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Synthesis of 1,2,5-oxathiazole-S-oxides by 1,3 dipolar cycloadditions of nitrile oxides to α-oxo sulfines

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General Procedures

All solvents were distilled prior to use by the following methods: dichloromethane was distilled from phosphorus pentoxide; ethyl acetate was distilled from potassium carbonate; acetone was distilled from potassium permanganate followed by potassium carbonate; toluene was distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves; and methanol was distilled from magnesium methoxide and stored over 3 Å molecular sieves. Distilled diethyl ether was obtained commercially from Riedel de Haën and HPLC grade acetonitrile, available from Labscan Ltd., was used for diazo transfer reactions. All reagents were used without further purification.

^{1}H (300.13 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer. ^{1}H NMR (400.13 MHz) and ^{13}C (100 MHz) spectra were recorded on a Bruker Avance 400 NMR spectrometer. All spectra were recorded at 20 °C, in deuterated chloroform ($CDCl_3$), using tetramethylsilane (TMS) as an internal standard, and on the Bruker Avance 400 NMR spectrometer unless otherwise stated. Chemical shifts (δ_H and δ_C) are reported as parts per million (ppm) relative to TMS and coupling constants are expressed in Hertz (Hz). Splitting patterns in ^{1}H NMR spectra are designated as s (singlet), br s (broad singlet), br d (broad doublet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), qd (quartet of doublets), m (multiplet) and ABq (AB quartet). ^{13}C NMR spectra were calibrated using the solvent signals *i.e.* $CDCl_3$: δ_C 77.0 ppm. All spectroscopic details for compounds previously made were in agreement with those reported unless otherwise stated. Diastereomeric ratios (d.r.) and product ratios were determined by ^{1}H NMR spectroscopy. Infrared spectra were recorded Perkin Elmer FTIR UATR2 spectrometer. Continuous flow reactions were carried out on Vaportec R-Series or E-Series flow reactors.

Wet flash column chromatography was carried out on silica gel using Kieselgel 60, 0.040-0.063 mm (Merck). Thin layer chromatography (TLC) was carried out on precoated silica gel plates (Merck 60 PF254). Visualisation was achieved by UV light detection (254 nm), vanillin staining, iodine staining and potassium permanganate staining as appropriate.

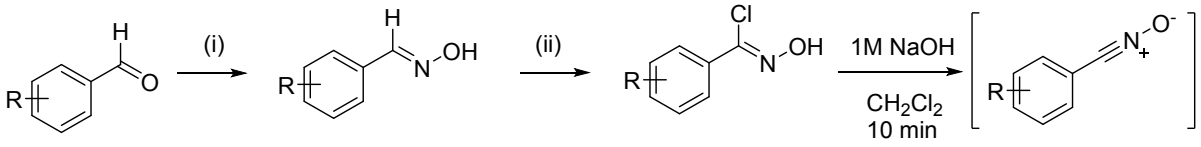
Low resolution mass spectra were recorded on a Waters Quattro Micro triple quadrupole instrument in electrospray ionization (ESI) mode using 50% acetonitrile-water containing 0.1% formic acid as eluent; samples were made up in acetonitrile. High resolution precise mass spectra (HRMS) were recorded on a Waters LCT Premier TOF LC-MS instrument in electrospray ionization (ESI) mode using 50% acetonitrile-water containing 0.1% formic acid as eluent; samples were made up in acetonitrile.

Single crystal X-ray analysis was conducted by Dr. S. E. Lawrence, and Dr. Uday Khandivalli, Department of Chemistry, University College Cork using a Nonium Mach 3 diffractometer with graphite monochromatised Mo-Kα radiation (λ = 0.71069 Å). Calculations were performed on a PC with the SHELXL-97 (G.M. Sheldrick, University of Gottingen, 1998) and Platon (A.L. Spek, University of Utrecht, 1998) suite of programs.

Oximes and Nitrile Oxides

The known imidoyl chloride[1] and oxime[2] precursors were generated using procedures described previously in the literature. Due to the tendency of nitrile oxide dipoles to dimerise forming the corresponding furoxan,[3] nitrile oxide dipoles are generally generated *in situ* by slow addition of a base such as triethylamine. The desired imidoyl chloride is added to a biphasic 1:1 mixture of dichloromethane and 1M NaOH at room temperature, to generate the nitrile oxide dipole. Successful dehydrohalogenation is achieved in approx. 10 minutes at which point the organic layer is separated and dried and the nitrile oxide solution can then be added to the α-diazosulfoxide without characterisation.

Table 1: Conditions and yields for the sequence of reactions to generate the range of nitrile oxide dipoles.



R	Oxime (%)	Imidoyl Chloride (%)
H	-[b]	54%
4-NO_2	84%	79%
4-F	98%	39% [4]
2,5-di-fluoro	47%	93% [5]
4-t-Butyl	89%	73% [5]

Dimerization of the nitrile oxide did not prove to be a problem in practice.

(i) $NH_2OH.HCl$, NaOH, H_2O/Ethanol 1:1, 1 - 2 h in most cases, except for the 2,5-difluoro derivative for which 16 h were needed.
(ii) NCS, DMF, rt, 1 - 5 hr. If the chlorination reactions were slow to start for the electron deficient oximes (as evidenced by the absence of a colour change) the reaction was heated to 40°C. If the reaction still did not start HCl vapour from the headspace of a bottle of conc. HCl was bubbled through the reaction mixture from a glass syringe. [6]
[a] Oximes were used without purification except for the *p*-nitro derived oxime which was recrystallized from ethanol : water, 3: 1. Yields are

reported for crude products.
[b] Benzaldoxime was commercially available from Sigma-Aldrich.

Synthesis of Oximes

(*E*)-4-Nitrobenzaldoxime[7]

p-Nitrobenzaldehyde (8.54 g, 56.5 mmol, 1 eq), hydroxylamine hydrochloride (3.93 g, 56.5 mmol, 1 eq) and anhydrous sodium acetate (11.59 g, 141.3 mmol, 2.5 eq) were heated under reflux in aqueous ethanol (90%, 100 mL) for 24 h. The solvent was then removed under reduced pressure. The resulting residue was dissolved in sodium hydroxide solution (2 M, 20 mL) and water (20 mL) and subsequently filtered, leaving a dark orange solution of the oxime anion in the filtrate. The filtrate was acidified with acetic acid resulting in the precipitation of the oxime as a pale yellow solid. The crystals were isolated by vacuum filtration and washed with water. The solid was recrystallized from ethanol: water (3 : 1) to yield the oxime as a yellow solid (6.95 g, 84 %). Found C, 58.77; H 5.49; N 22.50, $C_7H_6N_2O_3$ requires C, 59.01; H 4.95 ; N 22.94; mp 125 – 126°C (lit.[6] 119 – 120°C); ν_{max}/cm^{-1} (neat) 1605, 1532, 1347; δ_H (300 MHz, $CDCl_3$) 7.75 (2H, d, *J* 8.7, 2 x Aromatic CH), 7.98 (1 H, s, OH), 8.21 (1H, s, CH), 8.25 (2H, d, *J* 8.7, 2 x Aromatic CH); δ_C (100 MHz, $CDCl_3$) 124.1 (1 signal corresponding to 2 x Aromatic CH), 127.7 (1 signal corresponding to 2 x Aromatic CH), 138.2 (Cq, 1 x Aromatic Cq), 148.5 (CH, CH=N), 148.6 (Cq, 1 x Aromatic Cq). Spectroscopic characteristics are in good agreement with the literature.[7]

Typical procedure for all other oximes:

(*E*)-4-Fluorobenzaldehyde oxime[7]

To a suspension of the 4-fluorobenzaldehyde (1.5 g, 12.08 mmol, 1 eq) in water/ethanol/ice (1 : 1 : 2, 12 mL) was added hydroxylamine hydrochloride in one portion (0.84 g, 12.08 mmol, 1 eq). NaOH solution (1.20 g NaOH, 2.5 eq, 50% in water) was added dropwise over 10 min keeping the temperature under 30°C. The reaction mixture was stirred for 1 h at room temperature, after which TLC analysis (40% ethyl acetate, 60% hexane as eluent) showed complete consumption of starting material. The reaction mixture was extracted with ether (20 mL), the aqueous layer was separated and acidified to pH 6 with concentrated HCl. The aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure to give the oxime as a white crystalline solid (1.65 g, 98%). ν_{max}/cm^{-1} (neat) 3256, 1606, 1509; δ_H (400 MHz, $CDCl_3$) 7.04 – 7.12 (2H, m, 2 x Aromatic CH), 7.54 – 7.57 (2H, m, 2 x Aromatic CH), 8.14 (1H, s, CH=N), 9.13 (1H, br s, OH); δ_C (100 MHz, $CDCl_3$) 116.0 (2 x CH, 2 x Aromatic CH, d, $^2J_{CF}$ 22.0), 128.1 (Cq, 1 x Aromatic Cq, $^4J_{CF}$ 3.3), 128.9 (2 x CH, 2 x Aromatic CH, d, $^3J_{CF}$ 8.4), 149.4 (CH, CH=N), 163.8 (ArCF, d, $^1J_{CF}$ 250.5); m/z (ESI+) 140 [$(M+H)^+$, 20%]; HRMS (ESI+): Exact mass calculated for C_7H_7NOF $[M+H]^+$, 140.0512. Found 140.0519. The spectral data are in agreement with those reported in the literature.[7]

(*E*)-4-(*tert*-Butyl)benzaldehyde oxime[5,8]

White crystalline solid (1.56 g, 89 %). mp 88 – 90° C; ν_{max}/cm^{-1} (neat) 3252, 1607, 1510; δ_H (400 MHz, $CDCl_3$) 1.36 (9H, s, 3 x CH_3), 7.41 (2H, d, *J* 7.8, 2 x Aromatic CH), 7.50 – 7.59 (2H, m, 2 x Aromatic CH), 8.13 (1H, s, CH=N), 9.0 (1H, br s , OH); δ_C (100 MHz, $CDCl_3$) 31.2 (1 signal corresponding to 3 x CH_3), 34.9 [Cq, $Cq(CH_3)_3$], 125.8 (2 x CH, 2 x Aromatic CH),

126.9 (CH, 2 x Aromatic CH), 129.1 (Cq, 1 x Aromatic Cq), 150.2 (CH, CH=N), 153.5 (Cq, 1 x Aromatic Cq). HRMS (ESI+): Exact mass calculated for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1232. Found 178.1225

(*E*)-2, 5-Difluorobenzaldehyde oxime [8,9]

White crystalline solid (1.44 g, 47%). mp 104 - 106° C; ν_{max}/cm^{-1} (neat) 3232, 1488, 1191, 805; δ_H (400 MHz, $CDCl_3$) 7.00 – 7.20 (2H, asymmetric multiplet, 2 x Aromatic CH), 7.42 – 7.46 (1H, m, 1 x Aromatic CH), 8.33 (1H, br s, CH=N), 8.63 (1H, br s, OH); δ_C(100 MHz, $CDCl_3$) 112.9 (dd, $^2J_{CF}$ 25.5, $^3J_{CF}$ 3.3, Aromatic CH), 117.2 (dd, $^2J_{CF}$ 24.4, $^3J_{CF}$ 8.4, Aromatic CH) 118.2 (dd, $^2J_{CF}$ 24.8, $^3J_{CF}$ 9.0, Aromatic CH), 121.1 (dd, $^2J_{CF}$ 13.2, $^3J_{CF}$ 8.4, Aromatic Cq), 143.5 (apparent br t, J_{CF} 2.8, CH=N), 156.8 (dd, $^1J_{CF}$ 248.4, $^4J_{CF}$ 2.6, ArCF), 158.7 (dd, $^1J_{CF}$ 243.0, $^4J_{CF}$ 2.4, ArCF). m/z (ESI+) 158 [$(M+H)^+$, 80%]. HRMS (ESI+): Exact mass calculated for $C_7H_6NOF_2$ $[M+H]^+$ 158.0417 Found 158.0417.

Synthesis of Imidoyl chlorides

Benzohydroximoyl chloride[10-12]

Chlorine gas (generated by the dropwise addition of concentrated hydrochloric acid to solid potassium permanganate) was bubbled through a cooled (-10°C) solution of benzaldoxime (3.00 g, 0.24 mol) in chloroform (36 mL), with a calcium chloride guard tube fitted to the reaction flask. The temperature was maintained at -10°C by use of a cryocooler and the chlorine gas caused the solution to go from clear through yellow, yellow/orange, green, blue/green, green, yellow and finally dark orange, indicating saturation. Excess chlorine gas was purged with nitrogen and the colour changed to a pale yellow. The solvent was removed by concentration under reduced pressure and the resulting residue was dissolved in hexane and placed in a freezer overnight. The resultant solid was isolated by vacuum filtration to yield benzohydroximoyl chloride as a white solid (1.94 g, 50%). δ_H (400 MHz, $CDCl_3$) 7.37-7.52 (3H, m, 3 x Aromatic CH), 7.82-7.85 (2H, m, Aromatic CH), 8.61 (1H, s, OH). Spectral characteristics are in agreement with those reported in the literature.

Typical procedure for the synthesis of all other imidoyl chlorides:

***N*-Hydroxy-4-nitrobenzimidoyl chloride**

To a solution of the oxime (4 g, 24.1 mmol, 1 eq) in DMF (35 mL) was added the first portion of NCS (0.578 g, 0.043 mmol, 0.2 eq) and the reaction mixture is heated to 40°C. A small amount of HCl gas, extracted from the headspace of a conc. HCl bottle, is bubbled through the solution to initiate the reaction.[6] The remaining portion of NCS (2.61 g, 0.196 mmol, 0.8 eq) was added in small portions over 20 min while keeping the reaction temperature below 45°C. The mixture was stirred at room temperature overnight, poured on to water (300 mL) and extracted with ether (3 x 90 mL). The organic layers were combined and washed with brine (20 mL), dried with $MgSO_4$ and concentrated under reduced pressure to give the imidoyl chloride as a pale yellow crystalline solid (3.68 g, 76%). mp: 124-125 °C; ν_{max}/cm^{-1} (neat) 3112, 1601, 1523; δ_H (300 MHz, $CDCl_3$) 8.04 (2H, d, *J* 9.0, 2 x Aromatic CH), 8.26 (2H, d, *J* 9.0, 2 x Aromatic CH), 8.41 (1H, br s, OH),; δ_C (75.5 MHz) 123.6 (CH, 2 x Aromatic CH), 128.0 (CH, 2 x Aromatic CH), 138.21 (Cq, Aromatic Cq-NO_2), 138.25 (Cq, 1 x Aromatic Cq), 145.5 (Cq, C=N).

4-(*tert*-Butyl)-*N*-hydroxybenzimidoyl chloride[5]

Colourless oily residue (0.435 g, 73%). ν_{max}/cm^{-1} (neat) 2962, 1607, 1249, 936; δ_H (400 MHz, $CDCl_3$) 1.30 (9H, s, 3 x CH_3), 7.40 (2H, d, *J* 8.8, 2 x Aromatic CH), 7.75 (2H, d, *J* 8.8, 2 x Aromatic CH), 9.85 (1H, s, OH). δ_C (100 MHz, $CDCl_3$) 31.2 (3 x CH_3), 34.9 [Cq, $Cq(CH_3)_3$], 125.6 (CH, 2 x Aromatic CH), 127.1 (CH, 2 x Aromatic CH), 129.8 (Cq, 1 x Aromatic Cq), 140.1 (Cq, C=N), 154.1 (Cq, 1 x Aromatic Cq). HRMS (ESI+): Exact mass calculated for $C_{11}H_{15}NO^{35}Cl$ $[M+H]^+$, 212.0842. Found 212.0839.

4-Fluoro-*N*-hydroxybenzimidoyl chloride [4]

White crystalline solid (~92% pure, 8% residual starting material) (0.79 g, 36%*). mp 59 - 61° C; ν_{max}/cm^{-1} (neat) 3368, 1598, 1505, 1234; δ_H (400 MHz, $CDCl_3$) 7.09 (2H, t, *J* 9.7, 8.3, 2 x Aromatic CH), 7.81 – 7.84 (2H, m, 2 x Aromatic CH), 8.64 (1H, br s, OH); δ_C (100 MHz, $CDCl_3$) 115.7 (2 x CH, d, $^2J_{CF}$ 22.4, 2 x Aromatic CH), 128.6 (d, $^4J_{CF}$ 3.3, 1 x Aromatic Cq), 129.3 (2 x CH, d, $^3J_{CF}$ 8.8, 2 x Aromatic CH), 139.1 (Cq, C=N), 164.2 (Cq, 1 x Aromatic CF, d, $^1J_{CF}$ 251.6); HRMS (ESI+): Exact mass calculated for $C_7H_5{}^{35}ClFNO$ $[M+H]^+$, 174.0122 Found 174.0115. *Corrected yield for the presence of the residual starting material.

2,5-difluoro-*N*-hydroxybenzimidoyl chloride[5]

White crystalline solid (1.53 g, 93 %). mp 118 - 120° C; ν_{max}/cm^{-1} (neat) 3283, 1490, 1167, 990; δ_H (400 MHz, $CDCl_3$) 7.11 – 7.15 (2H, m, 2 x Aromatic CH), 7.38 – 7.41 (1H, m, 1 x Aromatic CH) 8.81 (1H, br s, OH); δ_C (100 MHz, $CDCl_3$) 117.3 (CH, dd, $^2J_{CF}$ 18.4, $^3J_{CF}$ 10.0, ArCH-3), 117.9 (CH, dd, $^2J_{CF}$ 23.1, $^3J_{CF}$ 10.4, ArCH-6), 118.7 (CH, dd, $^2J_{CF}$ 19.1, $^3J_{CF}$ 13.7, ArCH-4), 122.1 (dd, $^2J_{CF}$ 12.7, $^3J_{CF}$ 9.0, ArC-1), 134.3 (d, $^3J_{CF}$ 4.7, C=N), 155.9 (dd, $^1J_{CF}$ 253.2, $^4J_{CF}$ 4.0, 1 x ArCF), 158.2 (dd, $^1J_{CF}$ 245.3, $^4J_{CF}$ 4.0, 1 x ArCF); HRMS (ESI+): Exact mass calculated for $C_7H_5NOF_2{}^{35}Cl$ $[M+H]^+$, 192.0028 Found 192.0029.

^{1}H and ^{13}C NMR spectra

Dipolar cycloadditions of α-diazosulfoxide **1** with nitrile oxides.

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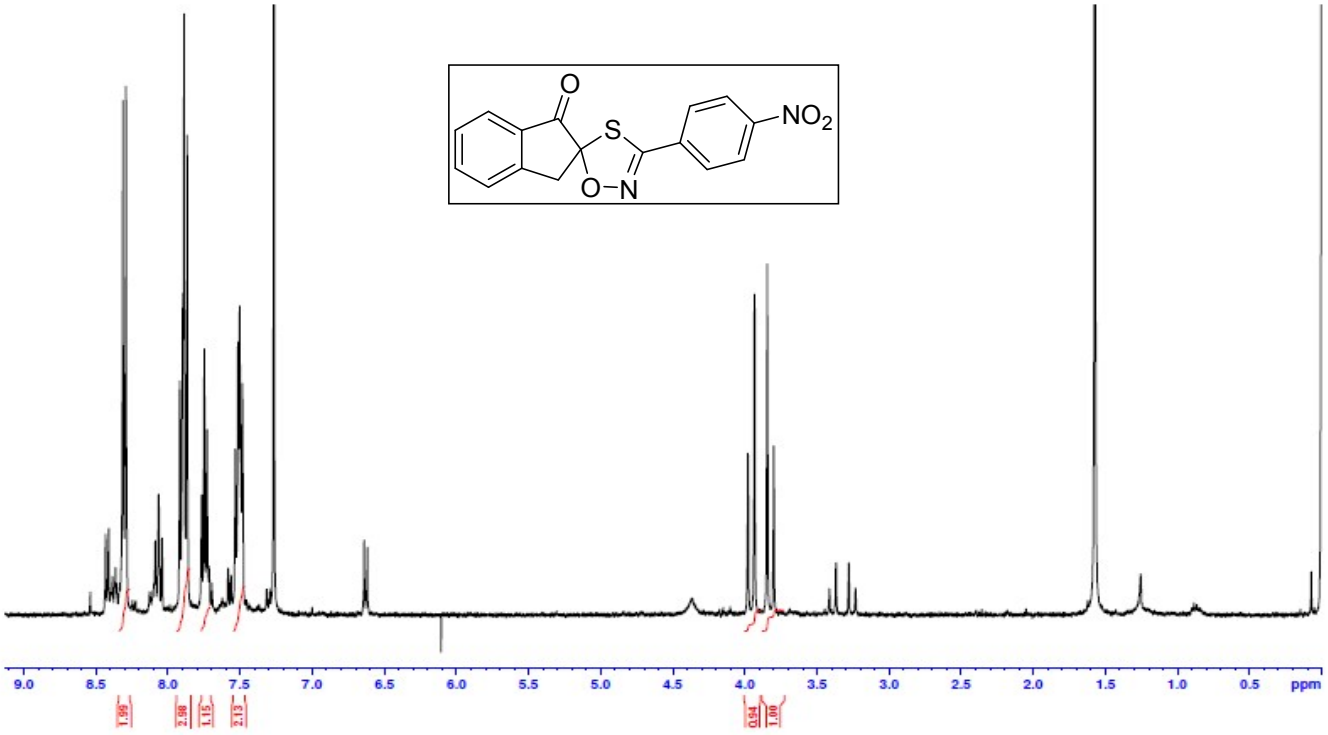


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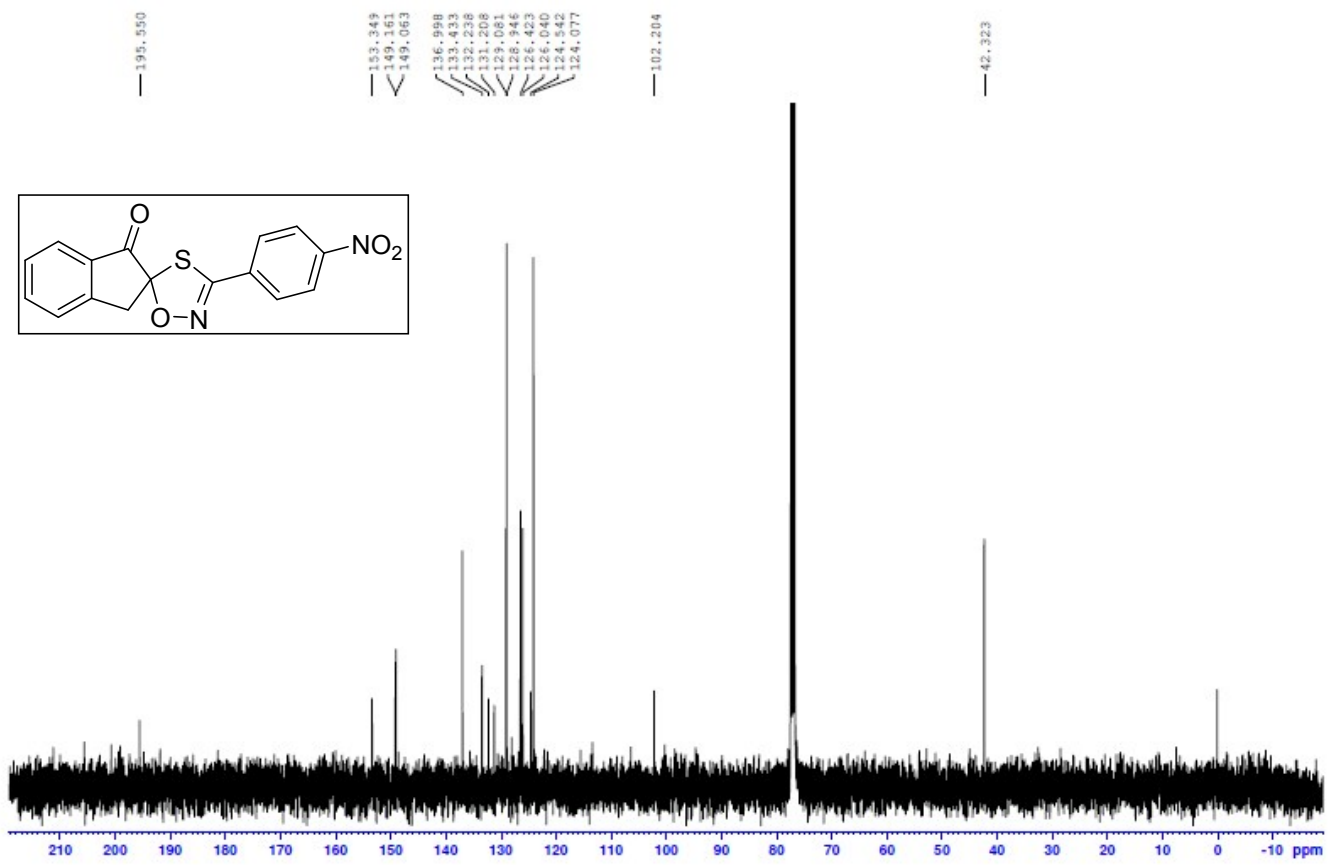


