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Synthesis and Reactivity of α-Sulfenyl-β-chloroenones, including Oxidation and Stille Cross-Coupling to form Chalcone Derivatives

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1. Experimental Section

1.1 General Procedures

Solvents were distilled prior to use as follows: dichloromethane was distilled from phosphorous pentoxide, ethyl acetate was distilled from potassium carbonate, and hexane was distilled prior to use. Organic phases were dried using anhydrous magnesium sulfate. All commercial reagents were used without further purification.

Proton (300 MHz) and carbon (75 MHz) NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer. Proton (400 MHz) and carbon (100 MHz) NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. All spectra were recorded at either 300 K (27 °C) or room temperature (*ca.* 20 °C) in deuterated chloroform ($CDCl_3$), unless otherwise stated, using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ_H and δ_C) are reported in parts per million (ppm) relative to TMS and coupling constants (*J*) are expressed in Hertz (Hz). Splitting patterns in ^{1}H NMR spectra are designated as s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), qd (quartet of doublets), and m (multiplet). ^{13}C NMR spectra were assigned with the aid of DEPT experiments. Compounds which were assigned with the aid of DEPT experiments were assigned by identifying the carbon type (CH_3, CH_2, CH or C).

Infrared spectra were measured using universal ATR sampling accessories on a Perkin Elmer Spectrum Two spectrometer. Flash chromatography was performed using Kieselgel silica gel 60, 0.040-0.063 mm (Merck). Thin layer chromatography (TLC) was carried out on pre-coated silica gel plates (Merck 60 PF_{254}). Visualisation was achieved by UV (254 nm) light detection and vanillin staining.

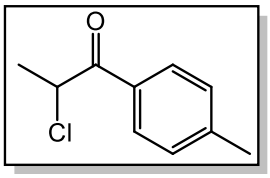
Nominal mass spectra were recorded on a Waters Quattro Micro triple quadrupole spectrometer in electrospray ionisation (ESI) mode using 50% water/acetonitrile containing 0.1% formic acid as eluent; samples were made up in acetonitrile. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier Time of Flight spectrometer in electrospray ionisation (ESI) mode using 50% water/acetonitrile containing 0.1% formic acid as eluent; samples were made up in acetonitrile.

Elemental analyses were performed by the Microanalysis Laboratory, National University of Ireland, Cork, using Perkin Elmer 240 and Exeter Analytical CE440 elemental analysers.

Melting points were carried out on a uni-melt Thomas Hoover Capillary melting point apparatus and are uncorrected.

1.2 Synthesis of α-Chloroketones

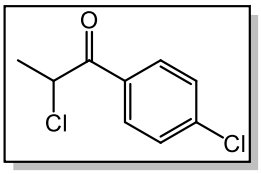
2-Chloro-1-(*p*-tolyl)propan-1-one S1[1]



Unrecrystallised *N*-chlorosuccinimide (NCS) (8.95 g, 67 mmol) was added to a stirring solution of 4'-methylpropiophenone (9.93 g, 10 mL, 67 mmol) and *p*-toluenesulfonic acid monohydrate (19.12 g, 100.5 mmol, 1.5 eq) in acetonitrile (150 mL). The mixture was stirred under reflux conditions for 4 hours. Upon cooling, the solvent was evaporated under reduced pressure and the resulting residue was dissolved in dichloromethane (50 mL) and washed with water (2 x 20 mL). The organic layer was dried over magnesium sulfate and concentrated *in vacuo* to give the chloride **S1** (8.69 g, 71%) as an orange oil which crystallised to a cream solid, mp 44-46°C (Lit.[1] states an oil). No further purification was required; ν_{max}/cm^{-1} (ATR) 2982, 2934, 1686 (C=O), 1607, 1180, 952, 752, 612; δ_H (400 MHz, $CDCl_3$): 1.73 [3H, d, *J* 6.7, C(3)H_3], 2.42 (3H, s, ArCH_3), 5.24 [1H, q, *J* 6.7, C(2)*H*], 7.28 (2H, d, *J* 8.2, Ar*H*), 7.91 (2H, d, *J* 8.3, Ar*H*); δ_C (75 MHz, $CDCl_3$): 20.1 [CH_3, *C*(3)H_3], 21.8 (CH_3, Ar*C*H_3), 52.8 [CH, *C*(2)H], 129.1, 129.5 (2 x CH signals, 4 x aromatic *C*H), 131.5, 144.8 (2 x C, aromatic *C*), 193.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{12}O^{35}Cl[M+H^+]$ 183.0577. Found 183.0568; m/z (ES+) 183.3 $[(C_{10}H_{11}O^{35}Cl)+H^+]$, 33%. $^{35}Cl/^{37}Cl$ pattern visible at 183 and 185 in a 3:1 ratio.

Spectroscopic characteristics are consistent with those previously reported. [1]

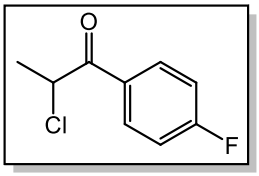
2-Chloro-1-(4-chlorophenyl)propan-1-one S2[2-3]



The title compound was prepared following the procedure outlined for **S1** using NCS (0.80 g, 6.0 mmol), *p*-toluenesulfonic acid monohydrate (1.65 g, 8.7 mmol), and 4'-chloropropiophenone (1.01 g, 6.0 mmol) in acetonitrile (50 mL) to give the crude *α-chloroketone* as a yellow oil. Following purification by column chromatography on silica gel using hexane-dichloromethane (70:30) as eluent, the pure *α-chloroketone* **S2** (0.88 g, 72%) was obtained as a white solid, mp 51-53° C (Lit.[2-3] states 56-58 °C); ν_{max}/cm^{-1} (ATR) 2984, 1684 (C=O), 1589, 1089, 845; δ_H (400 MHz, $CDCl_3$): 1.74 [3H, d, *J* 6.6, C(3)H_3], 5.18 [1H, q, *J* 6.6, C(2)*H*], 7.46 (2H, d, *J* 8.8, Ar*H*), 7.96 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 19.8 [*C*(3)H_3], 52.6 [*C*(2)H], 129.1, 130.4 (2 x signals, 4 x aromatic *C*H), 132.5, 140.2 (2 x aromatic *C*), 192.4 (*C*O); m/z (ES+) 203.0 $[(C_9H_8O^{35}Cl_2)+H^+]$; m/z (ES-) 201.2 $[(C_9H_8O^{35}Cl_2)+H^+]$, 4%.

Spectroscopic characteristics are consistent with those previously reported. [2-3]

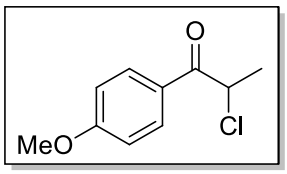
2-Chloro-1-(4-fluorophenyl)propan-1-one S3[4]



The title compound was prepared following the procedure outlined for **S1** using NCS (3.85 g, 28.8 mmol), *p*-toluenesulfonic acid monohydrate (8.24 g, 43.2 mmol), and 4'-fluoropropiophenone (4.38 g, 28.8 mmol) in acetonitrile (100 mL) to give the crude *α-chloroketone* **S3** (4.81 g, 89%) as a yellow oil. No purification was carried out; ν_{max}/cm^{-1} (ATR) 2986, 2936, 1690 (C=O), 1595, 1507, 1234, 1158, 954, 847, 610, 587; δ_H (400 MHz, $CDCl_3$): 1.74 [3H, d, *J* 6.7, C(3)*H*$_3$], 5.20 [1H, q, *J* 6.6, C(2)*H*], 7.12-7.19 (2H, m, Ar*H*), 8.02-8.12 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 19.8 [*C*(3)H$_3$], 52.6 [*C*(2)H], 115.9 (1 x signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 130.5 (d, $^4J_{CF}$ 2.9, aromatic *C*), 131.8 (1 x signal, 2 x CH, d, $^3J_{CF}$ 9.4, aromatic *C*H), 166.0 (d, $^1J_{CF}$ 256.2, aromatic *C*), 192.1 (*C*O); HRMS (ES+): Exact mass calculated for $C_9H_9OF^{35}Cl[M+H^+]$ 187.0326. Found 187.0318.

Spectroscopic characteristics are consistent with those previously reported.[4]

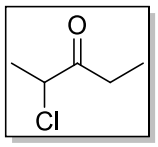
2-Chloro-1-(4-methoxyphenyl)propan-1-one S4[2, 5]



The title compound was prepared following the procedure outlined for **S1** using NCS (0.90 g, 6.7 mmol), *p*-toluenesulfonic acid monohydrate (1.93 g, 10.1 mmol), and 4'-methoxypropiophenone (1.00 g, 6.7 mmol) in acetonitrile (75 mL) to give to give the crude *α-chloroketone* **S4** (1.16 g, 87 %) as a yellow oil. No purification was carried out; ν_{max}/cm^{-1} (film) 3077 (CH), 2936 (CH), 1684 (CO), 1601 (aromatic); δ_H (300 MHz, $CDCl_3$) 1.71 [3H, d, *J* 6.7, C(3)*H*$_3$], 3.85 (3H, s, OC*H*$_3$), 5.23 [1H, q, *J* 6.7, C(2)*H*], 6.94 (2H, d, *J* 9.0, Ar*H*), 7.97 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 20.1 [CH_3, *C*(3)H$_3$], 52.7 [CH, *C*(2)H], 55.5 (CH_3, O*C*H$_3$), 114.0 (CH, aromatic *C*H), 126.8 (C, aromatic *C*), 131.4 (CH, aromatic *C*H), 164.0 (C, aromatic *C*), 192.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{12}O_2{}^{35}Cl[M+H]^+$ 199.0526. Found 199.0519; m/z (ES+) 199.0 [($C_{10}H_{11}O_2{}^{35}Cl$)+H^+], 82%, 201.0 [($C_{10}H_{11}O_2{}^{37}Cl$)+H^+], 30%.

Spectroscopic characteristics were consistent with those previously reported.[2, 5]

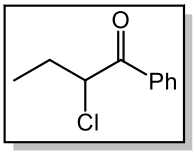
2-Chloropentan-3-one S5[6]



A solution of 3-pentanone (7.00 g, 8.61 mL, 81.3 mmol) in carbon tetrachloride (30 mL) was heated to 45 °C and sulfuryl chloride (12.07g, 7.25 mL, 89.4 mmol) was added dropwise over 2 h. The resulting mixture was stirred for a further 3 h at 45 °C. On completion the carbon tetrachloride was removed by distillation under atmospheric pressure at 85 °C. The residue was then purified by distillation under reduced pressure (85 °C, 62 mmHg) to give the *α-chloroketone* **S5** as a pale yellow oil (7.80 g, 80%); ν_{max}/cm^{-1} (film) 2984 (CH), 2942 (CH), 1725 (CO), 1448; δ_H (300 MHz, $CDCl_3$) 1.10 (3H, t, *J* 7.3, CH_2CH_3), 1.61 (3H, d, *J* 6.9, $CHCH_3$), 2.60-2.84 (2H, m, CH_2CH_3), 4.38 (1H, q, *J* 6.9, *C*HCl); δ_C (75.5 MHz, $CDCl_3$) 7.7 (CH_3, CH_2CH_3), 20.1 (CH_3, $CHCH_3$), 31.6 (CH_2, CH_2CH_3), 58.2 (CH, *C*HCl), 206.0 (C, *C*O).

Spectroscopic characteristics were consistent with those previously reported. [6]

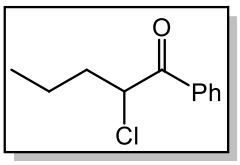
2-Chloro-1-phenylbutan-1-one S6 [7]



The title compound was prepared following the procedure outlined for **S1** using NCS (4.50 g, 33.7 mmol), *p*-toluenesulfonic acid monohydrate (9.61 g, 50.5 mmol), and butyrophenone (5.0 g, 4.9 mL, 33.7 mmol) in acetonitrile (90 mL) to give the crude α-*chloroketone* as a colourless oil. Following purification by column chromatography on silica gel using hexane-dichloromethane (70:30) as eluent, the pure *α-chloroketone* **S6** (4.57 g, 74%) was obtained as a colourless oil; ν_{max}/cm^{-1} (ATR) 2991 (CH), 2974 (CH), 2931 (CH), 1689 (C=O), 1597 (aromatic), 686; δ_H (400 MHz): 1.02 [3H, t, *J* 7.4, C(4)H_3], 1.91-2.05 [1H, m, one of C(3)H_2], 2.06-2.19 [1H, m, one of C(3)H_2], 5.07 [1H, overlapping dd, *J* 7.9, 5.7, C(2)*H*], 7.35-7.45 (2H, m, Ar*H*), 7.47-7.55 (1H, m, Ar*H*), 7.90-8.00 (2H, m, Ar*H*); δ_C (100 MHz): 10.8 [CH_3, *C*(4)H_3], 27.1 [CH_2, *C*(3)H_2], 59.4 [CH, *C*(2)H], 128.8, 128.9, 133.7 (3 x CH signals, 5 x aromatic *C*H), 134.6 (C, aromatic *C*), 193.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{12}O^{35}Cl[M+H^+]$ 183.0577. Found 183.0570; m/z (ES+) 182.4 $(C_{10}H_{11}O^{35}Cl)^+$, 32%, 183.4 $[(C_{10}H_{11}O^{35}Cl)+H^+]$, 5%.

Spectroscopic characteristics are consistent with those previously reported. [7]

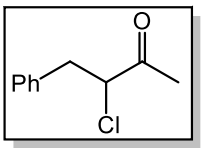
2-Chloro-1-phenylpentan-1-one S7[8]



The title compound was prepared following the procedure outlined for **S1** using NCS (2.67 g, 20 mmol), *p*-toluenesulfonic acid monohydrate (5.71 g, 30 mmol), and valerophenone (3.24 g, 3.33 mL, 20 mmol) in acetonitrile (90 mL) to give the crude α-*chloroketone* as an orange oil. Following purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent, the pure *α-chloroketone* **S7** (2.89 g, 73%) was obtained as a colourless oil; ν_{max}/cm^{-1} (ATR) 2962, 2934, 2874, 1689 (C=O), 1596 (aromatic), 1448, 686; δ_H (400 MHz): 0.98 [3H, t, *J* 7.4, C(5)H_3], 1.40-1.66 [2H, m, C(4)H_2], 1.94-2.16 [2H, m, C(3)H_2], 5.12 [1H, overlapping dd, *J* 8.2, 5.7, C(2)*H*], 7.45-7.53 (2H, m, Ar*H*), 7.56-7.64 (1H, m, Ar*H*), 7.97-8.04 (2H, m, Ar*H*); δ_C (100 MHz): 13.5 [CH_3, *C*(5)H_3], 19.5 [CH_2, *C*(4)H_2], 35.6 [CH_2, *C*(3)H_2], 57.5 [CH, *C*(2)H], 128.8, 128.9, 133.7 (3 x CH signals, 5 x aromatic *C*H), 134.6 (C, aromatic *C*), 193.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{11}H_{14}O^{35}Cl[M+H^+]$ 197.0733. Found 197.0724; m/z (ES+) 197.3 $[(C_{11}H_{13}O^{35}Cl)+H^+]$, 32%. $^{35}Cl/^{37}Cl$ pattern visible at 197 and 199 in a 3:1 ratio.

Spectroscopic characteristics are consistent with those previously reported. [8]

3-Chloro-4-phenylbutan-2-one S8[3]

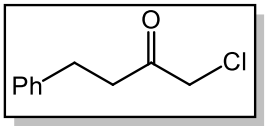


The title compound was prepared following the procedure outlined for **S1** using NCS (2.67 g, 20 mmol), *p*-toluenesulfonic acid monohydrate (5.71 g, 30 mmol), and 4-phenyl-2-butanone (2.96 g, 2.98 mL, 20 mmol) in acetonitrile (90 mL) to give the crude *α-chloroketone* as a yellow oil which also contained the by-products **S9** and **S10**. Following purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent, the pure *α-chloroketone* **S8** (1.03 g, 28%) was obtained as a colourless oil; ν_{max}/cm^{-1} (ATR) 3064, 3031, 1714 (C=O), 1357, 697; δ_H (400 MHz): 2.28 (3H, s, CH_3), 3.07 [1H, A of ABX system, J_{AB} 14.3, J_{AX} 8.1, one of C(4)H_2], 3.33 [1H, B of ABX system, J_{AB} 14.3, J_{BX} 6.1, one of C(4)H_2], 4.40 [1H, X of ABX system, dd, *J* 8.0, 6.2, C(3)*H*], 7.19-7.40 (5H, m, Ar*H*); δ_C (100 MHz): 26.8 (CH_3), 39.8 [*C*(4)H_2], 63.8 [*C*(3)H], 127.2, 128.6, 129.4 (3 x signals, 5 x aromatic *C*H), 136.2 (aromatic *C*), 202.6 (*C*O).

Spectroscopic characteristics are consistent with those previously reported. [3]

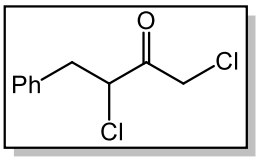
Other impure fractions contained the chlorinated products **S9** and **S10** which could not be isolated.

1-Chloro-4-phenylbutan-2-one S9[9]



Characteristic signals due to **S9**: δ_H (400 MHz): 2.86-2.98 (4H, m, C*H*$_2$C*H*$_2$), 4.01 (2H, s, C*H*$_2$Cl).

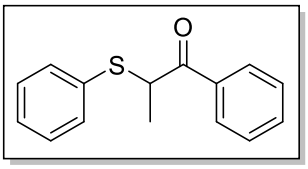
1,3-Dichloro-4-phenylbutan-2-one S10



Characteristic signals tentatively assigned as **S10**: δ_H (400 MHz): 4.23 (1H, A of AB system, J_{AB} 16.0, one of C*H*$_2$Cl), 4.32 (1H, B of AB system, J_{AB} 15.9, one of C*H*$_2$Cl), 4.70 [1H, X of ABX system, *J* 7.6, 6.3, C(3)*H*Cl].

1.3 Synthesis of α-Sulfenylketones

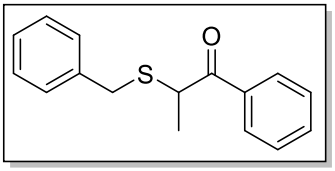
1-Phenyl-2-(phenylthio)propan-1-one 3a[10]



Thiophenol (1.30 g, 1.21 mL, 11.8 mmol) was added to a solution of freshly prepared sodium ethoxide [prepared from sodium (0.272 g, 11.8 mmol) in dry ethanol (20 mL) at 0 °C] while stirring under nitrogen. After stirring for 20 min under nitrogen, a solution of 2-chloropropiophenone (1.66 g, 9.8 mmol) in dry ethanol (20 mL) was added gradually over 15 min to the reaction mixture. Following stirring for 16 h at room temperature, the reaction was quenched by the addition of water (20 mL) and dichloromethane (20 mL). The combined organic layers were washed with sodium hydroxide (1 M, 2 x 30 mL), water (30 mL) and brine (30 mL), dried and concentrated under reduced pressure to give the *α-thioketone* **3a** (2.31 g, 97%) as a pale yellow oil. No further purification was required; ν_{max}/cm^{-1} (film) 3059 (CH), 2973 (CH), 1680 (CO); δ_H (300 MHz, $CDCl_3$) 1.52 [3H, d, *J* 6.8, C(3)*H*$_3$], 4.61 [1H, q, *J* 6.8, C(2)*H*], 7.20-7.54 (8H, m, Ar*H*), 7.95 (2H, dd, *J* 1.3, 8.4, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 17.1 [CH_3, *C*(3)H_3], 46.2 [CH, *C*(2)H], 128.6, 128.7, 129.0 (3 x CH, aromatic *C*H), 131.8 (C, aromatic *C*), 133.1, 134.9 (2 x CH, aromatic *C*H) 135.7 (C, aromatic *C*), 196.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{15}H_{15}OS[M+H]^+$ 243.0844. Found 243.0845; m/z (ES+) 243.0 [($C_{15}H_{14}OS$)+H^+], 100%.

Spectroscopic characteristics were consistent with those previously reported. [10]

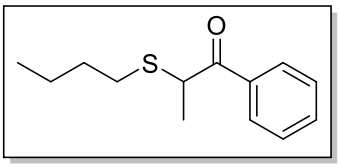
2-(Benzylthio)-1-phenylpropan-1-one 3b[11]



This was synthesised following the procedure described for **3a** using benzyl mercaptan (1.47 g, 1.39 mL, 11.8 mmol), 2-chloropropiophenone (1.66 g, 9.8 mmol) in dry ethanol (20 mL) and freshly prepared sodium ethoxide [prepared from sodium (0.272 g, 11.8 mmol) in dry ethanol (20 mL) at 0 °C]. The crude *α-thioketone* **3b** was obtained as an orange oil. Following purification by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent, the pure *α-thioketone* **3b** (1.37 g, 54%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3085 (CH), 2972 (CH), 1677 (CO); δ_H (300 MHz, $CDCl_3$) 1.54 [3H, d, *J* 6.9, C(3)*H*$_3$], 3.62 (1H, A of AB system, J_{AB} 12.9, one of SC*H*$_2$), 3.74 (1H, B of AB system, J_{AB} 12.9, one of SC*H*$_2$), 4.26 [1H, q, *J* 6.9, C(2)*H*], 7.19-7.52 (8H, m, Ar*H*), 7.84 (2H, dd, *J* 1.3, 8.4, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 16.7 [CH_3, *C*(3)H_3], 34.2 (CH_2, C*H*$_2$), 42.0 [CH, *C*(2)H], 127.3, 128.6, 129.2, 133.1 (4 x CH, aromatic *C*H) 135.6, 137.3 (2 x C, 2 x aromatic *C*), 196.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{17}OS[M+H]^+$ 257.1000. Found 257.1001; m/z (ES+) 257.1 [($C_{16}H_{16}OS$)+H^+], 100%.

Spectroscopic characteristics were consistent with those previously reported.[11]

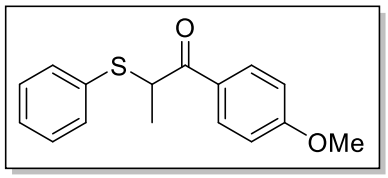
2-(Butylthio)-1-phenylpropan-1-one 3c



This was synthesised following the procedure described for **3a** using *n*-butanethiol (1.06 g, 1.27 mL, 11.8 mmol), 2-chloropropiophenone (1.66 g, 9.8 mmol) in dry ethanol (30 mL) and freshly prepared sodium ethoxide [prepared from sodium (0.272 g, 11.8 mmol) in dry ethanol (30 mL) at 0 °C]. The crude *α-thioketone* **3c** was obtained as a yellow oil. Following purification by column chromatography on silica gel using hexane-ethyl acetate as eluent (gradient elution 2-40% ethyl acetate), the pure *α-thioketone* **3c** (1.29 g, 64%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3061 (CH), 2959 (CH), 1678 (CO), 1596 (aromatic); δ_H (300 MHz, $CDCl_3$) 0.83 (3H, t, *J* 7.3, CH_2CH_3), 1.27-1.37 (2H, m, CH_2CH_3), 1.41-1.51 (2H, m, $CH_2CH_2CH_3$), 1.55 [3H, d, *J* 6.9, C(3)*H*$_3$], 2.32-2.57 (2H, m, SC*H*$_2$), 4.32 [1H, q, *J* 6.9, C(2)*H*], 7.40-7.45 (2H, m, Ar*H*), 7.46-7.55 (1H, m, Ar*H*) 7.98-8.02 (2H, m, Ar*H)*; δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, CH_2CH_3), 16.4 [CH_3, *C*(3)H_3], 22.0 (CH_2, CH_2CH_3), 28.3 (CH_2, SCH_2), 31.3 (CH_2, $CH_2CH_2CH_3$), 41.4 [CH, *C*(2)H], 128.5, 132.9 (2 x CH ,2 signals for 3 x aromatic *C*H) 135.7 (C, aromatic *C*), 196.0 (C, *C*O);

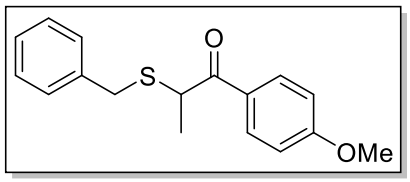
HRMS (ES+): Exact mass calculated for $C_{13}H_{19}OS[M+H]^+$ 223.1157. Found 223.1156; m/z (ES+) 223.1 [$(C_{16}H_{18}OS)+H^+$], 100%.

1-(4-Methoxyphenyl)-2-(phenylthio)propan-1-one 3d



This was synthesised following the procedure described for **3a** using thiophenol (0.58 g, 0.54 mL, 5.3 mmol), 2-chloro-1-(4-methoxyphenyl)propan-1-one **S4** (0.88 g, 4.4 mmol) in dry methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (122 mg, 5.3 mmol) in dry methanol (15 mL) at 0°C]. The crude *α-thioketone* **3d** was isolated as a yellow oil. This was purified by chromatography on silica gel using hexane-ethyl acetate as eluent (gradient elution 0-20% ethyl acetate) to give the pure *α-thioketone* **3d** (0.83 g, 69%) as a yellow oil; ν_{max}/cm^{-1} (film) 3058 (CH), 2969 (CH), 1671 (CO), 1598 (aromatic); δ_H (300 MHz, $CDCl_3$) 1.51 [3H, d, *J* 6.9, C(3)H_3], 3.83 (3H, s, OCH_3), 4.60 [1H, q, *J* 6.9, C(2)*H*], 6.89 (2H, d, *J* 9.0, Ar*H*), 7.25-7.37 (5H, m, Ar*H*), 7.93 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 17.3 [CH_3, *C*(3)H_3], 46.0 [CH, *C*(2)H], 55.5 (CH_3, O*C*H_3), 113.8, 128.4, 128.9, 131.0 (4 x CH, aromatic *C*H), 132.2 (C, aromatic *C*), 134.3 (CH, aromatic *C*H), 163.5 (C, aromatic *C*), 195.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{17}O_2S[M+H]^+$ 273.0949. Found 273.0938; m/z (ES+) 273.0 [$(C_{16}H_{16}O_2S)+H^+$], 42%, 289.0 (100%).

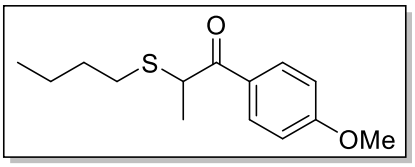
2-(Benzylthio)-1-(4-methoxyphenyl)propan-1-one 3e



This was synthesised following the procedure described for **3a** using benzyl mercaptan (0.621 g, 0.59 mL, 5.0 mmol), 2-chloro-1-(4-methoxyphenyl)propan-1-one **S4** (0.825 g, 4.2 mmol) in dry methanol (20 mL) and freshly prepared sodium methoxide [prepared from sodium (0.115 g, 5.0 mmol) in dry methanol (10 mL) at 0 °C]. The crude *α-thioketone* **3e** was obtained as a yellow oil. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent, and further recrystallised from methanol to give the pure *α-thioketone* **3e** (1.01 g, 84%) as a white solid, mp 61-63 °C; (Found C, 71.10; H, 6.34; S, 11.20. $C_{17}H_{18}O_2S$ requires C, 71.30; H, 6.34; S, 11.20%); ν_{max}/cm^{-1} (KBr) 3064 (CH), 2930 (CH), 1668 (CO), 1600 (aromatic); δ_H (400 MHz, $CDCl_3$) 1.55 [3H, d, *J* 6.9, C(3)H_3], 3.65 (1H, A of AB system, J_{AB} 13.0, one of SCH_2), 3.76 (1H, B of AB system, J_{AB} 13.0, one of SCH_2), 3.86 (3H, s, OCH_3), 4.25 [1H, q, *J* 6.9, C(2)*H*], 6.88 (2H, d,

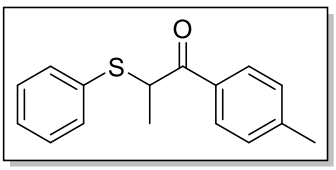
J 8.9, Ar*H*), 7.21-7.30 (5H, m, Ar*H*), 7.85 (2H, d, *J* 8.9, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 16.8 [CH_3, *C*(3)H_3], 34.2 (CH_2, *C*H_2), 41.7 [CH, *C*(2)H], 55.5 (CH_3, O*C*H_3), 113.7, 127.1 (2 x CH, aromatic *C*H) 128.4 (C, aromatic *C*), 128.5, 129.2, 130.9 (3 x CH, aromatic *C*H), 137.5, 163.5 (2 x C, 2 x aromatic *C*), 195.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{19}O_2S[M+H]^+$ 287.1106. Found 287.1099; m/z (ES+) 287.0 [($C_{17}H_{18}O_2S$)+H^+], 100%.

2-(Butylthio)-1-(4-methoxyphenyl)propan-1-one 3f



This was synthesised following the procedure described for **3a** using *n*-butanethiol (0.45 g, 0.54 mL, 5.0 mmol), 2-chloro-1-(4-methoxyphenyl)propan-1-one **S4** (0.825 g, 4.2 mmol) in dry methanol (20 mL) and freshly prepared sodium methoxide [prepared from sodium (0.115 g, 5.0 mmol) in dry methanol (20 mL) at 0 °C]. The crude *α-thioketone* **3f** was obtained as a yellow oil. Following purification by column chromatography on silica gel using hexane-ethyl acetate as eluent (gradient elution 2-20% ethyl acetate), the pure *α-thioketone* **3f** (0.85 g, 81%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 2959 (CH), 2931 (CH), 1669 (CO), 1601 (aromatic); δ_H (300 MHz, $CDCl_3$) 0.85 (3H, t, *J* 7.3, CH_2CH_3), 1.26-1.38 (2H, m, CH_2CH_3), 1.42-1.50 (2H, m, $CH_2CH_2CH_3$), 1.54 [3H, d, *J* 6.9, C(3)H_3], 2.34-2.59 (2H, m, S*C*H_2), 3.86 (3H, s, O*C*H_3), 4.30 [1H, q, *J* 6.9, C(2)*H*], 6.93 (2H, d, *J* 9.0, Ar*H*), 8.01 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, CH_2CH_3), 16.6 [CH_3, *C*(3)H_3], 22.0 (CH_2, *C*H_2CH_3), 28.4 (CH_2, S*C*H_2), 31.4 (CH_2, *C*$H_2CH_2CH_3$), 41.9 [CH, *C*(2)H], 55.4 (CH_3, O*C*H_3), 113.7 (CH, aromatic *C*H), 128.4 (C, aromatic *C*), 130.9 (CH, aromatic *C*H), 163.4 (C, aromatic *C*), 195.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{14}H_{21}O_2S[M+H]^+$ 253.1262. Found 253.1252; m/z (ES+) 253.1 [($C_{14}H_{20}O_2S$)+H^+], 58%, 269.1 (100%).

2-(Phenylthio)-1-(*p*-tolyl)propan-1-one 3g[12]

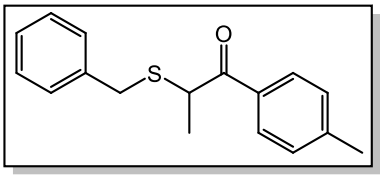


This was synthesised following the procedure described for **3a** using thiophenol (3.31 g, 3.08 mL, 30.1 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (5.00 g, 27.4 mmol) in dry methanol (30 mL) and freshly prepared sodium methoxide [prepared from sodium (0.757 g, 32.9 mmol) in dry methanol (50 mL) at 0 °C]. The crude *α-thioketone* **3g** was obtained as an orange oil. Following purification by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent, the pure *α-thioketone* **3g** (4.33 g, 62%) was isolated as a yellow oil; ν_{max}/cm^{-1}

(film) 3056 (CH), 2972 (CH), 1676 (CO), 1606 (aromatic); δ_H (300 MHz, $CDCl_3$) 1.50 [3H, d, *J* 6.9, C(3)H_3], 2.36 (3H, s, ArCH_3), 4.60 [1H, q, *J* 6.9, C(2)*H*], 7.12-7.39 (7H, m, Ar*H*), 7.84 (2H, d, *J* 8.3, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 17.2 [CH_3, *C*(3)H_3], 21.7 (CH_3, Ar*C*H_3), 46.2 [CH, *C*(2)H], 128.5, 128.8, 129.0, 129.4 (4 x CH, aromatic *C*H), 132.0, 133.1 (2 x C, 2 x aromatic *C*), 134.5 (CH, aromatic *C*H), 144.0 (C, aromatic *C*), 196.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{17}OS[M+H]^+$ 257.1000. Found 257.0992; m/z (ES+) 257.2 [($C_{16}H_{16}OS$)+H^+], 66%, 273.2 (100%).

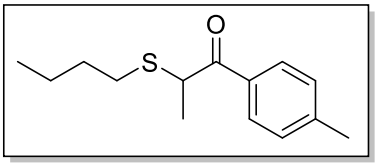
Spectroscopic characteristics were consistent with those previously reported.[12]

2-(Benzylthio)-1-(*p*-tolyl)propan-1-one 3h



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (1.89 g, 1.78 mL, 15.2 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (2.53 g, 13.8 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.38 g, 16.6 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a yellow solid which was recrystallised from methanol to give the pure *α-thioketone* **3h** (2.27 g, 61%) as a white solid, mp 43-44°C; ν_{max}/cm^{-1} (ATR) 1664 (C=O), 1602, 1234, 756, 698; δ_H (400 MHz, $CDCl_3$): 1.55 (3H, d, *J* 6.9, C(3)H_3), 2.40 (3H, s, ArCH_3), 3.64 (1H, A of AB system, J_{AB} 12.9, one of SCH_2), 3.75 (1H, B of AB system, J_{AB} 12.9, one of SCH_2), 4.26 [1H, q, *J* 6.9, C(2)*H*], 7.19-7.35 (7H, m, Ar*H*), 7.76 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.7 [*C*(3)H_3], 21.7 (Ar*C*H_3), 34.1 (S*C*H_2), 41.9 [*C*(2)H], 127.1, 128.5, 128.7, 129.1, 129.2 (5 signals for 9 x aromatic *C*H), 133.0, 137.3, 143.9 (3 x aromatic *C*), 196.1 (*C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{19}OS[M+H^+]$ 271.1157. Found 271.1157; m/z (ES+) 271.3 [($C_{17}H_{18}OS$)+H^+], 100%.

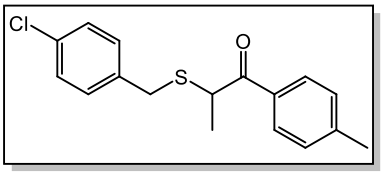
2-(Butylthio)-1-(*p*-tolyl)propan-1-one 3i



This was synthesised following the procedure described for **3a** using *n*-butanethiol (2.97 g, 3.55 mL, 32.9 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (5.00 g, 27.4 mmol) in dry methanol (30 mL) and freshly prepared sodium methoxide [prepared from sodium (0.757 g, 32.9 mmol) in dry methanol (50 mL) at 0 °C] to give the pure *α-thioketone* **3i** as an orange oil (6.22 g, 97%). No further purification was required; ν_{max}/cm^{-1} (film) 3030 (CH), 2958 (CH), 1674 (CO), 1608 (aromatic); δ_H (300 MHz, $CDCl_3$) 0.84 (3H, t, *J* 7.3, CH_2CH_3), 1.28-1.36 (2H, m, CH_2CH_3), 1.42-

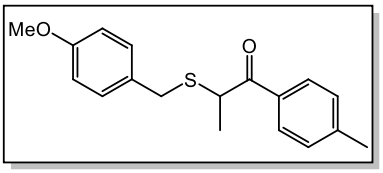
1.49 (2H, m, CH_2CH_2CH_3), 1.55 [3H, d, *J* 6.9, C(3)H_3], 2.33-2.58 (2H, m, SCH_2), 2.40 (3H, s, ArCH_3), 4.30 [1H, q, *J* 6.9, C(2)*H*], 7.25 (2H, d, *J* 8.0, Ar*H*), 7.91 (2H, d, *J* 8.3, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, CH_2CH_3), 16.5 [CH_3, *C*(3)H_3], 21.6 (CH_3, Ar*C*H_3), 22.0 (CH_2, *C*H_2CH_3), 28.4 (CH_2, S*C*H_2), 31.4 (CH_2, *C*H_2CH_2CH_3), 41.4 [CH, *C*(2)H], 128.7, 129.2 (2 x CH, aromatic *C*H), 133.1, 143.7 (2 x C, 2 x aromatic *C*), 195.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{14}H_{21}OS[M+H]^+$ 237.1313. Found 237.1313; m/z (ES+) 237.2 [($C_{14}H_{20}OS$)+H^+], 60%, 253.2 (100%).

2-((4-Chlorobenzyl)thio)-1-(*p*-tolyl)propan-1-one 3j



The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (1.13 g, 0.94 mL, 7.1 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (1.19 g, 6.5 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.179 g, 7.8 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as an off-white solid which was recrystallised from methanol to give the pure *α-thioketone* **3j** (1.48 g, 75%) as a cream solid, mp 45-47°C; Found C, 67.00; H, 5.64. $C_{17}H_{17}OSCl$ requires C, 66.98; H, 5.62; ν_{max}/cm^{-1} (ATR) 2930, 1667 (C=O), 1605; δ_H (400 MHz, $CDCl_3$): 1.53 [3H, d, *J* 6.9, C(3)H_3], 2.41 (3H, s, ArCH_3), 3.57 (1H, A of AB system, J_{AB} 13.2, one of SCH_2), 3.69 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.27 [1H, q, *J* 6.9, C(2)*H*], 7.11-7.30 (6H, m, Ar*H*), 7.77 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.8 [CH_3, *C*(3)H_3], 21.7 (CH_3, Ar*C*H_3), 33.3 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 128.6, 128.7, 129.3, 130.5 (4 x CH signals, 8 x aromatic *C*H), 132.9, 136.1, 144.0 (3 x C signals, 4 x aromatic *C*), 195.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OS^{35}Cl[M+H^+]$ 305.0767. Found 305.0763; m/z (ES+) 305.2 [($C_{17}H_{17}OS^{35}Cl$)+H^+], 100%, 307.2 [($C_{17}H_{17}OS^{37}Cl$)+H^+], 42%.

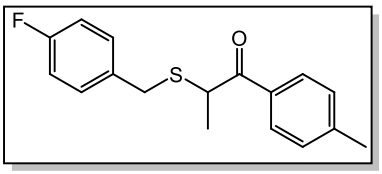
2-((4-Methoxybenzyl)thio)-1-(*p*-tolyl)propan-1-one 3k



The title compound was prepared following the procedure outlined for **3a** using (4-methoxyphenyl)methanethiol (0.933 g, 0.84 mL, 6.1 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (1.00 g, 5.5 mmol) in methanol (5 mL) and freshly prepared sodium methoxide [prepared from sodium (0.139 g, 6.1 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as an orange oil which was purified by column

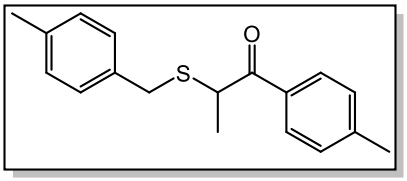
chromatography on silica gel (hexane-dichloromethane 50:50) to give the pure *α-thioketone* **3k** (1.30 g, 79%) as a white solid, mp 50-52°C; Found C, 71.92; H, 6.72. $C_{18}H_{20}O_2S$ requires C, 71.97; H, 6.71; ν_{max}/cm^{-1} (ATR) 2958, 2931, 1662 (C=O), 1606, 1509, 1237, 1174; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.9, C(3)H_3], 2.40 (3H, s, ArCH_3), 3.59 (1H, A of AB system, J_{AB} 12.9, one of SCH_2), 3.71 (1H, B of AB system, J_{AB} 12.9, one of SCH_2), 3.78 (3H, s, OCH_3), 4.26 [1H, q, *J* 6.9, C(2)*H*], 6.80 (2H, d, *J* 8.6, Ar*H*), 7.17 (2H, d, *J* 8.6, Ar*H*), 7.22 (2H, d, *J* 8.2, Ar*H*), 7.78 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.7 [CH_3, *C*(3)H_3], 21.7 (CH_3, Ar*C*H_3), 33.6 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 55.3 (CH_3, O*C*H_3), 113.9, 128.7 (2 x CH signals, 4 x aromatic *C*H), 129.2 (C, aromatic *C*), 129.2, 130.3 (2 x CH signals, 4 x aromatic *C*H), 133.0, 143.9, 158.7 (3 x C, aromatic *C*), 196.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{21}O_2S[M+H^+]$ 301.1262. Found 301.1270.

2-((4-Fluorobenzyl)thio)-1-(*p*-tolyl)propan-1-one 3l



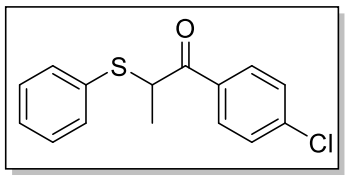
The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.754 g, 0.65 mL, 5.3 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (0.804 g, 4.4 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.122 g, 5.3 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as an cream solid which was recrystallised from methanol to give the pure *α-thioketone* **3l** (0.555 g, 44%) as a cream solid, mp 52-53°C; ν_{max}/cm^{-1} (ATR) 3030, 2966, 2924, 1662 (C=O), 1604, 1505, 1219, 829; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.9, C(3)H_3], 2.41 (3H, s, ArCH_3), 3.60 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 3.72 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.28 [1H, q, *J* 6.9, C(2)*H*], 6.95 (2H, t, *J* 8.7, Ar*H*), 7.18- 7.25 (4H, m, Ar*H*), 7.79 (2H, d, *J* 8.3, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.6 [CH_3, *C*(3)H_3], 21.6 (CH_3, Ar*C*H_3), 33.2 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H), 128.6, 129.3 (2 x CH signals, 4 x aromatic *C*H), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 132.9 (C, aromatic *C*), 133.1 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 144.0 (C, aromatic *C*), 161.9 (C, d, $^1J_{CF}$ 245.7, aromatic *C*), 196.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OSF[M+H^+]$ 289.1062. Found 289.1056.

2-((4-Methybenzyl)thio)-1-(*p*-tolyl)propan-1-one 3m



The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.553 g, 0.54 mL, 4.0 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (0.666 g, 3.6 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.101 g, 4.4 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3m** (0.75 g, 72%) as a white solid, mp 76-77°C; Found C, 76.10; H, 7.11. $C_{18}H_{20}OS$ requires C, 76.01; H, 7.09; ν_{max}/cm^{-1} (ATR) 1670 (C=O), 1603, 1236, 755; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.9, C(3)H_3], 2.32 (3H, s, ArCH_3), 2.41 (3H, s, ArCH_3), 3.60 (1H, A of AB system, J_{AB} 12.8, one of SCH_2), 3.73 (1H, B of AB system, J_{AB} 12.8, one of SCH_2), 4.26 [1H, q, *J* 6.8, C(2)*H*], 7.08 (2H, d, *J* 7.9, Ar*H*), 7.14 (2H, d, *J* 8.0, Ar*H*), 7.22 (2H, d, *J* 8.0, Ar*H*), 7.77 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.7 [CH_3, *C*(3)H_3], 21.1, 21.7 (2 x CH_3, Ar*C*H_3), 33.9 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 128.7, 129.1, 129.2 (3 x CH signals, 8 x aromatic *C*H), 133.1, 134.2, 136.8, 143.9 (4 x C, aromatic *C*), 196.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{21}OS[M+H^+]$ 285.1313. Found 285.1310; m/z (ES+) 285.2 [($C_{18}H_{20}OS$)+H^+], 60%.

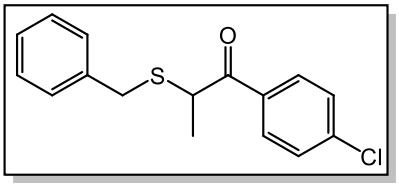
1-(4-Chlorophenyl)-2-(phenylthio)propan-1-one 3n



This was synthesised following the procedure described for **3a** using thiophenol (1.30 g, 1.21 mL, 11.8 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (2.00 g, 9.9 mmol) in dry methanol (20 mL) and freshly prepared sodium methoxide [prepared from sodium (0.272 g, 11.8 mmol) in dry methanol (20 mL) at 0 °C]. The *α-thioketone* **3n** (2.36 g, 87%) was isolated as a yellow oil. By ^{1}H NMR spectroscopy, this product was seen to also contain 4'-chloropropiophenone (5%, q, δ_H 2.97 ppm), no purification was carried out; ν_{max}/cm^{-1} (film) 3058 (CH), 2972 (CH), 1680 (CO), 1589 (aromatic); δ_H (300 MHz, $CDCl_3$) 1.51 [3H, d, *J* 6.9, C(3)H_3] C(3)H_3], 4.53 [1H, q, *J* 6.9, C(2)*H*], 7.20-7.41 (5H, m, Ar*H*), 7.39 (2H, d, *J* 8.7, Ar*H*), 7.87 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 16.9 [CH_3, *C*(3)H_3], 46.1 [CH, *C*(2)H], 128.9, 129.0, 130.1 (3 x CH, aromatic *C*H), 131.4, 134.0 (2 x C, 2 x aromatic *C*), 134.8 (CH, aromatic *C*H), 139.5 (C, aromatic *C*), 194.9 (C, *C*O); 4 CH signals seen for 5 aromatic *C*H; HRMS (ES+): Exact mass

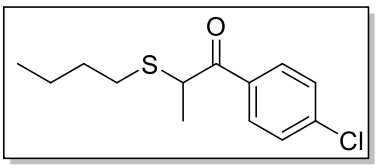
calculated for $C_{15}H_{14}OS^{35}Cl[M+H]^+$ 277.0376. Found 277.0311; m/z (ES+) 277.1 [$(C_{15}H_{13}OS^{35}Cl)+H^+$], 22%, 279.1 [$(C_{15}H_{13}OS^{37}Cl)+H^+$], 12%, 293.1 (100%).

2-(Benzylthio)-1-(4-chlorophenyl)propan-1-one 3o



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (0.596 g, 0.56 mL, 4.8 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (0.893 g, 4.4 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.122 g, 5.3 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3o** (0.747 g, 58%) as a white solid, mp 65-67°C; ν_{max}/cm^{-1} (ATR) 2934, 1672 (C=O), 1587, 1331, 1091, 946, 710, 698; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.6, C(3)H_3], 3.63 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 3.76 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.20 [1H, q, *J* 6.9, C(2)*H*], 7.22- 7.32 (5H, m, Ar*H*), 7.37 (2H, d, *J* 8.8, Ar*H*), 7.76 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.5 [*C*(3)H_3], 34.2 (S*C*H_2), 42.0 [*C*(2)H], 127.3, 128.6, 128.8, 129.2, 130.0 (5 x signals, 9 x aromatic *C*H), 133.9, 137.1, 139.4 (3 x aromatic *C*), 195.1 (*C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{16}OS^{35}Cl[M+H^+]$ 291.0610. Found 291.0598; m/z (ES+) 291.2 [$(C_{16}H_{15}OS^{35}Cl)+H^+$], 10%.

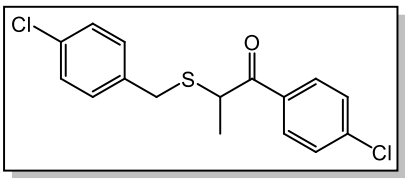
2-(Butylthio)-1-(4-chlorophenyl)propan-1-one 3p



This was synthesised following the procedure described for **3a** using *n*-butanethiol (1.07 g, 1.27 mL, 11.8 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (2.00 g, 9.9 mmol) in dry methanol (30 mL) and freshly prepared sodium methoxide [prepared from sodium (0.272 g, 11.8 mmol) in dry methanol (30 mL) at 0 °C] to give the *α-thioketone* **3p** as a yellow oil (2.15 g, 85%). By ^{1}H NMR spectroscopy this product was seen to also contain 4'-chloropropiophenone (6%), no purification was carried out; ν_{max}/cm^{-1} (film) 2960 (CH), 2360 (CH), 1678 (CO), 1590 (aromatic); δ_H (300 MHz, $CDCl_3$) 0.85 (3H, t, *J* 7.3, CH_2CH_3), 1.28-1.36 (2H, m, CH_2CH_3), 1.41-1.49 (2H, m, $CH_2CH_2CH_3$), 1.55 [3H, d, *J* 6.9, C(3)H_3], 2.30-2.57 (2H, m, SCH_2), 4.26 [1H, q, *J* 6.9, C(2)*H*], 7.42 (2H, d, *J* 8.7, Ar*H*), 7.95 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, CH_2CH_3), 16.2 [CH_3, *C*(3)H_3], 22.0 (CH_2, CH_2CH_3), 28.3 (CH_2, SCH_2), 31.3 (CH_2, $CH_2CH_2CH_3$), 41.5 [CH, *C*(2)H], 128.8, 130.0 (2 x CH, aromatic *C*H) 133.9, 139.3 (2 x C, 2 x

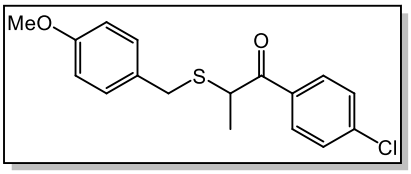
aromatic *C*), 194.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{13}H_{18}OS^{35}Cl[M+H]^+$ 257.0767. Found 257.0780; m/z (ES+) 273.1 (100%), 275.1 (36%).

2-((4-Chlorobenzyl)thio)-1-(4-chlorophenyl)propan-1-one 3q



The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.841 g, 0.70 mL, 5.3 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (0.893 g, 4.4 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.122 g, 5.3 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3q** (0.988 g, 69%) as a white crystalline solid, mp 87-88°C; Found C, 59.13; H, 4.36. $C_{16}H_{14}OSCl_2$ requires C, 59.09; H, 4.34; ν_{max}/cm^{-1} (ATR) 2974, 2934, 1669 (C=O), 1588 (aromatic), 1489, 1093, 504; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.9, C(3)H_3], 3.57 (1H, A of AB system, J_{AB} 13.2, one of SCH_2), 3.70 (1H, B of AB system, J_{AB} 13.2, one of SCH_2), 4.22 [1H, q, *J* 6.9, C(2)*H*], 7.16 (2H, d, *J* 8.5, Ar*H*), 7.23 (2H, d, *J* 8.5, Ar*H*), 7.40 (2H, d, *J* 8.7, Ar*H*), 7.80 (2H, d, *J* 8.7, Ar*H*); δ_C (75 MHz, $CDCl_3$): 16.5 [CH_3, *C*(3)H_3], 33.2 (CH_2, S*C*H_2), 42.1 [CH, *C*(2)H], 128.7, 128.9, 130.0, 130.5 (4 x CH signals, 8 x aromatic *C*H), 133.1, 133.7, 135.7, 139.6 (4 x C, aromatic *C*), 194.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{15}OS^{35}Cl_2[M+H^+]$ 325.0221. Found 325.0218; m/z (ES+) 325.7 [$(C_{16}H_{14}OS^{35}Cl_2)+H^+$], 12%. $^{35}Cl/^{37}Cl$ pattern visible in HRMS at 325, 327 and 329 in a 9:6:1 ratio.

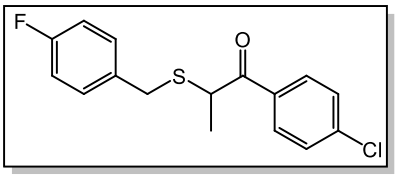
1-(4-Chlorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one 3r



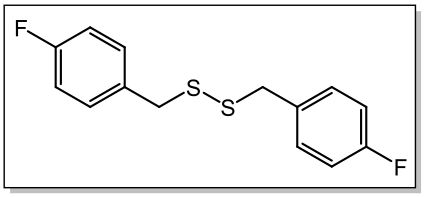
The title compound was prepared following the procedure outlined for **3a** using (4-methoxyphenyl)methanethiol (0.848 g, 0.76 mL, 5.5 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (1.02 g, 5.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3r** (1.02 g, 64%) as a white solid (mp 49-51°C), which contained *approx*. 4% disulfide **S11**[13] (Full details described in the synthesis of **3y**) (δ_H 3.59 ppm, s; δ_H 3.79 ppm, s; δ_H 6.85 ppm, d, *J* 8.7); Found C, 63.73; H, 5.38. $C_{17}H_{17}O_2SCl$ requires C, 63.64; H, 5.34; ν_{max}/cm^{-1} (ATR) 2966, 2929, 2836, 1678 (C=O), 1585,

1509, 1507, 1227, 1028, 824, 760, 523; δ_H (400 MHz, $CDCl_3$): 1.56 [3H, d, *J* 6.8, C(3)H_3], 3.58 (1H, A of AB system, J_{AB} 12.9, one of SCH_2), 3.72 (1H, B of AB system, J_{AB} 12.9, one of SCH_2), 3.79 (3H, s, OCH_3), 4.19 [1H, q, *J* 6.8, C(2)*H*], 6.81 (2H, d, *J* 8.7, Ar*H*), 7.16 (2H, d, *J* 8.7, Ar*H*), 7.38 (2H, d, *J* 8.7, Ar*H*), 7.78 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.4 [CH_3, *C*(3)H_3], 33.5 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 55.3 (CH_3, O*C*H_3), 113.9, 128.7 (2 x CH signals, 4 x aromatic *C*H), 128.9 (C, aromatic *C*), 130.0, 130.2 (2 x CH signals, 4 x aromatic *C*H), 133.8, 139.3, 158.8 (3 x C, aromatic *C*), 195.1 (C, *C*O).

1-(4-Chlorophenyl)-2-((4-fluorobenzyl)thio)propan-1-one 3s

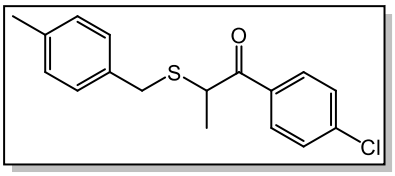


The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.61 g, 0.52 mL, 4.3 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (0.80 g, 3.9 mmol) in methanol (5 mL) and freshly prepared sodium methoxide [prepared from sodium (0.107 g, 4.7 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3s** (0.782 g, 65%) as a white crystalline solid (mp 58-60°C), which contained *approx*. 3% disulfide **S12**[14] (s, δ_H 3.57 ppm); Found C, 62.44; H, 4.63. $C_{16}H_{14}OSClF$ requires C, 62.23; H, 4.57; ν_{max}/cm^{-1} (ATR) 3084, 2979, 2934, 1672 (C=O), 1590, 1508, 1329, 1223, 840, 528, 485; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.9, C(3)H_3], 3.58 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 3.71 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.21 [1H, q, *J* 6.9, C(2)*H*], 6.95 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*), 7.19 (2H, dd, *J* 8.7, J_{FH} 5.3, Ar*H*), 7.39 (2H, d, *J* 8.7, Ar*H*), 7.81 (2H, d, *J* 8.7, Ar*H*); δ_C (75 MHz, $CDCl_3$): 16.5 [CH_3, *C*(3)H_3], 33.1 (CH_2, S*C*H_2), 42.1 [CH, *C*(2)H], 115.4 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H), 128.9, 130.0 (2 x CH signals, 4 x aromatic *C*H), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 132.8 (C, d, $^4J_{CF}$ 3.3, aromatic *C*), 133.8, 139.5 (2 x C, aromatic *C*), 162.0 (C, d, $^1J_{CF}$ 246.0, aromatic *C*), 194.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{15}OS^{35}ClF[M+H^+]$ 309.0516. Found 309.0515.



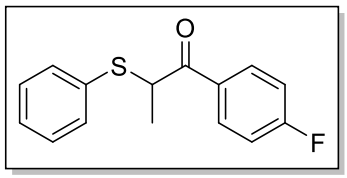
Characteristic signal due to **S12**[14]: δ_H (400 MHz, $CDCl_3$) 3.57 (4H, s, SCH_2).

1-(4-Chlorophenyl)-2-((4-methybenzyl)thio)propan-1-one 3t



The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.608 g, 0.60 mL, 4.4 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (0.812 g, 4.0 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.11 g, 4.8 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3t** (0.892 g, 73%) as a white solid, mp 92-93°C; Found C, 66.99; H, 5.63. $C_{17}H_{17}OSCl$ requires C, 66.98; H, 5.62; ν_{max}/cm^{-1} (ATR) 2933, 1905, 1671 (C=O), 1587 (aromatic), 1091, 946, 732; δ_H (400 MHz, $CDCl_3$): 1.56 [3H, d, *J* 6.7, C(3)H_3], 2.33 (3H, s, ArCH_3), 3.58 (1H, A of AB system, J_{AB} 13.0, one of SCH_2), 3.72 (1H, B of AB system, J_{AB} 13.0, one of SCH_2), 4.19 [1H, q, *J* 6.7, C(2)*H*], 7.09 (2H, d, *J* 8.0, Ar*H*), 7.13 (2H, d, *J* 8.1, Ar*H*), 7.37 (2H, d, *J* 8.4, Ar*H*), 7.77 (2H, d, *J* 8.5, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.5 [CH_3, *C*(3)H_3], 21.1 (CH_3, Ar*C*H_3), 33.9 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 128.8, 129.1, 129.3, 130.1 (4 x CH signals, 8 x aromatic *C*H), 133.8, 133.9, 137.0, 139.4 (4 x C, aromatic *C*), 195.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OS^{35}Cl[M+H^+]$ 305.0767. Found 305.0762; m/z (ES+) 305.2 [($C_{17}H_{17}OS^{35}Cl$)+H^+], 10%. $^{35}Cl/^{37}Cl$ pattern visible in HRMS at 305 and 307 in a 3:1 ratio.

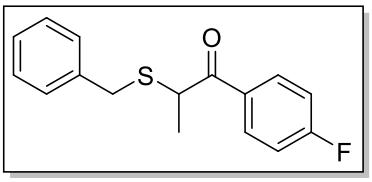
1-(4-Fluorophenyl)-2-(phenylthio)propan-1-one 3u



This was synthesised following the procedure described for **3a** using thiophenol (0.68 g, 0.63 mL, 6.2 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (0.95 g, 5.1 mmol) in dry methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.143 g, 6.2 mmol) in dry methanol (15 mL) at 0 °C]. The crude *α-thioketone* **3u** was obtained as a yellow oil which was purified by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent. The *α-thioketone* **3u** (0.78 g, 59%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3074 (CH), 2976 (CH), 1679 (CO), 1598 (aromatic); δ_H (300 MHz, $CDCl_3$) 1.52 (3H, d, *J* 6.9, CH_3), 4.58 (1H, q, *J* 6.9, C*H*), 7.03-7.11 (2H, m, Ar*H*), 7.21-7.36 (5H, m, Ar*H*), 7.91-8.01 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 17.0 (CH_3, *C*H_3), 46.1 (CH, *C*H), 115.7 (CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 128.8, 129.0 (2 × CH, aromatic *C*H), 131.3 (CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 131.5 (C, aromatic *C*), 132.0 (C, d, $^4J_{CF}$ 2.9, aromatic *C*), 134.7 (CH, aromatic *C*H), 165.7 (C, d, $^1J_{CF}$

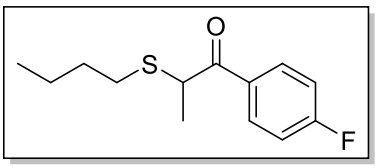
255.0, aromatic *C*), 194.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{15}H_{14}OSF[M+H]^+$ 261.0749. Found 261.0726; m/z (ES+) 261.0 [$(C_{15}H_{13}OSF)+H^+$], 12%, 277.0 (100%).

2-(Benzylthio)-1-(4-fluorophenyl)propan-1-one 3v



This was synthesised following the procedure described for **3a** using benzyl mercaptan (0.93 g, 0.88 mL, 7.5 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (1.16 g, 6.3 mmol) in dry methanol (20 mL) and freshly prepared sodium methoxide [prepared from sodium (0.173 g, 7.5 mmol) in dry methanol (20 mL) at 0 °C]. The crude *α-thioketone* **3v** was obtained as a yellow oil. Following purification by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent, the pure *α-thioketone* **3v** (1.32 g, 77%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3064 (CH), 2929 (CH), 1677 (CO), 1597 (aromatic); δ_H (300 MHz, $CDCl_3$) 1.56 [3H, d, *J* 6.8, C(3)H_3], 3.63 (1H, A of AB system, J_{AB} 13.0, one of SCH_2), 3.76 (1H, B of AB system, J_{AB} 13.0, one of SCH_2), 4.21 [1H, q, *J* 6.8, C(2)*H*], 7.05 (2H, overlapping dd appears as t, *J* 8.7, *J* 8.7, Ar*H*), 7.19-7.32 (5H, m, Ar*H*), 7.80-7.89 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 16.6 [CH_3, *C*(3)H_3], 34.2 (CH_2, CH_2), 41.9 [CH, *C*(2)H], 115.6 (CH, d, $^2J_{CF}$ 21.9, aromatic *C*H), 127.3, 128.6, 129.2 (3 x CH, aromatic *C*H), 131.3 (CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 131.9 (C, d, $^4J_{CF}$ 3.0, aromatic *C*), 137.2 (C, aromatic *C*), 165.6 (C, d, $^1J_{CF}$ 254.8, aromatic *C*), 194.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{16}OSF[M+H]^+$ 275.0906. Found 275.0891; m/z (ES+) 275.1 [$(C_{16}H_{15}OSF)+H^+$], 14%, 291.0 (100%).

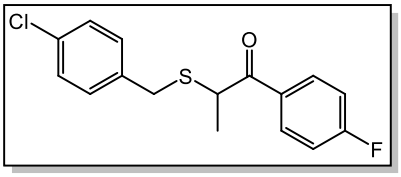
2-(Butylthio)-1-(4-fluorophenyl)propan-1-one 3w



This was synthesised following the procedure described for **3a** using *n*-butanethiol (0.68 g, 0.81 mL, 7.5 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (1.16 g, 6.3 mmol) in dry methanol (20 mL) and freshly prepared sodium methoxide [prepared from sodium (0.173 g, 7.5 mmol) in dry methanol (20 mL) at 0 °C]. The crude *α-thioketone* **3w** was obtained as a yellow oil. Following purification by column chromatography on silica gel using hexane-ethyl acetate (96:4) as eluent, the pure *α-thioketone* **3w** (1.16 g, 77 %) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3076 (CH), 2960 (CH), 1678 (CO), 1598 (aromatic); δ_H (300 MHz, $CDCl_3$) 0.85 (3H, t, *J* 6.9, CH_2CH_3), 1.26-1.39 (2H, m, CH_2CH_3), 1.42-1.52 (2H, m, $CH_2CH_2CH_3$), 1.56 [3H, d, *J* 6.9, C(3)H_3], 2.32-2.58 (2H, m, SCH_2), 4.28 [1H, q, *J* 6.9, C(2)*H*], 7.13 (2H, overlapping dd

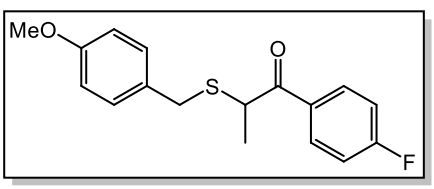
appears as t, *J* 8.7, *J* 8.7, Ar*H*), 8.03-8.07 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, CH_2CH_3), 16.3 [CH_3, *C*(3)H_3], 22.0 (CH_2, CH_2CH_3), 28.3 (CH_2, SCH_2), 31.3 (CH_2, $CH_2CH_2CH_3$), 41.4 [CH, *C*(2)H], 115.6 (CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 131.2 (CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 131.9 (C, d, $^4J_{CF}$ 3.0, aromatic *C*), 165.6 (C, d, $^1J_{CF}$ 254.7, aromatic *C*), 194.5 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{13}H_{18}OSF[M+H]^+$ 241.1062. Found 241.1068; m/z (ES+) 239.2 (4%), 257.1 (100%).

2-((4-Chlorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one 3x



The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.87 g, 0.72 mL, 5.5 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (0.93 g, 5.0 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as an off-white solid which was recrystallised from methanol to give the pure *α-thioketone* **3x** (0.88 g, 57%) as an off-white solid, mp 100-102°C; Found C, 62.38; H, 4.64. $C_{16}H_{14}OSClF$ requires C, 62.23; H, 4.57; ν_{max}/cm^{-1} (ATR) 2933, 1672 (C=O), 1594 (aromatic), 1491, 1157, 836, 502; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, *J* 6.9, C(3)H_3], 3.59 (1H, A of AB system, J_{AB} 13.2, one of SCH_2), 3.71 (1H, B of AB system, J_{AB} 13.2, one of SCH_2), 4.23 [1H, q, *J* 6.9, C(2)*H*], 7.09 (2H, dd appears as t, *J* 8.7, Ar*H*), 7.16 (2H, d, *J* 8.6, Ar*H*), 7.23 (2H, d, *J* 8.5, Ar*H*), 7.89 (2H, dd, *J* 8.9, J_{FH} 5.4, Ar*H*); δ_C (75 MHz, $CDCl_3$): 16.6 [CH_3, *C*(3)H_3], 33.3 (CH_2, SCH_2), 42.0 [CH, *C*(2)H], 115.7 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 128.6, 130.5 (2 x CH signals, 4 x aromatic *C*H), 131.2 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.2, aromatic *C*H), 131.7 (C, d, $^4J_{CF}$ 3.1, aromatic *C*), 133.1, 135.8 (2 x C, aromatic *C*), 165.7 (C, d, $^1J_{CF}$ 255.3, aromatic *C*), 194.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{15}OFS^{35}Cl[M+H^+]$ 309.0516. Found 309.0504; m/z (ES-) 307.2 [$(C_{16}H_{14}OFS^{35}Cl)-H^+$], 19%. $^{35}Cl/^{37}Cl$ pattern visible in HRMS at 309 and 311 in a 3:1 ratio.

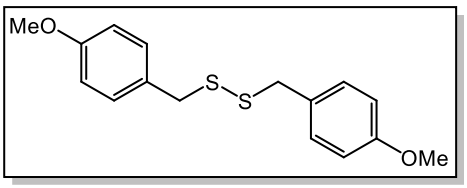
1-(4-Fluorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one 3y



The title compound was prepared following the procedure outlined for **3a** using (4-methoxyphenyl)methanethiol (0.848 g, 0.76 mL, 5.5 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3**

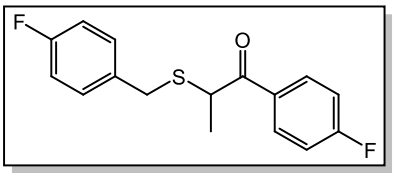
(0.933 g, 5.0 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as an off-white solid which was recrystallised from methanol to give the *α-thioketone* **3y** (0.727 g, 48%) as an off-white solid, mp 48-51°C; Found C, 66.62; H, 5.74. $C_{17}H_{17}O_2FS$ requires C, 67.08; H, 5.63; ν_{max}/cm^{-1} (ATR) 3008, 2952, 2820, 1668 (C=O), 1594, 1510, 1348, 1237, 1222, 1031, 847, 597, 511; δ_H (400 MHz, $CDCl_3$): 1.56 [3H, d, *J* 6.8, C(3)H_3], 3.59 (1H, A of AB system, J_{AB} 13.0, one of SCH_2), 3.72 (1H, B of AB system, J_{AB} 13.0, one of SCH_2), 3.78 (3H, s, OCH_3), 4.21 [1H, q, *J* 6.8, C(2)*H*], 6.81 (2H, d, *J* 8.7, Ar*H*), 7.07 (2H, dd appears as t, *J* 8.7, Ar*H*), 7.16 (2H, d, *J* 8.7, Ar*H*), 7.87 (2H, dd, *J* 8.9, J_{FH} 5.4, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.5 [CH_3, *C*(3)H_3], 33.5 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 55.3 (CH_3, O*C*H_3), 113.9 (1 x CH signal, 2 x aromatic *C*H), 115.5 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 129.0 (C, aromatic *C*), 130.2 (1 x CH signal, 2 x aromatic *C*H), 131.2 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 131.8 (C, d, $^4J_{CF}$ 2.8, aromatic *C*), 158.8 (C, aromatic *C*), 165.6 (C, d, $^1J_{CF}$ 254.8, aromatic *C*), 194.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}O_2FS[M+H^+]$ 305.1012. Found 305.1003.

Approx. 13% of the disulfide by-product **S11** was present in the NMR sample.



Characteristic signals due to **S11**[13]: δ_H (400 MHz, $CDCl_3$) 3.59 (4H, s, SCH_2), 3.79 (6H, s, OCH_3), 6.85 (4H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 42.7 (CH_2, 2 x S*C*H_2), 113.8 (1 x CH signal, 4 x aromatic *C*H), 129.4 (C, 2 x aromatic *C*), 130.5 (1 x CH signal, 4 x aromatic *C*H), 159.0 (C, 2 x aromatic *C*).

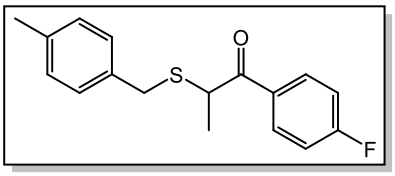
2-((4-Fluorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one 3z



The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.782 g, 0.68 mL, 5.5 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (0.933 g, 5.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.135 g, 6.0 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as an off-white solid which was recrystallised from methanol to give the pure *α-thioketones* **3z** (1.02 g, 70%) as a cream solid, mp 68-70°C; Found C, 65.50; H, 4.86. $C_{16}H_{14}OSF_2$ requires C, 65.74; H, 4.83; ν_{max}/cm^{-1} (ATR) 2977, 2933, 1669 (C=O), 1593, 1505, 1333, 1220, 1154, 950. 848, 833; δ_H (400 MHz, $CDCl_3$): 1.56 [3H, d, *J* 6.9,

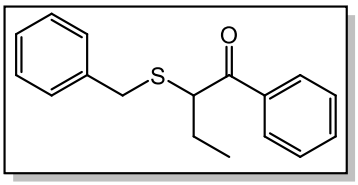
C(3)H_3], 3.59 (1H, A of AB system, J_{AB} 13.0, one of SCH_2), 3.73 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.23 [1H, q, *J* 6.9, C(2)*H*], 6.95 (2H, dd appears as t, *J* 8.7, Ar*H*), 7.09 (2H, dd appears as t, *J* 8.7, Ar*H*), 7.20 (2H, dd, *J* 8.7, J_{FH} 5.3, Ar*H*), 7.91 (2H, dd, *J* 8.9, J_{FH} 5.4, Ar*H*); δ_C (75 MHz, $CDCl_3$): 16.6 [CH_3, *C*(3)H_3], 33.2 (CH_2, S*C*H_2), 42.0 [CH, *C*(2)H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.2, aromatic *C*H), 115.6 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.3, aromatic *C*H), 130.6 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 131.2 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.2, aromatic *C*H), 131.7 (C, d, $^4J_{CF}$ 2.9, aromatic *C*), 132.9 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 161.9 (C, d, $^1J_{CF}$ 246.0, aromatic *C*), 165.6 (C, d, $^1J_{CF}$ 255.0, aromatic *C*), 194.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{15}OF_2S[M+H^+]$ 293.0812. Found 293.0807.

1-(4-Fluorophenyl)-2-((4-methylbenzyl)thio)- propan-1-one 3aa



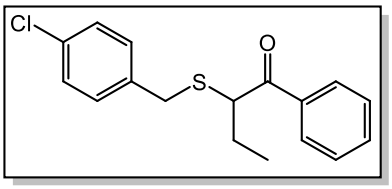
The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.608 g, 0.60 mL, 4.4 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (0.742 g, 4.0 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.110 g, 4.8 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a white solid which was recrystallised from methanol to give the pure *α-thioketone* **3aa** (0.749 g, 65%) as a white solid, mp 87-88°C; Found C, 70.95; H, 5.99. $C_{17}H_{17}OFS$ requires C, 70.80; H, 5.94; ν_{max}/cm^{-1} (ATR) 2980, 2935, 2861, 1673 (C=O), 1594, 1505, 1332, 1229, 1156, 848, 476; δ_H (400 MHz, $CDCl_3$): 1.56 [3H, d, *J* 6.8, C(3)H_3], 2.33 (3H, s, ArCH_3), 3.60 (1H, A of AB system, J_{AB} 12.9, one of SCH_2), 3.73 (1H, B of AB system, J_{AB} 12.9, one of SCH_2), 4.21 [1H, q, *J* 6.8, C(2)*H*], 7.03-7.18 (6H, m, Ar*H*), 7.86 (2H, dd, *J* 8.9, J_{FH} 5.4, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.6 [CH_3, *C*(3)H_3], 21.1 (CH_3, Ar*C*H_3), 33.9 (CH_2, S*C*H_2), 41.9 [CH, *C*(2)H], 115.6 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 129.1, 129.3 (2 x CH signals, 4 x aromatic *C*H), 131.3 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 131.9 (C, d, $^4J_{CF}$ 2.9, aromatic *C*), 134.0, 137.0 (2 x C, aromatic *C*), 165.6 (C, d, $^1J_{CF}$ 254.9, aromatic *C*), 194.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OFS[M+H^+]$ 289.1062. Found 289.1060; m/z (ES+) 289.2 [$(C_{17}H_{17}OFS)+H^+$], 12%.

2-(Benzylthio)-1-phenylbutan-1-one 3bb



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (0.683 g, 0.64 mL, 5.5 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.913 g, 5.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography using gradient elution (hexane:ethyl acetate, 0-2% ethyl acetate) afforded the product **3bb** (0.489 g, 36%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3068, 3034, 2982, 2948, 2879, 1673 (C=O), 1596 (aromatic), 699; δ_H (400 MHz): 0.97 [3H, t, *J* 7.4, C(4)*H*$_3$], 1.81-1.92 [1H, symmetrical m, one of C(3)*H*$_2$], 2.04-2.15 [1H, symmetrical m, one of C(3)*H*$_2$], 3.59 (1H, A of AB system, J_{AB} 12.9, one of SC*H*$_2$), 3.71 (1H, B of AB system, J_{AB} 12.9, one of SC*H*$_2$), 4.04 [1H, t, *J* 7.3, C(2)*H*], 7.17-7.28 (5H, m, Ar*H*), 7.38-7.43 (2H, m, Ar*H*), 7.50-7.54 (1H, m, Ar*H*), 7.85-7.88 (2H, m, Ar*H*); δ_C (100 MHz): 12.0 [CH$_3$, *C*(4)H$_3$], 23.8 [CH$_2$, *C*(3)H$_2$], 34.1 (CH$_2$, S*C*H$_2$), 49.0 [CH, *C*(2)H], 127.1, 128.50, 128.53, 128.58, 129.2, 133.0 (6 x CH signals, 10 x aromatic *C*H), 136.3, 137.4 (2 x C, aromatic *C*), 196.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{19}OS[M+H^+]$ 271.1157. Found 271.1146; m/z (ES+) 271.3 [$(C_{17}H_{18}OS)+H^+$], 90%.

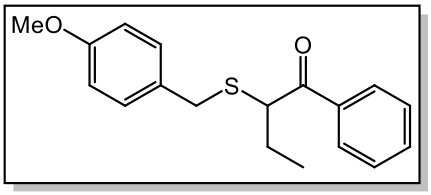
2-((4-Chlorobenzyl)thio)-1-phenylbutan-1-one 3cc



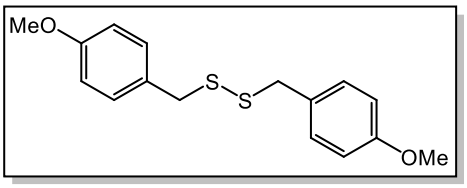
The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.873 g, 0.72 mL, 5.5 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.913 g, 5.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a pale-yellow oil. Column chromatography on silica gel (95:5 hexane:ethyl acetate) afforded the product **3cc** (1.36 g, 89%) as a yellow oil; ν_{max}/cm^{-1} (ATR) 3061, 2966, 2931, 2873, 1672 (C=O), 1595 (aromatic), 1489, 1091, 687; δ_H (400 MHz): 0.98 [3H, t, *J* 7.4, C(4)*H*$_3$], 1.79-1.90 [1H, symmetrical m, one of C(3)*H*$_2$], 2.03-2.14 [1H, symmetrical m, one of C(3)*H*$_2$], 3.55 (1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$), 3.67 (1H, B of AB system, J_{AB} 13.1, one of SC*H*$_2$), 4.04 [1H, t, *J* 7.3, C(2)*H*], 7.15 (2H, d, *J* 8.5, Ar*H*), 7.21 (2H, d, *J* 8.5, Ar*H*), 7.41-7.45 (2H, m, Ar*H*), 7.53-7.57 (1H, m, Ar*H*), 7.86-7.89 (2H, m, Ar*H*); δ_C (100 MHz): 12.0

[CH_3, *C*(4)H_3], 23.8 [CH_2, *C*(3)H_2], 33.2 (CH_2, S*C*H_2), 49.1 [CH, *C*(2)H], 128.4, 128.5, 128.6, 130.4 (4 x CH signals, 8 x aromatic *C*H), 132.9 (C, aromatic *C*), 133.0 (CH, aromatic *C*H), 136.0, 136.1 (2 x C, aromatic *C*), 195.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OS^{35}Cl[M+H^+]$ 305.0767. Found 305.0762. $^{35}Cl/^{37}Cl$ pattern visible in HRMS at 305 and 307 in a 3:1 ratio.

2-((4-Methoxybenzyl)thio)-1-phenylbutan-1-one 3dd

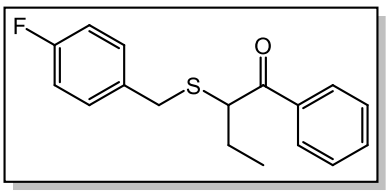


The title compound was prepared following the procedure outlined for **3a** using 4-methoxybenzyl mercaptan (0.463 g, 0.41 mL, 3.0 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.50 g, 2.7 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (74 mg, 3.2 mmol) in methanol (15 mL) at 0°C]. The product **3dd** (0.795 g, 98%) was obtained as a pale orange oil which contained *approx*. 5% disulfide **S11**[13] impurity. No purification was carried out; ν_{max}/cm^{-1} (ATR) 2964, 2932, 2873, 2835, 1672 (C=O), 1609 (aromatic), 1509, 1243, 688; δ_H (400 MHz): 0.98 [3H, t, *J* 7.3, C(4)*H*$_3$], 1.80-1.94 [1H, symmetrical m, one of C(3)*H*$_2$], 2.03-2.17 [1H, symmetrical m, one of C(3)*H*$_2$], 3.55 (1H, A of AB system, J_{AB} 12.8, one of SC*H*$_2$), 3.68 (1H, B of AB system, J_{AB} 12.8, one of SC*H*$_2$), 3.76 (3H, s, OC*H*$_3$), 4.03 [1H, t, *J* 7.3, C(2)*H*], 6.79 (2H, d, *J* 8.7, Ar*H*), 7.15 (2H, d, *J* 8.6, Ar*H*), 7.39-7.47 (2H, m, Ar*H*), 7.51-7.57 (1H, m, Ar*H*), 7.85-7.93 (2H, m, Ar*H*); δ_C (100 MHz): 12.0 [CH_3, *C*(4)H_3], 23.8 [CH_2, *C*(3)H_2], 33.5 (CH_2, S*C*H_2), 49.0 [CH, *C*(2)H], 55.2 (CH_3, O*C*H_3), 113.9, 128.4, 128.5 (3 x CH signals, 6 x aromatic *C*H), 129.2 (C, aromatic *C*), 130.3, 132.9 (2 x CH signals, 3 x aromatic *C*H), 136.2, 158.7 (2 x C, aromatic *C*), 196.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{21}O_2S[M+H^+]$ 301.1262. Found 301.1261.



Characteristic signals due to **S11**[13]: δ_H (400 MHz, $CDCl_3$) 3.58 (4H, s, SC*H*$_2$), 3.78 (6H, s, OC*H*$_3$).

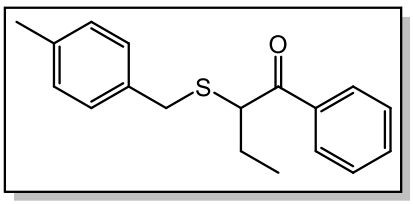
2-((4-Fluorobenzyl)thio)-1-phenylbutan-1-one 3ee



The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.427 g, 0.36 mL, 3.0 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.50 g, 2.7

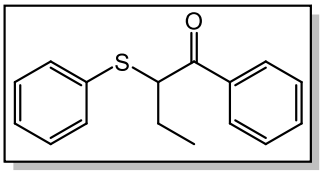
mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (74 mg, 3.2 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography on silica gel (99:1 hexane:ethyl acetate) afforded the product **3ee** (0.592 g 76%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3065, 2967, 2931, 2874, 1672 (C=O), 1597 (aromatic), 1507, 1220, 687; δ_H (400 MHz): 0.99 [3H, t, *J* 7.4, C(4)*H*$_3$], 1.78-1.93 [1H, symmetrical m, one of C(3)*H*$_2$], 2.02-2.18 [1H, symmetrical m, one of C(3)*H*$_2$], 3.57 (1H, A of AB system, J_{AB} 13.4, one of SC*H*$_2$), 3.69 (1H, B of AB system, J_{AB} 13.3, one of SC*H*$_2$), 4.04 [1H, t, *J* 7.3, C(2)*H*], 6.93 (2H, t, *J* 8.7, Ar*H*), 7.19 (2H, dd, *J* 8.6, J_{FH} 5.4, Ar*H*), 7.40-7.49 (2H, m, Ar*H*), 7.52-7.60 (1H, m, Ar*H*), 7.86-7.95 (2H, m, Ar*H*); δ_C (100 MHz): 12.0 [CH_3, *C*(4)H_3], 23.8 [CH_2, *C*(3)H_2], 33.2 (CH_2, S*C*H_2), 49.1 [CH, *C*(2)H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H), 128.4, 128.6 (2 x CH signals, 4 x aromatic *C*H), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 133.1 (CH, aromatic *C*H), 133.1 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 136.2 (C, aromatic *C*), 161.9 (C, d, $^1J_{CF}$ 245.7, aromatic *C*), 195.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OSF[M+H^+]$ 289.1062. Found 289.1052; m/z (ES+) 289.2 [($C_{17}H_{17}OSF$)+H^+], 16%.

2-((4-Methylbenzyl)thio)-1-phenylbutan-1-one 3ff



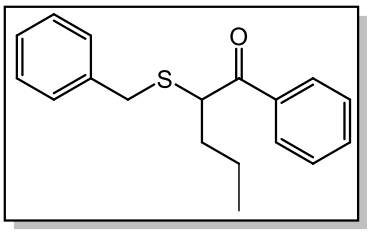
The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.415 g, 0.41 mL, 3.0 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.502 g, 2.7 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (74 mg, 3.2 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a yellow oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **3ff** (0.592 g, 77%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3052, 3024, 2965, 2928, 2873, 1673 (C=O), 1596 (aromatic), 1446, 1221, 709, 687; δ_H (400 MHz): 0.98 [3H, t, *J* 7.3, C(4)*H*$_3$], 1.80-1.94 [1H, symmetrical m, one of C(3)*H*$_2$], 2.03-2.18 [1H, symmetrical m, one of C(3)*H*$_2$], 2.31 (3H, s, ArC*H*$_3$), 3.56 (1H, A of AB system, J_{AB} 12.7, one of SC*H*$_2$), 3.69 (1H, B of AB system, J_{AB} 12.7, one of SC*H*$_2$), 4.03 [1H, t, *J* 7.3, C(2)*H*], 7.06 (2H, d, *J* 7.8, Ar*H*), 7.12 (2H, d, *J* 7.8, Ar*H*), 7.38-7.47 (2H, m, Ar*H*), 7.50-7.59 (1H, m, Ar*H*), 7.87 (2H, d, *J* 7.6, Ar*H*); δ_C (100 MHz): 12.1 [CH_3, *C*(4)H_3], 21.1 (CH_3, Ar*C*H_3), 23.8 [CH_2, *C*(3)H_2], 33.8 (CH_2, S*C*H_2), 49.0 [CH, *C*(2)H], 128.50, 128.53, 129.1, 129.2, 132.9 (5 x CH signals, 9 x aromatic *C*H), 134.2, 136.3, 136.8 (3 x C, aromatic *C*), 196.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{21}OS[M+H^+]$ 285.1313. Found 285.1313; m/z (ES+) 285.2 [($C_{18}H_{20}OS$)+H^+], 26%.

1-Phenyl-2-(phenylthio)butan-1-one 3gg



The title compound was prepared following the procedure outlined for **3a** using thiophenol (0.364 g, 0.34 mL, 3.3 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.548 g, 3.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (83 mg, 3.6 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a yellow oil. Column chromatography on silica gel (90:10 hexane:ethyl acetate) afforded the product **3gg** (0.66 g, 86%) as a yellow oil; ν_{max}/cm^{-1} (ATR) 3058, 2966, 2930, 2874, 1675 (C=O), 1446, 745, 687; δ_H (400 MHz): 1.05 [3H, t, *J* 7.4, C(4)H_3], 1.80-1.94 [1H, symmetrical m, one of C(3)H_2], 1.97-2.11 [1H, symmetrical m, one of C(3)H_2], 4.37 [1H, t, *J* 7.2, C(2)*H*], 7.21-7.31 (3H, m, Ar*H*), 7.31-7.38 (2H, m, Ar*H*), 7.39-7.47 (2H, m, Ar*H*), 7.51-7.58 (1H, m, Ar*H*), 7.91 (2H, d, *J* 7.4, Ar*H*); δ_C (100 MHz): 11.9 [CH_3, *C*(4)H_3], 24.3 [CH_2, *C*(3)H_2], 53.4 [CH, *C*(2)H], 128.50, 128.54, 128.56, 128.9 (4 x CH signals, 8 x aromatic *C*H), 132.2 (C, aromatic *C*), 133.0, 134.4 (2 x CH, aromatic *C*H), 136.4 (C, aromatic *C*), 196.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{17}OS[M+H^+]$ 257.1000. Found 257.1001; m/z (ES+) 257.3 [$(C_{16}H_{16}OS)+H^+$], 100%.

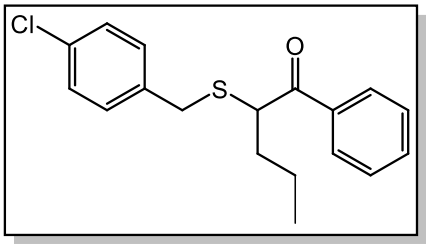
2-(Benzylthio)-1-phenylpentan-1-one 3hh



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (0.385 g, 0.36 mL, 3.1 mmol), 2-chloro-1-phenylpentan-1-one **S7** (0.55 g, 2.8 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (78 mg, 3.4 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **3hh** (0.687 g, 86%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3061, 3028, 2957, 2930, 2871, 1671 (C=O), 1596 (aromatic), 698, 687; δ_H (400 MHz): 0.89 [3H, t, *J* 7.4, C(5)H_3], 1.30-1.49 [2H, m, C(4)H_2], 1.75-1.87 [1H, symmetrical m, one of C(3)H_2], 2.01-2.12 [1H, symmetrical m, one of C(3)H_2], 3.60 (1H, A of AB system, J_{AB} 12.9, one of SCH_2), 3.72 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.12 [1H, t, *J* 7.3, C(2)*H*], 7.17-7.30 (5H, m, Ar*H*), 7.41 (2H, t, *J* 7.7, Ar*H*), 7.53 (1H, t, *J* 7.6, Ar*H*), 7.86 (2H, d, *J* 7.3, Ar*H*); δ_C (100 MHz): 13.9 [CH_3, *C*(5)H_3], 20.7 [CH_2, *C*(4)H_2], 32.7 [CH_2, *C*(3)H_2 or S*C*H_2], 34.2 [CH_2, *C*(3)H_2 or S*C*H_2], 47.0 [CH, *C*(2)H], 127.2, 128.49, 128.50, 128.6, 129.2, 133.0 (6 x CH signals,

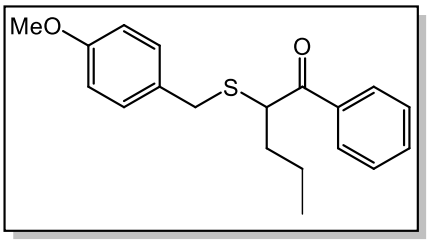
10 x aromatic *C*H), 136.3, 137.4 (2 x C, aromatic *C*), 196.0 (C, *C*O); m/z (ES+) 285.2 [($C_{18}H_{20}OS$)+H^+], 18%.

2-((4-Chlorobenzyl)thio)-1-phenylpentan-1-one 3ii



The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.492 g, 0.41 mL, 3.1 mmol), 2-chloro-1-phenylpentan-1-one **S7** (0.55 g, 2.8 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (78 mg, 3.4 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **3ii** (0.648 g, 73%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3061, 2958, 2930, 2871, 1672 (C=O), 1596 (aromatic), 1489, 1091, 687; δ_H (400 MHz): 0.90 [3H, t, *J* 7.4, C(5)H_3], 1.28-1.52 [2H, m, C(4)H_2], 1.73-1.85 [1H, symmetrical m, one of C(3)H_2], 1.98-2.12 [1H, symmetrical m, one of C(3)H_2], 3.56 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 3.68 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 4.12 [1H, t, *J* 7.3, C(2)*H*], 7.16 (2H, d, *J* 8.4, Ar*H*), 7.21 (2H, d, *J* 8.4, Ar*H*), 7.39-7.49 (2H, m, Ar*H*), 7.52-7.59 (1H, m, Ar*H*), 7.84-7.92 (2H, m, Ar*H*); δ_C (100 MHz): 13.8 [CH_3, *C*(5)H_3], 20.6 [CH_2, *C*(4)H_2], 32.6 [CH_2, *C*(3)H_2 or S*C*H_2], 33.4 [CH_2, *C*(3)H_2 or S*C*H_2], 47.0 [CH, *C*(2)H], 128.4, 128.6, 130.5 (3 x CH signals, 8 x aromatic *C*H), 132.9 (C, aromatic *C*), 133.1 (CH, aromatic *C*H), 136.0, 136.1 (2 x C, aromatic *C*), 195.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{20}OSCl$[M+H^+] 319.0923. Found 319.0916; m/z (ES+) 319.2 [($C_{18}H_{19}OS^{35}Cl$)+H^+], 100%, 321.2 [($C_{18}H_{19}OS^{37}Cl$)+H^+], 40%.

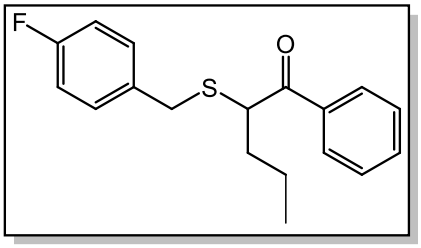
2-((4-Methoxybenzyl)thio)-1-phenylpentan-1-one 3jj



The title compound was prepared following the procedure outlined for **3a** using 4-methoxybenzyl mercaptan (0.424 g, 0.38mL, 2.8mmol), 2-chloro-1-phenylpentan-1-one **S7** (0.50 g, 2.5 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (69 mg, 3.0 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a yellow oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **3jj** (0.494 g, 63%) as a yellow oil; ν_{max}/cm^{-1} (ATR) 2957, 2934, 2871, 2834, 1673 (C=O), 1609

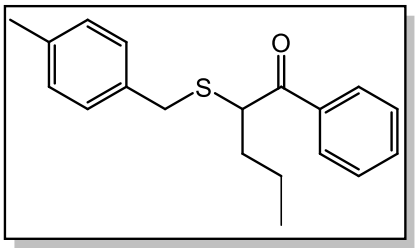
(aromatic), 1510, 1241, 688; δ_H (400 MHz): 0.90 [3H, t, *J* 7.4, C(5)H_3], 1.28-1.52 [2H, m, C(4)H_2], 1.75-1.87 [1H, symmetrical m, one of C(3)H_2], 2.00-2.13 [1H, symmetrical m, one of C(3)H_2], 3.56 (1H, A of AB system, J_{AB} 12.8, one of SCH_2), 3.68 (1H, B of AB system, J_{AB} 12.8, one of SCH_2),3.76 (3H, s, OCH_3), 4.11 [1H, t, *J* 7.3, C(2)*H*], 6.78 (2H, d, *J* 8.6, Ar*H*), 7.15 (2H, d, *J* 8.6, Ar*H*), 7.41 (2H, t, *J* 7.7, Ar*H*), 7.53 (1H, t, *J* 7.8, Ar*H*), 7.87 (2H, d, *J* 7.5, Ar*H*); δ_C (100 MHz): 13.8 [CH_3, *C*(5)H_3], 20.7 [CH_2, *C*(4)H_2], 32.7 [CH_2, *C*(3)H_2 or SCH_2], 33.6 [CH_2, *C*(3)H_2 or SCH_2], 47.0 [CH, *C*(2)H], 55.2 (CH_3, OCH_3), 113.9 (1 x CH signal, 2 x aromatic *C*H), 128.4, 128.5 (2 x CH signals, 4 x aromatic *C*H), 129.2 (C, aromatic *C*), 130.2, 132.9 (2 x CH signals, 3 x aromatic *C*H), 136.3, 158.7 (2 x C, aromatic *C*), 196.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{19}H_{23}O_2S$[M+H^+] 315.1419. Found 315.1422; m/z (ES-) 313.3 [($C_{19}H_{22}O_2S$)-H^+], 10%.

2-((4-Fluorobenzyl)thio)-1-phenylpentan-1-one 3kk



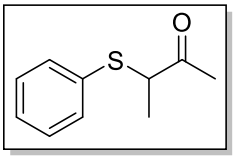
The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.391 g, 0.33 mL, 2.8 mmol), 2-chloro-1-phenylpentan-1-one **S7** (0.50 g, 2.5 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (69 mg, 3.0mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a yellow oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **3kk** (0.614 g, 81%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 2958, 2934, 2871, 1672 (C=O), 1597 (aromatic), 1507, 1222, 687; δ_H (400 MHz): 0.89 [3H, t, *J* 7.4, C(5)H_3], 1.28-1.52 [2H, m, C(4)H_2], 1.73-1.87 [1H, symmetrical m, one of C(3)H_2], 1.98-2.12 [1H, symmetrical m, one of C(3)H_2], 3.57 (1H, A of AB system, J_{AB} 13.0, one of SCH_2), 3.69 (1H, B of AB system, J_{AB} 13.0, one of SCH_2), 4.12 [1H, t, *J* 7.3, C(2)*H*], 6.92 (2H, dd appears as t, *J* 8.7, Ar*H*), 7.18 (2H, dd, *J* 8.6, J_{FH} 5.4, Ar*H*), 7.42 (2H, t, *J* 7.7, Ar*H*), 7.53 (1H, t, *J* 7.6, Ar*H*), 7.85-7.93 (2H, m, Ar*H*); δ_C (100 MHz): 13.8 [CH_3, *C*(5)H_3], 20.6 [CH_2, *C*(4)H_2], 32.6 [CH_2, *C*(3)H_2 or SCH_2], 33.2 [CH_2, *C*(3)H_2 or SCH_2], 47.0 [CH, *C*(2)H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.6, aromatic *C*H), 128.4, 128.6 (2 x CH signals, 4 x aromatic *C*H), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 133.0 (CH, aromatic *C*H), 133.1 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 136.2 (C, aromatic *C*), 161.9 (C, d, $^1J_{CF}$ 245.7, aromatic *C*), 195.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{20}OFS$[M+H^+] 303.1219. Found 303.1214; m/z (ES+) 303.2 [($C_{18}H_{19}OFS$)+H^+], 100%.

2-((4-Methylbenzyl)thio)-1-phenylpentan-1-one 3ll



The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.511 g, 0.5 mL, 3.7 mmol), 2-chloro-1-phenylpentan-1-one **S7** (0.661 g, 3.3 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (92 mg, 4.0 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **3ll** (0.823 g, 82%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3052, 3023, 2957, 2929, 2871, 1672 (C=O), 1598 (aromatic), 1446, 687; δ_H (400 MHz): 0.90 [3H, t, *J* 7.3, C(5)H_3], 1.30-1.53 [2H, m, C(4)H_2], 1.75-1.94 [1H, symmetrical m, one of C(3)H_2], 2.01-2.20 [1H, symmetrical m, one of C(3)H_2], 2.31 (3H, s, ArCH_3), 3.57 (1H, A of AB system, J_{AB} 12.8, one of SCH_2), 3.70 (1H, B of AB system, J_{AB} 12.7, one of SCH_2), 4.11 [1H, t, *J* 7.5, C(2)*H*], 7.02-7.23 (4H, m, Ar*H*), 7.41 (2H, t, *J* 7.6, Ar*H*), 7.54 (1H, t, *J* 7.4, Ar*H*), 7.86 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz): 13.8 [CH_3, *C*(5)H_3], 20.6 [CH_2, *C*(4)H_2], 21.1 (CH_3, Ar*C*H_3), 32.6 [CH_2, *C*(3)H_2 or S*C*H_2], 33.9 [CH_2, *C*(3)H_2 or S*C*H_2], 46.9 [CH, *C*(2)H], 128.50, 128.52, 129.1, 129.2, 132.9 (5 x CH signals, 9 x aromatic *C*H), 134.1, 136.2, 136.8 (3 x C, aromatic *C*), 196.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{19}H_{23}OS[M+H^+]$ 299.1470. Found 299.1471; m/z (ES+) 299.3 [$(C_{19}H_{22}OS)+H^+$], 92%.

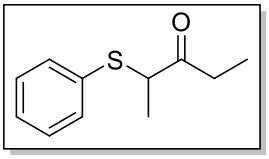
3-(Phenylthio)butan-2-one 5a[15]



The title compound was prepared following the procedure outlined for **3a** using thiophenol (8.64 g, 8.10 mL, 78.5 mmol), 3-chloro-2-butanone (6.96 g, 6.60 mL, 70.4 mmol) and freshly prepared sodium ethoxide [prepared from sodium (1.85 g, 78.5 mmol) in dry ethanol (150 mL) at 0°C] to give the *α-thioketone* **5a** (9.75 g, 83%) as an orange oil which required no further purification; ν_{max}/cm^{-1} (film) 3000 (CH), 1705 (CO), 1571; δ_H (300 MHz, $CDCl_3$) 1.40 (3H, d, *J* 6.9, CHCH_3), 2.25 (3H, s, COCH_3), 3.75 (1H, q, *J* 6.9, C*H*SPh), 7.20-7.45 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 16.1 (CH_3, CH*C*H_3), 26.4 (CH_3, CO*C*H_3), 52.1 (CH, *C*HSPh), 128.0, 129.1, 132.7 (3 x CH, aromatic *C*H), 137.8 (C, aromatic *C*), 205.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{13}OS[M+H^+]$ 181.0687. Found 181.0689; m/z (ES+) 181.1 [$(C_{10}H_{12}OS)+H^+$], 24%, 197.0 (100%).

Spectroscopic characteristics were consistent with those previously reported.[15]

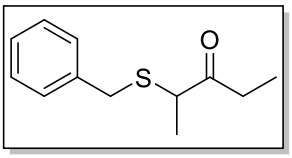
2-(Phenylthio)pentan-3-one 5b[16]



The title compound was prepared following the procedure outlined for **3a** using thiophenol (1.04 g, 0.96 mL, 9.4 mmol), 2-chloropentan-3-one **S5** (0.95 g, 7.9 mmol) in ethanol (10 mL) and freshly prepared sodium ethoxide [prepared from sodium (0.217 g, 9.4 mmol) in dry ethanol (10 mL) at 0°C]. The crude *α-thioketone* **5b** was isolated as an orange oil. The *α-thioketone* **5b** (1.31 g, 86%) was isolated as a yellow oil which contained some unidentified impurities (~18%); ν_{max}/cm^{-1} (film) 3060 (CH), 2977 (CH), 2936 (CH), 1710 (CO), 1439; δ_H (300 MHz, $CDCl_3$) 1.05 (3H, t, *J* 7.3, CH_2CH_3), 1.41 (3H, d, *J* 7.1, $CHCH_3$), 2.48-2.62 (1H, m, one of CH_2CH_3), 2.67-2.80 (1H, m, one of CH_2CH_3), 3.78 (1H, q, *J* 7.1, *CH*SPh), 7.26-7.39 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 8.1, 16.3 (2 x CH_3, CH_2CH_3 and $CHCH_3$), 32.4 (CH_2, CH_2CH_3), 51.2 (CH, *C*HSPh), 128.0, 129.1, 132.8 (3 x CH, aromatic *C*H), 136.2 (C, aromatic *C*), 208.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{11}H_{15}OS[M+H^+]$ 195.0844. Found 195.0838; m/z (ES+) 195.1 $[(C_{11}H_{14}OS)+H^+]$, 26%.

Spectroscopic characteristics were consistent with those previously reported.[16]

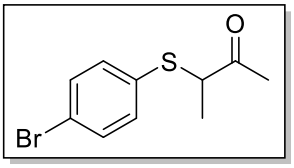
2-(Benzylthio)pentan-3-one 5c[11]



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (1.71 g, 1.11 mL, 9.4 mmol), 2-chloropentan-3-one **S5** (0.95 g, 7.9 mmol) and freshly prepared sodium ethoxide [prepared from sodium (0.217 g, 9.4 mmol) in dry ethanol (20 mL) at 0°C] to give the crude *α-thioketone* **5c** as an orange oil. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to remove the dibenzyl disulfide **S13** impurity seen in the ^{1}H NMR spectrum of the crude material as a characteristic singlet at 3.59 ppm. The pure *α-thioketone* **5c** (0.77 g, 50%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3063 (CH), 2976 (CH), 2935 (CH), 1707 (CO), 1454; δ_H (300 MHz, $CDCl_3$) 1.04 (3H, t, *J* 7.3, CH_2CH_3), 1.36 (3H, d, *J* 7.1, $CHCH_3$), 2.47-2.69 (2H, m, CH_2CH_3), 3.31 (1H, q, *J* 7.1, *CH*SBn), 3.59 (1H, A of AB system, *J* 13.1, one of SCH_2), 3.67 (1H, B of AB system, *J* 13.1, one of SCH_2), 7.18-7.30 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 8.3 (CH_3, CH_2CH_3), 15.9 (CH_3, $CHCH_3$), 31.4 (CH_2, CH_2CH_3), 34.8 (CH_2, SCH_2), 47.3 (CH, *C*HSBn), 127.2, 128.5, 129.1 (3 x CH, aromatic *C*H), 137.5 (C, aromatic *C*), 208.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{12}H_{17}OS[M+H^+]$ 209.1000. Found 209.0920; m/z (ES+) 209.1 $[(C_{12}H_{16}OS)+H^+]$, 62%.

Spectroscopic characteristics were consistent with those previously reported. [11]

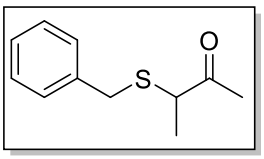
3-[(4-Bromophenyl)thio]butan-2-one 5d[17]



The title compound was prepared following the procedure outlined for **3a** using 4-bromothiophenol (8.51 g, 45.0 mmol), 3-chloro-2-butanone (4.36 g, 4.13 mL, 40.9 mmol) and freshly prepared sodium ethoxide [prepared from sodium (1.04 g, 45.0 mmol) in dry ethanol (135 mL) at 0°C] to give the crude *α-thioketone* **5d** as an orange oil. This was purified by column chromatography on silica gel using hexane-ethyl acetate (80:20) as eluent. The pure *α-thioketone* **5d** (6.11 g, 58%) was isolated as an orange oil; ν_{max}/cm^{-1} (film) 3079 (CH), 2974 (CH), 1710 (CO), 1473; δ_H (400 MHz, $CDCl_3$) 1.41 (3H, d, *J* 7.1, CHC*H*$_3$), 2.29 (3H, s, COC*H*$_3$), 3.73 (1H, q, *J* 7.1, C*H*SAr), 7.22 (2H, d, *J* 8.4, Ar*H*), 7.42 (2H, d, *J* 8.4, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 16.0 (CH_3, CH*C*H$_3$), 26.2 (CH_3, CO*C*H$_3$), 51.9 (CH, *C*HSAr), 123.0, 131.8 (2 x C, 2 x aromatic *C*), 132.2, 134.2 (2 x CH, aromatic *C*H), 205.1 (C, *C*O); m/z (ES+) 275.1 [($C_{10}H_{11}{}^{79}BrOS$)+H_2O^+], 96%, 277.1 [($C_{10}H_{11}{}^{81}BrOS$)+H_2O^+], 100%.

Spectroscopic characteristics were consistent with those previously reported.[17]

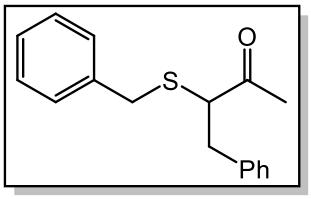
3-(Benzylthio)butan-2-one 5e[11]



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (10.48 g, 9.91 mL, 84.4 mmol), 3-chloro-2-butanone (7.50 g, 7.11 mL, 70.4 mmol) and freshly prepared sodium ethoxide [prepared from sodium (1.94 g, 84.4 mmol) in dry ethanol (150 mL) at 0°C] to give the crude *α-thioketone* **5e** as an orange oil. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent. The pure *α-thioketone* **5f** (11.7 g, 86%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3000 (CH), 1714 (CO), 1583; δ_H (300 MHz, $CDCl_3$) 1.35 (3H, d, *J* 7.2, CHC*H*$_3$), 2.22 (3H, s, COC*H*$_3$), 3.25 (1H, q, *J* 7.2, C*H*SBn), 3.59 (1H, A of AB system, *J* 13.2, one of SC*H*$_2$), 3.65 (1H, B of AB system, *J* 13.2, one of SC*H*$_2$), 7.18-7.32 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 15.9 (CH_3, CH*C*H$_3$), 25.5 (CH_3, CO*C*H$_3$), 35.0 (CH_2, S*C*H$_2$), 48.2 (CH, *C*HSBn), 127.2, 128.6, 129.1 (3 x CH, aromatic *C*H), 137.5 (C, aromatic *C*), 205.6 (C, *C*O); m/z (ES+) 195.1 [($C_{11}H_{14}O$)+H^+], 20%, 211.0 (100%).

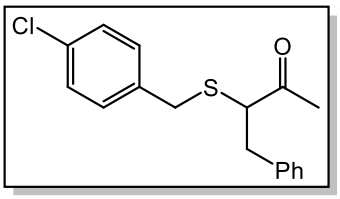
Spectroscopic characteristics were consistent with those previously reported.[11]

3-(Benzylthio)-4-phenylbutan-2-one 10a



The title compound was prepared following the procedure outlined for **3a** using benzyl mercaptan (0.295 g, 0.28 mL, 2.4 mmol), 3-chloro-4-phenylbutan-2-one **S8** (0.395 g, 2.1 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (59 mg, 2.6 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a yellow oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **10a** (0.454 g, 77%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3085, 3061, 3028, 2920, 2850, 1702 (C=O), 1494, 1453, 1353, 696; δ_H (400 MHz): 2.14 (3H, s, C*H*$_3$), 2.90 [1H, overlapping dd, *J* 14.1, 6.9, one of C(4)*H*$_2$], 3.17 [1H, overlapping dd, *J* 14.1, 8.5, one of C(4)*H*$_2$], 3.46 [1H, t, *J* 7.7, C(3)*H*], 3.61 (2H, s, SC*H*$_2$), 7.11 (2H, d, *J* 7.0, Ar*H*), 7.18-7.32 (8H, m, Ar*H*); δ_C (100 MHz): 27.0 (CH_3, *C*H_3), 35.2 [CH_2, S*C*H_2 or *C*(4)H_2], 36.5 [CH_2, S*C*H_2 or *C*(4)H_2], 54.5 [CH, *C*(3)H], 126.7, 127.3, 128.5, 128.6, 128.9, 129.1 (6 x CH signals, 10 x aromatic *C*H), 137.2, 138.1 (2 x C, aromatic *C*), 204.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{19}OS[M+H^+]$ 271.1157. Found 271.1153.

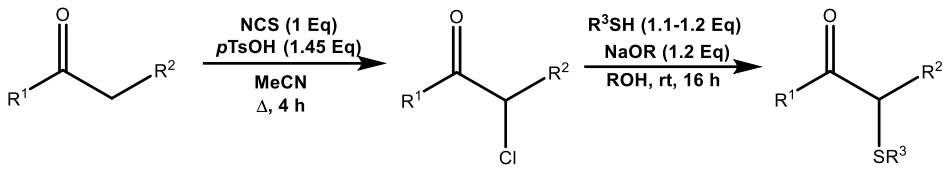
3-((4-Chlorobenzyl)thio)-4-phenylbutan-2-one S14



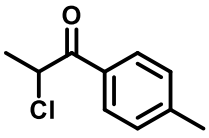
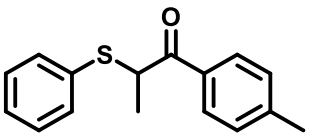
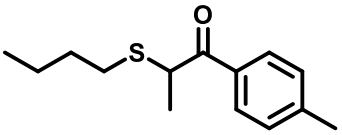
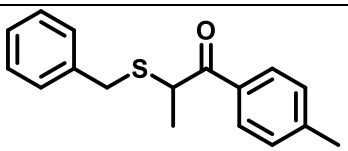
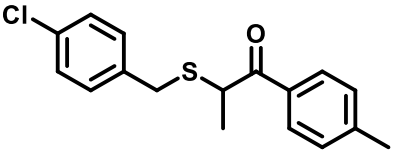
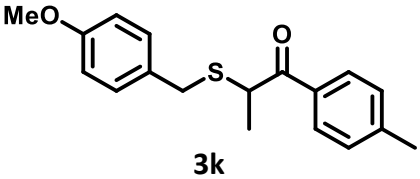
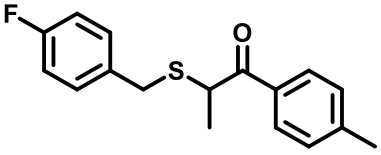
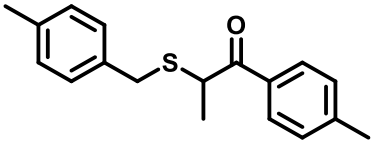
The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.247 g, 0.23 mL, 1.7 mmol), 3-chloro-4-phenylbutan-2-one **S8** (0.288 g, 1.5 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (43 mg, 1.8 mmol) in methanol (20 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography on silica gel (50:50 hexane:dichloromethane) afforded the product **S14** (0.353 g, 74%) as a colourless oil; ν_{max}/cm^{-1} (ATR) 3085, 3062, 3028, 2919, 1702 (C=O), 1489, 1353, 1091, 697, 499; δ_H (400 MHz): 2.17 (3H, s, C*H*$_3$), 2.89 [1H, overlapping dd, *J* 14.1, 7.1, one of C(4)*H*$_2$], 3.15 [1H, overlapping dd, *J* 14.1, 8.5, one of C(4)*H*$_2$], 3.43 [1H, t, *J* 7.7, C(3)*H*], 3.55 (1H, A of AB system, J_{AB} 13.4, SC*H*$_2$), 3.59 (1H, B of AB system, J_{AB} 13.4, SC*H*$_2$), 7.11 (2H, d, *J* 7.5, Ar*H*), 7.14-7.32 (7H, m, Ar*H*); δ_C (100 MHz): 26.8 (CH_3, *C*H_3), 34.4 [CH_2, S*C*H_2 or *C*(4)H_2], 36.4 [CH_2, S*C*H_2 or *C*(4)H_2], 54.4 [CH, *C*(3)H], 126.7, 128.5, 128.7, 128.9, 130.4 (5 x CH signals, 9 x aromatic *C*H), 133.1,

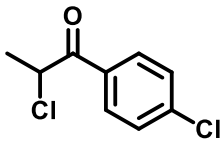
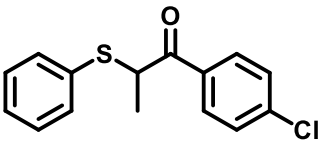
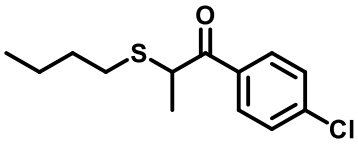
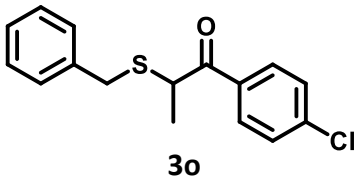
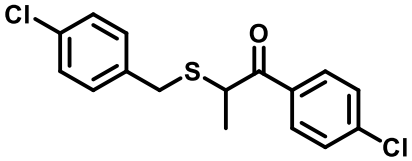
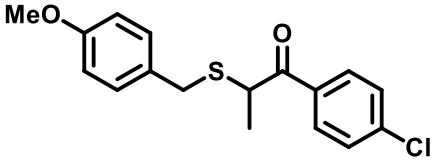
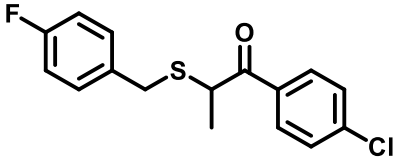
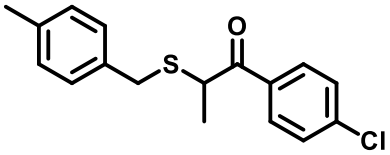
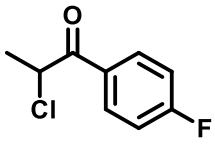
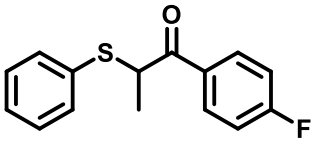
135.7, 137.9 (3 x C, aromatic *C*), 204.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OS^{35}Cl[M+H^+]$ 305.0767. Found 305.0760.

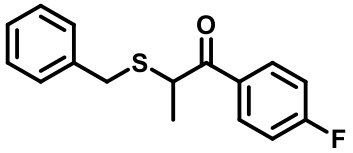
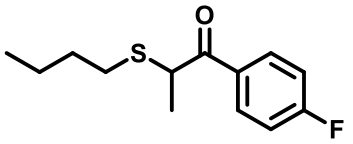
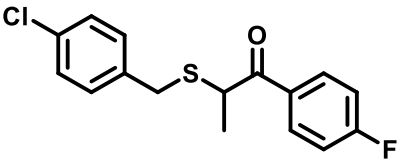
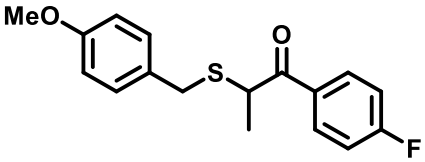
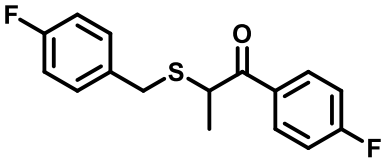
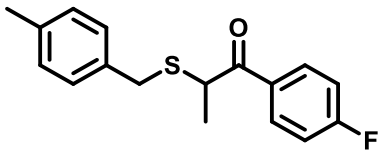
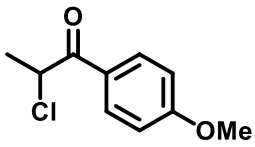
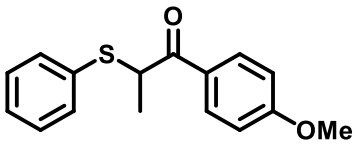
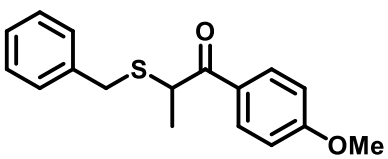
1.4 Table of α-chloroketones and α-sulfenylketones

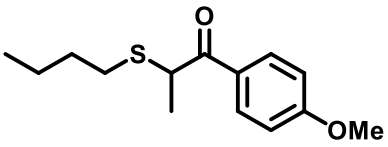
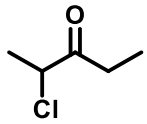
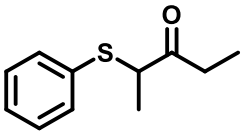
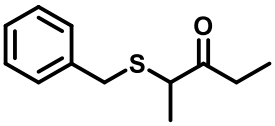
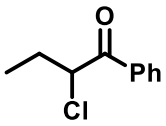
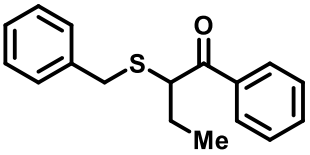
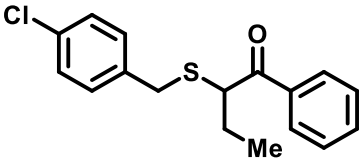
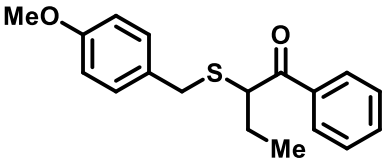
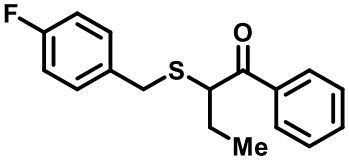
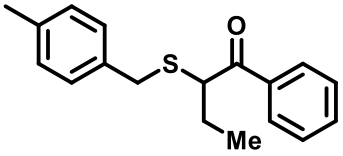


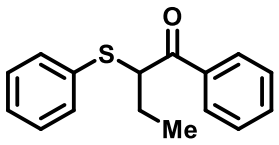
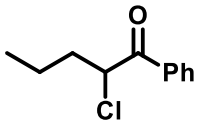
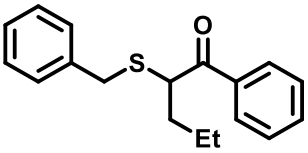
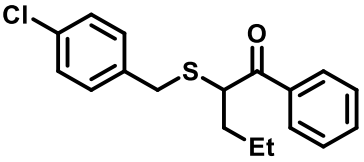
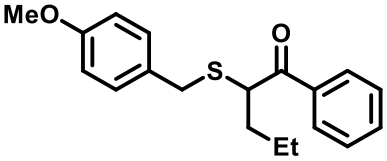
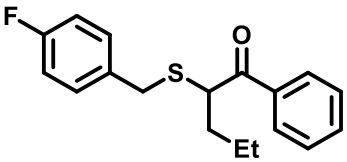
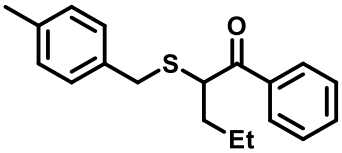
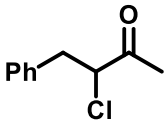
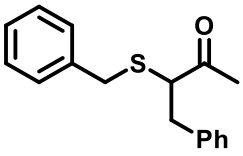
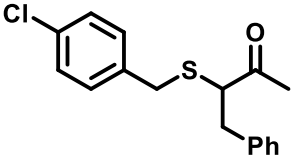
Ketone α-Chloroketone α-Sulfenylketone

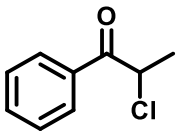
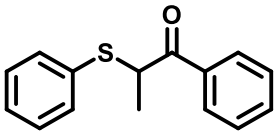
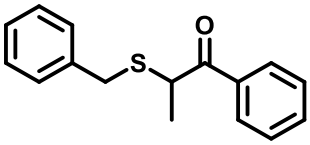
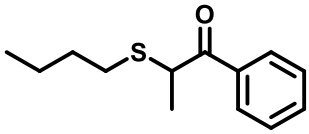
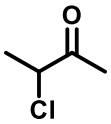
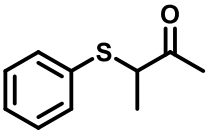
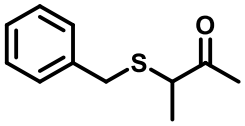
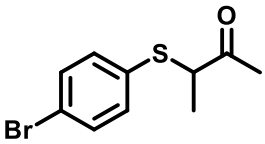
α-Chloroketone	% Yield	α-Sulfenylketone	% Yield
 **S1**[1]	71	 **3g**[12]	62
		 **3i**	97
		 **3h**	61
		 **3j**	72
		 **3k**	79
		 **3l**	44
		 **3m**	72

 **S2**[2-3]	72	 **3n**	87
		 **3p**	85
		 **3o**	58
		 **3q**	69
		 **3r**	64
		 **3s**	65
		 **3t**	73
 **S3**[4]	89	 **3u**	59

		 **3v**	77
		 **3w**	77
		 **3x**	57
		 **3y**	48
		 **3z**	70
		 **3aa**	65
 **S4**[2, 5]	87	 **3d**	69
		 **3e**	84

		 **3f**	81
 **S5**[6]	80[a]	 **5b**[16]	86
		 **5c**[11]	50
 **S6**[7]	74	 **3bb**	36
		 **3cc**	89
		 **3dd**	98
		 **3ee**	76
		 **3ff**	77

		 **3gg**	86
 **S7**[8]	73	 **3hh**	86
		 **3ii**	73
		 **3jj**	63
		 **3kk**	81
		 **3ll**	82
 **S8**[3]	28	 **10a**	77
		 **S16**	74

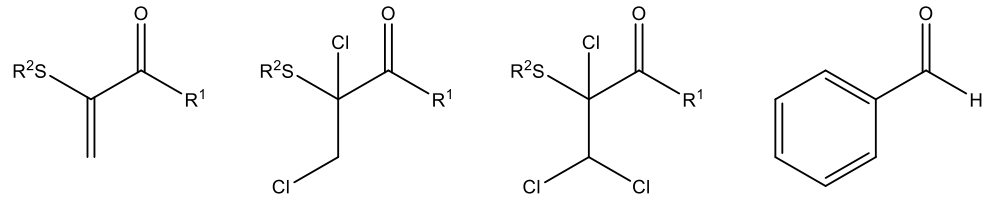
	Commercially available	 **3a**[10]	97
		 **3b**[11]	54
		 **3c**	64
	Commercially available	 **5a**[15]	83
		 **5e**[11]	86
		 **5d**[17]	58
[a] Reaction carried out in CCl_4 at 45°C for 2 h using 1.1 Eq. sulfuryl chloride			

1.5 Synthesis of α-Sulfenyl-β-chloroenones

1.5.1 Synthesis of α-sulfenyl-β-chloropropenones

**Note* Commercially available un-recrystallised N-chlorosuccinimide was used throughout the reactions in this section. It was determined that recrystallised NCS had no impact on the efficiency or outcome of the reactions and so recrystallisation was deemed an unnecessary step.*[18]

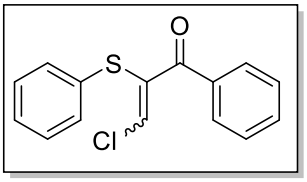
In some of the experiments described below, signals corresponding to the key intermediates and by-products were seen in the ^{1}H NMR spectra of the crude product mixtures and are listed within the experimental description.



α,β-Unsaturated ketone | Trichloride | Dichloride | Benzaldehyde

A number of ^{1}H NMR spectra contain a singlet between δ_H 1.55 and 1.58 ppm. This peak is due to water which was present in the $CDCl_3$.

(*Z*)-3-Chloro-1-phenyl-2-(phenylthio)prop-2-en-1-one Z-4a and (*E*)-3-chloro-1-phenyl-2-(phenylthio)prop-2-en-1-one E-4a



N-chlorosuccinimide (0.59 g, 4.4 mmol, 1.95 eq) was added in one portion to a solution of the sulfide 1-phenyl-2-(phenylthio)propan-1-one **3a** (0.60 g, 2.2 mmol) in toluene (25 mL). The flask was immediately immersed in an oil bath at 90 °C and heating was maintained for 16 h with stirring. The reaction mixture was cooled to 0 °C and the succinimide by-product was removed by filtration. The solvent was evaporated at reduced pressure to give the crude product as an orange oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4a** and **Z-4a**, in a ratio of 2:1, in addition to signals due to the dichloride **S15** (A of AB system, δ_H 3.99, *J* 11.8 and B of AB system, δ_H 4.05, *J* 11.8) and the trichloride **S16** (s, δ_H 6.21 ppm).The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the major

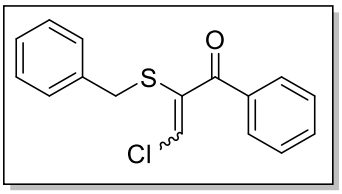
fraction as the desired β-*chloroenone* (0.46 g, 68%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4a** and **Z-4a** in a ratio of 2.2:1, a trace of the dichloride and trichloride were still present in this fraction; ν_{max}/cm^{-1} (film) 3060 (CH), 1669 (CO), 1597 (aromatic), 1243, 689.

Z-4a: δ_H (300 MHz, $CDCl_3$) 6.90 (1H, s, C*H*Cl), 7.08-7.59 (8H, m, Ar*H*), 7.62-7.70 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 128.05 (CH, *C*HCl), 128.07, 128.3, 128.6, 128.7, 129.0, 129.27, 129.30, 129.6, 132.3, 132.4, 133.2, 134.0 (CH, aromatic *C*H), 130.9, 136.4, 140.5 [3 x C, 2 x aromatic *C* and *C*(2)S], 190.8 (C, *C*O).

E-4a: δ_H (300 MHz, $CDCl_3$) 6.71 (1H, s, C*H*Cl), 7.08-7.59 (8H, m, Ar*H*), 7.82-7.88 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 121.8 (CH, *C*HCl), 128.07, 128.3, 128.6, 128.7, 129.0, 129.27, 129.30, 129.6, 132.3, 132.4, 133.2, 134.0 (CH, aromatic *C*H), 129.5, 134.5, 135.1 [3 x C, 2 x aromatic *C* and *C*(2)S], 191.0 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{15}H_{12}OS^{35}Cl[M+H]^+$ 275.0297. Found 275.0299; m/z (ES+) 275.1 [$(C_{15}H_{11}OS^{35}Cl)+H^+$], 16%, 277.1 [$(C_{15}H_{11}OS^{37}Cl)+H^+$], 6%.

(*Z*)-2-(Benzylthio)-3-chloro-1-phenylprop-2-en-1-one Z-4b and (*E*)-2-(benzylthio)-3-chloro-1-phenylprop-2-en-1-one E-4b



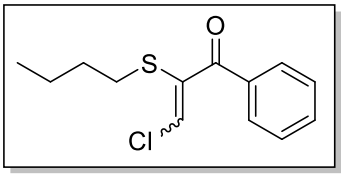
This was prepared following the procedure described for **4a** using 2-(benzylthio)-1-phenylpropan-1-one **3b** (0.26 g, 1.0 mmol), *N*-chlorosuccinimide (0.264 g, 1.9 mmol, 1.95 eq) and toluene (20 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4b** and **E-4b**, in a ratio of 1:1, in addition to signals due to the α,β-unsaturated ketone **S17** (2 x d, δ_H 6.05, *J* 2.0 and δ_H 6.26 ppm, *J* 2.0) and benzaldehyde **S18** (s, δ_H 10.01 ppm). This was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-2% ethyl acetate) as eluent to give the major fraction of β-*chloroenone* (0.253 g, 86%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4b** and **E-4b** in a ratio of 1.1:1, a slight trace of the α,β-unsaturated ketone and benzaldehyde **S18** were present as less than 2% of this fraction; ν_{max}/cm^{-1} (film) 3062 (CH), 2927 (CH), 1666 (CO), 1597 (aromatic), 1243.

Z-4b: δ_H (300 MHz, $CDCl_3$) 4.02 (2H, s, SC*H*$_2$), 6.66 (1H, s, C*H*Cl), 7.12-7.63 (10H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 35.8 (CH_2, S*C*H_2), 127.4, 127.5, 128.4, 128.6, 128.9, 129.2, 129.3, 129.7, 129.8 (CH, aromatic *C*H), 130.3 (CH, *C*HCl), 133.3 (CH, aromatic *C*H), 133.5 (C, aromatic *C*), 134.2 (CH, aromatic *C*H), 134.3, 136.5, 136.7, 137.1, 140.0 [C, aromatic *C* and *C*(2)S], 190.6 (C, *C*O).

E-4b: δ_H (300 MHz, $CDCl_3$) 3.88 (2H, s, SC*H*$_2$), 6.45 (1H, s, C*H*Cl), 7.12-7.63 (8H, m, Ar*H*), 7.91 (2H, d, *J* 7.1, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 38.6 (CH_2, S*C*H_2), 122.1 (CH, *C*HCl), 127.4, 127.5, 128.4, 128.6, 128.9, 129.2, 129.3, 129.7, 129.8, 133.3 (CH, aromatic *C*H), 133.5 (C, aromatic *C*), 134.2 (CH, aromatic *C*H), 134.3, 136.5, 136.7, 137.1, 140.0 [C, aromatic *C* and *C*(2)S], 191.8 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{16}H_{14}OS^{35}Cl[M+H]^+$ 289.0454. Found 289.0457; m/z (ES+) 289.0 [($C_{16}H_{13}OS^{35}Cl$)+H^+], 52%, 291.0 [($C_{16}H_{13}OS^{37}Cl$)+H^+], 20%, 307.1 (56%), 305.1 (100%).

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-phenylprop-2-en-1-one Z-4c and (*E*)-2-(*n*-butylthio)-3-chloro-1-phenylprop-2-en-1-one Z-4c



This was prepared following the procedure described for **4a** using 2-(butylthio)-1-phenylpropan-1-one **3c** (0.60 g, 2.7 mmol), *N*-chlorosuccinimide (0.70 g, 5.3 mmol, 1.95 eq) and toluene (20 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4c** and **E-4c**, in a ratio of 1:1.8. This was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-2% ethyl acetate) as eluent. The major isomer **E-4c** (70 mg, 10%) was isolated as a yellow oil; ν_{max}/cm^{-1} (film) 3064 (CH), 2959 (CH), 1670 (CO), 1596 (aromatic), 1220.

E-4c (less polar)**:** δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.3, CH_2CH_3), 1.32-1.42 (2H, m, C*H*$_2$CH$_3$), 1.52-1.62 (2H, m, C*H*$_2$CH$_2$CH$_3$), 2.60-2.68 (2H, m, SC*H*$_2$), 6.59 (1H, s, C*H*Cl), 7.49 (2H, t, *J* 7.6, Ar*H*), 7.58-7.63 (1H, m, Ar*H*), 7.92-7.99 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.53 (CH_3, CH*C*H$_3$), 21.6 (CH_2, *C*H$_2$CH$_3$), 31.2 (CH_2, *C*H$_2$CH$_2$CH$_3$), 33.3 (CH_2, S*C*H$_2$), 119.3 (CH, *C*HCl), 128.9, 129.6, 134.1 (3 x CH, aromatic *C*H), 134.2, 134.9 [2 x C, aromatic *C* and *C*(2)S], 191.7 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{13}H_{16}OS^{35}Cl[M+H]^+$ 255.0610. Found 255.0617; m/z (ES+) 297.2 [$(C_{13}H_{15}OS^{35}Cl)+CNCH_3^+$], 100%, 299.2 [$(C_{13}H_{15}OS^{37}Cl)+CNCH_3^+$], 30%.

The major fraction isolated after chromatography contained the β-*chloroenone* (0.52 g, 75%) as a yellow oil and a mixture of *Z* and *E* isomers **Z-4c** and **E-4c** in a ratio of 1:1.5; ν_{max}/cm^{-1} (film) 3064 (CH), 2960 (CH), 1670 (CO), 1596 (aromatic), 1222.

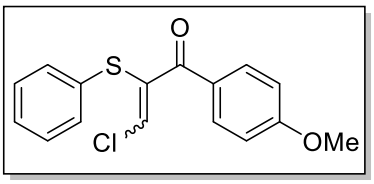
E-4c (less polar): δ_H (400 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.3, CH_2CH_3), 1.32-1.42 (2H, m, CH_2CH_3), 1.52-1.62 (2H, m, $CH_2CH_2CH_3$), 2.60-2.68 (2H, m, SCH_2), 6.59 (1H, s, *C*HCl), 7.49 (2H, t, *J* 7.6, Ar*H*), 7.58-7.63 (1H, m, Ar*H*), 7.92-7.99 (2H, m, Ar*H*).

Spectroscopic characteristics were consistent with those above.

Z-4c (more polar): δ_H (400 MHz, $CDCl_3$) 0.83 (3H, t, *J* 7.3, CH_2CH_3), 1.32-1.42 (2H, m, CH_2CH_3), 1.47-1.62 (2H, m, $CH_2CH_2CH_3$), 2.68-2.72 (2H, m, SCH_2), 6.69 (1H, s, *C*HCl), 7.45-7.50 (2H, m, Ar*H*), 7.58-7.63 (1H, m, Ar*H*), 7.88-7.90 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.49 (CH_3, $CHCH_3$), 21.6 (CH_2, CH_2CH_3), 31.4 (CH_2, SCH_2), 32.1 (CH_2, $CH_2CH_2CH_3$), 126.8 (CH, *C*HCl), 128.7, 129.8, 133.7 (3 x CH, aromatic *C*H), 136.4, 140.1 [2 x C, aromatic *C* and *C*(2)S], 190.8 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{13}H_{16}OS^{35}Cl[M+H]^+$ 255.0610. Found 255.0610 (100%); m/z (ES+) 457.1 (100%).

(*Z*)-3-Chloro-1-(4-methoxyphenyl)-2-(phenylthio)prop-2-en-1-one Z-4d and (*E*)-3-chloro-1-(4-methoxyphenyl)-2-(phenylthio)prop-2-en-1-one E-4d



This was prepared following the procedure described for **4a** using 1-(4-methoxyphenyl)-2-(phenylthio)propan-1-one **3d** (0.232 g, 0.9 mmol), *N*-Chlorosuccinimide (0.248 g, 1.9 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy this was seen to contain 70% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4d** and **E-4d**, in a ratio of 1:1.75 and the α,β-unsaturated ketone **S19** (3%). Following purification by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent, the β-*chloroenone* **4d** (0.241 g, 88%) was isolated in the major fraction as a yellow oil and a mixture of *Z* and *E* isomers **Z-4d** and **E-4d** in a ratio of 1.6:1. ^{1}H NMR spectroscopy showed a trace of α,β-unsaturated ketone **S19**

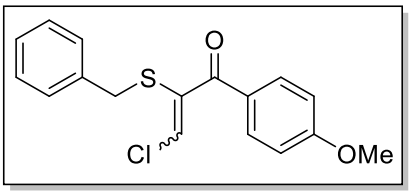
(1%) was still present in this sample - [(d, δ_H 6.00 ppm, *J* 2.0) and (d, δ_H 6.18 ppm, *J* 2.0)]; ν_{max}/cm^{-1} (film) 3058 (CH), 2934 (CH), 1659 (CO), 1598 (aromatic), 1253.

Z-4d (more polar): δ_H (300 MHz, $CDCl_3$) 3.83 (3H, s, OC*H*$_3$), 6.79 (1H, s, C*H*Cl), 6.83 (2H, d, *J* 9.0, Ar*H*), 7.10-7.16 (3H, m, Ar*H*), 7.20-7.29 (2H, m, Ar*H*), 7.73 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 55.5 (CH_3, O*C*H$_3$) 113.6 (CH, aromatic *C*H), 126.0 (CH, *C*HCl), 128.1, 129.0 (2 x CH, aromatic *C*H), 129.1, 130.9 [2 x C, aromatic *C* and *C*(2)S], 131.9, 132.6 (2 x CH, aromatic *C*H), 140.4, 163.8 (2 x C, 2 x aromatic *C*), 189.2 (C, *C*O).

E-4d (less polar): δ_H (300 MHz, $CDCl_3$) 3.85 (3H, s, OC*H*$_3$), 6.64 (1H, s, C*H*Cl), 6.90 (2H, d, *J* 9.0, Ar*H*), 7.20-7.29 (2H, m, Ar*H*), 7.38-7.44 (3H, m, Ar*H*), 7.84 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 55.6 (CH_3, O*C*H$_3$) 114.0 (CH, aromatic *C*H), 121.0 (CH, *C*HCl), 127.5 [C, aromatic *C* or *C*(2)S], 128.5, 129.3 (2 x CH, aromatic *C*H), 131.2 [C, aromatic *C* or *C*(2)S], 132.1, 132.4 (2 x CH, aromatic *C*H), 135.4 [C, aromatic *C* or *C*(2)S], 164.3 (C, aromatic *C*), 189.6 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{16}H_{14}O_2S^{35}Cl[M+H]^+$ 305.0403. Found 305.0390; m/z (ES+) 305.1 [($C_{16}H_{13}O_2S^{35}Cl$)+H^+], 100%, 307.0 [($C_{16}H_{13}O_2S^{37}Cl$)+H^+], 40%.

(*Z*)-2-(Benzylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one Z-4e and (*E*)-2-(benzylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one E-4e



This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-(4-methoxyphenyl)propan-1-one **3e** (0.67 g, 2.3 mmol), *N*-chlorosuccinimide (0.61 g, 4.6 mmol, 1.95 eq) and toluene (20 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4e** and **E-4e**, in a ratio of 3:1, in addition to signals due to the α,β-unsaturated ketone **S20** (2 x d, δ_H 5.99, *J* 2.0 and δ_H 6.16 ppm, *J* 2.0) and benzaldehyde **S18** (s, δ_H 10.01 ppm). This was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-5% ethyl acetate) as eluent to give the major fraction of β-*chloroenone* (0.43 g, 57%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4e** and **E-4e** in a ratio of 4.3:1, a trace of the α,β-unsaturated ketone **S20** and the dichloride **S21** (A of AB system, δ_H 4.14, *J* 12.9 and B of AB

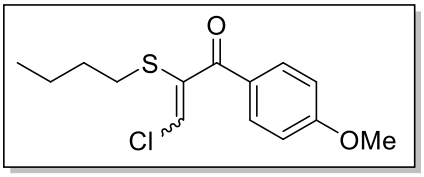
system, δ_H 4.37, *J* 12.9) were also present (<2%); ν_{max}/cm^{-1} (film) 3062 (CH), 3031 (CH), 2935 (CH), 1654 (CO), 1598 (aromatic), 1253.

Z-4e (more polar): δ_H (400 MHz, $CDCl_3$) 3.83 (3H, s, OC*H*$_3$), 3.97 (2H, s, SC*H*$_2$), 6.56 (1H, s, C*H*Cl), 6.84 (2H, d, *J* 9.0, Ar*H*), 7.12-7.22 (5H, m, Ar*H*), 7.56 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 35.7 (CH_2, S*C*H$_2$), 55.6 (CH_3, O*C*H$_3$), 113.7 (CH, aromatic *C*H), 127.1 (CH, *C*HCl), 127.4, 128.5, 129.3, 132.3 (4 x CH, aromatic *C*H), 137.1, 139.8 [2 x C, aromatic *C* and *C*(2)S], 163.9 (C, aromatic *C*), 189.2 (C, *C*O).

E-4e (less polar): δ_H (400 MHz, $CDCl_3$) 3.86 (3H, s, OC*H*$_3$), 3.88 (2H, s, SC*H*$_2$), 6.41 (1H, s, C*H*Cl), 6.95 (2H, d, *J* 9.0, Ar*H*), 7.12-7.22 (5H, m, Ar*H*), 7.90 (2H, d, *J* 9.0, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 38.5 (CH_2, S*C*H$_2$), 55.7 (CH_3, O*C*H$_3$), 114.2 (CH, aromatic *C*H), 121.2 (CH, *C*HCl), 127.5, 128.6, 129.2, 132.2 (4 x CH, aromatic *C*H), 132.2, 133.7, 136.6 [3 x C, 2 x aromatic *C* and *C*(2)S], 164.5 (C, aromatic *C*), 190.4 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{17}H_{16}O_2S^{35}Cl[M+H]^+$ 319.0560. Found 319.0565; m/z (ES+) 319.1 [($C_{17}H_{15}O_2S^{35}Cl$)+H^+], 100%, 321.1 [($C_{17}H_{15}O_2S^{37}Cl$)+H^+], 40%.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one Z-4f and (*E*)-2-(*n*-butylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one E-4f



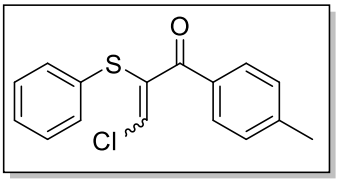
This was prepared following the procedure described above for **4a** using 2-(butylthio)-1-(4-methoxyphenyl)propan-1-one **3f** (0.15 g, 0.6 mmol), *N*-chlorosuccinimide (0.155 g, 1.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4f** and **E-4f**, in a ratio of 2.1:1. This was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-5% ethyl acetate) as eluent to give the major fraction of pure β-*chloroenone* (0.15 g, 89%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4f** and **E-4f** in a ratio of 2.3:1; ν_{max}/cm^{-1} (film) 3062 (CH), 2960 (CH), 1658 (CO), 1598 (aromatic), 1254, 1168.

Z-4f (more polar): δ_H (300 MHz, $CDCl_3$) 0.80-0.95 (3H, m, CH_2CH_3), 1.28-1.43 (2H, m, CH_2CH_3), 1.45-1.66 (2H, m, $CH_2CH_2CH_3$), 2.62-2.71 (2H, m, SCH_2), 3.89 (3H, s, OCH_3), 6.58 (1H, s, CHCl), 6.92-6.99 (2H, m, ArH), 7.89-7.98 (2H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 13.5 (CH_3, CH_2CH_3), 21.6 (CH_2, CH_2CH_3), 31.3 (CH_2, SCH_2), 32.0 (CH_2, $CH_2CH_2CH_3$), 55.5 (CH_3,OCH_3), 114.0 (CH, aromatic CH), 124.0 (CH, CHCl), 129.0 [C, aromatic C or C(2)S], 132.4 (CH, aromatic CH), 140.0, 164.2 [2 x C, 2 x aromatic C or aromatic C and C(2)S], 189.4 (C, CO).

E-4f (less polar): δ_H (300 MHz, $CDCl_3$) 0.80-0.95 (3H, m, CH_2CH_3), 1.28-1.43 (2H, m, CH_2CH_3), 1.45-1.66 (2H, m, $CH_2CH_2CH_3$), 2.62-2.71 (2H, m, SCH_2), 3.89 (3H, s, OCH_3), 6.55 (1H, s, CHCl), 6.92-6.99 (2H, m, ArH), 7.89-7.98 (2H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, CH_2CH_3), 21.6 (CH_2, CH_2CH_3), 31.2 (CH_2, $CH_2CH_2CH_3$), 33.7 (CH_2, SCH_2), 55.6 (CH_3,OCH_3), 114.2 (CH, aromatic CH), 118.4 (CH, CHCl), 127.2 [C, aromatic C or C(2)S], 132.1 (CH, aromatic CH), 135.1, 164.4 [2 x C, 2 x aromatic C or aromatic C and C(2)S], 190.3 (C, CO).

HRMS (ES+): Exact mass calculated for $C_{14}H_{18}O_2S^{35}Cl[M+H]^+$ 285.0716. Found 285.0710; m/z (ES+) 285.1 [$(C_{14}H_{17}O_2S^{35}Cl)+H^+$], 100%, 287.1 [$(C_{14}H_{17}O_2S^{37}Cl)+H^+$], 40%.

(*Z*)-3-Chloro-2-(phenylthio)-1-(*p*-tolyl)prop-2-en-1-one Z-4g and (*E*)-3-chloro-2-(phenylthio)-1-(*p*-tolyl)prop-2-en-1-one Z-4g



This was prepared following the procedure described above for **4a** using 2-(phenylthio)-1-(*p*-tolyl)propan-1-one **3g** (0.20 g, 0.8 mmol), *N*-chlorosuccinimide (0.203 g, 1.6 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. By ^{1}H NMR spectroscopy this was seen to contain the β-chloroenone as the major component as a mixture of *Z* and *E* isomers, **Z-4g** and **E-4g**, in a ratio of 1.5:1. Purification by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent isolated the major fraction as the desired β-*chloroenone* (0.147 g, 65%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4g** and **Z-4g** in a ratio of 1.7:1; ν_{max}/cm^{-1} (film) 3059 (CH), 1667 (CO), 1605 (aromatic), 1257.

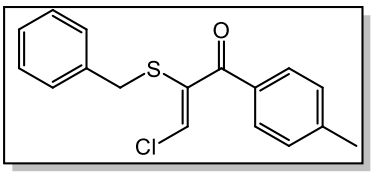
Z-4g (more polar): δ_H (400 MHz, $CDCl_3$) 2.38 (3H, s, $ArCH_3$), 6.86 (1H, s, CHCl), 7.11-7.35 (7H, m, ArH), 7.62 (2H, d, *J* 8.2, ArH); δ_C (75.5 MHz, $CDCl_3$) 21.7 (CH_3, aromatic CH_3), 127.4 (CH, CHCl), 128.0, 128.5, 128.99, 129.04, 129.3, 129.5, 129.6, 129.8 (CH, aromatic CH), 131.0 [C,

aromatic *C* or *C*(2)S], 132.3, 132.4, 134.2 (3 x CH, aromatic *C*H), 133.8, 140.5 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 144.3 (C, aromatic *C*), 190.4 (C, *C*O).

E-4g (less polar): δ_H (400 MHz, $CDCl_3$) 2.41 (3H, s, ArCH_3), 6.68 (1H, s, C*H*Cl), 7.11-7.35 (7H, m, Ar*H*), 7.77 (2H, d, *J* 8.3, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 21.8 (CH_3, aromatic *C*H_3), 121.4 (CH, *C*HCl), 128.0, 128.5, 128.99, 129.04, 129.3, 129.5, 129.6, 129.8 (CH, aromatic *C*H), 131.2, 132.0 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 132.3, 132.4, 134.2 (3 x CH, aromatic *C*H), 135.3 [C, aromatic *C* or *C*(2)S], 145.9 (C, aromatic *C*), 190.7 (C, *C*O).

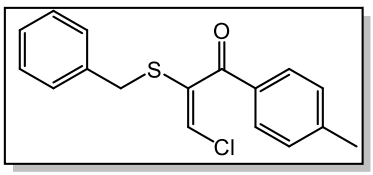
HRMS (ES+): Exact mass calculated for $C_{16}H_{14}OS^{35}Cl[M+H]^+$ 289.0454. Found 289.0446; m/z (ES+) 289.2 [($C_{16}H_{13}OS^{35}Cl$)+H^+], 42%, 292.2 [($C_{16}H_{13}OS^{37}Cl$)+H^+], 30%.

(*Z*)-2-(Benzylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one Z-4h and (*E*)-2-(Benzylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one E-4h



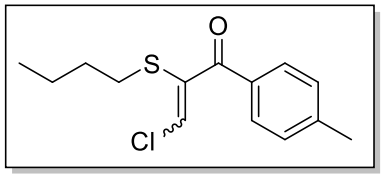
This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-(*p*-tolyl)propan-1-one **3h** (1.04 g, 3.8 mmol), *N*-chlorosuccinimide (1.00 g, 7.5 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was isolated as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (96%, *Z* : *E* 2.5:1) as well as the α,β-unsaturated ketone side product **S22** (4%, 2 x s, δ_H 5.75 and 5.79 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4h** (0.463 g, 40%) as a yellow oil and pure **E-4h** (0.182 g, 16%) as a colourless oil.

Z-4h (more polar): ν_{max}/cm^{-1} (ATR) 3060, 3030, 1656 (C=O), 1602, 1243, 1177, 734, 696; δ_H (400 MHz, $CDCl_3$): 2.39 (3H, s, ArCH_3), 4.01 (2H, s, SCH_2), 6.64 (1H, s, C*H*Cl), 7.14-7.22 (7H, m, Ar*H*), 7.42 (2H, d, *J* 8.0, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H_3), 35.8 (CH_2, S*C*H_2), 127.3 [CH, *C*(3)H], 128.5, 129.1, 129.2, 130.0 (4 x CH signals, 9 x aromatic *C*H), 134.0, 137.1, 139.9, 144.3 [4 x C, 3 x aromatic *C* and *C*(2)S], 190.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{16}OS^{35}Cl[M+H^+]$ 303.0610. Found 303.0602; m/z (ES+) 303.2 [($C_{17}H_{15}OS^{35}Cl$)+H^+], 100%, 305.2 [($C_{17}H_{15}OS^{37}Cl$)+H^+], 40%.



E-4h (less polar): ν_{max}/cm^{-1} (ATR) 3028, 2912, 1658 (C=O), 1602, 1453, 1302, 1231, 1176, 699; δ_H (400 MHz, $CDCl_3$): 2.43 (3H, s, ArC*H*$_3$), 3.87 (2H, s, SC*H*$_2$), 6.43 (1H, s, C*H*Cl), 7.18-7.34 (7H, m, Ar*H*), 7.82 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 38.5 (CH_2, S*C*H$_2$), 121.6 [CH, *C*(3)H], 127.4, 128.5, 129.2, 129.6, 129.8 (5 x CH signals, 9 x aromatic *C*H), 131.8, 133.6, 136.6, 145.3 [4 x C, 3 x aromatic *C* and *C*(2)S], 191.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{16}OS^{35}Cl[M+H^+]$ 303.0610. Found 303.0605; m/z (ES+) 303.2 [$(C_{17}H_{15}OS^{35}Cl)+H^+$], 100%, 305.2 [$(C_{17}H_{15}OS^{37}Cl)+H^+$], 44%.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one Z-4i and (*E*)-2-(*n*-butylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one E-4i



This was prepared following the procedure described above for **4a** using 2-(butylthio)-1-(*p*-tolyl)propan-1-one **3i** (0.20 g, 0.8 mmol), *N*-chlorosuccinimide (0.221 g, 1.7 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy this product was seen to contain 88% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4i** and **E-4i**, in a ratio of 1.3:1. This was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-2% ethyl acetate) as eluent to give the major fraction of pure β-*chloroenone* (0.12 g, 53%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4i** and **E-4i** in a ratio of 1.3:1, other fractions isolated contained varying ratios of *Z* and *E* isomers but were not as pure; ν_{max}/cm^{-1} (film) 3061 (CH), 2959 (CH), 1663 (CO), 1605 (aromatic), 1178.

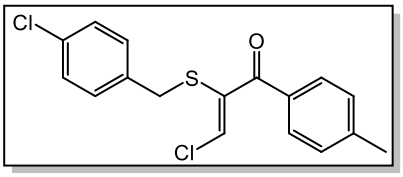
Z-4i (more polar): δ_H (300 MHz, $CDCl_3$) 0.78-0.96 (3H, m, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.44-1.61 (2H, m, $CH_2CH_2CH_3$), 2.43 (3H, s, ArC*H*$_3$), 2.61-2.72 (2H, m, SC*H*$_2$), 6.64 (1H, s, C*H*Cl), 7.23-7.30 (2H, m, Ar*H*), 7.78-7.91 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.5 (CH_3, $CHCH_3$), 21.6 (CH_2, CH_2CH_3), 21.8 (CH_3, Ar*C*H$_3$), 31.3 (CH_2, S*C*H$_2$), 32.1 (CH_2, $CH_2CH_2CH_3$), 125.7 (CH, *C*HCl), 129.4, 130.1 (2 x CH, aromatic *C*H), 133.8, 140.2, 144.9, 145.3 [4 x C, 2 x aromatic *C* and *C*(2)S], 190.5 (C, *C*O).

E-4i (less polar): δ_H (300 MHz, $CDCl_3$) 0.78-0.96 (3H, m, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.44-1.61 (2H, m, $CH_2CH_2CH_3$), 2.43 (3H, s, ArC*H*$_3$), 2.61-2.72 (2H, m, SC*H*$_2$), 6.57 (1H, s, C*H*Cl),

7.23-7.30 (2H, m, Ar*H*), 7.78-7.91 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH_3, $CHCH_3$), 21.6 (CH_2, CH_2CH_3), 21.9 (CH3, $ArCH_3$), 31.2 (CH_2, $CH_2CH_2CH_3$), 33.3 (CH_2, SCH_2), 118.9 (CH, *C*HCl), 129.6, 129.8 (2 x CH, aromatic *C*H), 131.7, 135.0, 140.2, 145.3 [4 x C, 2 x aromatic *C* and *C*(2)S], 191.4 (C, *C*O).

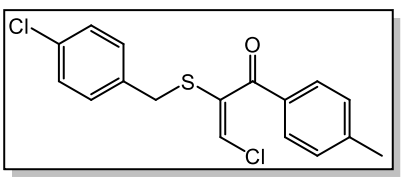
HRMS (ES+): Exact mass calculated for $C_{14}H_{18}OS^{35}Cl[M+H]^+$ 269.0767. Found 269.0765; m/z (ES+) 269.1 [$(C_{14}H_{17}OS^{35}Cl)+H^+$], 68%, 271.1 [$(C_{13}H_{14}OS^{37}ClF)+H^+$], 26%, 323.1 (100%).

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4j and (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4j



This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-(*p*-tolyl)propan-1-one **3j** (2.03 g, 6.7 mmol), *N*-chlorosuccinimide (1.74 g, 13.0 mmol, 1.95 eq) and toluene (25 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (83%, *Z* : *E* 2.8:1) and the α,β-unsaturated ketone side product **S23** (6%, 2 x s, δ_H 5.75 and 5.78 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (60:40) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4j** (0.733 g, 32%) as a yellow oil and pure **E-4j** (0.414 g, 18%) as a yellow oil.

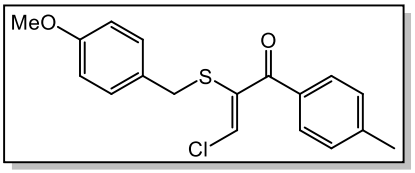
Z-4j (more polar)**:** ν_{max}/cm^{-1} (ATR) 3049, 2921, 1654 (C=O), 1602, 1489, 1243, 1090, 731; δ_H (400 MHz, $CDCl_3$): 2.41 (3H, s, $ArCH_3$), 3.97 (2H, s, SCH_2), 6.65 (1H, s, C*H*Cl), 7.12 (4H, s, Ar*H*), 7.18 (2H, d, *J* 7.9, Ar*H*), 7.41 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, $ArCH_3$), 35.0 (CH_2, SCH_2), 128.6, 129.1 (2 x CH signals, 4 x aromatic *C*H), 129.3 [CH, *C*(3)H], 129.9, 130.6 (2 x CH signals, 4 x aromatic *C*H), 133.2, 133.8, 135.7 (3 x C, aromatic *C*), 139.4 [C, *C*(2)S], 144.6 (C, aromatic *C*), 190.1 (C, *C*O); m/z (ES+) 337.1 [$(C_{17}H_{14}OS^{35}Cl_2)+H^+$], 20%, 339.1 [$(C_{17}H_{14}OS^{35}Cl^{37}Cl)+H^+$], 10%.



E-4j (less polar)**:** ν_{max}/cm^{-1} (ATR) 3064, 2922, 1659 (C=O), 1603, 1489, 1287, 1224, 1175, 829, 791; δ_H (400 MHz, $CDCl_3$): 2.43 (3H, s, $ArCH_3$), 3.82 (2H, s, SCH_2), 6.45 (1H, s, C*H*Cl), 7.21-7.32 (6H, m, Ar*H*), 7.80 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, $ArCH_3$), 37.8 (CH_2, SCH_2), 122.4 [CH, *C*(3)H], 128.6, 129.6, 129.8, 130.5

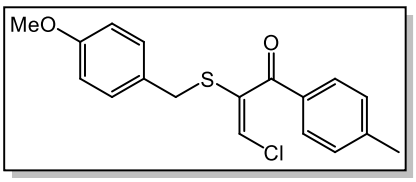
(4 x CH signals, 8 x aromatic *C*H), 131.5 (C, aromatic *C*), 132.8 [C, *C*(2)S], 133.3, 135.3, 145.4 (3 x C, aromatic *C*), 191.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OS^{35}Cl_2[M+H^+]$ 337.0221. Found 337.0224; m/z (ES+) 337.1 [$(C_{17}H_{14}OS^{35}Cl_2)+H^+$], 18%. $^{35}Cl/^{37}Cl$ pattern visible at 337, 339 and 341 in a 9:6:1 ratio.

(*Z*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4k and (*E*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4k



This was prepared following the procedure described above for **4a** using 2-((4-methoxybenzyl)thio)-1-(*p*-tolyl)propan-1-one **3k** (0.457 g, 1.5 mmol), *N*-chlorosuccinimide (0.397 g, 3.0 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (83%, *Z* : *E* 2.6:1) and the impurity 1-(chloromethyl)-4-methoxybenzene **S24** (17%, s, δ_H 4.57 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (30:70) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4k** (0.197 g, 39%) as an orange oil and pure **E-4k** (60 mg, 12%) as an off-white solid (mp 85-87°C).

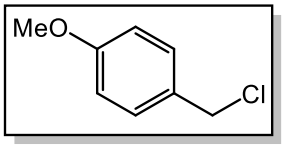
Z-4k (more polar): ν_{max}/cm^{-1} (ATR) 3033, 2999, 2953, 2933, 2834, 1655 (C=O), 1603, 1509, 1239, 730; δ_H (400 MHz, $CDCl_3$): 2.40 (3H, s, ArC*H*$_3$), 3.73 (3H, s, OC*H*$_3$), 3.96 (2H, s, SC*H*$_2$), 6.62 (1H, s, C*H*Cl), 6.70 (2H, d, *J* 8.6, Ar*H*), 7.10 (2H, d, *J* 8.6, Ar*H*), 7.17 (2H, d, *J* 8.1, Ar*H*), 7.45 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H$_3$), 35.2 (CH_2, S*C*H$_2$), 55.2 (CH_3, O*C*H$_3$), 113.9 (1 x CH signal, 2 x aromatic *C*H), 128.5 [CH, *C*(3)H], 129.0 (C, aromatic *C*), 129.1, 130.1, 130.4 (3 x CH signals, 6 x aromatic *C*H), 134.0 (C, aromatic *C*), 140.1 [C, *C*(2)S], 144.3, 158.8 [2 x C, 2 x aromatic *C*), 190.3 (C, *C*O); m/z (ES+) 121.3 [$(C_8H_9O)^+$], 100%; m/z (ES-) 35.3 [$(^{35}Cl)^+$], 100%, 37.3 [$(^{37}Cl)^+$], 24%.



E-4k (less polar)**:** ν_{max}/cm^{-1} (ATR) 3100, 2957, 2913, 2835, 1661 (C=O), 1603, 1508, 1234, 1176, 829; δ_H (400 MHz, $CDCl_3$): 2.43 (3H, s, ArC*H*$_3$), 3.79 (3H, s, OC*H*$_3$), 3.84 (2H, s, SC*H*$_2$), 6.43 (1H, s, C*H*Cl), 6.82 (2H, d, *J* 8.7, Ar*H*), 7.21 (2H, d, *J* 8.7, Ar*H*), 7.28 (2H, d, *J* 8.2, Ar*H*), 7.82 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 38.1 (CH_2, S*C*H$_2$), 55.2 (CH_3, O*C*H$_3$), 113.9 (1 x CH signal, 2 x aromatic *C*H), 121.4 [CH,

C(3)H], 128.5 [C, aromatic *C* or *C*(2)S], 129.6, 129.8, 130.4 (3 x CH signals, 6 x aromatic *C*H), 131.7, 133.7, 145.3, 158.9 [4 x C, 4 x aromatic *C* or 3 x aromatic *C* and *C*(2)S], 191.5 (C, *C*O).

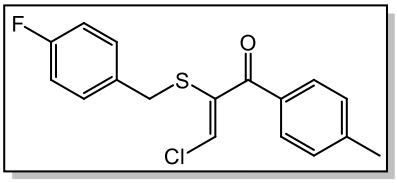
1-(Chloromethyl)-4-methoxybenzene S24[19]



δ_H (400 MHz, $CDCl_3$): 3.81 (3H, s, OC*H*$_3$), 4.57 (2H, s, C*H*$_2$Cl), 6.88 (2H, d, *J* 8.7, Ar*H*), 7.31 (2H, d, *J* 8.7, Ar*H*); δ_C (75 MHz, $CDCl_3$): 46.3 (CH_2, *C*H_2Cl), 55.3 (CH_3, O*C*H_3), 114.1 (1 x CH signal, 2 x aromatic *C*H), 129.7 (C, aromatic *C*), 130.1 (1 x CH signal, 2 x aromatic *C*H), 159.6 (C, aromatic *C*).

Spectroscopic characteristics are consistent with those previously reported. [19]

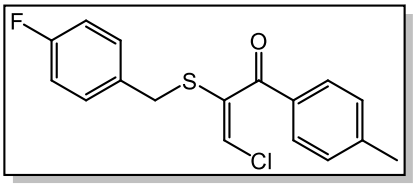
(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4l and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4l



This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)propan-1-one **3l** (0.423 g, 1.5 mmol), *N*-chlorosuccinimide (0.382 g, 2.9 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. The ^{1}H NMR spectrum showed the presence of two β-chloroenone isomers (92%, *Z* : *E* 2.7:1) and the α,β-unsaturated ketone side product **S25** (8%, 2 x s, δ_H 5.76 and 5.79 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4l** (0.215 g, 46%) as a colourless oil and pure **E-4l** (68 mg, 15%) as a colourless oil.

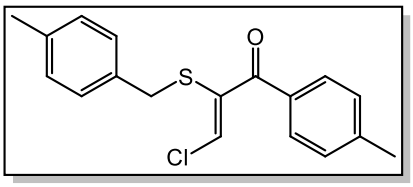
Z-4l (more polar)**:** ν_{max}/cm^{-1} (ATR) 3047, 2921, 1655 (C=O), 1602, 1506, 1243, 1222, 824, 731; δ_H (400 MHz, $CDCl_3$): 2.40 (3H, s, ArC*H*$_3$), 3.98 (2H, s, SC*H*$_2$), 6.65 (1H, s, C*H*Cl), 6.86 (2H, overlapping dd appears as t, *J* 8.6, Ar*H*), 7.12-7.24 (4H, m, Ar*H*), 7.43 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H_3), 35.0 (CH_2, S*C*H_2), 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H), 129.1 (1 x CH signal, 2 x aromatic *C*H), 129.2 [CH, *C*(3)H], 129.9 (1 x CH signal, 2 x aromatic *C*H), 130.8 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.2, aromatic *C*H), 132.9 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 133.9 (C, aromatic *C*), 139.5 [C, *C*(2)S], 144.5 (C, aromatic *C*), 162.0 (C, d, $^1J_{CF}$ 246.4, aromatic *C*), 190.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OFS^{35}Cl[M+H^+]$

321.0516. Found 321.0501; m/z (ES+) 321.1 [($C_{17}H_{14}OFS^{35}Cl$)+H^+], 100%, 323.1 [($C_{17}H_{14}OFS^{37}Cl$)+H^+], 40%.



E-4l (less polar): ν_{max}/cm^{-1} (ATR) 3066, 2922, 1659 (C=O), 1602, 1507, 1287, 1222, 829; δ_H (400 MHz, $CDCl_3$): 2.43 (3H, s, ArC*H*$_3$), 3.84 (2H, s, SC*H*$_2$), 6.44 (1H, s, C*H*Cl), 6.97 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*), 7.23-7.33 (4H, m, Ar*H*), 7.81 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 37.7 (CH_2, S*C*H$_2$), 115.4 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H), 122.2 [CH, *C*(3)H], 129.6, 129.8 (2 x CH signals, 4 x aromatic *C*H), 130.8 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 131.6 (C, aromatic *C*), 132.4 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 133.0 [C, *C*(2)S], 145.4 (C, aromatic *C*), 162.1 (C, d, $^1J_{CF}$ 246.2, aromatic *C*), 191.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OFS^{35}Cl$[M+H^+] 321.0516. Found 321.0506; m/z (ES+) 321.1 [($C_{17}H_{14}OFS^{35}Cl$)+H^+], 100%, 323.1 [($C_{17}H_{14}OFS^{37}Cl$)+H^+], 40%.

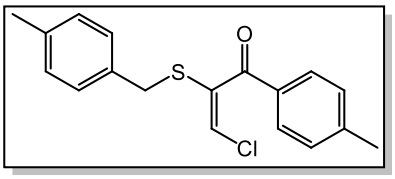
(*Z*)-3-Chloro-2-((4-methylbenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4m and (*E*)-3-Chloro-2-((4-methylbenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4m



This was prepared following the procedure described above for **4a** using 2-((4-methylbenzyl)thio)-1-(*p*-tolyl)propan-1-one **3m** (0.613 g, 2.2 mmol), *N*-chlorosuccinimide (0.562 g, 4.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (96%, *Z* : *E* 2.7:1) and the α,β-unsaturated ketone side product **S26** (4%, 2 x s, δ_H 5.76 and 5.80 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4m** (0.159 g, 23%) as a pale yellow oil and pure **E-4m** (61 mg, 9%) as a yellow oil.

Z-4m (more polar)**:** ν_{max}/cm^{-1} (ATR) 3045, 2913, 1656 (C=O), 1602, 1543, 1240, 1081, 873, 806, 734; δ_H (400 MHz, $CDCl_3$): 2.27 (3H, s, ArC*H*$_3$), 2.41 (3H, s, ArC*H*$_3$), 3.97 (2H, s, SC*H*$_2$), 6.62 (1H, s, C*H*Cl), 6.98 (2H, d, *J* 7.9, Ar*H*), 7.08 (2H, d, *J* 8.0, Ar*H*), 7.17 (2H, d, *J* 7.9, Ar*H*), 7.45 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.0 (CH_3, Ar*C*H$_3$), 21.7 (CH_3, Ar*C*H$_3$), 35.5 (CH_2, S*C*H$_2$), 128.5

[CH, *C*(3)H], 129.0, 129.1, 130.0 (3 x CH signals, 8 x aromatic *C*H), 133.9, 134.0, 137.0 (3 x C, aromatic *C*), 140.0 [C, *C*(2)S], 144.3 (C, aromatic *C*), 190.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{18}OS^{35}Cl[M+H^+]$ 317.0767. Found 317.0764; m/z (ES+) 317.1 $[(C_{18}H_{17}OS^{35}Cl)+H^+]$, 29%, 319.1 $[(C_{18}H_{17}OS^{37}Cl)+H^+]$, 10%.

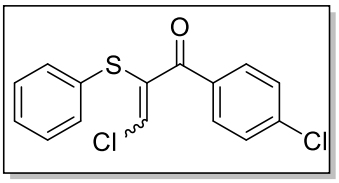


E-4m (less polar)**:** ν_{max}/cm^{-1} (ATR) 3048, 3026, 2920, 2861, 1657 (C=O), 1603, 1513, 1243, 1177, 731; δ_H (400 MHz, $CDCl_3$): 2.32 (3H, s, ArC*H*$_3$), 2.43 (3H, s, ArC*H*$_3$), 3.85 (2H, s, SC*H*$_2$), 6.44 (1H, s, C*H*Cl), 7.10 (2H, d, *J* 7.8, Ar*H*), 7.17 (2H, d, *J* 8.0, Ar*H*), 7.28 (2H, d, *J* 7.9, Ar*H*), 7.83 (2H, d, *J* 7.8, Ar*H*); HRMS (ES+): Exact mass calculated for $C_{18}H_{18}OS^{35}Cl[M+H^+]$ 317.0767. Found 317.0767; m/z (ES+) 317.1 $[(C_{18}H_{17}OS^{35}Cl)+H^+]$, 100%, 319.1 $[(C_{18}H_{17}OS^{37}Cl)+H^+]$, 44%.

The major fraction obtained contained a mixture of the *E* and *Z* isomers in a ratio of *Z*:*E* 2.8:1 (0.277 g, 40%) giving an overall yield of 72%.

^{1}H and ^{13}C NMR spectra recorded after storage at room temperature for 20 months indicated partial interconversion of the E and Z.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-(phenylthio)prop-2-en-1-one Z-4n and (*E*)-3-chloro-1-(4-chlorophenyl)-2-(phenylthio)prop-2-en-1-one E-4n



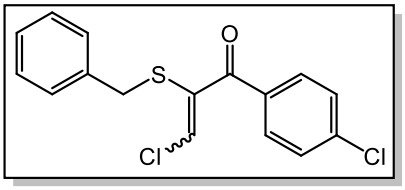
This was prepared following the procedure described above for **4a** using 1-(4-chlorophenyl)-2-(phenylthio)propan-1-one **3n** (0.20 g, 0.7 mmol), *N*-chlorosuccinimide (0.188 g, 1.4 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4n** and **E-4n**, in a ratio of 1.7:1, in addition to signals due to the dichloride **S27** (A of AB system, δ_H 3.96, *J* 11.8 and B of AB system, δ_H 4.04, *J* 11.8) and the trichloride **S28** (s, δ_H 6.17 ppm). Purification by column chromatography on silica gel using hexane-ethyl acetate (99:1) as eluent gave the major fraction as the desired β-*chloroenone* (0.118 g, 53%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4n** and **E-4n** in a ratio of 2.1:1, which contained a trace of the dichloride **S27** and trichloride **S28**; ν_{max}/cm^{-1} (film) 3060 (CH), 1671 (CO), 1586 (aromatic), 1248, 1091.

Z-4n (more polar): δ_H (300 MHz, $CDCl_3$) 6.90 (1H, s, C*H*Cl), 7.08-7.48 (7H, m, Ar*H*), 7.61 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 127.7 (CH, *C*HCl), 128.3, 128.6, 128.7, 129.11, 129.13, 129.4, 130.5 (7 x CH, aromatic CH), 130.6 [C, aromatic *C* or *C*(2)S], 130.9, 132.4, 132.5 (3 x CH, aromatic *C*H), 134.7, 139.7, 140.2 [3 x C, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 189.7 (C, *C*O).

E-4n (less polar): δ_H (300 MHz, $CDCl_3$) 6.72 (1H, s, C*H*Cl), 7.08-7.48 (7H, m, Ar*H*), 7.78 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 122.0 (CH, *C*HCl), 128.3, 128.6, 128.7, 129.11, 129.13, 129.4, 130.5, 130.9 (8 x CH, aromatic *C*H), 132.0 [C, aromatic *C* or *C*(2)S], 132.4, 132.5 (2 x CH, aromatic *C*H), 132.9, 134.9, 140.5 [3 x C, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 189.9 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{15}H_{11}OS^{35}Cl_2[M+H]^+$ 308.9908. Found 308.9917; m/z (ES+) 309.0 [$(C_{15}H_{10}OS^{35}Cl_2)+H^+$], 100%, 311.0 [$(C_{15}H_{10}OS^{35}Cl^{37}Cl)+H^+$], 62%, 313.0 [$(C_{15}H_{10}OS^{37}Cl_2)+H^+$], 14%.

(*Z*)-2-(Benzylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one Z-4o and (*E*)-2-(Benzylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one E-4o



This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-(4-chlorophenyl)propan-1-one **3o** (0.596 g, 2.1 mmol), *N*-chlorosuccinimide (0.527 g, 4.0 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. The ^{1}H NMR spectrum showed the presence of two isomers (*Z*:*E* 1.7:1) as well as *approx*. 19% of the dichloride precursor **S29** (A of AB system, δ_H 4.07 ppm, J_{AB} 11.9; B of AB system, δ_H 4.25 ppm, J_{AB} 11.9). Attempts to remove the dichloride by column chromatography proved unsuccessful and so a Lewis acid was used to convert the dichloride precursor to the desired α-*thio*-β-*chloroenone* as follows. A solution of zinc chloride in ether (4.2 mL of a 1M solution, 4.2 mmol) was added to a stirring solution of the dichloride/α-thio-β-chloroenone mixture (0.506 g, 1.4 mmol) in dichloromethane (10 mL). The solution was heated at reflux for 18 h under nitrogen. The reaction was quenched with water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated to give the α-*thio*-

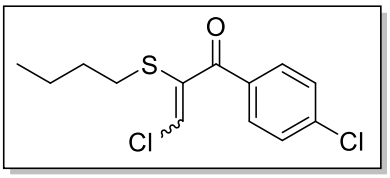
β-*chloroenones* **Z-4o** and **E-4o** (ratio *Z*:*E* 2.4:1) (0.319 g, 48%) as an orange oil. No further purification was carried out; ν_{max}/cm^{-1} (ATR) 3085, 3061, 3030, 1660 (C=O), 1584, 1246, 1089, 1012, 698; δ_H (400 MHz, $CDCl_3$) 3.87 (2H, s, S*CH*$_2$, *E* isomer), 4.00 (2H, s, S*CH*$_2$, *Z* isomer), 6.46 (1H, s, *CH*Cl, *E* isomer), 6.64 (1H, s, *CH*Cl, *Z* isomer), 7.05-7.33 [7H and 5H, m, Ar*H*, *Z* and *E* isomer, containing (7.30, 2H, d, *J* 8.7, Ar*H*, *Z* isomer)], 7.38 (2H, d, *J* 8.6, Ar*H*, *Z* isomer), 7.42 (2H, d, *J* 8.6, Ar*H*, *E* isomer), 7.81 (2H, d, *J* 8.6, Ar*H*, *E* isomer); HRMS (ES+): Exact mass calculated for $C_{16}H_{13}OS^{35}Cl_2[M+H^+]$ 323.0064. Found 323.0059. $^{35}Cl/^{37}Cl$ pattern visible in HRMS at 323, 325 and 327 in a 9:6:1 ratio.

^{1}H and ^{13}C NMR spectra were recorded after storage at room temperature for 42 months and were seen to contain an altered ratio of Z and E isomers (Z:E 4:1 assigned from ^{1}H NMR spectrum).

Z-4o: δ_C (100 MHz, $CDCl_3$): 35.7 (CH_2, S*C*H$_2$), 127.4 (CH, 1 x aromatic *C*H), 128.5, 128.7, 129.3 (3 x CH signal, 6 x aromatic *C*H), 130.4 [CH, *C*(3)H], 131.1 (1 x CH signal, 2 x aromatic *C*H), 134.9, 137.0 (2 x C, aromatic *C*), 139.7 [C, *C*(2)S], 139.8 (C, aromatic *C*), 189.3 (C, *C*O).

Only characteristic signals for **E-4o** *could be observed*; δ_C (100 MHz, $CDCl_3$): 38.6 (CH_2, S*C*H$_2$), 122.5 [CH, *C*(3)H], 190.6 (C, *C*O).

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one Z-4p and (*E*)-2-(*n*-butylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one E-4p



This was prepared following the procedure described above for **4a** using 2-(butylthio)-1-(4-chlorophenyl)propan-1-one **3p** (1.76 g, 6.9 mmol), *N*-chlorosuccinimide (1.79 g, 13.5 mmol, 1.95 eq) and toluene (40 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a brown oil. By ^{1}H NMR spectroscopy, this product was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4p** and **E-4p**, in a ratio of 1:2. This was purified by column chromatography on silica gel using hexane as eluent. The major isomer **E-4p** (25 mg, 13%) was isolated as a clear oil.

E-4p (less polar): ν_{max}/cm^{-1} (film) 3067 (CH), 2960 (CH), 1674 (CO), 1586 (aromatic), 1094; δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.3, CH_2CH_3), 1.24-1.41 (2H, m, CH_2CH_3), 1.52-1.68 (2H, m,

C*H*$_2$CH$_2$CH$_3$), 2.60-2.65 (2H, m, SC*H*$_2$), 6.59 (1H, s, C*H*Cl), 7.68 (2H, d, *J* 8.7, Ar*H*), 7.90 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.52 (CH_3, CH*C*H$_3$), 21.6 (CH_2, *C*H$_2$CH$_3$), 31.1 (CH_2, *C*H$_2$CH$_2$CH$_3$), 33.4 (CH_2, S*C*H$_2$), 119.7 (CH, *C*HCl), 129.3, 131.0 (2 x CH, aromatic *C*H), 132.5, 134.6, 140.7 [3 x C, 2 x aromatic *C* and *C*(2)S], 190.4 (C, *C*O). HRMS (ES+): Exact mass calculated for $C_{13}H_{15}OS^{35}Cl_2[M+H]^+$ 289.0221. Found 289.0212; m/z (ES+) 186.4 (100%), 187.5 (14%).

The major fraction isolated after chromatography contained the β-*chloroenone* (1.31 g, 66%) as an orange oil and a mixture of *Z* and *E* isomers **Z-4p** and **E-4p** in a ratio of 1:1.3; ν_{max}/cm^{-1} (film) 3067 (CH), 2960 (CH), 1670 (CO), 1587 (aromatic), 1092.

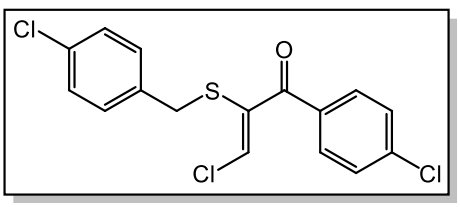
E-4p (less polar): δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.3, CH$_2$C*H*$_3$), 1.24-1.41 (2H, m, C*H*$_2$CH$_3$), 1.52-1.68 (2H, m, C*H*$_2$CH$_2$CH$_3$), 2.60-2.65 (2H, m, SC*H*$_2$), 6.59 (1H, s, C*H*Cl), 7.68 (2H, d, *J* 8.7, Ar*H*), 7.90 (2H, d, *J* 8.7, Ar*H*).

Spectroscopic characteristics were consistent with those reported above.

Z-4p (more polar): δ_H (300 MHz, $CDCl_3$) 0.84 (3H, t, *J* 7.3, CH$_2$C*H*$_3$), 1.20-1.26 (2H, m, C*H*$_2$CH$_3$), 1.45-1.51 (2H, m, C*H*$_2$CH$_2$CH$_3$), 2.65-2.70 (2H, m, SC*H*$_2$), 6.70 (1H, s, C*H*Cl), 7.46 (2H, d, *J* 8.7, Ar*H*), 7.86 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.48 (CH_3, CH*C*H$_3$), 21.5 (CH_2, *C*H$_2$CH$_3$), 31.5 (CH_2, S*C*H$_2$), 32.0 (CH_2, *C*H$_2$CH$_2$CH$_3$), 126.9 (CH, *C*HCl), 129.0, 131.2 (2 x CH, aromatic *C*H), 134.4, 139.8, 140.3 [3 x C, 2 x aromatic *C* and *C*(2)S], 189.7 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{13}H_{15}OS^{35}Cl_2[M+H]^+$ 289.0221. Found 289.0222; m/z (ES+) 186.4 (100%).

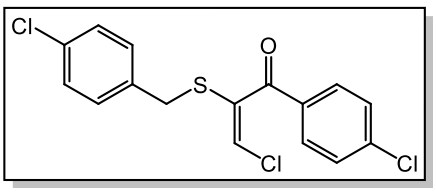
(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one Z-4q and (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one E-4q



This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)propan-1-one **3q** (2.00 g, 6.2 mmol), *N*-chlorosuccinimide (1.60 g, 12.0 mmol, 1.95 eq) and toluene (25 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (90%, *Z*:*E* 2.7:1) and the α,β-unsaturated ketone side product **S30** (3%, 2 x s, δ_H 5.75 and 5.83 ppm). Purification by column

chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave pure **E-4q** (0.354 g, 16%) as a colourless oil. Further column chromatography (hexane-dichloromethane, 70:30) gave the α-*thio*-β-*chloroenone* **Z-4q** (0.45 g, 20%) as a yellow oil.

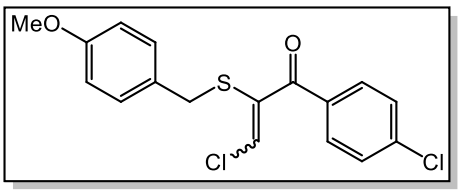
Z-4q (more polar)**:** ν_{max}/cm^{-1} (ATR) 3088, 3051, 1659 (C=O), 1584, 1488, 1245, 1089, 808, 737; δ_H (400 MHz, $CDCl_3$): 3.98 (2H, s, SC*H*$_2$), 6.68 (1H, s, C*H*Cl), 7.09-7.17 (4H, m, Ar*H*), 7.31-7.44 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 35.1 (CH_2, S*C*H$_2$), 128.7, 128.8, 130.6 (3 x CH signals, 6 x aromatic *C*H), 130.7 [CH, *C*(3)H], 131.0 (1 x CH signal, 2 x aromatic *C*H), 133.3, 134.7, 135.6, 139.2, 140.0 [5 x C, 4 x aromatic *C* and *C*(2)S], 189.2 (C, *C*O).



E-4q (less polar)**:** ν_{max}/cm^{-1} (ATR) 3066, 1665 (C=O), 1585, 1488, 1286, 1218, 1091, 1013, 836; δ_H (400 MHz, $CDCl_3$): 3.81 (2H, s, SC*H*$_2$), 6.47 (1H, s, C*H*Cl), 7.17-7.30 (4H, m, Ar*H*), 7.45 (2H, d, *J* 8.5, Ar*H*), 7.82 (2H, d, *J* 8.6, Ar*H*); δ_C (100 MHz, $CDCl_3$): 37.8 (CH_2, S*C*H$_2$), 123.3 [CH, *C*(3)H], 128.7, 129.3, 130.5, 131.0 (4 x CH signals, 8 x aromatic *C*H), 132.3, 132.4, 133.4, 135.1, 140.8 [5 x C, 4 x aromatic *C* and *C*(2)S], 190.5 (C, *C*O).

HRMS was recorded for another sample which contained a mixture of Z and E isomers in a ratio of 1.7:1; HRMS (ES+): Exact mass calculated for $C_{16}H_{12}OS^{35}Cl_3[M+H^+]$ 356.9674. Found 356.9669.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one Z-4r and (*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one E-4r

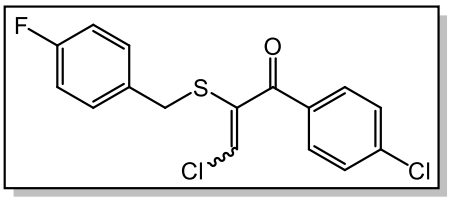


This was prepared following the procedure described above for **4a** using 1-(4-chlorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one **3r** (0.642 g, 2.0 mmol), *N*-chlorosuccinimide (0.521 g, 3.9 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (60%, *Z*:*E* 2.3:1) and the impurity 1-(chloromethyl)-4-methoxybenzene **S24**[19] (40%, s, δ_H 4.56 ppm). Following purification by column chromatography on silica gel using hexane-ethyl acetate (gradient elution, 1-5% ethyl acetate) as eluent, the α-*thio*-β-*chloroenones* **Z-4r** and **E-4r** (*Z*:*E* 9:1) (0.275 g, 39%) were

obtained as an orange crystalline solid; mp 61-65°C; ν_{max}/cm^{-1} (ATR) 2959, 2930, 2835, 1666 (C=O), 1607, 1584, 1509, 1246, 1173, 1089, 831, 738; δ_H (400 MHz, $CDCl_3$): 3.73 (3H, s, OC*H*$_3$, *Z* isomer), 3.79 (3H, s, OC*H*$_3$, *E* isomer), 3.84 (2H, s, SC*H*$_2$, *E* isomer), 3.96 (2H, s, SC*H*$_2$, *Z* isomer), 6.46 (1H, s, C*H*Cl, *E* isomer), 6.62 (1H, s, C*H*Cl, *Z* isomer), 6.68 (2H, d, *J* 8.6, Ar*H*, *Z* isomer), 6.81 (2H, d, *J* 8.7, Ar*H*, *E* isomer), 7.07 (2H, d, *J* 8.6, Ar*H*, *Z* isomer), 7.19 (2H, d, *J* 8.8, Ar*H*, *E* isomer), 7.32 (2H, d, *J* 8.6, Ar*H*, *Z* isomer), 7.41 (2H, d, *J* 8.6, Ar*H*, *Z* isomer) 7.44 (2H, d, *J* 8.7, Ar*H*, *E* isomer), 7.83 (2H, d, *J* 8.7, Ar*H*, *E* isomer); m/z (ES+) 353.1 [($C_{17}H_{14}O_2S^{35}Cl_2$)+$H^+$], 5%.

^{1}H and ^{13}C NMR spectra were recorded after storage at room temperature for 36 months and it was seen that all of the E isomer had converted to the Z isomer; **Z-4r:** δ_C (100 MHz, $CDCl_3$): 35.2 (CH_2, S*C*H$_2$), 55.2 (CH_3, O*C*H$_3$), 113.9, 128.6 (2 x CH signals, 4 x aromatic *C*H), 128.9 (C, aromatic *C*), 129.6 [CH, *C*(3)H], 130.5, 131.1 (2 x CH signals, 4 x aromatic *C*H), 134.9 (C, aromatic *C*), 139.7 [C, *C*(2)S], 139.8, 158.9 [2 x C, 2 x aromatic *C*), 189.3 (C, *C*O).

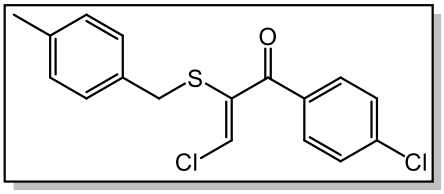
(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)prop-2-en-1-one Z-4s and (*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)prop-2-en-1-one E-4s



This was prepared following the procedure described above for **4a** using 1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)propan-1-one **3s** (0.617 g, 2.0 mmol), *N*-chlorosuccinimide (0.521 g, 3.9 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (*approx*. 90%, *Z*:*E* 2.2:1) and the α,β-unsaturated ketone side product **S31** (4%, 2 x s, δ_H 5.75 and 5.83 ppm). Following purification by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent, the α-*thio*-β-*chloroenones* **Z-4s** and **E-4s** (0.424 g, 62%) were obtained as an orange oil containing a mixture of the *E* and *Z* isomers in a ratio of *Z*:*E* 2.5:1; ν_{max}/cm^{-1} (ATR) 3053, 1660 (C=O), 1584, 1506, 1221, 1090, 738; δ_H (400 MHz, $CDCl_3$) 3.83 (2H, s, SC*H*$_2$, *E* isomer), 3.98 (2H, s, SC*H*$_2$, *Z* isomer), 6.46 (1H, s, C*H*Cl, *E* isomer), 6.67 (1H, s, C*H*Cl, *Z* isomer), 6.86 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*, *Z* isomer), 6.97 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*, *E* isomer), 7.14 (2H, overlapping dd, *J* 8.8, J_{FH} 5.3, Ar*H*, *Z* isomer), 7.22-7.29 (2H, m, Ar*H*,

E isomer), 7.32-7.38 (2H, m, Ar*H*, *Z* isomer), 7.39-7.49 (2H and 2H, m, Ar*H*, *Z* and *E* isomer), 7.83 (2H, d, *J* 8.8, Ar*H*, *E* isomer); δ_C (100 MHz, $CDCl_3$): 35.0 (CH_2, S*C*H_2, *Z* isomer), 37.8 (CH_2, S*C*H_2, *E* isomer), 115.4 (1 x CH signal, 4 x CH, d, $^2J_{CF}$ 21.6, aromatic *C*H, *Z* and *E* isomer), 123.1 [CH, *C*(3)H, *E* isomer], 128.8 (1 x CH signal, 2 x aromatic *C*H, *Z* isomer), 129.3 (1 x CH signal, 2 x aromatic *C*H, *E* isomer), 130.5 [CH, *C*(3)H, *Z* isomer], 130.8 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H, *E* isomer), 130.9 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.2, aromatic *C*H, *Z* isomer), 131.0 (1 x CH signal, 2 x aromatic *C*H, *E* isomer), 131.1 (1 x CH signal, 2 x aromatic *C*H, *Z* isomer), 132.3 (C, d, $^4J_{CF}$ 3.3, aromatic *C*, *E* isomer), 132.8 (C, d, $^4J_{CF}$ 3.2, aromatic *C*, *Z* isomer), 132.4, 132.5, (2 x C, C_q, *E* isomer), 134.8, 139.3, 140.0 [3 x C, 2 x aromatic *C* and *C*(2)S, *Z* isomer], 140.8 (C, C_q, *E* isomer), 162.0 (C, d, $^1J_{CF}$ 246.8, aromatic *C*, *Z* isomer), 162.1 (C, d, $^1J_{CF}$ 246.4, aromatic *C*, *E* isomer), 189.2 (C, *C*O, *Z* isomer), 190.5 (C, *C*O, *E* isomer); HRMS (ES+): Exact mass calculated for $C_{16}H_{12}OFS^{35}Cl_2[M+H^+]$ 340.9970. Found 340.9979.

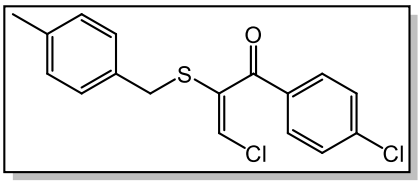
(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one Z-4t and (*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one E-4t



This was prepared following the procedure described above for **4a** using 1-(4-chlorophenyl)-2-((4-methybenzyl)thio)propan-1-one **3t** (0.71 g, 2.3 mmol), *N*-chlorosuccinimide (0.607 g, 4.5 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (93%, *Z*:*E* 2.5:1) and the α,β-unsaturated ketone side product **S32** (3%, 2 x s, δ_H 5.73 and 5.82 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (70:30) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4t** (0.26 g, 33%) as an orange oil and pure **E-4t** (0.101 g, 13%) as a white solid (mp 84-86°C).

Z-4t (more polar)**:** ν_{max}/cm^{-1} (ATR) 3314, 3088, 3049, 2920, 2860, 1660 (C=O), 1584, 1245, 1089, 808, 737; δ_H (400 MHz, $CDCl_3$): 2.26 (3H, s, ArCH_3), 3.97 (2H, s, SCH_2), 6.62 (1H, s, C*H*Cl), 6.92-7.11 (4H, m, Ar*H*), 7.28-7.44 (4H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.0 (CH_3, Ar*C*H_3), 35.5 (CH_2, S*C*H_2), 128.6, 129.21, 129.25 (3 x CH signals, 6 x aromatic *C*H), 129.7 [CH, *C*(3)H], 131.1 (1 x CH signal, 2 x aromatic *C*H), 133.9, 134.9, 137.2, 139.7, 139.8 [5 x C, 4 x aromatic *C* and

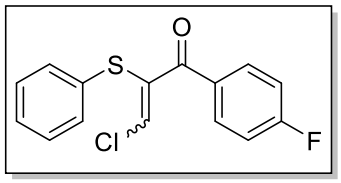
C(2)S], 189.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OS^{35}Cl_2$[M+H$^+$] 337.0221. Found 337.0230.



E-4t (less polar)**:** ν_{max}/cm^{-1} (ATR) 3330, 3066, 3024, 2921, 1668 (C=O), 1586, 1287, 1220, 839; δ_H (400 MHz, $CDCl_3$): 2.32 (3H, s, ArC*H*$_3$), 3.84 (2H, s, SC*H*$_2$), 6.47 (1H, s, C*H*Cl), 7.06-7.20 (4H, m, Ar*H*), 7.41-7.48 (2H, m, Ar*H*), 7.79-7.86 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.1 (CH_3, Ar*C*H$_3$), 38.3 (CH_2, S*C*H$_2$), 122.1 [CH, *C*(3)H], 129.1, 129.2, 129.3, 131.0 (4 x CH signals, 8 x aromatic *C*H), 132.6, 133.2, 133.2, 137.3, 140.6 [5 x C, 4 x aromatic *C* and *C*(2)S], 190.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OS^{35}Cl_2$[M+H$^+$] 337.0221. Found 337.0226; m/z (ES+) 337.1 [($C_{17}H_{14}OS^{35}Cl_2$)+H$^+$], 5%.

Relative stereochemistry was assigned for **4t** *by a NOESY experiment.*

(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-(phenylthio)prop-2-en-1-one Z-4u and (*E*)-3-chloro-1-(4-fluorophenyl)-2-(phenylthio)prop-2-en-1-one E-4u



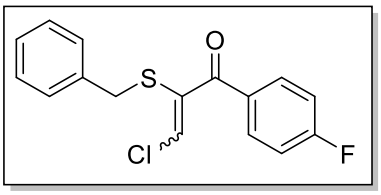
This was prepared following the procedure described above for **4a** using 1-(4-fluorophenyl)-2-(phenylthio)propan-1-one **3u** (0.15 g, 0.5 mmol), *N*-chlorosuccinimide (0.15 g, 1.1 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy this was seen to contain β-chloroenone as the major component as a mixture of *Z* and *E* isomers, **Z-4u** and **E-4u**, in a ratio of 1.3:1. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the β-*chloroenone* (0.106 g, 63%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4u** and **E-4u** in a ratio of 3.8:1, containing *approx.* 1% of the α,β-unsaturated ketone **S33**; ν_{max}/cm^{-1} (film) 3060 (CH), 1666 (CO), 1597 (aromatic), 1237.

Z-4u (more polar): δ_H (300 MHz, $CDCl_3$) 6.88 (1H, s, C*H*Cl), 6.98-7.45 (7H, m, Ar*H*), 7.68-7.75 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 115.5 (CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 127.2 (CH, *C*HCl), 128.2 (CH, aromatic *C*H), 129.1 (CH, aromatic *C*H), 130.6 [C, aromatic *C* or *C*(2)S], 131.9 (CH, d, $^3J_{CF}$ 9.5, aromatic *C*H), 132.5 (CH, aromatic *C*H), 132.6 (C, d, $^4J_{CF}$ 2.9, aromatic *C*), 140.3 [C, aromatic *C* or *C*(2)S], 165.7 (C, d, $^1J_{CF}$ 255.7, aromatic *C*), 189.4 (C, *C*O).

E-4u (less polar): δ_H (300 MHz, $CDCl_3$) 6.71 (1H, s, C*H*Cl), 6.98-7.45 (7H, m, Ar*H*), 7.82-7.92 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 116.0 (CH, d, $^2J_{CF}$ 22.1, aromatic *C*H), 121.8 (CH, *C*HCl), 128.2 (CH, aromatic *C*H), 128.7, 129.4 (2 x CH, aromatic *C*H), 130.7 [C, aromatic *C* or *C*(2)S], 130.9 (C, d, $^4J_{CF}$ 2.8, aromatic *C*), 132.4 (CH, d, $^3J_{CF}$ 10.0, aromatic *C*H), 135.0 [C, aromatic *C* or *C*(2)S], 166.3 (C, d, $^1J_{CF}$ 256.7, aromatic *C*), 189.6 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{15}H_{11}OS^{35}ClF[M+H]^+$ 293.0203. Found 293.0195; m/z (ES+) 367.0 (100%), 293.1 [$(C_{15}H_{10}OS^{35}ClF)+H^+$], 31%, 295.0 [$(C_{15}H_{10}OS^{37}ClF)+H^+$], 12%, 291.1 (80%).

(*Z*)-2-(Benzylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one Z-4v and (*E*)-2-(benzylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one E-4v



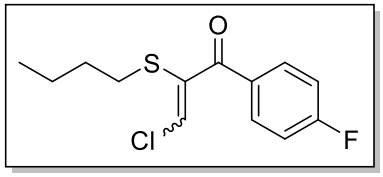
This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-(4-fluorophenyl)propan-1-one **3v** (0.53 g, 1.9 mmol), *N*-chlorosuccinimide (0.50 g, 3.8 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy, this was seen to contain β-chloroenone a mixture of *Z* and *E* isomers, **Z-4v** and **E-4v**, in a ratio of 1.4:1, in addition to signals due to the α,β-unsaturated ketone **S34** (2 x d, δ_H 6.05, *J* 2.0 and δ_H 6.26 ppm, *J* 2.0) and benzaldehyde **S18** (s, δ_H 10.01 ppm). Following purification by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-2% ethyl acetate) as eluent, the β-*chloroenone* (0.45 g, 76%) was isolated as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4v** and **E-4v** in a ratio of 2:1, a trace of the α,β-unsaturated ketone **S34** and benzaldehyde **S18** were also present; ν_{max}/cm^{-1} (film) 3064 (CH), 3032 (CH), 2931 (CH), 1663 (CO), 1597 (aromatic), 1239.

Z-4v (more polar): δ_H (300 MHz, $CDCl_3$) 4.01 (2H, s, S*CH*$_2$), 6.62 (1H, s, C*H*Cl), 6.98-7.30 (7H, m, Ar*H*), 7.43-7.51 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 35.7 (CH_2, S*C*H_2), 115.6 (CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 128.5, 129.3 (2 x CH, aromatic *C*H), 129.5 (CH, *C*HCl), 132.4 (CH, d, $^3J_{CF}$ 9.5, aromatic *C*H), 132.9 (C, d, $^4J_{CF}$ 3.1, aromatic *C*), 137.1, 139.7 [2 x C, aromatic *C* and *C*(2)S], 165.7 (C, d, $^1J_{CF}$ 255.9, aromatic *C*), 189.0 (C, *C*O).

