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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 (CDCl₃), 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 ¹H 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). ¹³C 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 (CH₃, CH₂, 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 PF₂₅₄). Visualisation was achieved by UV (254 nm) light detection and vanillin staining.

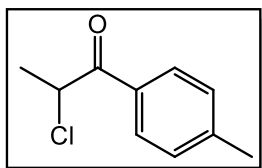
Nominal mass spectra were recorded on a Waters Quattro Micro triple quadrupole spectrometer in electrospray ionisation (ESI) mode using 50% water/acetonitrile containing 0.1% formic acid as eluent; samples were made up in acetonitrile. High resolution mass spectra (HRMS) were recorded on a Waters LCT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

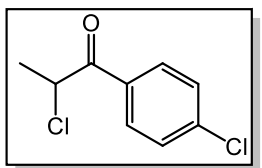
2-Chloro-1-(*p*-tolyl)propan-1-one **S1**¹



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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArCH₃), 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 [CH₃, C(3)*H*₃], 21.8 (CH₃, ArCH₃), 52.8 [CH, C(2)*H*], 129.1, 129.5 (2 x CH signals, 4 x aromatic CH), 131.5, 144.8 (2 x C, aromatic C), 193.3 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₀H₁₂O³⁵Cl[M+H⁺] 183.0577. Found 183.0568; *m/z* (ES⁺) 183.3 [(C₁₀H₁₁O³⁵Cl)+H⁺], 33%. ³⁵Cl/³⁷Cl pattern visible at 183 and 185 in a 3:1 ratio.

Spectroscopic characteristics are consistent with those previously reported.¹

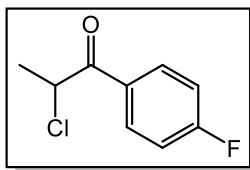
2-Chloro-1-(4-chlorophenyl)propan-1-one **S2**²⁻³



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); $\nu_{\text{max}}/\text{cm}^{-1}$ (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 CH), 132.5, 140.2 (2 x aromatic C), 192.4 (CO); *m/z* (ES⁺) 203.0 [(C₉H₈O³⁵Cl₂)+H⁺]; *m/z* (ES⁻) 201.2 [(C₉H₈O³⁵Cl₂)+H⁺], 4%.

Spectroscopic characteristics are consistent with those previously reported.²⁻³

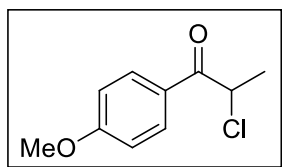
2-Chloro-1-(4-fluorophenyl)propan-1-one **S3**⁴



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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, $^2J_{\text{CF}}$ 22.0, aromatic CH), 130.5 (d, $^4J_{\text{CF}}$ 2.9, aromatic C), 131.8 (1 x signal, 2 x CH, d, $^3J_{\text{CF}}$ 9.4, aromatic CH), 166.0 (d, $^1J_{\text{CF}}$ 256.2, aromatic C), 192.1 (CO); HRMS (ES+): Exact mass calculated for $\text{C}_9\text{H}_9\text{OF}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 187.0326. Found 187.0318.

Spectroscopic characteristics are consistent with those previously reported.⁴

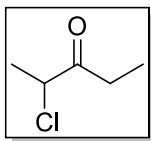
2-Chloro-1-(4-methoxyphenyl)propan-1-one **S4**^{2, 5}



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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, OCH_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 , OCH_3), 114.0 (CH, aromatic CH), 126.8 (C, aromatic C), 131.4 (CH, aromatic CH), 164.0 (C, aromatic C), 192.2 (C, CO); HRMS (ES+): Exact mass calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2^{35}\text{Cl}[\text{M}+\text{H}]^+$ 199.0526. Found 199.0519; m/z (ES+) 199.0 [$(\text{C}_{10}\text{H}_{11}\text{O}_2^{35}\text{Cl})+\text{H}^+$], 82%, 201.0 [$(\text{C}_{10}\text{H}_{11}\text{O}_2^{37}\text{Cl})+\text{H}^+$], 30%.

Spectroscopic characteristics were consistent with those previously reported.^{2, 5}

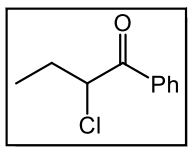
2-Chloropentan-3-one S5⁶



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 suluryl 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%); $\nu_{\max}/\text{cm}^{-1}$ (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, CHCl); 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, CHCl), 206.0 (C, CO).

Spectroscopic characteristics were consistent with those previously reported.⁶

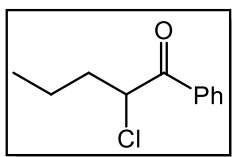
2-Chloro-1-phenylbutan-1-one S6⁷



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; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 2991 (CH), 2974 (CH), 2931 (CH), 1689 (C=O), 1597 (aromatic), 686; δ_{H} (400 MHz): 1.02 [3H, t, J 7.4, $\text{C}(4)\text{H}_3$], 1.91-2.05 [1H, m, one of $\text{C}(3)\text{H}_2$], 2.06-2.19 [1H, m, one of $\text{C}(3)\text{H}_2$], 5.07 [1H, overlapping dd, J 7.9, 5.7, $\text{C}(2)\text{H}$], 7.35-7.45 (2H, m, ArH), 7.47-7.55 (1H, m, ArH), 7.90-8.00 (2H, m, ArH); δ_{C} (100 MHz): 10.8 [CH_3 , $\text{C}(4)\text{H}_3$], 27.1 [CH_2 , $\text{C}(3)\text{H}_2$], 59.4 [CH, $\text{C}(2)\text{H}$], 128.8, 128.9, 133.7 (3 x CH signals, 5 x aromatic CH), 134.6 (C, aromatic C), 193.6 (C, CO); HRMS (ES+): Exact mass calculated for $\text{C}_{10}\text{H}_{12}\text{O}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 183.0577. Found 183.0570; m/z (ES+) 182.4 ($\text{C}_{10}\text{H}_{11}\text{O}^{35}\text{Cl}$)⁺, 32%, 183.4 [$(\text{C}_{10}\text{H}_{11}\text{O}^{35}\text{Cl})+\text{H}^+$], 5%.

Spectroscopic characteristics are consistent with those previously reported.⁷

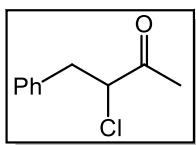
2-Chloro-1-phenylpentan-1-one **S7**⁸



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; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 2962, 2934, 2874, 1689 (C=O), 1596 (aromatic), 1448, 686; δ_{H} (400 MHz): 0.98 [3H, t, J 7.4, C(5)H₃], 1.40-1.66 [2H, m, C(4)H₂], 1.94-2.16 [2H, m, C(3)H₂], 5.12 [1H, overlapping dd, J 8.2, 5.7, C(2)H], 7.45-7.53 (2H, m, ArH), 7.56-7.64 (1H, m, ArH), 7.97-8.04 (2H, m, ArH); δ_{C} (100 MHz): 13.5 [CH₃, C(5)H₃], 19.5 [CH₂, C(4)H₂], 35.6 [CH₂, C(3)H₂], 57.5 [CH, C(2)H], 128.8, 128.9, 133.7 (3 x CH signals, 5 x aromatic CH), 134.6 (C, aromatic C), 193.7 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₁H₁₄O³⁵Cl[M+H⁺] 197.0733. Found 197.0724; m/z (ES⁺) 197.3 [(C₁₁H₁₃O³⁵Cl)+H⁺], 32%. ³⁵Cl/³⁷Cl 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

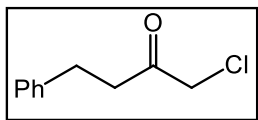


The title compound was prepared following the procedure outlined for **S1** using NCS (2.67 g, 20 mmol), *p*-toluenesulfonic acid monohydrate (5.71 g, 30 mmol), and 4-phenyl-2-butanone (2.96 g, 2.98 mL, 20 mmol) in acetonitrile (90 mL) to give the crude α -chloroketone as a yellow oil which also contained 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; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3064, 3031, 1714 (C=O), 1357, 697; δ_{H} (400 MHz): 2.28 (3H, s, CH₃), 3.07 [1H, A of ABX system, J_{AB} 14.3, J_{AX} 8.1, one of C(4)H₂], 3.33 [1H, B of ABX system, J_{AB} 14.3, J_{BX} 6.1, one of C(4)H₂], 4.40 [1H, X of ABX system, dd, J 8.0, 6.2, C(3)H], 7.19-7.40 (5H, m, ArH); δ_{C} (100 MHz): 26.8 (CH₃), 39.8 [C(4)H₂], 63.8 [C(3)H], 127.2, 128.6, 129.4 (3 x signals, 5 x aromatic CH), 136.2 (aromatic C), 202.6 (CO).

Spectroscopic characteristics are consistent with those previously reported.³

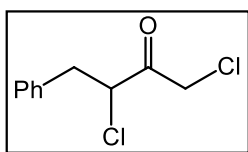
Other impure fractions contained the chlorinated products **S9** and **S10** which could not be isolated.

1-Chloro-4-phenylbutan-2-one **S9**⁹



Characteristic signals due to **S9**: δ_H (400 MHz): 2.86-2.98 (4H, m, CH_2CH_2), 4.01 (2H, s, CH_2Cl).

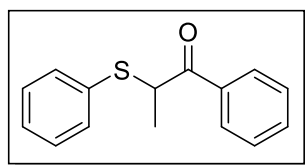
1,3-Dichloro-4-phenylbutan-2-one **S10**



Characteristic signals tentatively assigned as **S10**: δ_H (400 MHz): 4.23 (1H, A of AB system, J_{AB} 16.0, one of CH_2Cl), 4.32 (1H, B of AB system, J_{AB} 15.9, one of CH_2Cl), 4.70 [1H, X of ABX system, J 7.6, 6.3, $C(3)HCl$].

1.3 Synthesis of α -Sulfenylketones

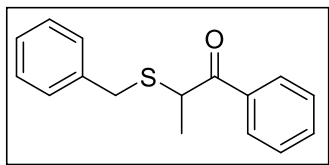
1-Phenyl-2-(phenylthio)propan-1-one **3a**¹⁰



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, ArH), 7.95 (2H, dd, J 1.3, 8.4, ArH); 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 CH), 131.8 (C, aromatic C), 133.1, 134.9 (2 x CH, aromatic CH) 135.7 (C, aromatic C), 196.3 (C, CO); 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

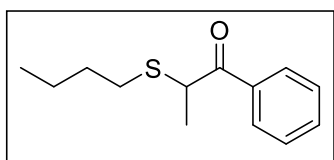
2-(Benzylthio)-1-phenylpropan-1-one **3b**¹¹



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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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 SCH₂), 3.74 (1H, B of AB system, J_{AB} 12.9, one of SCH₂), 4.26 [1H, q, J 6.9, C(2) H], 7.19-7.52 (8H, m, ArH), 7.84 (2H, dd, J 1.3, 8.4, ArH); δ_{C} (75.5 MHz, CDCl_3) 16.7 [CH₃, C(3) H_3], 34.2 (CH₂, CH₂), 42.0 [CH, C(2) H], 127.3, 128.6, 129.2, 133.1 (4 x CH, aromatic CH) 135.6, 137.3 (2 x C, 2 x aromatic C), 196.4 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₇OS[M+H]⁺ 257.1000. Found 257.1001; m/z (ES⁺) 257.1 [(C₁₆H₁₆OS)+H⁺], 100%.

Spectroscopic characteristics were consistent with those previously reported.¹¹

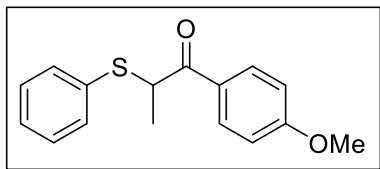
2-(Butylthio)-1-phenylpropan-1-one **3c**



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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3061 (CH), 2959 (CH), 1678 (CO), 1596 (aromatic); δ_{H} (300 MHz, CDCl_3) 0.83 (3H, t, J 7.3, CH₂CH₃), 1.27-1.37 (2H, m, CH₂CH₃), 1.41-1.51 (2H, m, CH₂CH₂CH₃), 1.55 [3H, d, J 6.9, C(3) H_3], 2.32-2.57 (2H, m, SCH₂), 4.32 [1H, q, J 6.9, C(2) H], 7.40-7.45 (2H, m, ArH), 7.46-7.55 (1H, m, ArH) 7.98-8.02 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 13.6 (CH₃, CH₂CH₃), 16.4 [CH₃, C(3) H_3], 22.0 (CH₂, CH₂CH₃), 28.3 (CH₂, SCH₂), 31.3 (CH₂, CH₂CH₂CH₃), 41.4 [CH, C(2) H], 128.5, 132.9 (2 x CH, 2 signals for 3 x aromatic CH) 135.7 (C, aromatic C), 196.0 (C, CO);

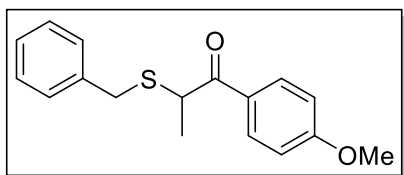
HRMS (ES⁺): Exact mass calculated for C₁₃H₁₉OS[M+H]⁺ 223.1157. Found 223.1156; m/z (ES⁺) 223.1 [(C₁₆H₁₈OS)+H⁺], 100%.

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 **54** (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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3058 (CH), 2969 (CH), 1671 (CO), 1598 (aromatic); δ_{H} (300 MHz, CDCl₃) 1.51 [3H, d, J 6.9, C(3)H₃], 3.83 (3H, s, OCH₃), 4.60 [1H, q, J 6.9, C(2)H], 6.89 (2H, d, J 9.0, ArH), 7.25-7.37 (5H, m, ArH), 7.93 (2H, d, J 9.0, ArH); δ_{C} (75.5 MHz, CDCl₃) 17.3 [CH₃, C(3)H₃], 46.0 [CH, C(2)H], 55.5 (CH₃, OCH₃), 113.8, 128.4, 128.9, 131.0 (4 x CH, aromatic CH), 132.2 (C, aromatic C), 134.3 (CH, aromatic CH), 163.5 (C, aromatic C), 195.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₇O₂S[M+H]⁺ 273.0949. Found 273.0938; m/z (ES⁺) 273.0 [(C₁₆H₁₆O₂S)+H⁺], 42%, 289.0 (100%).

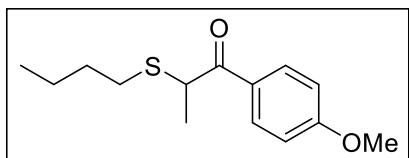
2-(Benzylthio)-1-(4-methoxyphenyl)propan-1-one **3e**



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 **54** (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. C₁₇H₁₈O₂S requires C, 71.30; H, 6.34; S, 11.20%); $\nu_{\max}/\text{cm}^{-1}$ (KBr) 3064 (CH), 2930 (CH), 1668 (CO), 1600 (aromatic); δ_{H} (400 MHz, CDCl₃) 1.55 [3H, d, J 6.9, C(3)H₃], 3.65 (1H, A of AB system, J_{AB} 13.0, one of SCH₂), 3.76 (1H, B of AB system, J_{AB} 13.0, one of SCH₂), 3.86 (3H, s, OCH₃), 4.25 [1H, q, J 6.9, C(2)H], 6.88 (2H, d,

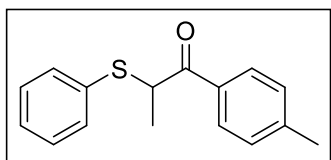
J 8.9, Ar*H*), 7.21-7.30 (5*H*, m, Ar*H*), 7.85 (2*H*, d, *J* 8.9, Ar*H*); δ_c (75.5 MHz, CDCl₃) 16.8 [CH₃, C(3)H₃], 34.2 (CH₂, CH₂), 41.7 [CH, C(2)H], 55.5 (CH₃, OCH₃), 113.7, 127.1 (2 x CH, aromatic CH) 128.4 (C, aromatic C), 128.5, 129.2, 130.9 (3 x CH, aromatic CH), 137.5, 163.5 (2 x C, 2 x aromatic C), 195.2 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₉O₂S[M+H]⁺ 287.1106. Found 287.1099; *m/z* (ES⁺) 287.0 [(C₁₇H₁₈O₂S)+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; $\nu_{\max}/\text{cm}^{-1}$ (film) 2959 (CH), 2931 (CH), 1669 (CO), 1601 (aromatic); δ_H (300 MHz, CDCl₃) 0.85 (3*H*, t, *J* 7.3, CH₂CH₃), 1.26-1.38 (2*H*, m, CH₂CH₃), 1.42-1.50 (2*H*, m, CH₂CH₂CH₃), 1.54 [3*H*, d, *J* 6.9, C(3)H₃], 2.34-2.59 (2*H*, m, SCH₂), 3.86 (3*H*, s, OCH₃), 4.30 [1*H*, q, *J* 6.9, C(2)H], 6.93 (2*H*, d, *J* 9.0, Ar*H*), 8.01 (2*H*, d, *J* 9.0, Ar*H*); δ_c (75.5 MHz, CDCl₃) 13.6 (CH₃, CH₂CH₃), 16.6 [CH₃, C(3)H₃], 22.0 (CH₂, CH₂CH₃), 28.4 (CH₂, SCH₂), 31.4 (CH₂, CH₂CH₂CH₃), 41.9 [CH, C(2)H], 55.4 (CH₃, OCH₃), 113.7 (CH, aromatic CH), 128.4 (C, aromatic C), 130.9 (CH, aromatic CH), 163.4 (C, aromatic C), 195.0 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₄H₂₁O₂S[M+H]⁺ 253.1262. Found 253.1252; *m/z* (ES⁺) 253.1 [(C₁₄H₂₀O₂S)+H⁺], 58%, 269.1 (100%).

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

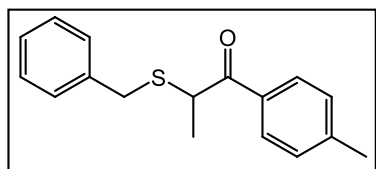


This was synthesised following the procedure described for **3a** using thiophenol (3.31 g, 3.08 mL, 30.1 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (5.00 g, 27.4 mmol) in dry methanol (30 mL) and freshly prepared sodium methoxide [prepared from sodium (0.757 g, 32.9 mmol) in dry methanol (50 mL) 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; $\nu_{\max}/\text{cm}^{-1}$

(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, Ar CH_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 [CH₃, C(3) H_3], 21.7 (CH₃, Ar CH_3), 46.2 [CH, C(2) H], 128.5, 128.8, 129.0, 129.4 (4 x CH, aromatic CH), 132.0, 133.1 (2 x C, 2 x aromatic C), 134.5 (CH, aromatic CH), 144.0 (C, aromatic C), 196.0 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{17}\text{OS}[\text{M}+\text{H}]^+$ 257.1000. Found 257.0992; m/z (ES⁺) 257.2 [$(\text{C}_{16}\text{H}_{16}\text{OS})+\text{H}^+$], 66%, 273.2 (100%).

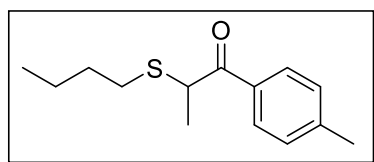
Spectroscopic characteristics were consistent with those previously reported.¹²

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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, Ar CH_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 CH_3), 34.1 (SCH_2), 41.9 [C(2) H], 127.1, 128.5, 128.7, 129.1, 129.2 (5 signals for 9 x aromatic CH), 133.0, 137.3, 143.9 (3 x aromatic C), 196.1 (CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{19}\text{OS}[\text{M}+\text{H}]^+$ 271.1157. Found 271.1157; m/z (ES⁺) 271.3 [$(\text{C}_{17}\text{H}_{18}\text{OS})+\text{H}^+$], 100%.

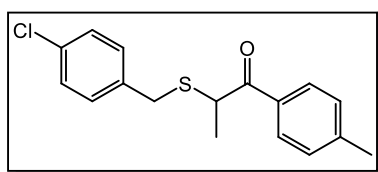
2-(Butylthio)-1-(*p*-tolyl)propan-1-one **3i**



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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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-

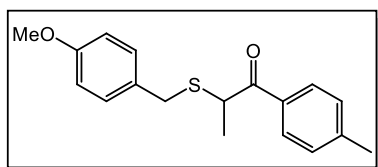
1.49 (2H, m, CH₂CH₂CH₃), 1.55 [3H, d, *J* 6.9, C(3)H₃], 2.33-2.58 (2H, m, SCH₂), 2.40 (3H, s, ArCH₃), 4.30 [1H, q, *J* 6.9, C(2)H], 7.25 (2H, d, *J* 8.0, ArH), 7.91 (2H, d, *J* 8.3, ArH); δ_c (75.5 MHz, CDCl₃) 13.6 (CH₃, CH₂CH₃), 16.5 [CH₃, C(3)H₃], 21.6 (CH₃, ArCH₃), 22.0 (CH₂, CH₂CH₃), 28.4 (CH₂, SCH₂), 31.4 (CH₂, CH₂CH₂CH₃), 41.4 [CH, C(2)H], 128.7, 129.2 (2 x CH, aromatic CH), 133.1, 143.7 (2 x C, 2 x aromatic C), 195.8 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₄H₂₁OS[M+H]⁺ 237.1313. Found 237.1313; *m/z* (ES⁺) 237.2 [(C₁₄H₂₀OS)+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. C₁₇H₁₇OSCl requires C, 66.98; H, 5.62; $\nu_{\max}$ /cm⁻¹ (ATR) 2930, 1667 (C=O), 1605; δ_H (400 MHz, CDCl₃): 1.53 [3H, d, *J* 6.9, C(3)H₃], 2.41 (3H, s, ArCH₃), 3.57 (1H, A of AB system, *J*_{AB} 13.2, one of SCH₂), 3.69 (1H, B of AB system, *J*_{AB} 13.1, one of SCH₂), 4.27 [1H, q, *J* 6.9, C(2)H], 7.11-7.30 (6H, m, ArH), 7.77 (2H, d, *J* 8.2, ArH); δ_c (100 MHz, CDCl₃): 16.8 [CH₃, C(3)H₃], 21.7 (CH₃, ArCH₃), 33.3 (CH₂, SCH₂), 41.9 [CH, C(2)H], 128.6, 128.7, 129.3, 130.5 (4 x CH signals, 8 x aromatic CH), 132.9, 136.1, 144.0 (3 x C signals, 4 x aromatic C), 195.9 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₈OS³⁵Cl[M+H]⁺ 305.0767. Found 305.0763; *m/z* (ES⁺) 305.2 [(C₁₇H₁₇OS³⁵Cl)+H⁺], 100%, 307.2 [(C₁₇H₁₇OS³⁷Cl)+H⁺], 42%.

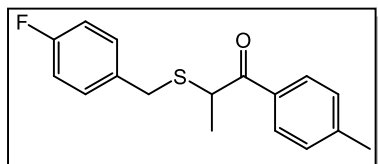
2-((4-Methoxybenzyl)thio)-1-(*p*-tolyl)propan-1-one **3k**



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

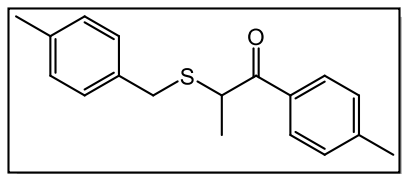
chromatography on silica gel (hexane-dichloromethane 50:50) to give the pure α -thioketone **3k** (1.30 g, 79%) as a white solid, mp 50-52°C; Found C, 71.92; H, 6.72. $C_{18}H_{20}O_2S$ requires C, 71.97; H, 6.71; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 2958, 2931, 1662 (C=O), 1606, 1509, 1237, 1174; δ_H (400 MHz, $CDCl_3$): 1.55 [3H, d, J 6.9, C(3) H_3], 2.40 (3H, s, Ar CH_3), 3.59 (1H, A of AB system, J_{AB} 12.9, one of SCH₂), 3.71 (1H, B of AB system, J_{AB} 12.9, one of SCH₂), 3.78 (3H, s, OCH₃), 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 [CH₃, C(3) H_3], 21.7 (CH₃, Ar CH_3), 33.6 (CH₂, SCH₂), 41.9 [CH, C(2) H], 55.3 (CH₃, OCH₃), 113.9, 128.7 (2 x CH signals, 4 x aromatic CH), 129.2 (C, aromatic C), 129.2, 130.3 (2 x CH signals, 4 x aromatic CH), 133.0, 143.9, 158.7 (3 x C, aromatic C), 196.2 (C, CO); 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**



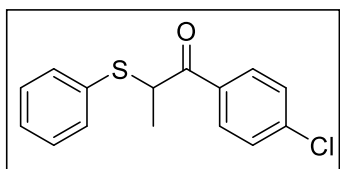
The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.754 g, 0.65 mL, 5.3 mmol), 2-chloro-1-(*p*-tolyl)propan-1-one **S1** (0.804 g, 4.4 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.122 g, 5.3 mmol) in methanol (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; $\nu_{\max}/\text{cm}^{-1}$ (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, Ar CH_3), 3.60 (1H, A of AB system, J_{AB} 13.1, one of SCH₂), 3.72 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 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 [CH₃, C(3) H_3], 21.6 (CH₃, Ar CH_3), 33.2 (CH₂, SCH₂), 41.9 [CH, C(2) H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic CH), 128.6, 129.3 (2 x CH signals, 4 x aromatic CH), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for $C_{17}H_{18}OSF$ [M+H⁺] 289.1062. Found 289.1056.

2-((4-Methylbenzyl)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; $\nu_{\max}/\text{cm}^{-1}$ (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, Ar CH_3), 2.41 (3H, s, Ar CH_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 CH_3), 33.9 (CH $_2$, SCH $_2$), 41.9 [CH, C(2) H], 128.7, 129.1, 129.2 (3 x CH signals, 8 x aromatic CH), 133.1, 134.2, 136.8, 143.9 (4 x C, aromatic C), 196.2 (C, CO); 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%.

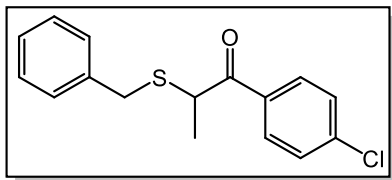
1-(4-Chlorophenyl)-2-(phenylthio)propan-1-one **3n**



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 ^1H NMR spectroscopy, this product was seen to also contain 4'-chloropropiophenone (5%, q, δ_{H} 2.97 ppm), no purification was carried out; $\nu_{\max}/\text{cm}^{-1}$ (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], 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 CH), 131.4, 134.0 (2 x C, 2 x aromatic C), 134.8 (CH, aromatic CH), 139.5 (C, aromatic C), 194.9 (C, CO); 4 CH signals seen for 5 aromatic CH; HRMS (ES $^+$): Exact mass

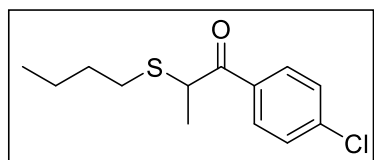
calculated for $C_{15}H_{14}OS^{35}Cl[M+H]^+$ 277.0376. Found 277.0311; m/z (ES+) 277.1 $[(C_{15}H_{13}OS^{35}Cl)+H^+]$, 22%, 279.1 $[(C_{15}H_{13}OS^{37}Cl)+H^+]$, 12%, 293.1 (100%).

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 SCH₂), 3.76 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 4.20 [1H, q, J 6.9, C(2) H], 7.22- 7.32 (5H, m, ArH), 7.37 (2H, d, J 8.8, ArH), 7.76 (2H, d, J 8.7, ArH); δ_C (100 MHz, $CDCl_3$): 16.5 [C(3) H_3], 34.2 (SCH₂), 42.0 [C(2) H], 127.3, 128.6, 128.8, 129.2, 130.0 (5 x signals, 9 x aromatic CH), 133.9, 137.1, 139.4 (3 x aromatic C), 195.1 (CO); 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%.

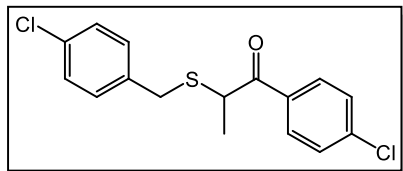
2-(Butylthio)-1-(4-chlorophenyl)propan-1-one **3p**



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 1H 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, CH₂CH₃), 1.28-1.36 (2H, m, CH₂CH₃), 1.41-1.49 (2H, m, CH₂CH₂CH₃), 1.55 [3H, d, J 6.9, C(3) H_3], 2.30-2.57 (2H, m, SCH₂), 4.26 [1H, q, J 6.9, C(2) H], 7.42 (2H, d, J 8.7, ArH), 7.95 (2H, d, J 8.7, ArH); δ_C (75.5 MHz, $CDCl_3$) 13.6 (CH₃, CH₂CH₃), 16.2 [CH₃, C(3) H_3], 22.0 (CH₂, CH₂CH₃), 28.3 (CH₂, SCH₂), 31.3 (CH₂, CH₂CH₂CH₃), 41.5 [CH, C(2) H], 128.8, 130.0 (2 x CH, aromatic CH) 133.9, 139.3 (2 x C, 2 x

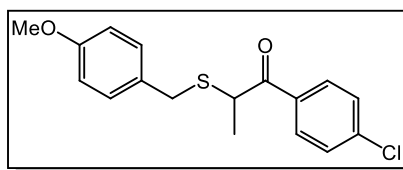
aromatic C), 194.7 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₃H₁₈OS³⁵Cl[M+H]⁺ 257.0767. Found 257.0780; m/z (ES⁺) 273.1 (100%), 275.1 (36%).

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. C₁₆H₁₄OSCl₂ requires C, 59.09; H, 4.34; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 2974, 2934, 1669 (C=O), 1588 (aromatic), 1489, 1093, 504; δ_{H} (400 MHz, CDCl₃): 1.55 [3H, d, *J* 6.9, C(3)H₃], 3.57 (1H, A of AB system, *J*_{AB} 13.2, one of SCH₂), 3.70 (1H, B of AB system, *J*_{AB} 13.2, one of SCH₂), 4.22 [1H, q, *J* 6.9, C(2)H], 7.16 (2H, d, *J* 8.5, ArH), 7.23 (2H, d, *J* 8.5, ArH), 7.40 (2H, d, *J* 8.7, ArH), 7.80 (2H, d, *J* 8.7, ArH); δ_{C} (75 MHz, CDCl₃): 16.5 [CH₃, C(3)H₃], 33.2 (CH₂, SCH₂), 42.1 [CH, C(2)H], 128.7, 128.9, 130.0, 130.5 (4 x CH signals, 8 x aromatic CH), 133.1, 133.7, 135.7, 139.6 (4 x C, aromatic C), 194.9 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₅OS³⁵Cl₂[M+H]⁺ 325.0221. Found 325.0218; m/z (ES⁺) 325.7 [(C₁₆H₁₄OS³⁵Cl₂)+H⁺], 12%. ³⁵Cl/³⁷Cl pattern visible in HRMS at 325, 327 and 329 in a 9:6:1 ratio.

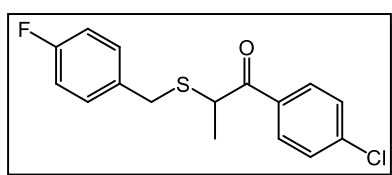
1-(4-Chlorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one **3r**



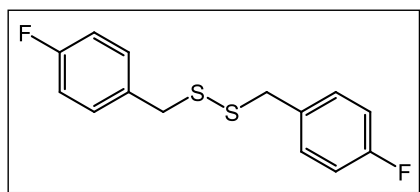
The title compound was prepared following the procedure outlined for **3a** using (4-methoxyphenyl)methanethiol (0.848 g, 0.76 mL, 5.5 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (1.02 g, 5.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 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. C₁₇H₁₇O₂SCl requires C, 63.64; H, 5.34; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, $\text{C}(3)\text{H}_3$], 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, $\text{C}(2)\text{H}$], 6.81 (2H, d, J 8.7, ArH), 7.16 (2H, d, J 8.7, ArH), 7.38 (2H, d, J 8.7, ArH), 7.78 (2H, d, J 8.7, ArH); δ_{C} (100 MHz, CDCl_3): 16.4 [CH_3 , $\text{C}(3)\text{H}_3$], 33.5 (CH_2 , SCH_2), 41.9 [CH , $\text{C}(2)\text{H}$], 55.3 (CH_3 , OCH_3), 113.9, 128.7 (2 x CH signals, 4 x aromatic CH), 128.9 (C, aromatic C), 130.0, 130.2 (2 x CH signals, 4 x aromatic CH), 133.8, 139.3, 158.8 (3 x C, aromatic C), 195.1 (C, CO).

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

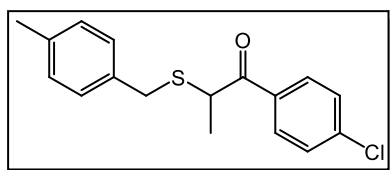


The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.61 g, 0.52 mL, 4.3 mmol), 2-chloro-1-(4-chlorophenyl)propan-1-one **S2** (0.80 g, 3.9 mmol) in methanol (5 mL) and freshly prepared sodium methoxide [prepared from sodium (0.107 g, 4.7 mmol) in methanol (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. $\text{C}_{16}\text{H}_{14}\text{OSClF}$ requires C, 62.23; H, 4.57; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, $\text{C}(3)\text{H}_3$], 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, $\text{C}(2)\text{H}$], 6.95 (2H, overlapping dd appears as t, J 8.7, ArH), 7.19 (2H, dd, J 8.7, J_{FH} 5.3, ArH), 7.39 (2H, d, J 8.7, ArH), 7.81 (2H, d, J 8.7, ArH); δ_{C} (75 MHz, CDCl_3): 16.5 [CH_3 , $\text{C}(3)\text{H}_3$], 33.1 (CH_2 , SCH_2), 42.1 [CH , $\text{C}(2)\text{H}$], 115.4 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 21.5, aromatic CH), 128.9, 130.0 (2 x CH signals, 4 x aromatic CH), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 8.1, aromatic CH), 132.8 (C, d, $^4J_{\text{CF}}$ 3.3, aromatic C), 133.8, 139.5 (2 x C, aromatic C), 162.0 (C, d, $^1J_{\text{CF}}$ 246.0, aromatic C), 194.9 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{15}\text{OS}^{35}\text{ClF}[\text{M}+\text{H}^+]$ 309.0516. Found 309.0515.



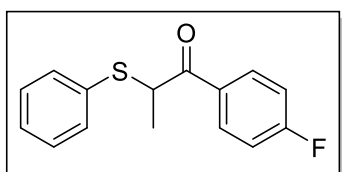
Characteristic signal due to **S12**¹⁴: δ_{H} (400 MHz, CDCl_3) 3.57 (4H, s, SCH_2).

1-(4-Chlorophenyl)-2-((4-methylbenzyl)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; $\nu_{\max}/\text{cm}^{-1}$ (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, Ar CH_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 CH_3), 33.9 (CH_2 , SCH_2), 41.9 [CH , C(2) H], 128.8, 129.1, 129.3, 130.1 (4 x CH signals, 8 x aromatic CH), 133.8, 133.9, 137.0, 139.4 (4 x C, aromatic C), 195.2 (C, CO); 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.

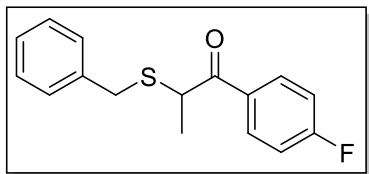
1-(4-Fluorophenyl)-2-(phenylthio)propan-1-one **3u**



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; $\nu_{\max}/\text{cm}^{-1}$ (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, CH), 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 , CH_3), 46.1 (CH, CH), 115.7 (CH, d, $^2J_{CF}$ 21.8, aromatic CH), 128.8, 129.0 (2 x CH, aromatic CH), 131.3 (CH, d, $^3J_{CF}$ 9.3, aromatic CH), 131.5 (C, aromatic C), 132.0 (C, d, $^4J_{CF}$ 2.9, aromatic C), 134.7 (CH, aromatic CH), 165.7 (C, d, $^1J_{CF}$

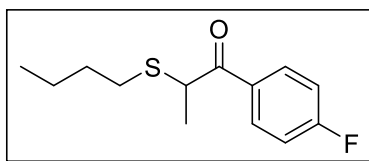
255.0, aromatic C), 194.7 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₅H₁₄OSF[M+H]⁺ 261.0749. Found 261.0726; m/z (ES⁺) 261.0 [(C₁₅H₁₃OSF)+H⁺], 12%, 277.0 (100%).

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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3064 (CH), 2929 (CH), 1677 (CO), 1597 (aromatic); δ_{H} (300 MHz, CDCl₃) 1.56 [3H, d, J 6.8, C(3)H₃], 3.63 (1H, A of AB system, J_{AB} 13.0, one of SCH₂), 3.76 (1H, B of AB system, J_{AB} 13.0, one of SCH₂), 4.21 [1H, q, J 6.8, C(2)H], 7.05 (2H, overlapping dd appears as t, J 8.7, J 8.7, ArH), 7.19-7.32 (5H, m, ArH), 7.80-7.89 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl₃) 16.6 [CH₃, C(3)H₃], 34.2 (CH₂, CH₂), 41.9 [CH, C(2)H], 115.6 (CH, d, $^2J_{\text{CF}}$ 21.9, aromatic CH), 127.3, 128.6, 129.2 (3 x CH, aromatic CH), 131.3 (CH, d, $^3J_{\text{CF}}$ 9.3, aromatic CH), 131.9 (C, d, $^4J_{\text{CF}}$ 3.0, aromatic C), 137.2 (C, aromatic C), 165.6 (C, d, $^1J_{\text{CF}}$ 254.8, aromatic C), 194.8 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₆OSF[M+H]⁺ 275.0906. Found 275.0891; m/z (ES⁺) 275.1 [(C₁₆H₁₅OSF)+H⁺], 14%, 291.0 (100%).

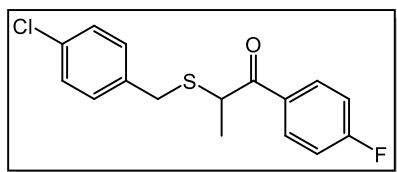
2-(Butylthio)-1-(4-fluorophenyl)propan-1-one **3w**



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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3076 (CH), 2960 (CH), 1678 (CO), 1598 (aromatic); δ_{H} (300 MHz, CDCl₃) 0.85 (3H, t, J 6.9, CH₂CH₃), 1.26-1.39 (2H, m, CH₂CH₃), 1.42-1.52 (2H, m, CH₂CH₂CH₃), 1.56 [3H, d, J 6.9, C(3)H₃], 2.32-2.58 (2H, m, SCH₂), 4.28 [1H, q, J 6.9, C(2)H], 7.13 (2H, overlapping dd

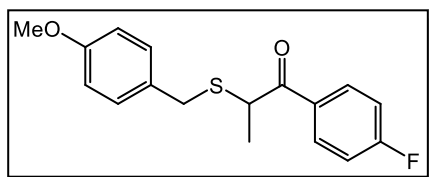
appears as t, J 8.7, J 8.7, ArH), 8.03-8.07 (2H, m, ArH); δ_C (75.5 MHz, CDCl₃) 13.6 (CH₃, CH₂CH₃), 16.3 [CH₃, C(3)H₃], 22.0 (CH₂, CH₂CH₃), 28.3 (CH₂, SCH₂), 31.3 (CH₂, CH₂CH₂CH₃), 41.4 [CH, C(2)H], 115.6 (CH, d, $^2J_{CF}$ 21.8, aromatic CH), 131.2 (CH, d, $^3J_{CF}$ 9.3, aromatic CH), 131.9 (C, d, $^4J_{CF}$ 3.0, aromatic C), 165.6 (C, d, $^1J_{CF}$ 254.7, aromatic C), 194.5 (C, CO); HRMS (ES+): Exact mass calculated for C₁₃H₁₈OSF[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. C₁₆H₁₄OSClF 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, CDCl₃): 1.55 [3H, d, J 6.9, C(3)H₃], 3.59 (1H, A of AB system, J_{AB} 13.2, one of SCH₂), 3.71 (1H, B of AB system, J_{AB} 13.2, one of SCH₂), 4.23 [1H, q, J 6.9, C(2)H], 7.09 (2H, dd appears as t, J 8.7, ArH), 7.16 (2H, d, J 8.6, ArH), 7.23 (2H, d, J 8.5, ArH), 7.89 (2H, dd, J 8.9, J_{FH} 5.4, ArH); δ_C (75 MHz, CDCl₃): 16.6 [CH₃, C(3)H₃], 33.3 (CH₂, SCH₂), 42.0 [CH, C(2)H], 115.7 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic CH), 128.6, 130.5 (2 x CH signals, 4 x aromatic CH), 131.2 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.2, aromatic CH), 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, CO); HRMS (ES+): Exact mass calculated for C₁₆H₁₅OFS³⁵Cl[M+H]⁺ 309.0516. Found 309.0504; m/z (ES-) 307.2 [(C₁₆H₁₄OFS³⁵Cl)-H⁺], 19%. ³⁵Cl/³⁷Cl pattern visible in HRMS at 309 and 311 in a 3:1 ratio.

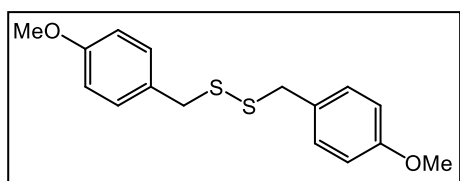
1-(4-Fluorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one **3y**



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. C₁₇H₁₇O₂FS requires C, 67.08; H, 5.63; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3008, 2952, 2820, 1668 (C=O), 1594, 1510, 1348, 1237, 1222, 1031, 847, 597, 511; δ_{H} (400 MHz, CDCl₃): 1.56 [3H, d, J 6.8, C(3)H₃], 3.59 (1H, A of AB system, J_{AB} 13.0, one of SCH₂), 3.72 (1H, B of AB system, J_{AB} 13.0, one of SCH₂), 3.78 (3H, s, OCH₃), 4.21 [1H, q, J 6.8, C(2)H], 6.81 (2H, d, J 8.7, ArH), 7.07 (2H, dd appears as t, J 8.7, ArH), 7.16 (2H, d, J 8.7, ArH), 7.87 (2H, dd, J 8.9, J_{FH} 5.4, ArH); δ_{C} (100 MHz, CDCl₃): 16.5 [CH₃, C(3)H₃], 33.5 (CH₂, SCH₂), 41.9 [CH, C(2)H], 55.3 (CH₃, OCH₃), 113.9 (1 x CH signal, 2 x aromatic CH), 115.5 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 21.8, aromatic CH), 129.0 (C, aromatic C), 130.2 (1 x CH signal, 2 x aromatic CH), 131.2 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 9.3, aromatic CH), 131.8 (C, d, $^4J_{\text{CF}}$ 2.8, aromatic C), 158.8 (C, aromatic C), 165.6 (C, d, $^1J_{\text{CF}}$ 254.8, aromatic C), 194.9 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₈O₂FS[M+H⁺] 305.1012. Found 305.1003.

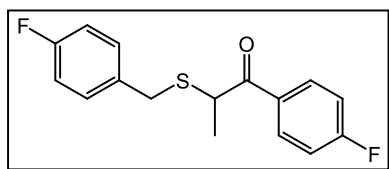
Approx. 13% of the disulfide by-product **S11** was present in the NMR sample.



Characteristic signals due to **S11**¹³: δ_{H} (400 MHz, CDCl₃) 3.59 (4H, s, SCH₂), 3.79 (6H, s, OCH₃), 6.85 (4H, d, J 8.7, ArH); δ_{C} (100 MHz, CDCl₃): 42.7 (CH₂, 2 x SCH₂), 113.8 (1 x CH signal, 4 x aromatic CH), 129.4 (C, 2 x aromatic C),

130.5 (1 x CH signal, 4 x aromatic CH), 159.0 (C, 2 x aromatic C).

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

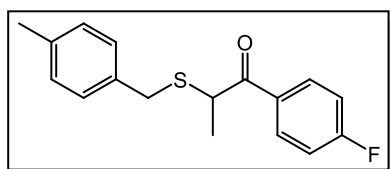


The title compound was prepared following the procedure outlined for **3a** using 4-fluorobenzylthiol (0.782 g, 0.68 mL, 5.5 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (0.933 g, 5.0 mmol) in methanol (10 mL) and freshly

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. C₁₆H₁₄OSF₂ requires C, 65.74; H, 4.83; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 2977, 2933, 1669 (C=O), 1593, 1505, 1333, 1220, 1154, 950. 848, 833; δ_{H} (400 MHz, CDCl₃): 1.56 [3H, d, J 6.9,

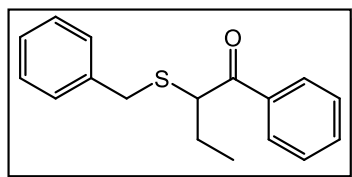
C(3)H₃], 3.59 (1H, A of AB system, J_{AB} 13.0, one of SCH₂), 3.73 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 4.23 [1H, q, J 6.9, C(2)H], 6.95 (2H, dd appears as t, J 8.7, ArH), 7.09 (2H, dd appears as t, J 8.7, ArH), 7.20 (2H, dd, J 8.7, J_{FH} 5.3, ArH), 7.91 (2H, dd, J 8.9, J_{FH} 5.4, ArH); δ_C (75 MHz, CDCl₃): 16.6 [CH₃, C(3)H₃], 33.2 (CH₂, SCH₂), 42.0 [CH, C(2)H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.2, aromatic CH), 115.6 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.3, aromatic CH), 130.6 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic CH), 131.2 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.2, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₅OF₂S[M+H⁺] 293.0812. Found 293.0807.

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



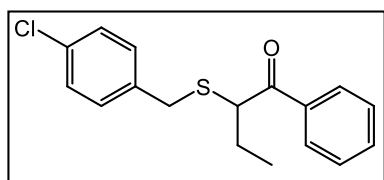
The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.608 g, 0.60 mL, 4.4 mmol), 2-chloro-1-(4-fluorophenyl)propan-1-one **S3** (0.742 g, 4.0 mmol) in methanol (15 mL) and freshly prepared sodium methoxide [prepared from sodium (0.110 g, 4.8 mmol) in 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. C₁₇H₁₇OFS 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, CDCl₃): 1.56 [3H, d, J 6.8, C(3)H₃], 2.33 (3H, s, ArCH₃), 3.60 (1H, A of AB system, J_{AB} 12.9, one of SCH₂), 3.73 (1H, B of AB system, J_{AB} 12.9, one of SCH₂), 4.21 [1H, q, J 6.8, C(2)H], 7.03-7.18 (6H, m, ArH), 7.86 (2H, dd, J 8.9, J_{FH} 5.4, ArH); δ_C (100 MHz, CDCl₃): 16.6 [CH₃, C(3)H₃], 21.1 (CH₃, ArCH₃), 33.9 (CH₂, SCH₂), 41.9 [CH, C(2)H], 115.6 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.8, aromatic CH), 129.1, 129.3 (2 x CH signals, 4 x aromatic CH), 131.3 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.3, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₈OFS[M+H⁺] 289.1062. Found 289.1060; m/z (ES⁺) 289.2 [(C₁₇H₁₇OFS)+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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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 SCH₂), 3.71 (1H, B of AB system, J_{AB} 12.9, one of SCH₂), 4.04 [1H, t, J 7.3, C(2) H], 7.17-7.28 (5H, m, ArH), 7.38-7.43 (2H, m, ArH), 7.50-7.54 (1H, m, ArH), 7.85-7.88 (2H, m, ArH); δ_{C} (100 MHz): 12.0 [CH₃, C(4) H_3], 23.8 [CH₂, C(3) H_2], 34.1 (CH₂, SCH₂), 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 CH), 136.3, 137.4 (2 x C, aromatic C), 196.0 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₉OS[M+H⁺] 271.1157. Found 271.1146; m/z (ES⁺) 271.3 [(C₁₇H₁₈OS)+H⁺], 90%.

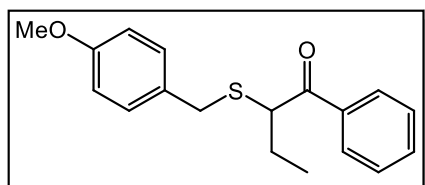
2-((4-Chlorobenzyl)thio)-1-phenylbutan-1-one **3cc**



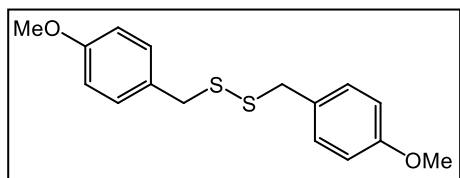
The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.873 g, 0.72 mL, 5.5 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.913 g, 5.0 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (0.138 g, 6.0 mmol) in methanol (15 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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 SCH₂), 3.67 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 4.04 [1H, t, J 7.3, C(2) H], 7.15 (2H, d, J 8.5, ArH), 7.21 (2H, d, J 8.5, ArH), 7.41-7.45 (2H, m, ArH), 7.53-7.57 (1H, m, ArH), 7.86-7.89 (2H, m, ArH); δ_{C} (100 MHz): 12.0

[CH₃, C(4)H₃], 23.8 [CH₂, C(3)H₂], 33.2 (CH₂, SCH₂), 49.1 [CH, C(2)H], 128.4, 128.5, 128.6, 130.4 (4 x CH signals, 8 x aromatic CH), 132.9 (C, aromatic C), 133.0 (CH, aromatic CH), 136.0, 136.1 (2 x C, aromatic C), 195.9 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₈OS³⁵Cl[M+H⁺] 305.0767. Found 305.0762. ³⁵Cl/³⁷Cl pattern visible in HRMS at 305 and 307 in a 3:1 ratio.

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

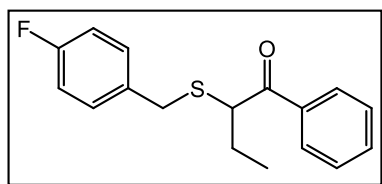


The title compound was prepared following the procedure outlined for **3a** using 4-methoxybenzyl mercaptan (0.463 g, 0.41 mL, 3.0 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.50 g, 2.7 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (74 mg, 3.2 mmol) in methanol (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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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)H₃], 1.80-1.94 [1H, symmetrical m, one of C(3)H₂], 2.03-2.17 [1H, symmetrical m, one of C(3)H₂], 3.55 (1H, A of AB system, J_{AB} 12.8, one of SCH₂), 3.68 (1H, B of AB system, J_{AB} 12.8, one of SCH₂), 3.76 (3H, s, OCH₃), 4.03 [1H, t, J 7.3, C(2)H], 6.79 (2H, d, J 8.7, ArH), 7.15 (2H, d, J 8.6, ArH), 7.39-7.47 (2H, m, ArH), 7.51-7.57 (1H, m, ArH), 7.85-7.93 (2H, m, ArH); δ_{C} (100 MHz): 12.0 [CH₃, C(4)H₃], 23.8 [CH₂, C(3)H₂], 33.5 (CH₂, SCH₂), 49.0 [CH, C(2)H], 55.2 (CH₃, OCH₃), 113.9, 128.4, 128.5 (3 x CH signals, 6 x aromatic CH), 129.2 (C, aromatic C), 130.3, 132.9 (2 x CH signals, 3 x aromatic CH), 136.2, 158.7 (2 x C, aromatic C), 196.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₈H₂₁O₂S[M+H⁺] 301.1262. Found 301.1261.



Characteristic signals due to **S11**¹³: δ_{H} (400 MHz, CDCl₃) 3.58 (4H, s, SCH₂), 3.78 (6H, s, OCH₃).

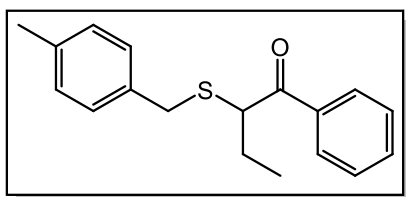
2-((4-Fluorobenzyl)thio)-1-phenylbutan-1-one **3ee**



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

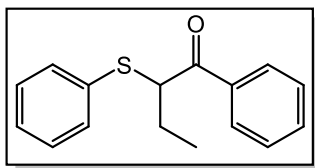
mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (74 mg, 3.2 mmol) in methanol (15 mL) at 0°C]. The crude product was obtained as a colourless oil. Column chromatography on silica gel (99:1 hexane:ethyl acetate) afforded the product **3ee** (0.592 g 76%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ (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 SCH₂), 3.69 (1H, B of AB system, J_{AB} 13.3, one of SCH₂), 4.04 [1H, t, J 7.3, C(2) H], 6.93 (2H, t, J 8.7, ArH), 7.19 (2H, dd, J 8.6, J_{FH} 5.4, ArH), 7.40-7.49 (2H, m, ArH), 7.52-7.60 (1H, m, ArH), 7.86-7.95 (2H, m, ArH); δ_{C} (100 MHz): 12.0 [CH₃, C(4) H_3], 23.8 [CH₂, C(3) H_2], 33.2 (CH₂, SCH₂), 49.1 [CH, C(2) H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 21.5, aromatic CH), 128.4, 128.6 (2 x CH signals, 4 x aromatic CH), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 8.1, aromatic CH), 133.1 (CH, aromatic CH), 133.1 (C, d, $^4J_{\text{CF}}$ 3.2, aromatic C), 136.2 (C, aromatic C), 161.9 (C, d, $^1J_{\text{CF}}$ 245.7, aromatic C), 195.9 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₈OSF[M+H⁺] 289.1062. Found 289.1052; m/z (ES⁺) 289.2 [(C₁₇H₁₇OSF)+H⁺], 16%.

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



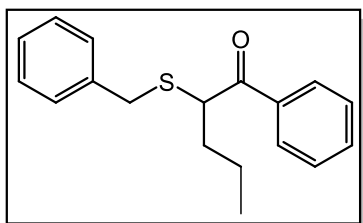
The title compound was prepared following the procedure outlined for **3a** using 4-methylbenzylthiol (0.415 g, 0.41 mL, 3.0 mmol), 2-chloro-1-phenylbutan-1-one **S6** (0.502 g, 2.7 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (74 mg, 3.2 mmol) in methanol (20 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; $\nu_{\max}/\text{cm}^{-1}$ (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, ArCH₃), 3.56 (1H, A of AB system, J_{AB} 12.7, one of SCH₂), 3.69 (1H, B of AB system, J_{AB} 12.7, one of SCH₂), 4.03 [1H, t, J 7.3, C(2) H], 7.06 (2H, d, J 7.8, ArH), 7.12 (2H, d, J 7.8, ArH), 7.38-7.47 (2H, m, ArH), 7.50-7.59 (1H, m, ArH), 7.87 (2H, d, J 7.6, ArH); δ_{C} (100 MHz): 12.1 [CH₃, C(4) H_3], 21.1 (CH₃, ArCH₃), 23.8 [CH₂, C(3) H_2], 33.8 (CH₂, SCH₂), 49.0 [CH, C(2) H], 128.50, 128.53, 129.1, 129.2, 132.9 (5 x CH signals, 9 x aromatic CH), 134.2, 136.3, 136.8 (3 x C, aromatic C), 196.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₈H₂₁OS[M+H⁺] 285.1313. Found 285.1313; m/z (ES⁺) 285.2 [(C₁₈H₂₀OS)+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; $\nu_{\max}/\text{cm}^{-1}$ (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, ArH), 7.31-7.38 (2H, m, ArH), 7.39-7.47 (2H, m, ArH), 7.51-7.58 (1H, m, ArH), 7.91 (2H, d, J 7.4, ArH); δ_{C} (100 MHz): 11.9 [CH₃, C(4) H_3], 24.3 [CH₂, 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 CH), 132.2 (C, aromatic C), 133.0, 134.4 (2 x CH, aromatic CH), 136.4 (C, aromatic C), 196.0 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₇OS[M+H⁺] 257.1000. Found 257.1001; m/z (ES⁺) 257.3 [(C₁₆H₁₆OS)+H⁺], 100%.

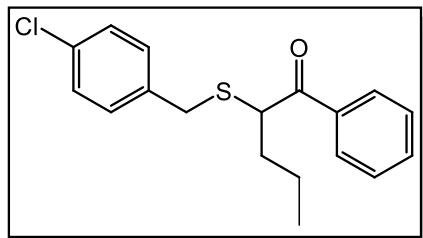
2-(Benzylthio)-1-phenylpentan-1-one **3hh**



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; $\nu_{\max}/\text{cm}^{-1}$ (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 SCH₂), 3.72 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 4.12 [1H, t, J 7.3, C(2) H], 7.17-7.30 (5H, m, ArH), 7.41 (2H, t, J 7.7, ArH), 7.53 (1H, t, J 7.6, ArH), 7.86 (2H, d, J 7.3, ArH); δ_{C} (100 MHz): 13.9 [CH₃, C(5) H_3], 20.7 [CH₂, C(4) H_2], 32.7 [CH₂, C(3) H_2 or SCH₂], 34.2 [CH₂, C(3) H_2 or SCH₂], 47.0 [CH, C(2) H], 127.2, 128.49, 128.50, 128.6, 129.2, 133.0 (6 x CH signals,

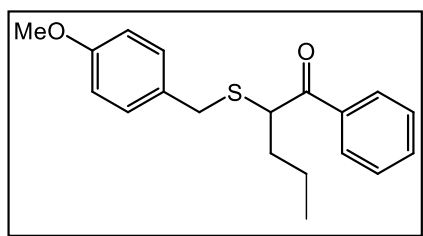
10 x aromatic CH), 136.3, 137.4 (2 x C, aromatic C), 196.0 (C, CO); m/z (ES+) 285.2 $[(C_{18}H_{20}OS)+H^+]$, 18%.

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; $\nu_{\max}/\text{cm}^{-1}$ (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 SCH₂), 3.68 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 4.12 [1H, t, J 7.3, C(2) H], 7.16 (2H, d, J 8.4, ArH), 7.21 (2H, d, J 8.4, ArH), 7.39-7.49 (2H, m, ArH), 7.52-7.59 (1H, m, ArH), 7.84-7.92 (2H, m, ArH); δ_C (100 MHz): 13.8 [CH₃, C(5) H_3], 20.6 [CH₂, C(4) H_2], 32.6 [CH₂, C(3) H_2 or SCH₂], 33.4 [CH₂, C(3) H_2 or SCH₂], 47.0 [CH, C(2) H], 128.4, 128.6, 130.5 (3 x CH signals, 8 x aromatic CH), 132.9 (C, aromatic C), 133.1 (CH, aromatic CH), 136.0, 136.1 (2 x C, aromatic C), 195.9 (C, CO); 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%.

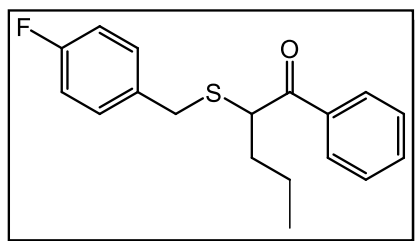
2-((4-Methoxybenzyl)thio)-1-phenylpentan-1-one **3jj**



The title compound was prepared following the procedure outlined for **3a** using 4-methoxybenzyl mercaptan (0.424 g, 0.38 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, 3.0 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; $\nu_{\max}/\text{cm}^{-1}$ (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 SCH₂), 3.68 (1H, B of AB system, J_{AB} 12.8, one of SCH₂), 3.76 (3H, s, OCH₃), 4.11 [1H, t, J 7.3, C(2) H], 6.78 (2H, d, J 8.6, ArH), 7.15 (2H, d, J 8.6, ArH), 7.41 (2H, t, J 7.7, ArH), 7.53 (1H, t, J 7.8, ArH), 7.87 (2H, d, J 7.5, ArH); δ_{C} (100 MHz): 13.8 [CH₃, C(5) H_3], 20.7 [CH₂, C(4) H_2], 32.7 [CH₂, C(3) H_2 or SCH₂], 33.6 [CH₂, C(3) H_2 or SCH₂], 47.0 [CH, C(2) H], 55.2 (CH₃, OCH₃), 113.9 (1 x CH signal, 2 x aromatic CH), 128.4, 128.5 (2 x CH signals, 4 x aromatic CH), 129.2 (C, aromatic C), 130.2, 132.9 (2 x CH signals, 3 x aromatic CH), 136.3, 158.7 (2 x C, aromatic C), 196.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₉H₂₃O₂S[M+H⁺] 315.1419. Found 315.1422; m/z (ES⁻) 313.3 [(C₁₉H₂₂O₂S)-H⁺], 10%.

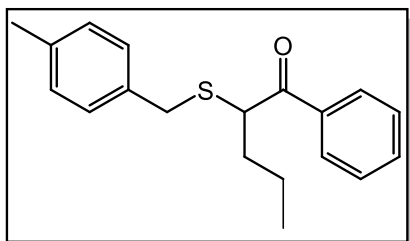
2-((4-Fluorobenzyl)thio)-1-phenylpentan-1-one **3kk**



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, 3.0 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 **3kk** (0.614 g, 81%) as a colourless oil; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 2958, 2934, 2871, 1672 (C=O), 1597

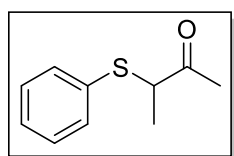
(aromatic), 1507, 1222, 687; δ_{H} (400 MHz): 0.89 [3H, t, J 7.4, C(5) H_3], 1.28-1.52 [2H, m, C(4) H_2], 1.73-1.87 [1H, symmetrical m, one of C(3) H_2], 1.98-2.12 [1H, symmetrical m, one of C(3) H_2], 3.57 (1H, A of AB system, J_{AB} 13.0, one of SCH₂), 3.69 (1H, B of AB system, J_{AB} 13.0, one of SCH₂), 4.12 [1H, t, J 7.3, C(2) H], 6.92 (2H, dd appears as t, J 8.7, ArH), 7.18 (2H, dd, J 8.6, J_{FH} 5.4, ArH), 7.42 (2H, t, J 7.7, ArH), 7.53 (1H, t, J 7.6, ArH), 7.85-7.93 (2H, m, ArH); δ_{C} (100 MHz): 13.8 [CH₃, C(5) H_3], 20.6 [CH₂, C(4) H_2], 32.6 [CH₂, C(3) H_2 or SCH₂], 33.2 [CH₂, C(3) H_2 or SCH₂], 47.0 [CH, C(2) H], 115.3 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH), 128.4, 128.6 (2 x CH signals, 4 x aromatic CH), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 8.1, aromatic CH), 133.0 (CH, aromatic CH), 133.1 (C, d, $^4J_{\text{CF}}$ 3.2, aromatic C), 136.2 (C, aromatic C), 161.9 (C, d, $^1J_{\text{CF}}$ 245.7, aromatic C), 195.9 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₈H₂₀OFS[M+H⁺] 303.1219. Found 303.1214; m/z (ES⁺) 303.2 [(C₁₈H₁₉OFS)+H⁺], 100%.

2-((4-Methylbenzyl)thio)-1-phenylpentan-1-one **3II**



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 **3II** (0.823 g, 82%) as a colourless oil; $\nu_{\max}/\text{cm}^{-1}$ (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, Ar CH_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 CH_3), 32.6 [CH $_2$, C(3) H_2 or SCH $_2$], 33.9 [CH $_2$, C(3) H_2 or SCH $_2$], 46.9 [CH, C(2) H], 128.50, 128.52, 129.1, 129.2, 132.9 (5 x CH signals, 9 x aromatic CH), 134.1, 136.2, 136.8 (3 x C, aromatic C), 196.1 (C, CO); HRMS (ES $^{+}$): Exact mass calculated for C $_{19}\text{H}_{23}\text{OS}$ [M+H $^{+}$] 299.1470. Found 299.1471; m/z (ES $^{+}$) 299.3 [(C $_{19}\text{H}_{22}\text{OS}$)+H $^{+}$], 92%.

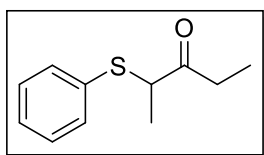
3-(Phenylthio)butan-2-one **5a**¹⁵



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; $\nu_{\max}/\text{cm}^{-1}$ (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, CHSPh), 7.20-7.45 (5H, m, Ar H); δ_{C} (75.5 MHz, CDCl $_3$) 16.1 (CH $_3$, CHCH $_3$), 26.4 (CH $_3$, COCH $_3$), 52.1 (CH, CHSPh), 128.0, 129.1, 132.7 (3 x CH, aromatic CH), 137.8 (C, aromatic C), 205.6 (C, CO); HRMS (ES $^{+}$): Exact mass calculated for C $_{10}\text{H}_{13}\text{OS}$ [M+H $^{+}$] 181.0687. Found 181.0689; m/z (ES $^{+}$) 181.1 [(C $_{10}\text{H}_{12}\text{OS}$)+H $^{+}$], 24%, 197.0 (100%).

Spectroscopic characteristics were consistent with those previously reported.¹⁵

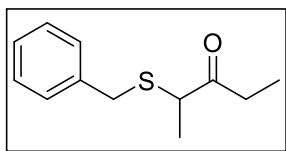
2-(Phenylthio)pentan-3-one **5b**¹⁶



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%); $\nu_{\max}/\text{cm}^{-1}$ (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, CHSPH), 7.26-7.39 (5H, m, ArH); 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, CHSPH), 128.0, 129.1, 132.8 (3 x CH, aromatic CH), 136.2 (C, aromatic C), 208.4 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{11}\text{H}_{15}\text{OS}[\text{M}+\text{H}^+]$ 195.0844. Found 195.0838; m/z (ES⁺) 195.1 [$(\text{C}_{11}\text{H}_{14}\text{OS})+\text{H}^+$], 26%.

Spectroscopic characteristics were consistent with those previously reported.¹⁶

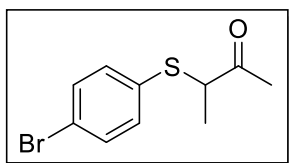
2-(Benzylthio)pentan-3-one **5c**¹¹



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 ^1H 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; $\nu_{\max}/\text{cm}^{-1}$ (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, CHSBn), 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, ArH); 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, CHSBn), 127.2, 128.5, 129.1 (3 x CH, aromatic CH), 137.5 (C, aromatic C), 208.2 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{12}\text{H}_{17}\text{OS}[\text{M}+\text{H}^+]$ 209.1000. Found 209.0920; m/z (ES⁺) 209.1 [$(\text{C}_{12}\text{H}_{16}\text{OS})+\text{H}^+$], 62%.

Spectroscopic characteristics were consistent with those previously reported.¹¹

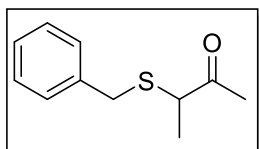
3-[(4-Bromophenyl)thio]butan-2-one **5d**¹⁷



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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3079 (CH), 2974 (CH), 1710 (CO), 1473; δ_{H} (400 MHz, CDCl_3) 1.41 (3H, d, J 7.1, CHCH_3), 2.29 (3H, s, COCH_3), 3.73 (1H, q, J 7.1, CHSAr), 7.22 (2H, d, J 8.4, ArH), 7.42 (2H, d, J 8.4, ArH); δ_{C} (75.5 MHz, CDCl_3) 16.0 (CH_3 , CHCH_3), 26.2 (CH_3 , COCH_3), 51.9 (CH, CHSAr), 123.0, 131.8 (2 x C, 2 x aromatic C), 132.2, 134.2 (2 x CH, aromatic CH), 205.1 (C, CO); m/z (ES+) 275.1 [$(\text{C}_{10}\text{H}_{11}^{79}\text{BrOS})+\text{H}_2\text{O}^+$], 96%, 277.1 [$(\text{C}_{10}\text{H}_{11}^{81}\text{BrOS})+\text{H}_2\text{O}^+$], 100%.

Spectroscopic characteristics were consistent with those previously reported.¹⁷

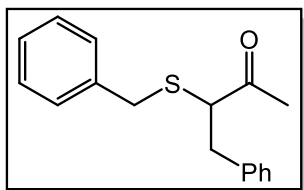
3-(Benzylthio)butan-2-one **5e**¹¹



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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3000 (CH), 1714 (CO), 1583; δ_{H} (300 MHz, CDCl_3) 1.35 (3H, d, J 7.2, CHCH_3), 2.22 (3H, s, COCH_3), 3.25 (1H, q, J 7.2, CHSBn), 3.59 (1H, A of AB system, J 13.2, one of SCH_2), 3.65 (1H, B of AB system, J 13.2, one of SCH_2), 7.18-7.32 (5H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 15.9 (CH_3 , CHCH_3), 25.5 (CH_3 , COCH_3), 35.0 (CH_2 , SCH_2), 48.2 (CH, CHSBn), 127.2, 128.6, 129.1 (3 x CH, aromatic CH), 137.5 (C, aromatic C), 205.6 (C, CO); m/z (ES+) 195.1 [$(\text{C}_{11}\text{H}_{14}\text{O})+\text{H}^+$], 20%, 211.0 (100%).

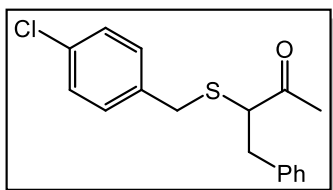
Spectroscopic characteristics were consistent with those previously reported.¹¹

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; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3085, 3061, 3028, 2920, 2850, 1702 (C=O), 1494, 1453, 1353, 696; δ_{H} (400 MHz): 2.14 (3H, s, CH_3), 2.90 [1H, overlapping dd, J 14.1, 6.9, one of $\text{C}(4)\text{H}_2$], 3.17 [1H, overlapping dd, J 14.1, 8.5, one of $\text{C}(4)\text{H}_2$], 3.46 [1H, t, J 7.7, $\text{C}(3)\text{H}$], 3.61 (2H, s, SCH_2), 7.11 (2H, d, J 7.0, ArH), 7.18-7.32 (8H, m, ArH); δ_{C} (100 MHz): 27.0 (CH_3 , CH_3), 35.2 [CH_2 , SCH_2 or $\text{C}(4)\text{H}_2$], 36.5 [CH_2 , SCH_2 or $\text{C}(4)\text{H}_2$], 54.5 [CH , $\text{C}(3)\text{H}$], 126.7, 127.3, 128.5, 128.6, 128.9, 129.1 (6 x CH signals, 10 x aromatic CH), 137.2, 138.1 (2 x C, aromatic C), 204.1 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{19}\text{OS}[\text{M}+\text{H}^+]$ 271.1157. Found 271.1153.

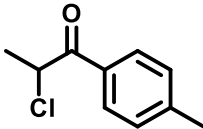
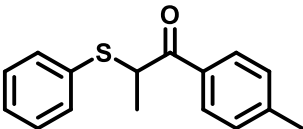
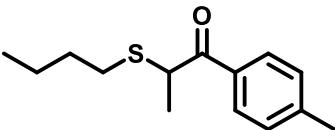
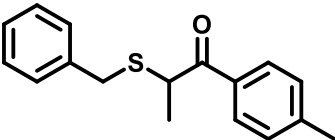
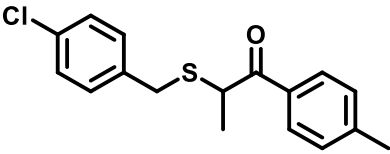
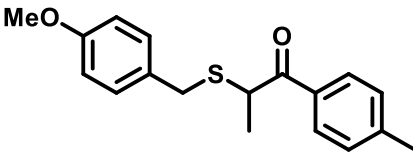
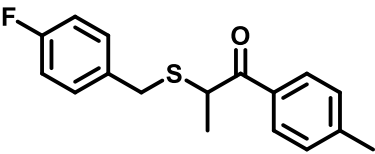
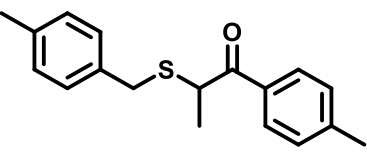
3-((4-Chlorobenzyl)thio)-4-phenylbutan-2-one **S14**

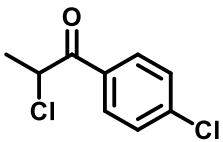
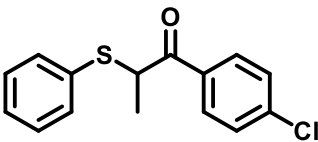
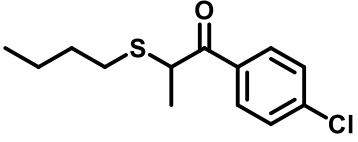
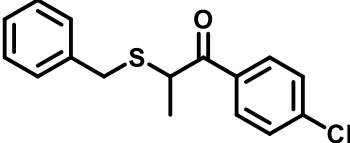
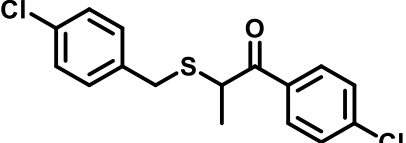
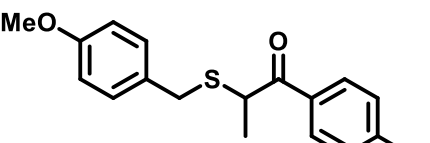
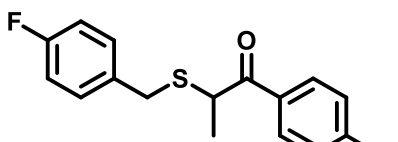
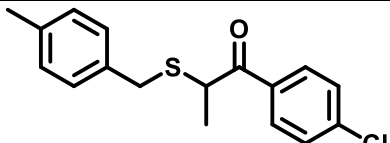
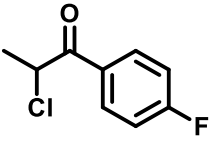
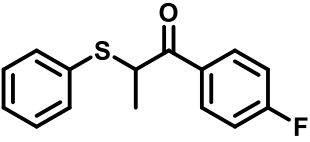


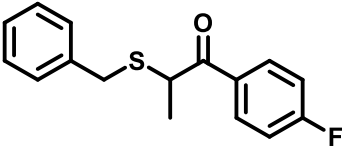
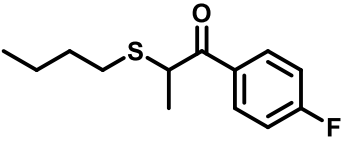
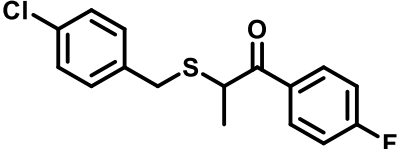
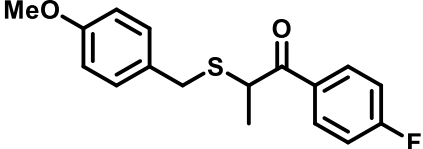
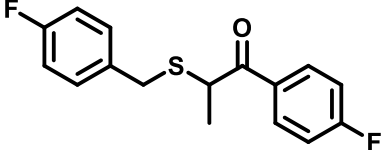
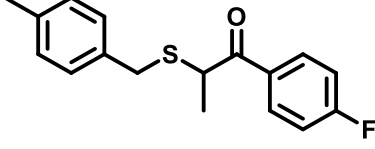
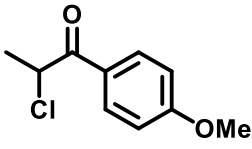
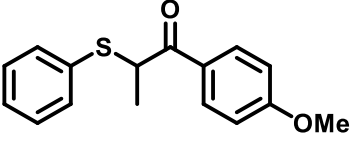
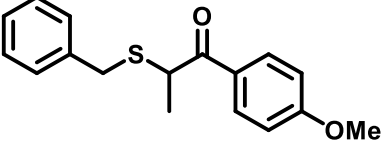
The title compound was prepared following the procedure outlined for **3a** using 4-chlorobenzylthiol (0.247 g, 0.23 mL, 1.7 mmol), 3-chloro-4-phenylbutan-2-one **S8** (0.288 g, 1.5 mmol) in methanol (10 mL) and freshly prepared sodium methoxide [prepared from sodium (43 mg, 1.8 mmol) in methanol (20 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3085, 3062, 3028, 2919, 1702 (C=O), 1489, 1353, 1091, 697, 499; δ_{H} (400 MHz): 2.17 (3H, s, CH_3), 2.89 [1H, overlapping dd, J 14.1, 7.1, one of $\text{C}(4)\text{H}_2$], 3.15 [1H, overlapping dd, J 14.1, 8.5, one of $\text{C}(4)\text{H}_2$], 3.43 [1H, t, J 7.7, $\text{C}(3)\text{H}$], 3.55 (1H, A of AB system, J_{AB} 13.4, SCH_2), 3.59 (1H, B of AB system, J_{AB} 13.4, SCH_2), 7.11 (2H, d, J 7.5, ArH), 7.14-7.32 (7H, m, ArH); δ_{C} (100 MHz): 26.8 (CH_3 , CH_3), 34.4 [CH_2 , SCH_2 or $\text{C}(4)\text{H}_2$], 36.4 [CH_2 , SCH_2 or $\text{C}(4)\text{H}_2$], 54.4 [CH , $\text{C}(3)\text{H}$], 126.7, 128.5, 128.7, 128.9, 130.4 (5 x CH signals, 9 x aromatic CH), 133.1,

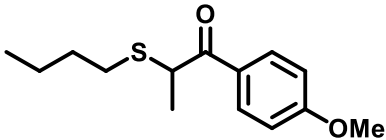
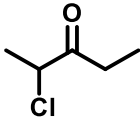
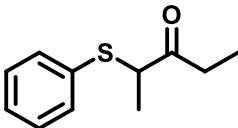
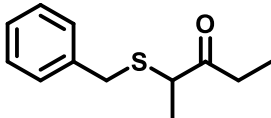
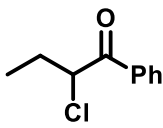
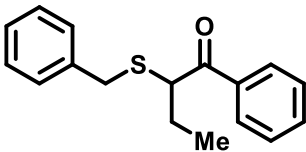
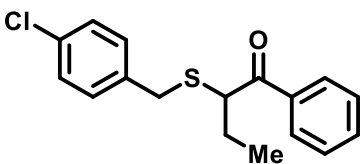
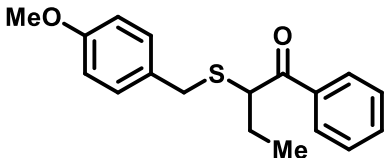
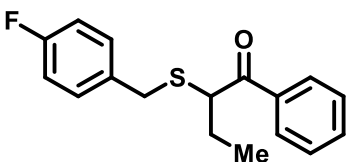
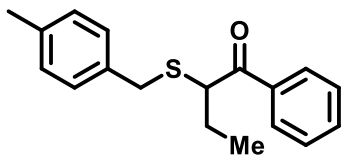
135.7, 137.9 (3 x C, aromatic C), 204.0 (C, CO); HRMS (ES+): Exact mass calculated for $C_{17}H_{18}OS^{35}Cl[M+H^+]$ 305.0767. Found 305.0760.

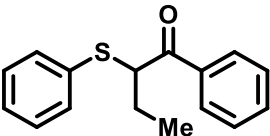
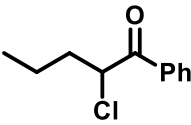
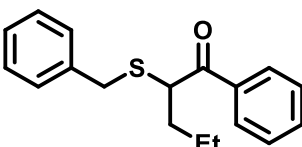
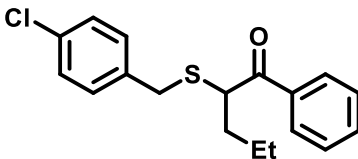
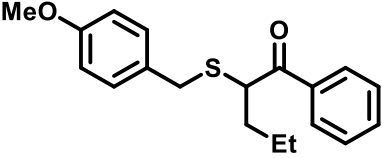
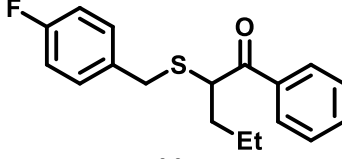
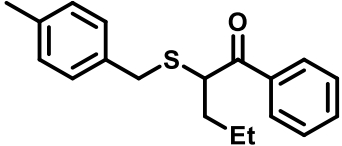
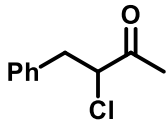
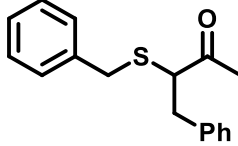
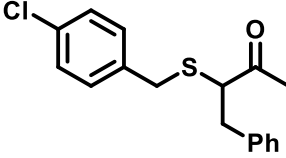
1.4 Table of α -chloroketones and α -sulfenylketones

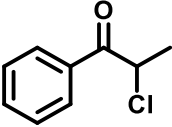
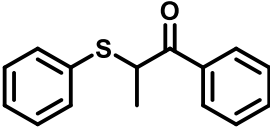
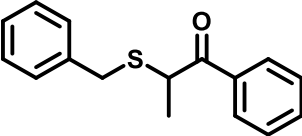
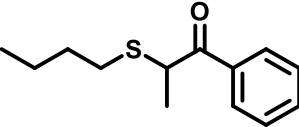
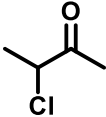
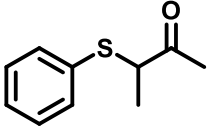
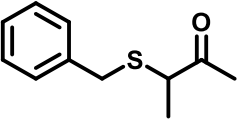
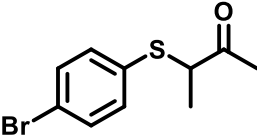
$ \begin{array}{ccccc} \text{R}^1-\text{C}(=\text{O})-\text{CH}_2-\text{R}^2 & \xrightarrow[\text{MeCN, } \Delta, 4 \text{ h}]{\text{NCS (1 Eq), } p\text{TsOH (1.45 Eq)}} & \text{R}^1-\text{C}(=\text{O})-\text{CH}(\text{Cl})-\text{R}^2 & \xrightarrow[\text{ROH, rt, 16 h}]{\text{R}^3\text{SH (1.1-1.2 Eq), NaOR (1.2 Eq)}} & \text{R}^1-\text{C}(=\text{O})-\text{CH}(\text{SR}^3)-\text{R}^2 \\ \text{Ketone} & & \alpha\text{-Chloroketone} & & \alpha\text{-Sulfenylketone} \end{array} $			
α -Chloroketone	% Yield	α -Sulfenylketone	% Yield
 S1 ¹	71	 3g ¹²	62
		 3i	97
		 3h	61
		 3j	72
		 3k	79
		 3l	44
		 3m	72

 S2²⁻³	72	 3n	87
		 3p	85
		 3o	58
		 3q	69
		 3r	64
		 3s	65
		 3t	73
 S3⁴	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
 S5⁶	80 ^a	 5b¹⁶	86
		 5c¹¹	50
 S6⁷	74	 3bb	36
		 3cc	89
		 3dd	98
		 3ee	76
		 3ff	77

		 3gg	86
 S7⁸	73	 3hh	86
		 3ii	73
		 3jj	63
		 3kk	81
		 3ll	82
 S8³	28	 10a	77
		 S16	74

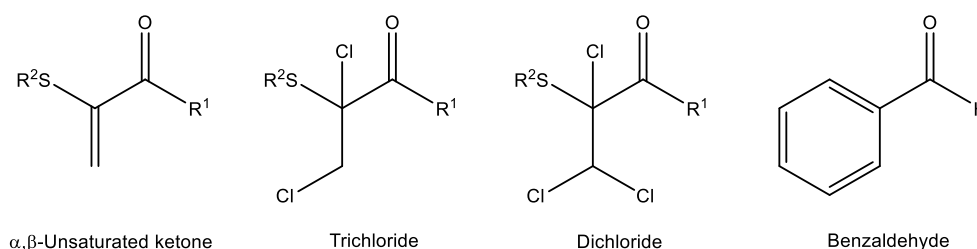
	Commercially available	 3a¹⁰	97
		 3b¹¹	54
		 3c	64
	Commercially available	 5a¹⁵	83
		 5e¹¹	86
		 5d¹⁷	58
^a Reaction carried out in CCl ₄ at 45°C for 2 h using 1.1 Eq. sulfonyl chloride			

1.5 Synthesis of α -Sulfenyl- β -chloroenones

1.5.1 Synthesis of α -sulfenyl- β -chloropropenones

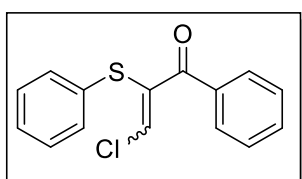
Note Commercially available un-recrystallised *N*-chlorosuccinimide was used throughout the reactions in this section. It was determined that recrystallised NCS had no impact on the efficiency or outcome of the reactions and so recrystallisation was deemed an unnecessary step.¹⁸

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



A number of ^1H 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 ^1H NMR spectroscopy, this was seen to contain the β -chloroenone as a mixture of *Z* and *E* isomers, **Z-4a** and **E-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

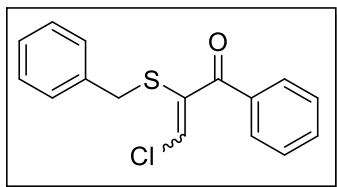
fraction as the desired β -chloroenone (0.46 g, 68%) as a yellow oil and an inseparable mixture of *Z* and *E* isomers **Z-4a** and **E-4a** in a ratio of 2.2:1, a trace of the dichloride and trichloride were still present in this fraction; $\nu_{\max}/\text{cm}^{-1}$ (film) 3060 (CH), 1669 (CO), 1597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

Z-4a: δ_{H} (300 MHz, CDCl_3) 6.90 (1H, s, CHCl), 7.08-7.59 (8H, m, ArH), 7.62-7.70 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 128.05 (CH, CHCl), 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 CH), 130.9, 136.4, 140.5 [3 x C, 2 x aromatic C and C(2)S], 190.8 (C, CO).

E-4a: δ_{H} (300 MHz, CDCl_3) 6.71 (1H, s, CHCl), 7.08-7.59 (8H, m, ArH), 7.82-7.88 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 121.8 (CH, CHCl), 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 CH), 129.5, 134.5, 135.1 [3 x C, 2 x aromatic C and C(2)S], 191.0 (C, CO).

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

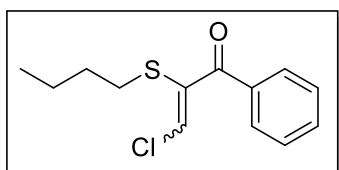
h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^1H NMR spectroscopy, this was seen to contain the β -chloroenone as a mixture of *Z* and *E* isomers, **Z-4b** and **E-4b**, in a ratio of 1:1, in addition to signals due to 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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3062 (CH), 2927 (CH), 1666 (CO), 1597 (aromatic), 1243.

Z-4b: δ_{H} (300 MHz, CDCl_3) 4.02 (2H, s, SCH_2), 6.66 (1H, s, CHCl), 7.12-7.63 (10H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 35.8 (CH_2 , SCH_2), 127.4, 127.5, 128.4, 128.6, 128.9, 129.2, 129.3, 129.7, 129.8 (CH, aromatic CH), 130.3 (CH, CHCl), 133.3 (CH, aromatic CH), 133.5 (C, aromatic C), 134.2 (CH, aromatic CH), 134.3, 136.5, 136.7, 137.1, 140.0 [C, aromatic C and $\text{C}(2)\text{S}$], 190.6 (C, CO).

E-4b: δ_{H} (300 MHz, CDCl_3) 3.88 (2H, s, SCH_2), 6.45 (1H, s, CHCl), 7.12-7.63 (8H, m, ArH), 7.91 (2H, d, J 7.1, ArH); δ_{C} (75.5 MHz, CDCl_3) 38.6 (CH_2 , SCH_2), 122.1 (CH, CHCl), 127.4, 127.5, 128.4, 128.6, 128.9, 129.2, 129.3, 129.7, 129.8, 133.3 (CH, aromatic CH), 133.5 (C, aromatic C), 134.2 (CH, aromatic CH), 134.3, 136.5, 136.7, 137.1, 140.0 [C, aromatic C and $\text{C}(2)\text{S}$], 191.8 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{14}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}]^+$ 289.0454. Found 289.0457; m/z (ES⁺) 289.0 [$(\text{C}_{16}\text{H}_{13}\text{OS}^{35}\text{Cl})+\text{H}^+$], 52%, 291.0 [$(\text{C}_{16}\text{H}_{13}\text{OS}^{37}\text{Cl})+\text{H}^+$], 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 E-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 ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, CH_2CH_3), 1.52-1.62 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60-2.68 (2H, m, SCH_2), 6.59 (1H, s, CHCl), 7.49 (2H, t, J 7.6, ArH), 7.58-7.63 (1H, m, ArH), 7.92-7.99 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 13.53 (CH_3 , CHCH_3), 21.6 (CH_2 , CH_2CH_3), 31.2 (CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 33.3 (CH_2 , SCH_2), 119.3 (CH, CHCl), 128.9, 129.6, 134.1 (3 x CH, aromatic CH), 134.2, 134.9 [2 x C, aromatic C and $\text{C}(2)\text{S}$], 191.7 (C, CO).

HRMS (ES⁺): Exact mass calculated for C₁₃H₁₆OS³⁵Cl[M+H]⁺ 255.0610. Found 255.0617; m/z (ES⁺) 297.2 [(C₁₃H₁₅OS³⁵Cl)+CNCH₃⁺], 100%, 299.2 [(C₁₃H₁₅OS³⁷Cl)+CNCH₃⁺], 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; $\nu_{\max}/\text{cm}^{-1}$ (film) 3064 (CH), 2960 (CH), 1670 (CO), 1596 (aromatic), 1222.

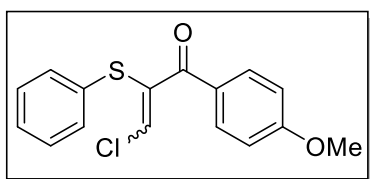
E-4c (less polar): δ_{H} (400 MHz, CDCl₃) 0.88 (3H, t, *J* 7.3, CH₂CH₃), 1.32-1.42 (2H, m, CH₂CH₃), 1.52-1.62 (2H, m, CH₂CH₂CH₃), 2.60-2.68 (2H, m, SCH₂), 6.59 (1H, s, CHCl), 7.49 (2H, t, *J* 7.6, ArH), 7.58-7.63 (1H, m, ArH), 7.92-7.99 (2H, m, ArH).

Spectroscopic characteristics were consistent with those above.

Z-4c (more polar): δ_{H} (400 MHz, CDCl₃) 0.83 (3H, t, *J* 7.3, CH₂CH₃), 1.32-1.42 (2H, m, CH₂CH₃), 1.47-1.62 (2H, m, CH₂CH₂CH₃), 2.68-2.72 (2H, m, SCH₂), 6.69 (1H, s, CHCl), 7.45-7.50 (2H, m, ArH), 7.58-7.63 (1H, m, ArH), 7.88-7.90 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl₃) 13.49 (CH₃, CHCH₃), 21.6 (CH₂, CH₂CH₃), 31.4 (CH₂, SCH₂), 32.1 (CH₂, CH₂CH₂CH₃), 126.8 (CH, CHCl), 128.7, 129.8, 133.7 (3 x CH, aromatic CH), 136.4, 140.1 [2 x C, aromatic C and C(2)S], 190.8 (C, CO).

HRMS (ES⁺): Exact mass calculated for C₁₃H₁₆OS³⁵Cl[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 ¹H 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. ¹H NMR spectroscopy showed a trace of α,β -unsaturated ketone **S19**

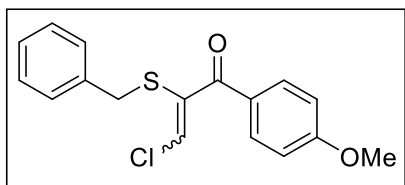
(1%) was still present in this sample - [(d, δ_{H} 6.00 ppm, J 2.0) and (d, δ_{H} 6.18 ppm, J 2.0)]; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3058 (CH), 2934 (CH), 1659 (CO), 1598 (aromatic), 1253.

Z-4d (more polar): δ_{H} (300 MHz, CDCl_3) 3.83 (3H, s, OCH_3), 6.79 (1H, s, CHCl), 6.83 (2H, d, J 9.0, ArH), 7.10-7.16 (3H, m, ArH), 7.20-7.29 (2H, m, ArH), 7.73 (2H, d, J 9.0, ArH); δ_{C} (75.5 MHz, CDCl_3) 55.5 (CH_3 , OCH_3) 113.6 (CH, aromatic CH), 126.0 (CH, CHCl), 128.1, 129.0 (2 x CH, aromatic CH), 129.1, 130.9 [2 x C, aromatic C and C(2)S], 131.9, 132.6 (2 x CH, aromatic CH), 140.4, 163.8 (2 x C, 2 x aromatic C), 189.2 (C, CO).

E-4d (less polar): δ_{H} (300 MHz, CDCl_3) 3.85 (3H, s, OCH_3), 6.64 (1H, s, CHCl), 6.90 (2H, d, J 9.0, ArH), 7.20-7.29 (2H, m, ArH), 7.38-7.44 (3H, m, ArH), 7.84 (2H, d, J 9.0, ArH); δ_{C} (75.5 MHz, CDCl_3) 55.6 (CH_3 , OCH_3) 114.0 (CH, aromatic CH), 121.0 (CH, CHCl), 127.5 [C, aromatic C or C(2)S], 128.5, 129.3 (2 x CH, aromatic CH), 131.2 [C, aromatic C or C(2)S], 132.1, 132.4 (2 x CH, aromatic CH), 135.4 [C, aromatic C or C(2)S], 164.3 (C, aromatic C), 189.6 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}^{35}\text{Cl}[\text{M}+\text{H}]^+$ 305.0403. Found 305.0390; m/z (ES⁺) 305.1 [$(\text{C}_{16}\text{H}_{13}\text{O}_2\text{S}^{35}\text{Cl})+\text{H}^+$], 100%, 307.0 [$(\text{C}_{16}\text{H}_{13}\text{O}_2\text{S}^{37}\text{Cl})+\text{H}^+$], 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 ^1H 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

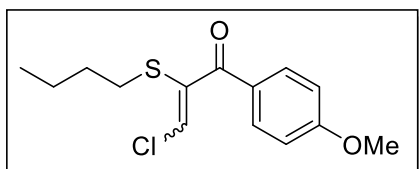
system, δ_{H} 4.37, J 12.9) were also present (<2%); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3062 (CH), 3031 (CH), 2935 (CH), 1654 (CO), 1598 (aromatic), 1253.

Z-4e (more polar): δ_{H} (400 MHz, CDCl_3) 3.83 (3H, s, OCH_3), 3.97 (2H, s, SCH_2), 6.56 (1H, s, CHCl), 6.84 (2H, d, J 9.0, ArH), 7.12-7.22 (5H, m, ArH), 7.56 (2H, d, J 9.0, ArH); δ_{C} (75.5 MHz, CDCl_3) 35.7 (CH_2 , SCH_2), 55.6 (CH_3 , OCH_3), 113.7 (CH, aromatic CH), 127.1 (CH, CHCl), 127.4, 128.5, 129.3, 132.3 (4 x CH, aromatic CH), 137.1, 139.8 [2 x C, aromatic C and $\text{C}(2)\text{S}$], 163.9 (C, aromatic C), 189.2 (C, CO).

E-4e (less polar): δ_{H} (400 MHz, CDCl_3) 3.86 (3H, s, OCH_3), 3.88 (2H, s, SCH_2), 6.41 (1H, s, CHCl), 6.95 (2H, d, J 9.0, ArH), 7.12-7.22 (5H, m, ArH), 7.90 (2H, d, J 9.0, ArH); δ_{C} (75.5 MHz, CDCl_3) 38.5 (CH_2 , SCH_2), 55.7 (CH_3 , OCH_3), 114.2 (CH, aromatic CH), 121.2 (CH, CHCl), 127.5, 128.6, 129.2, 132.2 (4 x CH, aromatic CH), 132.2, 133.7, 136.6 [3 x C, 2 x aromatic C and $\text{C}(2)\text{S}$], 164.5 (C, aromatic C), 190.4 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{S}^{35}\text{Cl}[\text{M}+\text{H}]^+$ 319.0560. Found 319.0565; m/z (ES⁺) 319.1 [$(\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}^{35}\text{Cl})+\text{H}^+$], 100%, 321.1 [$(\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}^{37}\text{Cl})+\text{H}^+$], 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



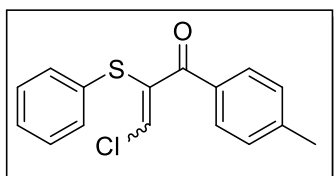
This was prepared following the procedure described above for **4a** using 2-(butylthio)-1-(4-methoxyphenyl)propan-1-one **3f** (0.15 g, 0.6 mmol), *N*-chlorosuccinimide (0.155 g, 1.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 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 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 55.5 (CH_3 , OCH_3), 114.0 (CH, aromatic CH), 124.0 (CH, CHCl), 129.0 [C, aromatic C or $\text{C}(2)\text{S}$], 132.4 (CH, aromatic CH), 140.0, 164.2 [2 x C, 2 x aromatic C or aromatic C and $\text{C}(2)\text{S}$], 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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 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 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 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 $\text{C}(2)\text{S}$], 132.1 (CH, aromatic CH), 135.1, 164.4 [2 x C, 2 x aromatic C or aromatic C and $\text{C}(2)\text{S}$], 190.3 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{S}^{35}\text{Cl}[\text{M}+\text{H}]^+$ 285.0716. Found 285.0710; m/z (ES⁺) 285.1 [$(\text{C}_{14}\text{H}_{17}\text{O}_2\text{S}^{35}\text{Cl})+\text{H}^+$], 100%, 287.1 [$(\text{C}_{14}\text{H}_{17}\text{O}_2\text{S}^{37}\text{Cl})+\text{H}^+$], 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 E-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 ^1H 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 **E-4g** in a ratio of 1.7:1; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3059 (CH), 1667 (CO), 1605 (aromatic), 1257.

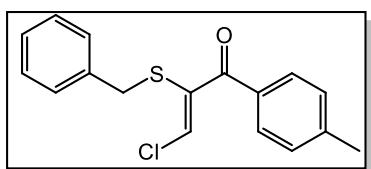
Z-4g (more polar): δ_{H} (400 MHz, CDCl_3) 2.38 (3H, s, ArCH_3), 6.86 (1H, s, CHCl), 7.11-7.35 (7H, m, ArH), 7.62 (2H, d, J 8.2, ArH); δ_{C} (75.5 MHz, CDCl_3) 21.7 (CH_3 , aromatic CH_3), 127.4 (CH, CHCl), 128.0, 128.5, 128.99, 129.04, 129.3, 129.5, 129.6, 129.8 (CH, aromatic CH), 131.0 [C,

aromatic C or C(2)S], 132.3, 132.4, 134.2 (3 x CH, aromatic CH), 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, CO).

E-4g (less polar): δ_{H} (400 MHz, CDCl_3) 2.41 (3H, s, ArCH_3), 6.68 (1H, s, CHCl), 7.11-7.35 (7H, m, ArH), 7.77 (2H, d, J 8.3, ArH); δ_{C} (75.5 MHz, CDCl_3) 21.8 (CH_3 , aromatic CH_3), 121.4 (CH, CHCl), 128.0, 128.5, 128.99, 129.04, 129.3, 129.5, 129.6, 129.8 (CH, aromatic CH), 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 CH), 135.3 [C, aromatic C or C(2)S], 145.9 (C, aromatic C), 190.7 (C, CO).

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

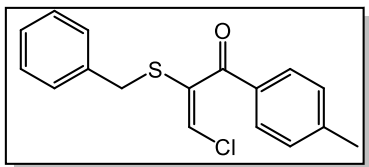
(Z)-2-(Benzylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one Z-4h and (E)-2-(Benzylthio)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one E-4h



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 ^1H 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.

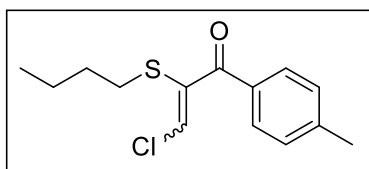
Z-4h (more polar): $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3060, 3030, 1656 (C=O), 1602, 1243, 1177, 734, 696; δ_{H} (400 MHz, CDCl_3) 2.39 (3H, s, ArCH_3), 4.01 (2H, s, SCH_2), 6.64 (1H, s, CHCl), 7.14-7.22 (7H, m, ArH), 7.42 (2H, d, J 8.0, ArH); δ_{C} (100 MHz, CDCl_3) 21.7 (CH_3 , ArCH_3), 35.8 (CH_2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



E-4h (less polar): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3028, 2912, 1658 (C=O), 1602, 1453, 1302, 1231, 1176, 699; δ_{H} (400 MHz, CDCl_3): 2.43 (3H, s, ArCH_3), 3.87 (2H, s, SCH_2), 6.43 (1H, s, CHCl), 7.18-7.34 (7H, m, ArH), 7.82 (2H, d, J 8.2, ArH); δ_{C} (100 MHz, CDCl_3): 21.8

(CH_3 , ArCH_3), 38.5 (CH_2 , SCH_2), 121.6 [CH , $\text{C}(3)\text{H}$], 127.4, 128.5, 129.2, 129.6, 129.8 (5 x CH signals, 9 x aromatic CH), 131.8, 133.6, 136.6, 145.3 [4 x C, 3 x aromatic C and $\text{C}(2)\text{S}$], 191.4 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{16}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 303.0610. Found 303.0605; m/z (ES⁺) 303.2 [$(\text{C}_{17}\text{H}_{15}\text{OS}^{35}\text{Cl})+\text{H}^+$], 100%, 305.2 [$(\text{C}_{17}\text{H}_{15}\text{OS}^{37}\text{Cl})+\text{H}^+$], 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 ^1H 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; $\nu_{\max}/\text{cm}^{-1}$ (film)

3061 (CH), 2959 (CH), 1663 (CO), 1605 (aromatic), 1178.

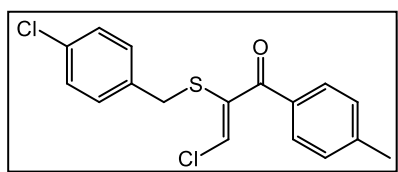
Z-4i (more polar): δ_{H} (300 MHz, CDCl_3) 0.78-0.96 (3H, m, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.44-1.61 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.43 (3H, s, ArCH_3), 2.61-2.72 (2H, m, SCH_2), 6.64 (1H, s, CHCl), 7.23-7.30 (2H, m, ArH), 7.78-7.91 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 13.5 (CH_3 , CHCH_3), 21.6 (CH_2 , CH_2CH_3), 21.8 (CH_3 , ArCH_3), 31.3 (CH_2 , SCH_2), 32.1 (CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 125.7 (CH, CHCl), 129.4, 130.1 (2 x CH, aromatic CH), 133.8, 140.2, 144.9, 145.3 [4 x C, 2 x aromatic C and $\text{C}(2)\text{S}$], 190.5 (C, CO).

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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.43 (3H, s, ArCH_3), 2.61-2.72 (2H, m, SCH_2), 6.57 (1H, s, CHCl),

7.23-7.30 (2H, m, ArH), 7.78-7.91 (2H, m, ArH); δ_c (75.5 MHz, CDCl₃) 13.6 (CH₃, CHCH₃), 21.6 (CH₂, CH₂CH₃), 21.9 (CH₃, ArCH₃), 31.2 (CH₂, CH₂CH₂CH₃), 33.3 (CH₂, SCH₂), 118.9 (CH, CHCl), 129.6, 129.8 (2 x CH, aromatic CH), 131.7, 135.0, 140.2, 145.3 [4 x C, 2 x aromatic C and C(2)S], 191.4 (C, CO).

HRMS (ES⁺): Exact mass calculated for C₁₄H₁₈OS³⁵Cl[M+H]⁺ 269.0767. Found 269.0765; m/z (ES⁺) 269.1 [(C₁₄H₁₇OS³⁵Cl)+H⁺], 68%, 271.1 [(C₁₃H₁₄OS³⁷ClF)+H⁺], 26%, 323.1 (100%).

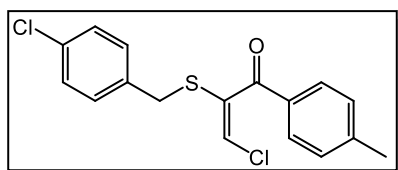
(Z)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(p-tolyl)prop-2-en-1-one Z-4j and (E)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(p-tolyl)prop-2-en-1-one E-4j



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 ¹H 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, CDCl₃): 2.41 (3H, s, ArCH₃), 3.97 (2H, s, SCH₂), 6.65 (1H, s, CHCl), 7.12 (4H, s, ArH), 7.18 (2H, d, *J* 7.9, ArH), 7.41 (2H, d, *J* 8.2, ArH); δ_c (100 MHz, CDCl₃): 21.7 (CH₃, ArCH₃), 35.0 (CH₂, SCH₂), 128.6, 129.1 (2 x CH signals, 4 x aromatic CH), 129.3 [CH, C(3)H], 129.9, 130.6 (2 x CH signals, 4 x aromatic CH), 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, CO); m/z (ES⁺) 337.1 [(C₁₇H₁₄OS³⁵Cl₂)+H⁺], 20%, 339.1 [(C₁₇H₁₄OS³⁵Cl³⁷Cl)+H⁺], 10%.

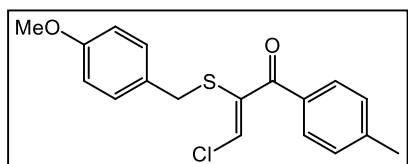


E-4j (less polar): ν_{max}/cm^{-1} (ATR) 3064, 2922, 1659 (C=O), 1603, 1489, 1287, 1224, 1175, 829, 791; δ_H (400 MHz, CDCl₃): 2.43 (3H, s, ArCH₃), 3.82 (2H, s, SCH₂), 6.45 (1H, s, CHCl), 7.21-7.32 (6H, m, ArH), 7.80 (2H, d, *J* 8.2, ArH); δ_c (100

MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 37.8 (CH₂, SCH₂), 122.4 [CH, C(3)H], 128.6, 129.6, 129.8, 130.5

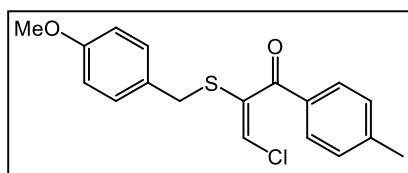
(4 x CH signals, 8 x aromatic CH), 131.5 (C, aromatic C), 132.8 [C, C(2)S], 133.3, 135.3, 145.4 (3 x C, aromatic C), 191.3 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₅OS³⁵Cl₂[M+H⁺] 337.0221. Found 337.0224; m/z (ES⁺) 337.1 [(C₁₇H₁₄OS³⁵Cl₂)+H⁺], 18%. ³⁵Cl/³⁷Cl pattern visible at 337, 339 and 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 ¹H 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).

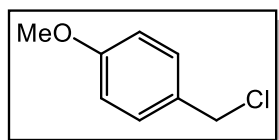
Z-4k (more polar): ν_{max}/cm⁻¹ (ATR) 3033, 2999, 2953, 2933, 2834, 1655 (C=O), 1603, 1509, 1239, 730; δ_H (400 MHz, CDCl₃): 2.40 (3H, s, ArCH₃), 3.73 (3H, s, OCH₃), 3.96 (2H, s, SCH₂), 6.62 (1H, s, CHCl), 6.70 (2H, d, *J* 8.6, ArH), 7.10 (2H, d, *J* 8.6, ArH), 7.17 (2H, d, *J* 8.1, ArH), 7.45 (2H, d, *J* 8.2, ArH); δ_C (100 MHz, CDCl₃): 21.7 (CH₃, ArCH₃), 35.2 (CH₂, SCH₂), 55.2 (CH₃, OCH₃), 113.9 (1 x CH signal, 2 x aromatic CH), 128.5 [CH, C(3)H], 129.0 (C, aromatic C), 129.1, 130.1, 130.4 (3 x CH signals, 6 x aromatic CH), 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, CO); m/z (ES⁺) 121.3 [(C₈H₉O)⁺], 100%; m/z (ES⁻) 35.3 [(³⁵Cl)⁺], 100%, 37.3 [(³⁷Cl)⁺], 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, CDCl₃): 2.43 (3H, s, ArCH₃), 3.79 (3H, s, OCH₃), 3.84 (2H, s, SCH₂), 6.43 (1H, s, CHCl), 6.82 (2H, d, *J* 8.7, ArH), 7.21 (2H, d, *J* 8.7, ArH), 7.28 (2H, d, *J* 8.2, ArH), 7.82 (2H, d, *J* 8.2, ArH); δ_C (100 MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 38.1 (CH₂, SCH₂), 55.2 (CH₃, OCH₃), 113.9 (1 x CH signal, 2 x aromatic CH), 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 CH), 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, CO).

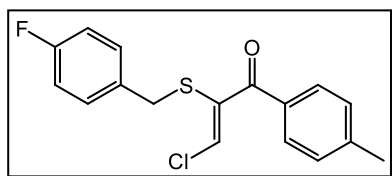
1-(Chloromethyl)-4-methoxybenzene **S24**¹⁹



δ_H (400 MHz, $CDCl_3$): 3.81 (3H, s, OCH_3), 4.57 (2H, s, CH_2Cl), 6.88 (2H, d, J 8.7, ArH), 7.31 (2H, d, J 8.7, ArH); δ_C (75 MHz, $CDCl_3$): 46.3 (CH_2 , CH_2Cl), 55.3 (CH_3 , OCH_3), 114.1 (1 x CH signal, 2 x aromatic CH), 129.7 (C, aromatic C), 130.1 (1 x CH signal, 2 x aromatic CH), 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-4I** and (*E*)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)prop-2-en-1-one **E-4I**

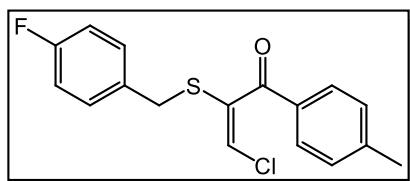


This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-(*p*-tolyl)propan-1-one **3I** (0.423 g, 1.5 mmol), *N*-chlorosuccinimide (0.382 g, 2.9 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture

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 1H 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-4I** (0.215 g, 46%) as a colourless oil and pure **E-4I** (68 mg, 15%) as a colourless oil.

Z-4I (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, $ArCH_3$), 3.98 (2H, s, SCH_2), 6.65 (1H, s, $CHCl$), 6.86 (2H, overlapping dd appears as t, J 8.6, ArH), 7.12-7.24 (4H, m, ArH), 7.43 (2H, d, J 8.2, ArH); δ_C (100 MHz, $CDCl_3$): 21.7 (CH_3 , $ArCH_3$), 35.0 (CH_2 , SCH_2), 115.3 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic CH), 129.1 (1 x CH signal, 2 x aromatic CH), 129.2 [CH, C(3)H], 129.9 (1 x CH signal, 2 x aromatic CH), 130.8 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.2, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for $C_{17}H_{15}OFS^{35}Cl$ [$M+H^+$]

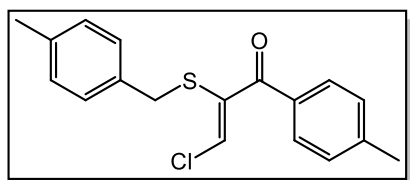
321.0516. Found 321.0501; m/z (ES+) 321.1 $[(C_{17}H_{14}OFS^{35}Cl)+H^+]$, 100%, 323.1 $[(C_{17}H_{14}OFS^{37}Cl)+H^+]$, 40%.



E-4l (less polar): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3066, 2922, 1659 (C=O), 1602, 1507, 1287, 1222, 829; δ_{H} (400 MHz, CDCl_3): 2.43 (3H, s, ArCH_3), 3.84 (2H, s, SCH_2), 6.44 (1H, s, CHCl), 6.97 (2H, overlapping dd appears as t, J 8.7, ArH), 7.23-7.33 (4H, m, ArH), 7.81 (2H, d, J 8.2, ArH); δ_{C} (100 MHz, CDCl_3): 21.8 (CH_3 , ArCH_3), 37.7 (CH_2 , SCH_2), 115.4 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 21.5, aromatic CH), 122.2 [CH, $\text{C}(3)\text{H}$], 129.6, 129.8 (2 x CH signals, 4 x aromatic CH), 130.8 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 8.1, aromatic CH), 131.6 (C, aromatic C), 132.4 (C, d, $^4J_{\text{CF}}$ 3.2, aromatic C), 133.0 [C, $\text{C}(2)\text{S}$], 145.4 (C, aromatic C), 162.1 (C, d, $^1J_{\text{CF}}$ 246.2, aromatic C), 191.4 (C, CO); HRMS (ES+): Exact mass calculated for $\text{C}_{17}\text{H}_{15}\text{OFS}^{35}\text{Cl}[\text{M}+H^+]$

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

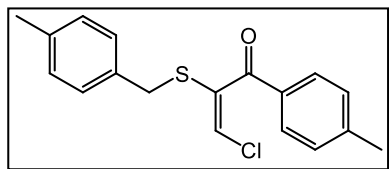


This was prepared following the procedure described above for **4a** using 2-((4-methylbenzyl)thio)-1-(p-tolyl)propan-1-one **3m** (0.613 g, 2.2 mmol), *N*-chlorosuccinimide (0.562 g, 4.2 mmol, 1.95 eq) and toluene

(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 ^1H 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): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3045, 2913, 1656 (C=O), 1602, 1543, 1240, 1081, 873, 806, 734; δ_{H} (400 MHz, CDCl_3): 2.27 (3H, s, ArCH_3), 2.41 (3H, s, ArCH_3), 3.97 (2H, s, SCH_2), 6.62 (1H, s, CHCl), 6.98 (2H, d, J 7.9, ArH), 7.08 (2H, d, J 8.0, ArH), 7.17 (2H, d, J 7.9, ArH), 7.45 (2H, d, J 8.2, ArH); δ_{C} (100 MHz, CDCl_3): 21.0 (CH_3 , ArCH_3), 21.7 (CH_3 , ArCH_3), 35.5 (CH_2 , SCH_2), 128.5

[CH, C(3)H], 129.0, 129.1, 130.0 (3 x CH signals, 8 x aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for C₁₈H₁₈OS³⁵Cl[M+H⁺] 317.0767. Found 317.0764; m/z (ES⁺) 317.1 [(C₁₈H₁₇OS³⁵Cl)+H⁺], 29%, 319.1 [(C₁₈H₁₇OS³⁷Cl)+H⁺], 10%.

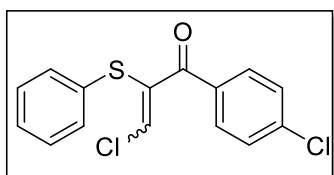


E-4m (less polar): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3048, 3026, 2920, 2861, 1657 (C=O), 1603, 1513, 1243, 1177, 731; δ_{H} (400 MHz, CDCl₃): 2.32 (3H, s, ArCH₃), 2.43 (3H, s, ArCH₃), 3.85 (2H, s, SCH₂), 6.44 (1H, s, CHCl), 7.10 (2H, d, *J* 7.8, ArH), 7.17 (2H, d, *J* 8.0, ArH), 7.28 (2H, d, *J* 7.9, ArH), 7.83 (2H, d, *J* 7.8, ArH); HRMS (ES⁺): Exact mass calculated for C₁₈H₁₈OS³⁵Cl[M+H⁺] 317.0767. Found 317.0767; m/z (ES⁺) 317.1 [(C₁₈H₁₇OS³⁵Cl)+H⁺], 100%, 319.1 [(C₁₈H₁₇OS³⁷Cl)+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%.

¹H and ¹³C 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

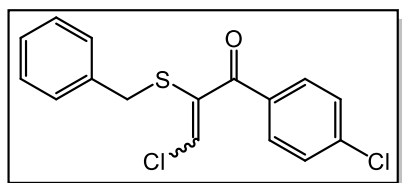
°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow oil. By ¹H NMR spectroscopy, this was seen to contain the β-chloroenone as a mixture of *Z* and *E* isomers, **Z-4n** and **E-4n**, in a ratio of 1.7:1, in addition to signals 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**; $\nu_{\max}/\text{cm}^{-1}$ (film) 3060 (CH), 1671 (CO), 1586 (aromatic), 1248, 1091.

Z-4n (more polar): δ_{H} (300 MHz, CDCl_3) 6.90 (1H, s, CHCl), 7.08-7.48 (7H, m, ArH), 7.61 (2H, d, J 8.7, ArH); δ_{C} (75.5 MHz, CDCl_3) 127.7 (CH, CHCl), 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 CH), 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, CO).

E-4n (less polar): δ_{H} (300 MHz, CDCl_3) 6.72 (1H, s, CHCl), 7.08-7.48 (7H, m, ArH), 7.78 (2H, d, J 8.7, ArH); δ_{C} (75.5 MHz, CDCl_3) 122.0 (CH, CHCl), 128.3, 128.6, 128.7, 129.11, 129.13, 129.4, 130.5, 130.9 (8 x CH, aromatic CH), 132.0 [C, aromatic C or C(2)S], 132.4, 132.5 (2 x CH, aromatic CH), 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, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{15}\text{H}_{11}\text{OS}^{35}\text{Cl}_2[\text{M}+\text{H}]^+$ 308.9908. Found 308.9917; m/z (ES⁺) 309.0 [$(\text{C}_{15}\text{H}_{10}\text{OS}^{35}\text{Cl}_2)+\text{H}^+$], 100%, 311.0 [$(\text{C}_{15}\text{H}_{10}\text{OS}^{35}\text{Cl}^{37}\text{Cl})+\text{H}^+$], 62%, 313.0 [$(\text{C}_{15}\text{H}_{10}\text{OS}^{37}\text{Cl}_2)+\text{H}^+$], 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 ^1H 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-

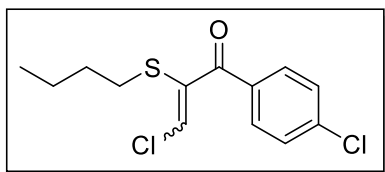
β -chloroenones **Z-4o** and **E-4o** (ratio Z:E 2.4:1) (0.319 g, 48%) as an orange oil. No further purification was carried out; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3085, 3061, 3030, 1660 (C=O), 1584, 1246, 1089, 1012, 698; δ_{H} (400 MHz, CDCl_3) 3.87 (2H, s, SCH_2 , *E* isomer), 4.00 (2H, s, SCH_2 , *Z* isomer), 6.46 (1H, s, CHCl , *E* isomer), 6.64 (1H, s, CHCl , *Z* isomer), 7.05-7.33 [7H and 5H, m, *ArH*, *Z* and *E* isomer, containing (7.30, 2H, d, *J* 8.7, *ArH*, *Z* isomer)], 7.38 (2H, d, *J* 8.6, *ArH*, *Z* isomer), 7.42 (2H, d, *J* 8.6, *ArH*, *E* isomer), 7.81 (2H, d, *J* 8.6, *ArH*, *E* isomer); HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{13}\text{OS}^{35}\text{Cl}_2[\text{M}+\text{H}^+]$ 323.0064. Found 323.0059. $^{35}\text{Cl}/^{37}\text{Cl}$ pattern visible in HRMS at 323, 325 and 327 in a 9:6:1 ratio.

^1H 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 ^1H NMR spectrum).

Z-4o: δ_{C} (100 MHz, CDCl_3): 35.7 (CH_2 , SCH_2), 127.4 (CH, 1 x aromatic CH), 128.5, 128.7, 129.3 (3 x CH signal, 6 x aromatic CH), 130.4 [CH, C(3)H], 131.1 (1 x CH signal, 2 x aromatic CH), 134.9, 137.0 (2 x C, aromatic C), 139.7 [C, C(2)S], 139.8 (C, aromatic C), 189.3 (C, CO).

Only characteristic signals for **E-4o** could be observed; δ_{C} (100 MHz, CDCl_3): 38.6 (CH_2 , SCH_2), 122.5 [CH, C(3)H], 190.6 (C, CO).

(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 ^1H 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): $\nu_{\max}/\text{cm}^{-1}$ (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,

$\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60-2.65 (2H, m, SCH_2), 6.59 (1H, s, CHCl), 7.68 (2H, d, J 8.7, ArH), 7.90 (2H, d, J 8.7, ArH); δ_{C} (75.5 MHz, CDCl_3) 13.52 (CH_3 , CHCH_3), 21.6 (CH_2 , CH_2CH_3), 31.1 (CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 33.4 (CH_2 , SCH_2), 119.7 (CH , CHCl), 129.3, 131.0 (2 x CH , aromatic CH), 132.5, 134.6, 140.7 [3 x C , 2 x aromatic C and $\text{C}(2)\text{S}$], 190.4 (C , CO). HRMS (ES^+): Exact mass calculated for $\text{C}_{13}\text{H}_{15}\text{OS}^{35}\text{Cl}_2[\text{M}+\text{H}]^+$ 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3067 (CH), 2960 (CH), 1670 (CO), 1587 (aromatic), 1092.

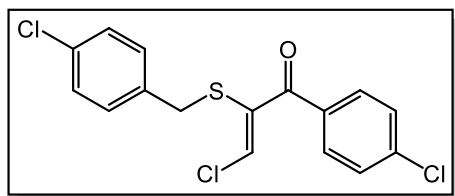
E-4p (less polar): δ_{H} (300 MHz, CDCl_3) 0.89 (3H, t, J 7.3, CH_2CH_3), 1.24-1.41 (2H, m, CH_2CH_3), 1.52-1.68 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60-2.65 (2H, m, SCH_2), 6.59 (1H, s, CHCl), 7.68 (2H, d, J 8.7, ArH), 7.90 (2H, d, J 8.7, ArH).

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_2CH_3), 1.20-1.26 (2H, m, CH_2CH_3), 1.45-1.51 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.65-2.70 (2H, m, SCH_2), 6.70 (1H, s, CHCl), 7.46 (2H, d, J 8.7, ArH), 7.86 (2H, d, J 8.7, ArH); δ_{C} (75.5 MHz, CDCl_3) 13.48 (CH_3 , CHCH_3), 21.5 (CH_2 , CH_2CH_3), 31.5 (CH_2 , SCH_2), 32.0 (CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 126.9 (CH , CHCl), 129.0, 131.2 (2 x CH , aromatic CH), 134.4, 139.8, 140.3 [3 x C , 2 x aromatic C and $\text{C}(2)\text{S}$], 189.7 (C , CO).

HRMS (ES^+): Exact mass calculated for $\text{C}_{13}\text{H}_{15}\text{OS}^{35}\text{Cl}_2[\text{M}+\text{H}]^+$ 289.0221. Found 289.0222; m/z (ES^+) 186.4 (100%).

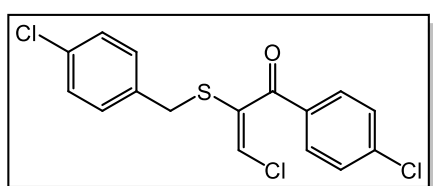
(Z)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one Z-4q and **(E)-3-Chloro-2-((4-chlorobenzyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one E-4q**



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 ^1H 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.

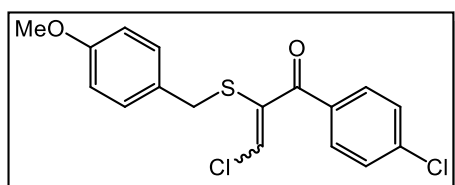
Z-4q (more polar): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3088, 3051, 1659 (C=O), 1584, 1488, 1245, 1089, 808, 737; δ_{H} (400 MHz, CDCl_3): 3.98 (2H, s, SCH_2), 6.68 (1H, s, CHCl), 7.09-7.17 (4H, m, ArH), 7.31-7.44 (4H, m, ArH); δ_{C} (100 MHz, CDCl_3): 35.1 (CH_2 , SCH_2), 128.7, 128.8, 130.6 (3 x CH signals, 6 x aromatic CH), 130.7 [CH, $\text{C}(3)\text{H}$], 131.0 (1 x CH signal, 2 x aromatic CH), 133.3, 134.7, 135.6, 139.2, 140.0 [5 x C, 4 x aromatic C and $\text{C}(2)\text{S}$], 189.2 (C, CO).



E-4q (less polar): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3066, 1665 (C=O), 1585, 1488, 1286, 1218, 1091, 1013, 836; δ_{H} (400 MHz, CDCl_3): 3.81 (2H, s, SCH_2), 6.47 (1H, s, CHCl), 7.17-7.30 (4H, m, ArH), 7.45 (2H, d, J 8.5, ArH), 7.82 (2H, d, J 8.6, ArH); δ_{C} (100 MHz, CDCl_3): 37.8 (CH_2 , SCH_2), 123.3 [CH, $\text{C}(3)\text{H}$], 128.7, 129.3, 130.5, 131.0 (4 x CH signals, 8 x aromatic CH), 132.3, 132.4, 133.4, 135.1, 140.8 [5 x C, 4 x aromatic C and $\text{C}(2)\text{S}$], 190.5 (C, CO).

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 $\text{C}_{16}\text{H}_{12}\text{OS}^{35}\text{Cl}_3[\text{M}+\text{H}^+]$ 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

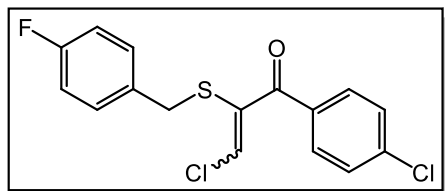


This was prepared following the procedure described above for **4a** using 1-(4-chlorophenyl)-2-((4-methoxybenzyl)thio)propan-1-one **3r** (0.642 g, 2.0 mmol), *N*-chlorosuccinimide (0.521 g, 3.9 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, OCH_3 , Z isomer), 3.79 (3H, s, OCH_3 , E isomer), 3.84 (2H, s, SCH_2 , E isomer), 3.96 (2H, s, SCH_2 , Z isomer), 6.46 (1H, s, CHCl , E isomer), 6.62 (1H, s, CHCl , Z isomer), 6.68 (2H, d, J 8.6, ArH, Z isomer), 6.81 (2H, d, J 8.7, ArH, E isomer), 7.07 (2H, d, J 8.6, ArH, Z isomer), 7.19 (2H, d, J 8.8, ArH, E isomer), 7.32 (2H, d, J 8.6, ArH, Z isomer), 7.41 (2H, d, J 8.6, ArH, Z isomer) 7.44 (2H, d, J 8.7, ArH, E isomer), 7.83 (2H, d, J 8.7, ArH, E isomer); m/z (ES+) 353.1 $[(\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}^{35}\text{Cl}_2)+\text{H}^+]$, 5%.

^1H 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 , SCH_2), 55.2 (CH_3 , OCH_3), 113.9, 128.6 (2 x CH signals, 4 x aromatic CH), 128.9 (C, aromatic C), 129.6 [CH, C(3)H], 130.5, 131.1 (2 x CH signals, 4 x aromatic CH), 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, CO).

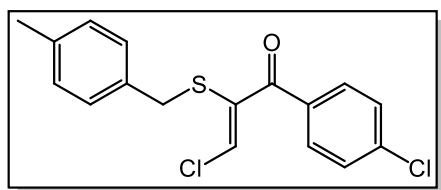
(Z)-3-Chloro-1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)prop-2-en-1-one Z-4s and (E)-3-Chloro-1-(4-chlorophenyl)-2-((4-fluorobenzyl)thio)prop-2-en-1-one E-4s



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 ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3053, 1660 (C=O), 1584, 1506, 1221, 1090, 738; δ_{H} (400 MHz, CDCl_3) 3.83 (2H, s, SCH_2 , E isomer), 3.98 (2H, s, SCH_2 , Z isomer), 6.46 (1H, s, CHCl , E isomer), 6.67 (1H, s, CHCl , Z isomer), 6.86 (2H, overlapping dd appears as t, J 8.7, ArH, Z isomer), 6.97 (2H, overlapping dd appears as t, J 8.7, ArH, E isomer), 7.14 (2H, overlapping dd, J 8.8, J_{FH} 5.3, ArH, Z isomer), 7.22-7.29 (2H, m, ArH,

E isomer), 7.32-7.38 (2H, m, ArH, *Z* isomer), 7.39-7.49 (2H and 2H, m, ArH, *Z* and *E* isomer), 7.83 (2H, d, *J* 8.8, ArH, *E* isomer); δ_{C} (100 MHz, CDCl_3): 35.0 (CH_2 , SCH_2 , *Z* isomer), 37.8 (CH_2 , SCH_2 , *E* isomer), 115.4 (1 x CH signal, 4 x CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH, *Z* and *E* isomer), 123.1 [CH, C(3)H, *E* isomer], 128.8 (1 x CH signal, 2 x aromatic CH, *Z* isomer), 129.3 (1 x CH signal, 2 x aromatic CH, *E* isomer), 130.5 [CH, C(3)H, *Z* isomer], 130.8 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 8.1, aromatic CH, *E* isomer), 130.9 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 8.2, aromatic CH, *Z* isomer), 131.0 (1 x CH signal, 2 x aromatic CH, *E* isomer), 131.1 (1 x CH signal, 2 x aromatic CH, *Z* isomer), 132.3 (C, d, $^4J_{\text{CF}}$ 3.3, aromatic C, *E* isomer), 132.8 (C, d, $^4J_{\text{CF}}$ 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, $^1J_{\text{CF}}$ 246.8, aromatic C, *Z* isomer), 162.1 (C, d, $^1J_{\text{CF}}$ 246.4, aromatic C, *E* isomer), 189.2 (C, CO, *Z* isomer), 190.5 (C, CO, *E* isomer); HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{12}\text{OFS}^{35}\text{Cl}_2[\text{M}+\text{H}^+]$ 340.9970. Found 340.9979.

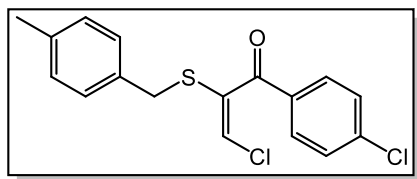
(*Z*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one *Z*-4t and (*E*)-3-Chloro-1-(4-chlorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one *E*-4t



This was prepared following the procedure described above for **4a** using 1-(4-chlorophenyl)-2-((4-methylbenzyl)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 ^1H 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): $\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3314, 3088, 3049, 2920, 2860, 1660 (C=O), 1584, 1245, 1089, 808, 737; δ_{H} (400 MHz, CDCl_3): 2.26 (3H, s, ArCH₃), 3.97 (2H, s, SCH_2), 6.62 (1H, s, CHCl), 6.92-7.11 (4H, m, ArH), 7.28-7.44 (4H, m, ArH); δ_{C} (100 MHz, CDCl_3): 21.0 (CH_3 , ArCH₃), 35.5 (CH_2 , SCH_2), 128.6, 129.21, 129.25 (3 x CH signals, 6 x aromatic CH), 129.7 [CH, C(3)H], 131.1 (1 x CH signal, 2 x aromatic CH), 133.9, 134.9, 137.2, 139.7, 139.8 [5 x C, 4 x aromatic C and

C(2)S], 189.3 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₅OS³⁵Cl₂[M+H⁺] 337.0221. Found 337.0230.

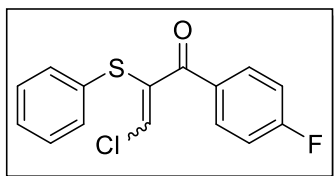


E-4t (less polar): $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3330, 3066, 3024, 2921, 1668 (C=O), 1586, 1287, 1220, 839; δ_{H} (400 MHz, CDCl₃): 2.32 (3H, s, ArCH₃), 3.84 (2H, s, SCH₂), 6.47 (1H, s, CHCl), 7.06-7.20 (4H, m, ArH), 7.41-7.48 (2H, m, ArH), 7.79-7.86

(2H, m, ArH); δ_{C} (100 MHz, CDCl₃): 21.1 (CH₃, ArCH₃), 38.3 (CH₂, SCH₂), 122.1 [CH, C(3)H], 129.1, 129.2, 129.3, 131.0 (4 x CH signals, 8 x aromatic CH), 132.6, 133.2, 133.2, 137.3, 140.6 [5 x C, 4 x aromatic C and C(2)S], 190.6 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₅OS³⁵Cl₂[M+H⁺] 337.0221. Found 337.0226; m/z (ES⁺) 337.1 [(C₁₇H₁₄OS³⁵Cl₂)+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

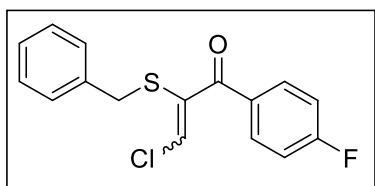
for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ¹H NMR spectroscopy this was seen to contain β -chloroenone as the major component as a mixture of *Z* and *E* isomers, **Z-4u** and **E-4u**, in a ratio of 1.3:1. The 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**; $\nu_{\max}/\text{cm}^{-1}$ (film) 3060 (CH), 1666 (CO), 1597 (aromatic), 1237.

Z-4u (more polar): δ_{H} (300 MHz, CDCl₃) 6.88 (1H, s, CHCl), 6.98-7.45 (7H, m, ArH), 7.68-7.75 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl₃) 115.5 (CH, d, ²J_{CF} 22.0, aromatic CH), 127.2 (CH, CHCl), 128.2 (CH, aromatic CH), 129.1 (CH, aromatic CH), 130.6 [C, aromatic C or C(2)S], 131.9 (CH, d, ³J_{CF} 9.5, aromatic CH), 132.5 (CH, aromatic CH), 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, CO).

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

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



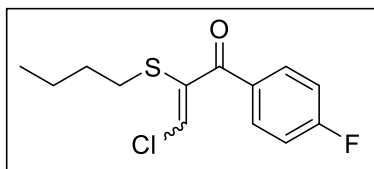
This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-(4-fluorophenyl)propan-1-one **3v** (0.53 g, 1.9 mmol), *N*-chlorosuccinimide (0.50 g, 3.8 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90 °C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. By ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, SCH_2), 6.62 (1H, s, CHCl), 6.98-7.30 (7H, m, ArH), 7.43-7.51 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 35.7 (CH_2 , SCH_2), 115.6 (CH, d, $^2J_{\text{CF}}$ 22.0, aromatic CH), 128.5, 129.3 (2 x CH, aromatic CH), 129.5 (CH, CHCl), 132.4 (CH, d, $^3J_{\text{CF}}$ 9.5, aromatic CH), 132.9 (C, d, $^4J_{\text{CF}}$ 3.1, aromatic C), 137.1, 139.7 [2 x C, aromatic C and $\text{C}(2)\text{S}$], 165.7 (C, d, $^1J_{\text{CF}}$ 255.9, aromatic C), 189.0 (C, CO).

E-4v (less polar): δ_{H} (300 MHz, CDCl_3) 3.88 (2H, s, SCH_2), 6.45 (1H, s, CHCl), 6.98-7.30 (7H, m, ArH), 7.89-7.98 (2H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 38.5 (CH_2 , SCH_2), 116.1 (CH, d, $^2J_{\text{CF}}$ 22.2, aromatic CH), 122.2 (CH, CHCl), 128.0 (CH, d, $^3J_{\text{CF}}$ 9.1, aromatic CH), 128.5, 129.2 (2 x CH, aromatic CH), 130.6 (C, d, $^4J_{\text{CF}}$ 3.0, aromatic C), 133.1, 136.4 [2 x C, aromatic C and $\text{C}(2)\text{S}$], 166.3 (C, d, $^1J_{\text{CF}}$ 256.8, aromatic C), 190.2 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{13}\text{OS}^{35}\text{ClF}[\text{M}+\text{H}]^+$ 307.0360. Found 307.0367; m/z (ES⁺) 307.1 [$(\text{C}_{16}\text{H}_{12}\text{OS}^{35}\text{ClF})+\text{H}^+$], 100%, 309.1 [$(\text{C}_{16}\text{H}_{12}\text{OS}^{37}\text{ClF})+\text{H}^+$], 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 ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 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); δ_{C} (75.5 MHz, CDCl_3) 13.54 (CH_3 , CHCH_3), 21.6 (CH_2 , CH_2CH_3), 31.1 (CH_2 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 33.3 (CH_2 , SCH_2), 116.2 (CH, d, $^2J_{\text{CF}}$ 22.2, aromatic CH), 119.5 (CH, CHCl), 130.6 (C, d, $^4J_{\text{CF}}$ 2.8 aromatic C), 132.4 (CH, d, $^3J_{\text{CF}}$ 9.6, aromatic CH), 134.5 [C, $\text{C}(2)\text{S}$], 166.4 (C, d, $^1J_{\text{CF}}$ 256.7, aromatic C), 190.2 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{13}\text{H}_{15}\text{OS}^{35}\text{ClF}[\text{M}+\text{H}]^+$ 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3071 (CH), 2960 (CH), 1668 (CO), 1597 (aromatic), 1239, 1154.

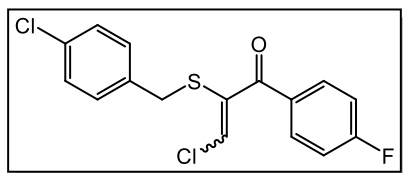
E-4w (less polar): δ_{H} (300 MHz, CDCl_3) 0.89 (3H, t, J 7.5, CH_2CH_3), 1.30-1.42 (2H, m, CH_2CH_3), 1.54-1.65 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.61-2.66 (2H, m, SCH_2), 6.60 (1H, s, CHCl), 7.12-7.20 (2H, m, ArH), 7.92-8.02 (2H, m, ArH).

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, $\text{CH}_2\text{CH}_2\text{CH}_3$), 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 , $\text{CH}_2\text{CH}_2\text{CH}_3$), 116.0 (CH, d, $^2J_{\text{CF}}$ 22.0, aromatic CH), 126.3 (CH, CHCl), 132.6 (CH, d, $^3J_{\text{CF}}$ 9.5, aromatic CH), 132.9 (C, d, $^4J_{\text{CF}}$ 3.2 aromatic C), 139.8 [C, $\text{C}(2)\text{S}$], 166.1 (C, d, $^1J_{\text{CF}}$ 256.5, aromatic C), 189.4 (C, CO).

HRMS (ES⁺): Exact mass calculated for $\text{C}_{13}\text{H}_{15}\text{OS}^{35}\text{ClF}[\text{M}+\text{H}]^+$ 273.0516. Found 273.0518; m/z (ES⁺) 273.2 [$(\text{C}_{13}\text{H}_{14}\text{OS}^{35}\text{ClF})+\text{H}^+$], 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

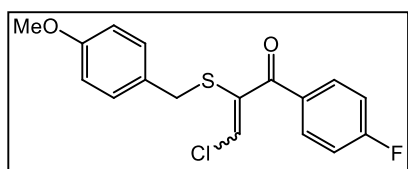
(15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^1H NMR spectrum showed the presence of two isomers (88%, *Z*:*E* 2.2:1) and the α,β -unsaturated ketone side product **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;

$\nu_{\max}/\text{cm}^{-1}$ (ATR) 3064, 1658 (C=O), 1595, 1503, 1489, 1235, 1153; δ_{H} (400 MHz, CDCl_3) 3.83 (2H, s, SCH_2 , *E* isomer), 3.97 (2H, s, SCH_2 , *Z* isomer), 6.47 (1H, s, CHCl , *E* isomer), 6.65 (1H, s, CHCl , *Z* isomer), 7.05 (2H, overlapping dd appears as t, J 8.6, *ArH*, *Z* isomer), 7.09-7.18 (2H and 6H, m, *ArH*, *Z* and *E* isomer), 7.19-7.29 (2H, m, *ArH*, *Z* isomer), 7.52 (2H, overlapping dd, J 8.9, J_{FH} 5.4, *ArH*, *Z* isomer), 7.91 (2H, overlapping dd, J 8.9, J_{FH} 5.4, *ArH*, *E* isomer); HRMS (ES⁺): Exact mass calculated for $\text{C}_{16}\text{H}_{12}\text{OFS}^{35}\text{Cl}_2[\text{M}+\text{H}^+]$ 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 , SCH_2), 115.6 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 22.0, aromatic CH), 128.6 (1 x CH signal, 2 x aromatic CH), 129.8 [CH, C(3)H], 130.6 (1 x CH signal, 2 x aromatic CH), 132.4 (1 x CH signal, 2 x CH, d, $^3J_{\text{CF}}$ 9.4, aromatic CH), 132.7 (C, d, $^4J_{\text{CF}}$ 2.9, aromatic C), 133.3, 135.6 (2 x C, aromatic C), 139.2 [C, C(2)S], 165.9 (C, d, $^1J_{\text{CF}}$ 256.5, aromatic C), 188.9 (C, CO).

Characteristic signals observed for **E-4x**: δ_{C} (75 MHz, CDCl_3): 37.8 (CH_2 , SCH_2), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{\text{CF}}$ 22.2, aromatic CH), 123.0 [CH, C(3)H], 128.7 (1 x CH signal, 2 x aromatic CH), 130.5 (1 x CH signal, 2 x aromatic CH), 133.4, 135.1 (2 x C signals, 2 x C_q), 166.4 (C, d, $^1J_{\text{CF}}$ 257.0, aromatic C), 190.1 (C, CO).

(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



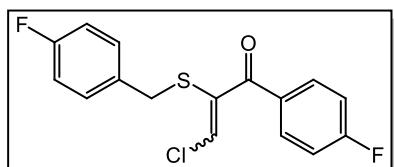
This was prepared following the procedure described above for **4a** using 1-(4-fluorophenyl)-2-((4-methoxybenzyl)thio)-propan-1-one **3y** (0.617 g, 2.0 mmol), *N*-chlorosuccinimide (0.523 g, 3.9 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. The ^1H 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; $\nu_{\max}/\text{cm}^{-1}$ (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, OCH_3 , *Z* isomer), 3.77 (3H, s, OCH_3 , *E* isomer), 3.83 (2H, s, SCH_2 , *E* isomer), 3.95 (2H, s, SCH_2 , *Z* isomer), 6.44 (1H, s, CHCl , *E* isomer), 6.60 (1H, s, CHCl , *Z* isomer), 6.67 (2H, d, J 8.6, *ArH*, *Z* isomer), 6.81 (2H, d, J

8.7, ArH, *E* isomer), 6.98-7.23 (4H and 4H, m, ArH, *Z* and *E* isomer), 7.52 (2H, overlapping dd, *J* 8.9, *J*_{FH} 5.4, ArH, *Z* isomer), 7.92 (2H, overlapping dd, *J* 8.9, *J*_{FH} 5.4, ArH, *E* isomer); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₅O₂FS³⁵Cl[M+H⁺] 337.0465. Found 337.0452.

¹H and ¹³C 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 ¹H NMR spectrum); **Z-4y**: δ_C (100 MHz, CDCl₃): 35.2 (CH₂, SCH₂), 55.25 (CH₃, OCH₃), 113.8 (1 x CH signal, 2 x aromatic CH), 115.5 (1 x CH signal, 2 x CH, d, ²*J*_{CF} 22.0, aromatic CH), 128.94 (C, aromatic C), 128.97 [CH, C(3)H], 130.5 (2 x CH, aromatic CH), 132.5 (2 x CH, d, ³*J*_{CF} 9.4, aromatic CH), 132.8 (C, d, ⁴*J*_{CF} 3.1, aromatic C), 139.8 [C, C(2)S], 158.9 (C, aromatic C), 165.8 (C, d, ¹*J*_{CF} 256.4, aromatic C), 189.0 (C, CO).

Characteristic signals observed for **E-4y**: δ_C (100 MHz, CDCl₃): 38.1 (CH₂, SCH₂), 55.27 (CH₃, OCH₃), 113.9 (1 x CH signal, 2 x aromatic CH), 116.1 (1 x CH signal, 2 x CH, d, ²*J*_{CF} 21.9, aromatic CH), 122.0 [CH, C(3)H], 128.3 (C, aromatic C), 130.3 (1 x CH signal, 2 x aromatic CH), 132.4 (2 x CH, d, ³*J*_{CF} 9.8, aromatic CH), 159.0 (C, aromatic C), 190.8 (C, CO).

(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

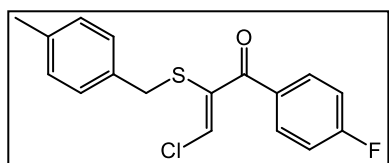


This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-(4-fluorophenyl)propan-1-one **3z** (0.584 g, 2.0 mmol), *N*-chlorosuccinimide (0.521 g, 3.9 mmol, 1.95 eq) and toluene

(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 ¹H 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, CDCl₃) 3.84 (2H, s, SCH₂, *E* isomer), 3.97 (2H, s, SCH₂, *Z* isomer), 6.46 (1H, s, CHCl, *E* isomer), 6.65 (1H, s, CHCl, *Z* isomer), 6.85 (2H, overlapping dd appears as t, *J* 8.6, ArH, *Z* isomer), 6.96 (2H, overlapping dd appears as t, *J* 8.6, ArH, *E* isomer), 7.05 (2H, overlapping dd

appears as t, J 8.6, ArH, *Z* isomer), 7.10-7.19 (2H and 2H, m, ArH, *Z* and *E* isomer), 7.21-7.30 (2H, m, ArH, *E* isomer), 7.55 (2H, overlapping dd, J 8.7, J_{FH} 5.4, ArH, *Z* isomer), 7.92 (2H, overlapping dd, J 8.8, J_{FH} 5.4, ArH, *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 CH, *Z* isomer), 115.44 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.5, aromatic CH, *E* isomer), 115.7 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic CH, *Z* isomer), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.1, aromatic CH, *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 CH, *E* isomer), 130.9 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic CH, *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 CH, *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, CO, *Z* isomer), 190.2 (C, CO, *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%.

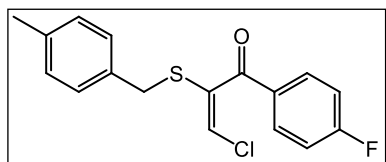
(*Z*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one *Z*-4aa and (*E*)-3-Chloro-1-(4-fluorophenyl)-2-((4-methylbenzyl)thio)prop-2-en-1-one *E*-4aa



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 1H 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, ArCH₃), 3.97 (2H, s, SCH_2), 6.61 (1H, s, CHCl), 6.92-7.11

(6H, m, ArH), 7.50 (2H, overlapping dd, J 8.6, J_{FH} 5.4, ArH); δ_C (100 MHz, $CDCl_3$): 21.0 (CH_3 , Ar CH_3), 35.5 (CH_2 , SCH_2), 115.4 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.0, aromatic CH), 129.0 [CH, C(3)H], 129.1, 129.2 (2 x CH signals, 4 x aromatic CH), 132.5 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.4, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for $C_{17}H_{15}OFS^{35}Cl$ [M+H⁺] 321.0516. Found 321.0514.

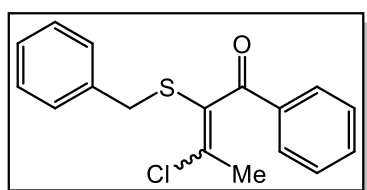


E-4aa (less polar): ν_{max}/cm^{-1} (ATR) 3072, 3024, 2921, 1660 (C=O), 1594, 1503, 1286, 1233, 1154; δ_H (400 MHz, $CDCl_3$): 2.32 (3H, s, Ar CH_3), 3.85 (2H, s, SCH_2), 6.46 (1H, s, $CHCl$), 7.05-

7.21 (6H, m, ArH), 7.92 (2H, overlapping dd, J 8.7, J_{FH} 5.4, ArH); δ_C (100 MHz, $CDCl_3$): 21.1 (CH_3 , Ar CH_3), 38.3 (CH_2 , SCH_2), 116.1 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.1, aromatic CH), 121.8 [CH, C(3)H], 129.0, 129.2 (2 x CH signals, 4 x aromatic CH), 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 CH), 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, CO); 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 -Sulphenyl- 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**

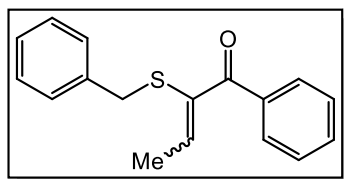


This was prepared following the procedure described above for **4a** using 2-(benzylthio)-1-phenylbutan-1-one **3bb** (which contained 7% disulfide **S38**²⁰) (1.40 g, 5.2 mmol), *N*-chlorosuccinimide (1.35 g, 10.1 mmol, 1.95 eq) and toluene (25

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. ¹H 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**

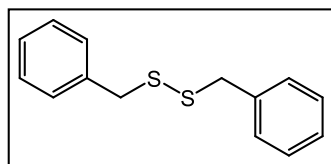
and **E-4bb** in a ratio of 1:1.6; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3084, 3061, 3029, 2918, 1661 (C=O), 1595, 1579, 1242, 690; δ_{H} (300 MHz, CDCl_3): 2.07 [6H, s, C(4) H_3 , *E* and *Z* isomer], 3.79 (2H, s, SCH_2 , *Z* isomer), 3.82 (2H, s, SCH_2 , *E* isomer), 7.12-7.34 (5H and 5H, m, *ArH*, *E* and *Z* isomer), 7.41-7.51 (2H and 2H, m, *ArH*, *E* and *Z* isomer), 7.54-7.63 (1H and 1H, m, *ArH*, *E* and *Z* isomer), 7.86-7.95 (2H and 2H, m, *ArH*, *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 , SCH_2 , *Z* isomer), 39.1 (CH_2 , SCH_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 CH, *E* and *Z* isomer), 130.1 [C, C(2)*S*, *Z* isomer], 133.7 (CH, aromatic CH, *E* isomer), 134.0 (CH, aromatic CH, *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, CO, *E* isomer), 192.2 (C, CO, *Z* isomer); HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{16}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 303.0610. Found 303.0599; m/z (ES⁺) 303.1 [($\text{C}_{17}\text{H}_{15}\text{OS}^{35}\text{Cl}$)+ H^+], 100%, 305.1 [($\text{C}_{17}\text{H}_{15}\text{OS}^{37}\text{Cl}$)+ H^+], 42%.

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



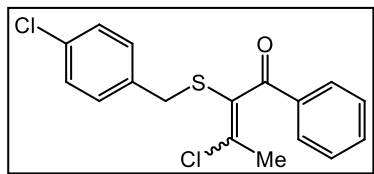
(More polar than **4bb**): orange oil (86mg, 6%); $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3082, 3060, 3028, 2909, 1654 (C=O), 1595, 1257, 694; δ_{H} (300 MHz, CDCl_3): 1.89 [3H, d, *J* 6.9, C(4) H_3], 3.93 (2H, s, SCH_2), 6.47 [1H, q, *J* 6.9, C(3)*H*], 7.18 (5H, s, *ArH*), 7.28-7.38 (2H, m, *ArH*), 7.41-7.52 (3H, m, *ArH*); δ_{C} (75 MHz, CDCl_3): 16.1 [CH_3 , C(4) H_3], 36.4 (CH_2 , SCH_2), 127.0, 128.0, 128.4, 129.2, 129.6, 132.1 (6 x CH signals, 10 x aromatic CH), 136.8 [C, C(2)*S*], 137.8, 138.1 (2 x C, aromatic C), 144.9 [CH, C(3)*H*], 194.0 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{17}\text{OS}[\text{M}+\text{H}^+]$ 269.1000. Found 269.0995; m/z (ES⁺) 269.2 [($\text{C}_{17}\text{H}_{16}\text{OS}$)+ H^+], 100%.

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



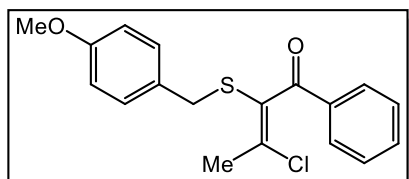
Characteristic signals due to **S38**²⁰: δ_{H} (400 MHz, CDCl_3): 3.59 (4H, s, SCH_2).

(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



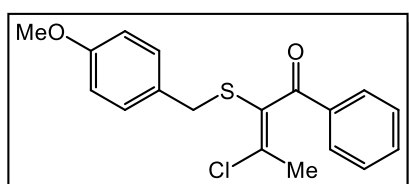
This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-phenylbutan-1-one **3cc** (0.574 g, 1.9 mmol), *N*-chlorosuccinimide (0.491 g, 3.7 mmol, 1.95 eq) and toluene (15 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a yellow/green oil. ¹H 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, CDCl₃): 2.06 [CH₃, C(4)H₃, *Z* isomer], 2.08 [CH₃, C(4)H₃, *E* isomer], 3.75 (2H, s, SCH₂, *Z* isomer), 3.78 (2H, s, SCH₂, *E* isomer), 7.15 (4H, s, ArH, *Z* isomer), 7.26 (4H, s, ArH, *E* isomer), 7.41-7.51 (2H and 2H, m, ArH, *E* and *Z* isomer), 7.57-7.63 (1H and 1H, m, ArH, *E* and *Z* isomer), 7.83-7.93 (2H and 2H, m, ArH, *E* and *Z* isomer); δ_C (100 MHz, CDCl₃): 22.8 [CH₃, C(4)H₃, *E* isomer], 24.8 [CH₃, C(4)H₃, *Z* isomer], 36.6 (CH₂, SCH₂, *Z* isomer), 38.3 (CH₂, SCH₂, *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 CH, *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 CH, *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 CH, *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, CO, *E* and *Z* isomer); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₅OS³⁵Cl₂[M+H⁺] 337.0221. Found 337.0222; *m/z* (ES⁺) 337.1 [(C₁₇H₁₄OS³⁵Cl₂)+H⁺], 100%, 339.1 [(C₁₇H₁₄OS³⁵Cl³⁷Cl)+H⁺], 76%. ³⁵Cl/³⁷Cl 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. ¹H 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.

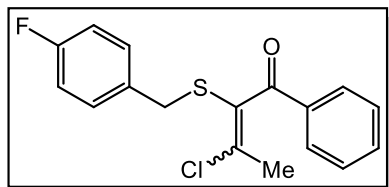
E-4dd (less polar): ν_{max}/cm⁻¹ (ATR) 2954, 2932, 2835, 1661 (C=O), 1608, 1510, 1239, 1174, 1032, 691; δ_H (400 MHz, CDCl₃): 2.10 [3H, s, C(4)H₃], 3.79 (5H, s, OCH₃ and SCH₂), 6.81 (2H, d, *J* 8.7, ArH), 7.23 (2H, d, *J* 8.6, ArH), 7.42-7.52 (2H, m, ArH), 7.54-7.63 (1H, m, ArH), 7.89-7.96 (2H, m, ArH); δ_C (100 MHz, CDCl₃): 22.9 [CH₃, C(4)H₃], 38.6 (CH₂, SCH₂), 55.3 (CH₃, OCH₃), 113.8 (1 x CH signal, 2 x CH, aromatic CH), 126.4 [C, C(2)S], 128.7 (1 x CH signal, 2 x aromatic CH), 129.0 (C, aromatic C), 129.6, 130.4, 133.7 (3 x CH signals, 5 x aromatic CH), 134.4 (C, aromatic C), 137.3 [C, C(3)Cl], 158.9 (C, aromatic C), 192.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₈H₁₈O₂SCl[M+H⁺] 333.0716. Found 333.0709; m/z (ES⁺) 333.2[(C₁₈H₁₇O₂S³⁵Cl)+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, CDCl₃): 2.06 [3H, s, C(4)H₃], 3.73 (3H, s, OCH₃), 3.75 (2H, s, SCH₂), 6.72 (2H, d, *J* 8.7, ArH), 7.11 (2H, d, *J* 8.6, ArH), 7.37-7.67 (3H, m, ArH), 7.86-8.05 (2H, m, ArH); δ_C (75 MHz, CDCl₃): 24.6 [CH₃, C(4)H₃], 36.8 (CH₂, SCH₂), 55.2 (CH₃, OCH₃), 113.8 (1 x CH signal, 2 x aromatic CH), 128.3 (C, C_q), 128.8, 129.6, 130.2 (3 x CH signals, 6 x aromatic CH), 133.8 (C, C_q), 134.0 (CH, aromatic CH), 134.1, 135.5 (2 x C, C_q), 158.9 (C, aromatic C), 192.2 (C, CO)

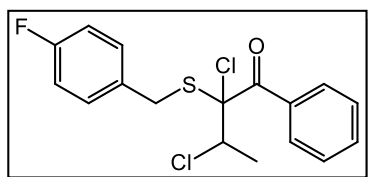
Relative stereochemistry was assigned for **4dd** by NOESY experiments.