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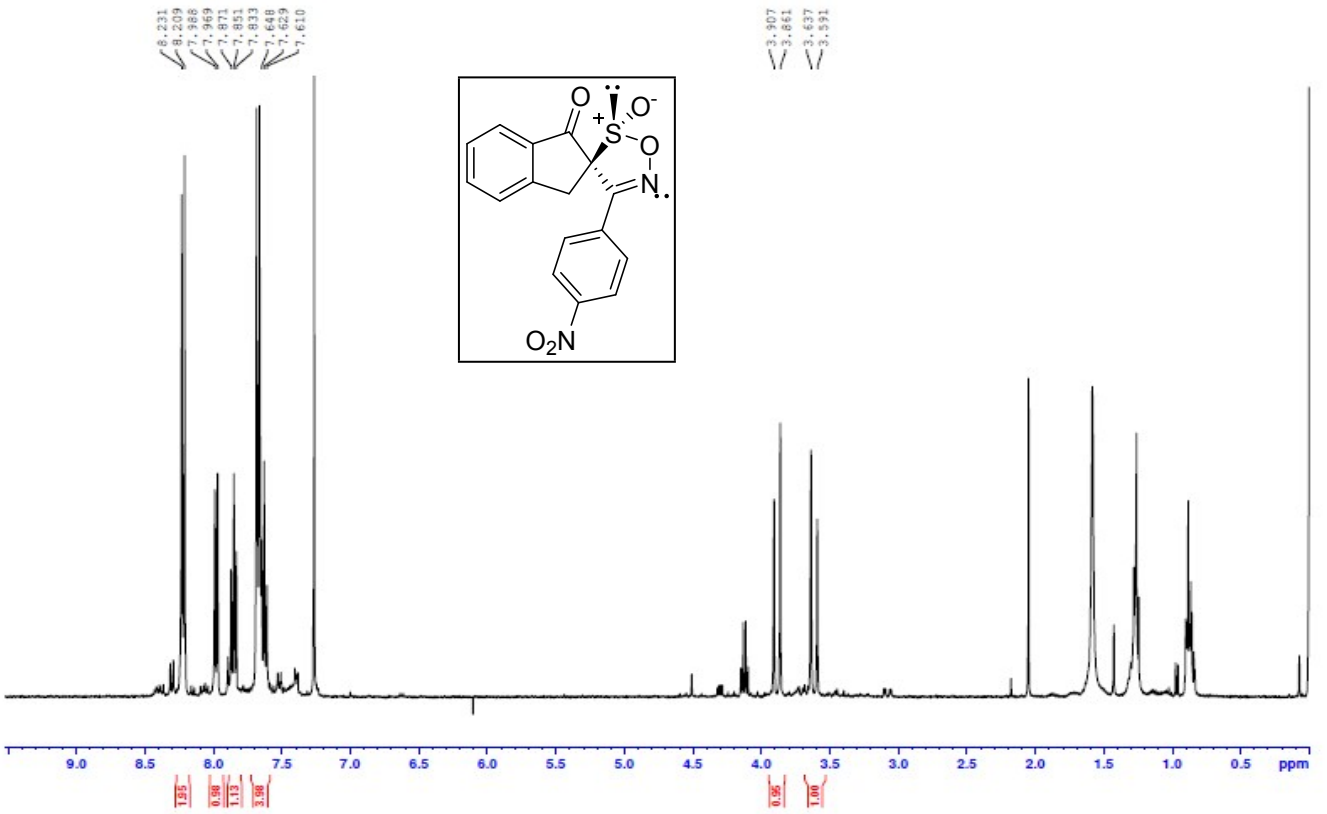


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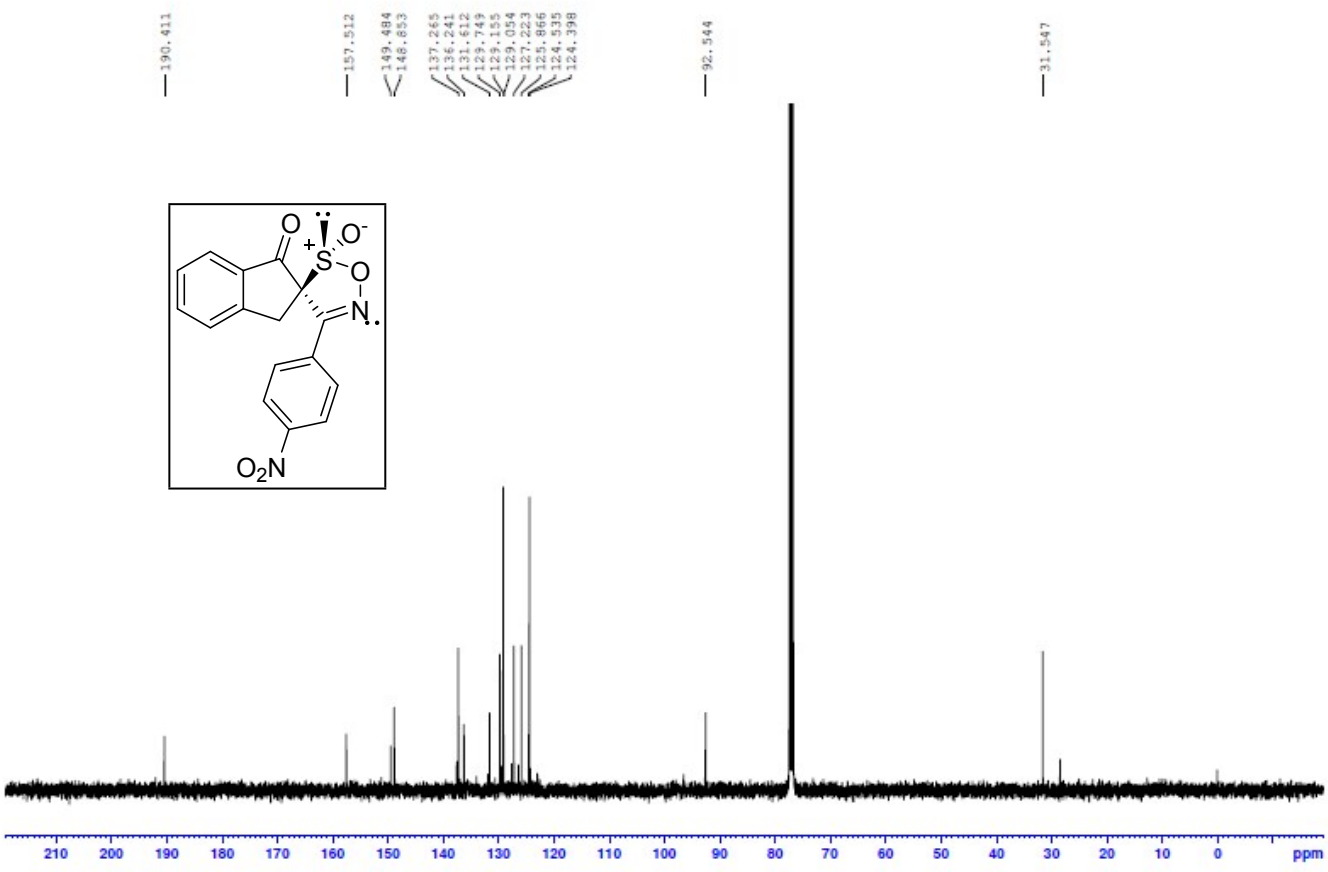


Figure S 4

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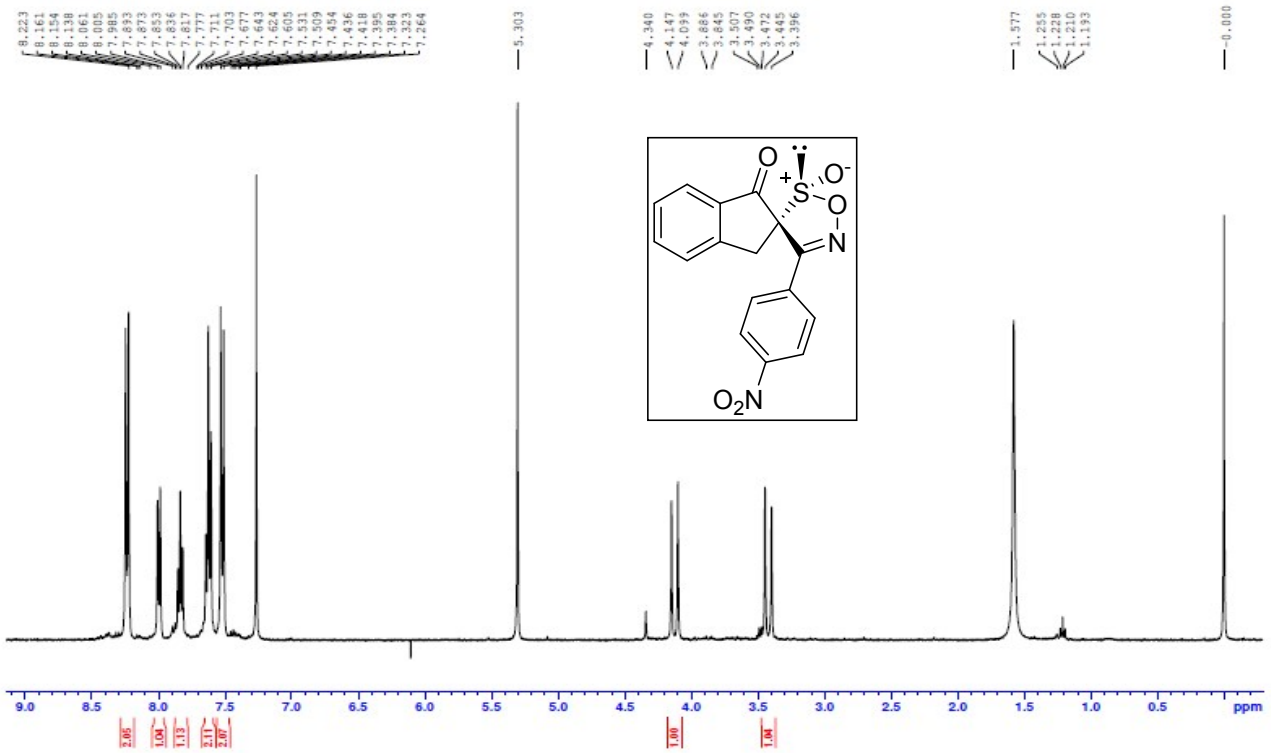


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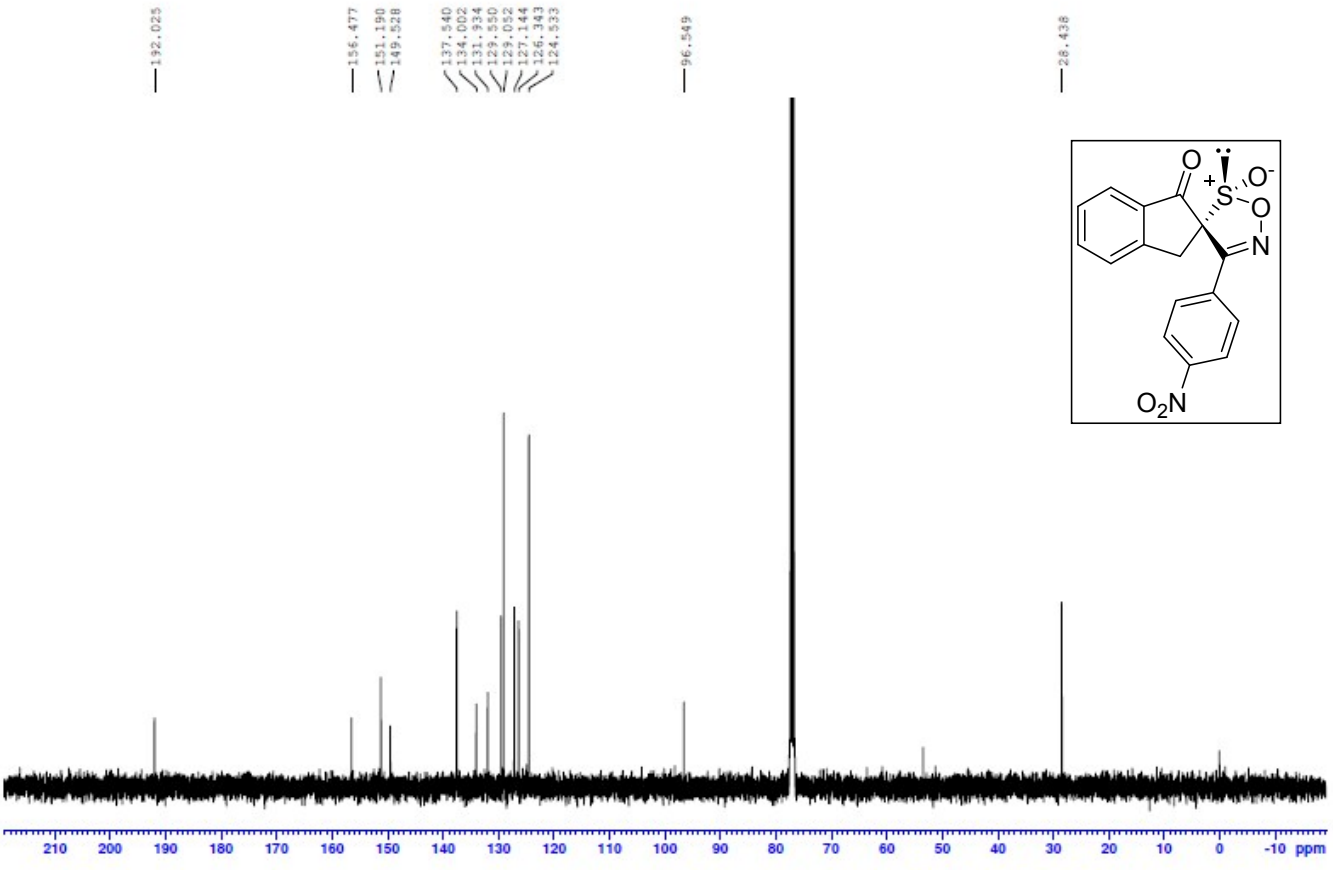


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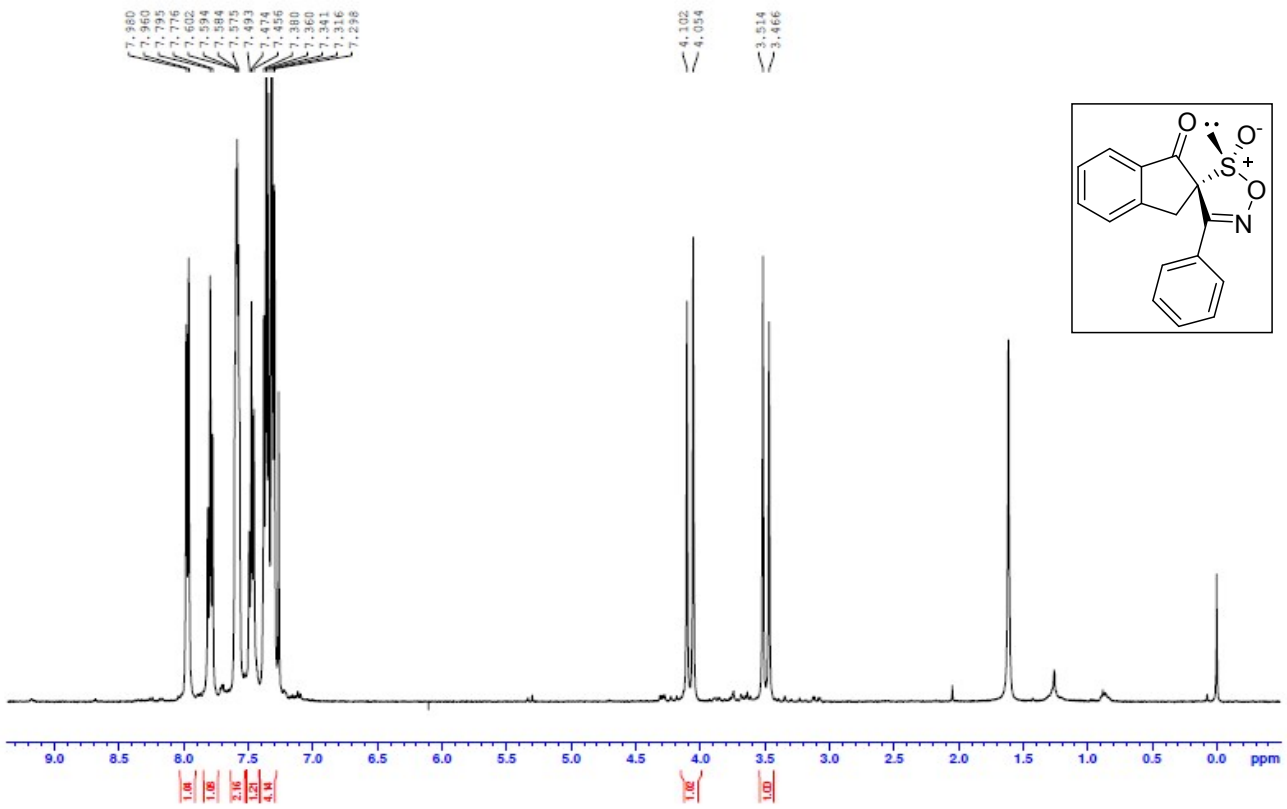


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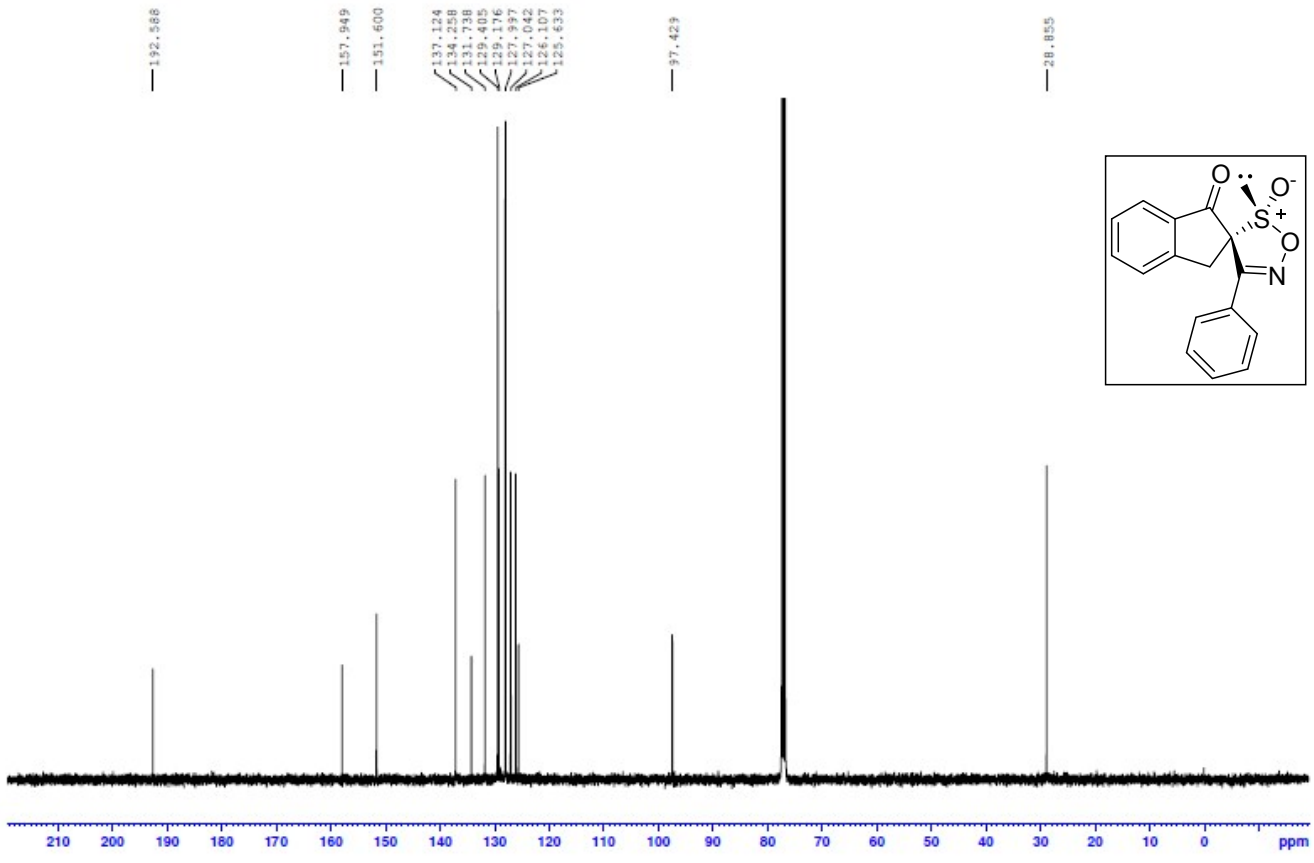


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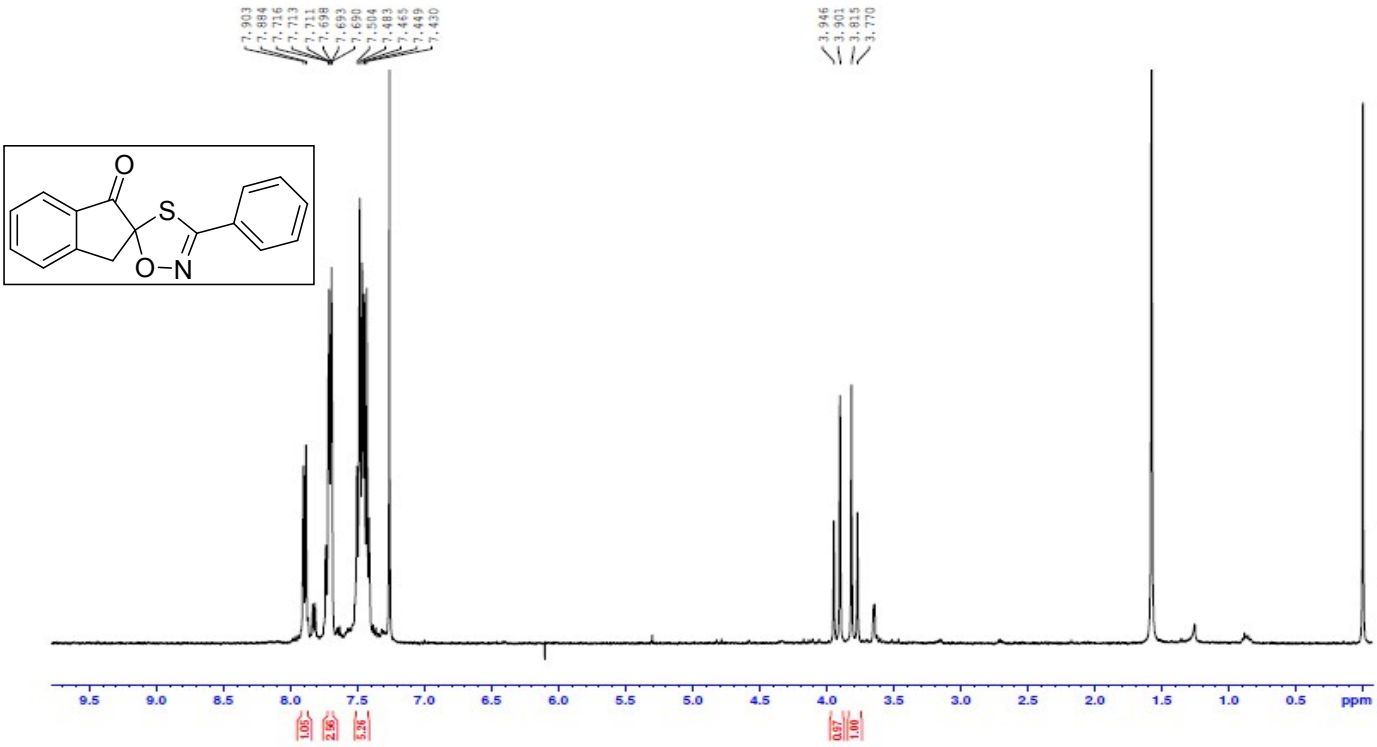


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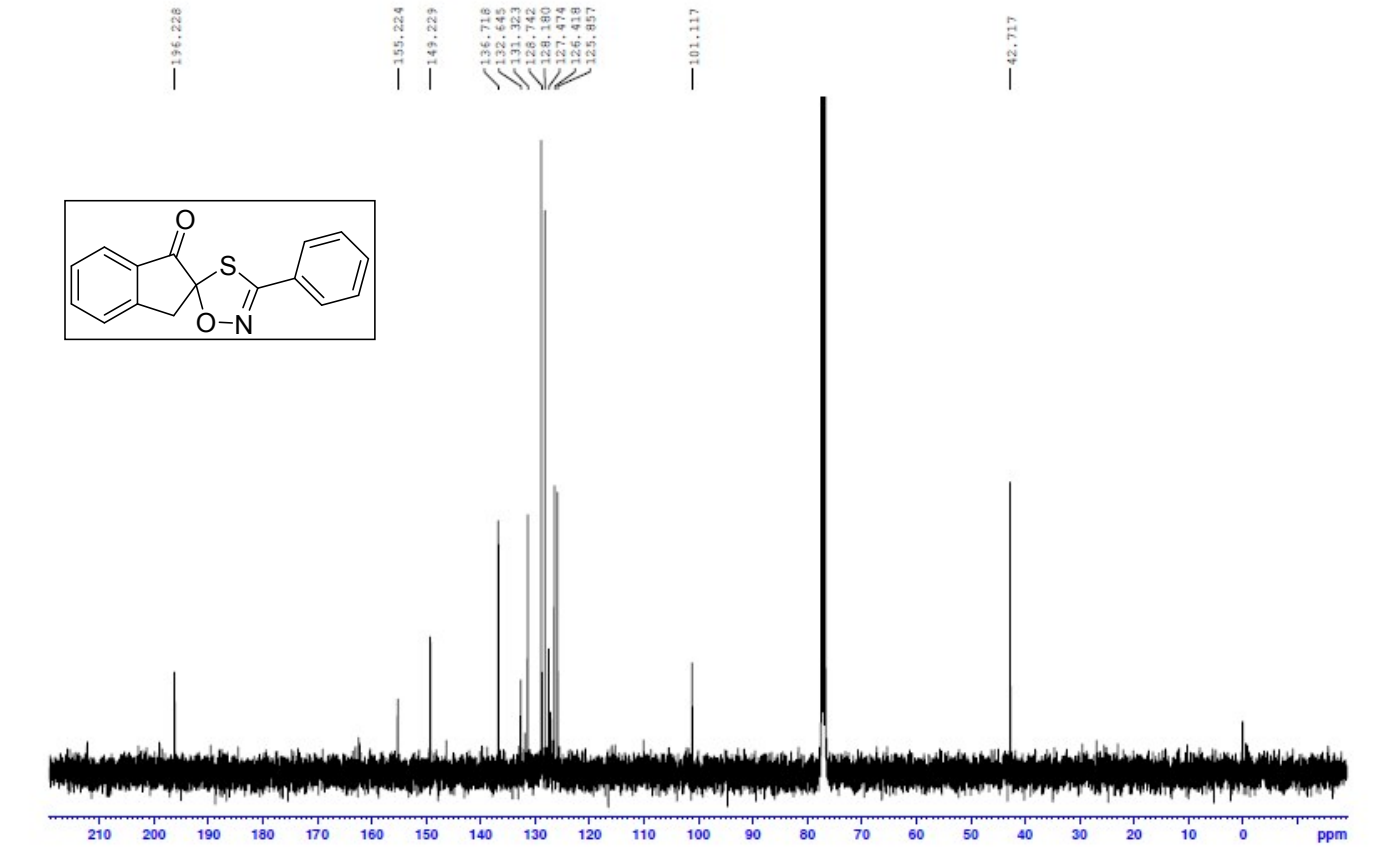


