Supporting Information

Lewis Acid-Assisted Ir(III) Reductive Elimination Enables Construction of Seven-Membered-Ring Sulfoxides

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1. General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at ambient temperature on a Bruker DPX 400 (400 MHz) or a Bruker DPX 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm) and coupling constants (*J*) are quoted in Hertz (Hz). Data are reported as follows: Chemical shift (multiplicity, coupling constants, number of protons). Coupling constants (*J*) were quoted to the nearest 0.1 Hz and multiplicity reported according to the following convention: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Where coincident coupling constants have been observed, the apparent (app) multiplicity of the proton resonance has been reported.

Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at ambient temperature on a Bruker DPX 400 (100 MHz) or a Bruker DPX 600 (151 MHz) spectrometer. Chemical shift (δ) was measured in ppm and quoted to the nearest 0.1 ppm relative to the residual solvent peaks in $CDCl_3$ (77.16 ppm).

Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded at ambient temperature on a Bruker DPX 400 (376 MHz) or a Bruker DPX 600 (565 MHz) spectrometer. Chemical shift (δ) was measured in ppm and quoted to the nearest 0.01 ppm.

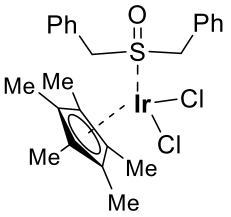
High-resolution mass spectrometry (HRMS) was performed on an Agilent Technologies 6230 TOF LC/MS under the conditions of electrospray ionization (ESI) in a positive mode using CH_2Cl_2 as the solvent.

Reactions were carried out under an atmosphere of air unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by use of UV light (254 nm). Column chromatography was performed using GENERAL-REAGENT silica gel (200-300 mesh). Unless otherwise specified, all reagents were purchased from commercial suppliers and directly used without further purification.

2. Stoichiometric Reactions between Ir(III) Salts and Dibenzyl Sulfoxide

2.1 Coordination of Ir(III) Salts and Dibenzyl Sulfoxide

The synthesis was adapted from the reported literatures.[1, 2] Under air atmosphere, to an NMR tube was added [Cp*IrCl$_2$]$_2$ (19.9 mg, 0.025 mmol), dibenzyl sulfoxide (**1a**; 11.6 mg, 0.05 mmol) and CDCl$_3$ solvent (0.5 mL), the mixture was shakend for 5 min to be a clarified solution, and then standing at rt for 1 h for NMR analysis. A complex: Cp*IrCl$_2$(BnS(O)Bn) formed quantitatively.



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 (s, 10H), 4.90 (br, 2H), 4.16 (d, *J* = 13.4 Hz, 2H), 4.15 (s, 15H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 132.1, 129.2, 128.7, 128.6, 93.9, 56.1, 8.6.

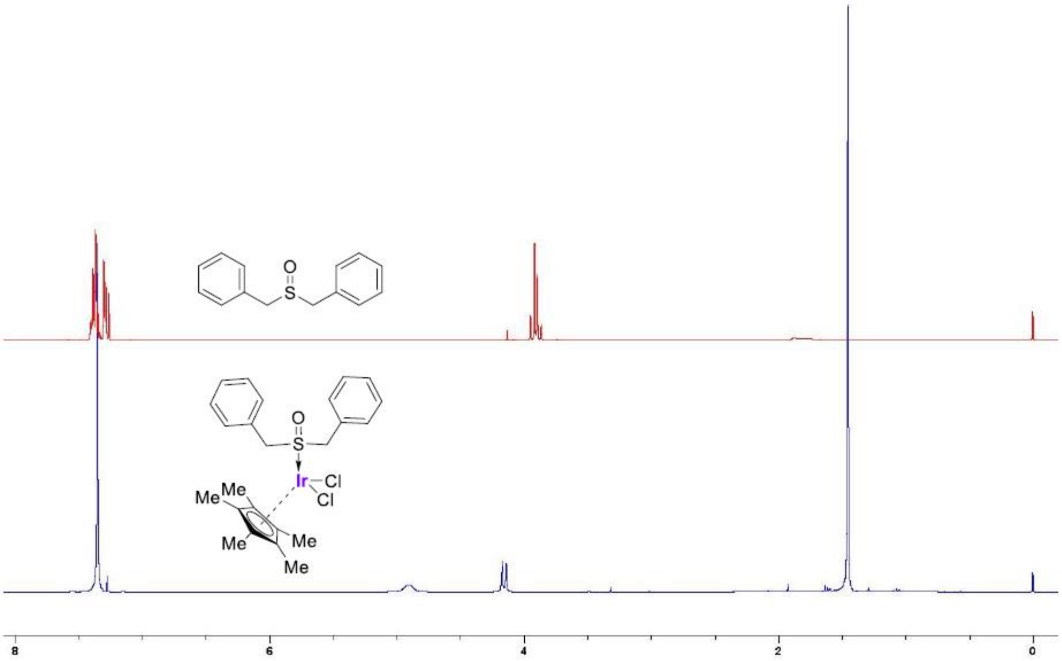


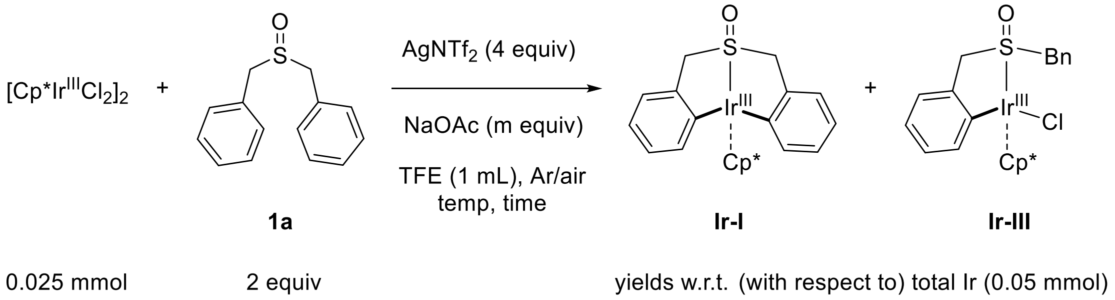
Figure S1. Comparison between the ^{1}H NMR spectra of dibenzyl sulfoxide and its complex with Cp*IrCl$_2$.

2.2 Procedures for the Synthesis of Ir(III) Sulfoxide Metallacycle

Under Ar: To an 8 mL glass vial was added a stirrer, [Cp*IrCl$_2$]$_2$ (19.9 mg, 0.025 mmol), dibenzyl sulfoxide (**1a**; 11.6 mg, 0.05 mmol) and NaOAc (41.0 mg, 0.50 mmol). The vial was then transferred into a glovebox. AgNTf$_2$ (38.8 mg, 0.10 mmol) was added to the vial, followed by the addition of solvent (1 mL). The vial was then capped to be sealed, taken out of the glovebox and placed into a pre-heated aluminium block. After the reaction, the mixture was diluted with CH_2Cl_2 and filtered through a short plug of silica gel eluting with EtOAc. The filtrate was concentrated under reduced pressure, and the residue was taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. Sometimes the residue was further purified by column chromatography eluting with a solvent mixture of Petroleum Ether/EtOAc 6/1 (v/v).

Under Air: Inside a glovebox, to an 8 mL glass vial was added AgNTf$_2$ (38.8 mg, 0.10 mmol). The vial was then taken out of the glovebox. To the vial was added a stirrer, [Cp*IrCl$_2$]$_2$ (19.9 mg, 0.025 mmol), dibenzyl sulfoxide (**1a**; 11.6 mg, 0.05 mmol), NaOAc (20 equiv; 41.0 mg, 0.50 mmol) and a solvent (1 mL). The vial was then placed into a pre-heated aluminium block. After the reaction, the mixture was diluted with CH_2Cl_2 and filtered through a short plug of silica gel eluting with EtOAc. The filtrate was concentrated under reduced pressure, and the residue was taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard.

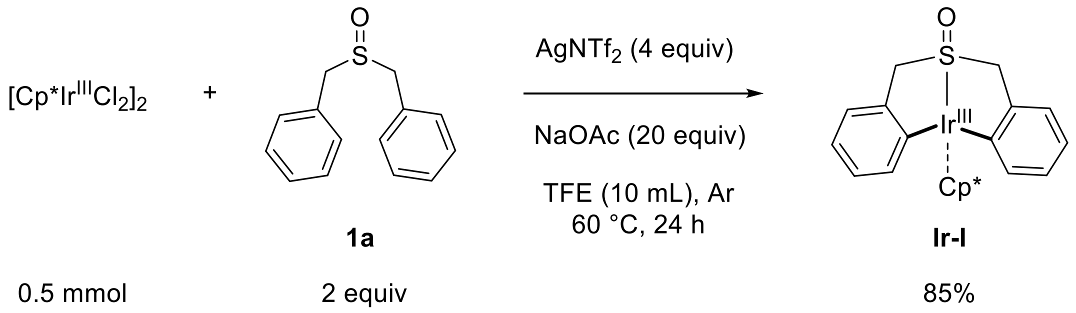
Table S1. Stoichiometric Reactions between [Cp*IrCl$_2$]$_2$ and Dibenzyl Sulfoxide



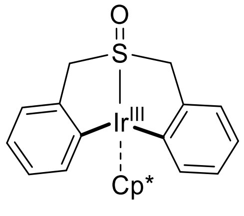
entry	air/Ar	m equiv	temp/°C	time/h	**Ir-I** yield/%[a]	**Ir-III** yield/%[a]
1	Ar	8	r.t.	24	9	0
2	Ar	8	r.t.	84	19	5
3	air	8	r.t.	84	16	5
4	Ar	8	40	12	26	9
5	Ar	8	50	12	57	14
6	Ar	8	60	12	66	13
7	Ar	8	60	24	85	13
8	**Ar**	**20**	**60**	**24**	**80 (72)[d]**	**3**
9	Ar	8	70	12	76	10
10	Ar	8	80	7	71	8
11	Ar	8	80	24	64	10
12	Ar	8	90	12	60	8
13[b]	air	4	80	14	15	10
14[b,c]	air	8	80	12	46	8
15[b]	Ar	20	60	24	31	5
16[b]	air	20	60	24	47	trace
17[b]	Ar	20	r.t.	24	6	8

[a]NMR yield; [b]DCE as the solvent; [c]8 equiv **1a**; [d]Isolated yield in parentheses.

2.3 Scale-up Reaction for the Synthesis of Ir-I Metallacycle



To a 30-mL glass vial was added a stirrer, [Cp*IrCl$_2$]$_2$ (398.3 mg, 0.50 mmol), dibenzyl sulfoxide (**1a**; 230.3 mg, 1.0 mmol) and NaOAc (20 equiv; 820.3 mg, 10 mmol). The vial was then transferred into a glovebox. AgNTf$_2$ (4 equiv; 776.0 mg, 2.0 mmol) was added to the vial, followed by the addition of TFE solvent (10 mL). The vial was then capped to be sealed, taken out of the glovebox and placed into a pre-heated aluminium block at 60 °C for 24 h. After the reaction, the mixture was diluted with CH$_2$Cl$_2$ and filtered through a pad of celite, evaporated to dryness. The residue was purified by column chromatography eluting with a solvent mixture of Petroleum Ether/EtOAc 6/1 (v/v) to afford the desired product: **Ir-I** (474.5 mg, 0.85 mmol) as a yellow solid in 85% isolated yield.



Ir-I

R$_f$ = 0.40 (Petroleum Ether/EtOAc = 5/1).

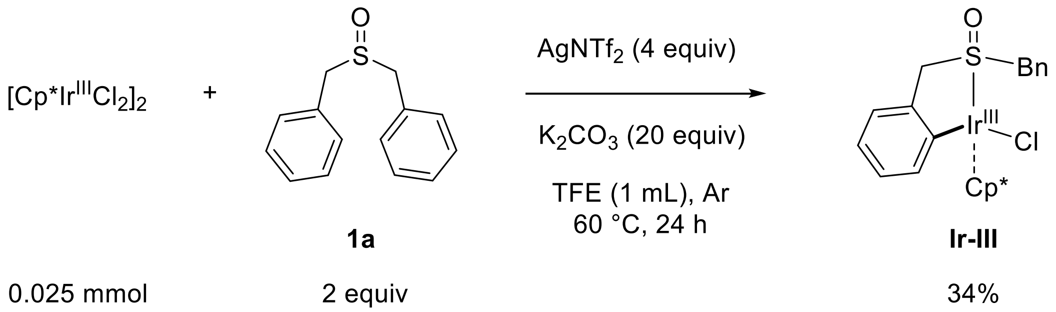
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.07 (d, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 7.3 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 2H), 4.67 and 4.58 (ABq system, *J* = 15.7 Hz, 4H), 1.86 (s, 15H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 147.6, 140.3, 136.7, 127.0, 121.9, 120.3, 96.1, 74.5, 8.7.

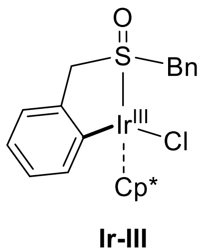
HRMS (ESI, m/z) found [M+H]$^+$ 557.1486, C$_{24}$H$_{28}$IrOS$^+$ requires 557.1485.

The crystal structure is shown in the X-ray Crystallographic Data section.

2.4 Synthesis of Ir-III Metallacycle



To an 8 mL glass vial was added a stirrer, $[Cp^*IrCl_2]_2$ (19.9 mg, 0.025 mmol), dibenzyl sulfoxide (**1a**; 11.6 mg, 0.05 mmol) and K_2CO_3 (20 equiv; 69.1 mg, 0.50 mmol). The vial was then transferred into a glovebox. $AgNTf_2$ (38.8 mg, 0.10 mmol) was added to the vial, followed by the addition of TFE solvent (1 mL). The vial was then capped to be sealed, taken out of the glovebox and placed into a pre-heated aluminium block at 60 °C for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2 and filtered through a plug of celite, evaporated to dryness. The residue was purified by preparative TLC to afford **Ir-III** (10.0 mg, 0.017 mmol) in 34% yield as a yellow solid.



Ir-III

R_f = 0.40 (Petroleum Ether/EtOAc = 5/1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.36 (m, 3H), 7.34 (d, J = 7.5 Hz, 1H), 7.23 (dd, J = 6.6, 3.0 Hz, 2H), 7.14 (d, J = 7.4 Hz, 1H), 7.11–7.07 (m, 1H), 6.97 (t, J = 7.4 Hz, 1H), 4.56 (dd, J = 14.5, 2.2 Hz, 1H), 4.52 (d, J = 14.6 Hz, 1H), 4.06 (d, J = 14.5 Hz, 1H), 3.99 (d, J = 14.6 Hz, 1H), 1.77 (s, 15H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 138.4, 138.0, 131.6, 129.3, 128.7, 128.7, 128.2, 123.9, 121.5, 95.5, 68.0, 56.4, 8.8.

HRMS (ESI, m/z) found $[M–Cl]^+$ 557.1464, $C_{24}H_{28}IrOS^+$ requires 557.1485.

The crystal structure is shown in the X-ray Crystallographic Data section.

3. Stoichiometric Reactions between Ir-I Metallacycle with Oxidants and Lewis Acids

3.1 Experimental Procedures

Without any oxidant at 90 °C under Ar (Scheme 3, entry 1). Inside a glovebox, to an 8 mL glass vial was added a stirrer, **Ir-I** (0.05 mmol, 27.8 mg) and TFE solvent (0.5 mL). The vial was then capped to be sealed, taken out of the glovebox and placed into a pre-heated aluminium block at 90 °C for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2, and passed through a short pipet column on silica gel eluting with EtOAc. It was evaporated to dryness, and taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. **Ir-I** was recovered quantitatively.

With air as an oxidant (Scheme 3, entries 2-4). Under air atmosphere, to an 8 mL glass vial was added a stirrer, **Ir-I** (0.05 mmol, 27.8 mg) and TFE solvent (0.5 mL). The vial was then capped to be sealed and placed into a pre-heated aluminium block at a specified temperature for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2, and passed through a short pipet column on silica gel eluting with EtOAc. It was evaporated to dryness, and taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard.

At 90 °C for 24 h, **Ir-I** was recovered in 57% yield, together with 26% yield of **2a (Scheme 3, entry 2)**.

At 60 °C for 24 h, **Ir-I** was recovered in 74% yield, together with 8% yield of **2a (Scheme 3, entry 3)**.

At rt for 24 h, **Ir-I** was recovered in 96% yield, together with trace yield of **2a (Scheme 3, entry 4)**.

With 1.2 equiv oxidant under Ar (Scheme 3, entries 5-13). Inside a glovebox, to an 8 mL glass vial was added a stirrer, **Ir-I** (0.05 mmol, 27.8 mg), an oxidant (1.2 equiv; 0.06 mmol) and TFE solvent (0.5 mL). The vial was then capped to be sealed, taken out of the glovebox and placed into an aluminium block at rt for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2, (20 μL NEt_3 was added for entries 13 and 14) and passed through a short pipet column on silica gel eluting with EtOAc. It was evaporated to dryness, and taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard.

With 1.2 equiv AgOAc (10.0 mg, 0.06 mmol), **Ir-I** was recovered in 94% yield, together with trace yield of **2a (Scheme 3, entry 5)**.

With 1.2 equiv $Cu(OAc)_2$ (10.9 mg, 0.06 mmol), **Ir-I** was recovered quantitatively **(Scheme 3, entry 6)**.

With 1.2 equiv $PhI(OAc)_2$ (19.3 mg, 0.06 mmol), **Ir-I** was recovered in 54% yield, together with 13% yield of **2a (Scheme 3, entry 7)**.

With 1.2 equiv CAN (ceric ammonium nitrate; 32.9 mg, 0.06 mmol), **Ir-I** was recovered in 85% yield, together with trace yield of **2a (Scheme 3, entry 8)**.

With 1.2 equiv $Ce(SO_4)_2$ (19.9 mg, 0.06 mmol), **Ir-I** was recovered quantitatively, together with trace yield of **2a (Scheme 3, entry 9)**.

With 1.2 equiv V_2O_5 (10.9 mg, 0.06 mmol), **Ir-I** was recovered quantitatively **(Scheme 3, entry 10)**.

With 1.2 equiv Oxone (36.9 mg, 0.06 mmol), **Ir-I** was recovered in 76% yield, together with 11% yield of **2a (Scheme 3, entry 11)**.

With 1.2 equiv MnO_2 (5.2 mg, 0.06 mmol), **Ir-I** was recovered quantitatively, together with trace yield of **2a (Scheme 3, entry 12)**.

With 1.2 equiv $Mn(OAc)_3{\cdot}2H_2O$ (16.1 mg, 0.06 mmol), **Ir-I** was recovered in 52% yield, together with 37% yield of **2a (Scheme 3, entry 13)**.

With 0.2 equiv oxidant of $Mn(OAc)_3{\cdot}2H_2O$ under air (Scheme 3, entries 14-18): Under air atmosphere, to an 8 mL glass vial was added a stirrer, **Ir-I** (0.05 mmol, 27.8 mg), $Mn(OAc)_3{\cdot}2H_2O$ (0.2 equiv; 2.7 mg, 0.01 mmol), additive (0.2/0.4 equiv) and TFE solvent (0.5 mL). The vial was then capped to be sealed and placed into an aluminium block at rt for 24 h. After the reaction, the mixture was diluted by CH_2Cl_2 with the addition of 20 μL NEt_3 and passed through a short pipet column on silica gel eluting with EtOAc. It was evaporated to dryness, and taken for NMR analysis with

1,1,2,2-tetrachloroethane as the internal standard.

Without any additive, **Ir-I** was recovered in 63% yield, together with 22% yield of **2a (Scheme 3, entry 14)**.

With 0.2 equiv $Mg(NTf_2)_2$ (5.8 mg, 0.01 mmol) additive, **Ir-I** was recovered in 18% yield, together with 68% yield of **2a (Scheme 3, entry 15)**.

With 0.2 equiv $Mg(ClO_4)_2$ (2.2 mg, 0.01 mmol) additive, **Ir-I** was recovered in 24% yield, together with 56% yield of **2a (Scheme 3, entry 16)**.

With 0.4 equiv $AgNTf_2$ (7.8 mg, 0.02 mmol) additive, **Ir-I** was recovered in 32% yield, together with 43% yield of **2a (Scheme 3, entry 17)**.

With 0.2 equiv AgTFA (2.2 mg, 0.01 mmol) additive, **Ir-I** was recovered in 50% yield, together with 40% yield of **2a (Scheme 3, entry 18)**.

With 0.2 equiv $Mg(NTf_2)_2$ under air (Scheme 3, entry 19). Under air atmosphere, to an 8 mL glass vial was added a stirrer, **Ir-I** (0.05 mmol, 27.8 mg), $Mg(NTf_2)_2$ (5.8 mg, 0.01 mmol) and TFE solvent (0.5 mL). The vial was then capped to be sealed and placed into an aluminium block at rt for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2, and passed through a short pipet column on silica gel eluting with EtOAc. It was evaporated to dryness, and taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. **Ir-I** was recovered in 73% yield, together with 14% yield of **2a**.

3.2 Investigations on the Lewis Acid Effects

Ir-I with $Mg(NTf_2)_2$

Inside a glovebox, to an NMR tube was added **Ir-I** (0.05 mmol, 27.8 mg), $Mg(NTf_2)_2$ (29.1 mg, 0.05 mmol) and $CDCl_3$ solvent (0.5 mL). The NMR tube was then capped. The mixture was shakend for 1 min, and then taken out of the glovebox for NMR analysis. ^1H NMR spectra show a significant down-field chemical shift of the benzylic protons of **Ir-I**, which indicates the coordination of $Mg(NTf_2)_2$ with **Ir-I,** thus supporting the function of $Mg(NTf_2)_2$ as a Lewis acid.

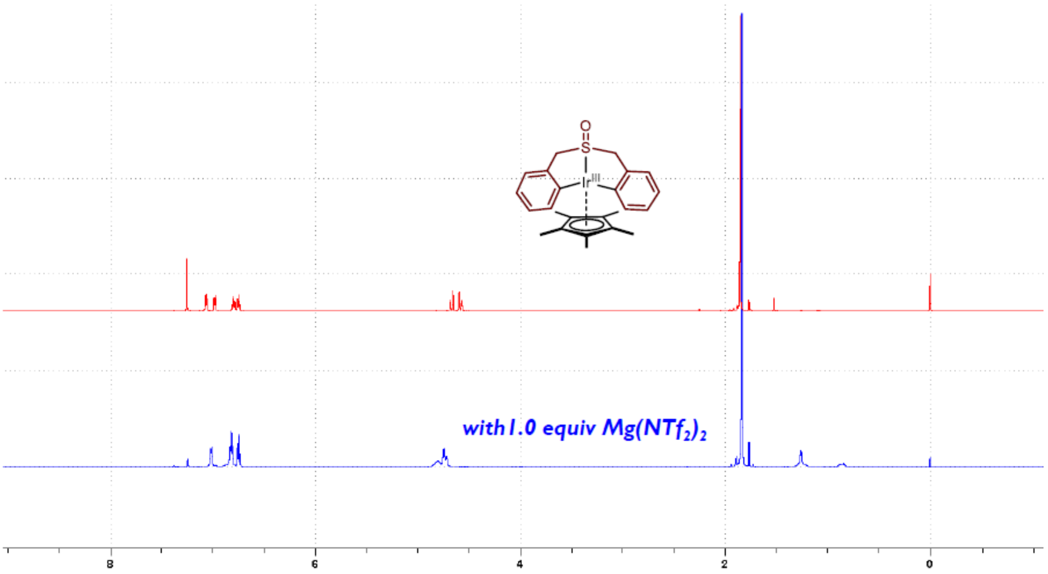


Figure S2. Comparison between the ^{1}H NMR spectra of **Ir-I** with or without $Mg(NTf_2)_2$ additive.

Ir-I with AgTFA

Inside a glovebox, to an NMR tube was added **Ir-I** (0.05 mmol, 27.8 mg), AgTFA (13.3 mg, 0.06 mmol) and $CDCl_3$ solvent (0.5 mL). The NMR tube was then capped. The mixture was shakend for 1 min, and then taken out of the glovebox, standing at rt for 6 d for NMR analysis. ^{1}H NMR spectra show a significant down-field chemical shift of the benzylic protons of **Ir-I**, which indicates the coordination of AgTFA with **Ir-I**. Furthrmore, a single crystal suitable for X-ray diffraction characterization was obtained by the vapor diffusion method with chloroform solvent and hexane precipitant. These results strongly support the function of AgTFA as a Lewis acid.

For the details of the X-ray crystallographic data, please refer to the corresponding X-ray Crystallographic Data section.

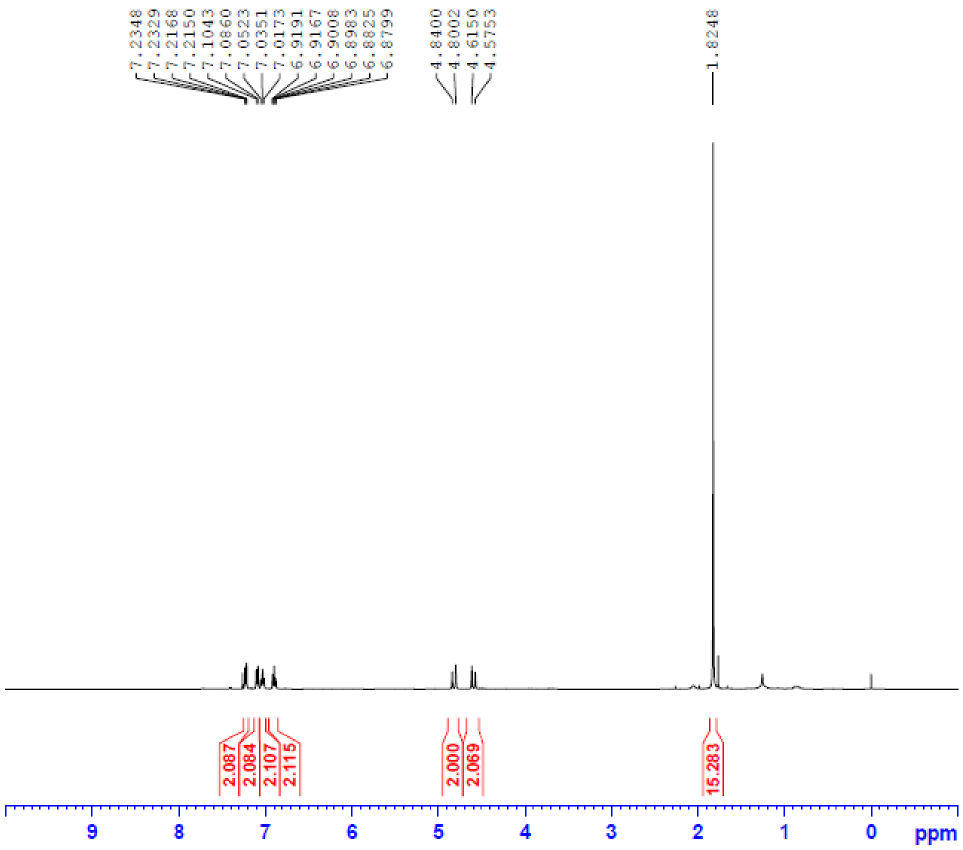


Figure S3. ^{1}H NMR spectrum of **Ir-I** with AgTFA additive at rt for 6 d.

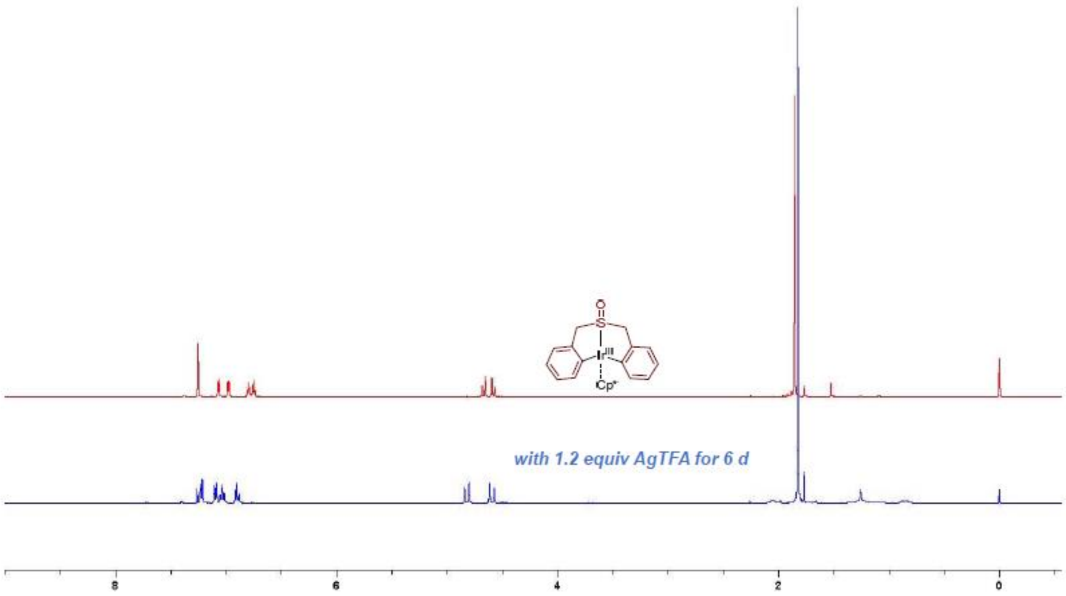


Figure S4. Comparison between the ^{1}H NMR spectra of **Ir-I** with or without AgTFA additive.

Ir-I with $AgNTf_2$

Inside a glovebox, to an NMR tube was added **Ir-I** (0.05 mmol, 27.8 mg), $AgNTf_2$ (23.3 mg, 0.06 mmol) and $CDCl_3$ solvent (0.5 mL). The NMR tube was then capped. The mixture was shakend for 1 min, and then taken out of the glovebox, standing at rt for 24 h for NMR analysis. ^1H NMR spectra show a significant down-field chemical shift of the benzylic protons of **Ir-I**, which indicates the coordination of $AgNTf_2$ with **Ir-I,** thus supporting the function of $AgNTf_2$ as a Lewis acid.

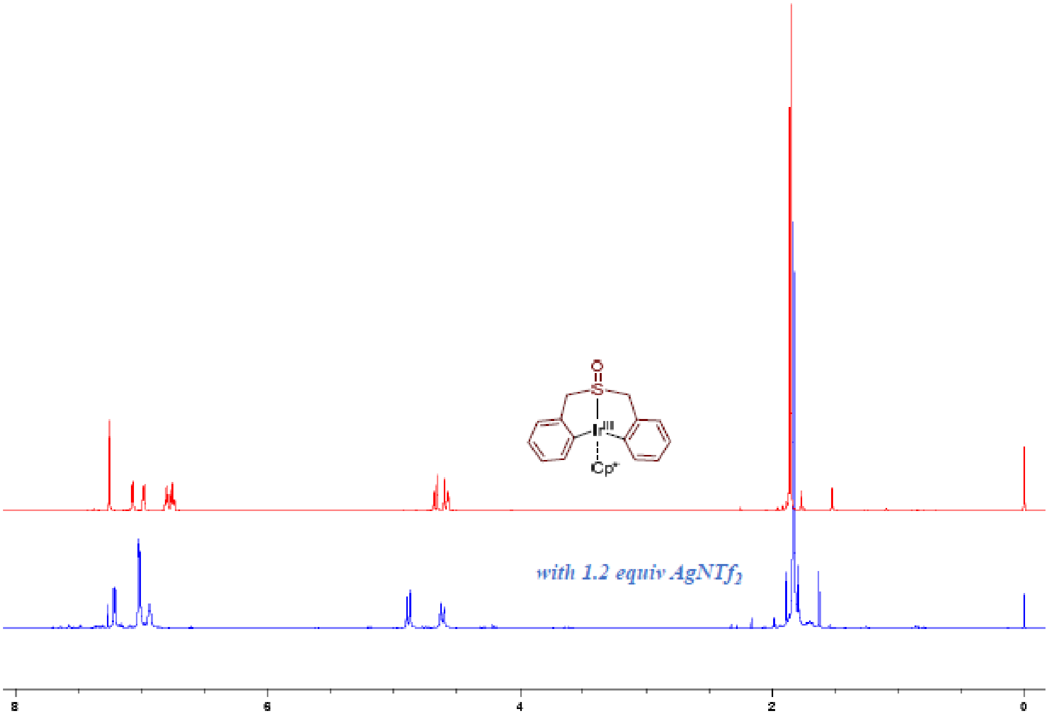


Figure S5. Comparison between the ^1H NMR spectra of **Ir-I** with or without $AgNTf_2$ additive.

4. Development of Catalytic Reactions

Experimental Procedures for Scheme 7

With 10 mol% Ir-I catalyst, 20 mol% $Mn(OAc)_3·2H_2O$ (Scheme 7, entries 1-4). Under air atmosphere, to an 8 mL glass vial was added **Ir-I** (5.6 mg, 0.01 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol), dibenzyl sulfoxide (23.0 mg, 0.10 mmol), without or with additive (0.02 mmol, 20 mol%) and TFE solvent (0.5 mL). The vial was capped under air and placed into a pre-heated aluminum block at 90 °C for 24 h. After the reaction, the mixture was diluted by CH_2Cl_2 with the addition 20 μL NEt_3 and passed through a short pipet column on silica gel eluting with EtOAc. The filtrate was evaporated to dryness. The residue was taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard.

Without any additive, **2a** was obtained in 38% yield **(Scheme 7, entry 1)**.

With 20 mol% $Mg(NTf_2)_2$ (11.7 mg, 0.02 mmol), **2a** was obtained in quantitative yield **(Scheme 7, entry 2)**.

With 20 mol% $Mg(ClO_4)_2$ (4.5 mg, 0.02 mmol), **2a** was obtained in quantitative yield **(Scheme 7, entry 3)**.

With 20 mol% $AgNTf_2$ (7.8 mg, 0.02mmol), **2a** was obtained in quantitative yield **(Scheme 7, entry 4)**.

With 5 mol% $[Cp^*IrCl_2]_2$ under air (Scheme 7, entry 5). Under air atmosphere, to an 8 mL glass vial was added a stirrer, $[Cp^*IrCl_2]$ (4.0 mg, 0.005 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), dibenzyl sulfoxide (**1a**; 23.0 mg, 0.10 mmol) and TFE solvent (0.5 mL). The vial was capped under air and placed into a pre-heated aluminum block at 90 °C for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2 and filtered through a plug of celite and evaporated to dryness. The residue was taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. **2a** was obtained in <5% yield, together with quantitative recovery of **1a**.

With $Mn(OAc)_3·2H_2O$ (Scheme 7, entries 6-8). Under air atmosphere, to an 8 mL glass vial was added a catalyst, 5 mol% or 20 mol% $Mn(OAc)_3·2H_2O$, dibenzyl sulfoxide (23.0 mg, 0.10 mmol), without or with $AgNTf_2$ additive and TFE solvent (0.5 mL). The vial was capped under air and placed into a pre-heated aluminum block at 90 °C for 24 h. After the reaction, the mixture was diluted by CH_2Cl_2 with the addition of 20 μL NEt_3 and passed through a short pipet column on silica gel eluting with EtOAc. The filtrate was evaporated to dryness. The residue was taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard.

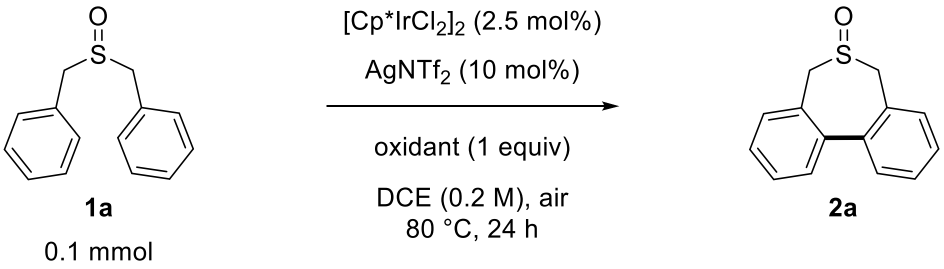
With 5 mol% $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), 20 mol% $AgNTf_2$ (7.8 mg, 0.020 mmol) and 20 mol% $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol), **2a** was obtained in 93% yield **(Scheme 7, entry 6)**.

With 1 mol% $[Cp^*IrCl_2]$ (1.6 mg, 0.002 mmol), 4 mol% $AgNTf_2$ (3.1 mg, 0.008 mmol) and 5 mol% $Mn(OAc)_3·2H_2O$ (2.7 mg, 0.010 mmol), dibenzyl sulfoxide (46.1 mg, 0.20 mmol) and TFE solvent (1.0 mL), **2a** was obtained in 92% yield **(Scheme 7, entry 7)**.

With 5 mol% $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), 10 mol% $AgNTf_2$ (3.9 mg, 0.010 mmol) and 20 mol% $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol), **2a** was obtained in 0% yield **(Scheme 7, entry 8)**.

Investigations of Other Reaction Parameters

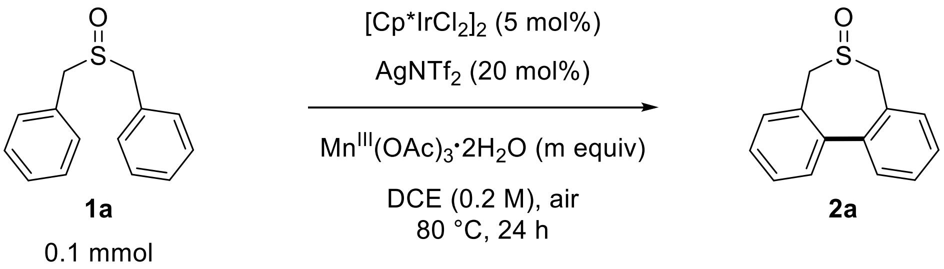
Table S2. Oxidant Effects



entry	oxidant	**2a** yield/%[a]
1	$Cu(OAc)_2$	8
2	BQ	< 5
3	AgOAc	16
4	Ag_2CO_3	15
5	$Cu(OAc)_2$ (10 mol%), 1 atm O_2	13
6	Ag_2O	5
7	$K_2S_2O_8$	< 5
8	$PhI(OAc)_2$	< 5
9	$NaIO_4$	< 5
10	I_2	< 5
11	*m*CPBA	< 5
12	MnO_2	32[b]
13[c]	$Mn^{III}(OAc)_3 \cdot 2H_2O$	88[b]
14[c]	$Co^{II}(NO_3)_2 \cdot 6H_2O$	< 5
15[c]	$Fe^{III}(NO_3)_3 \cdot 9H_2O$	< 5
16[c]	$Mn^{III}(acac)_3$	< 5
17[c]	MnO	44[b]
18[c]	$Mn^{II}(OAc)_2$	76[b]
19[c]	$Mn^{II}Br_2 \cdot 4H_2O$	< 5

[a]NMR yield; [b]Isolated yield; [c]5 mol% $[Cp^*IrCl_2]_2$ and 20 mol% $AgNTf_2$.

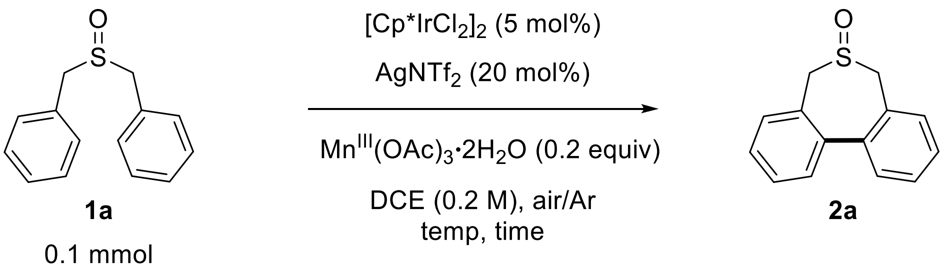
Table S3. Mn^{III}(OAc)$_3$·2H$_2$O Loading Effects



entry	m	**2a** yield/%[a]
1	1	88
2	0.5	95
3	0.2	83 (86)[b]
4	0.1	51

[a] Isolated yield; [b] NMR yield in parentheses.

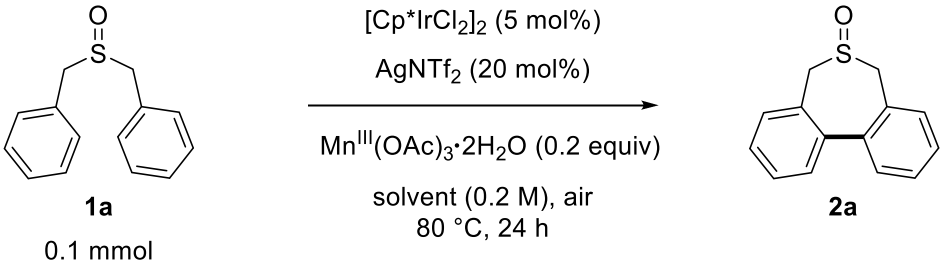
Table S4. Temperature and Atmosphere Effects



entry	temp/°C	time/h	air/Ar	**2a** yield/%[a]
1	50	24	air	12
2	60	24	air	30
3	70	24	air	60
4	80	24	air	86
5	80	24	Ar	14
6	90	9	air	94
7	100	4	air	93

[a] NMR yield.

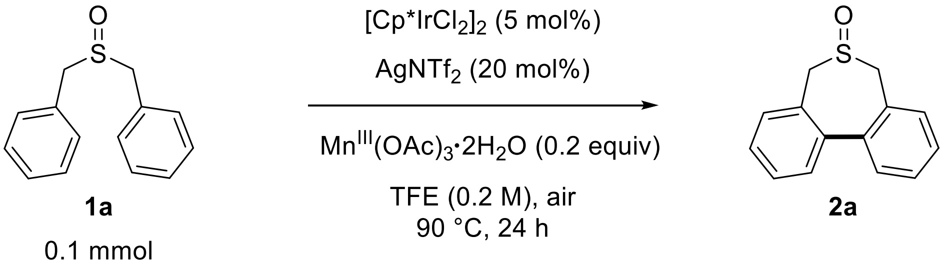
Table S5. Solvent Effects



entry	solvent	**2a** yield/%[a]
1	CH_3CN	< 5
2	PhCl	31
3	$PhCF_3$	30
4	1,4-dioxane	30
5	*t*-amyl-OH	29
6	HFIP	95
7	TFE	92
8	$PhCH_3$	26
9	acetone	26
10	DMF	< 5
11	DMSO	< 5
12	$CHCl_3$	11
13	DCE	86

[a]NMR yield.

Table S6. Investigations of Rh, Ru, and Pd Catalytic System



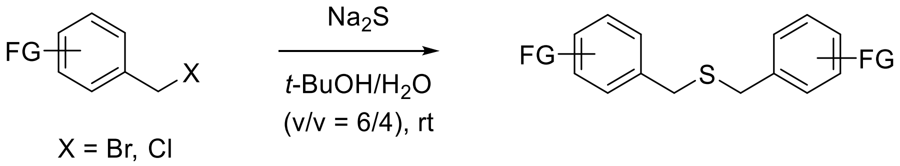
entry	variation	**2a** yield[a]/%
1	none	93
2	$Pd(OAc)_2$ (10 mol%) in place of $[Cp^*IrCl_2]_2$ and $AgNTf_2$	0
3	$Pd(OAc)_2$ (10 mol%) in place of $[Cp^*IrCl_2]_2$ and $AgNTf_2$; and AgOAc (2 equiv) in place of $Mn^{III}(OAc)_3{\cdot}2H_2O$ (0.2 equiv)	0
4	the conditions of entry 3, with additional BQ (0.5 equiv)	0
5	$[Cp^*RhCl_2]_2$ in place of $[Cp^*IrCl_2]_2$	0
6	[(*p*-cymene)$RuCl_2]_2$ in place of $[Cp^*IrCl_2]_2$	0
7[b]	$PdCl_2$ (10 mol%) in place of $[Cp^*IrCl_2]_2$ and $AgNTf_2$; AgOAc (4 equiv) in place of $Mn^{III}(OAc)_3{\cdot}2H_2O$; 1,1,2,2-tetrachloroethane (TTCE) in place of TFE solvent; with PhI (2 equiv) and AcOH (4 equiv) at 100 °C for 48 h	0
8	$Pd(OAc)_2$ (10 mol%) in place of $[Cp^*IrCl_2]_2$ and $AgNTf_2$; DCE in place of TFE solvent at 80 °C for 24 h	0
9	$Pd(OAc)_2$ (10 mol%) in place of $[Cp^*IrCl_2]_2$ and $AgNTf_2$; DCE in place of TFE solvent at 80 °C for 24 h; AgOAc (2 equiv) in place of $Mn^{III}(OAc)_3{\cdot}2H_2O$ (0.2 equiv)	0
10	$Pd(OAc)_2$ (10 mol%) in place of $[Cp^*IrCl_2]_2$ and $AgNTf_2$; DCE in place of TFE solvent at 80 °C for 24 h; $AgCO_3$ (2 equiv) in place of $Mn^{III}(OAc)_3{\cdot}2H_2O$ (0.2 equiv)	0
11	the conditions of entry 10, with additional BQ (0.5 equiv)	

[a] NMR yield; [b] Zhang's conditions (Y. Zhang, *Org Lett*, 2014, **16**, 4574-4577).

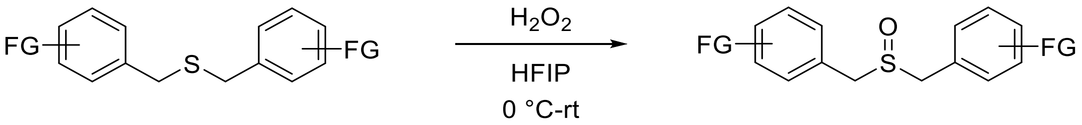
5. Synthesis of Sulfoxide Substrate and Characterization

5.1 Synthesis of Symmetric Sulfoxides

General Procedures:

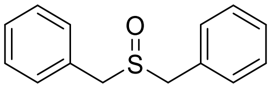


The synthesis was adapted from the reported literature.[3] To a stirred solution of benzylic bromide/chloride (10 mmol) in *t*-BuOH (6 mL) at rt was added an aqueous solution (4 mL) of Na_2S (8 mmol) in one portion, the mixture was stirred at rt for 1-24 h. Upon the completion of the reaction as monitored by TLC analysis, the mixture was diluted with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated to give the corresponding bis-benzylic sulfide, which was directly involved into the next step without further purification.



The synthesis was adapted from the reported literature.[4] To a stirred solution of the bis-benzylic sulfide (1 mmol) in HFIP (sometimes with CH_2Cl_2/$CHCl_3$ to increase the solubility of sulfide) at 0 °C was added 30% aq. H_2O_2 (1.1 mmol) in one portion. The mixture was stirred at 0 °C or allowed to warm to rt for 0.5-24 h. Upon the completion of the reaction as monitored by TLC analysis, the mixture was quenched by adding Na_2SO_3 and reaction for 30 min. The mixture was then filtered and washed with CH_2Cl_2. The filtrate was concentrated and purified by column chromatography on silica gel (Petroleum Ether/EtOAc 4/1 to pure EtOAc) to afford the desired symmetric bis-benzylic sulfoxides in 50-100% total yield (over two steps).

(Sulfinylbis(methylene))dibenzene (1a; purchased from commercial suppliers)



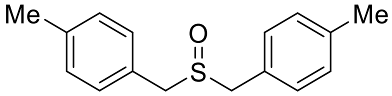
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40–7.27 (m, 10H), 3.92 and 3.87 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 130.2, 129.0, 128.4, 57.4.

The obtained NMR spectral data are in good agreement with those reported in literature.[5]

4,4'-(Sulfinylbis(methylene))bis(methylbenzene) (1b)



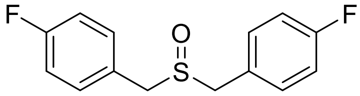
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (br, 8H), 3.90 and 3.88 (ABq system, *J* = 13.0 Hz, 4H), 2.35 (s, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.4, 130.2, 129.8, 126.9, 56.8, 21.3.

HRMS (ESI, m/z) found [M+H]$^+$ 259.1148, $C_{16}H_{19}SO^+$ requires 259.1151.

4,4'-(Sulfinylbis(methylene))bis(fluorobenzene) (1c)



Physical Sate: White solid.

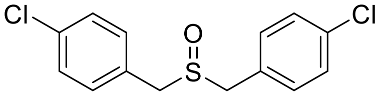
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29–7.24 (m, 4H), 7.10–7.04 (m, 4H), 3.91 and 3.84 (ABq system, *J* = 13.1 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 162.8 (d, *J* = 247.0 Hz), 131.8 (d, *J* = 8.4 Hz), 125.7 (d, *J* = 3.2 Hz), 116.1 (d, *J* = 21.6 Hz), 56.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ –113.04.

HRMS (ESI, m/z) found [M+H]$^+$ 267.0647, $C_{14}H_{13}F_2SO^+$ requires 267.0650.

4,4'-(Sulfinylbis(methylene))bis(chlorobenzene) (1d)



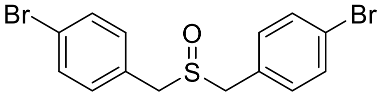
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36 (d, *J* = 7.7 Hz, 4H), 7.22 (d, *J* = 7.9 Hz, 4H), 3.88 and 3.81 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.8, 131.5, 129.4, 128.5, 55.6.

HRMS (ESI, m/z) found [M+H]$^+$ 299.0056, $C_{14}H_{13}Cl_2SO^+$ requires 299.0059.

4,4'-(Sulfinylbis(methylene))bis(bromobenzene) (1e)



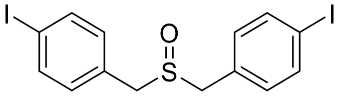
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51 (d, *J* = 7.9 Hz, 4H), 7.16 (d, *J* = 7.9 Hz, 4H), 3.87 and 3.80 (ABq system, *J* = 13.1 Hz, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 132.3, 131.8, 129.0, 123.0, 56.6.

HRMS (ESI, m/z) found [M+H]$^+$ 386.9044, $C_{14}H_{13}Br_2SO^+$ requires 386.9048.

4,4'-(Sulfinylbis(methylene))bis(iodobenzene) (1f)



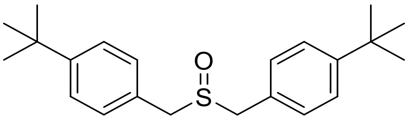
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, *J* = 8.3 Hz, 4H), 7.02 (d, *J* = 8.3 Hz, 4H), 3.84 and 3.78 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.3,132.0, 129.6, 94.6, 56.8.

HRMS (ESI, m/z) found [M+H]$^+$ 482.8770, $C_{14}H_{13}I_2SO^+$ requires 482.8771.

4,4'-(Sulfinylbis(methylene))bis(*tert*-butylbenzene) (1g)



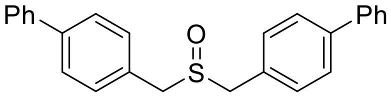
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.39 (d, *J* = 7.9 Hz, 4H), 7.22 (d, *J* = 7.5 Hz, 4H), 3.92 and 3.87 (ABq system, *J* = 13.0 Hz, 4H), 1.32 (s, 18H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 151.7, 130.0, 126.8, 126.1, 56.7, 34.8, 31.4.

HRMS (ESI, m/z) found [M+H]$^+$ 343.2087, $C_{22}H_{31}SO^+$ requires 343.2090.

4,4''-(Sulfinylbis(methylene))di-1,1'-biphenyl (1h)



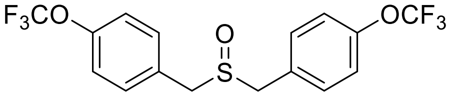
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (t, *J* = 8.3 Hz, 8H), 7.43 (t, *J* = 7.6 Hz, 5H), 7.40–7.36 (m, 5H), 4.01 and 3.97 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 141.5, 140.5, 130.8, 129.1, 129.0, 127.8, 127.7, 127.2, 57.1.

HRMS (ESI, m/z) found [M+H]$^+$ 383.1460, $C_{26}H_{23}OS^+$ requires 383.1464.

4,4'-(Sulfinylbis(methylene))bis((trifluoromethoxy)benzene) (1i)



Physical Sate: White solid.

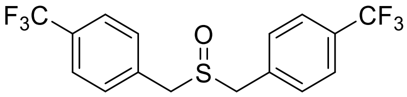
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 (d, *J* = 8.7 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 4H), .3.94 and 3.85 (ABq system, *J* = 13.1 Hz, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 149.5, 131.7, 128.7, 121.6, 120.5 (q, *J* = 256.7 Hz), 56.6.