E-4v (less polar): δ_H (300 MHz, $CDCl_3$) 3.88 (2H, s, SC*H*$_2$), 6.45 (1H, s, C*H*Cl), 6.98-7.30 (7H, m, Ar*H*), 7.89-7.98 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 38.5 (CH_2, S*C*H_2), 116.1 (CH, d, $^2J_{CF}$ 22.2, aromatic *C*H), 122.2 (CH, *C*HCl), 128.0 (CH, d, $^3J_{CF}$ 9.1, aromatic *C*H), 128.5, 129.2 (2 x CH, aromatic *C*H), 130.6 (C, d, $^4J_{CF}$ 3.0, aromatic *C*), 133.1, 136.4 [2 x C, aromatic *C* and *C*(2)S], 166.3 (C, d, $^1J_{CF}$ 256.8, aromatic *C*), 190.2 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{16}H_{13}OS^{35}ClF[M+H]^+$ 307.0360. Found 307.0367; m/z (ES+) 307.1 [$(C_{16}H_{12}OS^{35}ClF)+H^+$], 100%, 309.1 [$(C_{16}H_{12}OS^{37}ClF)+H^+$], 39%.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one Z-4w and (*E*)-2-(*n*-butylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one E-4w



This was prepared following the procedure described above for **4a** using 2-(butylthio)-1-(4-fluorophenyl)propan-1-one **3w** (0.15 g, 0.6 mmol), *N*-chlorosuccinimide (0.163 g, 1.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^{1}H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4w** and **E-4w**, in a ratio of 1:1.2. This was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-2% ethyl acetate) as eluent to give the major isomer **E-4w** (30 mg, 18%) as a yellow oil; ν_{max}/cm^{-1} (film) 2960 (CH), 1672 (CO), 1597 (aromatic), 1232, 1154.

E-4w (less polar): δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.3, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.54-1.65 (2H, m, $CH_2CH_2CH_3$), 2.61-2.66 (2H, m, SC*H*$_2$), 6.60 (1H, s, C*H*Cl), 7.12-7.20 (2H, m, Ar*H*), 7.92-8.02 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 13.54 (CH_3, $CHCH_3$), 21.6 (CH_2, CH_2CH_3), 31.1 (CH_2, $CH_2CH_2CH_3$), 33.3 (CH_2, S*C*H_2), 116.2 (CH, d, $^2J_{CF}$ 22.2, aromatic *C*H), 119.5 (CH, *C*HCl), 130.6 (C, d, $^4J_{CF}$ 2.8 aromatic *C*), 132.4 (CH, d, $^3J_{CF}$ 9.6, aromatic *C*H), 134.5 [C, *C*(2)S], 166.4 (C, d, $^1J_{CF}$ 256.7, aromatic *C*), 190.2 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{13}H_{15}OS^{35}ClF[M+H]^+$ 273.0516. Found 273.0504; m/z (ES+) 289.1 (62%), 291.1 (24%), 335.0 (100%).

The major fraction isolated after chromatography contained the β-*chloroenone* **4w** (0.124 g, 73%) as a yellow oil and a mixture of *Z* and *E* isomers **Z-4w** and **E-4w** in a ratio of 1:1.1; ν_{max}/cm^{-1} (film) 3071 (CH), 2960 (CH), 1668 (CO), 1597 (aromatic), 1239, 1154.

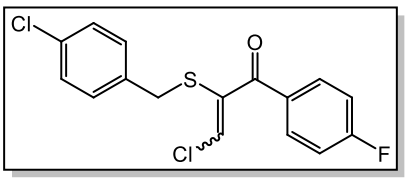
E-4w (less polar): δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.5, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.54-1.65 (2H, m, $CH_2CH_2CH_3$), 2.61-2.66 (2H, m, SCH_2), 6.60 (1H, s, CHCl), 7.12-7.20 (2H, m, ArH), 7.92-8.02 (2H, m, ArH).

Spectroscopic characteristics are consistent with above.

Z-4w (more polar): δ_H (300 MHz, $CDCl_3$) 0.84 (3H, t, *J* 7.4, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.43-1.65 (2H, m, $CH_2CH_2CH_3$), 2.67-2.71 (2H, m, SCH_2), 6.68 (1H, s, CHCl), 7.12-7.20 (2H, m, ArH), 7.92-8.02 (2H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 13.50 (CH_3, $CHCH_3$), 21.6 (CH_2, CH_2CH_3), 31.4 (CH_2, SCH_2), 32.0 (CH_2, $CH_2CH_2CH_3$), 116.0 (CH, d, $^2J_{CF}$ 22.0, aromatic CH), 126.3 (CH, CHCl), 132.6 (CH, d, $^3J_{CF}$ 9.5, aromatic CH), 132.9 (C, d, $^4J_{CF}$ 3.2 aromatic C), 139.8 [C, C(2)S], 166.1 (C, d, $^1J_{CF}$ 256.5, aromatic C), 189.4 (C, CO).

HRMS (ES+): Exact mass calculated for $C_{13}H_{15}OS^{35}ClF[M+H]^+$ 273.0516. Found 273.0518; m/z (ES+) 273.2 [$(C_{13}H_{14}OS^{35}ClF)+H^+$], 4%, 493.0 (100%), 327.1 (40%).

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one Z-4x and (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one E-4x



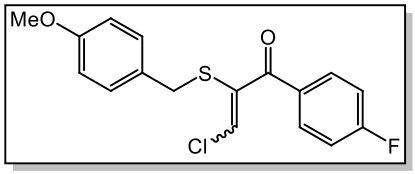
This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one **3x** (0.617 g, 2.0 mmol), *N*-chlorosuccinimide (0.521 g, 3.9 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (88%, *Z*:*E* 2.2:1) and the α,β-unsaturated ketone side product **S35** (6%, 2 x s, δ_H 5.73 and 5.80 ppm). Following purification by column chromatography on silica gel by gradient elution using hexane-ethyl acetate (0-5% ethyl acetate) as eluent, the α-*thio*-β-*chloroenones* **Z-4x** and **E-4x** (0.448 g, 66%, yellow oil) were obtained as a mixture of *E* and *Z* isomers in a ratio of *Z*:*E* 2.2:1;

ν_{max}/cm^{-1} (ATR) 3064, 1658 (C=O), 1595, 1503, 1489, 1235, 1153; δ_H (400 MHz, $CDCl_3$) 3.83 (2H, s, SC*H*$_2$, *E* isomer), 3.97 (2H, s, SC*H*$_2$, *Z* isomer), 6.47 (1H, s, C*H*Cl, *E* isomer), 6.65 (1H, s, C*H*Cl, *Z* isomer), 7.05 (2H, overlapping dd appears as t, *J* 8.6, Ar*H*, *Z* isomer), 7.09-7.18 (2H and 6H, m, Ar*H*, *Z* and *E* isomer), 7.19-7.29 (2H, m, Ar*H*, *Z* isomer), 7.52 (2H, overlapping dd, *J* 8.9, J_{FH} 5.4, Ar*H*, *Z* isomer), 7.91 (2H, overlapping dd, *J* 8.9, J_{FH} 5.4, Ar*H*, *E* isomer); HRMS (ES+): Exact mass calculated for $C_{16}H_{12}OFS^{35}Cl_2$[M+H$^+$] 340.9970. Found 340.9964.

^{13}C NMR spectrum was recorded after storage at room temperature for 1 month; **Z-4x:** δ_C (75 MHz, $CDCl_3$): 35.1 (CH_2, S*C*H$_2$), 115.6 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 128.6 (1 x CH signal, 2 x aromatic *C*H), 129.8 [CH, *C*(3)H], 130.6 (1 x CH signal, 2 x aromatic *C*H), 132.4 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.4, aromatic *C*H), 132.7 (C, d, $^4J_{CF}$ 2.9, aromatic *C*), 133.3, 135.6 (2 x C, aromatic *C*), 139.2 [C, *C*(2)S], 165.9 (C, d, $^1J_{CF}$ 256.5, aromatic *C*), 188.9 (C, *C*O).

Characteristic signals observed for **E-4x:** δ_C (75 MHz, $CDCl_3$): 37.8 (CH_2, S*C*H$_2$), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.2, aromatic *C*H), 123.0 [CH, *C*(3)H], 128.7 (1 x CH signal, 2 x aromatic *C*H), 130.5 (1 x CH signal, 2 x aromatic *C*H), 133.4, 135.1 (2 x C signals, 2 x C_q), 166.4 (C, d, $^1J_{CF}$ 257.0, aromatic *C*), 190.1 (C, *C*O).

(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one Z-4y and (*E*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one E-4y



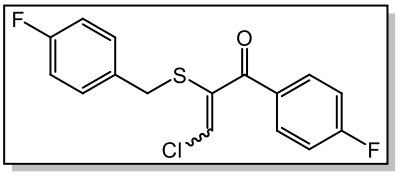
This was prepared following the procedure described above for **4a** using 1-(4-fluorophenyl)-2-((4-methoxybenzyl)thio)-propan-1-one **3y** (0.617 g, 2.0 mmol), *N*-chlorosuccinimide (0.523 g, 3.9 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (*Z*:*E* 2.6:1). Following purification by column chromatography on silica gel by gradient elution using hexane-ethyl acetate (0-5% ethyl acetate) as eluent, the α-*thio*-β-*chloroenones* **Z-4y** and **E-4y** (0.276 g, 40%, orange oil) were obtained as a mixture of *E* and *Z* isomers in a ratio of *Z*:*E* 2.8:1; ν_{max}/cm^{-1} (ATR) 2956, 2933, 2836, 1659 (C=O), 1595, 1509, 1234, 1153, 1031, 823, 743, 597; δ_H (400 MHz, $CDCl_3$) 3.71 (3H, s, OC*H*$_3$, *Z* isomer), 3.77 (3H, s, OC*H*$_3$, *E* isomer), 3.83 (2H, s, SC*H*$_2$, *E* isomer), 3.95 (2H, s, SC*H*$_2$, *Z* isomer), 6.44 (1H, s, C*H*Cl, *E* isomer), 6.60 (1H, s, C*H*Cl, *Z* isomer), 6.67 (2H, d, *J* 8.6, Ar*H*, *Z* isomer), 6.81 (2H, d, *J*

8.7, Ar*H*, *E* isomer), 6.98-7.23 (4H and 4H, m, Ar*H*, *Z* and *E* isomer), 7.52 (2H, overlapping dd, *J* 8.9, J_{FH} 5.4, Ar*H*, *Z* isomer), 7.92 (2H, overlapping dd, *J* 8.9, J_{FH} 5.4, Ar*H*, *E* isomer); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}O_2FS^{35}Cl[M+H^+]$ 337.0465. Found 337.0452.

^{1}H and ^{13}C NMR spectra were recorded after storage at room temperature for 42 months and was seen to contain an altered ratio of Z and E isomers (Z:E 4.4:1 assigned from ^{1}H NMR spectrum); **Z-4y:** δ_C (100 MHz, $CDCl_3$): 35.2 (CH_2, S*C*H_2), 55.25 (CH_3, O*C*H_3), 113.8 (1 x CH signal, 2 x aromatic *C*H), 115.5 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 128.94 (C, aromatic *C*), 128.97 [CH, *C*(3)H], 130.5 (2 x CH, aromatic *C*H), 132.5 (2 x CH, d, $^3J_{CF}$ 9.4, aromatic *C*H), 132.8 (C, d, $^4J_{CF}$ 3.1, aromatic *C*,), 139.8 [C, *C*(2)S], 158.9 (C, aromatic *C*), 165.8 (C, d, $^1J_{CF}$ 256.4, aromatic *C*), 189.0 (C, *C*O).

Characteristic signals observed for **E-4y**: δ_C (100 MHz, $CDCl_3$): 38.1 (CH_2, S*C*H_2), 55.27 (CH_3, O*C*H_3), 113.9 (1 x CH signal, 2 x aromatic *C*H), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.9, aromatic *C*H), 122.0 [CH, *C*(3)H], 128.3 (C, aromatic *C*), 130.3 (1 x CH signal, 2 x aromatic *C*H), 132.4 (2 x CH, d, $^3J_{CF}$ 9.8, aromatic *C*H), 159.0 (C, aromatic *C*), 190.8 (C, *C*O).

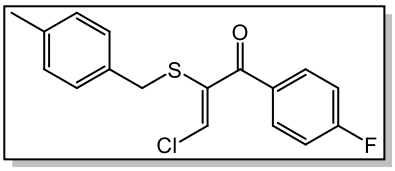
(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one Z-4z and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one E-4z



This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one **3z** (0.584 g, 2.0 mmol), *N*-chlorosuccinimide (0.521 g, 3.9 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. The ^{1}H NMR spectrum showed the presence of two isomers (93%, *Z*:*E* 2.6:1) and the α,β-unsaturated ketone side product **S36** (3%, 2 x s, δ_H 5.73 and 5.80 ppm). Following purification by column chromatography on silica gel using hexane-ethyl acetate (gradient 0-4% ethyl acetate) as eluent, the pure α-*thio*-β-*chloroenones* **Z-4z** and **E-4z** (*Z*:*E* 3:1) (0.416 g, 64%) were obtained as a yellow oil; ν_{max}/cm^{-1} (ATR) 3071, 1659 (C=O), 1595, 1504, 1222, 1154; δ_H (400 MHz, $CDCl_3$) 3.84 (2H, s, S*C*H_2, *E* isomer), 3.97 (2H, s, S*C*H_2, *Z* isomer), 6.46 (1H, s, C*H*Cl, *E* isomer), 6.65 (1H, s, C*H*Cl, *Z* isomer), 6.85 (2H, overlapping dd appears as t, *J* 8.6, Ar*H*, *Z* isomer), 6.96 (2H, overlapping dd appears as t, *J* 8.6, Ar*H*, *E* isomer), 7.05 (2H, overlapping dd

appears as t, *J* 8.6, Ar*H*, *Z* isomer), 7.10-7.19 (2H and 2H, m, Ar*H*, *Z* and *E* isomer), 7.21-7.30 (2H, m, Ar*H*, *E* isomer), 7.55 (2H, overlapping dd, *J* 8.7, J_{FH} 5.4, Ar*H*, *Z* isomer), 7.92 (2H, overlapping dd, *J* 8.8, J_{FH} 5.4, Ar*H*, *E* isomer); δ_C (100 MHz, $CDCl_3$): 35.0 (CH_2, SCH_2, *Z* isomer), 37.8 (CH_2, SCH_2, *E* isomer), 115.41 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H, *Z* isomer), 115.44 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic *C*H, *E* isomer), 115.7 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic *C*H, *Z* isomer), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.1, aromatic *C*H, *E* isomer), 122.8 [CH, *C*(3)H, *E* isomer], 129.7 [CH, *C*(3)H, *Z* isomer], 130.5 (C, d, $^4J_{CF}$ 2.8, aromatic *C*, *E* isomer), 130.8 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.0, aromatic *C*H, *E* isomer), 130.9 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H, *Z* isomer), 132.3 (C, d, $^4J_{CF}$ 3.3, aromatic *C*, *E* isomer), 132.4 (1 x CH signal, 4 x CH, d, $^3J_{CF}$ 9.4, aromatic *C*H, *Z* and *E* isomer), 132.6 [C, *C*(2)S, *E* isomer], 132.7 (C, d, $^4J_{CF}$ 3.0, aromatic *C*, *Z* isomer), 132.8 (C, d, $^4J_{CF}$ 3.2, aromatic *C*, *Z* isomer), 139.3 [C, *C*(2)S, *Z* isomer], 162.0 (C, d, $^1J_{CF}$ 246.6, aromatic *C*, *Z* isomer), 162.1 (C, d, $^1J_{CF}$ 246.3, aromatic *C*, *E* isomer), 165.9 (C, d, $^1J_{CF}$ 256.4, aromatic *C*, *Z* isomer), 166.4 (C, d, $^1J_{CF}$ 257.2, aromatic *C*, *E* isomer), 188.9 (C, *C*O, *Z* isomer), 190.2 (C, *C*O, *E* isomer); HRMS (ES+): Exact mass calculated for $C_{16}H_{12}OF_2S^{35}Cl[M+H^+]$ 325.0265. Found 325.0261; m/z (ES-) 323.2 [$(C_{16}H_{11}OF_2S^{35}Cl)-H^+$], 6%.

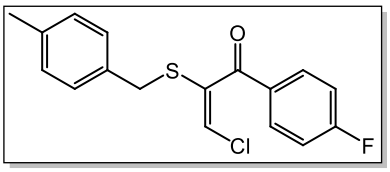
(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one Z-4aa and (*E*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one E-4aa



This was prepared following the procedure described above for **4a** using 1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)-propan-1-one **3aa** (0.50 g, 1.7 mmol), *N*-chlorosuccinimide (0.452 g, 3.4 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^{1}H NMR spectrum showed the presence of two isomers (86%, *Z*:*E* 2.3:1) and the α,β-unsaturated ketone side product **S37** (6%, 2 x s, δ_H 5.73 and 5.80 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the pure α-*thio*-β-*chloroenone* **Z-4aa** (0.245 g, 45%) as a yellow oil and pure **E-4aa** (93 mg, 17%) as a yellow oil.

Z-4aa (more polar)**:** ν_{max}/cm^{-1} (ATR) 3049, 2921, 1659 (C=O), 1595, 1503, 1234, 1153, 743, 597; δ_H (400 MHz, $CDCl_3$): 2.26 (3H, s, ArCH_3), 3.97 (2H, s, SCH_2), 6.61 (1H, s, C*H*Cl), 6.92-7.11

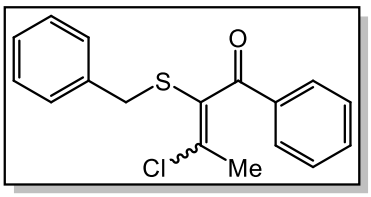
(6H, m, Ar*H*), 7.50 (2H, overlapping dd, *J* 8.6, J_{FH} 5.4, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.0 (CH_3, Ar*C*H_3), 35.5 (CH_2, S*C*H_2), 115.4 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 129.0 [CH, *C*(3)H], 129.1, 129.2 (2 x CH signals, 4 x aromatic *C*H), 132.5 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.4, aromatic *C*H), 132.9 (C, d, $^4J_{CF}$ 3.0, aromatic *C*), 133.9, 137.1, 139.8 [3 x C, 2 x aromatic *C* and *C*(2)S], 165.8 (C, d, $^1J_{CF}$ 255.9, aromatic *C*), 189.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OFS^{35}Cl[M+H^+]$ 321.0516. Found 321.0514.



E-4aa (less polar)**:** ν_{max}/cm^{-1} (ATR) 3072, 3024, 2921, 1660 (C=O), 1594, 1503, 1286, 1233, 1154; δ_H (400 MHz, $CDCl_3$): 2.32 (3H, s, Ar*C*H_3), 3.85 (2H, s, S*C*H_2), 6.46 (1H, s, *C*HCl), 7.05-7.21 (6H, m, Ar*H*), 7.92 (2H, overlapping dd, *J* 8.7, J_{FH} 5.4, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.1 (CH_3, Ar*C*H_3), 38.3 (CH_2, S*C*H_2), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.1, aromatic *C*H), 121.8 [CH, *C*(3)H], 129.0, 129.2 (2 x CH signals, 4 x aromatic *C*H), 130.6 (C, d, $^4J_{CF}$ 2.8, aromatic *C*), 132.4 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.7, aromatic *C*H), 133.2, 133.4, 137.3 [3 x C, 2 x aromatic *C* and *C*(2)S], 166.4 (C, d, $^1J_{CF}$ 256.7, aromatic *C*), 190.2 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OFS^{35}Cl$ $[M+H^+]$ 321.0516. Found 321.0505; m/z (ES+) 321.1 $[(C_{17}H_{14}FOS^{35}Cl)+H^+]$, 10%.

1.5.2 Preparation of α-Sulfenyl-β-Chlorobutenones

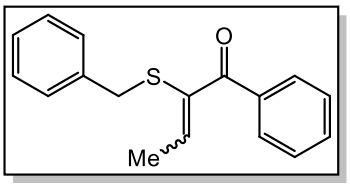
(*Z*)-2-(Benzylthio)-3-chloro-1-phenylbut-2-en-1-one Z-4bb and (*E*)-2-(Benzylthio)-3-chloro-1-phenylbut-2-en-1-one E-4bb



This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-phenylbutan-1-one **3bb** (which contained 7% disulfide **S38**[20]) (1.40 g, 5.2 mmol), *N*-chlorosuccinimide (1.35 g, 10.1 mmol, 1.95 eq) and toluene (25 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectrum analysis showed this product to contain 86% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4bb** and **E-4bb**, in a ratio of 1:1.7, the α,β-unsaturated ketone **S39** (*approx*. 10%) and the disulfide **S38**[20] (3%). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (1.05 g, 67%) as a yellow oil and an inseparable mixture of Z and *E* isomers **Z-4bb**

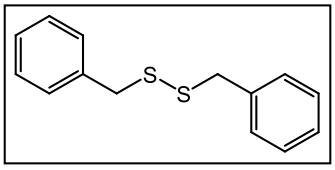
and **E-4bb** in a ratio of 1:1.6; ν_{max}/cm^{-1} (ATR) 3084, 3061, 3029, 2918, 1661 (C=O), 1595, 1579, 1242, 690; δ_H (300 MHz, $CDCl_3$): 2.07 [6H, s, C(4)*H*$_3$, *E* and *Z* isomer], 3.79 (2H, s, SC*H*$_2$, *Z* isomer), 3.82 (2H, s, SC*H*$_2$, *E* isomer), 7.12-7.34 (5H and 5H, m, Ar*H*, *E* and *Z* isomer), 7.41-7.51 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.54-7.63 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.86-7.95 (2H and 2H, m, Ar*H*, *E* and *Z* isomer); δ_C (75 MHz, $CDCl_3$): 22.8 [CH_3, C(4)H_3, *E* isomer], 24.7 [CH_3, C(4)H_3, *Z* isomer], 37.4 (CH_2, S*C*H$_2$, *Z* isomer), 39.1 (CH_2, S*C*H$_2$, *E* isomer), 126.2 [C, *C*(2)S, *E* isomer], 127.3, 127.4, 128.4, 128.5, 128.7, 128.8, 129.1, 129.2, 129.63, 129.67 (10 x CH signals, 18 x aromatic *C*H, *E* and *Z* isomer), 130.1 [C, *C*(2)S, *Z* isomer], 133.7 (CH, aromatic *C*H, *E* isomer), 134.0 (CH, aromatic *C*H, *Z* isomer), 134.3 [C, *C*(3)Cl, *Z* isomer], 134.4 (C, aromatic *C*, *E* isomer), 135.5, 136.3 (2 x C, aromatic *C*, *Z* isomer), 137.0 (C, aromatic *C*, *E* isomer), 137.7 [C, *C*(3)Cl, *E* isomer], 192.0 (C, *C*O, *E* isomer), 192.2 (C, *C*O, *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{17}H_{16}OS^{35}Cl[M+H^+]$ 303.0610. Found 303.0599; m/z (ES+) 303.1 [($C_{17}H_{15}OS^{35}Cl$)+H^+], 100%, 305.1 [($C_{17}H_{15}OS^{37}Cl$)+H^+], 42%.

2-(Benzylthio)-1-phenylbut-2-en-1-one S39



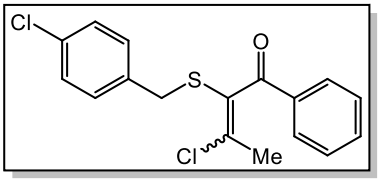
(More polar than **4bb**): orange oil (86mg, 6%); ν_{max}/cm^{-1} (ATR) 3082, 3060, 3028, 2909, 1654 (C=O), 1595, 1257, 694; δ_H (300 MHz, $CDCl_3$): 1.89 [3H, d, *J* 6.9, C(4)*H*$_3$], 3.93 (2H, s, SC*H*$_2$), 6.47 [1H, q, *J* 6.9, C(3)*H*], 7.18 (5H, s, Ar*H*), 7.28-7.38 (2H, m, Ar*H*), 7.41-7.52 (3H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$): 16.1 [CH_3, *C*(4)H_3], 36.4 (CH_2, S*C*H$_2$), 127.0, 128.0, 128.4, 129.2, 129.6, 132.1 (6 x CH signals, 10 x aromatic *C*H), 136.8 [C, *C*(2)S], 137.8, 138.1 (2 x C, aromatic *C*), 144.9 [CH, *C*(3)H], 194.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{17}OS[M+H^+]$ 269.1000. Found 269.0995; m/z (ES+) 269.2 [($C_{17}H_{16}OS$)+H^+], 100%.

E/Z stereochemistry not assigned but only one isomer present.



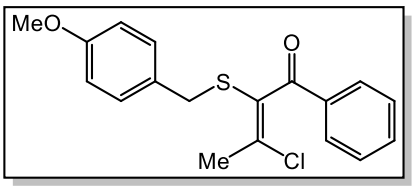
Characteristic signals due to **S38**[20]: δ_H (400 MHz, $CDCl_3$): 3.59 (4H, s, SC*H*$_2$).

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylbut-2-en-1-one Z-4cc and (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylbut-2-en-1-one E-4cc



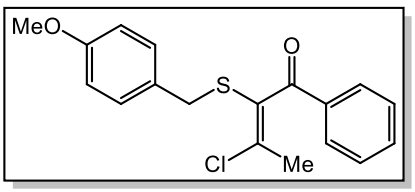
This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-phenylbutan-1-one **3cc** (0.574 g, 1.9 mmol), *N*-chlorosuccinimide (0.491 g, 3.7 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow/green oil. ^{1}H NMR spectroscopy showed this product to contain 81% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4cc** and **E-4cc**, in a ratio of 1:1.3, the α,β-unsaturated ketone **S40** (12%) (q, δ_H 6.51 ppm, *J* 6.8; d, δ_H 1.92 ppm, *J* 6.9) and the dichloride **S41** (7%) (q, δ_H 4.77 ppm, *J* 6.7; d, δ_H 1.76 ppm, *J* 6.5). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (0.467 g, 74%) as a yellow oil and as an inseparable mixture of Z and *E* isomers **Z-4cc** and **E-4cc** in a ratio of 1:1.4. A trace of the dichloride **S41** (*approx*. 5%) was still present in this fraction; ν_{max}/cm^{-1} (ATR) 3061, 2918, 1660 (C=O), 1595, 1489, 1242, 691; δ_H (400 MHz, $CDCl_3$): 2.06 [CH_3, C(4)*H*$_3$, *Z* isomer], 2.08 [CH_3, C(4)*H*$_3$, *E* isomer], 3.75 (2H, s, SC*H*$_2$, *Z* isomer), 3.78 (2H, s, SC*H*$_2$, *E* isomer), 7.15 (4H, s, Ar*H*, *Z* isomer), 7.26 (4H, s, Ar*H*, *E* isomer), 7.41-7.51 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.57-7.63 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.83-7.93 (2H and 2H, m, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 22.8 [CH_3, *C*(4)H$_3$, *E* isomer], 24.8 [CH_3, *C*(4)H$_3$, *Z* isomer], 36.6 (CH_2, S*C*H$_2$, *Z* isomer), 38.3 (CH_2, S*C*H$_2$, *E* isomer), 125.6 [C, *C*(2)S, *E* isomer], 128.5, 128.6, 128.8, 128.9 (4 x CH signals, 8 x aromatic *C*H, *E* and *Z* isomer), 129.4 (C, aromatic *C*, *E* isomer), 129.5 [C, *C*(2)S, *Z* isomer], 129.6, 129.7, 130.4, 130.6 (4 x CH signals, 8 x aromatic *C*H, *E* and *Z* isomer), 133.20, 133.23 (2 x C, aromatic *C*, *E* and *Z* isomer), 133.8, 134.1 (2 x CH, aromatic *C*H, *E* and *Z* isomer), 134.2 (C, aromatic *C*, *Z* isomer), 135.1 [C, *C*(3)Cl, *Z* isomer], 135.3 (C, aromatic *C*, *Z* isomer), 135.7 (C, aromatic *C*, *E* isomer), 138.1 [C, *C*(3)Cl, *E* isomer], 191.9, 192.1 (2 x C, *C*O, *E* and *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}OS^{35}Cl_2$[M+H$^+$] 337.0221. Found 337.0222; m/z (ES+) 337.1 [($C_{17}H_{14}OS^{35}Cl_2$)+H$^+$], 100%, 339.1 [($C_{17}H_{14}OS^{35}Cl^{37}Cl$)+H$^+$], 76%. ^{35}Cl/^{37}Cl pattern visible at 337, 339 and 341 in a 9:6:1 ratio.

(*Z*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylbut-2-en-1-one Z-4dd and (*E*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylbut-2-en-1-one E-4dd



This was prepared following the procedure described above for **4a** using 2-((4-methoxybenzyl)thio)-1-phenylbutan-1-one **3dd** (0.399 g, 1.3 mmol), *N*-chlorosuccinimide (0.345 g, 2.6 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 59% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4dd** and **E-4dd**, in a ratio of 1:1.2, and the impurity **S42**[19] (41%, s, δ_H 4.56 ppm). Purification by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 0-10% ethyl acetate) as eluent gave the pure α-*thio*-β-*chloroenone* **E-4dd** (0.109 g, 25%) as a yellow oil and **Z-4dd** (0.13 g, 29%) as an orange oil.

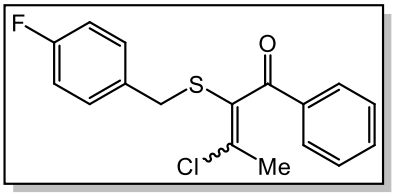
E-4dd (less polar): ν_{max}/cm^{-1} (ATR) 2954, 2932, 2835, 1661 (C=O), 1608, 1510, 1239, 1174, 1032, 691; δ_H (400 MHz, $CDCl_3$): 2.10 [3H, s, C(4)H_3], 3.79 (5H, s, OCH_3 and SCH_2), 6.81 (2H, d, *J* 8.7, Ar*H*), 7.23 (2H, d, *J* 8.6, Ar*H*), 7.42-7.52 (2H, m, Ar*H*), 7.54-7.63 (1H, m, Ar*H*), 7.89-7.96 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 22.9 [CH_3, C(4)H_3], 38.6 (CH_2, SCH_2), 55.3 (CH_3, OCH_3), 113.8 (1 x CH signal, 2 x CH, aromatic *C*H), 126.4 [C, *C*(2)S], 128.7 (1 x CH signal, 2 x aromatic *C*H), 129.0 (C, aromatic *C*), 129.6, 130.4, 133.7 (3 x CH signals, 5 x aromatic *C*H), 134.4 (C, aromatic *C*), 137.3 [C, *C*(3)Cl], 158.9 (C, aromatic *C*), 192.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{18}H_{18}O_2SCl$[M+H$^+$] 333.0716. Found 333.0709; m/z (ES+) 333.2[($C_{18}H_{17}O_2S^{35}Cl$)+H$^+$], 10%.



Z-4dd (more polar): ν_{max}/cm^{-1} (ATR) 2955, 2932, 2835, 1661 (C=O), 1608, 1595, 1579, 1510, 1240, 1174, 690; δ_H (400 MHz, $CDCl_3$): 2.06 [3H, s, C(4)H_3], 3.73 (3H, s, OCH_3), 3.75 (2H, s, SCH_2), 6.72 (2H, d, *J* 8.7, Ar*H*), 7.11 (2H, d, *J* 8.6, Ar*H*), 7.37-7.67 (3H, m, Ar*H*), 7.86-8.05 (2H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$): 24.6 [CH_3, C(4)H_3], 36.8 (CH_2, SCH_2), 55.2 (CH_3, OCH_3), 113.8 (1 x CH signal, 2 x aromatic *C*H), 128.3 (C, C_q), 128.8, 129.6, 130.2 (3 x CH signals, 6 x aromatic *C*H), 133.8 (C, C_q), 134.0 (CH, aromatic *C*H), 134.1, 135.5 (2 x C, C_q), 158.9 (C, aromatic *C*), 192.2 (C, *C*O)

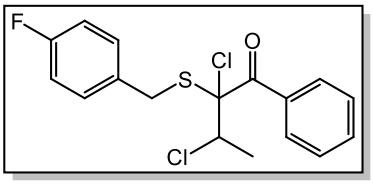
*Relative stereochemistry was assigned for **4dd** by NOESY experiments.*

(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylbut-2-en-1-one Z-4ee and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylbut-2-en-1-one E-4ee



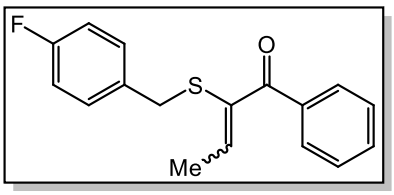
This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-phenylbutan-1-one **3ee** (0.389 g, 1.3 mmol), *N*-chlorosuccinimide (0.333 g, 2.5 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a green/yellow oil. ^{1}H NMR spectroscopy showed this product to contain 70% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4ee** and **E-4ee**, in a ratio of 1:1.4, the α,β-unsaturated ketones **S43a** and **S43b** (*Z* : *E* 9 : 1, 20%) (q, δ_H 6.50 ppm, *J* 6.9; q, δ_H 6.13 ppm, *J* 7.2) and the dichloride **S44** (7%) (q, δ_H 4.78 ppm, *J* 6.5). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (0.269 g, 65%) as a yellow oil and as an inseparable mixture of Z and *E* isomers **Z-4ee** and **E-4ee** in a ratio of 1:1.4. Some of the dichloride **S44** (*approx*. 7%) was still present in this fraction; ν_{max}/cm^{-1} (ATR) 1661 (C=O), 1597, 1508, 1243, 1223, 692; δ_H (400 MHz, $CDCl_3$): 2.06 [3H, s, C(4)*H*$_3$, *Z* isomer], 2.09 [3H, s, C(4)*H*$_3$, *E* isomer], 3.76 (2H, s, SC*H*$_2$, *Z* isomer), 3.80 (2H, s, SC*H*$_2$, *E* isomer), 6.88 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*, *Z* isomer), 6.97 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*, *E* isomer), 7.17 (2H, dd, *J* 8.6, J_{FH} 5.4, Ar*H*, *Z* isomer), 7.29 (2H, dd, *J* 8.6, J_{FH} 5.4, Ar*H*, *E* isomer), 7.40-7.53 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.56-7.65 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.83-7.96 (2H and 2H, m, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 22.8 [CH_3, *C*(4)H$_3$, *E* isomer], 24.7 [CH_3, *C*(4)H$_3$, *Z* isomer], 36.6 (CH_2, S*C*H$_2$, *Z* isomer), 38.3 (CH_2, S*C*H$_2$, *E* isomer), 115.2 (1 x CH signal, 2 x CH, d, $^{2}J_{CF}$ 21.6, aromatic *C*H, *Z* isomer), 115.3 (1 x CH signal, 2 x CH, d, $^{2}J_{CF}$ 21.5, aromatic *C*H, *E* isomer), 125.9 [C, *C*(2)S, *E* isomer], 128.7, 128.8, 129.6, 129.7 (4 x signals, 9 x C, [8 x aromatic *C*H, *E* and *Z* isomer] and [*C*(2)S, *Z* isomer]), 130.7 (1 x CH signal, 2 x CH, d, $^{3}J_{CF}$ 8.2, aromatic *C*H, *Z* isomer), 130.8 (1 x CH signal, 2 x CH, d, $^{3}J_{CF}$ 8.1, aromatic *C*H, *E* isomer), 132.3 (C, d, $^{4}J_{CF}$ 3.0, aromatic *C*, *Z* isomer), 132.9 (C, d, $^{4}J_{CF}$ 3.2, aromatic *C*, *E* isomer), 133.8, 134.1 (2 x CH, aromatic *C*H, *E* and *Z* isomer), 134.3 (C, aromatic *C*, *E* or *Z* isomer), 135.0 [C, *C*(3)Cl, *Z* isomer], 135.4 (C, aromatic *C*, *E* or *Z* isomer), 137.8 [C, *C*(3)Cl, *E* isomer], 162.0 (C, d, $^{1}J_{CF}$ 245.9, aromatic *C*, *Z* isomer), 162.1 (C, d, $^{1}J_{CF}$ 246.2, aromatic *C*, *E* isomer), 191.9, 192.1 (2 x C, *C*O, *E* and *Z* isomer); HRMS (ES+): Exact mass calculated for

$C_{17}H_{15}OFS^{35}Cl[M+H^+]$ 321.0516. Found 321.0504; m/z (ES+) 321.1 [$(C_{17}H_{14}OSF^{35}Cl)+H^+$], 100%, 323.1 [$(C_{17}H_{14}OSF^{37}Cl)+H^+$], 40%.



Characteristic signals due to the dichloride **S44**: δ_H (400 MHz, $CDCl_3$) 1.76 [3H, d, *J* 6.6, C(4)*H*$_3$], 3.92 (1H, B of AB system, J_{AB} 12.4, SC*H*$_2$), 4.78 [1H, q, *J* 6.5, C(3)*H*], 8.07 (2H, d, *J* 7.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 20.0 [CH_3, *C*(4)H_3], 36.3 (CH_2, S*C*H_2), 59.5 [CH, *C*(3)H], 115.7 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.7, aromatic *C*H).

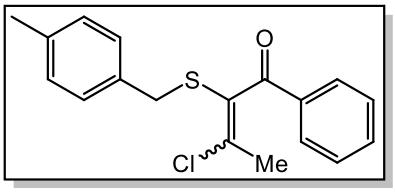
2-((4-Fluorobenzyl)thio)-1-phenylbut-2-en-1-one S43



(more polar): orange oil (55 mg, 14%); ν_{max}/cm^{-1} (ATR) 3064, 2926, 1657 (C=O), 1596, 1507, 1221, 711, 688; δ_H (400 MHz, $CDCl_3$): 1.91 [3H, d, *J* 6.9, C(4)*H*$_3$], 3.91 (2H, s, SC*H*$_2$), 6.50 [1H, q, *J* 6.9, C(3)*H*], 6.89 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*), 7.16 (2H, overlapping dd, *J* 8.6, J_{FH} 5.4, Ar*H*), 7.36 (2H, t, *J* 7.6, Ar*H*), 7.42-7.55 (3H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.1 [CH_3, *C*(4)H_3], 35.6 (CH_2, S*C*H_2), 115.2 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.4, aromatic *C*H), 128.1, 129.6 (2 x CH signals, 4 x aromatic *C*H), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic *C*H), 132.2 (CH, aromatic *C*H), 133.9 (C, d, $^4J_{CF}$ 3.1, aromatic *C*), 136.5, 137.6 [2 x C, aromatic *C* and *C*(2)S], 144.8 [CH, *C*(3)H], 161.9 (C, d, $^1J_{CF}$ 245.8, aromatic *C*), 194.0 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{16}OFS[M+H^+]$ 287.0906. Found 287.0901.

E/Z stereochemistry not assigned but only one isomer present.

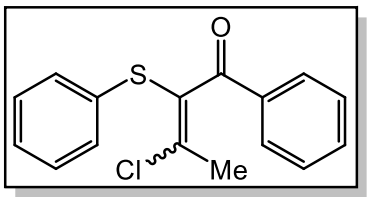
(*Z*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylbut-2-en-1-one Z-4ff and (*E*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylbut-2-en-1-one E-4ff



This was prepared following the procedure described above for **4a** using 2-((4-methylbenzyl)thio)-1-phenylbutan-1-one **3ff** (0.511 g, 1.8 mmol), *N*-chlorosuccinimide (0.468 g, 3.5 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 82% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4ff** and **E-4ff**, in a ratio of 1:1.4, the α,β-unsaturated ketone **S45** (16%) (q, δ_H 6.47 ppm, *J* 6.9; s, δ_H 3.90 ppm; d,

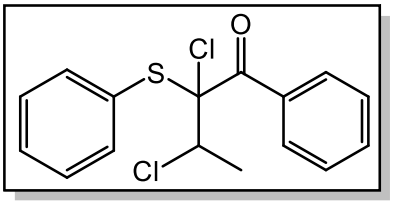
δ_H 1.91 ppm, *J* 6.9) and the dichloride **S46** (2%) (q, δ_H 5.24 ppm, *J* 6.8). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the desired α-*thio*-β-*chloroenone* (0.359 g, 63%, yellow oil) as an inseparable mixture of Z and *E* isomers **Z-4ff** and **E-4ff** in a ratio of 1:1.8; ν_{max}/cm^{-1} (ATR) 3052, 3025, 3003, 2919, 1661 (C=O), 1595, 1448, 1242, 691; δ_H (400 MHz, $CDCl_3$): 2.06 [3H, s, C(4)H_3, *Z* isomer], 2.11 [3H, s, C(4)H_3, *E* isomer], 2.27 (3H, s, ArCH_3, *Z* isomer), 2.32 (3H, s, ArCH_3, *E* isomer), 3.76 (2H, s, SCH_2, *Z* isomer), 3.79 (2H, s, SCH_2, *E* isomer), 7.00 (2H, d, *J* 8.0, Ar*H*, *Z* isomer), 7.08 (2H and 2H, d, *J* 8.0, Ar*H*, *E* and *Z* isomer), 7.19 (2H, d, *J* 8.0, Ar*H*, *E* isomer), 7.41-7.50 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.54-7.62 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.86-7.95 (2H and 2H, m, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 21.1 (CH_3, Ar*C*H_3, *Z* isomer), 21.2 (CH_3, Ar*C*H_3, *E* isomer), 22.9 [CH_3, C(4)H_3, *E* isomer], 24.7 [CH_3, C(4)H_3, *Z* isomer], 37.0 (CH_2, S*C*H_2, *Z* isomer), 38.8 (CH_2, S*C*H_2, *E* isomer), 126.5 [C, *C*(2)S, *E* isomer], 128.7, 128.8, 129.0, 129.12, 129.14, 129.6, 129.7 (7 x CH signals, 16 x aromatic *C*H, *E* and *Z* isomer), 130.3 [C, *C*(2)S, *Z* isomer], 133.2 (C, C_q, *E* or *Z* isomer), 133.7 [1 x signal, 2 x C, (1 x aromatic *C*H, *E* isomer) and (1 x C_q, *E* or *Z* isomer)], 133.8 (C, C_q, *E* or *Z* isomer), 134.0 (CH, aromatic *C*H, *Z* isomer), 134.4, 135.5, 137.0, 137.1, 137.2 (5 x C, C_q, *E* and *Z* isomer), 192.1 (C, *C*O, *E* isomer), 192.2 (C, *C*O, *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{18}H_{18}OS^{35}Cl[M+H^+]$ 317.0767. Found 317.0758; m/z (ES+) 317.1 [$(C_{18}H_{17}OS^{35}Cl)+H^+$], 20%, 319.1 [$(C_{18}H_{17}OS^{37}Cl)+H^+$], 10%. $^{35}Cl/^{37}Cl$ pattern visible at 317 and 319 in a 3:1 ratio.

(*Z*)-3-Chloro-1-phenyl-2-(phenylthio)but-2-en-1-one Z-4gg and (*E*)-3-Chloro-1-phenyl-2-(phenylthio)but-2-en-1-one E-4gg



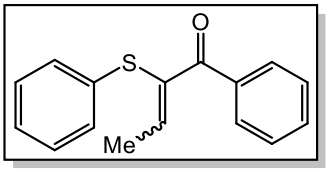
This was prepared following the procedure described above for **4a** using 1-phenyl-2-(phenylthio)butan-1-one **3gg** (0.502 g, 2.0 mmol), *N*-chlorosuccinimide (0.518 g, 3.9 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 66% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4gg** and **E-4gg**, in a ratio of 1:1.4, the α,β-unsaturated ketone **S47** (11%) and the dichloride **S48** (23%). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (0.287 g, 50%) as a yellow oil and an inseparable

mixture of Z and *E* isomers **Z-4gg** and **E-4gg** in a ratio of 1:1.2; ν_{max}/cm^{-1} (ATR) 3059, 1665 (C=O), 1595, 1579, 1448, 1439, 1240, 1132, 740, 687; δ_H (400 MHz, $CDCl_3$): 2.22 [3H, s, C(4)H_3, minor], 2.57 [3H, s, C(4)H_3, major], 7.07-7.64 (8H and 8H, m, Ar*H*, major and minor), 7.70 (2H, d, *J* 7.3, Ar*H*, minor) 7.80 (2H, d, *J* 7.2, Ar*H*, major); δ_C (100 MHz, $CDCl_3$): 23.7 [CH_3, *C*(4)H_3, major], 24.7 [CH_3, *C*(4)H_3, minor], 127.7, 127.8, 128.1, 128.4, 128.6, 128.8, 129.1, 129.3, 129.5, 130.8, 131.4, 132.4, 133.1, 133.6 [14 x signals, 24 x C, (20 x aromatic *C*H, major and minor) and (4 x C_q, major and minor)], 134.7, 135.1, 135.9, 137.2 (4 x C, C_q, major and minor), 191.4, 191.8 (2 x C, *C*O, major and minor);



Characteristic signals due to the dichloride **S48a** (assigned from ^{1}H NMR spectrum of crude material): δ_H (400 MHz, $CDCl_3$) 1.95 [3H, d, *J* 6.5, C(4)H_3], 4.78 [1H, q, *J* 6.5, C(3)*H*]; Characteristic signals due to the dichloride **S48b**: δ_H (400 MHz, $CDCl_3$) 1.51 [3H, d, *J* 6.4, C(4)H_3], 4.67 [1H, q, *J* 6.3, C(3)*H*].

1-Phenyl-2-(phenylthio)but-2-en-1-one S47

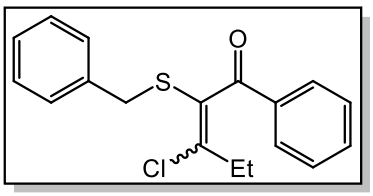


S47a: (more polar): yellow oil (47 mg, 9%); ν_{max}/cm^{-1} (ATR) 3058, 1660 (C=O), 1596, 1579, 1476, 1446, 1253, 1024, 687;δ_H (400 MHz, $CDCl_3$): 2.13 [3H, d, *J* 6.9, C(4)H_3], 6.83 [1H, q, *J* 6.9, C(3)*H*], 7.07-7.60 (8H, m, Ar*H*), 7.69 (2H, d, *J* 7.6, Ar*H*); δ_C (100 MHz, $CDCl_3$): 16.5 [CH_3, *C*(4)H_3], 126.6, 128.1, 128.9, 129.3, 129.7, 132.3 (6 x CH signals, 10 aromatic *C*H), 134.2, 136.8, 137.3 (3 x C, C_q), 144.7 [CH, *C*(3)H], 194.1 (C, *C*O). *This fraction contained characteristic signals due to* **S47b** (5%): δ_H (400 MHz, $CDCl_3$): 1.80 [3H, d, *J* 7.2, C(4)H_3], 6.47 [1H, q, *J* 7.1, C(3)*H*].

E/Z stereochemistry not assigned.

1.5.3 Preparation of α-Sulfenyl-β-Chloropentenones

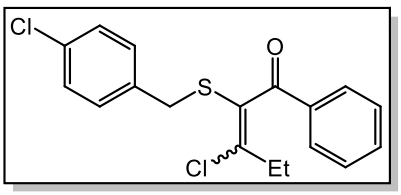
(*Z*)-2-(Benzylthio)-3-chloro-1-phenylpent-2-en-1-one Z-4hh and (*E*)-2-(Benzylthio)-3-chloro-1-phenylpent-2-en-1-one E-4hh



This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-phenylpentan-1-one **3hh** (0.554 g, 1.9 mmol), *N*-chlorosuccinimide (0.506 g, 3.8 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C

for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 88% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4hh** and **E-4hh**, in a ratio of 1:1.4 and the α,β-unsaturated ketone **S49** (11%) (δ_H, t, 6.39 ppm, *J* 7.3; δ_H, s, 3.92 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (0.409 g, 67%) as a yellow oil and as an inseparable mixture of Z and *E* isomers **Z-4hh** and **E-4hh** in a ratio of 1:1.4; ν_{max}/cm^{-1} (ATR) 3029, 3061, 2975, 2935, 2875, 1661 (C=O), 1596 (aromatic), 1449, 1238, 689; δ_H (400 MHz, $CDCl_3$): 0.95 [3H, t, *J* 7.4, C(5)H_3, *E* isomer], 1.05 [3H, t, *J* 7.3, C(5)H_3, *Z* isomer], 2.30 [2H, q, *J* 7.3, C(4)H_2, *Z* isomer], 2.52 [2H, q, *J* 7.4, C(4)H_2, *E* isomer], 3.78 (2H, s, SCH_2, *Z* isomer), 3.81 (2H, s, SCH_2, *E* isomer), 7.12-7.38 (5H and 5H, m, Ar*H*, *E* and *Z* isomer), 7.43-7.50 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.56-7.62 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.92 (2H and 2H, d, *J* 7.6, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 11.8 [CH_3, *C*(5)H_3, *E* isomer], 12.5 [CH_3, *C*(5)H_3, *Z* isomer], 28.9 [CH_2, *C*(4)H_2, *E* isomer], 31.1 [CH_2, *C*(4)H_2, *Z* isomer], 37.3 (CH_2, S*C*H_2, *Z* isomer), 39.0 (CH_2, S*C*H_2, *E* isomer), 125.4 [C, *C*(2)S, *E* isomer], 127.3, 127.4, 128.4, 128.5, 128.7, 128.8, 129.1, 129.2 (8 x CH signals, 14 x aromatic *C*H, *E* and *Z* isomer), 129.4 [C, C_q, *Z* isomer], 129.6, 133.7, 134.1 (3 x CH signals, 6 x aromatic *C*H, *E* and *Z* isomer), 134.4, 135.6, 136.3, 137.2, 140.2 (5 x C, C_q, *E* and *Z* isomer), 143.2 [C, *C*(3)Cl, *E* isomer], 191.6 (C, *C*O, *E* isomer), 192.0 (C, *C*O, *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{18}H_{18}OS^{35}Cl[M+H^+]$ 317.0767. Found 317.0670; m/z (ES+) 317.1 [$(C_{18}H_{18}OS^{35}Cl)+H^+$], 100%, 319.1 [$(C_{18}H_{18}OS^{37}Cl)+H^+$], 40%.

(Z)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylpent-2-en-1-one Z-4ii and (E)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylpent-2-en-1-one E-4ii

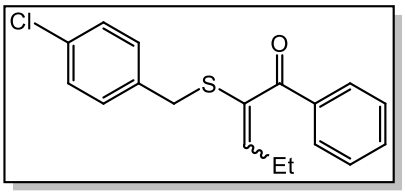


This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-phenylpentan-1-one **3ii** (0.524 g, 1.6 mmol), N-chlorosuccinimide (0.427 g, 3.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 91% β-chloroenone as a mixture of Z and E isomers, **Z-4ii** and **E-4ii**, in a ratio of 1:1.4 and the α,β-unsaturated ketone **S50** (9%) (δ_H, t, 6.40 ppm, J 7.3; δ_H, s, 3.89 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50)

as eluent gave the α-thio-β-chloroenone (0.397 g, 69%, yellow oil) as an inseparable mixture of Z and E isomers **Z-4ii** and **E-4ii** in a ratio of 1:1.2; ν_{max}/cm^{-1} (ATR) 2976, 2935, 2875, 1660 (C=O), 1595 (aromatic), 1489, 1238, 689; δ_H (400 MHz, $CDCl_3$): 0.97 [3H, t, J 7.4, C(5)H_3, E isomer], 1.04 [3H, t, J 7.3, C(5)H_3, Z isomer], 2.29 [2H, q, J 7.3, C(4)H_2, Z isomer], 2.51 [2H, q, J 7.4, C(4)H_2, E isomer], 3.74 (2H, s, SCH_2, Z isomer), 3.77 (2H, s, SCH_2, E isomer), 7.15 (4H, s, ArH, E isomer), 7.23-7.29 (4H, m, ArH, Z isomer), 7.43-7.50 (2H and 2H, m, ArH, E and Z isomer), 7.56-7.62 (1H and 1H, m, ArH, E and Z isomer), 7.89 (2H and 2H, t, J 8.3, ArH, E and Z isomer); δ_C (100 MHz, $CDCl_3$): 11.9 [CH_3, C(5)H_3, E isomer], 12.5 [CH_3, C(5)H_3, Z isomer], 28.9 [CH_2, C(4)H_2, E isomer], 31.2 [CH_2, C(4)H_2, Z isomer], 36.6 (CH_2, SCH_2, Z isomer), 38.1 (CH_2, SCH_2, E isomer), 124.9 [C, C(2)S, E isomer], 128.5, 128.6 (2 x CH signals, 4 x aromatic CH, E and Z isomer), 128.7 (C, C_q, E or Z isomer), 128.80, 128.83, 129.6, 130.5, 130.6 (5 x CH signals, 12 x aromatic CH, E and Z isomer), 133.2 (C, C_q, E or Z isomer), 133.8, 134.1 (2 x CH, aromatic CH, E and Z isomer), 134.3, 135.1, 135.4, 135.8, 141.1, 143.6 (6 x C signals, 7 x C_q, E and Z isomer), 191.5 (C, CO, E isomer), 191.9 (C, CO, Z isomer); HRMS (ES+): Exact mass calculated for $C_{18}H_{17}OS^{35}Cl_2$[M+H^+] 351.0377. Found 351.0367; m/z (ES+) 351.1 [($C_{18}H_{17}OS^{35}Cl_2$)+H^+], 100%, 353.1 [($C_{18}H_{17}OS^{35}Cl^{37}Cl$)+$H^+$], 70%.

*Relative stereochemistry assigned for **4ii** by a NOESY experiment*.

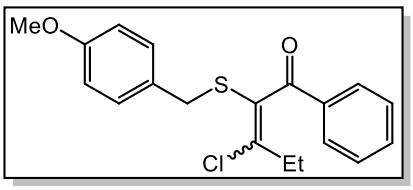
2-((4-Chlorobenzyl)thio)-1-phenylpent-2-en-1-one S50



(More polar): orange oil (28 mg, 5%); ν_{max}/cm^{-1} (ATR) 2965, 2917, 1666 (C=O), 1595, 1489, 1091, 688; δ_H (400 MHz, $CDCl_3$): 0.94 [3H, d, J 7.5, C(5)H_3], 2.36 [2H, dq appears as quintet, J 7.5, C(4)H_2], 3.89 (2H, s, SCH_2), 6.40 [1H, t, J 7.3, C(3)H], 7.00-7.20 (4H, m, ArH), 7.32-7.41 (2H, m, ArH), 7.42-7.55 (3H, m, ArH); δ_C (100 MHz, $CDCl_3$): 12.8 [CH_3, C(5)H_3], 23.8 [CH_2, C(4)H_2], 35.7 (CH_2, SCH_2), 128.1, 128.5, 129.6, 130.5, 132.3 (5 x CH signals, 9 x aromatic CH) 132.8, 134.5, 136.8, 137.6 (4 x C, C_q), 151.4 [CH, C(3)H], 193.9 (C, CO).

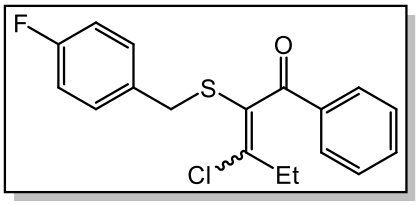
E/Z stereochemistry not assigned but only one isomer present.

(*Z*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylpent-2-en-1-one Z-4jj and (*E*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylpent-2-en-1-one E-4jj



This was prepared following the procedure described above for **4a** using 2-((4-methoxybenzyl)thio)-1-phenylpentan-1-one **3jj** (0.388 g, 1.2 mmol), *N*-chlorosuccinimide (0.321 g, 2.4 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 85% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4jj** and **E-4jj**, in a ratio of 1:1.2 and the impurity **S42**[19] (15%) (s, δ_H 4.56 ppm). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (0.278 g, 65%) as a yellow oil and an inseparable mixture of Z and *E* isomers **Z-jj** and **E-4jj** in a ratio of 1:1.3; ν_{max}/cm^{-1} (ATR) 2973, 2934, 2834, 1661 (C=O), 1609, 1510, 1236, 690; δ_H (400 MHz, $CDCl_3$): 0.99 [3H, t, *J* 7.4, C(5)*H*$_3$, *E* isomer], 1.05 [3H, t, *J* 7.3, C(5)*H*$_3$, *Z* isomer], 2.30 [2H, q, *J* 7.3, C(4)*H*$_2$, *Z* isomer], 2.54 [2H, q, *J* 7.4, C(4)*H*$_2$, *E* isomer], 3.74 (2H, s, SC*H*$_2$, *Z* isomer), 3.75 (3H, s, OC*H*$_3$, *Z* isomer), 3.78 (2H, s, SC*H*$_2$, *E* isomer), 3.78 (3H, s, OC*H*$_3$, *E* isomer), 6.73 (2H, d, *J* 8.5, Ar*H*, *Z* isomer), 6.81 (2H, d, *J* 8.5, Ar*H*, *E* isomer), 7.12 (2H, d, *J* 8.5, Ar*H*, *Z* isomer), 7.24 (2H, d, *J* 8.6, Ar*H*, *E* isomer), 7.44-7.51 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.56-7.63 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.92 (2H and 2H, d, *J* 7.9, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 11.9 [CH_3, *C*(5)H_3, *E* isomer], 12.5 [CH_3, *C*(5)H_3, *Z* isomer], 28.9 [CH_2, *C*(4)H_2, *E* isomer], 31.1 [CH_2, *C*(4)H_2, *Z* isomer], 36.7 (CH_2, S*C*H_2, *Z* isomer), 38.4 (CH_2, S*C*H_2, *E* isomer), 55.2 (CH_3, O*C*H_3, *Z* isomer), 55.3 (CH_3, O*C*H_3, *E* isomer), 113.8 (1 x CH signal, 4 x aromatic *C*H, *E* and *Z* isomer), 125.6 (C, aromatic *C*, *Z* isomer), 128.2 (C, C_q, *E* isomer), 128.7, 128.8 (2 x CH signals, 4 x aromatic *C*H, *E* and *Z* isomer), 129.1 (C, C_q, *E* isomer), 129.6 [C, *C*(2)S, *Z* isomer], 129.6, 130.3, 130.4, 133.7, 134.0 (5 x CH signals, 10 x aromatic *C*H, *E* and *Z* isomer), 134.4, 135.6 (2 x C, aromatic *C*, *E* and *Z* isomer), 139.6 [C, *C*(3)Cl, *Z* isomer], 142.8 [C, *C*(3)Cl, *E* isomer], 158.9 (1 x C signal, 2 x aromatic *C*, *E* and *Z* isomer), 191.7 (C, *C*O, *E* isomer), 192.1 (C, *C*O, *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{19}H_{20}O_2S^{35}Cl$ [M+H$^+$] 347.0873. Found 347.0866.

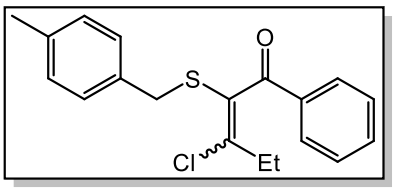
(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylpent-2-en-1-one Z-4kk and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylpent-2-en-1-one E-4kk



This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-phenylpentan-1-one **3kk** (0.401 g, 1.3 mmol), *N*-chlorosuccinimide (0.346 g, 2.6 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 75% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4kk** and **E-4kk**, in a ratio of 1:1.1 and the α,β-unsaturated ketones (*Z*:*E* 6.7:1, 19%) **S51a** (δ_H, t, 6.40 ppm, *J* 7.3) and **S51b** (δ_H, t, 6.02 ppm, *J* 7.9). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the major fraction as the desired α-*thio*-β-*chloroenone* (0.282 g, 63%) as a yellow oil and an inseparable mixture of Z and *E* isomers **Z-4kk** and **E-4kk** in a ratio of 1:1.1; ν_{max}/cm^{-1} (ATR) 2976, 2935, 2875, 1660 (C=O), 1597 (aromatic), 1507, 1221, 838, 812, 689; δ_H (400 MHz, $CDCl_3$): 0.97 [3H, t, *J* 7.4, C(5)*H*$_3$, *E* isomer], 1.04 [3H, t, *J* 7.3, C(5)*H*$_3$, *Z* isomer], 2.29 [2H, q, *J* 7.3, C(4)*H*$_2$, *Z* isomer], 2.51 [2H, q, *J* 7.4, C(4)*H*$_2$, *E* isomer], 3.75 (2H, s, SC*H*$_2$, *Z* isomer), 3.78 (2H, s, SC*H*$_2$, *E* isomer), 6.88 (2H, t, *J* 8.7, Ar*H*, *Z* isomer), 6.96 (2H, t, *J* 8.7, Ar*H*, *E* isomer), 7.16-7.21 (2H, m, Ar*H*, *Z* isomer), 7.28-7.33 (2H, m, Ar*H*, *E* isomer), 7.43-7.50 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.56-7.62 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.88-7.93 (2H and 2H, m, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 11.9 [CH_3, *C*(5)H$_3$, *E* isomer], 12.5 [CH_3, *C*(5)H$_3$, *Z* isomer], 28.9 [CH_2, *C*(4)H$_2$, *E* isomer], 31.2 [CH_2, *C*(4)H$_2$, *Z* isomer], 36.6 (CH_2, S*C*H$_2$, *Z* isomer), 38.1 (CH_2, S*C*H$_2$, *E* isomer), 115.2 (1 x CH signal, 2 x CH, d, $^{2}J_{CF}$ 21.5, aromatic *C*H, *Z* isomer), 115.3 (1 x CH signal, 2 x CH, d, $^{2}J_{CF}$ 21.4, aromatic *C*H, *E* isomer), 125.0 [C, *C*(2)S, *E* isomer], 128.8 (1 x CH signal, 4 x CH, aromatic *C*H, *E* and *Z* isomer), 128.9 [C, *C*(2)S, *Z* isomer], 129.6 (1 x CH signal, 4 x CH, aromatic *C*H, *E* and *Z* isomer), 130.8 (1 x CH signal, 2 x CH, d, $^{3}J_{CF}$ 9.1, aromatic *C*H, *Z* isomer), 130.9 (1 x CH signal, 2 x CH, d, $^{3}J_{CF}$ 8.3, aromatic *C*H, *E* isomer), 132.2 (C, d, $^{4}J_{CF}$ 3.2, aromatic *C*, *Z* isomer), 133.1 (C, d, $^{4}J_{CF}$ 3.2, aromatic *C*, *E* isomer), 133.7, 134.1 (2 x CH, aromatic *C*H, *E* and *Z* isomer), 134.3, 135.5 (2 x C, aromatic *C*, *E* and *Z* isomer), 140.9 [C, *C*(3)Cl, *Z* isomer], 143.4 [C, *C*(3)Cl, *E* isomer], 162.0 (C, d, $^{1}J_{CF}$ 246.1, aromatic *C*, *Z* isomer), 162.1 (C, d, $^{1}J_{CF}$ 246.1, aromatic *C*, *E* isomer), 191.5 (C, *C*O, *E* isomer), 191.9 (C, *C*O, *Z* isomer); HRMS (ES+): Exact mass

calculated for $C_{18}H_{17}OFS^{35}Cl[M+H^+]$ 335.0673. Found 335.0659; m/z (ES+) 335.1 $[(C_{18}H_{17}OFS^{35}Cl)+H^+]$, 70%, 337.1 $[(C_{18}H_{17}OFS^{37}Cl)+H^+]$, 30%.

(*Z*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylpent-2-en-1-one Z-4ll and (*E*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylpent-2-en-1-one E-4ll



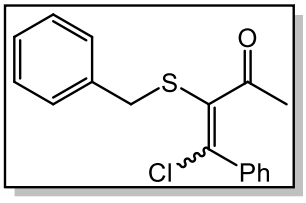
This was prepared following the procedure described above for **4a** using 2-((4-methylbenzyl)thio)-1-phenylpentan-1-one **3ll** (0.73 g, 2.4 mmol), *N*-chlorosuccinimide (0.637 g, 4.7 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 86% β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4ll** and **E-4ll**, in a ratio of 1:1.4 and the α,β-unsaturated ketones **S52a** (8%) (δ_H, t, 6.37 ppm, *J* 7.3; δ_H, s, 3.89 ppm) and **S52b** (δ_H, t, 6.03 ppm, *J* 7.7). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave the desired α-*thio*-β-*chloroenone* (0.576 g, 72%, yellow oil) as an inseparable mixture of Z and *E* isomers **Z-4ll** and **E-4ll** in a ratio of 1:1.4; ν_{max}/cm^{-1} (ATR) 2975, 2934, 2874, 1662 (C=O), 1596, 1448, 1238, 810, 689; δ_H (400 MHz, $CDCl_3$): 0.99 [3H, t, *J* 7.4, C(5)H_3, *E* isomer], 1.05 [3H, t, *J* 7.3, C(5)H_3, *Z* isomer], 2.25-2.40 (8H, m, [2H, C(4)H_2, *Z* isomer] containing (2.27, 3H, s, ArCH_3, *Z* isomer) and (2.31, 3H, s, ArCH_3, *E* isomer)), 2.56 [2H, q, *J* 7.4, C(4)H_2, *E* isomer], 3.74 (2H, s, SCH_2, *Z* isomer), 3.78 (2H, s, SCH_2, *E* isomer), 7.00 (2H, d, *J* 8.0, Ar*H*, *Z* isomer), 7.08 (2H and 2H, d, *J* 6.3, Ar*H*, *E* and *Z* isomer), 7.19 (2H, d, *J* 8.0, Ar*H*, *E* isomer), 7.43-7.51 (2H and 2H, m, Ar*H*, *E* and *Z* isomer), 7.56-7.63 (1H and 1H, m, Ar*H*, *E* and *Z* isomer), 7.92 (2H and 2H, d, *J* 8.3, Ar*H*, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 11.9 [CH_3, *C*(5)H_3, *E* isomer], 12.6 [CH_3, *C*(5)H_3, *Z* isomer], 21.1 (1 x CH_3 signal, 2 x Ar*C*H_3, *E* and *Z* isomer), 29.0 [CH_2, *C*(4)H_2, *E* isomer], 31.1 [CH_2, *C*(4)H_2, *Z* isomer], 36.9 (CH_2, S*C*H_2, *Z* isomer), 38.7 (CH_2, S*C*H_2, *E* isomer), 125.7 [C, *C*(2)S, *E* isomer], 128.7, 128.8, 129.0, 129.11, 129.14, 129.6 (6 x signals, 17 x C, (16 x aromatic *C*H, *E* and *Z* isomer) and [C, *C*(2)S, *Z* isomer]), 133.1 (C, aromatic *C*, *Z* isomer), 133.7 (CH, aromatic *C*H, *E* isomer), 133.9 (C, aromatic *C*, *E* isomer), 134.0 (CH, aromatic *C*H, *Z* isomer), 134.4, 135.6, 137.0, 137.1 (4 x C, aromatic *C*, *E* and *Z* isomer), 139.4 [C, *C*(3)Cl, *Z* isomer], 142.8 [C, *C*(3)Cl, *E* isomer], 191.7 (C, *C*O, *E* isomer), 192.1 (C, *C*O, *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{19}H_{20}OS^{35}Cl[M+H^+]$ 331.0923. Found 331.0923; m/z (ES+) 331.2 $[(C_{19}H_{20}OS^{35}Cl)+H^+]$, 60%, 333.2 $[(C_{19}H_{20}OS^{37}Cl)+H^+]$, 25%.

1.5.4 Preparation of α-Sulfenyl-β-Phenyl-β-Chloroenones

Reaction of 3-(benzylthio)-4-phenylbutan-2-one 10a with NCS: (*Z*)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one Z-13a, (*E*)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one E-13a, 3-(Benzylthio)-3,4-dichloro-4-phenylbutan-2-one 12a and (*E*)-3-(Benzylthio)-4-phenylbut-3-en-2-one 11a

These compounds were prepared following the procedure described above for **4a** using 3-(benzylthio)-4-phenylbutan-2-one **10a** (0.308 g, 1.1 mmol), *N*-chlorosuccinimide (0.296 g, 2.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 15 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a brown oil. ^{1}H NMR spectroscopy showed this product to contain a mixture of the α-thio-β-chloroenones **Z-13a** and **E-13a** (42%, *Z*:*E* 1.3:1), the dichlorides **12a** and **12b** (41%, 3.2:1) and the α,β-unsaturated ketone **11a** (17%). Purification by column chromatography on silica gel using hexane-dichloromethane (50:50) as eluent gave three major fractions. The first gave the dichlorides **12a** and **12b** (0.106 g, 27%, 3.7:1) as a yellow oil and an inseparable mixture of isomers. The second fraction gave the desired α-*thio*-β-*chloroenones* (33 mg, 9%) as a yellow oil and an inseparable mixture of Z and *E* isomers **Z-13a** and **E-13a** in a ratio of 2.9:1. The third fraction gave the α,β-unsaturated ketone **11a** (43 mg, 14%) as an orange oil. Another fraction was obtained containing the β-chloroenones **Z-13a** and **E-13a** (88 mg, 24%, yellow oil) however, this fraction also contained *approx*. 20% dichloride **12**.

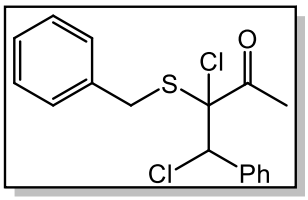
(*Z*)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one Z-13a and (*E*)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one E-13a



ν_{max}/cm^{-1} (ATR) 3060, 3029, 2921, 1691 (C=O), 1351, 1234, 1190, 745, 693; δ_H (400 MHz, $CDCl_3$): 1.63 (3H, s, C*H*$_3$, *Z* isomer), 2.47 (3H, s, C*H*$_3$, *E* isomer), 3.74 (2H, s, SC*H*$_2$, *E* isomer), 3.99 (2H, s, SC*H*$_2$, *Z* isomer), 7.12 (2H, d, *J* 7.9, *E* isomer), 7.17-7.42 (10H and 8H, m, Ar*H*, *Z* and *E* isomer); δ_C (100 MHz, $CDCl_3$): 28.8 [CH_3, C(O)*C*H$_3$, *E* isomer], 30.5 [CH_3, C(O)*C*H$_3$, *Z* isomer], 36.9 (CH_2, S*C*H$_2$, *Z* isomer), 38.5 (CH_2, S*C*H$_2$, *E* isomer), 127.4, 127.5, 127.9, 128.60, 128.62, 128.7, 129.0, 129.20, 129.27, 129.3, 129.8 (11 x CH signals, 20 x aromatic *C*H, *Z* and *E* isomer), 131.1 [C, *C*(3)S, *E* isomer], 132.8 (C, *C*$_q$, *E* isomer), 135.4 (C, *C*$_q$, *Z* isomer), 135.8 [C,

C(3)S, *Z* isomer], 135.9, 136.6 (2 x C, C_q, *E* isomer), 136.8, 137.4 (2 x C, C_q, *Z* isomer), 199.2 (C, *C*O, *Z* isomer), 199.3 (C, *C*O, *E* isomer); HRMS (ES+): Exact mass calculated for $C_{17}H_{16}OS^{35}Cl[M+H^+]$ 303.0610. Found 303.0595; m/z (ES+) 303.2 [$(C_{17}H_{15}OS^{35}Cl)+H^+$], 30%.

3-(Benzylthio)-3,4-dichloro-4-phenylbutan-2-one 12a and 12b (ratio 3.7:1)

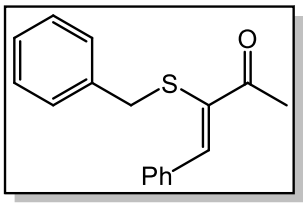


ν_{max}/cm^{-1} (ATR) 3061, 3029, 2967, 2923, 1693 (C=O), 1494, 1453, 1352, 1234, 1191, 746, 694; δ_H (400 MHz, $CDCl_3$): 2.26 (3H, s, C*H*$_3$, minor), 2.58 (3H, s, C*H*$_3$, major), 3.31 (1H, A of AB system, J_{AB} 11.5, one of SC*H*$_2$, major), 3.59 (1H, B of AB system, J_{AB} 11.5, one of SC*H*$_2$, major), 3.85 (1H, A of AB system, J_{AB} 11.3, one of SC*H*$_2$, minor), 3.91 (1H, B of AB system, J_{AB} 11.4, one of SC*H*$_2$, minor), 5.64 [1H, s, C(4)*H*Cl, major], 5.66 [1H, s, C(4)*H*Cl, minor], 7.06-7.47 (8H and 8H, m, Ar*H*, major and minor), 7.48-7.56 (2H, m, Ar*H*, minor), 7.59-7.70 (2H, m, Ar*H*, major); HRMS (ES+): Exact mass calculated for $C_{17}H_{17}OS^{35}Cl_2[M+H^+]$ 339.0377. Found 339.0392; m/z (ES+) 341.1 [$(C_{17}H_{16}OS^{37}Cl_2)+H^+$], 50%.

^{1}H and ^{13}C NMR spectra were recorded after storage at room temperature for 40 months and were seen to contain ***12a*** *(51%) as well as the* β*-chloroenones* ***Z-13a*** *(33%) and* ***Z-13a*** *(16%). None of the dichloride* ***12b*** *remained in this sample*; **12a:** δ_H (400 MHz, $CDCl_3$): 2.58 (3H, s, C*H*$_3$), 3.31 (1H, A of AB system, J_{AB} 11.5, one of SC*H*$_2$), 3.59 (1H, B of AB system, J_{AB} 11.5, one of SC*H*$_2$), 5.64 [1H, s, C(4)*H*Cl], 7.06-7.56 (8H, m, Ar*H*), 7.58-7.70 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 26.0 [CH_3, C(O)*C*H$_3$], 36.2 (CH_2, S*C*H$_2$), 64.7[CH, *C*(4)HCl], 86.3 (C, C_q), 127.8, 128.0, 128.7, 129.4, 129.6, 130.0 (6 x CH signal, 10 x aromatic *C*H), 134.3, 134.9 (2 x C, C_q), 197.8 (C, *C*O).

Characteristic peaks for **Z-13a** *and* **E-13a** (*Z*:*E* 2:1): δ_H (400 MHz, $CDCl_3$): 1.63 (3H, s, C*H*$_3$, *Z* isomer), 2.47 (3H, s, C*H*$_3$, *E* isomer), 3.74 (2H, s, SC*H*$_2$, *E* isomer), 3.99 (2H, s, SC*H*$_2$, *Z* isomer); δ_C (100 MHz, $CDCl_3$): 28.8 [CH_3, C(O)*C*H$_3$, *E* isomer], 30.5 [CH_3, C(O)*C*H$_3$, *Z* isomer], 36.9 (CH_2, S*C*H$_2$, *Z* isomer), 38.5 (CH_2, S*C*H$_2$, *E* isomer), 199.2 (C, *C*O, *Z* isomer), 199.3 (C, *C*O, *E* isomer).

(*Z*)-3-(Benzylthio)-4-phenylbut-3-en-2-one 11a[21]



ν_{max}/cm^{-1} (ATR) 3060, 3027, 2922, 1673 (C=O), 1219, 1203, 1179, 754, 690; δ_H (400 MHz, $CDCl_3$): 2.36 (3H, s, C*H*$_3$), 3.91 (2H, s, SC*H*$_2$), 7.11-7.25 (5H, m, Ar*H*), 7.34-7.42 (3H, m, Ar*H*), 7.63 [1H, s, C(4)H],

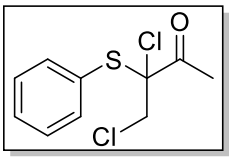
7.72 (2H, d, *J* 7.9, Ar*H*); δ_C (100 MHz, $CDCl_3$): 27.3 [CH_3, C(O)*C*H_3)], 38.0 (CH_2, S*C*H_2), 127.1, 128.3, 128.4, 129.1, 129.6, 130.7 (6 x CH signals, 10 x aromatic *C*H), 134.6, 135.3, 137.4 [3 x C, 2 x aromatic *C* and *C*(2)S], 143.2 [CH, *C*(4)H], 198.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{17}OS[M+H^+]$ 269.1000. Found 269.0988; m/z (ES+) 269.2 [$(C_{17}H_{16}OS)+H^+$], 50%.

Spectroscopic characteristics are consistent with those previously reported.[21] Stereochemistry was assigned in the literature, based on a crystal structure of a similar compound.

1.5.5 Synthesis of Dichlorides

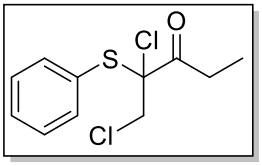
Note *Commercially available un-recrystallised N-chlorosuccinimide was used throughout the reactions in this section. It was determined that recrystallised NCS had no impact on the efficiency or outcome of the reactions and so recrystallisation was deemed an unnecessary step.*[18]

3,4-Dichloro-3-(phenylthio)butan-2-one S53



The α-thioketone 2-(phenylthio)butan-3-one **5a** (0.20 g, 1.1 mmol), *N*-chlorosuccinimide (0.386 g, 2.9 mmol, 2.6 eq) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 h. The resulting reaction mixture was cooled to 0 °C and the excess *N*-chlorosuccimide was removed by filtration. The crude mixture was evaporated under reduced pressure to give the crude product as an orange oil. Analysis of the crude product by ^{1}H NMR spectroscopy showed *approx.* 80% conversion to the desired dichloride **S53** was achieved. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent, the *dichloride* **S53** was obtained as a yellow oil (0.188 g, 69%); ν_{max}/cm^{-1} (film) 3000 (CH), 2990 (CH), 2939 (CH), 1710 (CO), 1560, 1434; δ_H (300 MHz, $CDCl_3$) 2.49 (3H, s, CH_3), 3.95 (1H, A of AB system, *J* 12.0, one of CH_2Cl), 4.15 (1H, B of AB system, *J* 12.0, one of CH_2Cl), 7.38-7.57 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 25.2 (CH_3, *C*H_3), 48.4 (CH_2, *C*H_2Cl), 80.9 [C, *C*(2)S], 127.8 (C, aromatic *C*), 129.5, 131.1, 137.2 (3 x CH, aromatic *C*H), 197.3 (C, *C*O).

1,2-Dichloro-2-(phenylthio)pentan-3-one S54

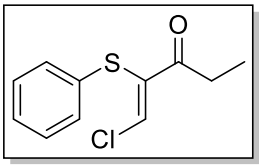


The α-thioketone 2-(phenylthio)pentan-3-one **5b**, (0.20 g, 1.03 mmol), unrecrystallised *N*-chlorosuccinimide (0.358 g, 2.7 mmol, 2.6 eq) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 h. The resulting reaction mixture was cooled to 0 °C and the excess *N*-chlorosuccinimide was removed by filtration. The crude mixture was evaporated under reduced pressure to give the crude product as an orange oil. ^{1}H NMR spectroscopy showed the crude product to contain a mixture of the dichloride **S54** (57%), the trichloride **S55** (9%) and the *Z* isomer of the corresponding β-chloroenone **Z-9b** (*approx*. 34%), the *E* β-chloroenone **E-9b** (<2%) [C(3)*H*, s, δ_H 6.67 ppm] and the benzyl chloride **S56** (s, δ_H 4.59 ppm). Complete separation of these components by column chromatography on silica gel using hexane-ethyl acetate as eluent (gradient elution 0-2% ethyl acetate) was not possible. The product mixture was isolated as a yellow oil (0.168 g) and characterised by ^{1}H NMR spectroscopy as a mixture of three compounds, 1,2-dichloro-2-(phenylthio)pentan-3-one **S54** (57%), (*Z*)-2-(phenylthio)-1-chloropent-1-en-3-one **Z-9b** (32%), 1,1,2-trichloro-2-(phenylthio)pentan-3-one **S55** (11%) and (*E*)-2-(phenylthio)-1-chloropent-1-en-3-one **E-9b** (<2%). No further purification was attempted and this product was carried forward to the reaction with zinc chloride where the dichloride and trichloride formed here eliminate to give the β-chloroenone; ν_{max}/cm^{-1} (film) 3058 (CH), 2979 (CH), 2939 (CH), 1717 (CO), 1542, 1434;

1,2-Dichloro-2-(phenylthio)pentan-3-one S54

δ_H (300 MHz, $CDCl_3$) 1.11 (3H, t, *J* 7.2, CH_2CH_3), 2.86 (2H, q, *J* 7.2, CH_2CH_3), 3.86 (1H, A of AB system, *J* 11.8, one of CH_2Cl), 4.03 (1H, B of AB system, *J* 11.8, one of CH_2Cl), 7.22-7.56 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 8.3 (CH_3, CH_2CH_3), 31.2 (CH_2, CH_2CH_3), 48.7 (CH_2, CH_2Cl), 81.3 [C, *C*(2)S], 127.7 (C, aromatic *C*), 129.4, 131.0, 137.30 (3 x CH, aromatic *C*H), 200.5 (C, *C*O).

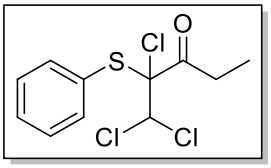
(*Z*)-2-(Phenylthio)-1-chloropent-1-en-3-one Z-9b



δ_H (300 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.2, CH_2CH_3), 2.61 (2H, q, *J* 7.2, CH_2CH_3), 7.18-7.33 (5H, m, Ar*H*), 7.50 (1H, s, C*H*Cl); δ_C (75.5 MHz, $CDCl_3$) 8.1 (CH_3, CH_2CH_3), 33.5 (CH_2, CH_2CH_3), 127.1, 128.8, 129.5 (3 x CH,

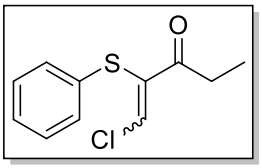
aromatic *C*H), 133.5 [C, aromatic *C* or *C*(2)S], 136.2 (CH, *C*HCl), 138.0 [C, aromatic *C* or *C*(2)S], 198.7 (C, *C*O).

1,1,2-Trichloro-2-(phenylthio)pentan-3-one S55



δ_H (300 MHz, $CDCl_3$) 0.98 (3H, t, *J* 7.1, CH_2CH_3), 2.70 (2H, q, *J* 7.2, CH_2CH_3), 6.18 (1H, s, $CHCl_2$), 7.22-7.56 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 8.0 (CH_3, CH_2CH_3), 32.9 (CH_2, CH_2CH_3), 74.8 (CH, $CHCl_2$), 86.6 [C, *C*(2)S], 127.6 (C, aromatic *C*), 129.6, 131.4, 137.25 (3 x CH, aromatic *C*H), 200.3 (C, *C*O).

(*Z*)-1-Chloro-2-(phenylthio)pent-1-en-3-one Z-9b and (*E*)-1-chloro-2-(phenylthio)pent-1-en-3-one E-9b



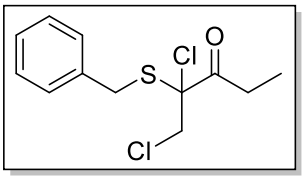
A solution of zinc chloride in ether (3.30 mL of a 1M solution, 3.3 mmol) was added to a stirring solution of a mixture containing the compounds, 1,2-dichloro-2-(phenylthio)pentan-3-one **S54** (57%), (*Z*)-2-(phenylthio)-1-chloropent-1-en-3-one **Z-9b** (32%), 1,1,2-trichloro-2-(phenylthio)pentan-3-one **S55** (11%) and (*E*)-2-(phenylthio)-1-chloropent-1-en-3-one **E-9b** (<2%) (0.289 g, 1.1 mmol) in dichloromethane (15 mL). The resulting solution was heated under reflux for 18 h. The cooled reaction mixture was quenched by addition of water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated at reduced pressure to give the crude β-*chloroenone* as a brown oil. ^{1}H NMR spectroscopy of the crude product showed the desired β-chloroenones **Z-9b** and **E-9b** formed as the major product in a ratio of 15:1. The crude product mixture was purified by column chromatography using hexane-ethyl acetate (96:4) as eluent. The major fraction isolated after chromatography contained the β-*chloroenones* **Z-9b** and **E-9b** (0.11 g, 47% yield over two steps from the sulfide) as a yellow oil and an inseparable mixture of *Z* and *E* isomers in a ratio of 15:1 (ratio was unchanged after chromatography); ν_{max}/cm^{-1} (film) 3057 (CH), 2980 (CH), 2939 (CH), 1708 (CO), 1440;

Z-9b: δ_H (300 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.2, CH_2CH_3), 2.61 (2H, q, *J* 7.2, CH_2CH_3), 7.18-7.33 (5H, m, Ar*H*), 7.50 (1H, s, C*H*Cl); δ_C (75.5 MHz, $CDCl_3$) 8.1 (CH_3, CH_2CH_3), 33.5 (CH_2, CH_2CH_3), 127.1, 128.8, 129.5 (3 x CH, aromatic *C*H), 133.5 [C, aromatic *C* or *C*(2)S], 136.2 (CH, *C*HCl), 138.0 [C, aromatic *C* or *C*(2)S], 198.7 (C, *C*O).

Characteristic signals due to **E-9b**: δ_H (300 MHz, $CDCl_3$) 1.00 (3H, t, *J* 7.4, CH_2CH_3), 2.61 (2H, q, *J* 7.2, CH_2CH_3), 6.67 (1H, s, C*H*Cl), 7.18-7.33 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 7.6 (CH_3, CH_2CH_3), 35.2 (CH_2, CH_2CH_3), 123.8 (CH, *C*HCl), 127.9, 130.4 (CH, aromatic *C*H), 200.4 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{11}H_{12}OS^{35}Cl[M+H^+]$ 227.0297. Found 227.0296.

2-(Benzylthio)-1,2-dichloropentan-3-one S57



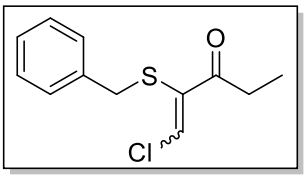
N-Chlorosuccinimide (0.251 g, 1.9 mmol) was added in one portion to a solution of 2-(benzylthio)pentan-3-one **5c** (0.20 g, 0.96 mmol) in toluene (8 mL). The flask was immediately immersed in an oil bath at 90 °C and heating was maintained for 2 h with stirring. The reaction mixture was cooled to 0 °C and the succinimide by-product was removed by filtration. The solvent was evaporated at reduced pressure to give the crude product as a brown oil. ^{1}H NMR spectroscopy showed the crude product to contain a mixture of the dichloride **S57** (44%) and both the *Z* **Z-9c** and *E* **E-9c** isomers of the corresponding β-chloroenone (55%) in a ratio of 2.2:1 respectively and a trace of benzyl chloride **S56** (singlet at δ_H 4.59 ppm). Separation was attempted by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent; the isolated product was obtained as a yellow oil (0.166 g), however, further analysis by ^{1}H NMR spectroscopy showed this product still contained a mixture of three compounds, the dichloride 2-(benzylthio)-1,2-dichloropentan-3-one **S57** (46%), and both the *Z* **Z-9c** and *E* **E-9c** isomers of the β-chloroenone in a ratio of 1.5:1, (*Z*)-2-(benzylthio)-1-chloropent-1-en-3-one **Z-9c** (32%) and (*E*)-2-(benzylthio)-1-chloropent-1-en-3-one **E-9c** (21%). No further purification was attempted and this product was characterised as a mixture and carried forward to the reaction with zinc chloride where the dichloride formed here undergoes an elimination reaction to give the corresponding β-chloroenone; ν_{max}/cm^{-1} (film) 3063 (CH), 2978 (CH), 2938 (CH), 1690 (CO), 1541, 1495, 1454;

2-(Benzylthio)-1,2-dichloropentan-3-one S57

δ_H (300 MHz, $CDCl_3$) 1.10 (3H, t, *J* 7.2, CH_2CH_3), 2.87 (2H, q, *J* 7.2, CH_2CH_3), 3.85 (2H, s, SCH_2), 3.88 (1H, A of AB system, *J* 11.9, one of CH_2Cl), 4.17 (1H, B of AB system, *J* 11.9, one of CH_2Cl), 7.21-7.33 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 8.3 (CH_3, CH_2CH_3), 30.5 (CH_2, CH_2CH_3), 36.2 (CH_2, SCH_2), 49.1 (CH_2, CH_2Cl), 80.3 [C, *C*(2)S], 127.9, 128.8, 129.3 (3 x CH, aromatic *C*H), 135.2 (C, aromatic *C*), 200.0 (C, *C*O).

Spectral characteristics of *Z* **Z-9c** and *E* **E-9c** were consistent with those described below.

(*Z*)-2-(Benzylthio)-1-chloropent-1-en-3-one Z-9c and (*E*)-2-(benzylthio)-1-chloropent-1-en-3-one E-9c

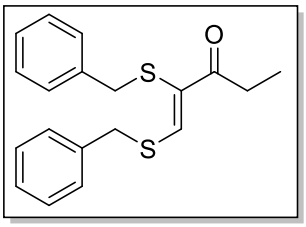


The title compounds were synthesized using the procedure described above for **Z-9b** and **E-9b** using a solution of zinc chloride in ether (1.80 mL of a 1M solution, 1.8 mmol) and a mixture containing the dichloride 2-(benzylthio)-1,2-dichloropentan-3-one **S57** (46%), (*Z*)-2-(benzylthio)-1-chloropent-1-en-3-one **Z-9c** (32%) and (*E*)-2-(benzylthio)-1-chloropent-1-en-3-one **E-9c** (21%) (0.166 g, 0.6 mmol) in dichloromethane (15 mL). The reaction was quenched by addition of water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated at reduced pressure to give the crude product as a dark yellow oil. ^{1}H NMR spectroscopy of the crude product showed the dichloride had converted to the desired β-chloroenones **Z-9c** and **E-9c** (ratio 17:1 respectively). The bis-sulfide impurity, 1,2-bis(benzylthio)pent-1-en-3-one **S58** (*approx.* 18%), was also seen in the ^{1}H NMR spectrum of the crude product characterised by the presence of a singlet at δ_H 7.99 ppm. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate (gradient elution 4-30% ethyl acetate) as eluent. The major fraction isolated contained the pure β-*chloroenone* **Z-9c** and **E-9c** in a ratio of 14:1 (59 mg, 27% yield over two steps from the sulfide) as a yellow oil; ν_{max}/cm^{-1} (film) 3051 (CH), 2984 (CH), 2936 (CH), 1688 (CO), 1454;

Z-9c: δ_H (300 MHz, $CDCl_3$) 0.99 (3H, t, *J* 7.2, CH_2CH_3), 2.49 (2H, q, *J* 7.2, CH_2CH_3), 4.00 (2H, s, SCH_2), 7.22-7.32 (5H, m, Ar*H*), 7.35 (1H, s, C*H*Cl); δ_C (75.5 MHz, $CDCl_3$) 8.1 (CH_3, CH_2CH_3), 33.2 (CH_2, CH_2CH_3), 37.2 (CH_2, SCH_2), 127.4, 128.54, 129.0 (3 x CH, aromatic *C*H), 135.7 (CH, *C*HCl), 137.3, 139.0 [2 x C, aromatic *C* and *C*(2)S], 197.7 (C, *C*O).

E-9c: δ_H (300 MHz, $CDCl_3$) 1.11 (3H, t, *J* 7.2, CH_2CH_3), 2.73 (2H, q, *J* 7.2, CH_2CH_3), 3.82 (2H, s, SCH_2), 6.31 (1H, s, C*H*Cl), 7.21-7.33 (5H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 7.5 (CH_3, CH_2CH_3), 35.0 (CH_2, CH_2CH_3), 38.7 (CH_2, SCH_2), 122.2 (CH, *C*HCl), 127.5, 128.50, 129.1 (3 x CH, aromatic *C*H), 135.5, 136.6 [2 x C, aromatic *C* and *C*(2)S], 201.9 (C, *C*O).

HRMS (ES+): Exact mass calculated for $C_{12}H_{14}OS^{35}Cl[M+H^+]$ 241.0454. Found 241.0447; m/z (ES+) 241.1 [$(C_{12}H_{13}OS^{35}Cl)+H^+$], 30%, 243.1 [$(C_{12}H_{13}OS^{37}Cl)+H^+$], 10%.



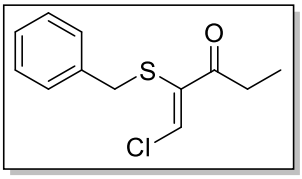
Characteristic signals assigned as the bis-sulfide impurity **S58** were seen in the ^{1}H NMR spectrum of a more polar fraction; δ_H (300 MHz, $CDCl_3$) 0.91 (3H, t, *J* 7.2, CH_2CH_3), 2.40 (2H, q, *J* 7.2, CH_2CH_3), 3.89 (2H, s, one of SCH_2), 4.05 (2H, s, one of SCH_2), 7.11-7.39 (10H, m, Ar*H*), 7.99 (1H, s, C*H*SBn); δ_C (75.5 MHz, $CDCl_3$) 8.5 (CH_3, CH_2CH_3), 31.6 (CH_2, CH_2CH_3), 37.4 (CH_2, one of SCH_2), 38.7 (CH_2, one of SCH_2), 127.2 (CH, aromatic *C*H), 127.4 [C, aromatic *C* or *C*(2)S], 127.8, 128.4, 128.8, 129.0, 129.1 (5 x CH, aromatic *C*H), 136.8, 137.8 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 154.3 (CH, CHSBn), 196.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{19}H_{21}OS_2$[M+H$^+$] 329.1034. Found 329.1022; m/z (ES+) 329.0 [($C_{19}H_{20}OS_2$)+H$^+$], 46%.

Reaction of 2-(benzylthio)pentan-3-one S60 and NCS using Microwave Methods

This reaction was undertaken using the method described above for **S57** using the α-thioketone 2-(benzylthio)pentan-3-one **5c** (0.20 g, 0.96 mmol), unrecrystallised *N*-chlorosuccinimide (0.334 g, 2.5 mmol) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 h. The resulting reaction mixture was cooled to 0 °C and the excess *N*-chlorosuccimide was removed by filtration. The crude mixture was evaporated under reduced pressure to give the crude product as a brown oil. ^{1}H NMR spectroscopy of the crude product showed no evidence of any dichloride formation and the major product was seen to be the corresponding β-chloroenone as a 17:1 mixture of the *Z* isomer **Z-9c** and *E* isomer **E-9c** with a trace of benzyl chloride **S56** (s, δ_H 4.59 ppm). Purification by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent afforded the pure β-*chloroenones* **Z-9c** and **E-9c** in a ratio of 35:1 (0.163 g, 61%) as a yellow oil.

A further fraction isolated from the column contained both the *Z* and *E* isomers of the β-chloroenone **Z-9c** and **E-9c** (21 mg, 8%) in a ratio of 13:1 respectively.

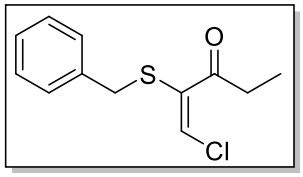
(*Z*)-2-(Benzylthio)-1-chloropent-1-en-3-one Z-9c



ν_{max}/cm^{-1} (film) 3051 (CH), 2984 (CH), 2936 (CH), 1688 (CO), 1454; δ_H (300 MHz, $CDCl_3$) 0.99 (3H, t, *J* 7.2, CH_2CH_3), 2.49 (2H, q, *J* 7.2, CH_2CH_3), 4.00 (2H, s, SCH_2), 7.22-7.32 (5H, m, Ar*H*)*, 7.35 (1H, s, C*H*Cl); δ_C (75.5 MHz, $CDCl_3$) 8.1 (CH_3, CH_2CH_3), 33.2 (CH_2, CH_2CH_3), 37.2 (CH_2, SCH_2), 127.4,

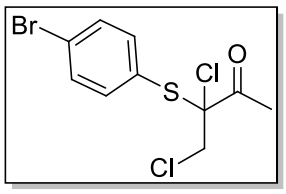
128.5, 129.0 (3 x CH, aromatic *C*H), 135.7 (CH, *C*HCl), 137.3, 139.0 [2 x C, aromatic *C* and *C*(2)S], 197.7 (C, *C*O).

(*E*)-2-(Benzylthio)-1-chloropent-1-en-3-one E-9c



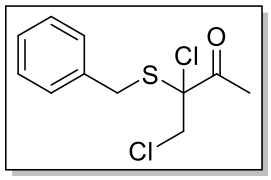
δ_H (300 MHz, $CDCl_3$) 1.11 (3H, t, *J* 7.2, CH_2CH_3), 2.73 (2H, q, *J* 7.2, CH_2CH_3), 3.82 (2H, s, SCH_2), 6.31 (1H, s, C*H*Cl), 7.21-7.33 (5H, m, Ar*H*).

3-[(4-Bromophenyl)thio]-3,4-dichlorobutan-2-one S59



The α-thioketone **5d** (0.30 g, 1.2 mmol), *N*-chlorosuccinimide (0.404 g, 3.0 mmol, 2.6 eq) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 h. The resulting reaction mixture was cooled to 0 °C and the excess *N*-chlorosuccimide was removed by filtration. The crude mixture was evaporated under reduced pressure to give the crude product as an orange oil. ^{1}H NMR spectroscopy of the crude compound showed the dichloride **S59** to be the major component. The crude product was purified by column chromatography on silica gel using hexane-ethyl acetate (90:10) as eluent, the pure *dichloride* **S59** was obtained as a yellow oil (0.134 g, 35%); ν_{max}/cm^{-1} (film) 2923 (CH), 1719 (CO), 1566, 1472; δ_H (300 MHz, $CDCl_3$) 2.48 (3H, s, CH_3), 3.92 (1H, A of AB system, *J* 12.0, one of CH_2Cl), 3.85 (1H, B of AB system, *J* 12.0, one of CH_2Cl), 7.42 (2H, d, *J* 8.4, Ar*H*), 7.54 (2H, d, *J* 8.4, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 25.5 (CH_3, CH_3), 48.2 (CH_2, CH_2Cl), 80.9 [C, *C*(2)S], 126.2, 126.8 (2 x C, 2 x aromatic *C*), 132.9, 138.5 (2 x CH, aromatic *C*H), 197.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{10}OS^{35}Cl_2{}^{79}Br[M+H^+]$ 327.8914. Found 327.0786; m/z (ES+) 292.0 [$(C_{10}H_9OS^{35}Cl_2{}^{79}Br)$-$^{35}Cl^-$], 25% 79.8 (100%).

3-(Benzylthio)-3,4-dichlorobutan-2-one S60



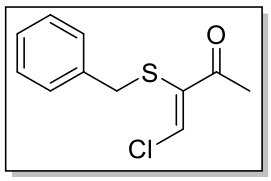
The α-thioketone **5e** (0.20 g, 1.0 mmol), *N*-chlorosuccinimide (0.358 g, 2.7 mmol, 2.6 eq) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 h. The resulting reaction mixture was cooled to 0 °C and the excess *N*-chlorosuccimide was removed by filtration. The crude mixture

was evaporated under reduced pressure to give the crude product as an orange oil. ^{1}H NMR spectroscopy of the crude product showed a complex mixture of the dichloride **S60**, the *Z* isomer of the β-chloroenone **Z-9e** and the trichloride **S61** had formed along with a minor amount of benzyl chloride **S56** (s, δ_H 4.59 ppm). Separation was attempted by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent. A small amount of (*Z*)-3-(benzylthio)-4-chlorobut-3-en-2-one **Z-9e** (10 mg, 4%) was isolated as a yellow oil, however the major fraction obtained was a yellow oil (0.166 g), which was a mixture of three compounds, 3-(benzylthio)-3,4-dichlorobutan-2-one **S60** (35%), (*Z*)-3-(benzylthio)-4-chlorobut-3-en-2-one **Z-9e** (32%) and the over-chlorination product the trichloride **S61**, 3-(benzylthio)-3,4,4-trichlorobutan-2-one (33%). No further purification was attempted and this product was carried forward as a mixture and reacted with zinc chloride.

3-(Benzylthio)-3,4-dichlorobutan-2-one S60

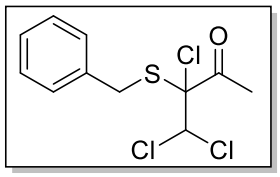
Characteristic signals: δ_H (300 MHz, $CDCl_3$) 2.46 (3H, s, C*H*$_3$), 3.84 (2H, s, SC*H*$_2$), 3.90 (1H, A of AB system, *J* 12.0, one of C*H*$_2$Cl), 4.14 (1H, B of AB system, *J* 12.0, one of C*H*$_2$Cl).

(*Z*)-3-[(Benzyl)thio]-4-chlorobut-3-en-2-one Z-9e



δ_H (300 MHz, $CDCl_3$) 2.19 (3H, s, C*H*$_3$), 4.01 (2H, s, SC*H*$_2$), 7.22-7.30 (5H, m, Ar*H*), 7.40 (1H, s, C*H*Cl).

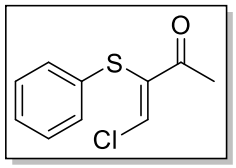
3-(Benzylthio)-3,4,4-trichlorobutan-2-one S61



Characteristic signals: δ_H (300 MHz, $CDCl_3$) 2.54 (3H,s, C*H*$_3$), 6.26 (1H, s, C*H*Cl_2).

1.5.6 Zinc Chloride Catalysed Elimination of Dichlorides to α-Sulfenyl-β-chloroenones

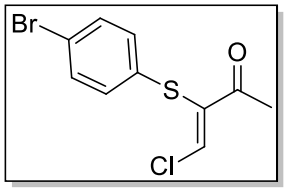
(*Z*)-4-Chloro-3-(phenylthio)but-3-en-2-one Z-9a



The title compound was synthesized using the procedure described above for **Z-9b** and **E-9b** using a solution of zinc chloride in ether (1.80 mL of a 1M solution, 1.8 mmol, 3 eq) and the dichloride **S53**, (0.15 g, 0.6

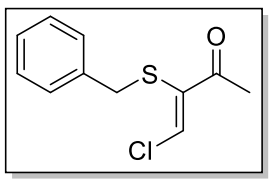
mmol) in dichloromethane (15 mL). The reaction was quenched by addition of water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated at reduced pressure to give the crude product as a dark yellow oil. The ^{1}H NMR spectrum of this crude product showed the *Z* isomer of the β-*chloroenone* **Z-9a** was the major product. Following purification by column chromatography using hexane-ethyl acetate (95:5) as eluent, the pure β-*chloroenone* **Z-9a** (79 mg, 62%) was obtained as a yellow oil; ν_{max}/cm^{-1} (film) 3051 (CH), 1721 (CO), 1536; δ_H (300 MHz, $CDCl_3$) 2.24 (3H, s, C*H*$_3$), 7.23-7.34 (5H, m, Ar*H*), 7.52 (1H, s, C*H*Cl); δ_C (75.5 MHz, $CDCl_3$) 28.0 (CH_3, *C*H_3), 127.2, 129.0, 129.5 (3 x CH, aromatic *C*H), 133.4 [C, aromatic *C* or *C*(2)S], 136.8 (CH, *C*HCl), 138.5 [C, aromatic *C* or *C*(2)S], 195.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{10}H_{10}OS^{35}Cl[M+H^+]$ 213.0141. Found 213.0134; m/z (ES+) 211.1 [$(C_{10}H_9OS^{35}Cl)-H^+$], 4%, 287.0 (100%), 288.0 (20%).

(*Z*)-3-[(4-Bromophenyl)thio]-4-chlorobut-3-en-2-one Z-9d



The title compound was synthesized using the procedure described above for **Z-9b** and **E-9b** using a solution of zinc chloride in ether (1.23 mL of a 1M solution, 1.2 mmol, 3 eq) and the dichloride **S59** (0.134 g, 0.4 mmol) in dichloromethane (15 mL). The reaction was quenched by addition of water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated at reduced pressure to give the crude product as a dark yellow oil. ^{1}H NMR spectroscopy of the crude product showed the tentatively assigned β-chloroenone **Z-9d** as the major product. The compound was not recovered following attempted purification by column chromatography using hexane-ethyl acetate (90:10) as eluent. Characteristic signals for the tentatively assigned β-chloroenone from the ^{1}H NMR spectrum of the crude product; δ_H (400 MHz, $CDCl_3$) 2.27 (3H, s, C*H*$_3$), 7.12 (2H, d, *J* 8.4, Ar*H*), 7.42 (2H, d, *J* 8.2, Ar*H*), 7.58 (1H, s, C*H*Cl).

(*Z*)-3-[(Benzyl)thio]-4-chlorobut-3-en-2-one Z-9e



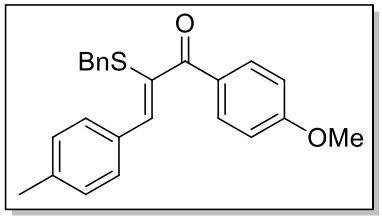
The title compound was synthesized using the procedure described above for **Z-9b** and **E-9b** using a solution of zinc chloride in ether (1.80 mL of a 1M solution, 1.8 mmol) and a mixture containing three compounds, 3-(benzylthio)-3,4-dichlorobutan-2-one **S60** (35%), (*Z*)-3-(benzylthio)-4-

chlorobut-3-en-2-one (32%) **Z-9e** and 3-(benzylthio)-3,4,4-trichlorobutan-2-one **S61** (33%) (0.166 g, 0.6 mmol) in dichloromethane (15 mL). The reaction was quenched by addition of water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated at reduced pressure to give the crude product as a dark yellow oil. ^{1}H NMR spectroscopy of the crude product showed the dichloride had eliminated successfully to form the desired β-chloroenone **Z-9e**. Following purification by column chromatography using hexane-ethyl acetate (95:5) as eluent, a fraction was recovered (49 mg) which contained the β-*chloroenone* **Z-9e** but this was not isolated as a pure compound. Characteristic signals*;* ν_{max}/cm^{-1} (film) 3030 (CH), 2984 (CH), 2925 (CH), 1686 (CO), 1542; δ_H (400 MHz, $CDCl_3$) 2.19 (3H, s, C*H*$_3$), 4.01 (2H, s, SC*H*$_2$), 7.22-7.30 (5H, m, Ar*H*), 7.40 (1H, s, C*H*Cl); δ_C (75.5 MHz, $CDCl_3$) 27.6 (CH_3, *C*H$_3$), 37.2 (CH_2, S*C*H$_2$), 127.4, 128.5, 129.0 (3 x CH, aromatic *C*H), 137.3 (CH, *C*HCl), 137.3, 139.4 [C, aromatic *C* and *C*(2)S], 194.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{11}H_{12}OS^{35}Cl[M+H^+]$ 227.0297. Found 227.0296.

1.6 Synthesis of Chalcones

The following compounds were synthesised following a procedure described by Aguilar-Aguilar and Peña Cabrera.[22]

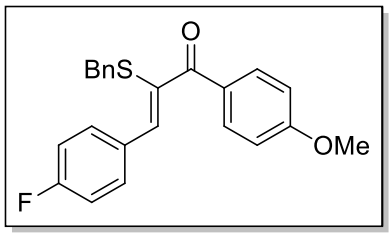
(*Z*)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-(*p*-tolyl)prop-2-en-1-one 14



The β-chloroenones ***Z*-4e** and ***E*-4e** (ratio 4:1) (200 mg, 0.63 mmol) and the aryl stannane, 4-(tributylstannyl)toluene **36b**[23] (287 mg, 0.75 mmol) were dissolved in anhydrous acetonitrile (5mL) under nitrogen. The mixture was then purged with nitrogen for 5 min whereupon the palladium catalyst, $(CH_3CN)_2PdCl_2$ (5%) was added and the reaction mixture was stirred at room temperature for 2h. The mixture was then washed with hexane (3 x 20mL) to remove the tin by-products and the remaining acetonitrile phase was evaporated under reduced pressure to give the crude *chalcone* as an orange oil. ^{1}H NMR spectroscopy showed the crude product to contain 9% β-chloroenone starting material as the *E* isomer **4e** and 91% *Z* chalcone ***Z*-14**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (99:1) as eluent to give the *Z chalcone* ***Z*-14** (204 mg, 86%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 2918 (CH), 1650 (CO), 1598 (aromatic), 1251; δ_H (300 MHz, $CDCl_3$) 2.37 (3H, s, ArC*H*$_3$), 3.87 (3H, s, OC*H*$_3$), 3.98 (2H, s, SC*H*$_2$), 6.87 (2H, d, *J* 8.9, Ar*H*), 6.95 [1H, s, C(3)*H*], 7.11-7.21 (7H, m, Ar*H*),

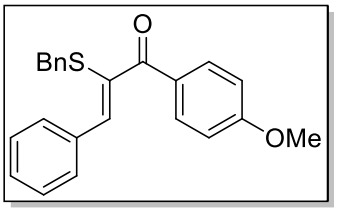
7.57 (2H, d, *J* 8.1, Ar*H*), 7.67 (2H, d, *J* 8.9, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 21.4 (CH_3, Ar*C*H_3), 36.8 (CH_2, S*C*H_2), 55.5 (CH_3, O*C*H_3), 113.5, 127.2, 128.4, 129.0, 129.3 (5 x CH, aromatic *C*H), 130.0 [C, aromatic *C* or *C*(2)S], 130.3 (CH, aromatic *C*H), 132.2 [C, aromatic *C* or *C*(2)S], 132.4 (CH, aromatic *C*H), 134.9, 137.4 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 138.3 [CH, *C*(3)H], 139.1 [C, aromatic *C* or *C*(2)S], 163.3 (C, aromatic *C*), 192.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{24}H_{23}SO_2$[M+H$^+$] 375.1419. Found 375.1412; m/z (ES+) 375.2 [($C_{24}H_{22}SO_2$)+H$^+$], 100%.

(*Z*)-2-(Benzylthio)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 15



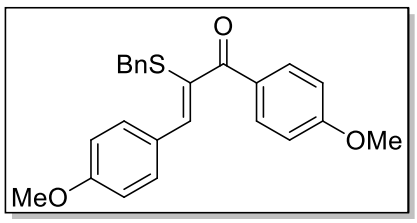
The title compound was prepared following the procedure described above for **14** using the β-chloroenones **Z-4e** and ***E*-4e** (ratio 4:1) (155 mg, 0.5 mmol), tributyl(4-fluorophenyl)stannane **36c**[24] (227 mg, 0.6 mmol) and anhydrous acetonitrile (5 mL). The crude chalcone was obtained as a yellow oil. ^{1}H NMR analysis showed the crude product to contain 18% β-chloroenone starting material as a mixture of *Z* and *E* isomers ***Z*-4e** and ***E*-4e** in a ratio of 1:3 and 82% *Z* chalcone ***Z*-15**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z chalcone* ***Z*-15** (124 mg, 66%) as a yellow oil; ν_{max}/cm^{-1} (film) 2967 (CH), 1650 (CO), 1599 (aromatic), 1464, 1423; δ_H (300 MHz, $CDCl_3$) 3.79 (3H, s, O*CH*$_3$), 3.97 (2H, s, S*CH*$_2$), 6.79 (2H, d, *J* 8.7, Ar*H*), 6.83 [1H, s, C(3)*H*], 6.97 (2H, t, *J* 8.7, Ar*H*), 7.07 (5H, s, Ar*H*), 7.53-7.61 (4H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 35.7 (CH_2, S*C*H_2), 54.5 (CH_3, O*C*H_3), 112.3 (CH, aromatic *C*H), 114.3 (CH, d, $^2J_{CF}$ 21.5, aromatic *C*H), 126.2, 127.4, 128.3 (3 x CH, aromatic *C*H), 128.7, 129.9 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 131.1 (CH, d, $^3J_{CF}$ 9.1, aromatic *C*H), 131.4 (CH, aromatic *C*H), 134.5 (C, d, $^4J_{CF}$ 2.1, aromatic *C*), 135.5 [CH, *C*(3)H], 136.2 [C, aromatic *C* or *C*(2)S], 161.5 (C, d, $^1J_{CF}$ 250.3, aromatic *C*), 162.5 (C, aromatic *C*), 191.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{20}SO_2F$[M+H$^+$] 379.1168. Found 379.1160; m/z (ES+) 379.3 [($C_{23}H_{19}SO_2F$)+H$^+$], 100%.

(*Z*)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one 16



The title compound was prepared following the procedure described above for **14** using the β-chloroenones ***Z*-4e** and ***E*-4e** (ratio 4:1) (155 mg, 0.5 mmol) and phenyltributylstannane **36a** (220 mg, 0.6 mmol) and anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ^{1}H NMR analysis showed the crude product to contain 39% β-chloroenone starting material as a mixture of *Z* and *E* isomers ***Z*-4e** and ***E*-4e** in a ratio of 2:1 and 59% *Z* chalcone ***Z*-16**. A signal tentatively assigned as the C(3)H proton of the *E* chalcone ***E*-16** (<2%) was observed as a singlet at δ_H 6.60 ppm. The crude product mixture was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z chalcone* ***Z*-16** (115 mg, 59%) as a yellow oil, which also contained *Z* β-chloroenone starting material ***Z*-4e** (14% by integration of the ^{1}H NMR spectrum); ν_{max}/cm^{-1} (film) 2933 (CH), 1651 (CO), 1599 (aromatic), 1253; δ_H (300 MHz, $CDCl_3$) 3.87 (3H, s, OC*H*$_3$), 3.98 (2H, s, SC*H*$_2$), 6.87 (2H, d, *J* 8.8, Ar*H*), 6.94 [1H, s, C(3)*H*], 7.16 (5H, m, Ar*H*), 7.25-7.39 (3H, m, Ar*H*), 7.65 (2H, d, *J* 7.4, Ar*H*), 7.69 (2H, d, *J* 8.8, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.8 (CH_2, S*C*H$_2$), 55.5 (CH_3, O*C*H$_3$), 113.6, 127.2, 128.3, 128.4, 128.7, 129.3 (6 x CH, aromatic *C*H), 129.8 [C, aromatic *C* or *C*(2)S], 130.2, 132.4 (2 x CH, aromatic *C*H), 135.0, 136.0, 137.3 [3 x C, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 137.4 [CH, *C*(3)H], 163.5 (C, aromatic *C*OCH$_3$), 192.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{21}SO_2$[M+H$^+$] 361.1268. Found 361.1262; m/z (ES+) 361.3 [($C_{23}H_{20}SO_2$)+H$^+$], 100%.

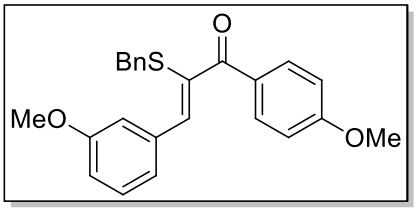
(*Z*)-2-(Benzylthio)-1,3-bis(4-methoxyphenyl)prop-2-en-1-one 17



This was prepared following the procedure described for **14** using the β-chloroenones ***Z*-4e** and ***E*-4e** (ratio 4:1) (155 mg, 0.5 mmol), tributyl(4-methoxyphenyl)stannane **36d**[23] (238 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ^{1}H NMR analysis showed the crude product to contain 9% β-chloroenone starting material as the *E* isomer ***E*-4e** only and 91% *Z* chalcone ***Z*-17**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z chalcone* ***Z*-17** (137 mg, 70%) as a yellow oil; ν_{max}/cm^{-1} (film) 2919 (CH), 1650 (CO), 1600 (aromatic), 1508, 1252; δ_H (400 MHz, $CDCl_3$) 3.84 (3H, s, OC*H*$_3$), 3.88 (3H, s, OC*H*$_3$), 3.99 (2H,

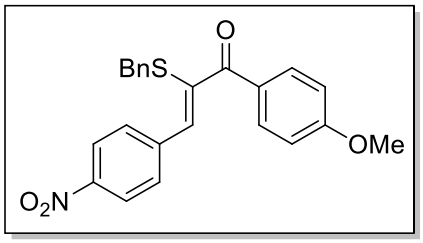
s, SCH_2), 6.87 (2H, d, *J* 8.8, Ar*H*), 6.90 (2H, d, *J* 8.8, Ar*H*), 6.97 [1H, s, C(3)*H*], 7.11-7.19 (5H, m, Ar*H*), 7.63 (2H, d, *J* 8.8, Ar*H*), 7.68 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.8 (CH_2, S*C*H_2), 55.3 (CH_3, O*C*H_3), 55.5 (CH_3, O*C*H_3), 113.5, 113.8, 127.1 (3 x CH, aromatic *C*H), 127.7 (C, aromatic *C*), 128.4, 129.3 (2 x CH, aromatic *C*H), 130.3 [C, aromatic *C* or *C*(2)S], 132.2, 132.3 (2 x CH, aromatic *C*H), 133.4, 137.5 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 139.0 [CH, *C*(3)H], 163.0, 163.1 (2 x C, 2 x aromatic *C*OCH_3), 193.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{24}H_{23}SO_3$[M+H^+] 391.1368. Found 391.1380; m/z (ES+) 391.3 [($C_{24}H_{22}SO_3$)+H^+], 100%.

(*Z*)-2-(Benzylthio)-3-(3-methoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 18



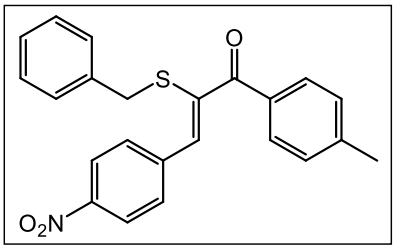
This was prepared following the procedure described for **14i** using the β-chloroenones ***Z*-4e** and ***E*-4e** (ratio 4:1) (155 mg, 0.5 mmol), tributyl(3-methoxyphenyl)stannane **36e**[23] (238 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ^{1}H NMR spectroscopy showed the crude product to contain 10% β-chloroenone starting material as the *E* isomer ***E*-4e** only and 90% *Z* chalcone ***Z*-18**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z chalcone* ***Z*-18** (162 mg, 83%) as a yellow oil; ν_{max}/cm^{-1} (film) 2917 (CH), 1649 (CO), 1598 (aromatic), 1249, 1169; δ_H (400 MHz, $CDCl_3$) 3.81 (3H, s, O*C*H_3), 3.87 (3H, s, O*C*H_3), 3.97 (2H, s, S*C*H_2), 6.87 (3H, d, *J* 8.9, Ar*H*), 6.91 [1H, s, C(3)*H*], 7.09-7.32 (8H, m, Ar*H*), 7.69 (2H, d, *J* 8.9, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.8 (CH_2, S*C*H_2), 55.3 (CH_3, O*C*H_3), 55.5 (CH_3, O*C*H_3), 113.6, 114.8, 115.0, 122.9, 127.2, 128.4, 129.26, 129.33 (8 x CH, aromatic *C*H), 129.8 [C, aromatic *C* or *C*(2)S], 132.4 (CH, aromatic *C*H), 136.3 [C, aromatic *C* or *C*(2)S], 137.2 [CH, *C*(3)H], 137.3 [C, aromatic *C* or *C*(2)S], 159.4, 163.5 (2 x C, 2 x aromatic C), 192.6 (C, *C*O), signal for 1 x aromatic C could not be seen in the ^{13}C NMR spectrum; HRMS (ES+): Exact mass calculated for $C_{24}H_{23}SO_3$[M+H^+] 391.1368. Found 391.1360; m/z (ES+) 391.4 [($C_{24}H_{22}SO_3$)+H^+], 100%.

(*Z*)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one 19



This was prepared following the procedure described for **14** using the β-chloroenones ***Z*-4e** and ***E*-4e** (ratio 4:1) (155 mg, 0.5 mmol), 4-(tri-*n*-butylstannyl)nitrobenzene **36f**[25] (240 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as an orange oil. ^{1}H NMR spectroscopy showed the crude product to contain 9% β-chloroenone starting material as the *E* isomer ***E*-4e** and 89% *Z* chalcone ***Z*-19**. A signal tentatively assigned as the C(3)H proton of the *E* chalcone product ***E*-19** (<1%) was observed as a singlet at δ_H 6.60 ppm. This was purified by column chromatography on silica gel using hexane-ethyl acetate (85:15) as eluent to give the *Z chalcone* ***Z*-19** (176 mg, 87%) as a bright yellow oil; ν_{max}/cm^{-1} (film) 2955 (CH), 1650 (CO), 1598 (aromatic), 1515 (NO_2), 1342 (NO_2), 1253; δ_H (400 MHz, $CDCl_3$) 3.89 (3H, s, OC*H*$_3$), 3.98 (2H, s, SC*H*$_2$), 6.85 [1H, s, C(3)*H*], 6.91 (2H, d, *J* 8.9, Ar*H*), 7.17 (5H, s, Ar*H*), 7.74 (2H, d, *J* 8.6, Ar*H*), 7.78 (2H, d, *J* 8.9, Ar*H*), 8.21 (2H, d, *J* 8.8, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.9 (CH_2, S*C*H$_2$), 55.6 (CH_3, O*C*H$_3$), 113.8, 123.6, 127.6, 128.6 (4 x CH, aromatic *C*H), 128.9 [C, aromatic *C* or *C*(2)S], 129.3, 130.4 (2 x CH, aromatic *C*H), 131.8 [CH, *C*(3)H], 132.5 (CH, aromatic *C*H), 136.5, 140.9, 141.4 [3 x C, 2 x aromatic *C* and *C*(2)S], 146.8 (C, aromatic *C*NO$_2$), 164.0 (C, aromatic *C*OCH$_3$), 191.7 (C, *C*O), signal for 1 x aromatic C not seen in ^{13}C NMR spectrum; HRMS (ES+): Exact mass calculated for $C_{23}H_{20}NSO_4$[M+H$^+$] 406.1113. Found 406.1133; m/z (ES+) 406.3 [($C_{23}H_{19}SO_4N$)+H$^+$], 5%.

(*Z*)-2-(Benzylthio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 20



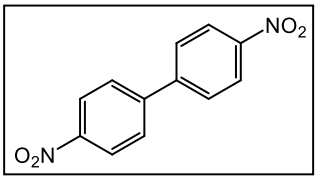
This was prepared following the procedure described for **14** from the β-chloroenones *Z*-**4h** and *E*-**4h** (*Z* : *E*, 14 : 1) (105 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (151 mg, 0.4 mmol), and $(CH_3CN)_2PdCl_2$ (4 mg, 17 µmol, 5 mol %) in anhydrous acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 24 h. The crude *chalcone* was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 4% β-chloroenone starting material **E-4h,** and *approx.* 62% chalcone *Z*-**20** as well as bi-aryl **37**[26] (δ_H, d, 7.79 ppm, *J* 8.8 and δ_H, d, 8.36 ppm, *J* 8.8). This was purified by column chromatography on silica gel using hexane–

dichloromethane (gradient 70–100% dichloromethane) as eluent, to give the *chalcones Z*-**20** and *E*-**20** (*Z* : *E*, 10.6 : 1) (51 mg, 38%) as a bright yellow viscous gum. The bi-aryl **37**[26] was isolated in a less polar fraction as a white solid.

Z-**20**: ν_{max}/cm^{-1} (neat) 3029, 2921, 1651 (C=O), 1601, 1514 (NO_2), 1339 (NO_2), 1243, 1177, 689; δ_H (400 MHz, $CDCl_3$): 2.43 (3H, s, ArC*H*$_3$), 3.99 (2H, s, SC*H*$_2$), 6.89 [1H, s, C(3)*H*], 7.11–7.36 (7H, m, Ar*H*), 7.63 (2H, d, *J* 8.2, Ar*H*), 7.73 (2H, d, *J* 8.9, Ar*H*), 8.20 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H$_3$), 36.9 (CH_2, S*C*H$_2$), 123.5, 127.5, 128.6, 129.2, 129.3, 130.2, 130.5, 133.3 [8 × CH, aromatic *C*H and *C*(3)H], 133.7, 136.6, 140.7, 141.2, 144.5, 146.9 [6 × C, 5 × aromatic *C* and *C*(2)S], 192.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{20}NO_3S[M+H^+]$ 390.1164. Found 390.1164.

Characteristic signals tentatively assigned as *E*-**20**: δ_H (400 MHz, $CDCl_3$): 2.38 (3H, s, ArC*H*$_3$), 3.97 (2H, s, SC*H*$_2$), 6.87 [1H, s, C(3)*H*], 7.81 (2H, d, *J* 8.2, Ar*H*), 7.98 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 37.6 (CH_2, S*C*H$_2$), 123.8, 128.7, 128.9, 129.1, 129.7, 129.8 [6 × CH, aromatic *C*H or 10 × aromatic *C*H and *C*(3)H], 136.1, 139.5, 141.1, 145.6 (4 × C, *C*q), 193.6 (C, *C*O).

4,4'-Dinitro-1,1'-biphenyl 37[26]

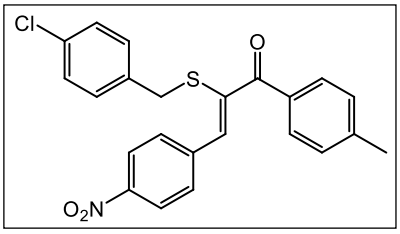


(less polar): white solid (7 mg, 8%); ν_{max}/cm^{-1} (neat) 1598, 1512 (NO_2), 1340 (NO_2), 1107, 850, 737; δ_H (400 MHz, $CDCl_3$): 7.79 (4H, d, *J* 8.8, Ar*H*), 8.37 (4H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 124.4, 128.3 (2 × CH signals, 8 × aromatic *C*H), 145.0, 148.0 (2 × C, 4 × aromatic *C*).

Spectroscopic details were consistent with those previously reported.[26]

This reaction was also carried out with a shorter reaction time of 2 h using the β-chloroenones *Z*-**4h** and *E*-**4h** (*Z* : *E*, 5.2 : 1) (60 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **36f**[27] (99 mg, 0.24 mmol), and $(CH_3CN)_2PdCl_2$ (3 mg, 10 µmol, 5 mol %) in acetonitrile (5 mL). After work up, ^{1}H NMR spectroscopy showed this material to contain *approx*. 24% β-chloroenone starting materials *Z*-**4h** and *E*-**4h** (*Z* : *E*, 1.8 : 1) and 76% chalcone *Z*-**20**. Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the *chalcone Z*-**20** (14 mg, 18%) as a bright yellow oil .

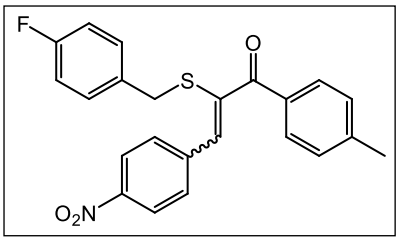
(*Z*)-2-((4-Chlorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *Z*-21



This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4j** and *E*-**4j** (*Z* : *E*, 4.5 : 1) (123 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (157 mg, 0.4 mmol), and $(CH_3CN)_2PdCl_2$ (4 mg, 15 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 5 h and after work-up, the crude product was obtained as a brown residue. ^{1}H NMR spectroscopy showed this product to contain 4% β-chloroenone starting material *E*-**4j**, 22% bi-aryl **37**[26], and *approx.* 74% chalcone *Z*-**21**. Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave a yellow solid. This was recrystallised from isopropyl alcohol to give the *chalcone Z*-**21** (65 mg, 43%) as a bright yellow powder (mp 106–108°C) which contained *approx*. 6% bi-aryl **37.**[26]

Z-**21:** ν_{max}/cm^{-1} (neat) 3029, 2924, 2851, 1723, 1655 (C=O), 1602, 1516 (NO_2), 1341 (NO_2); δ_H (400 MHz, $CDCl_3$): 2.44 (3H, s, ArC*H*$_3$), 3.97 (2H, s, SC*H*$_2$), 6.90 [1H, s, C(3)*H*], 7.03–7.18 (4H, m, Ar*H*), 7.23 (2H, d, *J* 8.0, Ar*H*), 7.59 (2H, d, *J* 8.1, Ar*H*), 7.73 (2H, d, *J* 8.7, Ar*H*), 8.22 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H$_3$), 36.1 (CH_2, S*C*H$_2$), 123.5, 128.7, 129.2, 130.2, 130.5, 130.7 (6 × CH, aromatic *C*H), 133.4, 133.5 [2 × C, 2 × aromatic *C* or 1 × aromatic *C* and *C*(2)S], 133.6 [CH, *C*(3)H], 135.2, 140.1, 141.1, 144.7, 147.0 [5 × C, 5 × aromatic *C* or 4 × aromatic *C* and *C*(2)S], 192.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{19}NO_3S^{35}Cl$[M+H$^+$] 424.0774. Found 424.0753.

(*Z*)-2-((4-Fluorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *Z*-22 and (*E*)-2-((4-fluorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-22



This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4l** and *E*-**4l** (*Z* : *E*, 3.4 : 1) (33 mg, 0.1 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (64 mg, 0.1 mmol), and $(CH_3CN)_2PdCl_2$ (2 mg, 8 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred under reflux for 5 h and after work-up, the crude product was obtained as a brown residue. ^{1}H NMR spectroscopy showed this material to contain *approx*. 14% β-chloroenone starting materials *Z*-**4l** and *E*-**4l** (*Z* : *E*, 1 : 1.4), 35% chalcones *Z*-**22** and *E*-**22** (*Z* : *E*, 6.3 : 1) in addition to the bi-

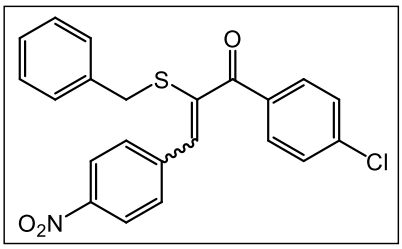
aryl **37**[26] (δ_H, d, 8.36 ppm, *J* 8.8). Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the *chalcones Z*-**22** and *E*-**22** (*Z* : *E*, 3.2 : 1; 11 mg, 28%) as a bright yellow oil; ν_{max}/cm^{-1} (neat) 3071, 3038, 2922, 2850, 1655 (C=O), 1601, 1508 (NO_2), 1340 (NO_2), 1226; δ_H (400 MHz, $CDCl_3$): 2.38 (3H, s, ArC*H*$_3$, *E* isomer), 2.44 (3H, s, ArC*H*$_3$, *Z* isomer), 3.92 (2H, s, SC*H*$_2$, *E* isomer), 3.98 (2H, s, SC*H*$_2$, *Z* isomer), 6.78–7.02 [3H and 3H, m, Ar*H* and C(3)*H*, *Z* and *E* isomer, containing (6.84, 2H, overlapping dd appears as t, *J* 8.6, Ar*H*, *Z* isomer), [6.90, 1H and 1H, s, C(3)*H*, *Z* and *E* isomer], and (6.95, 2H, overlapping dd appears as t, *J* 8.6, Ar*H*, *E* isomer)], 7.11 (2H, dd, *J* 8.4, J_{FH} 5.4, Ar*H*, *Z* isomer), 7.16–7.35 (2H and 6H, m, Ar*H*, *Z* and *E* isomer), 7.62 (2H, d, *J* 8.1, Ar*H*, *Z* isomer), 7.74 (2H, d, *J* 8.7, Ar*H*, *Z* isomer), 7.80 (2H, d, *J* 8.1, Ar*H*, *E* isomer), 7.99 (2H, d, *J* 8.8, Ar*H*, *E* isomer), 8.22 (2H, d, *J* 8.8, Ar*H*, *Z* isomer); HRMS (ES+): Exact mass calculated for $C_{23}H_{19}NO_3FS[M+H^+]$ 408.1070. Found 408.1057.

*^{1}H and ^{13}C NMR spectra were recorded after 60 months (sample was stored neat at room temperature). No degradation was visible, however, the product was seen to have isomerised to give the chalcones Z-***22** *and E-***22** *in an altered ratio of Z : E, 2.2 : 1 (by ^{1}H NMR spectroscopy).*

δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H$_3$, *Z* isomer), 21.8 (CH_3, Ar*C*H$_3$, *E* isomer), 36.0 (CH_2, S*C*H$_2$, *Z* isomer), 36.8 (CH_2, S*C*H$_2$, *E* isomer), 115.4 (1 × CH, d, $^2J_{CF}$ 21.6, aromatic *C*H, *Z* and *E* isomer), 123.5, 123.8, 128.7, 129.2, 129.75 (5 × CH, aromatic *C*H, *Z* and *E* isomer), 129.79 [CH, *C*(3)H, *E* isomer], 129.8, 130.2, 130.5 (3 × CH, aromatic *C*H, *Z* and *E* isomer), 130.7 (1 × CH, d, $^3J_{CF}$ 8.2, aromatic *C*H, *E* isomer), 130.9 (1 × CH, d, $^3J_{CF}$ 8.2, aromatic *C*H, *Z* isomer), 131.8 (C, C_q, *Z* or *E* isomer), 132.0 (C, d, $^4J_{CF}$ 3.6, aromatic *C*, *E* isomer), 132.4 (C, d, $^4J_{CF}$ 3.3, aromatic *C*, *Z* isomer), 133.4 [1 x CH, *C*(3)H, *Z* isomer], 133.6, 138.8, 140.3, 141.0, 141.1, 144.6, 145.7, 146.8, 146.9 (9 × C, C_q, *Z* and *E* isomer), 162.0 (C, d, $^1J_{CF}$ 246.6, aromatic *C*, *Z* isomer), 162.1 (C, d, $^1J_{CF}$ 246.6, aromatic *C*, *E* isomer), 192.7 (C, *C*O, *Z* isomer), 193.5 (C, *C*O, *E* isomer).

This reaction was also carried out at room temperature using the β-chloroenones *Z*-**4l** and *E*-**4l** (*Z* : *E*, 3.4 : 1) (66 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **37f**[25] (99 mg, 0.24 mmol), and $(CH_3CN)_2PdCl_2$ (3 mg, 10 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 5 h. After work up, ^{1}H NMR spectroscopy showed this material to contain *approx*. 77% β-chloroenone starting materials *Z*-**4l** and *E*-**4l** (*Z* : *E*, 3.2 : 1) and 23% chalcones *Z*-**22** and *E*-**22** (*Z* : *E*, 9.6 : 1). Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the *chalcones Z*-**22** and *E*-**22** (*Z* : *E*, 4.9 : 1; 3 mg, 4%, approximately 80% pure) as a bright yellow oil.

(*Z*)-2-(Benzylthio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-23 and (*E*)-2-(Benzylthio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *E*-23

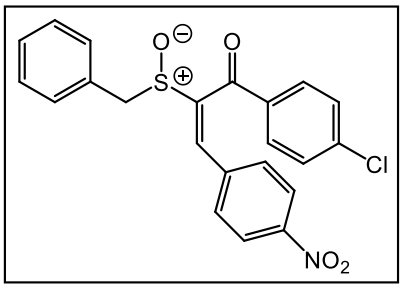


This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4o** and *E*-**4o** (*Z* : *E*, 2.4 : 1) (80 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **37**[25] (123 mg, 0.3 mmol), and $(CH_3CN)_2PdCl_2$ (3 mg, 12 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 5 h and after work-up, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain *approx.* 7% β-chloroenone starting material *E*-**4o** (s, δ_H 6.47 ppm), 8% bi-aryl **37**[26], and 85% chalcones *Z*-**23** and *E*-**23** (*Z* : *E*, 8.4 : 1). Following column chromatography on silica gel using dichloromethane (100%) as eluent gave the *chalcones Z*-**23** and *E*-**23** (*Z* : *E*, 4.6 : 1) (66 mg, 64%) as a yellow semi-solid; ν_{max}/cm^{-1} (neat) 3060, 1655 (C=O), 1584, 1509 (NO_2), 1340 (NO_2), 1244, 693; δ_H (400 MHz, $CDCl_3$) 3.97 (2H, s, SC*H*$_2$, *E* isomer), 4.01 (2H, s, SC*H*$_2$, *Z* isomer), 6.89 [1H, s, C(3)*H*, *Z* isomer], 6.92 [1H, s, C(3)*H*, *E* isomer], 7.09–7.43 [7H and 9H, m, Ar*H*, *Z* and *E* isomer containing (7.37, 2H, d, *J* 8.6, Ar*H*, *Z* isomer)], 7.56 (2H, d, *J* 8.6, Ar*H*, *Z* isomer), 7.75 (2H, d, *J* 8.7, Ar*H*, *Z* isomer), 7.80 (2H, d, *J* 8.7, Ar*H*, *E* isomer), 8.00 (2H, d, *J* 8.8, Ar*H*, *E* isomer), 8.22 (2H, d, *J* 8.8, Ar*H*, *Z* isomer).

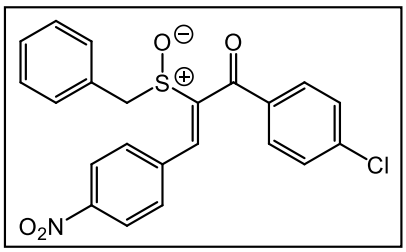
*^{1}H and ^{13}C NMR spectra were recorded after 32 months (sample was stored neat at room temperature). The ^{1}H NMR spectrum was seen to contain approx. 52% chalcones Z-***23** *and E-***23** *(Z : E, 2.9 : 1) and what is believed to be the α-sulfinyl chalcones Z-***40o** *and E-***40o** *(48%, Z : E, 1.1 : 1). Only characteristic signals could be assigned from the ^{13}C NMR spectrum.*

Characteristic signals due to *Z*-**40o:** δ_C (100 MHz, $CDCl_3$): 36.7 (CH_2, S*C*H$_2$), 134.7 [CH, *C*(3)H], 191.9 (C, *C*O).

Characteristic signals due to *E*-**40o:** δ_C (100 MHz, $CDCl_3$): 37.7 (CH_2, S*C*H$_2$), 129.9 [CH, *C*(3)H], 192.7 (C, *C*O).

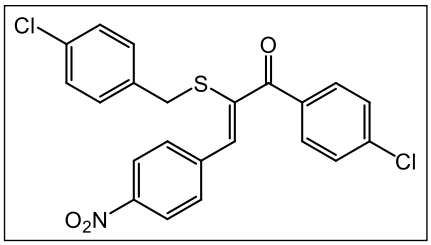


Characteristic signals tentatively assigned as *E*-**40o:** δ_H (400 MHz, $CDCl_3$): 4.17 (1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$), 4.38 (1H, B of AB system, J_{AB} 13.0, one of SC*H*$_2$), 7.07 [1H, s, C(3)*H*]; δ_C (100 MHz, $CDCl_3$): 59.5 (CH_2, S*C*H_2), 134.4 [CH, *C*(3)H], 192.1 (C, *C*O).



Characteristic signals tentatively assigned as *Z*-**40o:** δ_H (400 MHz, $CDCl_3$): 4.46 (1H, A of AB system, J_{AB} 12.2, one of SC*H*$_2$), 4.97 (1H, B of AB system, J_{AB} 12.2, one of SC*H*$_2$); δ_C (100 MHz, $CDCl_3$): 59.2 (CH_2, S*C*H_2), 141.0 [CH, *C*(3)H], 191.7 (C, *C*O).

(*Z*)-2-((4-Chlorobenzyl)thio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-24



This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4q** and *E*-**4q** (*Z* : *E*, 1.7 : 1) (63 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (91 mg, 0.2 mmol), and $(CH_3CN)_2PdCl_2$ (2 mg, 9 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred under reflux for 5 h and after work-up, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain 8% β-chloroenone starting material *E*-**4q**, 19% bi-aryl **37**[26], and *approx.* 52% chalcones *Z*-**24** and *E*-**24** (*Z* : *E*, 8.3 : 1). Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the *chalcones Z*-**24** and *E*-**24**(*Z* : *E*, 30.7 : 1) (37 mg, 47%) as a yellow solid; mp 96–99°C.

Z-**24:** ν_{max}/cm^{-1} (neat) 2921, 1656 (C=O), 1586, 1508 (NO_2), 1336 (NO_2), 1250, 1091; δ_H (400 MHz, $CDCl_3$): 3.97 (2H, s, SC*H*$_2$), 6.91 [1H, s, C(3)*H*], 7.06 (2H, d, *J* 8.5, Ar*H*), 7.11 (2H, d, *J* 8.5, Ar*H*), 7.40 (2H, d, *J* 8.5, Ar*H*), 7.57 (2H, d, *J* 8.5, Ar*H*), 7.75 (2H, d, *J* 8.9, Ar*H*), 8.23 (2H, d, *J* 8.8, Ar*H*).

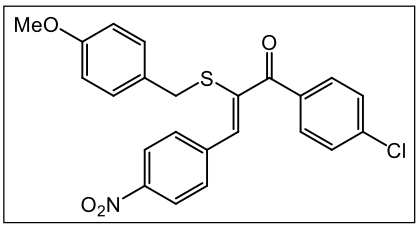
^{1}H and ^{13}C NMR spectra were recorded after 27 months (sample was stored neat at room temperature). No degradation was visible, however, the product was seen to have isomerised

*to give the chalcones Z-***24** *and E-***24** *in an altered ratio of Z : E, 15.4 : 1 (by ^{1}H NMR spectroscopy).*

Z-**24:** δ_C (100 MHz, $CDCl_3$): 36.1 (CH_2, S*C*H_2), 123.6, 128.7, 128.87, 130.6, 130.7, 131.3 (6 × CH, aromatic *C*H), 133.5, 134.5 [2 × C, 2 × aromatic *C* or 1 × aromatic *C* and *C*(2)S], 134.9 [1 x CH, *C*(3)H], 135.1, 139.5, 140.1, 140.6, 147.2 [5 × C, 5 × aromatic *C* or 4 × aromatic *C* and *C*(2)S], 191.7 (C, *C*O).

Characteristic signals due to *E*-**24:** δ_H (400 MHz, $CDCl_3$): 3.90 (2H, s, SC*H*$_2$), 6.94 [1H, s, C(3)*H*], 7.36 (2H, d, *J* 8.5, Ar*H*), 7.80 (2H, d, *J* 8.6, Ar*H*), 8.01 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 123.9, 128.83, 129.3, 130.4, 130.9 (5 × CH).

(*Z*)-1-(4-Chlorophenyl)-2-((4-methoxybenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-25



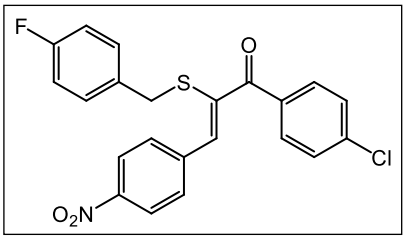
This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4r** and *E*-**4r** (*Z* : *E*, 9 : 1) (70 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (99 mg, 0.24 mmol), and $(CH_3CN)_2PdCl_2$ (2 mg, 10 μmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 2 h and after work-up, the crude product was obtained as a brown residue. ^{1}H NMR spectroscopy showed this product to contain *approx.* 51% β-chloroenone starting materials *Z*-**4r** and *E*-**4r**(*Z* : *E*, 5.4 : 1), 13% bi-aryl **37**[26], and 36% chalcone *Z*-**25**. Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the *chalcone Z*-**25** (8 mg, 9%) as a bright yellow oil which contained *approx*. 22% bi-aryl **37**[26] (δ_H, d, 7.79 ppm, *J* 8.9 and δ_H, d, 8.36 ppm, *J* 8.9); ν_{max}/cm^{-1} (neat) 3076, 2934, 2836, 1723, 1660 (C=O), 1592, 1512 (NO_2), 1341 (NO_2), 1250, 849; δ_H (400 MHz, $CDCl_3$): 3.72 (3H, s, OC*H*$_3$), 3.97 (2H, s, SC*H*$_2$), 6.66 (2H, d, *J* 8.7, Ar*H*), 6.86 [1H, s, C(3)*H*], 7.03 (2H, d, *J* 8.7, Ar*H*), 7.38 (2H, d, *J* 8.7, Ar*H*), 7.59 (2H, d, *J* 8.6, Ar*H*), 7.76 (2H, d, *J* 8.6, Ar*H*), 8.22 (2H, d, *J* 8.9, Ar*H*).

*^{1}H and ^{13}C NMR spectra of this sample were recorded after 65 months following storage at room temperature. The ^{1}H NMR spectrum showed isomerisation had occurred to give two chalcone isomers Z-***25** *and E-***25** *(Z : E, 5 : 1; 78%) with 22% bi-aryl* **37**[26] *still present.*

Z-**25**: δ_C (100 MHz, $CDCl_3$): 36.3 (CH_2, S*C*H_2), 55.25 (CH_3, O*C*H_3), 113.9, 123.6, 128.7, 130.6, 131.4 (5 × CH , aromatic *C*H), 133.9 [1 x CH, *C*(3)H], 134.6, 139.8 (2 × C, 2 × aromatic *C*), 140.3 [1 x C, *C*(2)S], 140.92, 140.97, 147.0, 159.0 (4 × C, aromatic *C*), 191.8 (C, *C*O).

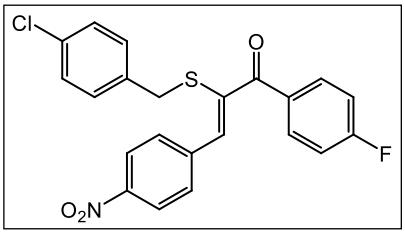
Characteristic signals due to *E*-**25**: δ_H (400 MHz, $CDCl_3$): 3.77 (3H, s, OC*H*$_3$), 3.93 (2H, s, SC*H*$_2$), 6.79 (2H, d, *J* 8.6, Ar*H*), 6.92 [1H, s, C(3)*H*], 7.17–7.29 (4H, m, Ar*H*), 7.34 (2H, d, *J* 8.6, Ar*H*), 8.00 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 37.2 (CH_2, S*C*H_2), 55.28 (CH_3, O*C*H_3), 123.9, 129.3 (2 × CH, aromatic *C*H), 129.6 [1 x CH, *C*(3)H], 130.3, 130.9 (2 × CH, aromatic *C*H).

(*Z*)-1-(4-Chlorophenyl)-2-((4-fluorobenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-26



This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4s** and *E*-**4s** (*Z* : *E*, 2.5 : 1) (108 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (148 mg, 0.3 mmol), and $(CH_3CN)_2PdCl_2$ (4 mg, 15 µmol, 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 5 h and after work-up, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain *approx*. 15% β-chloroenone starting materials *Z*-**4s** and *E*-**4s** (*Z* : *E*, 1.2 : 1), 75% chalcone *Z*-**26**, and 10% bi-aryl **37**[26]. Purification by column chromatography on silica gel using hexane–ethyl acetate (gradient elution 5–10% ethyl acetate) as eluent gave a yellow solid which was recrystallised from isopropyl alcohol to give the *chalcone Z*-**26** (23 mg, 18%) as a fine yellow powder, mp 96–98°C; ν_{max}/cm^{-1} (neat) 1659 (C=O), 1588, 1508, 1342, 1243, 1220, 1089, 751; δ_H (400 MHz, $CDCl_3$): 3.98 (2H, s, SC*H*$_2$), 6.85 (2H, t, *J* 8.7, Ar*H*), 6.91 [1H, s, C(3)*H*], 7.10 (2H, dd, *J* 8.6, J_{FH} 5.4, Ar*H*), 7.40 (2H, d, *J* 8.6, Ar*H*), 7.60 (2H, d, *J* 8.6, Ar*H*), 7.75 (2H, d, *J* 8.7, Ar*H*), 8.23 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 36.0 (CH_2, S*C*H_2), 115.5 (1 × CH, d, $^2J_{CF}$ 21.6, aromatic *C*H), 123.6, 128.8, 130.6 (3 × CH, aromatic *C*H), 131.0 (1 × CH, d, $^3J_{CF}$ 8.2, aromatic *C*H), 131.3 (1 × CH, aromatic *C*H), 132.3 (1 x C, d, $^4J_{CF}$ 3.2, aromatic *C*), 134.5 [1 x C, aromatic *C* or *C*(2)S], 134.7 [1 x CH, *C*(3)H], 139.7, 140.1, 140.7, 147.1 [4 × C, 4 × aromatic *C* or 3 × aromatic *C* and *C*(2)S], 162.1 (C, d, $^1J_{CF}$ 247.1, aromatic *C*), 191.8 (C, *C*O); HRMS (ES−): Exact mass calculated for $C_{22}H_{14}NO_3FS^{35}Cl[M-H^+]$ 426.0367. Found 426.0364; m/z (ES−) 426.1 [($C_{22}H_{15}NO_3FS^{35}Cl$)−$H^+$], 10%.

(*Z*)-2-((4-Chlorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-27

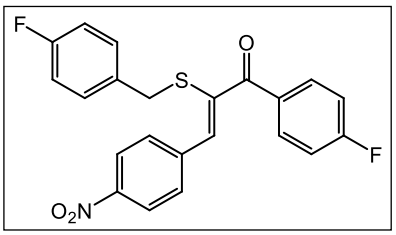


This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4x** and *E*-**4x** (*Z* : *E*, 2.2 : 1) (86 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (123 mg, 0.3 mmol), and $(CH_3CN)_2PdCl_2$ (3 mg, 12 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred under reflux for 5 h and after work-up, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain *approx.* 24% β-chloroenones starting material *Z*-**4x** and *E*-**4x** (*Z* : *E*, 1 **:** 3.7), 11% bi-aryl **37**[26], and 65% chalcones *Z*-**27** and *E*-**27** (*Z* : *E*, 8.8 : 1). The crude product was recrystallised from isopropyl alcohol to give the pure *Z chalcone Z*-**27** (21 mg, 20%) as a yellow powder; mp 117–120°C.

Z-**27:** ν_{max}/cm^{-1} (neat) 1655 (C=O), 1591, 1508, 1336, 1234, 599, 497; δ_H (400 MHz, $CDCl_3$): 3.97 (2H, s, SC*H*$_2$), 6.90 [1H, s, C(3)*H*], 7.04–7.14 (6H, m, Ar*H*), 7.68 (2H, dd, *J* 8.6, J_{FH} 5.4, Ar*H*), 7.75 (2H, d, *J* 8.8, Ar*H*), 8.24 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 36.1 (CH_2, S*C*H$_2$), 115.7 (1 × CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 123.6, 128.7, 130.6, 130.7 (4 × CH, aromatic *C*H), 132.4 (1 x C, d, $^4J_{CF}$ 3.0, aromatic *C*), 132.6 (1 × CH, d, $^3J_{CF}$ 9.5, aromatic *C*H), 133.5 [1 x C, aromatic *C* or *C*(2)S], 134.3 [1 x CH, *C*(3)H], 135.1, 139.6, 140.7, 147.1 [4 × C, 4 × aromatic *C* or 3 × aromatic *C* and *C*(2)S], 165.9 (1 x C, d, $^1J_{CF}$ 256.6, aromatic *C*), 191.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{22}H_{16}NO_3FS^{35}Cl[M+H^+]$ 428.0523. Found 428.0531.

Characteristic signals due to *E*-**27:** δ_H (400 MHz, $CDCl_3$): 3.92 (2H, s, SC*H*$_2$), 6.94 [1H, s, C(3)*H*], 7.78 (2H, d, *J* 8.9, Ar*H*), 7.89 (2H, dd, *J* 8.9, J_{FH} 5.4, Ar*H*), 8.00 (2H, d, *J* 8.8, Ar*H*), 8.36 (2H, d, *J* 8.9, Ar*H*).

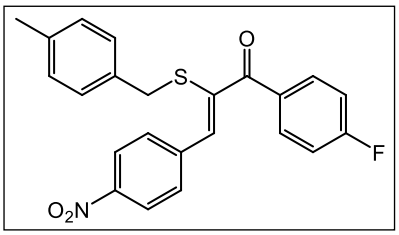
(*Z*)-2-((4-Fluorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-28



This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4z** and *E*-**4z** (*Z* : *E*, 3 : 1) (111 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (152 mg, 0.3 mmol), and $(CH_3CN)_2PdCl_2$ (4 mg, 15 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 6 h and after work-up, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed this product to contain *approx.* 10% *E* β-chloroenone starting material *E*-**4z**, 10% bi-aryl **37**[26], and

80% chalcone *Z*-**28**. Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the desired product, which was recrystallised from isopropyl alcohol to give the *chalcone Z*-**28** (29 mg, 24%) as a bright yellow powder; mp 90–91°C; ν_{max}/cm^{-1} (neat) 1658 (C=O), 1592, 1504, 1335, 1234, 822, 685; δ_H (400 MHz, $CDCl_3$): 3.97 (2H, s, SCH_2), 6.84 (2H, t, *J* 8.7, Ar*H*), 6.89 [1H, s, C(3)*H*], 7.08–7.13 (4H, m, Ar*H*), 7.70–7.77 (4H, m, Ar*H*), 8.23 (2H, d, *J* 8.9, Ar*H*); δ_C (100 MHz, $CDCl_3$): 36.0 (CH_2, SCH_2), 115.5 (1 × CH, d, $^2J_{CF}$ 21.6, aromatic *C*H), 115.7 (1 × CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 123.6, 130.6 (2 × CH, aromatic *C*H), 131.0 (1 × CH, d, $^3J_{CF}$ 8.2, aromatic *C*H), 132.3 (1 x C, d, $^4J_{CF}$ 3.3, aromatic *C*), 132.5 (1 x C, d, $^4J_{CF}$ 2.9, aromatic *C*), 132.6 (1 × CH, d, $^3J_{CF}$ 9.5, aromatic *C*H), 134.0 [1 x CH, *C*(3)H], 139.8 [1 x C, *C*(2)S], 140.8, 147.1 (2 × C, 2 × aromatic *C*), 162.1 (1 x C, d, $^1J_{CF}$ 247.2, aromatic *C*), 165.9 (1 x C, d, $^1J_{CF}$ 256.4, aromatic *C*), 191.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{22}H_{16}NO_3F_2S$ [M+H$^+$] 412.0819. Found 412.0837.

(*Z*)-1-(4-Fluorophenyl)-2-((4-methylbenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one *Z*-29



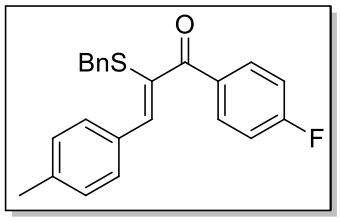
This was prepared following the procedure described above for **14** using the β-chloroenones *Z*-**4aa** and *E*-**4aa** (*Z* : *E*, 14 : 1) (162 mg, 0.5 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (249 mg, 0.6 mmol), and $(CH_3CN)_2PdCl_2$ (6 mg, 25 µmol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 24 h and after work-up, the crude product was obtained as a brown residue. ^{1}H NMR spectroscopy showed this product to contain *approx.* 6% β-chloroenone starting material *E*-**4aa**, 8% bi-aryl **37**[26], and 86% chalcone *Z*-**29**. Purification by column chromatography on silica gel using hexane–dichloromethane (40:60) as eluent gave the *chalcone Z*-**29** (105 mg, 51%) as a bright yellow solid; mp 95–99°C.

Z-**29**: Found C, 67.51; H, 4.94; N, 3.57. $C_{23}H_{18}NO_3SF$ requires C, 67.80; H, 4.45; N, 3.44; ν_{max}/cm^{-1} (neat) 3027, 2918, 1658 (C=O), 1590, 1502 (NO_2), 1332 (NO_2), 1249, 1234, 1078, 686; δ_H (400 MHz, $CDCl_3$): 2.25 (3H, s, ArCH_3), 3.96 (2H, s, SCH_2), 6.86 [1H, s, C(3)*H*], 6.95 (2H, d, *J* 7.9, Ar*H*), 7.02 (2H, d, *J* 8.0, Ar*H*), 7.08 (2H, t, *J* 8.6, Ar*H*), 7.71 (2H, dd, *J* 8.9, J_{FH} 5.4, Ar*H*), 7.75 (2H, d, *J* 8.7, Ar*H*), 8.21 (2H, d, *J* 8.9, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.0 (CH_3, ArCH_3), 36.6 (CH_2, SCH_2), 115.6 (1 × CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 123.6, 129.2, 129.3, 130.5 (4 × CH, aromatic *C*H), 132.6 (1 x C, d, $^4J_{CF}$ 3.0, aromatic *C*), 132.7 (1 × CH, d, $^3J_{CF}$ 9.4, aromatic *C*H), 133.3 [1 x C, aromatic *C* or *C*(2)S], 133.4 [1 x CH, *C*(3)H], 137.4, 140.5, 141.0, 147.0 [4 × C, 4 ×

aromatic *C* or 3 × aromatic *C* and *C*(2)S], 165.8 (1 x C, d, $^{1}J_{CF}$ 256.1, aromatic *C*), 191.5 (C, *C*O); HRMS (ES−): Exact mass calculated for $C_{23}H_{17}NO_3FS[M-H^+]$ 406.0913. Found 406.0924; m/z (ES−) 406.2 $[(C_{23}H_{18}NO_3SF)-H^+]$, 30%.

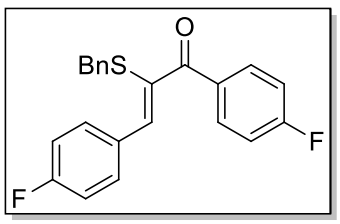
Characteristic signals due to *E*-**15aa:** δ_H (400 MHz, $CDCl_3$): 2.31 (3H, s, ArCH_3), 3.95 (2H, s, SCH_2), 6.91 [1H, s, C(3)*H*], 7.18 (2H, d, *J* 8.0, Ar*H*), 7.90 (2H, dd, *J* 8.8, J_{FH} 5.4, Ar*H*), 7.99 (2H, d, *J* 8.9, Ar*H*).

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(*p*-tolyl)prop-2-en-1-one 30



This was prepared following the procedure described for **14** using the β-chloroenones ***Z*-4v** and ***E*-4v** (ratio 2.2:1) (150 mg, 0.5 mmol), 4-(tributylstannyl)toluene **36b**[23] (150 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was recovered as an orange oil and by ^{1}H NMR spectroscopy, complete conversion of **4v** to the chalcone was evident. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the pure *Z chalcone* ***Z*-30** (166 mg, 92%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 2921 (CH), 1655 (CO), 1597 (aromatic), 1239; δ_H (400 MHz, $CDCl_3$) 2.38 (3H, s, ArCH_3), 4.00 (2H, s, SCH_2), 6.97 [1H, s, C(3)*H*], 7.03 (2H, t, *J* 8.7, Ar*H*), 7.14 (5H, s, Ar*H*), 7.20 (2H, d, *J* 8.0 Ar*H*), 7.55-7.59 (4H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 21.5 (CH_3, Ar*C*H$_3$), 36.7 (CH_2, S*C*H$_2$), 115.3 (CH, d, $^{2}J_{CF}$ 21.8, aromatic *C*H), 127.2, 128.5, 129.1, 129.4, 130.5 (5 x CH, aromatic *C*H), 131.9 (C, aromatic *C*), 132.5 (CH, d, $^{3}J_{CF}$ 9.1, aromatic *C*H), 133.8 (C, d, $^{4}J_{CF}$ 3.0, aromatic *C*), 134.6, 137.4, 139.6 [3 x C, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 140.4 [CH, *C*(3)H], 165.4 (C, d, $^{1}J_{CF}$ 252.8, aromatic *C*), 192.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{20}SOF[M+H^+]$ 363.1219. Found 363.1222; m/z (ES+) 363.3 $[(C_{23}H_{19}SOF)+H^+]$, 10%.

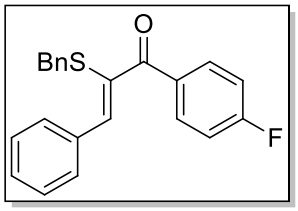
(*Z*)-2-(Benzylthio)-1,3-bis(4-fluorophenyl)prop-2-en-1-one 31



This was prepared following the procedure described for **14**using the β-chloroenones ***Z*-4v** and ***E*-4v** (ratio 2.2:1) (150 mg, 0.5 mmol), tributyl(4-fluorophenyl)stannane **36c**[24] (227 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was isolated as a yellow oil. ^{1}H NMR analysis showed the crude product to contain 22% β-chloroenone starting material as a mixture of *Z* and *E* isomers ***Z*-4v** and ***E*-4v**

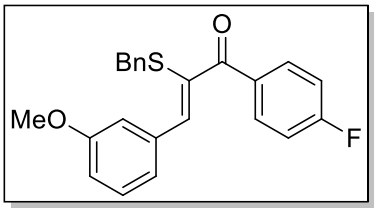
in a ratio of 1:1.2 and 78% *Z* chalcone *Z*-**31**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z chalcone* ***Z*-31** (137 mg, 75%) as a yellow oil; ν_{max}/cm^{-1} (film) 3032 (CH), 1657 (CO), 1598 (aromatic), 1505, 1236, 846; δ_H (400 MHz, $CDCl_3$) 4.00 (2H, s, SCH_2), 6.94 [1H, s, C(3)*H*], 7.02-7.09 (4H, m, Ar*H*), 7.15 (5H, s, Ar*H*), 7.53-7.72 (4H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.7 (CH_2, SCH_2), 115.4 (CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 115.5 (CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 127.3, 128.5, 129.4 (3 x CH, aromatic *C*H), 130.8 (C, d, $^4J_{CF}$ 3.3, aromatic *C*), 132.4 (CH, d, $^3J_{CF}$ 8.4, aromatic *C*H), 132.5 (CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 133.5 (C, d, $^4J_{CF}$ 2.9, aromatic *C*), 135.2, 137.2 [2 x C, aromatic *C* and *C*(2)S], 138.6 [CH, *C*(3)H], 162.8 (C, d, $^1J_{CF}$ 254.8, aromatic *C*), 165.5 (C, d, $^1J_{CF}$ 251.3, aromatic *C*), 192.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{22}H_{17}SOF_2$[M+H^+] 367.0968. Found 367.0960; m/z (ES+) 367.3 [($C_{22}H_{16}SOF_2$)+H^+], 100%.

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one 32



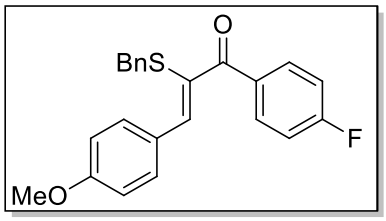
The title compound was prepared following the procedure described above for **14** using the β-chloroenones ***Z*-4v** and ***E*-4v** (ratio 2.2:1) (150 mg, 0.5 mmol) and phenyltributylstannane **36a** (220 mg, 0.6 mmol) and anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ^{1}H NMR analysis showed the crude product to contain 63% β-chloroenone starting material as a mixture of *Z* and *E* isomers ***Z*-4e** and ***E*-4e** in a ratio of 2.5:1 and37% *Z* chalcone ***Z*-32**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z chalcone* ***Z*-32i** (61 mg, 35%) as a yellow oil; this fraction also contained *Z* β-chloroenone starting material ***Z*-4v** (9% by integration of the ^{1}H NMR spectrum); ν_{max}/cm^{-1} (film) 2932 (CH), 1657 (CO), 1597 (aromatic), 1240; δ_H (400 MHz, $CDCl_3$) 3.99 (2H, s, SCH_2), 6.97 [1H, s, C(3)*H*], 7.04 (2H, t, *J* 8.7, Ar*H*), 7.15 (5H, s, Ar*H*), 7.31-7.41 (3H, m, Ar*H*), 7.57-7.64 (2H, m, Ar*H*), 7.66 (2H, d, *J* 7.5, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.7 (CH_2, SCH_2), 115.4 (CH, $^2J_{CF}$ 21.9, aromatic *C*H), 127.3, 128.4, 128.5, 129.1, 129.4, 130.3 (5 x CH, aromatic *C*H), 132.5 (CH, d, $^3J_{CF}$ 9.0, aromatic *C*H), 133.5 (C, d, $^4J_{CF}$ 3.1, aromatic *C*), 134.7, 135.6, 137.3 [3 x C, 2 x aromatic *C* and *C*(2)S], 139.4 [CH, *C*(3)H], 165.4 (C, d, $^1J_{CF}$ 254.6, aromatic *C*), 192.5 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{22}H_{18}SOF$[M+H^+] 349.1062. Found 349.1050; m/z (ES+) 365.3 (8%).

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(3-methoxyphenyl)prop-2-en-1-one 34



This was prepared following the procedure described for **14** using the β-chloroenones ***Z*-4v** and ***E*-4v** (ratio 2.2:1) (150 mg, 0.5 mmol), tributyl(3-methoxyphenyl)stannane **36e**[23] (238 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* **34** was obtained as a yellow oil. ^{1}H NMR spectroscopy showed the crude product to contain 30% β-chloroenone starting material as a mixture of *Z* and *E* isomers **Z-4v** and ***E*-4v** in a ratio of 1:2 and 70% *Z* chalcone *Z*-**34**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (97:3) as eluent to give the pure *Z chalcone* ***Z*-34** (123 mg, 65%) as a yellow oil; ν_{max}/cm^{-1} (film) 2921 (CH), 1655 (CO), 1597 (aromatic), 1237; δ_H (400 MHz, $CDCl_3$) 3.82 (3H, s, OC*H*$_3$), 4.00 (2H, s, SC*H*$_2$), 6.90 (1H, d, *J* 9.0, Ar*H*), 6.93 [1H, s, C(3)*H*], 7.04 (2H, t, *J* 8.7, Ar*H*), 7.14 (5H, s, Ar*H*), 7.18-7.32 (3H, m, Ar*H*), 7.56-7.62 (2H, m, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.6 (CH_2, S*C*H$_2$), 55.4 (CH_3, O*C*H$_3$), 115.1 (CH, aromatic *C*H), 115.4 (CH, d, $^2J_{CF}$ 21.8, aromatic *C*H), 123.1, 127.3, 128.5, 129.35, 129.41 (5 x CH, aromatic *C*H), 132.6 (CH, d, $^3J_{CF}$ 9.3, aromatic *C*H), 133.5 (C, d, $^4J_{CF}$ 2.8, aromatic *C*), 135.9, 137.3 [2 x C, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 139.3 [CH, *C*(3)H], 159.4 (C, aromatic *C*OCH$_3$), 165.5 (C, d, $^1J_{CF}$ 254.7, aromatic *C*), 192.4 (C, *C*O), signal for 1 x aromatic C and 1 x aromatic CH (possibly overlapping with aromatic CH signal at δ_C 128.5 ppm) not seen in ^{13}C NMR spectrum; HRMS (ES+): Exact mass calculated for $C_{23}H_{20}SO_2F$[M+H$^+$] 379.1168. Found 379.1170; m/z (ES+) 379.3 [($C_{23}H_{19}SO_2F$)+H$^+$], 100%.

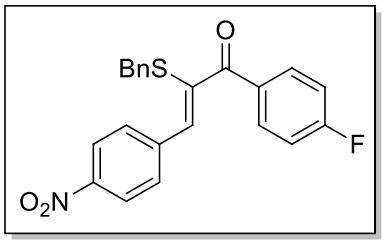
(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one 33



This was prepared following the procedure described for **14**using the β-chloroenones ***Z*-4v** and ***E*-4v** (ratio 2.2:1) (150 mg, 0.5 mmol), tributyl(4-methoxyphenyl)stannane **36d**[23] (238 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ^{1}H NMR spectroscopy showed the crude product to contain 12% β-chloroenone starting material as the *E* isomer ***E*-4v** only and 88% *Z* chalcone ***Z*-33**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (97:3) as eluent to give the *Z chalcone* ***Z*-33**(146 mg, 77%) as a yellow oil; ν_{max}/cm^{-1} (film) 2932 (CH), 1652 (CO), 1598 (aromatic), 1508, 1253; δ_H (400 MHz, $CDCl_3$) 3.84 (3H, s, OC*H*$_3$), 4.01 (2H, s, SC*H*$_2$), 6.91 (2H, d, *J* 8.9, Ar*H*), 6.99 [1H, s, C(3)*H*], 7.03

(2H, t, *J* 8.7, Ar*H*), 7.15 (5H, s, Ar*H*), 7.50-7.59 (2H, m, Ar*H*), 7.70 (2H, d, *J* 8.7, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.7 (CH_2, S*C*H_2), 55.4 (CH_3, O*C*H_3), 113.8 (CH, aromatic *C*H), 115.2 (CH, d, $^2J_{CF}$ 21.9, aromatic *C*H), 127.2, 128.4, 129.4 (3 x CH, aromatic *C*H), 132.4 (CH, d, $^3J_{CF}$ 8.4, aromatic *C*H), 132.9 [C, aromatic *C* or *C*(2)S], 134.0 (C, d, $^4J_{CF}$ 2.8, aromatic *C*), 137.5 [C, aromatic *C* or *C*(2)S], 141.0 [CH, *C*(3)H], 160.4 (C, aromatic *C*OCH_3), 165.3 (C, d, $^1J_{CF}$ 253.9, aromatic *C*), 192.8 (C, *C*O), signal for 1 x aromatic CH (possibly overlapping with aromatic CH signal at δ_C 132.4 ppm) could not be seen in the ^{13}C NMR spectrum; HRMS (ES+): Exact mass calculated for $C_{23}H_{20}SO_2F[M+H^+]$ 379.1168. Found 379.1160; m/z (ES+) 379.3 [$(C_{23}H_{19}SO_2F)+H^+$], 32%.

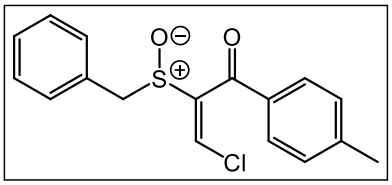
(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 35



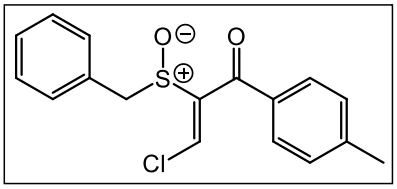
This was prepared following the procedure described for **14**from the β-chloroenones ***Z*-4v** and ***E*-4v** (ratio 2.2:1) (150 mg, 0.5 mmol), 4-(tri-*n*-butylstannyl)nitrobenzene **36f**[25] (240 mg, 0.6 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in acetonitrile (5 mL). The crude *chalcone* was obtained as an orange oil. ^{1}H NMR spectroscopy showed the crude product to contain 14% β-chloroenone starting material as a mixture of *Z* and *E* isomers ***Z*-4v** and ***E*-4v** in a ratio of 1:4 and 80% *Z* chalcone ***Z*-35**. Signals tentatively assigned as the C(3)H proton and the SCH_2 protons of the *E* chalcone ***E*-35** (6%) were observed as a singlet at δ_H 6.66 ppm and a singlet at δ_H 3.88 ppm. This was purified by column chromatography on silica gel using hexane-ethyl acetate (95:5) as eluent to give the *Z chalcone* ***Z*-35** (154 mg, 78%) as a bright yellow oil (contains a minor amount of the *E* chalcone, <5%); ν_{max}/cm^{-1} (film) 3064 (CH), 1659 (CO), 1596 (aromatic), 1517 (NO_2), 1343 (NO_2), 1239; δ_H (400 MHz, $CDCl_3$) 4.00 (2H, s, S*C*H_2), 6.88 [1H, s, C(3)*H*], 7.08 (2H, t, *J* 8.6, Ar*H*), 7.11-7.19 (5H, m, Ar*H*), 7.67-7.73 (2H, m, Ar*H*), 7.75 (2H, d, *J* 8.6, Ar*H*), 8.82 (2H, d, *J* 8.8, Ar*H*); δ_C (75.5 MHz, $CDCl_3$) 36.9 (CH_2, S*C*H_2), 115.7 (CH, d, $^2J_{CF}$ 22.0, aromatic *C*H), 123.6, 127.6, 128.6, 129.3, 130.6 (5 x CH, aromatic *C*H), 132.7 (CH, d, $^3J_{CF}$ 9.5, aromatic *C*H), 133.9 [CH, *C*(3)H], 136.6, 140.3, 141.0 [3 x C, 2 x aromatic *C* and *C*(2)S], 147.1 (C, aromatic *C*NO_2), 165.9 (C, d, $^1J_{CF}$ 256.2, aromatic *C*H), 191.6 (C, *C*O), signal for 1 x aromatic C not seen in ^{13}C NMR spectrum; HRMS (ES+): Exact mass calculated for $C_{22}H_{17}NSO_3F[M+H^+]$ 394.0913. Found 394.0919; m/z (ES+) 317.3 (100%); m/z (ES-) 394.2 (8%).

1.7 Oxidation of α-Sulfenyl-β-chloroenones

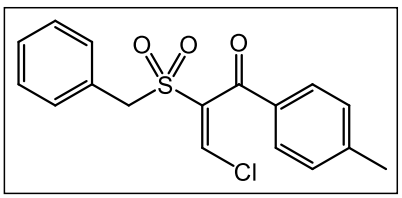
(*E*)-2-(Benzylsulfinyl)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one *E*-38h



A solution of Oxone® (824 mg, 1.3 mmol) in water (5 mL) was added dropwise to a stirring solution of the sulfide *Z*-**4h** (203 mg, 0.6 mmol) in acetone (10 mL) at room temperature. A white precipitate formed immediately. After stirring for 2 h, water (15 mL) was added and the aqueous solution was extracted with dichloromethane (3 × 15 mL). The organic layers were washed with water (2 × 10 mL) and brine (10 mL), dried, and concentrated under reduced pressure to give a yellow solid. ^{1}H NMR spectroscopy showed this product to contain 90% of the *E* sulfoxide *E*-**38h** with *approx*. 6% of the *Z* sulfoxide *Z*-**38h** and 4% of the *E* sulfone *E*-**S62**. The product was recrystallised from methanol to give the *sulfoxide E*-**38h** (112 mg, 53%) as an off-white solid (mp 86–88°C), which contained *approx*. 3% *E* sulfone *E*-**S62**; ν_{max}/cm^{-1} (neat) 3048, 1654 (C=O), 1599, 1284, 1225, 1175, 1061 (S–O), 704; δ_H (400 MHz, $CDCl_3$): 2.45 (3H, s, ArC*H*$_3$), 4.14 (1H, A of AB system, J_{AB} 13.0, one of SC*H*$_2$), 4.36 (1H, B of AB system, J_{AB} 13.0, one of SC*H*$_2$), 6.57 (1H, s, C*H*Cl), 7.27–7.38 (7H, m, Ar*H*), 7.85 (2H, d, *J* 8.1, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.9 (CH_3, Ar*C*H$_3$), 59.8 (CH_2, S*C*H$_2$), 127.9 [CH, aromatic *C*H or *C*(3)H], 128.1 (C, aromatic *C*), 128.4 (1 × CH signal, 2 × CH, aromatic *C*H), 128.6 [CH, aromatic *C*H or *C*(3)H], 129.8, 130.0, 131.1 (3 × CH signals, 6 × CH, aromatic *C*H), 133.0, 142.8, 146.2 [3 × C, 2 × aromatic *C* and *C*(2)S], 189.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{16}O_2S^{35}Cl$[M+H$^+$] 319.0560. Found 319.0550; m/z (ES+) 319.2 [($C_{17}H_{15}O_2S^{35}Cl$)+H$^+$], 11%.

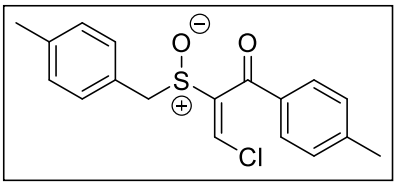


Characteristic signals tentatively assigned as *Z*-**38h**: δ_H (400 MHz, $CDCl_3$) 2.43 (3H, s, ArC*H*$_3$), 4.61 (1H, A of AB system, J_{AB} 12.4, one of SC*H*$_2$), 4.72 (1H, B of AB system, J_{AB} 12.3, one of SC*H*$_2$), 6.88 (1H, s, C*H*Cl).



Characteristic signals due to *E*-**S62**: δ_H (400 MHz, $CDCl_3$) 4.56 (2H, s, SC*H*$_2$), 7.00 (1H, s, C*H*Cl).

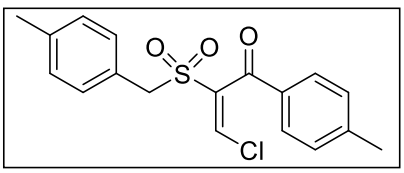
3-Chloro-2-((4-methylbenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one 38m



This was prepared following the procedure described above for **38h** using the sulfide ***Z*-4h** (0.25 g, 0.8 mmol, 1 eq) in acetone (10 mL) and Oxone® (0.51 g, 1.7 mmol, 2.1 eq) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h and following work-up, the crude sulfoxide was obtained as a yellow oil. The ^{1}H NMR spectrum of the crude product showed approximately 98.5% conversion of the starting material. There was 89% conversion to the desired products with the presence of two isomers *Z*-**38m** and *E*-**38m** (Z:E 1 : 8.8) and 9% conversion to the sulfone product **S63** (s, δ 4.52 ppm). The crude sulfoxide was recrystallised from methanol to give the *E*-sulfoxide **38m** (0.10 g, 36.9%) an off-white solid, mp 129–130°C.

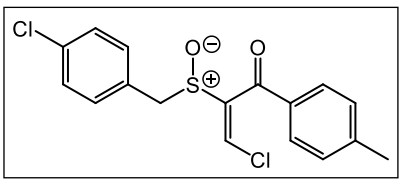
***E*-38m** (less polar): υ_{max}/cm^{-1} (neat) 1651 cm^{-1} (C=O), 1053.25 cm^{-1} (S-O); δ_H (400 MHz, $CDCl_3$): 2.35 [3H, s, aromatic C*H*$_3$], 2.45 [3H, s, aromatic C*H*$_3$], 4.10 [1H, A of AB system, J_{AB} 13.4, one of SC*H*$_2$], 4.32 [1H, B of AB system, J_{AB} 13.0, one of SC*H*$_2$], 6.60 [1H, s, C*H*Cl], 7.13–7.22 [4H, m, aromatic *H*], 7.33 [2H, d, *J* 8.0, aromatic *H*], 7.86 [2H, d, *J* 8.2, aromatic *H*]; δ_c (75 MHz, $CDCl_3$): 21.3 [CH_3, aromatic *C*H$_3$], 21.9 [CH_3, aromatic *C*H$_3$], 59.6 [CH_2, S*C*H$_2$], 125.0 [1 x CH signal, *C*(3)H], 127.8 [1 x C signal, *C*(2)S], 129.2, 129.8, 130.0, 130.9 [4 x CH signals, 4 x aromatic *C*H], 133.0, 138.6, 143.0, 146.2 [4 x C signals, 4 x aromatic *C*], 189.7 [1 x C signal, *C*O]; m/z (ES+): 333.2 [($C_{18}H_{17}{}^{35}ClO_2S$)+H$^+$], 20%. ^{35}Cl/^{37}Cl pattern visible at 333.2 and 335.2in a 3:1 ratio. HRMS (ES+): Exact mass calculated for $C_{18}H_{17}{}^{35}ClO_2S$ [M+H$^+$], 333.071055; Found 333.07101.

Characteristic signals due to *Z*-**38m** : δ_H (400 MHz, $CDCl_3$): 4.58 [1H, A of AB system, J_{AB} 12.3, one of SC*H*$_2$], 4.67 [1H, B of AB system, J_{AB} 12.3, one of SC*H*$_2$].



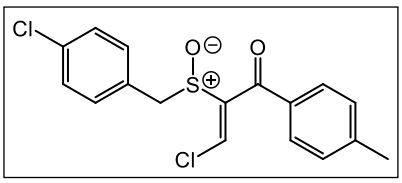
Characteristic signals due to **(*E*)-3-chloro-2-((4-methylbenzyl)sulfonyl)-1-(p-tolyl)prop-2-en-1-one S63**: δ_H (400 MHz, $CDCl_3$) 4.52 (2H, s, SC*H*$_2$).

(*E*)-3-Chloro-2-((4-chlorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-38t

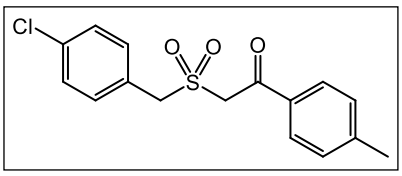


This was prepared following the procedure described above for **38h** using the sulfide *Z*-**4t** (0.26 g, 0.7 mmol) in acetone (10 mL) and Oxone® (0.94 g, 1.5 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h

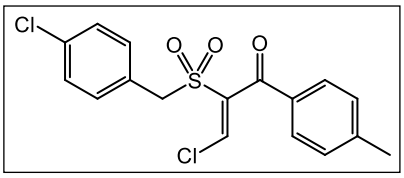
and following the work-up, the crude product was obtained as an off-white semisolid. ^{1}H NMR spectroscopy showed this product to contain the desired *sulfoxide* as a mixture of *Z* and *E* isomers, *Z*-**38t** and *E*-**38t**, in a ratio of 2.8 : 1. A small quantity of the retro-Claisen sulfone impurity **39a** (<2%) as well as peaks which could correspond to the *Z* and *E* sulfone products *Z*-**S64** and *E*-**S64** (9%) (*Z* : *E,* 1.8 : 1) were also observed. A subsequent ^{1}H NMR spectrum, obtained prior to chromatography, showed that isomerisation to the *E* sulfoxide *E*-**38t** had occurred, after storage at room temperature over a 6 day period, with only trace quantities of the *Z* sulfoxide *Z*-**38t** visible. Purification by column chromatography on silica gel using hexane–ethyl acetate (70 : 30) as eluent gave the *sulfoxide E*-**38t** (205 mg, 76%) as a colourless viscous gum, which contained 3% retro-Claisen sulfone impurity **39a**. No trace of the *Z* sulfoxide *Z*-**38t** was observed after column chromatography; ν_{max}/cm^{-1} (neat) 3051, 1651 (C=O), 1602, 1490, 1227, 1176, 1061 (S–O), 834, 501, 470; δ_H (400 MHz, $CDCl_3$): 2.44 (3H, s, ArC*H*$_3$), 4.13 (1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$), 4.31 (1H, B of AB system, J_{AB} 13.1, one of SC*H*$_2$), 6.55 (1H, s, C*H*Cl), 7.23 (2H, d, *J* 8.5, Ar*H*), 7.30–7.36 (4H, m, Ar*H*), 7.85 (2H, d, *J* 8.3, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.9 (CH_3, Ar*C*H$_3$), 58.6 (CH_2, S*C*H$_2$), 126.3 [C, aromatic *C* or C(2)S], 128.1 [CH, *C*(3)H], 128.6, 129.8, 130.0, 132.4 (4 × CH signals, 8 × CH, aromatic *C*H), 132.8, 134.8, 142.3, 146.4 [4 × C, 4 × aromatic *C* or 3 × aromatic *C* and *C*(2)S], 189.6 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{15}O_2S^{35}Cl_2$[M+H$^+$] 353.0170. Found 353.0168; m/z (ES+) 353.1 [($C_{17}H_{14}O_2S^{35}Cl_2$)+H$^+$], 10%.



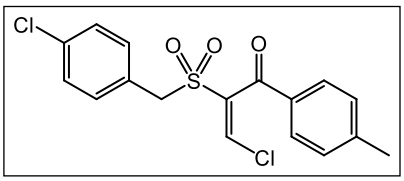
Characteristic signals tentatively assigned as *Z*-**38t**: δ_H (400 MHz, $CDCl_3$) 2.42 (3H, s, ArC*H*$_3$), 4.59 (1H, A of AB system, J_{AB} 12.4, one of SC*H*$_2$), 4.66 (1H, B of AB system, J_{AB} 12.3, one of SC*H*$_2$), 6.90 (1H, s, C*H*Cl), 7.80 (2H, d, *J* 8.2, Ar*H*).



Characteristic signals tentatively assigned as **39a**: δ_H (400 MHz, $CDCl_3$) 2.43 (3H, s, ArC*H*$_3$), 4.37 (2H, s, SC*H*$_2$), 4.51 (2H, s, SC*H*$_2$), 7.48 (2H, d, *J* 8.5, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 56.7, 58.9 (2 × CH_2, S*C*H$_2$), 129.3, 129.7 (CH, aromatic *C*H), 189.0 (C, *C*O).

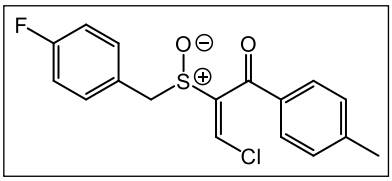


Characteristic signals tentatively assigned as *Z*-**S64**: δ_H (400 MHz, $CDCl_3$) 4.52 (2H, s, SCH_2), 7.11 (1H, s, C*H*Cl).

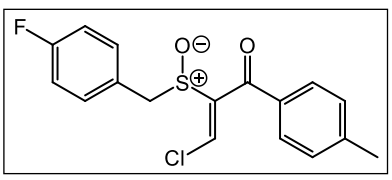


Characteristic signals tentatively assigned as *E*-**S64**: δ_H (400 MHz, $CDCl_3$) 4.53 (2H, s, SCH_2), 7.07 (1H, s, C*H*Cl).

(*E*)-3-Chloro-2-((4-fluorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-38aa



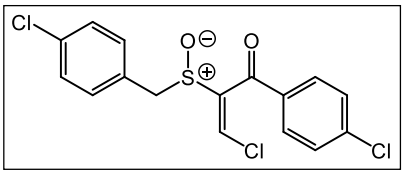
This was prepared following the procedure described above for **38h** using the sulfide *Z*-**4aa** (146 mg, 0.4 mmol) in acetone (10 mL) and Oxone® (559 mg, 0.9 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h and following the work-up, the crude product was obtained as a white solid. ^{1}H NMR spectroscopy showed this product to contain the desired *sulfoxide* as a mixture of *Z* and *E* isomers, *Z*-**38aa** and *E*-**38aa**, in a ratio of 1 : 1.03. Purification by column chromatography on silica gel using hexane–ethyl acetate (70 : 30) as eluent gave the *sulfoxide* *E*-**38aa** (117 mg, 77%) as a colourless viscous gum. A more polar fraction contained a mixture of *E* and *Z* isomers (8 mg, 5%) in a ratio of 1 : 1.05; ν_{max}/cm^{-1} (neat) 3048, 2921, 1651 (C=O), 1602, 1508, 1316, 1295, 1223, 1177, 1060 (S–O), 834; δ_H (400 MHz, $CDCl_3$): 2.45 (3H, s, ArCH_3), 4.14 (1H, A of AB system, J_{AB} 13.2, one of SCH_2), 4.32 (1H, B of AB system, J_{AB} 13.2, one of SCH_2), 6.53 (1H, s, C*H*Cl), 7.05 (2H, overlapping dd appears as t, *J* 8.6, Ar*H*), 7.20–7.40 (4H, m, Ar*H*), 7.85 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.9 (CH_3, Ar*C*H_3), 58.6 (CH_2, S*C*H_2), 115.4 (1 × CH signal, 2 × CH, d, $^2J_{CF}$ 21.6, aromatic *C*H), 123.6 (C, d, $^4J_{CF}$ 3.2, aromatic *C*), 128.0 [CH, *C*(3)H], 129.8, 130.0 (2 × CH signals, 4 × CH, aromatic *C*H), 132.8 (C, aromatic *C*), 132.9 (1 × CH signal, 2 × CH, d, $^3J_{CF}$ 8.4, aromatic *C*H), 142.3 [C, *C*(2)S], 146.4 (C, aromatic *C*), 163.0 (C, d, $^1J_{CF}$ 248.0, aromatic *C*), 189.7 (C, *C*O).



Characteristic signals tentatively assigned as *Z*-**38aa**: δ_H (400 MHz, $CDCl_3$) 2.43 (3H, s, ArCH_3), 4.59 (1H, A of AB system, J_{AB} 12.4, one of SCH_2), 4.68 (1H, B of AB system, J_{AB} 12.4, one of

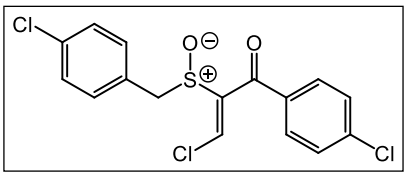
SC*H*$_2$), 6.89 (1H, s, C*H*Cl), 7.40 (2H, dd, *J* 8.5, J_{FH} 5.3, Ar*H*), 7.82 (2H, d, *J* 8.2, Ar*H*).

(*E*)-3-Chloro-2-((4-chlorobenzyl)sulfinyl)-1-(4-chlorophenyl)prop-2-en-1-one *E*-38q

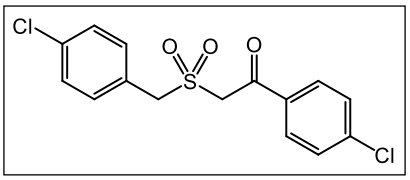


This was prepared following the procedure described above for **38h** using the sulfide *Z*-**4q** (198 mg, 0.5 mmol) in acetone (10 mL) and Oxone® (682 mg, 1.1 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h and following the work-up, the crude product was obtained as an off-white solid. ^{1}H NMR spectroscopy showed this product to contain the desired *sulfoxide* as a mixture of *Z* and *E* isomers, *Z*-**38q** and *E*-**38q**, in a ratio of 2.4 : 1. A small quantity of starting material *Z*-**4q** (4%) and retro-Claisen sulfone impurity **39b** (6%) could also be seen. Purification by column chromatography on silica gel using dichloromethane (100%) as eluent gave the *sulfoxide E*-**38q** (80 mg, 39%) as a colourless viscous gum. The retro-Claisen sulfone impurity **39b** (7 mg, 4%) was isolated in a less polar fraction.

E-**38q**: ν_{max}/cm^{-1} (neat) 3054, 1659 (C=O), 1586, 1490, 1222, 1092, 1063 (S–O), 1012, 841; δ_H (400 MHz, $CDCl_3$): 4.16 (1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$), 4.34 (1H, B of AB system, J_{AB} 13.1, one of SC*H*$_2$), 6.58 (1H, s, C*H*Cl), 7.22 (2H, d, *J* 8.4, Ar*H*), 7.34 (2H, d, *J* 8.4, Ar*H*), 7.50 (2H, d, *J* 8.7, Ar*H*), 7.87 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 58.8 (CH_2, S*C*H$_2$), 126.2 (C, aromatic *C*), 128.7 (1 × CH signal, 2 × CH, aromatic *C*H), 129.2 [CH, *C*(3)H], 129.5, 131.1, 132.4 (3 × CH signals, 6 × CH, aromatic *C*H), 133.6, 135.0, 141.7, 141.8 [4 × C, 3 × aromatic *C* and *C*(2)S], 189.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{16}H_{12}O_2S^{35}Cl_3$[M+H$^+$] 372.9624. Found 372.9617; m/z (ES+) 373.0 [($C_{16}H_{11}O_2S^{35}Cl_3$)+H$^+$], 14%.



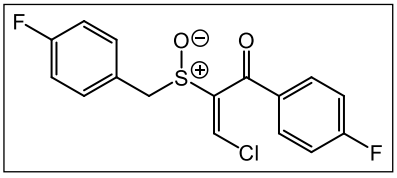
Characteristic signals tentatively assigned as *Z*-**38q**: δ_H (400 MHz, $CDCl_3$) 4.58 (1H, A of AB system, J_{AB} 12.4, one of SC*H*$_2$), 4.64 (1H, B of AB system, J_{AB} 12.4, one of SC*H*$_2$), 6.90 (1H, s, C*H*Cl).



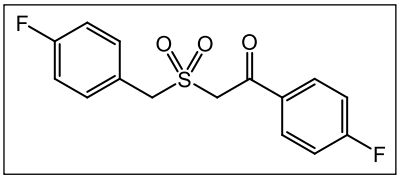
39b (less polar than *Z*-**38q**): white solid (7 mg, 4%); ν_{max}/cm^{-1} (neat) 2968, 2923, 1685 (C=O), 1589, 1491, 1323; δ_H (400 MHz, $CDCl_3$): 4.35 (2H, s, SC*H*$_2$), 4.49 (2H, s, SC*H*$_2$), 7.39 (2H, d, *J* 8.4, Ar*H*), 7.49 (4H, dd appears as t, *J* 8.0, Ar*H*), 7.91 (2H, d, *J* 8.6, Ar*H*); δ_C (100 MHz, $CDCl_3$): 56.8, 58.9 (2 × CH_2, S*C*H$_2$), 126.0 (C, aromatic *C*), 129.4,

129.5, 130.5, 132.4 (4 × CH signals, 8 × CH, aromatic *C*H), 134.0, 135.7, 141.6 (3 × C, aromatic *C*), 188.3 (C, *C*O).

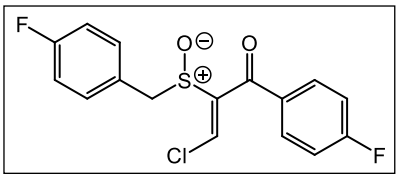
(*E*)-3-Chloro-2-((4-fluorobenzyl)sulfinyl)-1-(4-fluorophenyl)prop-2-en-1-one *E*-38z



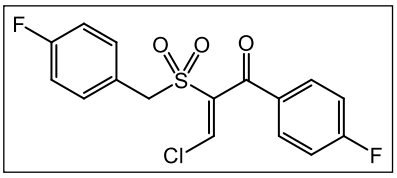
This was prepared following the procedure described above for **38h** using the sulfide *Z*-**4z** (218 mg, 0.7 mmol) in acetone (10 mL) and Oxone® (826 mg, 1.3 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h and following the work-up, the crude product was obtained as a yellow viscous gum. ^{1}H NMR spectroscopy showed this product to contain the desired *sulfoxide* as a mixture of *Z* and *E* isomers, *Z*-**38z** and *E*-**38z**, in a ratio of 1.5 : 1 with *approx*. 3% retro-Claisen sulfone impurity **39c** (δ_H, 2H, s, 4.38 ppm and δ_H, 2H, s, 4.50 ppm) and 9% tentatively assigned sulfones *Z*-**S65** and *E*-**S65** (*Z* : *E,* 4 : 1) (δ_H, 2H, s, 4.49 ppm and δ_H, 2H, s, 4.53 ppm). Purification by column chromatography on silica gel using hexane–ethyl acetate (70 : 30) as eluent gave the *sulfoxide E*-**38z** (123 mg, 54%) as a colourless viscous gum which was seen to contain *approx*. 5% retro-Claisen sulfone impurity **39c**; ν_{max}/cm^{-1} (neat) 3053, 1658 (C=O), 1592, 1506, 1297, 1223, 1154, 1059 (S–O), 848, 730; δ_H (400 MHz, $CDCl_3$): 4.16 (1H, A of AB system, J_{AB} 13.2, one of SC*H*$_2$), 4.34 (1H, B of AB system, J_{AB} 13.2, one of SC*H*$_2$), 6.55 (1H, s, C*H*Cl), 7.05 (2H, overlapping dd appears as t, *J* 8.7, Ar*H*), 7.20 (2H, overlapping dd appears as t, *J* 8.5, Ar*H*), 7.27 (2H, dd, *J* 8.5, J_{FH} 5.4, Ar*H*), 7.98 (2H, dd, *J* 8.9, J_{FH} 5.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 58.7 (CH_2, S*C*H$_2$), 115.5 (1 × CH signal, 2 × CH, d, $^2J_{CF}$ 21.9, aromatic *C*H), 116.4 (1 × CH signal, 2 × CH, d, $^2J_{CF}$ 22.2, aromatic *C*H), 123.5 (C, d, $^4J_{CF}$ 3.3, aromatic *C*), 128.7 [CH, *C*(3)H], 131.8 (C, d, $^4J_{CF}$ 3.0, aromatic *C*), 132.6 (1 × CH signal, 2 × CH, d, $^3J_{CF}$ 9.9, aromatic *C*H), 132.9 (1 × CH signal, 2 × CH, d, $^3J_{CF}$ 8.4, aromatic *C*H), 142.0 [C, *C*(2)S], 163.0 (C, d, $^1J_{CF}$ 248.5, aromatic *C*), 166.8 (C, d, $^1J_{CF}$ 258.4, aromatic *C*), 188.6 (C, *C*O); m/z (ES+) 341.1 [($C_{16}H_{11}O_2S^{35}ClF_2$)+H$^+$], 26%.