Figure S 10

thermodynamic isomer **27** and regiosiomer **29**,, regio : thermodynamic, 0.73 : 1, **29** : **27**

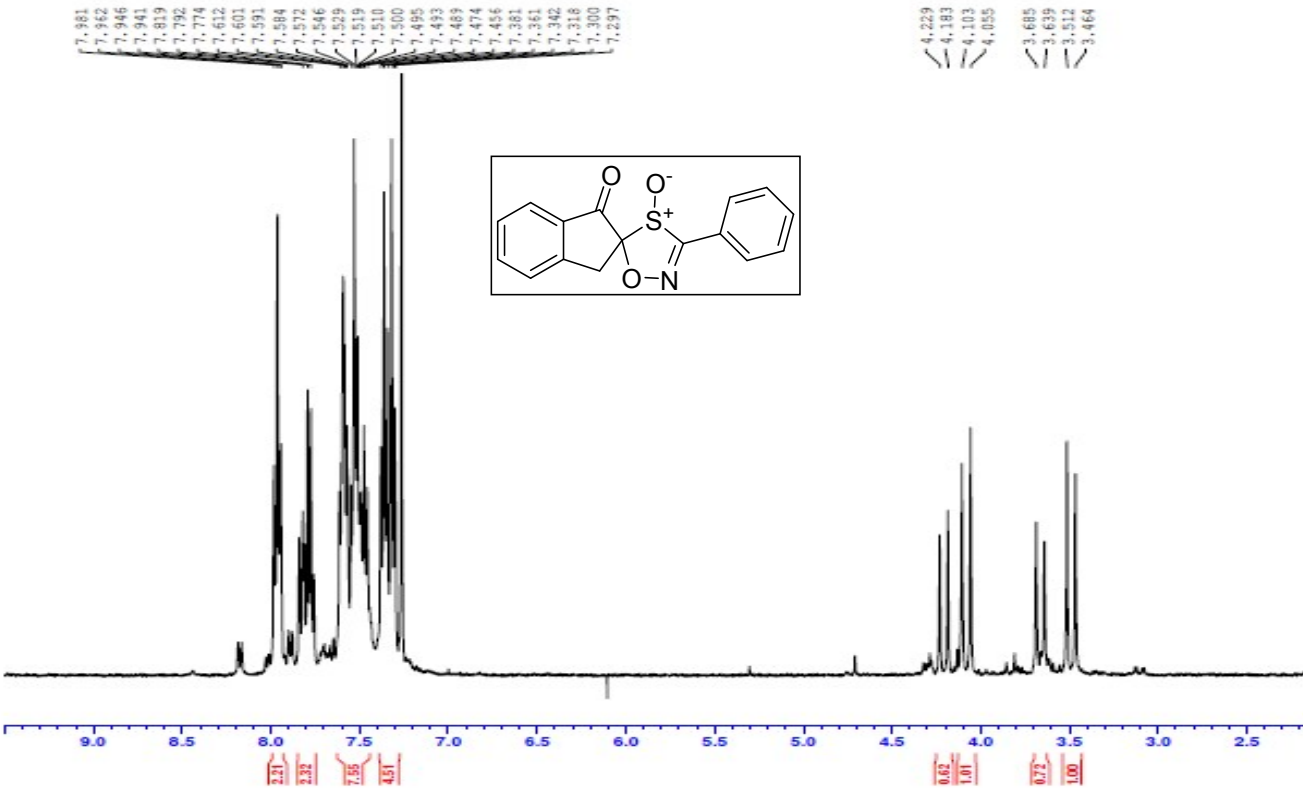


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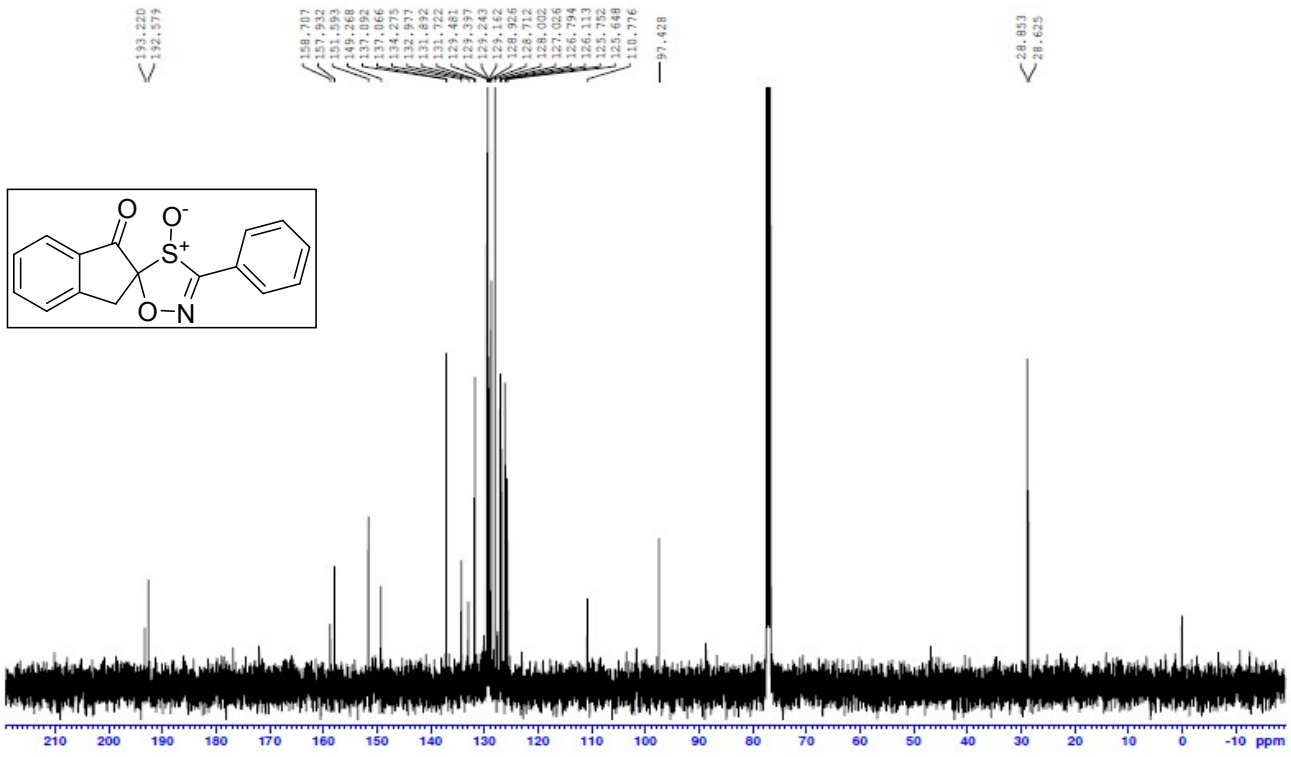


Figure S 12

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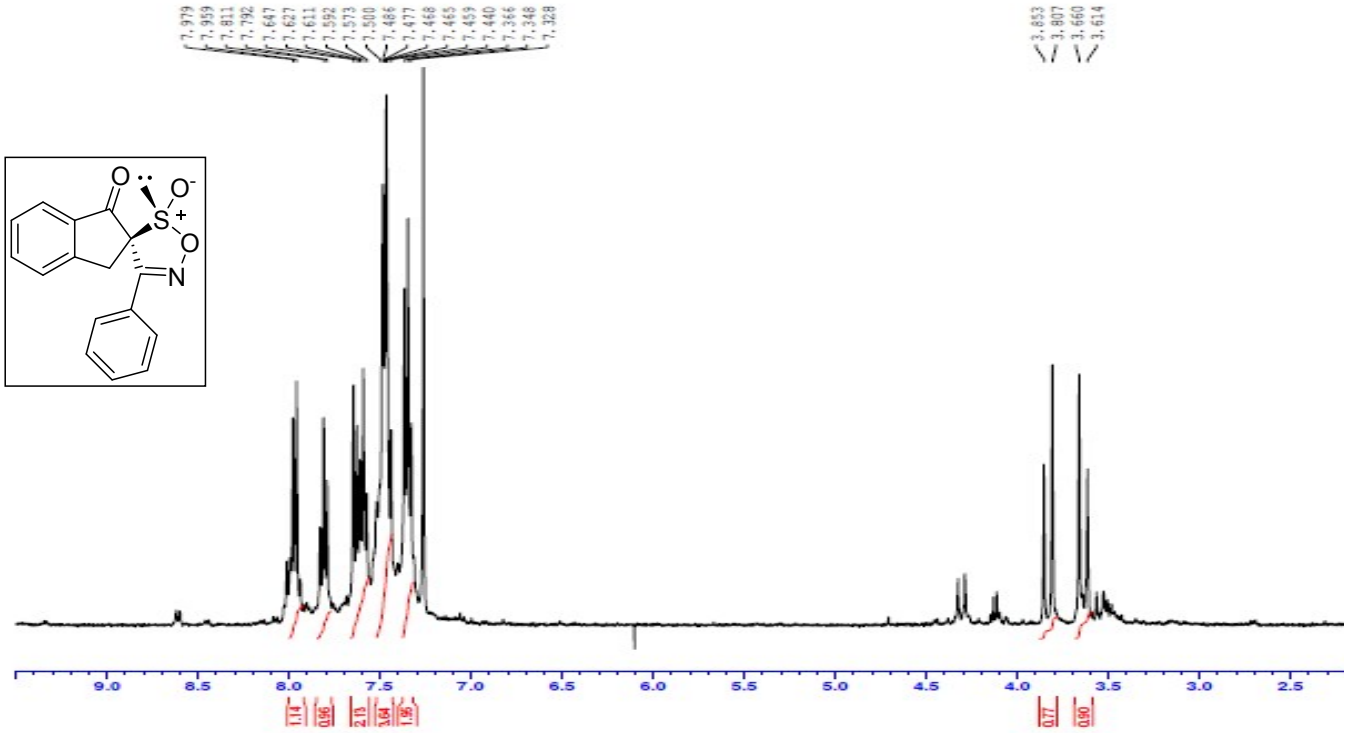


Figure S 13

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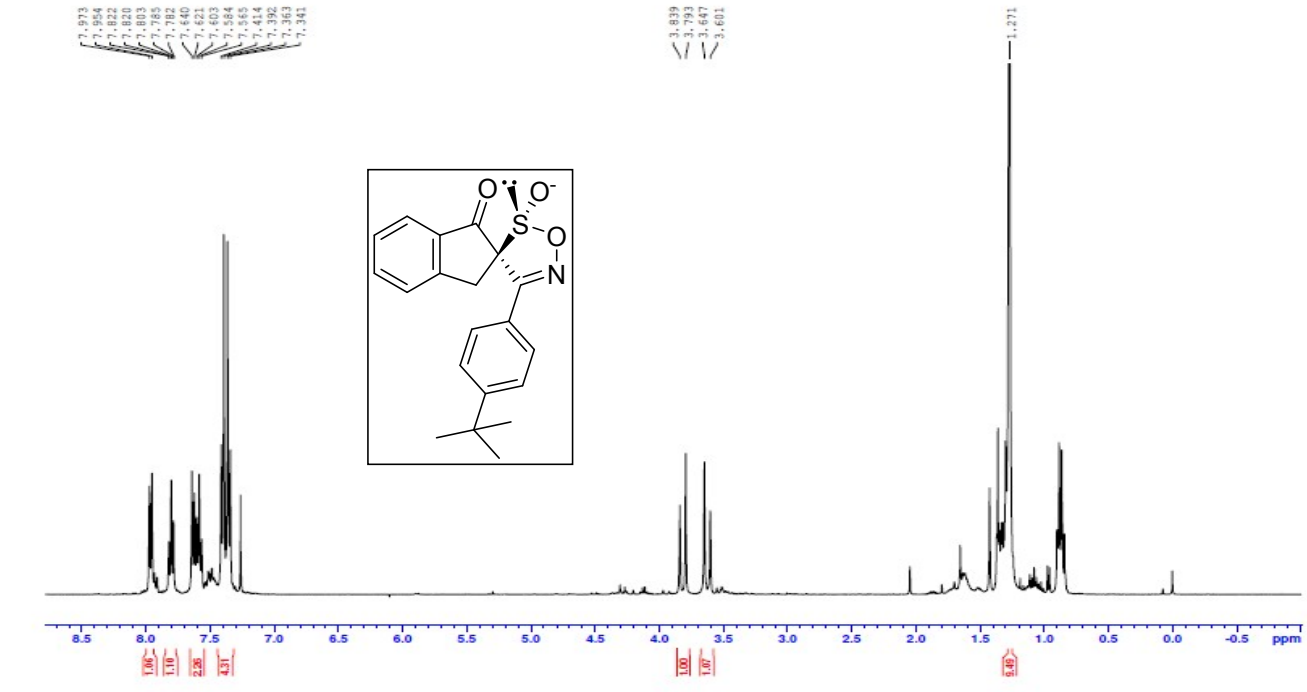


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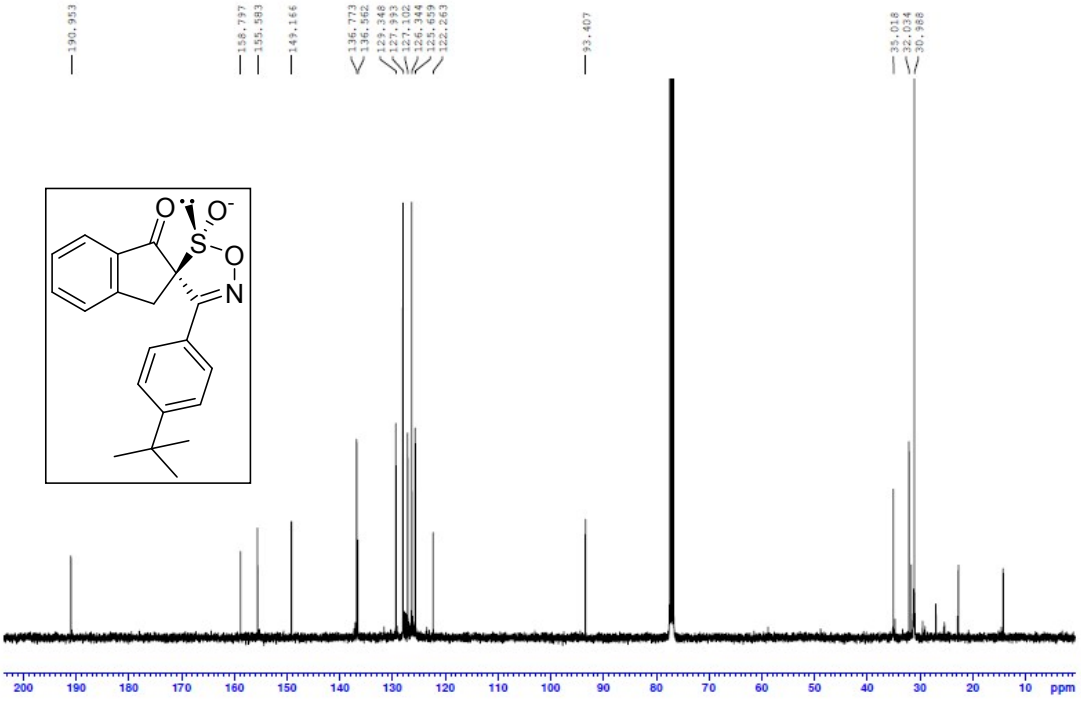


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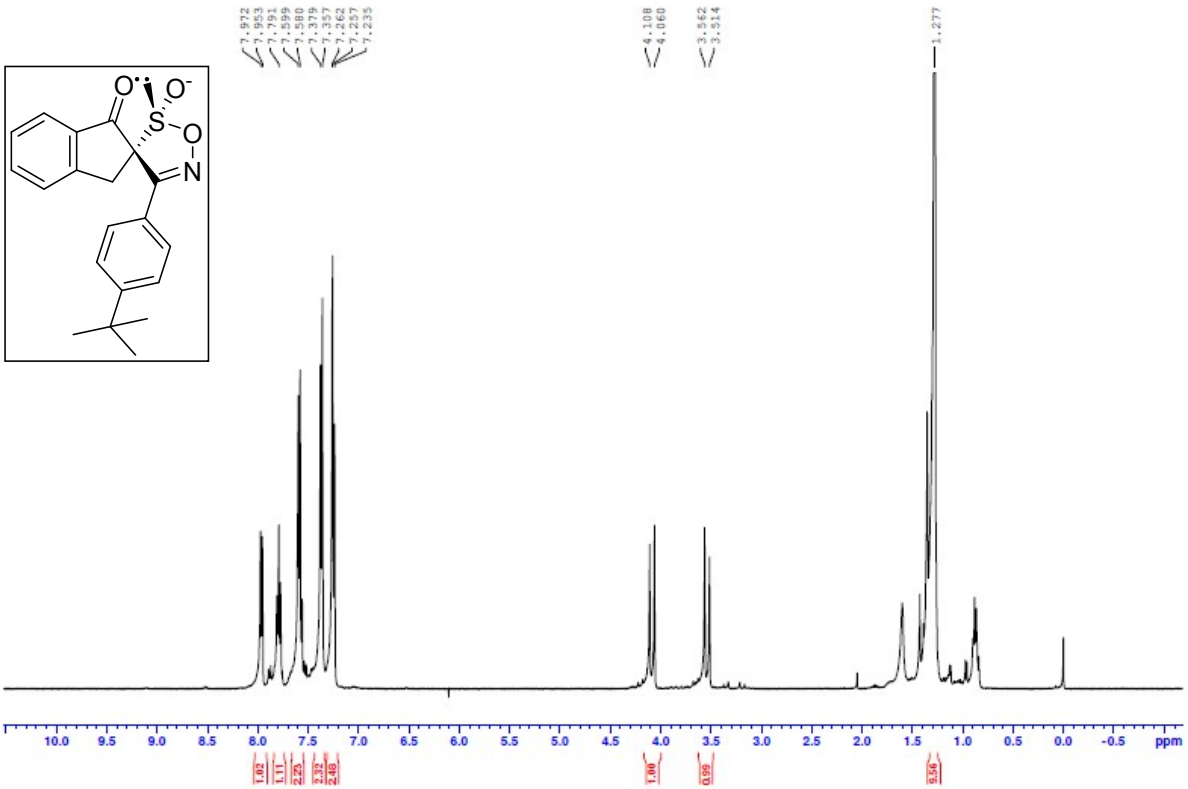


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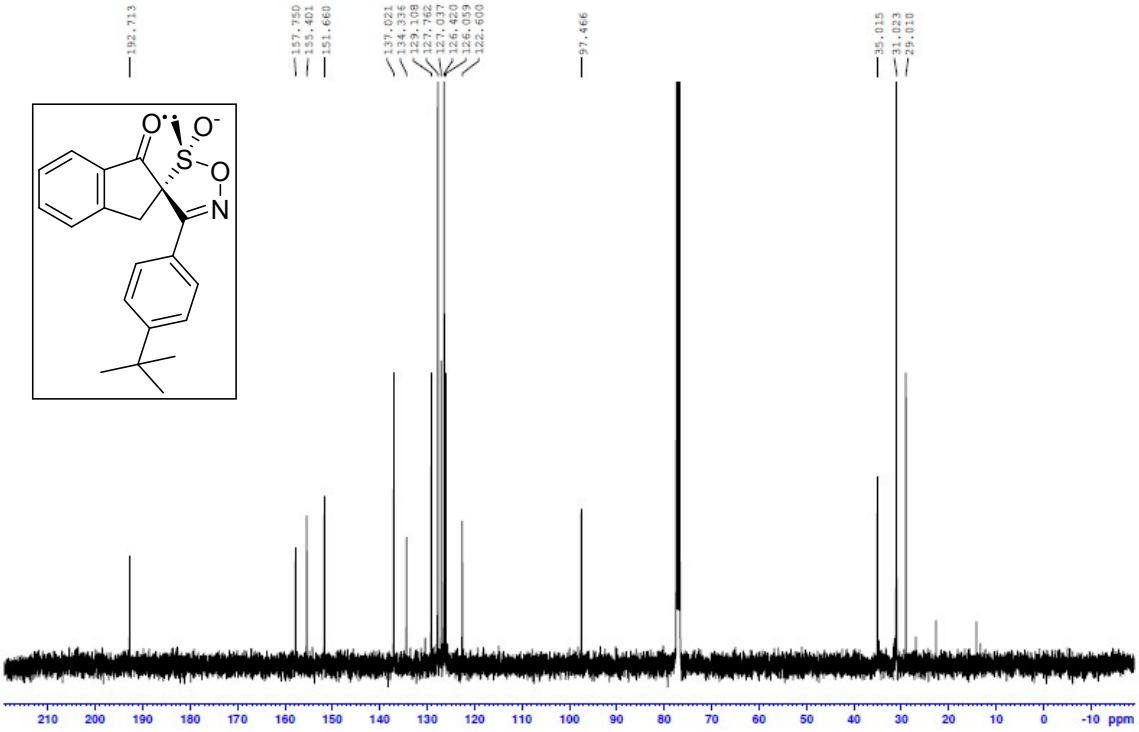