^{19}F NMR (565 MHz, CDCl$_3$) δ –57.84.

HRMS (ESI, m/z) found [M+H]$^+$ 399.0481, $C_{16}H_{13}F_6O_3S^+$ requires 399.0484.

4,4'-(Sulfinylbis(methylene))bis((trifluoromethyl)benzene) (1j)



Physical Sate: White solid.

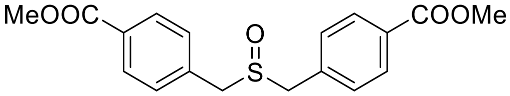
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, *J* = 8.0 Hz, 4H), 7.43 (d, *J* = 8.0 Hz, 4H), 4.01 and 3.91 (ABq system, *J* = 12.9 Hz, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.0, 130.9 (q, *J* = 32.8 Hz), 130.6, 126.09 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.4 Hz), 57.3.

^{19}F NMR (376 MHz, CDCl$_3$) δ –62.73.

HRMS (ESI, m/z) found [M+H]$^+$ 367.0584, $C_{16}H_{13}F_6OS^+$ requires 367.0586.

Dimethyl 4,4'-(sulfinylbis(methylene))dibenzoate (1k)



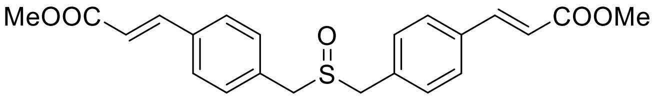
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, *J* = 8.3 Hz, 4H), 7.37 (d, *J* = 8.3 Hz, 4H), 3.92 (s, 6H), 3.97 and 3.92 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.7, 135.0, 130.4, 130.3, 130.3, 57.3, 52.4.

HRMS (ESI, m/z) found [M+H]$^+$ 347.0944, $C_{18}H_{19}O_5S^+$ requires 347.0948.

Dimethyl 3,3'-((sulfinylbis(methylene))bis(4,1-phenylene))(2*E*,2'*E*)-diacrylate (1l)



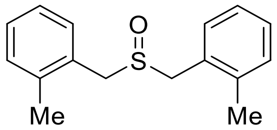
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, *J* = 16.0 Hz, 2H), 7.53 (d, *J* = 6.9 Hz, 4H), 7.32 (d, *J* = 7.6 Hz, 4H), 6.45 (dd, *J* = 16.0, 1.3 Hz, 2H), 3.95 and 3.88 (ABq system, *J* = 13.0 Hz, 4H), 3.81 (d, *J* = 1.5 Hz, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.4, 144.0, 134.7, 132.2, 130.8, 128.7, 118.7, 57.3, 51.9.

HRMS (ESI, m/z) found [M+H]$^+$ 399.1258, $C_{22}H_{23}O_5S^+$ requires 399.1261.

2,2'-(Sulfinylbis(methylene))bis(methylbenzene) (1m)



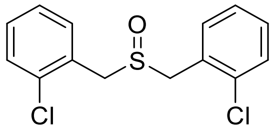
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.26–7.19 (m, 8H), 4.07 and 4.06 (ABq system, *J* = 13.3 Hz, 4H), 2.25 (s, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 137.4, 131.2, 131.0, 129.2, 128.8, 126.7, 56.9, 19.8.

HRMS (ESI, m/z) found $[M+H]^+$ 259.1150, $C_{16}H_{19}SO^+$ requires 259.1151.

2,2'-(Sulfinylbis(methylene))bis(chlorobenzene) (1n)



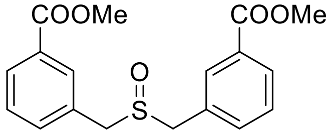
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43–7.41 (m, 4H), 7.31–7.27 (m, 4H), 4.35 and 4.08 (ABq system, *J* = 12.9 Hz, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.6, 132.7, 130.1, 130.0, 128.7, 127.4, 56.1.

HRMS (ESI, m/z) found $[M+H]^+$ 299.0058, $C_{14}H_{13}Cl_2SO^+$ requires 299.0059.

Dimethyl 3,3'-(sulfinylbis(methylene))dibenzoate (1o)



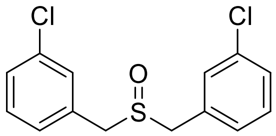
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.96 (s, 2H), 7.55–7.45 (m, 4H), 3.92 (s, 6H), 4.00 and 3.92 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.6, 134.7, 131.2, 131.0, 130.4, 129.7, 129.2, 57.0, 52.4.

HRMS (ESI, m/z) found $[M+H]^+$ 347.0947, $C_{18}H_{19}O_5S^+$ requires 347.0948.

3,3'-(Sulfinylbis(methylene))bis(chlorobenzene) (1p)



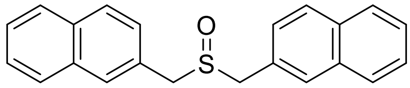
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ7.33–7.28(m, 6H), 7.19 (d, *J* = 6.4 Hz, 2H), 3.91 and 3.88 (ABq system, *J* = 13.2 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 135.0, 131.9, 130.4, 130.2, 128.9, 128.4, 57.0.

HRMS (ESI, m/z) found $[M+H]^+$ 299.0057, $C_{14}H_{13}Cl_2SO^+$ requires 299.0059.

2,2'-(Sulfinylbis(methylene))dinaphthalene (1q)



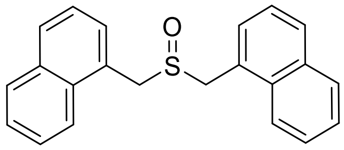
Physical Sate: Light brown solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86–7.79 (m, 6H), 7.76 (s, 2H), 7.52–7.48 (m, 4H), 7.39 (dd, *J* = 8.4, 1.8 Hz, 2H), 4.12 and 4.08 (ABq system, *J* = 13.0 Hz, 4H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 133.5, 133.2, 129.6, 128.9, 128.0, 127.9, 127.7, 127.6, 126.7, 126.6, 57.9.

HRMS (ESI, m/z) found $[M+H]^+$ 331.1148, $C_{22}H_{19}SO^+$ requires 331.1151.

1,1'-(Sulfinylbis(methylene))dinaphthalene (1r)



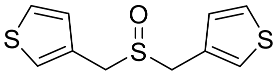
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 (t, *J* = 7.9 Hz, 4H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.51–7.44 (m, 6H), 7.40 (t, *J* = 7.8 Hz, 2H), 4.51 and 4.49 (ABq system, *J* = 13.2 Hz, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.1, 131.8, 129.6, 129.4, 129.1, 126.9, 126.3, 125.6, 123.4, 57.1.

HRMS (ESI, m/z) found $[M+H]^+$ 331.1146, $C_{22}H_{19}SO^+$ requires 331.1151.

3,3'-(Sulfinylbis(methylene))dithiophene (1s)



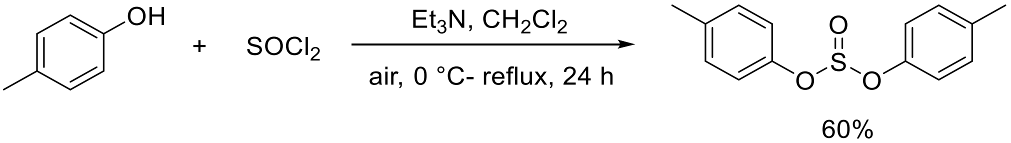
Physical Sate: Light brown solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.37 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.27 (s, 2H), 7.06 (dd, *J* = 5.0, 1.3 Hz, 2H), 3.96 and 3.86 (ABq system, *J* = 13.5 Hz, 4H).

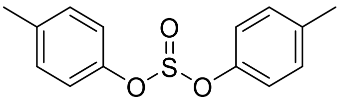
^{13}C NMR (151 MHz, CDCl$_3$) δ 129.8, 128.7, 126.8, 125.3, 51.2.

HRMS (ESI, m/z) found [M+H]$^+$ 242.9962, $C_{10}H_{11}OS_3^+$ requires 242.9967.

Synthesis of di-*p*-tolyl sulfite (1t)



To a stirred solution of 4-methylphenol (2.16 g, 20 mmol) in CH_2Cl_2 was added thionyl chloride (10 mmol) and Et_3N (0.5 mL) at 0 °C, the mixture was then heated to refluxing temperature for 24 h. The mixture was quenched with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (Petroleum Ether/EtOAc 40/1) to the desired product (1.57 g, 6.0 mmol) as a colorless oil in 60% yield.



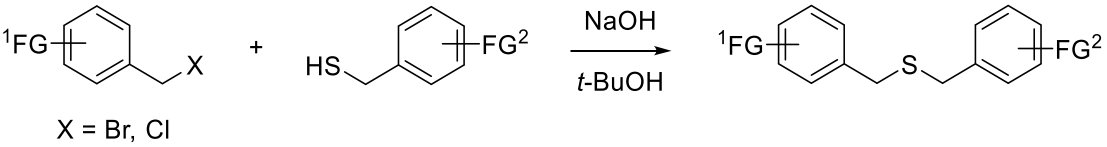
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.17 (d, *J* = 8.1 Hz, 4H), 7.07 (d, *J* = 7.8 Hz, 4H), 2.34 (s, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 146.3, 136.4, 130.5, 122.2, 21.0.

HRMS (ESI, m/z) found [M+Na]$^+$ 285.0556, $C_{14}H_{14}NaO_3S^+$ requires 285.0556.

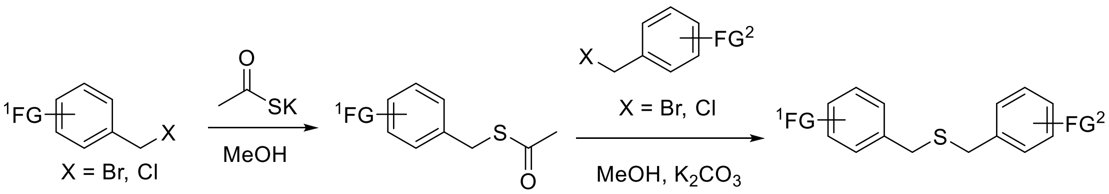
5.2 Synthesis of Non-Symmetric Sulfoxides

General Procedures:



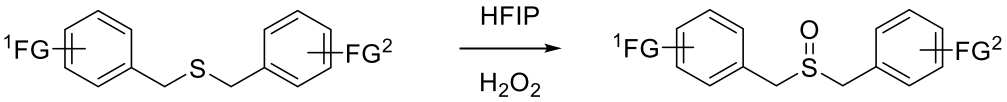
Unless otherwise stated, **method A** was employed.

Method A: The synthesis was adapted from the reported literature.[6] To a stirred solution of benzylic bromide/chloride (10 mmol) and benzylic thiol (11 mmol) in *t*-BuOH (5 mL) at rt was added NaOH (0.60 g, 15 mmol) in portions. The mixture was stirred at rt for 0.5-24 h. Upon the completion of the reaction as monitored by TLC analysis, the mixture was diluted with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated to give the corresponding bis-benzylic sulfide, which was directly involved into the next step without further purification.



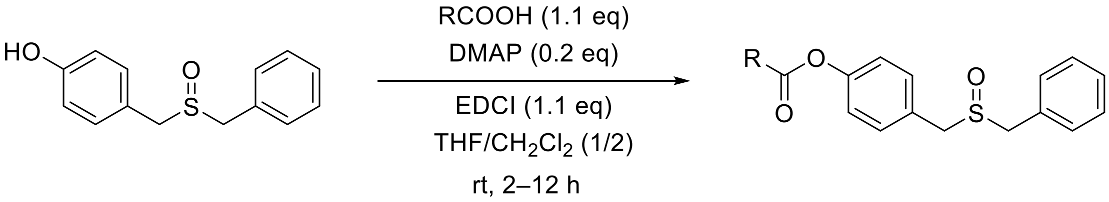
Method B: The synthesis was adapted from the reported literatures.[7, 8] To a stirred solution of benzylic bromide/chloride (5 mmol) in MeOH (10 mL) at rt under air was added potassium thioacetate (5 mmol), the mixture was stirred at rt for 0.5-3 h until the complete consumption of the benzylic bromide/chloride. The mixture was diluted with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated to give the corresponding benzylic thioacetate without further purification.

To the above benzylic thioacetate in MeOH (10 mL) was added another benzylic bromide/chloride (5 mmol), potassium carbonate (K_2CO_3, 6 mmol), the mixture was reacted at rt for 1-24 h until the complete consumption of the benzylic bromide/chloride. The mixture was diluted with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated to give the corresponding bis-benzylic sulfide, which was either purified by column chromatography or directly involved into the next step without further purification.



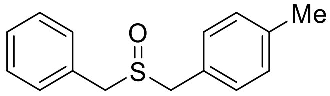
The synthesis was adapted from the reported literature.[4] To a stirred solution of the bis-benzylic sulfide (1 mmol) in HFIP (sometimes with CH_2Cl_2/$CHCl_3$ to increase the solubility of sulfide) at 0 °C was added 30% aq. H_2O_2 (1.1 mmol) in one portion. The mixture was stirred at 0 °C or allowed to warm to rt for 0.5-24 h. Upon the completion of the reaction as monitored by TLC analysis, the mixture was quenched by adding Na_2SO_3 and reaction for 30 min. The mixture was then filtered and washed with CH_2Cl_2. The filtrate was concentrated and purified by column chromatography on silica gel (Petroleum Ether/EtOAc 4/1 to pure EtOAc) to afford the desired unsymmetric bis-benzylic sulfoxides in 50-100% total yield (over two/three steps).

Method C:



Steglich Esterification: To a 30-mL glass vial was added a stirrer, 4-((benzylsulfinyl)methyl)phenol (246.3 mg, 1.0 mmol), RCOOH (1.1 mmol), 4-dimethylaminopyridine (DMAP; 24.4 mg, 0.2 mmol), 1-ethyl-(3-dimethylaminopropyl)carbonyldiimide hydrochloride (EDCI; 210.9 mg, 1.1 mmol) and THF/CH_2Cl_2 (1.7 mL/3.4 mL) mixed solvent. The mixture was stirred at rt for 2–12 h. After the reaction, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (Petroleum Ether/EtOAc 4/1 to EtOAc Petroleum Ether 1/4) to afford the desired sulfoxides in 60-95% yield.

1-((Benzylsulfinyl)methyl)-4-methylbenzene (3a)



Physical Sate: White solid.

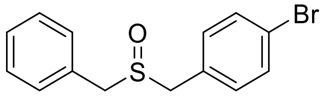
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40–7.27 (m, 5H), 7.18 (s, 4H), 3.93–3.83 (m, 4H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.4, 130.3, 130.3, 130.1, 129.8, 129.1, 128.4, 127.0, 57.2, 57.1, 21.3.

HRMS (ESI, m/z) found $[M+H]^+$ 245.0992, $C_{15}H_{17}OS^+$ requires 245.0995.

The obtained NMR spectral data are in good agreement with those reported in literature.[9]

1-((Benzylsulfinyl)methyl)-4-bromobenzene (3b)



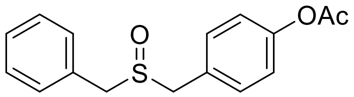
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.50 (d, J = 8.1 Hz, 2H), 7.41–7.33 (m, 3H), 7.29 (d, J = 6.8 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 3.92 (s, 2H), 3.87 (d, J = 13.1 Hz, 1H), 3.76 (d, J = 13.1 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 132.2, 131.9, 130.2, 129.9, 129.3, 129.2, 128.6, 122.8, 57.6, 56.4.

HRMS (ESI, m/z) found $[M+H]^+$ 308.9940, $C_{14}H_{14}BrOS^+$ requires 308.9943.

4-((Benzylsulfinyl)methyl)phenyl acetate (3c; via method C)



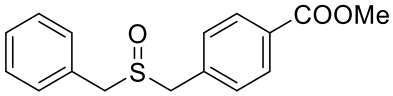
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.42–7.33 (m, 3H), 7.31–7.28 (m, 4H), 7.11 (d, *J* = 8.5 Hz, 2H), 3.97–3.87 (m, 3H), 3.82 (d, *J* = 13.2 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 169.4, 150.9, 131.3, 130.3, 130.1, 129.2, 128.6, 127.9, 122.3, 57.5, 56.6, 21.3.

HRMS (ESI, m/z) found [M+H]$^+$ 289.0891, $C_{16}H_{17}O_3S^+$ requires 289.0893.

Methyl 4-((benzylsulfinyl)methyl)benzoate (3d)



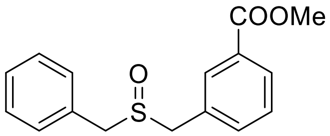
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.40–7.35 (m, 5H), 7.29 (d, *J* = 7.4 Hz, 2H), 3.96 (d, *J* = 13.2 Hz, 1H), 3.94 (s, 2H), 3.92 (s, 3H), 3.87 (d, *J* = 12.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 166.7, 135.4, 130.3, 130.3, 130.2, 129.9, 129.2, 128.7, 57.8, 56.9, 52.4.

HRMS (ESI, m/z) found [M+H]$^+$ 289.0891, $C_{16}H_{17}O_3S^+$ requires 289.0893.

Methyl 3-((benzylsulfinyl)methyl)benzoate (3e)



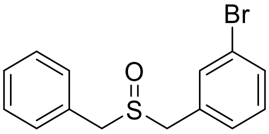
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.95 (s, 1H), 7.51–7.29 (m, 7H), 4.00–3.88 (m, 7H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 166.8, 134.9, 131.3, 131.0, 130.5, 130.2, 129.8, 129.6, 129.2, 128.8, 57.6, 56.5, 52.4.

HRMS (ESI, m/z) found [M+H]$^+$ 289.0891, $C_{16}H_{17}O_3S^+$ requires 289.0893.

1-((Benzylsulfinyl)methyl)-3-bromobenzene (3f)



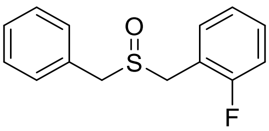
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.48 (d, *J* = 7.3 Hz, 1H), 7.41–7.35 (m, 4H), 7.30 (d, *J* = 6.9 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 3.96 and 3.94 (ABq system, *J* = 13.2 Hz, 2H), 3.87 and 3.78 (ABq system, *J* = 13.1 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 133.1, 132.6, 131.7, 130.6, 130.2, 129.8, 129.2, 129.0, 128.7, 123.0, 57.8, 56.5.

HRMS (ESI, m/z) found $[M+H]^+$ 308.9941, $C_{14}H_{14}BrOS^+$ requires 308.9943.

1-((Benzylsulfinyl)methyl)-2-fluorobenzene (3g)



Physical Sate: White solid.

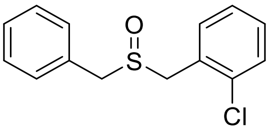
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40–7.33 (m, 5H), 7.31 (d, *J* = 6.6 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 9.2 Hz, 1H), 4.09 (d, *J* = 13.0 Hz, 1H), 4.03-3.89 (m, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 161.2 (d, *J* = 247.4 Hz), 132.6 (d, *J* = 4.0 Hz), 130.5 (d, *J* = 8.0 Hz), 130.3, 130.2, 129.1, 128.5, 124.7 (d, *J* = 3.3 Hz), 117.8 (d, *J* = 15.2 Hz), 115.8 (d, *J* = 21.8 Hz), 58.1, 50.8.

^{19}F NMR (565 MHz, CDCl$_3$) δ –116.27.

HRMS (ESI, m/z) found $[M+H]^+$ 249.0741, $C_{14}H_{14}FOS^+$ requires 249.0744.

1-((Benzylsulfinyl)methyl)-2-chlorobenzene (3h)



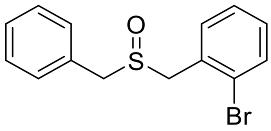
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43–7.26 (m, 9H), 4.25 (d, *J* = 12.9 Hz, 1H), 4.04 (s, 2H), 3.95 (d, *J* = 12.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.6, 132.7, 130.3, 130.1, 130.0, 129.1, 128.8, 128.7, 127.4, 58.4, 55.7.

HRMS (ESI, m/z) found $[M+H]^+$ 265.0446, $C_{14}H_{14}ClOS^+$ requires 265.0448.

1-((Benzylsulfinyl)methyl)-2-bromobenzene (3i)



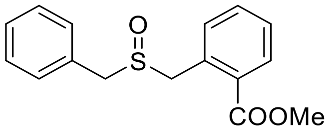
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.41–7.28 (m, 7H), 7.20 (td, *J* = 7.7, 1.8 Hz, 1H), 4.26 (d, *J* = 12.9 Hz, 1H), 4.04 (s, 2H), 3.92 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 133.3, 132.7, 130.9, 130.3, 130.2, 129.1, 128.6, 128.0, 125.1, 58.6, 58.4.

HRMS (ESI, m/z) found $[M+H]^+$ 308.9942, $C_{14}H_{14}BrOS^+$ requires 308.9943.

Methyl 2-((benzylsulfinyl)methyl)benzoate (3j)



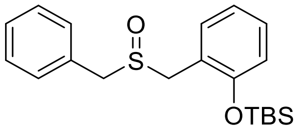
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.06 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.45–7.34 (m, 7H), 4.81 (d, *J* = 12.3 Hz, 1H), 4.12 (d, *J* = 13.0 Hz, 1H), 4.00 (d, *J* = 13.1 Hz, 1H), 3.91 (d, *J* = 12.3 Hz, 1H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.5, 133.1, 132.9, 131.7, 130.5, 130.3, 129.3, 129.0, 128.7, 128.5, 58.2, 57.5, 52.3.

HRMS (ESI, m/z) found $[M+H]^+$ 289.0891, $C_{16}H_{17}O_3S^+$ requires 289.0893.

(2-((Benzylsulfinyl)methyl)phenoxy)(tert-butyl)dimethylsilane (3k)



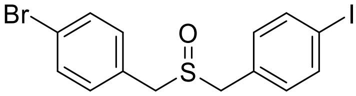
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36–7.27 (m, 6H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.89 (dd, *J* = 12.7, 9.0 Hz, 2H), 0.96 (s, 9H), 0.23 (s, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 154.1, 132.4, 130.8, 130.3, 129.7, 129.0, 128.3, 121.6, 121.1, 118.5, 58.4, 53.7, 26.0, 18.4, –3.9, –4.0.

HRMS (ESI, m/z) found [M+H]$^+$ 361.1648, $C_{20}H_{29}O_2SSi^+$ requires 361.1652.

1-Bromo-4-(((4-iodobenzyl)sulfinyl)methyl)benzene (3l; via method B)



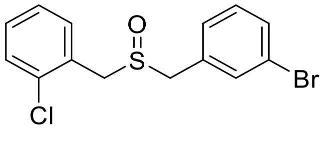
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 3.85 (dd, *J* = 13.1, 8.6 Hz, 2H), 3.78 (dd, *J* = 13.1, 5.0 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 138.3, 132.3, 132.0, 131.8, 129.6, 129.0, 122.9, 94.6, 56.8, 56.7.

HRMS (ESI, m/z) found [M+H]$^+$ 434.8903, $C_{14}H_{13}BrIOS^+$ requires 434.8910.

1-(((3-Bromobenzyl)sulfinyl)methyl)-2-chlorobenzene (3m; via method B)



Physical Sate: White solid.

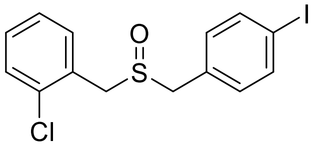
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.48 (d, *J* = 7.1 Hz, 1H), 7.45 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.33–7.22 (m, 4H), 4.24 (d, *J* = 12.9 Hz, 1H), 4.00

(d, *J* = 13.0 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 3.89 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.6, 133.1, 132.6, 132.6, 131.7, 130.5, 130.1, 130.0, 128.9, 128.6, 127.5, 123.0, 57.5, 56.0.

HRMS (ESI, m/z) found [M+H]$^+$ 342.9547, $C_{14}H_{13}BrClOS^+$ requires 342.9554.

1-Chloro-2-(((4-iodobenzyl)sulfinyl)methyl)benzene (3n; via method B)



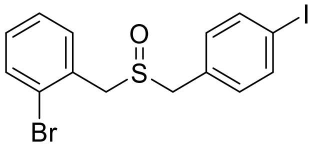
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72–7.69 (m, 2H), 7.44–7.42 (m, 1H), 7.37 (dd, *J* = 7.0, 2.4 Hz, 1H), 7.34–7.27 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 4.22 (d, *J* = 12.9 Hz, 1H), 3.96 (d, *J* = 12.9 Hz, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.86 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.2, 134.6, 132.6, 132.1, 130.1, 130.1, 129.9, 128.7, 127.5, 94.5, 57.5, 56.0.

HRMS (ESI, m/z) found [M+H]$^+$ 390.9407, $C_{14}H_{13}ClIOS^+$ requires 390.9415.

1-Bromo-2-(((4-iodobenzyl)sulfinyl)methyl)benzene (3o; via method B)



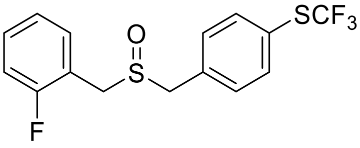
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73–7.69 (m, 2H), 7.61 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.40–7.28 (m, 2H), 7.22 (td, *J* = 7.8, 1.9 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 4.24 (d, *J* = 12.9 Hz, 1H), 3.98 (d, *J* = 7.5 Hz, 1H), 3.95 (d, *J* = 7.4 Hz, 1H), 3.88 (d, *J* = 13.1 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.2, 133.4, 132.6, 132.1, 130.5, 130.3, 129.9, 128.1, 125.1, 94.5, 58.5, 57.6.

HRMS (ESI, m/z) found [M+H]$^+$ 434.8908, $C_{14}H_{13}BrIOS^+$ requires 434.8910.

(4-(((2-Fluorobenzyl)sulfinyl)methyl)phenyl)(trifluoromethyl)sulfane (3p; via method B)



Physical Sate: White solid.

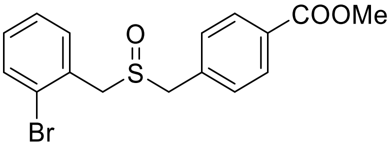
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.37–7.34 (m, 4H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 (d, *J* = 9.8 Hz, 1H), 4.11 (dd, *J* = 13.2, 1.1 Hz, 1H), 3.96 (t, *J* = 13.3 Hz, 2H), 3.84 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 161.1 (d, *J* = 247.4 Hz), 136.7 , 133.6 , 132.5 (d, *J* = 7.0 Hz), 131.4 , 130.7 (d, *J* = 8.5 Hz), 129.6 (q, *J* = 308.5 Hz), 124.9 (d, *J* = 4.2 Hz), 124.8 , 117.3 (d, *J* = 15.2 Hz), 115.9 (d, *J* = 21.7 Hz), 57.2 , 51.1.

^{19}F NMR (565 MHz, CDCl$_3$) δ –42.47, –116.25.

HRMS (ESI, m/z) found [M+H]$^+$ 349.0337, $C_{15}H_{13}F_4OS_2^+$ requires 349.0338.

Methyl 4-(((2-bromobenzyl)sulfinyl)methyl)benzoate (3q; via method B)



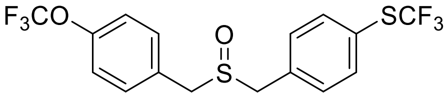
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 4.26 (d, *J* = 12.9 Hz, 1H), 4.08 (d, *J* = 12.9 Hz, 1H), 4.02 (d, *J* = 12.9 Hz, 1H), 3.97 (d, *J* = 12.9 Hz, 1H), 3.92 (s, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 166.7, 135.4, 133.4, 132.7, 130.5, 130.4, 130.3, 130.3, 128.1, 125.1, 58.7, 58.1, 52.4.

HRMS (ESI, m/z) found [M+H]$^+$ 366.9996, $C_{16}H_{16}BrO_3S^+$ requires 366.9998.

(4-(((4-(Trifluoromethoxy)benzyl)sulfinyl)methyl)phenyl)(trifluoromethyl)sulfane (3r; via method B)



Physical Sate: White solid.

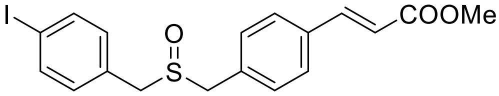
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.95 (dd, *J* = 13.1, 5.6 Hz, 2H), 3.87 (dd, *J* = 13.1, 5.0 Hz, 2H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 149.6, 136.8, 133.2, 131.7, 131.3, 129.6 (q, *J* = 308.2 Hz), 128.6, 125.0, 121.5, 120.5 (q, *J* = 257.6 Hz), 57.0, 56.8.

^{19}F NMR (565 MHz, CDCl$_3$) δ –42.44, –57.84.

HRMS (ESI, m/z) found [M+H]$^+$ 415.0253, $C_{16}H_{13}F_6O_2S_2^+$ requires 415.0256.

Methyl (*E*)-3-(4-(((4-iodobenzyl)sulfinyl)methyl)phenyl)acrylate (3s; via method B)



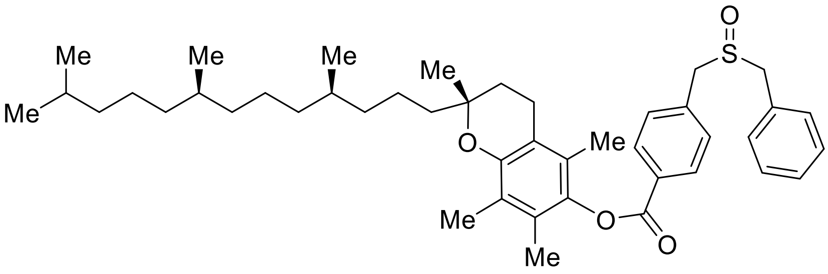
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73–7.70 (m, 2H), 7.66 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.45 (d, *J* = 16.1 Hz, 1H), 3.93 (d, *J* = 13.0 Hz, 1H), 3.87 (d, *J* = 11.9 Hz, 2H), 3.82 (s, 3H), 3.79 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.4, 144.0, 138.3, 134.8, 132.2, 132.1, 130.8, 129.6, 128.7, 118.7, 94.6, 57.2, 56.8, 51.9.

HRMS (ESI, m/z) found [M+H]$^+$ 441.0015, $C_{18}H_{18}IO_3S^+$ requires 441.0016.

(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-((benzylsulfinyl)methyl)benzoate (s5a)



Steglich Esterification: To a 30-mL glass vial was added a stirrer, 4-((benzylsulfinyl)methyl)benzoic acid (274.3 mg, 1.0 mmol), (+)-α-tocopherol (473.8 mg, 1.1 mmol), DMAP (24.4 mg, 0.2 mmol), EDCI (210.9 mg, 1.1 mmol) and THF/CH_2Cl_2 (1.7 mL/3.4 mL) mixed solvent. The mixture was stirred at rt for 12 h. After the reaction, the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel (Petroleum Ether/EtOAc 2/1 to EtOAc Petroleum Ether 1/4) to afford the desired sulfoxide (**s5a**; 446.6 mg, 0.65 mmol) in 65% yield.

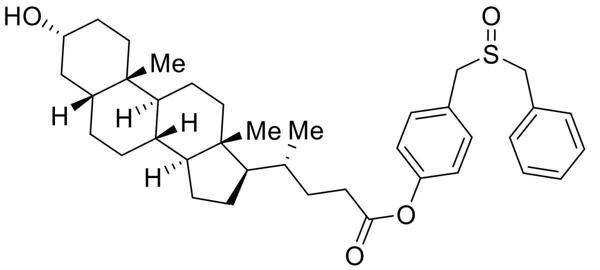
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, *J* = 8.2 Hz, 2H), 7.48–7.29 (m, 7H), 4.05–3.95 (m, 3H), 3.89 (d, *J* = 13.0 Hz, 1H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.12 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.89–1.74 (m, 2H), 1.57–1.01 (m, 24H), 0.88–0.84 (m, 12H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 164.8, 149.7, 140.7, 136.0, 130.8, 130.6, 130.2, 129.9, 129.8, 129.2, 129.1, 128.7, 127.0, 125.2, 123.3, 117.6, 75.2, 57.9, 56.8, 40.6, 39.7, 39.5, 37.6, 37.4, 32.9, 32.9, 32.8, 31.4, 31.1, 28.1, 24.9, 24.6, 24.3, 23.8, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.4, 12.0.

HRMS (ESI, m/z) found $[M+H]^+$ 687.4441, $C_{44}H_{63}O_4S^+$ requires 687.4442.

4-((Benzylsulfinyl)methyl)phenyl (4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (s5b; via method C)



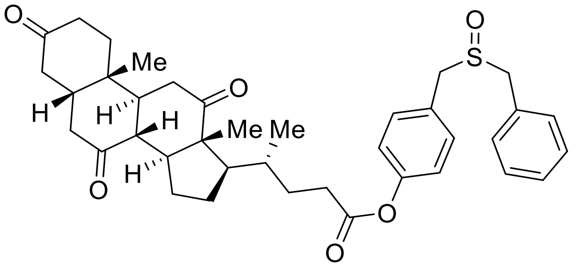
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38–7.34 (m, 3H), 7.33–7.21 (m, 4H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.98–3.86 (m, 3H), 3.83 (d, *J* = 13.1 Hz, 1H), 3.60 (tt, *J* = 10.7, 4.7 Hz, 1H), 2.64–2.55 (m, 1H), 2.51–2.43 (m, 1H), 2.05–1.04 (m, 27H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.92 (s, 3H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.7, 151.0, 131.3, 130.3, 130.1, 129.1, 128.6, 127.7, 122.3, 71.9, 57.5, 56.6, 56.6, 56.1, 42.9, 42.2, 40.5, 40.3, 36.6, 36.0, 35.5, 35.5, 34.7, 31.5, 31.0, 30.7, 28.4, 27.3, 26.5, 24.3, 23.5, 20.9, 18.4, 12.2.

HRMS (ESI, m/z) found $[M+H]^+$ 605.3662, $C_{38}H_{53}O_4S^+$ requires 605.3659.

4-((Benzylsulfinyl)methyl)phenyl (4*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (s5c; via method C)



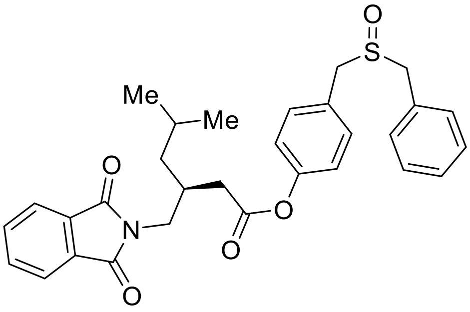
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40–7.34 (m, 3H), 7.32–7.25 (m, 4H), 7.11–7.08 (m, 2H), 3.98–3.86 (m, 3H), 3.82 (d, *J* = 13.1 Hz, 1H), 2.98–2.78 (m, 3H), 2.69–2.61 (m, 1H), 2.57–2.48 (m, 1H), 2.41–1.82 (m, 14H), 1.67–1.45 (m, 2H), 1.40–1.21 (m, 6H), 1.09 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 212.0, 209.1, 208.7, 172.3, 150.8, 131.2, 130.1, 130.0, 129.0, 128.4, 127.7, 122.1, 57.4, 56.9, 56.4, 51.8, 49.0, 46.8, 45.7, 45.5, 45.0, 42.8, 38.7, 36.5, 36.0, 35.5, 35.2, 31.6, 30.4, 27.7, 25.1, 21.9, 18.7, 11.9.

HRMS (ESI, m/z) found [M+H]$^+$ 631.3088, $C_{38}H_{47}O_6S^+$ requires 631.3088.

4-((Benzylsulfinyl)methyl)phenyl (3*S*)-3-((1,3-dioxoisoindolin-2-yl)methyl)-5-methylhexanoate (s5d; via method C)



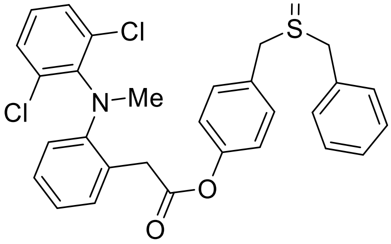
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.86–7.80 (m, 2H), 7.74–7.70 (m, 2H), 7.42–7.32 (m, 3H), 7.29–7.25 (m, 4H), 7.08 (d, *J* = 8.5 Hz, 2H) 3.98–3.64 (m, 6H), 2.72–2.42 (m, 3H), 1.82 (hept, *J* = 6.7 Hz, 1H), 1.39–1.27 (m, 2H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 171.0, 168.8, 150.8, 134.2, 132.1, 131.2, 130.2, 130.1, 129.1, 128.5, 127.7, 123.4, 122.3, 57.4, 56.6, 41.8, 41.8, 37.7, 33.0, 25.4, 22.9, 22.7.

HRMS (ESI, m/z) found [M+H]$^+$ 518.1998, $C_{30}H_{32}NO_5S^+$ requires 518.1996.

4-((Benzylsulfinyl)methyl)phenyl 2-(2-((2,6-dichlorophenyl)(methyl)amino)phenyl)acetate (s5e; via method C)



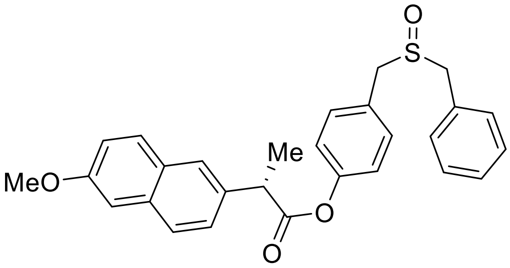
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40–7.32 (m, 3H), 7.32–7.26 (m, 5H), 7.25–7.17 (m, 4H), 7.05–6.94 (m, 4H), 3.94–3.83 (m, 3H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.56 (s, 2H), 3.30 (s, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 169.4, 150.9, 148.2, 143.6, 135.5, 131.9, 131.1, 130.2, 130.1, 129.9, 129.1, 128.5, 128.1, 127.5, 127.4, 124.5, 122.1, 122.0, 120.6, 57.4, 56.5, 40.7, 37.4.

HRMS (ESI, m/z) found $[M+H]^+$ 538.1004, $C_{29}H_{26}Cl_2NO_3S^+$ requires 538.1005.

4-((Benzylsulfinyl)methyl)phenyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (s5f; via method C)



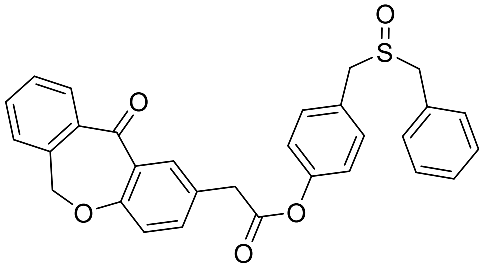
Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80–7.65 (m, 3H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.33–7.28 (m, 3H), 7.24–7.20 (m, 6H), 6.99 (d, *J* = 8.1 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 1H), 3.91–3.69 (m, 7H), 1.67 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 173.0, 157.8, 150.9, 135.0, 133.9, 131.1, 130.1, 130.0, 129.3, 128.9, 128.4, 127.7, 127.7, 127.4, 126.2, 126.1, 121.9, 119.2, 105.6, 57.2, 57.2, 56.4, 56.4, 55.3, 45.5, 18.5.

HRMS (ESI, m/z) found $[M+H]^+$ 459.1624, $C_{28}H_{27}O_4S^+$ requires 459.1625.

4-((Benzylsulfinyl)methyl)phenyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (s5g; via method C)



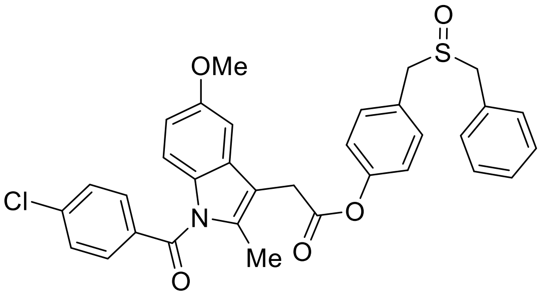
Physical Sate: White solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.22 (d, *J* = 2.3 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.57–7.42 (m, 3H), 7.34 (dd, *J* = 10.5, 7.8 Hz, 4H), 7.30–7.23 (m, 4H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H), 3.99–3.67 (m, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 190.8, 169.7, 160.7, 150.8, 140.4, 136.3, 135.5, 132.9, 132.6, 131.2, 130.2, 130.0, 129.5, 129.3, 129.0, 128.4, 127.9, 127.1, 125.3, 122.0, 121.3, 73.7, 57.3, 56.4, 40.3.

HRMS (ESI, m/z) found $[M+H]^+$ 497.1417, $C_{30}H_{25}O_5S^+$ requires 497.1417.

4-((Benzylsulfinyl)methyl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (s5h; via method C)



Physical Sate: White solid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71–7.62 (m, 2H), 7.50–7.44 (m, 2H), 7.41–7.33 (m, 3H), 7.28–7.26 (m, 4H), 7.12–7.02 (m, 3H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.95–3.75 (m, 9H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 169.2, 168.4, 156.2, 150.9, 139.5, 136.3, 133.9, 131.3, 130.9, 130.5, 130.2, 130.0, 129.3, 129.1, 128.5, 128.0, 122.0, 115.1, 111.9, 111.9, 101.3, 57.5, 56.4, 55.8, 30.6, 13.5.

HRMS (ESI, m/z) found $[M+H]^+$ 586.1448, $C_{33}H_{29}ClNO_5S^+$ requires 586.1449.

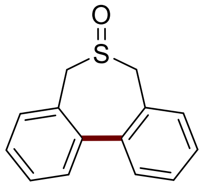
6. Construction of Seven-Membered-Ring Sulfoxides

General Procedures:

Inside a glovebox, $AgNTf_2$ (7.8 mg, 0.020 mmol) was added into an 8 mL glass vial. After the addition, the vial was taken outside of the glovebox. To the vial was added a stirrer, $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3\cdot 2H_2O$ (5.4 mg, 0.020 mmol), a sulfoxide (0.10 mmol) and TFE solvent (0.5 mL). The vial was capped under air and placed into a pre-heated aluminum block at 90 °C for 24 h. After the reaction, the mixture was diluted by CH_2Cl_2 with the addition of 20 μL NEt_3 and passed through a short pipet column on silica gel eluting with EtOAc. The filtrate was evaporated to dryness. The residue was taken for NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. The residue was either purified by column chromatography or preparative TLC to afford the desired seven-membered-ring sulfoxide.

6.1 With Symmetric Sulfoxides

5,7-Dihydrodibenzo[c,e]thiepine 6-oxide (2a)



Isolated as a white solid in 90% yield (20.5 mg, 0.090 mmol) by pipet column chromatography (1/1 Petroleum Ether/EtOAc) according to the general procedures using (sulfinylbis(methylene))dibenzene (**1a**; 23.0 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3\cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.42 (m, 6H), 7.38–7.32 (m, 2H), 4.21 (d, *J* = 11.9 Hz, 1H), 3.79 (d, *J* = 14.2 Hz, 1H), 3.49 (d, *J* = 14.2 Hz, 1H), 3.27 (d, *J* = 11.8 Hz, 1H).

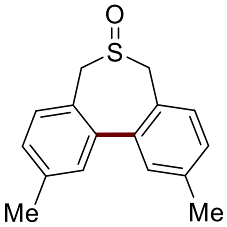
The obtained ^{1}H NMR spectral data are in good agreement with those reported in literature.[10]

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.5, 131.7, 129.9, 129.7, 129.6, 129.4, 129.1, 129.0, 128.5, 128.4, 128.1, 55.8, 53.3.

HRMS (ESI, m/z) found $[M+H]^+$ 229.0680, $C_{14}H_{13}OS^+$ requires 229.0682.

The crystal structure is shown in the X-ray Crystallographic Data section.

2,10-Dimethyl-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2b)



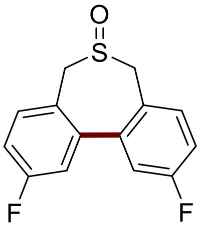
Isolated as a white solid in 63% yield (16.2 mg, 0.063 mmol) by preparative TLC (v/v 2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis(methylbenzene) (**1b**; 25.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 80 °C for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 3H), 7.13 (dd, *J* = 7.5, 1.6 Hz, 1H), 4.16 (d, *J* = 11.9 Hz, 1H), 3.73 (d, *J* = 14.2 Hz, 1H), 3.45 (d, *J* = 14.2 Hz, 1H), 3.22 (d, *J* = 11.9 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 139.5, 138.9, 131.5, 130.1, 129.8, 129.7, 129.1, 128.6, 126.7, 125.4, 55.5, 53.1, 21.4.

HRMS (ESI, m/z) found $[M+H]^+$ 257.0992, $C_{16}H_{17}OS^+$ requires 257.0995.

2,10-Difluoro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2c)



Isolated as a white solid in 70% yield (18.5 mg, 0.070 mmol) by preparative TLC (v/v 2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis(fluorobenzene) (**1c**; 26.6 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) in HFIP solvent (0.5 mL) at 90 °C for 24 h.

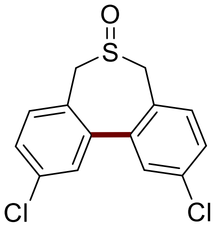
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (dd, *J* = 8.3, 5.5 Hz, 1H), 7.36 (dd, *J* = 8.4, 5.4 Hz, 1H), 7.20–7.13 (m, 3H), 7.07 (td, *J* = 8.3, 2.7 Hz, 1H), 4.21 (d, *J* = 12.1 Hz, 1H), 3.79 (d, *J* = 14.4 Hz, 1H), 3.43 (d, *J* = 14.3 Hz, 1H), 3.18 (d, *J* = 12.1 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 163.3 (d, *J* = 249.9 Hz), 163.1 (d, *J* = 249.0 Hz), 141.6 (d, *J* = 10.2 Hz), 141.5 (d, *J* = 10.7 Hz), 133.6 (d, *J* = 8.6 Hz), 131.8 (d, *J* = 8.6 Hz), 125.7 (d, *J* = 3.1 Hz), 124.3 (d, *J* = 3.4 Hz), 116.5 (d, *J* = 22.5 Hz), 116.0 (d, *J* = 22.6 Hz), 115.9 (d, *J* = 21.3 Hz), 115.5 (d, *J* = 21.7 Hz), 54.9 , 52.5.

^{19}F NMR (376 MHz, CDCl$_3$) δ –111.19, –112.11.

HRMS (ESI, m/z) found $[M+H]^+$ 265.0490, $C_{14}H_{11}F_2OS^+$ requires 265.0493.

2,10-Dichloro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2d)



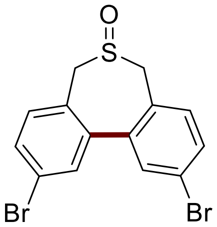
Isolated as a white solid in 77% yield (22.9 mg, 0.077 mmol) by preparative TLC (v/v 2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis(chlorobenzene) (**1d**; 29.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56–7.28 (m, 6H), 4.21 (d, *J* = 12.1 Hz, 1H), 3.79 (d, *J* = 14.3 Hz, 1H), 3.42 (d, *J* = 14.3 Hz, 1H), 3.18 (d, *J* = 12.1 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 140.8, 135.7, 135.2, 133.1, 131.2, 129.4, 129.0, 128.9, 128.7, 128.2, 127.0, 55.2, 52.6.

HRMS (ESI, m/z) found $[M+H]^+$ 296.9901, $C_{14}H_{11}Cl_2OS^+$ requires 296.9902.

2,10-Dibromo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2e)



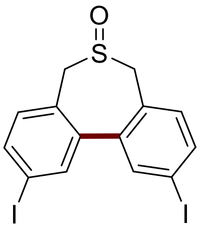
Isolated as a white solid in 80% yield (30.9 mg, 0.080 mmol) by preparative TLC (v/v 2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis(bromobenzene) (**1e**; 38.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 48 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.0 Hz, 1H), 7.58 (dt, *J* = 4.7, 2.6 Hz, 2H), 7.50 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 3.77 (d, *J* = 14.3 Hz, 1H), 3.41 (d, *J* = 14.2 Hz, 1H), 3.16 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.9, 133.3, 132.2, 132.0, 131.8, 131.7, 131.4, 128.7, 127.5, 123.7, 123.2, 55.3, 52.8.

HRMS (ESI, m/z) found $[M+H]^+$ 384.8888 $C_{14}H_{11}Br_2OS^+$ requires 384.8892.

2,10-Diiodo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2f)



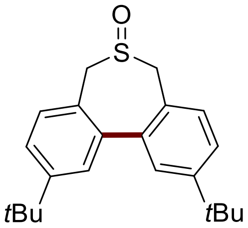
Isolated as a white solid in 90% yield (43.2 mg, 0.090 mmol) by pipet column chromatography (1/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(mthylene))bis(iodobenzene) (**1f**; 48.2 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 100 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83–7.76 (m, 3H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 4.17 (d, *J* = 12.1 Hz, 1H), 3.75 (d, *J* = 14.3 Hz, 1H), 3.40 (d, *J* = 14.4 Hz, 1H), 3.16 (d, *J* = 12.2 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 140.9, 140.8, 138.1, 138.0, 137.7, 137.6, 133.3, 131.5, 129.3, 128.1, 95.3, 94.8, 55.5, 53.0.

HRMS (ESI, m/z) found [M+H]$^+$ 480.8614, $C_{14}H_{11}I_2OS^+$ requires 480.8614.

2,10-Di-*tert*-butyl-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2g)



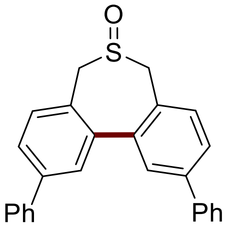
Isolated as a white solid in 88% yield (29.9 mg, 0.088 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis(*tert*-butylbenzene) (**1g**; 34.2 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47–7.43 (m, 3H), 7.36 (dd, J = 8.0, 1.7 Hz, 2H), 7.29 (d, J = 8.0 Hz, 1H), 4.19 (d, J = 11.8 Hz, 1H), 3.76 (d, J = 14.2 Hz, 1H), 3.48 (d, J = 14.2 Hz, 1H), 3.25 (d, J = 11.8 Hz, 1H), 1.39 (s, 9H), 1.37 (s, 9H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 152.8, 152.3, 140.7, 131.3, 129.6, 126.8, 126.4, 126.0, 125.6, 125.5, 125.0, 55.6, 53.0, 35.0, 34.9, 31.5, 31.4.

HRMS (ESI, m/z) found [M+H]$^+$ 341.1932, $C_{22}H_{29}OS^+$ requires 341.1934.

2,10-Diphenyl-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2h)



Isolated as a white solid in 71% yield (27.0 mg, 0.071 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4''-(sulfinylbis(methylene))di-1,1'-biphenyl (**1h**; 38.2 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020

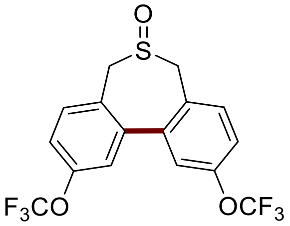
mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.74 (d, *J* = 15.2 Hz, 2H), 7.69–7.61 (m, 5H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.46 (q, *J* = 7.4 Hz, 5H), 7.39 (d, *J* = 7.6 Hz, 2H), 4.30 (d, *J* = 12.0 Hz, 1H), 3.87 (d, *J* = 14.3 Hz, 1H), 3.60 (d, *J* = 14.2 Hz, 1H), 3.38 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 142.7, 142.2, 141.0, 141.0, 140.3, 140.1, 132.2, 130.7, 130.4, 129.1, 129.1, 129.0, 128.6, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.5, 127.3, 127.3, 127.2, 126.8, 55.7, 53.2.

HRMS (ESI, m/z) found $[M+H]^+$ 381.1305, $C_{26}H_{21}OS^+$ requires 381.1308.

2,10-Bis(trifluoromethoxy)-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2i)



Isolated as a white solid in 76% yield (30.1 mg, 0.076 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis((trifluoromethoxy)benzene) (**1i**; 39.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 48 h.