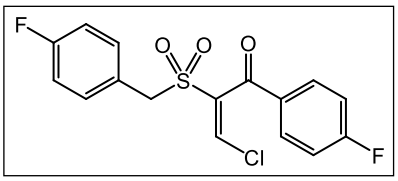
Characteristic signals due to **39c**: δ_H (400 MHz, $CDCl_3$) 4.38 (2H, s, SC*H*$_2$), 4.50 (2H, s, SC*H*$_2$), 7.53 (2H, dd, *J* 8.6, J_{FH} 5.3, Ar*H*); δ_C (100 MHz, $CDCl_3$): 56.7, 58.7 (2 × CH_2, S*C*H$_2$), 116.3 (2 × CH, d, $^2J_{CF}$ 22.2, aromatic *C*H), 123.4 (C, d, $^4J_{CF}$ 3.3, aromatic *C*), 132.1 (2 × CH, d, $^3J_{CF}$ 9.8, aromatic *C*H), 187.9 (C, *C*O).



Characteristic signals tentatively assigned as *Z*-**38z** (from ^{1}H NMR spectrum of crude material): δ_H (400 MHz, $CDCl_3$) 4.58 (1H, A of AB system, J_{AB} 12.4, one of SCH_2), 4.66 (1H, B of AB system, J_{AB} 12.5, one of SCH_2), 6.89 (1H, s, C*H*Cl).



Characteristic signals tentatively assigned as *Z*-**S65**: δ_H (400 MHz, $CDCl_3$) 4.49 (2H, s, SCH_2).



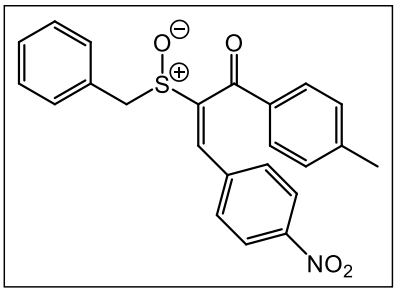
Characteristic signals tentatively assigned as *E*-**S65**: δ_H (400 MHz, $CDCl_3$) 4.53 (2H, s, SCH_2).

1.8 Synthesis of Chalcones from α-Sulfinyl-β-chloroenones

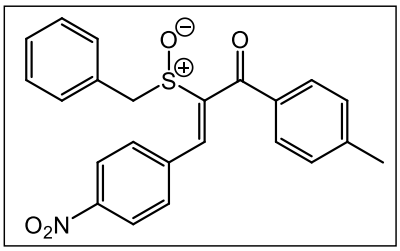
The following compounds were synthesised following a procedure described by Aguilar-Aguilar and Peña Cabrera. [22]

(*E*)-2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-40h and (*Z*)-2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *Z*-40h

The sulfoxide *E*-**14h** (135 mg, 0.4 mmol) and the aryl stannane, tributyl(4-nitrophenyl)stannane **36f**[25] (210 mg, 0.5 mmol), were dissolved in anhydrous acetonitrile (10 mL) under nitrogen. The mixture was then purged with nitrogen for 5 min whereupon the palladium catalyst, $(CH_3CN)_2PdCl_2$ (5 mg, 20 µmol, 5 mol %) was added and the reaction mixture was stirred at room temperature for 2 h. The mixture was then washed with hexane (3 × 20 mL) to remove the tin by-products and the remaining acetonitrile phase was evaporated under reduced pressure to give the crude *chalcone* as an orange solid. ^{1}H NMR spectroscopy showed this product to contain *approx.* 6% β-chloroenone starting material *E*-**14h**, 22% bi-aryl **37**[26] (δ_H d, 8.36 ppm), and 71% chalcones *Z*-**40h** and *E*-**40h** (*Z* : *E*, 1 : 4.5). Purification by column chromatography on silica gel using dichloromethane (100%) as eluent afforded the pure *chalcone E*-**4h** (80 mg, 47%) as a pale yellow solid. A more polar fraction from the column was removed using hexane–ethyl acetate (50 : 50) as eluent. This fraction contained the *chalcone Z*-**40h** (13 mg, 8%) as an orange oil.

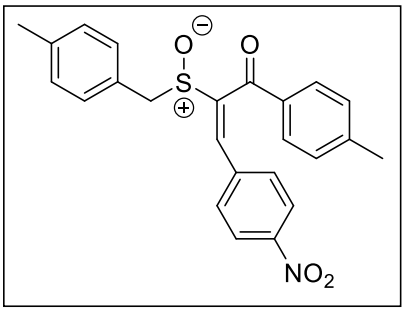


E-**140h** (less polar): mp 52–56°C; ν_{max}/cm^{-1} (neat) 3063, 3027, 2921, 2848, 1626 (C=O), 1601, 1514 (NO_2), 1341 (NO_2), 1056, 734; δ_H (400 MHz, $CDCl_3$): 2.36 (3H, s, ArC*H*$_3$), 4.12 (1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$), 4.35 (1H, B of AB system, J_{AB} 13.1, one of SC*H*$_2$), 7.04 [1H, s, C(3)*H*], 7.17 (2H, d, *J* 8.1, Ar*H*), 7.25–7.34 (7H, m, Ar*H*), 7.76 (2H, d, *J* 8.2, Ar*H*), 8.01 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 59.4 (CH_2, S*C*H$_2$), 123.7 (1 × CH, aromatic *C*H), 128.2 [1 x C, aromatic *C* or *C*(2)S], 128.3, 128.5, 129.8, 129.9, 130.1, 131.0 (6 × CH, aromatic *C*H), 132.6 [1 x C, aromatic *C* or *C*(2)S], 133.3 [1 x CH, *C*(3)H], 139.0, 145.3, 146.4, 147.7 [4 × C, 4 × aromatic *C* or 3 × aromatic *C* and *C*(2)S], 192.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{20}NO_4S[M+H^+]$ 406.1113. Found 406.1100; m/z (ES+) 406.1 $[(C_{23}H_{19}NO_4S)+H^+]$, 100%.



Z-**40h** (more polar): ν_{max}/cm^{-1} (neat) 3030, 2979, 2918, 1655 (C=O), 1601, 1511 (NO_2), 1343 (NO_2), 1039, 754, 704; δ_H (400 MHz, $CDCl_3$): 2.45 (3H, s, ArC*H*$_3$), 4.44 (1H, A of AB system, J_{AB} 12.2, one of SC*H*$_2$), 4.97 (1H, B of AB system, J_{AB} 12.2, one of SC*H*$_2$), 6.95 (2H, d, *J* 8.4, Ar*H*), 7.11–7.45 [8H, m, containing [7.25, 1H, s, C(3)*H*] and Ar*H*], 7.91 (2H, d, *J* 8.2, Ar*H*), 8.02 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 59.2 (CH_2, S*C*H$_2$), 123.2, 128.7, 128.9 (3 × CH, aromatic *C*H), 129.3 [1 x C, aromatic *C* or *C*(2)S], 129.5, 130.4, 130.5, 130.9 (4 × CH, aromatic *C*H), 134.6, 138.1 [2 × C, 2 × aromatic *C* or aromatic *C* and *C*(2)S], 140.7 [1 x CH, *C*(3)H], 143.7, 145.6, 147.8 [3 × C, 3 × aromatic *C* or 2 × aromatic *C* and *C*(2)S], 192.4 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{20}NO_4S[M+H^+]$ 406.1113. Found 406.1115.

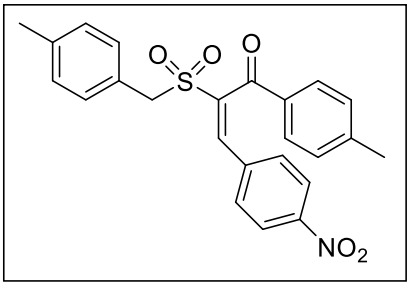
2-((4-Methylbenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40m



This was prepared following the procedure described above for **40h** using the sulfoxide 3-Chloro-2-((4-methylbenzyl)sulfiniyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-**14h** (0.04 g, 0.1 mmol, 1 eq), tributyl(4-nitrophenyl)stannane **36f**[25] (0.06 g, 0.1 mmol, 1.3 eq) and $(CH_3CN)_2PdCl_2$ (0.0016 g, 0.006 mmol 5 mol %) in acetonitrile (15 mL). The reaction mixture was stirred under reflux for 5 h, and following work-up, the crude chalcone was

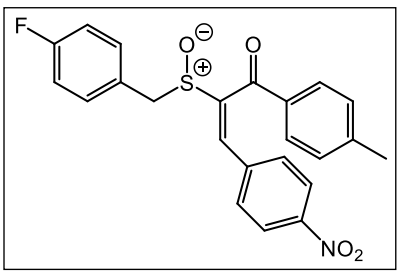
obtained as a light amber oil. The ^{1}H NMR spectrum of the crude product showed approximately 90% *E* chalcone *E*-**40m** with 10% of the tentatively assigned sulfone **S66** as a singlet at δ 4.59 ppm. The crude chalcone was purified by column chromatography on silica gel using dichloromethane (100%) as eluent to give the pure *E*-chalcone *E*-**40m** (0.035 g, 70%) as a bright yellow oil.

E-40m: υ_{max}/cm^{-1} (neat) 1645 cm^{-1} (C=O), 1518 (NO_2), 1060.88 cm^{-1} (S-O); δ_H (500 MHz, $CDCl_3$): 2.29 (3H, s, ArC*H*$_3$), 2.36 (3H, s, ArC*H*$_3$), 4.07 (1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$), 4.32 (1H, B of AB system, J_{AB} 13.1, one of SC*H*$_2$), 7.07 – 7.13 [3H, m, Ar*H* and C(3)*H*], 7.15 – 7.23 (4H, m, Ar*H*), 7.30 (2H, d, *J* 8.8, Ar*H*), 7.76 (2H, d, *J* 8.3, Ar*H*), 8.01 (2H, d, *J* 8.8, Ar*H*); δ_C (125 MHz, $CDCl_3$): 21.2 (CH_3, aromatic *C*H$_3$), 21.9 (CH_3, aromatic *C*H$_3$), 59.4 (CH_2, S*C*H$_2$), 123.8 (1 x CH, aromatic *C*H), 125.3 [1 x C signal, aromatic *C* or *C*(2)S], 129.1, 129.9, 130.1, 130.9 [4 x CH, aromatic *C*H), 132.7 (1 x C signal, aromatic *C*), 133.1 [1 x CH signal, *C*(3)H], 138.5, 139.1 (2 x C signals, 2 x aromatic *C*), 145.8 [1 x C signal, aromatic *C* or *C*(2)S], 146.4, 147.8 (2 x C signals, 2 x aromatic *C*), 192.8 (1 x C signal, *C*O); m/z (ES+): 420.2 [($C_{24}H_{21}NO_4S$)+H$^+$], 34%. HRMS (ES+): Exact mass calculated for $C_{24}H_{21}NO_4S$ [M+H$^+$] 420.126405. Found 420.12630.



Characteristic signals for **(*E*)-2-((4-methylbenzyl)sulfonyl)-3-(4-nitrophenyl)-1-(p-tolyl)prop-2-en-1-one S66**: δ_H (400 MHz, $CDCl_3$) 4.59 (2H, s, SC*H*$_2$).

(*E*)-2-((4-Fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-40aa



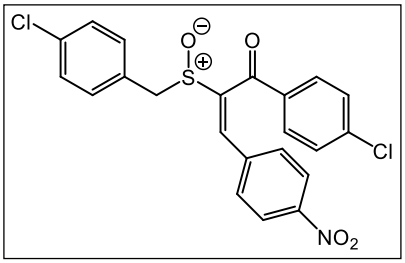
This was prepared following the procedure described above for **40h** using the sulfoxide *E*-**14aa** (109 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (161 mg, 0.4 mmol), and $(CH_3CN)_2PdCl_2$ (4 mg, 16 µmol, 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 24 h and after work-up, the crude product was obtained as a brown oil. ^{1}H NMR spectroscopy showed *approx*. 94% conversion to the *chalcone E*-**40aa**. Trace quantities of the *Z* chalcone *Z*-**40aa** (3%) were also visible. Purification by column chromatography on silica gel using

hexane–ethyl acetate (70 : 30) as eluent gave the *chalcone E*-**40aa** (101 mg, 74%) as a yellow solid, mp 48–52°C.

E-**40aa**: ν_{max}/cm^{-1} (neat) 1645 (C=O), 1599, 1507 (NO_2), 1342 (NO_2), 1225, 1059, 830; δ_H (400 MHz, $CDCl_3$): 2.37 (3H, s, ArC*H*$_3$), 4.11 (1H, A of AB system, J_{AB} 13.3, one of SC*H*$_2$), 4.32 (1H, B of AB system, J_{AB} 13.2, one of SC*H*$_2$), 6.94–7.09 [3H, m, containing (6.99, 2H, dd appears as t, *J* 8.2, Ar*H*) and [7.01, 1H, s, C(3)*H*)]], 7.18 (2H, d, *J* 8.0, Ar*H*), 7.24–7.34 (4H, m, Ar*H*), 7.76 (2H, d, *J* 8.2, Ar*H*), 8.02 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 58.2 (CH_2, S*C*H$_2$), 115.3 (1 × CH, d, $^2J_{CF}$ 21.6, aromatic *C*H), 123.83 (1 x C, d, $^4J_{CF}$ 3.4, aromatic *C*), 123.86 (1 × CH, aromatic *C*H), 129.8, 129.9, 130.0 (3 × CH, aromatic *C*H), 132.5 (1 x C, aromatic *C*), 132.8 (1 × CH, d, $^3J_{CF}$ 8.3, aromatic *C*H), 133.3 [1 x CH, *C*(3)H], 138.8 (1 x C, aromatic *C*), 144.9 [1 x C, *C*(2)S], 146.6, 147.8 (2 × C, aromatic *C*), 162.9 (C, d, $^1J_{CF}$ 247.6, aromatic *C*), 192.8 (C, *C*O); m/z (ES+) 424.1 [($C_{23}H_{18}FNO_4S$)+H^+], 68%.

Characteristic signals tentatively assigned as *Z*-**40aa**: δ_H (400 MHz, $CDCl_3$): 4.45 (1H, A of AB system, J_{AB} 12.2, one of SC*H*$_2$), 4.86 (1H, B of AB system, J_{AB} 12.2, one of SC*H*$_2$).

(*E*)-2-((4-Chlorobenzyl)sulfinyl)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *E*-40q



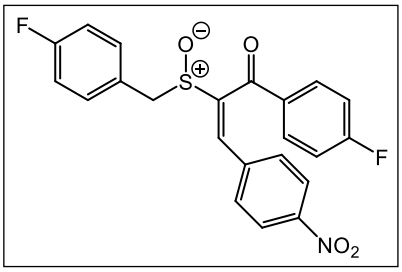
This was prepared following the procedure described above for **40h** using the sulfoxide *E*-**14q** (50 mg, 0.1 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (65 mg, 0.1 mmol), and $(CH_3CN)_2PdCl_2$ (2 mg, 6 µmol, 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 21 h and after work-up, the crude product was obtained as an orange oil. ^{1}H NMR spectroscopy showed *approx*. 20% sulfoxide starting material *E*-**14q**, 68% chalcones *Z*-**40q** and *E*-**40q** (*Z* : *E*, 1 : 5.7) and 12% bi-aryl **37**[26]. Purification by column chromatography on silica gel using dichloromethane (100%) as eluent gave the *chalcone E*-**40q** (27 mg, 45%) as a yellow solid, mp 43–46°C; ν_{max}/cm^{-1} (neat) 2924, 2853, 1651 (C=O), 1586, 1520, 1345 (NO_2), 1225, 1093, 836; δ_H (400 MHz, $CDCl_3$): 4.14 (1H, A of AB system, J_{AB} 13.2, one of SC*H*$_2$), 4.34 (1H, B of AB system, J_{AB} 13.2, one of SC*H*$_2$), 7.06 [1H, s, C(3)*H*], 7.20–7.50 [8H, m, Ar*H*, containing (7.36, 2H, d, *J* 8.7, Ar*H*)], 7.78 (2H, d, *J* 8.7, Ar*H*), 8.04 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 58.5 (CH_2, S*C*H$_2$), 123.9 (1 × CH, aromatic *C*H), 126.3 [1 x C, aromatic *C* or *C*(2)S], 128.5, 129.6, 130.1, 130.9, 132.3 (5 × CH, aromatic *C*H), 133.2 [1 x C, aromatic *C* or *C*(2)S], 134.3 [1 x CH, *C*(3)H],

134.8, 138.4, 141.9, 144.2, 148.0 [5 × C, 5 × aromatic *C* or 4 × aromatic *C* and *C*(2)S], 192.1 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{22}H_{16}NO_4S^{35}Cl_2$[M+H$^+$] 460.0177. Found 460.0160; m/z (ES+) 460.0 [($C_{22}H_{15}NO_4S^{35}Cl_2$)+H$^+$], 12%.

Characteristic signals tentatively assigned as *Z*-**40q**: δ_H (400 MHz, $CDCl_3$): 4.44 (1H, A of AB system, J_{AB} 12.2, one of SC*H*$_2$), 4.83 (1H, B of AB system, J_{AB} 12.2, one of SC*H*$_2$).

*A ^{1}H NMR spectrum was recorded for a sample of E-***40q** *which had been stored at room temperature for 4 months. The spectrum showed approx. 3% Z-***40q** *to be present in the sample.*

(*E*)-2-((4-Fluorobenzyl)sulfinyl)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *E*-40z



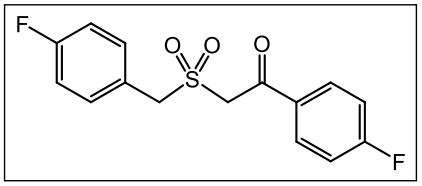
This was prepared following the procedure described above for **40h** using the sulfoxide *E*-**14z** (containing 5% of the oxidation by-product **39c**) (118 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (172 mg, 0.4 mmol), and $(CH_3CN)_2PdCl_2$ (4 mg, 18 µmol, 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 21 h and after work-up, the crude product was obtained as a brown residue. ^{1}H NMR spectroscopy showed formation of the *E* chalcone *E*-**40z** and trace quantities of the *Z* chalcone *Z*-**40z** (<2%). The bi-aryl **37**[26] accounted for *approx*. 20% of the mixture. The oxidation by-product **39c** was unaffected by the reaction and accounted for *approx*. 7% of the mixture. Purification by column chromatography on silica gel using ethyl acetate (100%) as eluent gave the *chalcone E*-**40z** (103 mg, 69%) as an orange solid, mp 51–54°C.

E-**40z**: ν_{max}/cm^{-1} (neat) 3072, 1648 (C=O), 1591, 1507, 1342, 1222, 1153, 1059, 841; δ_H (400 MHz, $CDCl_3$): 4.15 (1H, A of AB system, J_{AB} 13.3, one of SC*H*$_2$), 4.35 (1H, B of AB system, J_{AB} 13.2, one of SC*H*$_2$), 6.93–7.15 [5H, m, 4 × Ar*H* and C(3)*H*], 7.24–7.34 (4H, m, Ar*H*), 7.89 (2H, dd, *J* 8.7, J_{FH} 5.3, Ar*H*), 8.04 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 58.4 (CH_2, S*C*H$_2$), 115.3 (1 × CH, d, $^2J_{CF}$ 21.6, aromatic *C*H), 116.5 (1 × CH, d, $^2J_{CF}$ 22.2, aromatic *C*H), 123.6 (1 x C, d, $^4J_{CF}$ 3.0, aromatic *C*), 123.9, 130.1 (2 × CH, aromatic *C*H), 131.4 (1 x C, d, $^4J_{CF}$ 2.9, aromatic *C*), 132.5 (1 × CH, d, $^3J_{CF}$ 9.9, aromatic *C*H), 132.8 (1 × CH, d, $^3J_{CF}$ 8.3, aromatic *C*H), 134.1 [1 x CH, *C*(3)H], 138.5 (1 x C, aromatic *C*), 144.4 [1 x C, *C*(2)S], 148.0 (1 x C, aromatic *C*), 163.0 (1 x C, d, $^1J_{CF}$

248.2, aromatic *C*), 166.8 (1 x C, d, $^{1}J_{CF}$ 259.5, aromatic *C*), 191.7 (C, *C*O). HRMS (ES+): Exact mass calculated for $C_{22}H_{16}NO_4F_2S[M+H^+]$ 428.0768. Found 428.0778.

Characteristic signals tentatively assigned as *Z*-**40z**: δ_H (400 MHz, $CDCl_3$): 4.45 (1H, A of AB system, J_{AB} 12.5, one of SCH_2), 4.85 (1H, B of AB system, J_{AB} 12.4, one of SCH_2).

2-((4-Fluorobenzyl)sulfonyl)-1-(4-fluorophenyl)ethan-1-one 39c

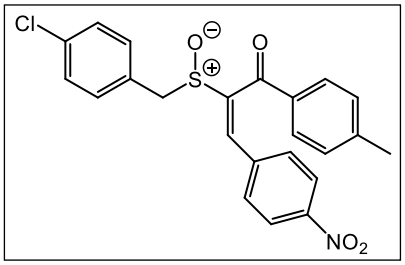


39c (less polar than *E*-**40z**): fine yellow crystals (16 mg, 14%); mp 150–153°C; ν_{max}/cm^{-1} (neat) 2961, 2922, 1679 (C=O), 1594, 1504, 1303, 1133 (S=O), 1124, 996, 834, 824, 517; δ_H (400 MHz, $CDCl_3$): 4.36 (2H, s, SCH_2), 4.50 (2H, s, SCH_2), 7.11 (2H, t, *J* 8.6, Ar*H*), 7.15–7.24 (2H, m, Ar*H*), 7.49–7.61 (2H, m, Ar*H*), 7.98–8.07 (2H, m, Ar*H*); δ_C (100 MHz, $CDCl_3$): 56.7, 58.7 (2 × CH_2, S*C*H_2), 116.2 (1 × CH, d, $^{2}J_{CF}$ 21.6, aromatic *C*H), 116.3 (1 × CH, d, $^{2}J_{CF}$ 22.2, aromatic *C*H), 123.4 (1 x C, d, $^{4}J_{CF}$ 3.5, aromatic *C*), 132.1 (1 × CH, d, $^{3}J_{CF}$ 9.8, aromatic *C*H), 133.0 (1 × CH, d, $^{3}J_{CF}$ 8.5, aromatic *C*H), 187.9 (C, *C*O); m/z (ES−) 309.2 [$(C_{15}H_{12}F_2O_3S)-H^+$], 42%. 3 × C_q were not observed.

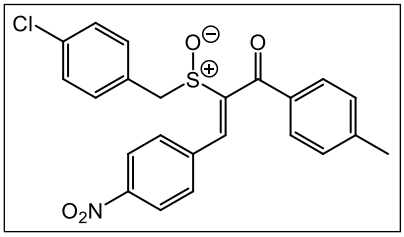
Impurity (*approx*. 20%) present in this sample; δ_H (400 MHz, $CDCl_3$): 7.25–7.45 (m); δ_C (100 MHz, $CDCl_3$): 115.9, 131.2 (1 x C, d, $^{4}J_{CF}$ 9.3, aromatic *C*), 141.1.

(*E*)-2-((4-Chlorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *E*-40t and (*Z*)-2-((4-Chlorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one *Z*-40t

This was prepared following the procedure described above for **40h** using the sulfoxides *Z*-**14t** and *E*-**14t** (*Z* : *E*, 5 : 1) (161 mg, 0.4 mmol), tributyl(4-nitrophenyl)stannane **36f**[25] (225 mg, 0.5 mmol), and $(CH_3CN)_2PdCl_2$ (6 mg, 20 µmol, 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 21 h and after work-up, the crude product was obtained as an orange gel. ^{1}H NMR spectroscopy 39% sulfoxide starting materials *Z*-**14t** and *E*-**14t** (*Z* : *E*, 1 : 1), 56% chalcones *Z*-**40t** and *E*-**40t** (*Z* : *E*, 2.5 : 1, *Z* isomer is major isomer), and 5% enone **S67**. Purification by column chromatography on silica gel using dichloromethane (100%) as eluent gave the *chalcone E*-**40t** (43 mg, 22%) as a yellow solid, mp 50–54°C. Further chromatography using hexane–ethyl acetate (50 : 50) as eluent gave the enone **S67** (6 mg) as an orange oil and the pure *chalcone Z*-**40t** (19 mg, 10%) as a yellow semisolid.

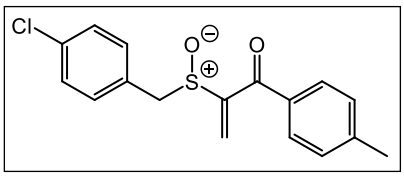


E-**40t** (less polar): ν_{max}/cm^{-1} (neat) 3037, 2921, 1644 (C=O), 1600, 1519 (NO_2), 1342 (NO_2), 1060, 726; δ_H (400 MHz, $CDCl_3$): 2.37 (3H, s, ArC*H*$_3$), 4.10 (1H, A of AB system, J_{AB} 13.2, one of SC*H*$_2$), 4.31 (1H, B of AB system, J_{AB} 13.2, one of SC*H*$_2$), 7.02 [1H, s, C(3)*H*], 7.18 (2H, d, *J* 8.0, Ar*H*), 7.25–7.31 (6H, m, Ar*H*), 7.76 (2H, d, *J* 8.3, Ar*H*), 8.02 (2H, d, *J* 8.8, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.9 (CH_3, Ar*C*H$_3$), 58.3 (CH_2, S*C*H$_2$), 123.8 (1 × CH, aromatic *C*H), 126.5 (1 x C, aromatic *C*), 128.5, 129.8, 129.9, 130.1, 132.43 (5 × CH, aromatic *C*H), 132.48 (1 x C, aromatic *C*), 133.3 [1 x CH, *C*(3)H], 134.7, 138.7 (2 × C, aromatic *C*), 144.9 [1 x C, *C*(2)S], 146.7, 147.8 (2 × C, aromatic *C*), 192.8 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{19}NO_4S^{35}Cl[M+H^+]$ 440.0723. Found 440.0707; m/z (ES+) 440.1 [($C_{23}H_{18}NO_4S^{35}Cl$)+H^+], 100%, 442.1 [($C_{23}H_{18}NO_4S^{37}Cl$)+H^+], 40%.



Z-**40t** (more polar): ν_{max}/cm^{-1} (neat) 2922, 2855, 1650 (C=O), 1601, 1519 (NO_2), 1343 (NO_2), 1055, 727; δ_H (400 MHz, $CDCl_3$): 2.45 (3H, s, ArC*H*$_3$), 4.43 (1H, A of AB system, J_{AB} 12.2, one of SC*H*$_2$), 4.85 (1H, B of AB system, J_{AB} 12.2, one of SC*H*$_2$), 7.12 (2H, d, *J* 8.6, Ar*H*), 7.15–7.40 [7H, m, containing (7.19, 2H, d, *J* 8.4, Ar*H*), 7.23 [1H, s, C(3)*H*], 7.33 (2H, d, *J* 8.0, Ar*H*) and Ar*H*], 7.91 (2H, d, *J* 8.2, Ar*H*), 8.09 (2H, d, *J* 8.7, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.8 (CH_3, Ar*C*H$_3$), 58.6 (CH_2, S*C*H$_2$), 123.3 (1 × CH, aromatic *C*H), 127.7 (1 x C, aromatic *C*), 129.0, 129.6, 130.4, 130.5, 132.1 (5 × CH, aromatic *C*H), 134.3, 134.9, 138.0 [3 × C, 3 × aromatic *C* or 2 × aromatic *C* and *C*(2)S], 140.7 [1 x CH, *C*(3)H], 143.7, 145.8, 147.9 [3 × C, 3 × aromatic *C* or 2 × aromatic *C* and *C*(2)S], 192.2 (C, *C*O); m/z (ES+) 440.1 [($C_{23}H_{18}NO_4S^{35}Cl$)+H^+], 34%, 442.1 [($C_{23}H_{18}NO_4S^{37}Cl$)+H^+], 16%.

2-((4-Chlorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one S67

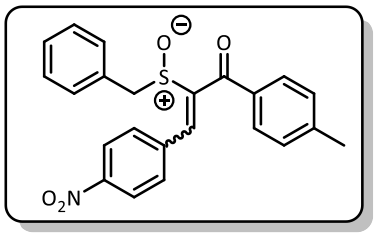


S67: orange oil (6 mg, 4%); ν_{max}/cm^{-1} (neat) 3031, 2920, 1666 (C=O), 1603, 1489, 1178, 1091, 1014, 830, 502; δ_H (400 MHz, $CDCl_3$): 2.45 (3H, s, ArC*H*$_3$), 4.08 (1H, A of AB system, J_{AB} 13.4, one of SC*H*$_2$), 4.30 (1H, B of AB system, J_{AB} 13.4, one of SC*H*$_2$), 6.38, 6.40 [2 × 1H, s, C(3)*H*$_2$], 7.12 (2H, d, *J* 8.4, Ar*H*), 7.24–7.33 (4H, m, Ar*H*), 7.59 (2H, d, *J* 8.2, Ar*H*); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3, Ar*C*H$_3$), 57.2 (CH_2, S*C*H$_2$), 127.9 [1 x C, aromatic *C* or *C*(2)S], 128.5, 129.4, 129.5, 131.7 (4 × CH, aromatic *C*H), 132.5 [CH_2, *C*(3)H$_2$], 133.4, 134.4, 144.8, 150.1 [4 × C, 4 × aromatic *C* or 3 × aromatic *C* and *C*(2)S], 192.1 (C, *C*O).

The reaction was also carried out using the sulfoxide *E*-**40t** (93 mg, 0.26 mmol) with all other reactants scaled accordingly. The reaction mixture was stirred at room temperature for 26 h and after work-up, the impure product was obtained as a brown residue. ^{1}H NMR spectroscopy showed formation of the chalcone *E*-**4t** with complete consumption of the starting material *E*-**40t**. Following column chromatography on silica gel using hexane–ethyl acetate (70 : 30) as eluent, the *chalcone E*-**40t** (52 mg, 46%) was obtained as an orange gel.

1.9 Oxidation of Chalcones

2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40h

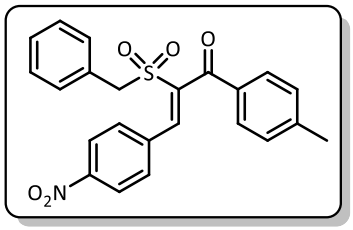


A solution of Oxone® (0.06 g, 0.2 mmol, 2.1 eq) in water (2.5 mL) was added dropwise to a stirring solution of 2-(benzylthio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **20** (0.04 g, 0.1 mmol, 1 eq) in acetone (5 mL) at room temperature. A cloudy-yellow precipitate formed immediately and the solution was stirred for a further 2 h. After 2 h, water (15 mL) was added and the aqueous solution was extracted with dichloromethane (3 x 15 mL). The organic layer was then washed with water (2 x 10 mL) and brine (10 mL), dried, filtered and concentrated under reduced pressure to give the crude sulfoxide as a yellow semi-solid. ^{1}H NMR spectroscopy showed this product to contain approximately 85.5% chalone as a mixture of two isomers *Z*-**40h** and *E*-**40h** (Z:E; 10.5 : 1) along with unreacted starting material *Z*-**20** (*Z* isomer, 6.5%) and the tentatively assigned sulfone **S68** (8%, s, δ_H 4.62 ppm). The crude sulfoxide was purified by column chromatography using hexane:ethyl acetate (80:20) as eluent to give the pure sulfoxide **40h** (0.02 g, 46.8%) as a yellow semi-solid. The pure sulfoxide was isolated as a mixture of isomers *Z*-**40h** and *E*-**40h** (Z:E; 3.6 : 1) which could not be separated.

Z-40h: υ_{max}/cm^{-1} (neat) 1655 cm^{-1} (C=O), 1512 (NO_2), 1040; δ_H (400 MHz, $CDCl_3$): 2.37 [3H, s, aromatic C*H*$_3$], 4.44 [1H, A of AB system, *J* 12.4, one of SC*H*$_2$], 4.99 [1H, B of AB system, *J* 12.4, one of SC*H*$_2$], 6.95 [2H, d, *J* 9.4, aromatic *H*], 7.21 – 7.44 [8H, m, containing (7.25, 1H, s, C(3)*H*) and aromatic *H*], 7.92 [2H, d, *J* 8.1, aromatic *H*], 8.02 [2H, d, *J* 8.9, aromatic *H*]; δ_c (100 MHz, $CDCl_3$): 21.9 [CH_3, aromatic *C*H_3], 59.2 [CH_2, S*C*H_2], 123.2, 128.7, 128.9 [3 x CH signals, aromatic *C*H], 129.3 [1 x C signal, aromatic *C* or *C*(2)S], 129.6, 130.4, 130.6, 130.9 [4 x CH signals, aromatic *C*H], 134.6, 138.2 [2 x C signals, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 140.7 [1 x CH signal, *C*(3)H], 143.6, 145.6, 147.8 [3 x C signals, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S],

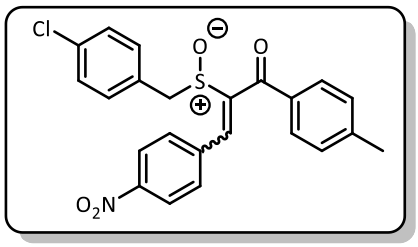
192.5 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{33}H_{29}{}^{35}Cl_2NO_4S$ [M+H$^+$] 606.091194. Found 606.09120.

Characteristic E-40h signals: δ_H (400 MHz, $CDCl_3$): 2.37 [3H, s, aromatic C*H*$_3$], 4.13 [1H, A of AB system, J_{AB} 13.4, one of SC*H*$_2$], 4.36 [1H, B of AB system, J_{AB} 13.4, one of SC*H*$_2$], 7.05 [1H, s, C(3)*H*], 7.18 [2H, d, *J* 7.9, aromatic *H*], 7.76 [2H, d, *J* 7.9, aromatic *H*]; δ_c (100 MHz, $CDCl_3$): 59.5 [CH_2, S*C*H$_2$], 123.8, 128.4, 128.6, 129.85, 129.88, 130.1, 131.0 [7 x CH signals, aromatic *C*H], 132.6 [1 x C signal, aromatic *C* or *C*(2)S], 133.3 [1 x CH signal, *C*(3)H], 139.0, 145.3, 146.5, 147.8 [4 x C signals, 4 x aromatic *C* or 3 x aromatic *C* and *C*(2)S].



Characteristic signals tentatively assigned as **(*Z*)-2-(benzylsulfonyl)-3-(4-nitrophenyl)-1-(p-tolyl)prop-2-en-1-one S68**: δ_H (400 MHz, $CDCl_3$) 4.62 (2H, s, SC*H*$_2$).

2-((4-Chlorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40j



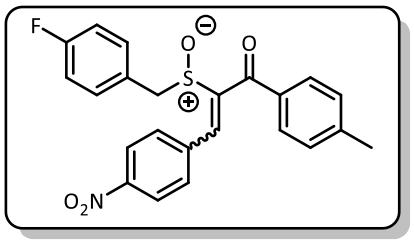
2-((4-Chlorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **21** (0.01 g, 0.03 mmol, 1 eq) in acetone (5 mL) and a solution of Oxone® (0.02 g, 0.06 mmol, 2.1 eq) in water (2.5 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h.** The crude oxidised chalcone was isolated as a yellow semi-solid. ^{1}H NMR spectroscopy showed this product to contain 75% chalcone as a mixture of isomers *Z*-**40j** and *E*-**40j** (Z:E; 4.5 : 1) along with unreacted starting material *Z*-**21** (*Z* isomer, 25%) remaining. The crude mixture was purified by column chromatography on silica gel using dichloromethane as eluent to give the pure sulfoxide (0.018 g, 59%) as an off-white to yellow solid. The pure sulfoxide was isolated as a mixture of isomers *Z*-**40j** and *E*-**40j** (Z:E; 8 : 1) which could not be separated.

Z-40j: υ_{max}/cm^{-1} (neat) 1650 cm^{-1} (C=O), 1518 (NO_2), 1040; δ_H (500 MHz, $CDCl_3$): 2.46 [3H, s, aromatic C*H*$_3$], 4.43 [1H, A of AB system, J_{AB} 12.3, one of SC*H*$_2$], 4.83 [1H, B of AB system, J_{AB} 12.3, 7.13 [2 H, d, *J* 8.5, aromatic *H*], 7.20 [2H, d, *J* 8.5, aromatic *H*], 7.23 [1H, s, C(3)*H*], 7.24 – 7.30 [2H, m, aromatic *H*], 7.33 [2H, d, *J* 8.0, aromatic *H*], 7.91 [2H, d, *J* 8.3, aromatic *H*], 8.09 [2H, d, *J* 8.6, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 21.9 [CH_3, aromatic *C*H$_3$], 58.7 [CH_2, S*C*H$_2$],

123.3 [1 x CH signal, aromatic *C*H], 127.7 [1 x C signal, aromatic *C*], 129.0, 129.6, 130.4, 130.6, 132.1 [5 x CH signals, aromatic *C*H], 134.4, 134.9, 138.1 [3 x C signals, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 140.7 [1 x CH signal, *C*(3)H], 143.9, 145.8, 147.9 [3 x C signals, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 192.2 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{23}H_{18}{}^{35}ClNO_4S$ [M+H$^+$] 440.0718. Found 440.0717.

Characteristic E-40j signals: δ_H (500 MHz, $CDCl_3$): 2.37 [3H, s, aromatic CH_3], 4.10 [1H, A of AB system, J_{AB} 13.2, one of SCH_2], 4.32 [1H, B of AB system, J_{AB} 13.2, one of SCH_2], 7.03 [1H, s, C(3)*H*], 7.76 [2H, d, *J* 8.4, aromatic *H*], 8.02 [2H, d, *J* 8.4, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.4 [CH_2, S*C*H_2], 123.9, 128.5, 129.85, 129.93, 130.1, 132.4 [6 x CH signals, aromatic *C*H].

2-((4-Fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40l



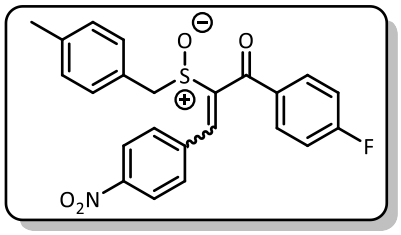
2-((4-Fluorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **22** (0.11 g, 0.03 mmol, 1 eq) in acetone (5 mL) and a solution of Oxone® (0.17 g, 0.06 mmol, 2.1 eq) in water (2.5 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h.** The crude oxidised chalcone was isolated as a yellow semi-solid. ^{1}H NMR spectroscopy showed this product to contain 94% chalcone as a mixture of isomers *Z*-**40l** and *E*-**40l** (Z:E; 16 : 1) along with unreacted starting material *Z*-**22** (*Z* isomer, 6%) . The crude mixture was purified by column chromatography on silica gel using hexane:ethyl acetate (20–40% ethyl acetate) as eluent to give the pure sulfoxide (0.06 g, 52.7%) as an off-white to yellow solid. The pure sample was collected as mixture of isomers *Z*-**40l** and *E*-**40l** (Z:E; 11.5 : 1) which could not be separated by column chromatography.

Z-40l: υ_{max}/cm^{-1} (neat) 1650 cm^{-1} (C=O), 1506 (NO_2), 1040; δ_H (500 MHz, $CDCl_3$): 2.46 [3H, s, aromatic CH_3], 4.44 [1H, A of AB system, J_{AB} 12.3, one of SCH_2], 4.87 [1H, B of AB system, J_{AB} 12.3, one of SCH_2], 6.96 [2H, dd appears as t, J_{FH} 8.6, aromatic *H*], 7.10 [2H, d, *J* 8.6, aromatic *H*], 7.26 [1H, s, C(3)*H*], 7.30 – 7.40 [4H, m, aromatic *H*], 7.92 [2H, d, *J* 8.1, aromatic *H*], 8.09 [2H, d, *J* 8.7, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 21.8 [CH_3, aromatic *C*H_3], 58.3 [CH_2, S*C*H_2], 115.9 [1 x CH signal, d, $^2J_{CF}$ 20.7, aromatic *C*H], 123.3 [1 x CH signal, aromatic *C*H], 125.2 [1 x C signal, d, $^4J_{CF}$ 3.0, aromatic *C*], 129.6, 130.4, 130.6 [3 x CH signals, aromatic *C*H], 132.6 [1 x CH signal, d, $^3J_{CF}$ 8.2, aromatic *C*H], 134.4, 138.1 [2 x C signals, aromatic *C* or aromatic *C* and

C(2)S], 140.7 [1 x CH signal, *C*(3)H], 143.8, 145.8, 147.9 [3 x C signal, 3 x aromatic *C* or aromatic *C* and *C*(2)S], 163.0 [1 x C signal, d, $^{1}J_{CF}$ 251.6, aromatic *C*], 192.4 [1 x C signal, *C*O]; m/z (ES+): 424.1 [($C_{23}H_{18}FNO_4S$)+H^+], 5%.

Characteristic E-40l signals: δ_H (500 MHz, $CDCl_3$): 2.37 [3H, s, aromatic C*H*$_3$], 4.11 [1H, A of AB system, J_{AB} 13.3, one of SC*H*$_2$], 4.32 [1H, B of AB system, J_{AB} 13.3, one of SC*H*$_2$], 7.77 [2H, d, *J* 8.1, aromatic *H*], 8.02 [2H, d, *J* 8.7, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 115.3 [1 x CH signal, d, $^{2}J_{CF}$ 20.8, aromatic *C*H], 123.8, 129.8, 129.9, 130.0 [4 x CH signals, aromatic *C*H].

1-(4-Fluorophenyl)-2-((4-methylbenzyl)sulfinyl)-3-(4-nitrophenyl)prop-2-en-1-one 40aa



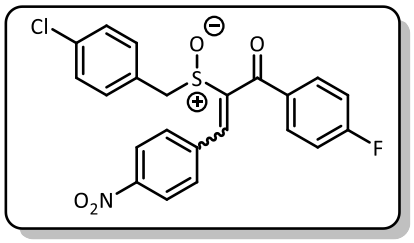
1-(4-Fluorophenyl)-2-((4-methylbenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one **29** (0.03 g, 0.07 mmol, 1 eq) in acetone (25 mL) and a solution of Oxone® (0.08 g, 0.3 mmol, 3.8 eq) in water (10 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h.** The solution was stirred for 6 h at room temperature and following work-up, the crude oxidised chalcone was isolated as a yellow semi-solid. ^{1}H NMR spectroscopy showed this product to contain 71% chalcone as a mixture of isomers *Z*-**40aa** and *E*-**40aa** (Z:E; 6.34 : 1) along with unreacted starting material *Z*-**29** (*Z* isomer, 29%). The crude mixture was purified by column chromatography on silica gel using hexane:ethyl acetate (70:30) to give the pure sulfoxide (0.01 g, 32.3%) as an off-white to yellow solid. The pure sample was collected as mixture of isomers *Z*-**40aa** and *E*-**40aa** (Z:E; 1 : 1.3) which could not be separated by column chromatography. υ_{max}/cm^{-1} (neat) 1656 (C=O), 1519 (NO_2); δ_H (500 MHz, $CDCl_3$): 2.29 [3H, s, *E* isomer, aromatic C*H*$_3$], 2.29 [3H, s, *Z* isomer, aromatic C*H*$_3$], 4.11 [1H, A of AB system, J_{AB} 13.0, *E* isomer, one of SC*H*$_2$], 4.35 [1H, B of AB system, J_{AB} 13.0, *E* isomer, one of SC*H*$_2$], 4.41 [1H, A of AB system, J_{AB} 11.9, *Z* isomer, one of SC*H*$_2$], 4.90 [1H, B of AB system, J_{AB} 11.9, *Z* isomer, one of SC*H*$_2$], 6.96 – 7.33 [20H, m, overlapping signals of *E* and *Z* isomers, containing 2 x C(3)*H* and aromatic *H*], 7.88 [2H, dd, *J* 8.3, J_{FH} 4.7, *E* isomer, aromatic *H*], 8.03 [2H, d, *J* 8.3, aromatic *H*], 8.06 [2H, dd, *J* 8.8, J_{FH} 5.2, aromatic *H*]; HRMS (ES+): Exact Mass Calculated for $C_{23}H_{18}FNO_4S$ [M+H^+] 424.1013. Found 424.1017.

E-40aa: δ_c (125 MHz, $CDCl_3$): 29.7 [CH_3, aromatic *C*H_3], 59.5 [CH_2, S*C*H_2], 116.5 [1 x CH signal, d, $^{2}J_{CF}$ 22.2, aromatic *C*H], 123.8 [1 x CH signal, aromatic *C*H], 125.0 [1 x C signal, aromatic *C* or

C(2)S], 129.2, 130.1, 130.9 [3 x CH signal, aromatic *C*H], 131.6 [1 x C signal, d, $^{4}J_{CF}$ 3.1, aromatic *C*], 132.5 [1 x CH signal, d, $^{3}J_{CF}$ 9.7, aromatic *C*H], 133.9 [1 x CH signal, *C*(3)H], 138.6, 138.8, 145.2, 148.1 [4 x C signal, 4 x aromatic *C* or 3 x aromatic *C* and *C*(2)S], 166.7 [1 x C signal, d, ^{1}J 258.8, aromatic *C*], 191.7 [1 x C signal, *C*O].

Characteristic Z-40aa signals: δ_c (125 MHz, $CDCl_3$): 28.9 [CH_3, aromatic *C*H_3], 59.1 [CH_2, S*C*H_2], 116.1 [1 x CH signal, d, $^{2}J_{CF}$ 22.2, aromatic *C*H], 123.2 [1 x CH signal, aromatic *C*H], 126.0 [1 x C signal, aromatic *C* or *C*(2)S], 129.6, 130.5, 130.8 [3 x CH signals, aromatic *C*H], 133.2 [1 x CH signal, d, $^{3}J_{CF}$ 9.7, aromatic *C*H], 133.5 [1 x C signal, d, $^{4}J_{CF}$ 3.1, aromatic *C*], 140.2 [1 x CH signal, *C*(3)H], 191.3 [1 x C signal, *C*O].

2-((4-Chlorobenzyl)sulfinyl)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40x



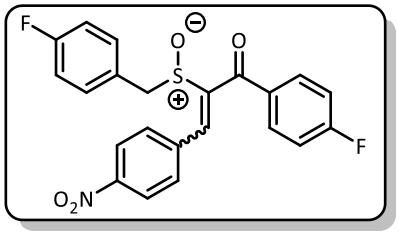
2-(4-Chlorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one **27** (0.03 g, 0.03 mmol, 1 eq), in acetone (7 mL) and a solution of Oxone® (0.05 g, 0.16 mmol, 2.1 eq) in water (2.5 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h.** The solution was stirred at 35°C for 7.5 h and following work-up, the crude oxidised chalcone was isolated as a yellow oil with the presence of some yellow solids. ^{1}H NMR spectroscopy showed this product to contain 90.9% chalcone as a mixture of isomers *Z*-**40x** and *E*-**40x** (Z:E; 10.4 : 1) along with residual starting material *Z*-**27** (*Z* isomer, 7.6%) and tentatively assigned sulfone **S69** (1.5%, s, δ_H 4.58 ppm). The crude mixture was purified by column chromatography on silica gel using dichloromethane as eluent to give the pure sulfoxide (0.026 g, 76%) as an off-white to yellow solid. The sulfoxide was collected as a mixture of isomers *Z*-**40x** and *E*-**40x** (Z:E; 6.7 : 1) which could not be separated using column chromatography.

Z-40x: υ_{max}/cm^{-1} (neat) 1657 cm^{-1} (C=O), 1519 (NO_2), 1049 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 4.43 [1H, A of AB system, J_{AB} 11.9, one of SCH_2], 4.82 [1H, B of AB system, J_{AB} 11.9, one of SCH_2], 7.13 [2H, d, *J* 8.8, aromatic *H*], 7.17 – 7.24 [5H, m, containing (7.21, 1H, s, C(3)*H*) and aromatic *H*], 7.25 – 7.32 [2H, m, aromatic *H*], 8.07 [2H, dd, *J* 8.8, J_{FH} 5.3, aromatic *H*], 8.10 [2H, d, *J* 8.8, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.8 [CH_2, S*C*H_2], 116.2 [1 x CH signal, d, $^{2}J_{CF}$ 22.1, aromatic *C*H], 123.4 [1 x CH signal, aromatic *C*H], 127.6 [1 x C signal, aromatic *C* or *C*(2)S], 129.1, 130.4,

132.1 [3 x CH signal, aromatic *C*H], 133.2 [1 x CH signal, d, $^{3}J_{CF}$ 9.9, aromatic *C*H], 133.3 [1 x C signal, d, $^{4}J_{CF}$ 2.6, aromatic *C*], 135.0, 137.8 [2 x C signal, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 140.4 [1 x CH signal, *C*(3)H], 143.7, 148.0 [2 x C signals, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 166.7 [1 x C signal, d, $^{1}J_{CF}$ 257.8, aromatic *C*], 191.1 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{22}H_{15}{}^{35}ClFNO_4S$ [M+H$^+$] 444.046711. Found 444.04692.

Characteristic E-40x signals: δ_H (500 MHz, $CDCl_3$): 4.14 [1H, A of AB system, J_{AB} 13.2, one of SC*H*$_2$], 4.35 [1H, B of AB system, J_{AB} 13.2, one of SC*H*$_2$], 7.89 [2H, dd, *J* 8.8, J_{FH} 5.3, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.5 [CH_2, S*C*H$_2$], 116.6 [1 x CH signal, d, $^{2}J_{CF}$ 22.1, aromatic *C*H], 123.9 [1 x CH signal, aromatic *C*H], 191.8 [1 x C signal, *C*O].

2-((4-Fluorobenzyl)sulfinyl)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40z



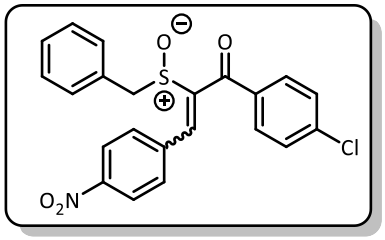
2-((4-Fluorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one **28** (0.06 g, 0.13 mmol, 1 eq) in acetone (8 mL) and a solution of Oxone® (0.08 g, 0.27 mmol, 2.1 eq) in water (2.5 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h.** The solution was stirred at 35°C for 7.5 h and following work-up, the crude sulfoxide was isolated as a yellow oil. ^{1}H NMR spectroscopy showed this product to contain 92.6% chalcone as a mixture of isomers *Z*-**40z** and *E*-**40z** (Z:E; 7 : 1) as well as residual starting material *Z*-**28** (*Z* isomer, 1.5%) and tentatively assigned sulfone **S70** (5.9%, s, δ_H 4.59 ppm). The crude sulfoxide was purified by column chromatography on silica gel using dichloromethane as eluent to give the pure sulfoxide (0.039g, 70%) as a yellow semi-solid. The pure sulfoxide was collected as a mixture of isomers *Z*-**40z** and *E*-**40z** (Z:E; 5.8 : 1) which could not be separated using column chromatography.

Z-40z: υ_{max}/cm^{-1} (neat) 1657 cm^{-1} (C=O), 1507 (NO_2), 1040 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 4.45 [1H, A of AB system, J_{AB} 12.4, one of SC*H*$_2$], 4.84 [1H, B of AB system, J_{AB} 12.4, one of SC*H*$_2$], 6.96 [2H, dd that appears as t, *J* 8.3, aromatic *H*], 7.12 [2H, d, *J* 8.3, aromatic *H*], 7.18 – 7.25 [3H, m, containing (7.25, 1H, s, C(3)*H*) and aromatic *H*], 7.36 [2H, dd, *J* 8.6, J_{FH} 5.3, aromatic *H*], 8.05 – 8.17 [4H, m, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.5 [CH_2, S*C*H$_2$], 116.0 [1 x CH signal, d, $^{2}J_{CF}$ 22.3, aromatic *C*H], 116.2 [1 x CH signal, d, $^{2}J_{CF}$ 22.3, aromatic *C*H], 123.4 [1 x CH signal, aromatic *C*H], 125.0 [1 x C signal, d, $^{4}J_{CF}$ 3.5, aromatic *C*], 130.4 [1 x CH signal, aromatic *C*H],

132.6 [1 x CH signal, d, $^{3}J_{CF}$ 8.5, aromatic *C*H], 133.2 [1 x CH signal, d, $^{3}J_{CF}$ 8.8, aromatic *C*H], 133.4 [1 x C signal, d, $^{4}J_{CF}$ 2.8, aromatic *C*], 137.9 [1 x C signal, aromatic *C*], 140.4 [1 x CH signal, *C*(3)H], 143.7 [1 x C signal, *C*(2)S], 148.0 [1 x C signal, aromatic *C*], 163.0 [1 x C signal, d, $^{1}J_{CF}$ 248.6, aromatic *C*], 166.6 [1 x C signal, d, $^{1}J_{CF}$ 257.8, aromatic *C*], 191.3 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{22}H_{15}F_2NO_4S$ [M+H$^+$] 428.0763. Found 428.0764.

Characteristic E-40z signals: δ_H (500 MHz, $CDCl_3$): 4.15 [1H, A of AB system, J_{AB} 13.3, one of SC*H*$_2$], 4.36 [1H, B of AB system, J_{AB} 13.3, one of SC*H*$_2$], 7.89 [2H, dd, *J* 9.0, J_{FH} 5.3, aromatic *H*], 8.03 [2H, d, *J* 9.0, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.4 [CH_2, S*C*H$_2$], 115.4 [1 x CH signal, d, $^{2}J_{CF}$ 21.6, aromatic *C*H], 116.6 [1 x CH signal, d, $^{2}J_{CF}$ 21.6, aromatic *C*H], 123.9, 130.1 [2 x CH signals, aromatic *C*H].

2-(Benzylsulfinyl)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40o



2-(Benzylthio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one **23** (0.03 g, 0.07 mmol, 1 eq) in acetone (10 mL) and a solution of Oxone® (0.05 g, 0.18 mmol, 2.6 eq) in water (5 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **40h.** The solution was stirred for 9.5 h at 30°C and following work-up, the crude oxidised chalcone was isolated as a yellow semi-solid. ^{1}H NMR spectroscopy showed this product to contain 87% chalcone as a mixture of isomers *Z*-**40o** and *E*-**40o** (Z:E; 3.9 : 1) along with unreacted starting material *Z*-**23** (*Z* isomer, 13%). The crude mixture was purified by column chromatography on silica gel using dichloromethane as eluent to give the pure sulfoxide (0.021 g, 73%) as an off-white to yellow solid. The pure product was collected as mixture of isomers *Z*-**40o** and *E*-**40o** (Z:E; 1 : 1.6) which could not be separated using column chromatography.

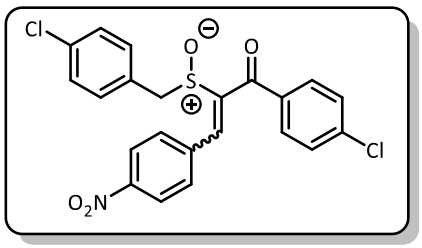
υ_{max}/cm^{-1} (neat) 1650 cm^{-1} (C=O), 1506 (NO_2), 1040 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 4.16 [1H, A of AB system, J_{AB} 13.3, *E* isomer, one of SCH_2], 4.38 [1H, B of AB system, J_{AB} 13.3, *E* isomer, one of SC*H*$_2$], 4.45 [1H, A of AB system, J_{AB} 12.3, *Z* isomer, one of SC*H*$_2$], 4.94 [1H, B of AB system, J_{AB} 12.3, *Z* isomer, one of SC*H*$_2$], 6.96 [2H, d, *J*, *Z* isomer, *J* 8.4, aromatic *H*], 7.08 [1H, s, *E* isomer, C(3)*H*], 7.21 – 7.42 [16H, m, *E* and *Z* isomer, containing (7.25, 1H, s, *Z* isomer, C(3)*H*] and aromatic *H*], 7.51 [1H, d, *Z* isomer, *J* 8.6, aromatic *H*], 7.77 [2H, d, *E* isomer, *J* 8.6, aromatic

H], 7.96 [2H, d, *Z* isomer, *J* 8.6, aromatic *H*], 8.02 [2H, d, *E* isomer, *J* 8.8, aromatic *H*], 8.03 [2H, d, *Z* isomer, *J* 8.8, aromatic *H*]; m/z (ES+): 424.1 [($C_{23}H_{18}FNO_4S$)+H^+], 5%.

E-40o δc (125 MHz, $CDCl_3$): 59.6 [CH_2, S*C*H_2], 123.9 [1 x CH signal, aromatic *C*H], 128.1 [1 x C signal, aromatic *C*], 128.4, 129.0, 129.5, 130.1, 130.9, 131.0 [6 x CH signals, aromatic *C*H], 133.4 [1 x C signal, aromatic *C*], 134.4 [1 x CH signal, *C*(3)H], 138.7, 141.8 [2 x C signals, aromatic *C*], 144.7 [1 x C signal, *C*(2)S], 148.0 [1 x C signal, aromatic *C*], 192.1 [1 x C signal, *C*O].

Characteristic Z-40o signals: δ_c (125 MHz, $CDCl_3$): 59.3 [CH_2, S*C*H_2], 123.3 [1 x CH signal, aromatic *C*H], 128.7, 128.8 [2 x CH signals, aromatic *C*H], 129.1 [1 x C signal, aromatic *C*], 129.2, 130.5, 130.9, 131.7 [4 x CH signals, aromatic *C*H], 135.4, 137.9 [2 x C signals, aromatic *C*], 140.9 [1 x CH signal, *C*(3)H], 141.1 [1 x C signal, aromatic *C*], 143.5 [1 x C signal, *C*(2)S], 191.8 [1 x C signal, *C*O].

2-((4-Chlorobenzyl)sulfinyl)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40q



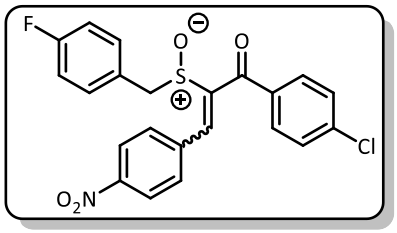
2-((4-Chlorobenzyl)thio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one **24** (0.03 g, 0.07 mmol, 1 eq) in acetone (10 mL) and a solution of Oxone® (0.09 g, 0.3 mmol, 4.4 eq) in water (10 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h**. The solution was stirred for 4 h at room temperature and following work-up, the crude oxidised chalcone was isolated as a yellow residue. The ^{1}H NMR spectrum of the crude product showed only 28% conversion to the desired product. A solution of mCPBA (0.02 g, 0.07 mmol, 1 eq) in dichloromethane (10 mL) was added to the crude material and the solution was stirred at room temperature for 1 h. After 1 h, the solution was quenched with saturated aqueous sodium bicarbonate (10mL). The aqueous layer was extracted with dichloromethane (2 x 10 mL). The combined organic layers were washed with water (2 x 10 mL) and brine (10 mL), dried over magnesium sulfate, filtered and concentrated to give the crude sulfoxide as a yellow residue. ^{1}H NMR spectroscopy showed this product to contain approximately 52% *Z*-chalcone *Z*-**40q** along with tentatively assigned sulfone **S71** (48%, s, δ_H 4.62 ppm). The crude sulfoxide was purified by column chromatography on silica gel using dichloromethane as eluent to give the pure *Z*-sulfoxide *Z*-**40q** (0.016 g, 56.4%) as an

off-white solid. On storage for 6 months at -20°C, the mixture isomerised to *Z*:*E* 1:3.5 prior to characterisation.

E-40q: υ_{max}/cm^{-1} (neat) 1651 cm^{-1} (C=O), 1519 (NO_2); δ_H (500 MHz, $CDCl_3$): 4.13 [1H, A of AB system, J_{AB} 13.1, one of SC*H*$_2$], 4.34 [1H, B of AB system, J_{AB} 13.1, one of SC*H*$_2$], 7.07 [1H, s, C(3)*H*], 7.22 – 7.31 [6H, m, aromatic *H*], 7.36 [2H, d, *J* 8.7, aromatic *H*], 7.78 [2H, d, *J* 8.7, aromatic *H*], 8.04 [2H, d, *J* 8.7, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.6 [CH_2, S*C*H$_2$], 124.0 [1 x CH signal, aromatic *C*H], 126.4 [1 x C signal, aromatic *C* or *C*(2)S], 128.6, 129.6, 130.1, 131.0, 132.4 [5 x CH signals, aromatic *C*H], 133.3 [1 x C signal, aromatic *C* or *C*(2)S], 134.4 [1 x CH signal, *C*(3)H], 134.8, 138.5, 142.0, 144.3, 148.1 [5 x C signals, 5 x aromatic *C* or 4 x aromatic *C* and *C*(2)S], 192.2 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{22}H_{15}{}^{35}Cl_2NO_4S$ [M+H$^+$] 460.0172. Found 460.0173.

Characteristic Z-40q signals: δ_H (500 MHz, $CDCl_3$): 4.44 [1H, A of AB system, J_{AB} 12.3, one of SC*H*$_2$], 4.82 [1H, B of AB system, J_{AB} 12.3, one of SC*H*$_2$], 7.51 [2H, d, *J* 8.9, aromatic *H*], 7.96 [2H, d, *J* 8.7, aromatic *H*], 8.10 [2H, d, *J* 8.9, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.8 [CH_2, S*C*H$_2$], 129.1, 129.3, 130.4, 131.7, 132.1 [5 x CH signals, aromatic *C*H].

1-(4-Chlorophenyl)-2-((4-fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)prop-2-en-1-one 40s



1-(4-Chlorophenyl)-2-((4-fluorobenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one **26** (0.03 g, 0.06 mmol, 1 eq) in acetone (5 mL) and a solution of Oxone® (0.04 g, 0.14 mmol, 2.1 eq) in water (10 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one **40h.** The solution was stirred for 23 h at room temperature and following work-up, the crude oxidised chalcone was isolated as a yellow oily solid. ^{1}H NMR spectroscopy showed this product to contain 82% chalcone as a mixture of isomers *Z*-**40s** and *E*-**40s** (Z:E; 4.8 : 1) along with 18% unreacted starting material *Z*-**26**. The crude mixture was purified by column chromatography on silica gel using dichloromethane as eluent to give the pure *Z*-sulfoxide *Z*-**40s** (0.010 g, 38.7%) as an off-white solid and the pure *E*-sulfoxide *E*-**40s** (0.0031, 11.7%) as a white solid. On storage for 6 months at -20°C, the *Z*-sulfoxide Z-**40s** isomerised to *Z*:*E* 7:1 prior to final characterisation.

Z-40s: υ_{max}/cm^{-1} (neat) 1657 cm^{-1} (C=O), 1506 (NO_2), 1036 cm^{-1}; δ_H (500 MHz, $CDCl_3$): 4.44 [1H, A of AB system, J_{AB} 12.5, one of SC*H*$_2$], 4.83 [1H, B of AB system, J_{AB} 12.5, one of SC*H*$_2$], 6.96

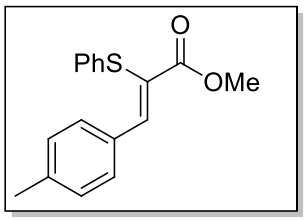
[2H, t, *J* 8.4, aromatic *H*], 7.11 [2H, d, *J* 8.5, aromatic *H*], 7.23 [1H, s, C(3)*H*], 7.35 [2H, dd, *J* 8.7, J_{FH} 5.3, aromatic *H*], 7.52 [2H, d, *J* 8.7, aromatic *H*], 7.96 [2H, d, *J* 8.7, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.5 [CH_2, S*C*H_2], 116.0 [1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.4, aromatic *C*H], 123.4 [1 x CH signal, 2 x aromatic *C*H], 125.0 [1 x C signal, d, $^4J_{CF}$ 2.4, aromatic *C*], 129.3, 130.5, 131.7 [3 x CH signal, 6 x aromatic *C*H], 132.6 [1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.8, aromatic *C*H], 135.3, 137.8 [2 x C signals, 2 x aromatic *C* or aromatic *C* and *C*(2)S], 140.8 [1 x CH signal, *C*(3)H], 141.3, 143.6, 148.1 [3 x C signals, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 163.0 [1 x C signal, d, $^1J_{CF}$ 248.6, aromatic *C*], 191.7 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{22}H_{15}{}^{35}ClFNO_4S$ [M+H$^+$] 444.0467. Found 444.0464.

E-40s: υ_{max}/cm^{-1} (neat) 1651 cm^{-1} (C=O), 1508 (NO_2); δ_H (500 MHz, $CDCl_3$): 4.14 [1H, A of AB system, J_{AB} 13.3, one of SCH_2], 4.34 [1H, B of AB system, J_{AB} 13.3, one of SCH_2], 6.99 [2H, t, *J* 8.7, aromatic *H*], 7.05 [1H, s, C(3)*H*], 7.24 – 7.28 [2H, m, aromatic *H*], 7.30 [2H, dd, *J* 8.7, J_{FH} 5.3, aromatic *H*], 7.36 [2H, d, *J* 8.7, aromatic *H*], 7.79 [2H, d, *J* 8.7, aromatic *H*]; δ_c (125 MHz, $CDCl_3$): 58.5 [CH_2, S*C*H_2], 115.4 [1 x CH signal, 2 x CH , d, $^2J_{CF}$ 21.7. aromatic *C*H], 123.7 [1 x C signal, d, $^4J_{CF}$ 2.9, aromatic *C*], 124.0, 129.6, 130.1, 130.9 [4 x CH signal, 8 x aromatic *C*H], 132.8 [1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.4, aromatic *C*H], 133.3 [1 x C signal, aromatic *C* or *C*(2)S], 134.3 [1 x CH signal, *C*(3)H], 138.5, 142.0, 144.4, 148.1 [4 x C signal, 4 x aromatic *C* or 3 x aromatic *C* and *C*(2)S], 163.0 [1 x C signal, d, $^1J_{CF}$ 248.8, aromatic *C*], 192.2 [1 x C signal, *C*O]; HRMS (ES+): Exact Mass Calculated for $C_{22}H_{15}{}^{35}ClFNO_4S$ [M+H$^+$] 444.0467. Found 444.0469.

1.10 Synthesis of Amide and Ester Derivatives

The following compounds were synthesised following a procedure described by Aguilar-Aguilar and Peña Cabrera.[22]

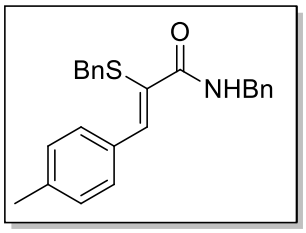
(*Z*)-Methyl 2-(phenylthio)-3-(*p*-tolyl)acrylate 44



This was prepared following the procedure described for **14** using the β-chloroester **41**[28] (200 mg, 0.88 mmol), 4-(tributylstannyl)toluene **36b**[23] (402 mg, 1.05 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude product was obtained as an orange oil which was seen by ^{1}H NMR spectroscopy to be a mixture of product **44** and starting material **41** in a ratio of 1:1.25 respectively. This was purified by column chromatography on silica gel using hexane-ethyl acetate (99:1) as eluent to give the pure *cinnamate* **44** (113 mg, 45 %) as a pale yellow oil; ν_{max}/cm^{-1} (film) 2949 (CH),

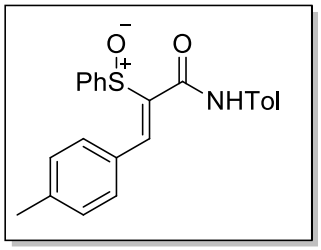
1721 (CO), 1594 (aromatic), 1255; δ_H (400 MHz, $CDCl_3$) 2.37 (3H, s, ArC*H*$_3$), 3.67 (3H, s, OC*H*$_3$), 7.20 (2H, d, *J* 8.1, Ar*H*), 7.21-7.29 (5H, m, Ar*H*), 7.76 (2H, d, *J* 8.2, Ar*H*), 8.13 [1H, s, C(3)*H*]; δ_C (75.5 MHz, $CDCl_3$) 21.5 (CH_3, Ar*C*H$_3$), 52.8 (CH_3, O*C*H$_3$), 123.5 (C, aromatic *C*), 126.2, 128.1, 129.0, 129.2, 131.0 (5 x CH, aromatic *C*H), 131.5, 135.7, 140.7 [3 x C, 3 x aromatic *C* or 2 x aromatic *C* and *C*(2)S], 146.7 [CH, *C*(3)H], 166.9 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{17}H_{17}SO_2$[M+H$^+$] 285.0949. Found 285.0949; m/z (ES+) 285.3 [($C_{17}H_{16}SO_2$)+H$^+$], 15%.

(*Z*)-*N*-Benzyl-2-(benzylthio)-3-(*p*-tolyl)acrylamide 45



This was prepared following the procedure described for **14** using the β-chloroacrylamide **42**[29] (67 mg, 0.21 mmol), 4-(tributylstannyl)toluene **36b**[23] (97 mg, 0.25 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude product was obtained as a brown oil which was seen by ^{1}H NMR analysis to be a mixture of product **45** and starting material **42** in a ratio of 1:8 respectively. This was purified by column chromatography on silica gel using hexane-ethyl acetate (90:10) as eluent to give the pure *acrylamide* **45** (8 mg, 10%) as a pale yellow oil; ν_{max}/cm^{-1} (film) 3350 (NH), 2920 (CH), 1650 (CO), 1577 (aromatic), 1512 (NH bend); δ_H (400 MHz, $CDCl_3$) 2.38 (3H, s, ArC*H*$_3$), 3.74 (2H, s, SC*H*$_2$), 4.43 (2H, d, *J* 5.8, NHC*H*$_2$), 7.06-7.09 (2H, m, Ar*H*), 7.17- 7.36 (10H, m, Ar*H*), 7.51 (1H, br s, N*H*), 7.75 (2H, d, *J* 8.2, Ar*H*), 8.16 [1H, s, C(3)*H*]; δ_C (75.5 MHz, $CDCl_3$) 21.5 (CH_3, Ar*C*H$_3$), 39.3 (CH_2, S*C*H$_2$), 44.4 (CH_2, NH*C*H$_2$), 125.1 (C, aromatic C), 127.4, 127.5, 127.8, 128.6, 128.7, 128.8, 129.1, 130.7 (8 x CH, aromatic *C*H), 132.0, 137.1, 138.1, 140.0 [4 x C, 4 x aromatic *C* or 3 x aromatic *C* and *C*(2)S], 144.4 [CH, *C*(3)H], 165.7 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{24}H_{24}SNO$[M+H$^+$] 374.1579. Found 374.1585; m/z (ES+) 374.4 [($C_{24}H_{23}SNO$)+H$^+$], 42%.

(*Z*)-2-(Phenylsulfinyl)-*N*,3-di-*p*-tolylacrylamide 46

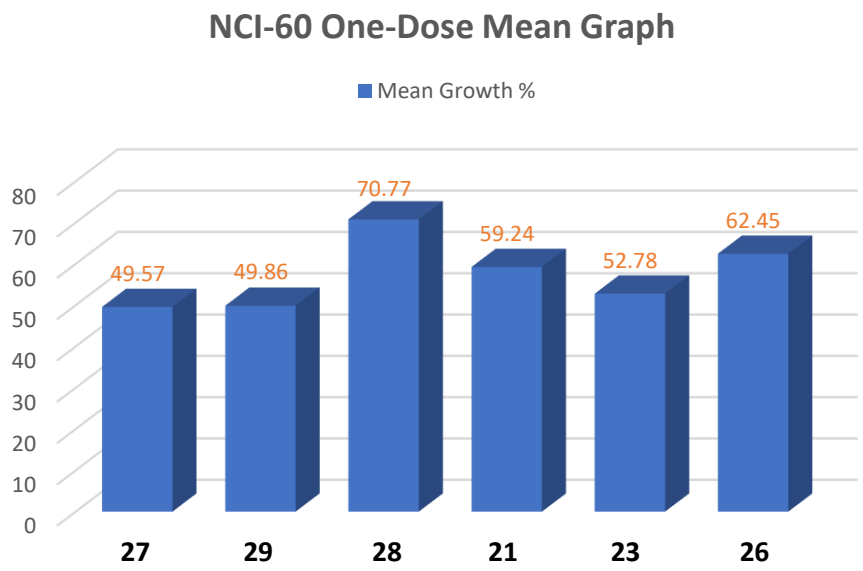


This was prepared following the procedure described for **14** using the sulfoxide **43**[30] (200 mg, 0.63 mmol), 4-(tributylstannyl)toluene **36b**[23] (286 mg, 0.75 mmol) and $(CH_3CN)_2PdCl_2$ (5%) in anhydrous acetonitrile (5 mL). The crude product was obtained as a yellow oil which was seen by ^{1}H NMR analysis to contain a mixture of

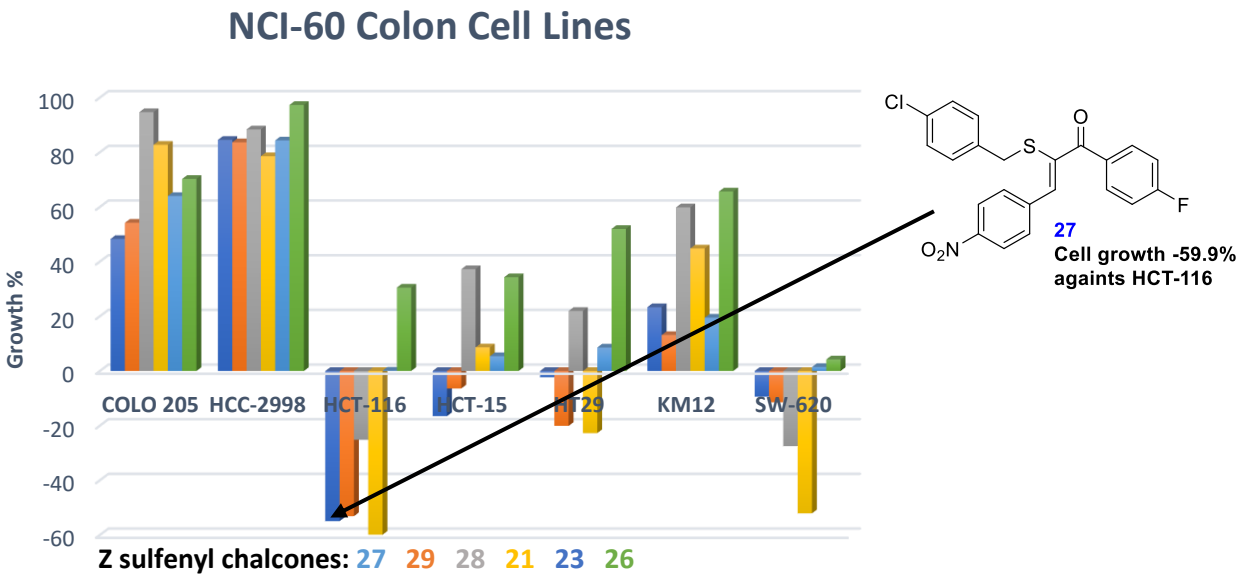
product **46** and starting material **43** in a ratio of 1.6:1 respectively. This was purified by column chromatography on silica gel using hexane-ethyl acetate (90:10) as eluent to give the pure *sulfoxide* **46** (139 mg, 59%) as a pale yellow solid. A sample was further recrystallised from methanol for crystal structure determination; mp 155-157 °C (after recrystallisation from methanol); Found (C, 73.54; H, 5.63; N, 3.71. $C_{23}H_{21}SNO_2$ requires C, 73.57; H, 5.64; N, 3.73%); ν_{max}/cm^{-1} (KBr) 3249 (NH), 2922 (CH), 1674 (CO), 1609 (aromatic), 1553 (NH bend); δ_H (400 MHz, $CDCl_3$) 2.28 (3H, s, ArCH_3), 2.42 (3H, s, ArCH_3), 7.07 (2H, d, *J* 8.0, Ar*H*), 7.27 (2H, d, *J* 8.0, Ar*H*), 7.32-7.48 (5H, m, Ar*H*), 7.59 (4H, d, *J* 8.0, Ar*H*), 8.34 [1H, s, C(3)*H*], 10.25 (1H, br s, N*H*); δ_C (75.5 MHz, $CDCl_3$) 20.1 (CH_3, Ar*C*H_3), 21.6 (CH_3, Ar*C*H_3), 120.6, 124.3, 129.4, 129.6, 129.7, 131.0, 131.1 (7 x CH, aromatic *C*H), 133.7, 134.1, 135.2, 141.5, 141.6 [5 x C, 5 x aromatic *C* or 4 x aromatic *C* and *C*(2)S], 147.6 [CH, *C*(3)H], 161.3 (C, *C*O); HRMS (ES+): Exact mass calculated for $C_{23}H_{22}SNO_2$[M+H^+] 376.1371. Found 376.1370; m/z (ES+) 376.3 [($C_{23}H_{21}SNO_2$)+H^+], 100%. Crystal Data: $C_{23}H_{21}NO_2S$, *M* = 375.47, monoclinic, *a* = 18.730(3) Å, *b* = 16.251(3) Å, *c* = 13.6888(19) Å, β = 103.468(5), *V* = 4052.0(12) $Å^3$, *T* = 300(2) K, space group *C*2/c, *Z* = 8, 13317 reflections measured, 3824 unique (R_{int} = 0.0599). The final R_1 values were 0.0518 ($I > 2\sigma(I)$) and 0.1056 (all data). The final $wR(F^2)$ values were 0.1104 ($I > 2\sigma(I)$) and 0.1308 (all data).

1.11 Biological evaluation of *Z* sulfenyl chalcones and *E*-sulfinyl chalcones

1.11.1 Biological evaluation of *Z* sulfenyl chalcones

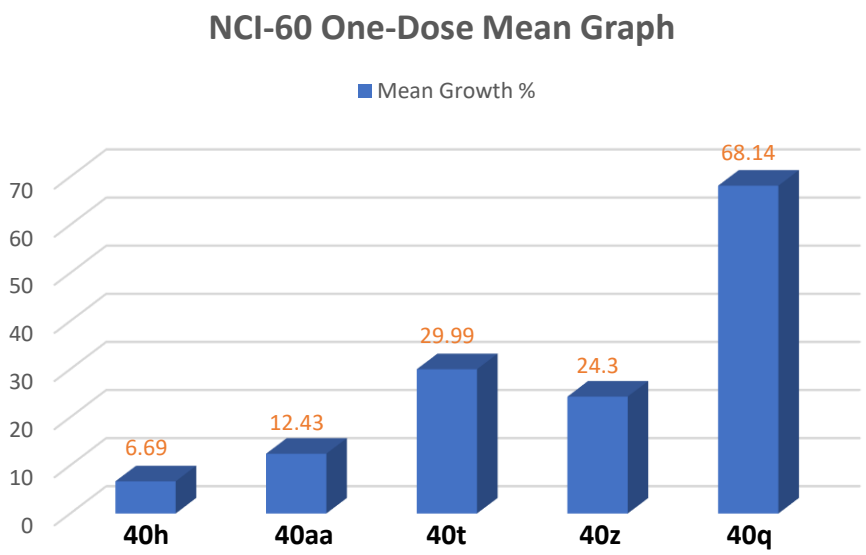


Graph 1: NCI-60 one-dose (10µM) mean cell growth of *Z* sulfenyl chalcones **27**, **29**, **28**, **21**, **23** and **26** across 60 cancer cell lines.

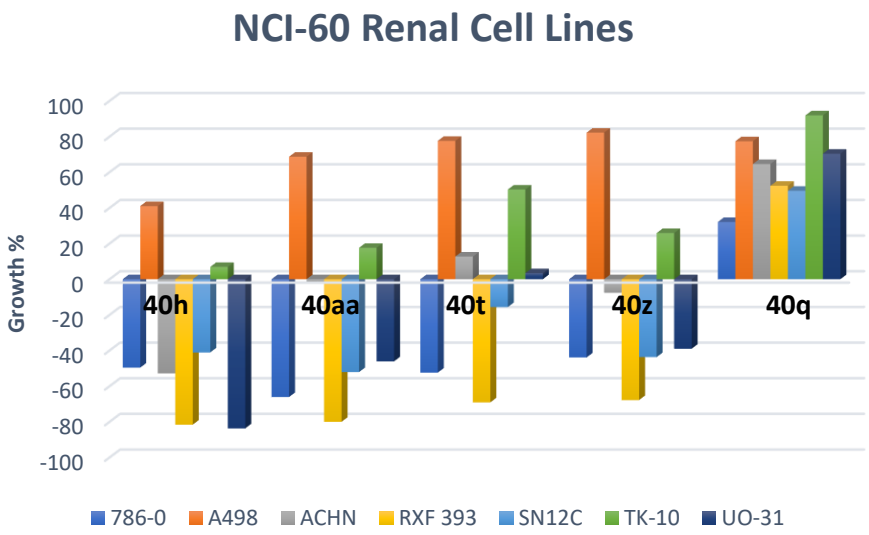


Graph 2: NCI-60 one-dose (10 µM) cell growth of *Z* sulfenyl chalcones against colon cell lines

1.11.2 Biological evaluation of *E* sulfinyl chalcones



Graph 3: NCI-60 one-dose (10µM) mean cell growth of *E* sulfinyl chalcones **40h**, **40aa**, **40t**, **40z** and **40q** against 60 cancer cell lines.



Graph 4: NCI-60 one-dose (10 µM) cell growth of *E* sulfinyl chalcones **40h**, **40aa**, **40t**, **40z** and **40q** against renal cell lines.

The following compounds were progressed for five-dose screening: **21**, **23**, **26**, **27**, **29** (*Z* sulfenyl chalcones) and **40h**, **40aa**, **40z**, **40t** (*E* sulfinyl chalcones).

1.12 ^{1}H and ^{13}C NMR spectra for compounds

1.12.1 α-Chloroketones:

2-Chloro-1-(*p*-tolyl)propan-1-one S1[1]

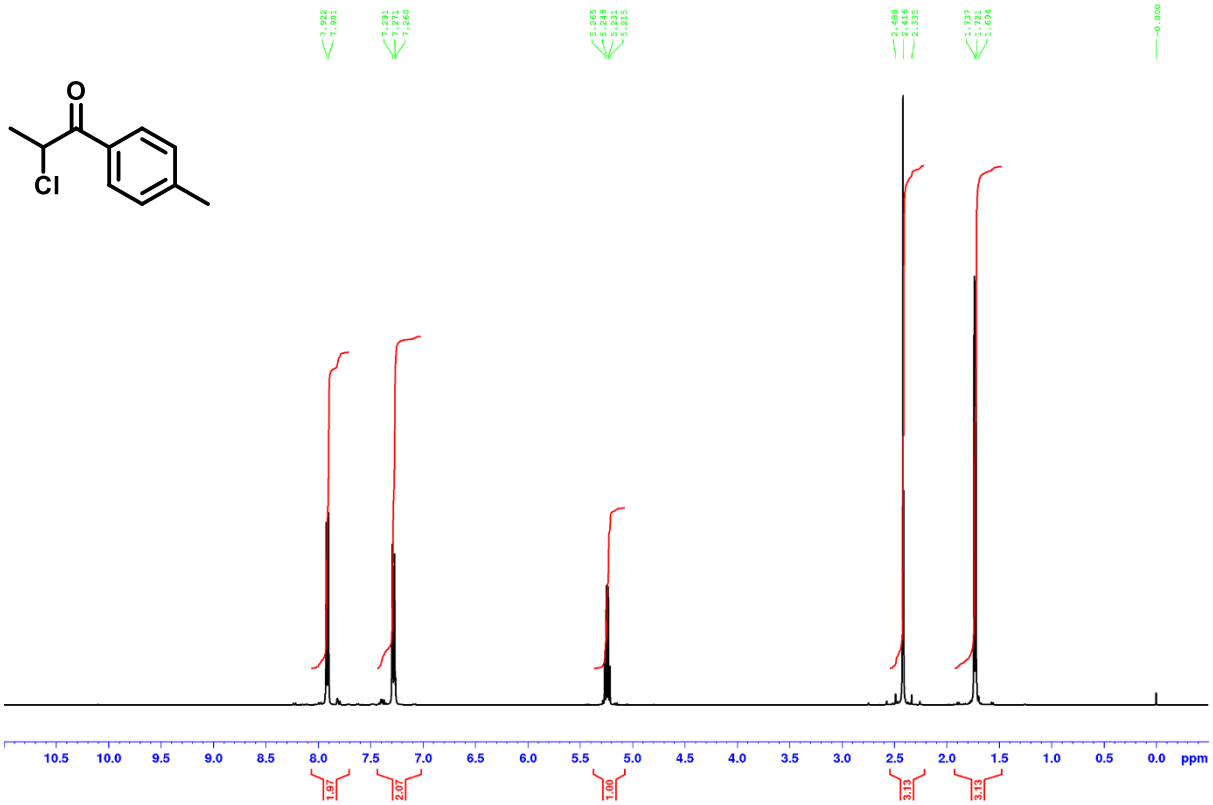


Figure S1: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S1**.

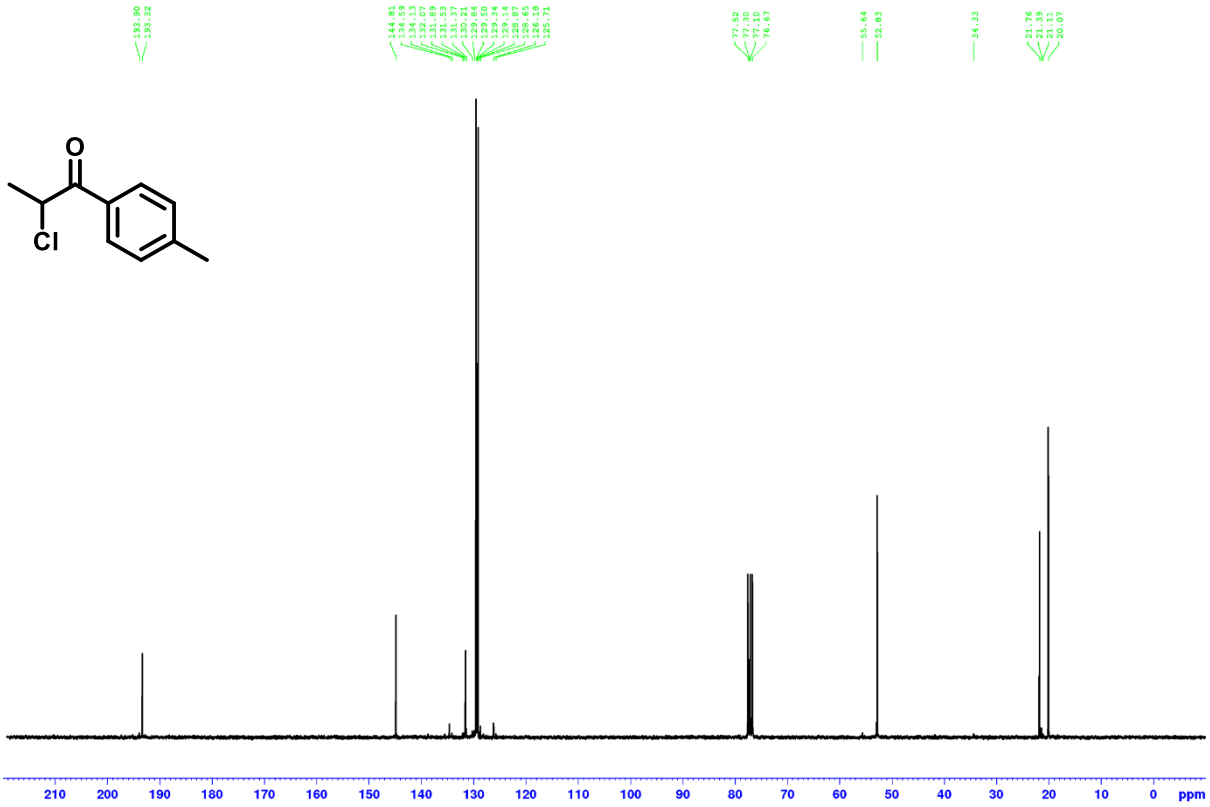


Figure S2: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **S1**.

2-Chloro-1-(4-chlorophenyl)propan-1-one S2[1, 3]

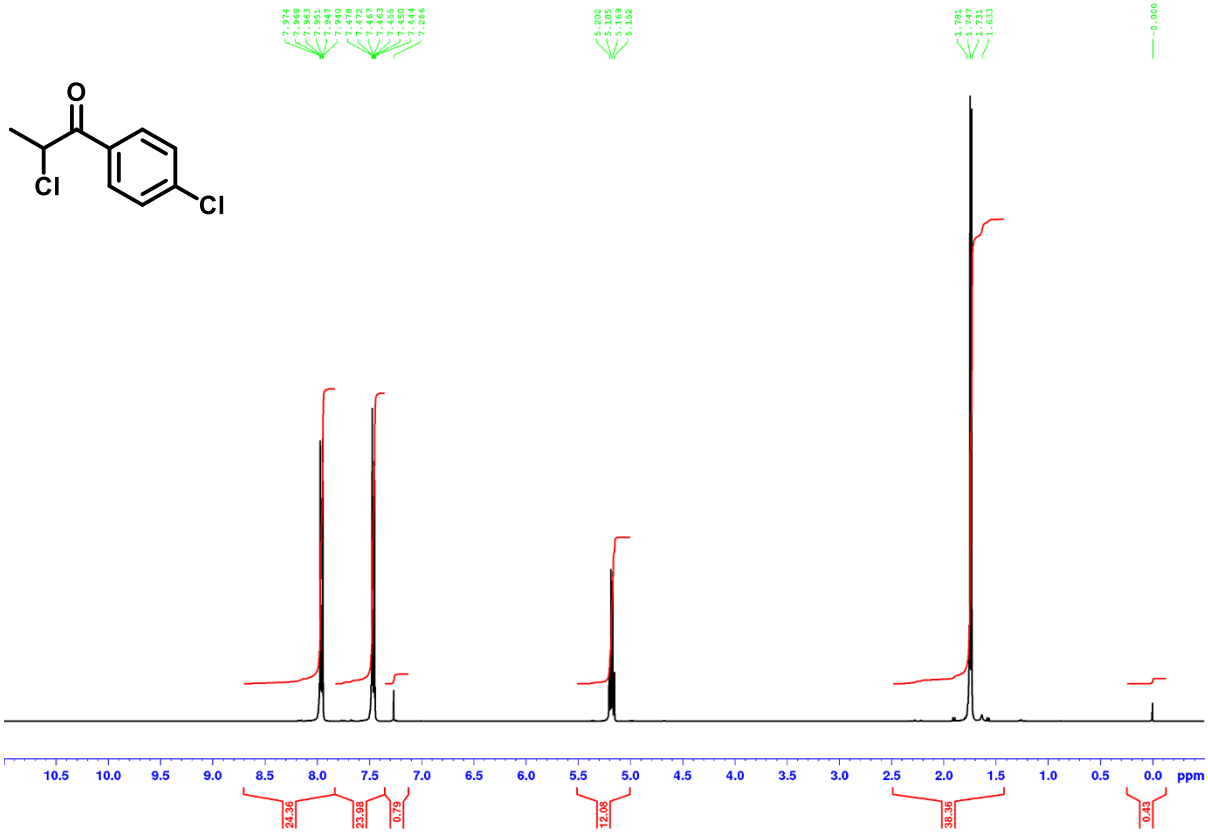


Figure S3: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S2**.

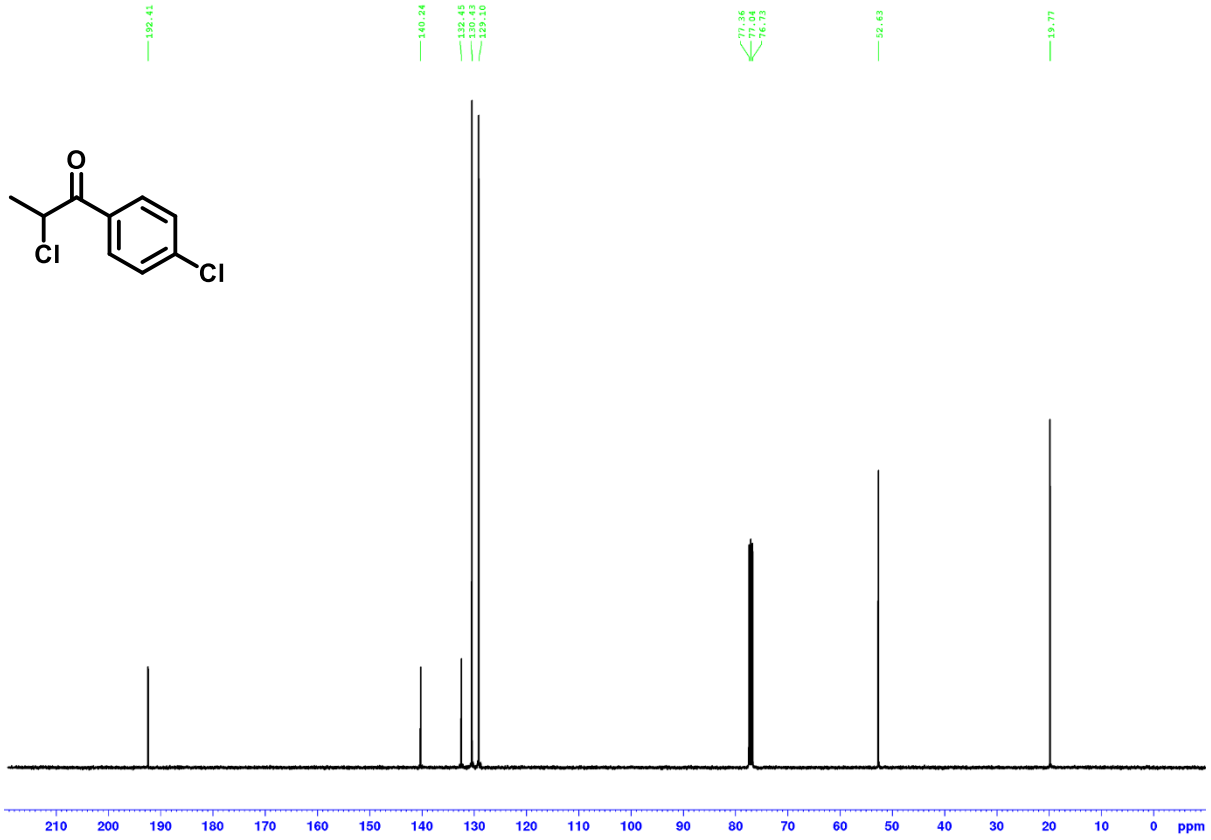


Figure S4: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S2**.

2-Chloro-1-(4-fluorophenyl)propan-1-one S3[4]

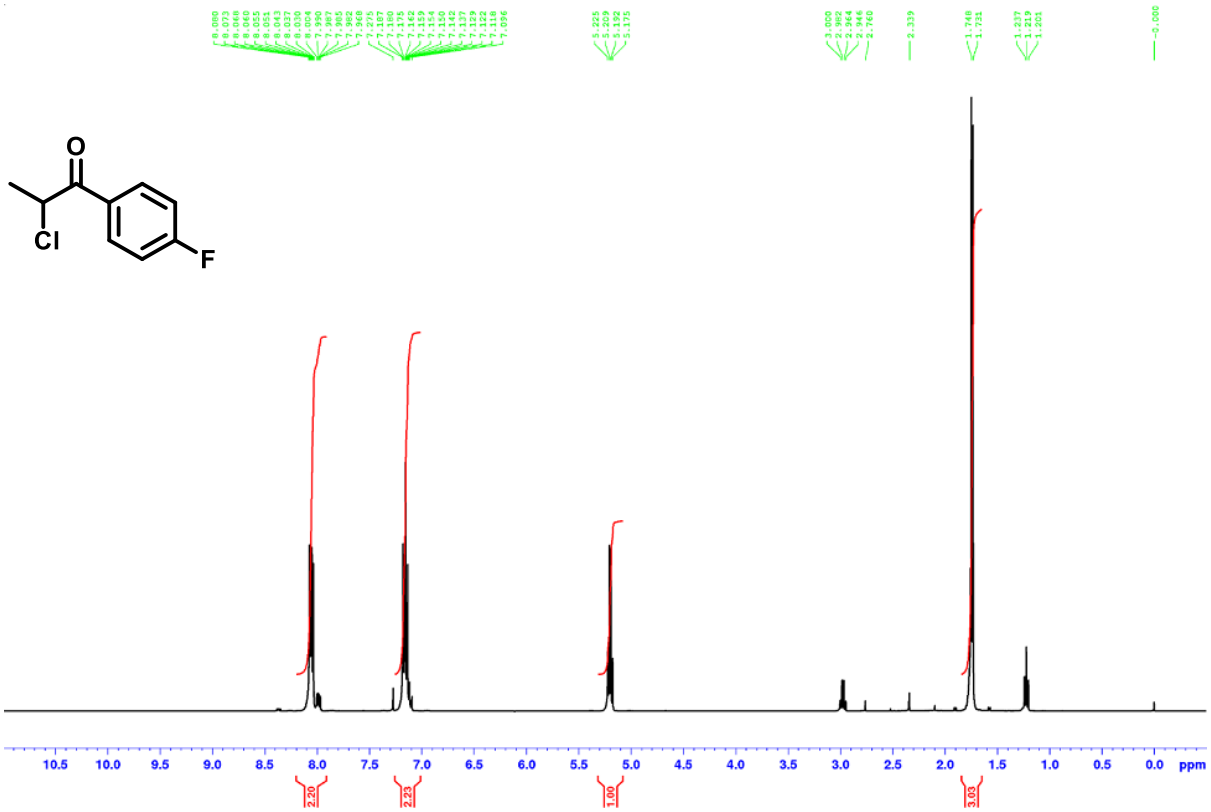


Figure S5: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S3**.

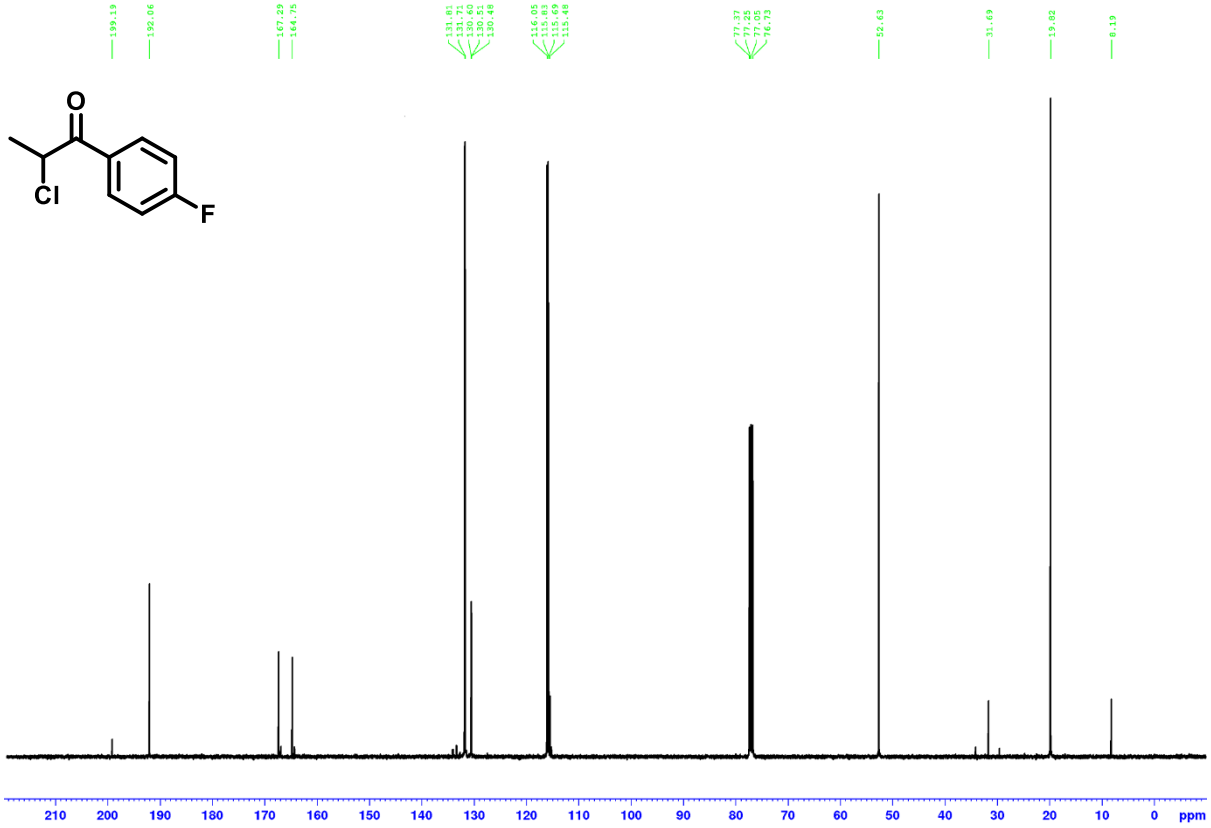


Figure S6: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S3**.

2-Chloro-1-(4-methoxyphenyl)propan-1-one S4[2, 5]

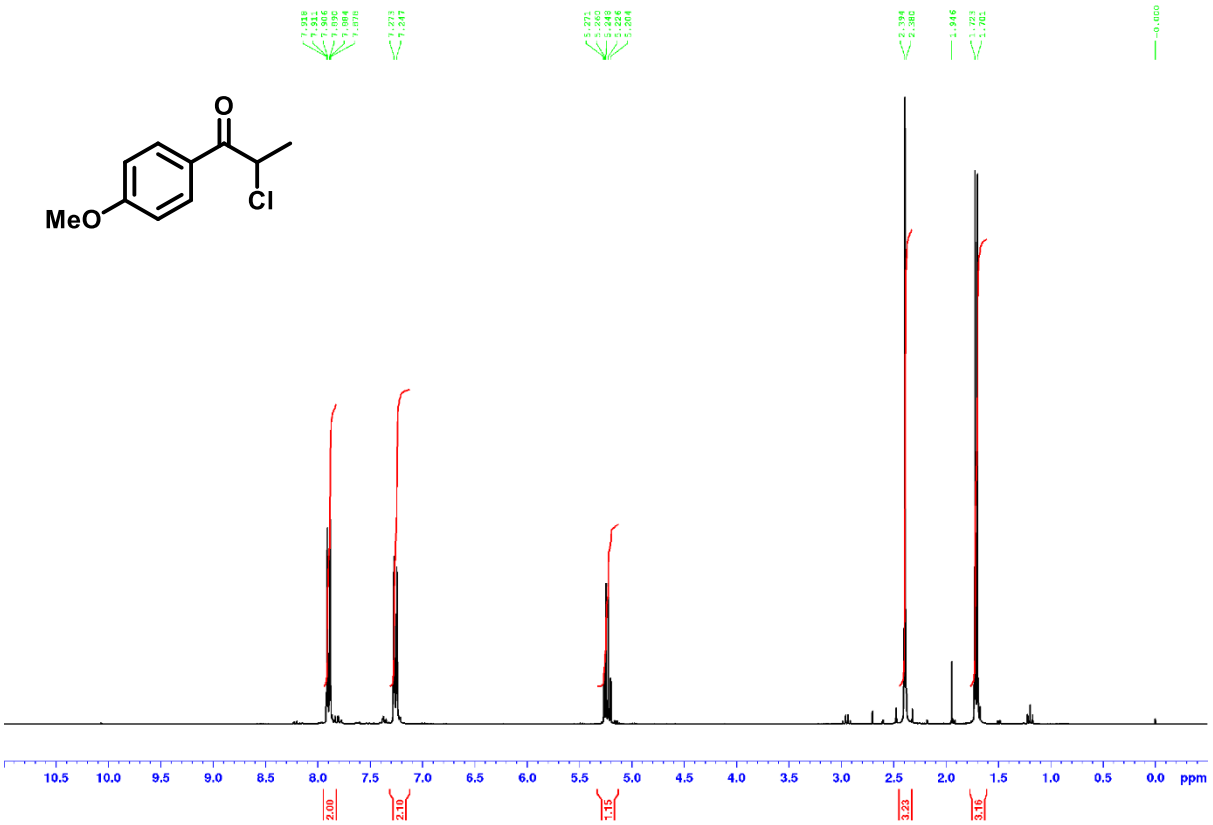


Figure S7: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S4**.

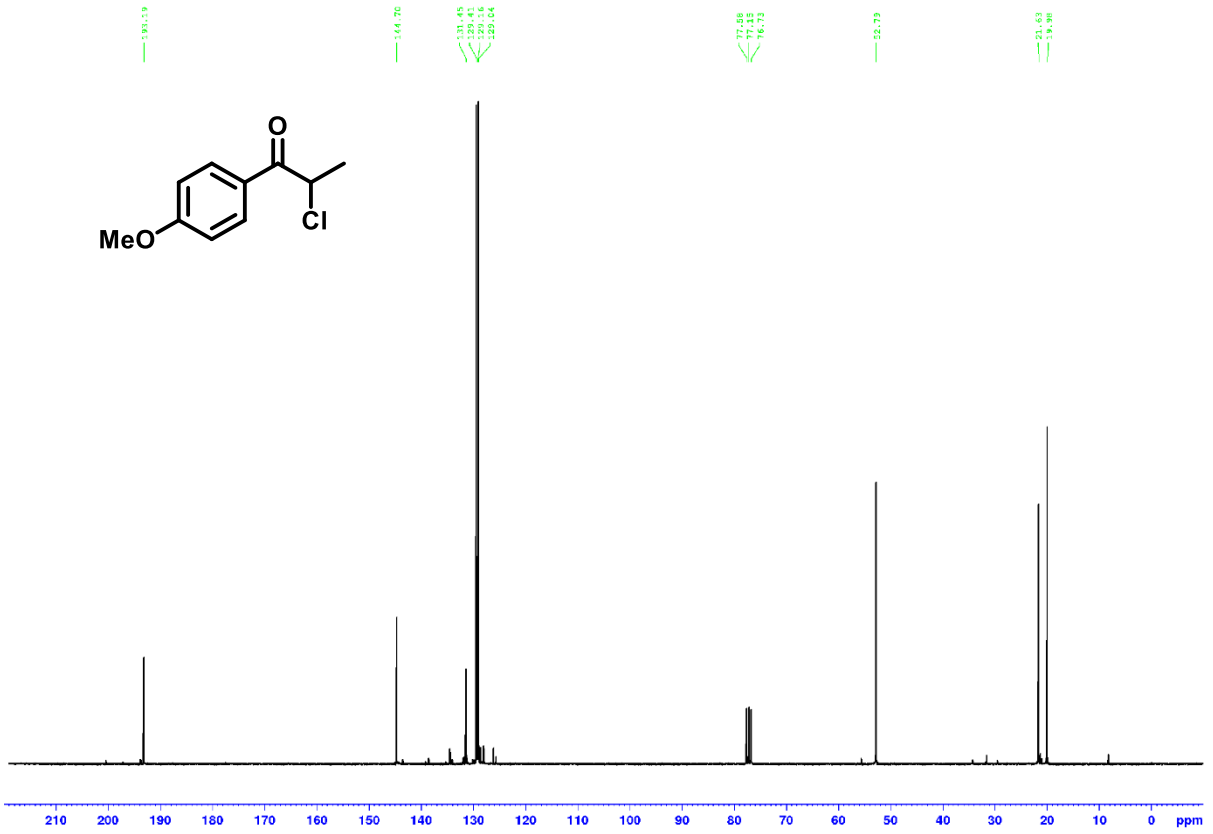


Figure S8: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **S4**.

2-Chloropentan-3-one S5[6]

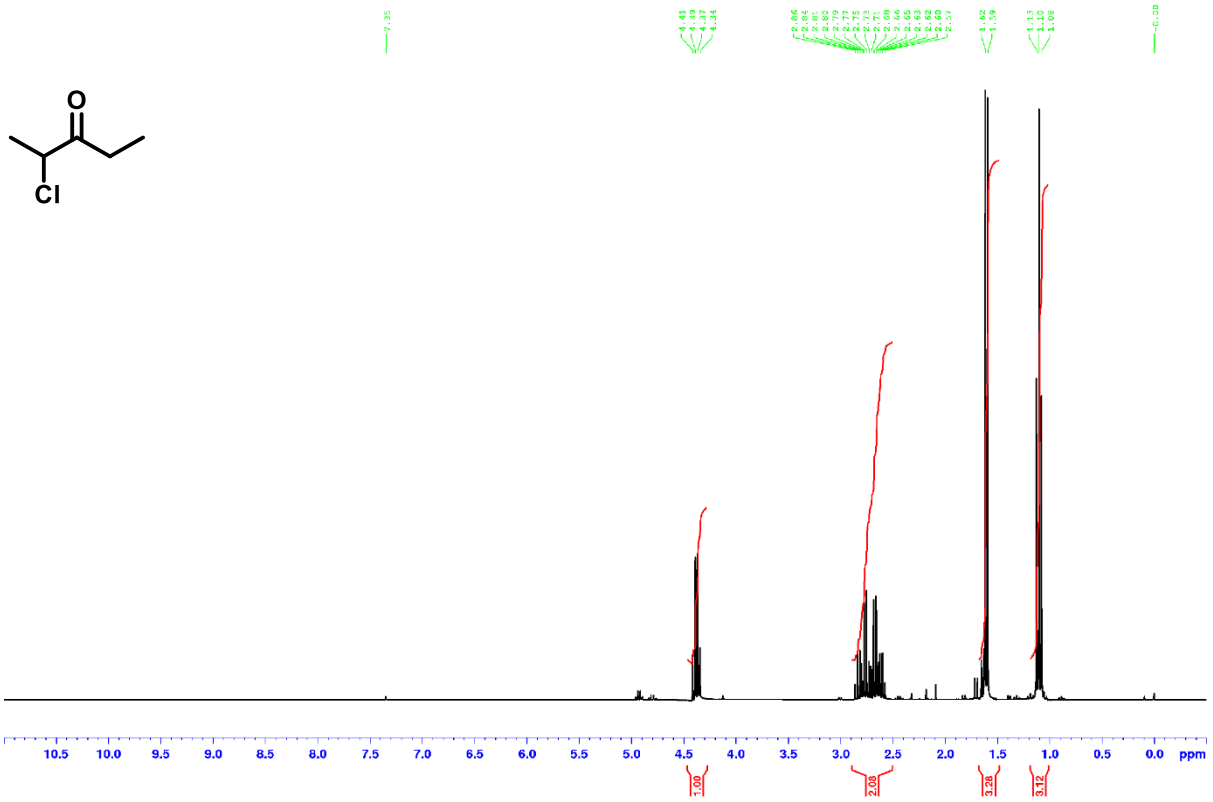


Figure S9: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S5**.

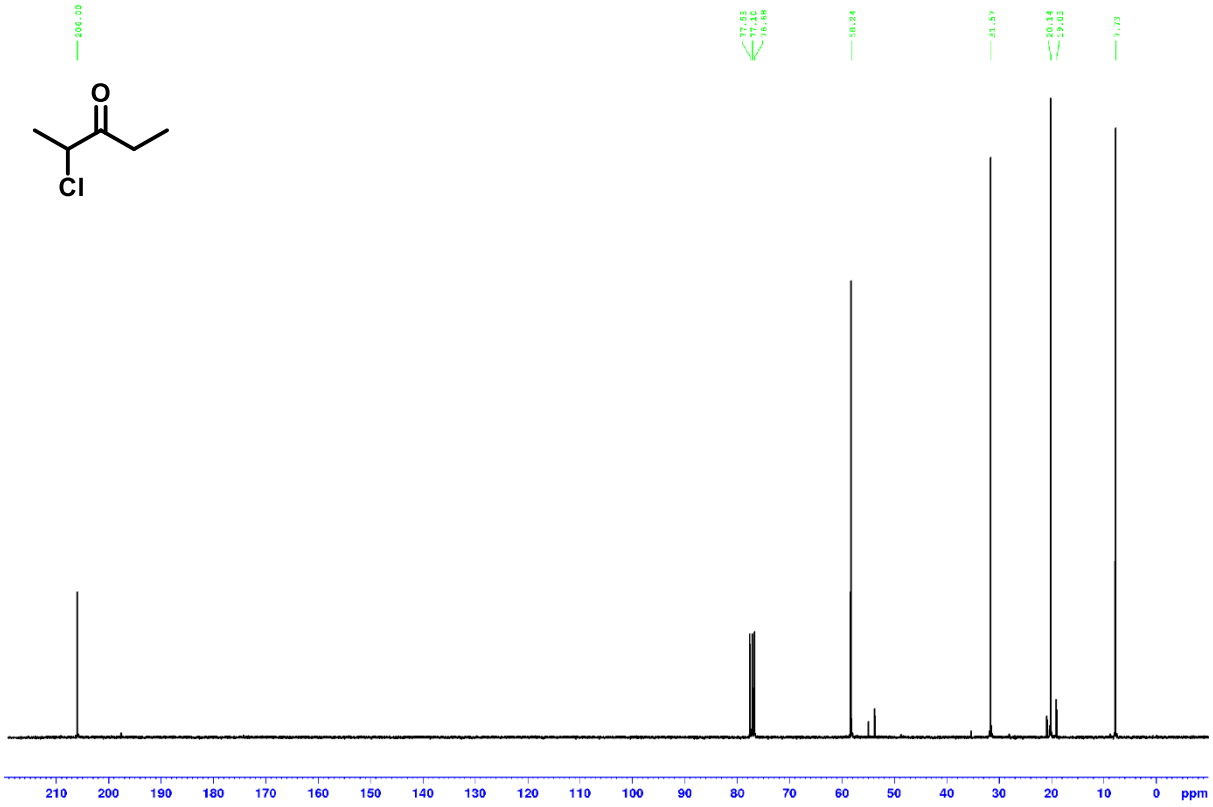


Figure S10: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **S5**.

2-Chloro-1-phenylbutan-1-one S6[7]

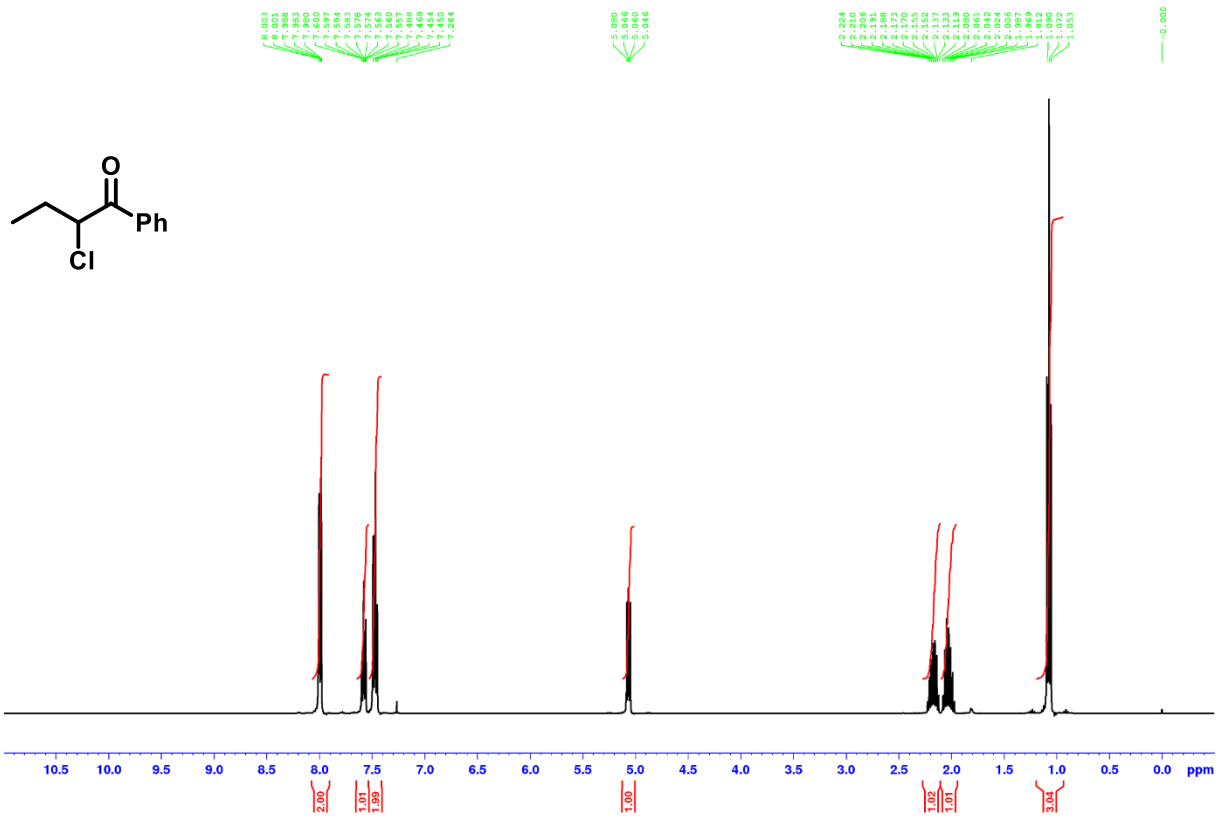


Figure S11: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S6.**

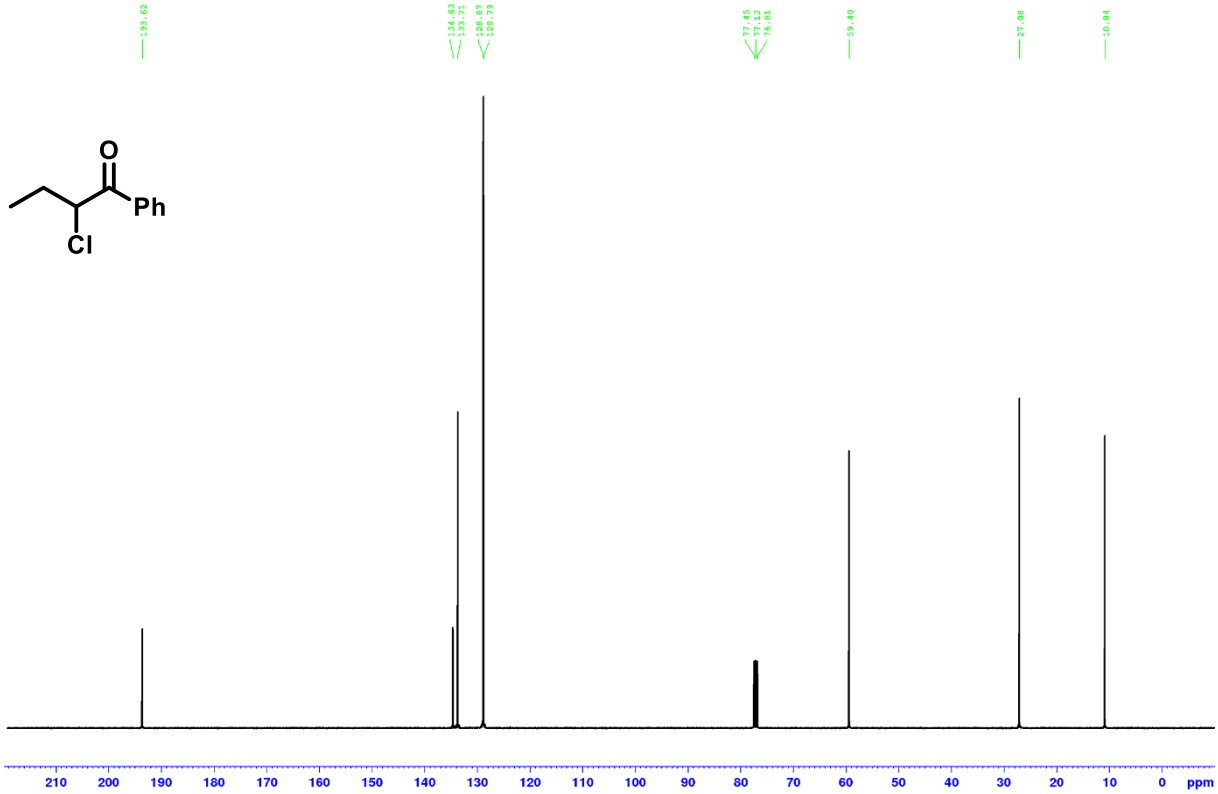


Figure S12: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S6**.

2-Chloro-1-phenylpentan-1-one S7[8]

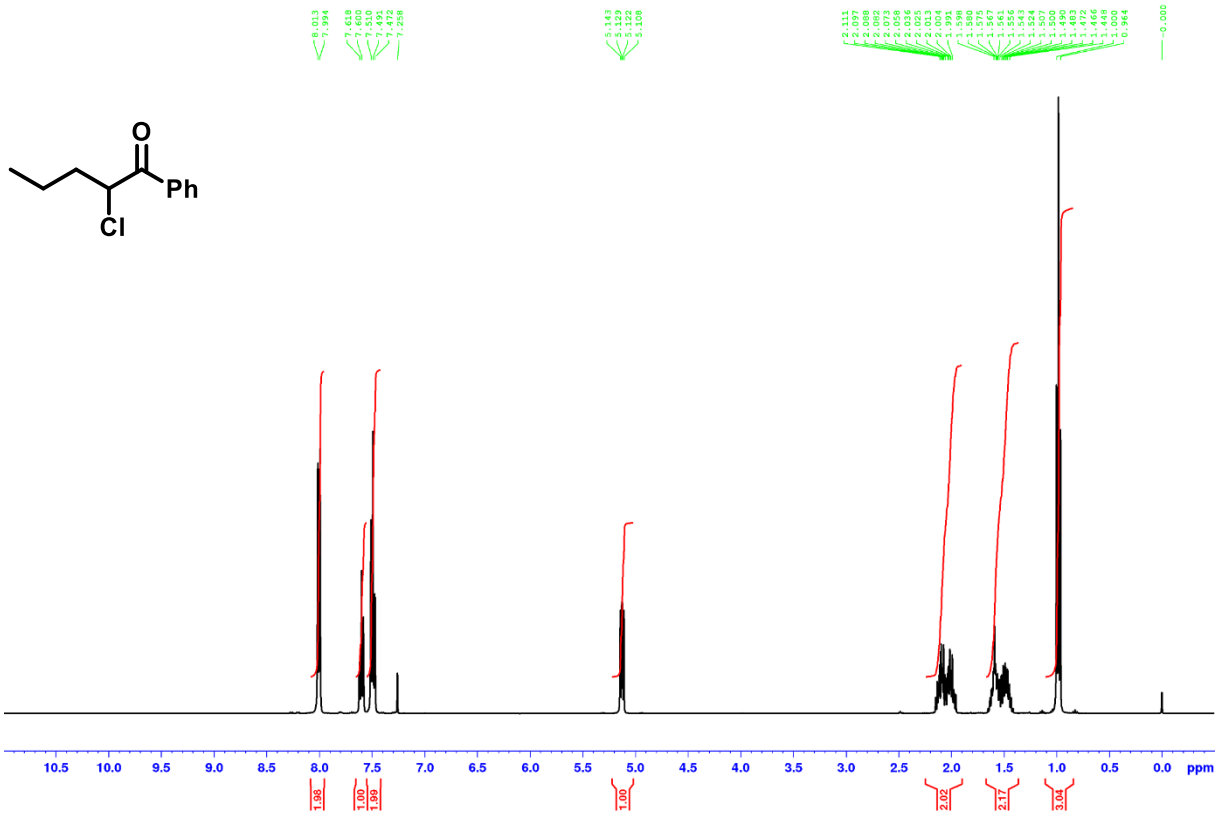


Figure S13: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S7**.

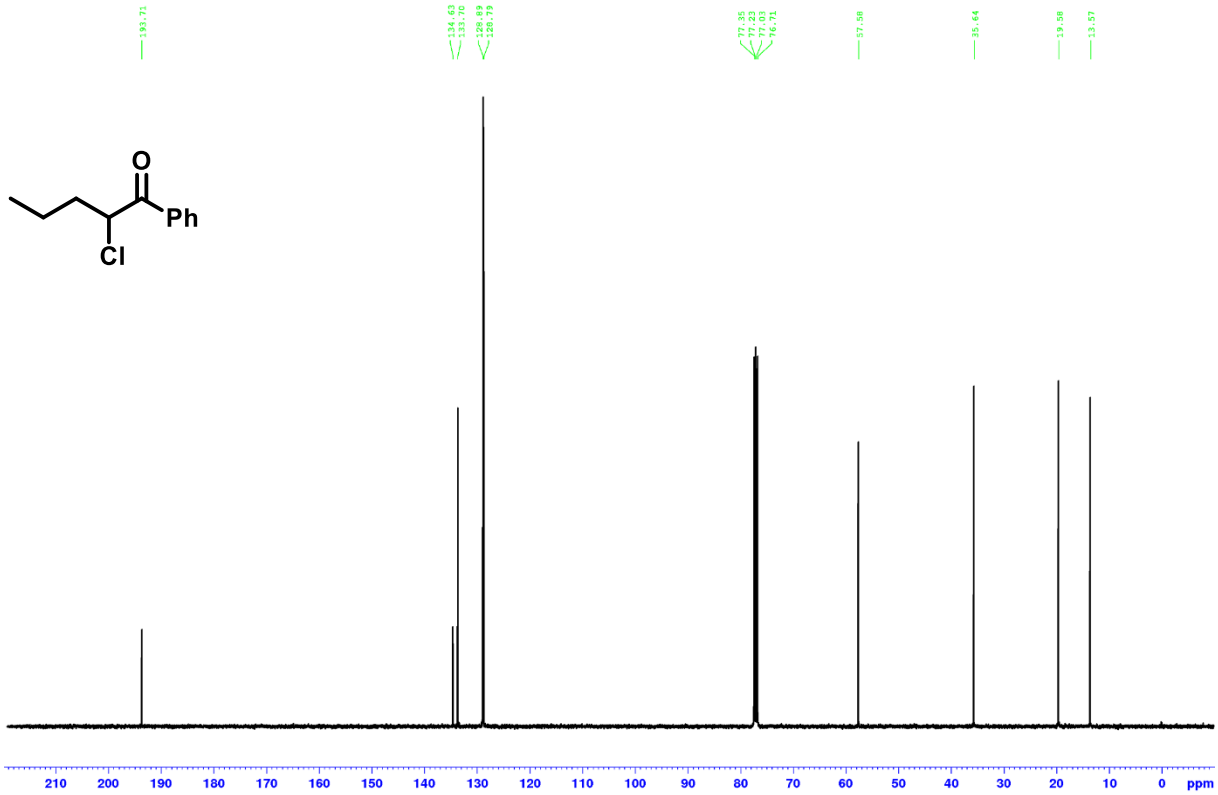


Figure S14: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S7**.

3-Chloro-4-phenylbutan-2-one S8[3]

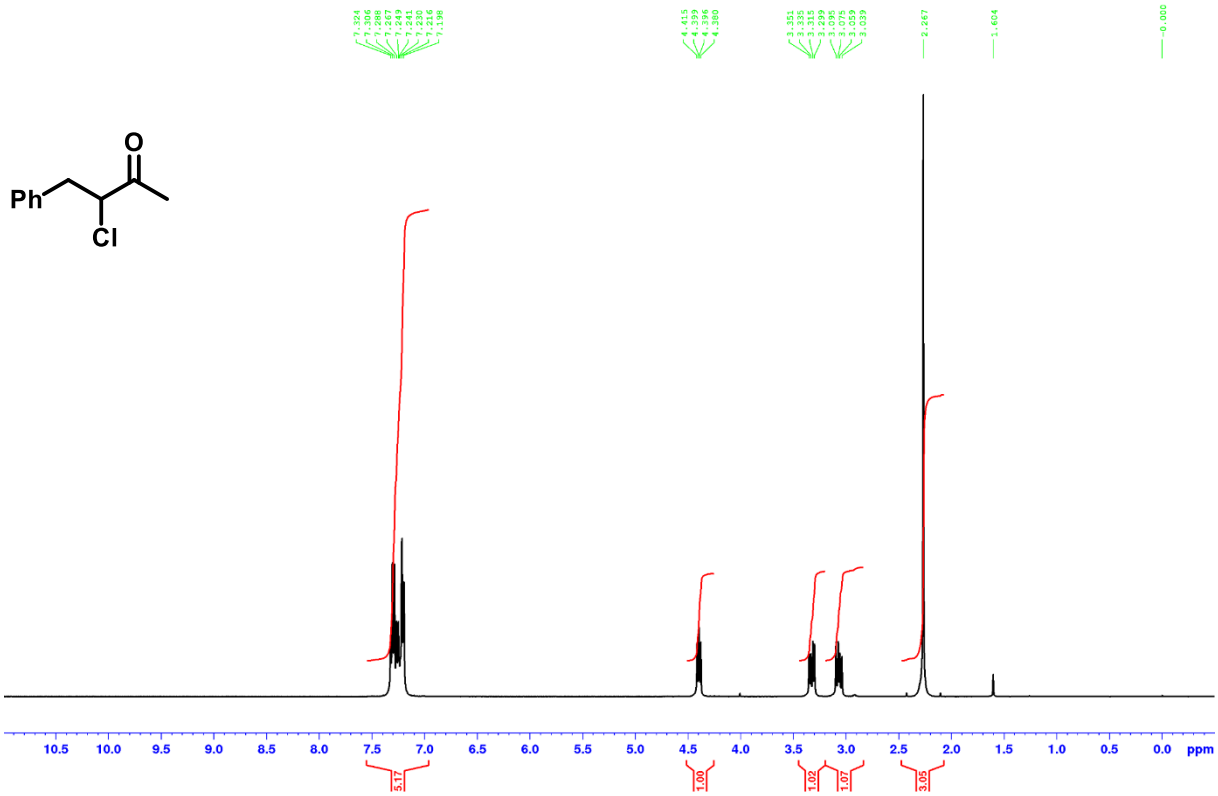


Figure S15: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S8**.

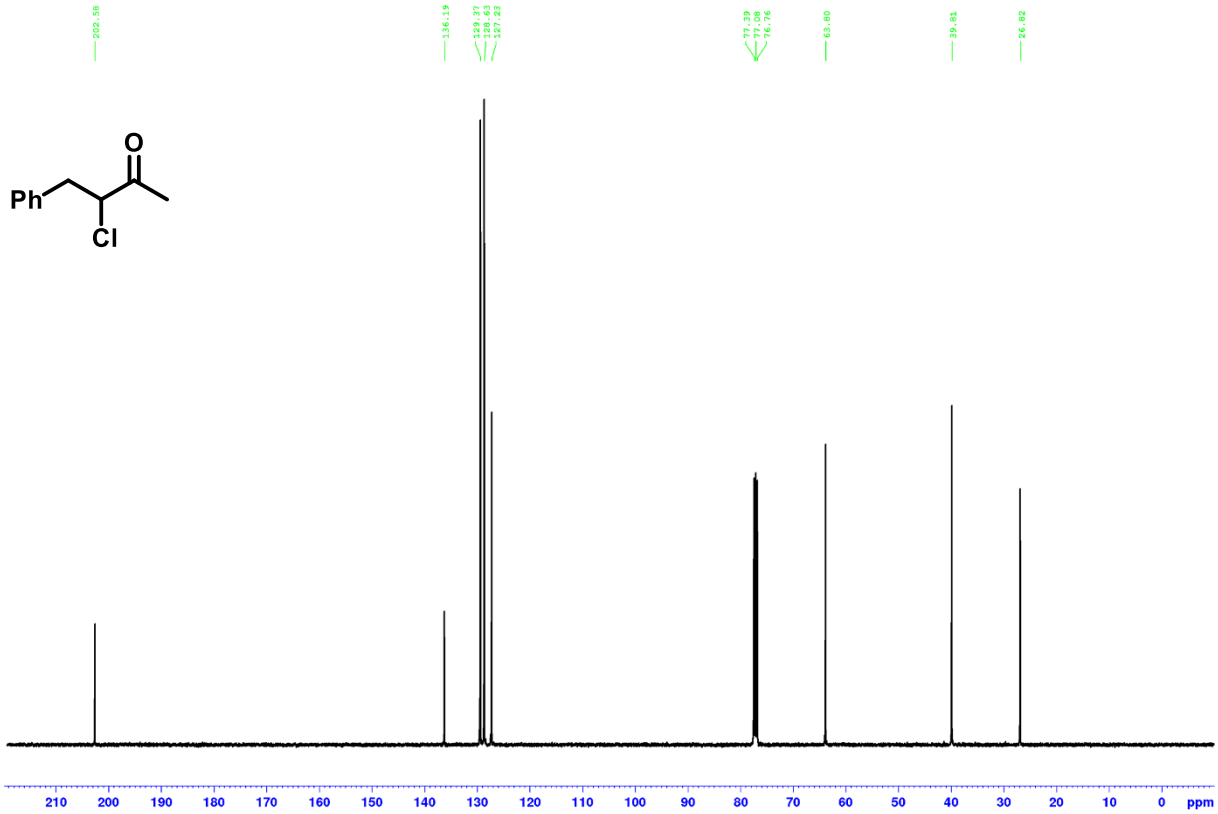


Figure S16: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S8**.

1.12.2 α-Sulphenylketones

1-Phenyl-2-(phenylthio)propan-1-one 3a[10]

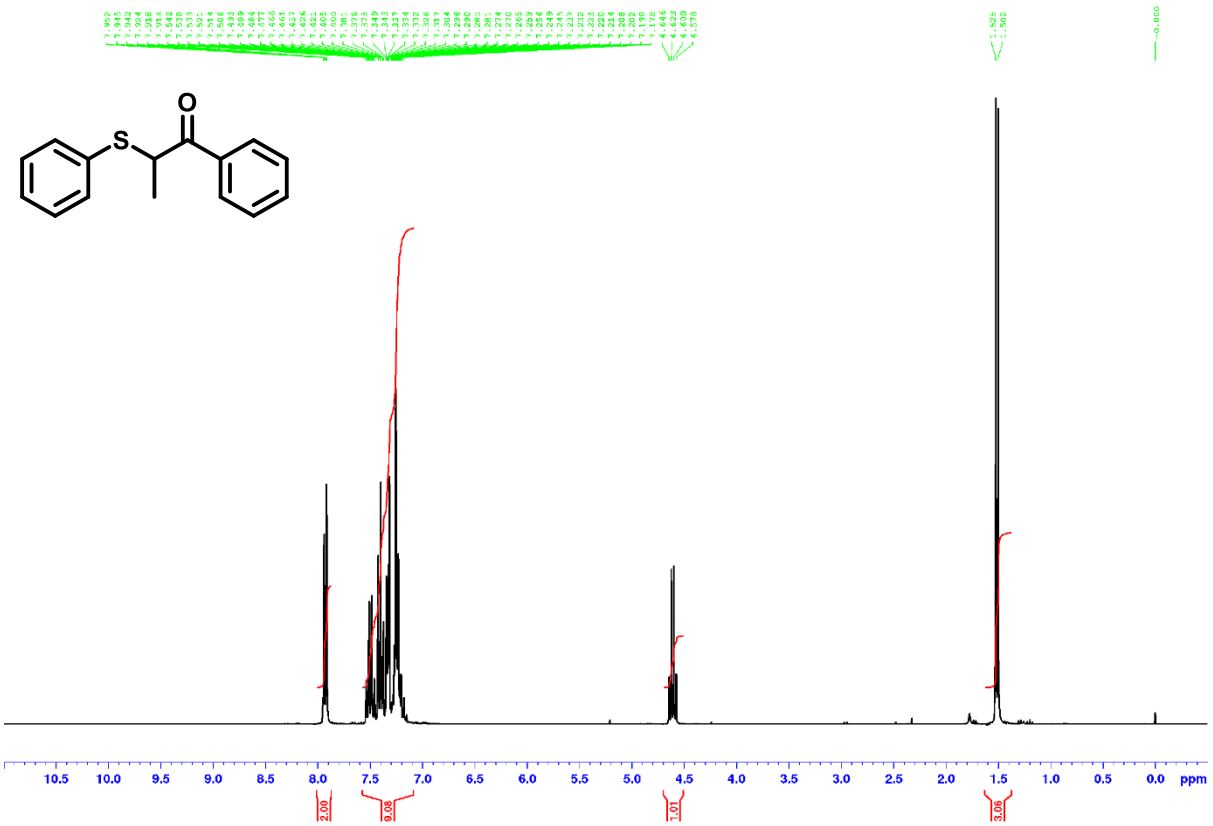


Figure S17: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3a**.

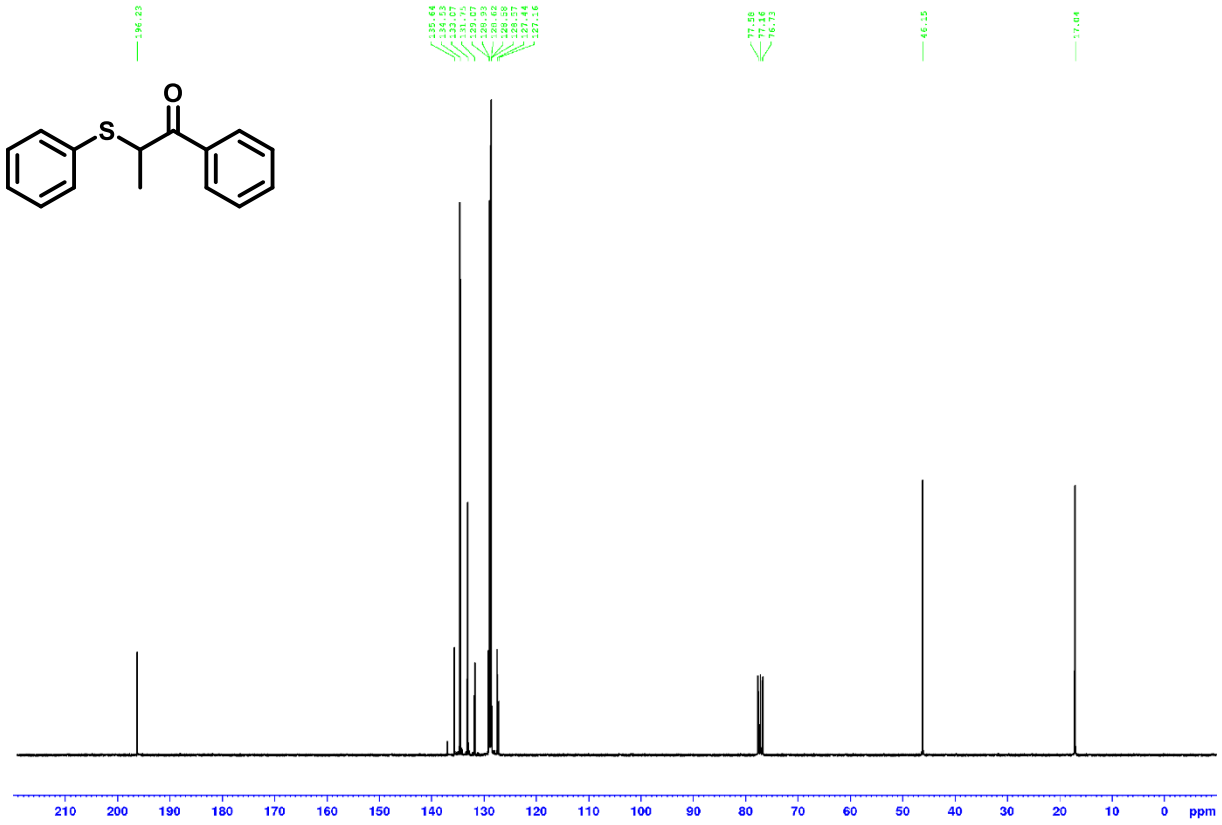


Figure S18: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3a**.

2-(Benzylthio)-1-phenylpropan-1-one 3b[11]

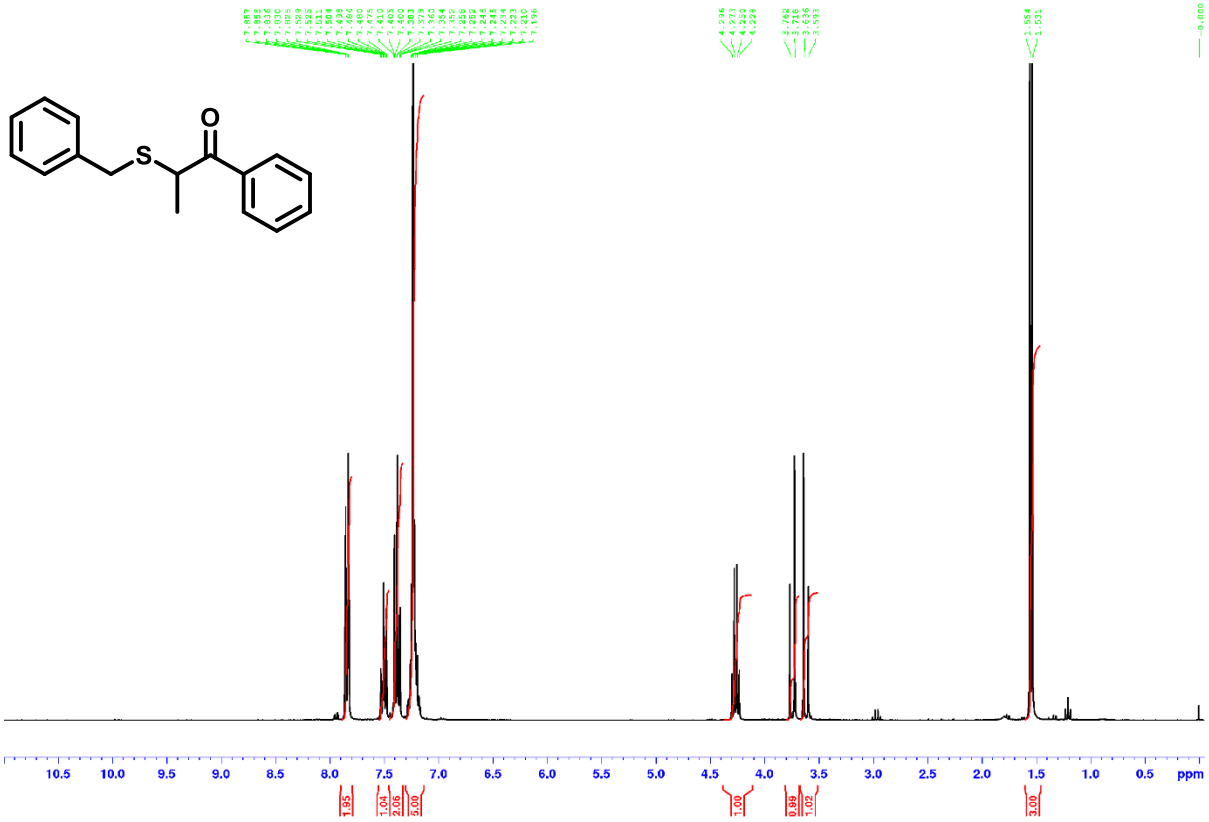


Figure S19: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3b**.

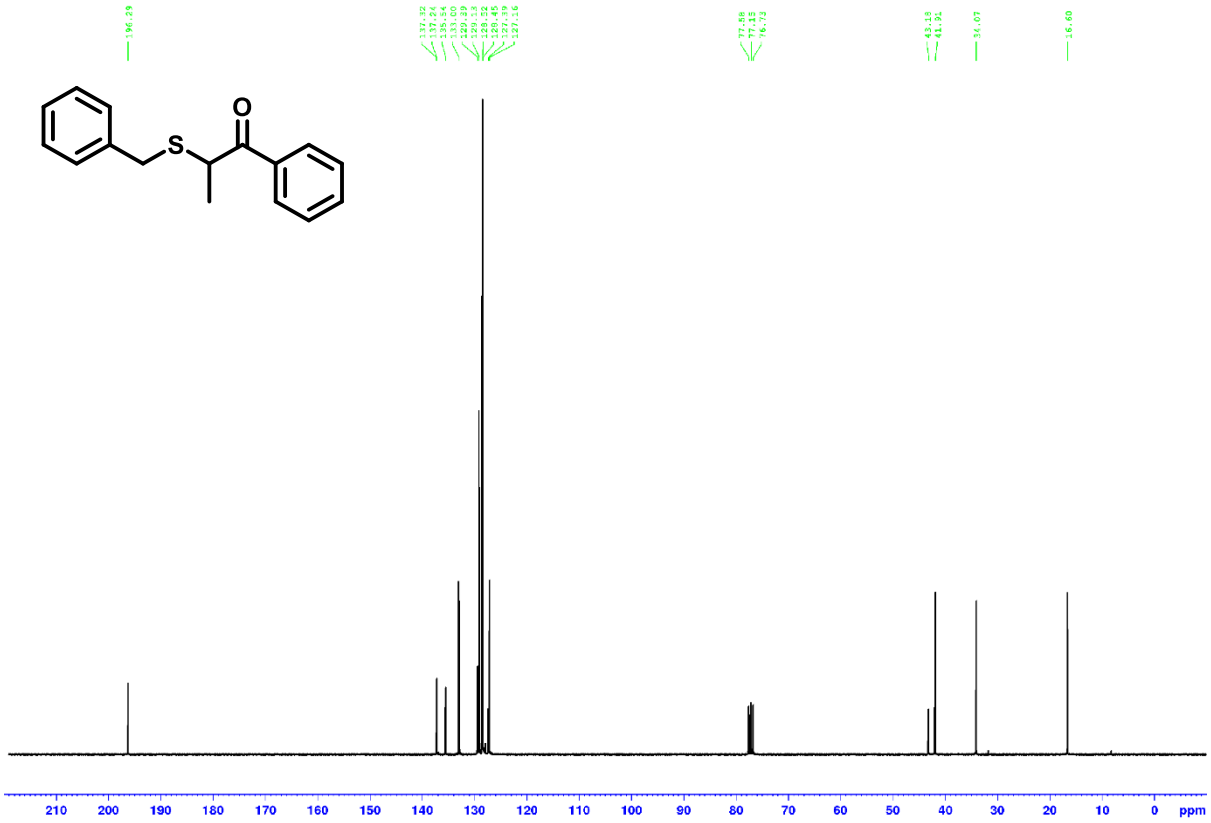


Figure S20: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3b**.

2-(Butylthio)-1-phenylpropan-1-one 3c

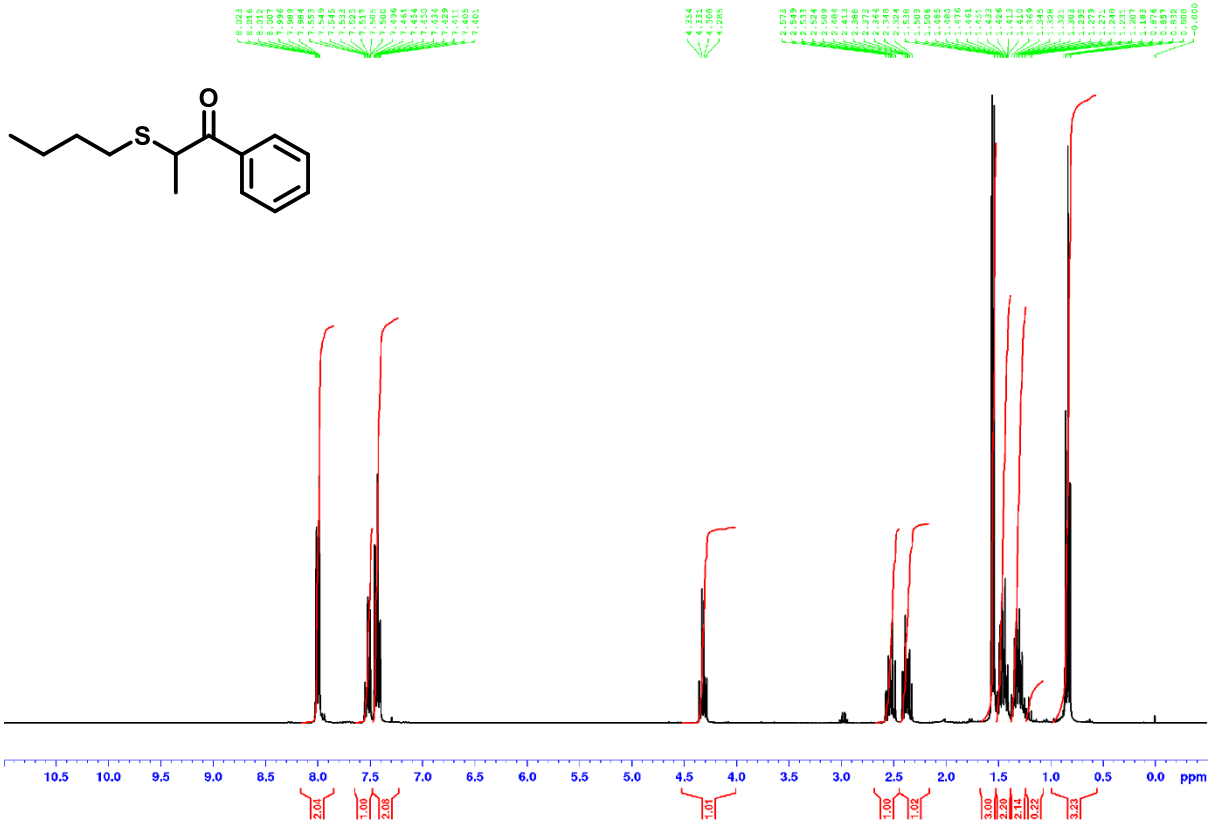


Figure S21: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3c**.

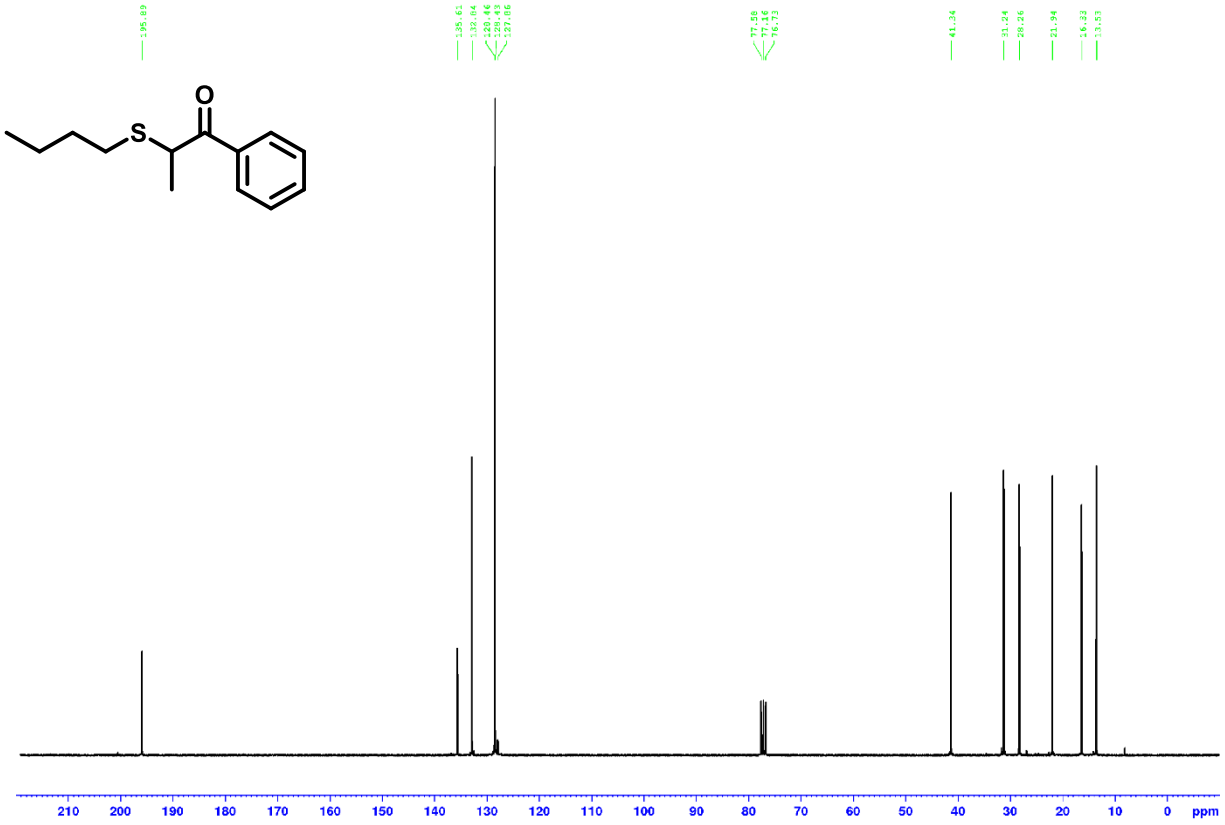


Figure S22: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3c**.

1-(4-Methoxyphenyl)-2-(phenylthio)propan-1-one 3d

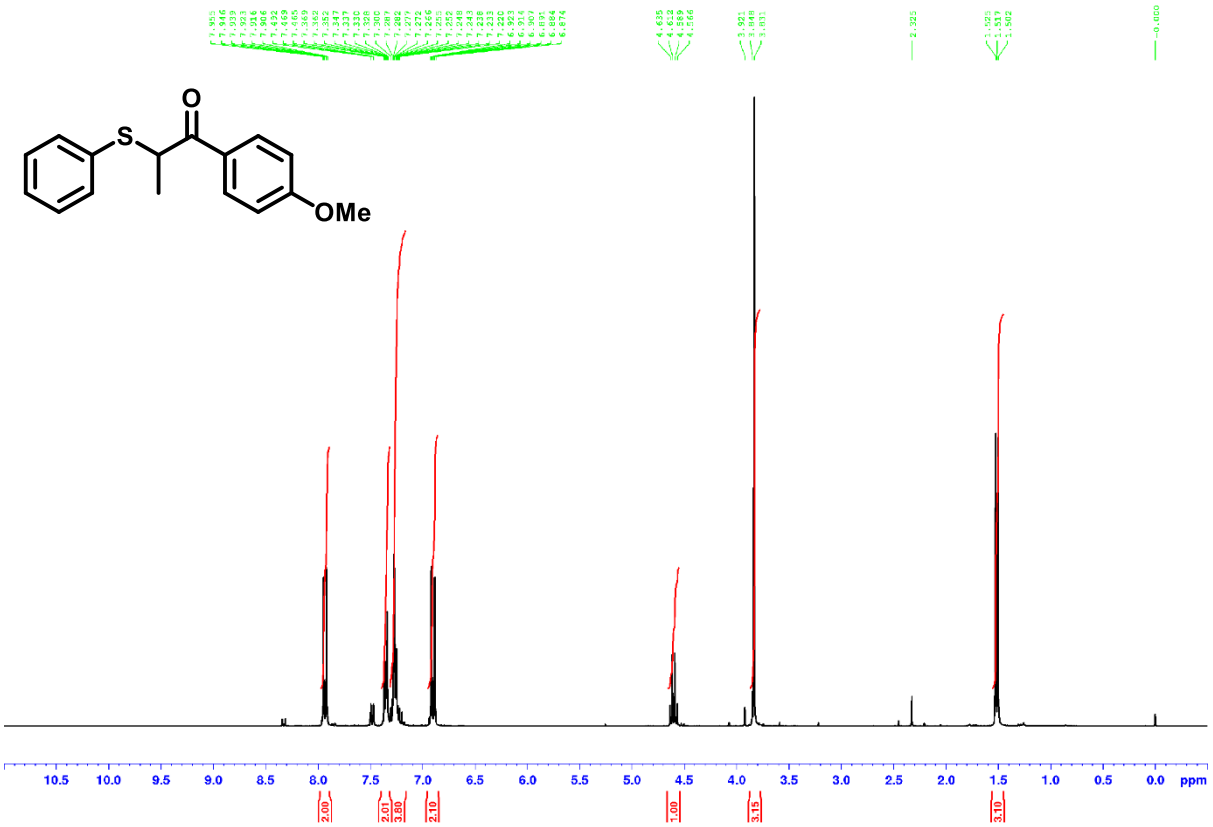


Figure S23: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3d**.

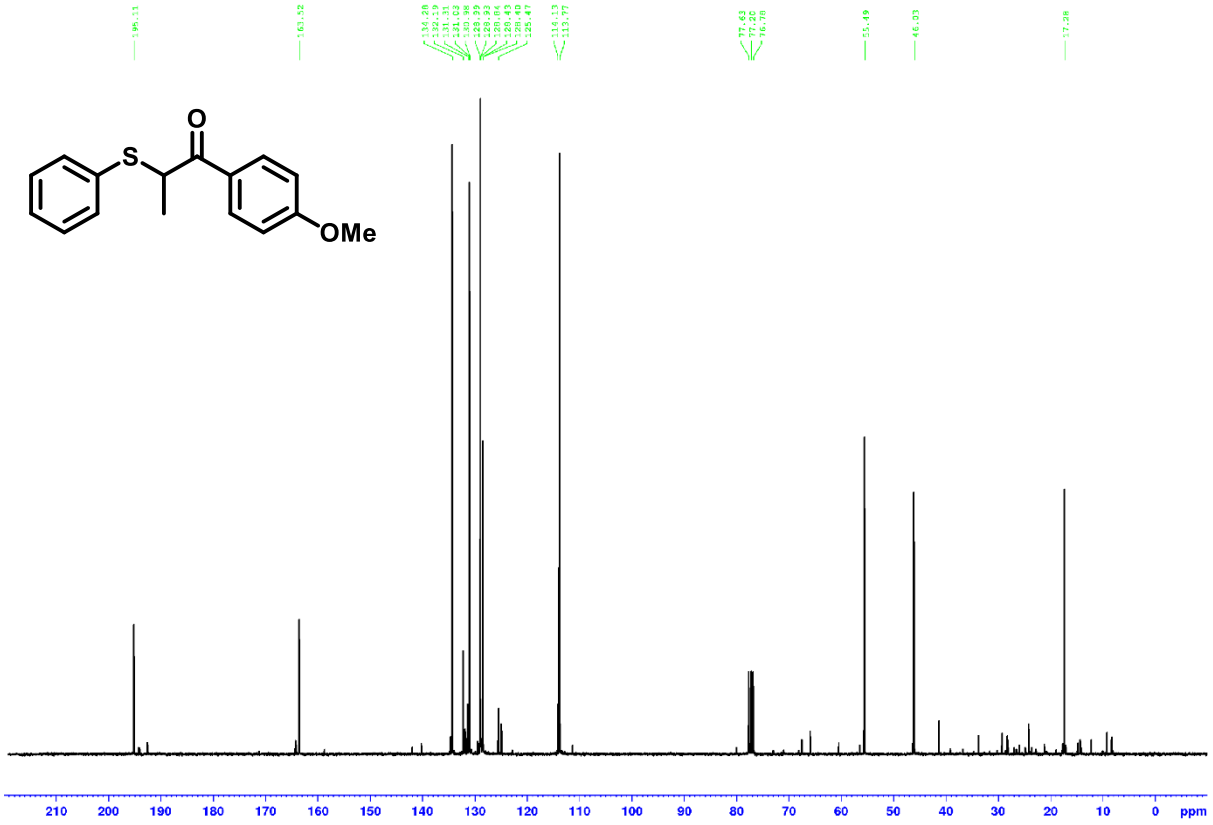


Figure S24: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3d**.

2-(Benzylthio)-1-(4-methoxyphenyl)propan-1-one 3e

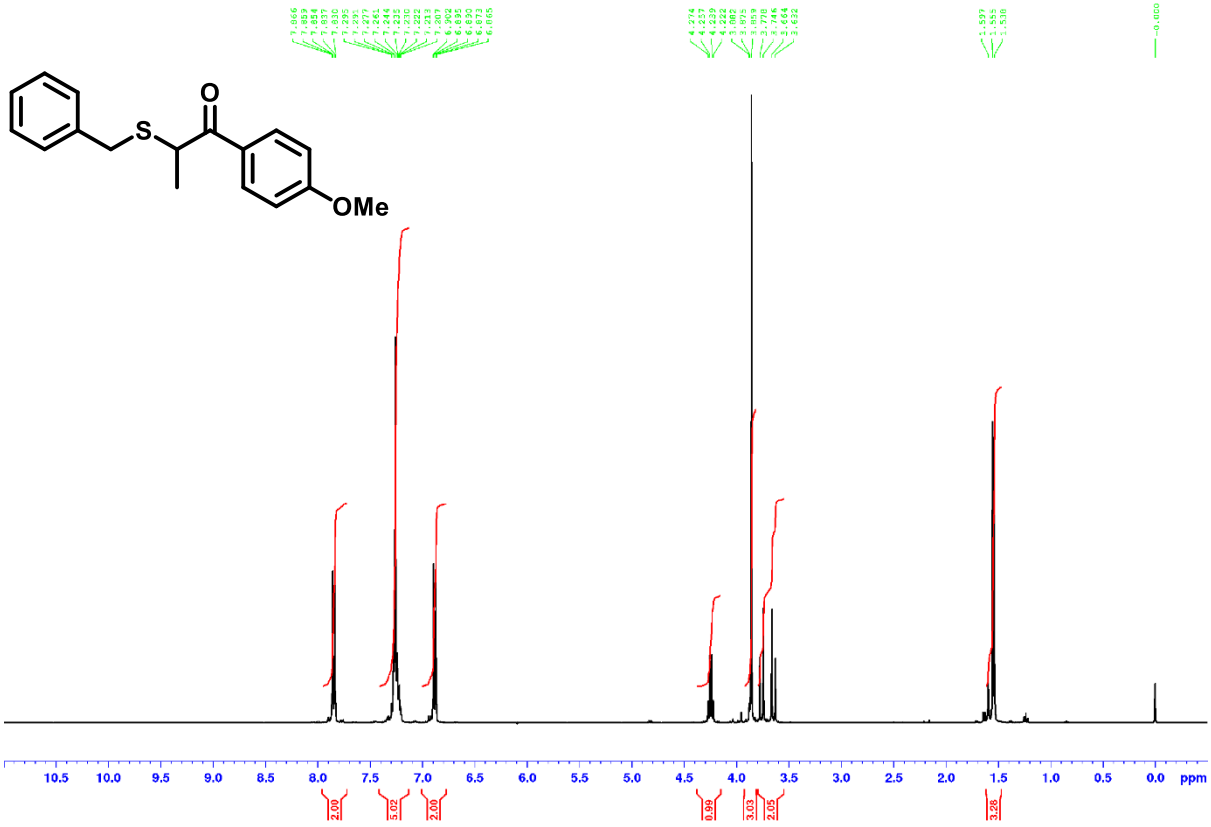


Figure S25: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**.

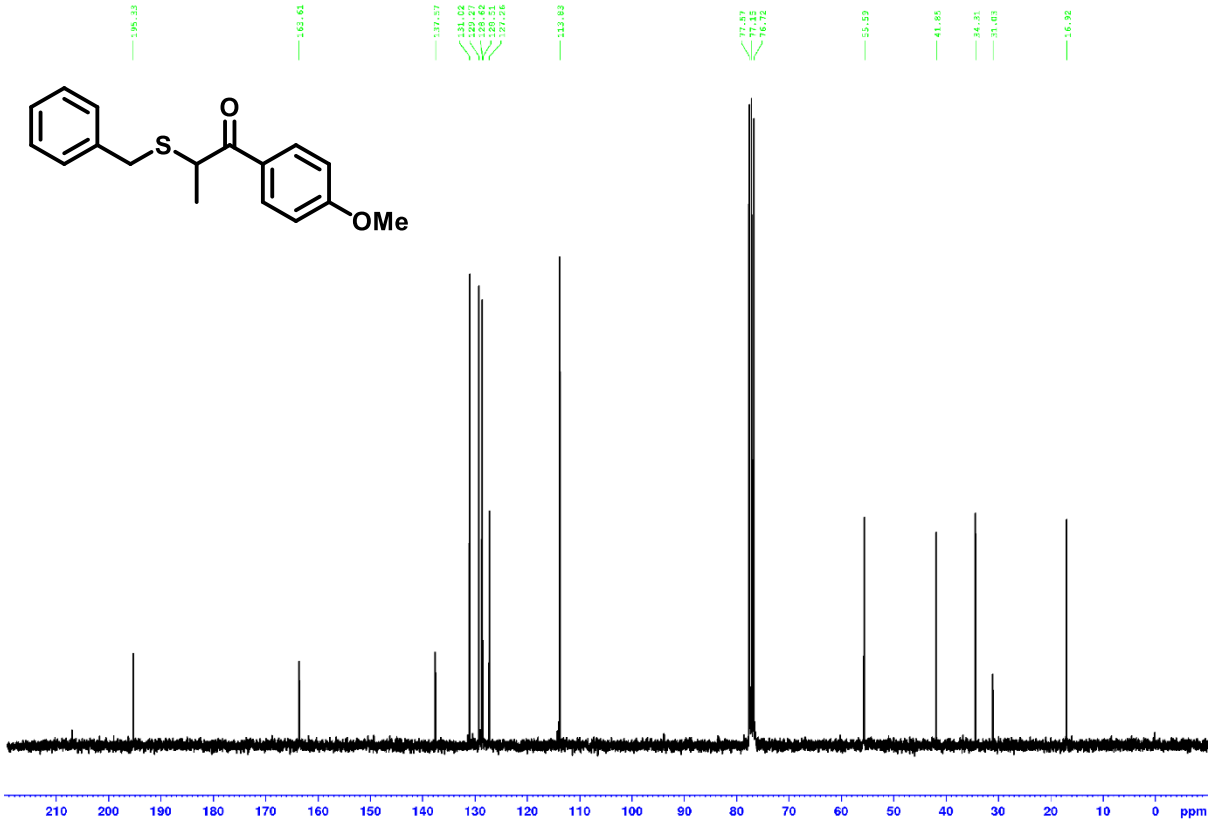


Figure S26: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3e**.

2-(Butylthio)-1-(4-methoxyphenyl)propan-1-one 3f

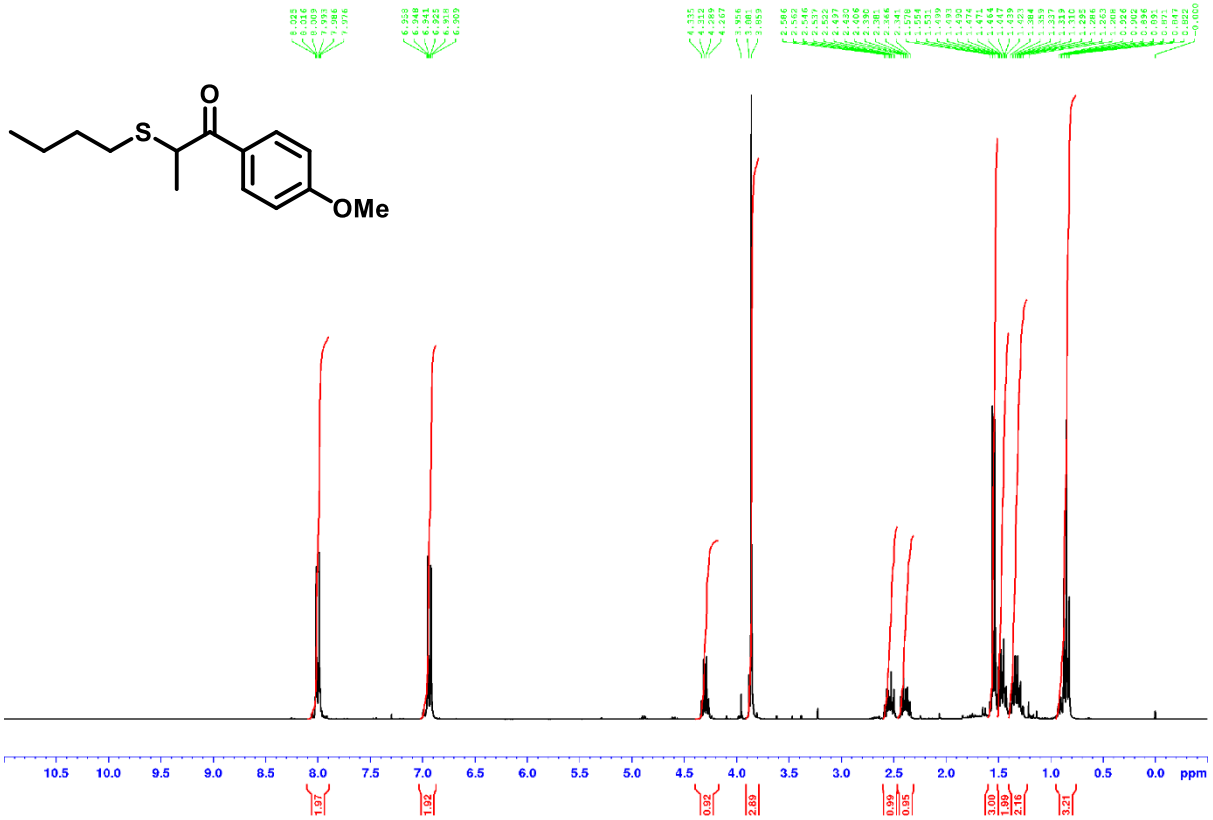


Figure S27: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3f**.

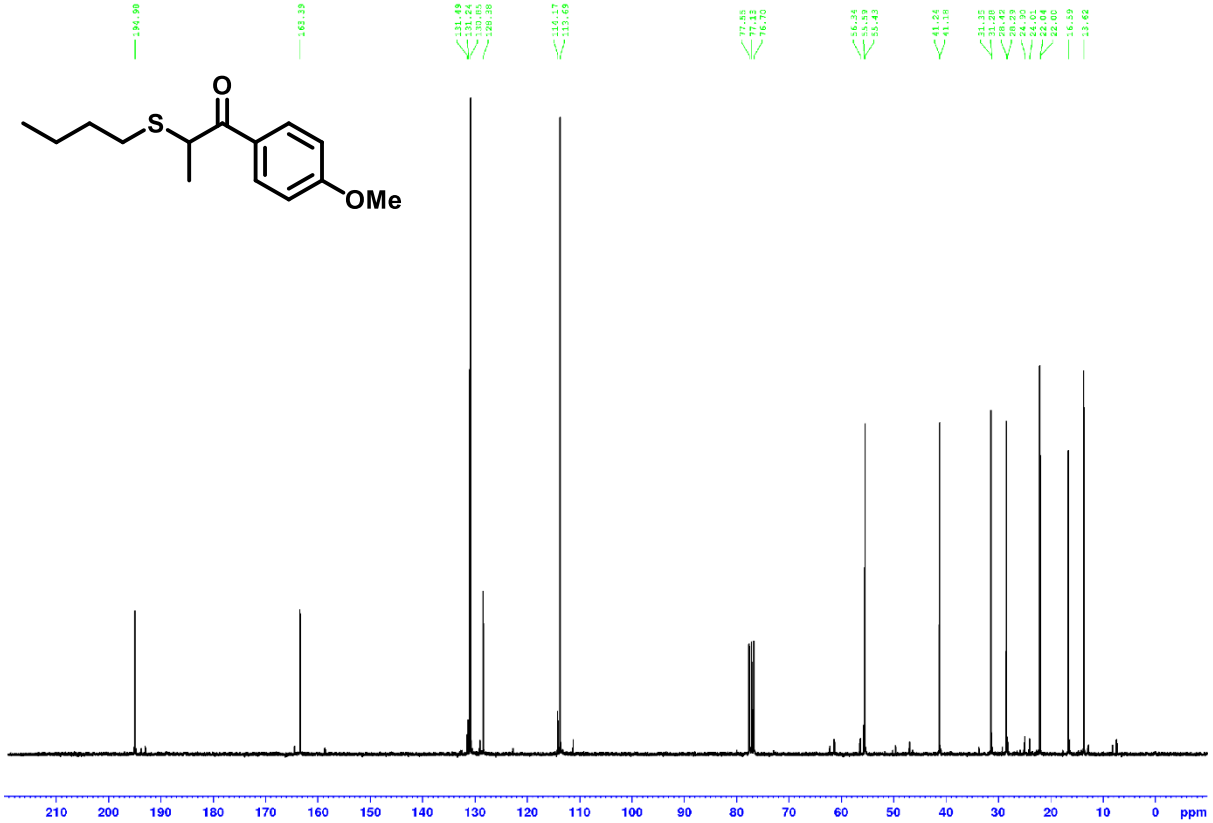


Figure S28: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3f**.

2-(Phenylthio)-1-(*p*-tolyl)propan-1-one 3g[12]

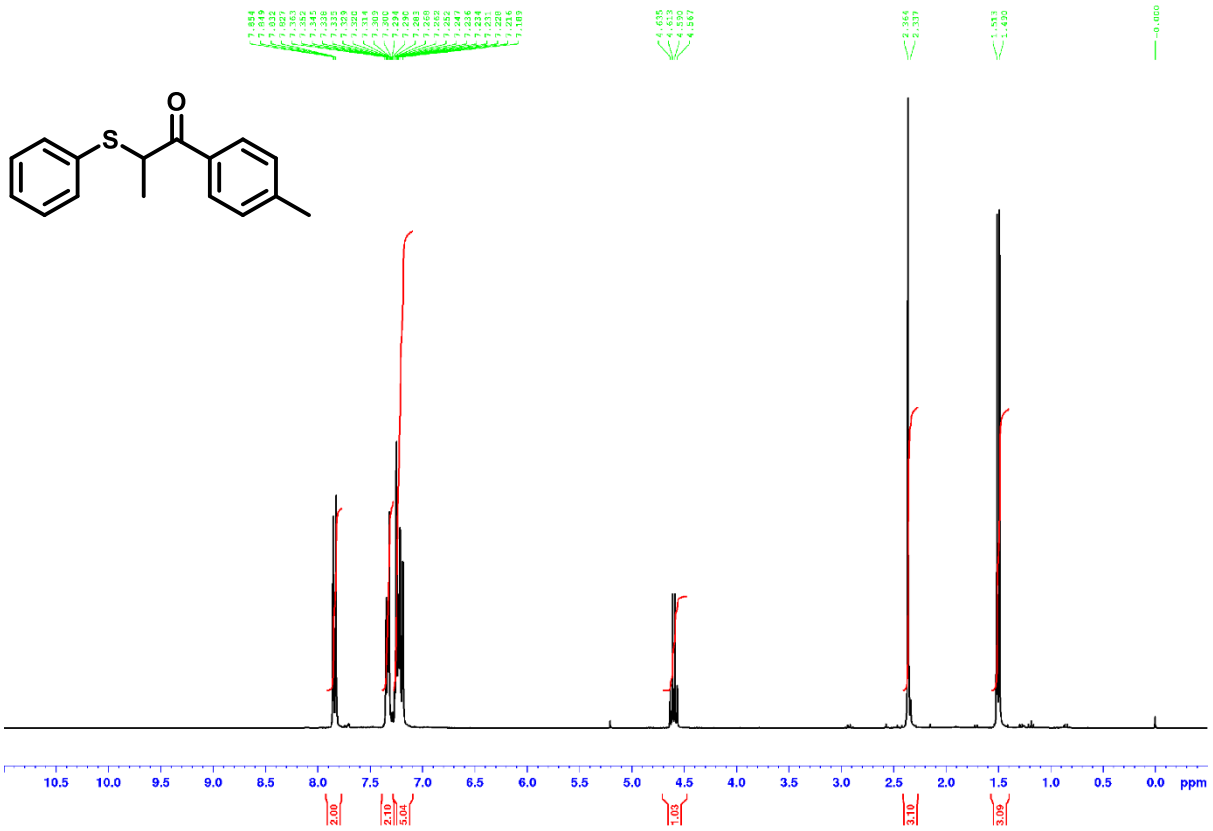


Figure S29: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3g**.

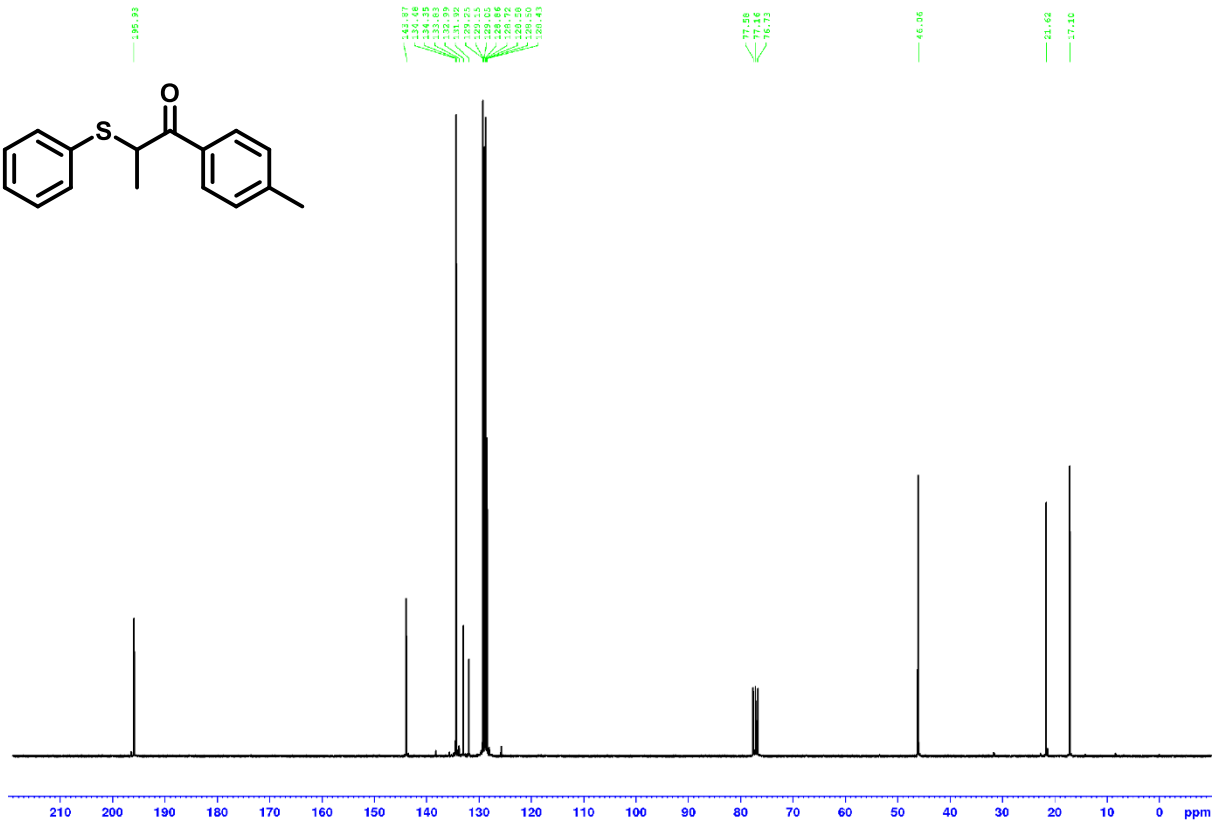


Figure S30: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3g**.

2-(Benzylthio)-1-(*p*-tolyl)propan-1-one 3h

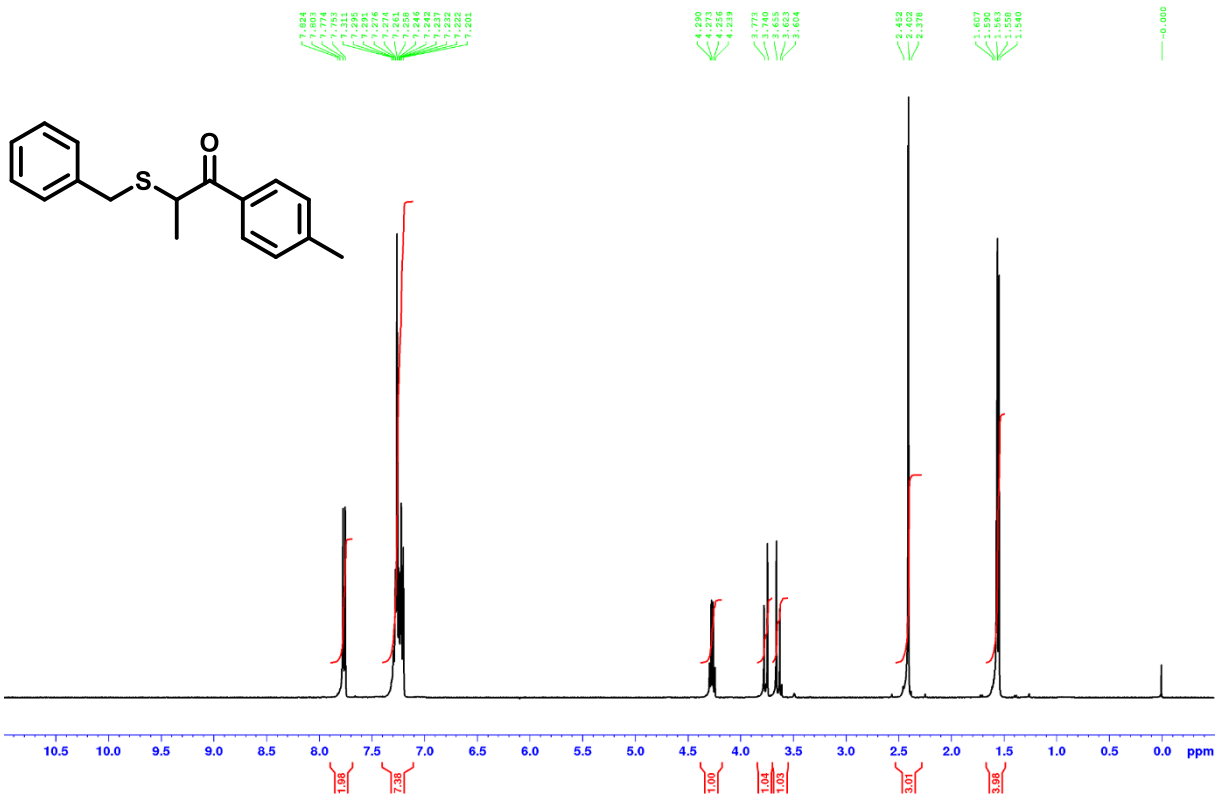


Figure S31: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**.

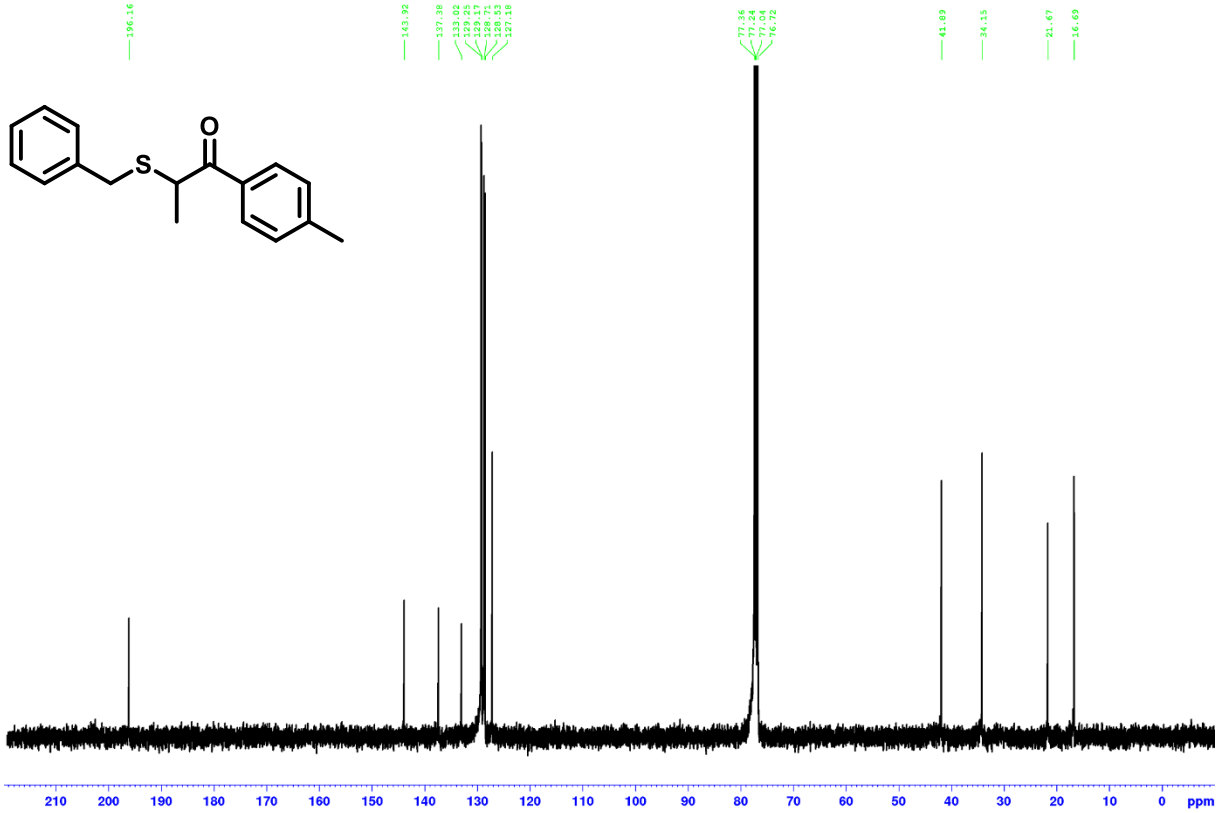


Figure S32: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3h**.

2-(Butylthio)-1-(*p*-tolyl)propan-1-one 3i

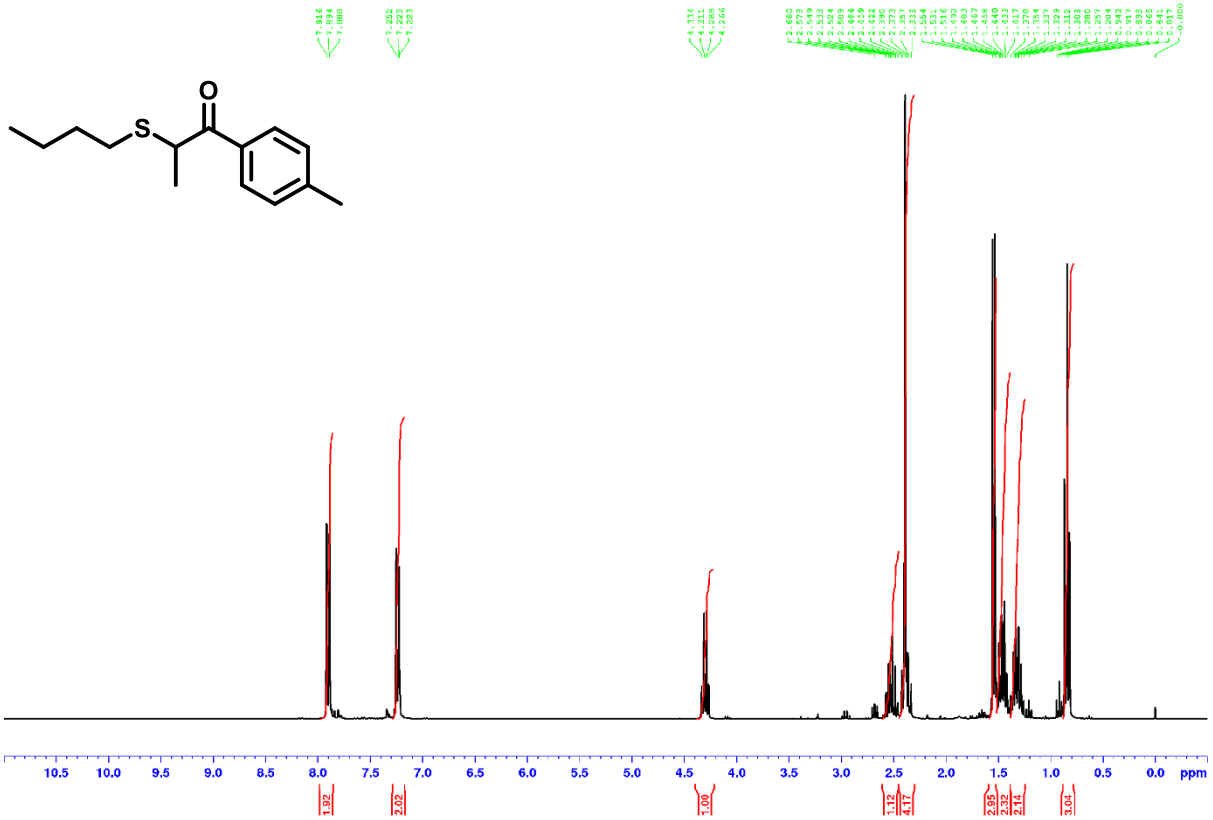


Figure S33: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3i**.

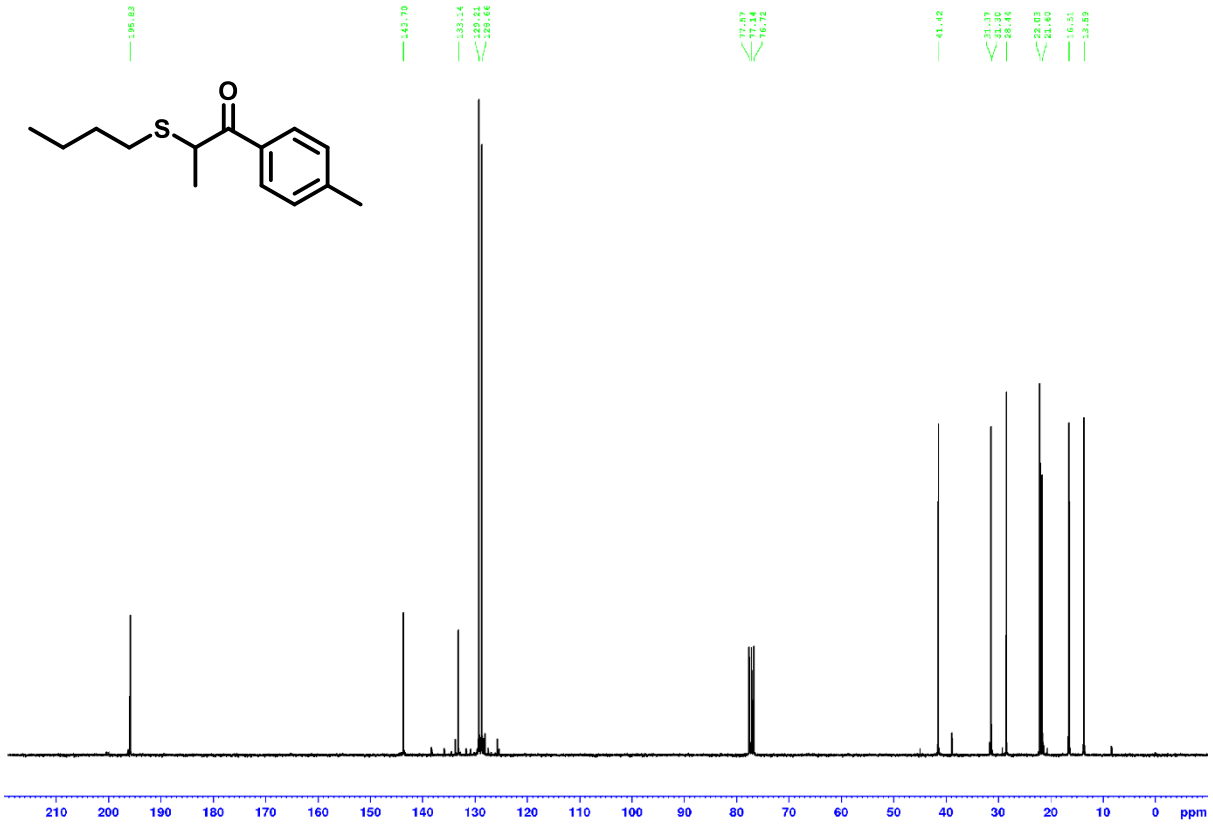


Figure S34: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3i**.

2-((4-Chlorobenzyl)thio)-1-(*p*-tolyl)propan-1-one 3j

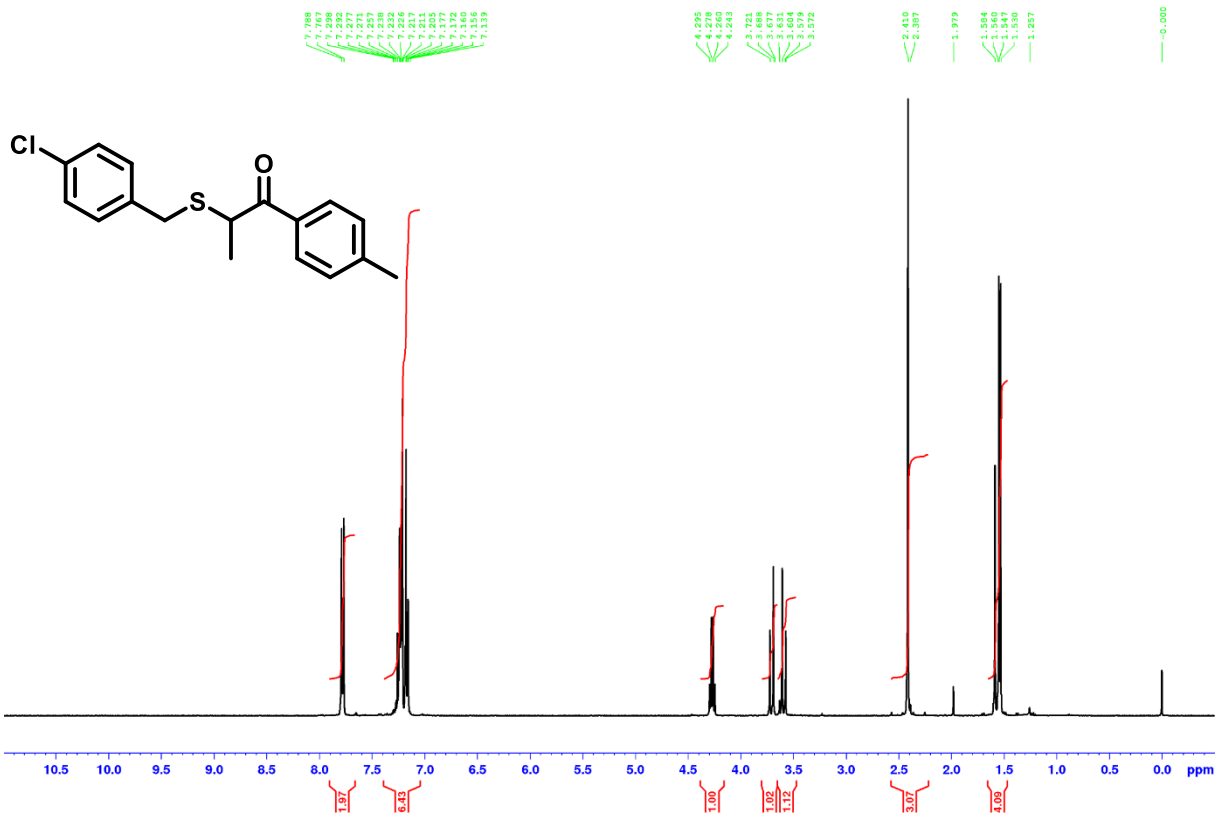


Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**.