Figure S 17

40

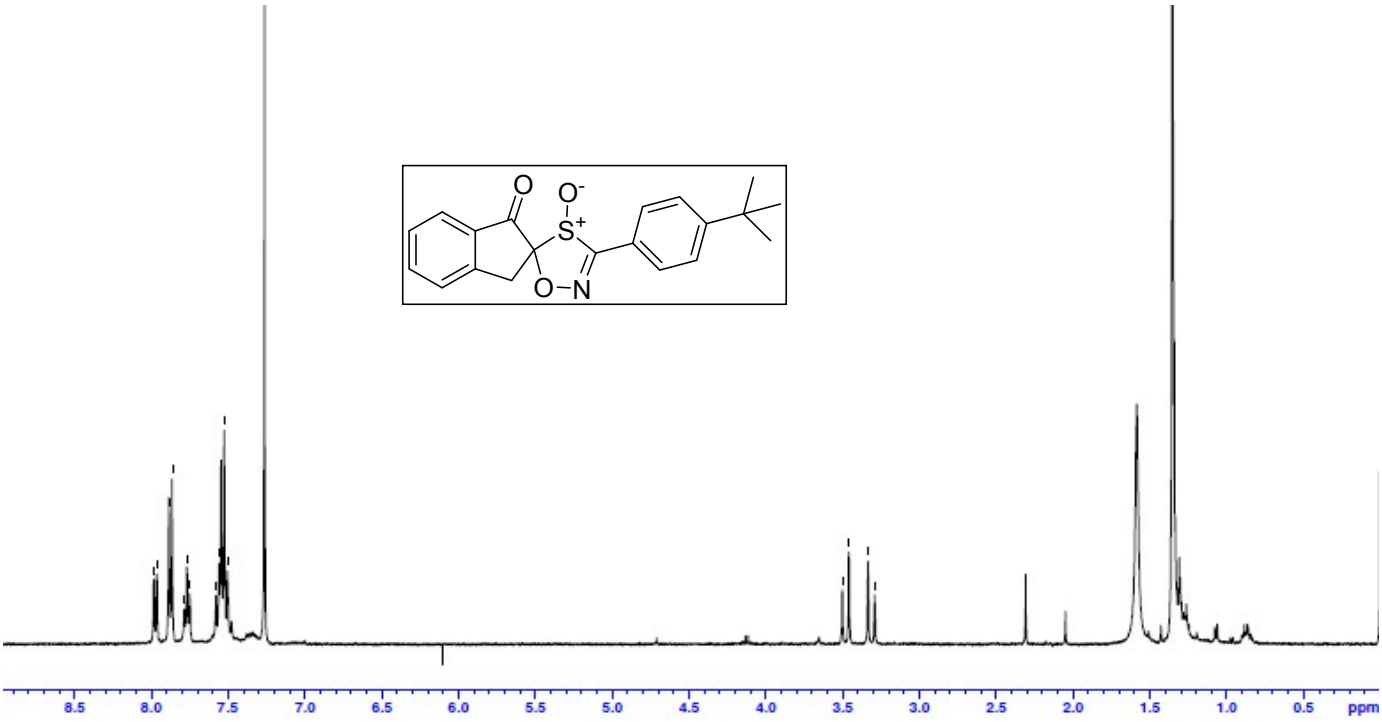


Figure S 18

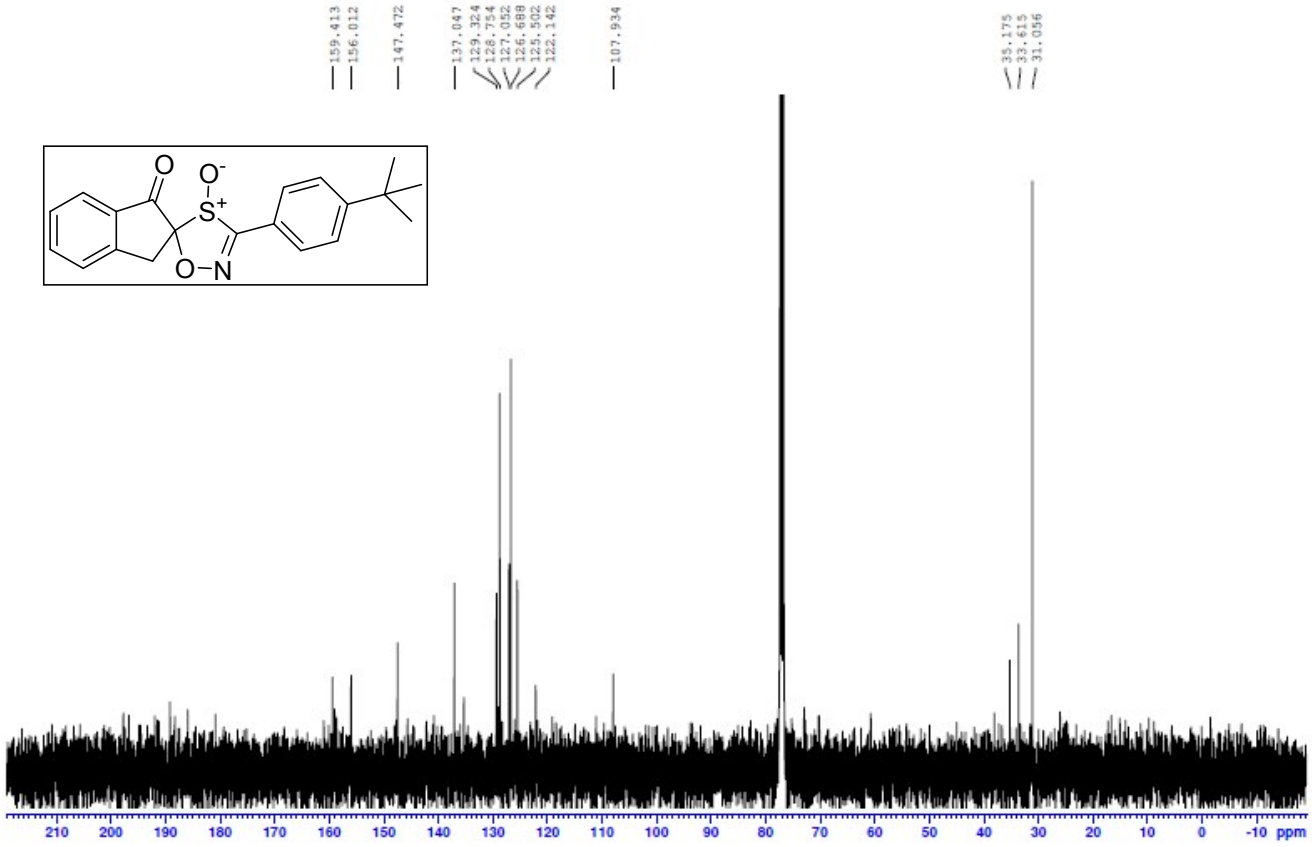


Figure S 19

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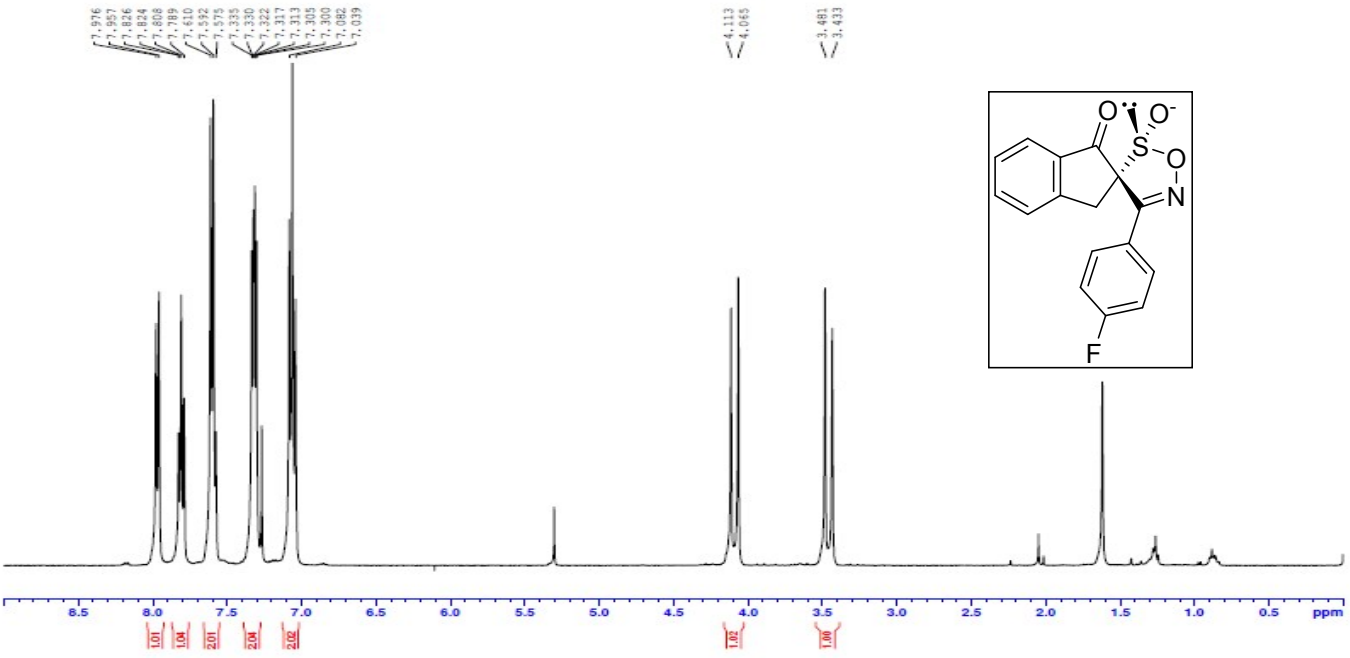


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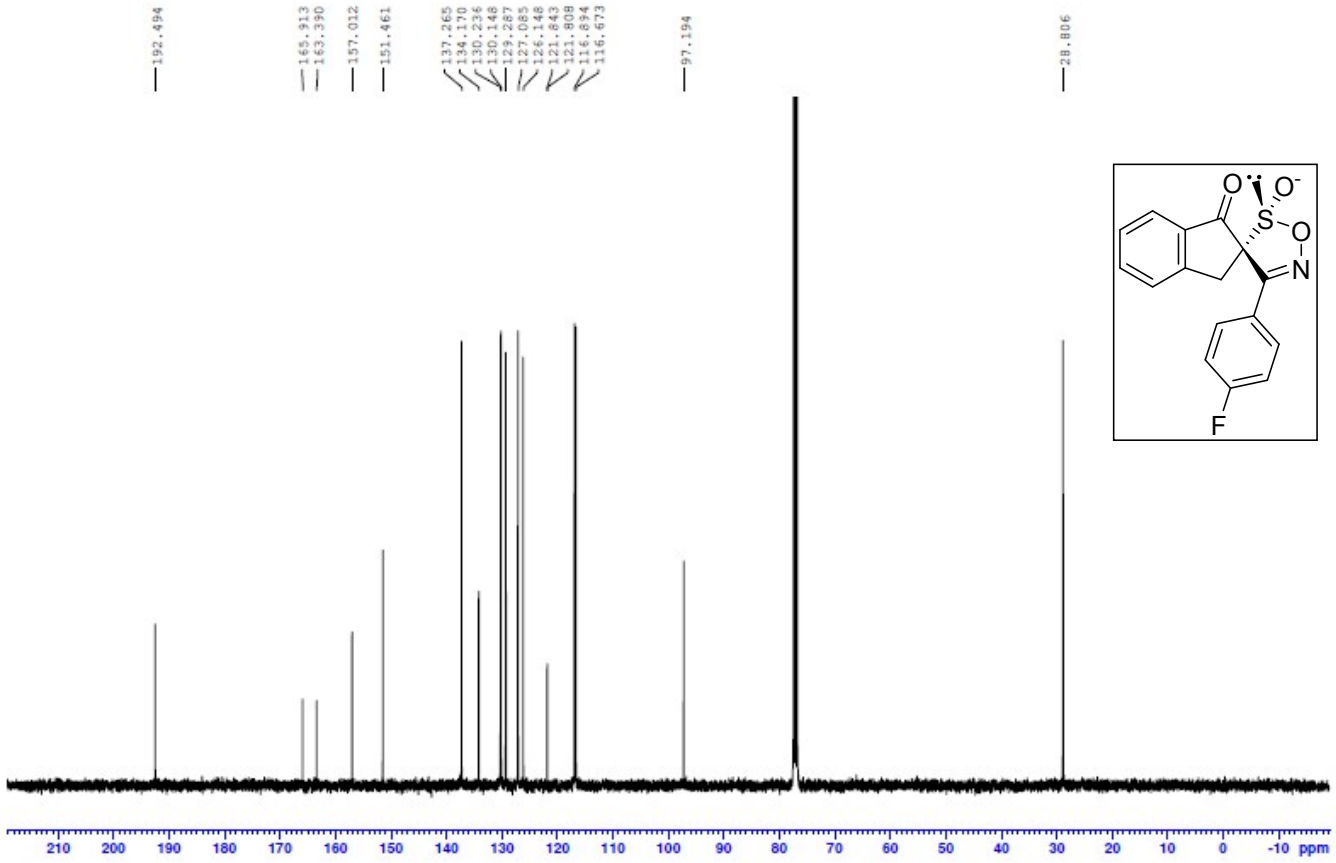


Figure S 21

32

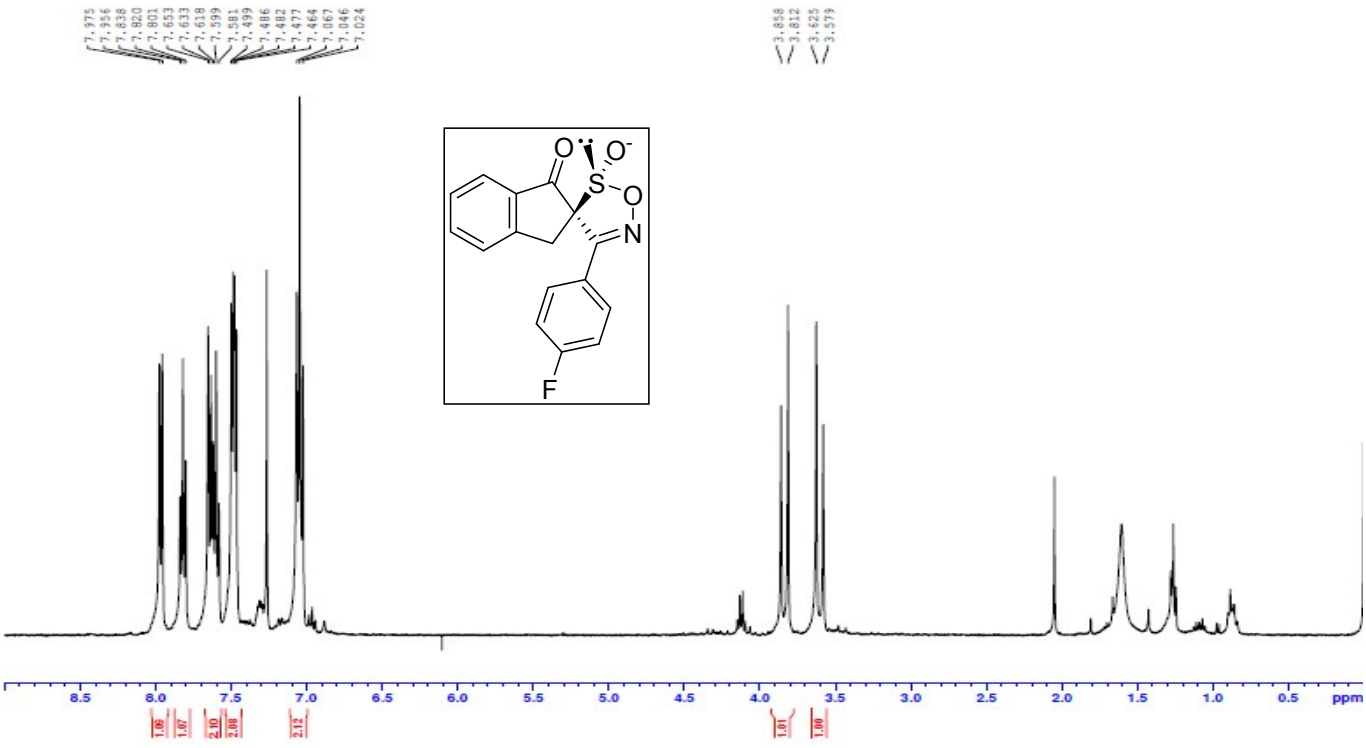


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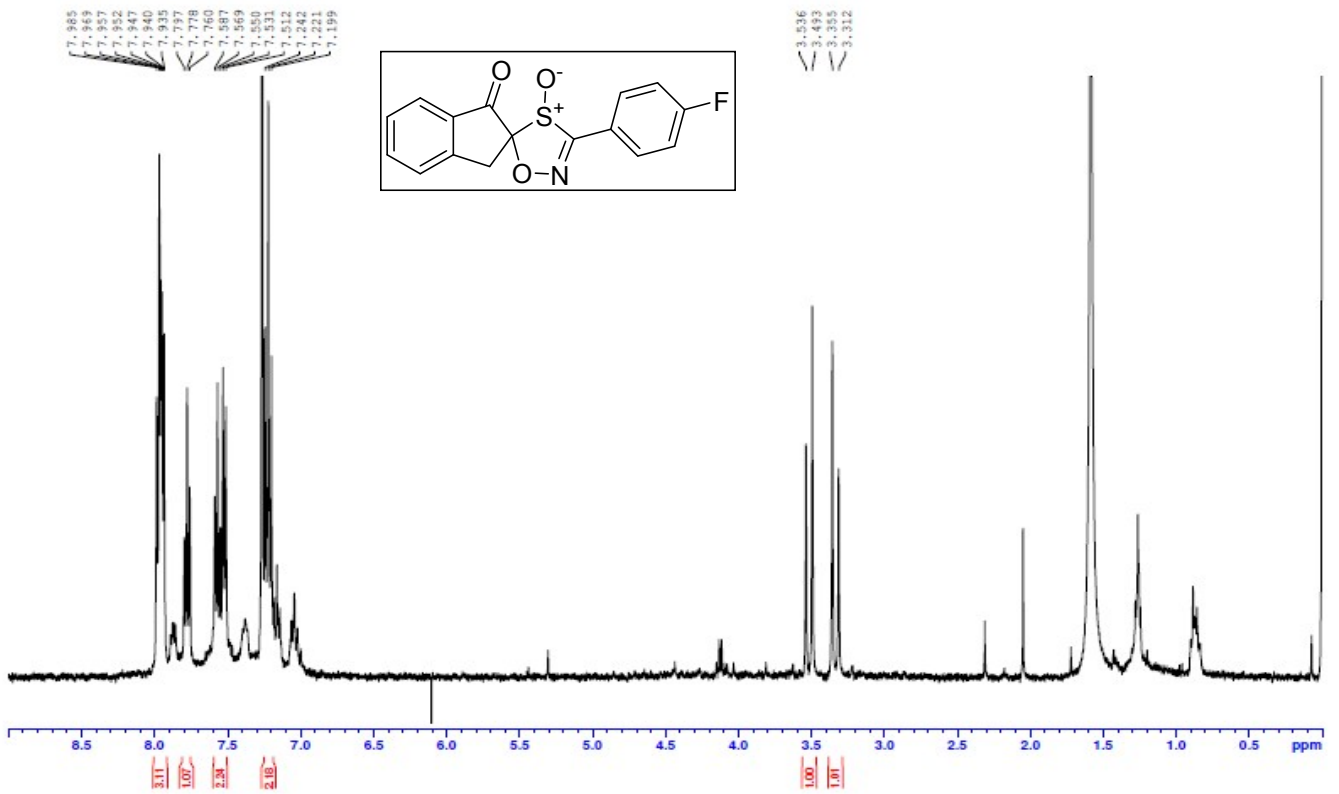


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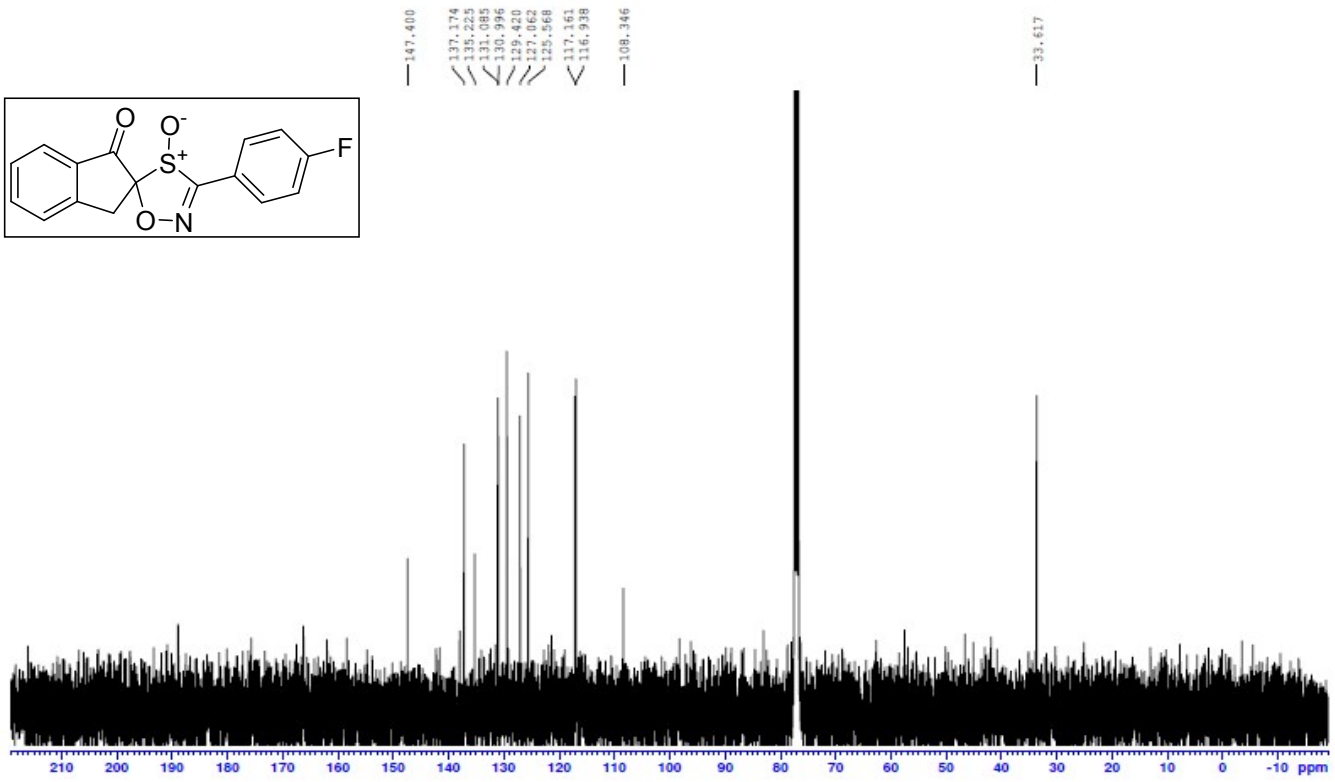


Figure S 24

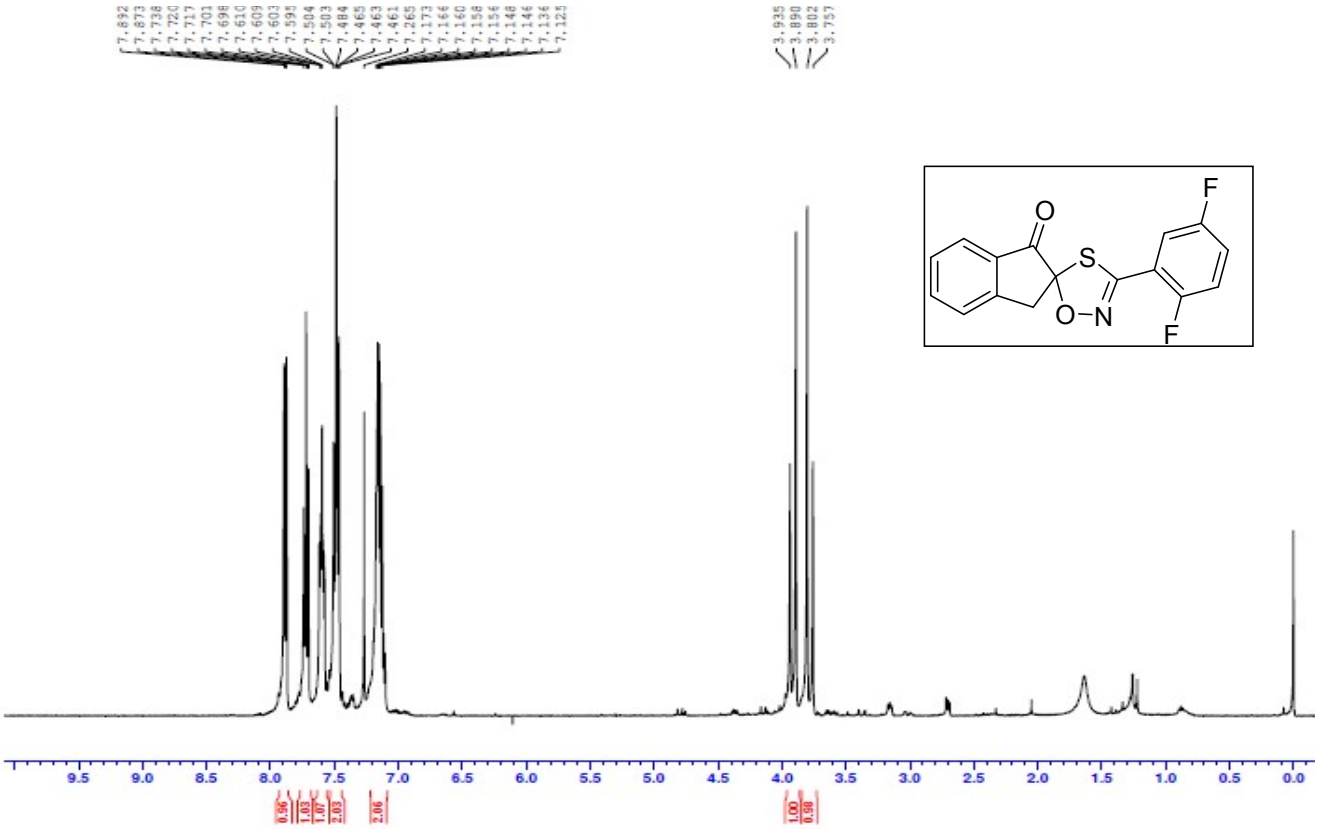


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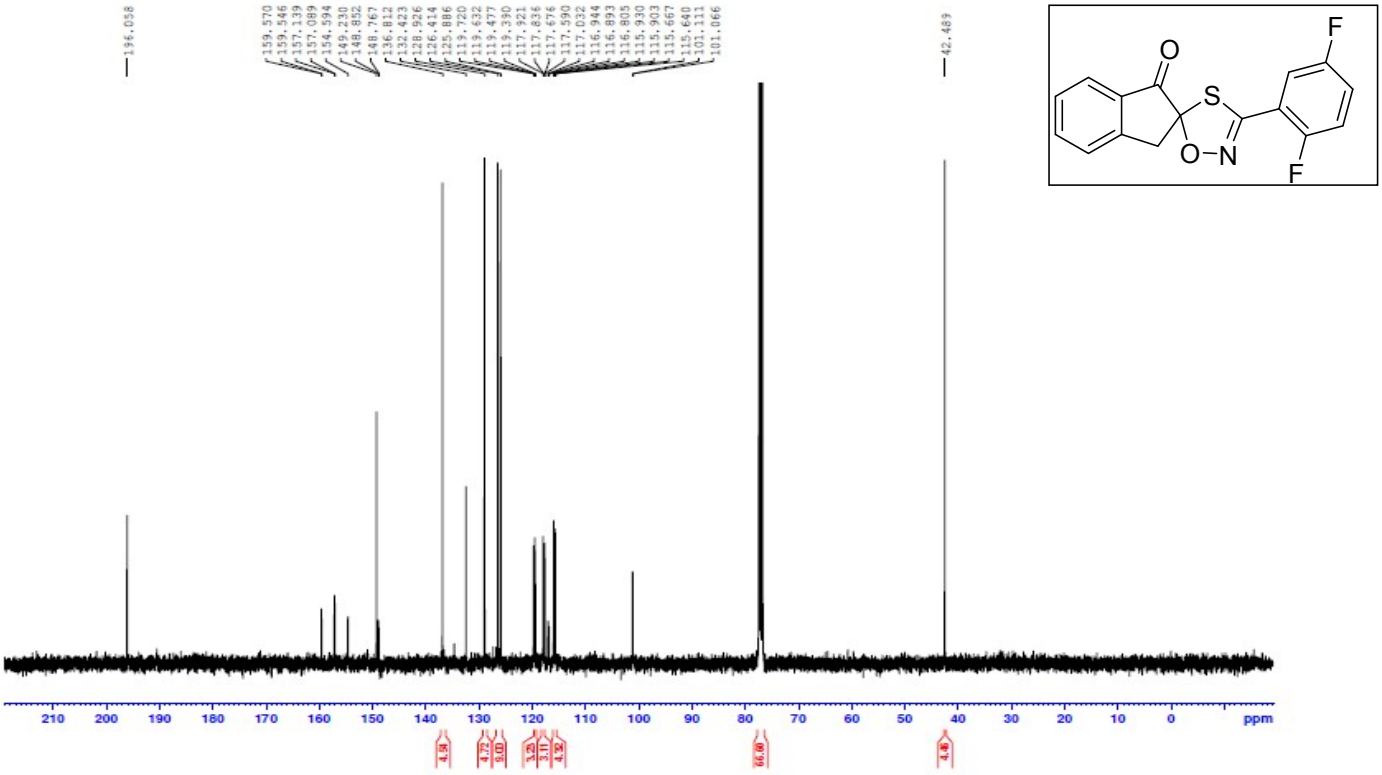