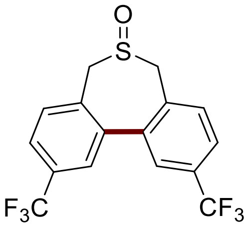
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.49 (d, *J* = 8.2 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.33 (s, 2H), 7.28 (d, *J* = 17.2 Hz, 2H), 4.27 (d, *J* = 12.2 Hz, 1H), 3.85 (d, *J* = 14.3 Hz, 1H), 3.47 (d, *J* = 14.4 Hz, 1H), 3.22 (d, *J* = 12.2 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 150.1, 149.8, 141.1, 141.0, 133.5, 131.6, 128.5, 127.3, 121.8, 121.5, 121.3, 120.9, 120.5 (q, *J* = 256.3 Hz), 120.4 (q, *J* = 258.0 Hz), 55.1, 52.6.

^{19}F NMR (565 MHz, CDCl$_3$) δ –57.76, –57.79.

HRMS (ESI, m/z) found $[M+H]^+$ 397.0325, $C_{16}H_{11}F_6O_3S^+$ requires 397.0328.

2,10-Bis(trifluoromethyl)-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2j)



Isolated as a white solid in 83% yield (30.2 mg, 0.083 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 4,4'-(sulfinylbis(methylene))bis((trifluoromethyl)benzene) (**1j**; 36.6 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 80 °C for 24 h.

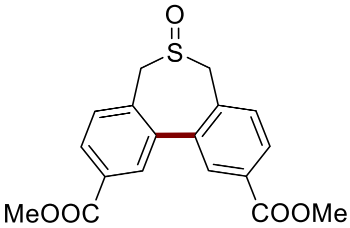
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76–7.72 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 18.7, 7.8 Hz, 2H), 4.34 (d, *J* = 12.0 Hz, 1H), 3.91 (d, *J* = 14.2 Hz, 1H), 3.50 (d, *J* = 14.2 Hz, 1H), 3.26 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 139.9, 133.7, 132.5, 132.4, 132.2 (q, *J* = 32.9 Hz), 131.7 (q, *J* = 33.1 Hz), 130.6, 126.2 (q, *J* = 3.8 Hz), 125.9 (q, *J* = 2.2 Hz), 125.7 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.8 Hz), 122.3 (q, *J* = 270.8 Hz), 55.7, 53.0.

^{19}F NMR (376 MHz, CDCl$_3$) δ –62.60, –62.67.

HRMS (ESI, m/z) found [M+H]$^+$ 365.0427, $C_{16}H_{11}F_6OS^+$ requires 365.0429.

Dimethyl 5,7-dihydrodibenzo[c,e]thiepine-2,10-dicarboxylate 6-oxide (2k)



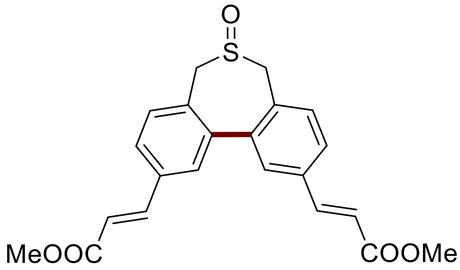
Isolated as a white solid in 73% yield (25.0 mg, 0.073 mmol) by preparative TLC (1/2 Petroleum Ether/EtOAc) according to the general procedures using dimethyl 4,4'-(sulfinylbis(methylene))dibenzoate (**1k**; 34.6 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, *J* = 1.8 Hz, 1H), 8.16 (d, *J* = 1.8 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H), 3.89 (d, *J* = 14.1 Hz, 1H), 3.48 (d, *J* = 14.1 Hz, 1H), 3.27 (d, *J* = 11.9 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.5, 166.3, 139.9, 139.8, 134.3, 133.4, 132.0, 131.5, 131.1, 130.6, 130.2, 130.1, 129.8, 129.6, 55.9, 53.3, 52.6, 52.5.

HRMS (ESI, m/z) found [M+H]$^+$ 345.0789, $C_{18}H_{17}O_5S^+$ requires 345.0791.

Dimethyl 3,3'-(6-oxido-5,7-dihydrodibenzo[c,e]thiepine-2,10-diyl)(2*E*,2'*E*)-diacrylate (2l)



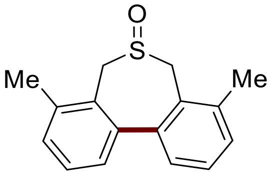
Isolated as a light yellow solid in 51% yield (20.2 mg, 0.051 mmol) by preparative TLC (1/1 Petroleum Ether/EtOAc) according to the general procedures using dimethyl 3,3'-((sulfinylbis(methylene))bis(4,1-phenylene))(2*E*,2'*E*)-diacrylate (**1l**; 39.8 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 (t, *J* = 15.6 Hz, 2H), 7.65–7.50 (m, 4H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.84 (d, *J* = 14.2 Hz, 1H), 3.83 (s, 3H), 3.83 (s, 3H), 3.49 (d, *J* = 14.2 Hz, 1H), 3.26 (d, *J* = 11.9 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.2, 167.1, 143.7, 143.4, 140.5, 140.5, 135.9, 135.4, 132.4, 131.6, 130.6, 130.6, 128.6, 128.3, 128.2, 128.0, 119.5, 119.3, 55.8, 53.2, 52.0, 52.0.

HRMS (ESI, m/z) found [M+H]$^+$ 397.1101, $C_{22}H_{21}O_5S^+$ requires 397.1104.

4,8-Dimethyl-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2m)



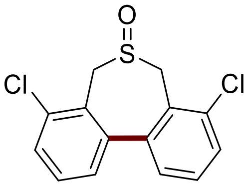
Isolated as a white solid in 81% yield (20.8 mg, 0.081 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 2,2'-(sulfinylbis(methylene))bis(methylbenzene) (**1m**; 25.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38–7.28 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 4.36 (d, *J* = 12.2 Hz, 1H), 4.31 (d, *J* = 14.4 Hz, 1H), 3.25 (d, *J* = 11.9 Hz, 1H), 3.13 (d, *J* = 14.4 Hz, 1H), 2.52 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.8, 141.6, 138.8, 136.7, 130.1, 129.8, 128.8, 128.4, 128.2, 127.9, 127.3, 126.7, 51.9, 48.9, 20.7, 20.3.

HRMS (ESI, m/z) found $[M+H]^+$ 257.0992, $C_{16}H_{17}OS^+$ requires 257.0995.

4,8-Dichloro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2n)



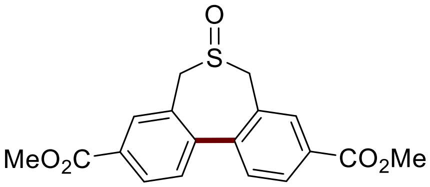
Isolated as a white solid in 82% yield (24.4 mg, 0.082 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 2,2'-(sulfinylbis(methylene))bis(chlorobenzene) (**1n**; 29.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 1H), 7.45–7.35 (m, 4H), 7.30 (d, *J* = 7.6 Hz, 1H), 4.85 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 14.4 Hz, 1H), 3.20 (d, *J* = 12.0 Hz, 1H), 3.13 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.2, 142.1, 136.6, 134.7, 130.1, 130.0, 129.6, 129.5, 128.1, 127.9, 127.7, 127.5, 52.5, 49.5.

HRMS (ESI, m/z) found $[M+H]^+$ 296.9902, $C_{14}H_{11}Cl_2OS^+$ requires 296.9902.

Dimethyl 5,7-dihydrodibenzo[c,e]thiepine-3,9-dicarboxylate 6-oxide (2o)



Isolated as a white solid in 48% yield (16.5 mg, 0.048 mmol) by preparative TLC (1/1 Petroleum Ether/EtOAc) according to the general procedures using dimethyl 3,3'-(sulfinylbis(methylene))dibenzoate (**1o**; 34.6 mg, 0.10 mmol), $AgNTf_2$ (15.6 mg, 0.040 mmol), $[Cp^*IrCl_2]_2$ (8.0 mg, 0.010 mmol), $Mn(OAc)_3·2H_2O$ (10.8 mg, 0.040 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

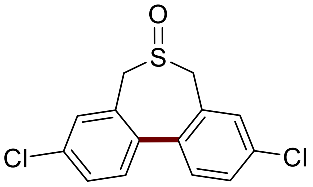
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.16 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.13 (s, 1H), 8.07 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 4.32 (d, *J* = 12.1 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.89 (d, *J* = 14.3 Hz, 1H), 3.47 (d, *J* = 14.3 Hz, 1H), 3.25 (d, *J* = 12.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.2, 144.0, 144.0, 132.8, 131.0, 130.8, 130.7, 130.5, 130.4, 130.1, 129.6, 129.2, 128.9, 55.7, 53.1, 52.6, 52.5.

HRMS (ESI, m/z) found $[M+H]^+$ 345.0789, $C_{18}H_{17}O_5S^+$ requires 345.0791.

The crystal structure is shown in the X-ray Crystallographic Data section.

3,9-Dichloro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (2p)



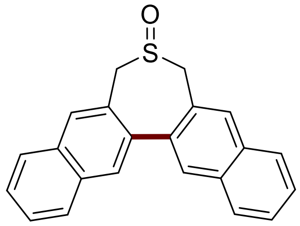
Isolated as a white solid in 54% yield (16.0 mg, 0.054 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 3,3'-(sulfinylbis(methylene))bis(chlorobenzene) (**1p**; 29.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 36 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.49 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.47–7.42 (m, 2H), 7.38 (dd, *J* = 5.2, 3.0 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 4.19 (d, *J* = 12.0 Hz, 1H), 3.77 (d, *J* = 14.3 Hz, 1H), 3.44 (d, *J* = 14.2 Hz, 1H), 3.23 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 137.9, 137.8, 134.7, 134.3, 131.7, 131.4, 130.6, 130.3, 130.2, 129.9, 129.8, 129.4, 55.6, 53.1.

HRMS (ESI, m/z) found [M+H]$^+$ 296.9902, $C_{14}H_{11}Cl_2OS^+$ requires 296.9902.

6,8-Dihydrodinaphtho[2,3-c:2',3'-e]thiepine 7-oxide (2q)



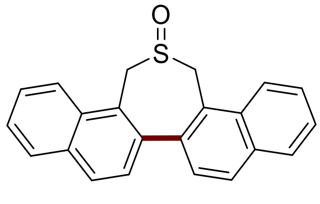
Isolated as a light brown solid in 42% yield (13.8 mg, 0.042 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 2,2'-(sulfinylbis(methylene))dinaphthalene (**1q**; 33.0 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, *J* = 6.5 Hz, 2H), 7.96–7.87 (m, 5H), 7.85 (s, 1H), 7.60–7.53 (m, 4H), 4.44 (d, *J* = 11.9 Hz, 1H), 3.97 (d, *J* = 14.3 Hz, 1H), 3.69 (d, *J* = 14.3 Hz, 1H), 3.45 (d, *J* = 12.0 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.3, 138.2, 133.8, 133.6, 133.2, 132.8, 131.1, 129.4, 128.8, 128.3, 128.1, 128.1, 128.0, 127.8, 127.4, 127.1, 127.0, 126.7, 125.1, 55.5, 53.3.

HRMS (ESI, m/z) found [M+H]$^+$ 329.0990, $C_{22}H_{17}OS^+$ requires 329.0995.

1,3-Dihydrodinaphtho[1,2-c:2',1'-e]thiepine 2-oxide (2r)



Isolated as a white solid in 40% yield (13.1 mg, 0.040 mmol) by preparative TLC (3/1

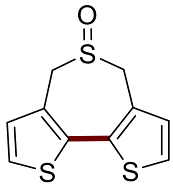
Petroleum Ether/EtOAc) according to the general procedures using 1,1'-(sulfinylbis(methylene))dinaphthalene (**1r**; 33.0 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in HFIP solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 13.8, 8.6 Hz, 2H), 8.02 (dd, *J* = 20.7, 8.4 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.70–7.63 (m, 3H), 7.59 (t, *J* = 7.7 Hz, 2H), 5.00 (d, *J* = 12.3 Hz, 1H), 4.81 (d, *J* = 14.8 Hz, 1H), 3.58 (d, *J* = 12.2 Hz, 1H), 3.45 (d, *J* = 15.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 139.6, 138.9, 133.8, 133.2, 133.0, 131.6, 129.7, 129.3, 129.0, 128.6, 127.9, 127.9, 127.4, 127.1, 127.0, 126.8, 126.7, 126.6, 124.4, 123.6, 51.5, 48.6.

HRMS (ESI, m/z) found $[M+H]^+$ 329.0993, $C_{22}H_{17}OS^+$ requires 329.0995.

4,6-Dihydrodithieno[3,2-c:2',3'-e]thiepine 5-oxide (2s)



Isolated as a light yellow solid in 50% yield (12.0 mg, 0.050 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 3,3'-(sulfinylbis(methylene))dithiophene (**1s**; 24.2 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

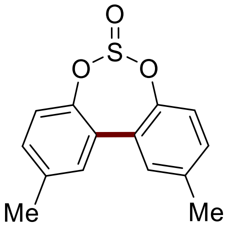
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 5.1 Hz, 2H), 7.16 (d, *J* = 5.1 Hz, 2H), 3.95 (d, *J* = 13.6 Hz, 2H), 3.71 (d, *J* = 13.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.0, 131.5, 130.0, 126.1, 51.5.

HRMS (ESI, m/z) found $[M+H]^+$ 240.9810, $C_{10}H_9OS_3^+$ requires 240.9810.

The crystal structure is shown in the X-ray Crystallographic Data section.

2,10-Dimethyldibenzo[d,f][1,3,2]dioxathiepine 6-oxide (2t)



Isolated as a viscous liquid in 43% yield (11.2 mg, 0.043 mmol) by preparative TLC (30/1 Petroleum Ether/EtOAc) according to the general procedures using di-p-tolyl sulfite (**1t**; 26.2 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3\cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE/DCE mixed solvent (0.3/0.4 mL) at 60 °C for 24 h.

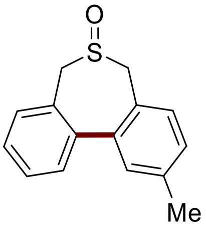
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.21 (q, *J* = 8.3 Hz, 4H), 2.44 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 137.5, 131.2, 130.1, 130.1, 123.1, 21.2.

HRMS (ESI, m/z) found $[M+H]^+$ 261.0576, $C_{14}H_{13}O_3S^+$ requires 261.0580.

6.2 With Non-Symmetric Sulfoxides

2-Methyl-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4a)



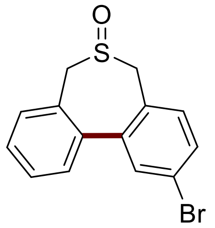
Isolated as a white solid in 95% yield (23.0 mg, 0.095 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-((benzylsulfinyl)methyl)-4-methylbenzene (**3a**; 24.4 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3\cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50–7.40 (m, 3H), 7.36–7.27 (m, 2H), 7.25–7.11 (m, 2H), 4.18 (t, *J* = 10.9 Hz, 1H), 3.76 (t, *J* = 12.7 Hz, 1H), 3.48 (t, *J* = 17.2 Hz, 1H), 3.26, 3.23 (d, *J* = 12.2 Hz, 1H), 2.44, 2.42 (s, 3H). dr = 1/1.

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.8, 140.7, 140.4, 140.4, 139.6, 139.0, 131.6, 131.5, 130.2, 129.9, 129.8, 129.8, 129.7, 129.5, 129.3, 129.2, 129.0, 129.0, 128.8, 128.4, 128.4, 128.0, 126.6, 125.3, 55.8, 55.4, 53.3, 53.1, 21.4.

HRMS (ESI, m/z) found $[M+H]^+$ 243.0836, $C_{15}H_{15}OS^+$ requires 243.0838.

2-Bromo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4b)



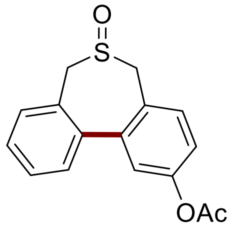
Isolated as a white solid in 85% yield (26.1 mg, 0.085 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using 1-((benzylsulfinyl)methyl)-4-bromobenzene (**3b**; 30.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.63–7.41 (m, 5H), 7.37 (s, 1H), 7.30, 7.24 (d, *J* = 8.2 Hz, 1H), 4.23, 4.17 (d, *J* = 12.1 Hz, 1H), 3.80, 3.76 (d, *J* = 14.2 Hz, 1H), 3.48, 3.43 (d, *J* = 13.7 Hz, 1H), 3.25, 3.20 (d, *J* = 11.6 Hz, 1H). dr = 1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 142.4, 139.2, 139.1, 133.1, 132.3, 131.9, 131.8, 131.4, 131.3, 131.1, 130.1, 129.7, 129.3, 129.2, 129.1, 128.9, 128.7, 128.4, 127.5, 123.5, 123.1, 55.8, 55.3, 53.2, 52.9.

HRMS (ESI, m/z) found $[M+H]^+$ 306.9784, $C_{14}H_{12}BrOS^+$ requires 306.9787.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl acetate (4c)



Isolated as a white solid in 72% yield (20.6 mg, 0.072 mmol) by preparative TLC (1/2 Petroleum Ether/EtOAc) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl acetate (**3c**; 28.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020

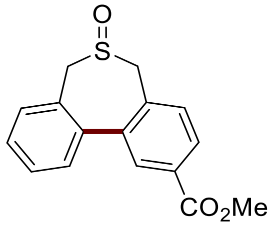
mmol) in TFE solvent (0.5 mL) at 90 °C for 12 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.53–7.35 (m, 5H), 7.24, 7.19 (d, *J* = 2.3 Hz, 1H), 7.16, 7.09 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.22, 4.20 (d, *J* = 10.9 Hz, 1H), 3.80, 3.78 (d, *J* = 14.4 Hz, 1H), 3.53, 3.46 (d, *J* = 13.7 Hz, 1H), 3.30, 3.22 (d, *J* = 11.8 Hz, 1H), 2.34, 2.33 (s, 3H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 169.4, 169.3, 151.5, 151.2, 141.9, 141.8, 139.7, 139.7, 132.8, 131.8, 130.9, 130.0, 129.6, 129.4, 129.2, 129.0, 128.9, 128.5, 128.4, 127.3, 126.1, 122.6, 122.3, 121.5, 121.2, 55.8, 55.2, 53.3, 52.8, 21.3, 21.2.

HRMS (ESI, m/z) found $[M+H]^+$ 287.0735, $C_{16}H_{15}O_3S^+$ requires 287.0736.

Methyl 5,7-dihydrodibenzo[c,e]thiepine-2-carboxylate 6-oxide (4d)



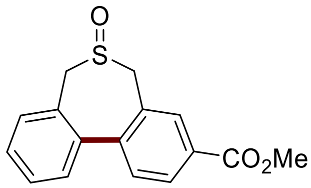
Isolated as a white solid in 94% yield (26.9 mg, 0.094 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using methyl 4-((benzylsulfinyl)methyl)benzoate (**3d**; 28.8 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.16, 8.11 (s, 1H), 8.09, 8.01 (d, *J* = 7.8 Hz, 1H), 7.56–7.43 (m, 4H), 7.38 (d, *J* = 4.1 Hz, 1H), 4.28, 4.24 (d, *J* = 12.1 Hz, 1H), 3.96, 3.95 (s, 3H), 3.86, 3.82 (d, *J* = 14.4 Hz, 1H), 3.52, 3.46 (d, *J* = 14.3 Hz, 1H), 3.30, 3.23 (d, *J* = 12.0 Hz, 1H). dr = 1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 166.5, 166.4, 140.7, 140.7, 139.5, 139.5, 134.3, 133.4, 131.7, 131.7, 131.2, 130.8, 130.3, 130.0, 129.9, 129.7, 129.5, 129.3, 129.2, 129.1, 129.0, 128.9, 128.5, 128.2, 55.8, 55.7, 53.2, 53.1, 52.4, 52.4.

HRMS (ESI, m/z) found $[M+H]^+$ 287.0734, $C_{16}H_{15}O_3S^+$ requires 287.0736.

Methyl 5,7-dihydrodibenzo[c,e]thiepine-3-carboxylate 6-oxide (4e)



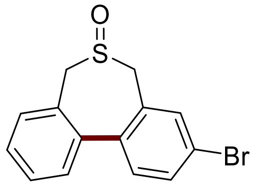
Isolated as a white solid in 53% yield (15.2 mg, 0.053 mmol) by preparative TLC (1/1 Petroleum Ether/EtOAc) according to the general procedures using methyl 3-((benzylsulfinyl)methyl)benzoate (**3e**; 28.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3\cdot2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19, 8.14 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.11, 8.05 (d, *J* = 1.8 Hz, 1H), 7.58–7.43 (m, 4H), 7.39 (d, *J* = 3.7 Hz, 1H), 4.28, 4.25 (d, *J* = 12.0 Hz, 1H), 3.96, 3.95 (s, 3H), 3.86, 3.82 (d, *J* = 14.3 Hz, 1H), 3.51, 3.45 (d, *J* = 14.3 Hz, 1H), 3.28, 3.24 (d, *J* = 12.1 Hz, 1H). dr = 1/1.

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 166.4, 145.2, 145.1, 139.6, 132.7, 131.9, 130.9, 130.7, 130.3, 130.2, 130.1, 130.1, 129.9, 129.7, 129.7, 129.6, 129.5, 129.3, 129.3, 129.0, 128.9, 128.8, 128.5, 55.9, 55.7, 53.2, 52.6, 52.4.

HRMS (ESI, m/z) found $[M+H]^+$ 287.0734, $C_{16}H_{15}O_3S^+$ requires 287.0736.

3-Bromo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4f)



Isolated as a white solid in 84% yield (25.8 mg, 0.084 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-((benzylsulfinyl)methyl)-3-bromobenzene (**3f**; 30.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3\cdot2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

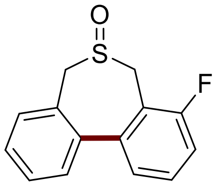
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.28 (m, 7H), 4.23, 4.15 (d, *J* = 11.9 Hz, 1H), 3.81, 3.74 (d, *J* = 14.3 Hz, 1H), 3.48, 3.45 (d, *J* = 13.6 Hz, 1H), 3.28, 3.22 (d, *J* = 11.9 Hz, 1H). dr = 1/1.

^{13}C NMR (100 MHz, CDCl$_3$) δ 139.5, 139.5, 139.4, 134.3, 132.6, 132.6, 132.2, 131.8, 131.7, 130.9, 130.5, 130.5, 130.1, 129.7, 129.6, 129.3, 129.3, 129.2, 128.9, 128.9, 128.5, 128.4, 122.4, 121.9, 55.9, 55.4, 53.3, 53.0.

HRMS (ESI, m/z) found $[M+H]^+$ 306.9785, $C_{14}H_{12}BrOS^+$ requires 306.9787.

The crystal structure is shown in the X-ray Crystallographic Data section.

4-Fluoro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4g)



Isolated as a white solid in 68% yield (16.7 mg, 0.068 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-((benzylsulfinyl)methyl)-2-fluorobenzene (**3g**; 24.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

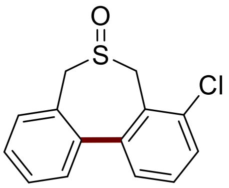
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57–7.33 (m, 5H), 7.31–7.06 (m, 2H), 4.62, 4.27 (d, *J* = 12.0 Hz, 1H), 4.37, 3.83 (d, *J* = 14.2 Hz, 1H), 3.49, 3.14 (d, *J* = 14.3 Hz, 1H), 3.33, 3.00 (d, *J* = 12.0, 1H). dr = 1.5/1.0.

^{13}C NMR (100 MHz, CDCl$_3$) δ 162.3 (d, *J* = 147.2 Hz), 159.8 (d, *J* = 147.3 Hz), 142.9, 142.9, 142.8, 142.7, 139.5 (d, *J* = 2.5 Hz), 139.3 (d, *J* = 2.1 Hz), 131.9, 130.5 (d, *J* = 9.2 Hz), 130.1 (d, *J* = 8.1 Hz), 129.8, 129.6 (d, *J* = 13.6 Hz), 129.2, 129.1, 129.0, 128.6, 128.4, 124.9 (d, *J* = 3.4 Hz), 124.6 (d, *J* = 3.1 Hz), 117.1 (d, *J* = 15.8 Hz), 116.6, 115.3 (d, *J* = 22.6 Hz), 114.9 (d, *J* = 22.5 Hz), 56.2, 53.7, 47.5, 45.4.

^{19}F NMR (376 MHz, CDCl$_3$) δ –116.83, –117.18.

HRMS (ESI, m/z) found $[M+H]^+$ 247.0586, $C_{14}H_{12}FOS^+$ requires 247.0587.

4-Chloro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4h)



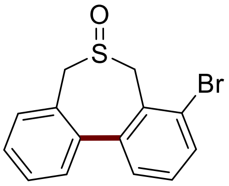
Isolated as a white solid in 50% yield (13.1 mg, 0.050 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-((benzylsulfinyl)methyl)-2-chlorobenzene (**3h**; 26.5 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55–7.33 (m, 7H), 4.77, 4.27 (d, *J* = 12.0 Hz, 1H), 4.72, 3.82 (d, *J* = 14.6 Hz, 1H), 3.44, 3.19 (d, *J* = 14.3 Hz, 1H), 3.36, 3.12 (d, *J* = 12.0 Hz, 1H). dr = 2.3/1.0.

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 142.8, 140.0, 140.0, 136.4, 134.6, 131.9, 130.0, 129.9, 129.6, 129.6, 129.5, 129.5, 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 128.0, 127.9, 127.7, 56.3, 53.9, 52.3, 49.1.

HRMS (ESI, m/z) found $[M+H]^+$ 263.0290, $C_{14}H_{12}ClOS^+$ requires 263.0292.

4-Bromo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4i)



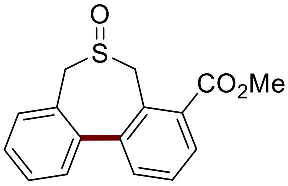
Isolated as a white solid in 80% yield (24.6 mg, 0.080 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-((benzylsulfinyl)methyl)-2-bromobenzene (**3i**; 30.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71, 7.59 (d, *J* = 8.0 Hz, 1H), 7.55–7.28 (m, 6H), 4.76, 4.27 (d, *J* = 12.0 Hz, 1H), 4.73, 3.83 (d, *J* = 14.5 Hz, 1H), 3.43, 3.25 (d, *J* = 14.3 Hz, 1H), 3.37, 3.18 (d, *J* = 12.0 Hz, 1H). dr = 2.6/1.0.

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 140.1, 132.9, 132.4, 131.8, 130.3, 129.8, 129.7, 129.6, 129.5, 129.1, 129.1, 128.8, 128.6, 128.5, 128.5, 128.4, 127.0, 125.1, 56.0, 55.0, 53.7, 51.4.

HRMS (ESI, m/z) found $[M+H]^+$ 306.9786, $C_{14}H_{12}BrOS^+$ requires 306.9787.

Methyl 5,7-dihydrodibenzo[c,e]thiepine-4-carboxylate 6-oxide (4j)



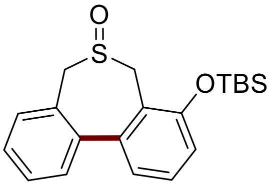
Isolated as a white solid in 60% yield (17.2 mg, 0.060 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using methyl 2-((benzylsulfinyl)methyl)benzoate (**3j**; 28.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02, 7.96 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64–7.33 (m, 6H), 5.41, 3.82 (d, *J* = 14.2 Hz, 1H), 5.12, 4.21 (d, *J* = 11.7 Hz, 1H), 3.97, 3.94 (s, 3H), 3.43, 3.19 (d, *J* = 14.1 Hz, 1H), 3.23, 3.12 (d, *J* = 11.5 Hz, 1H). dr = 3.0/1.0.

^{13}C NMR (151 MHz, CDCl$_3$) δ 167.2, 142.7, 142.6, 139.9, 133.2, 132.9, 131.7, 130.6, 130.6, 130.5, 130.3, 129.8, 129.7, 129.6, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.4, 55.5, 53.4, 52.8, 52.8, 47.0.

HRMS (ESI, m/z) found $[M+H]^+$ 287.0735, $C_{16}H_{15}O_3S^+$ requires 287.0736.

4-((*tert*-Butyldimethylsilyl)oxy)-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4k)



Isolated as a white solid in 48% yield (17.2 mg, 0.048 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using (2-((benzylsulfinyl)methyl)phenoxy)(*tert*-butyl)dimethylsilane (**3k**; 36.1 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol),

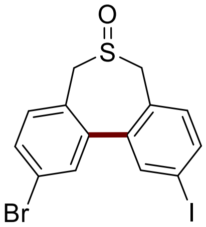
$Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52–7.27 (m, 5H), 7.03, 7.01 (d, *J* = 7.7 Hz, 1H), 6.95, 6.85 (d, *J* = 8.2 Hz, 1H), 4.71, 4.19 (d, *J* = 11.6 Hz, 1H), 4.56, 3.78 (d, *J* = 14.2 Hz, 1H), 3.47, 2.99 (d, *J* = 14.2 Hz, 1H), 3.39, 2.93 (d, *J* = 11.8 Hz, 1H), 1.05, 1.04 (s, 9H), 0.36, 0.32 (s, 3H), 0.30, 0.28 (s, 3H). dr = 5.7/1.0.

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 153.7, 142.6, 142.5, 140.8, 131.7, 129.8, 129.7, 129.7, 129.4, 129.3, 129.1, 128.9, 128.9, 128.5, 128.5, 128.0, 122.0, 121.6, 120.5, 120.2, 118.1, 117.7, 56.1, 53.9, 49.0, 46.2, 26.0, 25.9, 18.5, -3.9, -4.0.

HRMS (ESI, m/z) found $[M+H]^+$ 359.1493, $C_{20}H_{27}O_2SSi^+$ requires 359.1496.

2-Bromo-10-iodo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4l)



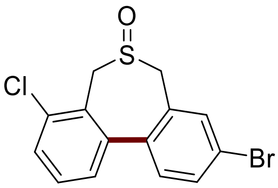
Isolated as a white solid in 62% yield (26.8 mg, 0.062 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-bromo-4-(((4-iodobenzyl)sulfinyl)methyl)benzene (**3l**; 43.5 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.67 (m, 2H), 7.63–7.46 (m, 2H), 7.29, 7.24 (d, *J* = 8.0 Hz, 1H), 7.16, 7.10 (d, *J* = 8.0 Hz, 1H), 4.18, 4.17 (d, *J* = 12.1 Hz, 1H), 3.76, 3.75 (d, *J* = 14.3 Hz, 1H), 3.41, 3.40 (d, *J* = 14.2 Hz, 1H), 3.17, 3.16 (d, *J* = 12.1 Hz, 1H). dr=1/1.

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.1, 141.0, 140.8, 138.1, 138.0, 137.7, 137.7, 133.4, 133.3, 132.3, 132.0, 131.8, 131.7, 131.5, 131.4, 129.4, 128.8, 128.2, 127.5, 123.7, 123.3, 95.3, 94.8, 55.5, 55.4, 53.0, 52.9.

HRMS (ESI, m/z) found $[M+H]^+$ 432.8753, $C_{14}H_{11}BrIOS^+$ requires 432.8753.

3-Bromo-8-chloro-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4m)



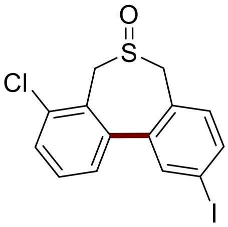
Isolated as a white solid in 79% yield (27.0 mg, 0.079 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-(((3-bromobenzyl)sulfinyl)methyl)-2-chlorobenzene (**3m**; 34.4 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.28 (m, 6H), 4.80, 4.74 (d, *J* = 14.4 Hz, 1H), 4.22, 3.79 (d, *J* = 14.3 Hz, 1H), 3.39, 3.31 (d, *J* = 14.2 Hz, 1H), 3.18, 3.13 (d, *J* = 12.0 Hz, 1H). dr = 2.5/1.0.

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.7, 141.6, 138.9, 138.8, 136.6, 134.8, 134.5, 132.7, 132.6, 132.2, 131.9, 130.9, 130.6, 130.3, 130.2, 129.9, 129.7, 129.4, 127.8, 127.7, 127.6, 127.5, 123.0, 122.5, 55.7, 53.5, 52.2, 49.1.

HRMS (ESI, m/z) found $[M+H]^+$ 340.9392, $C_{14}H_{11}BrClOS^+$ requires 340.9397.

8-Chloro-2-iodo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4n)



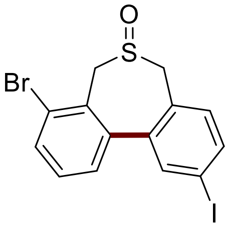
Isolated as a white solid in 64% yield (24.9 mg, 0.064 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-chloro-2-(((4-iodobenzyl)sulfinyl)methyl)benzene (**3n**; 39.1 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95–7.29 (m, 5H), 7.16, 7.10 (d, *J* = 8.0 Hz, 1H), 4.79, 4.22 (d, *J* = 12.1 Hz, 1H), 4.73, 3.78 (d, *J* = 14.4 Hz, 1H), 3.36, 3.17 (d, *J* = 14.3 Hz, 1H), 3.27, 3.09 (d, *J* = 12.0 Hz, 1H). dr = 2.3/1.0.

^{13}C NMR (151 MHz, CDCl$_3$) δ 141.9, 141.8, 141.3, 141.1, 138.3, 138.0, 137.6, 134.8, 133.3, 131.4, 130.2, 130.1, 129.7, 129.6, 129.5, 128.2, 128.0, 127.8, 127.6, 127.6, 95.2, 94.7, 55.8, 53.5, 52.2, 49.0.

HRMS (ESI, m/z) found [M+H]$^+$ 388.9251, $C_{14}H_{11}ClIOS^+$ requires 388.9258.

8-Bromo-2-iodo-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4o)



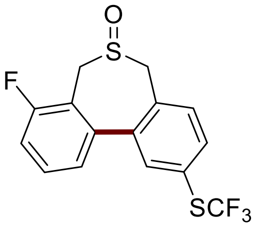
Isolated as a white solid in 76% yield (32.9 mg, 0.076 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using 1-bromo-2-(((4-iodobenzyl)sulfinyl)methyl)benzene (**3o**; 43.5 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86–7.58 (m, 3H), 7.41–7.28 (m, 2H), 7.16, 7.07 (d, *J* = 7.9 Hz, 1H), 4.78, 4.22 (d, *J* = 12.1 Hz), 4.75, 3.79 (d, *J* = 14.2 Hz, 1H), 3.35, 3.24 (d, *J* = 14.3 Hz, 1H), 3.29, 3.16 (d, *J* = 11.9 Hz, 1H). dr = 2.9/1.0.

^{13}C NMR (100 MHz, CDCl$_3$) δ 142.0, 141.2, 138.2, 138.0, 137.5, 133.4, 133.3, 132.9, 130.5, 129.8, 129.5, 128.4, 128.2, 125.2, 94.7, 55.0, 53.4.

HRMS (ESI, m/z) found [M+H]$^+$ 432.8753, $C_{14}H_{11}BrIOS^+$ requires 432.8753.

8-Fluoro-2-((trifluoromethyl)thio)-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4p)



Isolated as a white solid in 80% yield (27.7 mg, 0.080 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using (4-(((2-fluorobenzyl)sulfinyl)methyl)phenyl)(trifluoromethyl)sulfane (**3p**; 34.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

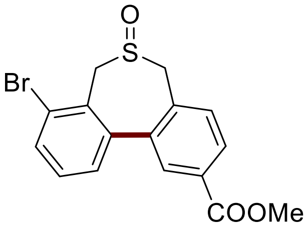
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83–7.61 (m, 2H), 7.54–7.41 (m, 2H), 7.33–7.07 (m, 2H), 4.66, 4.31 (d, *J* = 12.2 Hz, 1H), 4.41, 3.86 (d, *J* = 14.5 Hz, 1H), 3.49, 3.13 (d, *J* = 14.2 Hz, 1H), 3.33, 2.98 (d, *J* = 12.0 Hz, 1H). dr = 1.8/1.0.

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7 (d, *J* = 251.6 Hz), 160.4 (d, *J* = 250.5 Hz), 141.3 (d, *J* = 3.0 Hz), 141.1 (d, *J* = 3.1 Hz), 140.8 (d, *J* = 2.0 Hz), 140.7 (d, *J* = 1.9 Hz), 136.7, 136.3, 136.0, 132.9, 132.7, 131.7, 131.0, 130.9, 130.9, 130.4 (d, *J* = 8.9 Hz), 129.5 (q, *J* = 308.0 Hz), 129.4 (q, *J* = 308.0 Hz), 126.1, 125.6 (d, *J* = 1.9 Hz), 125.0 (d, *J* = 3.3 Hz), 124.7 (d, *J* = 3.3 Hz), 117.3 (d, *J* = 15.5 Hz), 116.7 (d, *J* = 16.3 Hz), 116.1 (d, *J* = 22.8 Hz), 115.7 (d, *J* = 22.0 Hz), 56.0, 53.4, 47.7 (d, *J* = 3.2 Hz), 45.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ –42.23, –116.22, –116.58.

HRMS (ESI, m/z) found $[M+H]^+$ 347.0180, $C_{15}H_{11}F_4OS_2^+$ requires 347.0182.

Methyl 8-bromo-5,7-dihydrodibenzo[c,e]thiepine-2-carboxylate 6-oxide (4q)



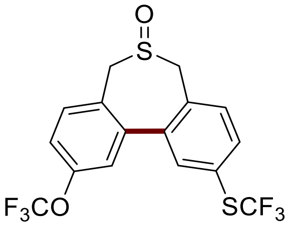
Isolated as a white solid in 69% yield (25.2 mg, 0.069 mmol) by preparative TLC (2/1 Petroleum Ether/EtOAc) according to the general procedures using methyl 4-(((2-bromobenzyl)sulfinyl)methyl)benzoate (**3q**; 36.7 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 48 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21–7.98 (m, 2H), 7.77–7.32 (m, 4H), 4.79, 4.34 (d, *J* = 12.0 Hz, 1H), 4.77, 3.90 (d, *J* = 14.4 Hz, 1H), 3.97, 3.95 (s, 3H), 3.46, 3.21 (d, *J* = 14.2 Hz, 1H), 3.42, 3.15 (d, *J* = 12.0 Hz, 1H). dr = 3.3/1.0.

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 141.7, 140.2, 133.4, 133.2, 132.8, 131.9, 130.8, 130.5, 130.3, 130.0, 129.8, 129.8, 129.6, 129.5, 128.6, 125.1, 55.0, 53.5, 52.5.

HRMS (ESI, m/z) found $[M+H]^+$ 364.9841, $C_{16}H_{14}BrO_3S^+$ requires 364.9842.

2-(Trifluoromethoxy)-10-((trifluoromethyl)thio)-5,7-dihydrodibenzo[c,e]thiepine 6-oxide (4r)



Isolated as a white solid in 63% yield (26.0 mg, 0.063 mmol) by preparative TLC (3/1 Petroleum Ether/EtOAc) according to the general procedures using (4-(((4-(trifluoromethoxy)benzyl)sulfinyl)methyl)phenyl)(trifluoromethyl)sulfane (**3r**; 41.4 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

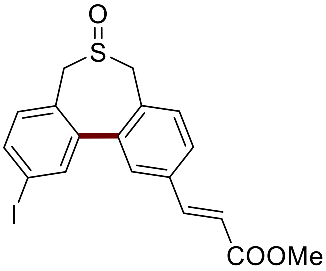
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.79–7.64 (m, 2H), 7.56–7.40 (m, 2H), 7.37–7.23 (m, 2H), 4.29, 4.27 (d, *J* = 12.1 Hz, 1H), 3.86, 3.84 (d, *J* = 14.4 Hz, 1H), 3.50, 3.45 (d, *J* = 14.4 Hz, 1H), 3.26, 3.22 (d, *J* = 12.1 Hz, 1H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 150.1, 149.8, 140.8, 140.7, 140.5, 140.4, 136.4, 136.4, 136.1, 133.4, 132.9, 132.6, 131.6, 131.6, 131.5, 131.2, 131.0, 129.4 (q, *J* = 308.4 Hz), 129.3 (q, *J* = 308.6 Hz), 128.4, 127.2, 121.8, 121.4, 121.2, 120.8, 120.5 (q, *J* = 258.3 Hz), 120.4 (q, *J* = 258.3 Hz), 55.5, 55.1, 52.9, 52.6.

^{19}F NMR (376 MHz, CDCl$_3$) δ –42.18, –42.19, –57.74, –57.77.

HRMS (ESI, m/z) found $[M+H]^+$ 413.0101, $C_{16}H_{11}F_6O_2S_2^+$ requires 413.0099.

Methyl (*E*)-3-(10-iodo-6-oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl)acrylate (4s)



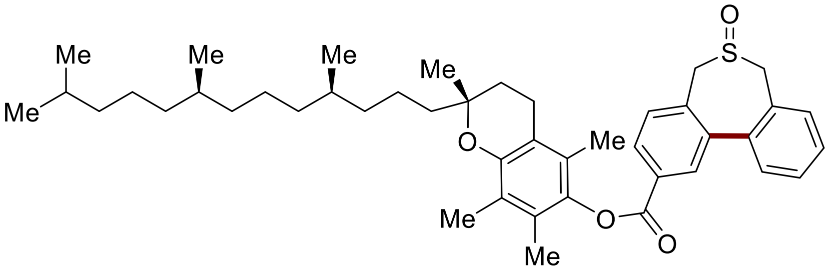
Isolated as a light yellow solid in 72% yield (31.6 mg, 0.072 mmol) by preparative TLC (1/1 Petroleum Ether/EtOAc) according to the general procedures using methyl (*E*)-3-(4-(((4-iodobenzyl)sulfinyl)methyl)phenyl)acrylate (**3s**; 44.0 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89–7.70 (m, 3H), 7.63–7.48 (m, 2H), 7.45, 7.39 (d, *J* = 8.2 Hz, 1H), 7.17, 7.11 (d, *J* = 8.0 Hz, 1H), 6.54, 6.51 (d, *J* = 16.0 Hz, 1H), 4.25, 4.19 (d, *J* = 12.0 Hz, 1H), 3.84, 3.83 (s, 3H), 3.81, 3.76 (d, *J* = 14.3 Hz, 1H), 3.48, 3.42 (d, *J* = 14.3 Hz, 1H), 3.25, 3.19 (d, *J* = 12.0 Hz, 1H). dr=1/1.

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 167.1, 143.6, 143.4, 141.8, 141.8, 139.7, 139.7, 138.2, 137.9, 137.7, 137.6, 136.0, 135.5, 133.4, 132.4, 131.6, 131.5, 130.6, 129.4, 129.0, 128.6, 128.4, 128.3, 128.2, 128.1, 119.6, 119.4, 95.4, 94.8, 55.8, 55.6, 53.2, 53.1, 52.0, 52.0.

HRMS (ESI, m/z) found $[M+H]^+$ 438.9860, $C_{18}H_{16}IO_3S^+$ requires 438.9859.

(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 5,7-dihydrodibenzo[c,e]thiepine-2-carboxylate 6-oxide (5a)



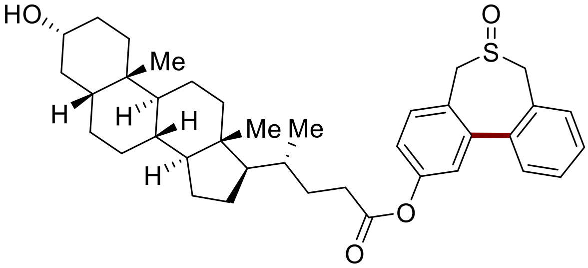
Isolated as a white solid in 65% yield (44.5 mg, 0.065 mmol) by preparative TLC (1/1 Petroleum Ether/EtOAc) according to the general procedures using (*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl 4-((benzylsulfinyl)methyl)benzoate (**s5a**; 68.7 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54–8.12 (m, 2H), 7.82–7.29 (m, 5H), 4.31, 4.28 (d, *J* = 11.9 Hz, 1H), 3.90, 3.85 (d, *J* = 14.2 Hz, 1H), 3.56, 3.53 (d, *J* = 14.2 Hz, 1H), 3.35, 3.30 (d, *J* = 11.9 Hz, 1H), 2.63 (s, 2H), 2.25–1.94 (m, 9H), 1.84–1.75 (m, 2H), 1.64–0.99 (m, 24H), 0.87–0.84 (m, 12H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 164.8, 164.6, 149.7, 141.1, 141.1, 140.7, 140.6, 139.6, 139.6, 135.0, 134.1, 132.0, 131.9, 130.9, 130.9, 130.7, 130.4, 130.2, 130.1, 129.9, 129.8, 129.8, 129.7, 129.4, 129.3, 129.1, 128.7, 128.5, 127.0, 126.9, 125.2, 125.1, 123.4, 117.7, 75.3, 75.3, 56.1, 56.0, 53.5, 53.3, 40.6, 39.7, 39.5, 37.6, 37.4, 32.9, 32.9, 32.8, 31.4, 31.1, 29.8, 29.5, 28.1, 27.4, 24.9, 24.6, 24.4, 23.8, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 14.3, 13.2, 12.4, 12.0.

HRMS (ESI, m/z) found [M+H]$^+$ 685.4284, $C_{44}H_{61}O_4S^+$ requires 685.4285.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl (4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (5b)



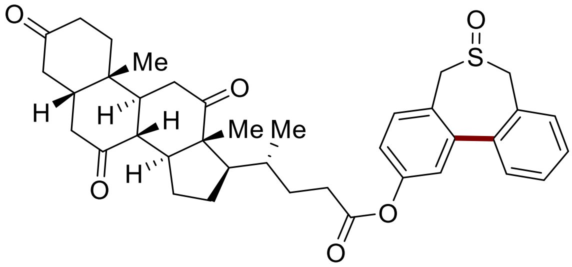
Isolated as a white solid in 63% yield (38.0 mg, 0.063 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl (4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (**s5b**; 60.5 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE/DCE mixed solvent (0.5 mL/0.25 mL) at 80 °C for 2 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.53–7.31 (m, 5H), 7.23, 7.18 (d, *J* = 2.4 Hz, 1H), 7.14, 7.07 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.22, 4.20 (d, *J* = 12.0 Hz, 1H), 3.79, 3.77 (d, *J* = 14.3 Hz, 1H), 3.62 (tt, *J* = 10.7, 4.7 Hz, 1H), 3.53, 3.45 (d, *J* = 14.3 Hz, 1H), 3.30, 3.22 (d, *J* = 12.0 Hz, 1H), 2.72–2.57 (m, 1H), 2.55–2.42 (m, 1H), 2.02–1.62 (m, 9H), 1.55–1.03 (m, 18H), 0.99 (t, *J* = 5.8 Hz, 3H), 0.92 (s, 3H), 0.67 (dd, *J* = 3.6, 2.1 Hz, 3H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 172.7, 151.6, 151.3, 141.8, 141.7, 139.8, 139.7, 132.7, 131.8, 130.9, 130.0, 129.6, 129.6, 129.4, 129.1, 129.0, 128.9, 128.4, 128.4, 127.1, 125.9, 122.7, 122.3, 121.5, 121.2, 71.9, 71.9, 56.6, 56.0, 55.7, 55.2, 53.3, 52.8, 42.9, 42.2, 40.5, 40.3, 36.5, 35.9, 35.5, 34.7, 31.5, 31.4, 31.0, 31.0, 30.6, 28.4, 27.3, 26.5, 24.3, 23.5, 20.9, 18.4, 12.2.

HRMS (ESI, m/z) found $[M+H]^+$ 603.3506, $C_{38}H_{51}O_4S^+$ requires 603.3503.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl (4*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (5c)



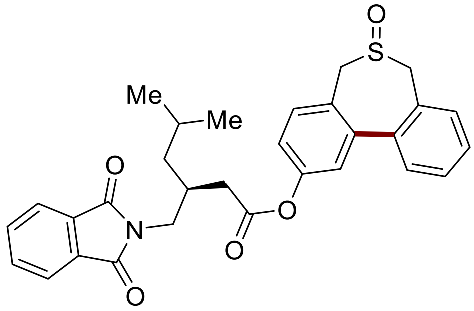
Isolated as a white solid in 60% yield (37.6 mg, 0.060 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl (4*R*)-4-((5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (**s5c**; 63.1 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 80 °C for 12 h.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59–7.28 (m, 5H), 7.26–7.04 (m, 2H), 4.22, 4.20 (d, *J* = 12.0 Hz, 1H), 3.80, 3.78 (d, *J* = 14.3 Hz, 1H), 3.53, 3.46 (d, *J* = 14.3 Hz, 1H), 3.29, 3.22 (d, *J* = 12.0 Hz, 1H), 2.98–2.82 (m, 3H), 2.75–2.50 (m, 2H), 2.40–1.78 (m, 14H), 1.71–1.47 (m, 2H), 1.47–1.20 (m, 6H), 1.10-1.09 (m, 3H), 0.99–0.87 (m, 3H). dr=1/1.

^{13}C NMR (101 MHz, CDCl$_3$) δ 212.0, 209.2, 209.1, 208.8, 172.4, 151.6, 151.3, 141.9, 141.8, 139.8, 139.7, 132.7, 131.8, 130.9, 130.0, 129.7, 129.6, 129.4, 129.1, 129.0, 128.9, 128.5, 128.4, 127.2, 126.0, 122.6, 122.3, 121.5, 121.2, 57.0, 55.8, 55.2, 53.3, 52.8, 51.9, 49.1, 46.9, 45.7, 45.7, 45.7, 45.1, 42.9, 38.7, 36.6, 36.1, 35.6, 35.4, 31.7, 31.6, 30.5, 27.8, 25.2, 22.0, 18.8, 12.0.

HRMS (ESI, m/z) found $[M+H]^+$ 629.2931, $C_{38}H_{45}O_6S^+$ requires 629.2931.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl (3*S*)-3-((1,3-dioxoisoindolin-2-yl)methyl)-5-methylhexanoate (5d)



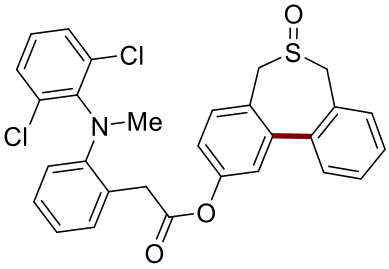
Isolated as a white solid in 75% yield (38.7 mg, 0.075 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl (3*S*)-3-((1,3-dioxoisoindolin-2-yl)methyl)-5-methylhexanoate (**s5d**; 51.7 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE/DCE solvent (0.3 mL/0.4 mL) at 90 °C for 20 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.86–7.76 (m, 2H), 7.72–7.60 (m, 2H), 7.56–7.29 (m, 5H), 7.22–7.01 (m, 2H), 4.24–4.15 (m, 1H), 3.85–3.66 (m, 3H), 3.52–3.38 (m, 1H), 3.28–3.15 (m, 1H), 2.69–2.50 (m, 3H), 1.82 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.45–1.19 (m, 2H), 1.03–0.97 (m, 3H), 0.98–0.92 (m, 3H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 171.0, 171.0, 170.9, 168.8, 151.5, 151.2, 141.7, 141.6, 139.8, 139.7, 134.1, 134.1, 132.6, 132.1, 131.7, 130.8, 130.0, 129.7, 129.6, 129.6, 129.5, 129.1, 129.1, 129.0, 128.8, 128.4, 127.2, 125.9, 123.4, 123.4, 122.7, 122.6, 122.3, 122.2, 121.6, 121.5, 121.2, 121.2, 55.7, 55.2, 53.3, 52.9, 41.9, 41.9, 41.8, 37.8, 37.7, 33.0, 32.9, 32.8, 25.5, 22.9, 22.8, 22.7, 22.7.

HRMS (ESI, m/z) found $[M+H]^+$ 516.1841, $C_{30}H_{30}NO_5S^+$ requires 516.1839.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl 2-(2-((2,6-dichlorophenyl)(methyl)amino)phenyl)acetate (5e)

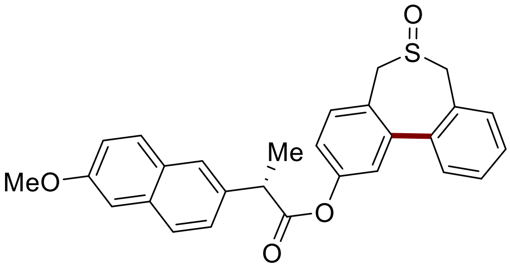


Isolated as a white solid in 52% yield (27.9 mg, 0.052 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl 2-(2-((2,6-dichlorophenyl)(methyl)amino)phenyl)acetate (**s5e**; 53.8 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE/DCE mixed solvent (0.5 mL/0.25 mL) at 80 °C for 5 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54–7.28 (m, 8H), 7.24–7.15 (m, 2H), 7.14–6.92 (m, 4H), 4.19, 4.17 (d, *J* = 12.0 Hz, 1H), 3.77, 3.75 (d, *J* = 14.3 Hz, 1H), 3.60, 3.58 (s, 2H), 3.48, 3.42 (d, *J* = 14.3 Hz, 1H), 3.31, 3.30 (s, 3H), 3.25, 3.18 (d, *J* = 12.0 Hz, 1H). dr=1/1.