(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



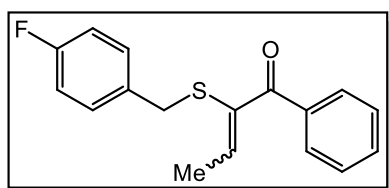
This was prepared following the procedure described above for **4a** using 2-((4-fluorobenzyl)thio)-1-phenylbutan-1-one **3ee** (0.389 g, 1.3 mmol), *N*-chlorosuccinimide (0.333 g, 2.5 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as a green/yellow oil. ¹H 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, CDCl₃): 2.06 [3H, s, C(4)H₃, *Z* isomer], 2.09 [3H, s, C(4)H₃, *E* isomer], 3.76 (2H, s, SCH₂, *Z* isomer), 3.80 (2H, s, SCH₂, *E* isomer), 6.88 (2H, overlapping dd appears as t, *J* 8.7, ArH, *Z* isomer), 6.97 (2H, overlapping dd appears as t, *J* 8.7, ArH, *E* isomer), 7.17 (2H, dd, *J* 8.6, *J*_{FH} 5.4, ArH, *Z* isomer), 7.29 (2H, dd, *J* 8.6, *J*_{FH} 5.4, ArH, *E* isomer), 7.40-7.53 (2H and 2H, m, ArH, *E* and *Z* isomer), 7.56-7.65 (1H and 1H, m, ArH, *E* and *Z* isomer), 7.83-7.96 (2H and 2H, m, ArH, *E* and *Z* isomer); δ_C (100 MHz, CDCl₃): 22.8 [CH₃, C(4)H₃, *E* isomer], 24.7 [CH₃, C(4)H₃, *Z* isomer], 36.6 (CH₂, SCH₂, *Z* isomer), 38.3 (CH₂, SCH₂, *E* isomer), 115.2 (1 x CH signal, 2 x CH, d, ²J_{CF} 21.6, aromatic CH, *Z* isomer), 115.3 (1 x CH signal, 2 x CH, d, ²J_{CF} 21.5, aromatic CH, *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 CH, *E* and *Z* isomer] and [C(2)S, *Z* isomer]), 130.7 (1 x CH signal, 2 x CH, d, ³J_{CF} 8.2, aromatic CH, *Z* isomer), 130.8 (1 x CH signal, 2 x CH, d, ³J_{CF} 8.1, aromatic CH, *E* isomer), 132.3 (C, d, ⁴J_{CF} 3.0, aromatic C, *Z* isomer), 132.9 (C, d, ⁴J_{CF} 3.2, aromatic C, *E* isomer), 133.8, 134.1 (2 x CH, aromatic CH, *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, ¹J_{CF} 245.9, aromatic C, *Z* isomer), 162.1 (C, d, ¹J_{CF} 246.2, aromatic C, *E* isomer), 191.9, 192.1 (2 x C, CO, *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, SCH_2), 4.78 [1H, q, J 6.5, C(3) H], 8.07 (2H, d, J 7.2, ArH); δ_C (100 MHz, $CDCl_3$): 20.0 [CH_3 , C(4) H_3], 36.3 (CH_2 , SCH_2), 59.5 [CH, C(3) H], 115.7 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.7, aromatic CH).

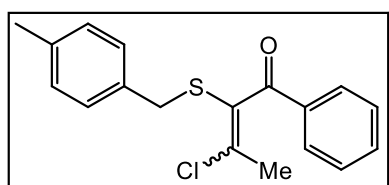
2-((4-Fluorobenzyl)thio)-1-phenylbut-2-en-1-one S43



(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, SCH_2), 6.50 [1H, q, J 6.9, C(3) H], 6.89 (2H, overlapping dd appears as t, J 8.7, ArH), 7.16 (2H, overlapping dd, J 8.6, J_{FH} 5.4, ArH), 7.36 (2H, t, J 7.6, ArH), 7.42-7.55 (3H, m, ArH); δ_C (100 MHz, $CDCl_3$): 16.1 [CH_3 , C(4) H_3], 35.6 (CH_2 , SCH_2), 115.2 (1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.4, aromatic CH), 128.1, 129.6 (2 x CH signals, 4 x aromatic CH), 130.7 (1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.1, aromatic CH), 132.2 (CH, aromatic CH), 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, CO); 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.

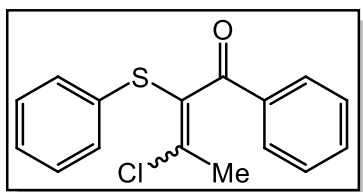
(Z)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylbut-2-en-1-one Z-4ff and (E)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylbut-2-en-1-one E-4ff



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. 1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, Ar CH_3 , *Z* isomer), 2.32 (3H, s, Ar CH_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 CH_3 , *Z* isomer), 21.2 (CH_3 , Ar CH_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 , SCH_2 , *Z* isomer), 38.8 (CH_2 , SCH_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 CH, *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 CH, *E* isomer) and (1 x C_q , *E* or *Z* isomer)], 133.8 (C, C_q , *E* or *Z* isomer), 134.0 (CH, aromatic CH, *Z* isomer), 134.4, 135.5, 137.0, 137.1, 137.2 (5 x C, C_q , *E* and *Z* isomer), 192.1 (C, CO, *E* isomer), 192.2 (C, CO, *Z* isomer); HRMS (ES⁺): Exact mass calculated for $\text{C}_{18}\text{H}_{18}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 317.0767. Found 317.0758; m/z (ES⁺) 317.1 [($\text{C}_{18}\text{H}_{17}\text{OS}^{35}\text{Cl}$)+ H^+], 20%, 319.1 [($\text{C}_{18}\text{H}_{17}\text{OS}^{37}\text{Cl}$)+ H^+], 10%. $^{35}\text{Cl}/^{37}\text{Cl}$ pattern visible at 317 and 319 in a 3:1 ratio.

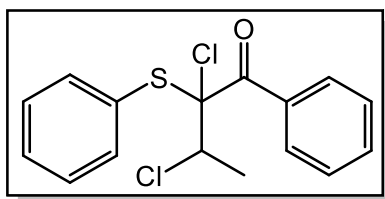
(*Z*)-3-Chloro-1-phenyl-2-(phenylthio)but-2-en-1-one **Z-4gg and (*E*)-3-Chloro-1-phenyl-2-(phenylthio)but-2-en-1-one **E-4gg****



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. ^1H 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

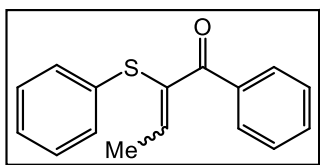
mixture of *Z* and *E* isomers **Z-4gg** and **E-4gg** in a ratio of 1:1.2; $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3059, 1665 (C=O), 1595, 1579, 1448, 1439, 1240, 1132, 740, 687; δ_{H} (400 MHz, CDCl_3): 2.22 [3H, s, C(4) H_3 , minor], 2.57 [3H, s, C(4) H_3 , major], 7.07-7.64 (8H and 8H, m, ArH, major and minor), 7.70 (2H, d, J 7.3, ArH, minor) 7.80 (2H, d, J 7.2, ArH, 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 CH, 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, CO, major and minor);



Characteristic signals due to the dichloride **S48a** (assigned from ^1H 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

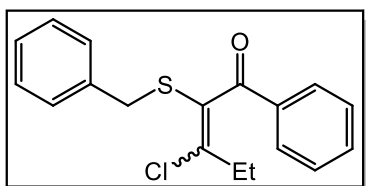


S47a: (more polar): yellow oil (47 mg, 9%); $\nu_{\max}/\text{cm}^{-1}$ (ATR) 3058, 1660 (C=O), 1596, 1579, 1476, 1446, 1253, 1024, 687; δ_{H} (400 MHz, CDCl_3): 2.13 [3H, d, J 6.9, C(4) H_3], 6.83 [1H, q, J 6.9, C(3) H], 7.07-7.60 (8H, m, ArH), 7.69 (2H, d, J 7.6, ArH); δ_{C} (100 MHz, CDCl_3): 16.5 [CH_3 , C(4) H_3], 126.6, 128.1, 128.9, 129.3, 129.7, 132.3 (6 x CH signals, 10 aromatic CH), 134.2, 136.8, 137.3 (3 x C, C_q), 144.7 [CH, C(3) H], 194.1 (C, CO). *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 -Sulphenyl- β -Chloropentenones

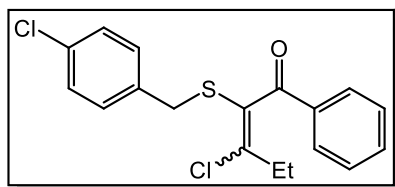
(*Z*)-2-(Benzylthio)-3-chloro-1-phenylpent-2-en-1-one **Z-4hh** and (*E*)-2-(Benzylthio)-3-chloro-1-phenylpent-2-en-1-one **E-4hh**



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. ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArH, *E* and *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), 7.92 (2H and 2H, d, *J* 7.6, ArH, *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 , SCH_2 , *Z* isomer), 39.0 (CH_2 , SCH_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 CH, *E* and *Z* isomer), 129.4 [C, C_q , *Z* isomer], 129.6, 133.7, 134.1 (3 x CH signals, 6 x aromatic CH, *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, CO, *E* isomer), 192.0 (C, CO, *Z* isomer); HRMS (ES $^+$): Exact mass calculated for $\text{C}_{18}\text{H}_{18}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 317.0767. Found 317.0670; *m/z* (ES $^+$) 317.1 [$(\text{C}_{18}\text{H}_{18}\text{OS}^{35}\text{Cl})+\text{H}^+$], 100%, 319.1 [$(\text{C}_{18}\text{H}_{18}\text{OS}^{37}\text{Cl})+\text{H}^+$], 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



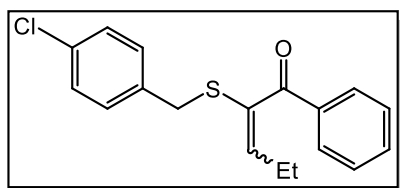
This was prepared following the procedure described above for **4a** using 2-((4-chlorobenzyl)thio)-1-phenylpentan-1-one **3ii** (0.524 g, 1.6 mmol), N-chlorosuccinimide (0.427 g, 3.2 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture

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. ^1H 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; $\nu_{\max}/\text{cm}^{-1}$ (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)H₃, E isomer], 1.04 [3H, t, J 7.3, C(5)H₃, Z isomer], 2.29 [2H, q, J 7.3, C(4)H₂, Z isomer], 2.51 [2H, q, J 7.4, C(4)H₂, E isomer], 3.74 (2H, s, SCH₂, Z isomer), 3.77 (2H, s, SCH₂, 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 [CH₃, C(5)H₃, E isomer], 12.5 [CH₃, C(5)H₃, Z isomer], 28.9 [CH₂, C(4)H₂, E isomer], 31.2 [CH₂, C(4)H₂, Z isomer], 36.6 (CH₂, SCH₂, Z isomer), 38.1 (CH₂, SCH₂, 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 C₁₈H₁₇OS³⁵Cl₂[M+H⁺] 351.0377. Found 351.0367; m/z (ES⁺) 351.1 [(C₁₈H₁₇OS³⁵Cl₂)+H⁺], 100%, 353.1 [(C₁₈H₁₇OS³⁵Cl³⁷Cl)+H⁺], 70%.

Relative stereochemistry assigned for 4ii by a NOESY experiment.

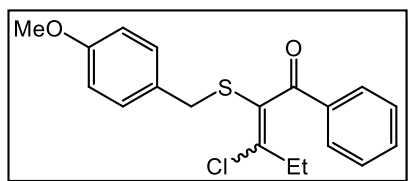
2-((4-Chlorobenzyl)thio)-1-phenylpent-2-en-1-one S50



(More polar): orange oil (28 mg, 5%); $\nu_{\max}/\text{cm}^{-1}$ (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)H₃], 2.36 [2H, dq appears as quintet, J 7.5, C(4)H₂], 3.89 (2H, s, SCH₂), 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 [CH₃, C(5)H₃], 23.8 [CH₂, C(4)H₂], 35.7 (CH₂, SCH₂), 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).

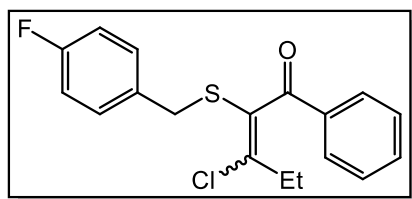
E/Z stereochemistry not assigned but only one isomer present.

(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. ¹H 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, CDCl₃): 0.99 [3H, t, *J* 7.4, C(5)H₃, *E* isomer], 1.05 [3H, t, *J* 7.3, C(5)H₃, *Z* isomer], 2.30 [2H, q, *J* 7.3, C(4)H₂, *Z* isomer], 2.54 [2H, q, *J* 7.4, C(4)H₂, *E* isomer], 3.74 (2H, s, SCH₂, *Z* isomer), 3.75 (3H, s, OCH₃, *Z* isomer), 3.78 (2H, s, SCH₂, *E* isomer), 3.78 (3H, s, OCH₃, *E* isomer), 6.73 (2H, d, *J* 8.5, ArH, *Z* isomer), 6.81 (2H, d, *J* 8.5, ArH, *E* isomer), 7.12 (2H, d, *J* 8.5, ArH, *Z* isomer), 7.24 (2H, d, *J* 8.6, ArH, *E* isomer), 7.44-7.51 (2H and 2H, m, ArH, *E* and *Z* isomer), 7.56-7.63 (1H and 1H, m, ArH, *E* and *Z* isomer), 7.92 (2H and 2H, d, *J* 7.9, ArH, *E* and *Z* isomer); δ_C (100 MHz, CDCl₃): 11.9 [CH₃, C(5)H₃, *E* isomer], 12.5 [CH₃, C(5)H₃, *Z* isomer], 28.9 [CH₂, C(4)H₂, *E* isomer], 31.1 [CH₂, C(4)H₂, *Z* isomer], 36.7 (CH₂, SCH₂, *Z* isomer), 38.4 (CH₂, SCH₂, *E* isomer), 55.2 (CH₃, OCH₃, *Z* isomer), 55.3 (CH₃, OCH₃, *E* isomer), 113.8 (1 x CH signal, 4 x aromatic CH, *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 CH, *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 CH, *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, CO, *E* isomer), 192.1 (C, CO, *Z* isomer); HRMS (ES⁺): Exact mass calculated for C₁₉H₂₀O₂S³⁵Cl [M+H⁺] 347.0873. Found 347.0866.

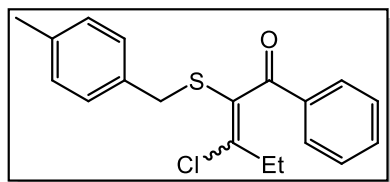
(Z)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylpent-2-en-1-one Z-4kk and (E)-3-Chloro-2-((4-fluorobenzyl)thio)-1-phenylpent-2-en-1-one E-4kk



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. ¹H 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, CDCl₃): 0.97 [3H, t, *J* 7.4, C(5)H₃, *E* isomer], 1.04 [3H, t, *J* 7.3, C(5)H₃, *Z* isomer], 2.29 [2H, q, *J* 7.3, C(4)H₂, *Z* isomer], 2.51 [2H, q, *J* 7.4, C(4)H₂, *E* isomer], 3.75 (2H, s, SCH₂, *Z* isomer), 3.78 (2H, s, SCH₂, *E* isomer), 6.88 (2H, t, *J* 8.7, ArH, *Z* isomer), 6.96 (2H, t, *J* 8.7, ArH, *E* isomer), 7.16-7.21 (2H, m, ArH, *Z* isomer), 7.28-7.33 (2H, m, ArH, *E* 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), 7.88-7.93 (2H and 2H, m, ArH, *E* and *Z* isomer); δ_C (100 MHz, CDCl₃): 11.9 [CH₃, C(5)H₃, *E* isomer], 12.5 [CH₃, C(5)H₃, *Z* isomer], 28.9 [CH₂, C(4)H₂, *E* isomer], 31.2 [CH₂, C(4)H₂, *Z* isomer], 36.6 (CH₂, SCH₂, *Z* isomer), 38.1 (CH₂, SCH₂, *E* isomer), 115.2 (1 x CH signal, 2 x CH, d, ²J_{CF} 21.5, aromatic CH, *Z* isomer), 115.3 (1 x CH signal, 2 x CH, d, ²J_{CF} 21.4, aromatic CH, *E* isomer), 125.0 [C, C(2)S, *E* isomer], 128.8 (1 x CH signal, 4 x CH, aromatic CH, *E* and *Z* isomer), 128.9 [C, C(2)S, *Z* isomer], 129.6 (1 x CH signal, 4 x CH, aromatic CH, *E* and *Z* isomer), 130.8 (1 x CH signal, 2 x CH, d, ³J_{CF} 9.1, aromatic CH, *Z* isomer), 130.9 (1 x CH signal, 2 x CH, d, ³J_{CF} 8.3, aromatic CH, *E* isomer), 132.2 (C, d, ⁴J_{CF} 3.2, aromatic C, *Z* isomer), 133.1 (C, d, ⁴J_{CF} 3.2, aromatic C, *E* isomer), 133.7, 134.1 (2 x CH, aromatic CH, *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, ¹J_{CF} 246.1, aromatic C, *Z* isomer), 162.1 (C, d, ¹J_{CF} 246.1, aromatic C, *E* isomer), 191.5 (C, CO, *E* isomer), 191.9 (C, CO, *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-4II and (E)-3-Chloro-2-((4-methylbenzyl)thio)-1-phenylpent-2-en-1-one E-4II



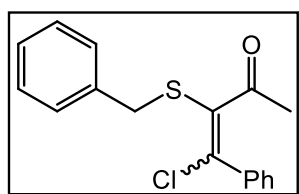
This was prepared following the procedure described above for **4a** using 2-((4-methylbenzyl)thio)-1-phenylpentan-1-one **3II** (0.73 g, 2.4 mmol), *N*-chlorosuccinimide (0.637 g, 4.7 mmol, 1.95 eq) and toluene (10 mL). The reaction mixture was heated at 90°C for 16 h. Following filtration and evaporation of the solvent at reduced pressure, the crude product was obtained as an orange oil. 1H NMR spectroscopy showed this product to contain 86% 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 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-4II** and **E-4II** 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, ArH, *Z* isomer), 7.08 (2H and 2H, d, *J* 6.3, ArH, *E* and *Z* isomer), 7.19 (2H, d, *J* 8.0, ArH, *E* isomer), 7.43-7.51 (2H and 2H, m, ArH, *E* and *Z* isomer), 7.56-7.63 (1H and 1H, m, ArH, *E* and *Z* isomer), 7.92 (2H and 2H, d, *J* 8.3, ArH, *E* and *Z* isomer); δ_C (100 MHz, $CDCl_3$): 11.9 [CH $_3$, C(5) H_3 , *E* isomer], 12.6 [CH $_3$, C(5) H_3 , *Z* isomer], 21.1 (1 x CH $_3$ signal, 2 x ArCH $_3$, *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 $_2$, SCH $_2$, *Z* isomer), 38.7 (CH $_2$, SCH $_2$, *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 CH, *E* and *Z* isomer) and [C, C(2)S, *Z* isomer]), 133.1 (C, aromatic C, *Z* isomer), 133.7 (CH, aromatic CH, *E* isomer), 133.9 (C, aromatic C, *E* isomer), 134.0 (CH, aromatic CH, *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, CO, *E* isomer), 192.1 (C, CO, *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. ^1H 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**.

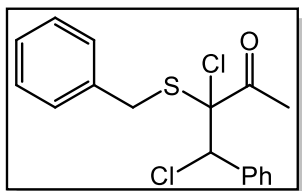
(Z)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one Z-13a and (E)-3-(Benzylthio)-4-chloro-4-phenylbut-3-en-2-one E-13a



$\nu_{\text{max}}/\text{cm}^{-1}$ (ATR) 3060, 3029, 2921, 1691 (C=O), 1351, 1234, 1190, 745, 693; δ_{H} (400 MHz, CDCl_3): 1.63 (3H, s, CH_3 , *Z* isomer), 2.47 (3H, s, CH_3 , *E* isomer), 3.74 (2H, s, SCH_2 , *E* isomer), 3.99 (2H, s, SCH_2 , *Z* isomer), 7.12 (2H, d, *J* 7.9, *E* isomer), 7.17-7.42 (10H and 8H, m, ArH, *Z* and *E* isomer); δ_{C} (100 MHz, CDCl_3): 28.8 [CH_3 , $\text{C}(\text{O})\text{CH}_3$, *E* isomer], 30.5 [CH_3 , $\text{C}(\text{O})\text{CH}_3$, *Z* isomer], 36.9 (CH_2 , SCH_2 , *Z* isomer), 38.5 (CH_2 , SCH_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 CH, *Z* and *E* isomer), 131.1 [C, $\text{C}(3)\text{S}$, *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, CO, *Z* isomer), 199.3 (C, CO, *E* isomer); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₆OS³⁵Cl[M+H⁺] 303.0610. Found 303.0595; *m/z* (ES⁺) 303.2 [(C₁₇H₁₅OS³⁵Cl)+H⁺], 30%.

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



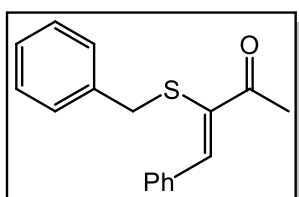
$\nu_{\max}/\text{cm}^{-1}$ (ATR) 3061, 3029, 2967, 2923, 1693 (C=O), 1494, 1453, 1352, 1234, 1191, 746, 694; δ_{H} (400 MHz, CDCl₃): 2.26 (3H, s, CH₃, minor), 2.58 (3H, s, CH₃, major), 3.31 (1H, A of AB system, *J*_{AB} 11.5, one of SCH₂, major), 3.59 (1H, B of AB system, *J*_{AB} 11.5, one of SCH₂,

major), 3.85 (1H, A of AB system, *J*_{AB} 11.3, one of SCH₂, minor), 3.91 (1H, B of AB system, *J*_{AB} 11.4, one of SCH₂, minor), 5.64 [1H, s, C(4)HCl, major], 5.66 [1H, s, C(4)HCl, minor], 7.06-7.47 (8H and 8H, m, ArH, major and minor), 7.48-7.56 (2H, m, ArH, minor), 7.59-7.70 (2H, m, ArH, major); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₇OS³⁵Cl₂[M+H⁺] 339.0377. Found 339.0392; *m/z* (ES⁺) 341.1 [(C₁₇H₁₆OS³⁷Cl₂)+H⁺], 50%.

¹H and ¹³C 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 **E-13a** (16%). None of the dichloride **12b** remained in this sample; **12a**: δ_{H} (400 MHz, CDCl₃): 2.58 (3H, s, CH₃), 3.31 (1H, A of AB system, *J*_{AB} 11.5, one of SCH₂), 3.59 (1H, B of AB system, *J*_{AB} 11.5, one of SCH₂), 5.64 [1H, s, C(4)HCl], 7.06-7.56 (8H, m, ArH), 7.58-7.70 (2H, m, ArH); δ_{C} (100 MHz, CDCl₃): 26.0 [CH₃, C(O)CH₃], 36.2 (CH₂, SCH₂), 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 CH), 134.3, 134.9 (2 x C, C_q), 197.8 (C, CO).

Characteristic peaks for **Z-13a** and **E-13a** (*Z*:*E* 2:1): δ_{H} (400 MHz, CDCl₃): 1.63 (3H, s, CH₃, *Z* isomer), 2.47 (3H, s, CH₃, *E* isomer), 3.74 (2H, s, SCH₂, *E* isomer), 3.99 (2H, s, SCH₂, *Z* isomer); δ_{C} (100 MHz, CDCl₃): 28.8 [CH₃, C(O)CH₃, *E* isomer], 30.5 [CH₃, C(O)CH₃, *Z* isomer], 36.9 (CH₂, SCH₂, *Z* isomer), 38.5 (CH₂, SCH₂, *E* isomer), 199.2 (C, CO, *Z* isomer), 199.3 (C, CO, *E* isomer).

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



$\nu_{\max}/\text{cm}^{-1}$ (ATR) 3060, 3027, 2922, 1673 (C=O), 1219, 1203, 1179, 754, 690; δ_{H} (400 MHz, CDCl₃): 2.36 (3H, s, CH₃), 3.91 (2H, s, SCH₂), 7.11-7.25 (5H, m, ArH), 7.34-7.42 (3H, m, ArH), 7.63 [1H, s, C(4)H],

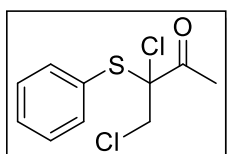
7.72 (2H, d, J 7.9, ArH); δ_c (100 MHz, $CDCl_3$): 27.3 [CH_3 , $C(O)CH_3$], 38.0 (CH_2 , SCH_2), 127.1, 128.3, 128.4, 129.1, 129.6, 130.7 (6 x CH signals, 10 x aromatic CH), 134.6, 135.3, 137.4 [3 x C, 2 x aromatic C and $C(2)S$], 143.2 [CH , $C(4)H$], 198.1 (C, CO); HRMS (ES+): Exact mass calculated 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

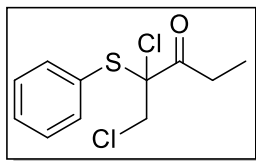
**Note* Commercially available un-recrystallised N -chlorosuccinimide was used throughout the reactions in this section. It was determined that recrystallised NCS had no impact on the efficiency or outcome of the reactions and so recrystallisation was deemed an unnecessary step.*¹⁸

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 -chlorosuccinimide 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 1H 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, ArH); δ_c (75.5 MHz, $CDCl_3$) 25.2 (CH_3 , CH_3), 48.4 (CH_2 , CH_2Cl), 80.9 [C, $C(2)S$], 127.8 (C, aromatic C), 129.5, 131.1, 137.2 (3 x CH, aromatic CH), 197.3 (C, CO).

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

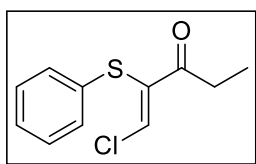


The α -thioketone 2-(phenylthio)pentan-3-one **5b**, (0.20 g, 1.03 mmol), unrecrystallised *N*-chlorosuccinimide (0.358 g, 2.7 mmol, 2.6 eq) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 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. ^1H 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%) [$\text{C}(3)\text{H}$, 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 ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArH); 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 CH), 200.5 (C, CO).

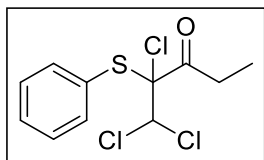
(Z)-2-(Phenylthio)-1-chloropent-1-en-3-one Z-9b



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, ArH), 7.50 (1H, s, CHCl); 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 CH), 200.5 (C, CO).

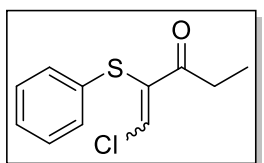
aromatic CH), 133.5 [C, aromatic C or C(2)S], 136.2 (CH, CHCl), 138.0 [C, aromatic C or C(2)S], 198.7 (C, CO).

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, ArH); 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 CH), 200.3 (C, CO).

(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



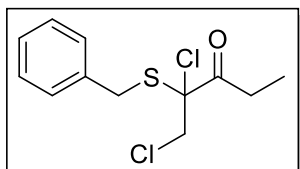
A solution of zinc chloride in ether (3.30 mL of a 1M solution, 3.3 mmol) was added to a stirring solution of a mixture containing the compounds, 1,2-dichloro-2-(phenylthio)pentan-3-one **S54** (57%), (Z)-2-(phenylthio)-1-chloropent-1-en-3-one **Z-9b** (32%), 1,1,2-trichloro-2-(phenylthio)pentan-3-one **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. ^1H 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); $\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArH), 7.50 (1H, s, CHCl); 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 CH), 133.5 [C, aromatic C or C(2)S], 136.2 (CH, CHCl), 138.0 [C, aromatic C or C(2)S], 198.7 (C, CO).

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, $CHCl$), 7.18-7.33 (5H, m, ArH); δ_C (75.5 MHz, $CDCl_3$) 7.6 (CH_3 , CH_2CH_3), 35.2 (CH_2 , CH_2CH_3), 123.8 (CH, $CHCl$), 127.9, 130.4 (CH, aromatic CH), 200.4 (C, CO).

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**



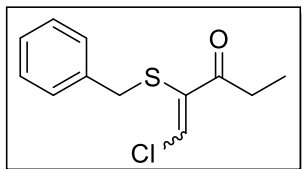
N-Chlorosuccinimide (0.251 g, 1.9 mmol) was added in one portion to a solution of 2-(benzylthio)pentan-3-one **5c** (0.20 g, 0.96 mmol) in toluene (8 mL). The flask was immediately immersed in an oil bath at 90 °C and heating was maintained for 2 h with stirring. The reaction mixture was cooled to 0 °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. 1H 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 1H 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, ArH); 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 CH), 135.2 (C, aromatic C), 200.0 (C, CO).

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

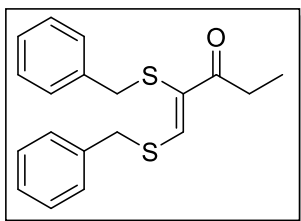


The title compounds were synthesized using the procedure described above for **Z-9b** and **E-9b** using a solution of zinc chloride in ether (1.80 mL of a 1M solution, 1.8 mmol) and a mixture containing the dichloride 2-(benzylthio)-1,2-dichloropentan-3-one **S57** (46%), (Z)-2-(benzylthio)-1-chloropent-1-en-3-one **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. ¹H 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 ¹H 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, CDCl₃) 0.99 (3H, t, *J* 7.2, CH₂CH₃), 2.49 (2H, q, *J* 7.2, CH₂CH₃), 4.00 (2H, s, SCH₂), 7.22-7.32 (5H, m, ArH), 7.35 (1H, s, CHCl); δ_C (75.5 MHz, CDCl₃) 8.1 (CH₃, CH₂CH₃), 33.2 (CH₂, CH₂CH₃), 37.2 (CH₂, SCH₂), 127.4, 128.54, 129.0 (3 x CH, aromatic CH), 135.7 (CH, CHCl), 137.3, 139.0 [2 x C, aromatic C and C(2)S], 197.7 (C, CO).

E-9c: δ_H (300 MHz, CDCl₃) 1.11 (3H, t, *J* 7.2, CH₂CH₃), 2.73 (2H, q, *J* 7.2, CH₂CH₃), 3.82 (2H, s, SCH₂), 6.31 (1H, s, CHCl), 7.21-7.33 (5H, m, ArH); δ_C (75.5 MHz, CDCl₃) 7.5 (CH₃, CH₂CH₃), 35.0 (CH₂, CH₂CH₃), 38.7 (CH₂, SCH₂), 122.2 (CH, CHCl), 127.5, 128.50, 129.1 (3 x CH, aromatic CH), 135.5, 136.6 [2 x C, aromatic C and C(2)S], 201.9 (C, CO).

HRMS (ES⁺): Exact mass calculated for C₁₂H₁₄OS³⁵Cl[M+H⁺] 241.0454. Found 241.0447; m/z (ES⁺) 241.1 [(C₁₂H₁₃OS³⁵Cl)+H⁺], 30%, 243.1 [(C₁₂H₁₃OS³⁷Cl)+H⁺], 10%.



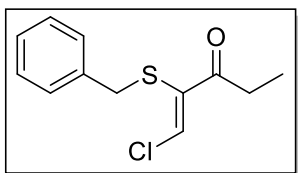
Characteristic signals assigned as the bis-sulfide impurity **S58** were seen in the ^1H NMR spectrum of a more polar fraction; δ_{H} (300 MHz, CDCl_3) 0.91 (3H, t, J 7.2, CH_2CH_3), 2.40 (2H, q, J 7.2, CH_2CH_3), 3.89 (2H, s, one of SCH_2), 4.05 (2H, s, one of SCH_2), 7.11-7.39 (10H, m, ArH), 7.99 (1H, s, CHSBn); 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 CH), 127.4 [C , aromatic C or $\text{C}(2)\text{S}$], 127.8, 128.4, 128.8, 129.0, 129.1 (5 x CH , aromatic CH), 136.8, 137.8 [2 x C , 2 x aromatic C or aromatic C and $\text{C}(2)\text{S}$], 154.3 (CH , CHSBn), 196.8 (C , CO); HRMS (ES^+): Exact mass calculated for $\text{C}_{19}\text{H}_{21}\text{OS}_2[\text{M}+\text{H}^+]$ 329.1034. Found 329.1022; m/z (ES^+) 329.0 [$(\text{C}_{19}\text{H}_{20}\text{OS}_2)+\text{H}^+$], 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*-chlorosuccinimide was removed by filtration. The crude mixture was evaporated under reduced pressure to give the crude product as a brown oil. ^1H 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.

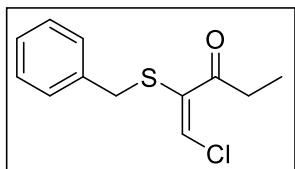
(*Z*)-2-(Benzylthio)-1-chloropent-1-en-3-one **Z-9c**



$\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArH)*, 7.35 (1H, s, CHCl); 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,

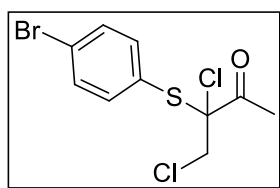
128.5, 129.0 (3 x CH, aromatic CH), 135.7 (CH, CHCl), 137.3, 139.0 [2 x C, aromatic C and C(2)S], 197.7 (C, CO).

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



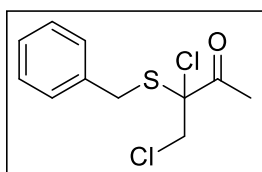
δ_H (300 MHz, $CDCl_3$) 1.11 (3H, t, J 7.2, CH_2CH_3), 2.73 (2H, q, J 7.2, CH_2CH_3), 3.82 (2H, s, SCH_2), 6.31 (1H, s, $CHCl$), 7.21-7.33 (5H, m, ArH).

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*-chlorosuccinimide was removed by filtration. The crude mixture was evaporated under reduced pressure to give the crude product as an orange oil. 1H 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, ArH), 7.54 (2H, d, J 8.4, ArH); 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 CH), 197.6 (C, CO); 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



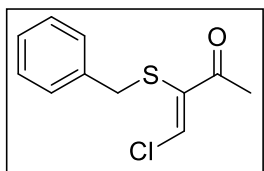
The α -thioketone **5e** (0.20 g, 1.0 mmol), *N*-chlorosuccinimide (0.358 g, 2.7 mmol, 2.6 eq) and toluene (2 mL) were placed in a sealed microwave tube. The microwave tube was placed in the microwave reactor at 120 °C, 200 W, 250 psi with stirring for 1 h. The resulting reaction mixture was cooled to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

was evaporated under reduced pressure to give the crude product as an orange oil. ^1H 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

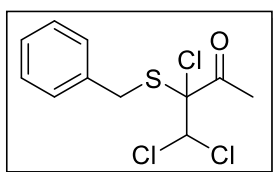
Characteristic signals: δ_{H} (300 MHz, CDCl_3) 2.46 (3H, s, CH_3), 3.84 (2H, s, SCH_2), 3.90 (1H, A of AB system, *J* 12.0, one of CH_2Cl), 4.14 (1H, B of AB system, *J* 12.0, one of CH_2Cl).

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



δ_{H} (300 MHz, CDCl_3) 2.19 (3H, s, CH_3), 4.01 (2H, s, SCH_2), 7.22-7.30 (5H, m, ArH), 7.40 (1H, s, CHCl).

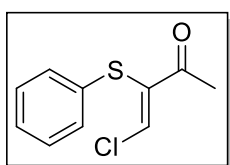
3-(Benzylthio)-3,4,4-trichlorobutan-2-one S61



Characteristic signals: δ_{H} (300 MHz, CDCl_3) 2.54 (3H, s, CH_3), 6.26 (1H, s, CHCl_2).

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

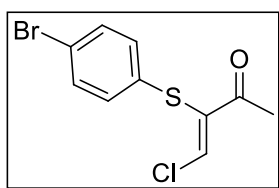
(*Z*)-4-Chloro-3-(phenylthio)but-3-en-2-one Z-9a



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

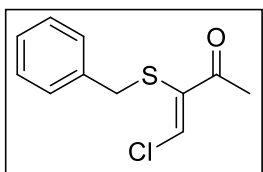
mmol) in dichloromethane (15 mL). The reaction was quenched by addition of water (15 mL) and the phases were separated. The organic layer was washed with water (20 mL) and brine (20 mL), dried and concentrated at reduced pressure to give the crude product as a dark yellow oil. The ^1H NMR spectrum of 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3051 (CH), 1721 (CO), 1536; δ_{H} (300 MHz, CDCl_3) 2.24 (3H, s, CH_3), 7.23-7.34 (5H, m, ArH), 7.52 (1H, s, CHCl); δ_{C} (75.5 MHz, CDCl_3) 28.0 (CH_3 , CH_3), 127.2, 129.0, 129.5 (3 x CH, aromatic CH), 133.4 [C, aromatic C or C(2)S], 136.8 (CH, CHCl), 138.5 [C, aromatic C or C(2)S], 195.6 (C, CO); HRMS (ES+): Exact mass calculated for $\text{C}_{10}\text{H}_{10}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}^+]$ 213.0141. Found 213.0134; m/z (ES+) 211.1 [$(\text{C}_{10}\text{H}_9\text{OS}^{35}\text{Cl})-\text{H}^+$], 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. ^1H 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 ^1H NMR spectrum of the crude product; δ_{H} (400 MHz, CDCl_3) 2.27 (3H, s, CH_3), 7.12 (2H, d, J 8.4, ArH), 7.42 (2H, d, J 8.2, ArH), 7.58 (1H, s, CHCl).

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



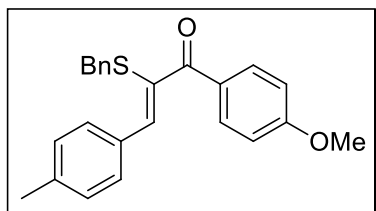
The title compound was synthesized using the procedure described above for **Z-9b** and **E-9b** using a solution of zinc chloride in ether (1.80 mL of a 1M solution, 1.8 mmol) and a mixture containing three compounds, 3-(benzylthio)-3,4-dichlorobutan-2-one **S60** (35%), (*Z*)-3-(benzylthio)-4-

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. ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3030 (CH), 2984 (CH), 2925 (CH), 1686 (CO), 1542; δ_{H} (400 MHz, CDCl_3) 2.19 (3H, s, CH_3), 4.01 (2H, s, SCH_2), 7.22-7.30 (5H, m, ArH), 7.40 (1H, s, CHCl); δ_{C} (75.5 MHz, CDCl_3) 27.6 (CH_3 , CH_3), 37.2 (CH_2 , SCH_2), 127.4, 128.5, 129.0 (3 x CH, aromatic CH), 137.3 (CH, CHCl), 137.3, 139.4 [C, aromatic C and $\text{C}(2)\text{S}$], 194.6 (C, CO); HRMS (ES $^{+}$): Exact mass calculated for $\text{C}_{11}\text{H}_{12}\text{OS}^{35}\text{Cl}[\text{M}+\text{H}^{+}]$ 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

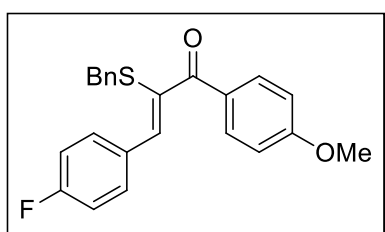
(Z)-2-(Benzylthio)-1-(4-methoxyphenyl)-3-(p-tolyl)prop-2-en-1-one **14**



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, $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (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. ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 2918 (CH), 1650 (CO), 1598 (aromatic), 1251; δ_{H} (300 MHz, CDCl_3) 2.37 (3H, s, ArCH_3), 3.87 (3H, s, OCH_3), 3.98 (2H, s, SCH_2), 6.87 (2H, d, J 8.9, ArH), 6.95 [1H, s, $\text{C}(3)\text{H}$], 7.11-7.21 (7H, m, ArH),

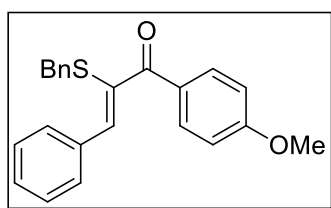
7.57 (2H, d, *J* 8.1, ArH), 7.67 (2H, d, *J* 8.9, ArH); δ_{C} (75.5 MHz, CDCl₃) 21.4 (CH₃, ArCH₃), 36.8 (CH₂, SCH₂), 55.5 (CH₃, OCH₃), 113.5, 127.2, 128.4, 129.0, 129.3 (5 x CH, aromatic CH), 130.0 [C, aromatic C or C(2)S], 130.3 (CH, aromatic CH), 132.2 [C, aromatic C or C(2)S], 132.4 (CH, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for C₂₄H₂₃SO₂[M+H⁺] 375.1419. Found 375.1412; *m/z* (ES⁺) 375.2 [(C₂₄H₂₂SO₂)+H⁺], 100%.

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



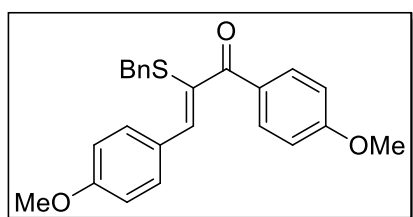
The title compound was prepared following the procedure described above for **14** using the β -chloroenones **Z-4e** and **E-4e** (ratio 4:1) (155 mg, 0.5 mmol), tributyl(4-fluorophenyl)stannane **36c**²⁴ (227 mg, 0.6 mmol) and anhydrous acetonitrile (5 mL). The crude chalcone was obtained as a yellow oil. ¹H 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, CDCl₃) 3.79 (3H, s, OCH₃), 3.97 (2H, s, SCH₂), 6.79 (2H, d, *J* 8.7, ArH), 6.83 [1H, s, C(3)H], 6.97 (2H, t, *J* 8.7, ArH), 7.07 (5H, s, ArH), 7.53-7.61 (4H, m, ArH); δ_{C} (75.5 MHz, CDCl₃) 35.7 (CH₂, SCH₂), 54.5 (CH₃, OCH₃), 112.3 (CH, aromatic CH), 114.3 (CH, d, ²*J*_{CF} 21.5, aromatic CH), 126.2, 127.4, 128.3 (3 x CH, aromatic CH), 128.7, 129.9 [2 x C, 2 x aromatic C or aromatic C and C(2)S], 131.1 (CH, d, ³*J*_{CF} 9.1, aromatic CH), 131.4 (CH, aromatic CH), 134.5 (C, d, ⁴*J*_{CF} 2.1, aromatic C), 135.5 [CH, C(3)H], 136.2 [C, aromatic C or C(2)S], 161.5 (C, d, ¹*J*_{CF} 250.3, aromatic C), 162.5 (C, aromatic C), 191.6 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₂₀SO₂F[M+H⁺] 379.1168. Found 379.1160; *m/z* (ES⁺) 379.3 [(C₂₃H₁₉SO₂F)+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. ^1H 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 ^1H NMR spectrum); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 2933 (CH), 1651 (CO), 1599 (aromatic), 1253; δ_{H} (300 MHz, CDCl_3) 3.87 (3H, s, OCH_3), 3.98 (2H, s, SCH_2), 6.87 (2H, d, J 8.8, ArH), 6.94 [1H, s, C(3)H], 7.16 (5H, m, ArH), 7.25-7.39 (3H, m, ArH), 7.65 (2H, d, J 7.4, ArH), 7.69 (2H, d, J 8.8, ArH); δ_{C} (75.5 MHz, CDCl_3) 36.8 (CH_2 , SCH_2), 55.5 (CH_3 , OCH_3), 113.6, 127.2, 128.3, 128.4, 128.7, 129.3 (6 x CH, aromatic CH), 129.8 [C, aromatic C or C(2)S], 130.2, 132.4 (2 x CH, aromatic CH), 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 COCH_3), 192.7 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{23}\text{H}_{21}\text{SO}_2[\text{M}+\text{H}^+]$ 361.1268. Found 361.1262; m/z (ES⁺) 361.3 [$(\text{C}_{23}\text{H}_{20}\text{SO}_2)+\text{H}^+$], 100%.

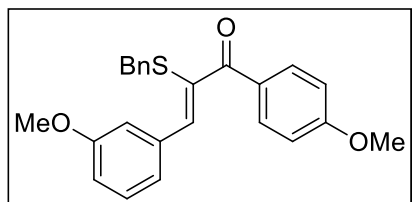
(Z)-2-(Benzylthio)-1,3-bis(4-methoxyphenyl)prop-2-en-1-one **17**



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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 2919 (CH), 1650 (CO), 1600 (aromatic), 1508, 1252; δ_{H} (400 MHz, CDCl_3) 3.84 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.99 (2H,

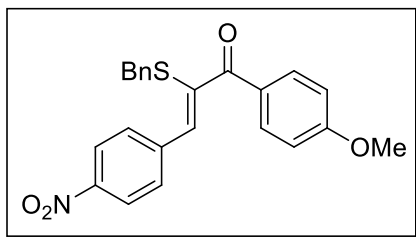
s, SCH₂), 6.87 (2H, d, *J* 8.8, ArH), 6.90 (2H, d, *J* 8.8, ArH), 6.97 [1H, s, C(3)H], 7.11-7.19 (5H, m, ArH), 7.63 (2H, d, *J* 8.8, ArH), 7.68 (2H, d, *J* 8.7, ArH); δ_C (75.5 MHz, CDCl₃) 36.8 (CH₂, SCH₂), 55.3 (CH₃, OCH₃), 55.5 (CH₃, OCH₃), 113.5, 113.8, 127.1 (3 x CH, aromatic CH), 127.7 (C, aromatic C), 128.4, 129.3 (2 x CH, aromatic CH), 130.3 [C, aromatic C or C(2)S], 132.2, 132.3 (2 x CH, aromatic CH), 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 COCH₃), 193.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₄H₂₃SO₃[M+H⁺] 391.1368. Found 391.1380; *m/z* (ES⁺) 391.3 [(C₂₄H₂₂SO₃)+H⁺], 100%.

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



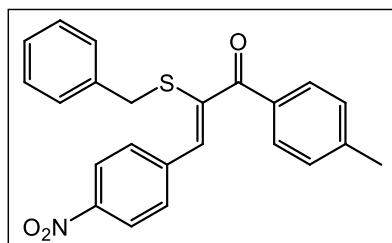
This was prepared following the procedure described for **14i** using the β-chloroenones **Z-4e** and **E-4e** (ratio 4:1) (155 mg, 0.5 mmol), tributyl(3-methoxyphenyl)stannane **36e**²³ (238 mg, 0.6 mmol) and (CH₃CN)₂PdCl₂ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ¹H 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, CDCl₃) 3.81 (3H, s, OCH₃), 3.87 (3H, s, OCH₃), 3.97 (2H, s, SCH₂), 6.87 (3H, d, *J* 8.9, ArH), 6.91 [1H, s, C(3)H], 7.09-7.32 (8H, m, ArH), 7.69 (2H, d, *J* 8.9, ArH); δ_C (75.5 MHz, CDCl₃) 36.8 (CH₂, SCH₂), 55.3 (CH₃, OCH₃), 55.5 (CH₃, OCH₃), 113.6, 114.8, 115.0, 122.9, 127.2, 128.4, 129.26, 129.33 (8 x CH, aromatic CH), 129.8 [C, aromatic C or C(2)S], 132.4 (CH, aromatic CH), 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, CO), signal for 1 x aromatic C could not be seen in the ¹³C NMR spectrum; HRMS (ES⁺): Exact mass calculated for C₂₄H₂₃SO₃[M+H⁺] 391.1368. Found 391.1360; *m/z* (ES⁺) 391.4 [(C₂₄H₂₂SO₃)+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 (CH₃CN)₂PdCl₂ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as an orange oil. ¹H 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; $\nu_{\max}/\text{cm}^{-1}$ (film) 2955 (CH), 1650 (CO), 1598 (aromatic), 1515 (NO₂), 1342 (NO₂), 1253; δ_H (400 MHz, CDCl₃) 3.89 (3H, s, OCH₃), 3.98 (2H, s, SCH₂), 6.85 [1H, s, C(3)H], 6.91 (2H, d, *J* 8.9, ArH), 7.17 (5H, s, ArH), 7.74 (2H, d, *J* 8.6, ArH), 7.78 (2H, d, *J* 8.9, ArH), 8.21 (2H, d, *J* 8.8, ArH); δ_C (75.5 MHz, CDCl₃) 36.9 (CH₂, SCH₂), 55.6 (CH₃, OCH₃), 113.8, 123.6, 127.6, 128.6 (4 x CH, aromatic CH), 128.9 [C, aromatic C or C(2)S], 129.3, 130.4 (2 x CH, aromatic CH), 131.8 [CH, C(3)H], 132.5 (CH, aromatic CH), 136.5, 140.9, 141.4 [3 x C, 2 x aromatic C and C(2)S], 146.8 (C, aromatic CNO₂), 164.0 (C, aromatic COCH₃), 191.7 (C, CO), signal for 1 x aromatic C not seen in ¹³C NMR spectrum; HRMS (ES⁺): Exact mass calculated for C₂₃H₂₀NSO₄[M+H⁺] 406.1113. Found 406.1133; *m/z* (ES⁺) 406.3 [(C₂₃H₁₉SO₄N)+H⁺], 5%.

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



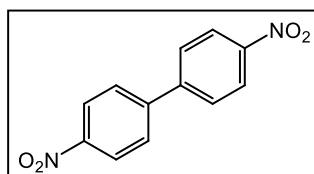
This was prepared following the procedure described for **14** from the β -chloroenones **Z-4h** and **E-4h** (*Z* : *E*, 14 : 1) (105 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**²⁵ (151 mg, 0.4 mmol), and (CH₃CN)₂PdCl₂ (4 mg, 17 μ mol, 5 mol %) in anhydrous acetonitrile (10 mL). The reaction mixture was stirred at room temperature for 24 h. The crude *chalcone* was obtained as an orange oil. ¹H 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: $\nu_{\max}/\text{cm}^{-1}$ (neat) 3029, 2921, 1651 (C=O), 1601, 1514 (NO₂), 1339 (NO₂), 1243, 1177, 689; δ_{H} (400 MHz, CDCl₃): 2.43 (3H, s, ArCH₃), 3.99 (2H, s, SCH₂), 6.89 [1H, s, C(3)H], 7.11–7.36 (7H, m, ArH), 7.63 (2H, d, *J* 8.2, ArH), 7.73 (2H, d, *J* 8.9, ArH), 8.20 (2H, d, *J* 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 21.7 (CH₃, ArCH₃), 36.9 (CH₂, SCH₂), 123.5, 127.5, 128.6, 129.2, 129.3, 130.2, 130.5, 133.3 [8 × CH, aromatic CH 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, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₂₀NO₃S[M+H⁺] 390.1164. Found 390.1164.

Characteristic signals tentatively assigned as *E-20*: δ_{H} (400 MHz, CDCl₃): 2.38 (3H, s, ArCH₃), 3.97 (2H, s, SCH₂), 6.87 [1H, s, C(3)H], 7.81 (2H, d, *J* 8.2, ArH), 7.98 (2H, d, *J* 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 37.6 (CH₂, SCH₂), 123.8, 128.7, 128.9, 129.1, 129.7, 129.8 [6 × CH, aromatic CH or 10 × aromatic CH and C(3)H], 136.1, 139.5, 141.1, 145.6 (4 × C, Cq), 193.6 (C, CO).

4,4'-Dinitro-1,1'-biphenyl **37**²⁶

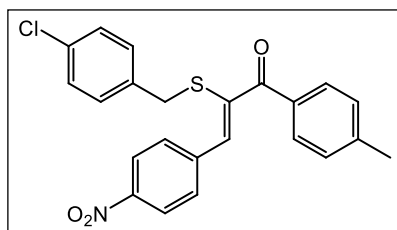


(less polar): white solid (7 mg, 8%); $\nu_{\max}/\text{cm}^{-1}$ (neat) 1598, 1512 (NO₂), 1340 (NO₂), 1107, 850, 737; δ_{H} (400 MHz, CDCl₃): 7.79 (4H, d, *J* 8.8, ArH), 8.37 (4H, d, *J* 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 124.4, 128.3 (2 × CH signals, 8 × aromatic CH), 145.0, 148.0 (2 × C, 4 × aromatic 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 (CH₃CN)₂PdCl₂ (3 mg, 10 μ mol, 5 mol %) in acetonitrile (5 mL). After work up, ¹H 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

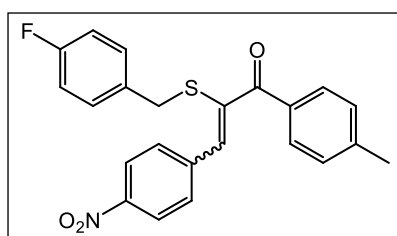


This was prepared following the procedure described above for **14** using the β -chloroenones **Z-4j** and **E-4j** (*Z* : *E*, 4.5 : 1) (123 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**²⁵ (157 mg, 0.4 mmol), and (CH₃CN)₂PdCl₂ (4 mg, 15 μ mol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred at

room temperature for 5 h and after work-up, the crude product was obtained as a brown residue. ¹H 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 (NO₂), 1341 (NO₂); δ_{H} (400 MHz, CDCl₃): 2.44 (3H, s, ArCH₃), 3.97 (2H, s, SCH₂), 6.90 [1H, s, C(3)H], 7.03–7.18 (4H, m, ArH), 7.23 (2H, d, *J* 8.0, ArH), 7.59 (2H, d, *J* 8.1, ArH), 7.73 (2H, d, *J* 8.7, ArH), 8.22 (2H, d, *J* 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 21.7 (CH₃, ArCH₃), 36.1 (CH₂, SCH₂), 123.5, 128.7, 129.2, 130.2, 130.5, 130.7 (6 $\times$ CH, aromatic CH), 133.4, 133.5 [2 $\times$ C, 2 $\times$ aromatic C or 1 $\times$ aromatic C and C(2)S], 133.6 [CH, C(3)H], 135.2, 140.1, 141.1, 144.7, 147.0 [5 $\times$ C, 5 $\times$ aromatic C or 4 $\times$ aromatic C and C(2)S], 192.6 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₁₉NO₃S³⁵Cl[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 (CH₃CN)₂PdCl₂ (2 mg, 8 μ mol, 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. ¹H 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-

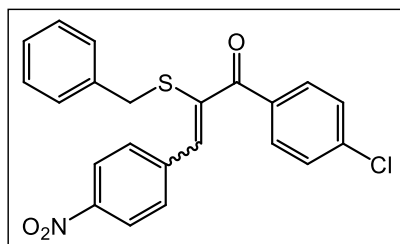
aryl **37**²⁶ (δ_{H} , d, 8.36 ppm, J 8.8). Purification by column chromatography on silica gel using hexane–ethyl acetate (95 : 5) as eluent gave the *chalcones* **Z-22** and **E-22** ($Z : E$, 3.2 : 1; 11 mg, 28%) as a bright yellow oil; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3071, 3038, 2922, 2850, 1655 (C=O), 1601, 1508 (NO_2), 1340 (NO_2), 1226; δ_{H} (400 MHz, CDCl_3): 2.38 (3H, s, ArCH_3 , *E* isomer), 2.44 (3H, s, ArCH_3 , *Z* isomer), 3.92 (2H, s, SCH_2 , *E* isomer), 3.98 (2H, s, SCH_2 , *Z* isomer), 6.78–7.02 [3H and 3H, m, ArH and C(3)H , *Z* and *E* isomer, containing (6.84, 2H, overlapping dd appears as t, J 8.6, ArH , *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, ArH , *E* isomer)], 7.11 (2H, dd, J 8.4, J_{FH} 5.4, ArH , *Z* isomer), 7.16–7.35 (2H and 6H, m, ArH , *Z* and *E* isomer), 7.62 (2H, d, J 8.1, ArH , *Z* isomer), 7.74 (2H, d, J 8.7, ArH , *Z* isomer), 7.80 (2H, d, J 8.1, ArH , *E* isomer), 7.99 (2H, d, J 8.8, ArH , *E* isomer), 8.22 (2H, d, J 8.8, ArH , *Z* isomer); HRMS (ES⁺): Exact mass calculated for $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{FS}[\text{M}+\text{H}^+]$ 408.1070. Found 408.1057.

¹H and ¹³C 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 ¹H NMR spectroscopy).

δ_{C} (100 MHz, CDCl_3): 21.7 (CH_3 , ArCH_3 , *Z* isomer), 21.8 (CH_3 , ArCH_3 , *E* isomer), 36.0 (CH_2 , SCH_2 , *Z* isomer), 36.8 (CH_2 , SCH_2 , *E* isomer), 115.4 (1 $\times$ CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH, *Z* and *E* isomer), 123.5, 123.8, 128.7, 129.2, 129.75 (5 $\times$ CH, aromatic CH, *Z* and *E* isomer), 129.79 [CH, C(3)H , *E* isomer], 129.8, 130.2, 130.5 (3 $\times$ CH, aromatic CH, *Z* and *E* isomer), 130.7 (1 $\times$ CH, d, $^3J_{\text{CF}}$ 8.2, aromatic CH, *E* isomer), 130.9 (1 $\times$ CH, d, $^3J_{\text{CF}}$ 8.2, aromatic CH, *Z* isomer), 131.8 (C, C_q , *Z* or *E* isomer), 132.0 (C, d, $^4J_{\text{CF}}$ 3.6, aromatic C, *E* isomer), 132.4 (C, d, $^4J_{\text{CF}}$ 3.3, aromatic C, *Z* isomer), 133.4 [1 $\times$ 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 $\times$ C, C_q , *Z* and *E* isomer), 162.0 (C, d, $^1J_{\text{CF}}$ 246.6, aromatic C, *Z* isomer), 162.1 (C, d, $^1J_{\text{CF}}$ 246.6, aromatic C, *E* isomer), 192.7 (C, CO, *Z* isomer), 193.5 (C, CO, *E* isomer).

This reaction was also carried out at room temperature using the β -chloroenones **Z-4I** and **E-4I** ($Z : E$, 3.4 : 1) (66 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **37f**²⁵ (99 mg, 0.24 mmol), and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (3 mg, 10 μmol , 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room temperature for 5 h. After work up, ¹H NMR spectroscopy showed this material to contain approx. 77% β -chloroenone starting materials **Z-4I** and **E-4I** ($Z : E$, 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



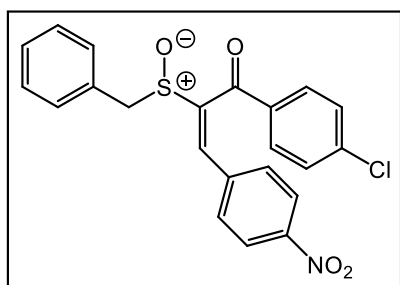
This was prepared following the procedure described above for **14** using the β -chloroenones **Z-4o** and **E-4o** (*Z* : *E*, 2.4 : 1) (80 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **37**²⁵ (123 mg, 0.3 mmol), and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (3 mg, 12 μmol , 5 mol %) in acetonitrile (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. ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3060, 1655 (C=O), 1584, 1509 (NO_2), 1340 (NO_2), 1244, 693; δ_{H} (400 MHz, CDCl_3) 3.97 (2H, s, SCH_2 , *E* isomer), 4.01 (2H, s, SCH_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, ArH, *Z* and *E* isomer containing (7.37, 2H, d, *J* 8.6, ArH, *Z* isomer)], 7.56 (2H, d, *J* 8.6, ArH, *Z* isomer), 7.75 (2H, d, *J* 8.7, ArH, *Z* isomer), 7.80 (2H, d, *J* 8.7, ArH, *E* isomer), 8.00 (2H, d, *J* 8.8, ArH, *E* isomer), 8.22 (2H, d, *J* 8.8, ArH, *Z* isomer).

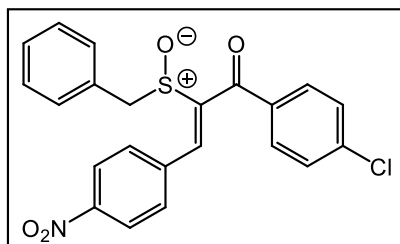
^1H and ^{13}C NMR spectra were recorded after 32 months (sample was stored neat at room temperature). The ^1H NMR spectrum was seen to contain *approx.* 52% chalcones **Z-23** and **E-23** (*Z* : *E*, 2.9 : 1) and what is believed to be the α -sulfinyl chalcones **Z-40o** and **E-40o** (48%, *Z* : *E*, 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 , SCH_2), 134.7 [CH, C(3)H], 191.9 (C, CO).

Characteristic signals due to **E-40o**: δ_{C} (100 MHz, CDCl_3): 37.7 (CH_2 , SCH_2), 129.9 [CH, C(3)H], 192.7 (C, CO).

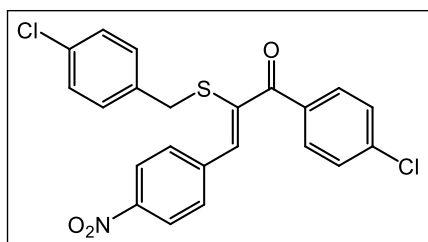


Characteristic signals tentatively assigned as **E-40o**: δ_H (400 MHz, $CDCl_3$): 4.17 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 4.38 (1H, B of AB system, J_{AB} 13.0, one of SCH_2), 7.07 [1H, s, C(3)H]; δ_C (100 MHz, $CDCl_3$): 59.5 (CH_2 , SCH_2), 134.4 [CH, C(3)H], 192.1 (C, CO).



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 SCH_2), 4.97 (1H, B of AB system, J_{AB} 12.2, one of SCH_2); δ_C (100 MHz, $CDCl_3$): 59.2 (CH_2 , SCH_2), 141.0 [CH, C(3)H], 191.7 (C, CO).

(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 μ mol, 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. 1H 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, SCH_2), 6.91 [1H, s, C(3)H], 7.06 (2H, d, J 8.5, ArH), 7.11 (2H, d, J 8.5, ArH), 7.40 (2H, d, J 8.5, ArH), 7.57 (2H, d, J 8.5, ArH), 7.75 (2H, d, J 8.9, ArH), 8.23 (2H, d, J 8.8, ArH).

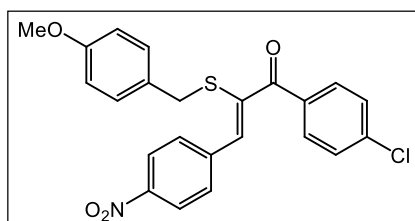
1H and ^{13}C NMR spectra were recorded after 27 months (sample was stored neat at room temperature). No degradation was visible, however, the product was seen to have isomerised

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

Z-24: δ_{C} (100 MHz, CDCl_3): 36.1 (CH_2 , SCH_2), 123.6, 128.7, 128.87, 130.6, 130.7, 131.3 ($6 \times \text{CH}$, aromatic CH), 133.5, 134.5 [$2 \times \text{C}$, $2 \times$ aromatic C or $1 \times$ aromatic C and $\text{C}(2)\text{S}$], 134.9 [$1 \times \text{CH}$, $\text{C}(3)\text{H}$], 135.1, 139.5, 140.1, 140.6, 147.2 [$5 \times \text{C}$, $5 \times$ aromatic C or $4 \times$ aromatic C and $\text{C}(2)\text{S}$], 191.7 (C, CO).

Characteristic signals due to **E-24**: δ_{H} (400 MHz, CDCl_3): 3.90 (2H, s, SCH_2), 6.94 [1H, s, $\text{C}(3)\text{H}$], 7.36 (2H, d, J 8.5, ArH), 7.80 (2H, d, J 8.6, ArH), 8.01 (2H, d, J 8.8, ArH); δ_{C} (100 MHz, CDCl_3): 123.9, 128.83, 129.3, 130.4, 130.9 ($5 \times \text{CH}$).

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



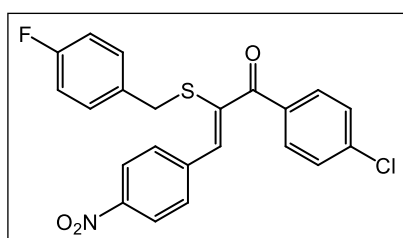
This was prepared following the procedure described above for **14** using the β -chloroenones **Z-4r** and **E-4r** (*Z* : *E*, 9 : 1) (70 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **36f**²⁵ (99 mg, 0.24 mmol), and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (2 mg, 10 μmol , 5 mol %) in acetonitrile (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. ^1H 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); $\nu_{\text{max}}/\text{cm}^{-1}$ (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, OCH_3), 3.97 (2H, s, SCH_2), 6.66 (2H, d, J 8.7, ArH), 6.86 [1H, s, $\text{C}(3)\text{H}$], 7.03 (2H, d, J 8.7, ArH), 7.38 (2H, d, J 8.7, ArH), 7.59 (2H, d, J 8.6, ArH), 7.76 (2H, d, J 8.6, ArH), 8.22 (2H, d, J 8.9, ArH).

^1H and ^{13}C NMR spectra of this sample were recorded after 65 months following storage at room temperature. The ^1H 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 , SCH_2), 55.25 (CH_3 , OCH_3), 113.9, 123.6, 128.7, 130.6, 131.4 ($5 \times \text{CH}$, aromatic CH), 133.9 [$1 \times \text{CH}$, $\text{C}(3)\text{H}$], 134.6, 139.8 ($2 \times \text{C}$, $2 \times \text{aromatic C}$), 140.3 [$1 \times \text{C}$, $\text{C}(2)\text{S}$], 140.92, 140.97, 147.0, 159.0 ($4 \times \text{C}$, aromatic C), 191.8 (C, CO).

Characteristic signals due to **E-25**: δ_{H} (400 MHz, CDCl_3): 3.77 (3H, s, OCH_3), 3.93 (2H, s, SCH_2), 6.79 (2H, d, J 8.6, ArH), 6.92 [1H, s, $\text{C}(3)\text{H}$], 7.17–7.29 (4H, m, ArH), 7.34 (2H, d, J 8.6, ArH), 8.00 (2H, d, J 8.8, ArH); δ_{C} (100 MHz, CDCl_3): 37.2 (CH_2 , SCH_2), 55.28 (CH_3 , OCH_3), 123.9, 129.3 ($2 \times \text{CH}$, aromatic CH), 129.6 [$1 \times \text{CH}$, $\text{C}(3)\text{H}$], 130.3, 130.9 ($2 \times \text{CH}$, aromatic CH).

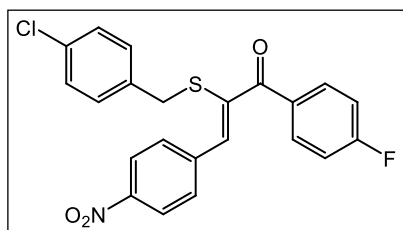
(Z)-1-(4-Chlorophenyl)-2-((4-fluorobenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one Z-26



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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (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. ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 1659 (C=O), 1588, 1508, 1342, 1243, 1220, 1089, 751; δ_{H} (400 MHz, CDCl_3): 3.98 (2H, s, SCH_2), 6.85 (2H, t, J 8.7, ArH), 6.91 [1H, s, $\text{C}(3)\text{H}$], 7.10 (2H, dd, J 8.6, J_{FH} 5.4, ArH), 7.40 (2H, d, J 8.6, ArH), 7.60 (2H, d, J 8.6, ArH), 7.75 (2H, d, J 8.7, ArH), 8.23 (2H, d, J 8.8, ArH); δ_{C} (100 MHz, CDCl_3): 36.0 (CH_2 , SCH_2), 115.5 ($1 \times \text{CH}$, d, $^2J_{\text{CF}}$ 21.6, aromatic CH), 123.6, 128.8, 130.6 ($3 \times \text{CH}$, aromatic CH), 131.0 ($1 \times \text{CH}$, d, $^3J_{\text{CF}}$ 8.2, aromatic CH), 131.3 ($1 \times \text{CH}$, aromatic CH), 132.3 ($1 \times \text{C}$, d, $^4J_{\text{CF}}$ 3.2, aromatic C), 134.5 [$1 \times \text{C}$, aromatic C or $\text{C}(2)\text{S}$], 134.7 [$1 \times \text{CH}$, $\text{C}(3)\text{H}$], 139.7, 140.1, 140.7, 147.1 [$4 \times \text{C}$, $4 \times \text{aromatic C}$ or $3 \times \text{aromatic C}$ and $\text{C}(2)\text{S}$], 162.1 (C, d, $^1J_{\text{CF}}$ 247.1, aromatic C), 191.8 (C, CO); HRMS (ES[−]): Exact mass calculated for $\text{C}_{22}\text{H}_{14}\text{NO}_3\text{F}^{35}\text{Cl}[\text{M}-\text{H}^+]$ 426.0367. Found 426.0364; m/z (ES[−]) 426.1 [$(\text{C}_{22}\text{H}_{15}\text{NO}_3\text{F}^{35}\text{Cl})-\text{H}^+$], 10%.

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



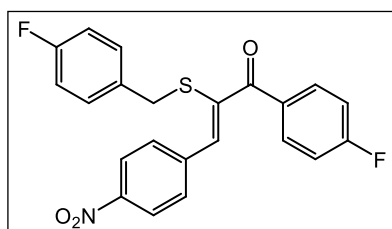
This was prepared following the procedure described above for **14** using the β -chloroenones **Z-4x** and **E-4x** (*Z* : *E*, 2.2 : 1) (86 mg, 0.2 mmol), tributyl(4-nitrophenyl)stannane **36f**²⁵ (123 mg, 0.3 mmol), and (CH₃CN)₂PdCl₂ (3 mg, 12 μ mol, 5 mol %) in acetonitrile (5 mL). The mixture was stirred under

reflux for 5 h and after work-up, the crude product was obtained as an orange oil. ¹H 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: $\nu_{\max}/\text{cm}^{-1}$ (neat) 1655 (C=O), 1591, 1508, 1336, 1234, 599, 497; δ_{H} (400 MHz, CDCl₃): 3.97 (2H, s, SCH₂), 6.90 [1H, s, C(3)H], 7.04–7.14 (6H, m, ArH), 7.68 (2H, dd, *J* 8.6, *J*_{FH} 5.4, ArH), 7.75 (2H, d, *J* 8.8, ArH), 8.24 (2H, d, *J* 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 36.1 (CH₂, SCH₂), 115.7 (1 $\times$ CH, d, ²*J*_{CF} 22.0, aromatic CH), 123.6, 128.7, 130.6, 130.7 (4 $\times$ CH, aromatic CH), 132.4 (1 $\times$ C, d, ⁴*J*_{CF} 3.0, aromatic C), 132.6 (1 $\times$ CH, d, ³*J*_{CF} 9.5, aromatic CH), 133.5 [1 $\times$ C, aromatic C or C(2)S], 134.3 [1 $\times$ CH, C(3)H], 135.1, 139.6, 140.7, 147.1 [4 $\times$ C, 4 $\times$ aromatic C or 3 $\times$ aromatic C and C(2)S], 165.9 (1 $\times$ C, d, ¹*J*_{CF} 256.6, aromatic C), 191.4 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₂H₁₆NO₃FS³⁵Cl[M+H⁺] 428.0523. Found 428.0531.

Characteristic signals due to **E-27**: δ_{H} (400 MHz, CDCl₃): 3.92 (2H, s, SCH₂), 6.94 [1H, s, C(3)H], 7.78 (2H, d, *J* 8.9, ArH), 7.89 (2H, dd, *J* 8.9, *J*_{FH} 5.4, ArH), 8.00 (2H, d, *J* 8.8, ArH), 8.36 (2H, d, *J* 8.9, ArH).

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

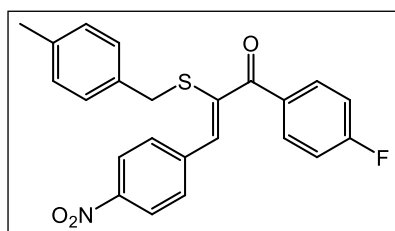


This was prepared following the procedure described above for **14** using the β -chloroenones **Z-4z** and **E-4z** (*Z* : *E*, 3 : 1) (111 mg, 0.3 mmol), tributyl(4-nitrophenyl)stannane **36f**²⁵ (152 mg, 0.3 mmol), and (CH₃CN)₂PdCl₂ (4 mg, 15 μ mol, 5 mol

%) 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. ¹H 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; $\nu_{\max}/\text{cm}^{-1}$ (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, ArH), 6.89 [1H, s, $\text{C}(3)\text{H}$], 7.08–7.13 (4H, m, ArH), 7.70–7.77 (4H, m, ArH), 8.23 (2H, d, J 8.9, ArH); δ_{C} (100 MHz, CDCl_3): 36.0 (CH_2 , SCH_2), 115.5 (1 $\times$ CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH), 115.7 (1 $\times$ CH, d, $^2J_{\text{CF}}$ 22.0, aromatic CH), 123.6, 130.6 (2 $\times$ CH, aromatic CH), 131.0 (1 $\times$ CH, d, $^3J_{\text{CF}}$ 8.2, aromatic CH), 132.3 (1 $\times$ C, d, $^4J_{\text{CF}}$ 3.3, aromatic C), 132.5 (1 $\times$ C, d, $^4J_{\text{CF}}$ 2.9, aromatic C), 132.6 (1 $\times$ CH, d, $^3J_{\text{CF}}$ 9.5, aromatic CH), 134.0 [1 $\times$ CH, $\text{C}(3)\text{H}$], 139.8 [1 $\times$ C, $\text{C}(2)\text{S}$], 140.8, 147.1 (2 $\times$ C, 2 $\times$ aromatic C), 162.1 (1 $\times$ C, d, $^1J_{\text{CF}}$ 247.2, aromatic C), 165.9 (1 $\times$ C, d, $^1J_{\text{CF}}$ 256.4, aromatic C), 191.4 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{22}\text{H}_{16}\text{NO}_3\text{F}_2\text{S}$ [$\text{M}+\text{H}^+$] 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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (6 mg, 25 μmol , 5 mol %) in acetonitrile (5 mL). The mixture was stirred at room

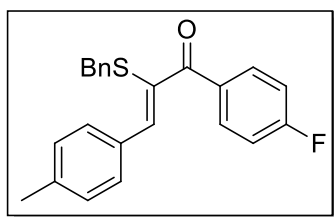
temperature for 24 h and after work-up, the crude product was obtained as a brown residue. ^1H NMR spectroscopy showed this product to contain *approx.* 6% β -chloroenone starting material **E-4aa**, 8% bi-aryl **37**²⁶, and 86% chalcone **Z-29**. Purification by column chromatography on silica gel using 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. $\text{C}_{23}\text{H}_{18}\text{NO}_3\text{SF}$ requires C, 67.80; H, 4.45; N, 3.44; $\nu_{\max}/\text{cm}^{-1}$ (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, $\text{C}(3)\text{H}$], 6.95 (2H, d, J 7.9, ArH), 7.02 (2H, d, J 8.0, ArH), 7.08 (2H, t, J 8.6, ArH), 7.71 (2H, dd, J 8.9, J_{FH} 5.4, ArH), 7.75 (2H, d, J 8.7, ArH), 8.21 (2H, d, J 8.9, ArH); δ_{C} (100 MHz, CDCl_3): 21.0 (CH_3 , ArCH_3), 36.6 (CH_2 , SCH_2), 115.6 (1 $\times$ CH, d, $^2J_{\text{CF}}$ 22.0, aromatic CH), 123.6, 129.2, 129.3, 130.5 (4 $\times$ CH, aromatic CH), 132.6 (1 $\times$ C, d, $^4J_{\text{CF}}$ 3.0, aromatic C), 132.7 (1 $\times$ CH, d, $^3J_{\text{CF}}$ 9.4, aromatic CH), 133.3 [1 $\times$ C, aromatic C or $\text{C}(2)\text{S}$], 133.4 [1 $\times$ CH, $\text{C}(3)\text{H}$], 137.4, 140.5, 141.0, 147.0 [4 $\times$ C, 4 $\times$

aromatic C or 3 × aromatic C and C(2)S], 165.8 (1 × C, d, $^1J_{CF}$ 256.1, aromatic C), 191.5 (C, CO); HRMS (ES⁻): Exact mass calculated for C₂₃H₁₇NO₃FS[M-H⁺] 406.0913. Found 406.0924; m/z (ES⁻) 406.2 [(C₂₃H₁₈NO₃SF)-H⁺], 30%.

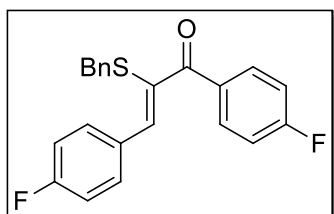
Characteristic signals due to **E-15aa**: δ_H (400 MHz, CDCl₃): 2.31 (3H, s, ArCH₃), 3.95 (2H, s, SCH₂), 6.91 [1H, s, C(3)H], 7.18 (2H, d, J 8.0, ArH), 7.90 (2H, dd, J 8.8, J_{FH} 5.4, ArH), 7.99 (2H, d, J 8.9, ArH).

(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 (CH₃CN)₂PdCl₂ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was recovered as an orange oil and by ¹H 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, CDCl₃) 2.38 (3H, s, ArCH₃), 4.00 (2H, s, SCH₂), 6.97 [1H, s, C(3)H], 7.03 (2H, t, J 8.7, ArH), 7.14 (5H, s, ArH), 7.20 (2H, d, J 8.0 ArH), 7.55–7.59 (4H, m, ArH); δ_C (75.5 MHz, CDCl₃) 21.5 (CH₃, ArCH₃), 36.7 (CH₂, SCH₂), 115.3 (CH, d, $^2J_{CF}$ 21.8, aromatic CH), 127.2, 128.5, 129.1, 129.4, 130.5 (5 × CH, aromatic CH), 131.9 (C, aromatic C), 132.5 (CH, d, $^3J_{CF}$ 9.1, aromatic CH), 133.8 (C, d, $^4J_{CF}$ 3.0, aromatic C), 134.6, 137.4, 139.6 [3 × C, 3 × aromatic C or 2 × aromatic C and C(2)S], 140.4 [CH, C(3)H], 165.4 (C, d, $^1J_{CF}$ 252.8, aromatic C), 192.6 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₂₀SOF[M+H⁺] 363.1219. Found 363.1222; m/z (ES⁺) 363.3 [(C₂₃H₁₉SOF)+H⁺], 10%.

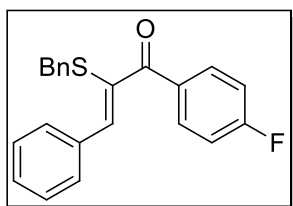
(Z)-2-(Benzylthio)-1,3-bis(4-fluorophenyl)prop-2-en-1-one **31**



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 (CH₃CN)₂PdCl₂ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was isolated as a yellow oil. ¹H 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**

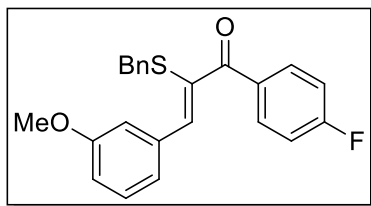
in a ratio of 1:1.2 and 78% *Z* chalcone **Z-31**. This was purified by column chromatography on silica gel using hexane-ethyl acetate (98:2) as eluent to give the *Z* chalcone **Z-31** (137 mg, 75%) as a yellow oil; $\nu_{\max}/\text{cm}^{-1}$ (film) 3032 (CH), 1657 (CO), 1598 (aromatic), 1505, 1236, 846; δ_{H} (400 MHz, CDCl_3) 4.00 (2H, s, SCH_2), 6.94 [1H, s, $\text{C}(3)\text{H}$], 7.02–7.09 (4H, m, ArH), 7.15 (5H, s, ArH), 7.53–7.72 (4H, m, ArH); δ_{C} (75.5 MHz, CDCl_3) 36.7 (CH_2 , SCH_2), 115.4 (CH, d, $^2J_{\text{CF}}$ 21.8, aromatic CH), 115.5 (CH, d, $^2J_{\text{CF}}$ 21.8, aromatic CH), 127.3, 128.5, 129.4 (3 x CH, aromatic CH), 130.8 (C, d, $^4J_{\text{CF}}$ 3.3, aromatic C), 132.4 (CH, d, $^3J_{\text{CF}}$ 8.4, aromatic CH), 132.5 (CH, d, $^3J_{\text{CF}}$ 9.3, aromatic CH), 133.5 (C, d, $^4J_{\text{CF}}$ 2.9, aromatic C), 135.2, 137.2 [2 x C, aromatic C and $\text{C}(2)\text{S}$], 138.6 [CH, $\text{C}(3)\text{H}$], 162.8 (C, d, $^1J_{\text{CF}}$ 254.8, aromatic C), 165.5 (C, d, $^1J_{\text{CF}}$ 251.3, aromatic C), 192.4 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{22}\text{H}_{17}\text{SOF}_2[\text{M}+\text{H}^+]$ 367.0968. Found 367.0960; m/z (ES⁺) 367.3 [$(\text{C}_{22}\text{H}_{16}\text{SOF}_2)+\text{H}^+$], 100%.

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



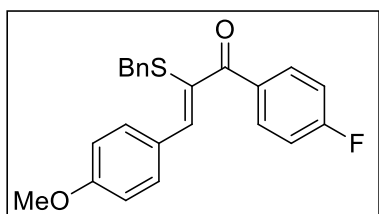
The title compound was prepared following the procedure described above for **14** using the β -chloroenones **Z-4v** and **E-4v** (ratio 2.2:1) (150 mg, 0.5 mmol) and phenyltributylstannane **36a** (220 mg, 0.6 mmol) and anhydrous acetonitrile (5 mL). The crude chalcone was obtained as a yellow oil. ^1H 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 and 37% *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 ^1H NMR spectrum); $\nu_{\max}/\text{cm}^{-1}$ (film) 2932 (CH), 1657 (CO), 1597 (aromatic), 1240; δ_{H} (400 MHz, CDCl_3) 3.99 (2H, s, SCH_2), 6.97 [1H, s, $\text{C}(3)\text{H}$], 7.04 (2H, t, J 8.7, ArH), 7.15 (5H, s, ArH), 7.31–7.41 (3H, m, ArH), 7.57–7.64 (2H, m, ArH), 7.66 (2H, d, J 7.5, ArH); δ_{C} (75.5 MHz, CDCl_3) 36.7 (CH_2 , SCH_2), 115.4 (CH, $^2J_{\text{CF}}$ 21.9, aromatic CH), 127.3, 128.4, 128.5, 129.1, 129.4, 130.3 (5 x CH, aromatic CH), 132.5 (CH, d, $^3J_{\text{CF}}$ 9.0, aromatic CH), 133.5 (C, d, $^4J_{\text{CF}}$ 3.1, aromatic C), 134.7, 135.6, 137.3 [3 x C, 2 x aromatic C and $\text{C}(2)\text{S}$], 139.4 [CH, $\text{C}(3)\text{H}$], 165.4 (C, d, $^1J_{\text{CF}}$ 254.6, aromatic C), 192.5 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{22}\text{H}_{18}\text{SOF}[\text{M}+\text{H}^+]$ 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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* **34** was obtained as a yellow oil. ¹H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 2921 (CH), 1655 (CO), 1597 (aromatic), 1237; δ_{H} (400 MHz, CDCl_3) 3.82 (3H, s, OCH_3), 4.00 (2H, s, SCH_2), 6.90 (1H, d, J 9.0, *ArH*), 6.93 [1H, s, C(3)*H*], 7.04 (2H, t, J 8.7, *ArH*), 7.14 (5H, s, *ArH*), 7.18-7.32 (3H, m, *ArH*), 7.56-7.62 (2H, m, *ArH*); δ_{C} (75.5 MHz, CDCl_3) 36.6 (CH_2 , SCH_2), 55.4 (CH_3 , OCH_3), 115.1 (CH, aromatic CH), 115.4 (CH, d, $^2J_{\text{CF}}$ 21.8, aromatic CH), 123.1, 127.3, 128.5, 129.35, 129.41 (5 x CH, aromatic CH), 132.6 (CH, d, $^3J_{\text{CF}}$ 9.3, aromatic CH), 133.5 (C, d, $^4J_{\text{CF}}$ 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 COCH_3), 165.5 (C, d, $^1J_{\text{CF}}$ 254.7, aromatic C), 192.4 (C, CO), 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 ¹³C NMR spectrum; HRMS (ES⁺): Exact mass calculated for $\text{C}_{23}\text{H}_{20}\text{SO}_2\text{F}[\text{M}+\text{H}^+]$ 379.1168. Found 379.1170; m/z (ES⁺) 379.3 [$(\text{C}_{23}\text{H}_{19}\text{SO}_2\text{F})+\text{H}^+$], 100%.

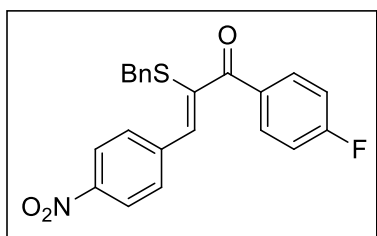
(Z)-2-(Benzylthio)-1-(4-fluorophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one **33**



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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (5%) in anhydrous acetonitrile (5 mL). The crude *chalcone* was obtained as a yellow oil. ¹H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 2932 (CH), 1652 (CO), 1598 (aromatic), 1508, 1253; δ_{H} (400 MHz, CDCl_3) 3.84 (3H, s, OCH_3), 4.01 (2H, s, SCH_2), 6.91 (2H, d, J 8.9, *ArH*), 6.99 [1H, s, C(3)*H*], 7.03

(2H, t, J 8.7, ArH), 7.15 (5H, s, ArH), 7.50-7.59 (2H, m, ArH), 7.70 (2H, d, J 8.7, ArH); δ_{C} (75.5 MHz, CDCl_3) 36.7 (CH_2 , SCH_2), 55.4 (CH_3 , OCH_3), 113.8 (CH, aromatic CH), 115.2 (CH, d, $^2J_{\text{CF}}$ 21.9, aromatic CH), 127.2, 128.4, 129.4 (3 x CH, aromatic CH), 132.4 (CH, d, $^3J_{\text{CF}}$ 8.4, aromatic CH), 132.9 [C, aromatic C or C(2)S], 134.0 (C, d, $^4J_{\text{CF}}$ 2.8, aromatic C), 137.5 [C, aromatic C or C(2)S], 141.0 [CH, C(3)H], 160.4 (C, aromatic COCH_3), 165.3 (C, d, $^1J_{\text{CF}}$ 253.9, aromatic C), 192.8 (C, CO), 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 $\text{C}_{23}\text{H}_{20}\text{SO}_2\text{F}[\text{M}+\text{H}^+]$ 379.1168. Found 379.1160; m/z (ES+) 379.3 [$(\text{C}_{23}\text{H}_{19}\text{SO}_2\text{F})+\text{H}^+$], 32%.

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

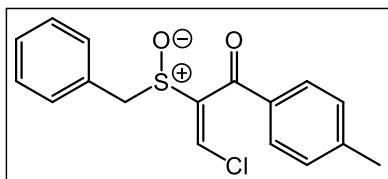


This was prepared following the procedure described for **14** from the β -chloroenones **Z-4v** and **E-4v** (ratio 2.2:1) (150 mg, 0.5 mmol), 4-(tri-*n*-butylstannyl)nitrobenzene **36f**²⁵ (240 mg, 0.6 mmol) and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (5%) in acetonitrile (5 mL).

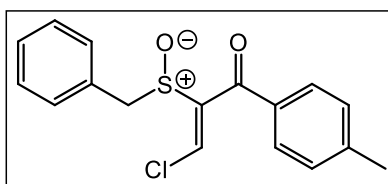
The crude *chalcone* was obtained as an orange oil. ^1H NMR spectroscopy showed the crude product to contain 14% β -chloroenone starting material as a mixture of *Z* and *E* isomers **Z-4v** and **E-4v** in a ratio of 1:4 and 80% *Z* *chalcone* **Z-35**. Signals tentatively assigned as the C(3)H proton 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%); $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3064 (CH), 1659 (CO), 1596 (aromatic), 1517 (NO_2), 1343 (NO_2), 1239; δ_{H} (400 MHz, CDCl_3) 4.00 (2H, s, SCH_2), 6.88 [1H, s, C(3)H], 7.08 (2H, t, J 8.6, ArH), 7.11-7.19 (5H, m, ArH), 7.67-7.73 (2H, m, ArH), 7.75 (2H, d, J 8.6, ArH), 8.82 (2H, d, J 8.8, ArH); δ_{C} (75.5 MHz, CDCl_3) 36.9 (CH_2 , SCH_2), 115.7 (CH, d, $^2J_{\text{CF}}$ 22.0, aromatic CH), 123.6, 127.6, 128.6, 129.3, 130.6 (5 x CH, aromatic CH), 132.7 (CH, d, $^3J_{\text{CF}}$ 9.5, aromatic CH), 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 CNO_2), 165.9 (C, d, $^1J_{\text{CF}}$ 256.2, aromatic CH), 191.6 (C, CO), signal for 1 x aromatic C not seen in ^{13}C NMR spectrum; HRMS (ES+): Exact mass calculated for $\text{C}_{22}\text{H}_{17}\text{NSO}_3\text{F}[\text{M}+\text{H}^+]$ 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

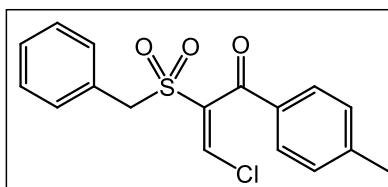
(*E*)-2-(Benzylsulfinyl)-3-chloro-1-(*p*-tolyl)prop-2-en-1-one *E*-38h



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 $\times$ 15 mL). The organic layers were washed with water (2 $\times$ 10 mL) and brine (10 mL), dried, and concentrated under reduced pressure to give a yellow solid. ¹H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3048, 1654 (C=O), 1599, 1284, 1225, 1175, 1061 (S–O), 704; δ_{H} (400 MHz, CDCl₃): 2.45 (3H, s, ArCH₃), 4.14 (1H, A of AB system, J_{AB} 13.0, one of SCH₂), 4.36 (1H, B of AB system, J_{AB} 13.0, one of SCH₂), 6.57 (1H, s, CHCl), 7.27–7.38 (7H, m, ArH), 7.85 (2H, d, J 8.1, ArH); δ_{C} (100 MHz, CDCl₃): 21.9 (CH₃, ArCH₃), 59.8 (CH₂, SCH₂), 127.9 [CH, aromatic CH or C(3)H], 128.1 (C, aromatic C), 128.4 (1 $\times$ CH signal, 2 $\times$ CH, aromatic CH), 128.6 [CH, aromatic CH or C(3)H], 129.8, 130.0, 131.1 (3 $\times$ CH signals, 6 $\times$ CH, aromatic CH), 133.0, 142.8, 146.2 [3 $\times$ C, 2 $\times$ aromatic C and C(2)S], 189.6 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₇H₁₆O₂S³⁵Cl[M+H⁺] 319.0560. Found 319.0550; m/z (ES⁺) 319.2 [(C₁₇H₁₅O₂S³⁵Cl)+H⁺], 11%.

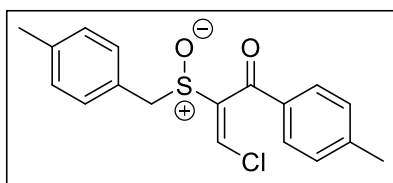


Characteristic signals tentatively assigned as *Z*-38h: δ_{H} (400 MHz, CDCl₃) 2.43 (3H, s, ArCH₃), 4.61 (1H, A of AB system, J_{AB} 12.4, one of SCH₂), 4.72 (1H, B of AB system, J_{AB} 12.3, one of SCH₂), 6.88 (1H, s, CHCl).



Characteristic signals due to *E*-S62: δ_{H} (400 MHz, CDCl₃) 4.56 (2H, s, SCH₂), 7.00 (1H, s, CHCl).

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

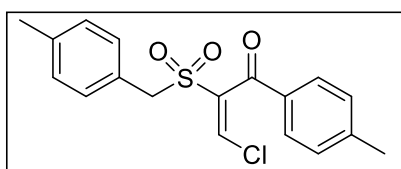


This was prepared following the procedure described above for **38h** using the sulfide **Z-4h** (0.25 g, 0.8 mmol, 1 eq) in acetone (10 mL) and Oxone® (0.51 g, 1.7 mmol, 2.1 eq) in water (5 mL). The reaction mixture was stirred at room

temperature for 2 h and following work-up, the crude sulfoxide was obtained as a yellow oil. The ^1H 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.

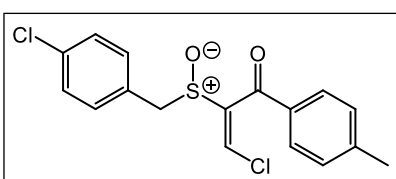
E-38m (less polar): $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 1651 cm^{-1} (C=O), 1053.25 cm^{-1} (S-O); δ_{H} (400 MHz, CDCl_3): 2.35 [3H, s, aromatic CH_3], 2.45 [3H, s, aromatic CH_3], 4.10 [1H, A of AB system, J_{AB} 13.4, one of SCH_2], 4.32 [1H, B of AB system, J_{AB} 13.0, one of SCH_2], 6.60 [1H, s, CHCl], 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 CH_3], 21.9 [CH_3 , aromatic CH_3], 59.6 [CH_2 , SCH_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 CH], 133.0, 138.6, 143.0, 146.2 [4 x C signals, 4 x aromatic C], 189.7 [1 x C signal, CO]; m/z (ES+): 333.2 [$(\text{C}_{18}\text{H}_{17}^{35}\text{ClO}_2\text{S})+\text{H}^+$], 20%. $^{35}\text{Cl}/^{37}\text{Cl}$ pattern visible at 333.2 and 335.2 in a 3:1 ratio. HRMS (ES+): Exact mass calculated for $\text{C}_{18}\text{H}_{17}^{35}\text{ClO}_2\text{S}$ [$\text{M}+\text{H}^+$], 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 SCH_2], 4.67 [1H, B of AB system, J_{AB} 12.3, one of SCH_2].



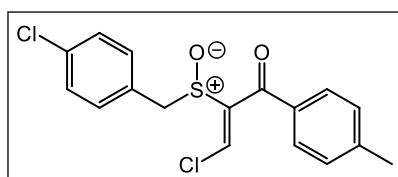
Characteristic signals due to **(E)-3-chloro-2-((4-methylbenzyl)sulfonyl)-1-(p-tolyl)prop-2-en-1-one S63**: δ_{H} (400 MHz, CDCl_3) 4.52 (2H, s, SCH_2).

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

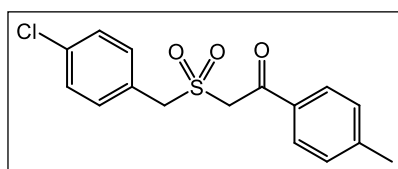


This was prepared following the procedure described above for **38h** using the sulfide **Z-4t** (0.26 g, 0.7 mmol) in acetone (10 mL) and Oxone® (0.94 g, 1.5 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h

and following the work-up, the crude product was obtained as an off-white semisolid. ^1H 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 ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArCH_3), 4.13 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 4.31 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 6.55 (1H, s, CHCl), 7.23 (2H, d, J 8.5, ArH), 7.30–7.36 (4H, m, ArH), 7.85 (2H, d, J 8.3, ArH); δ_{C} (100 MHz, CDCl_3): 21.9 (CH_3 , ArCH_3), 58.6 (CH_2 , SCH_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 $\times$ CH signals, 8 $\times$ CH, aromatic CH), 132.8, 134.8, 142.3, 146.4 [4 $\times$ C, 4 $\times$ aromatic C or 3 $\times$ aromatic C and C(2)S], 189.6 (C, CO); HRMS (ES $^{+}$): Exact mass calculated for $\text{C}_{17}\text{H}_{15}\text{O}_2\text{S}^{35}\text{Cl}_2[\text{M}+\text{H}^{+}]$ 353.0170. Found 353.0168; m/z (ES $^{+}$) 353.1 [$(\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}^{35}\text{Cl}_2)+\text{H}^{+}$], 10%.

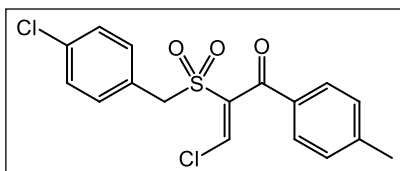


Characteristic signals tentatively assigned as **Z-38t**: δ_{H} (400 MHz, CDCl_3) 2.42 (3H, s, ArCH_3), 4.59 (1H, A of AB system, J_{AB} 12.4, one of SCH_2), 4.66 (1H, B of AB system, J_{AB} 12.3, one of SCH_2), 6.90 (1H, s, CHCl), 7.80 (2H, d, J 8.2, ArH).

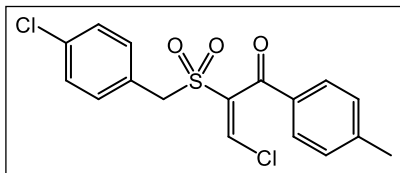


Characteristic signals tentatively assigned as **39a**: δ_{H} (400 MHz, CDCl_3) 2.43 (3H, s, ArCH_3), 4.37 (2H, s, SCH_2), 4.51 (2H, s, SCH_2), 7.48 (2H, d, J 8.5, ArH); δ_{C} (100 MHz, CDCl_3): 21.8 (CH_3 , ArCH_3), 56.7, 58.9 (2 $\times$ CH_2 , SCH_2), 129.3, 129.7 (CH, aromatic CH), 189.0 (C, CO).

aromatic CH), 189.0 (C, CO).

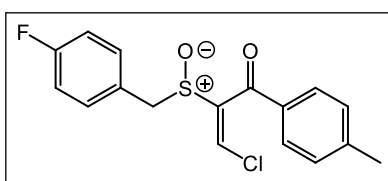


Characteristic signals tentatively assigned as **Z-S64**: δ_{H} (400 MHz, CDCl_3) 4.52 (2H, s, SCH_2), 7.11 (1H, s, CHCl).



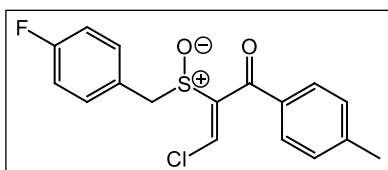
Characteristic signals tentatively assigned as **E-S64**: δ_{H} (400 MHz, CDCl_3) 4.53 (2H, s, SCH_2), 7.07 (1H, s, CHCl).

(*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

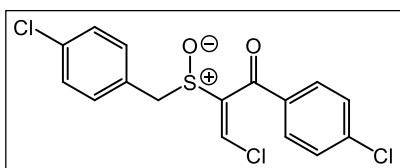
following the work-up, the crude product was obtained as a white solid. ^1H NMR spectroscopy showed this product to contain the desired *sulfoxide* as a mixture of *Z* and *E* isomers, **Z-38aa** and **E-38aa**, in a ratio of 1 : 1.03. Purification by column chromatography on silica gel using hexane–ethyl 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3048, 2921, 1651 ($\text{C}=\text{O}$), 1602, 1508, 1316, 1295, 1223, 1177, 1060 ($\text{S}=\text{O}$), 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, CHCl), 7.05 (2H, overlapping dd appears as t, J 8.6, ArH), 7.20–7.40 (4H, m, ArH), 7.85 (2H, d, J 8.2, ArH); δ_{C} (100 MHz, CDCl_3): 21.9 (CH_3 , ArCH_3), 58.6 (CH_2 , SCH_2), 115.4 (1 $\times$ CH signal, 2 $\times$ CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH), 123.6 (C, d, $^4J_{\text{CF}}$ 3.2, aromatic C), 128.0 [CH, $\text{C}(3)\text{H}$], 129.8, 130.0 (2 $\times$ CH signals, 4 $\times$ CH, aromatic CH), 132.8 (C, aromatic C), 132.9 (1 $\times$ CH signal, 2 $\times$ CH, d, $^3J_{\text{CF}}$ 8.4, aromatic CH), 142.3 [C, $\text{C}(2)\text{S}$], 146.4 (C, aromatic C), 163.0 (C, d, $^1J_{\text{CF}}$ 248.0, aromatic C), 189.7 (C, CO).



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

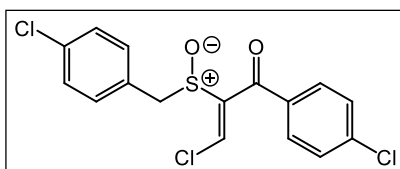
SCH₂), 6.89 (1H, s, CHCl), 7.40 (2H, dd, *J* 8.5, *J*_{FH} 5.3, ArH), 7.82 (2H, d, *J* 8.2, ArH).

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

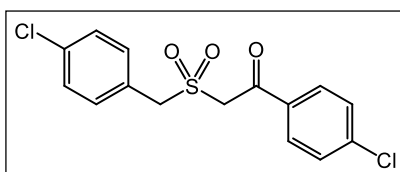


This was prepared following the procedure described above for **38h** using the sulfide **Z-4q** (198 mg, 0.5 mmol) in acetone (10 mL) and Oxone® (682 mg, 1.1 mmol) in water (5 mL). The reaction mixture was stirred at room temperature for 2 h and following the work-up, the crude product was obtained as an off-white solid. ¹H 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: $\nu_{\max}/\text{cm}^{-1}$ (neat) 3054, 1659 (C=O), 1586, 1490, 1222, 1092, 1063 (S–O), 1012, 841; δ_{H} (400 MHz, CDCl₃): 4.16 (1H, A of AB system, *J*_{AB} 13.1, one of SCH₂), 4.34 (1H, B of AB system, *J*_{AB} 13.1, one of SCH₂), 6.58 (1H, s, CHCl), 7.22 (2H, d, *J* 8.4, ArH), 7.34 (2H, d, *J* 8.4, ArH), 7.50 (2H, d, *J* 8.7, ArH), 7.87 (2H, d, *J* 8.7, ArH); δ_{C} (100 MHz, CDCl₃): 58.8 (CH₂, SCH₂), 126.2 (C, aromatic C), 128.7 (1 × CH signal, 2 × CH, aromatic CH), 129.2 [CH, C(3)H], 129.5, 131.1, 132.4 (3 × CH signals, 6 × CH, aromatic CH), 133.6, 135.0, 141.7, 141.8 [4 × C, 3 × aromatic C and C(2)S], 189.1 (C, CO); HRMS (ES⁺): Exact mass calculated for C₁₆H₁₂O₂S³⁵Cl₃[M+H⁺] 372.9624. Found 372.9617; *m/z* (ES⁺) 373.0 [(C₁₆H₁₁O₂S³⁵Cl₃)+H⁺], 14%.



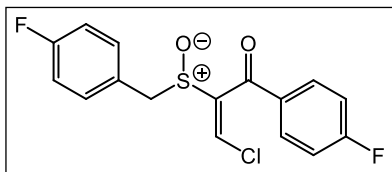
Characteristic signals tentatively assigned as **Z-38q**: δ_{H} (400 MHz, CDCl₃) 4.58 (1H, A of AB system, *J*_{AB} 12.4, one of SCH₂), 4.64 (1H, B of AB system, *J*_{AB} 12.4, one of SCH₂), 6.90 (1H, s, CHCl).



39b (less polar than **Z-38q**): white solid (7 mg, 4%); $\nu_{\max}/\text{cm}^{-1}$ (neat) 2968, 2923, 1685 (C=O), 1589, 1491, 1323; δ_{H} (400 MHz, CDCl₃): 4.35 (2H, s, SCH₂), 4.49 (2H, s, SCH₂), 7.39 (2H, d, *J* 8.4, ArH), 7.49 (4H, dd appears as t, *J* 8.0, ArH), 7.91 (2H, d, *J* 8.6, ArH); δ_{C} (100 MHz, CDCl₃): 56.8, 58.9 (2 × CH₂, SCH₂), 126.0 (C, aromatic C), 129.4,

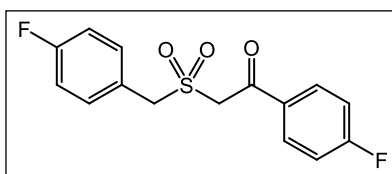
129.5, 130.5, 132.4 (4 × CH signals, 8 × CH, aromatic CH), 134.0, 135.7, 141.6 (3 × C, aromatic C), 188.3 (C, CO).

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



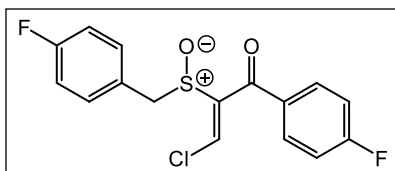
This was prepared following the procedure described above for **38h** using the sulfide **Z-4z** (218 mg, 0.7 mmol) in acetone (10 mL) and Oxone® (826 mg, 1.3 mmol) in water (5 mL). The

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. ¹H 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**; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 3053, 1658 (C=O), 1592, 1506, 1297, 1223, 1154, 1059 (S–O), 848, 730; δ_{H} (400 MHz, CDCl₃): 4.16 (1H, A of AB system, J_{AB} 13.2, one of SCH₂), 4.34 (1H, B of AB system, J_{AB} 13.2, one of SCH₂), 6.55 (1H, s, CHCl), 7.05 (2H, overlapping dd appears as t, J 8.7, ArH), 7.20 (2H, overlapping dd appears as t, J 8.5, ArH), 7.27 (2H, dd, J 8.5, J_{FH} 5.4, ArH), 7.98 (2H, dd, J 8.9, J_{FH} 5.2, ArH); δ_{C} (100 MHz, CDCl₃): 58.7 (CH₂, SCH₂), 115.5 (1 × CH signal, 2 × CH, d, $^2J_{\text{CF}}$ 21.9, aromatic CH), 116.4 (1 × CH signal, 2 × CH, d, $^2J_{\text{CF}}$ 22.2, aromatic CH), 123.5 (C, d, $^4J_{\text{CF}}$ 3.3, aromatic C), 128.7 [CH, C(3)H], 131.8 (C, d, $^4J_{\text{CF}}$ 3.0, aromatic C), 132.6 (1 × CH signal, 2 × CH, d, $^3J_{\text{CF}}$ 9.9, aromatic CH), 132.9 (1 × CH signal, 2 × CH, d, $^3J_{\text{CF}}$ 8.4, aromatic CH), 142.0 [C, C(2)S], 163.0 (C, d, $^1J_{\text{CF}}$ 248.5, aromatic C), 166.8 (C, d, $^1J_{\text{CF}}$ 258.4, aromatic C), 188.6 (C, CO); m/z (ES+) 341.1 [(C₁₆H₁₁O₂S³⁵ClF₂)+H⁺], 26%.

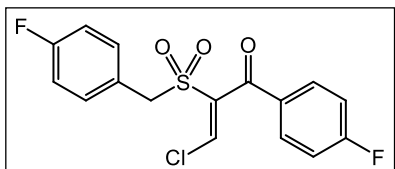


Characteristic signals due to **39c**: δ_{H} (400 MHz, CDCl₃) 4.38 (2H, s, SCH₂), 4.50 (2H, s, SCH₂), 7.53 (2H, dd, J 8.6, J_{FH} 5.3, ArH); δ_{C} (100 MHz, CDCl₃): 56.7, 58.7 (2 × CH₂, SCH₂), 116.3 (2 × CH, d, $^2J_{\text{CF}}$ 22.2, aromatic CH), 123.4 (C, d, $^4J_{\text{CF}}$ 3.3,

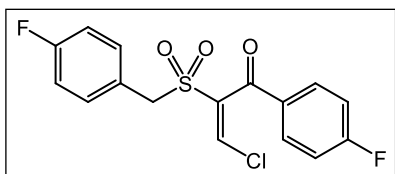
aromatic C), 132.1 (2 × CH, d, $^3J_{\text{CF}}$ 9.8, aromatic CH), 187.9 (C, CO).



Characteristic signals tentatively assigned as **Z-38z** (from ^1H 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, CHCl).



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



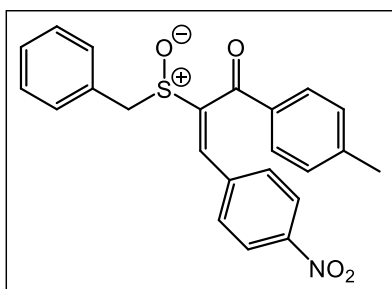
Characteristic signals tentatively assigned as **E-S65**: δ_{H} (400 MHz, CDCl_3) 4.53 (2H, s, SCH_2).

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

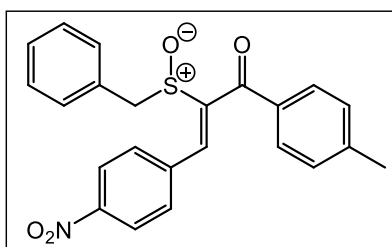
(E)-2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(p-tolyl)prop-2-en-1-one E-40h and **(Z)-2-(Benzylsulfinyl)-3-(4-nitrophenyl)-1-(p-tolyl)prop-2-en-1-one Z-40h**

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, $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (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 $\times$ 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. ^1H 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; $\nu_{\max}/\text{cm}^{-1}$ (neat) 3063, 3027, 2921, 2848, 1626 (C=O), 1601, 1514 (NO₂), 1341 (NO₂), 1056, 734; δ_{H} (400 MHz, CDCl₃): 2.36 (3H, s, ArCH₃), 4.12 (1H, A of AB system, J_{AB} 13.1, one of SCH₂), 4.35 (1H, B of AB system, J_{AB} 13.1, one of SCH₂), 7.04 [1H, s, C(3)H], 7.17 (2H, d, J 8.1, ArH), 7.25–7.34 (7H, m, ArH), 7.76 (2H, d, J 8.2, ArH),

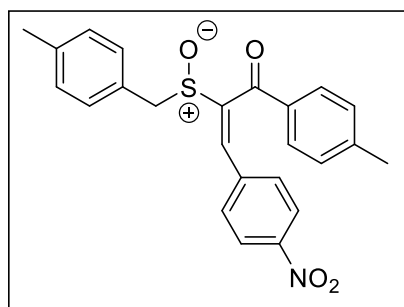
8.01 (2H, d, J 8.7, ArH); δ_{C} (100 MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 59.4 (CH₂, SCH₂), 123.7 (1 × CH, aromatic CH), 128.2 [1 × C, aromatic C or C(2)S], 128.3, 128.5, 129.8, 129.9, 130.1, 131.0 (6 × CH, aromatic CH), 132.6 [1 × C, aromatic C or C(2)S], 133.3 [1 × CH, C(3)H], 139.0, 145.3, 146.4, 147.7 [4 × C, 4 × aromatic C or 3 × aromatic C and C(2)S], 192.7 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₂₀NO₄S[M+H⁺] 406.1113. Found 406.1100; m/z (ES⁺) 406.1 [(C₂₃H₁₉NO₄S)+H⁺], 100%.



Z-40h (more polar): $\nu_{\max}/\text{cm}^{-1}$ (neat) 3030, 2979, 2918, 1655 (C=O), 1601, 1511 (NO₂), 1343 (NO₂), 1039, 754, 704; δ_{H} (400 MHz, CDCl₃): 2.45 (3H, s, ArCH₃), 4.44 (1H, A of AB system, J_{AB} 12.2, one of SCH₂), 4.97 (1H, B of AB system, J_{AB} 12.2, one of SCH₂), 6.95 (2H, d, J 8.4, ArH), 7.11–7.45 [8H, m, containing [7.25, 1H, s, C(3)H] and ArH], 7.91 (2H, d, J 8.2, ArH), 8.02 (2H, d, J 8.8, ArH); δ_{C}

(100 MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 59.2 (CH₂, SCH₂), 123.2, 128.7, 128.9 (3 × CH, aromatic CH), 129.3 [1 × C, aromatic C or C(2)S], 129.5, 130.4, 130.5, 130.9 (4 × CH, aromatic CH), 134.6, 138.1 [2 × C, 2 × aromatic C or aromatic C and C(2)S], 140.7 [1 × 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, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₂₀NO₄S[M+H⁺] 406.1113. Found 406.1115.

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

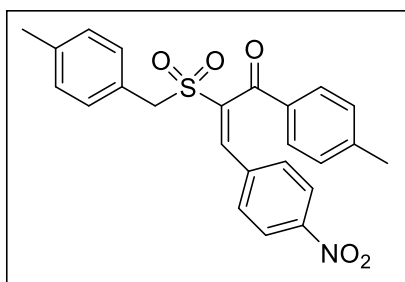


This was prepared following the procedure described above for **40h** using the sulfoxide 3-Chloro-2-((4-methylbenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one **E-14h** (0.04 g, 0.1 mmol, 1 eq), tributyl(4-nitrophenyl)stannane **36f**²⁵ (0.06 g, 0.1 mmol, 1.3 eq) and (CH₃CN)₂PdCl₂ (0.0016 g, 0.006 mmol 5 mol %) in acetonitrile (15 mL). The reaction

mixture was stirred under reflux for 5 h, and following work-up, the crude chalcone was

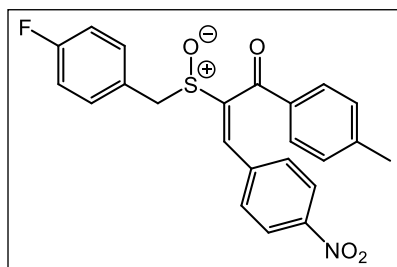
obtained as a light amber oil. The ^1H NMR spectrum of the crude product showed approximately 90% *E* chalcone **E-40m** with 10% of the tentatively assigned sulfone **S66** as a singlet at δ 4.59 ppm. The crude chalcone was purified by column chromatography on silica gel using dichloromethane (100%)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

E-40m: $\nu_{\text{max}}/\text{cm}^{-1}$ (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, ArCH_3), 2.36 (3H, s, ArCH_3), 4.07 (1H, A of AB system, J_{AB} 13.1, one of SCH_2), 4.32 (1H, B of AB system, J_{AB} 13.1, one of SCH_2), 7.07 – 7.13 [3H, m, ArH and $\text{C}(3)\text{H}$], 7.15 – 7.23 (4H, m, ArH), 7.30 (2H, d, J 8.8, ArH), 7.76 (2H, d, J 8.3, ArH), 8.01 (2H, d, J 8.8, ArH); δ_{C} (125 MHz, CDCl_3): 21.2 (CH_3 , aromatic CH_3), 21.9 (CH_3 , aromatic CH_3), 59.4 (CH_2 , SCH_2), 123.8 (1 x CH, aromatic CH), 125.3 [1 x C signal, aromatic C or $\text{C}(2)\text{S}$], 129.1, 129.9, 130.1, 130.9 [4 x CH, aromatic CH], 132.7 (1 x C signal, aromatic C), 133.1 [1 x CH signal, $\text{C}(3)\text{H}$], 138.5, 139.1 (2 x C signals, 2 x aromatic C), 145.8 [1 x C signal, aromatic C or $\text{C}(2)\text{S}$], 146.4, 147.8 (2 x C signals, 2 x aromatic C), 192.8 (1 x C signal, CO); m/z (ES+): 420.2 [$(\text{C}_{24}\text{H}_{21}\text{NO}_4\text{S})+\text{H}^+$], 34%. HRMS (ES+): Exact mass calculated for $\text{C}_{24}\text{H}_{21}\text{NO}_4\text{S}$ [$\text{M}+\text{H}^+$] 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, SCH_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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (4 mg, 16 μmol , 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 24

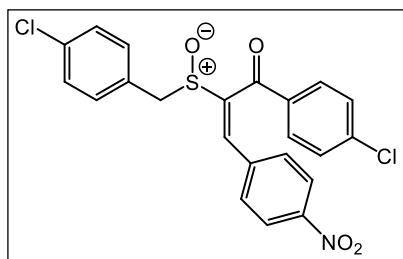
h and after work-up, the crude product was obtained as a brown oil. ^1H NMR spectroscopy showed approx. 94% conversion to the chalcone **E-40aa**. Trace quantities of the *Z* chalcone **40aa** (3%) were also visible. Purification by column chromatography on silica gel using

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: $\nu_{\max}/\text{cm}^{-1}$ (neat) 1645 (C=O), 1599, 1507 (NO₂), 1342 (NO₂), 1225, 1059, 830; δ_{H} (400 MHz, CDCl₃): 2.37 (3H, s, ArCH₃), 4.11 (1H, A of AB system, J_{AB} 13.3, one of SCH₂), 4.32 (1H, B of AB system, J_{AB} 13.2, one of SCH₂), 6.94–7.09 [3H, m, containing (6.99, 2H, dd appears as t, J 8.2, ArH) and [7.01, 1H, s, C(3)H]], 7.18 (2H, d, J 8.0, ArH), 7.24–7.34 (4H, m, ArH), 7.76 (2H, d, J 8.2, ArH), 8.02 (2H, d, J 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 58.2 (CH₂, SCH₂), 115.3 (1 × CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH), 123.83 (1 × C, d, $^4J_{\text{CF}}$ 3.4, aromatic C), 123.86 (1 × CH, aromatic CH), 129.8, 129.9, 130.0 (3 × CH, aromatic CH), 132.5 (1 × C, aromatic C), 132.8 (1 × CH, d, $^3J_{\text{CF}}$ 8.3, aromatic CH), 133.3 [1 × CH, C(3)H], 138.8 (1 × C, aromatic C), 144.9 [1 × C, C(2)S], 146.6, 147.8 (2 × C, aromatic C), 162.9 (C, d, $^1J_{\text{CF}}$ 247.6, aromatic C), 192.8 (C, CO); m/z (ES+) 424.1 [(C₂₃H₁₈FNO₄S)+H⁺], 68%.

Characteristic signals tentatively assigned as **Z-40aa**: δ_{H} (400 MHz, CDCl₃): 4.45 (1H, A of AB system, J_{AB} 12.2, one of SCH₂), 4.86 (1H, B of AB system, J_{AB} 12.2, one of SCH₂).

(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 (CH₃CN)₂PdCl₂ (2 mg, 6 μmol, 5 mol %) in acetonitrile (10 mL). The mixture was stirred at room temperature for 21 h

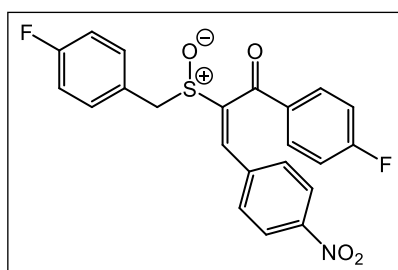
and after work-up, the crude product was obtained as an orange oil. ¹H NMR spectroscopy showed approx. 20% sulfoxide starting material **E-14q**, 68% chalcones **Z-40q** and **E-40q** (*Z* : *E*, 1 : 5.7) and 12% bi-aryl **37**²⁶. Purification by column chromatography on silica gel using dichloromethane (100%) as eluent gave the *chalcone E-40q* (27 mg, 45%) as a yellow solid, mp 43–46°C; $\nu_{\max}/\text{cm}^{-1}$ (neat) 2924, 2853, 1651 (C=O), 1586, 1520, 1345 (NO₂), 1225, 1093, 836; δ_{H} (400 MHz, CDCl₃): 4.14 (1H, A of AB system, J_{AB} 13.2, one of SCH₂), 4.34 (1H, B of AB system, J_{AB} 13.2, one of SCH₂), 7.06 [1H, s, C(3)H], 7.20–7.50 [8H, m, ArH, containing (7.36, 2H, d, J 8.7, ArH)], 7.78 (2H, d, J 8.7, ArH), 8.04 (2H, d, J 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 58.5 (CH₂, SCH₂), 123.9 (1 × CH, aromatic CH), 126.3 [1 × C, aromatic C or C(2)S], 128.5, 129.6, 130.1, 130.9, 132.3 (5 × CH, aromatic CH), 133.2 [1 × C, aromatic C or C(2)S], 134.3 [1 × 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, CO); HRMS (ES+): Exact mass calculated for C₂₂H₁₆NO₄S³⁵Cl₂[M+H⁺] 460.0177. Found 460.0160; m/z (ES+) 460.0 [(C₂₂H₁₅NO₄S³⁵Cl₂)+H⁺], 12%.

Characteristic signals tentatively assigned as **Z-40q**: δ_H (400 MHz, CDCl₃): 4.44 (1H, A of AB system, *J*_{AB} 12.2, one of SCH₂), 4.83 (1H, B of AB system, *J*_{AB} 12.2, one of SCH₂).

A ¹H 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 (CH₃CN)₂PdCl₂ (4 mg, 18 μmol, 5 mol %) in acetonitrile (10

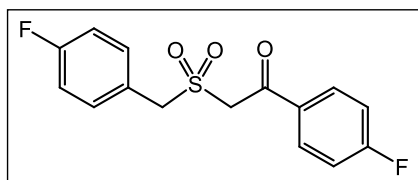
mL). The mixture was stirred at room temperature for 21 h and after work-up, the crude product was obtained as a brown residue. ¹H NMR spectroscopy showed formation of the *E* chalcone **E-40z** and trace quantities of the *Z* chalcone **Z-40z** (<2%). The bi-aryl **37**²⁶ accounted for approx. 20% of 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, CDCl₃): 4.15 (1H, A of AB system, *J*_{AB} 13.3, one of SCH₂), 4.35 (1H, B of AB system, *J*_{AB} 13.2, one of SCH₂), 6.93–7.15 [5H, m, 4 × ArH and C(3)H], 7.24–7.34 (4H, m, ArH), 7.89 (2H, dd, *J* 8.7, *J*_{FH} 5.3, ArH), 8.04 (2H, d, *J* 8.7, ArH); δ_C (100 MHz, CDCl₃): 58.4 (CH₂, SCH₂), 115.3 (1 × CH, d, ²*J*_{CF} 21.6, aromatic CH), 116.5 (1 × CH, d, ²*J*_{CF} 22.2, aromatic CH), 123.6 (1 × C, d, ⁴*J*_{CF} 3.0, aromatic C), 123.9, 130.1 (2 × CH, aromatic CH), 131.4 (1 × C, d, ⁴*J*_{CF} 2.9, aromatic C), 132.5 (1 × CH, d, ³*J*_{CF} 9.9, aromatic CH), 132.8 (1 × CH, d, ³*J*_{CF} 8.3, aromatic CH), 134.1 [1 × CH, C(3)H], 138.5 (1 × C, aromatic C), 144.4 [1 × C, C(2)S], 148.0 (1 × C, aromatic C), 163.0 (1 × C, d, ¹*J*_{CF}

248.2, aromatic C), 166.8 (1 x C, d, $^1J_{\text{CF}}$ 259.5, aromatic C), 191.7 (C, CO). HRMS (ES⁺): Exact mass calculated for C₂₂H₁₆NO₄F₂S[M+H⁺] 428.0768. Found 428.0778.

Characteristic signals tentatively assigned as **Z-40z**: δ_{H} (400 MHz, CDCl₃): 4.45 (1H, A of AB system, J_{AB} 12.5, one of SCH₂), 4.85 (1H, B of AB system, J_{AB} 12.4, one of SCH₂).

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



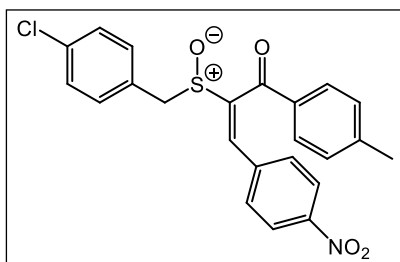
39c (less polar than **E-40z**): fine yellow crystals (16 mg, 14%); mp 150–153°C; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 2961, 2922, 1679 (C=O), 1594, 1504, 1303, 1133 (S=O), 1124, 996, 834, 824,

517; δ_{H} (400 MHz, CDCl₃): 4.36 (2H, s, SCH₂), 4.50 (2H, s, SCH₂), 7.11 (2H, t, J 8.6, ArH), 7.15–7.24 (2H, m, ArH), 7.49–7.61 (2H, m, ArH), 7.98–8.07 (2H, m, ArH); δ_{C} (100 MHz, CDCl₃): 56.7, 58.7 (2 x CH₂, SCH₂), 116.2 (1 x CH, d, $^2J_{\text{CF}}$ 21.6, aromatic CH), 116.3 (1 x CH, d, $^2J_{\text{CF}}$ 22.2, aromatic CH), 123.4 (1 x C, d, $^4J_{\text{CF}}$ 3.5, aromatic C), 132.1 (1 x CH, d, $^3J_{\text{CF}}$ 9.8, aromatic CH), 133.0 (1 x CH, d, $^3J_{\text{CF}}$ 8.5, aromatic CH), 187.9 (C, CO); m/z (ES[–]) 309.2 [(C₁₅H₁₂F₂O₃S)–H⁺], 42%. 3 x C_q were not observed.

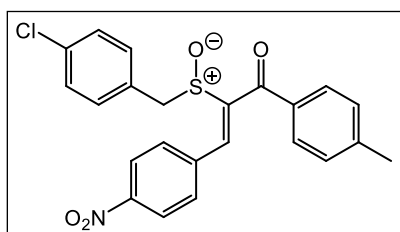
Impurity (approx. 20%) present in this sample; δ_{H} (400 MHz, CDCl₃): 7.25–7.45 (m); δ_{C} (100 MHz, CDCl₃): 115.9, 131.2 (1 x C, d, $^4J_{\text{CF}}$ 9.3, aromatic C), 141.1.

(**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 **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 (CH₃CN)₂PdCl₂ (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. ¹H 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.

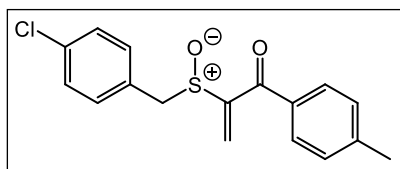


E-40t (less polar): $\nu_{\max}/\text{cm}^{-1}$ (neat) 3037, 2921, 1644 (C=O), 1600, 1519 (NO₂), 1342 (NO₂), 1060, 726; δ_{H} (400 MHz, CDCl₃): 2.37 (3H, s, ArCH₃), 4.10 (1H, A of AB system, J_{AB} 13.2, one of SCH₂), 4.31 (1H, B of AB system, J_{AB} 13.2, one of SCH₂), 7.02 [1H, s, C(3)H], 7.18 (2H, d, J 8.0, ArH), 7.25–7.31 (6H, m, ArH), 7.76 (2H, d, J 8.3, ArH), 8.02 (2H, d, J 8.8, ArH); δ_{C} (100 MHz, CDCl₃): 21.9 (CH₃, ArCH₃), 58.3 (CH₂, SCH₂), 123.8 (1 × CH, aromatic CH), 126.5 (1 × C, aromatic C), 128.5, 129.8, 129.9, 130.1, 132.43 (5 × CH, aromatic CH), 132.48 (1 × C, aromatic C), 133.3 [1 × CH, C(3)H], 134.7, 138.7 (2 × C, aromatic C), 144.9 [1 × C, C(2)S], 146.7, 147.8 (2 × C, aromatic C), 192.8 (C, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₁₉NO₄S³⁵Cl[M+H⁺] 440.0723. Found 440.0707; m/z (ES⁺) 440.1 [(C₂₃H₁₈NO₄S³⁵Cl)+H⁺], 100%, 442.1 [(C₂₃H₁₈NO₄S³⁷Cl)+H⁺], 40%.



Z-40t (more polar): $\nu_{\max}/\text{cm}^{-1}$ (neat) 2922, 2855, 1650 (C=O), 1601, 1519 (NO₂), 1343 (NO₂), 1055, 727; δ_{H} (400 MHz, CDCl₃): 2.45 (3H, s, ArCH₃), 4.43 (1H, A of AB system, J_{AB} 12.2, one of SCH₂), 4.85 (1H, B of AB system, J_{AB} 12.2, one of SCH₂), 7.12 (2H, d, J 8.6, ArH), 7.15–7.40 [7H, m, containing (7.19, 2H, d, J 8.4, ArH), 7.23 [1H, s, C(3)H], 7.33 (2H, d, J 8.0, ArH) and ArH], 7.91 (2H, d, J 8.2, ArH), 8.09 (2H, d, J 8.7, ArH); δ_{C} (100 MHz, CDCl₃): 21.8 (CH₃, ArCH₃), 58.6 (CH₂, SCH₂), 123.3 (1 × CH, aromatic CH), 127.7 (1 × C, aromatic C), 129.0, 129.6, 130.4, 130.5, 132.1 (5 × CH, aromatic CH), 134.3, 134.9, 138.0 [3 × C, 3 × aromatic C or 2 × aromatic C and C(2)S], 140.7 [1 × 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, CO); m/z (ES⁺) 440.1 [(C₂₃H₁₈NO₄S³⁵Cl)+H⁺], 34%, 442.1 [(C₂₃H₁₈NO₄S³⁷Cl)+H⁺], 16%.

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

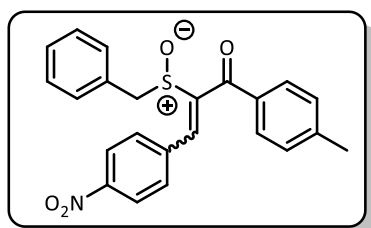


S67: orange oil (6 mg, 4%); $\nu_{\max}/\text{cm}^{-1}$ (neat) 3031, 2920, 1666 (C=O), 1603, 1489, 1178, 1091, 1014, 830, 502; δ_{H} (400 MHz, CDCl₃): 2.45 (3H, s, ArCH₃), 4.08 (1H, A of AB system, J_{AB} 13.4, one of SCH₂), 4.30 (1H, B of AB system, J_{AB} 13.4, one of SCH₂), 6.38, 6.40 [2 × 1H, s, C(3)H₂], 7.12 (2H, d, J 8.4, ArH), 7.24–7.33 (4H, m, ArH), 7.59 (2H, d, J 8.2, ArH); δ_{C} (100 MHz, CDCl₃): 21.7 (CH₃, ArCH₃), 57.2 (CH₂, SCH₂), 127.9 [1 × C, aromatic C or C(2)S], 128.5, 129.4, 129.5, 131.7 (4 × CH, aromatic CH), 132.5 [CH₂, C(3)H₂], 133.4, 134.4, 144.8, 150.1 [4 × C, 4 × aromatic C or 3 × aromatic C and C(2)S], 192.1 (C, CO).

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. ^1H 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**

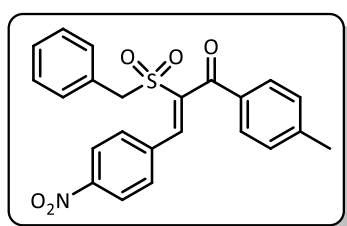


A solution of Oxone[®] (0.06 g, 0.2 mmol, 2.1 eq) in water (2.5 mL) was added dropwise to a stirring solution of 2-(benzylthio)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **20** (0.04 g, 0.1 mmol, 1 eq) in acetone (5 mL) at room temperature. A cloudy-yellow precipitate formed immediately and the 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. ^1H 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: $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 1655 cm^{-1} (C=O), 1512 (NO_2), 1040; δ_{H} (400 MHz, CDCl_3): 2.37 [3H, s, aromatic CH_3], 4.44 [1H, A of AB system, J 12.4, one of SCH_2], 4.99 [1H, B of AB system, J 12.4, one of SCH_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 CH_3], 59.2 [CH_2 , SCH_2], 123.2, 128.7, 128.9 [3 x CH signals, aromatic CH], 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 CH], 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],

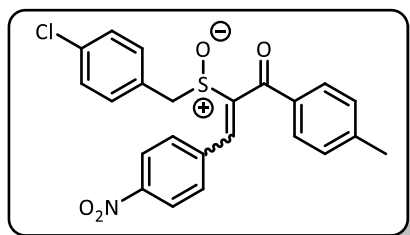
192.5 [1 x C signal, CO]; HRMS (ES+): Exact Mass Calculated for $C_{33}H_{29}^{35}Cl_2NO_4S$ [$M+H^+$] 606.091194. Found 606.09120.

Characteristic E-40h signals: δ_H (400 MHz, $CDCl_3$): 2.37 [3H, s, aromatic CH_3], 4.13 [1H, A of AB system, J_{AB} 13.4, one of SCH_2], 4.36 [1H, B of AB system, J_{AB} 13.4, one of SCH_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 , SCH_2], 123.8, 128.4, 128.6, 129.85, 129.88, 130.1, 131.0 [7 x CH signals, aromatic CH], 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, SCH_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-tolyl)prop-2-en-1-

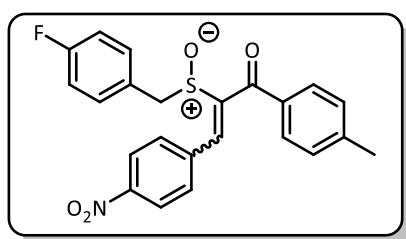
one **40h**. The crude oxidised chalcone was isolated as a yellow semi-solid. 1H NMR spectroscopy showed this product to contain 75% chalcone as a mixture of isomers **Z-40j** and **E-40j** (Z:E; 4.5 : 1) along with unreacted starting material **Z-21** (Z isomer, 25%) remaining. The crude mixture was 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: ν_{max}/cm^{-1} (neat) 1650 cm^{-1} (C=O), 1518 (NO_2), 1040; δ_H (500 MHz, $CDCl_3$): 2.46 [3H, s, aromatic CH_3], 4.43 [1H, A of AB system, J_{AB} 12.3, one of SCH_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 CH_3], 58.7 [CH_2 , SCH_2],

123.3 [1 x CH signal, aromatic CH], 127.7 [1 x C signal, aromatic C], 129.0, 129.6, 130.4, 130.6, 132.1 [5 x CH signals, aromatic CH], 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, CO]; HRMS (ES⁺): Exact Mass Calculated for C₂₃H₁₈³⁵ClNO₄S [M+H⁺] 440.0718. Found 440.0717.

Characteristic E-40j signals: δ_H (500 MHz, CDCl₃): 2.37 [3H, s, aromatic CH₃], 4.10 [1H, A of AB system, J_{AB} 13.2, one of SCH₂], 4.32 [1H, B of AB system, J_{AB} 13.2, one of SCH₂], 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, CDCl₃): 58.4 [CH₂, SCH₂], 123.9, 128.5, 129.85, 129.93, 130.1, 132.4 [6 x CH signals, aromatic CH].

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*-tolyl)prop-2-en-1-one **40h**.

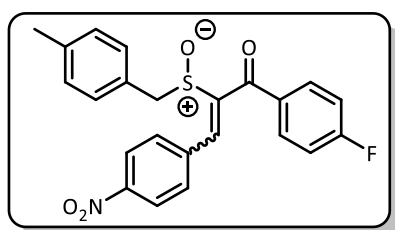
The crude oxidised chalcone was isolated as a yellow semi-solid. ¹H NMR spectroscopy showed this product to contain 94% chalcone as a mixture of isomers *Z*-**40l** and *E*-**40l** (Z:E; 16 : 1) along with unreacted starting material *Z*-**22** (*Z* isomer, 6%) . The crude mixture was purified by column 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: $\nu_{\max}/\text{cm}^{-1}$ (neat) 1650 cm⁻¹ (C=O), 1506 (NO₂), 1040; δ_H (500 MHz, CDCl₃): 2.46 [3H, s, aromatic CH₃], 4.44 [1H, A of AB system, J_{AB} 12.3, one of SCH₂], 4.87 [1H, B of AB system, J_{AB} 12.3, one of SCH₂], 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, CDCl₃): 21.8 [CH₃, aromatic CH₃], 58.3 [CH₂, SCH₂], 115.9 [1 x CH signal, d, ² J_{CF} 20.7, aromatic CH], 123.3 [1 x CH signal, aromatic CH], 125.2 [1 x C signal, d, ⁴ J_{CF} 3.0, aromatic C], 129.6, 130.4, 130.6 [3 x CH signals, aromatic CH], 132.6 [1 x CH signal, d, ³ J_{CF} 8.2, aromatic CH], 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, $^1J_{CF}$ 251.6, aromatic C], 192.4 [1 x C signal, CO]; m/z (ES+): 424.1 [(C₂₃H₁₈FNO₄S)+H⁺], 5%.

Characteristic E-40l signals: δ_H (500 MHz, CDCl₃): 2.37 [3H, s, aromatic CH₃], 4.11 [1H, A of AB system, J_{AB} 13.3, one of SCH₂], 4.32 [1H, B of AB system, J_{AB} 13.3, one of SCH₂], 7.77 [2H, d, J 8.1, aromatic H], 8.02 [2H, d, J 8.7, aromatic H]; δ_c (125 MHz, CDCl₃): 115.3 [1 x CH signal, d, $^2J_{CF}$ 20.8, aromatic CH], 123.8, 129.8, 129.9, 130.0 [4 x CH signals, aromatic CH].

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



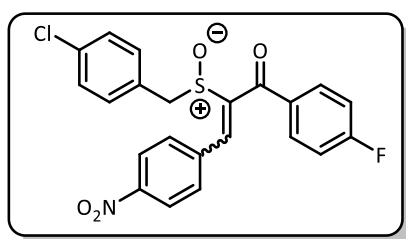
1-(4-Fluorophenyl)-2-((4-methylbenzyl)thio)-3-(4-nitrophenyl)prop-2-en-1-one **29** (0.03 g, 0.07 mmol, 1 eq) in acetone (25 mL) and a solution of Oxone® (0.08 g, 0.3 mmol, 3.8 eq) in water (10 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **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. 1H 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. ν_{max}/cm^{-1} (neat) 1656 (C=O), 1519 (NO₂); δ_H (500 MHz, CDCl₃): 2.29 [3H, s, *E* isomer, aromatic CH₃], 2.29 [3H, s, *Z* isomer, aromatic CH₃], 4.11 [1H, A of AB system, J_{AB} 13.0, *E* isomer, one of SCH₂], 4.35 [1H, B of AB system, J_{AB} 13.0, *E* isomer, one of SCH₂], 4.41 [1H, A of AB system, J_{AB} 11.9, *Z* isomer, one of SCH₂], 4.90 [1H, B of AB system, J_{AB} 11.9, *Z* isomer, one of SCH₂], 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 C₂₃H₁₈FNO₄S [M+H⁺] 424.1013. Found 424.1017.

E-40aa: δ_c (125 MHz, CDCl₃): 29.7 [CH₃, aromatic CH₃], 59.5 [CH₂, SCH₂], 116.5 [1 x CH signal, d, $^2J_{CF}$ 22.2, aromatic CH], 123.8 [1 x CH signal, aromatic CH], 125.0 [1 x C signal, aromatic C or

C(2)S], 129.2, 130.1, 130.9 [3 x CH signal, aromatic CH], 131.6 [1 x C signal, d, $^4J_{CF}$ 3.1, aromatic C], 132.5 [1 x CH signal, d, $^3J_{CF}$ 9.7, aromatic CH], 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, 1J 258.8, aromatic C], 191.7 [1 x C signal, CO].

Characteristic Z-40aa signals: δ_c (125 MHz, CDCl₃): 28.9 [CH₃, aromatic CH₃], 59.1 [CH₂, SCH₂], 116.1 [1 x CH signal, d, $^2J_{CF}$ 22.2, aromatic CH], 123.2 [1 x CH signal, aromatic CH], 126.0 [1 x C signal, aromatic C or C(2)S], 129.6, 130.5, 130.8 [3 x CH signals, aromatic CH], 133.2 [1 x CH signal, d, $^3J_{CF}$ 9.7, aromatic CH], 133.5 [1 x C signal, d, $^4J_{CF}$ 3.1, aromatic C], 140.2 [1 x CH signal, C(3)H], 191.3 [1 x C signal, CO].

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*-

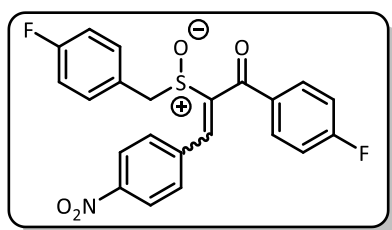
tolyl)prop-2-en-1-one **40h**. The solution was stirred at 35°C for 7.5 h and following work-up, the crude oxidised chalcone was isolated as a yellow oil with the presence of some yellow solids. ^1H NMR spectroscopy showed this product to contain 90.9% chalcone as a mixture of isomers **Z-40x** and **E-40x** (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: $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 1657 cm^{-1} (C=O), 1519 (NO₂), 1049 cm^{-1} ; δ_H (500 MHz, CDCl₃): 4.43 [1H, A of AB system, J_{AB} 11.9, one of SCH₂], 4.82 [1H, B of AB system, J_{AB} 11.9, one of SCH₂], 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, CDCl₃): 58.8 [CH₂, SCH₂], 116.2 [1 x CH signal, d, $^2J_{CF}$ 22.1, aromatic CH], 123.4 [1 x CH signal, aromatic CH], 127.6 [1 x C signal, aromatic C or C(2)S], 129.1, 130.4,

132.1 [3 x CH signal, aromatic CH], 133.2 [1 x CH signal, d, $^3J_{\text{CF}}$ 9.9, aromatic CH], 133.3 [1 x C signal, d, $^4J_{\text{CF}}$ 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, $^1J_{\text{CF}}$ 257.8, aromatic C], 191.1 [1 x C signal, CO]; HRMS (ES⁺): Exact Mass Calculated for C₂₂H₁₅³⁵ClFNO₄S [M+H⁺] 444.046711. Found 444.04692.

Characteristic E-40x signals: δ_{H} (500 MHz, CDCl₃): 4.14 [1H, A of AB system, J_{AB} 13.2, one of SCH₂], 4.35 [1H, B of AB system, J_{AB} 13.2, one of SCH₂], 7.89 [2H, dd, J 8.8, J_{FH} 5.3, aromatic H]; δ_{C} (125 MHz, CDCl₃): 58.5 [CH₂, SCH₂], 116.6 [1 x CH signal, d, $^2J_{\text{CF}}$ 22.1, aromatic CH], 123.9 [1 x CH signal, aromatic CH], 191.8 [1 x C signal, CO].

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



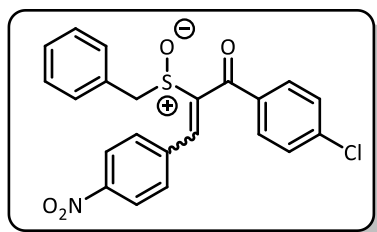
2-((4-Fluorobenzyl)thio)-1-(4-fluorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one **28** (0.06 g, 0.13 mmol, 1 eq) in acetone (8 mL) and a solution of Oxone[®] (0.08 g, 0.27 mmol, 2.1 eq) in water (2.5 mL) were used following the procedure for 2-(benzylsulfinyl)-3-(4-nitrophenyl)-1-(*p*-tolyl)prop-2-en-1-one **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. ¹H 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: ν_{max} /cm⁻¹ (neat) 1657 cm⁻¹ (C=O), 1507 (NO₂), 1040 cm⁻¹; δ_{H} (500 MHz, CDCl₃): 4.45 [1H, A of AB system, J_{AB} 12.4, one of SCH₂], 4.84 [1H, B of AB system, J_{AB} 12.4, one of SCH₂], 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, CDCl₃): 58.5 [CH₂, SCH₂], 116.0 [1 x CH signal, d, $^2J_{\text{CF}}$ 22.3, aromatic CH], 116.2 [1 x CH signal, d, $^2J_{\text{CF}}$ 22.3, aromatic CH], 123.4 [1 x CH signal, aromatic CH], 125.0 [1 x C signal, d, $^4J_{\text{CF}}$ 3.5, aromatic C], 130.4 [1 x CH signal, aromatic CH],

132.6 [1 x CH signal, d, $^3J_{\text{CF}}$ 8.5, aromatic CH], 133.2 [1 x CH signal, d, $^3J_{\text{CF}}$ 8.8, aromatic CH], 133.4 [1 x C signal, d, $^4J_{\text{CF}}$ 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, $^1J_{\text{CF}}$ 248.6, aromatic C], 166.6 [1 x C signal, d, $^1J_{\text{CF}}$ 257.8, aromatic C], 191.3 [1 x C signal, CO]; HRMS (ES+): Exact Mass Calculated for $\text{C}_{22}\text{H}_{15}\text{F}_2\text{NO}_4\text{S}$ $[\text{M}+\text{H}^+]$ 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 SCH_2], 4.36 [1H, B of AB system, J_{AB} 13.3, one of SCH_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 , SCH_2], 115.4 [1 x CH signal, d, $^2J_{\text{CF}}$ 21.6, aromatic CH], 116.6 [1 x CH signal, d, $^2J_{\text{CF}}$ 21.6, aromatic CH], 123.9, 130.1 [2 x CH signals, aromatic CH].

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. ^1H 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.

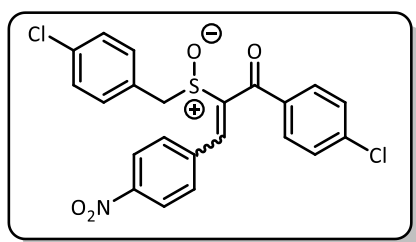
$\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 1650 cm^{-1} (C=O), 1506 (NO_2), 1040 cm^{-1} ; δ_{H} (500 MHz, CDCl_3): 4.16 [1H, A of AB system, J_{AB} 13.3, *E* isomer, one of SCH_2], 4.38 [1H, B of AB system, J_{AB} 13.3, *E* isomer, one of SCH_2], 4.45 [1H, A of AB system, J_{AB} 12.3, *Z* isomer, one of SCH_2], 4.94 [1H, B of AB system, J_{AB} 12.3, *Z* isomer, one of SCH_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 [(C₂₃H₁₈FNO₄S)+H⁺], 5%.

E-40o δ_c (125 MHz, CDCl₃): 59.6 [CH₂, SCH₂], 123.9 [1 x CH signal, aromatic CH], 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 CH], 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, CO].

Characteristic Z-40o signals: δ_c (125 MHz, CDCl₃): 59.3 [CH₂, SCH₂], 123.3 [1 x CH signal, aromatic CH], 128.7, 128.8 [2 x CH signals, aromatic CH], 129.1 [1 x C signal, aromatic C], 129.2, 130.5, 130.9, 131.7 [4 x CH signals, aromatic CH], 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, CO].

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*-

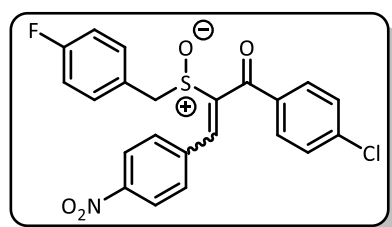
toly)prop-2-en-1-one **40h**. The solution was stirred for 4 h at room temperature and following work-up, the crude oxidised chalcone was isolated as a yellow residue. The ¹H NMR spectrum of the crude product showed only 28% conversion to the desired product. A solution of mCPBA (0.02 g, 0.07 mmol, 1 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. ¹H 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: $\nu_{\max}/\text{cm}^{-1}$ (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 SCH_2], 4.34 [1H, B of AB system, J_{AB} 13.1, one of SCH_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 , SCH_2], 124.0 [1 x CH signal, aromatic CH], 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 CH], 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, CO]; HRMS (ES⁺): Exact Mass Calculated for $\text{C}_{22}\text{H}_{15}^{35}\text{Cl}_2\text{NO}_4\text{S}$ [$\text{M}+\text{H}^+$] 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 SCH_2], 4.82 [1H, B of AB system, J_{AB} 12.3, one of SCH_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 , SCH_2], 129.1, 129.3, 130.4, 131.7, 132.1 [5 x CH signals, aromatic CH].

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*-tolyl)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. ^1H 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: $\nu_{\max}/\text{cm}^{-1}$ (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 SCH_2], 4.83 [1H, B of AB system, J_{AB} 12.5, one of SCH_2], 6.96

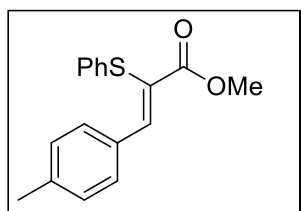
[2H, t, J 8.4, aromatic H], 7.11 [2H, d, J 8.5, aromatic H], 7.23 [1H, s, C(3) H], 7.35 [2H, dd, J 8.7, J_{FH} 5.3, aromatic H], 7.52 [2H, d, J 8.7, aromatic H], 7.96 [2H, d, J 8.7, aromatic H]; δ_c (125 MHz, $CDCl_3$): 58.5 [CH_2 , SCH_2], 116.0 [1 x CH signal, 2 x CH, d, $^2J_{CF}$ 22.4, aromatic CH], 123.4 [1 x CH signal, 2 x aromatic CH], 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 CH], 132.6 [1 x CH signal, 2 x CH, d, $^3J_{CF}$ 8.8, aromatic CH], 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, CO]; HRMS (ES⁺): Exact Mass Calculated for $C_{22}H_{15}^{35}ClFNO_4S$ [$M+H^+$] 444.0467. Found 444.0464.

E-40s: ν_{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 , SCH_2], 115.4 [1 x CH signal, 2 x CH, d, $^2J_{CF}$ 21.7, aromatic CH], 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 CH], 132.8 [1 x CH signal, 2 x CH, d, $^3J_{CF}$ 9.4, aromatic CH], 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, CO]; 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

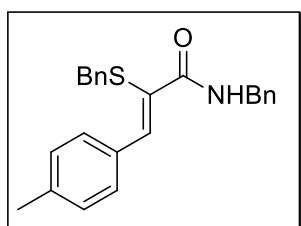
(Z)-Methyl 2-(phenylthio)-3-(*p*-tolyl)acrylate **44**



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 1H 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),

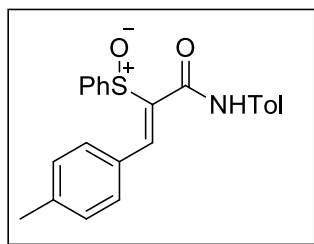
1721 (CO), 1594 (aromatic), 1255; δ_{H} (400 MHz, CDCl_3) 2.37 (3H, s, ArCH_3), 3.67 (3H, s, OCH_3), 7.20 (2H, d, J 8.1, ArH), 7.21-7.29 (5H, m, ArH), 7.76 (2H, d, J 8.2, ArH), 8.13 [1H, s, $\text{C}(3)\text{H}$]; δ_{C} (75.5 MHz, CDCl_3) 21.5 (CH_3 , ArCH_3), 52.8 (CH_3 , OCH_3), 123.5 (C, aromatic C), 126.2, 128.1, 129.0, 129.2, 131.0 (5 x CH, aromatic CH), 131.5, 135.7, 140.7 [3 x C, 3 x aromatic C or 2 x aromatic C and $\text{C}(2)\text{S}$], 146.7 [CH, $\text{C}(3)\text{H}$], 166.9 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{17}\text{H}_{17}\text{SO}_2[\text{M}+\text{H}^+]$ 285.0949. Found 285.0949; m/z (ES⁺) 285.3 [$(\text{C}_{17}\text{H}_{16}\text{SO}_2)+\text{H}^+$], 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 $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (5%) in anhydrous acetonitrile (5 mL). The crude product was obtained as a brown oil which was seen by ^1H 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; $\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3350 (NH), 2920 (CH), 1650 (CO), 1577 (aromatic), 1512 (NH bend); δ_{H} (400 MHz, CDCl_3) 2.38 (3H, s, ArCH_3), 3.74 (2H, s, SCH_2), 4.43 (2H, d, J 5.8, NHCH_2), 7.06-7.09 (2H, m, ArH), 7.17-7.36 (10H, m, ArH), 7.51 (1H, br s, NH), 7.75 (2H, d, J 8.2, ArH), 8.16 [1H, s, $\text{C}(3)\text{H}$]; δ_{C} (75.5 MHz, CDCl_3) 21.5 (CH_3 , ArCH_3), 39.3 (CH_2 , SCH_2), 44.4 (CH_2 , NHCH_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 CH), 132.0, 137.1, 138.1, 140.0 [4 x C, 4 x aromatic C or 3 x aromatic C and $\text{C}(2)\text{S}$], 144.4 [CH, $\text{C}(3)\text{H}$], 165.7 (C, CO); HRMS (ES⁺): Exact mass calculated for $\text{C}_{24}\text{H}_{24}\text{SNO}[\text{M}+\text{H}^+]$ 374.1579. Found 374.1585; m/z (ES⁺) 374.4 [$(\text{C}_{24}\text{H}_{23}\text{SNO})+\text{H}^+$], 42%.