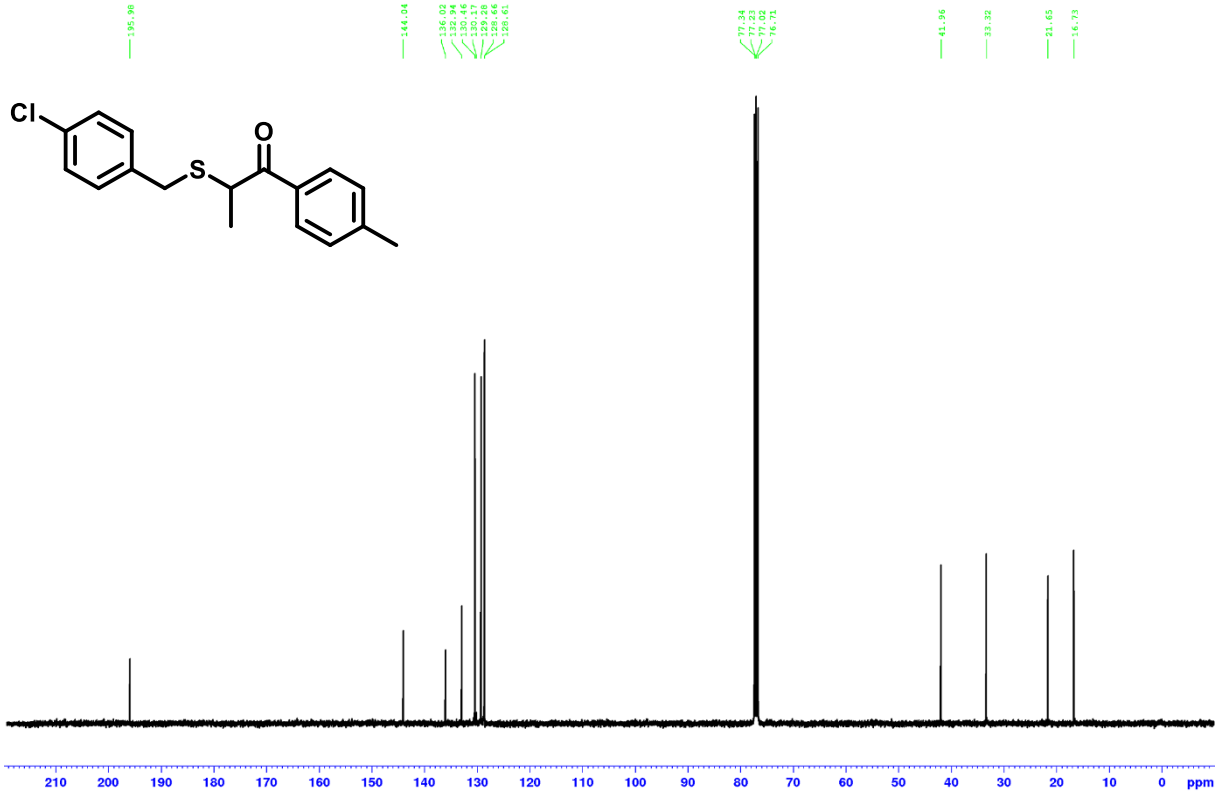


Figure S36: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3j**.

2-((4-Methoxybenzyl)thio)-1-(*p*-tolyl)propan-1-one 3k

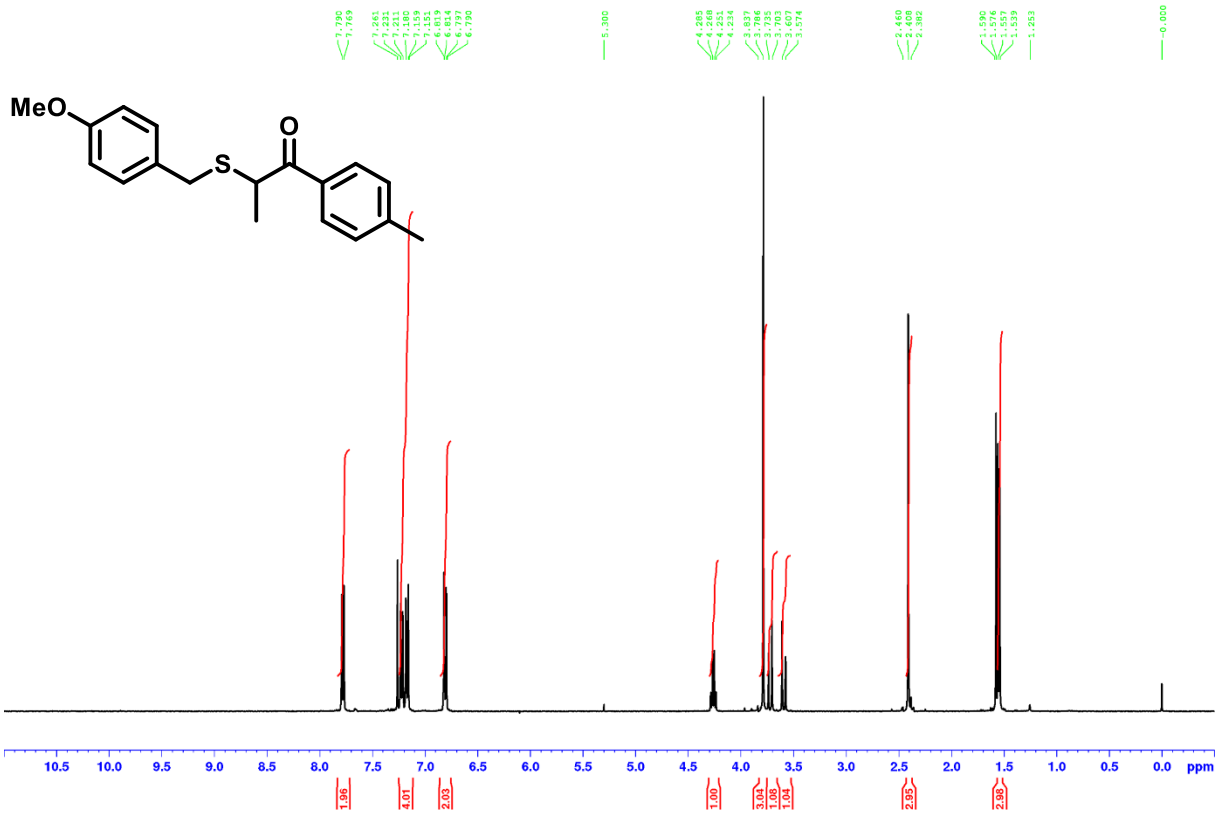


Figure S37: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**.



Figure S38: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3k**.

2-((4-Fluorobenzyl)thio)-1-(*p*-tolyl)propan-1-one 3l

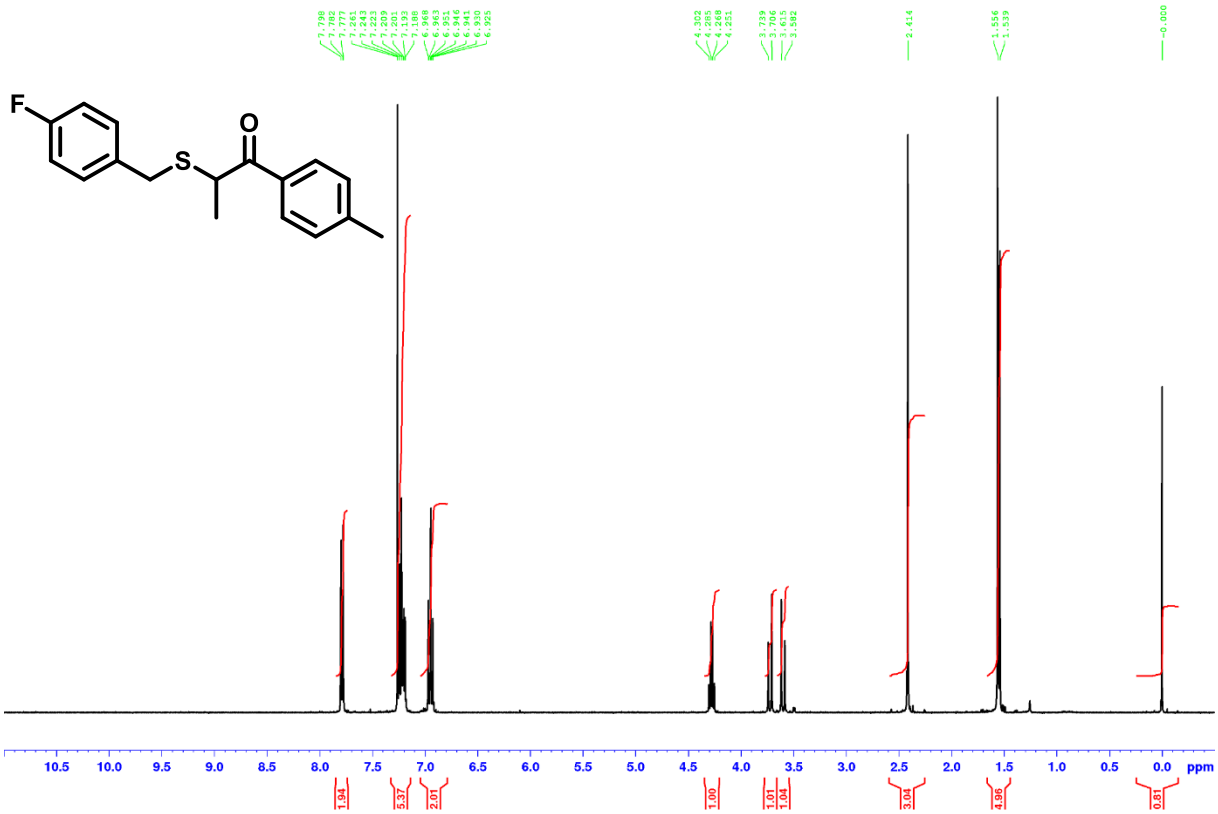


Figure S39: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l.**

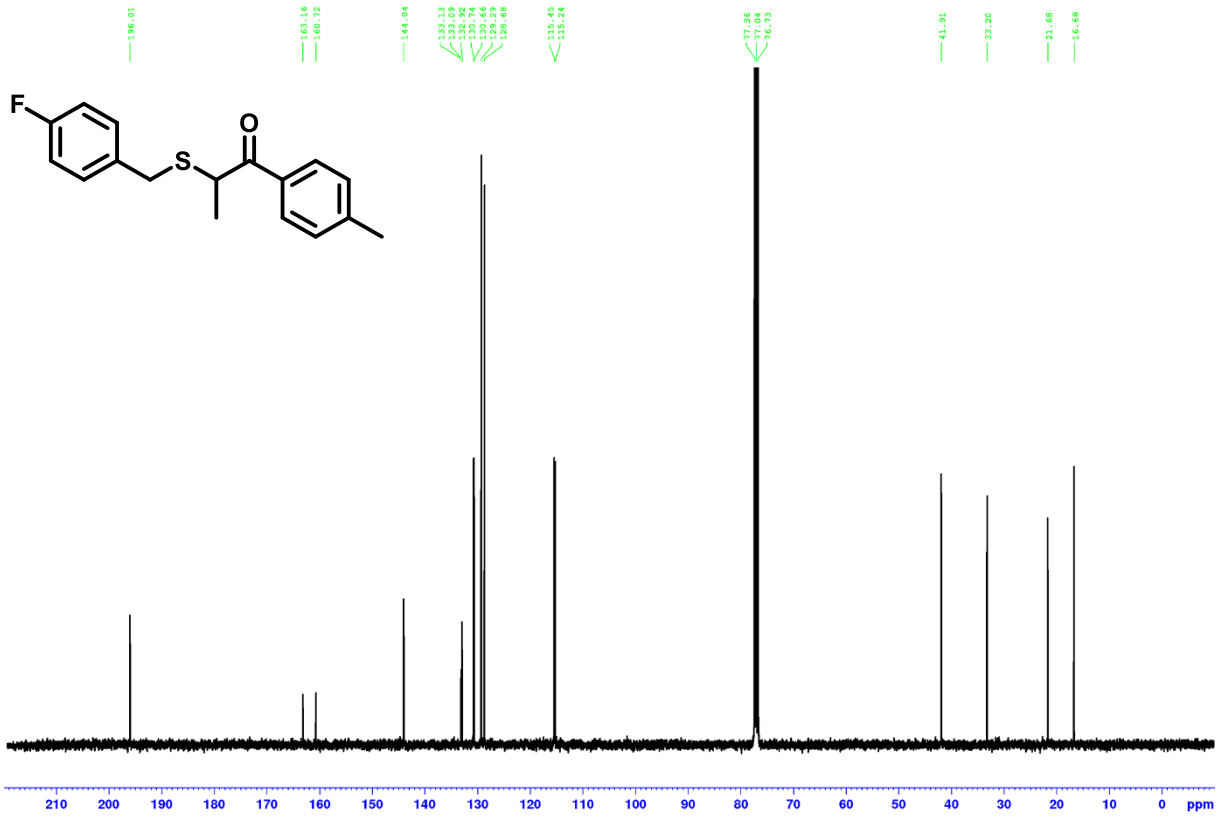


Figure S40: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3l**.

2-((4-Methybenzyl)thio)-1-(*p*-tolyl)propan-1-one 3m

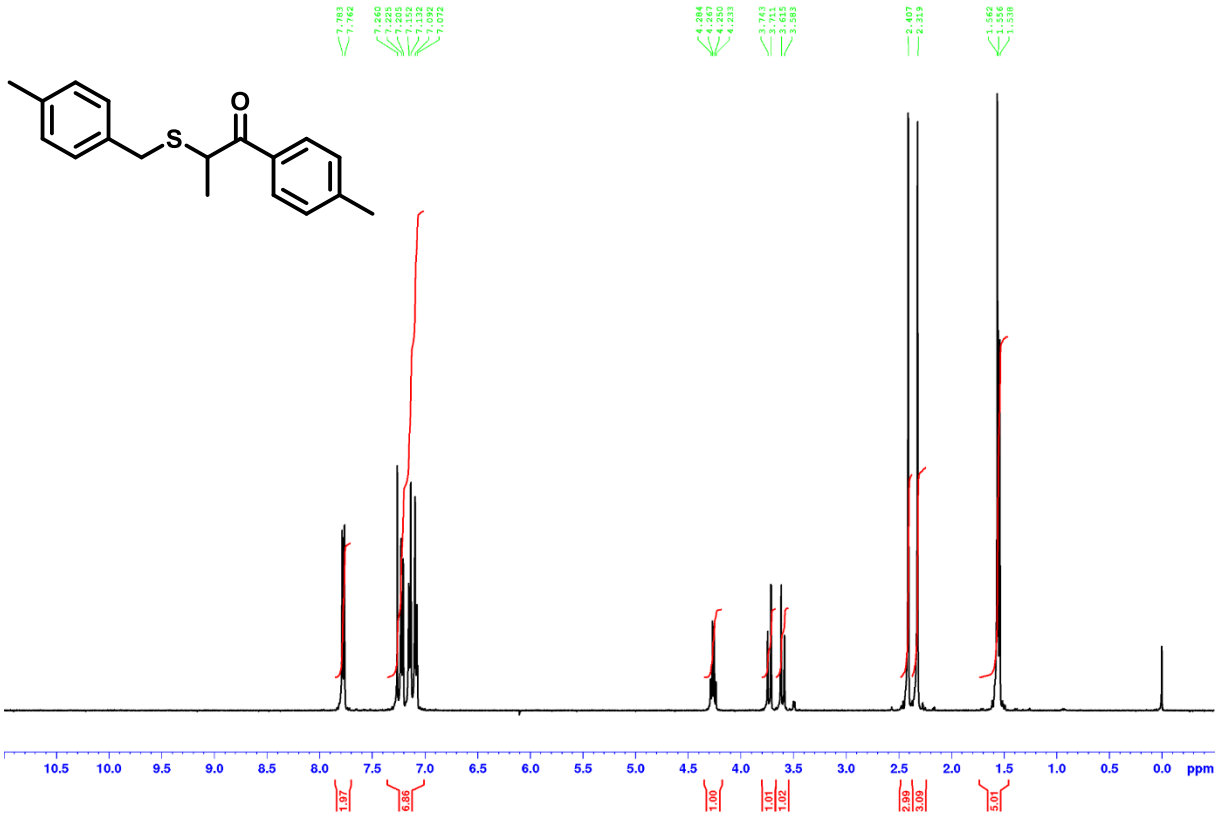


Figure S41: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**.

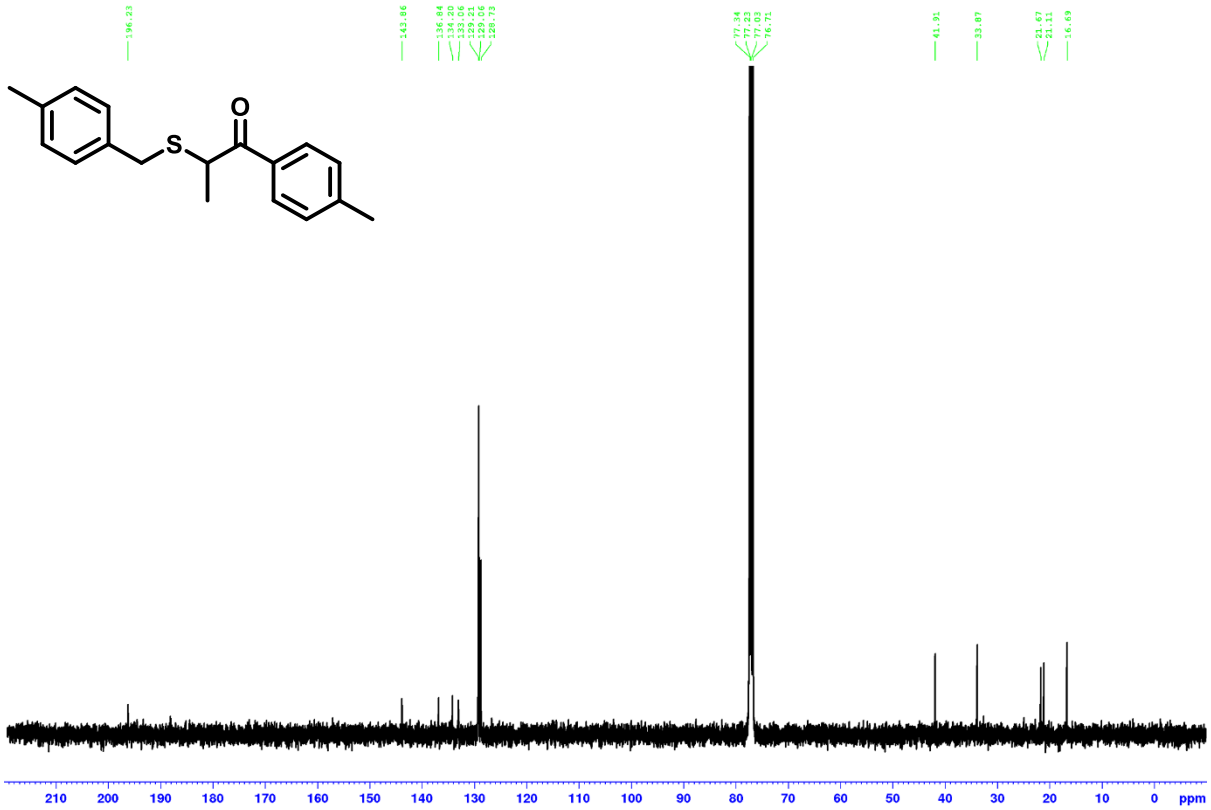


Figure S42: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3m**.

1-(4-Chlorophenyl)-2-(phenylthio)propan-1-one 3n

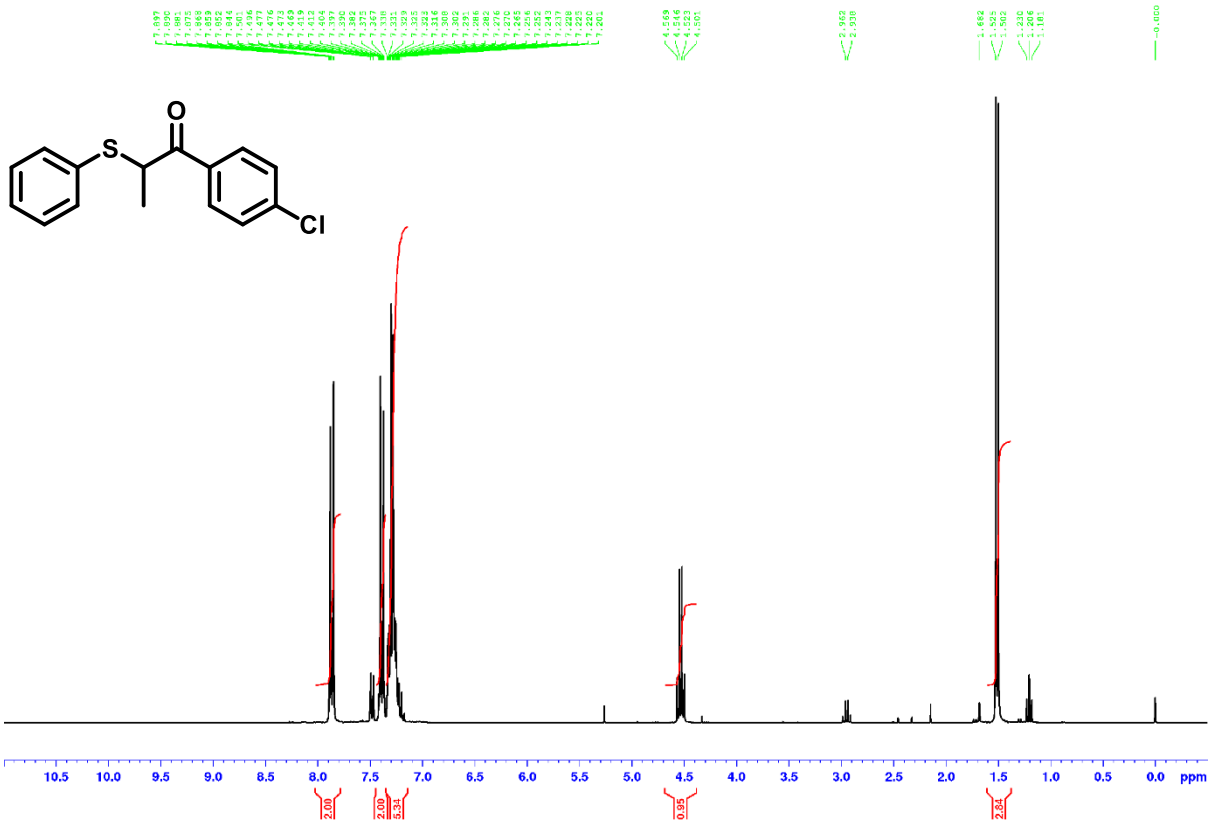


Figure S43: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3n**.

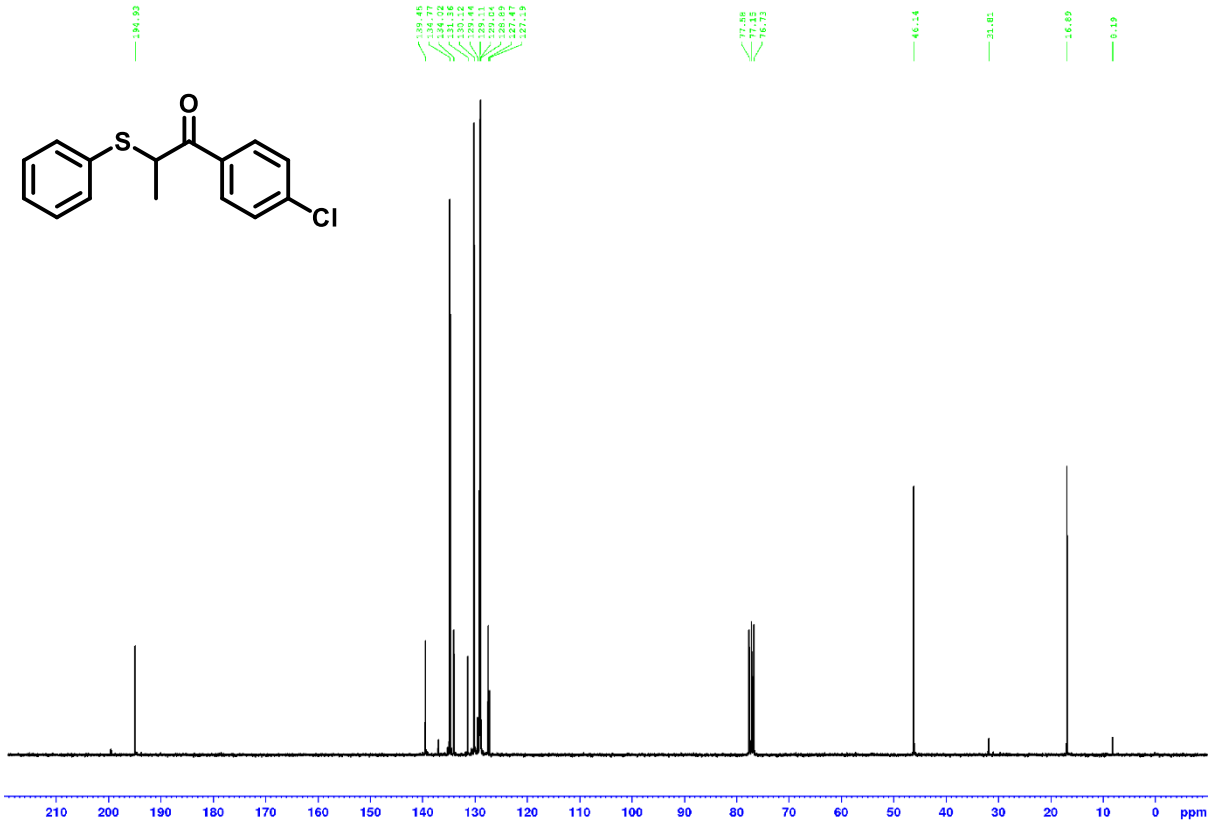


Figure S44: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3n**.

2-(Benzylthio)-1-(4-chlorophenyl)propan-1-one 3o

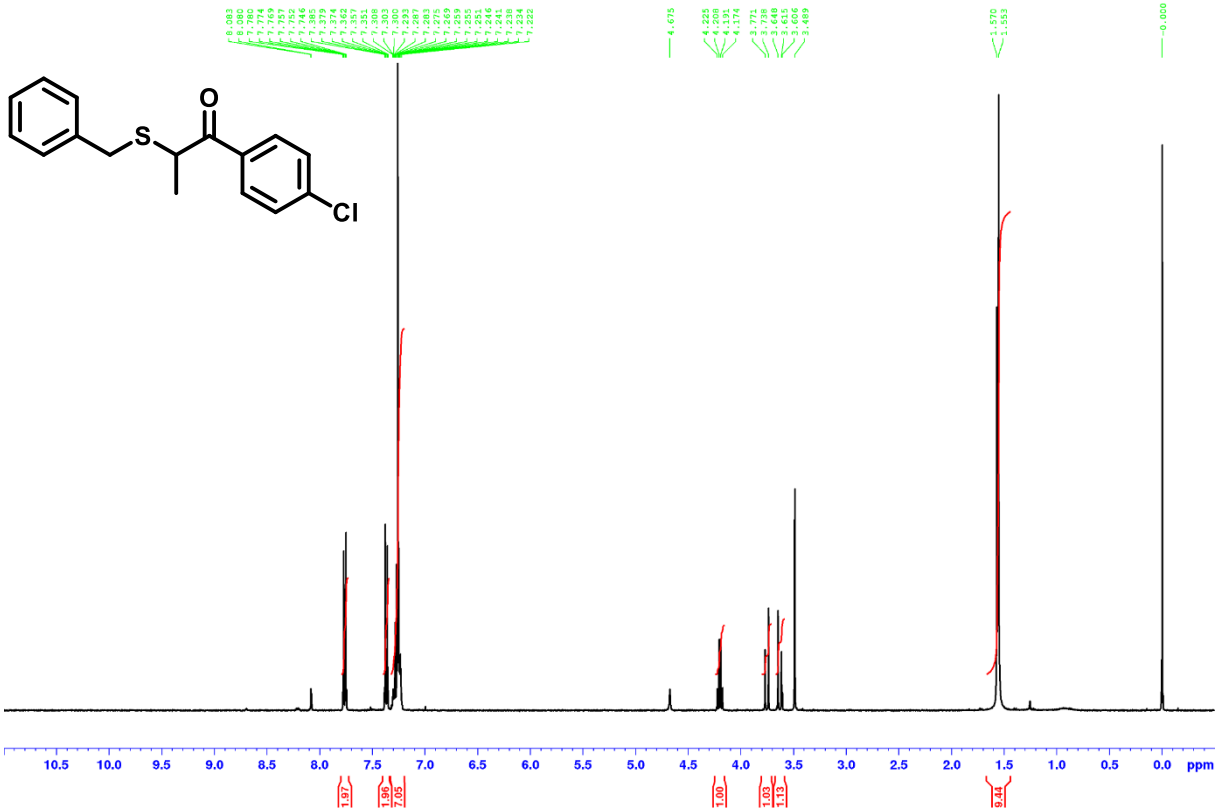


Figure S45: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**.

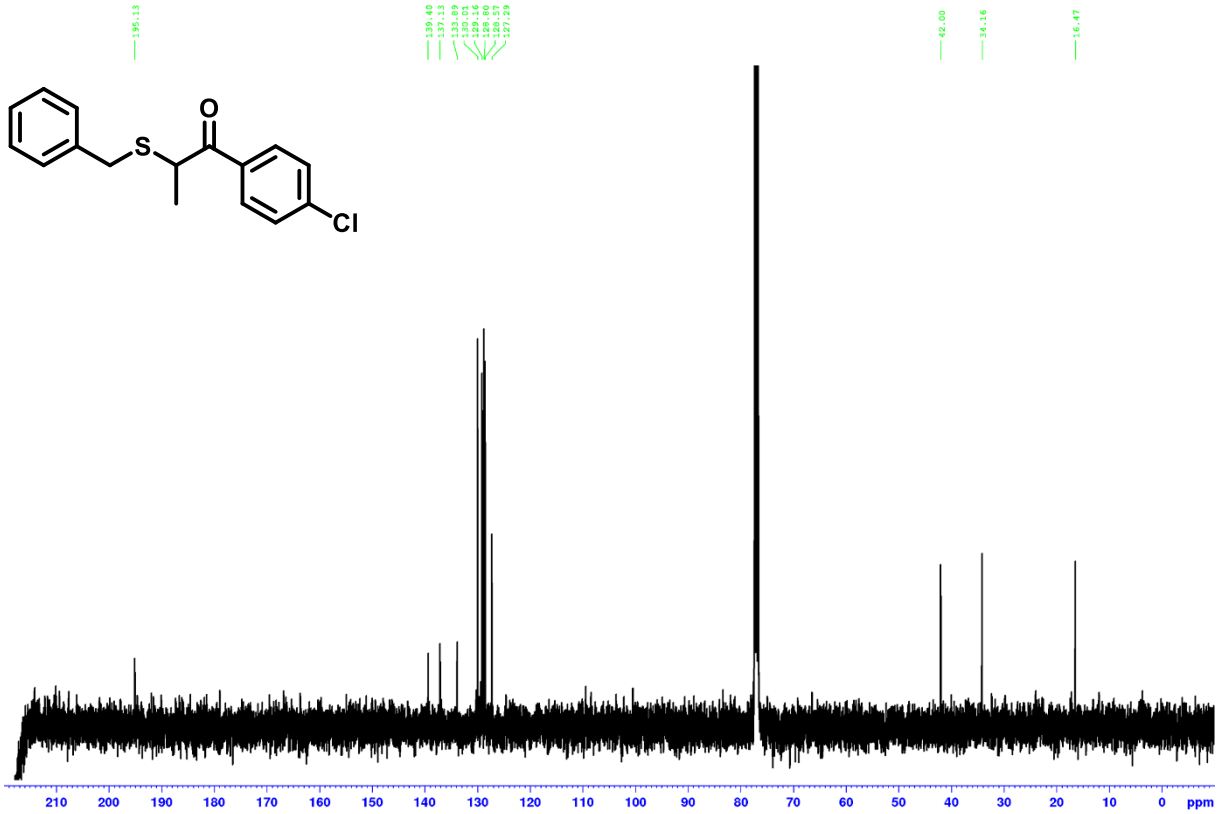


Figure S46: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3o**.

2-(Butylthio)-1-(4-chlorophenyl)propan-1-one 3p

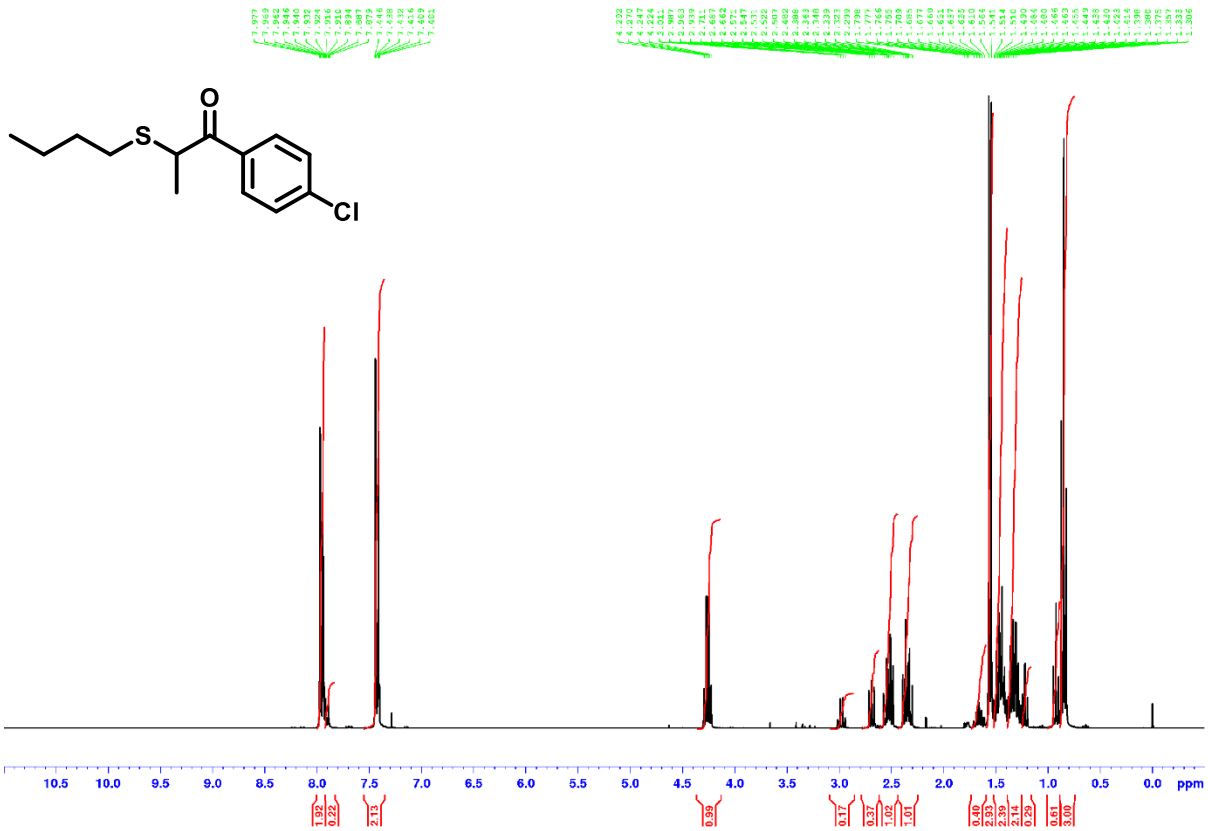


Figure S47: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3p**.

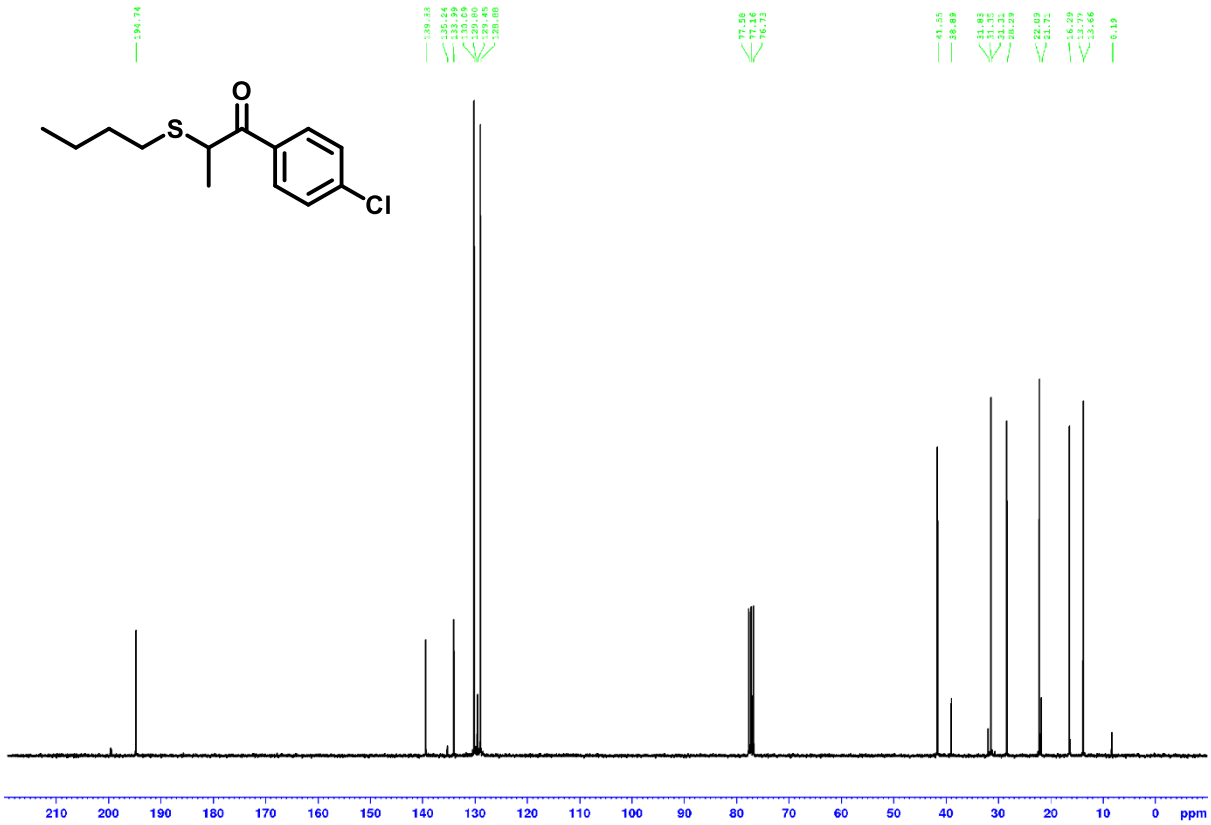


Figure S48: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3p**.

2-((4-Chlorobenzyl)thio)-1-(4-chlorophenyl)propan-1-one 3q

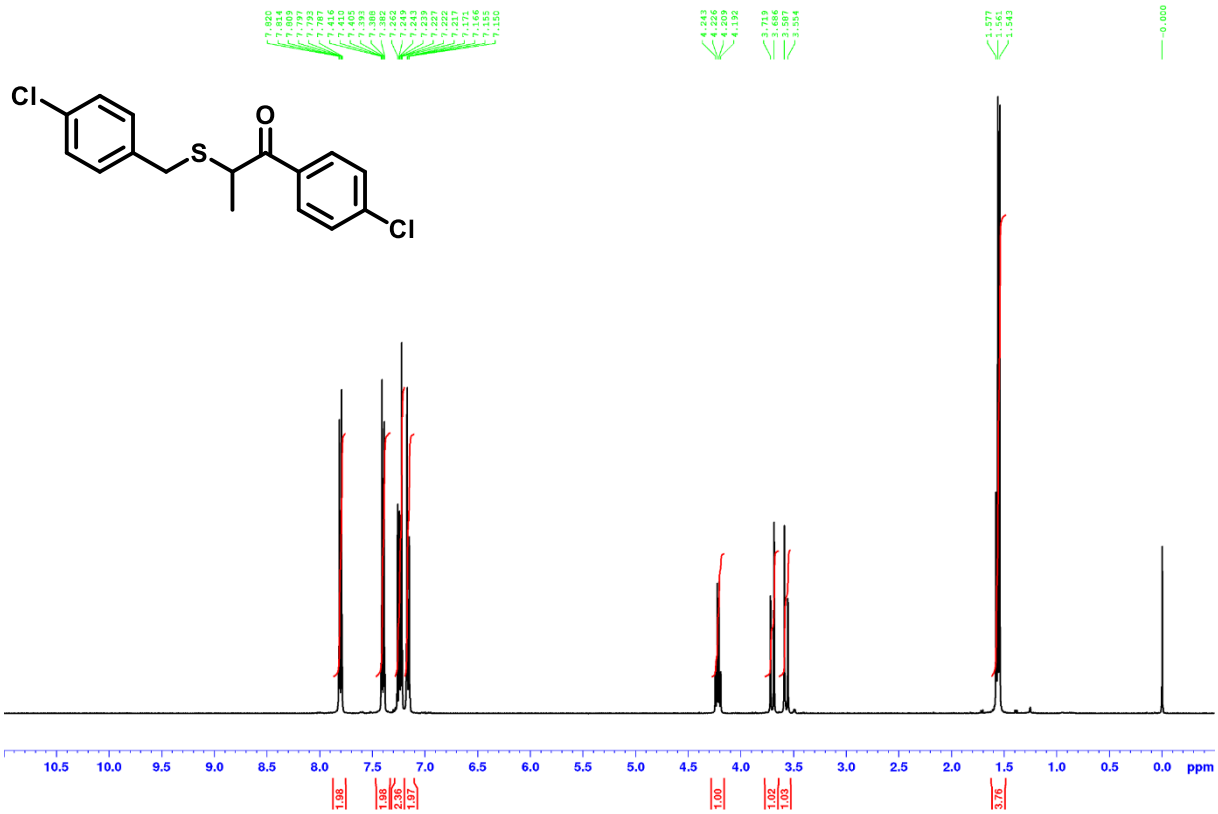


Figure S49: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**.

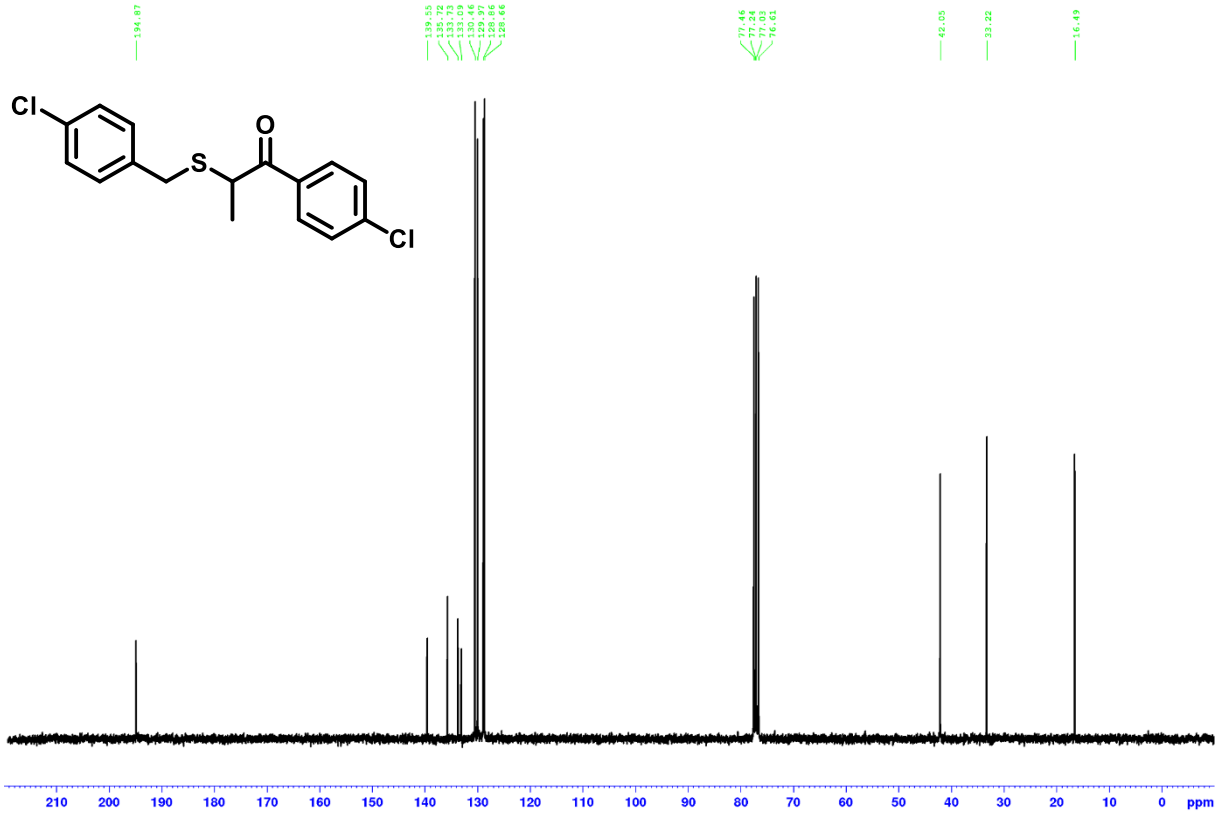


Figure S50: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3q**.

1-(4-Chlorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one 3r

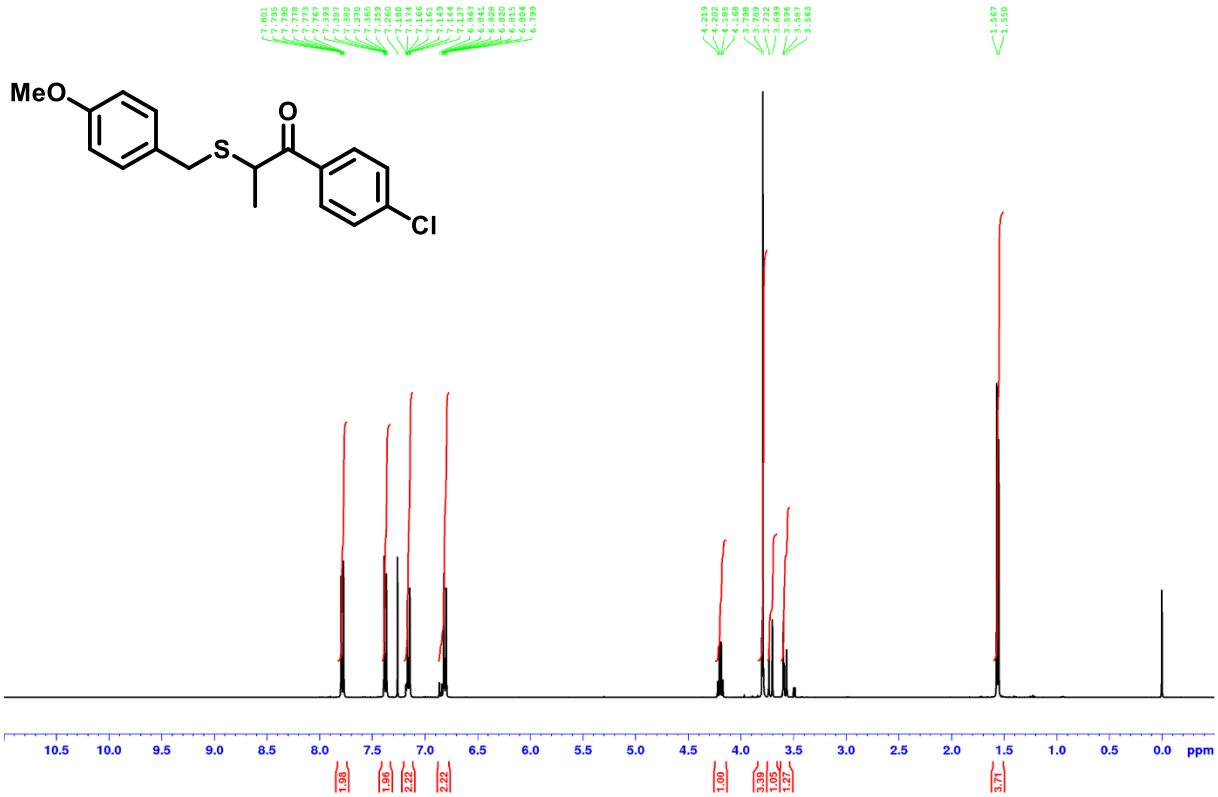


Figure S51: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**.

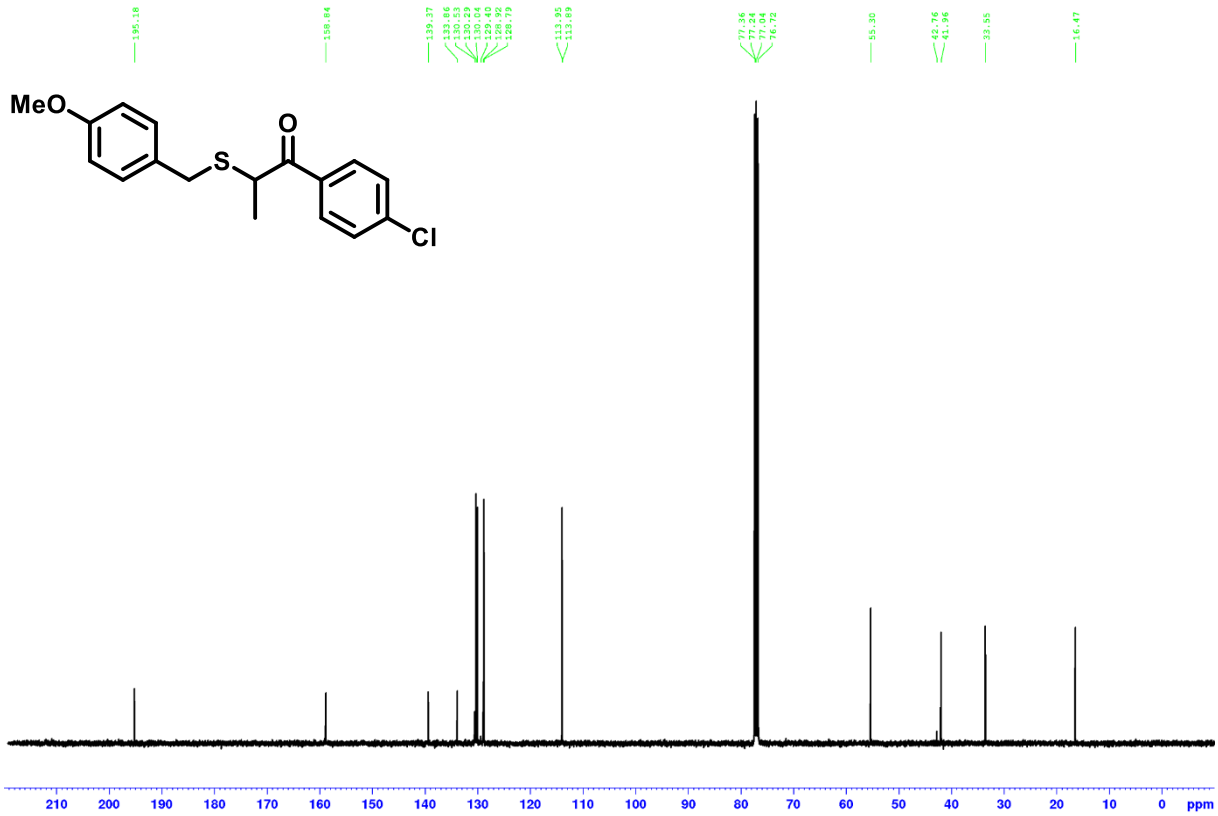


Figure S52: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3r**.

1-(4-Chlorophenyl)-2-((4-fluorobenzyl)thio)propan-1-one 3s

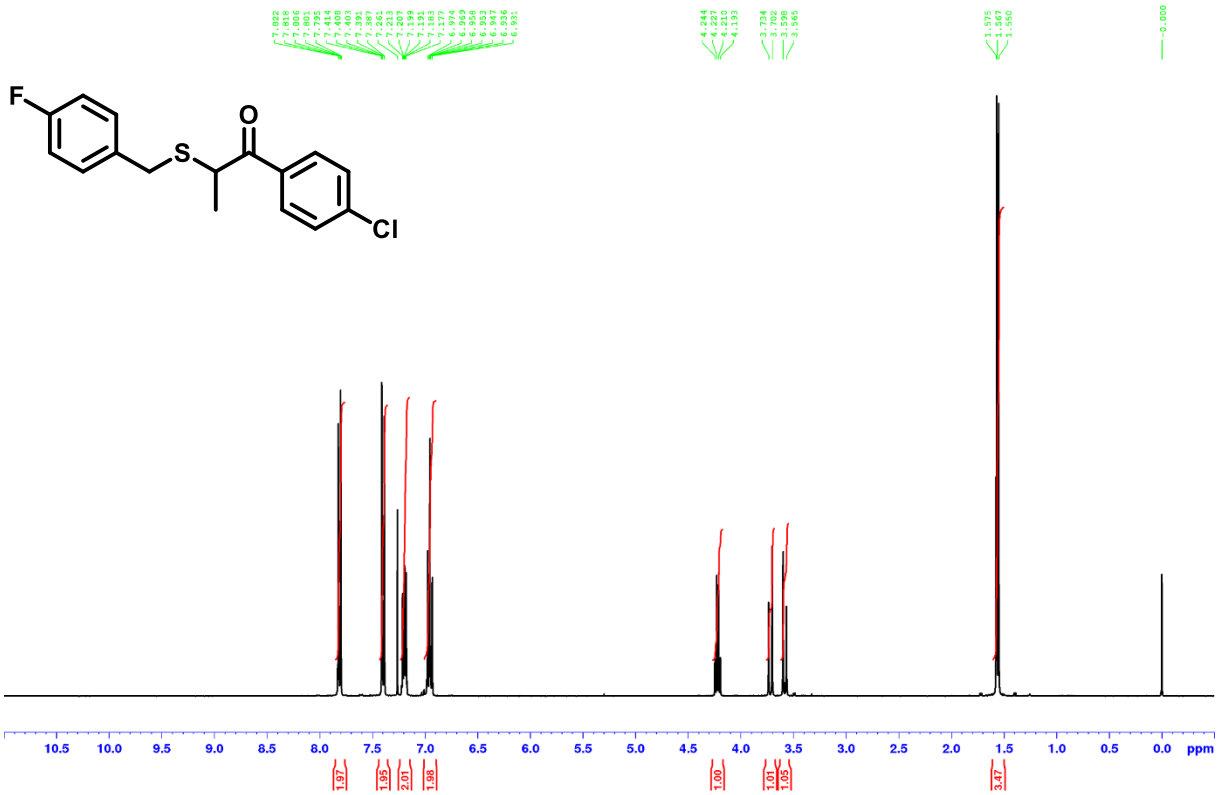


Figure S53: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3s**.

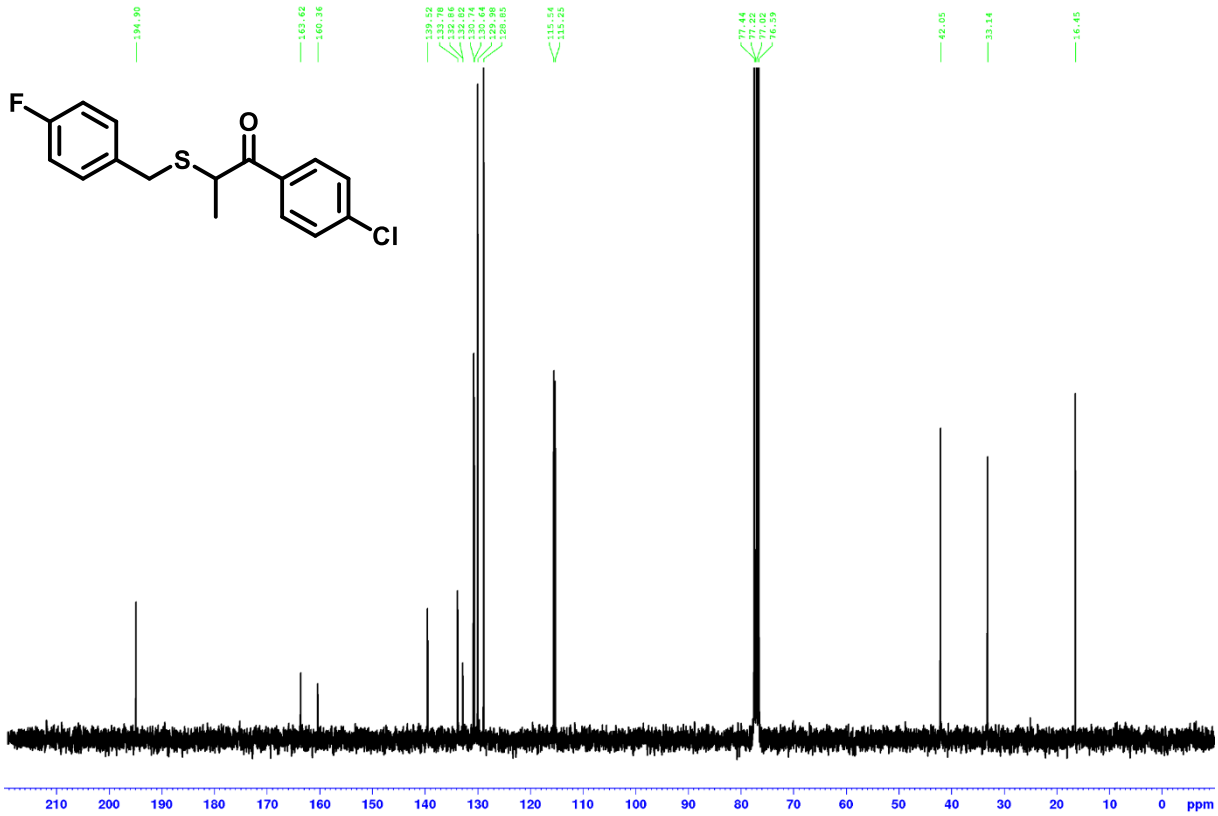


Figure S54: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3s**.

1-(4-Chlorophenyl)-2-((4-methybenzyl)thio)propan-1-one 3t

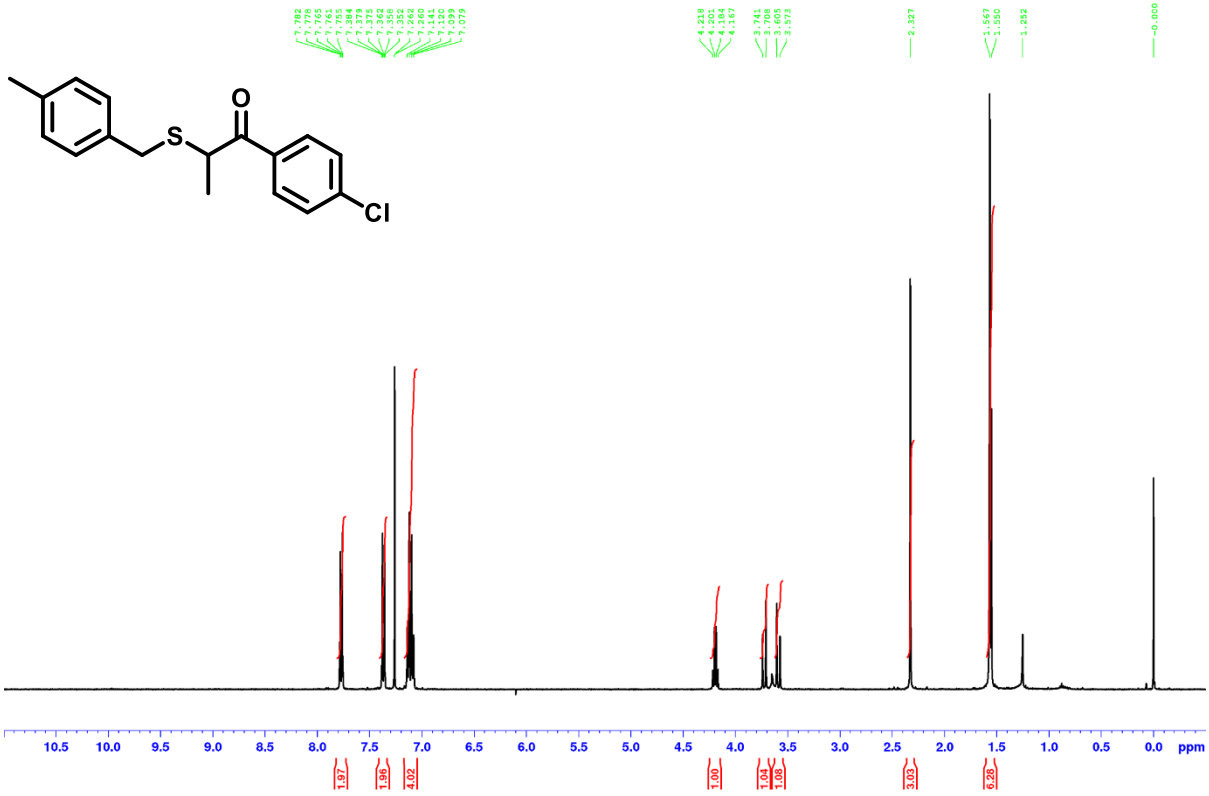


Figure S55: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3t**.

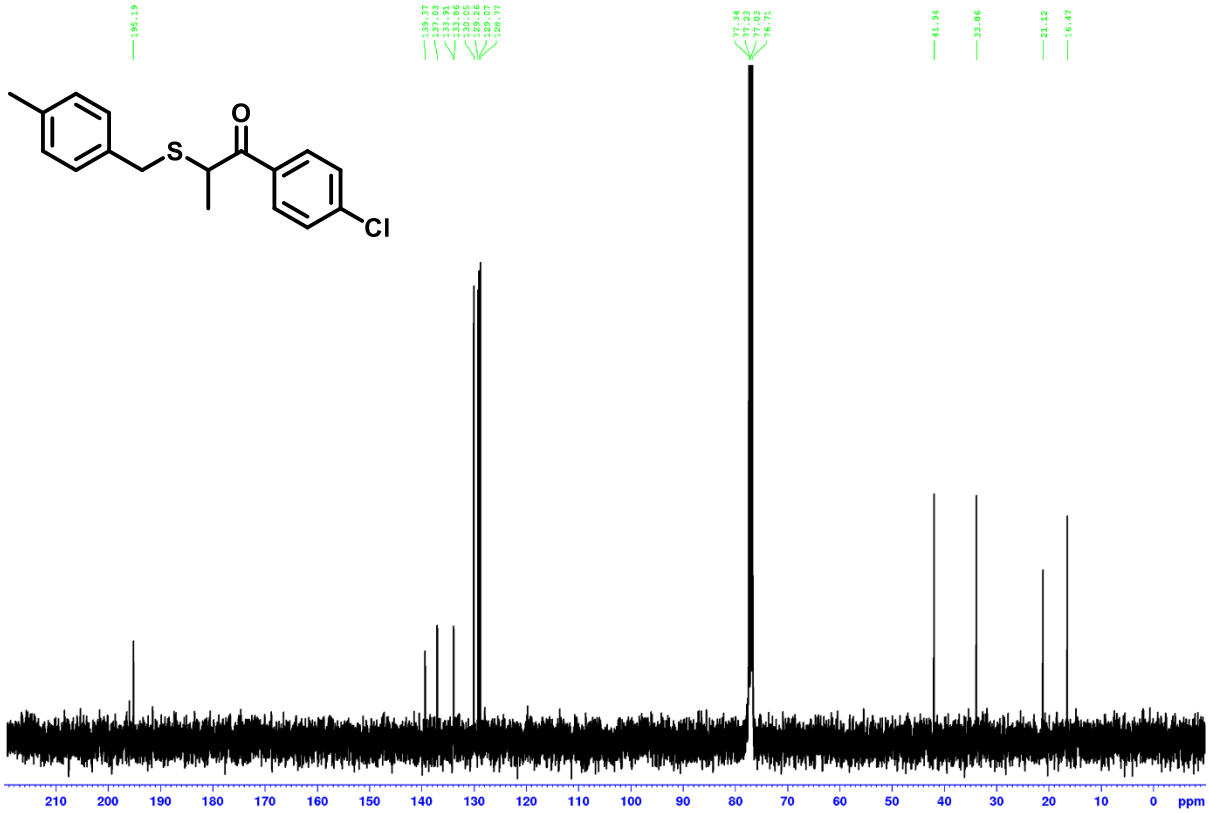


Figure S56: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3t**.

1-(4-Fluorophenyl)-2-(phenylthio)propan-1-one 3u

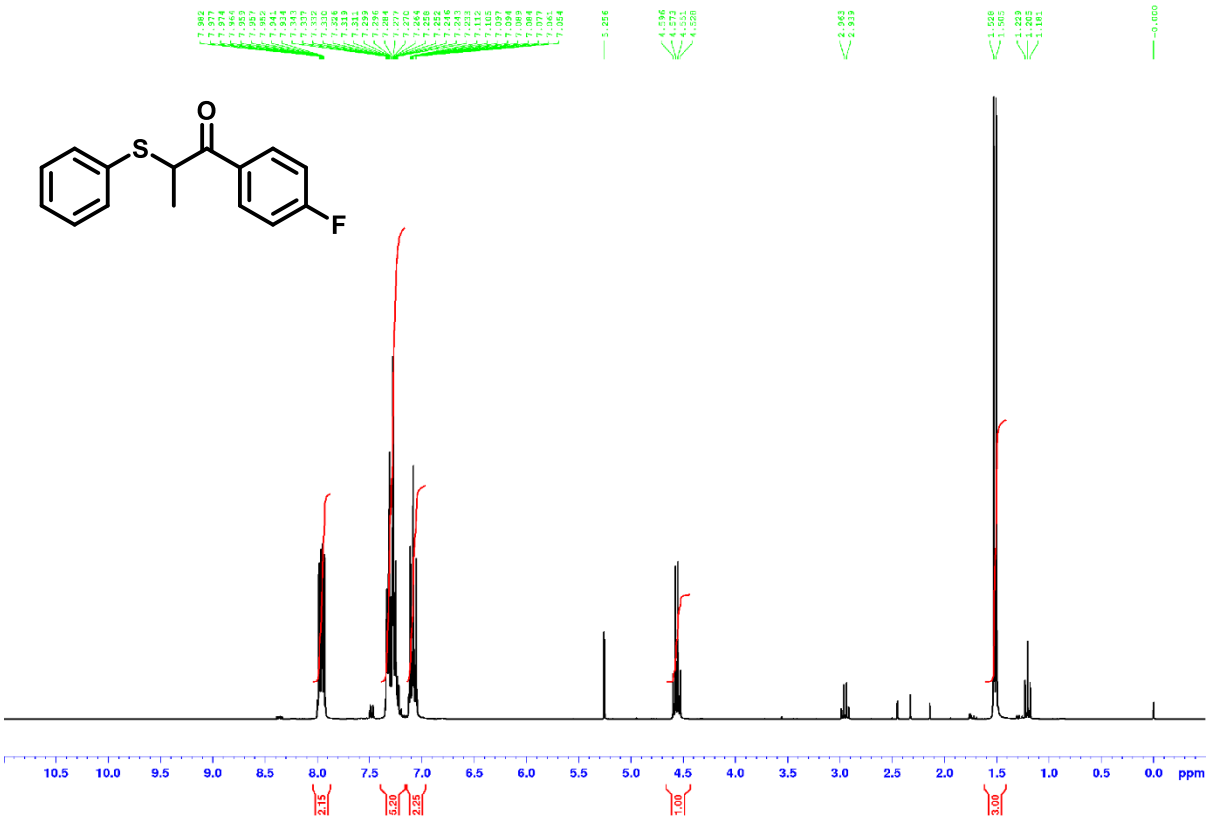


Figure S57: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3u**.

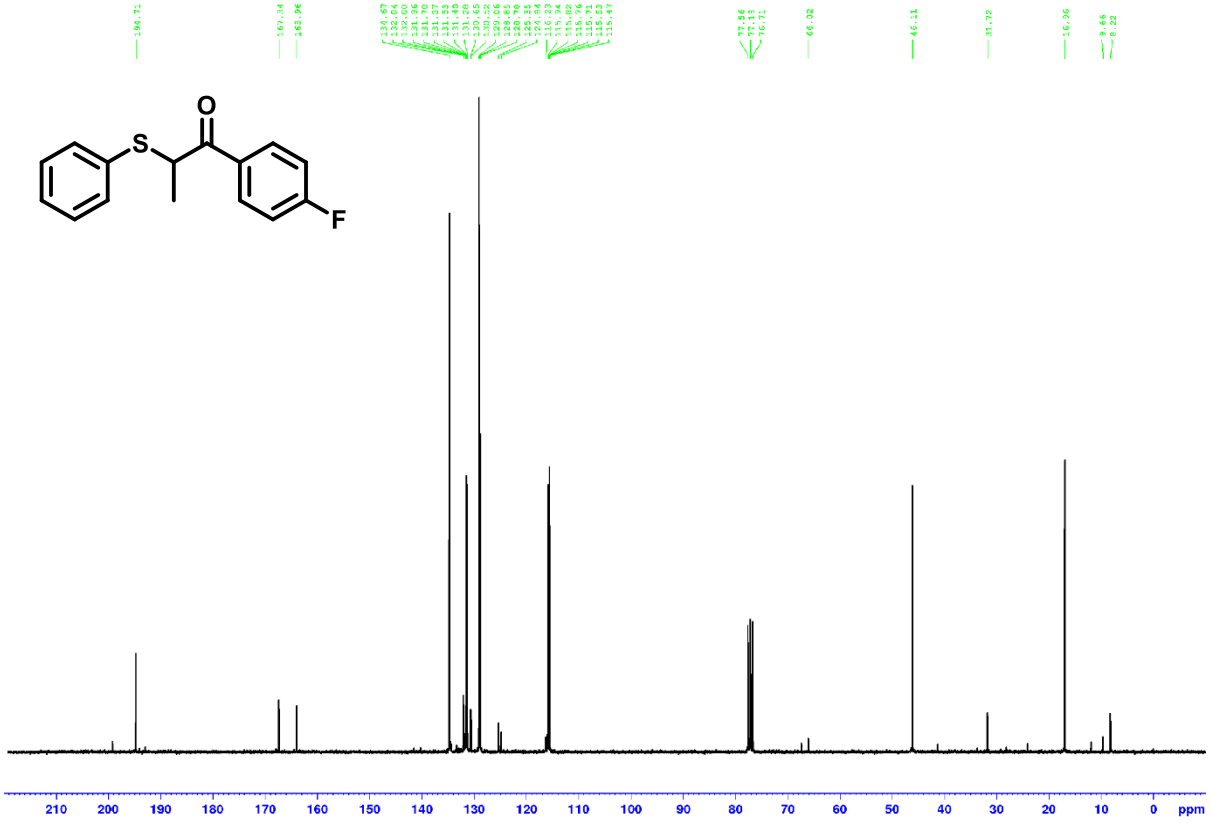


Figure S58: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3u**.

2-(Benzylthio)-1-(4-fluorophenyl)propan-1-one 3v

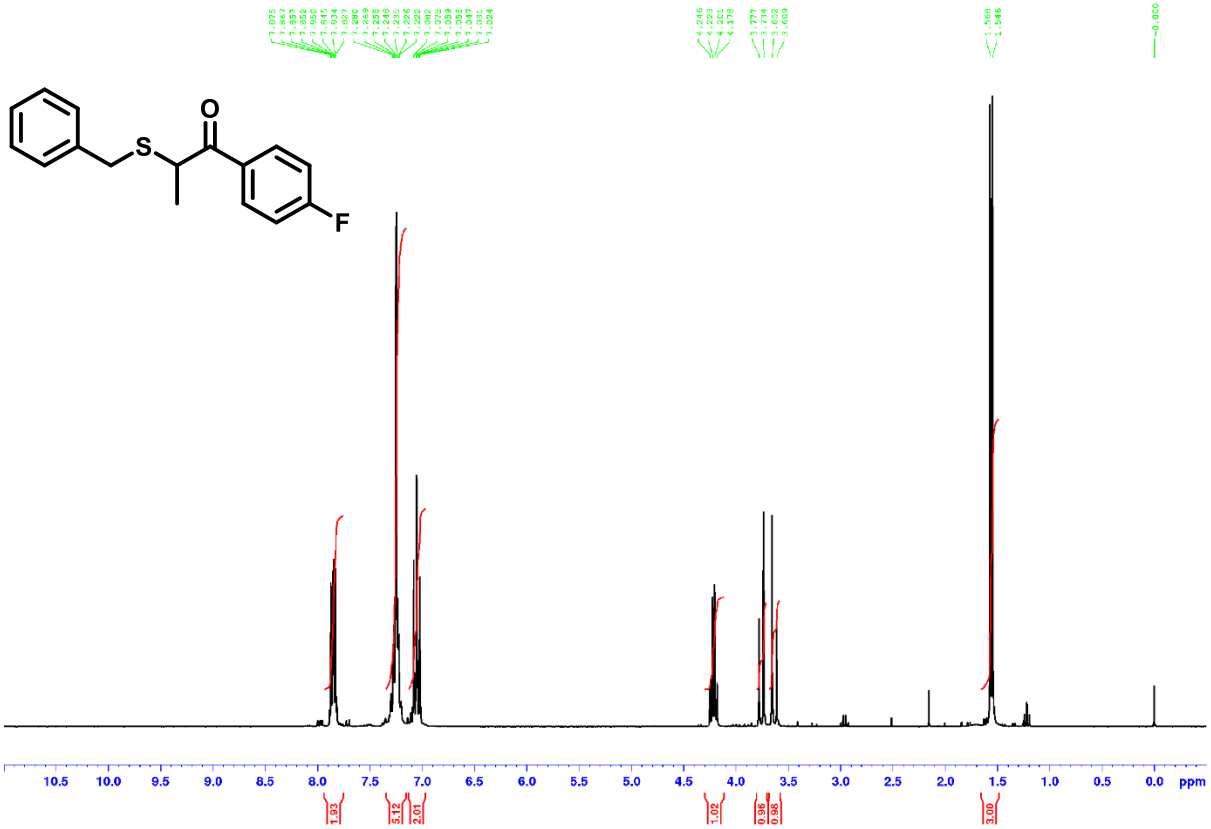


Figure S59: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3v**.

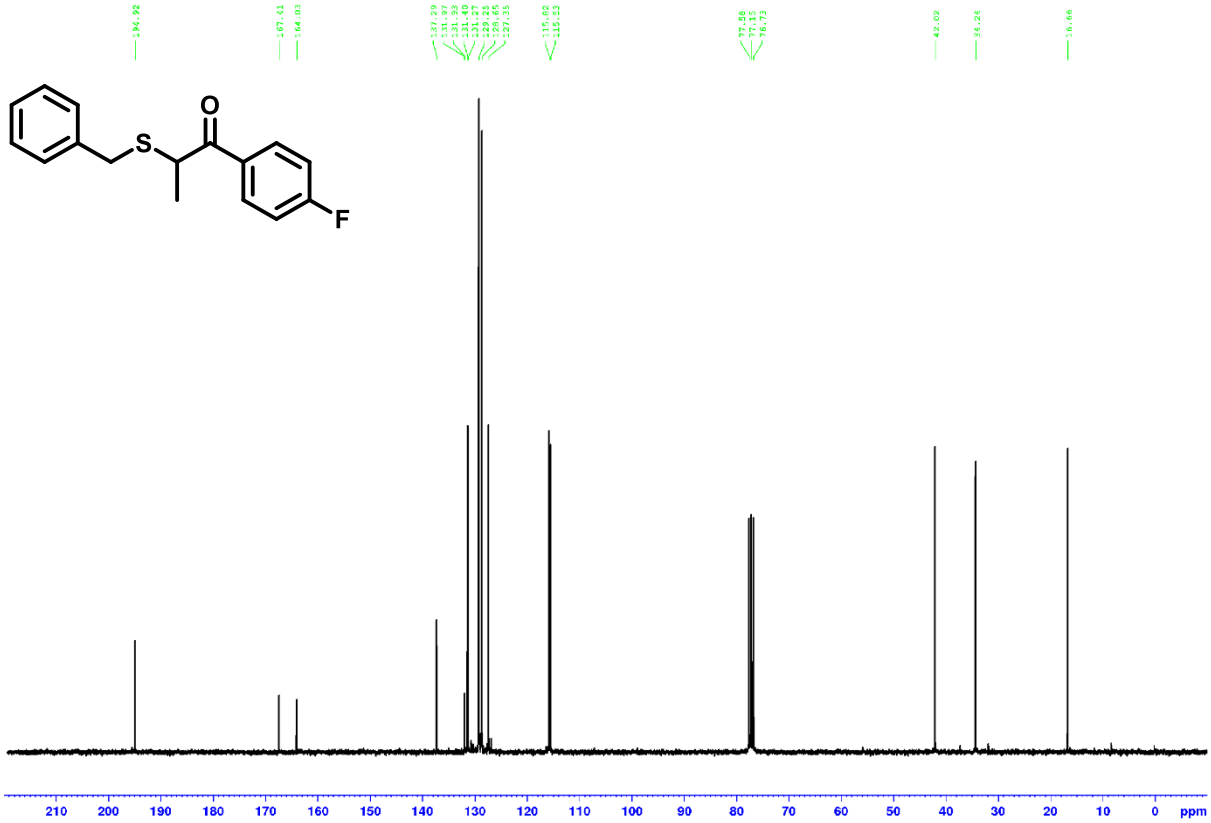


Figure S60: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3v**.

2-(Butylthio)-1-(4-fluorophenyl)propan-1-one 3w

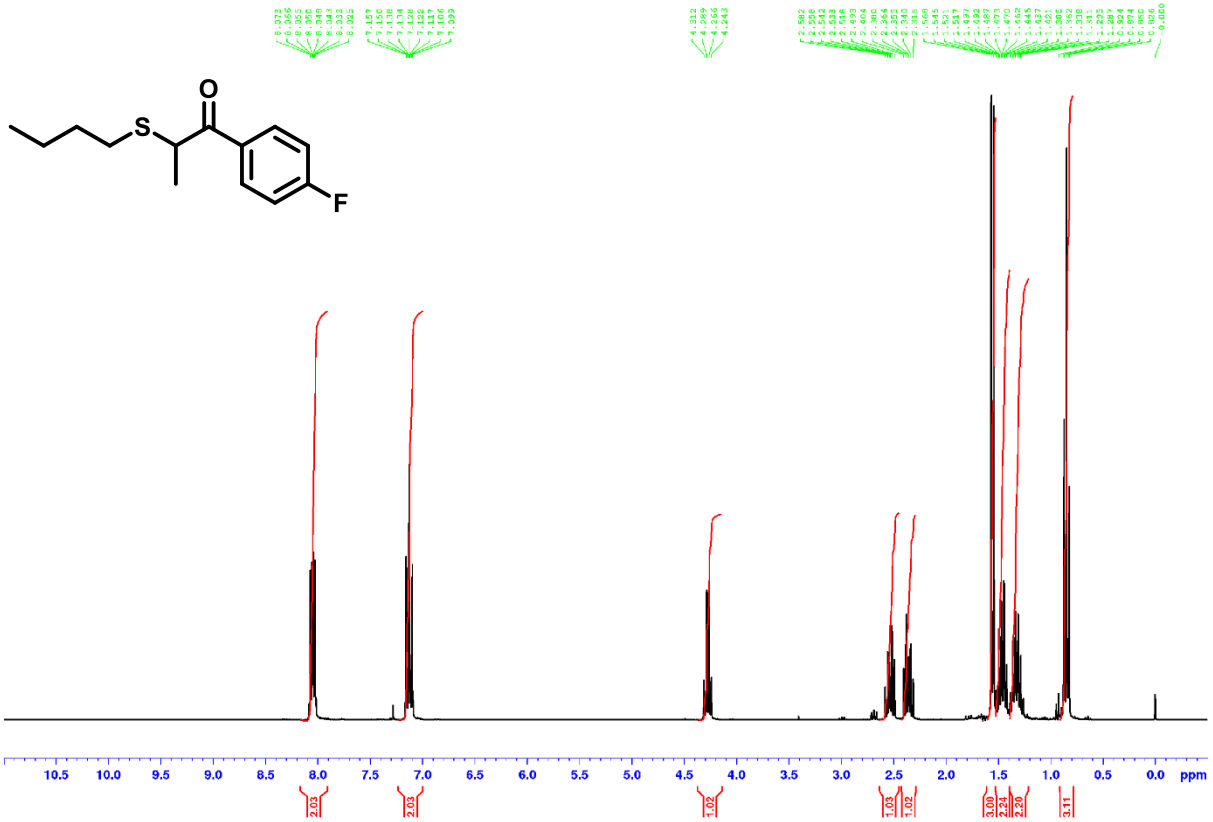


Figure S61: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **3w**.

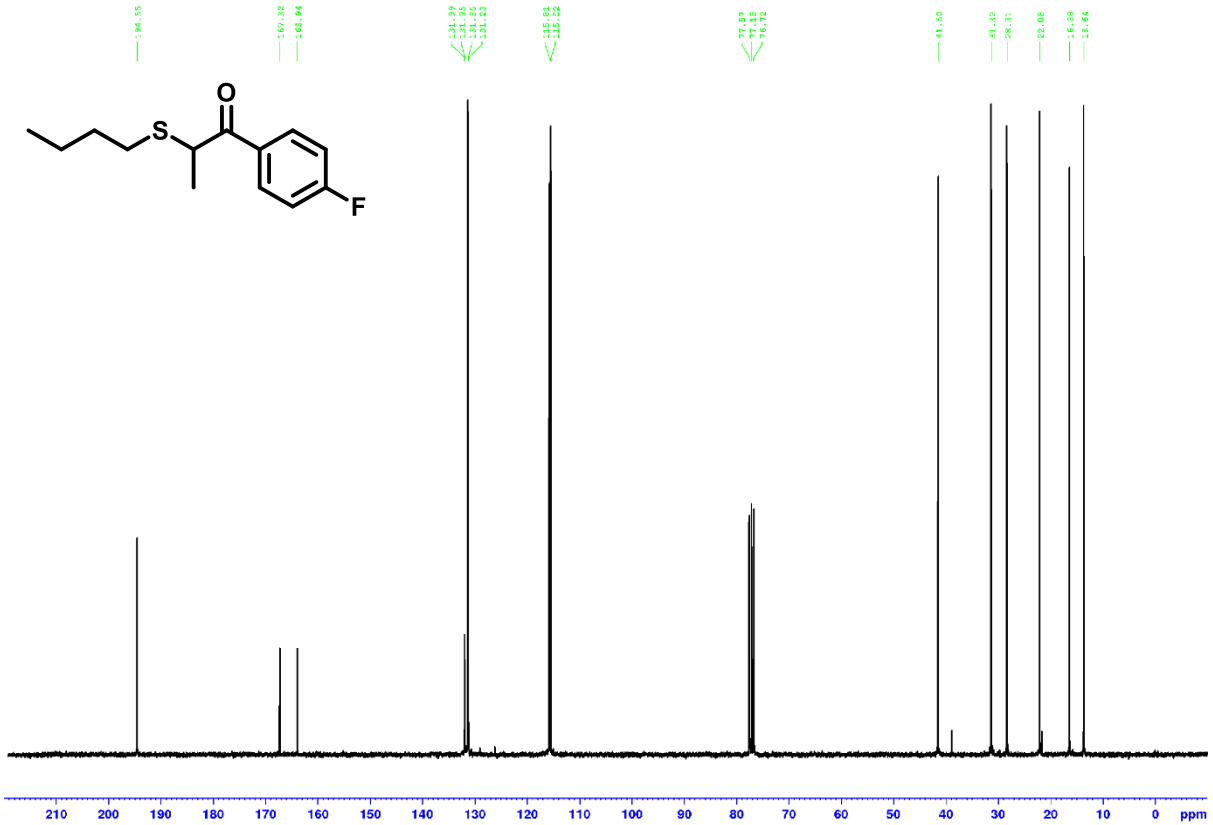


Figure S62: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3w**.

2-((4-Chlorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one 3x

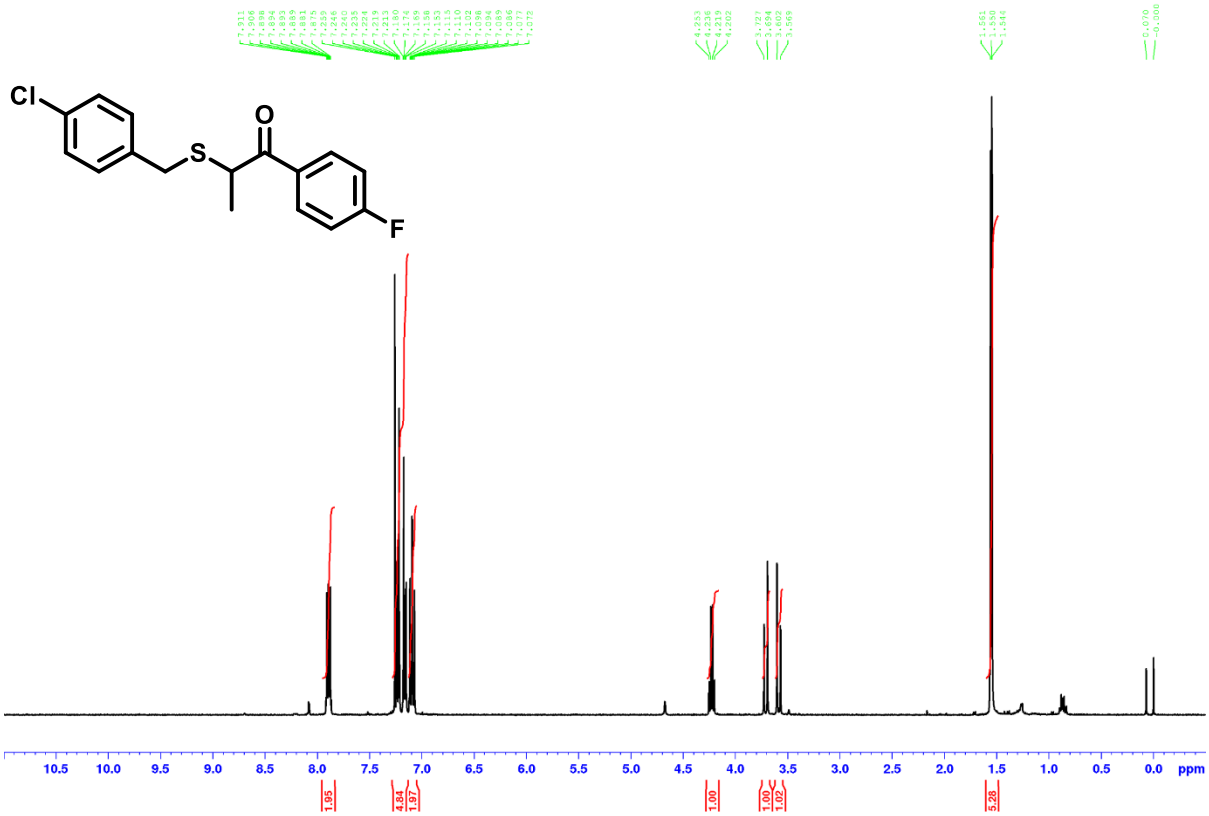


Figure S63: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3x**.

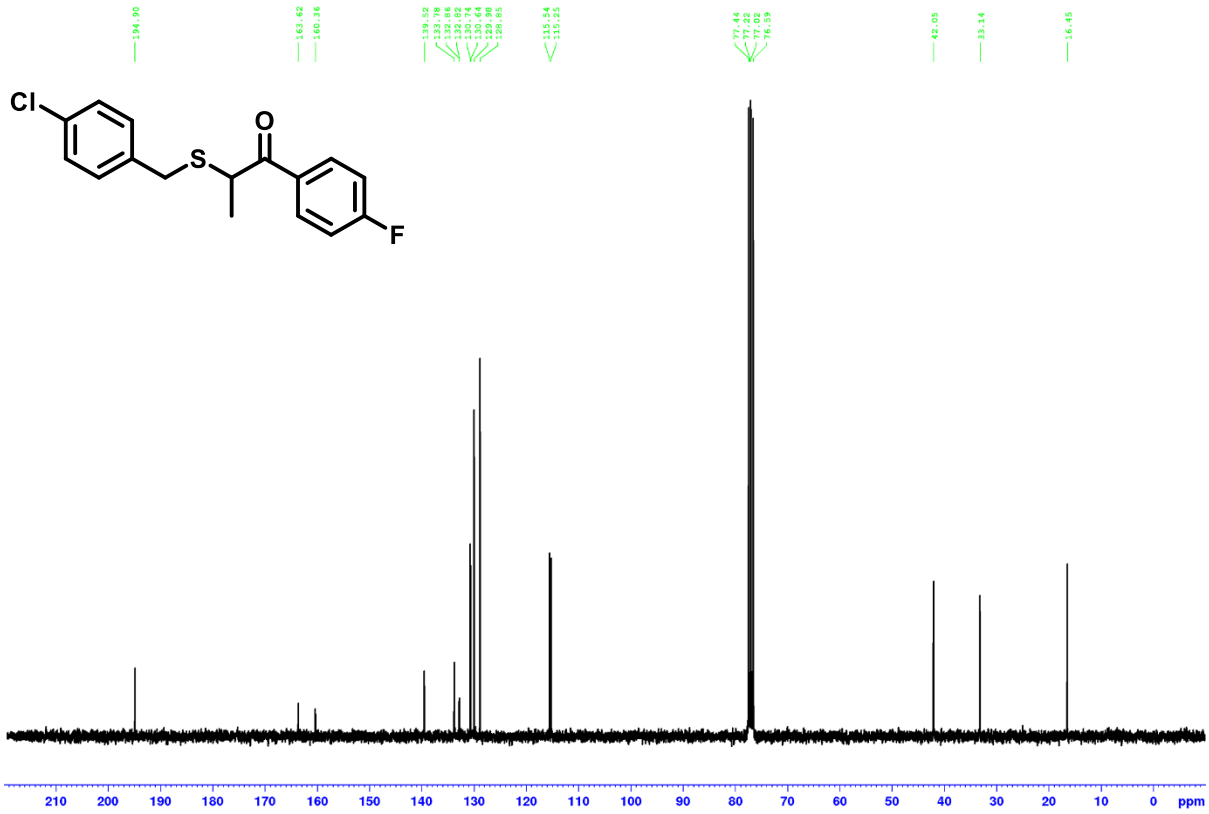


Figure S64: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3x**.

1-(4-Fluorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one 3y

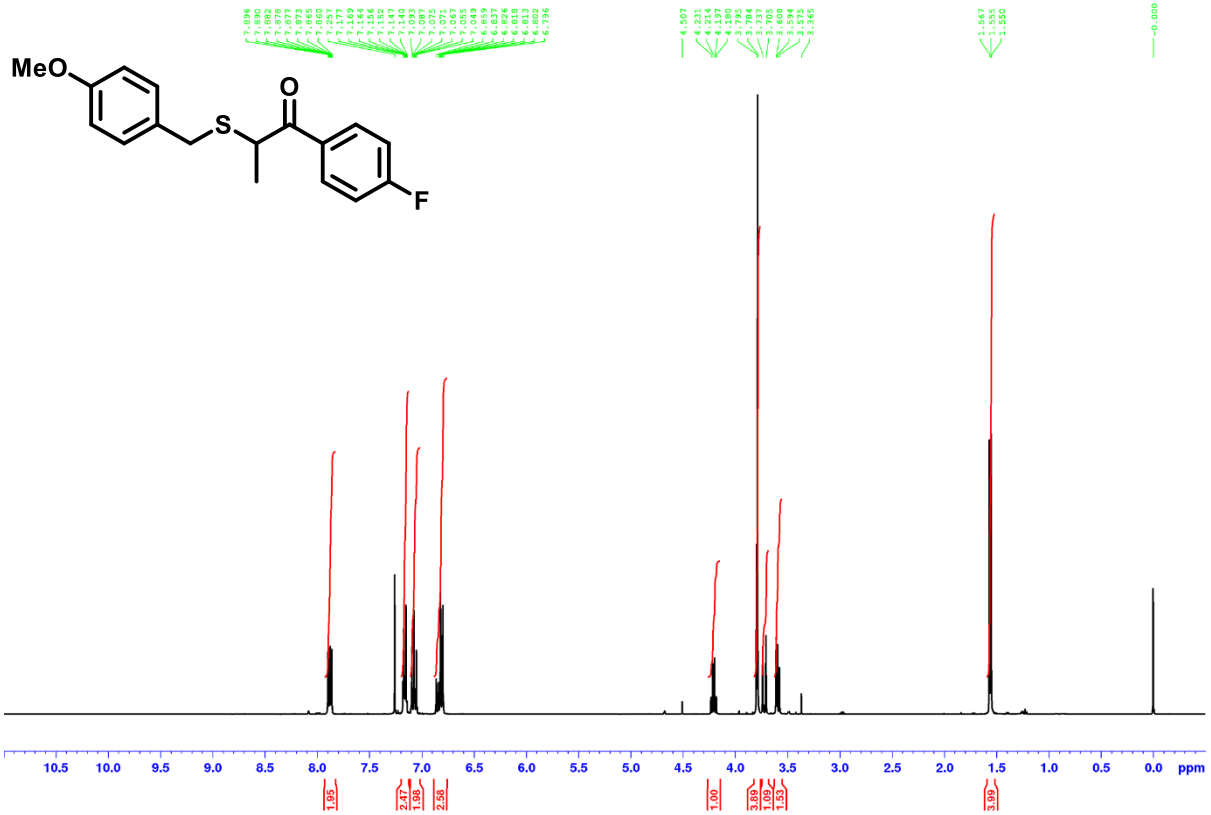


Figure S65: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3y**.

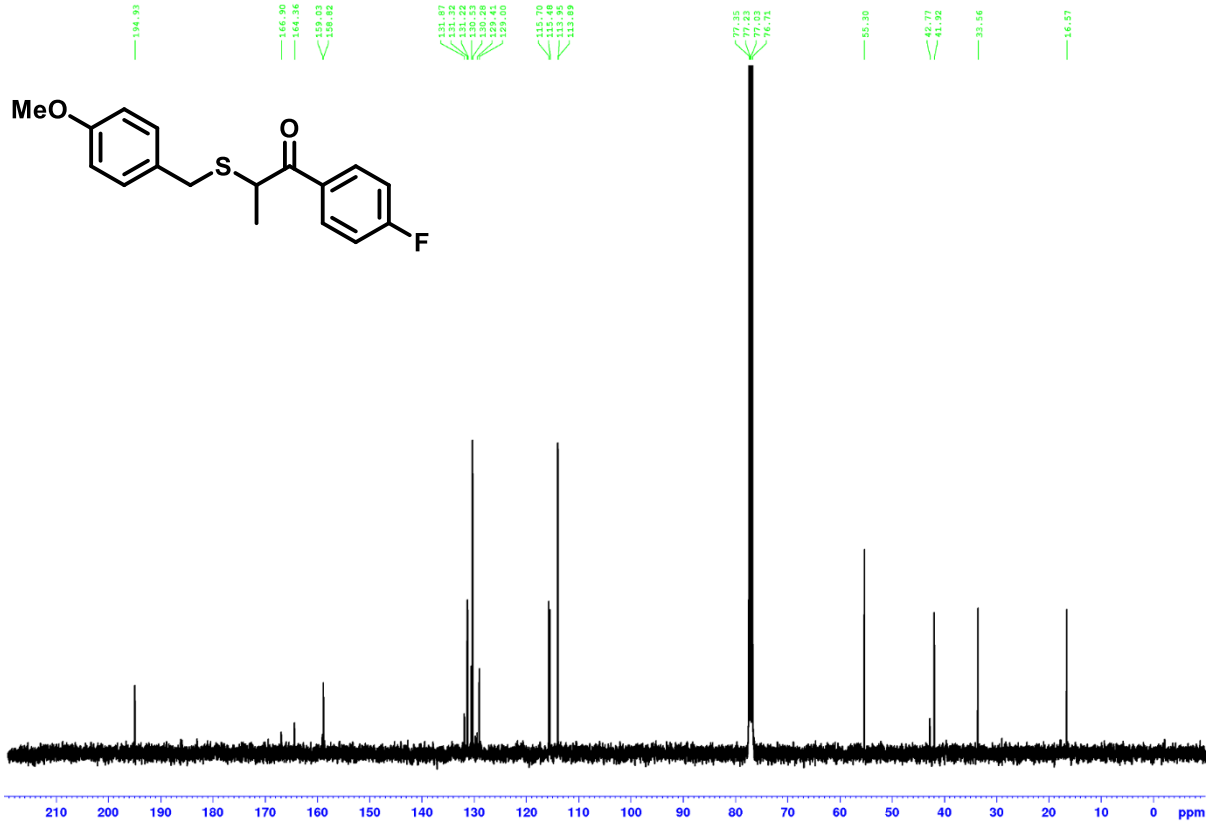


Figure S66: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3y**.

2-((4-Fluorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one 3z

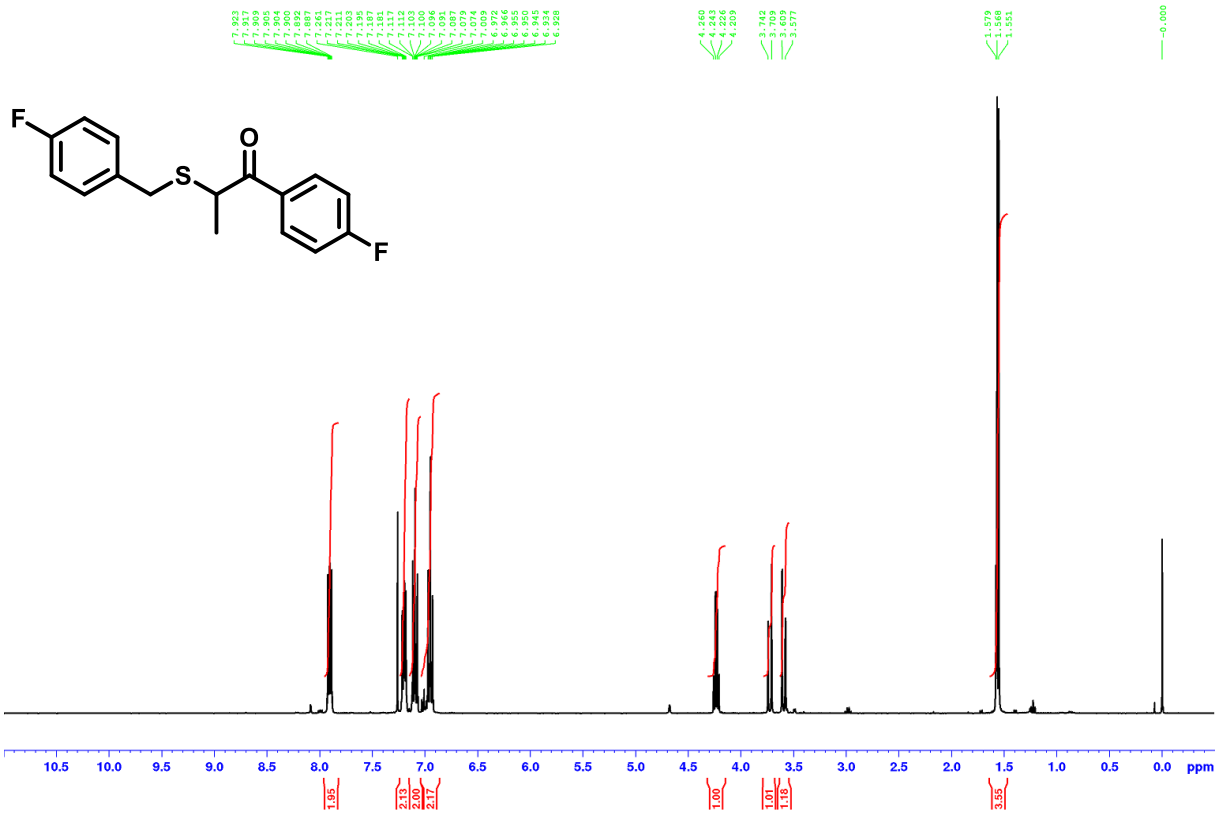


Figure S67: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3z**.

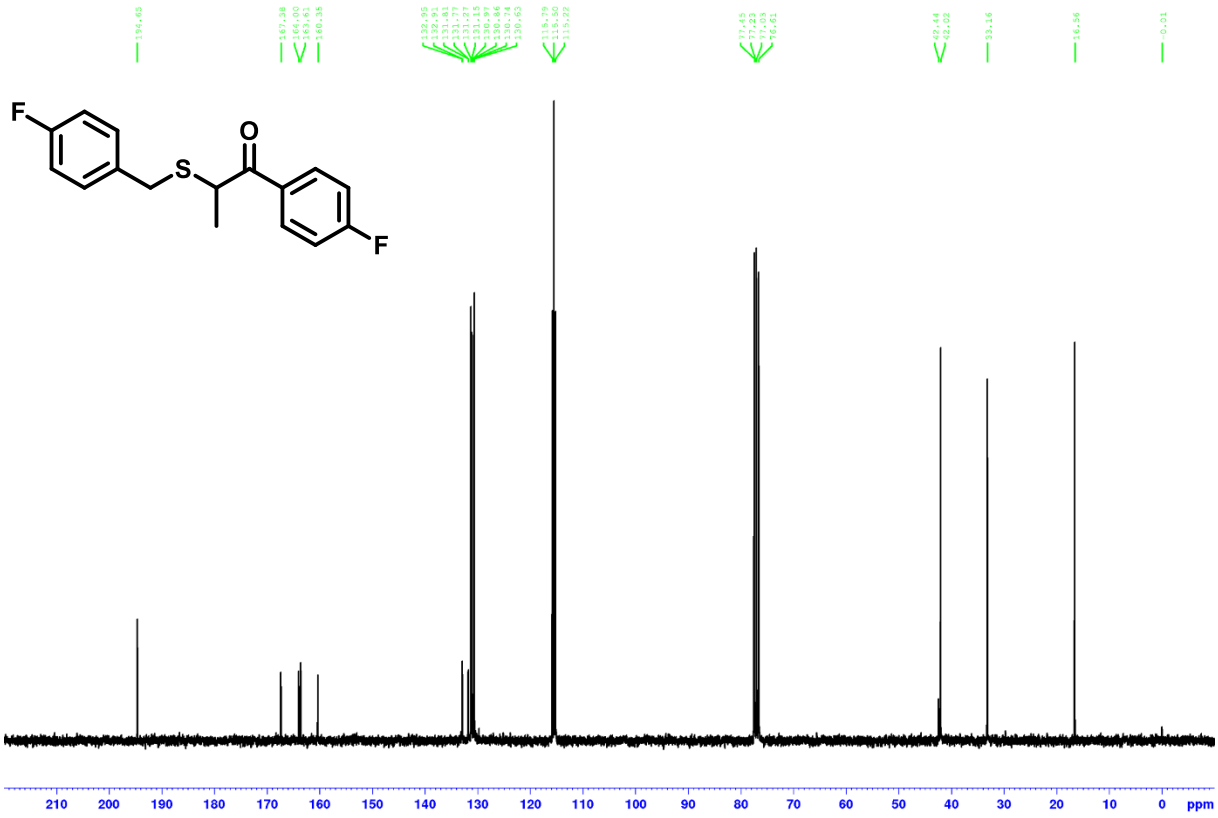


Figure S68: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **3z**.

1-(4-Fluorophenyl)-2-((4-methylbenzyl)thio)- propan-1-one 3aa

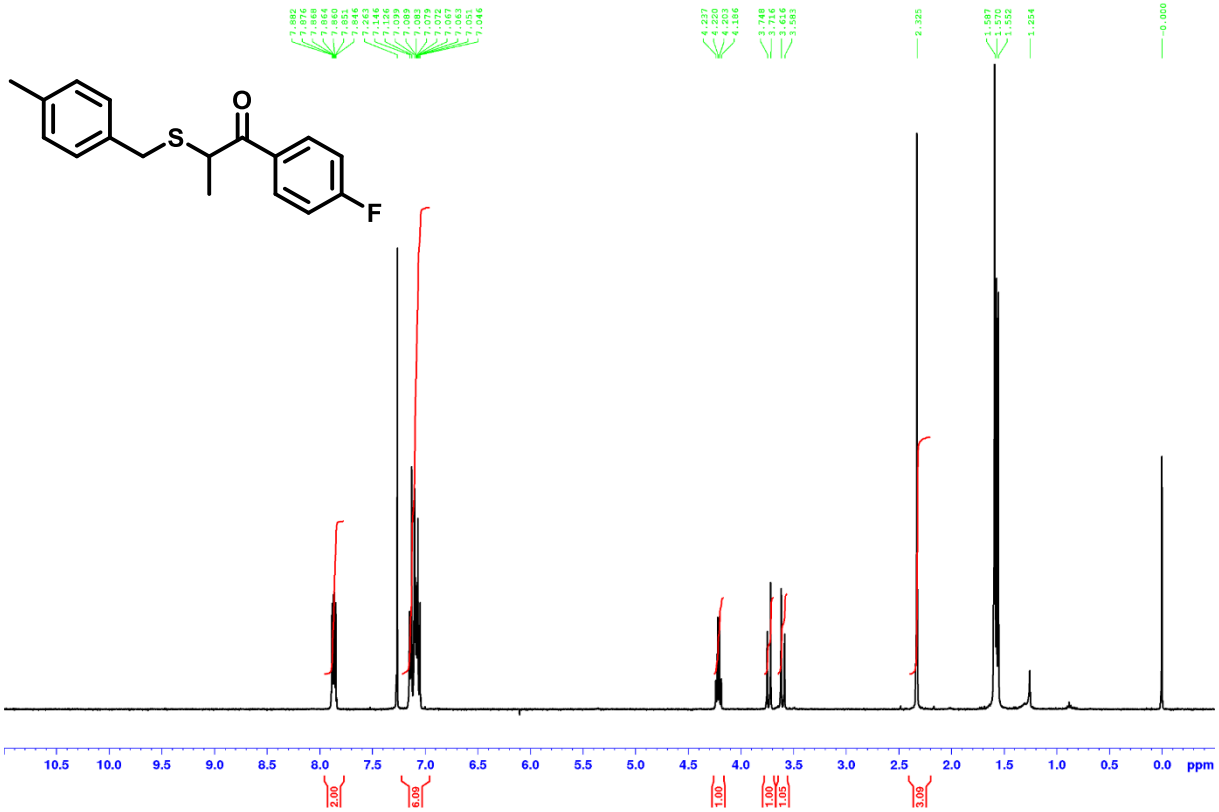


Figure S69: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**.

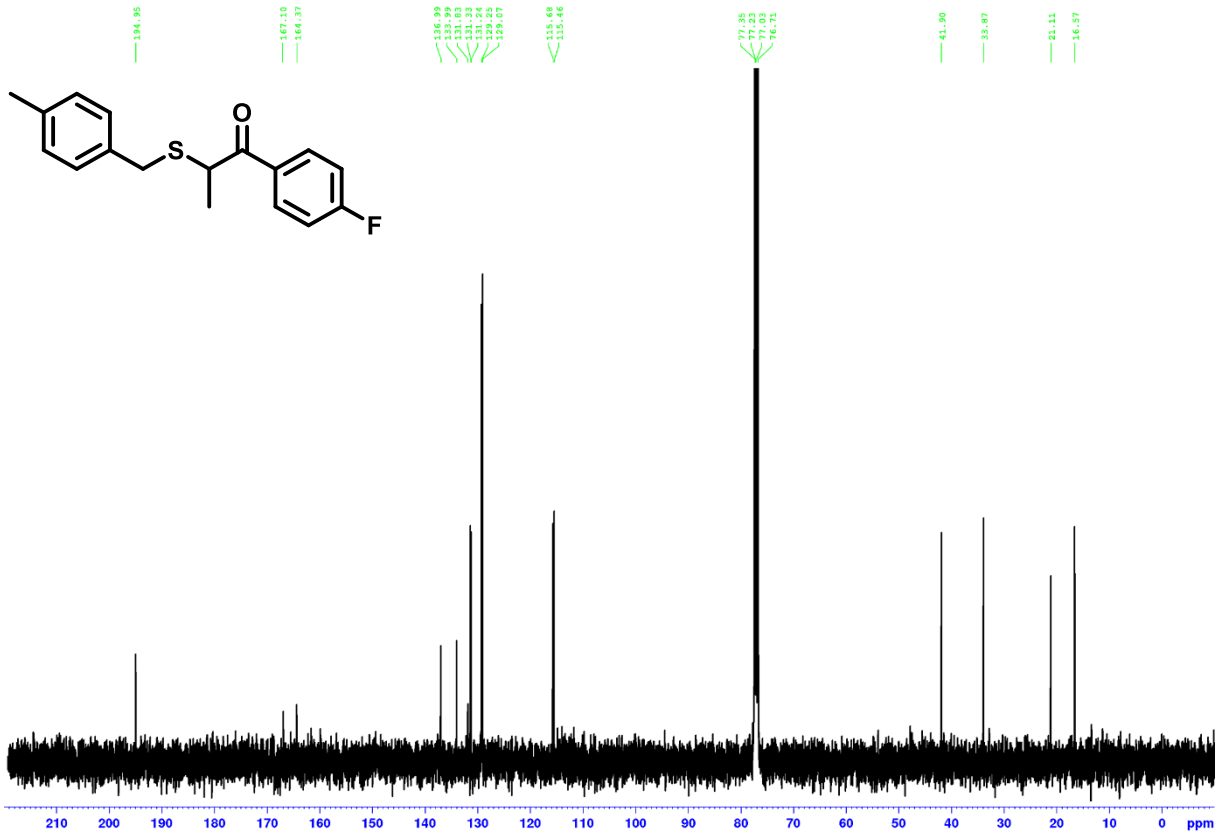


Figure S70: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3aa**.

2-(Benzylthio)-1-phenylbutan-1-one 3bb

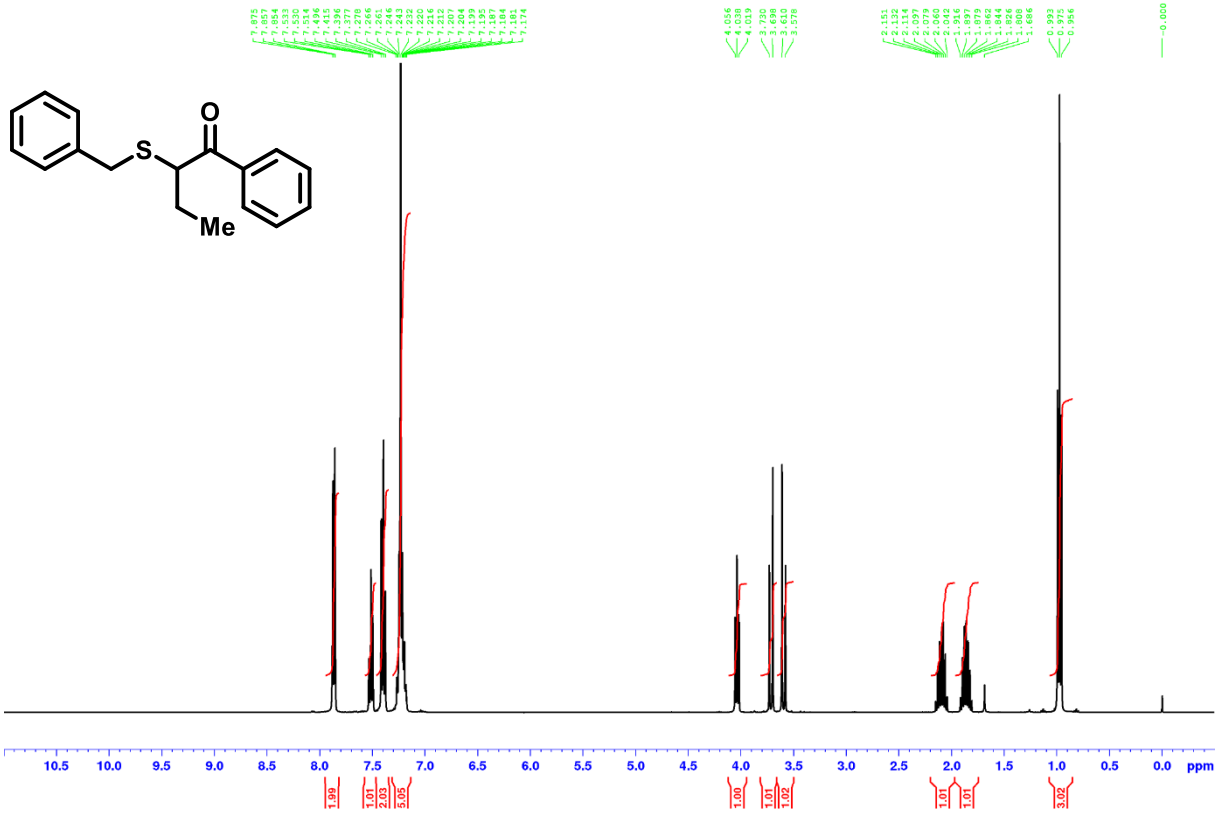


Figure S71: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3bb**.

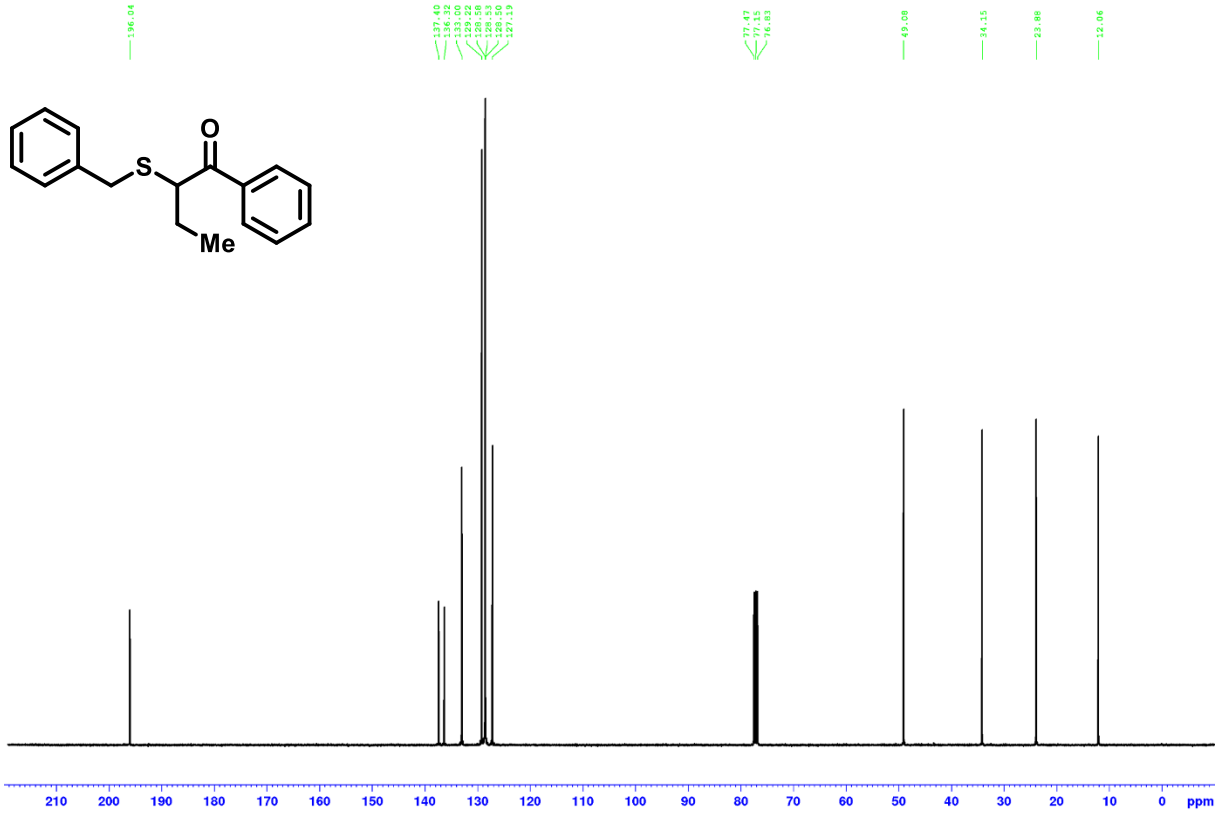


Figure S72: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3bb**.

2-((4-Chlorobenzyl)thio)-1-phenylbutan-1-one 3cc

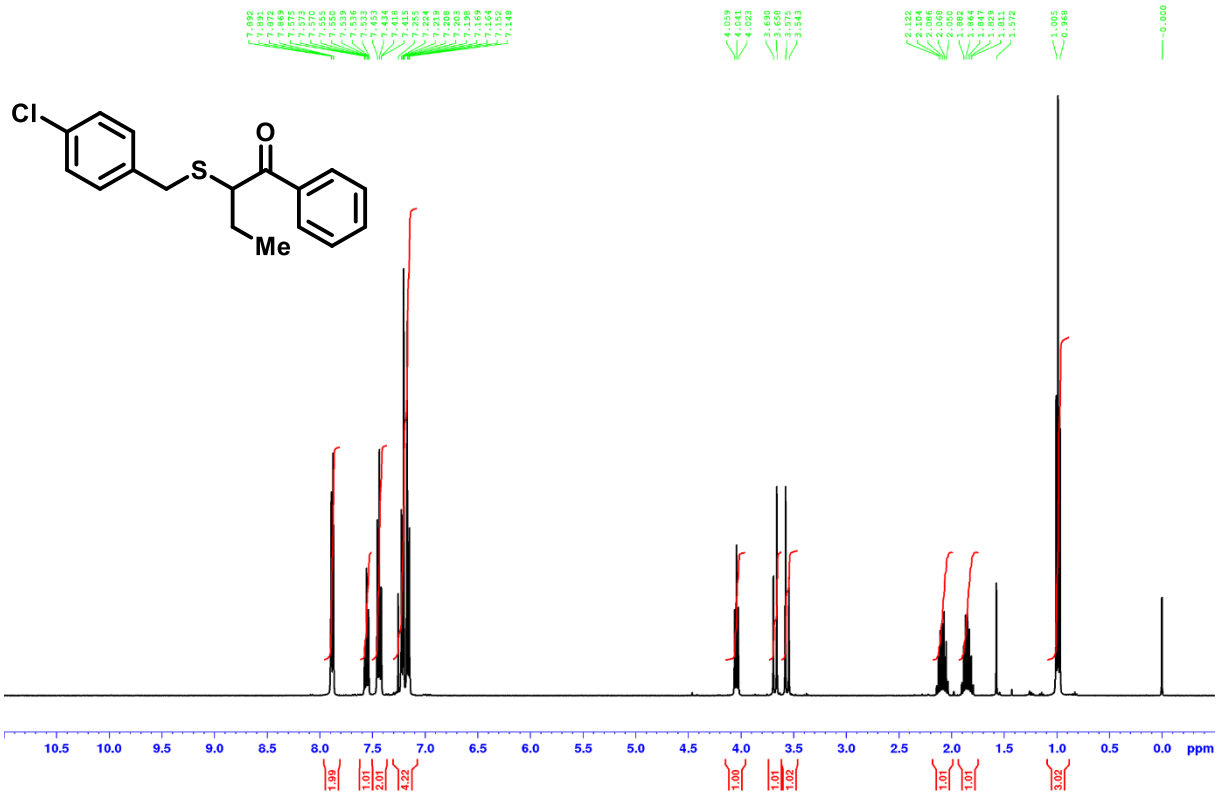


Figure S73: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3cc**.

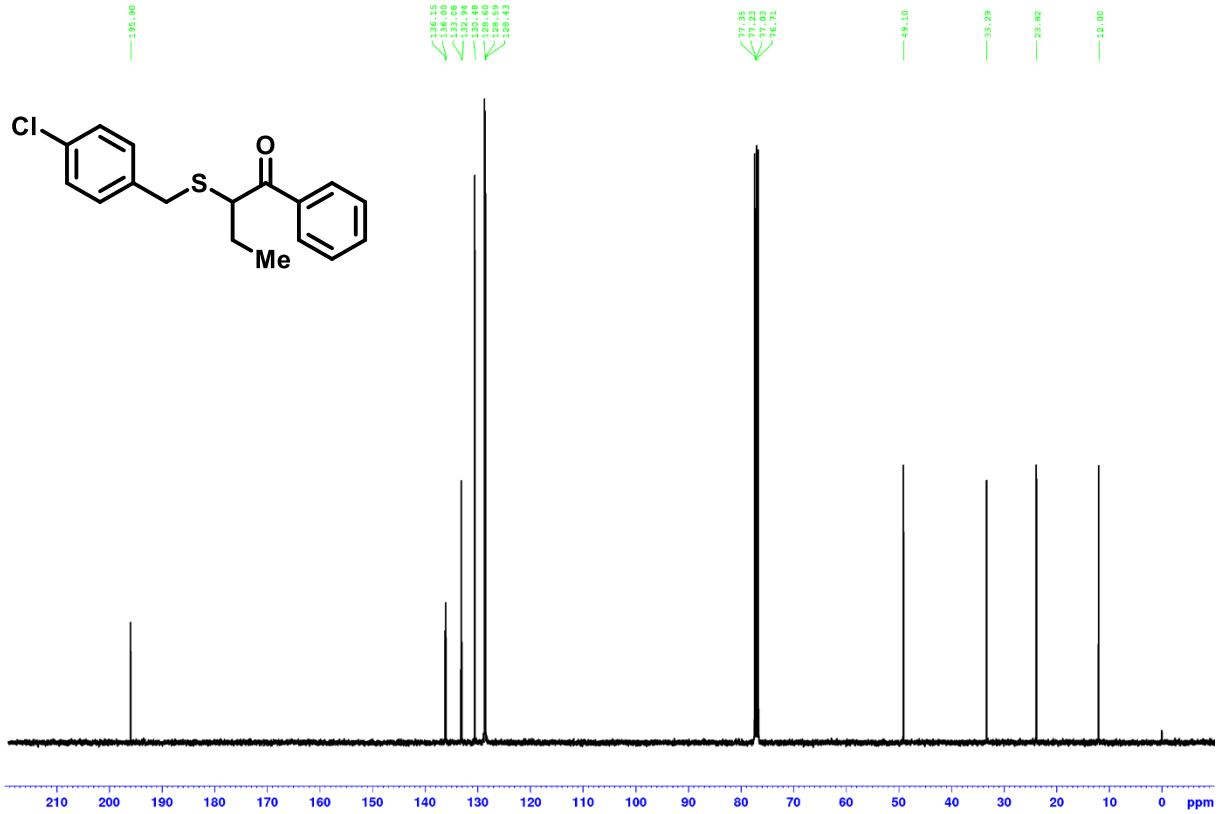


Figure S74: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3cc**.

2-((4-Methoxybenzyl)thio)-1-phenylbutan-1-one 3dd

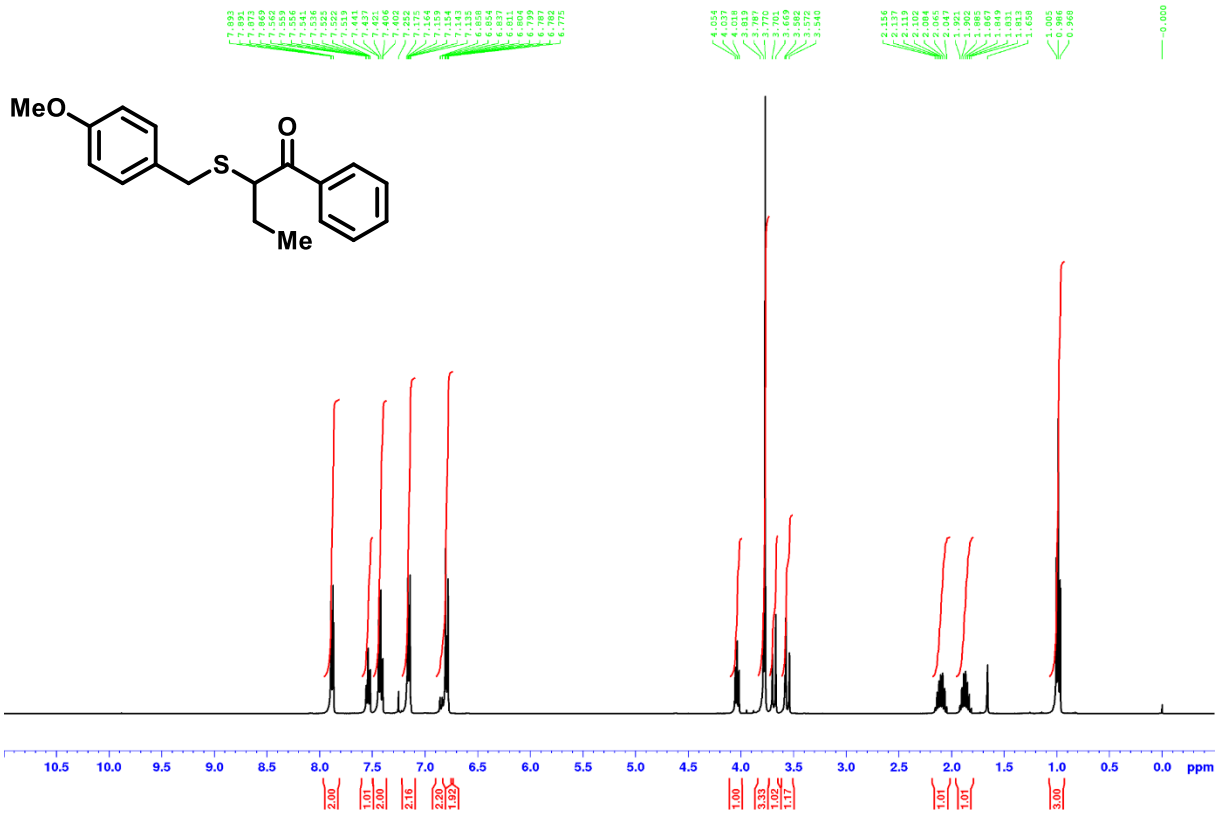


Figure S75: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3dd**.

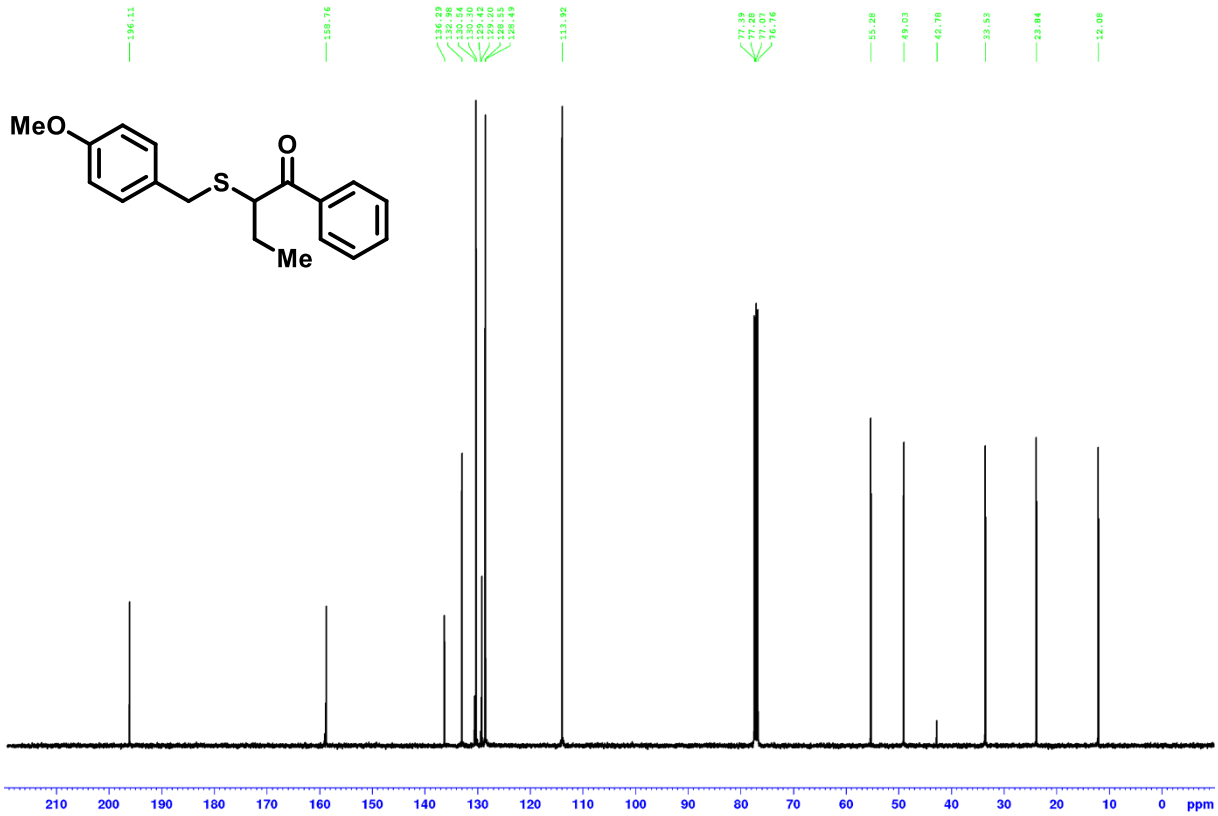


Figure S76: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3dd**.

2-((4-Fluorobenzyl)thio)-1-phenylbutan-1-one 3ee

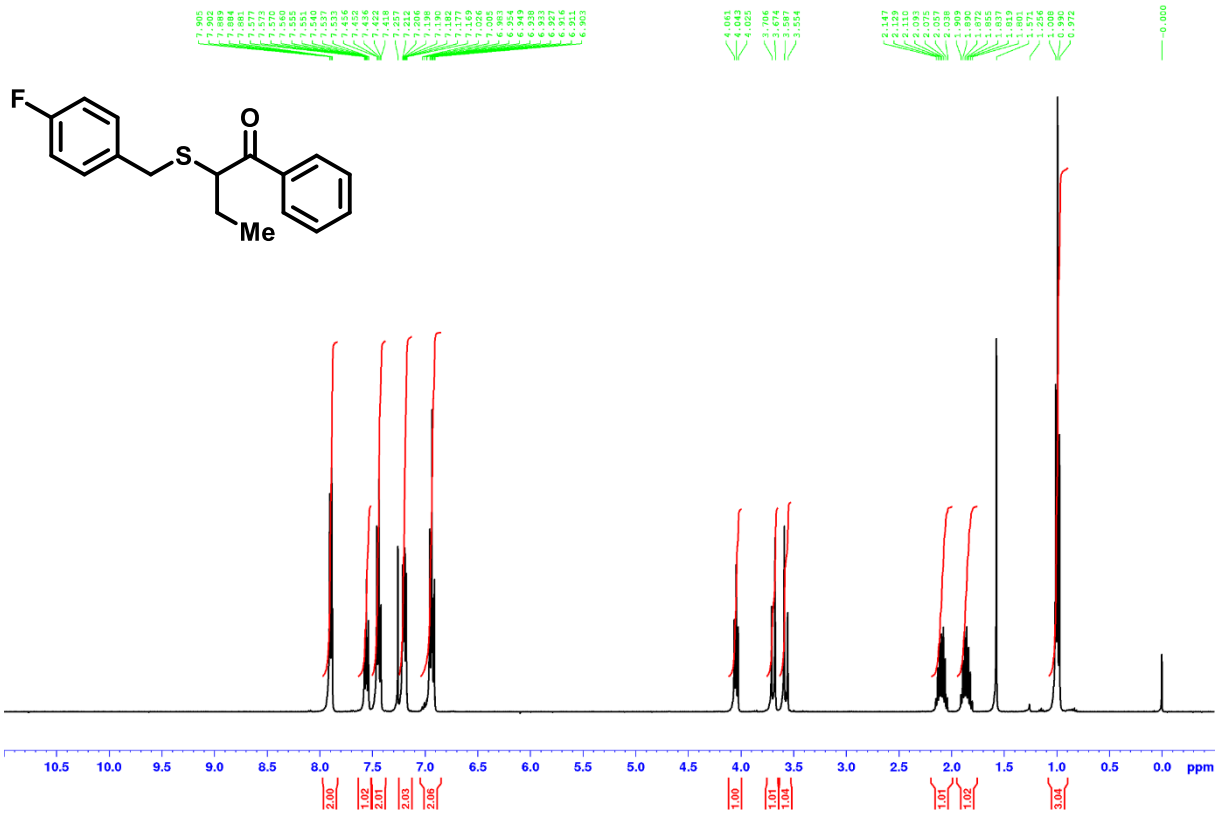


Figure S77: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ee**.

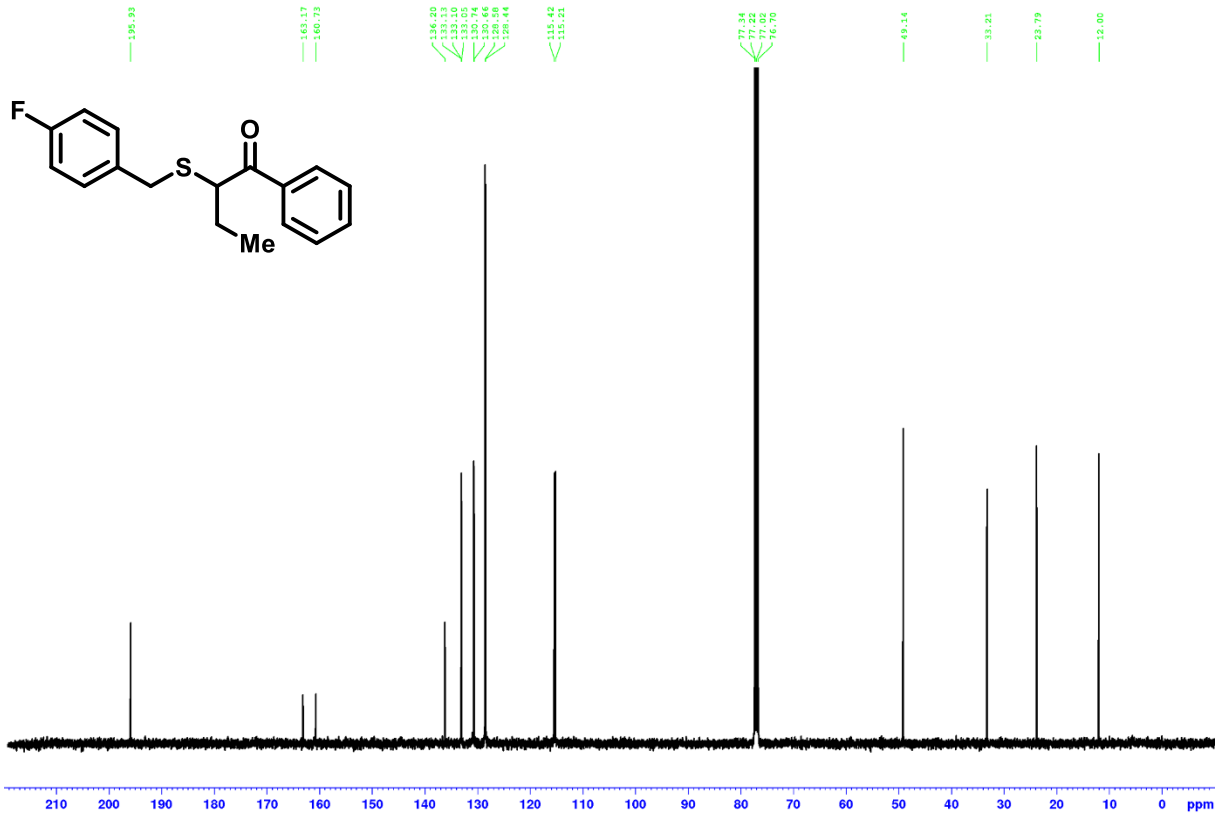


Figure S78: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3ee**.

2-((4-Methylbenzyl)thio)-1-phenylbutan-1-one 3ff

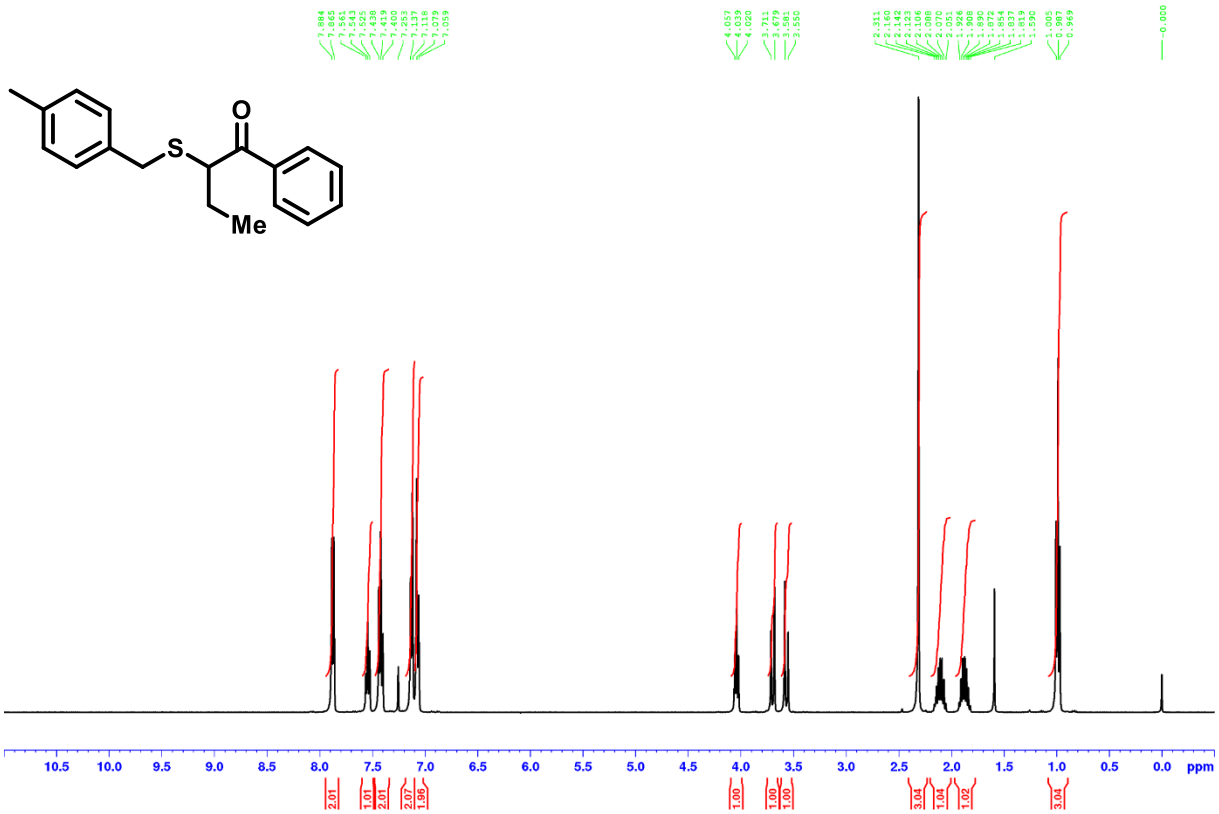


Figure S79: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ff**.

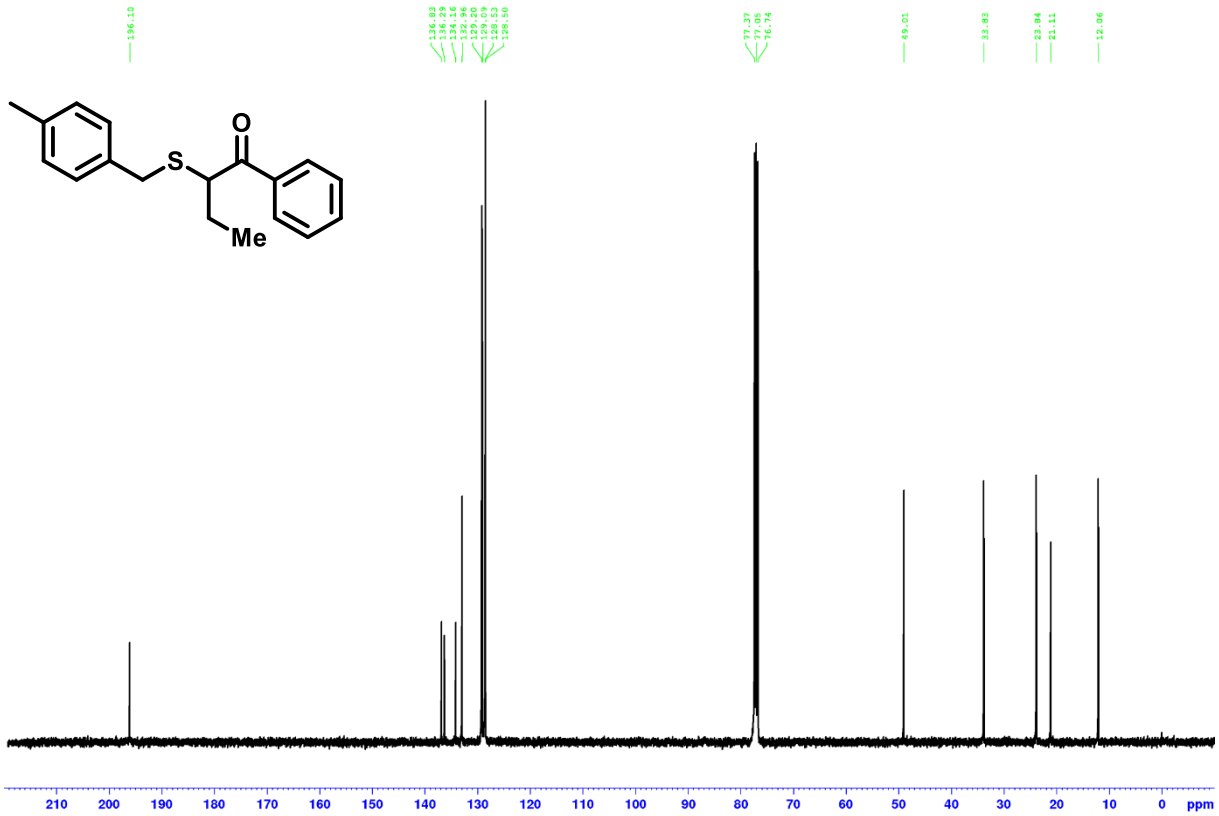


Figure S80: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3ff**.

1-Phenyl-2-(phenylthio)butan-1-one 3gg

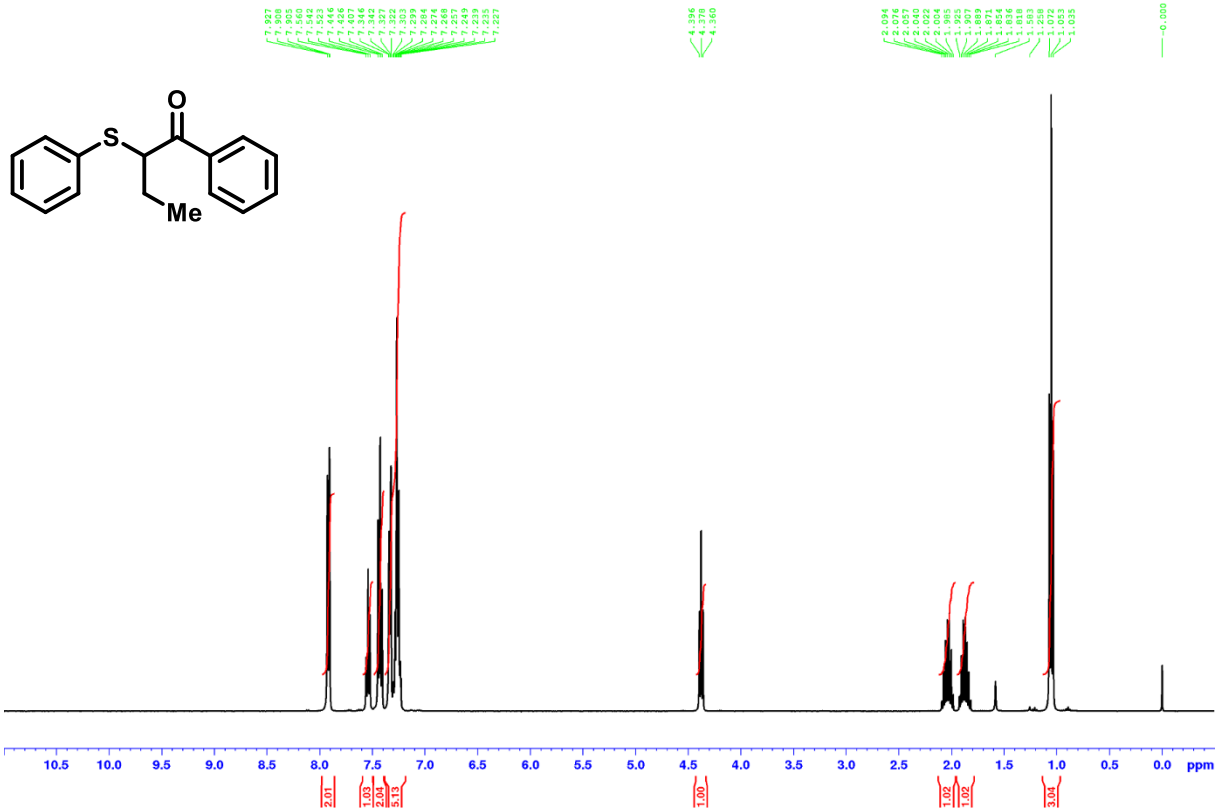


Figure S81: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3gg**.

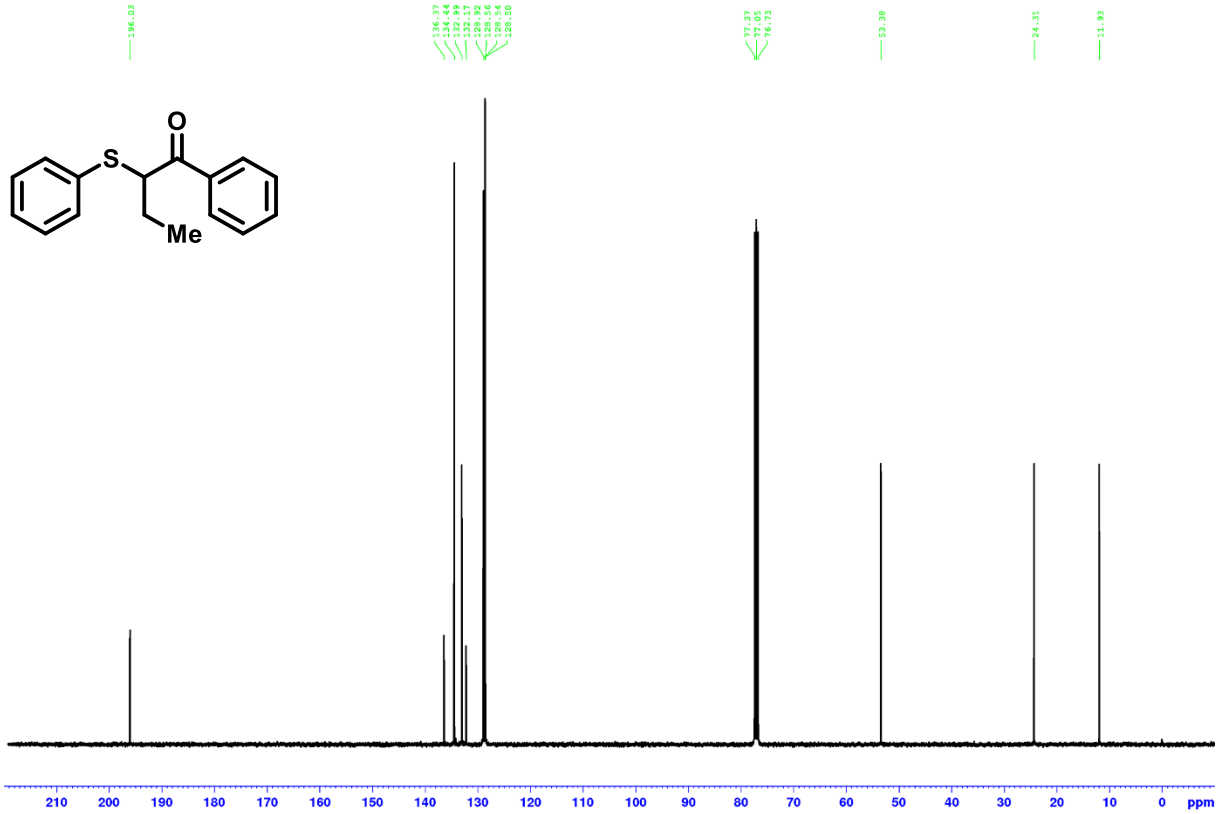


Figure S82: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3gg**.

2-(Benzylthio)-1-phenylpentan-1-one 3hh

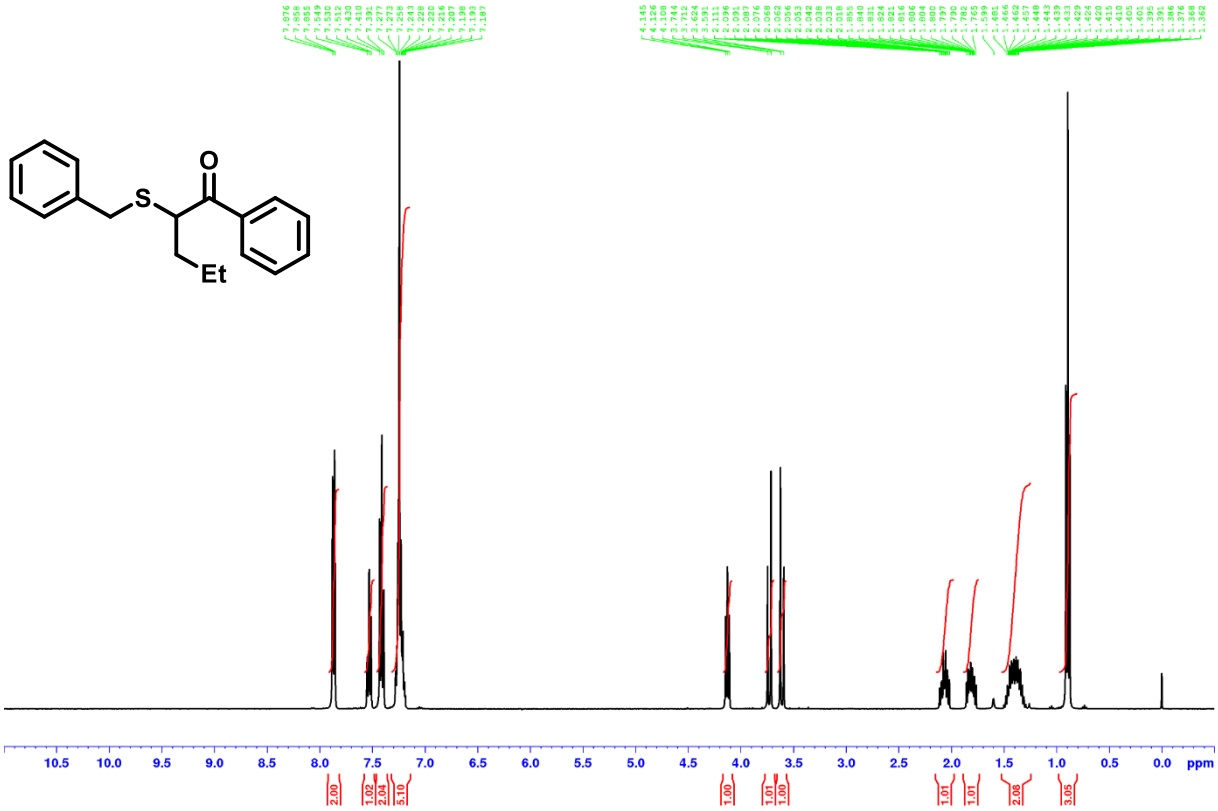


Figure S83: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3hh**.

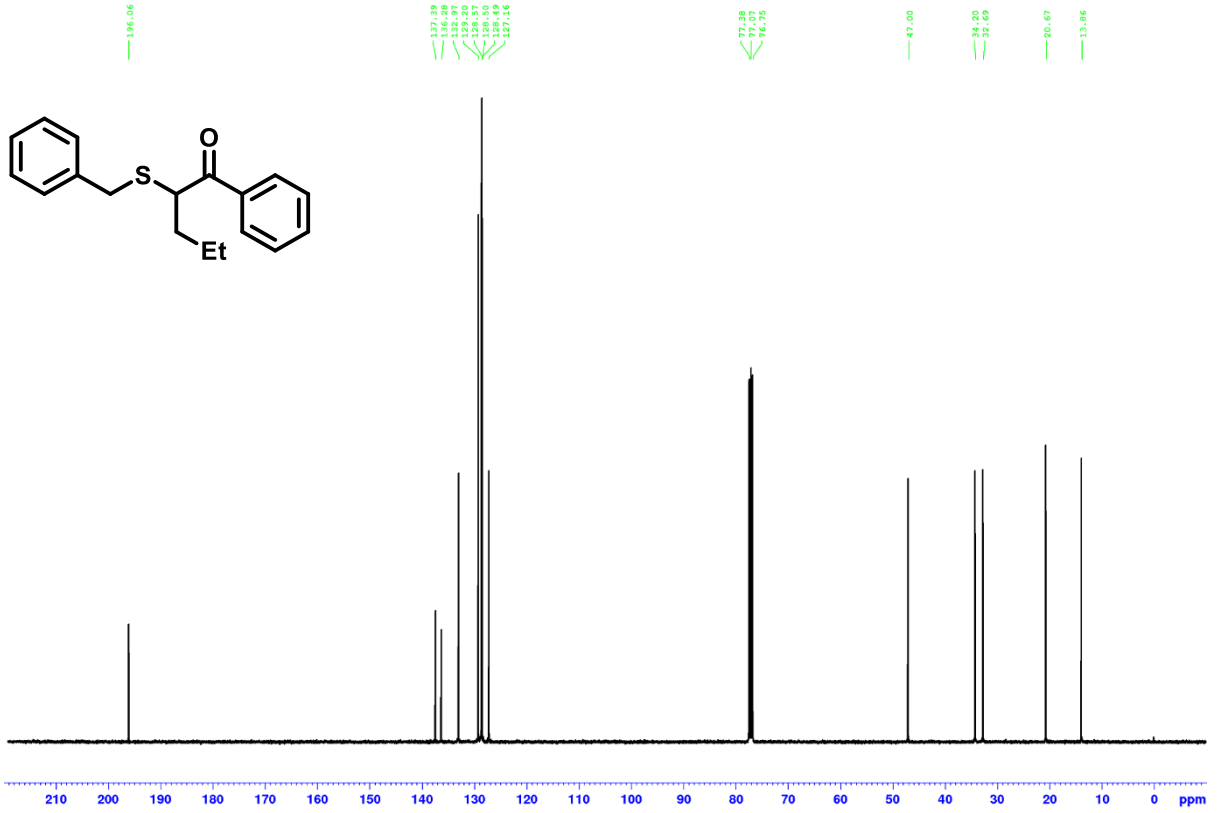


Figure S84: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3hh**.

2-((4-Chlorobenzyl)thio)-1-phenylpentan-1-one 3ii

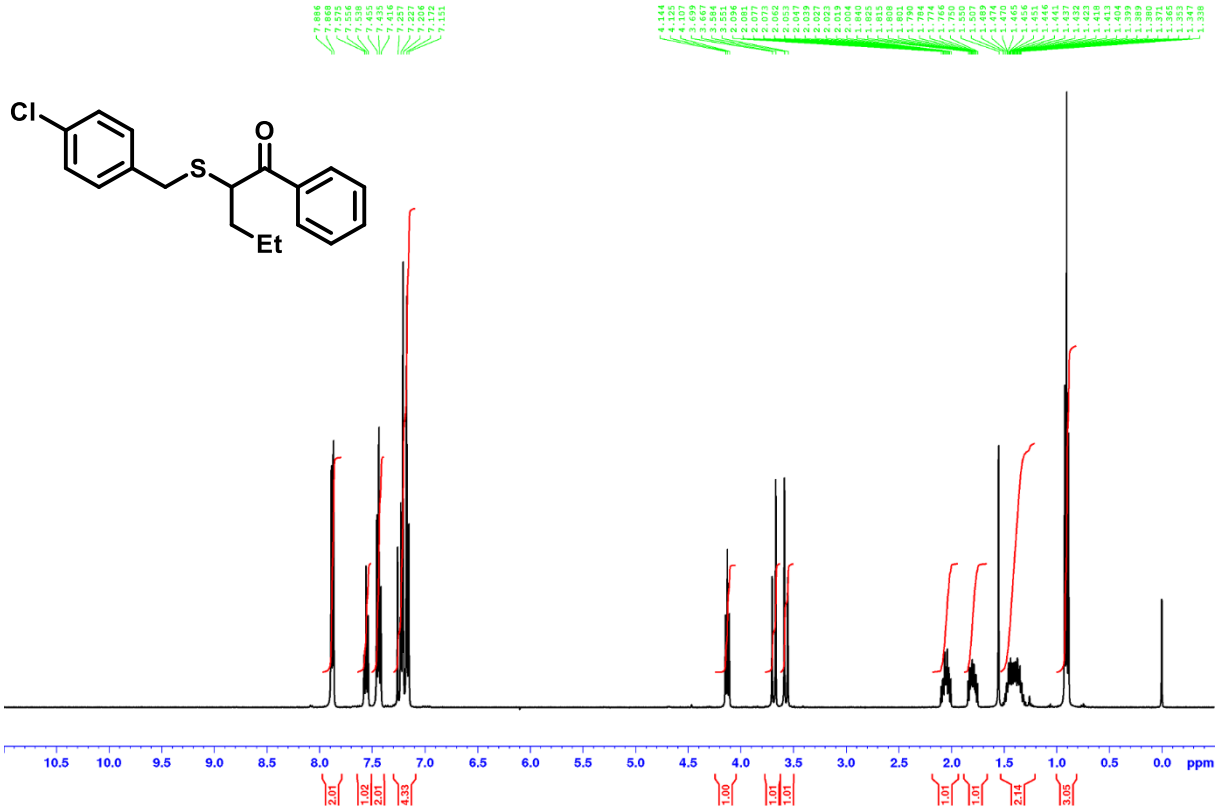


Figure S85: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ii**.

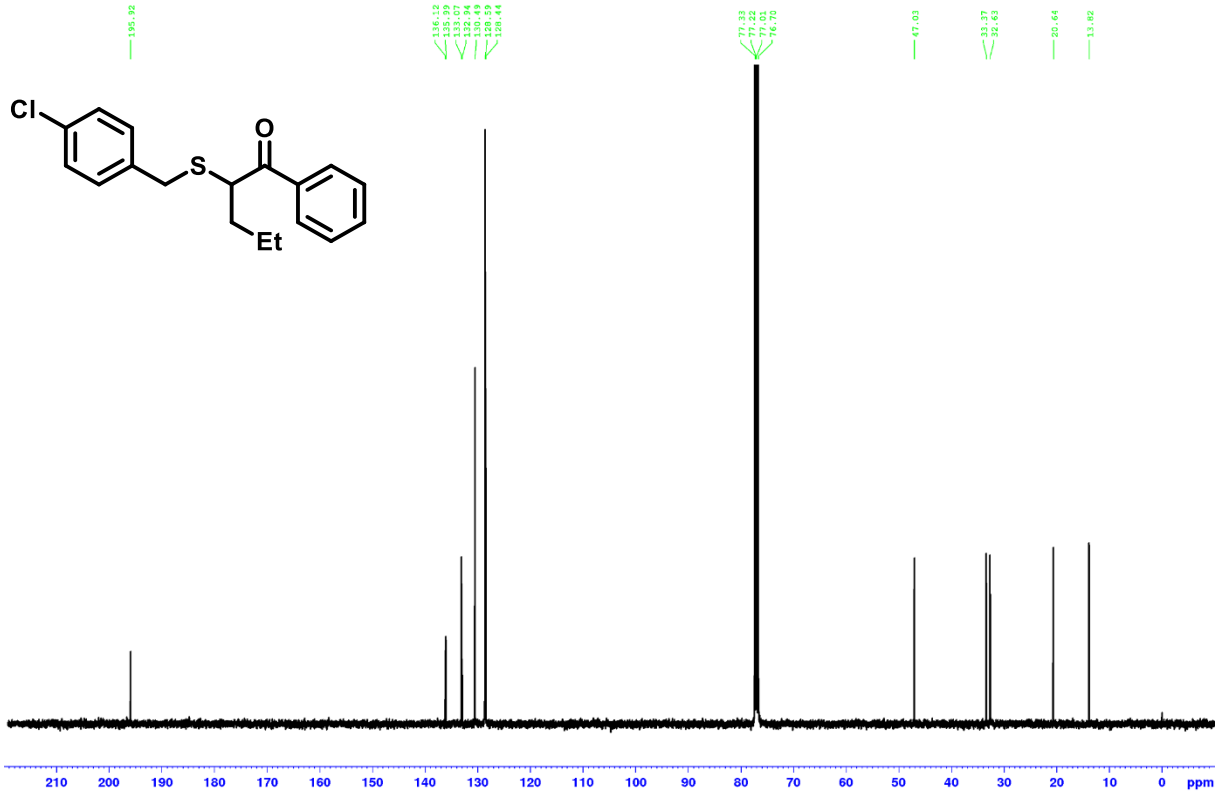


Figure S86: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3ii**.

2-((4-Methoxybenzyl)thio)-1-phenylpentan-1-one 3jj

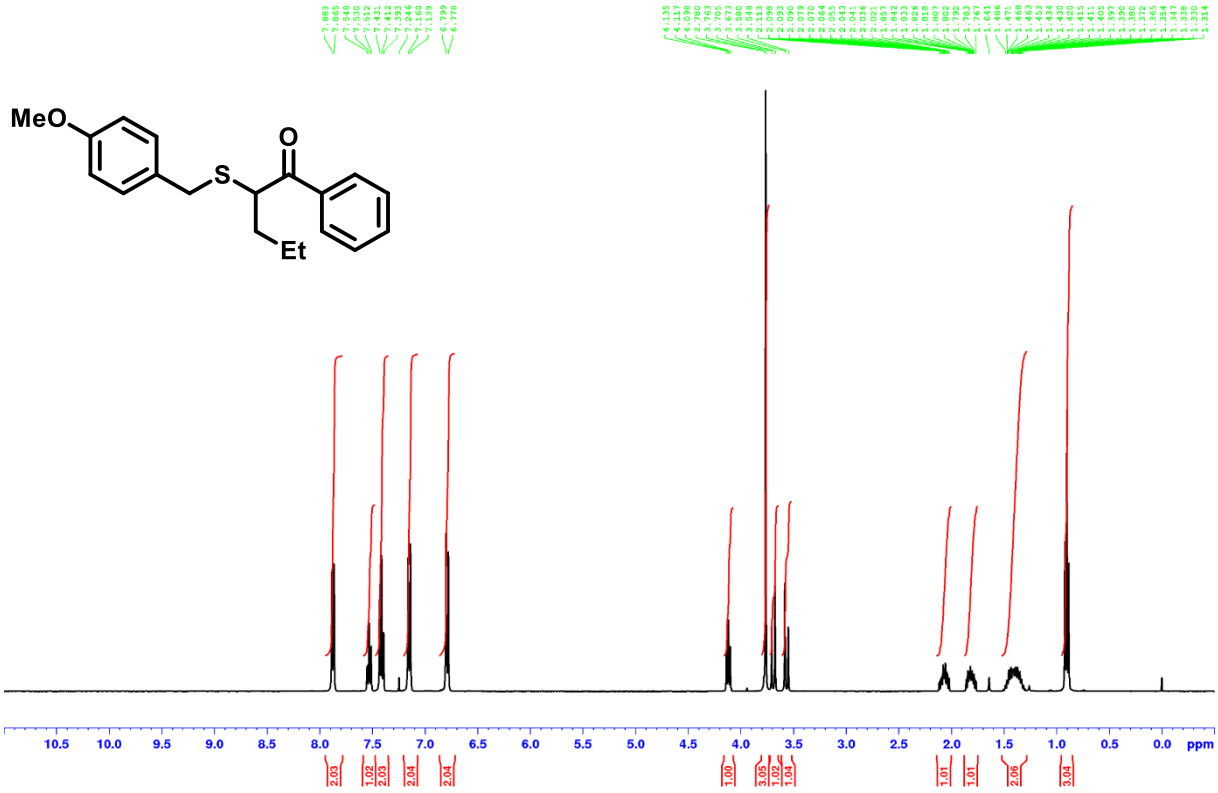


Figure S87: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3jj**.

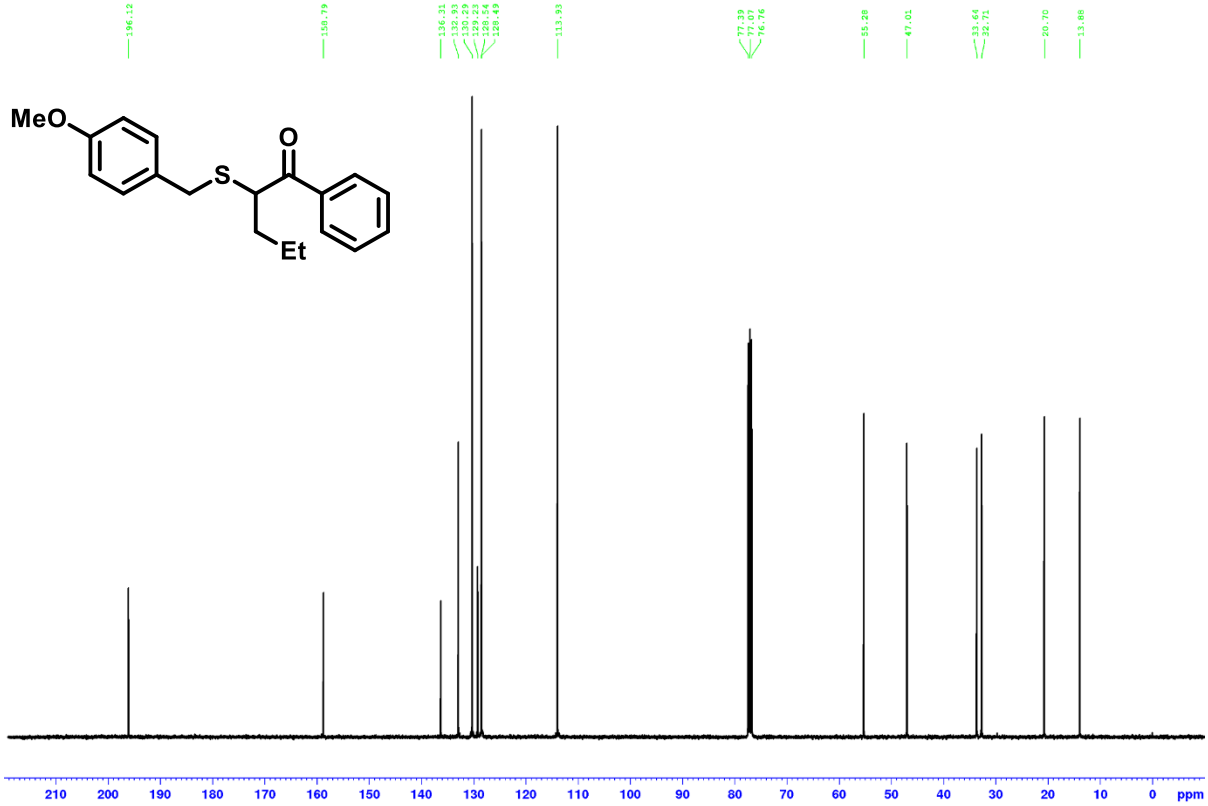


Figure S88: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3jj**.

2-((4-Fluorobenzyl)thio)-1-phenylpentan-1-one 3kk

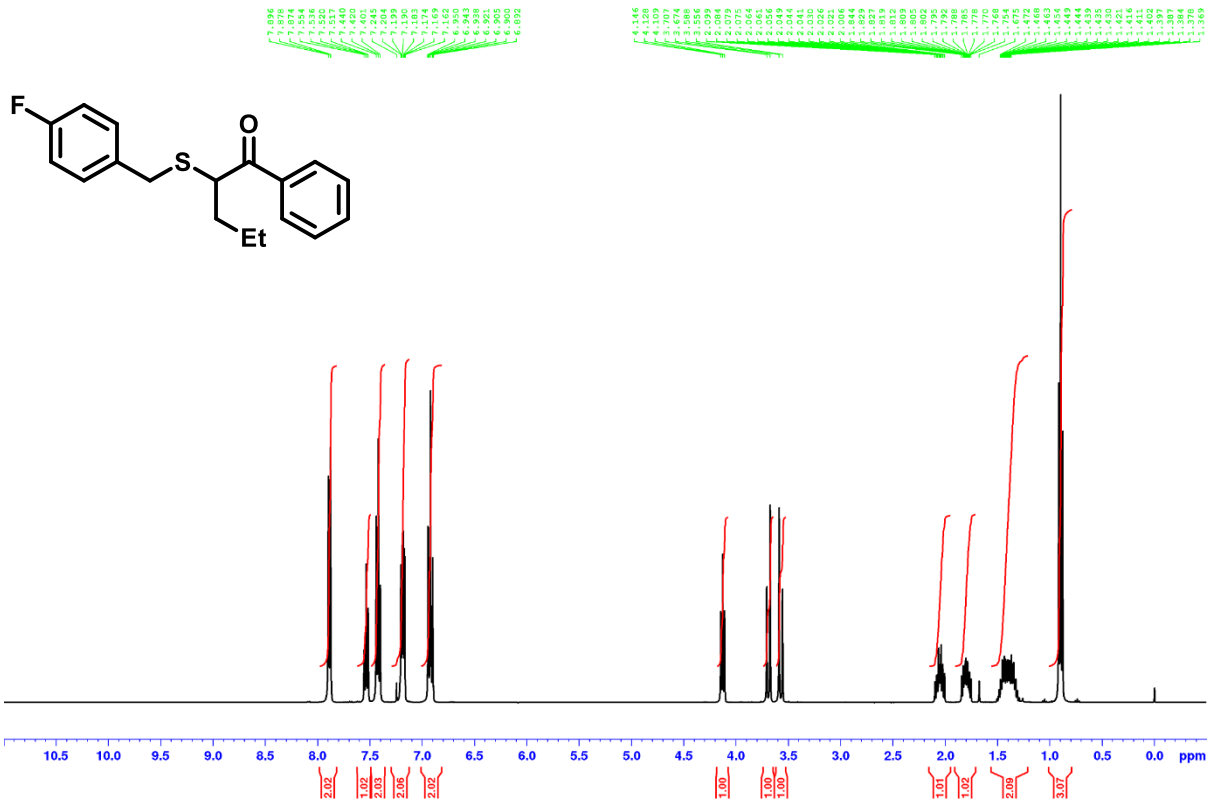


Figure S89: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3kk**.

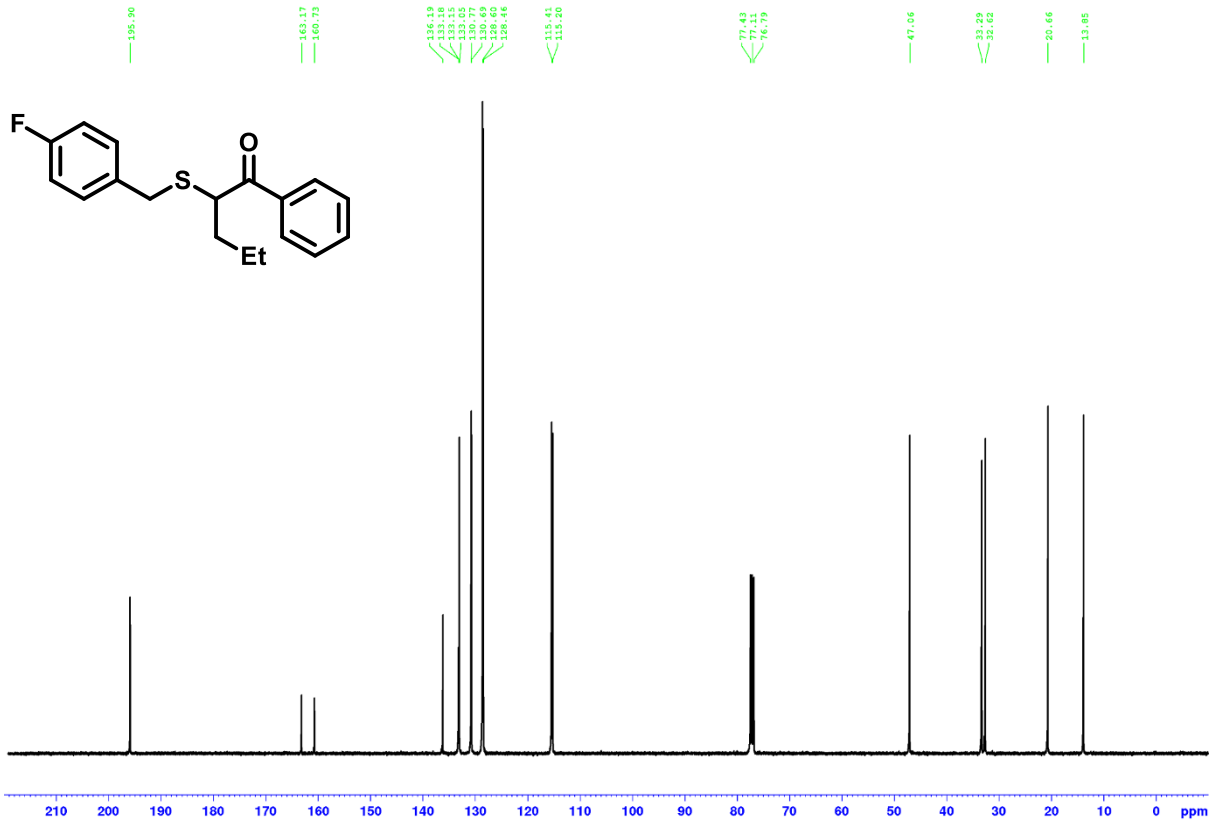


Figure S90: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3kk**.

2-((4-Methylbenzyl)thio)-1-phenylpentan-1-one 3ll

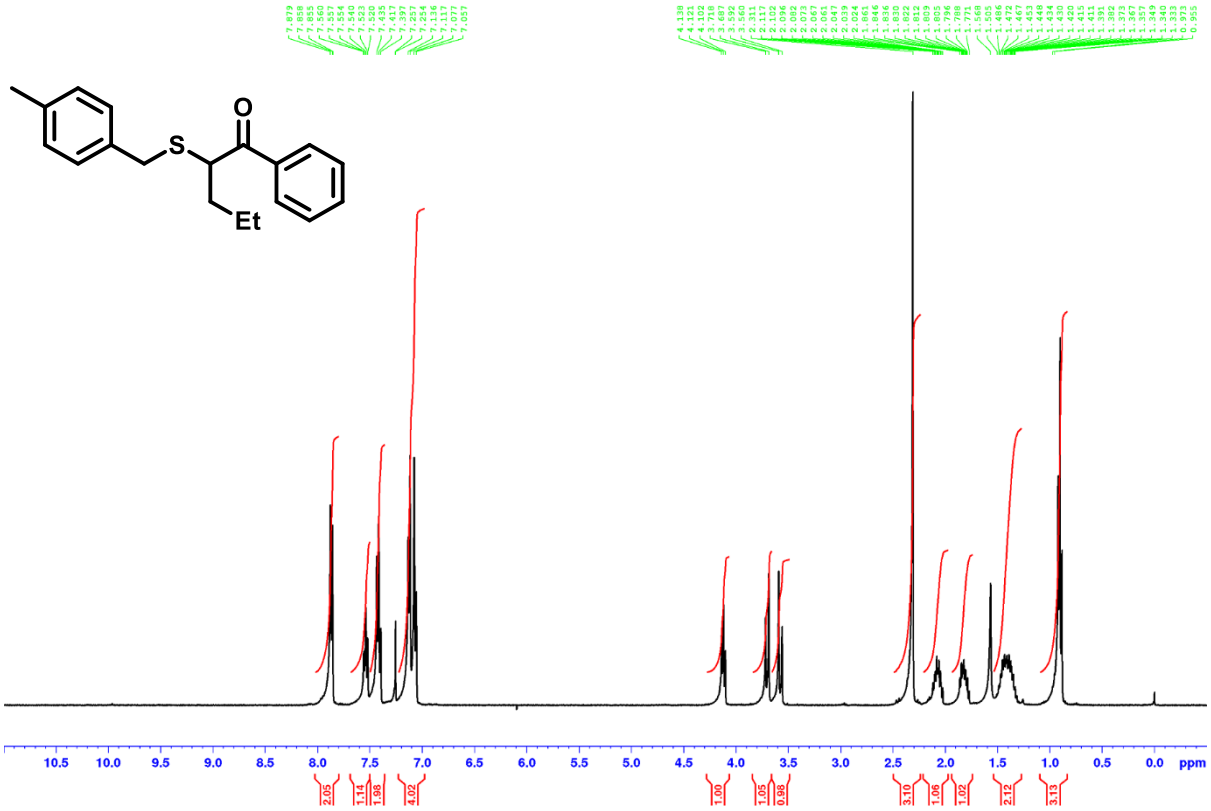


Figure S91: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ll**.

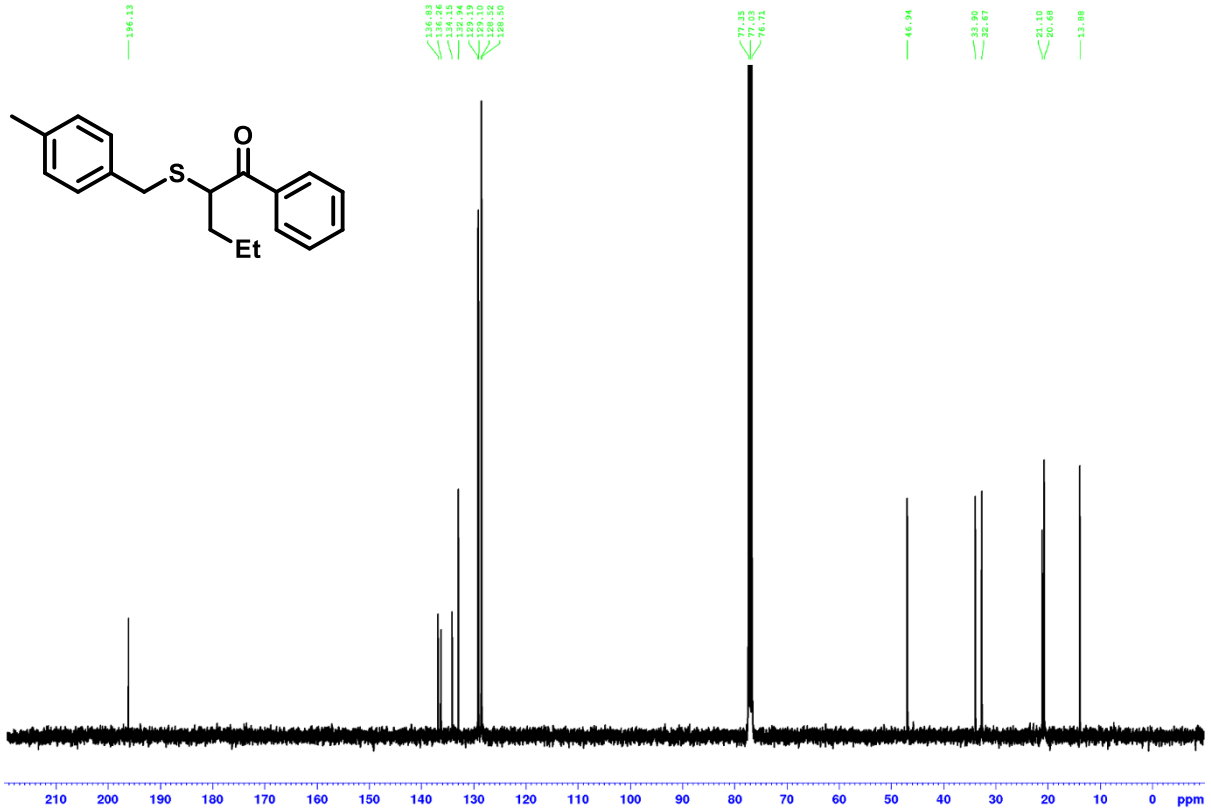


Figure S92: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **3ll**.

3-(Phenylthio)butan-2-one 5a[15]

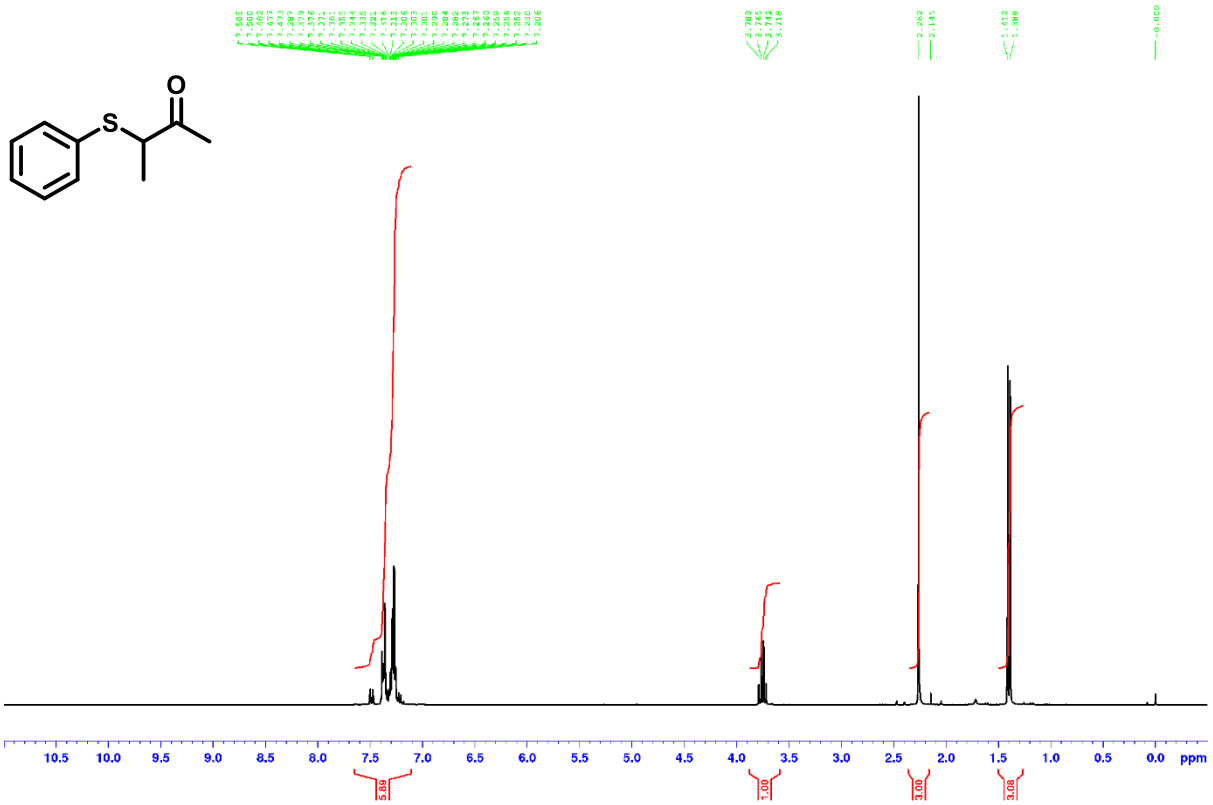


Figure S93: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5a**.

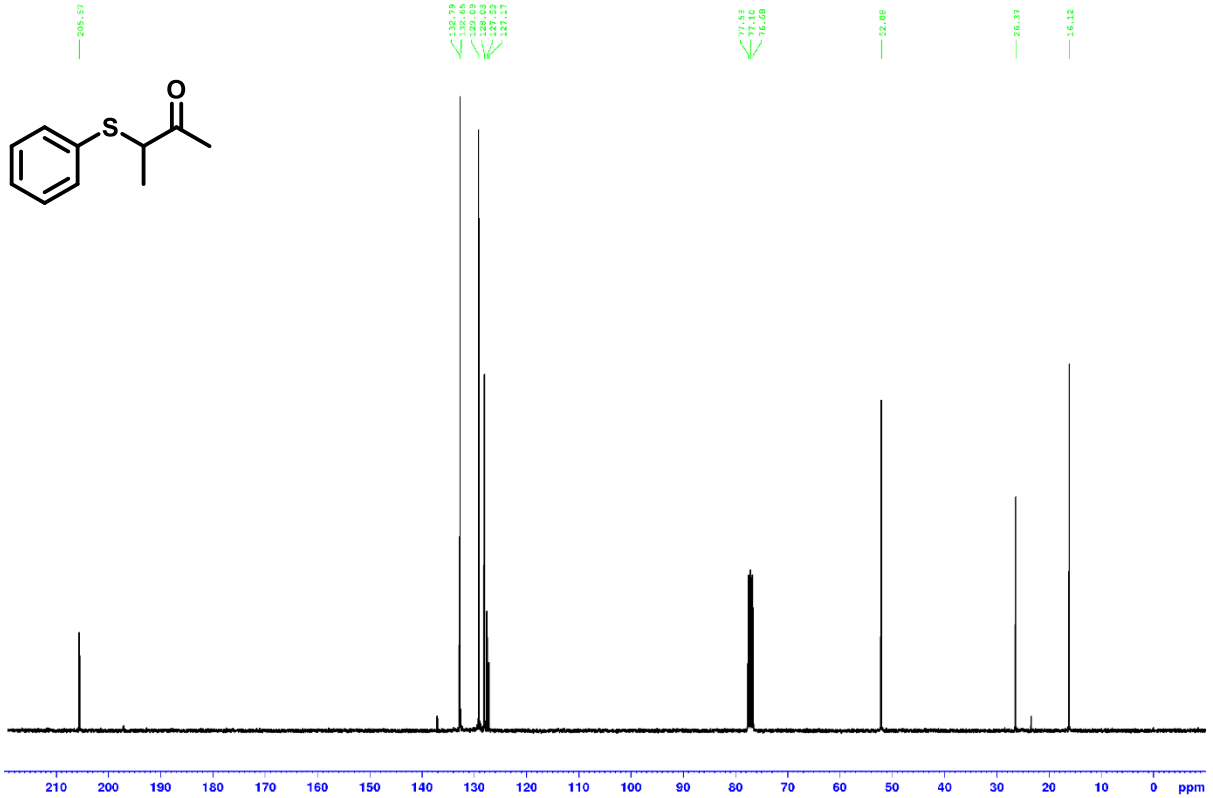


Figure S94: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **5a**.

2-(Phenylthio)pentan-3-one 5b[16]

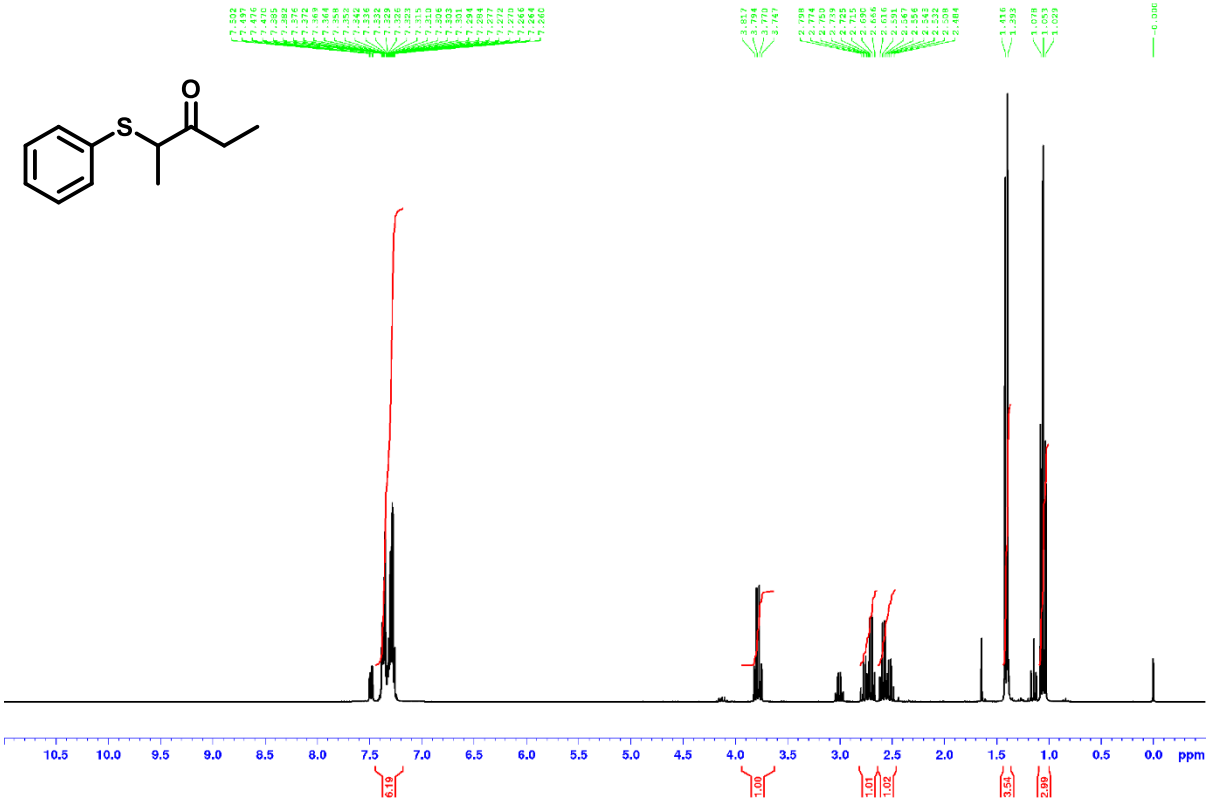


Figure S95: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5b**.

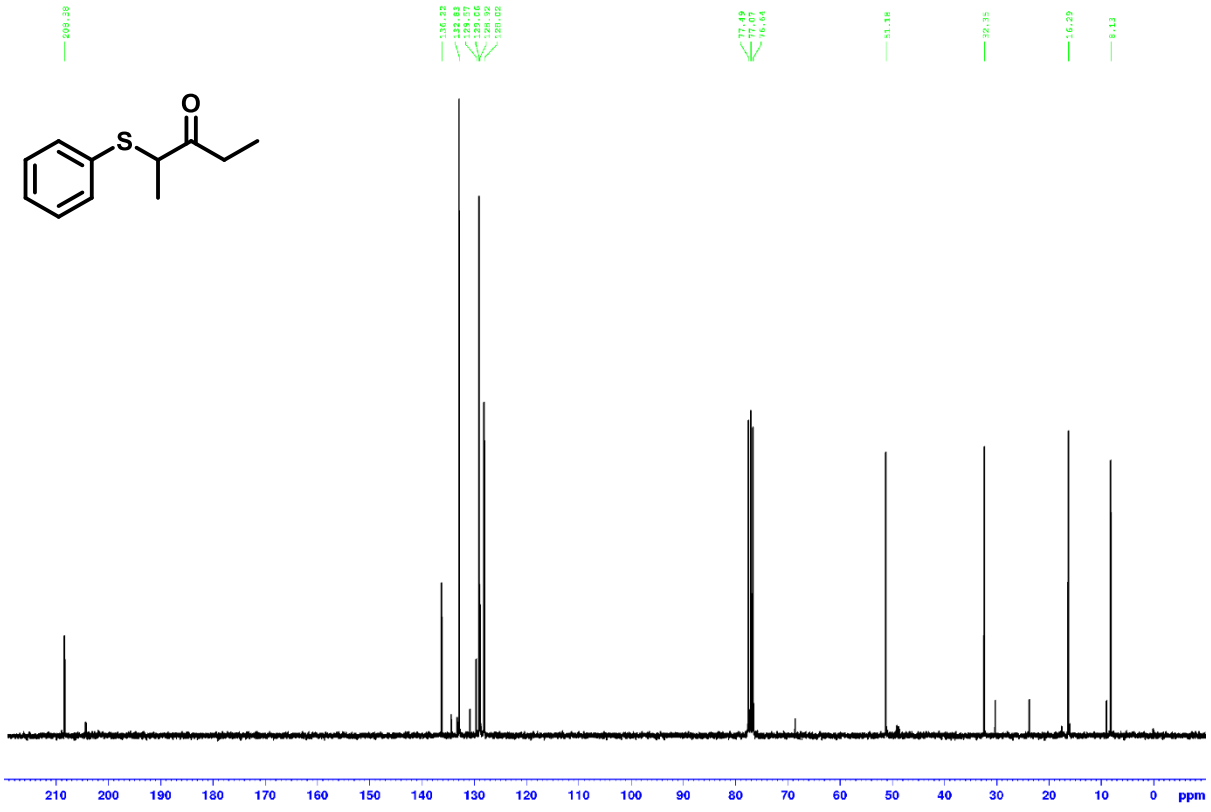


Figure S96: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **5b**.

2-(Benzylthio)pentan-3-one 5c[11]

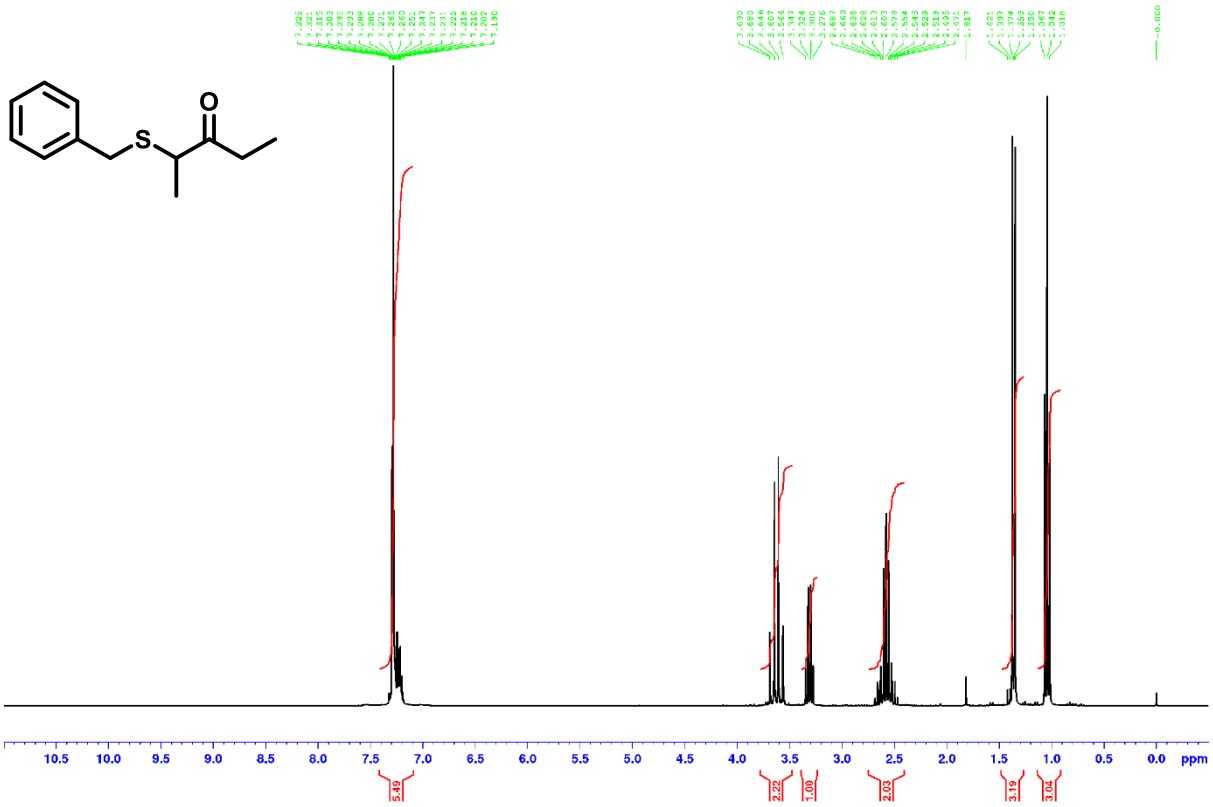


Figure S97: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5c**.