HRMS (ESI, m/z) found $[M+H]^+$ 536.0850, $C_{29}H_{24}Cl_2NO_3S^+$ requires 536.0848.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (5f)



Isolated as a white solid in 86% yield (39.3 mg, 0.086 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**s5f**; 45.9 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3·2H_2O$ (5.4 mg, 0.020 mmol) in TFE solvent (0.5 mL) at 80 °C for 14 h.

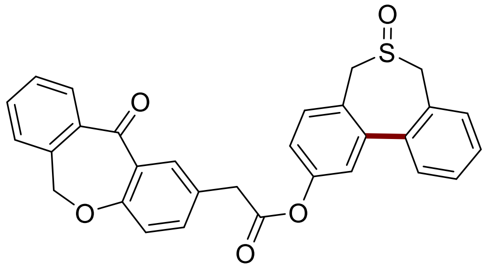
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80–7.67 (m, 3H), 7.55–7.28 (m, 6H), 7.20–6.94 (m, 4H), 4.24–4.05 (m, 2H), 3.91, 3.91 (s, 3H), 3.75, 3.74 (d, *J* = 14.1 Hz, 1H), 3.49–3.38

(m, 1H), 3.28–3.14 (m, 1H), 1.71, 1.70 (d, *J* = 6.8 Hz, 3H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 173.1, 157.9, 157.9, 151.7, 151.4, 141.8, 141.7, 139.7, 139.6, 135.0, 134.9, 134.9, 134.0, 132.7, 132.6, 131.7, 130.8, 129.9, 129.6, 129.6, 129.4, 129.4, 129.1, 129.0, 128.8, 128.4, 128.4, 127.6, 127.6, 127.2, 126.3, 126.2, 126.1, 126.1, 126.0, 122.5, 122.4, 122.1, 121.3, 121.3, 121.0, 121.0, 119.3, 119.3, 105.7, 55.7, 55.4, 55.2, 53.2, 52.8, 45.7, 18.6, 18.6, 18.6, 18.5.

HRMS (ESI, m/z) found [M+H]$^+$ 457.1465, $C_{28}H_{25}O_4S^+$ requires 457.1468.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (5g)



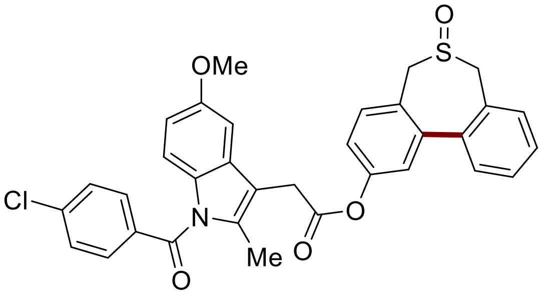
Isolated as a white solid in 42% yield (20.7 mg, 0.042 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (**s5g**; 49.7 mg, 0.10 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) in TFE/DCE mixed solvent (0.5 mL/0.5 mL) at 90 °C for 24 h.

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.23 (dd, *J* = 5.3, 2.4 Hz, 1H), 7.89 (dd, *J* = 7.8, 3.4 Hz, 1H), 7.63–7.30 (m, 10H), 7.24–7.13 (m, 1H), 7.08 (dt, *J* = 8.5, 2.9 Hz, 1H), 5.21 (s, 2H), 4.20, 4.19 (d, *J* = 12.1 Hz, 1H), 3.92, 3.91 (s, 2H), 3.79, 3.77 (d, *J* = 14.4 Hz, 1H), 3.52, 3.47 (d, *J* = 14.3 Hz, 1H), 3.29, 3.27 (d, *J* = 12.0 Hz, 1H). dr=1/1.

^{13}C NMR (151 MHz, CDCl$_3$) δ 190.9, 169.8, 160.8, 151.5, 151.2, 141.9, 141.8, 140.5, 140.5, 139.7, 139.6, 136.4, 136.4, 135.6, 133.0, 133.0, 132.8, 132.8, 131.8, 130.9, 130.0, 129.6, 129.6, 129.6, 129.5, 129.4, 129.2, 129.1, 128.9, 128.5, 128.4, 128.0, 128.0, 127.3, 127.1, 127.0, 126.2, 125.4, 122.5, 122.2, 121.5, 121.5, 121.4, 121.1, 73.8, 55.7, 55.2, 53.2, 52.8, 40.4.

HRMS (ESI, m/z) found [M+H]$^+$ 495.1262, $C_{30}H_{23}O_5S^+$ requires 495.1261.

6-Oxido-5,7-dihydrodibenzo[c,e]thiepin-2-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (5h)



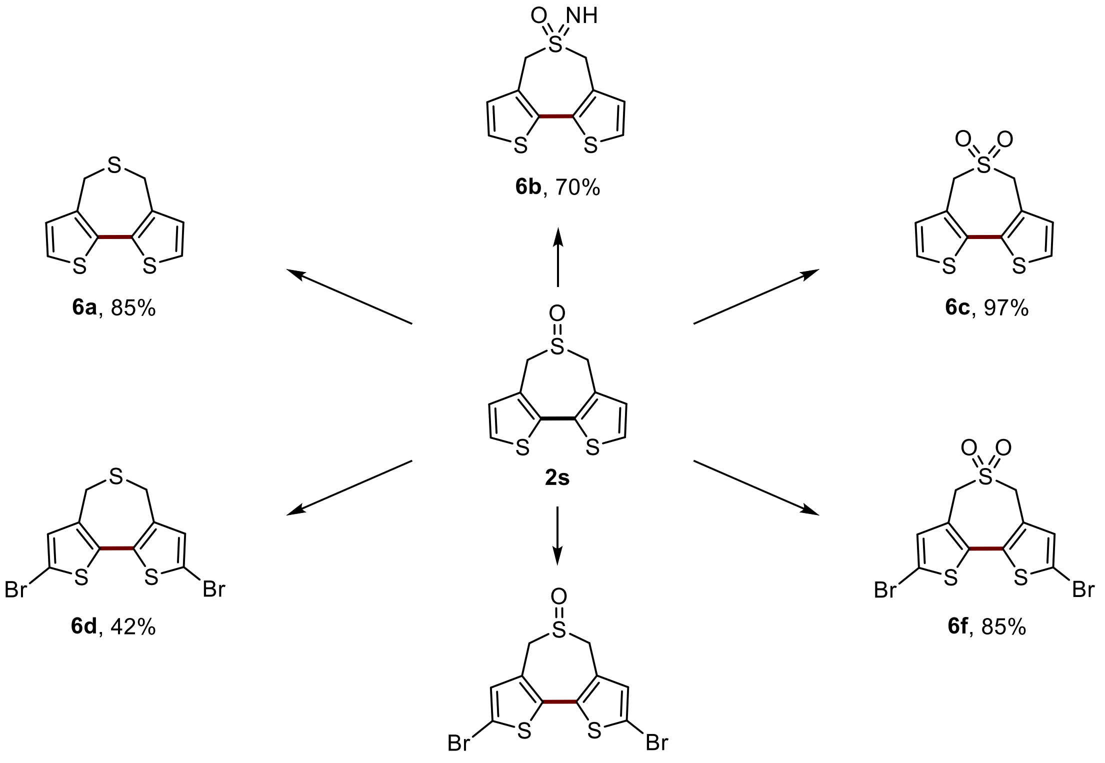
Isolated as a white solid in 78% yield (45.5 mg, 0.078 mmol) according to the general procedures using 4-((benzylsulfinyl)methyl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (**s5h**; 58.6 mg, 0.10 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol) in TFE/DCE mixed solvent (1.0 mL/0.5 mL) at 80 °C for 16 h.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.5, 3.2 Hz, 2H), 7.52–7.31 (m, 7H), 7.21, 7.16 (d, *J* = 2.4 Hz, 1H), 7.14–7.04 (m, 2H), 6.89 (dd, *J* = 8.9, 7.8 Hz, 1H), 6.70 (d, *J* = 9.0 Hz, 1H), 4.20, 4.19 (d, *J* = 11.2 Hz, 1H), 3.94, 3.93 (s, 2H), 3.84, 3.83 (s, 3H), 3.78, 3.77 (d, *J* = 14.4 Hz, 1H), 3.48, 3.44 (d, *J* = 14.3 Hz, 1H), 3.26, 3.22 (d, *J* = 12.0 Hz, 1H), 2.47 (s, 3H). dr=1/1.

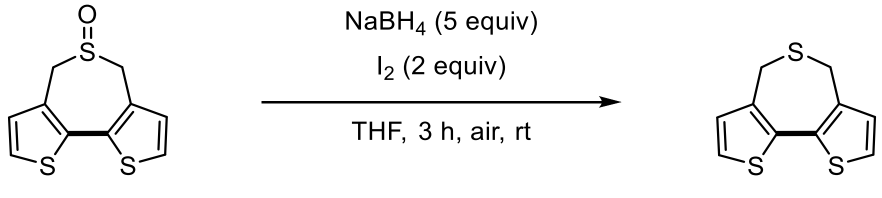
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.2, 169.2, 168.4, 156.2, 156.2, 151.5, 151.2, 141.9, 141.8, 139.6, 139.6, 139.5, 139.4, 136.5, 136.4, 133.9, 133.8, 132.7, 131.8, 131.3, 131.0, 130.9, 130.6, 130.5, 130.0, 129.6, 129.4, 129.3, 129.2, 129.0, 128.9, 128.5, 128.4, 127.4, 126.2, 122.5, 122.1, 121.3, 121.0, 115.1, 111.9, 111.8, 111.7, 101.4, 101.4, 55.9, 55.7, 55.1, 53.2, 52.8, 30.7, 30.6, 13.6, 13.5.

HRMS (ESI, m/z) found $[M+H]^+$ 584.1293, $C_{33}H_{27}ClNO_5S^+$ requires 584.1293.

7. Derivatizations of the Bithiophene-Based Seven-Membered-Ring Sulfoxide



Reduction of 2s to 6a



The conditions were adapted from the reported literature.[11] To a stirred solution of **2s** (24.0 mg, 0.10 mmol) and I_2 (50.8 mg, 0.20 mmol) in THF (1.0 mL) was added $NaBH_4$ (18.9 mg, 0.50 mmol) in one portion. The mixture was stirred at rt for 3 h. After the reaction, the solvent was evaporated to dryness. The residue was purified by by column chromatography (Petroleum Ether) on silica gel to afford the desired product **6a** (19.1 mg, 0.085 mmol) as a light-yellow solid in 85% yield.

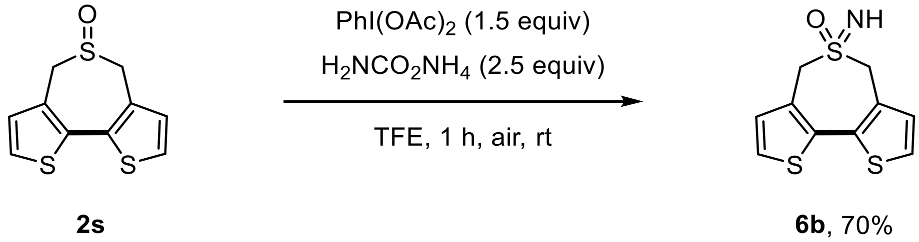
4,6-Dihydrodithieno[3,2-c:2',3'-e]thiepine (6a)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, J = 5.1 Hz, 2H), 6.92 (d, J = 5.1 Hz, 2H), 3.81 (s, 4H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 137.6, 133.2, 129.6, 123.9, 31.0.

HRMS (ESI, m/z) found $[M+H]^+$ 224.9859, $C_{10}H_9S_3^+$ requires 224.9861.

Imidation of 2s to 6b



The conditions were adapted from the reported literature.[12] To an 8 mL glass vial was added a stirrer, **2s** (48.1 mg, 0.20 mmol), PhI(OAc)$_2$ (96.6 mg, 0.30 mmol), $NH_2CO_2NH_4$ (39.0 mg, 0.50 mmol) and TFE (1.0 mL) at last. The mixture was stirred at rt for 1 h. After the reaction, the solvent was evaporated to dryness. The residue was purified by by column chromatography (1/4 Petroleum Ether/EtOAc) on silica gel to afford the desired product **6b** (35.8 mg, 0.14 mmol) as a light-yellow solid in 70% yield.

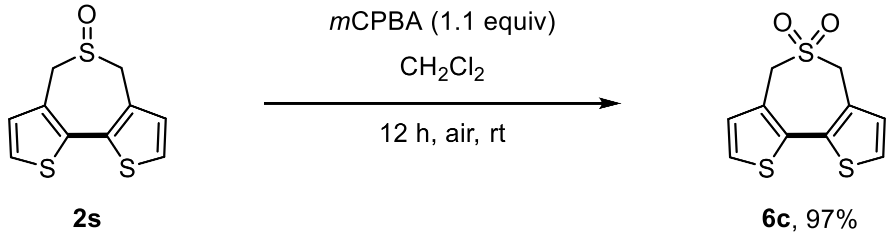
5-Imino-5,6-dihydro-4*H*-5λ^4-dithieno[3,2-c:2',3'-e]thiepine 5-oxide (6b)

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.41 (d, *J* = 5.1 Hz, 2H), 7.17 (d, *J* = 5.2 Hz, 2H), 4.19 (s, 4H), 2.81 (br, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 134.3, 130.2, 129.6, 127.4, 57.4.

HRMS (ESI, m/z) found $[M+H]^+$ 255.9914, $C_{10}H_{10}NOS_3^+$ requires 255.9919.

Oxidation of 2s to 6c



The conditions were adapted from the reported literature.[13] To a stirred solution of **2s** (24.0 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) was added *m*CPBA (22.3 mg, 0.10 mmol) in one portion. The mixture was stirred at rt for 12 h. After the reaction, K_2CO_3 (sat.

aq) was added to the reaction mixture to quench the reaction. The organic layer was collected. The aqueous layer was extracted with CH_2Cl_2 (5 mL) three times. The combined organic extracts were dried over Na_2SO_4, and concentrated to afford the desired product **6c** (25.0 mg, 0.097 mmol) as a light-yellow solid in 97% yield.

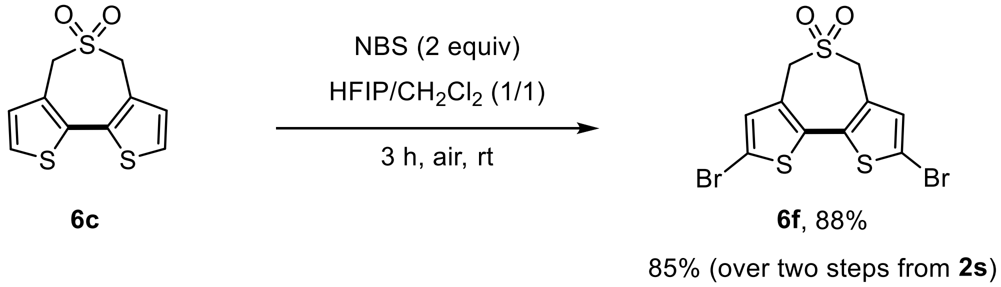
4,6-Dihydrodithieno[3,2-c:2',3'-e]thiepine 5,5-dioxide (6c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 5.2 Hz, 2H), 7.16 (d, *J* = 5.2 Hz, 2H), 4.15 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 129.6, 129.1, 127.7, 54.8.

HRMS (ESI, m/z) found $[M+H]^+$ 256.9753, $C_{10}H_9O_2S_3^+$ requires 256.9759.

Bromination of 6c to 6f



The conditions were adapted from the reported literature.[14] To an 8 mL glass vial was added a stirrer, **6c** (25.6 mg, 0.10 mmol), NBS (35.6 mg, 0.20 mmol), CH_2Cl_2 (1.0 mL) and HFIP (1.0 mL). The mixture was stirred at rt for 3 h. After the reaction, the solvent was evaporated to dryness. The residue was purified by by column chromatography (8/1 Petroleum Ether/EtOAc) on silica gel to afford the desired product **6f** (36.4 mg, 0.088 mmol) as a light-yellow solid in 88% yield.

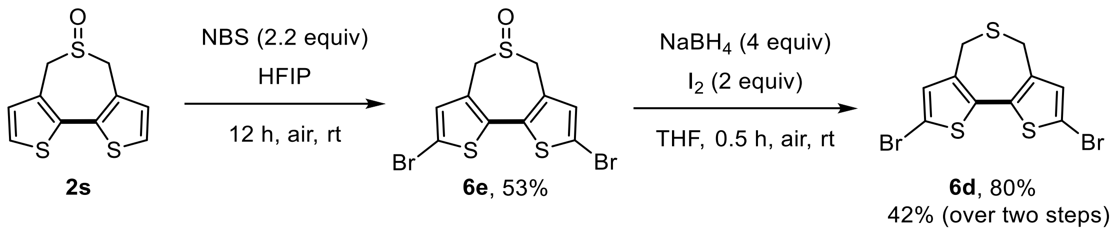
2,8-Dibromo-4,6-dihydrodithieno[3,2-c:2',3'-e]thiepine 5,5-dioxide (6f)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (s, 2H), 4.10 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 132.1, 129.8, 115.4, 54.5.

The crystal structure is shown in the X-ray Crystallographic Data section.

Bromination of 2s to 6d and 6e



The conditions were adapted from the reported literature.[14] To an 8 mL glass vial was added a stirrer, **2s** (24.0 mg, 0.10 mmol), NBS (39.1 mg, 0.22 mmol) and HFIP (1.0 mL). Unpon the addition of HFIP solvent, the color of the solution changed to dark blue-purple. The mixture was stirred at rt for 12 h. After the reaction, the color changed to dark green. The solvent was evaporated to dryness. The residue was purified by by column chromatography (1/1 Petroleum Ether/EtOAc) on silica gel to afford the desired product **6e** (21.1 mg, 0.053 mmol) as a light-yellow solid in 53% yield.

2,8-Dibromo-4,6-dihydrodithieno[3,2-c:2',3'-e]thiepine 5-oxide (6e)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13 (s, 2H), 3.90 (d, *J* = 13.6 Hz, 2H), 3.66 (d, *J* = 13.6 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 134.2, 132.8, 132.6, 114.0, 51.4.

HRMS (ESI, m/z) found $[M+H]^+$ 396.8016, $C_{10}H_7Br_2OS_3^+$ requires 396.8020.

To a stirred solution of **6e** (19.9 mg, 0.05 mmol) and I_2 (25.3 mg, 0.10 mmol) in THF (1.0 mL) was added $NaBH_4$ (7.6 mg, 0.20 mmol) in one portion. The mixture was stirred at rt for 0.5 h. After the reaction, the solvent was evaporated to dryness. The residue was purified by by column chromatography (Petroleum Ether) on silica gel to afford the desired product **6d** (15.3 mg, 0.04 mmol) as a light-yellow solid in 80% yield (42% total yield over two steps).

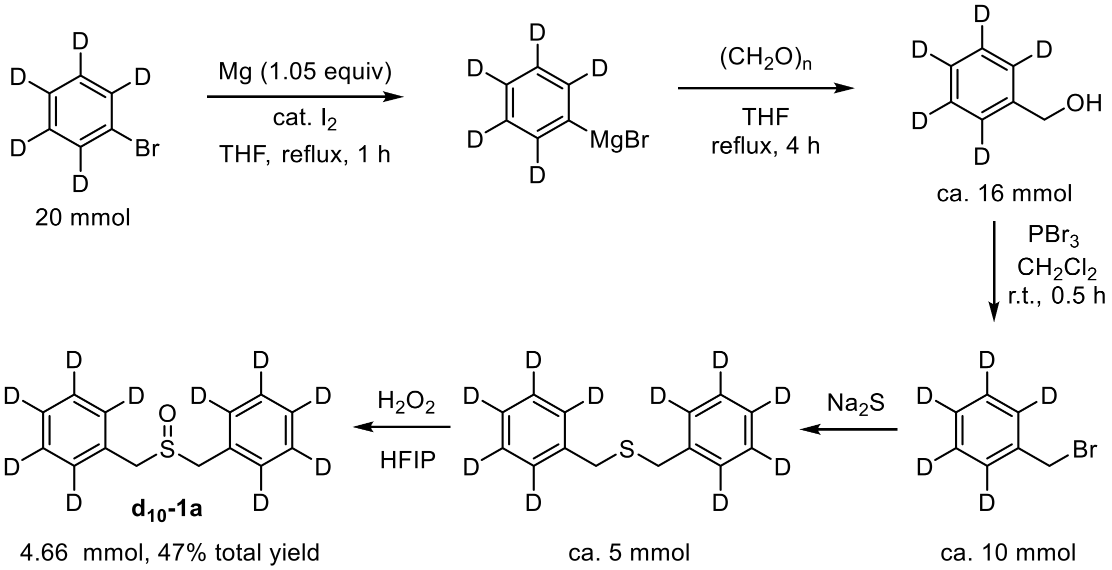
2,8-Dibromo-4,6-dihydrodithieno[3,2-c:2',3'-e]thiepine (6d)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.90 (s, 2H), 3.72 (s, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 138.5, 133.3, 132.1, 111.3, 30.7.

8. Kinetic Isotope Effects (KIE)

Synthesis of d_{10}-1a



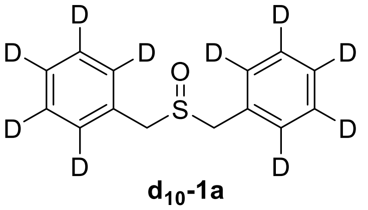
To a 100 mL 2-necked flask was added magnesium (510.3 mg, 21 mmol), and a crystal of iodine. Anhydrous THF (20 mL) was added via syringe under Ar atmosphere. d_5-Bromobenzene (d_5-PhBr; 2.1 mL, 3.24 g, 20 mmol) was added slowly to the stirred mixture via a syringe. After the complete addition of d_5-bromobenzene, the mixture was heated to reflux under Ar for 1 h to give a light black solution of d_5-PhMgBr. The resulting solution of d_5-PhMgBr was used for next step directly.[15]

To the solution of d_5-PhMgBr in THF at rt was added $(CH_2O)_n$ (660.7 mg, 22 mmol) in one portion under the flow of Ar. The mixture was futher heated to reflux under Ar for 4 h. The reaction was quenched with the addition of sat. NH_4Cl (aq). After extracting with EtOAc, the combined organic solvents were dried over anhydrous Na_2SO_4 and removed under reduced pressure to afford the crude residue of d_5-$PhCH_2OH$.

To the crude residue of d_5-$PhCH_2OH$ in CH_2Cl_2 (20 mL) at rt was added PBr_3 (750 μL, 2165 mg, 8 mmol) slowly, the resulting mixture was stirred at rt for 0.5 h. The reaction was quenched with the addition of sat. $NaHCO_3$ (aq), extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, and concentrated by rotary evaporation to give the crude residue of d_5-$PhCH_2Br$, which was involved into the next step without further purification.[16]

To a stirred solution of d_5-$PhCH_2Br$ in *t*-BuOH (6 mL) at rt was added an aqueous solution (4 mL) of Na_2S (8 mmol) in one portion, the mixture was stirred at rt overnight. After the completion of the reaction as monitored by TLC analysis, the mixture was diluted with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated to give the corresponding bis-benzylic sulfide (d_5-$PhCH_2SCH_2Ph$-d_5), which was directly involved into the next step without further purification.

To a stirred solution of the bis-benzylic sulfide in HFIP/$CHCl_3$ (5 mL/5 mL) at rt was added 30% aq. H_2O_2 (5 mmol) slowly. The mixture was stirred at rt for 0.5 h. Upon the completion of the reaction as monitored by TLC analysis, the mixture was quenched by adding Na_2SO_3 and reaction for 30 min. The mixture was then filtered and washed with CH_2Cl_2. The filtrate was concentrated and purified by column chromatography (1/1 Petroleum Ether/EtOAc) on silica gel to afford the desired symmetric bis-benzylic sulfoxides of **d_{10}-1a** (1.12 g, 4.67 mmol) as a white solid in 47% total yield.



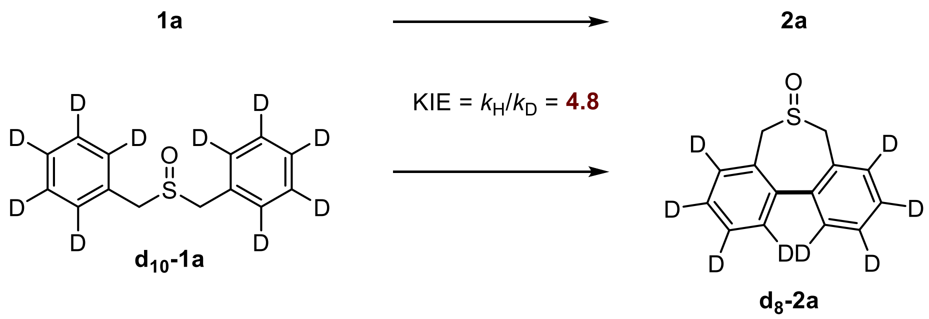
d_{10}-1a

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.92 and 3.89 (ABq system, *J* = 13.0 Hz, 4H).

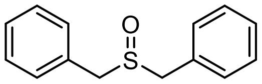
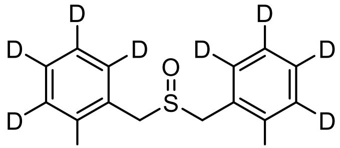
^{13}C NMR (151 MHz, $CDCl_3$) δ 130.0, 129.8 (t, *J* = 24.3 Hz), 128.6 (t, *J* = 24.3 Hz), 128.0 (t, *J* = 24.0 Hz), 57.3.

HRMS (ESI, m/z) found $[M+H]^+$ 241.1464, $C_{14}H_5D_{10}OS^+$ requires 241.1466.

KIE Determined from Two Parallel Reactions



According to the general procedure, dibenzyl sulfoxide (**1a**; 0.10 mmol, 23.0 mg) or **d$_{10}$-1a** (24.0 mg, 0.10 mmol), [Cp*IrCl$_2$]$_2$ (4.0 mg, 0.005 mmol), AgNTf$_2$ (7.8 mg, 0.020 mmol), and Mn(OAc)$_3$·2H$_2$O (5.4 mg, 0.020 mmol) were stirred in TFE solvent (0.5 mL) at 80 °C. Aliquots were taken at the indicated time intervals. The yield was determined by GC-FID using 1,1'-biphenyl as the internal standard.

	10 min	**20 min**	**30 min**	**40 min**	**50 min**
 **1a**	5.8%	13.9%	21.1%	27.5%	30.8%
 **d$_{10}$-1a**	1.1%	2.6%	4.0%	5.5%	7.0%

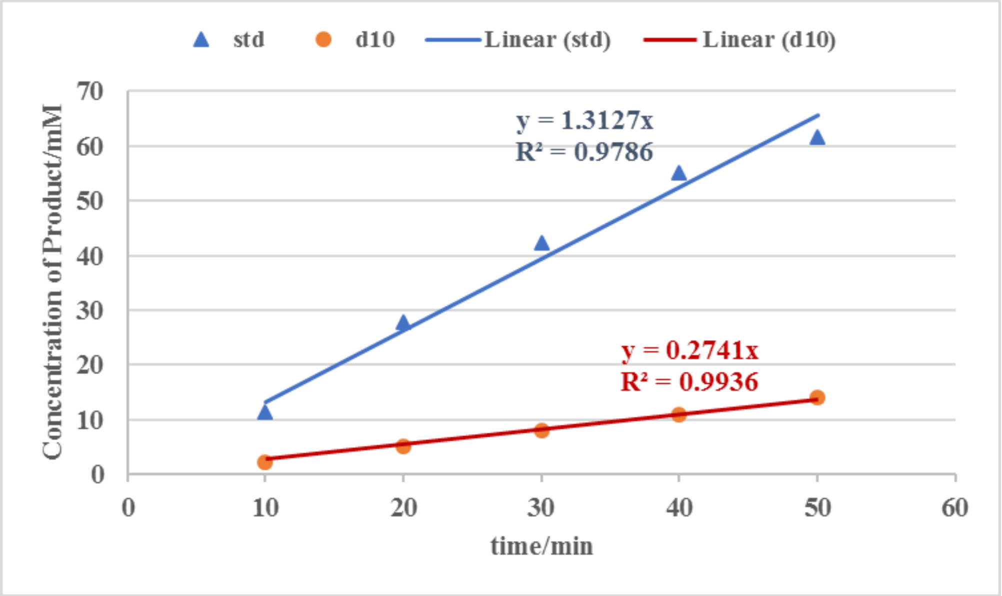
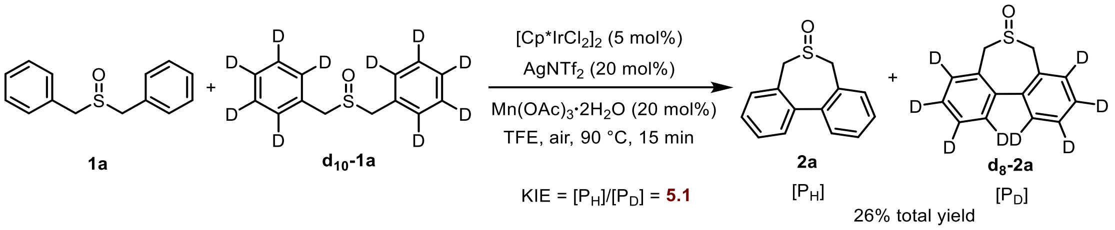


Figure S6. Linear model fitted plot of the concentration of products vs time.

KIE determined from an intermolecular competition



According to the general procedure, dibenzyl sulfoxide (**1a**; 0.05 mmol, 11.5 mg) and **d_{10}-1a** (12.0 mg, 0.05 mmol), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $AgNTf_2$ (7.8 mg, 0.020 mmol), and $Mn(OAc)_3 \cdot 2H_2O$ (5.4 mg, 0.020 mmol) were stirred in TFE solvent (0.5 mL) at 90 °C for 15 min. The reaction mixture was cooled to room temperature, diluted by CH_2Cl_2 with the addition of 20 μL NEt_3 and passed through a short pipet column on silica gel eluting with EtOAc, and concentrated in vacuo. The crude material was taken for ^1H NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard. **2a** and **d_8-2a** were formed in 26% total NMR yield. The crude material was purified by preparative TLC to provide the mixed products together with some starting materials for ^1H NMR analysis.

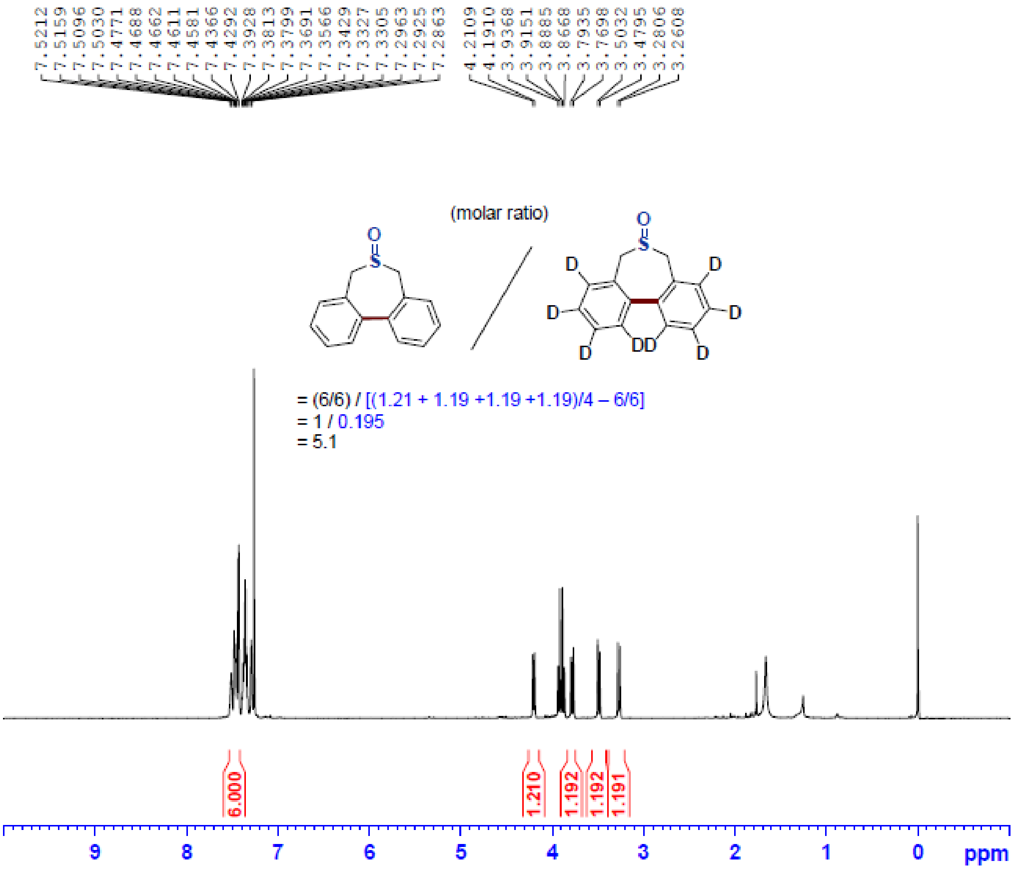


Figure S7. The ^{1}H NMR spectrum of the mixed products and their ratio analysis.

9. EPR Study

Inside a glovebox, $AgNTf_2$ (7.8 mg, 0.020 mmol) was added into an 8 mL glass vial. After the addition, the vial was taken outside of the glovebox. To the vial was added a stirrer, $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (5.4 mg, 0.020 mmol), dibenzyl sulfoxide (23.0 mg, 0.10 mmol) and TFE solvent (0.5 mL). The vial was capped under air and placed into a pre-heated aluminum block at 90 °C for 24 h. After the reaction, the mixture was diluted with CH_2Cl_2, and passed through a short pipet column on silica gel eluting with EtOAc. The filtrate was evaporated to dryness. The residue was dissloved in $CDCl_3$ solvent (0.6 mL) and taken for EPR (Electron Paramagnetic Resonance) analysis. Parameters for EPR-spectra acquisition: frequency: 9.840230 GHz, Xmin = 2500 G, Xmax = 4500 G, microwave power = 2.000 mW, modulation frequency = 100.00 kHz, modulation amplitude = 4.0 G, temperature = 298 K, EPR tube: A glass capillary was filled with the sample and placed inside a 4 mm EPR-tube.

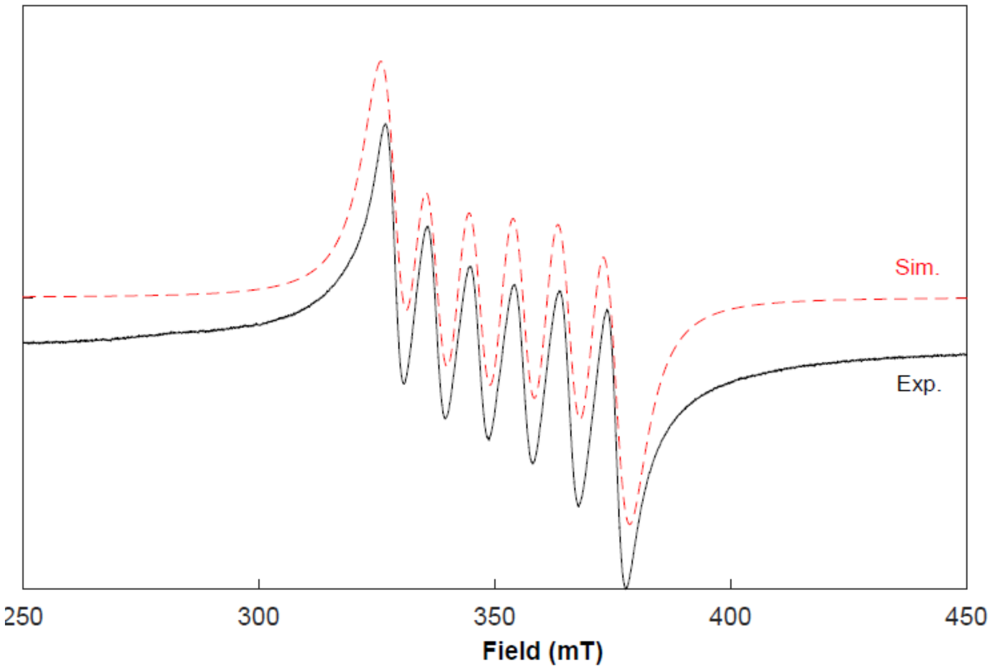


Figure S8. EPR spectrum (first harmonic) of the measured sample (black) and the simulated spectrum (red).

The obtained EPR spectrum has six lines with similar line intensities, which is what one expects for spin-5/2 nucleus coupling to the electron spin (hyperfine interaction).

The EPR signal therefore is in agreement with that of ^{55}Mn(II), which has the electronic configuration: [Ar] 3d^5 with an unpaired electron on a Mn(II) and the ground state nuclear spin quantum number (I) of ^{55}Mn is I = 5/2. EPR spectral simulation was performed with Easyspin software package using Matlab software.[17] RMSD of fit = 0.1952. The simulated heperfine coupling constant (A) value is A = 260.69 MHz. The simulated g-value of the radical is g_{iso} = 1.9949, which is also close to that of the reported Mn(II) (g_{iso} = 2.0).[18]

The Matlab/EasySpin code

```
clear, clc
[B,spc,Params] = eprload('0072b-1.DTA');
B = B/10;
spc = spc/max(abs(spc));
Sys.g = 2.00;                         % first guess
Sys.Nucs = '55Mn';                    % one nuclues
Sys.n = 1;
Sys.A = 260;                          % hyperfine coupling in MHz
Sys.lwpp = [5 5];                      % mT
Exp.mwFreq = 9.840230;                % X-band, static frequency, in units of GHz.
Exp.Range = [min(B) max(B)];
Exp.Harmonic = 1;                      % first harmonic (default)
[x,y] = garlic(Sys,Exp);               % for isotropic-limit and fast-motion cw EPR
y = y/max(abs(y));
plot(B,spc,'--r',x,y,':b');
Vary.g = 0.1;
Vary.A = 100;
Vary.lwpp = [10 10];                    % mT
FitOpt.Method = 'simplex fcn';
FitOpt.Scaling = 'lsq';
esfit('garlic',spc,Sys,Vary,Exp,[],FitOpt);
```

10. X-ray Crystallographic Data

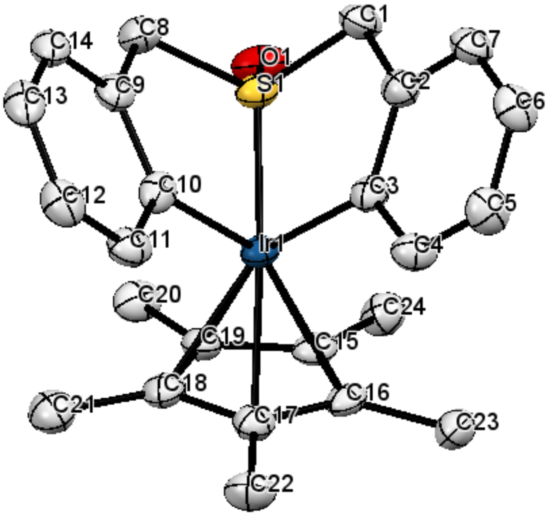


Figure S9. ORTEP presentation of the molecular structure with the numbering scheme for **Ir-I** (CCDC 1943600) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): Ir(1)–S(1): 2.1900(12); Ir(1)–C(3): 2.059(5); Ir(1)–C(10): 2.060(5); S(1)–O(1): 1.479(4); S(1)–C(1): 1.806(5); S(1)–C(8): 1.802(5). Bond angles (°): C(3)-Ir(1)-S(1): 83.50(14); C(10)-Ir(1)-S(1): 82.46(15).

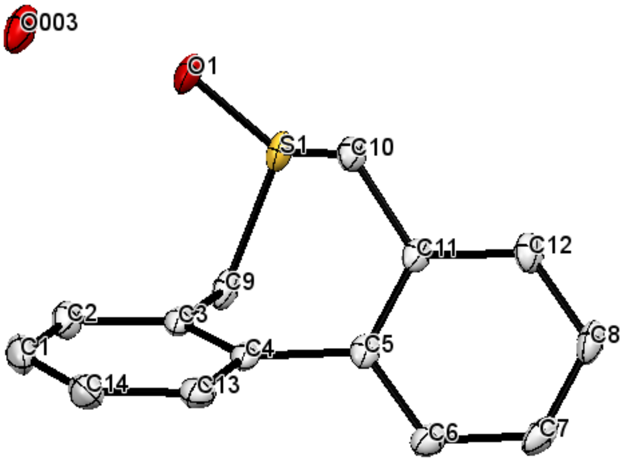


Figure S10. ORTEP presentation of the molecular structure with the numbering scheme for **2a**·H_2O (CCDC 1943599) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): S(1)–O(1): 1.5058(16); S(1)–C(10): 1.813(2); S(1)–C(9): 1.813(2). Bond angles (°): O(1)-S(1)-C(9): 107.48(10); O(1)-S(1)-C(10): 102.62(10).

Table S7. Crystallographic Data and Structure Refinement for Ir-I

Compound	**Ir-I**
CCDC deposition No.	1943600
Empirical formula	$C_{24}H_{27}IrOS$
Formula weight	555.71
Temperature	100.0 K
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 10.9930(5) Å alpha = 90° b = 14.5354(7) Å beta = 94.905(2)° c = 12.7588(7) Å gamma = 90°
Volume	2031.23(17) $Å^3$
Z; Calculated density	4; 1.817 g/cm^3
Absorption coefficient	6.687 mm^{-1}
F(000)	1088.0
Crystal size	0.32 × 0.28 × 0.19 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.256 to 55.08°.
Index ranges	$-14 \leq h \leq 14$, $-18 \leq k \leq 16$, $-16 \leq l \leq 15$
Reflections collected	26892
Independent reflections	4677 [R_{int} = 0.0711, R_{sigma} = 0.0422]
Data / restraints / parameters	4677/0/250
Goodness-of-fit on F2	1.059
Final R indices [I>2sigma(I)]	R_1 = 0.0388, wR_2 = 0.1051
R indices (all data)	R_1 = 0.0426, wR_2 = 0.1077
Largest diff. peak/hole	2.77 and −1.89 e $Å^{-3}$

Table S8. Crystallographic Data and Structure Refinement for 2a

Compound	**2a**·H_2O
CCDC deposition No.	1943599
Empirical formula	$C_{14}H_{14}O_2S$
Formula weight	246.31
Temperature	100.0 K
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 14.1140(12) Å alpha = 90° b = 5.0373(4) Å beta = 98.575(3)° c = 17.2267(15) Å gamma = 90°
Volume	1211.07(18) $Å^3$
Z; Calculated density	4; 1.340 g/cm^3
Absorption coefficient	0.253 mm^{-1}
F(000)	512.0
Crystal size	0.38 × 0.17 × 0.16 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	5.218 to 55.03°.
Index ranges	$-18 \leq h \leq 16$, $-6 \leq k \leq 6$, $-22 \leq l \leq 21$
Reflections collected	13053
Independent reflections	2799 [R_{int} = 0.1017, R_{sigma} = 0.0832]
Data / restraints / parameters	2799/0/158
Goodness-of-fit on F2	1.046
Final R indices [I>2sigma(I)]	R_1 = 0.0586, wR_2 = 0.1494
R indices (all data)	R_1 = 0.0839, wR_2 = 0.1641
Largest diff. peak/hole	0.59 and −0.57 e $Å^{-3}$

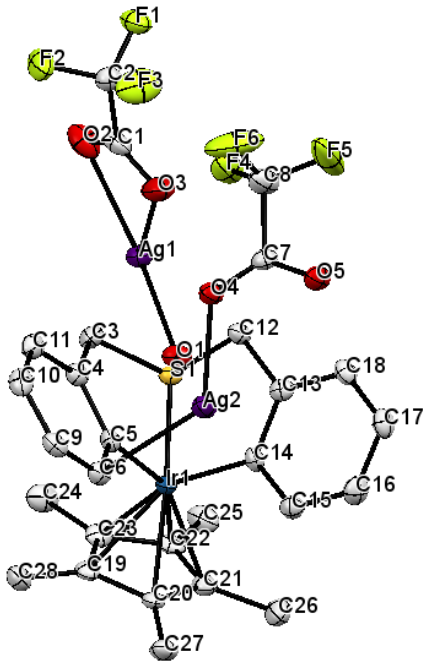


Figure S11. ORTEP presentation of the molecular structure (an asymmetric unit) with the numbering scheme for for **Ir-II** (CCDC 1943603) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): Ag(2)–C(6): 2.597(4); Ag(1)–O(1): 2.398(3); Ag(1)–O(2): 2.528(4); Ag(1)–O(3): 2.508(4); S(1)–O(1): 1.479(3); Ir(1)–S(1): 2.1802(10). Bond angles (°): S(1)-O(1)-Ag(1): 133.12(19); O(4)-Ag(2)-C(6): 117.60(13).

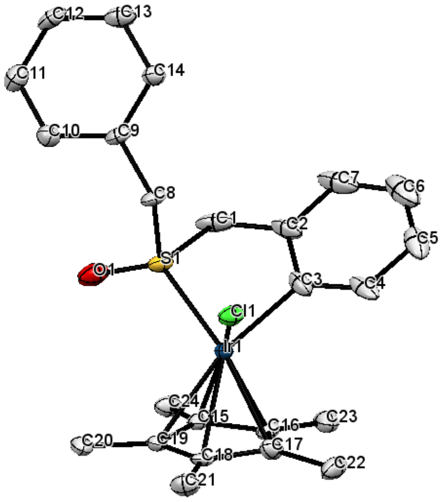


Figure S12. ORTEP presentation of the molecular structure with the numbering scheme for **Ir-III** (CCDC 1943601) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): Ir(1)–S(1): 2.2424(16); Ir(1)–C(3): 2.057(7); Ir(1)–Cl(1): 2.4000(16); S(1)–O(1): 1.473(5); S(1)–C(1): 1.796(8); S(1)–C(8): 1.817(7). Bond angles (°): C(3)-Ir(1)-S(1): 80.8(2); Cl(1)-Ir(1)-S(1): 94.62(6).

Table S9. Crystallographic Data and Structure Refinement for Ir-II

Compound	**Ir-II**
CCDC deposition No.	1943603
Empirical formula	$C_{28}H_{27}Ag_2F_6IrO_5S$
Formula weight	997.49
Temperature	100.0 K
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 9.9702(5) Å alpha = 89.3620(10)° b = 12.7689(6) Å beta = 73.4700(10)° c = 13.1134(6) Å gamma = 68.1400(10)°
Volume	1476.92(12) Å^3
Z; Calculated density	2; 2.243 g/cm^3
Absorption coefficient	5.953 mm^{-1}
F(000)	952.0
Crystal size	0.42 × 0.35 × 0.31 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.49 to 55.206°.
Index ranges	$-12 \le h \le 12$, $-16 \le k \le 16$, $-16 \le l \le 17$
Reflections collected	25782
Independent reflections	6804 [R_{int} = 0.0685, R_{sigma} = 0.0537]
Data / restraints / parameters	6804/0/394
Goodness-of-fit on F2	1.036
Final R indices [I>2sigma(I)]	R_1 = 0.0342, wR_2 = 0.0839
R indices (all data)	R_1 = 0.0369, wR_2 = 0.0856
Largest diff. peak/hole	2.83 and −1.58 e Å^{-3}

Table S10. Crystallographic Data and Structure Refinement for Ir-III

Compound	**Ir-III**
CCDC deposition No.	1943601
Empirical formula	$C_{24}H_{28}ClIrOS$
Formula weight	592.17
Temperature	100.0 K
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 8.5119(9) Å alpha = 90° b = 33.049(3) Å beta = 105.969(4)° c = 8.1129(7) Å gamma = 90°
Volume	2194.2(4) $Å^3$
Z; Calculated density	4; 1.793 g/cm^3
Absorption coefficient	6.314 mm^{-1}
F(000)	1166.0
Crystal size	0.42 × 0.36 × 0.19 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.93 to 54.996°.
Index ranges	$-10 \leq h \leq 11$, $-42 \leq k \leq 42$, $-10 \leq l \leq 8$
Reflections collected	28327
Independent reflections	5001 [R_{int} = 0.0755, R_{sigma} = 0.0480]
Data / restraints / parameters	5001/30/259
Goodness-of-fit on F2	1.189
Final R indices [I>2sigma(I)]	R_1 = 0.0461, wR_2 = 0.0973
R indices (all data)	R_1 = 0.0508, wR_2 = 0.0989
Largest diff. peak/hole	2.61 and −2.56 e $Å^{-3}$

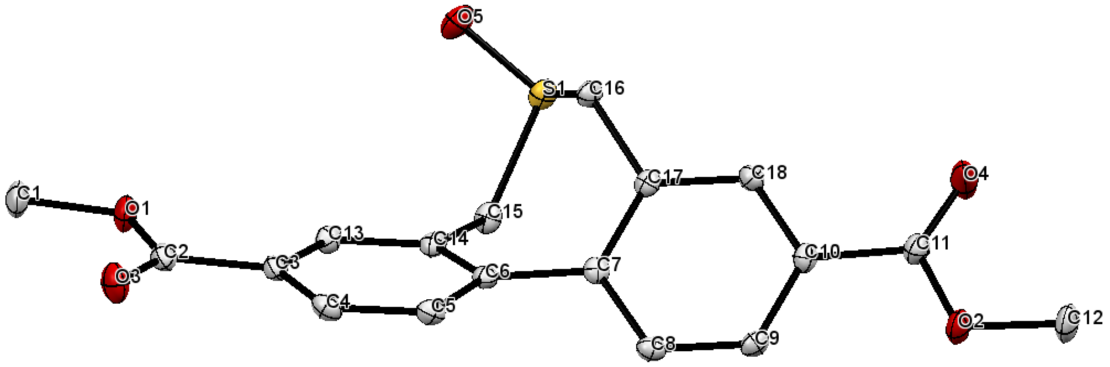


Figure S13. ORTEP presentation of the molecular structure with the numbering scheme for **2o** (CCDC 1943602) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): S(1)–O(5): 1.4998(12); S(1)–C(15): 1.8258(16); S(1)–C(16): 1.8197(15). Bond angles (°): O(5)-S(1)-C(15): 107.36(7); O(5)-S(1)-C(16): 103.68(7).

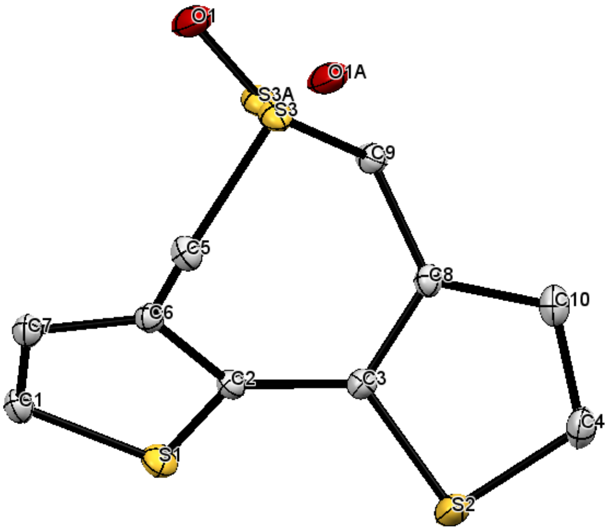


Figure S14. ORTEP presentation of the molecular structure with the numbering scheme for **2s** (CCDC 1943605) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): S(3)–O(1): 1.4950(10); S(3)–C(5): 1.8185(9); S(3)–C(9): 1.8263(8). Bond angles (°): O(1)-S(3)-C(5): 107.37(5); O(1)-S(3)-C(9): 103.88(5).