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

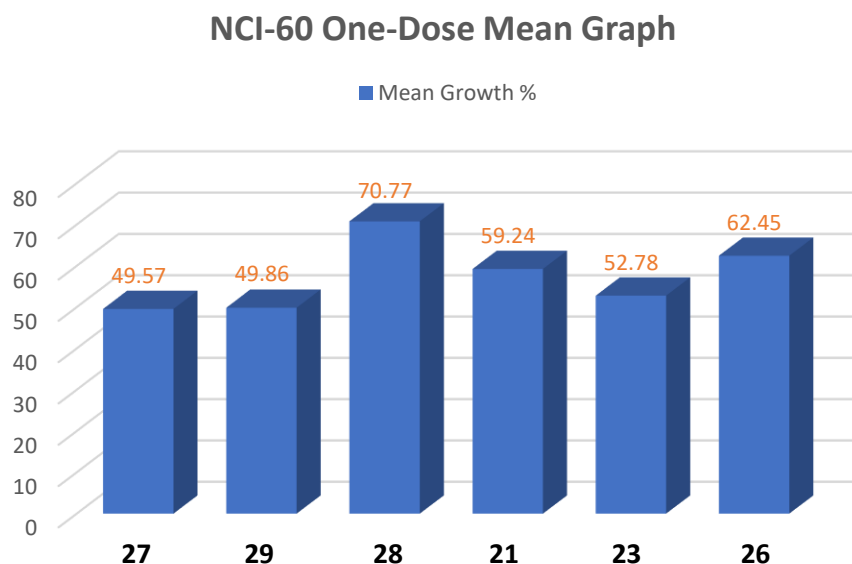


This was prepared following the procedure described for **14** using the sulfoxide **43**³⁰ (200 mg, 0.63 mmol), 4-(tributylstannyl)toluene **36b**²³ (286 mg, 0.75 mmol) and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$ (5%) in anhydrous acetonitrile (5 mL). The crude product was obtained as a yellow oil which was seen by ^1H NMR analysis to contain a mixture of

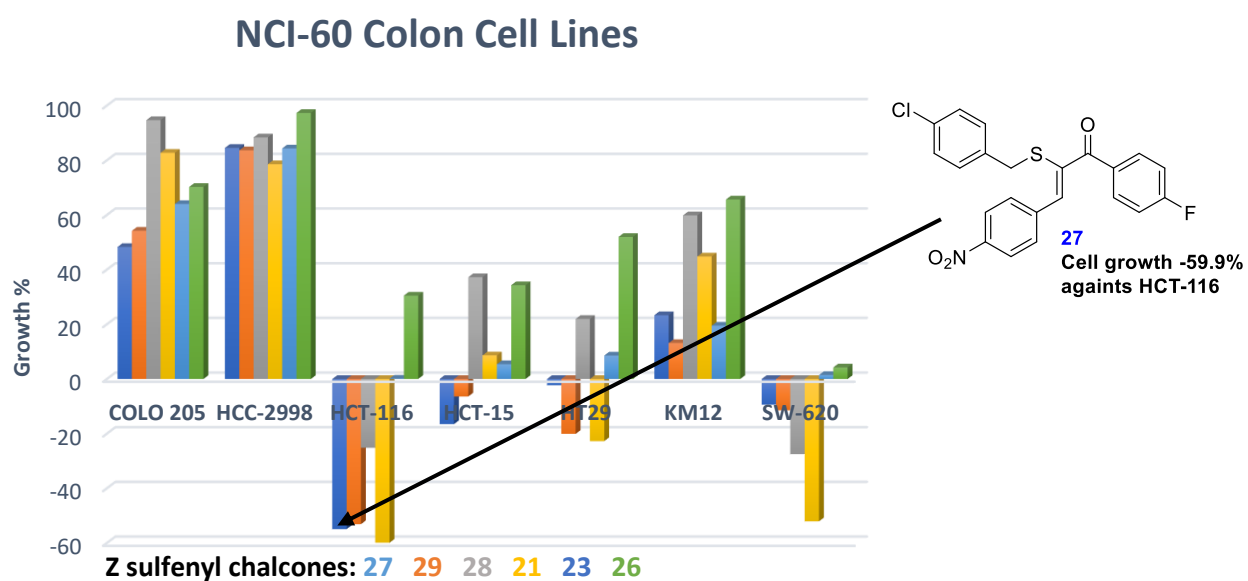
product **46** and starting material **43** in a ratio of 1.6:1 respectively. This was purified by column chromatography on silica gel using hexane-ethyl acetate (90:10) as eluent to give the pure *sulfoxide* **46** (139 mg, 59%) as a pale yellow solid. A sample was further recrystallised from methanol for crystal structure determination; mp 155-157 °C (after recrystallisation from methanol); Found (C, 73.54; H, 5.63; N, 3.71. C₂₃H₂₁SNO₂ requires C, 73.57; H, 5.64; N, 3.73%); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3249 (NH), 2922 (CH), 1674 (CO), 1609 (aromatic), 1553 (NH bend); δ_{H} (400 MHz, CDCl₃) 2.28 (3H, s, ArCH₃), 2.42 (3H, s, ArCH₃), 7.07 (2H, d, *J* 8.0, ArH), 7.27 (2H, d, *J* 8.0, ArH), 7.32-7.48 (5H, m, ArH), 7.59 (4H, d, *J* 8.0, ArH), 8.34 [1H, s, C(3)H], 10.25 (1H, br s, NH); δ_{C} (75.5 MHz, CDCl₃) 20.1 (CH₃, ArCH₃), 21.6 (CH₃, ArCH₃), 120.6, 124.3, 129.4, 129.6, 129.7, 131.0, 131.1 (7 x CH, aromatic CH), 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, CO); HRMS (ES⁺): Exact mass calculated for C₂₃H₂₂SNO₂[M+H⁺] 376.1371. Found 376.1370; *m/z* (ES⁺) 376.3 [(C₂₃H₂₁SNO₂)+H⁺], 100%. Crystal Data: C₂₃H₂₁NO₂S, *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) Å³, *T* = 300(2) K, space group C2/c, *Z* = 8, 13317 reflections measured, 3824 unique (*R*_{int} = 0.0599). The final *R*₁ values were 0.0518 (*I* > 2σ(*I*)) and 0.1056 (all data). The final *wR*(*F*²) values were 0.1104 (*I* > 2σ(*I*)) and 0.1308 (all data).

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

1.11.1 Biological evaluation of Z sulfenyl chalcones

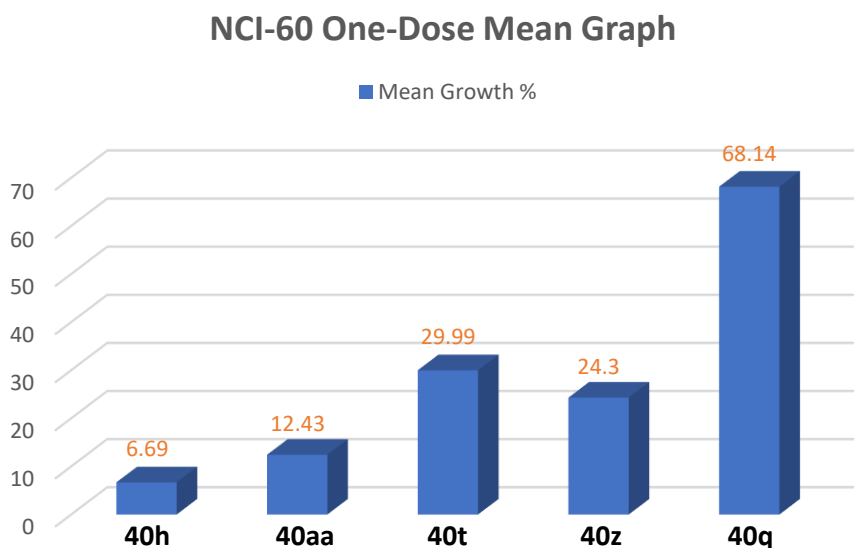


Graph 1: NCI-60 one-dose (10 μ M) mean cell growth of Z sulfenyl chalcones **27**, **29**, **28**, **21**, **23** and **26** across 60 cancer cell lines.

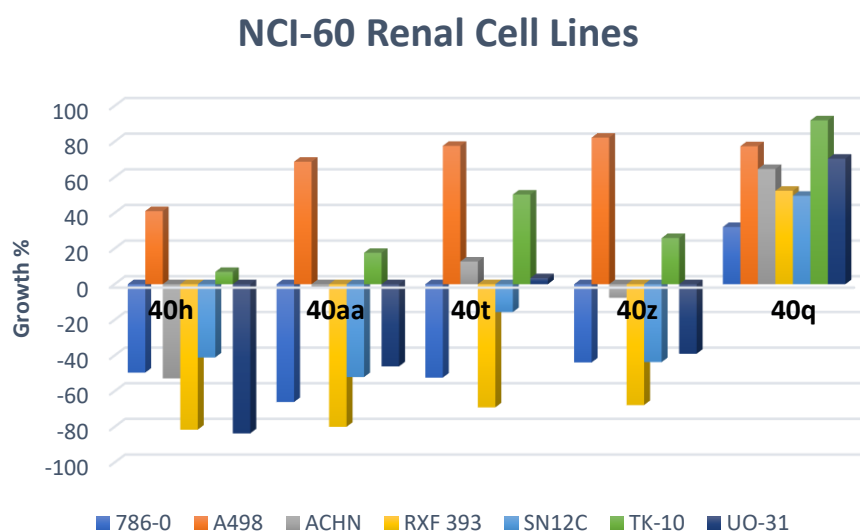


Graph 2: NCI-60 one-dose (10 μ M) cell growth of Z sulfenyl chalcones against colon cell lines

1.11.2 Biological evaluation of *E* sulfinyl chalcones



Graph 3: NCI-60 one-dose (10 μ M) 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 μ M) 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* sulfinyl chalcones) and **40h**, **40aa**, **40z**, **40t** (*E* sulfinyl chalcones).

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

1.12.1 α -Chloroketones:

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

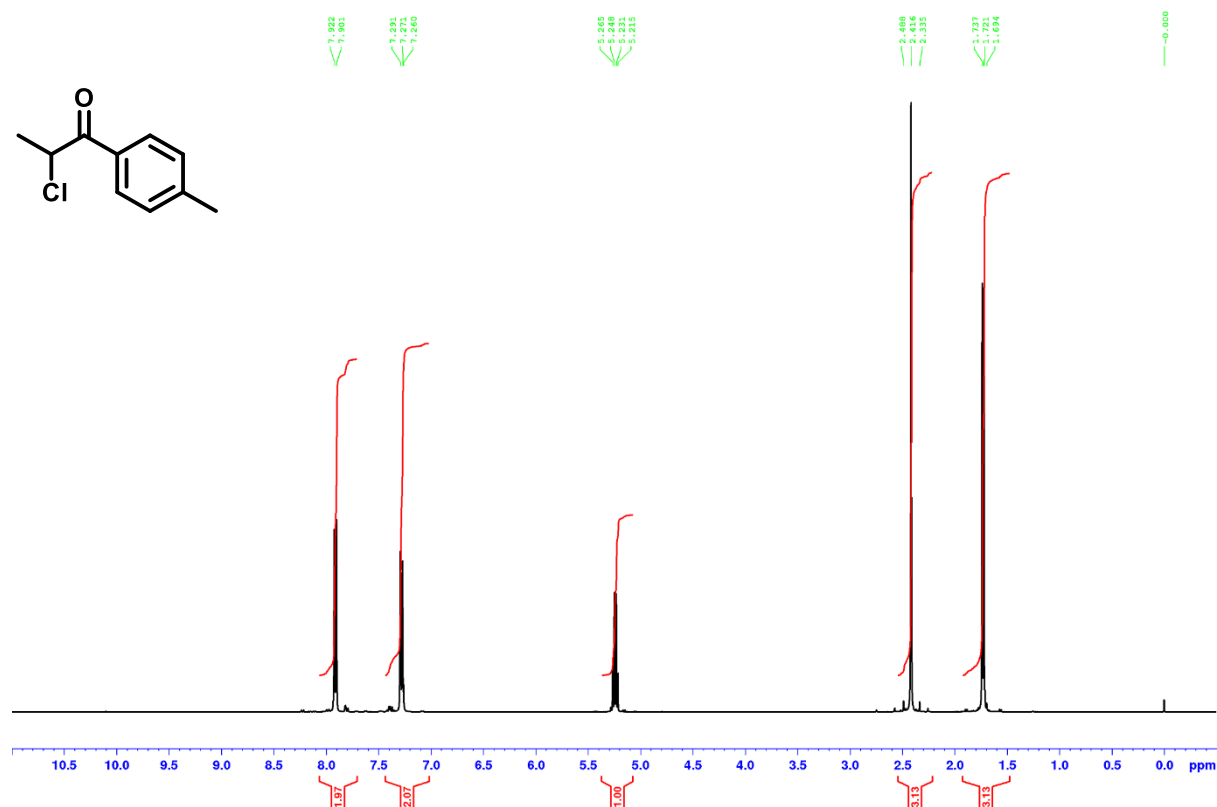


Figure S1: ^1H NMR (400 MHz, CDCl_3) spectrum of **S1**.

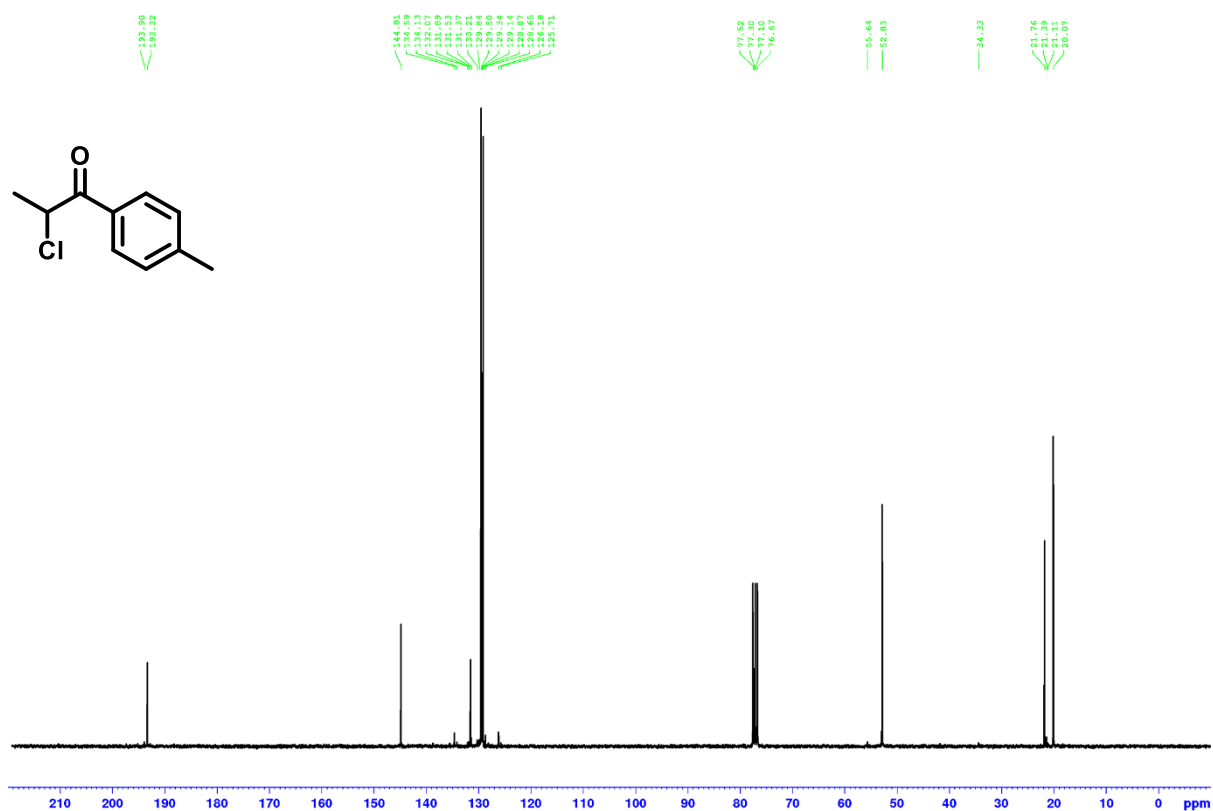


Figure S2: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **S1**.

2-Chloro-1-(4-chlorophenyl)propan-1-one S2^{1,3}

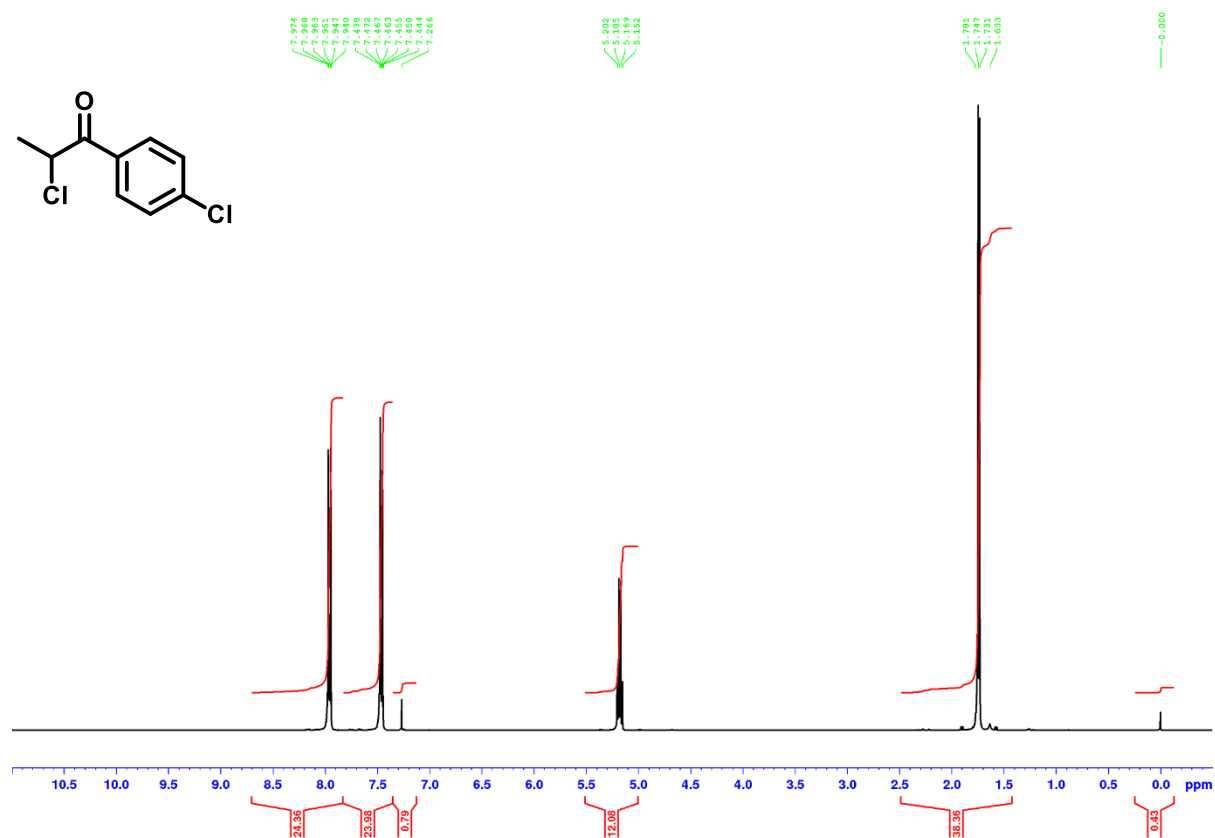


Figure S3: ¹H NMR (400 MHz, CDCl₃) spectrum of S2.

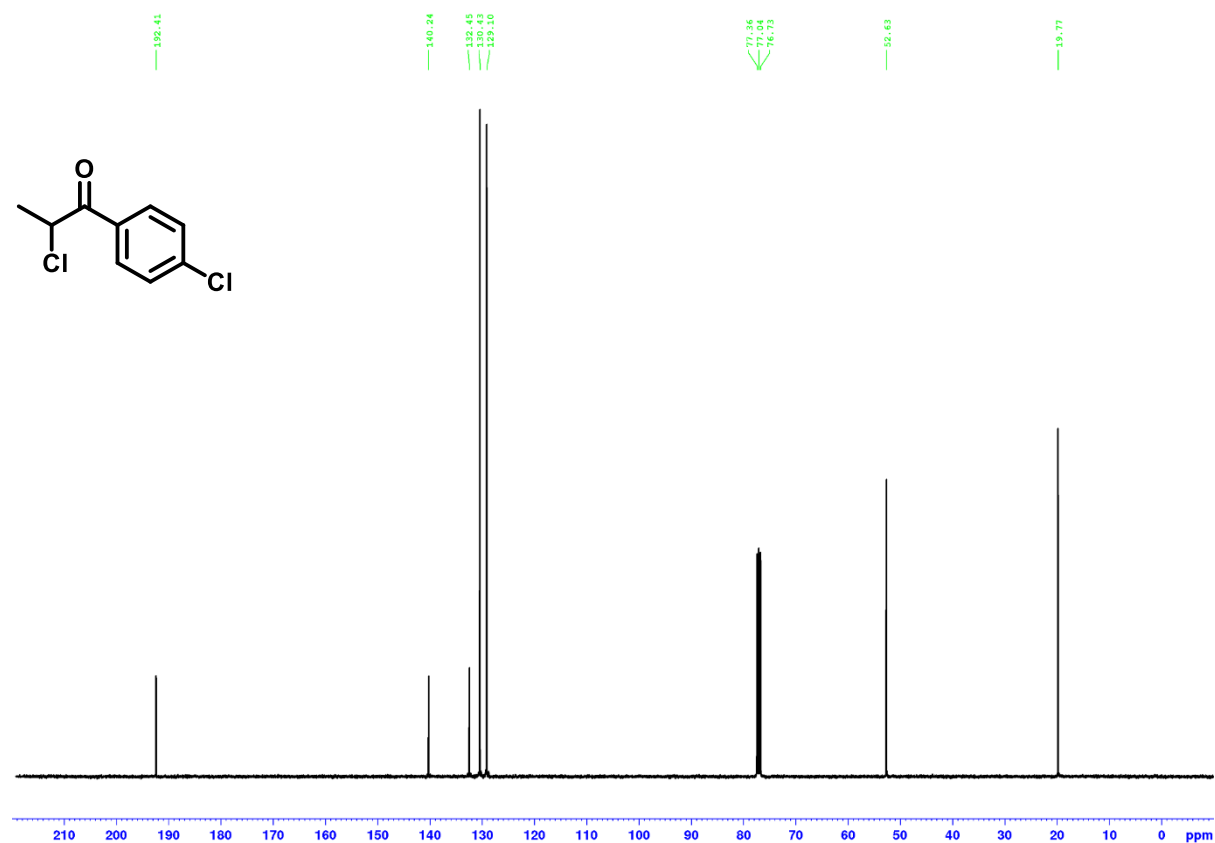


Figure S4: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of S2.

2-Chloro-1-(4-fluorophenyl)propan-1-one S3⁴

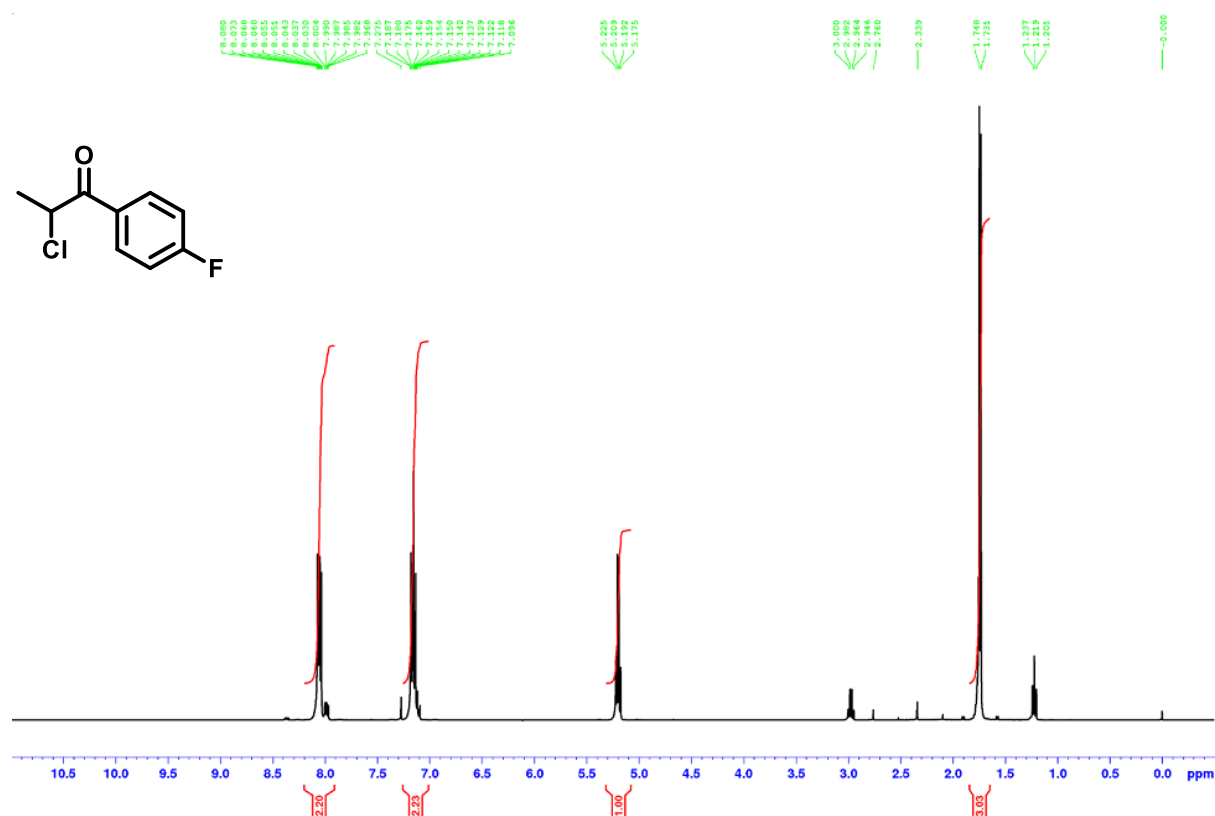


Figure S5: ¹H NMR (400 MHz, CDCl₃) spectrum of S3.

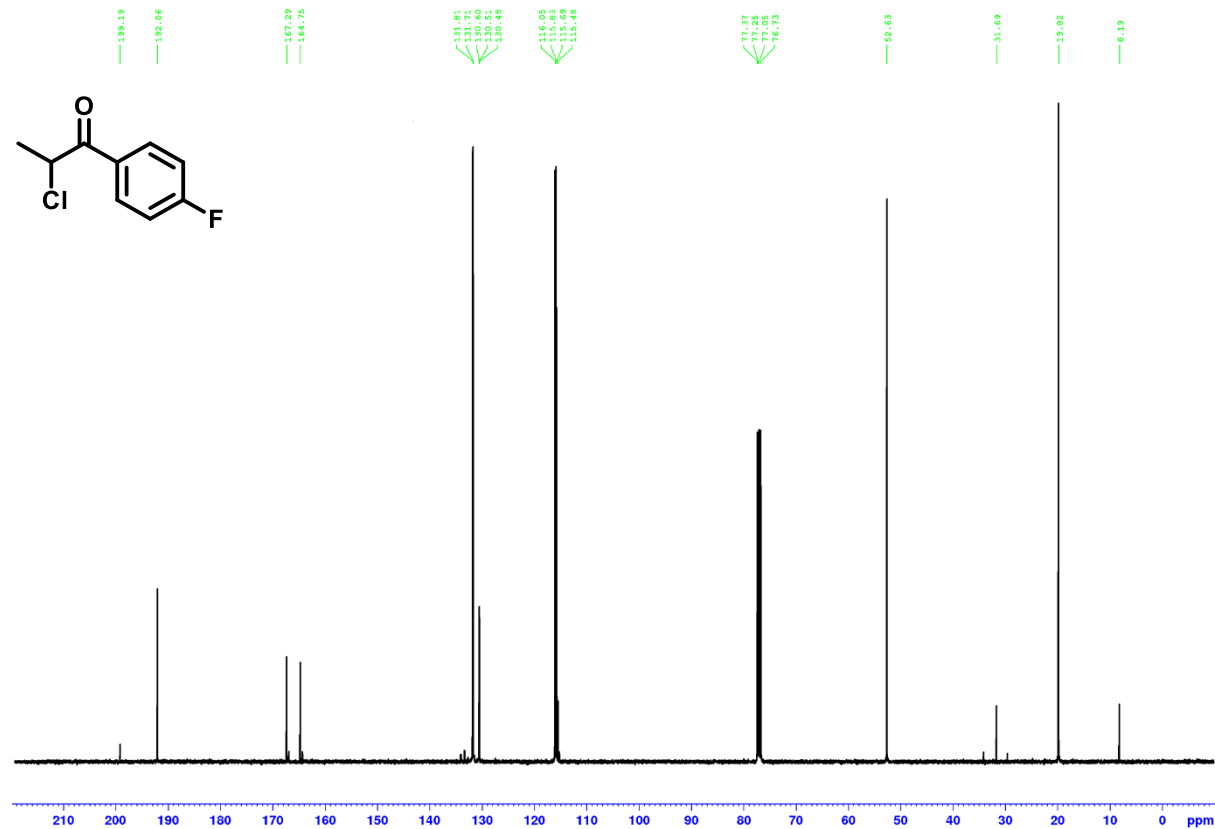


Figure S6: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of S3.

2-Chloro-1-(4-methoxyphenyl)propan-1-one S4^{2, 5}

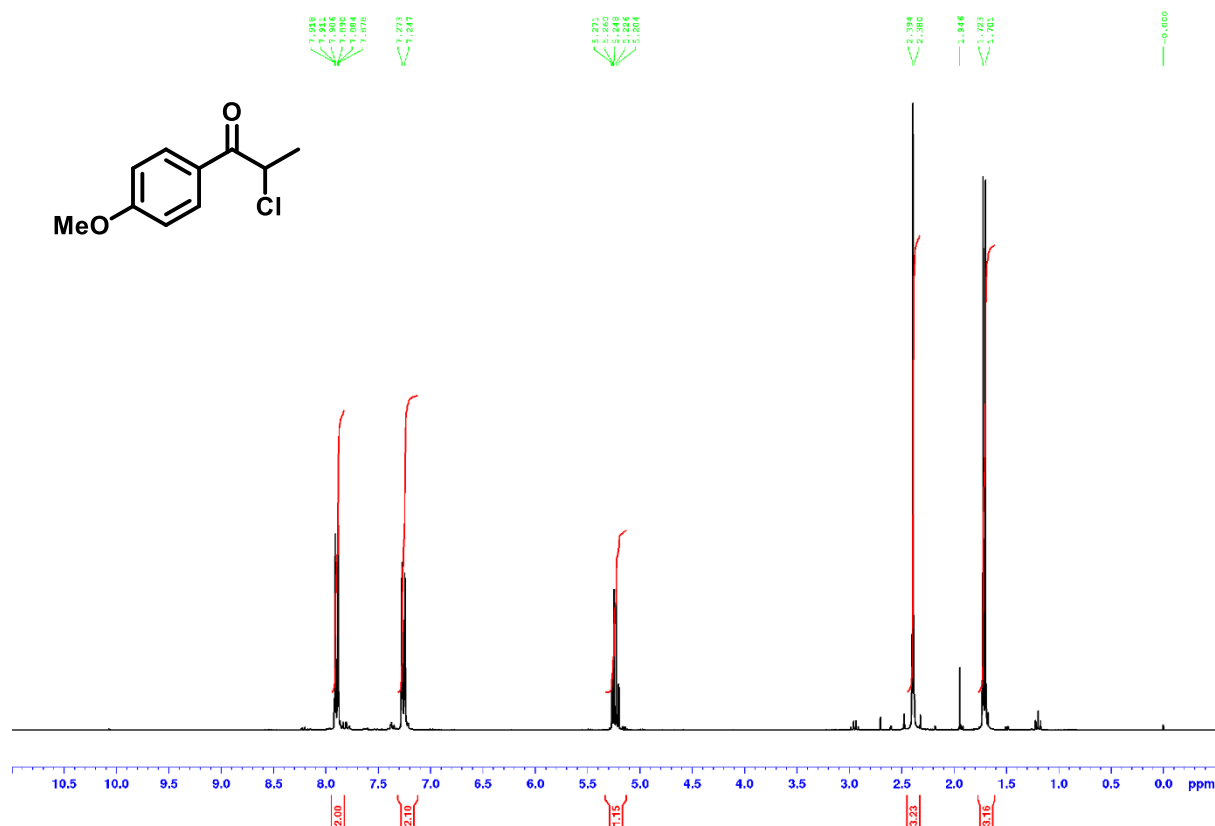


Figure S7: ¹H NMR (300 MHz, CDCl₃) spectrum of S4.

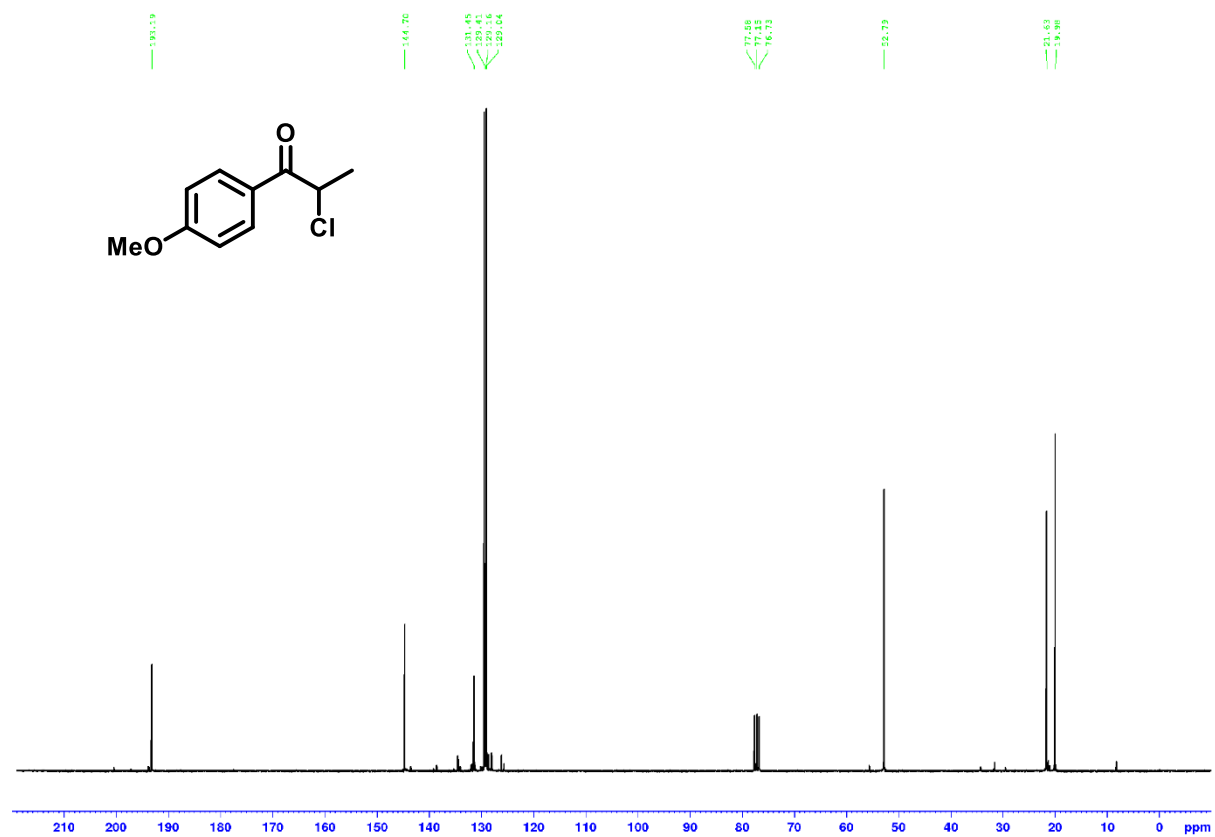


Figure S8: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of S4.

2-Chloropentan-3-one S5⁶

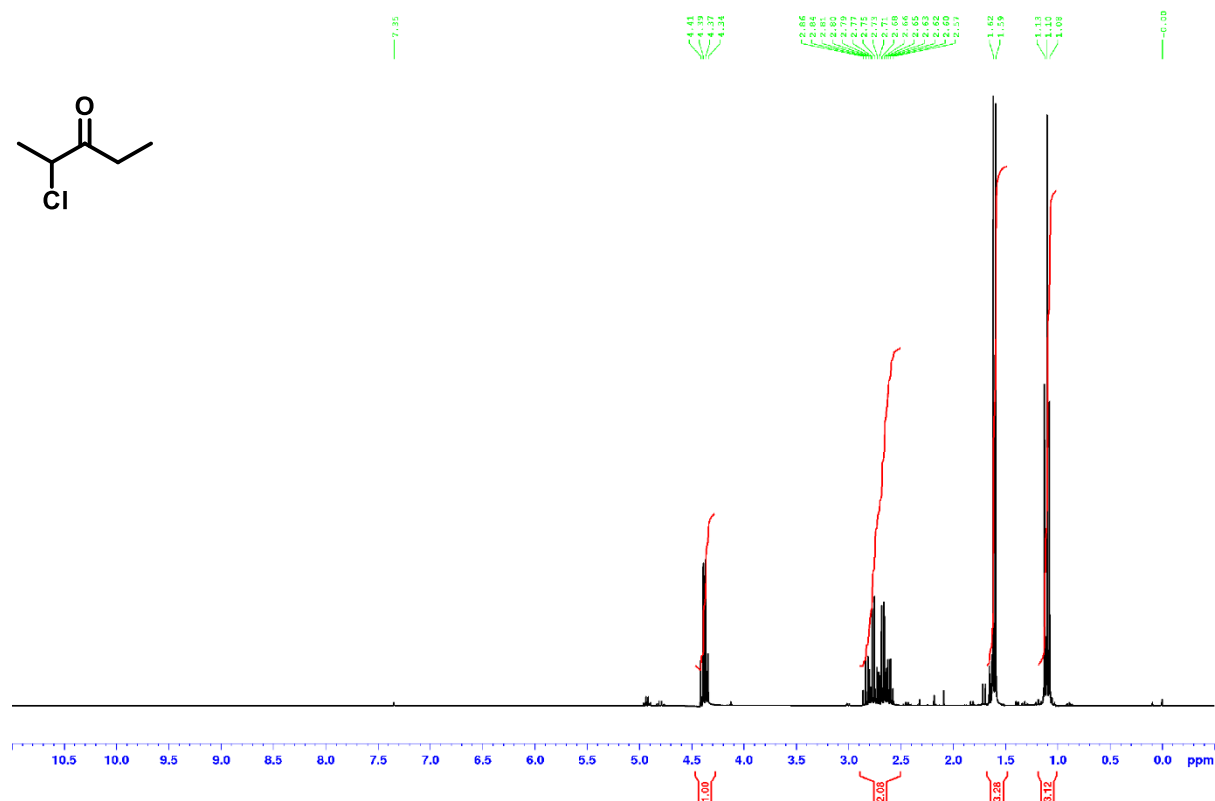


Figure S9: ¹H NMR (300 MHz, CDCl₃) spectrum of S5.

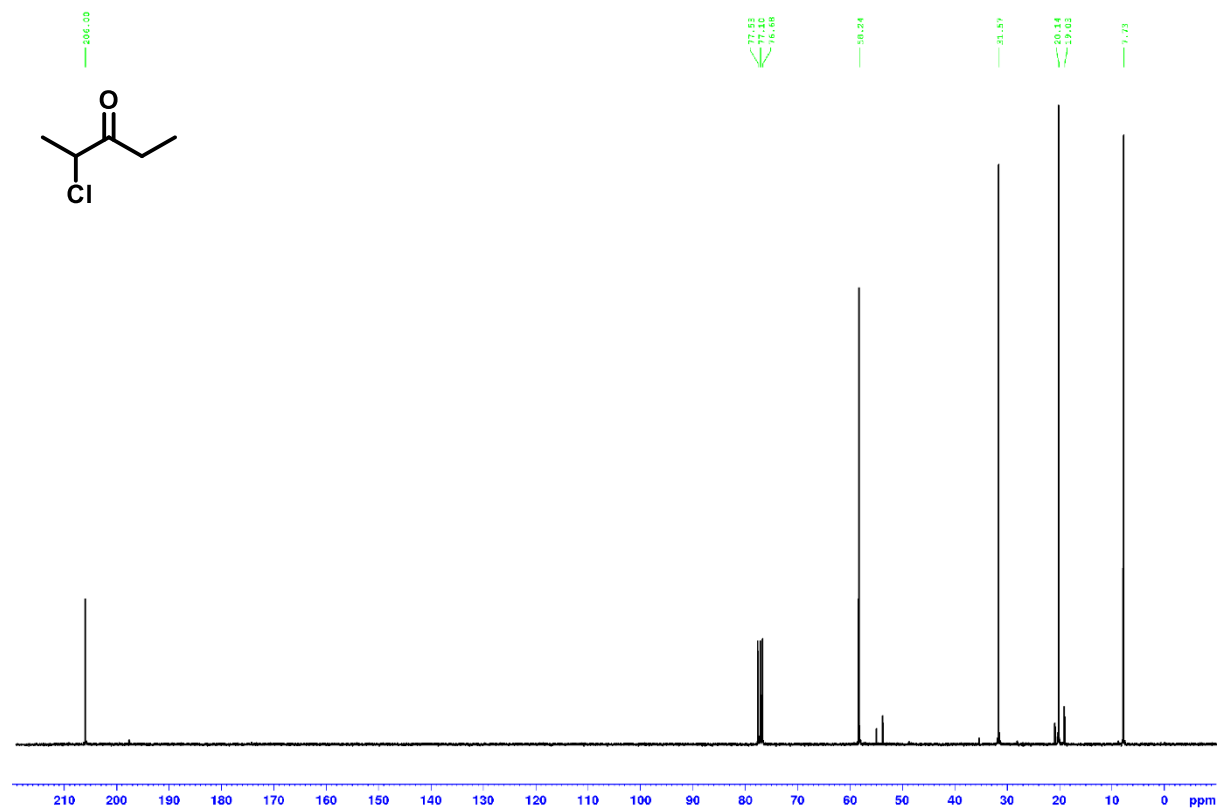


Figure S10: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of S5.

2-Chloro-1-phenylbutan-1-one S6⁷

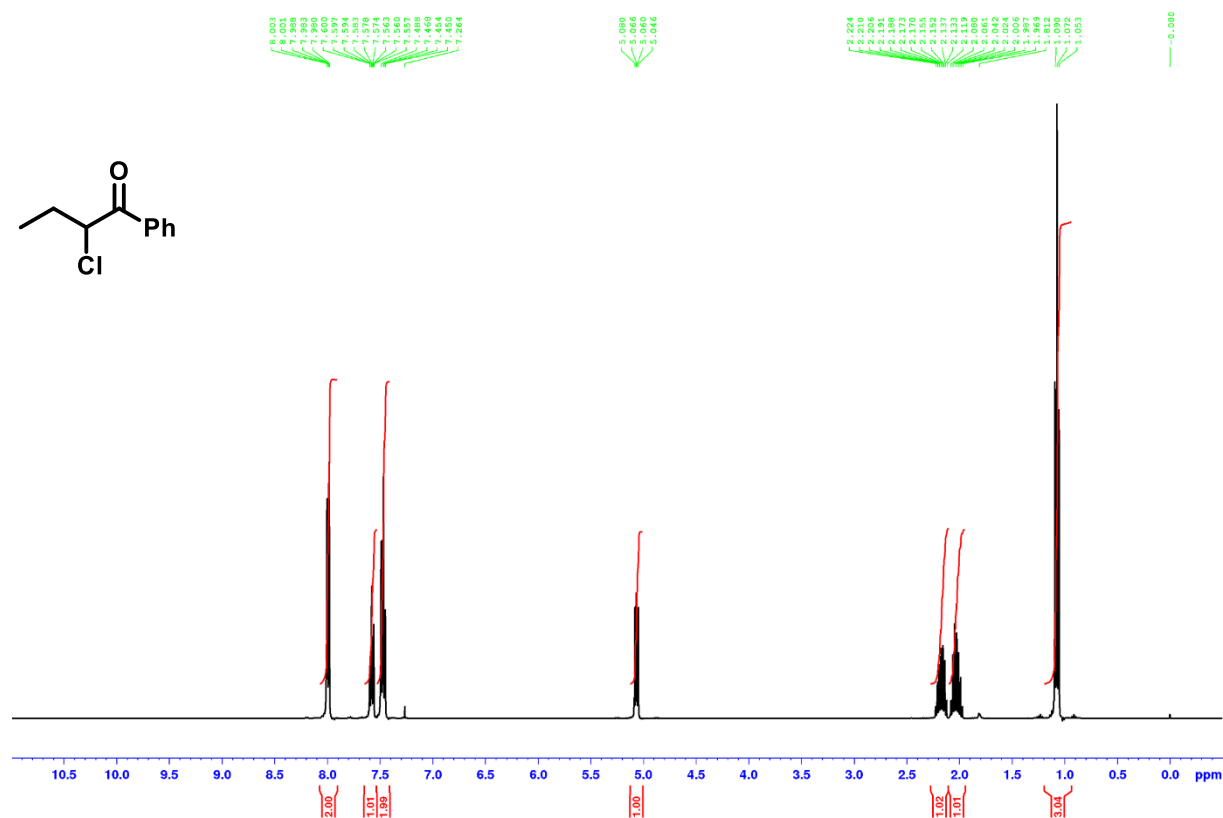


Figure S11: ¹H NMR (400 MHz, CDCl₃) spectrum of S6.

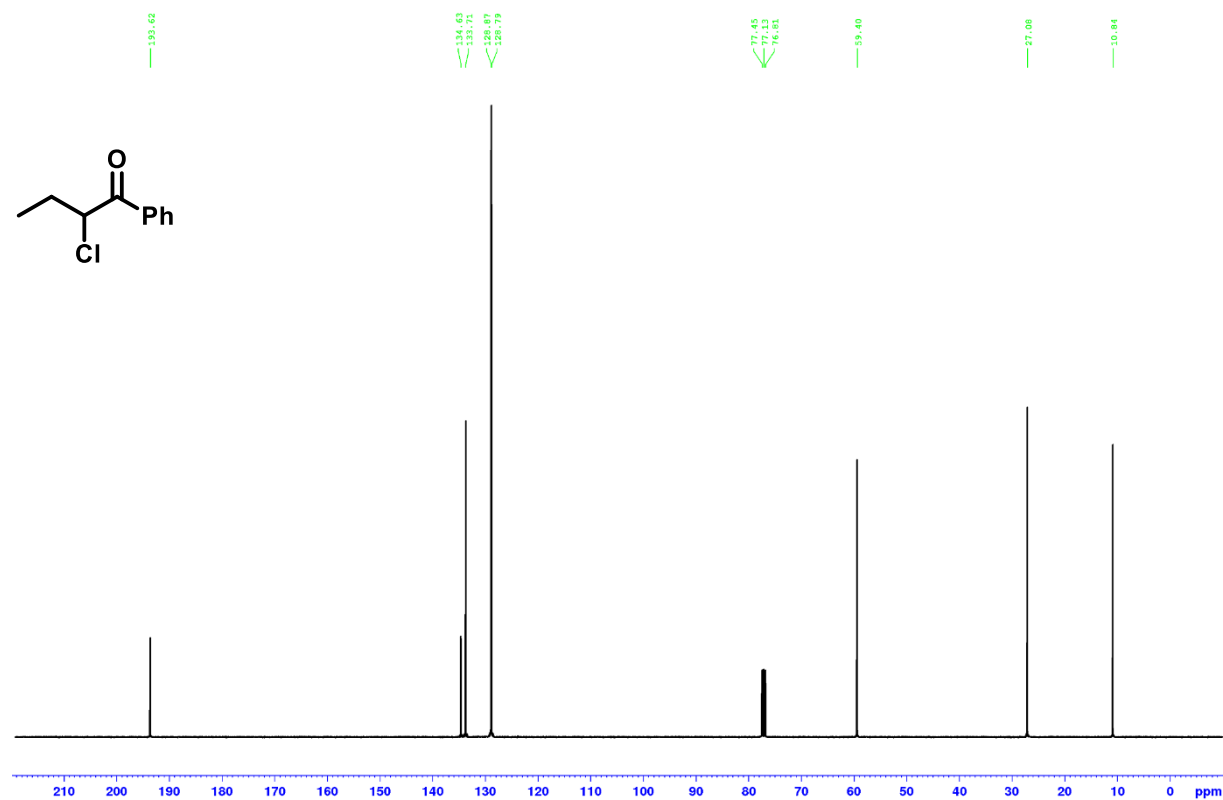


Figure S12: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of S6.

2-Chloro-1-phenylpentan-1-one S7⁸

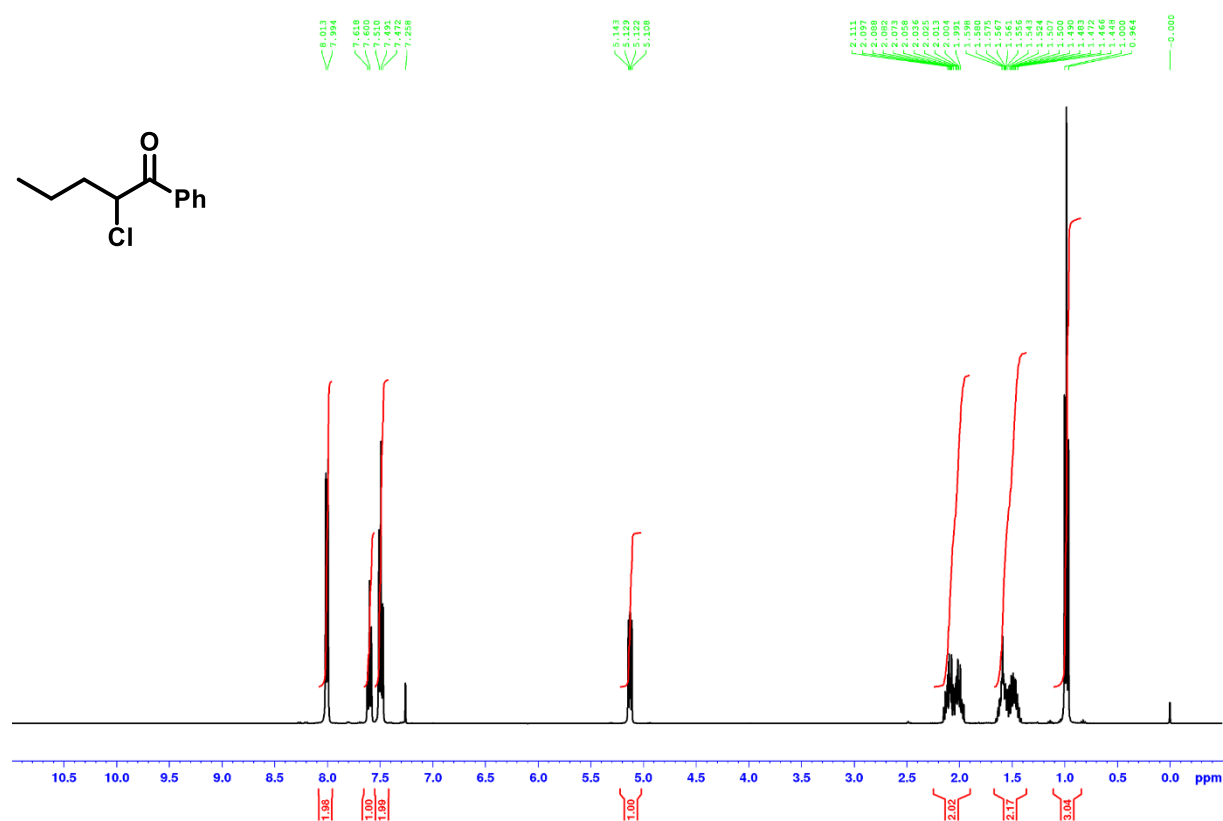


Figure S13: ¹H NMR (400 MHz, CDCl₃) spectrum of S7.

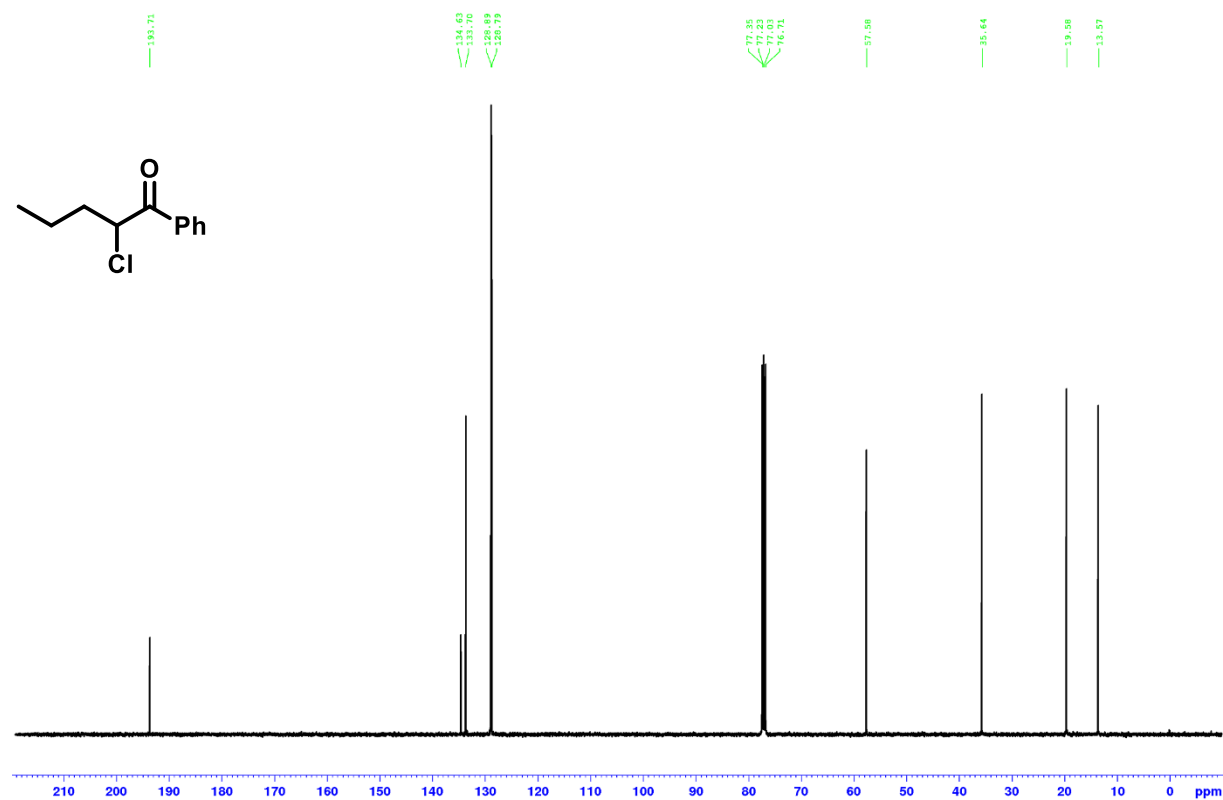


Figure S14: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of S7.

3-Chloro-4-phenylbutan-2-one S8³

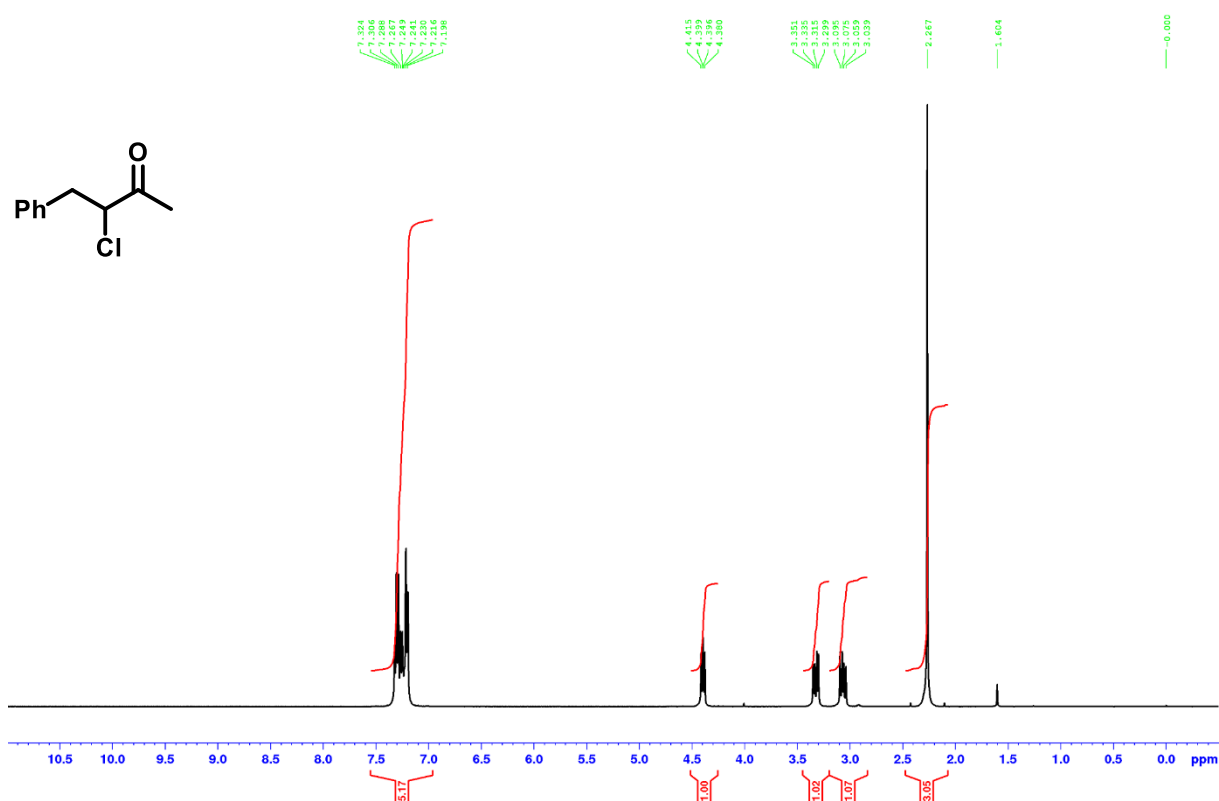


Figure S15: ¹H NMR (400 MHz, CDCl₃) spectrum of S8.

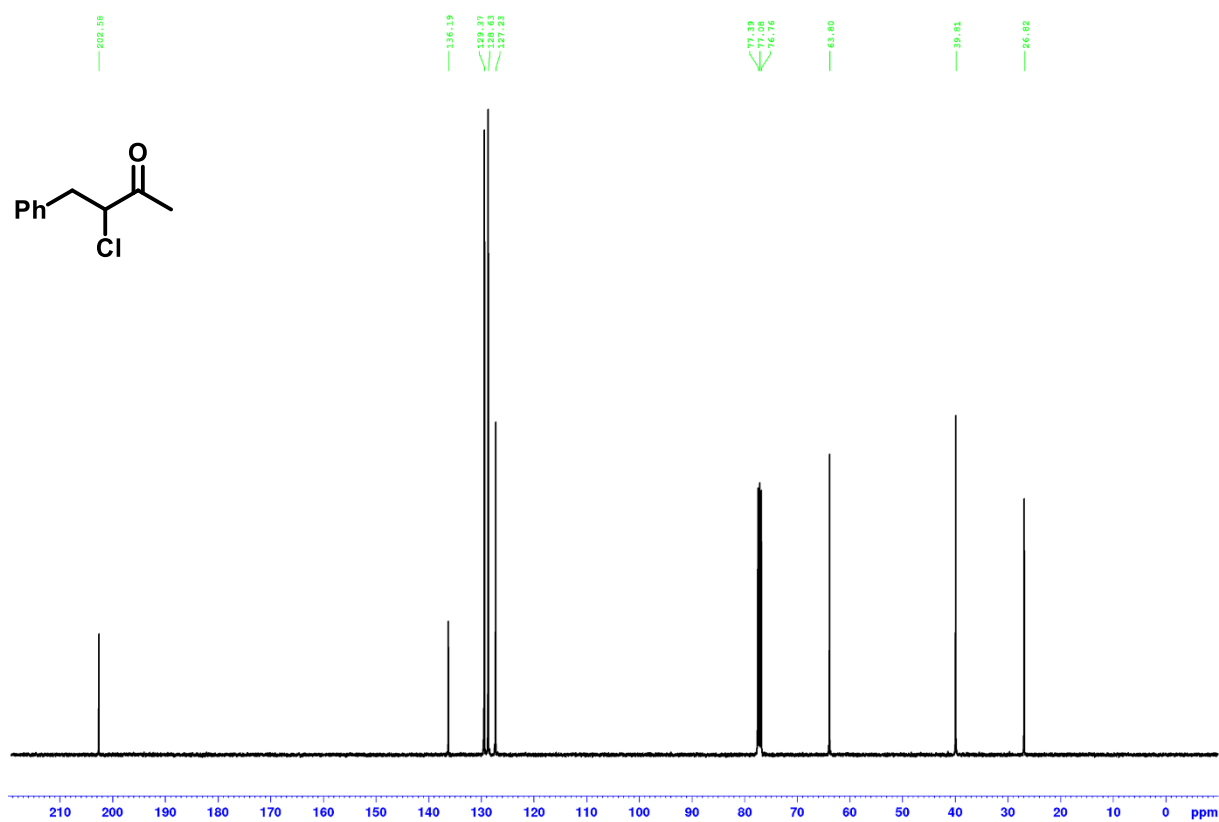


Figure S16: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of S8.

1.12.2 α -Sulphenylketones

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

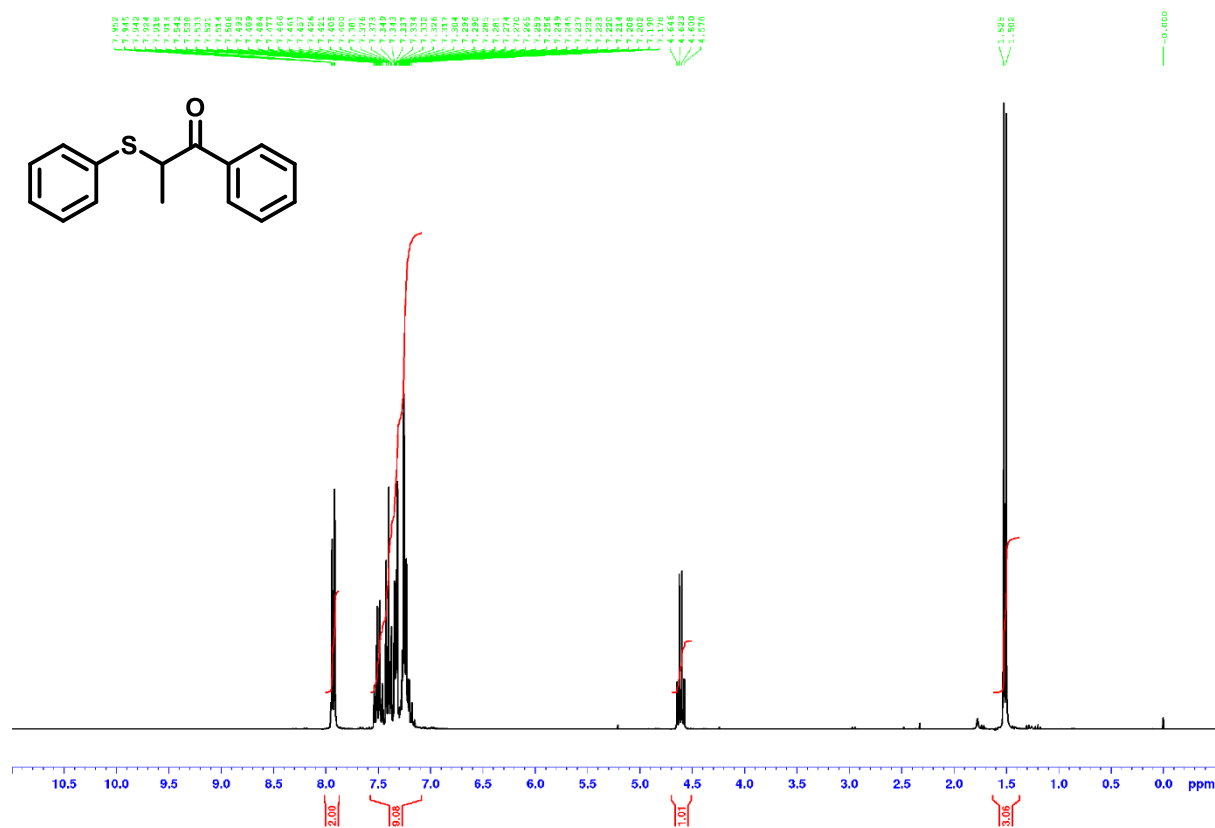


Figure S17: ¹H NMR (300 MHz, CDCl₃) spectrum of **3a**.

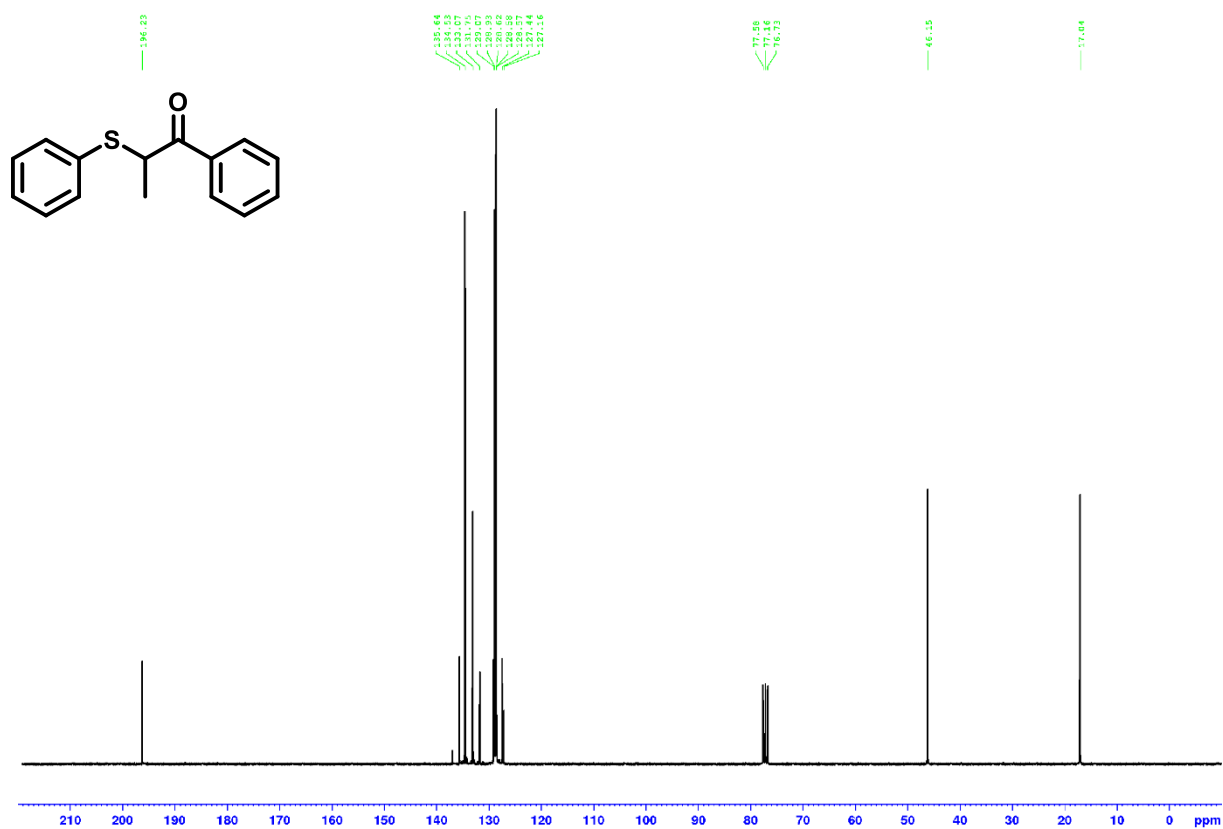


Figure S18: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3a**.

Chemical structure: CC(=O)SCc1ccccc1

¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
7.587, 7.582, 7.576, 7.571, 7.565, 7.560, 7.554, 7.549, 7.544, 7.538, 7.533, 7.528, 7.523, 7.518	1.95
7.487, 7.482, 7.476, 7.471, 7.465, 7.460, 7.454, 7.449, 7.444, 7.438, 7.433, 7.428, 7.423, 7.418	1.04
7.362, 7.357, 7.352, 7.346, 7.341, 7.336, 7.331, 7.326, 7.321, 7.316	2.00
3.626, 3.621, 3.616, 3.611, 3.606, 3.601, 3.596, 3.591, 3.586, 3.581, 3.576, 3.571, 3.566, 3.561, 3.556, 3.551, 3.546, 3.541, 3.536, 3.531, 3.526, 3.521, 3.516	1.00
1.544, 1.531	3.98
2.500	1.00

CC(=O)c1ccccc1SCc2ccccc2

149

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

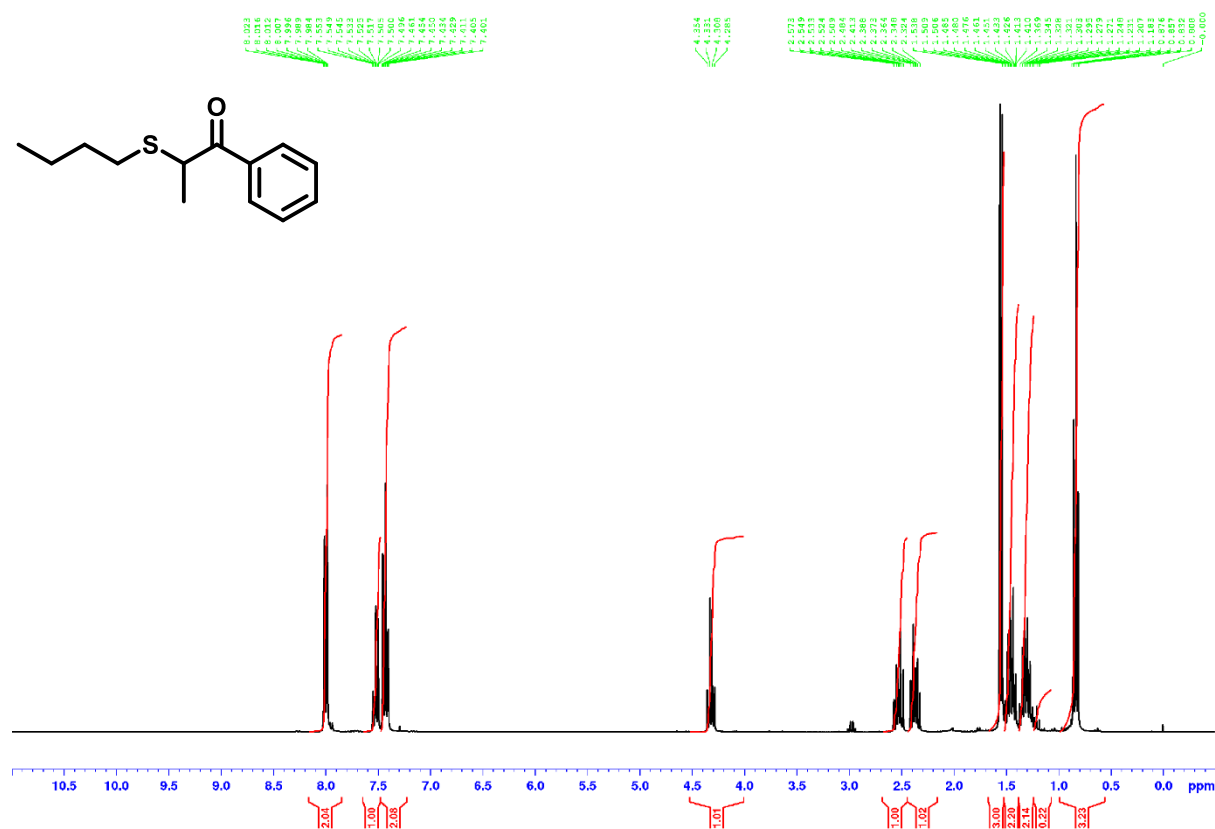


Figure S21: ¹H NMR (300 MHz, CDCl₃) spectrum of 3c.

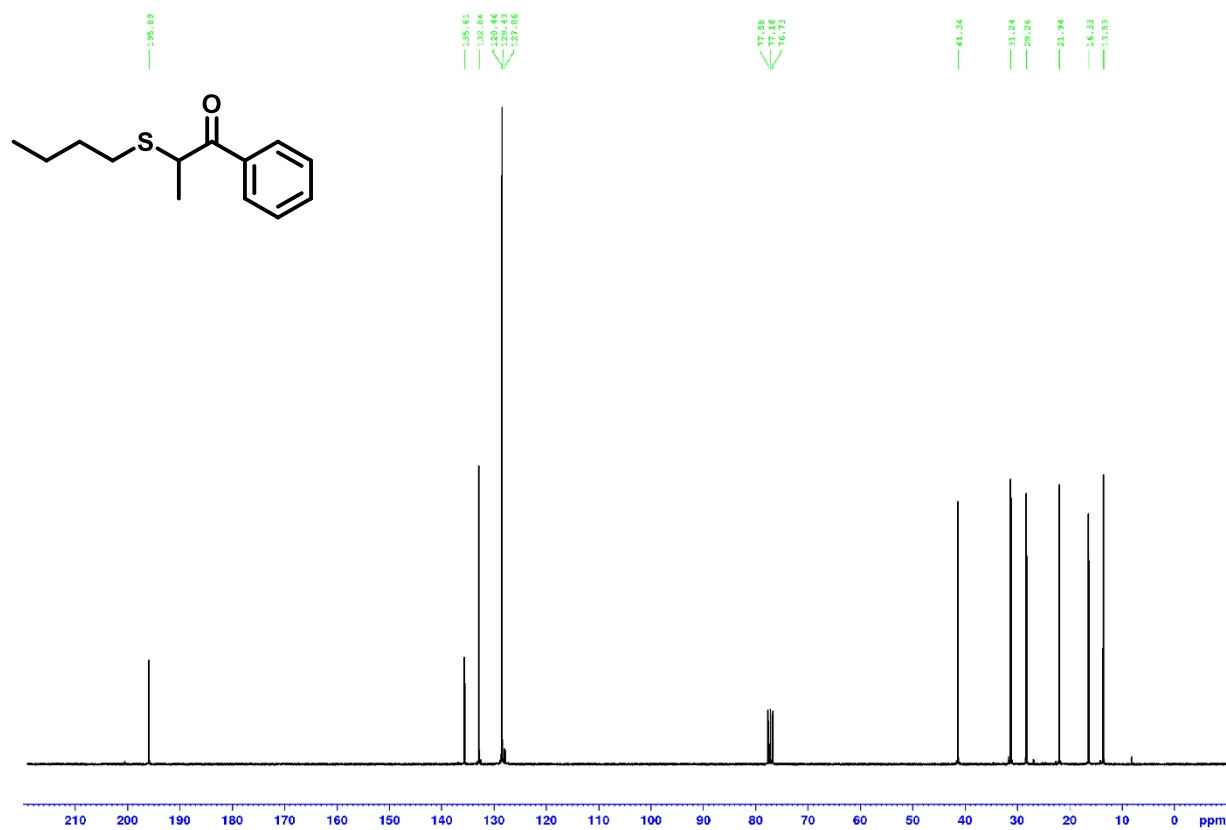


Figure S22: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of 3c.

Chemical structure: COc1ccc(cc1)C(=O)C(Sc2ccccc2)C

¹³C NMR peaks (ppm):

- 196.13
- 163.55
- 136.20
- 132.59
- 131.31
- 128.86
- 128.39
- 128.06
- 127.63
- 126.47
- 115.17
- 113.77
- 77.63
- 77.20
- 76.70
- 55.49
- 46.03
- 17.28

151

2-(Benzythio)-1-(4-methoxyphenyl)propan-1-one **3e**

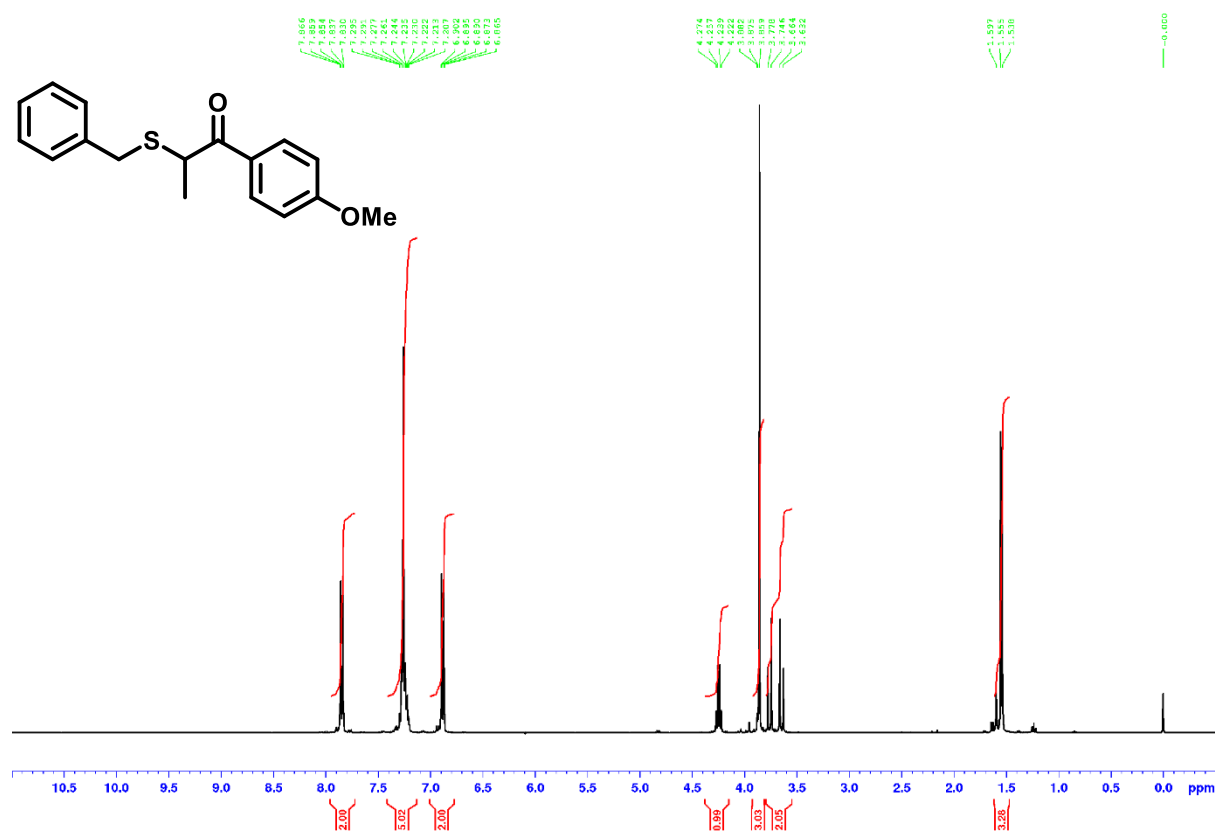


Figure S25: ¹H NMR (400 MHz, CDCl₃) spectrum of **3e**.

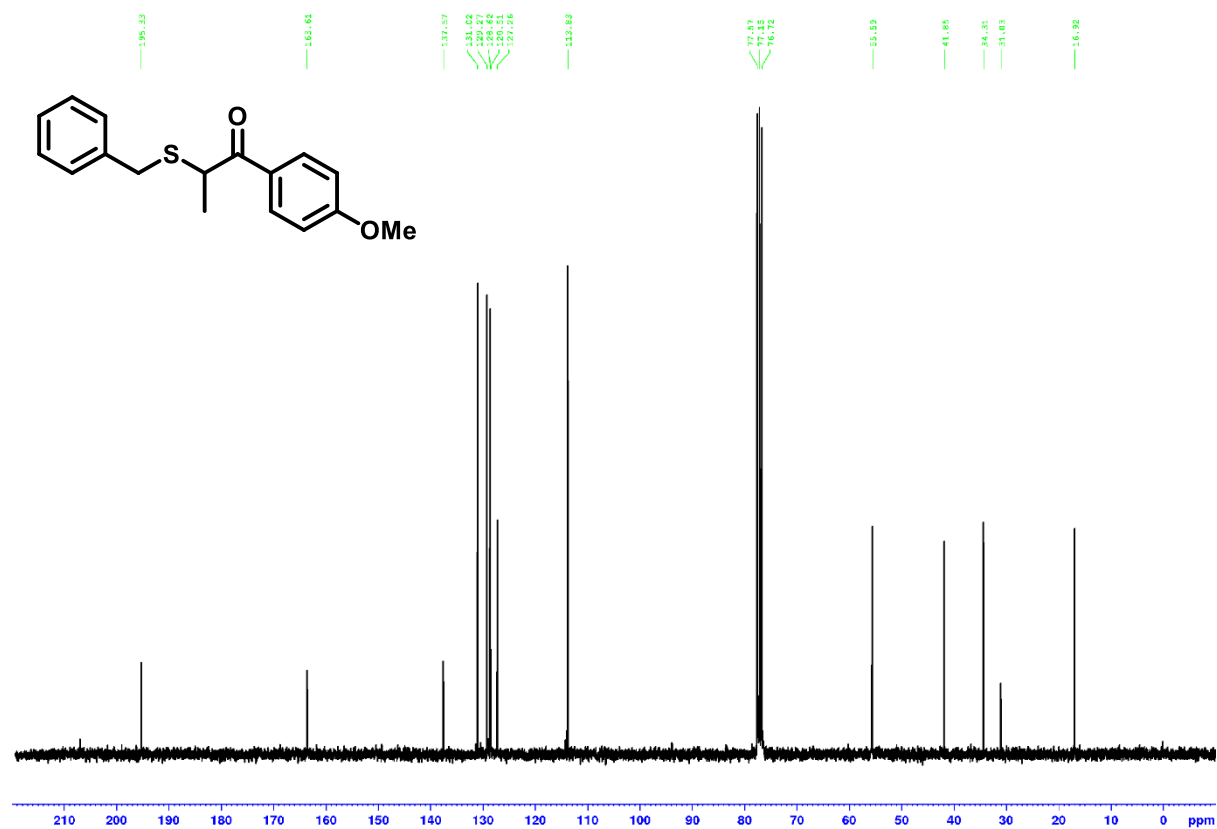


Figure S26: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3e**.

Chemical structure: CCCCSC(C)C(=O)c1ccc(OC)cc1

¹H NMR spectrum (CDCl₃) showing peaks and integrations:

- 7.8 ppm (d, 1.97H)
- 7.0 ppm (d, 1.97H)
- 3.8 ppm (s, 3.95H)
- 2.5 ppm (q, 2.99H)
- 2.1 ppm (s, 3.21H)
- 1.0 ppm (t, 3.21H)

Chemical structure: CCCCCSC(=O)C1=CC=C(OC)C=C1

¹³C NMR peaks (ppm): 194.90, 162.39, 131.49, 131.24, 130.05, 120.58, 115.67, 115.60, 77.85, 77.13, 76.70, 56.24, 55.59, 55.43, 41.24, 41.18, 31.35, 31.28, 29.49, 29.39, 24.90, 24.81, 22.64, 22.60, 16.59, 13.62.

153

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

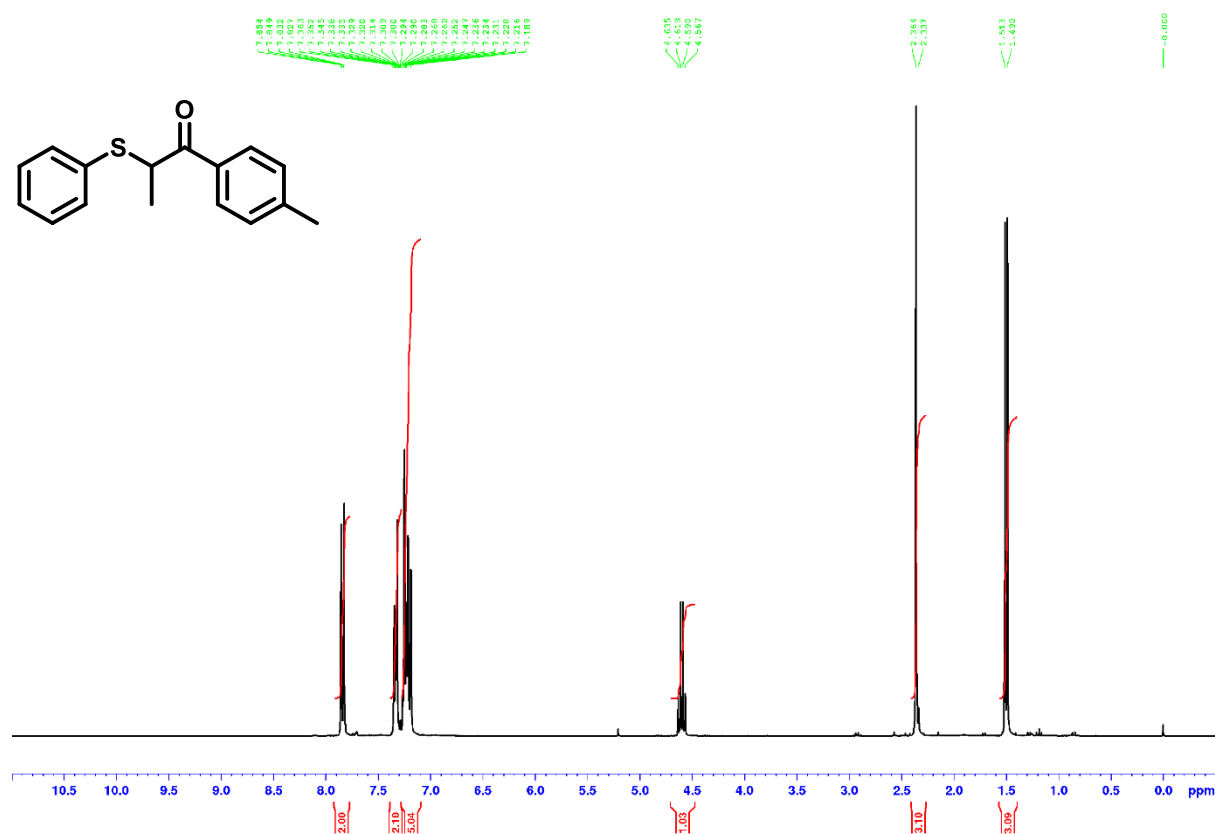


Figure S29: ¹H NMR (300 MHz, CDCl₃) spectrum of **3g**.

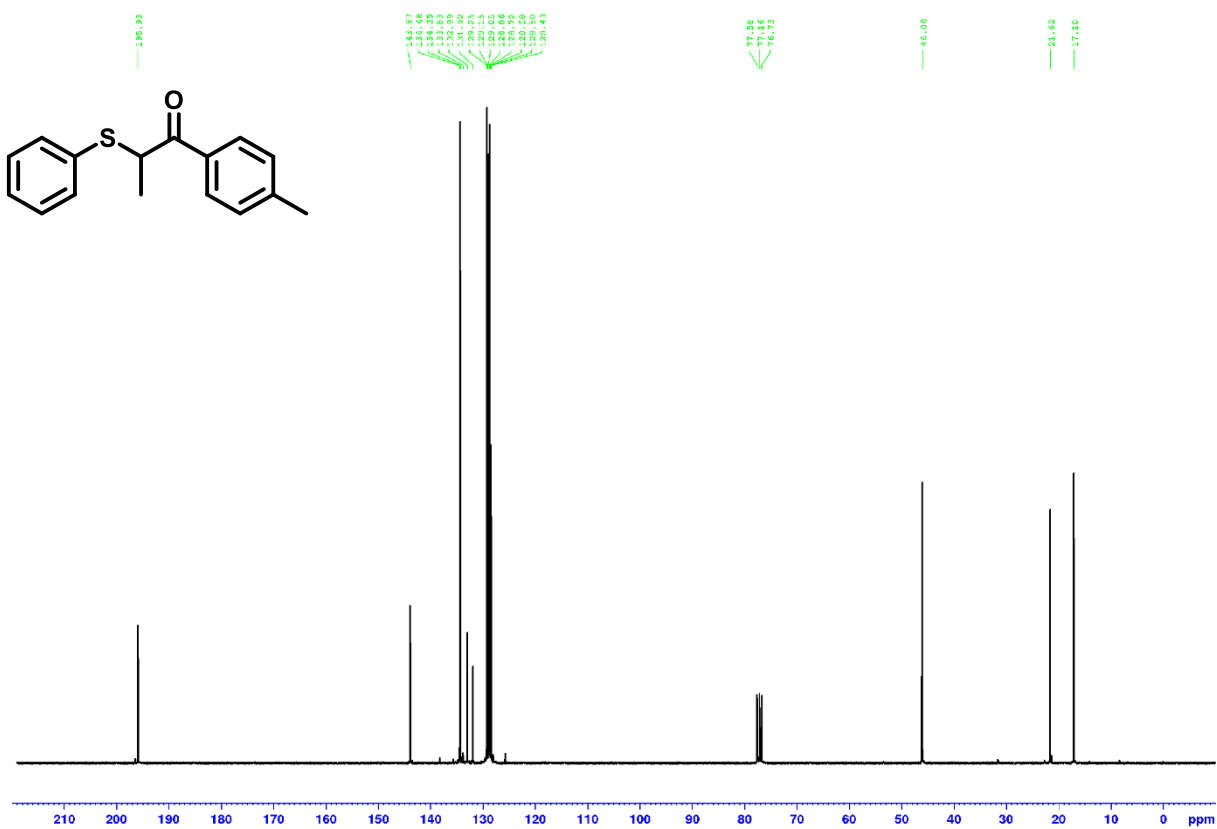


Figure S30: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3g**.

Chemical structure: CC(=O)C(CS)Cc1ccccc1

¹H NMR spectrum (400 MHz, CDCl₃) data:

Chemical Shift (ppm)	Integration
7.824, 7.774, 7.731, 7.595, 7.552, 7.516, 7.274, 7.246, 7.237, 7.201	1.98
7.174, 7.131, 7.095, 7.052, 7.016	1.98
3.778, 3.773, 3.655, 3.623, 3.604	1.98
3.655, 3.623, 3.604	1.98
2.522, 2.517, 2.512, 2.507	3.96
1.527, 1.505, 1.483, 1.461, 1.449	3.96

CC(=O)CSCc1ccccc1

13C NMR spectrum (CDCl₃) of 4-methylphenyl 1-phenylethyl ketone. The spectrum shows peaks at 196.16 ppm (C=O), 143.92 ppm (aromatic C), 137.38 ppm (aromatic C), 133.02 ppm (aromatic C), 129.25 ppm (aromatic C), 128.71 ppm (aromatic C), 128.53 ppm (aromatic C), 127.10 ppm (aromatic C), 77.36 ppm (CDCl₃), 77.24 ppm (CDCl₃), 77.04 ppm (CDCl₃), 76.72 ppm (CDCl₃), 41.09 ppm (CH₃), 34.15 ppm (CH₂), 21.67 ppm (CH₃), and 16.69 ppm (CH₃).

155

Chemical structure: CCCCSC(C)C(=O)c1ccc(C)cc1

¹H NMR spectrum (400 MHz, CDCl₃) data:

Chemical Shift (ppm)	Integration
7.81	1.02
7.22	2.02
4.31	1.00
2.53	1.12, 1.17
1.51	2.92, 2.39, 2.11
1.33	3.00
0.00	-

Chemical structure: CCCC(=O)c1ccc(C)cc1

¹³C NMR peaks (ppm):

- 195.83
- 143.79
- 133.14
- 129.21
- 128.66
- 77.87
- 77.54
- 76.72
- 41.42
- 31.93
- 31.30
- 28.44
- 22.03
- 21.44
- 16.51
- 13.89

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CC(=O)c1ccc(cc1)SCc2ccc(Cl)cc2

Chemical shift (ppm): 7.788, 7.767, 7.747, 7.728, 7.709, 7.690, 7.671, 7.651, 7.632, 7.613, 7.594, 7.575, 7.556, 7.537, 7.518, 7.499, 7.480, 7.461, 7.442, 7.423, 7.404, 7.385, 7.366, 7.347, 7.328, 7.309, 7.290, 7.271, 7.252, 7.233, 7.214, 7.195, 7.176, 7.157, 7.138, 7.119, 7.100, 7.081, 7.062, 7.043, 7.024, 7.005, 6.986, 6.967, 6.948, 6.929, 6.910, 6.891, 6.872, 6.853, 6.834, 6.815, 6.796, 6.777, 6.758, 6.739, 6.720, 6.701, 6.682, 6.663, 6.644, 6.625, 6.606, 6.587, 6.568, 6.549, 6.530, 6.511, 6.492, 6.473, 6.454, 6.435, 6.416, 6.397, 6.378, 6.359, 6.340, 6.321, 6.302, 6.283, 6.264, 6.245, 6.226, 6.207, 6.188, 6.169, 6.150, 6.131, 6.112, 6.093, 6.074, 6.055, 6.036, 6.017, 6.000, 5.981, 5.962, 5.943, 5.924, 5.905, 5.886, 5.867, 5.848, 5.829, 5.810, 5.791, 5.772, 5.753, 5.734, 5.715, 5.696, 5.677, 5.658, 5.639, 5.620, 5.601, 5.582, 5.563, 5.544, 5.525, 5.506, 5.487, 5.468, 5.449, 5.430, 5.411, 5.392, 5.373, 5.354, 5.335, 5.316, 5.297, 5.278, 5.259, 5.240, 5.221, 5.202, 5.183, 5.164, 5.145, 5.126, 5.107, 5.088, 5.069, 5.050, 5.031, 5.012, 5.000, 4.981, 4.962, 4.943, 4.924, 4.905, 4.886, 4.867, 4.848, 4.829, 4.810, 4.791, 4.772, 4.753, 4.734, 4.715, 4.696, 4.677, 4.658, 4.639, 4.620, 4.601, 4.582, 4.563, 4.544, 4.525, 4.506, 4.487, 4.468, 4.449, 4.430, 4.411, 4.392, 4.373, 4.354, 4.335, 4.316, 4.297, 4.278, 4.259, 4.240, 4.221, 4.202, 4.183, 4.164, 4.145, 4.126, 4.107, 4.088, 4.069, 4.050, 4.031, 4.012, 4.000, 3.981, 3.962, 3.943, 3.924, 3.905, 3.886, 3.867, 3.848, 3.829, 3.810, 3.791, 3.772, 3.753, 3.734, 3.715, 3.696, 3.677, 3.658, 3.639, 3.620, 3.601, 3.582, 3.563, 3.544, 3.525, 3.506, 3.487, 3.468, 3.449, 3.430, 3.411, 3.392, 3.373, 3.354, 3.335, 3.316, 3.297, 3.278, 3.259, 3.240, 3.221, 3.202, 3.183, 3.164, 3.145, 3.126, 3.107, 3.088, 3.069, 3.050, 3.031, 3.012, 3.000, 2.981, 2.962, 2.943, 2.924, 2.905, 2.886, 2.867, 2.848, 2.829, 2.810, 2.791, 2.772, 2.753, 2.734, 2.715, 2.696, 2.677, 2.658, 2.639, 2.620, 2.601, 2.582, 2.563, 2.544, 2.525, 2.506, 2.487, 2.468, 2.449, 2.430, 2.411, 2.392, 2.373, 2.354, 2.335, 2.316, 2.297, 2.278, 2.259, 2.240, 2.221, 2.202, 2.183, 2.164, 2.145, 2.126, 2.107, 2.088, 2.069, 2.050, 2.031, 2.012, 2.000, 1.981, 1.962, 1.943, 1.924, 1.905, 1.886, 1.867, 1.848, 1.829, 1.810, 1.791, 1.772, 1.753, 1.734, 1.715, 1.696, 1.677, 1.658, 1.639, 1.620, 1.601, 1.582, 1.563, 1.544, 1.525, 1.506, 1.487, 1.468, 1.449, 1.430, 1.411, 1.392, 1.373, 1.354, 1.335, 1.316, 1.297, 1.278, 1.259, 1.240, 1.221, 1.202, 1.183, 1.164, 1.145, 1.126, 1.107, 1.088, 1.069, 1.050, 1.031, 1.012, 1.000, 0.981, 0.962, 0.943, 0.924, 0.905, 0.886, 0.867, 0.848, 0.829, 0.810, 0.791, 0.772, 0.753, 0.734, 0.715, 0.696, 0.677, 0.658, 0.639, 0.620, 0.601, 0.582, 0.563, 0.544, 0.525, 0.506, 0.487, 0.468, 0.449, 0.430, 0.411, 0.392, 0.373, 0.354, 0.335, 0.316, 0.297, 0.278, 0.259, 0.240, 0.221, 0.202, 0.183, 0.164, 0.145, 0.126, 0.107, 0.088, 0.069, 0.050, 0.031, 0.012, 0.000, -0.019, -0.038, -0.057, -0.076, -0.095, -0.114, -0.133, -0.152, -0.171, -0.190, -0.209, -0.228, -0.247, -0.266, -0.285, -0.304, -0.323, -0.342, -0.361, -0.380, -0.399, -0.418, -0.437, -0.456, -0.475, -0.494, -0.513, -0.532, -0.551, -0.570, -0.589, -0.608, -0.627, -0.646, -0.665, -0.684, -0.703, -0.722, -0.741, -0.760, -0.779, -0.798, -0.817, -0.836, -0.855, -0.874, -0.893, -0.912, -0.931, -0.950, -0.969, -0.988, -1.007, -1.026, -1.045, -1.064, -1.083, -1.102, -1.121, -1.140, -1.159, -1.178, -1.197, -1.216, -1.235, -1.254, -1.273, -1.292, -1.311, -1.330, -1.349, -1.368, -1.387, -1.406, -1.425, -1.444, -1.463, -1.482, -1.501, -1.520, -1.539, -1.558, -1.577, -1.596, -1.615, -1.634, -1.653, -1.672, -1.691, -1.710, -1.729, -1.748, -1.767, -1.786, -1.805, -1.824, -1.843, -1.862, -1.881, -1.900, -1.919, -1.938, -1.957, -1.976, -1.995, -2.014, -2.033, -2.052, -2.071, -2.090, -2.109, -2.128, -2.147, -2.166, -2.185, -2.204, -2.223, -2.242, -2.261, -2.280, -2.299, -2.318, -2.337, -2.356, -2.375, -2.394, -2.413, -2.432, -2.451, -2.470, -2.489, -2.508, -2.527, -2.546, -2.565, -2.584, -2.603, -2.622, -2.641, -2.660, -2.679, -2.698, -2.717, -2.736, -2.755, -2.774, -2.793, -2.812, -2.831, -2.850, -2.869, -2.888, -2.907, -2.926, -2.945, -2.964

CC(=O)SCc1ccc(Cl)cc1

Chemical structure: CC(=O)SCc1ccc(Cl)cc1

¹³C NMR peaks (ppm): 195.98, 144.04, 135.00, 132.94, 130.46, 129.20, 128.66, 128.41, 77.34, 77.23, 77.02, 76.71, 41.96, 33.32, 21.65, 16.73.

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

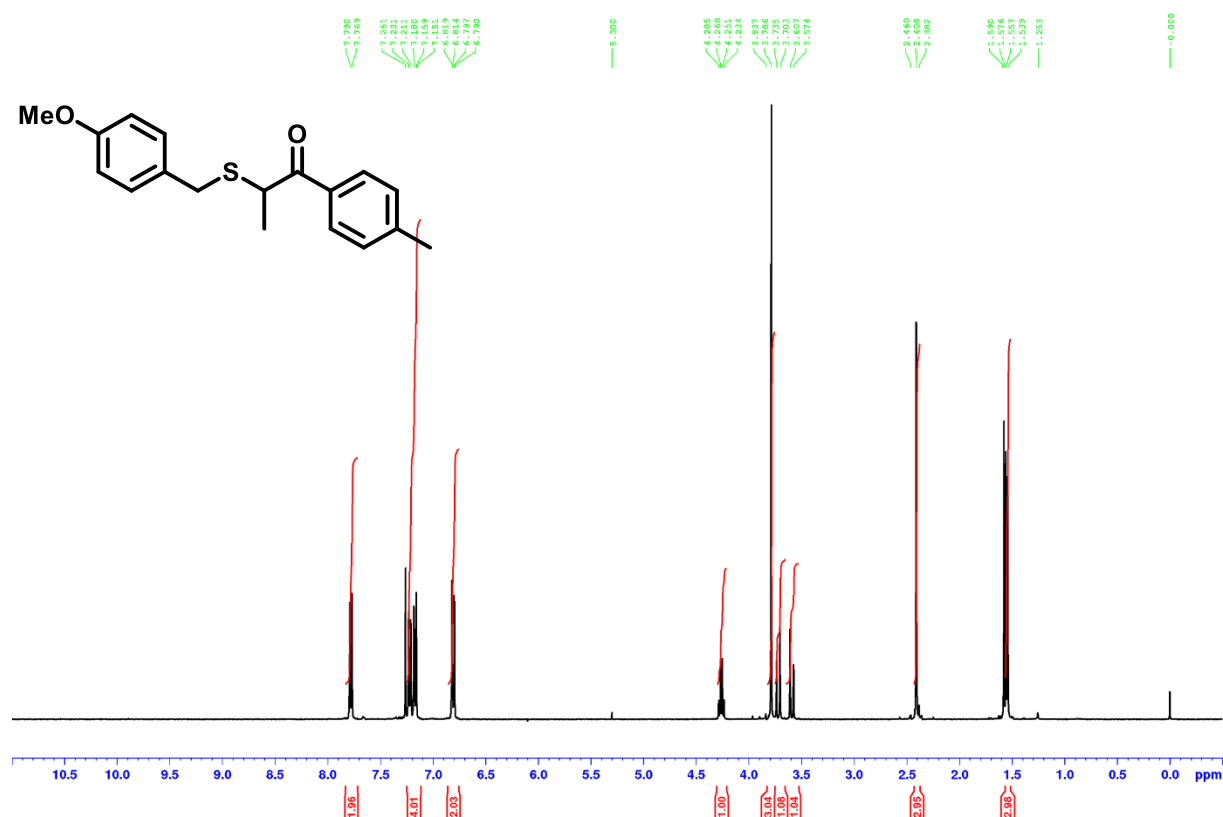


Figure S37: ¹H NMR (400 MHz, CDCl₃) spectrum of **3k**.

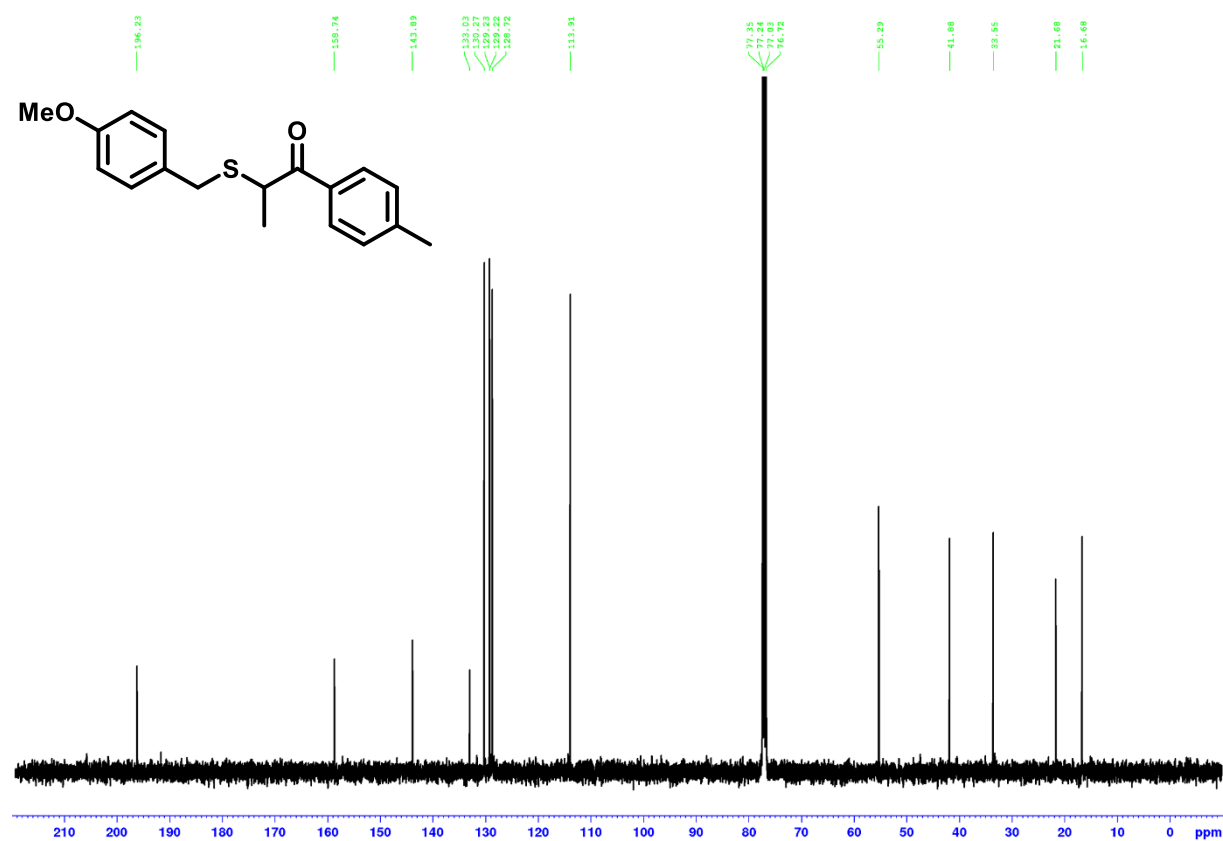


Figure S38: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3k**.

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

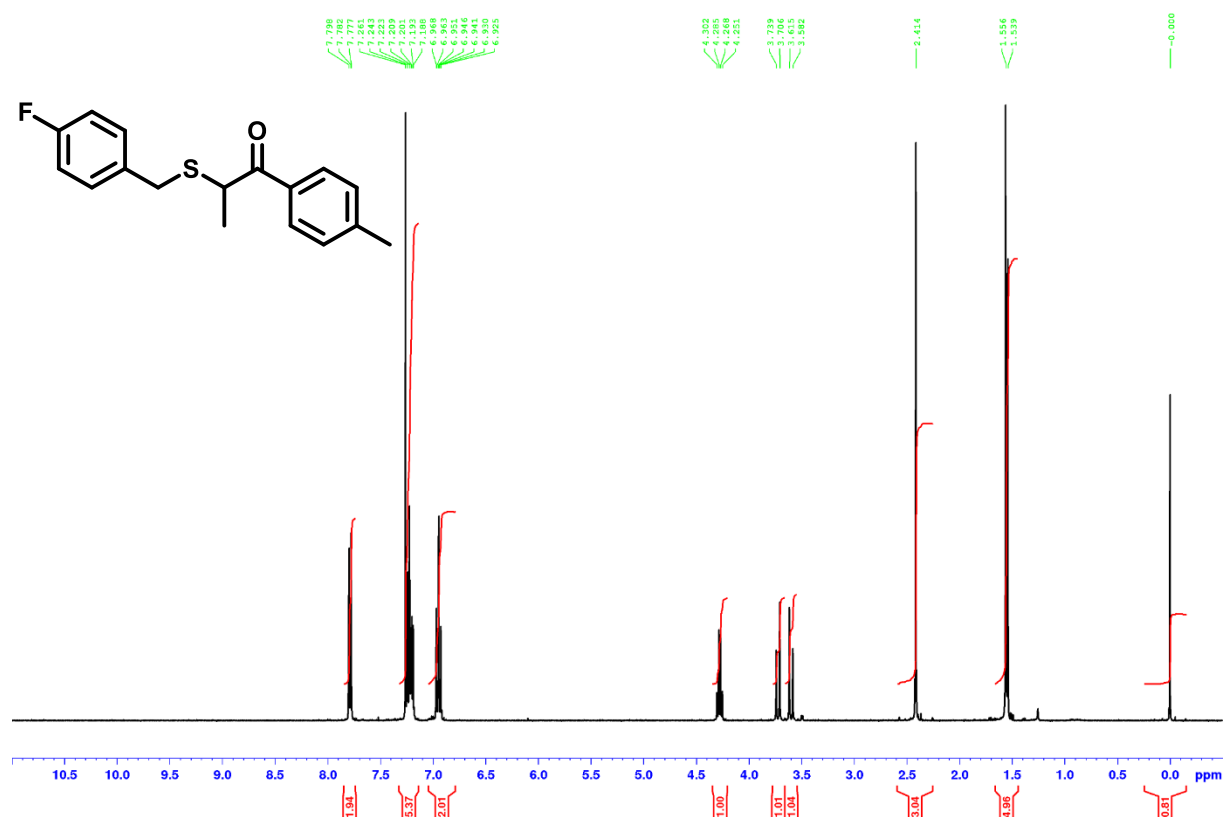


Figure S39: ¹H NMR (400 MHz, CDCl₃) spectrum of **3l**.

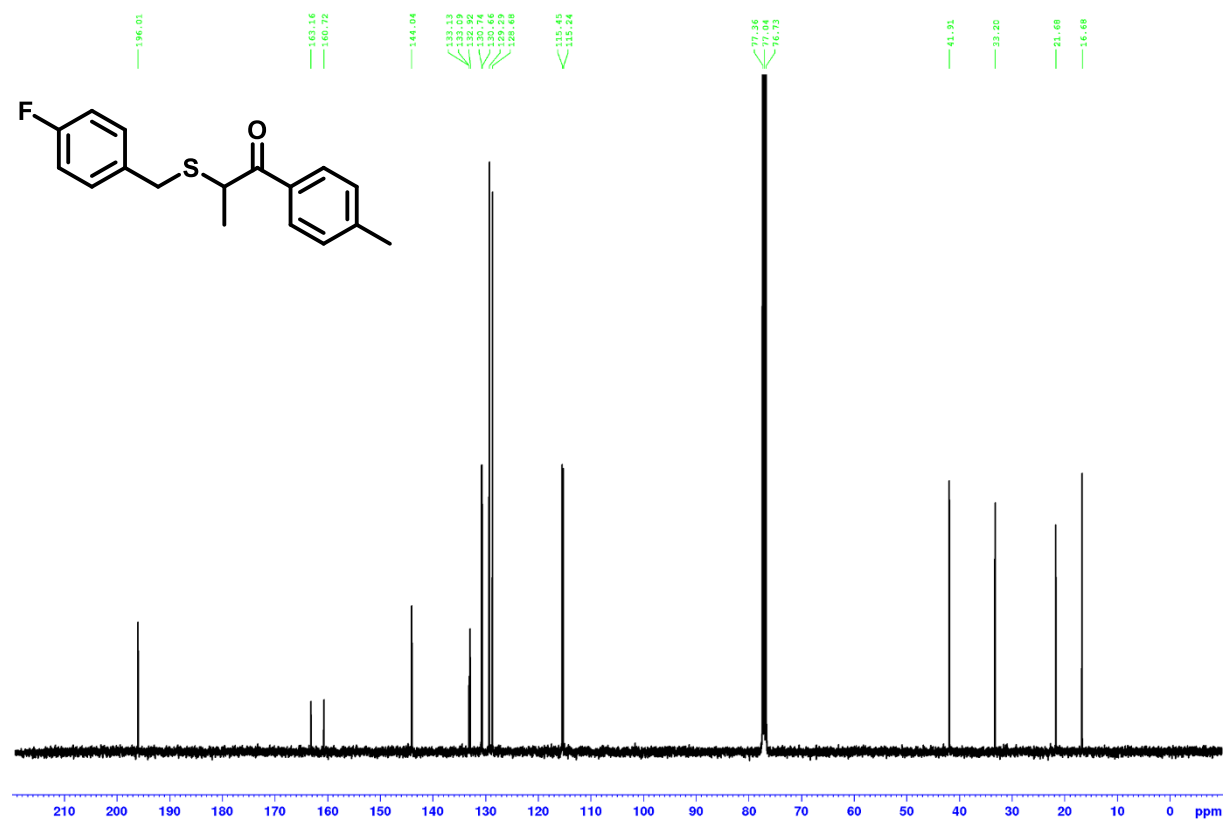


Figure S40: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3l**.

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

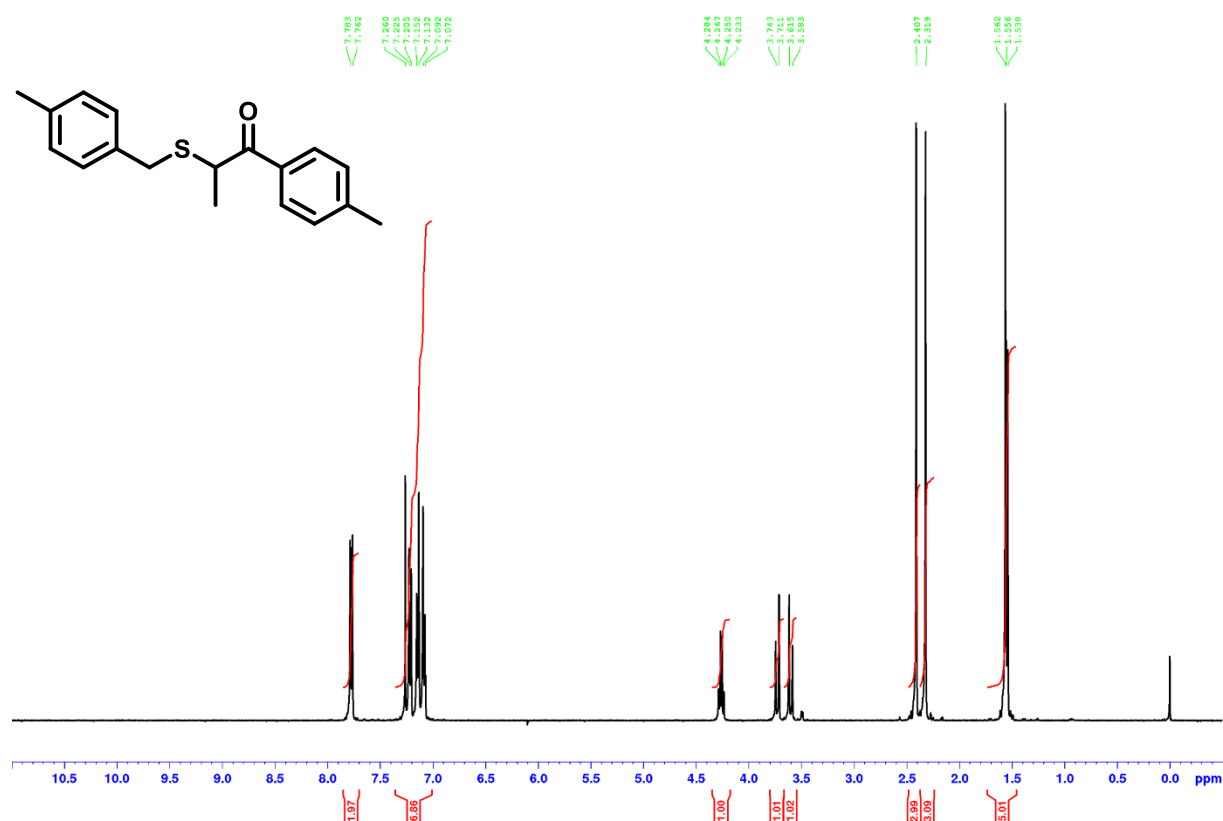


Figure S41: ¹H NMR (400 MHz, CDCl₃) spectrum of **3m**.

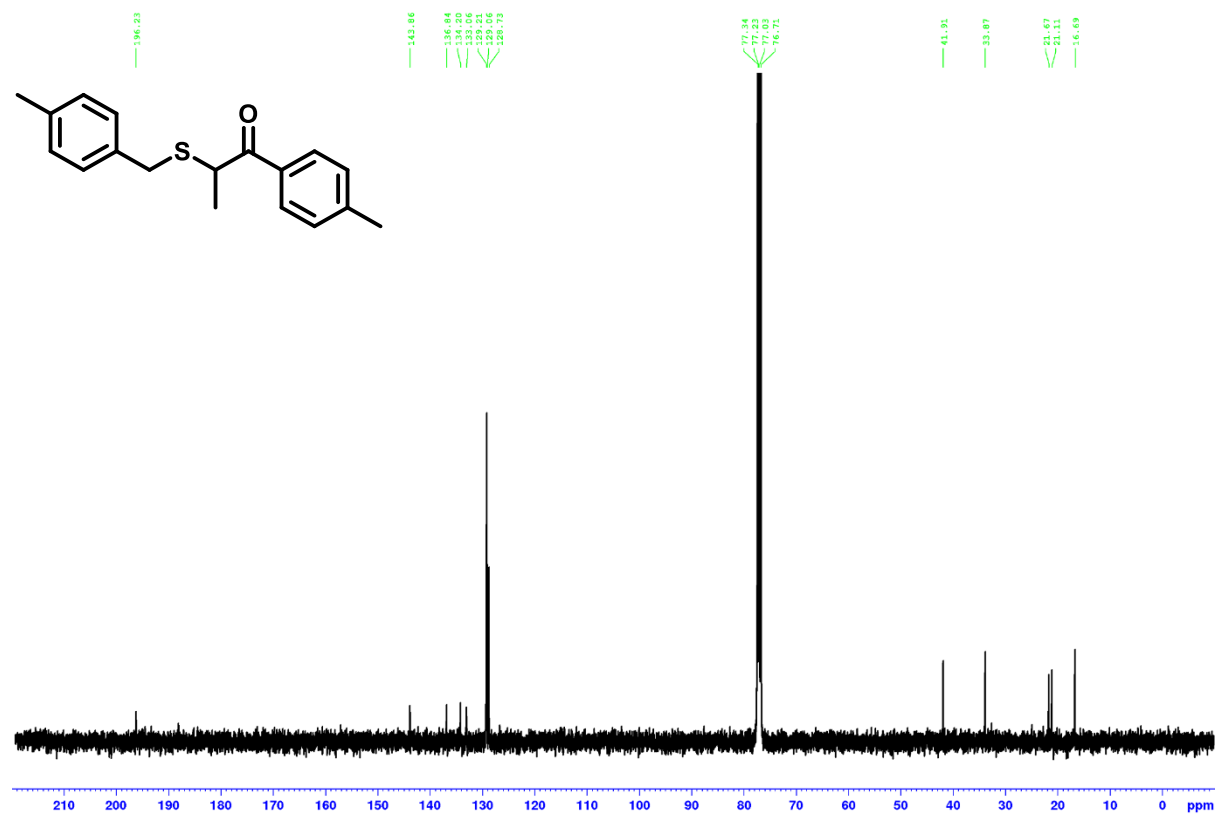


Figure S42: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3m**.

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

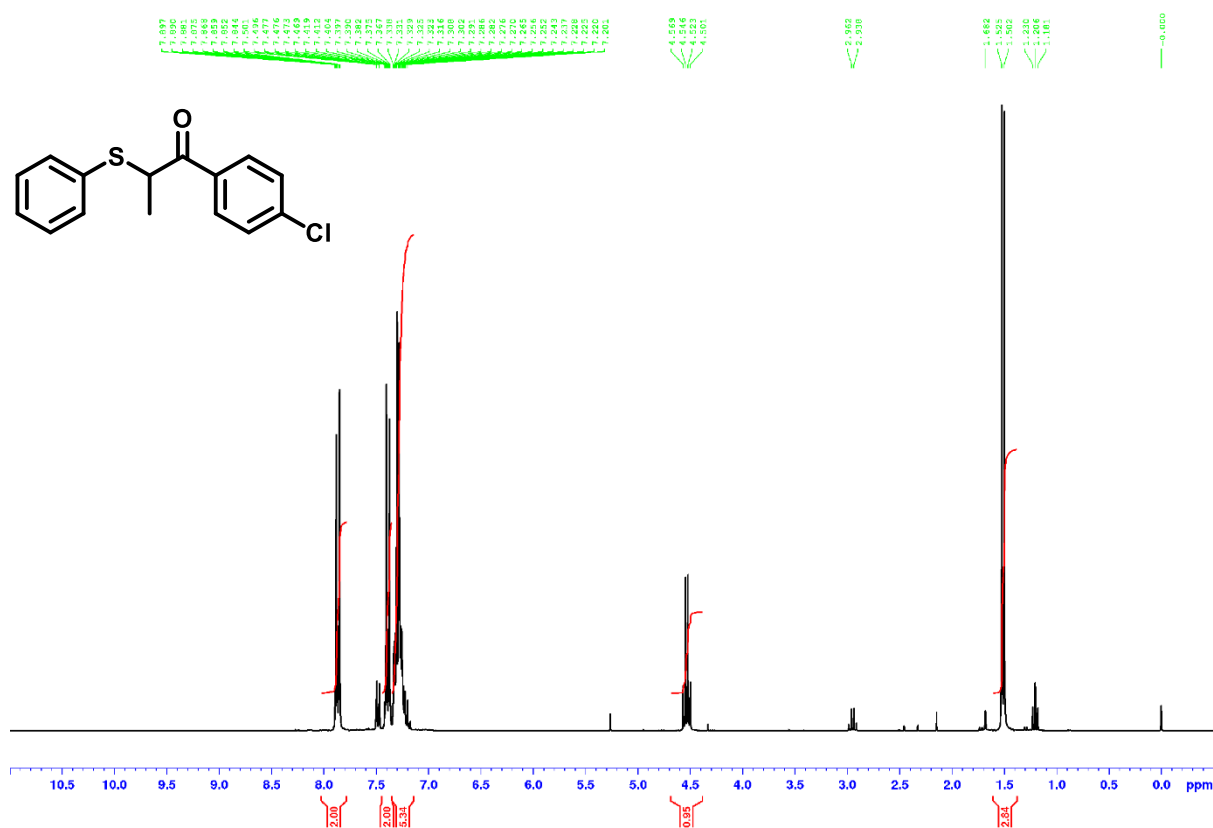


Figure S43: ¹H NMR (300 MHz, CDCl₃) spectrum of 3n.

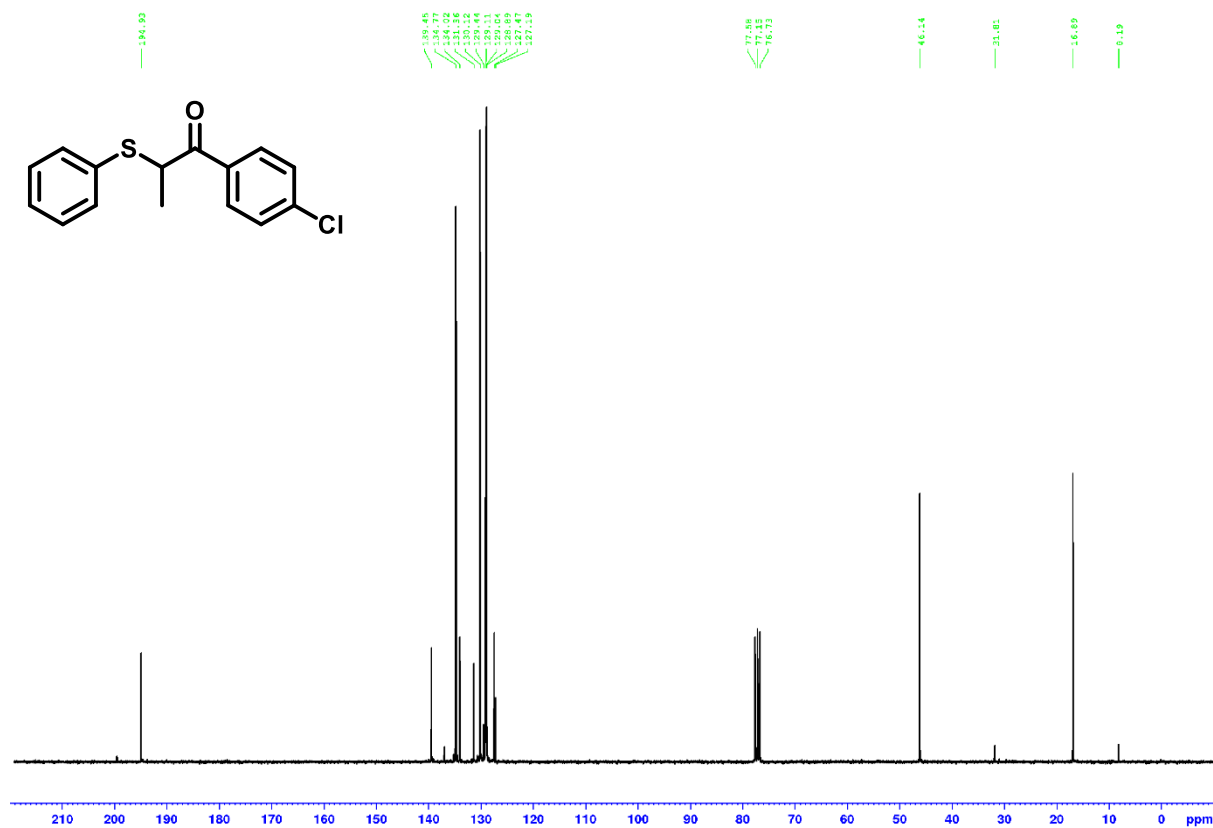


Figure S44: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of 3n.

2-(Benzythio)-1-(4-chlorophenyl)propan-1-one **3o**

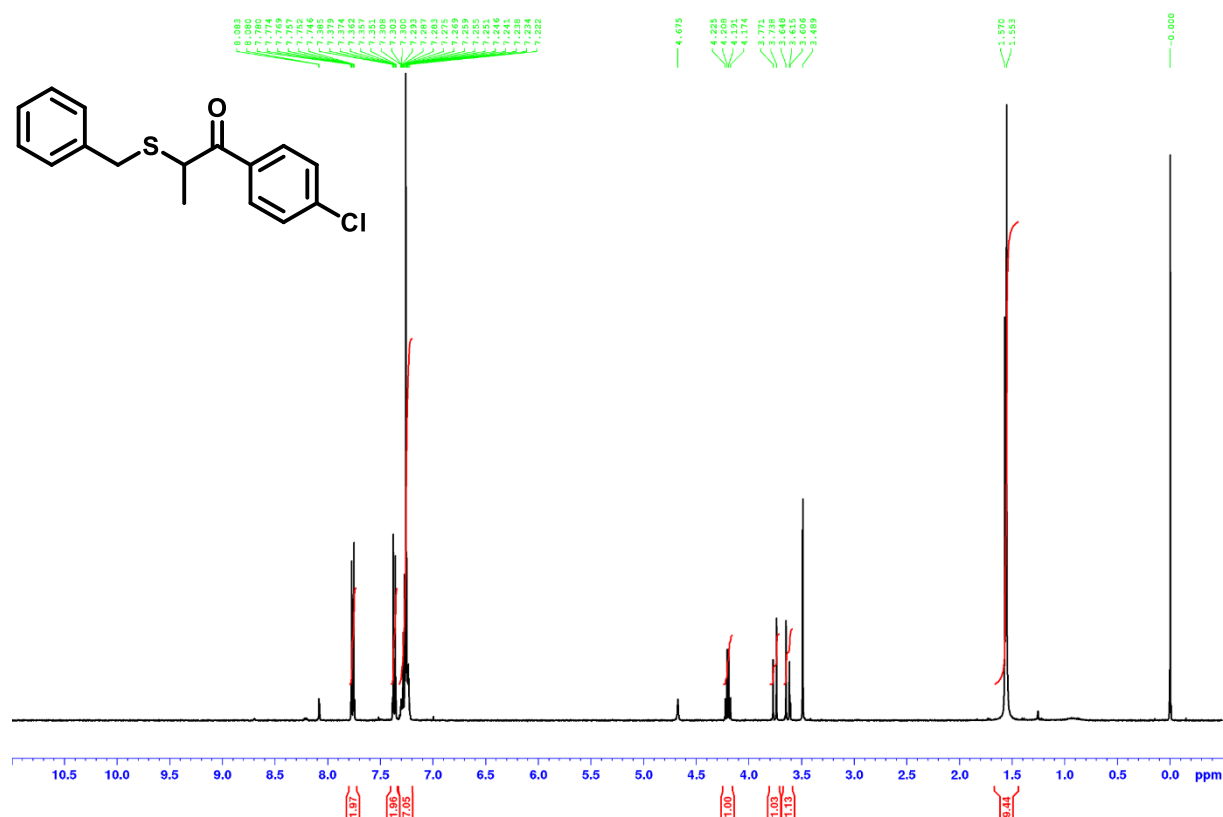


Figure S45: ¹H NMR (400 MHz, CDCl₃) spectrum of **3o**.

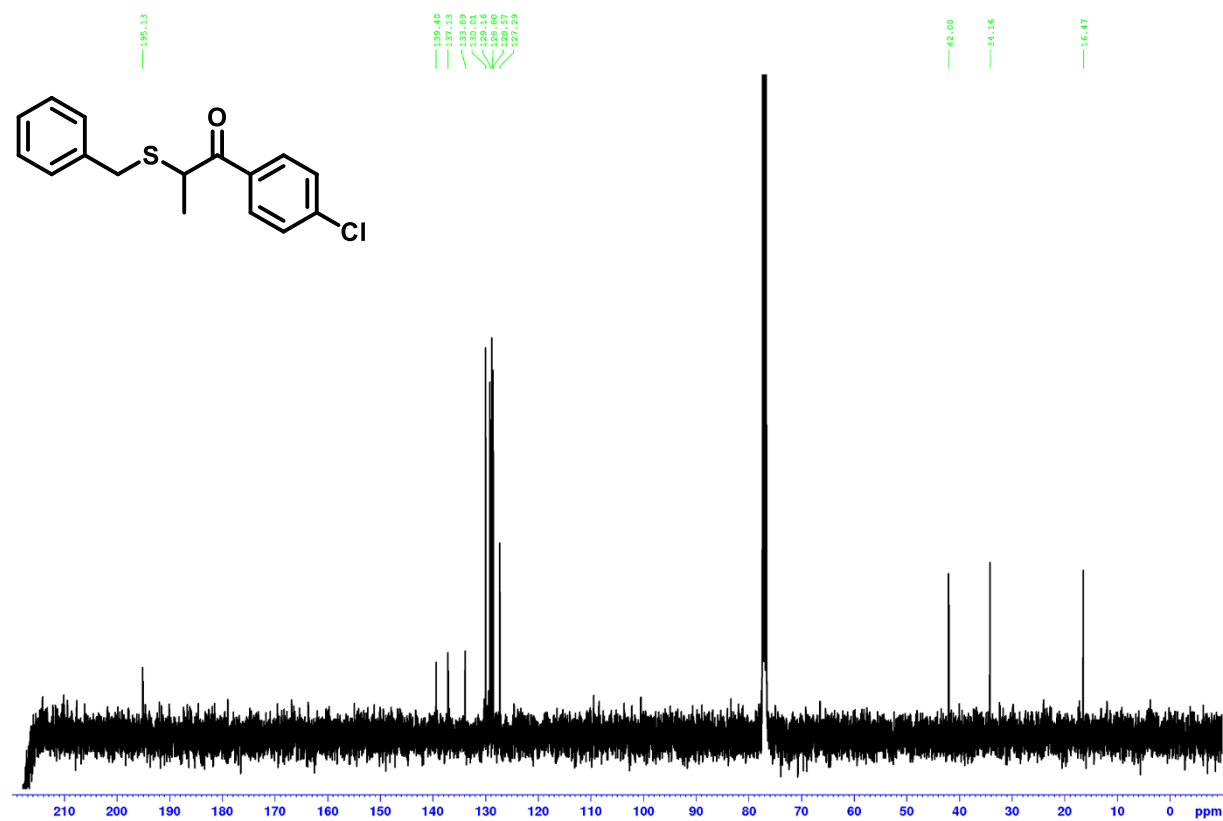


Figure S46: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3o**.

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

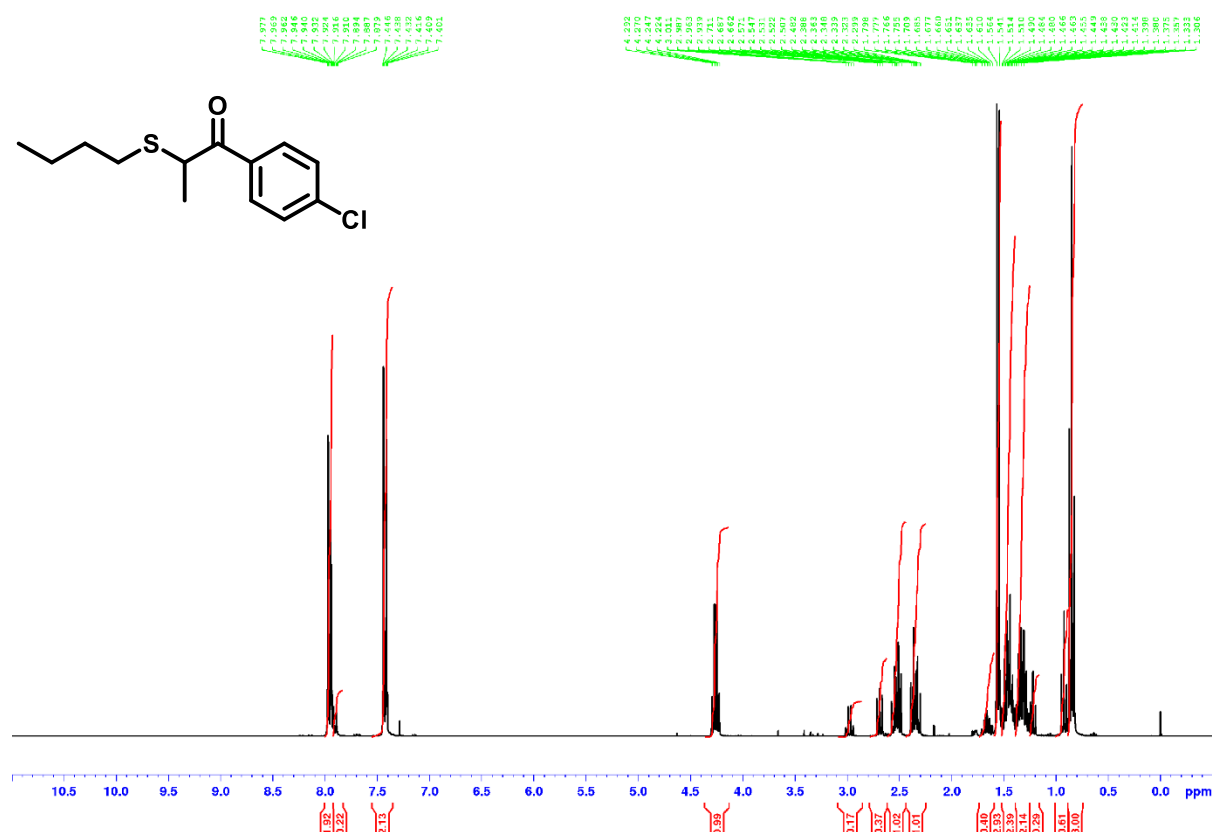
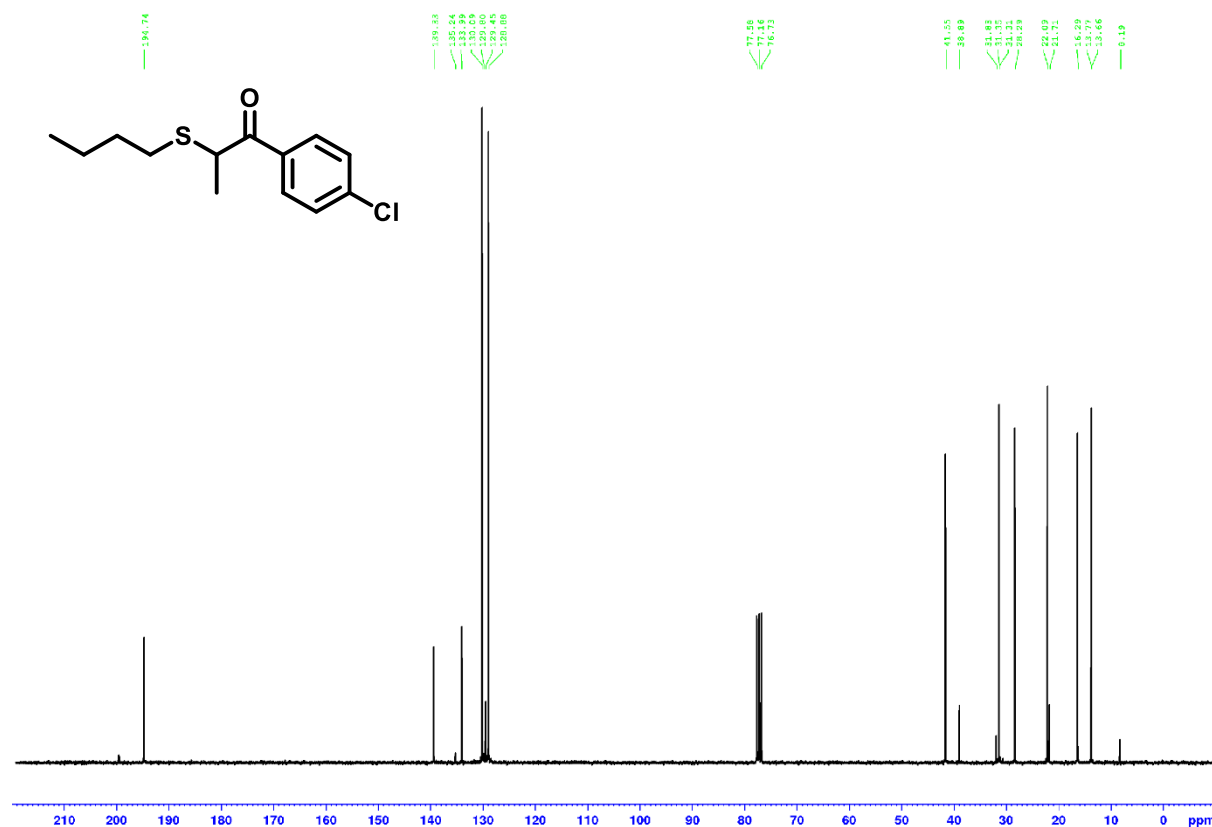


Figure S47: ¹H NMR (300 MHz, CDCl₃) spectrum of 3p.



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

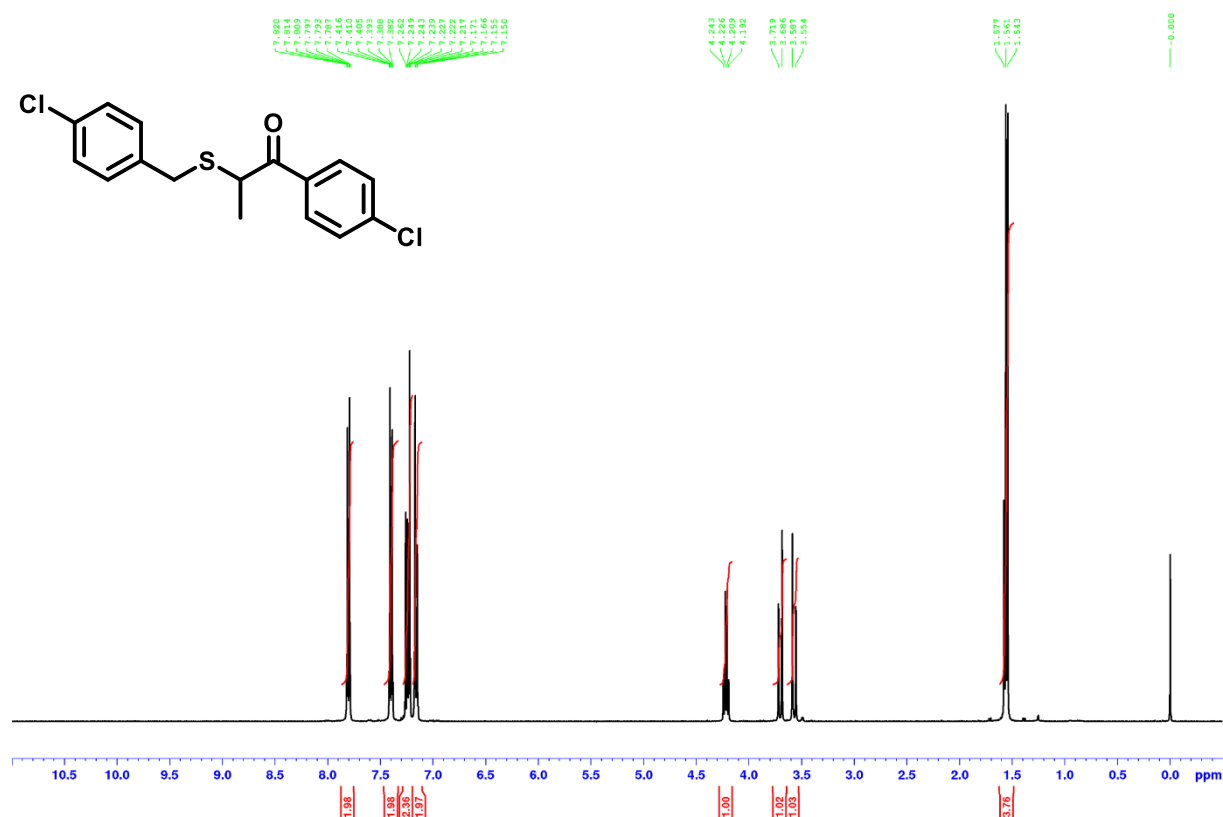


Figure S49: ¹H NMR (400 MHz, CDCl₃) spectrum of **3q**.

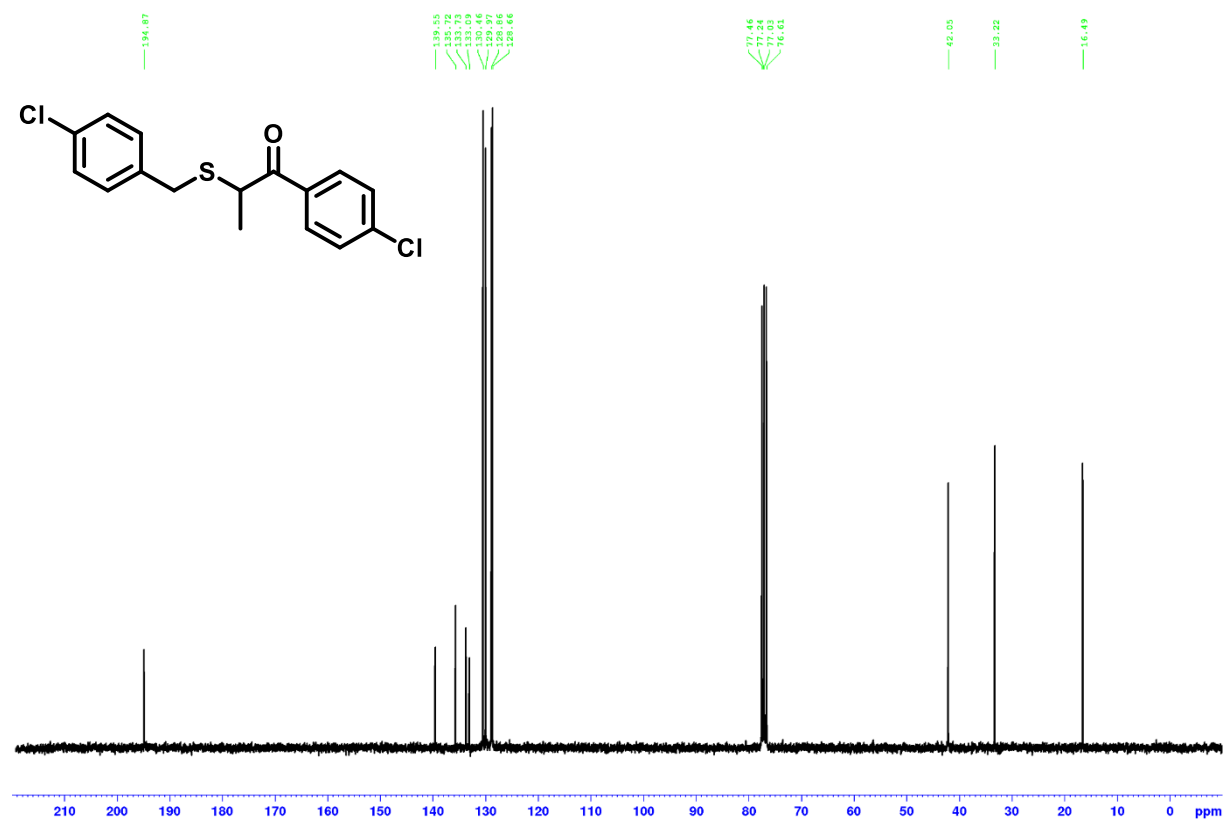


Figure S50: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3q**.

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

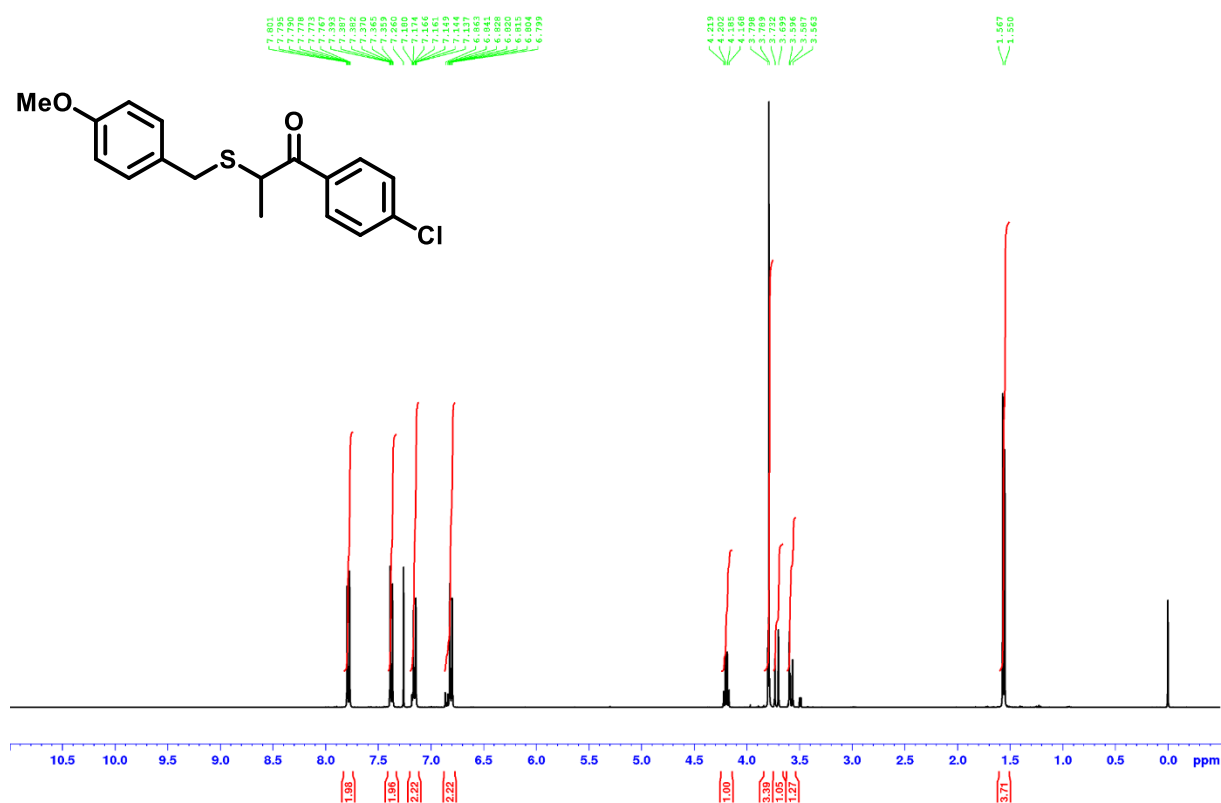
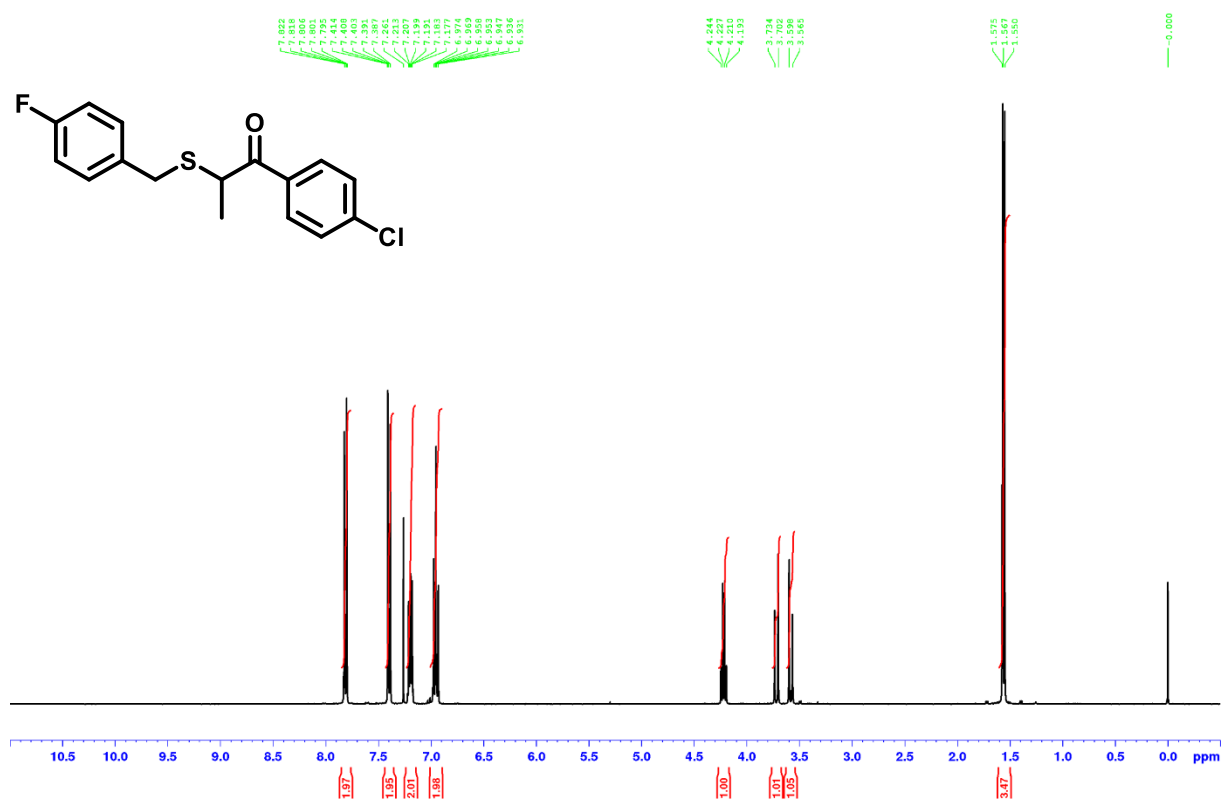


Figure S51: ¹H NMR (400 MHz, CDCl₃) spectrum of 3r.



Figure S52: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of 3r.

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



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

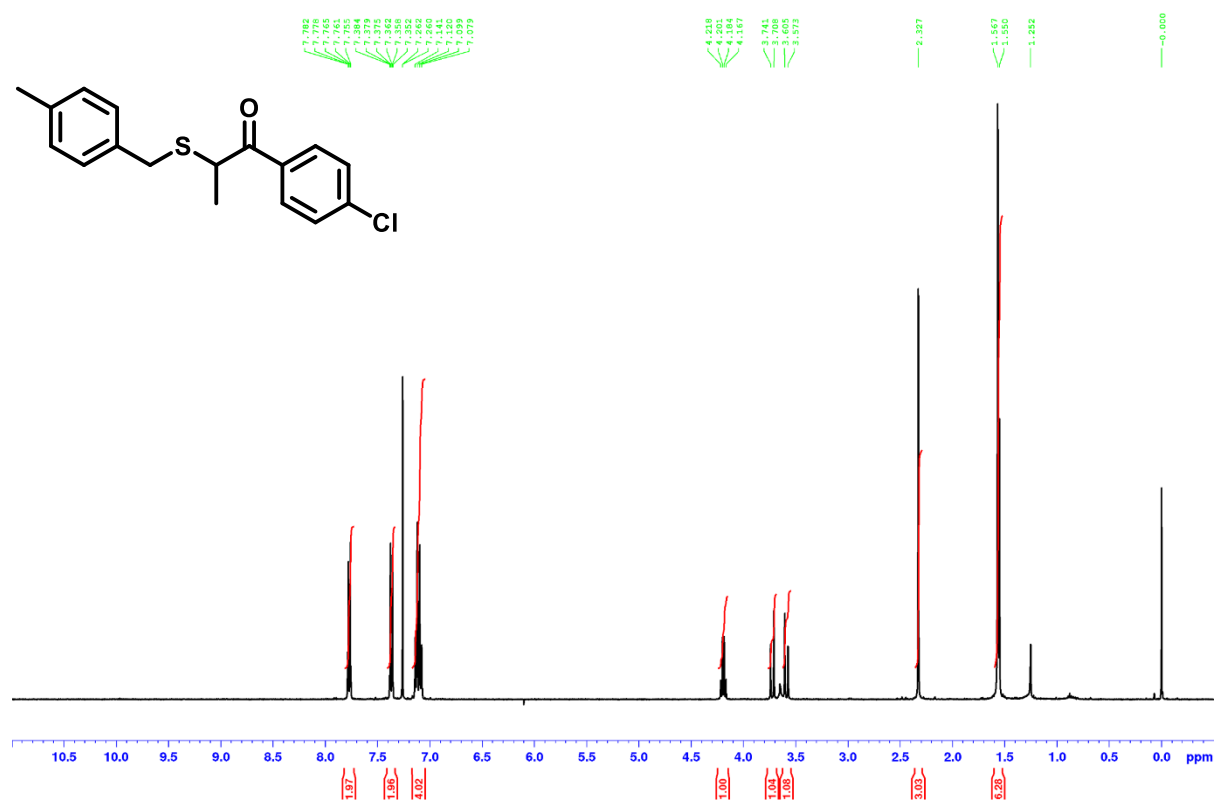


Figure S55: ¹H NMR (400 MHz, CDCl₃) spectrum of 3t.