Figure S 26

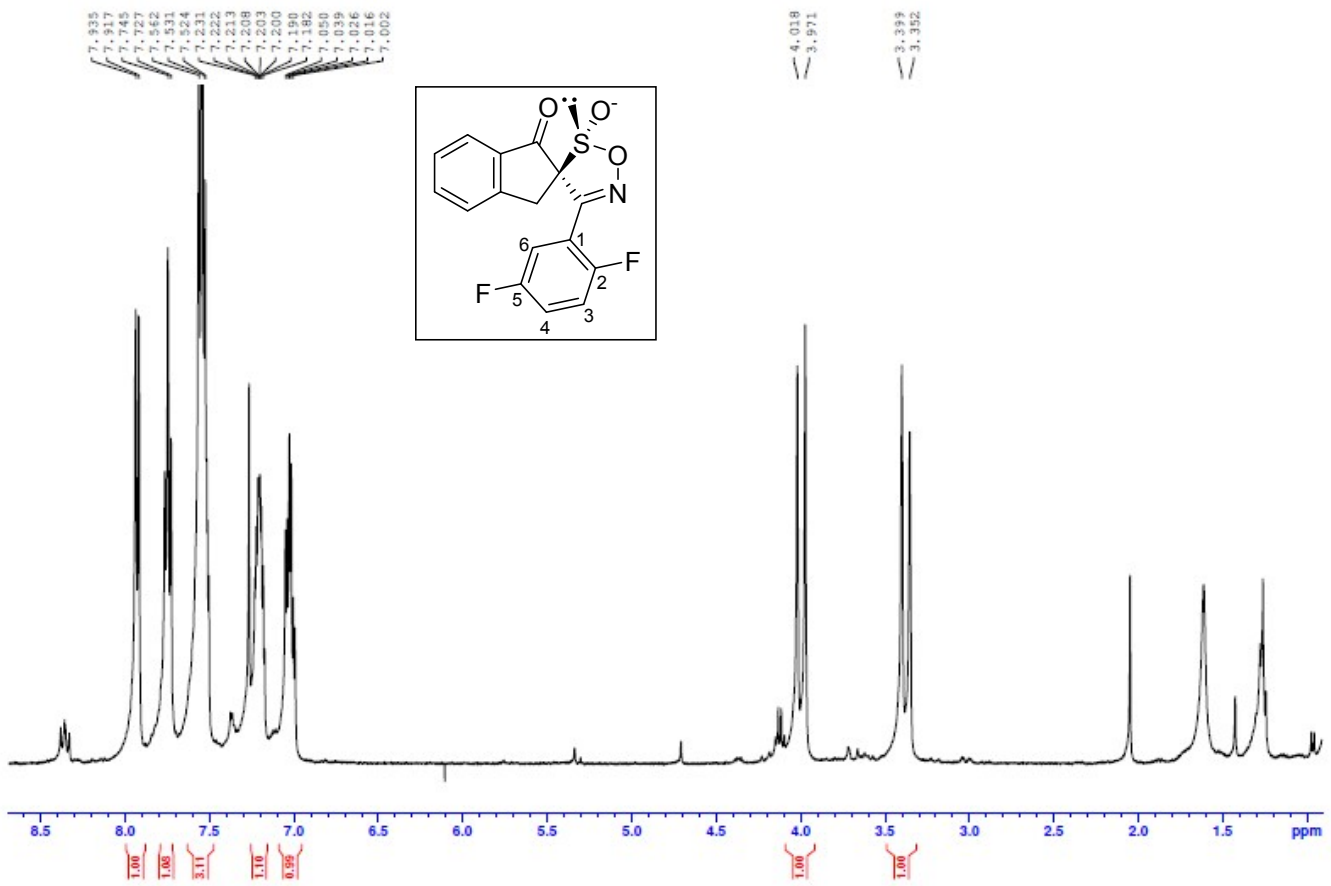


Figure S 27

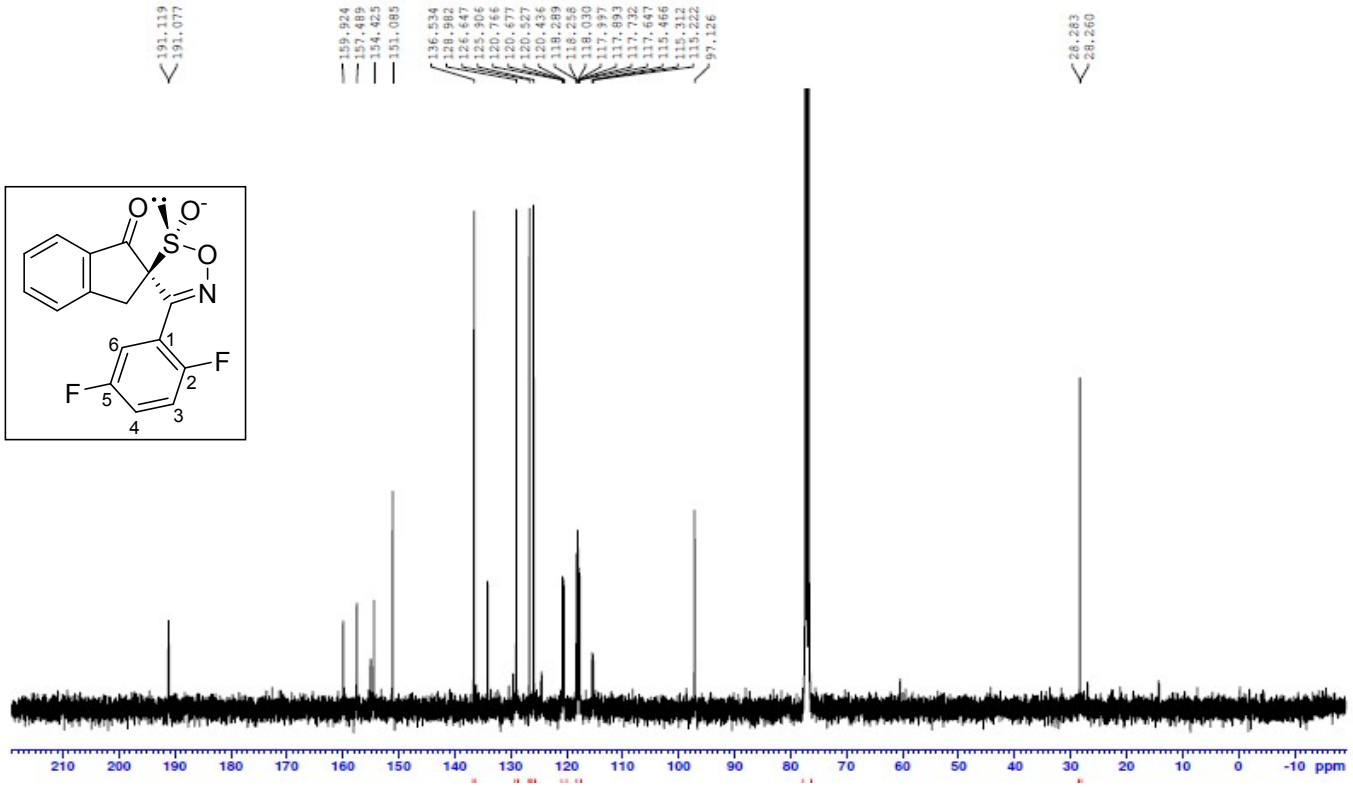
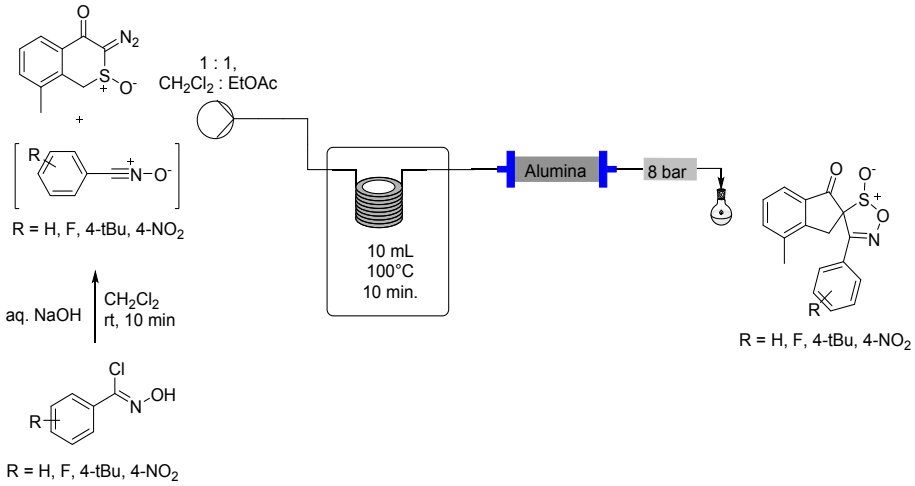


Figure S 28

Dipolar cycloadditions of α-diazosulfoxide **2** with nitrile oxides.



Scheme 1

42

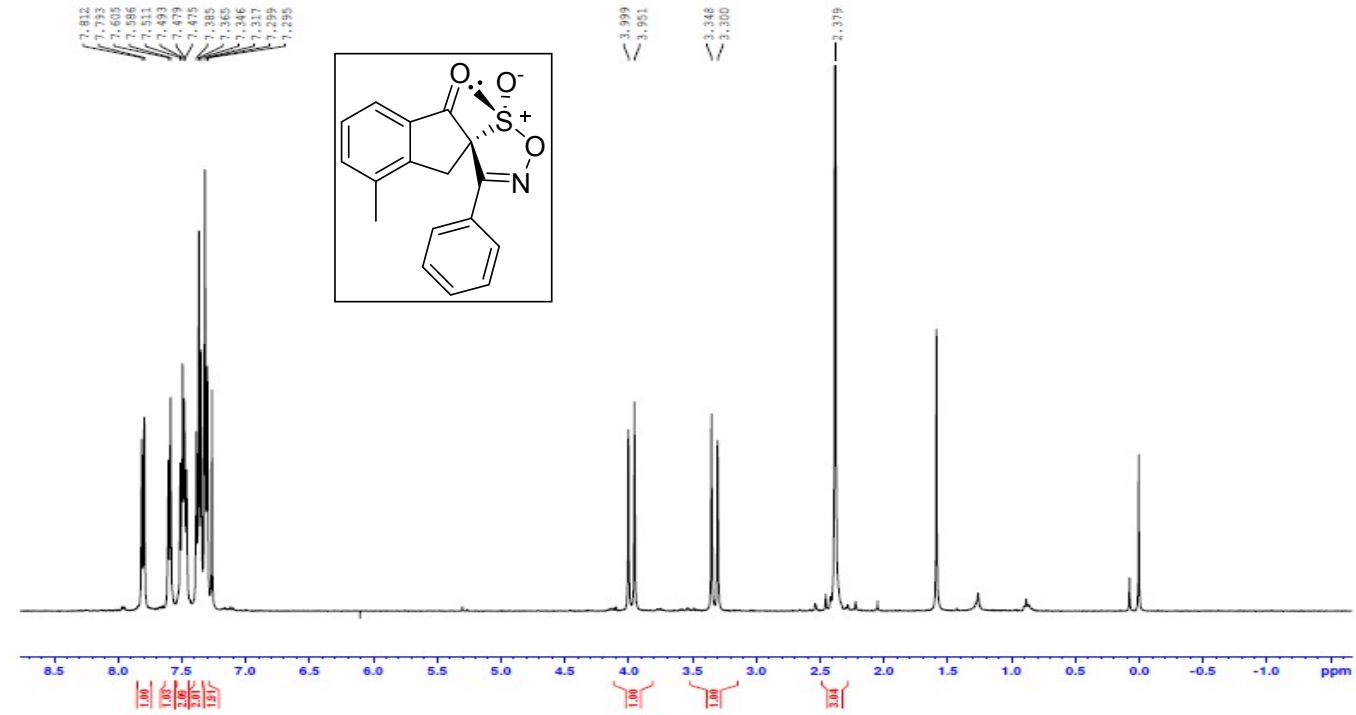


Figure S 29

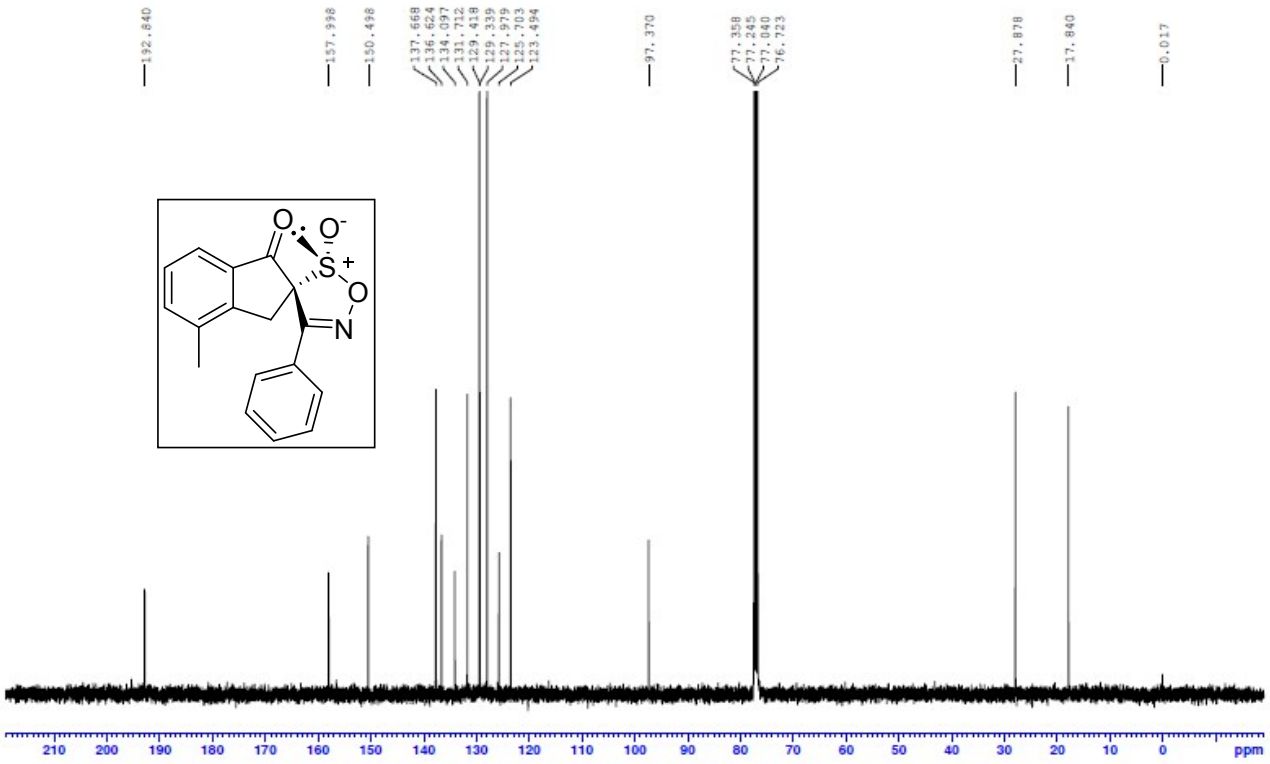


Figure S 30

45

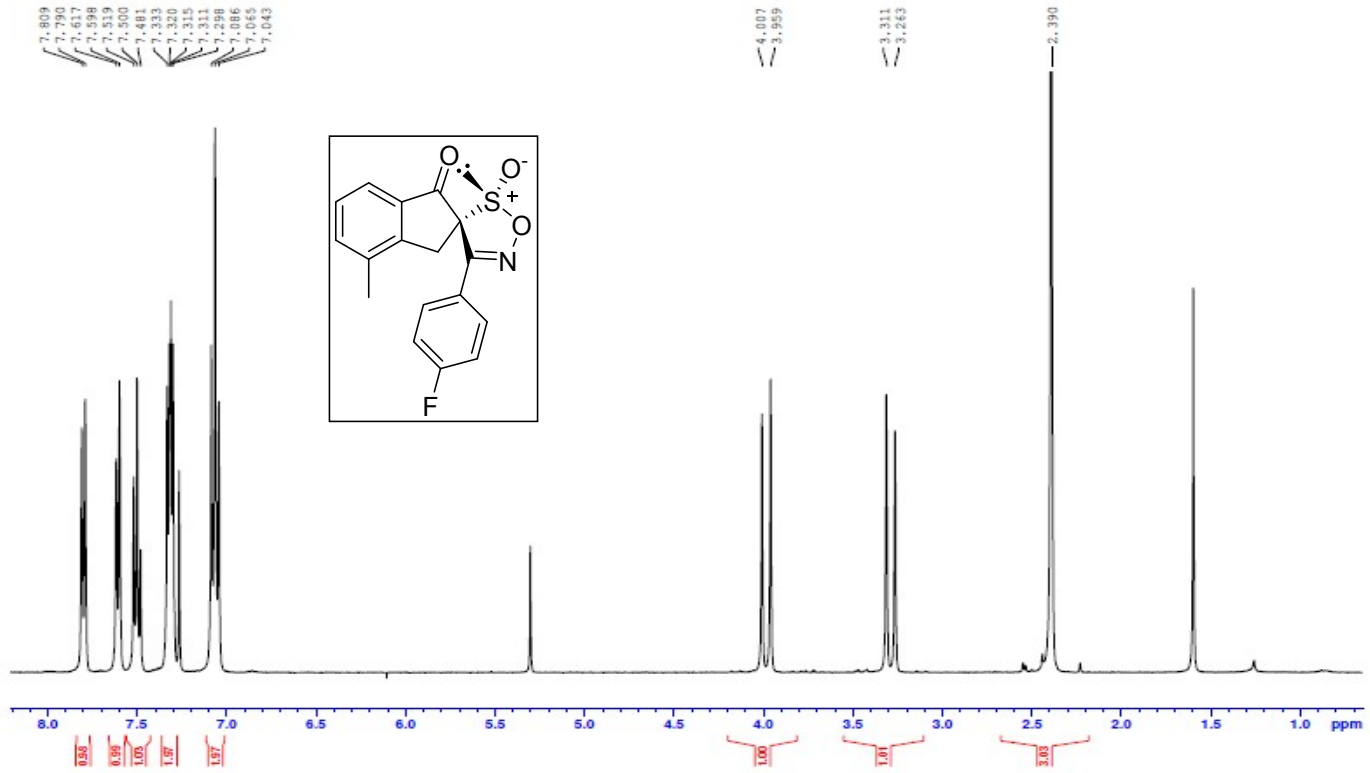


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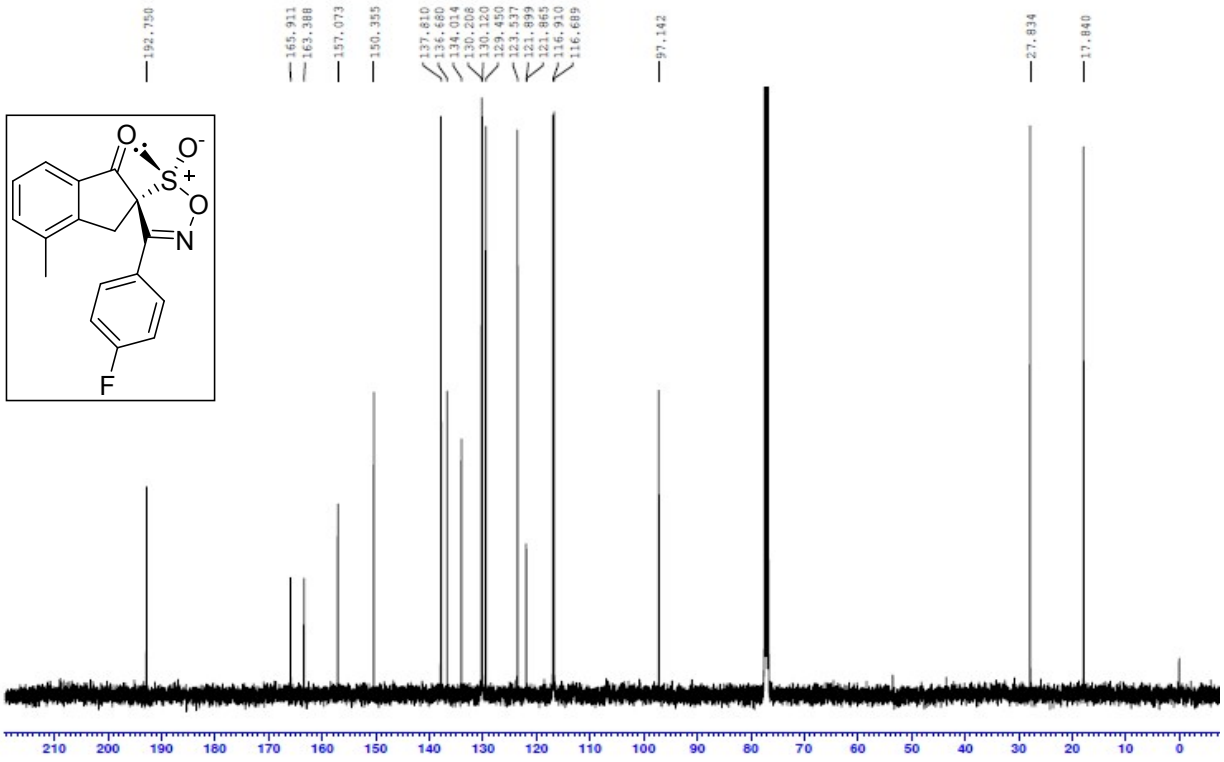