Table S11. Crystallographic Data and Structure Refinement for 2o

Compound	**2o**
CCDC deposition No.	1943602
Empirical formula	$C_{18}H_{16}O_5S$
Formula weight	344.37
Temperature	100.0 K
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 4.9916(3) Å alpha = 69.159(2)° b = 12.1921(6) Å beta = 87.173(2)° c = 13.9226(8) Å gamma = 79.345(2)°
Volume	778.09(8) $Å^3$
Z; Calculated density	2; 1.470 g/cm^3
Absorption coefficient	0.234 mm^{-1}
F(000)	360.0
Crystal size	0.38 × 0.06 × 0.05 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	6.03 to 55.138°.
Index ranges	$-6 \leq h \leq 6$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$
Reflections collected	11283
Independent reflections	3585 [R_{int} = 0.0379, R_{sigma} = 0.0389]
Data / restraints / parameters	3585/0/220
Goodness-of-fit on F2	1.047
Final R indices [I>2sigma(I)]	R_1 = 0.0370, wR_2 = 0.0906
R indices (all data)	R_1 = 0.0468, wR_2 = 0.0956
Largest diff. peak/hole	0.37 and −0.39 e $Å^{-3}$

Table S12. Crystallographic Data and Structure Refinement for 2s

Compound	**2s**
CCDC deposition No.	1943605
Empirical formula	$C_{10}H_8OS_3$
Formula weight	240.34
Temperature	100.0 K
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 8.1465(5) Å alpha = 90° b = 14.4371(8) Å beta = 100.673(2)° c = 8.8840(5) Å gamma = 90°
Volume	1026.79(10) $Å^3$
Z; Calculated density	4; 1.555 g/cm^3
Absorption coefficient	0.681 mm^{-1}
F(000)	496.0
Crystal size	0.42 × 0.36 × 0.32 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	5.454 to 90.716°.
Index ranges	$-16 \leq h \leq 15$, $-28 \leq k \leq 28$, $-17 \leq l \leq 17$
Reflections collected	44967
Independent reflections	8609 [R_{int} = 0.0482, R_{sigma} = 0.0375]
Data / restraints / parameters	8609/1/134
Goodness-of-fit on F2	1.028
Final R indices [I>2sigma(I)]	R_1 = 0.0397, wR_2 = 0.0953
R indices (all data)	R_1 = 0.0619, wR_2 = 0.1047
Largest diff. peak/hole	0.64 and −0.68 e $Å^{-3}$

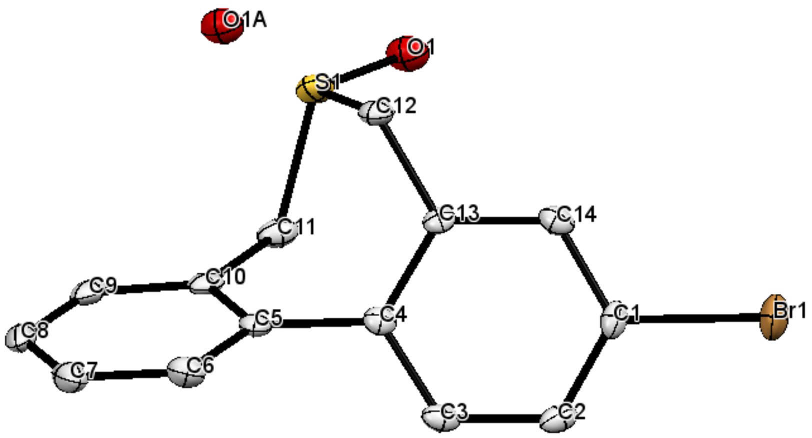


Figure S15. ORTEP presentation of the molecular structure with the numbering scheme for **4f** (CCDC 1943604) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): S(1)–O(5): 1.4998(12); S(1)–C(15): 1.8258(16); S(1)–C(16): 1.8197(15). Bond angles (°): O(5)-S(1)-C(15): 107.36(7); O(5)-S(1)-C(16): 103.68(7).

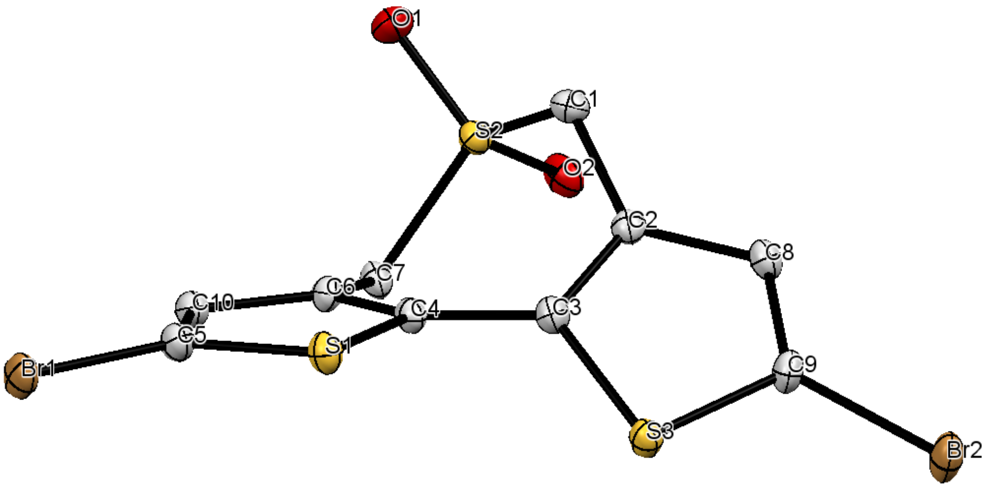


Figure S16. ORTEP presentation of the molecular structure with the numbering scheme for **6f** (CCDC 1971161) with hydrogen atoms omitted for clarity (50% probability displacement ellipsoids). Selected bond lengths (Å): S(2)–O(1): 1.438(2); S(2)–O(2): 1.446(2); S(2)–C(1): 1.792(3); S(2)–C(7): 1.806(3). Bond angles (°): C(1)-S(2)-C(7): 105.43(12); O(1)-S(2)-O(2): 117.53(12).

Table S13. Crystallographic Data and Structure Refinement for 4f

Compound	**4f**
CCDC deposition No.	1943604
Empirical formula	$C_{14}H_{11}BrOS$
Formula weight	307.20
Temperature	100.0 K
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 10.9587(9) Å alpha = 90° b = 15.1534(11) Å beta = 98.891(3) ° c = 7.3793(6) Å gamma = 90°
Volume	1210.69(17) $Å^3$
Z; Calculated density	4; 1.685 g/cm^3
Absorption coefficient	3.546 mm^{-1}
F(000)	616.0
Crystal size	0.39 × 0.36 × 0.28 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.624 to 55.06°.
Index ranges	$-14 \leq h \leq 14$, $-19 \leq k \leq 18$, $-9 \leq l \leq 9$
Reflections collected	16212
Independent reflections	2774 [R_{int} = 0.0492, R_{sigma} = 0.0347]
Data / restraints / parameters	2774/0/159
Goodness-of-fit on F2	1.136
Final R indices [I>2sigma(I)]	R_1 = 0.0307, wR_2 = 0.0687
R indices (all data)	R_1 = 0.0368, wR_2 = 0.0707
Largest diff. peak/hole	0.97 and −0.37 e $Å^{-3}$

Table S14. Crystallographic Data and Structure Refinement for 6f

Compound	**6f**
CCDC deposition No.	1971161
Empirical formula	$C_{10}H_6Br_2O_2S_3$
Formula weight	414.15
Temperature	100.0 K
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 5.8021(3) Å alpha = 73.356(2)° b = 10.4926(5) Å beta = 87.222(2) ° c = 10.9378(5) Å gamma = 79.5970(10)°
Volume	627.49(5) Å^3
Z; Calculated density	2; 2.192 g/cm^3
Absorption coefficient	6.942 mm^{-1}
F(000)	400.0
Crystal size	0.4 × 0.38 × 0.08 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.114 to 61.234°.
Index ranges	$-8 \leq h \leq 8$, $-14 \leq k \leq 15$, $-15 \leq l \leq 15$
Reflections collected	15988
Independent reflections	3865 [R_{int} = 0.0581, R_{sigma} = 0.0468]
Data / restraints / parameters	3865/0/155
Goodness-of-fit on F2	1.060
Final R indices [I>2sigma(I)]	R_1 = 0.0364, wR_2 = 0.1012
R indices (all data)	R_1 = 0.0433, wR_2 = 0.1059
Largest diff. peak/hole	1.44 and −0.87 e Å^{-3}

11. Computational Studies

1. Computational methods

Density functional theory (DFT) calculations were performed with Gaussian 16.[19] The geometries of all intermediates and transition states were optimized with the B_3LYP[20,21] functional at the 6-31G(d)[22-24] basis set (SDD[25] basis set for Ir, Ag). The intermediates on the potential energy surface (PES) were confirmed as such by harmonic frequency analysis, showing respectively zero and one imaginary frequency, at the same level of theory. The M06[26] functional proposed was used with a def_2-TZVP[27] basis set to calculate the single-point energies in the solvent. Solvation effects were taken into account by applying the SMD[28] solvation model with 2,2,2-TriFluoroEthanol (TFE) solvent in single-point energy calculations. The energies presented in this paper are the M06 calculated Gibbs free energies in TFE solvent with B_3LYP calculated thermodynamic corrections. ($G_{M06} = E_{solv\text{-}M06} + G_{corr\text{-}B3LYP,QH} + G_{corr\text{-}B3LYP}$).

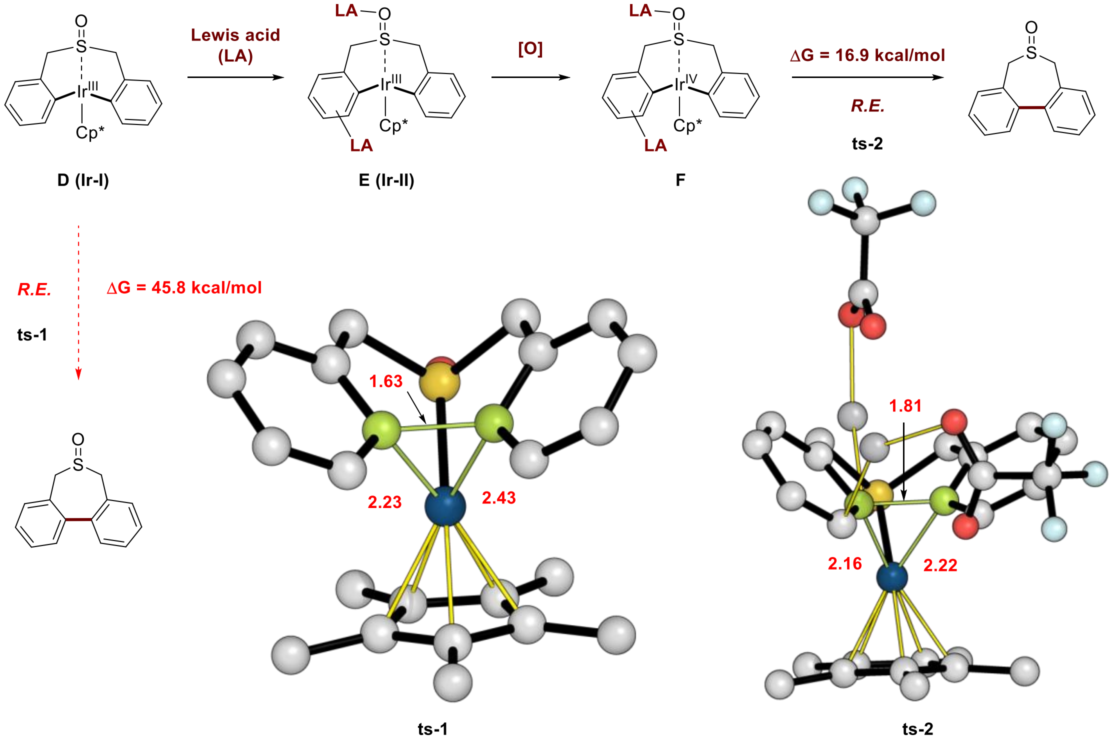


Figure S17. The activation free energy of the reductive elimination process.

To elucidate the importance of Lewis acid in this process, preliminary theoretical studies were conducted. As shown in Figure S17, the calculated activation free energy for direct reductive elimination of Ir(III) intermediate **D** (**Ir-I**) is enormous 45.8 kcal/mol, which indicated that direct C−C bond reductive elimination of Ir(III) intermediate **D** (**Ir-I**) would not occur under mild conditions. Assisted by Lewis acid, the facile oxidatively induced reductive elimination of C−C bond from Ir(IV) species **F** occurs with only a small activation energy of 16.9 kcal/mol.

2. Absolute energies, zero-point energies

Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 298K) for optimited structures are given below. Entropic quasi-harmonic treatment: frequency cut-off value of 100.0 wavenumbers was applied. QS = Grimme: Using a mixture of RRHO and Free-rotor vibrational entropies.[29]

Structure	E_SPC	E	ZPE	H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
D (Ir-I)	-1508.2	-1508.6	0.44595	-1507.8	0.0838	0.08076	-1507.8	-1507.8
E (Ir-II)	-2854.9	-2855.1	0.50379	-2854.3	0.14042	0.12498	-2854.5	-2854.4
F	-2854.7	-2854.8	0.50443	-2854.1	0.13812	0.12422	-2854.3	-2854.3
ts-1	-1508.2	-1508.5	0.44431	-1507.7	0.08333	0.08039	-1507.8	-1507.8
ts-2	-2854.7	-2854.8	0.50287	-2854.1	0.1393	0.12467	-2854.2	-2854.2

3. Optimized geometries

D (Ir-I)

Eopt -1508.606733

Ir	-0.399470	0.000196	0.023578
S	0.515024	-0.000625	2.068706
O	-0.299350	-0.000523	3.333740

C	2.920970	2.821045	0.414705
H	3.525780	3.193468	1.239798
C	1.092457	1.387002	-0.381362
C	1.379411	-1.847098	-1.679626
H	0.817446	-1.450652	-2.520791
C	1.900580	1.894712	0.666295
C	1.092014	-1.386867	-0.382149
C	-3.039291	1.571029	1.570847
H	-2.597782	1.217481	2.508174
H	-4.132052	1.534359	1.679806
H	-2.755272	2.619242	1.441695
C	-2.590655	0.729390	0.408954
C	1.899440	-1.895981	0.665344
C	3.165092	3.274980	-0.880466
H	3.957676	3.994410	-1.067387
C	1.379463	1.848497	-1.678471
H	0.816898	1.453270	-2.519810
C	2.388222	2.782057	-1.929413
H	2.575792	3.111375	-2.949077
C	-3.038871	-1.573248	1.568911
H	-2.753348	-2.620970	1.439095
H	-4.131774	-1.538156	1.677048
H	-2.598592	-1.219912	2.506890
C	-2.155091	-2.586817	-1.381665
H	-1.251751	-2.784592	-1.966589
H	-3.022528	-2.792089	-2.023732
H	-2.174461	-3.303599	-0.556468
C	-2.155611	2.588436	-1.378657
H	-2.176317	3.304284	-0.552686
H	-3.022393	2.793993	-2.021519
H	-1.251681	2.787313	-1.962312
C	-1.672907	0.001972	-3.175706
H	-1.119499	0.886260	-3.505627
H	-2.633855	0.002219	-3.710574
H	-1.119327	-0.881792	-3.506731
C	1.640525	1.456761	2.087945
H	1.060485	2.191406	2.661238
H	2.543036	1.215283	2.659211
C	3.163961	-3.275289	-0.882251
H	3.956278	-3.994910	-1.069574
C	2.387815	-2.780893	-1.931059

H	2.575737	-3.109242	-2.950970
C	2.919502	-2.822559	0.413268
H	3.523781	-3.196087	1.238248
C	-2.193671	1.172110	-0.883026
C	-1.888188	0.001028	-1.688514
C	-2.590411	-0.730015	0.408105
C	1.638958	-1.459209	2.087267
H	2.541348	-1.219295	2.659389
H	1.057728	-2.193791	2.659439
C	-2.193341	-1.171071	-0.884424

E (Ir-II)

Eopt -2855.092241

Ir	0.352143	-1.649048	-0.026387
Ag	-4.876972	-0.565479	-0.273327
Ag	2.992782	1.546159	1.261360
S	-1.708338	-0.772162	-0.092503
F	-7.229088	3.466125	-1.180855
F	7.425277	1.811366	-1.187629
F	-7.227140	3.368504	0.998261
F	-5.662788	4.460137	-0.046978
F	6.802438	3.813389	-0.622877
F	5.843256	2.810569	-2.305039
O	5.187370	0.777319	-0.098528
O	-2.975499	-1.651650	-0.209782
O	-4.364109	2.142556	-0.065805
C	2.093334	0.476657	-1.450244
H	2.943708	-0.077029	-1.063970
C	1.217631	-3.593275	0.909726
C	-6.437911	3.367109	-0.095394
C	1.923643	0.678680	3.395835
H	2.846934	0.697277	3.970579
C	-1.191115	-4.617079	0.800969
H	-2.112167	-4.202085	0.381053
H	-1.238054	-4.500151	1.886973
H	-1.178778	-5.693470	0.582440
C	2.145744	-3.024052	-0.060763
C	-1.874192	0.272168	1.410499
H	-2.371093	1.208567	1.136454
H	-2.560420	-0.305860	2.043111
C	-5.598740	2.067011	-0.146257

C	0.573377	-0.366771	1.590627
C	0.781891	0.045472	-1.180440
C	-0.271140	0.832049	-1.709154
C	5.270364	2.015016	-0.154426
C	-0.510925	0.422060	2.045121
C	0.025313	-3.949995	0.223751
C	0.211867	-3.660703	-1.196219
C	-0.012629	1.982497	-2.466727
H	-0.842985	2.571347	-2.850507
C	1.298511	2.371116	-2.736423
H	1.493490	3.261272	-3.327113
C	1.522980	-3.135642	-1.369308
C	-1.703774	0.409928	-1.492725
H	-2.099882	-0.194436	-2.320073
H	-2.408296	1.220614	-1.277680
C	1.797405	-0.209167	2.298463
H	2.622876	-0.882969	2.083388
C	-0.378905	1.317854	3.118657
H	-1.238371	1.906884	3.431097
C	1.522747	-3.842488	2.358061
H	0.610922	-3.972675	2.946687
H	2.090300	-3.021639	2.804829
H	2.124560	-4.754684	2.467073
C	6.364062	2.623781	-1.063198
C	2.353429	1.612230	-2.229148
H	3.381430	1.907288	-2.417809
C	3.604569	-2.750342	0.181739
H	3.807181	-2.530599	1.233624
H	3.983661	-1.909787	-0.405381
H	4.204949	-3.632604	-0.081082
C	-0.774390	-4.008785	-2.275943
H	-0.703692	-5.073546	-2.536940
H	-0.592466	-3.433550	-3.188002
H	-1.802901	-3.816044	-1.956042
C	0.829179	1.458837	3.794075
H	0.918415	2.147561	4.628288
C	2.198677	-2.826820	-2.671963
H	2.847234	-1.950901	-2.595166
H	1.476093	-2.637336	-3.469922
H	2.822447	-3.677390	-2.978553
O	-6.314148	1.012550	-0.261737

O	4.503457	2.870518	0.395583

F

Eopt -2854.839370

Ir	-0.531846	1.296596	-0.081662
Ag	4.899427	0.992021	0.533850
Ag	-3.201689	-1.775784	1.929861
S	1.663889	0.667860	0.005666
F	7.640202	-2.774912	-0.485103
F	-6.681757	-1.000611	-1.643433
F	5.866243	-3.832641	0.199910
F	6.006880	-3.159232	-1.870560
F	-6.293733	-3.131397	-1.453362
F	-4.919813	-1.872311	-2.586612
O	-4.471411	-0.446746	-0.101389
O	2.721629	1.651637	0.492359
O	4.361994	-1.497475	-0.309863
C	-1.670692	-0.842052	-1.927505
H	-2.627185	-0.539089	-1.517859
C	-1.141655	3.426967	0.691824
C	6.312242	-2.841951	-0.596657
C	-1.816531	-0.785384	3.594244
H	-2.608795	-0.669161	4.332002
C	1.048886	4.340792	-0.394272
H	1.686855	4.101315	-1.247731
H	1.613526	4.137443	0.518588
H	0.841889	5.418926	-0.428717
C	-2.331497	2.773443	0.211372
C	1.644781	-0.857286	1.031426
H	1.636503	-1.697860	0.329029
H	2.595117	-0.889832	1.570535
C	5.608245	-1.518059	-0.214833
C	-0.628360	0.099744	1.607480
C	-0.488069	-0.190225	-1.539886
C	0.744482	-0.626000	-2.094898
C	-4.858786	-1.622645	-0.244309
C	0.424035	-0.804867	1.908593
C	-0.248378	3.593098	-0.432864
C	-0.876052	3.037896	-1.605143
C	0.779740	-1.717408	-2.966856
H	1.731156	-2.063092	-3.362035

C	-0.406606	-2.361025	-3.331461
H	-0.374110	-3.199022	-4.021044
C	-2.166015	2.533803	-1.208365
C	2.018207	0.061708	-1.682919
H	2.240179	0.974072	-2.250817
H	2.905286	-0.579428	-1.635184
C	-1.732202	0.109107	2.502057
H	-2.504884	0.859882	2.391856
C	0.343926	-1.695379	2.990671
H	1.161754	-2.385307	3.181211
C	-0.924753	3.983245	2.068573
H	0.136698	4.026553	2.325696
H	-1.432850	3.390281	2.833457
H	-1.321696	5.005757	2.127600
C	-5.725180	-1.926918	-1.488758
C	-1.625848	-1.929252	-2.805487
H	-2.551491	-2.430712	-3.068902
C	-3.627353	2.612739	0.948472
H	-3.500979	2.729196	2.028078
H	-4.107238	1.653368	0.736028
H	-4.317233	3.404402	0.625346
C	-0.368660	3.122661	-3.016255
H	-0.769752	4.017565	-3.509349
H	-0.674550	2.255037	-3.606484
H	0.721946	3.191737	-3.055421
C	-0.769558	-1.704661	3.824455
H	-0.817410	-2.384056	4.669685
C	-3.243069	2.048285	-2.125101
H	-3.929431	1.359523	-1.626087
H	-2.833612	1.557512	-3.011485
H	-3.825554	2.914208	-2.471156
O	6.360240	-0.566971	0.164598
O	-4.566421	-2.618982	0.488910

ts-1

Eopt -1508.518894

Ir	0.390939	-0.226282	0.102379
S	-0.686386	-0.415603	2.051321
O	-0.135753	-0.855750	3.377446
C	-3.617314	-1.874471	-0.280905
H	-4.071955	-2.599154	0.391778

C	-1.921822	-0.115804	-0.635761
C	-0.787291	2.150859	-1.255158
H	-0.482557	1.716372	-2.199065
C	-2.572385	-1.085318	0.210572
C	-1.217717	1.284236	-0.199177
C	2.767280	-1.852161	1.670858
H	2.594911	-1.275128	2.584120
H	3.830486	-2.132253	1.641350
H	2.180474	-2.770927	1.755477
C	2.388332	-1.069864	0.442430
C	-1.538048	1.945489	1.044656
C	-4.038660	-1.816460	-1.605997
H	-4.851311	-2.445508	-1.956803
C	-2.362598	-0.124629	-1.991435
H	-1.937014	0.584458	-2.688079
C	-3.371566	-0.946873	-2.469667
H	-3.657207	-0.881236	-3.516297
C	3.698368	1.103170	1.136816
H	3.849726	2.128276	0.786108
H	4.689022	0.669432	1.335207
H	3.176628	1.156290	2.098989
C	2.845544	1.875673	-1.894030
H	1.917326	2.425825	-2.101284
H	3.331468	1.686958	-2.860524
H	3.496428	2.542612	-1.321355
C	1.566500	-3.066828	-1.085223
H	1.299942	-3.623245	-0.181816
H	2.447242	-3.557114	-1.528642
H	0.739272	-3.172533	-1.794134
C	1.364442	-0.621417	-3.142715
H	0.539871	-1.329152	-3.272032
H	2.196644	-0.961928	-3.776879
H	1.037498	0.346324	-3.538913
C	-2.072107	-1.492341	1.585448
H	-1.639921	-2.497824	1.546712
H	-2.846393	-1.477199	2.362141
C	-1.084318	4.138988	0.085868
H	-1.047935	5.218645	0.196416
C	-0.717921	3.528888	-1.117182
H	-0.369163	4.130807	-1.952591
C	-1.460259	3.331000	1.160804

H	-1.676588	3.785503	2.125028
C	1.852259	-1.623175	-0.781129
C	1.784517	-0.519711	-1.700789
C	2.931699	0.280764	0.143438
C	-1.772142	1.114813	2.262167
H	-2.804653	0.770568	2.387875
H	-1.447764	1.612479	3.179811
C	2.580439	0.599840	-1.154972

ts-2

Eopt -2854.798365

Ir	0.054645	-1.971838	0.006916
Ag	-5.107401	-0.120135	-0.236400
Ag	3.332621	1.966358	1.573725
S	-1.920531	-0.811743	-0.063988
F	-4.876646	4.678707	0.956355
F	7.348967	1.534424	-1.365230
F	-4.746975	4.728055	-1.221003
F	-6.663122	4.381304	-0.250105
F	6.745765	3.621434	-1.318235
F	5.680716	2.212988	-2.596489
O	5.040107	0.813039	-0.086540
O	-3.299946	-1.468299	-0.143771
O	-3.822581	2.302652	-0.133685
C	2.142693	0.130233	-1.164699
H	2.946822	-0.314353	-0.595073
C	0.788291	-3.860232	1.064845
C	-5.354420	4.130547	-0.178165
C	2.133747	0.479353	2.937849
H	3.035412	0.275844	3.515482
C	-1.737799	-4.568097	1.149494
H	-2.637194	-4.154427	0.685409
H	-1.741109	-4.285959	2.205325
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C	1.713806	-3.500848	0.009829
C	-1.848836	0.366829	1.329132
H	-2.382516	1.282388	1.044754
H	-2.405320	-0.124542	2.137154
C	-5.030448	2.617048	-0.191332
C	0.653860	-0.175370	1.041833
C	0.789721	-0.025747	-0.756123

C	-0.205534	0.631948	-1.562219
C	5.282434	2.017989	-0.28189
C	-0.402231	0.535443	1.725759
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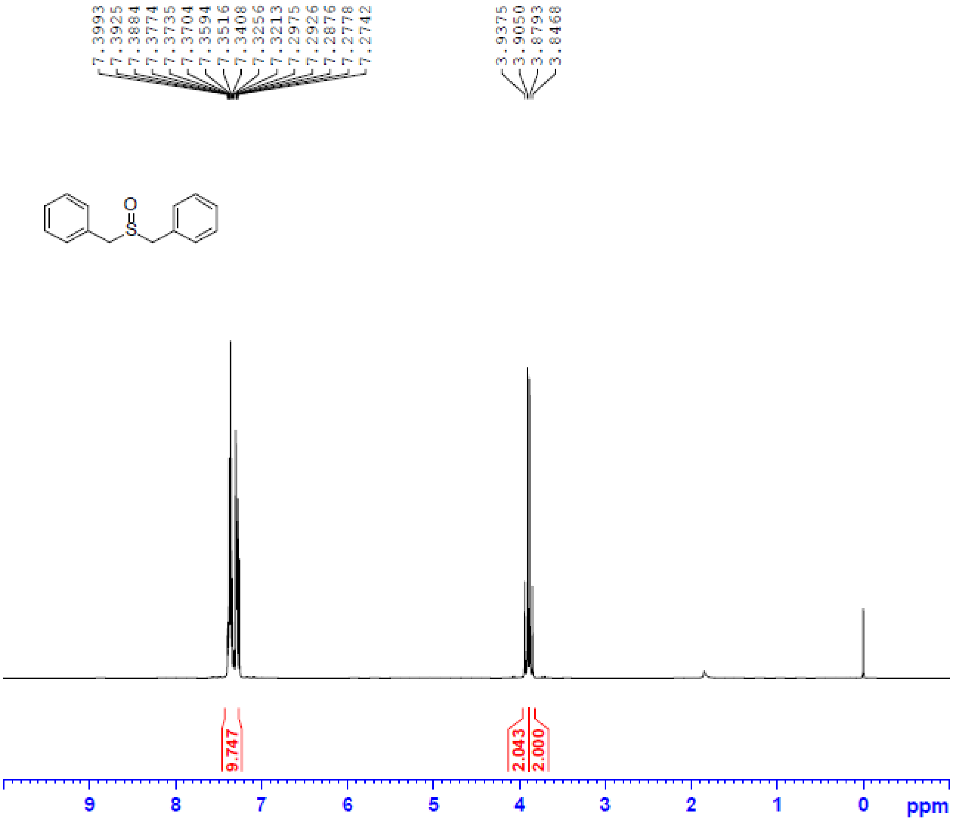
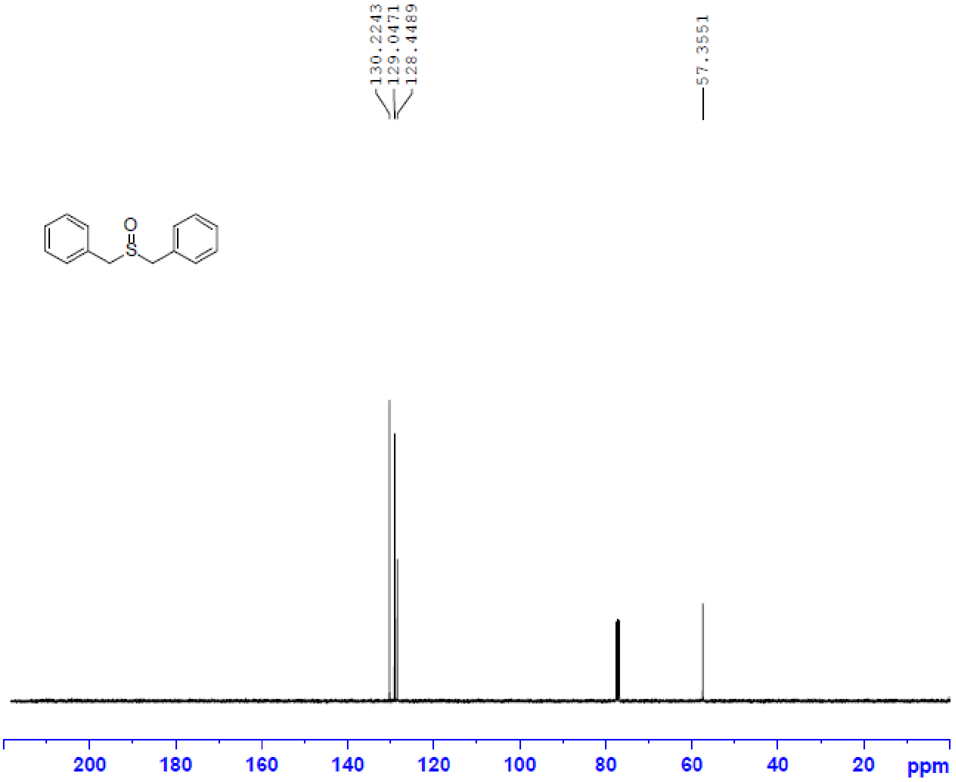
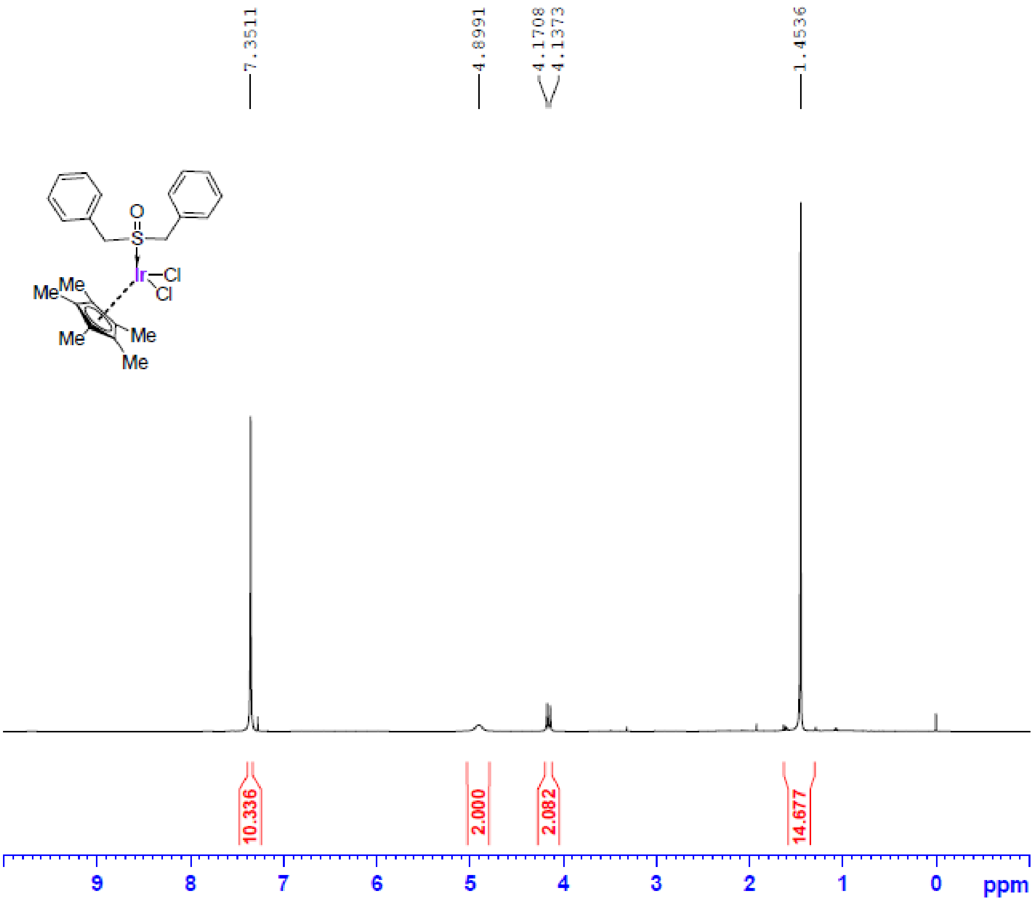
13. NMR Spectra