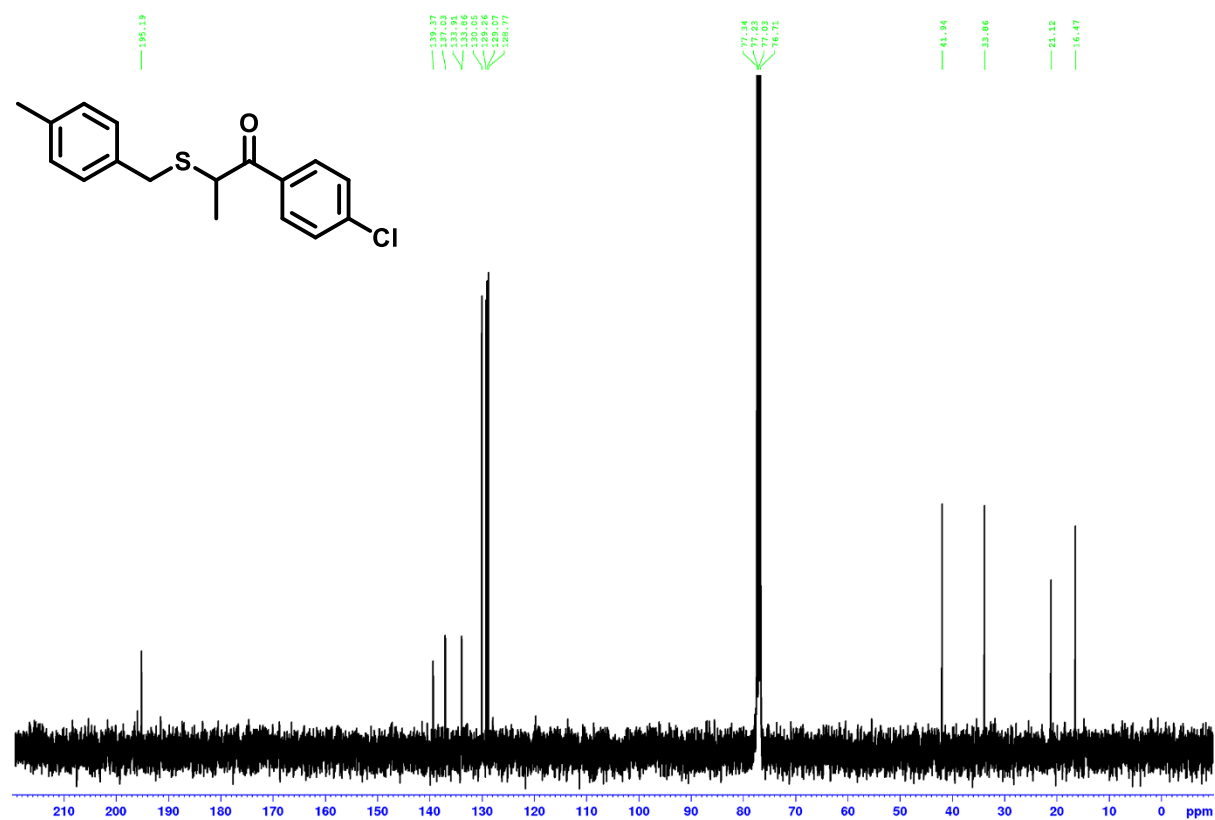
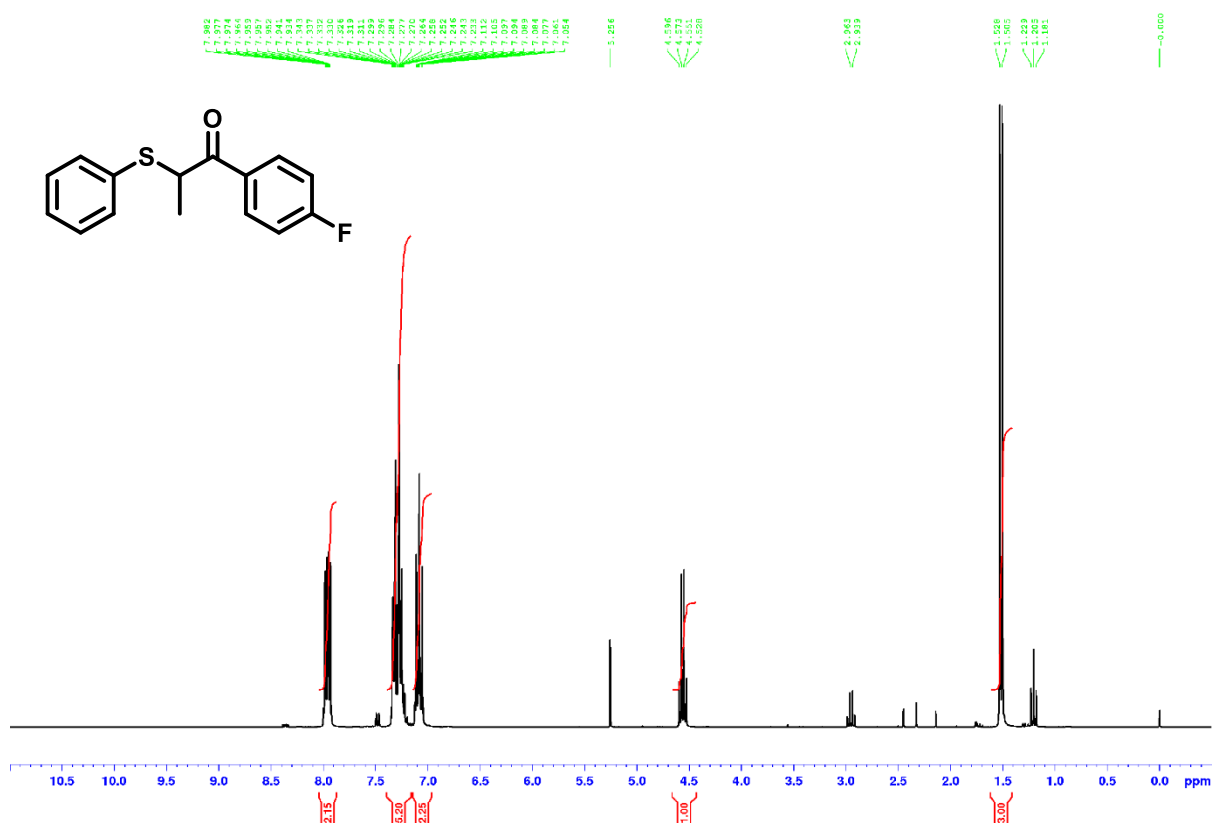


Figure S56: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of 3t.

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



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

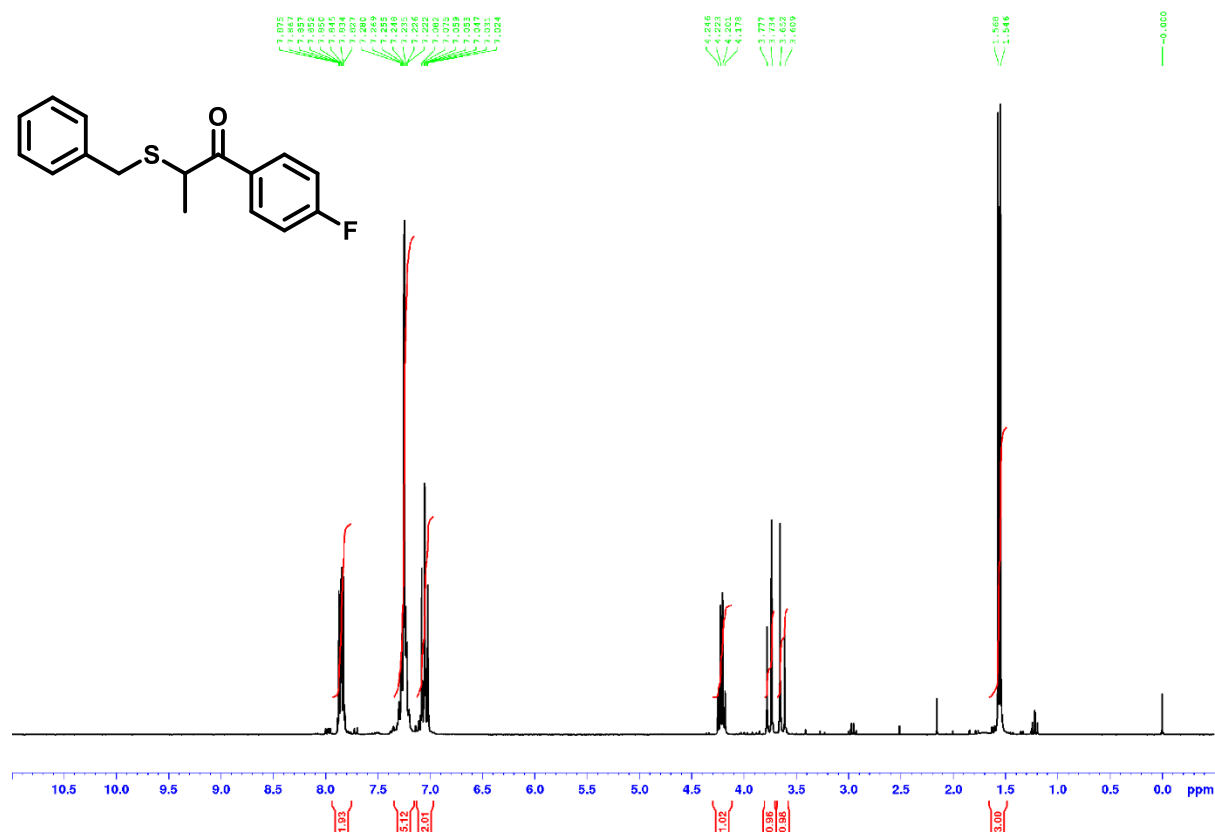


Figure S59: ¹H NMR (300 MHz, CDCl₃) spectrum of **3v**.

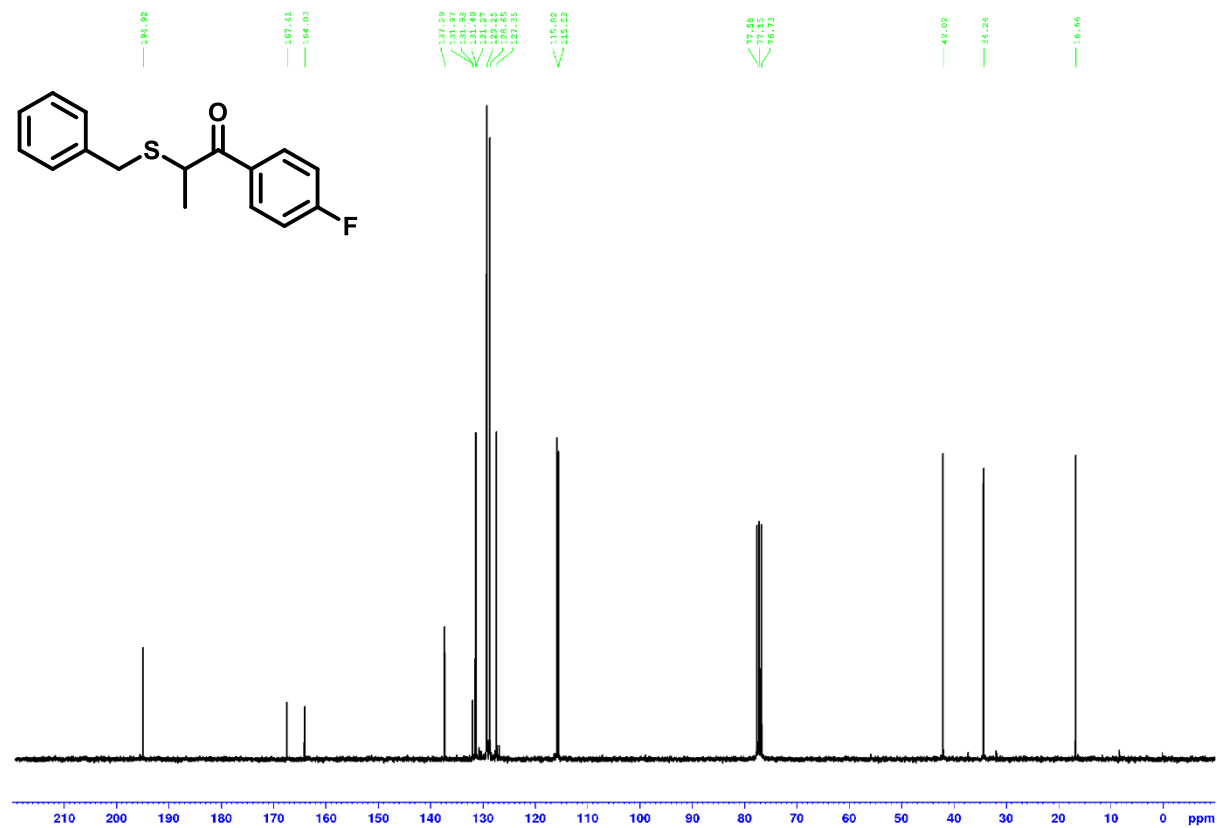


Figure S60: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3v**.

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

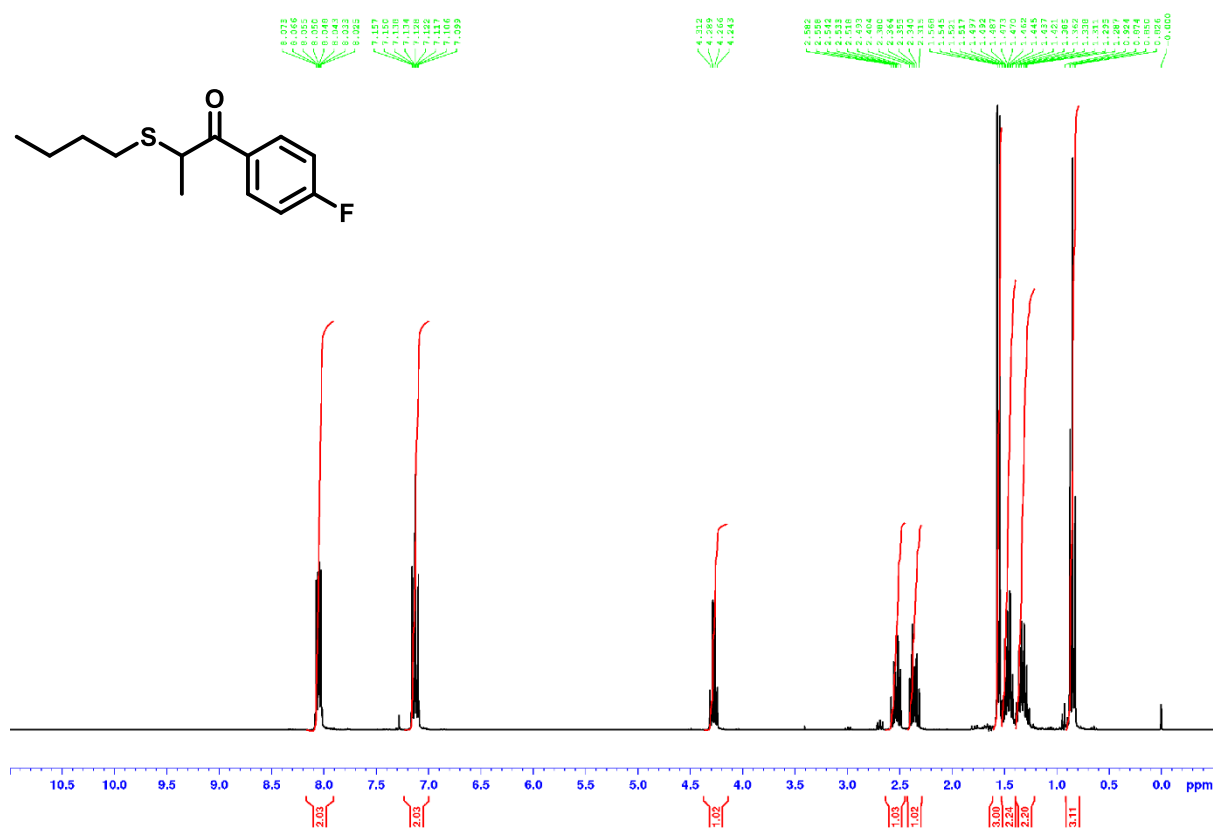


Figure S61: ¹H NMR (300 MHz, CDCl₃) spectrum of **3w**.



Figure S62: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3w**.

Chemical structure: Clc1ccc(cc1)CCSC(C)C(=O)c2ccc(F)cc2

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 10 ppm. The spectrum includes aromatic signals (7.0-8.0 ppm), a methylene signal (4.2 ppm), a methine signal (3.7 ppm), and a methyl signal (1.5 ppm). Integration values are provided below the baseline, and chemical shifts are labeled above the peaks.

Chemical Shift (ppm)	Integration
7.9211	1.93
7.8986	4.84
7.8844	1.97
7.8699	
7.8012	
7.7829	
7.7648	
7.7398	
7.7239	
7.7094	
7.6935	
7.6776	
7.6617	
7.6458	
7.6299	
7.6140	
7.5981	
7.5822	
7.5663	
7.5504	
7.5345	
4.213	1.00
4.238	
4.219	
4.202	
3.727	1.00
3.694	1.00
3.669	
1.561	2.28
1.550	
1.541	
0.005	
-0.006	

CC(=O)c1ccc(F)cc1SCc2ccc(Cl)cc2

Chemical structure: 4-(4-chlorobenzyl)-1-(4-fluorophenyl)ethan-1-one

¹³C NMR peaks (ppm):

- 194.90
- 146.36
- 140.38
- 138.59
- 135.78
- 132.86
- 132.62
- 130.74
- 130.64
- 128.85
- 115.54
- 115.25
- 77.44
- 77.22
- 77.02
- 76.59
- 42.05
- 33.14
- 16.45

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

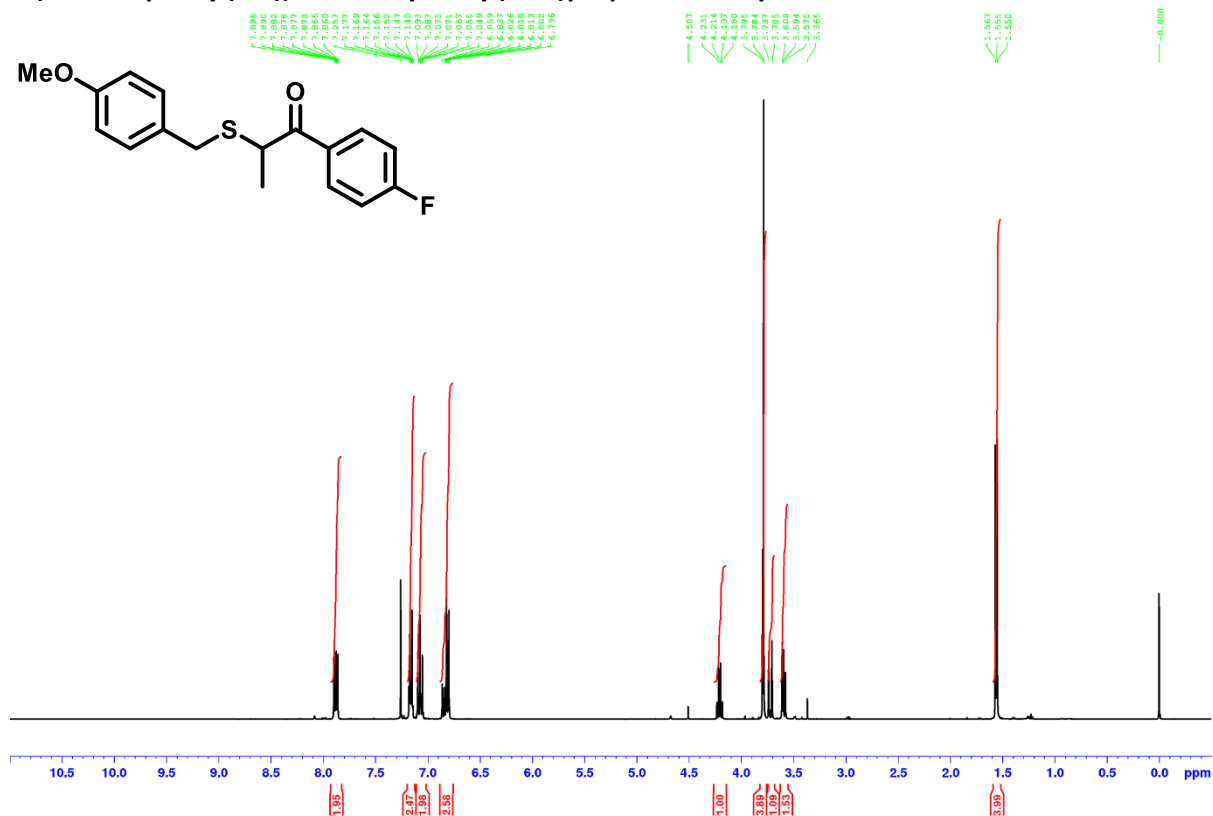


Figure S65: ¹H NMR (400 MHz, CDCl₃) spectrum of **3y**.

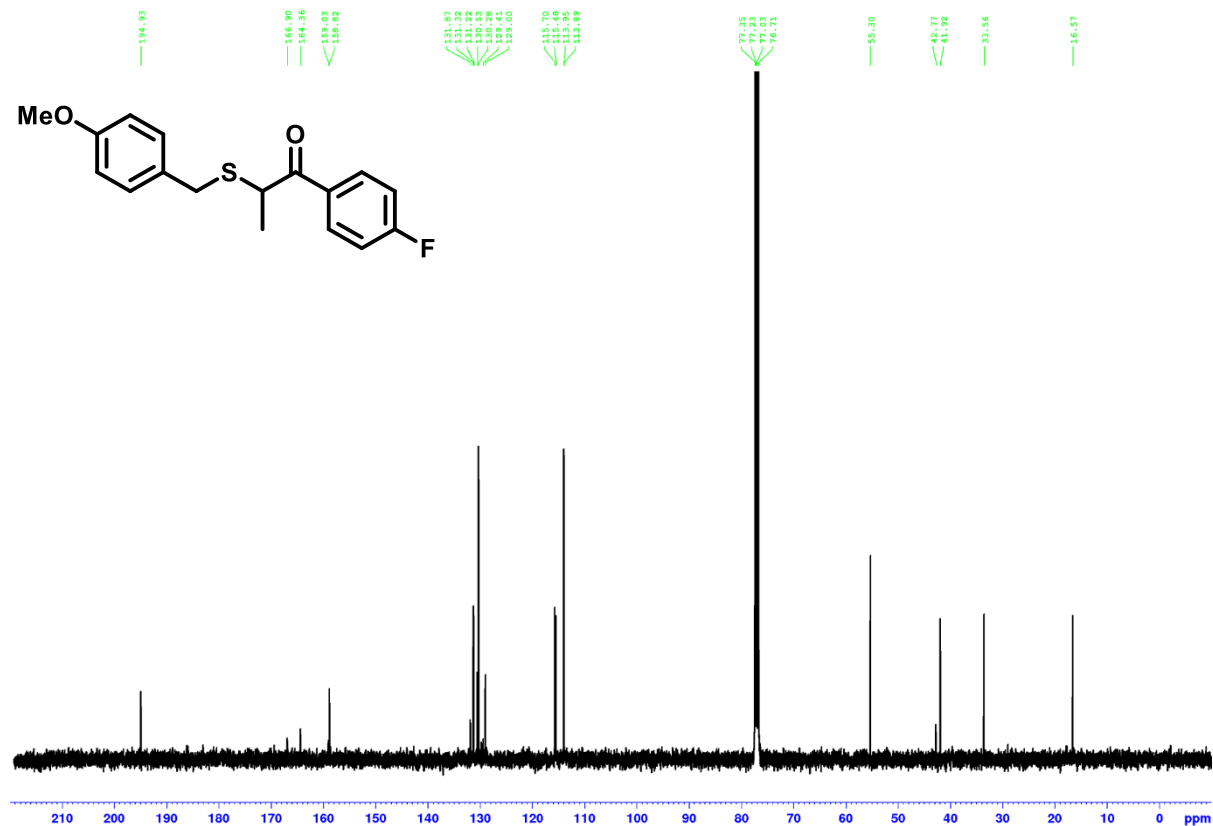


Figure S66: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3y**.

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

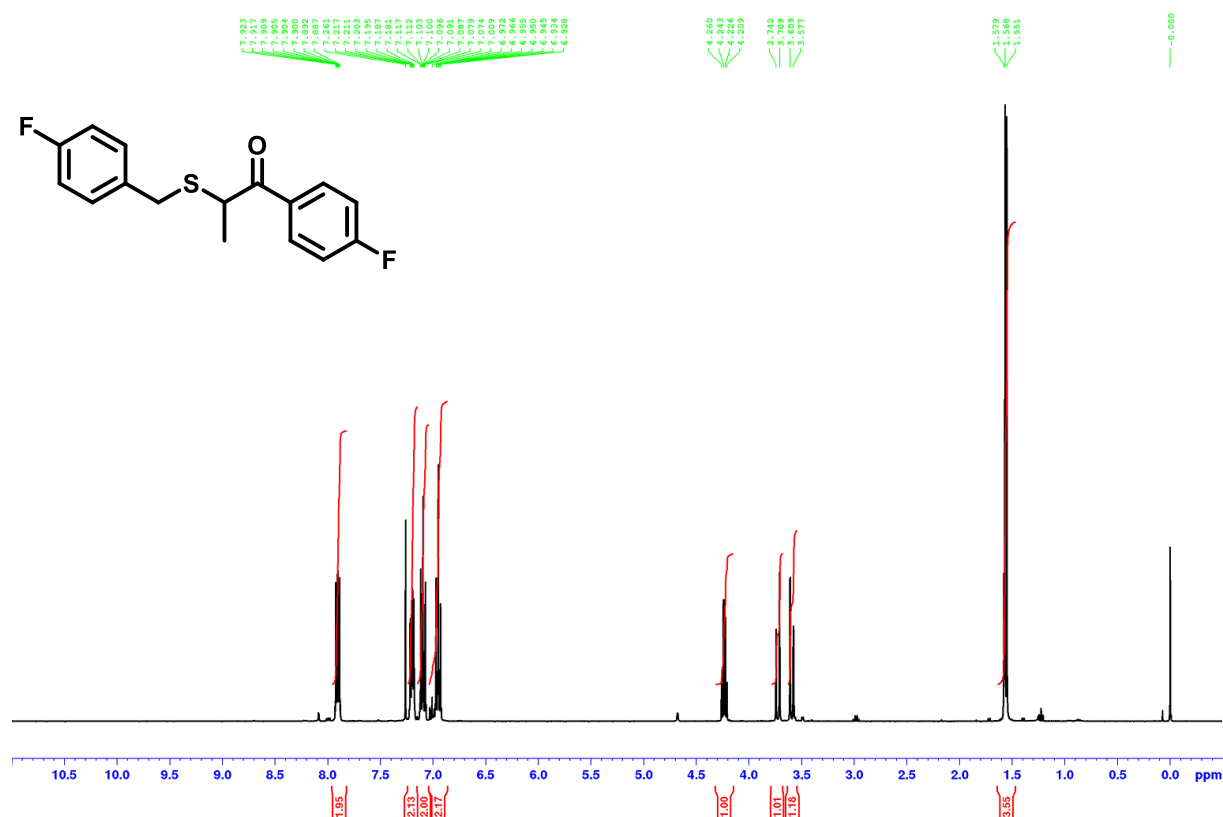


Figure S67: ¹H NMR (400 MHz, CDCl₃) spectrum of **3z**.

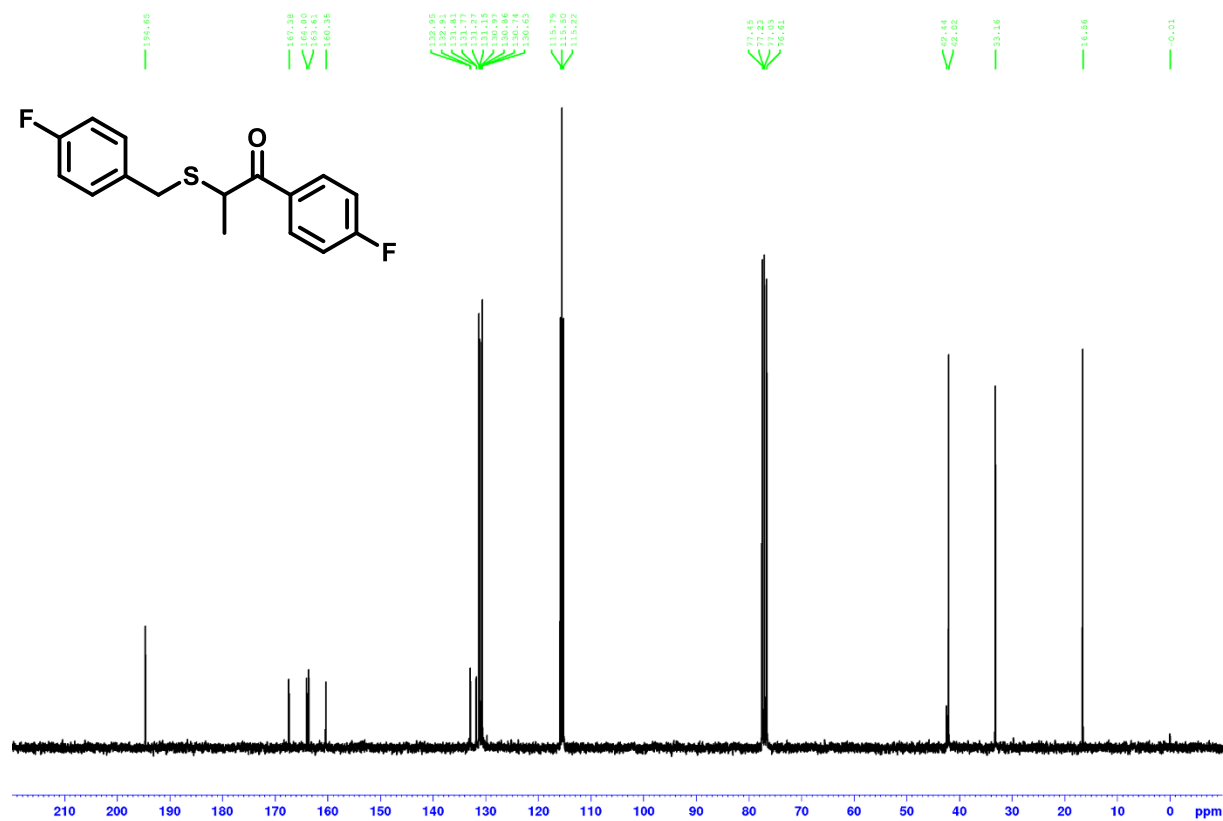


Figure S68: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **3z**.

CC1=CC=C(C=C1)CSC(C)C(=O)C2=CC=C(C=C2)F

Chemical shifts (ppm): 7.882, 7.876, 7.864, 7.855, 7.846, 7.838, 7.826, 7.815, 7.809, 7.803, 7.792, 7.787, 7.781, 7.751, 7.746, 4.257, 4.250, 4.203, 4.186, 3.749, 3.716, 3.696, 3.683, 2.325, 1.587, 1.570, 1.552, 1.524, -0.000.

Integration values: 2.00, 6.00, 1.00, 1.00, 1.00, 6.00.

Cc1ccc(cc1)CSC(C)C(=O)c2ccc(F)cc2

Chemical structure: 4-(4-methylphenyl)thioacetophenone

¹³C NMR peaks (ppm):

- 194.95
- 167.10
- 164.37
- 136.99
- 135.89
- 131.33
- 131.33
- 129.24
- 128.07
- 115.46
- 115.46
- 77.35
- 77.25
- 77.03
- 76.71
- 41.90
- 33.87
- 21.11
- 16.57

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

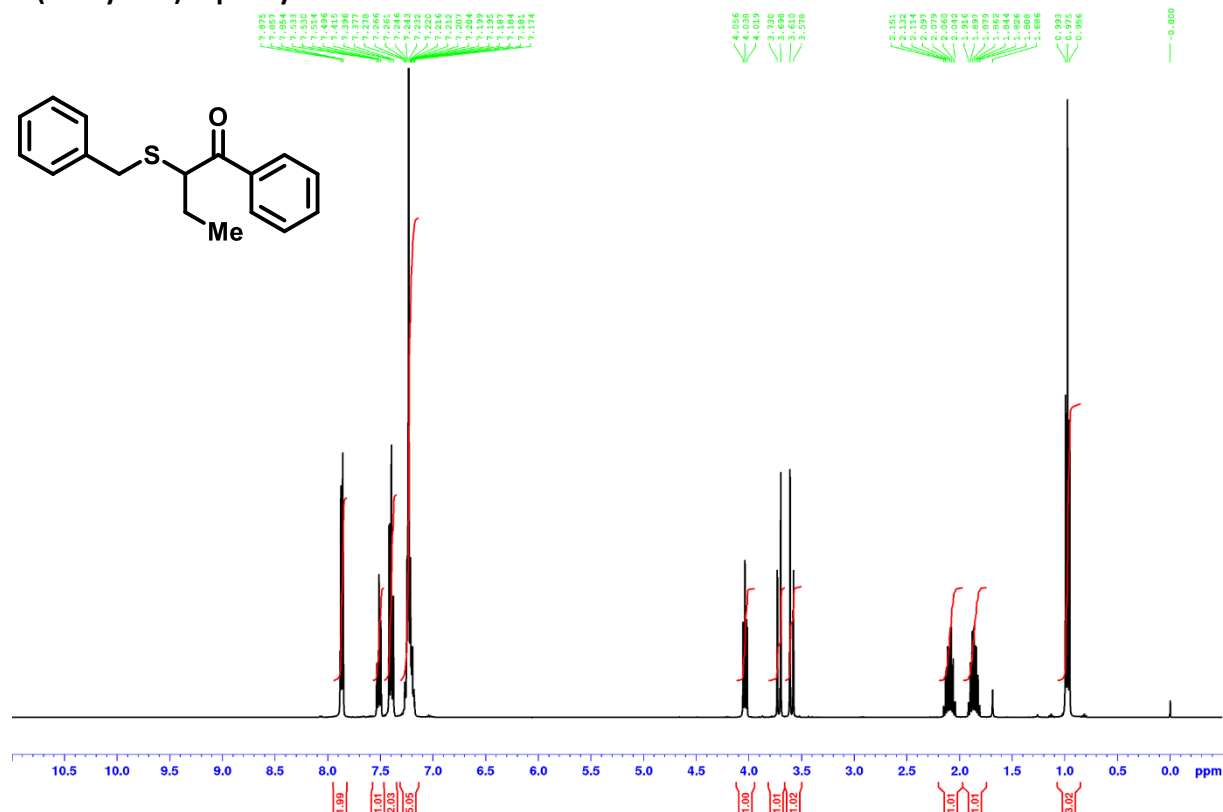


Figure S71: ¹H NMR (400 MHz, CDCl₃) spectrum of 3bb.

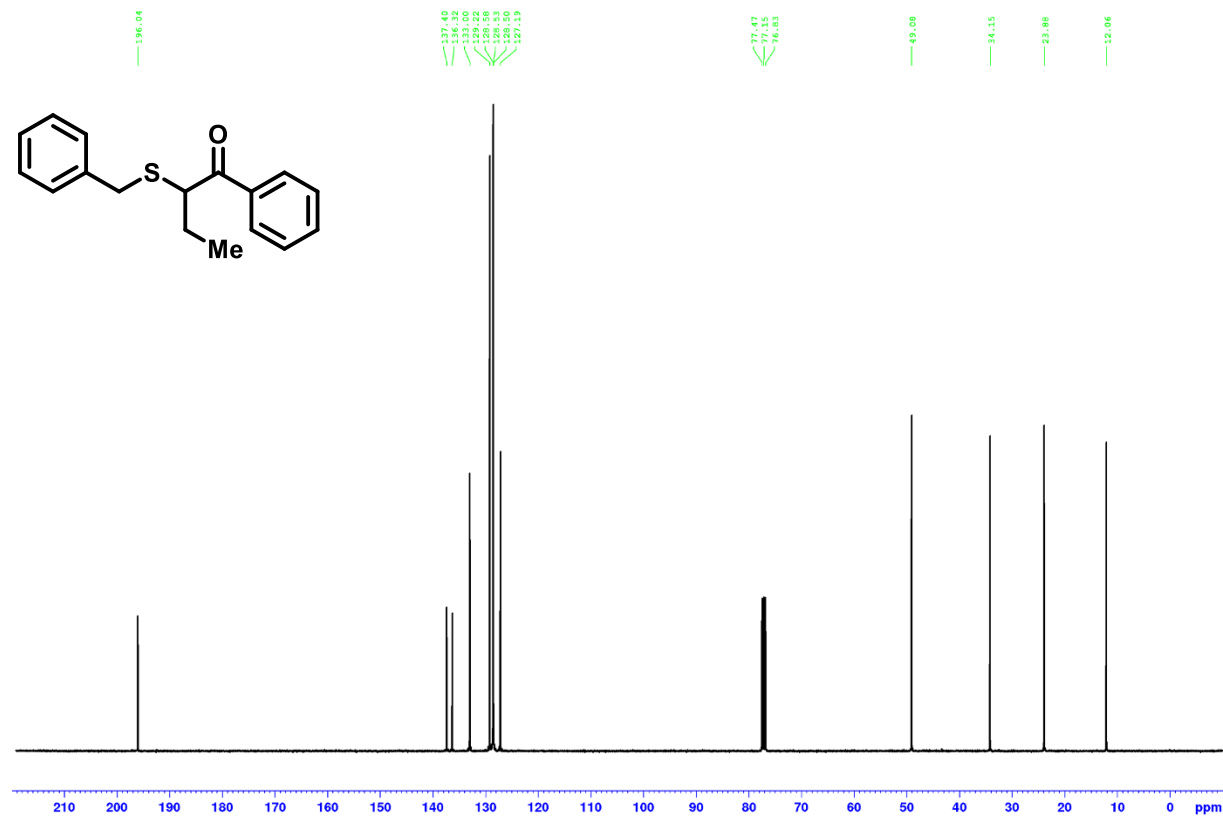


Figure S72: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of 3bb.

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

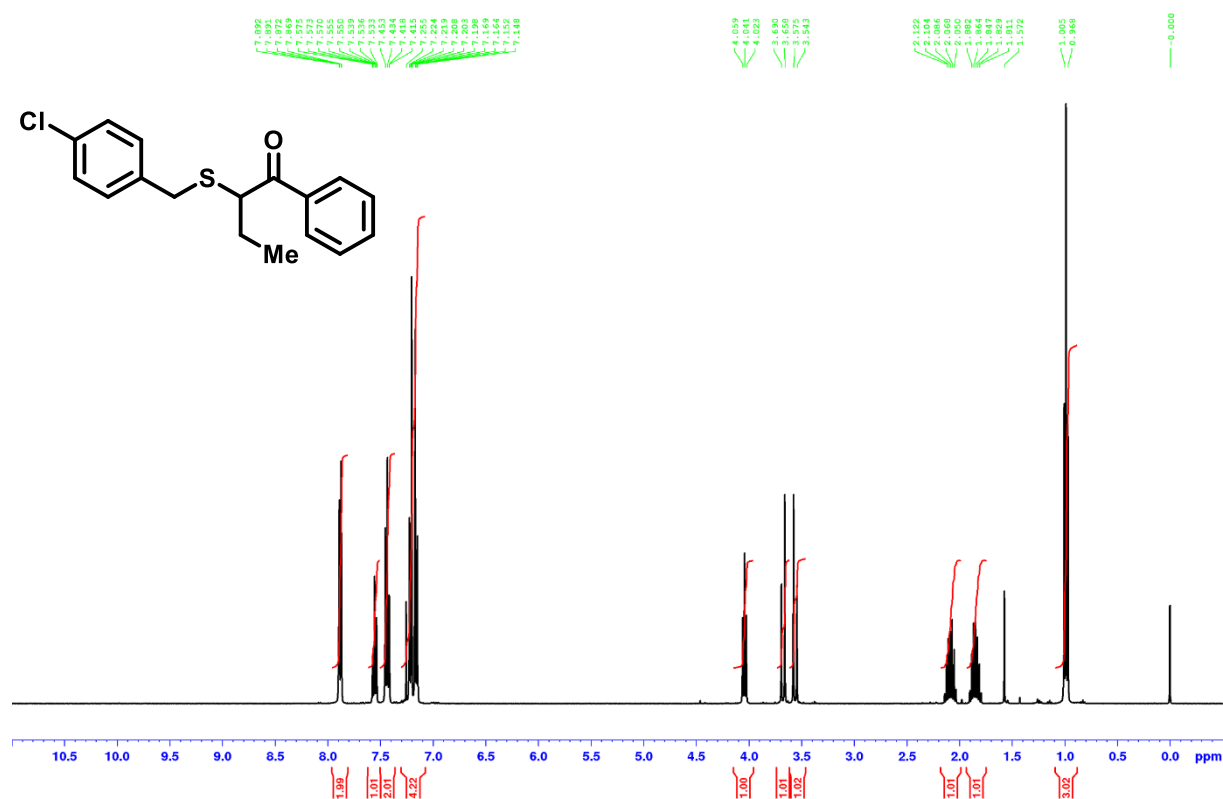


Figure S73: ¹H NMR (400 MHz, CDCl₃) spectrum of 3cc.

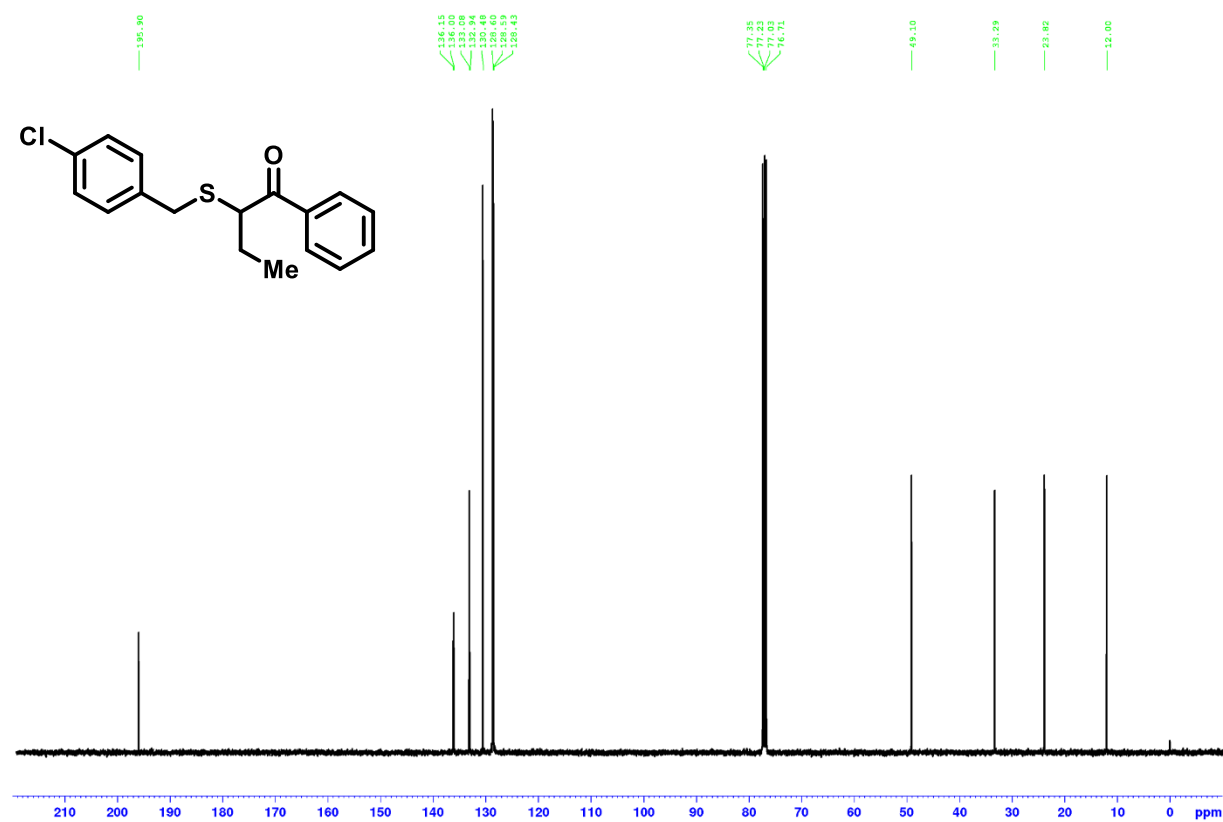


Figure S74: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of 3cc.

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

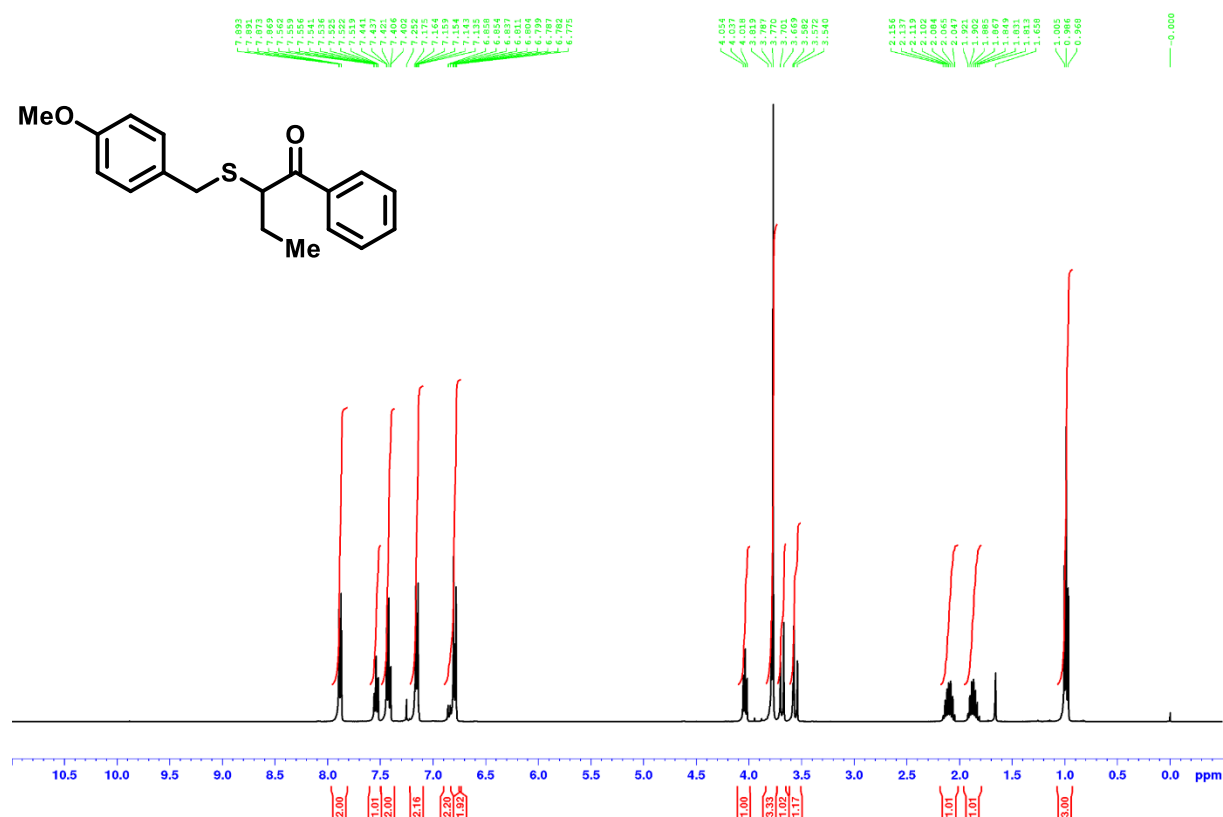


Figure S75: ¹H NMR (400 MHz, CDCl₃) spectrum of **3dd**.

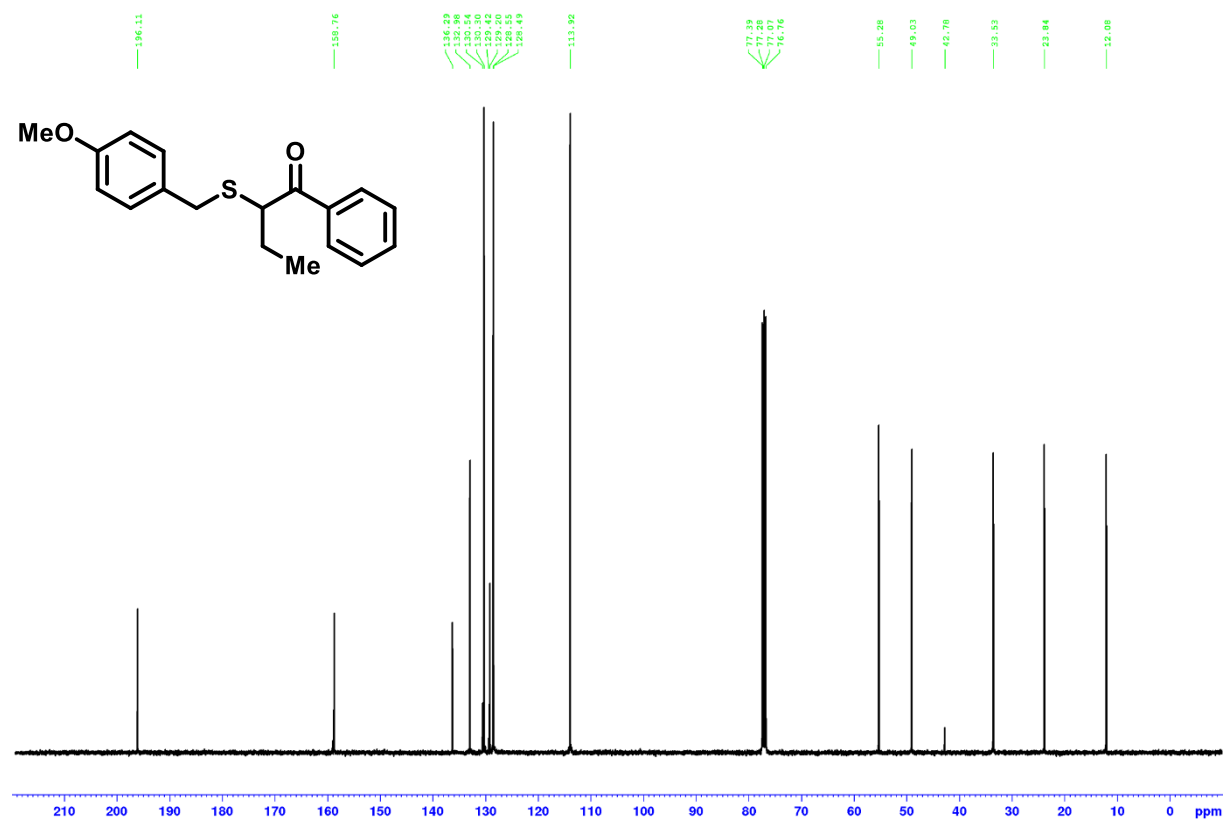


Figure S76: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3dd**.

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

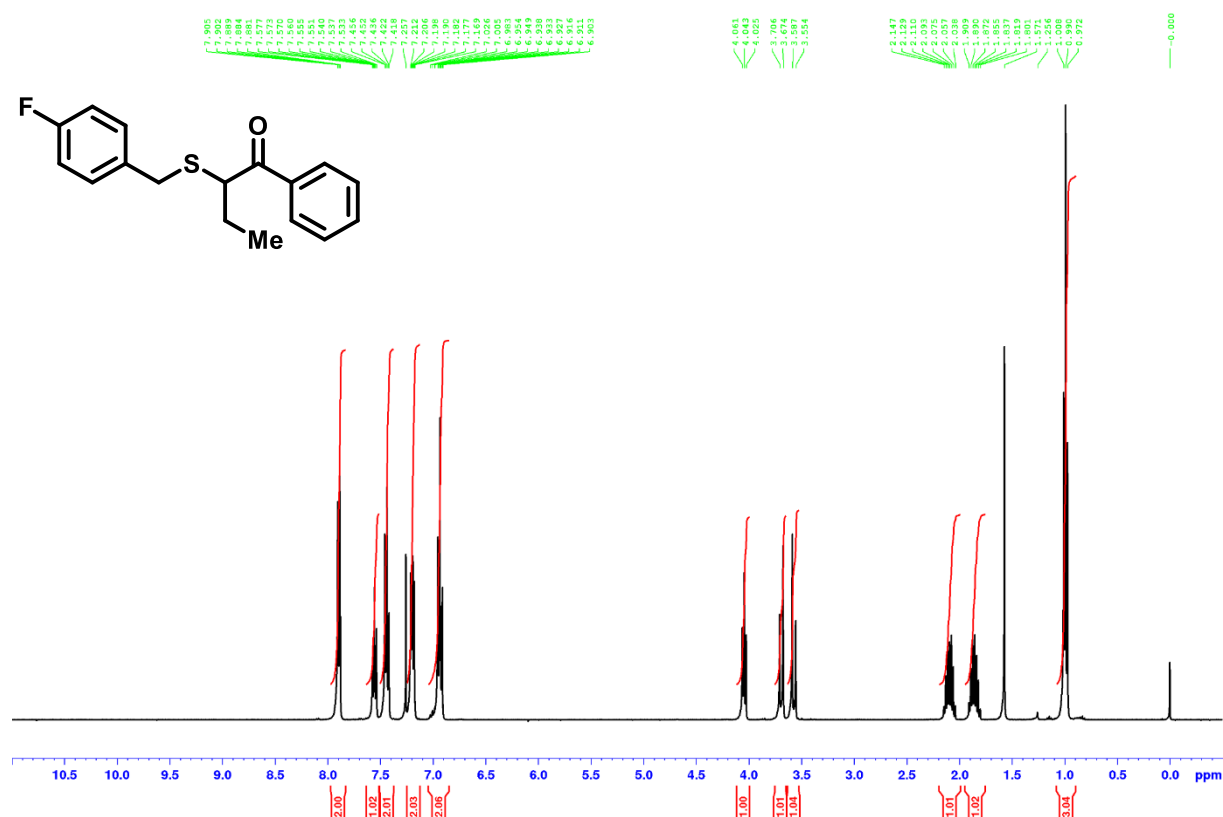


Figure S77: ¹H NMR (400 MHz, CDCl₃) spectrum of **3ee**.

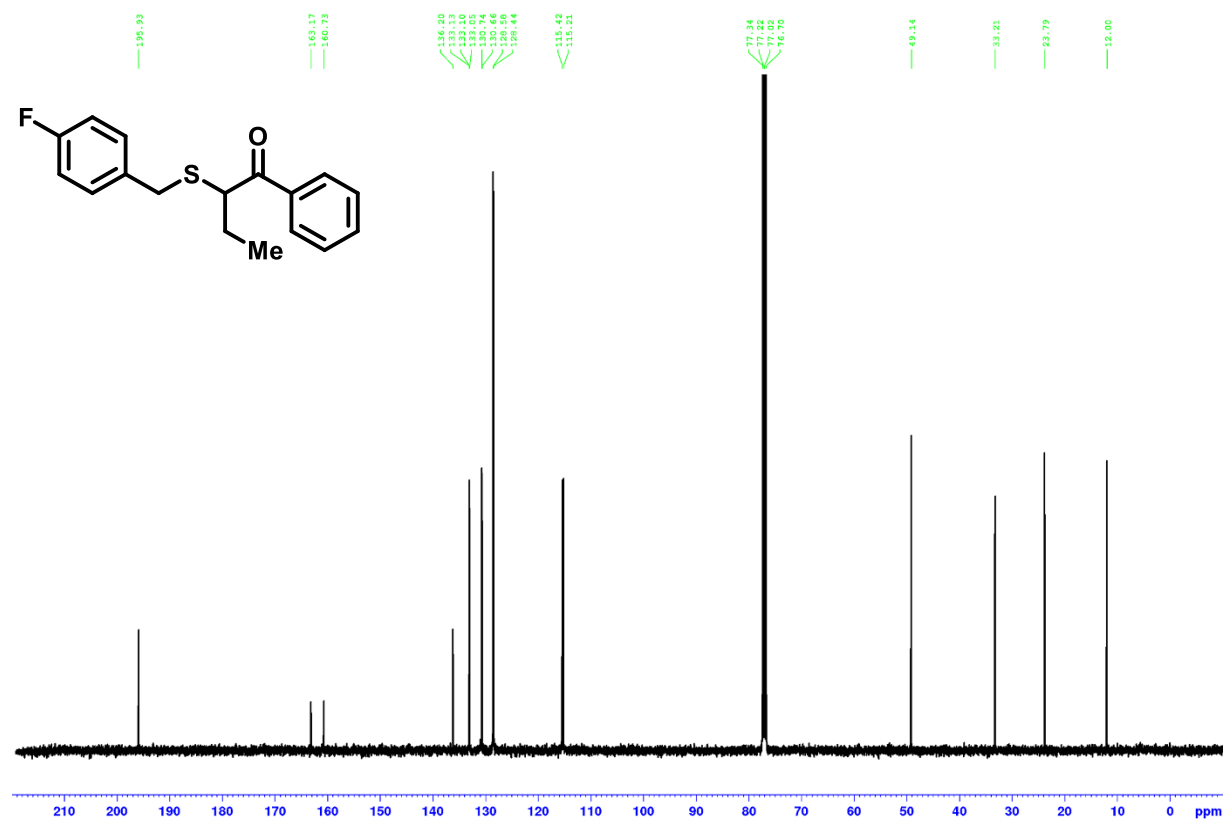


Figure S78: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3ee**.

Chemical structure: CC1(C)C(=O)CSCC2=CC=C(C)C=C2C1

¹H NMR spectrum (CDCl₃) showing peaks from 0.0 to 10.0 ppm. The spectrum includes aromatic signals (7.0-8.0 ppm), a methine signal (3.7 ppm), a methyl signal (2.5 ppm), and a p-tolyl methyl signal (2.3 ppm). Integration values are shown below the baseline, and chemical shifts are listed above the peaks.

Chemical structure: CC1=CC=C(C=C1)CCSC2(C)C(=O)C3=CC=CC=C3CC2

¹³C NMR peaks (ppm): 196.10, 136.03, 134.16, 133.76, 132.26, 128.09, 126.50, 77.37, 77.05, 76.74, 49.01, 33.83, 23.84, 21.11, 12.06.

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

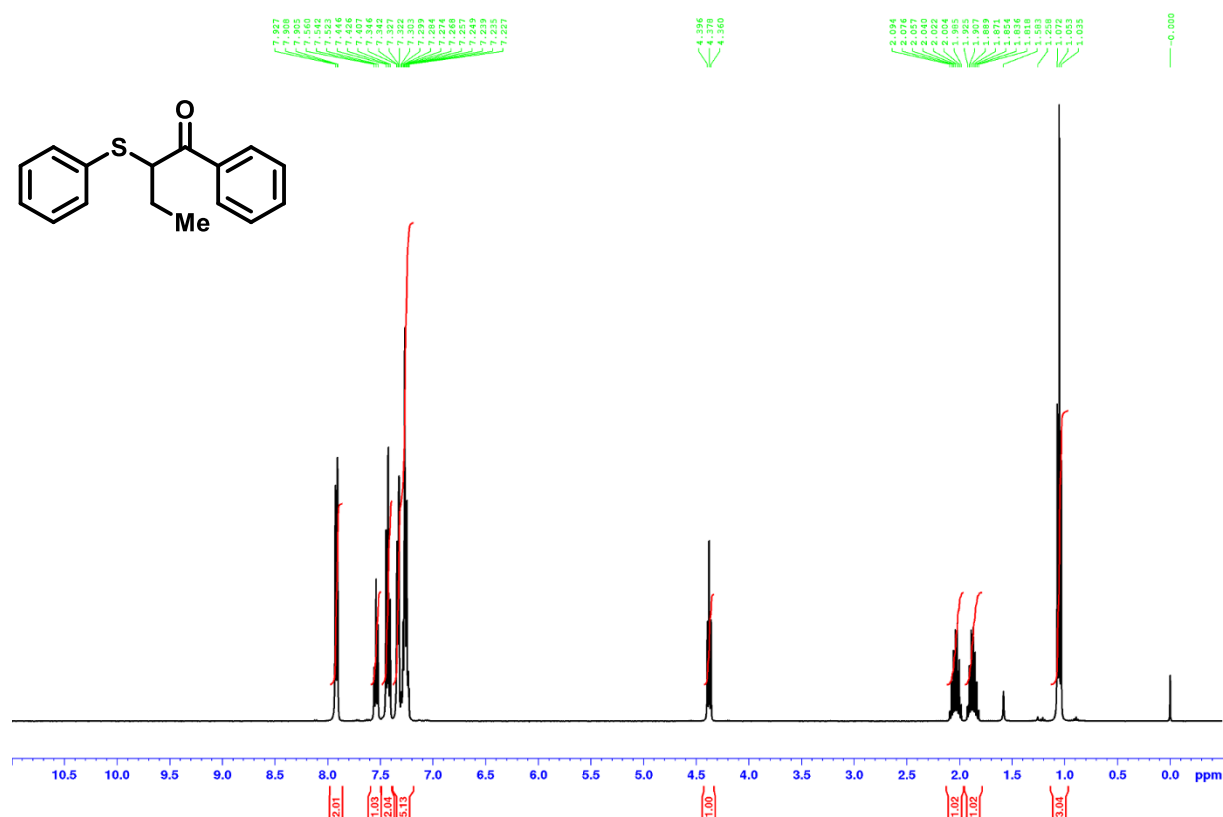


Figure S81: ¹H NMR (400 MHz, CDCl₃) spectrum of **3gg**.

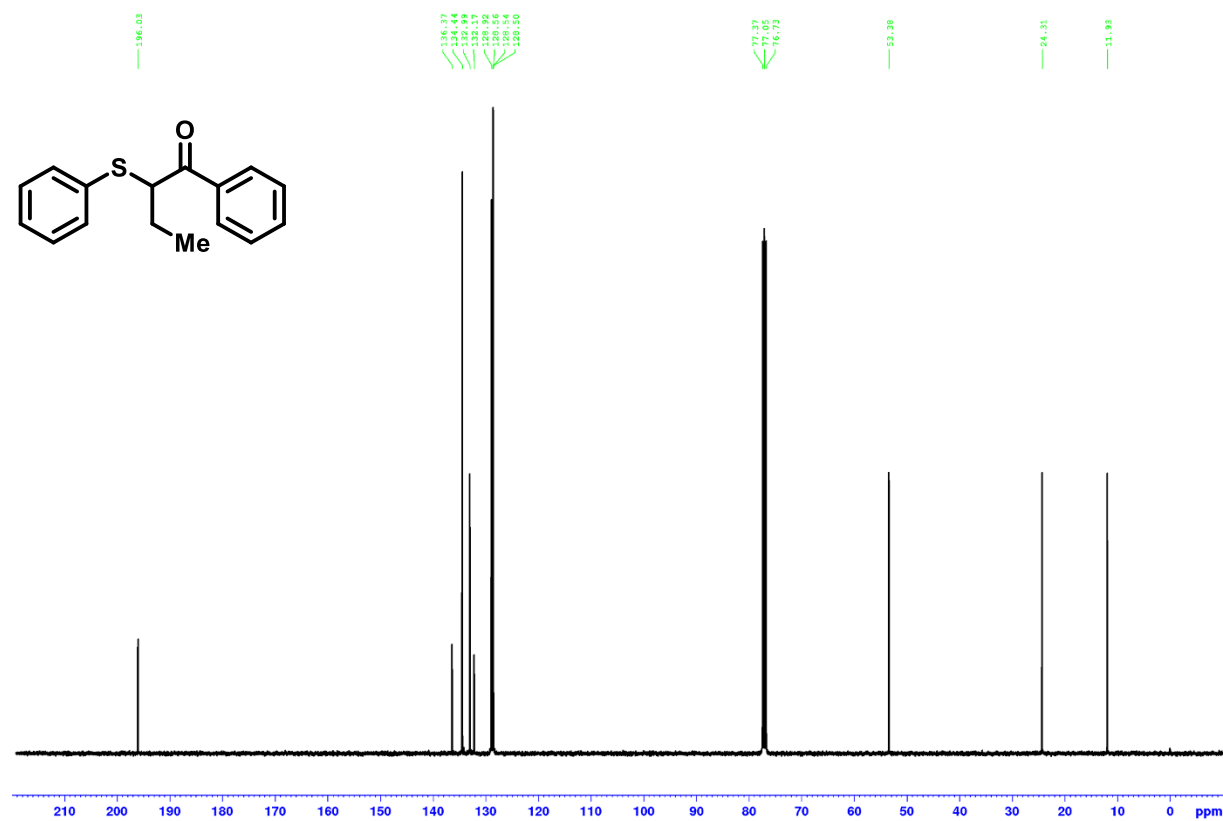


Figure S82: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3gg**.

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

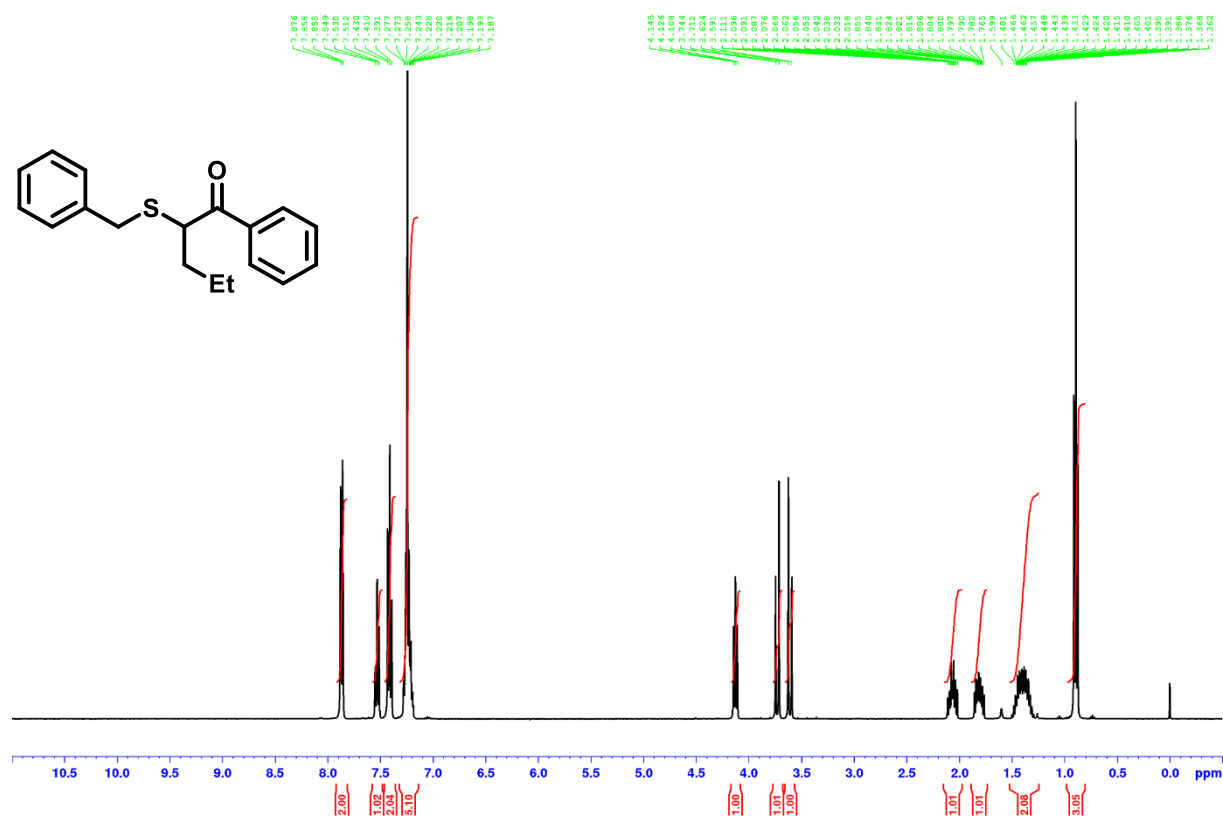


Figure S83: ¹H NMR (400 MHz, CDCl₃) spectrum of **3hh**.

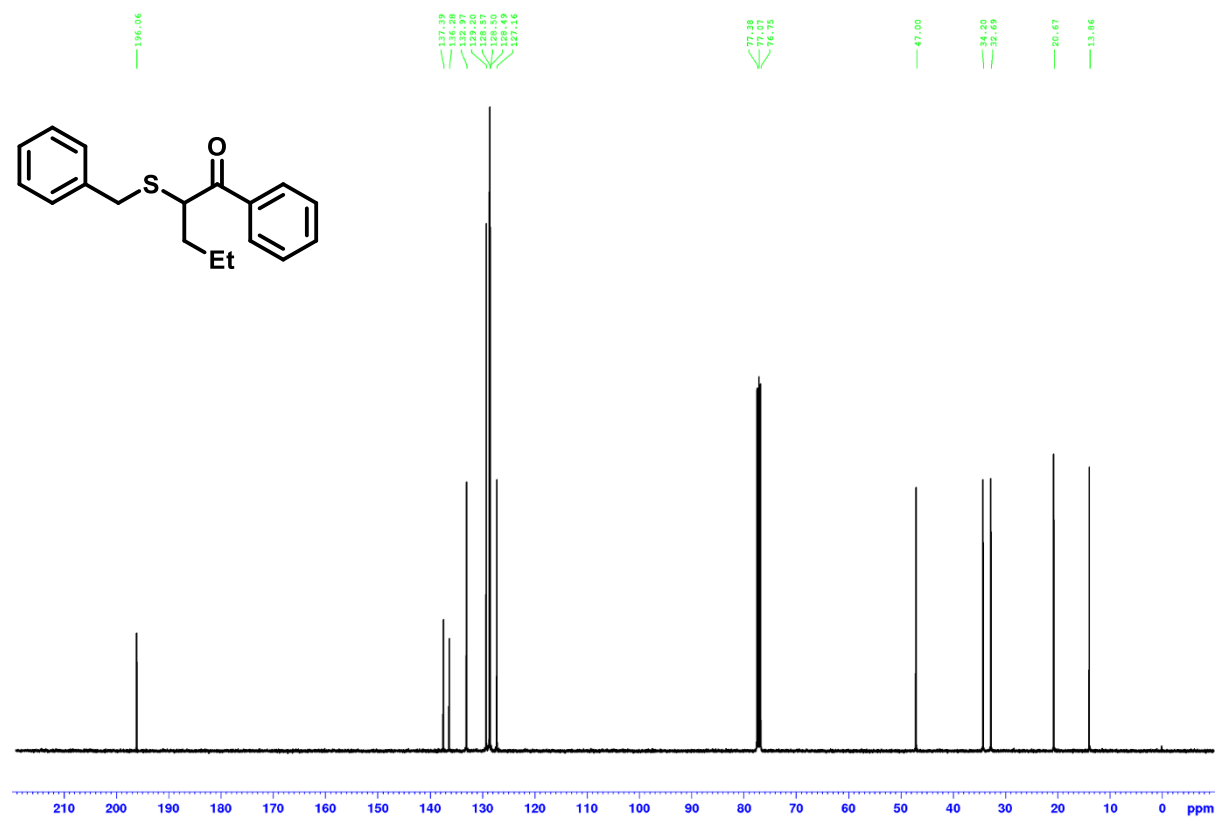


Figure S84: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3hh**.

Chemical structure: CCOC(=O)C(SCc1ccc(Cl)cc1)c2ccccc2

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. Integration values are provided below the peaks, and a list of chemical shifts (δ) is shown on the right.

Chemical shifts (δ): 7.866, 7.855, 7.817, 7.812, 7.792, 7.788, 7.738, 7.655, 7.652, 7.642, 7.632, 7.257, 7.254, 7.132, 7.122, 4.144, 4.135, 4.130, 3.699, 3.697, 3.684, 3.584, 3.551, 3.548, 3.546, 2.077, 2.075, 2.062, 2.053, 2.052, 2.039, 2.027, 2.024, 1.840, 1.838, 1.825, 1.823, 1.801, 1.799, 1.784, 1.782, 1.774, 1.772, 1.758, 1.756, 1.689, 1.687, 1.675, 1.665, 1.663, 1.651, 1.646, 1.644, 1.632, 1.630, 1.618, 1.616, 1.413, 1.411, 1.399, 1.397, 1.371, 1.369, 1.355, 1.353, 1.347, 1.335.

CCSC(C(=O)c1ccccc1)Cc2ccc(Cl)cc2

Chemical structure: CCSC(C(=O)c1ccccc1)Cc2ccc(Cl)cc2

¹³C NMR peaks (ppm):

- 195.92
- 136.12
- 135.09
- 133.89
- 132.94
- 132.80
- 128.59
- 126.44
- 77.33
- 77.02
- 76.70
- 47.03
- 33.37
- 32.63
- 20.64
- 13.82

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

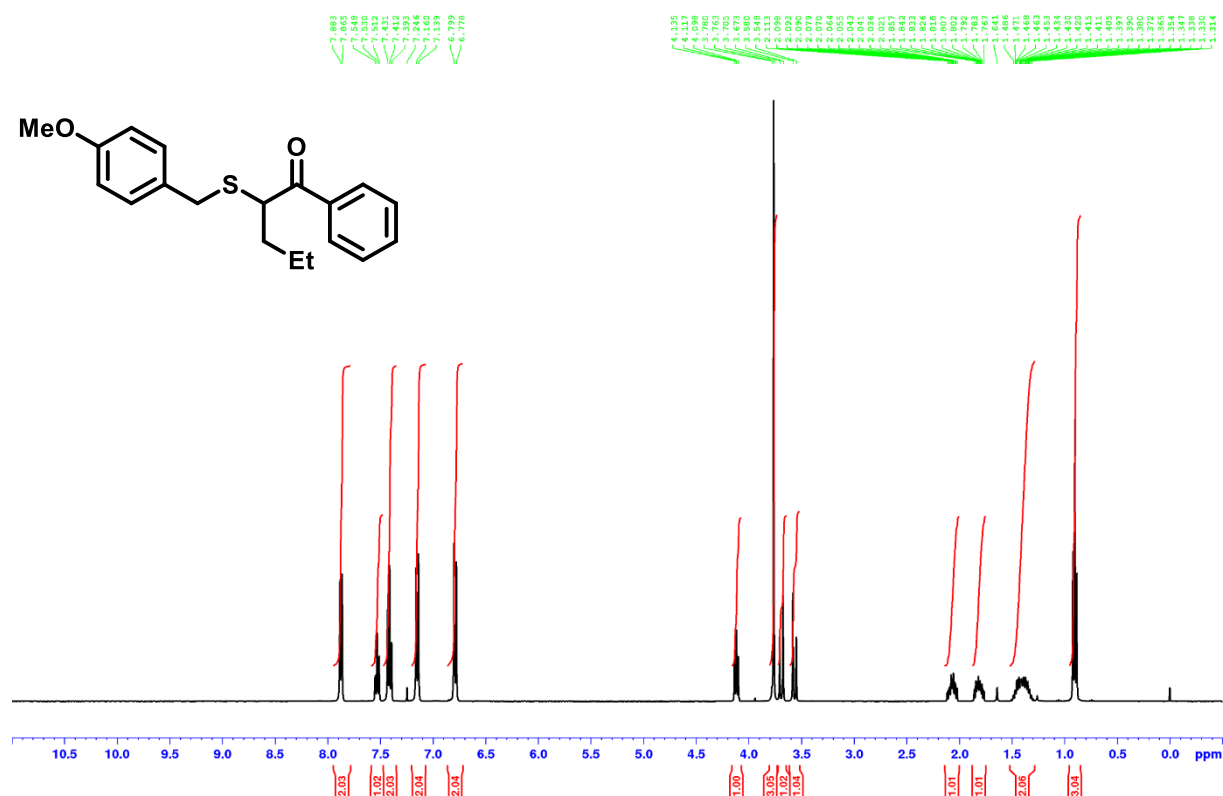


Figure S87: ¹H NMR (400 MHz, CDCl₃) spectrum of **3jj**.

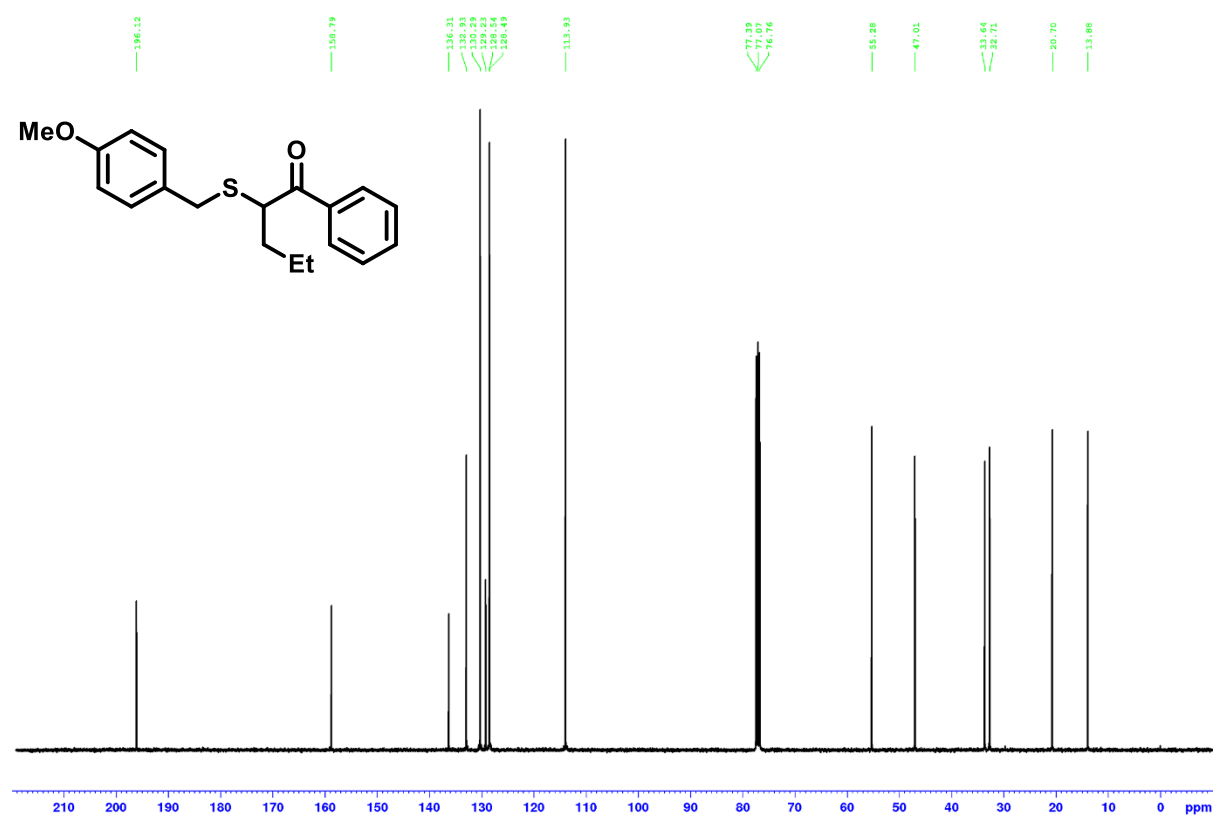


Figure S88: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3jj**.

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

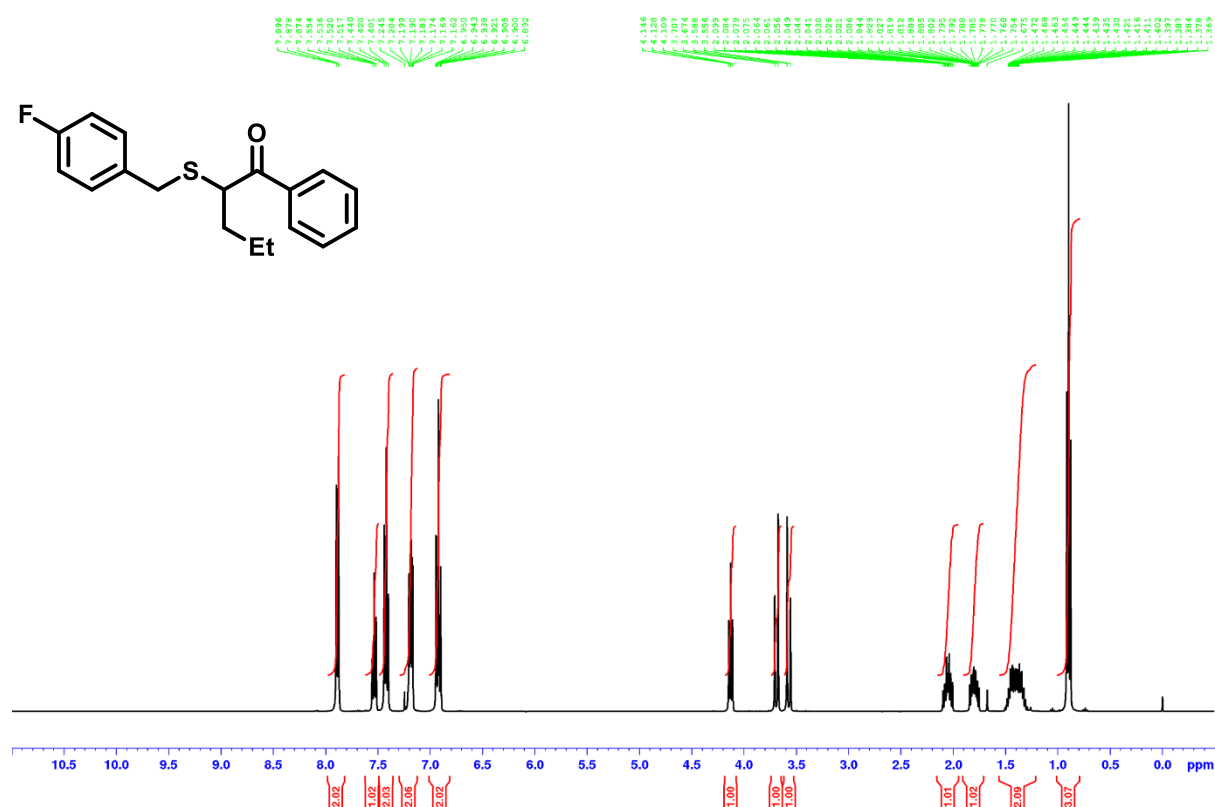


Figure S89: ¹H NMR (400 MHz, CDCl₃) spectrum of **3kk**.

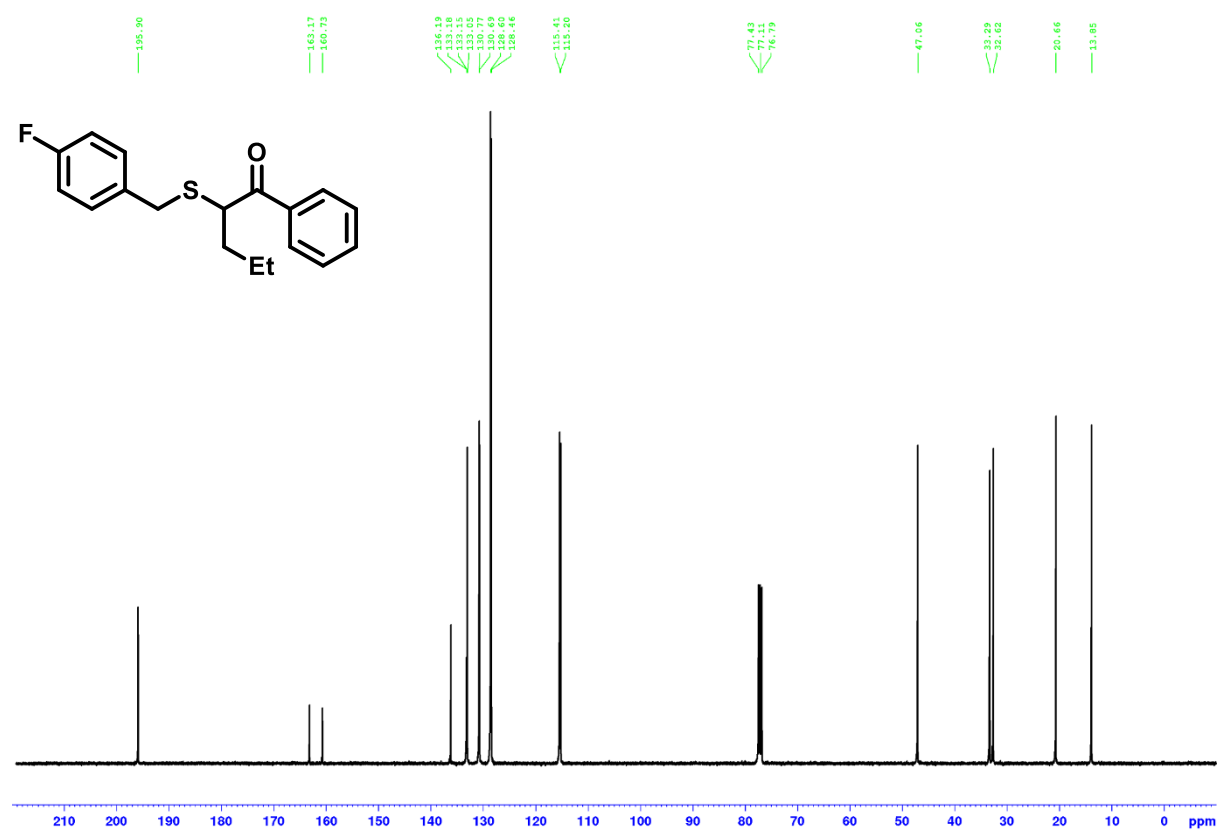


Figure S90: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **3kk**.

2-((4-Methylbenzyl)thio)-1-phenylpentan-1-one **3II**

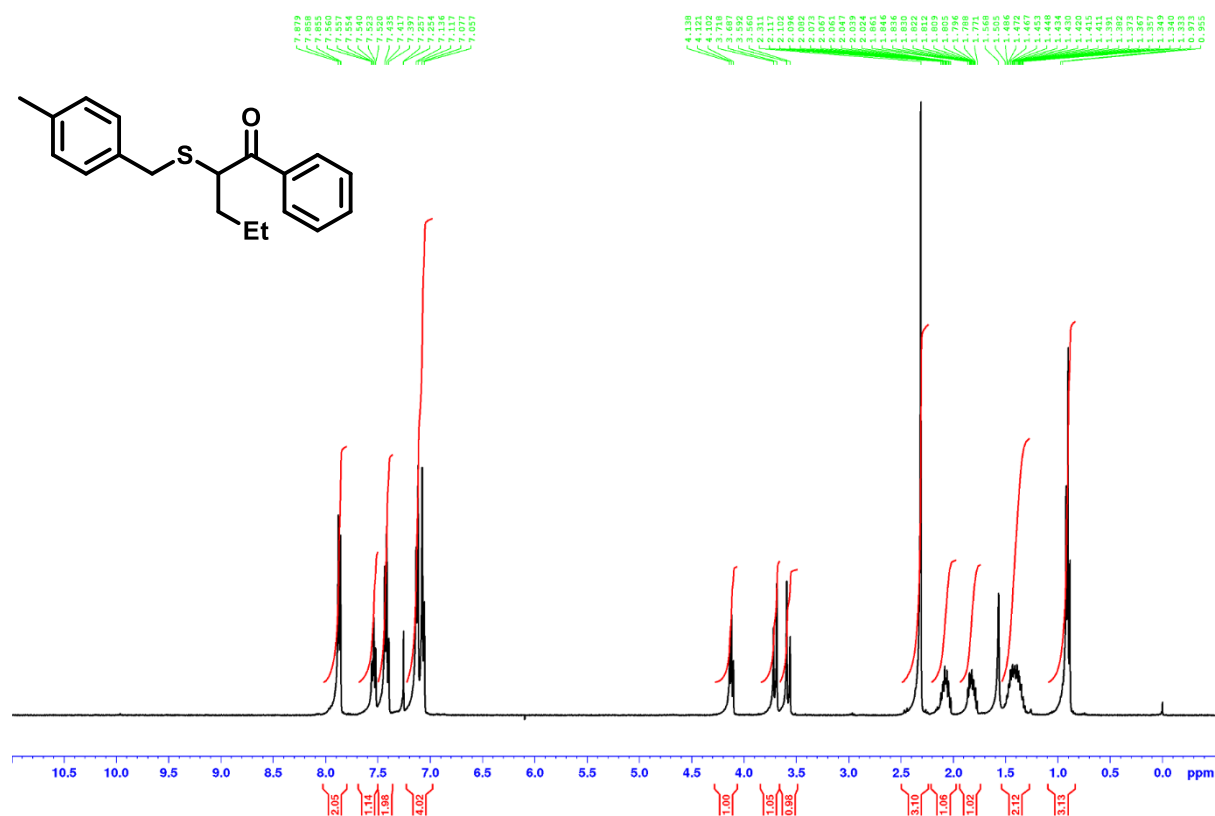


Figure S91: ^1H NMR (400 MHz, CDCl_3) spectrum of **3II**.

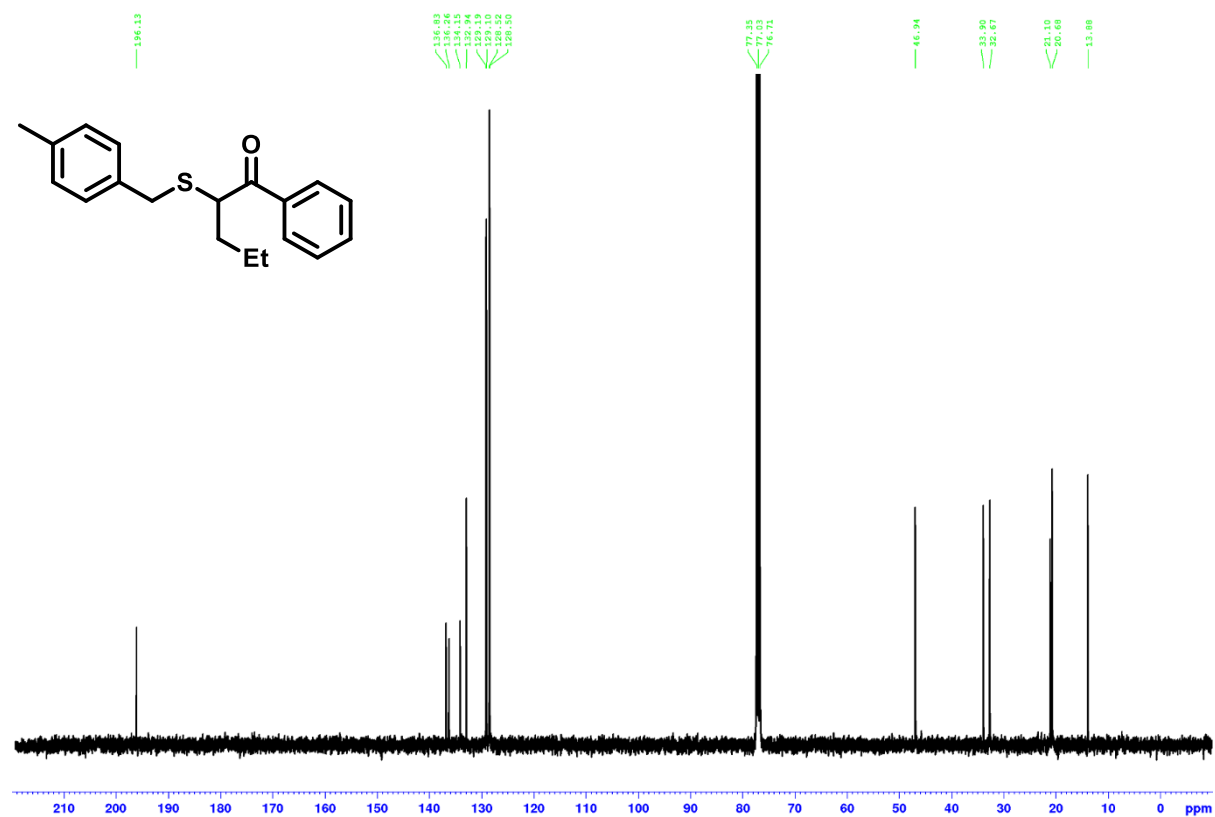


Figure S92: ^{13}C NMR (100.6 MHz, CDCl_3) spectrum of **3II**.

3-(Phenylthio)butan-2-one 5a¹⁵

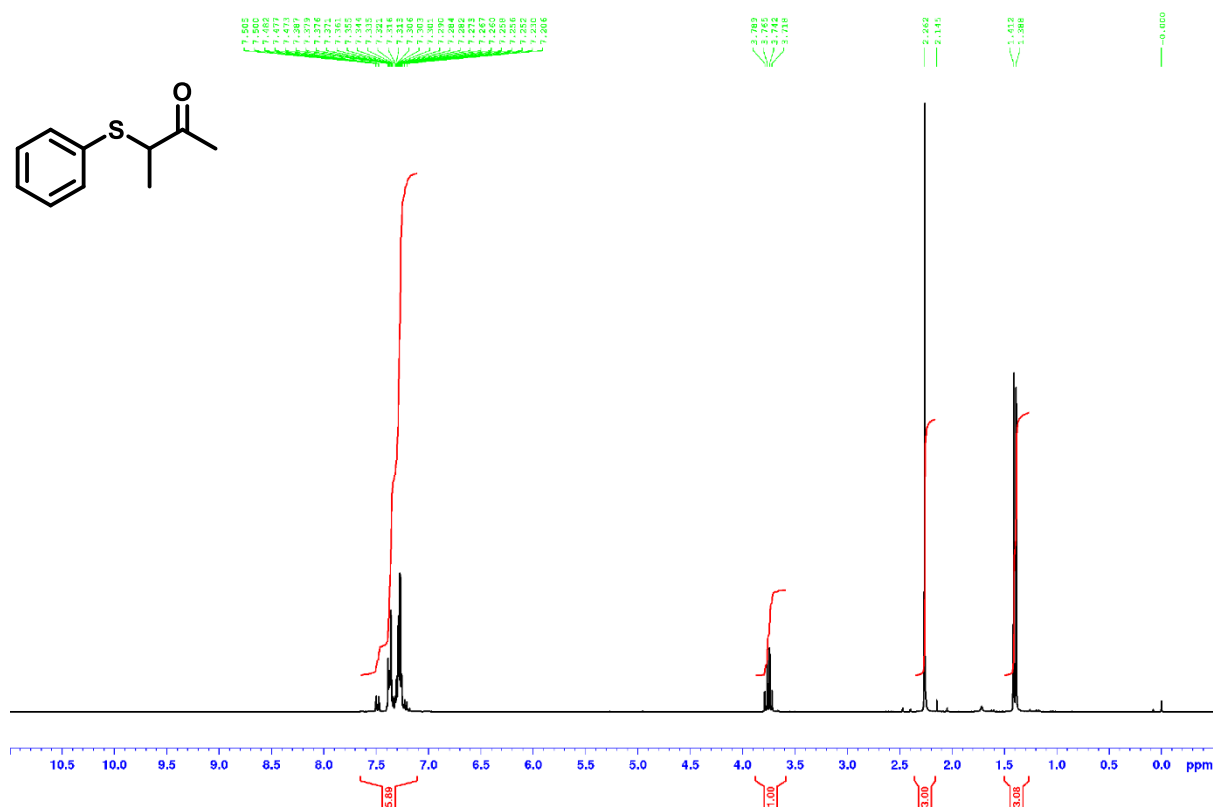


Figure S93: ¹H NMR (300 MHz, CDCl₃) spectrum of 5a.

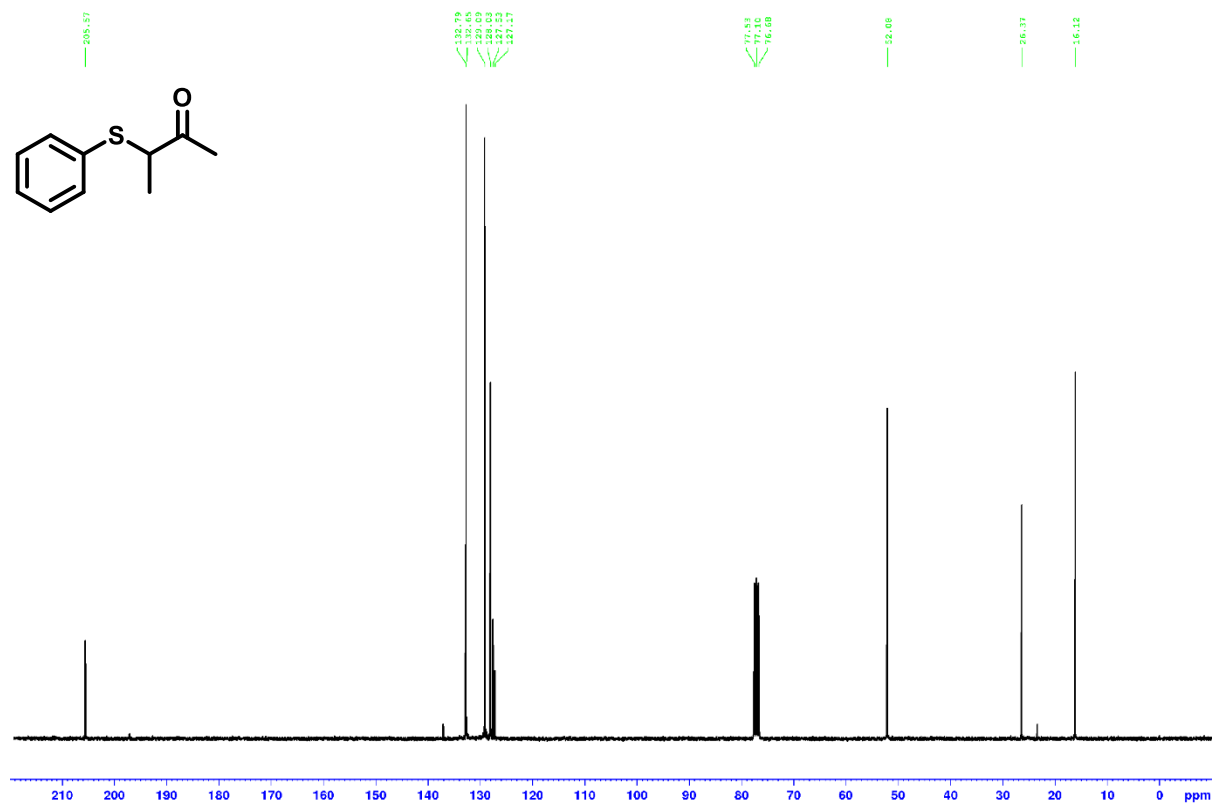


Figure S94: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of 5a.

2-(Phenylthio)pentan-3-one **5b**¹⁶

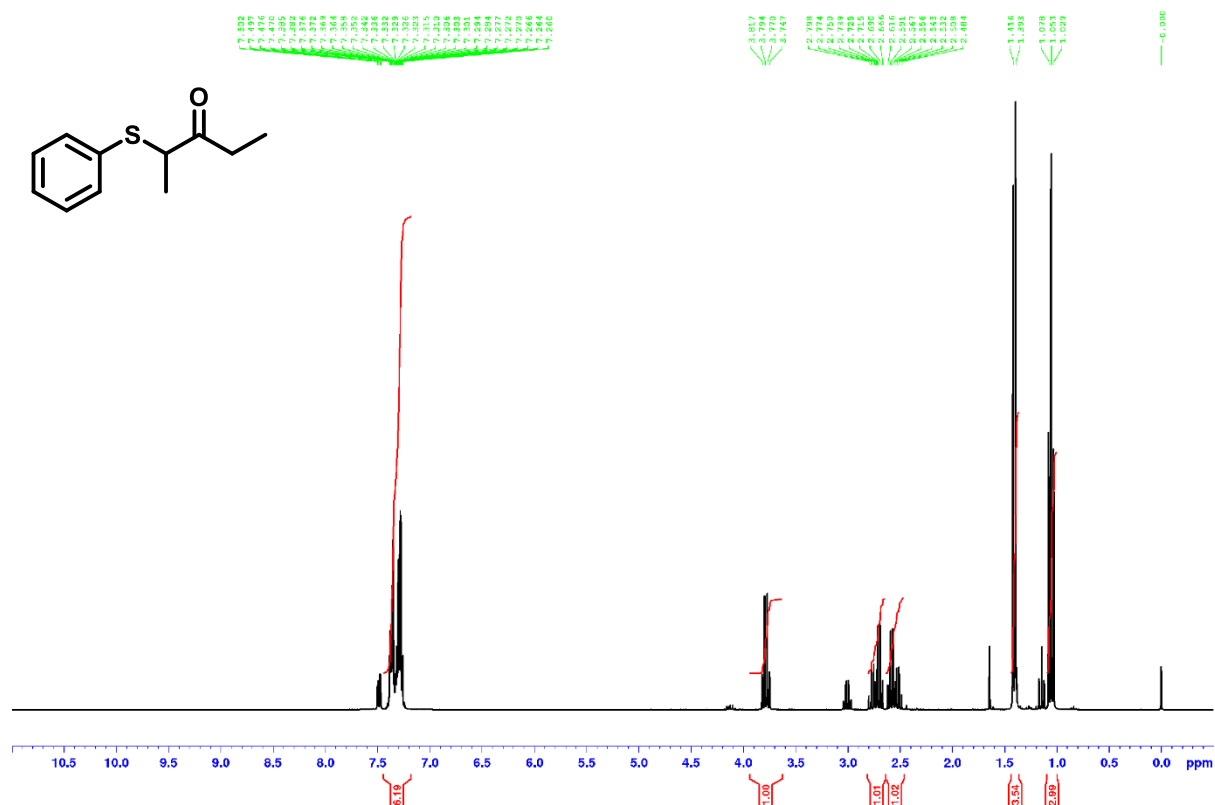


Figure S95: ¹H NMR (300 MHz, CDCl₃) spectrum of **5b**.

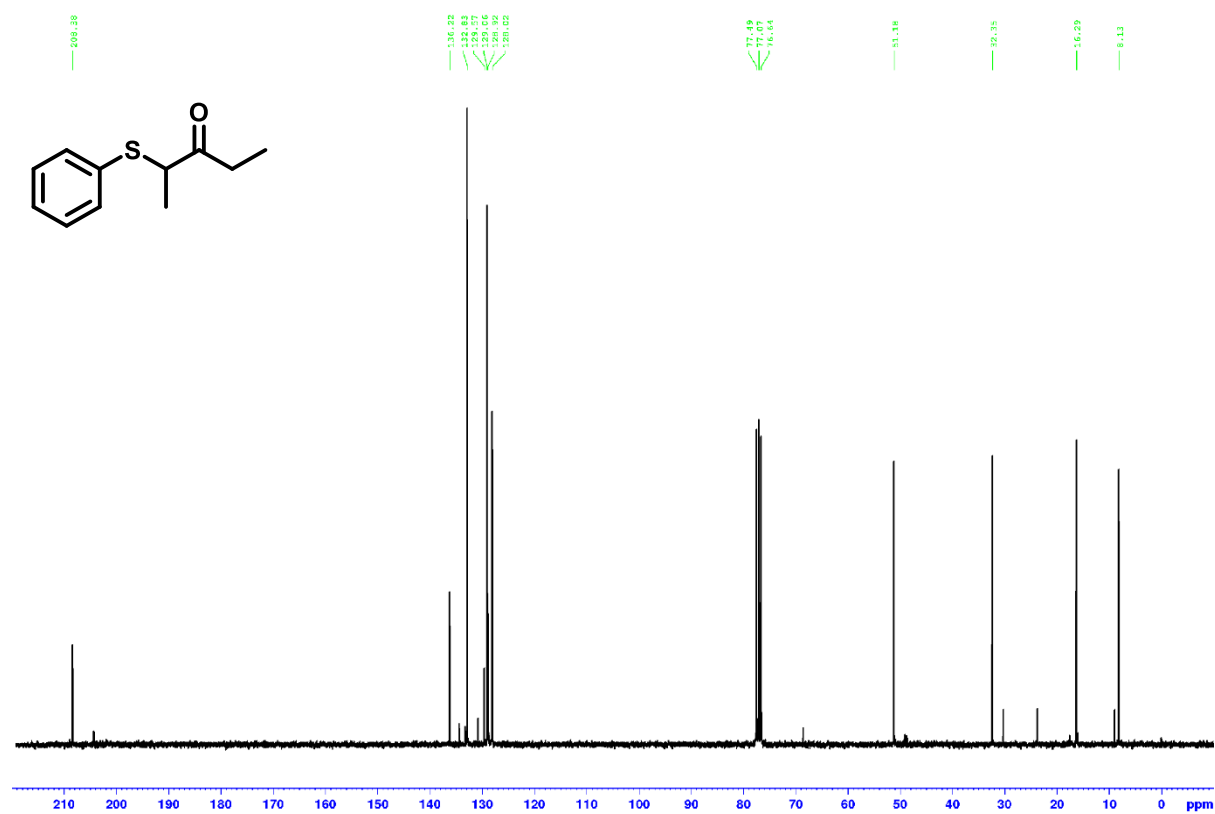


Figure S96: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **5b**.

CC(=O)C(C)SCc1ccccc1

¹H NMR spectrum (400 MHz, CDCl₃) of 1-(benzylthio)propan-2-one. The spectrum shows peaks at 7.25-7.19 ppm (aromatic, 5H), 3.60-3.50 ppm (CH₂, 2H), 2.57-2.53 ppm (CH₃, 3H), 1.74 ppm (CH, 1H), and 1.07-1.01 ppm (CH₃, 3H). Integration values are shown below the peaks: 5.00, 2.22, 1.00, 4.03, 1.19, and 3.00.

CC(=O)C(C)SCc1ccccc1

Chemical structure: CC(=O)C(C)SCc1ccccc1

¹³C NMR peaks (ppm):

- 208.17
- 137.52
- 135.15
- 132.03
- 129.65
- 128.40
- 127.59
- 77.59
- 77.37
- 76.14
- 47.30
- 36.77
- 31.32
- 15.94
- 0.28

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3-[(4-Bromophenyl)thio]butan-2-one 5d¹⁷

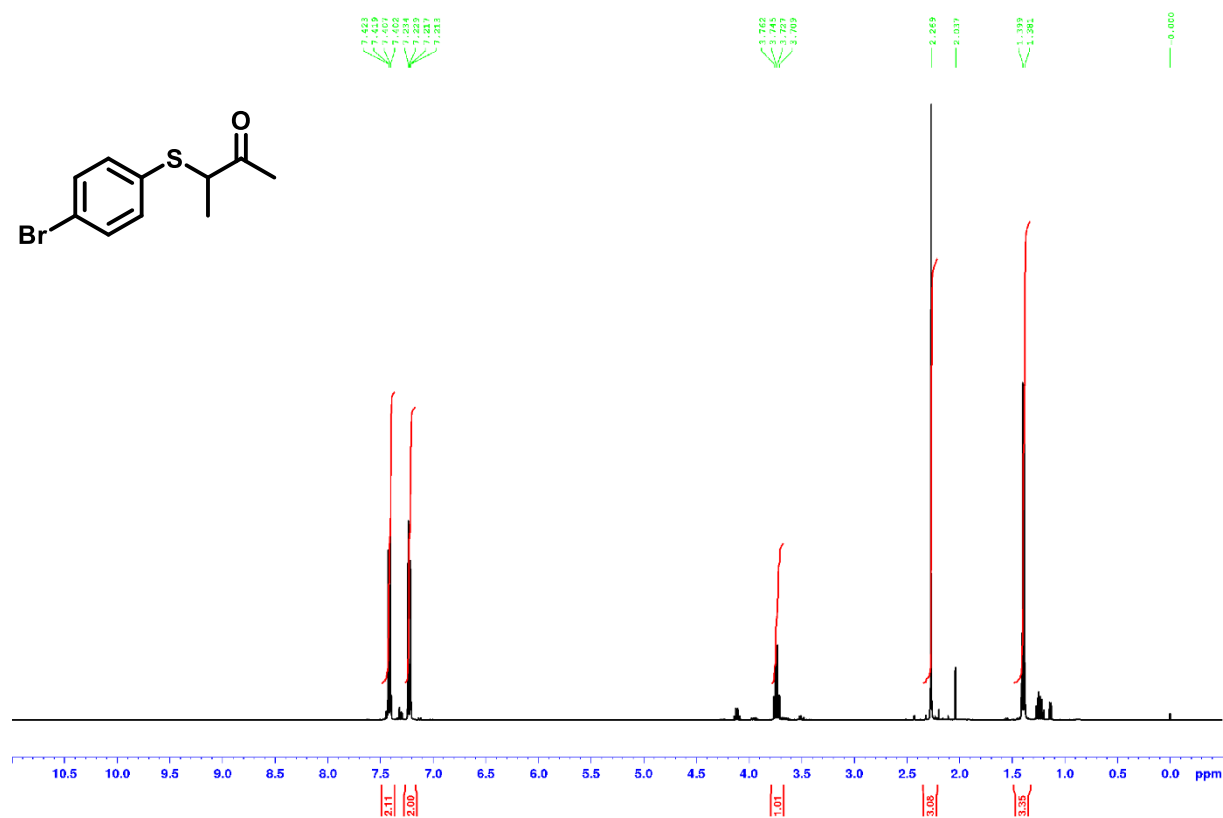


Figure S99: ¹H NMR (400 MHz, CDCl₃) spectrum of 5d.

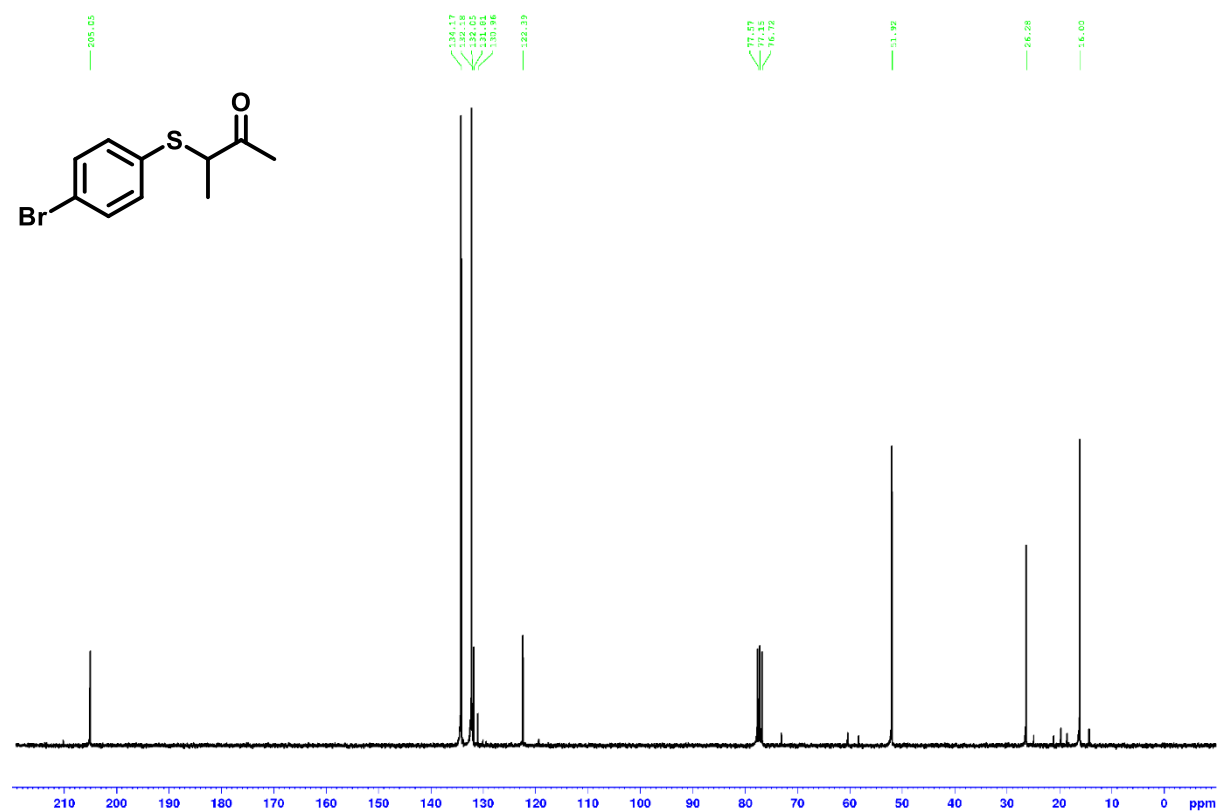


Figure S100: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of 5d.

3-(Benzylthio)butan-2-one 5e¹¹

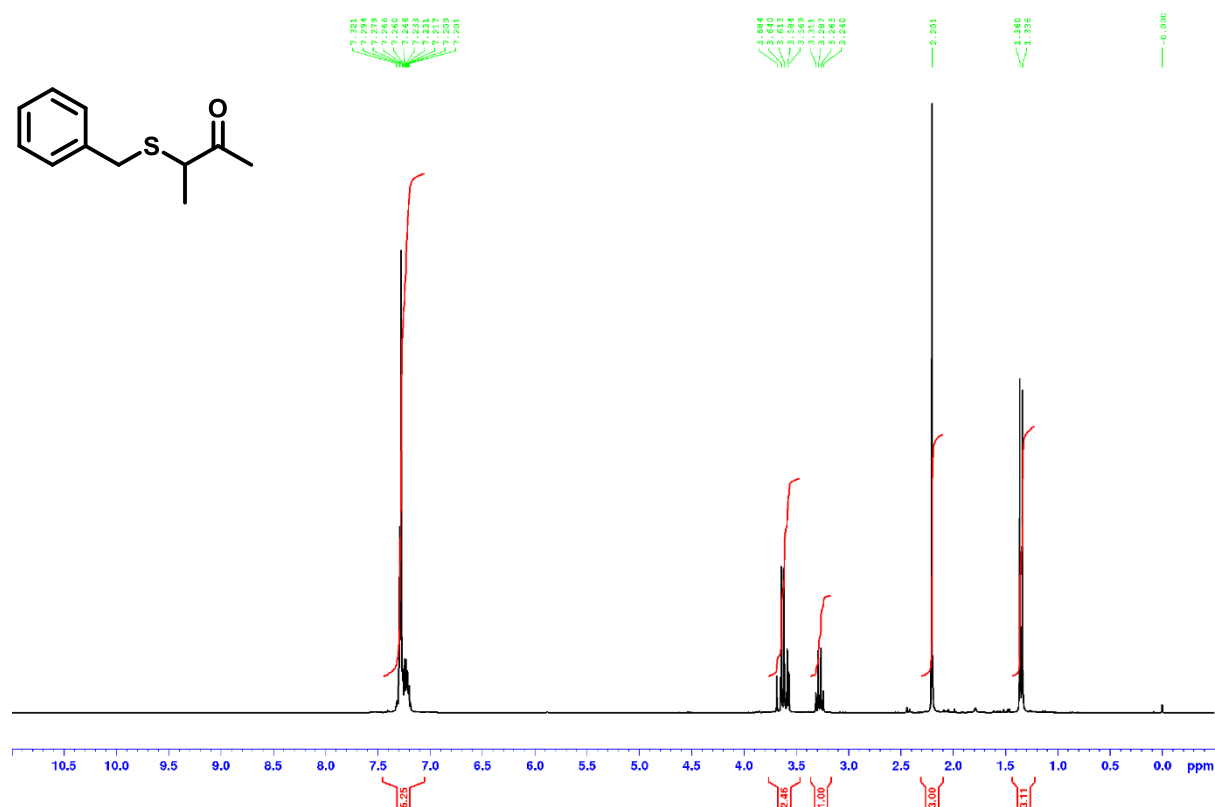


Figure S101: ¹H NMR (300 MHz, CDCl₃) spectrum of 5e.

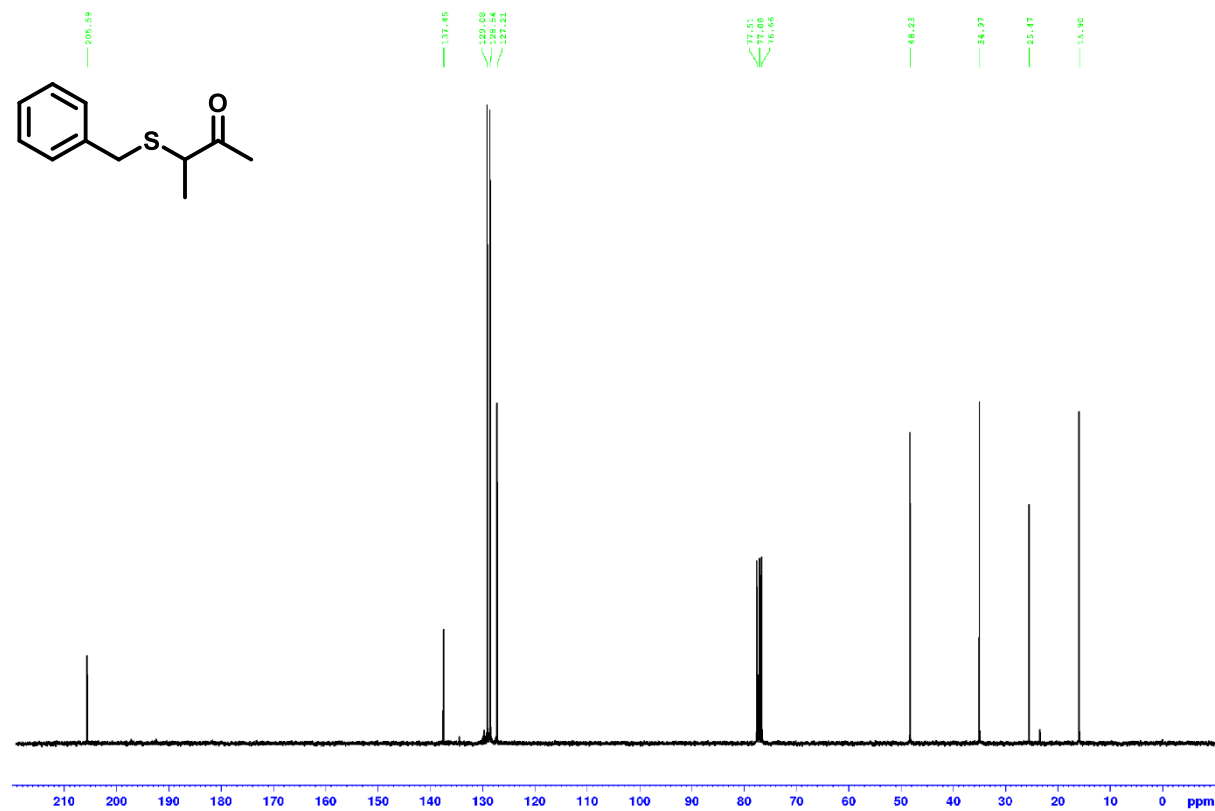


Figure S102: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of 5e.

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

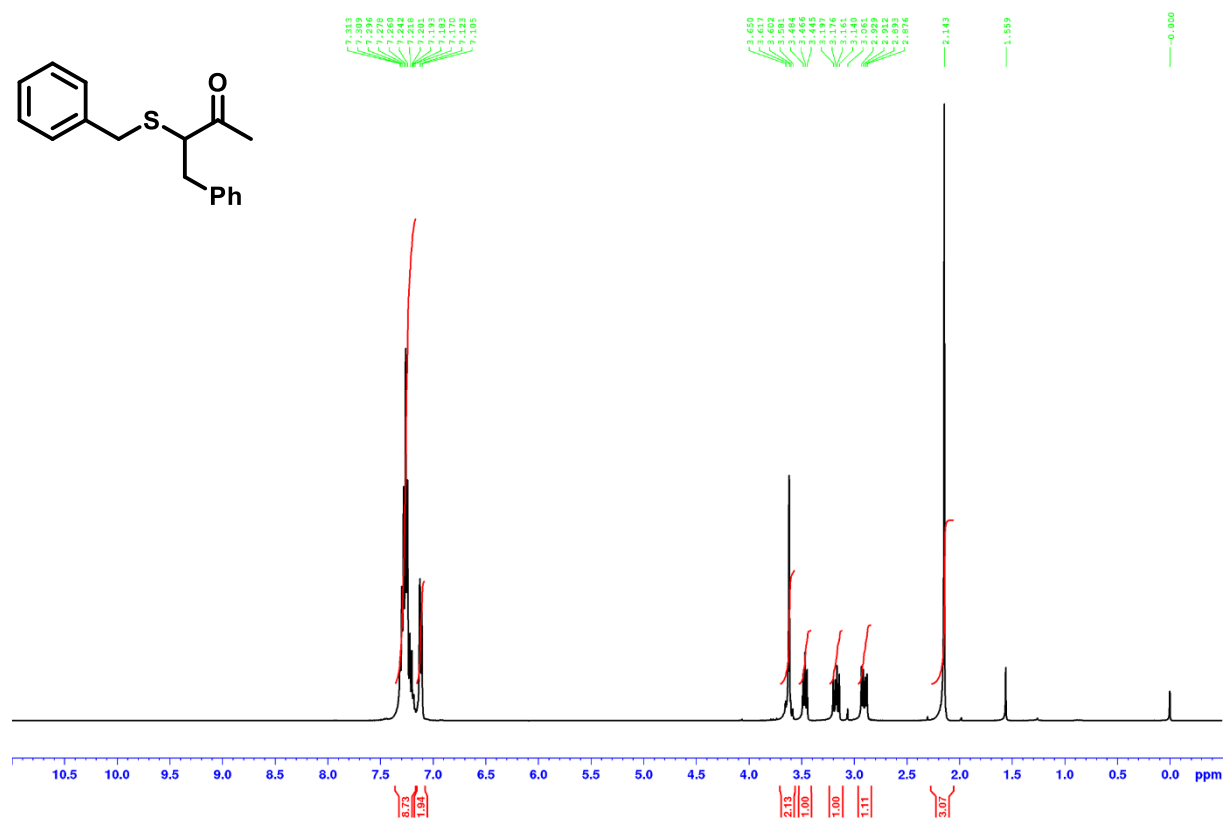


Figure S103: ¹H NMR (400 MHz, CDCl₃) spectrum of **10a**.

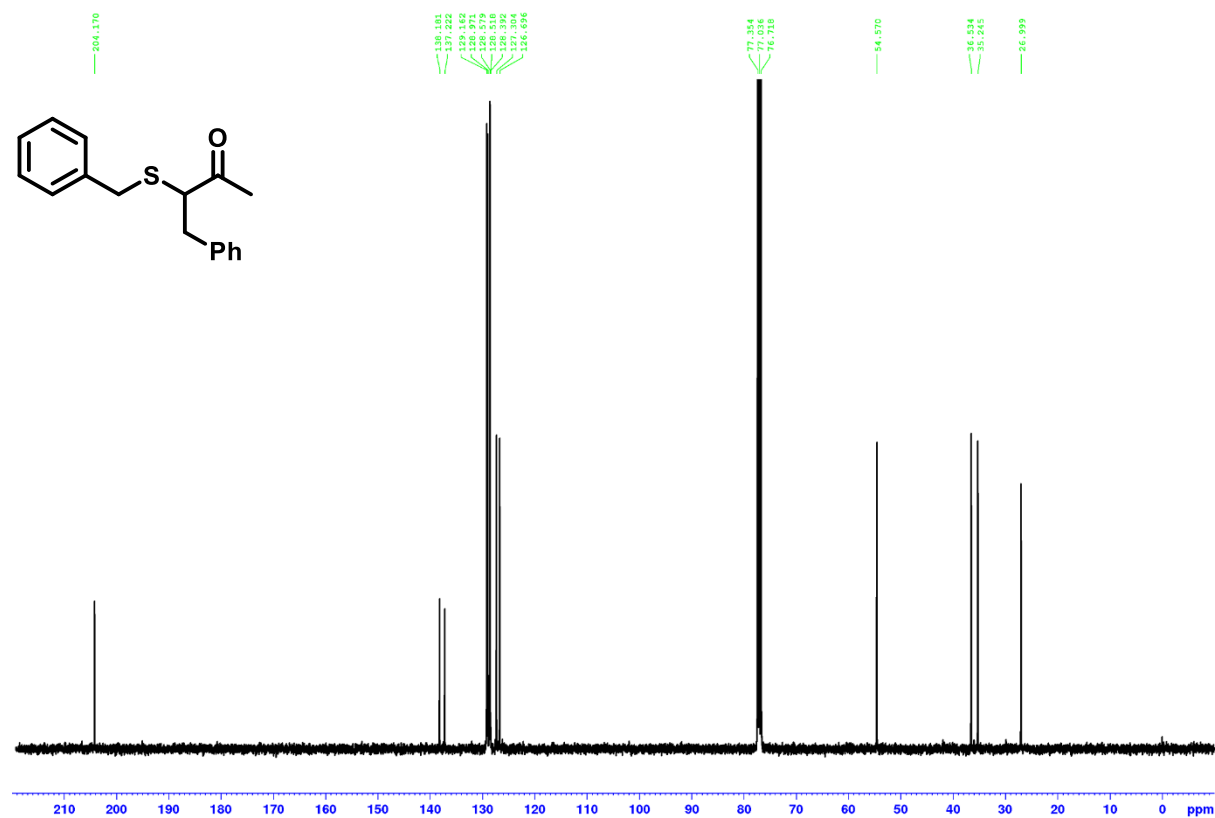


Figure S104: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **10a**.

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

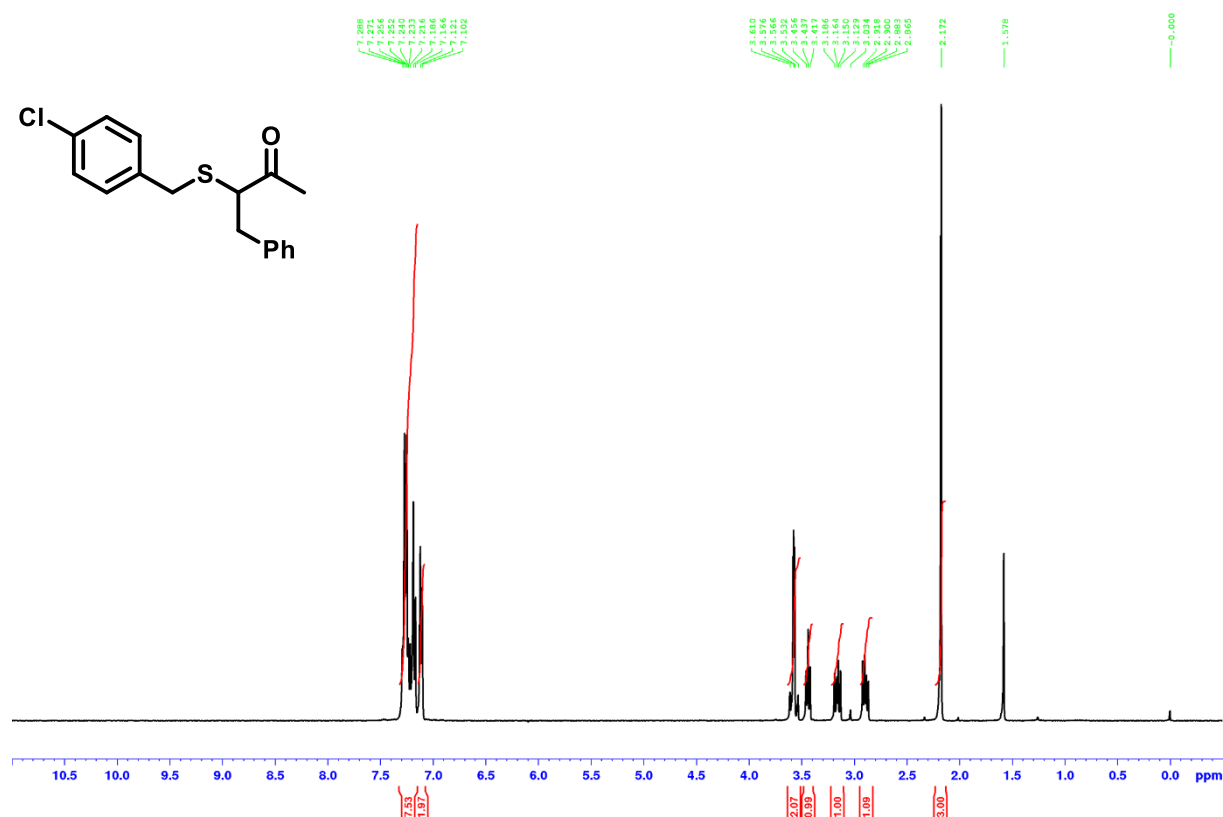


Figure S105: ¹H NMR (400 MHz, CDCl₃) spectrum of S14.

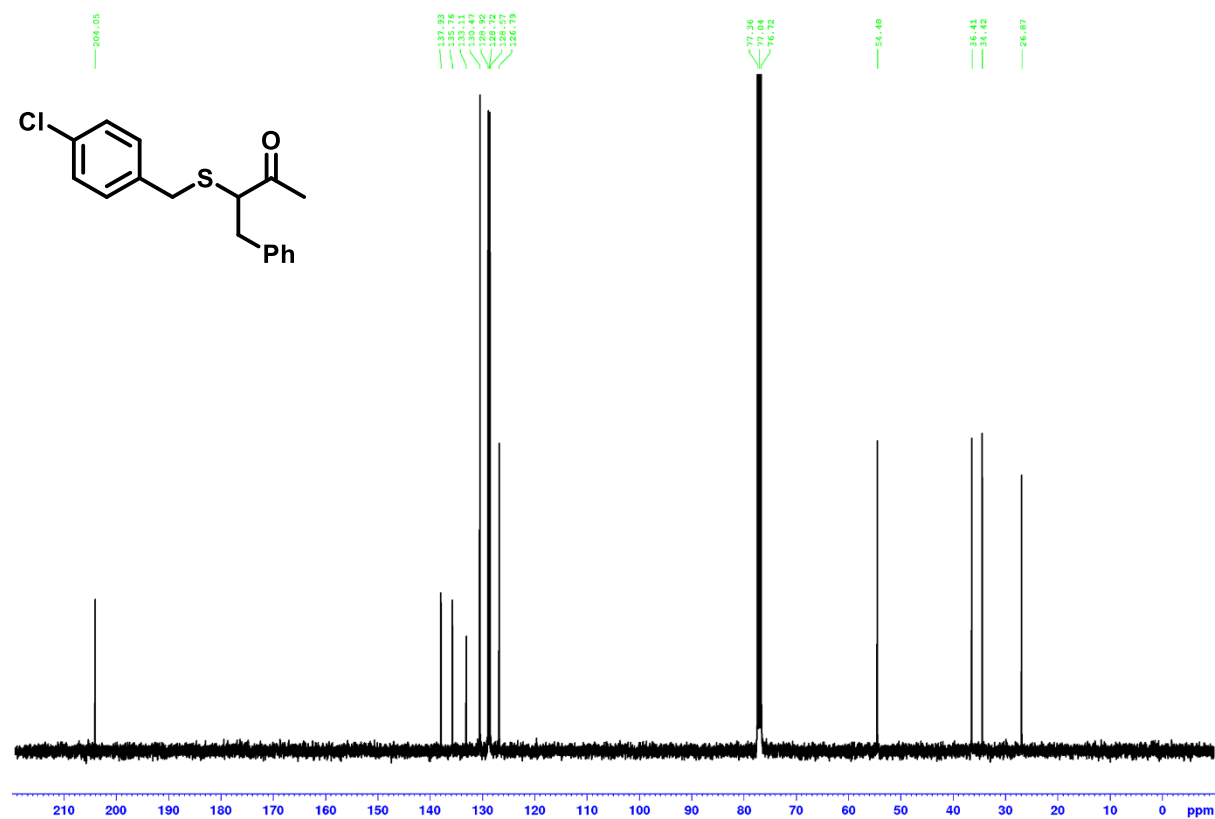


Figure S106: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of S14.

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

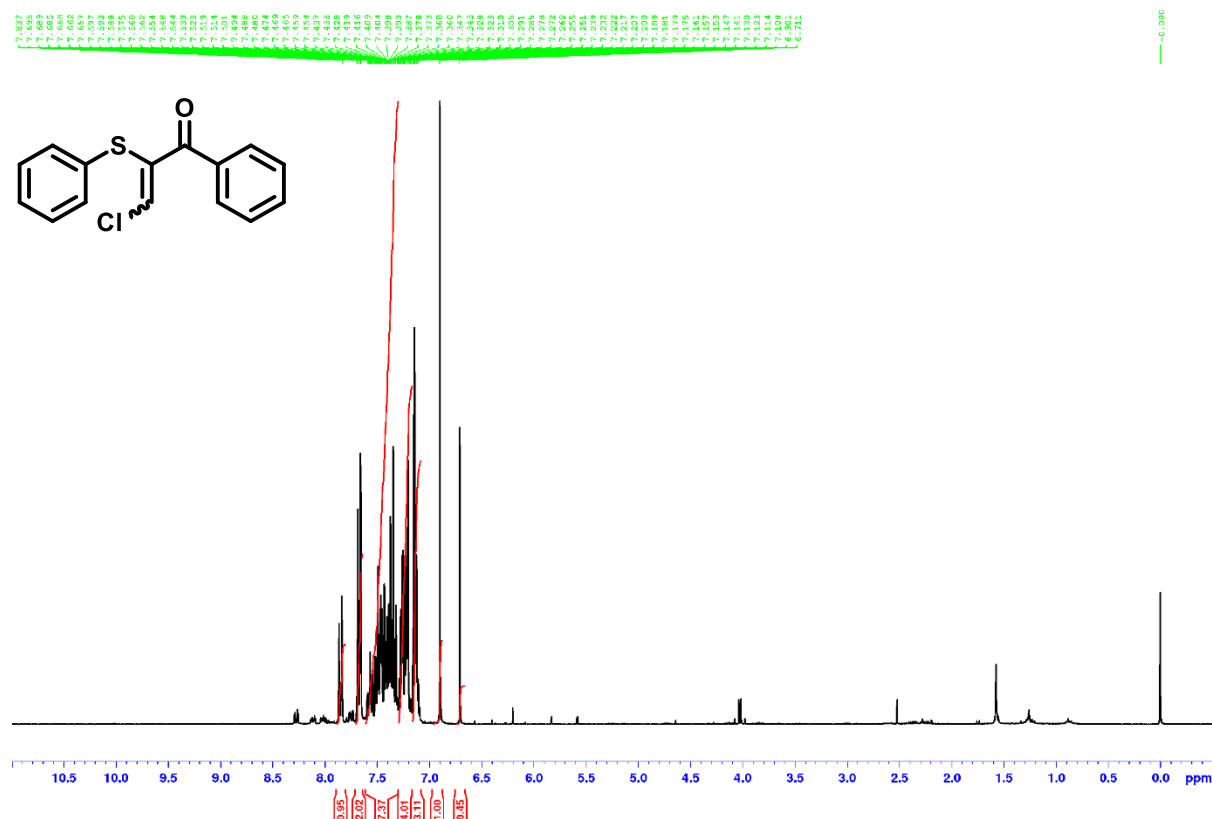


Figure S107: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4a** and **E-4a**.

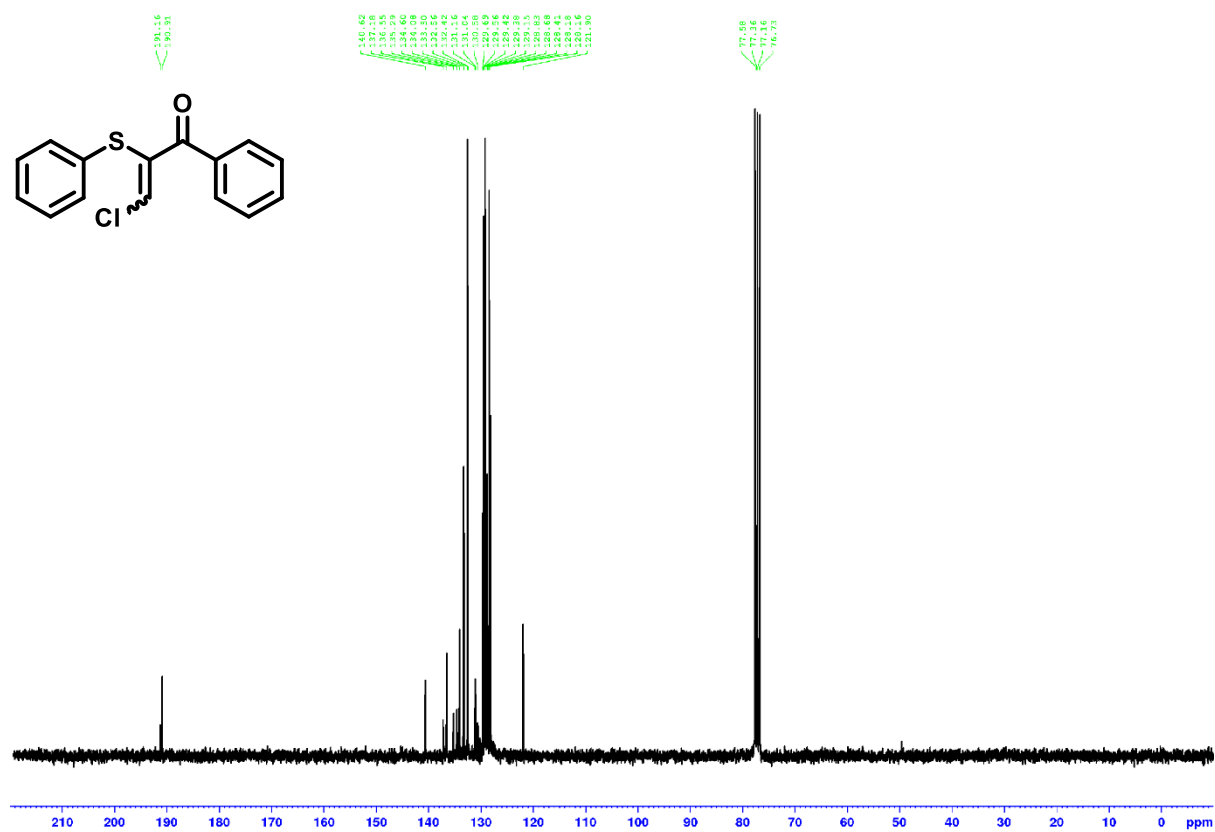


Figure S108: ^{13}C NMR (75.5 MHz, CDCl_3) spectrum of **Z-4a** and **E-4a**.

(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

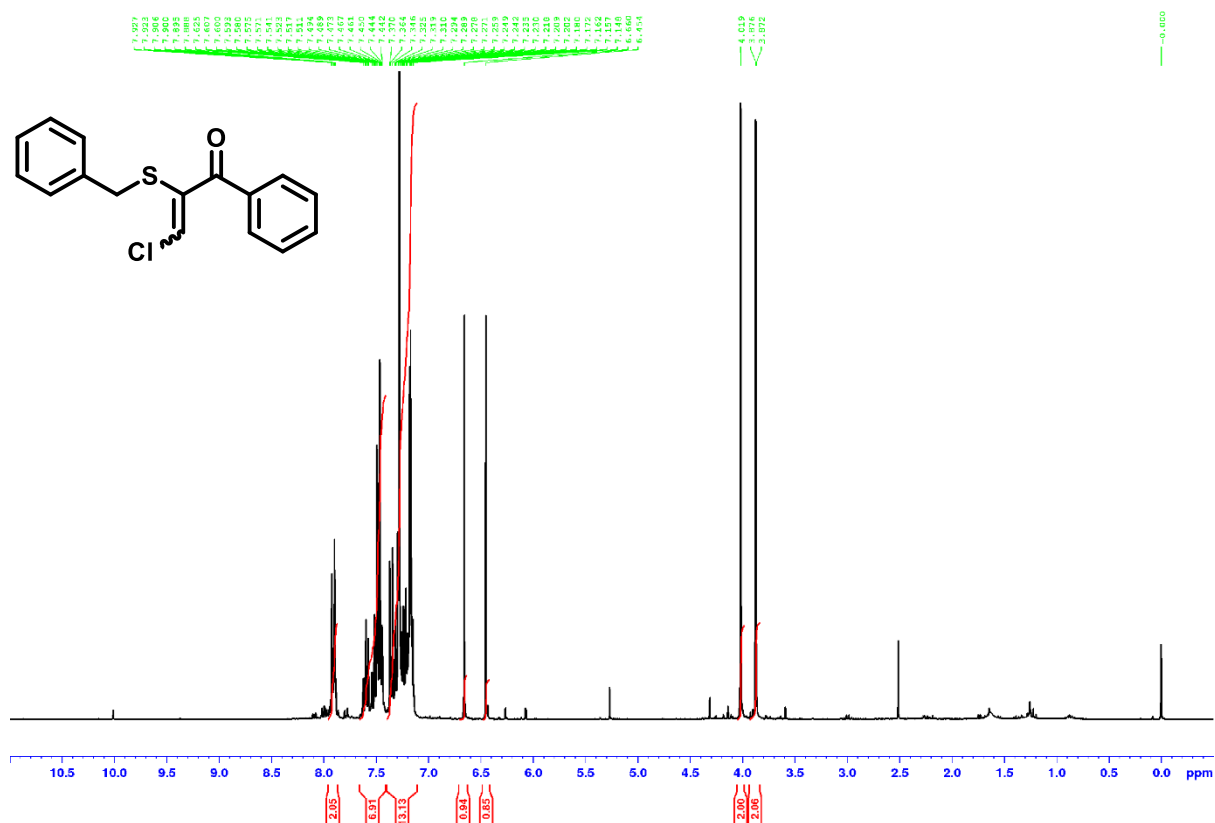


Figure S109: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4b** and **E-4b**.

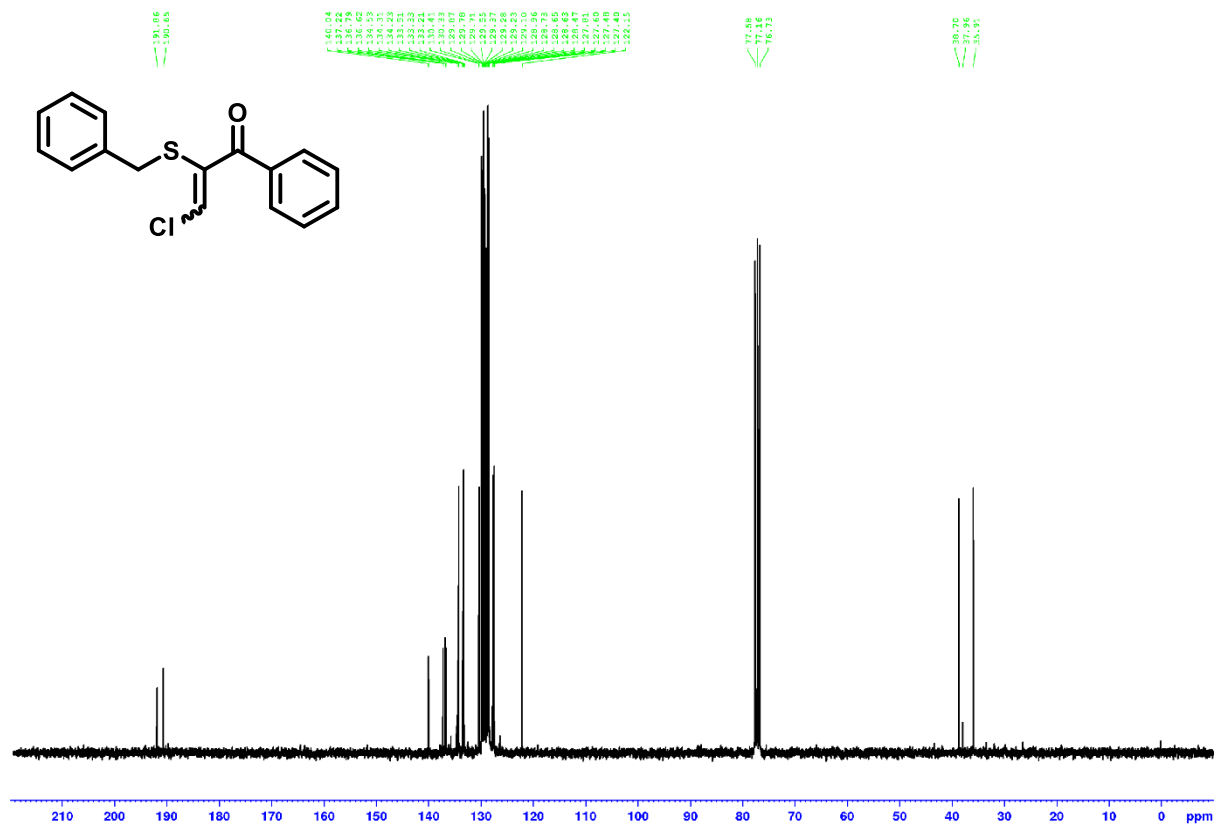


Figure S110: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4b** and **E-4b**.

(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

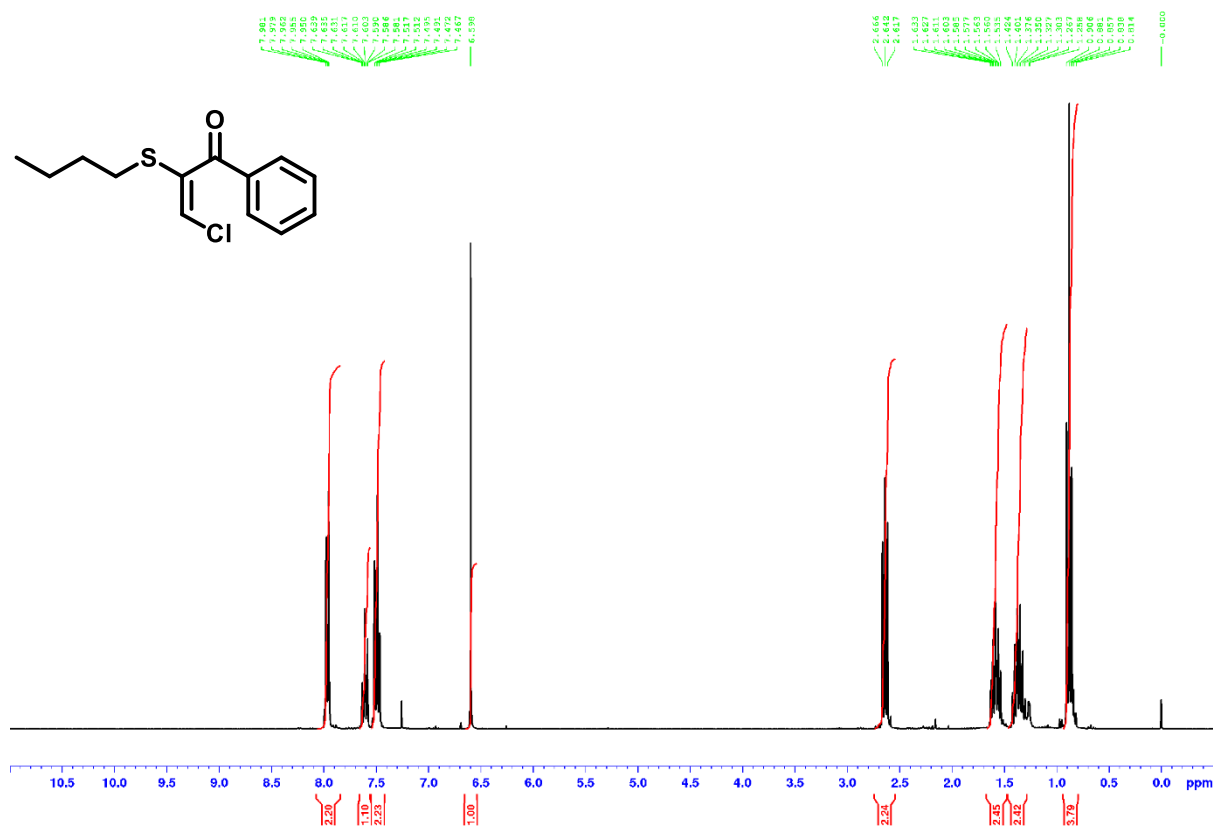


Figure S111: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-4c**.

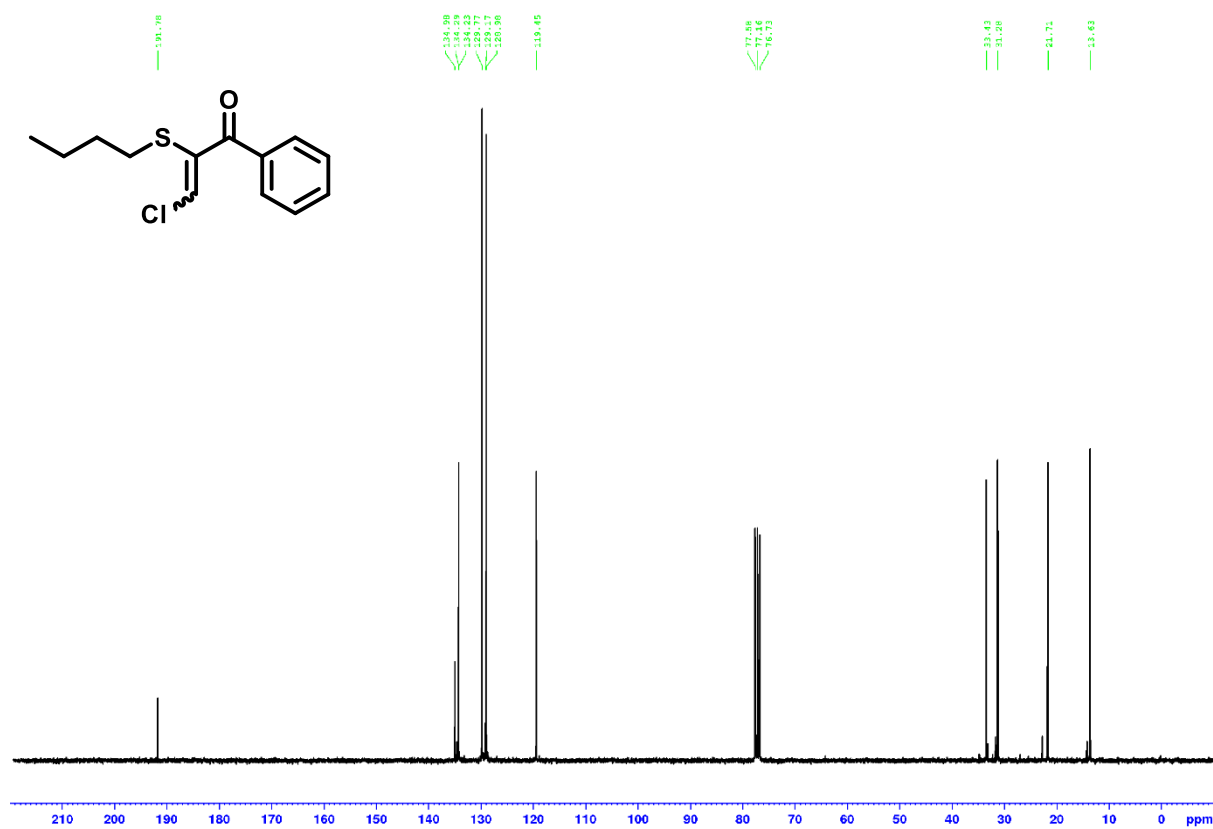


Figure S112: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4c** (95%) and **E-4c** (5%).