Figure S 32

47

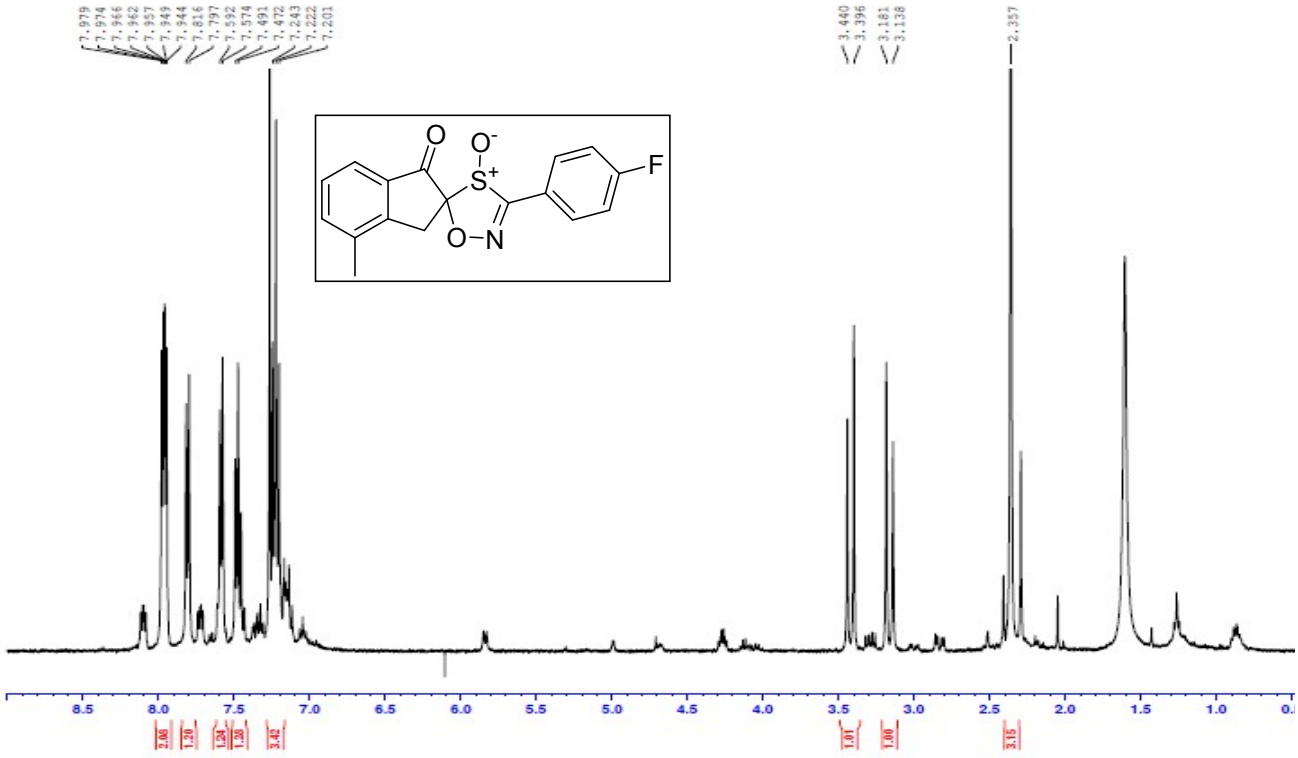


Figure S 33

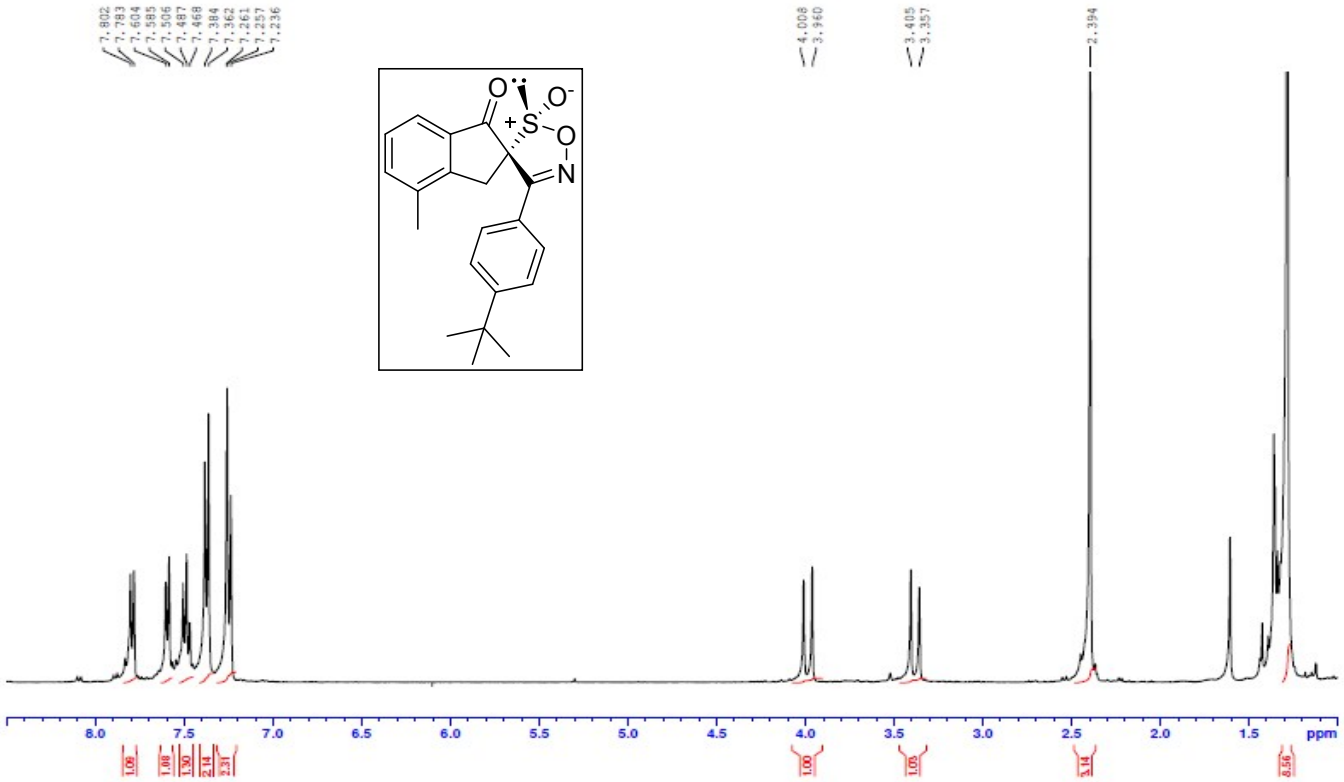


Figure S 34

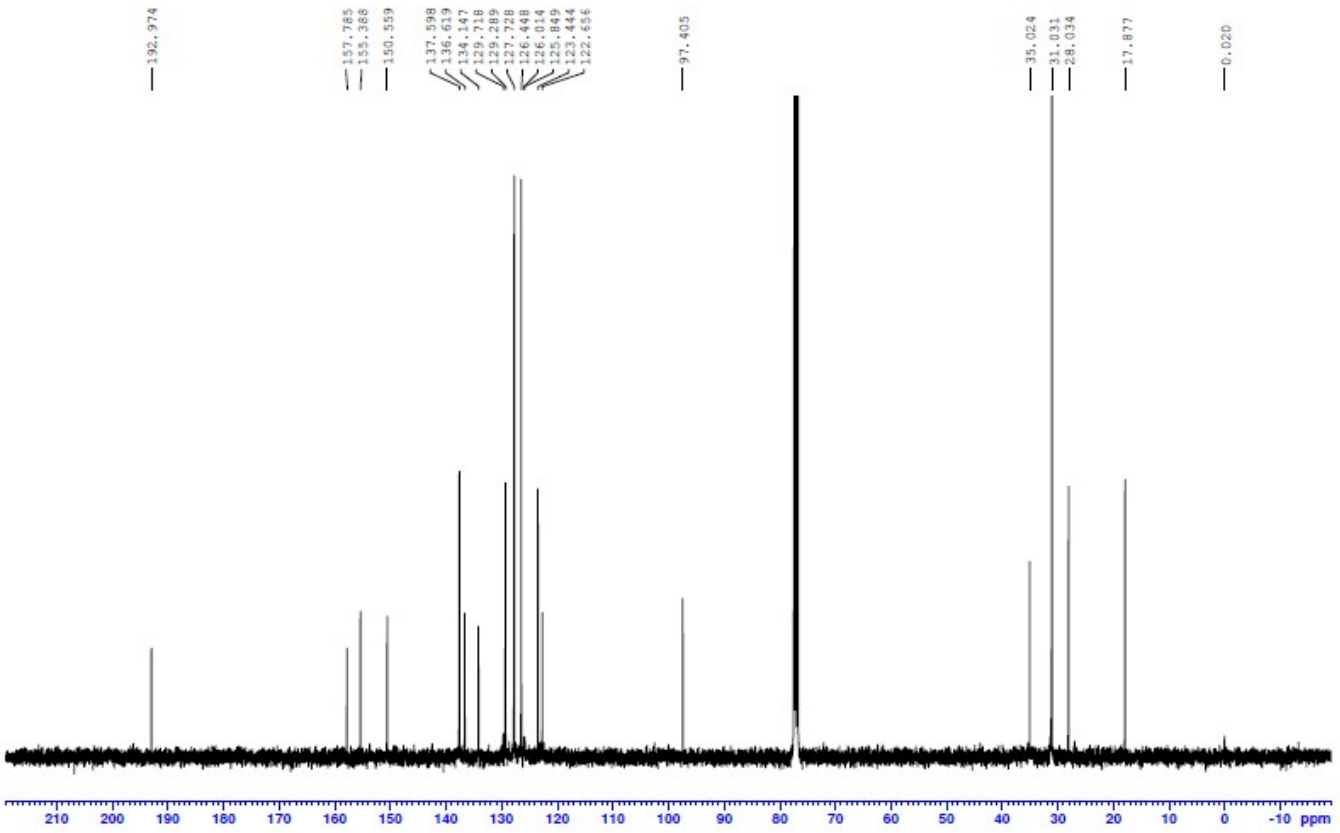


Figure S 35

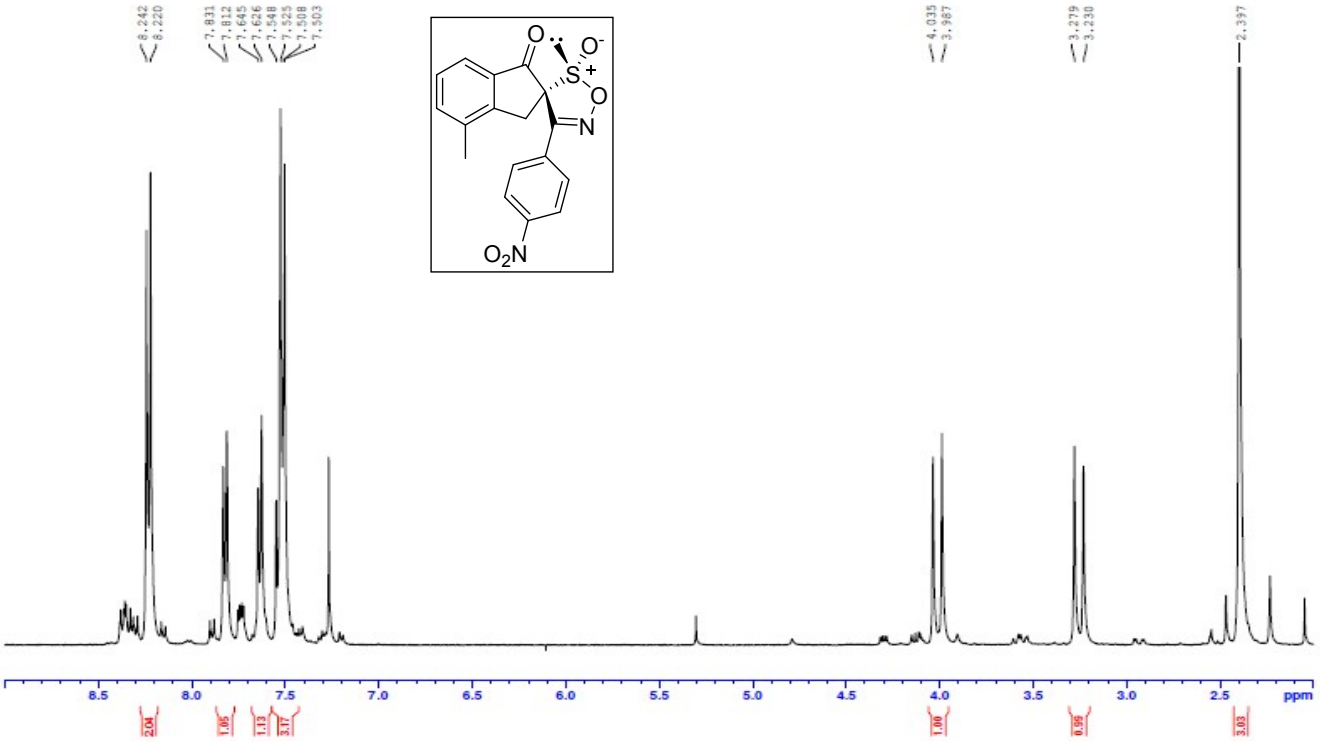


Figure S 36

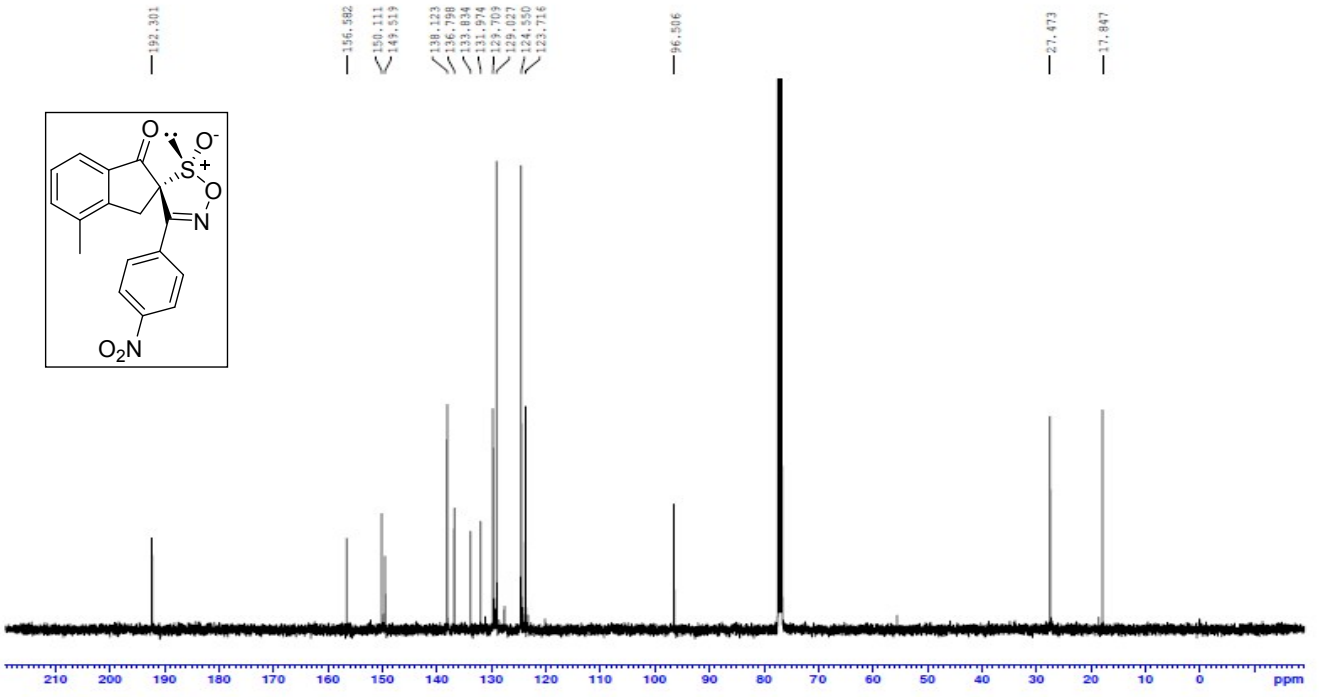
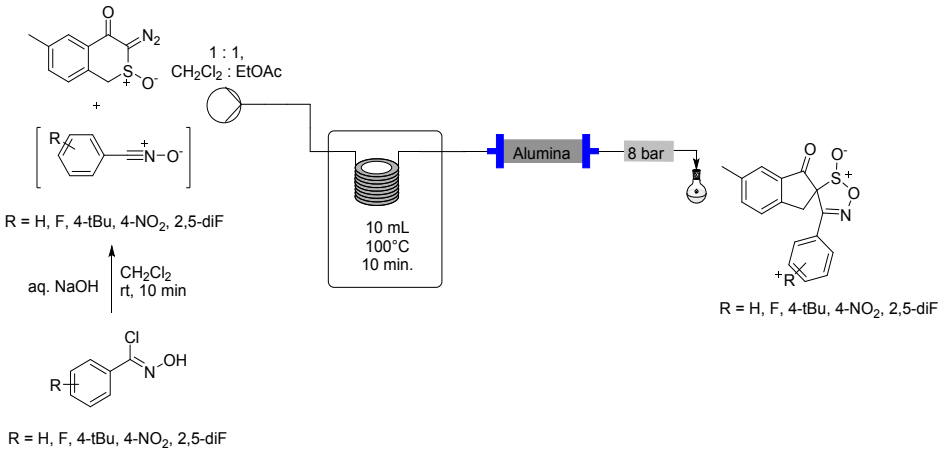


Figure S 37

Dipolar cycloaddition of α-diazosulfoxide **4** with nitrile oxides



Scheme 2

54

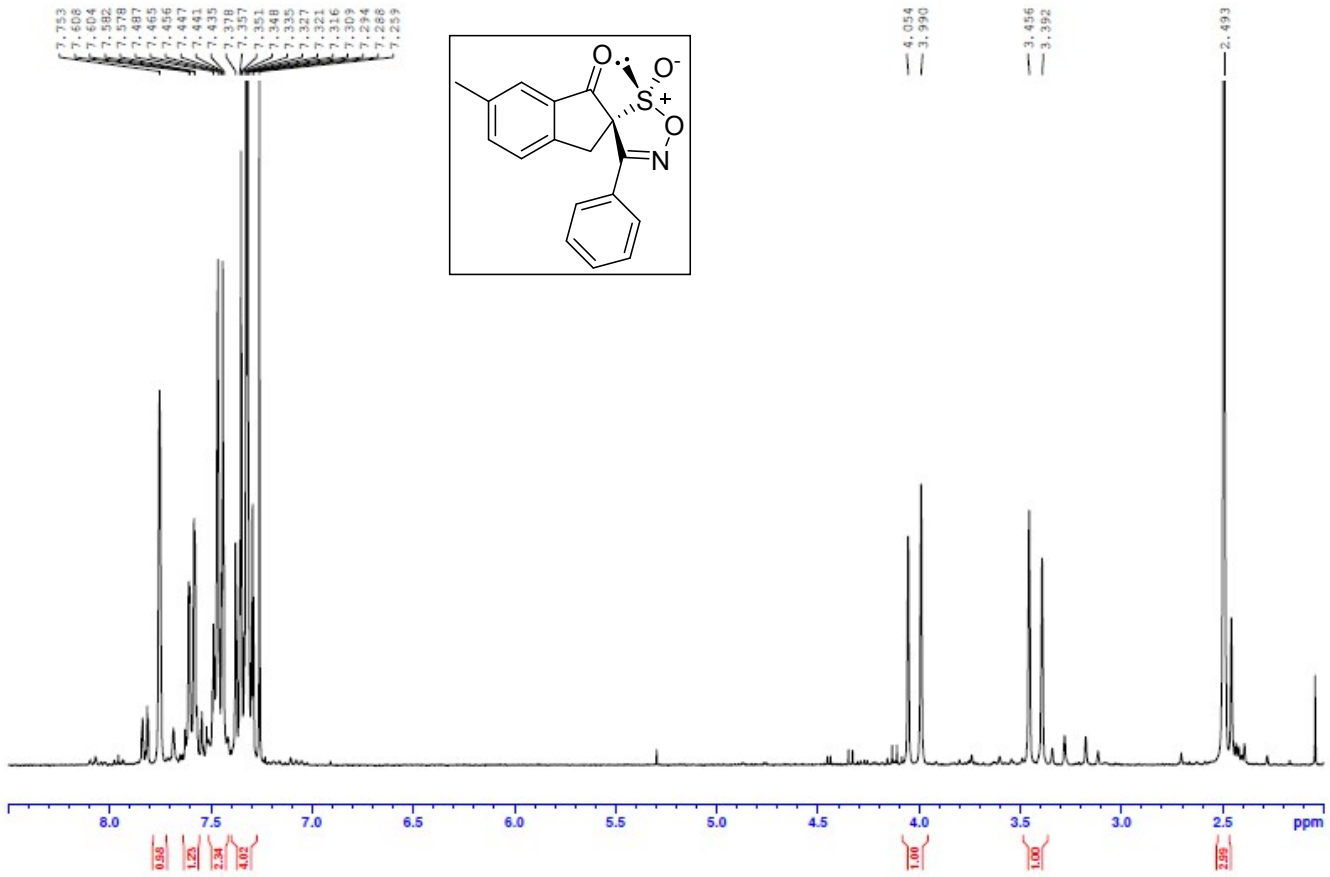


Figure S 38

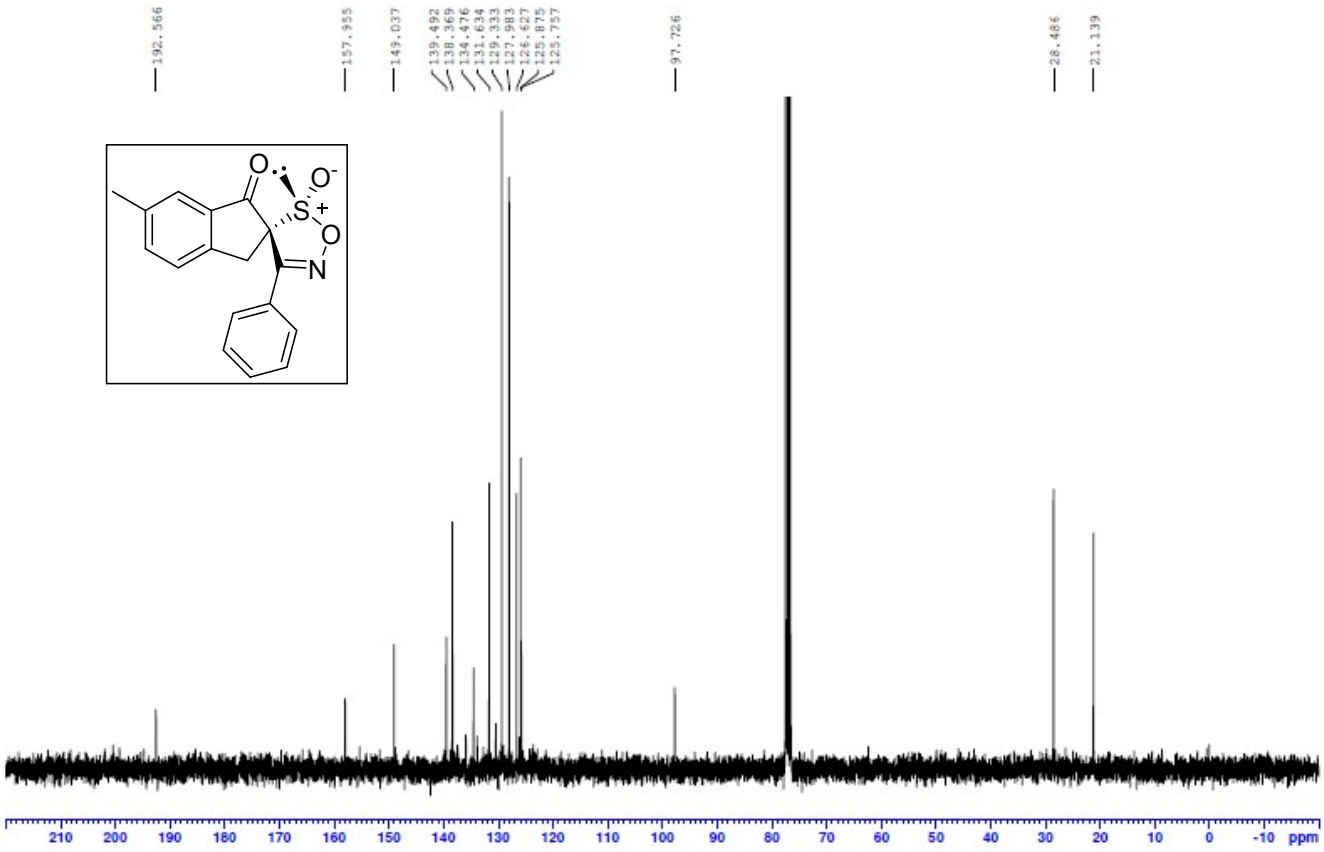
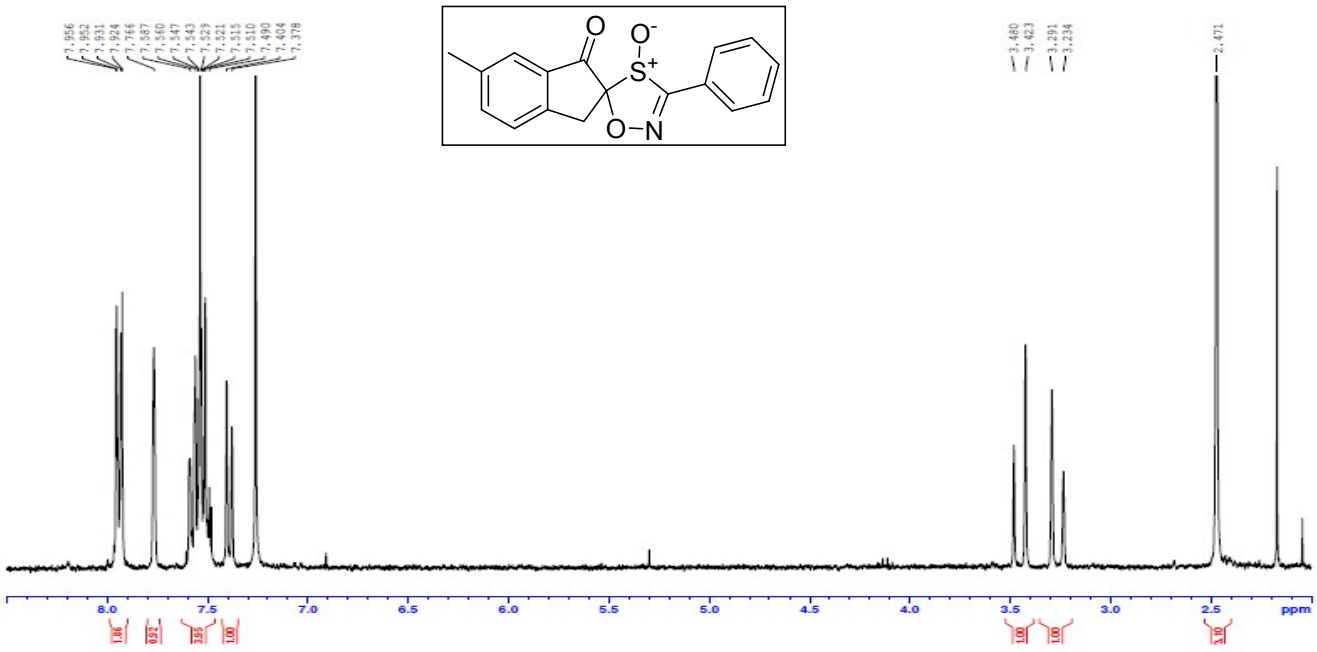
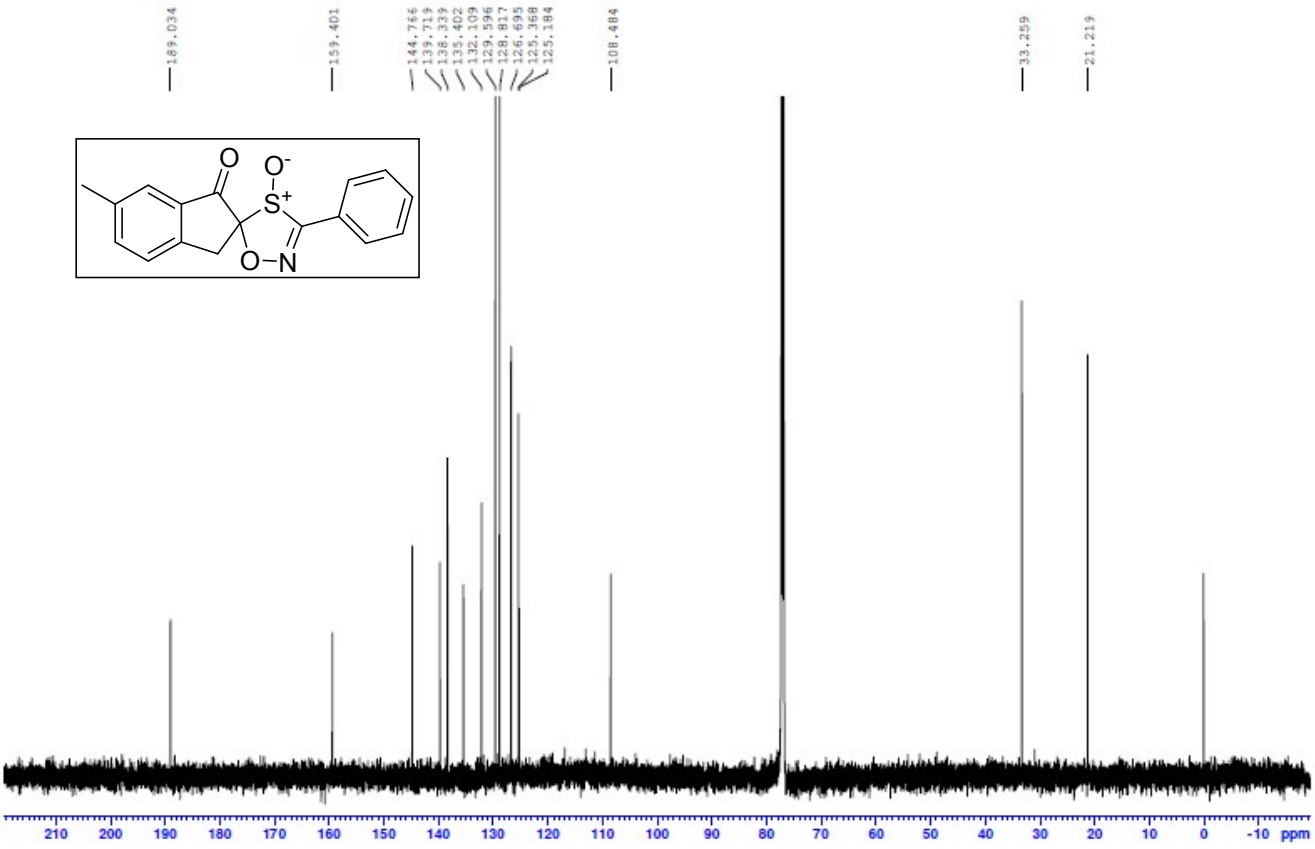