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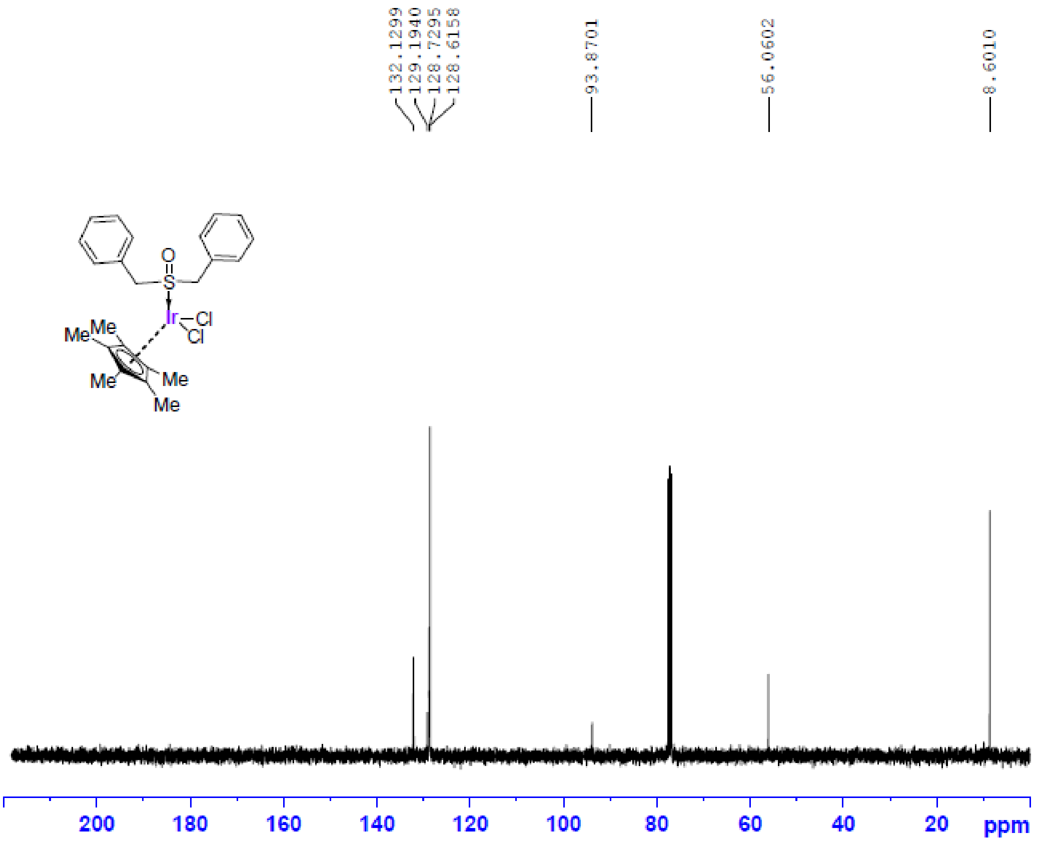
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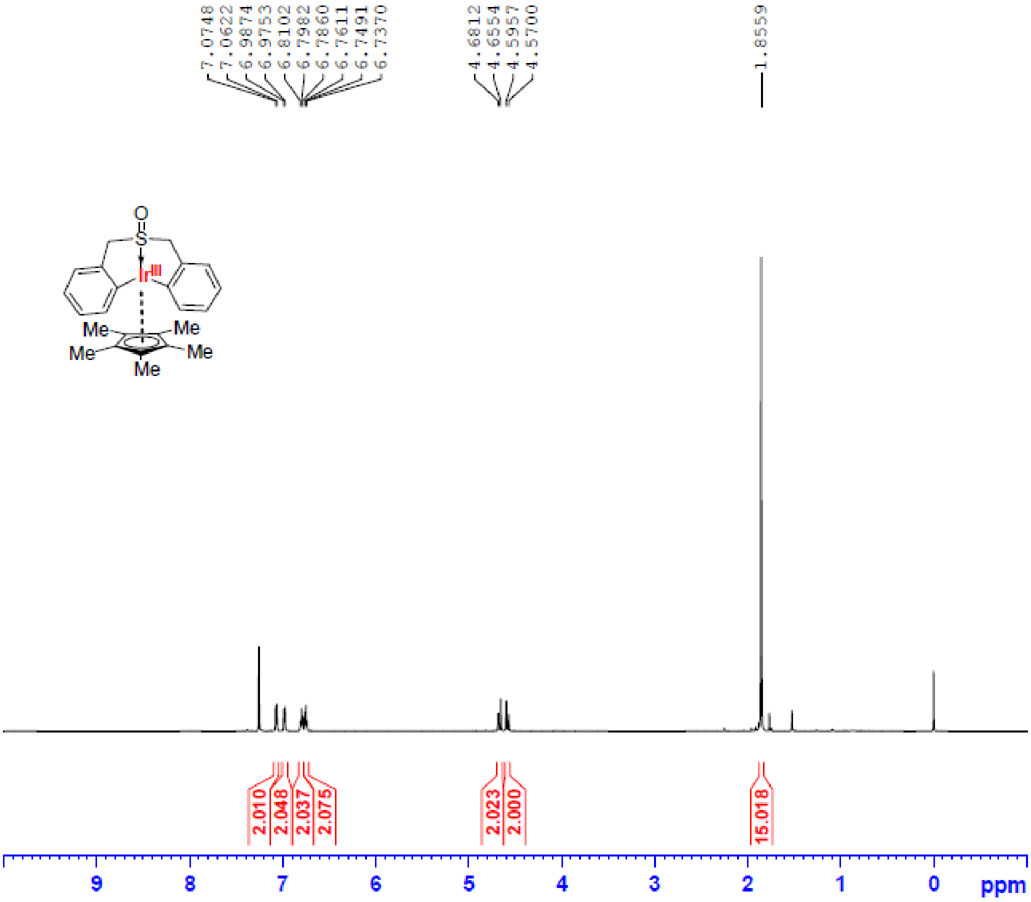
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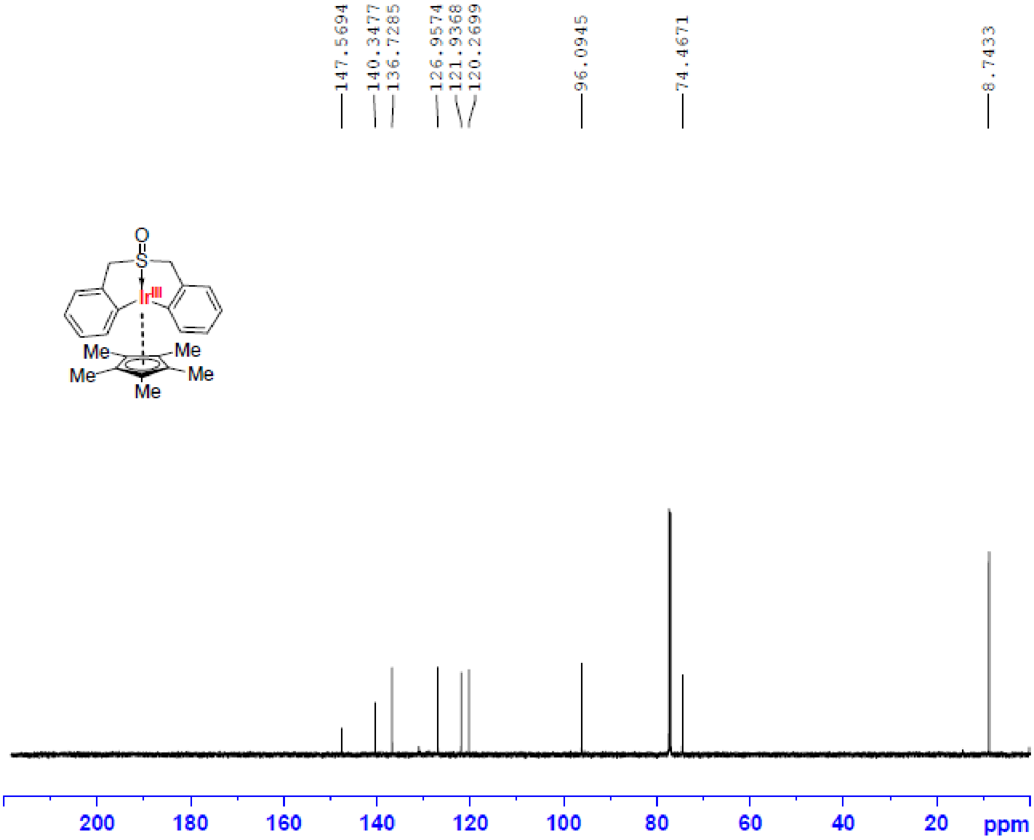
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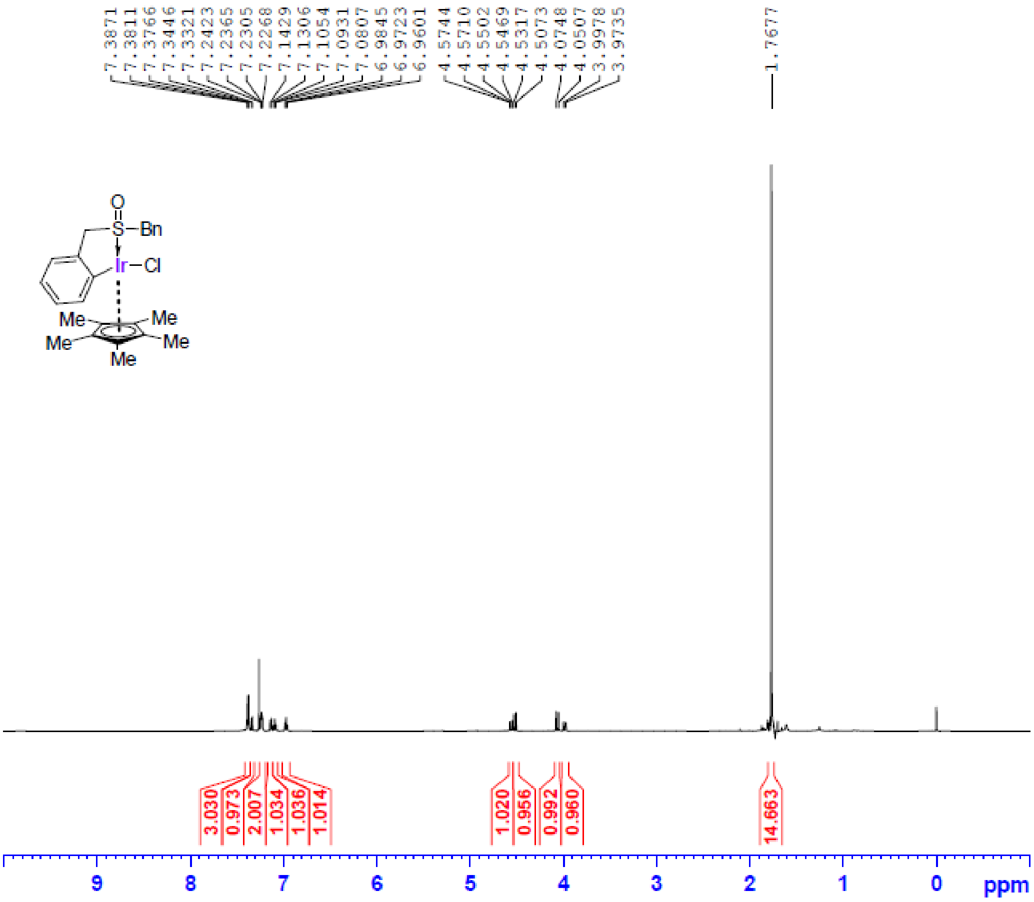
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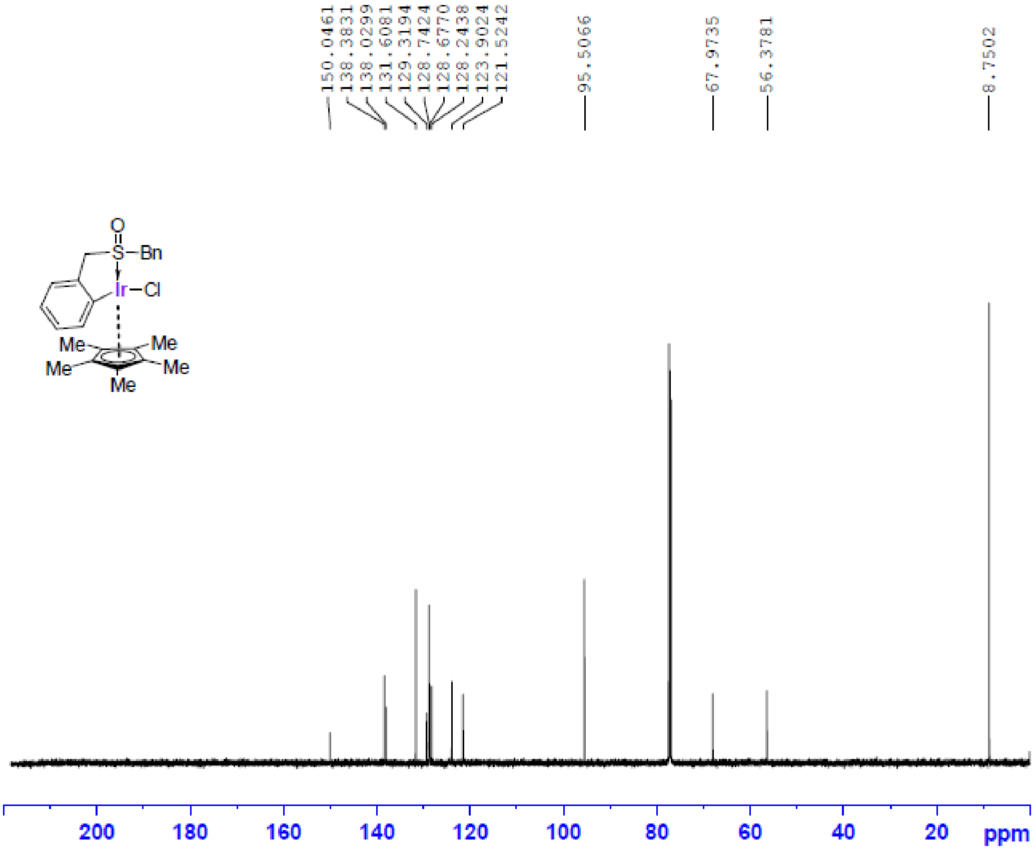
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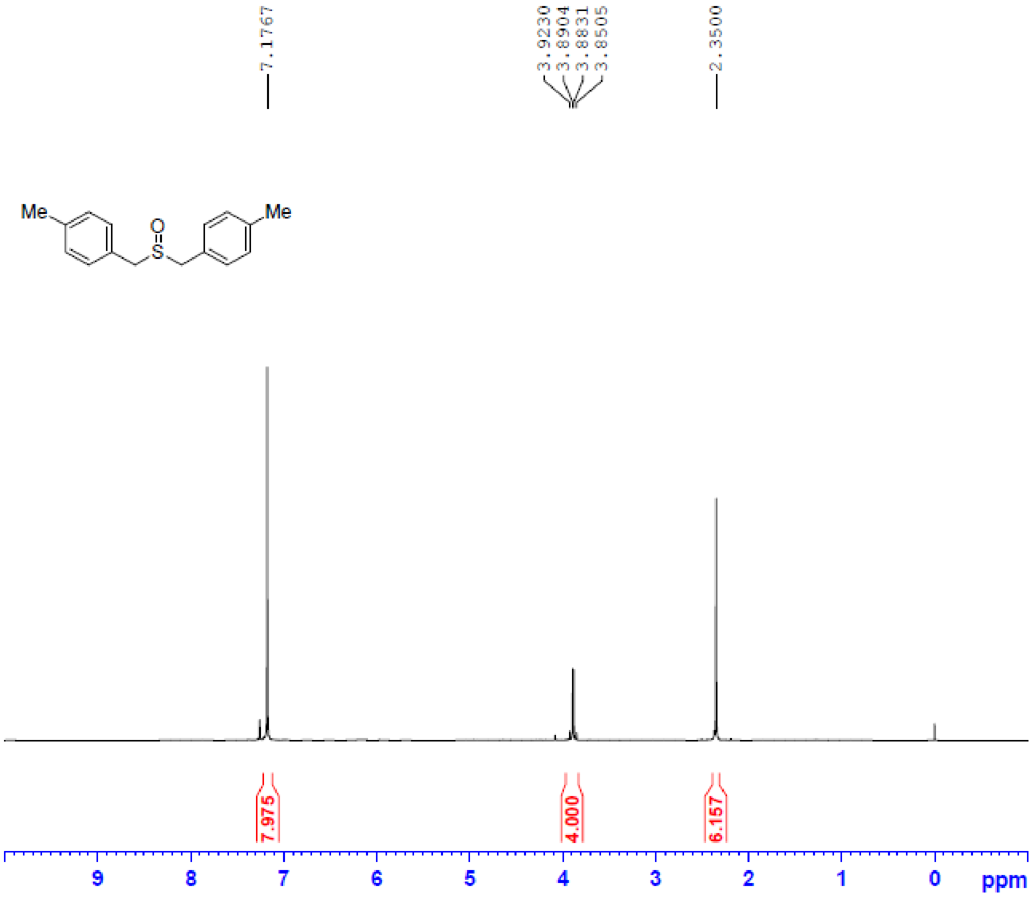
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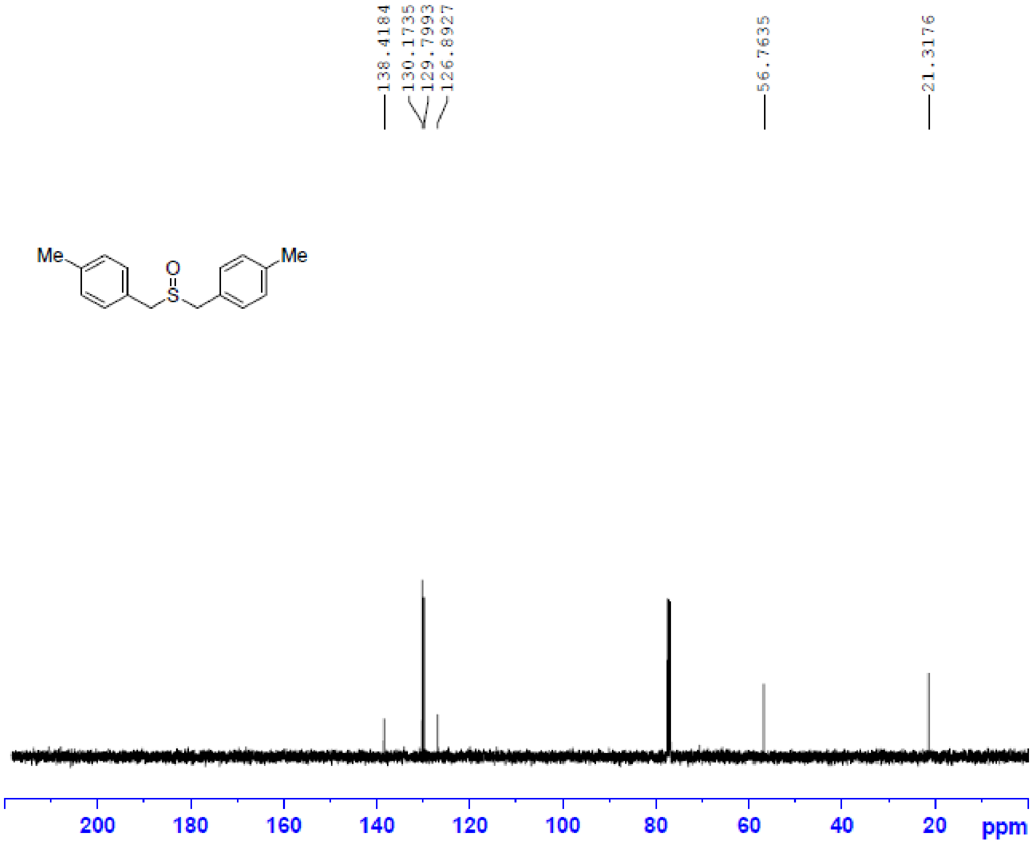
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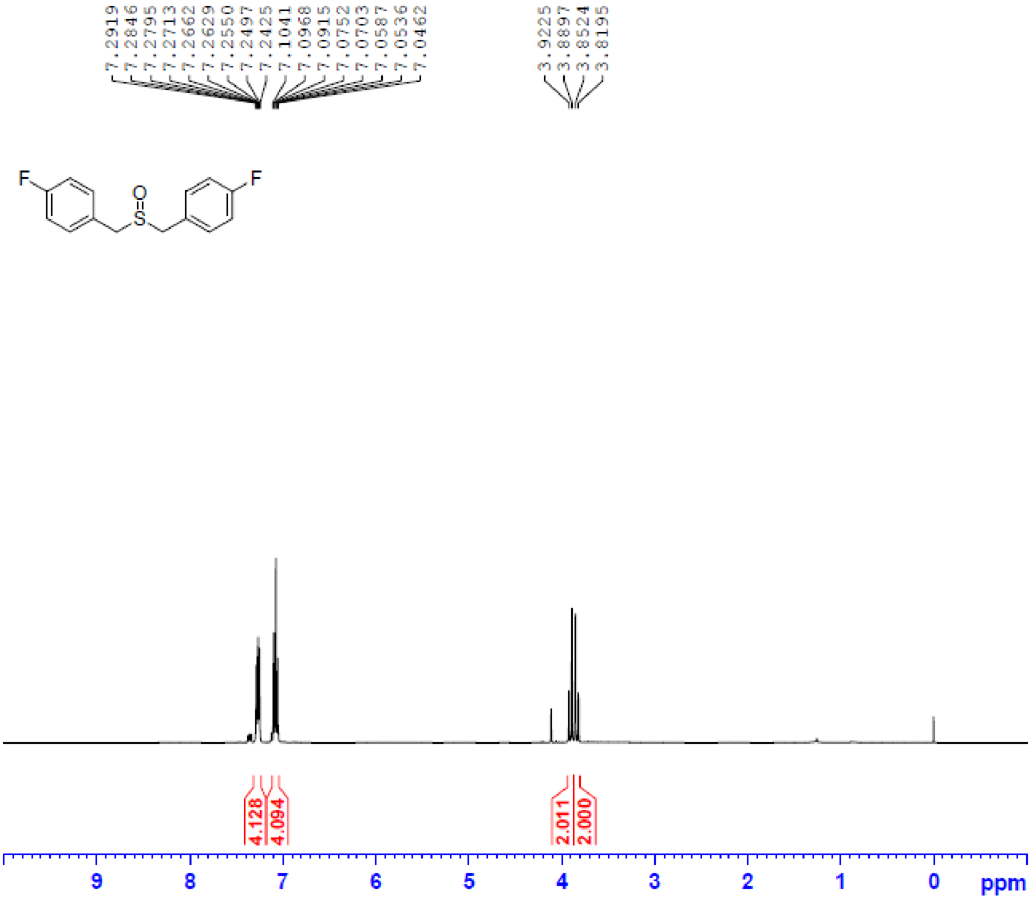
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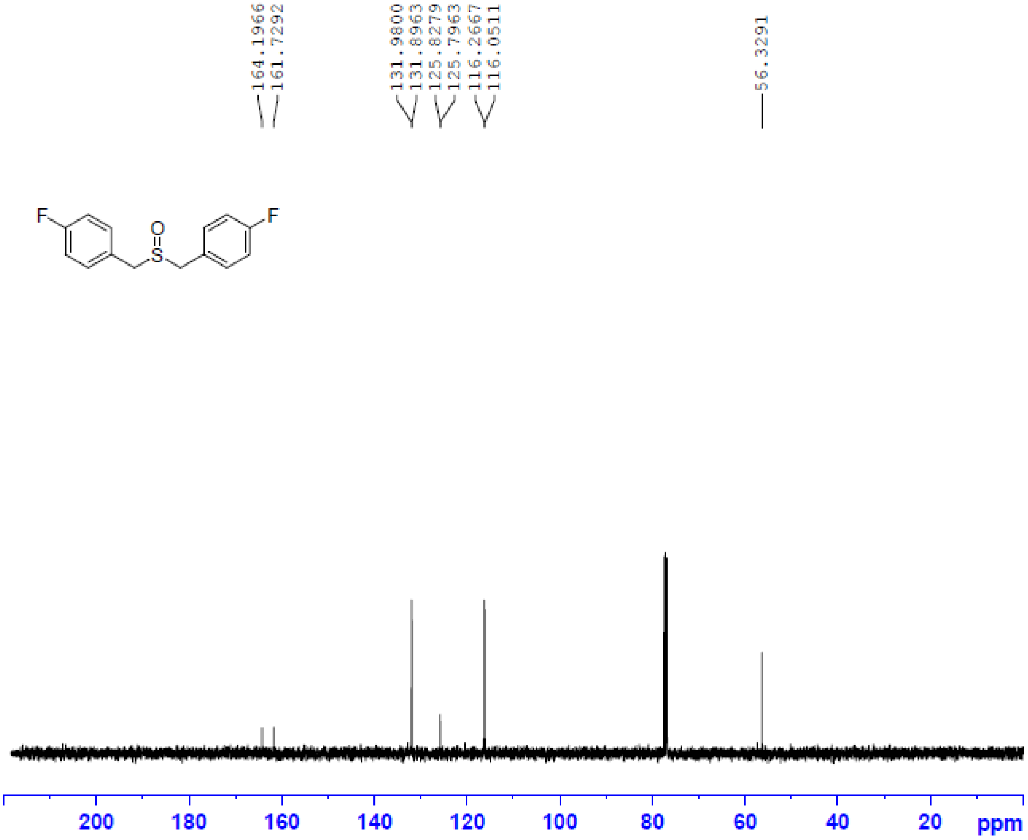
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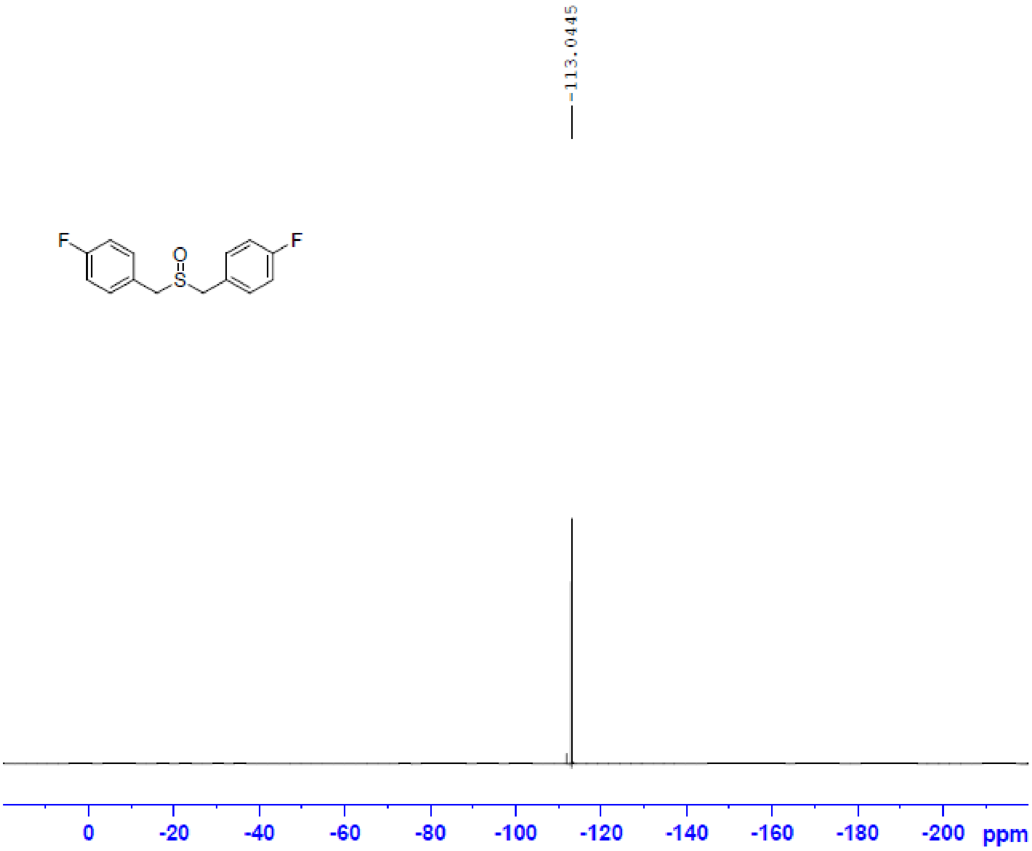
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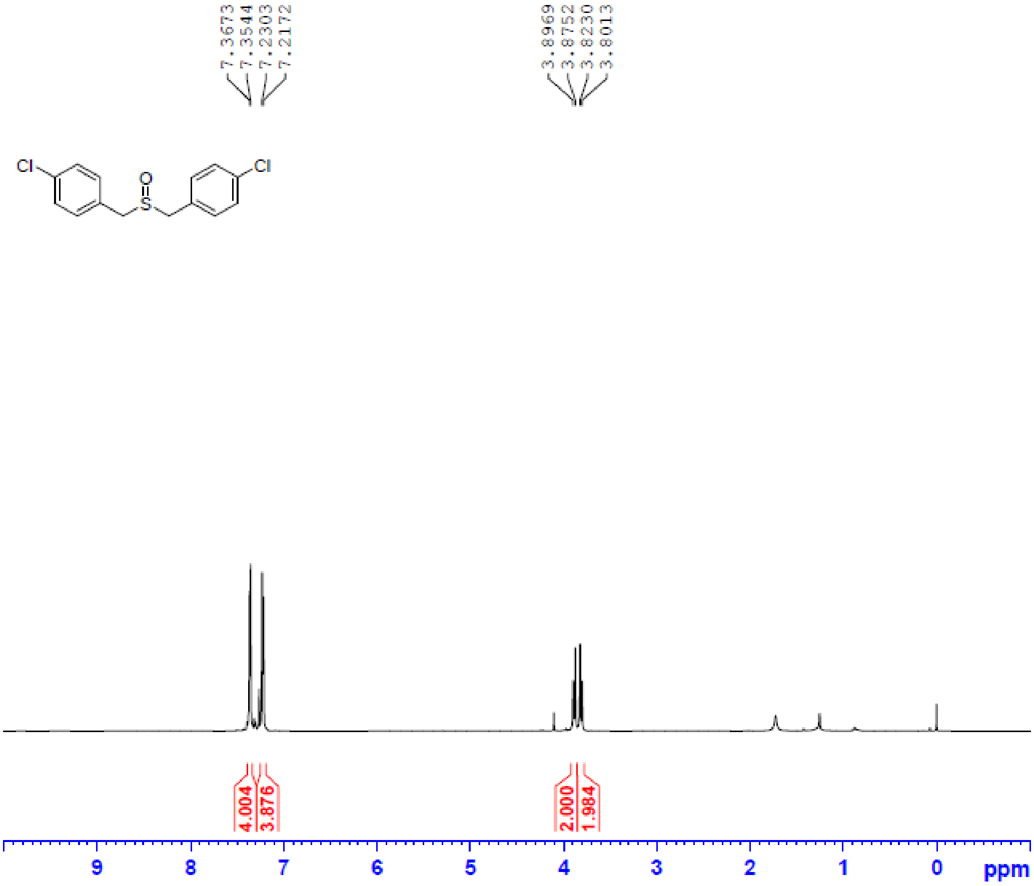
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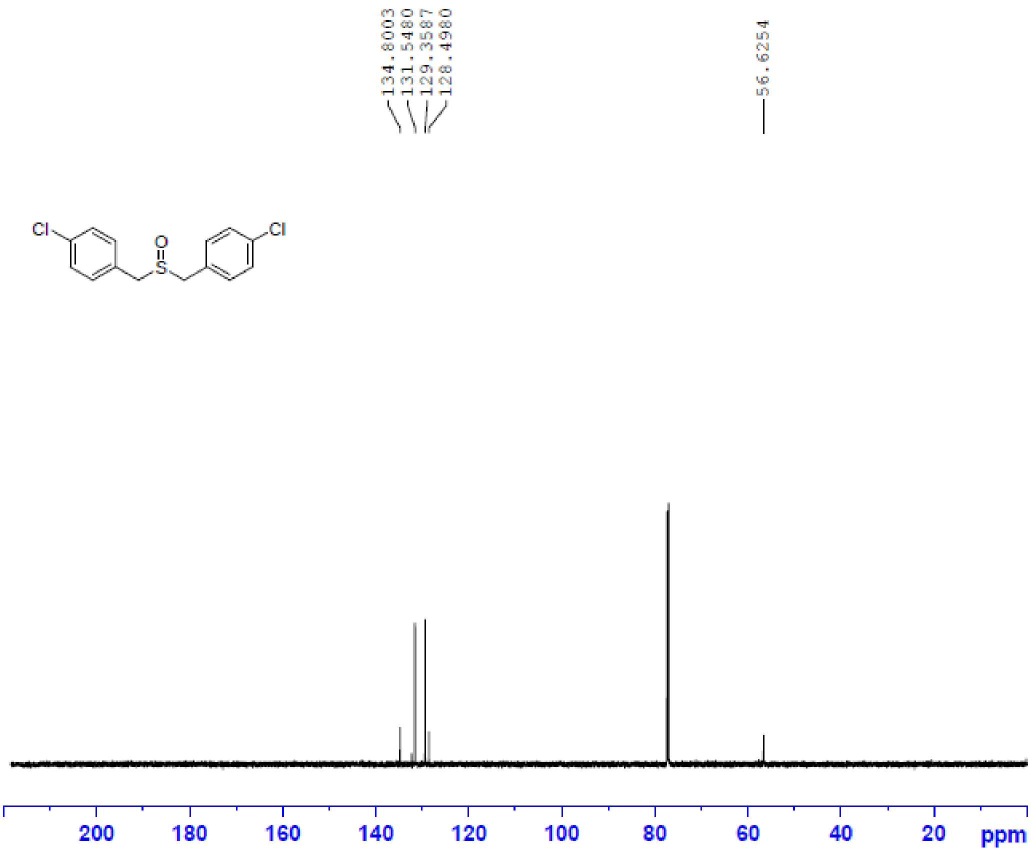
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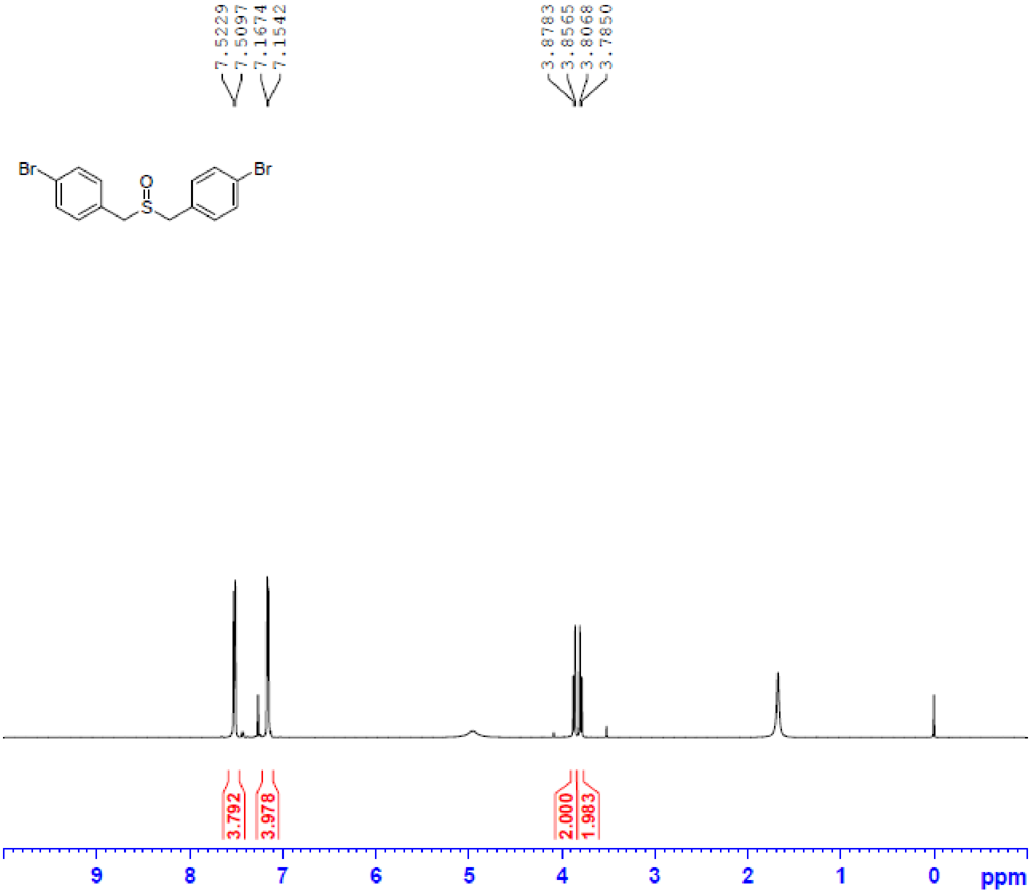
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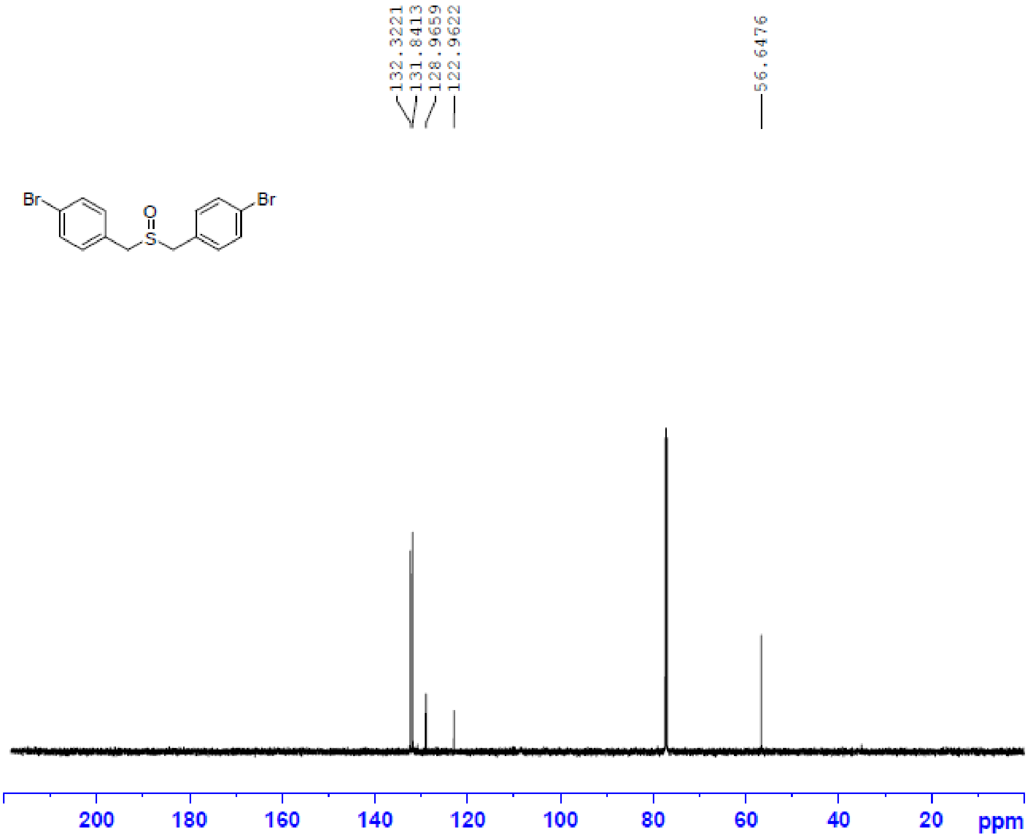
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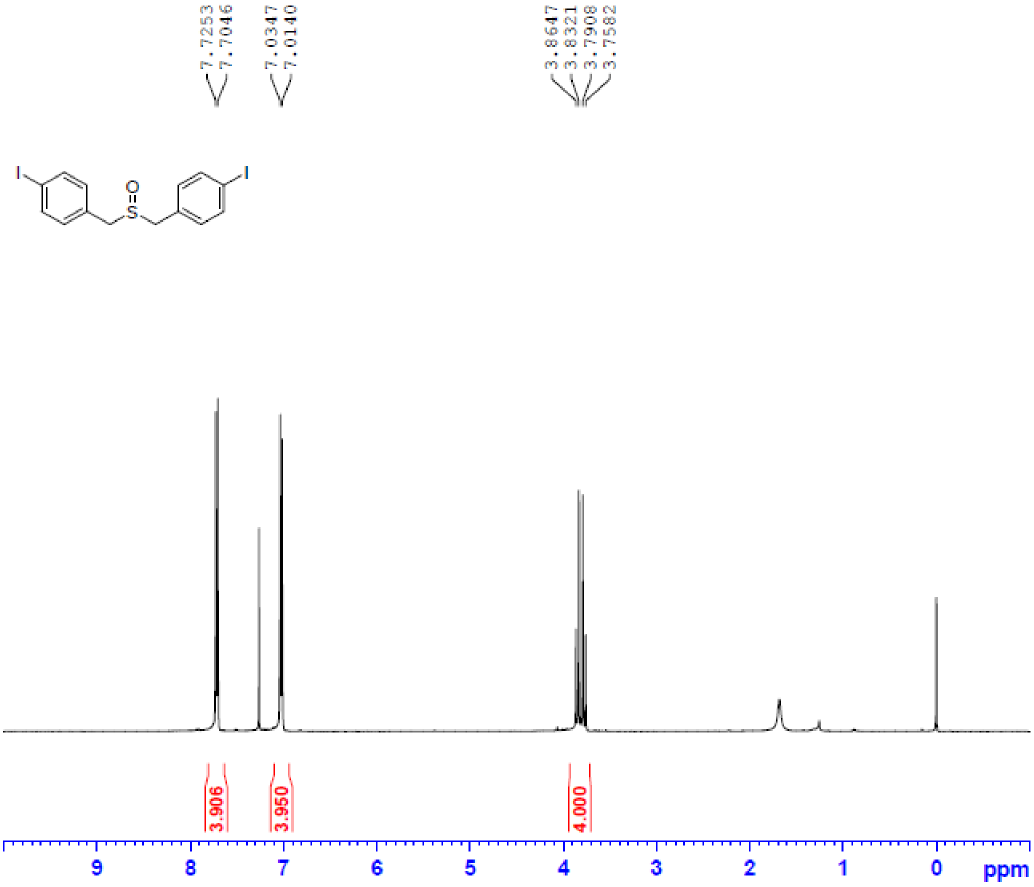
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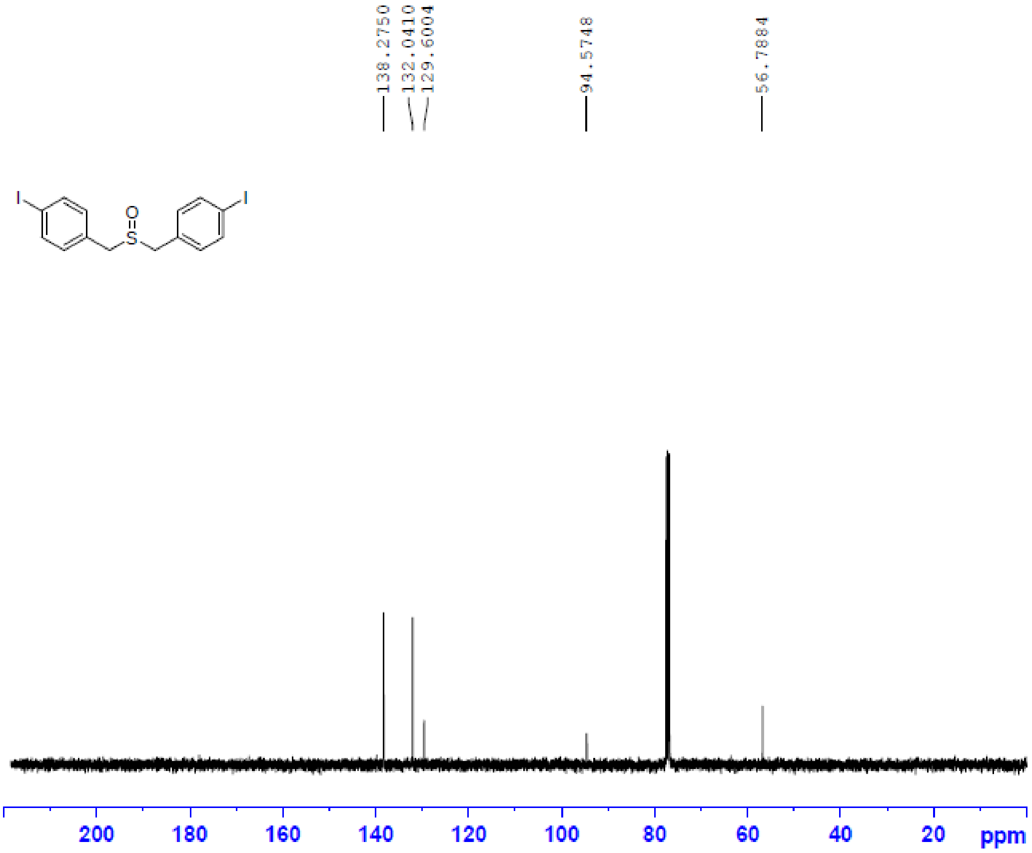
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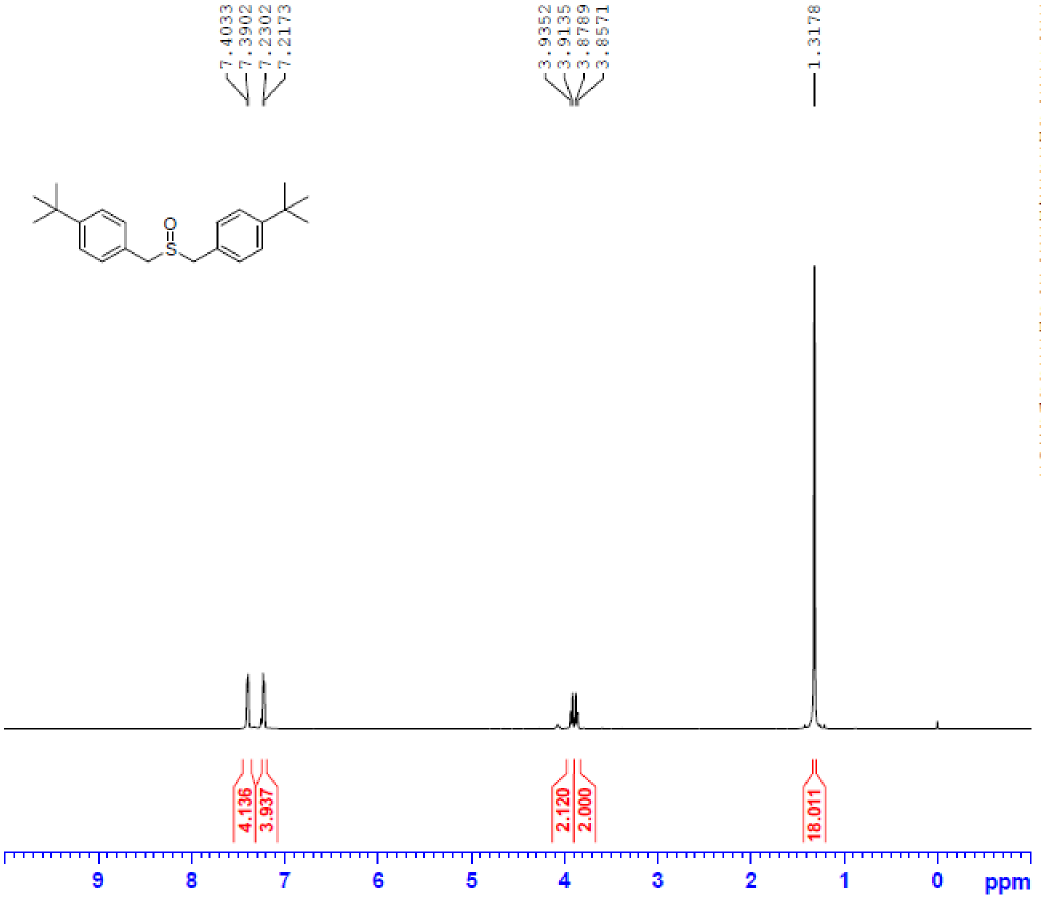
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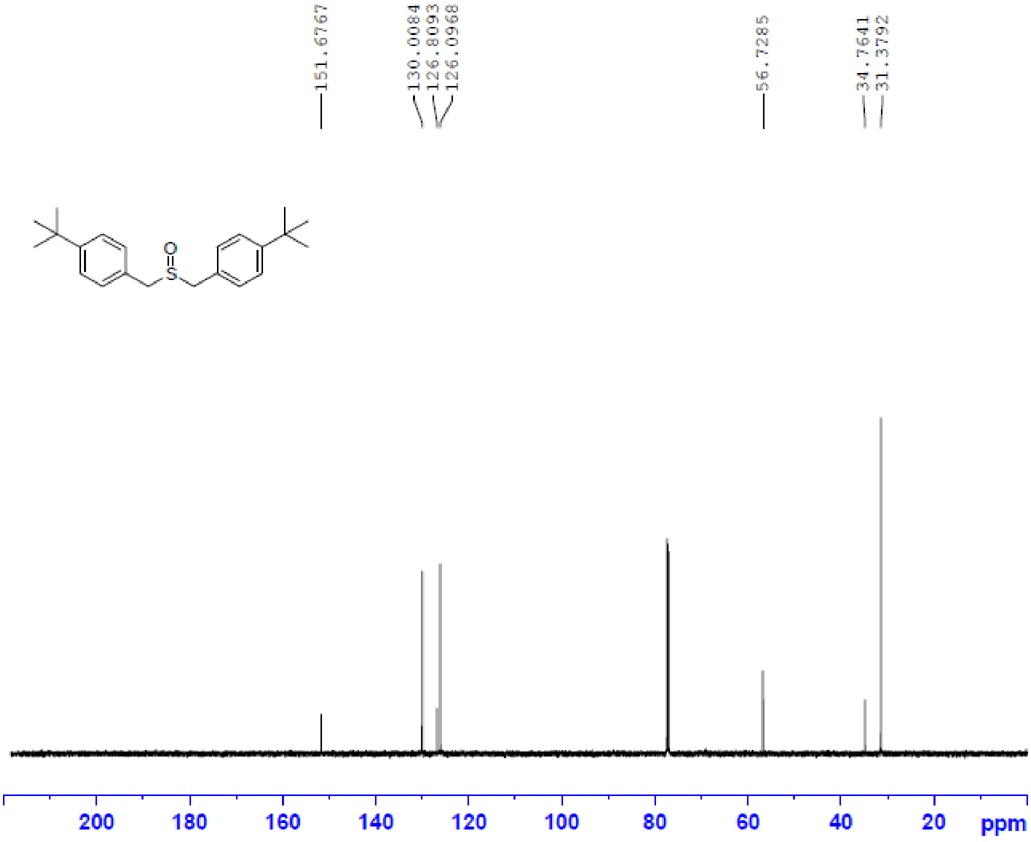
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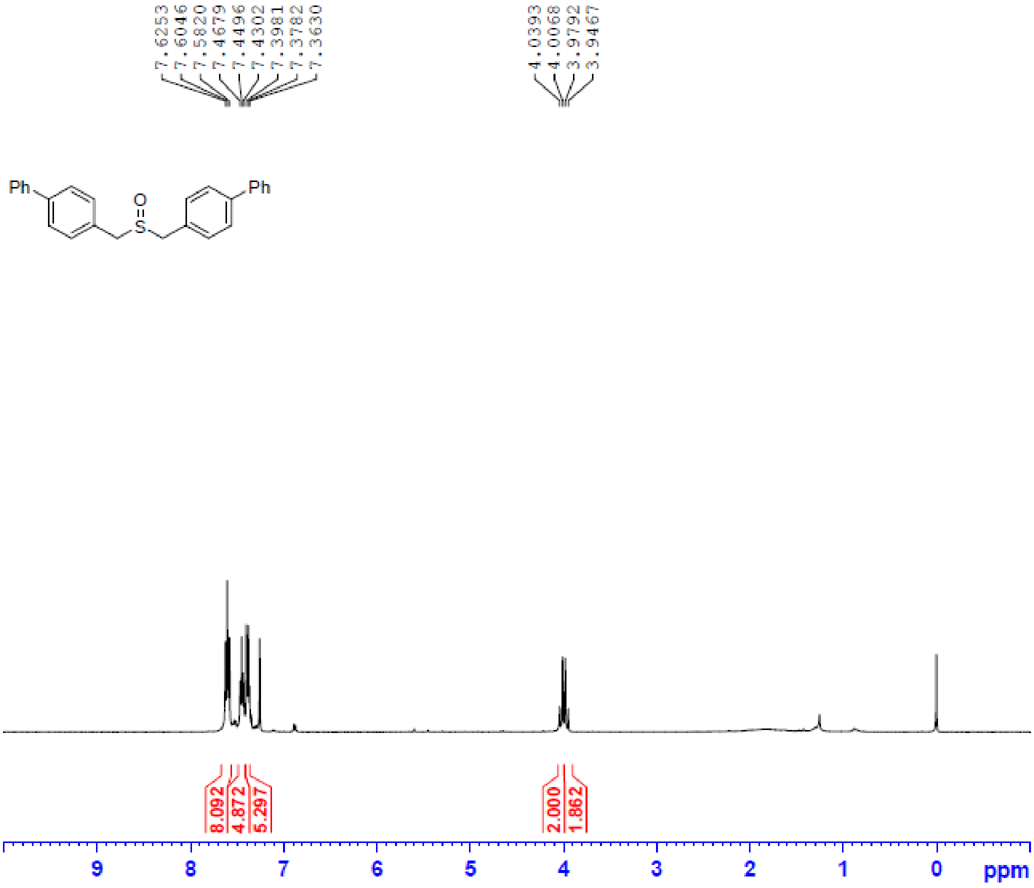
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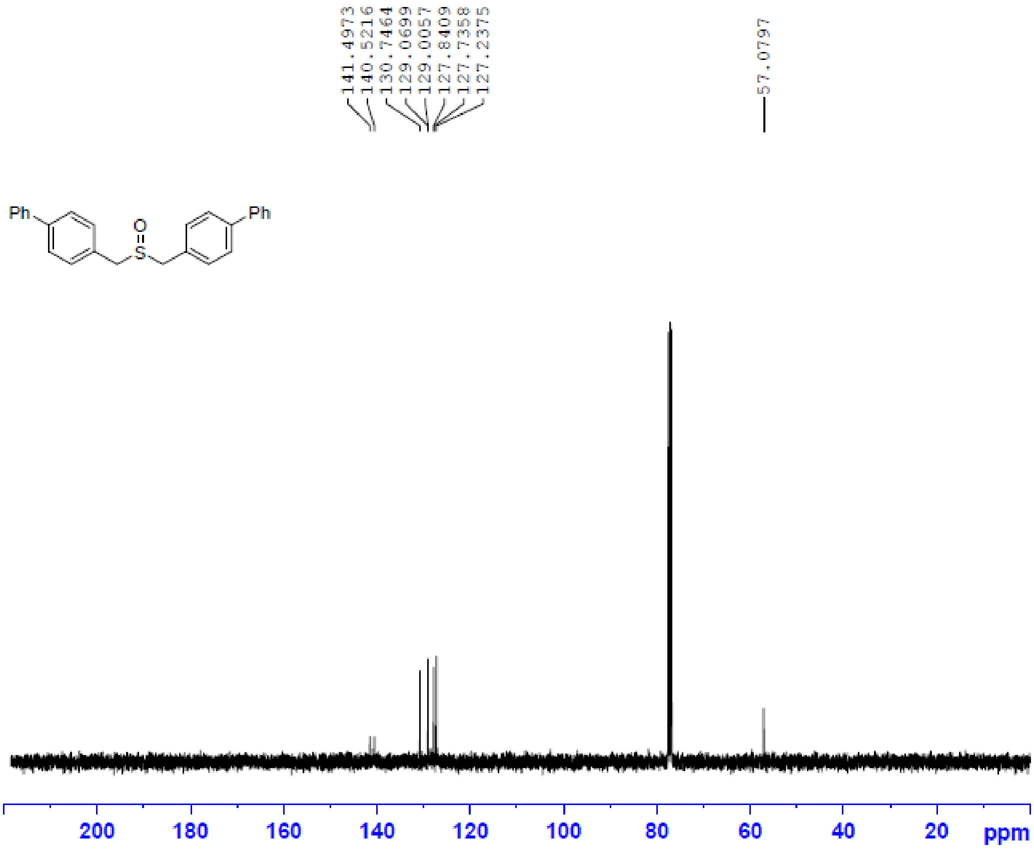
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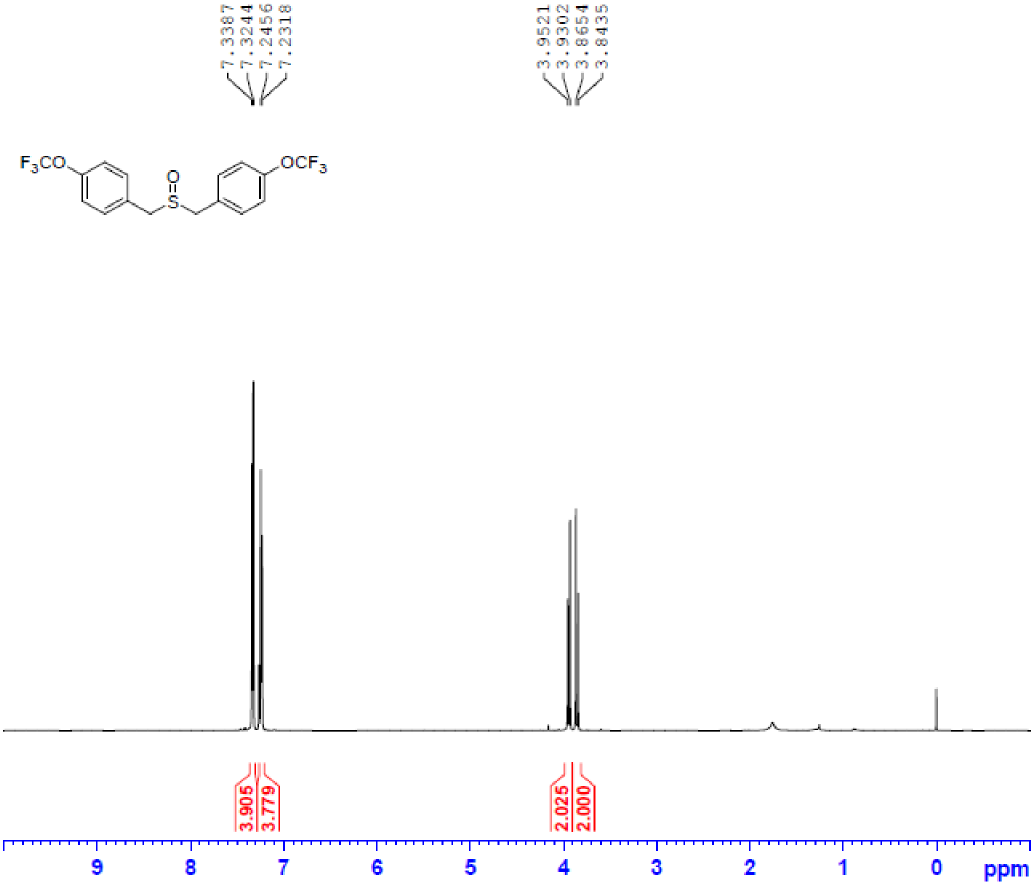
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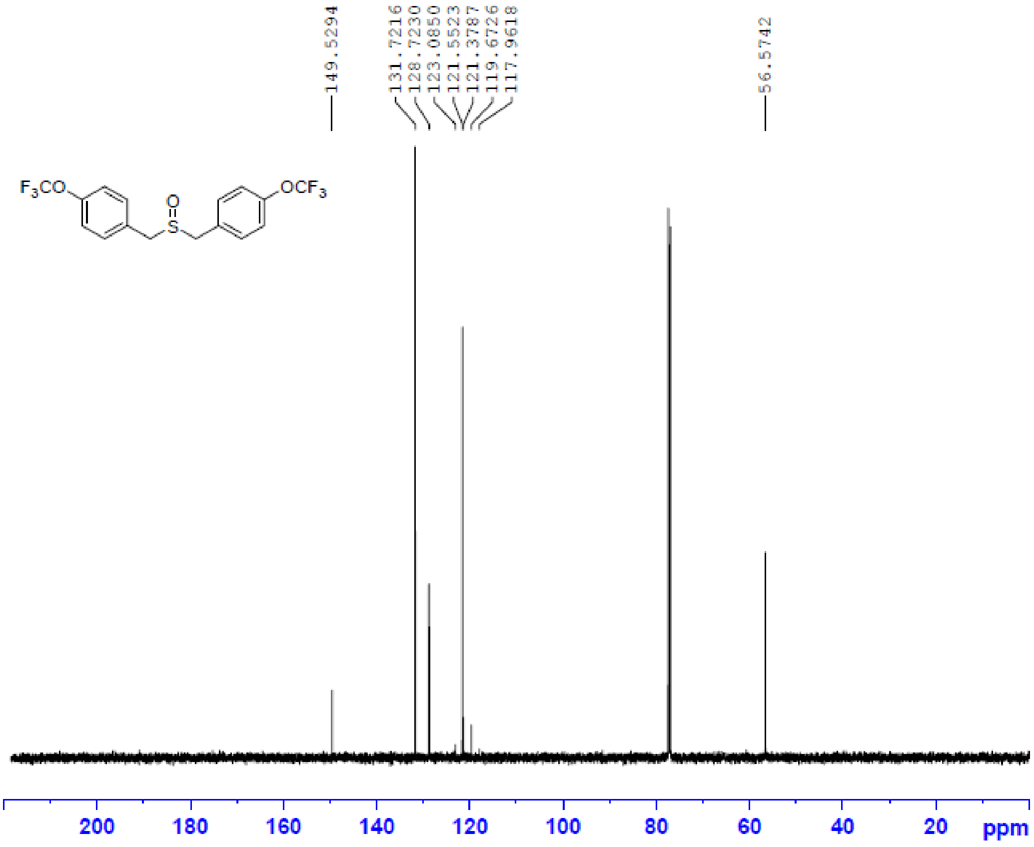
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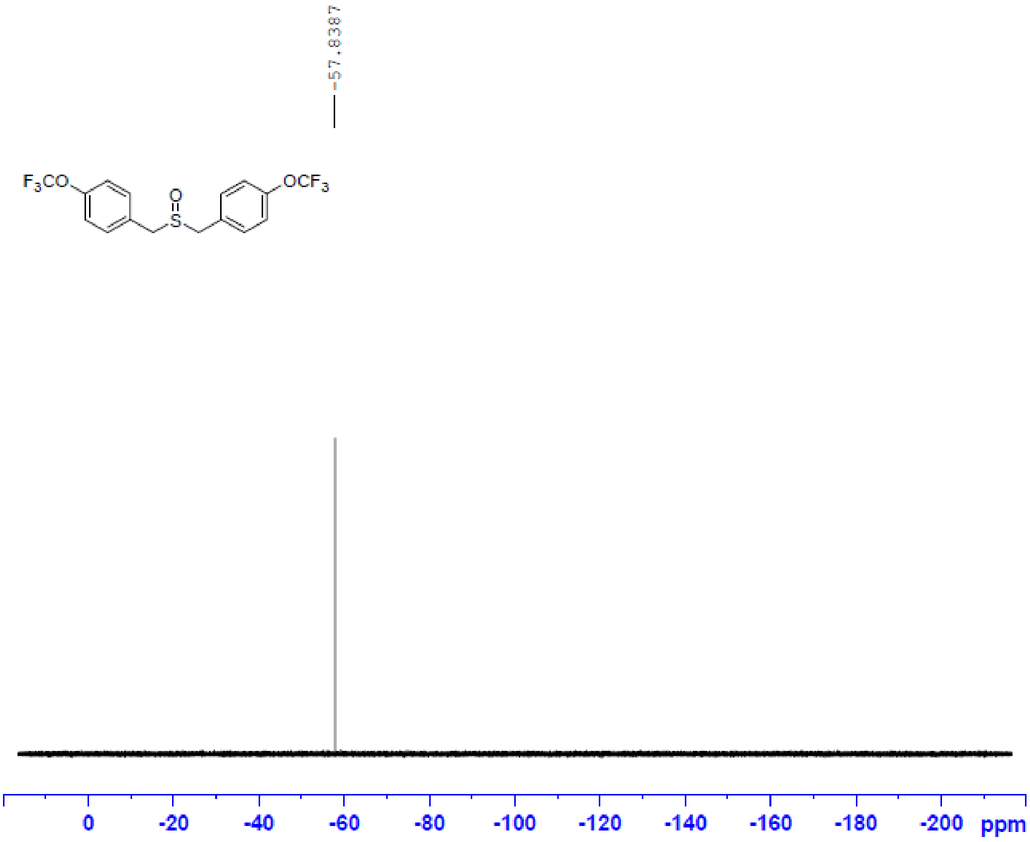
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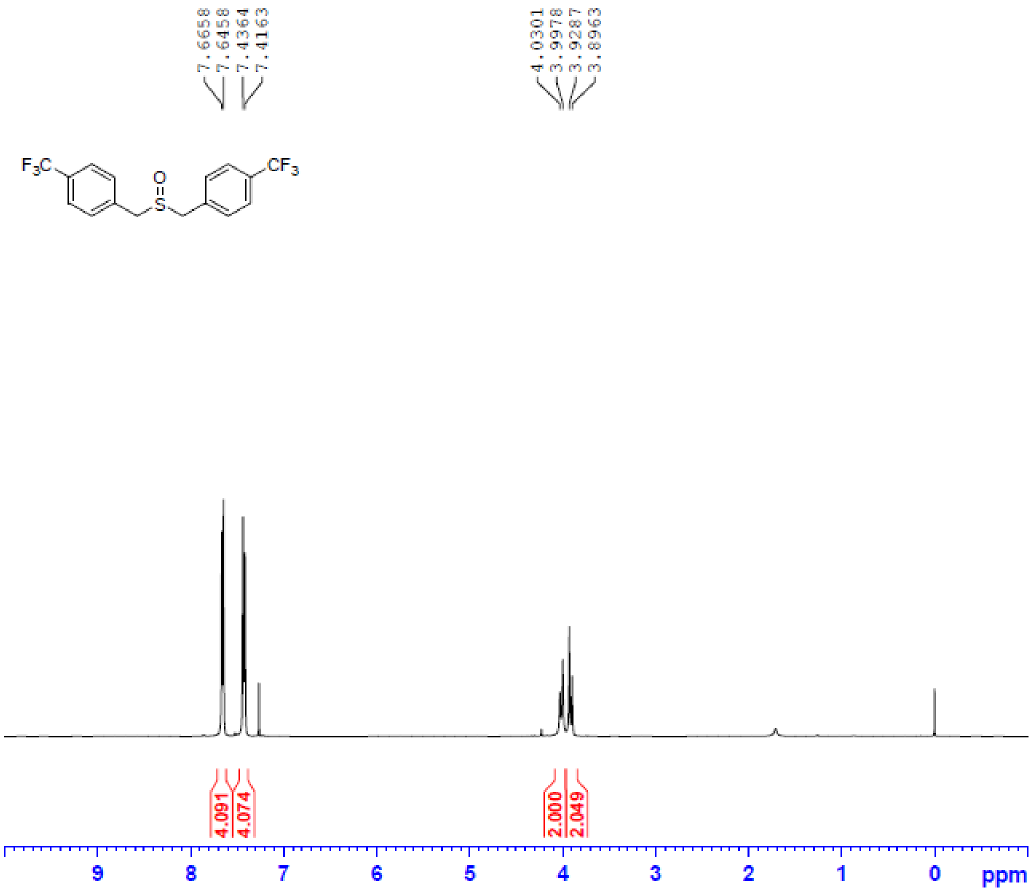
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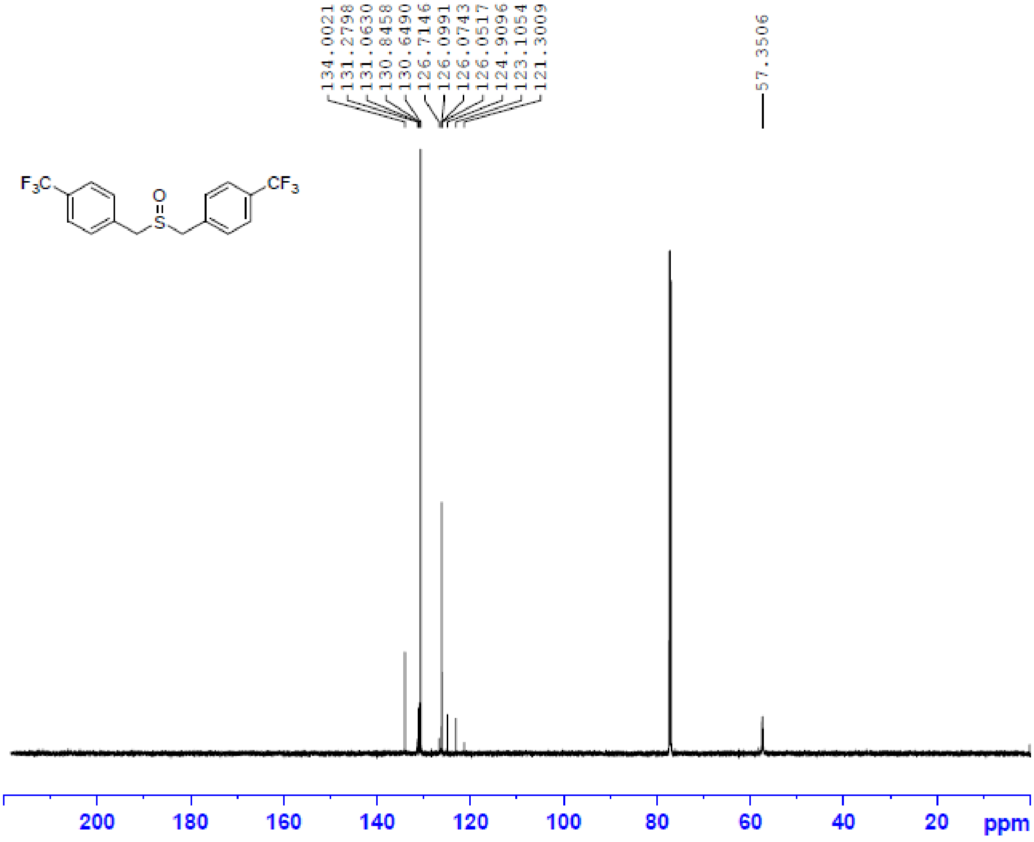
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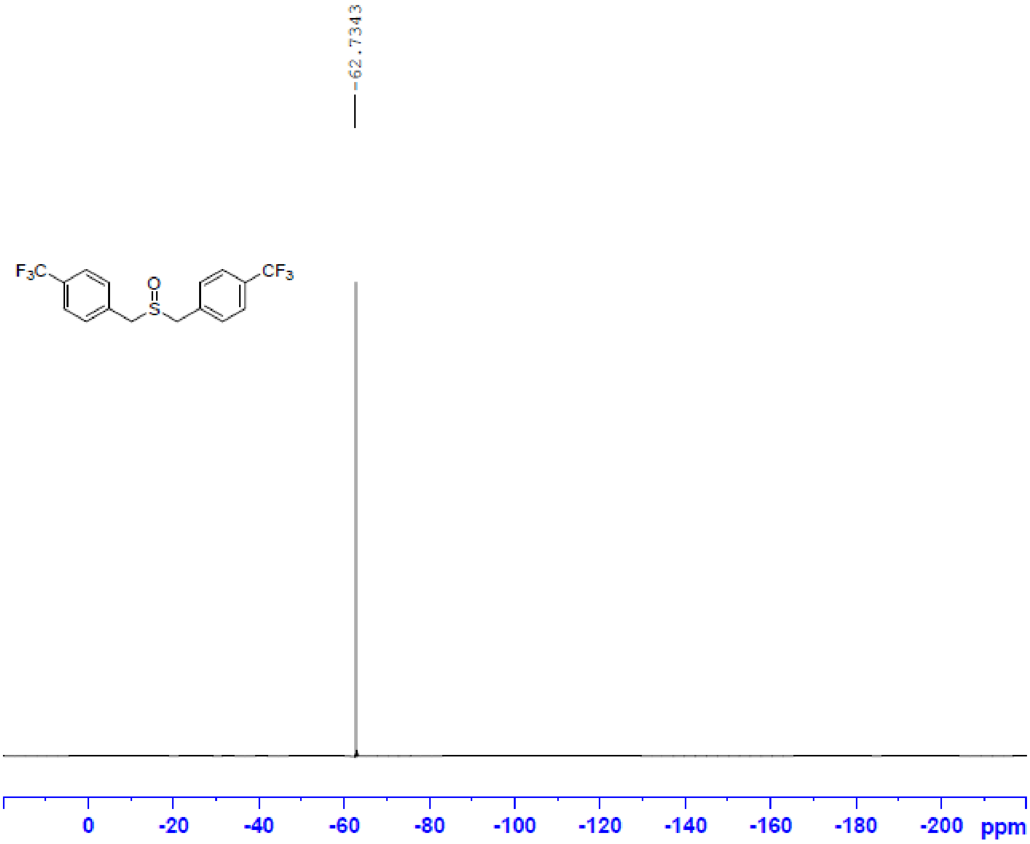
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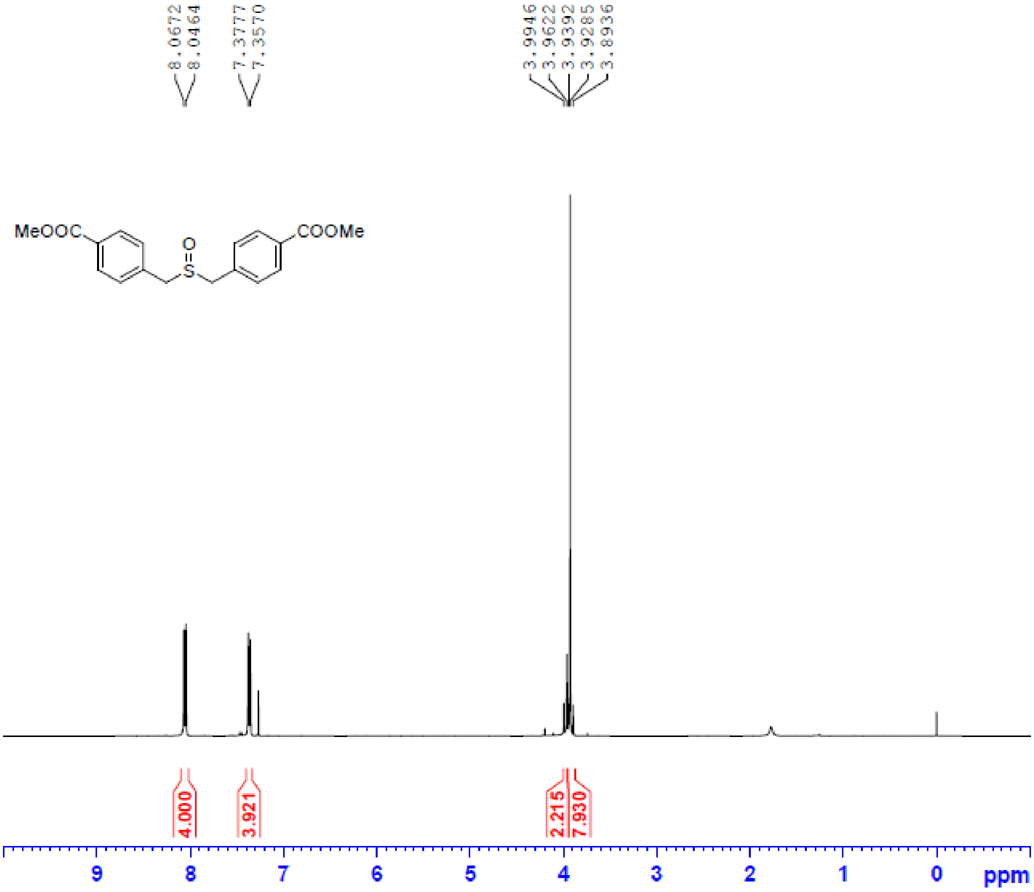
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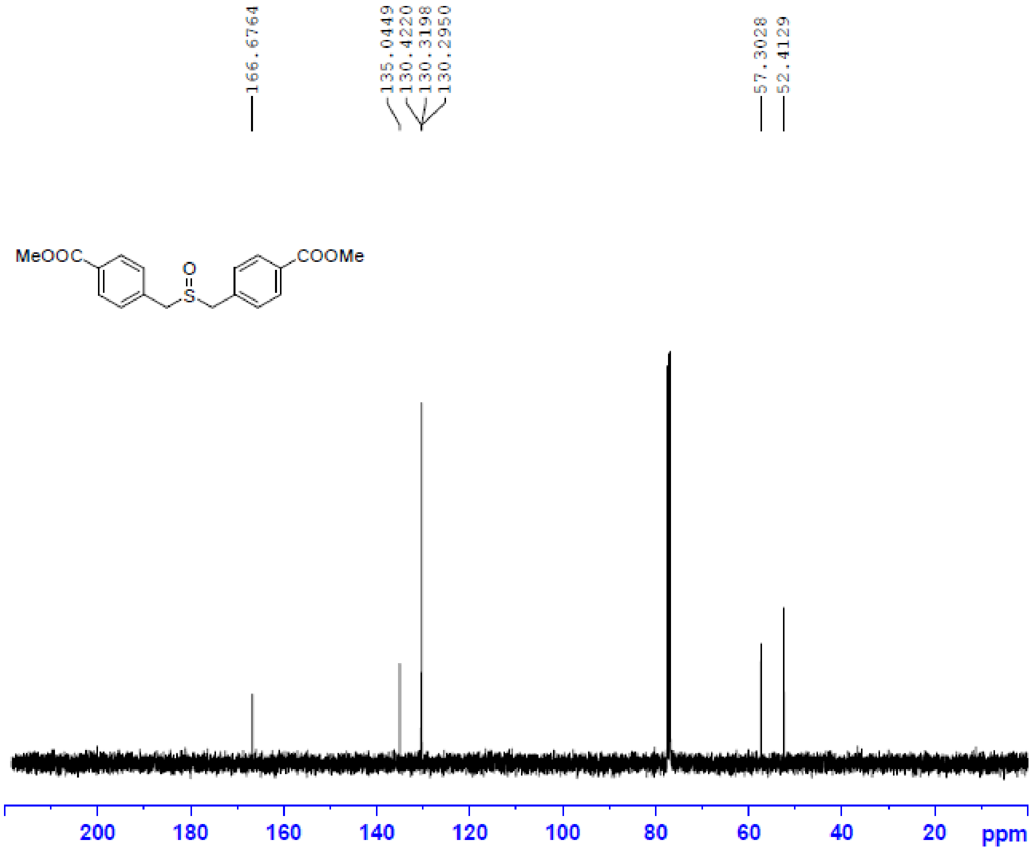
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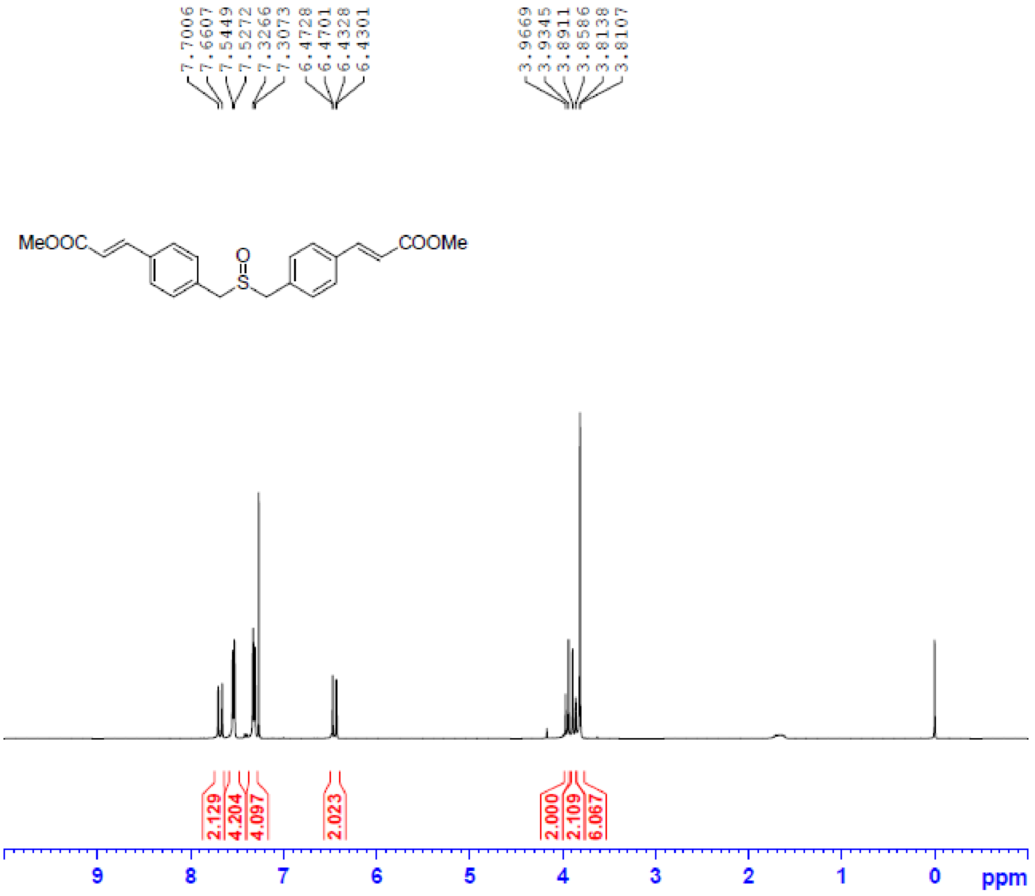
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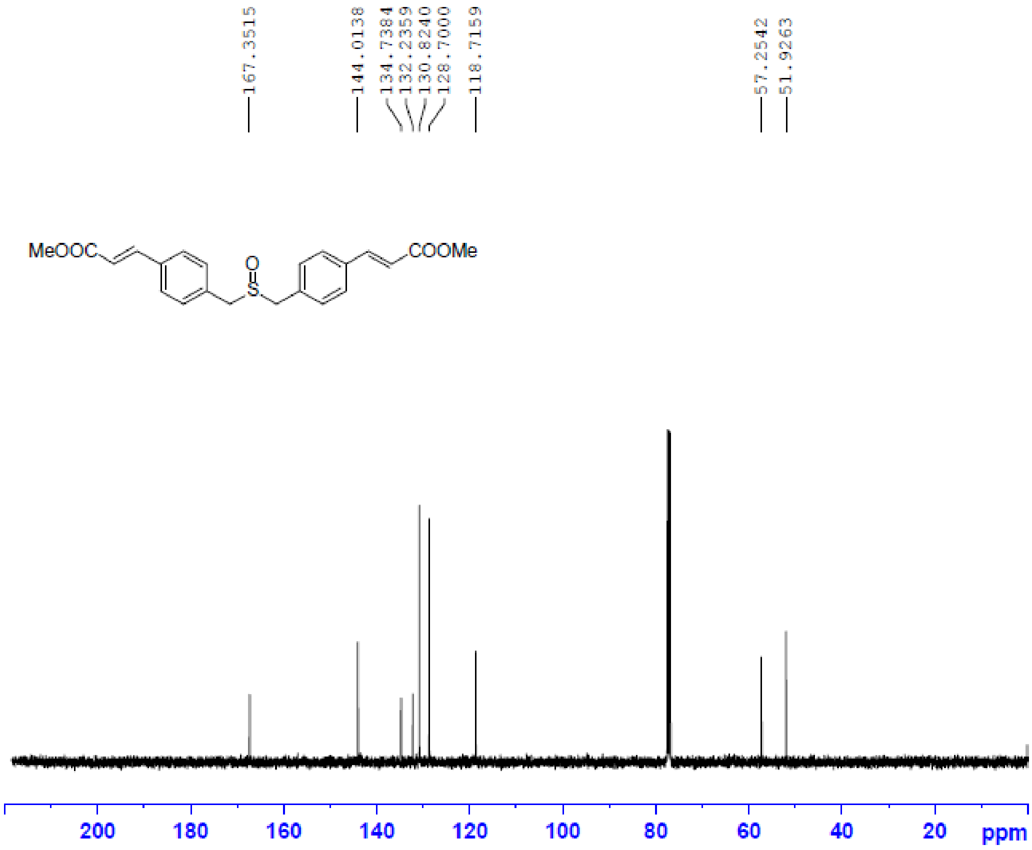
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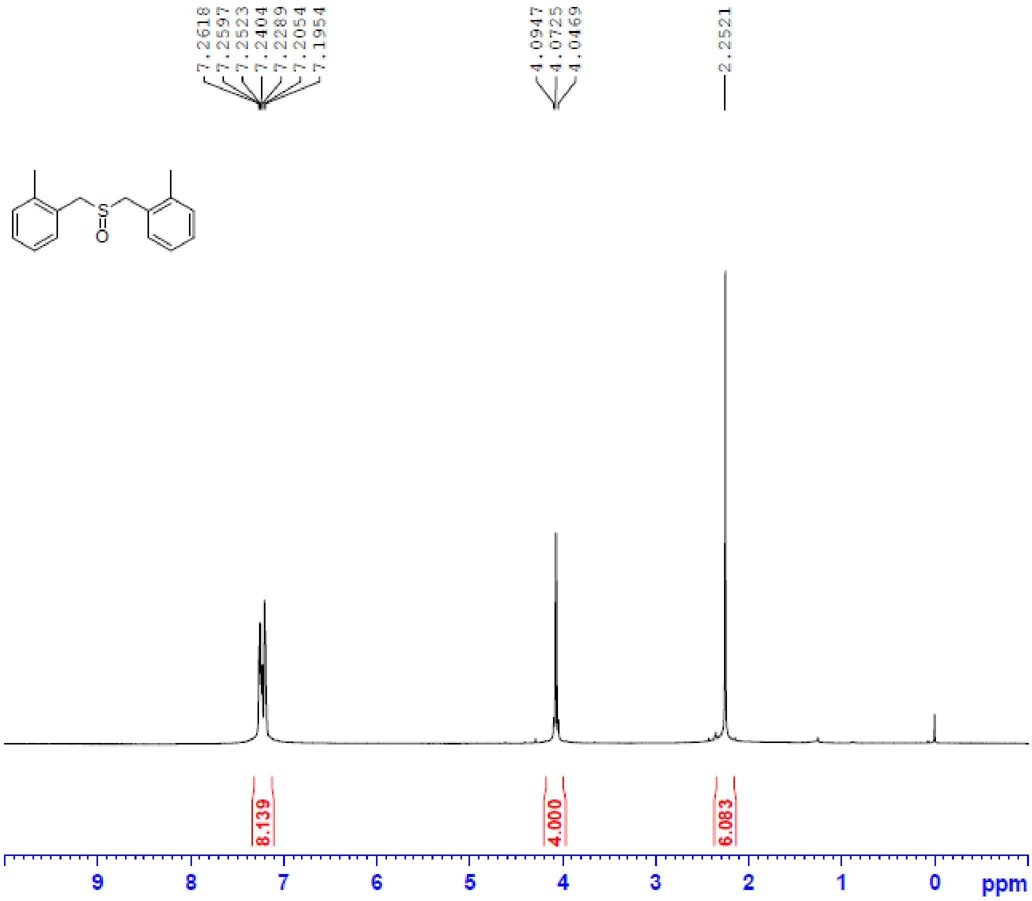
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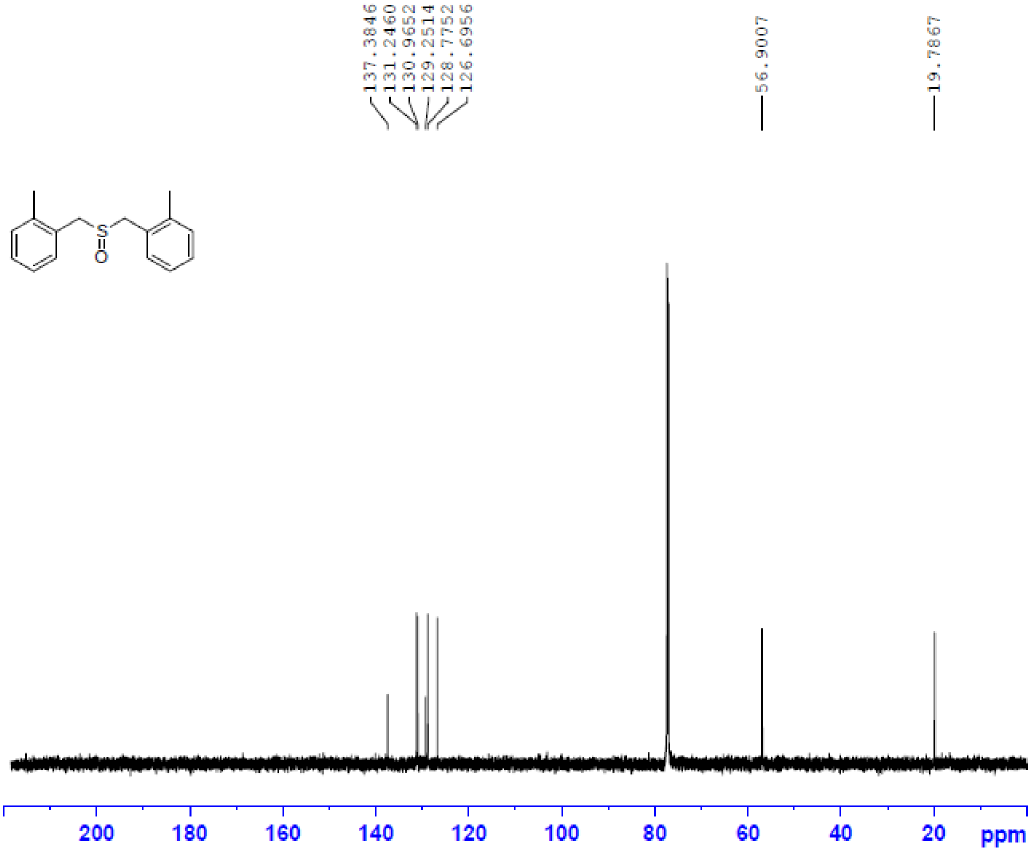
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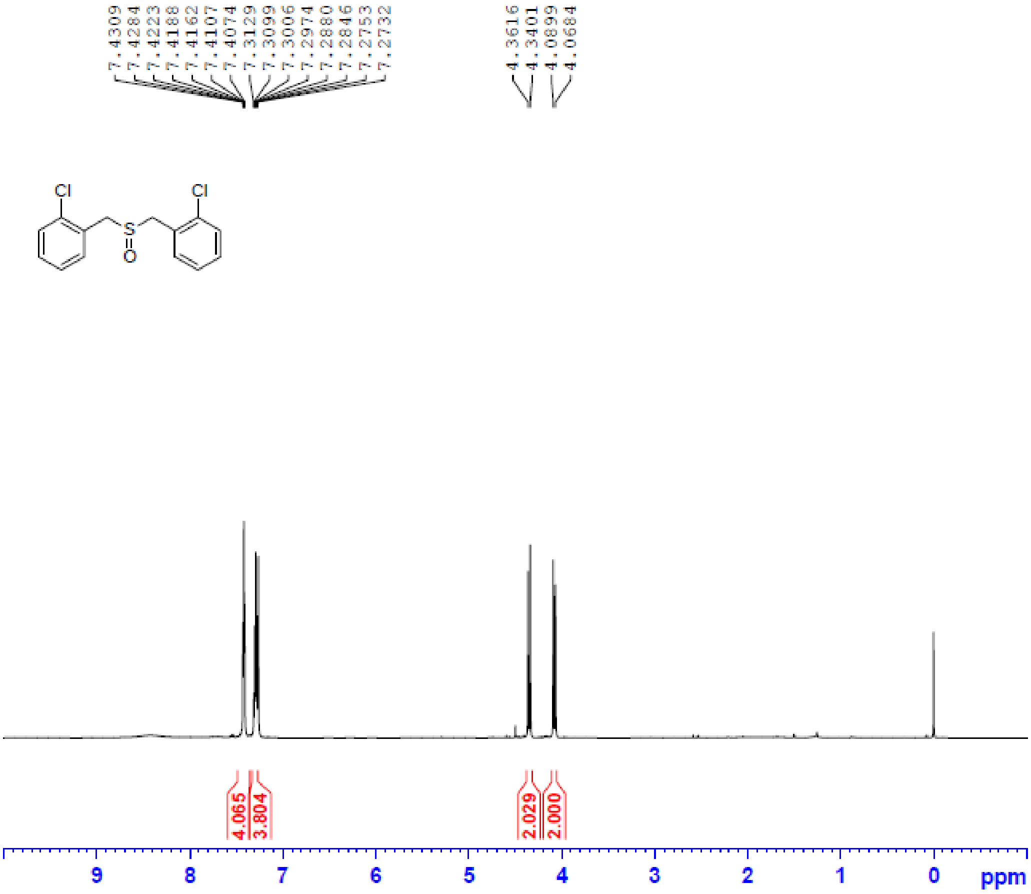
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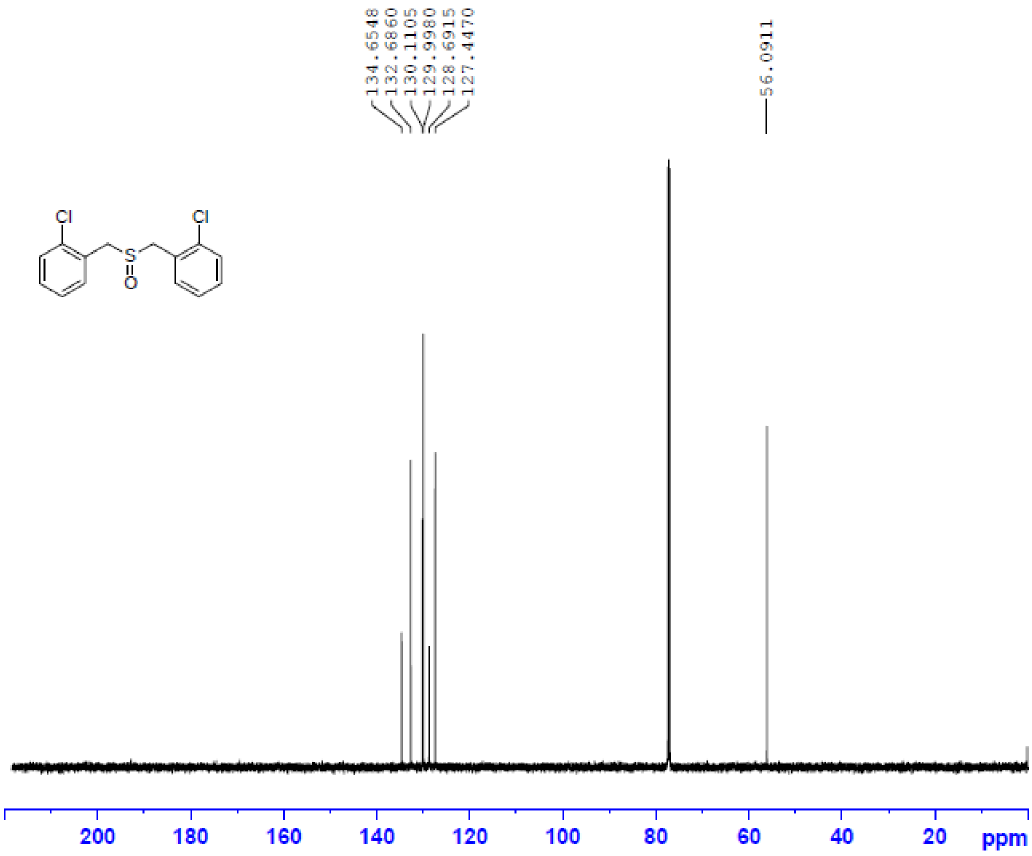
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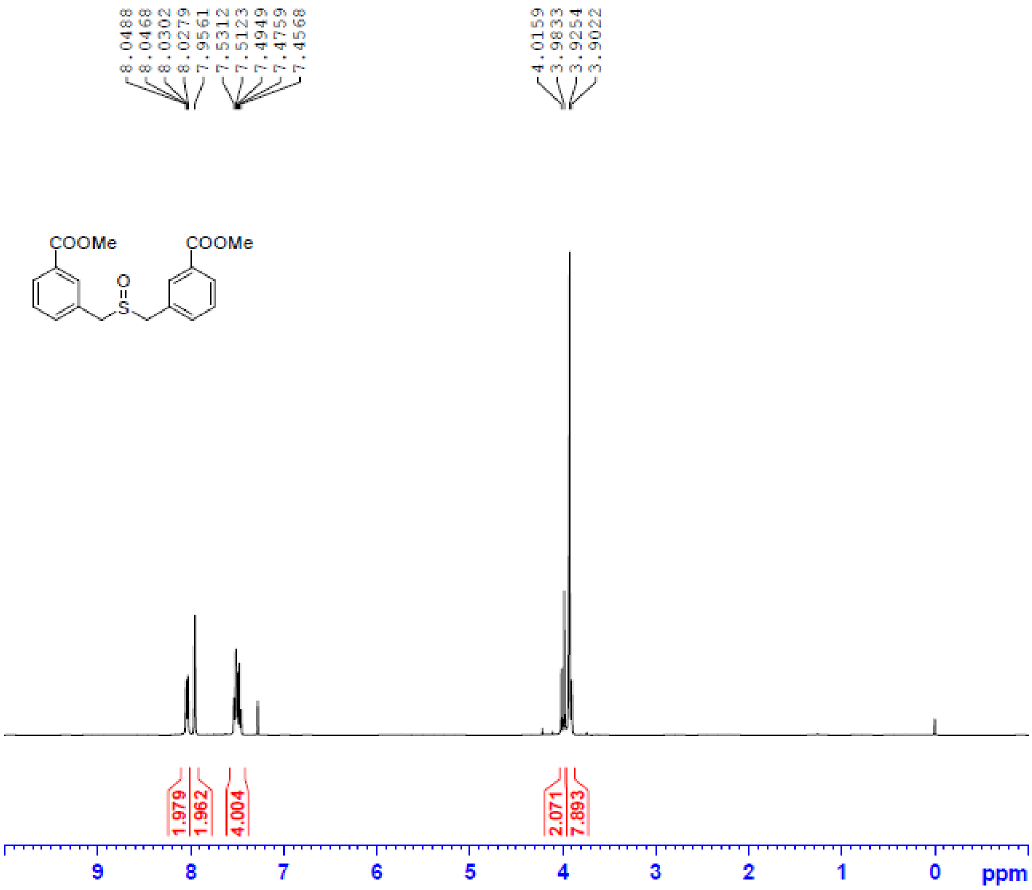
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COOMe
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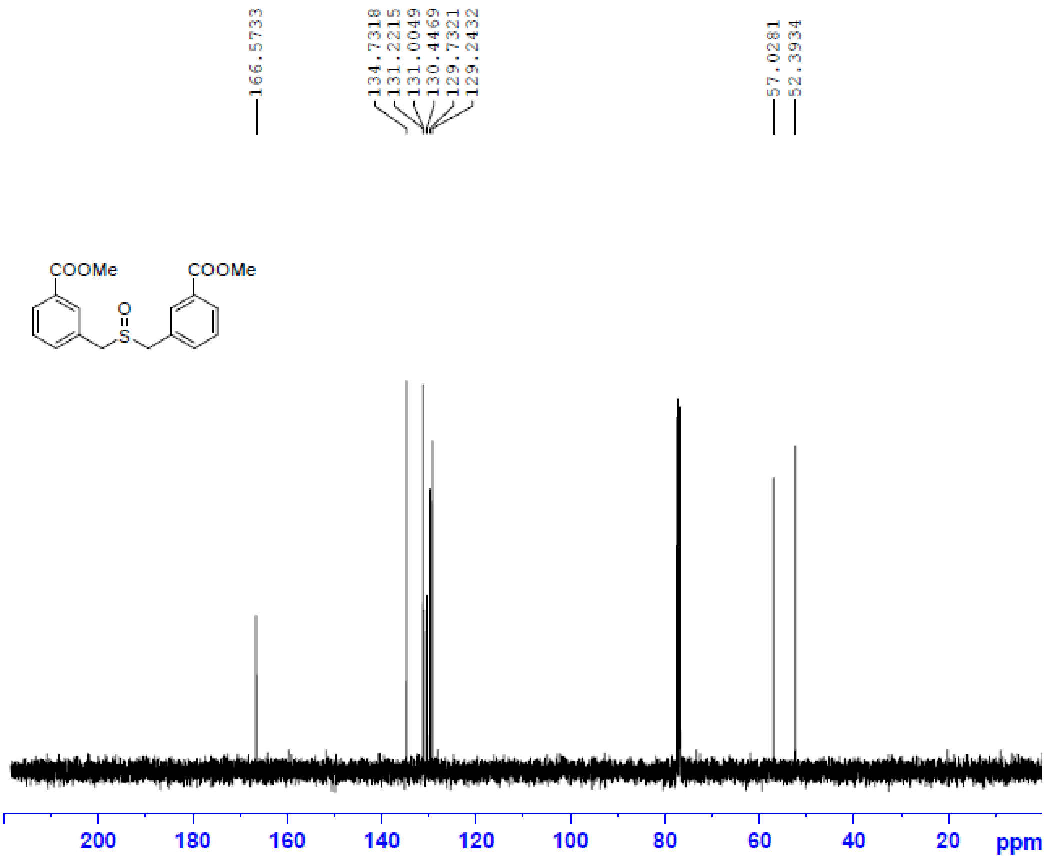
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COOMe
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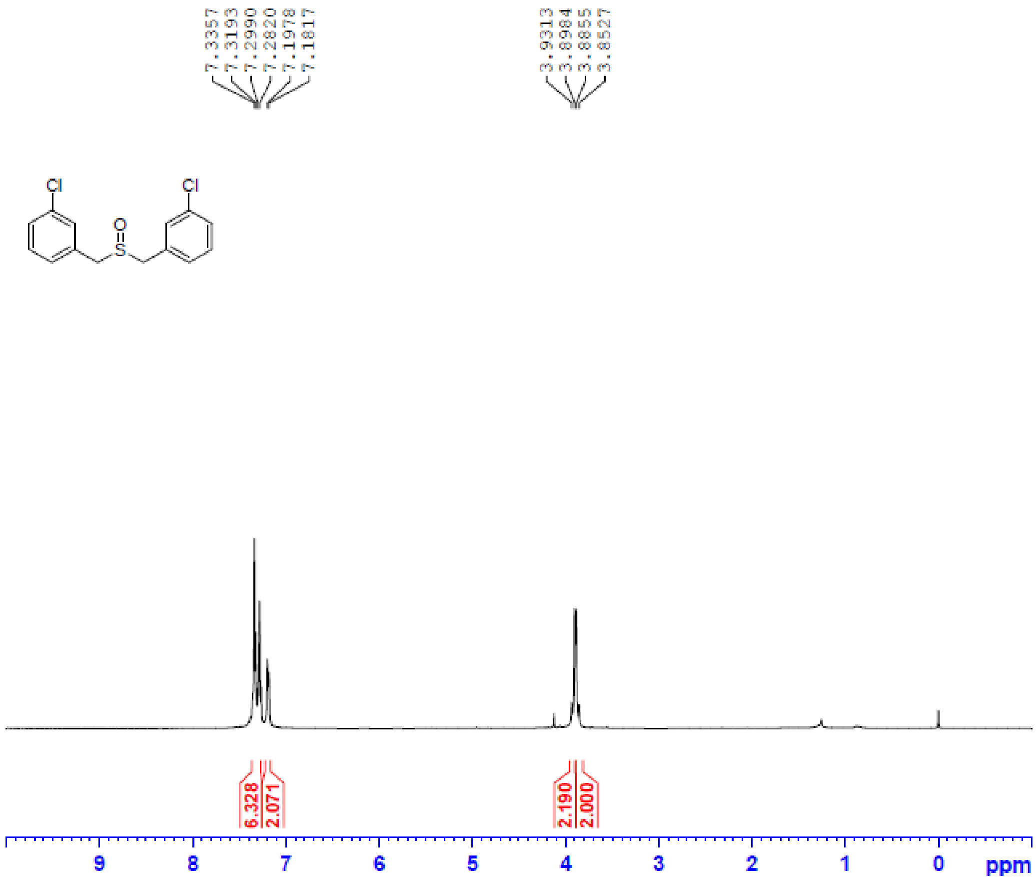
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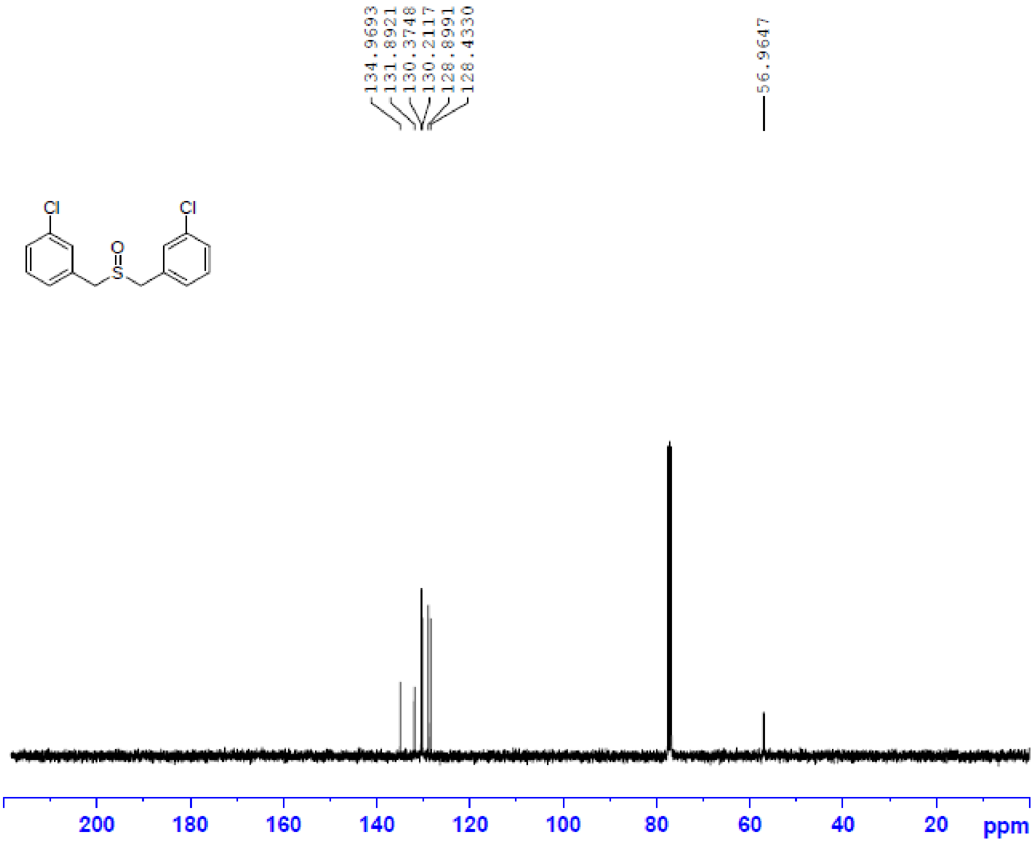
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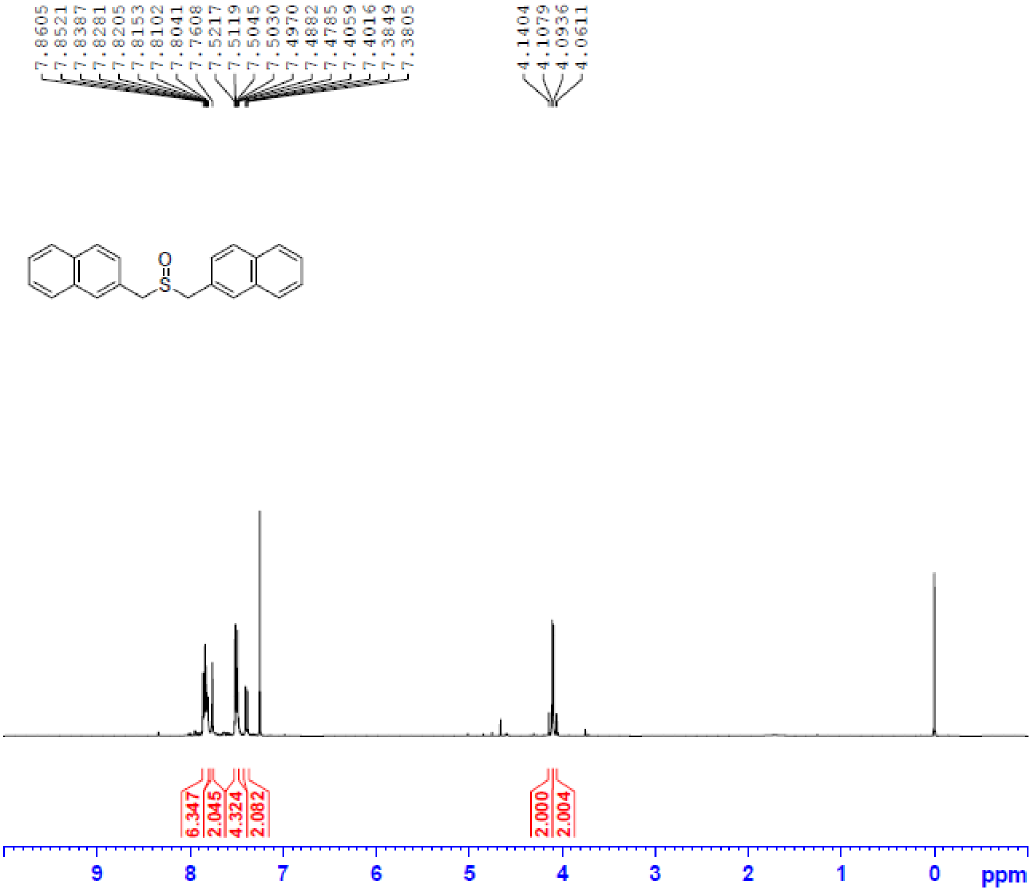
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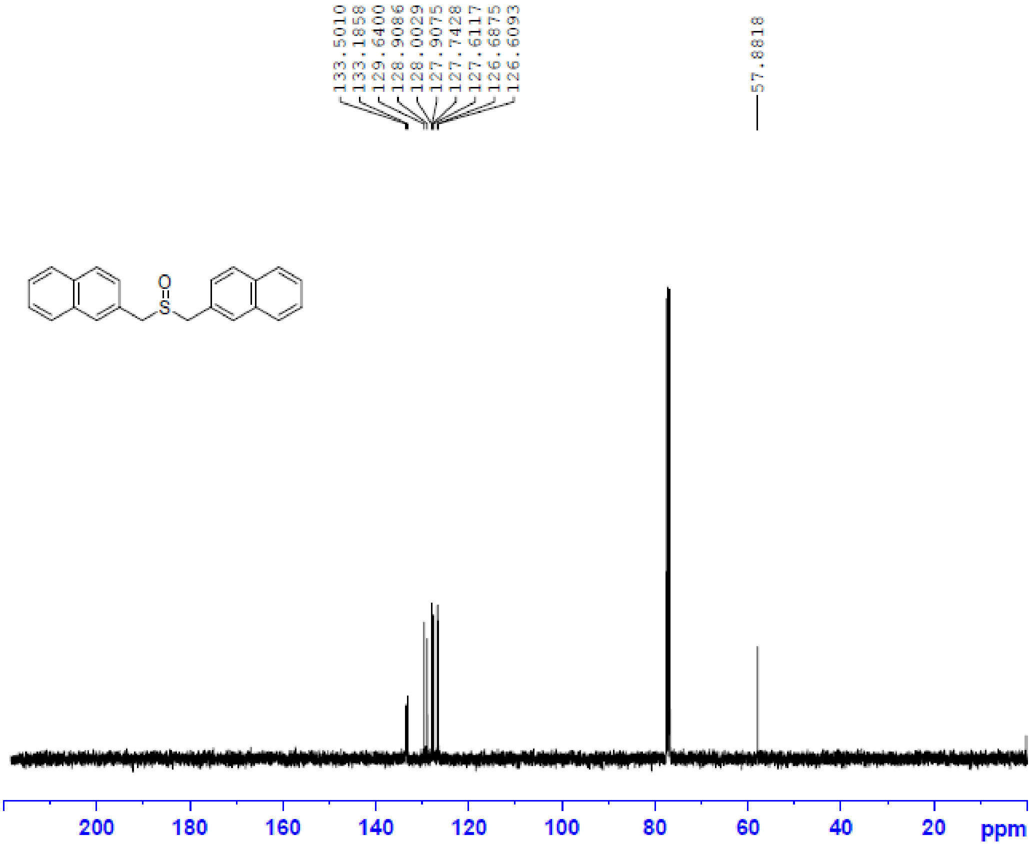
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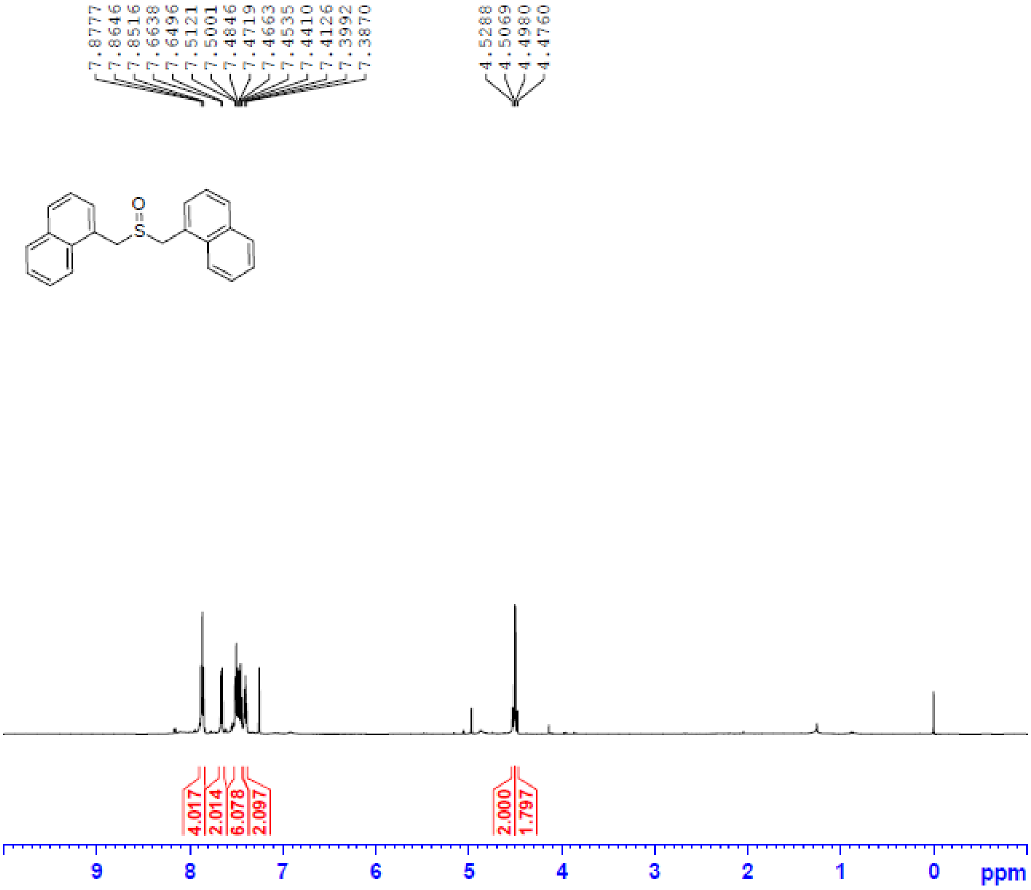
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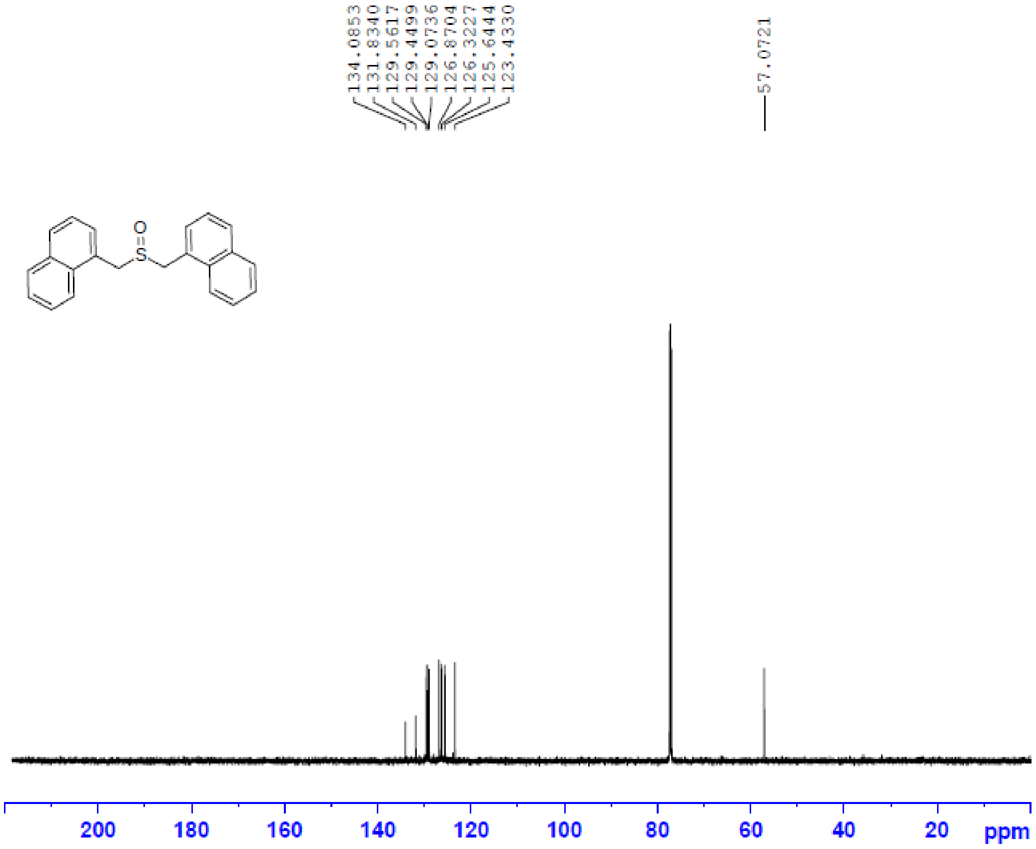
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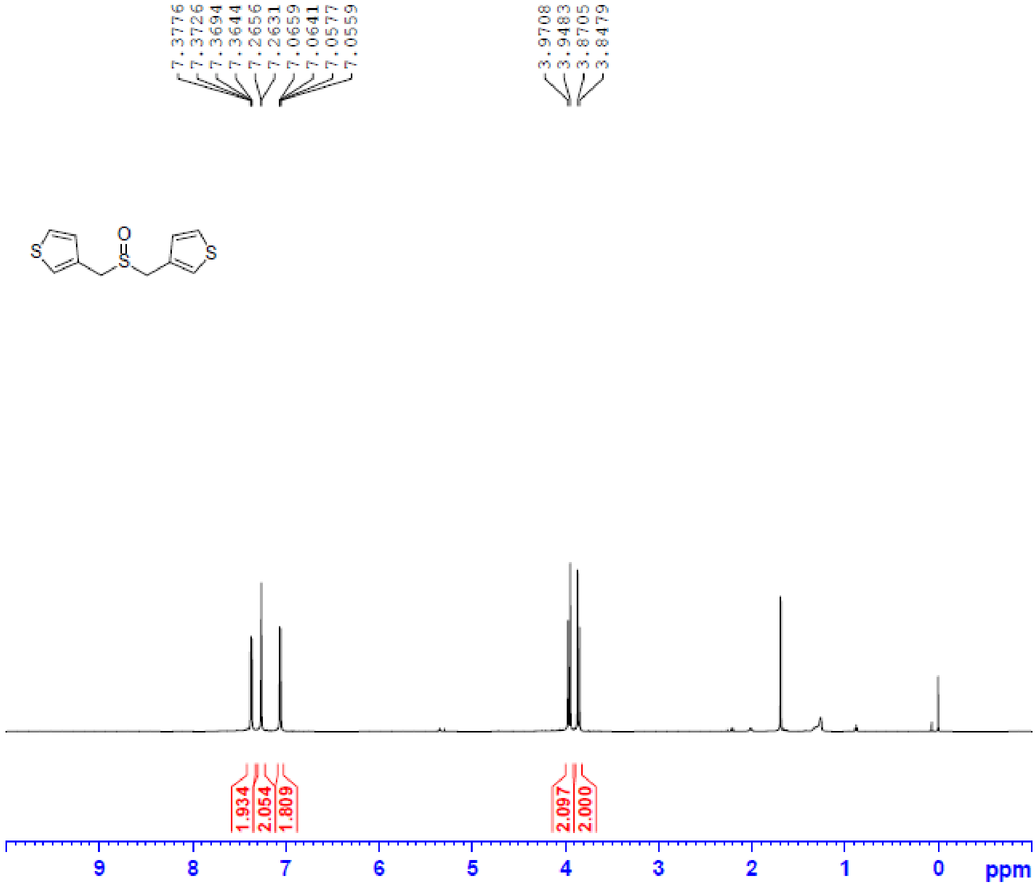
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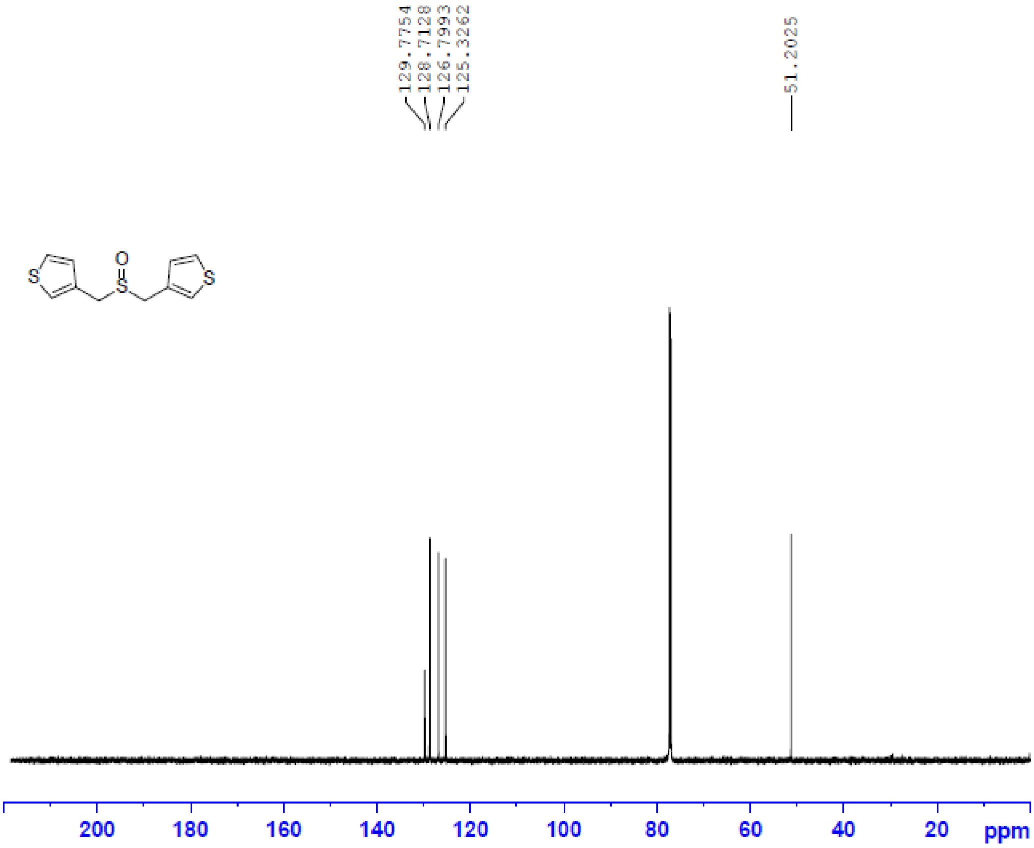
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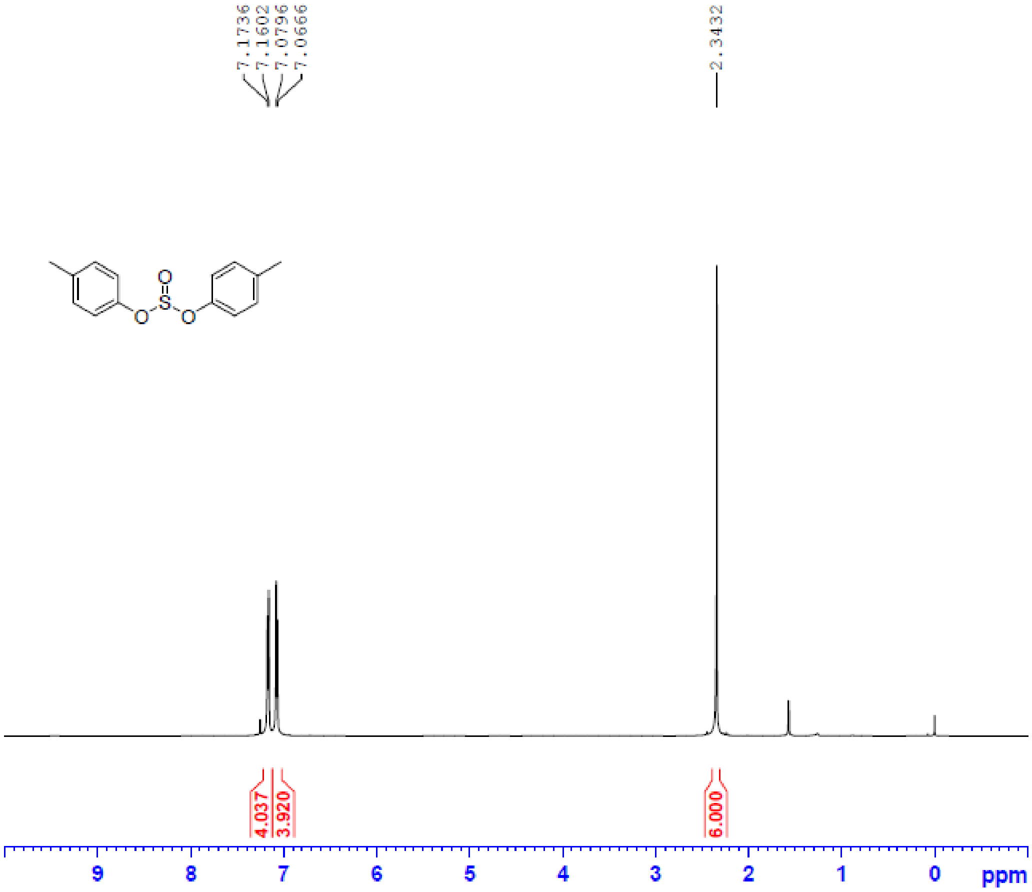
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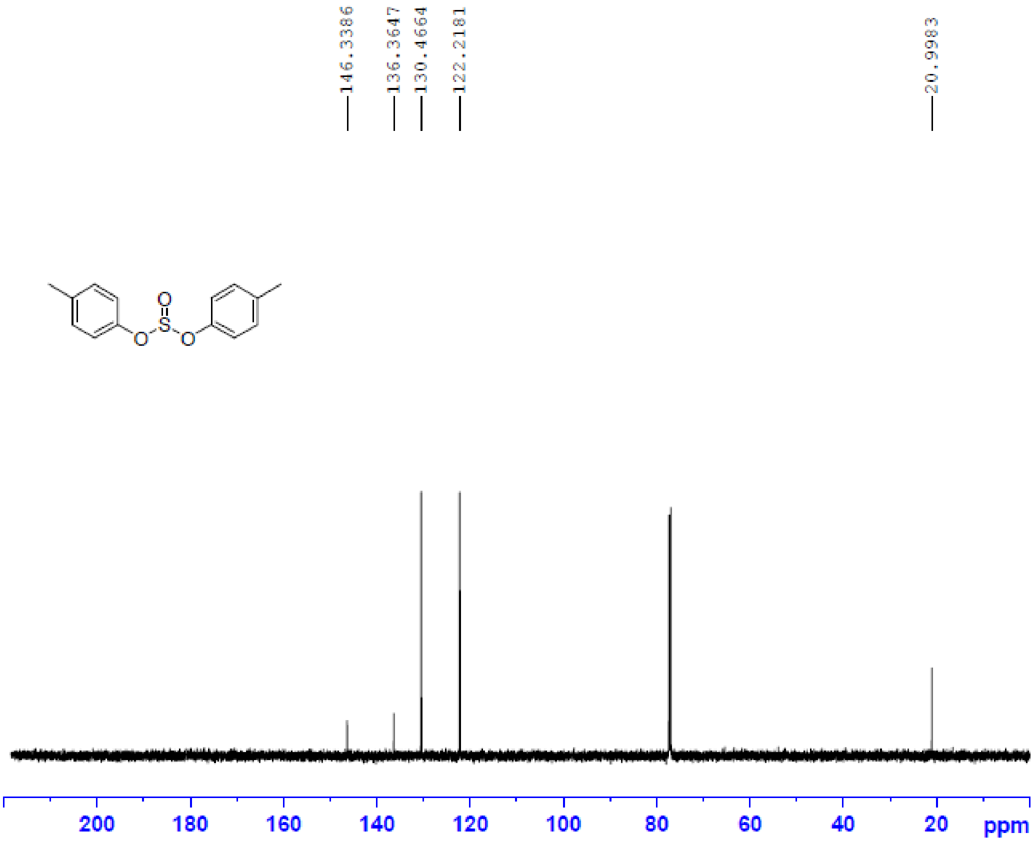
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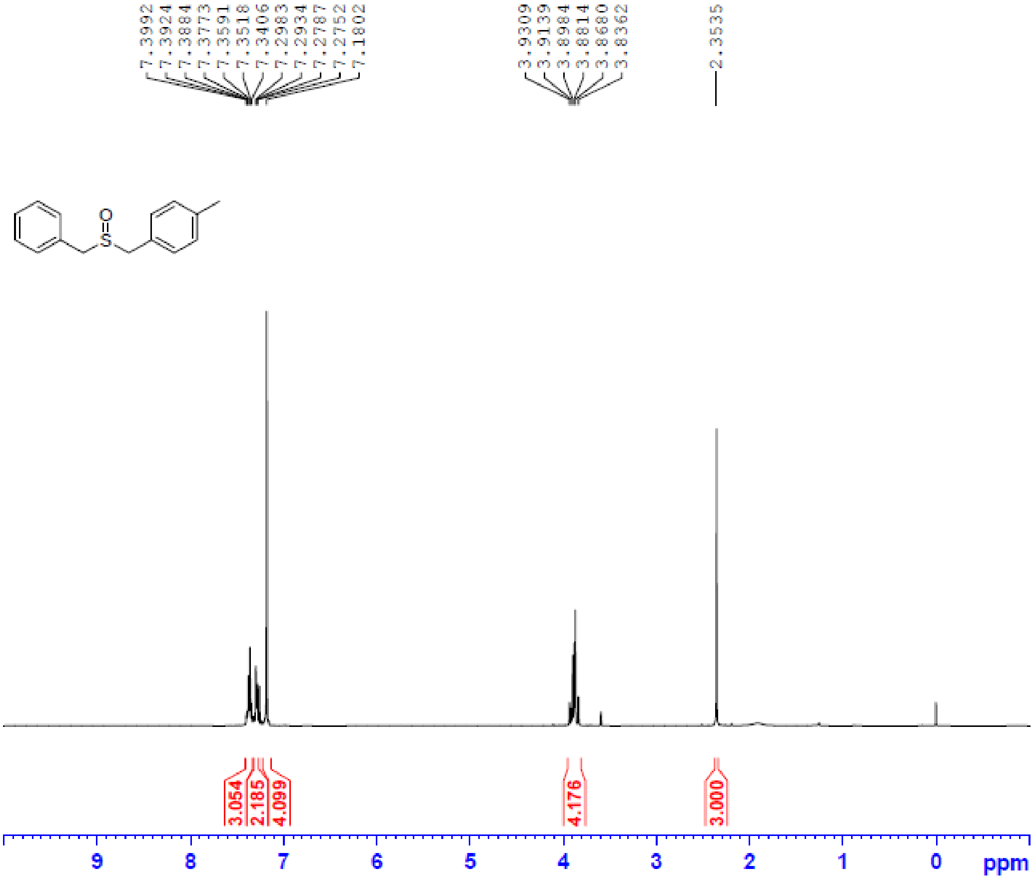
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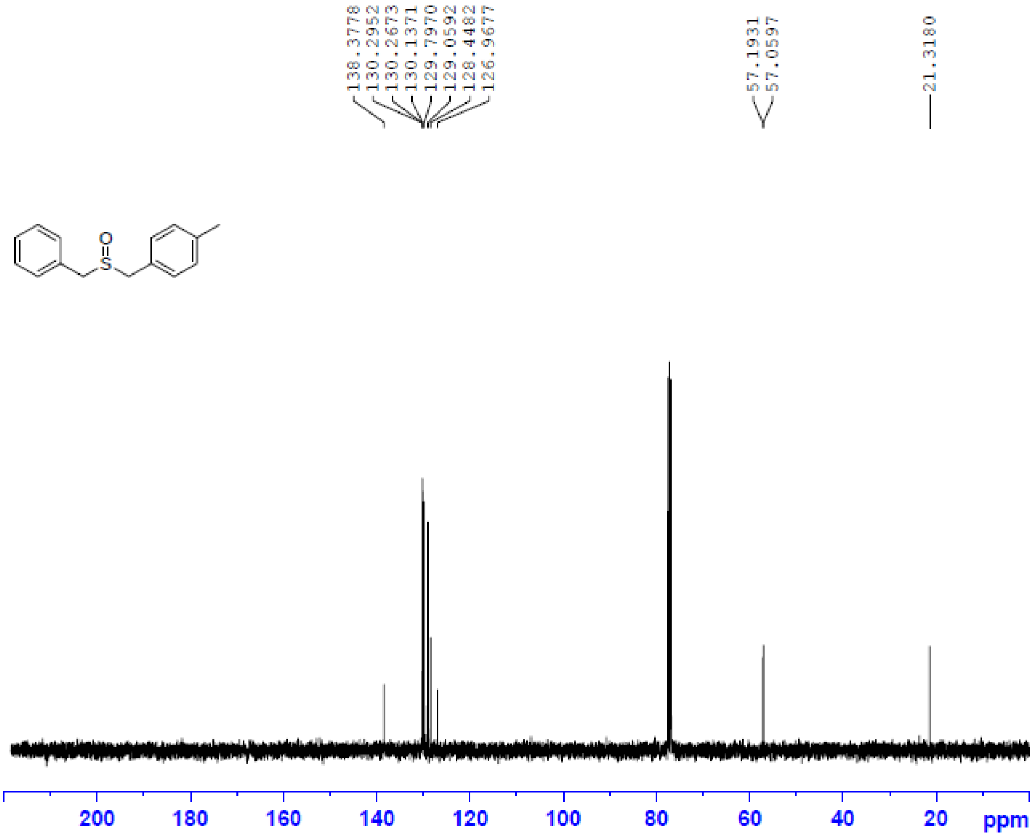
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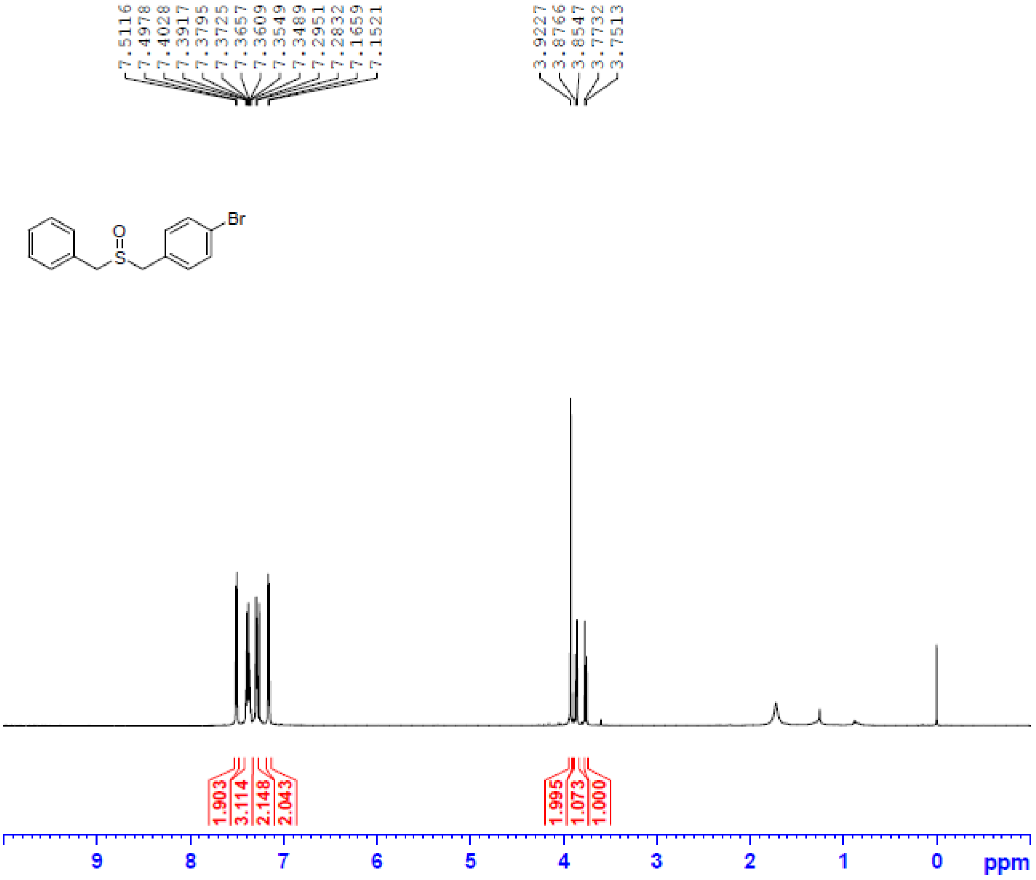
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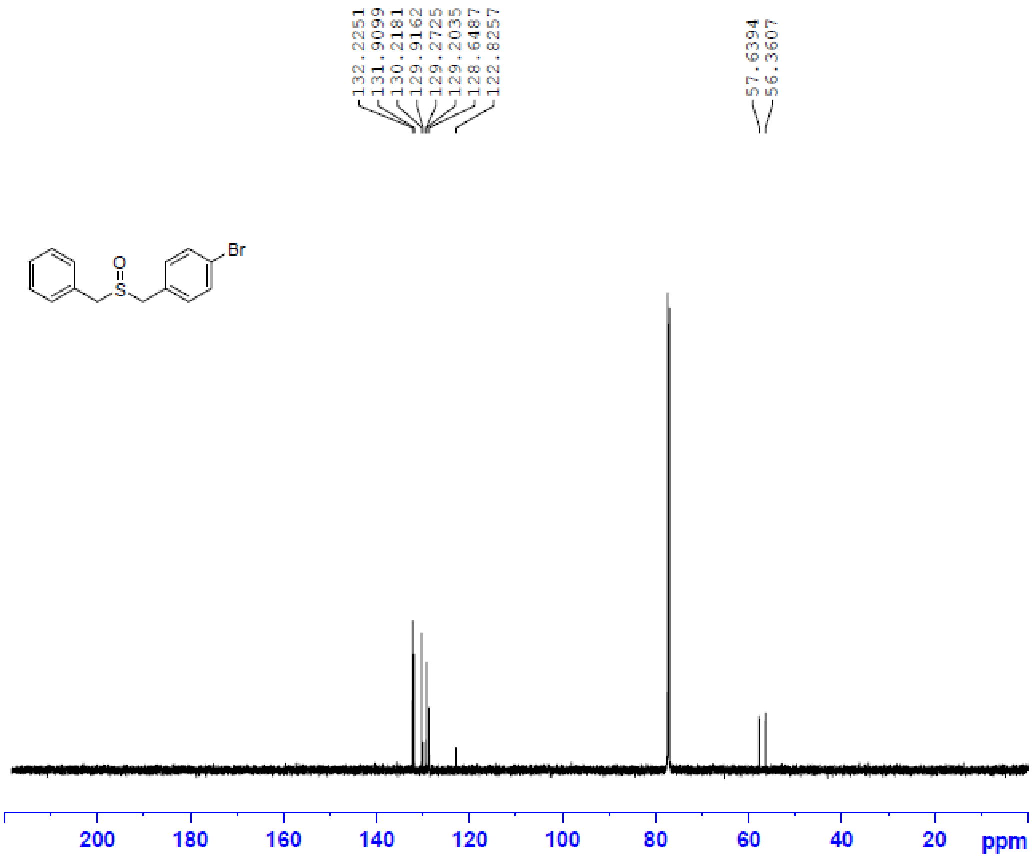
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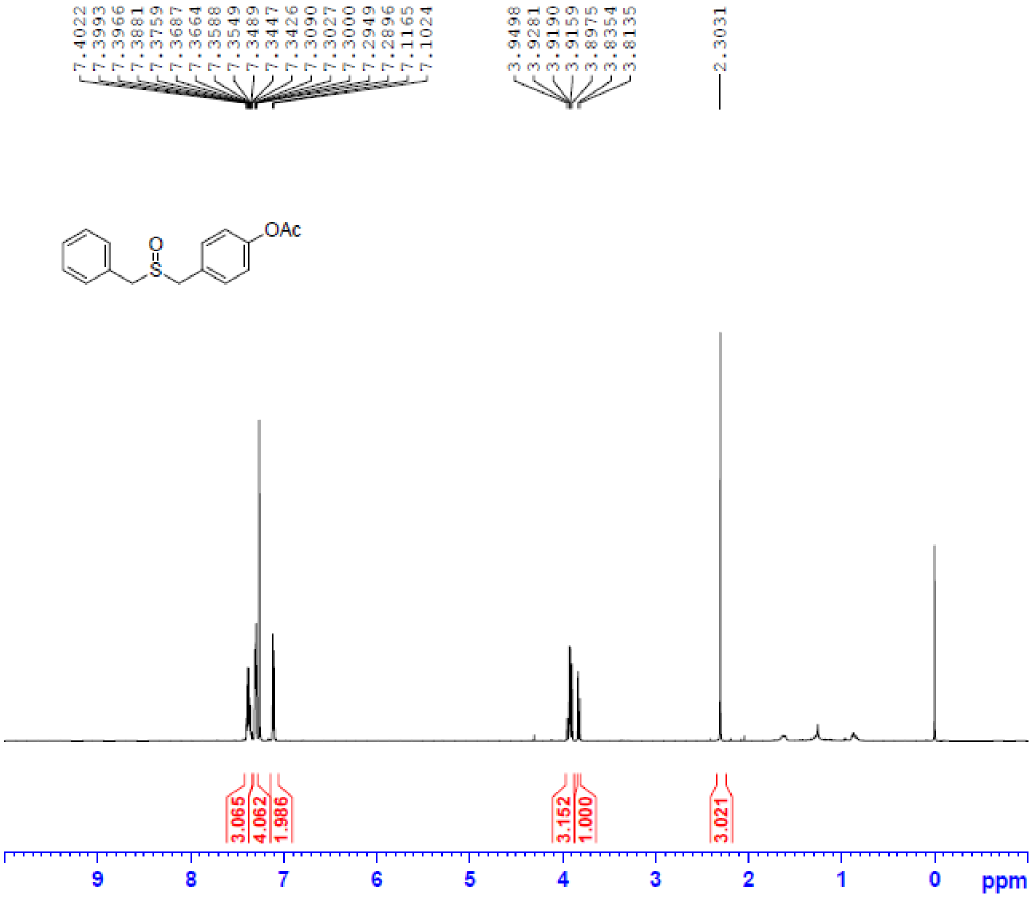
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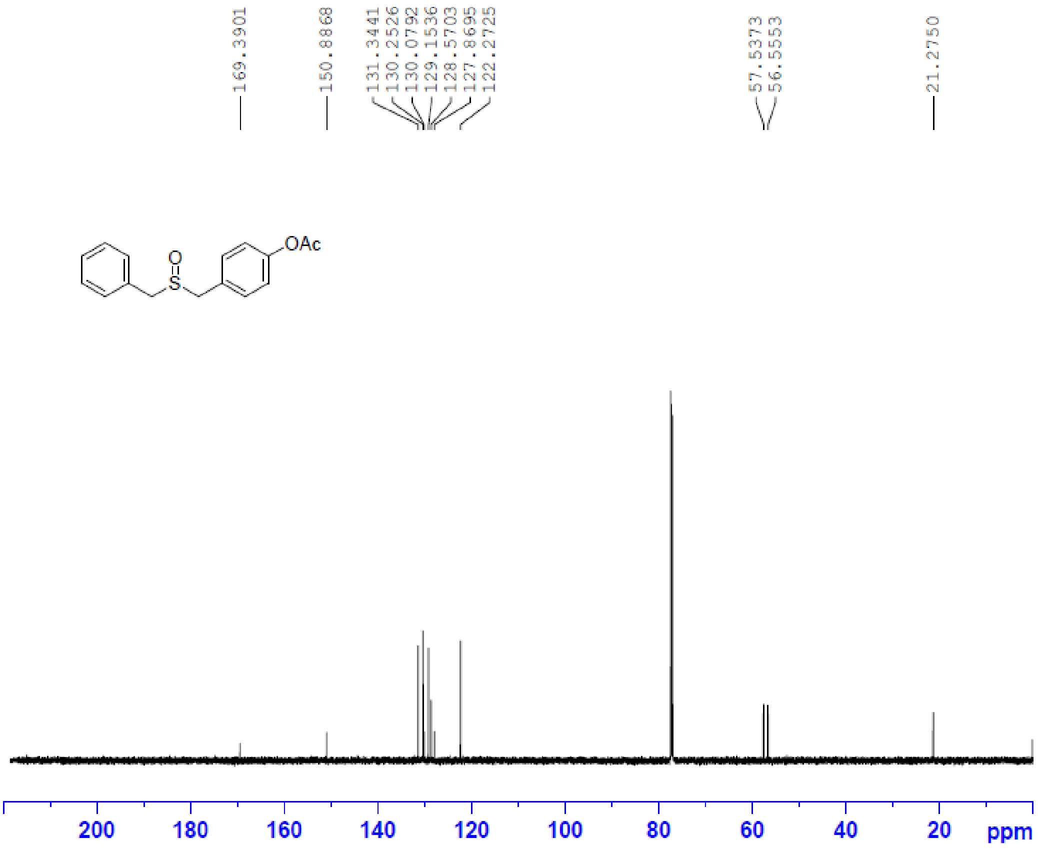