Chemical Structure: 4-methoxy-1-(2-chlorophenyl)butan-1-one

¹H NMR Data (ppm):

- 7.854, 7.848, 7.842, 7.824, 7.740, 7.735, 7.719, 7.710, 7.695, 7.689, 7.642, 7.619, 7.613, 7.595, 7.589, 7.583, 7.565, 7.559, 7.553, 7.535, 7.529, 7.523, 7.505, 7.499, 7.481, 7.475, 7.457, 7.451, 7.433, 7.427, 7.410, 7.404, 7.386, 7.380, 7.362, 7.356, 7.338, 7.332, 7.314, 7.308, 7.290, 7.284, 7.266, 7.260, 7.242, 7.236, 7.218, 7.212, 7.194, 7.188, 7.170, 7.164, 7.146, 7.140, 7.122, 7.116, 7.098, 7.092, 7.074, 7.068, 7.050, 7.044, 7.026, 7.020, 7.002, 6.996, 6.978, 6.972, 6.954, 6.948, 6.930, 6.924, 6.906, 6.900, 6.882, 6.876, 6.858, 6.852, 6.834, 6.828, 6.810, 6.804, 6.786, 6.780, 6.762, 6.756, 6.738, 6.732, 6.714, 6.708, 6.690, 6.684, 6.666, 6.660, 6.642, 6.636, 6.620, 6.614, 6.596, 6.590, 6.572, 6.566, 6.548, 6.542, 6.524, 6.518, 6.500, 6.494, 6.476, 6.470, 6.452, 6.446, 6.428, 6.422, 6.404, 6.398, 6.380, 6.374, 6.356, 6.350, 6.332, 6.326, 6.308, 6.302, 6.284, 6.278, 6.260, 6.254, 6.236, 6.230, 6.212, 6.206, 6.188, 6.182, 6.164, 6.158, 6.140, 6.134, 6.116, 6.110, 6.092, 6.086, 6.068, 6.062, 6.044, 6.038, 6.020, 6.014, 6.000, 5.994, 5.976, 5.970, 5.952, 5.946, 5.928, 5.922, 5.904, 5.898, 5.880, 5.874, 5.856, 5.850, 5.832, 5.826, 5.808, 5.802, 5.784, 5.778, 5.760, 5.754, 5.736, 5.730, 5.712, 5.706, 5.688, 5.682, 5.664, 5.658, 5.640, 5.634, 5.616, 5.610, 5.592, 5.586, 5.568, 5.562, 5.544, 5.538, 5.520, 5.514, 5.496, 5.490, 5.472, 5.466, 5.448, 5.442, 5.424, 5.418, 5.400, 5.394, 5.376, 5.370, 5.352, 5.346, 5.328, 5.322, 5.304, 5.298, 5.280, 5.274, 5.256, 5.250, 5.232, 5.226, 5.208, 5.202, 5.184, 5.178, 5.160, 5.154, 5.136, 5.130, 5.112, 5.106, 5.088, 5.082, 5.064, 5.058, 5.040, 5.034, 5.016, 5.010, 4.992, 4.986, 4.968, 4.962, 4.944, 4.938, 4.920, 4.914, 4.896, 4.890, 4.872, 4.866, 4.848, 4.842, 4.824, 4.818, 4.800, 4.794, 4.776, 4.770, 4.752, 4.746, 4.728, 4.722, 4.704, 4.698, 4.680, 4.674, 4.656, 4.650, 4.632, 4.626, 4.608, 4.602, 4.584, 4.578, 4.560, 4.554, 4.536, 4.530, 4.512, 4.506, 4.488, 4.482, 4.464, 4.458, 4.440, 4.434, 4.416, 4.410, 4.392, 4.386, 4.368, 4.362, 4.344, 4.338, 4.320, 4.314, 4.296, 4.290, 4.272, 4.266, 4.248, 4.242, 4.224, 4.218, 4.200, 4.194, 4.176, 4.170, 4.152, 4.146, 4.128, 4.122, 4.104, 4.098, 4.080, 4.074, 4.056, 4.050, 4.032, 4.026, 4.008, 4.002, 3.984, 3.978, 3.960, 3.954, 3.936, 3.930, 3.912, 3.906, 3.888, 3.882, 3.864, 3.858, 3.840, 3.834, 3.816, 3.810, 3.792, 3.786, 3.768, 3.762, 3.744, 3.738, 3.720, 3.714, 3.696, 3.690, 3.672, 3.666, 3.648, 3.642, 3.624, 3.618, 3.600, 3.594, 3.576, 3.570, 3.552, 3.546, 3.528, 3.522, 3.504, 3.498, 3.480, 3.474, 3.456, 3.450, 3.432, 3.426, 3.408, 3.402, 3.384, 3.378, 3.360, 3.354, 3.336, 3.330, 3.312, 3.306, 3.288, 3.282, 3.264, 3.258, 3.240, 3.234, 3.216, 3.210, 3.192, 3.186, 3.168, 3.162, 3.144, 3.138, 3.120, 3.114, 3.096, 3.090, 3.072, 3.066, 3.048, 3.042, 3.024, 3.018, 3.000, 2.994, 2.976, 2.970, 2.952, 2.946, 2.928, 2.922, 2.904, 2.898, 2.880, 2.874, 2.856, 2.850, 2.832, 2.826, 2.808, 2.802, 2.784, 2.778, 2.760, 2.754, 2.736, 2.730, 2.712, 2.706, 2.688, 2.682, 2.664, 2.658, 2.640, 2.634, 2.616, 2.610, 2.592, 2.586, 2.568, 2.562, 2.544, 2.538, 2.520, 2.514, 2.496, 2.490, 2.472, 2.466, 2.448, 2.442, 2.424, 2.418, 2.400, 2.394, 2.376, 2.370, 2.352, 2.346, 2.328, 2.322, 2.304, 2.298, 2.280, 2.274, 2.256, 2.250, 2.232, 2.226, 2.208, 2.202, 2.184, 2.178, 2.160, 2.154, 2.136, 2.130, 2.112, 2.106, 2.088, 2.082, 2.064, 2.058, 2.040, 2.034, 2.016, 2.010, 1.992, 1.986, 1.968, 1.962, 1.944, 1.938, 1.920, 1.914, 1.896, 1.890, 1.872, 1.866, 1.848, 1.842, 1.824, 1.818, 1.800, 1.794, 1.776, 1.770, 1.752, 1.746, 1.728, 1.722, 1.704, 1.698, 1.680, 1.674, 1.656, 1.650, 1.632, 1.626, 1.608, 1.602, 1.584, 1.578, 1.560, 1.554, 1.536, 1.530, 1.512, 1.506, 1.488, 1.482, 1.464, 1.458, 1.440, 1.434, 1.416, 1.410, 1.392, 1.386, 1.368, 1.362, 1.344, 1.338, 1.320, 1.314, 1.296, 1.290, 1.272, 1.266, 1.248, 1.242, 1.224, 1.218, 1.200, 1.194, 1.176, 1.170, 1.152, 1.146, 1.128, 1.122, 1.104, 1.098, 1.080, 1.074, 1.056, 1.050, 1.032, 1.026,

[illegible]

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(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**

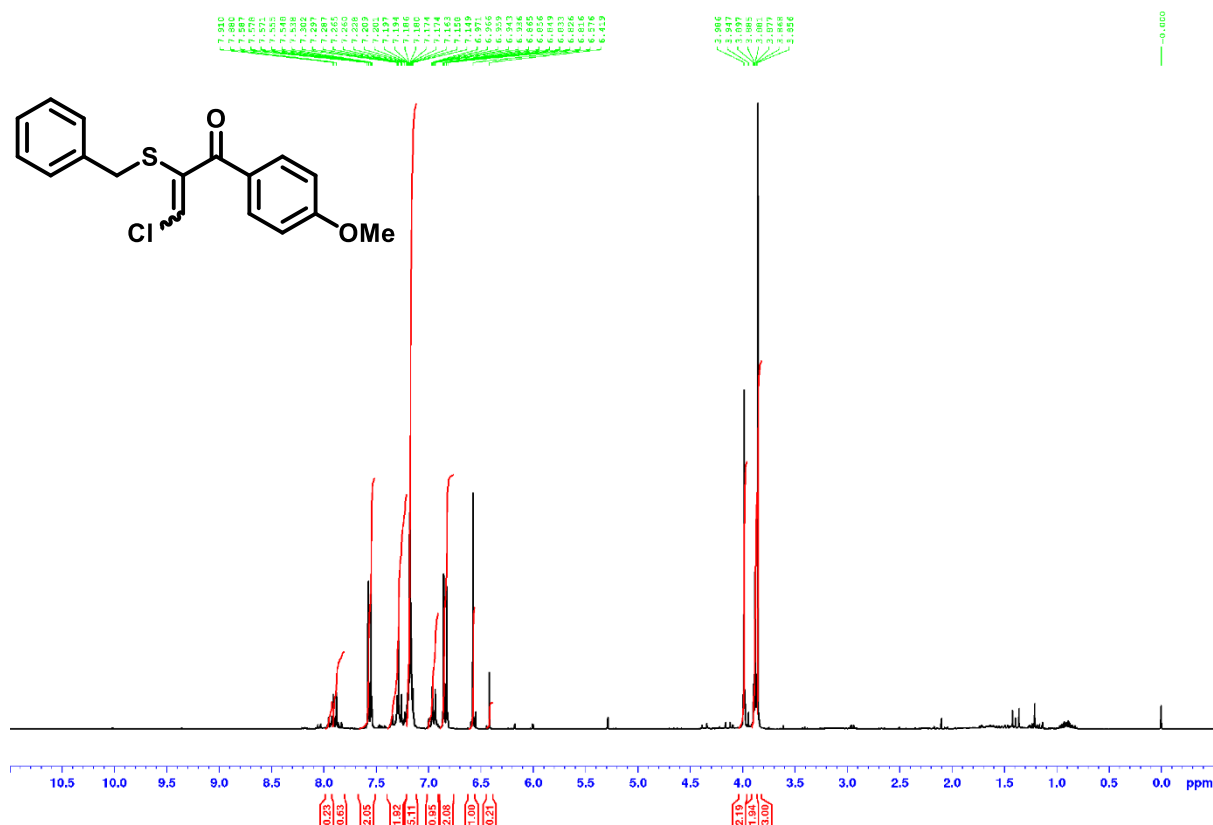


Figure S115: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4e** and **E-4e**.

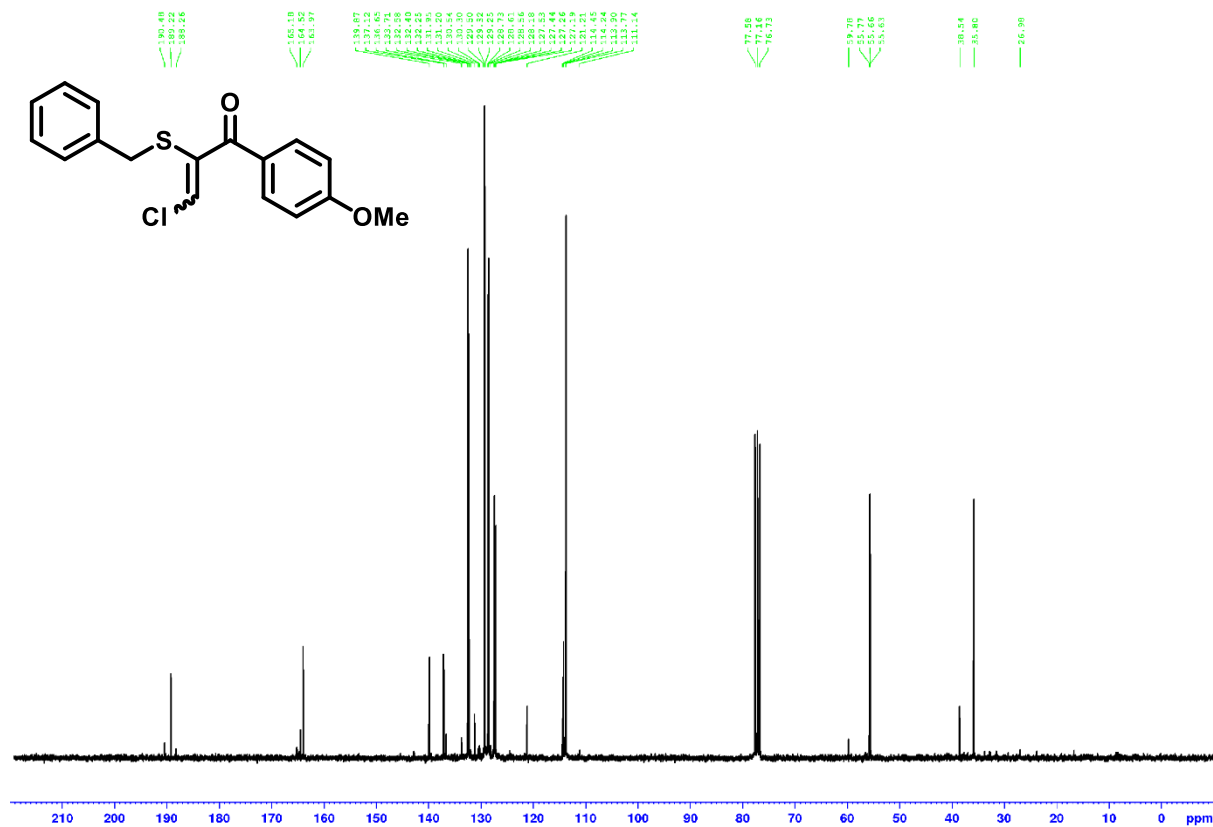


Figure S116: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4e** and **E-4e**.

(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**

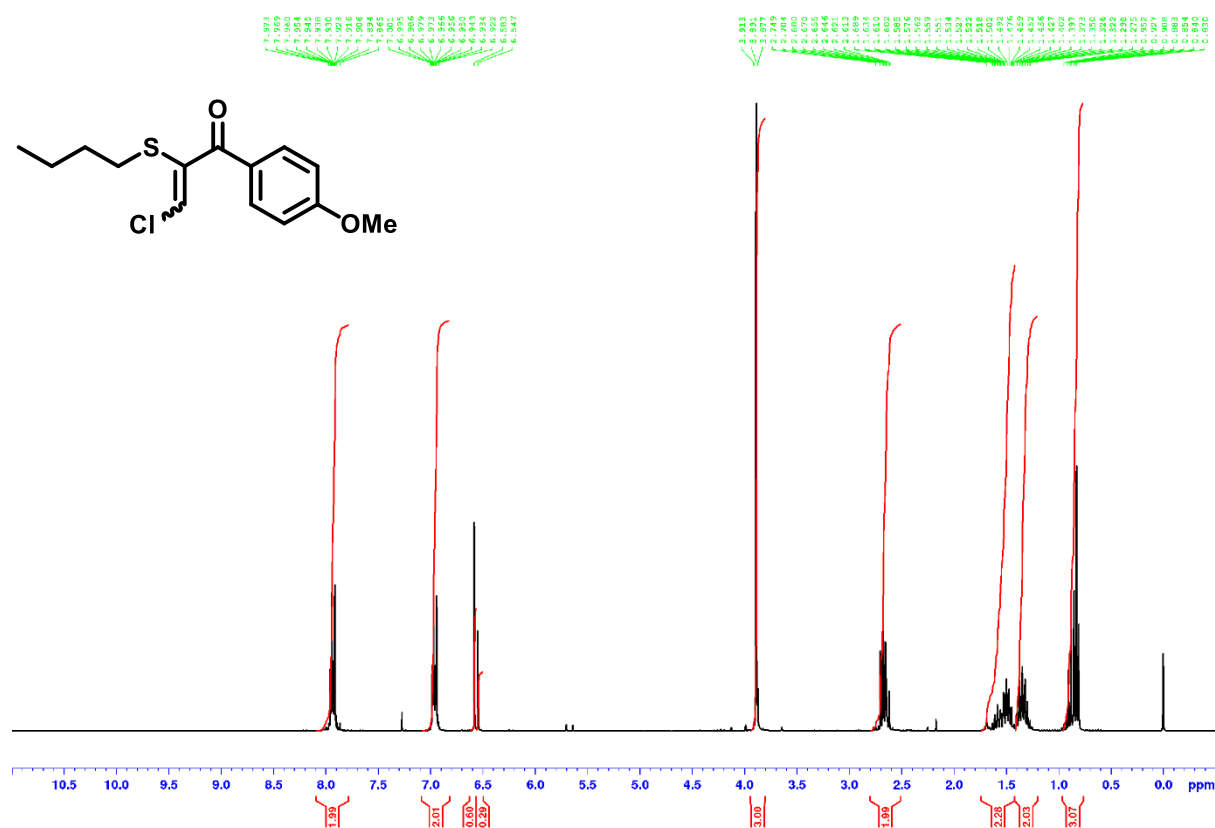


Figure S117: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4f** and **E-4f**.

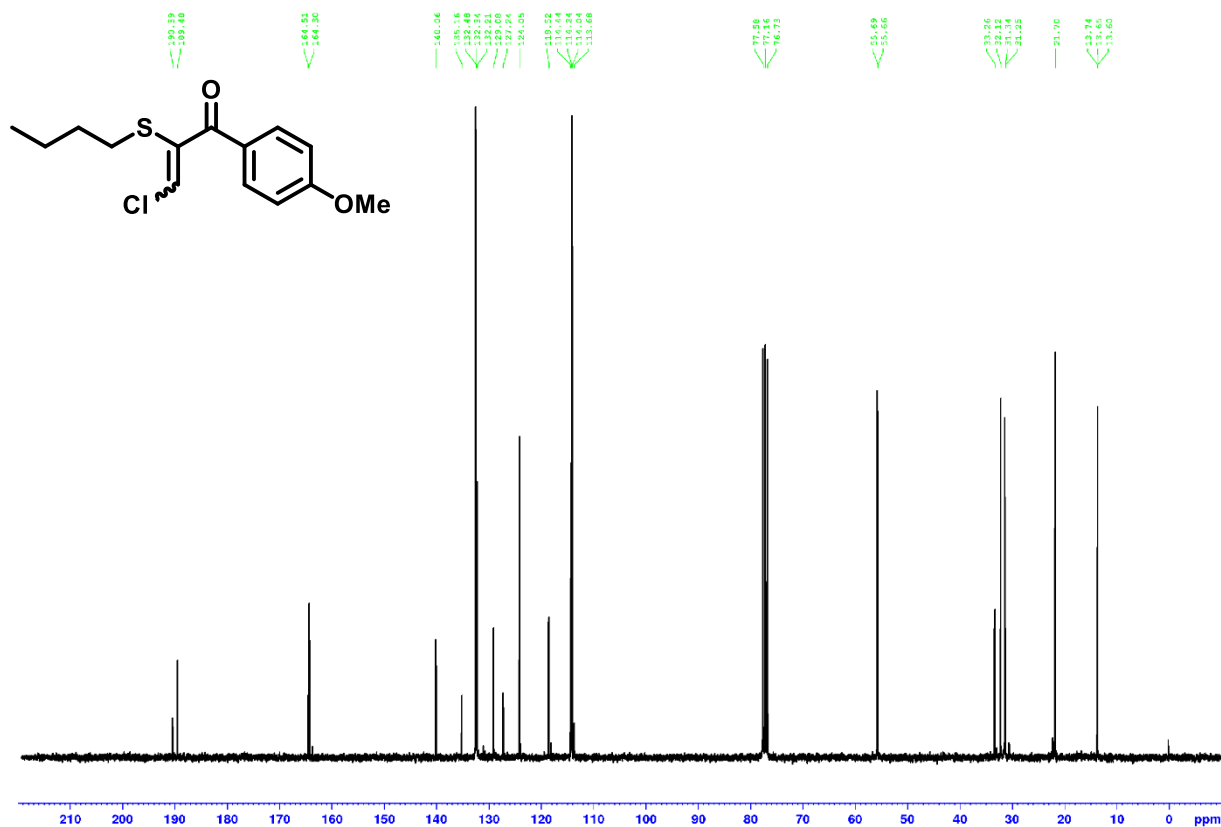


Figure S118: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4f** and **E-4f**.

(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

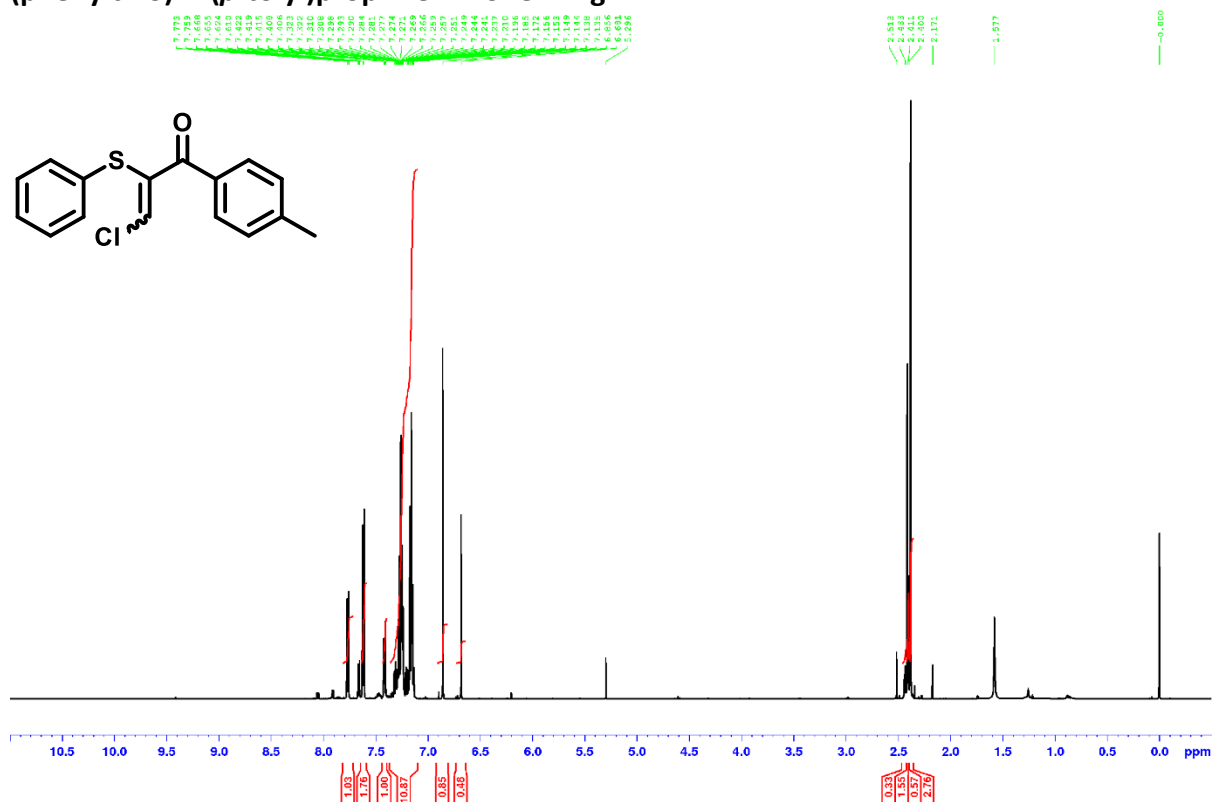


Figure S119: ¹H NMR (600 MHz, CDCl₃) spectrum of **Z-4g** and **E-4g**.

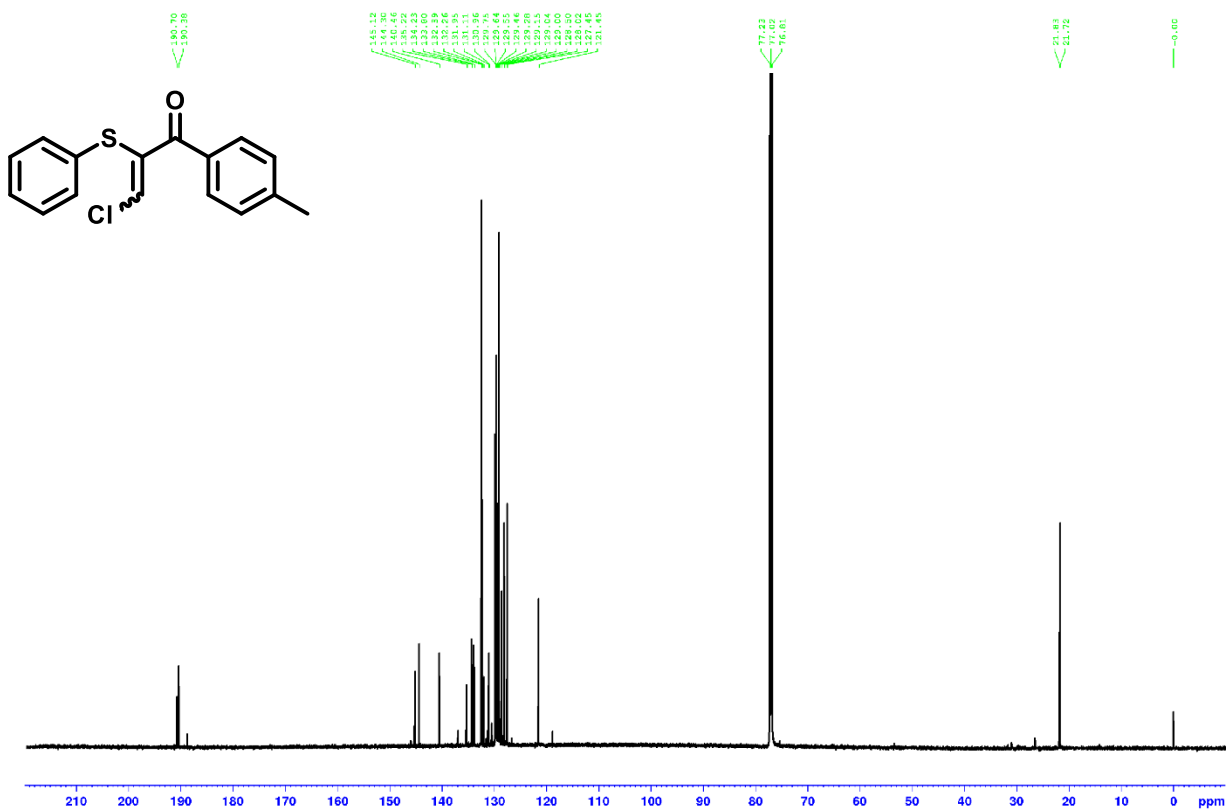


Figure S120: ¹³C NMR (150.8 MHz, CDCl₃) spectrum of **Z-4g** and **E-4g**.

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

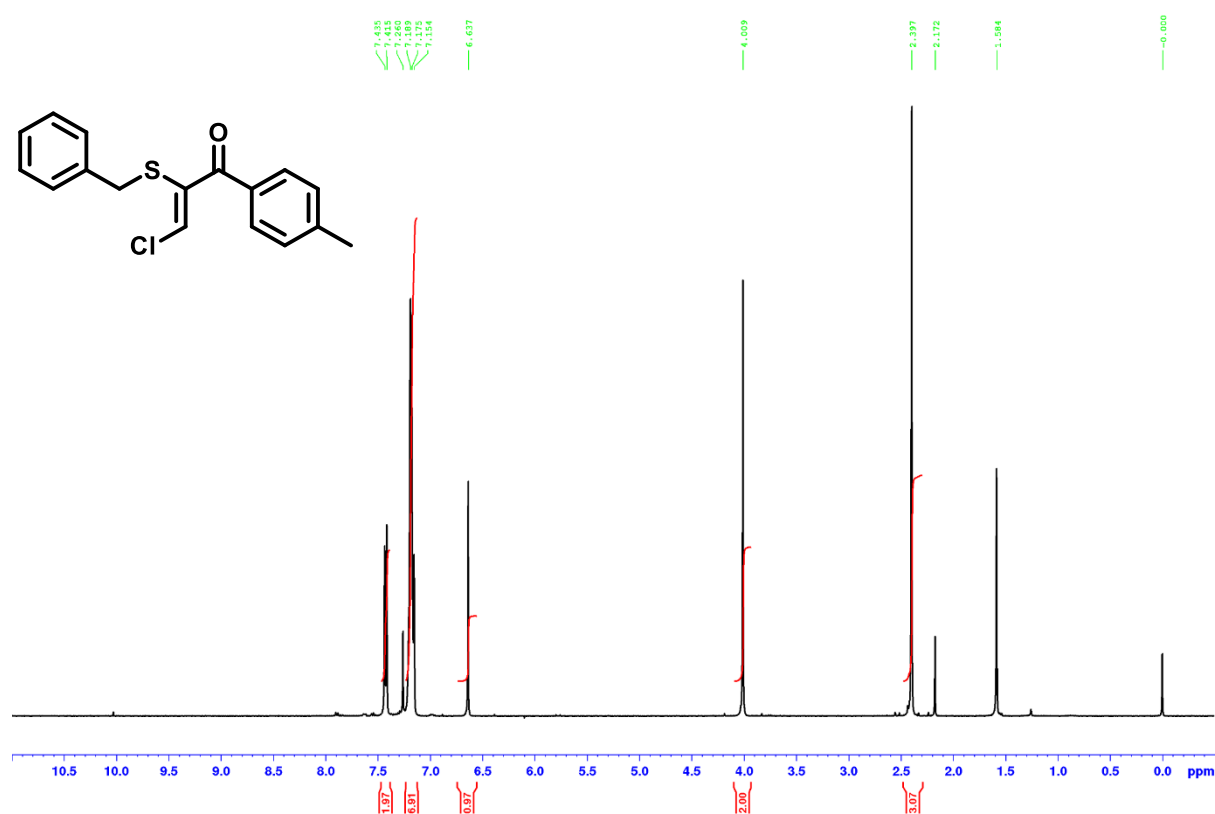


Figure S121: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4h.

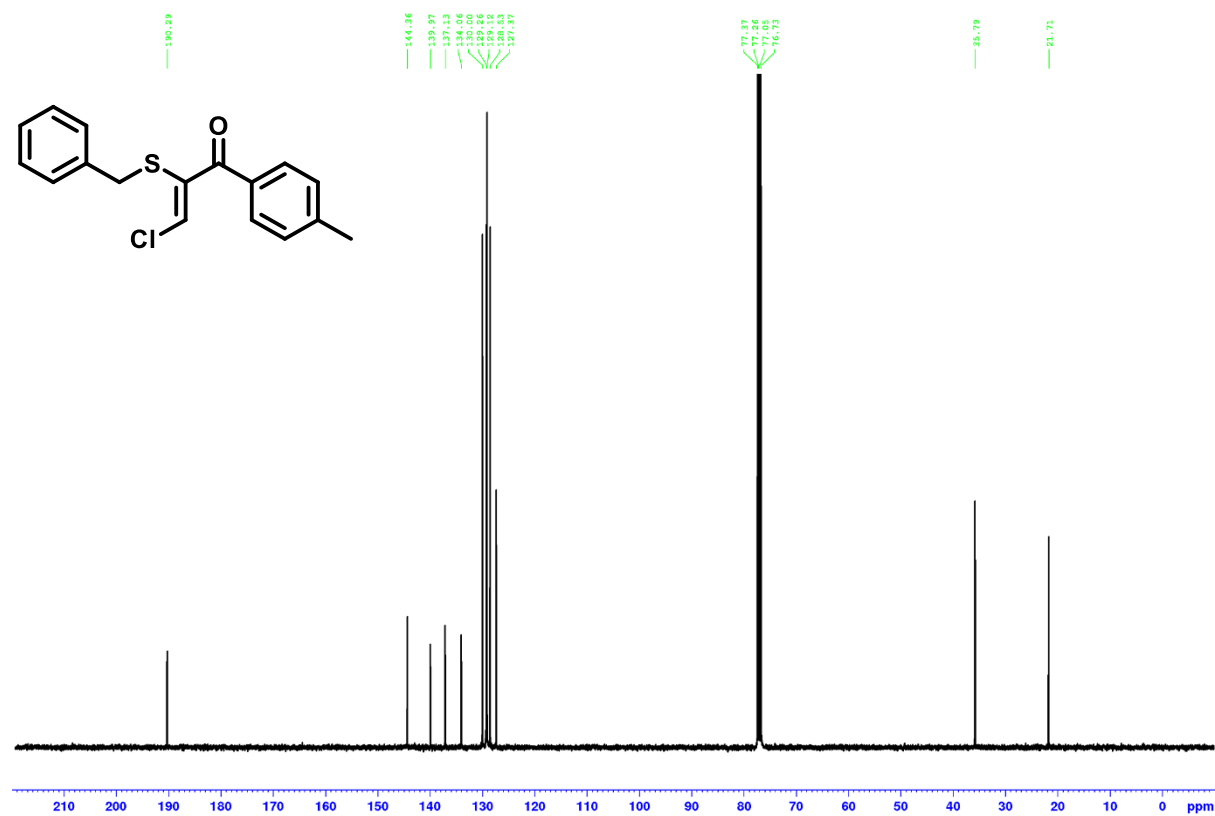


Figure S122: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of Z-4h.

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

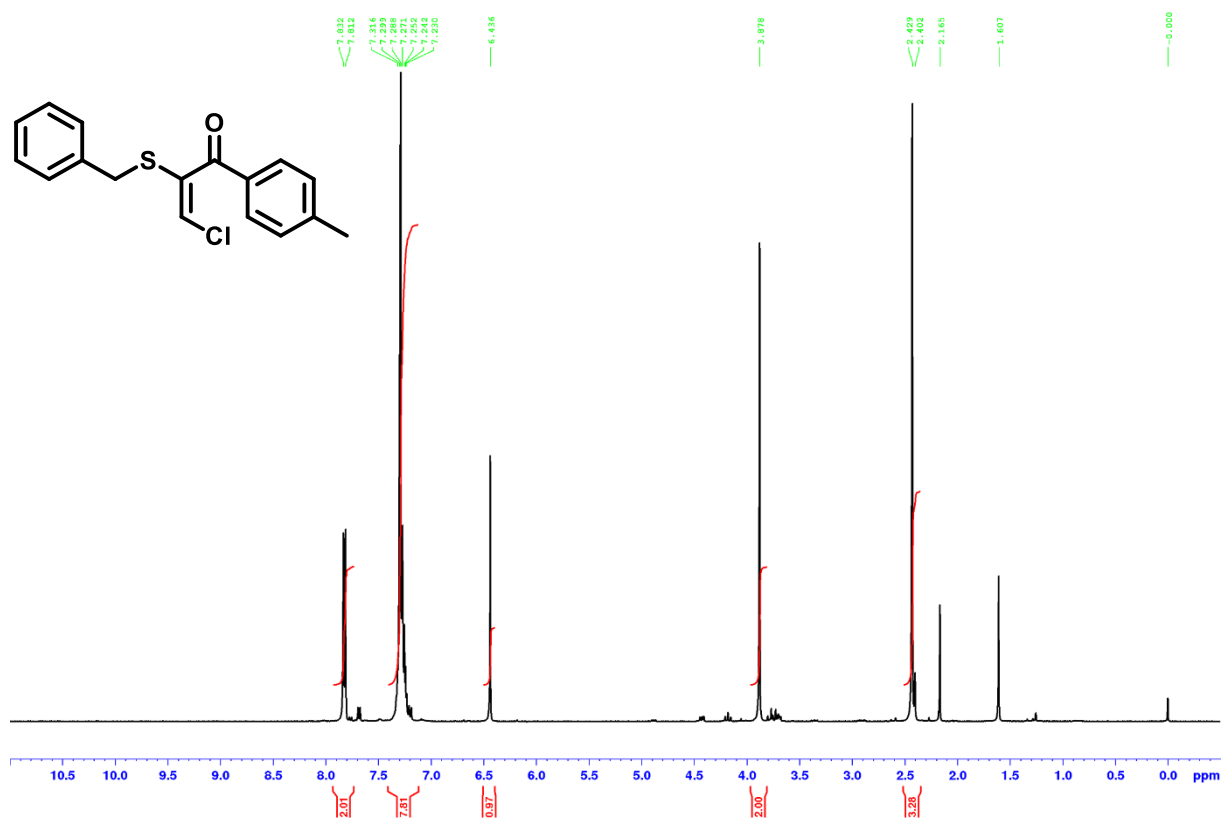


Figure S123: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-4h**.

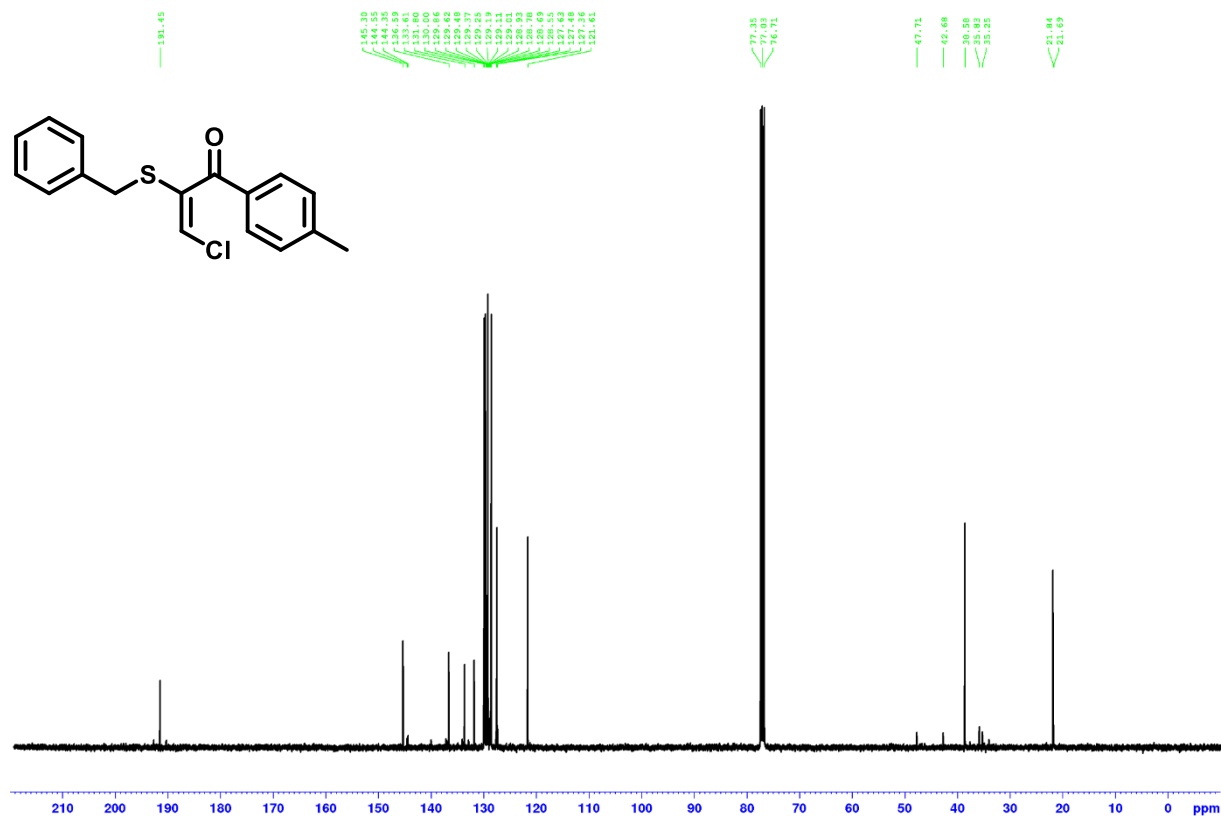


Figure S124: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **E-4h**.

(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

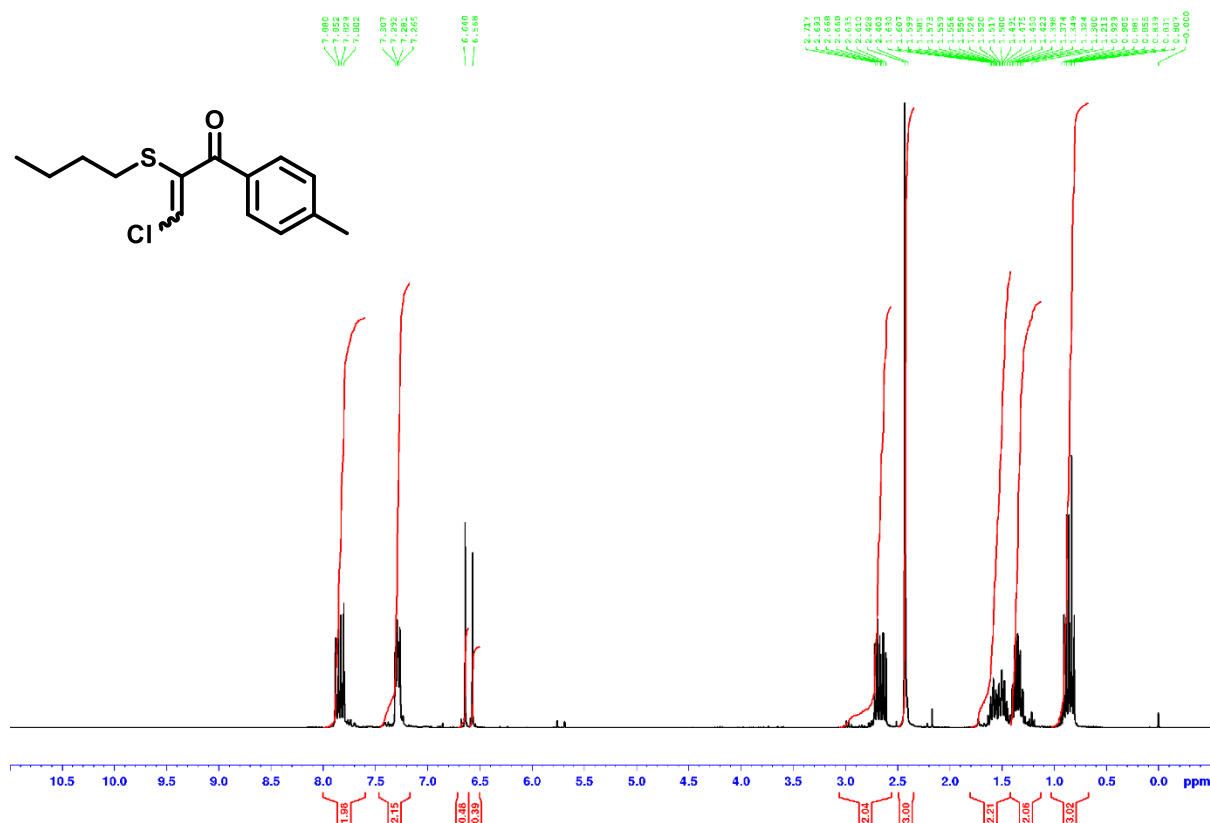


Figure S125: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4i** and **E-4i**.

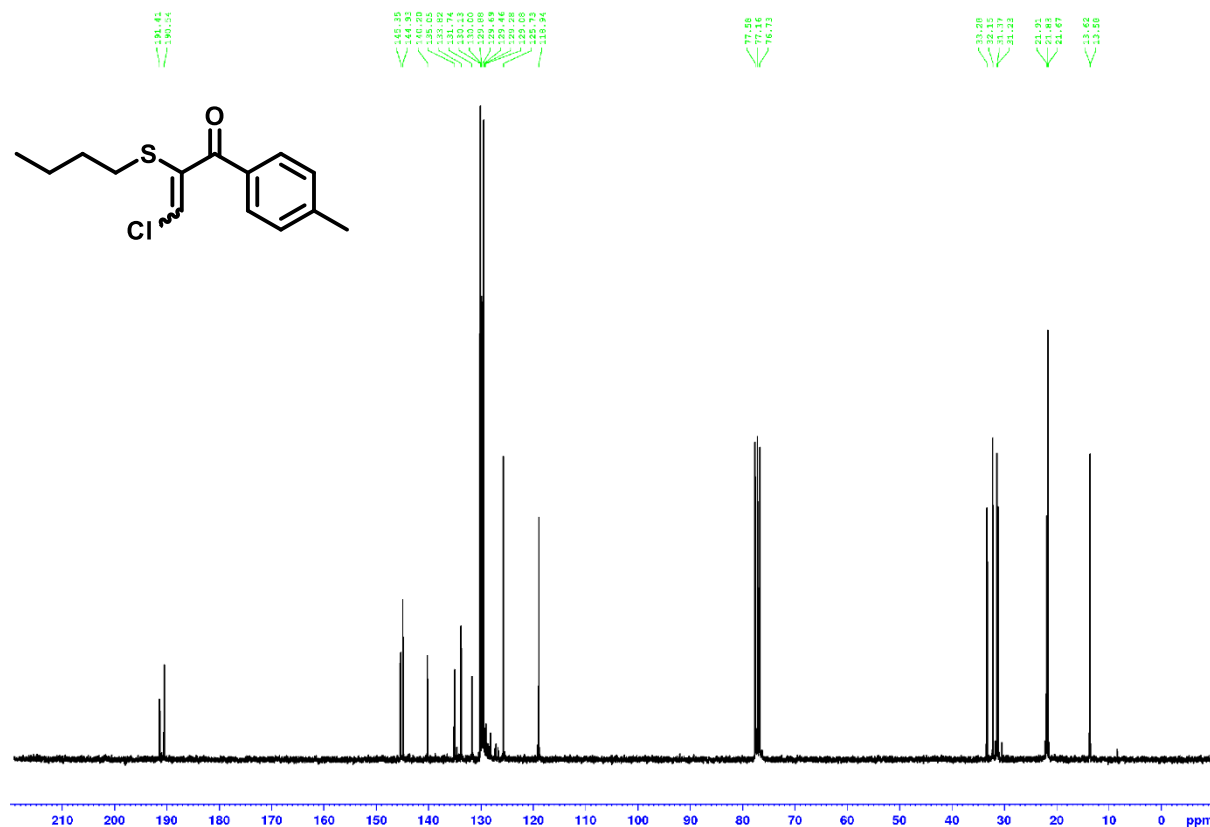


Figure S126: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4i** and **E-4i**.

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

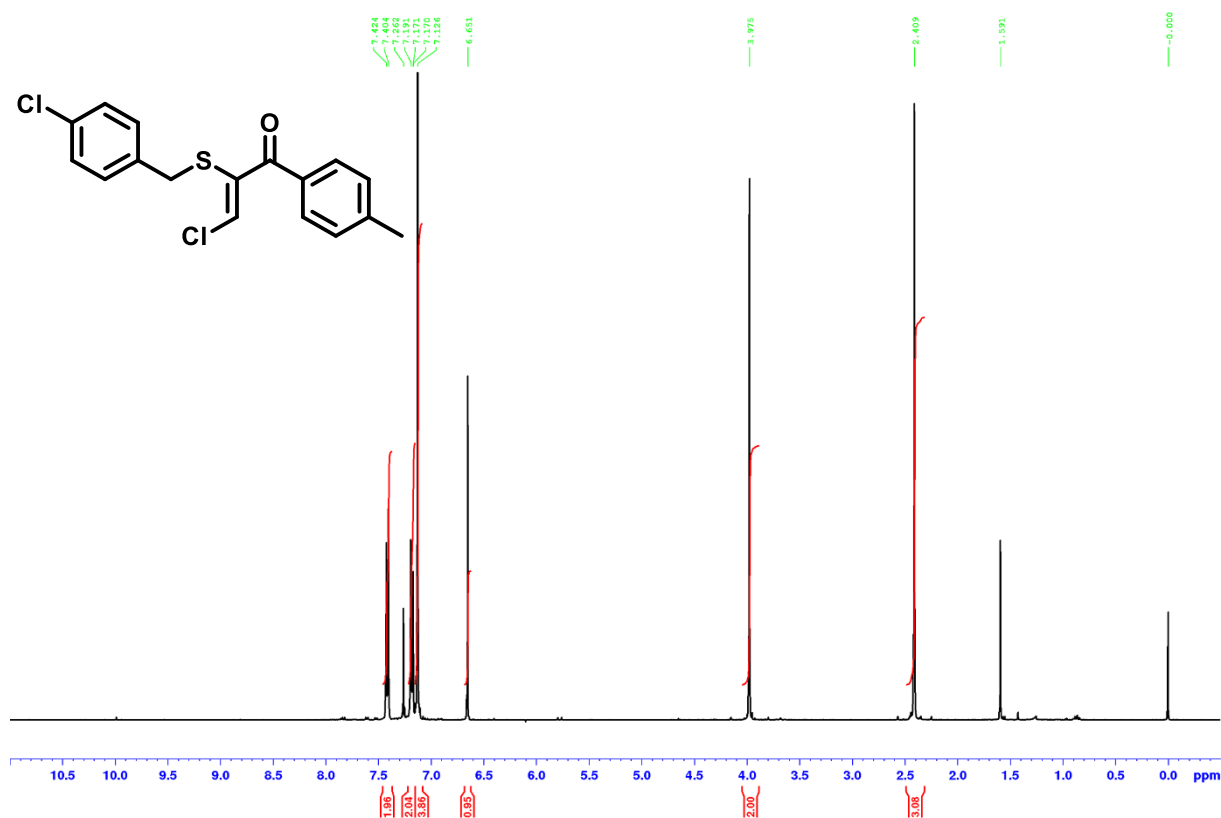


Figure S127: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4j.

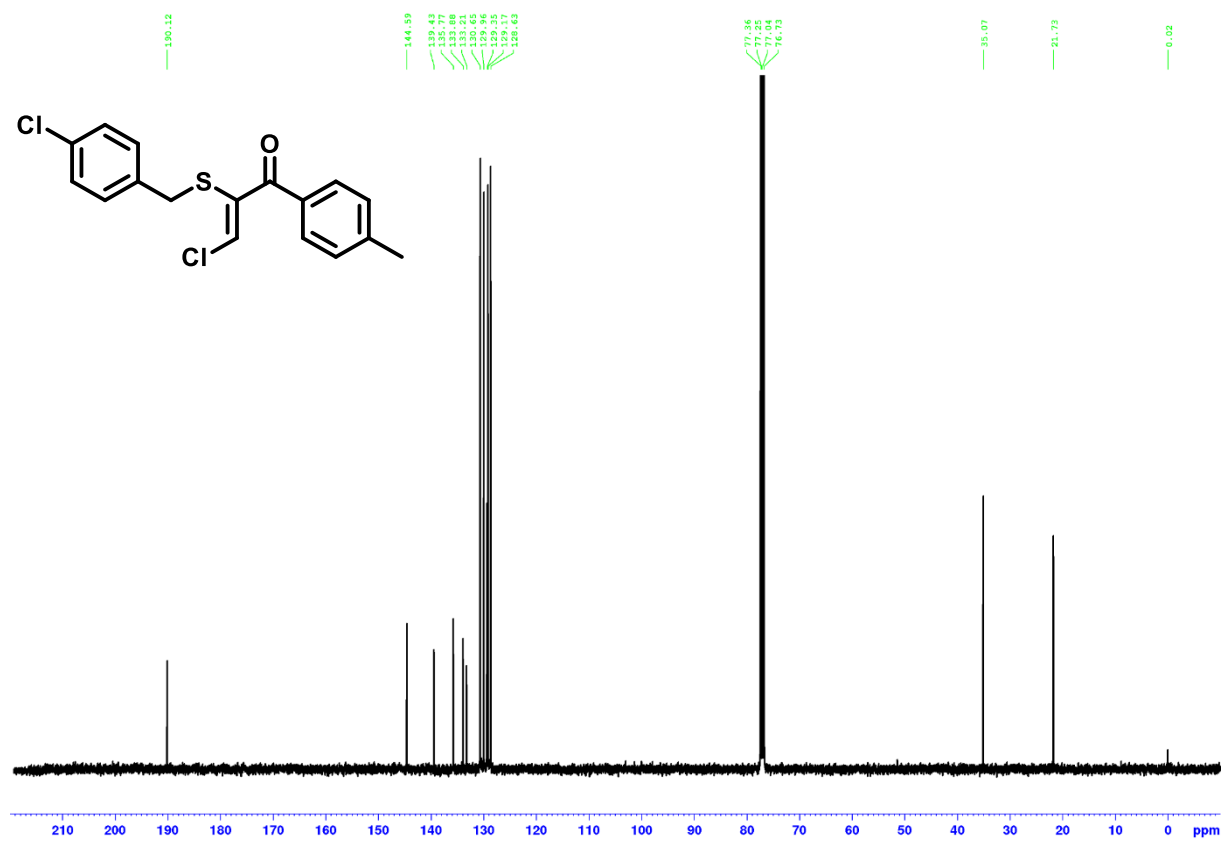


Figure S128: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of Z-4j.

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

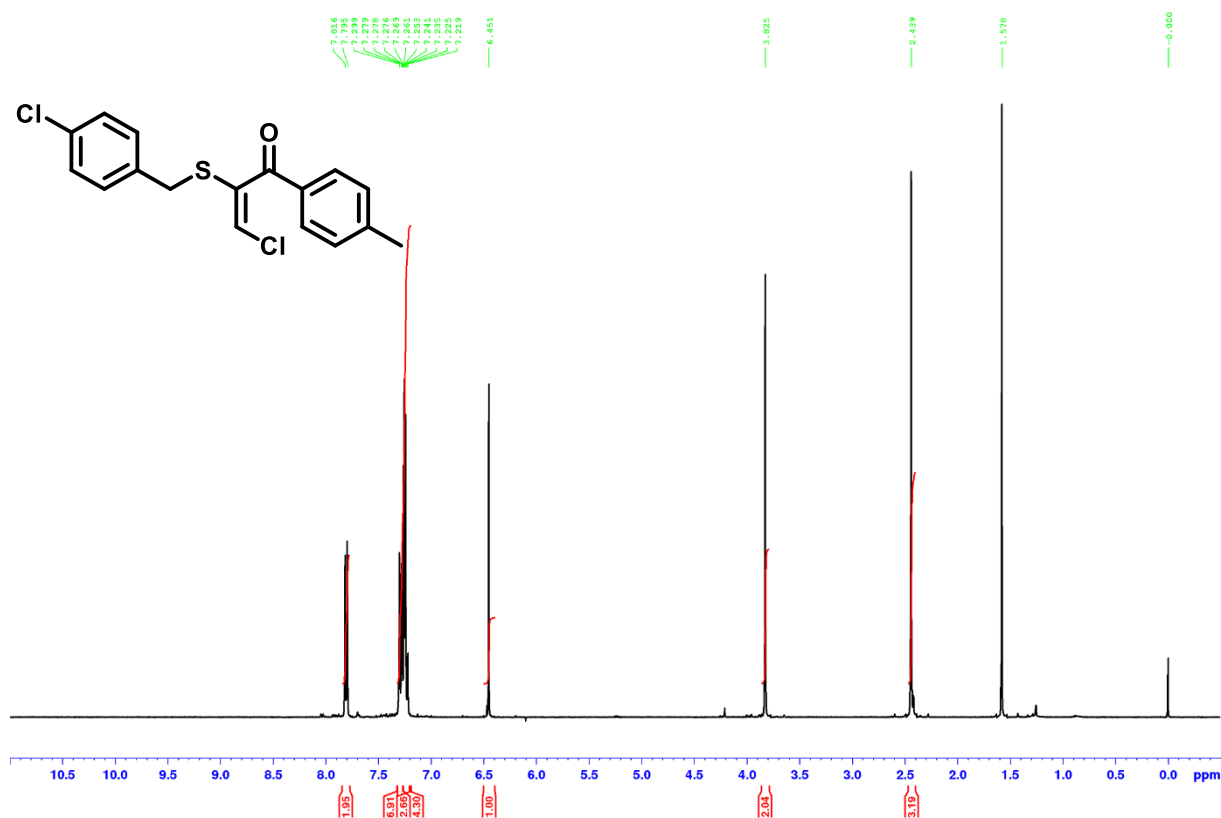


Figure S129: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-4j**.

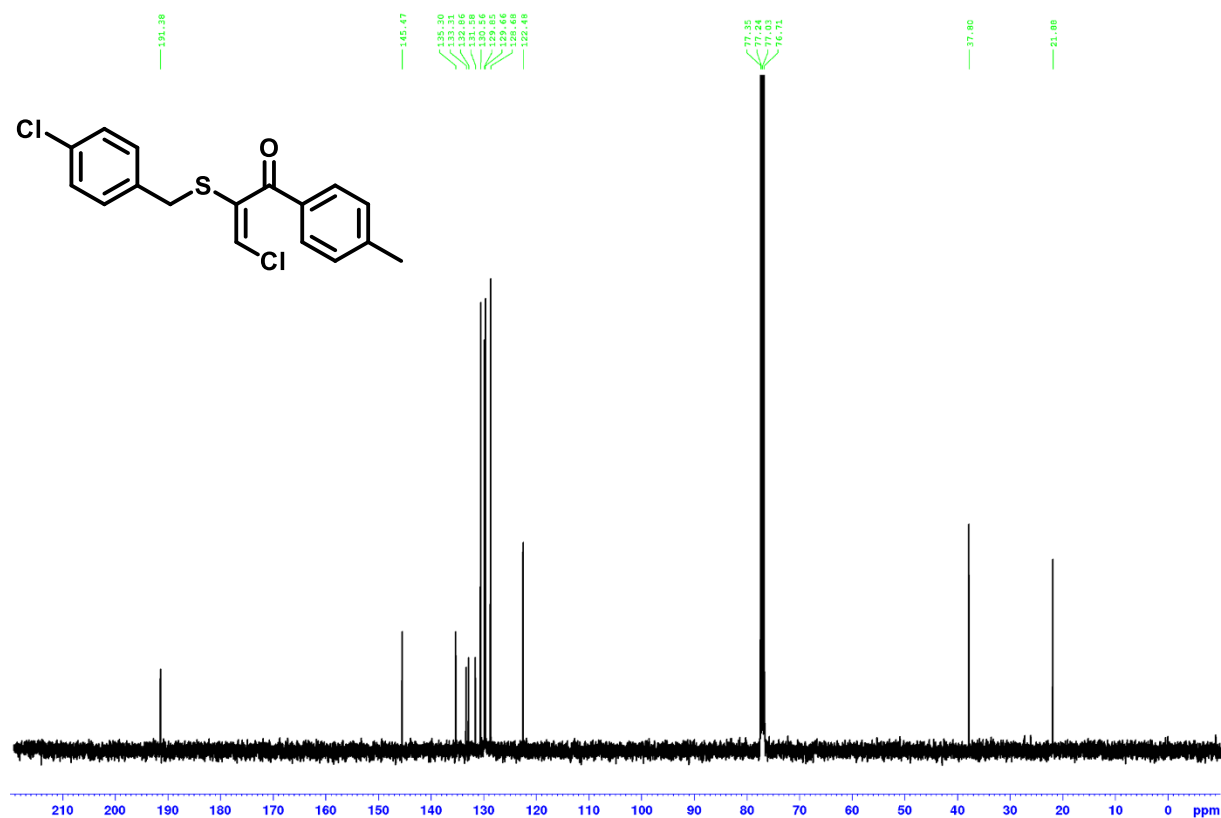


Figure S130: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **E-4j**.

Chemical structure: COc1ccc(cc1)CSC(=C(Cl)C(=O)c2ccc(C)cc2)

¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
7.466, 7.445, 7.422, 7.385, 7.364, 7.345, 7.326, 7.303, 7.284, 7.114, 7.093, 7.074, 7.055, 6.699, 6.681, 6.611, 6.611	2.15, 2.17, 2.22, 2.15, 1.00
5.301	
3.792, 3.735, 3.727	2.01, 2.15
2.401	3.10
1.574, 1.566	1.15
0.000	

Chemical structure: COc1ccc(cc1)CSC(=O)c2ccc(C)cc2

¹³C NMR peaks (ppm): 190.29, 159.87, 144.34, 140.05, 134.04, 133.05, 132.05, 129.09, 128.50, 127.50, 111.89, 77.35, 77.03, 76.71, 55.25, 35.27, 21.71.

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

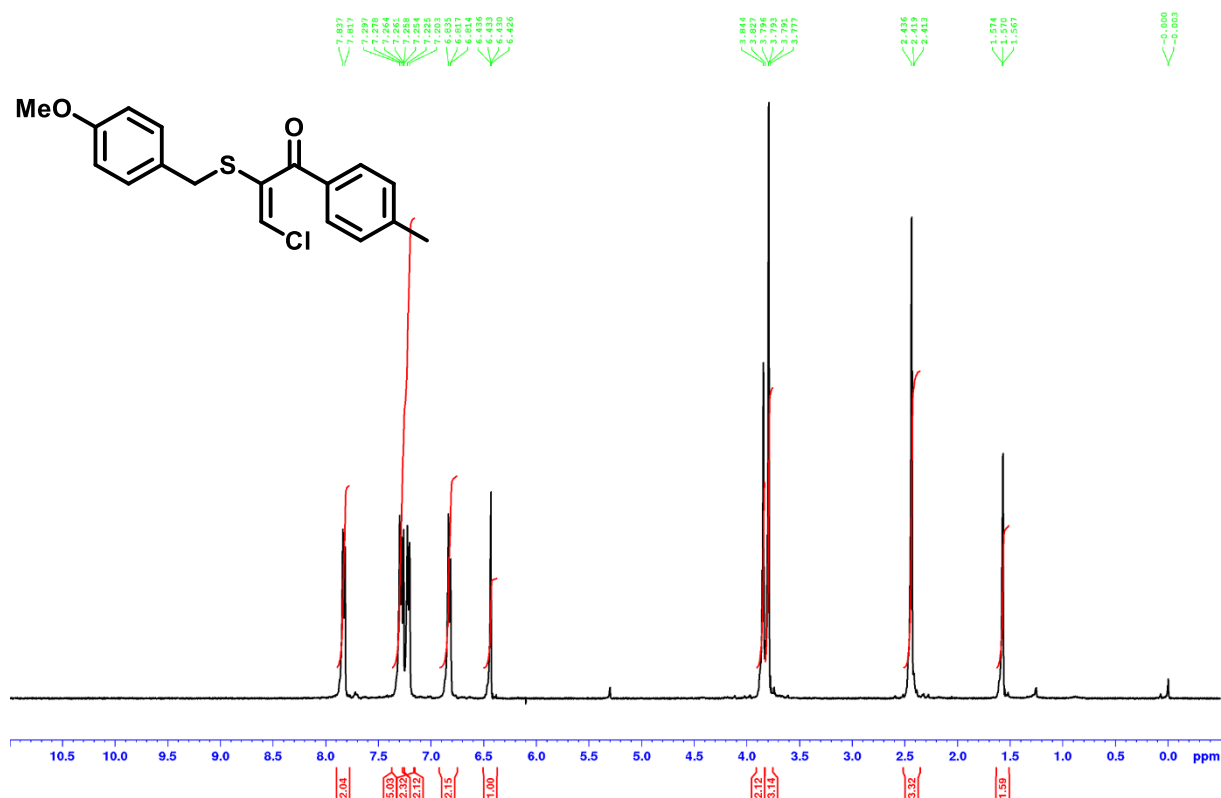


Figure S133: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-4k**.

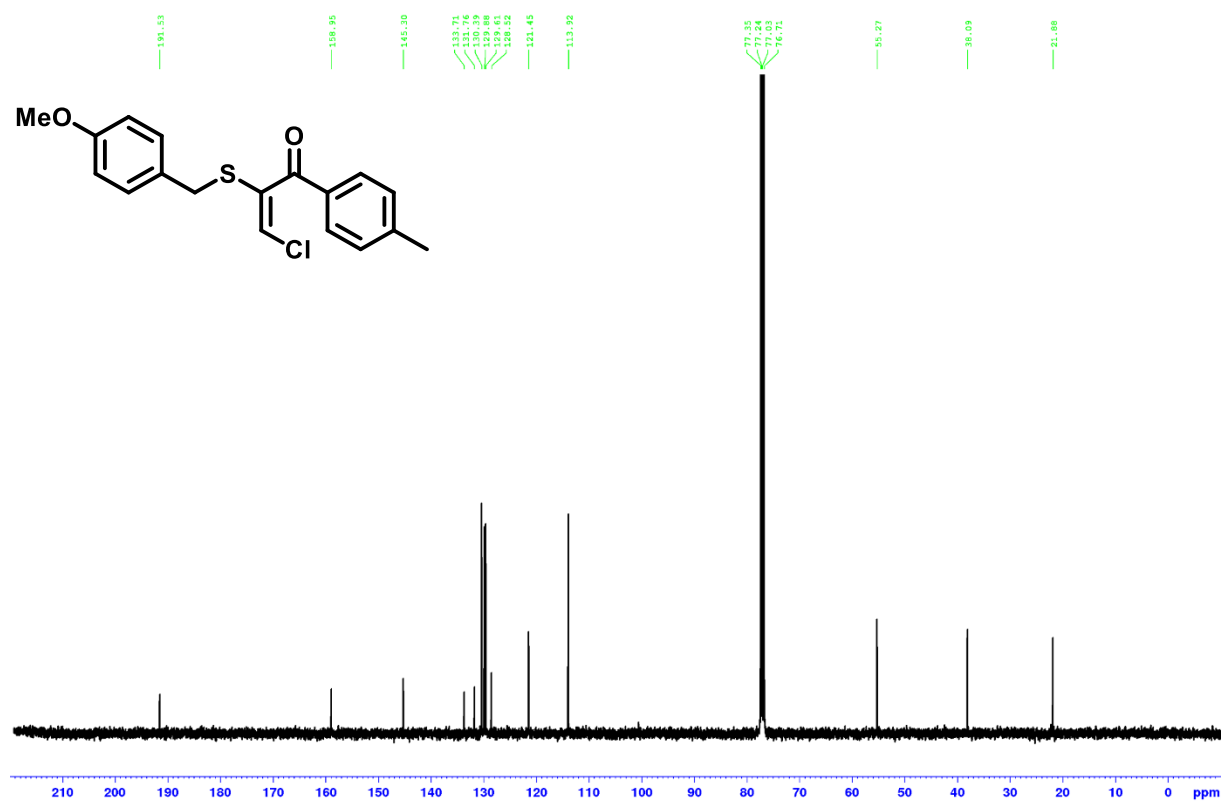


Figure S134: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **E-4k**.

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

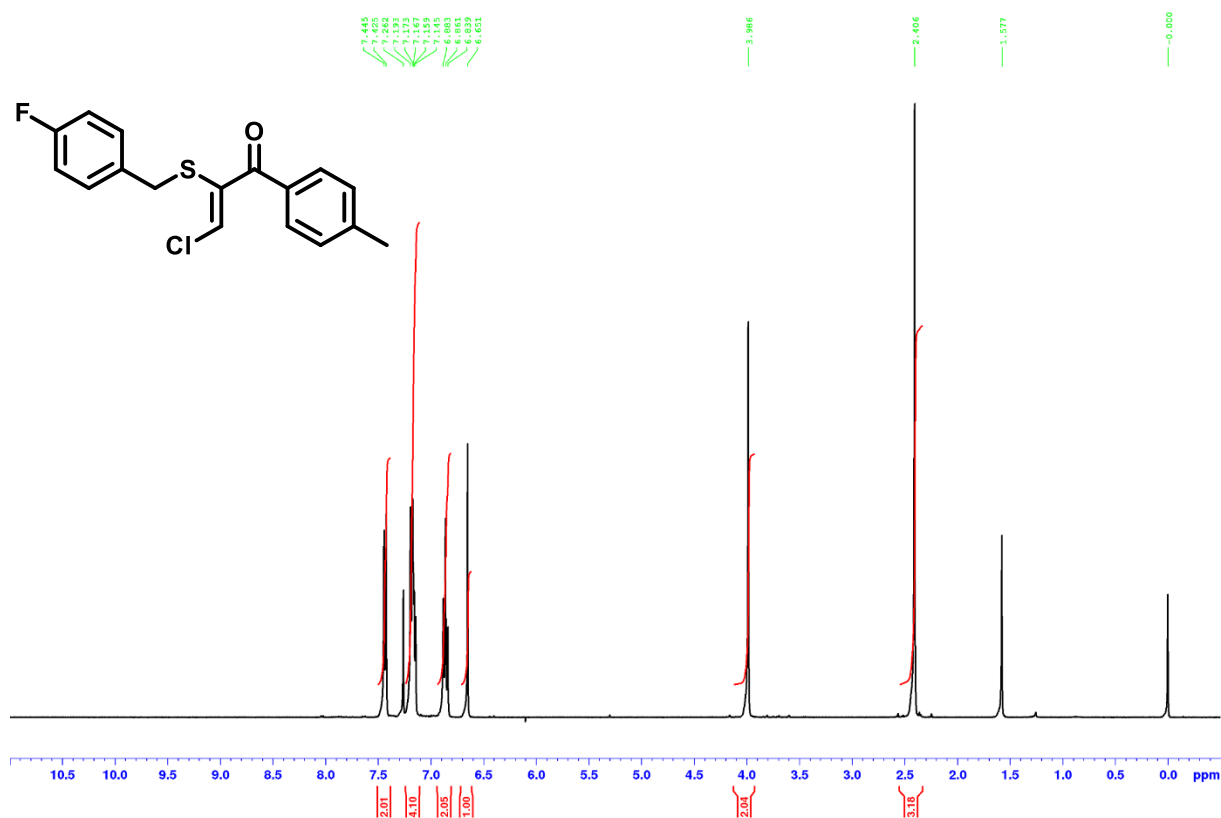


Figure S135: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4I.

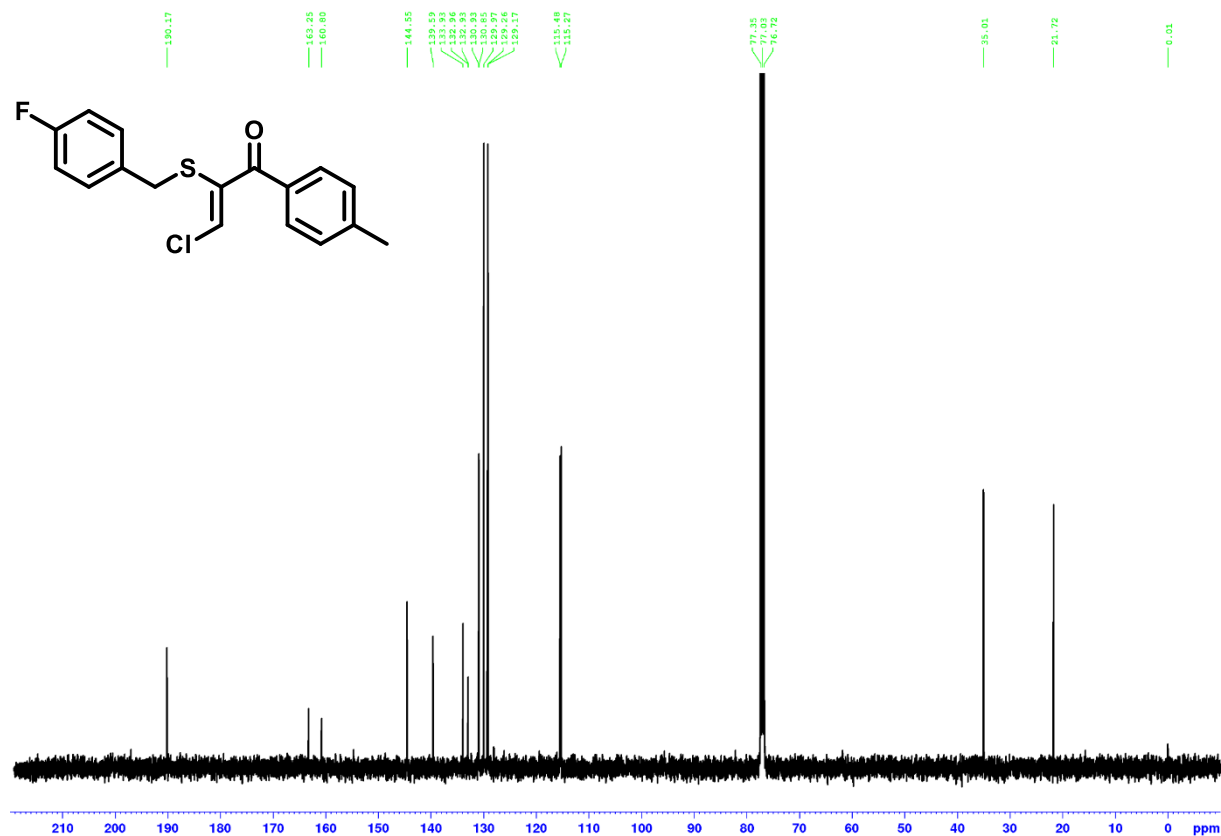


Figure S136: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of Z-4I.

(E)-3-Chloro-2-((4-fluorobenzyl)thio)-1-(p-tolyl)prop-2-en-1-one E-4I

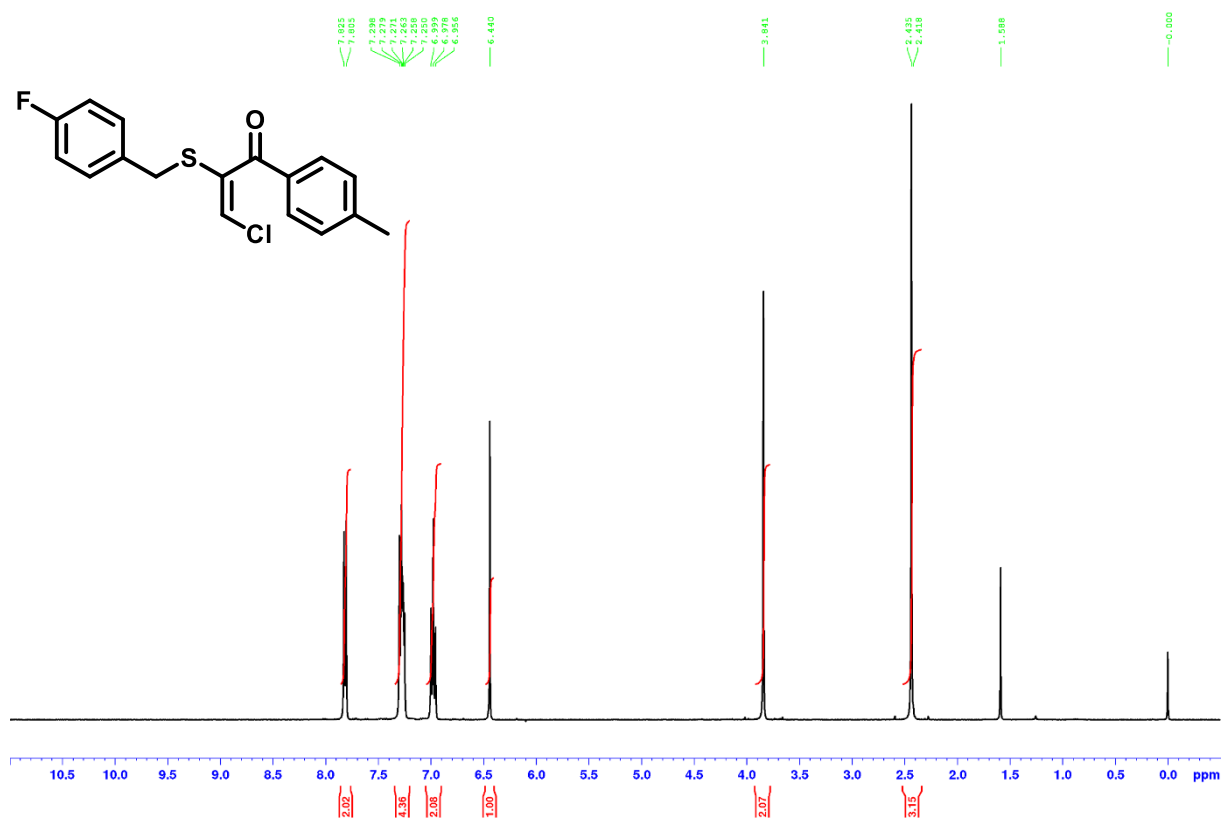


Figure S137: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-4I**.

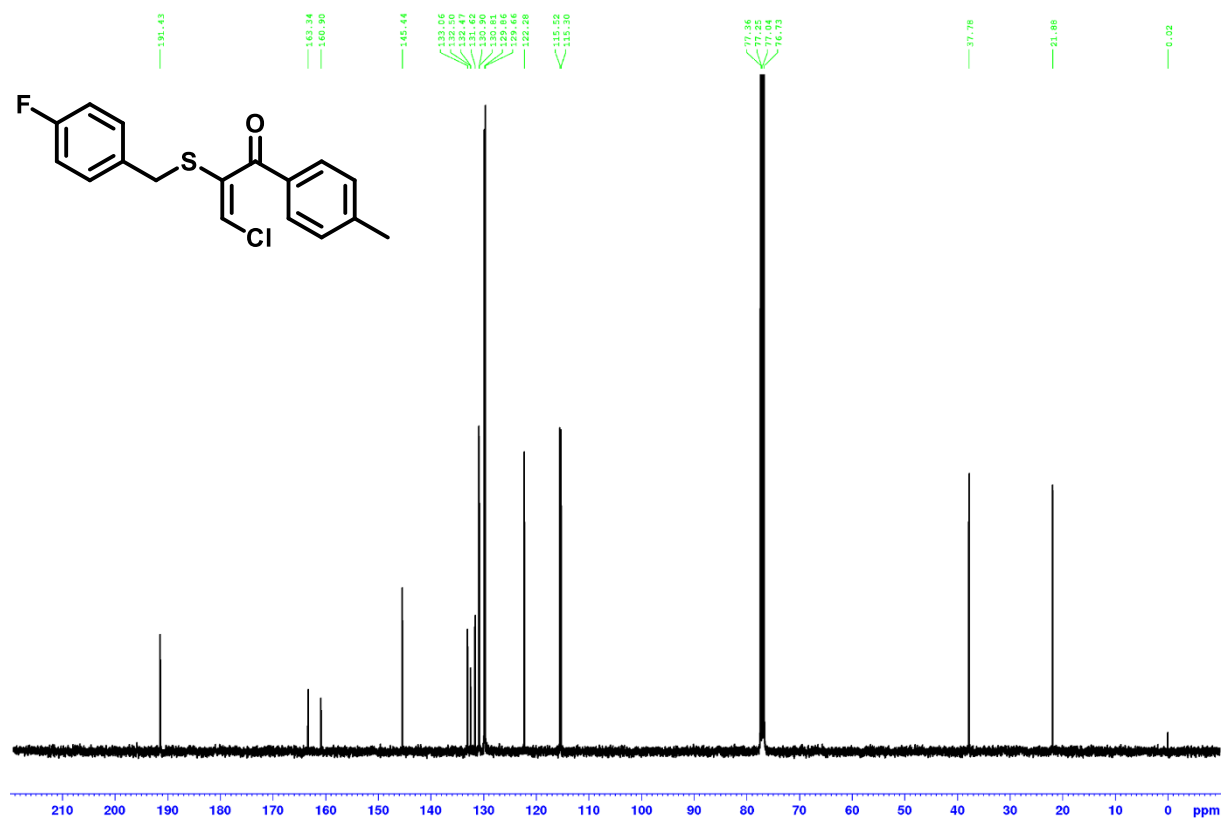


Figure S138: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **E-4I**.

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

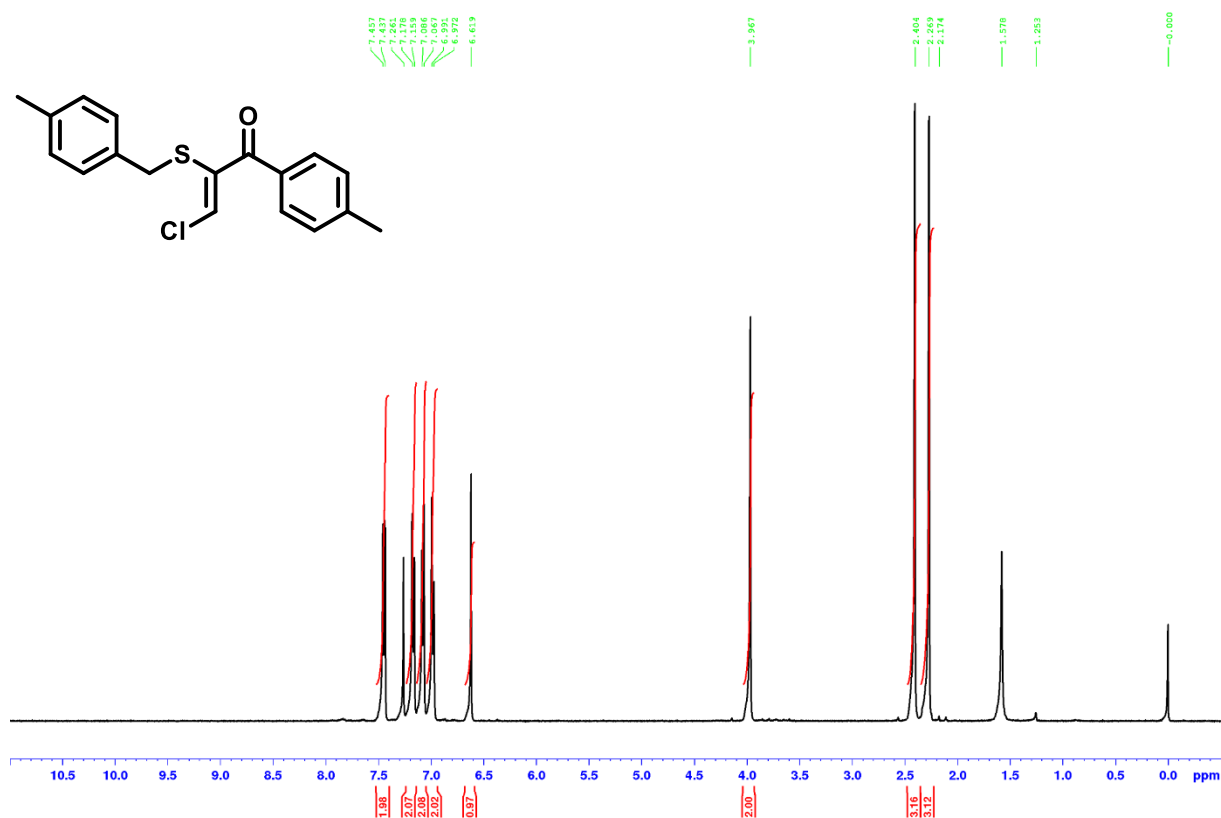


Figure S139: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4m**.

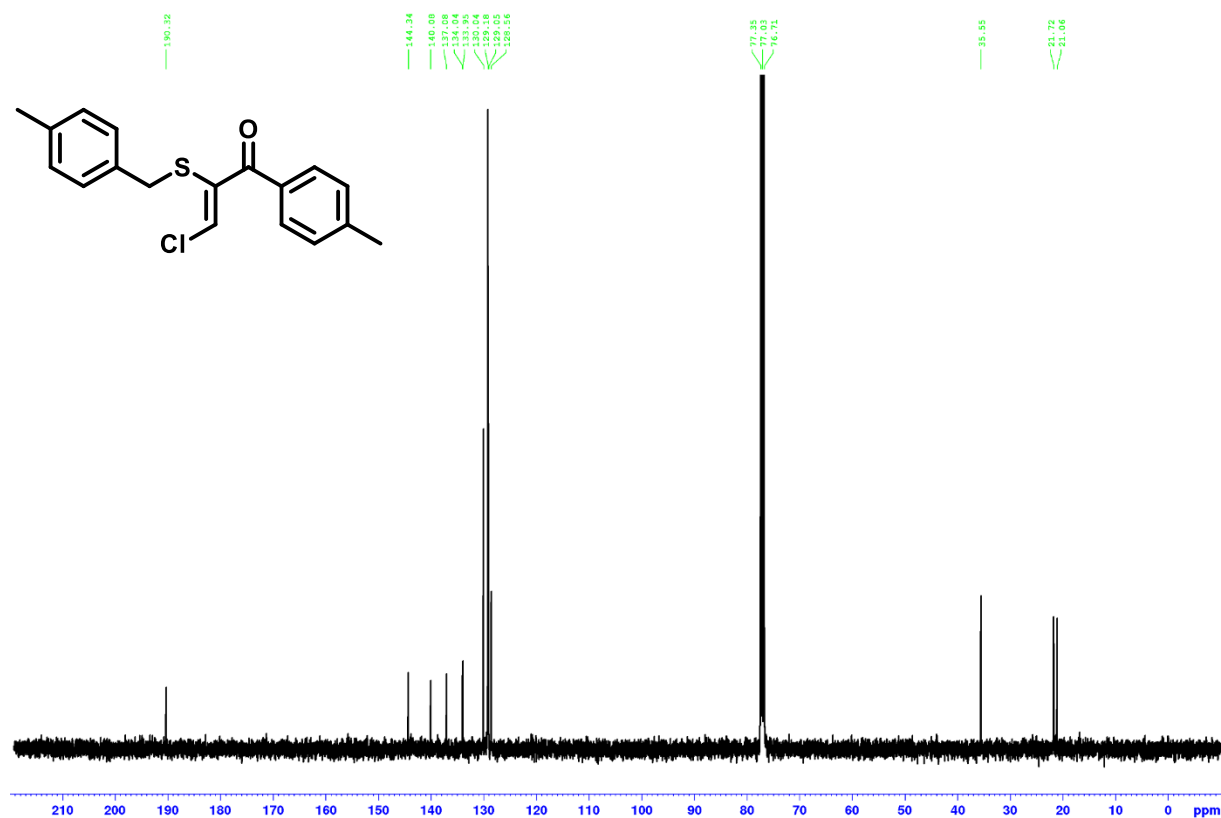


Figure S140: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4m**.

Chemical structure: Cc1ccc(cc1)C(=O)SCc2ccc(C)cc2

¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
7.716, 7.715, 7.723, 7.721, 7.727, 7.725, 7.735, 7.733, 7.746, 7.742, 7.737, 7.737	1.91, 2.11
6.444, 6.443, 6.441	0.97
3.950	2.00
2.414, 2.403, 2.395, 2.392	3.35, 3.37
1.586, 1.570, 1.564	
0.000, -0.002	

Cc1ccc(cc1)CSC(=C(Cl)C(=O)c2ccc(C)cc2)c3ccc(C)cc3

Chemical shifts (ppm): 7.837, 7.816, 7.807, 7.437, 7.395, 7.382, 7.365, 7.178, 7.162, 7.109, 7.097, 6.991, 6.652, 6.644, 3.947, 3.851, 2.486, 2.404, 2.384, 2.296, 2.269, 1.572, 0.000.

Integration values: 0.32, 0.10, 0.82, 1.00, 1.53, 1.41, 1.00, 0.48, 0.12, 1.00, 0.29, 4.10, 0.12.

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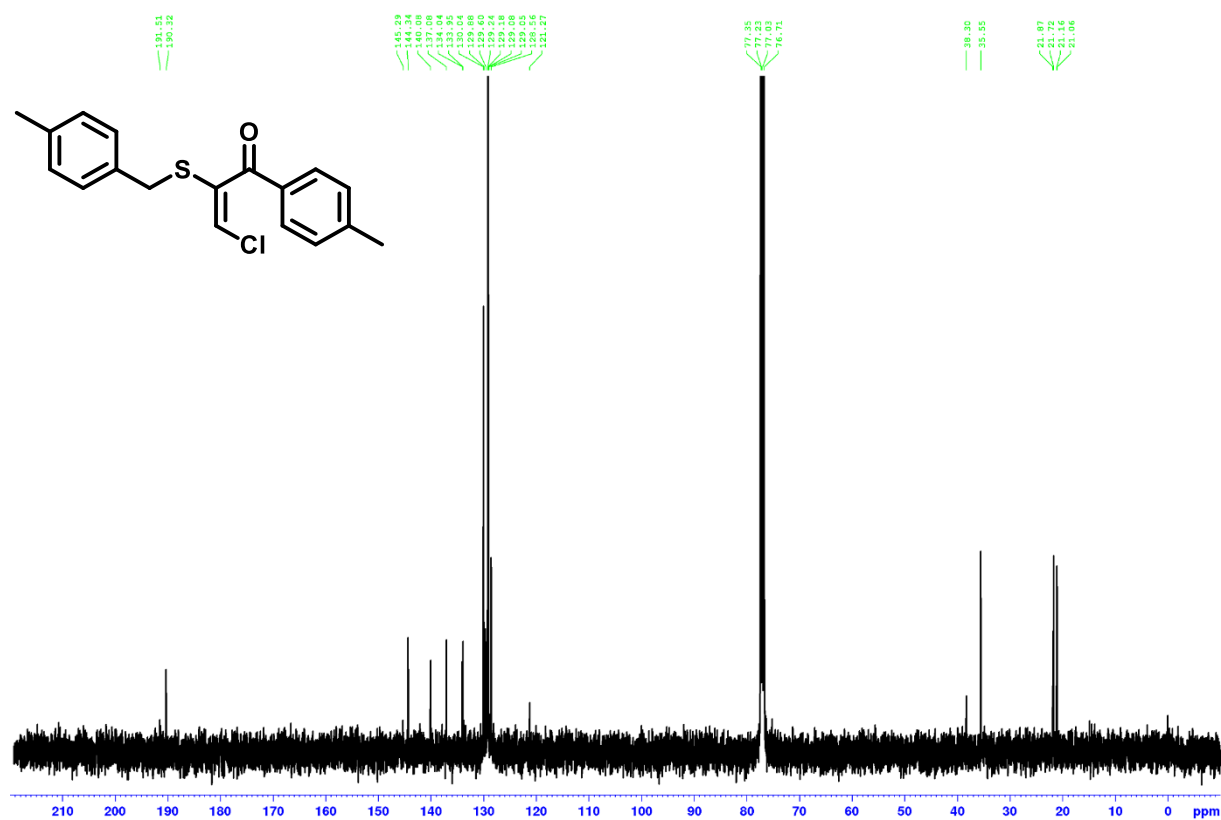


Figure S143: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **E-4m**.

(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

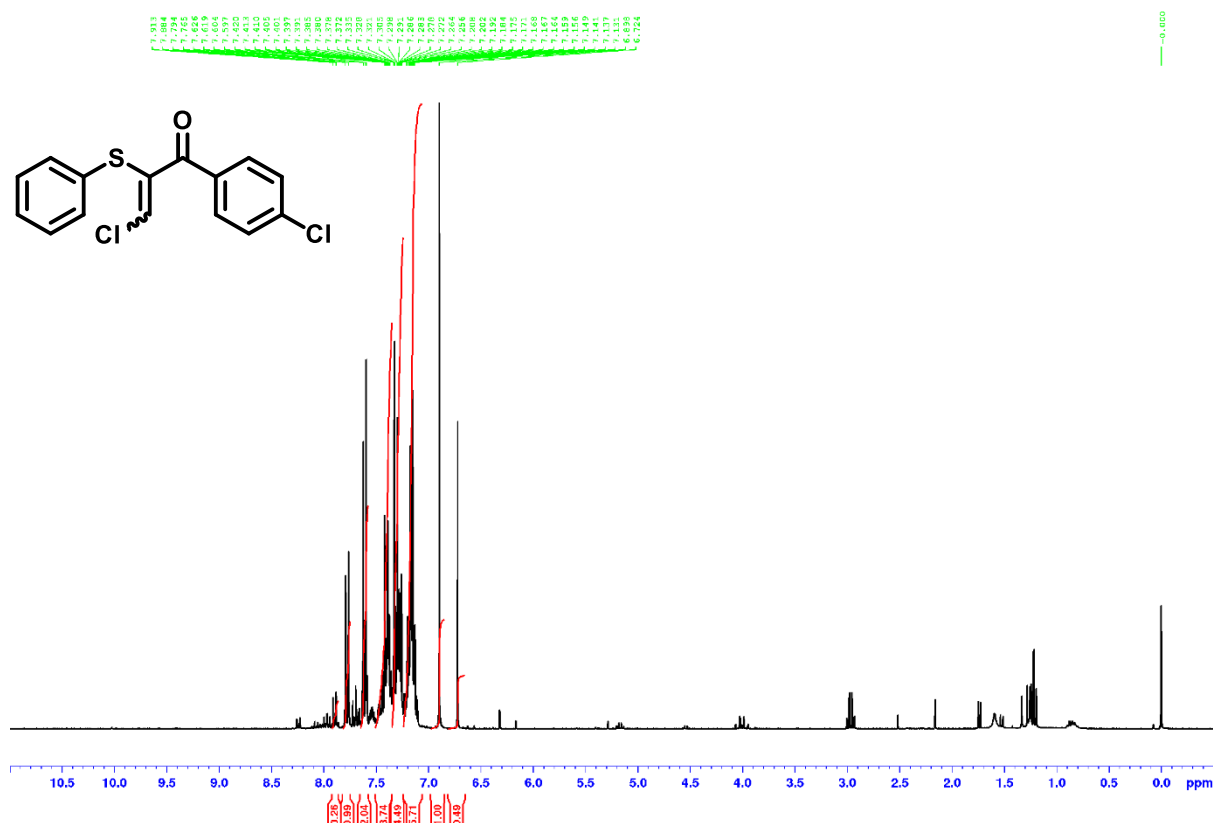


Figure S144: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4n** and **E-4n** which contains minor impurities.

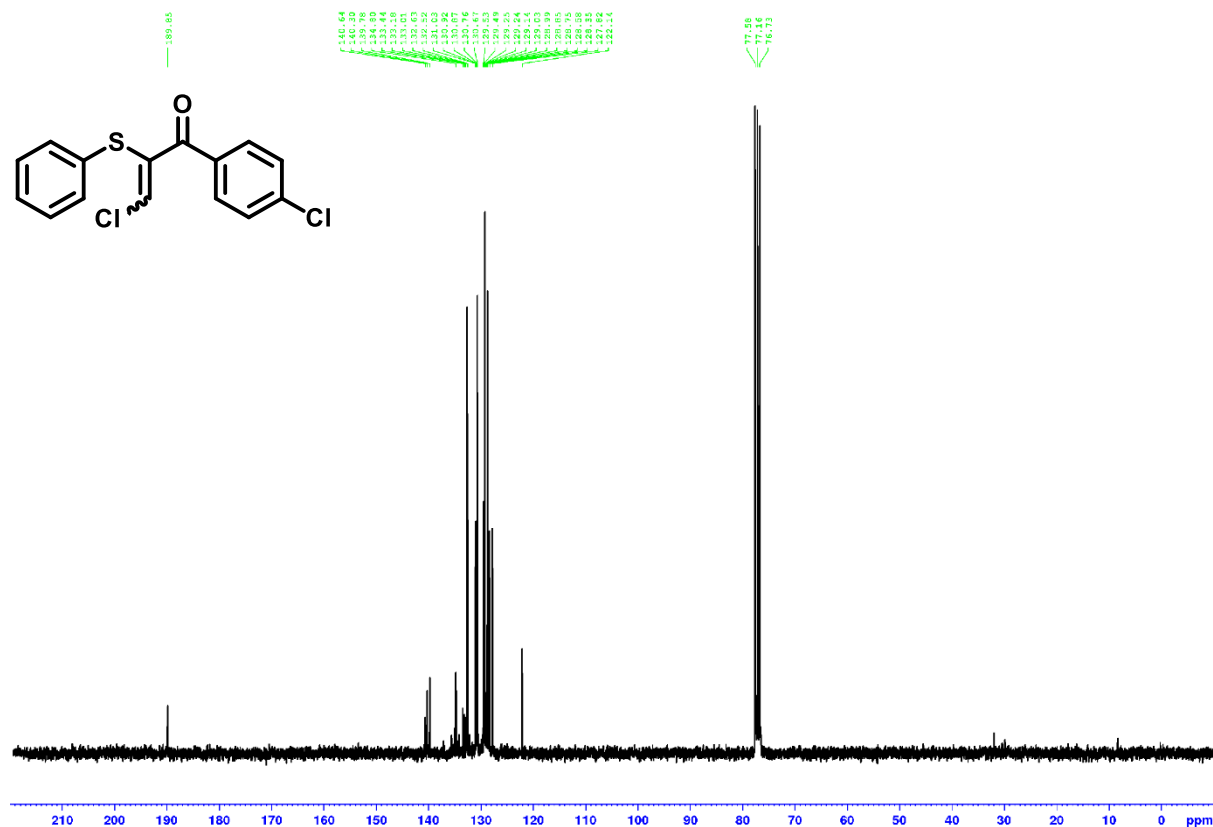


Figure S145: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4n** and **E-4n** which contains minor impurities.

Chemical structure: O=C(C=C(SCc1ccccc1)C(=O)c2ccc(Cl)cc2)

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.5-7.8 ppm) and a singlet at 4.0 ppm. The x-axis represents chemical shift in ppm, ranging from 10.5 to 0.0.

Peak list (ppm): 7.826, 7.815, 7.805, 7.795, 7.785, 7.775, 7.765, 7.755, 7.745, 7.735, 7.725, 7.715, 7.705, 7.695, 7.685, 7.675, 7.665, 7.655, 7.645, 7.635, 7.625, 7.615, 7.605, 7.595, 7.585, 7.575, 7.565, 7.555, 7.545, 7.535, 7.525, 7.515, 7.505, 7.495, 7.485, 7.475, 7.465, 7.455, 7.445, 7.435, 7.425, 7.415, 7.405, 7.395, 7.385, 7.375, 7.365, 7.355, 7.345, 7.335, 7.325, 7.315, 7.305, 7.295, 7.285, 7.275, 7.265, 7.255, 7.245, 7.235, 7.225, 7.215, 7.205, 7.195, 7.185, 7.175, 7.165, 7.155, 7.145, 7.135, 7.125, 7.115, 7.105, 7.095, 7.085, 7.075, 7.065, 7.055, 7.045, 7.035, 7.025, 7.015, 7.005, 6.995, 6.985, 6.975, 6.965, 6.955, 6.945, 6.935, 6.925, 6.915, 6.905, 6.895, 6.885, 6.875, 6.865, 6.855, 6.845, 6.835, 6.825, 6.815, 6.805, 6.795, 6.785, 6.775, 6.765, 6.755, 6.745, 6.735, 6.725, 6.715, 6.705, 6.695, 6.685, 6.675, 6.665, 6.655, 6.645, 6.635, 6.625, 6.615, 6.605, 6.595, 6.585, 6.575, 6.565, 6.555, 6.545, 6.535, 6.525, 6.515, 6.505, 6.495, 6.485, 6.475, 6.465, 6.455, 6.445, 6.435, 6.425, 6.415, 6.405, 6.395, 6.385, 6.375, 6.365, 6.355, 6.345, 6.335, 6.325, 6.315, 6.305, 6.295, 6.285, 6.275, 6.265, 6.255, 6.245, 6.235, 6.225, 6.215, 6.205, 6.195, 6.185, 6.175, 6.165, 6.155, 6.145, 6.135, 6.125, 6.115, 6.105, 6.095, 6.085, 6.075, 6.065, 6.055, 6.045, 6.035, 6.025, 6.015, 6.005, 5.995, 5.985, 5.975, 5.965, 5.955, 5.945, 5.935, 5.925, 5.915, 5.905, 5.895, 5.885, 5.875, 5.865, 5.855, 5.845, 5.835, 5.825, 5.815, 5.805, 5.795, 5.785, 5.775, 5.765, 5.755, 5.745, 5.735, 5.725, 5.715, 5.705, 5.695, 5.685, 5.675, 5.665, 5.655, 5.645, 5.635, 5.625, 5.615, 5.605, 5.595, 5.585, 5.575, 5.565, 5.555, 5.545, 5.535, 5.525, 5.515, 5.505, 5.495, 5.485, 5.475, 5.465, 5.455, 5.445, 5.435, 5.425, 5.415, 5.405, 5.395, 5.385, 5.375, 5.365, 5.355, 5.345, 5.335, 5.325, 5.315, 5.305, 5.295, 5.285, 5.275, 5.265, 5.255, 5.245, 5.235, 5.225, 5.215, 5.205, 5.195, 5.185, 5.175, 5.165, 5.155, 5.145, 5.135, 5.125, 5.115, 5.105, 5.095, 5.085, 5.075, 5.065, 5.055, 5.045, 5.035, 5.025, 5.015, 5.005, 4.995, 4.985, 4.975, 4.965, 4.955, 4.945, 4.935, 4.925, 4.915, 4.905, 4.895, 4.885, 4.875, 4.865, 4.855, 4.845, 4.835, 4.825, 4.815, 4.805, 4.795, 4.785, 4.775, 4.765, 4.755, 4.745, 4.735, 4.725, 4.715, 4.705, 4.695, 4.685, 4.675, 4.665, 4.655, 4.645, 4.635, 4.625, 4.615, 4.605, 4.595, 4.585, 4.575, 4.565, 4.555, 4.545, 4.535, 4.525, 4.515, 4.505, 4.495, 4.485, 4.475, 4.465, 4.455, 4.445, 4.435, 4.425, 4.415, 4.405, 4.395, 4.385, 4.375, 4.365, 4.355, 4.345, 4.335, 4.325, 4.315, 4.305, 4.295, 4.285, 4.275, 4.265, 4.255, 4.245, 4.235, 4.225, 4.215, 4.205, 4.195, 4.185, 4.175, 4.165, 4.155, 4.145, 4.135, 4.125, 4.115, 4.105, 4.095, 4.085, 4.075, 4.065, 4.055, 4.045, 4.035, 4.025, 4.015, 4.005, 3.995, 3.985, 3.975, 3.965, 3.955, 3.945, 3.935, 3.925, 3.915, 3.905, 3.895, 3.885, 3.875, 3.865, 3.855, 3.845, 3.835, 3.825, 3.815, 3.805, 3.795, 3.785, 3.775, 3.765, 3.755, 3.745, 3.735, 3.725, 3.715, 3.705, 3.695, 3.685, 3.675, 3.665, 3.655, 3.645, 3.635, 3.625, 3.615, 3.605, 3.595, 3.585, 3.575, 3.565, 3.555, 3.545, 3.535, 3.525, 3.515, 3.505, 3.495, 3.485, 3.475, 3.465, 3.455, 3.445, 3.435, 3.425, 3.415, 3.405, 3.395, 3.385, 3.375, 3.365, 3.355, 3.345, 3.335, 3.325, 3.315, 3.305, 3.295, 3.285, 3.275, 3.265, 3.255, 3.245, 3.235, 3.225, 3.215, 3.205, 3.195, 3.185, 3.175, 3.165, 3.155, 3.145, 3.135, 3.125, 3.115, 3.105, 3.095, 3.085, 3.075, 3.065, 3.055, 3.045, 3.035, 3.025, 3.015, 3.005, 2.995, 2.985, 2.975, 2.965, 2.955, 2.945, 2.935, 2.925, 2.915, 2.905, 2.895, 2.885, 2.875, 2.865, 2.855, 2.845, 2.835, 2.825, 2.815, 2.805, 2.795, 2.785, 2.775, 2.765, 2.755, 2.745, 2.735, 2.725, 2.715, 2.705, 2.695, 2.685, 2.675, 2.665, 2.655, 2.645, 2.635, 2.625, 2.615, 2.605, 2.595, 2.585, 2.575, 2.565, 2.555, 2.545, 2.535, 2.525, 2.515, 2.505, 2.495, 2.485, 2.475, 2.465, 2.455, 2.445, 2.435, 2.425, 2.415, 2.405, 2.395, 2.385, 2.375, 2.365, 2.355, 2.345, 2.335, 2.325, 2.315, 2.305, 2.295, 2.285, 2.275, 2.265,

Chemical structure: O=C(C=C(SCc1ccccc1)C(=O)c2ccc(Cl)cc2)

¹³C NMR spectrum (CDCl₃) showing peaks (ppm):

- 189.38
- 138.65
- 138.74
- 137.00
- 136.92
- 135.12
- 135.05
- 132.05
- 132.00
- 130.44
- 129.31
- 129.19
- 129.12
- 128.72
- 128.59
- 128.50
- 128.40
- 127.58
- 127.47
- 127.52
- 77.35
- 77.24
- 77.04
- 76.72
- 38.60
- 35.74
- 0.01

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Chemical structure: CCCCSC(=C(Cl)C(=O)c1ccc(Cl)cc1)

¹H NMR spectrum (400 MHz, CDCl₃) showing peaks from 0.0 to 10.0 ppm. Integration values are provided below the baseline.

Chemical Shift (ppm)	Integration
0.88	3.00
1.25	4.00
1.55	1.00
1.65	0.76
1.75	1.00
2.65	3.00
6.65	1.00
6.75	0.76
7.55	4.17
7.75	4.15

CCCCSC(=C(Cl)C(=O)c1ccc(Cl)cc1)C(F)(F)F

Chemical structure: CCCCSC(=C(Cl)C(=O)c1ccc(Cl)cc1)C(F)(F)F

¹³C NMR peaks (ppm):

- 193.22
- 165.24
- 143.10
- 132.62
- 131.22
- 129.59
- 128.59
- 127.46
- 114.50
- 77.58
- 77.16
- 76.73
- 59.94
- 55.80
- 37.99
- 31.99
- 22.99

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

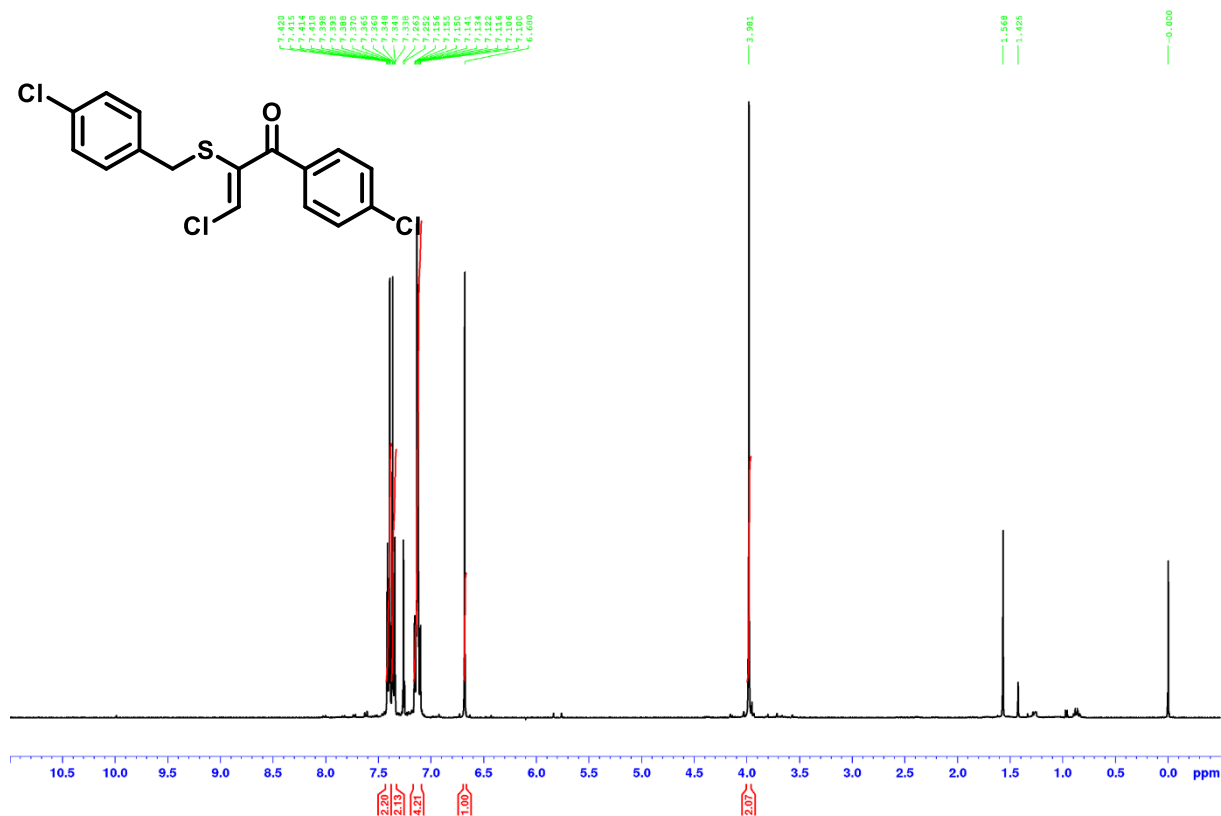


Figure S150: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4q**.

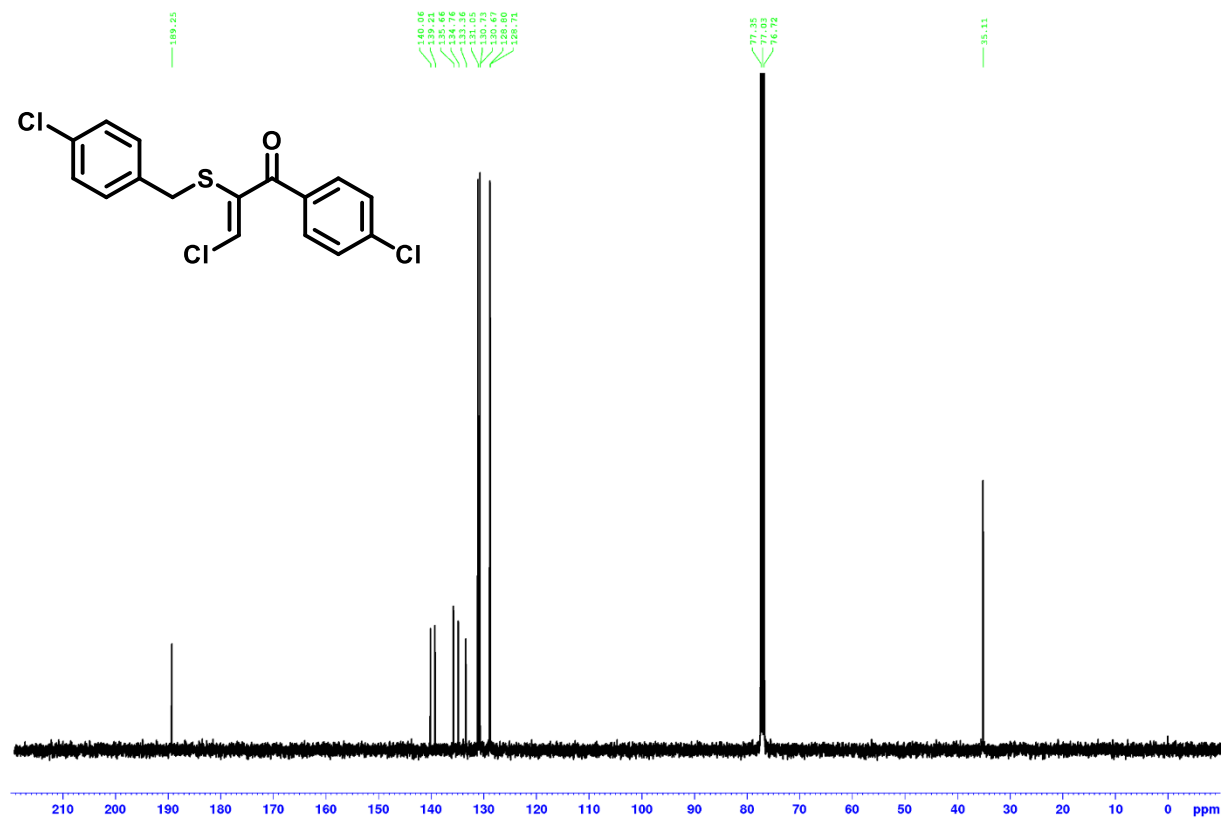


Figure S151: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4q**.

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

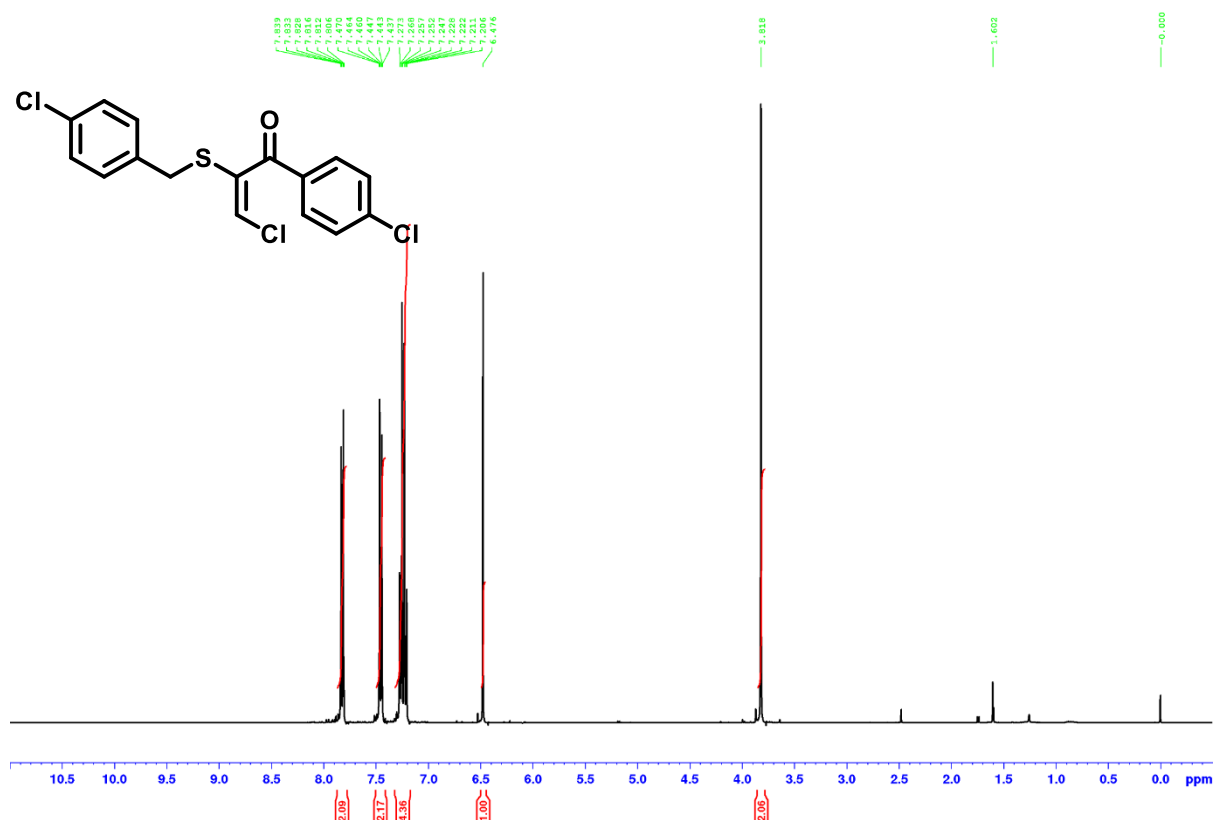


Figure S152: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-4q**.

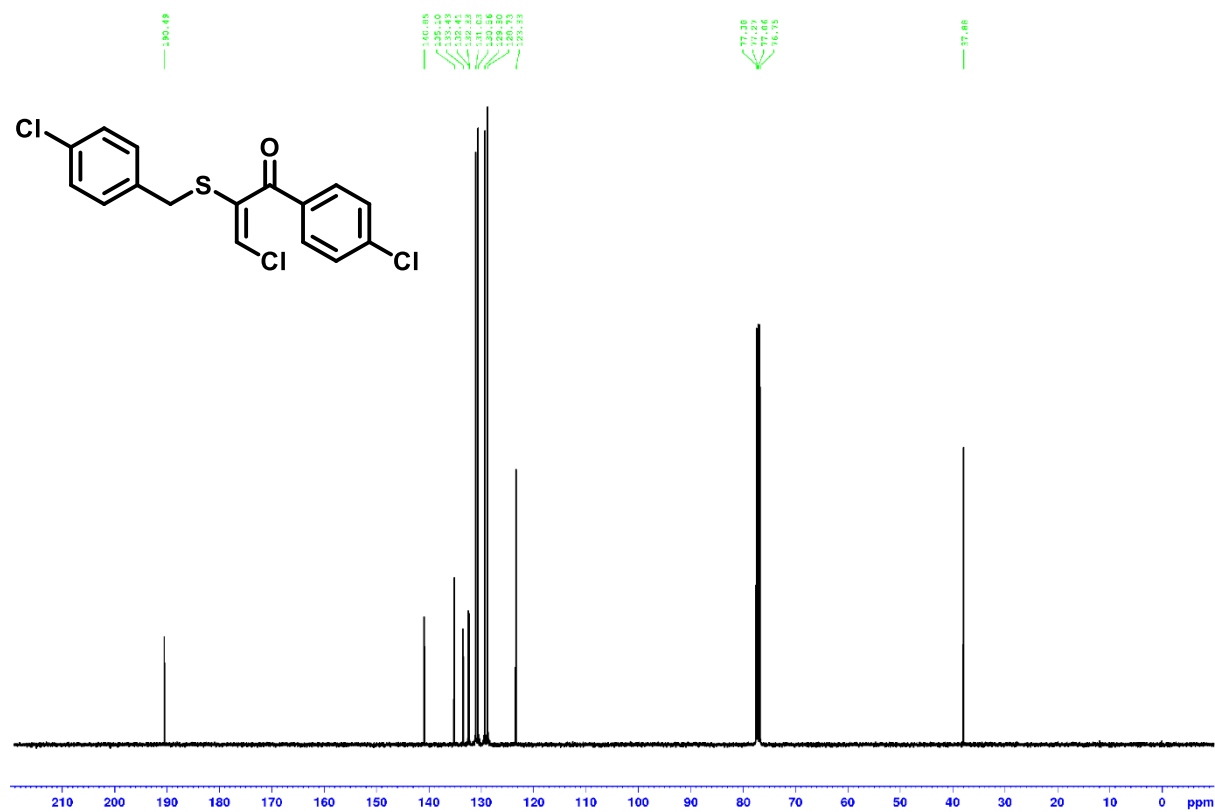


Figure S153: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **E-4q**.

(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

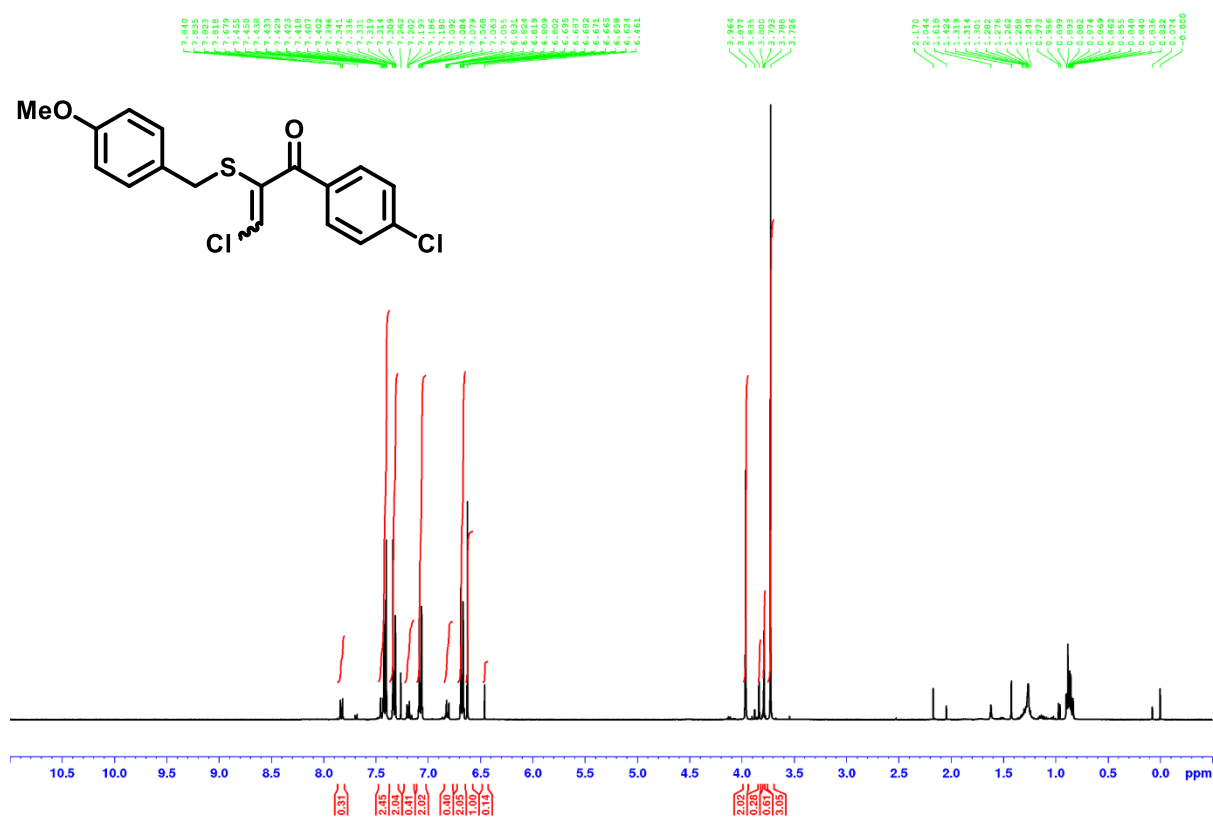


Figure S154: ^1H NMR (400 MHz, CDCl_3) spectrum of Z-4r and E-4r.

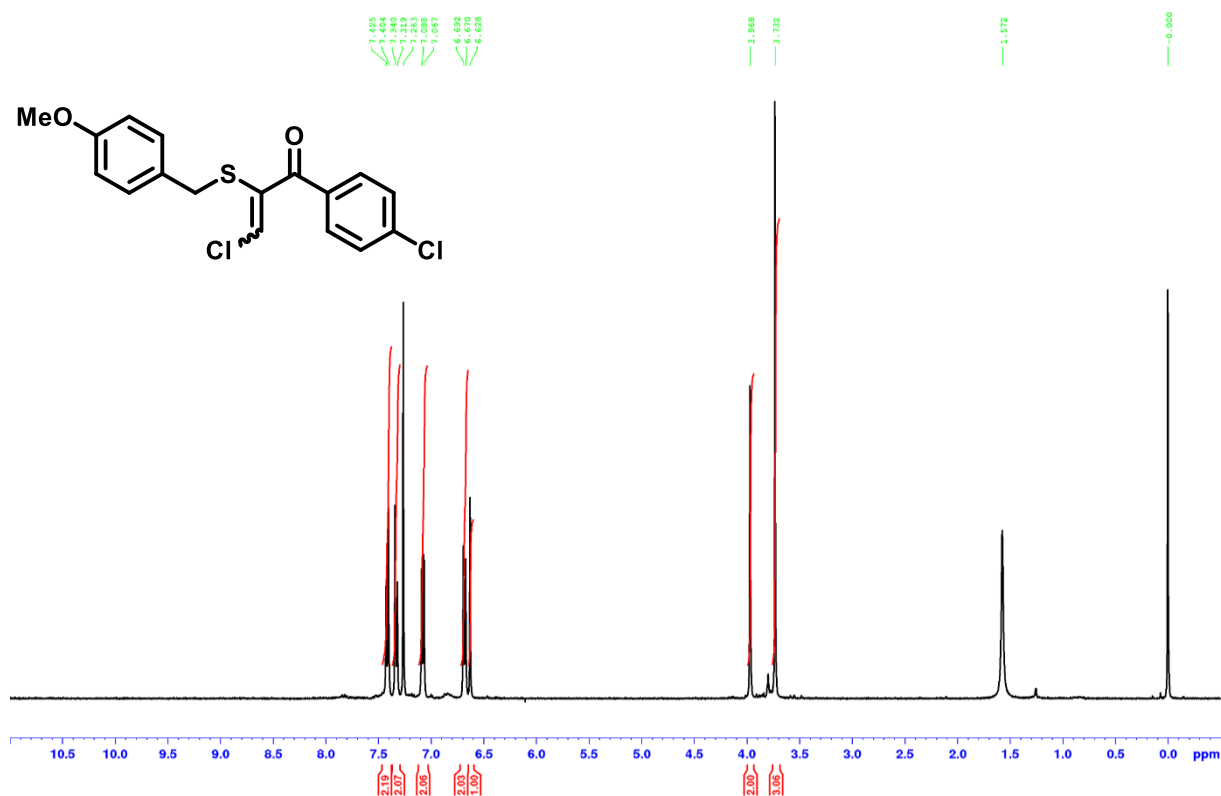


Figure S155: ^1H NMR (400 MHz, CDCl_3) spectrum of Z-4r and E-4r after storage at room temperature for 40 months.

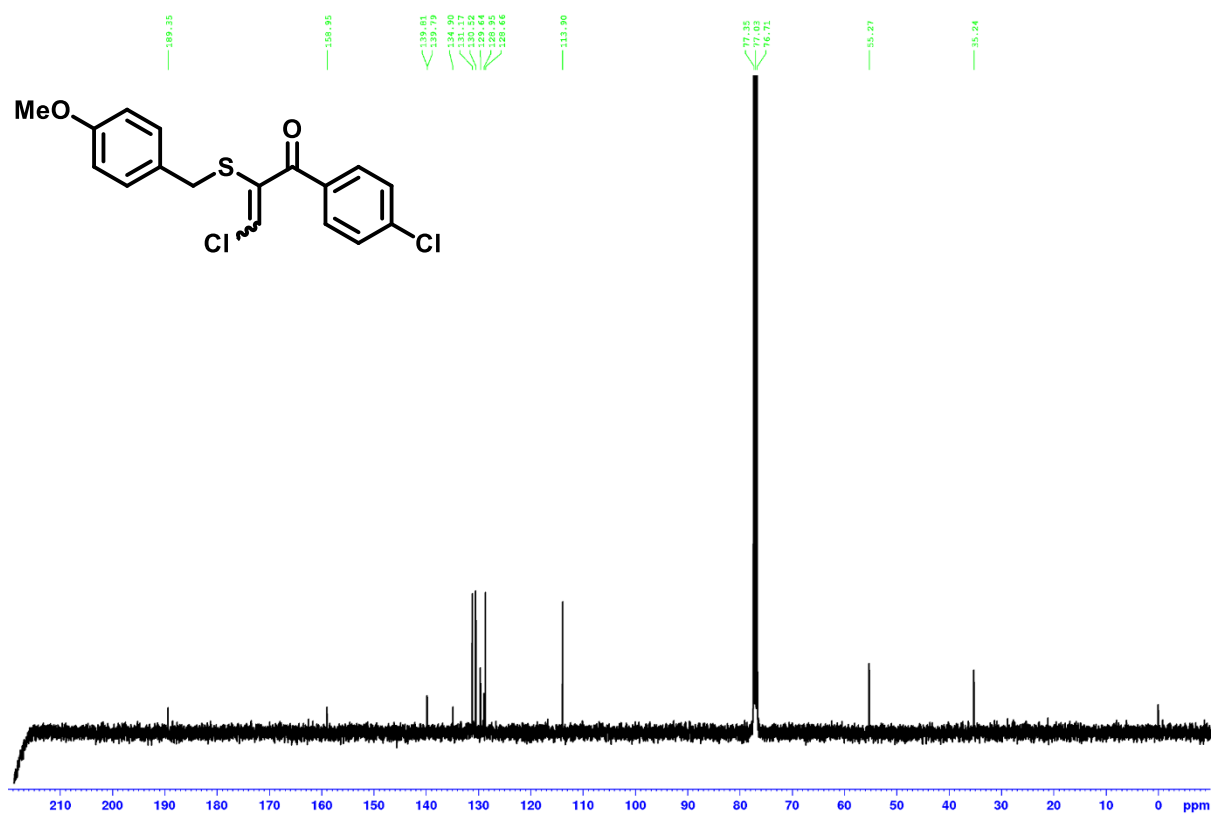


Figure S156: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4r** and **E-4r**.

(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

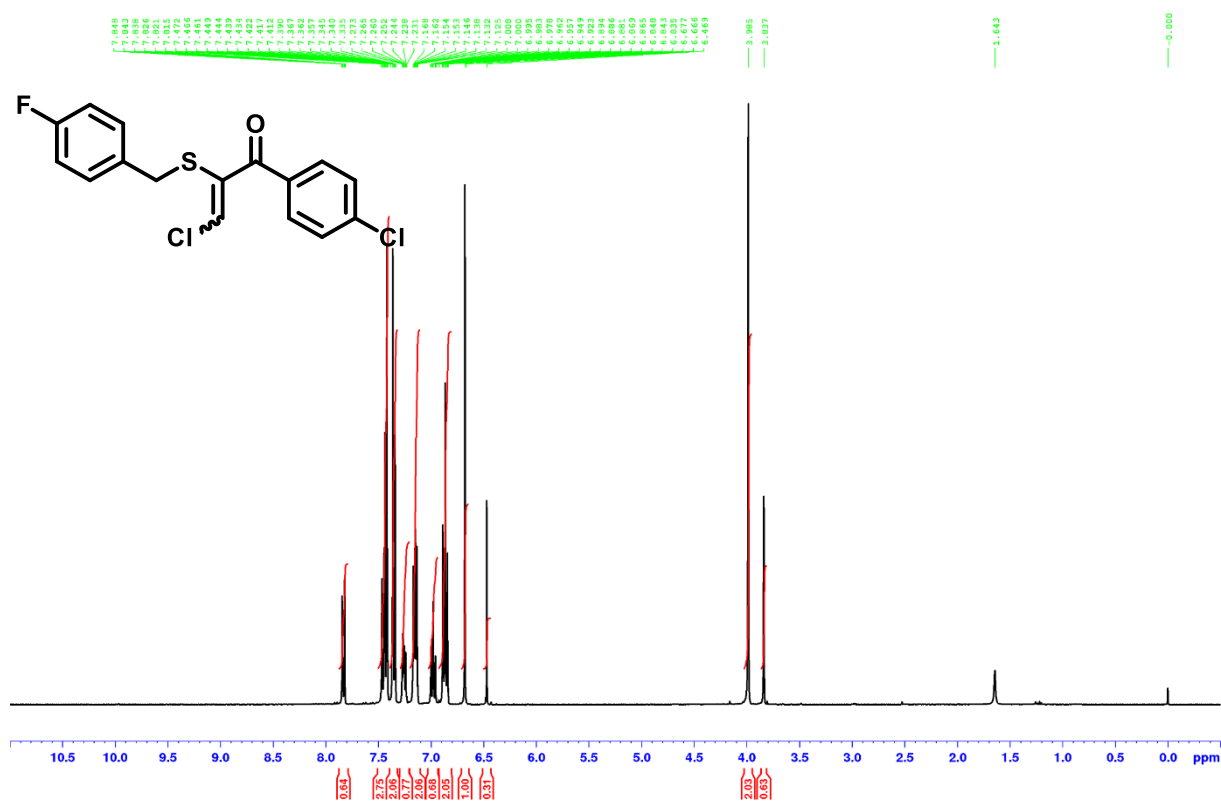


Figure S157: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4s and E-4s.

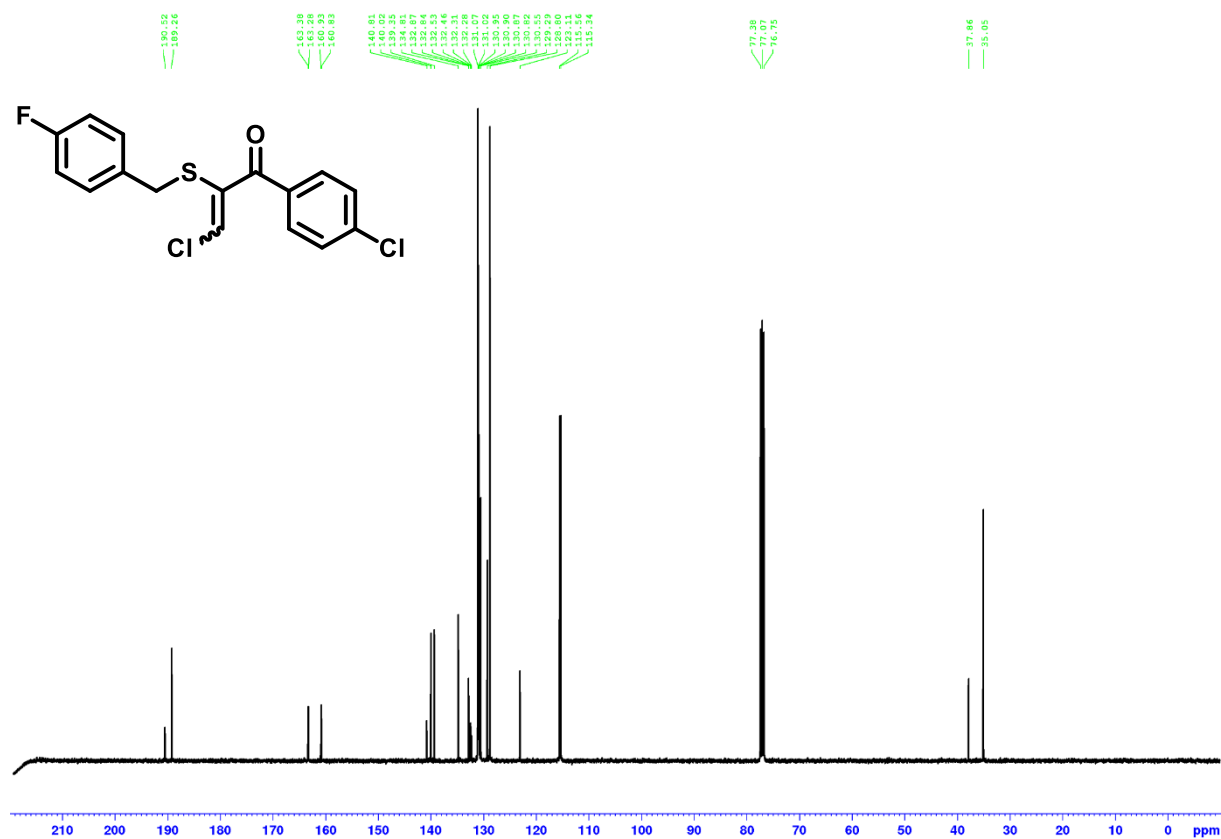


Figure S158: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of Z-4s and E-4s.

Chemical structure: CC1=CC=C(C=C1)SC(=C(Cl)C(=O)C2=CC=C(C=C2)Cl)

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The spectrum includes aromatic signals (6.5-7.5 ppm), a methine proton (3.973 ppm), a methyl group (2.466 ppm), and a solvent peak (1.578 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.403	0.96
7.399	2.00
7.382	2.00
7.371	2.17
7.356	2.00
7.350	2.17
7.305	2.00
7.286	2.00
7.061	1.00
6.955	1.00
6.623	1.00
3.973	2.05
2.466	3.21
1.578	2.05
-0.009	-

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

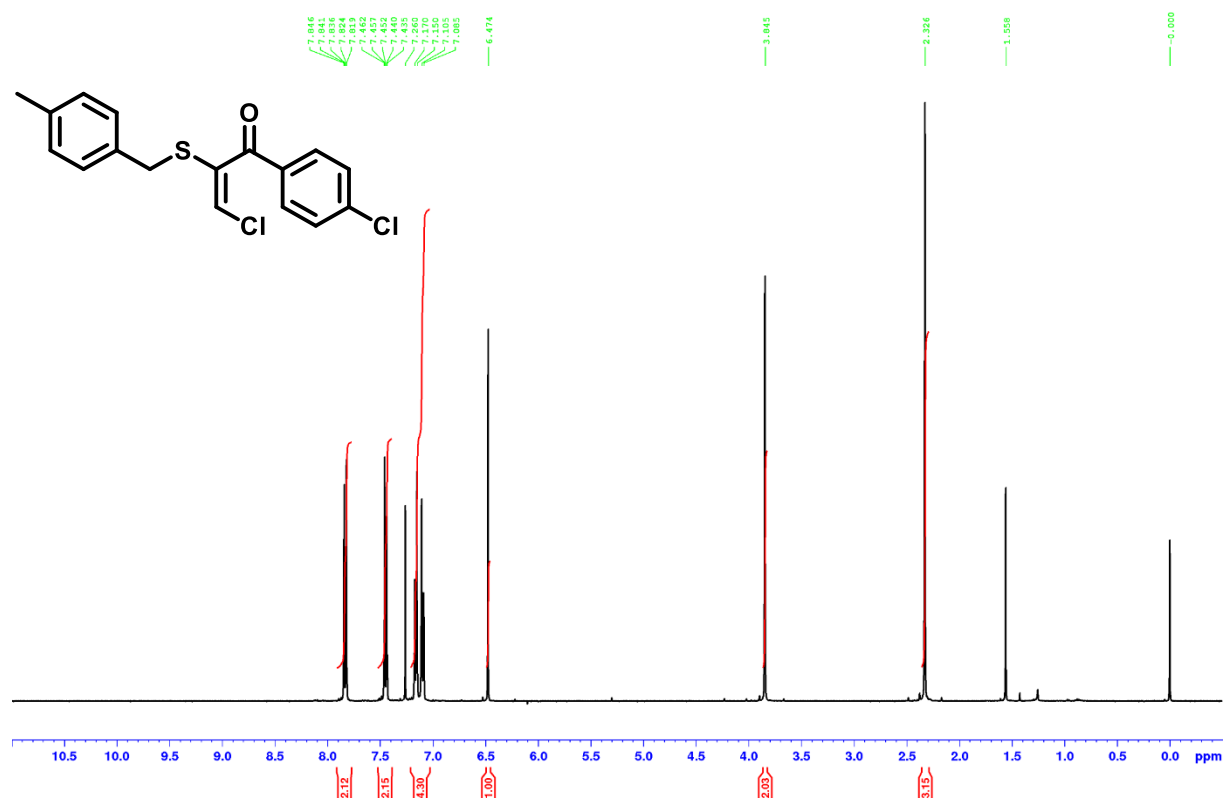


Figure S161: ¹H NMR (400 MHz, CDCl₃) spectrum of E-4t.

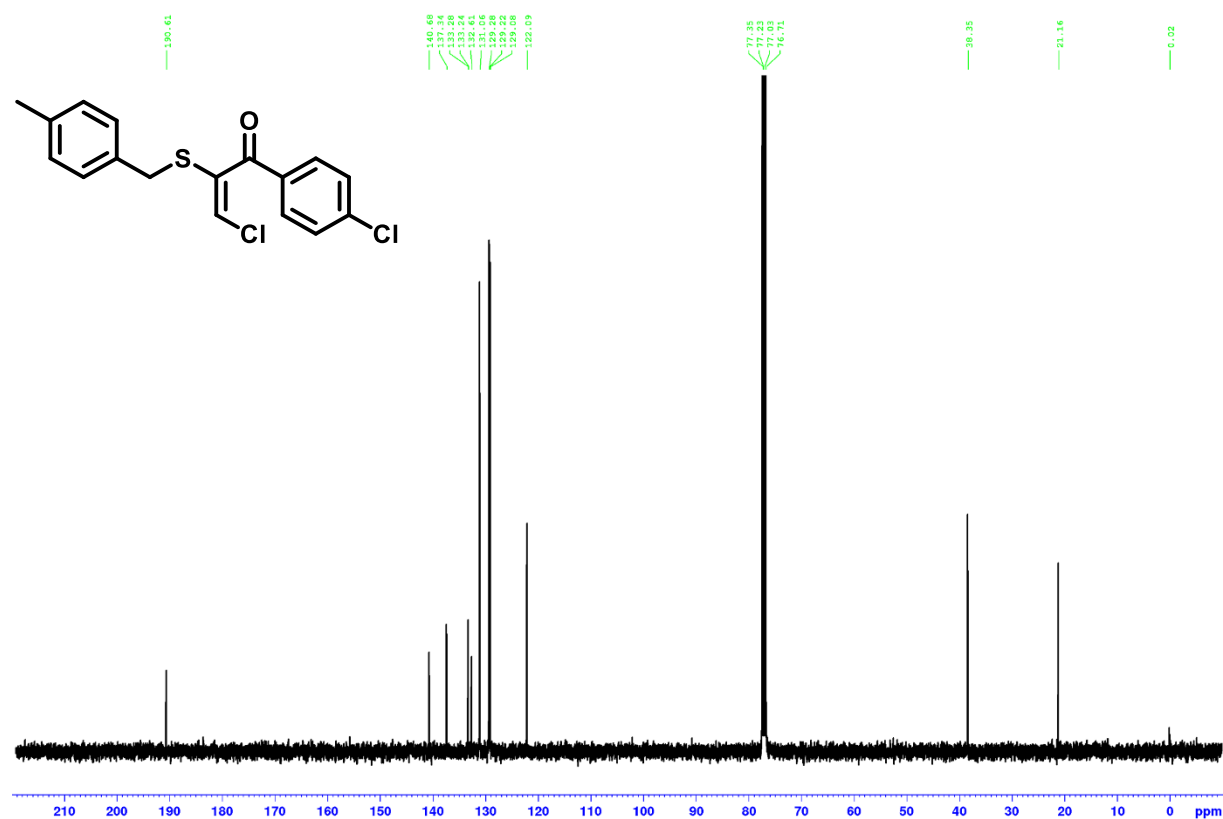
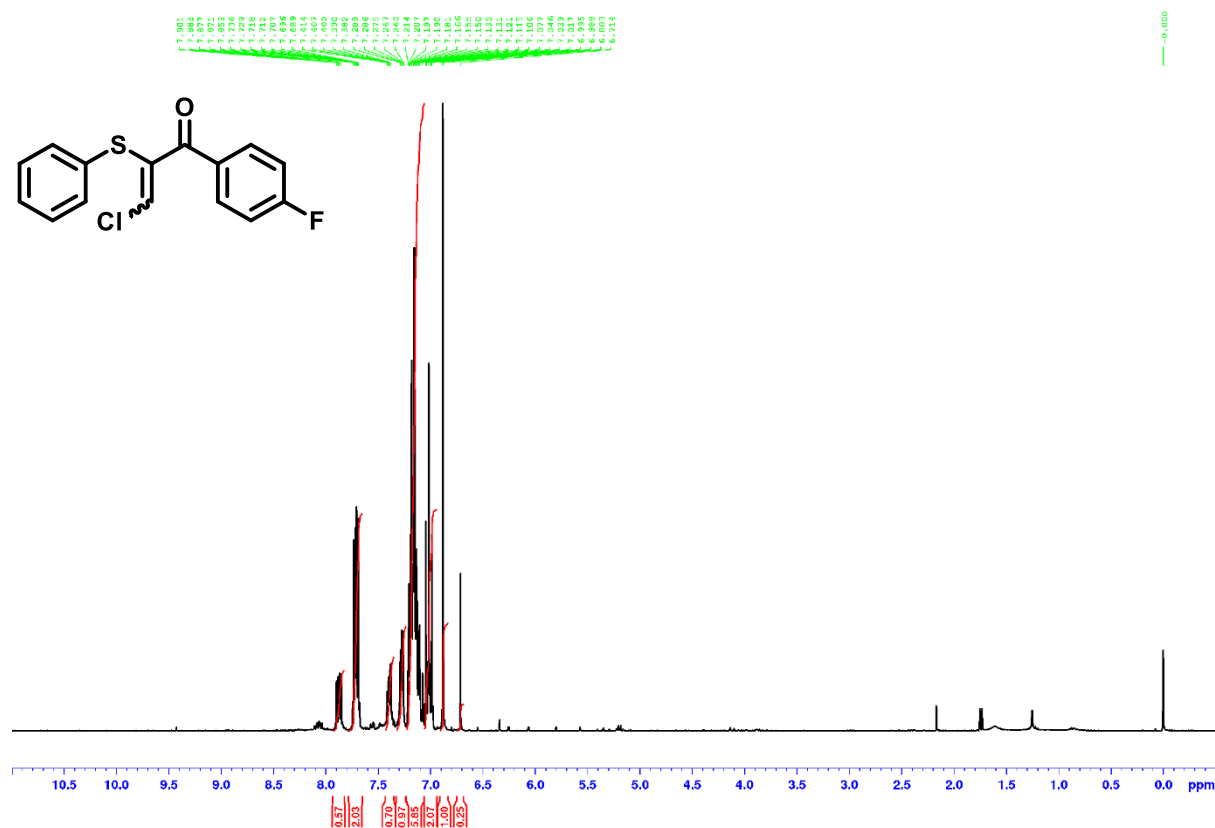


Figure S162: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of E-4t.

(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



(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

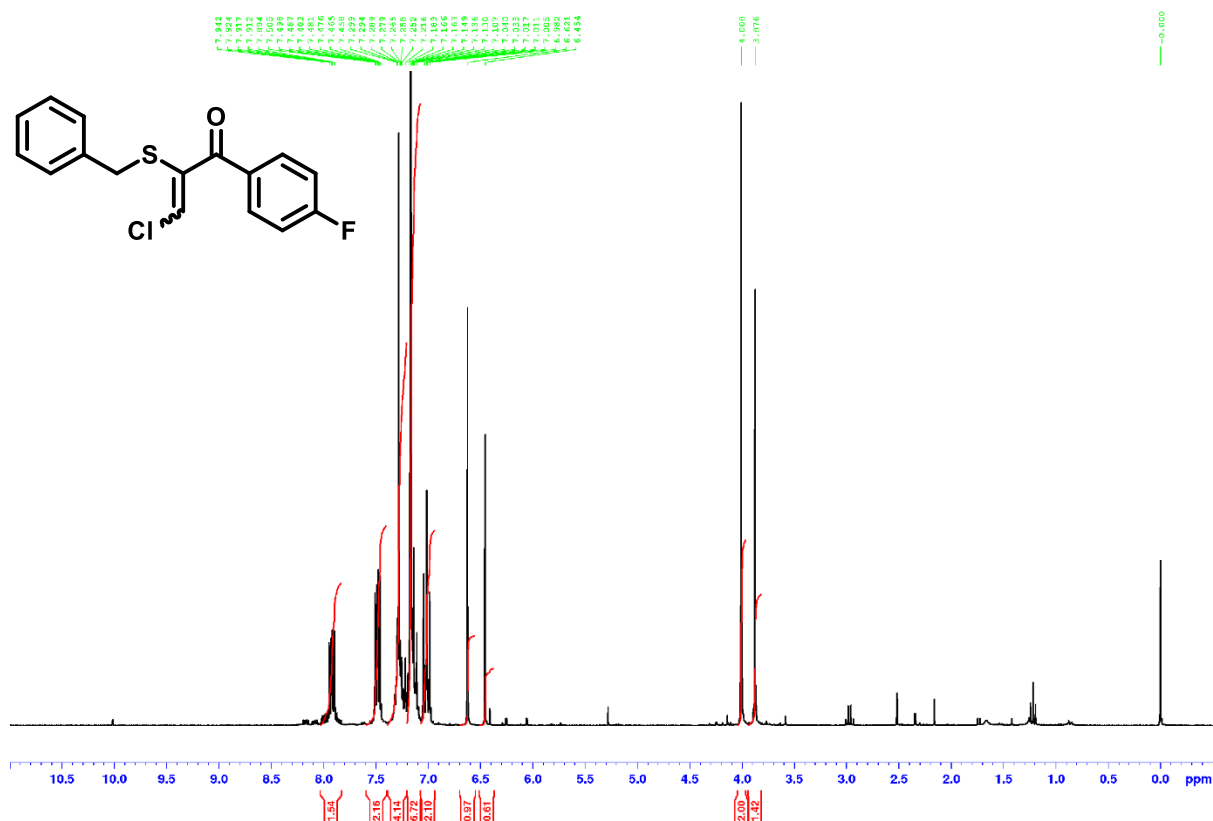


Figure S165: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4v** and **E-4v**.

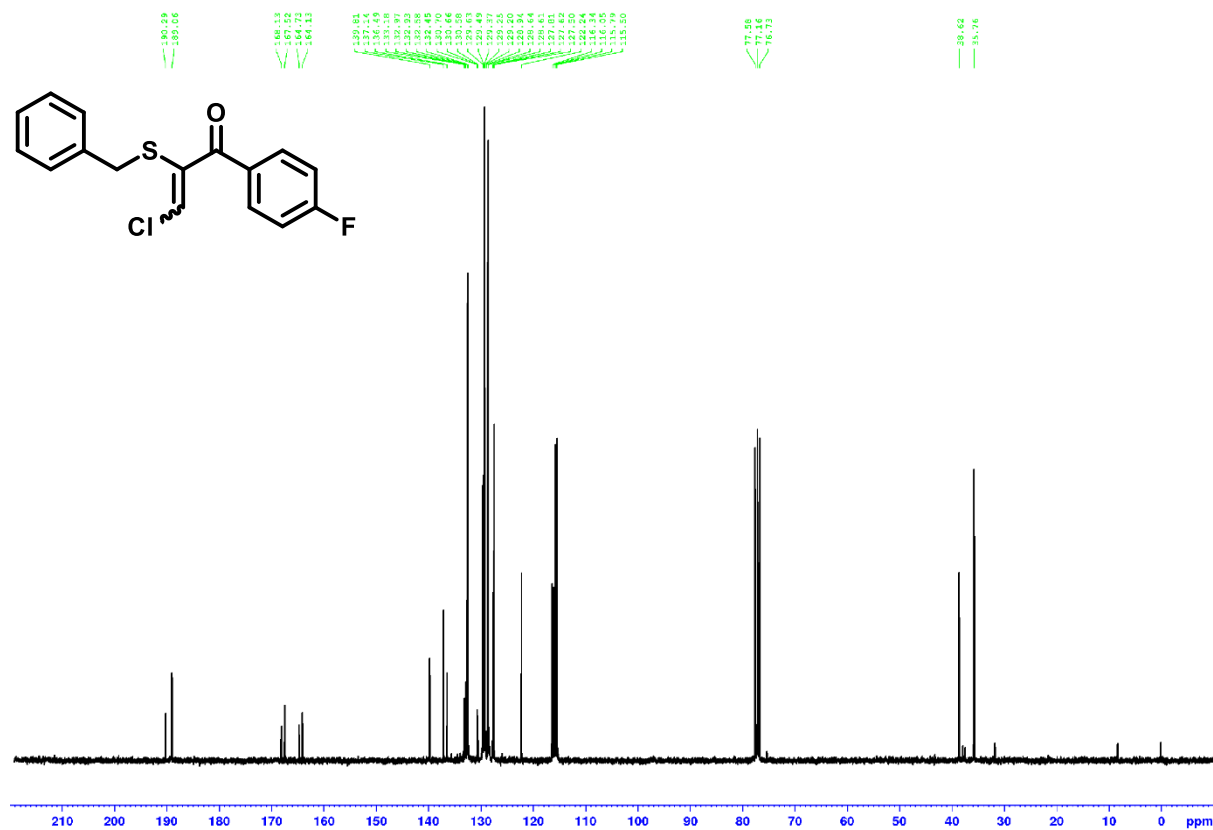
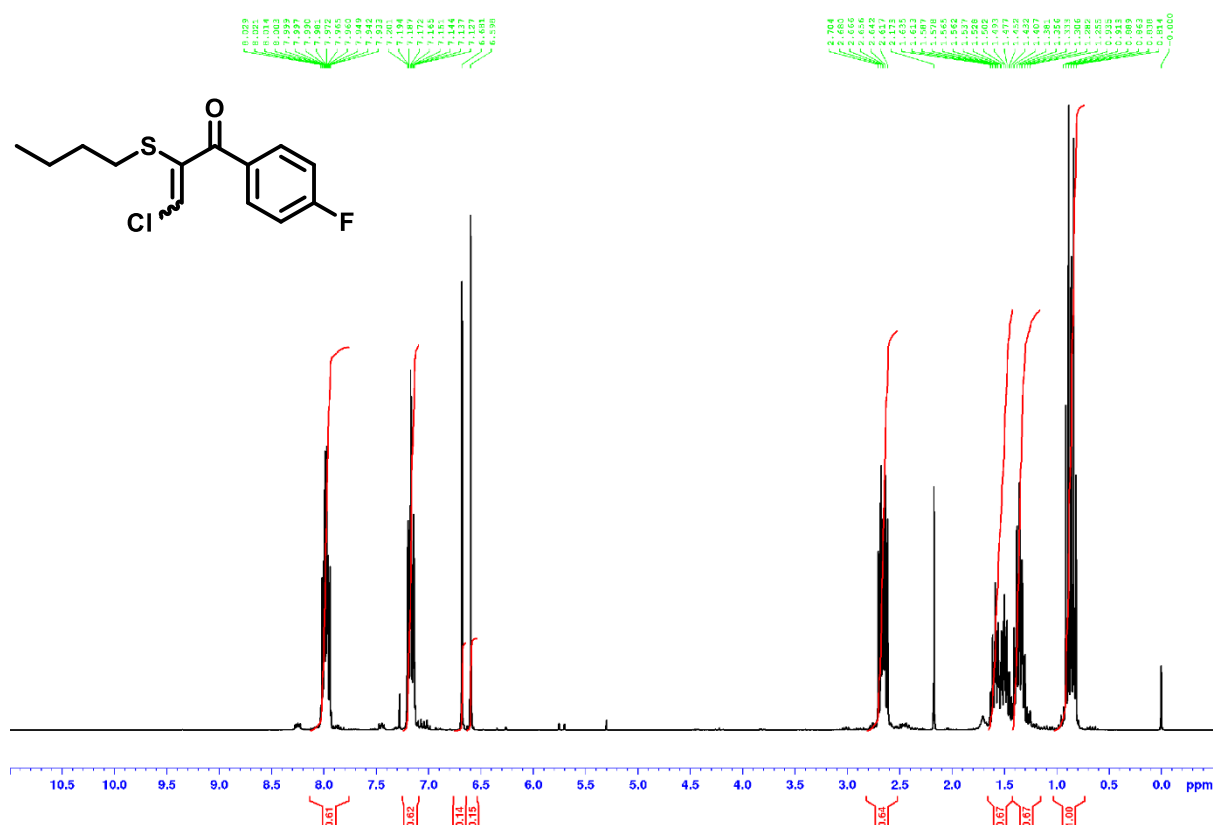


Figure S166: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4v** and **E-4v**.

(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



(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

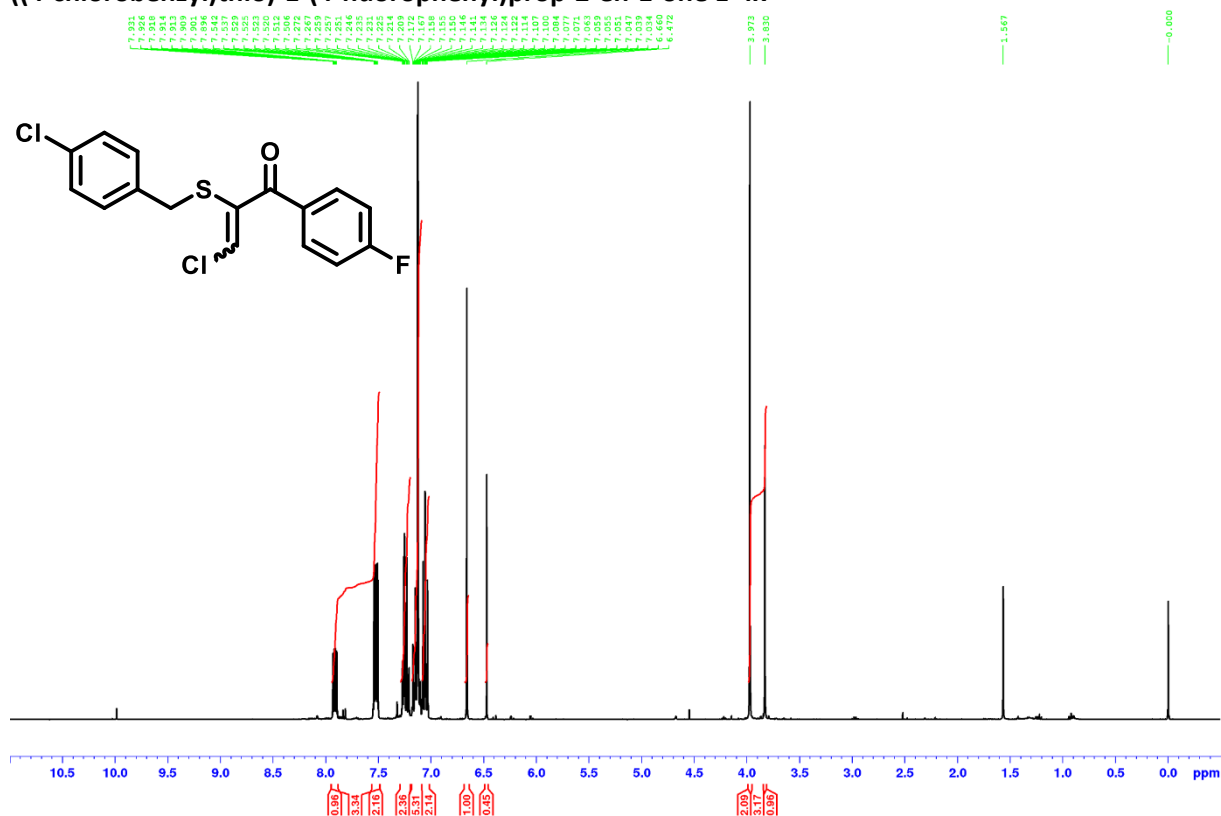


Figure S169: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4x** and **E-4x**.

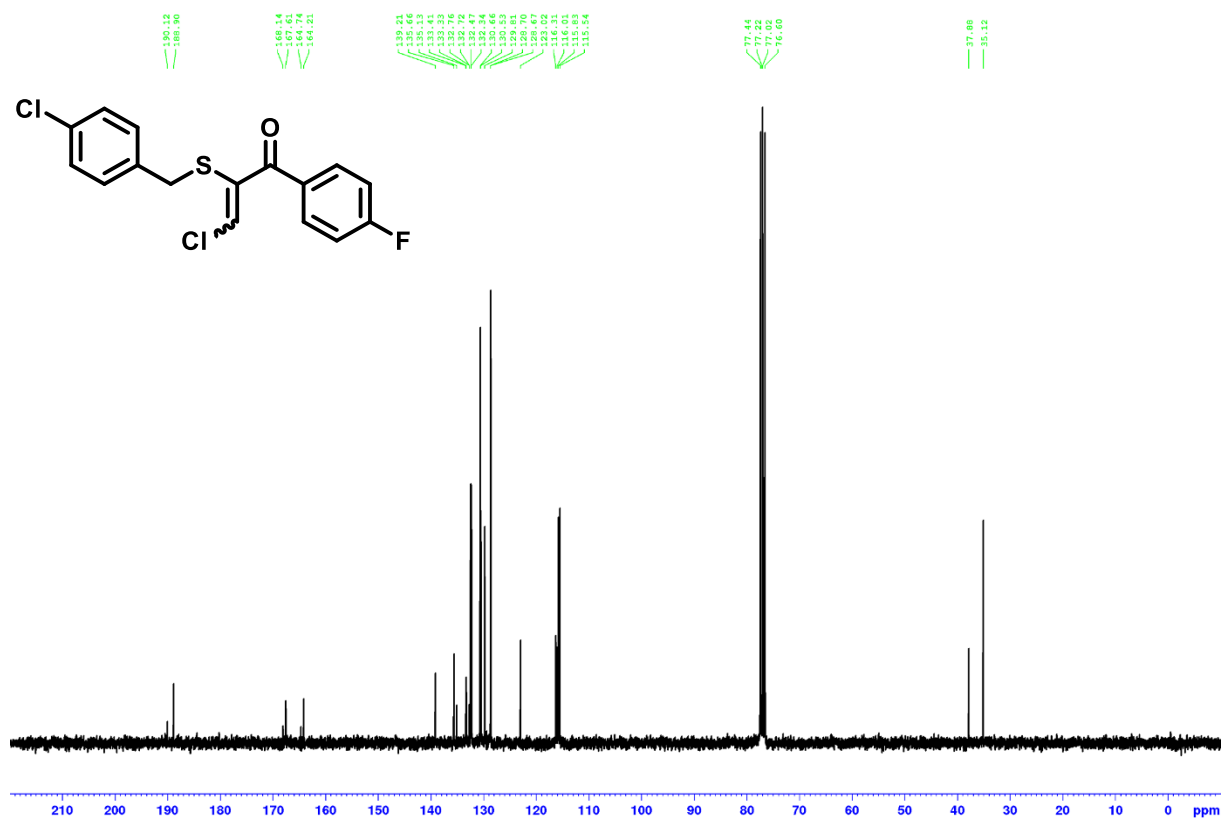


Figure S170: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4x** and **E-4x**.