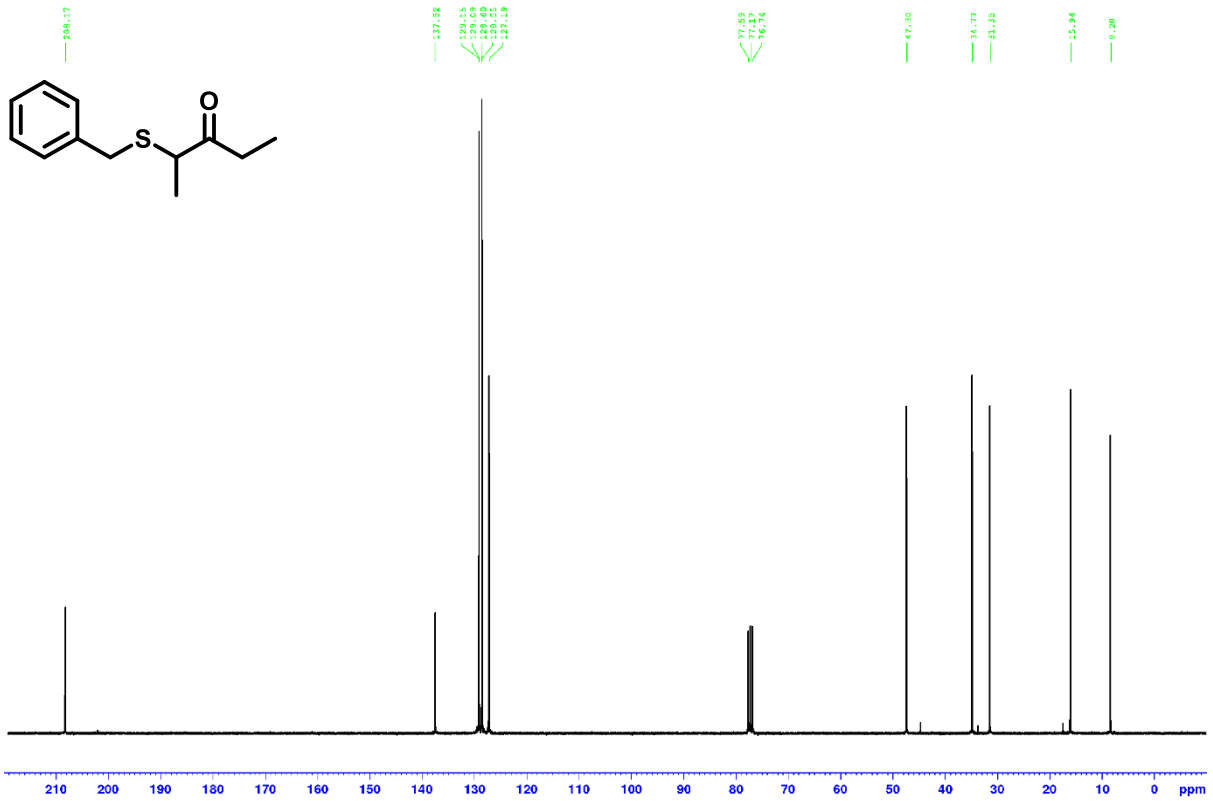


Figure S98: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **5c**.

3-[(4-Bromophenyl)thio]butan-2-one 5d[17]

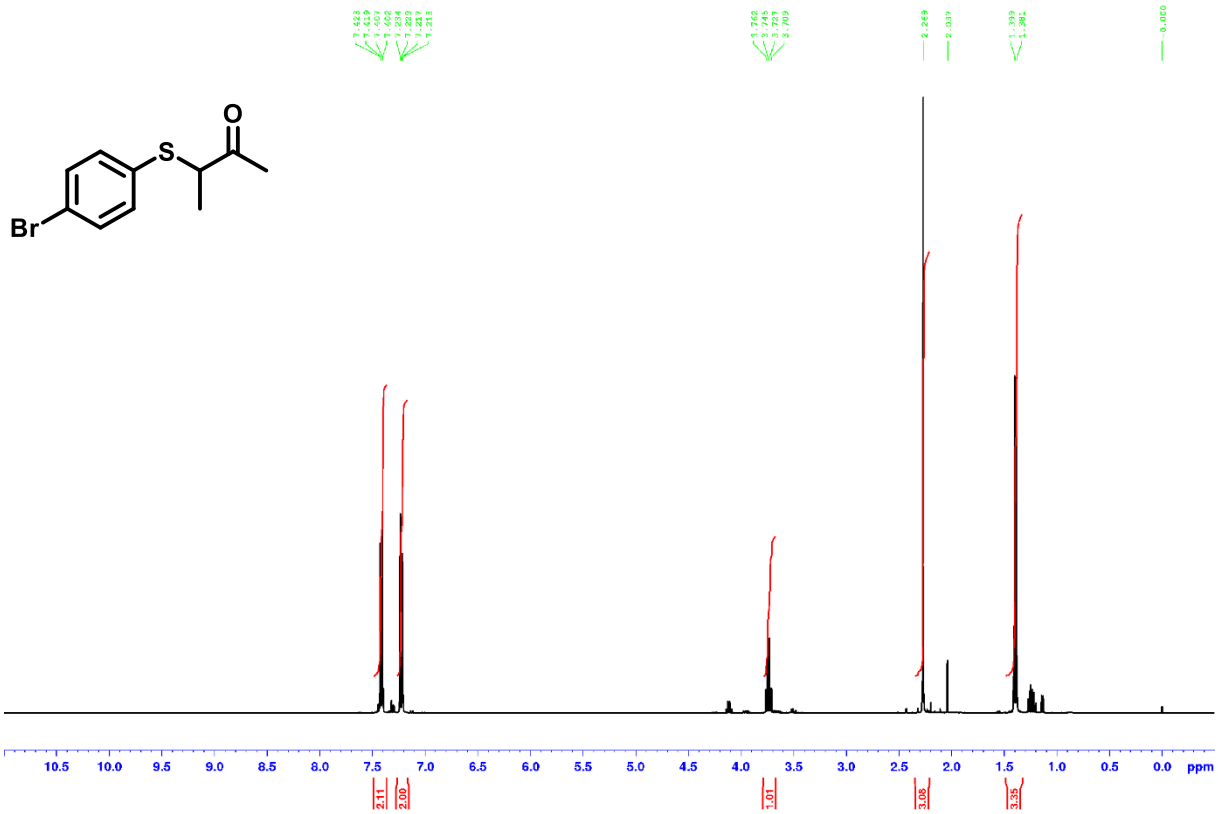


Figure S99: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5d**.

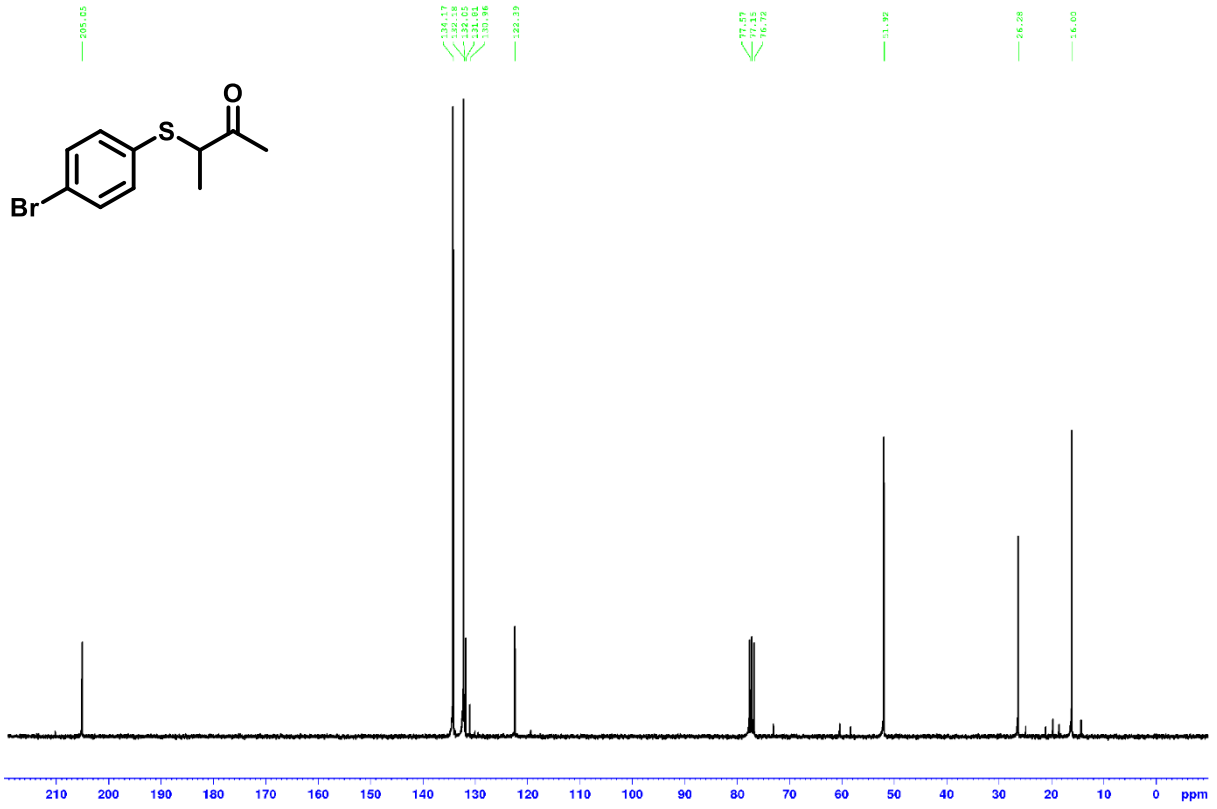


Figure S100: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **5d.**

3-(Benzylthio)butan-2-one 5e[11]

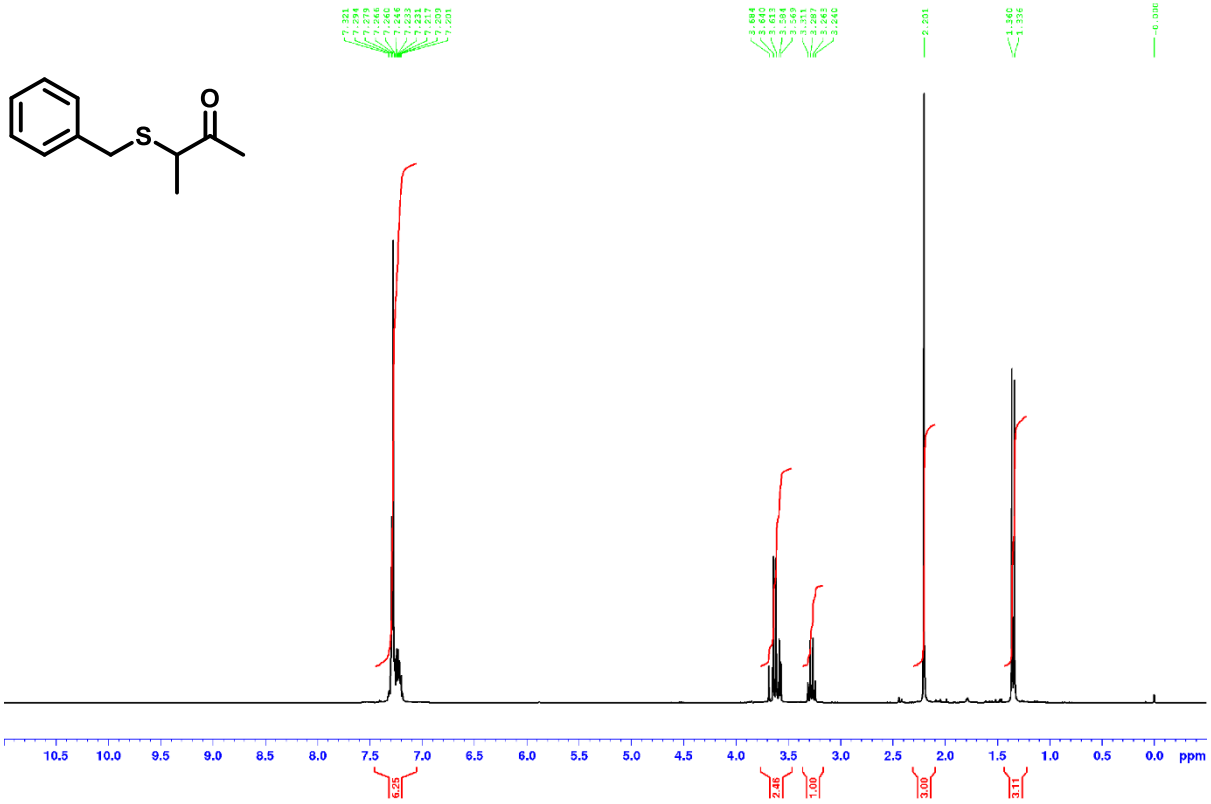


Figure S101: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **5e**.

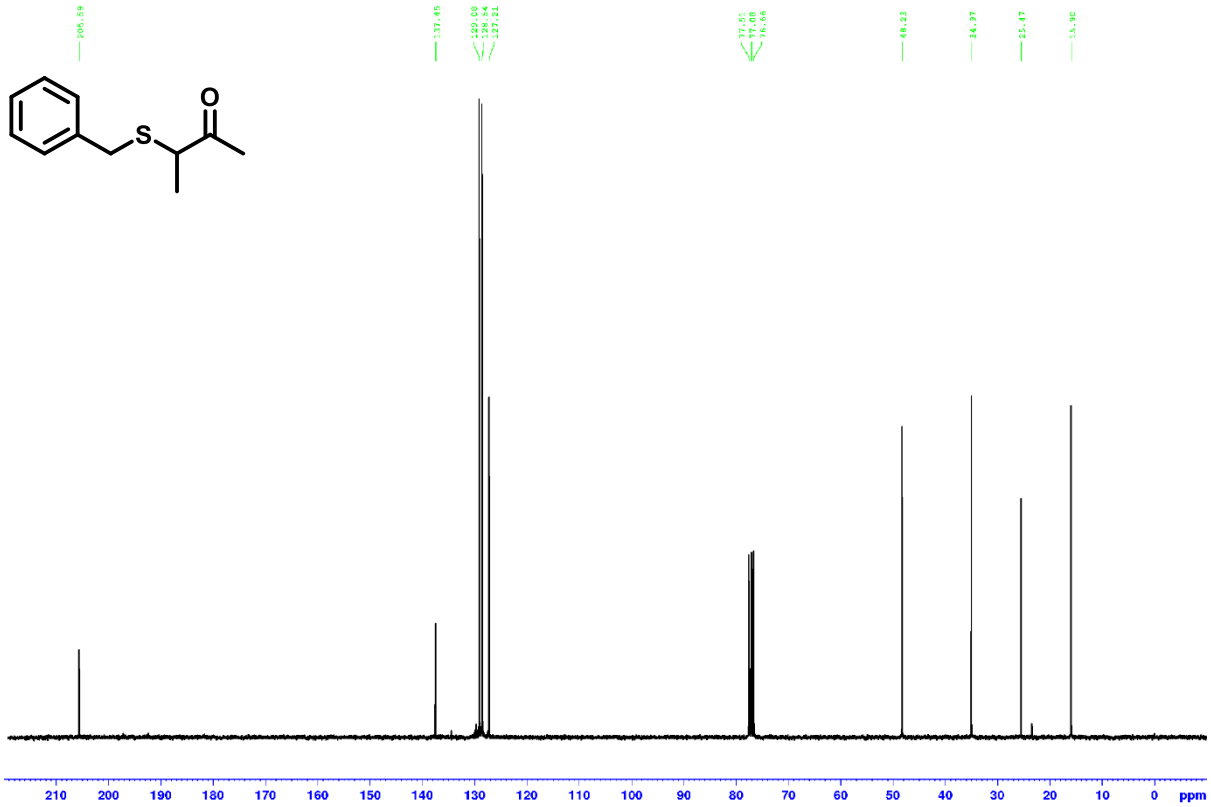


Figure S102: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **5e**.

3-(Benzylthio)-4-phenylbutan-2-one 10a

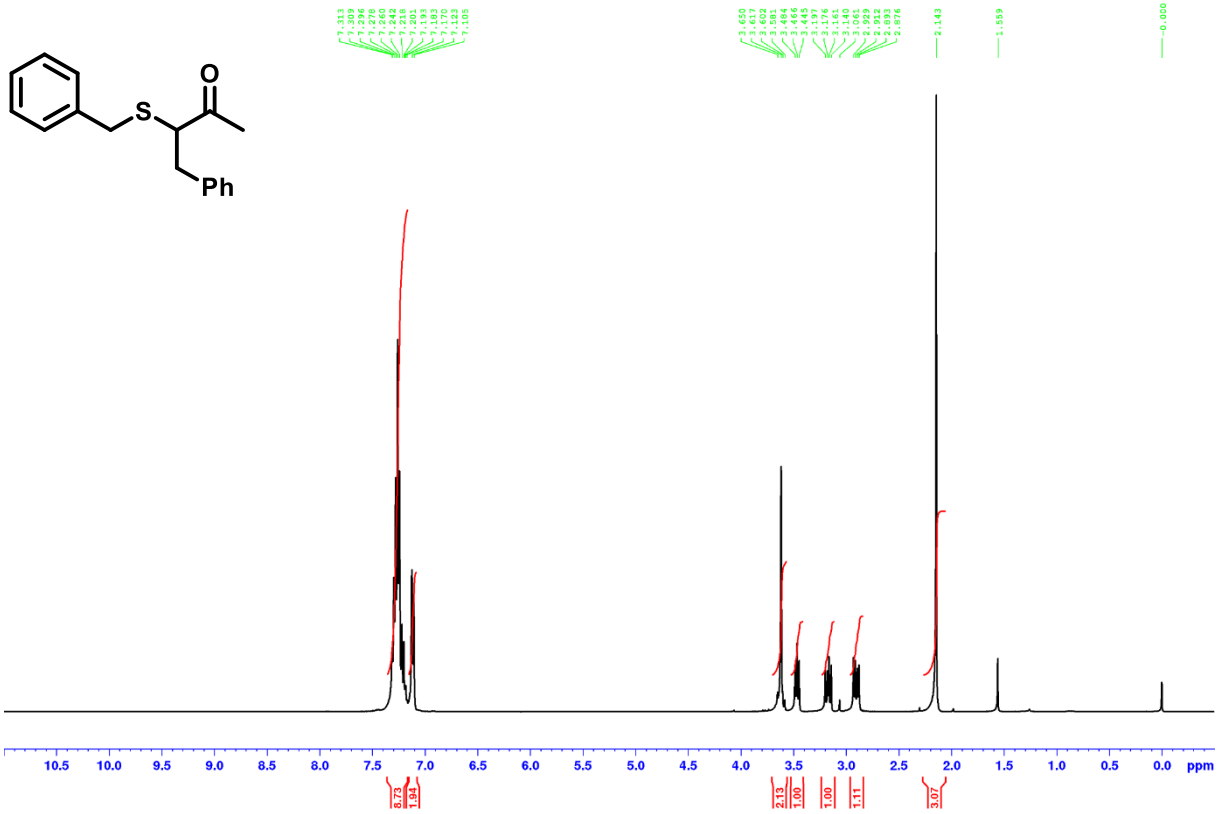


Figure S103: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10a**.

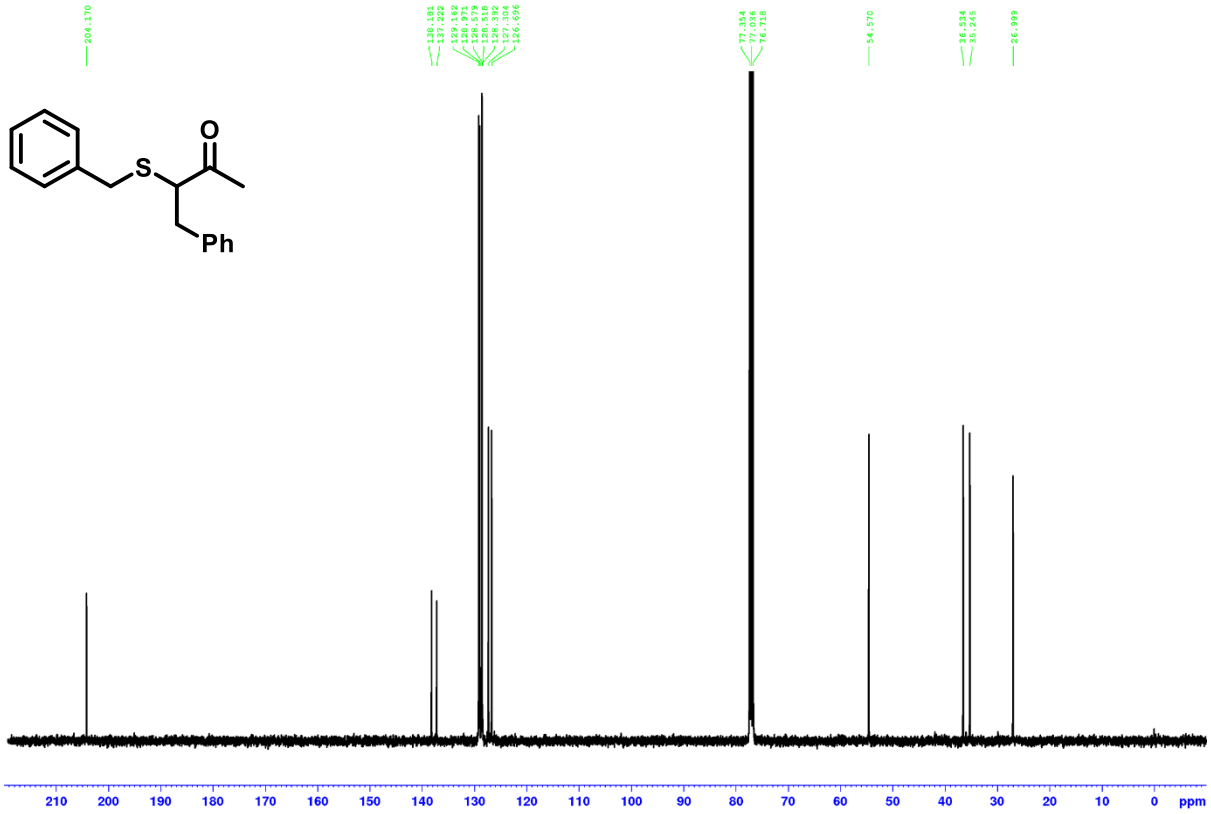


Figure S104: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **10a**.

3-((4-Chlorobenzyl)thio)-4-phenylbutan-2-one S14

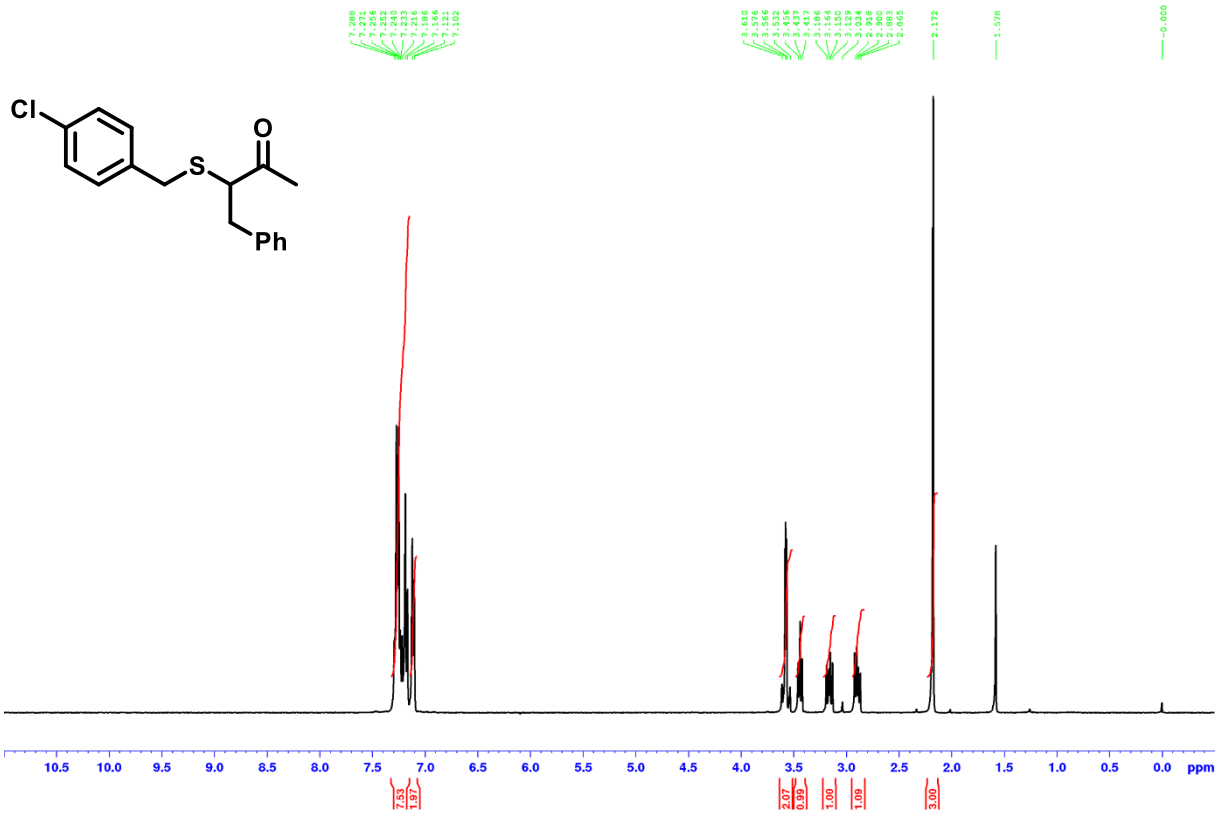


Figure S105: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S14**.

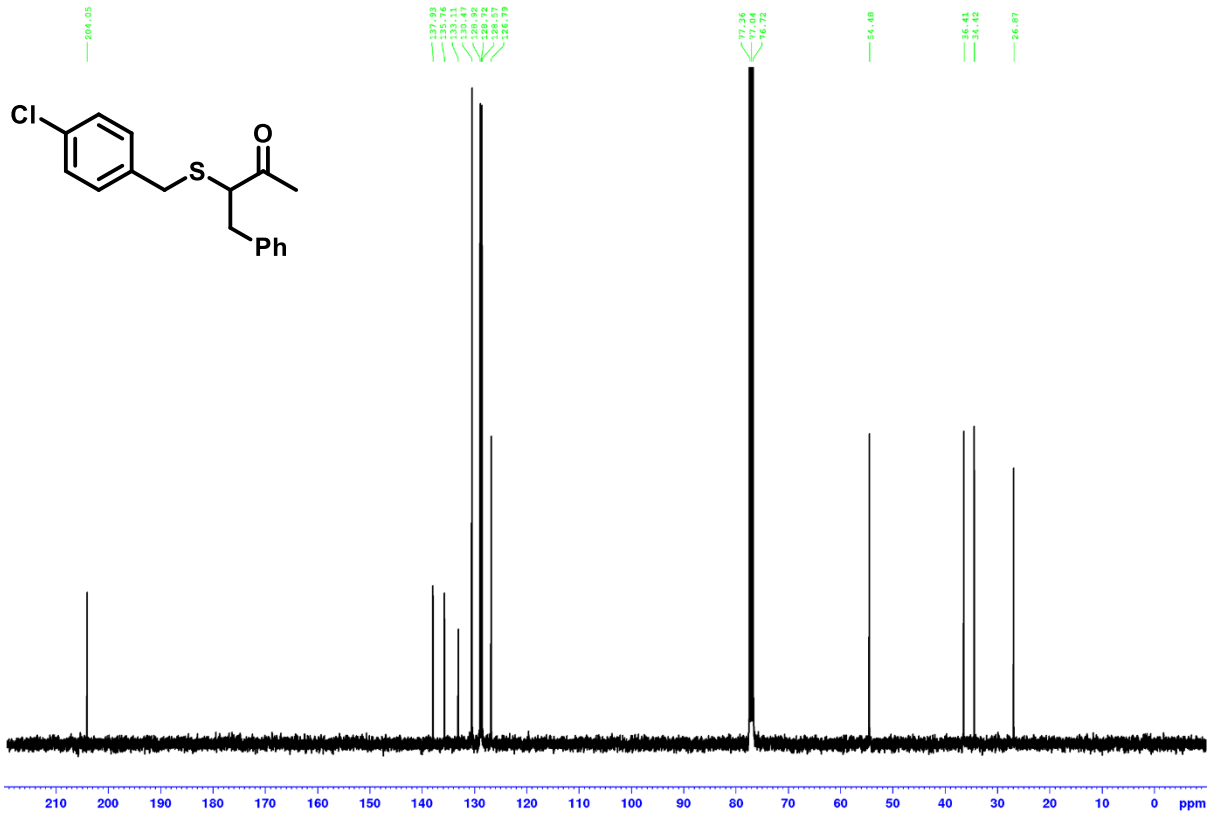


Figure S106: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S14**.

1.12.3 α-Sulfenyl-β-chloropropenones:

(*Z*)-3-Chloro-1-phenyl-2-(phenylthio)prop-2-en-1-one Z-4a and (*E*)-3-chloro-1-phenyl-2-(phenylthio)prop-2-en-1-one E-4a

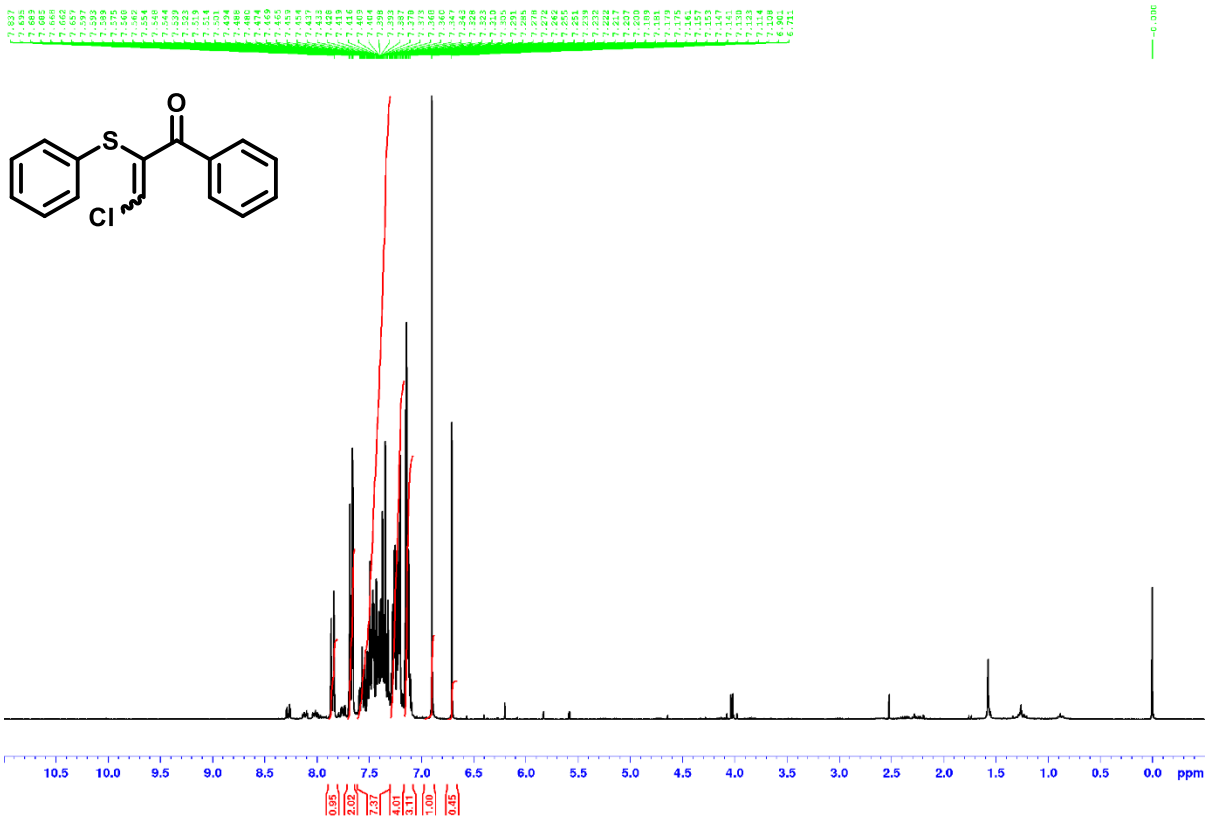


Figure S107: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4a** and **E-4a**.

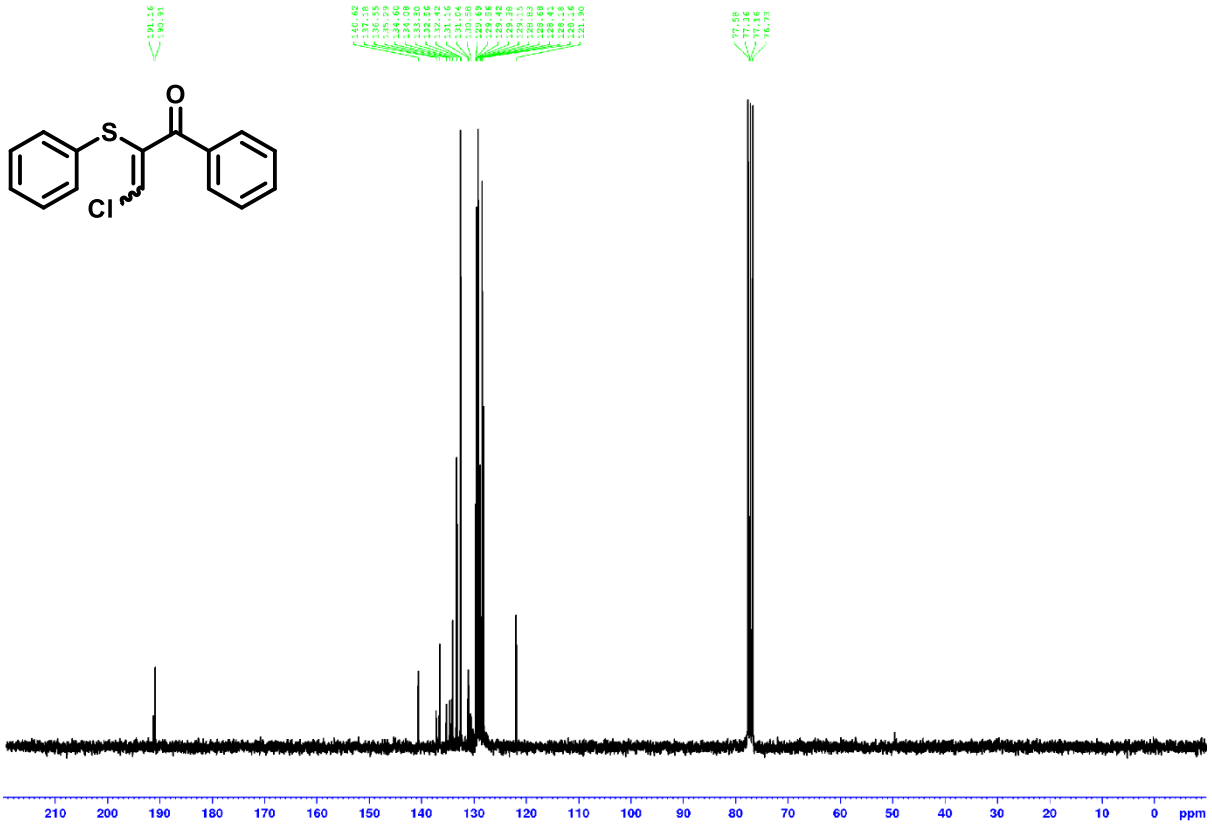


Figure S108: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4a** and **E-4a**.

(*Z*)-2-(Benzylthio)-3-chloro-1-phenylprop-2-en-1-one Z-4b and (*E*)-2-(benzylthio)-3-chloro-1-phenylprop-2-en-1-one E-4b

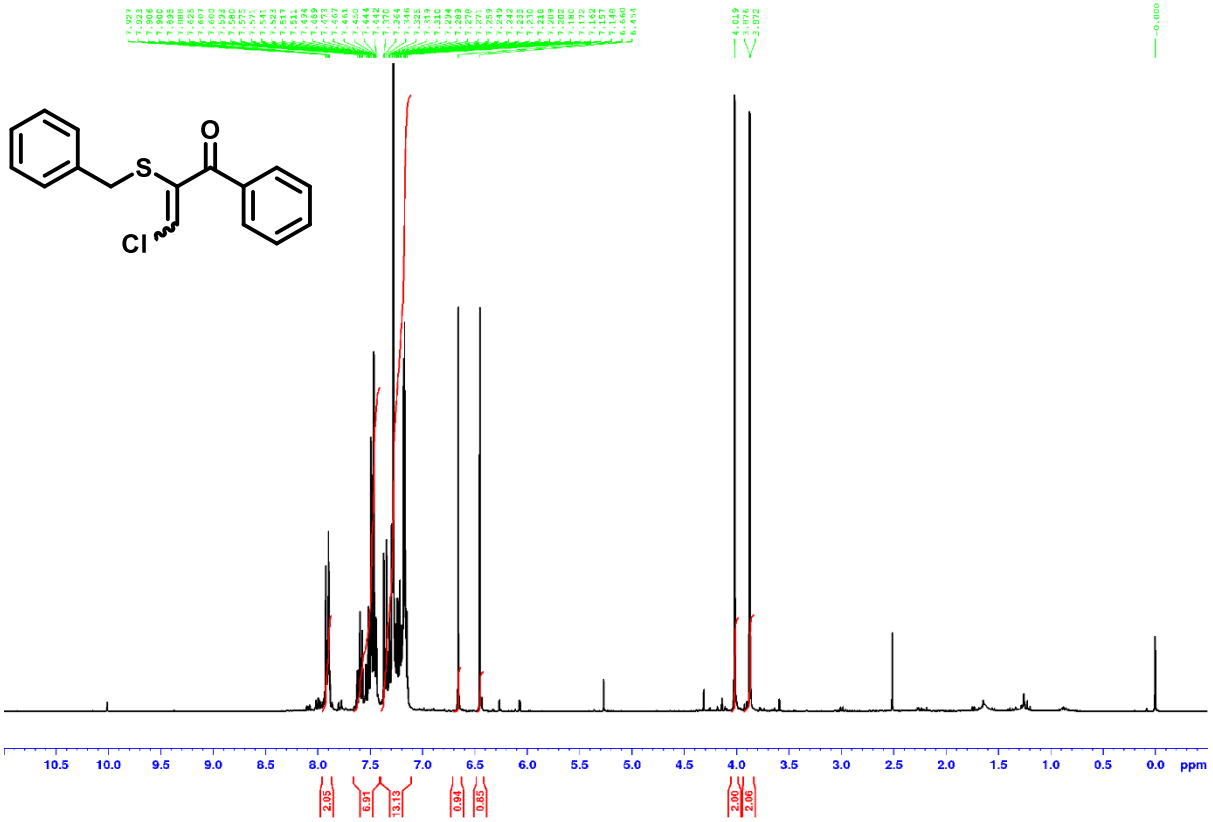


Figure S109: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4b** and **E-4b**.

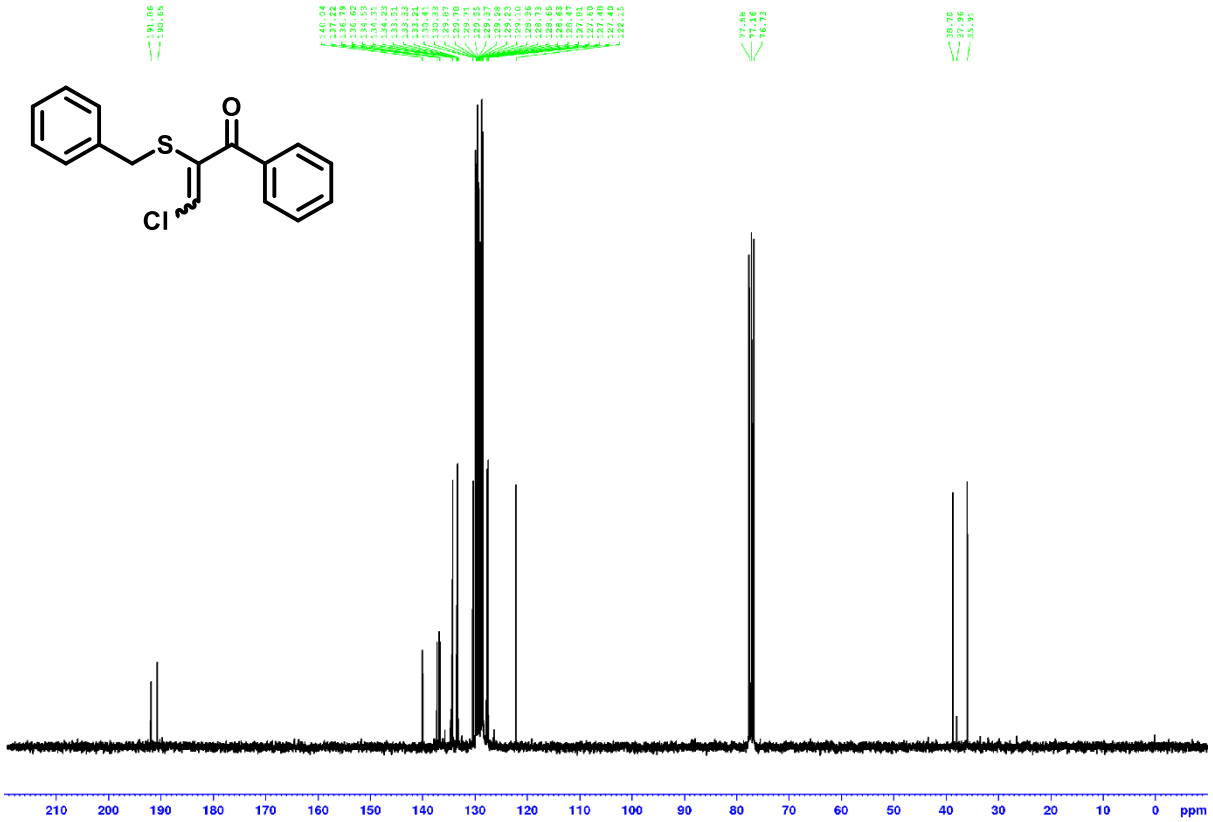


Figure S110: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4b** and **E-4b**.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-phenylprop-2-en-1-one Z-4c and (*E*)-2-(*n*-butylthio)-3-chloro-1-phenylprop-2-en-1-one E-4c

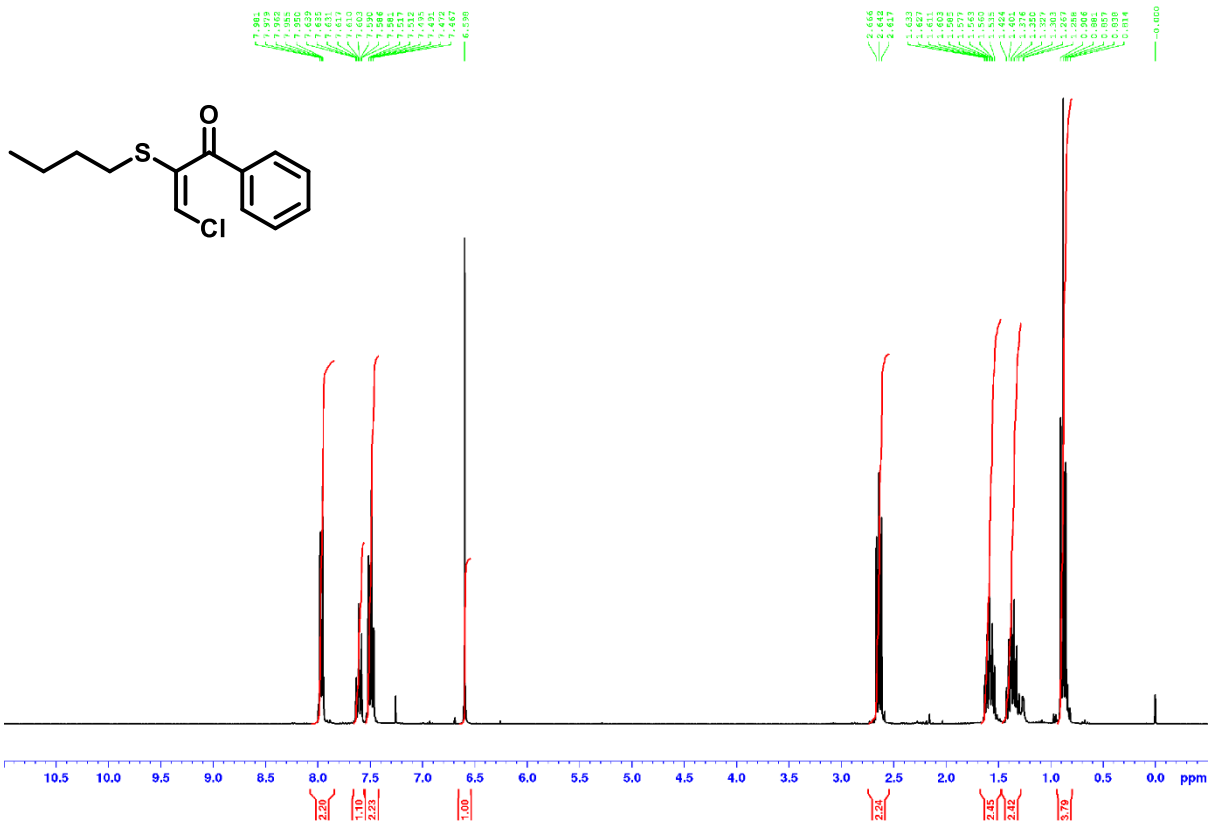


Figure S111: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4c**.

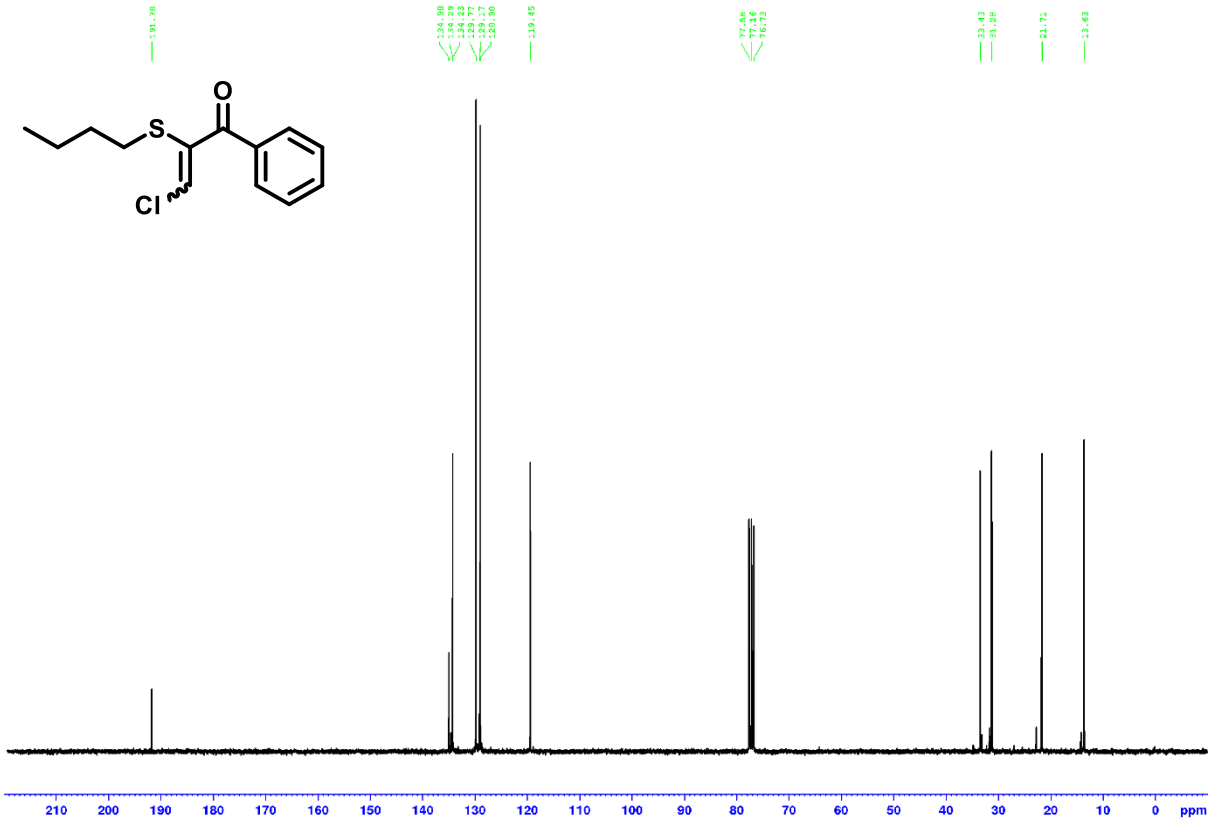


Figure S112: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4c (95%)** and **E-4c (5%)**.

(*Z*)-3-Chloro-1-(4-methoxyphenyl)-2-(phenylthio)prop-2-en-1-one Z-4d and (*E*)-3-chloro-1-(4-methoxyphenyl)-2-(phenylthio)prop-2-en-1-one E-4d

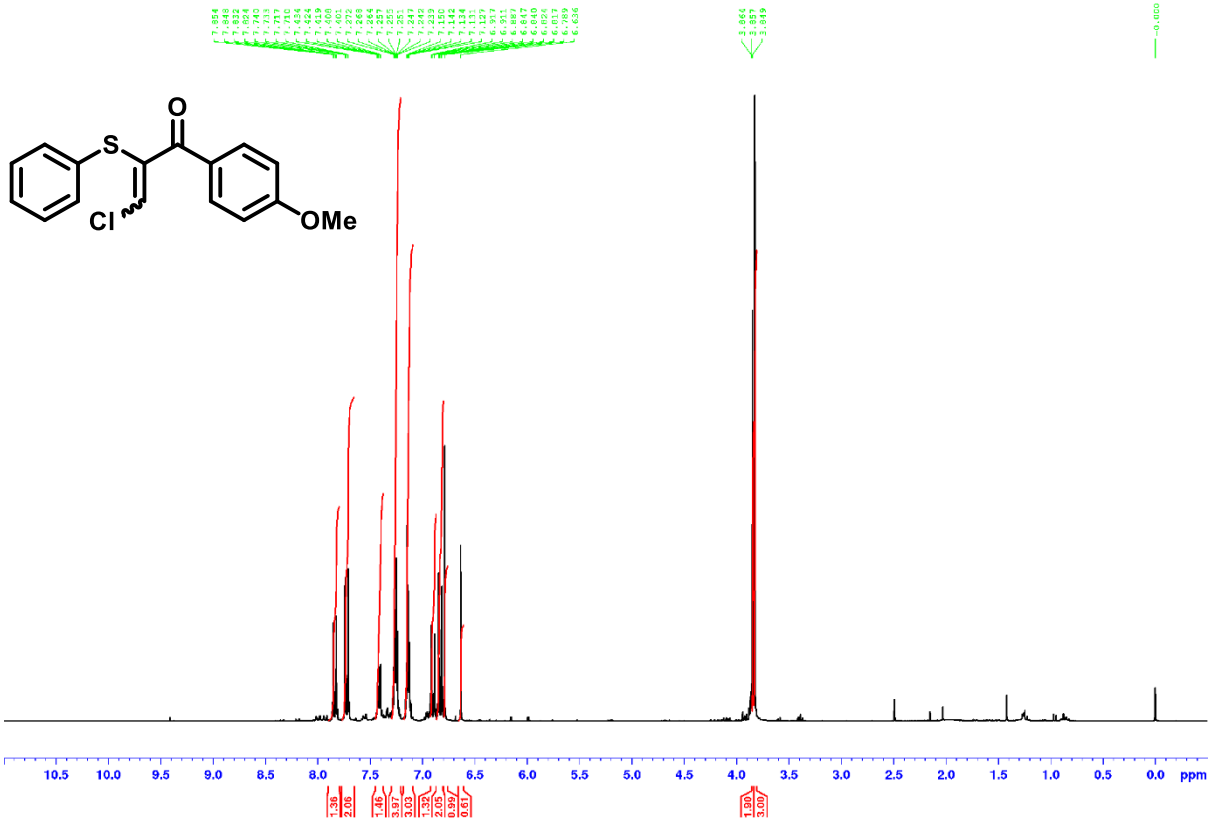


Figure S113: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4d** and **E-4d**.

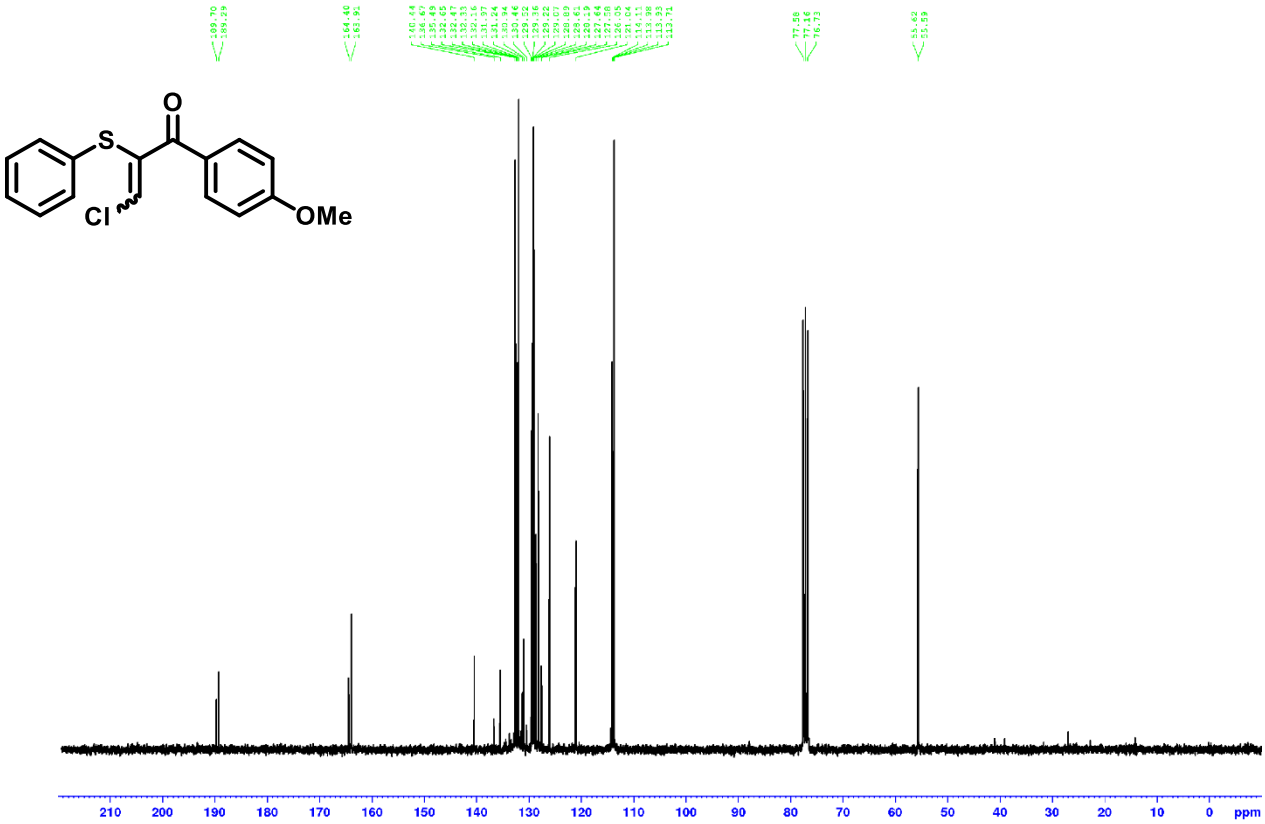


Figure S114: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4d** and **E-4d**.

(*Z*)-2-(Benzylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one Z-4e and (*E*)-2-(benzylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one E-4e

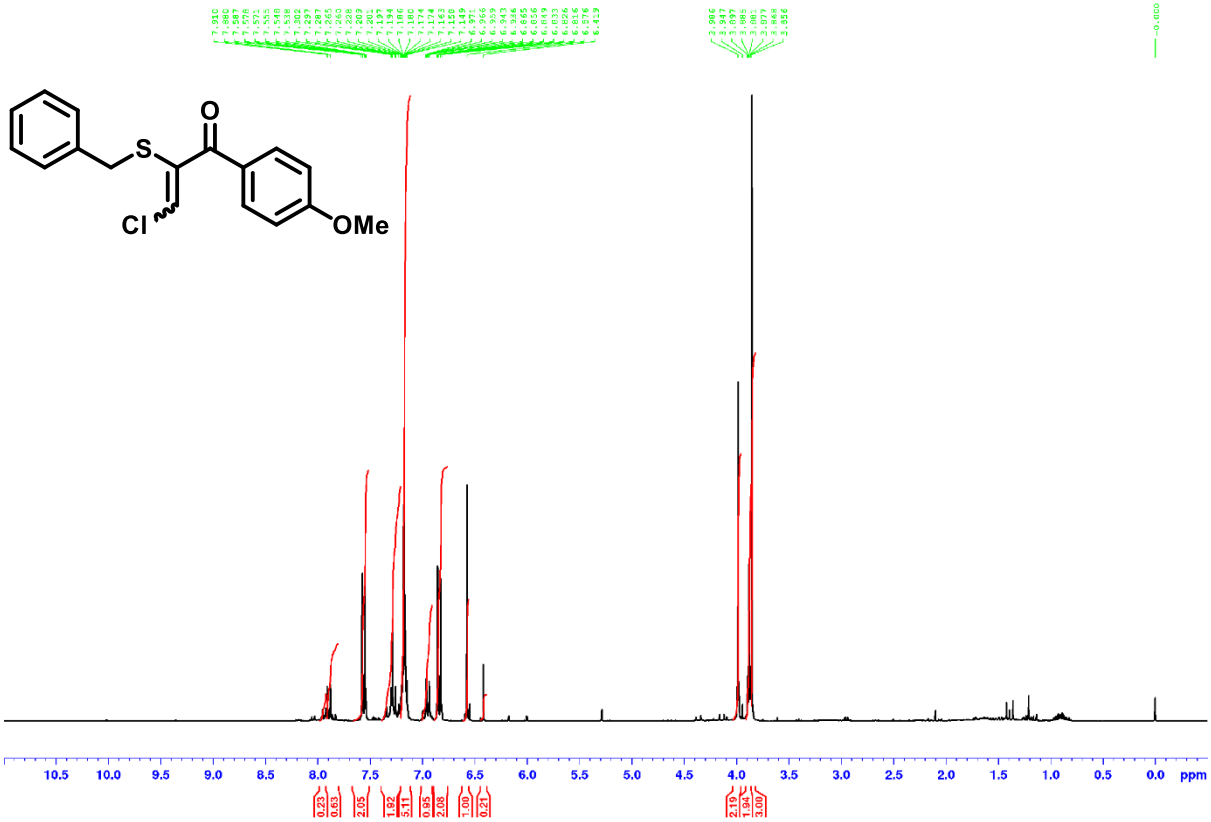


Figure S115: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4e** and **E-4e**.

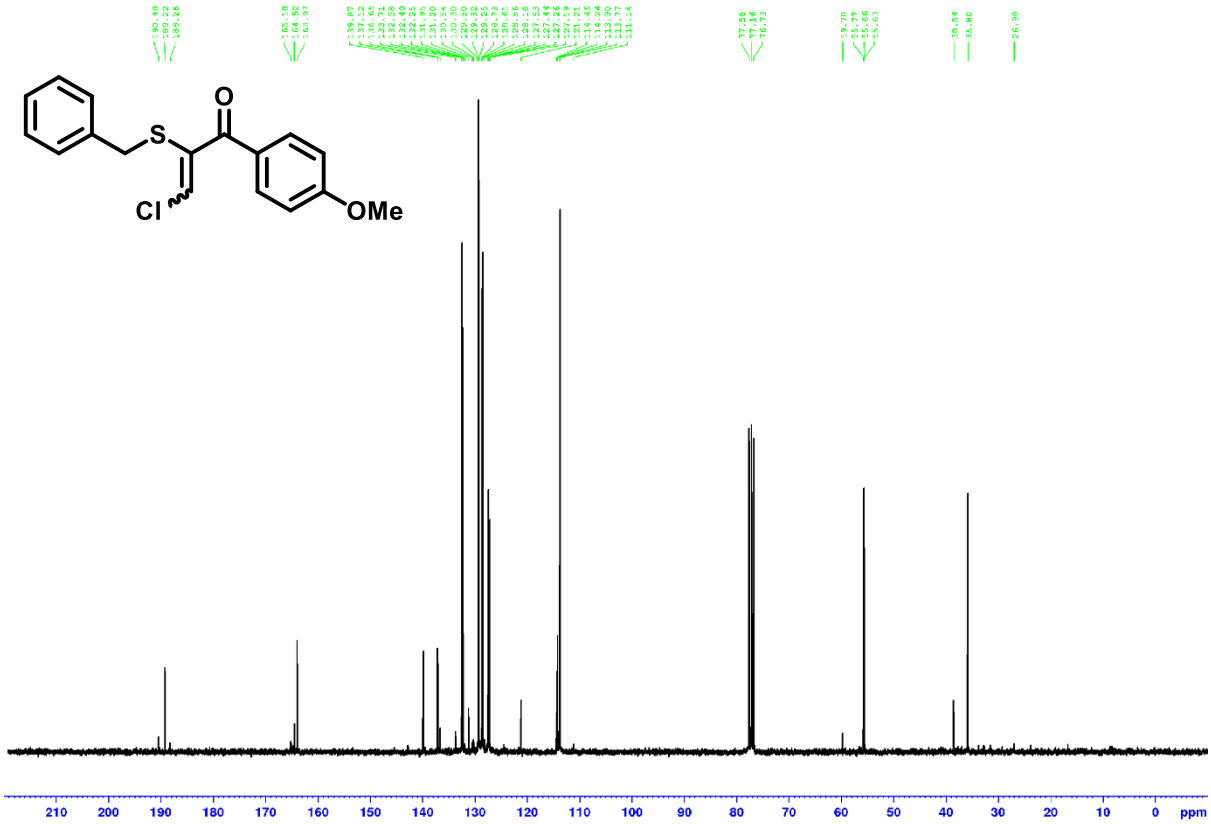


Figure S116: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4e** and **E-4e**.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one Z-4f and (*E*)-2-(*n*-butylthio)-3-chloro-1-(4-methoxyphenyl)prop-2-en-1-one E-4f

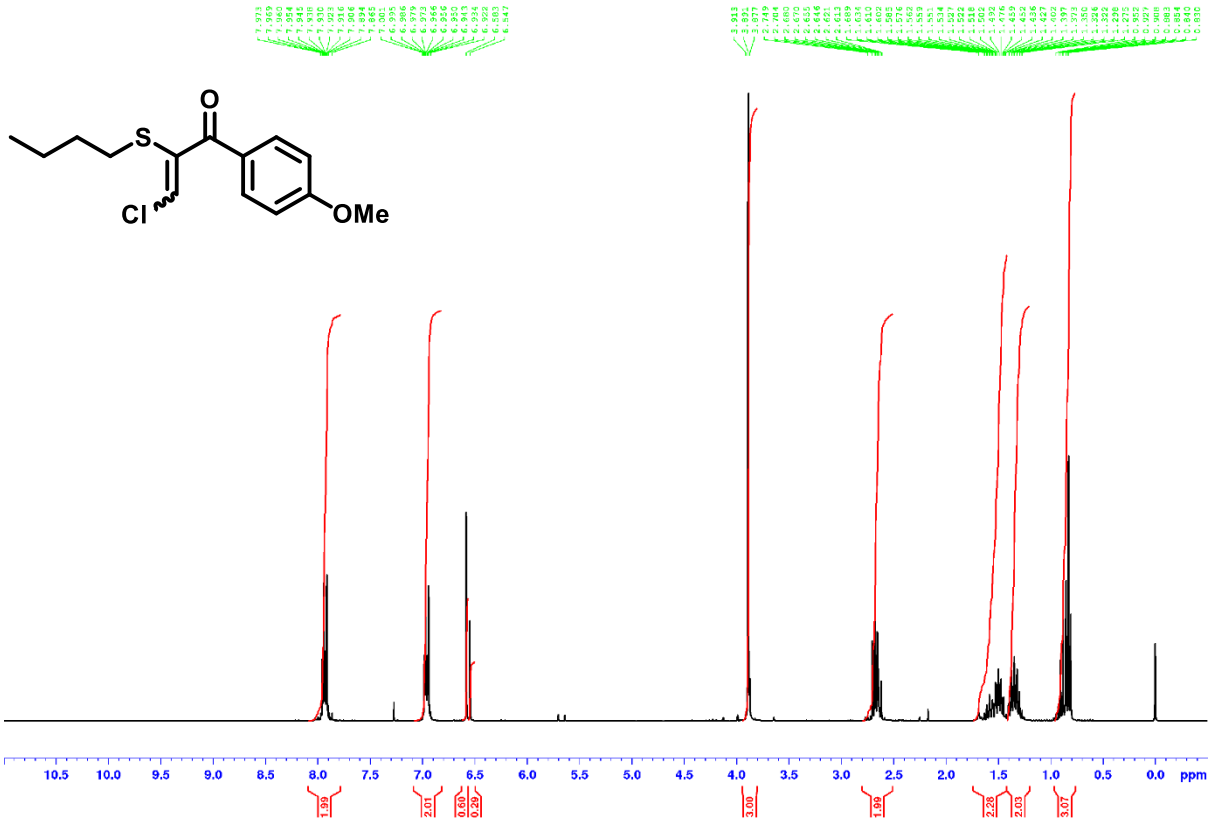


Figure S117: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4f** and **E-4f**.

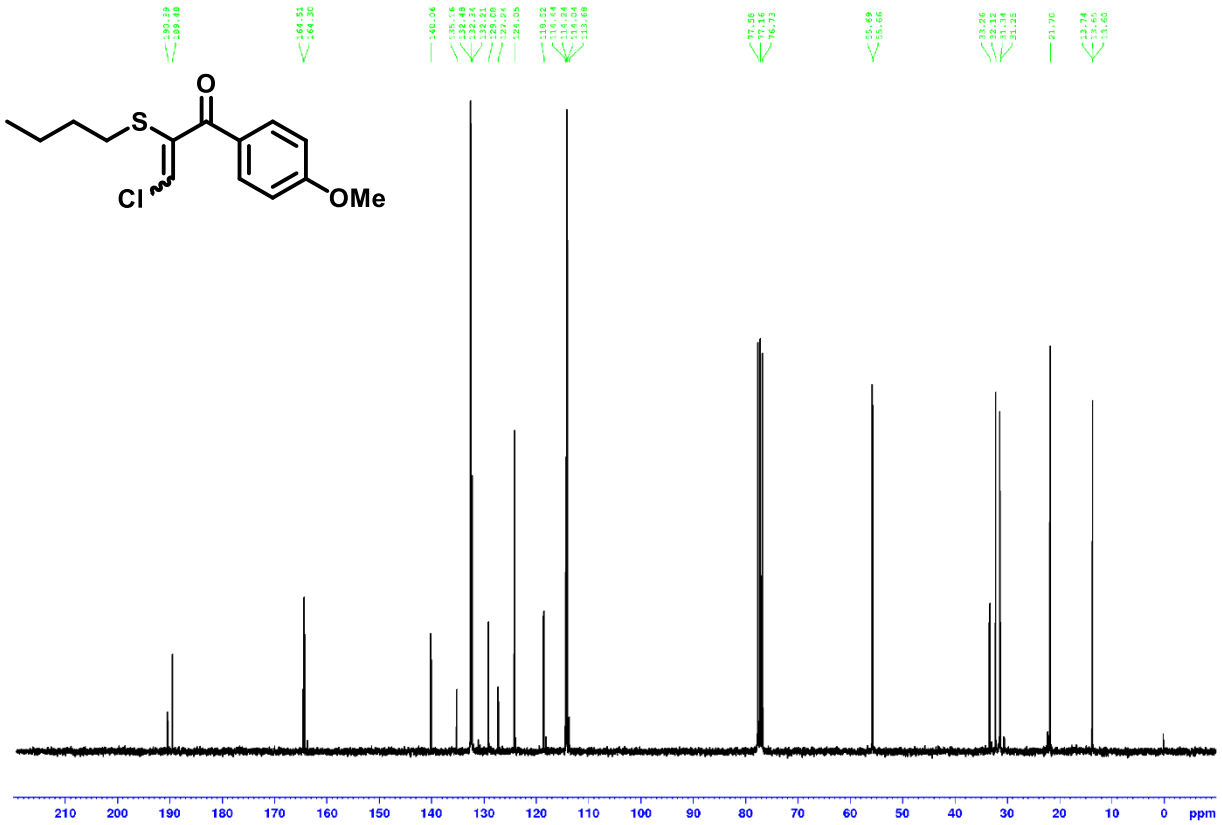


Figure S118: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4f** and **E-4f**.

(*Z*)-3-Chloro-2-(phenylthio)-1-(*p*-tolyl)prop-2-en-1-one Z-4g and (*E*)-3-chloro-2-(phenylthio)-1-(*p*-tolyl)prop-2-en-1-one E-4g

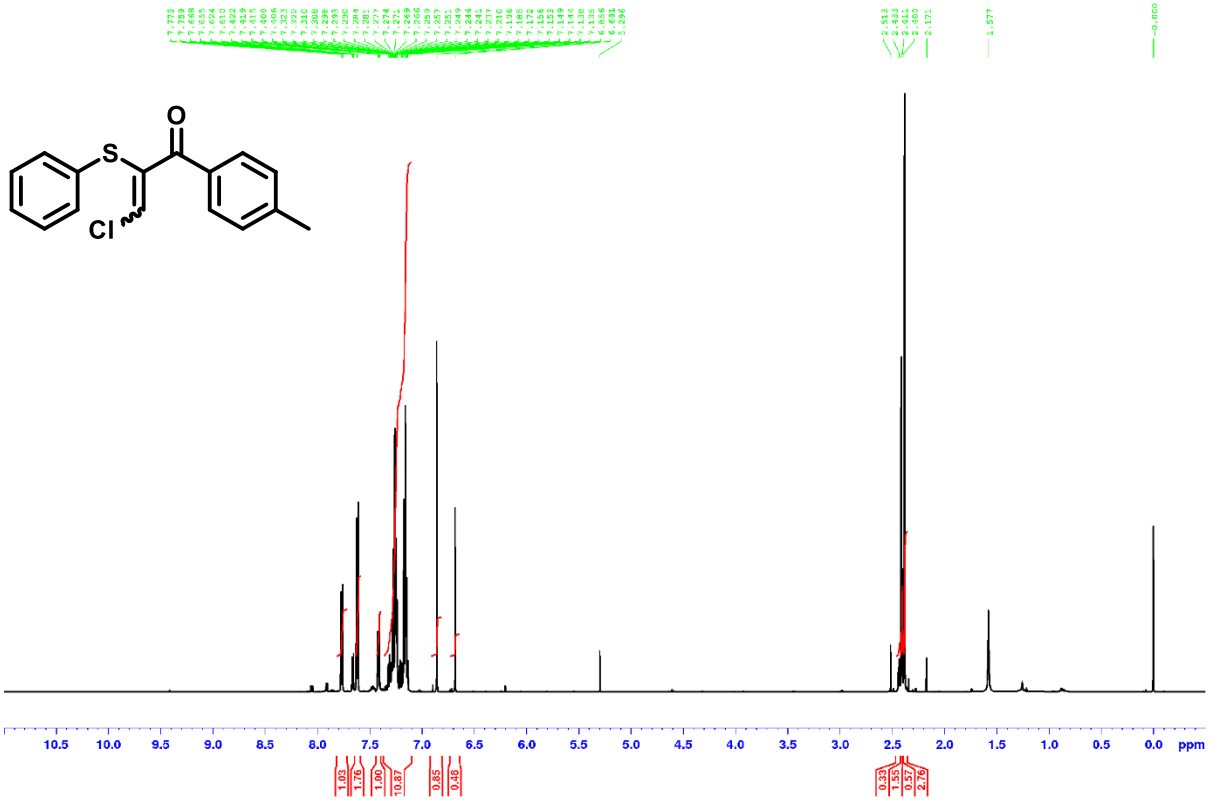


Figure S119: ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **Z-4g** and **E-4g**.

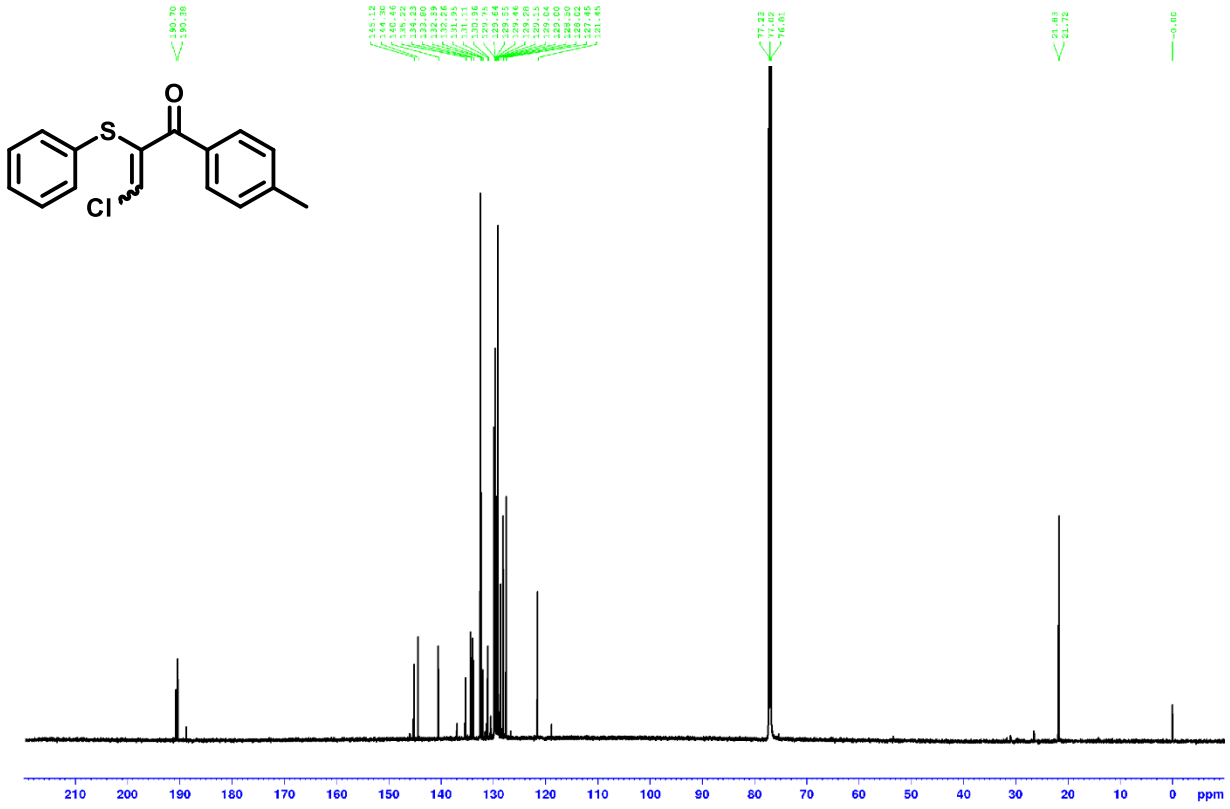


Figure S120: ^{13}C NMR (150.8 MHz, $CDCl_3$) spectrum of **Z-4g** and **E-4g**.

(*Z*)-2-(Benzylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one Z-4h

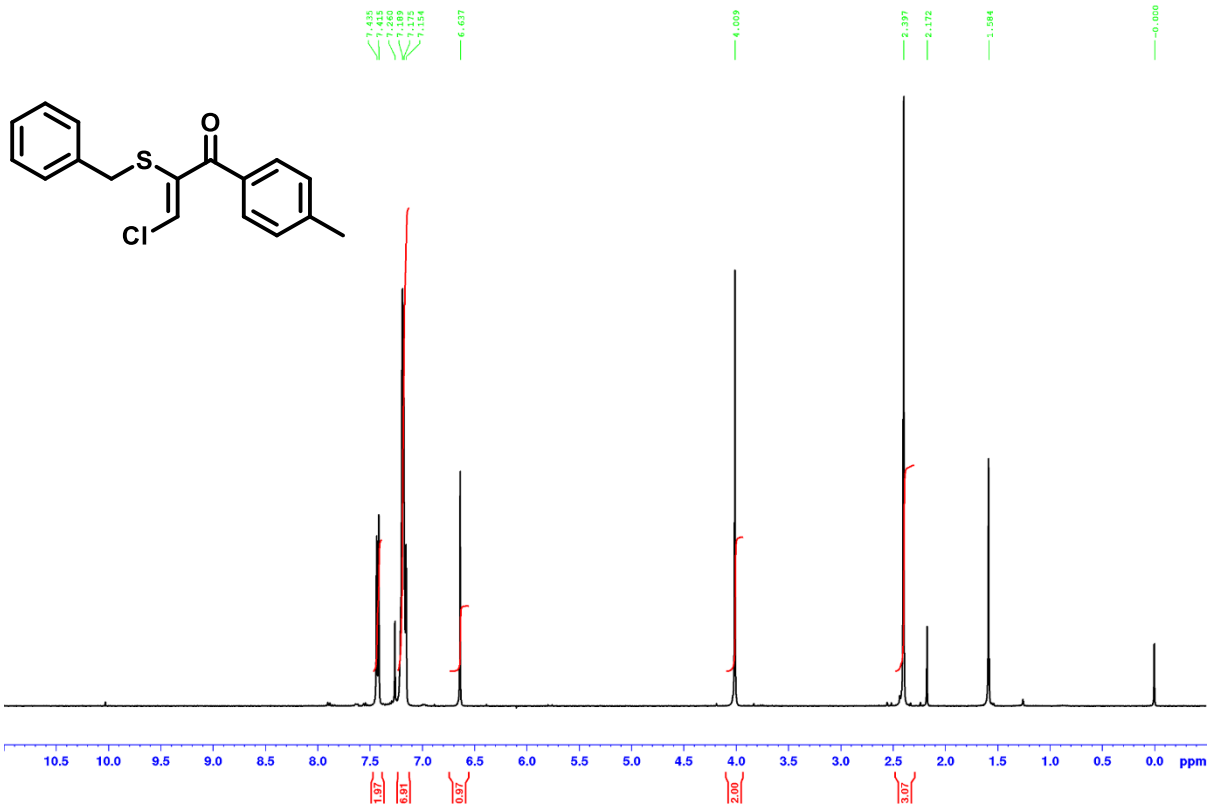


Figure S121: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4h**.

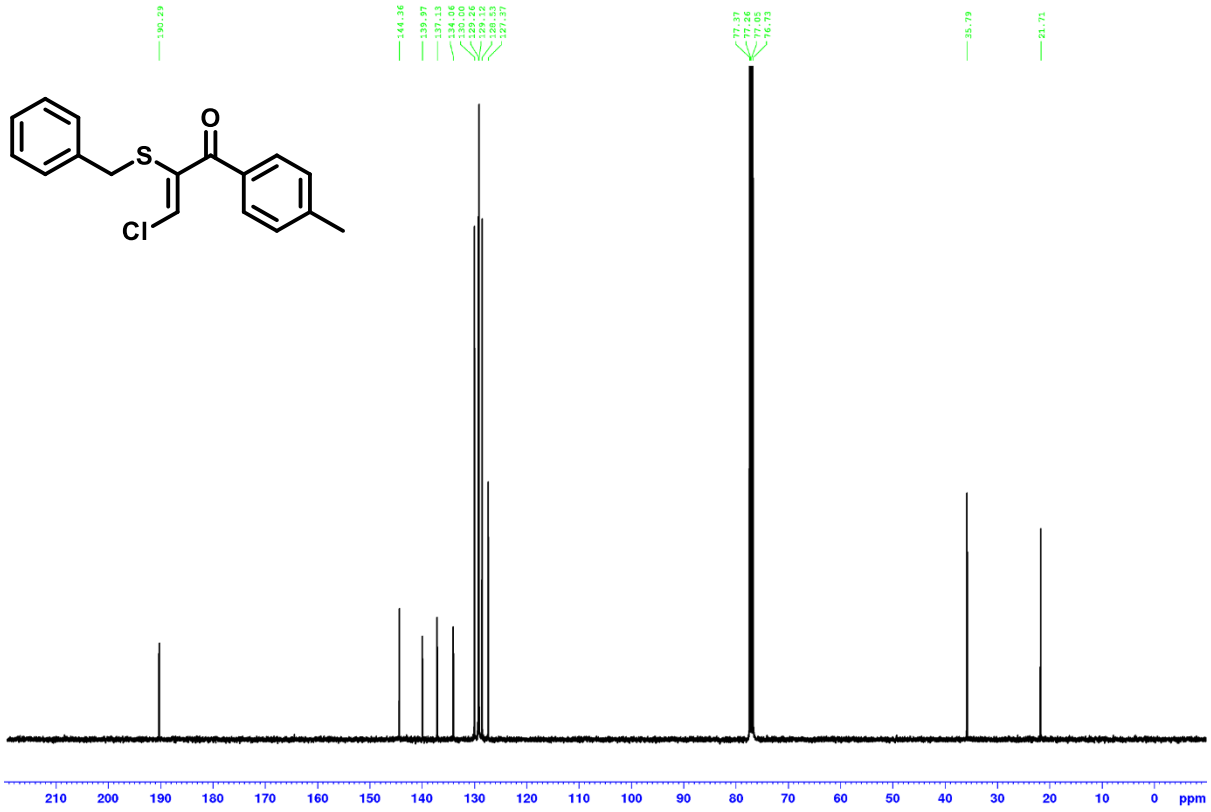


Figure S122: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4h**.

(*E*)-2-(Benzylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one E-4h

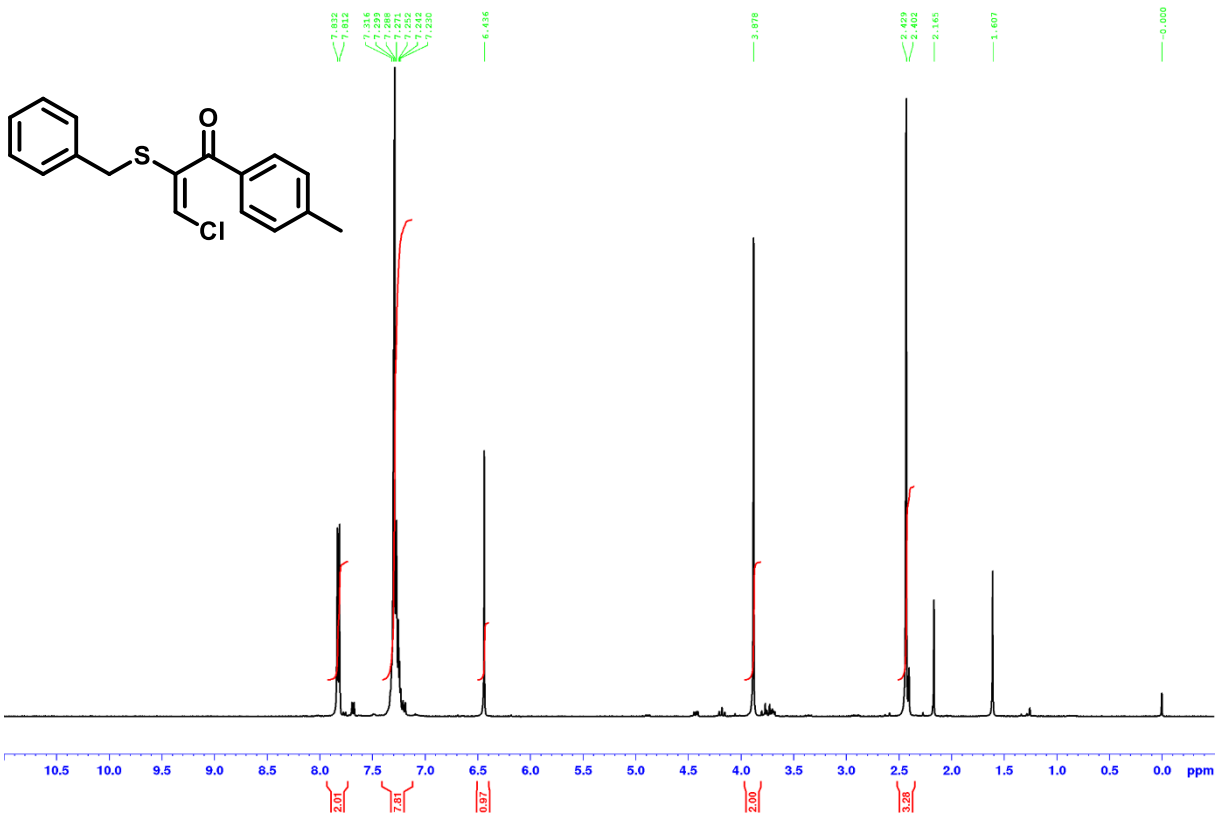


Figure S123: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4h**.

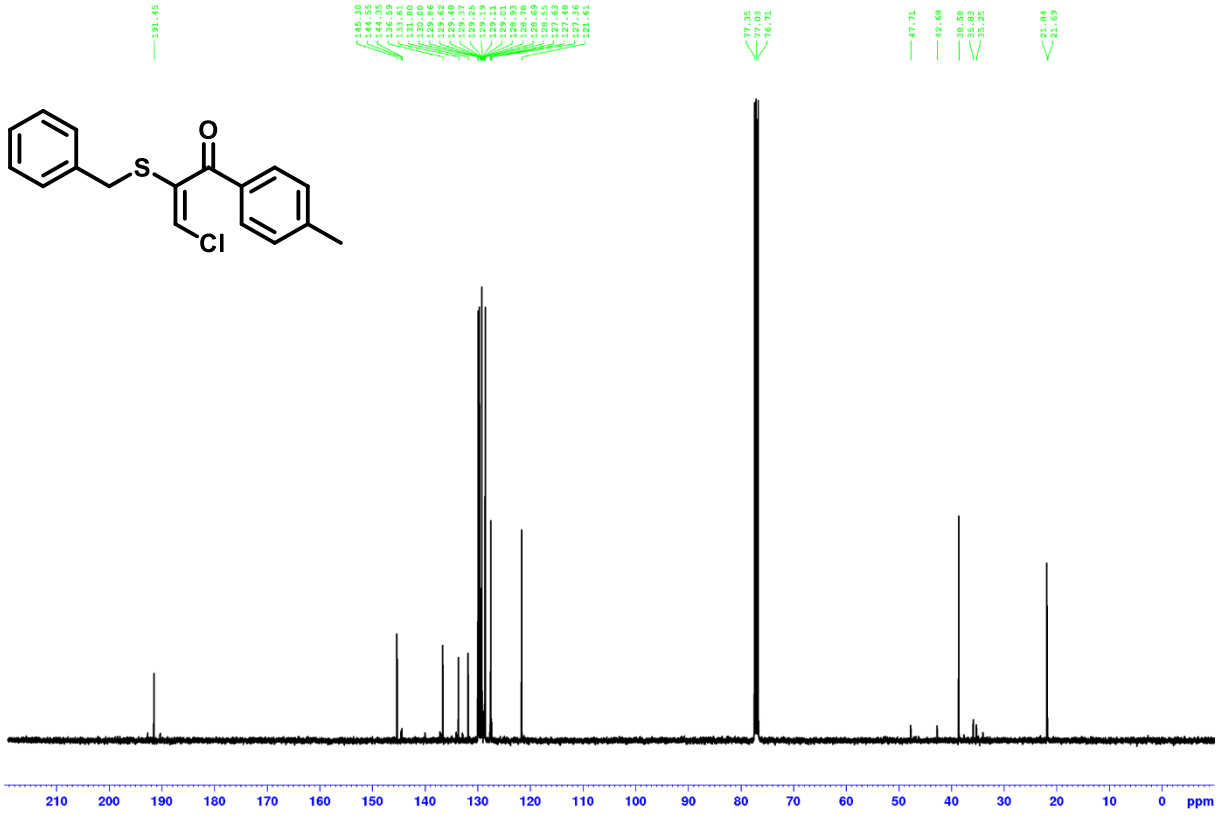


Figure S124: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4h**.

(*Z*)-2-(n-butylthio)-3-chloro-1-(p-tolyl)prop-2-en-1-one Z-4i and (*E*)-2-(butylthio)-3-chloro-1-(p-tolyl)prop-2-en-1-one E-4i

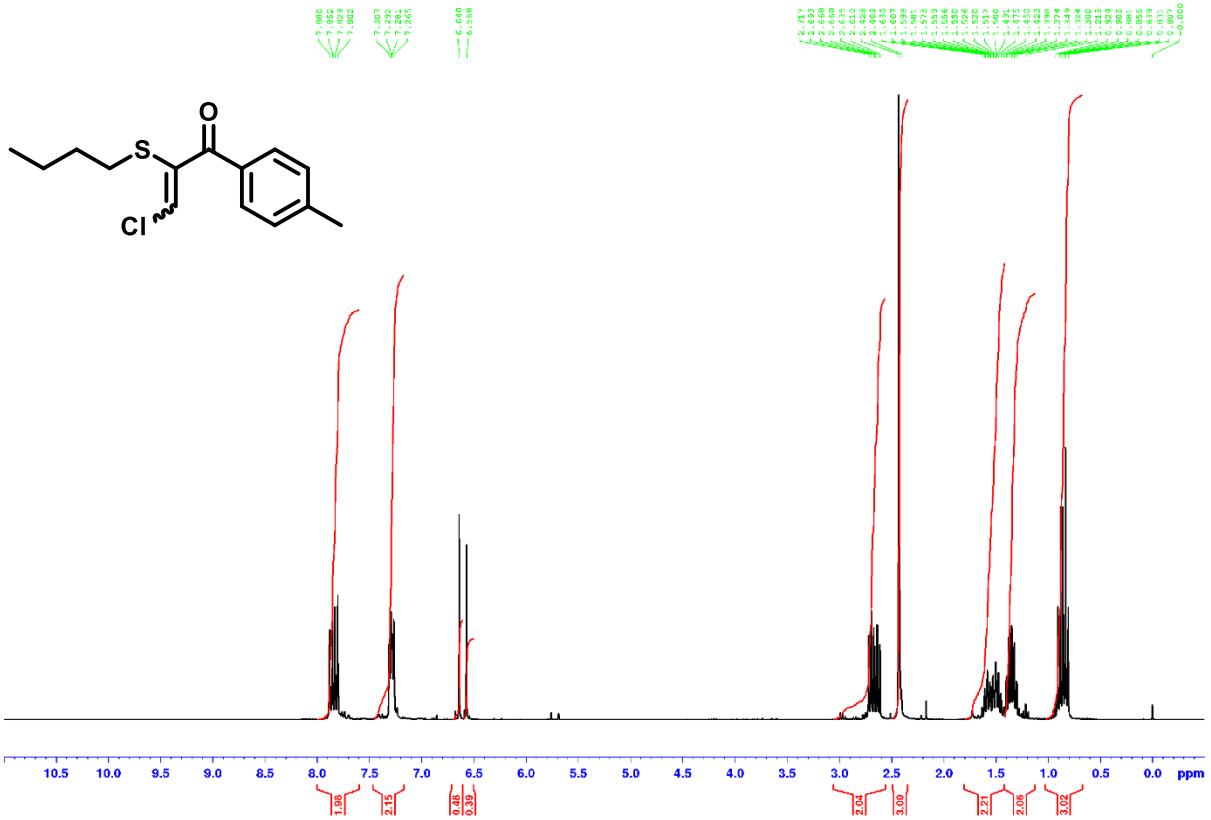


Figure S125: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4i** and **E-4i**.

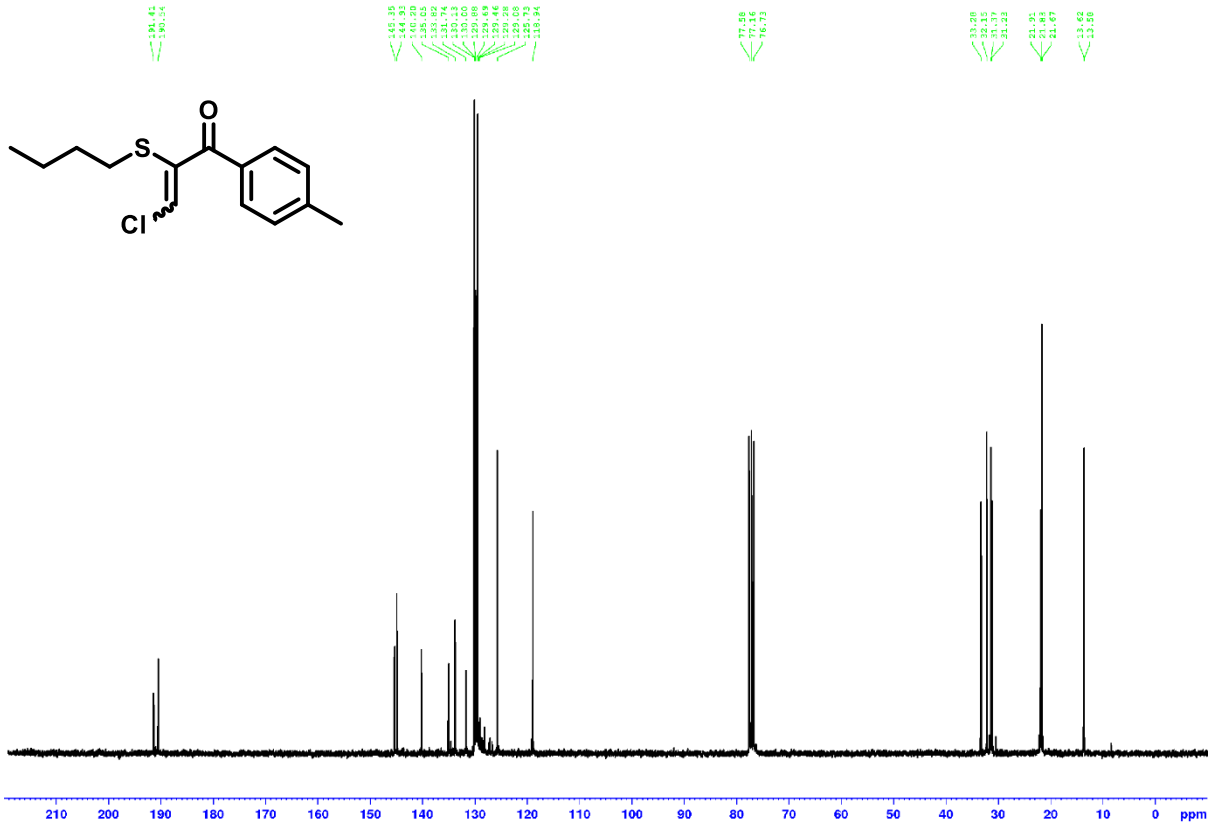


Figure S126: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4i** and **E-4i**.

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4j

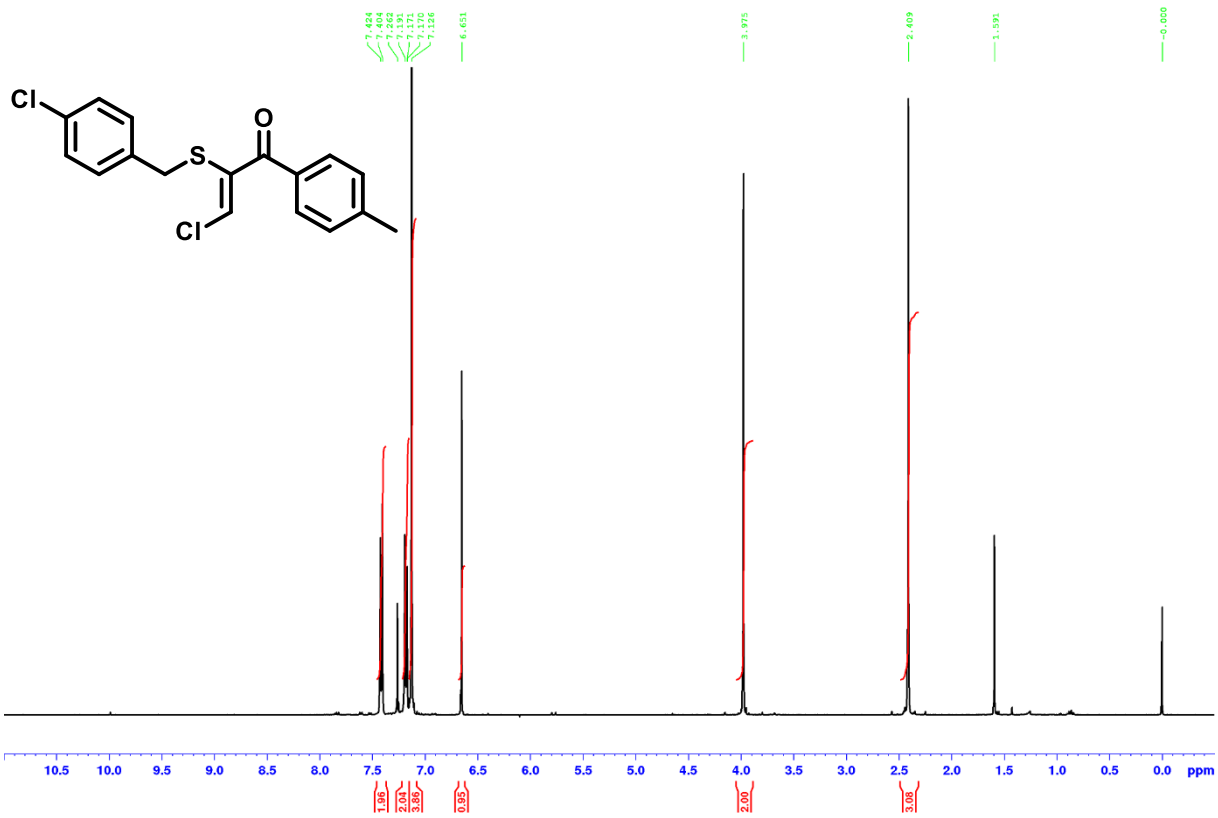


Figure S127: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4j.**

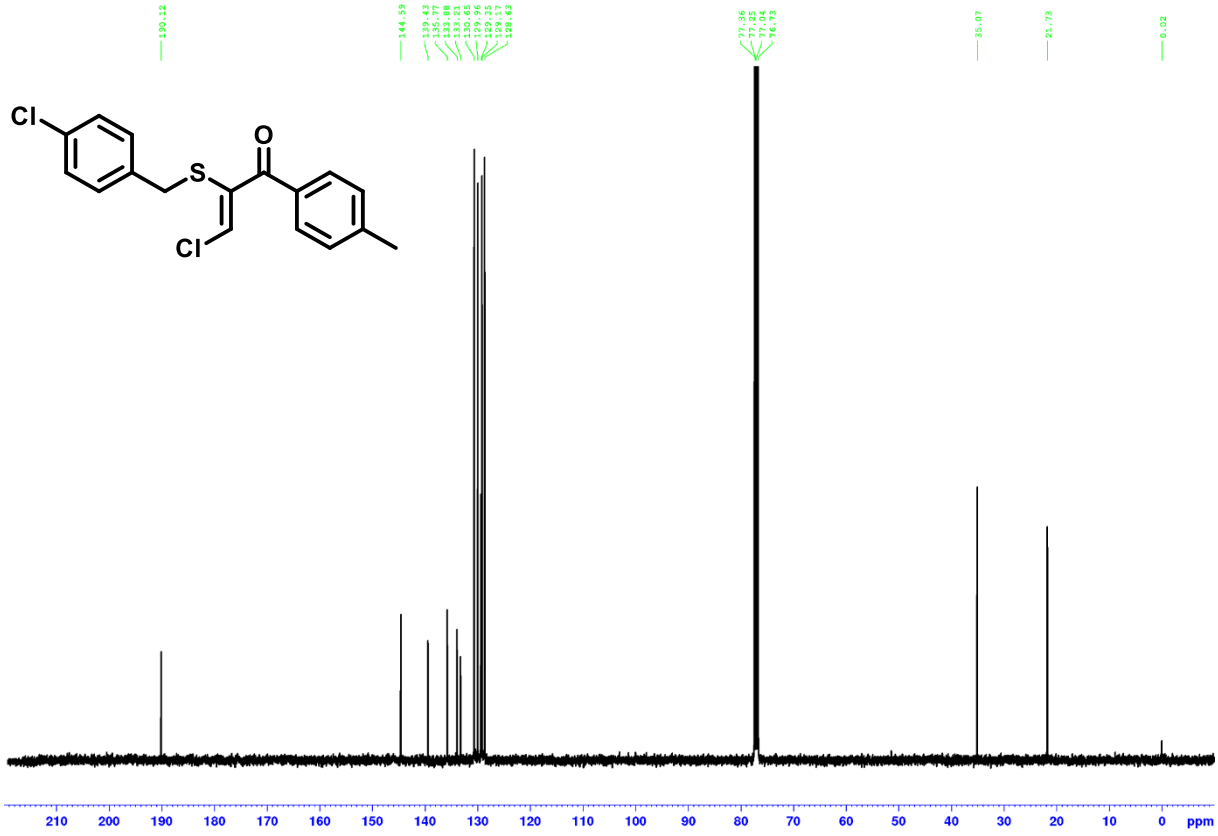


Figure S128: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4j**.

(*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4j

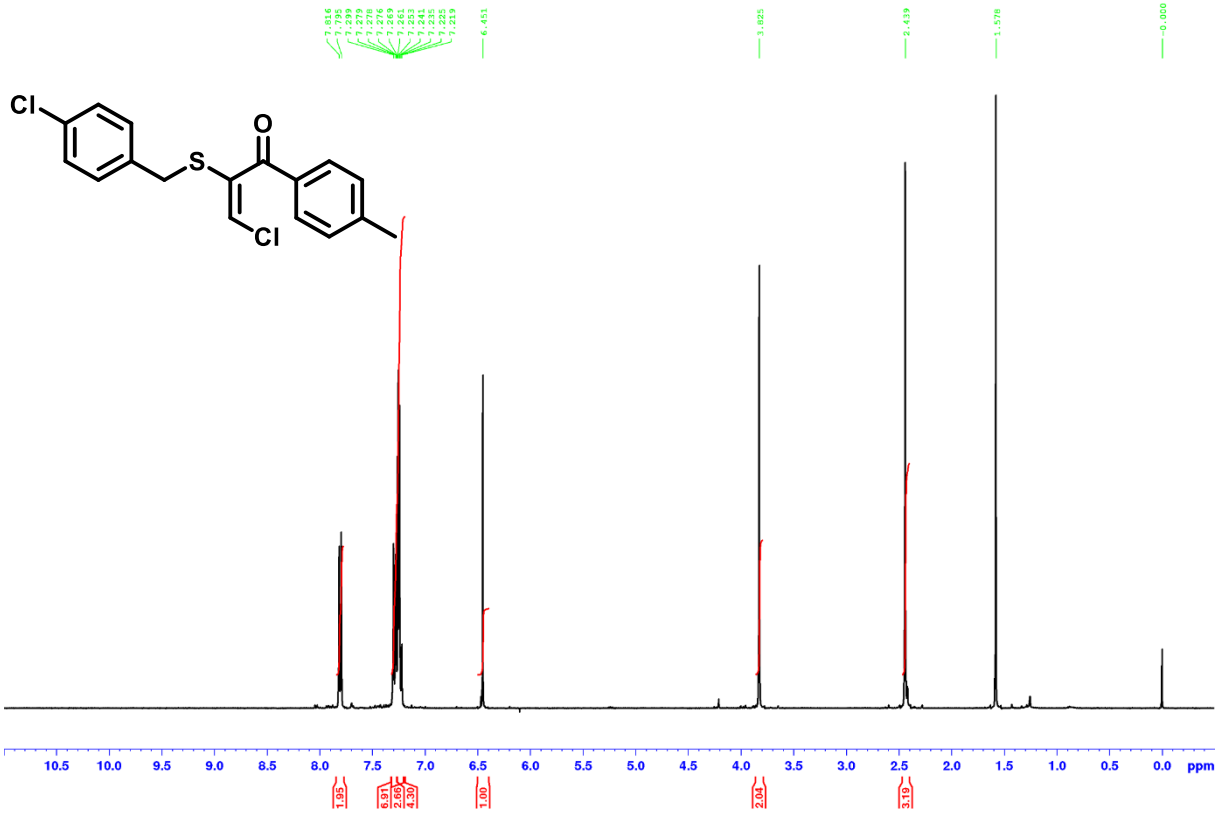


Figure S129: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4j**.

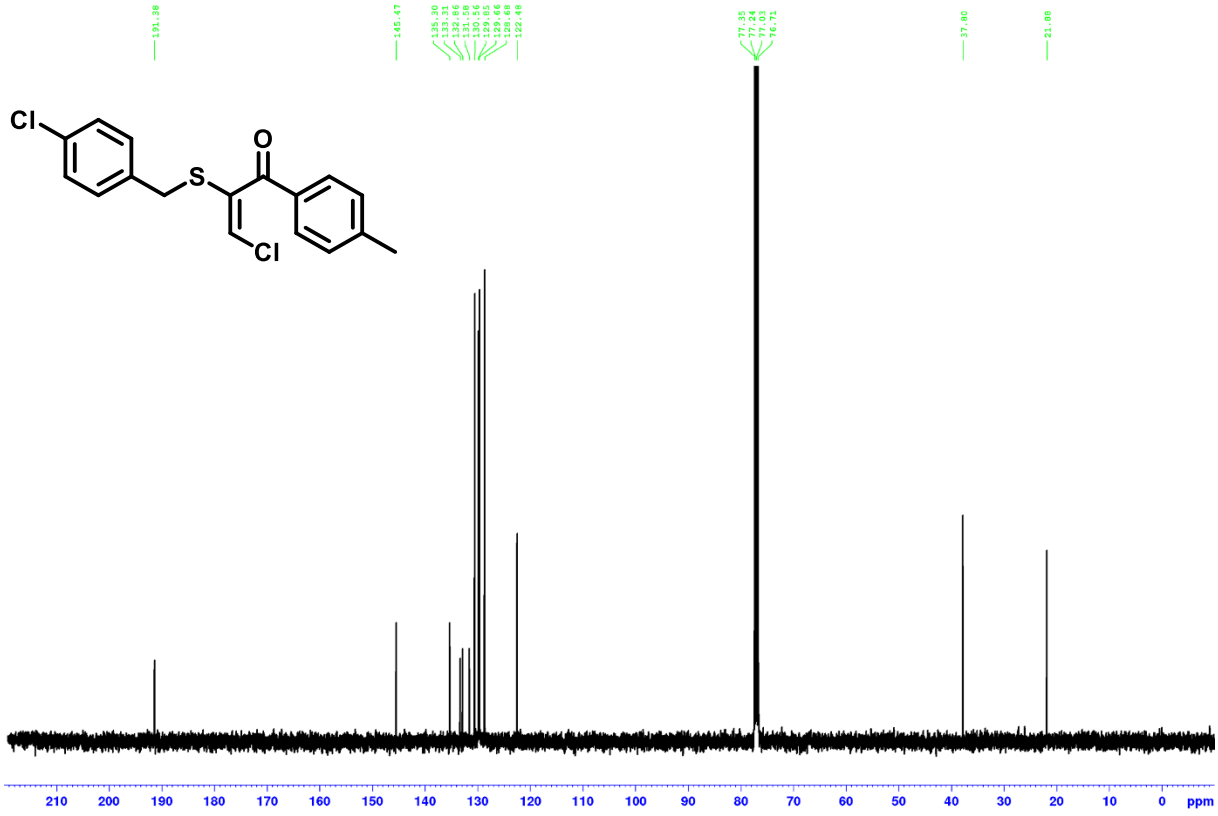


Figure S130: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4j**.

(*Z*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4k

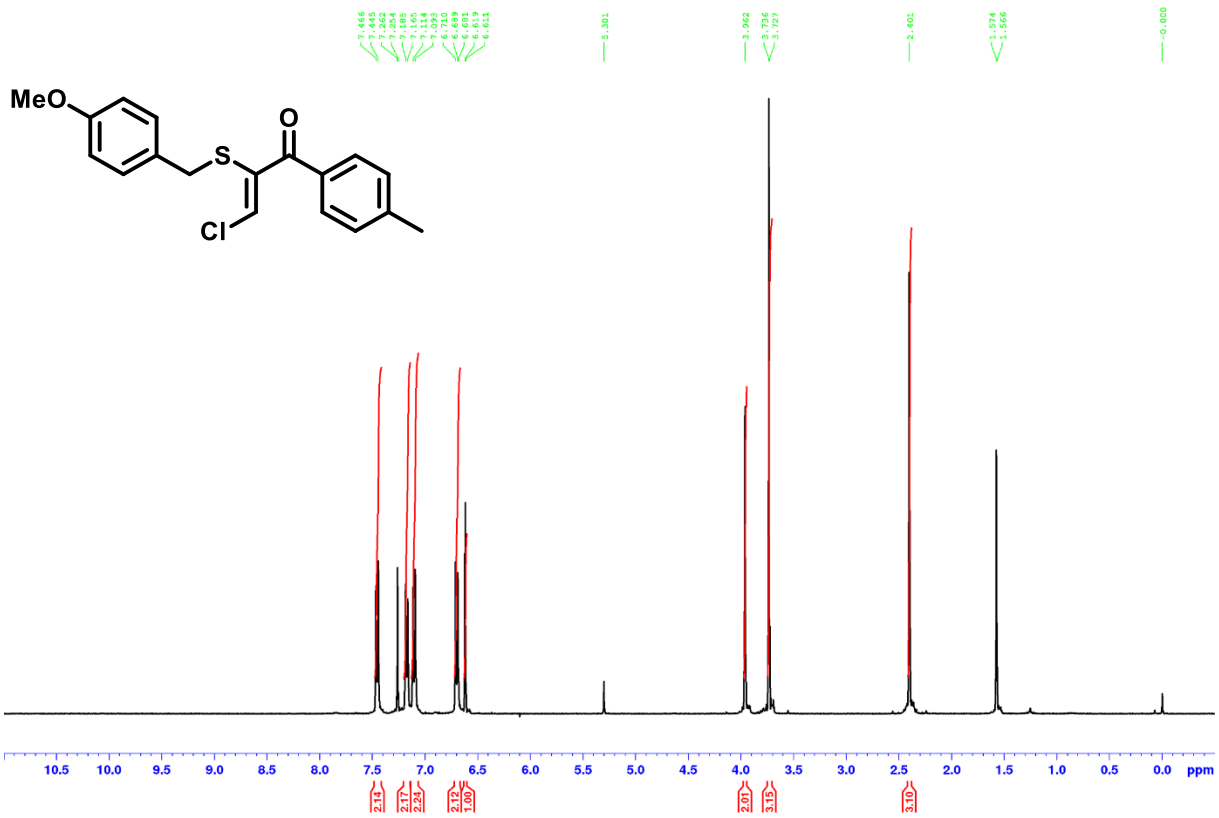


Figure S131: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4k**.

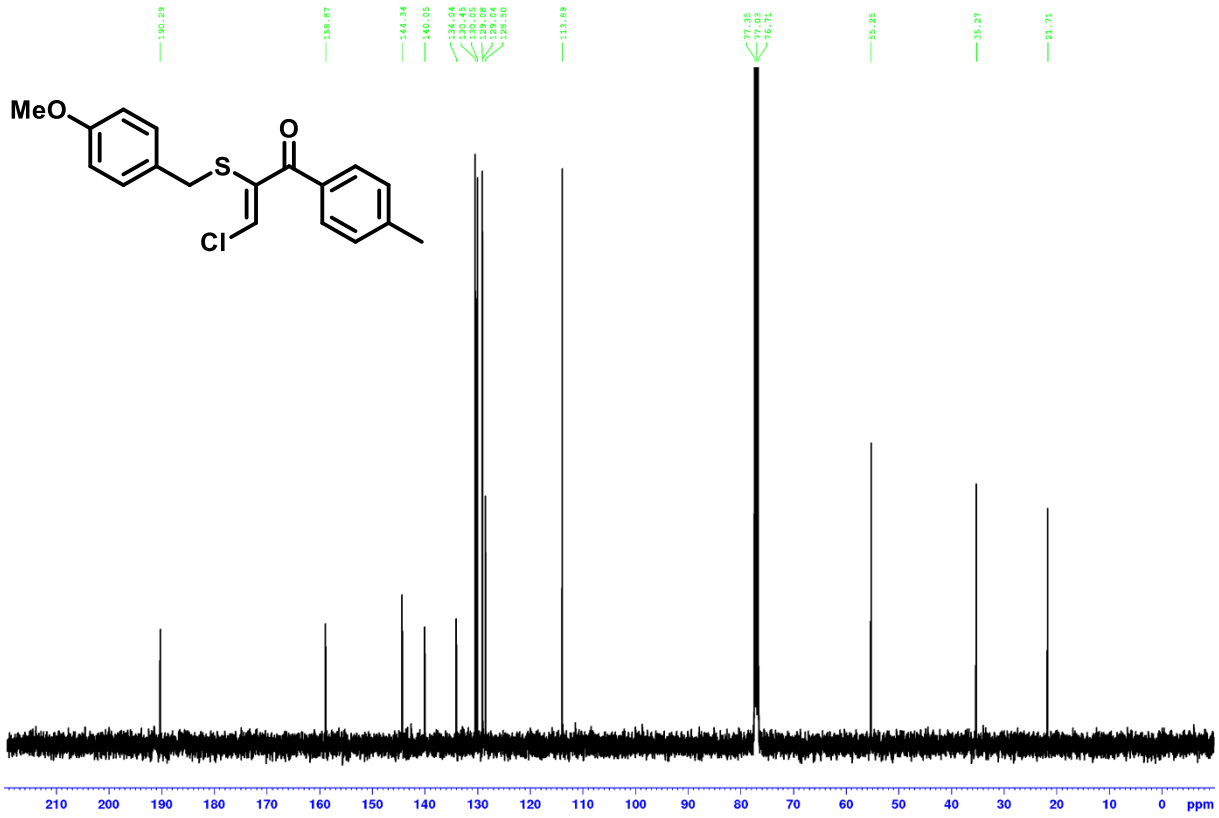


Figure S132: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4k**.

(*E*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4k

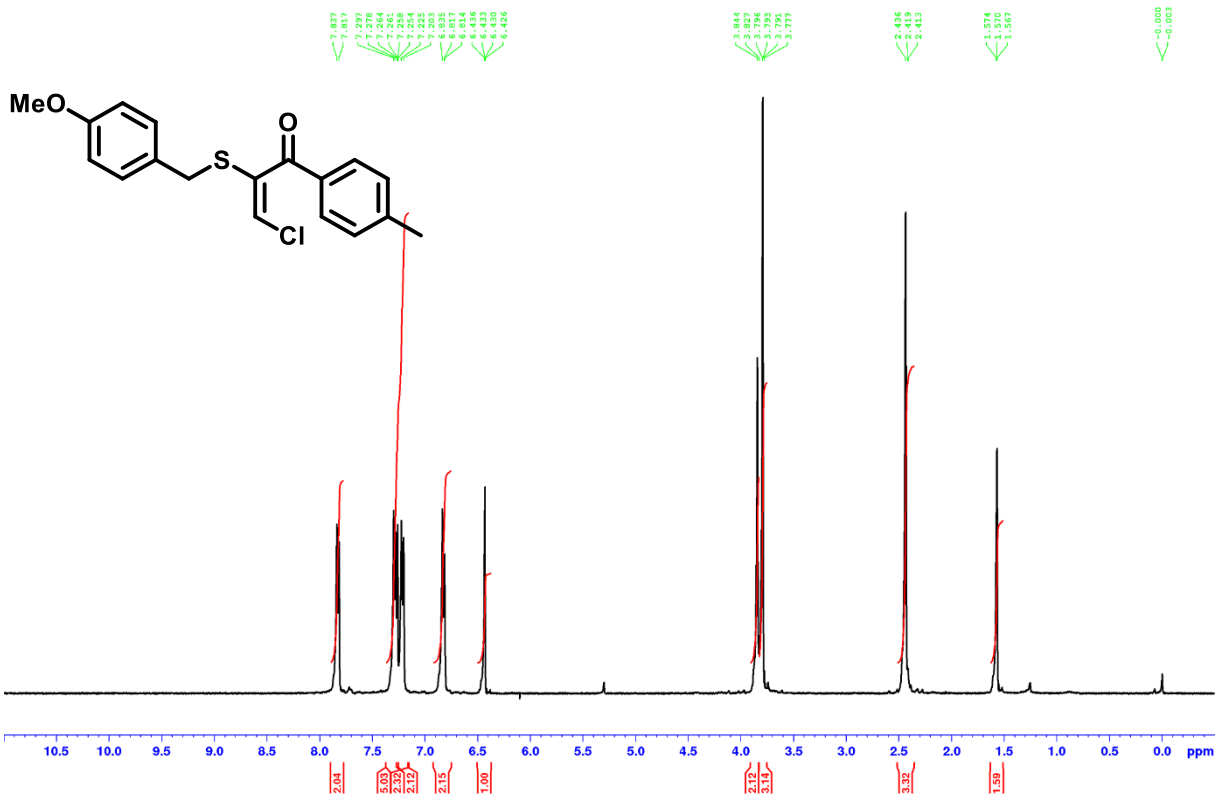


Figure S133: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4k**.

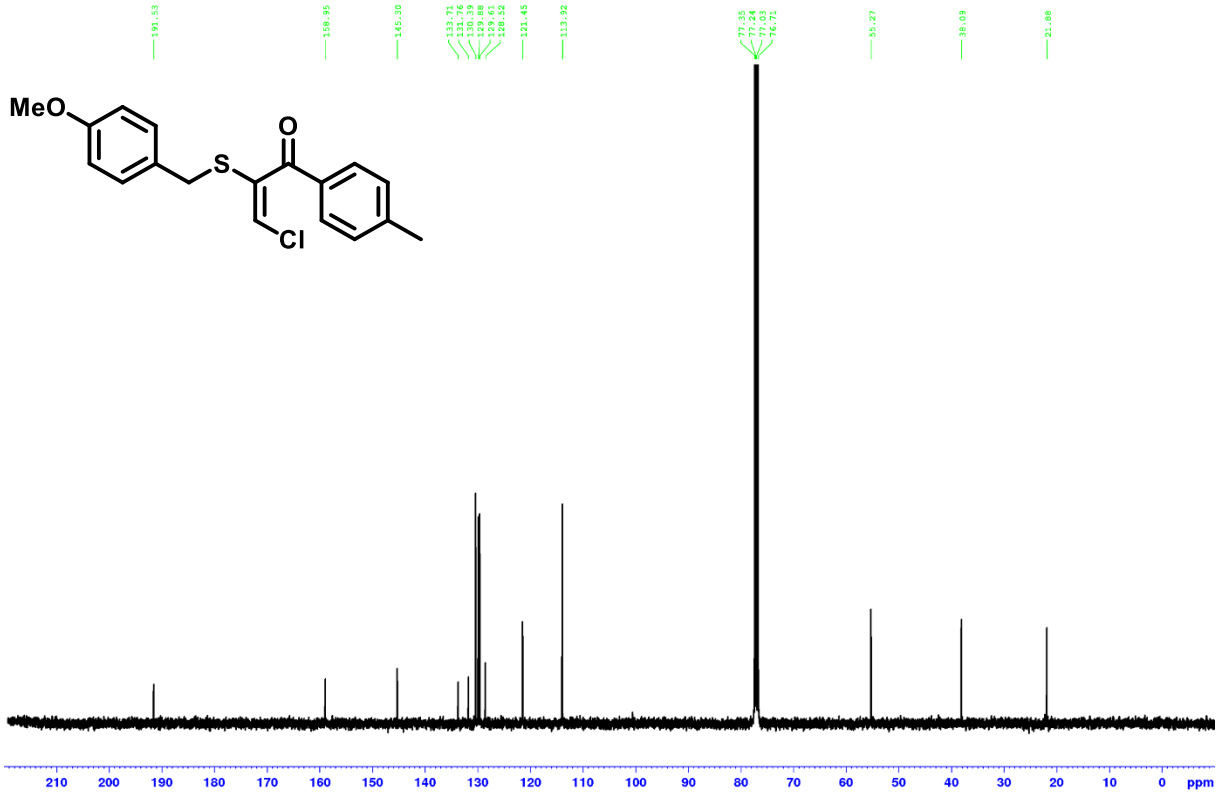


Figure S134: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4k**.

(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4l

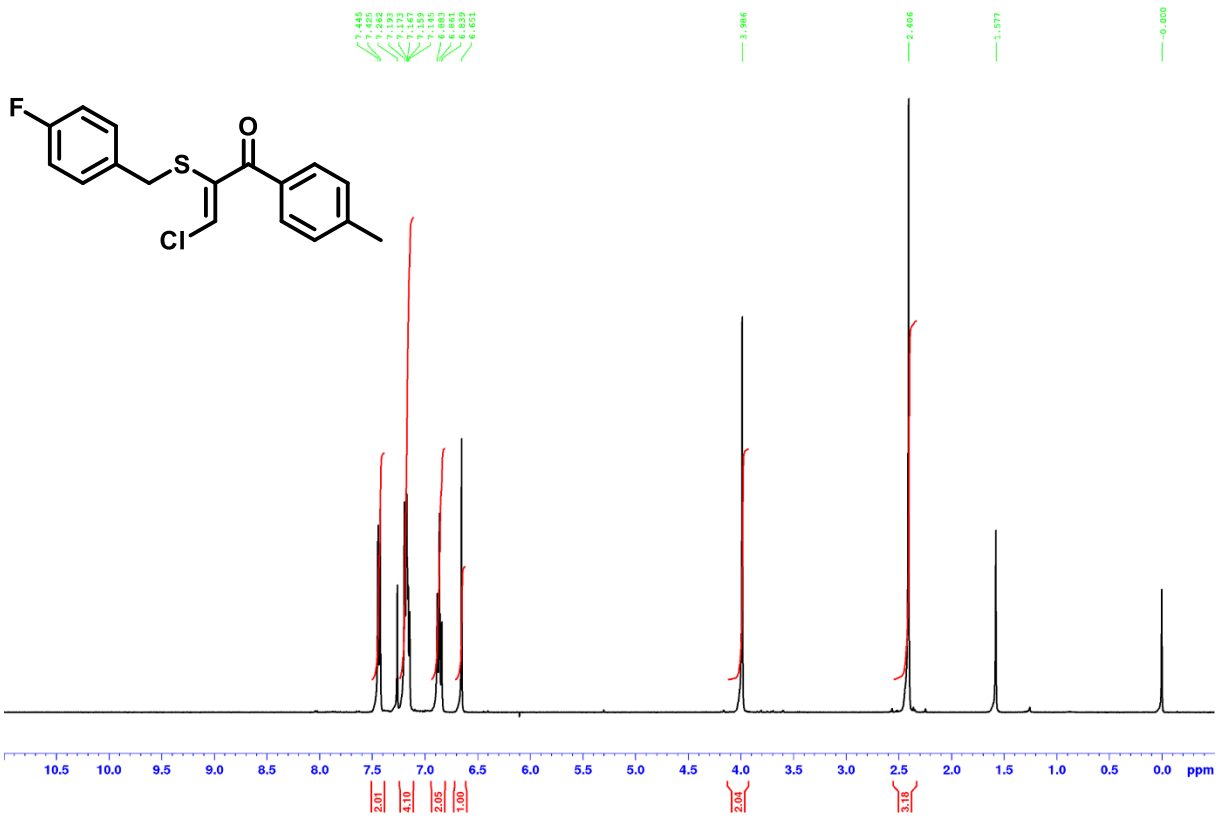


Figure S135: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4l**.

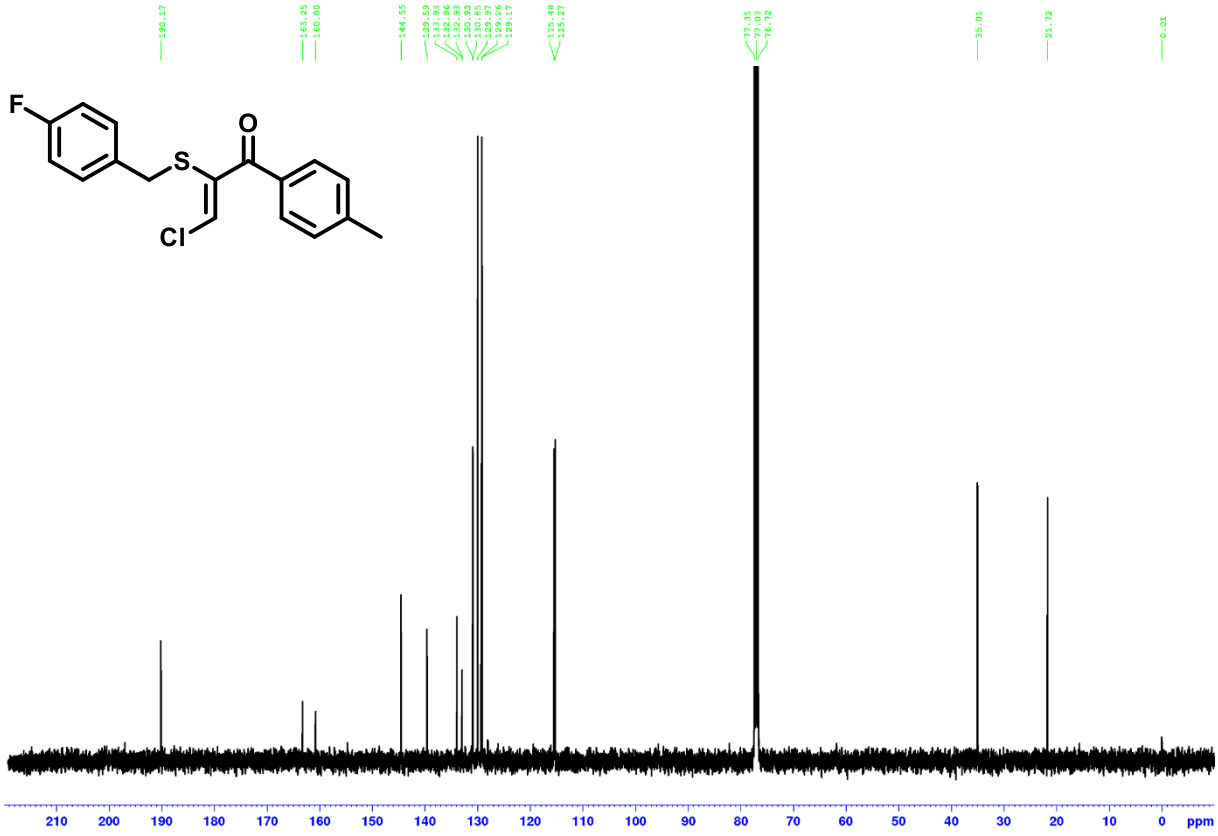


Figure S136: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4l.**

(*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4l

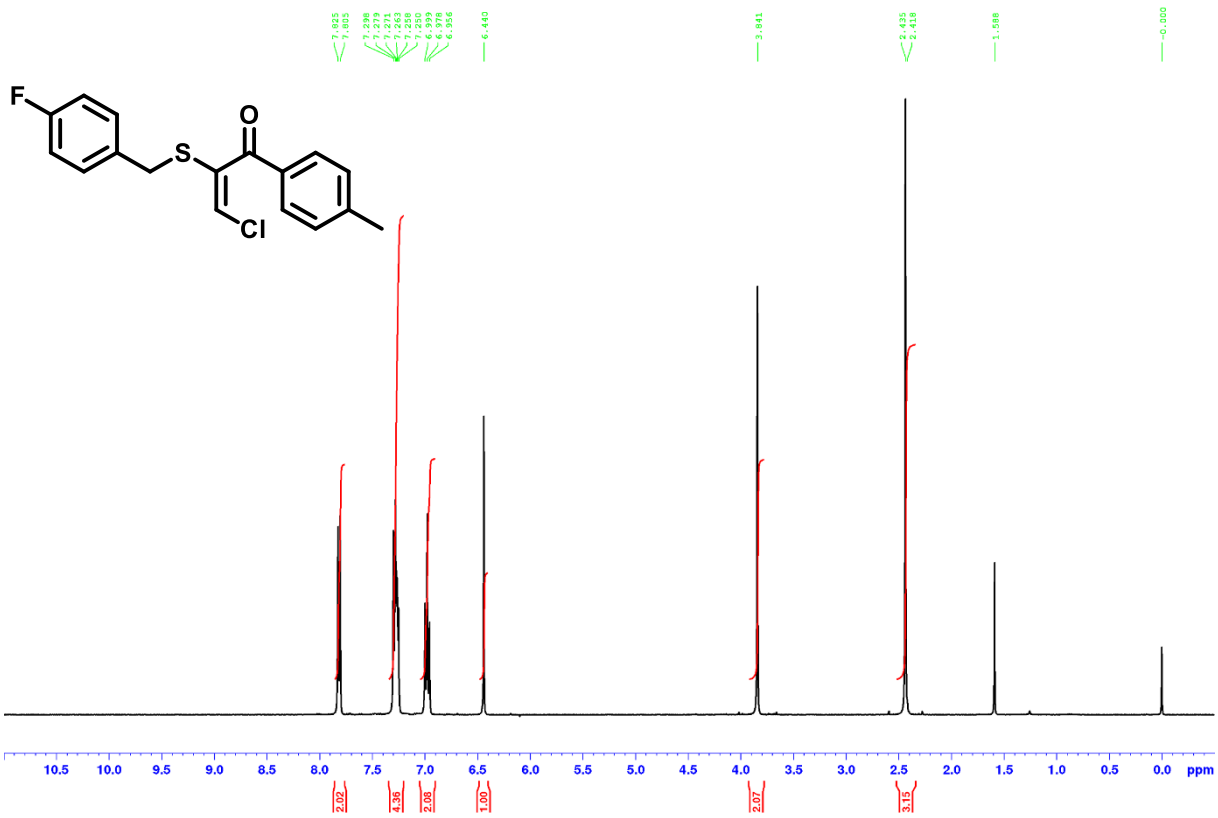


Figure S137: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4l**.

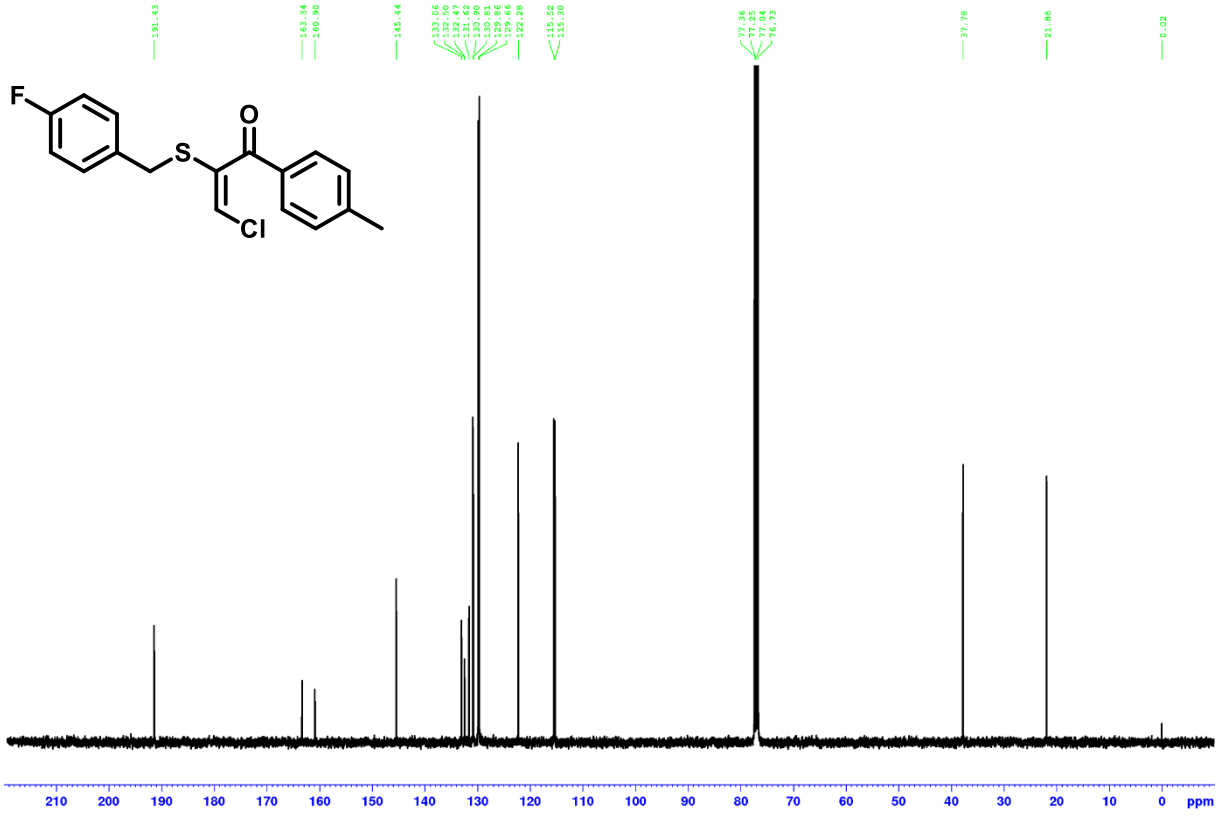


Figure S138: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4l**.

(*Z*)-3-Chloro-2-((4-methylbenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one Z-4m

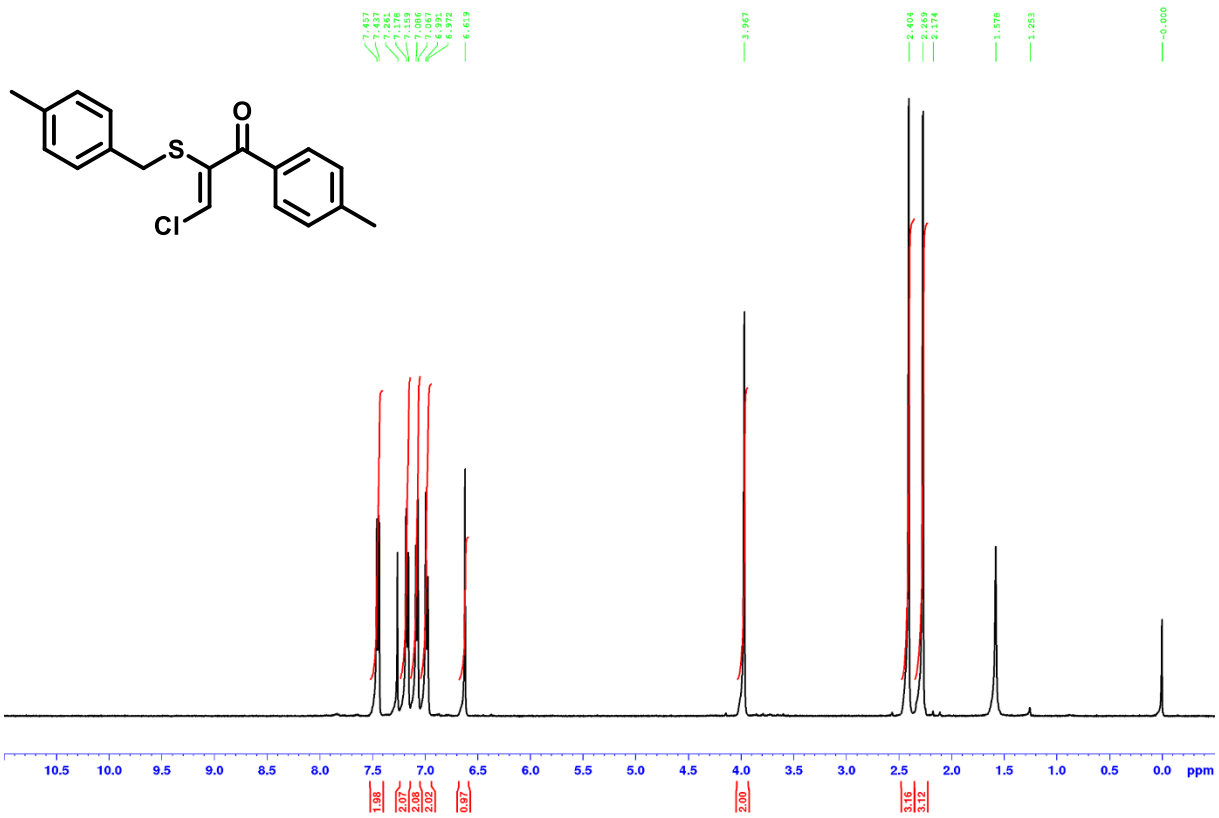


Figure S139: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4m**.

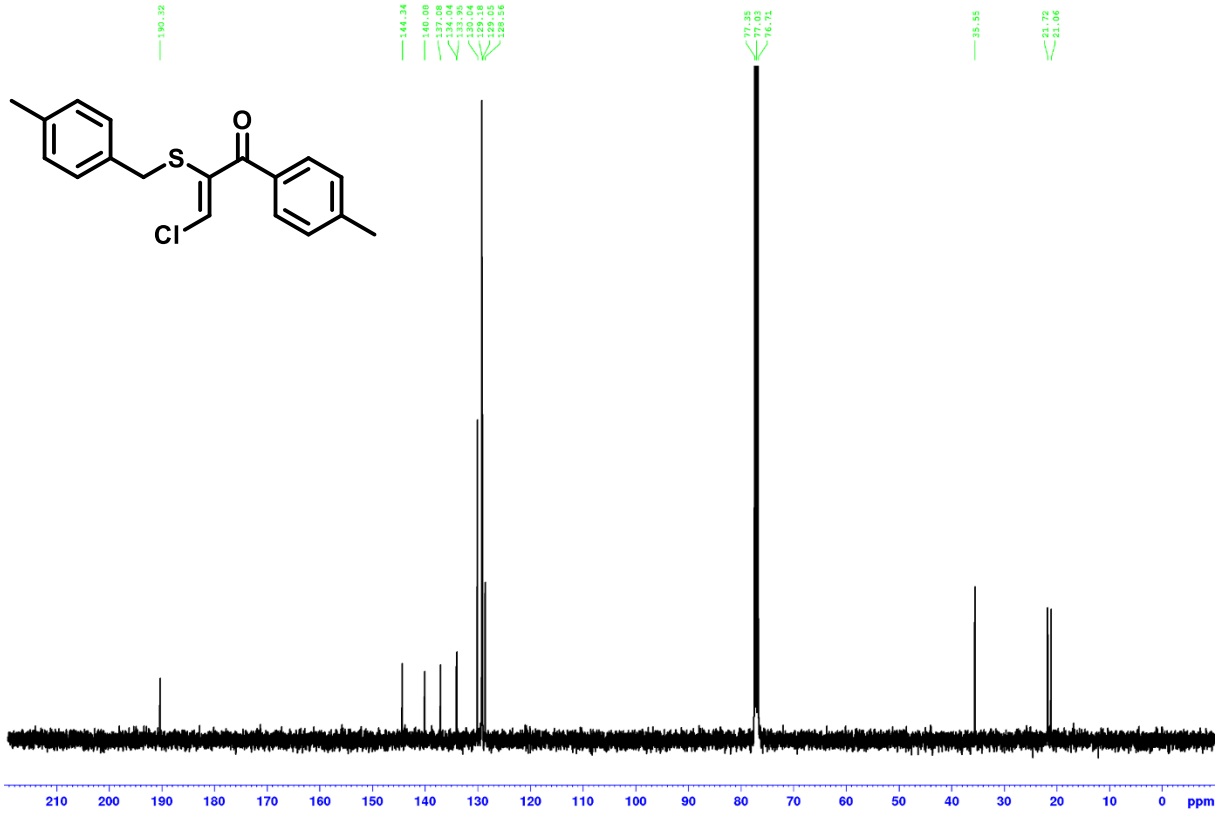


Figure S140: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4m**.

(*E*)-3-Chloro-2-((4-methylbenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one E-4m

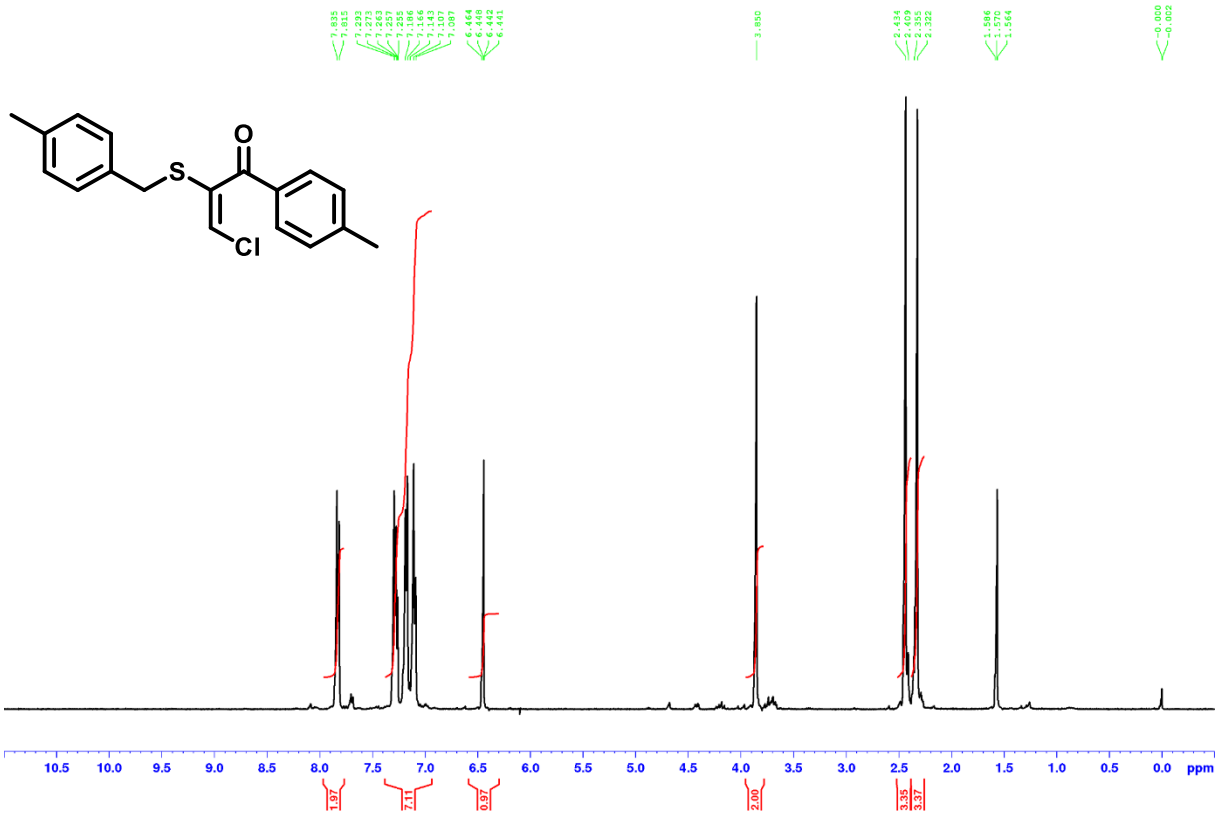


Figure S141: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4m**.

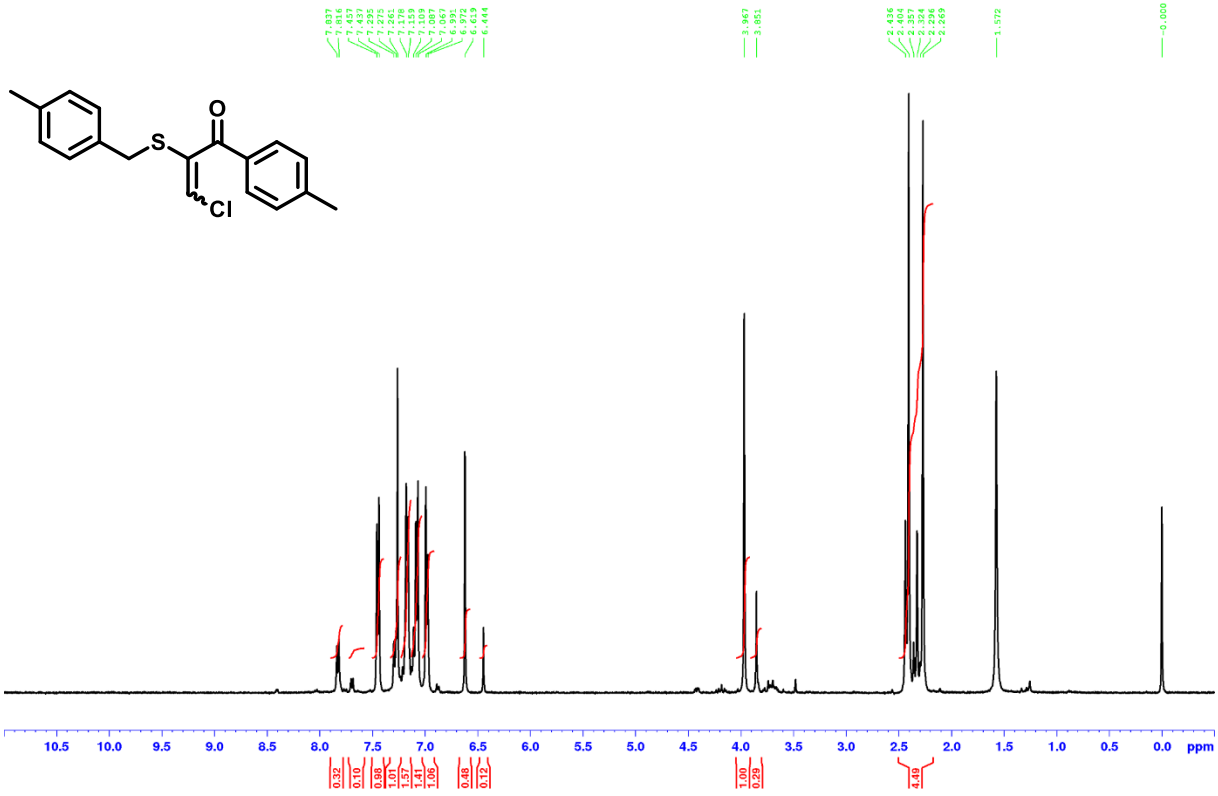


Figure S142: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4m** and **E-4m** after storage at room temperature for 40 months.

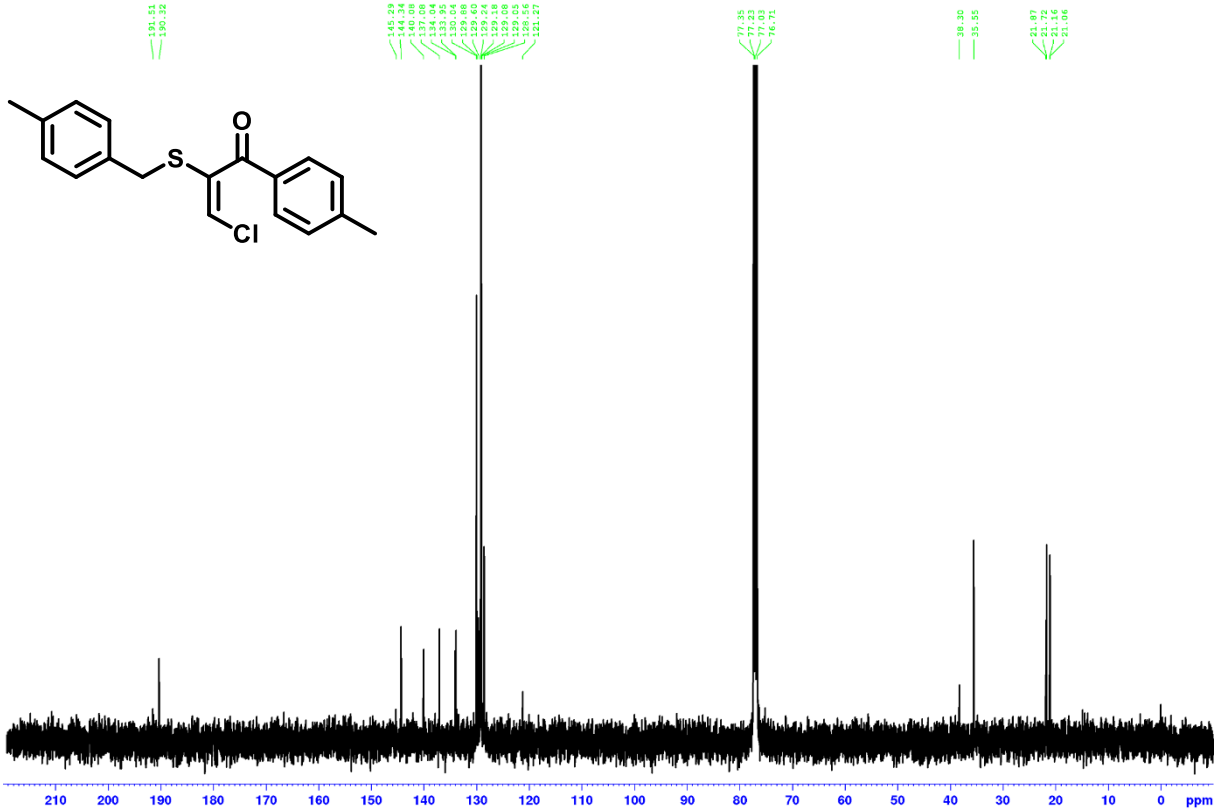


Figure S143: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4m**.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-(phenylthio)prop-2-en-1-one Z-4n and (*E*)-3-chloro-1-(4-chlorophenyl)-2-(phenylthio)prop-2-en-1-one E-4n

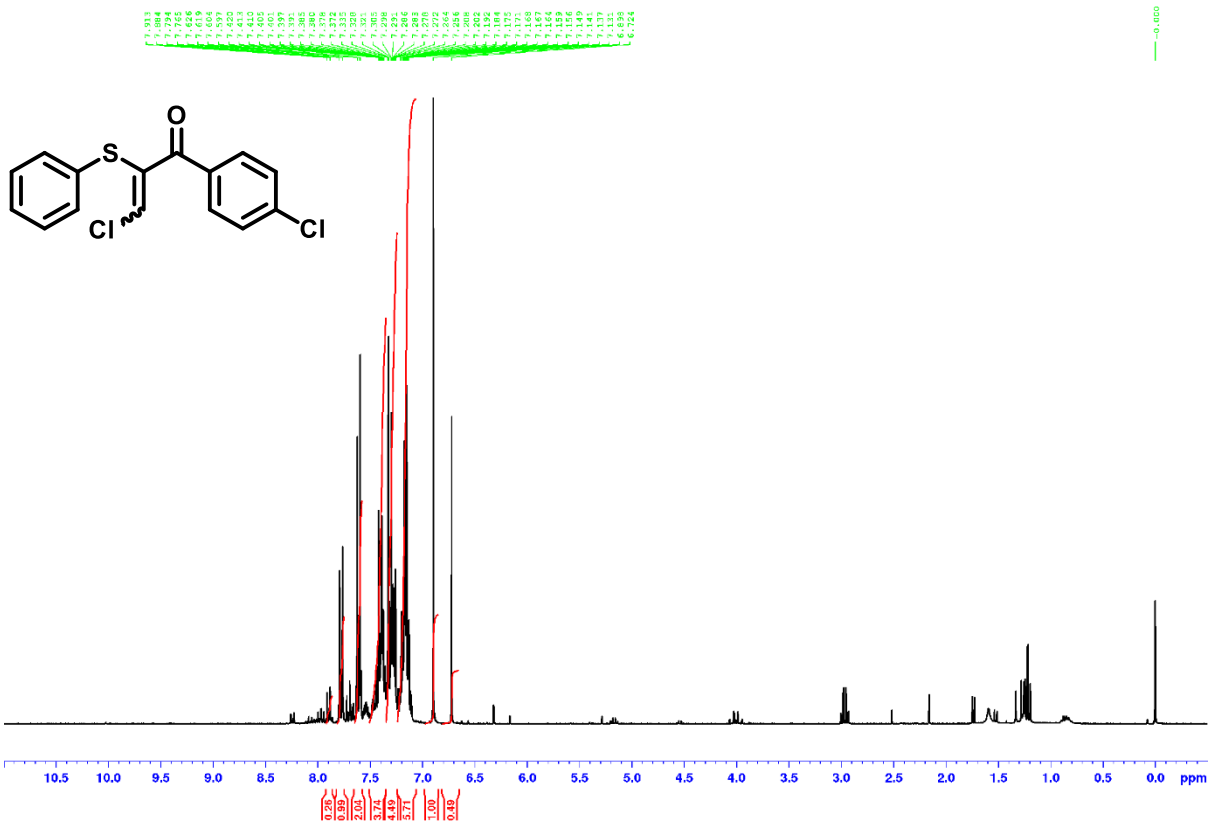


Figure S144: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4n** and **E-4n** which contains minor impurities.

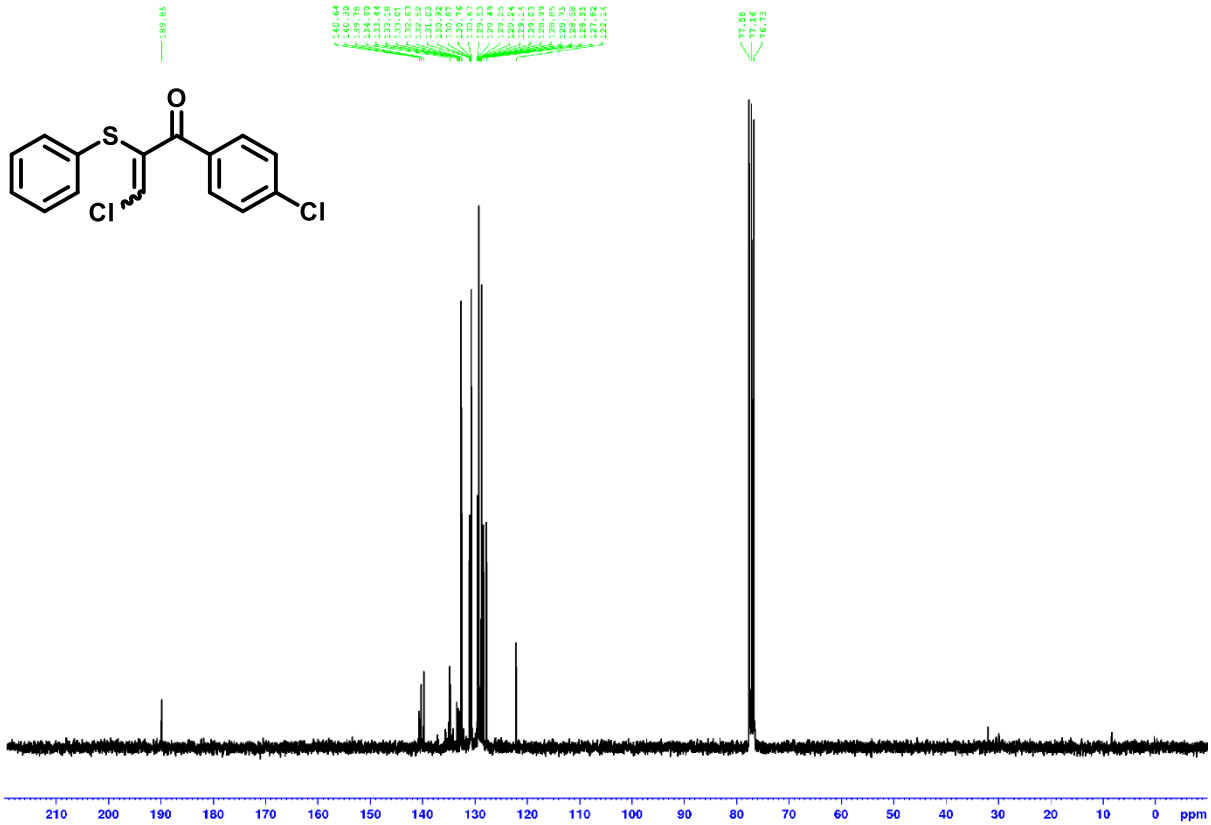


Figure S145: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4n** and **E-4n** which contains minor impurities.

(*Z*)-2-(Benzylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one Z-4o and (*E*)-2-(Benzylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one E-4o

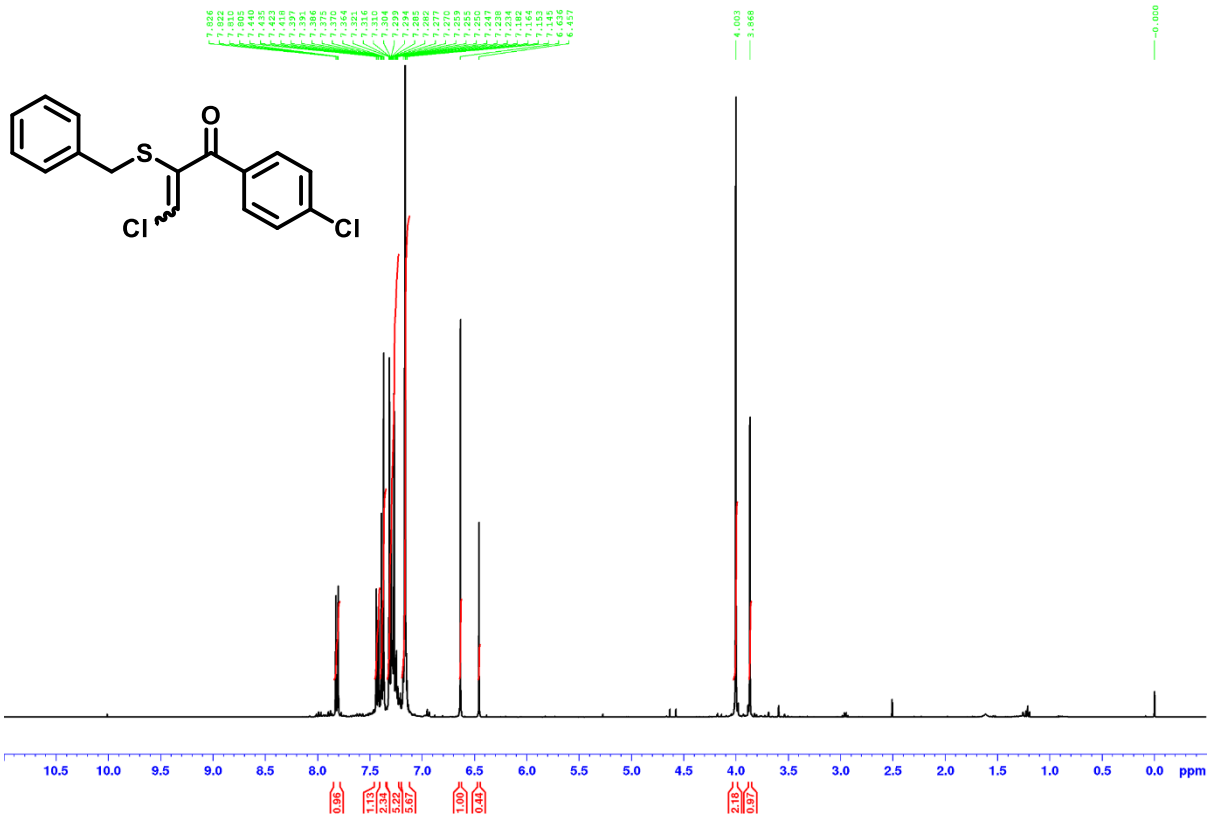


Figure S146: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4o** and **E-4o**.

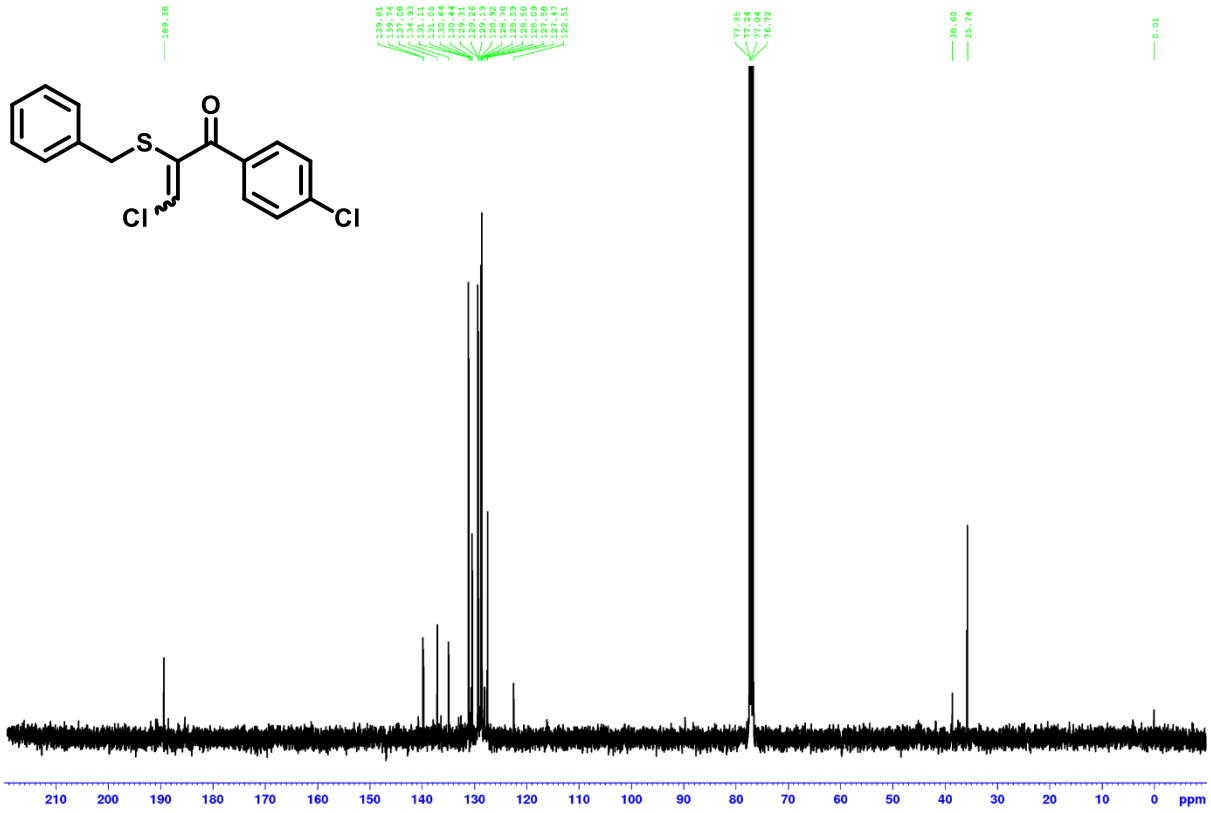


Figure S147: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4o** and **E-4o**.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one Z-4p and (*E*)-2-(*n*-butylthio)-3-chloro-1-(4-chlorophenyl)prop-2-en-1-one E-4p

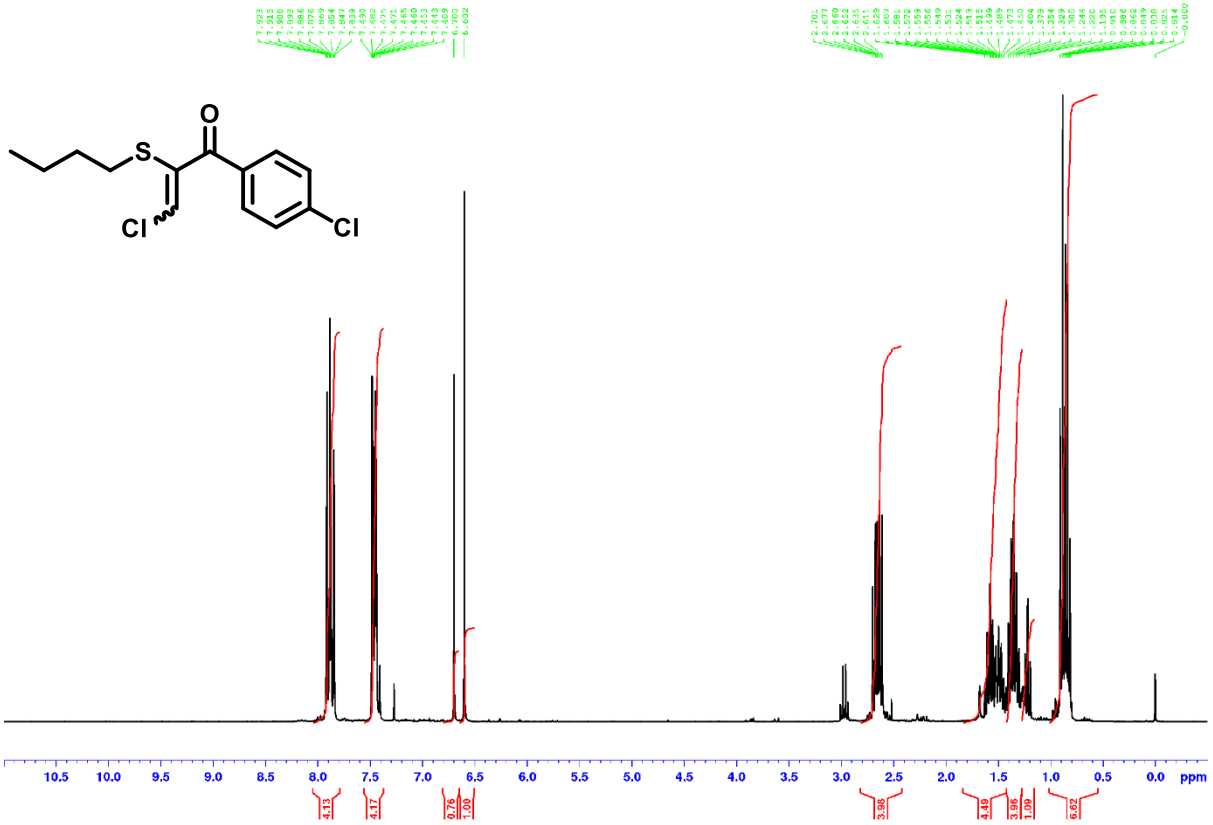


Figure S148: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4p** and **E-4p**.

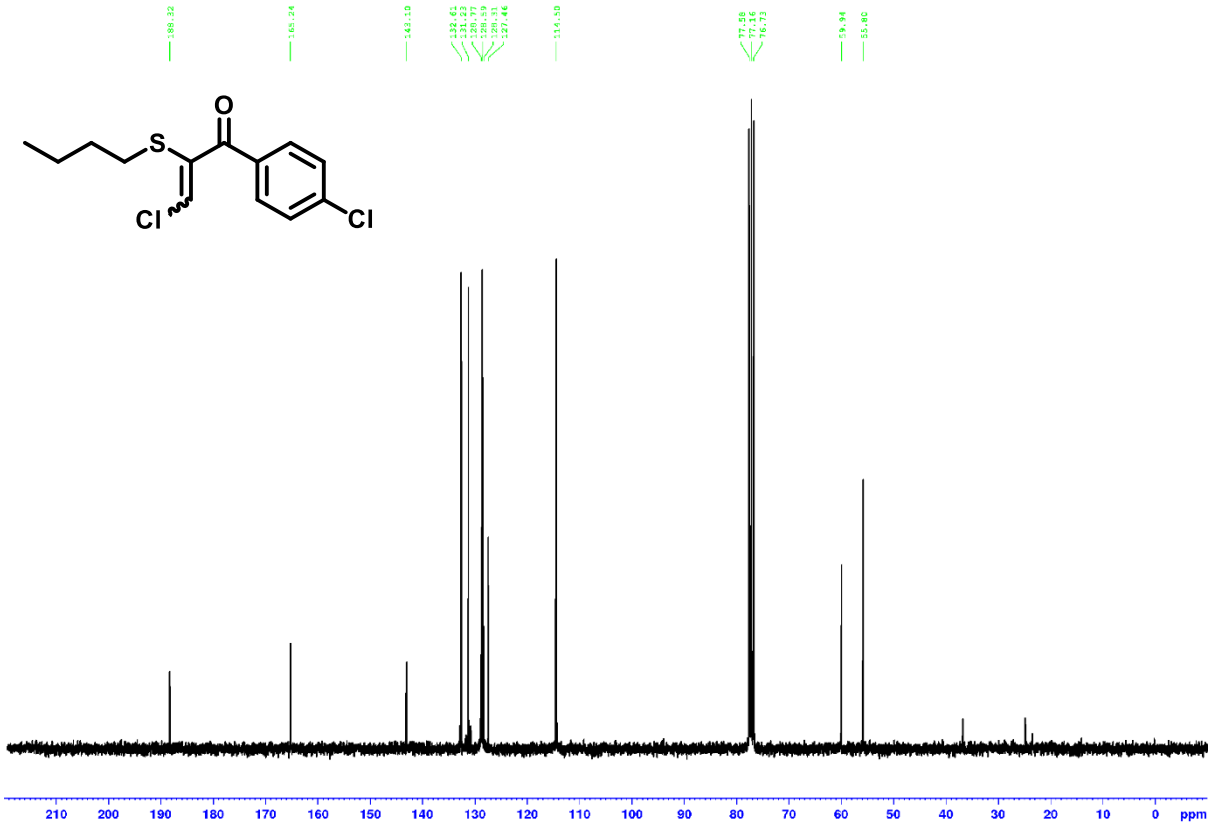


Figure S149: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4p** and **E-4p**.

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one Z-4q

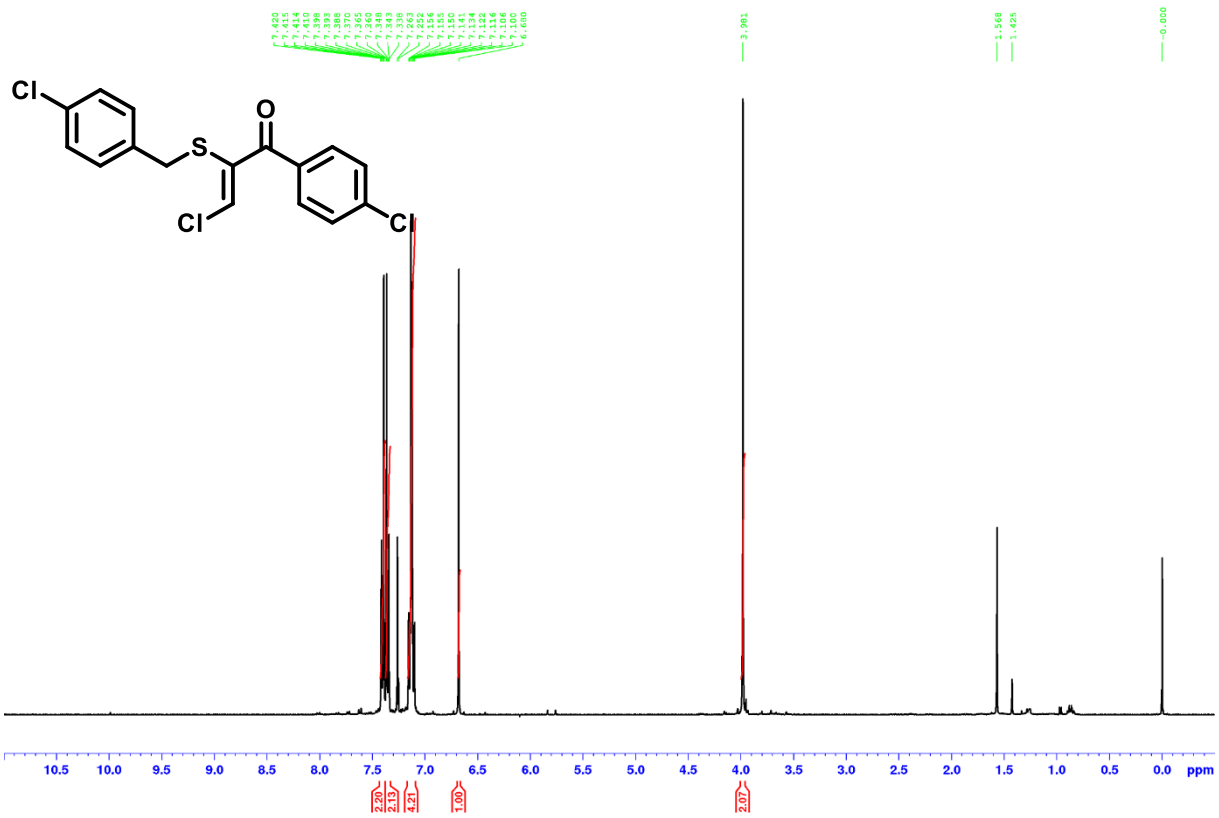


Figure S150: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4q**.

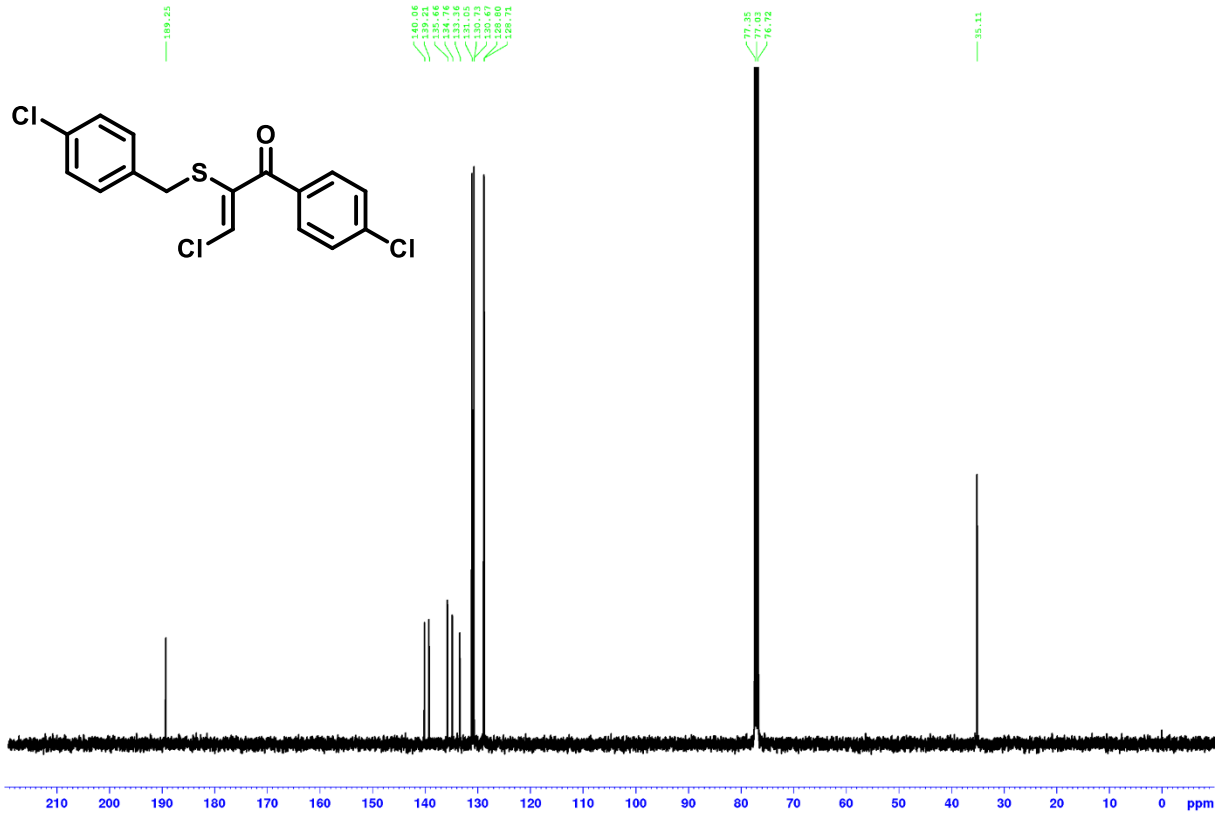


Figure S151: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4q**.

(*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one E-4q

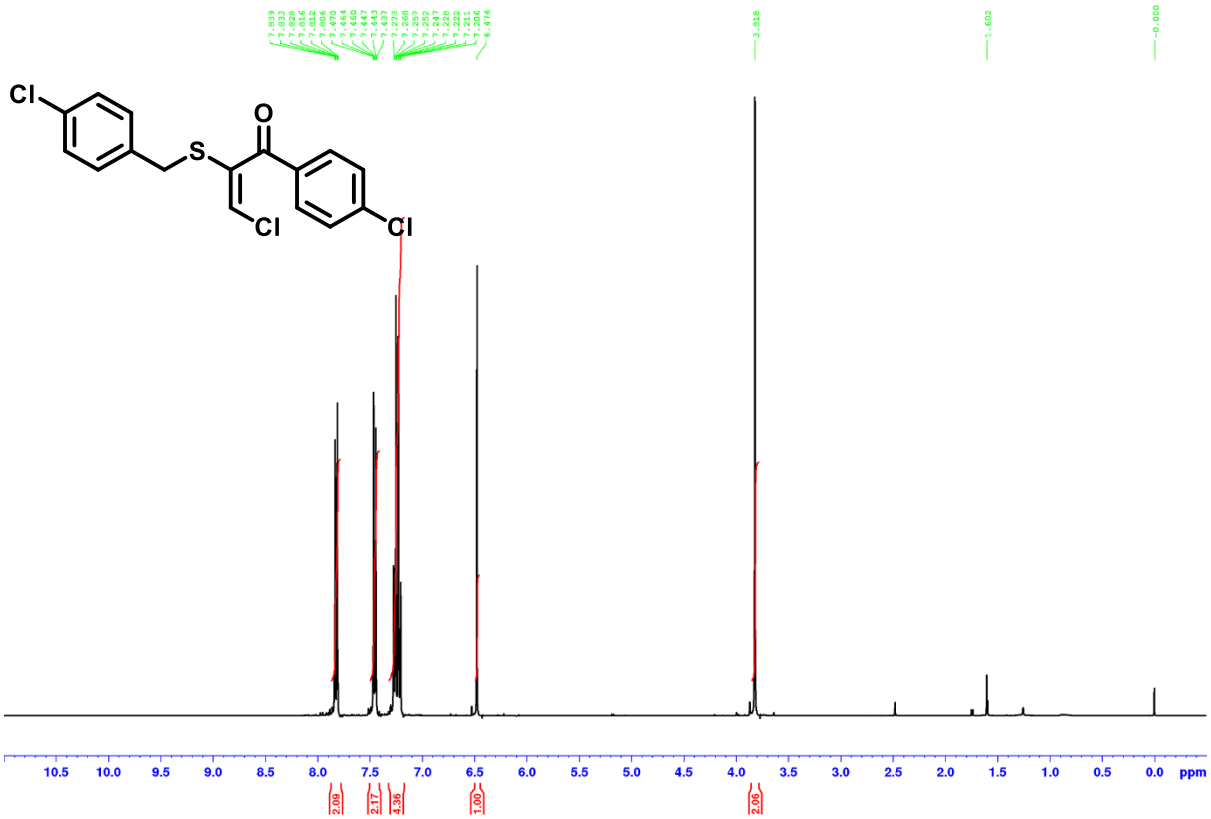


Figure S152: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4q**.

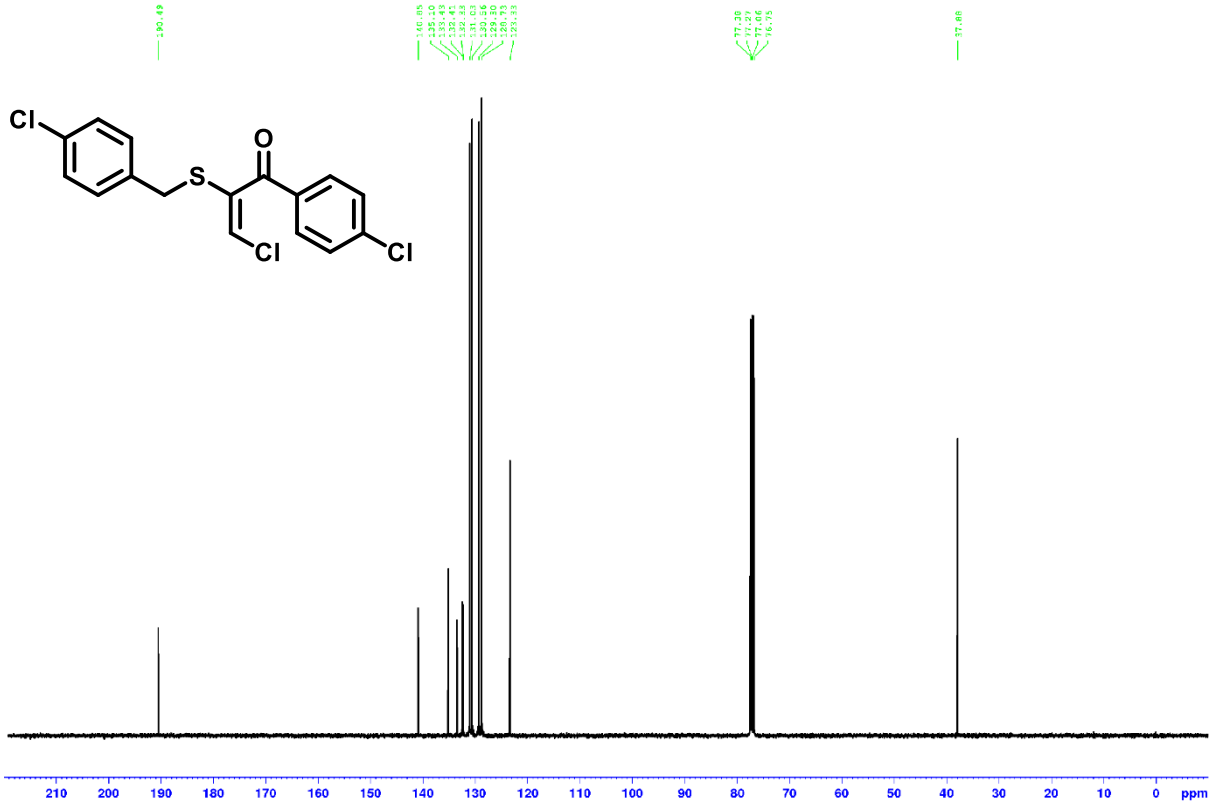


Figure S153: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4q**.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one Z-4r and (*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one E-4r

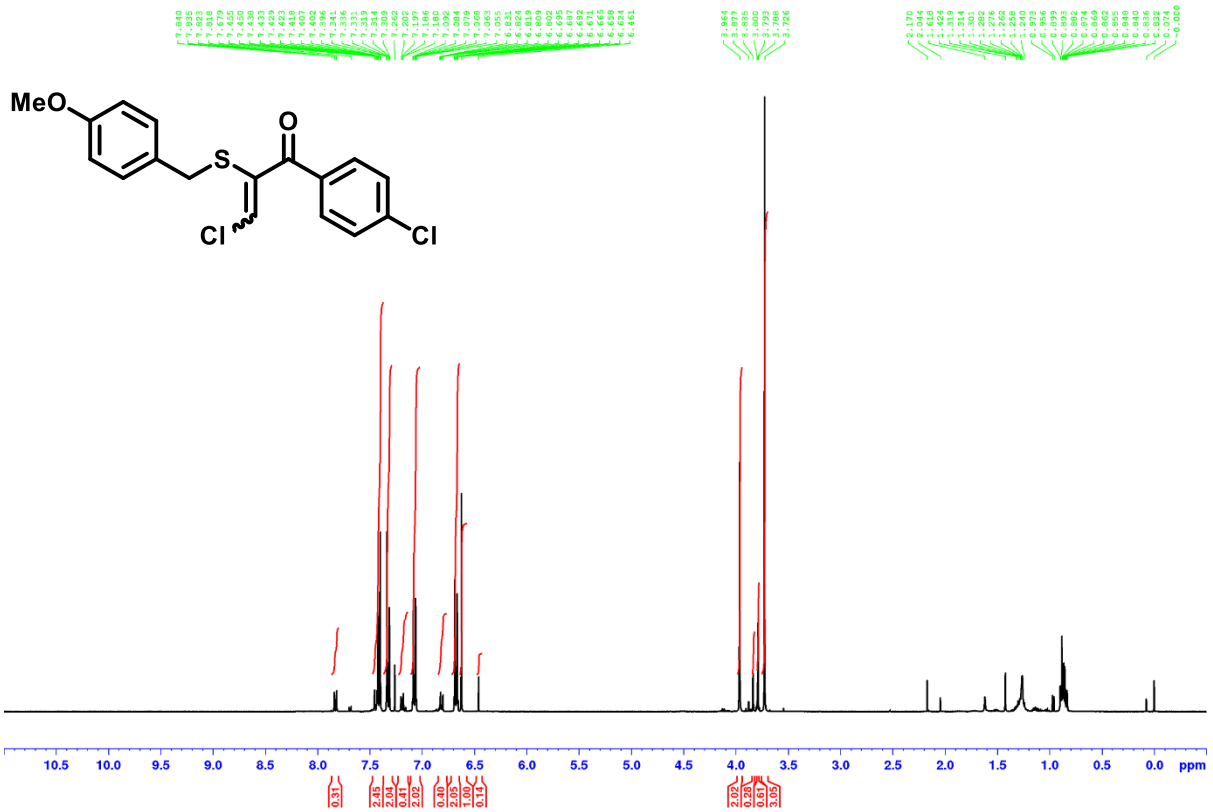


Figure S154: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4r** and **E-4r**.

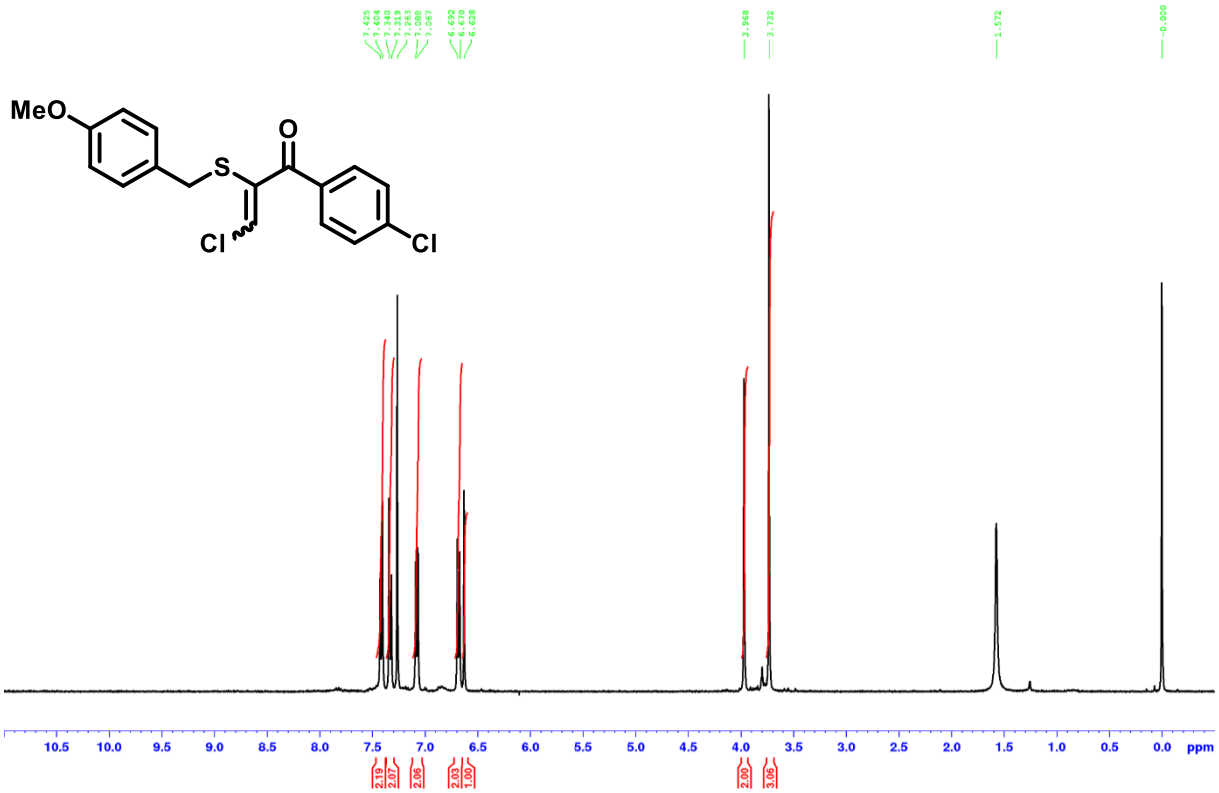


Figure S155: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4r** and **E-4r** after storage at room temperature for 40 months.

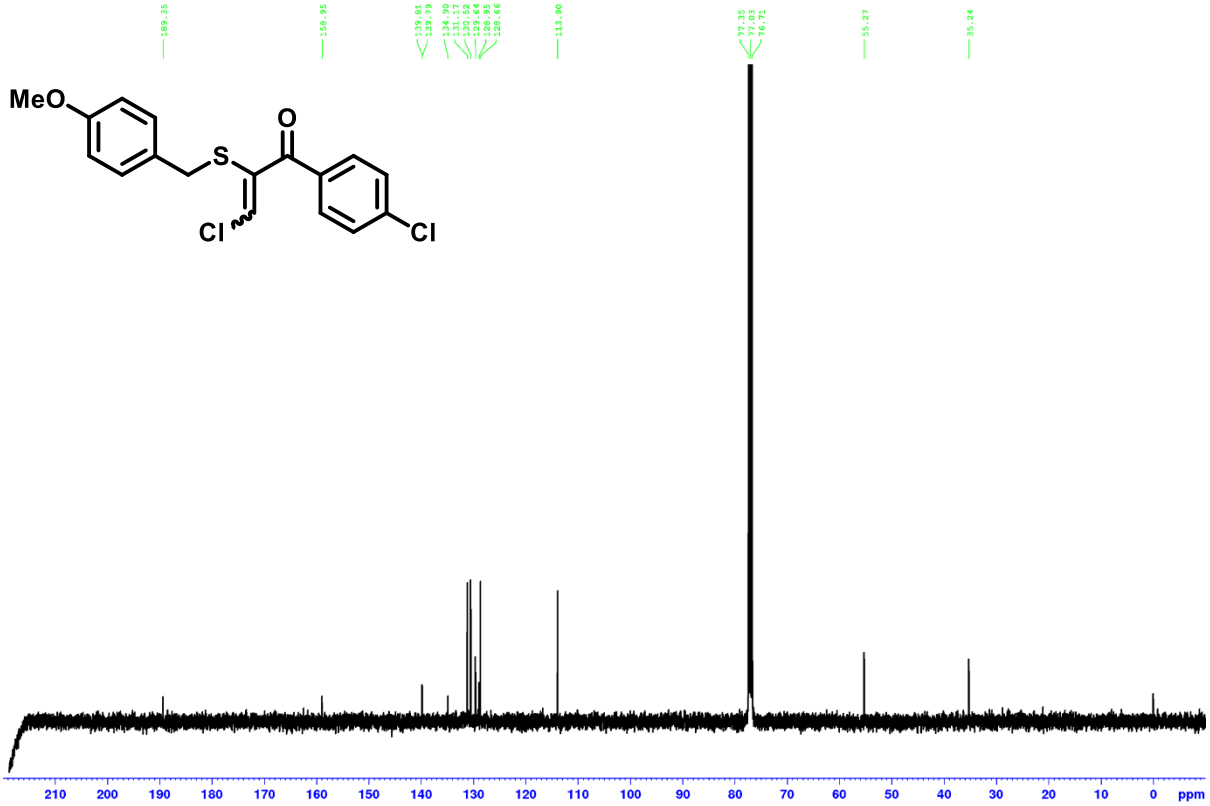


Figure S156: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4r** and **E-4r**.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)prop-2-en-1-one Z-4s and (*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)prop-2-en-1-one E-4s

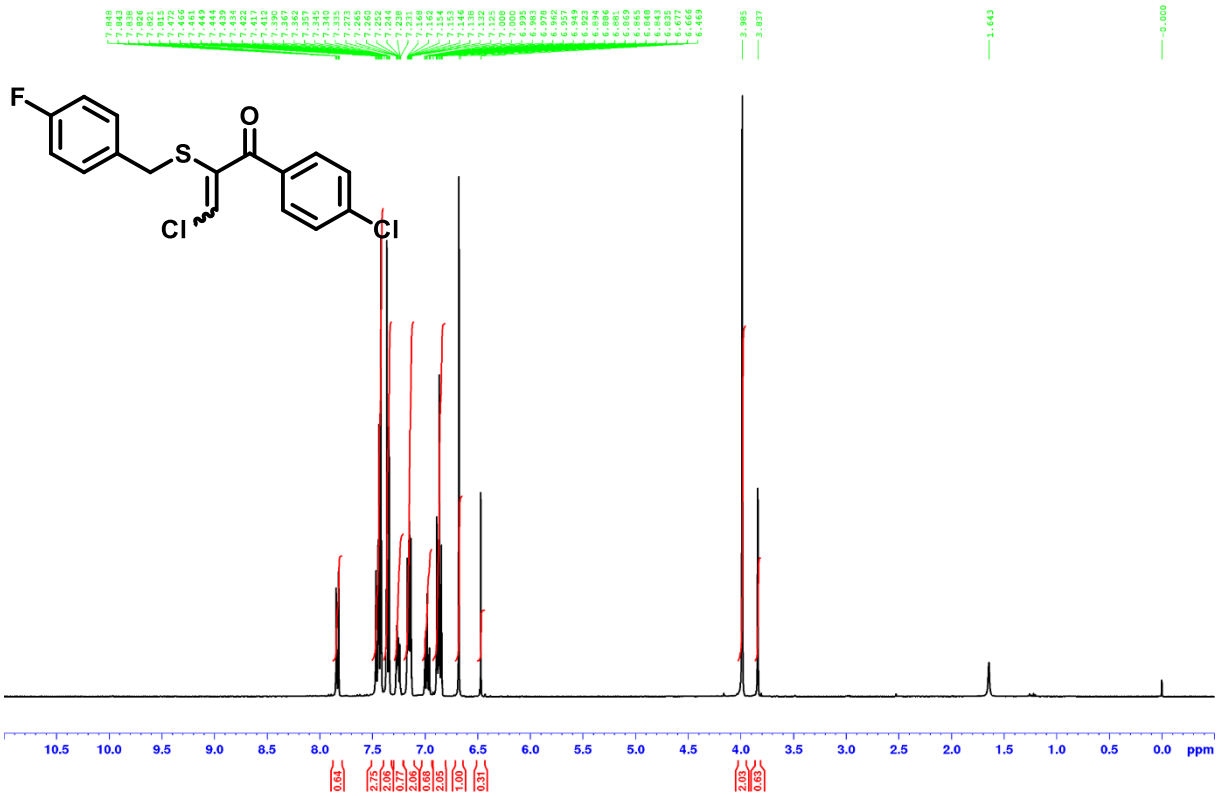


Figure S157: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4s** and **E-4s**.