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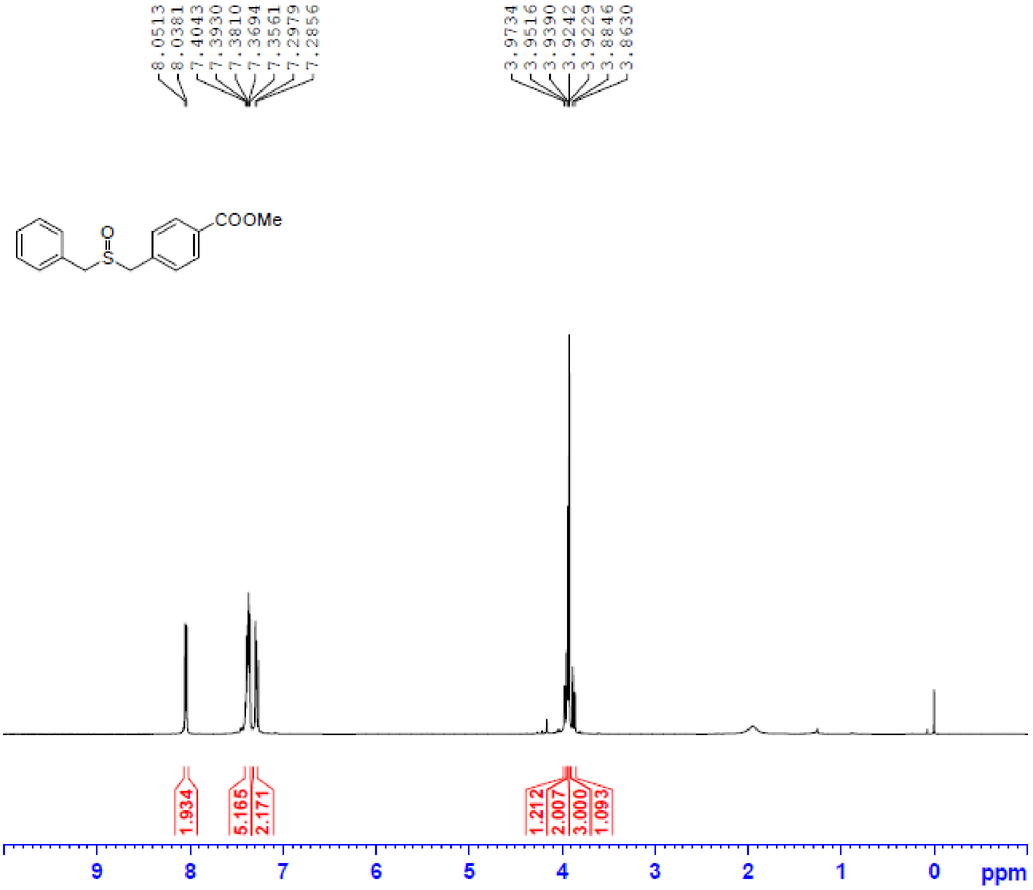