(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

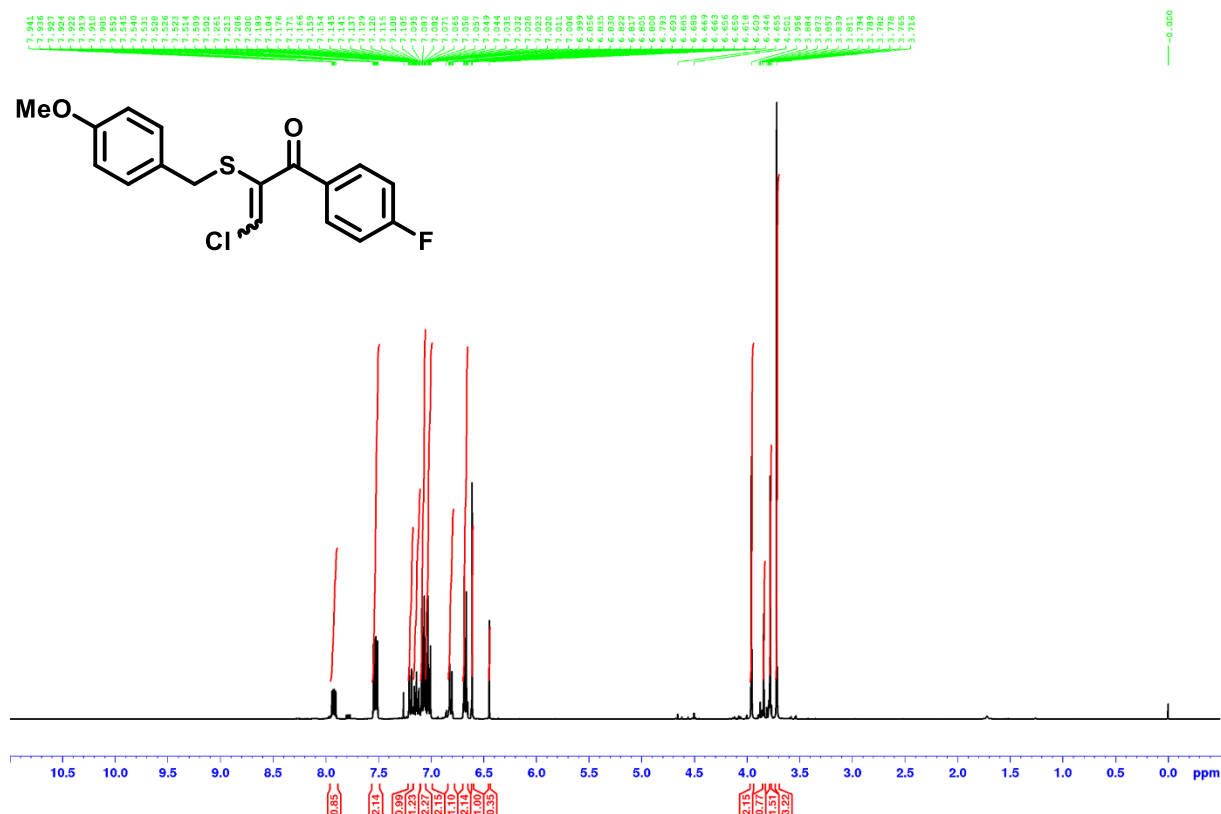


Figure S171: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4y and E-4y.

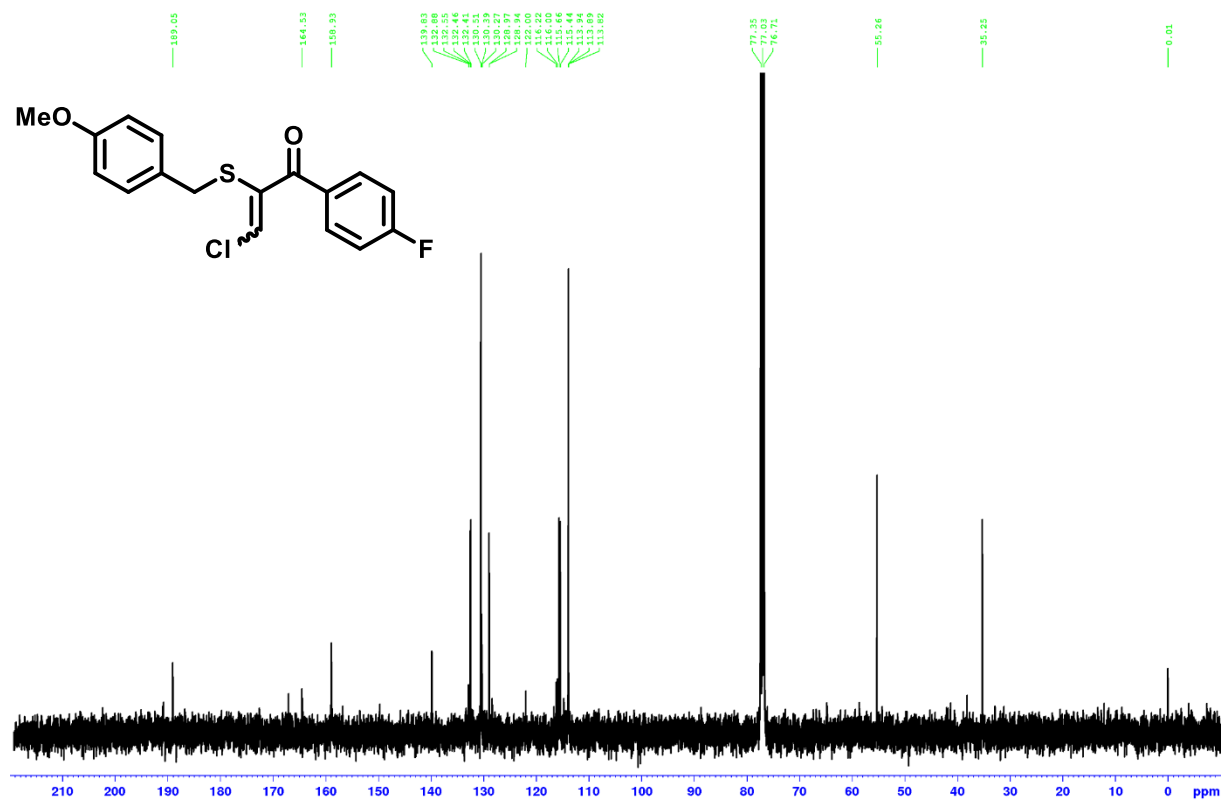


Figure S172: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of Z-4y and E-4y.

Fc1ccc(cc1)C(=O)S(Cc2ccc(F)cc2)C(=O)c3ccccc3

Chemical structure: 4-(4-chlorobenzyl)-4-(4-fluorophenyl)-2-thiophenecarboxylate

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.5-8.0 ppm) and aliphatic region (3.8 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.840	2.28
7.836	5.11
7.827	5.66
7.818	5.76
7.812	2.70
7.771	5.17
7.766	5.17
7.750	2.97
7.745	1.00
7.739	
7.724	
7.715	
7.714	
7.702	
7.692	
7.680	
7.672	
7.662	
7.652	
7.645	
7.640	
3.977	3.38
3.946	3.40
3.985	
2.159	
1.669	
-0.000	

Fc1ccc(cc1)C(=O)C(Cl)=S

13C NMR spectrum (CDCl₃) of 4-fluorobenzoyl chloride. The spectrum displays peaks corresponding to the aromatic and carbonyl carbons of the compound, as well as the solvent (CDCl₃) and TMS reference peak.

Chemical Shift (ppm)
190.22
188.25
167.16
164.62
163.22
160.86
139.37
138.86
138.78
138.78
138.75
138.48
138.38
138.09
138.01
137.91
129.74
129.69
129.39
116.07
115.90
115.56
115.54
115.34
115.31
77.35
77.14
77.01
76.72
37.84
35.02
0.01

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

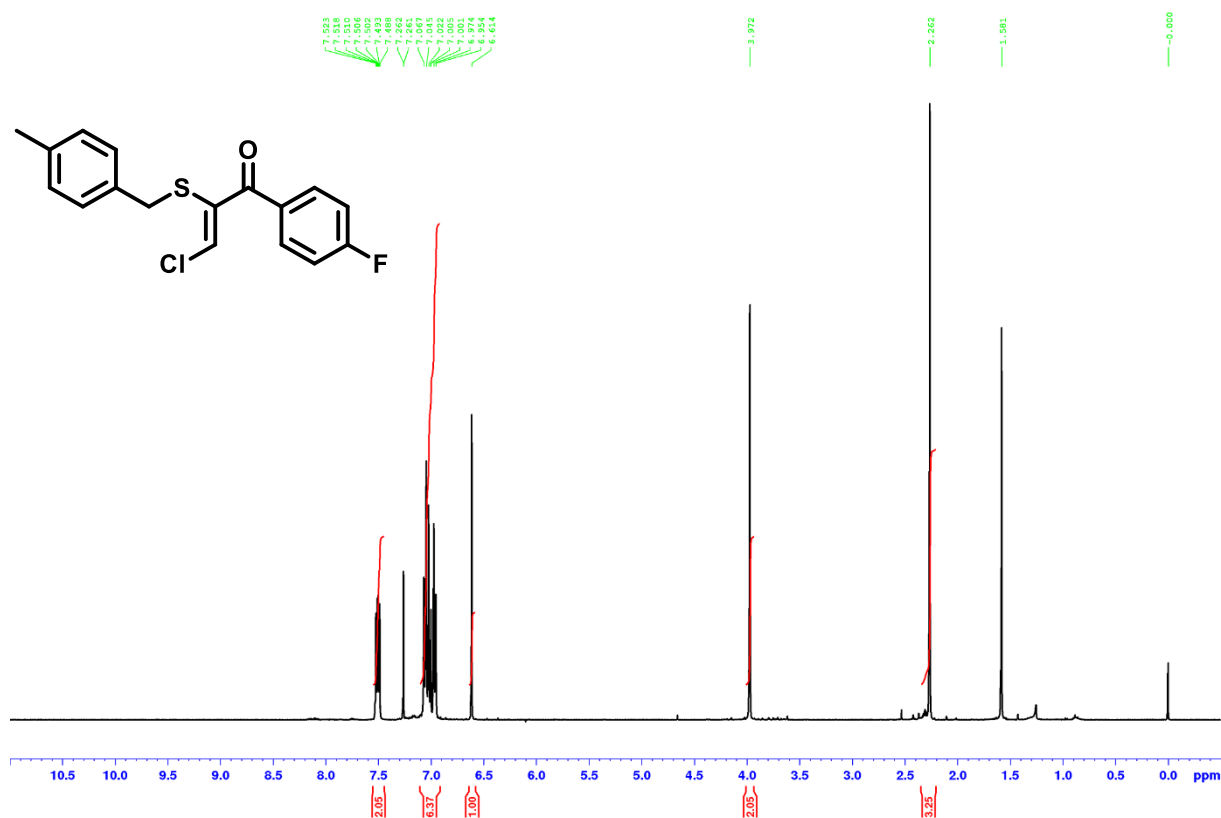


Figure S175: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4aa**.

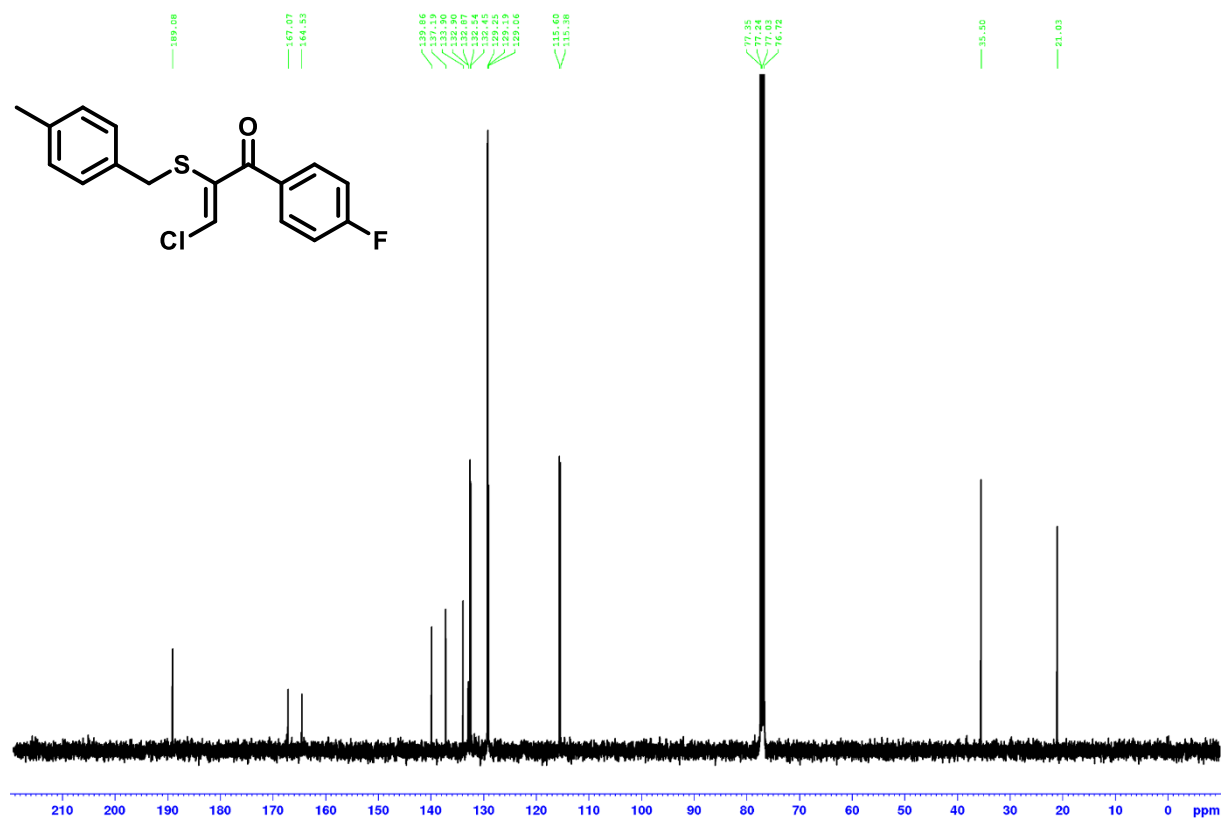


Figure S176: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4aa**.

[illegible]

Chemical structure: Cc1ccc(cc1)CSC(=O)c2cc(Cl)cc2-c3ccc(F)cc3

¹³C NMR spectrum (CDCl₃) peaks (ppm):

Peak (ppm)
190.28
146.11
147.66
137.32
133.41
133.57
132.57
132.42
132.40
130.60
128.27
127.61
126.80
116.21
115.99
77.35
77.14
77.03
76.72
38.34
21.15

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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

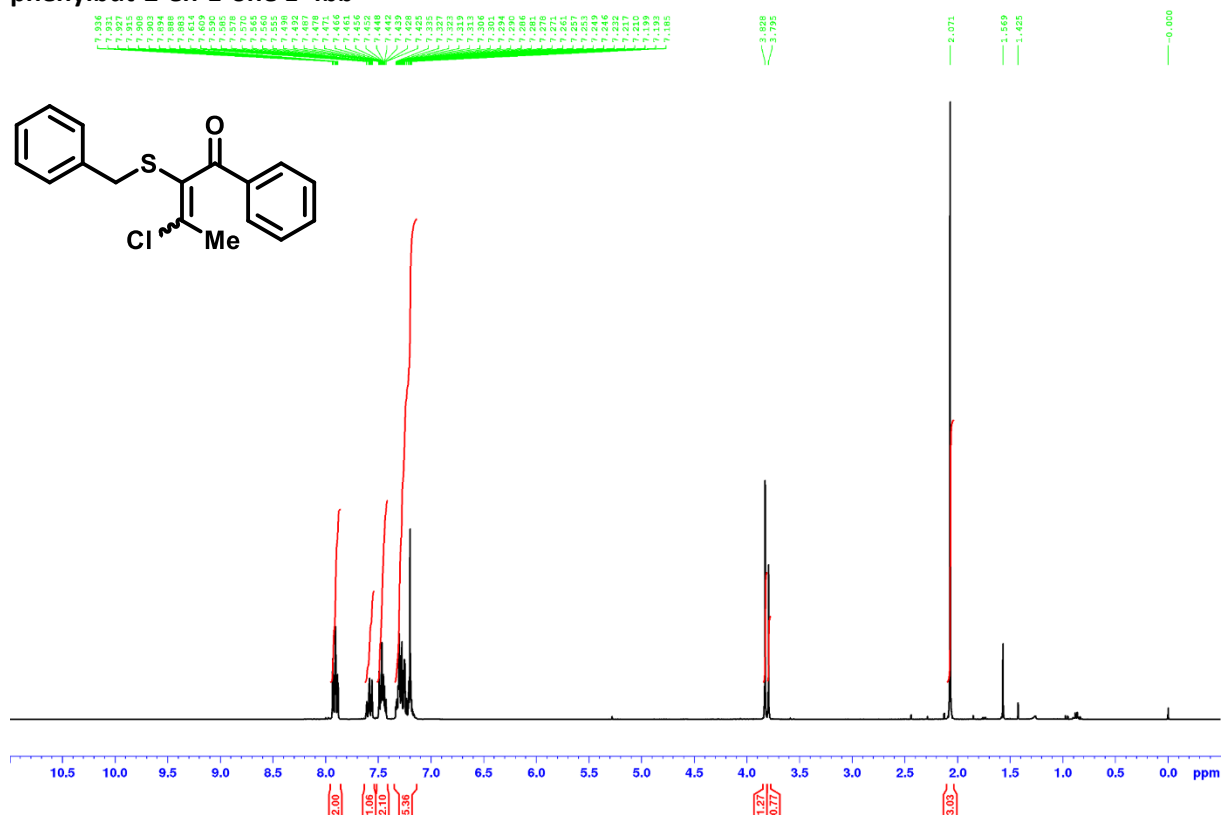


Figure S179: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-4bb** and **E-4bb**.

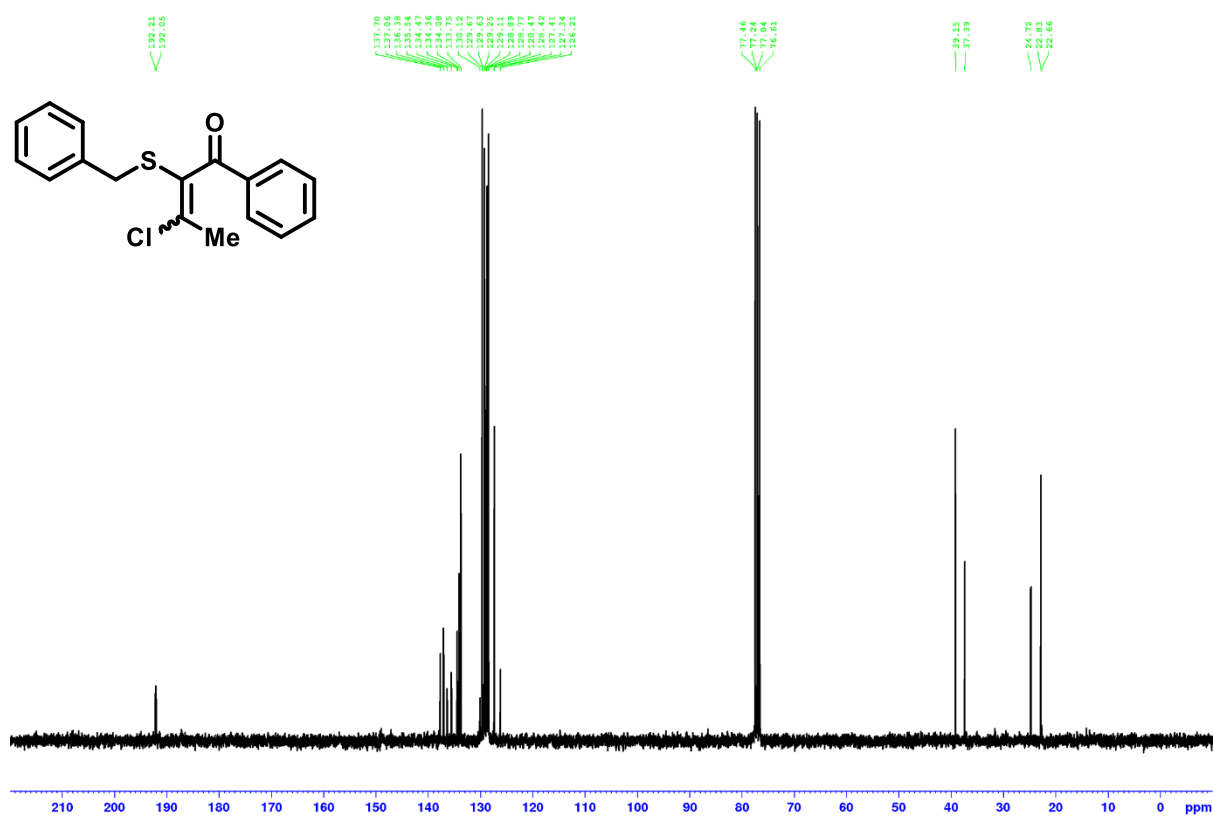


Figure S180: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-4bb** and **E-4bb**.

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

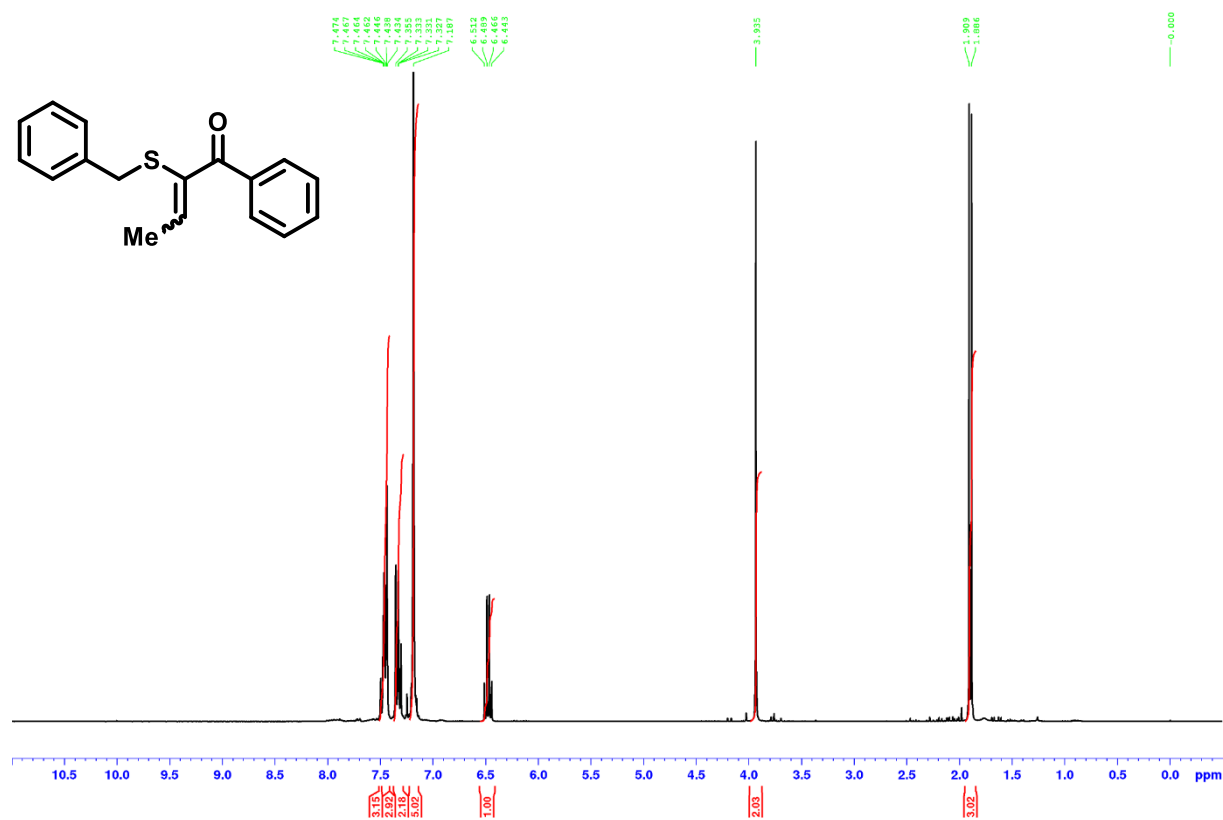


Figure S181: ¹H NMR (300 MHz, CDCl₃) spectrum of S39.

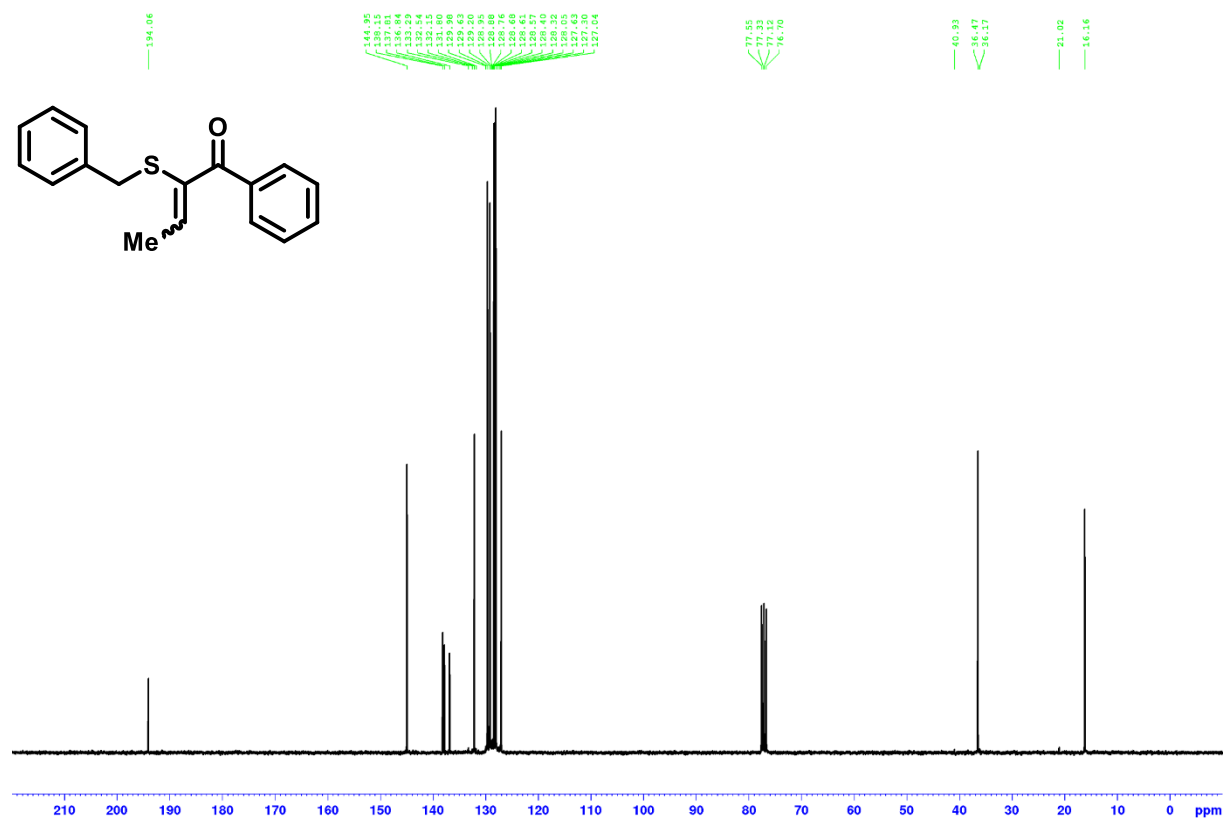


Figure S182: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of S39.

(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

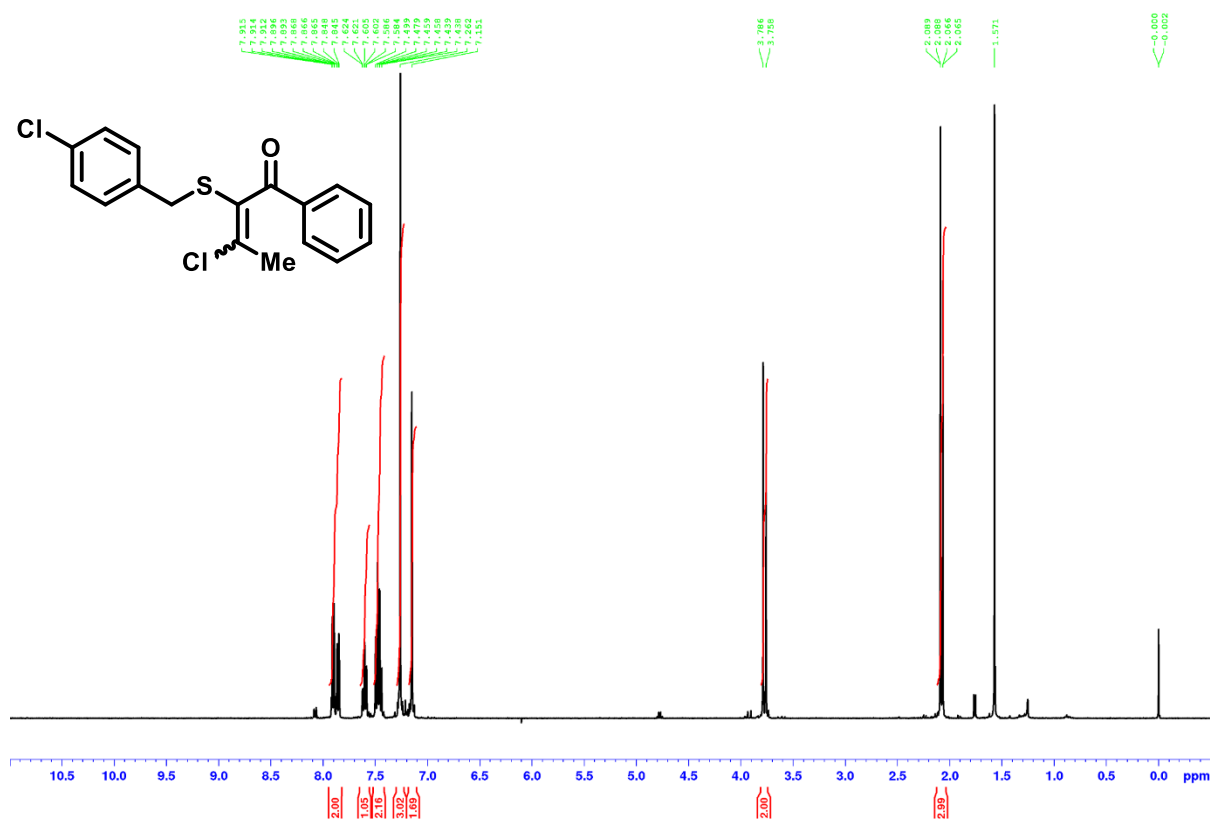


Figure S183: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4cc** and **E-4cc**.

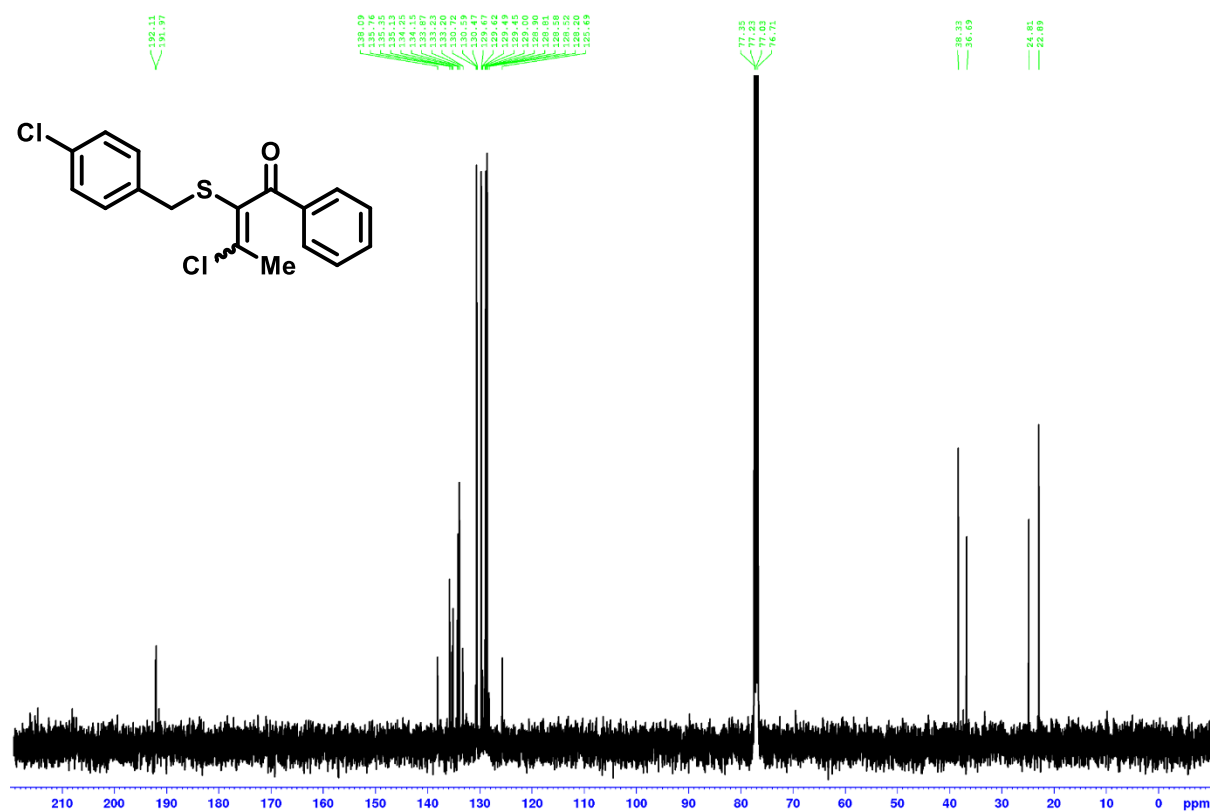


Figure S184: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4cc** and **E-4cc**.

Chemical structure of 4-(4-methoxybenzylthio)-2-chloro-1-phenylbutan-1-one:

COc1ccc(cc1)CS(=O)(C(=O)c2ccccc2)C(Cl)=C

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.5-8.0 ppm), a methoxy singlet (~3.8 ppm), a methylene quartet (~2.0 ppm), and a reference peak at 0 ppm. Integration values are shown below the peaks.

COc1ccc(CSC(=C(C)Cl)C(=O)c2ccccc2)cc1

192.12, 158.97, 137.34, 134.46, 133.76, 133.62, 133.42, 130.42, 129.69, 129.03, 128.77, 126.42, 113.65, 113.79, 77.36, 77.22, 77.04, 76.73, 55.30, 38.45, 22.91

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

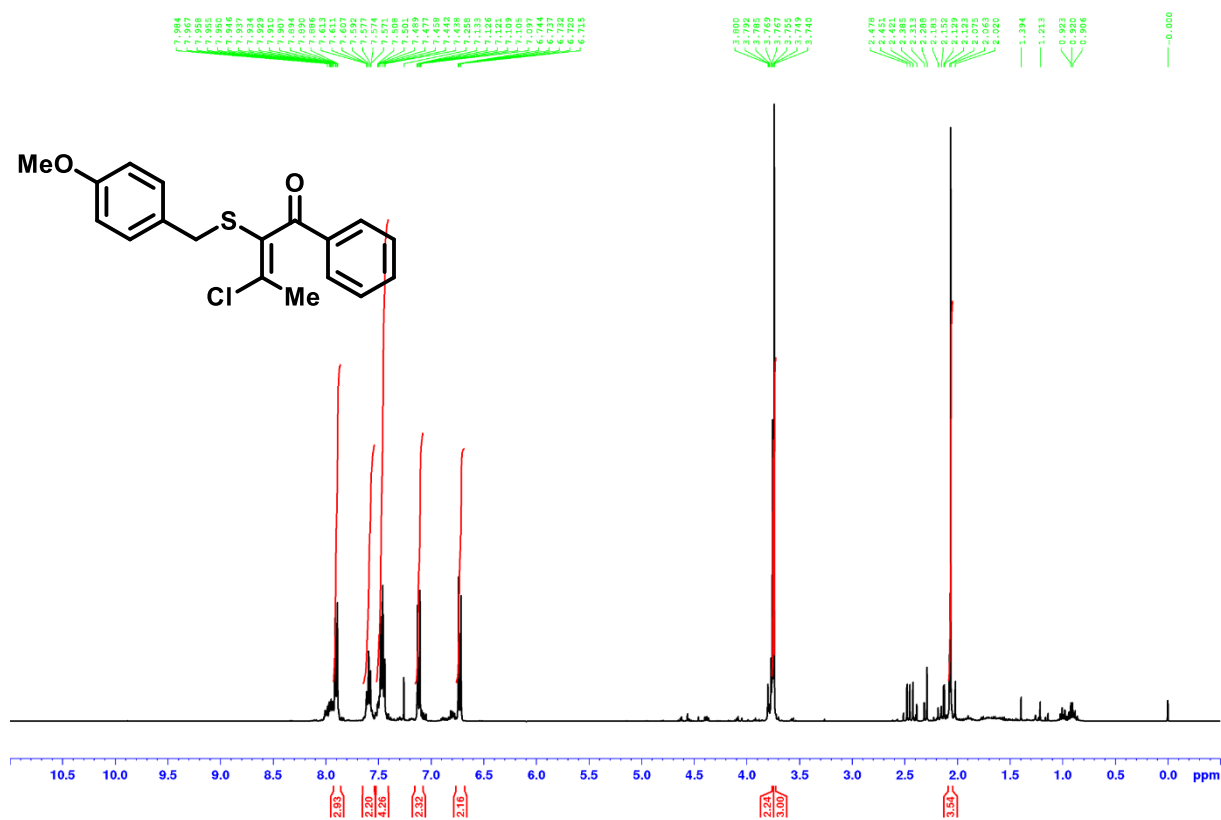


Figure S187: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4dd.

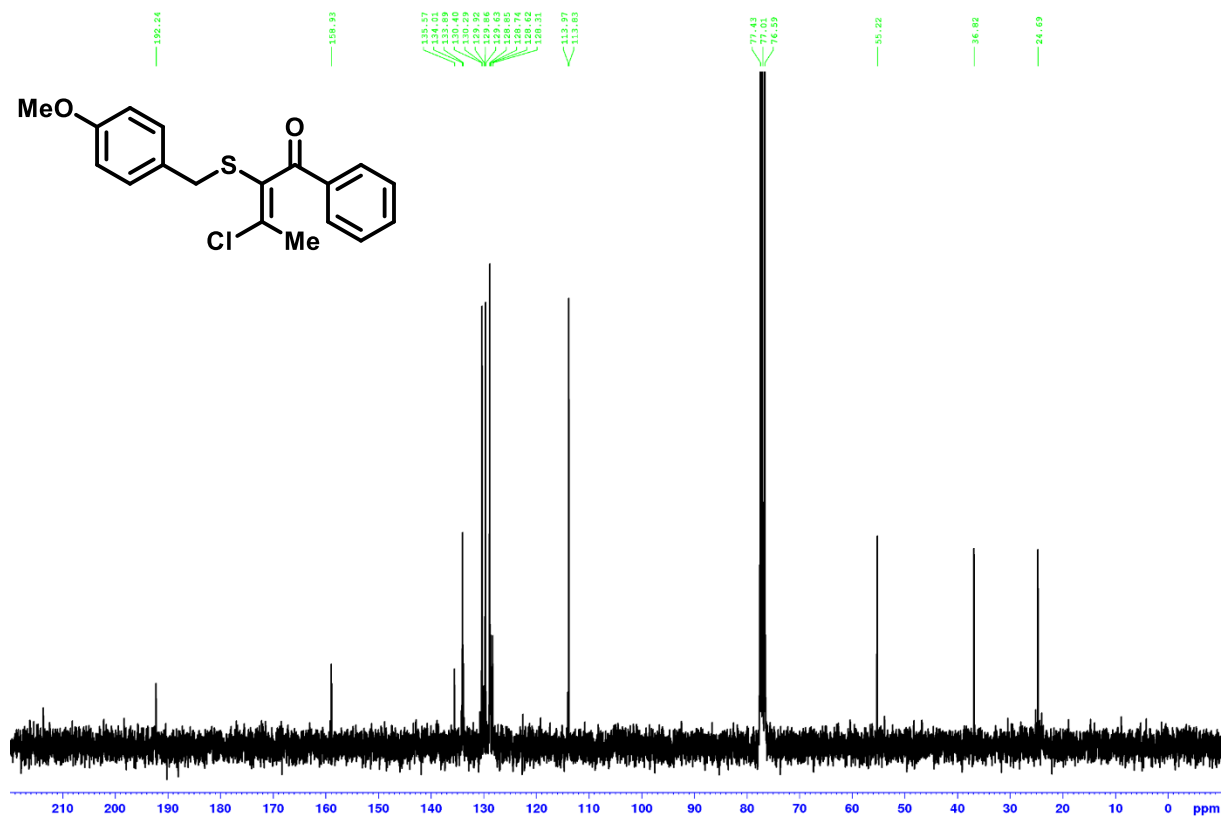


Figure S188: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of Z-4dd.

(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

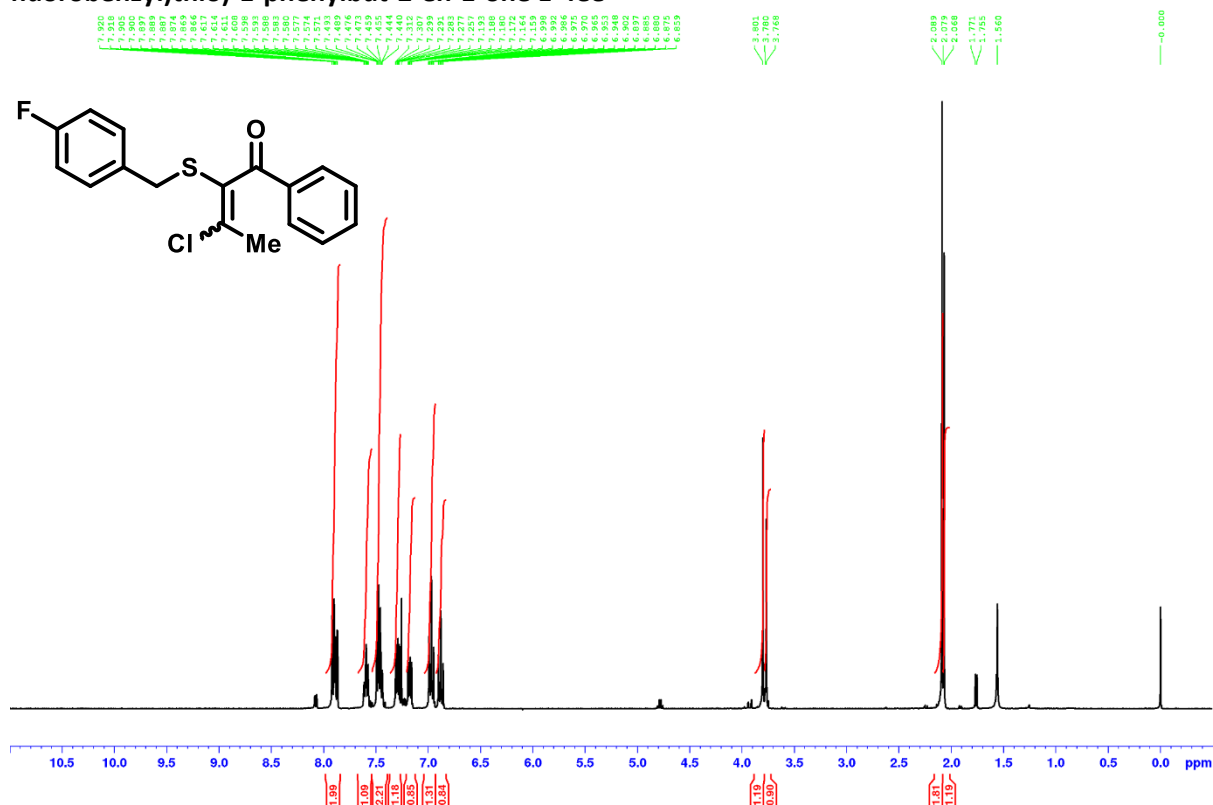


Figure S189: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4ee** and **E-4ee**.

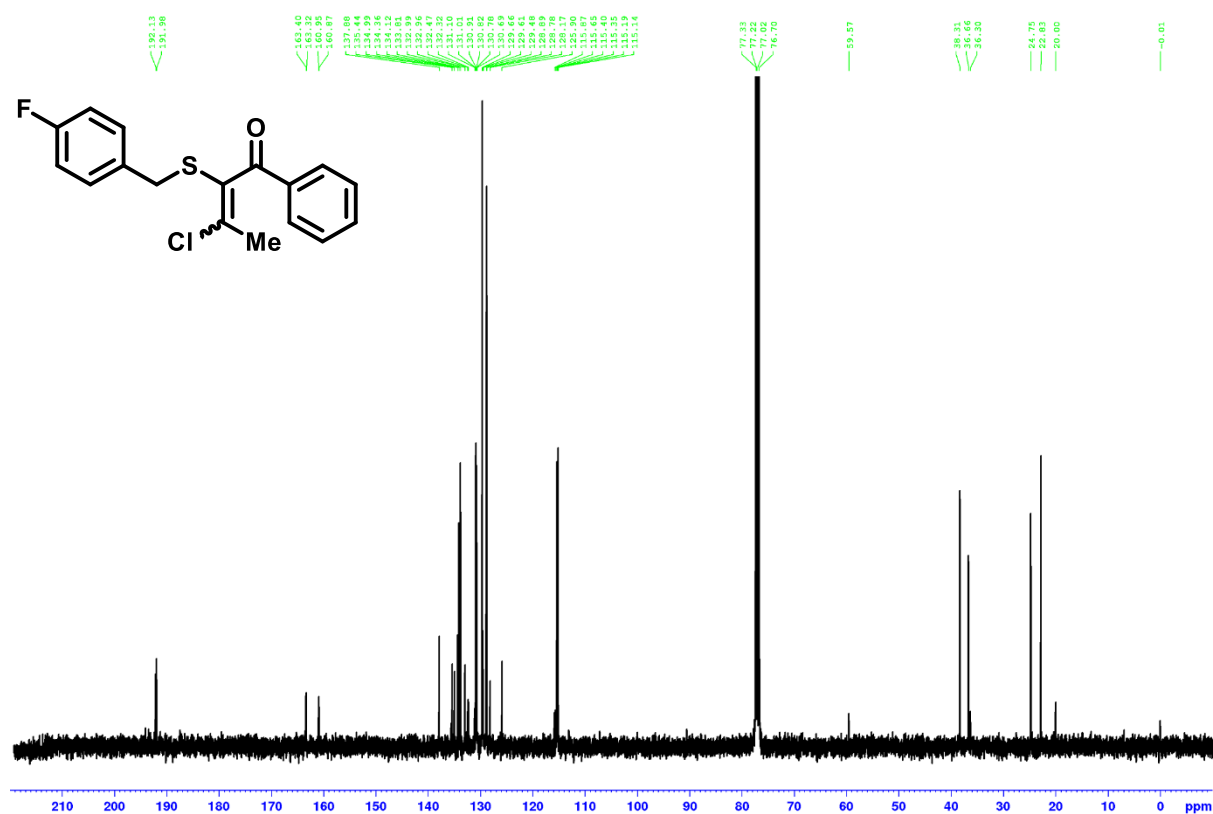


Figure S190: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4ee** and **E-4ee**.

CC(=C(SCc1ccc(F)cc1)C(=O)c2ccccc2)C

Chemical structure: (E)-1-(4-fluorophenyl)-2-methyl-3-phenylthio-2-propen-1-one

¹H NMR spectrum (CDCl₃) showing peaks from 0.0 to 10.5 ppm. The spectrum includes aromatic signals (6.5-7.5 ppm), a methine signal (3.919 ppm), and aliphatic signals (1.0-2.5 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.523	3.10
7.500	2.24
7.501	2.24
7.497	2.16
7.498	2.16
7.497	2.13
7.463	2.13
7.463	1.00
7.381	1.00
7.379	1.00
7.347	1.00
7.347	1.00
7.279	1.00
7.279	1.00
7.165	1.00
7.157	1.00
7.144	1.00
7.144	1.00
6.903	1.00
6.882	1.00
6.870	1.00
6.855	1.00
6.830	1.00
6.813	1.00
6.798	1.00
6.779	1.00
3.919	2.10
2.366	3.10
1.908	3.10
1.640	3.10
1.622	3.10
1.256	3.10
-0.000	3.10

C=C(C(=O)c1ccccc1)SCc2ccc(F)cc2

Chemical structure: C=C(C(=O)c1ccccc1)SCc2ccc(F)cc2

¹³C NMR spectrum (CDCl₃) peaks (ppm):

- 192.99
- 167.12
- 160.68
- 144.86
- 138.69
- 136.50
- 136.50
- 133.96
- 133.96
- 132.55
- 132.55
- 132.78
- 132.78
- 132.70
- 132.70
- 128.99
- 128.99
- 128.10
- 115.32
- 115.11
- 77.33
- 77.01
- 76.69
- 35.69
- 16.11
- 0.01

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Chemical structure: CC1=CC=C(C=C1)SC(=C(C)C(=O)C2=CC=CC=C2)C3=CC=C(C=C3)C

¹H NMR spectrum (CDCl₃) showing peaks from 0.0 to 10.0 ppm. The spectrum includes aromatic signals (6.8-7.7 ppm), a methine signal (6.2 ppm), a methoxy singlet (3.8 ppm), and aliphatic signals (2.1-2.6 ppm). Integration values are shown below the baseline, and chemical shift values are listed above the peaks.

Chemical Shift (ppm)	Integration
7.692, 7.620, 7.516, 7.501, 7.501, 7.502, 7.491, 7.491, 7.487, 7.487, 7.485, 7.484, 7.483, 7.483, 7.482, 7.482, 7.481, 7.481, 7.480, 7.480, 7.479, 7.479, 7.478, 7.478, 7.477, 7.477, 7.476, 7.476, 7.475, 7.475, 7.474, 7.474, 7.473, 7.473, 7.472, 7.472, 7.471, 7.471, 7.470, 7.470, 7.469, 7.469, 7.468, 7.468, 7.467, 7.467, 7.466, 7.466, 7.465, 7.465, 7.464, 7.464, 7.463, 7.463, 7.462, 7.462, 7.461, 7.461, 7.460, 7.460, 7.459, 7.459, 7.458, 7.458, 7.457, 7.457, 7.456, 7.456, 7.455, 7.455, 7.454, 7.454, 7.453, 7.453, 7.452, 7.452, 7.451, 7.451, 7.450, 7.450, 7.449, 7.449, 7.448, 7.448, 7.447, 7.447, 7.446, 7.446, 7.445, 7.445, 7.444, 7.444, 7.443, 7.443, 7.442, 7.442, 7.441, 7.441, 7.440, 7.440, 7.439, 7.439, 7.438, 7.438, 7.437, 7.437, 7.436, 7.436, 7.435, 7.435, 7.434, 7.434, 7.433, 7.433, 7.432, 7.432, 7.431, 7.431, 7.430, 7.430, 7.429, 7.429, 7.428, 7.428, 7.427, 7.427, 7.426, 7.426, 7.425, 7.425, 7.424, 7.424, 7.423, 7.423, 7.422, 7.422, 7.421, 7.421, 7.420, 7.420, 7.419, 7.419, 7.418, 7.418, 7.417, 7.417, 7.416, 7.416, 7.415, 7.415, 7.414, 7.414, 7.413, 7.413, 7.412, 7.412, 7.411, 7.411, 7.410, 7.410, 7.409, 7.409, 7.408, 7.408, 7.407, 7.407, 7.406, 7.406, 7.405, 7.405, 7.404, 7.404, 7.403, 7.403, 7.402, 7.402, 7.401, 7.401, 7.400, 7.400, 7.399, 7.399, 7.398, 7.398, 7.397, 7.397, 7.396, 7.396, 7.395, 7.395, 7.394, 7.394, 7.393, 7.393, 7.392, 7.392, 7.391, 7.391, 7.390, 7.390, 7.389, 7.389, 7.388, 7.388, 7.387, 7.387, 7.386, 7.386, 7.385, 7.385, 7.384, 7.384, 7.383, 7.383, 7.382, 7.382, 7.381, 7.381, 7.380, 7.380, 7.379, 7.379, 7.378, 7.378, 7.377, 7.377, 7.376, 7.376, 7.375, 7.375, 7.374, 7.374, 7.373, 7.373, 7.372, 7.372, 7.371, 7.371, 7.370, 7.370, 7.369, 7.369, 7.368, 7.368, 7.367, 7.367, 7.366, 7.366, 7.365, 7.365, 7.364, 7.364, 7.363, 7.363, 7.362, 7.362, 7.361, 7.361, 7.360, 7.360, 7.359, 7.359, 7.358, 7.358, 7.357, 7.357, 7.356, 7.356, 7.355, 7.355, 7.354, 7.354, 7.353, 7.353, 7.352, 7.352, 7.351, 7.351, 7.350, 7.350, 7.349, 7.349, 7.348, 7.348, 7.347, 7.347, 7.346, 7.346, 7.345, 7.345, 7.344, 7.344, 7.343, 7.343, 7.342, 7.342, 7.341, 7.341, 7.340, 7.340, 7.339, 7.339, 7.338, 7.338, 7.337, 7.337, 7.336, 7.336, 7.335, 7.335, 7.334, 7.334, 7.333, 7.333, 7.332, 7.332, 7.331, 7.331, 7.330, 7.330, 7.329, 7.329, 7.328, 7.328, 7.327, 7.327, 7.326, 7.326, 7.325, 7.325, 7.324, 7.324, 7.323, 7.323, 7.322, 7.322, 7.321, 7.321, 7.320, 7.320, 7.319, 7.319, 7.318, 7.318, 7.317, 7.317, 7.316, 7.316, 7.315, 7.315, 7.314, 7.314, 7.313, 7.313, 7.312, 7.312, 7.311, 7.311, 7.310, 7.310, 7.309, 7.309, 7.308, 7.308, 7.307, 7.307, 7.306, 7.306, 7.305, 7.305, 7.304, 7.304, 7.303, 7.303, 7.302, 7.302, 7.301, 7.301, 7.300, 7.300, 7.299, 7.299, 7.298, 7.298, 7.297, 7.297, 7.296, 7.296, 7.295, 7.295, 7.294, 7.294, 7.293, 7.293, 7.292, 7.292, 7.291, 7.291, 7.290, 7.290, 7.289, 7.289, 7.288, 7.288, 7.287, 7.287, 7.286, 7.286, 7.285, 7.285, 7.284, 7.284, 7.283, 7.283, 7.282, 7.282, 7.281, 7.281, 7.280, 7.280, 7.279, 7.279, 7.278, 7.278, 7.277, 7.277, 7.276, 7.276, 7.275, 7.275, 7.274, 7.274, 7.273, 7.273, 7.272, 7.272, 7.271, 7.271, 7.270, 7.270, 7.269, 7.269, 7.268, 7.268, 7.267, 7.267, 7.266, 7.266, 7.265, 7.265, 7.264, 7.264, 7.263, 7.263, 7.262, 7.262, 7.261, 7.261, 7.260, 7.260, 7.259, 7.259, 7.258, 7.258, 7.257, 7.257, 7.256, 7.256, 7.255, 7.255, 7.254, 7.254, 7.253, 7.253, 7.252, 7.252, 7.251, 7.251, 7.250, 7.250, 7.249, 7.249, 7.248, 7.248, 7.247, 7.247, 7.246, 7.246, 7.245, 7.245, 7.244, 7.244, 7.243, 7.243, 7.242, 7.242, 7.241, 7.241, 7.240, 7.240, 7.239, 7.239, 7.238, 7.238, 7.237, 7.237, 7.236, 7.236, 7.235, 7.235, 7.234, 7.234, 7.233, 7.233, 7.232, 7.232, 7.231, 7.231, 7.230, 7.230, 7.229, 7.229, 7.228, 7.228, 7.227, 7.227, 7.226, 7.226, 7.225, 7.225, 7.224, 7.224, 7.223, 7.223, 7.222, 7.222, 7.221, 7.221, 7.220, 7	

Chemical structure of 4-(4-methylphenyl)-2-chloro-1-phenylbut-3-en-1-one is shown above the spectrum.

The spectrum displays the following chemical shifts (ppm):

- 192.27
- 192.11
- 137.00
- 137.11
- 137.11
- 136.40
- 136.40
- 134.03
- 134.03
- 133.74
- 133.74
- 133.30
- 133.30
- 129.69
- 129.69
- 129.12
- 129.12
- 128.86
- 128.86
- 128.54
- 128.54
- 77.36
- 77.36
- 77.04
- 77.04
- 76.72
- 76.72
- 38.88
- 38.88
- 37.05
- 37.05
- 30.95
- 30.95
- 24.71
- 24.71
- 22.22
- 22.22
- 21.16
- 21.16
- 21.10
- 21.10

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(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

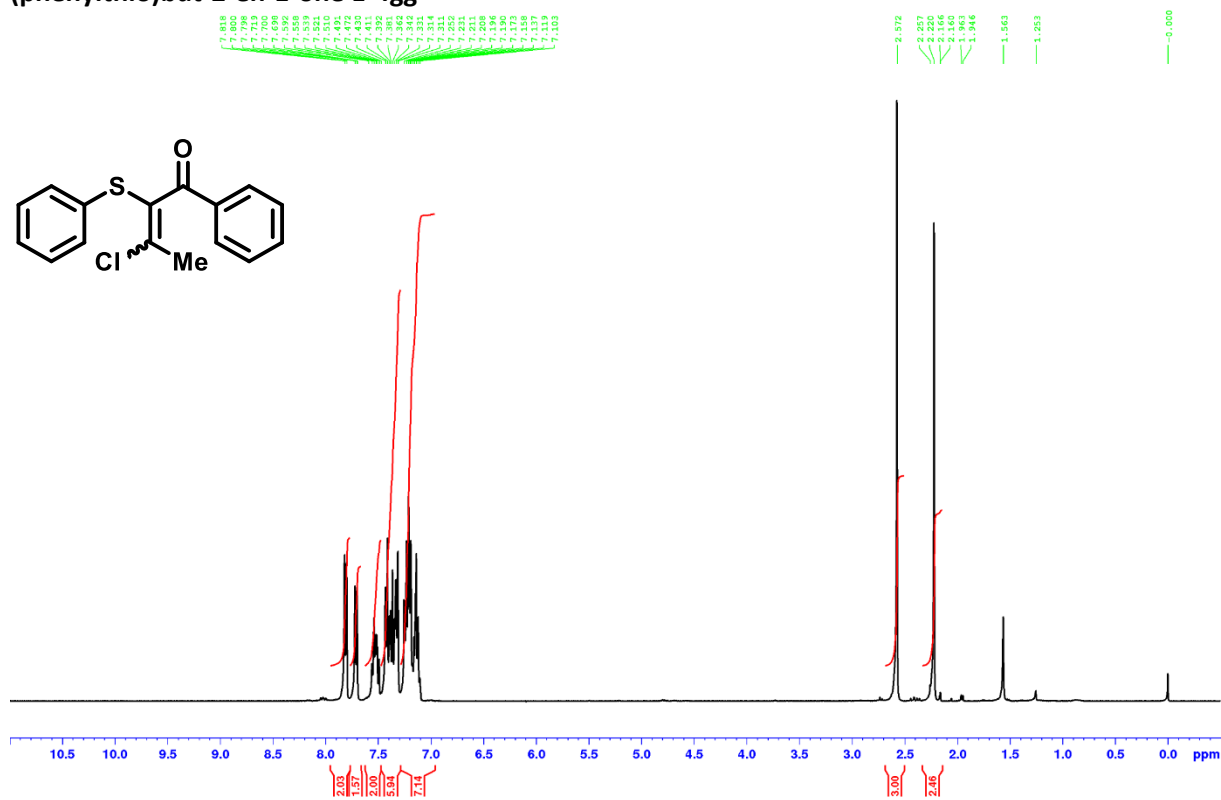


Figure S195: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4gg** and **E-4gg**.

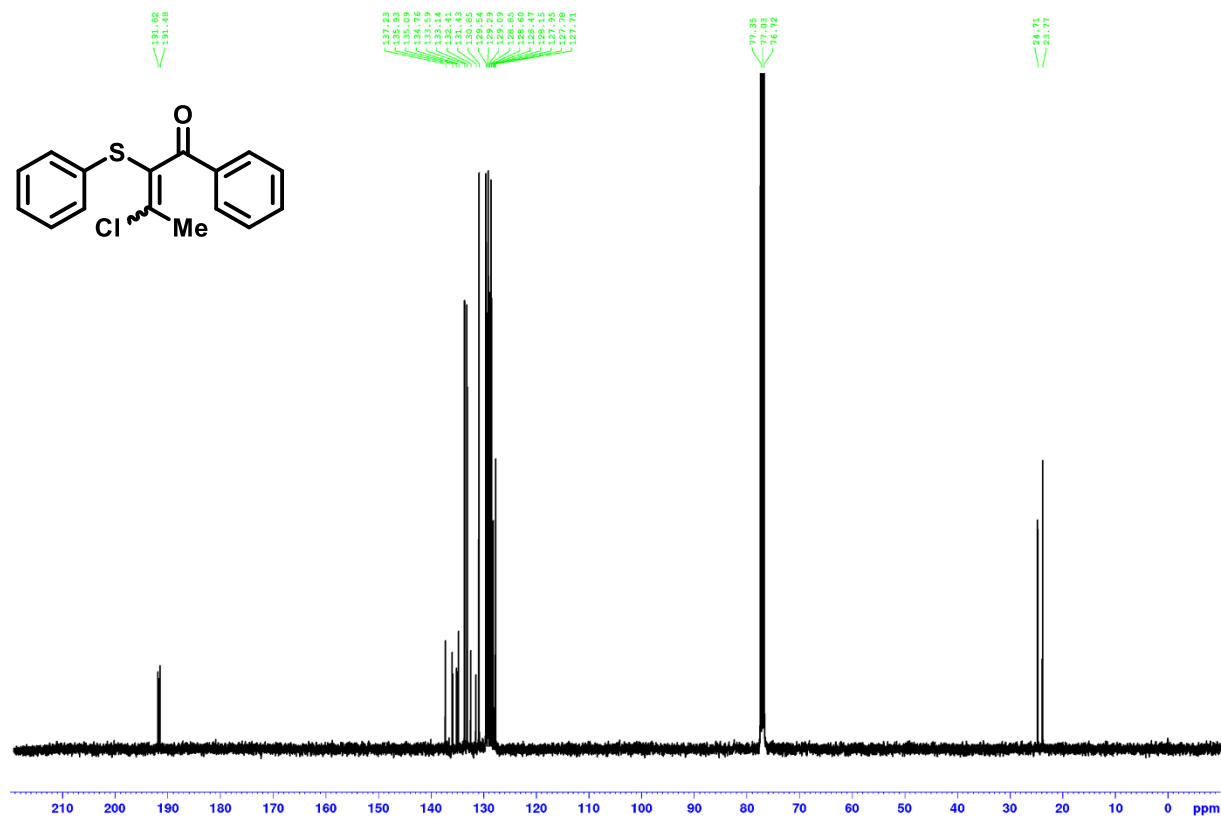


Figure S196: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4gg** and **E-4gg**.

Chemical structure: Cc1cc2ccccc2s1C(=O)c3ccccc3

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.5-7.7 ppm), a singlet for the methyl group (2.3 ppm), and a reference peak (0.0 ppm). Integration values are shown below the peaks, and chemical shifts are listed above the peaks.

Chemical Shift (ppm)	Integration
7.701	2.12
7.682	1.41
7.655	2.98
7.637	1.55
7.611	2.15
7.595	1.00
7.577	1.00
7.558	1.00
7.541	1.00
7.523	1.00
7.506	1.00
7.489	1.00
7.471	1.00
7.454	1.00
7.437	1.00
7.420	1.00
7.403	1.00
7.386	1.00
7.369	1.00
7.352	1.00
7.335	1.00
7.318	1.00
7.301	1.00
7.284	1.00
7.267	1.00
7.250	1.00
7.233	1.00
7.216	1.00
7.199	1.00
7.182	1.00
7.165	1.00
7.148	1.00
7.131	1.00
7.114	1.00
7.097	1.00
7.080	1.00
7.063	1.00
7.046	1.00
7.029	1.00
7.012	1.00
6.995	1.00
6.978	1.00
6.961	1.00
6.944	1.00
6.927	1.00
6.910	1.00
6.893	1.00
6.876	1.00
6.859	1.00
6.842	1.00
6.825	1.00
6.808	1.00
2.379	2.29
2.367	2.29
2.351	2.29
1.812	2.29
1.794	2.29
1.566	2.29
1.255	2.29
0.000	2.29

Cc1cc2ccccc2s1C(=O)c3ccccc3

¹³C NMR spectrum (CDCl₃) of 1-(4-methylphenyl)thiobenzophenone. The spectrum displays peaks corresponding to the aromatic and carbonyl carbons of the molecule, the solvent (CDCl₃), and the methyl group. The chemical structure of the compound is shown above the spectrum.

Chemical structure: Cc1cc2ccccc2s1C(=O)c3ccccc3

Peak list (ppm):

- 194.11
- 146.75
- 137.52
- 137.38
- 136.28
- 135.28
- 133.36
- 133.23
- 133.11
- 132.72
- 132.59
- 132.38
- 132.30
- 128.96
- 128.62
- 128.42
- 128.14
- 127.79
- 127.49
- 127.26
- 126.79
- 77.37
- 77.05
- 76.73
- 16.50

240

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

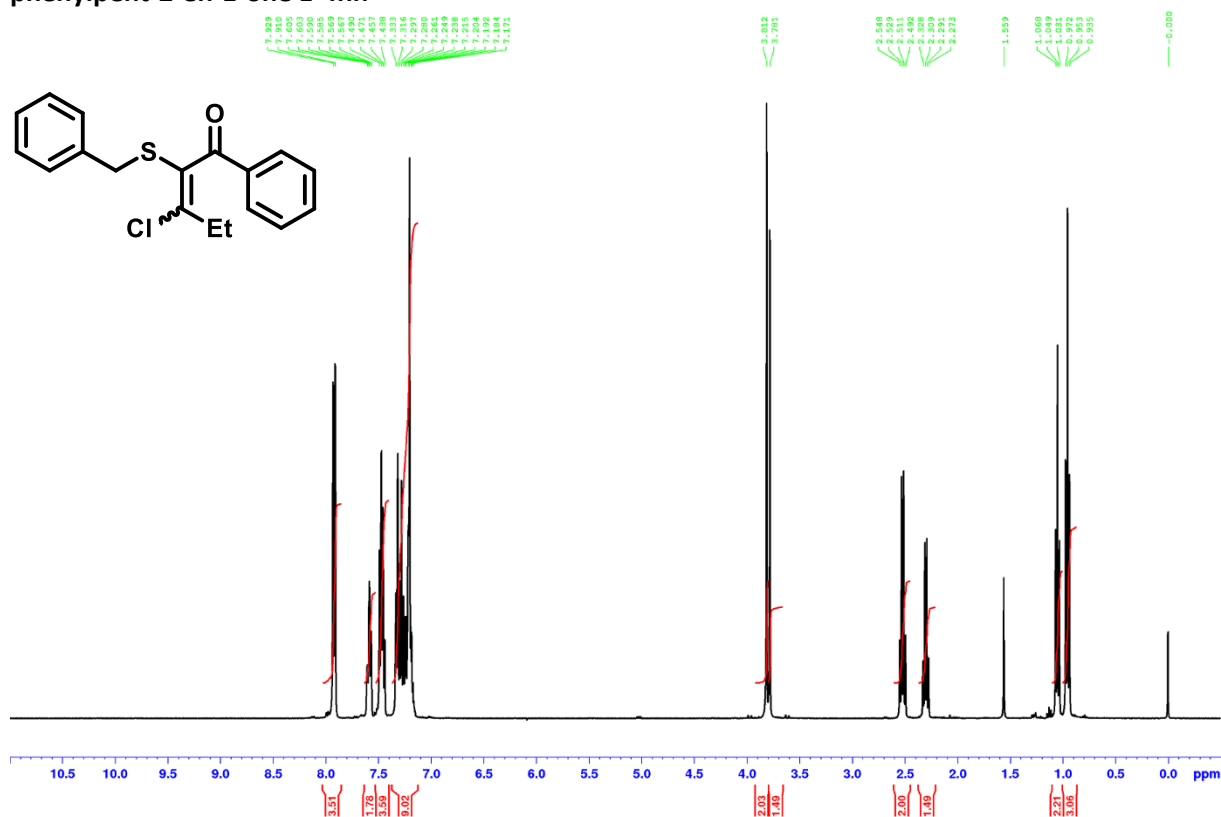


Figure S199: ^1H NMR (400 MHz, CDCl_3) spectrum of **Z-4hh** and **E-4hh**.

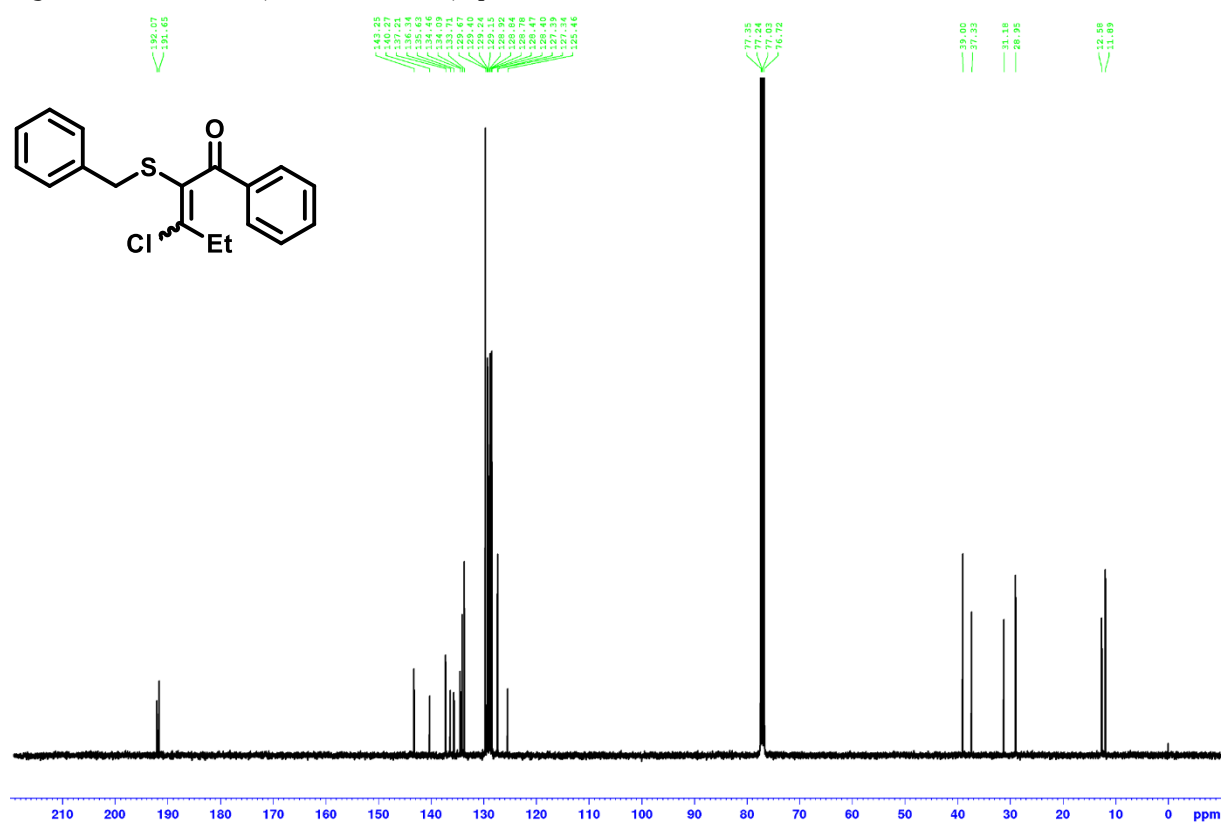


Figure S200: ^{13}C NMR (100.6 MHz, CDCl_3) spectrum of **Z-4hh** and **E-4hh**.

(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

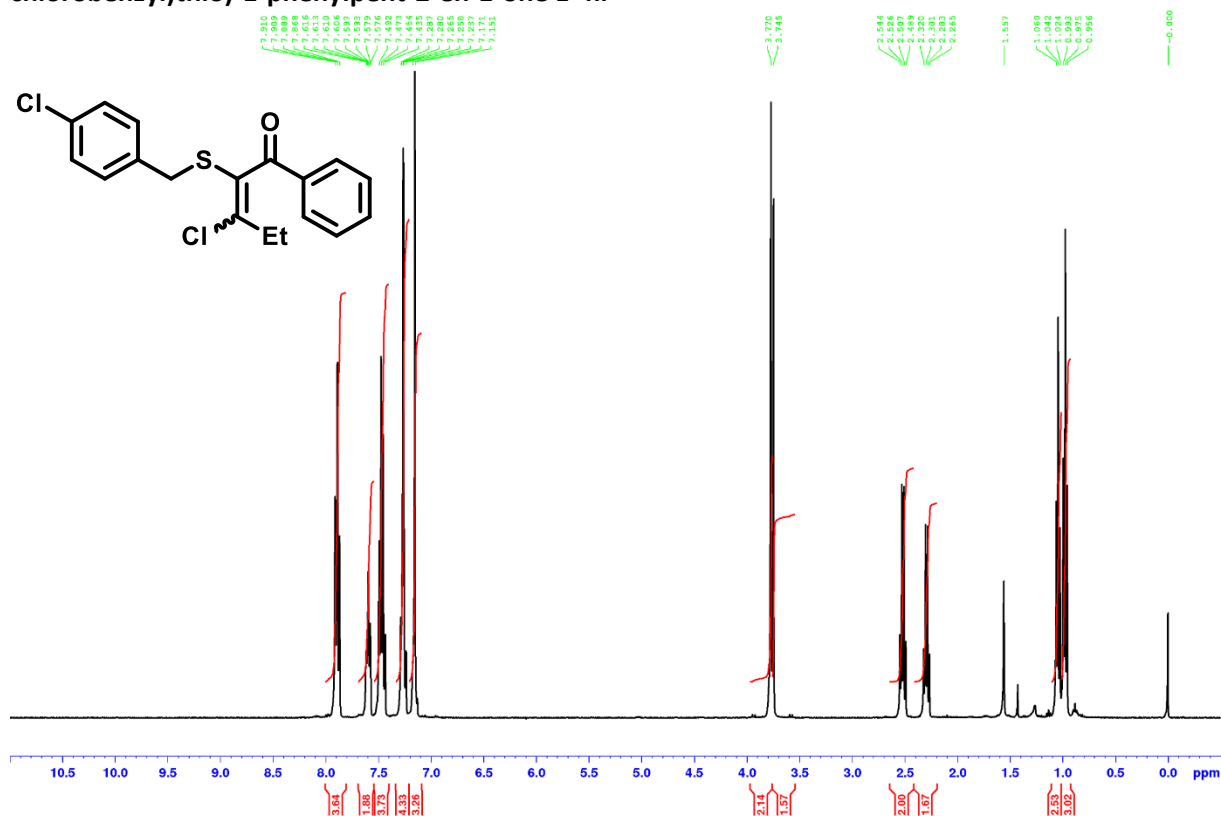


Figure S201: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4ii** and **E-4ii**.

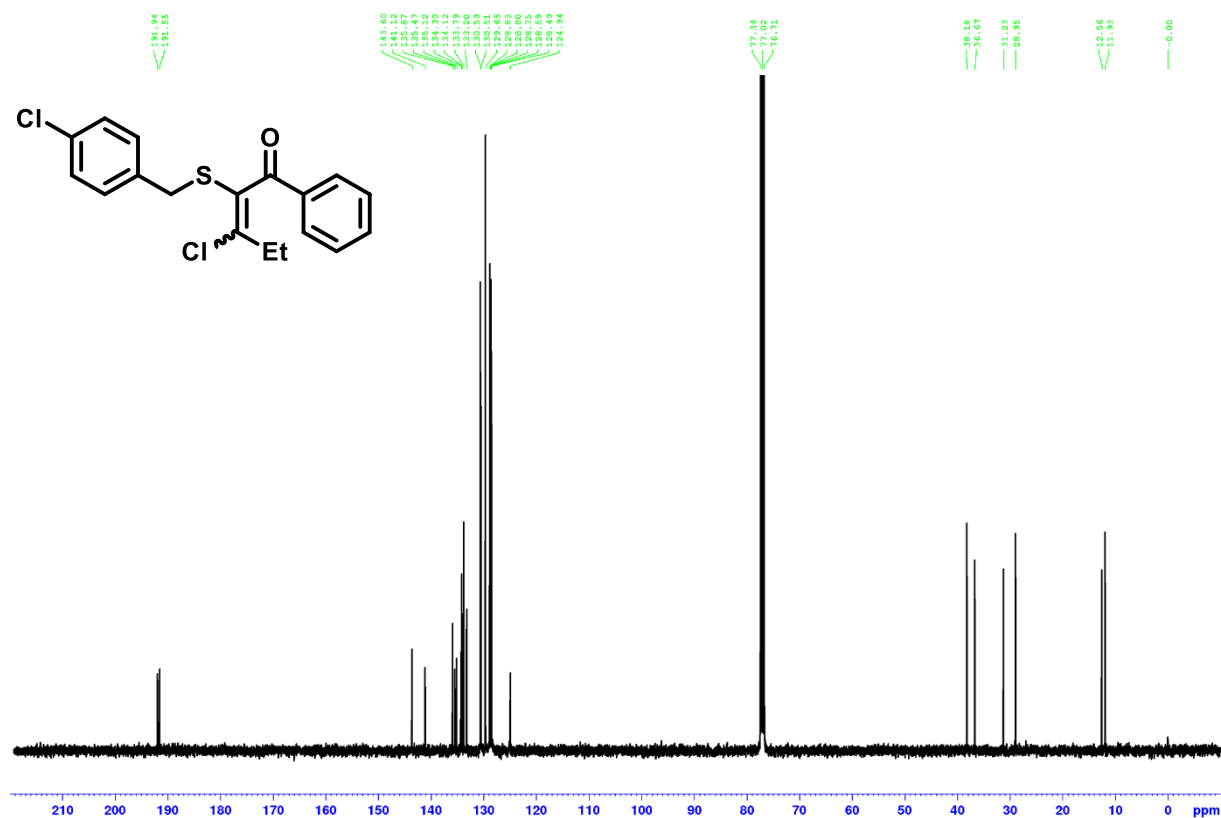


Figure S202: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4ii** and **E-4ii**.

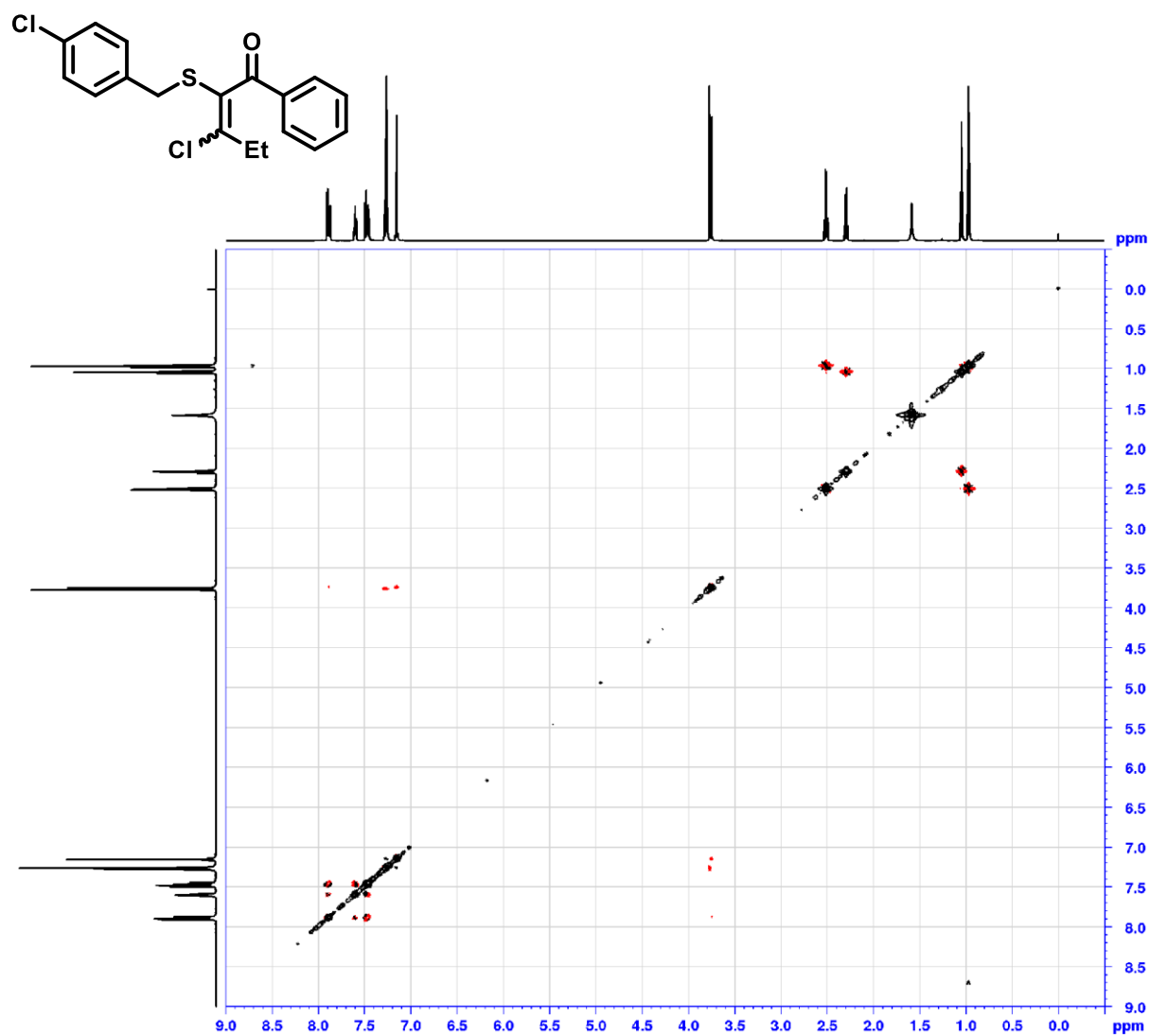


Figure S203: ^1H - ^1H NOESY (600 MHz, CDCl_3) spectrum of **Z-4ii** and **E-4ii**.

Chemical structure: CC(=O)(Cc1ccccc1)C(SCc2ccc(Cl)cc2)C

¹H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
7.500, 7.496, 7.493, 7.476, 7.455, 7.390, 7.351, 7.259, 7.160, 7.122	3.17, 2.00, 4.00
6.452, 6.389	0.84
3.893	1.97
2.386, 2.380, 2.348, 2.250	2.04
1.339	3.00
0.965, 0.943, 0.944	3.00
-0.000	-

CC=C(SCc1ccc(Cl)cc1)C(=O)c2ccccc2

Chemical structure: 4-(4-chlorobenzyl)-3-phenylbut-3-en-2-one

¹³C NMR peaks (ppm):

- 151.41
- 137.43
- 136.79
- 136.57
- 135.83
- 132.32
- 132.22
- 129.64
- 128.51
- 128.10
- 77.32
- 77.00
- 76.69
- 35.73
- 23.81
- 12.83
- 0.01

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(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

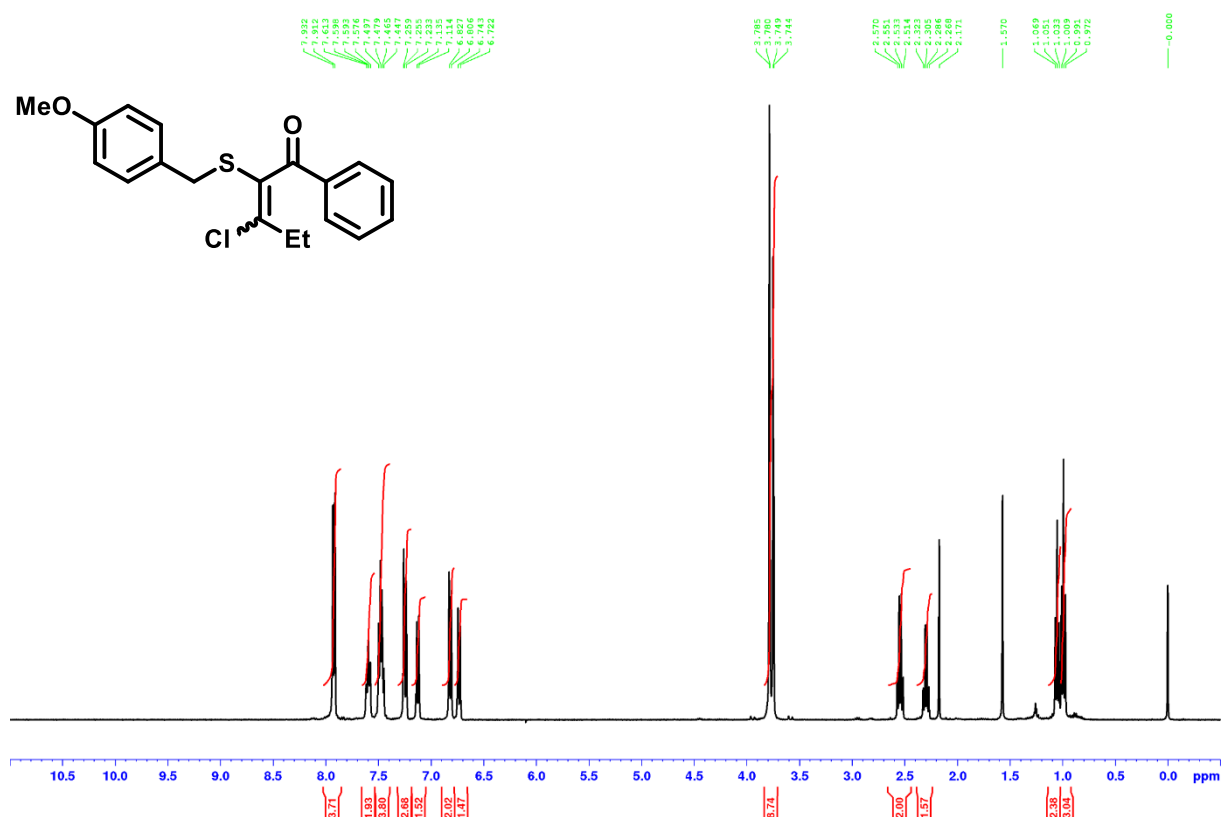


Figure S206: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-4jj and E-4jj.

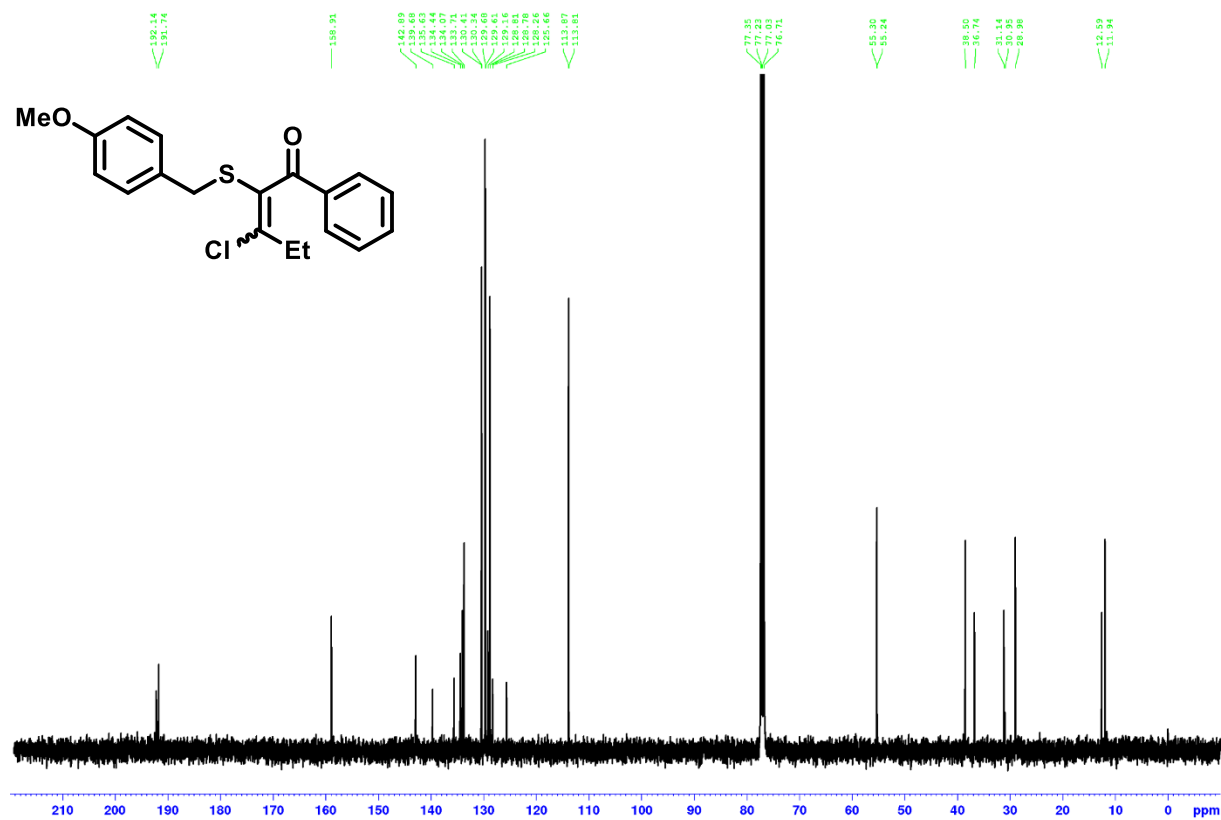


Figure S207: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of Z-4jj and E-4jj.

CC(=C(Cl)C(=O)c1ccccc1)SCc2ccc(F)cc2

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The spectrum includes a reference peak at 0 ppm and several multiplets in the aromatic region (6.8-7.8 ppm). The ethyl group is represented by a quartet at 2.5 ppm and a triplet at 1.0 ppm.

CC(=C(Cl)SCc1ccc(F)cc1)C(=O)c2ccccc2

Chemical Structure: 2-chloro-1-((4-fluorophenyl)methyl)-3-oxoprop-1-en-1-ylbenzene

¹³C NMR Peaks (ppm):

- 192.34, 191.99, 191.59
- 143.44, 140.98, 140.51, 139.51, 138.12, 134.12, 133.17, 132.92, 132.10, 130.83, 130.45, 129.45, 128.90, 128.60, 125.08, 115.32, 115.19, 113.19, 111.10
- 77.34, 77.02, 76.70 (solvent)
- 38.45, 36.61, 31.21, 20.92
- 12.55, 11.91

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

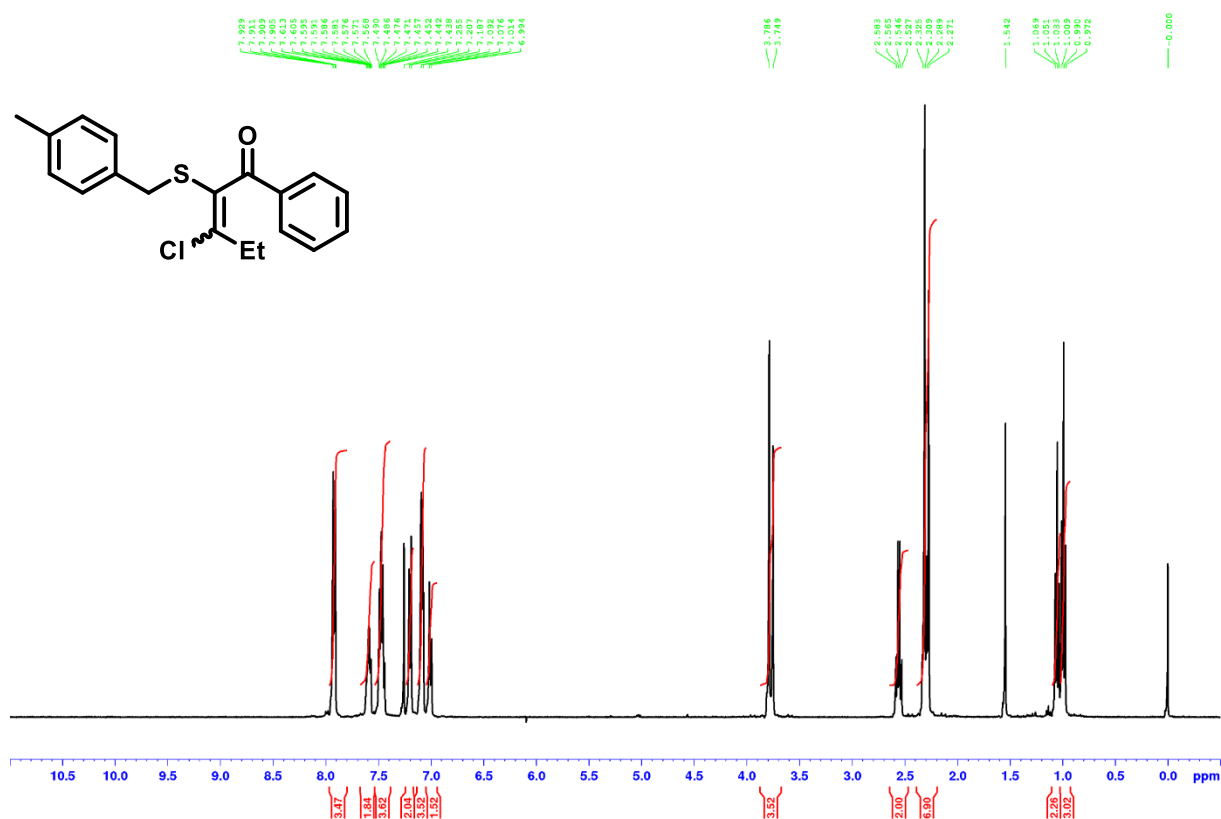


Figure S210: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-4II** and **E-4II**.

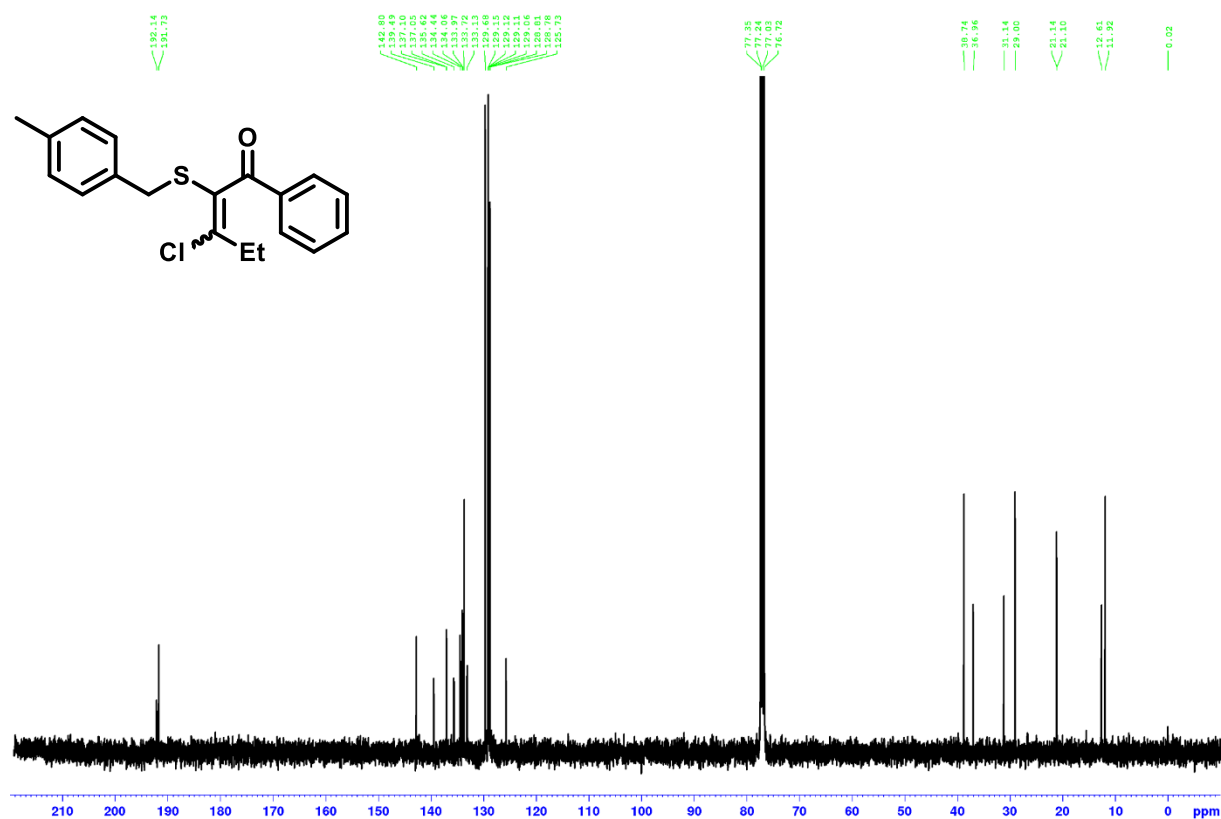


Figure S211: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **Z-4II** and **E-4II**.

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**

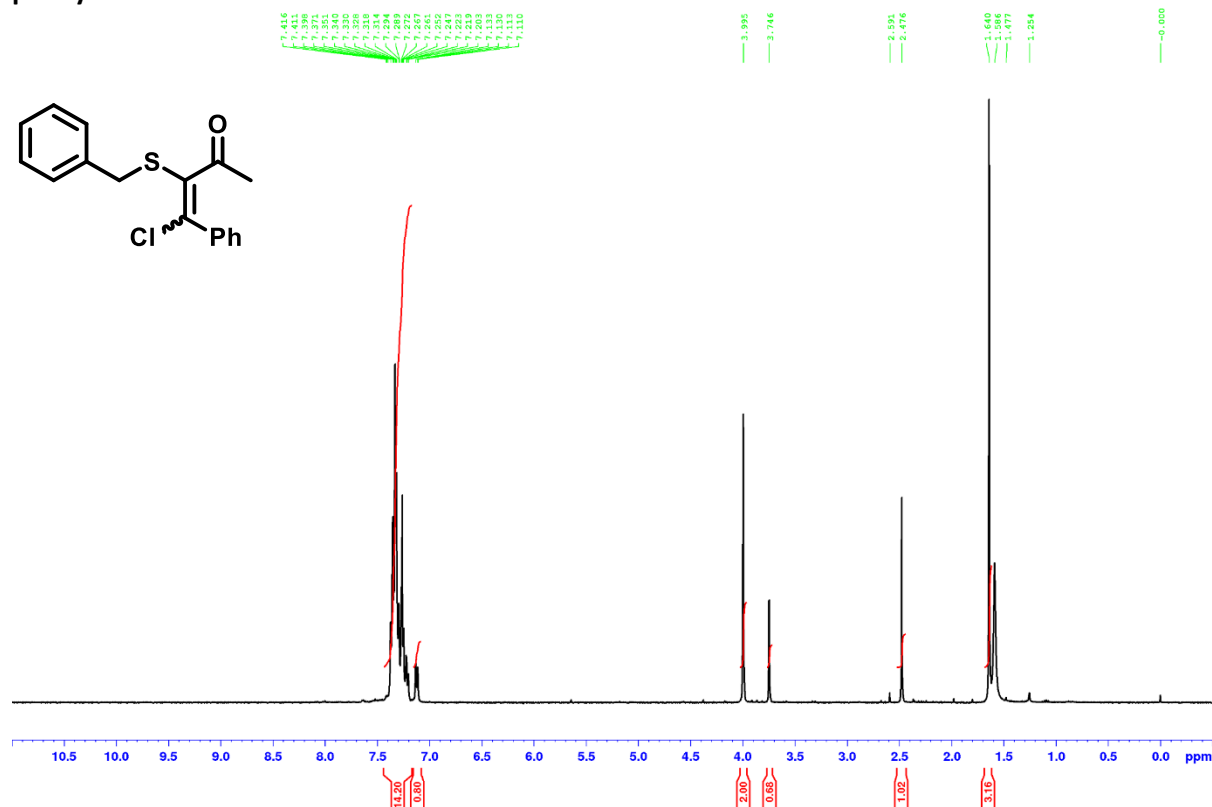


Figure S212: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-13a** and **E-13a**.

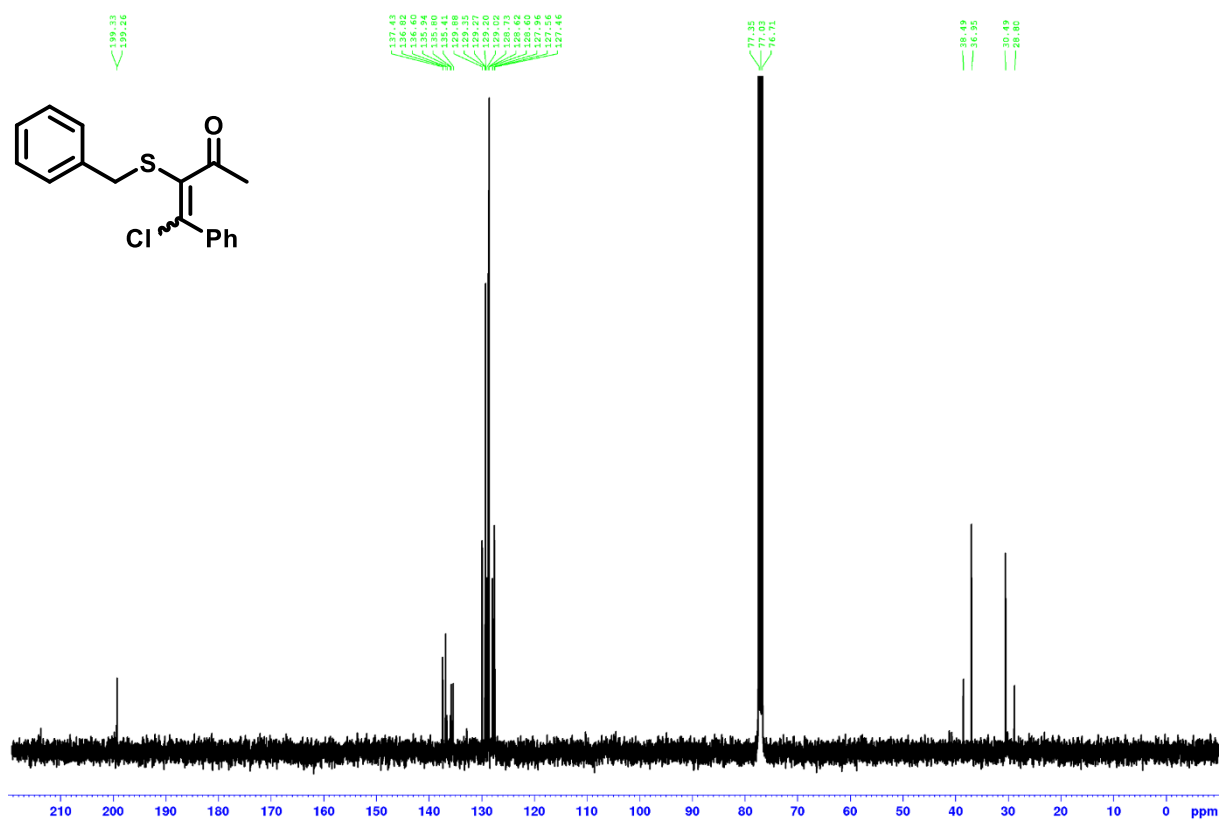


Figure S213: ^{13}C NMR (100.6 MHz, CDCl_3) spectrum of **Z-13a** and **E-13a**.

3-(Benzylthio)-3,4-dichloro-4-phenylbutan-2-one 12a/b

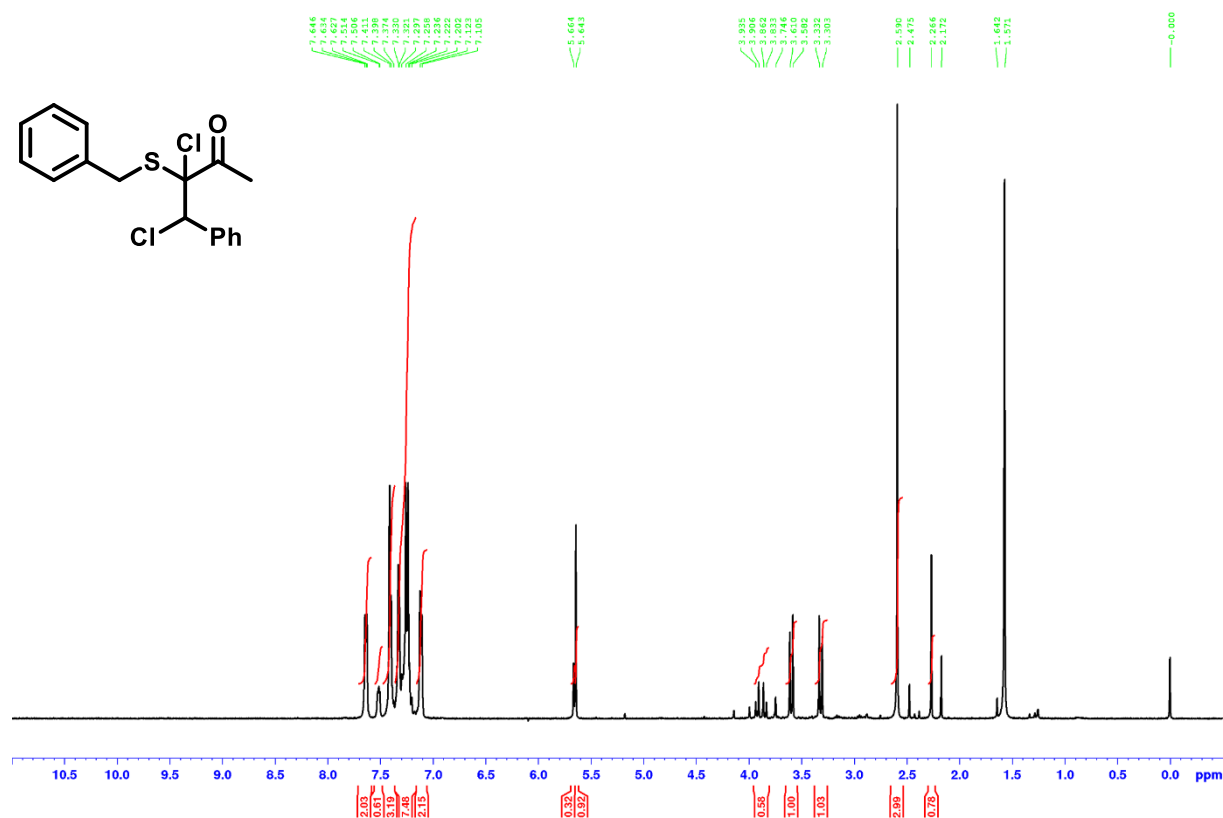


Figure S214: ¹H NMR (400 MHz, CDCl₃) spectrum of 12a/b.

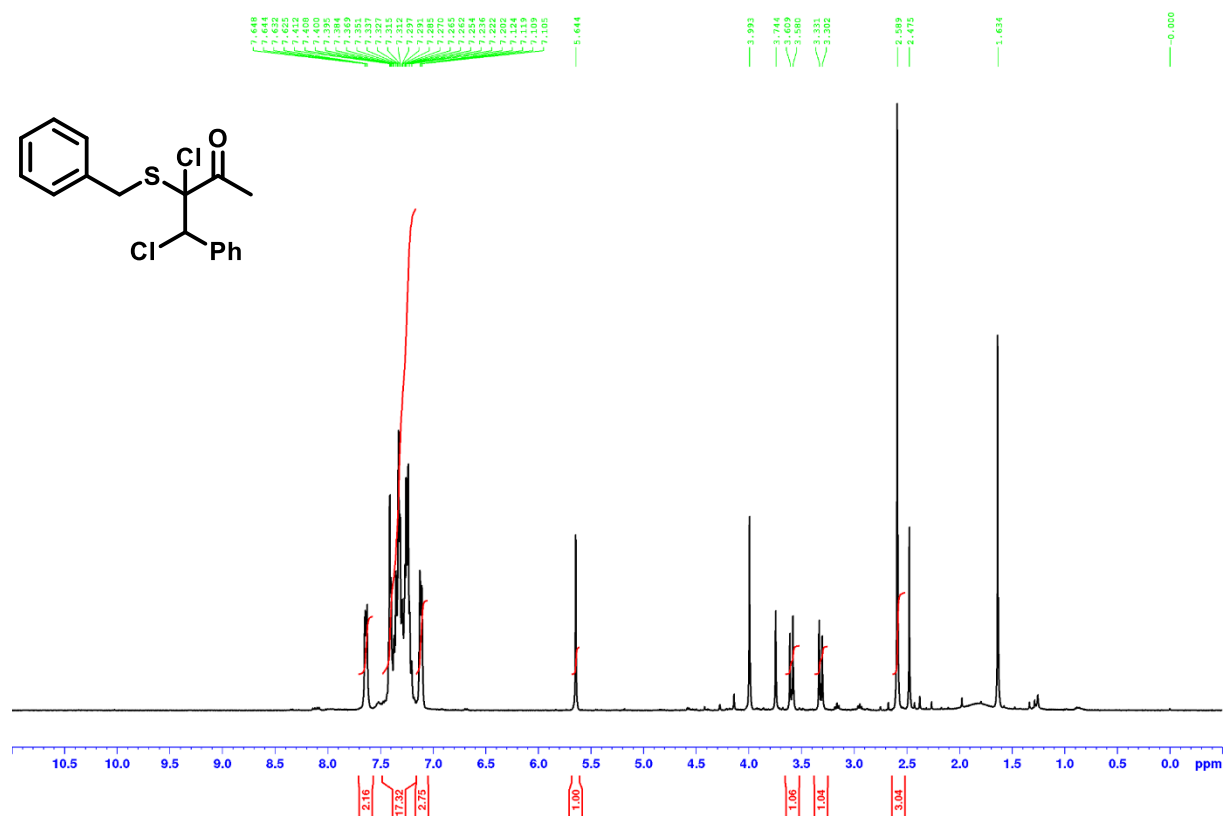


Figure S215: ¹H NMR (400 MHz, CDCl₃) spectrum of 12a/b after storage at room temperature for 40 months.

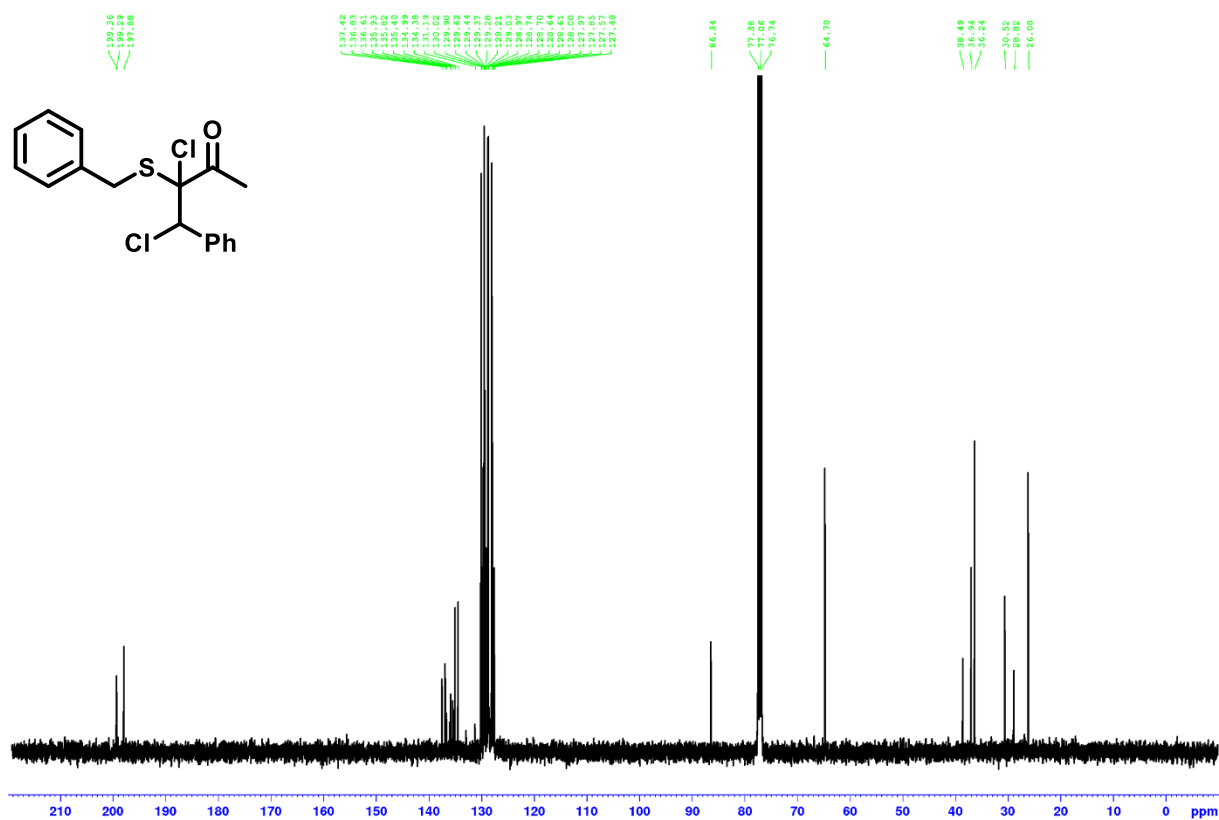


Figure S216: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **12a/b**.

(Z)-3-(Benzylthio)-4-phenylbut-3-en-2-one 11a²¹

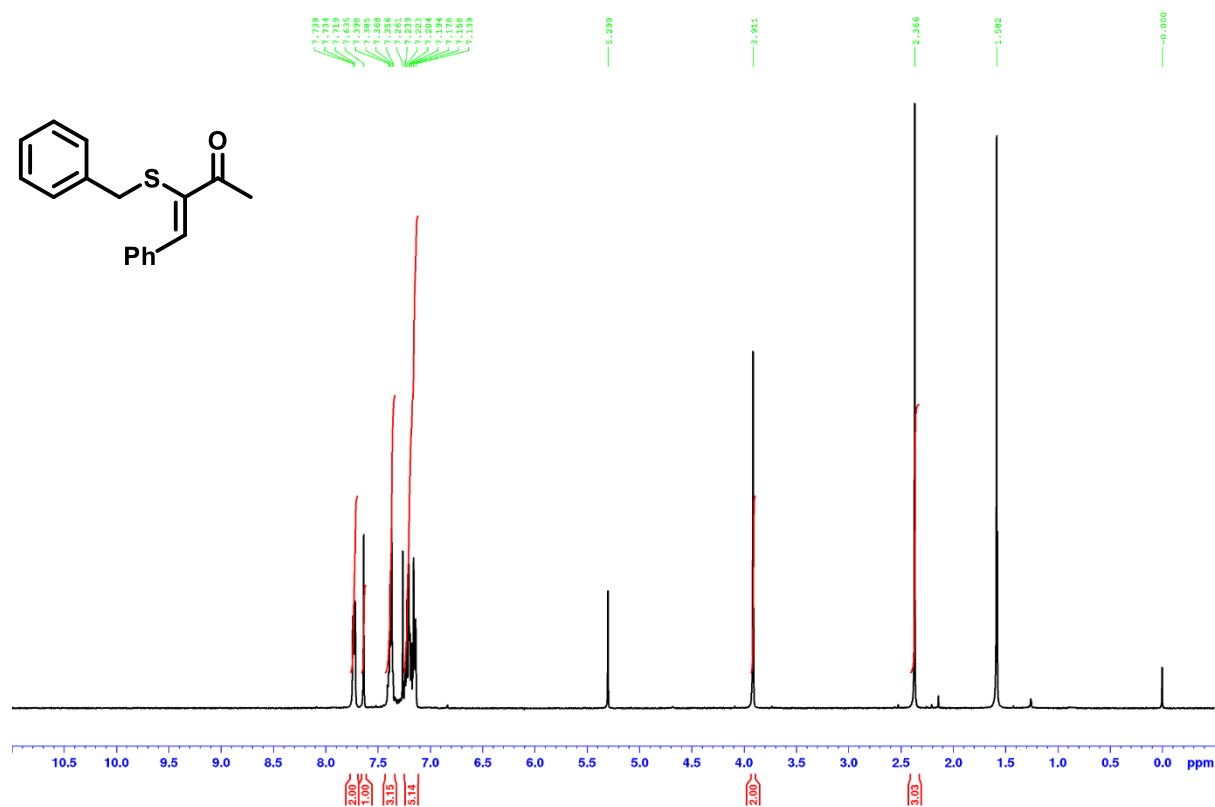


Figure S217: ¹H NMR (400 MHz, CDCl₃) spectrum of **11a**.

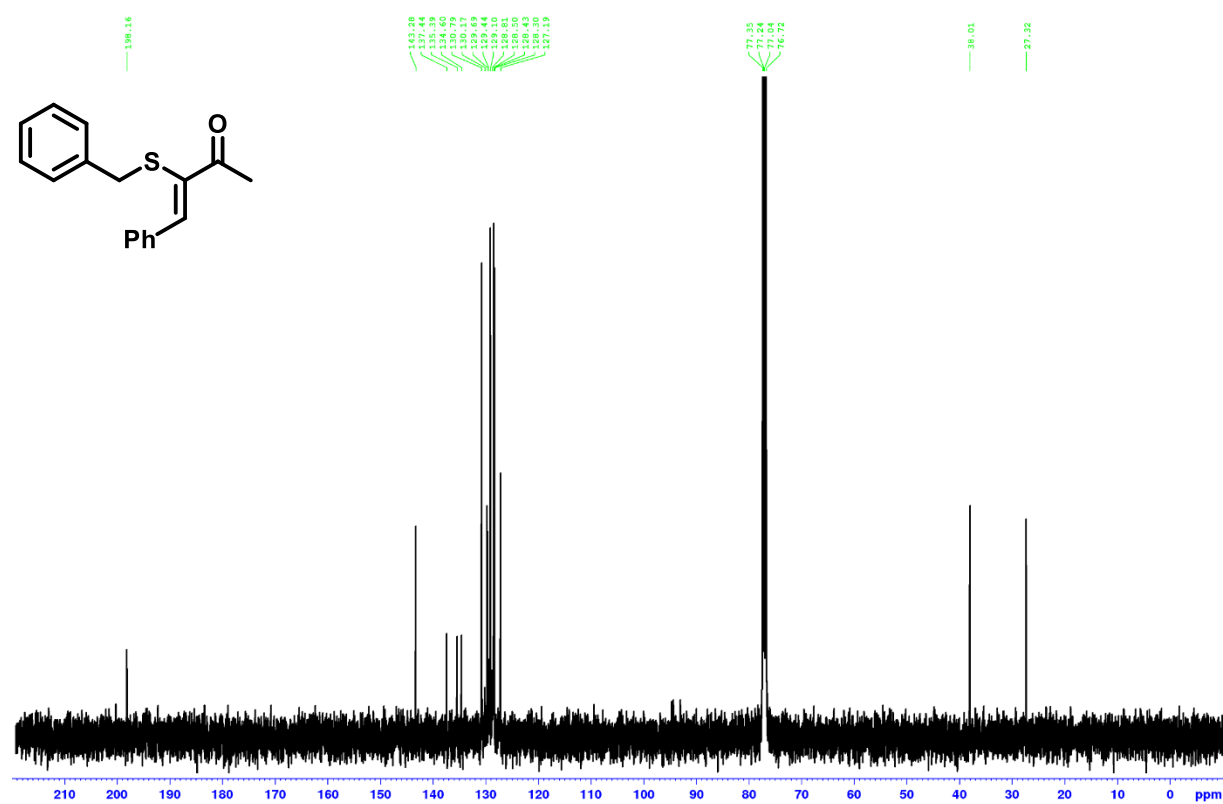


Figure S218: ¹³C NMR (100.6 MHz, CDCl₃) spectrum of **11a**.

1.12.7 Dichlorides:

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

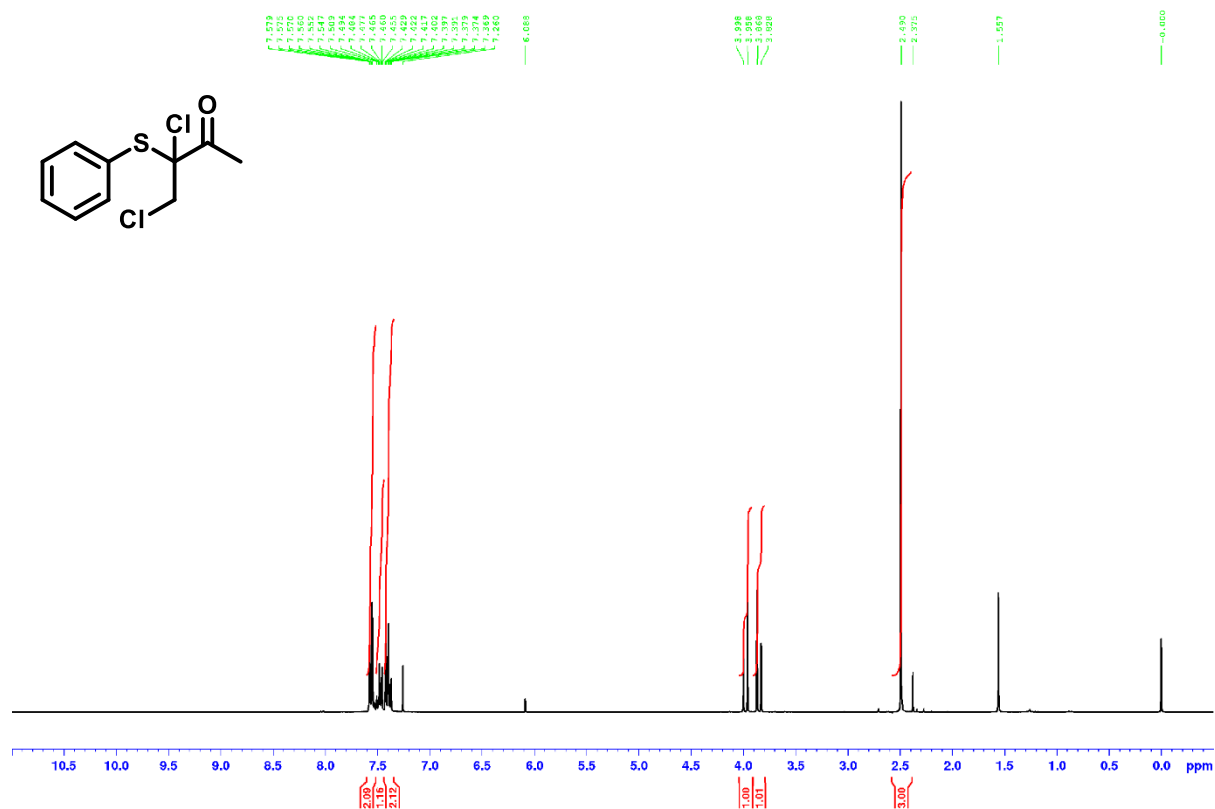


Figure S219: ¹H NMR (300 MHz, CDCl₃) spectrum of S53.

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

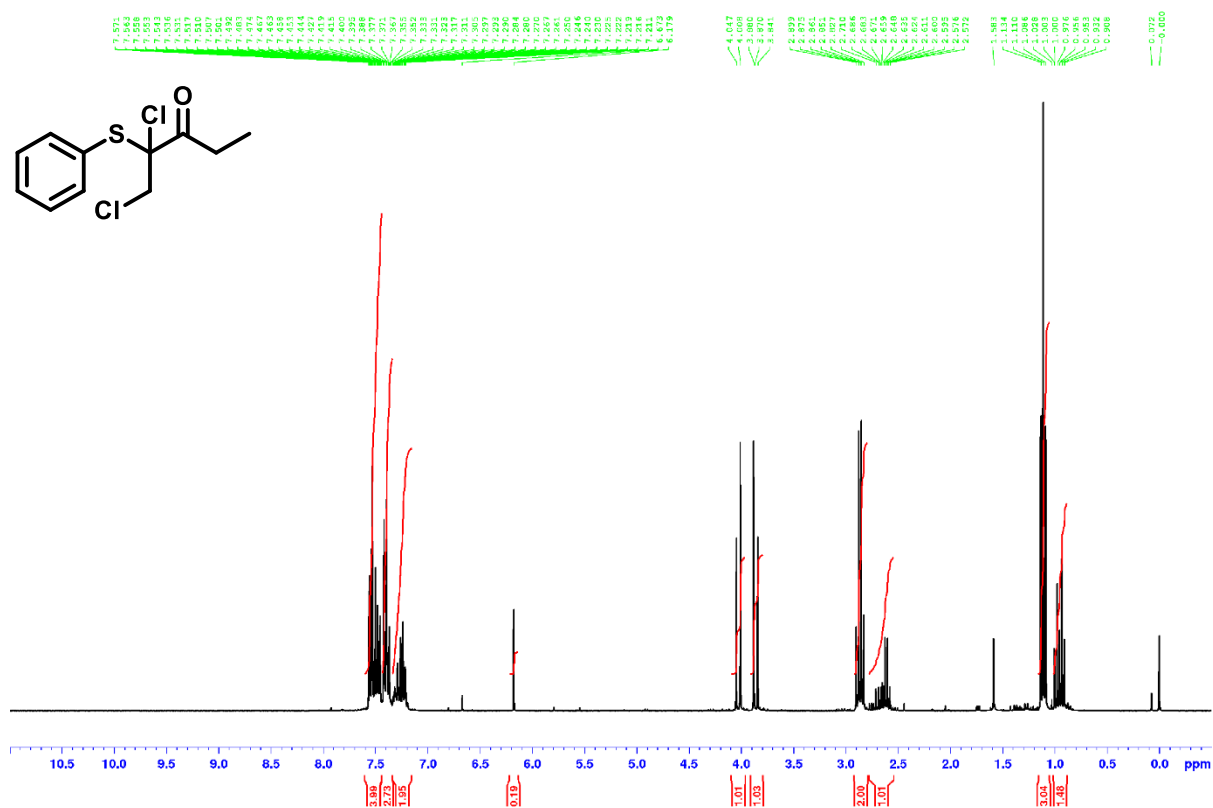


Figure S220: ¹H NMR (300 MHz, CDCl₃) spectrum of S54 (57%), Z-9b (32%), E-9b (<2%), S55 (11%).

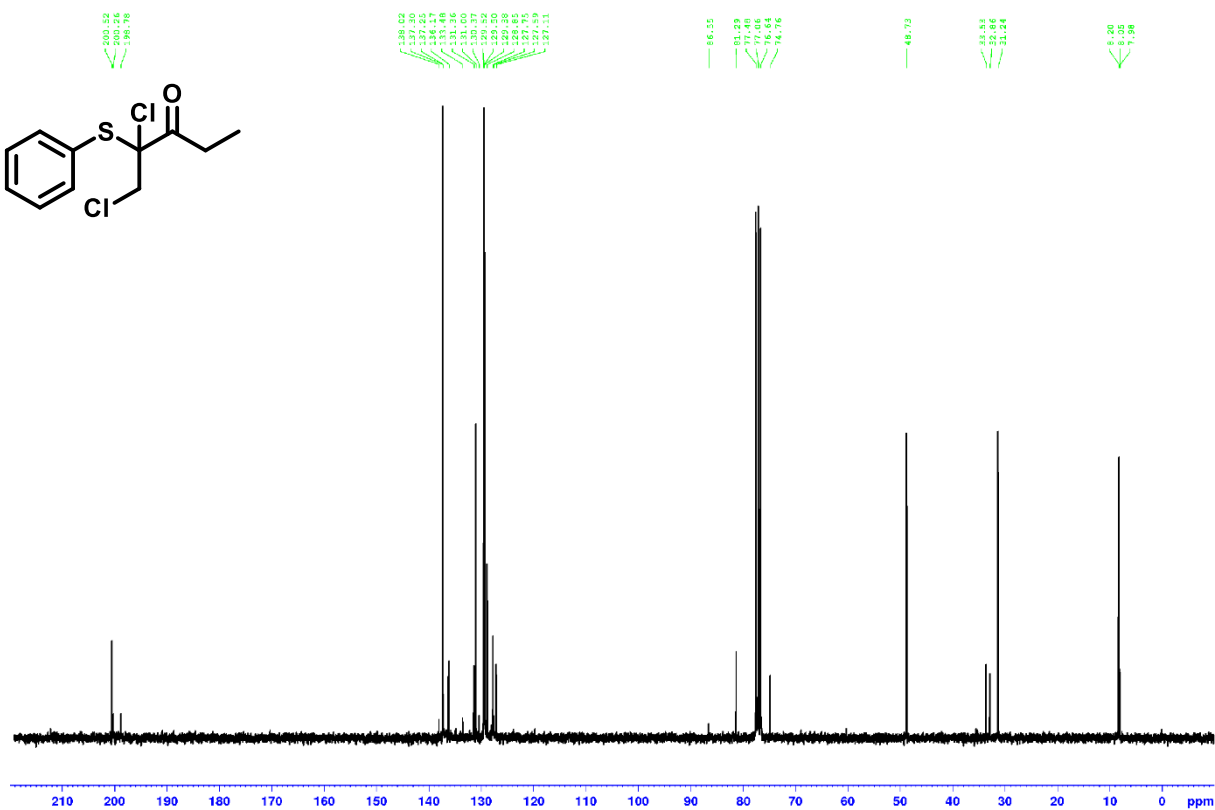


Figure S221: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of S54 (57%), Z-9b (32%), E-9b (<2%), S55 (11%).

(Z)-1-Chloro-2-(phenylthio)pent-1-en-3-one Z-9b

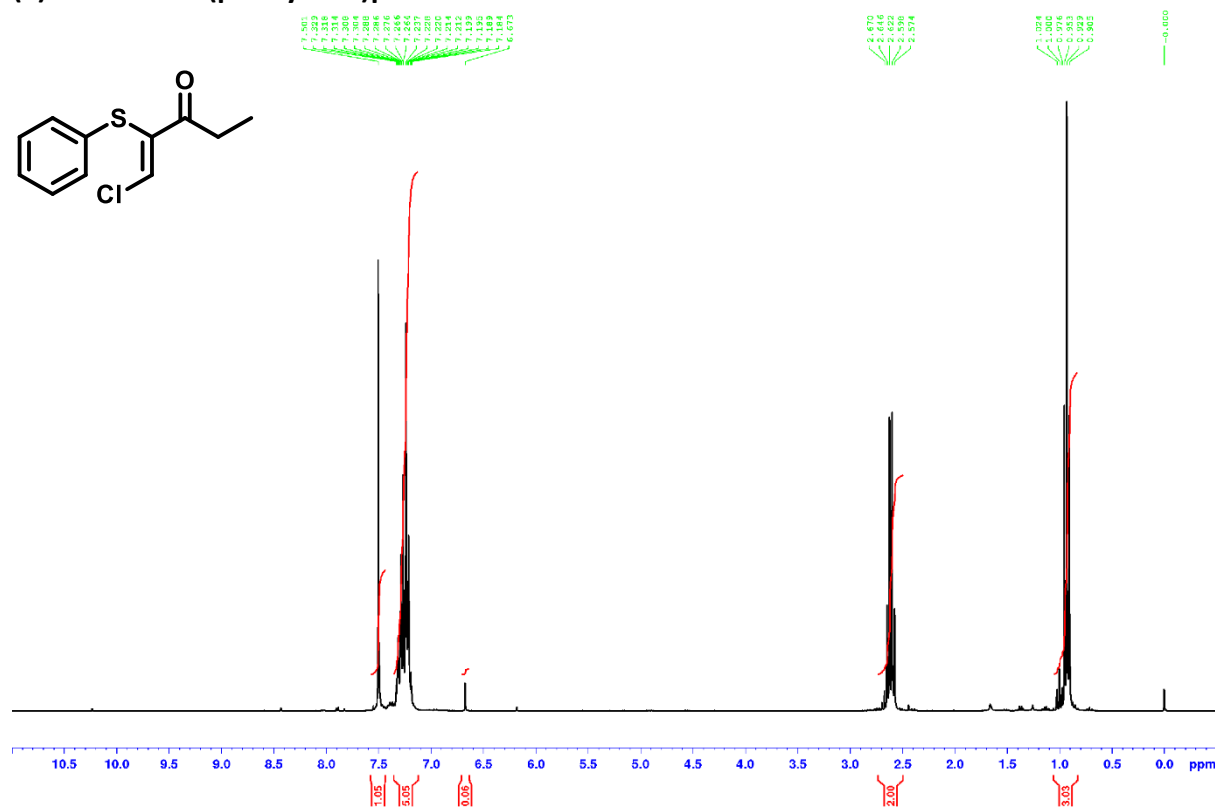


Figure S222: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-9b**.

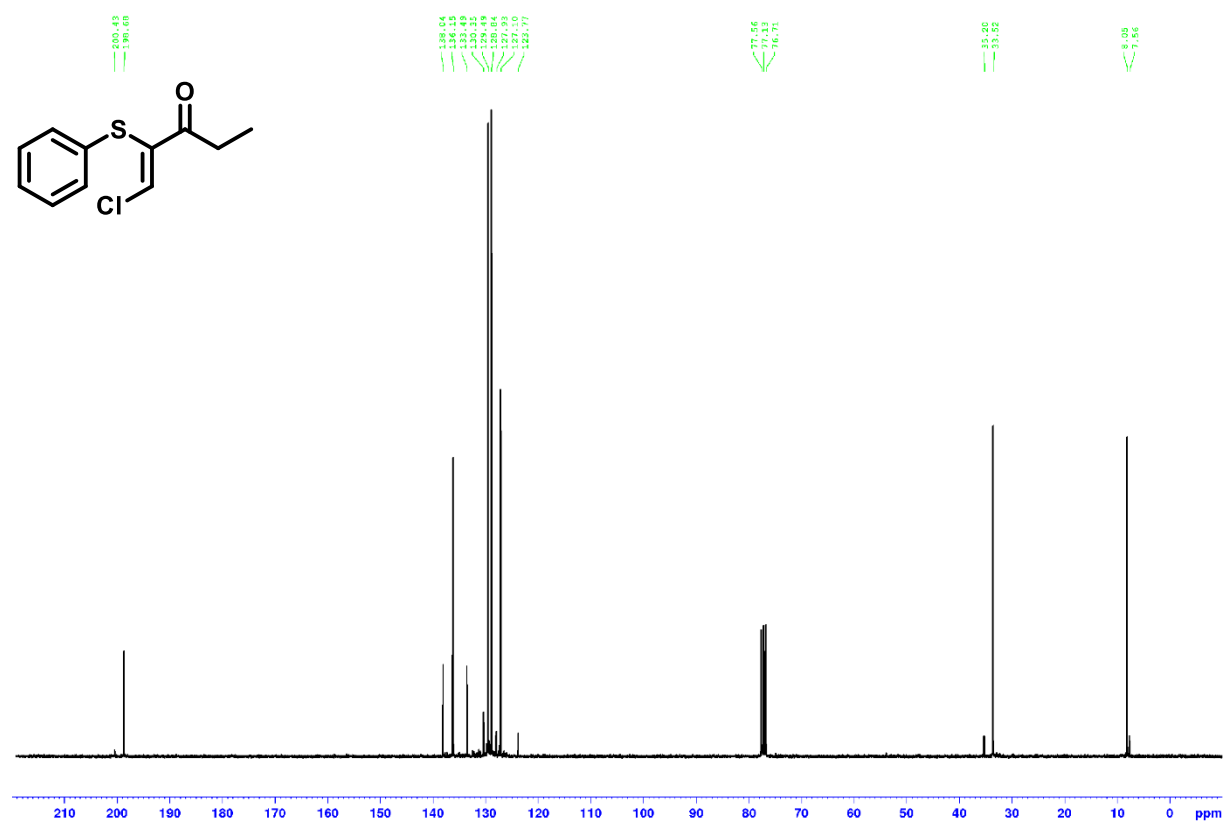
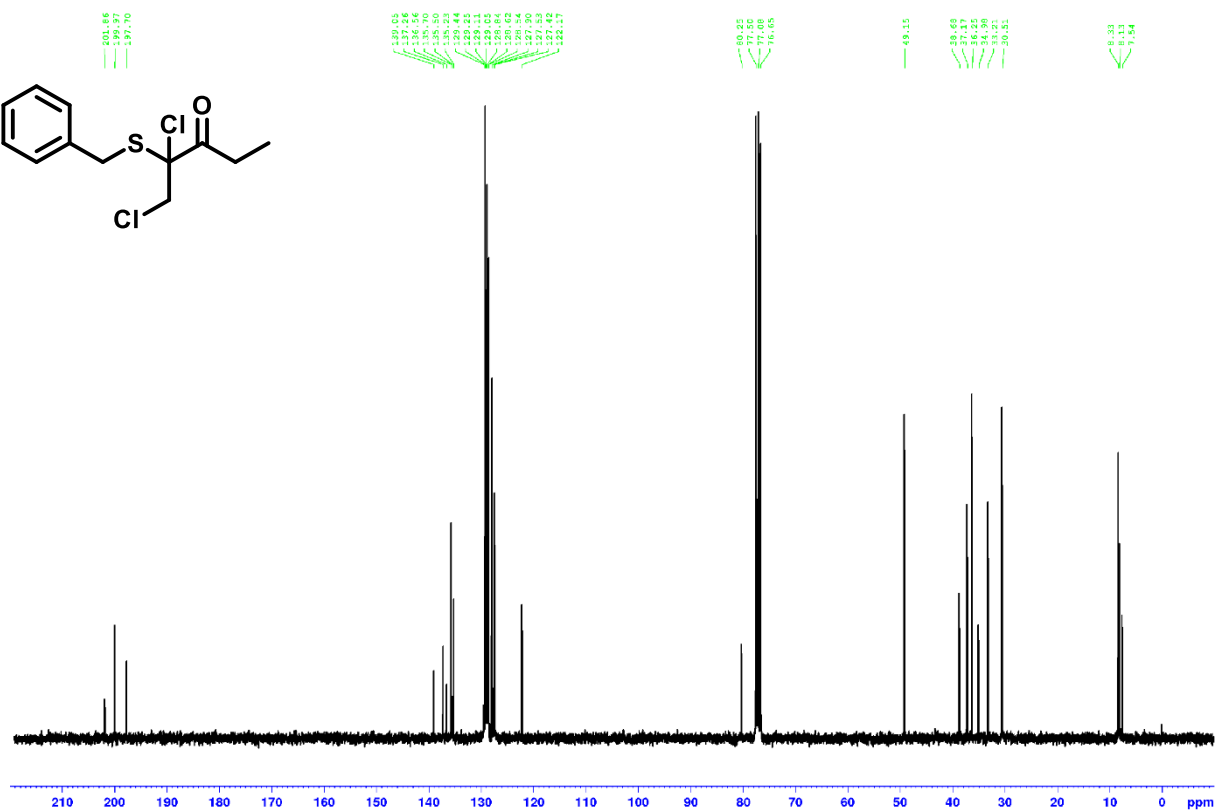
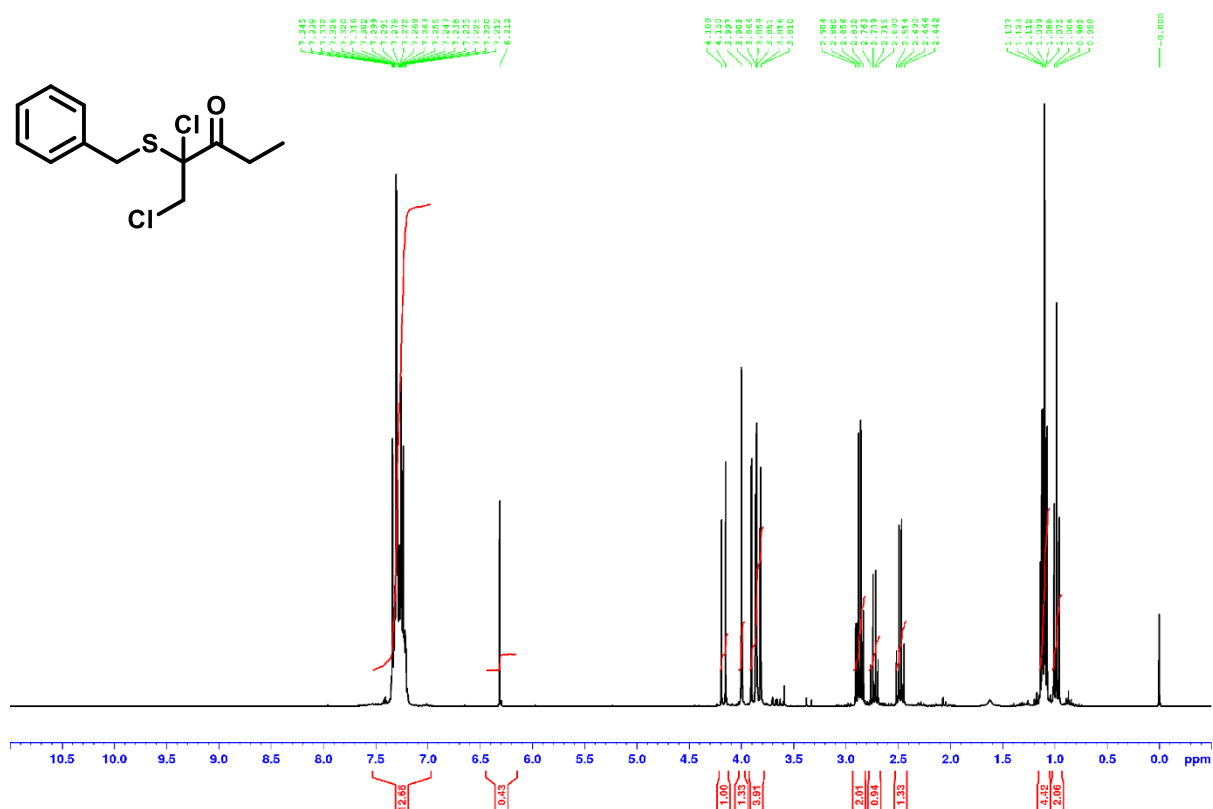


Figure S223: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-9b**.

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



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

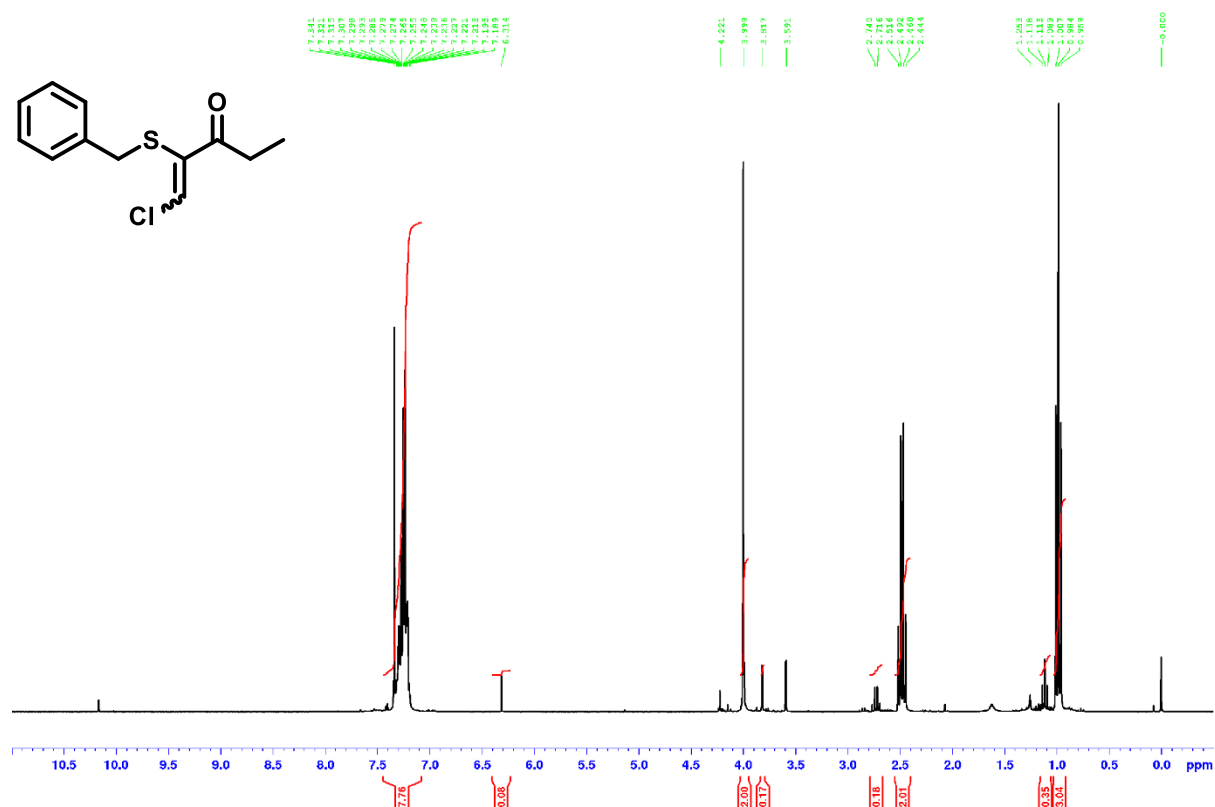


Figure S226: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-9c** and **E-9c**.

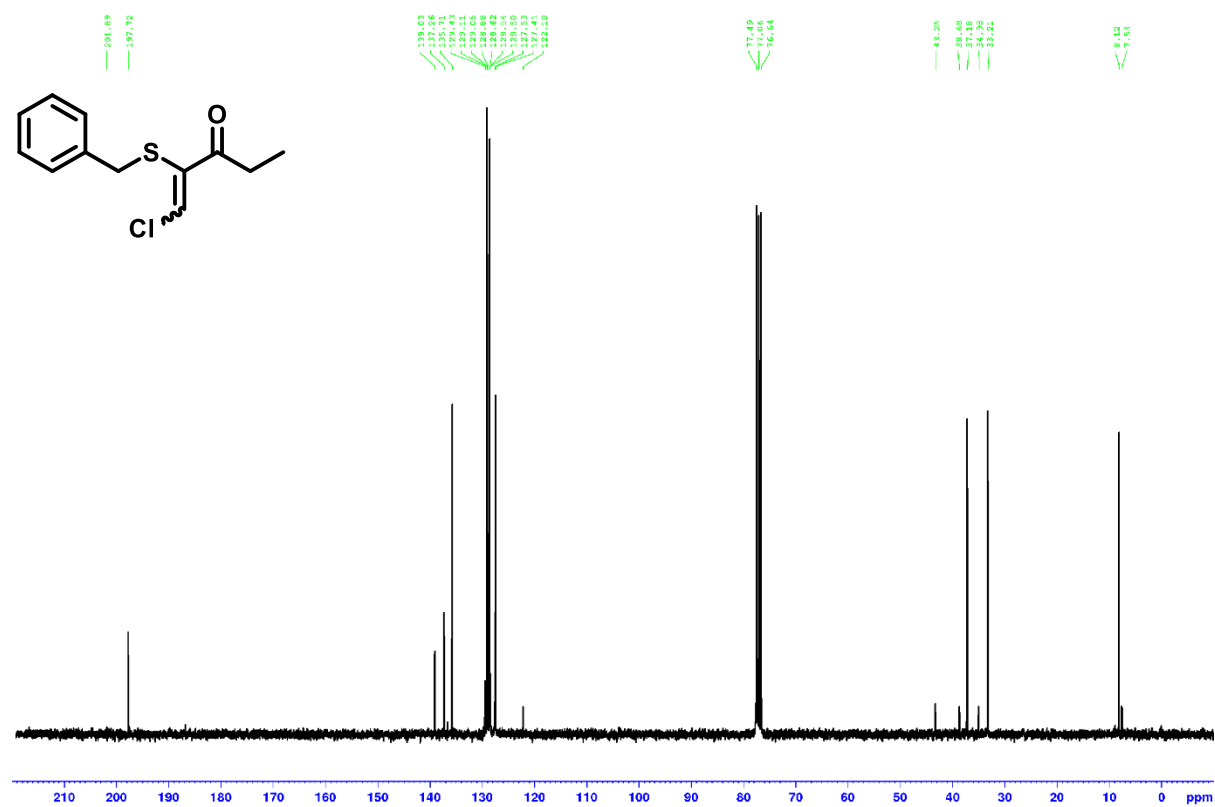
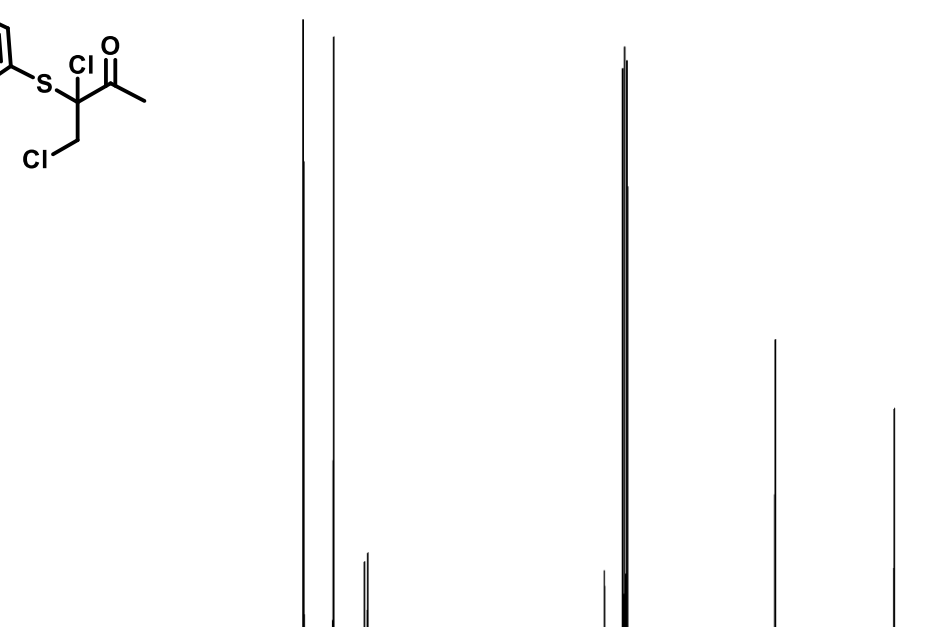


Figure S227: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-9c** and **E-9c**.

CC(=O)C(Cl)CSc1ccc(Br)cc1
CC(=O)C(Cl)C(Cl)Sc1ccc(Br)cc1

Chemical structure of 1-(4-bromophenyl)-2,2-dichloro-3-oxobutane is shown. The spectrum displays several peaks corresponding to the structure, with the following chemical shifts (ppm) labeled above the peaks:

- 197.02
- 138.02
- 138.45
- 132.89
- 132.72
- 126.03
- 126.22
- 80.21
- 77.62
- 77.69
- 76.60
- 48.20
- 25.45
- 0.00



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

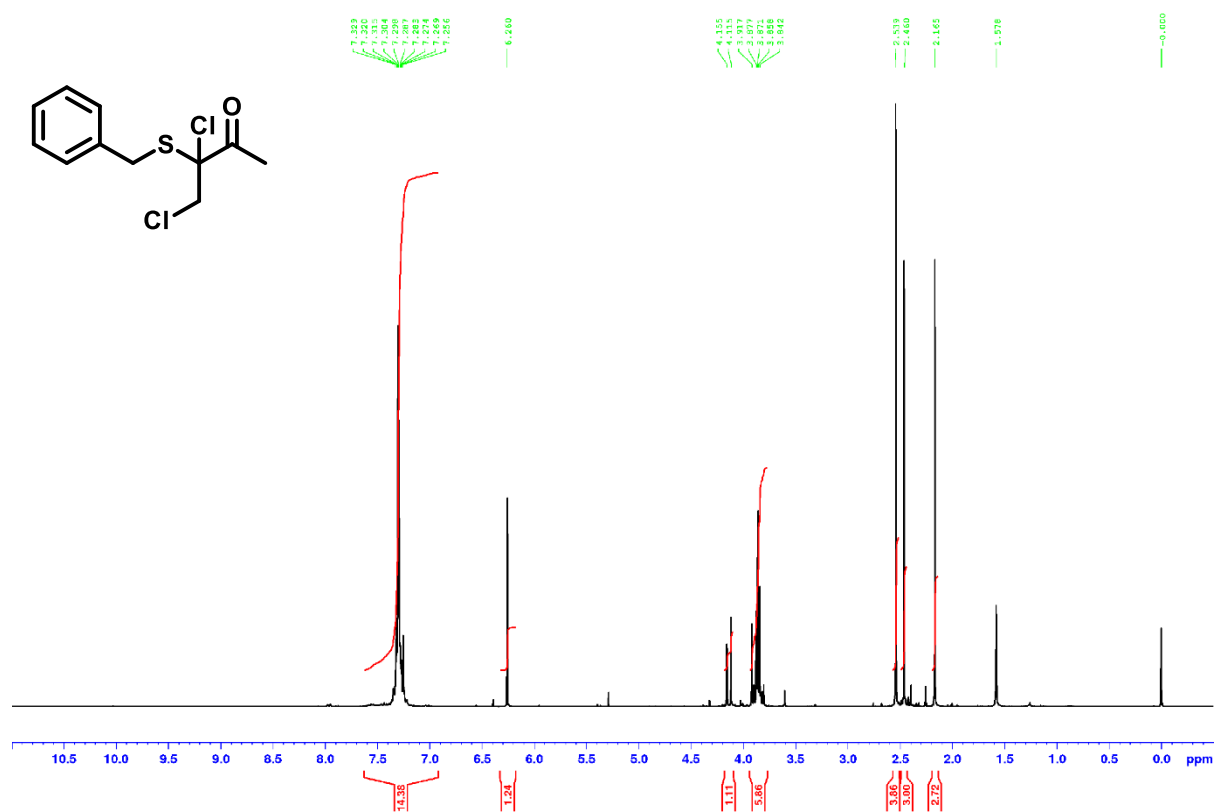


Figure S230: ¹H NMR (300 MHz, CDCl₃) spectrum of S60 (35%), Z-9e (32%), S61 (33%).