Figure S 39

56





57

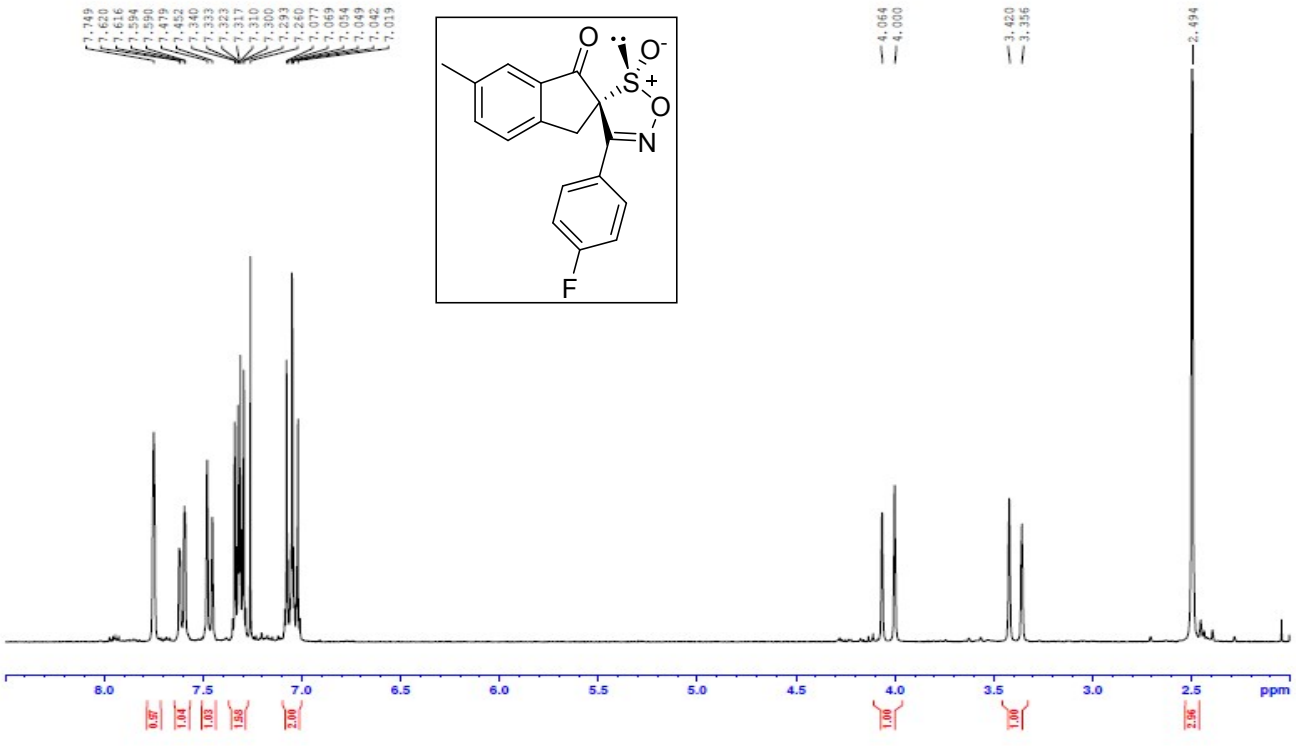


Figure S 40

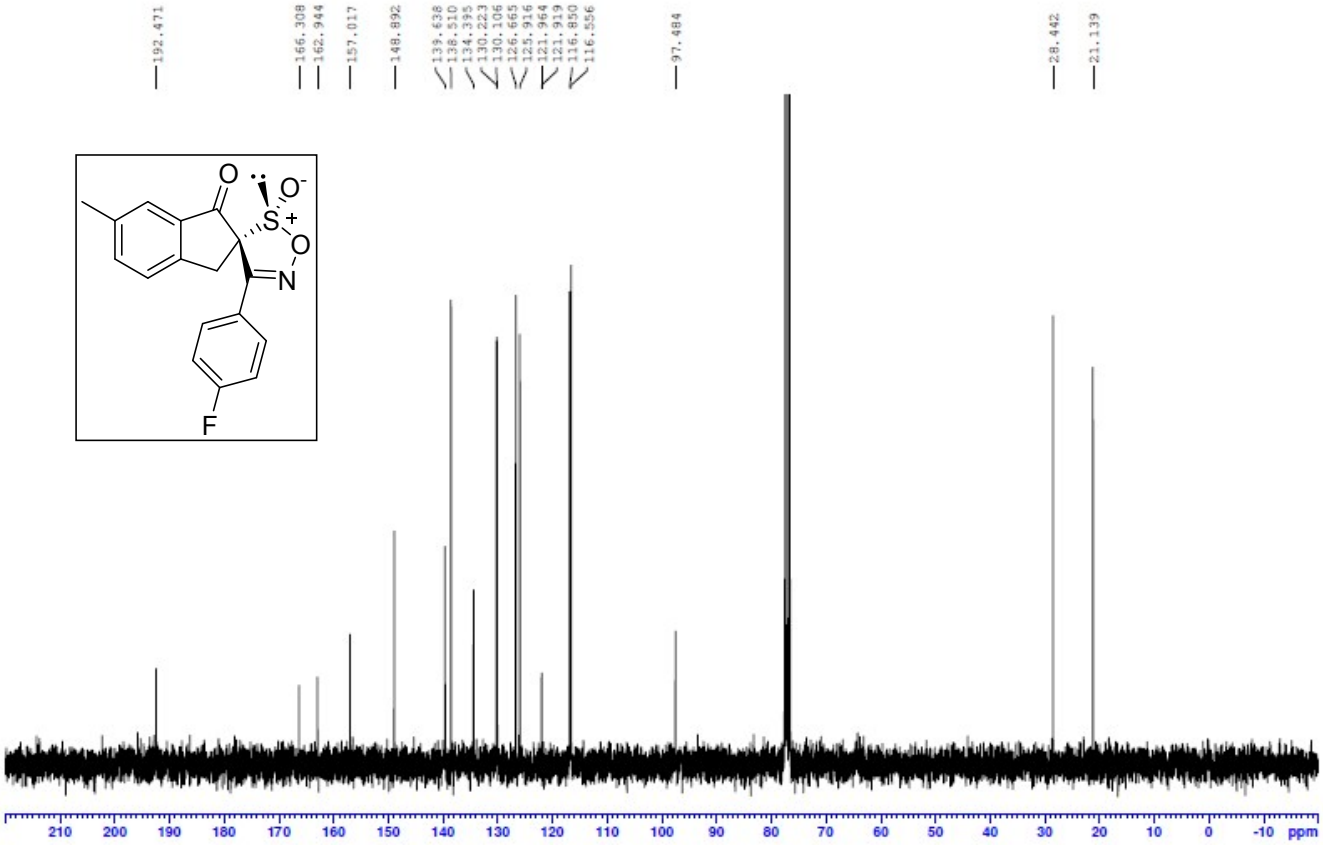


Figure S 41

58

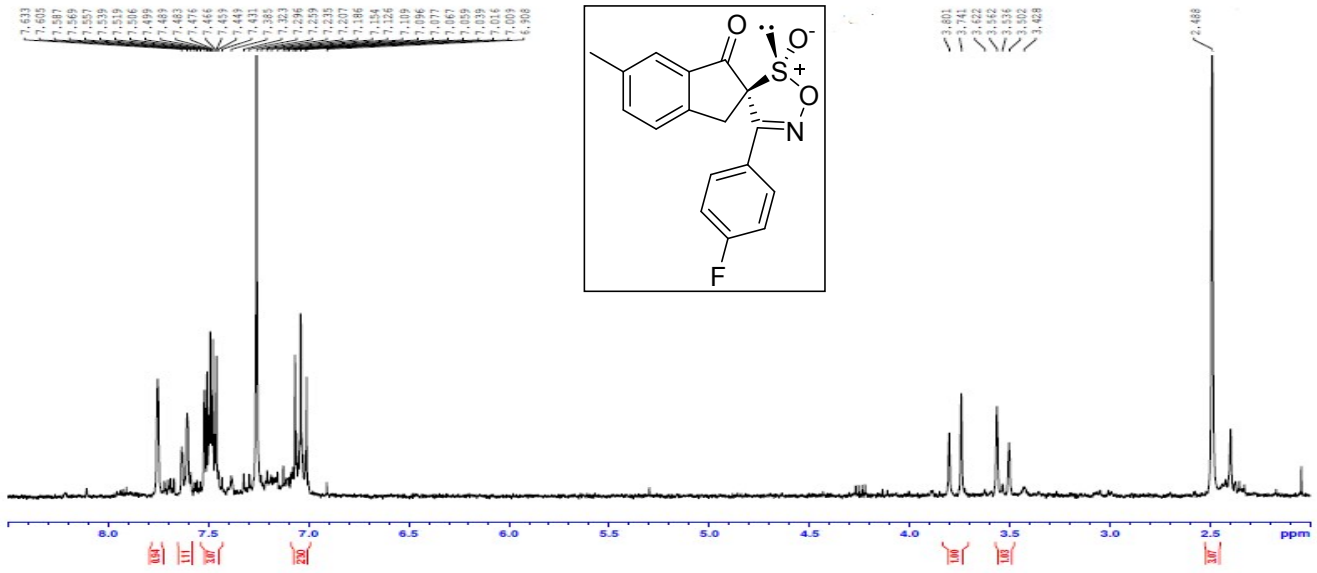


Figure S 42

59.

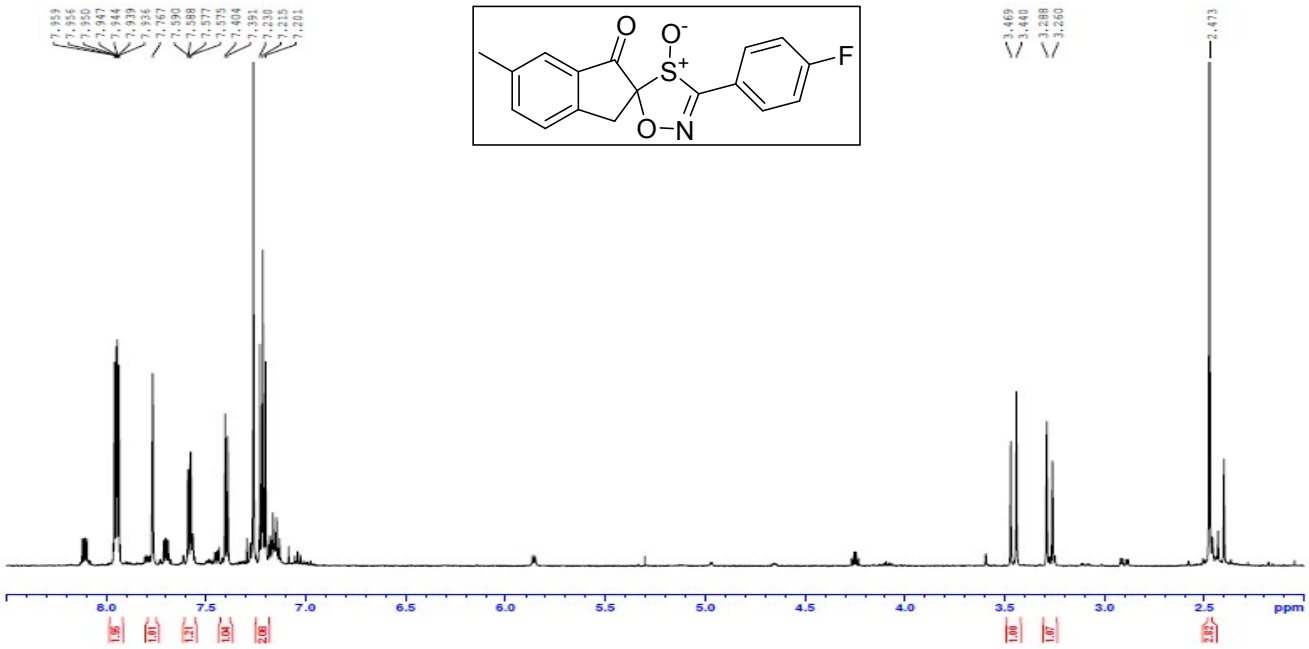


Figure S 43

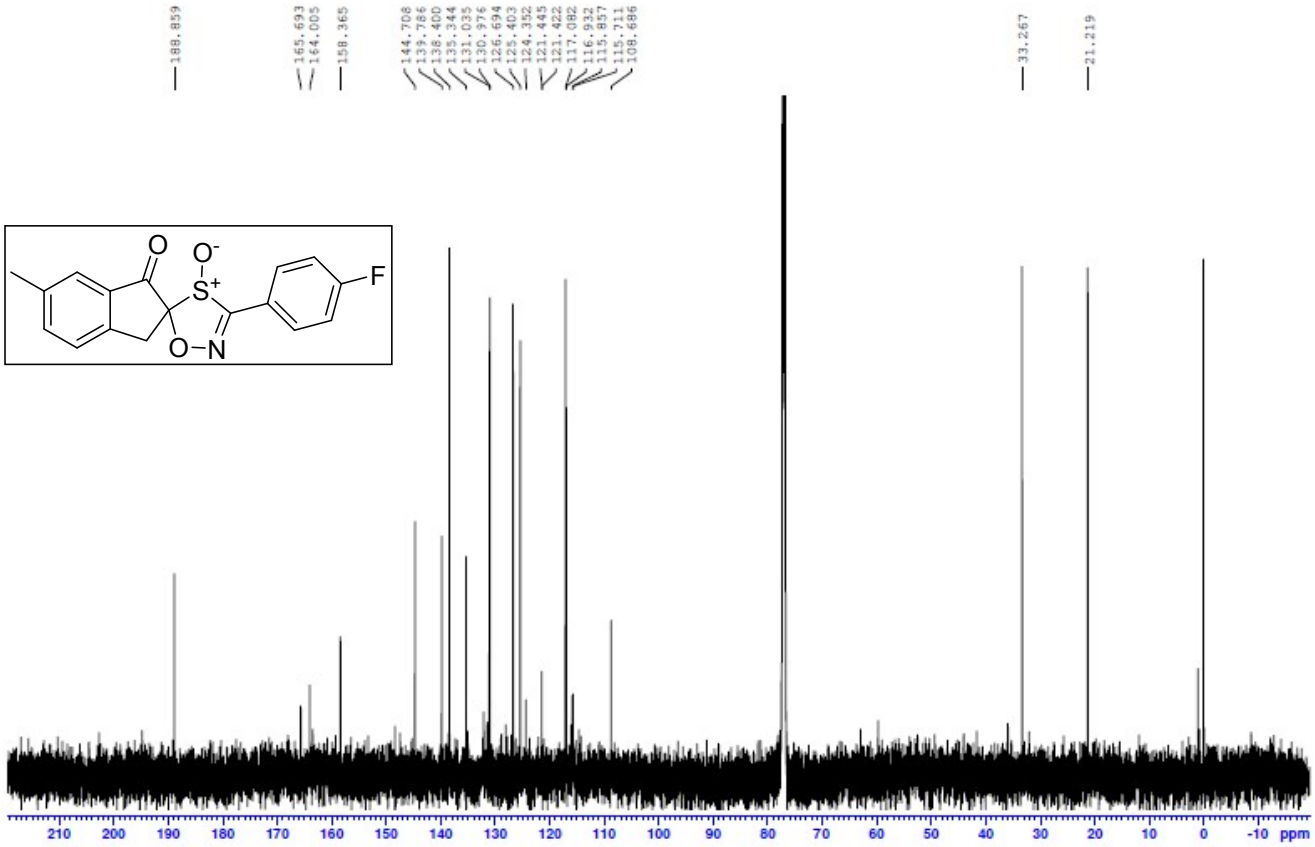


Figure S 44

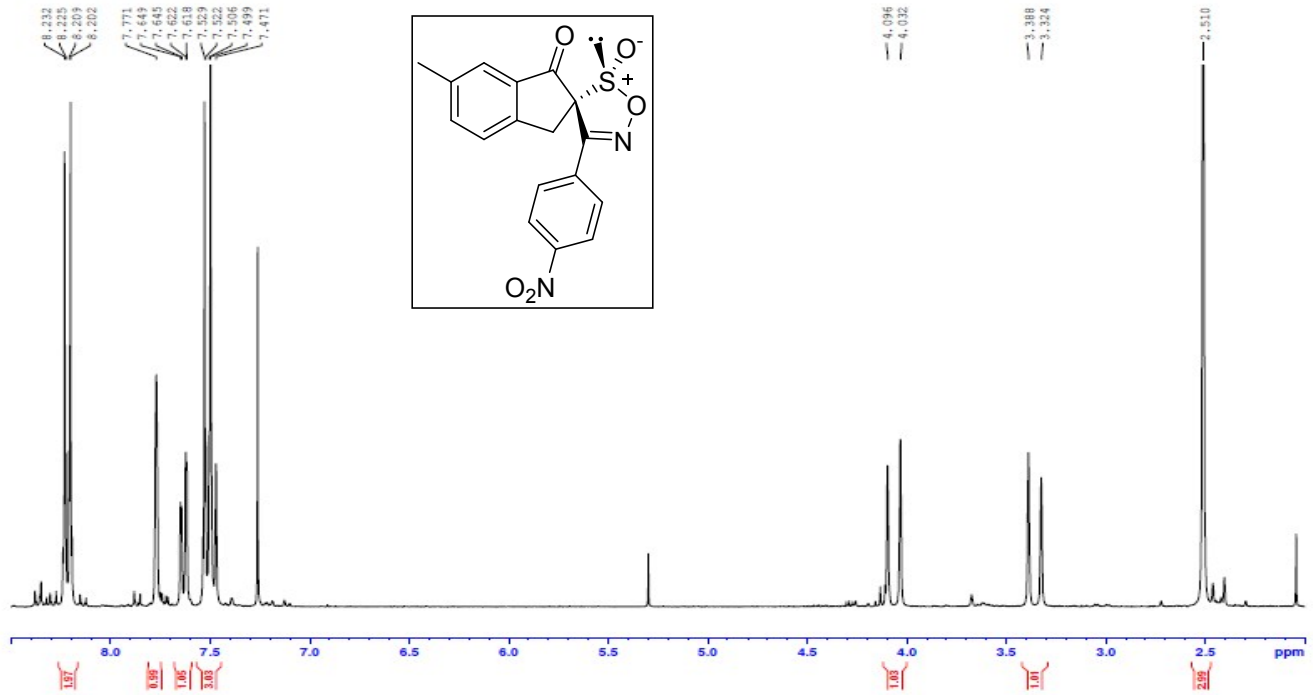


Figure S 45

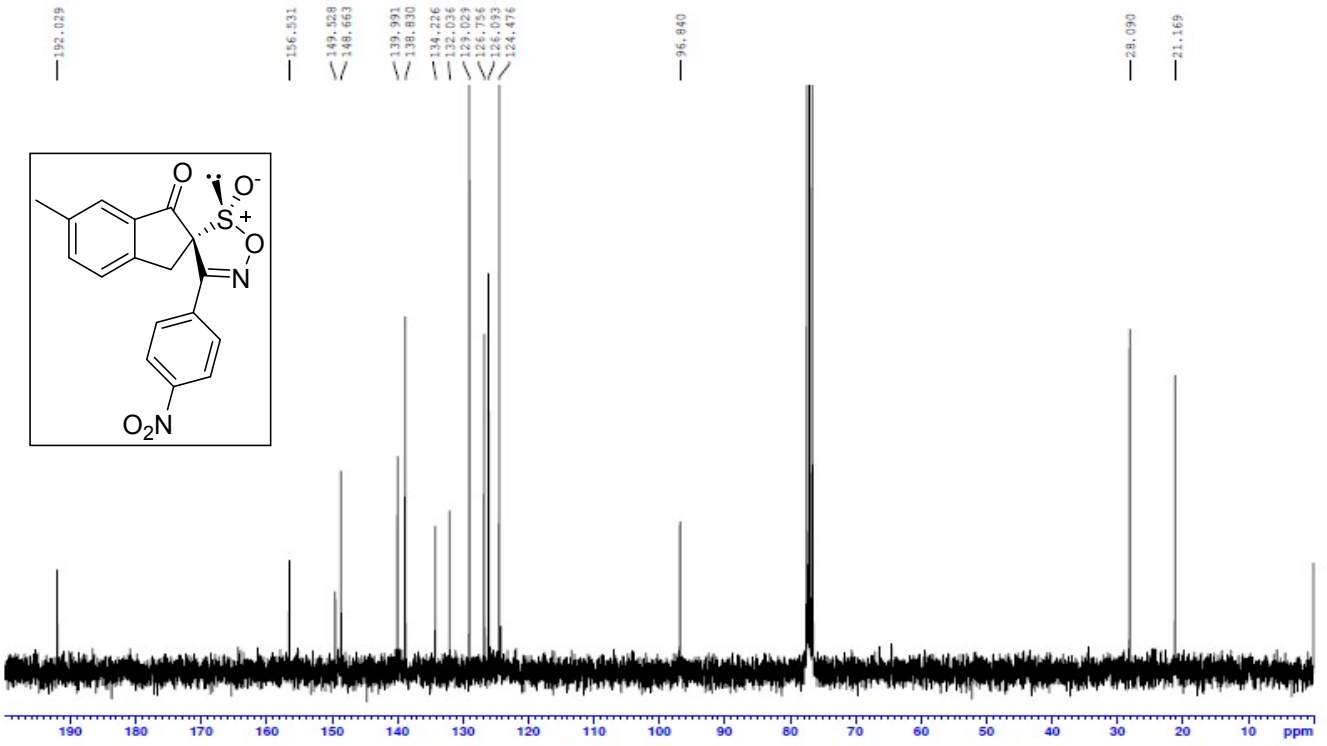


Figure S 46

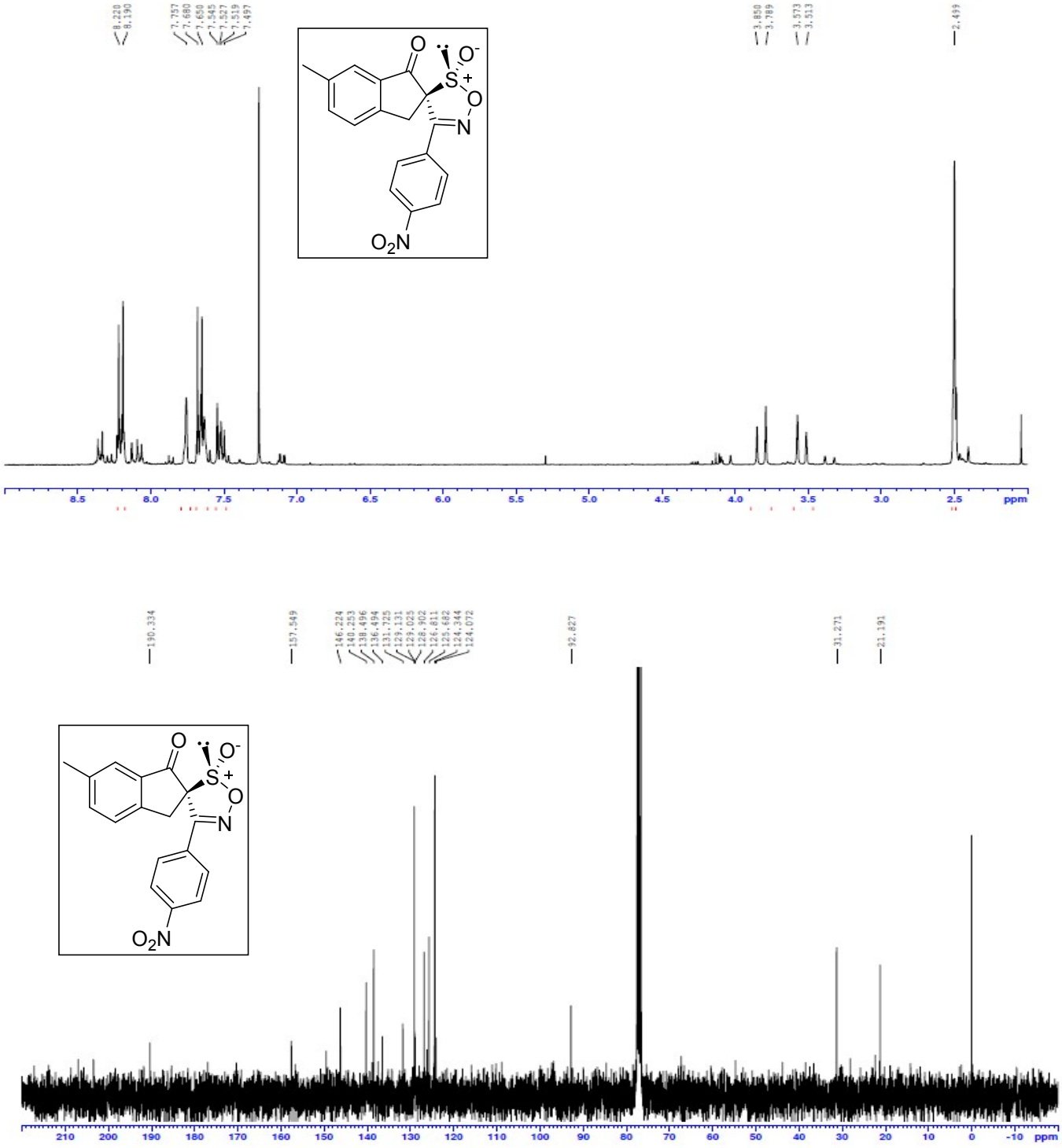

8.220
8.190
7.757
7.680
7.650
7.645
7.527
7.519
7.497
3.850
3.789
3.573
3.513
2.499
O
O-
S+
O
N
O2N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
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157.549
146.224
140.253
138.496
136.494
131.725
129.131
129.025
128.902
126.811
125.682
124.344
124.072
32.827
31.271
21.191
O
O-
S+
O
N
O2N
210
200
190
180
170
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70
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-10
ppm