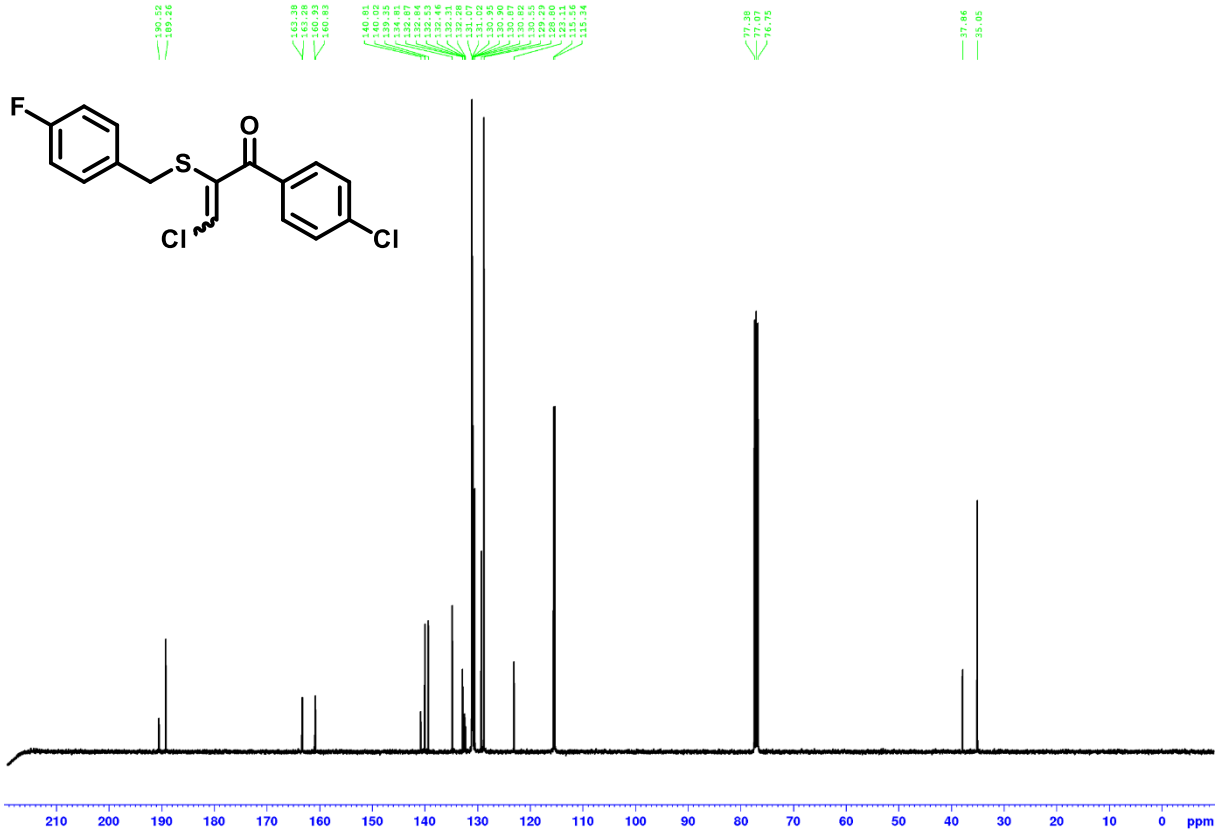


Figure S158: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4s** and **E-4s**.

(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one Z-4t

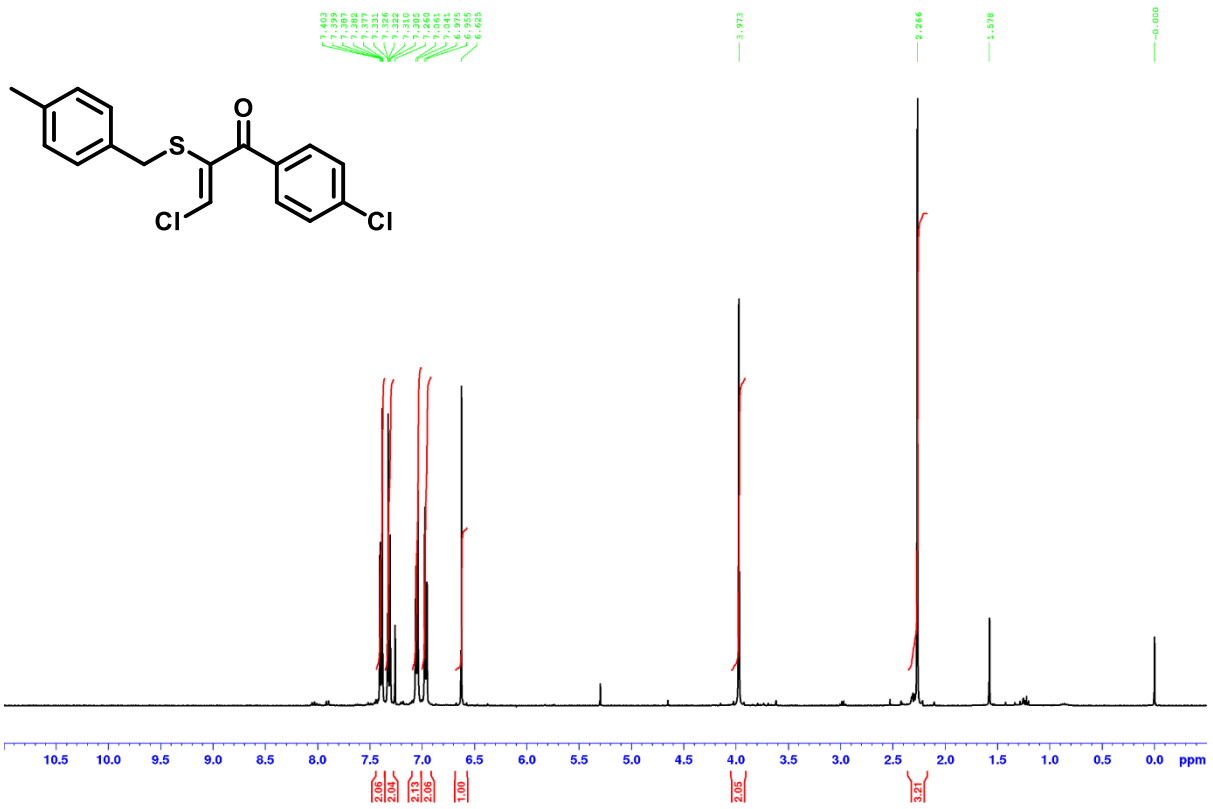


Figure S159: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4t**.

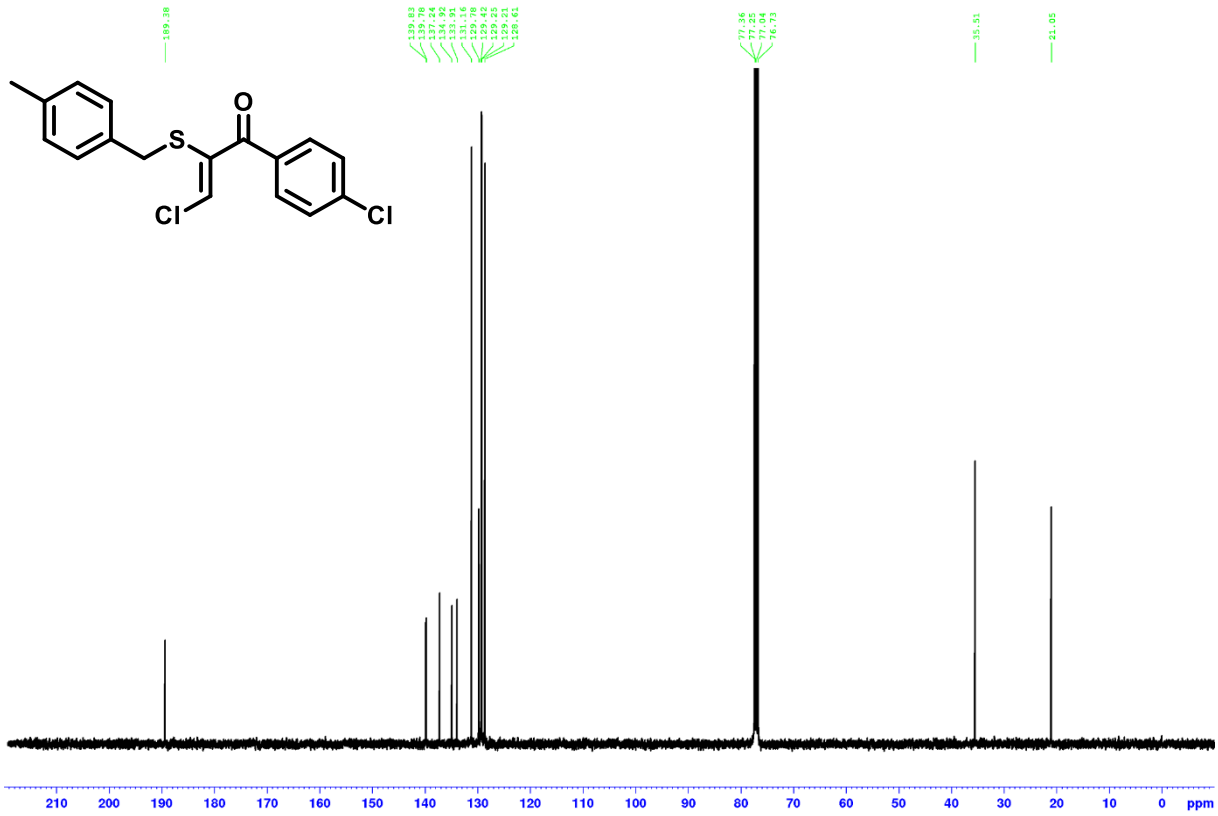


Figure S160: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4t**.

(*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one E-4t

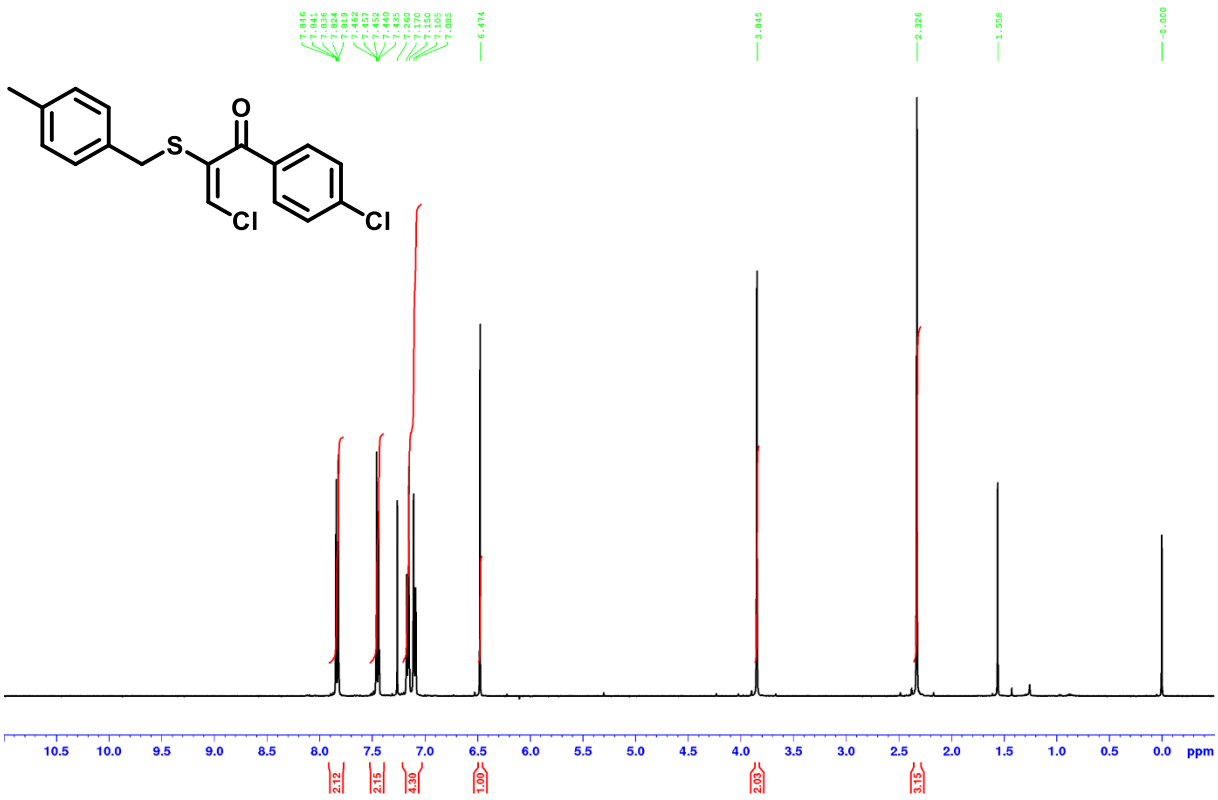


Figure S161: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4t**.

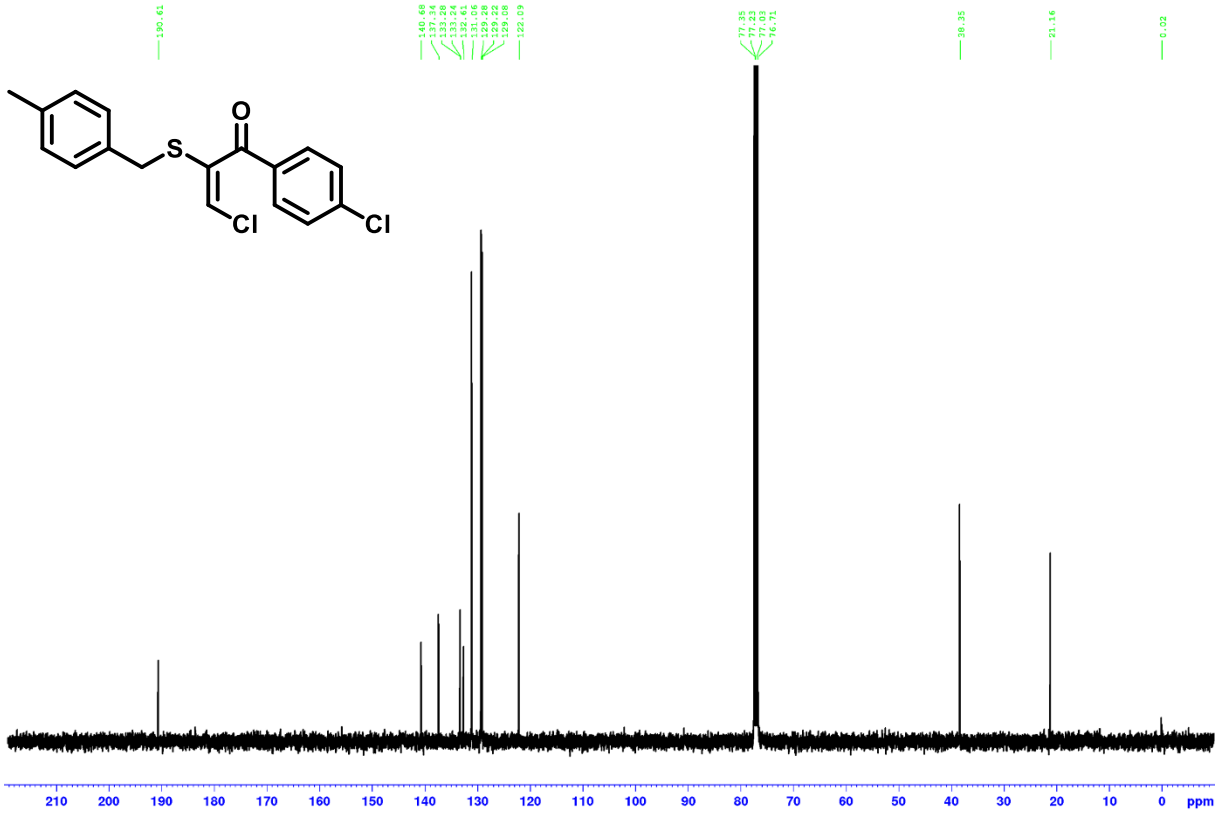


Figure S162: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4t**.

(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-(phenylthio)prop-2-en-1-one Z-4u and (*E*)-3-chloro-1-(4-fluorophenyl)-2-(phenylthio)prop-2-en-1-one E-4u

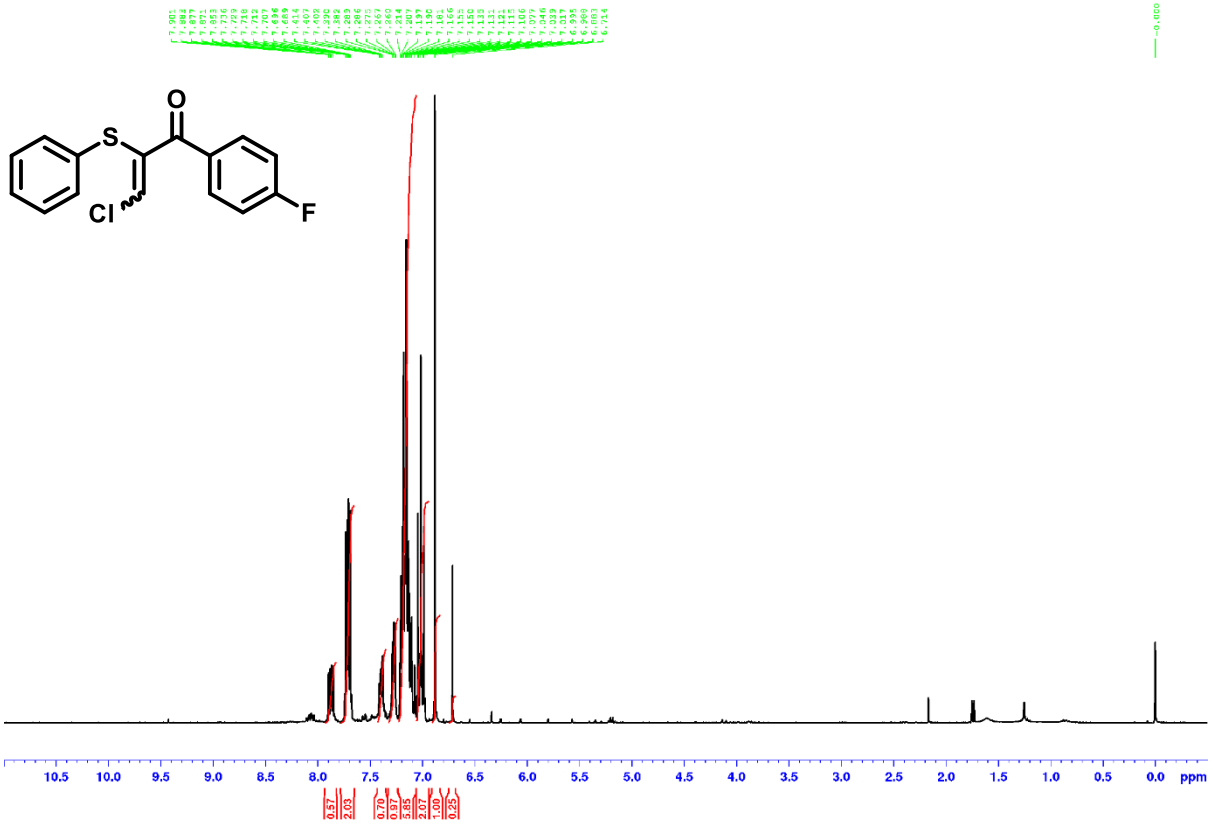


Figure S163: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4u** and **E-4u**.

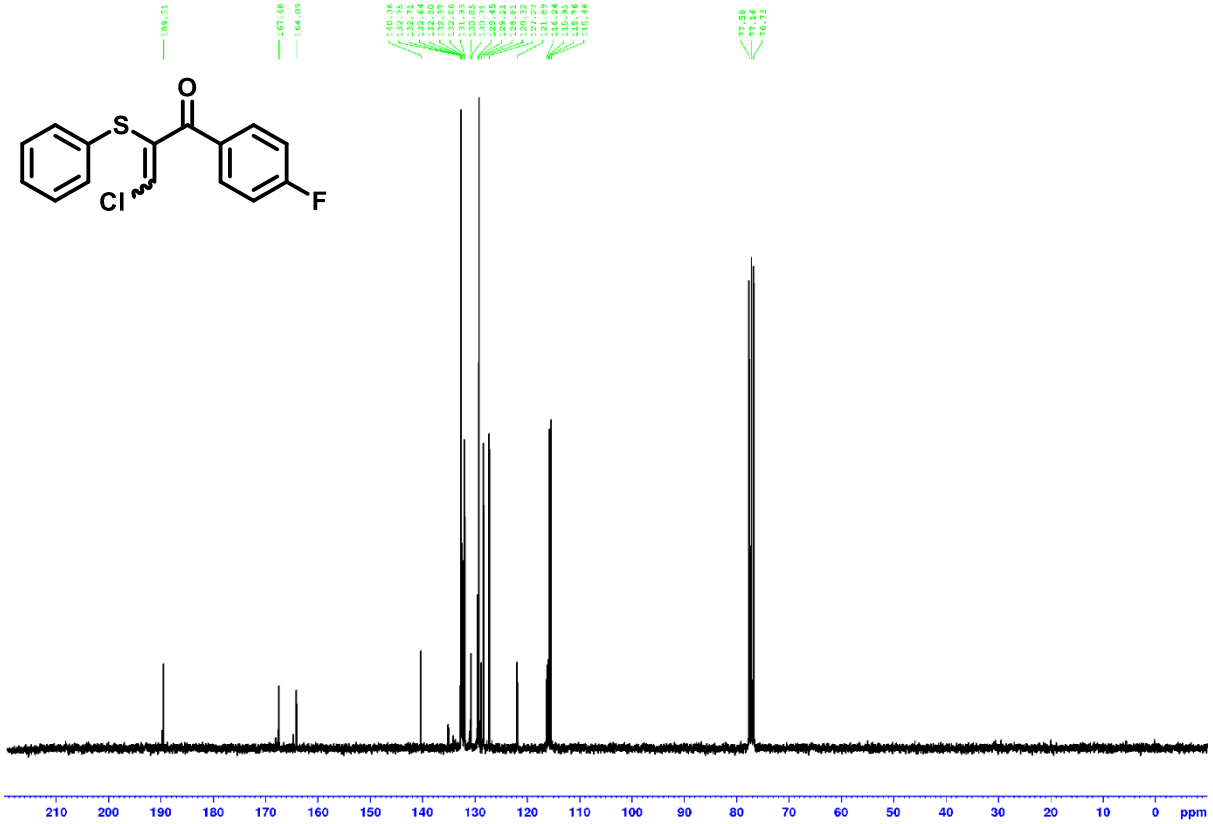


Figure S164: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4u** and **E-4u**.

(*Z*)-2-(Benzylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one Z-4v and (*E*)-2-(benzylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one E-4v

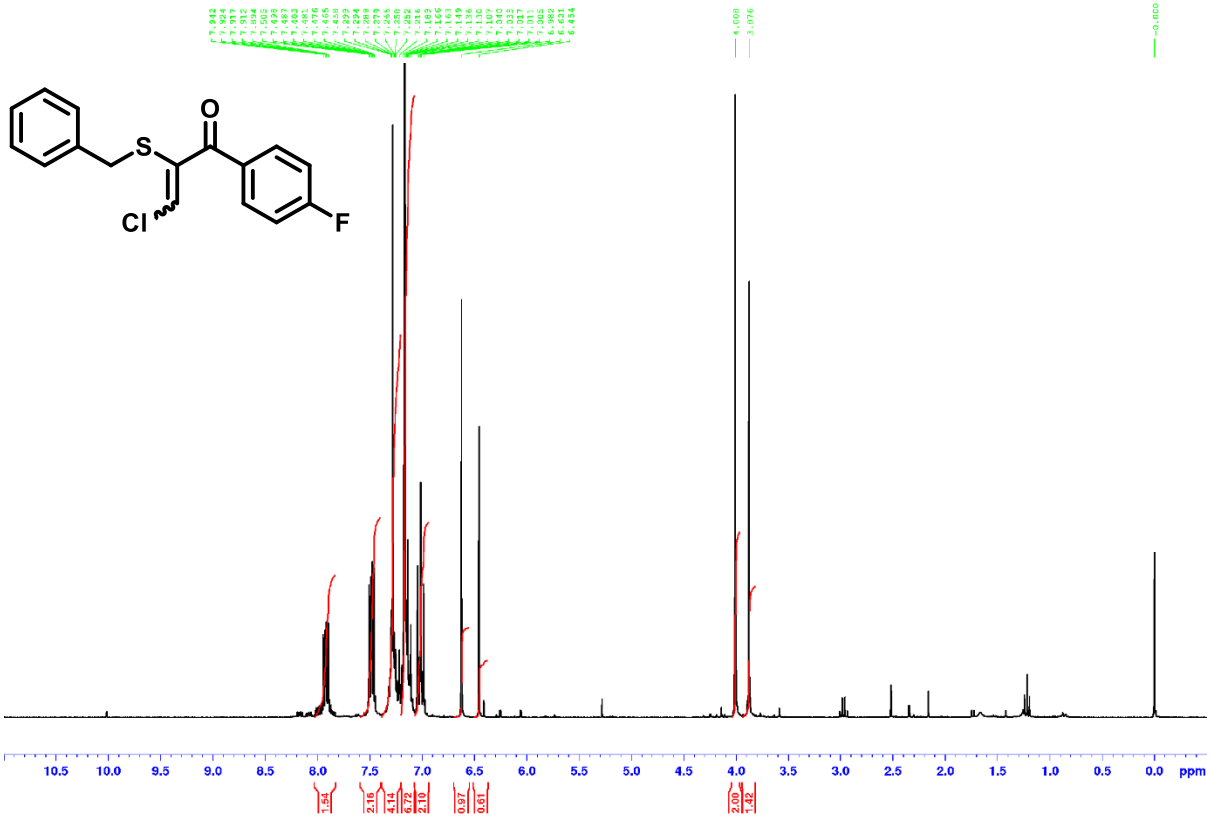


Figure S165: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4v** and **E-4v**.

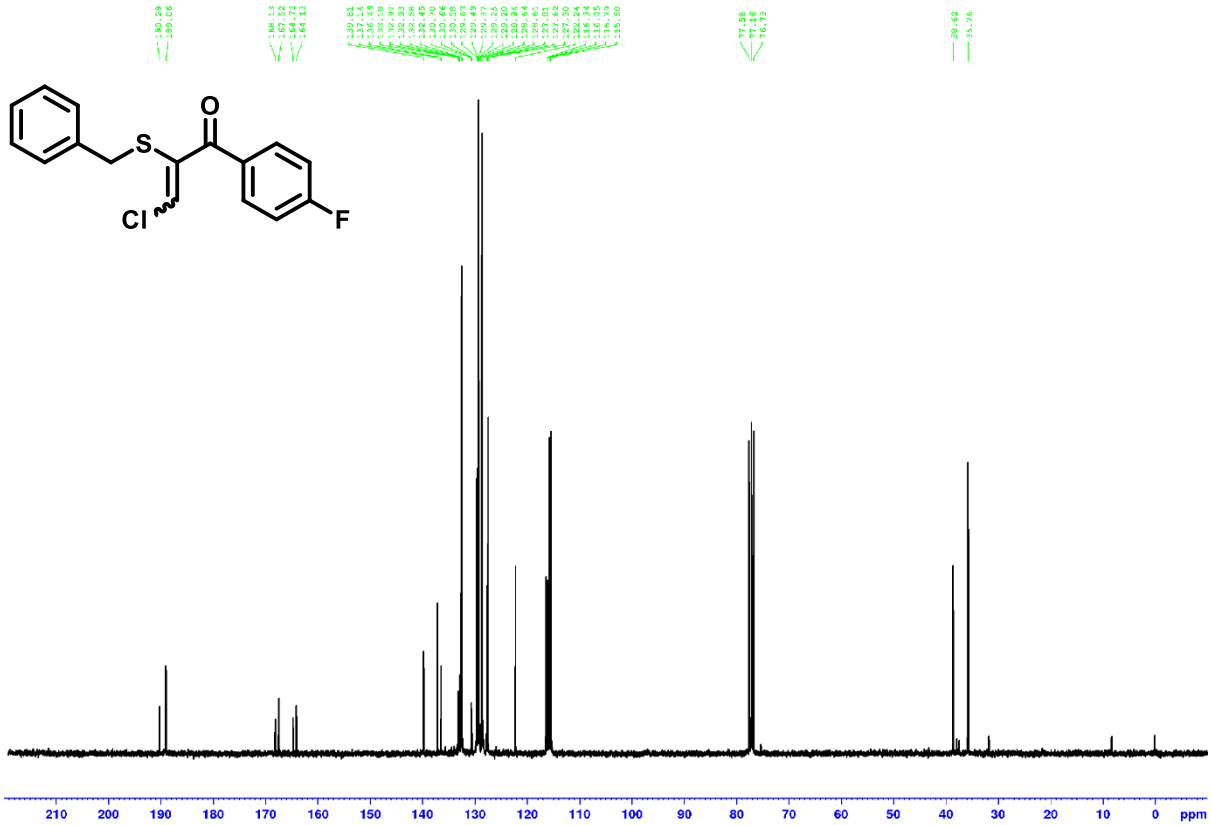


Figure S166: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4v** and **E-4v**.

(*Z*)-2-(*n*-Butylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one Z-4w and (*E*)-2-(*n*-butylthio)-3-chloro-1-(4-fluorophenyl)prop-2-en-1-one E-4w

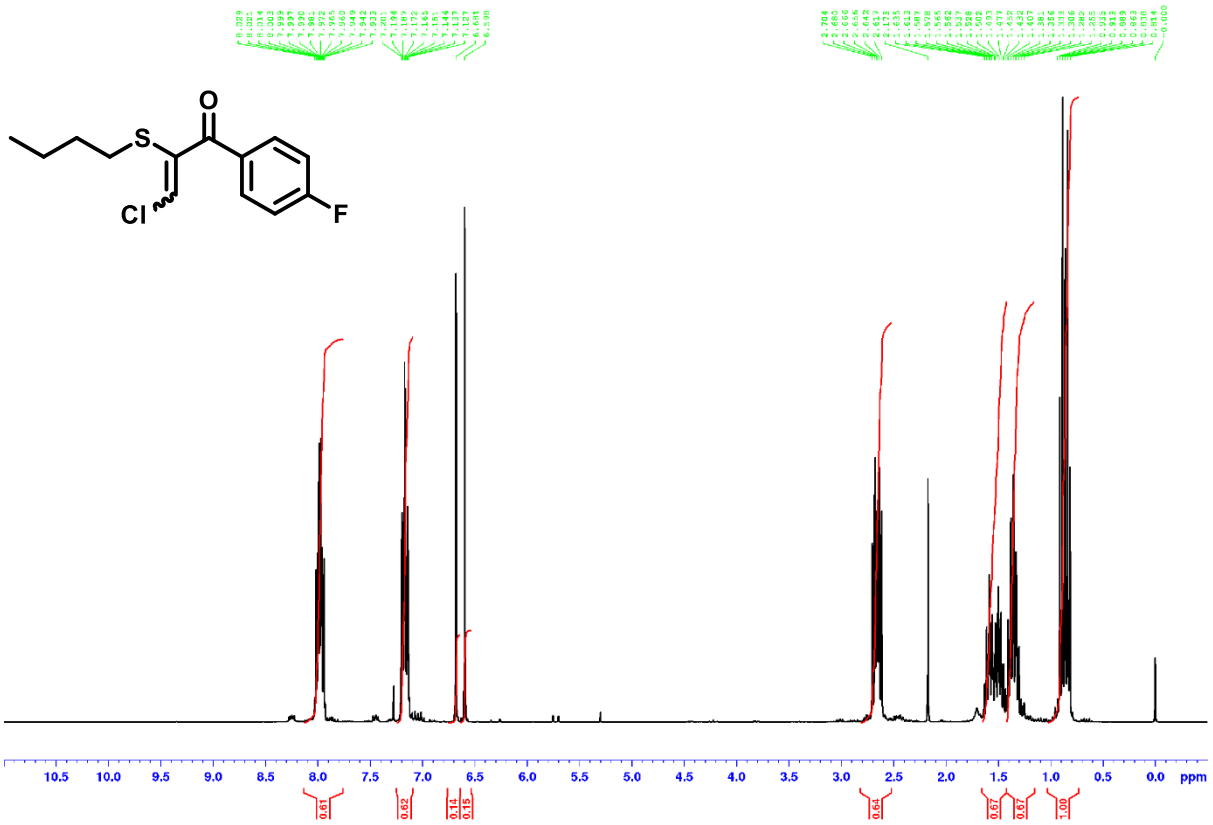


Figure S167: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4w** and **E-4w**.

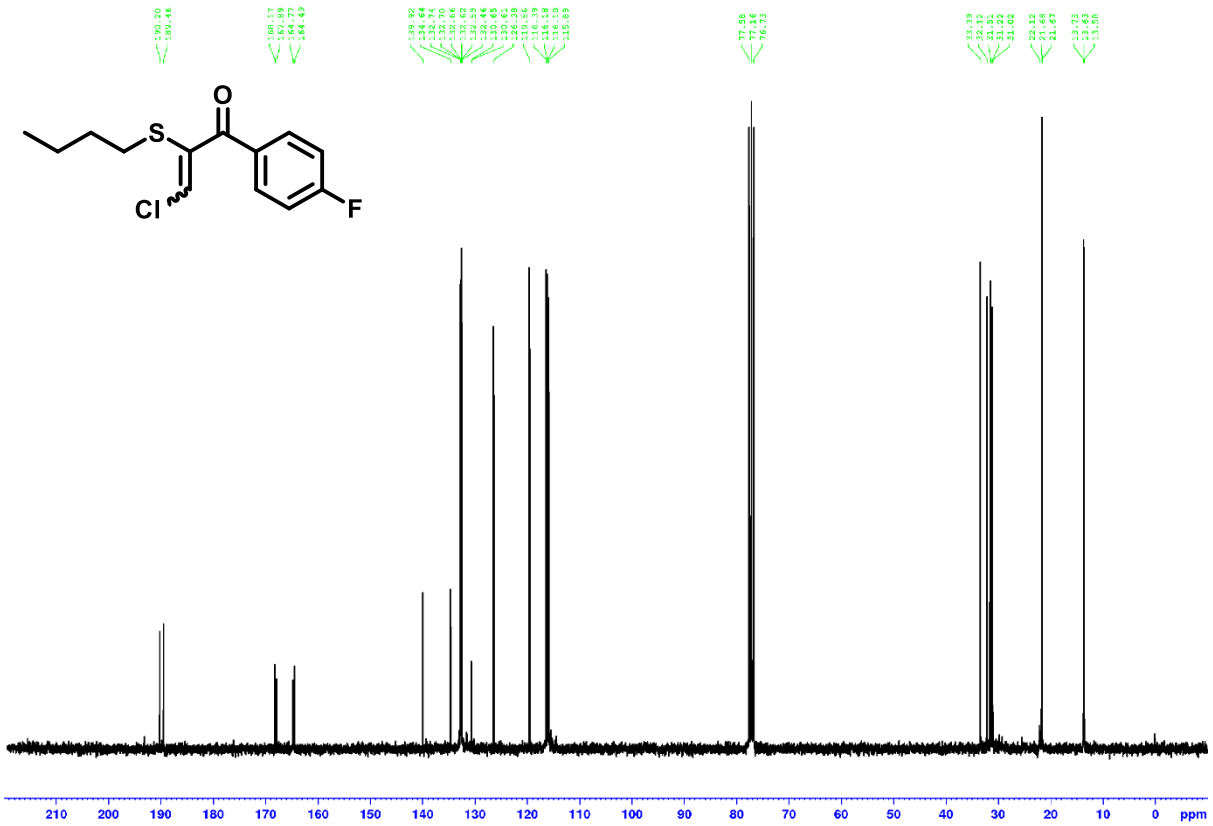


Figure S168: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4w** and **E-4w**.

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one and Z-4x (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one E-4x

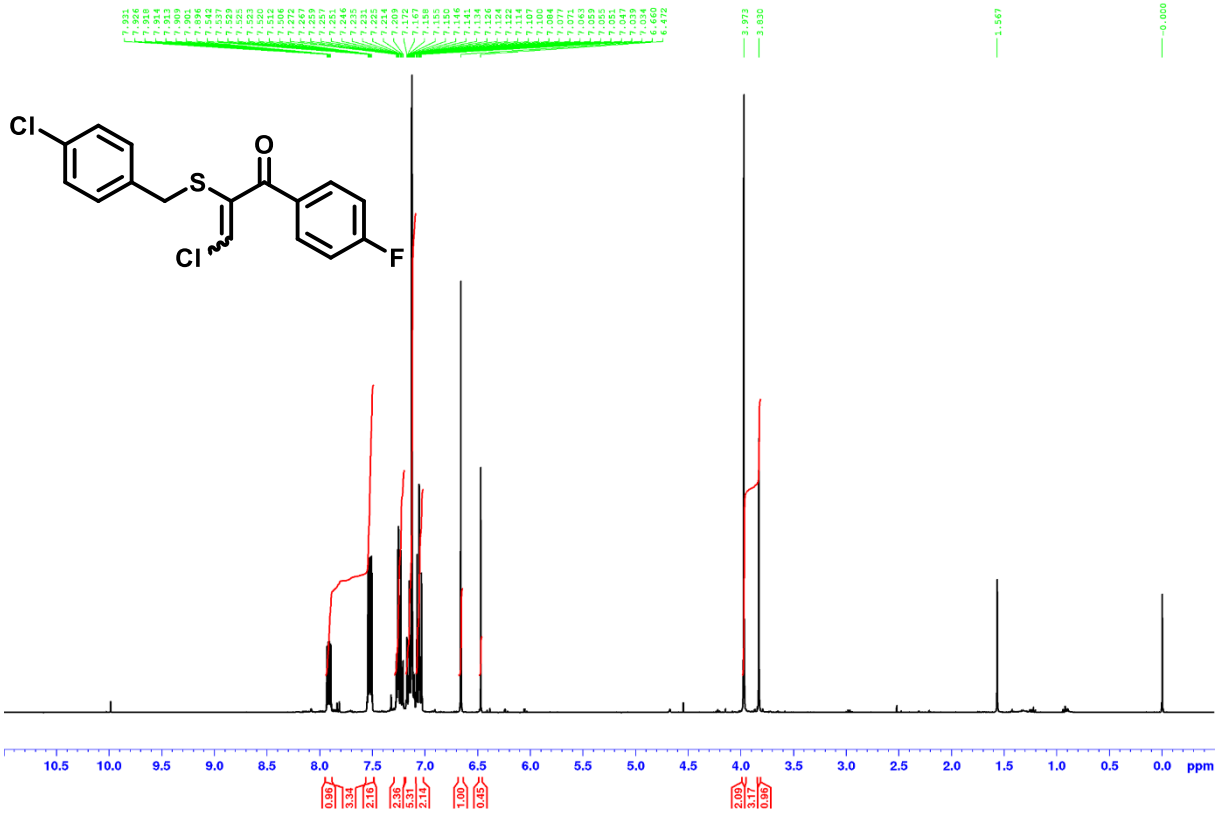


Figure S169: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4x** and **E-4x**.

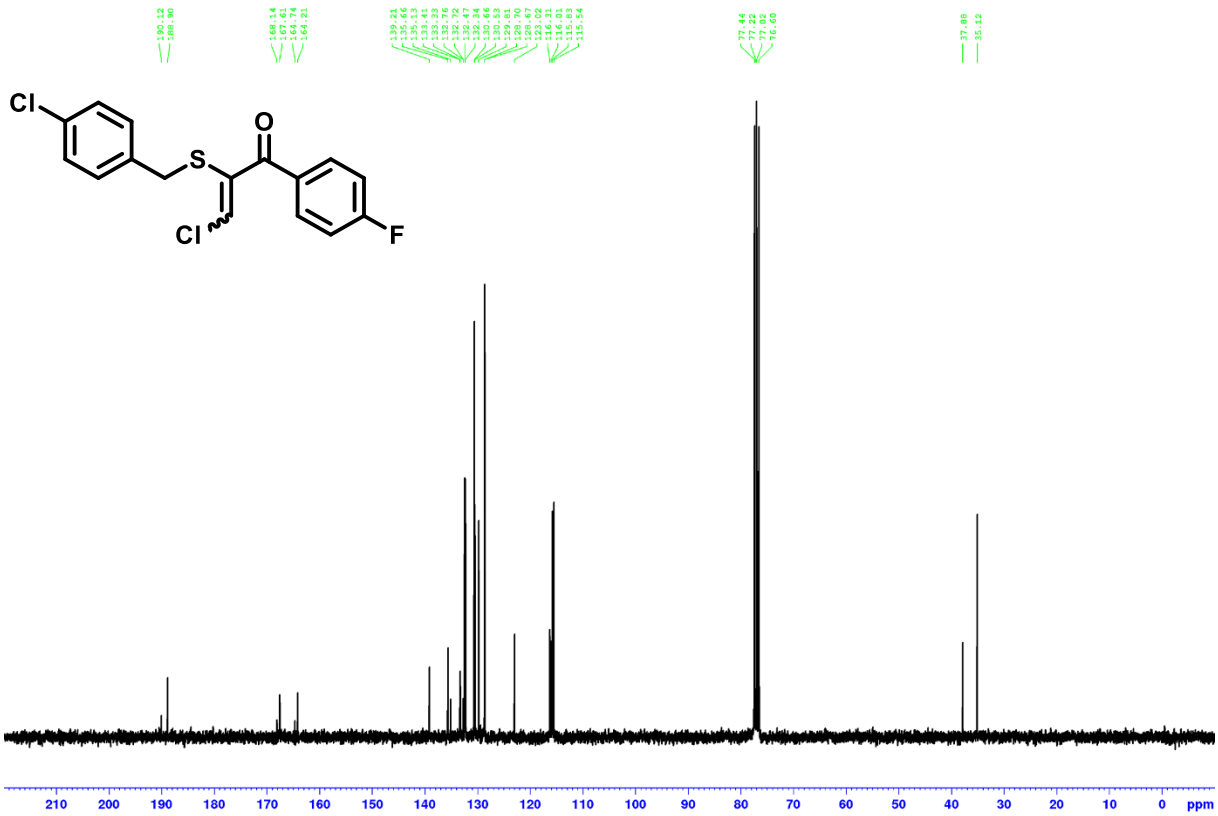


Figure S170: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4x** and **E-4x**.

(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one Z-4y and (*E*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methoxybenzyl)thio)prop-2-en-1-one E-4y

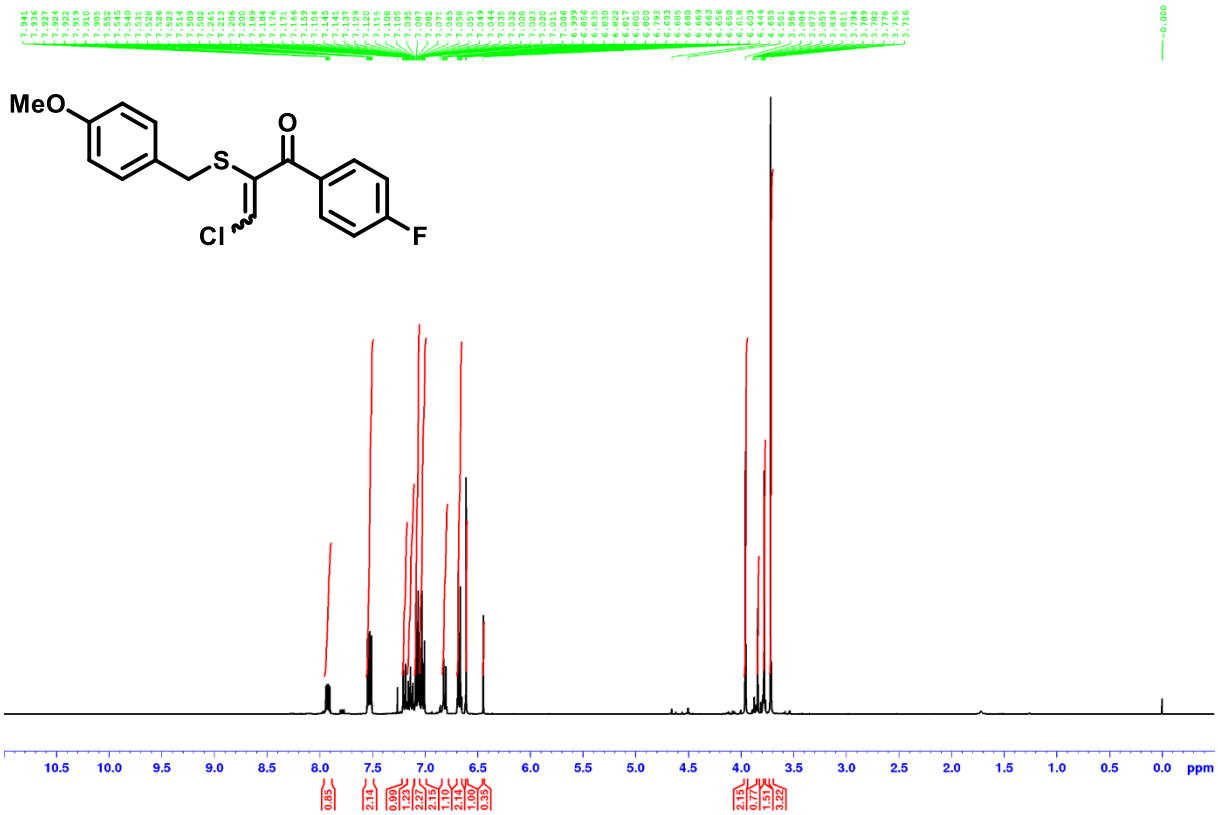


Figure S171: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4y** and **E-4y**.

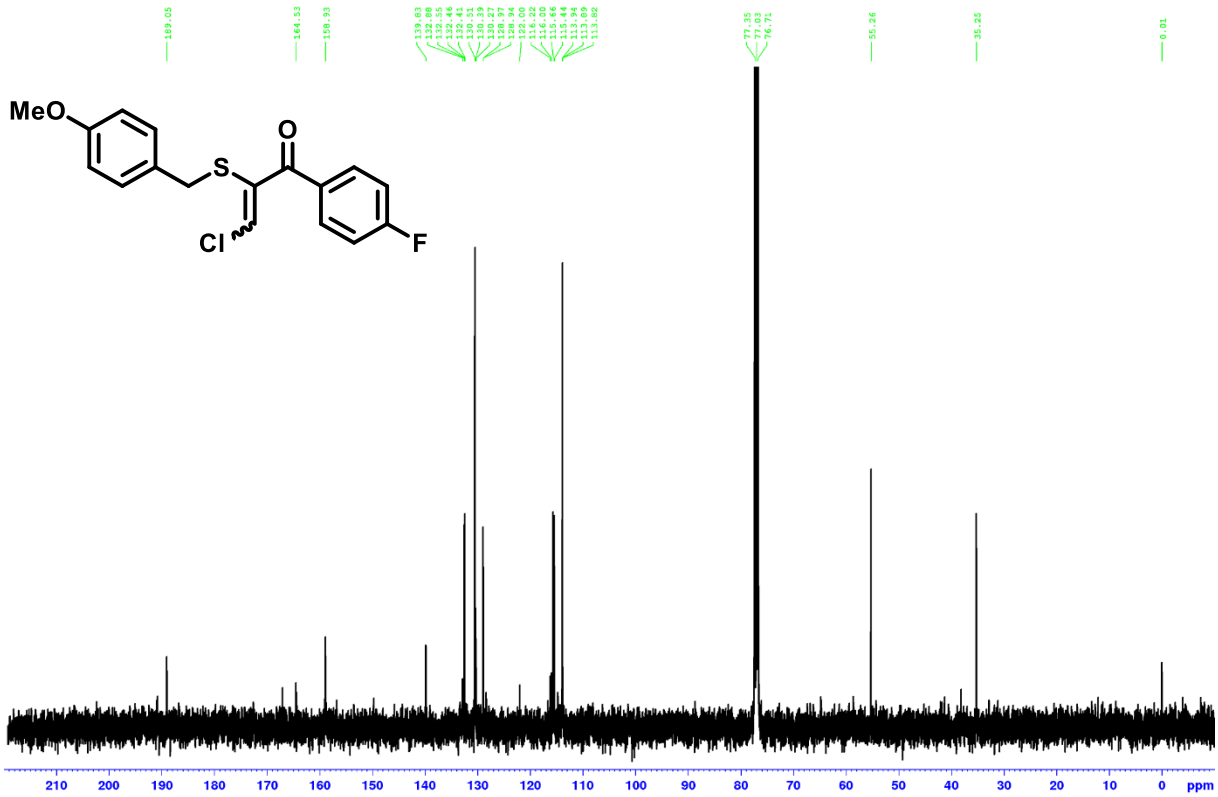


Figure S172: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4y** and **E-4y**.

(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one Z-4z and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(4-fluorophenyl)prop-2-en-1-one E-4z

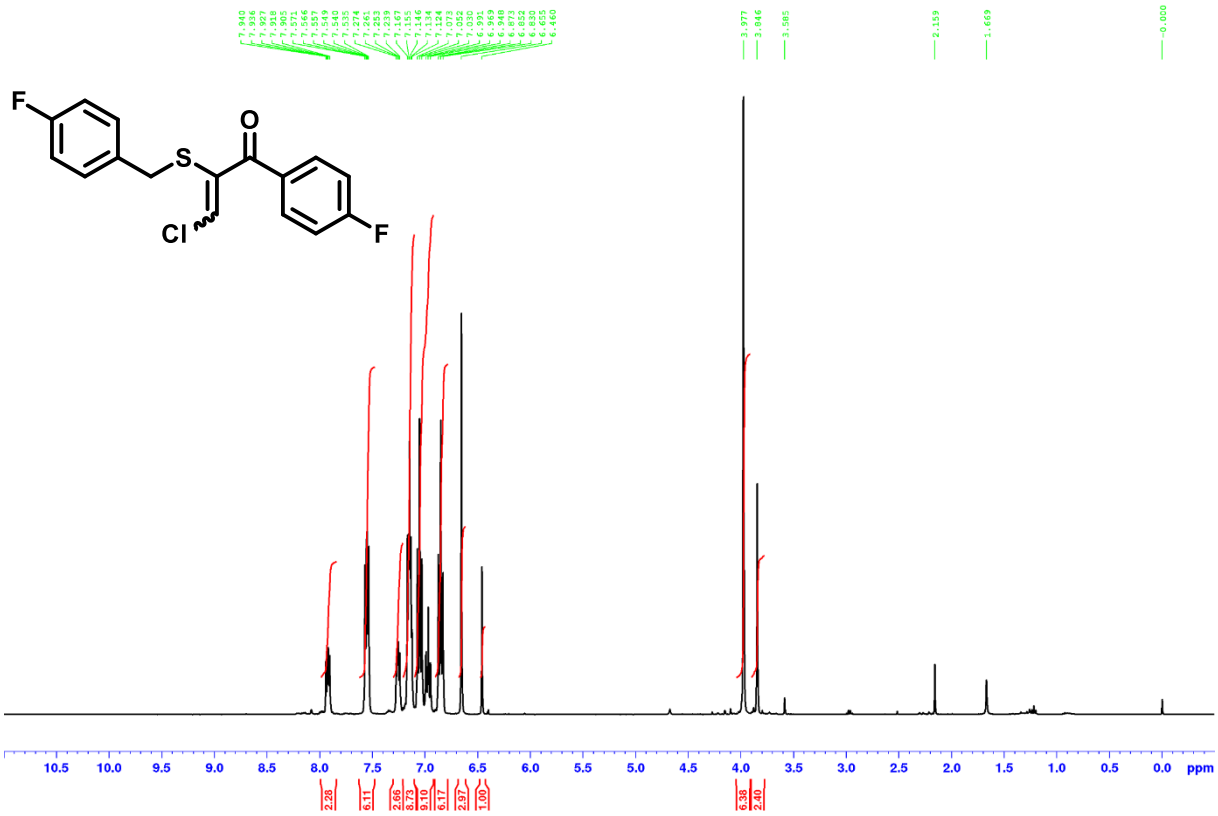


Figure S173: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4z** and **E-4z**.

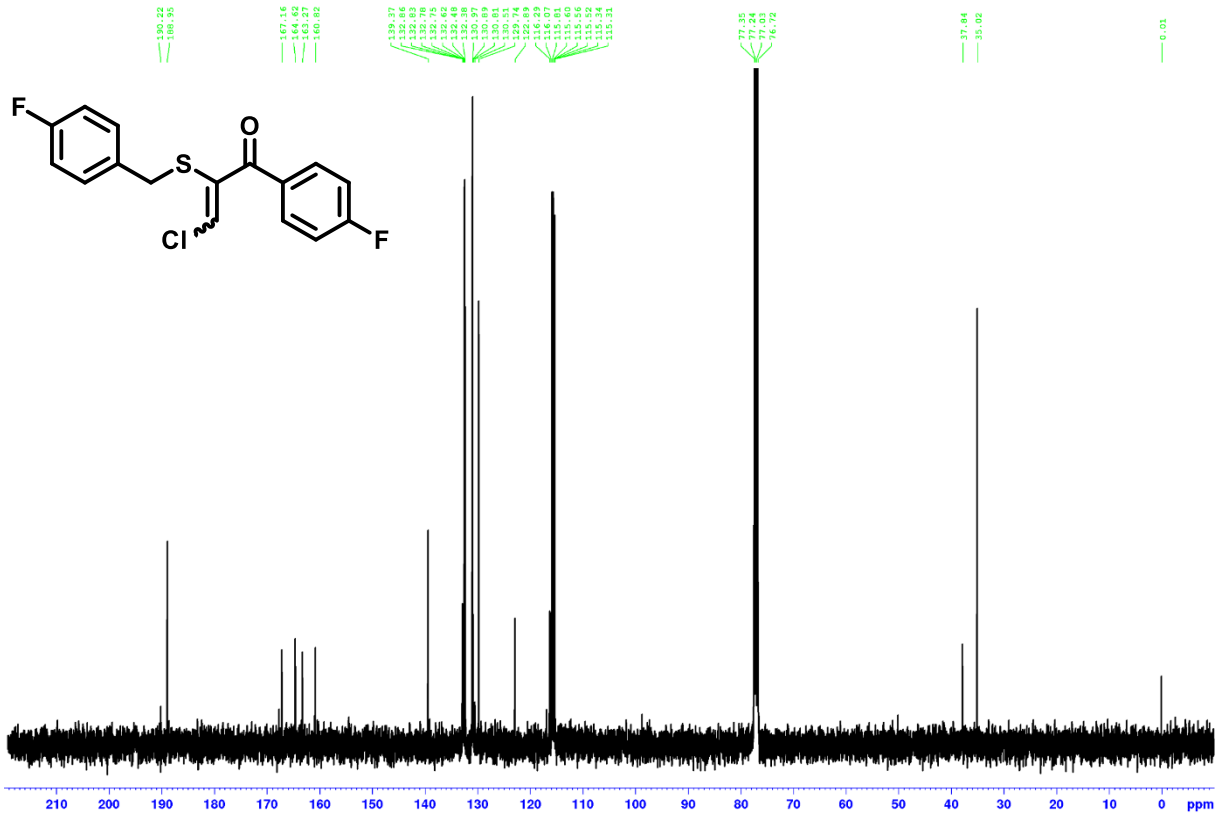


Figure S174: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4z** and **E-4z**.

(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one Z-4aa

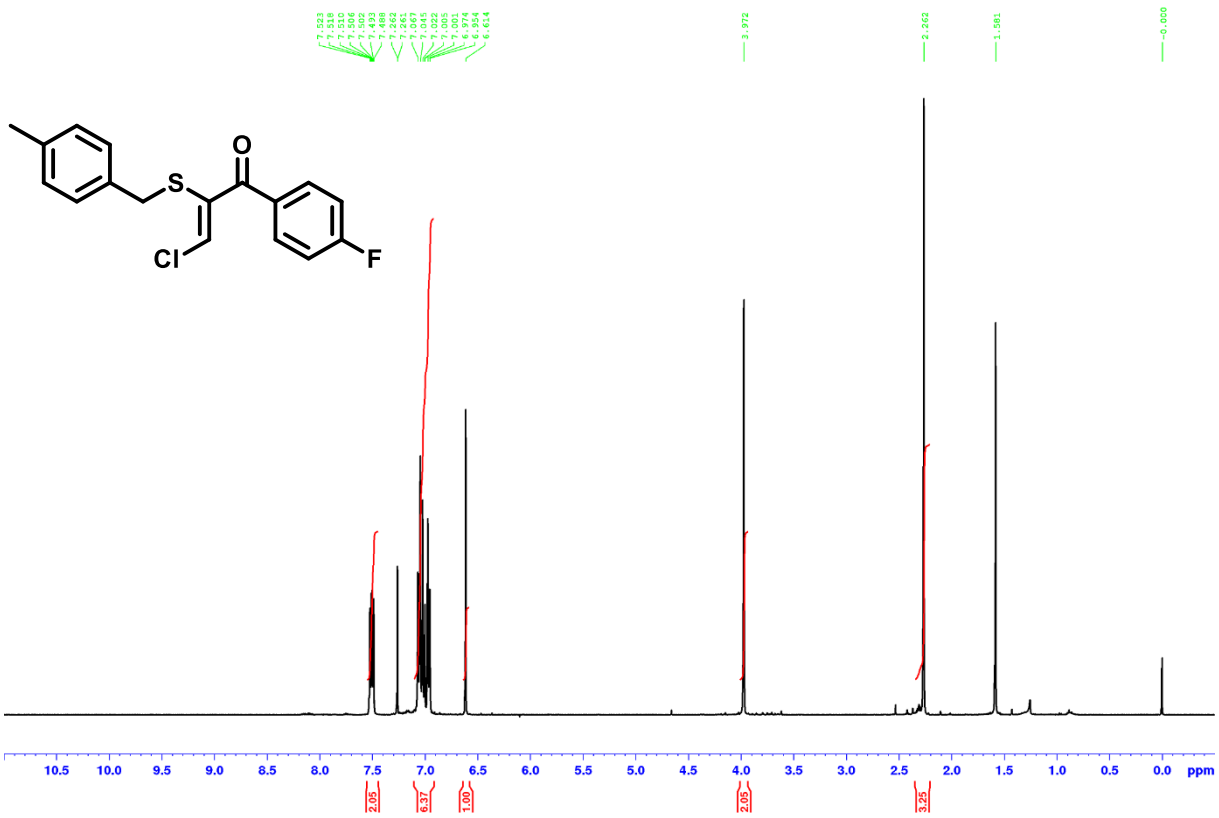


Figure S175: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4aa**.

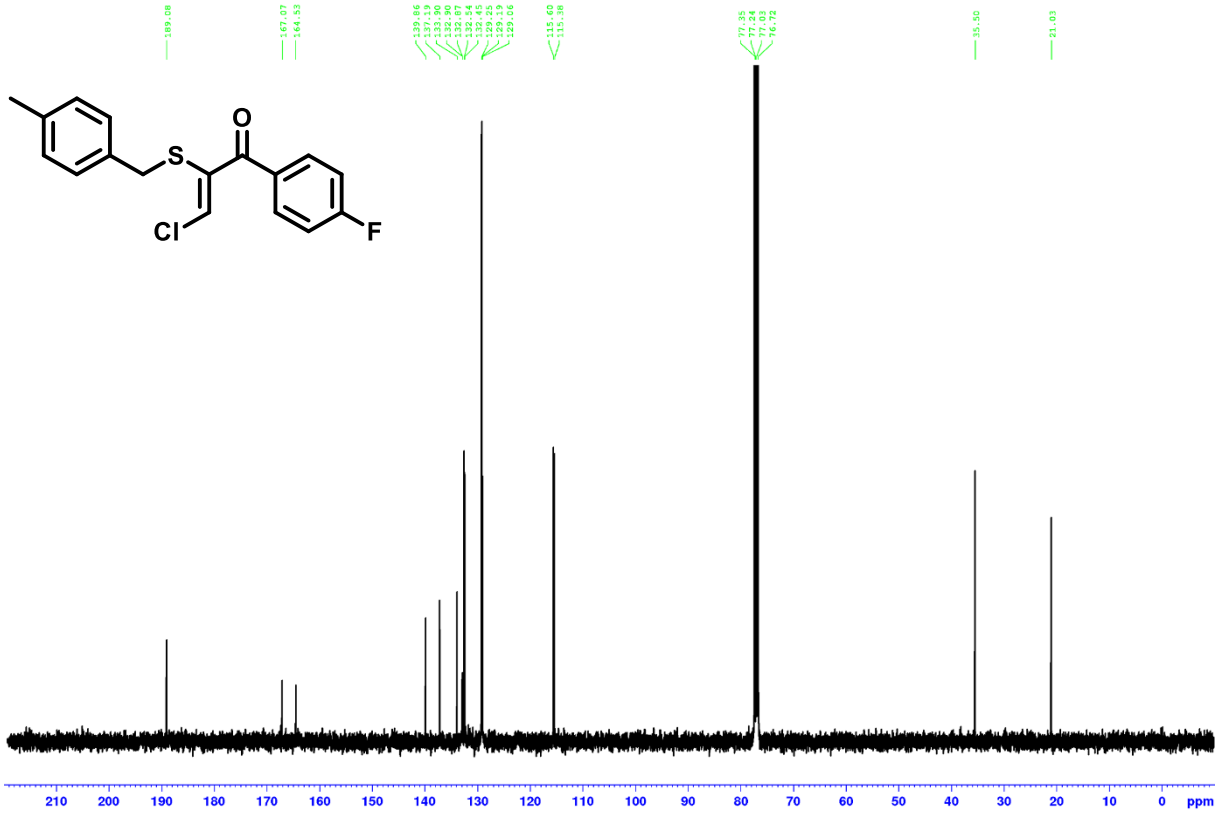


Figure S176: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4aa**.

(*E*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one E-4aa

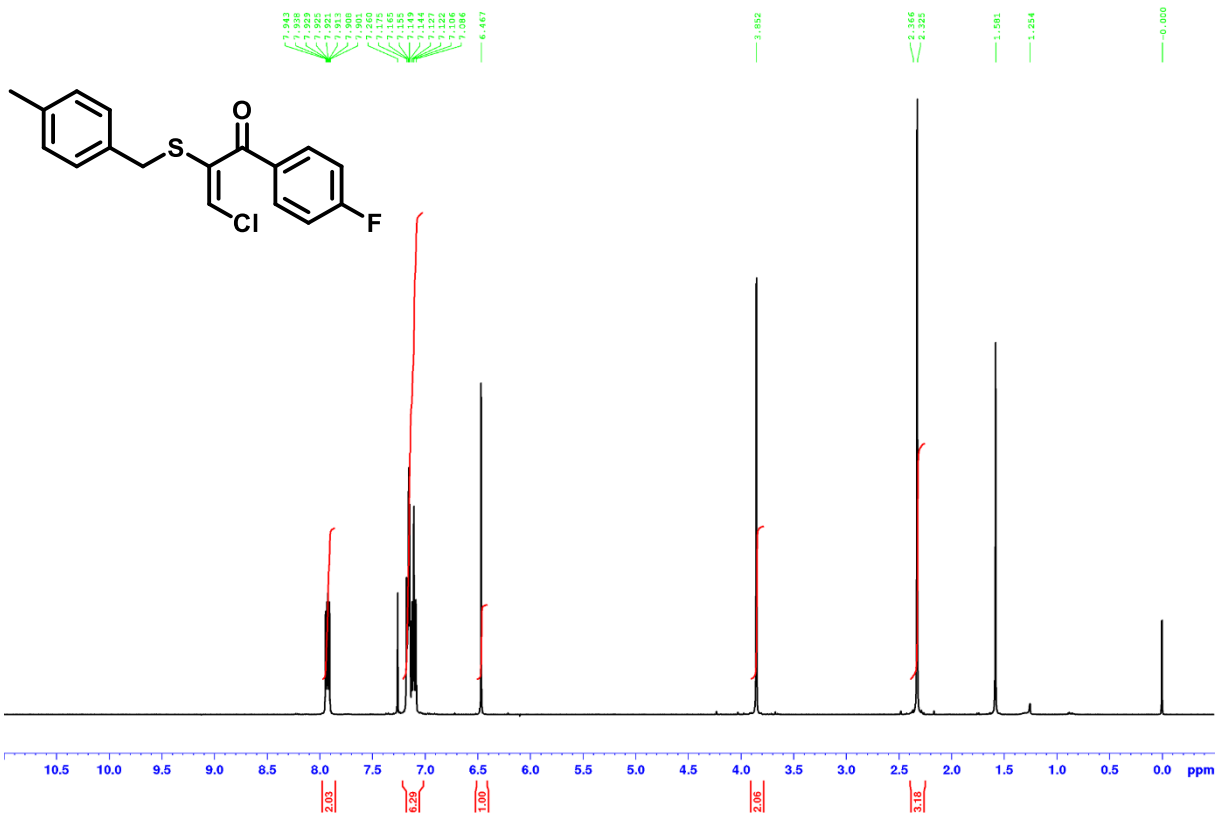


Figure S177: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4aa**.

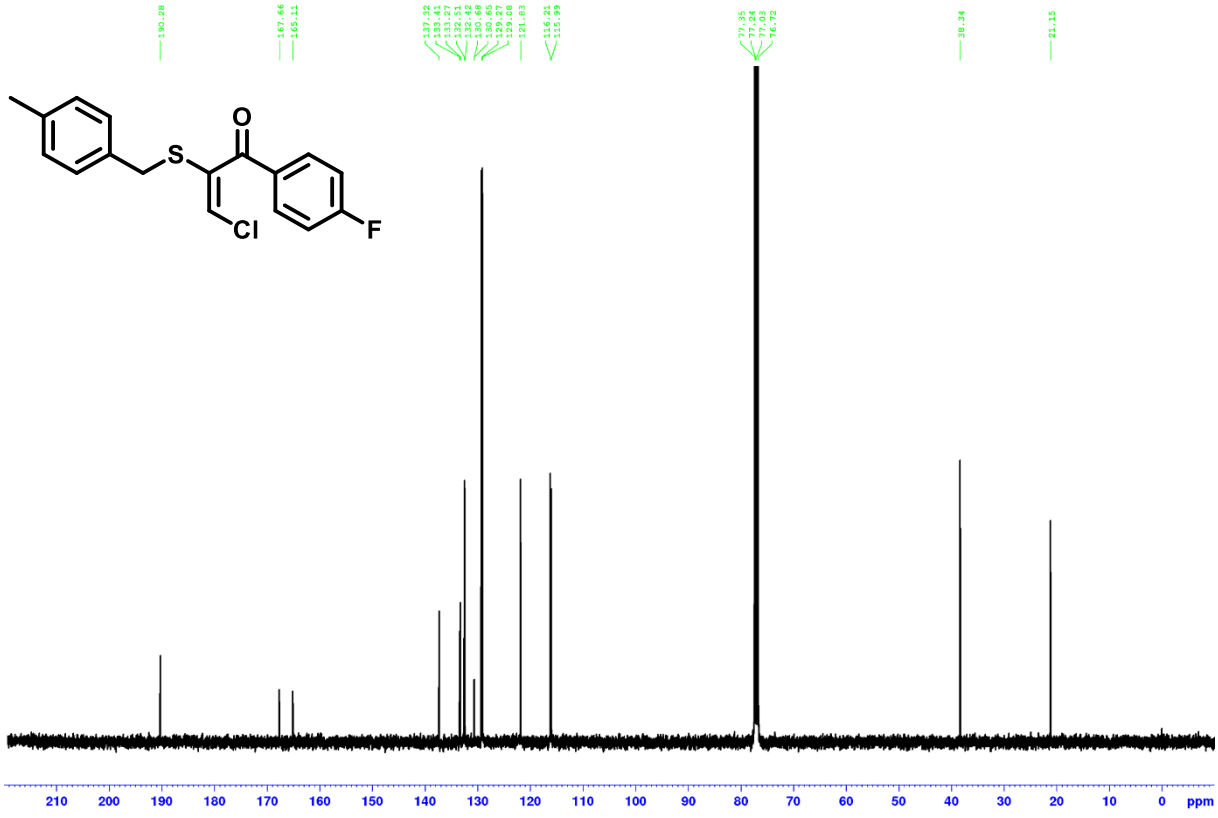


Figure S178: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4aa**.

1.12.4 α-Sulfenyl-β-Chlorobutenones:

(*Z*)-2-(Benzylthio)-3-chloro-1-phenylbut-2-en-1-one Z-4bb and (*E*)-2-(Benzylthio)-3-chloro-1-phenylbut-2-en-1-one E-4bb

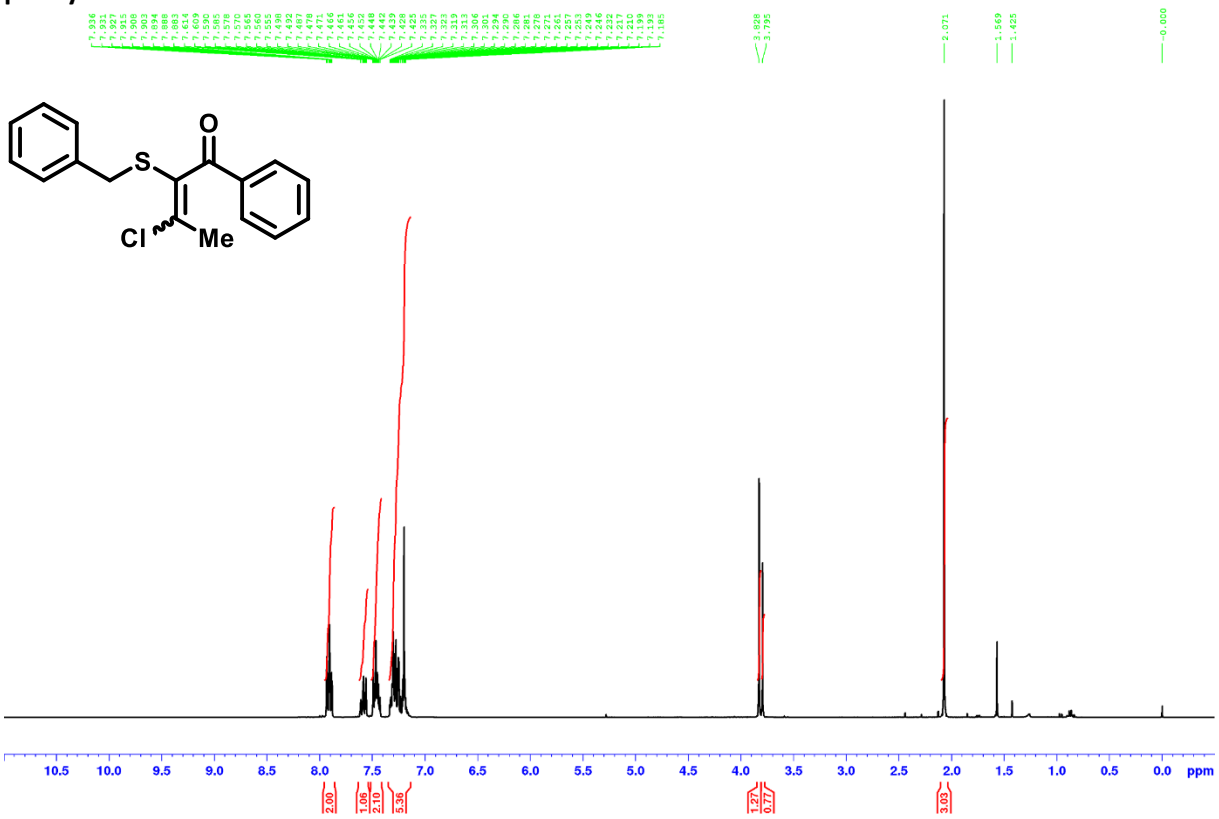


Figure S179: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-4bb** and **E-4bb**.

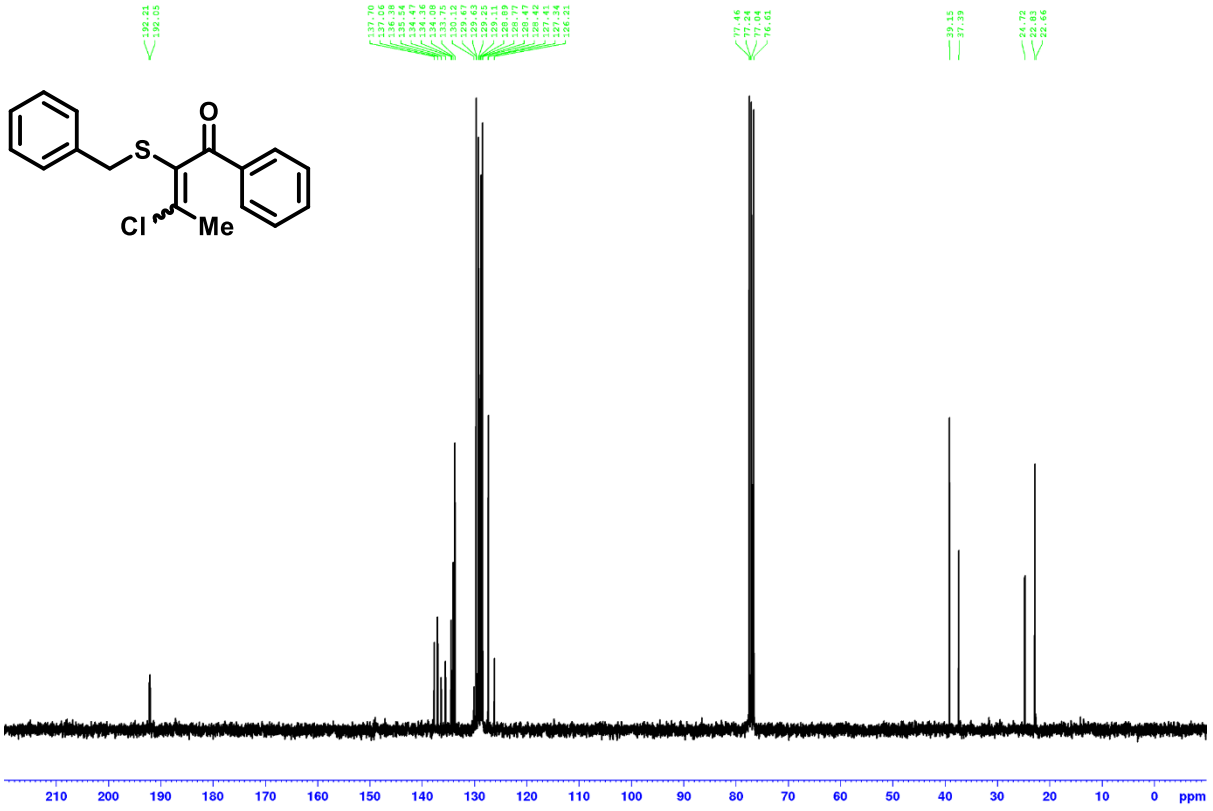


Figure S180: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4bb** and **E-4bb**.

2-(Benzylthio)-1-phenylbut-2-en-1-one S39

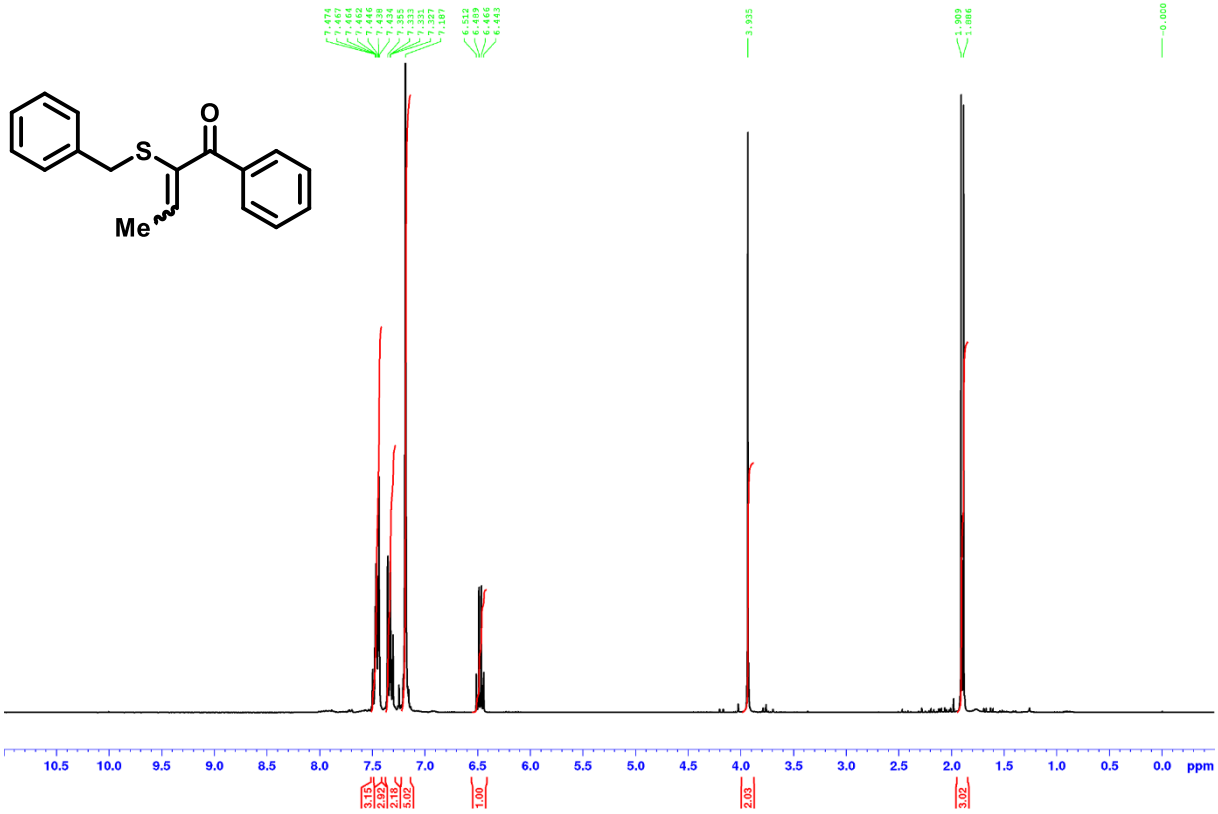


Figure S181: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S39**.

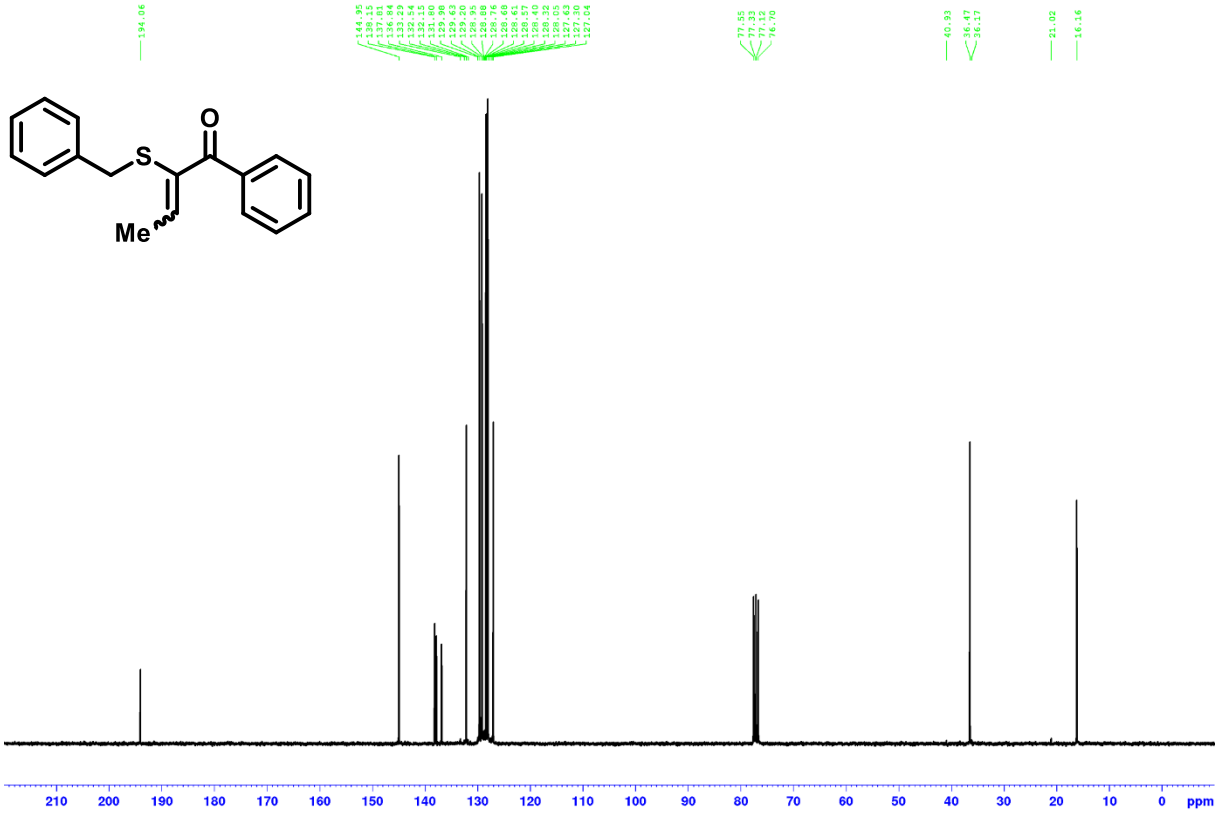


Figure S182: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **39**.

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylbut-2-en-1-one Z-4cc and (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylbut-2-en-1-one E-4cc

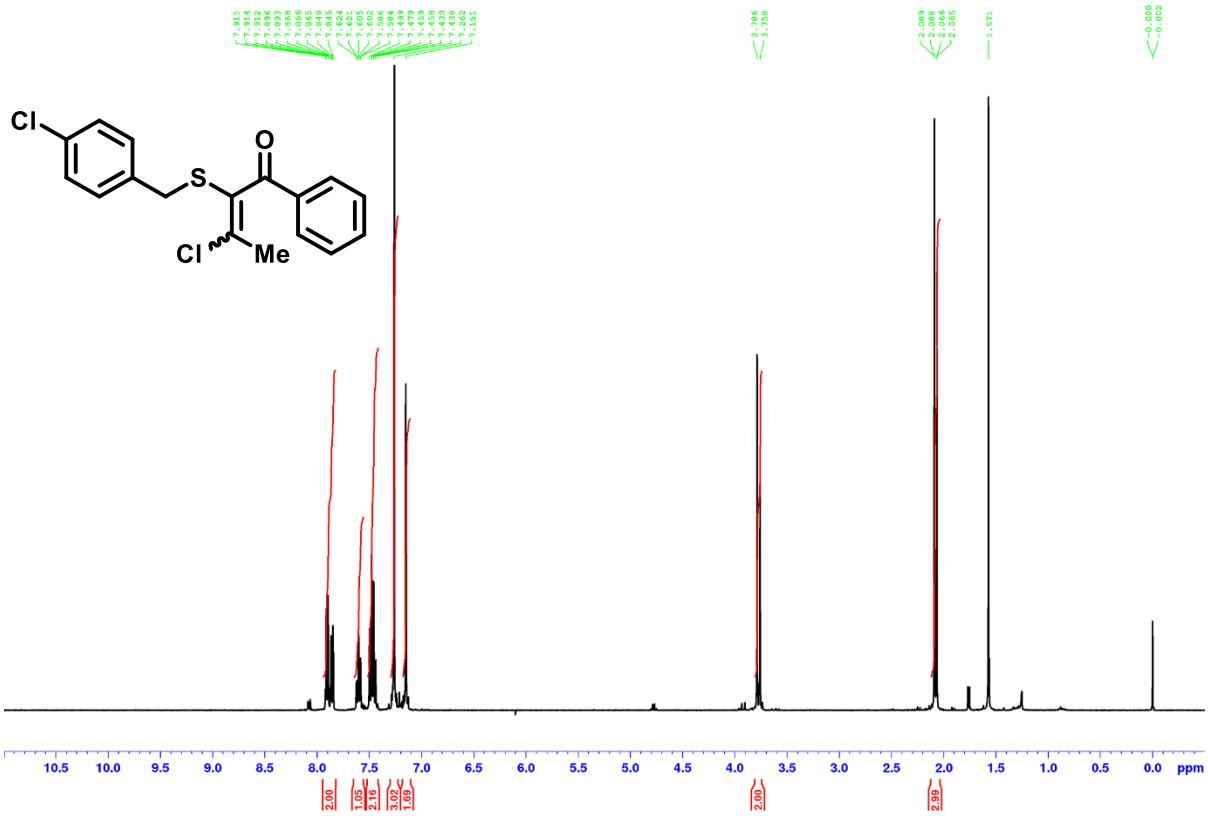


Figure S183: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4cc** and **E-4cc**.

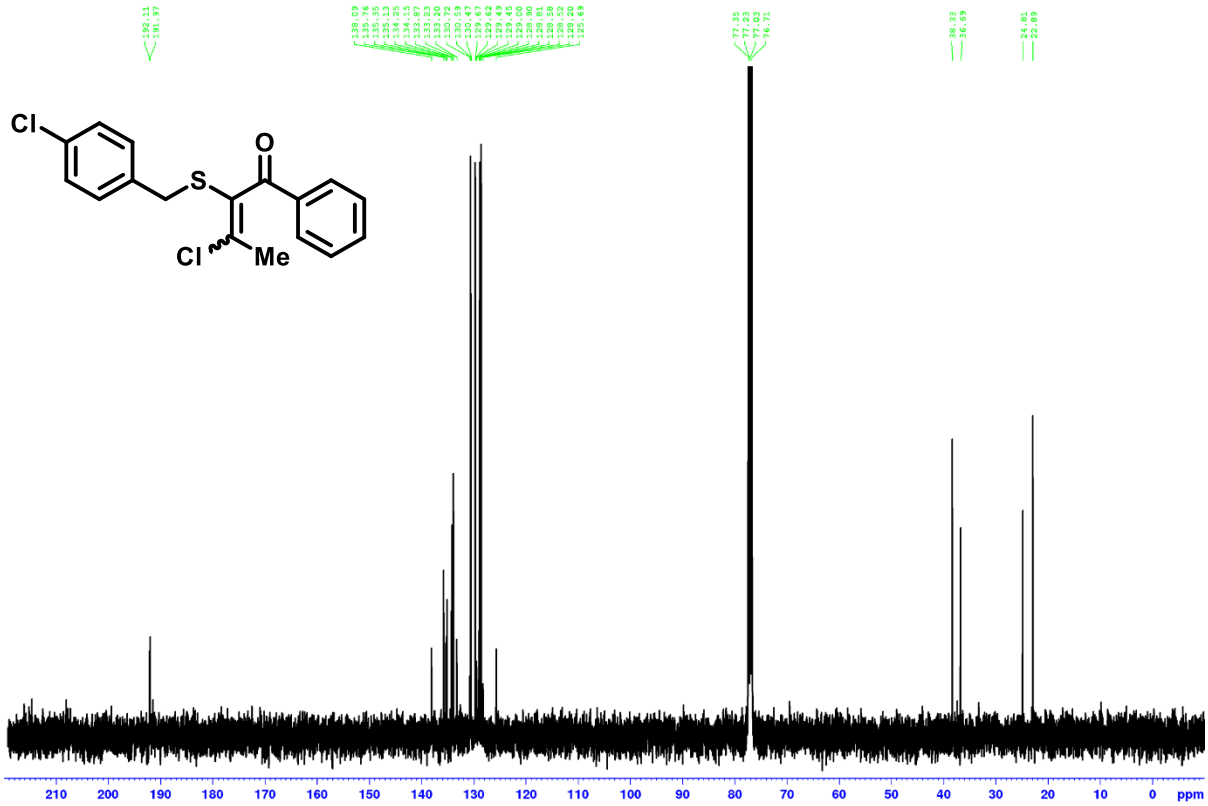


Figure S184: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4cc** and **E-4cc**.

(*E*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylbut-2-en-1-one E-4dd

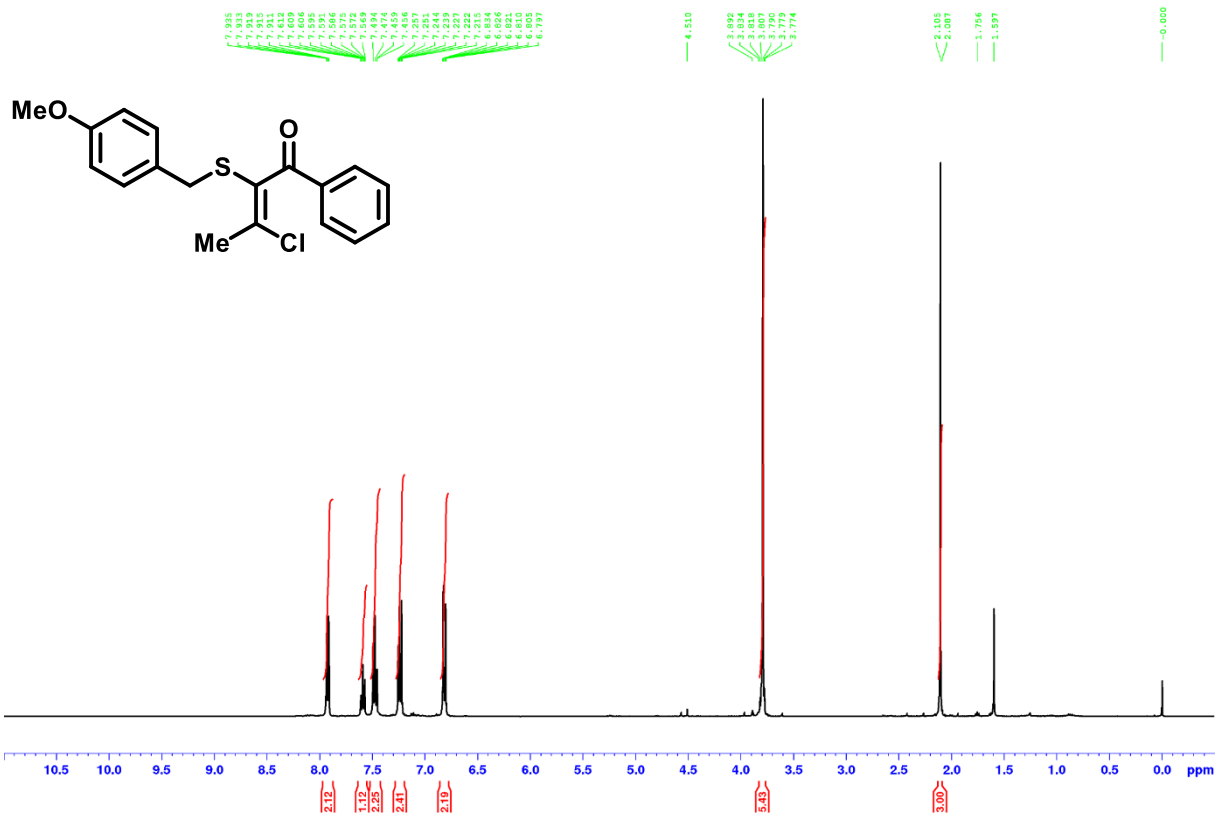


Figure S185: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **E-4dd**.

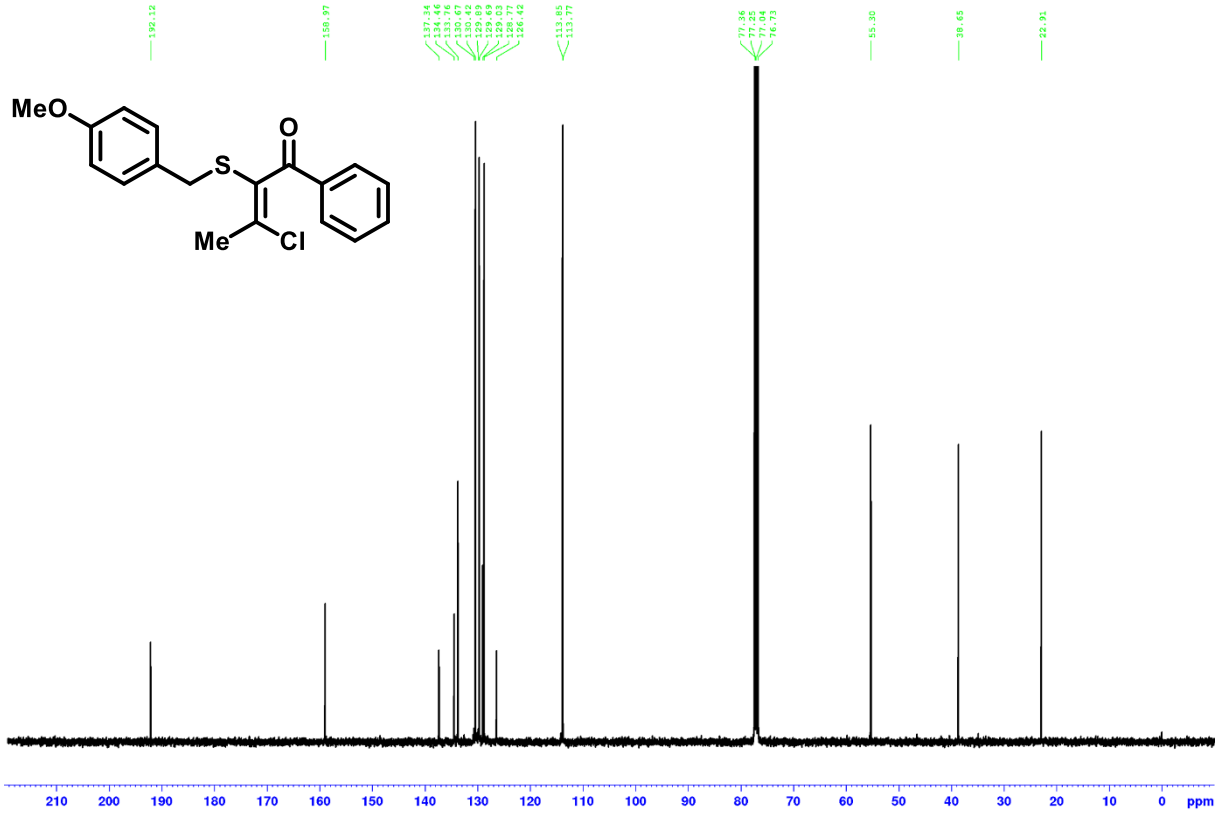


Figure S186: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **E-4dd**.

(*Z*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylbut-2-en-1-one Z-4dd

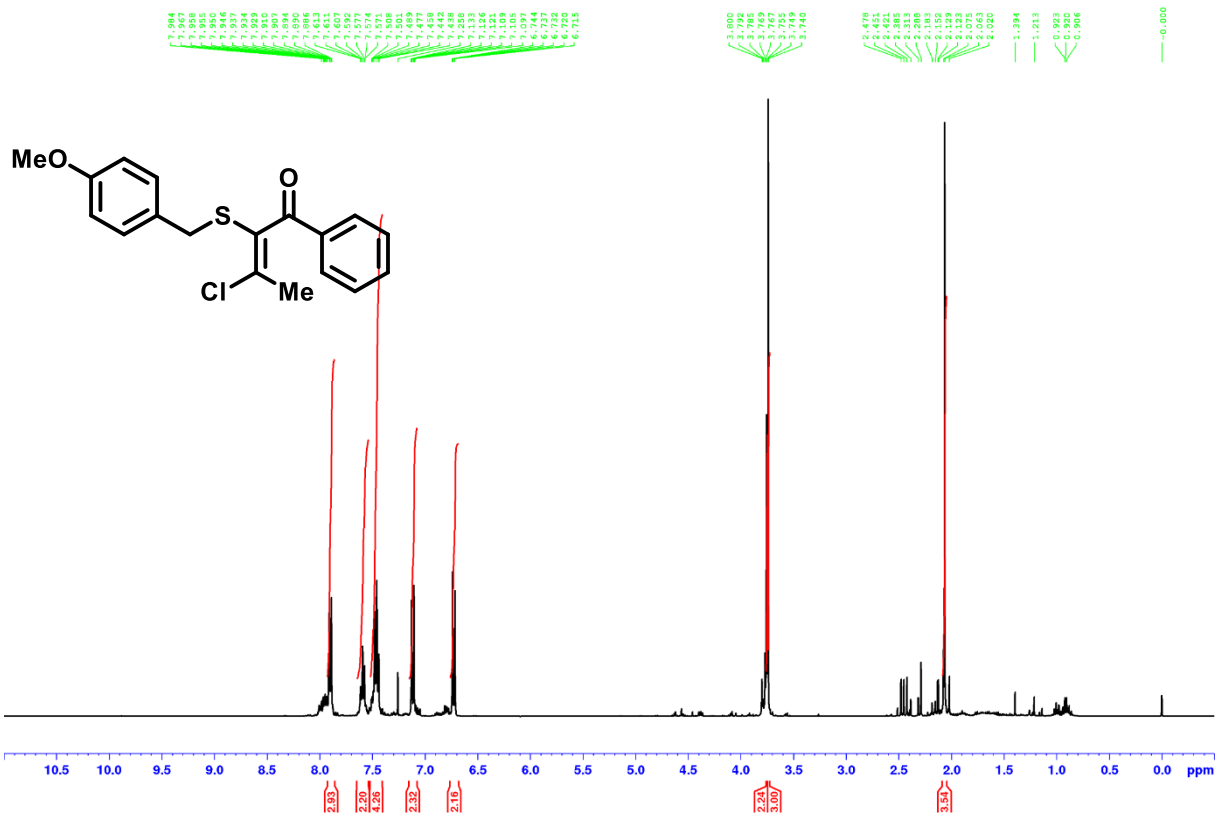


Figure S187: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4dd**.

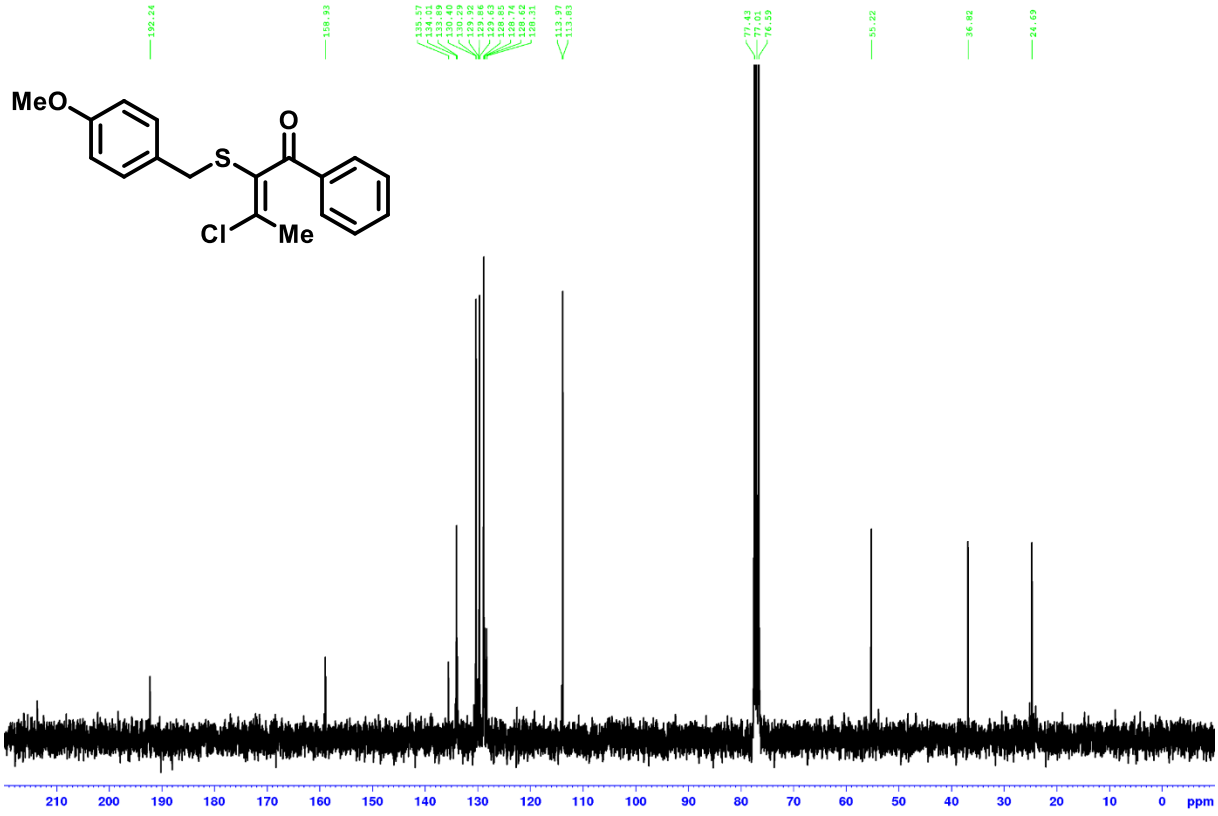


Figure S188: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-4dd**.

(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylbut-2-en-1-one Z-4ee and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylbut-2-en-1-one E-4ee

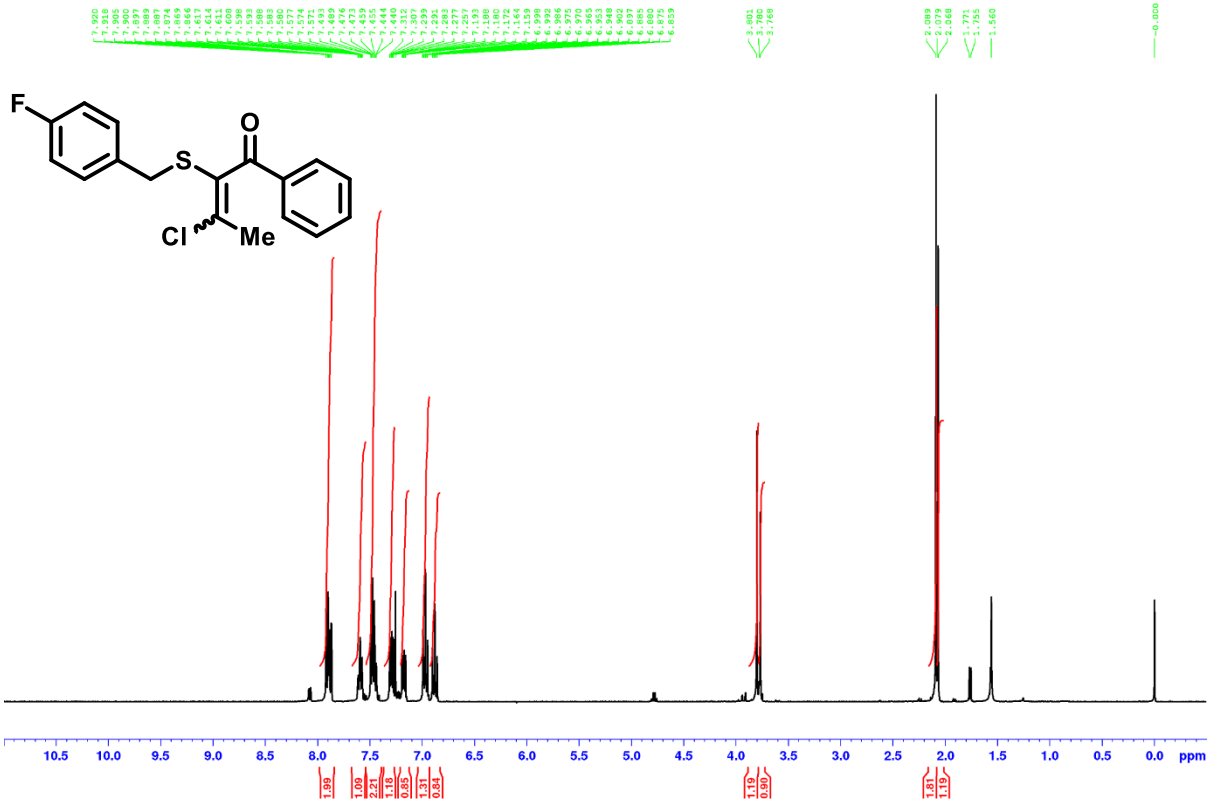


Figure S189: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4ee** and **E-4ee**.

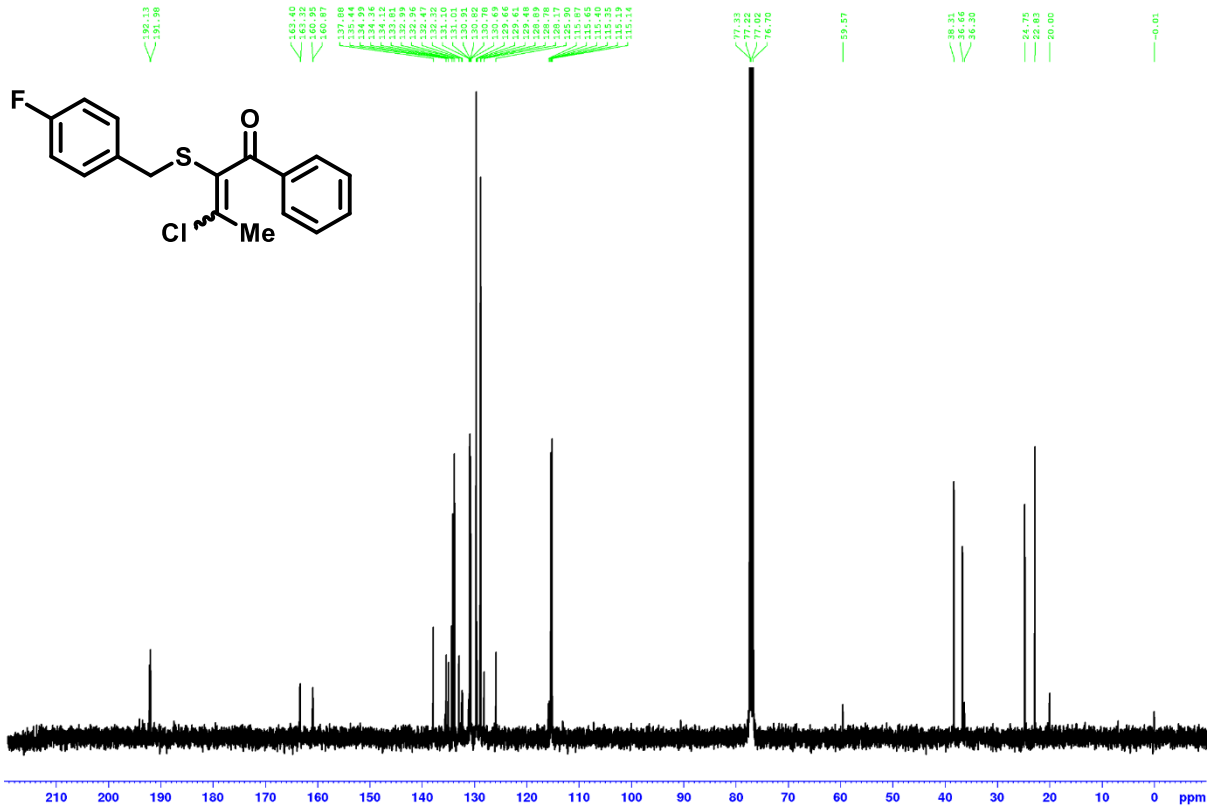


Figure S190: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4ee** and **E-4ee**.

2-((4-Fluorobenzyl)thio)-1-phenylbut-2-en-1-one S43

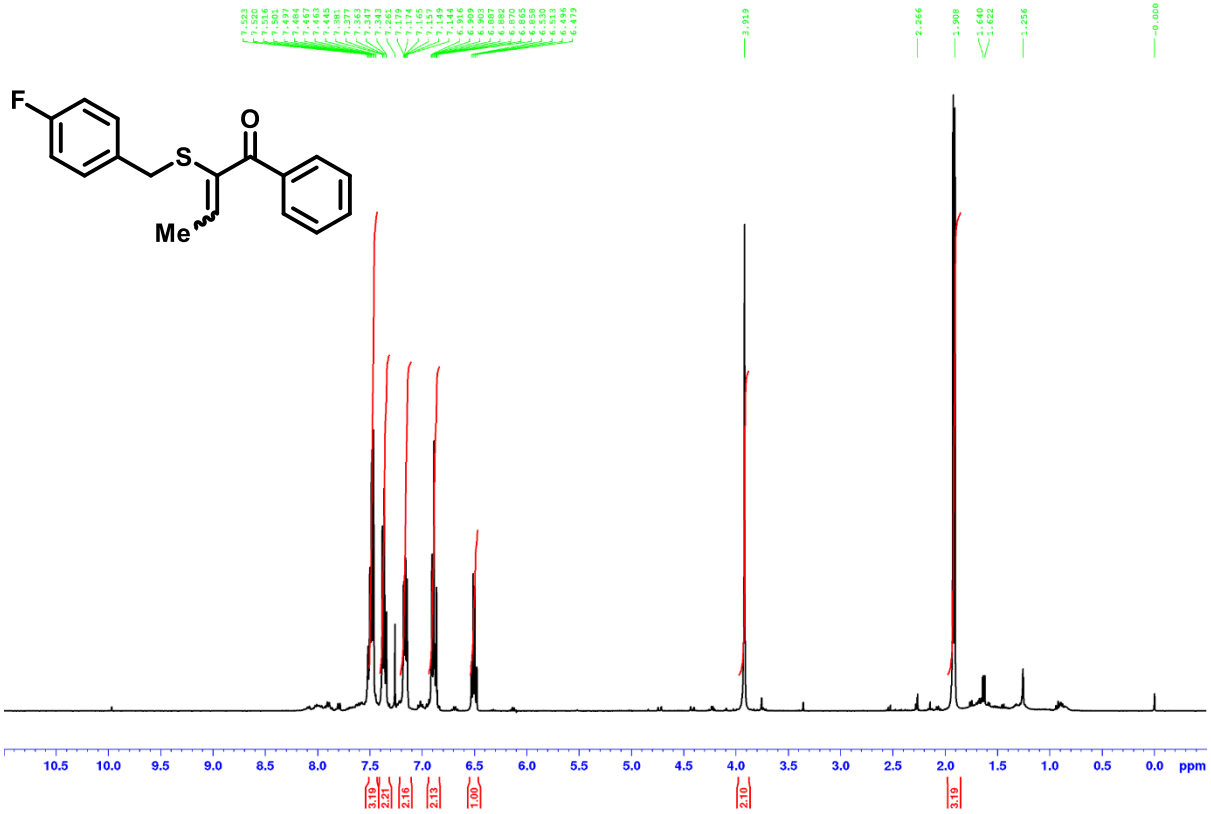


Figure S191: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S43**.

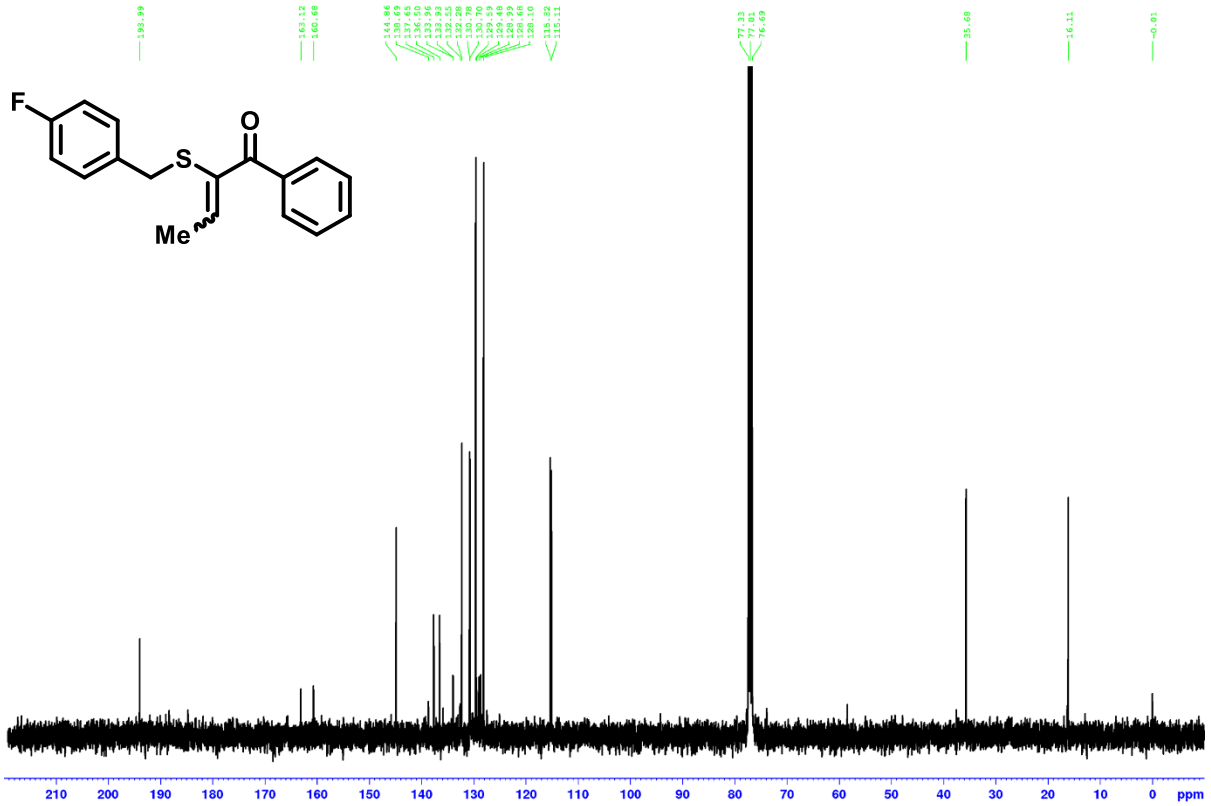


Figure S192: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S43**.

(*Z*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylbut-2-en-1-one Z-4ff and (*E*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylbut-2-en-1-one E-4ff

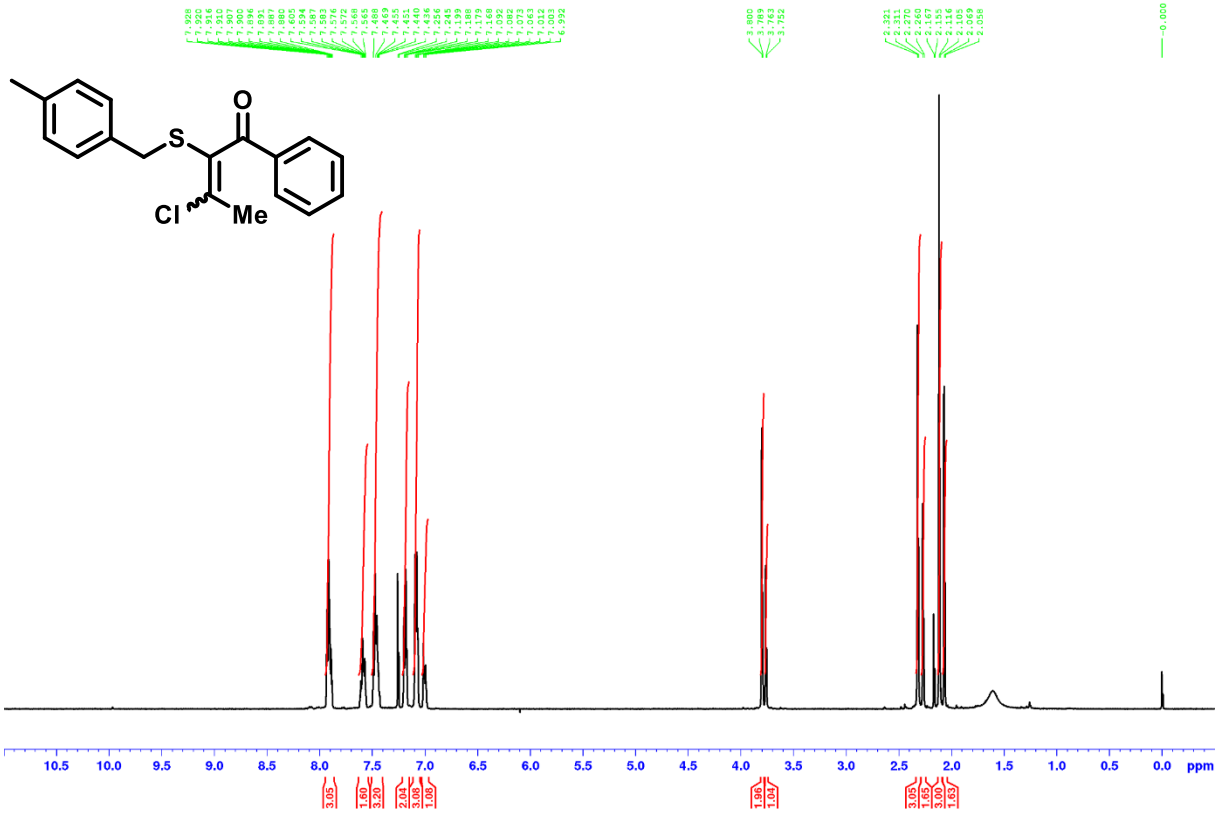


Figure S193: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4ff** and **E-4ff**.

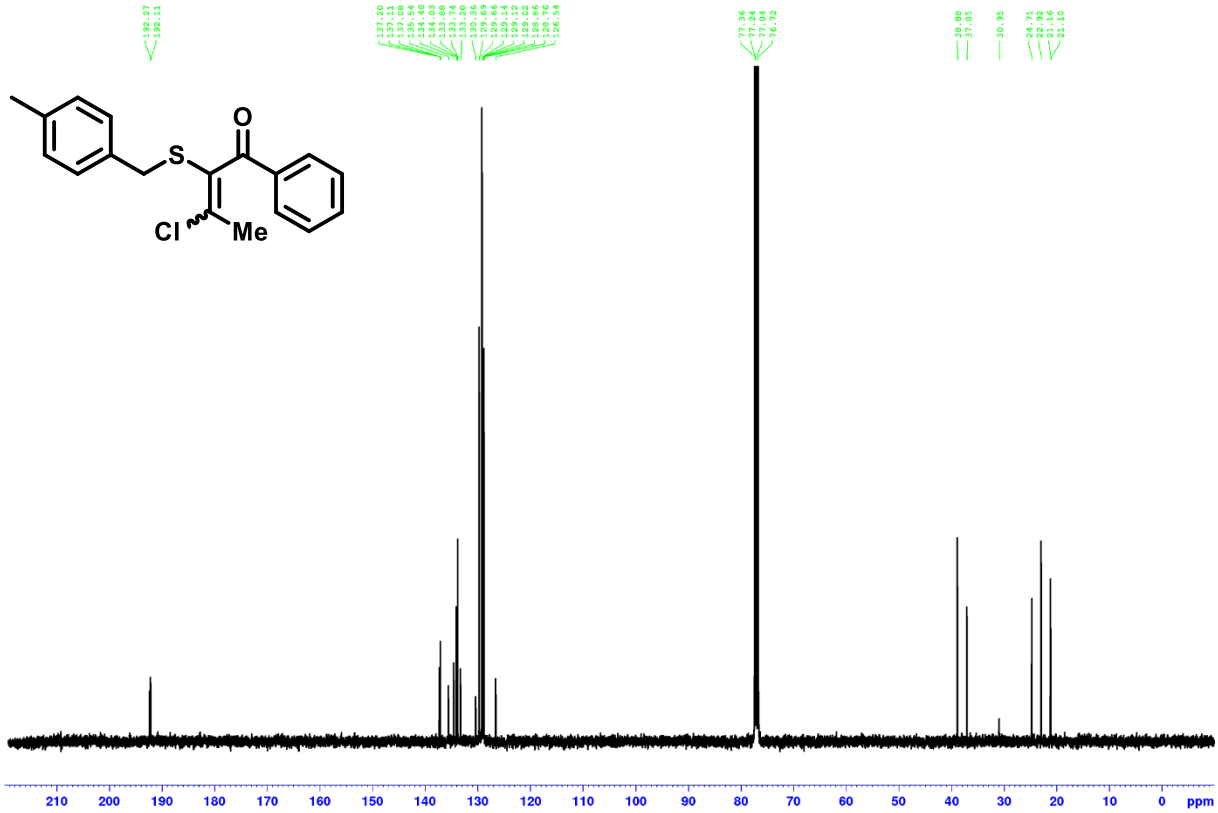


Figure S194: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4ff** and **E-4ff**.

(*Z*)-3-Chloro-1-phenyl-2-(phenylthio)but-2-en-1-one Z-4gg and (*E*)-3-Chloro-1-phenyl-2-(phenylthio)but-2-en-1-one E-4gg

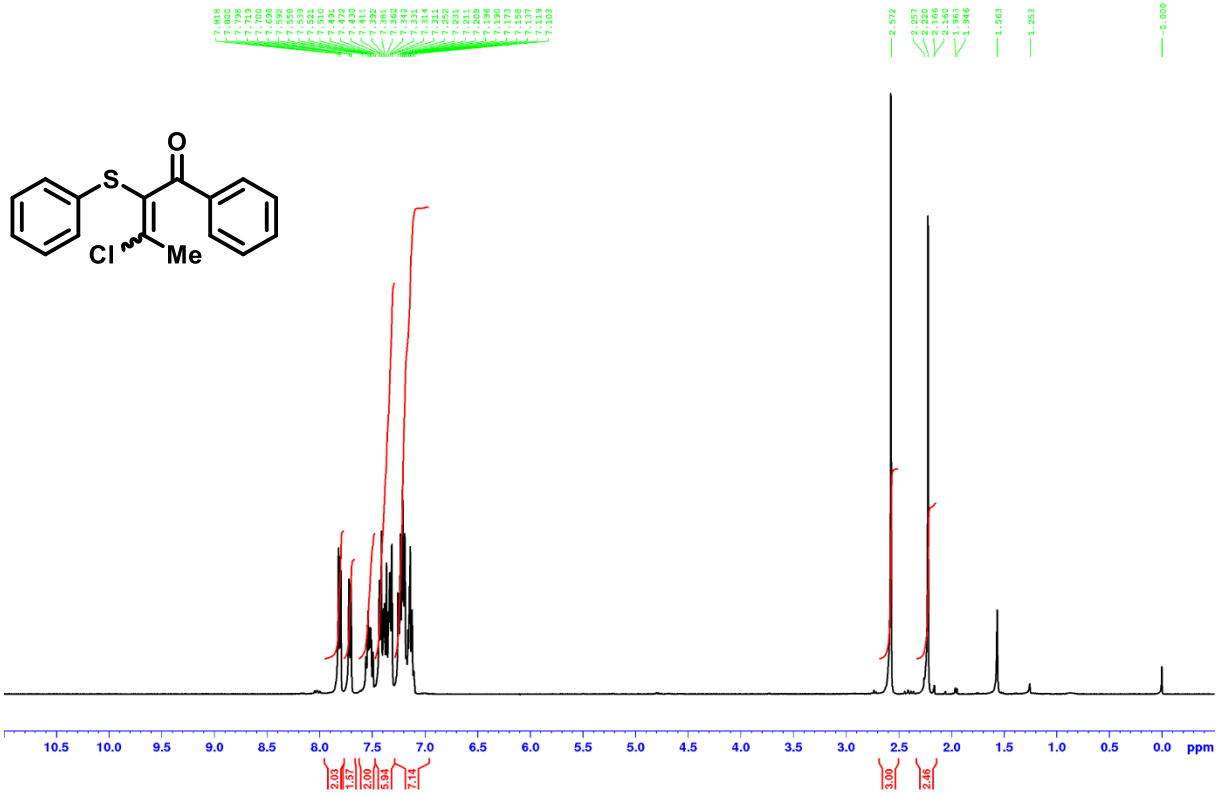


Figure S195: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4gg** and **E-4gg**.

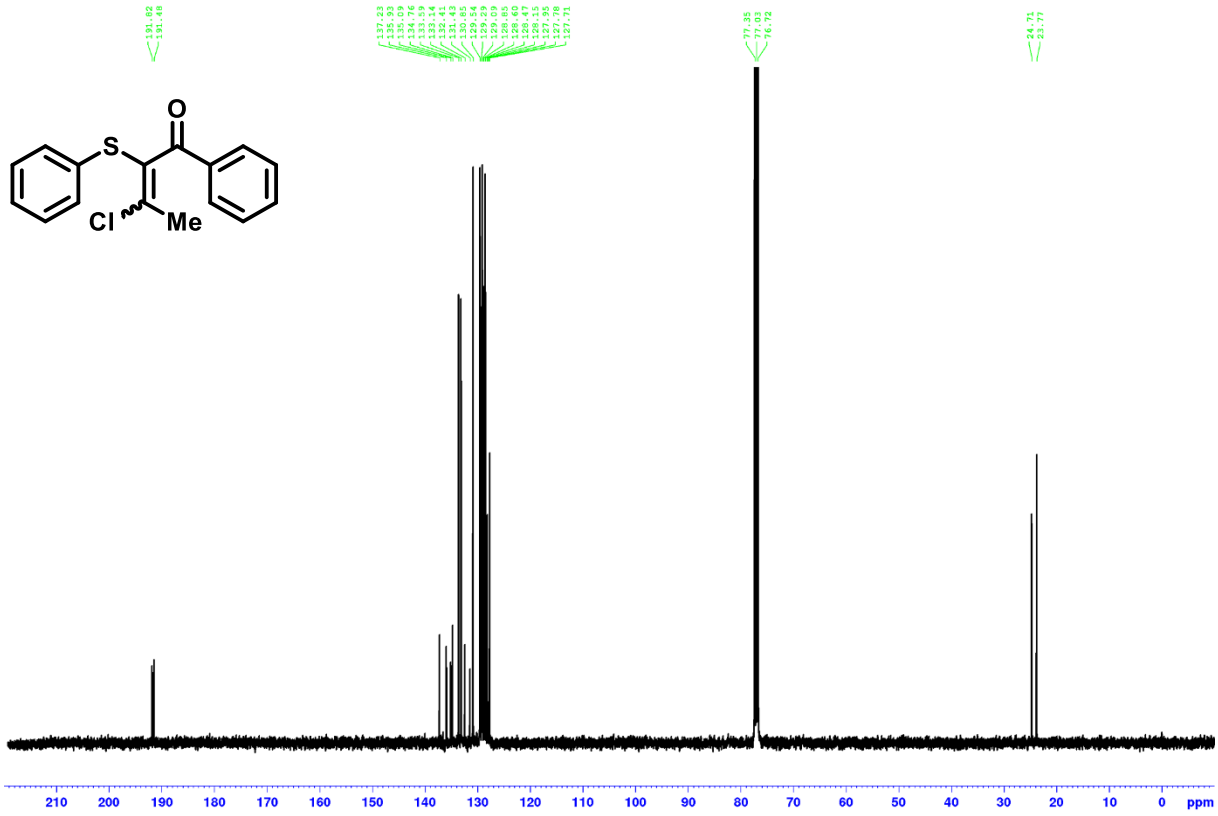


Figure S196: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4gg** and **E-4gg**.

1-Phenyl-2-(phenylthio)but-2-en-1-one S47

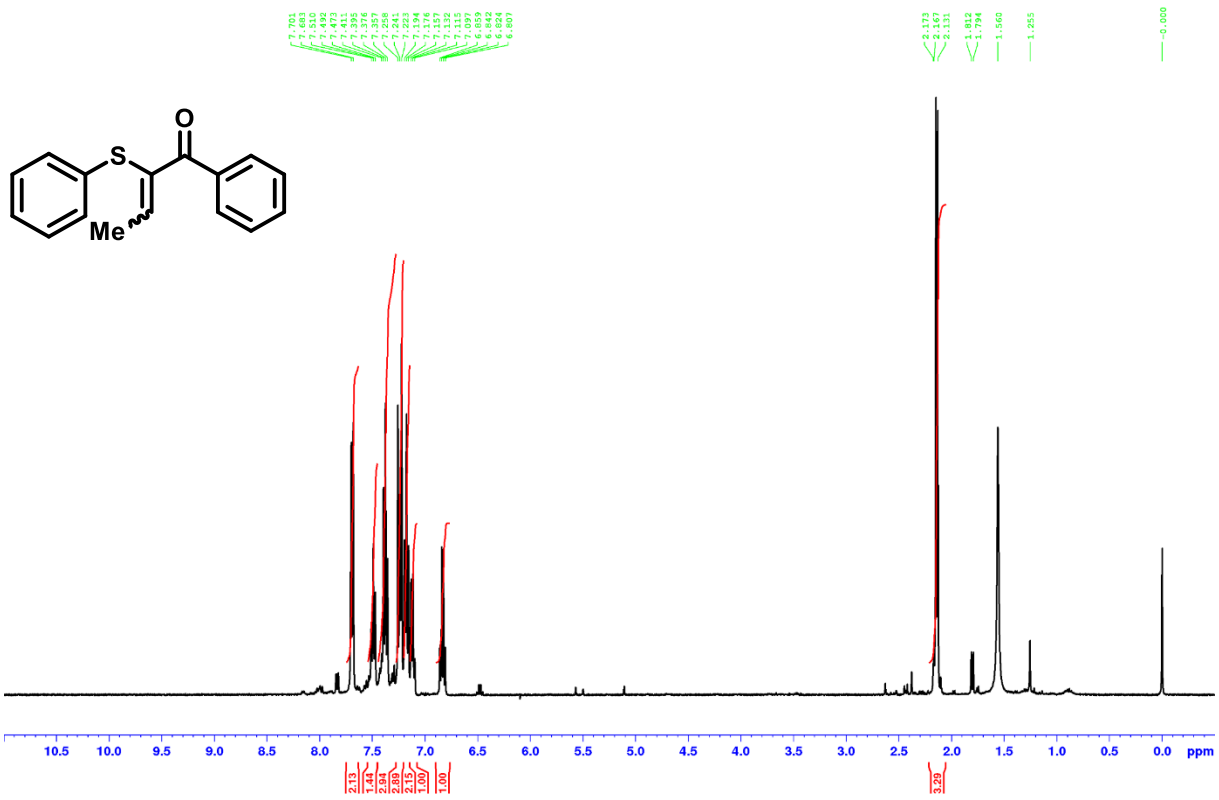


Figure S197: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S47.**

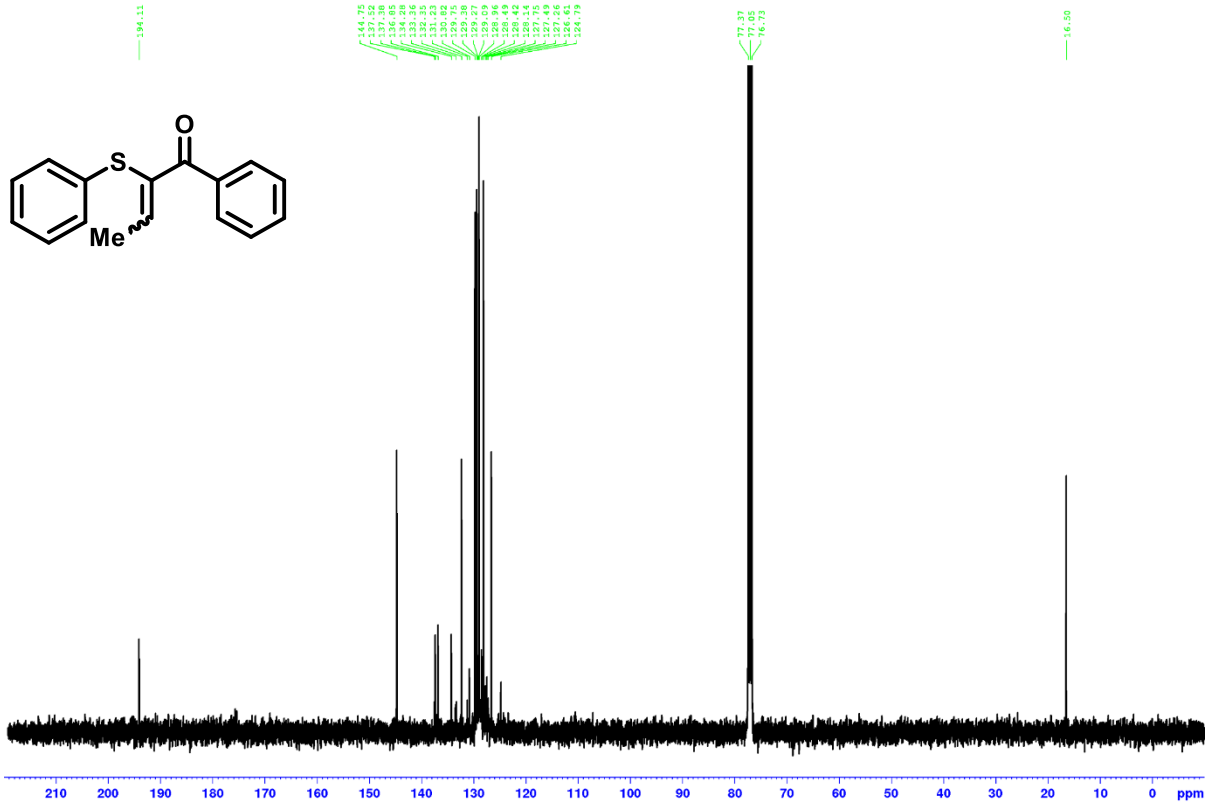


Figure S198: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S47**.

1.12.5 α-Sulfenyl-β-chloropentenones

(*Z*)-2-(Benzylthio)-3-chloro-1-phenylpent-2-en-1-one and Z-4hh (*E*)-2-(Benzylthio)-3-chloro-1-phenylpent-2-en-1-one E-4hh

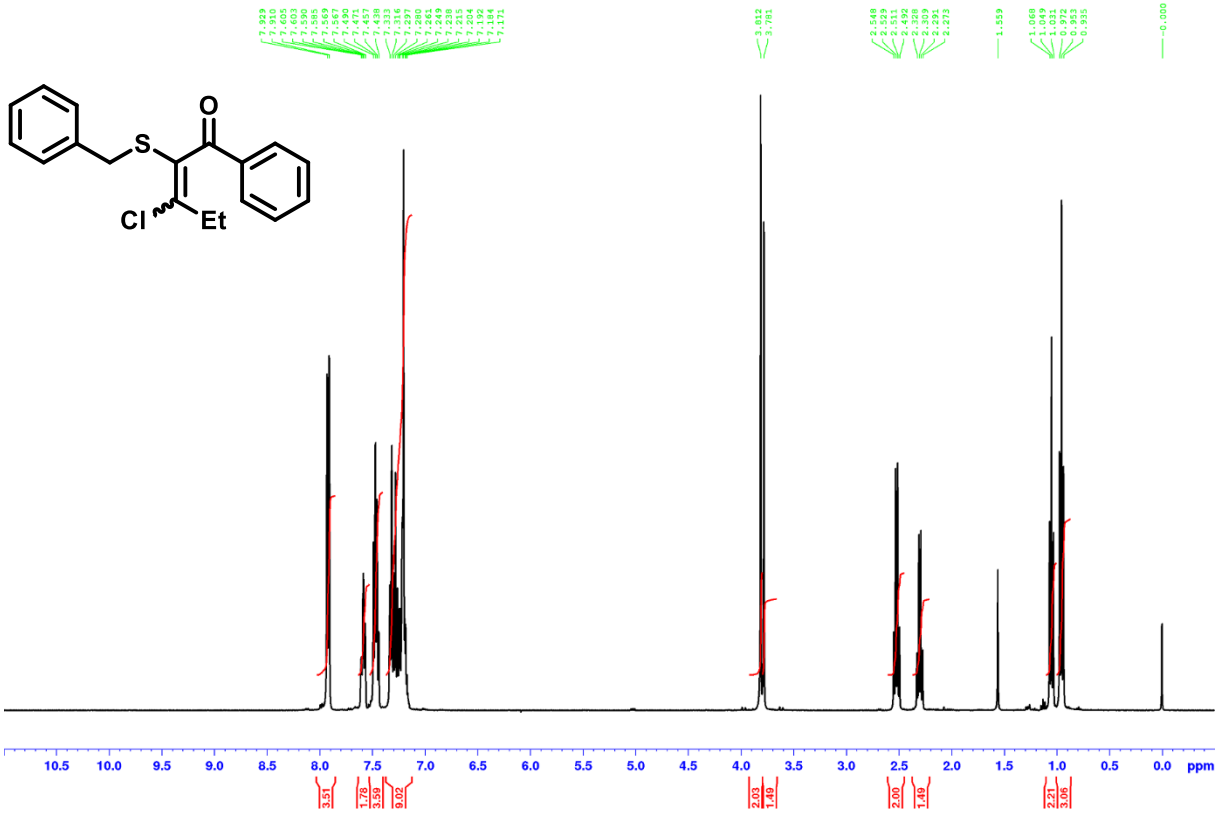


Figure S199: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4hh** and **E-4hh**.

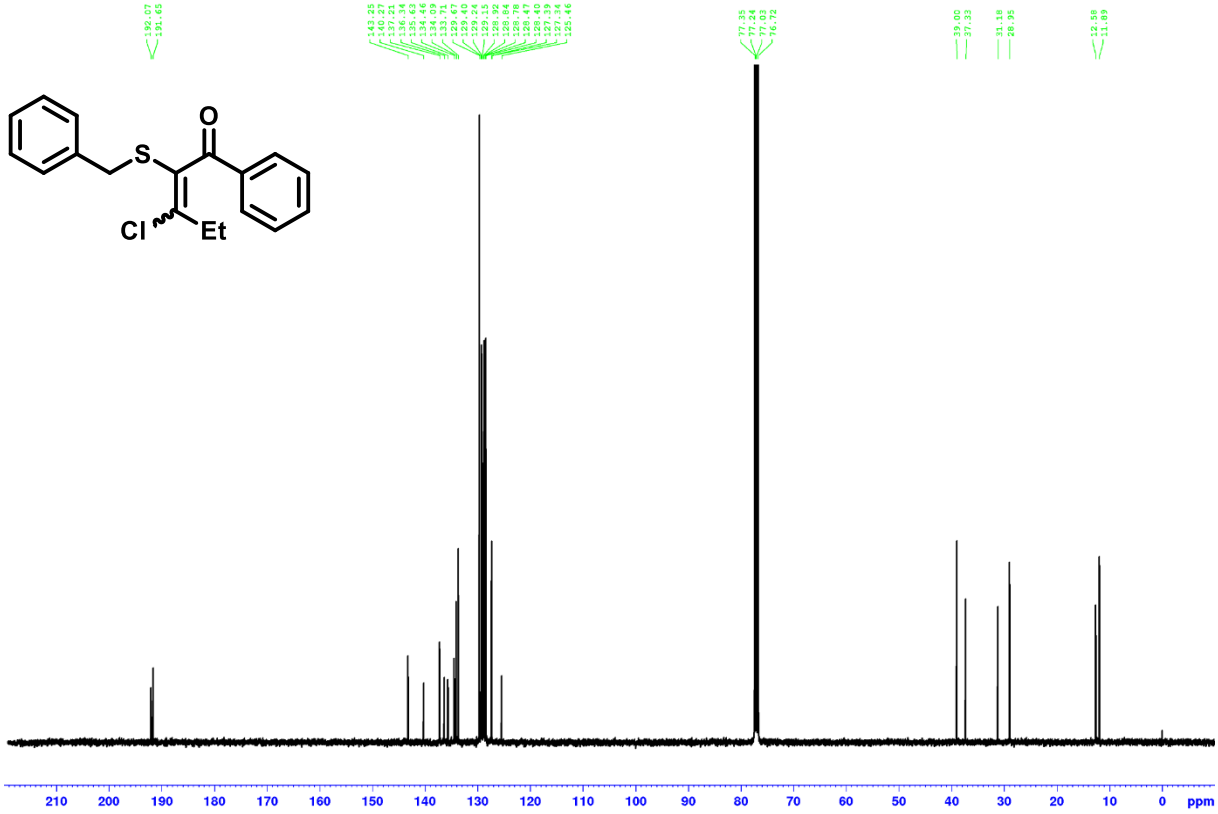


Figure S200: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4hh** and **E-4hh**.

(*Z*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylpent-2-en-1-one Z-4ii and (*E*)-3-Chloro-2-((4-chlorobenzyl)thio)-1-phenylpent-2-en-1-one E-4ii

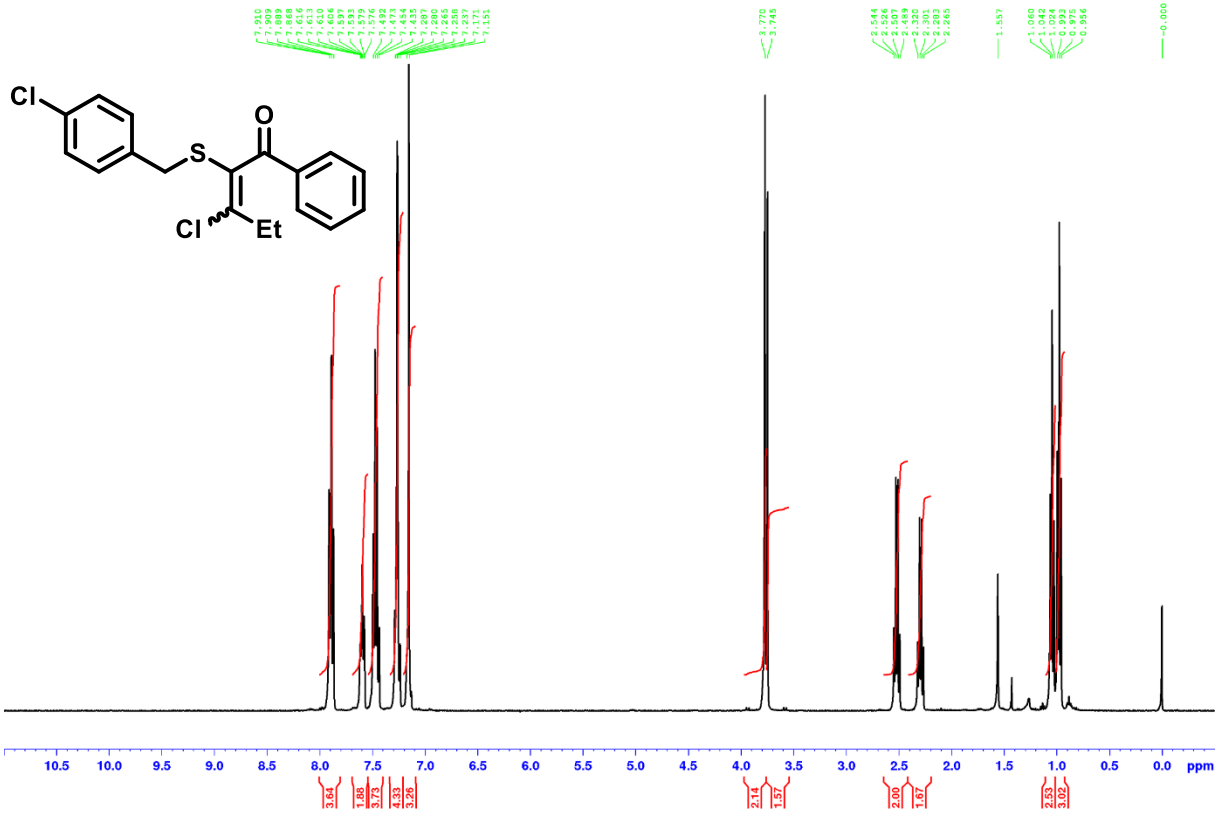


Figure S201: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4ii** and **E-4ii**.

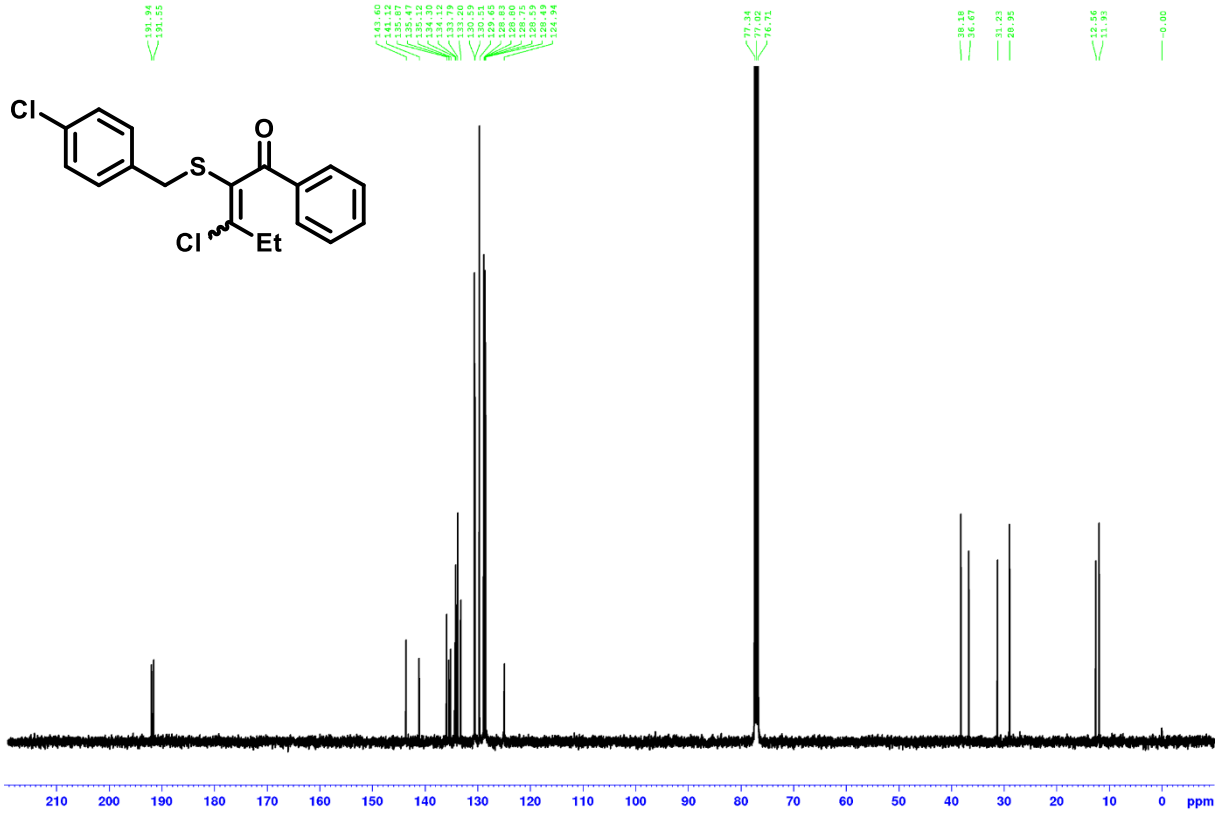


Figure S202: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4ii** and **E-4ii**.

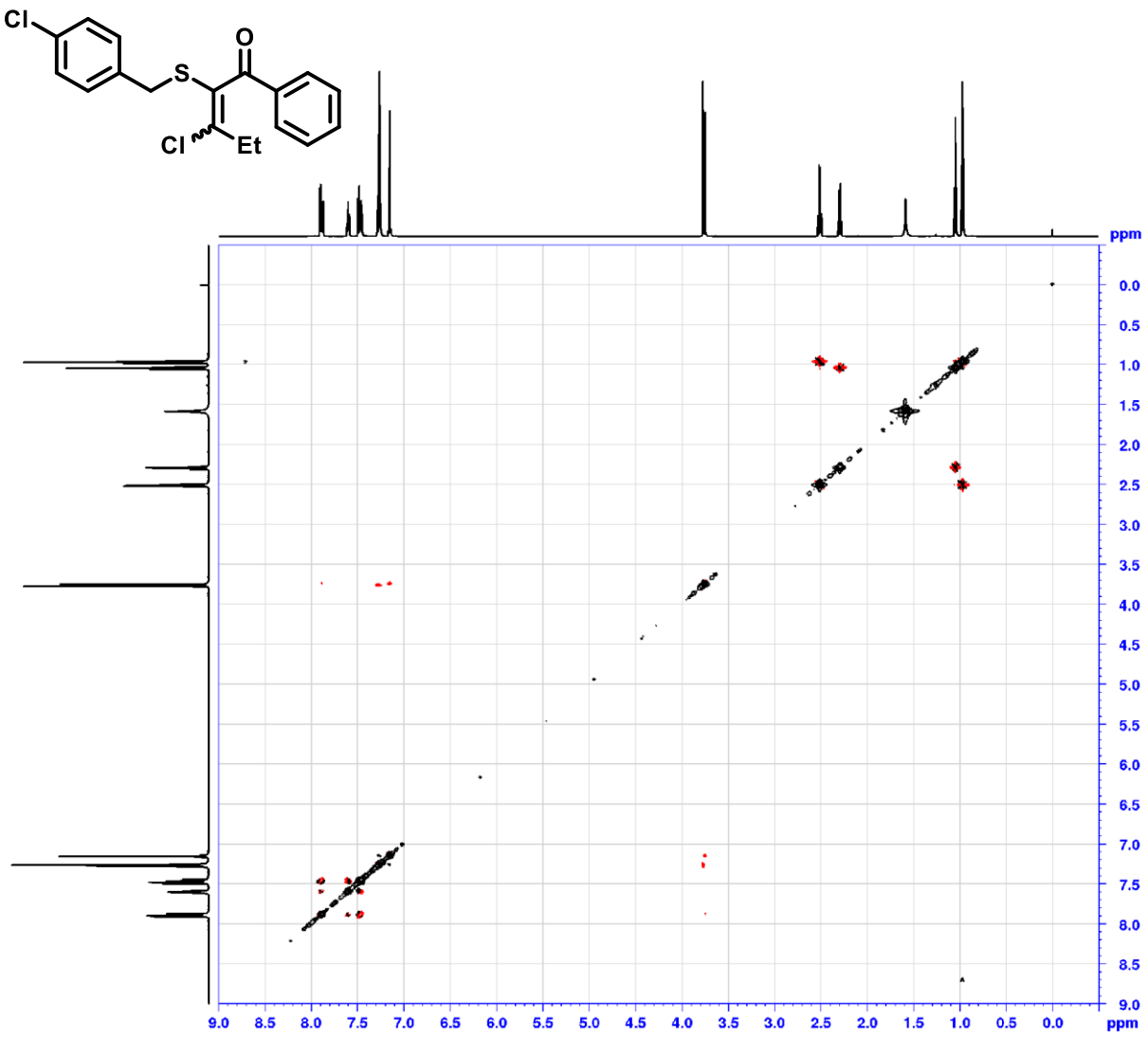


Figure S203: ^{1}H–^{1}H NOESY (600 MHz, $CDCl_3$) spectrum of **Z-4ii** and **E-4ii**.

2-((4-Chlorobenzyl)thio)-1-phenylpent-2-en-1-one S50

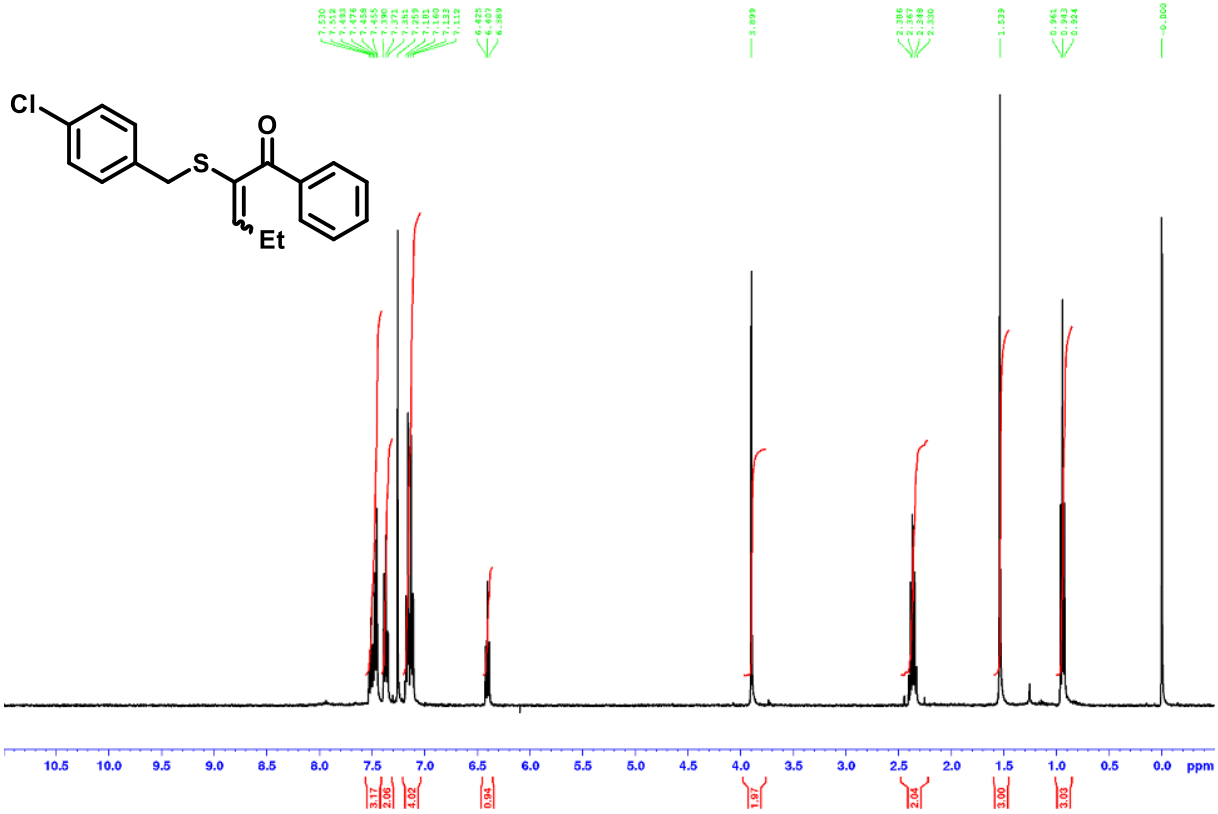


Figure S204: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S50**.

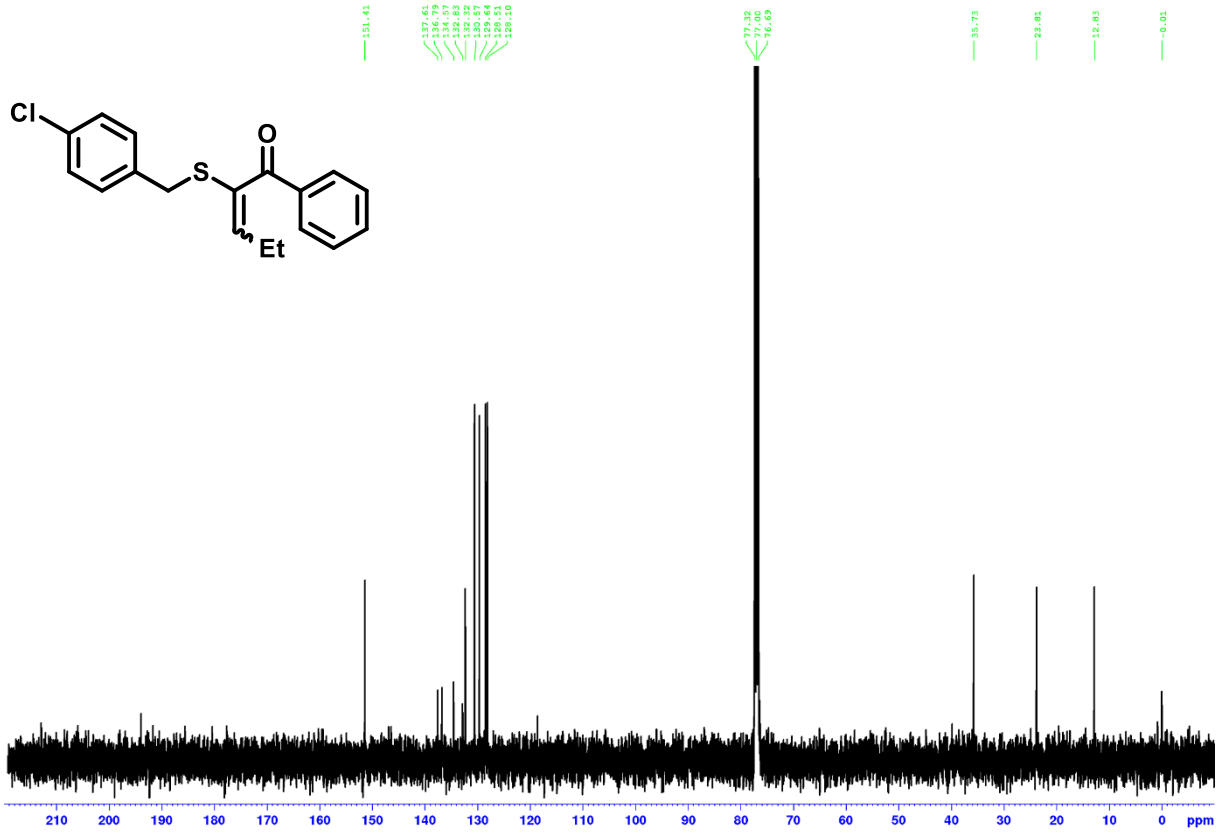


Figure S205: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **S50**.

(*Z*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylpent-2-en-1-one Z-4jj and (*E*)-3-Chloro-2-((4-methoxybenzyl)thio)-1-phenylpent-2-en-1-one E-4jj

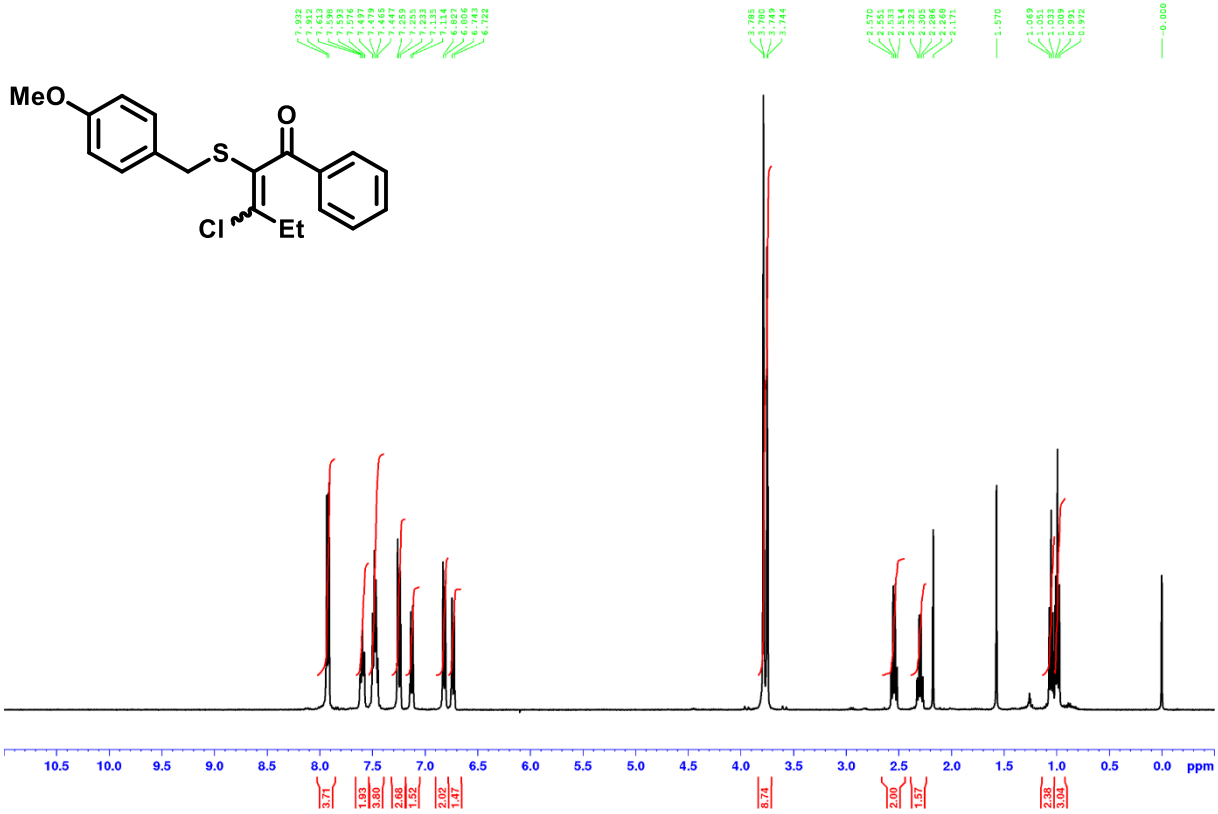


Figure S206: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4jj** and **E-4jj**.

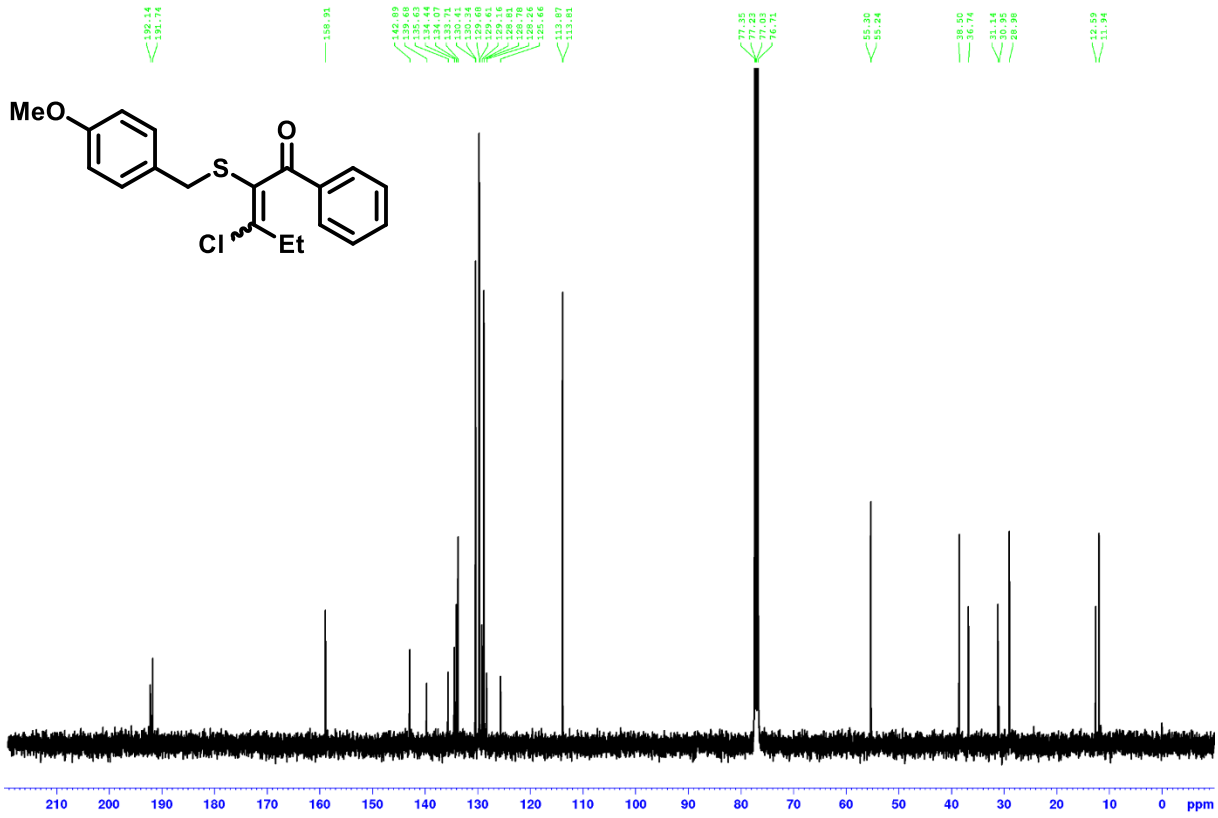


Figure S207: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4jj** and **E-4jj**.

(*Z*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylpent-2-en-1-one Z-4kk and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylpent-2-en-1-one E-4kk

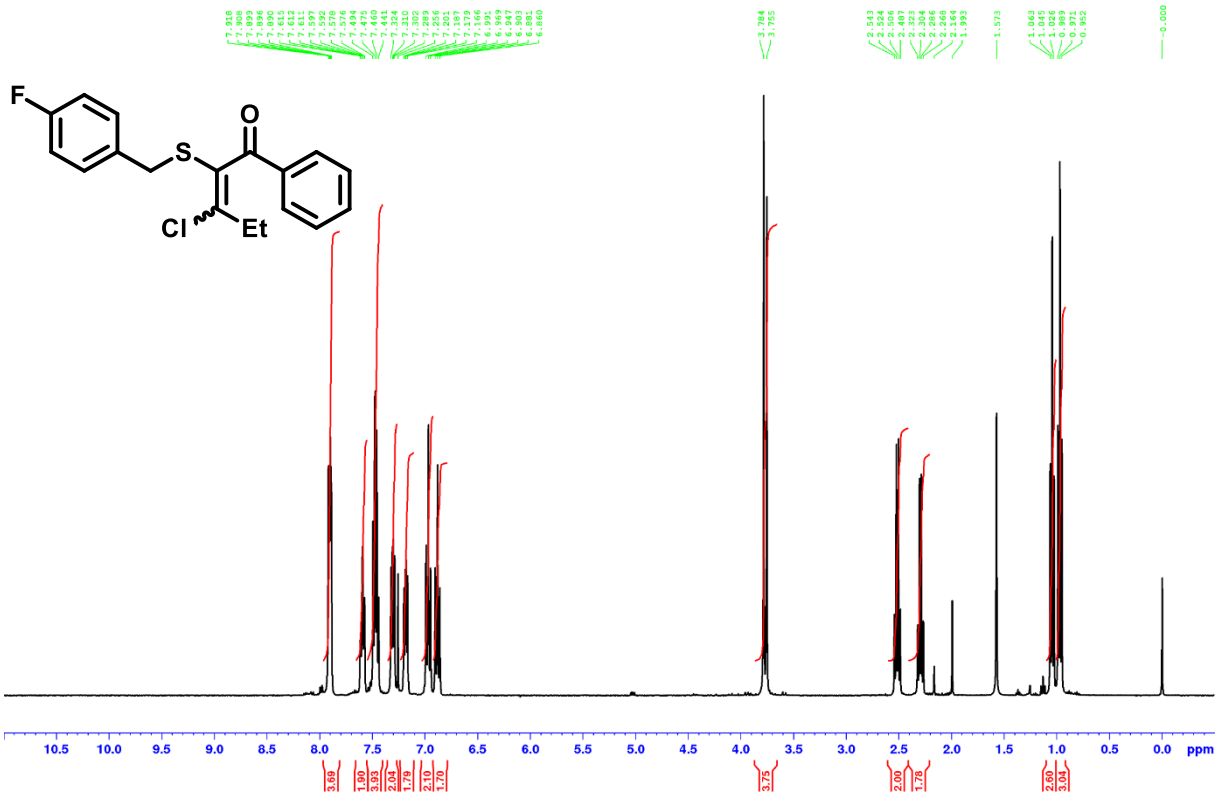


Figure S208: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4kk** and **E-4kk**.

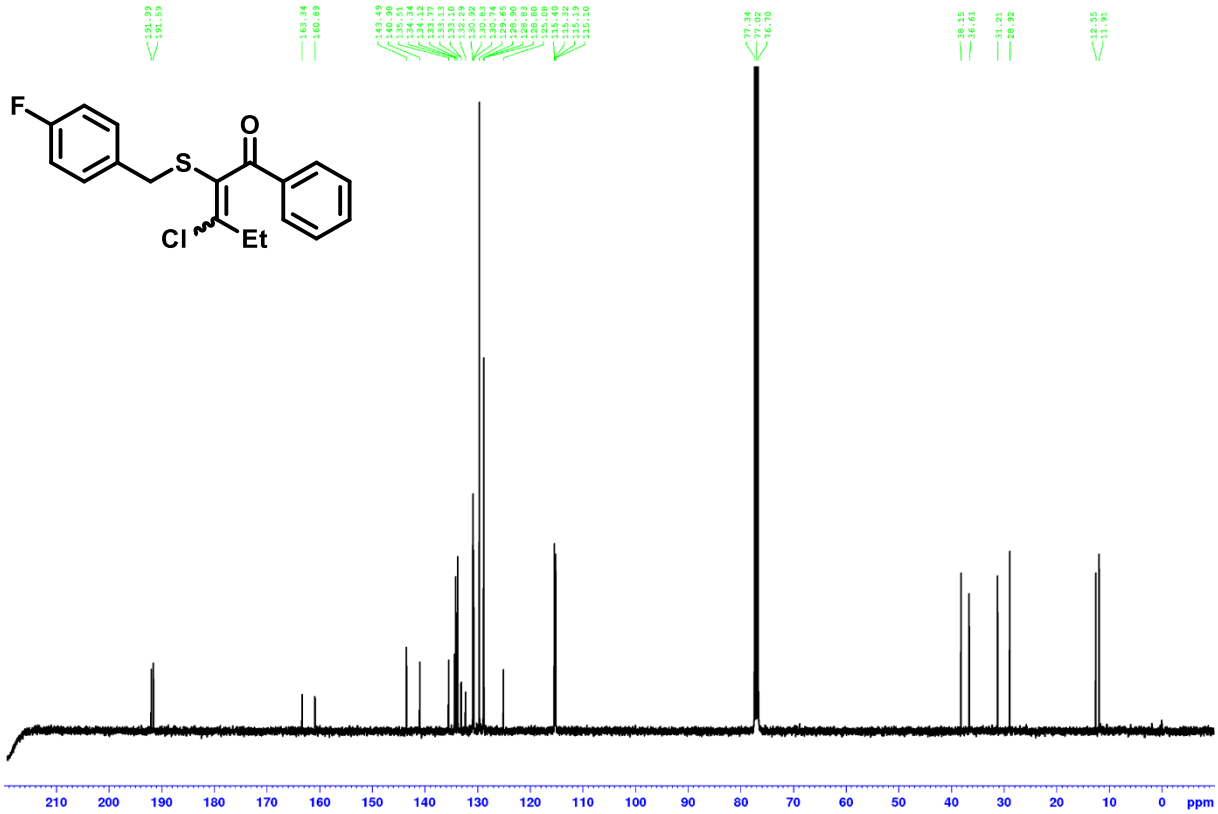


Figure S209: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4kk** and **E-4kk**.

(*Z*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylpent-2-en-1-one Z-4ll and (*E*)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylpent-2-en-1-one E-4ll

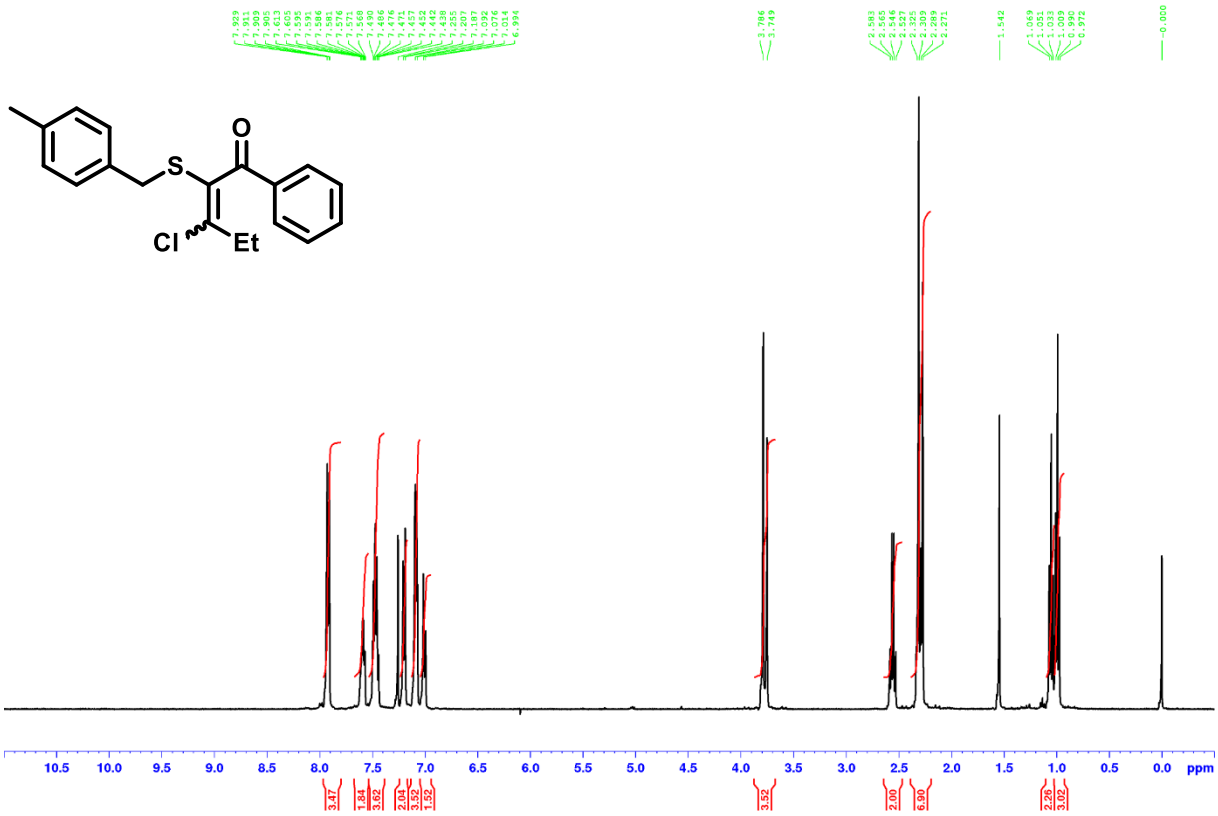


Figure S210: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-4ll** and **E-4ll**.

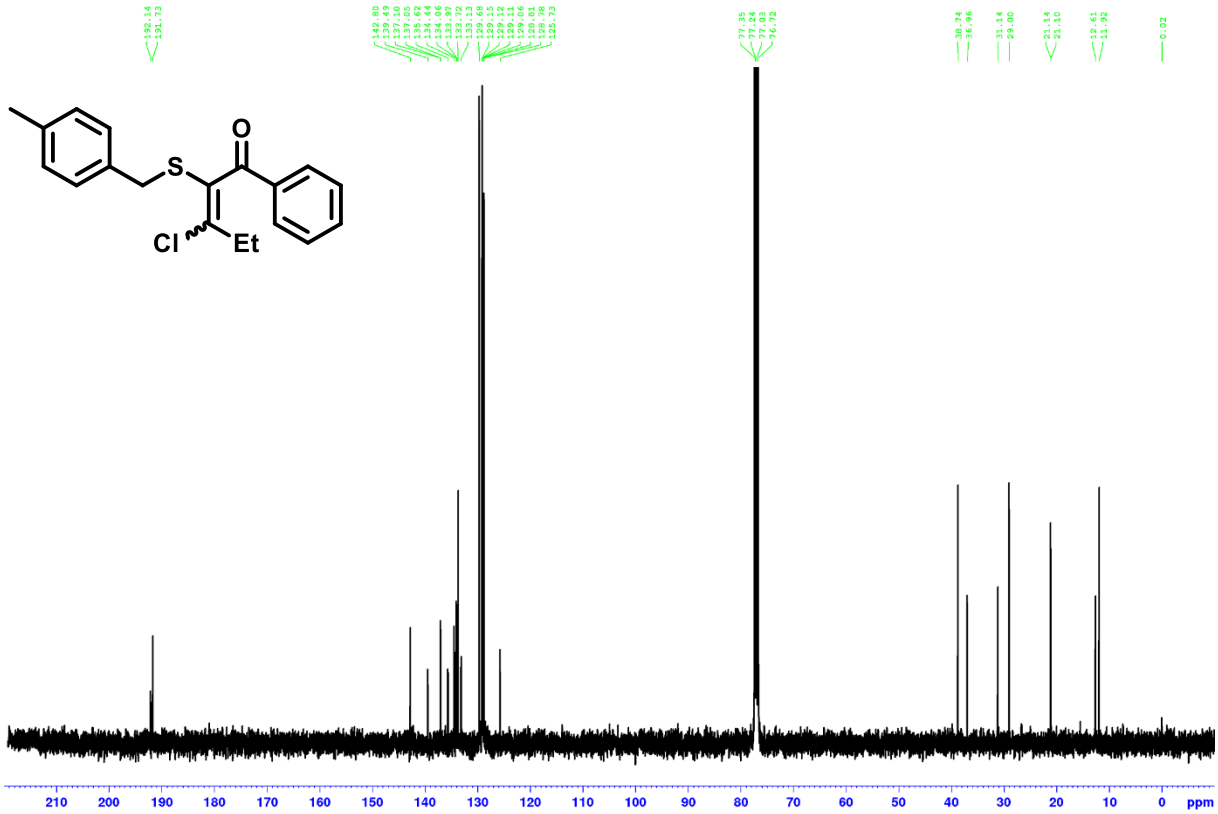


Figure S211: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-4ll** and **E-4ll**.

1.12.6 α-Sulfenyl-β-phenyl-β-chlorenones

(*Z*)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one Z-13a and (*E*)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one E-13a

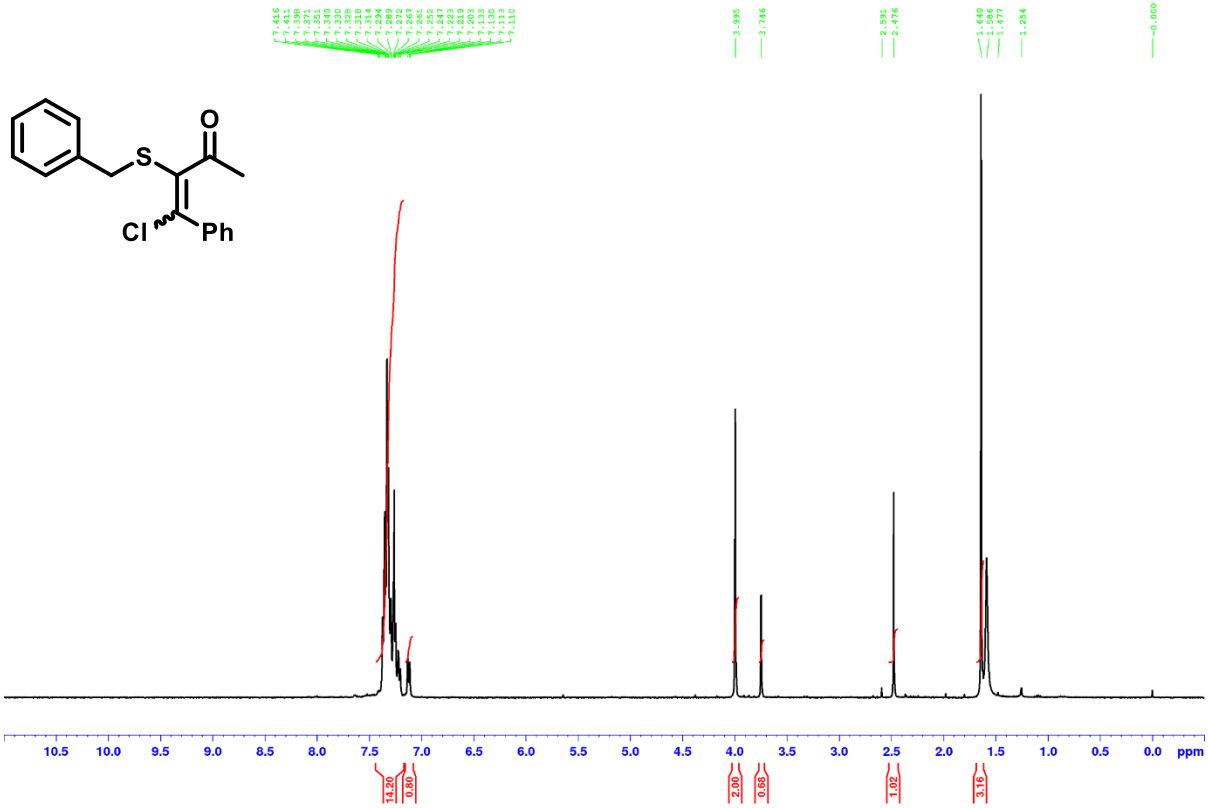


Figure S212: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Z-13a** and **E-13a**.

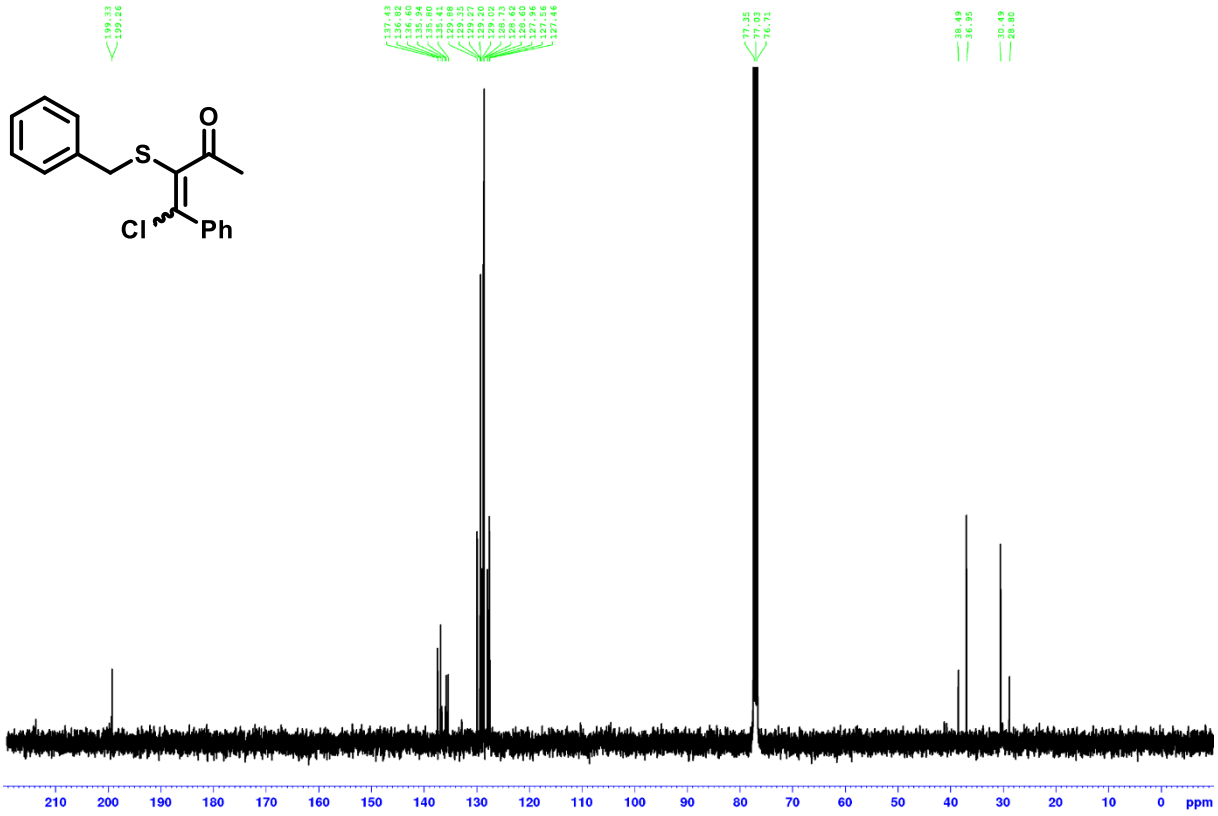


Figure S213: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **Z-13a** and **E-13a**.

3-(Benzylthio)-3,4-dichloro-4-phenylbutan-2-one 12a/b

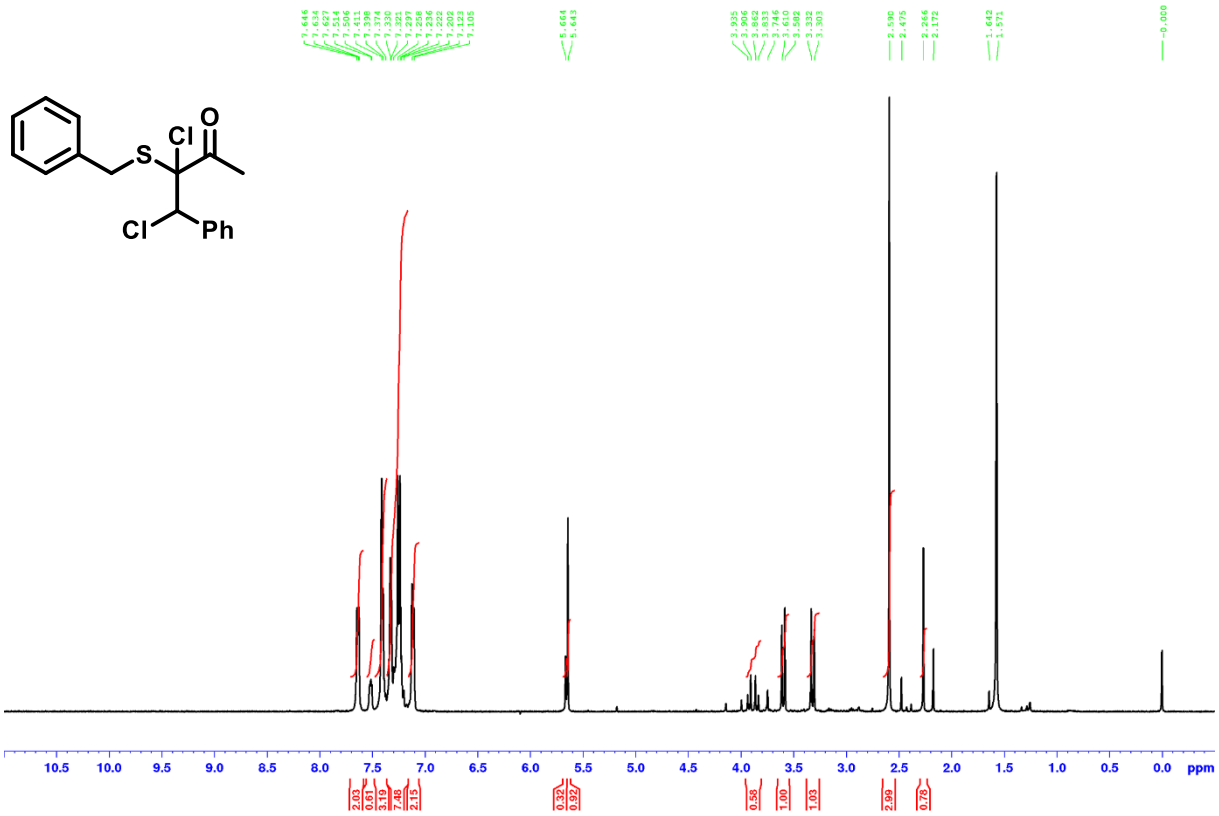


Figure S214: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12a/b**.

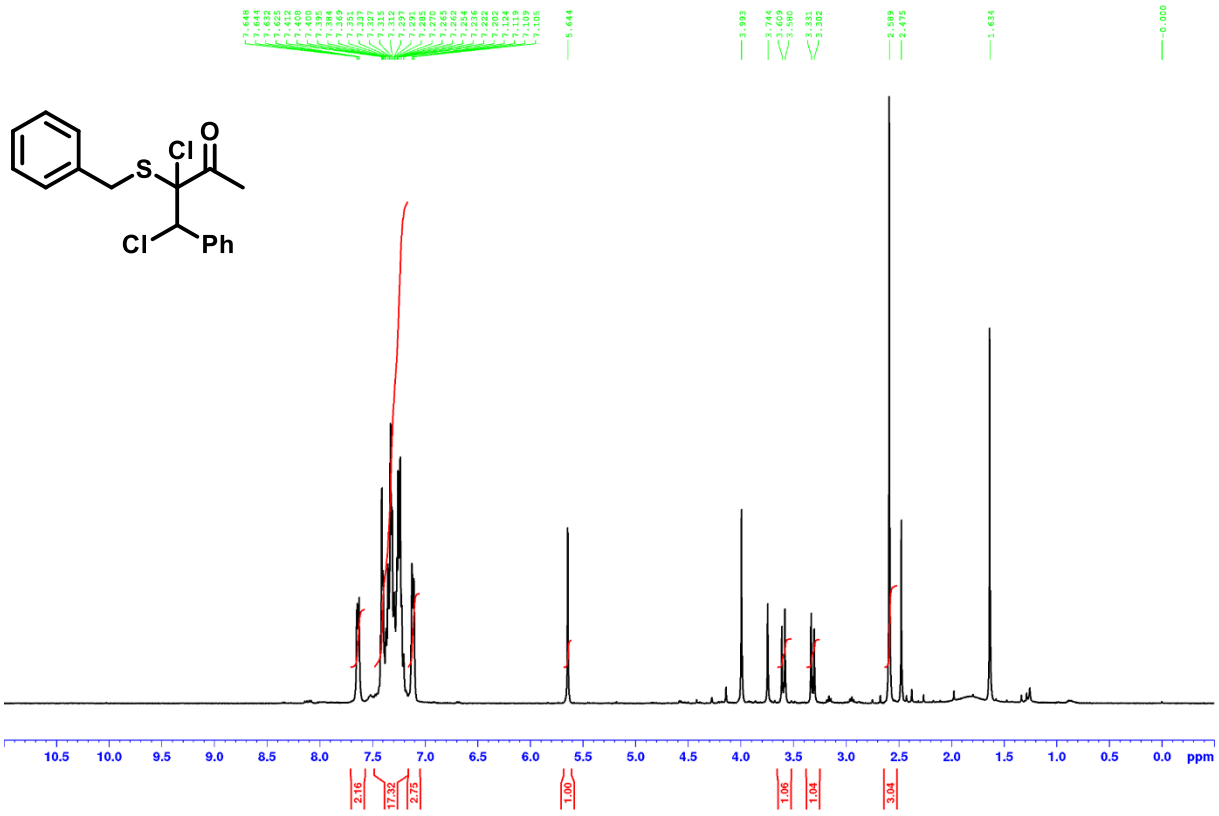


Figure S215: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12a/b** after storage at room temperature for 40 months.

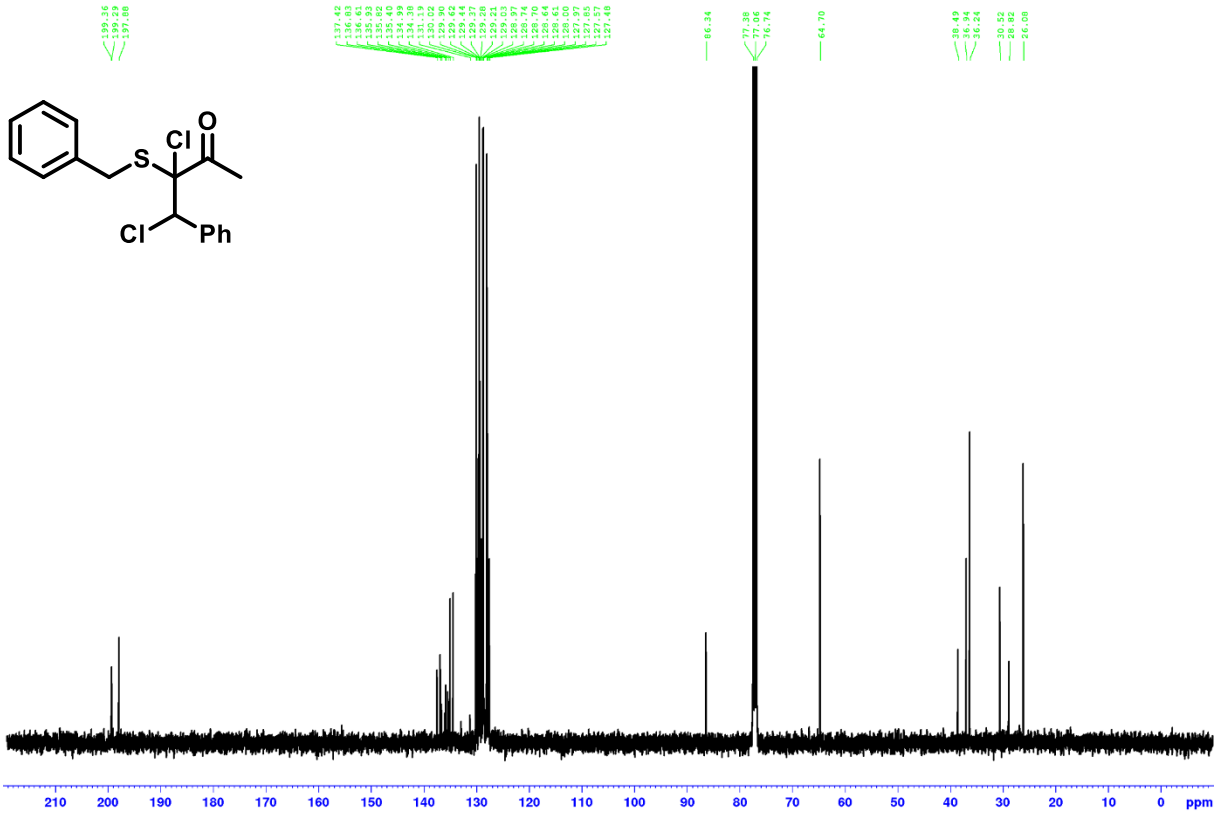


Figure S216: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **12a/b**.

(*Z*)-3-(Benzylthio)-4-phenylbut-3-en-2-one 11a[21]

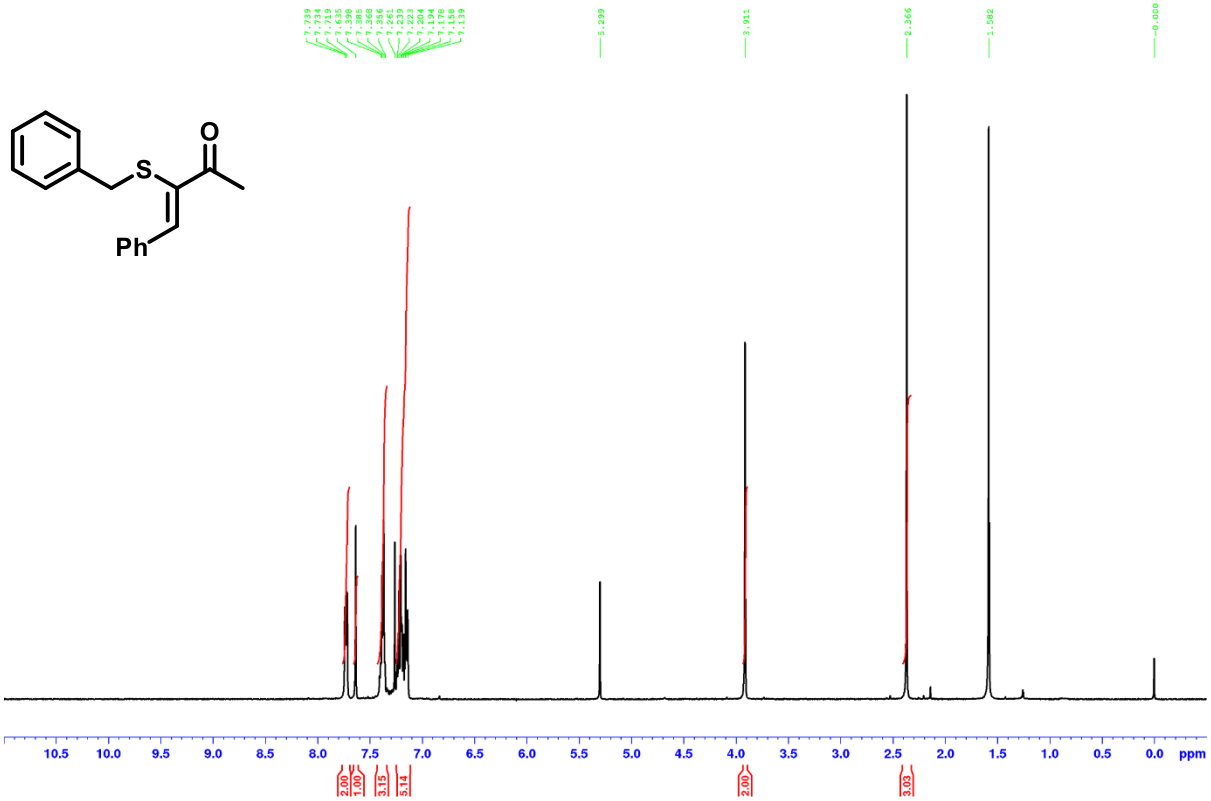


Figure S217: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11a**.