1.12.8 Zinc Chloride Catalysed Elimination to α -Sulfenyl- β -chloroenones:

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

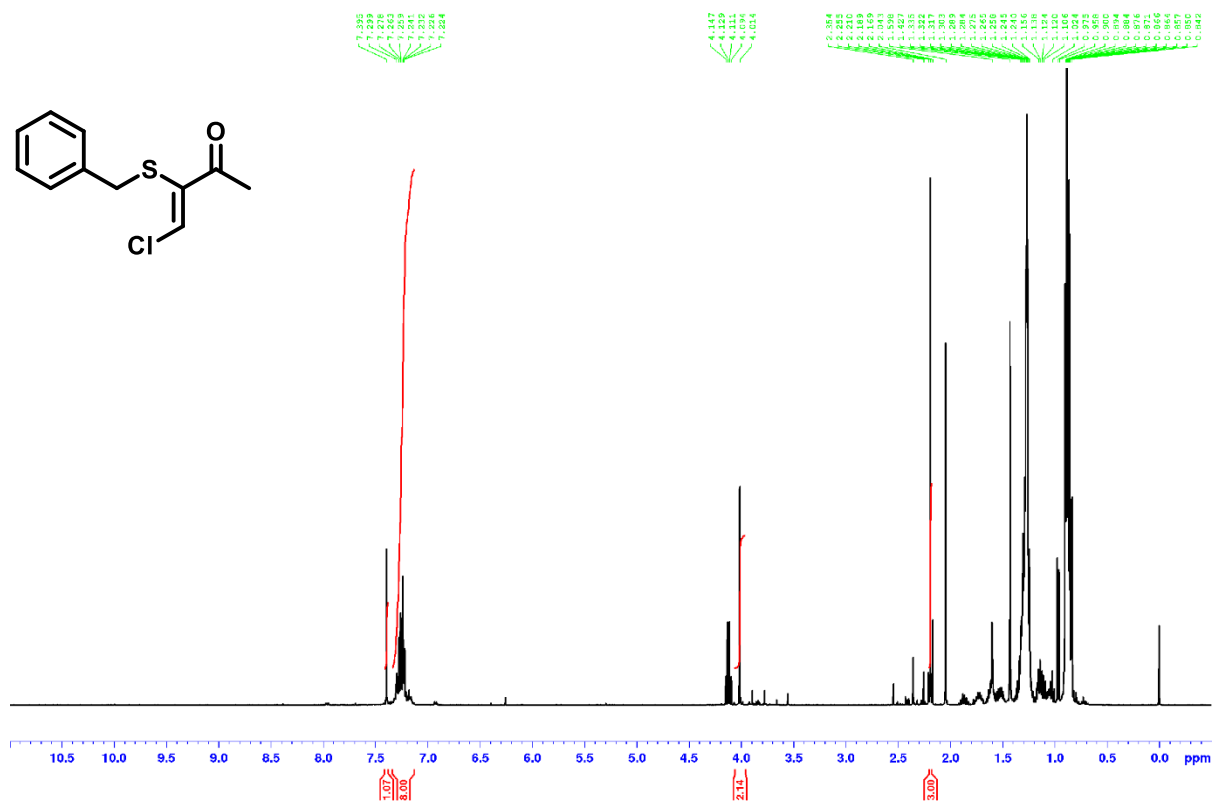


Figure S231: ¹H NMR (300 MHz, CDCl₃) spectrum of Z-9a.

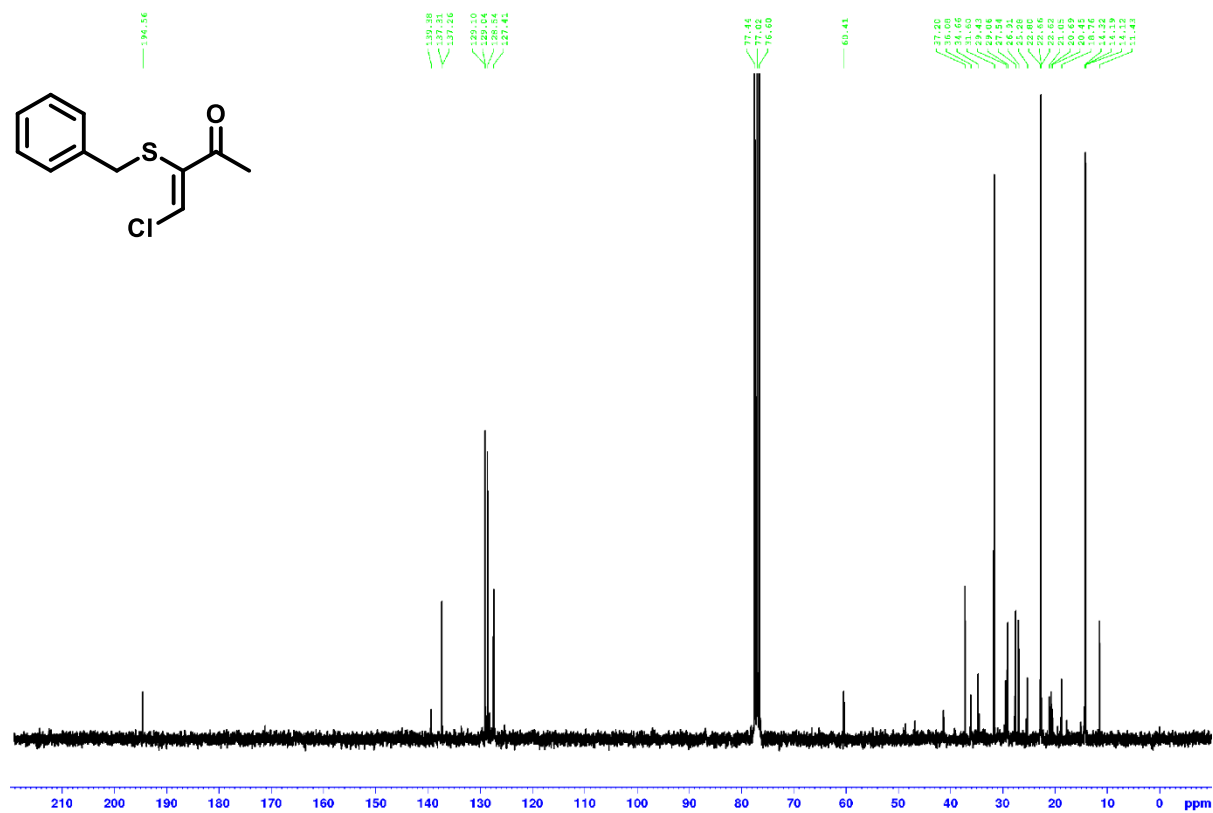


Figure S232: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of Z-9a.

1.12.9 Synthesis of Chalcones

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

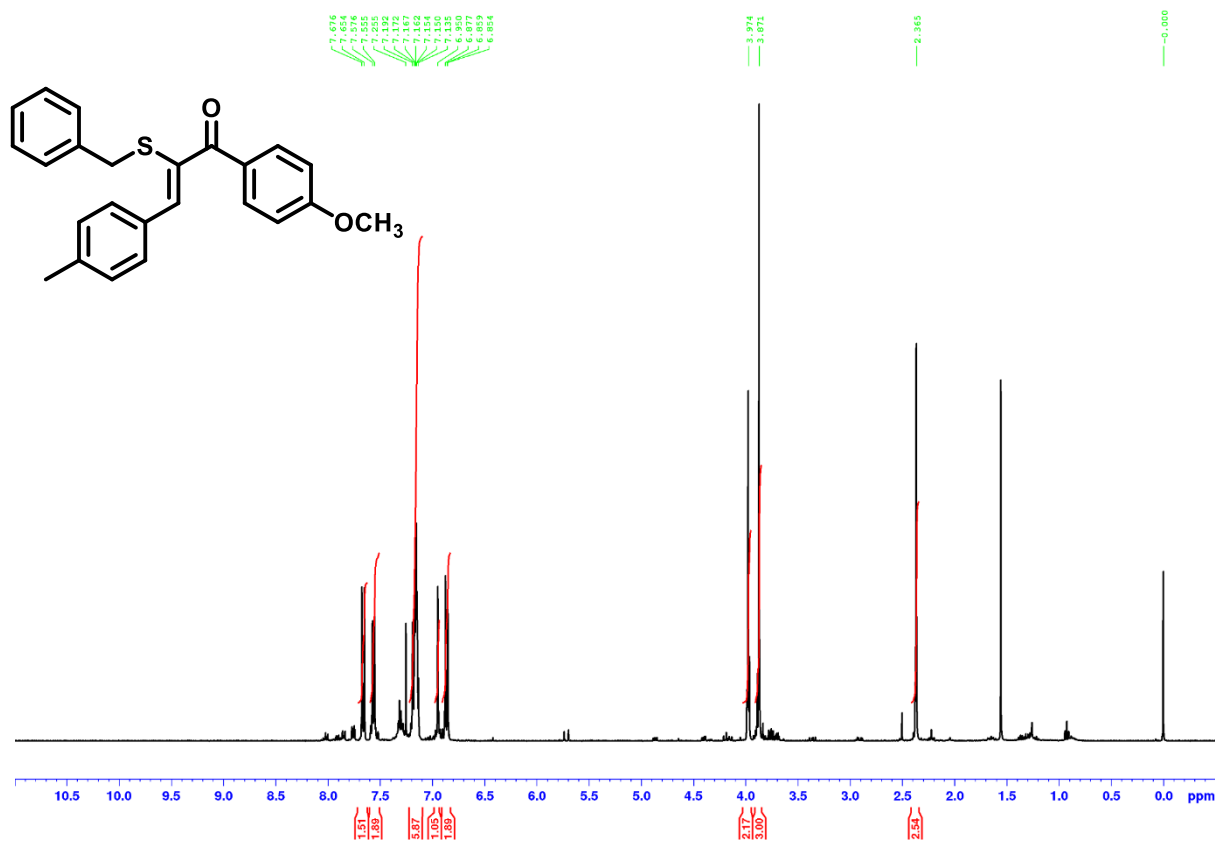


Figure S233: ¹H NMR (300 MHz, CDCl₃) spectrum of Z-14.

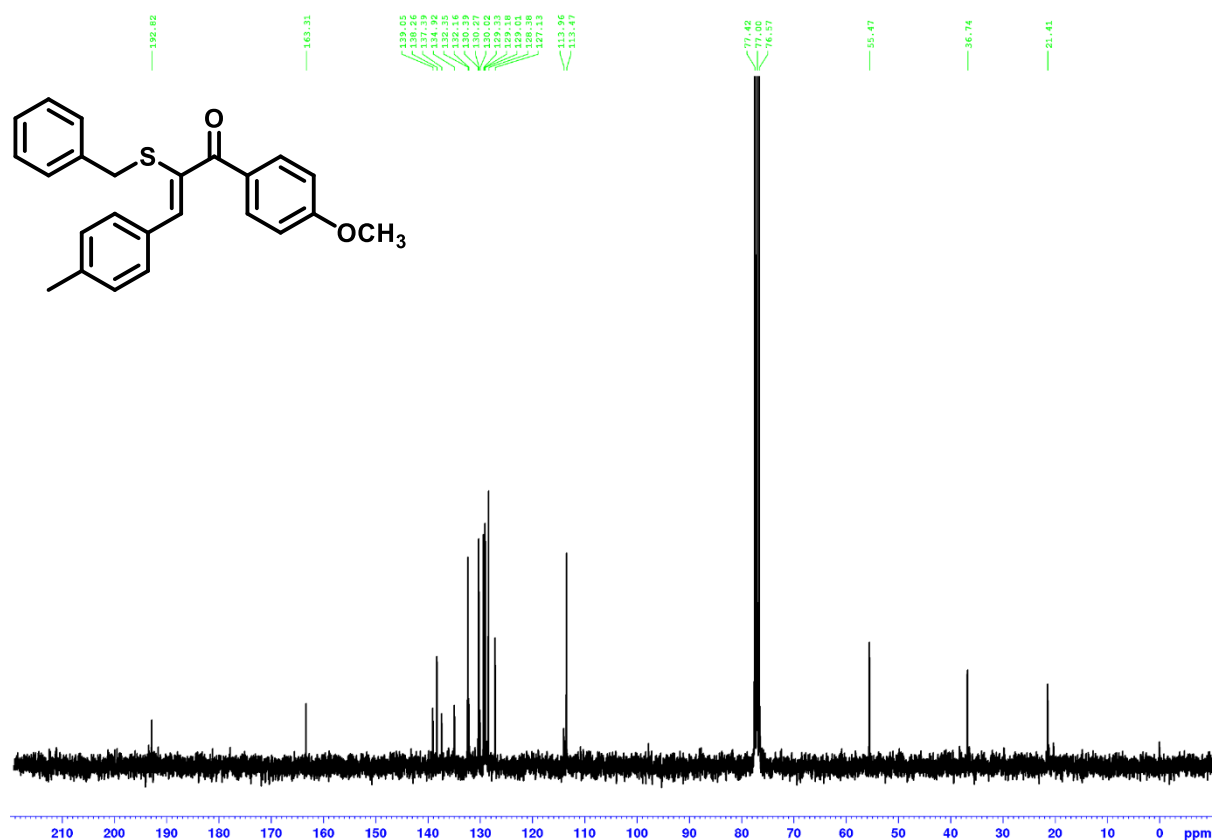


Figure S234: ^{13}C NMR (75.5 MHz, CDCl_3) spectrum of **Z-14**.

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

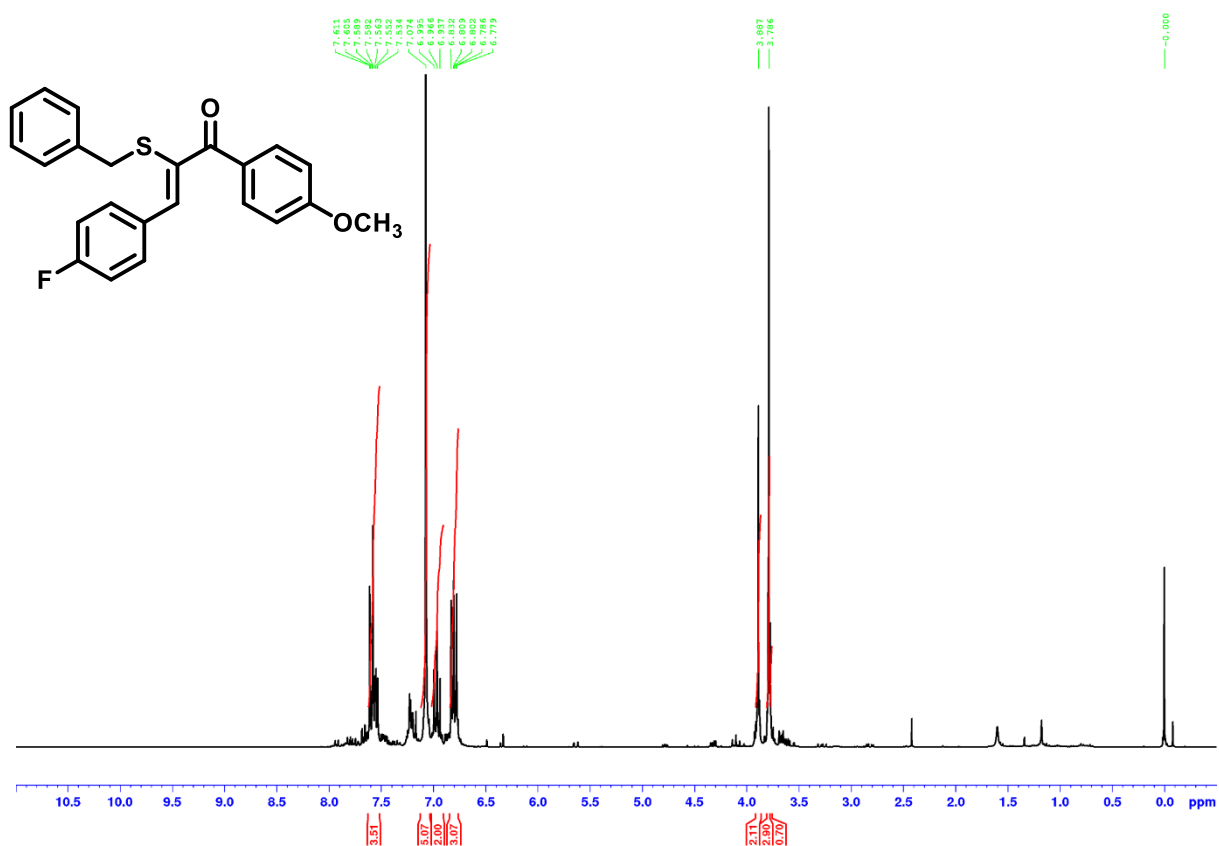


Figure S235: ¹H NMR (300 MHz, CDCl₃) spectrum of **Z-15**.

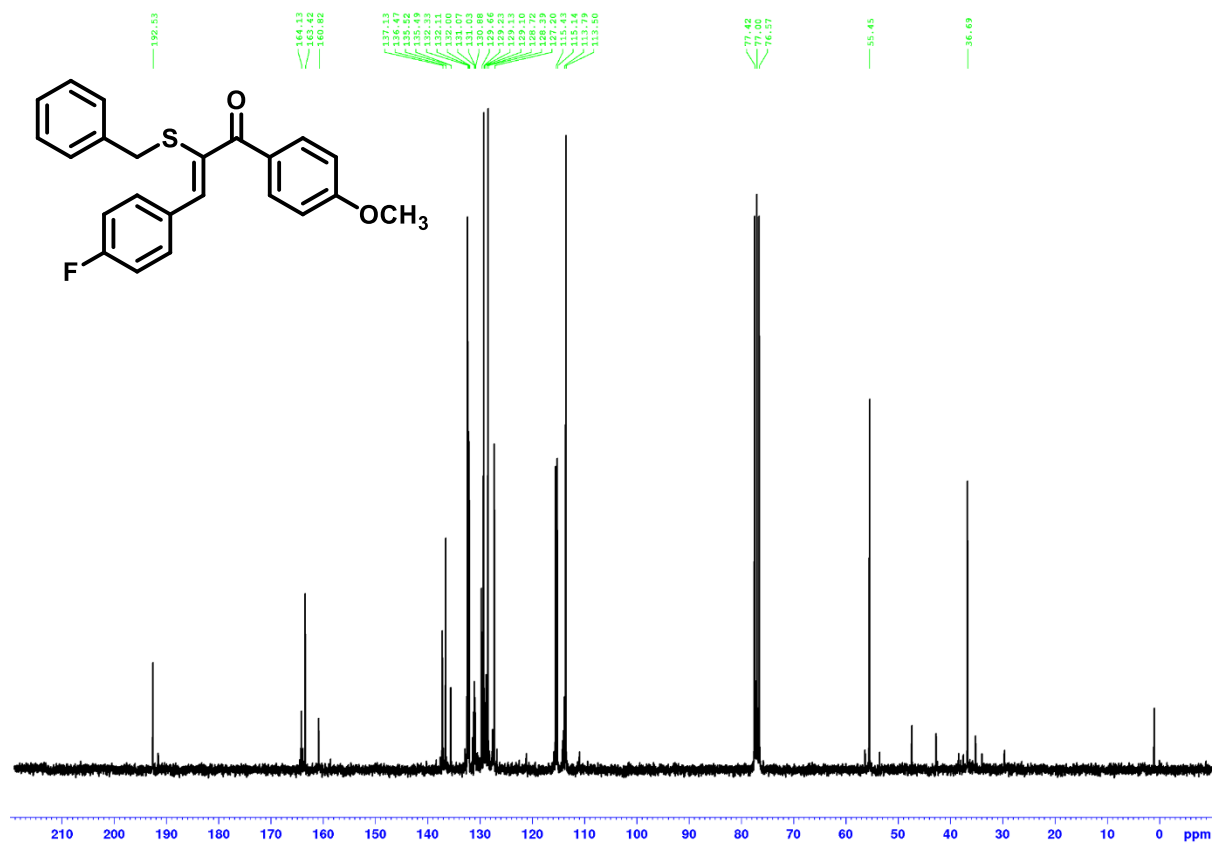


Figure S236: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-15**.

Chemical structure: COc1ccc(cc1)C(=O)C(=C(c2ccccc2)SCc3ccccc3)

¹H NMR spectrum (CDCl₃) showing peaks from 0 to 8 ppm. The spectrum includes aromatic signals (6.5-7.8 ppm), a methoxy singlet (3.8 ppm), and aliphatic signals (1.0-2.5 ppm). Integration values are shown below the peaks, and chemical shifts are listed above the peaks.

Chemical Shift (ppm)	Integration
7.712, 7.681, 7.633, 7.631, 7.571, 7.527, 7.511, 7.509, 7.455, 7.454, 6.943, 6.888, 6.843, 6.842, 6.574	1.92, 1.85, 2.29, 2.20, 1.15, 2.35
3.971, 3.869	3.00, 2.93
2.5, 1.5, 1.2, 0.0	-

Chemical structure: COc1ccc(cc1)C(=O)C(=C(c2ccccc2)SCc3ccccc3)

¹³C NMR spectrum (ppm):

- 192.62
- 163.41
- 137.33
- 137.22
- 135.96
- 135.95
- 135.88
- 135.27
- 135.25
- 135.21
- 135.13
- 135.00
- 130.90
- 130.73
- 129.73
- 129.29
- 129.13
- 129.11
- 128.98
- 128.72
- 128.65
- 128.52
- 128.25
- 128.18
- 128.16
- 127.17
- 113.82
- 113.51
- 55.46
- 36.72

264

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

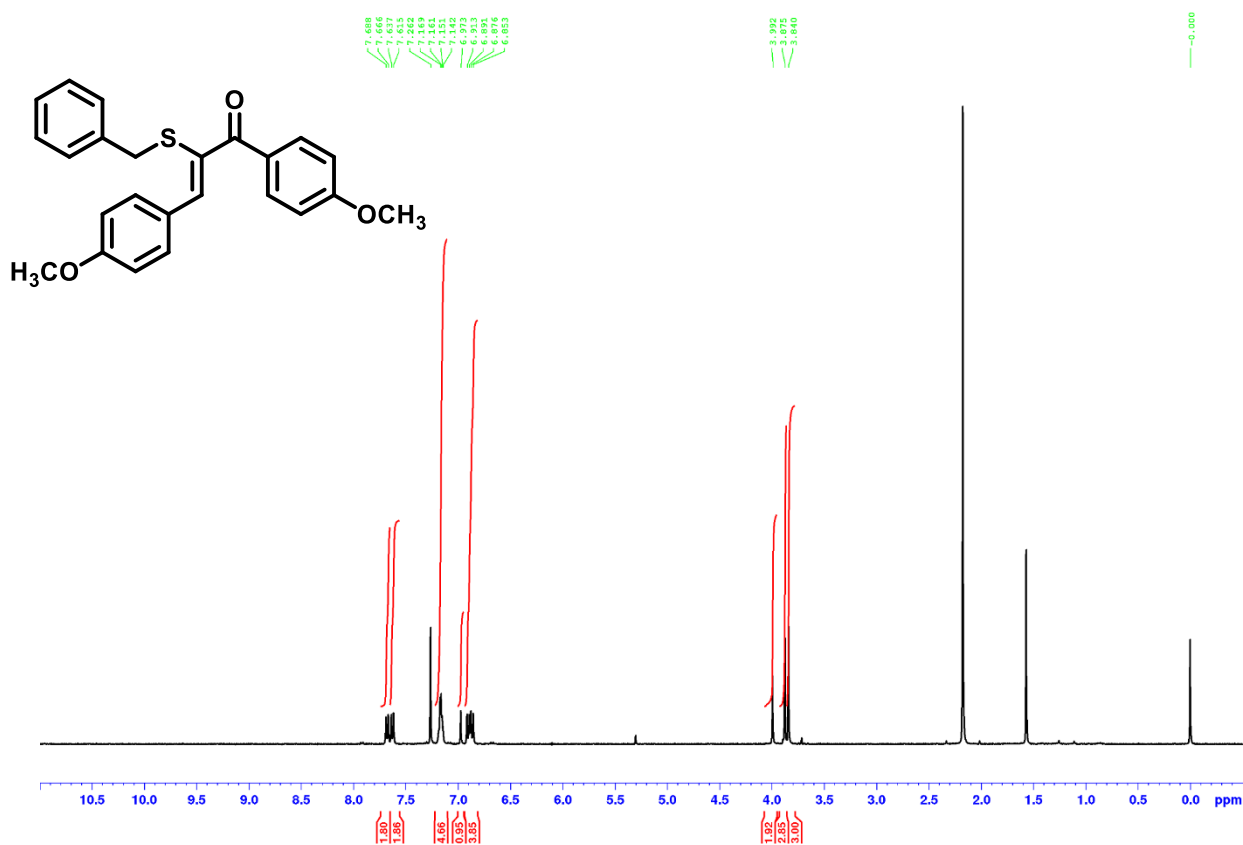


Figure S239: ^1H NMR (400 MHz, CDCl_3) spectrum of **Z-17**.

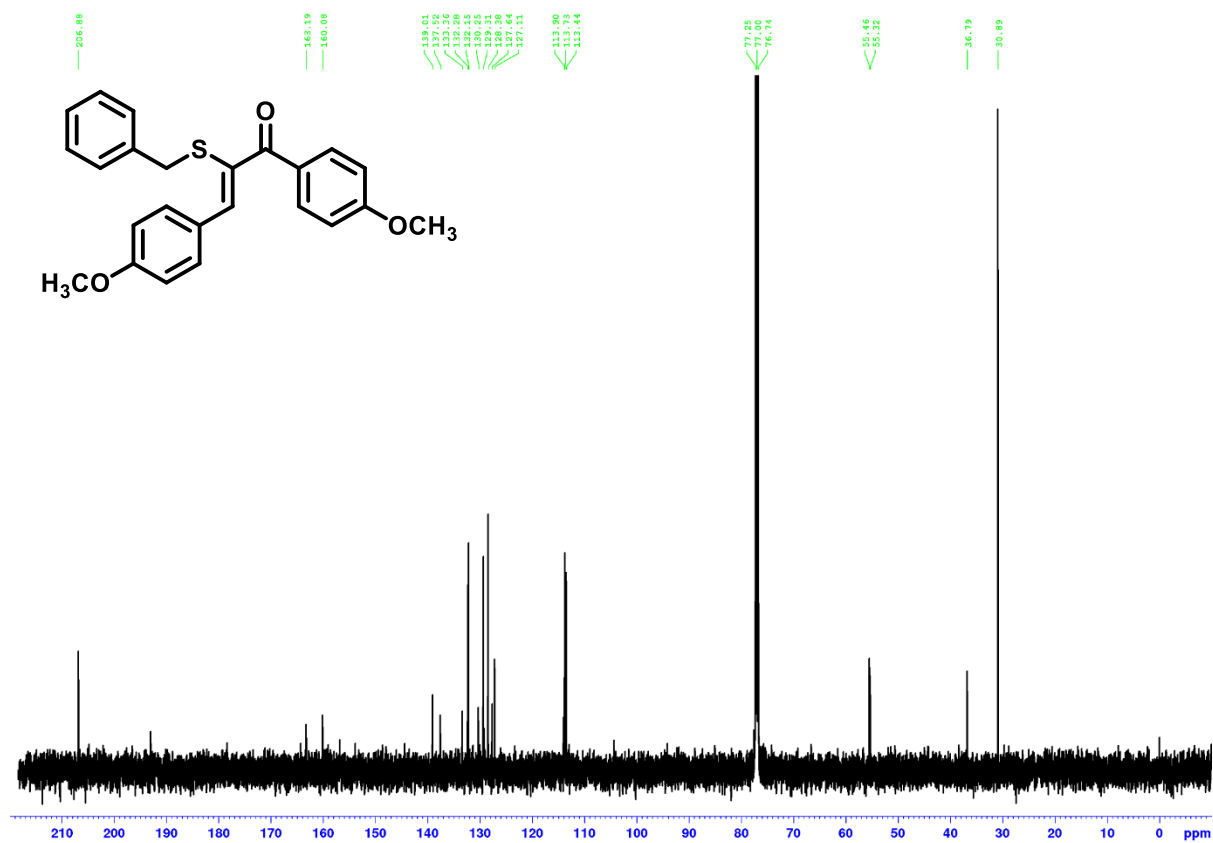


Figure S240: ^{13}C NMR (75.5 MHz, CDCl_3) spectrum of **Z-17**.

¹H NMR Spectrum (CDCl₃)

Chemical Structure: 4-methoxy-2-((4-methoxyphenyl)thio)benzoic acid

Peak Data:

Chemical Shift (ppm)	Integration
7.728, 7.701, 7.696, 7.678, 7.670, 7.533, 7.520, 7.512, 7.170, 7.159, 7.135, 7.130, 6.880, 6.865, 6.857, 6.849	1.95
7.520, 7.512, 7.170, 7.159, 7.135, 7.130	2.48
7.520, 7.512, 7.170, 7.159, 7.135, 7.130	5.97
7.520, 7.512, 7.170, 7.159, 7.135, 7.130	4.16
3.972, 3.871, 3.859	1.95
3.972, 3.871, 3.859	3.00
3.972, 3.871, 3.859	3.10
12.000	-

COc1ccc(cc1)C(=O)C(=C(c2ccc(OC)cc2)SCc3ccccc3)c4ccc(OC)cc4

13C NMR spectrum (CDCl₃) showing peaks at: 192.59, 165.45, 159.38, 137.28, 137.12, 136.42, 135.42, 133.76, 132.76, 132.59, 132.53, 128.39, 127.16, 122.06, 114.98, 114.74, 113.52, 77.42, 77.00, 76.57, 55.48, 55.49, 36.74 ppm.

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

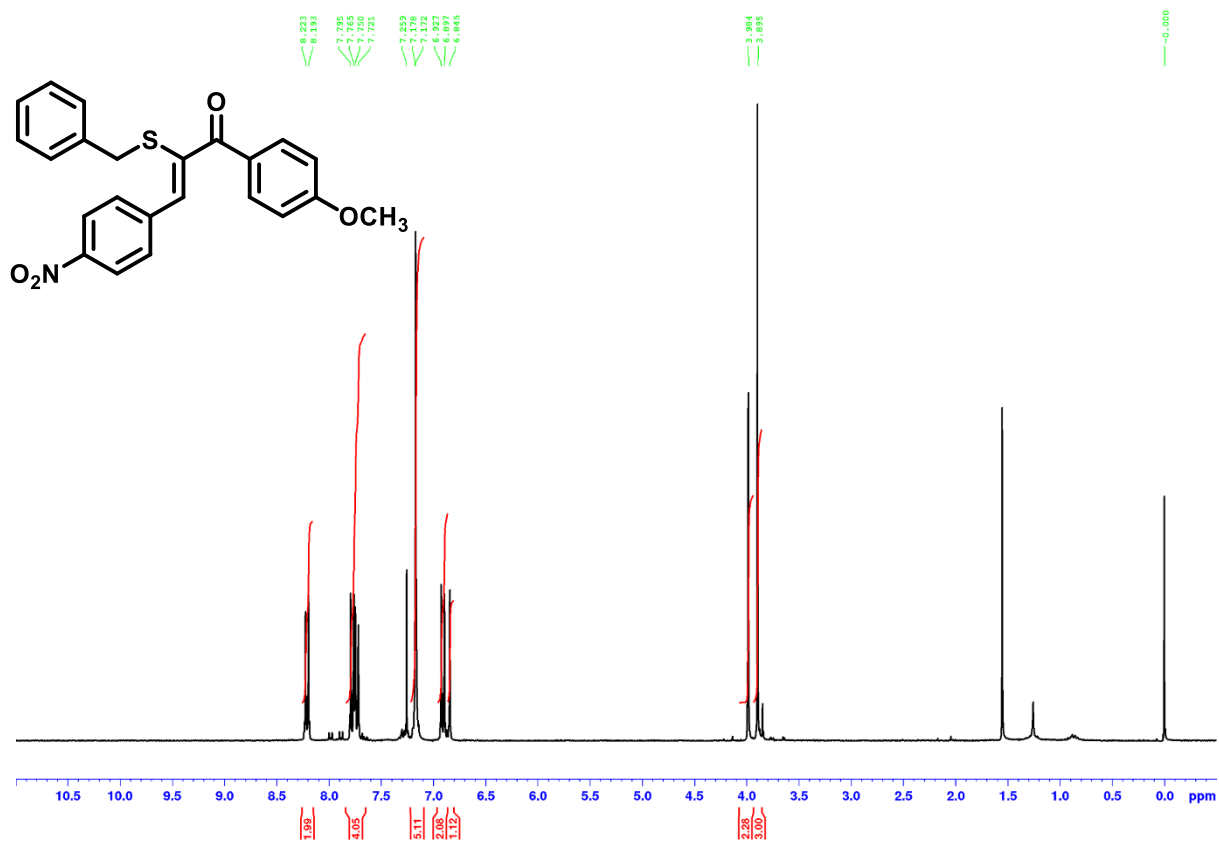
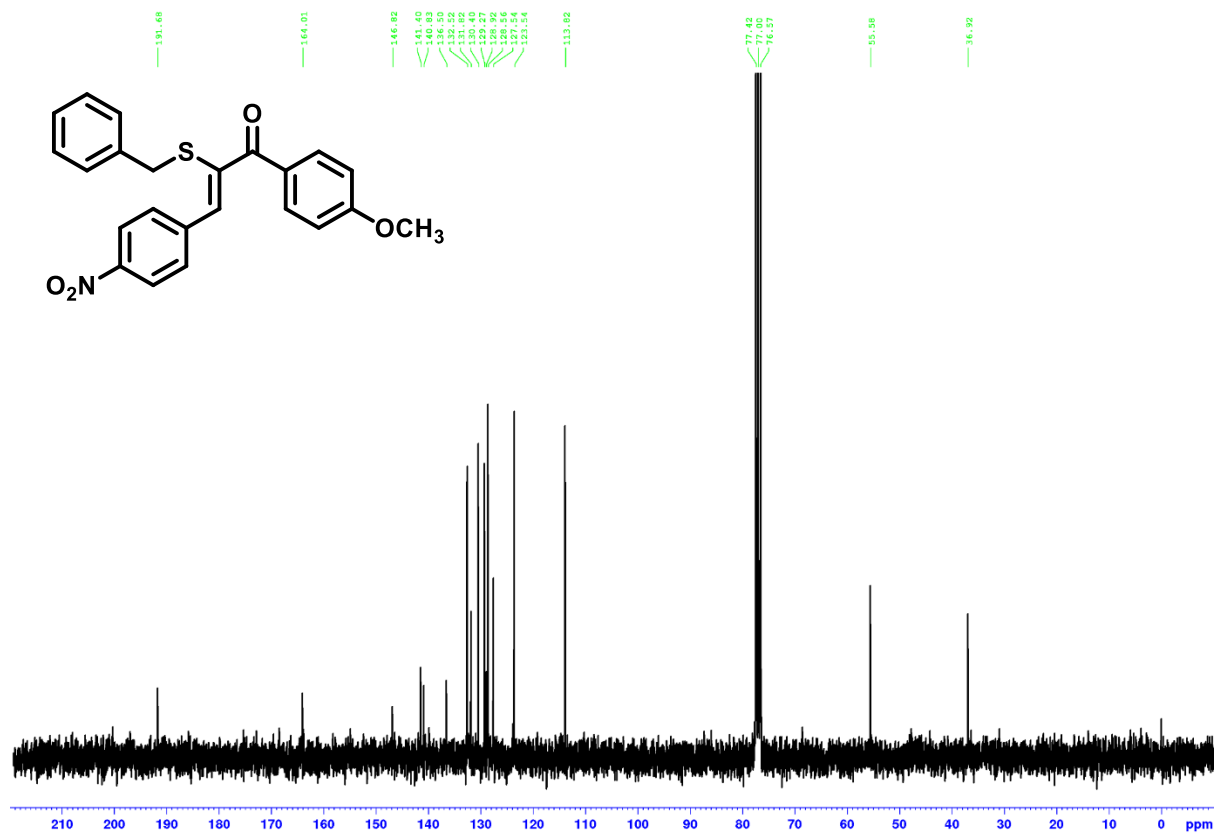


Figure S243: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-19**.



Chemical structure of (E)-4-(benzylthio)-1-(4-nitrophenyl)-2-methyl-1-buten-3-one:

CC(=C(C(=O)c1ccc(C)cc1)SCc2ccccc2)c3ccc([N+](=O)[O-])cc3

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.8-8.2 ppm) and aliphatic region (1.4-2.5 ppm). Integration values are shown below the peaks, and chemical shifts are listed above the peaks.

Chemical Shift (ppm)	Integration
8.217, 8.157, 8.119, 8.091, 8.072, 7.823, 7.803, 7.784, 7.640, 7.620, 7.585, 7.565, 7.260, 7.241, 7.221, 7.205, 7.180, 7.173, 7.157, 7.147, 7.127, 6.893, 6.876	2.00, 2.02, 1.97, 3.11, 1.07
4.037, 3.997, 3.975	2.23
2.436, 2.381	3.35
1.599, 1.423	
-0.009	

Chemical structure of (E)-1-(4-methylphenyl)-3-(4-nitrobenzyl)sulfonylethene:

Cc1ccc(cc1)C(=O)/C=C/CSc2ccc(cc2)[N+](=O)[O-]

¹³C NMR spectrum (CDCl₃) showing peaks (ppm):

- 146.91, 146.88, 146.85, 146.82, 146.55, 144.29, 144.26, 144.16, 143.78, 143.52, 143.46, 140.78, 139.52, 139.50, 138.74, 138.72, 138.62, 138.55, 138.53, 138.51, 138.50, 138.48, 138.47, 138.46, 138.45, 138.44, 138.43, 138.42, 138.41, 138.40, 138.39, 138.38, 138.37, 138.36, 138.35, 138.34, 138.33, 138.32, 138.31, 138.30, 138.29, 138.28, 138.27, 138.26, 138.25, 138.24, 138.23, 138.22, 138.21, 138.20, 138.19, 138.18, 138.17, 138.16, 138.15, 138.14, 138.13, 138.12, 138.11, 138.10, 138.09, 138.08, 138.07, 138.06, 138.05, 138.04, 138.03, 138.02, 138.01, 137.99, 137.98, 137.97, 137.96, 137.95, 137.94, 137.93, 137.92, 137.91, 137.90, 137.89, 137.88, 137.87, 137.86, 137.85, 137.84, 137.83, 137.82, 137.81, 137.80, 137.79, 137.78, 137.77, 137.76, 137.75, 137.74, 137.73, 137.72, 137.71, 137.70, 137.69, 137.68, 137.67, 137.66, 137.65, 137.64, 137.63, 137.62, 137.61, 137.60, 137.59, 137.58, 137.57, 137.56, 137.55, 137.54, 137.53, 137.52, 137.51, 137.50, 137.49, 137.48, 137.47, 137.46, 137.45, 137.44, 137.43, 137.42, 137.41, 137.40, 137.39, 137.38, 137.37, 137.36, 137.35, 137.34, 137.33, 137.32, 137.31, 137.30, 137.29, 137.28, 137.27, 137.26, 137.25, 137.24, 137.23, 137.22, 137.21, 137.20, 137.19, 137.18, 137.17, 137.16, 137.15, 137.14, 137.13, 137.12, 137.11, 137.10, 137.09, 137.08, 137.07, 137.06, 137.05, 137.04, 137.03, 137.02, 137.01, 137.00, 136.99, 136.98, 136.97, 136.96, 136.95, 136.94, 136.93, 136.92, 136.91, 136.90, 136.89, 136.88, 136.87, 136.86, 136.85, 136.84, 136.83, 136.82, 136.81, 136.80, 136.79, 136.78, 136.77, 136.76, 136.75, 136.74, 136.73, 136.72, 136.71, 136.70, 136.69, 136.68, 136.67, 136.66, 136.65, 136.64, 136.63, 136.62, 136.61, 136.60, 136.59, 136.58, 136.57, 136.56, 136.55, 136.54, 136.53, 136.52, 136.51, 136.50, 136.49, 136.48, 136.47, 136.46, 136.45, 136.44, 136.43, 136.42, 136.41, 136.40, 136.39, 136.38, 136.37, 136.36, 136.35, 136.34, 136.33, 136.32, 136.31, 136.30, 136.29, 136.28, 136.27, 136.26, 136.25, 136.24, 136.23, 136.22, 136.21, 136.20, 136.19, 136.18, 136.17, 136.16, 136.15, 136.14, 136.13, 136.12, 136.11, 136.10, 136.09, 136.08, 136.07, 136.06, 136.05, 136.04, 136.03, 136.02, 136.01, 136.00, 135.99, 135.98, 135.97, 135.96, 135.95, 135.94, 135.93, 135.92, 135.91, 135.90, 135.89, 135.88, 135.87, 135.86, 135.85, 135.84, 135.83, 135.82, 135.81, 135.80, 135.79, 135.78, 135.77, 135.76, 135.75, 135.74, 135.73, 135.72, 135.71, 135.70, 135.69, 135.68, 135.67, 135.66, 135.65, 135.64, 135.63, 135.62, 135.61, 135.60, 135.59, 135.58, 135.57, 135.56, 135.55, 135.54, 135.53, 135.52, 135.51, 135.50, 135.49, 135.48, 135.47, 135.46, 135.45, 135.44, 135.43, 135.42, 135.41, 135.40, 135.39, 135.38, 135.37, 135.36, 135.35, 135.34, 135.33, 135.32, 135.31, 135.30, 135.29, 135.28, 135.27, 135.26, 135.25, 135.24, 135.23, 135.22, 135.21, 135.20, 135.19, 135.18, 135.17, 135.16, 135.15, 135.14, 135.13, 135.12, 135.11, 135.10, 135.09, 135.08, 135.07, 135.06, 135.05, 135.04, 135.03, 135.02, 135.01, 135.00, 134.99, 134.98, 134.97, 134.96, 134.95, 134.94, 134.93, 134.92, 134.91, 134.90, 134.89, 134.88, 134.87, 134.86, 134.85, 134.84, 134.83, 134.82, 134.81, 134.80, 134.79, 134.78, 134.77, 134.76, 134.75, 134.74, 134.73, 134.72, 134.71, 134.70, 134.69, 134.68, 134.67, 134.66, 134.65, 134.64, 134.63, 134.62, 134.61, 134.60, 134.59, 134.58, 134.57, 134.56, 134.55, 134.54, 134.53, 134.52, 134.51, 134.50, 134.49, 134.48, 134.47, 134.46, 134.45, 134.44, 134.43, 134.42, 134.41, 134.40, 134.39, 134.38, 134.37, 134.36, 134.35, 134.34, 134.33, 134.32, 134.31, 134.30, 134.29, 134.28, 134.27, 134.26, 134.25, 134.24, 134.23, 134.22, 134.21, 134.20, 134.19, 134.18, 134.17, 134.16, 134.15, 134.14, 134.13, 134.12, 134.11, 134.10, 134.09, 134.08, 134.07, 134.06, 134.05, 134.04, 134.03, 134.02, 134.01, 134.00, 133.99, 133.98, 133.97, 133.96, 133.95, 133.94, 133.93, 133.92, 133.91, 133.90, 133.89, 133.88, 133.87, 133.86, 133.85, 133.84, 133.83, 133.82, 133.81, 133.80, 133.79, 133.78

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4,4'-Dinitro-1,1'-biphenyl **37**²⁶

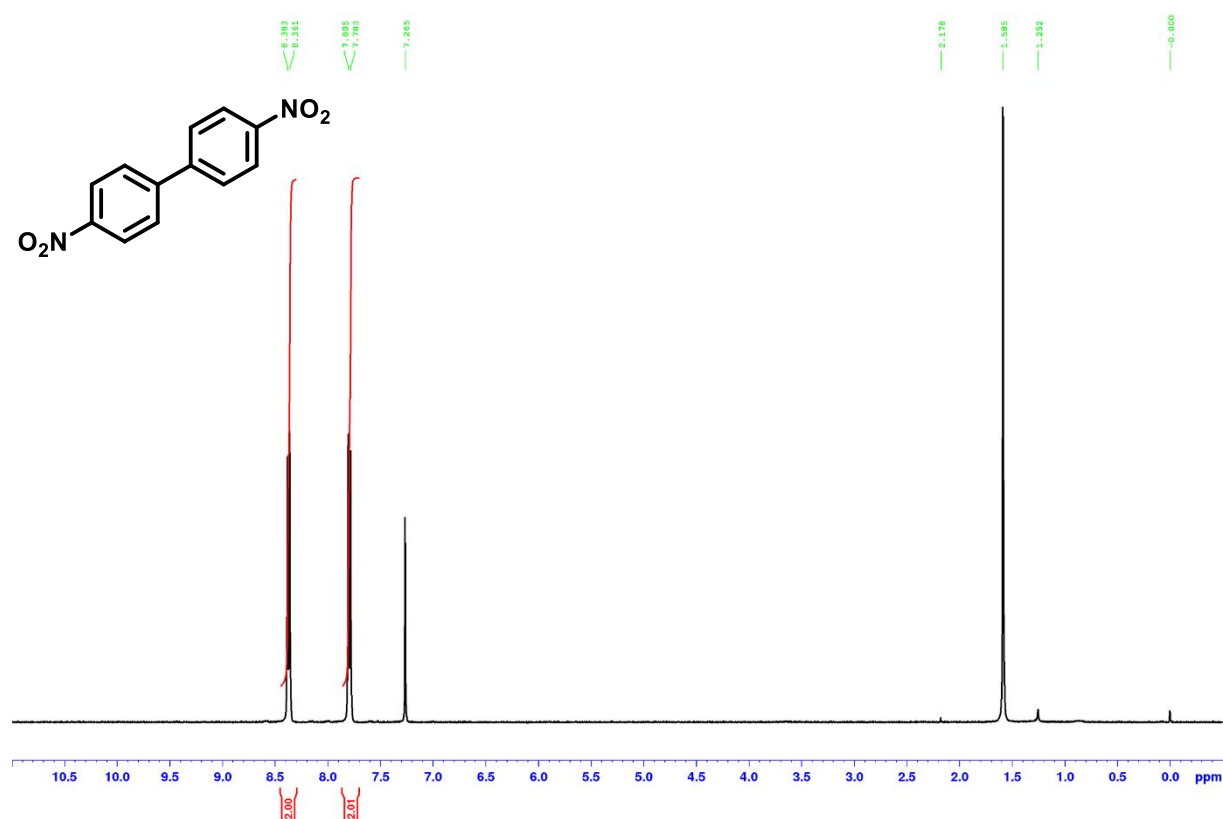


Figure S247: ¹H NMR (400 MHz, CDCl₃) spectrum of **37**²⁶

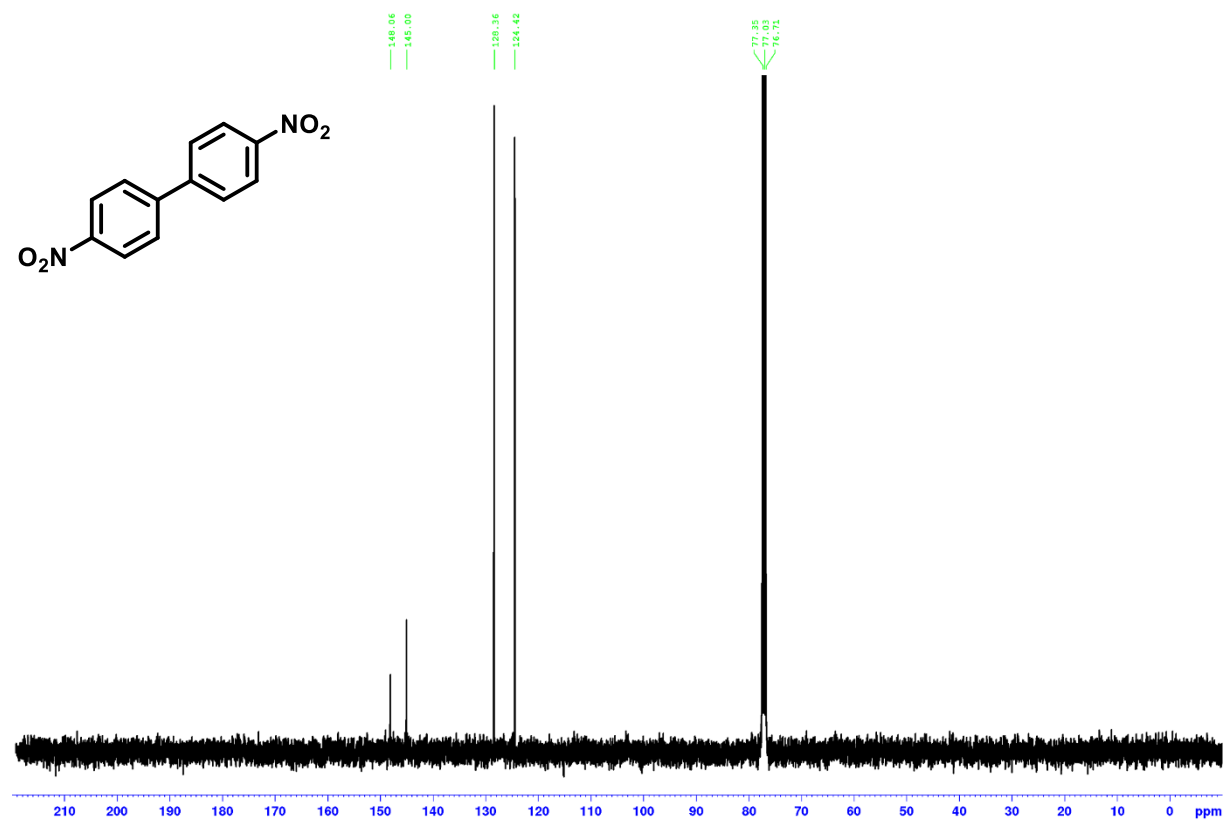


Figure S248: ¹³C NMR (100 MHz, CDCl₃) spectrum of **37**²⁶

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

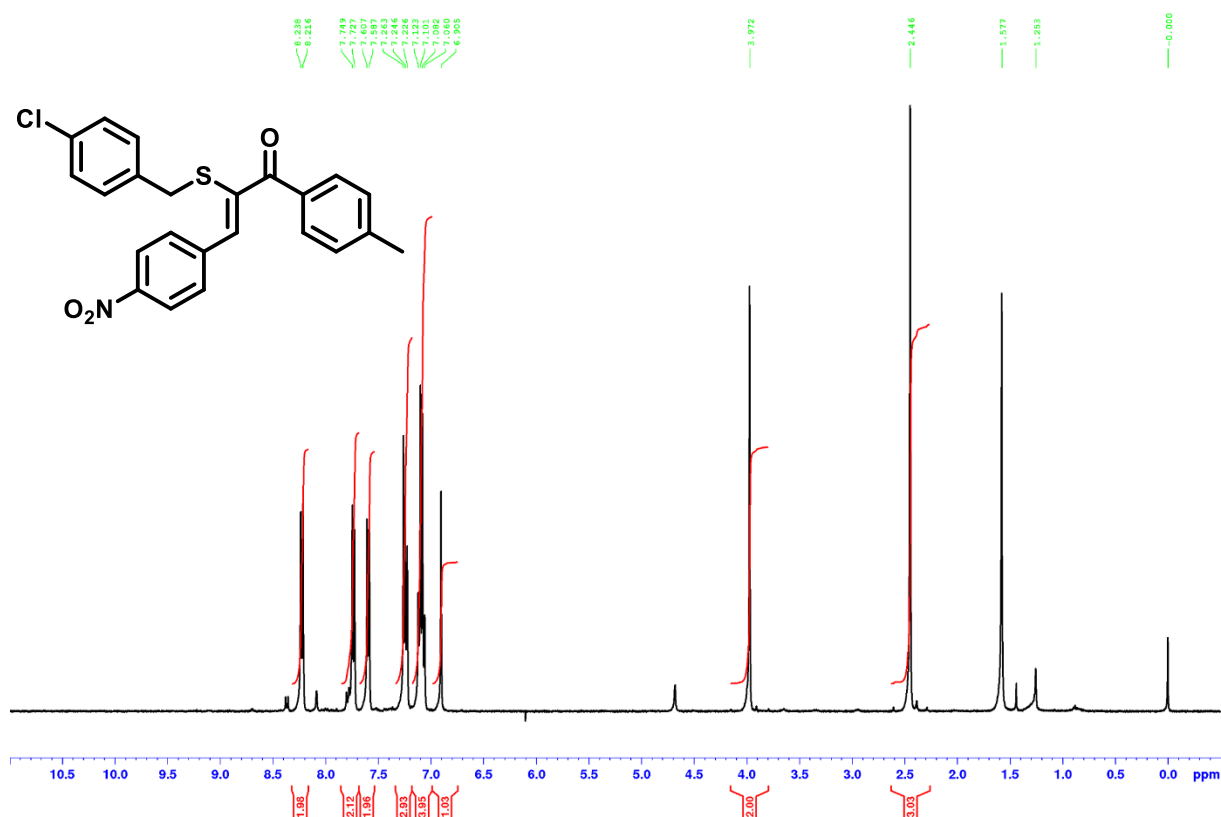


Figure S249: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-21**.

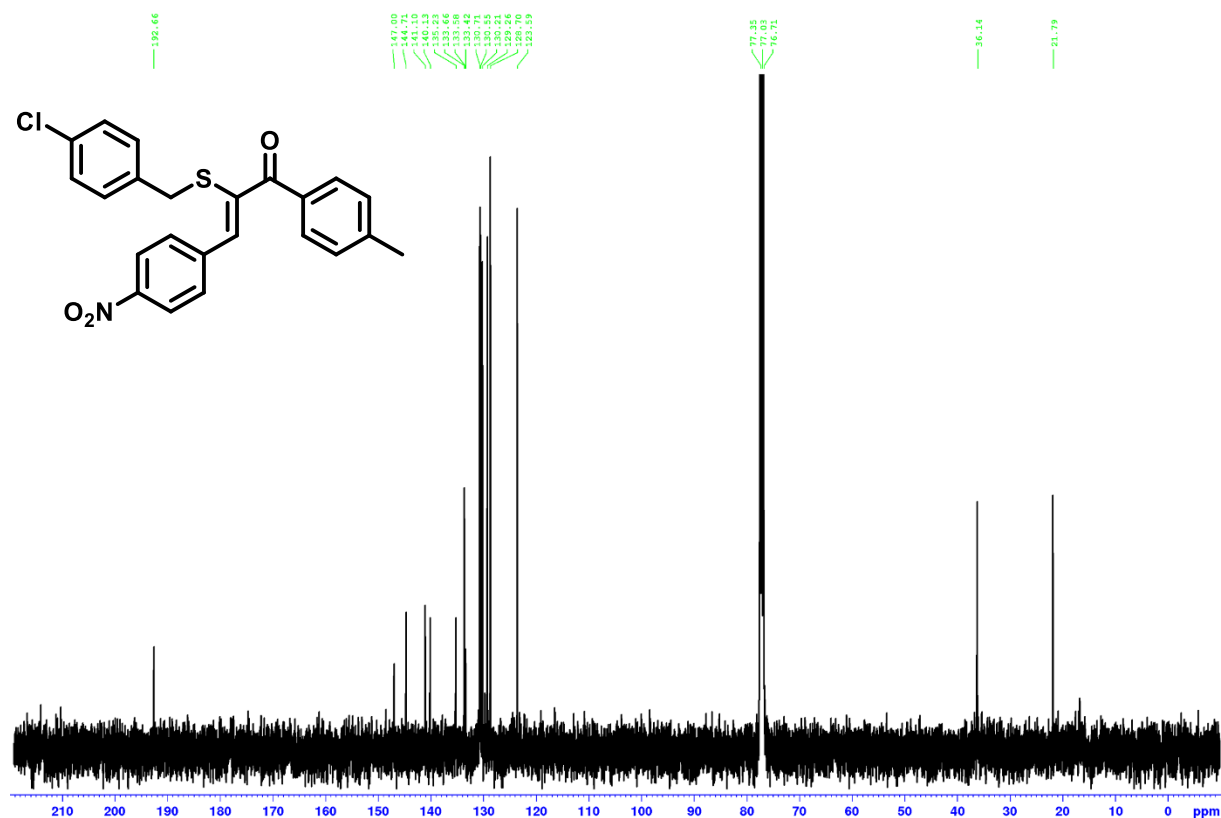
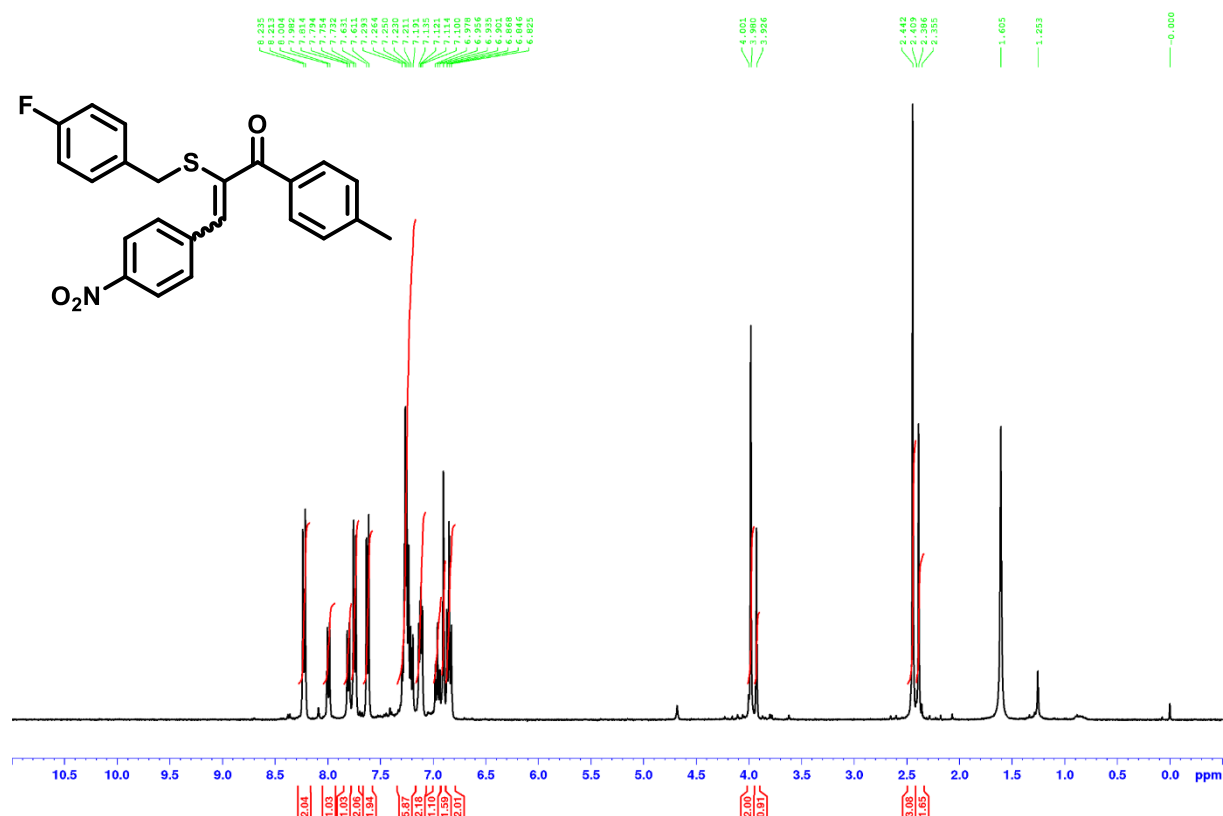


Figure S250: ¹³C NMR (100 MHz, CDCl₃) spectrum of **Z-21**.

(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



(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.

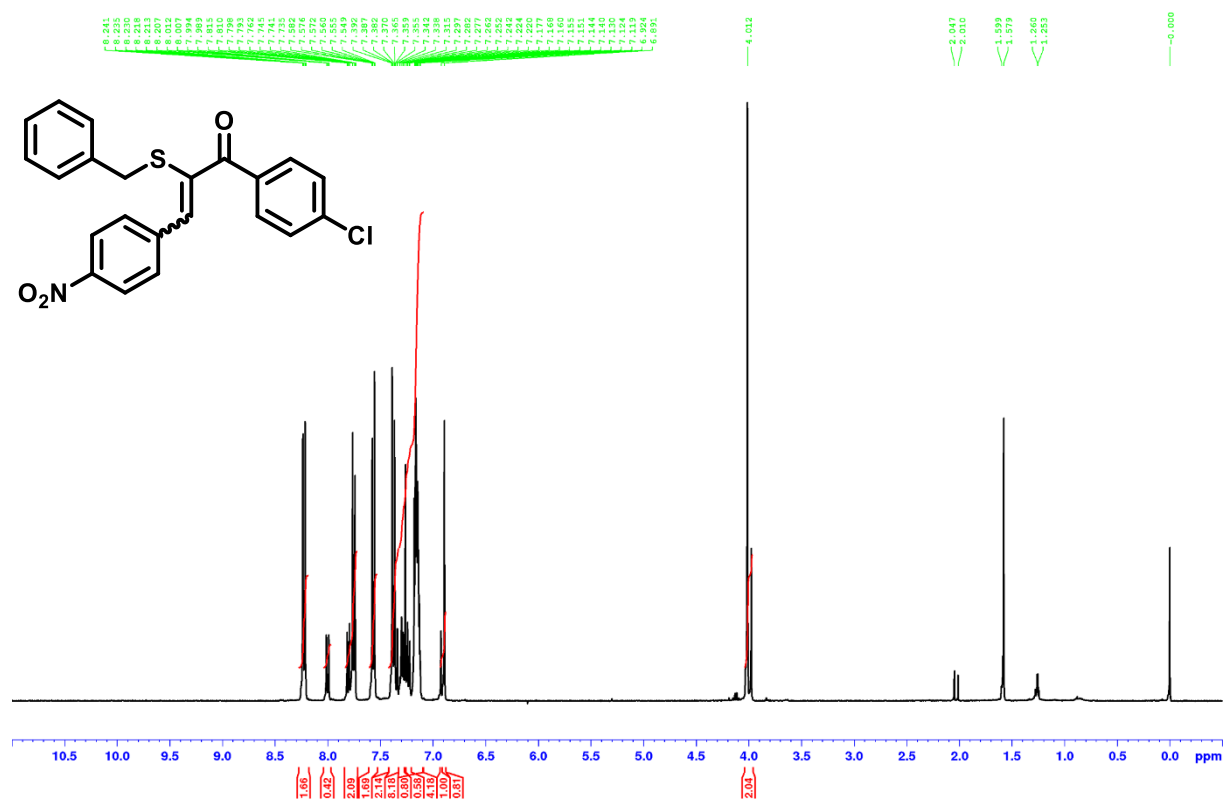


Figure S253: ^1H NMR (400 MHz, CDCl_3) spectrum of *Z*-23 and *E*-23 (*Z*:*E*, 4.6:1).

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

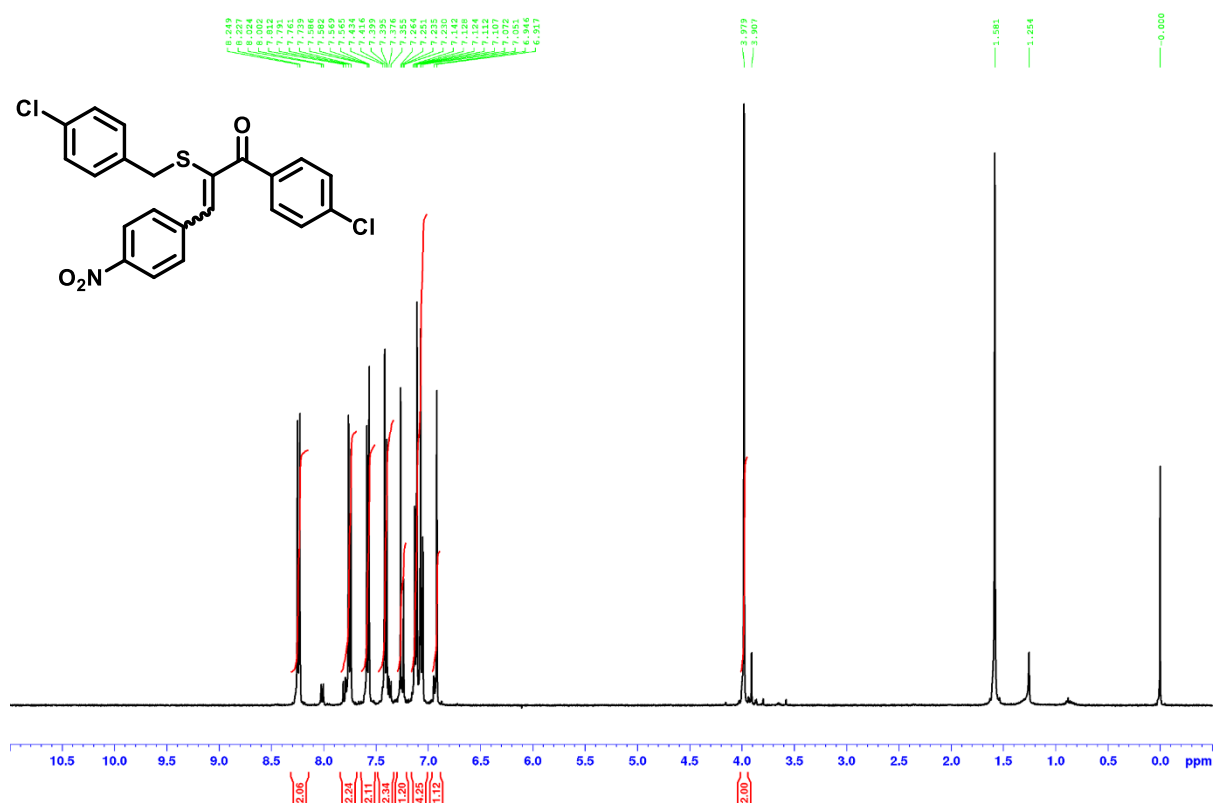


Figure S254: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-24** and **E-24** (Z:E, 30.7:1).

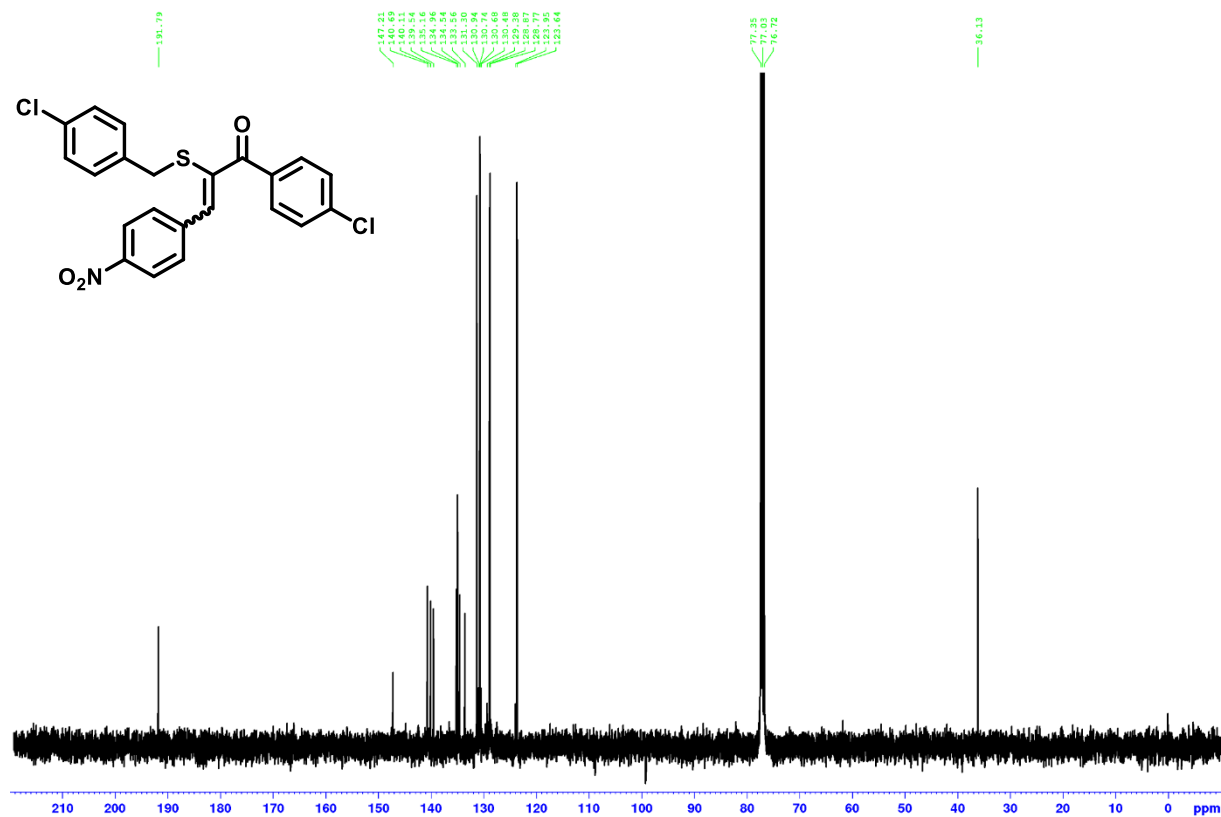


Figure 255: ¹³C NMR (100 MHz, CDCl₃) spectrum of **Z-24** and **E-24** (Z:E, 30.7:1).

Chemical Structure: 4-chlorobenzoyl 4-methoxybenzyl 4-nitrophenyl sulfide

¹H NMR Data (CDCl₃):

Chemical Shift (ppm)	Integration
8.580, 8.539, 8.514, 8.474, 8.454, 8.434, 8.414, 8.394, 8.374, 8.354, 8.334, 8.314, 8.294, 8.274, 8.254, 8.234, 8.214, 8.194, 8.174, 8.154, 8.134, 8.114, 8.094, 8.074, 8.054, 8.034, 8.014, 7.994, 7.974, 7.954, 7.934, 7.914, 7.894, 7.874, 7.854, 7.834, 7.814, 7.794, 7.774, 7.754, 7.734, 7.714, 7.694, 7.674, 7.654, 7.634, 7.614, 7.594, 7.574, 7.554, 7.534, 7.514, 7.494, 7.474, 7.454, 7.434, 7.414, 7.394, 7.374, 7.354, 7.334, 7.314, 7.294, 7.274, 7.254, 7.234, 7.214, 7.194, 7.174, 7.154, 7.134, 7.114, 7.094, 7.074, 7.054, 7.034, 7.014, 6.994, 6.974, 6.954, 6.934, 6.914, 6.894, 6.874, 6.854, 6.834, 6.814, 6.794, 6.774, 6.754, 6.734, 6.714, 6.694, 6.674, 6.654, 6.634, 6.614, 6.594, 6.574, 6.554, 6.534, 6.514, 6.494, 6.474, 6.454, 6.434, 6.414, 6.394, 6.374, 6.354, 6.334, 6.314, 6.294, 6.274, 6.254, 6.234, 6.214, 6.194, 6.174, 6.154, 6.134, 6.114, 6.094, 6.074, 6.054, 6.034, 6.014, 5.994, 5.974, 5.954, 5.934, 5.914, 5.894, 5.874, 5.854, 5.834, 5.814, 5.794, 5.774, 5.754, 5.734, 5.714, 5.694, 5.674, 5.654, 5.634, 5.614, 5.594, 5.574, 5.554, 5.534, 5.514, 5.494, 5.474, 5.454, 5.434, 5.414, 5.394, 5.374, 5.354, 5.334, 5.314, 5.294, 5.274, 5.254, 5.234, 5.214, 5.194, 5.174, 5.154, 5.134, 5.114, 5.094, 5.074, 5.054, 5.034, 5.014, 4.994, 4.974, 4.954, 4.934, 4.914, 4.894, 4.874, 4.854, 4.834, 4.814, 4.794, 4.774, 4.754, 4.734, 4.714, 4.694, 4.674, 4.654, 4.634, 4.614, 4.594, 4.574, 4.554, 4.534, 4.514, 4.494, 4.474, 4.454, 4.434, 4.414, 4.394, 4.374, 4.354, 4.334, 4.314, 4.294, 4.274, 4.254, 4.234, 4.214, 4.194, 4.174, 4.154, 4.134, 4.114, 4.094, 4.074, 4.054, 4.034, 4.014, 3.994, 3.974, 3.954, 3.934, 3.914, 3.894, 3.874, 3.854, 3.834, 3.814, 3.794, 3.774, 3.754, 3.734, 3.714, 3.694, 3.674, 3.654, 3.634, 3.614, 3.594, 3.574, 3.554, 3.534, 3.514, 3.494, 3.474, 3.454, 3.434, 3.414, 3.394, 3.374, 3.354, 3.334, 3.314, 3.294, 3.274, 3.254, 3.234, 3.214, 3.194, 3.174, 3.154, 3.134, 3.114, 3.094, 3.074, 3.054, 3.034, 3.014, 2.994, 2.974, 2.954, 2.934, 2.914, 2.894, 2.874, 2.854, 2.834, 2.814, 2.794, 2.774, 2.754, 2.734, 2.714, 2.694, 2.674, 2.654, 2.634, 2.614, 2.594, 2.574, 2.554, 2.534, 2.514, 2.494, 2.474, 2.454, 2.434, 2.414, 2.394, 2.374, 2.354, 2.334, 2.314, 2.294, 2.274, 2.254, 2.234, 2.214, 2.194, 2.174, 2.154, 2.134, 2.114, 2.094, 2.074, 2.054, 2.034, 2.014, 1.994, 1.974, 1.954, 1.934, 1.914, 1.894, 1.874, 1.854, 1.834, 1.814, 1.794, 1.774, 1.754, 1.734, 1.714, 1.694, 1.674, 1.654, 1.634, 1.614, 1.594, 1.574, 1.554, 1.534, 1.514, 1.494, 1.474, 1.454, 1.434, 1.414, 1.394, 1.374, 1.354, 1.334, 1.314, 1.294, 1.274, 1.254, 1.234, 1.214, 1.194, 1.174, 1.154, 1.134, 1.114, 1.094, 1.074, 1.054, 1.034, 1.014, 0.994, 0.974, 0.954, 0.934, 0.914, 0.894, 0.874, 0.854, 0.834, 0.814, 0.794, 0.774, 0.754, 0.734, 0.714, 0.694, 0.674, 0.654, 0.634, 0.614, 0.594, 0.574, 0.554, 0.534, 0.514, 0.494, 0.474, 0.454, 0.434, 0.414, 0.394, 0.374, 0.354, 0.334, 0.314, 0.294, 0.274, 0.254, 0.234, 0.214, 0.194, 0.174, 0.154, 0.134, 0.114, 0.094, 0.074, 0.054, 0.034, 0.014, -0.009, -0.029, -0.049, -0.069, -0.089, -0.109, -0.129, -0.149, -0.169, -0.189, -0.209, -0.229, -0.249, -0.269, -0.289, -0.309, -0.329, -0.349, -0.369, -0.389, -0.409, -0.429, -0.449, -0.469, -0.489, -0.509, -0.529, -0.549, -0.569, -0.589, -0.609, -0.629, -0.649, -0.669, -0.689, -0.709, -0.729, -0.749, -0.769, -0.789, -0.809, -0.829, -0.849, -0.869, -0.889, -0.909, -0.929, -0.949, -0.969, -0.989, -1.009, -1.029, -1.049, -1.069, -1.089, -1.109, -1.129, -1.149, -1.169, -1.189, -1.209, -1.229, -1.249, -1.269, -1.289, -1.309, -1.329, -1.349, -1.369, -1.389, -1.409, -1.429, -1.449, -1.469, -1.489, -1.509, -1.529, -1.549, -1.569, -1.589, -1.609, -1.629, -1.649, -1.669, -1.689, -1.709, -1.729, -1.749, -1.769, -1.789, -1.809, -1.829, -1.849, -1.869, -1.889, -1.909, -1.929, -1.949, -1.969, -1.989, -2.009, -2.029, -2.049, -2.069, -2.089, -2.109, -2.129, -2.149, -2.169, -2.189, -2.209, -2.229, -2.249, -2.269, -2.289, -2.309, -2.329, -2.349, -2.369, -2.389, -2.409, -2.429, -2.449, -2.469, -2.489, -2.509, -2.529, -2.549, -2.569, -2.589, -2.609, -2	

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

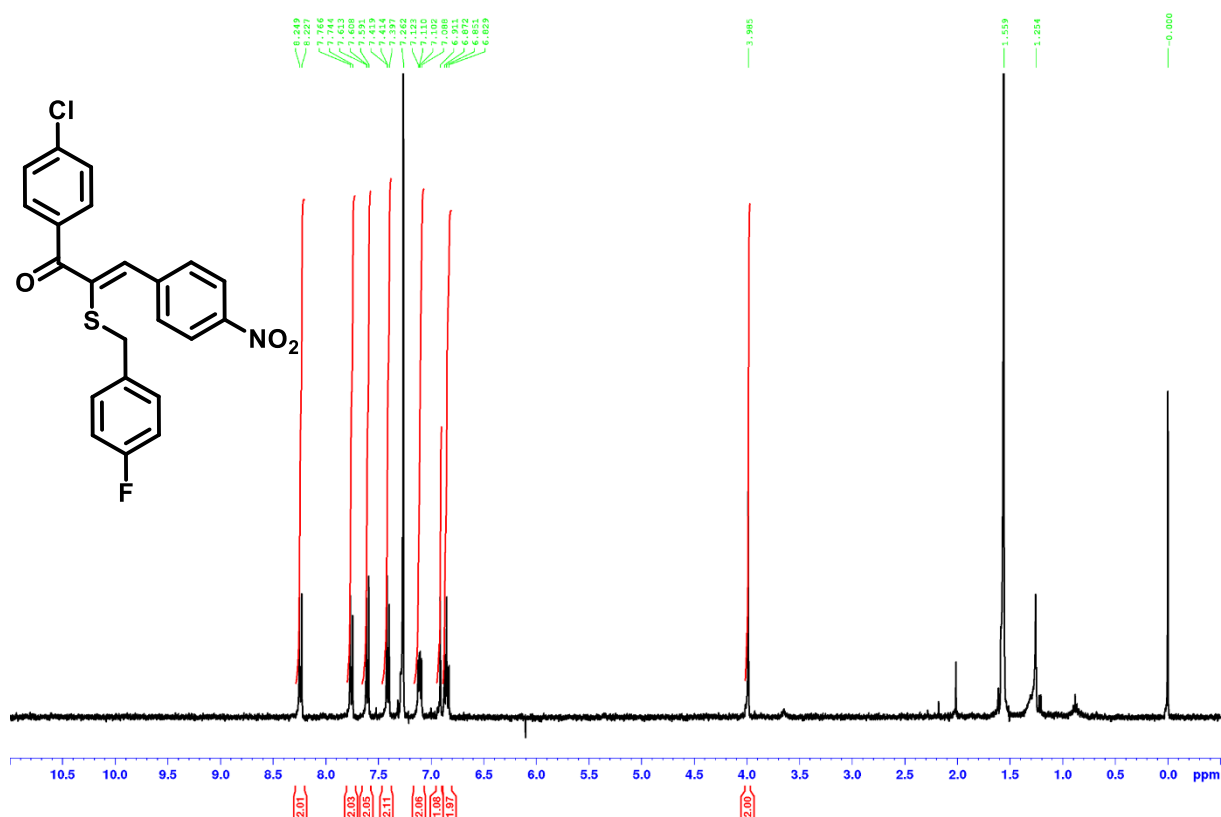


Figure S257: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-26.

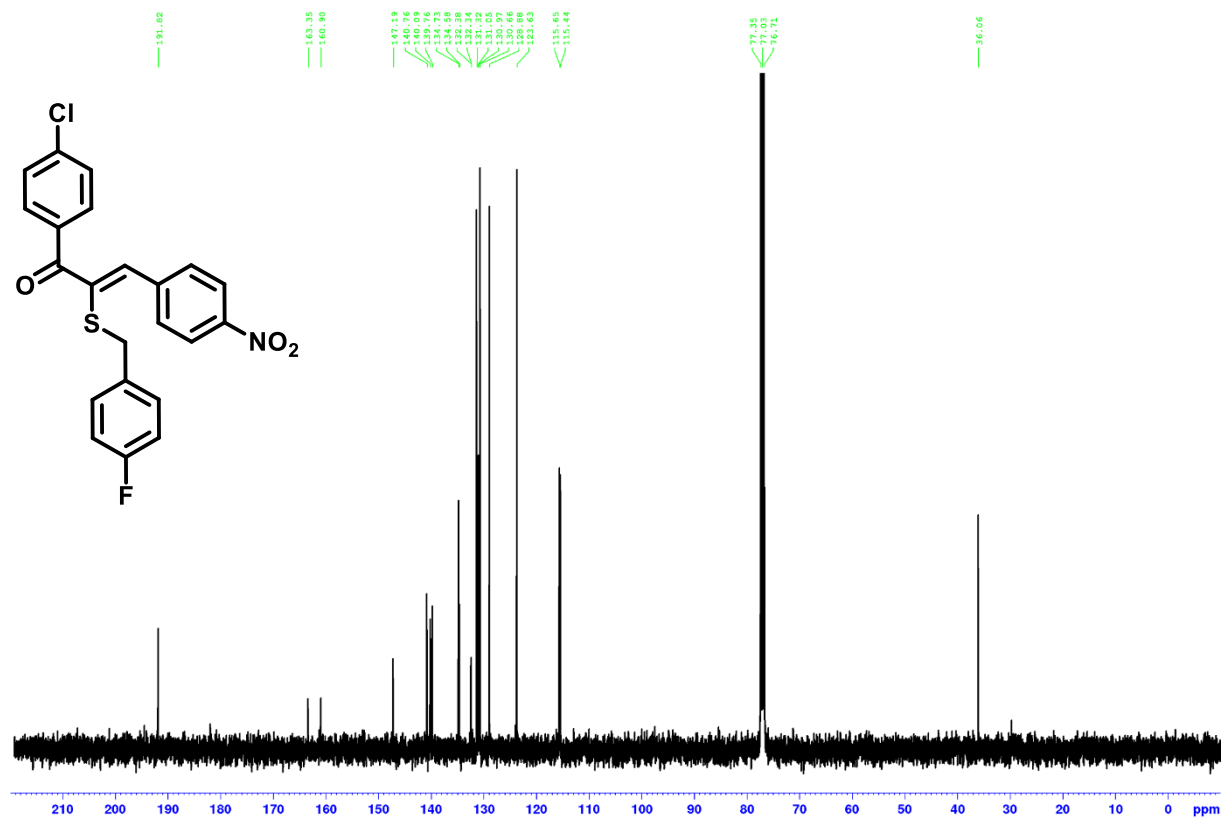


Figure S258: ¹³C NMR (100 MHz, CDCl₃) spectrum of Z-26.

O=[N+]([O-])c1ccc(cc1)/C=C/S(=O)(=O)c2ccc(cc2)C(=O)c3ccc(cc3)F

Chemical Structure: 4-chlorobenzyl 2-(4-fluorophenyl)-3-(4-nitrophenyl)acrylate

¹H NMR Data (CDCl₃):

Chemical Shift (ppm)	Integration
8.251, 8.238, 8.239, 8.215, 8.209, 8.197, 8.182, 8.168, 8.154, 8.140, 8.124, 8.107, 8.094, 8.086, 8.072, 8.055	2.00, 2.16, 1.97, 6.40, 1.00
3.977	2.14
1.560, 1.254	-
-0.000	-

Chemical structure of 4-chlorobenzyl 2-(4-fluorophenyl)-3-(4-nitrophenyl)acrylate is shown above the spectrum.

¹³C NMR peaks (ppm):

- 191.43
- 167.23
- 164.68
- 147.16
- 146.78
- 139.66
- 139.30
- 138.30
- 137.32
- 136.72
- 135.41
- 135.41
- 135.75
- 135.42
- 135.42
- 123.64
- 115.66
- 115.66
- 77.34
- 77.13
- 77.03
- 76.71
- 36.13

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

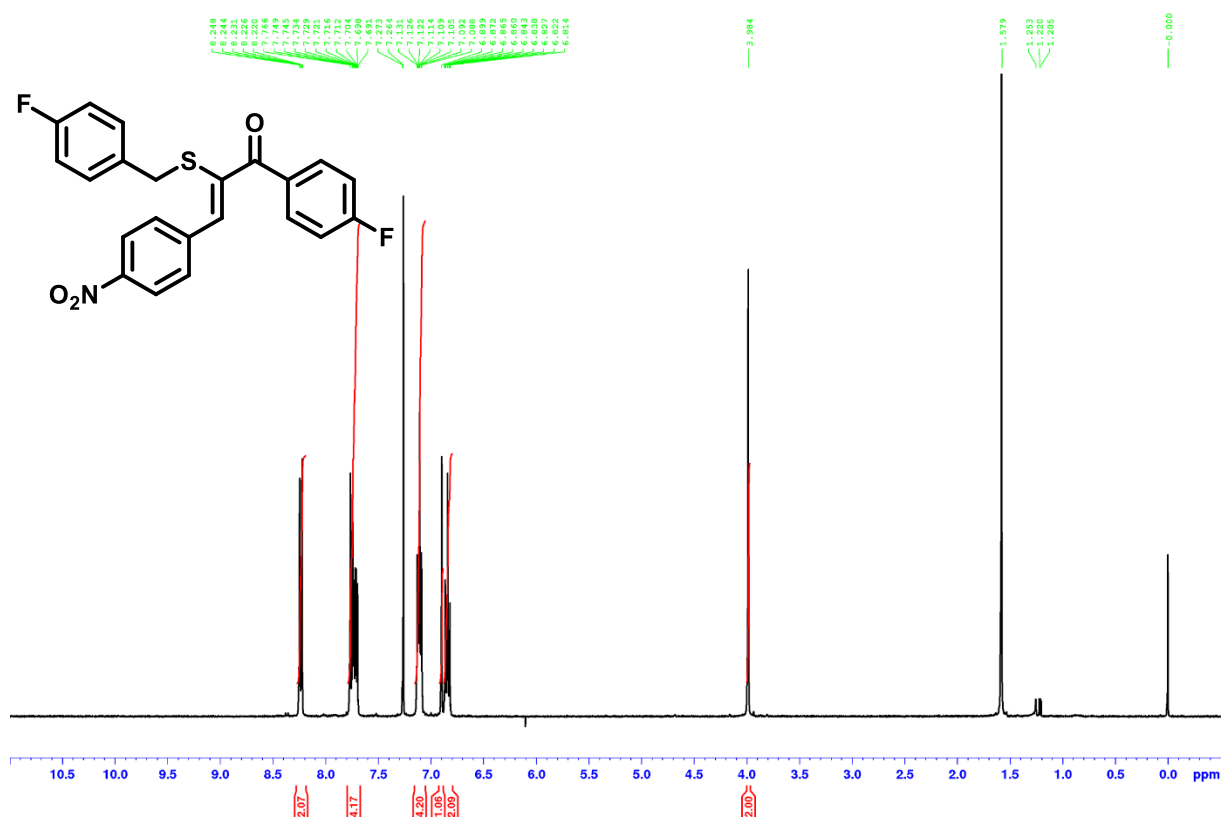


Figure S261: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-28**.

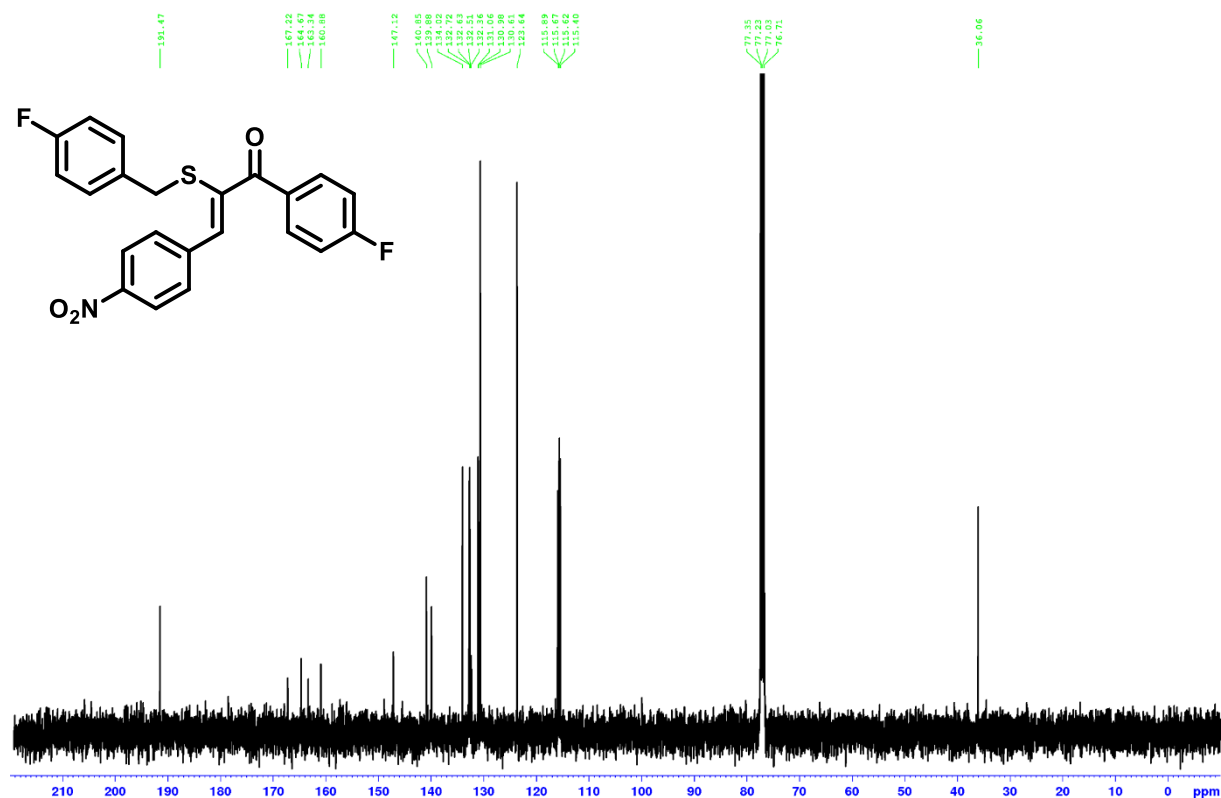


Figure S262: ¹³C NMR (100 MHz, CDCl₃) spectrum of **Z-28**.

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

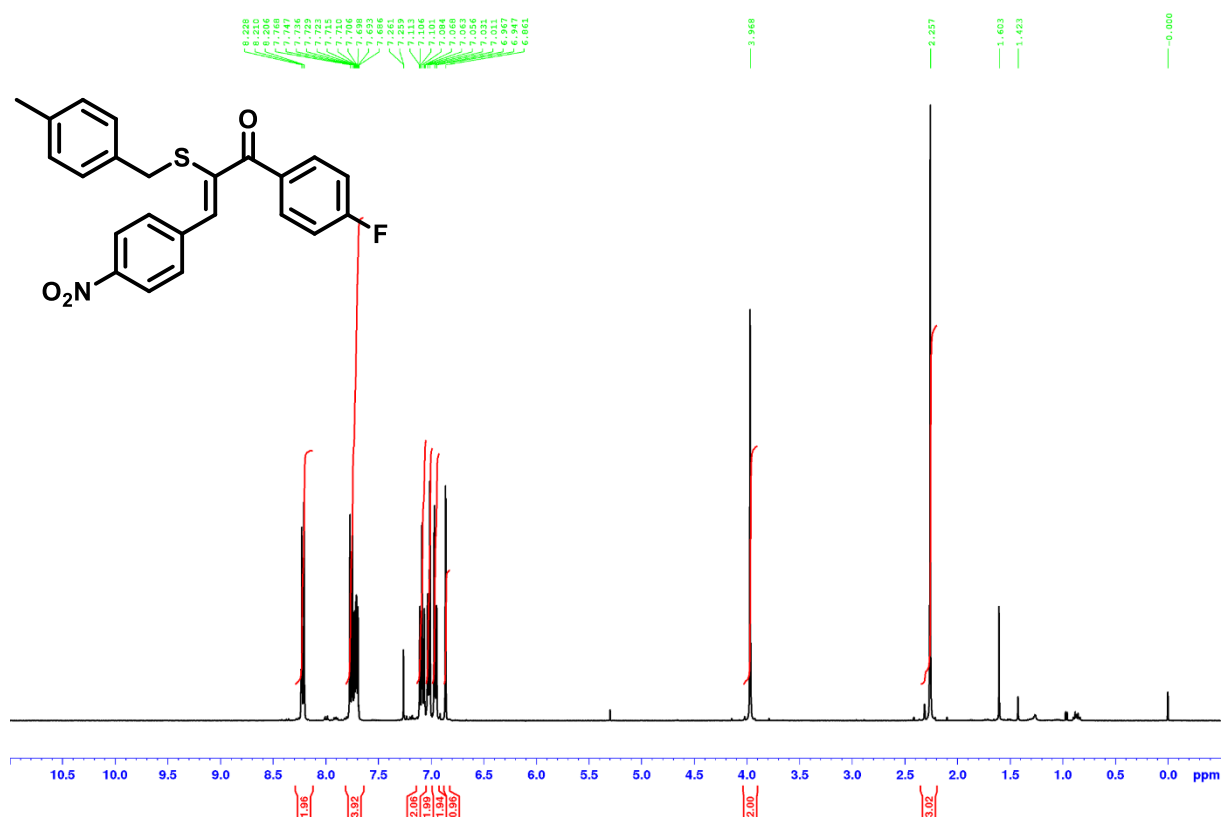


Figure S263: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-29**.

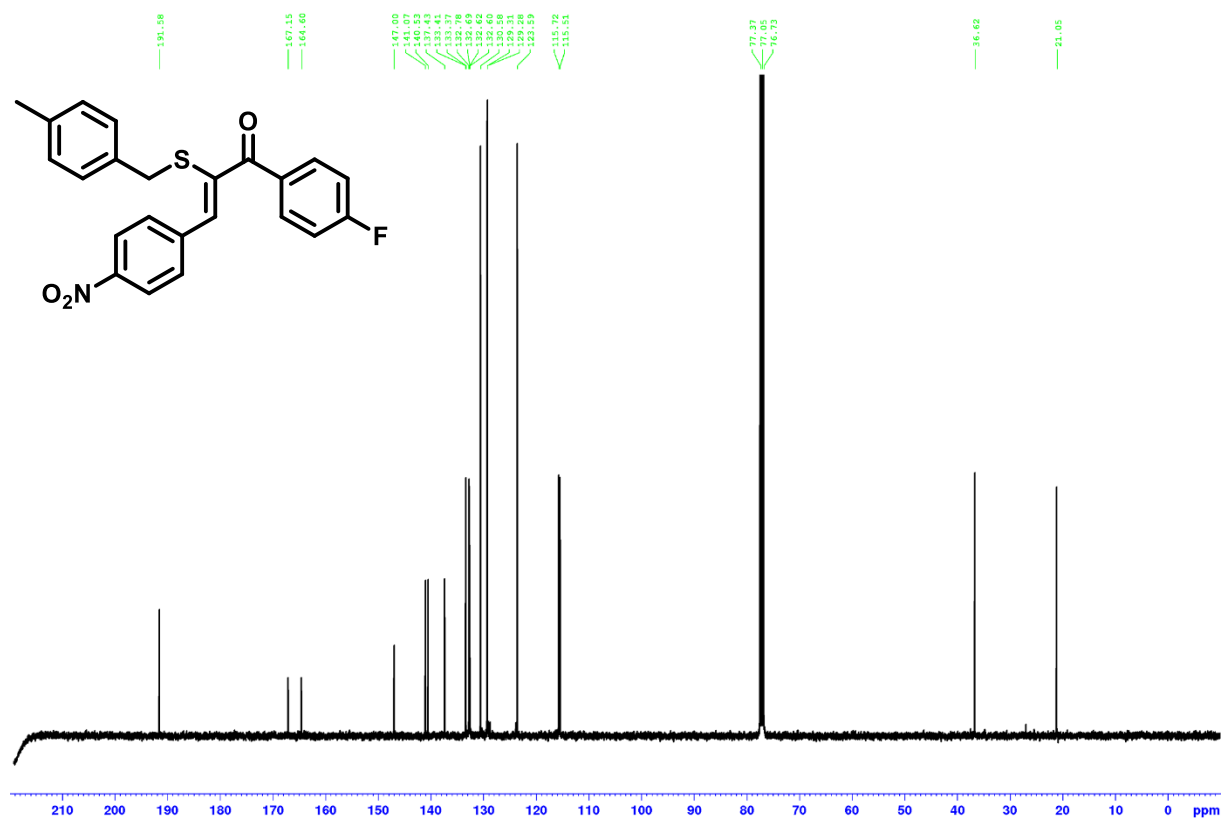


Figure S264: ¹³C NMR (100 MHz, CDCl₃) spectrum of **Z-29**.

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

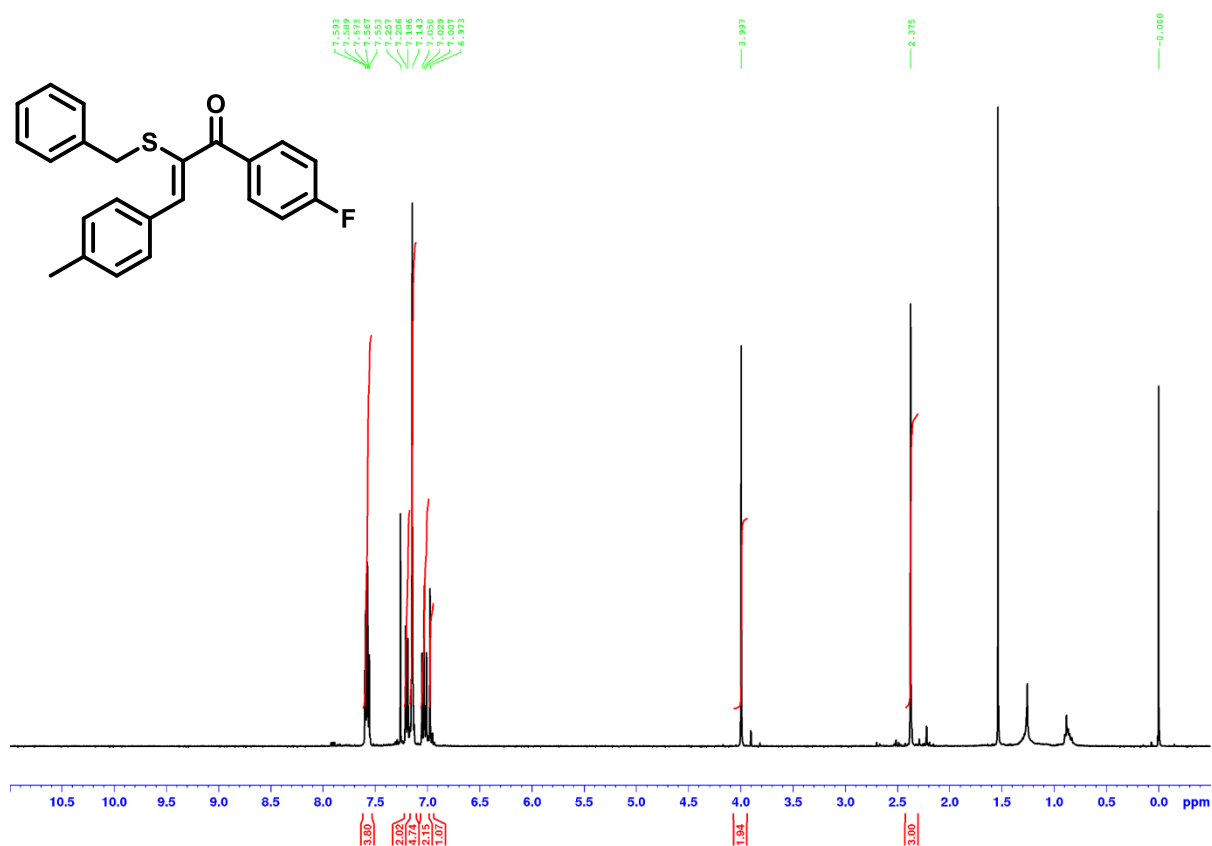


Figure S265: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-30**.

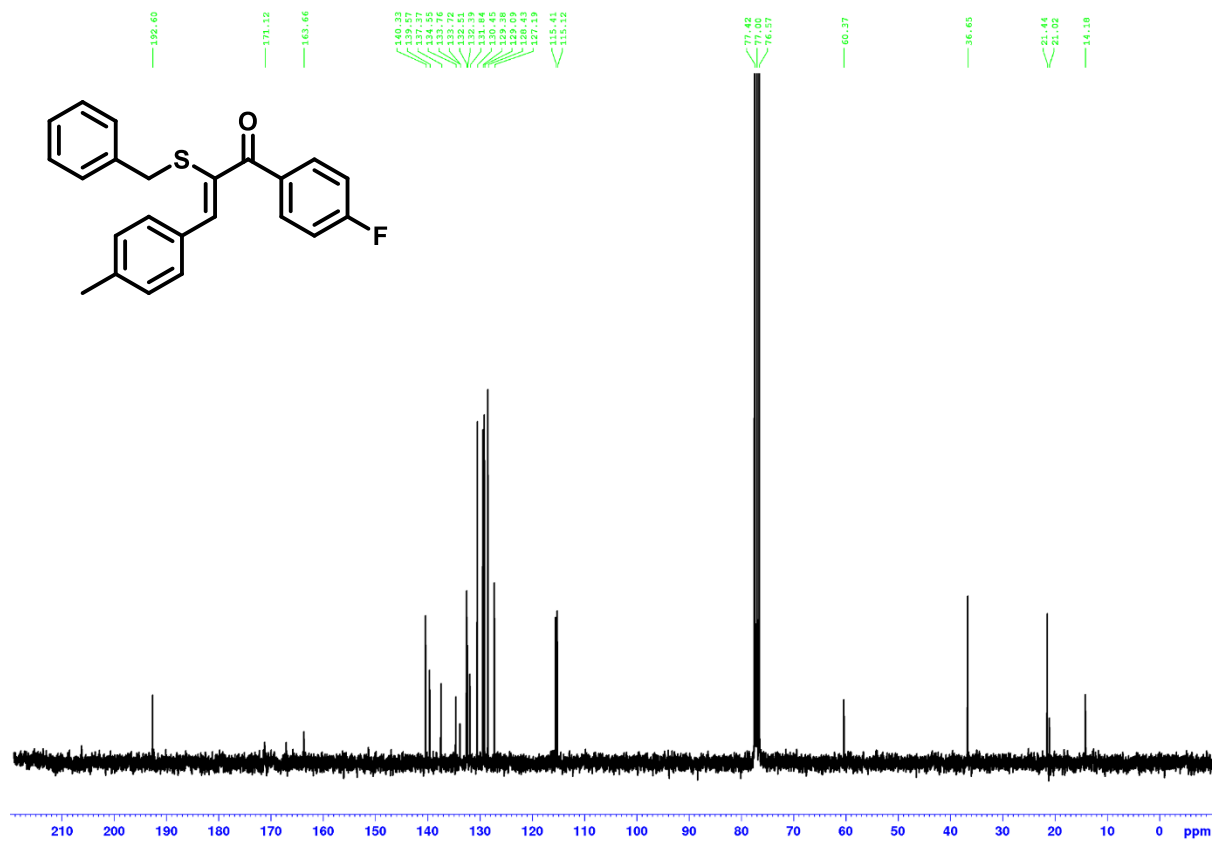


Figure S266: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-30**.

O=C(C=C(C1=CC=C(C=C1)SCC2=CC=CC=C2)C3=CC=C(C=C3)F)C4=CC=C(C=C4)F

Chemical structure of 4-(4-(benzylthio)phenyl)-2-(4-fluorophenyl)-1,3-butadiene-1-one is shown above the spectrum.

The spectrum displays several peaks in the aromatic region (6.5-8.0 ppm) and a singlet at 3.995 ppm. Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.607	1.06
7.566	1.33
7.525	4.68
7.484	4.10
7.443	1.00
3.995	1.88
0.000	-

280

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

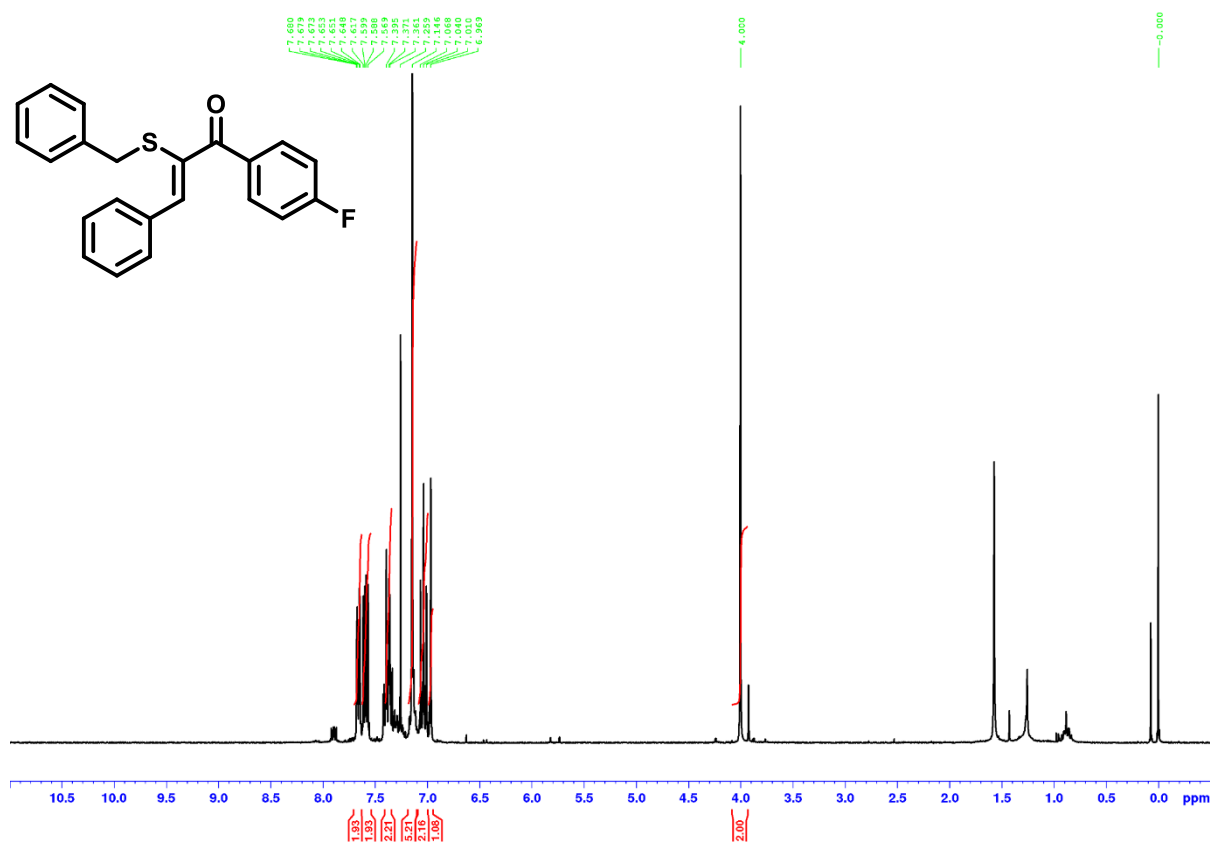


Figure S269: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-32**.

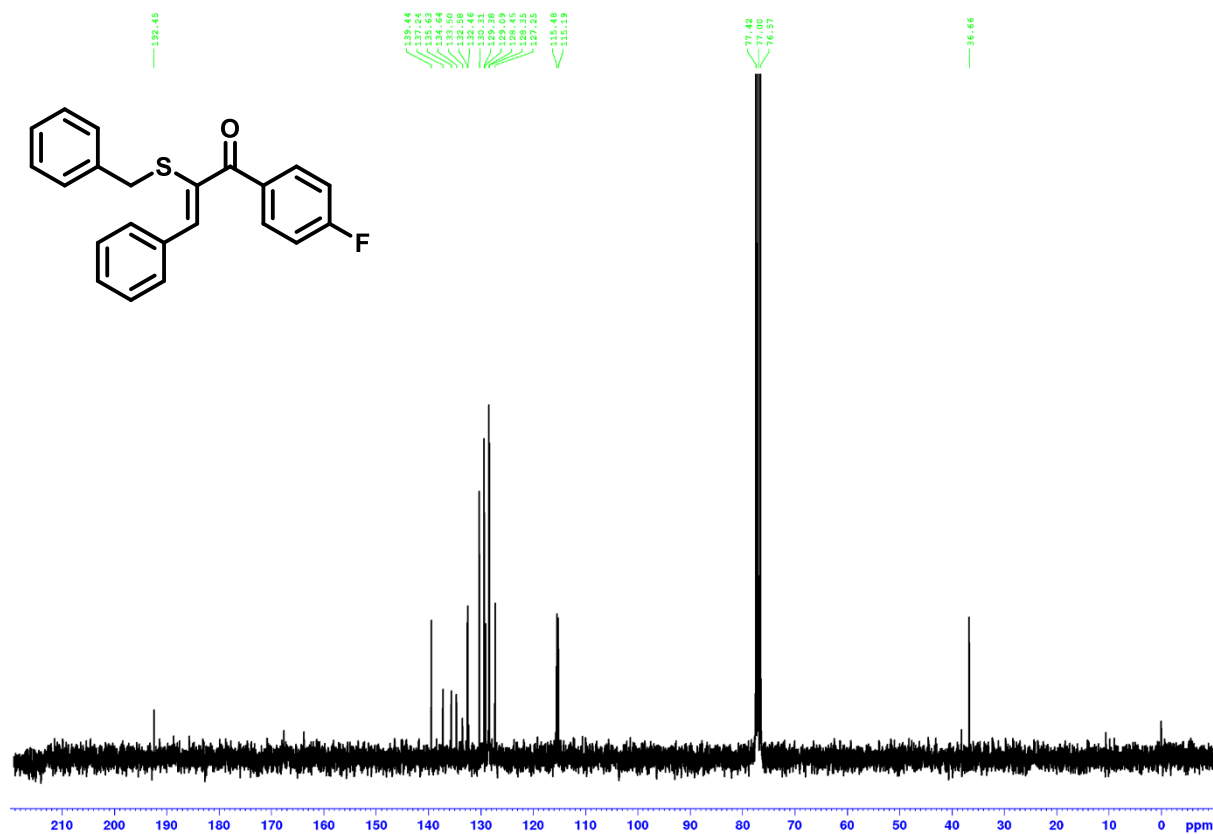


Figure S270: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-32**.

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

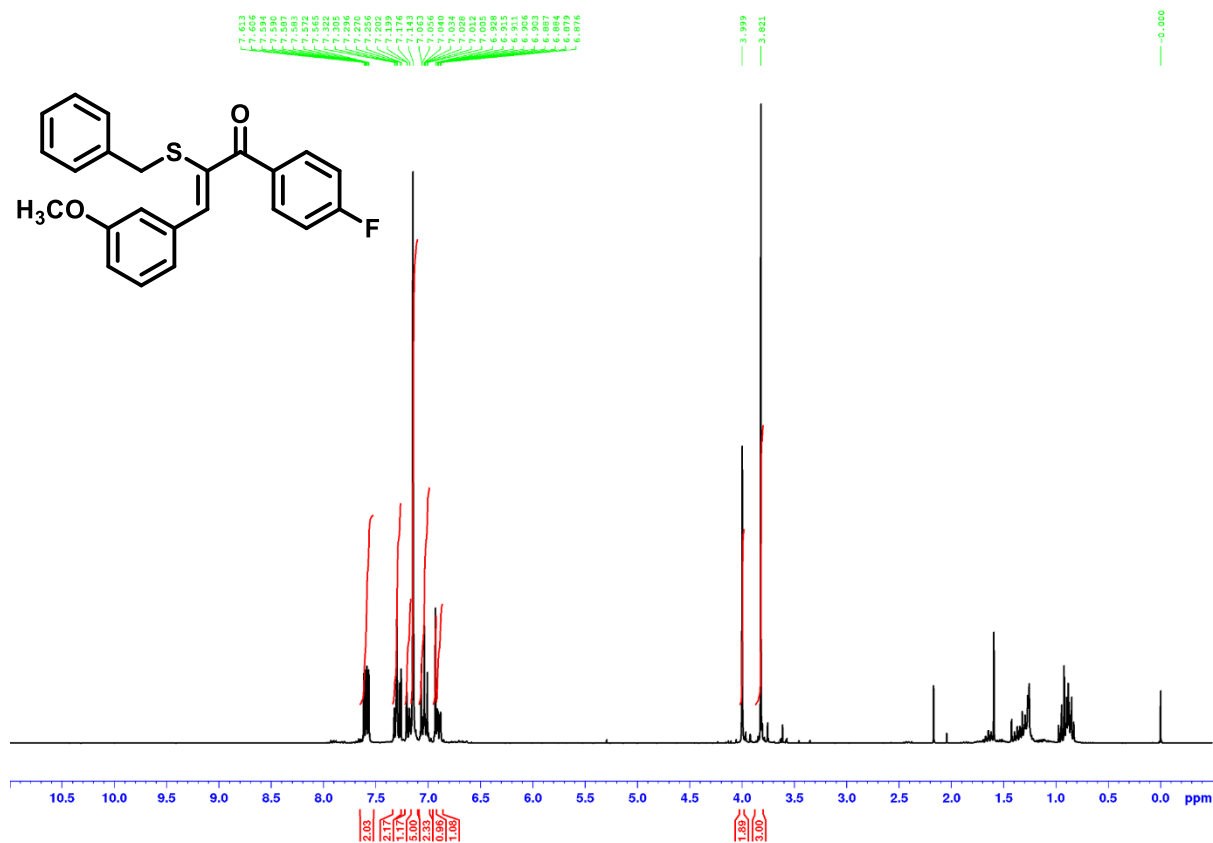


Figure S271: ^1H NMR (400 MHz, CDCl_3) spectrum of **Z-34**.

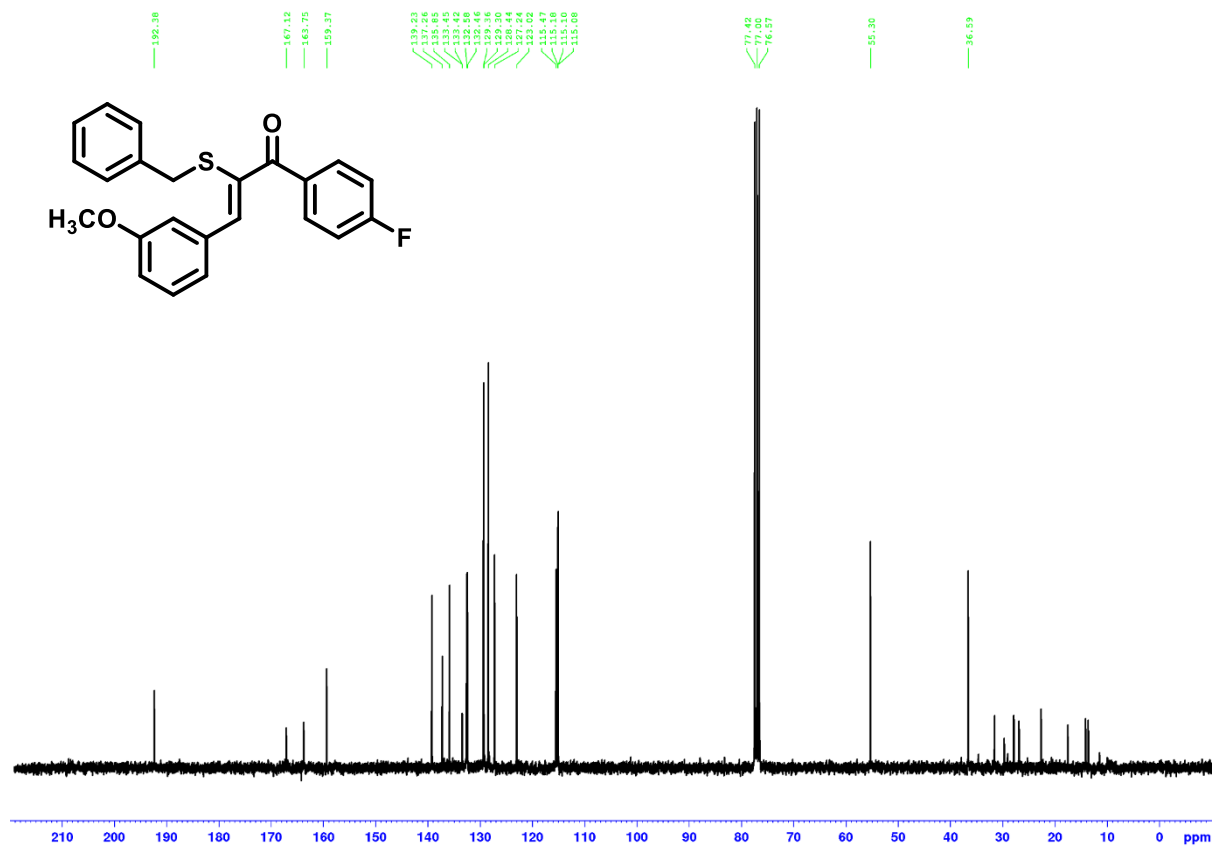


Figure S272: ^{13}C NMR (75.5 MHz, CDCl_3) spectrum of **Z-34**.

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

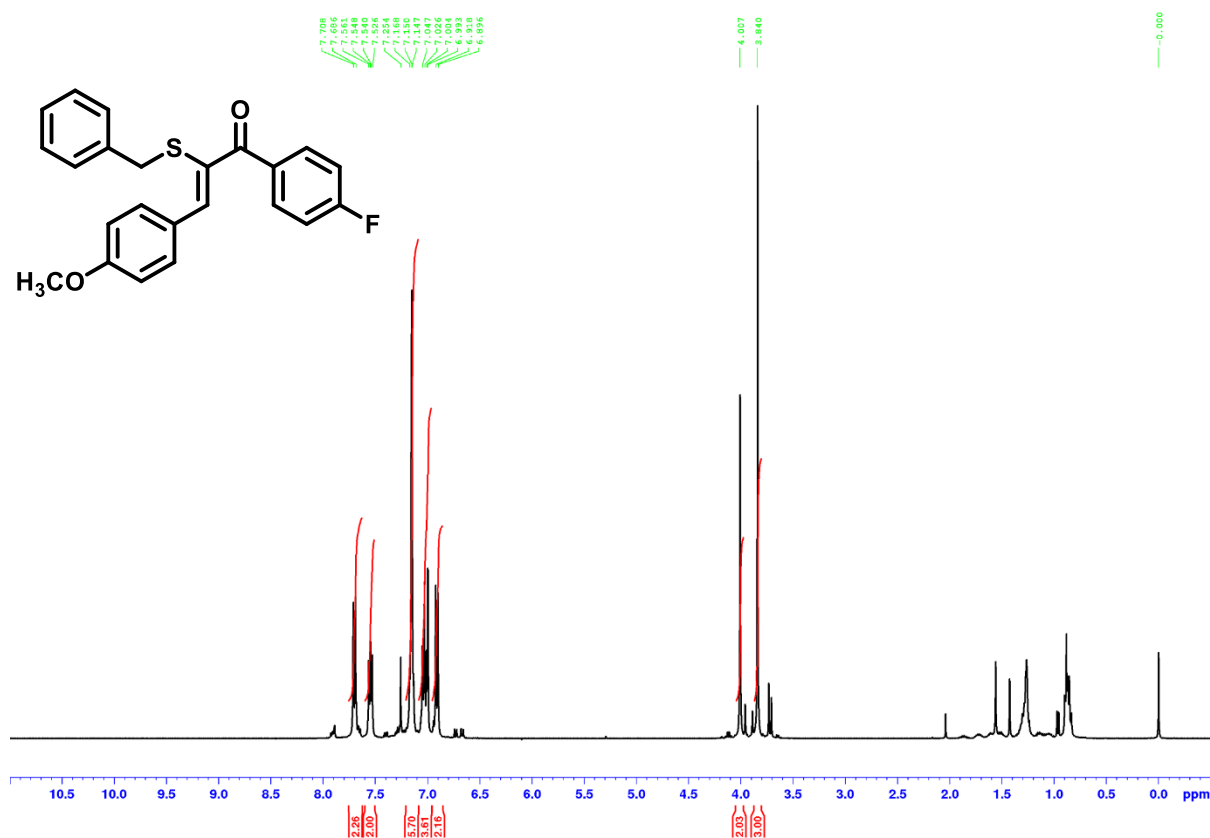


Figure S273: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-33**.

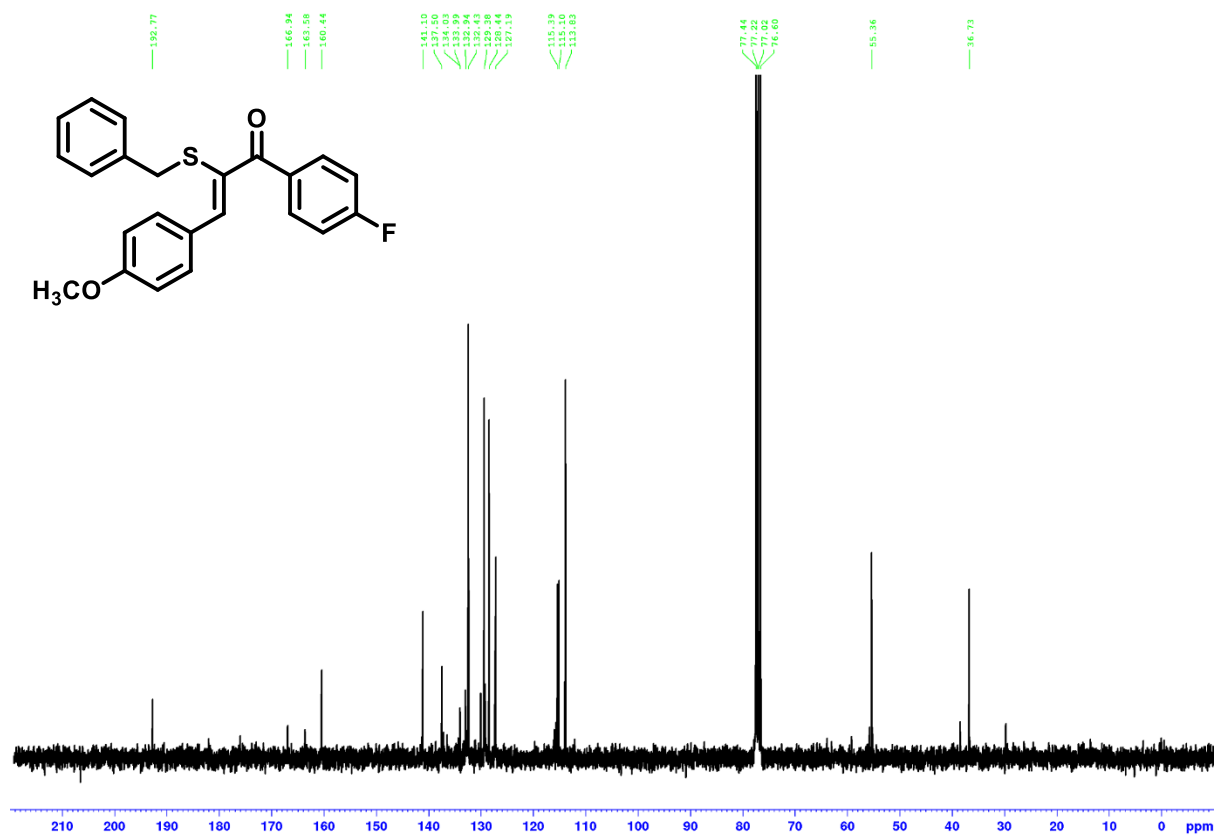


Figure S274: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **Z-33**.

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

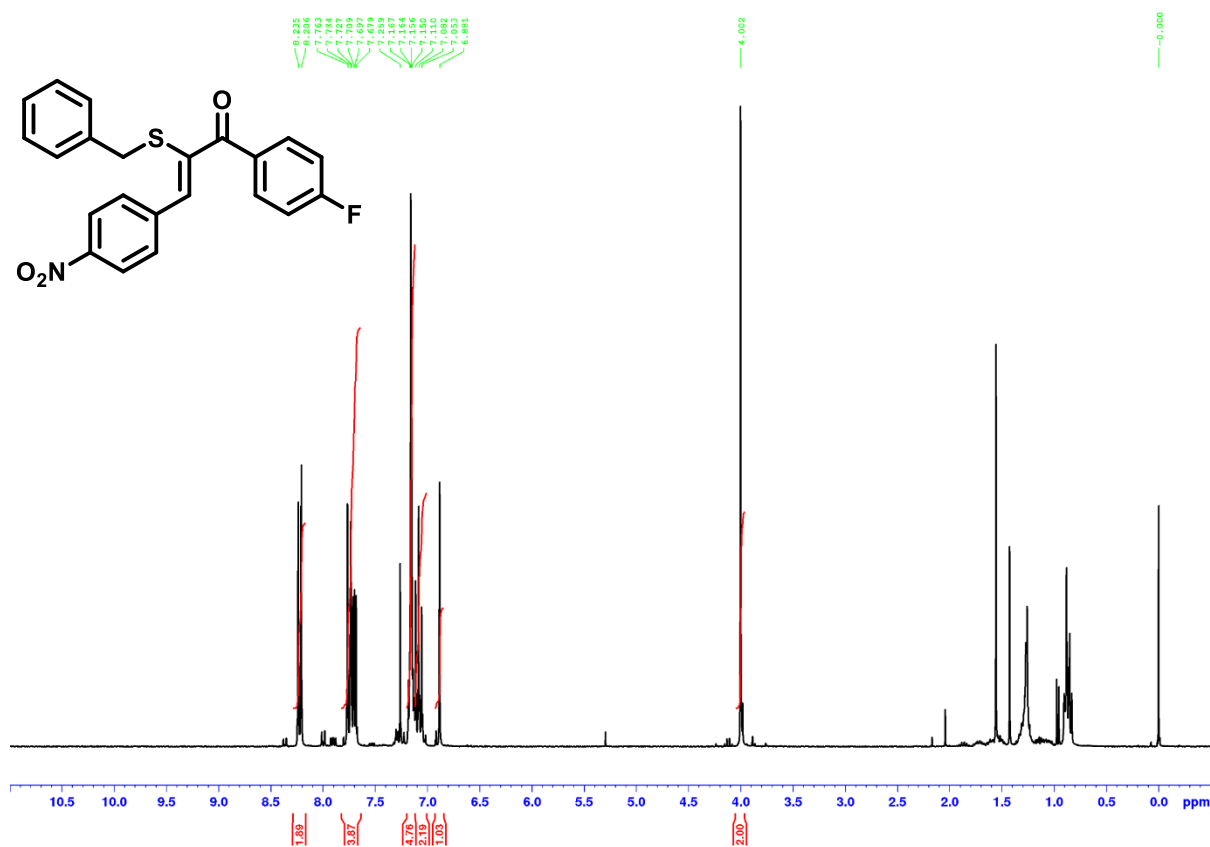


Figure S275: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-35.

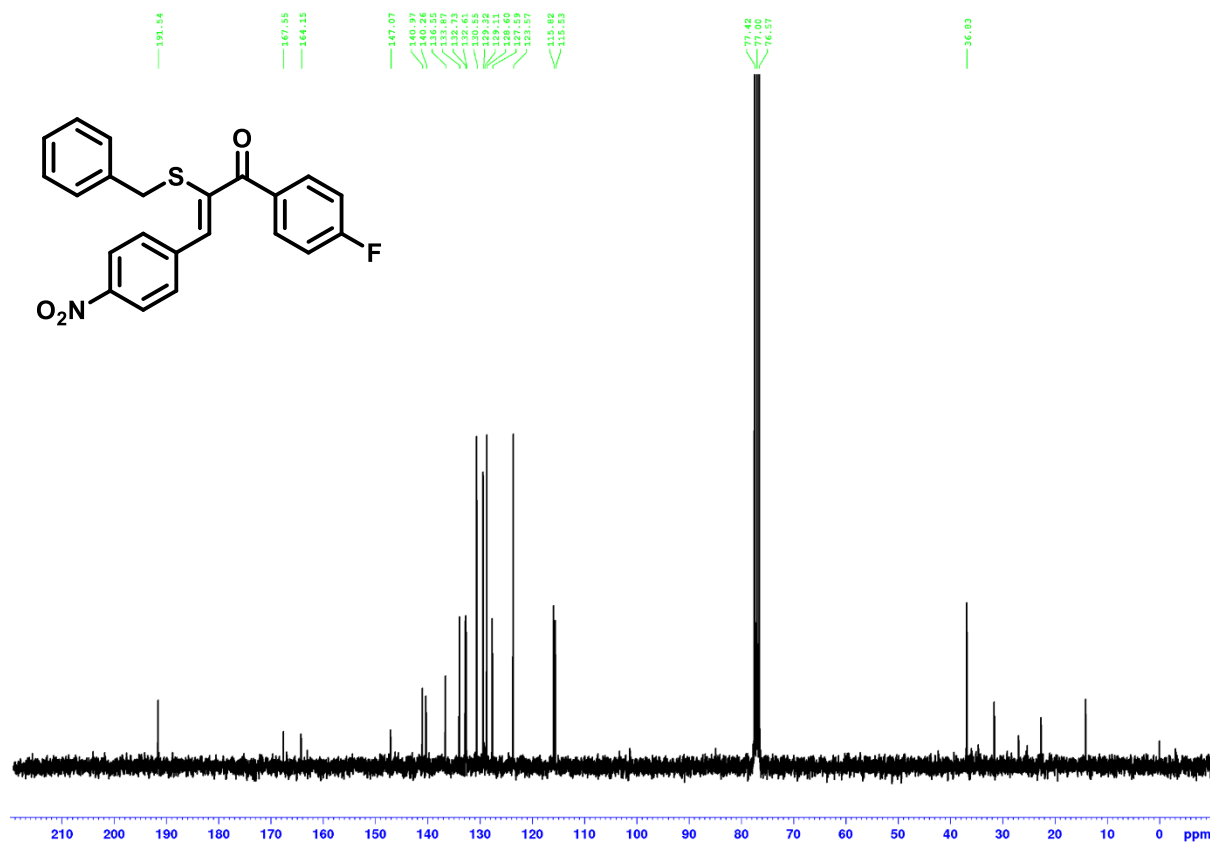


Figure S276: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of Z-35.

1.12.10 Oxidation of α -Sulfinyl- β -chloroenones

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

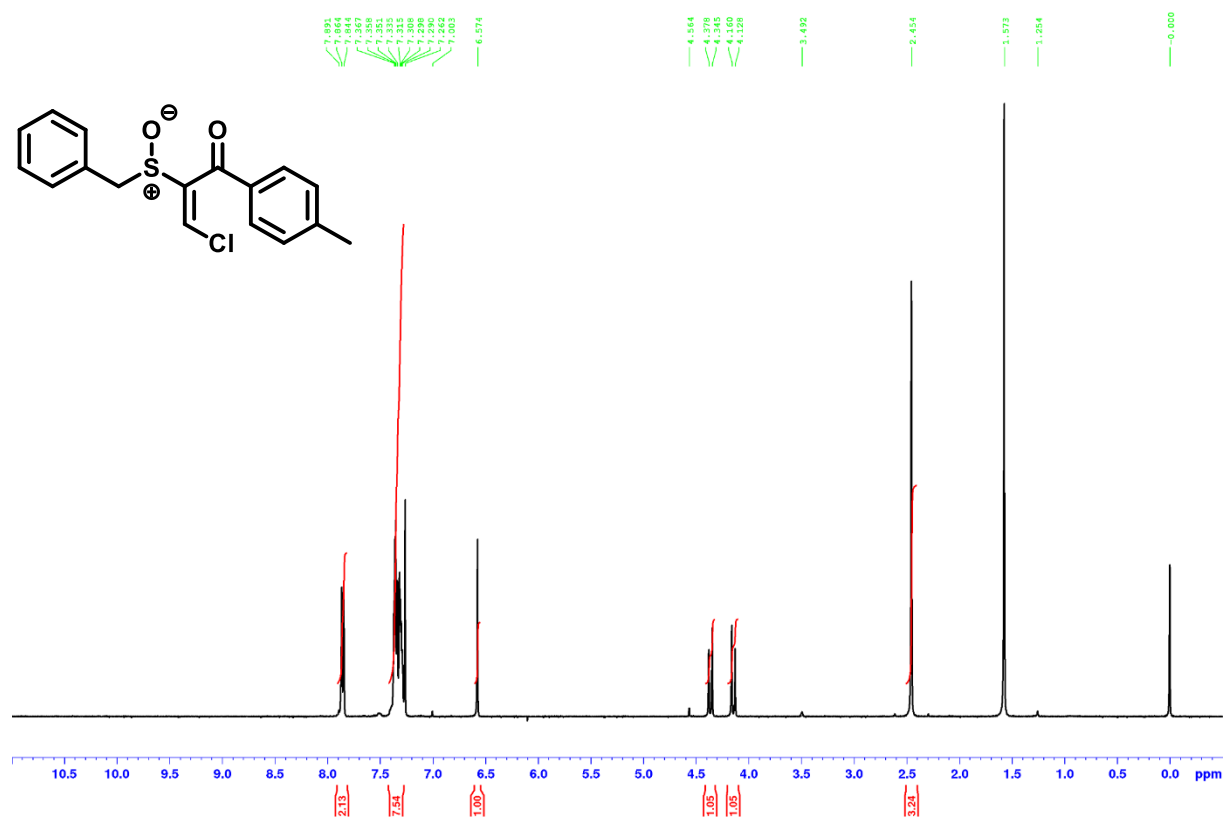


Figure S277: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-**38h**.

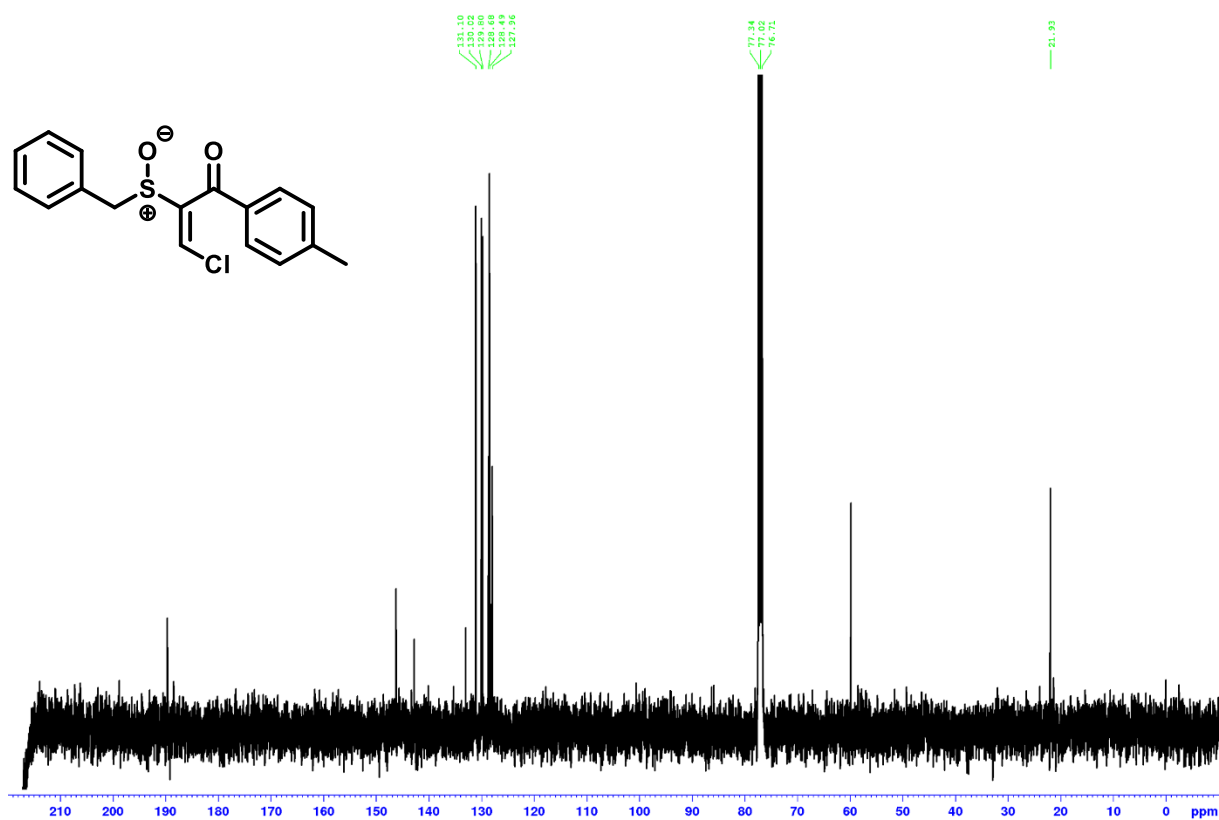


Figure S278: ^{13}C NMR (100 MHz, CDCl_3) spectrum of **E-38h**.

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

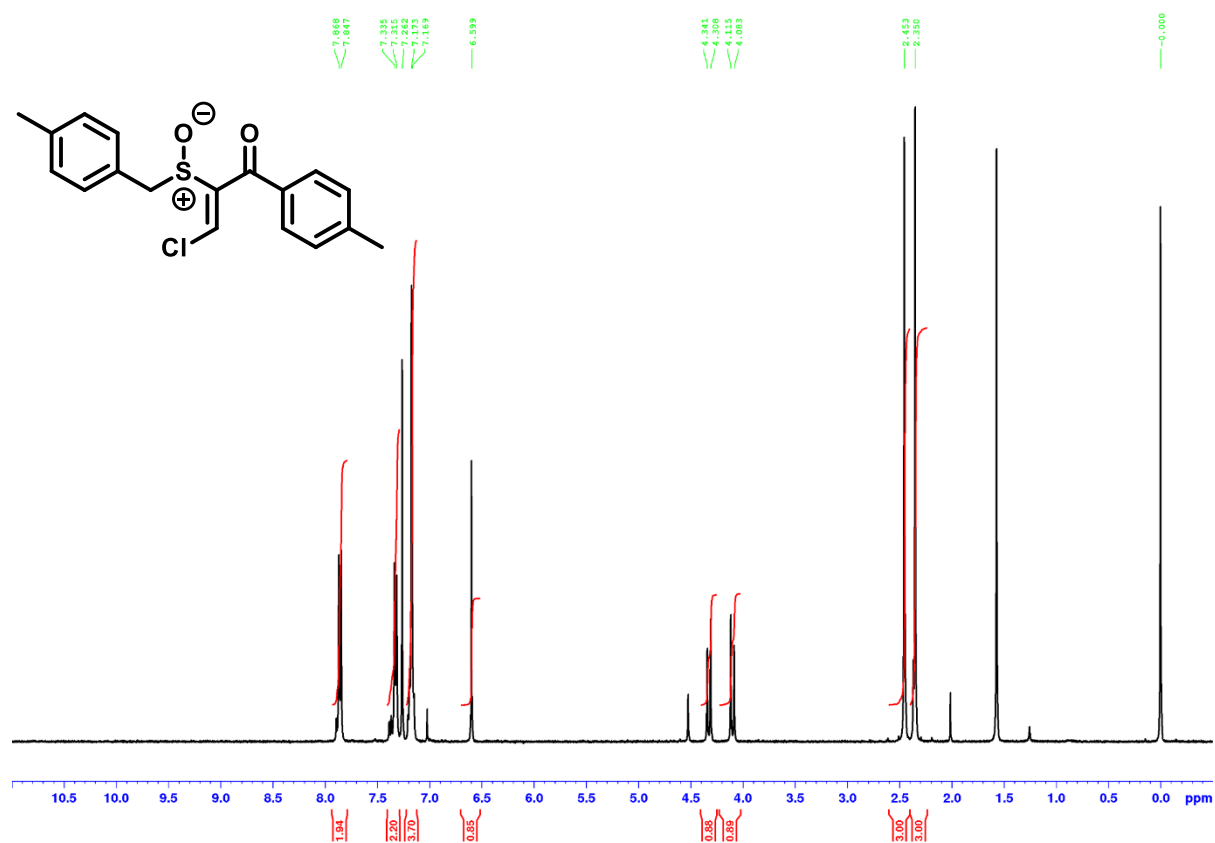


Figure S279: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-38m**.

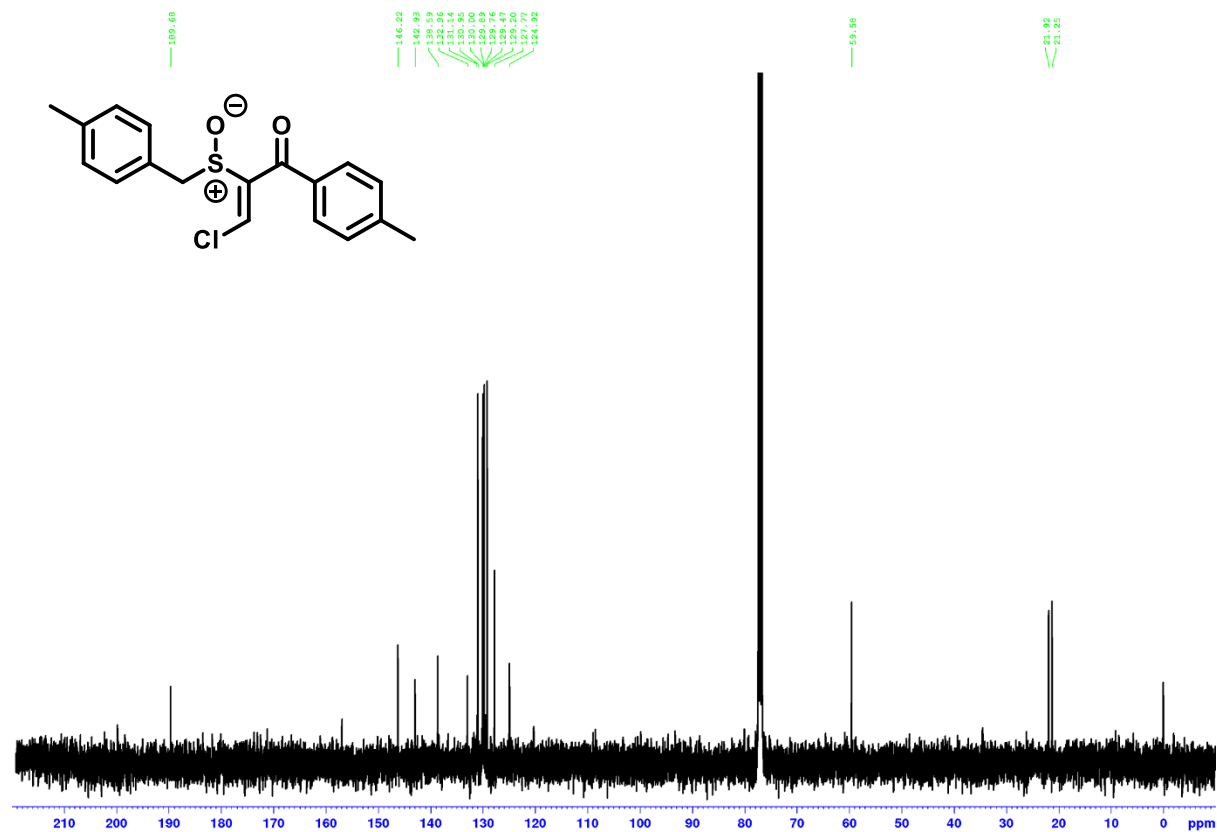


Figure S280: ¹³C NMR (100 MHz, CDCl₃) spectrum of **E-38m**.

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

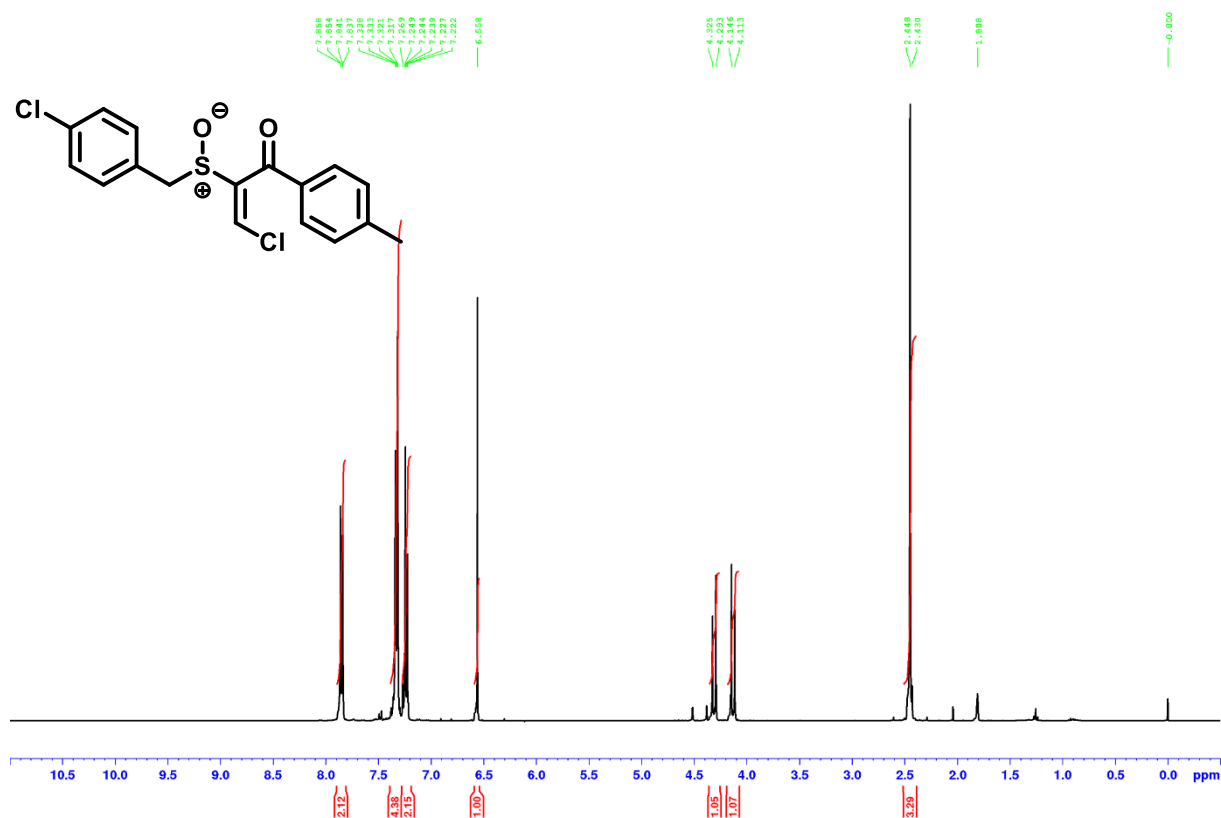


Figure S281: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-38t**.

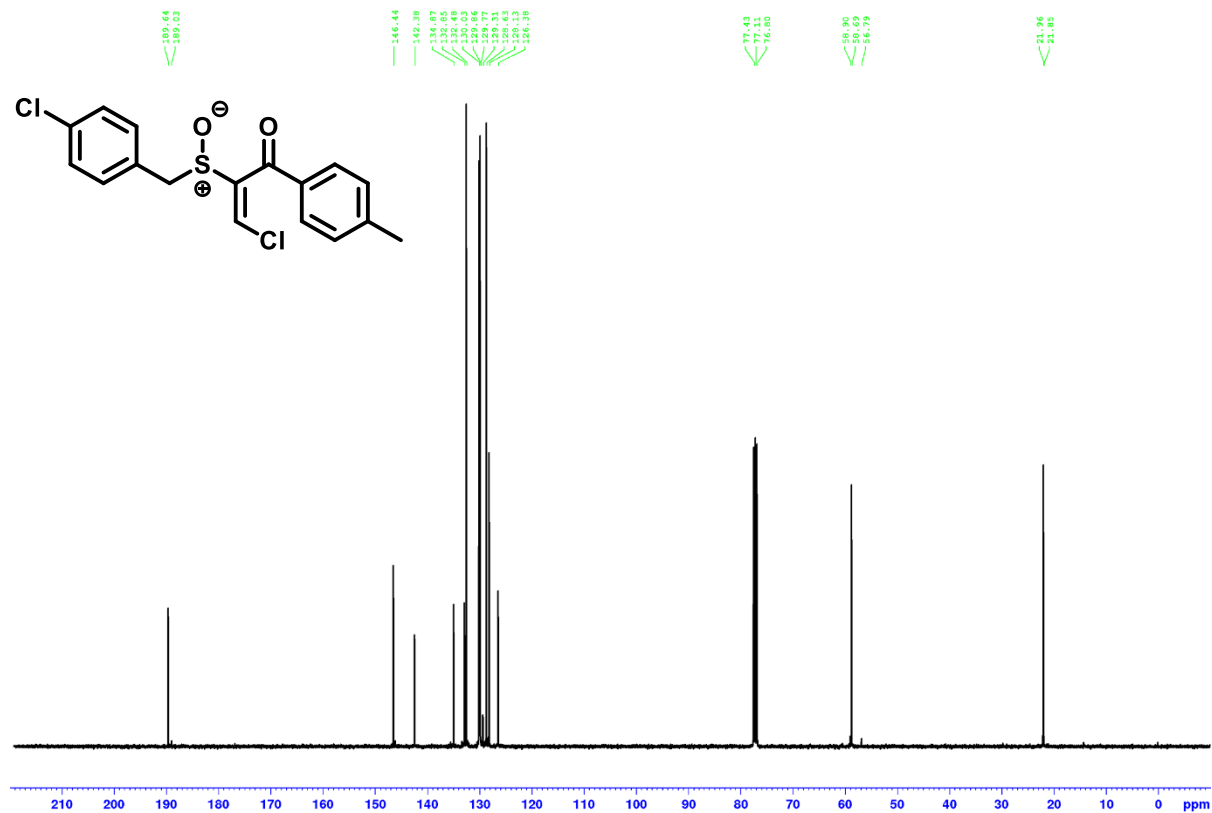


Figure S282: ¹³C NMR (100 MHz, CDCl₃) spectrum of **E-38t**.

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

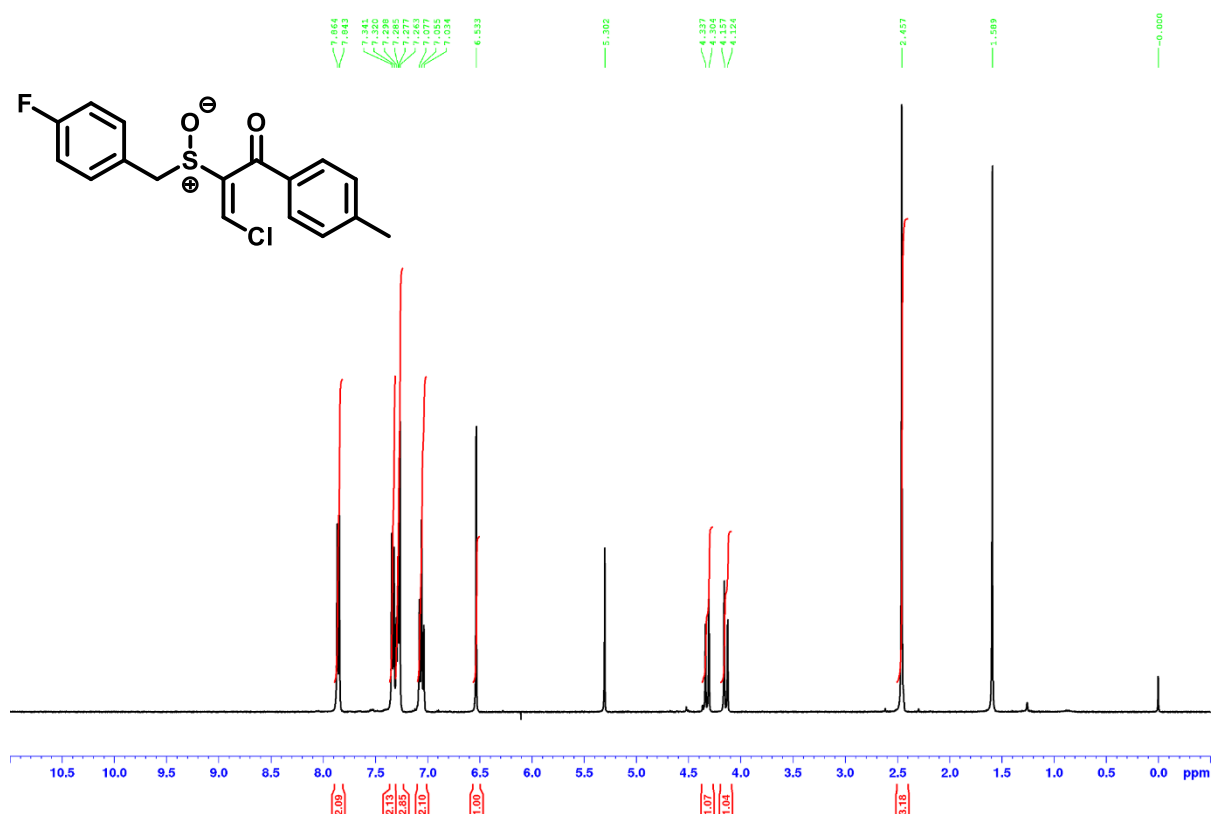


Figure S283: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-38aa.