Figure S 47

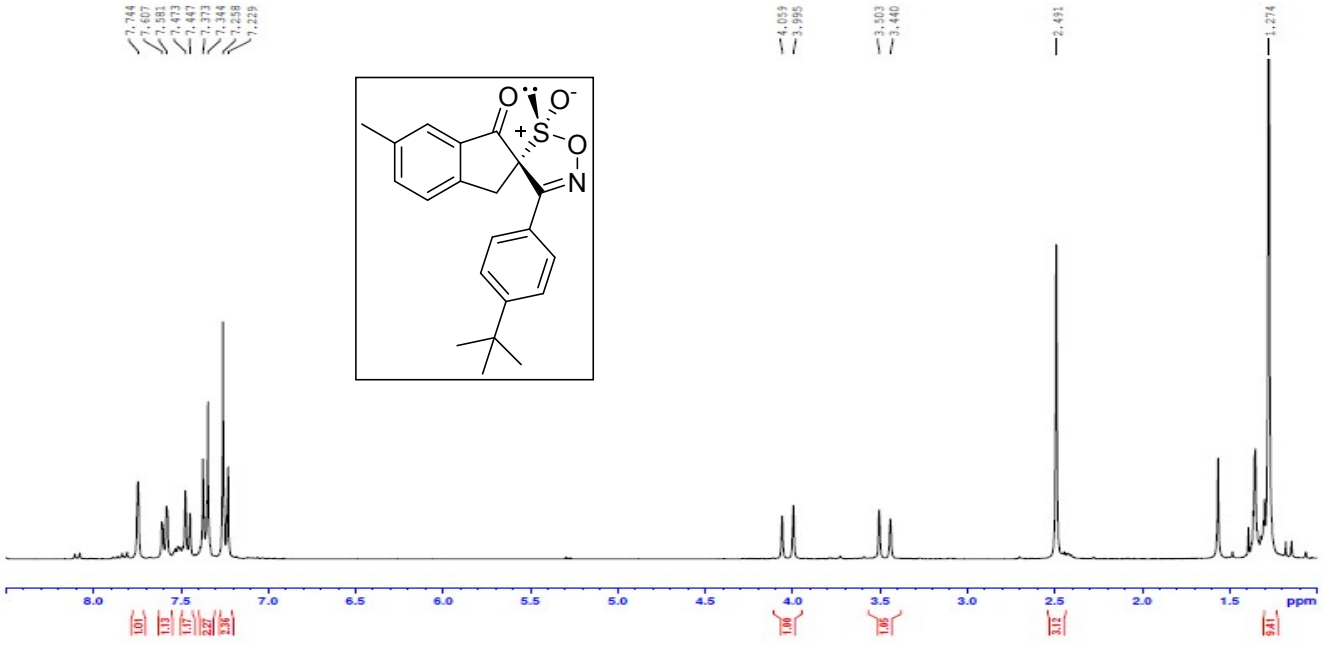


Figure S 48

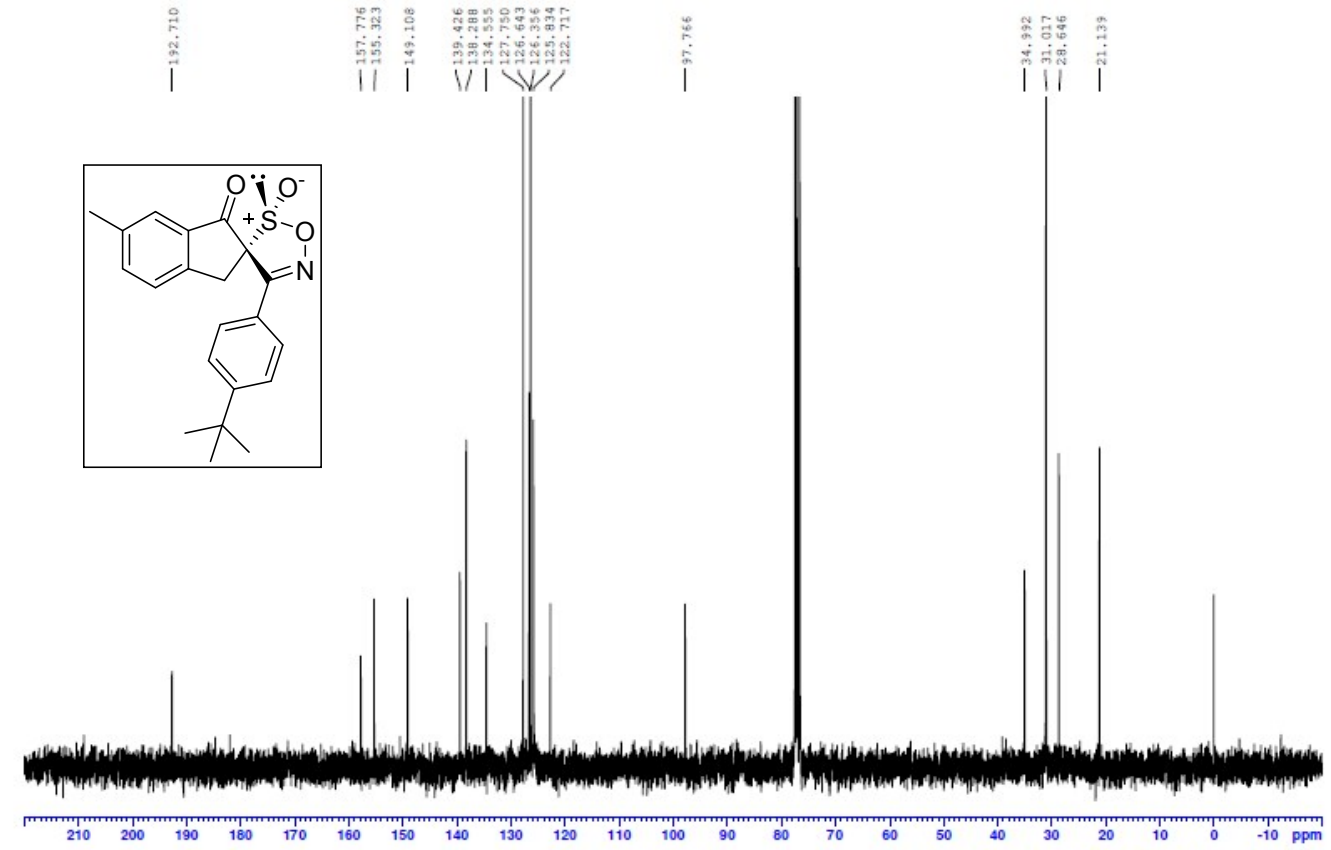


Figure S 49

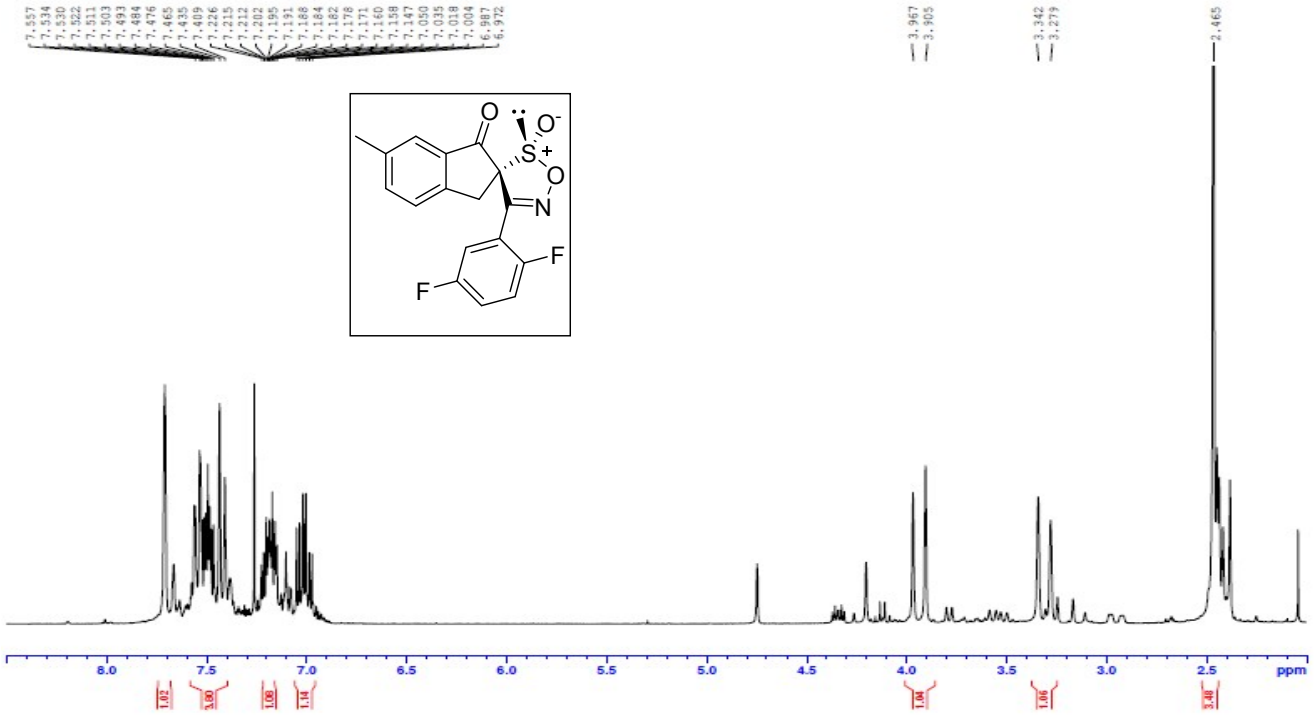


Figure S 50

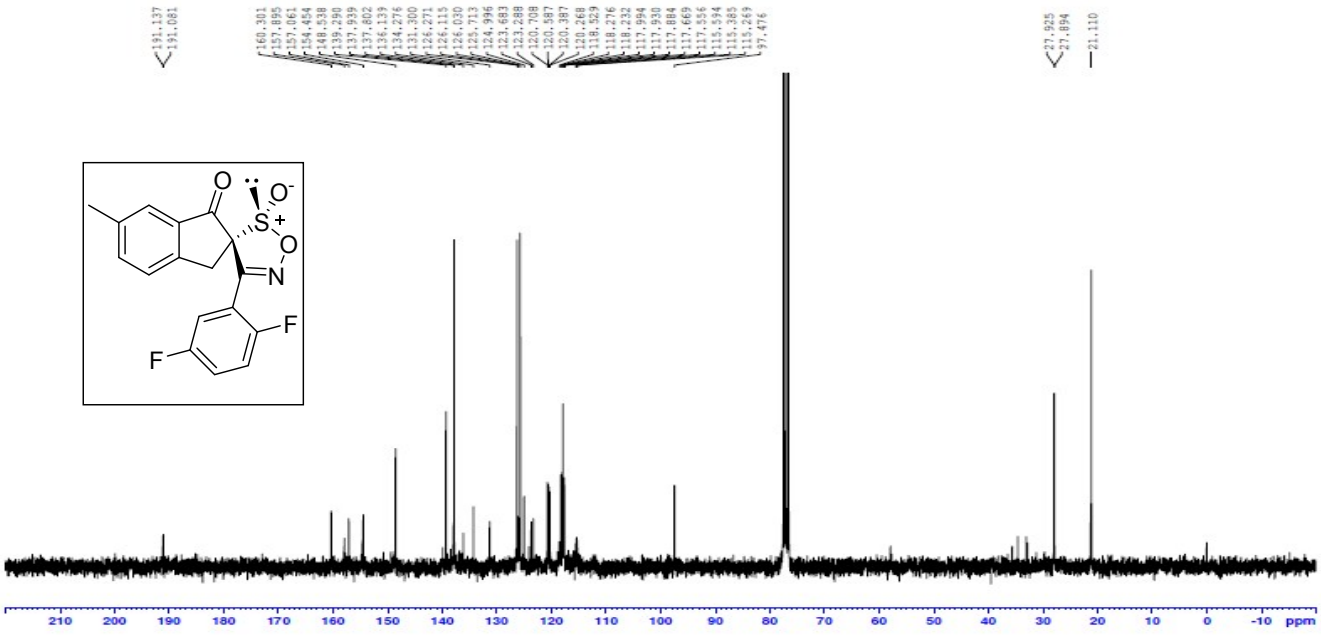


Figure S 51

Interconversion over time of kinetic 1,2,5-oxathiazole-S-oxide to thermodynamic 1,2,5-oxathiazole-*S*-oxide isomers

Example 1

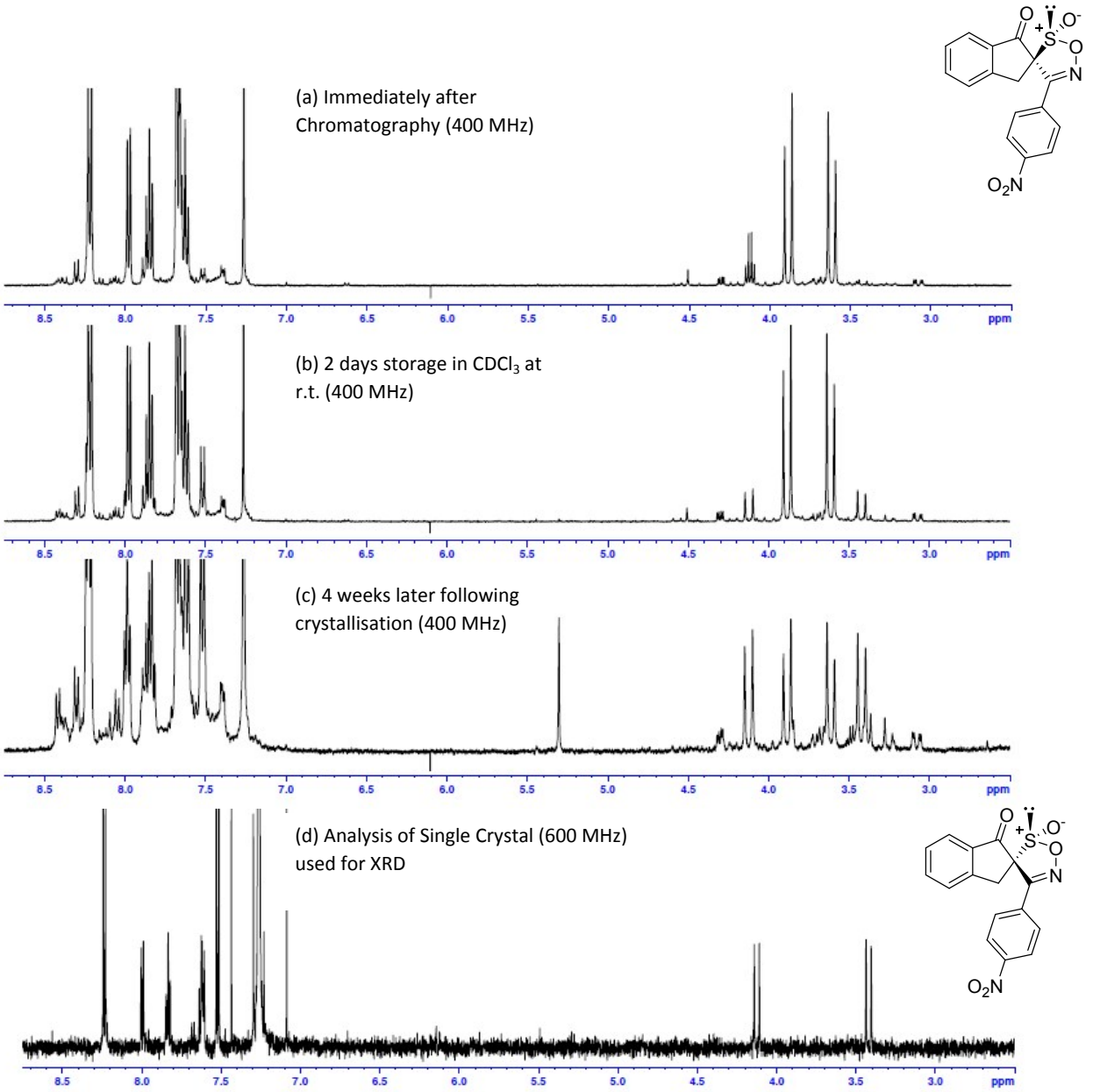


Figure 1: Continual monitoring of the interconversion of the kinetic oxathiazole-S-oxide isomer (top) to the thermodynamic isomer (bottom).

Example 2

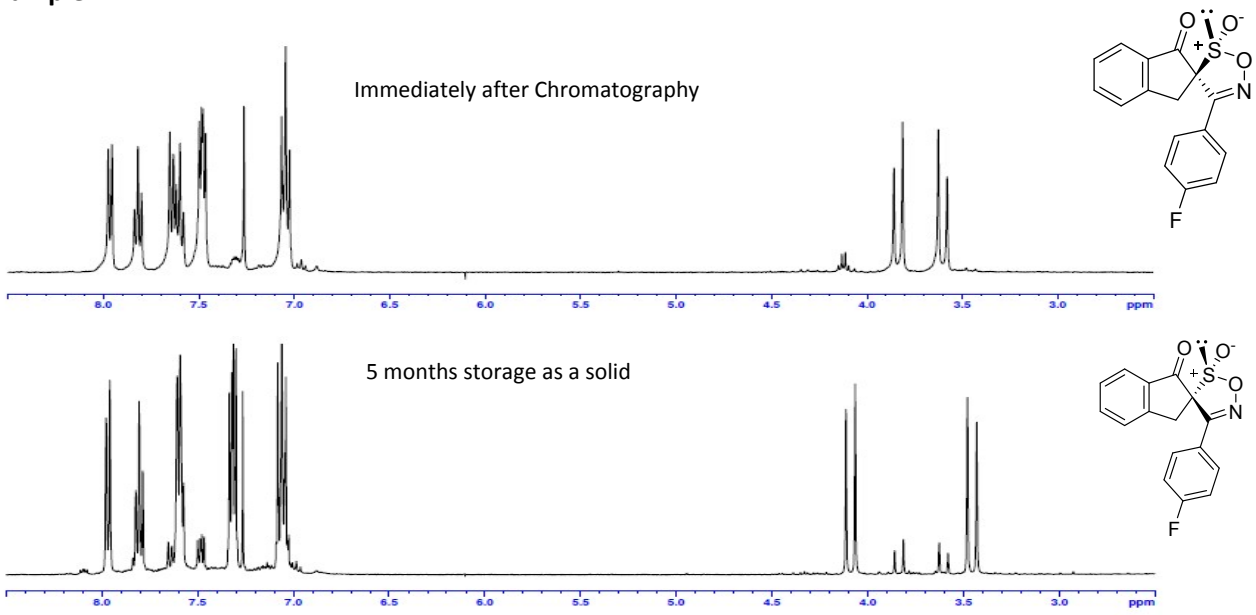


Figure 2: Comparison of the two ^{1}H NMR spectra highlights the conversion of the p-fluoro cycloadducts **32** *to* **31** *following a time lapse of 5 months on storage as a solid.*

Example 3

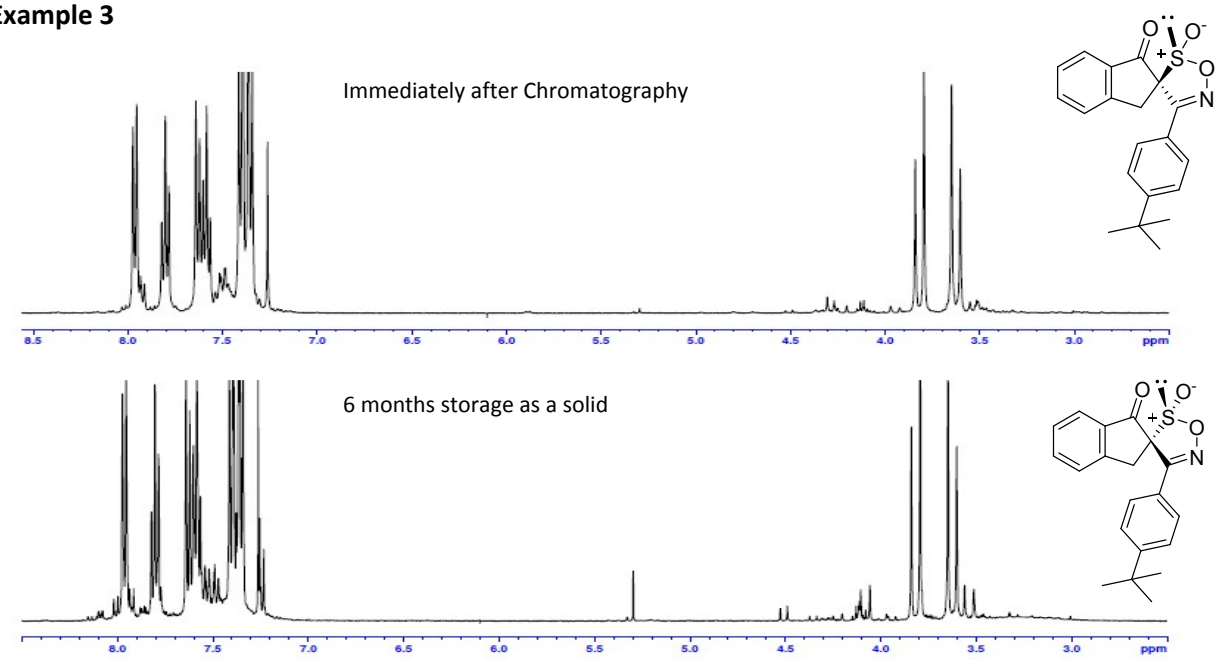


Figure 3: Stacked spectra of the kinetic 1,2,5-oxathiazole-S-oxide **35** *after purification by column chromatography on silica gel (top) with re-analysis of the material after 6 months (bottom), highlighting the slow rate of interconversion to the thermodynamic 1,2,5-oxathiazole-S-oxide* **34**.

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