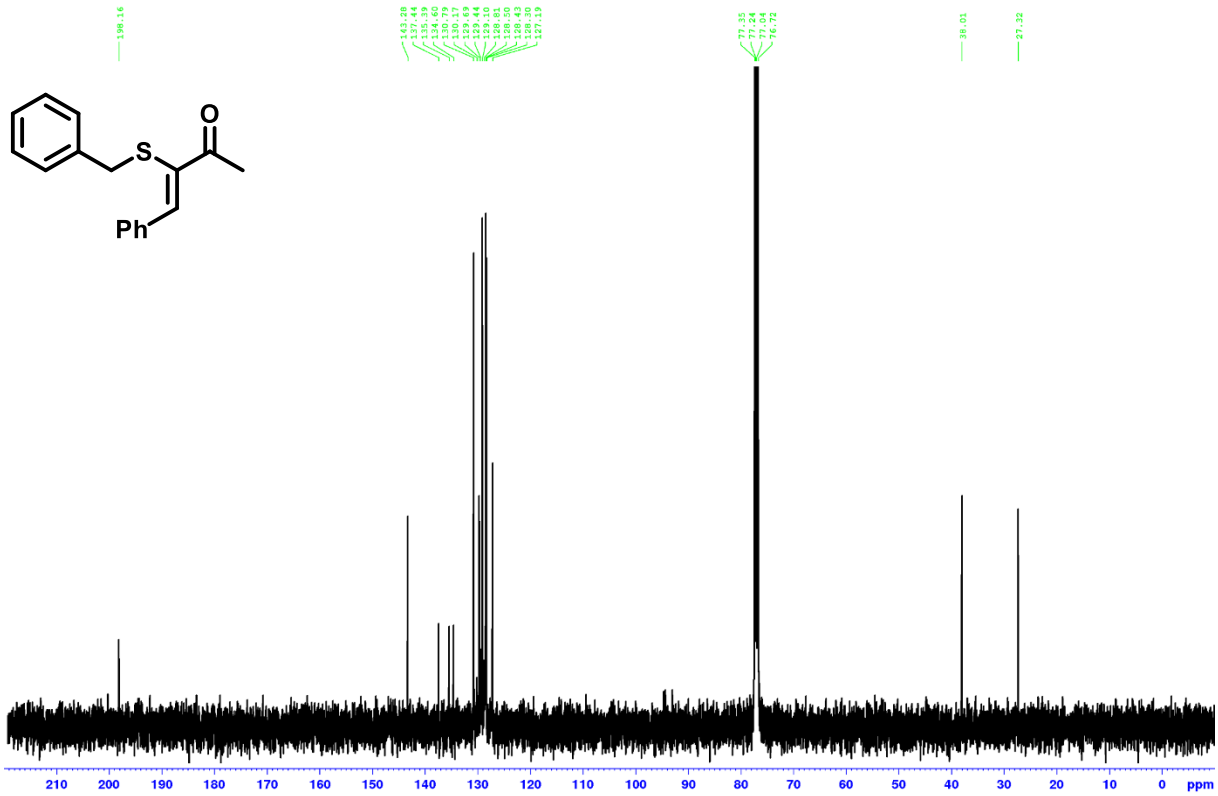


Figure S218: ^{13}C NMR (100.6 MHz, $CDCl_3$) spectrum of **11a**.

1.12.7 Dichlorides:

3,4-Dichloro-3-(phenylthio)butan-2-one S53

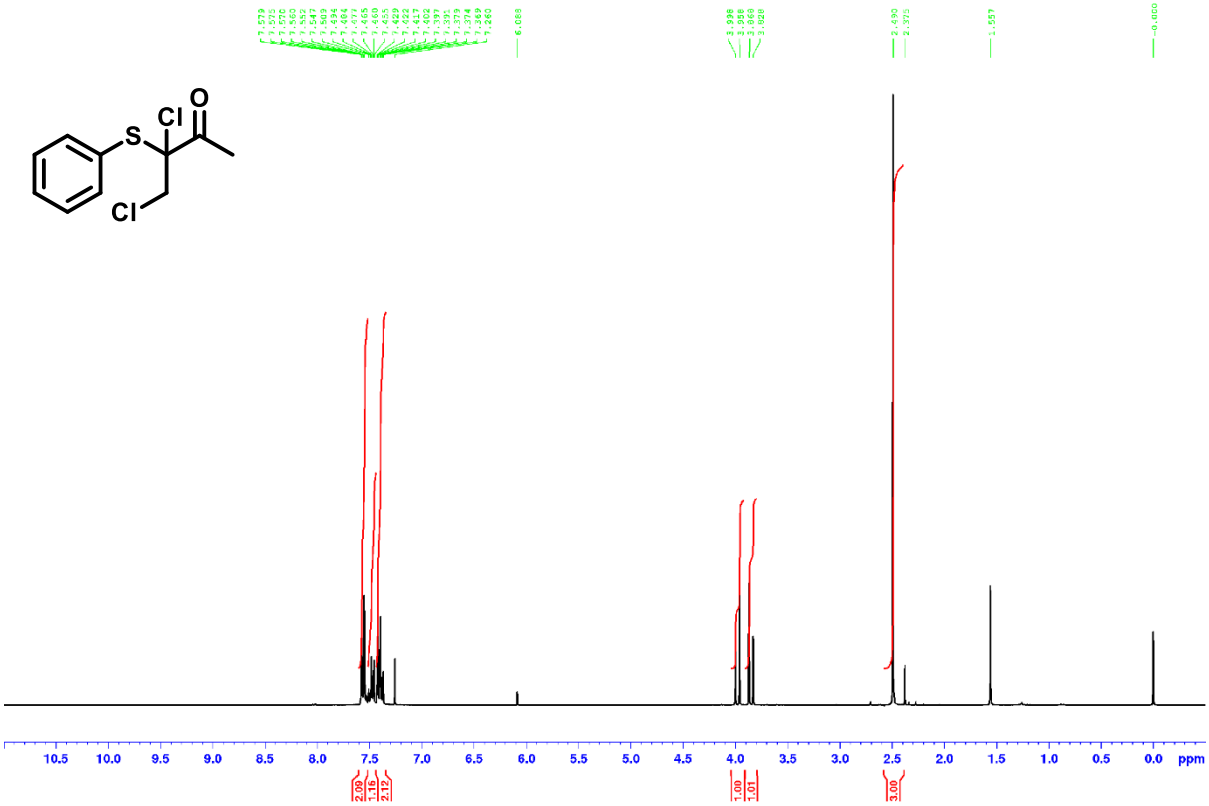


Figure S219: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S53.**

1,2-Dichloro-2-(phenylthio)pentan-3-one S54

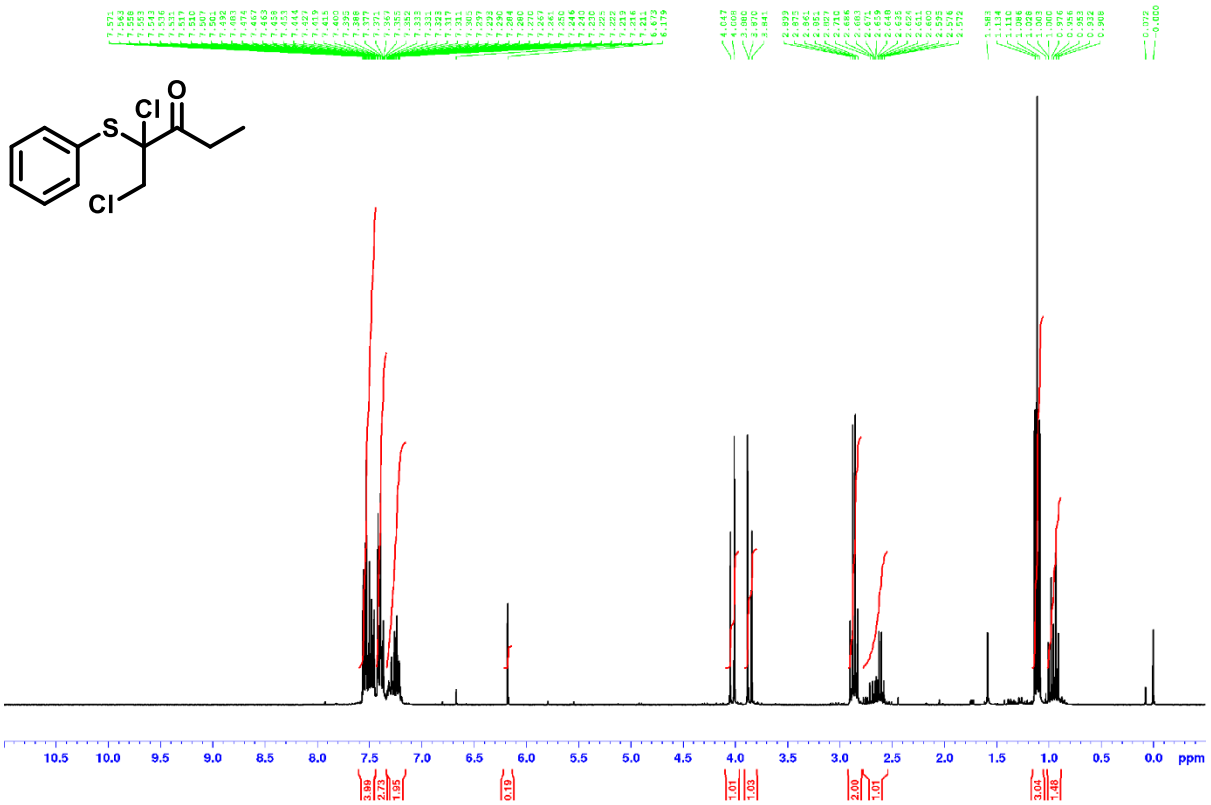


Figure S220: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S54 (57%), Z-9b (32%), E-9b (<2%), S55 (11%).**

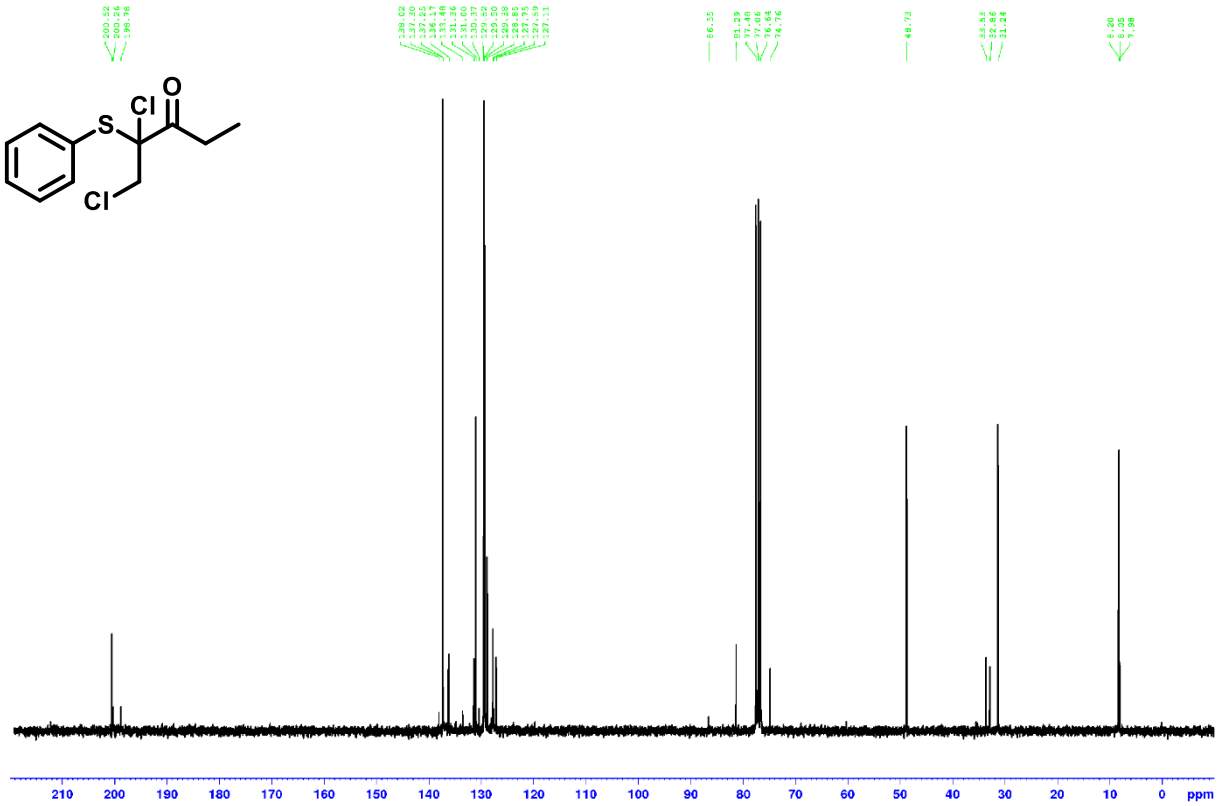


Figure S221: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **S54 (57%), Z-9b (32%), E-9b (<2%), S55 (11%).**

(*Z*)-1-Chloro-2-(phenylthio)pent-1-en-3-one Z-9b

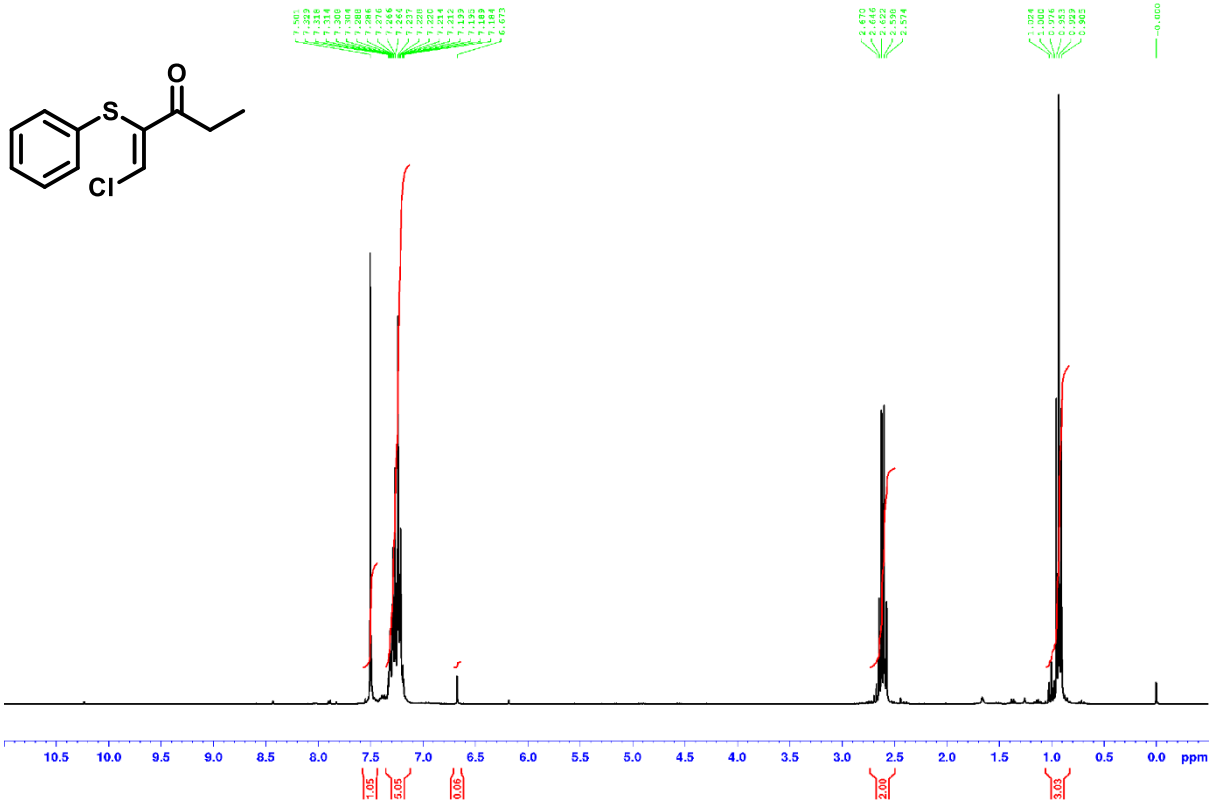


Figure S222: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-9b.**

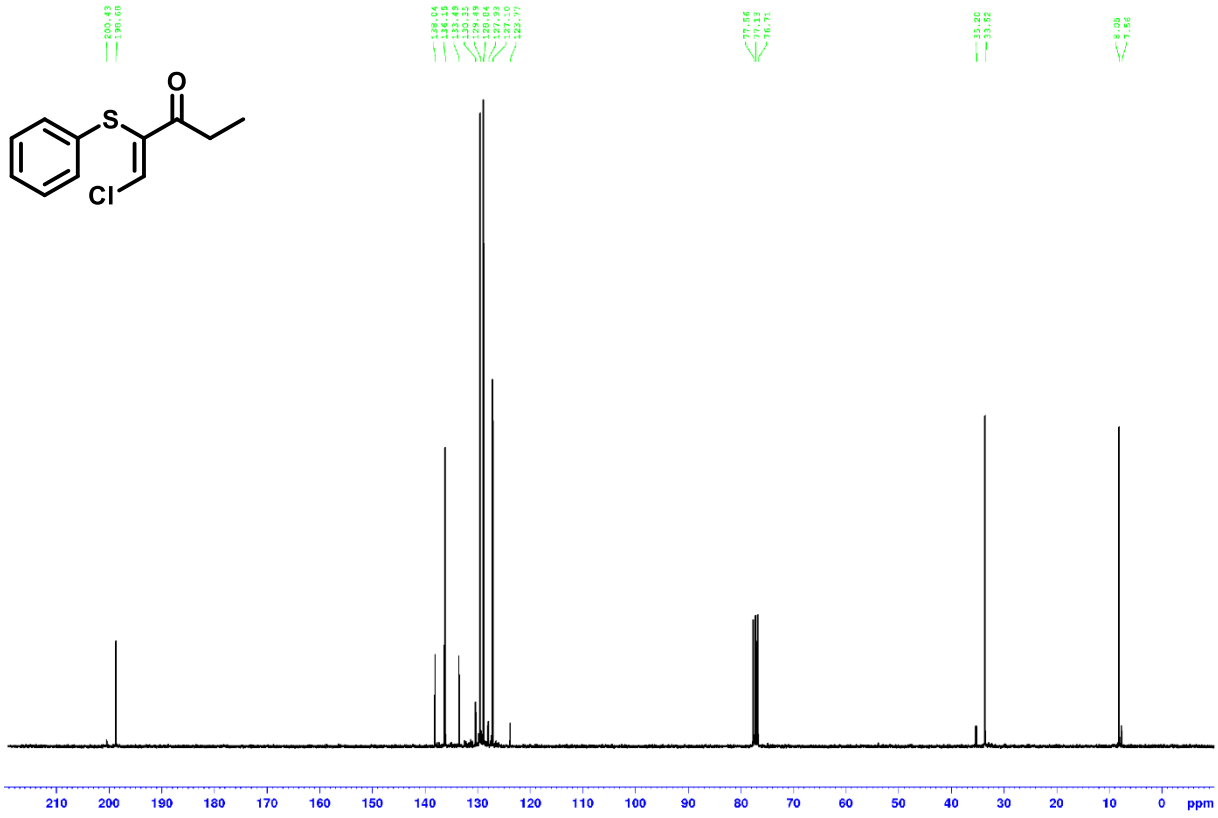


Figure S223: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-9b.**

2-(Benzylthio)-1,2-dichloropentan-3-one S57

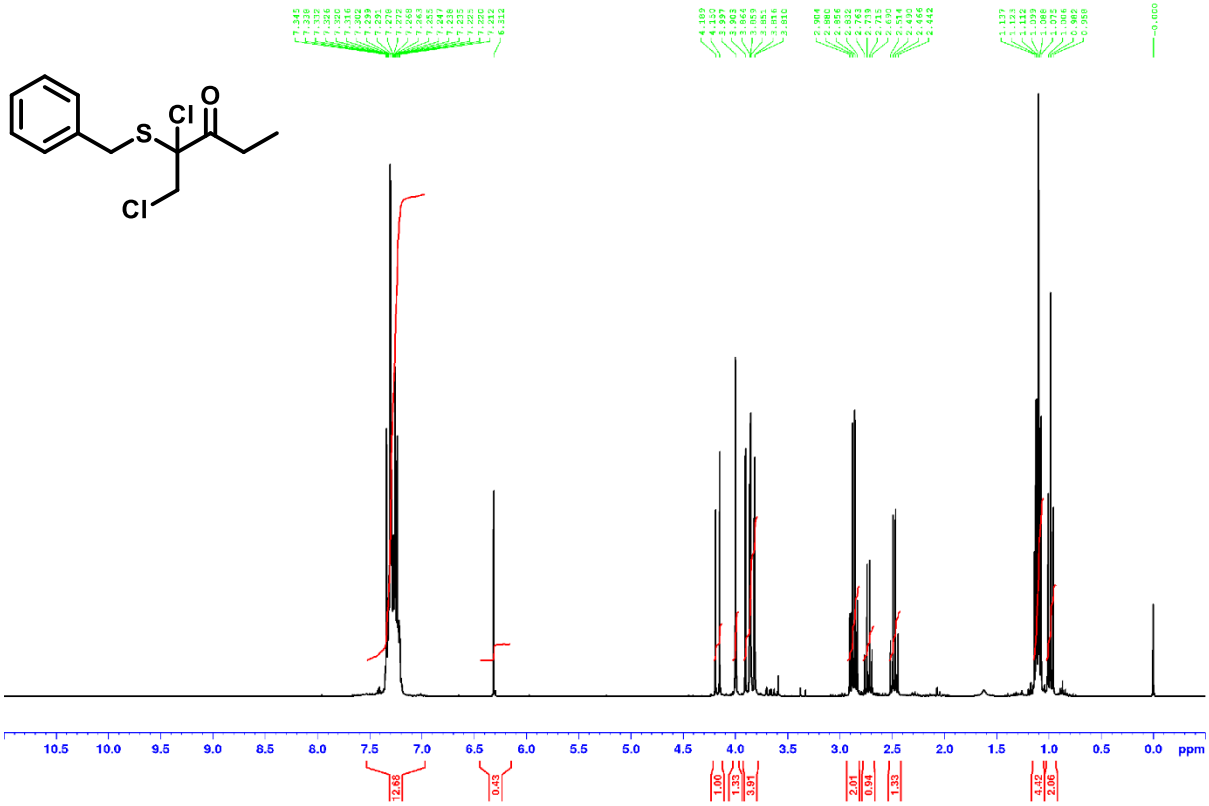


Figure S224: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S57 (46%), Z-9c (32%), E-9c (21%).**

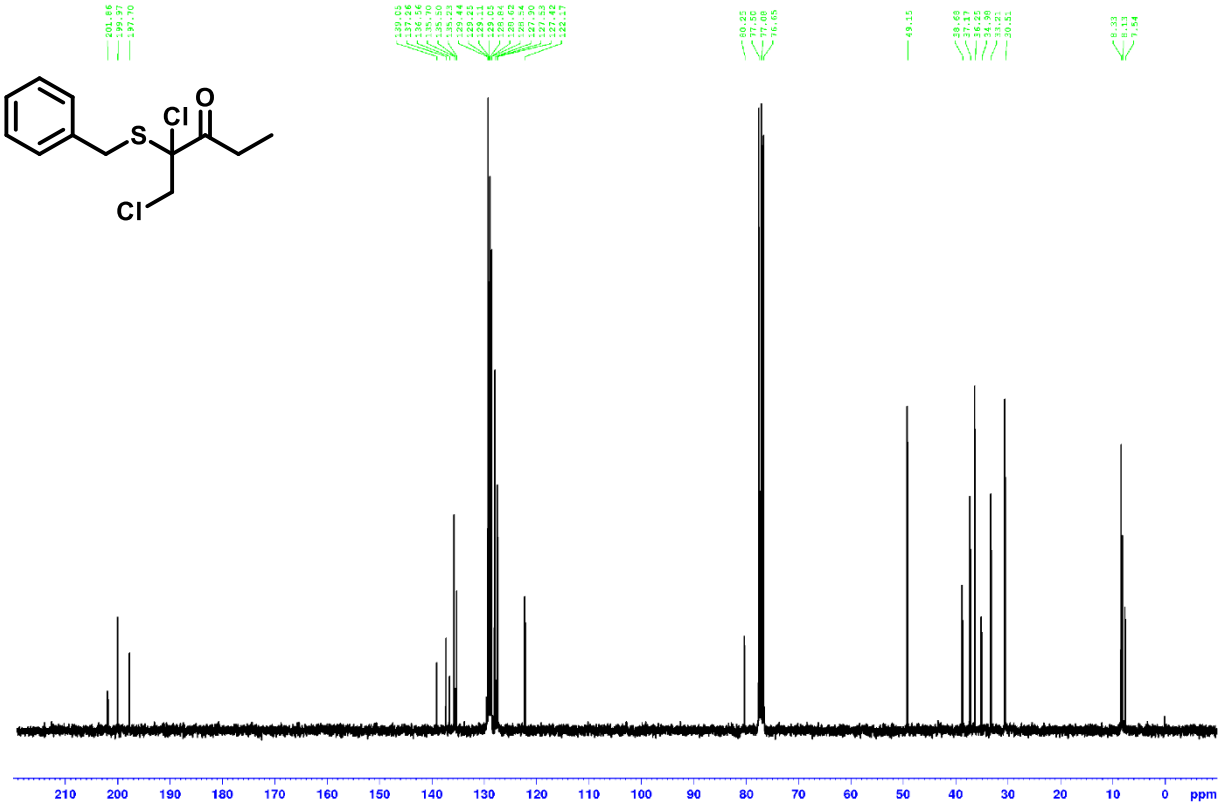


Figure S225: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **S57 (46%), Z-9c (32%), E-9c (21%).**

(*Z*)-2-(Benzylthio)-1-chloropent-1-en-3-one Z-9c and (*E*)-2-(benzylthio)-1-chloropent-1-en-3-one E-9c

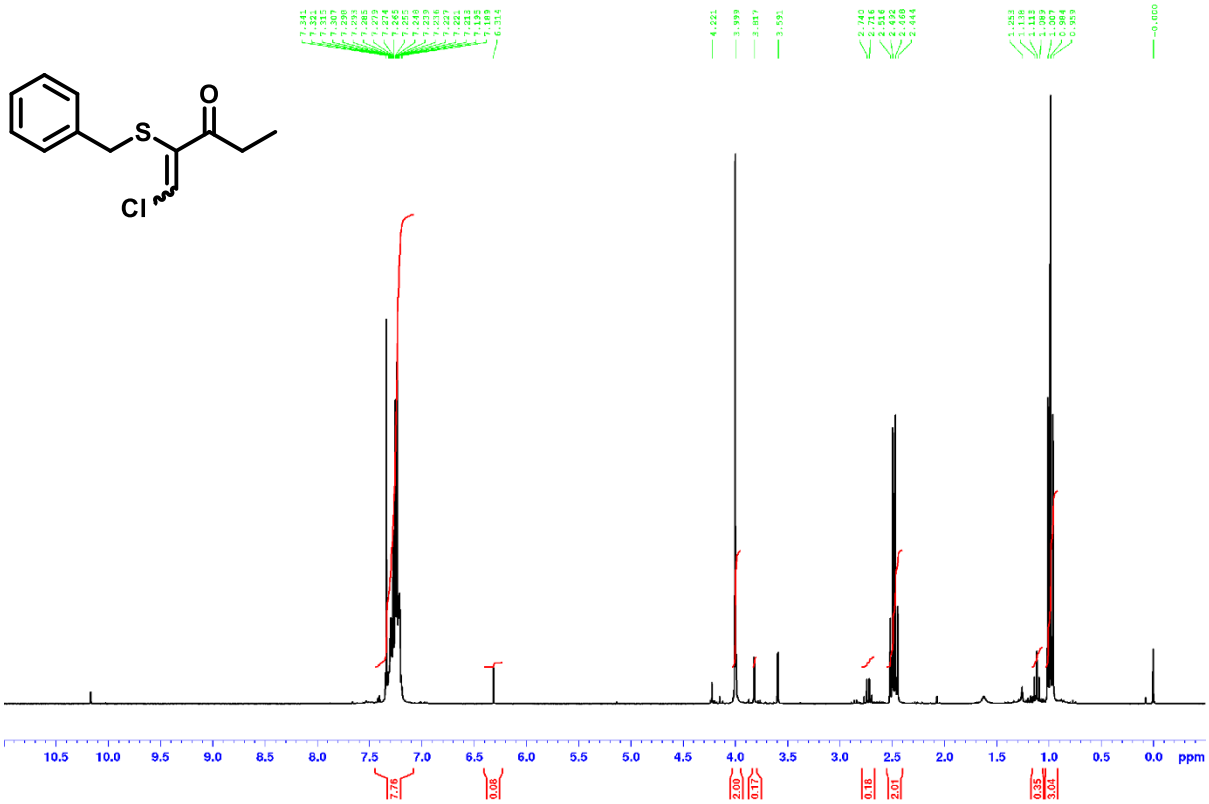


Figure S226: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-9c** and **E-9c.**

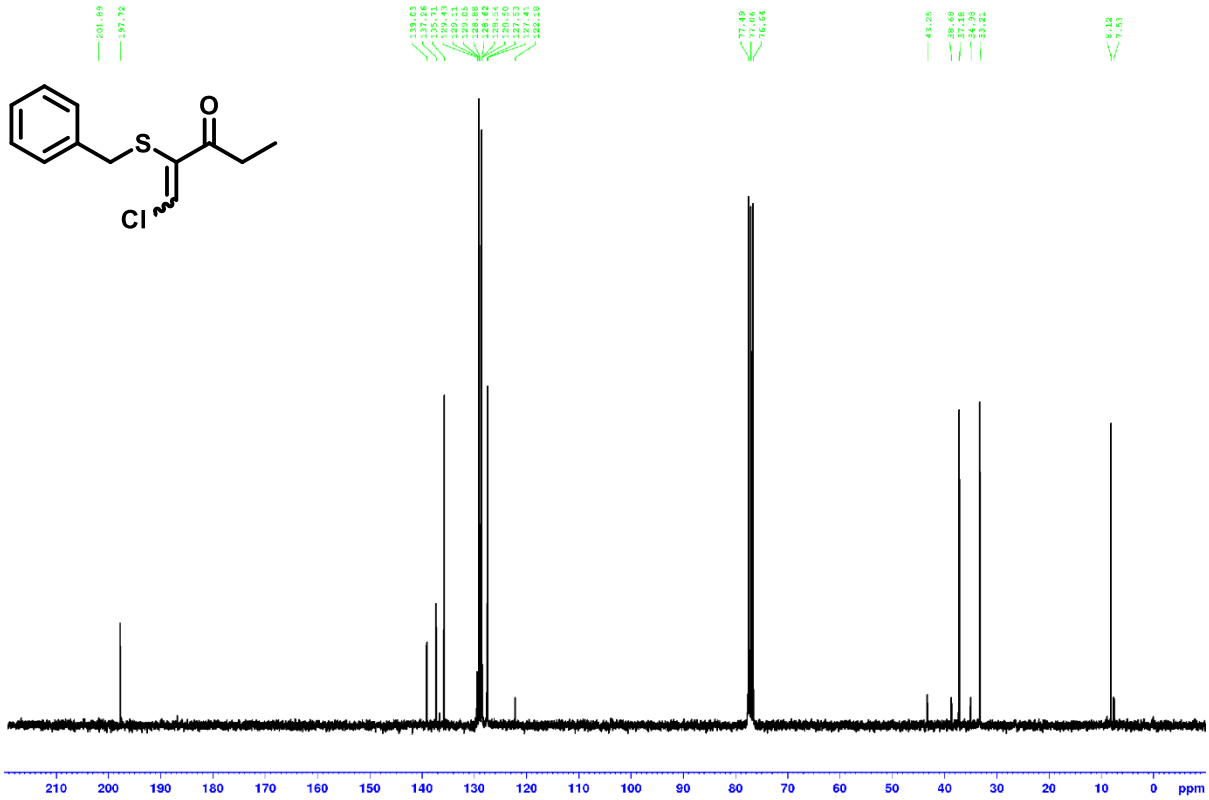


Figure S227: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-9c** and **E-9c.**

3-[(4-Bromophenyl)thio]-3,4-dichlorobutan-2-one S59[17]

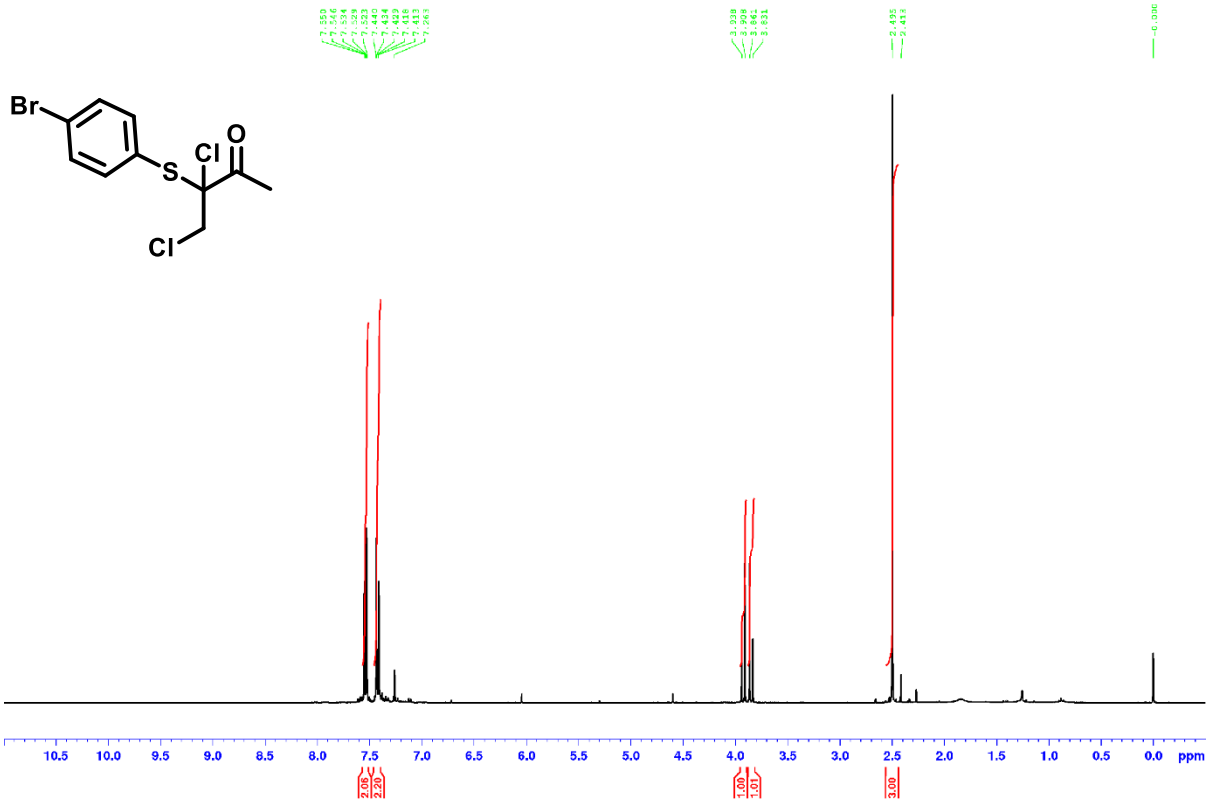


Figure S228: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S59.**

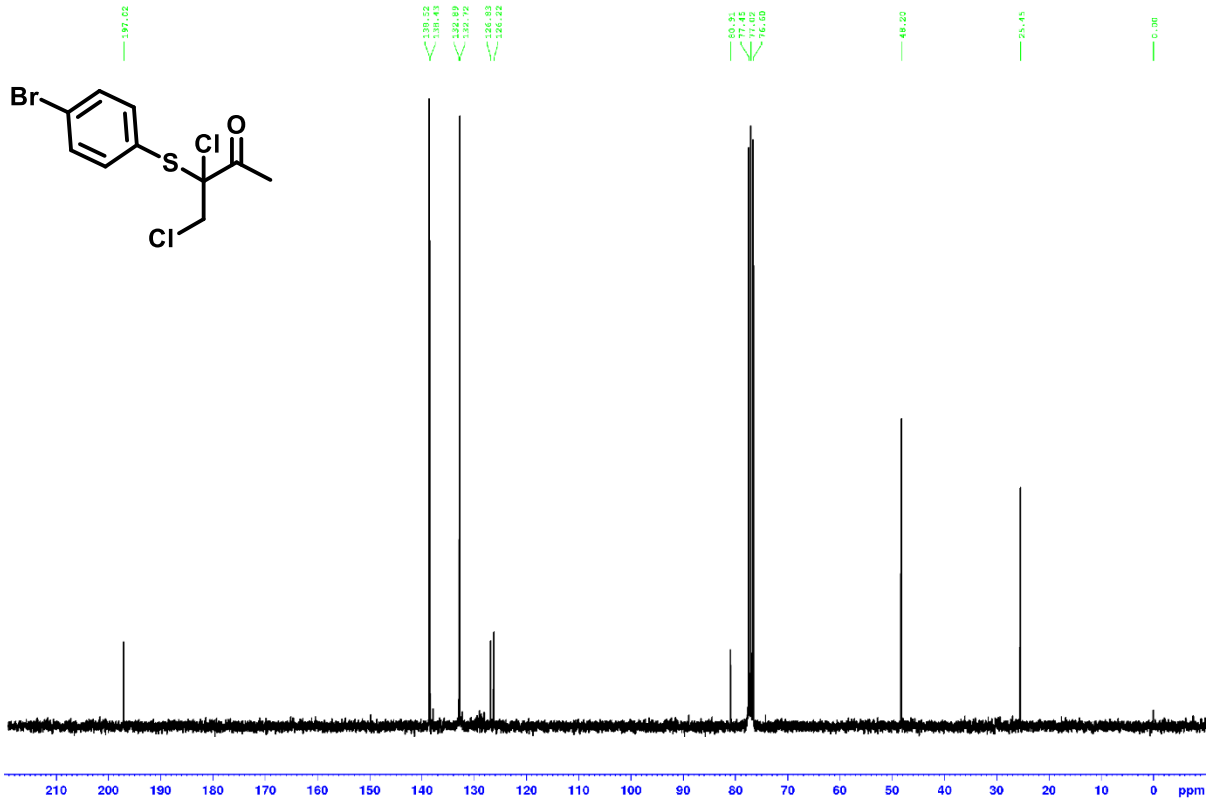


Figure S229: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **S59.**

3-(Benzylthio)-3,4-dichlorobutan-2-one S60

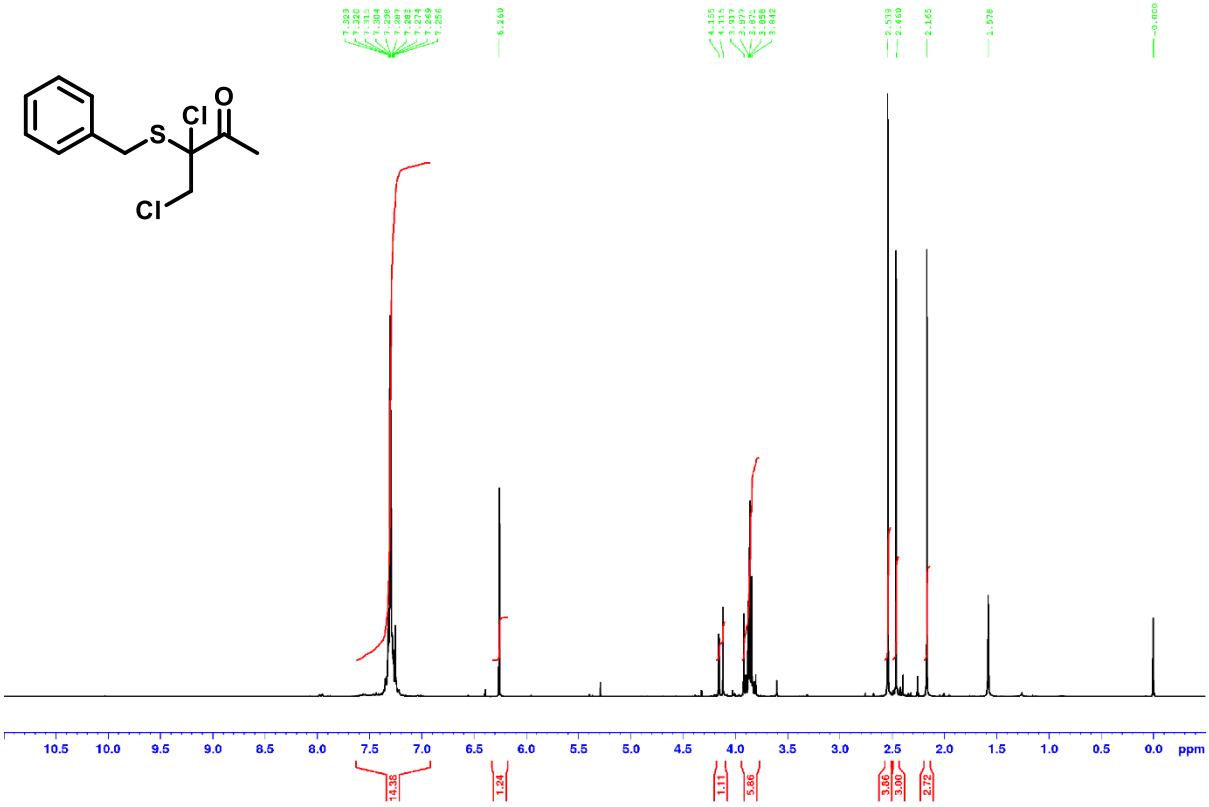


Figure S230: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **S60 (35%), Z-9e (32%), S61 (33%).**

1.12.8 Zinc Chloride Catalysed Elimination to α-Sulfenyl-β-chloroenones:

(*Z*)-3-[(Benzyl)thio]-4-chlorobut-3-en-2-one Z-9a

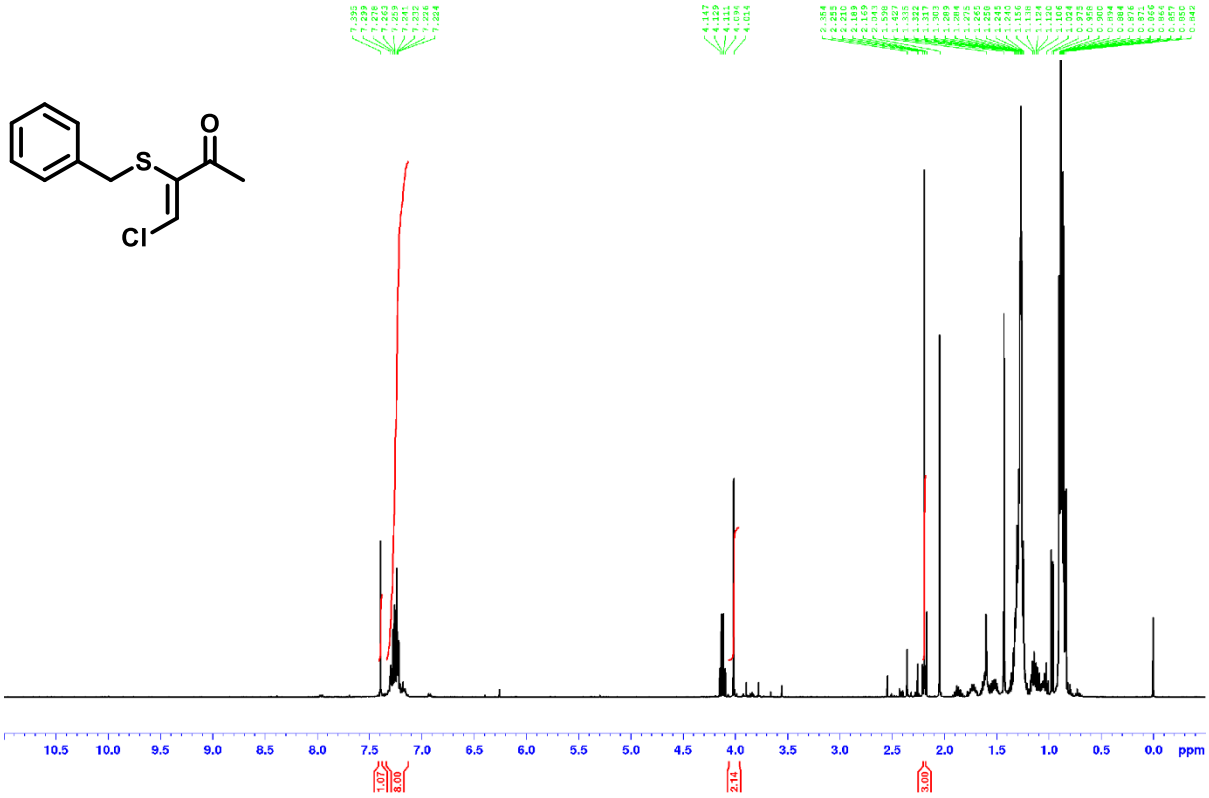


Figure S231: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-9a.**

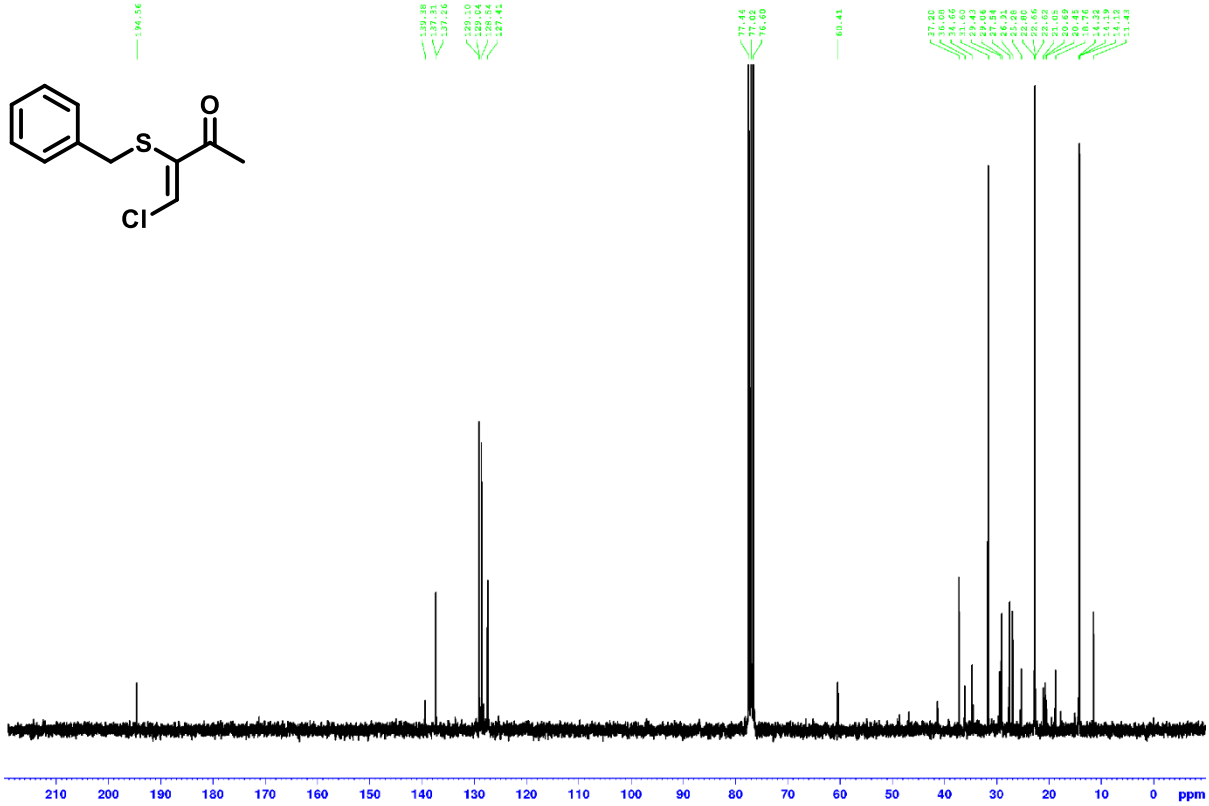


Figure S232: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-9a.**

1.12.9 Synthesis of Chalcones

(*Z*)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-(*p*-tolyl)prop-2-en-1-one 14

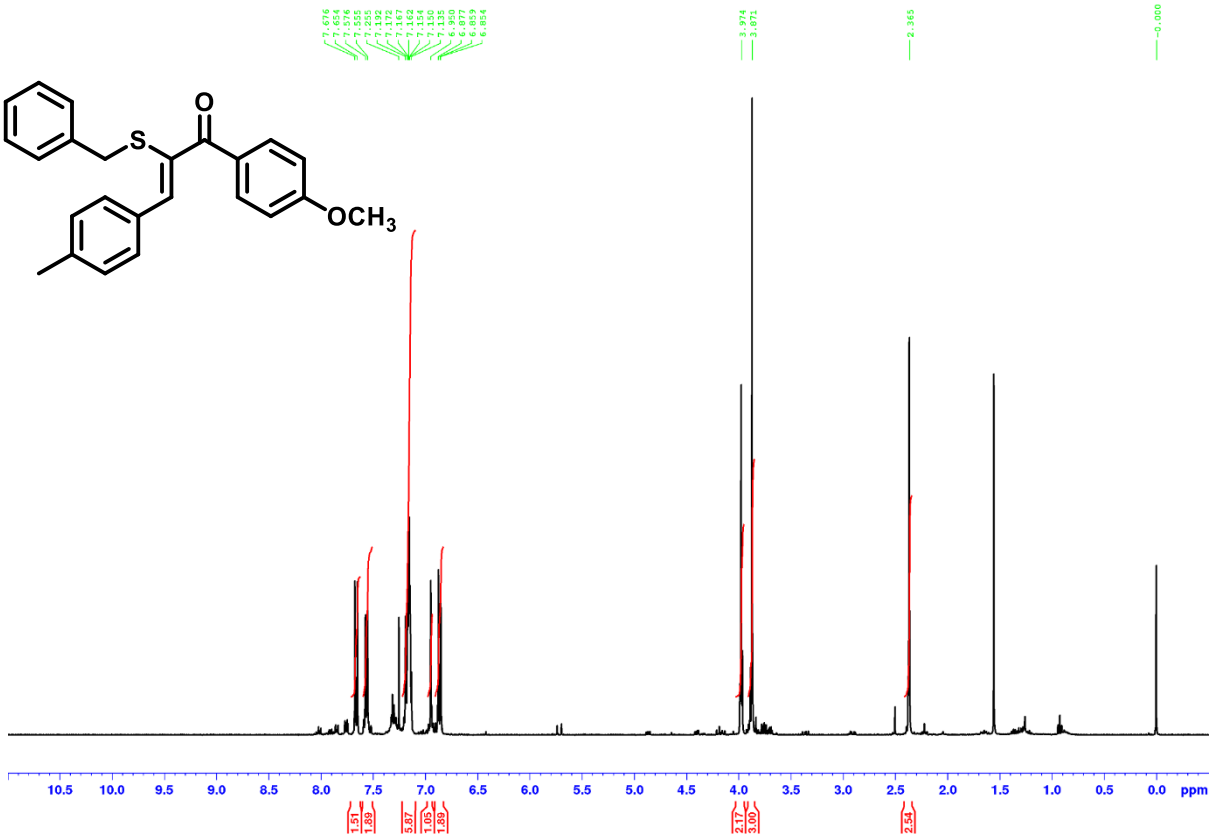


Figure S233: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ***Z*-14**.

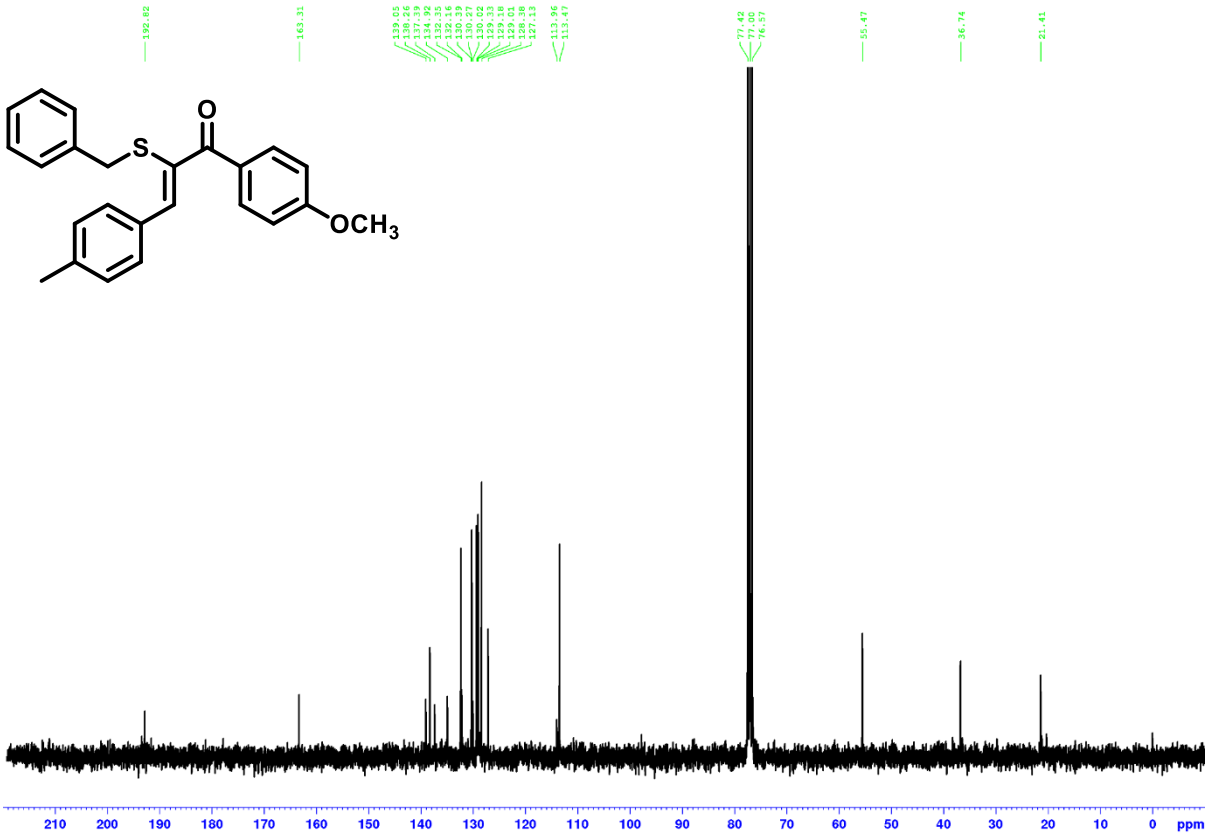


Figure S234: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-14.**

(*Z*)-2-(Benzylthio)-3-(4-fluorophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 15

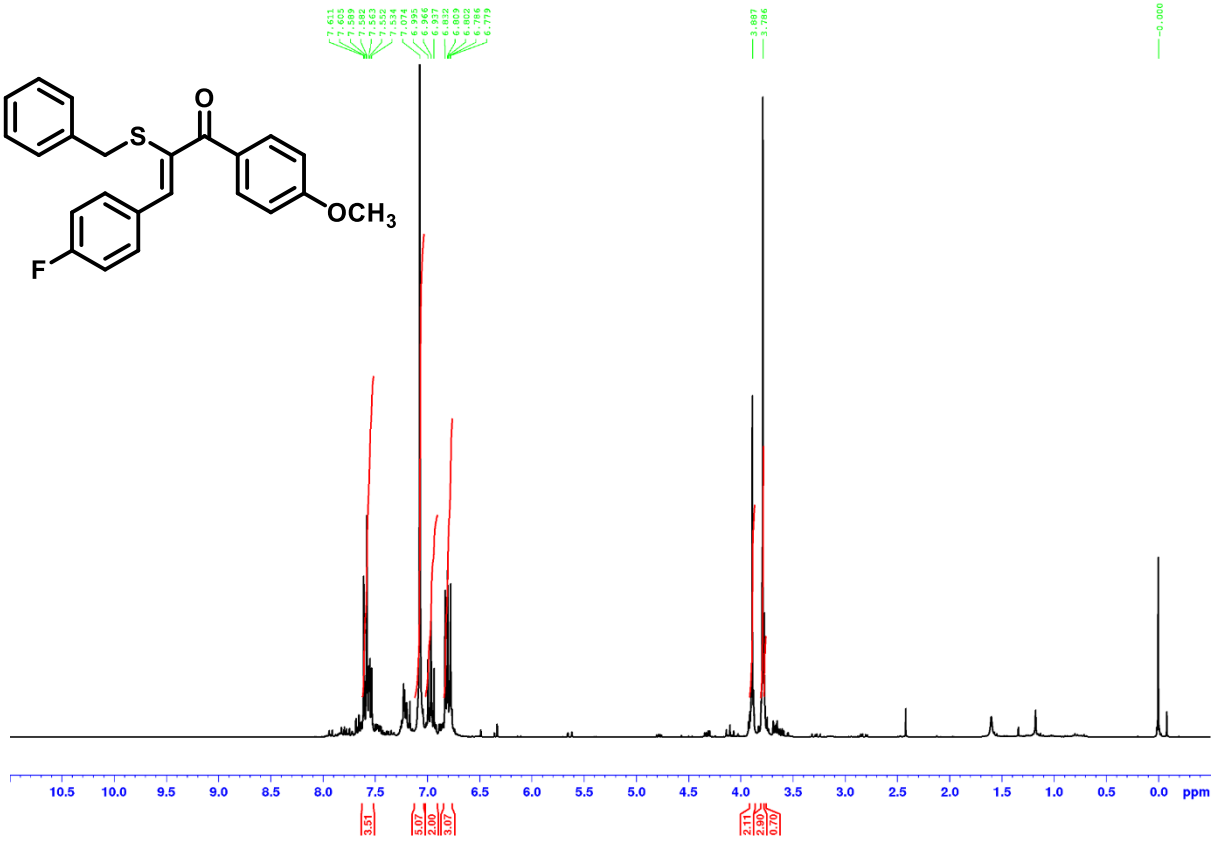


Figure S235: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **Z-15**.

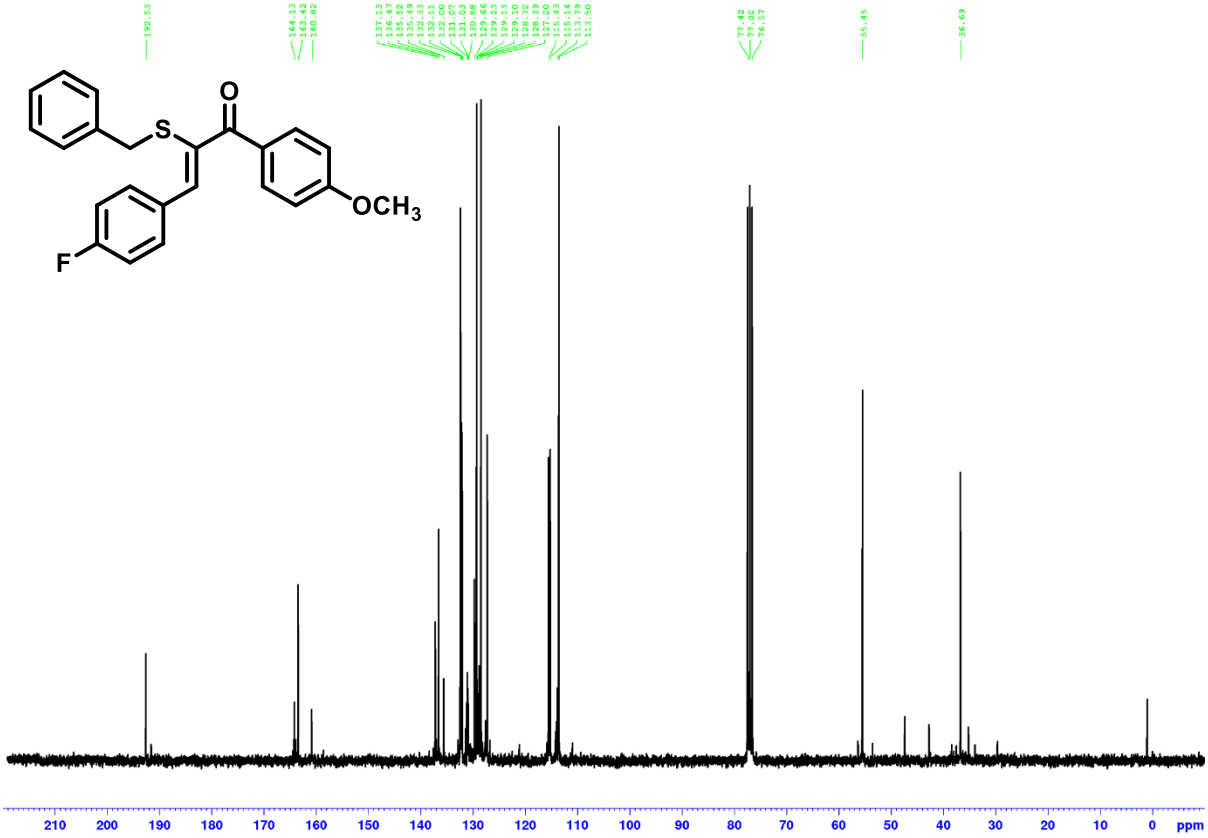


Figure S236: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **Z-15**.

(*Z*)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one 16

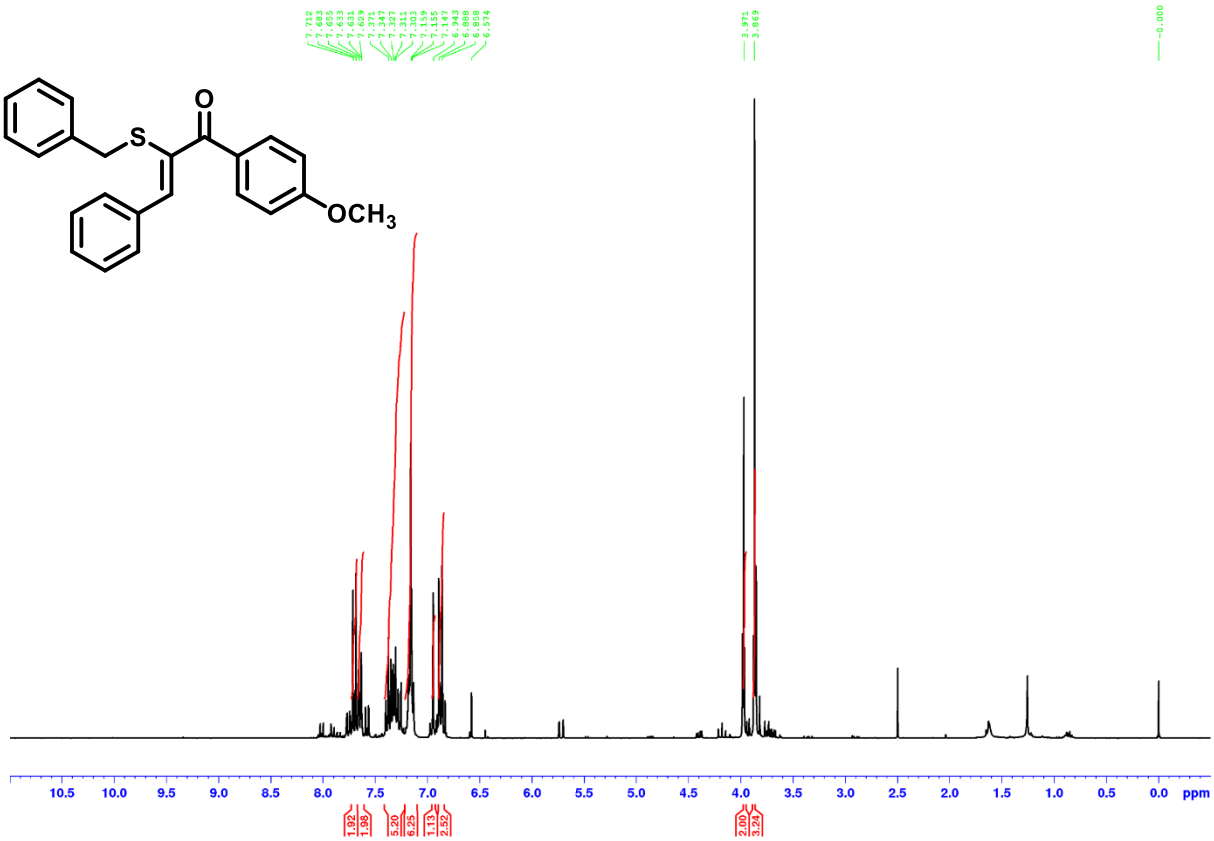


Figure S237: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ***Z*-16**.

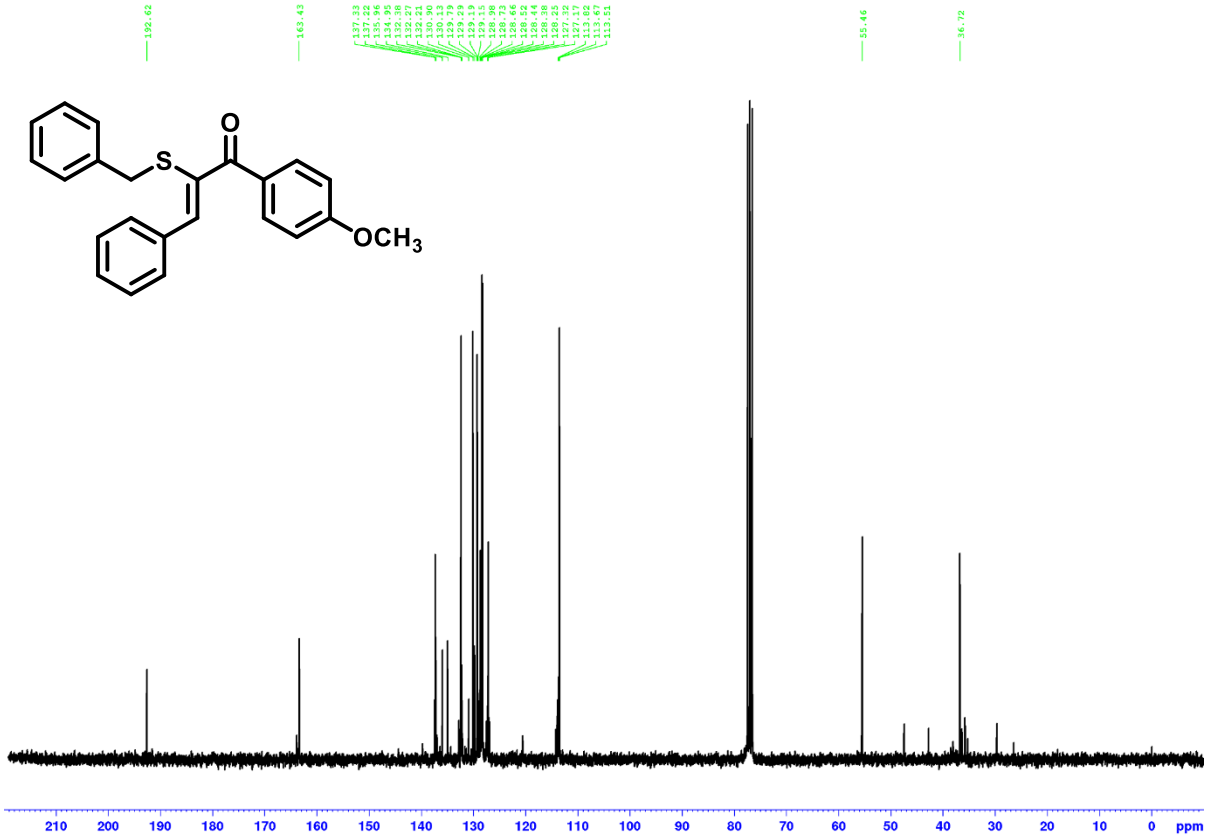


Figure S238: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-16**.

(*Z*)-2-(Benzylthio)-1,3-bis(4-methoxyphenyl)prop-2-en-1-one 17

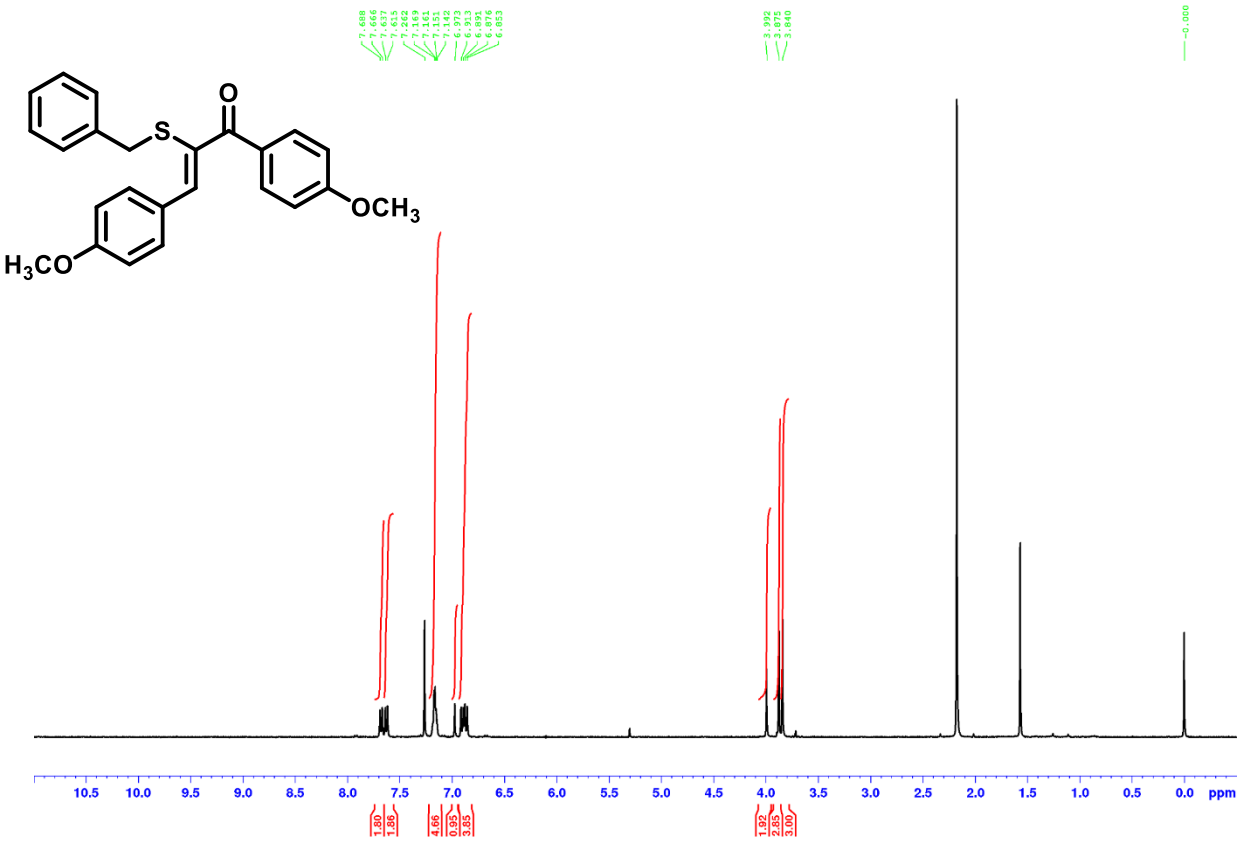


Figure S239: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-17**.

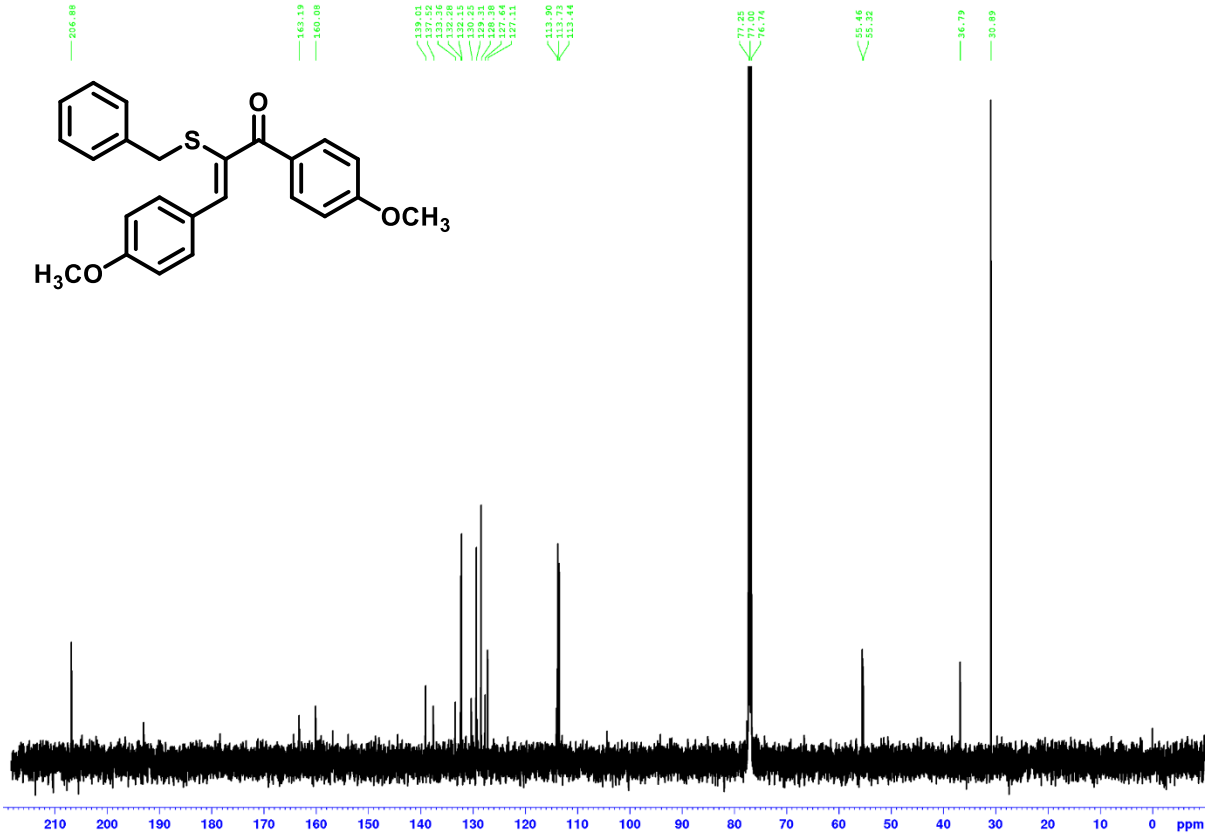


Figure S240: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-17**.

(*Z*)-2-(Benzylthio)-3-(3-methoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one 15ev

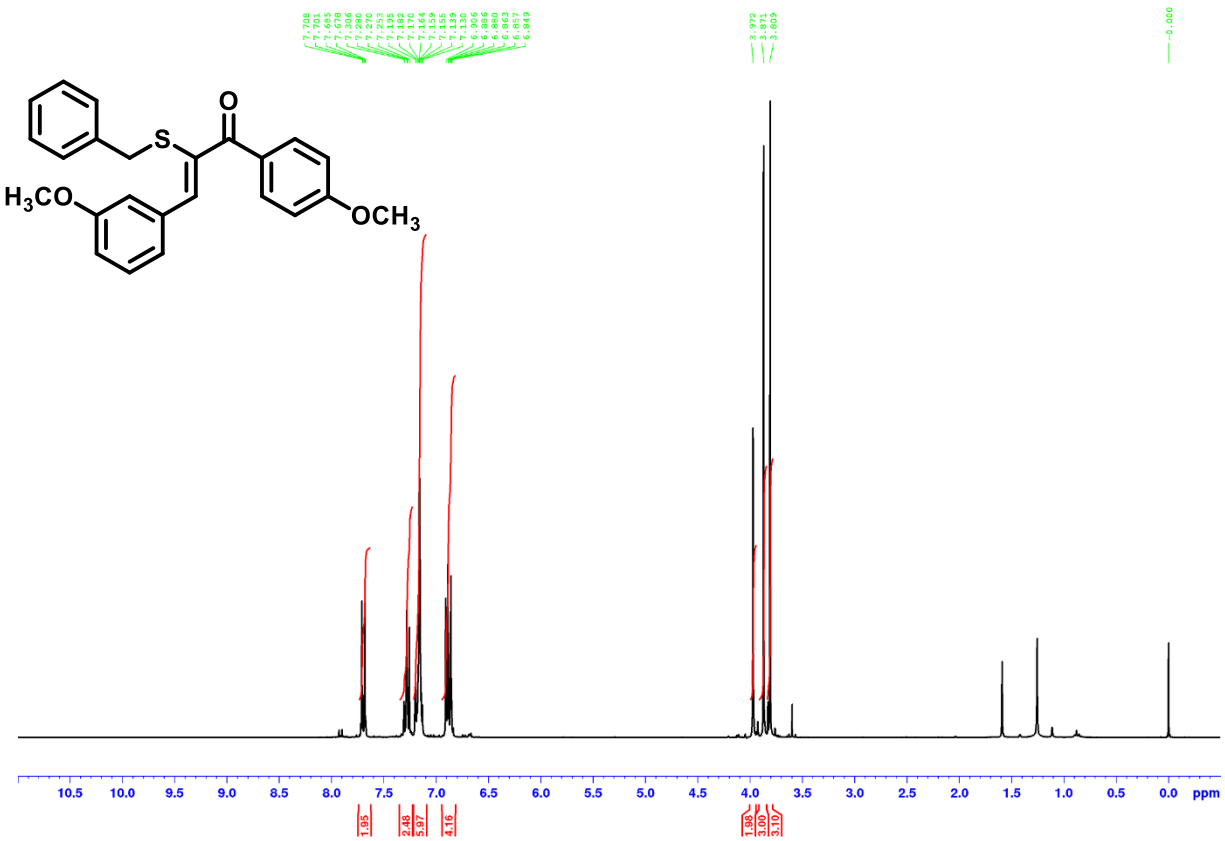


Figure S241: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-18**.

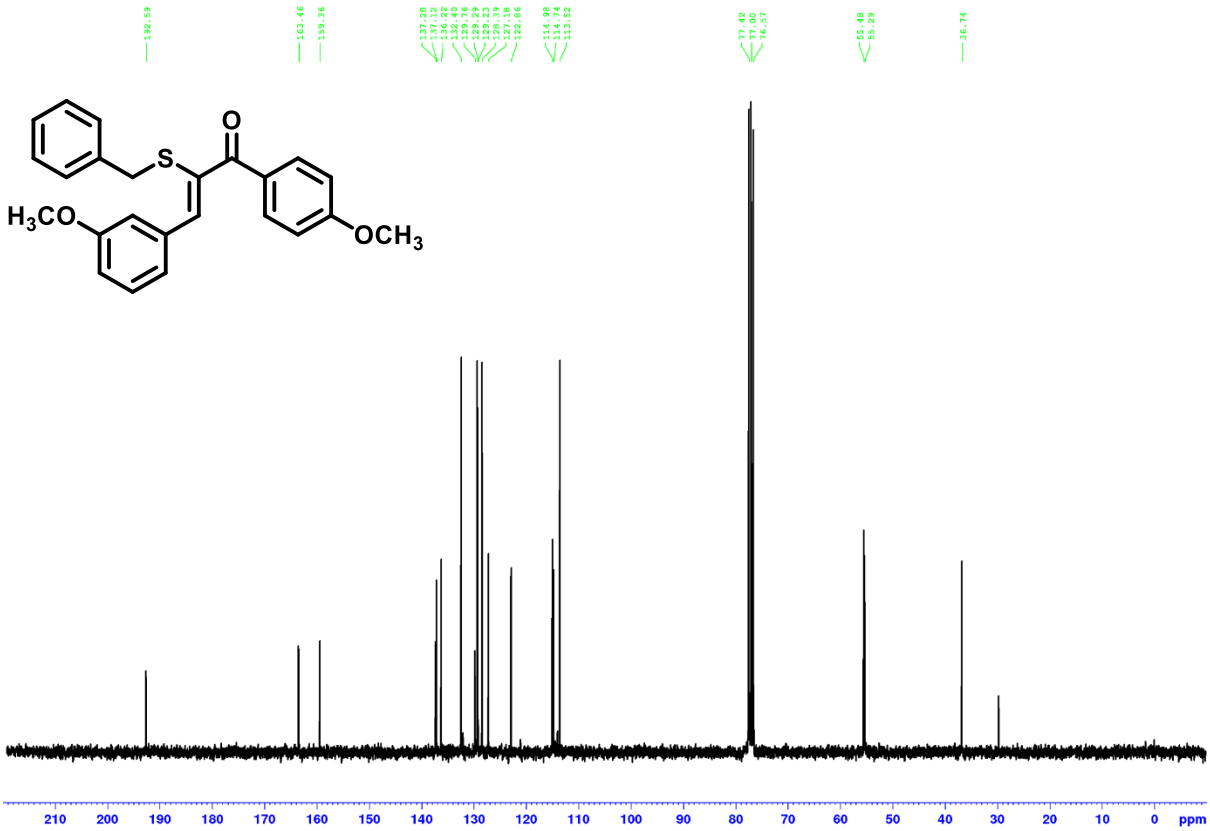


Figure S242: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-18.**

(*Z*)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-one 19

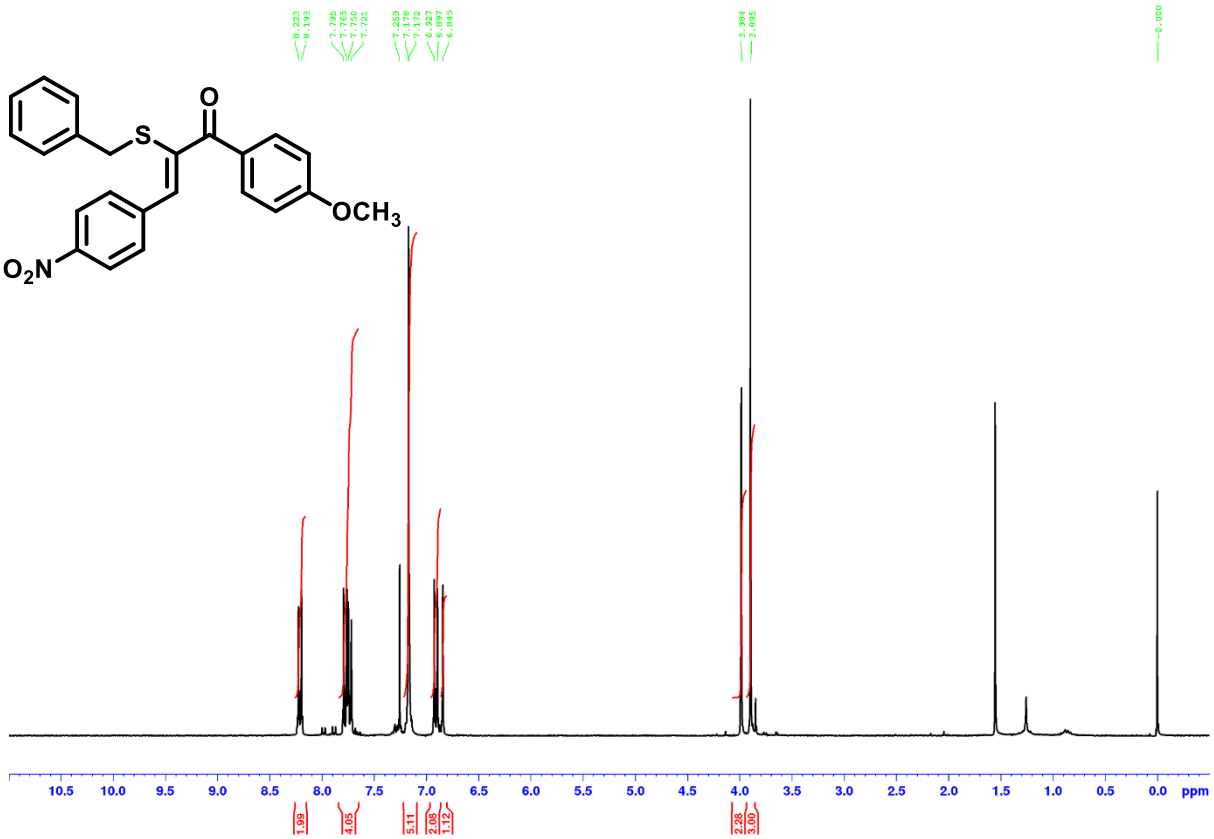


Figure S243: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-19**.

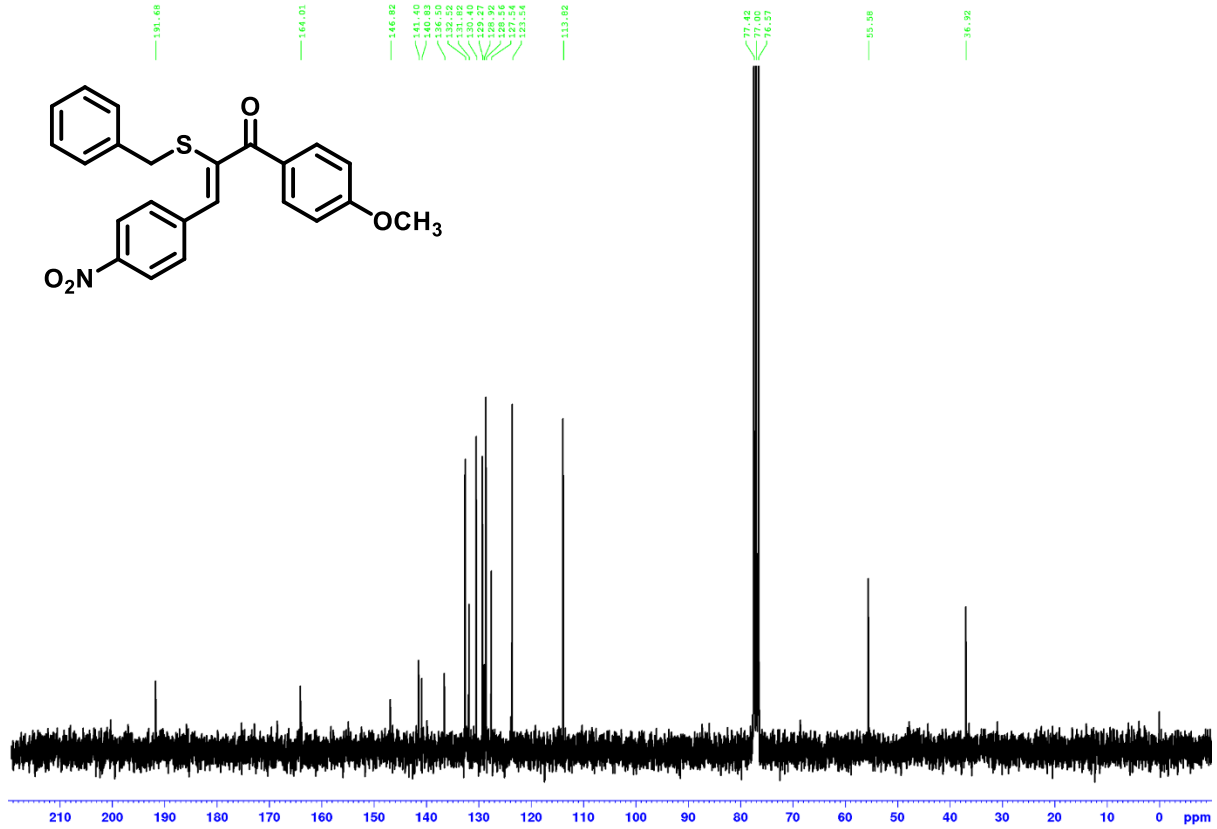


Figure S244: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-19**.

(*Z*)-2-(Benzylthio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 20

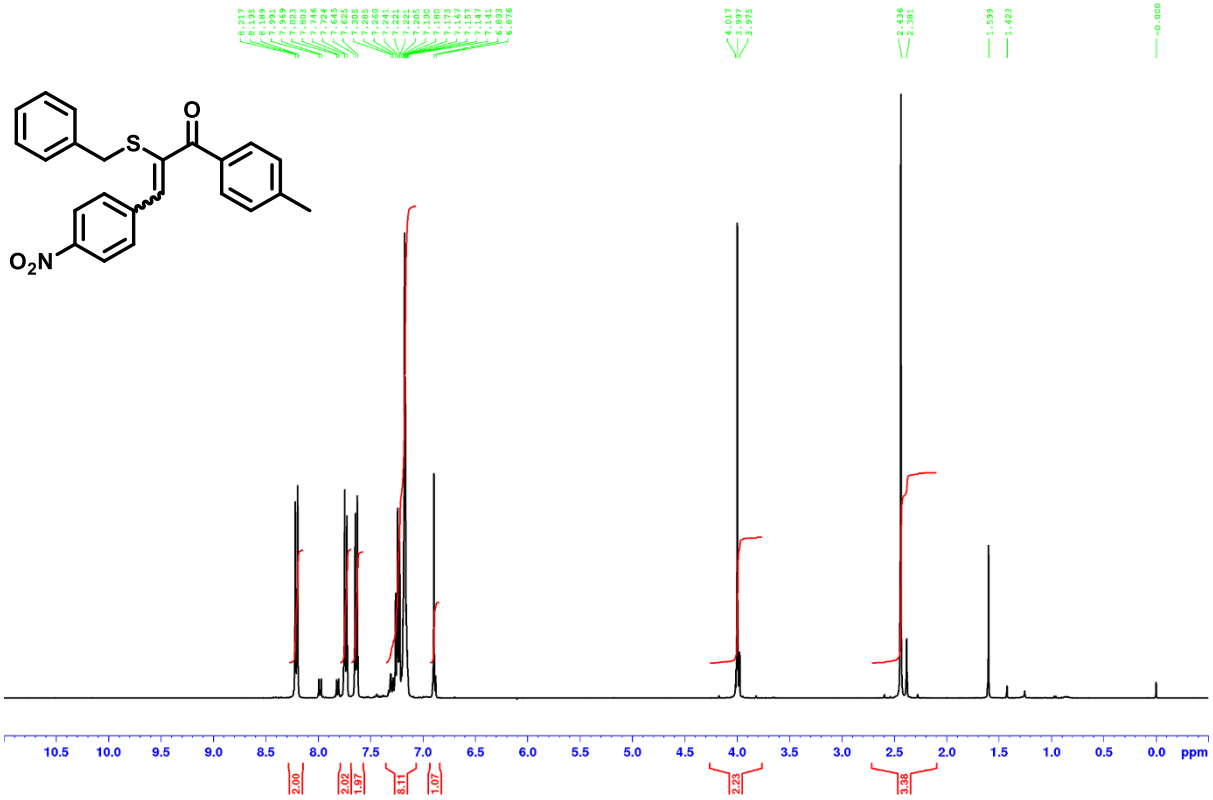


Figure S245: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Z-**20** and *E*-**20** (*Z*:*E*, 10.6:1).

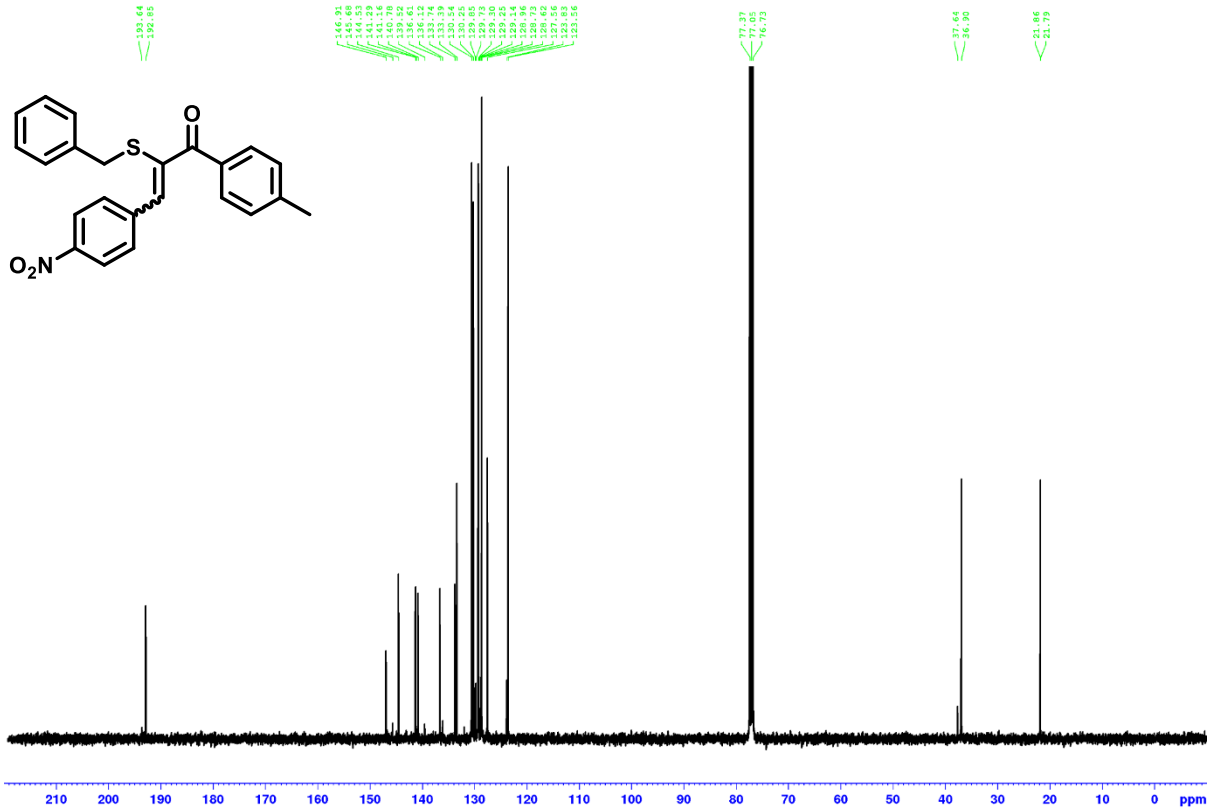


Figure S246: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Z-**20** and *E*-**20** (*Z*:*E*, 10.6:1).

4,4'-Dinitro-1,1'-biphenyl 37[26]

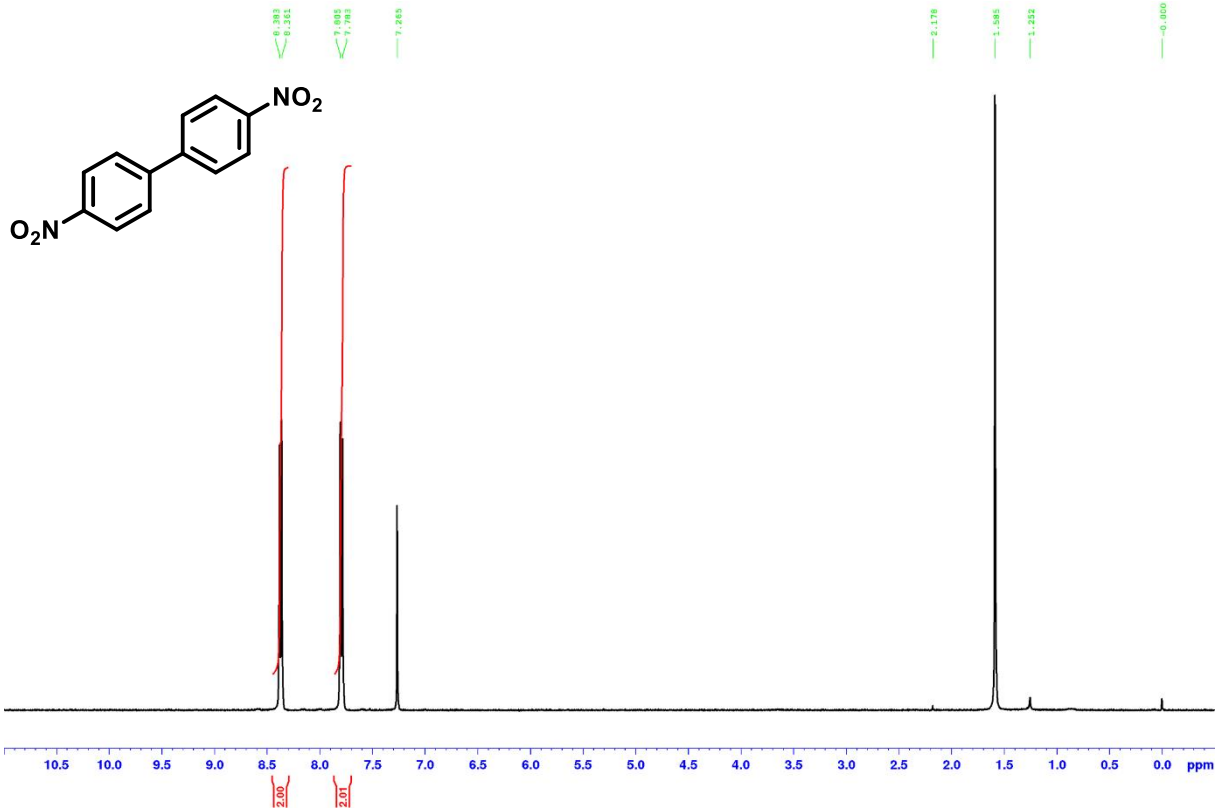


Figure S247: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **37**[26]

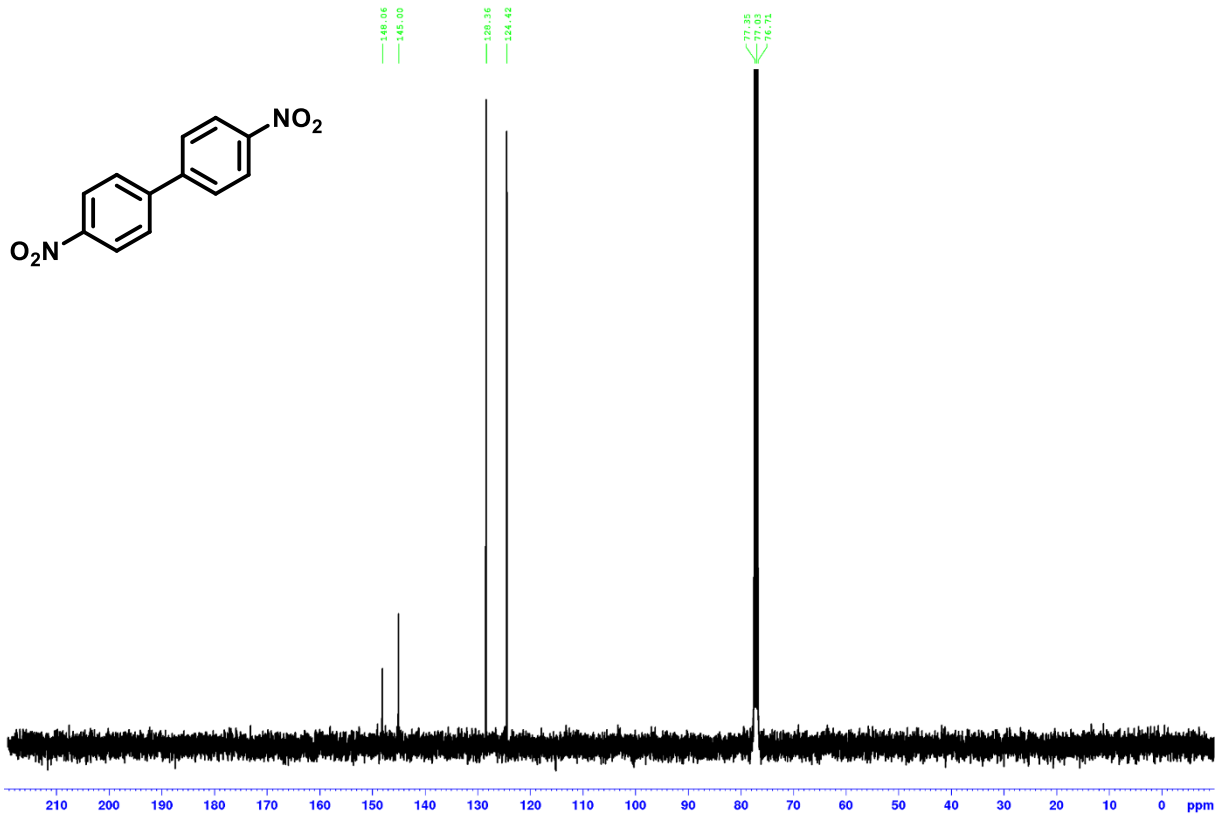


Figure S248: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **37**[26]

(*Z*)-2-((4-Chlorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 21

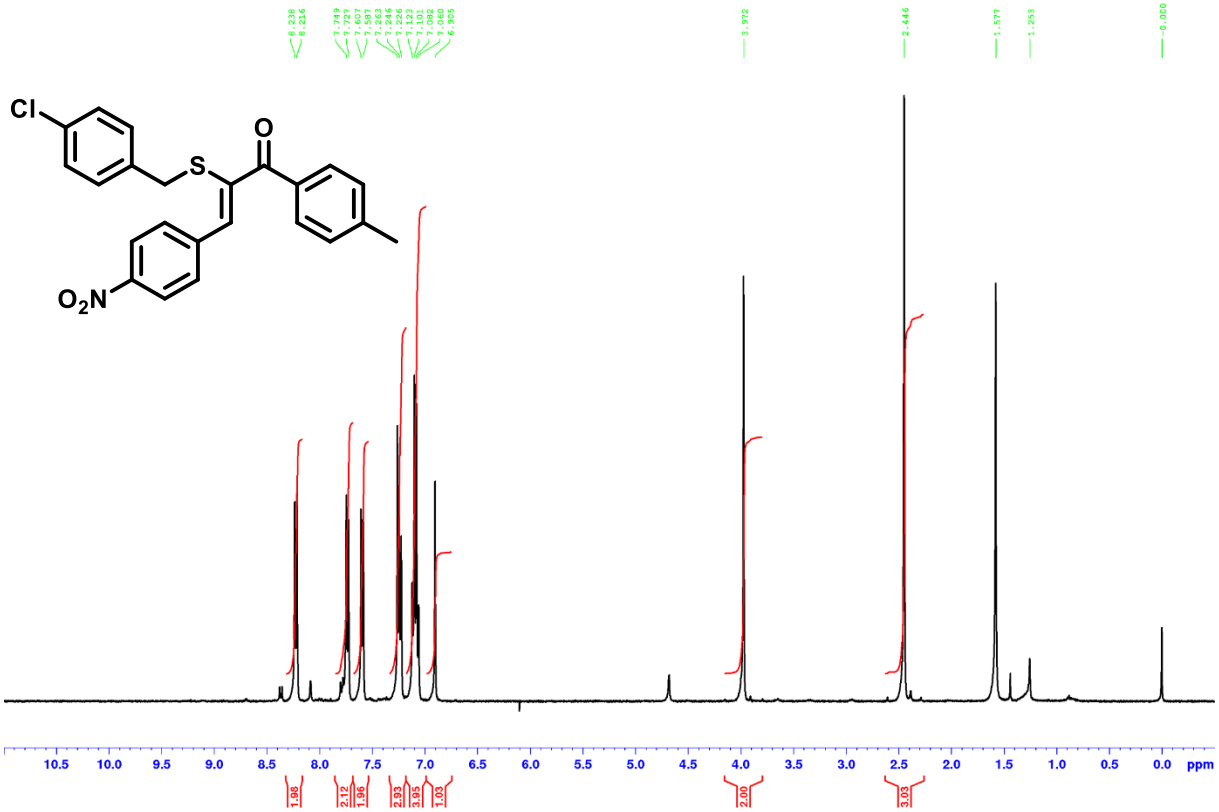


Figure S249: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-21**.

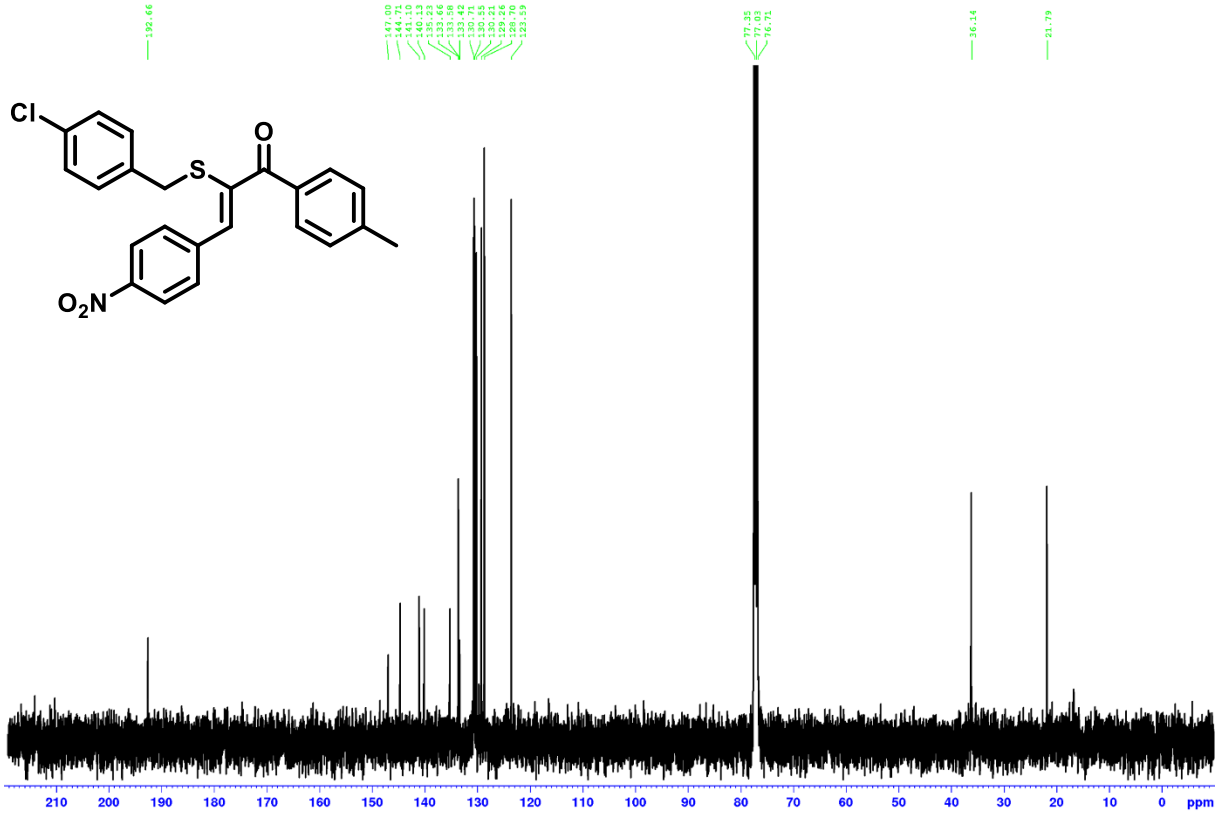


Figure S250: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***Z*-21**.

(*Z*)-2-((4-Fluorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 22 and (*E*)-2-((4-fluorobenzyl)thio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 22

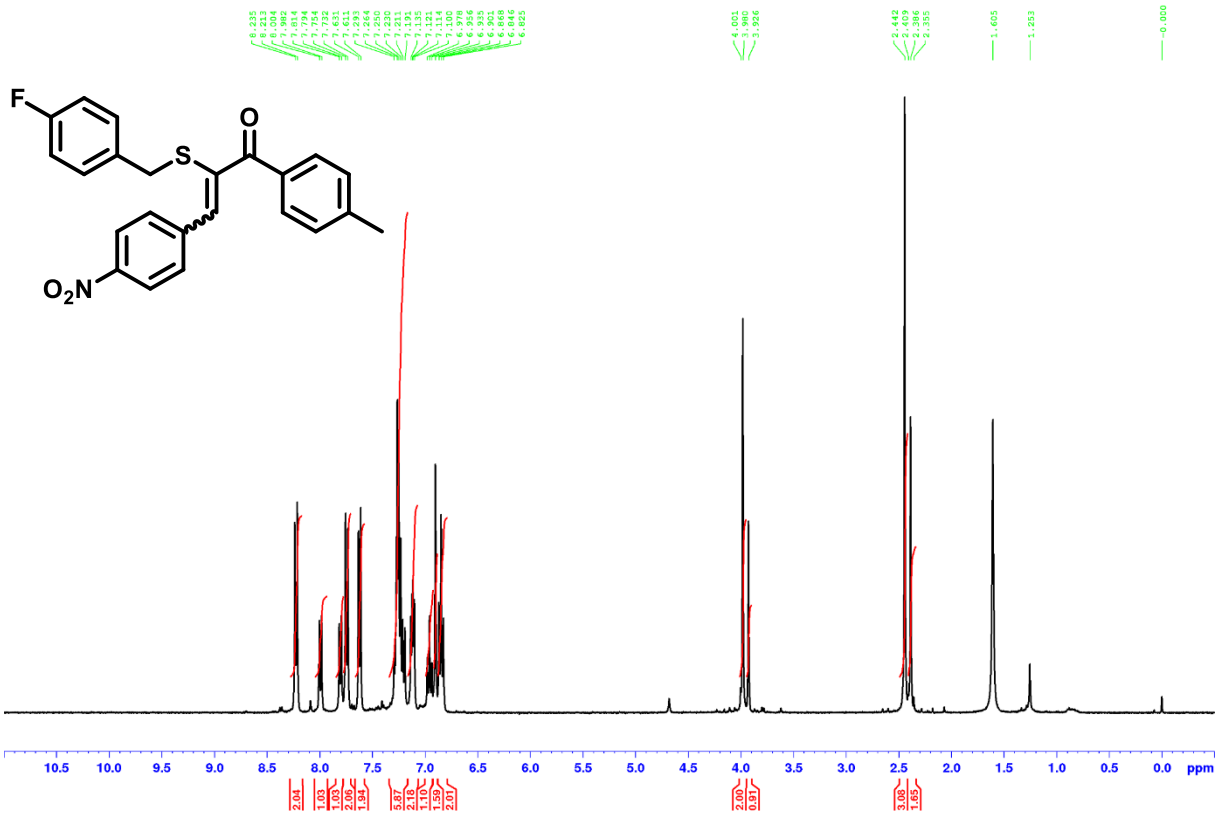


Figure S251: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**21**and *E*-**21** (*Z*:*E*, 3.2:1).

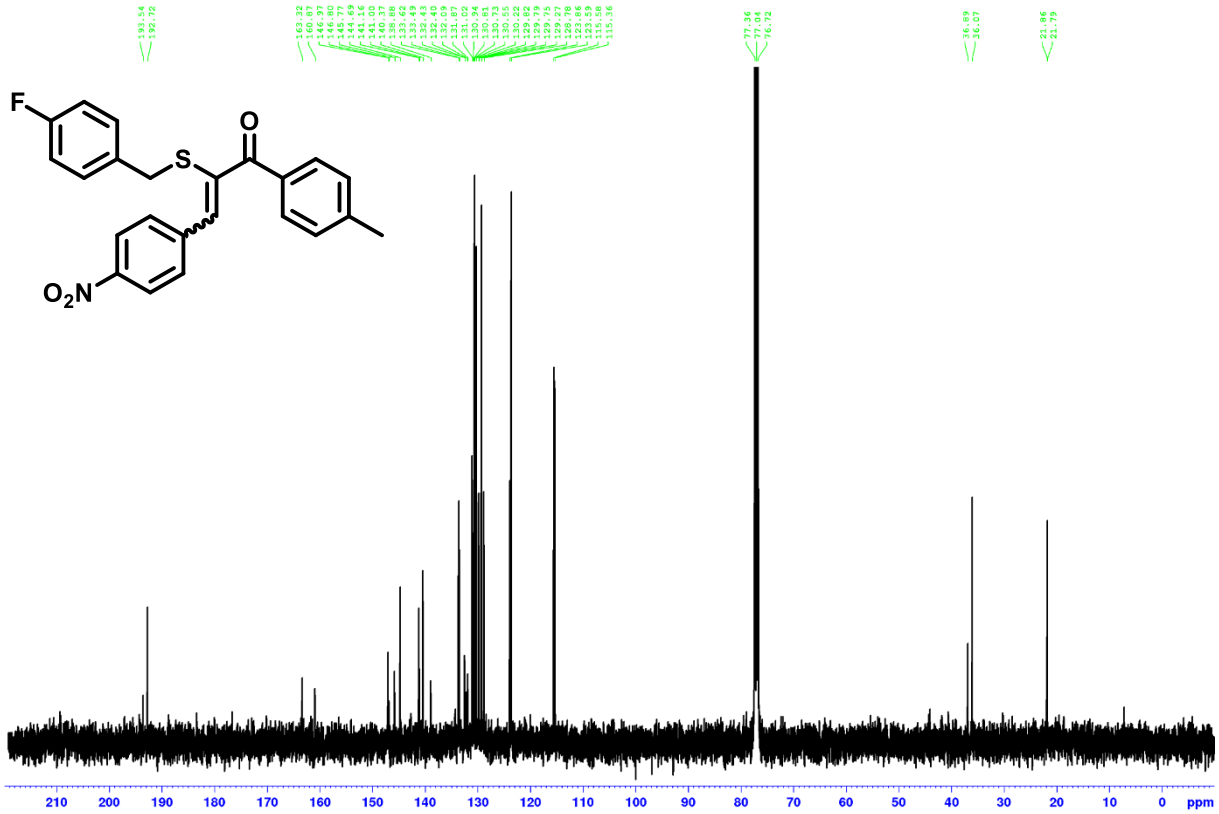


Figure S252: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Z*-**21** and *E*-**21** (*Z*:*E*, 3.2:1).

(*Z*)-2-(Benzylthio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 23 and (*E*)-2-(Benzylthio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 23.

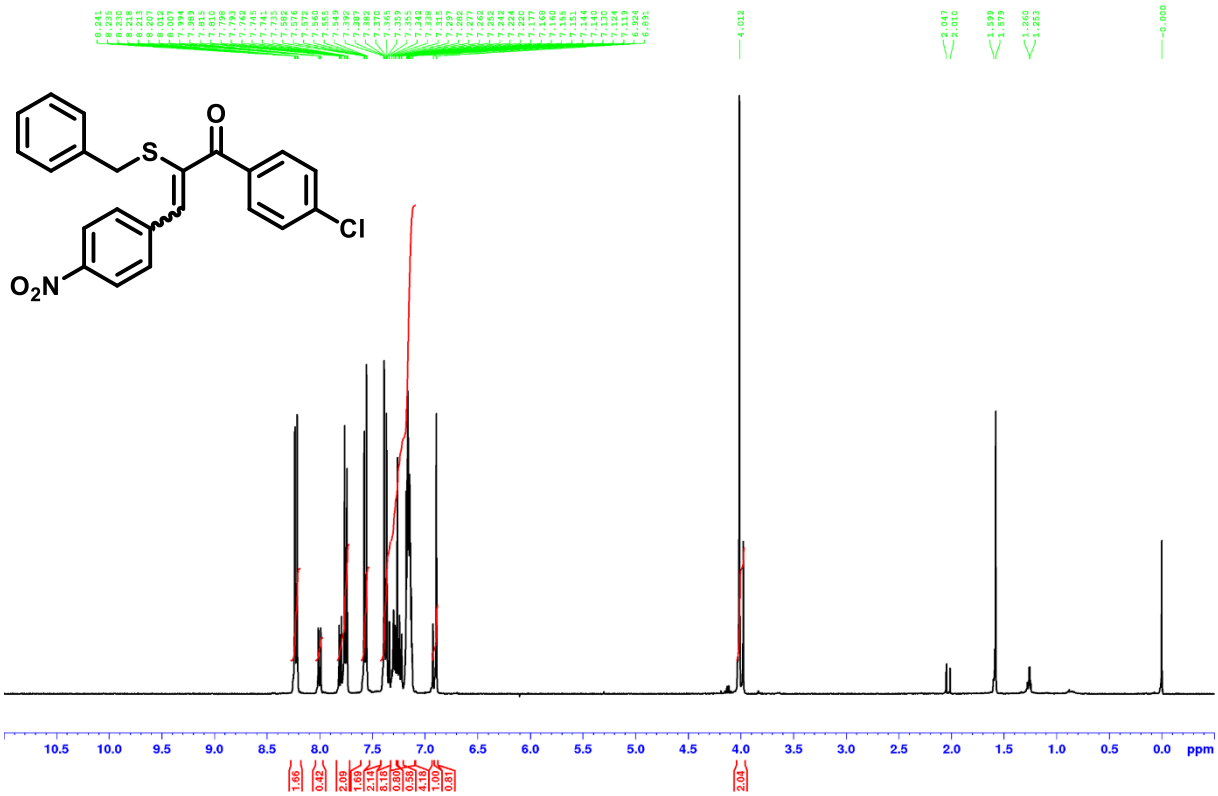


Figure S253: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**23** and *E*-**23** (*Z*:*E*, 4.6:1).

(*Z*)-2-((4-Chlorobenzyl)thio)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 24

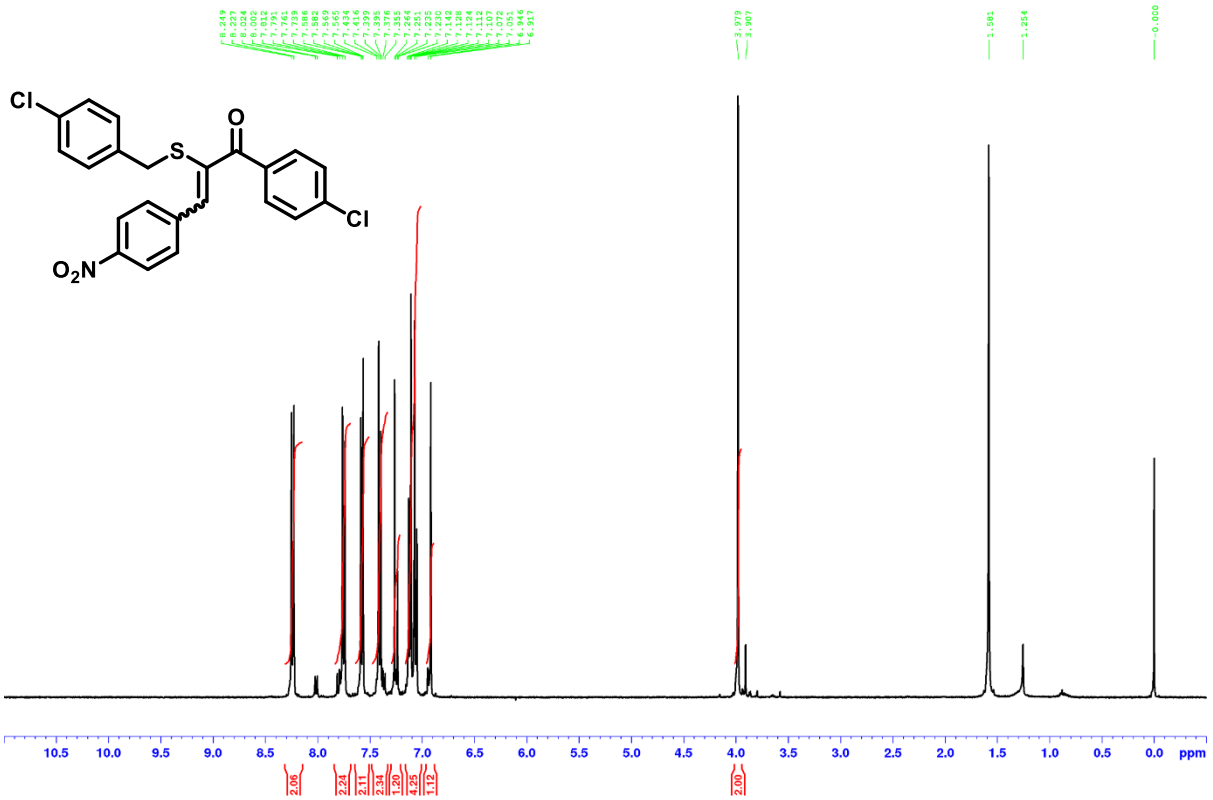


Figure S254: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**24** and *E*-**24** (*Z*:*E*, 30.7:1).

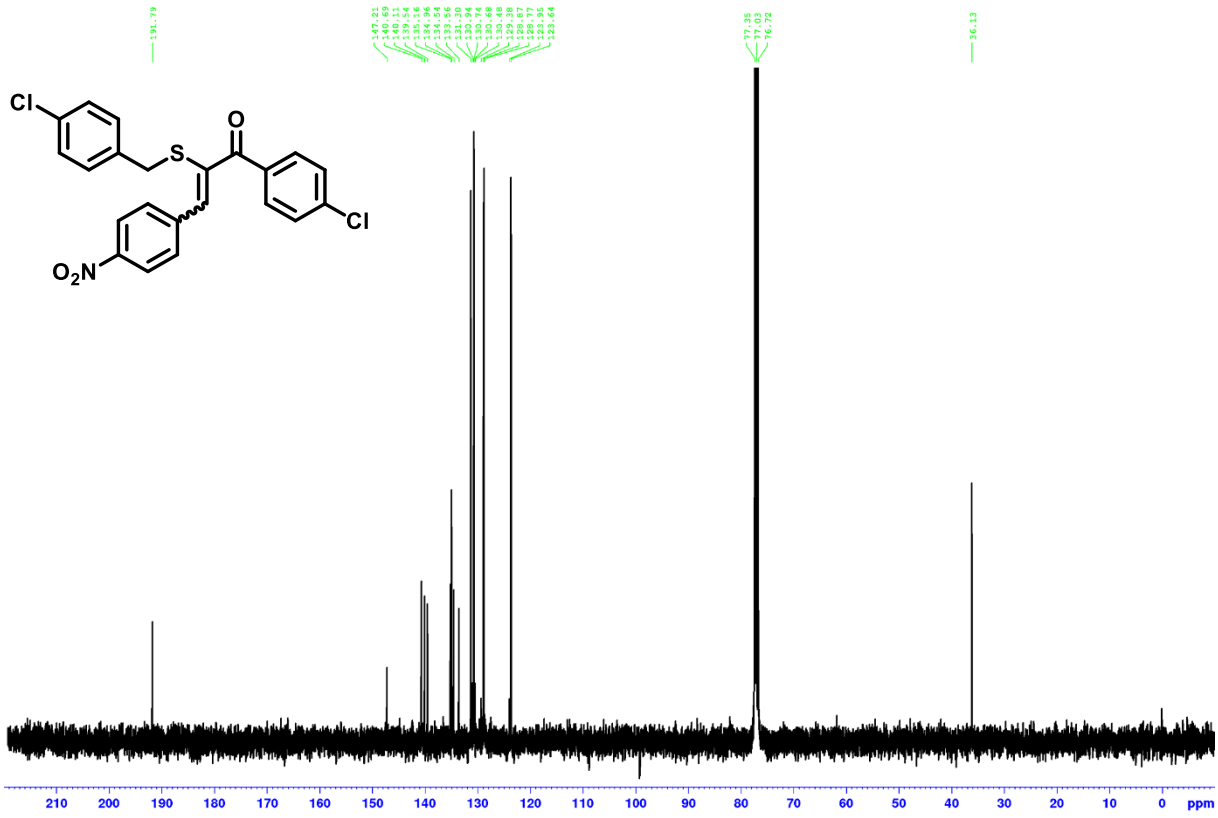


Figure 255: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Z*-**24** and *E*-**24** (*Z*:*E*, 30.7:1).

(*Z*)-1-(4-Chlorophenyl)-2-((4-methoxybenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one 25 and (*E*)-1-(4-Chlorophenyl)-2-((4-methoxybenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one 25

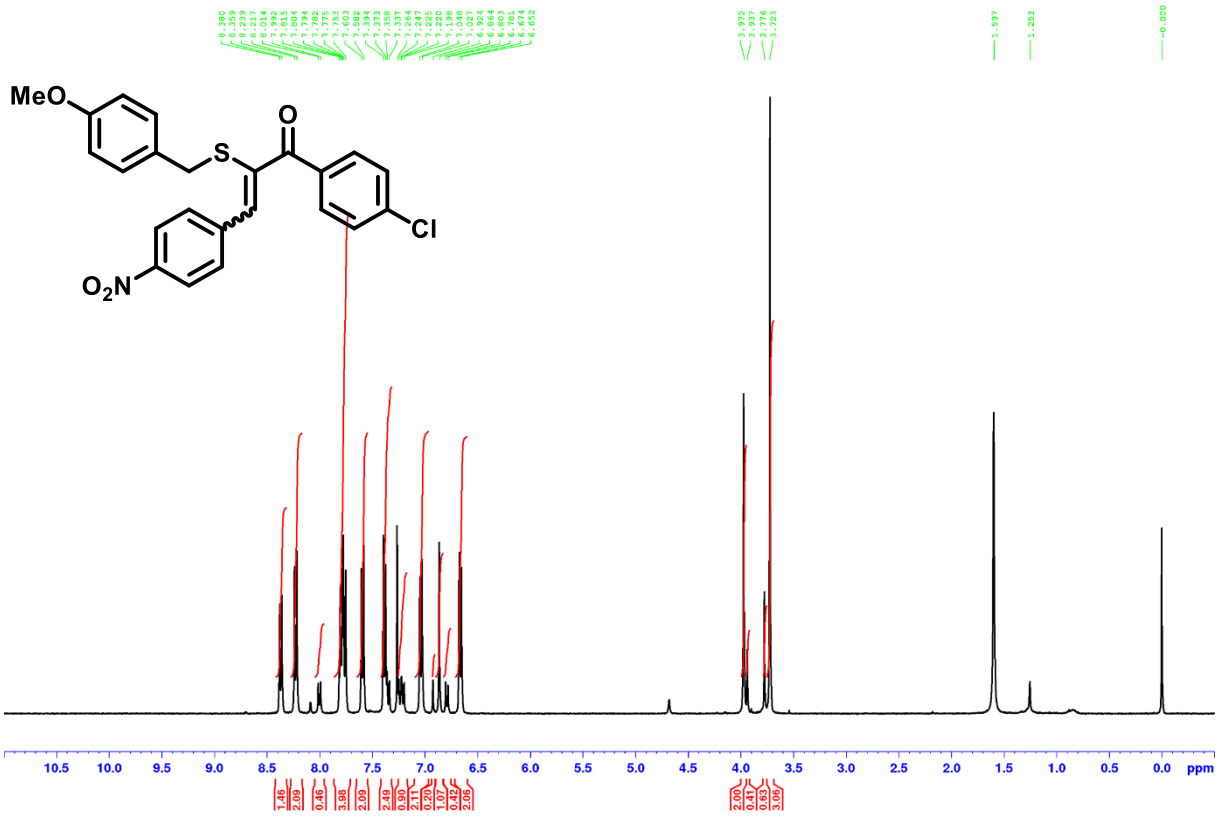


Figure S256: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**25** and *E*-**25** (*Z*:*E*, 5:1).

(*Z*)-1-(4-Chlorophenyl)-2-((4-fluorobenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one 26

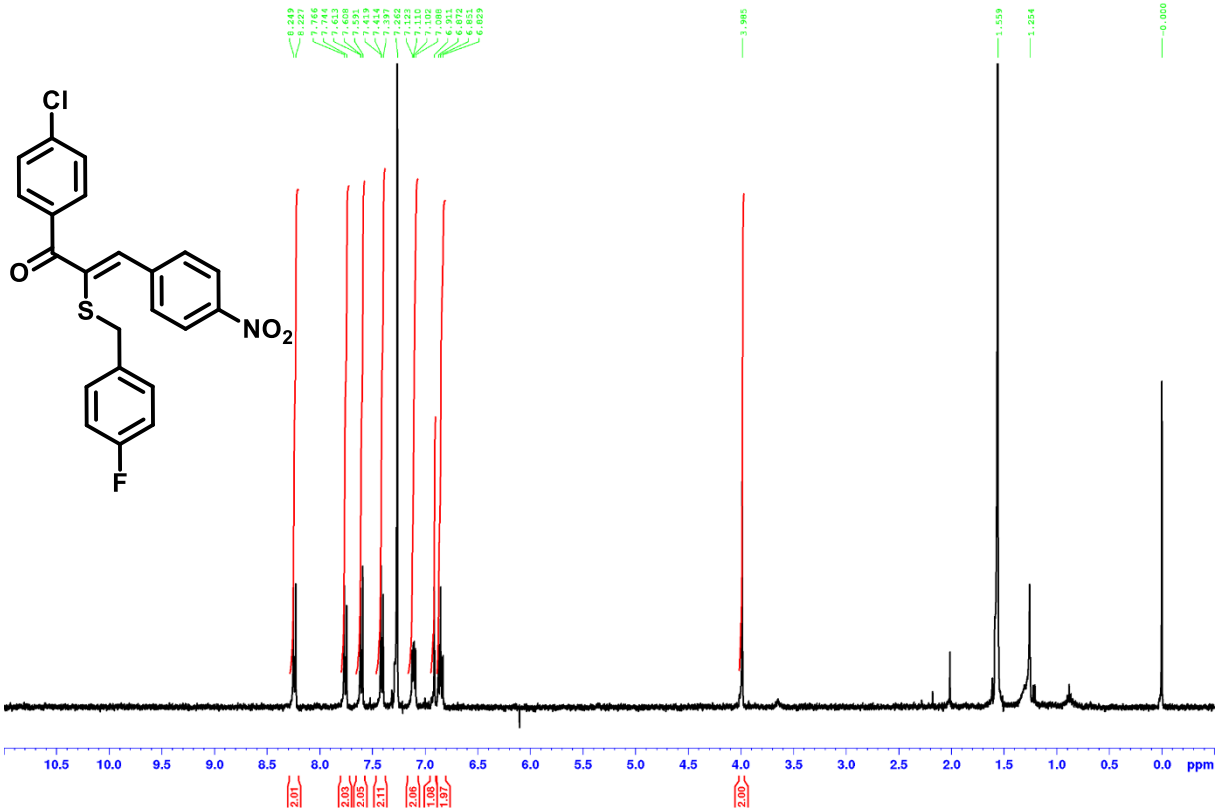


Figure S257: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**26**.

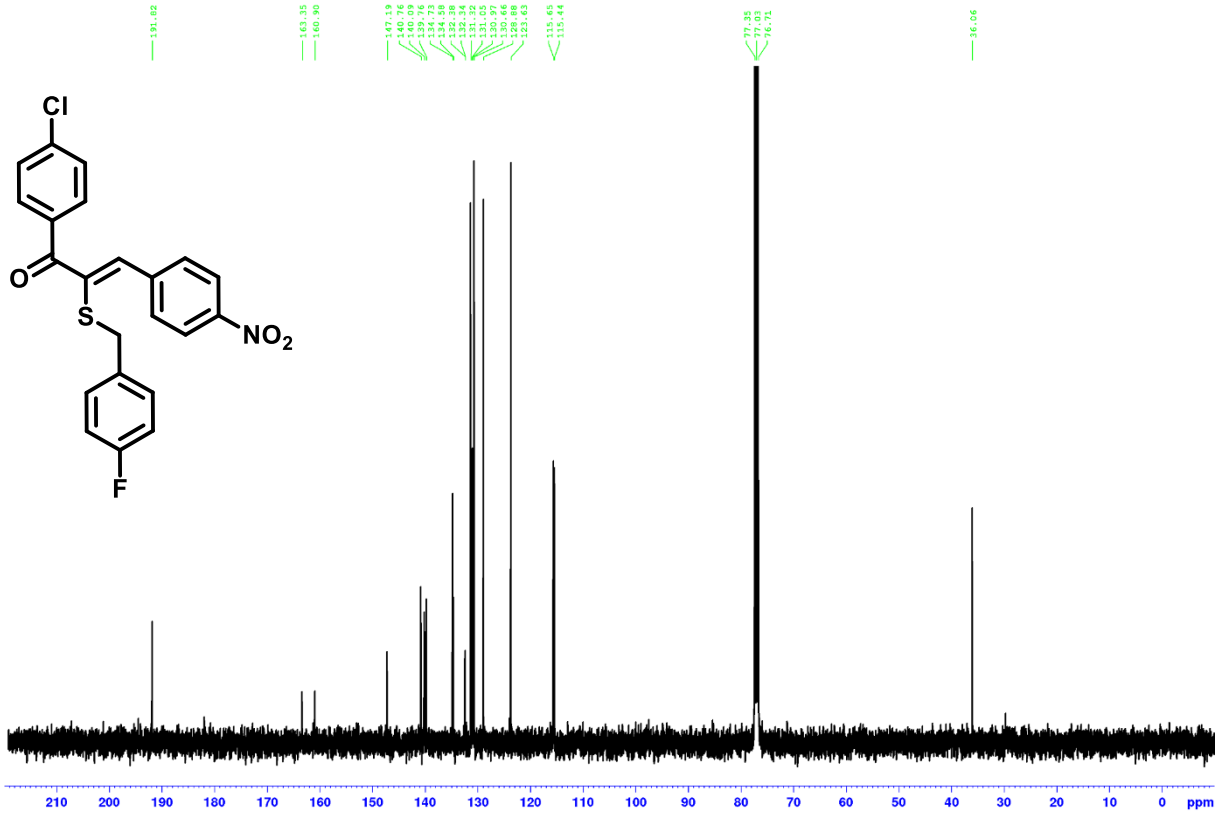


Figure S258: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***Z*-26**.

(*Z*)-2-((4-Chlorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 27

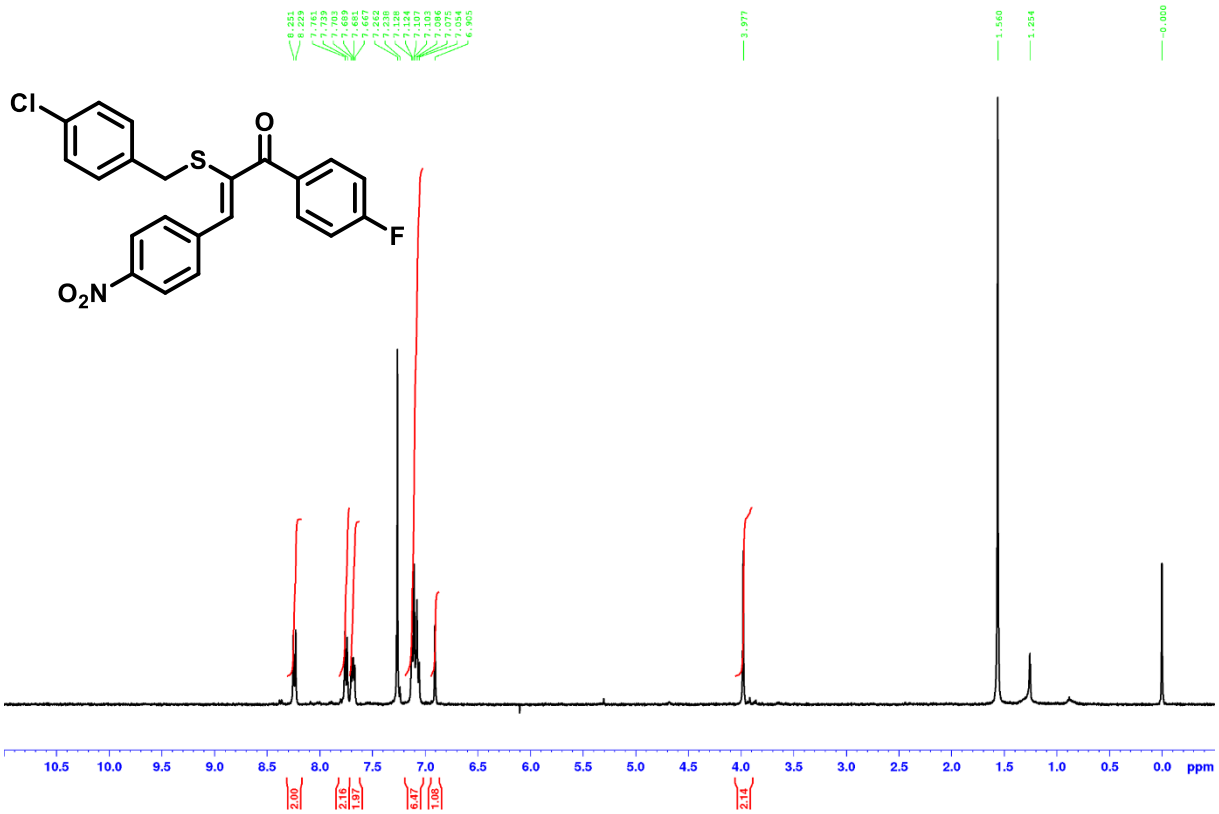


Figure S259: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-27**.

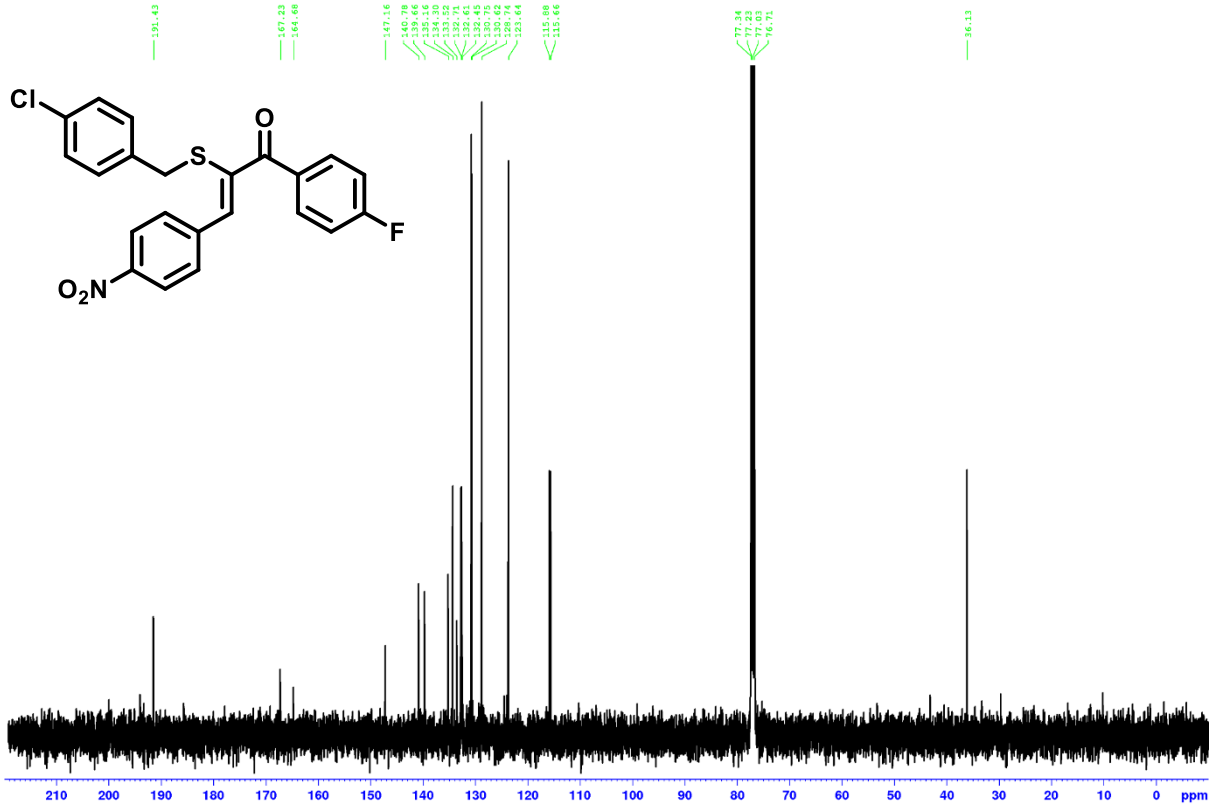


Figure S260: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***Z*-27**.

(*Z*)-2-((4-Fluorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 28

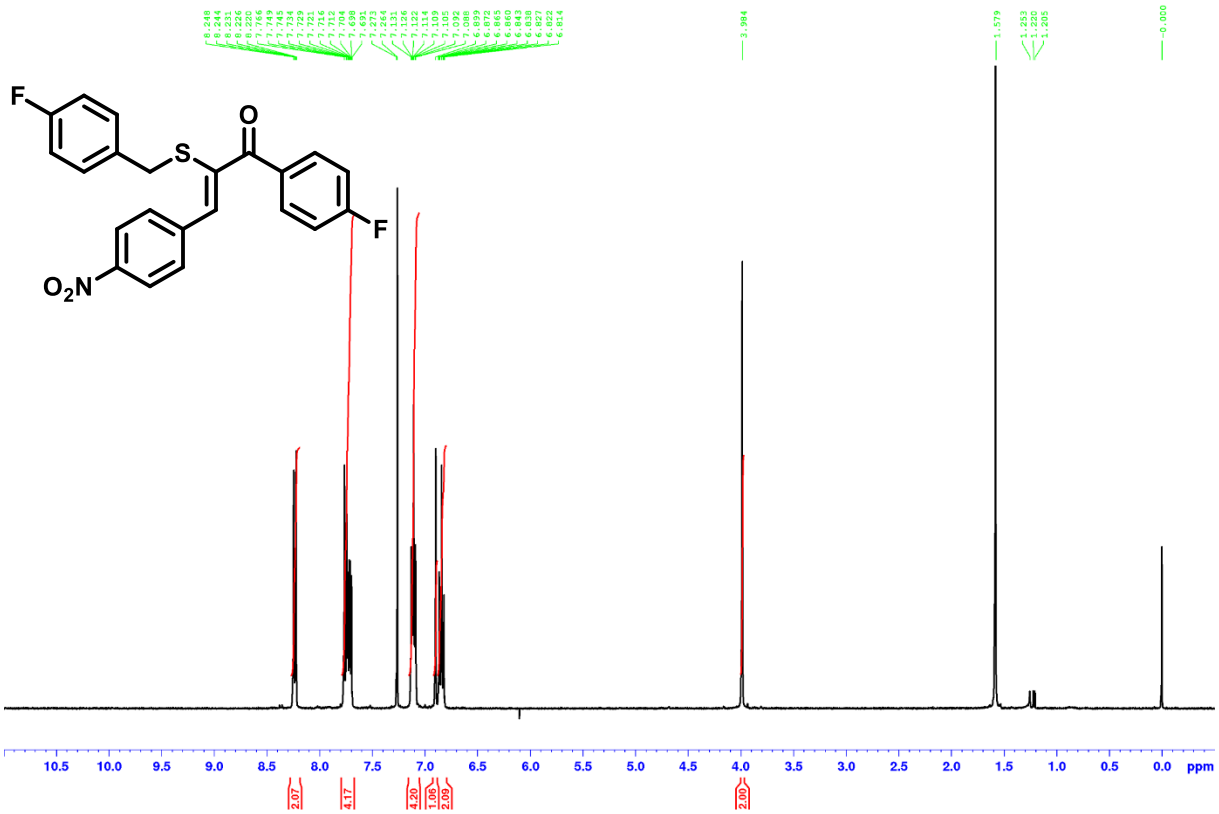


Figure S261: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-28**.

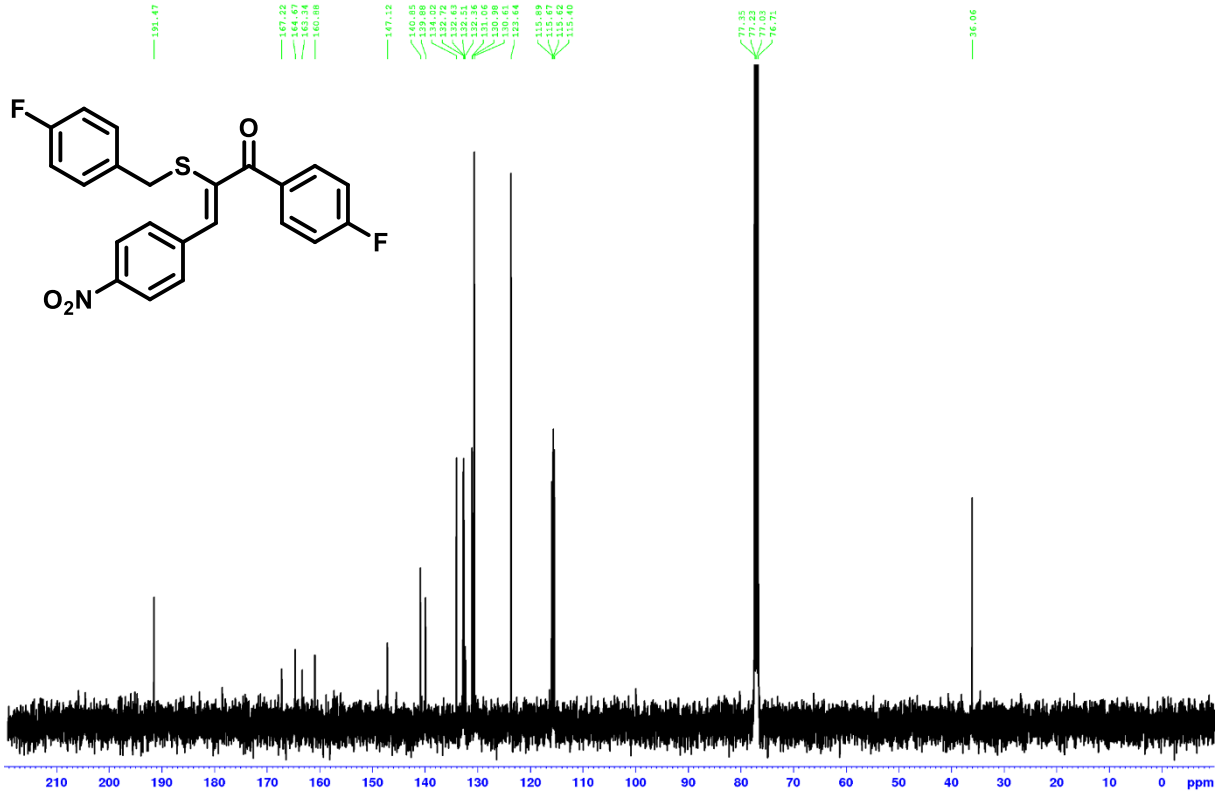


Figure S262: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***Z*-28**.

(*Z*)-1-(4-Fluorophenyl)-2-((4-methylbenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one 29

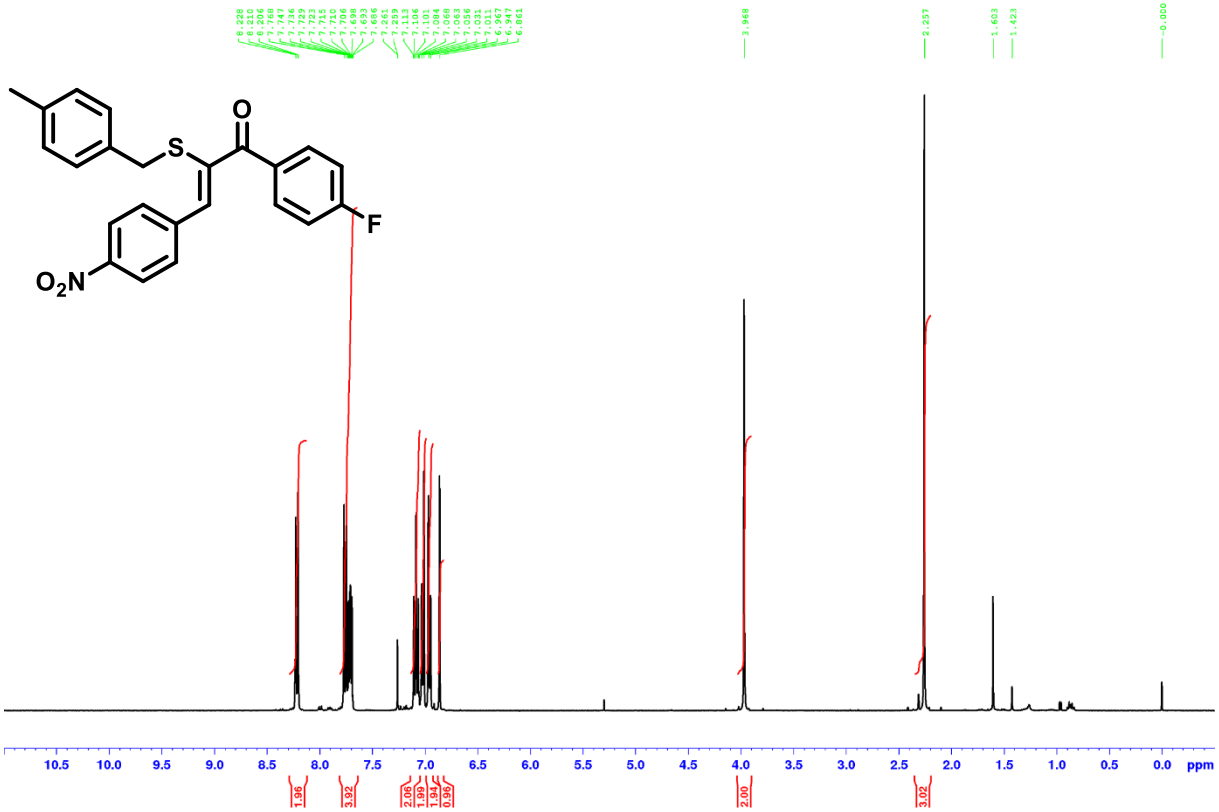


Figure S263: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-29**.

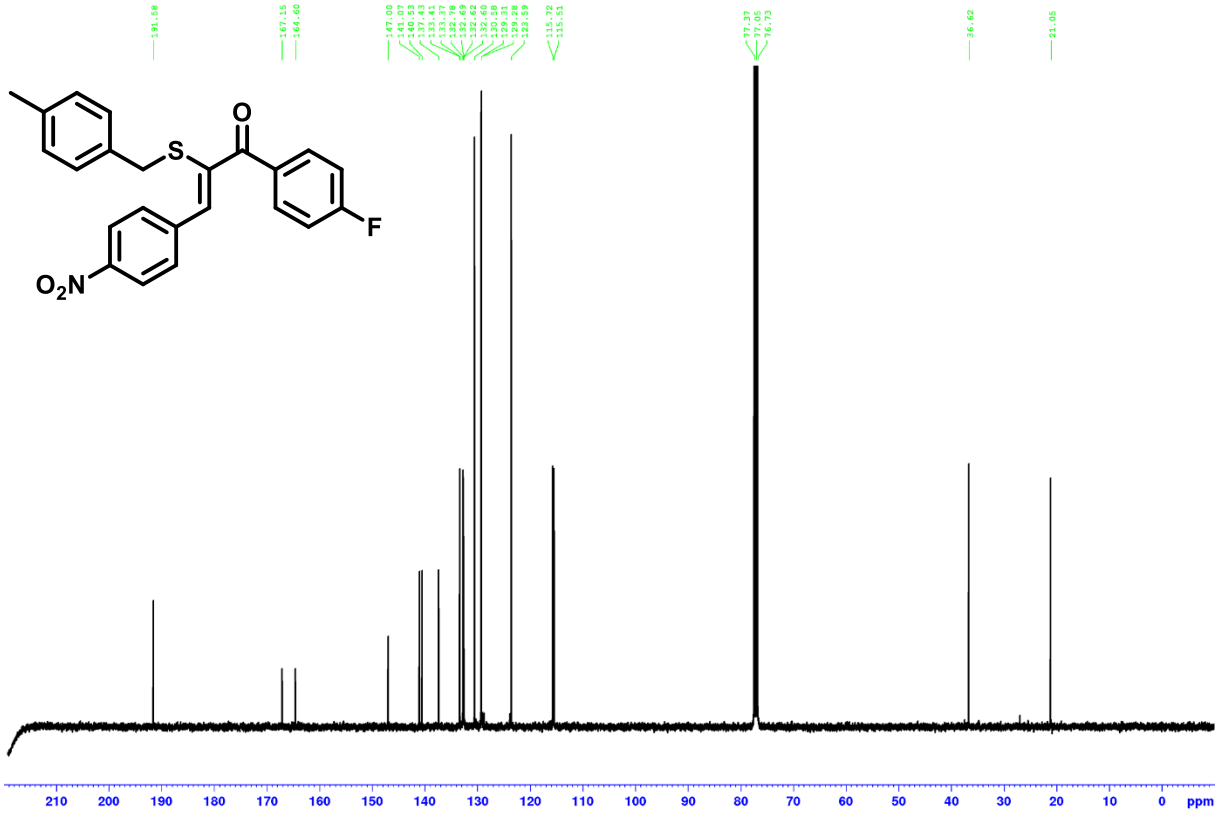


Figure S264: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***Z*-29**.

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(*p*-tolyl)prop-2-en-1-one 30

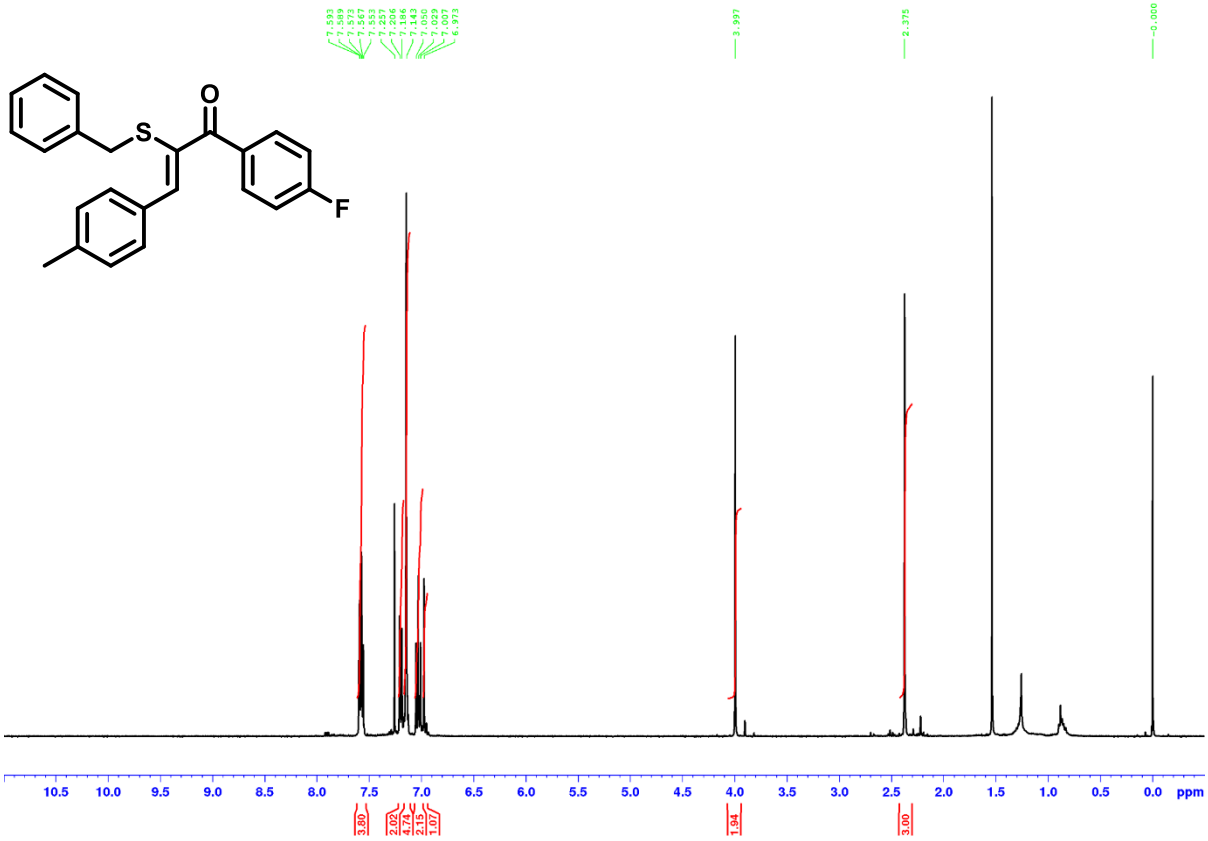


Figure S265: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-30**.

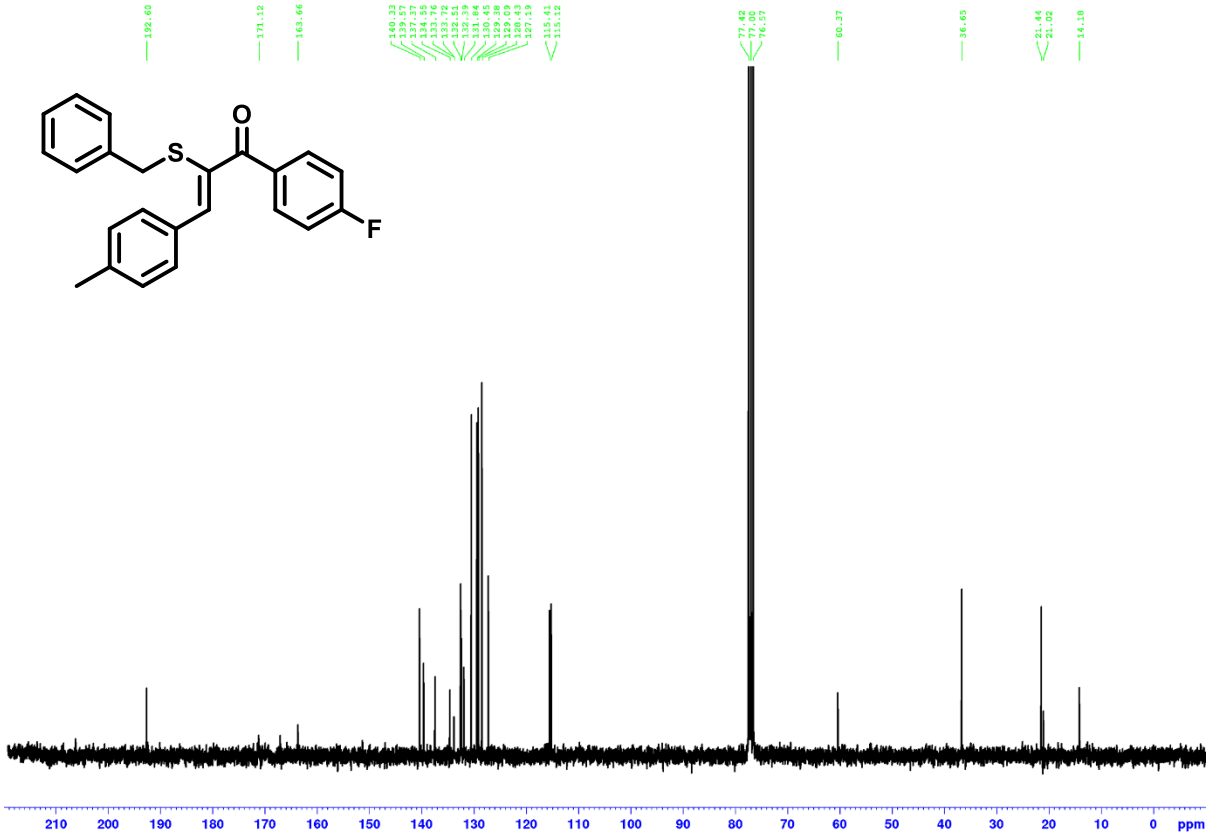


Figure S266: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-30**.

(*Z*)-2-(Benzylthio)-1,3-bis(4-fluorophenyl)prop-2-en-1-one 31

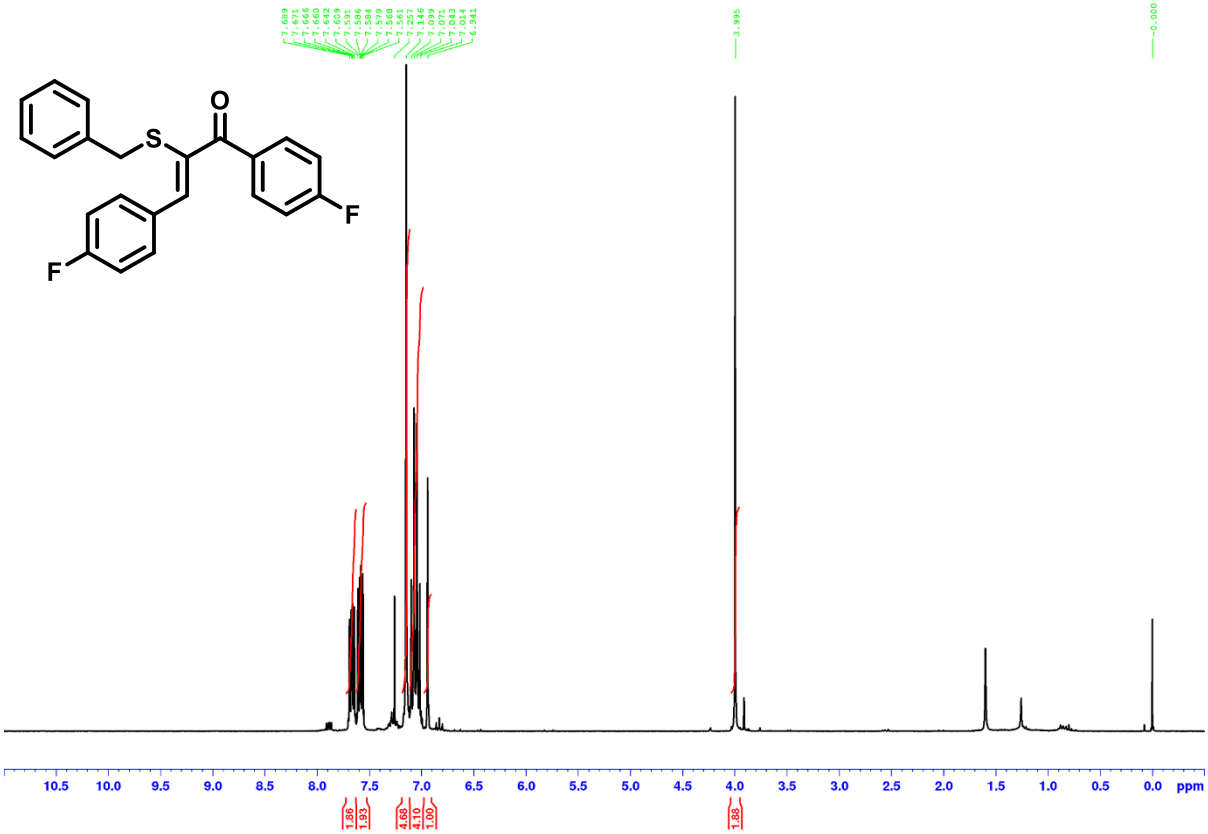


Figure S267: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-31**.

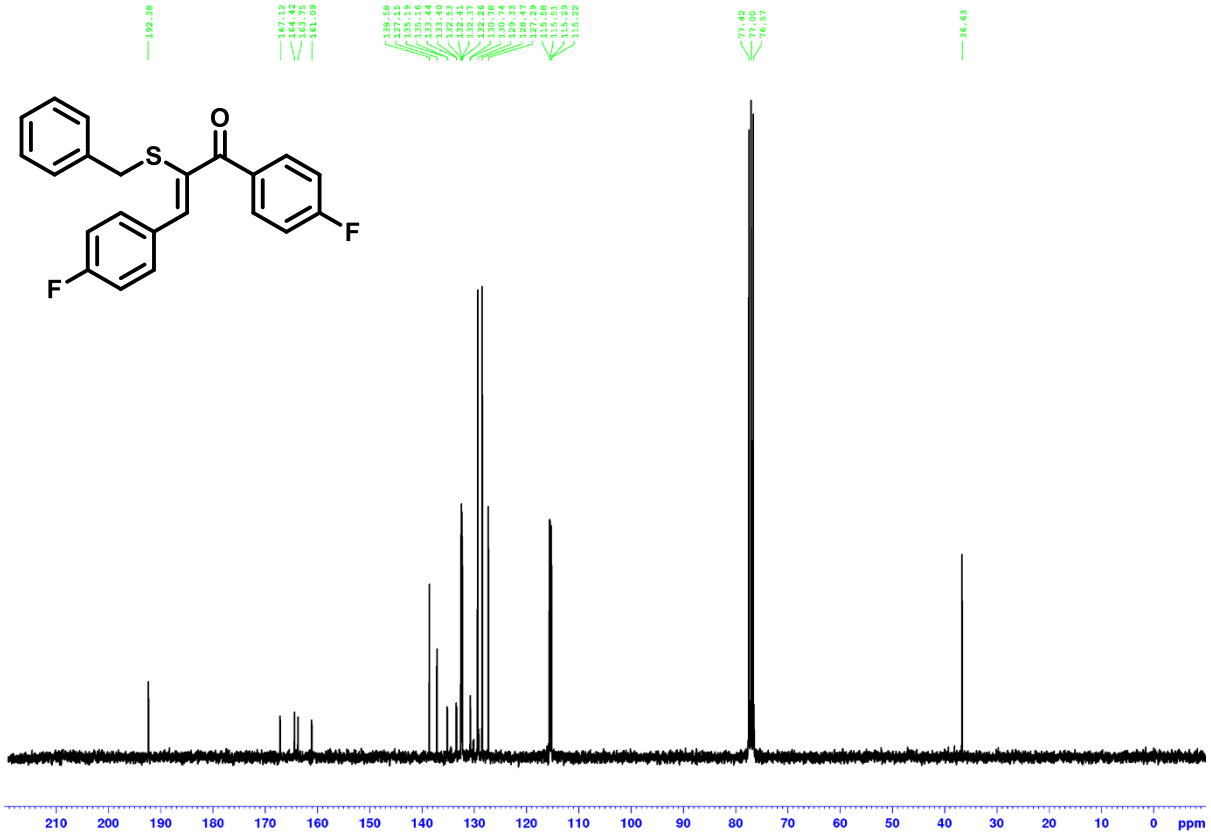


Figure S268: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-31**.

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-one 32

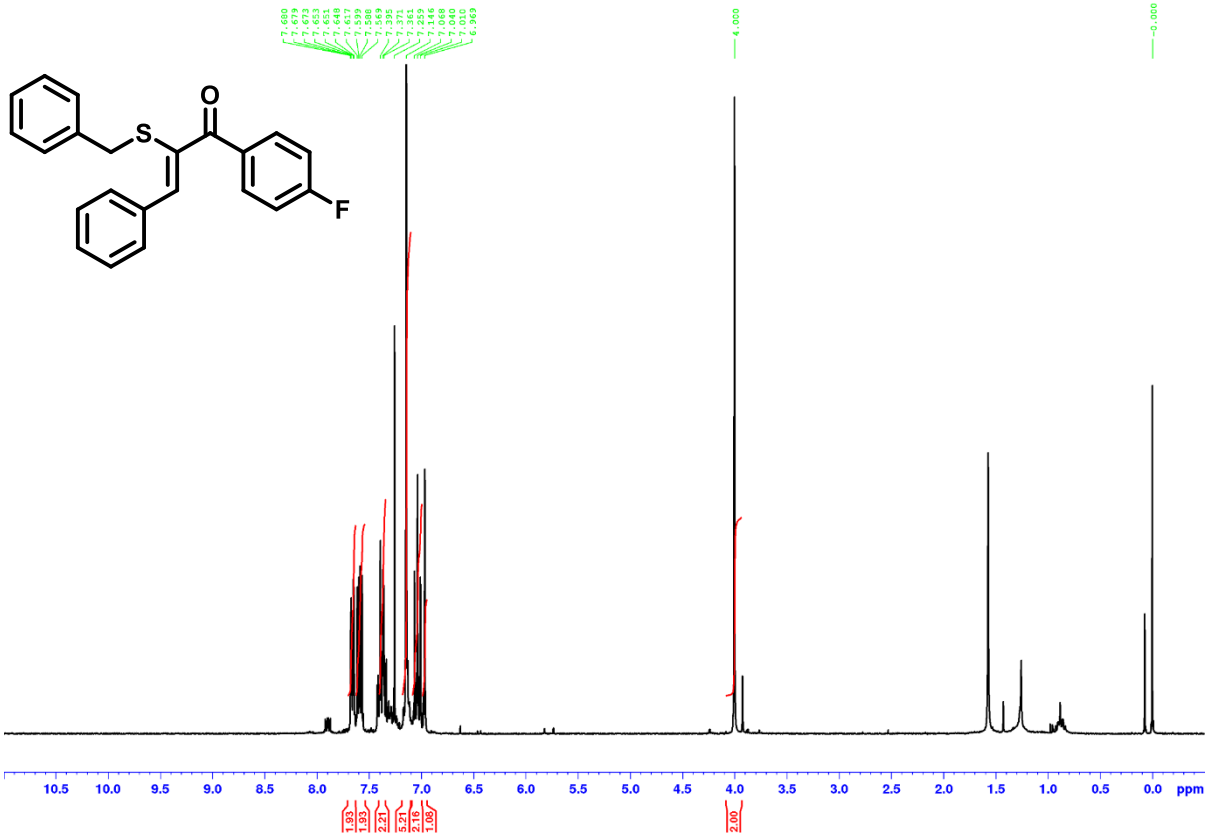


Figure S269: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-32**.

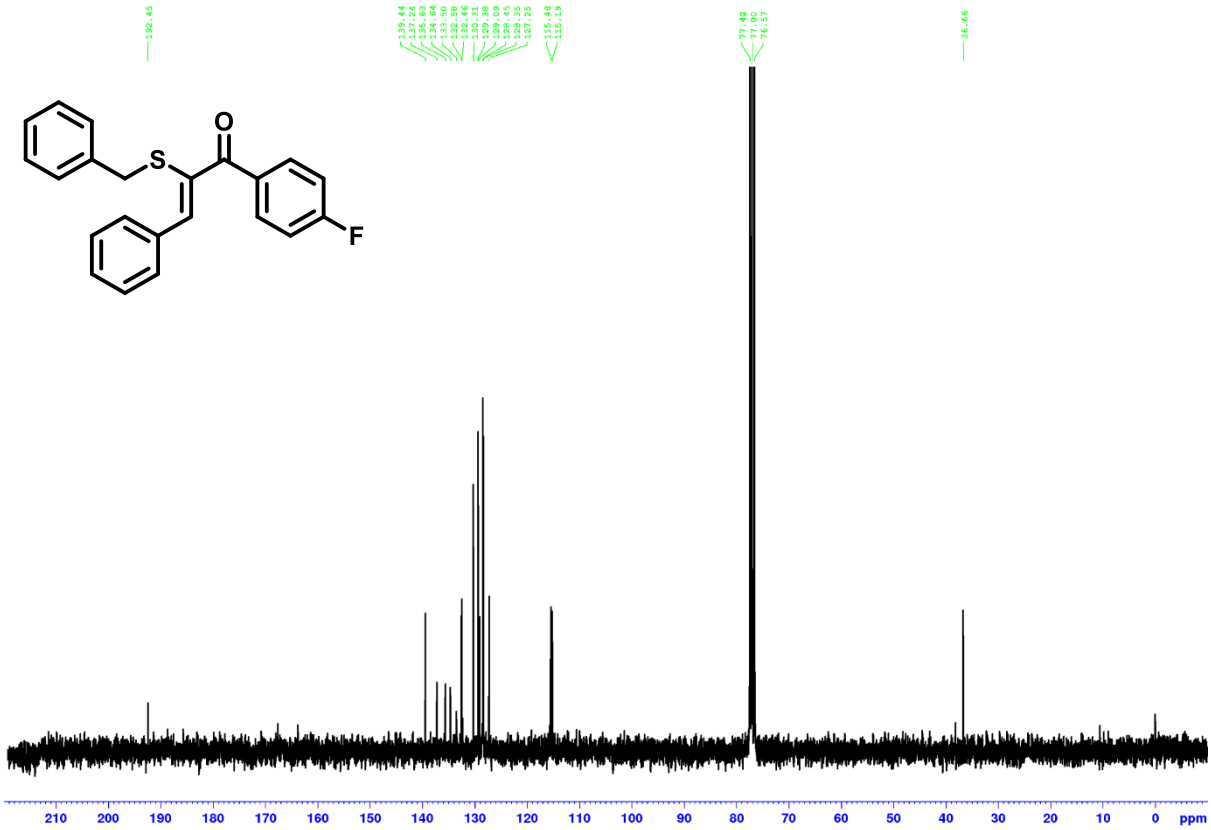


Figure S270: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-32**.

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(3-methoxyphenyl)prop-2-en-1-one 34

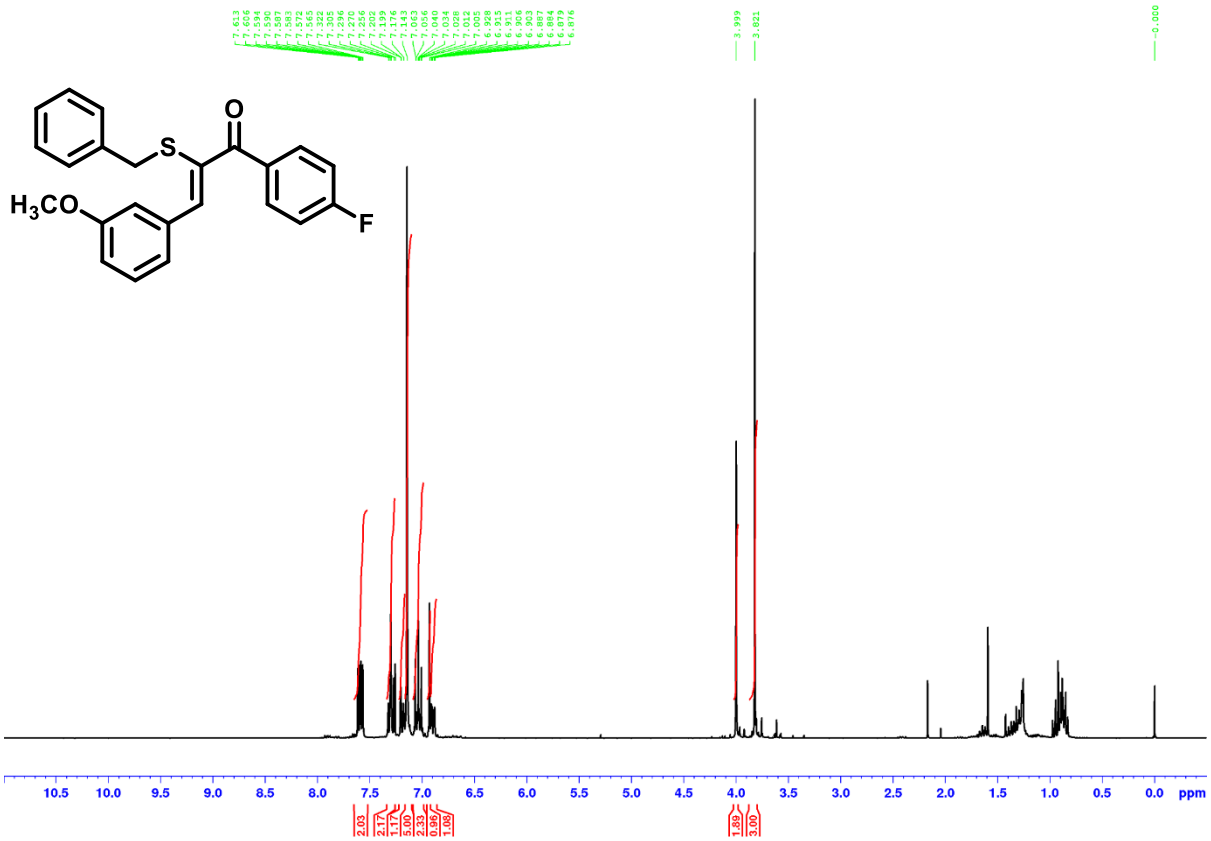


Figure S271: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-34**.

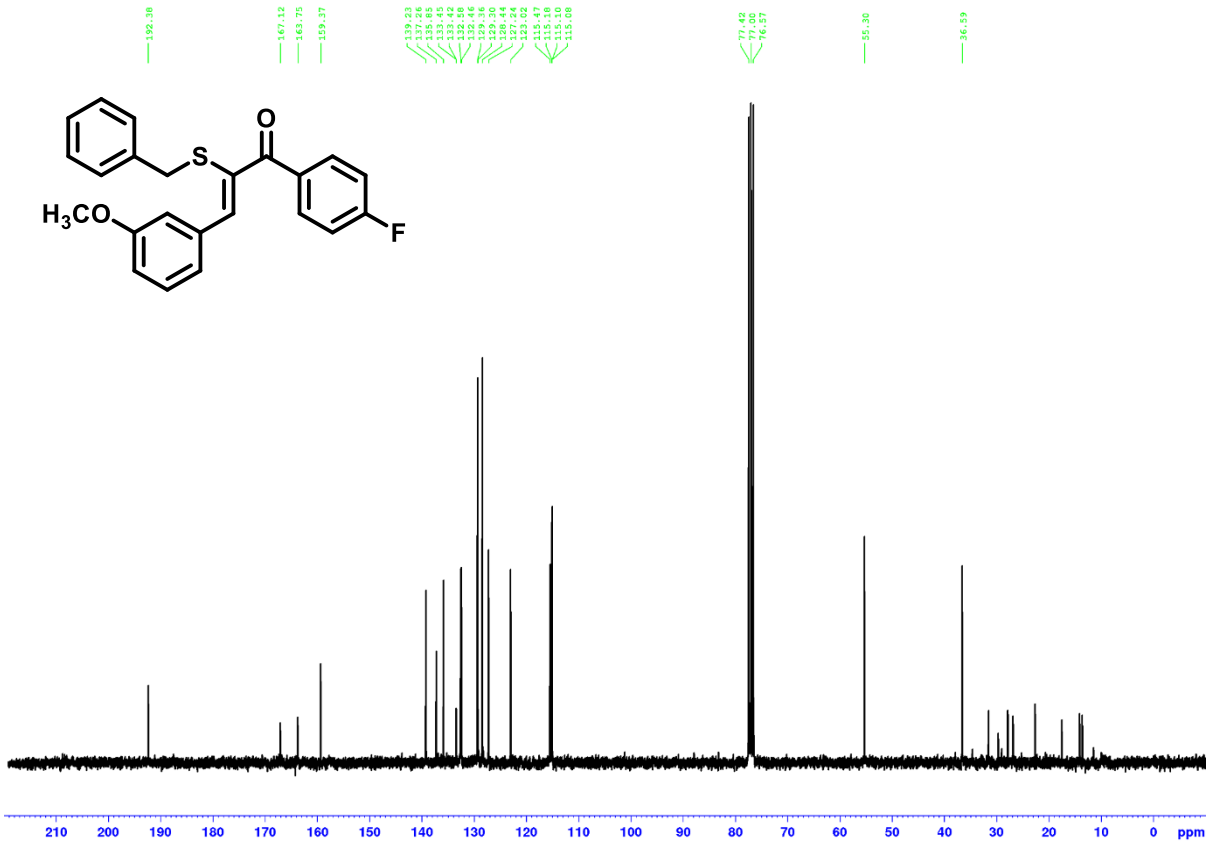


Figure S272: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-34**.

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one 33

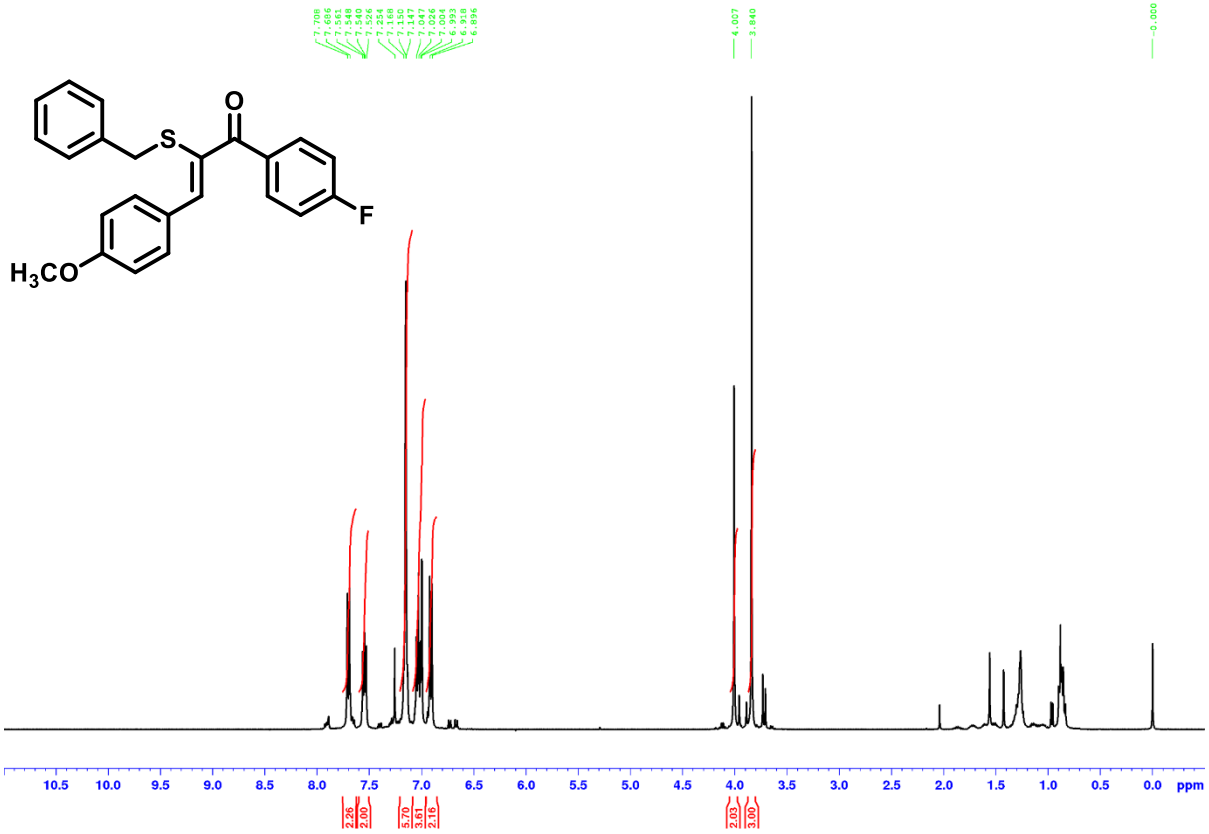


Figure S273: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-33**.

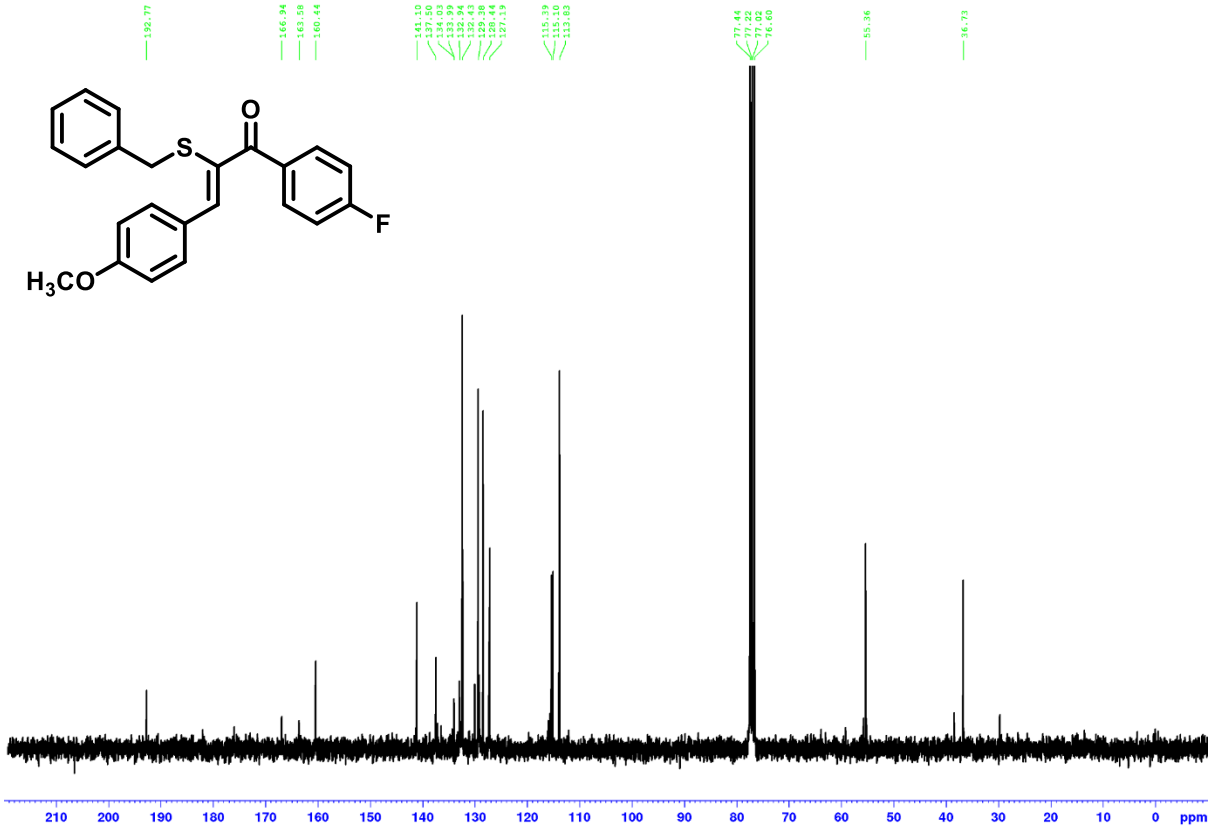


Figure S274: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-33**.

(*Z*)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 35

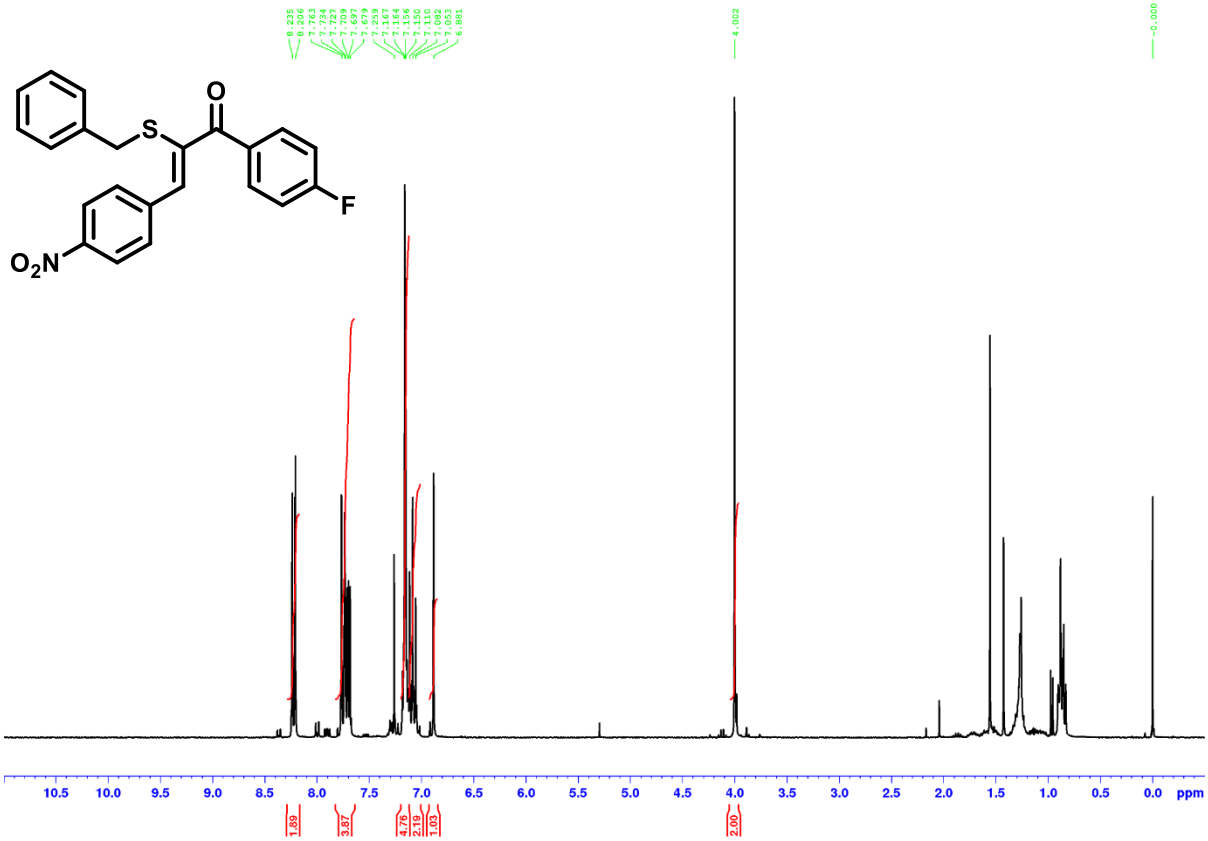


Figure S275: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-35**.

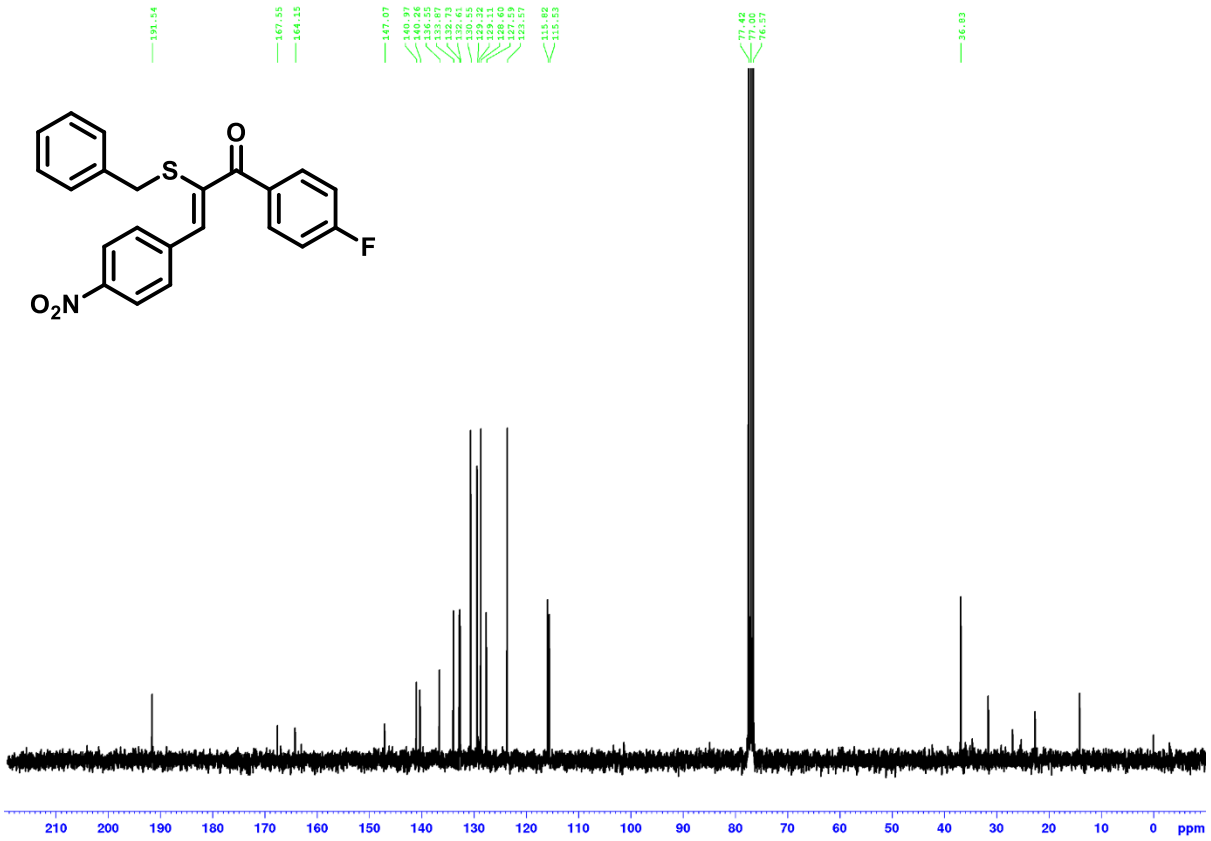


Figure S276: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of ***Z*-35**.

1.12.10 Oxidation of α-Sulfenyl-β-chloroenones

(*E*)-2-(Benzylsulfinyl)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one 38h

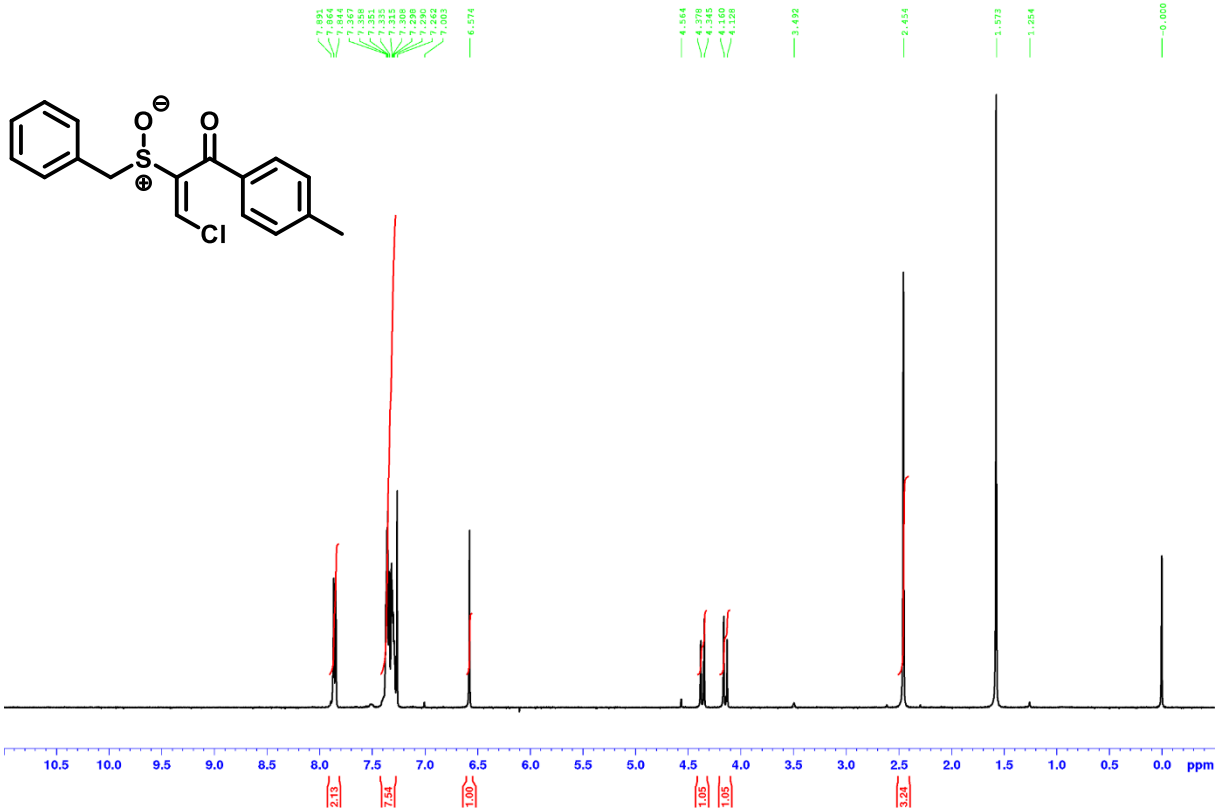


Figure S277: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-38h**.