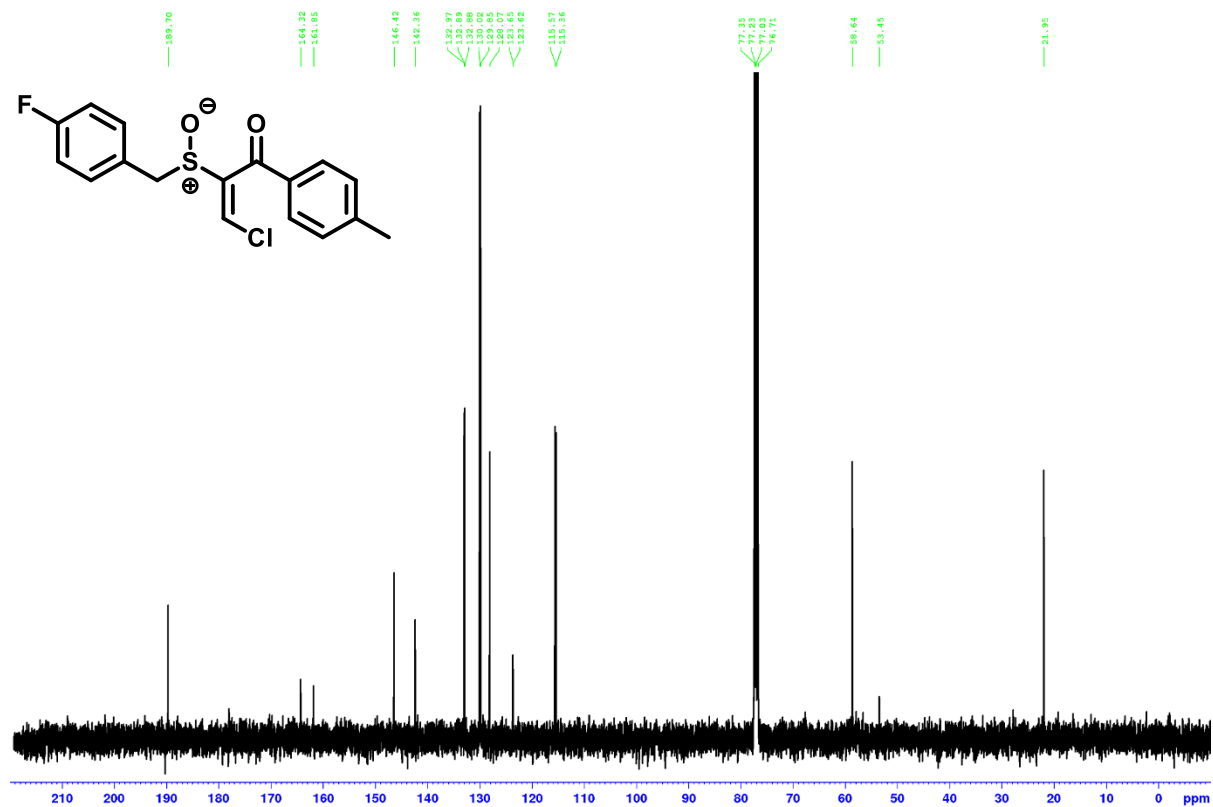


Figure S284: ¹³C NMR (100 MHz, CDCl₃) spectrum of *E*-38aa.

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

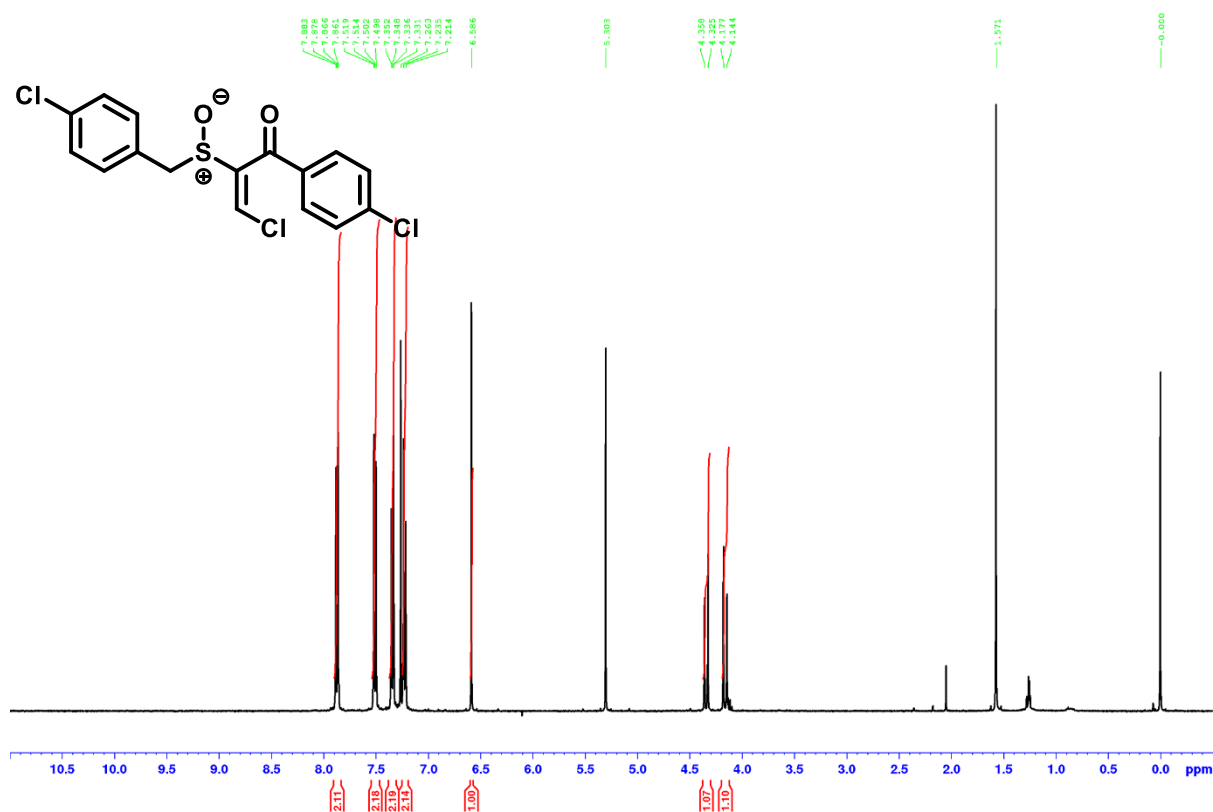


Figure S285: ¹H NMR (400 MHz, CDCl₃) spectrum of **E-38q**.

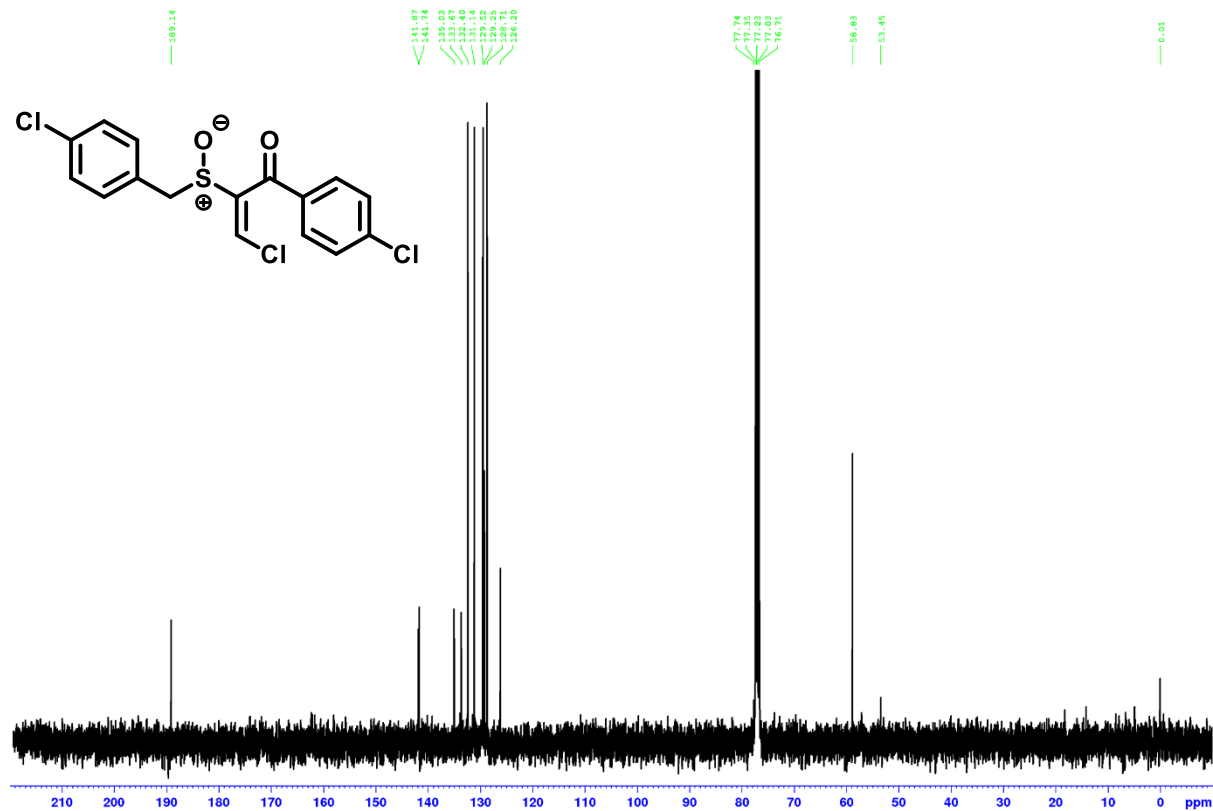


Figure S286: ¹³C NMR (100 MHz, CDCl₃) spectrum of **E-38q**.

Clc1ccc(cc1)CS(=O)(=O)CC(=O)c2ccc(Cl)cc2

Chemical structure: 4-chlorobenzyl 4-chlorobenzoate

¹³C NMR peaks (ppm):

- 188.28
- 142.65
- 136.71
- 134.05
- 133.46
- 132.46
- 129.46
- 128.46
- 127.34
- 126.71
- 77.34
- 77.03
- 76.71
- 56.92
- 56.05
- 0.01

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

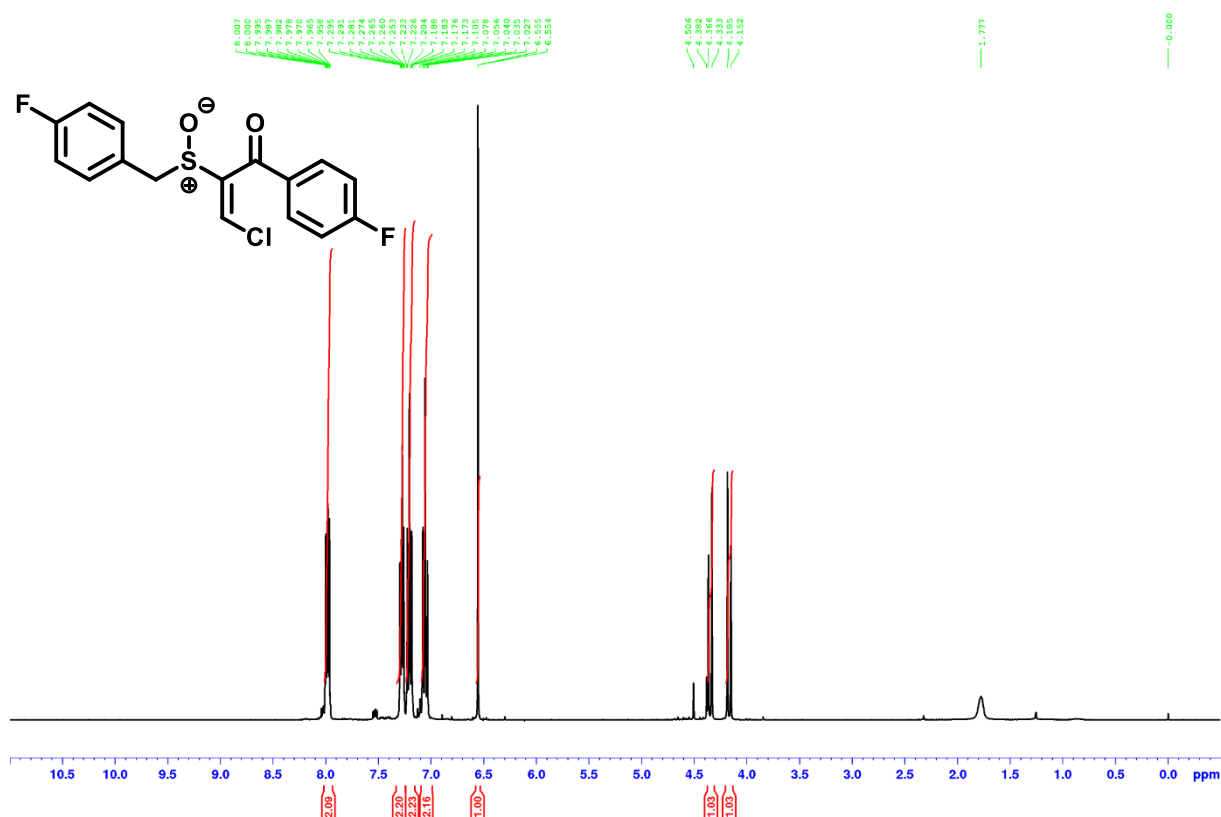


Figure S289: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-38z.

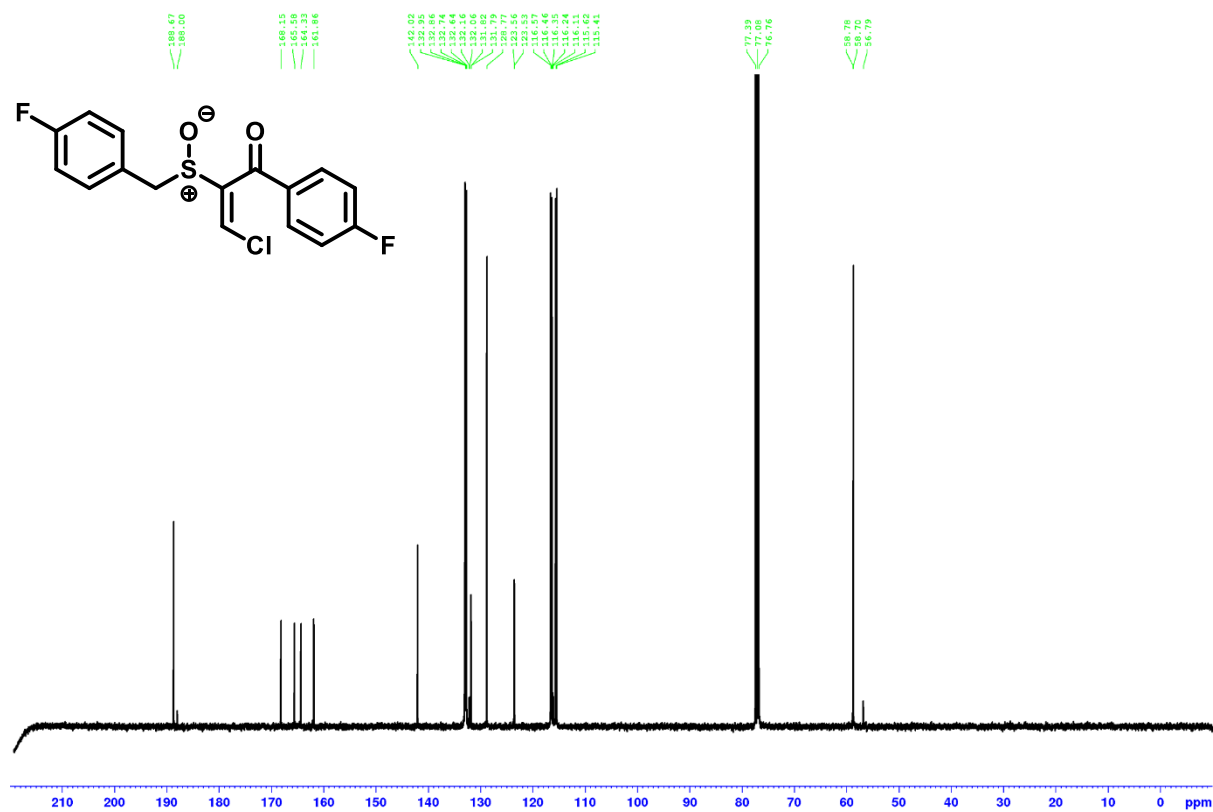


Figure S290: ¹³C NMR (100 MHz, CDCl₃) spectrum of *E*-38z.

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

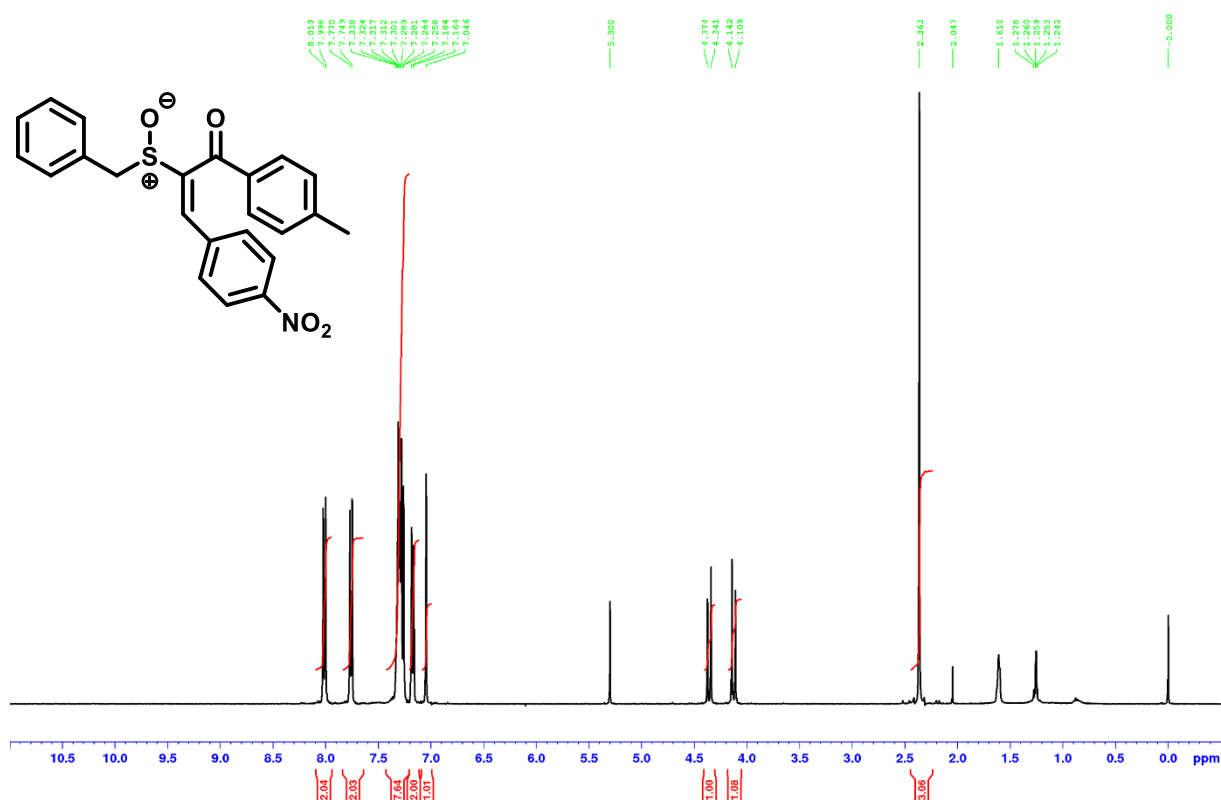


Figure S291: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-40h.

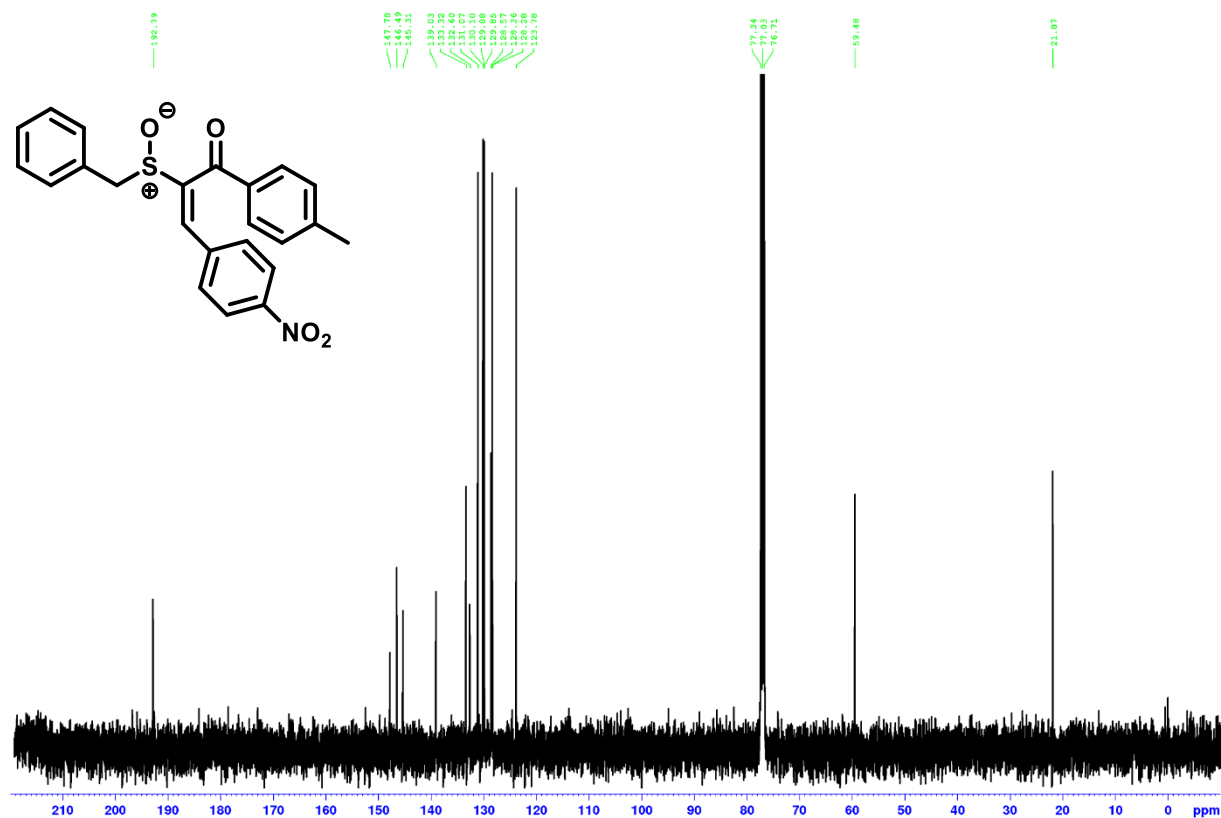


Figure S292: ¹³C NMR (100 MHz, CDCl₃) spectrum of *E*-40h.

[illegible][illegible]

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

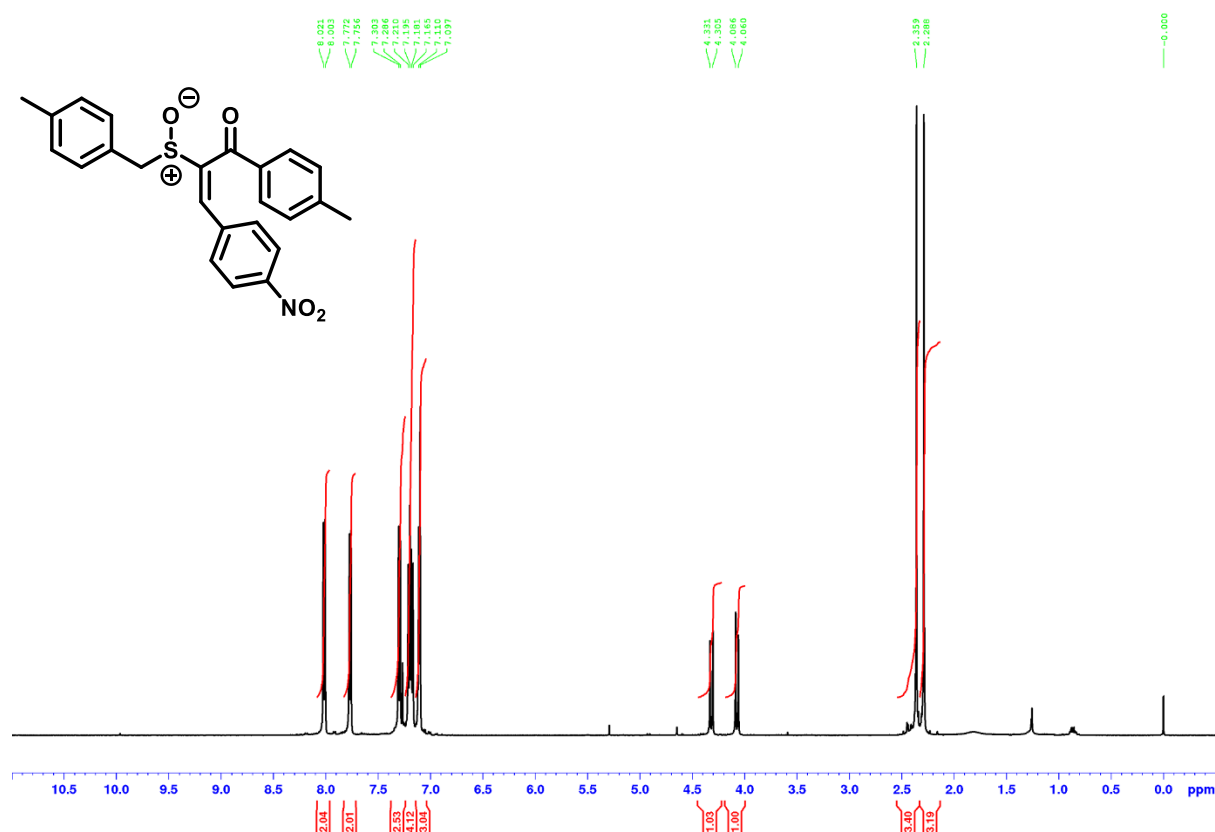
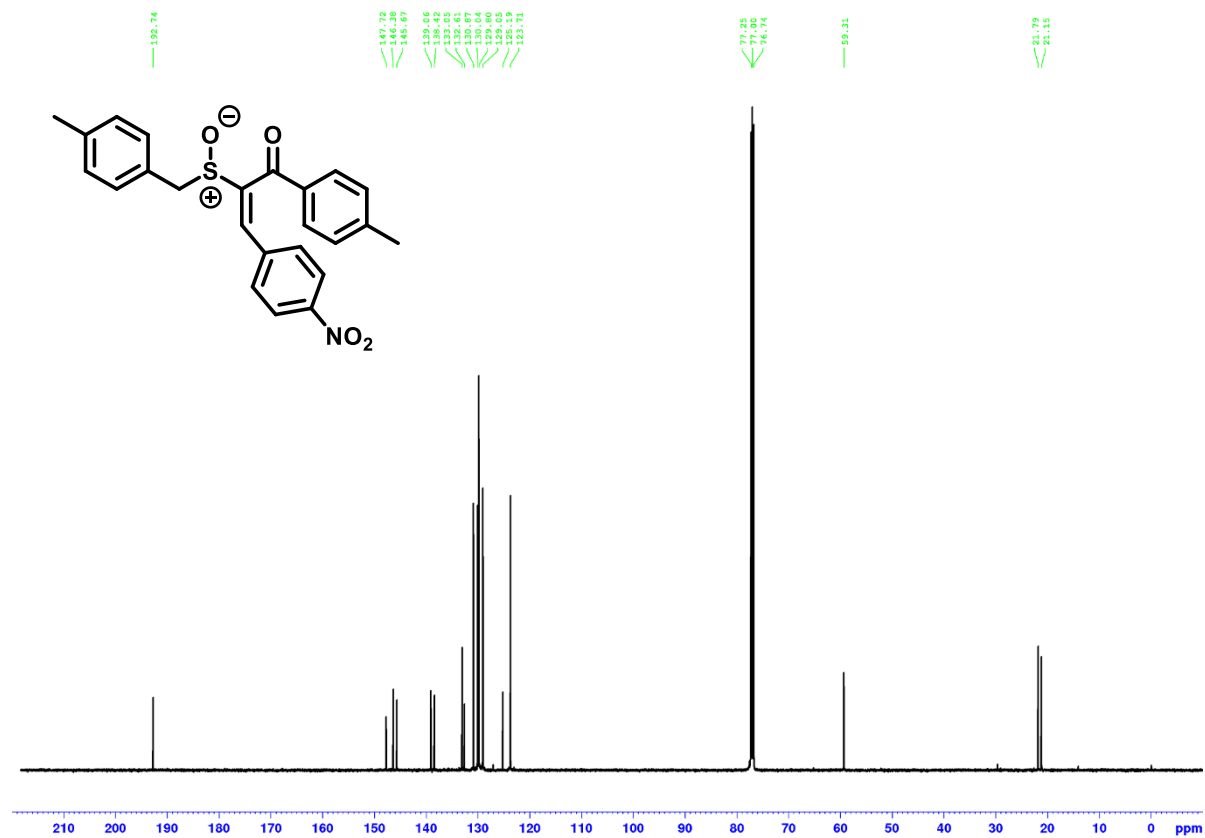


Figure S295: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-40m.



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

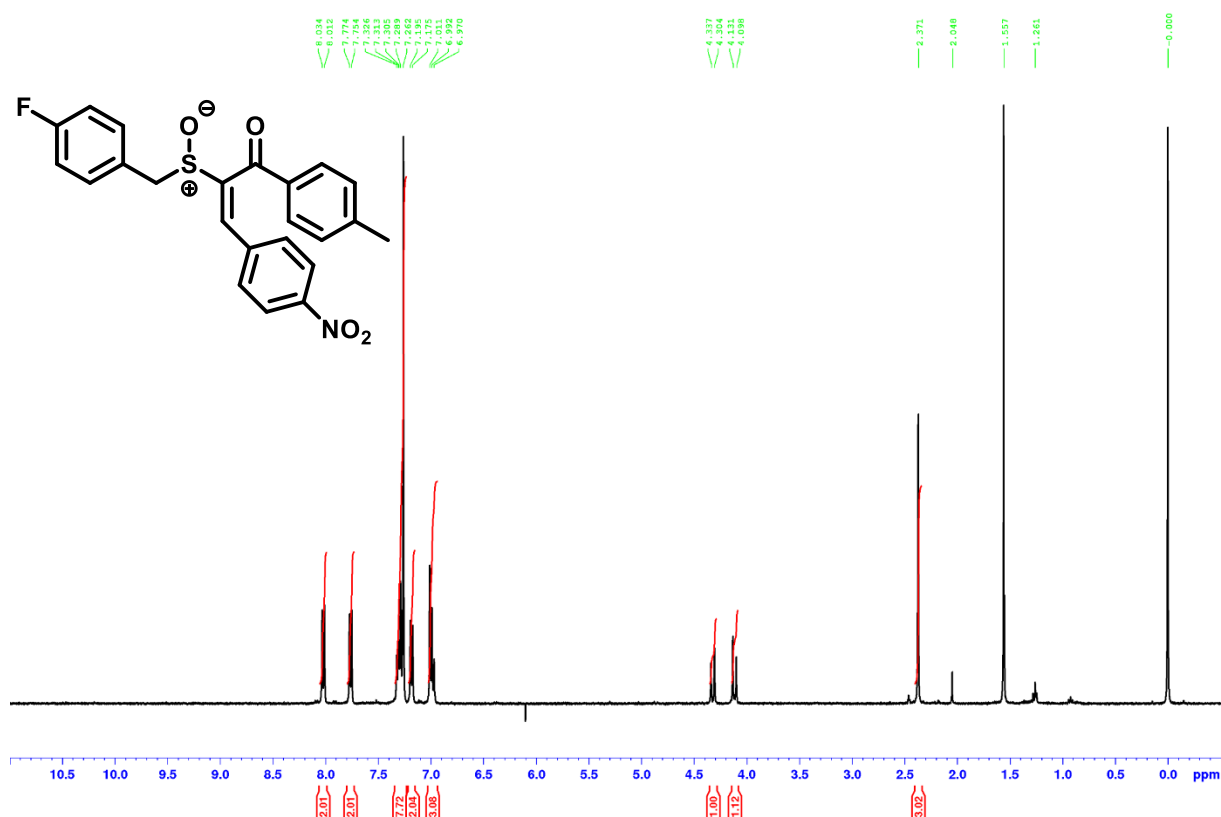


Figure S297: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-40aa.

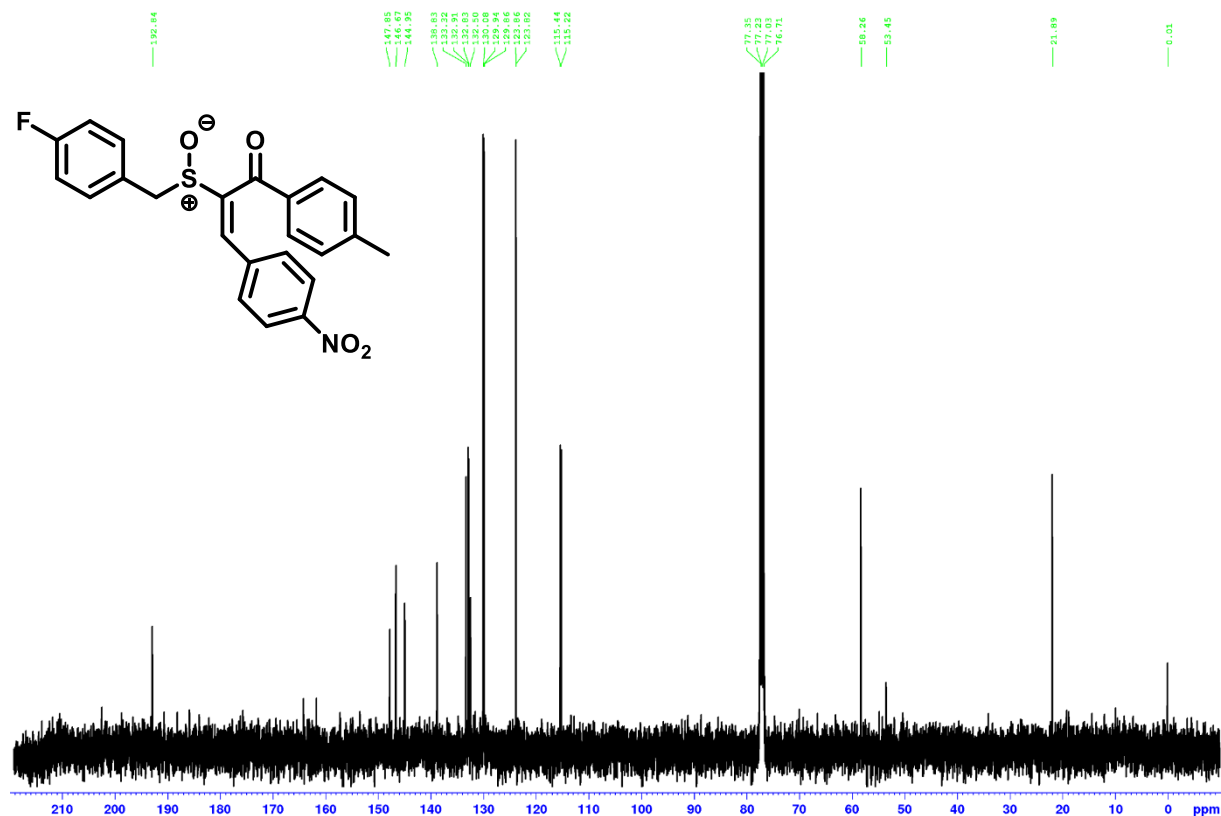


Figure S298: ¹³C NMR (100 MHz, CDCl₃) spectrum of *E*-40aa.

Chemical structure of compound 10 is shown in the top left. The structure is a 4-chlorobenzyl sulfonium ylide derivative. The sulfonium ylide is in equilibrium with a zwitterionic form (S⁺-O⁻). The sulfonium ylide is attached to a 4-nitrophenyl ring, which is in equilibrium with a zwitterionic form (S⁺-O⁻). The spectrum shows peaks for the aromatic protons (7.0-8.2 ppm), the 4-chlorobenzyl protons (4.1-4.3 ppm), the 4-nitrophenyl protons (7.2-7.6 ppm), the methoxy protons (3.8 ppm), and the dimethylamino protons (2.8 ppm). Integration values are shown below the peaks, and chemical shifts are listed above the peaks.

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

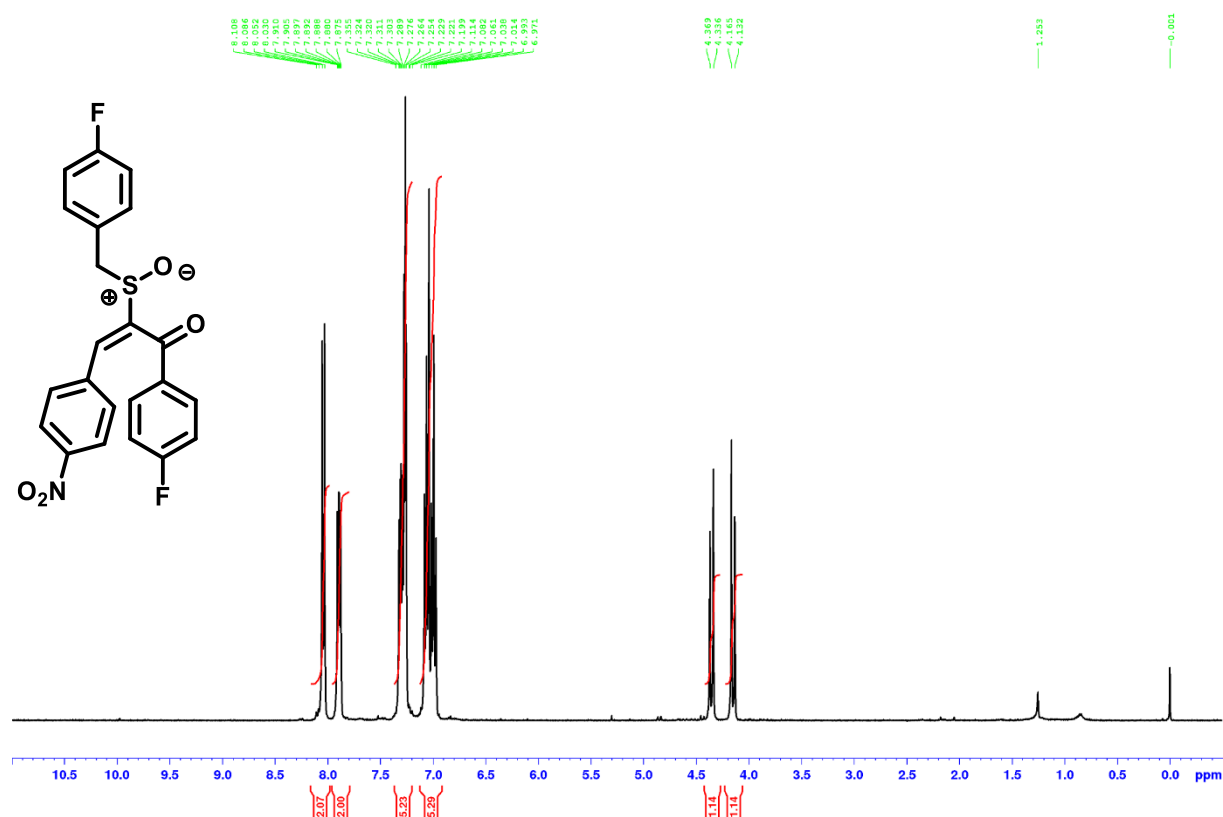


Figure S301: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-40z.

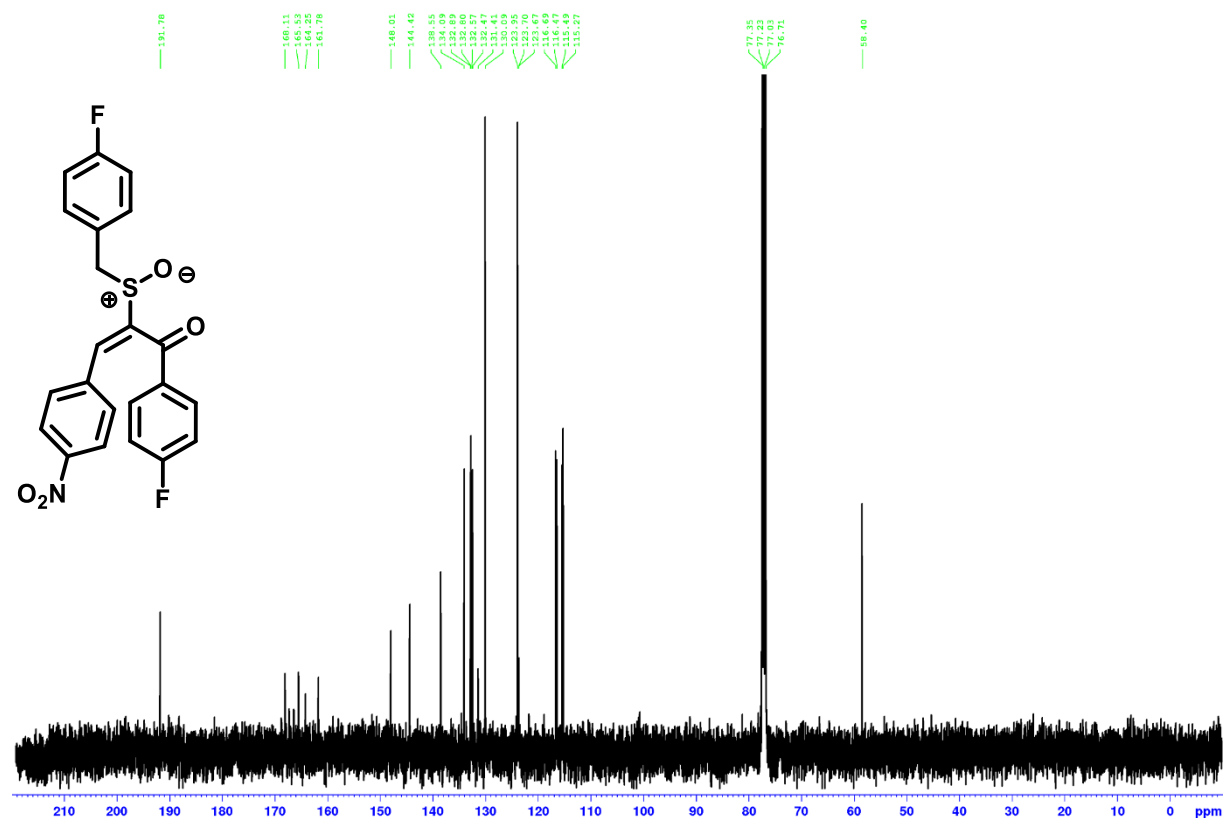


Figure S302: ¹³C NMR (100 MHz, CDCl₃) spectrum of *E*-40z.

Chemical structure of 4-(4-fluorophenyl)-2-(4-fluorophenyl)ethanesulfonamide:

N=S(=O)(Cc1ccc(F)cc1)Cc2ccc(F)cc2

¹H NMR spectrum (DMSO-d₆) showing peaks from 0 to 10 ppm. The spectrum includes aromatic signals (7.0-8.0 ppm), a methylene doublet (4.5 ppm), and a solvent peak (2.5 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
~8.0	3.25
~7.5	2.96
~7.3	0.66
~7.2	3.17
~7.1	2.16
~4.5	2.00
~4.4	2.00
2.5	-

Chemical structure: Fc1ccc(cc1)C(=O)CS(=O)(=O)Cc2ccc(F)cc2

¹³C NMR peaks (ppm):

- 167.96
- 166.02
- 165.11
- 141.16
- 139.05
- 138.26
- 137.96
- 136.15
- 135.96
- 135.76
- 131.40
- 129.40
- 128.40
- 116.49
- 116.38
- 116.27
- 116.13
- 115.92
- 77.35
- 77.33
- 77.31
- 77.03
- 76.71
- 58.79
- 56.78

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

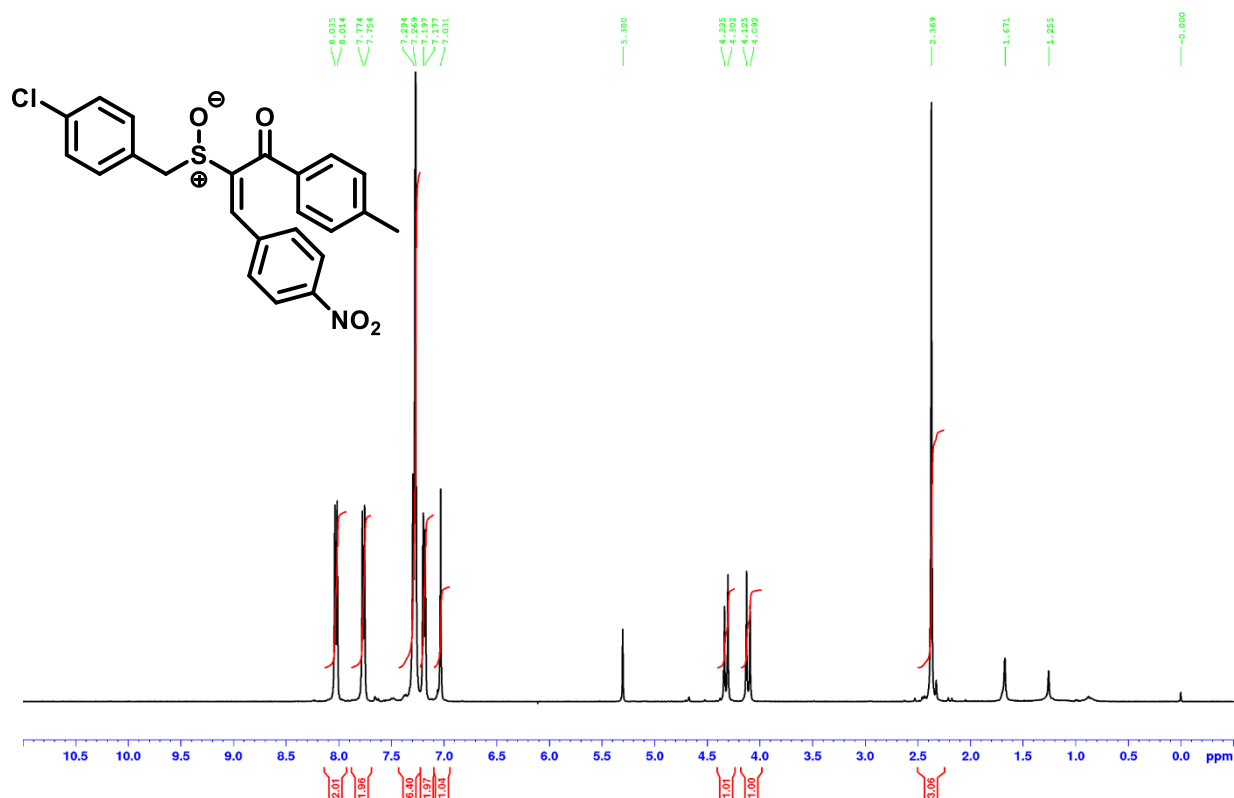


Figure S305: ¹H NMR (400 MHz, CDCl₃) spectrum of *E*-40t.

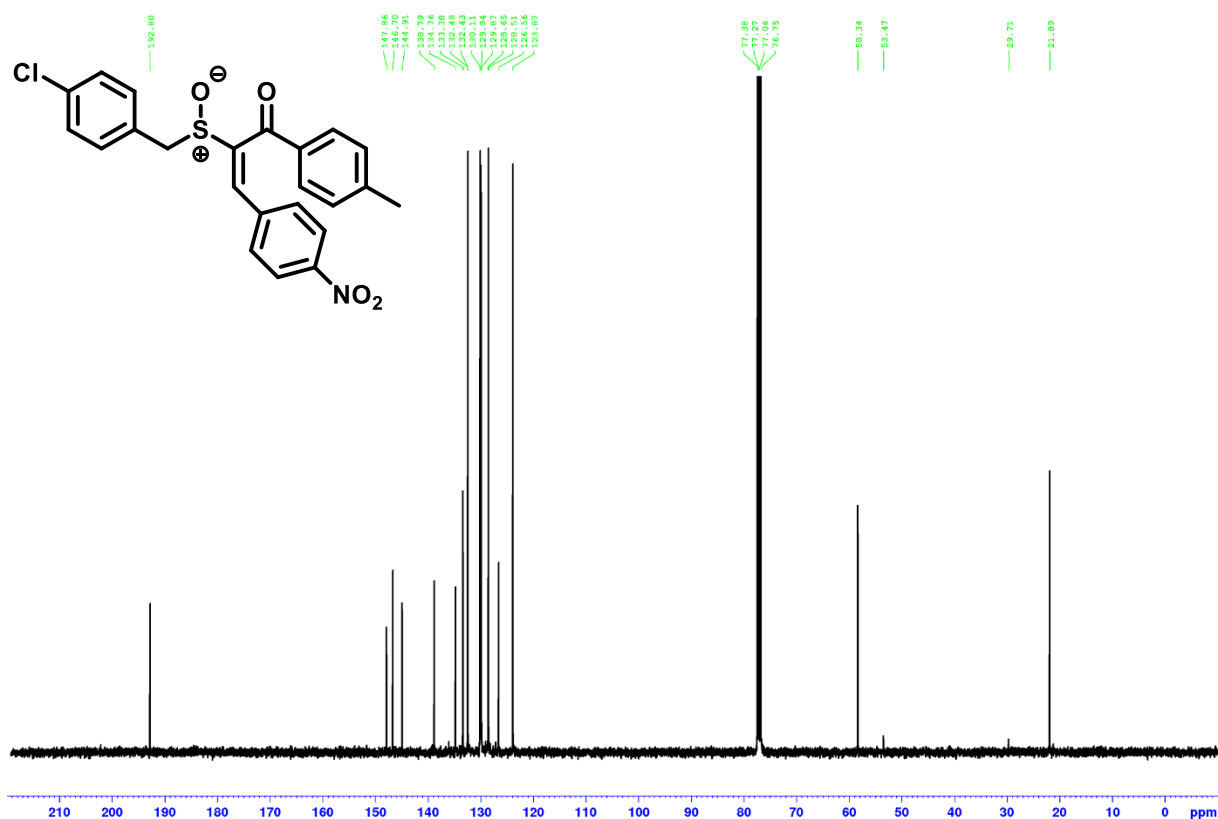


Figure S306: ¹³C NMR (100 MHz, CDCl₃) spectrum of *E*-40t.

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

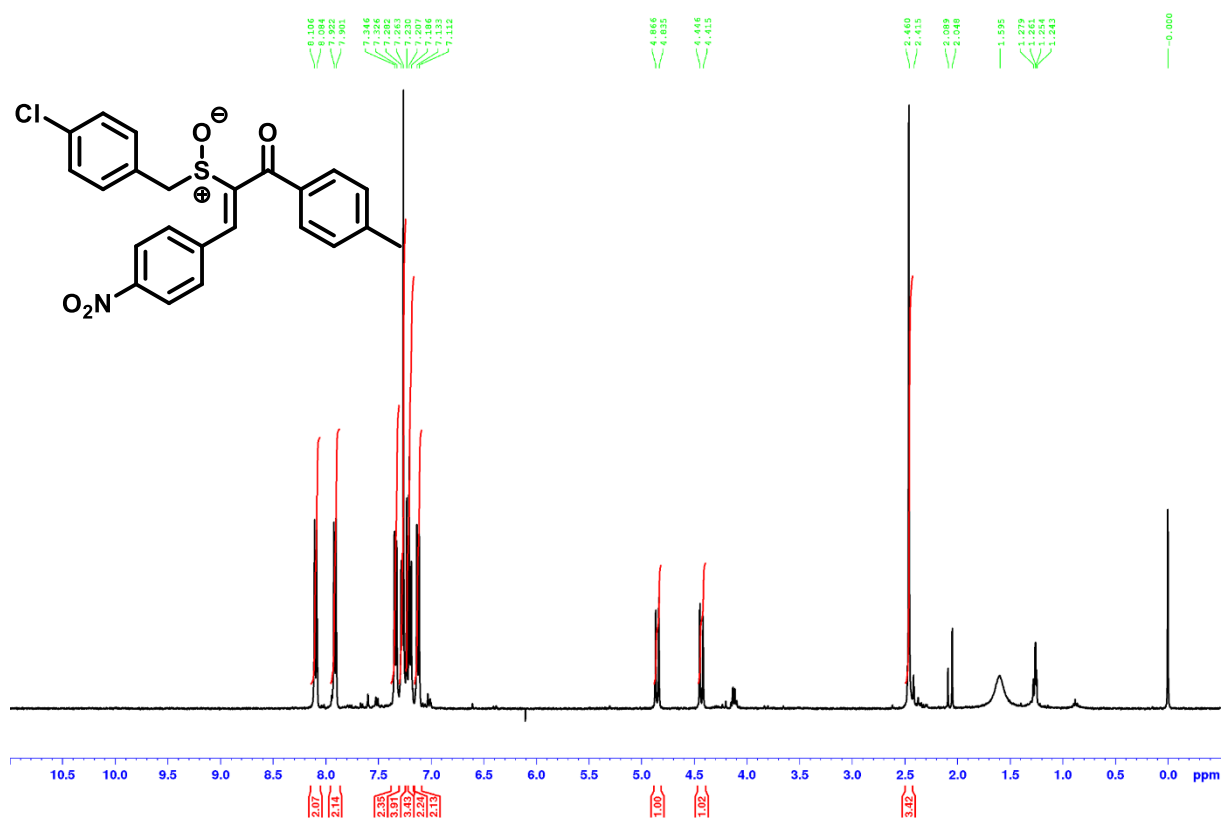


Figure S307: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-40t**.

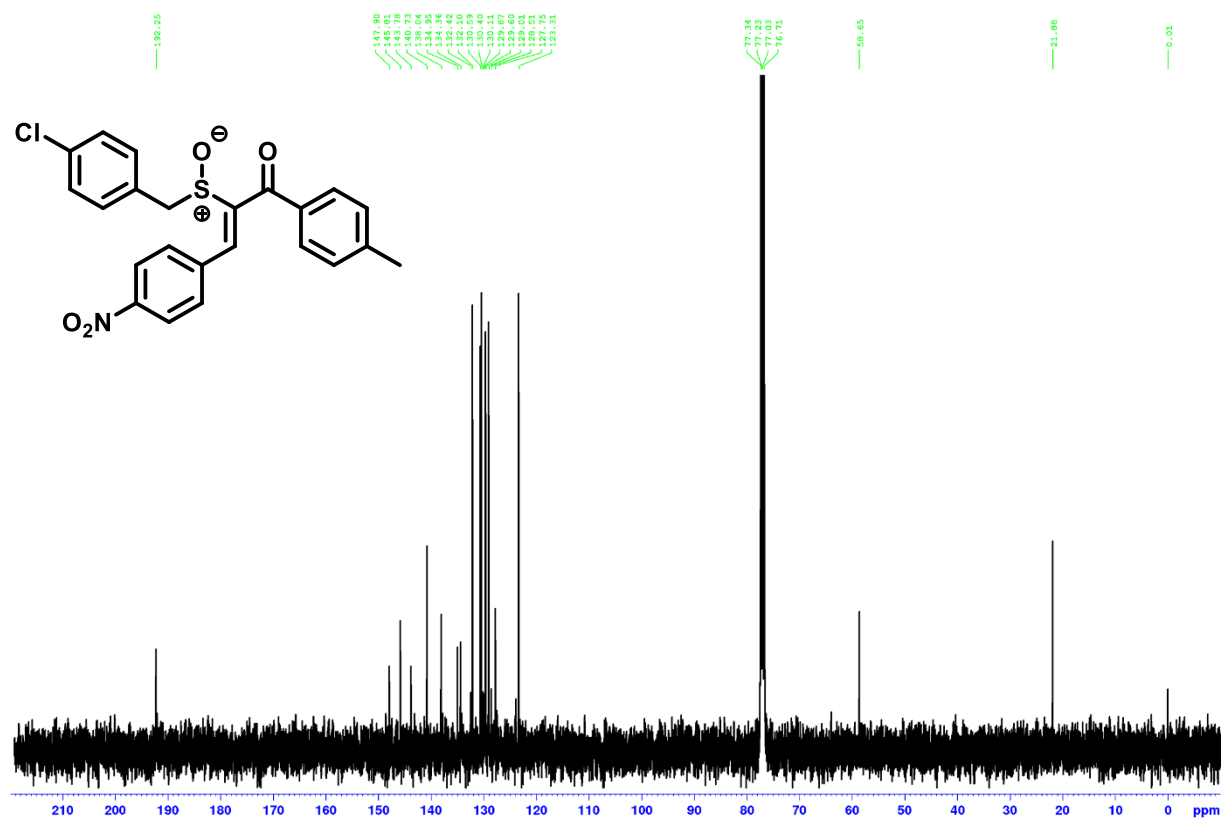


Figure S308: ¹³C NMR (100 MHz, CDCl₃) spectrum of **Z-40t**.

2-((4-Chlorobenzyl)sulfinyl)-1-(*p*-tolyl)prop-2-en-1-one S68

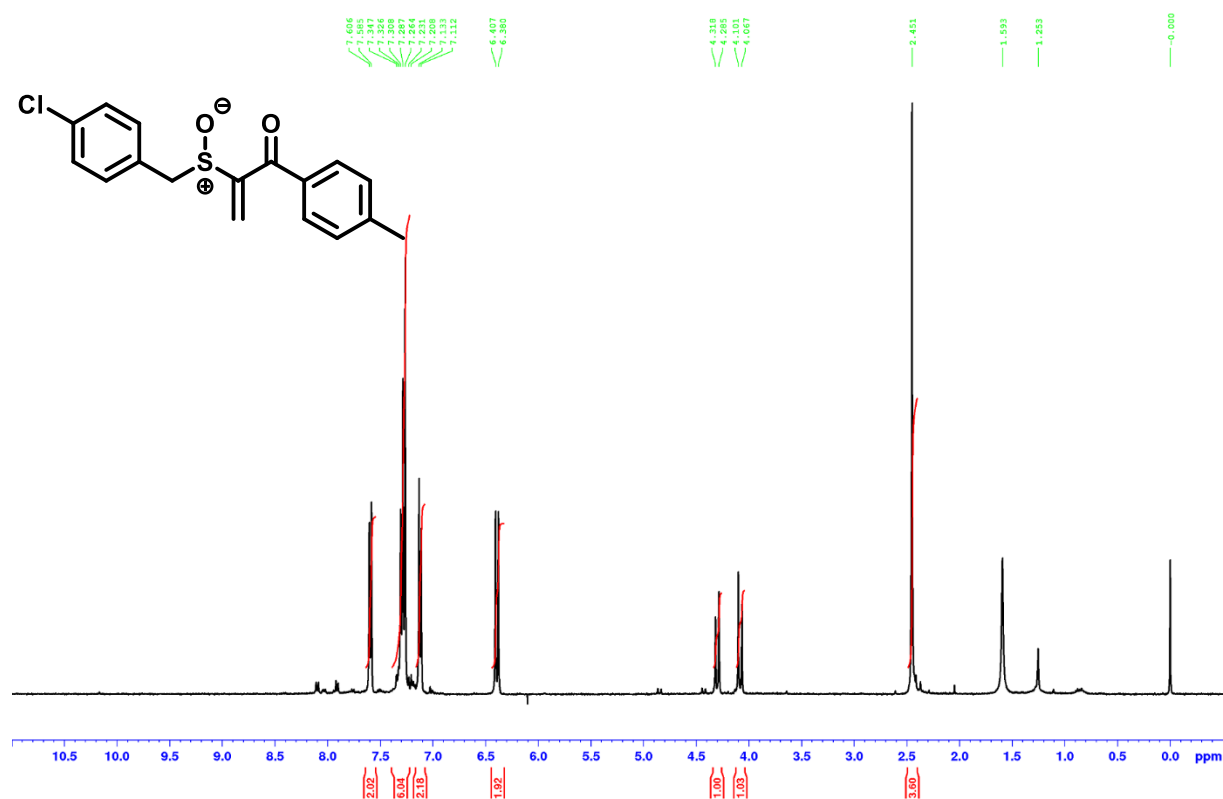


Figure S309: ¹H NMR (400 MHz, CDCl₃) spectrum of S68.

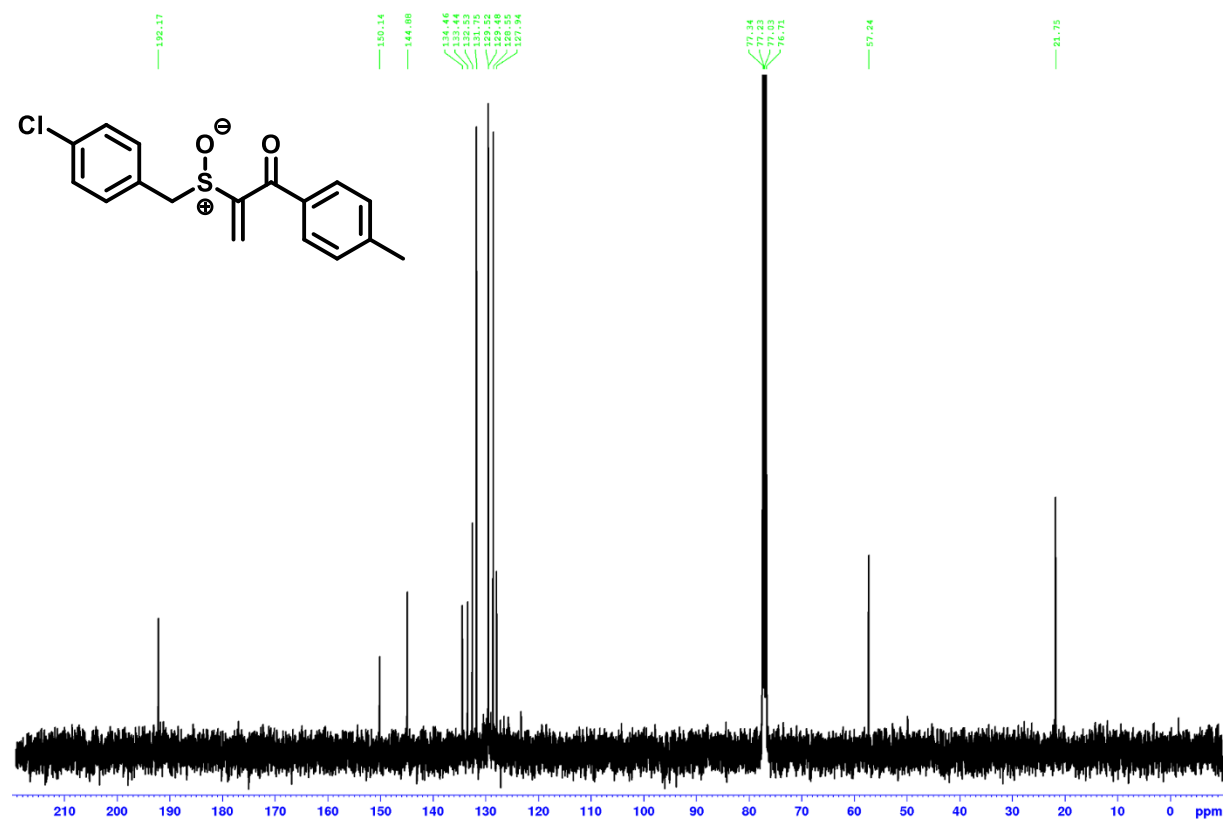


Figure S310: ¹³C NMR (100 MHz, CDCl₃) spectrum of S68.

1.12.12 Oxidation of Chalcones

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

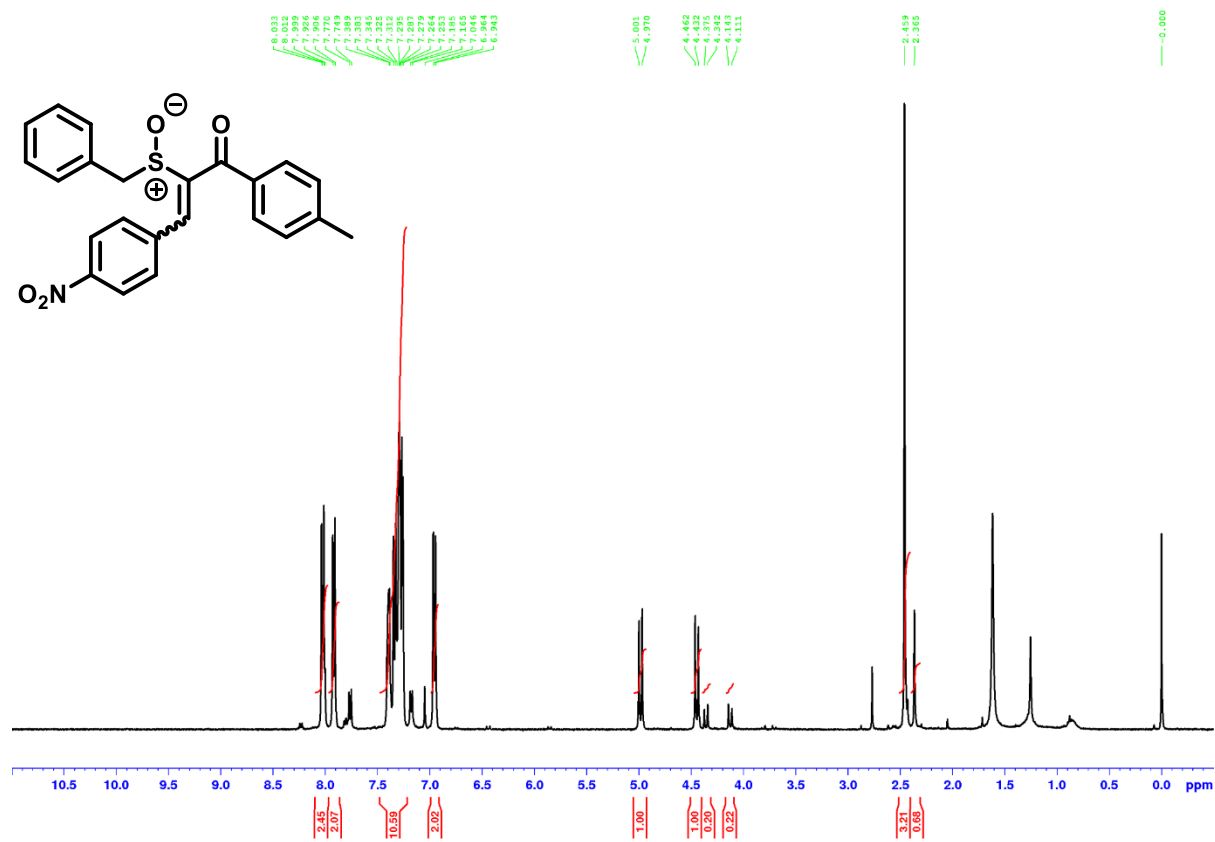


Figure S311: ¹H NMR (400 MHz, CDCl₃) spectrum of **Z-40h** and **E-40h** (Z:E, 3.6:1).

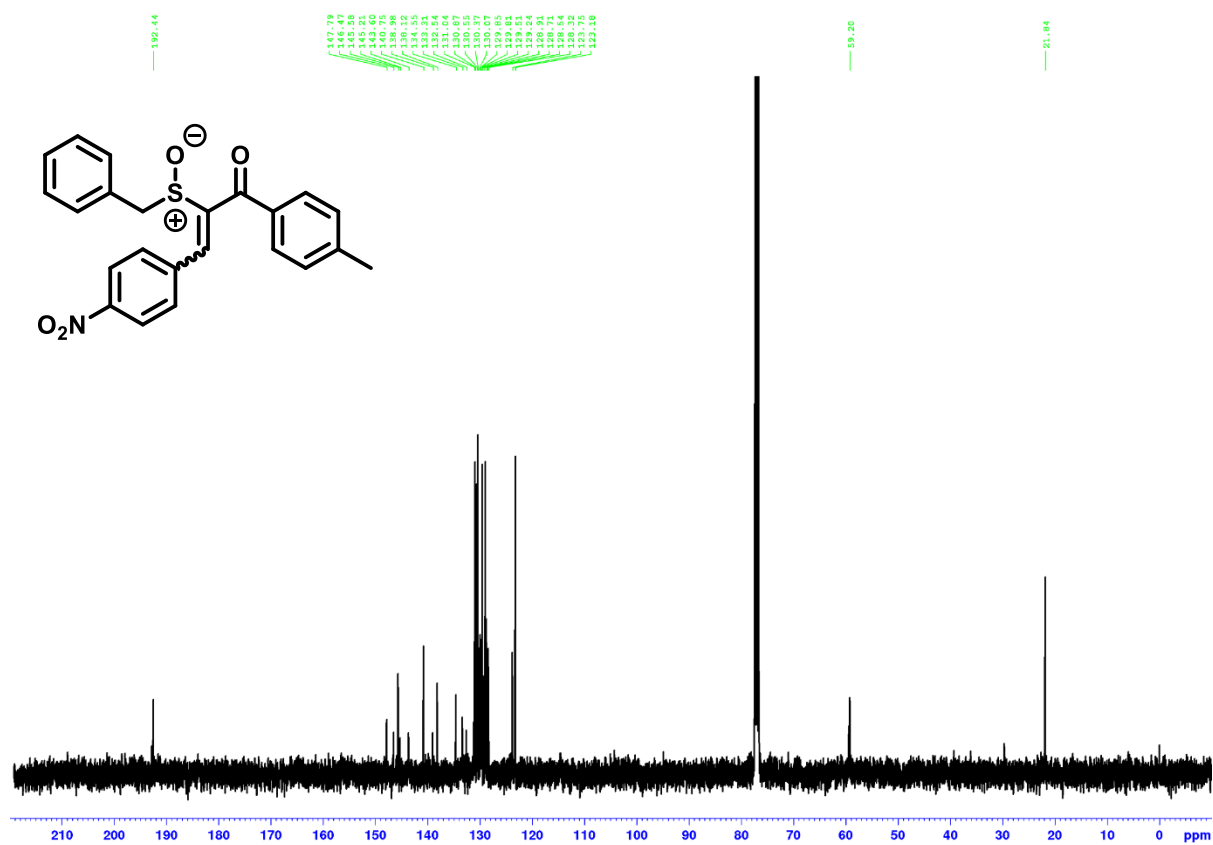


Figure S312: ¹³C NMR (100 MHz, CDCl₃) spectrum of **Z-40h** and **E-40h** (Z:E, 3.6:1).

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

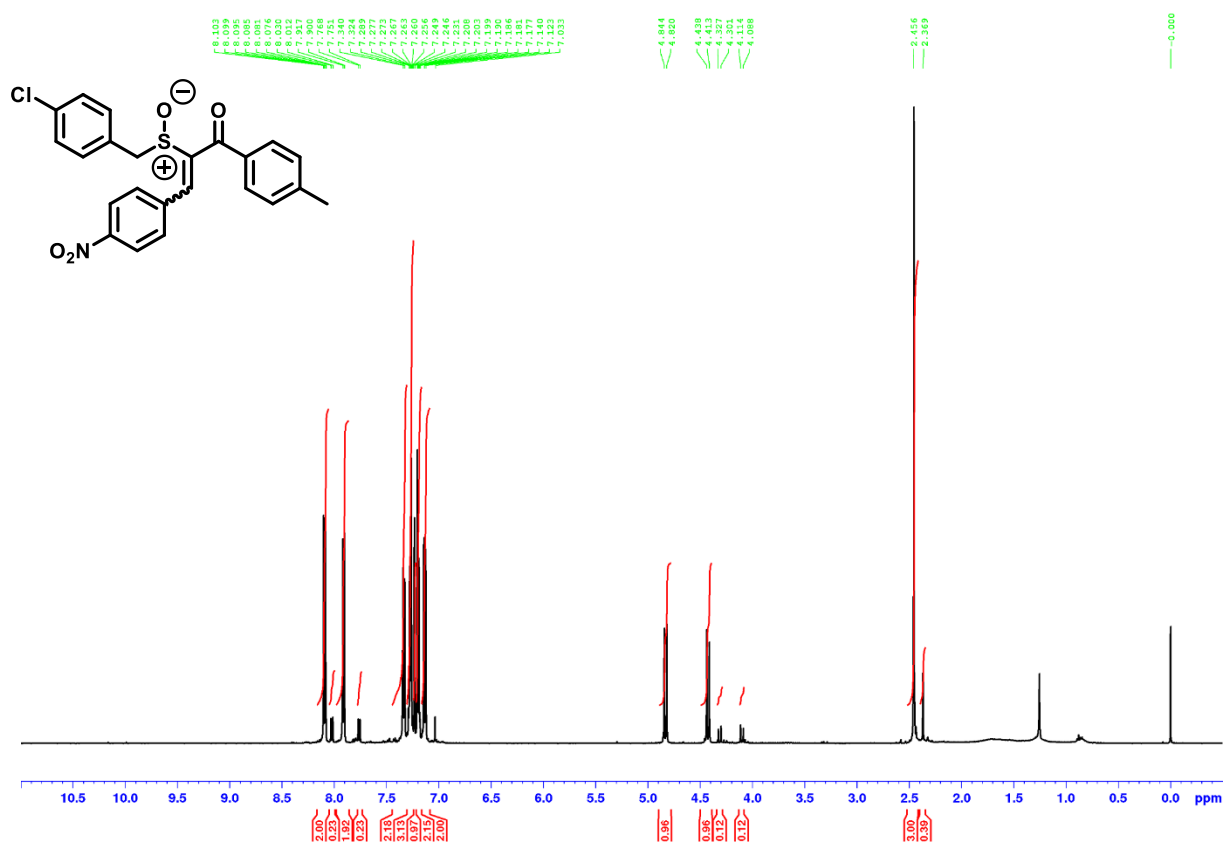


Figure S313: ¹H NMR (500 MHz, CDCl₃) spectrum of **Z-40j** and **E-40j** (Z:E, 8:1).

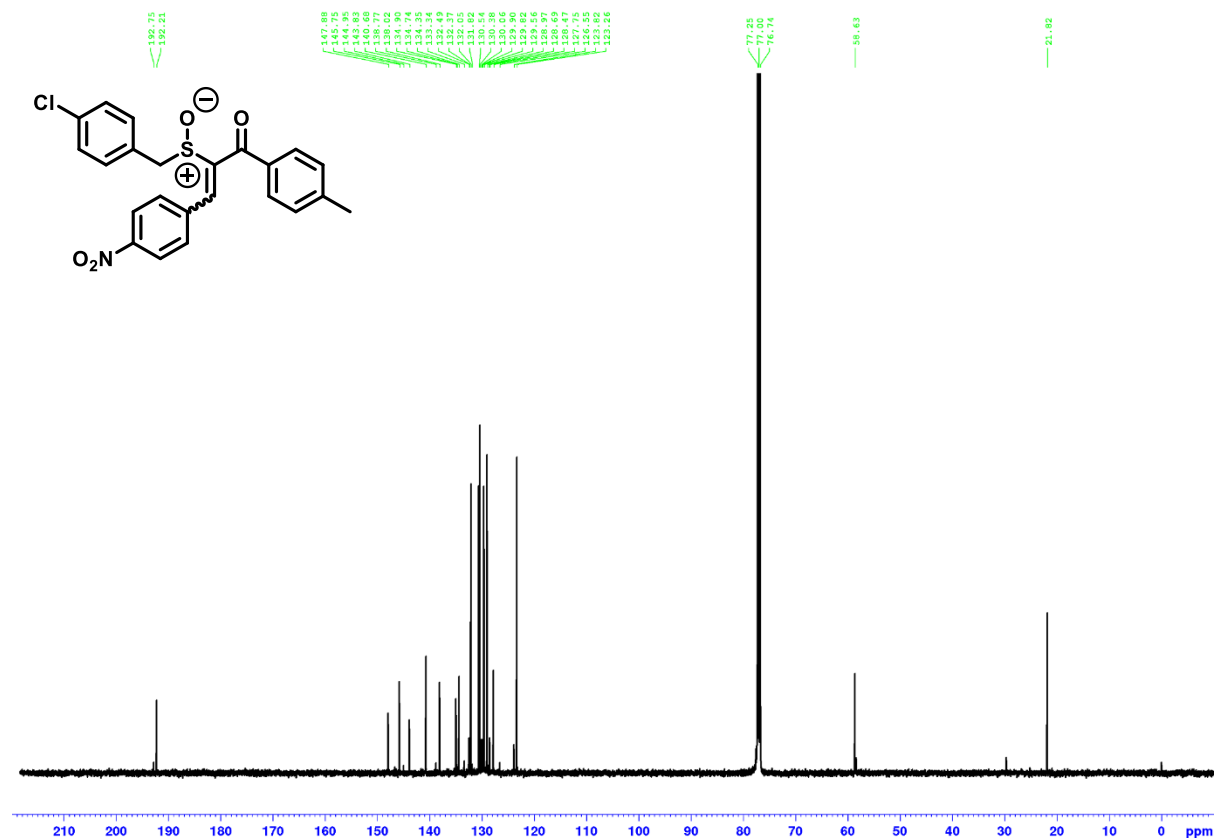


Figure S314: ¹³C NMR (125 MHz, CDCl₃) spectrum of **Z-40j** and **E-40j** (Z:E, 8:1).

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

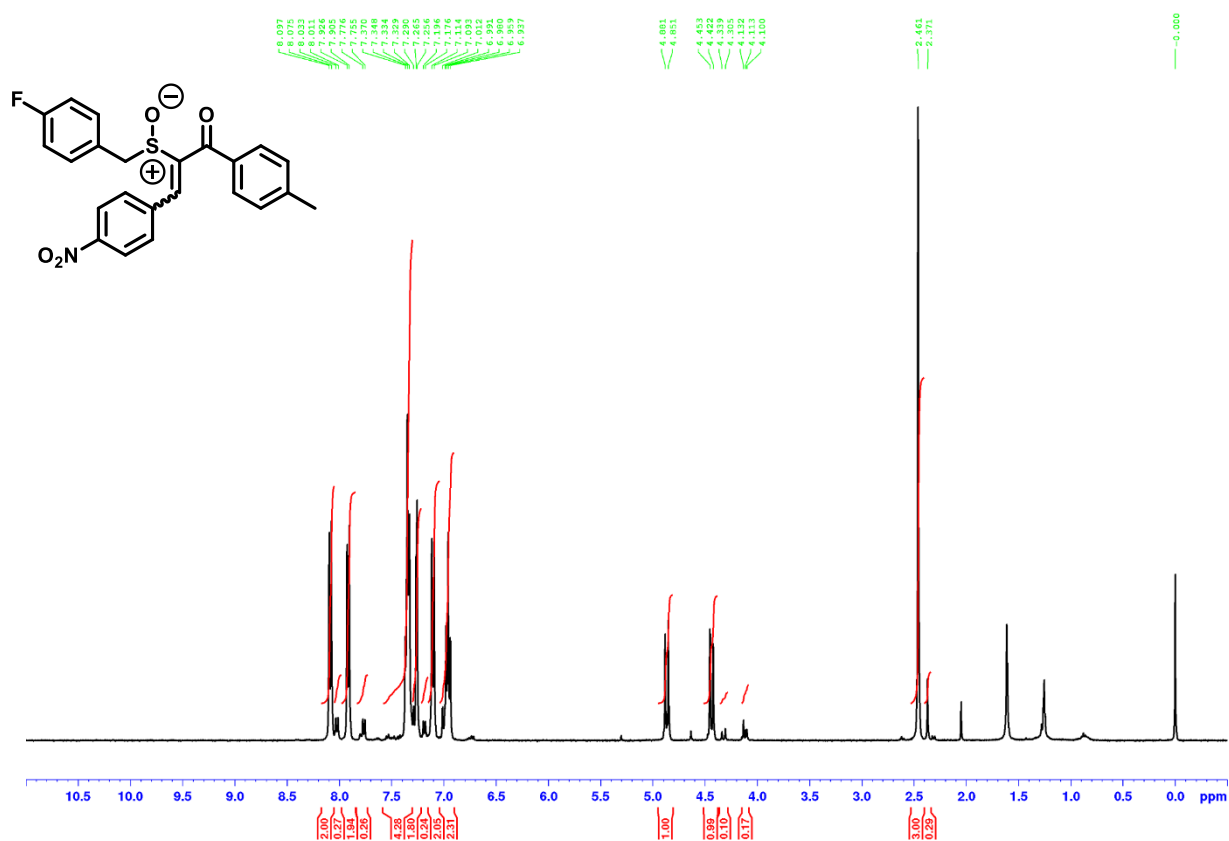


Figure S315: ¹H NMR (500 MHz, CDCl₃) spectrum of Z-40l and E-40l (Z:E, 11.5:1).

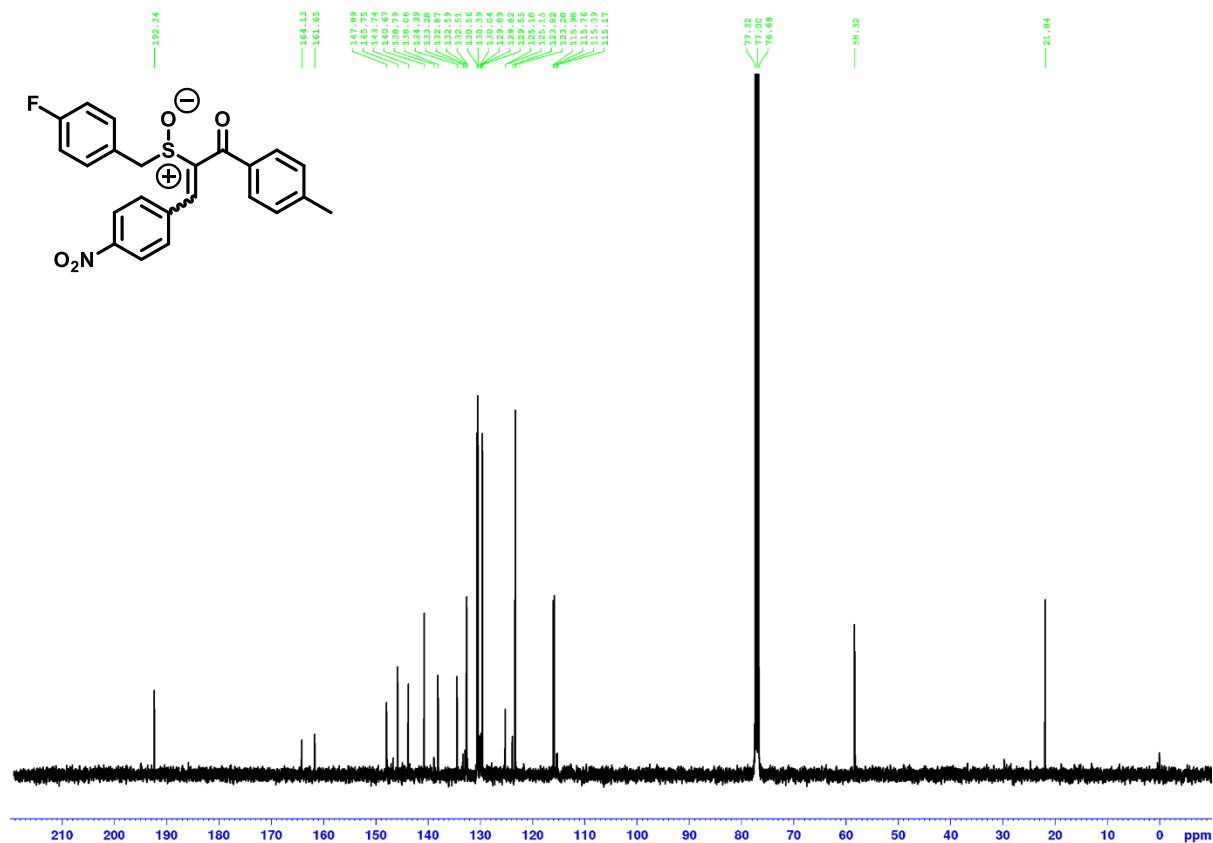


Figure S316: ¹³C NMR (125 MHz, CDCl₃) spectrum of Z-40l and E-40l (Z:E, 11.5:1)..

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

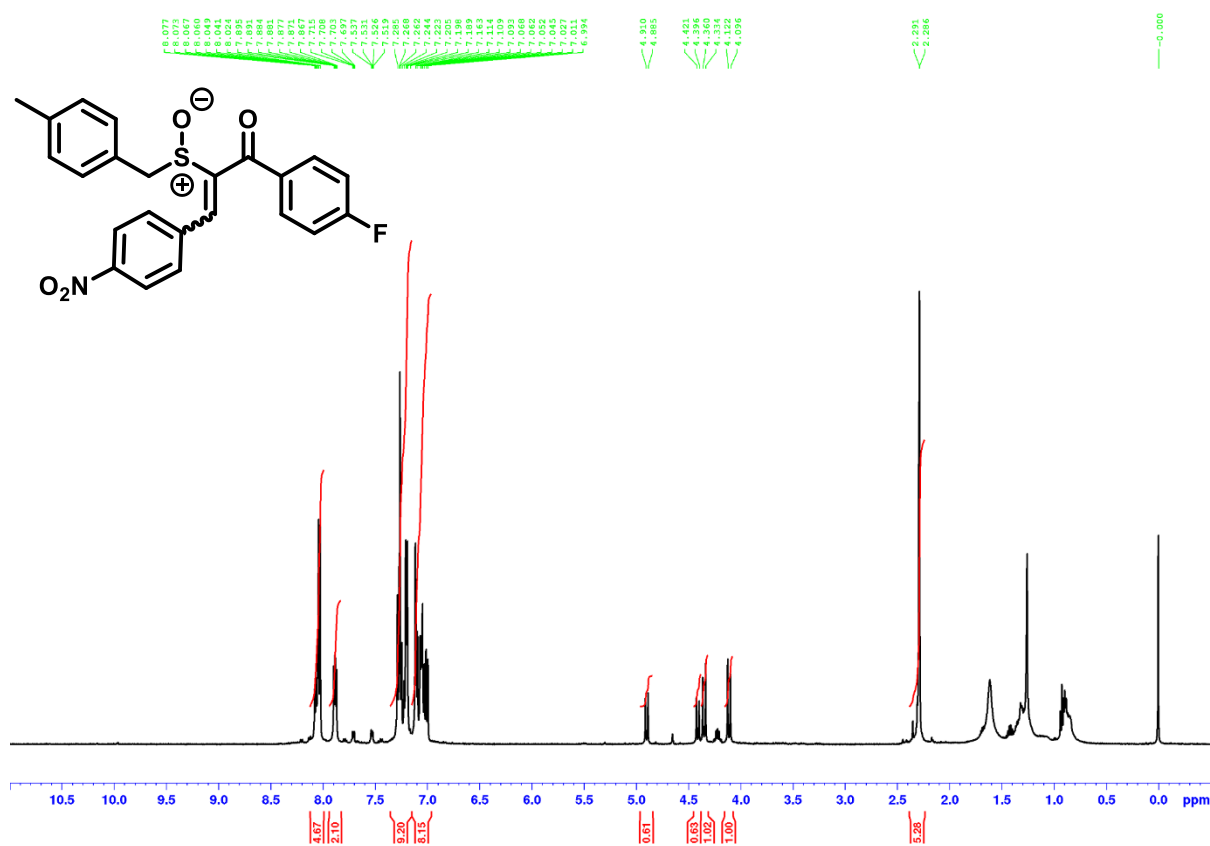


Figure S317: ¹H NMR (500 MHz, CDCl₃) spectrum of Z-40aa and E-40aa (Z:E, 1:1.3).

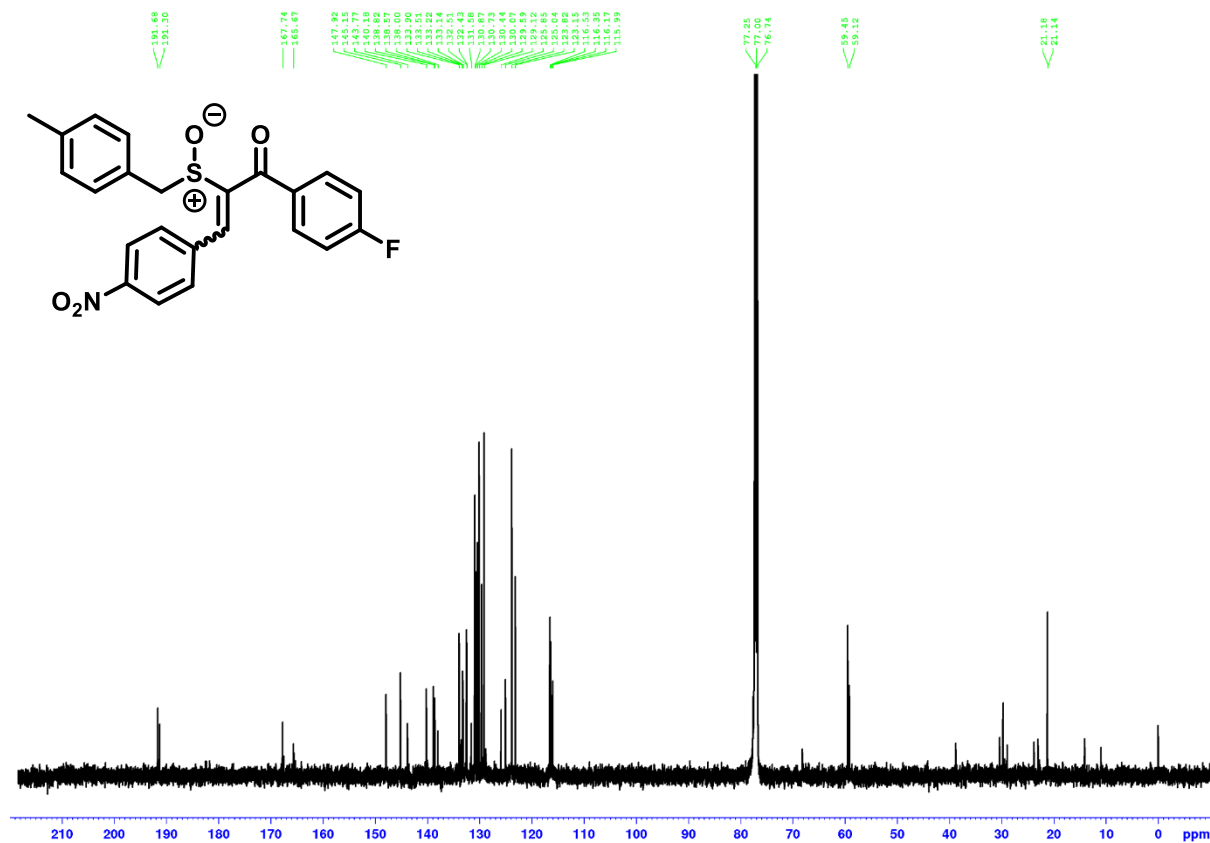


Figure S318: ¹³C NMR (125 MHz, CDCl₃) spectrum of Z-40aa and E-40aa (Z:E, 1:1.3).

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

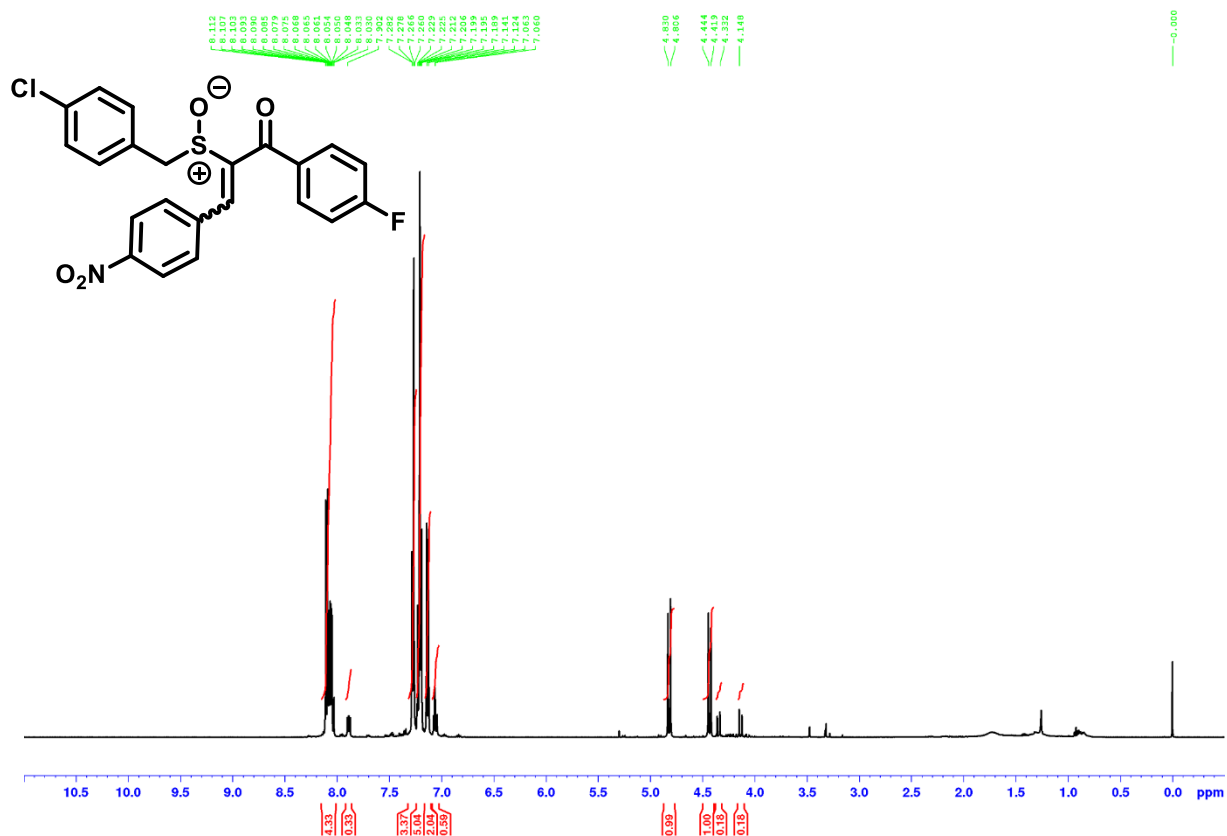


Figure S318: ¹H NMR (500 MHz, CDCl₃) spectrum of Z-40x and E-40x (Z:E, 6.7:1).

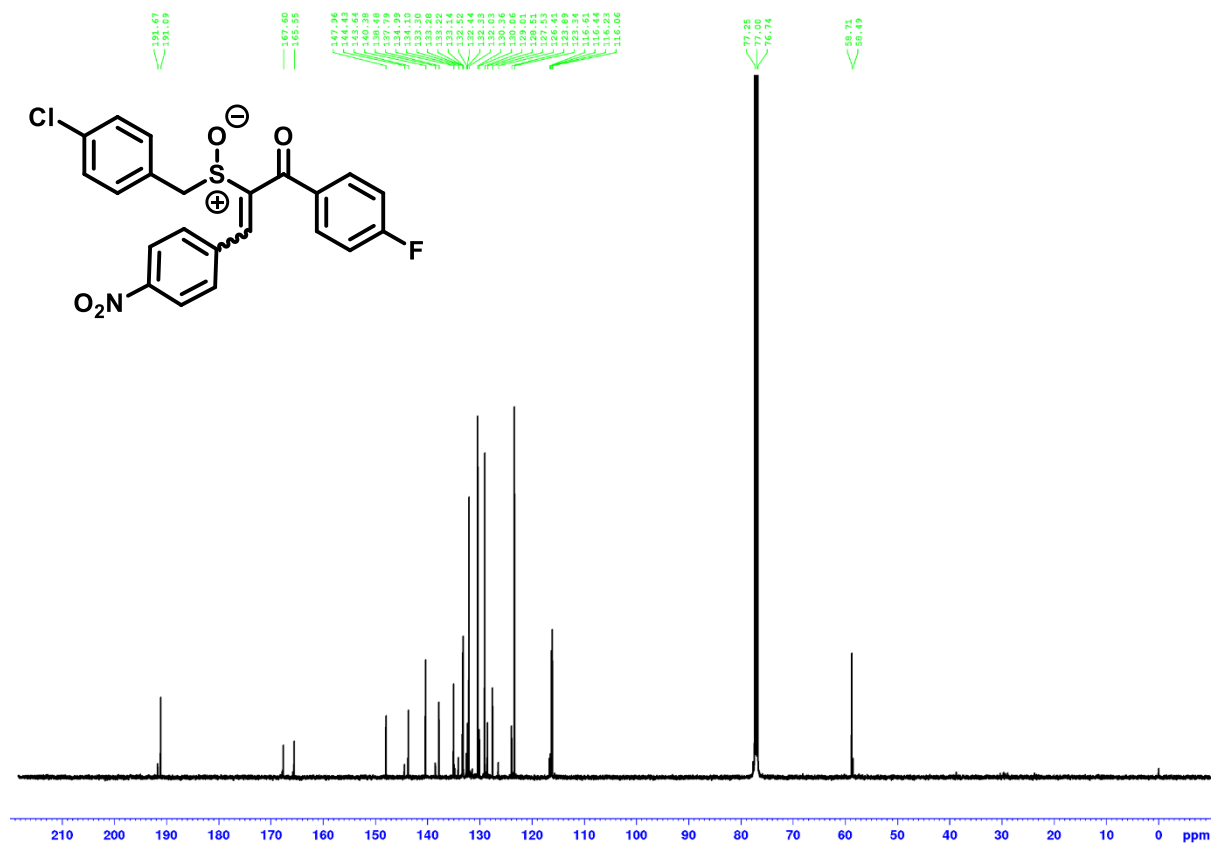


Figure S319: ¹³C NMR (125 MHz, CDCl₃) spectrum of Z-40x and E-40x (Z:E, 6.7:1).

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

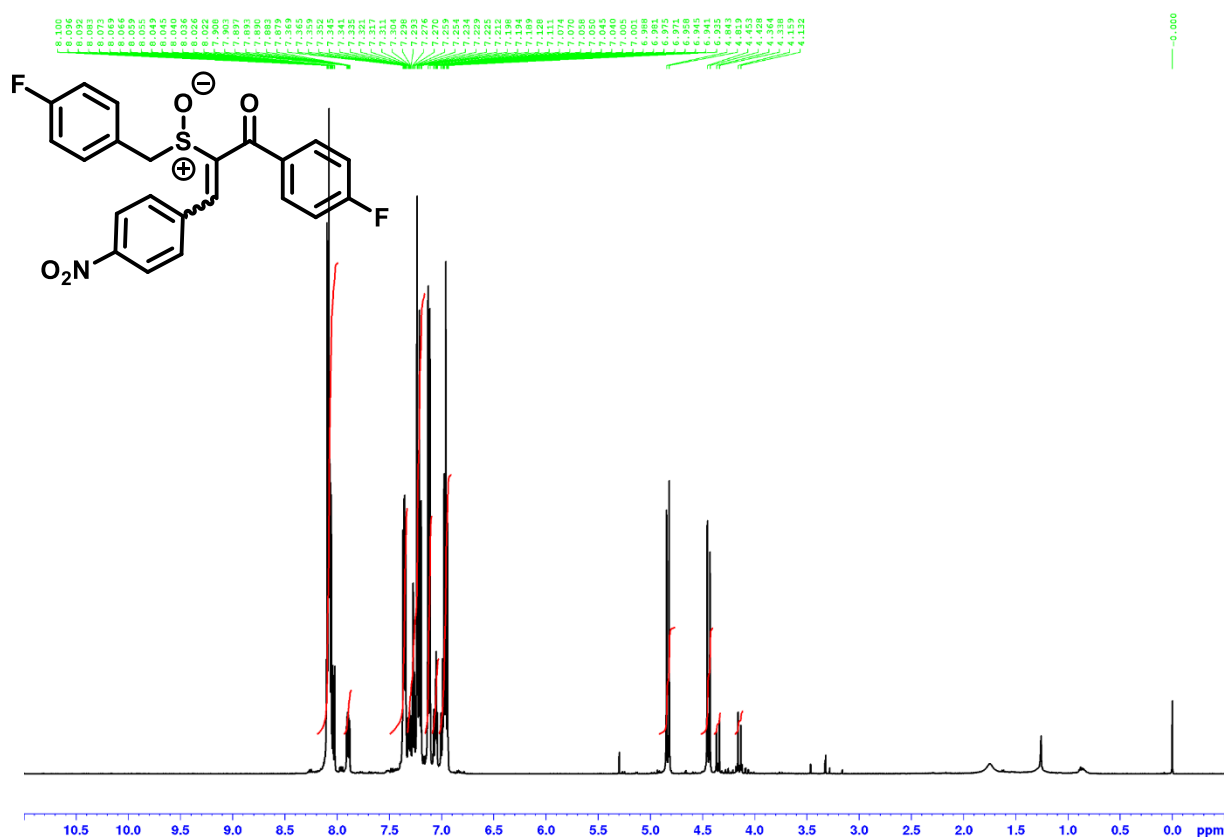


Figure S320: ¹H NMR (500 MHz, CDCl₃) spectrum of *Z*-40z and *E*-40z (Z:E, 5.8:1).

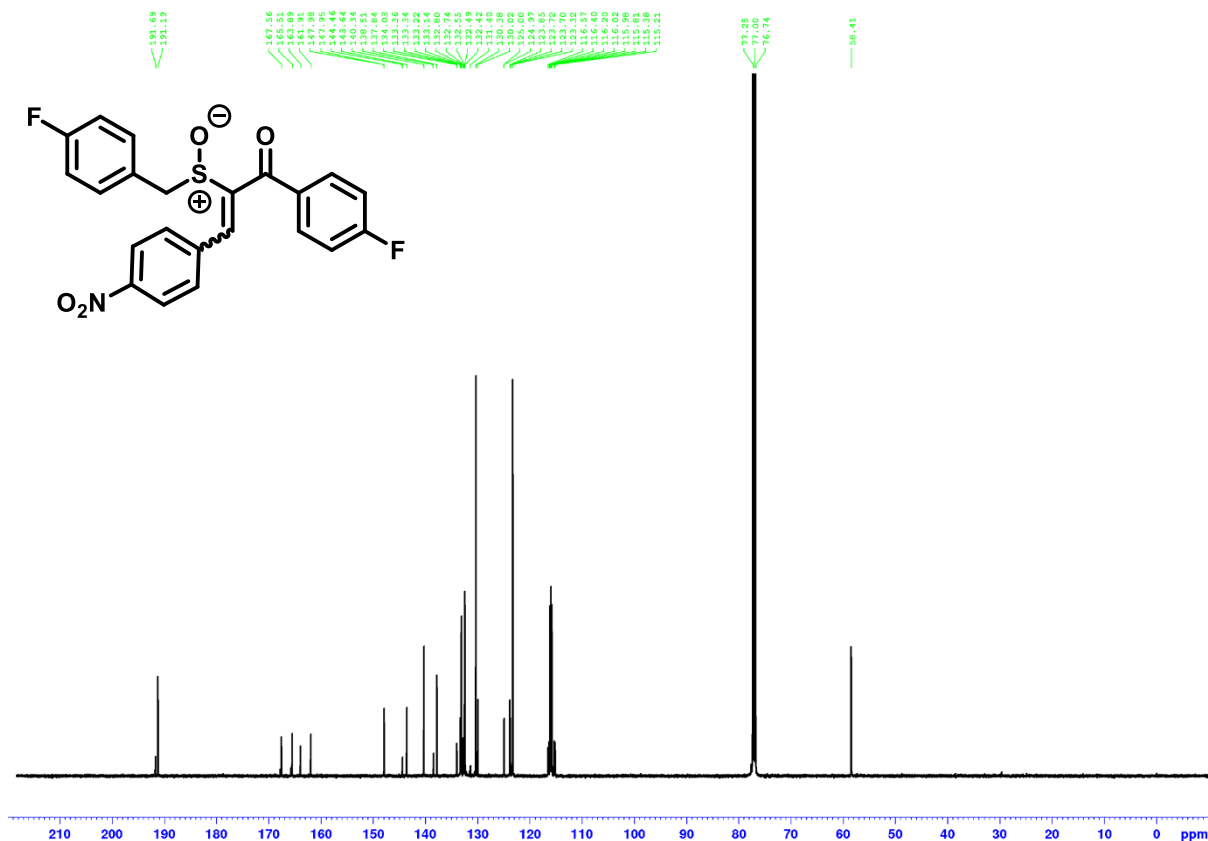


Figure S321: ¹³C NMR (125 MHz, CDCl₃) spectrum of *Z*-40z and *E*-40z (Z:E, 5.8:1).

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

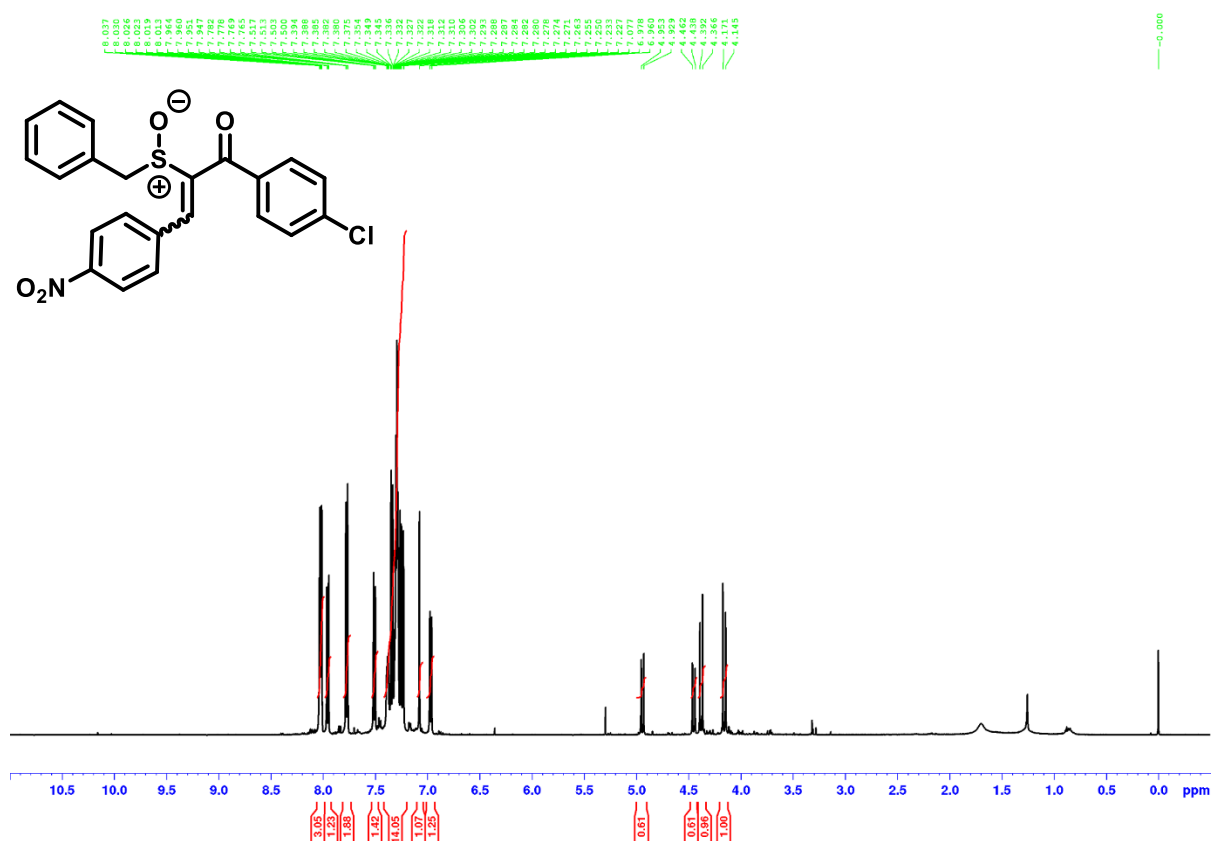


Figure S322: ¹H NMR (500 MHz, CDCl₃) spectrum of Z-40o and E-40o (Z:E, 1:1.6).

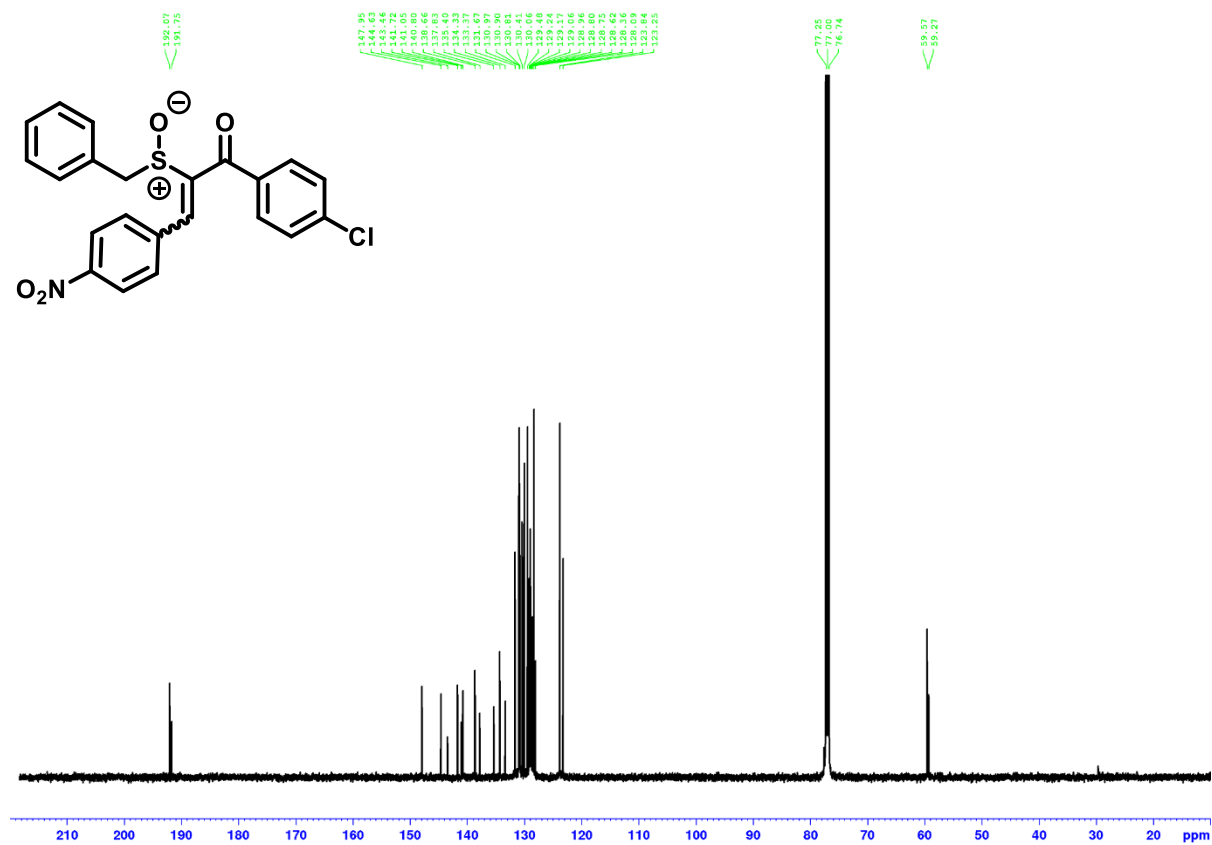


Figure S323: ¹³C NMR (125 MHz, CDCl₃) spectrum of Z-40o and E-40o (Z:E, 1:1.6).

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

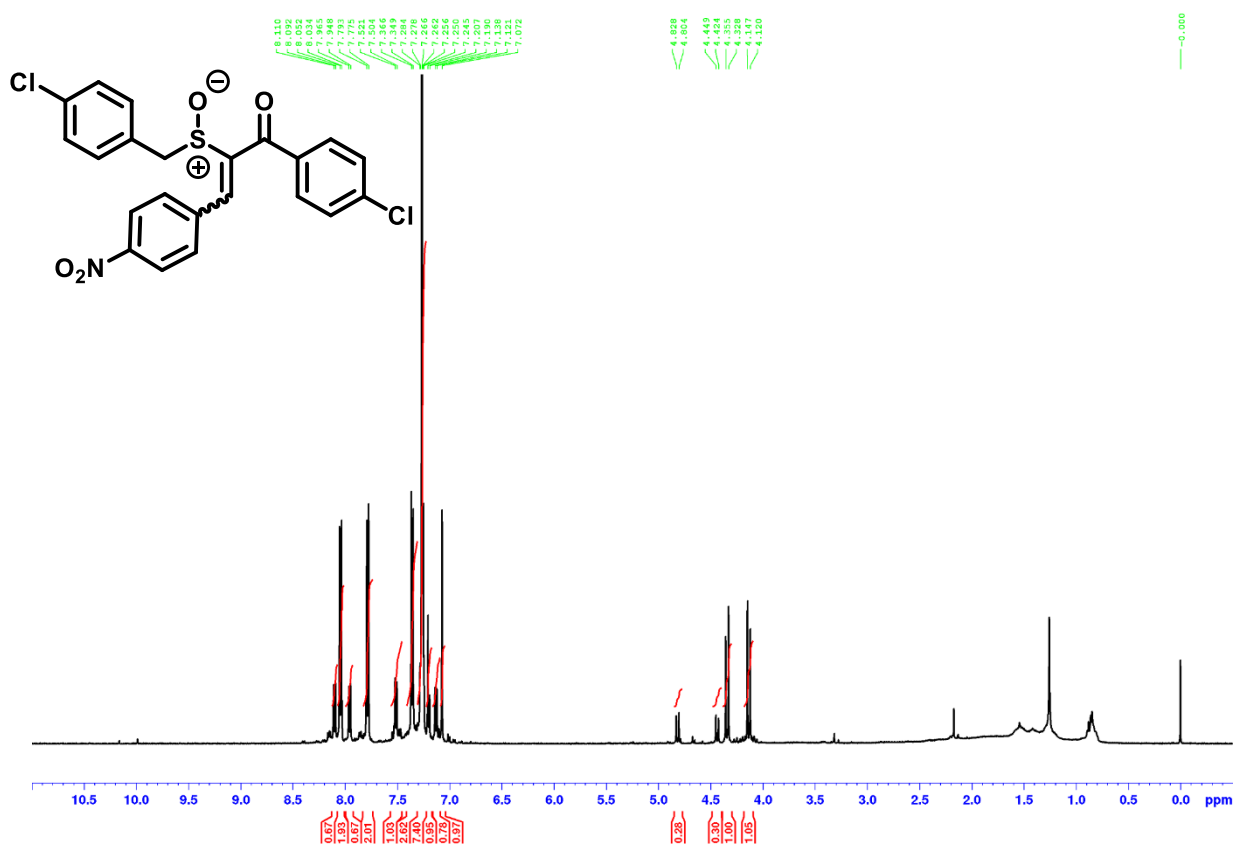


Figure S324: ¹H NMR (500 MHz, CDCl₃) spectrum of **Z-40q** and **E-40q** (Z:E, 1:3.5).

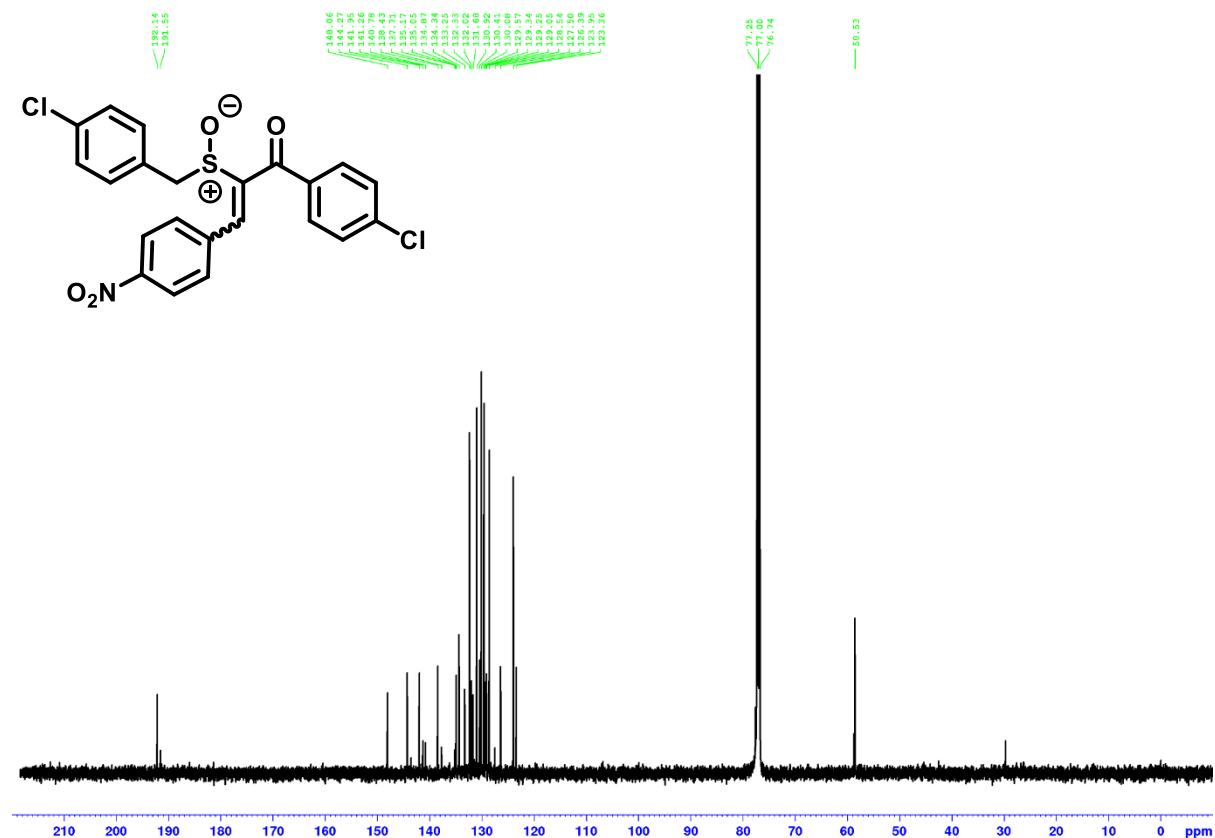


Figure S325: ¹³C NMR (125 MHz, CDCl₃) spectrum of **Z-40q** and **E-40q** (Z:E, 1:3.5).

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

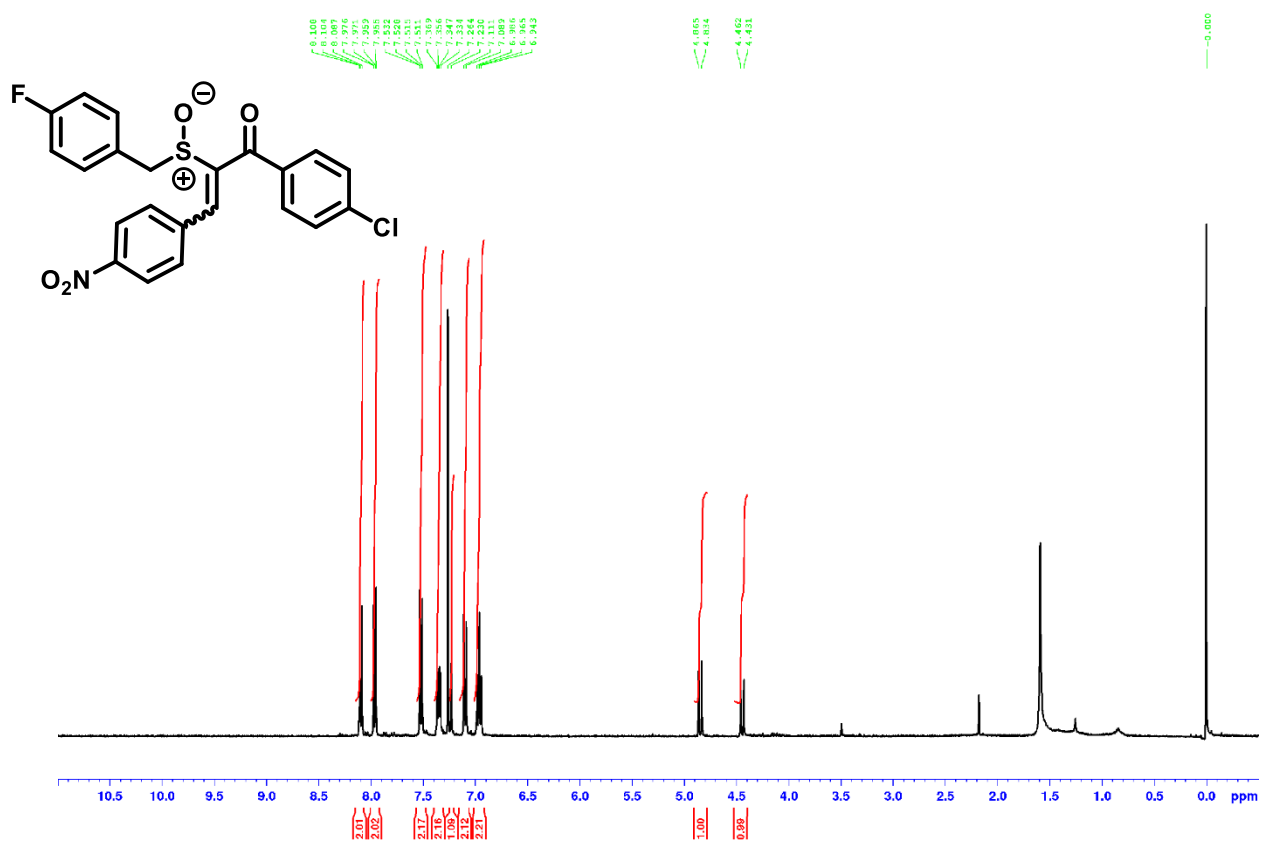


Figure S326: ¹H NMR (400 MHz, CDCl₃) spectrum of Z-16s after column chromatography.

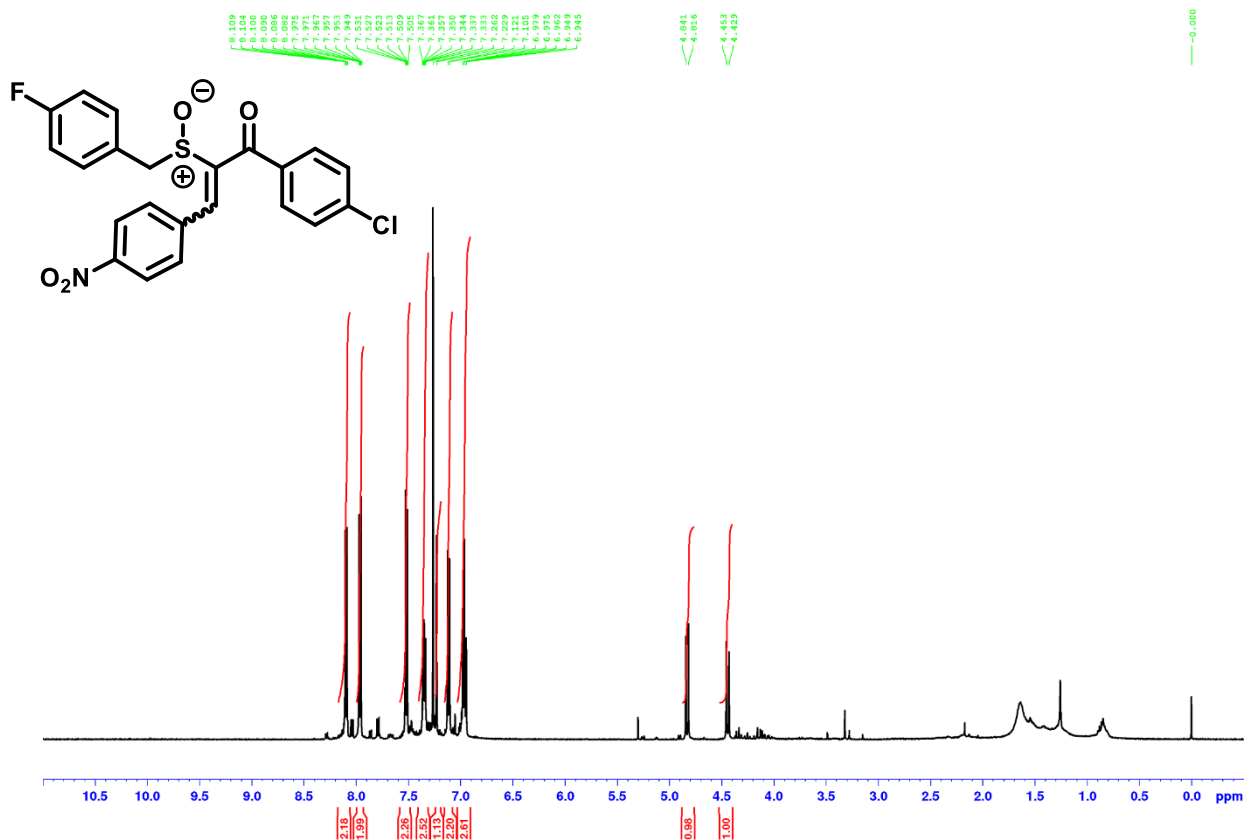


Figure S327: ¹H NMR (500 MHz, CDCl₃) spectrum of Z-40s after storage at -20°C for 6 months (Z:E, 7:1).

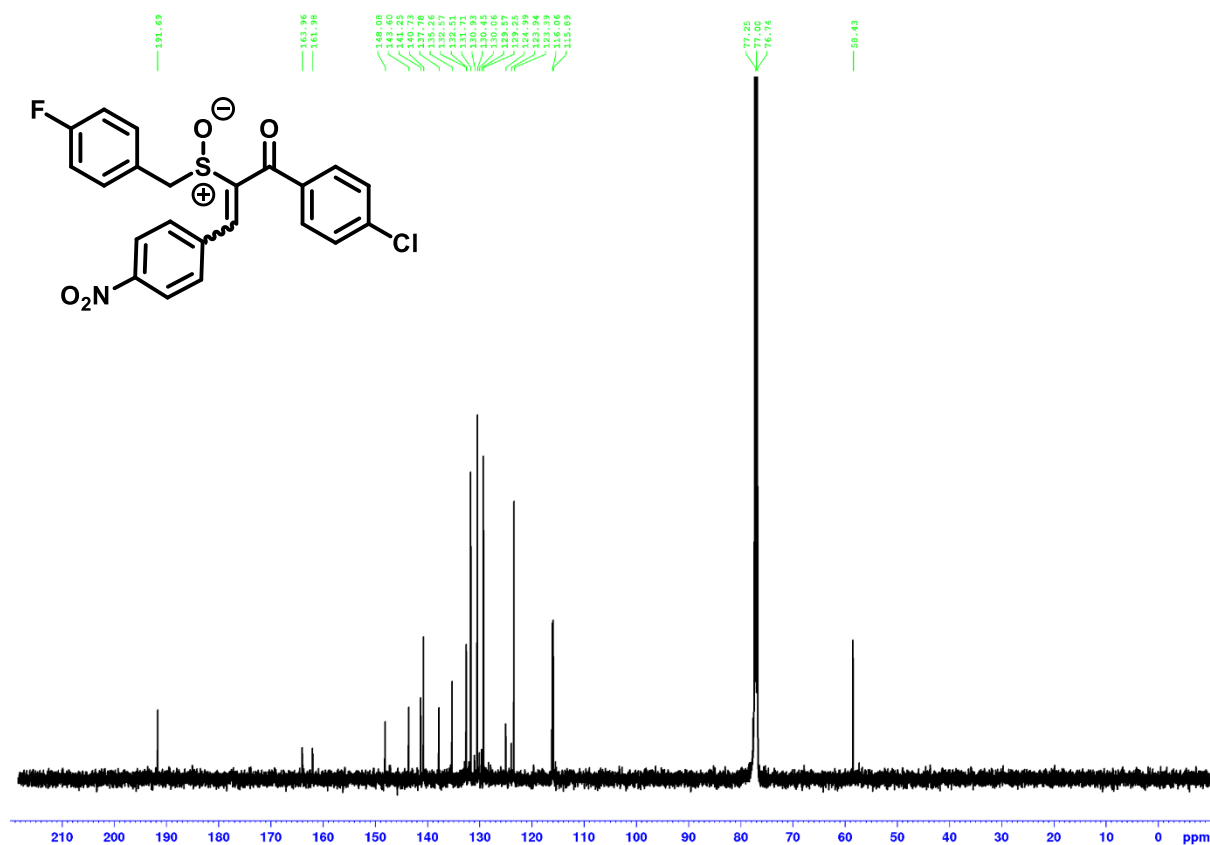


Figure S328: ¹³C NMR (125 MHz, CDCl₃) spectrum of **Z-40s** after storage at -20°C for 6 months (Z:E, 7:1).

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

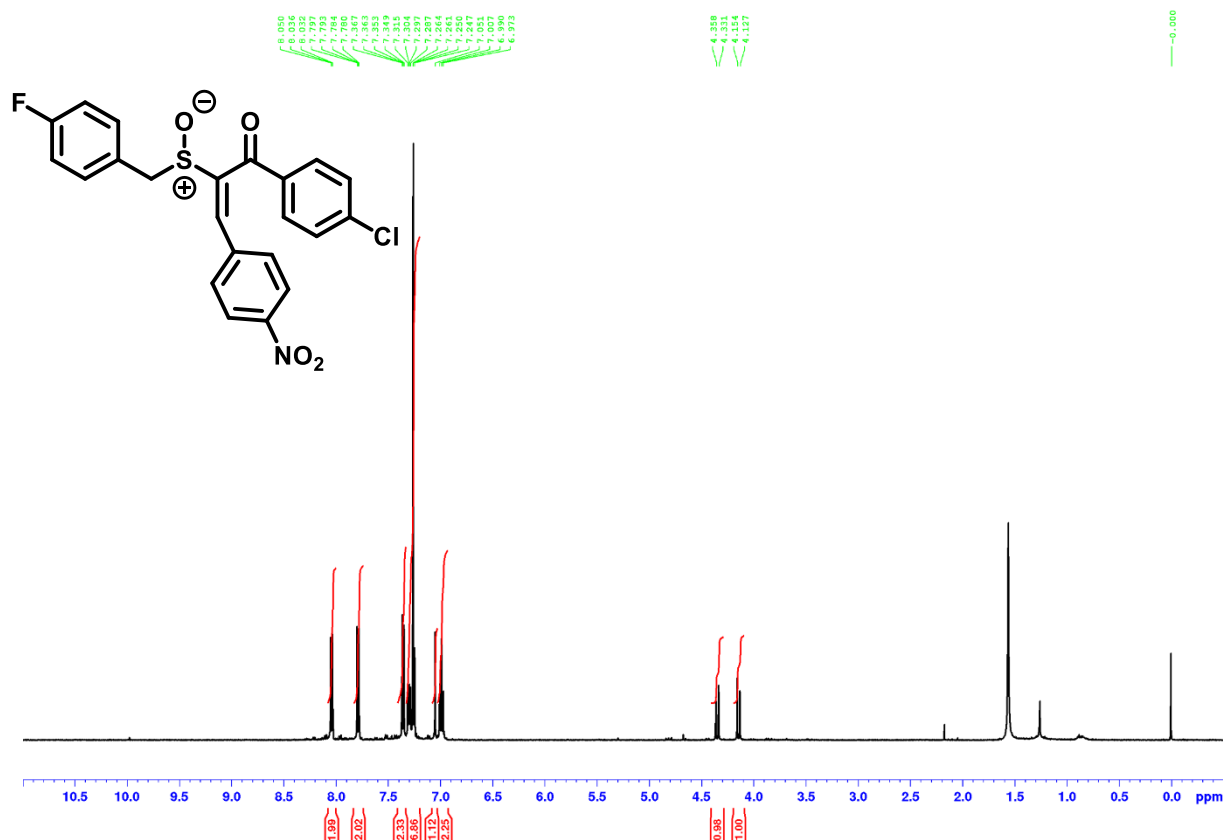


Figure S329: ¹H NMR (500 MHz, CDCl₃) spectrum of *E*-40s.

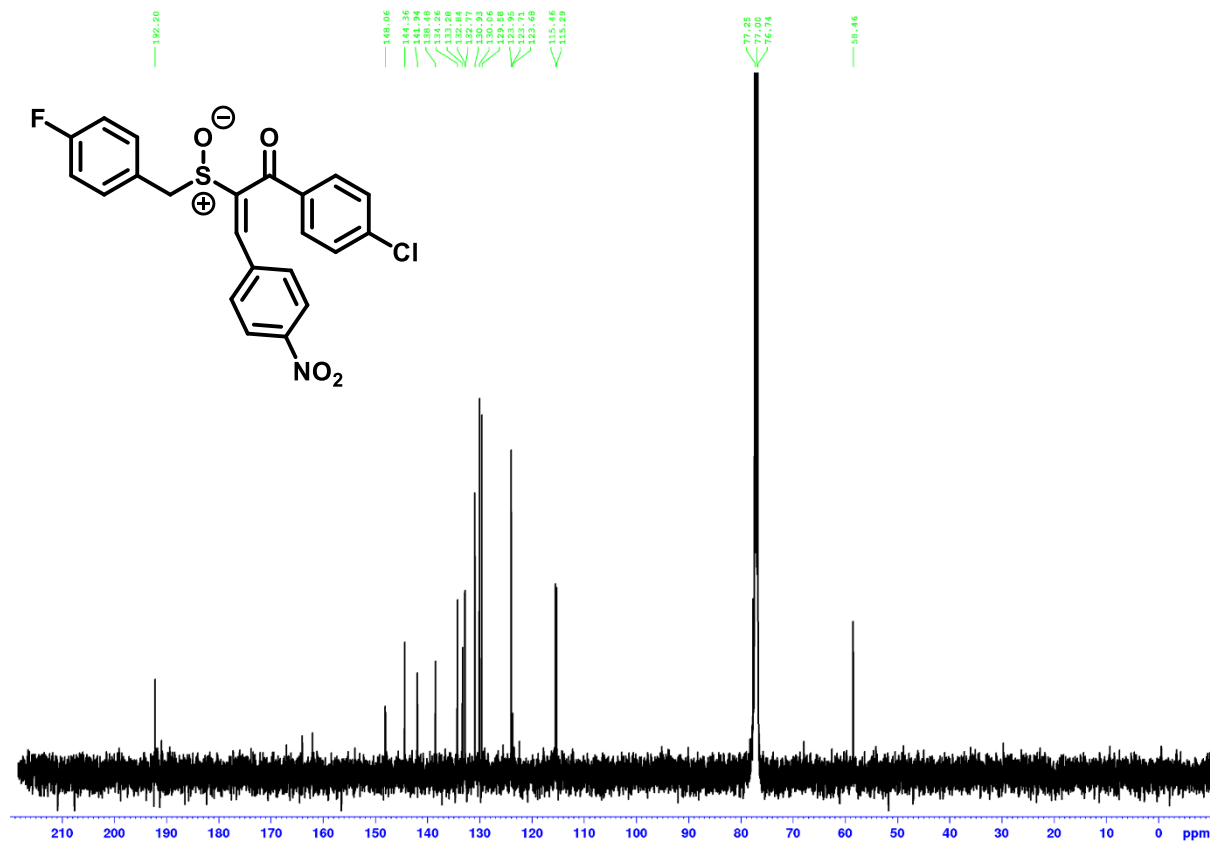


Figure S330: ¹³C NMR (125 MHz, CDCl₃) spectrum of *E*-40s.

1.12.13 Synthesis of Amide and Ester Derivatives

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

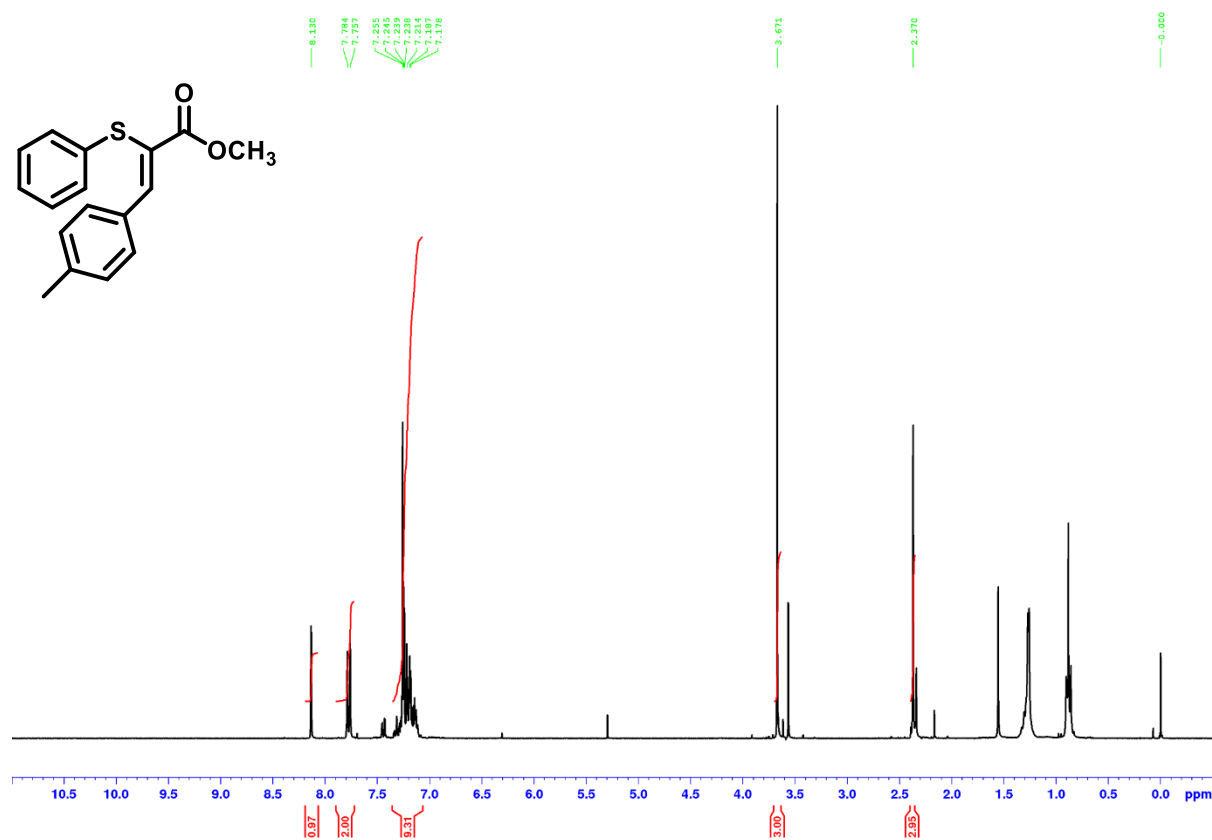


Figure S331: ¹H NMR (400 MHz, CDCl₃) spectrum of **44**.

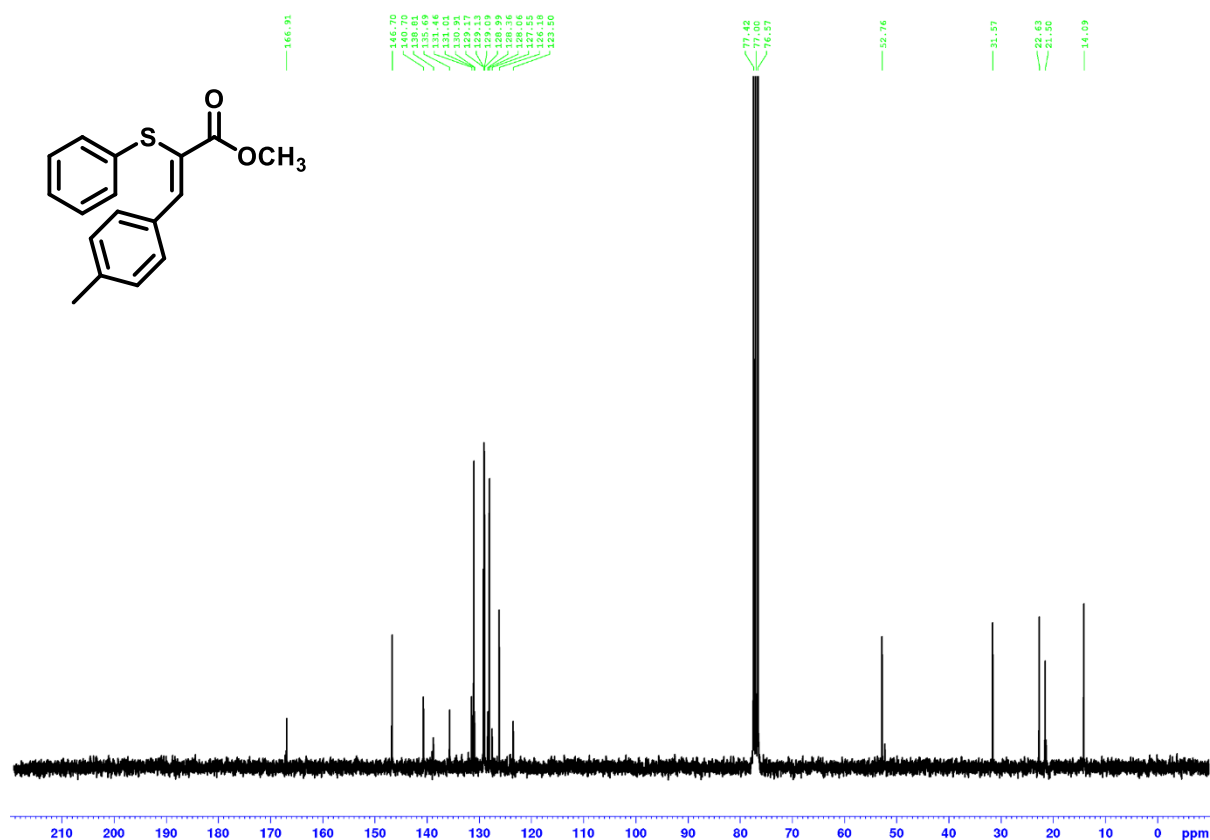


Figure S332: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **44**.

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

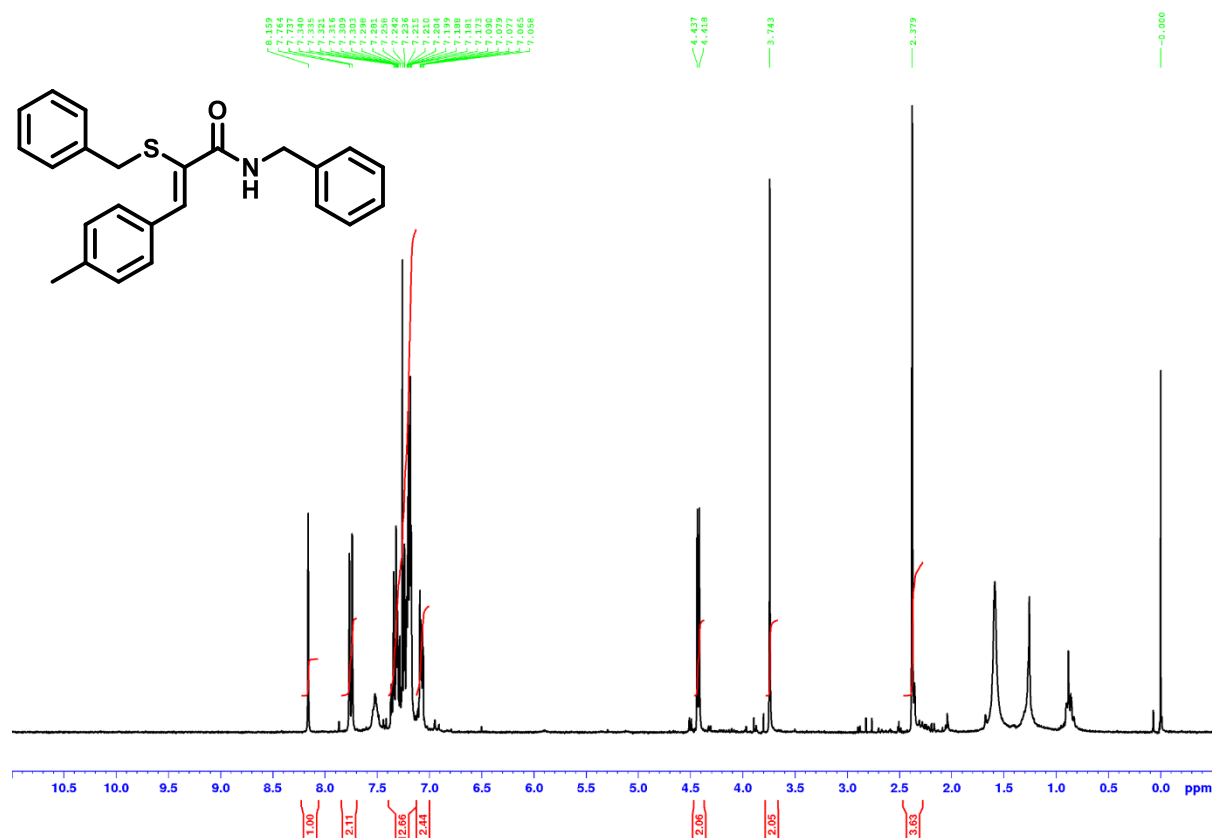


Figure S333: ¹H NMR (400 MHz, CDCl₃) spectrum of **45**.

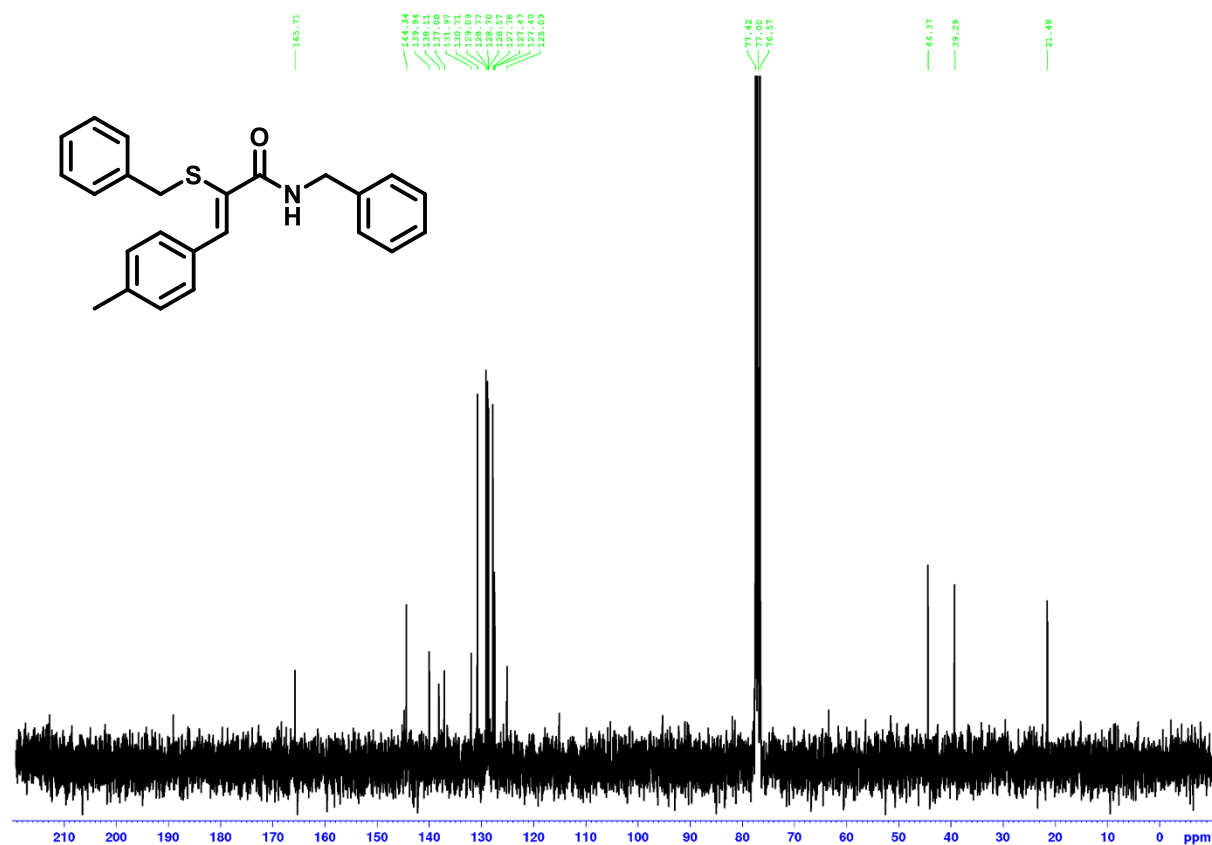


Figure S334: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **45**.

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

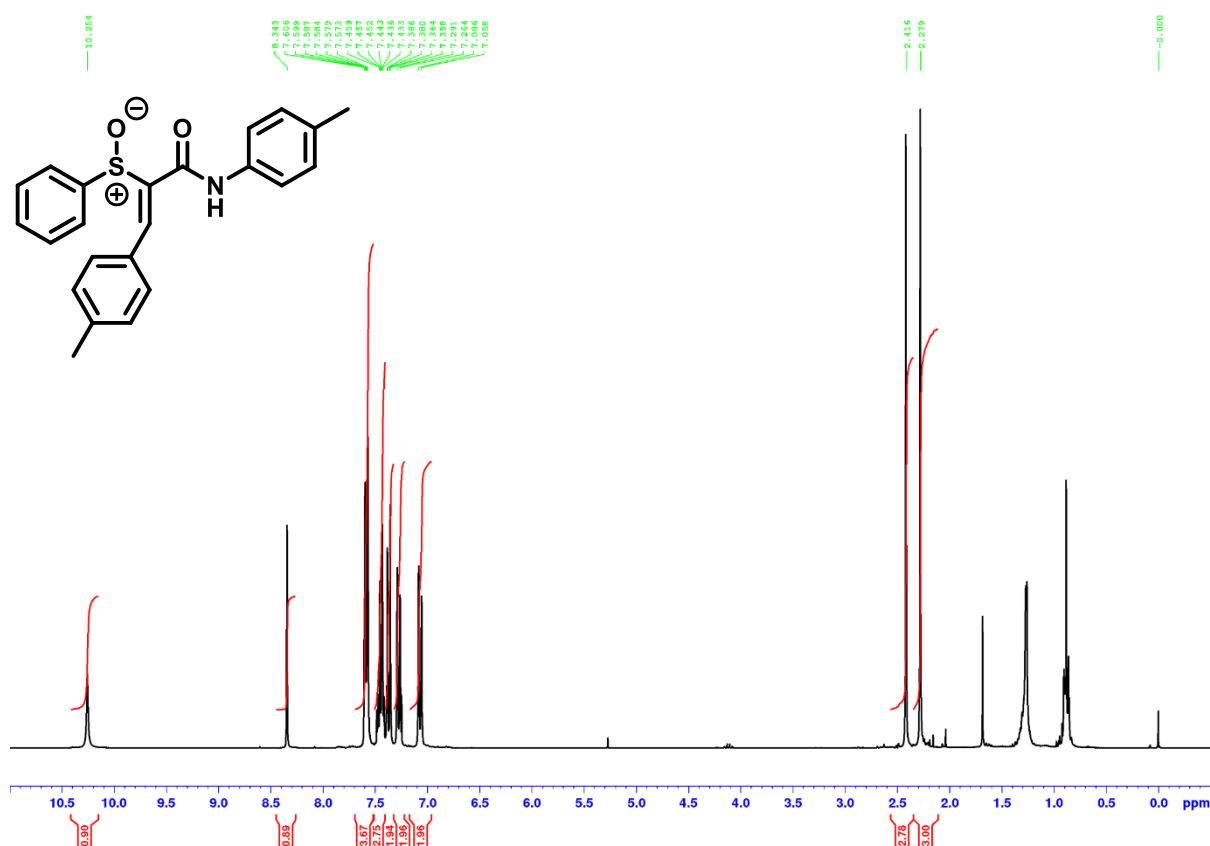


Figure S335: ¹H NMR (400 MHz, CDCl₃) spectrum of **46**.

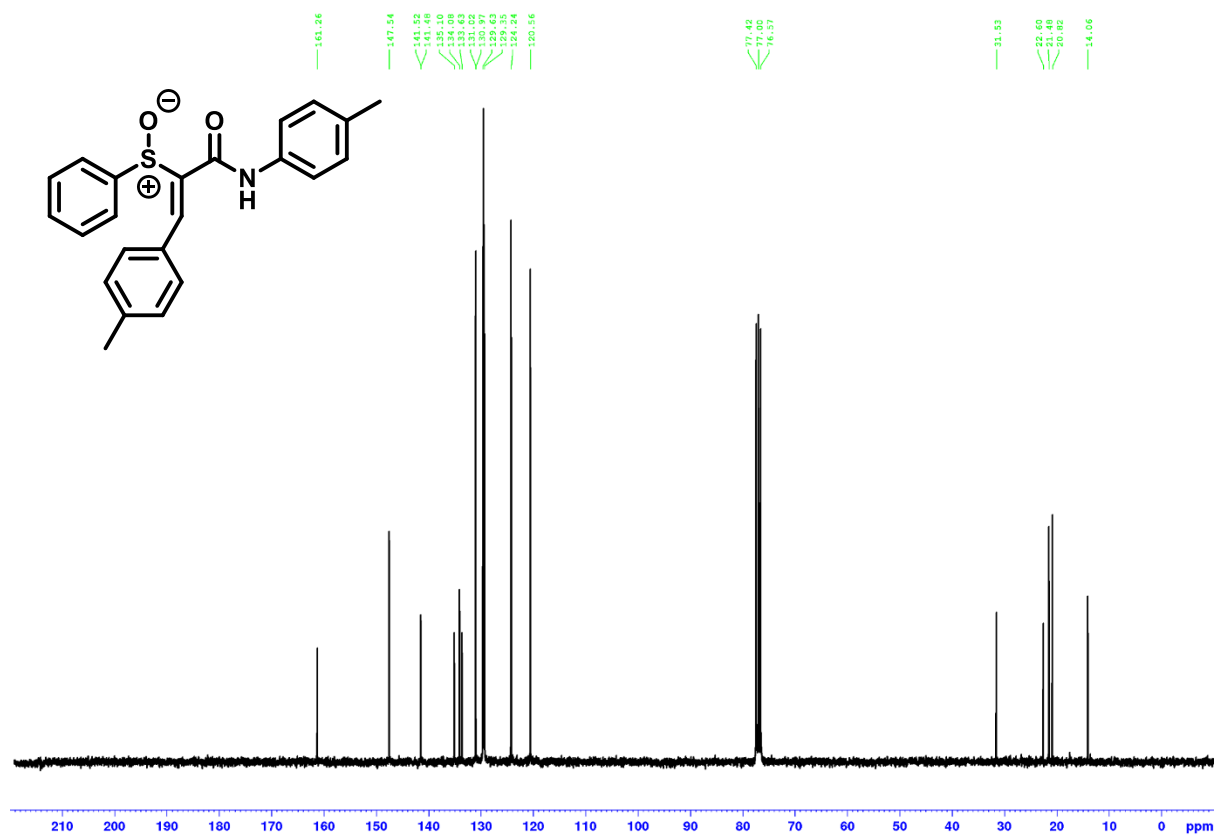


Figure S336: ¹³C NMR (75.5 MHz, CDCl₃) spectrum of **46**.

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