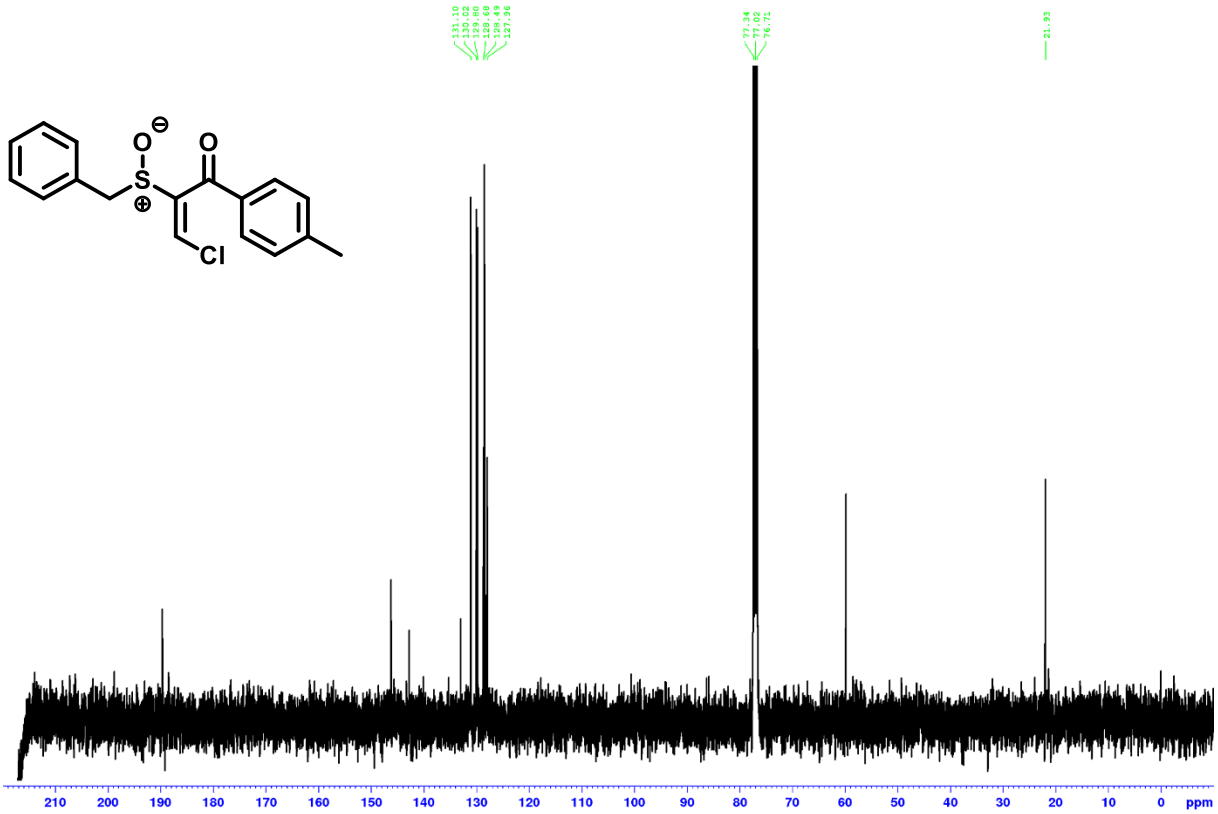


Figure S278: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-38h**.

3-Chloro-2-((4-methylbenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one 38m

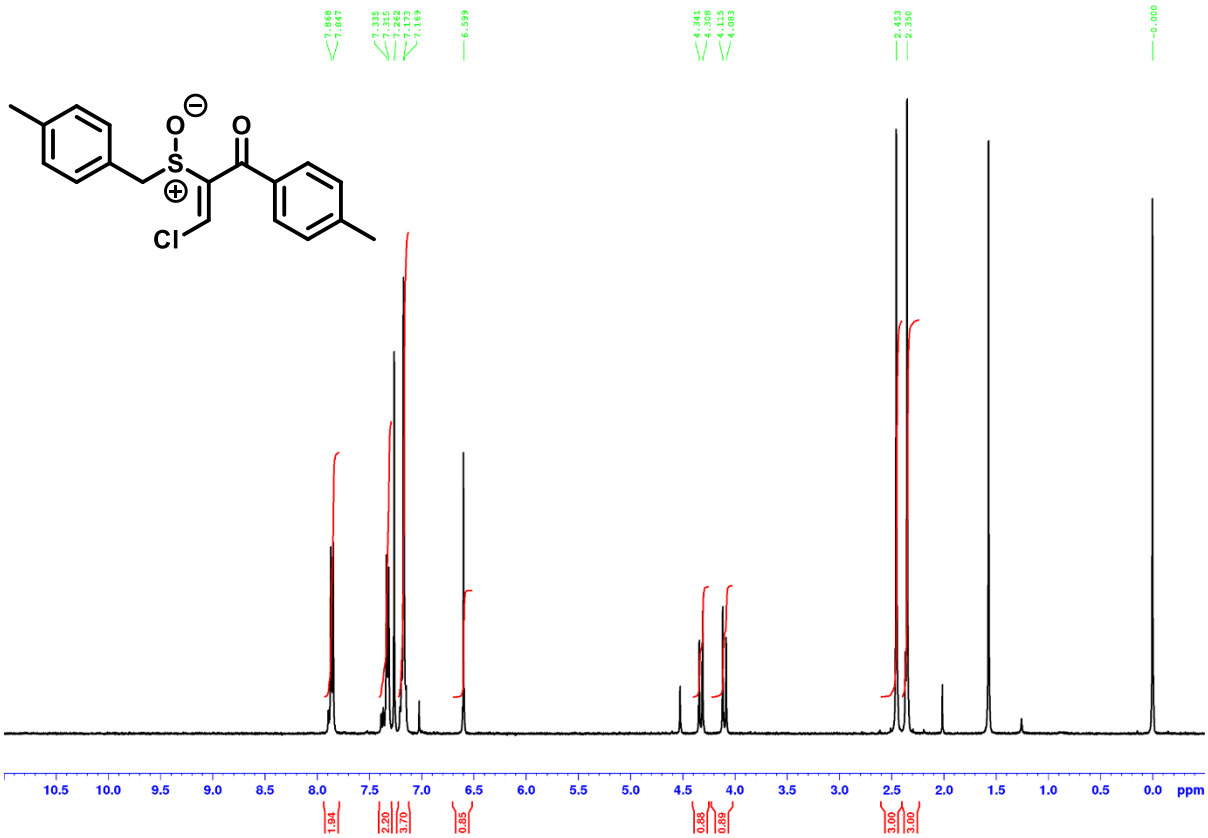


Figure S279: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-38m**.

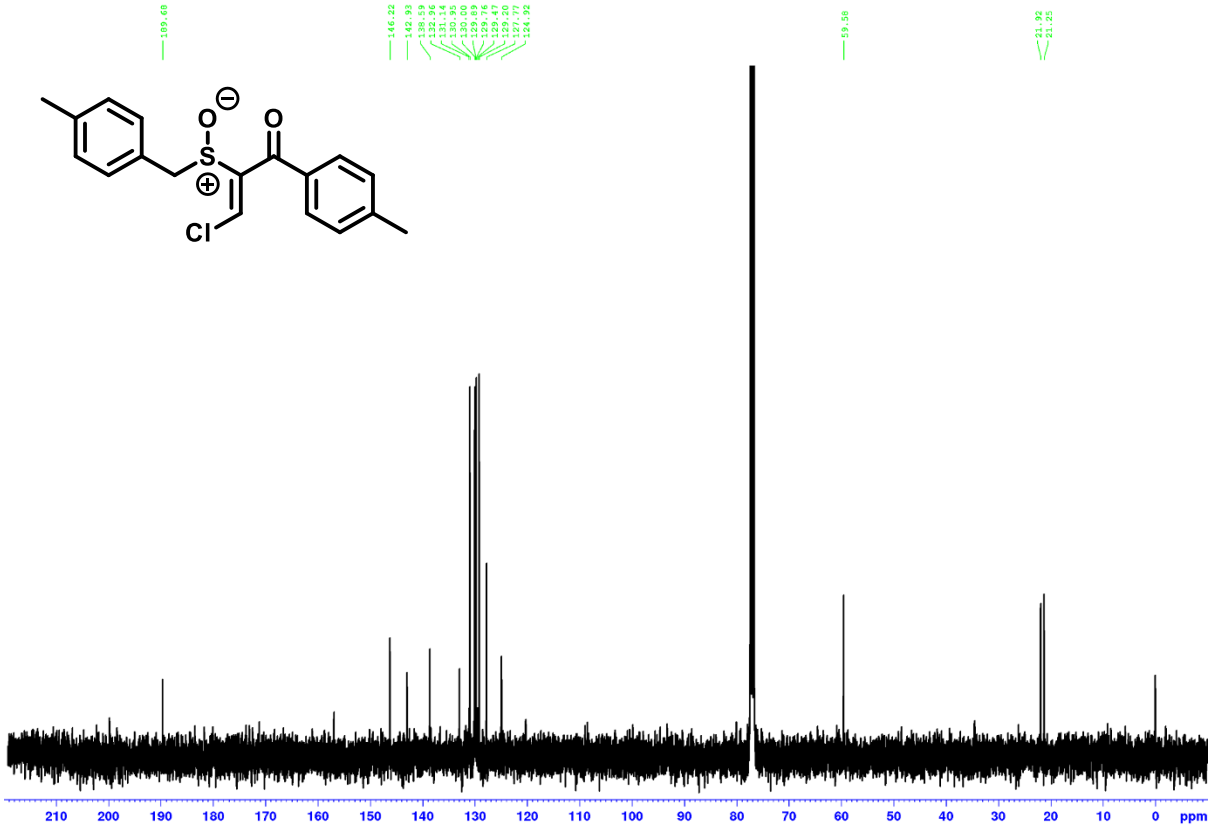


Figure S280: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-38m**.

(*E*)-3-Chloro-2-((4-chlorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one 38t

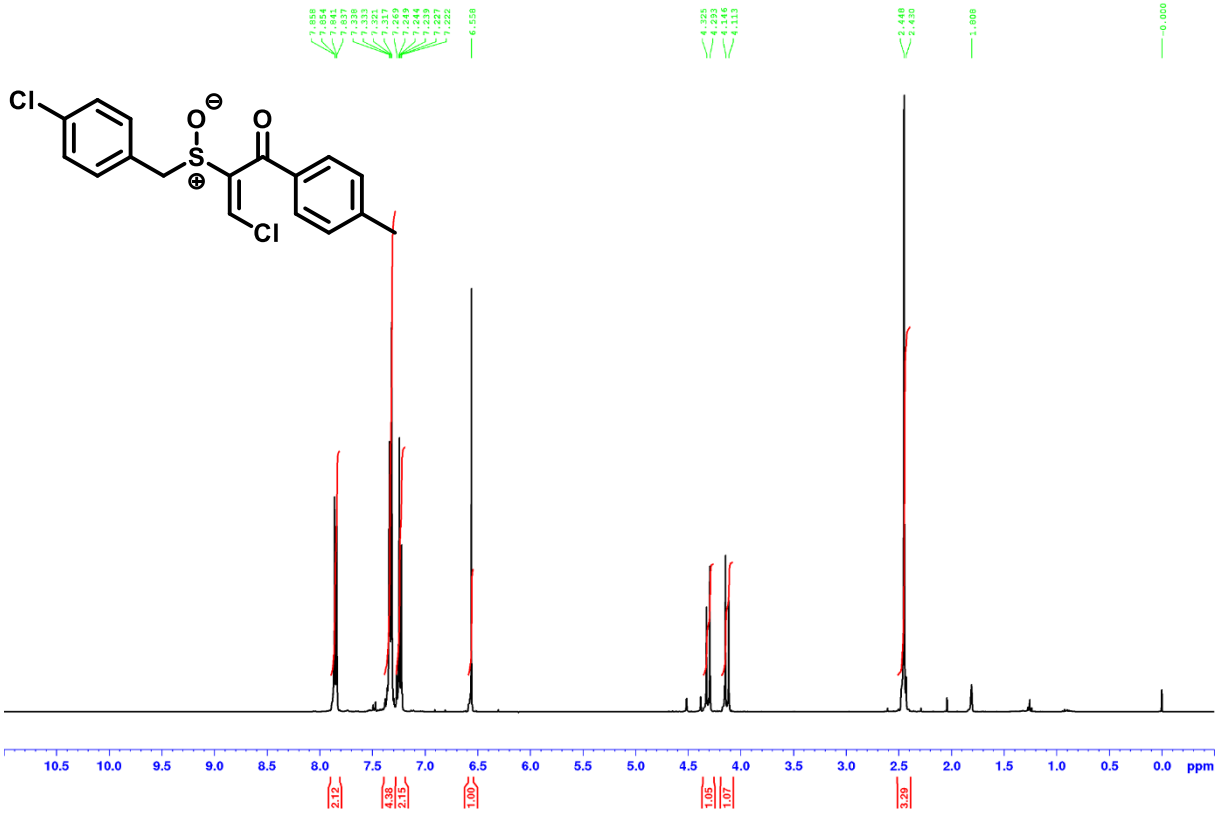


Figure S281: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-38t**.

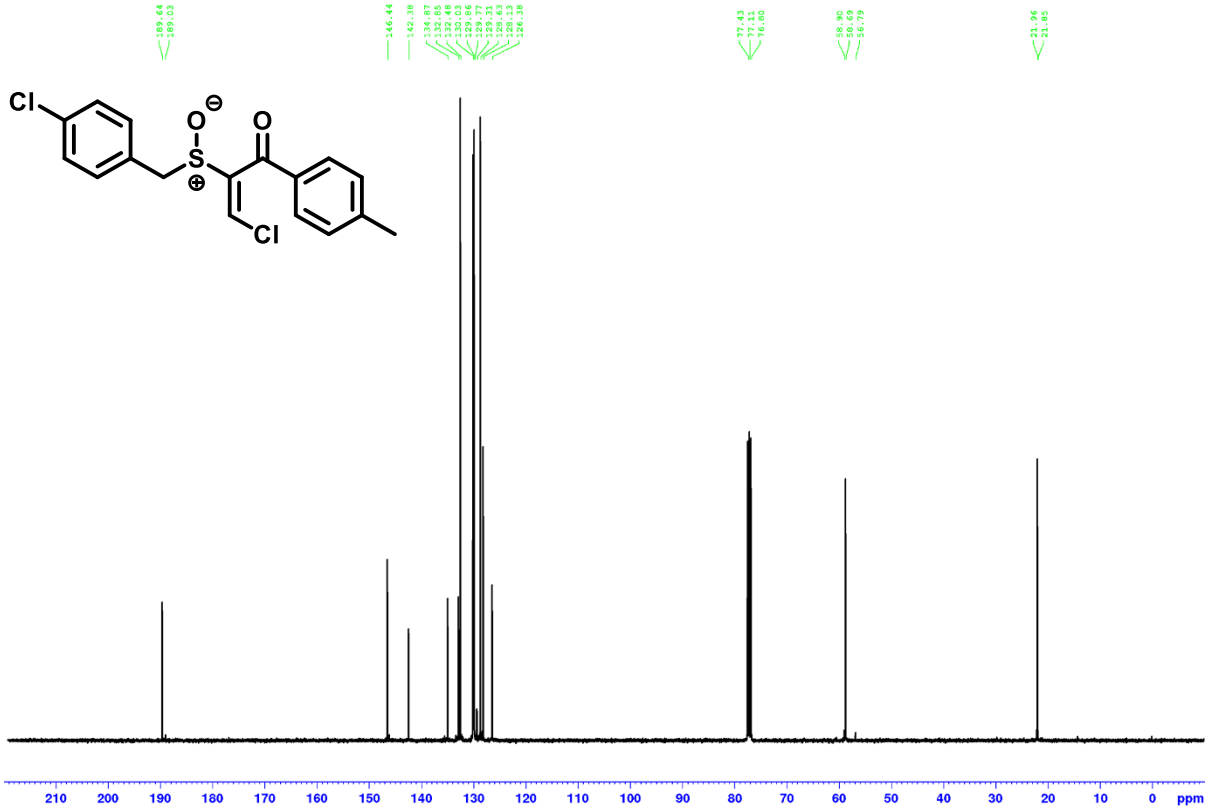


Figure S282: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-38t**.

(*E*)-3-Chloro-2-((4-fluorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one 38aa

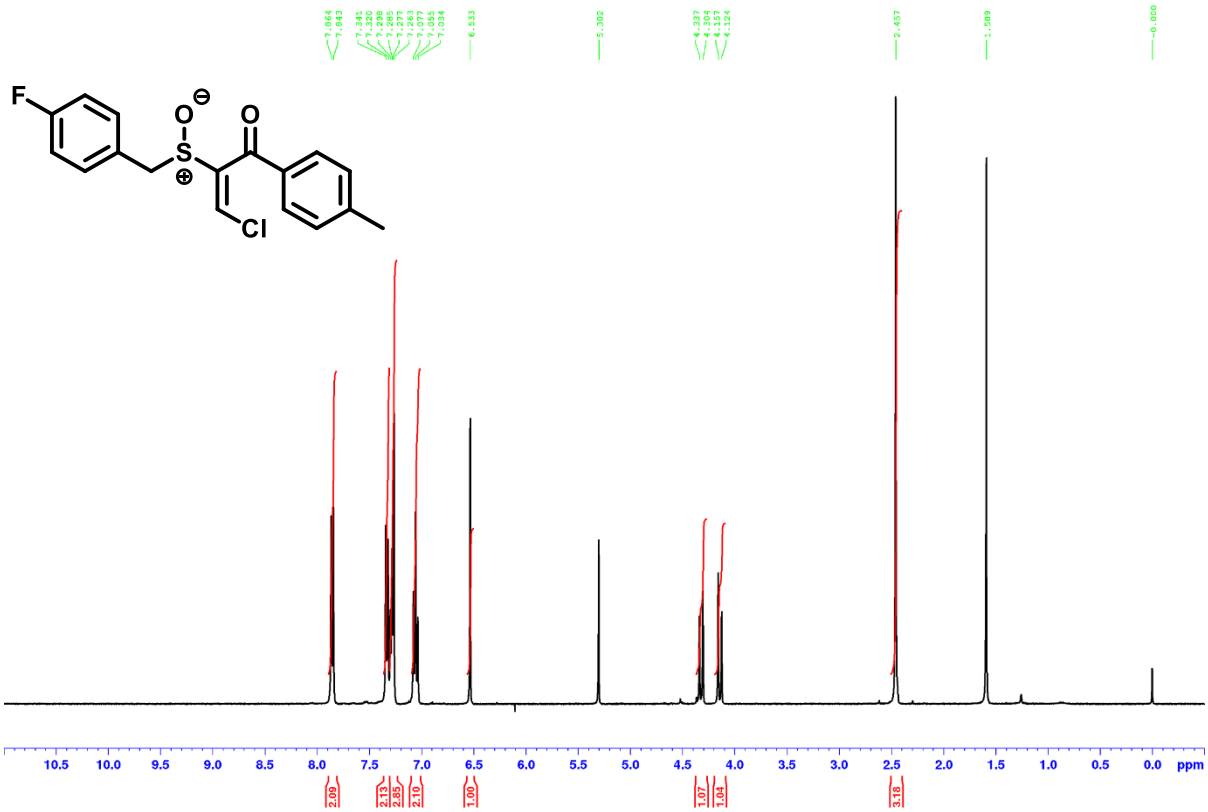


Figure S283: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-38aa**.

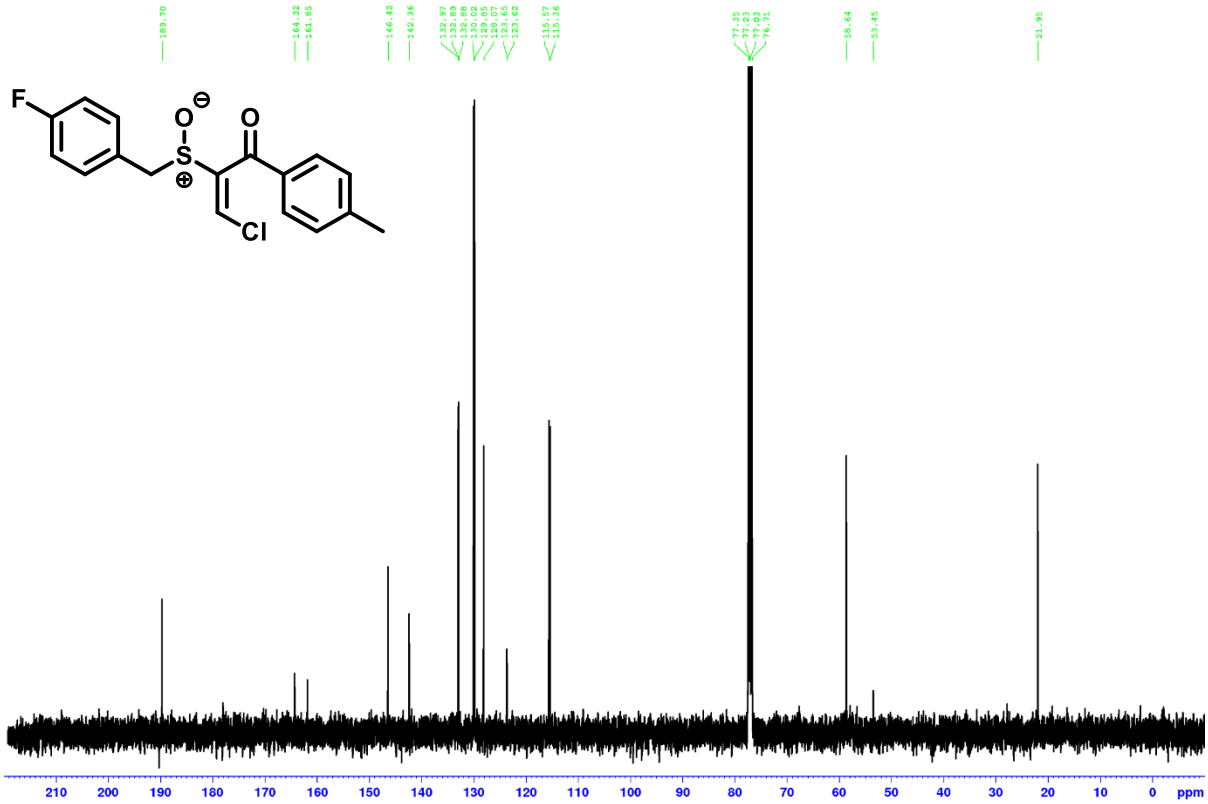


Figure S284: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-38aa**.

(*E*)-3-Chloro-2-((4-chlorobenzyl)sulfinyl)-1-(4-chlorophenyl)prop-2-en-1-one 38q

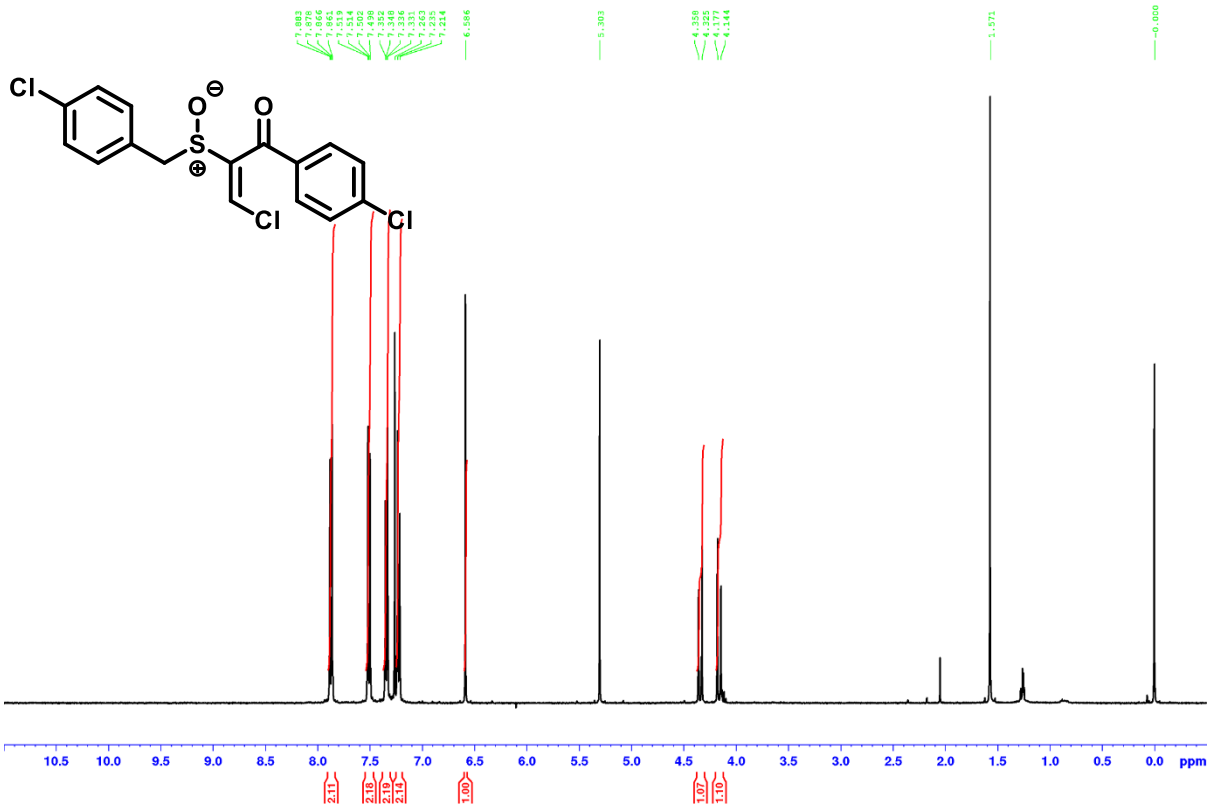


Figure S285: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-38q**.

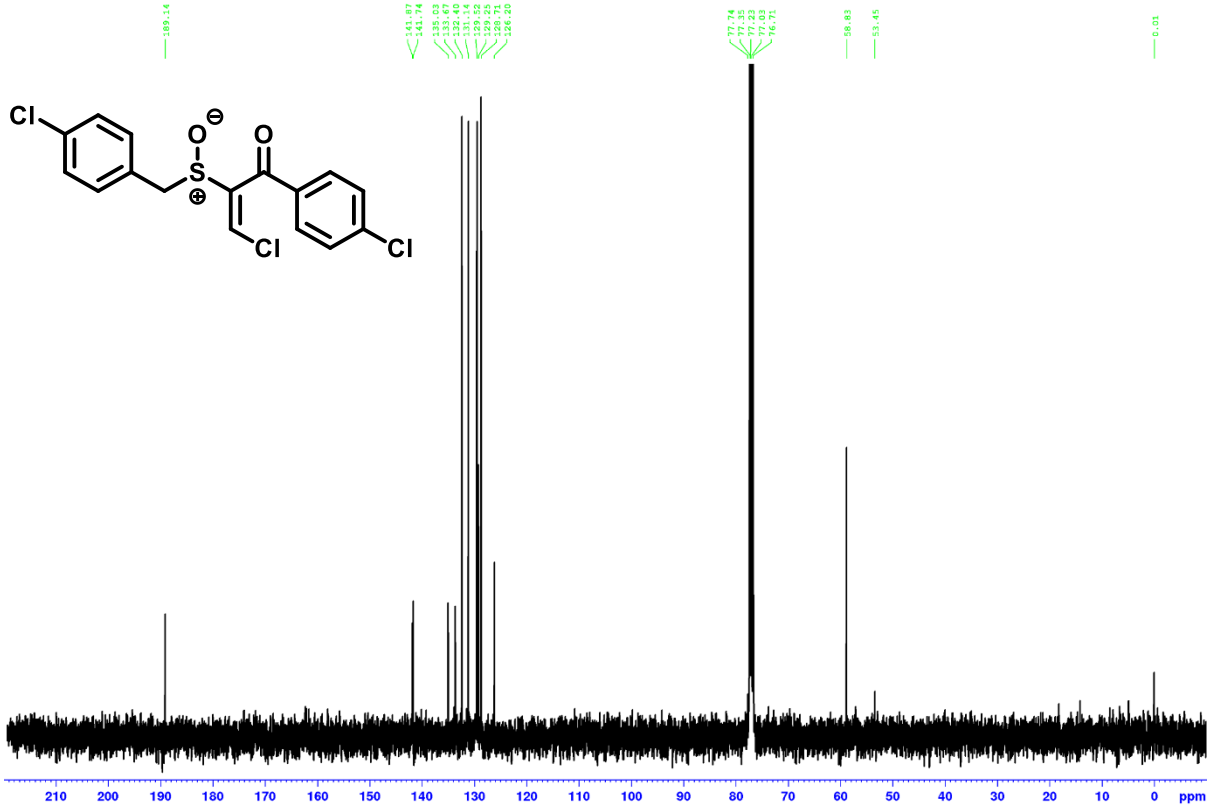


Figure S286: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-38q**.

2-((4-Chlorobenzyl)sulfonyl)-1-(4-chlorophenyl)ethan-1-one 39b

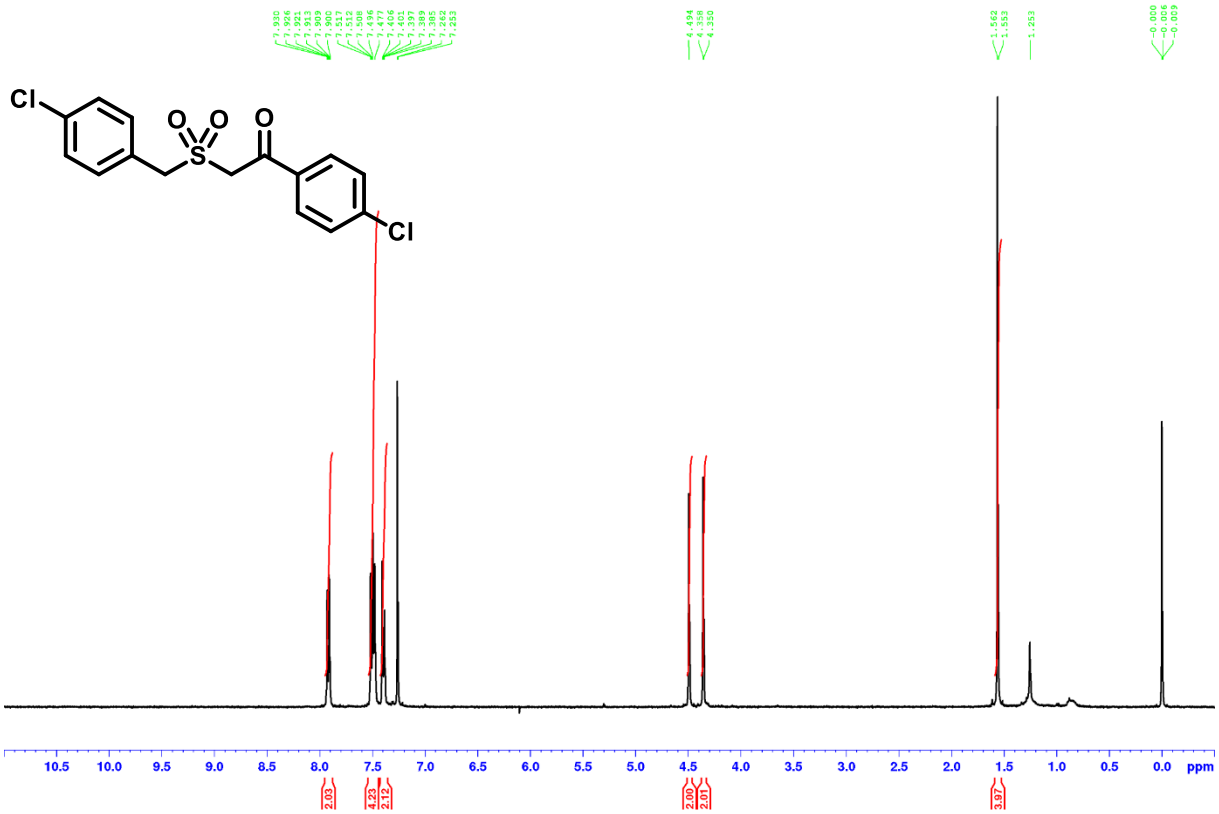


Figure S287: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **39b**.

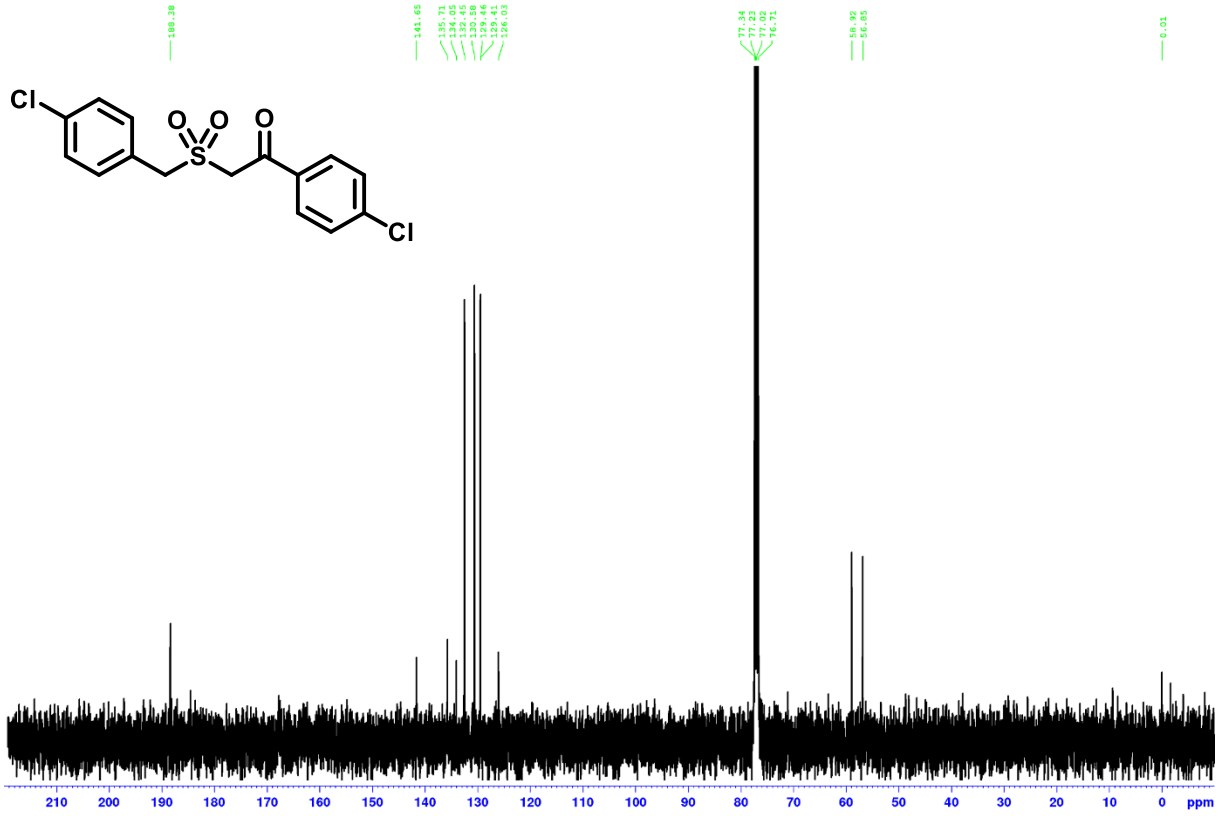


Figure S288: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **39b**.

(*E*)-3-Chloro-2-((4-fluorobenzyl)sulfinyl)-1-(4-fluorophenyl)prop-2-en-1-one 38z

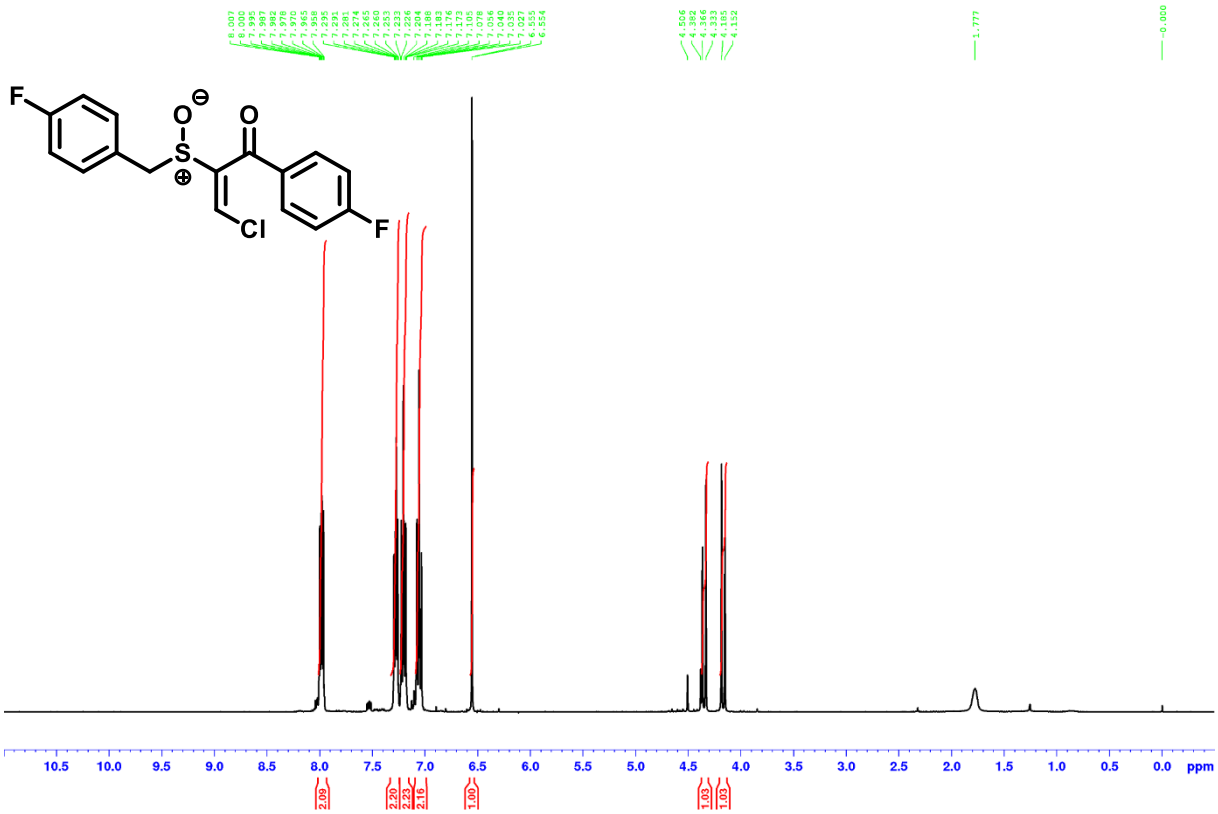


Figure S289: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-38z**.

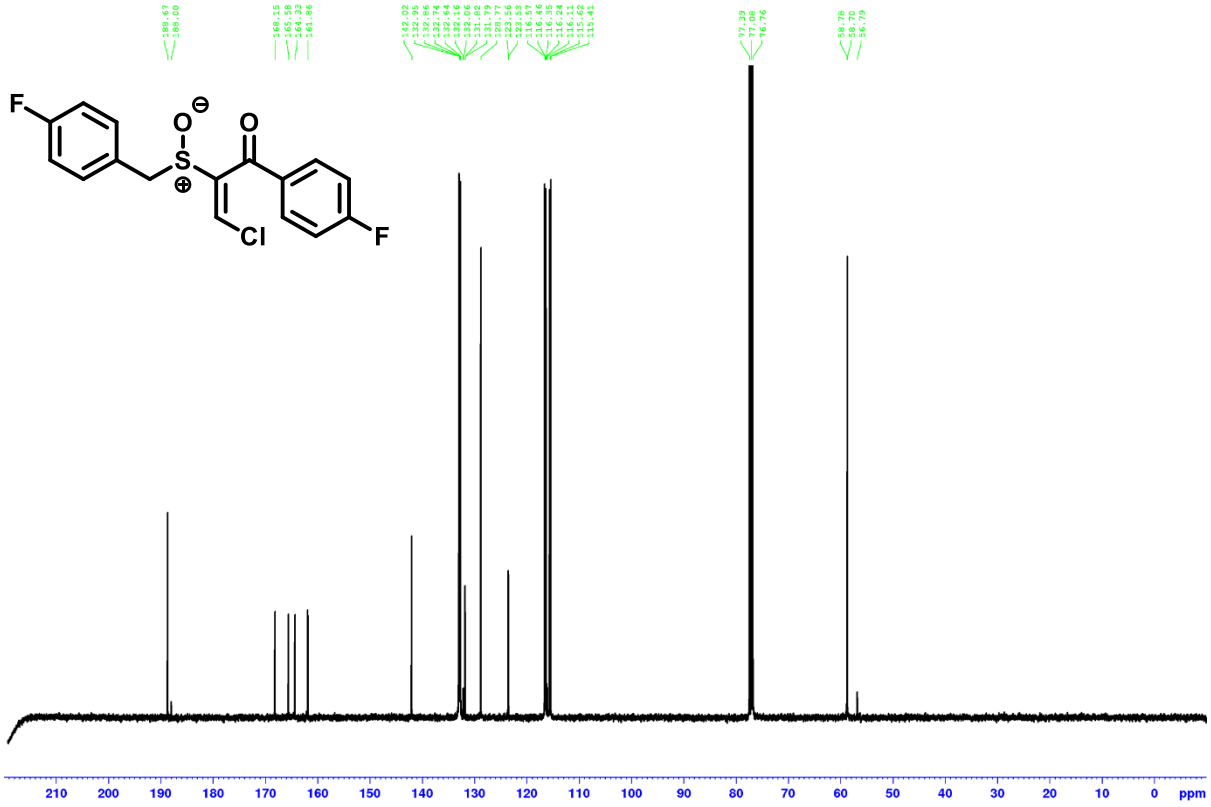


Figure S290: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-38z**.

1.12.11 Synthesis of Chalcones from α-Sulfinyl-β-chloroenones

(*E*)-2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40h

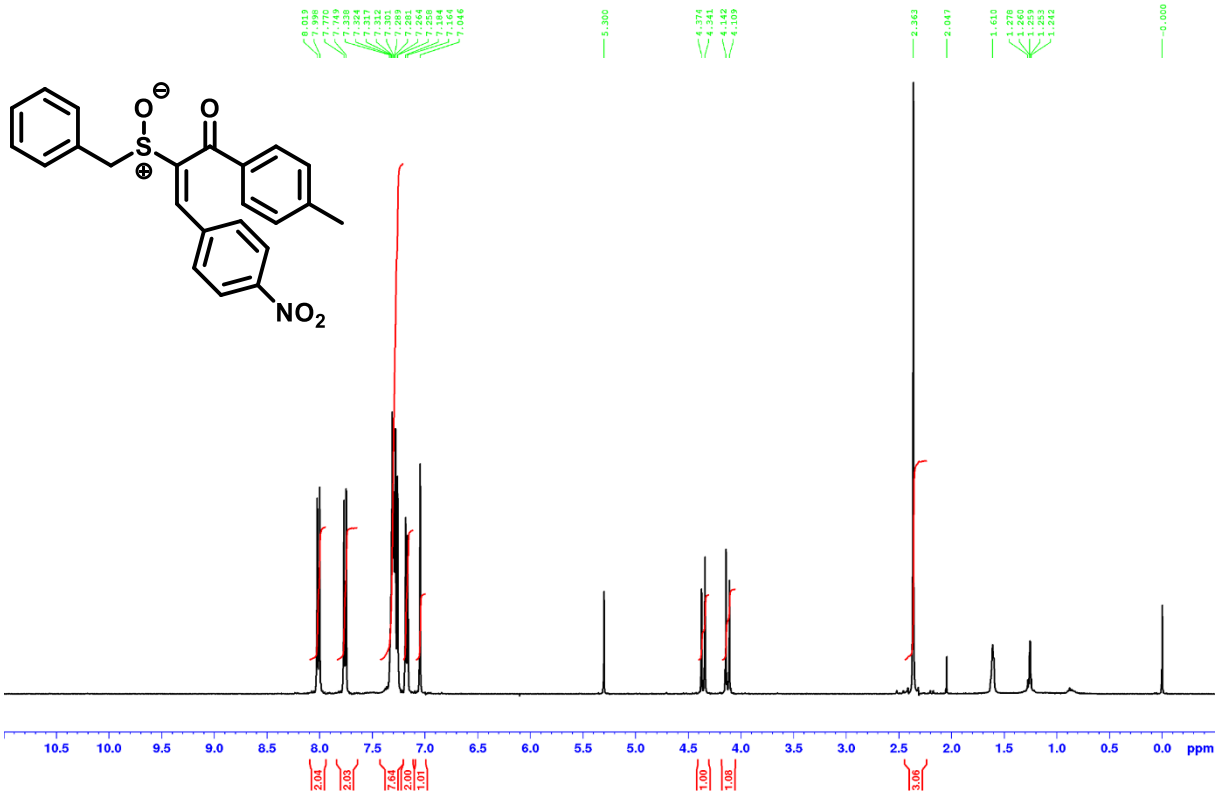


Figure S291: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-40h**.

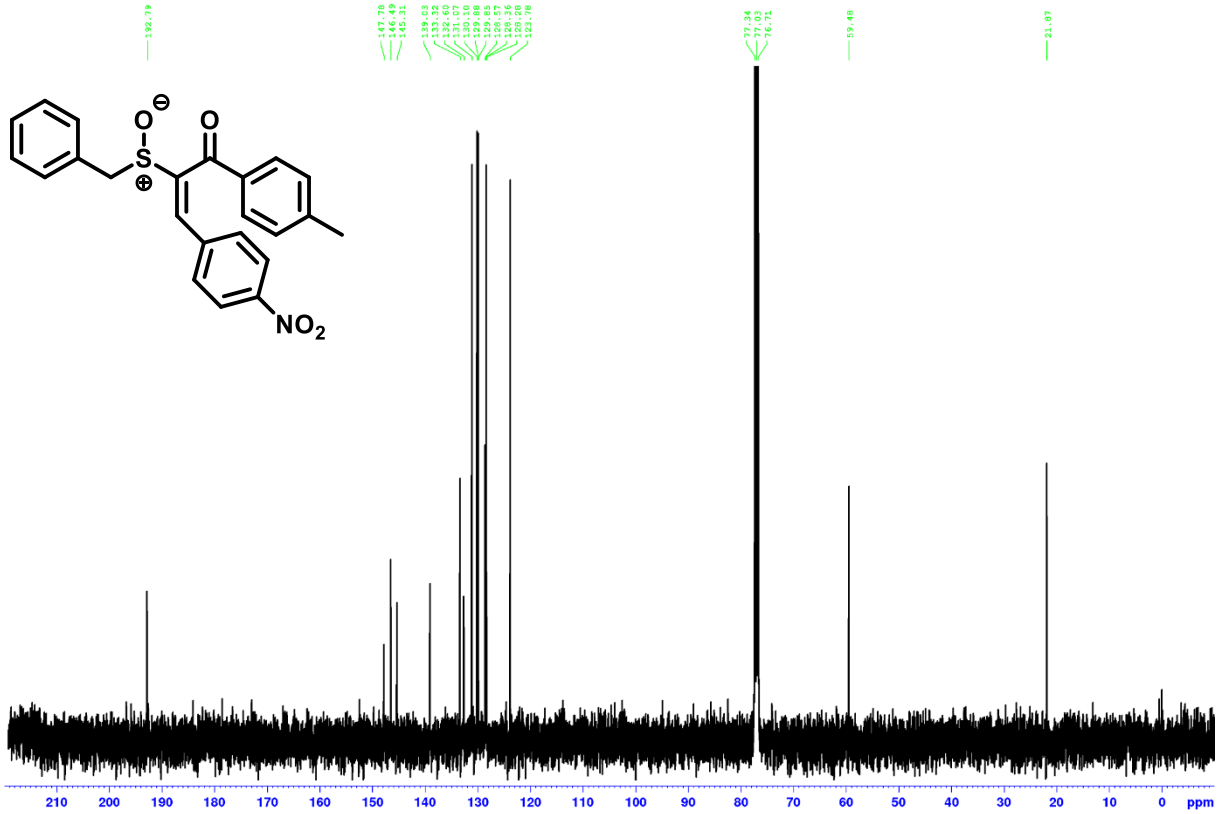


Figure S292: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-40h**.

(*Z*)-2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40h

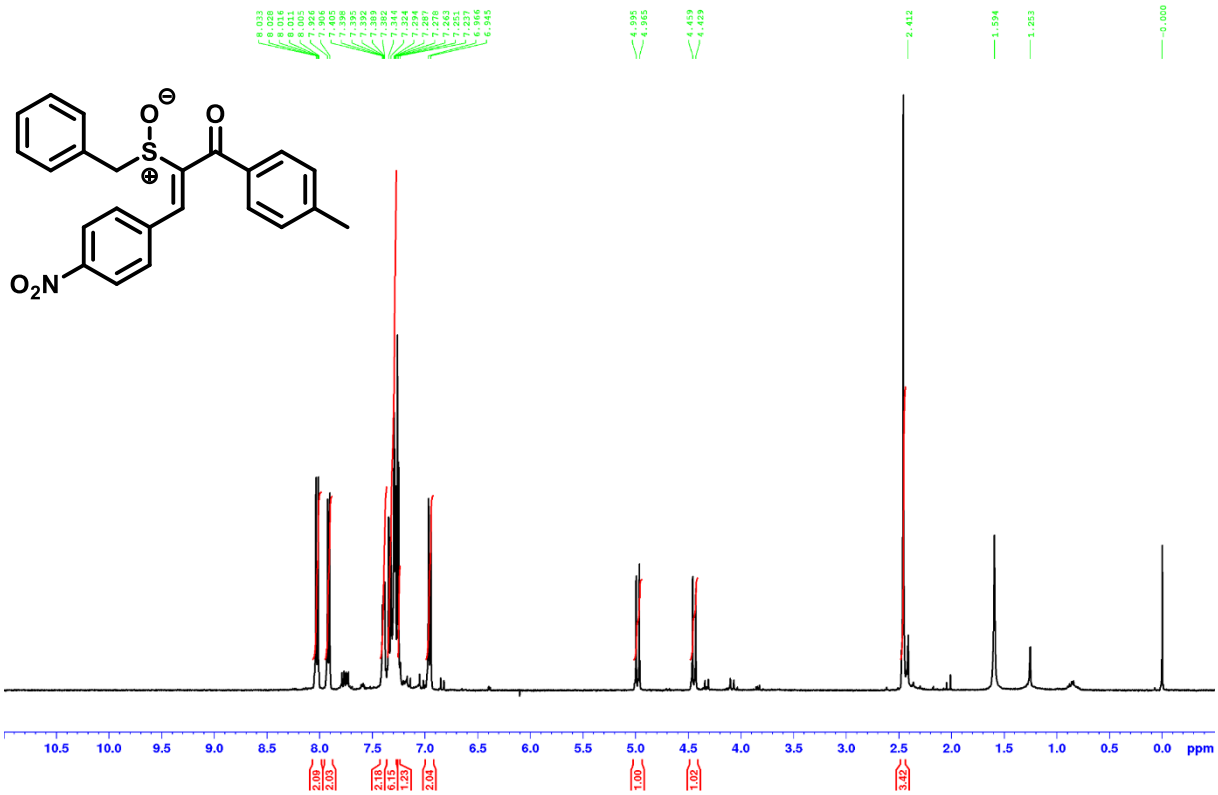


Figure S293: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**40h** which contains minor amounts of *E*-**40h** (<10%).

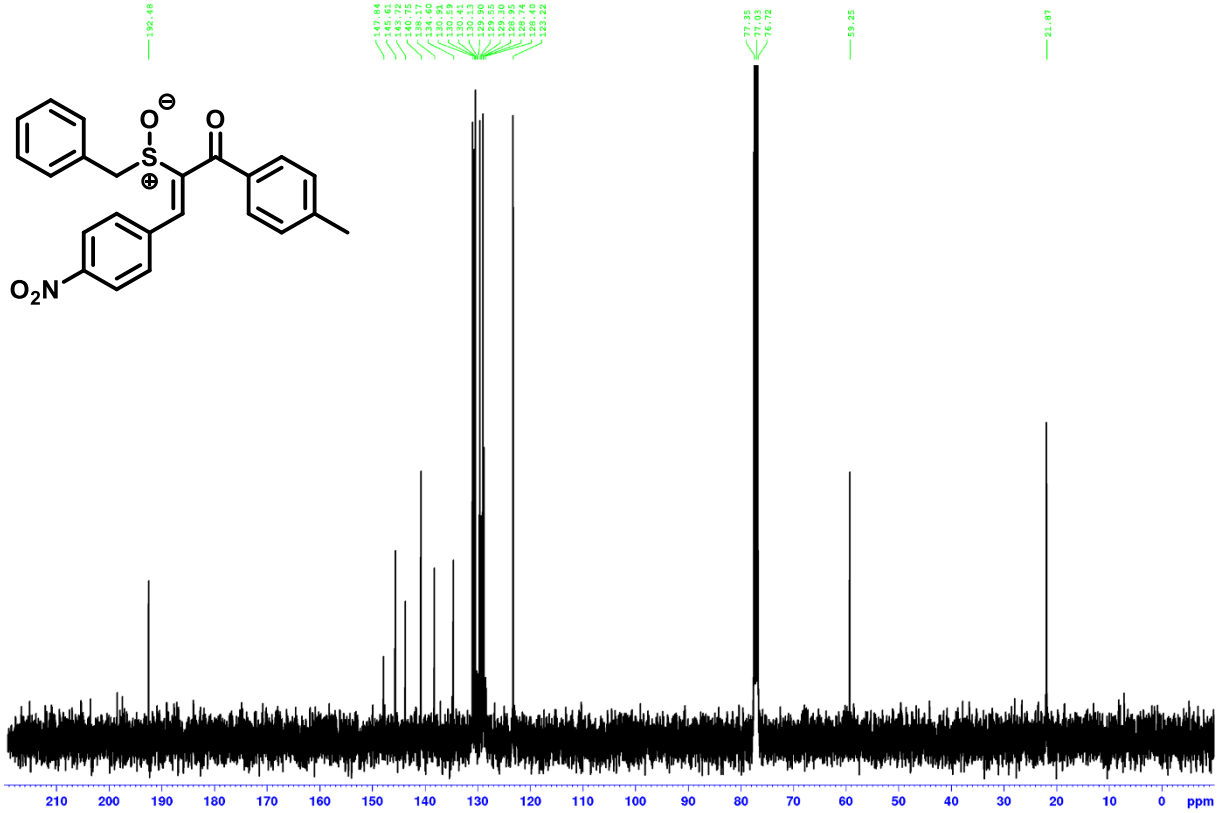


Figure S294: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Z*-**40h** which contains minor amounts of *E*-**40h** (<10%).

2-((4-Methylbenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40m

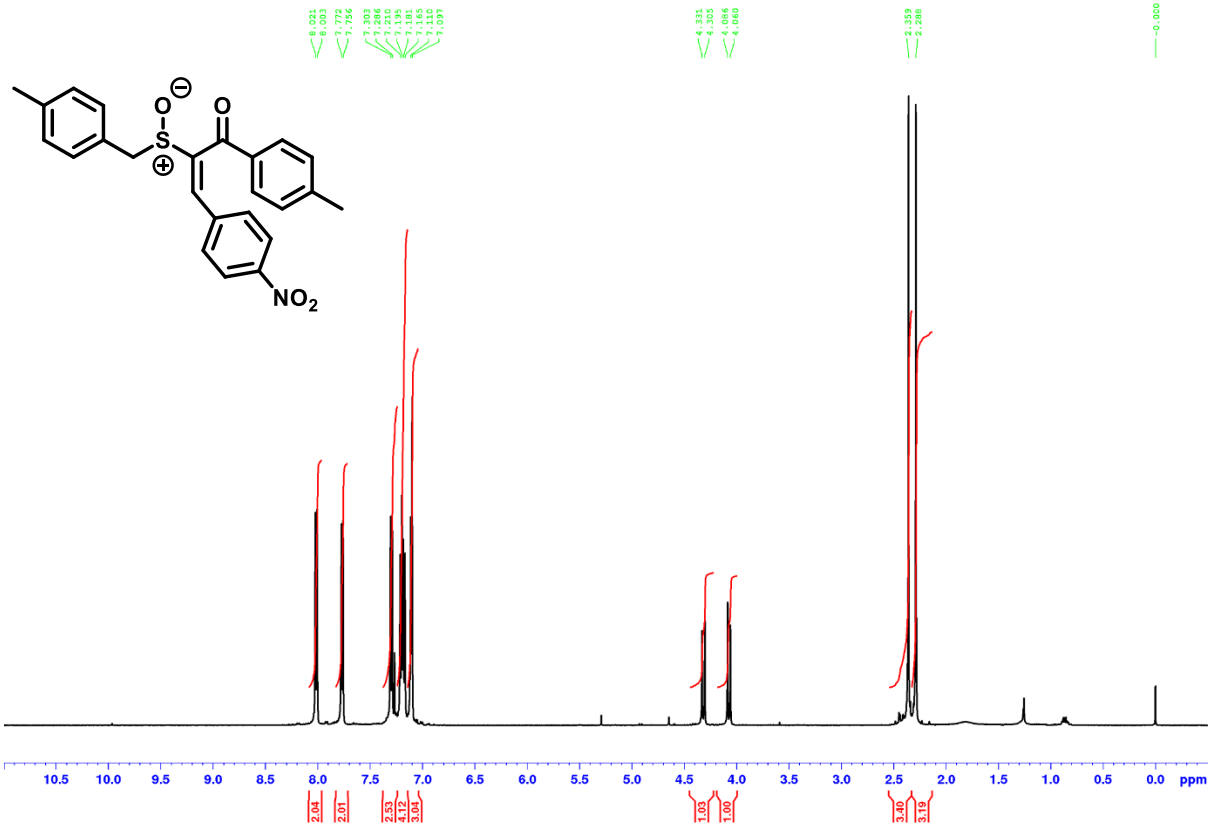


Figure S295: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-40m**.

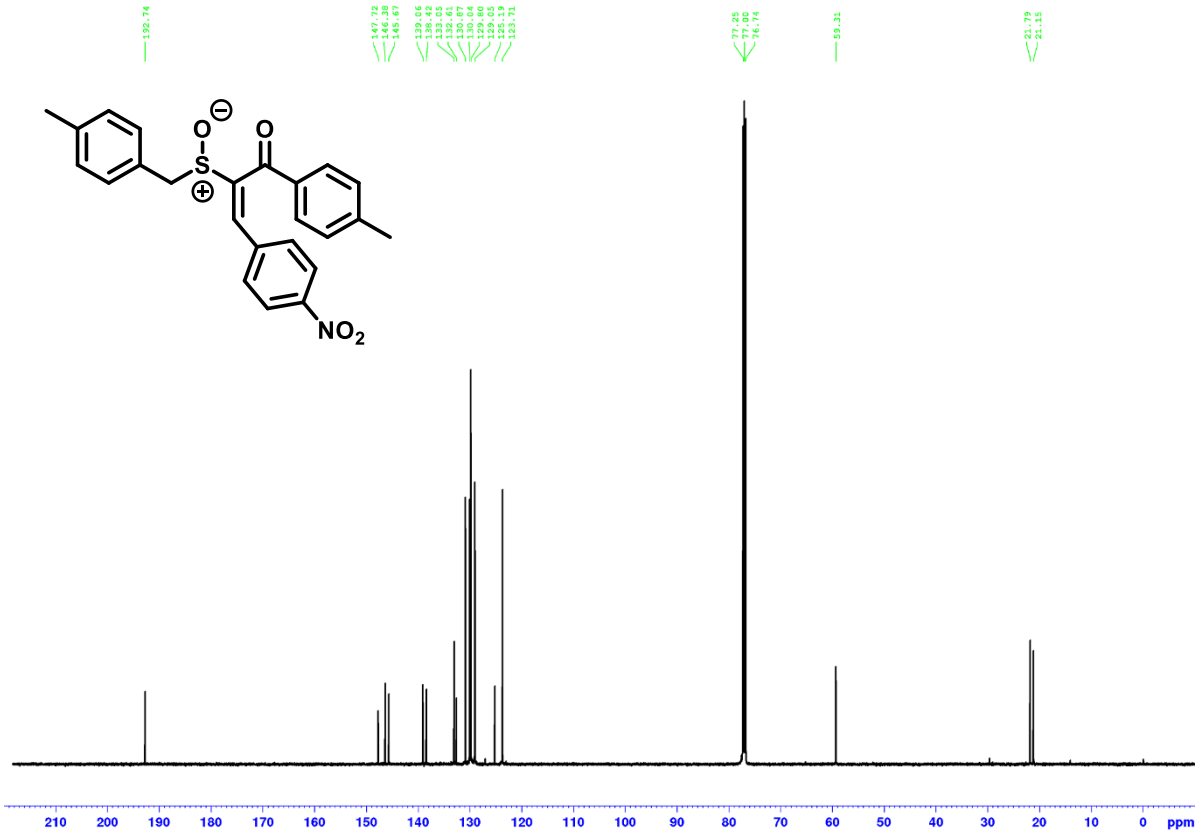


Figure S296: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-40m**.

(*E*)-2-((4-Fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40aa

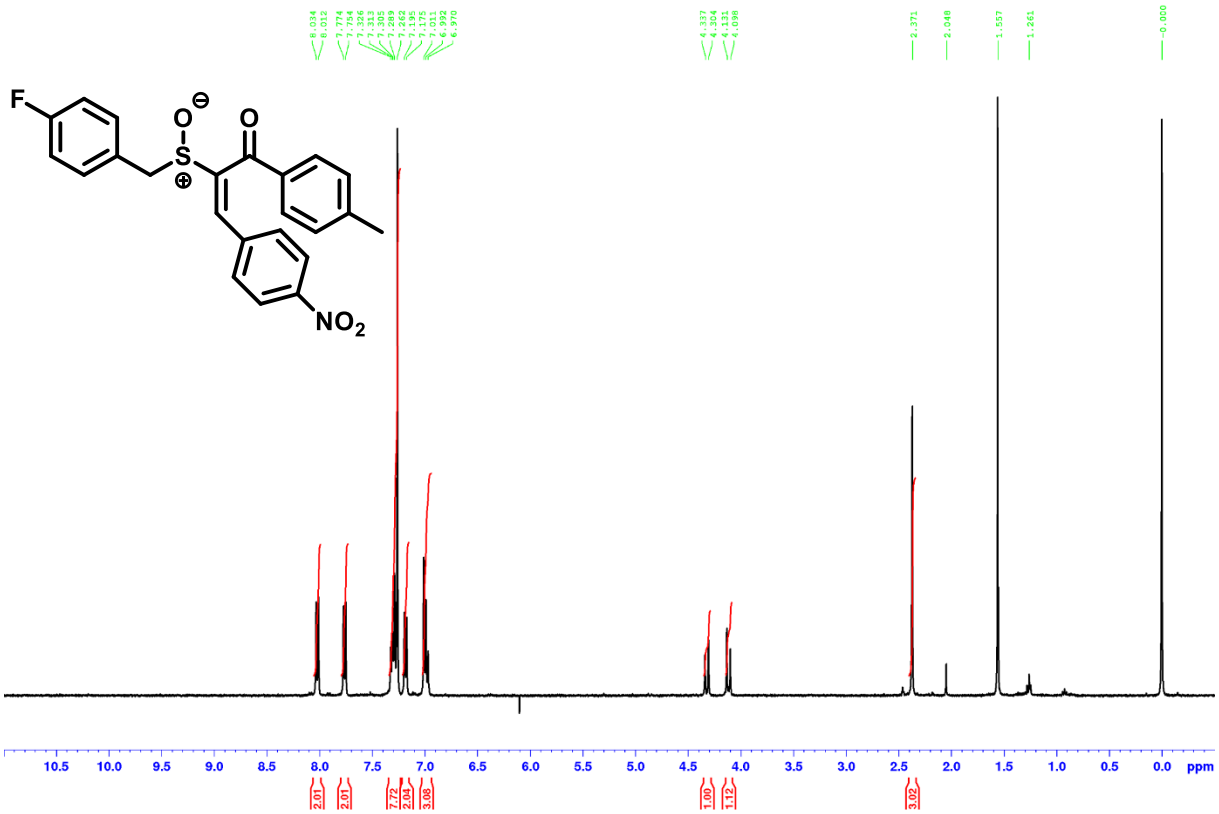


Figure S297: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-40aa**.

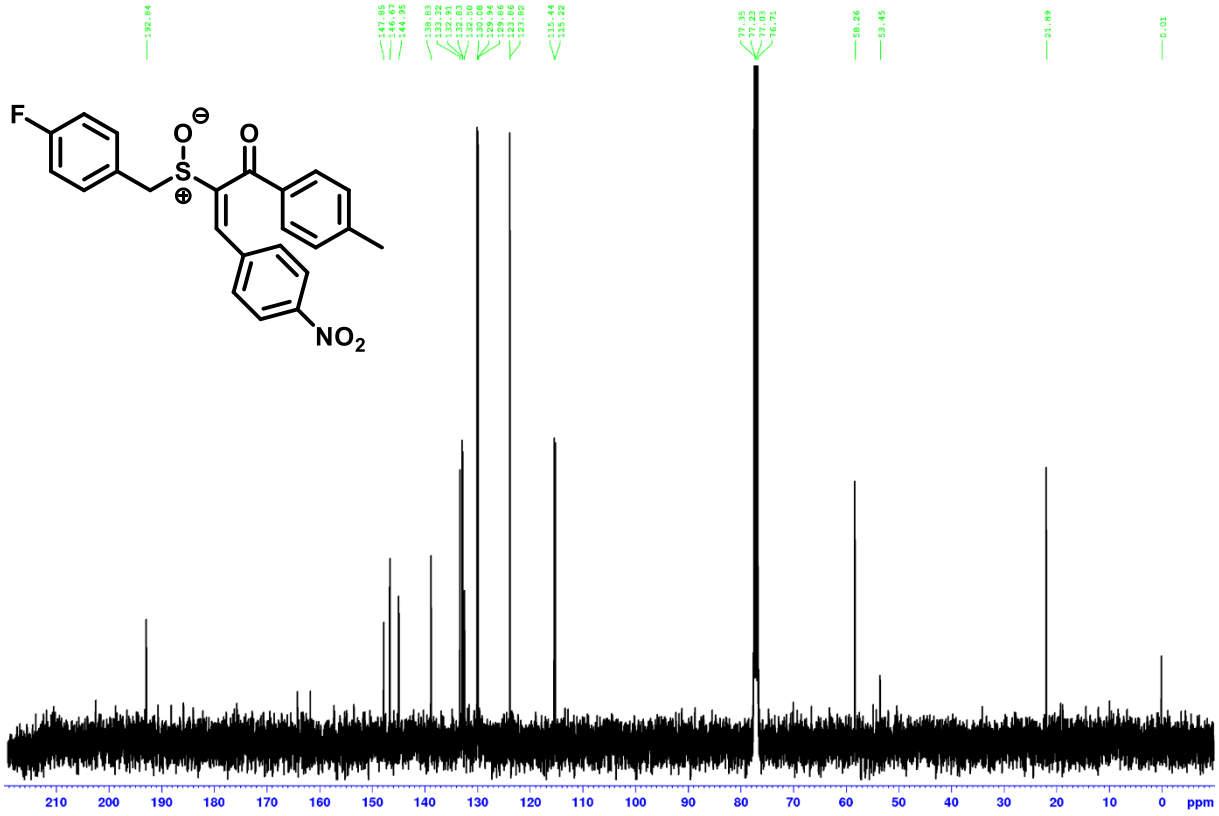


Figure S298: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-40aa**.

(*E*)-2-((4-Chlorobenzyl)sulfinyl)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40q

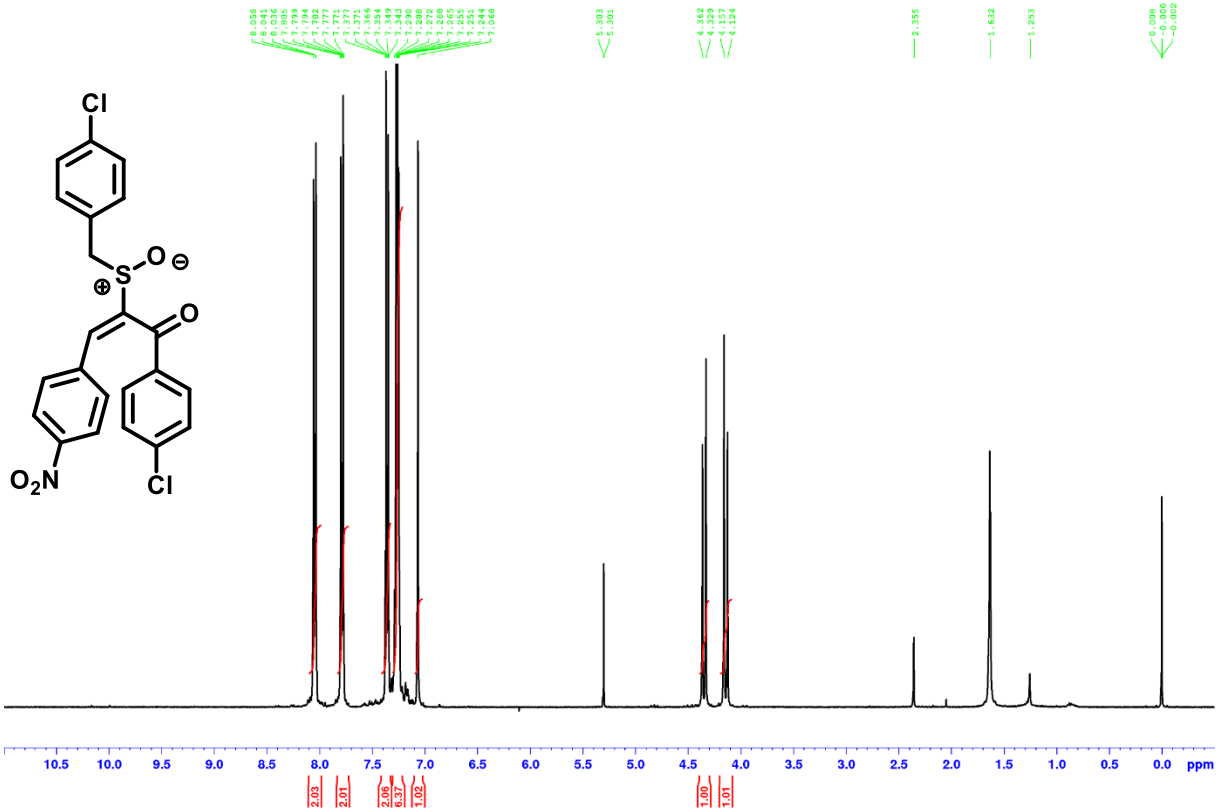


Figure S299: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*40q**.

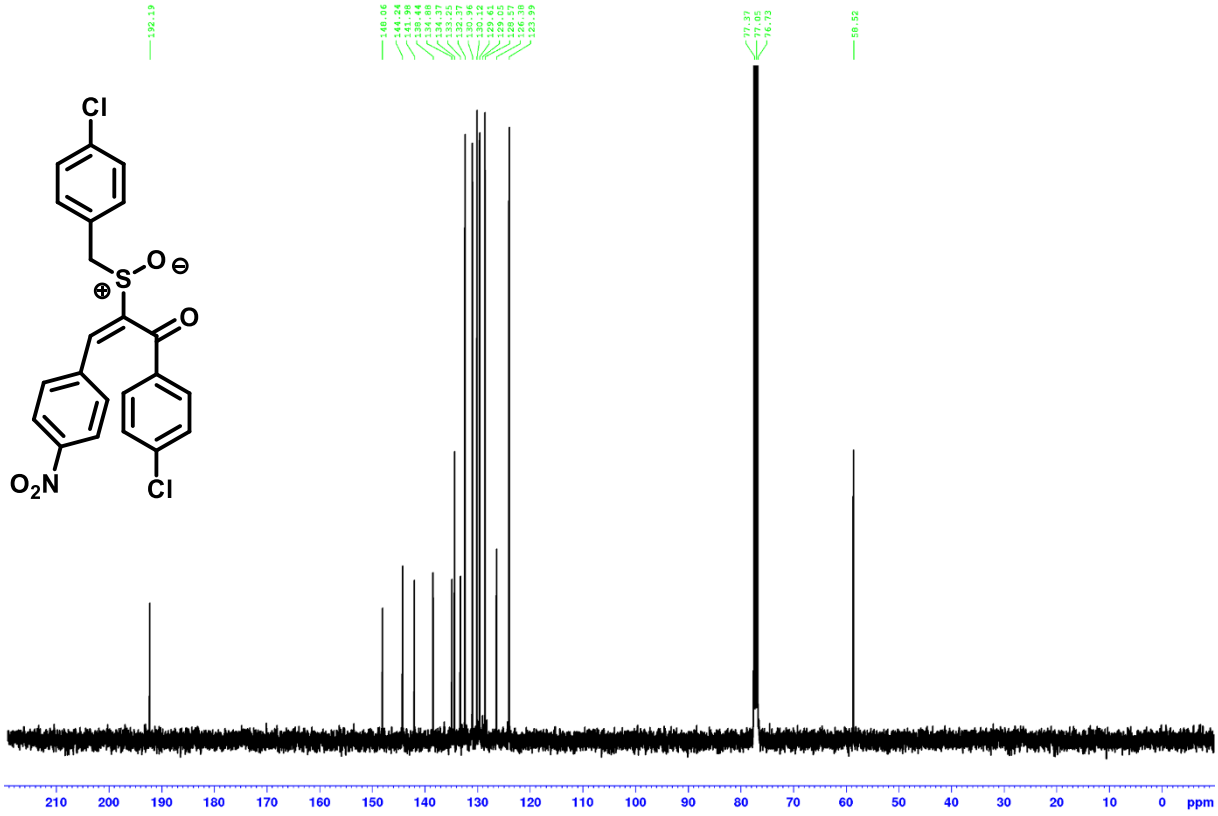


Figure S300: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-40q**.

(*E*)-2-((4-Fluorobenzyl)sulfinyl)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one *E*-40z

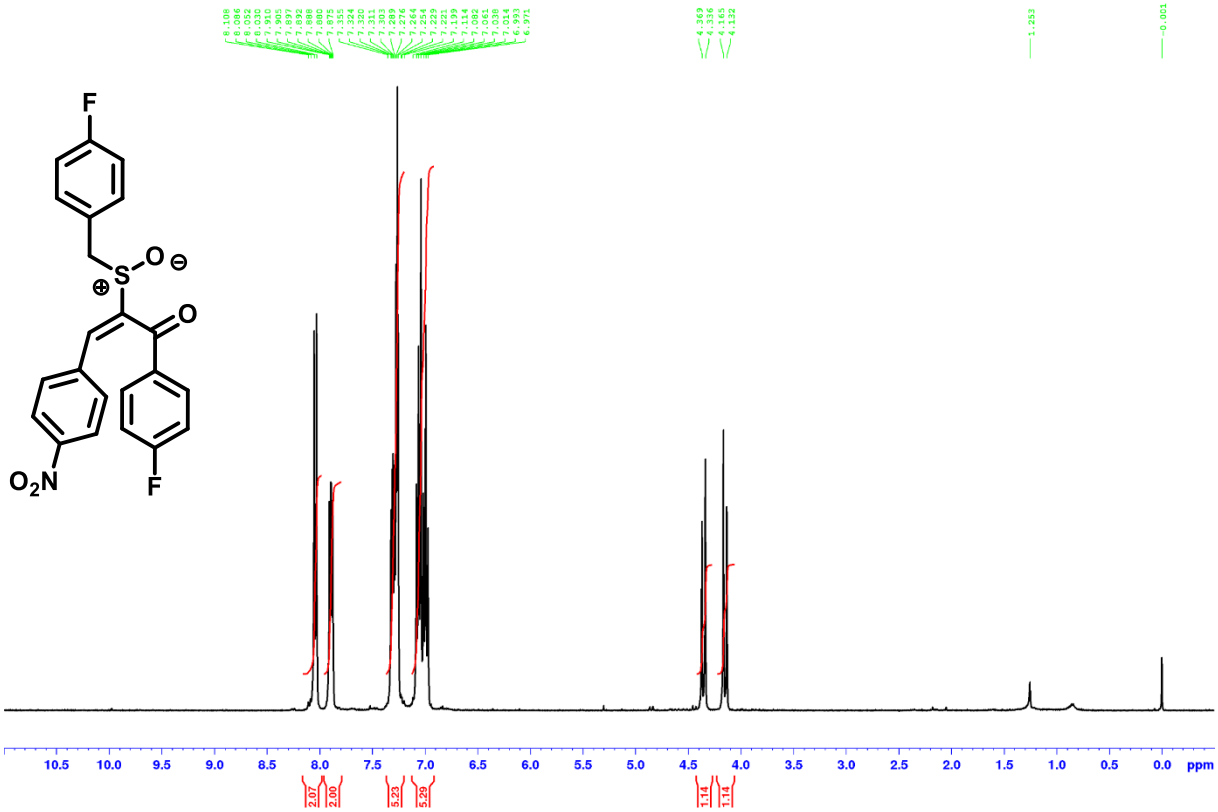


Figure S301: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-40z**.

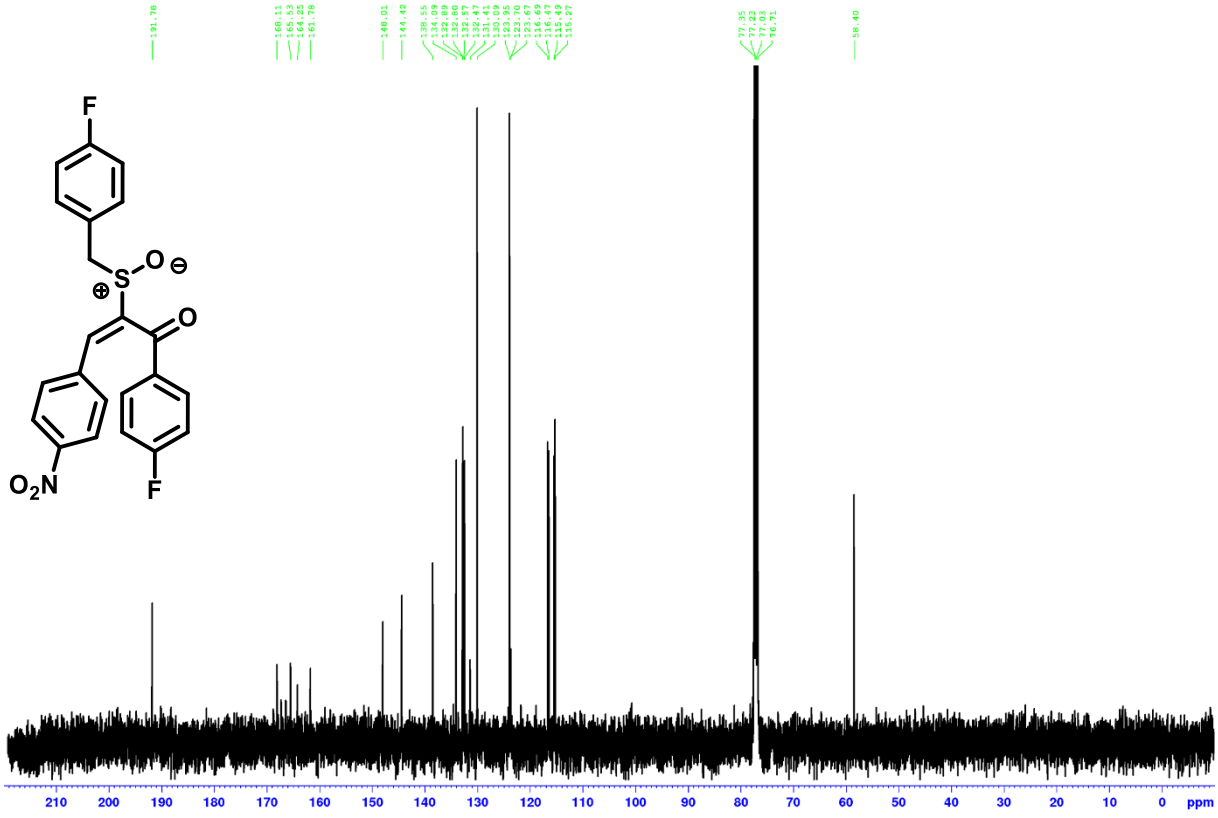


Figure S302: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-40z**.

2-((4-Fluorobenzyl)sulfonyl)-1-(4-fluorophenyl)ethan-1-one 39c

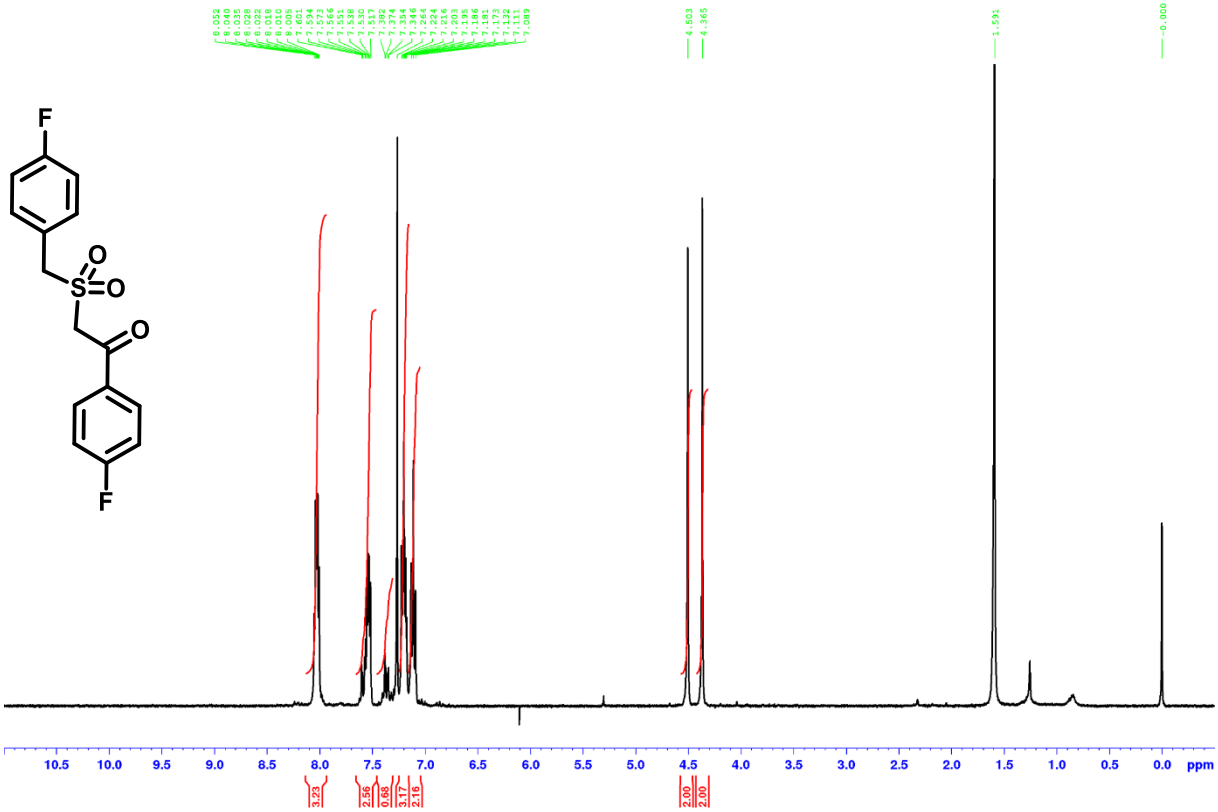


Figure S303: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **39c.**

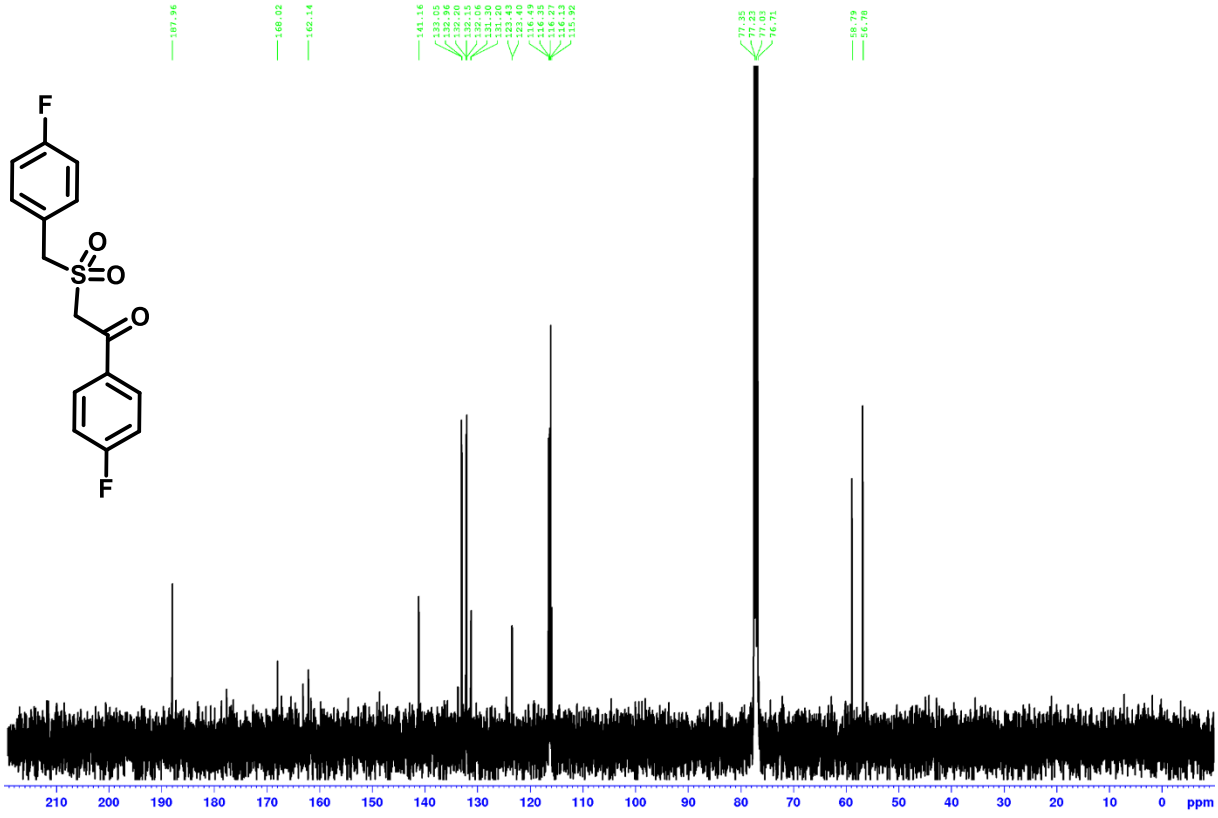


Figure S304: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **39c.**

(*E*)-2-((4-Chlorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40t

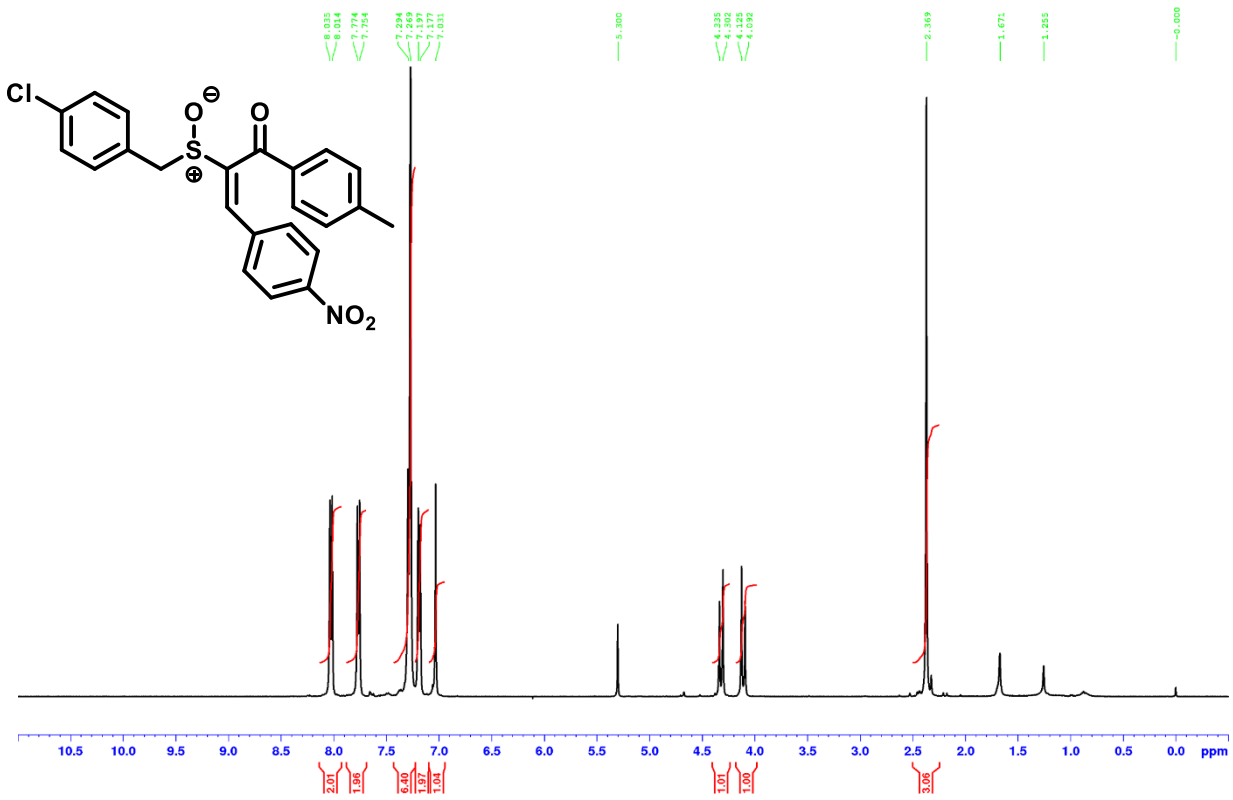


Figure S305: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***E*-40t**.

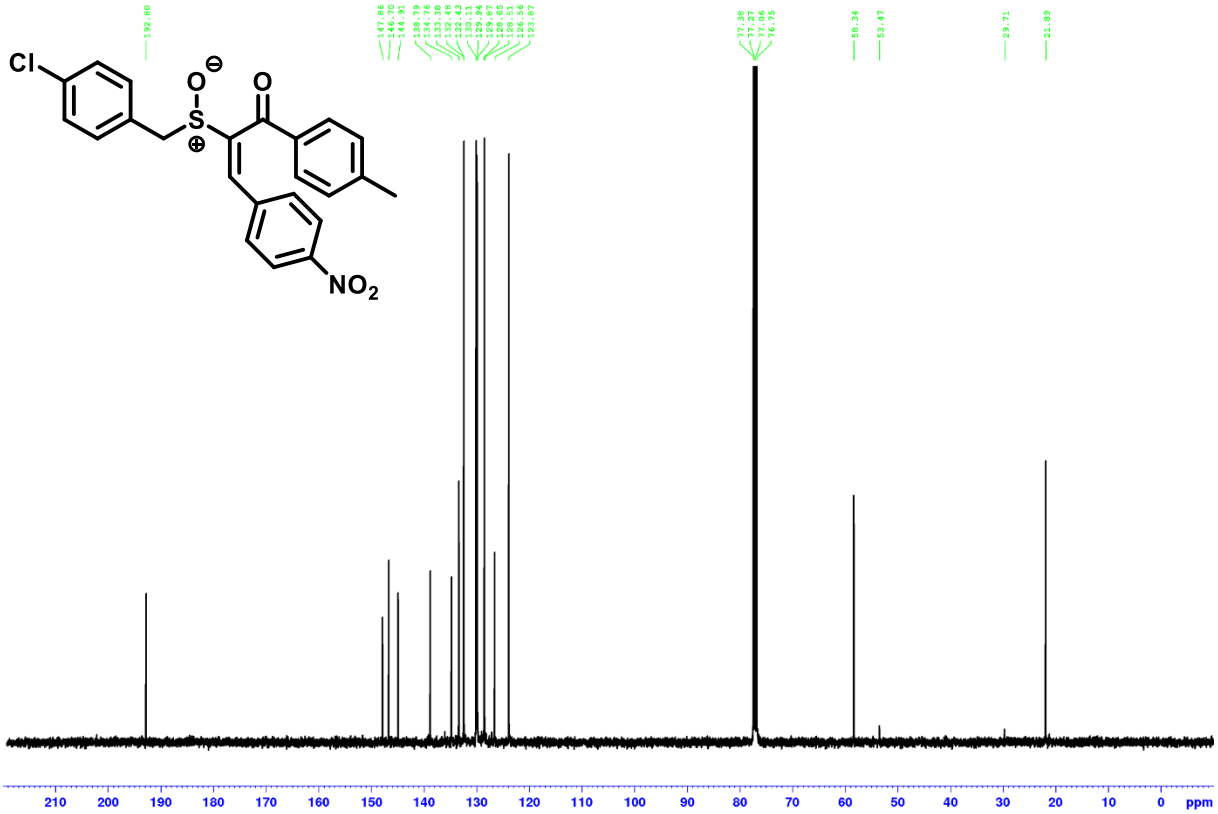


Figure S306: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***E*-40t**.

(*Z*)-2-((4-Chlorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40t

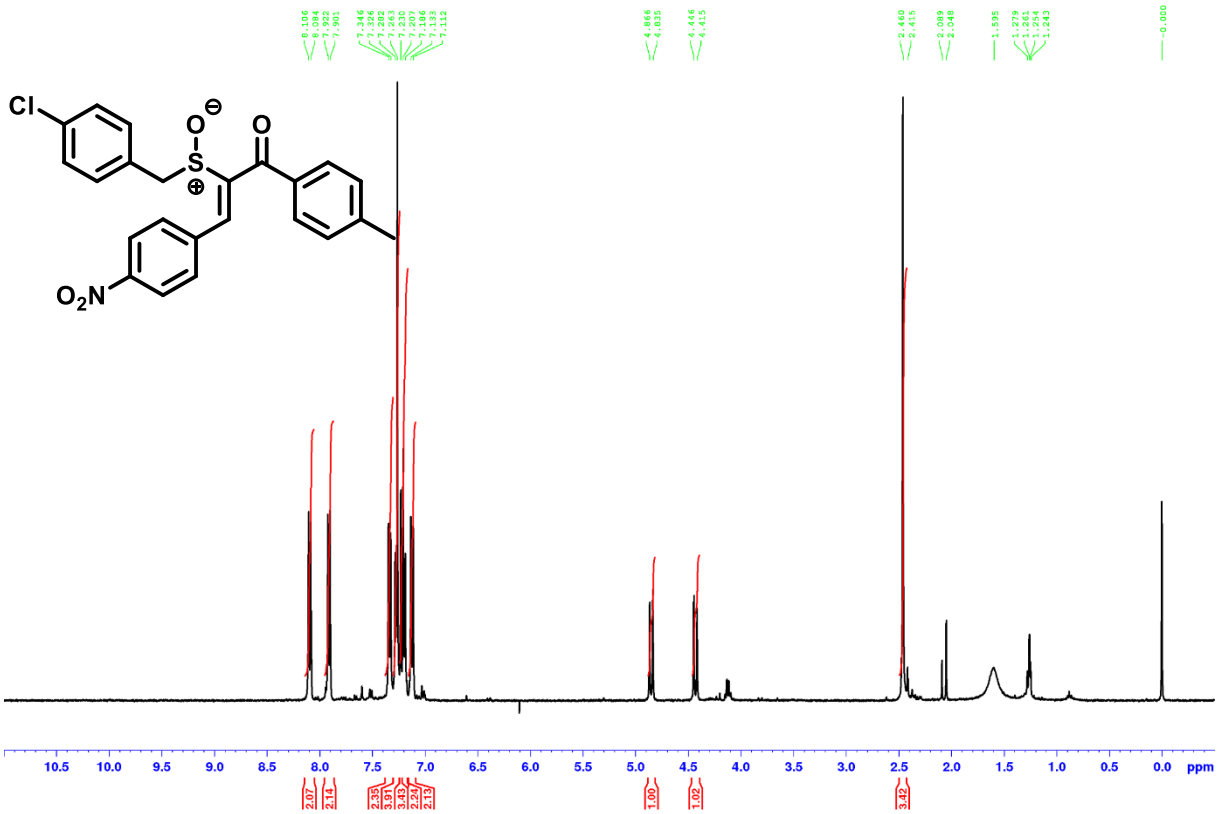


Figure S307: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***Z*-40t**.

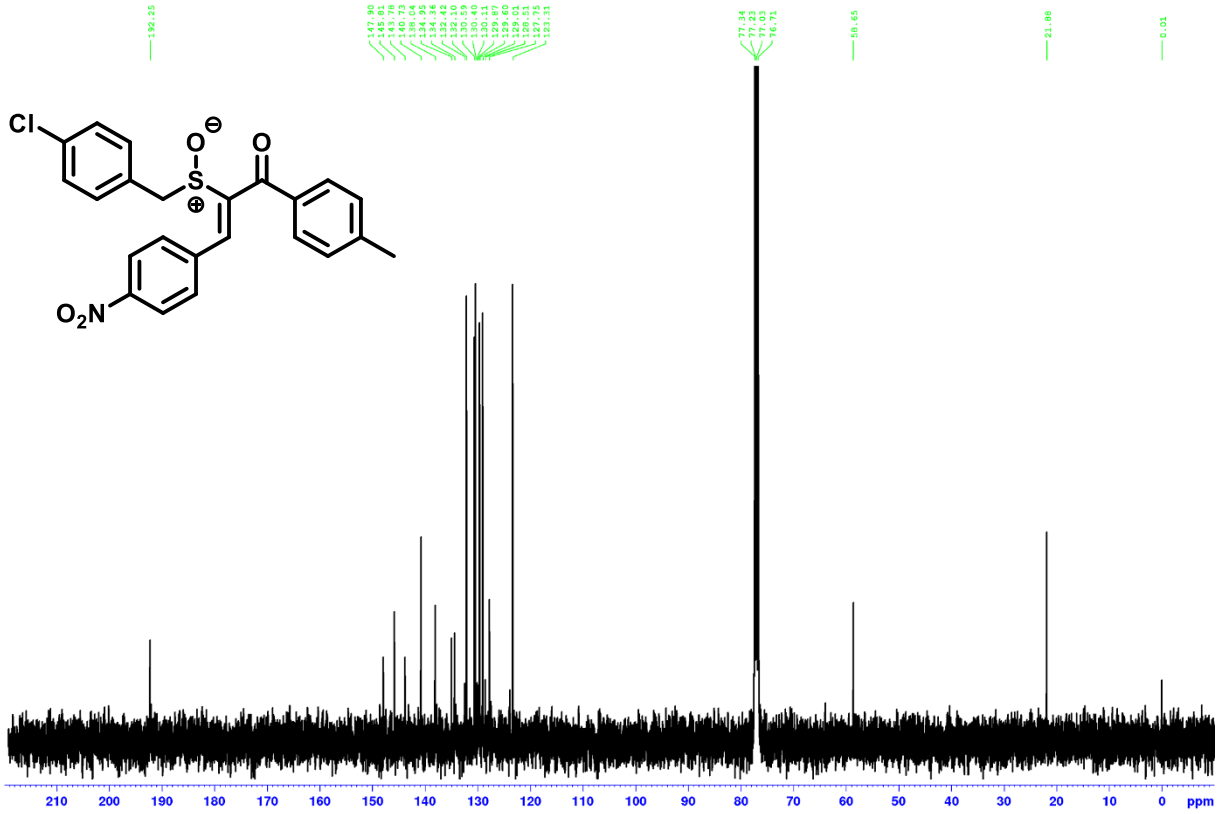


Figure S308: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***Z*-40t**.

2-((4-Chlorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one S68

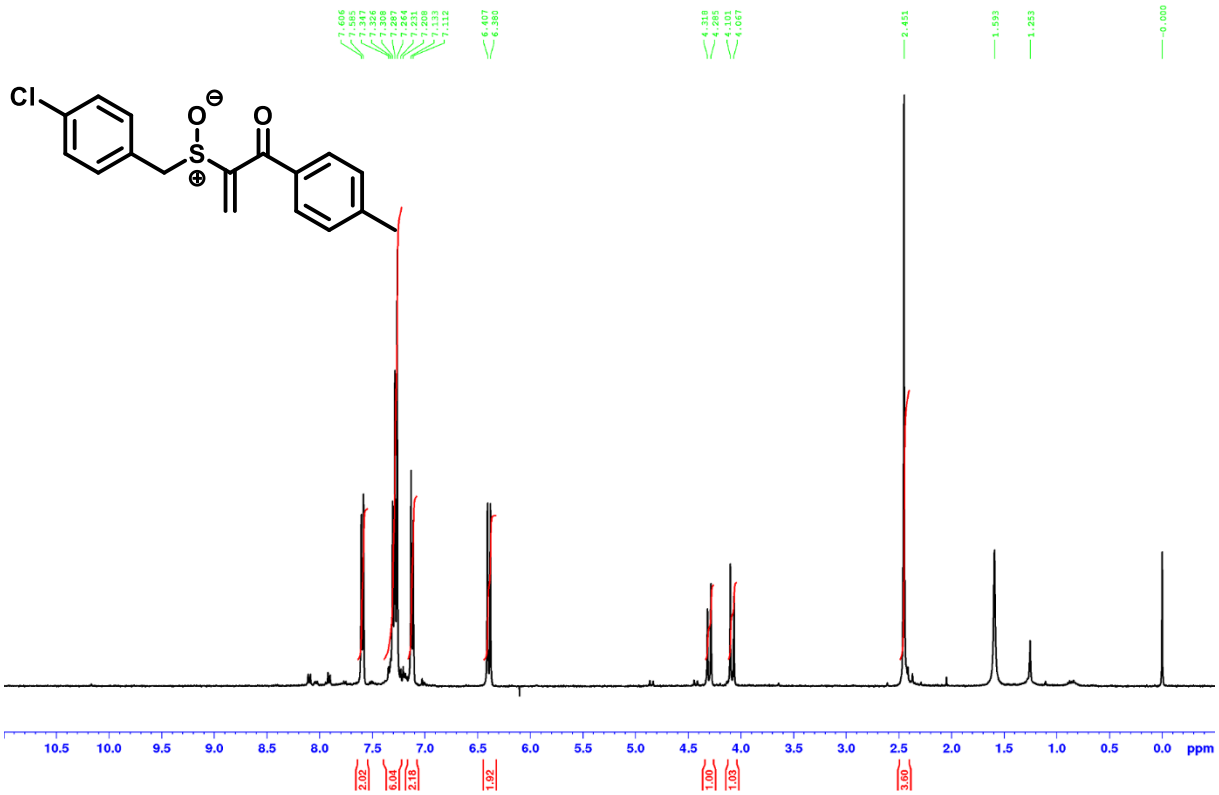


Figure S309: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S68.**

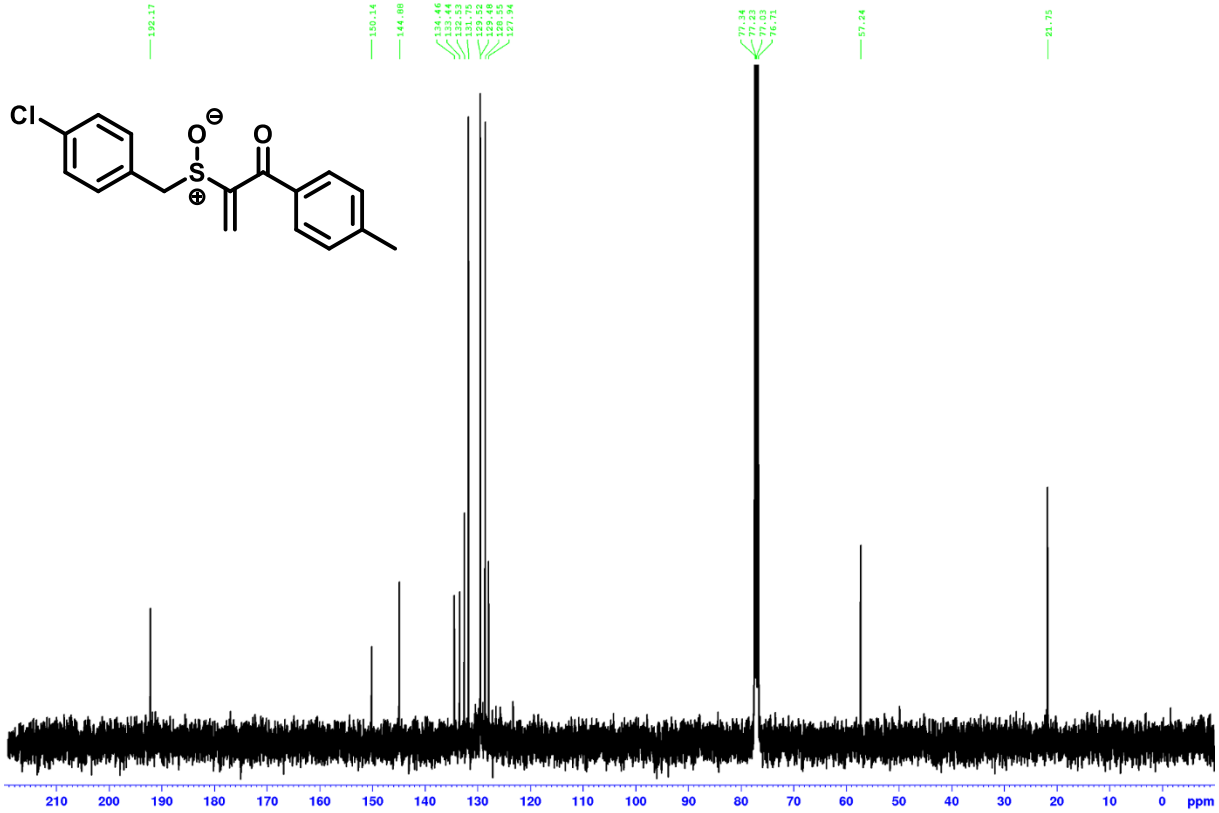


Figure S310: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S68.**

1.12.12 Oxidation of Chalcones

2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-toly)prop-2-en-1-one 40h

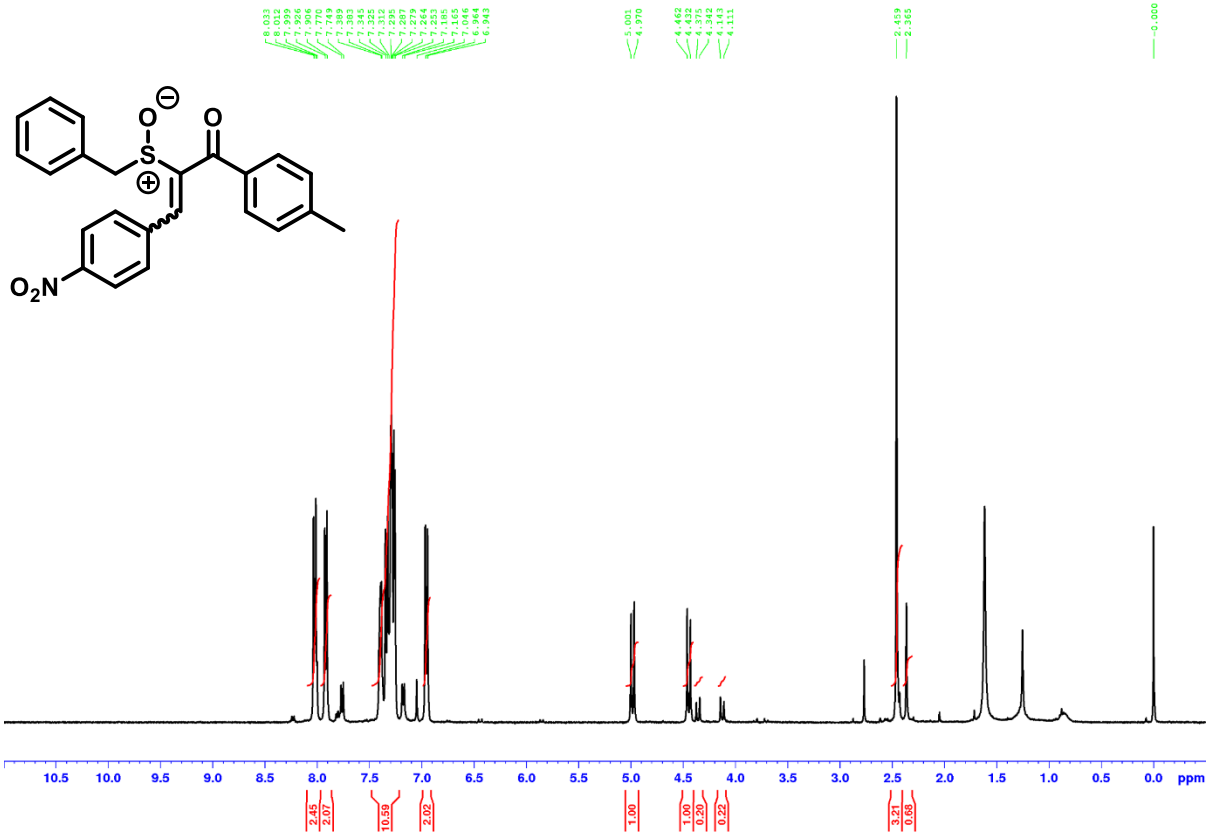


Figure S311: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**40h** and *E*-**40h** (*Z*:*E*, 3.6:1).

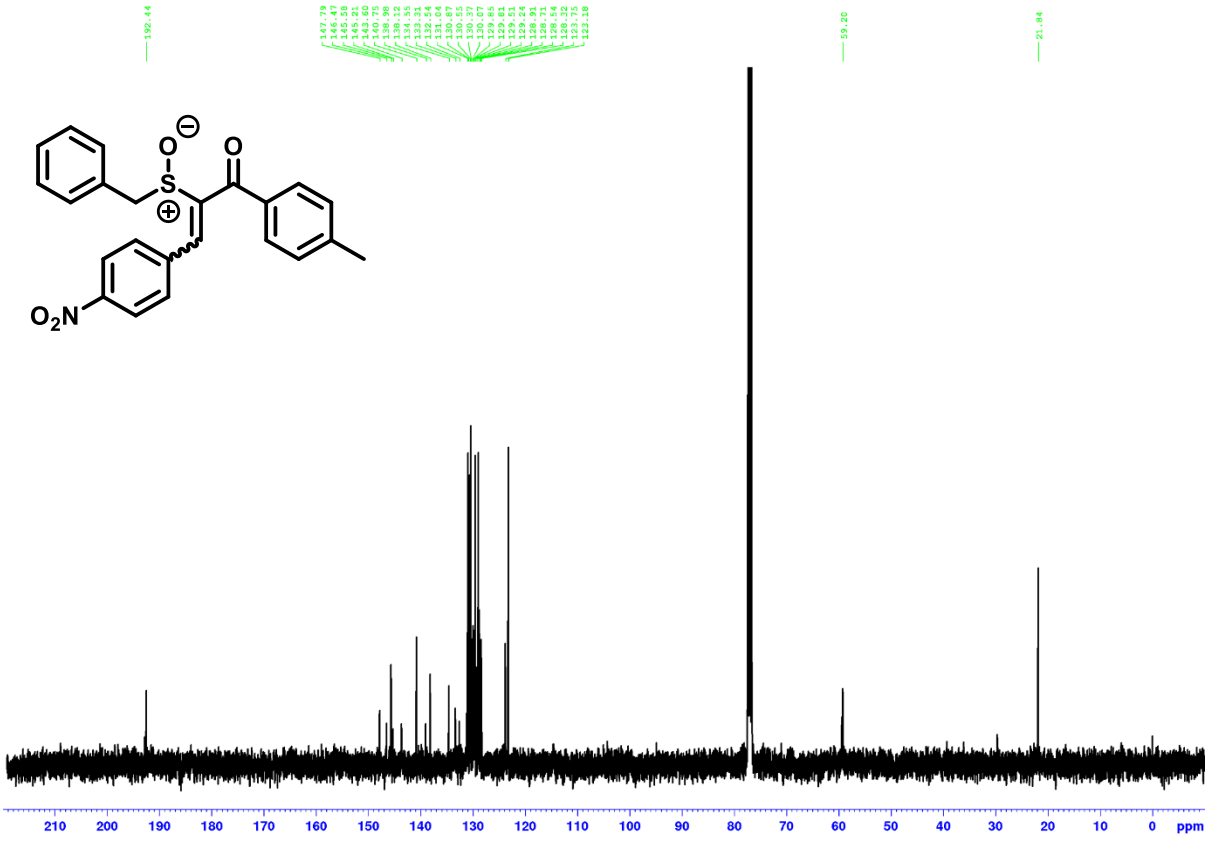


Figure S312: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of *Z*-**40h** and *E*-**40h** (*Z*:*E*, 3.6:1).

2-((4-Chlorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40j

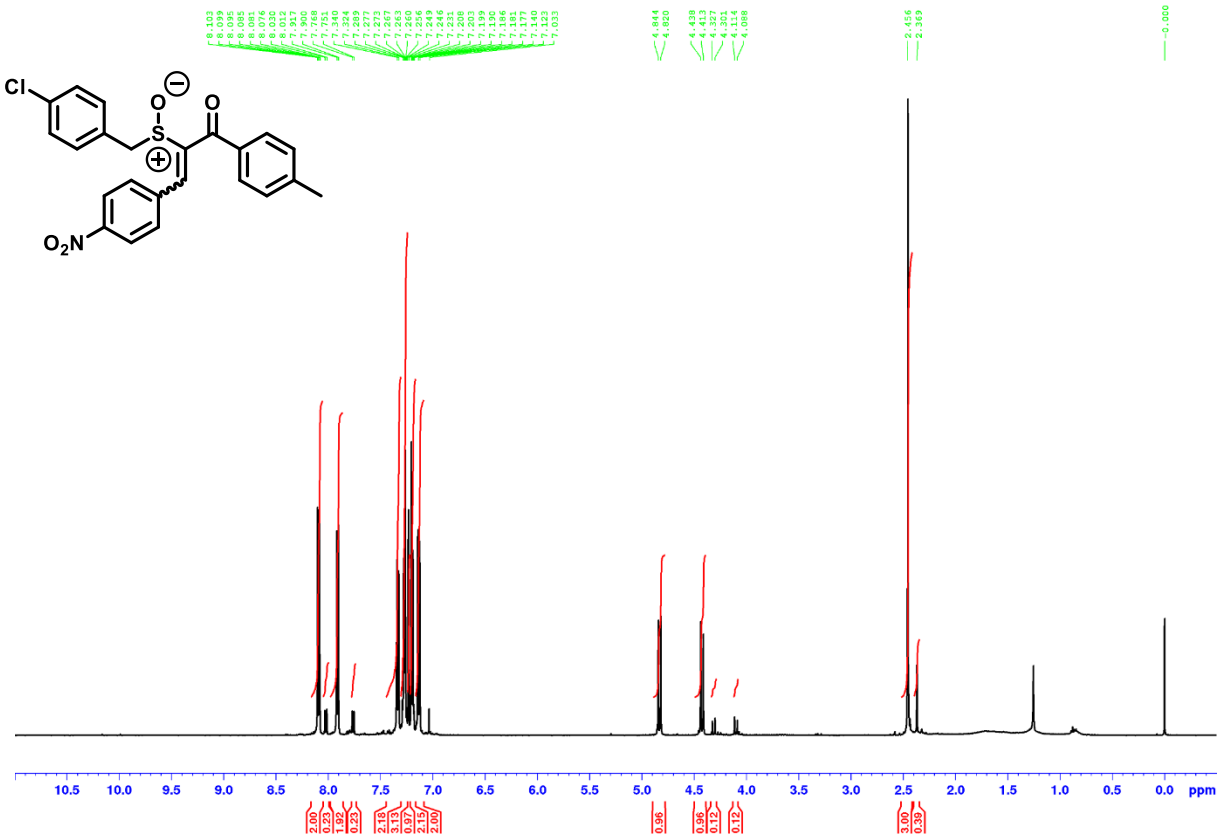


Figure S313: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40j** and *E*-**40j** (*Z*:*E*, 8:1).

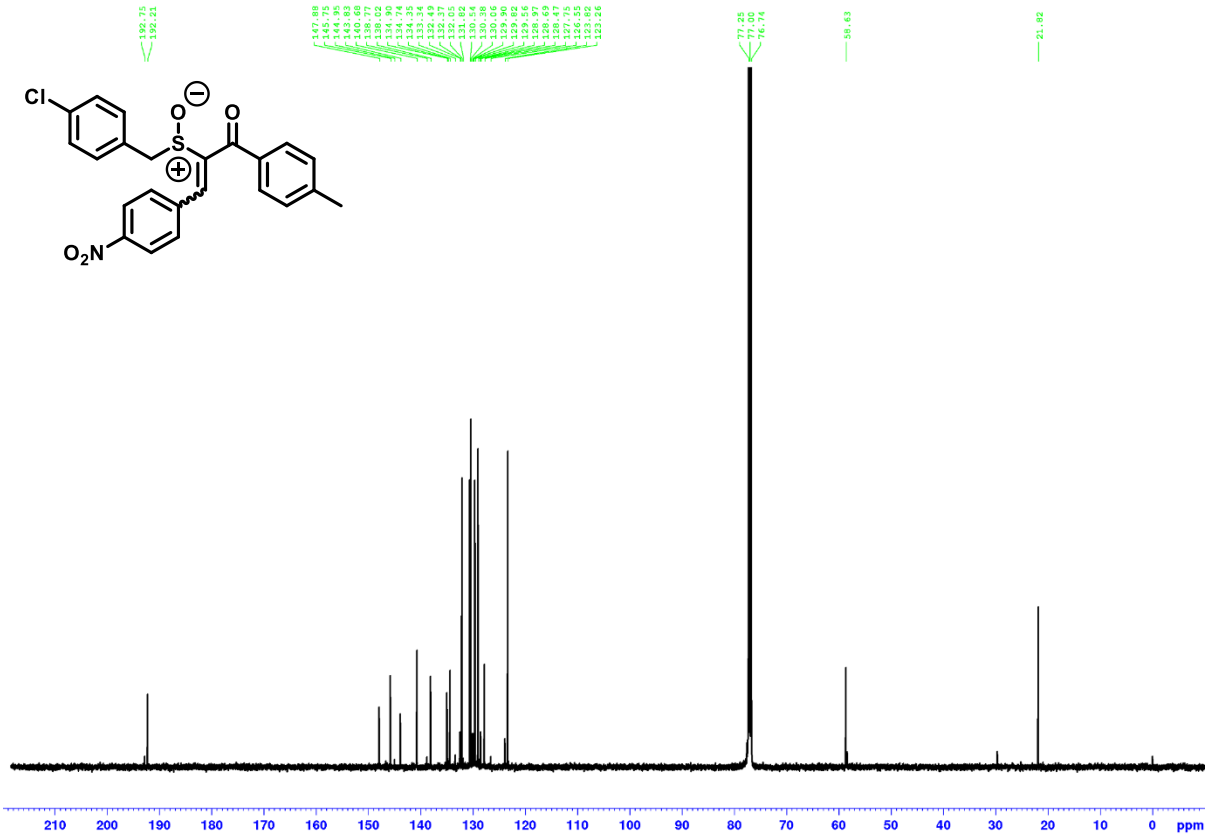


Figure S314: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40j** and *E*-**40j** (*Z*:*E*, 8:1).

2-((4-Fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one 40l

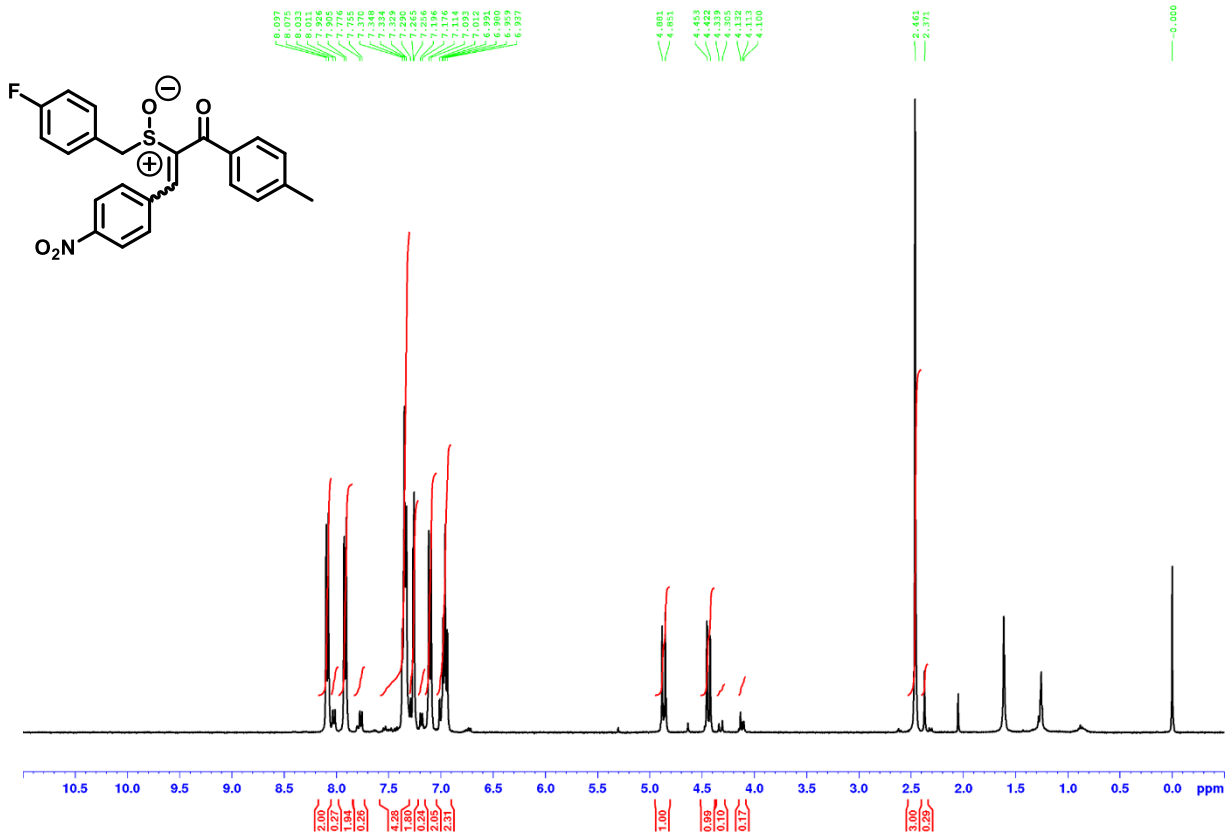


Figure S315: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40l** and *E*-**40l** (*Z*:*E*, 11.5:1).

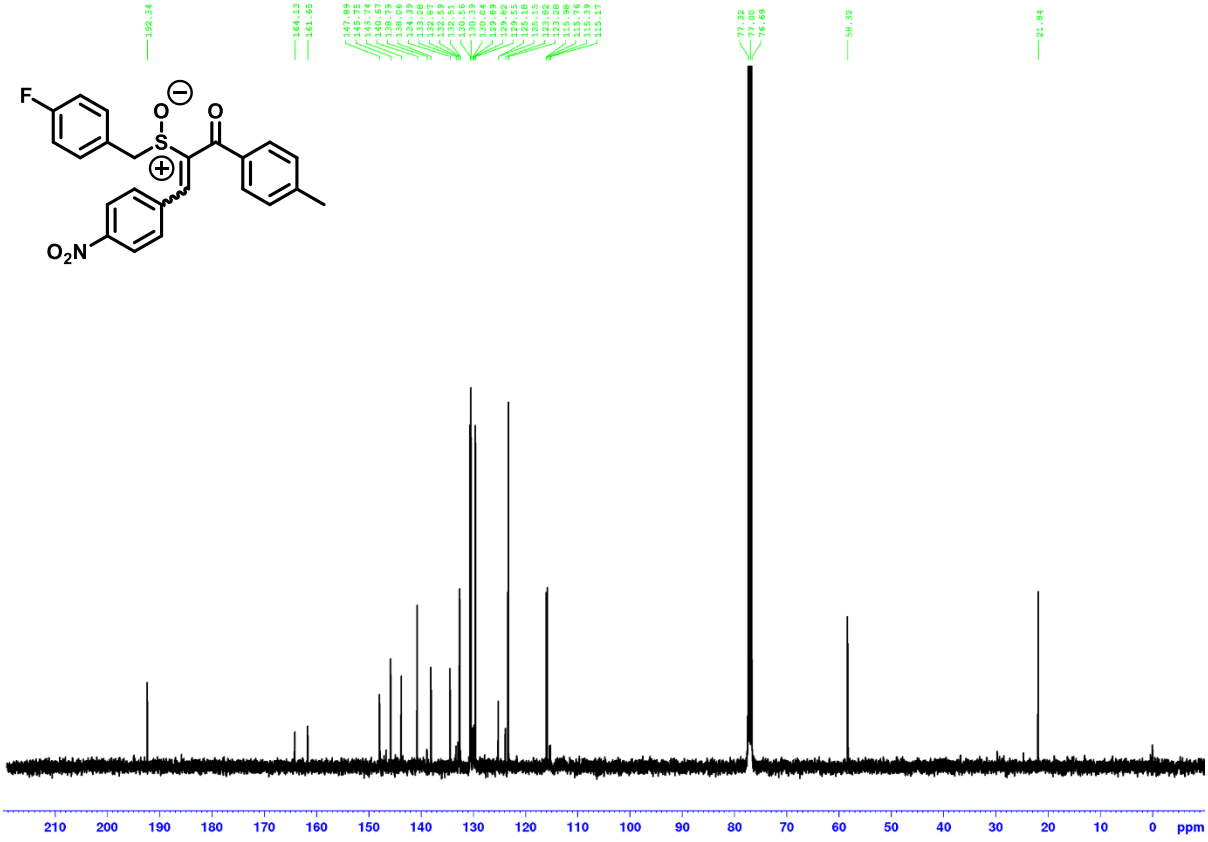


Figure S316: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40l** and *E*-**40l** (*Z*:*E*, 11.5:1)..

1-(4-Fluorophenyl)-2-((4-methylbenzyl)sulfinyl)-3-(4-nitrophenyl)prop-2-en-1-one 40aa

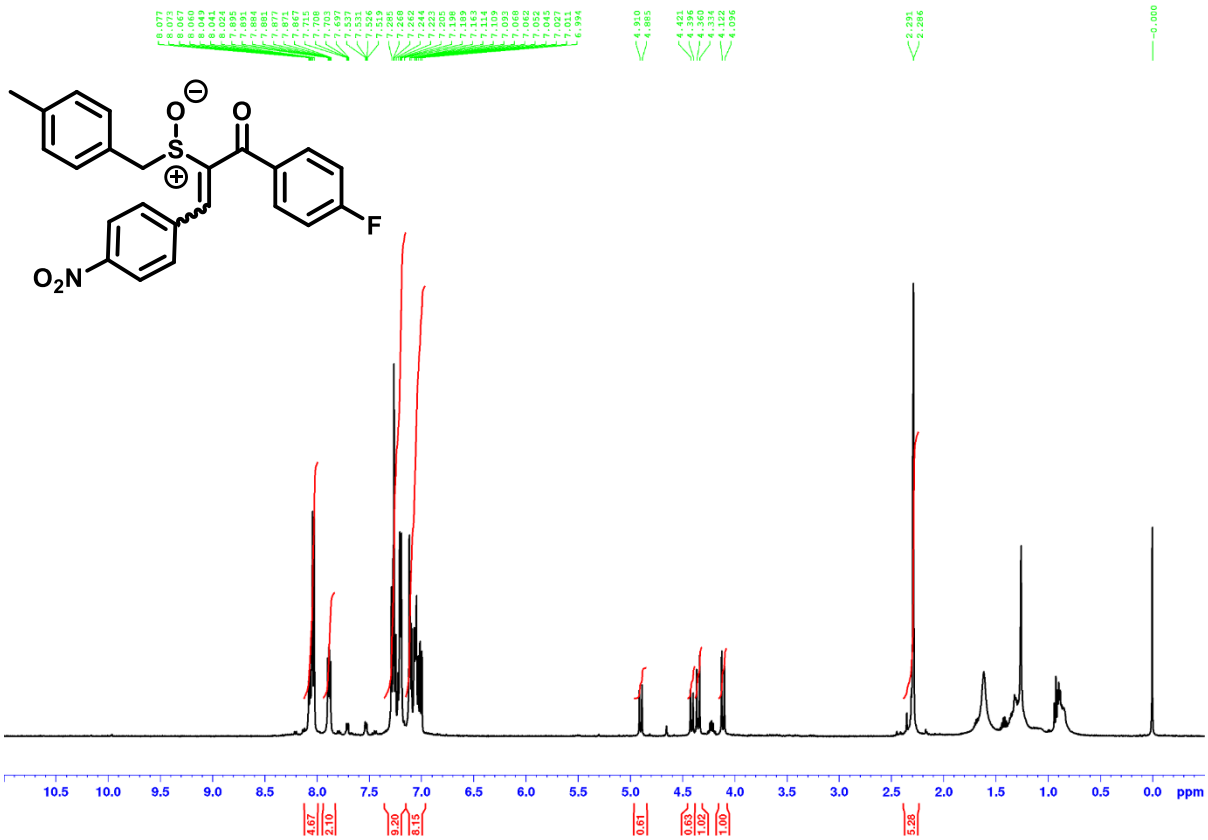


Figure S317: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40aa** and *E*-**40aa** (*Z*:*E*, 1:1.3).

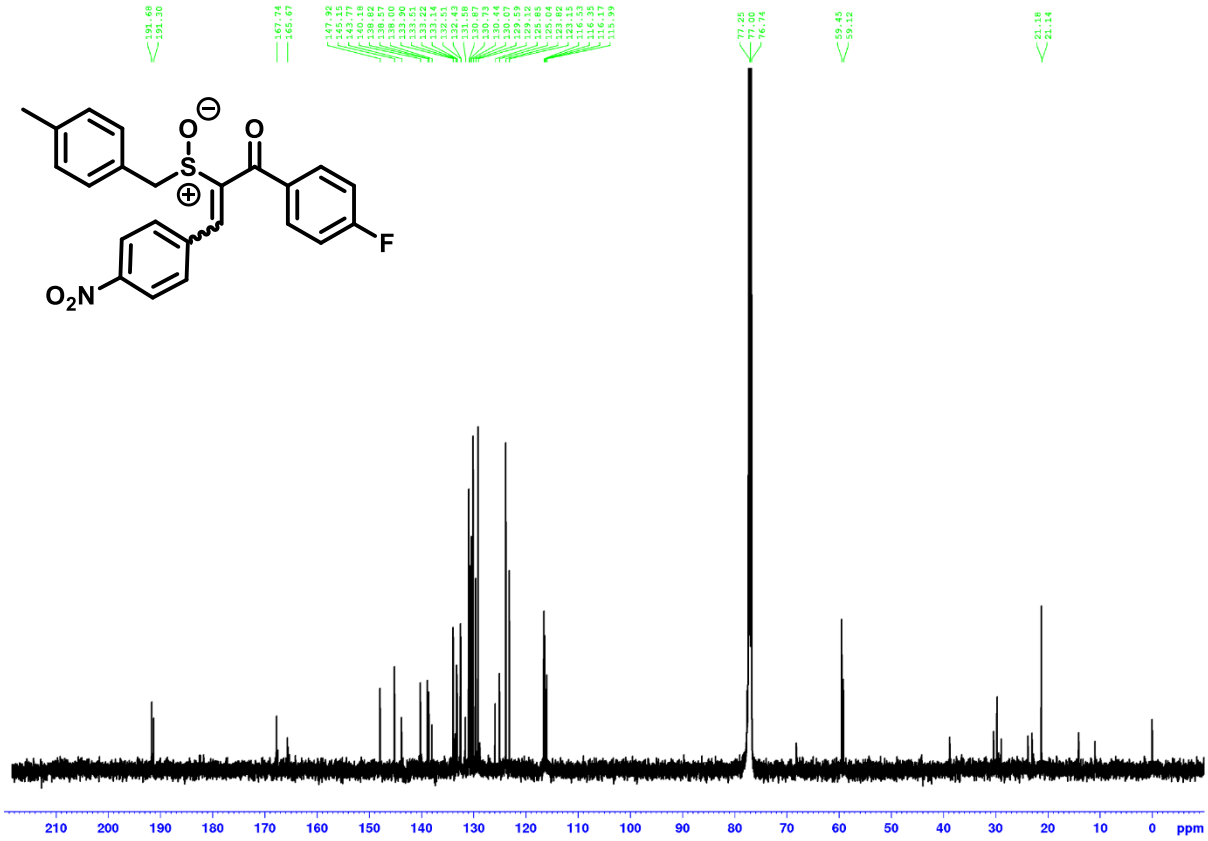


Figure S318: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40aa** and *E*-**40aa** (*Z*:*E*, 1:1.3).

2-((4-Chlorobenzyl)sulfinyl)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40x

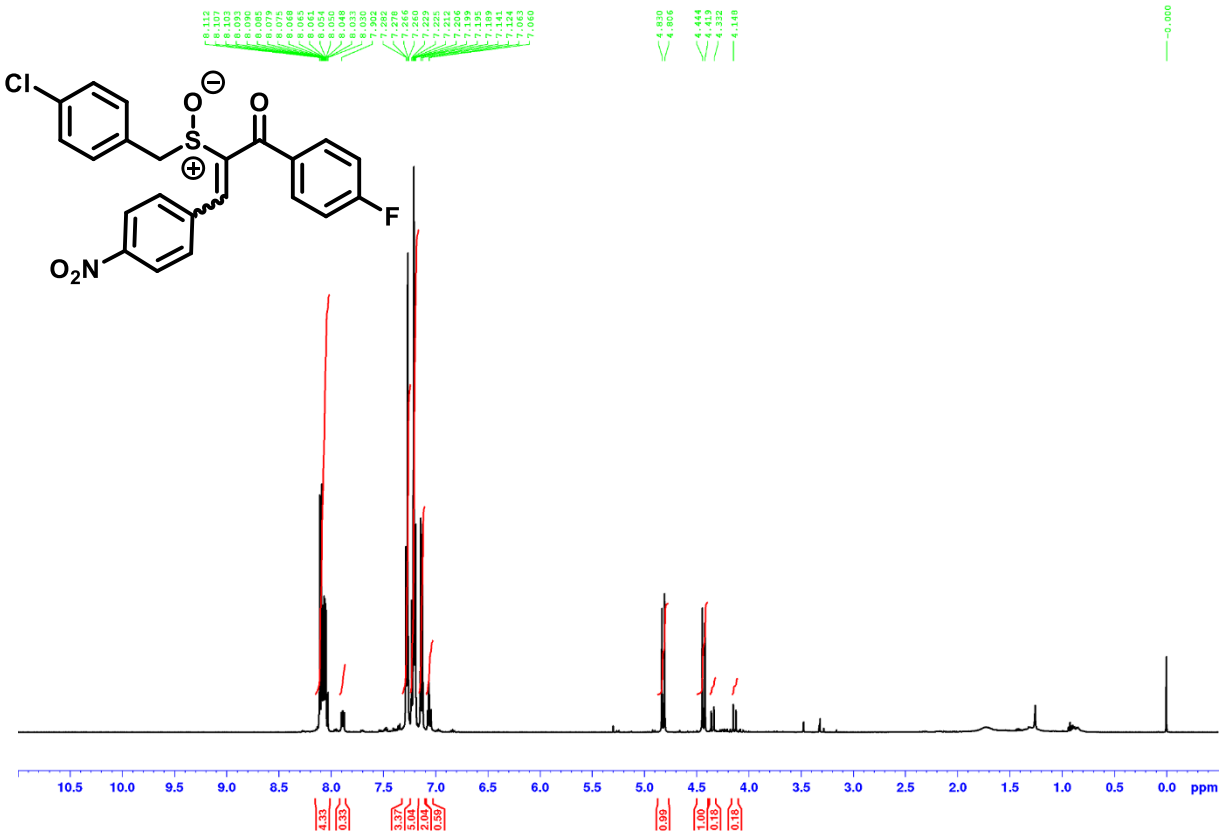


Figure S318: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40x** and *E*-**40x** (*Z*:*E*, 6.7:1).

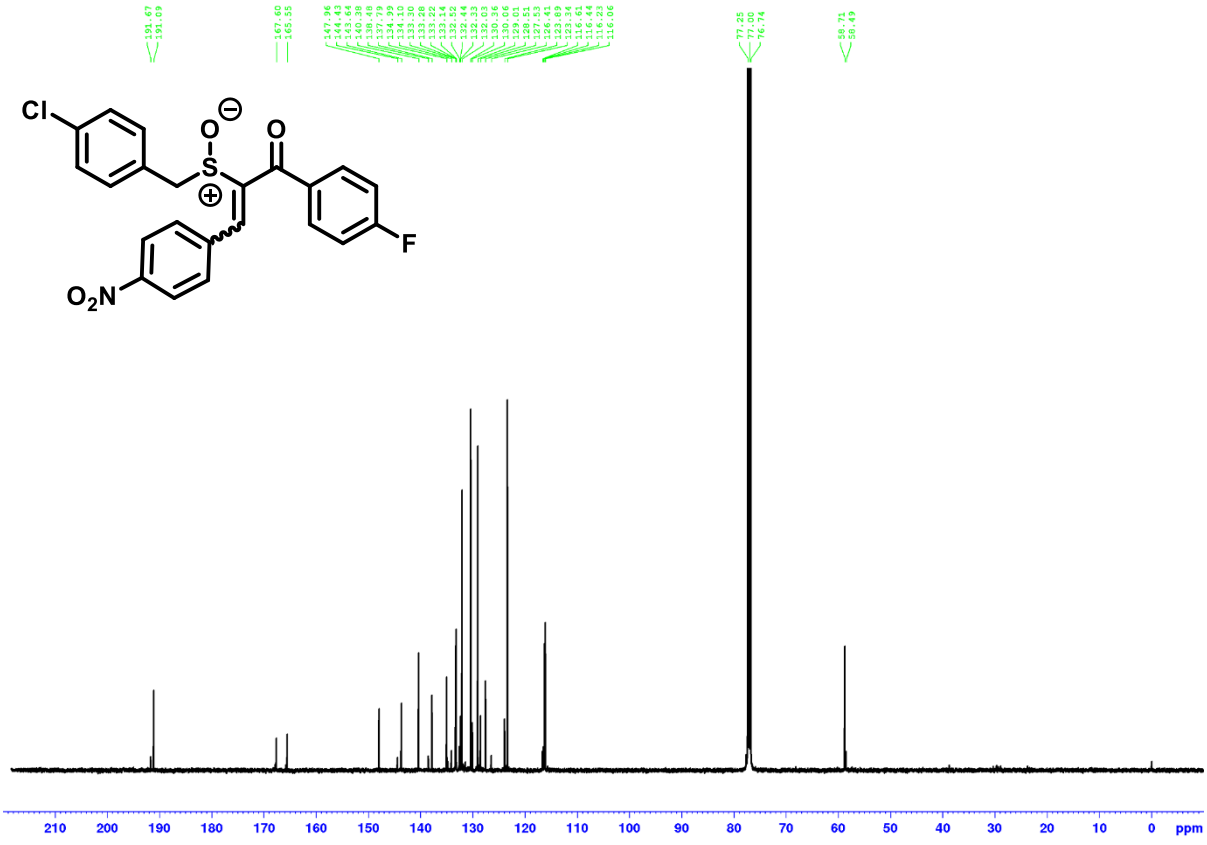


Figure S319: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40x** and *E*-**40x** (*Z*:*E*, 6.7:1).

2-((4-Fluorobenzyl)sulfinyl)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40z

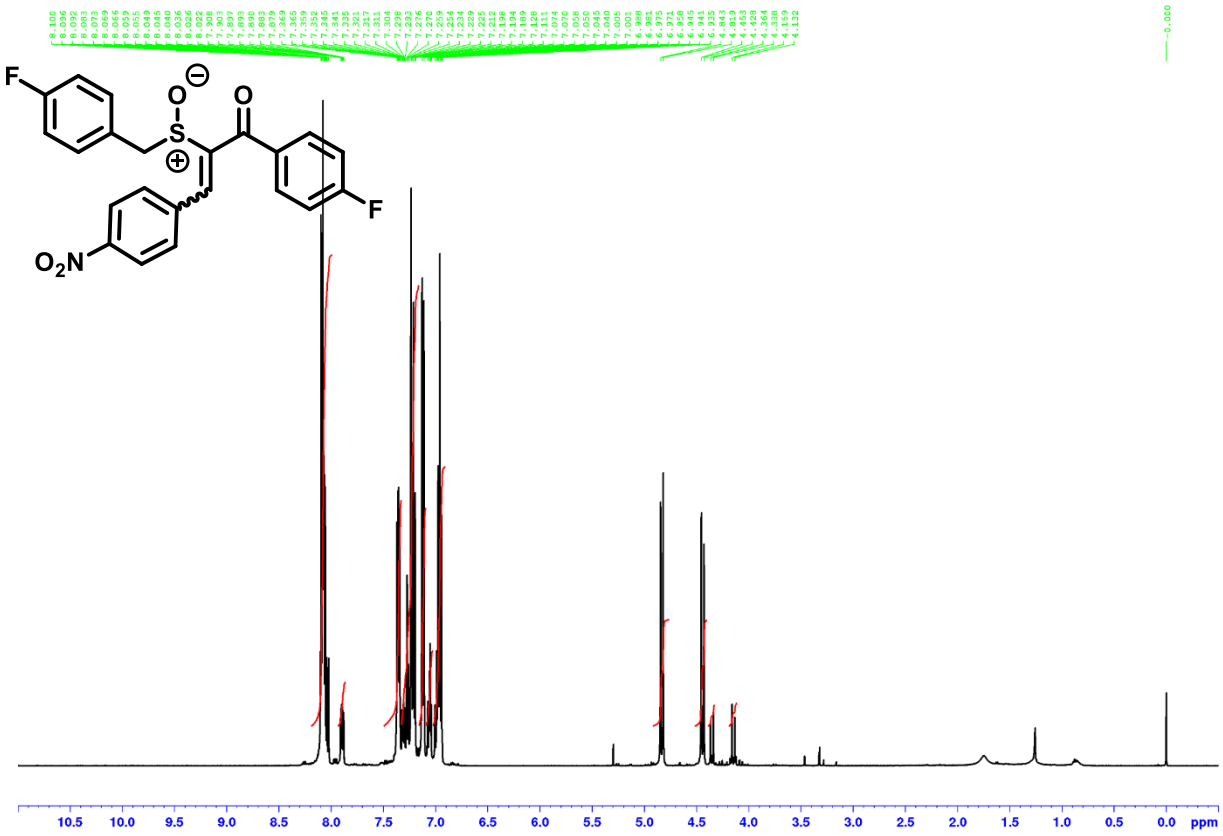


Figure S320: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40z** and *E*-**40z** (*Z*:*E*, 5.8:1).

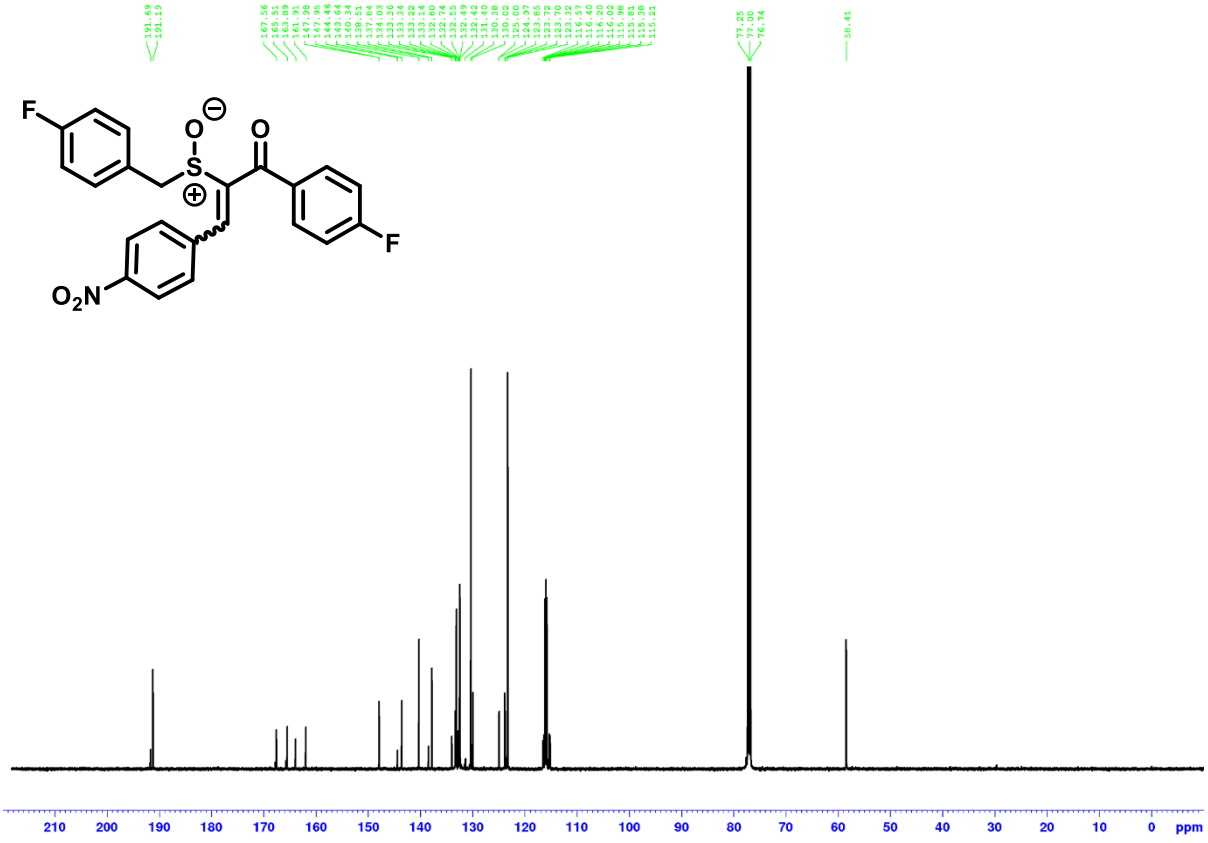


Figure S321: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40z** and *E*-**40z** (*Z*:*E*, 5.8:1).

2-(Benzylsulfinyl)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40o

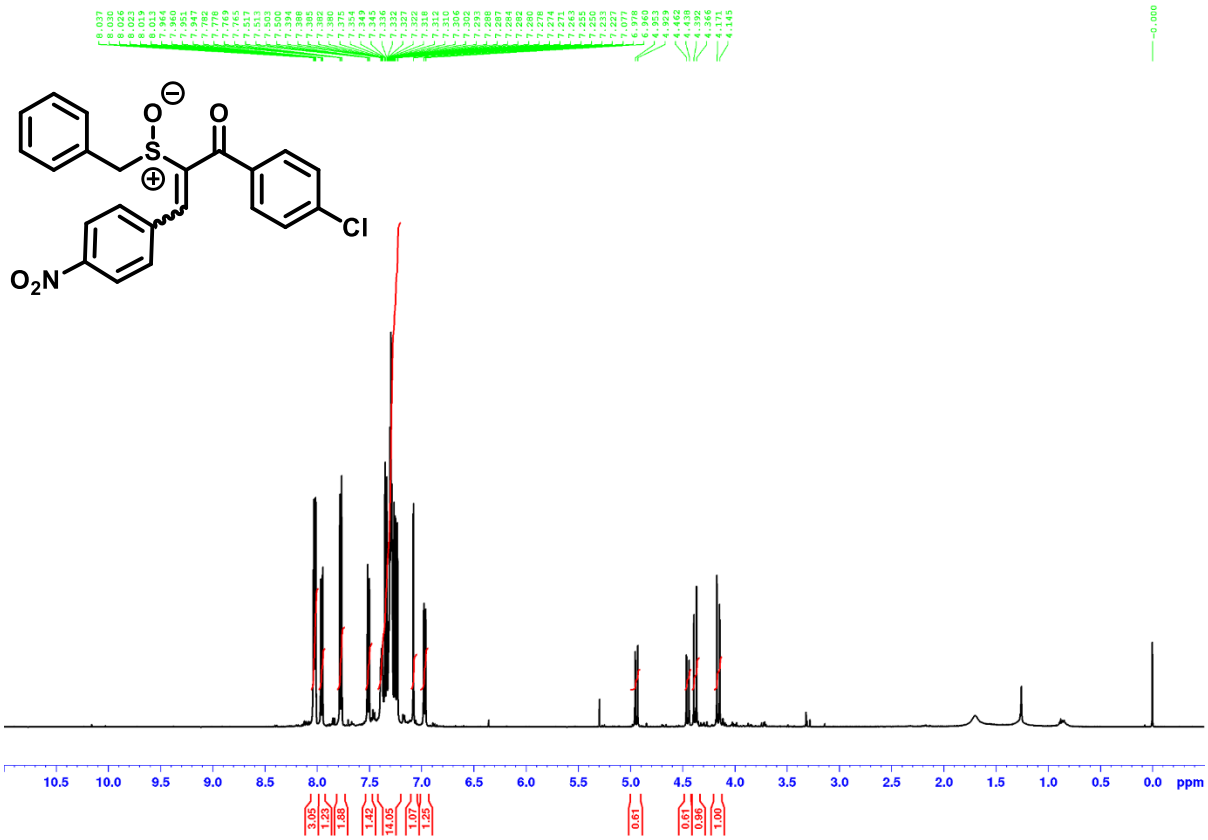


Figure S322: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40o** and *E*-**40o** (*Z*:*E*, 1:1.6).

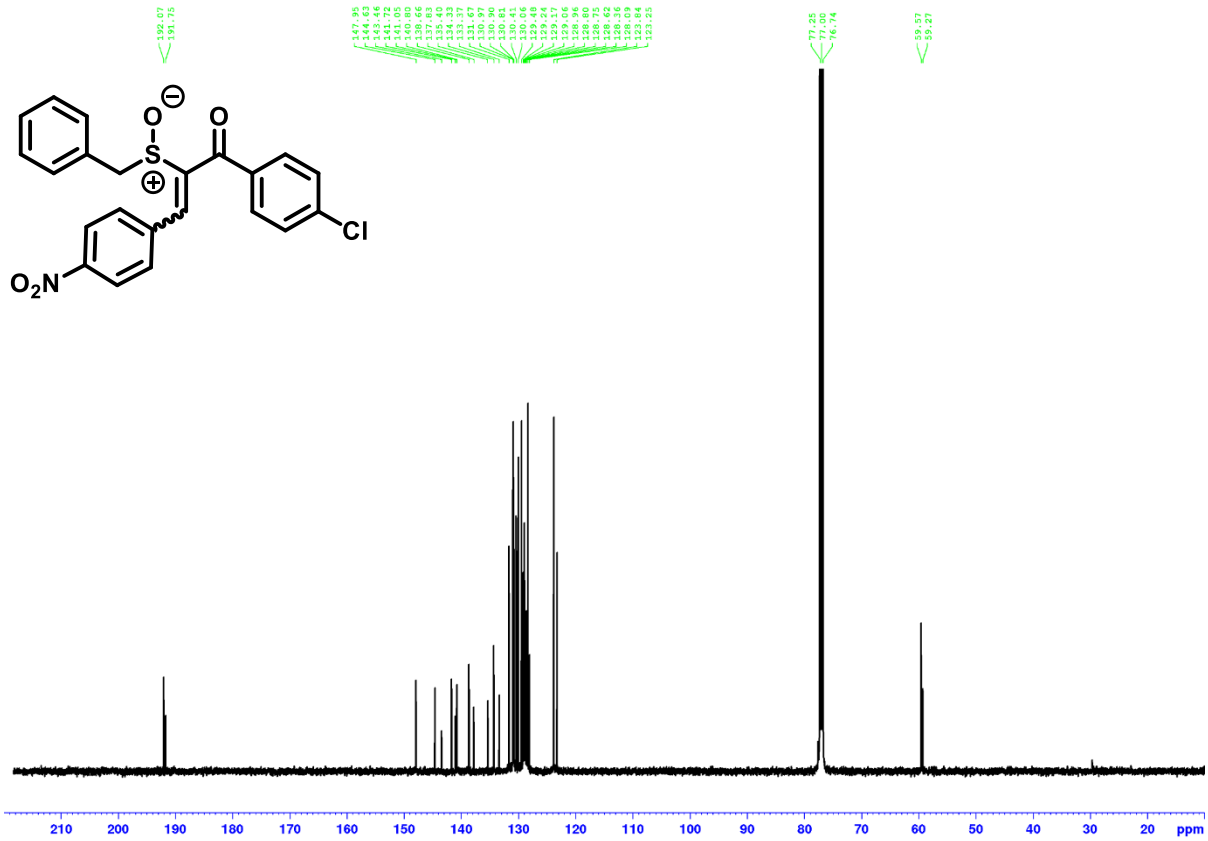


Figure S323: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40o** and *E*-**40o** (*Z*:*E*, 1:1.6).

2-((4-Chlorobenzyl)sulfinyl)-1-(4-chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one 40q

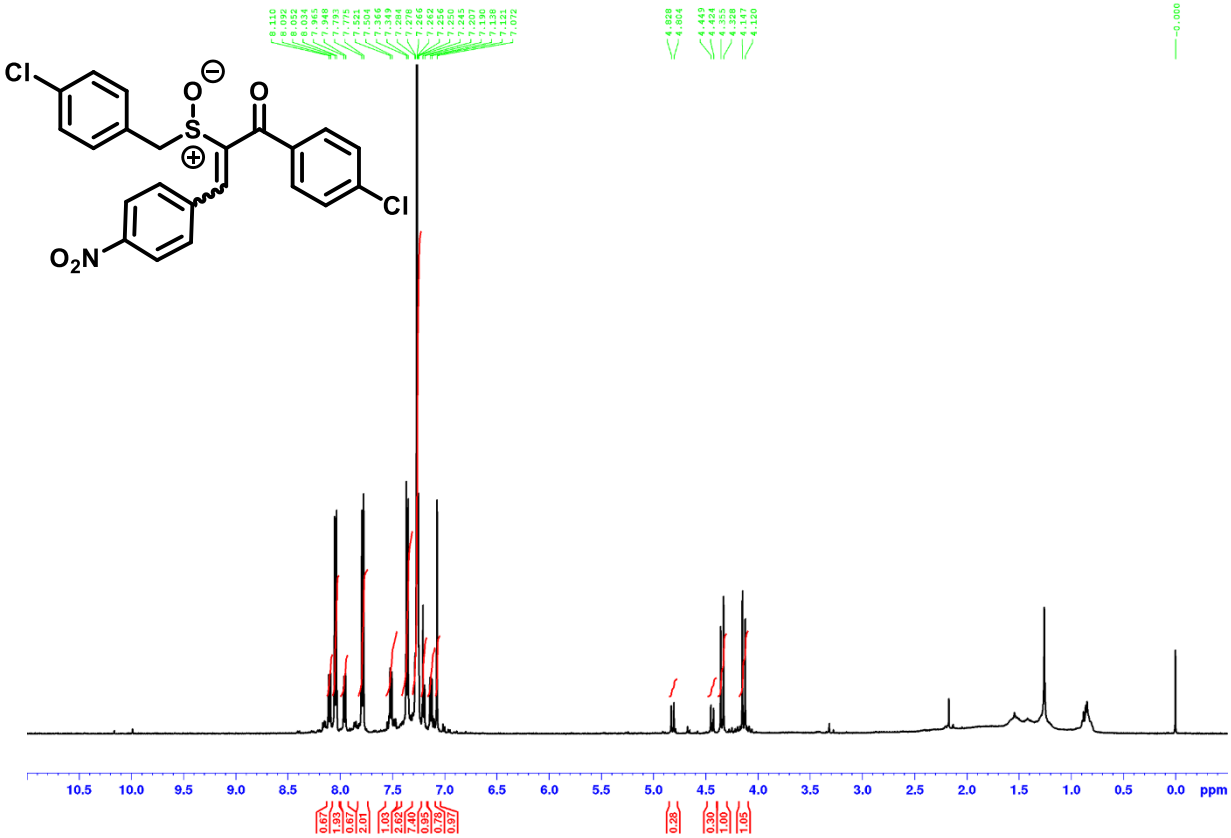


Figure S324: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40q** and *E*-**40q** (*Z*:*E*, 1:3.5).

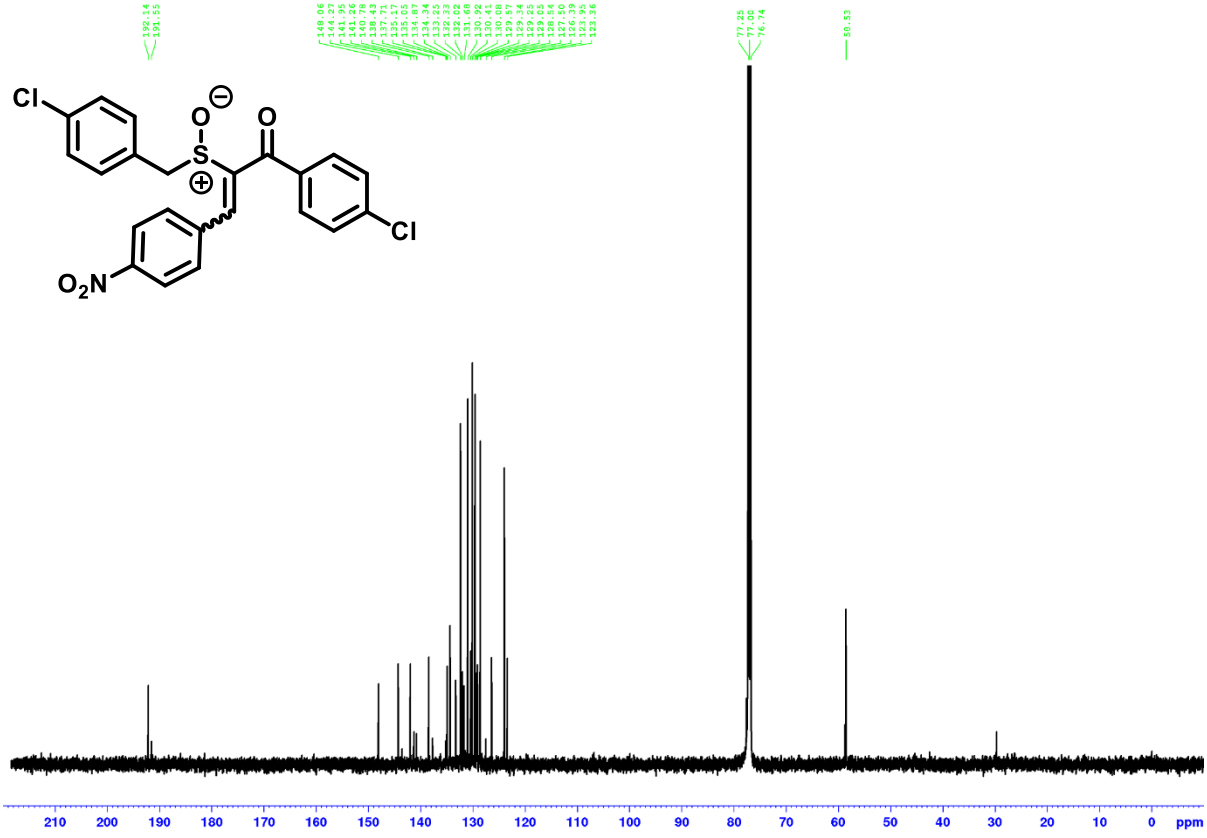


Figure S325: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40q** and *E*-**40q** (*Z*:*E*, 1:3.5).

(*Z*)-1-(4-Chlorophenyl)-2-((4-fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)prop-2-en-1-one 40s

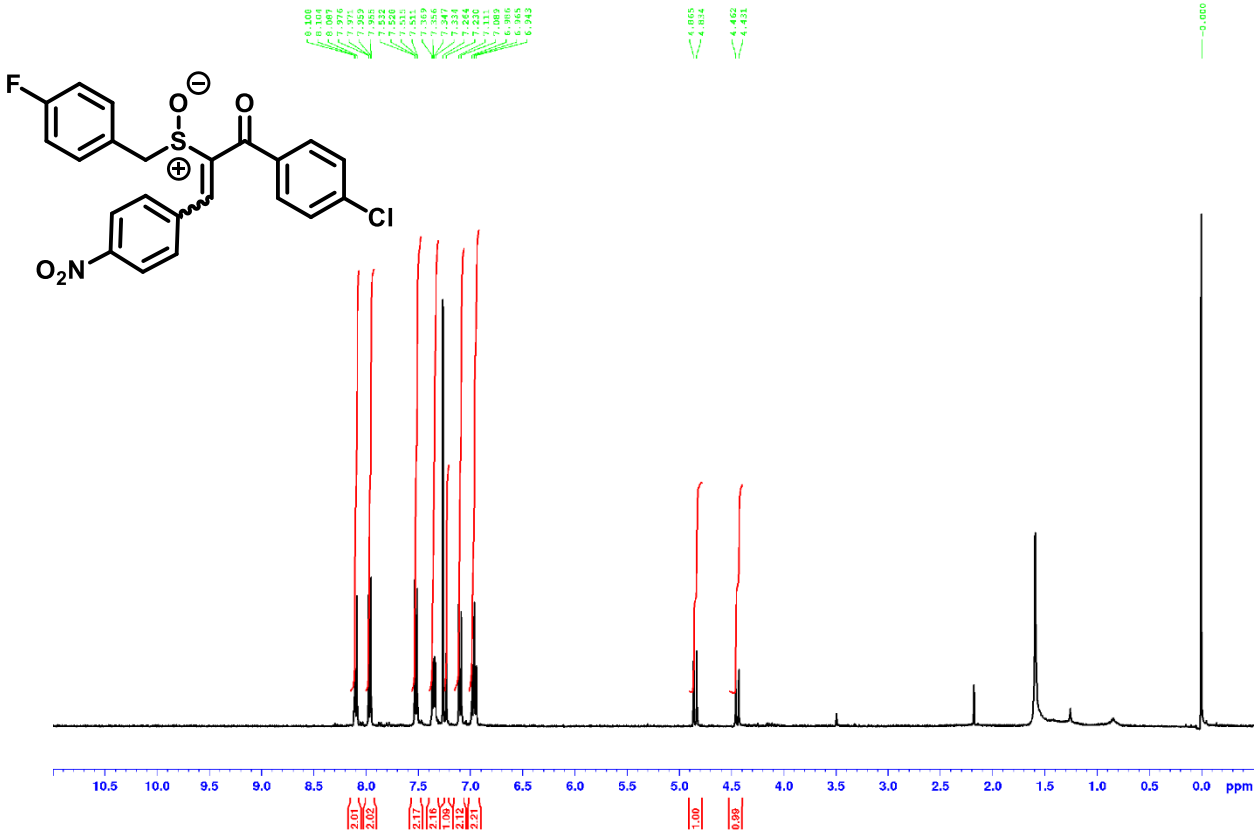


Figure S326: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *Z*-**16s** after column chromatography.

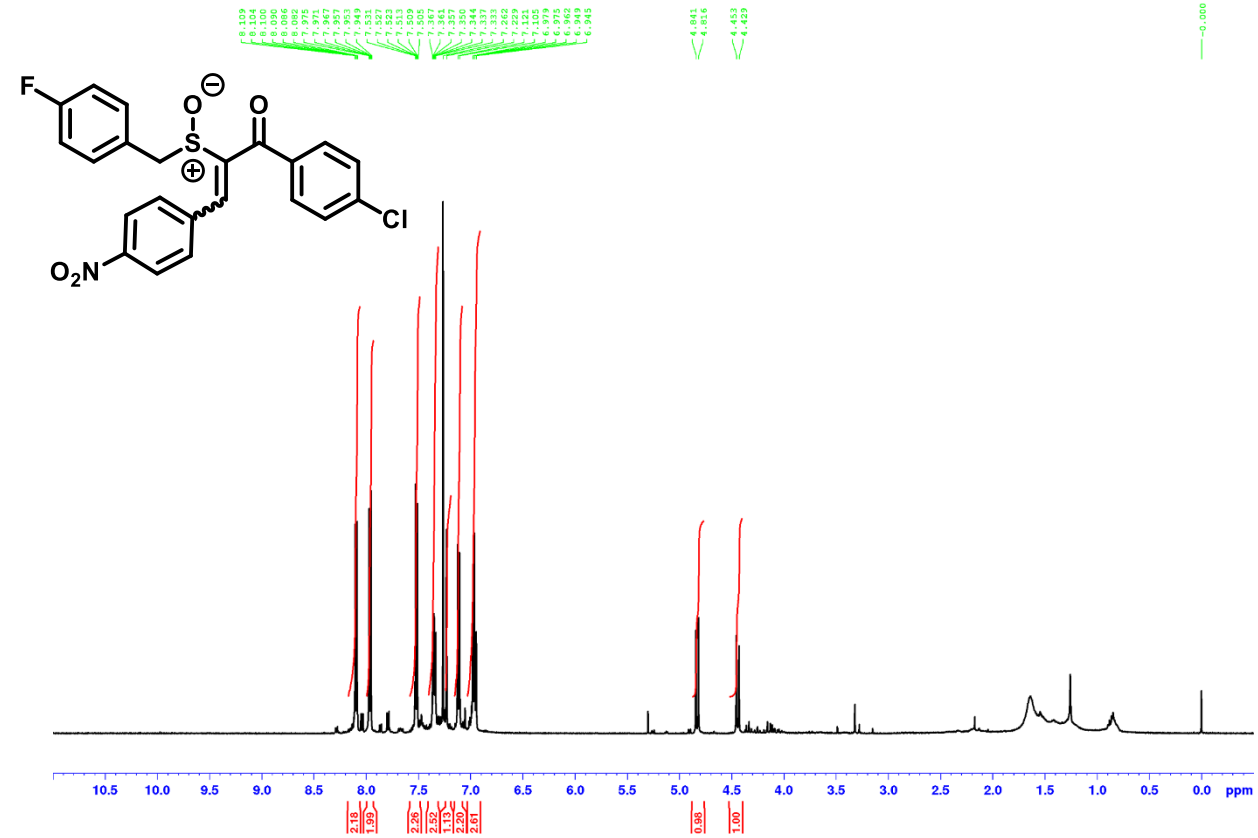


Figure S327: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *Z*-**40s** after storage at -20°C for 6 months (*Z*:*E*, 7:1).

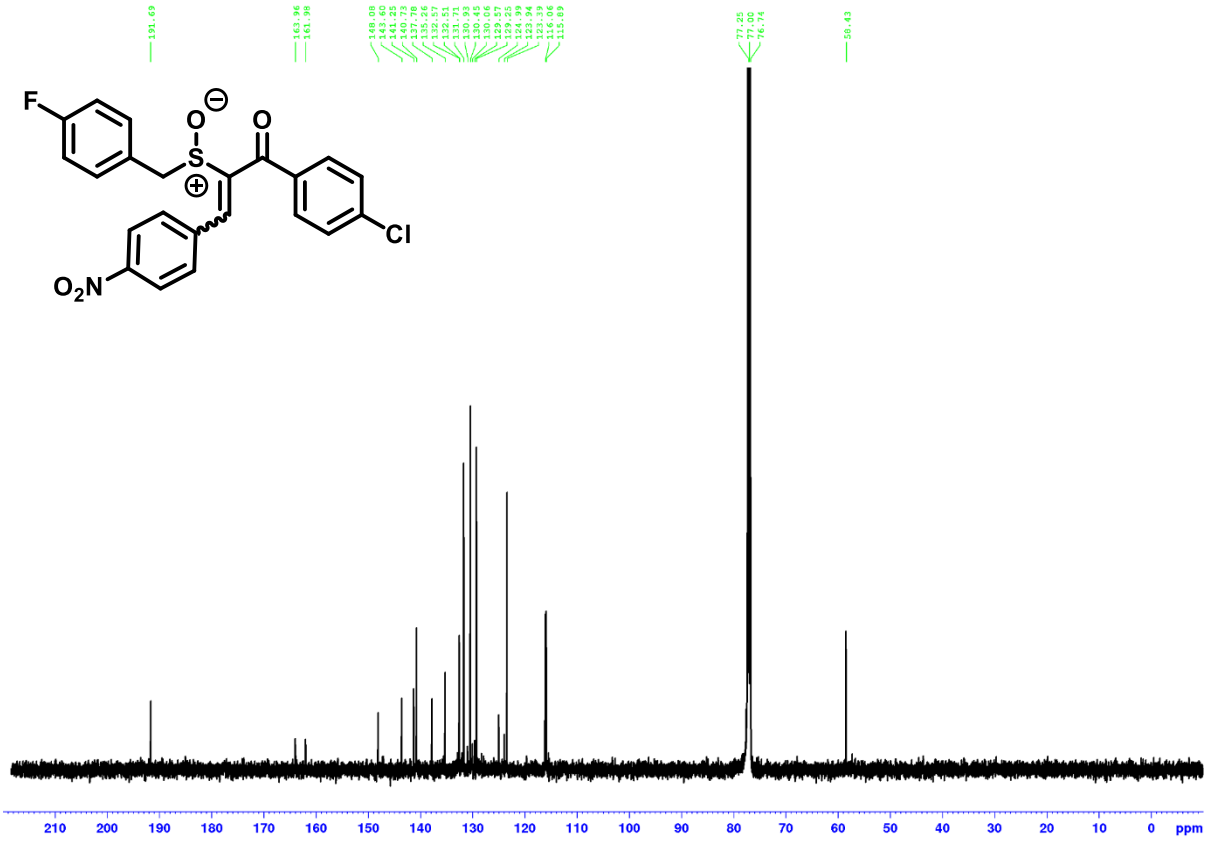


Figure S328: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *Z*-**40s** after storage at -20°C for 6 months (*Z*:*E*, 7:1).

(*E*)-1-(4-Chlorophenyl)-2-((4-fluorobenzyl)sulfinyl)-3-(4-nitrophenyl)prop-2-en-1-one 40s

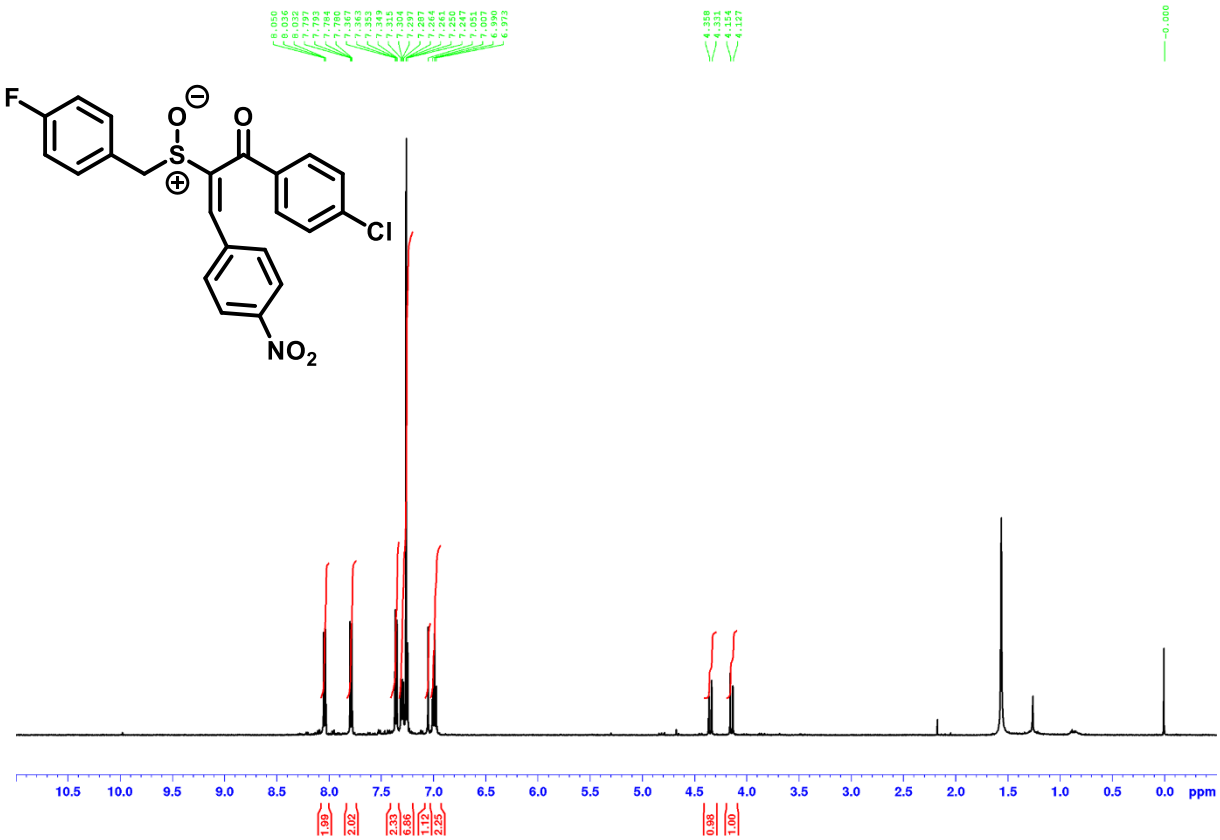


Figure S329: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of *E*-**40s**.

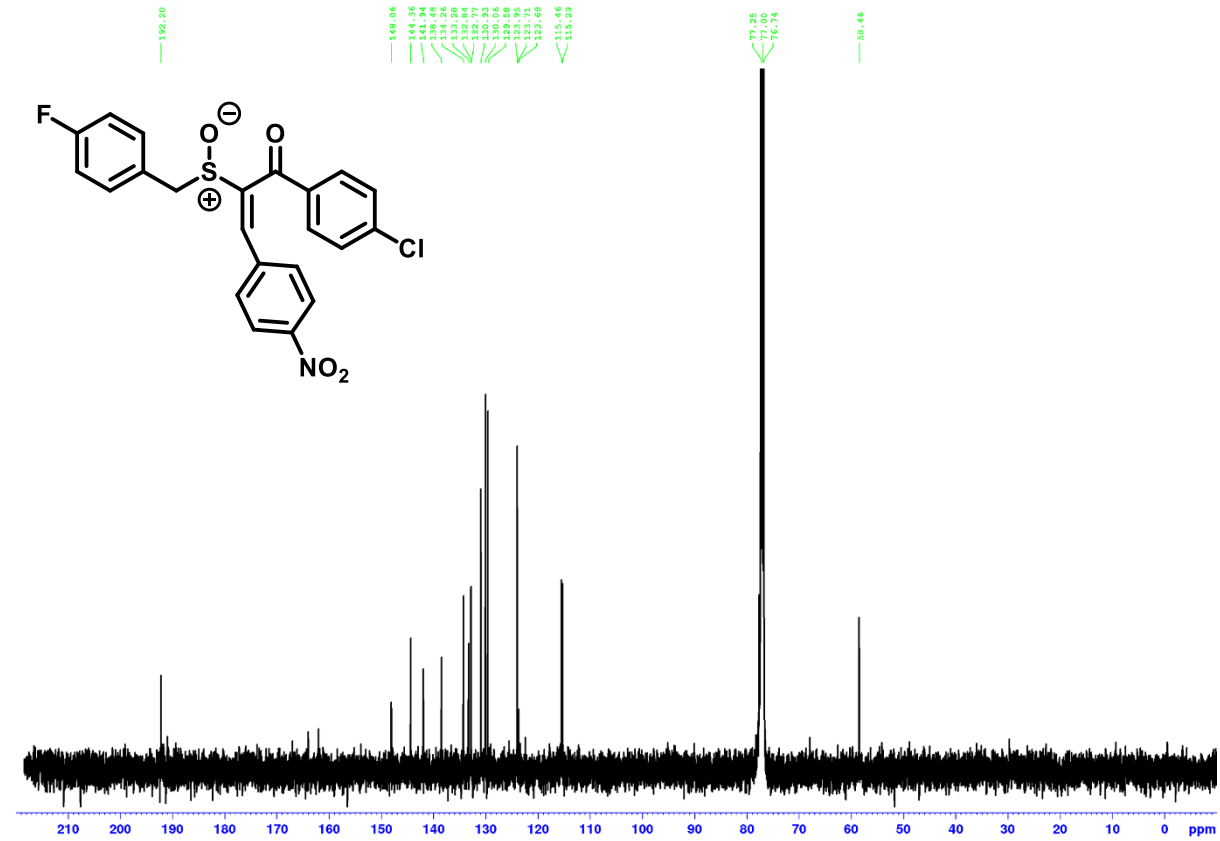


Figure S330: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of *E*-**40s**.

1.12.13 Synthesis of Amide and Ester Derivatives

(*Z*)-Methyl 2-(phenylthio)-3-(*p*-tolyl)acrylate 44

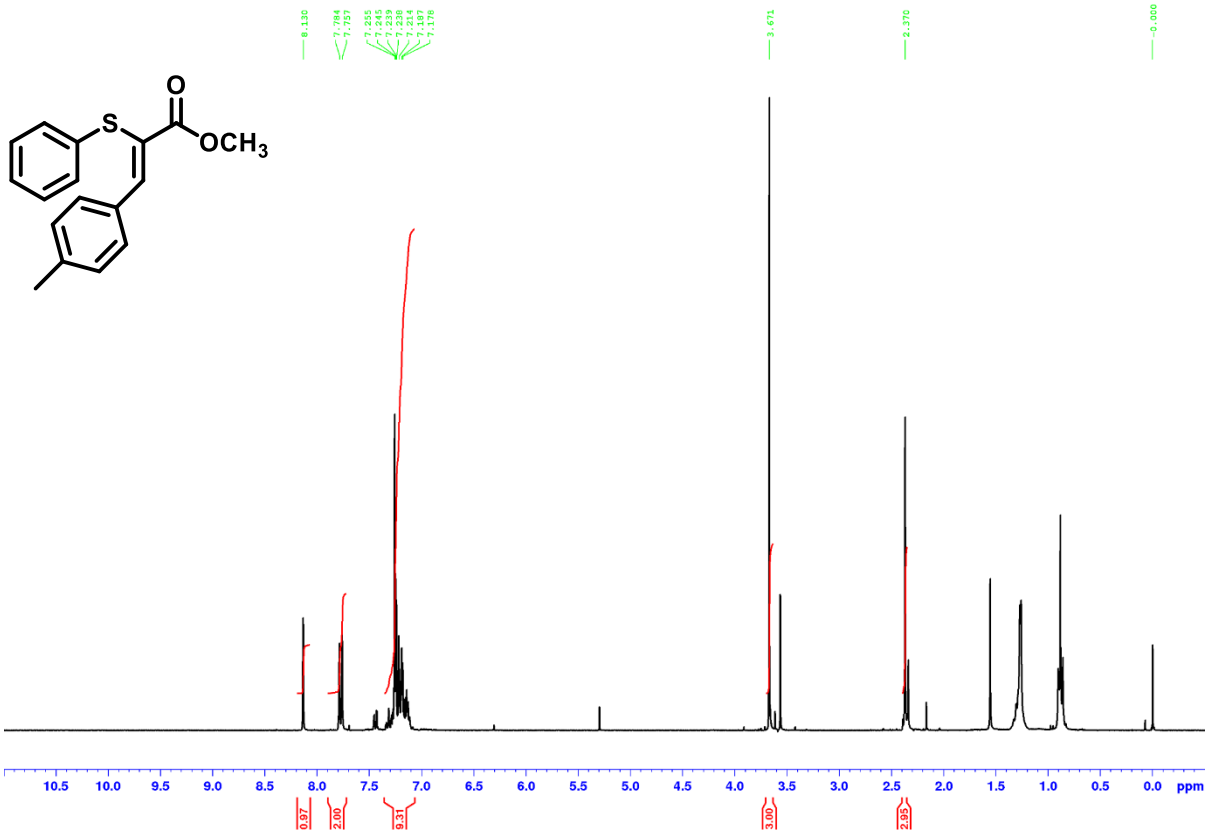


Figure S331: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **44**.

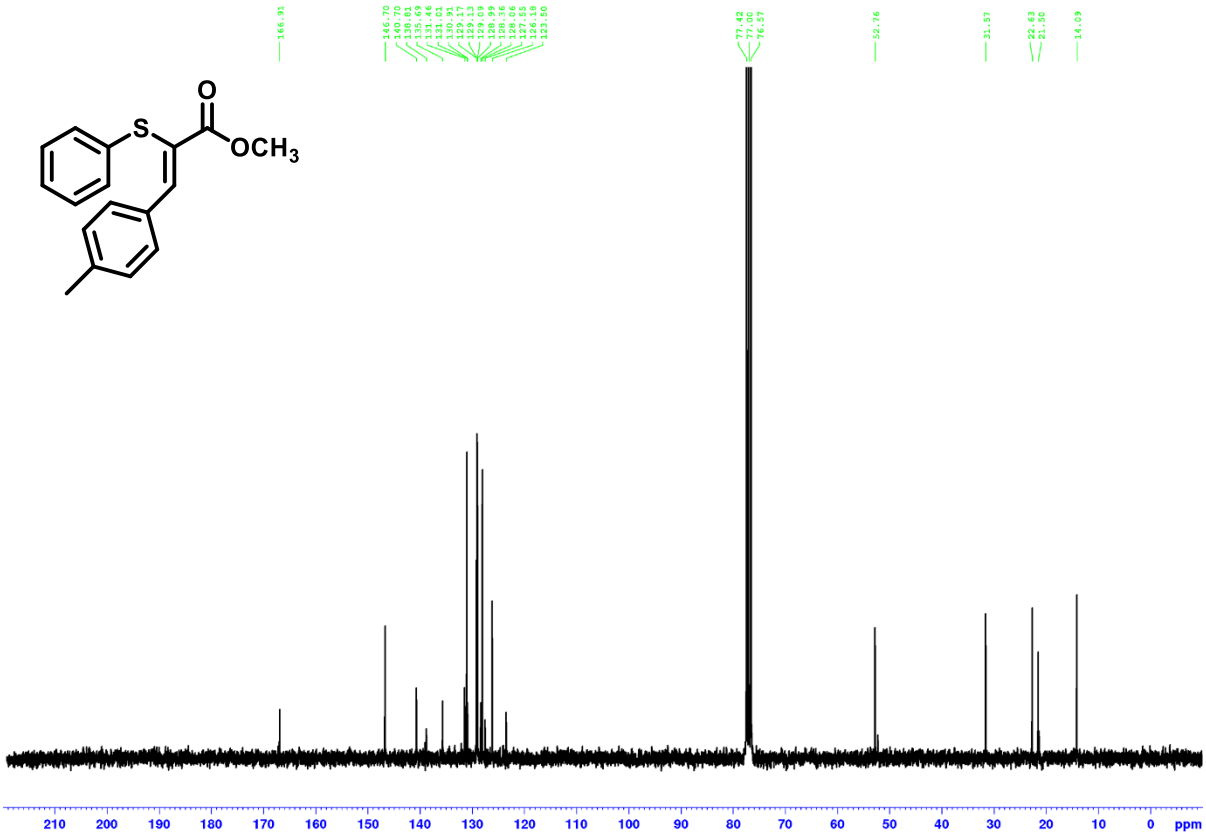


Figure S332: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **44**.

(*Z*)-*N*-Benzyl-2-(benzylthio)-3-(*p*-tolyl)acrylamide 45

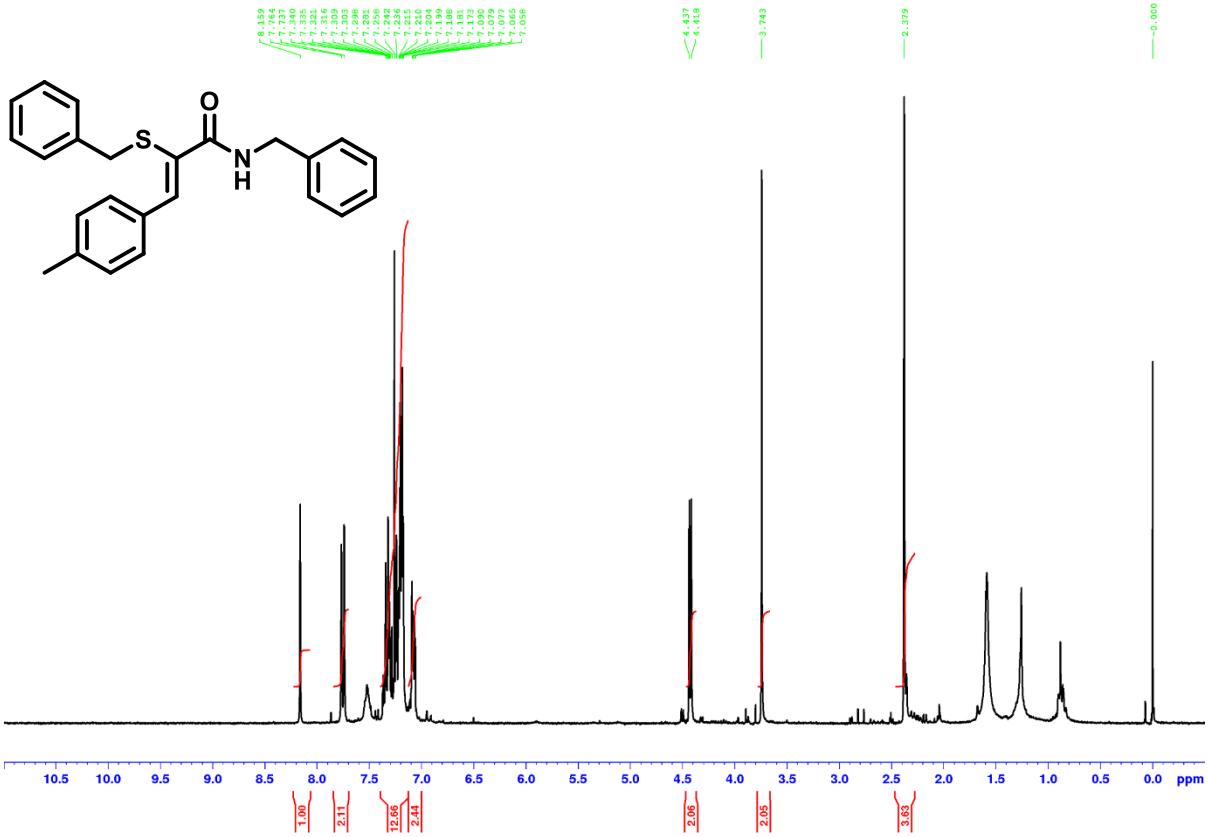


Figure S333: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **45**.

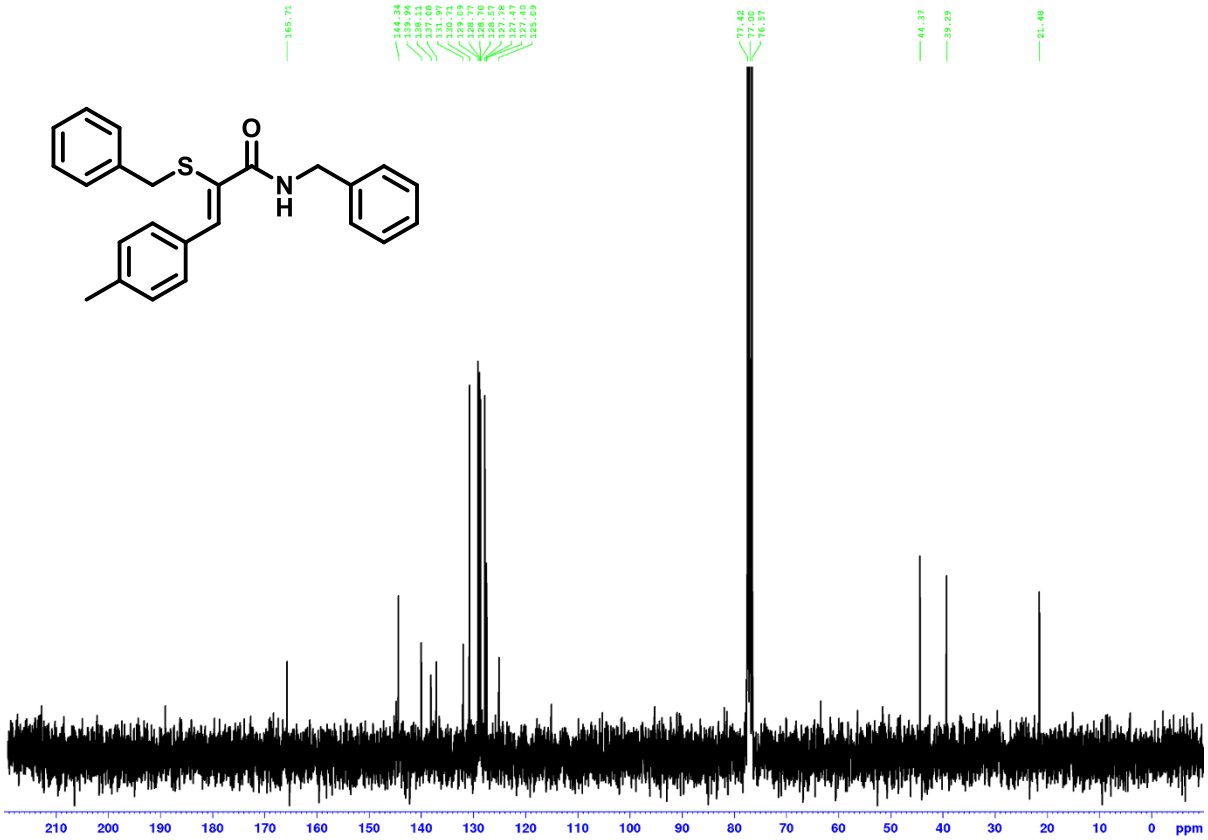


Figure S334: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **45**.

(*Z*)-2-(Phenylsulfinyl)-*N*,3-di-*p*-tolylacrylamide 46

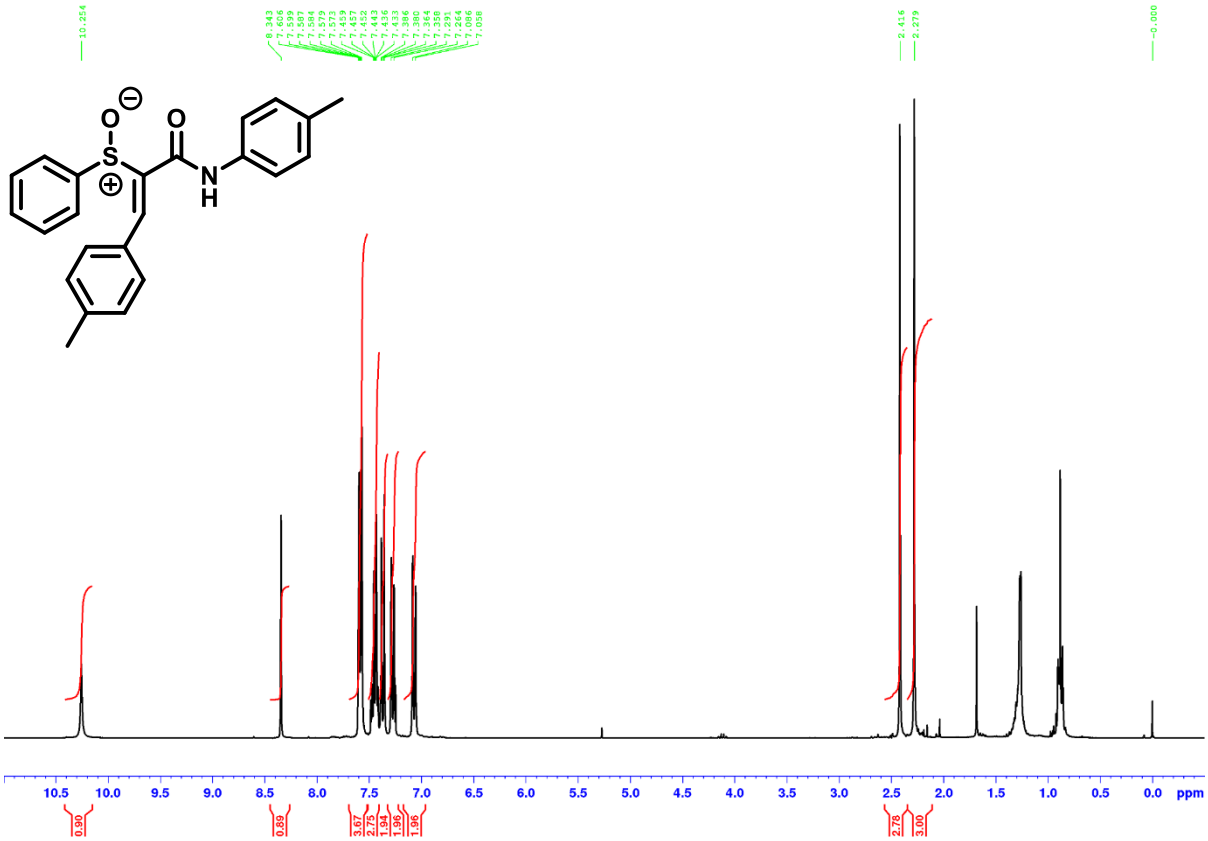


Figure S335: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **46**.

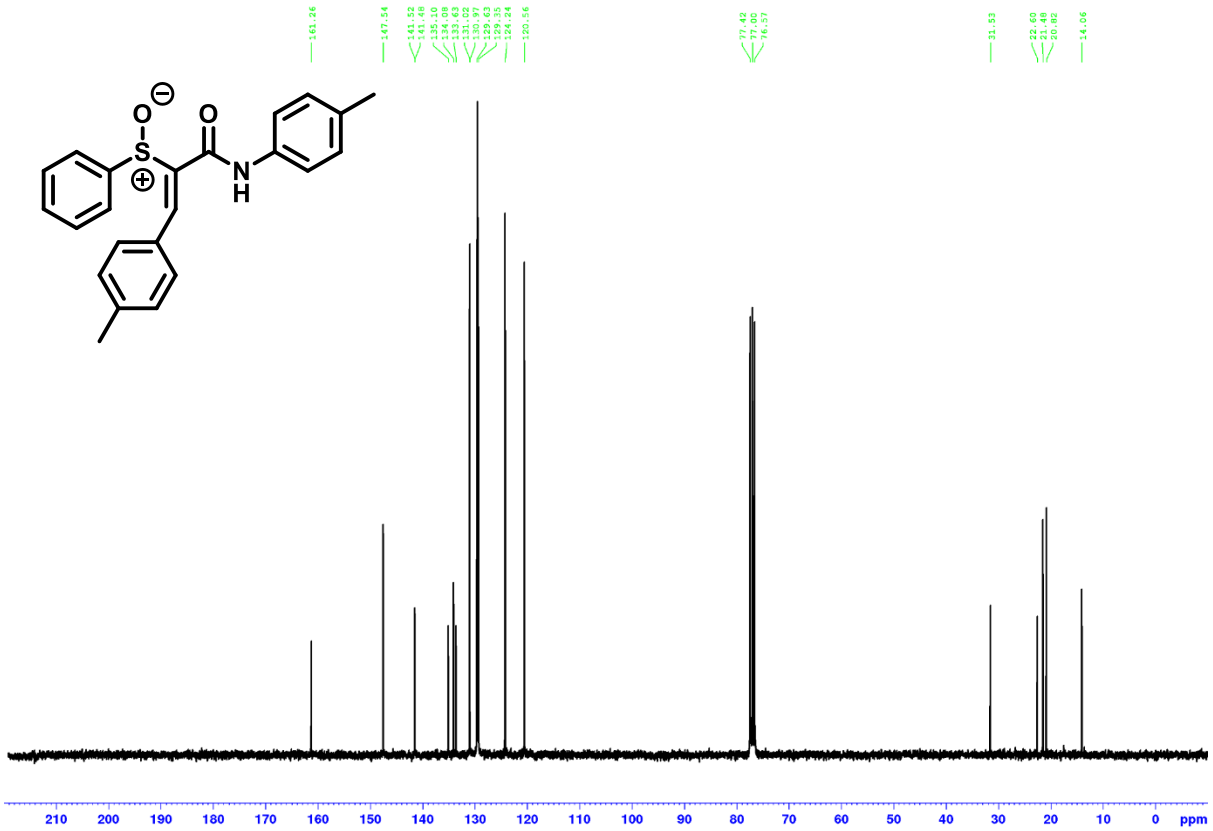


Figure S336: ^{13}C NMR (75.5 MHz, $CDCl_3$) spectrum of **46**.

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