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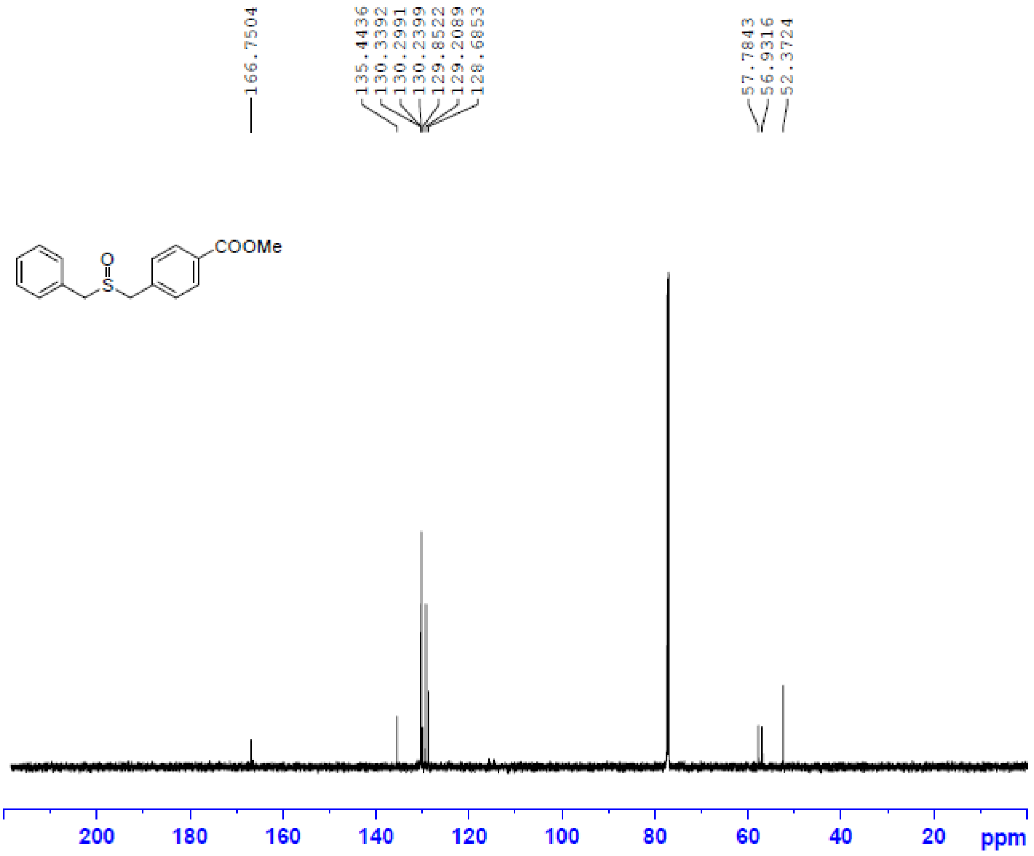
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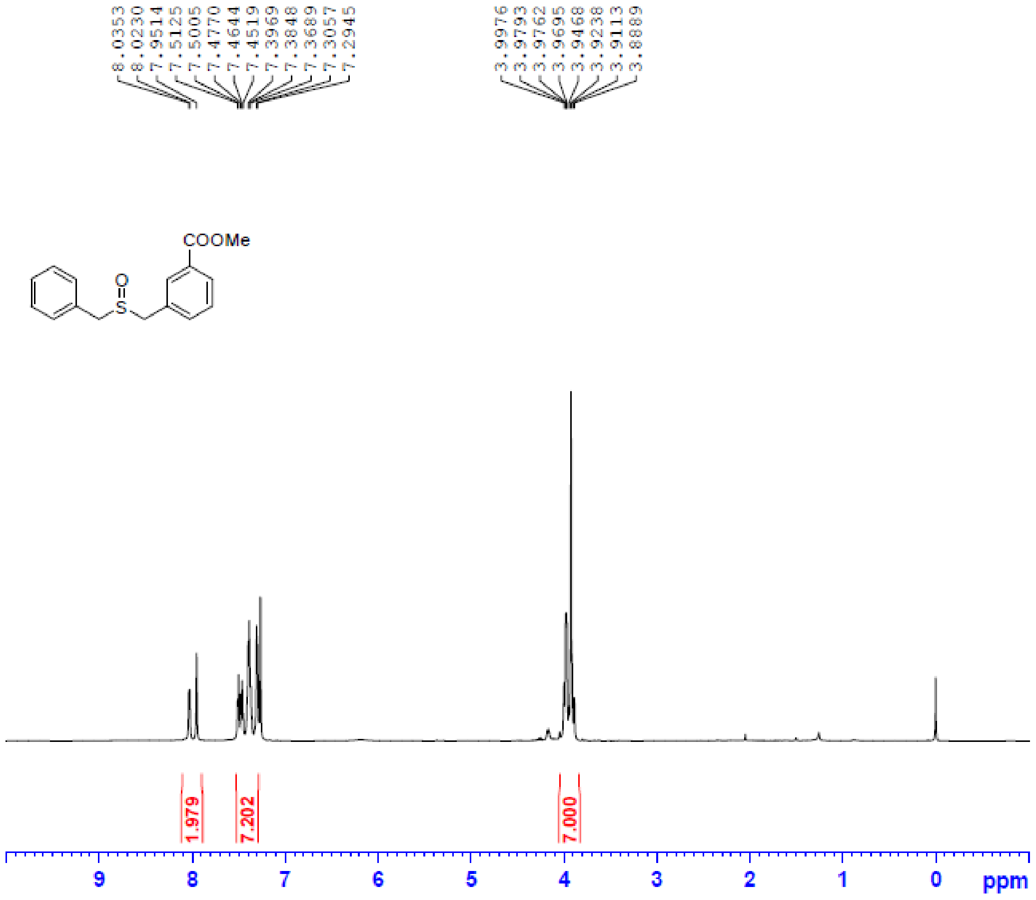
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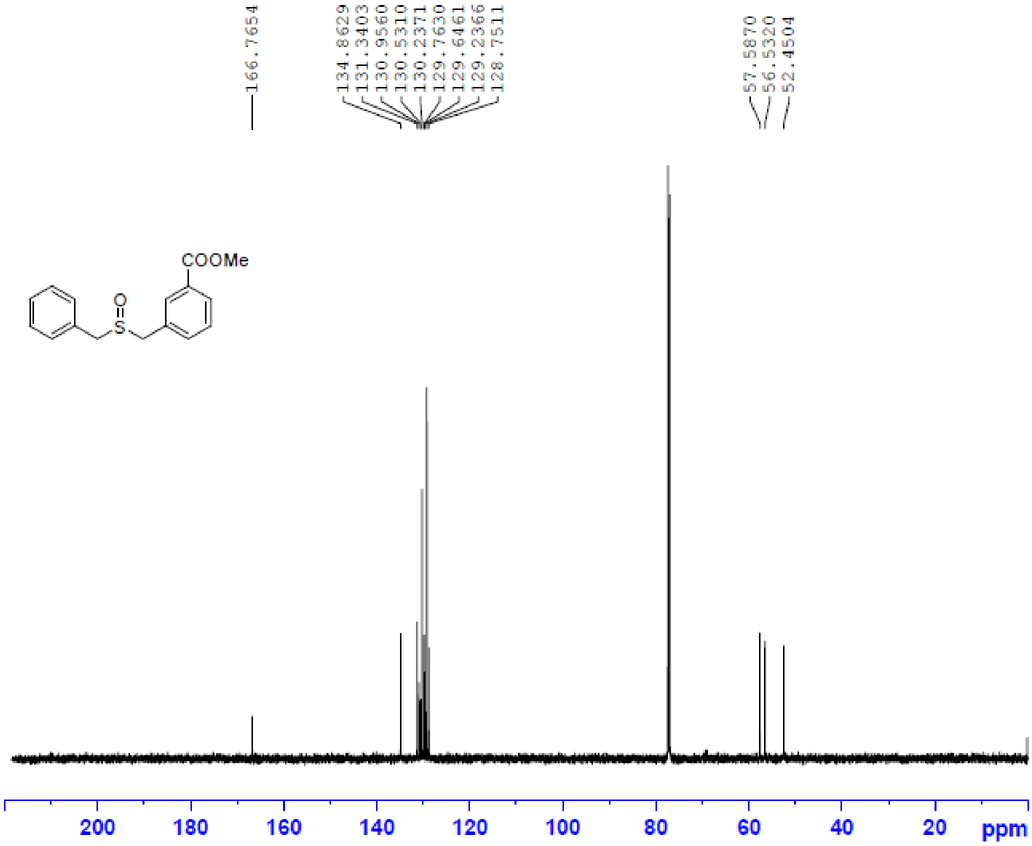
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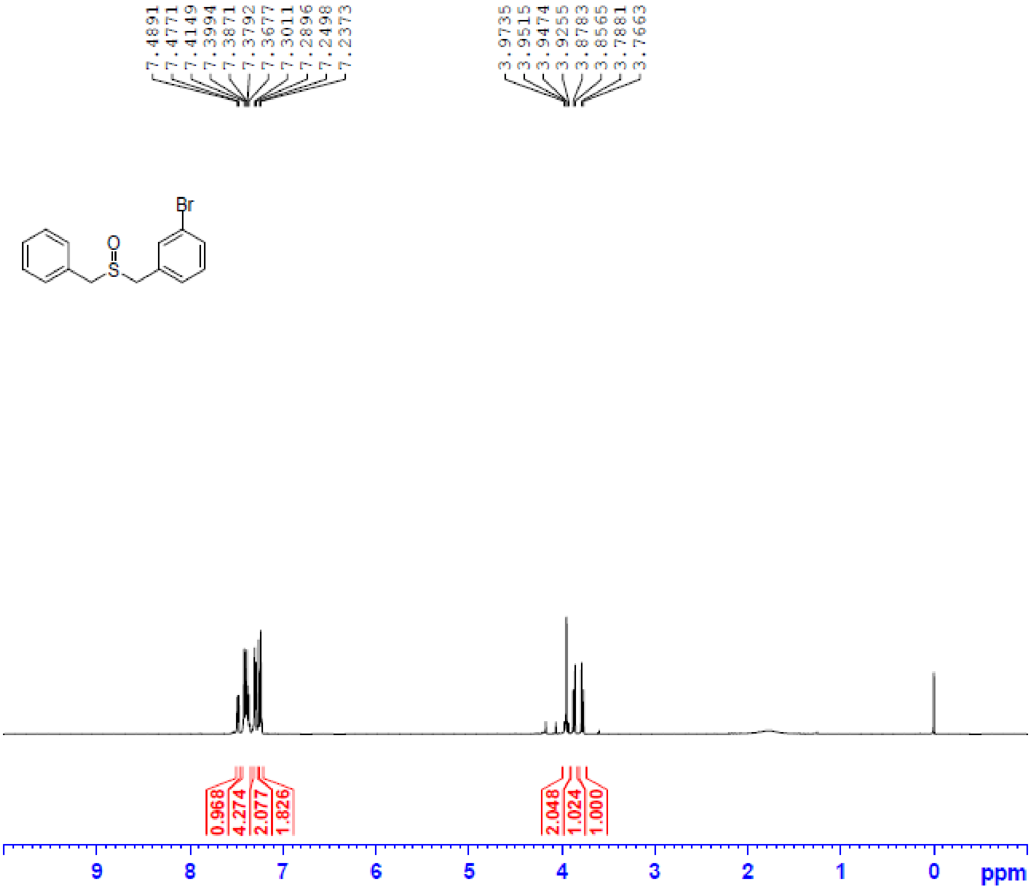
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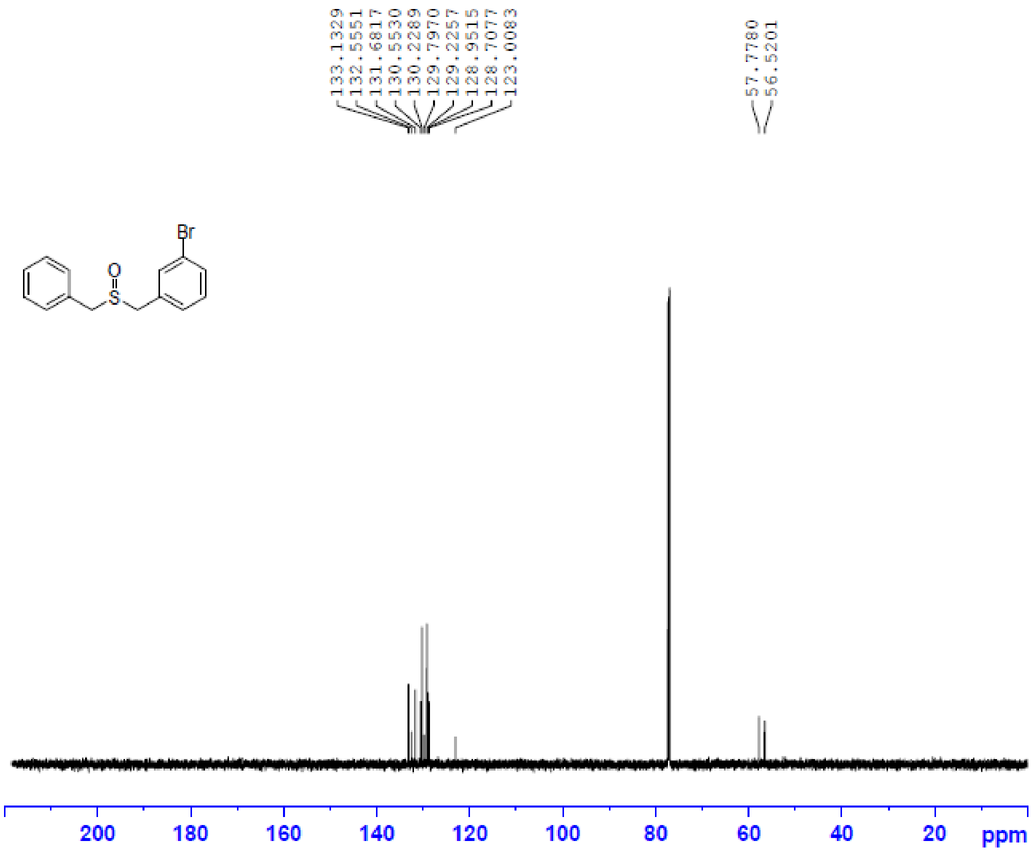
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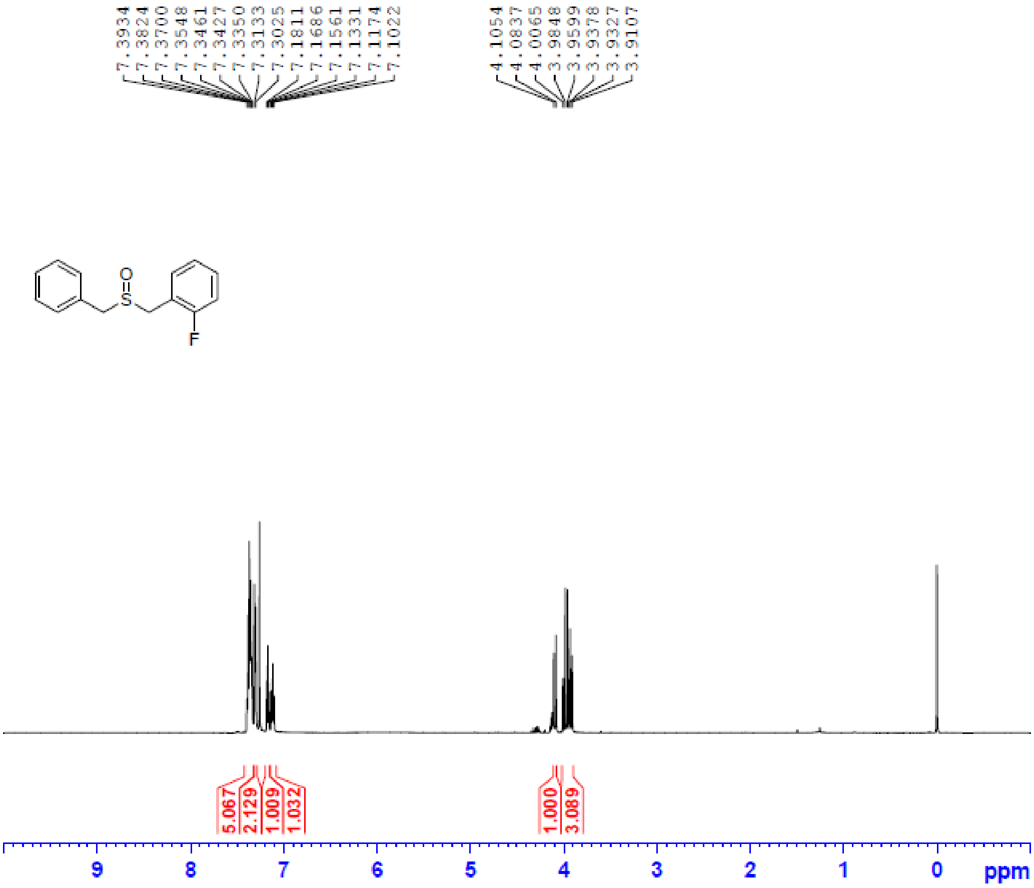
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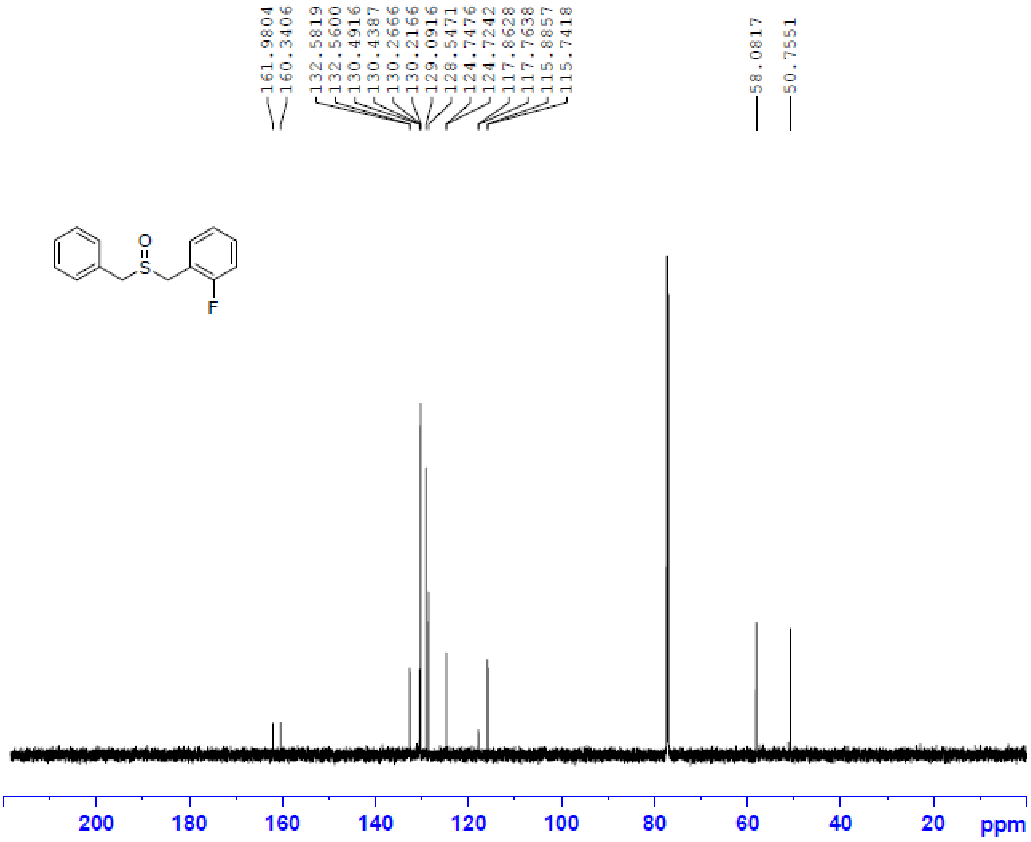
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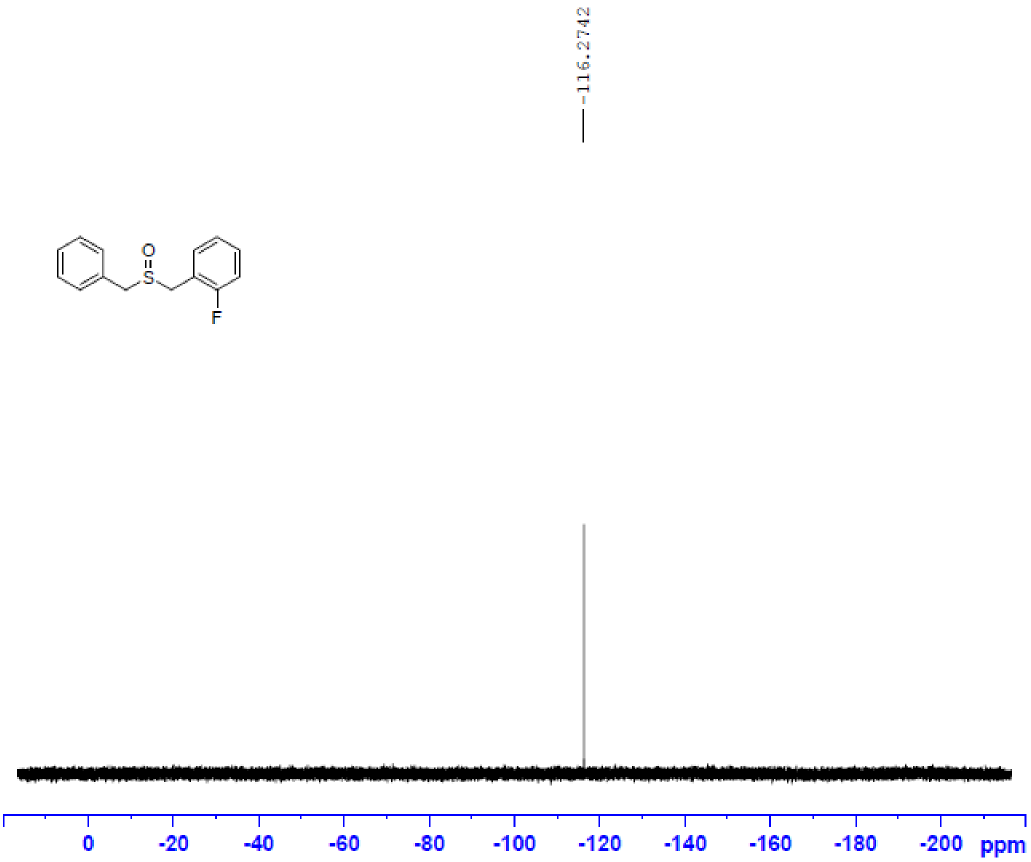
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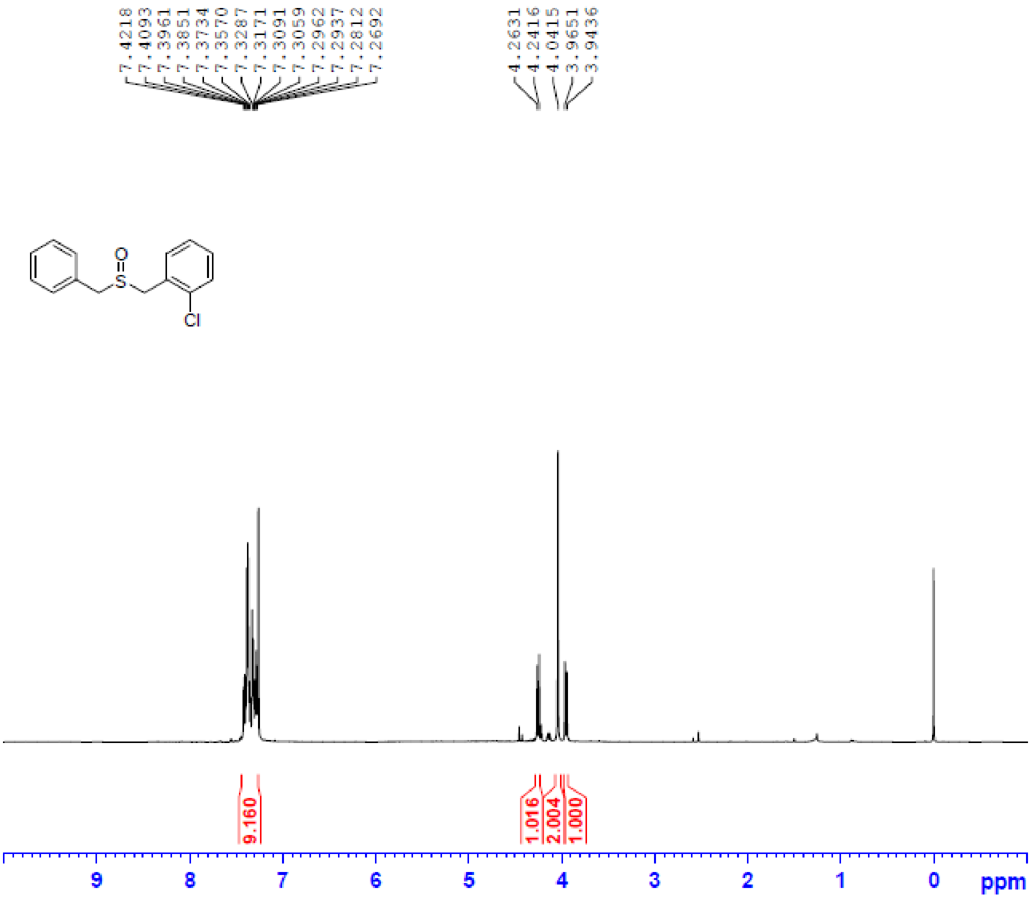
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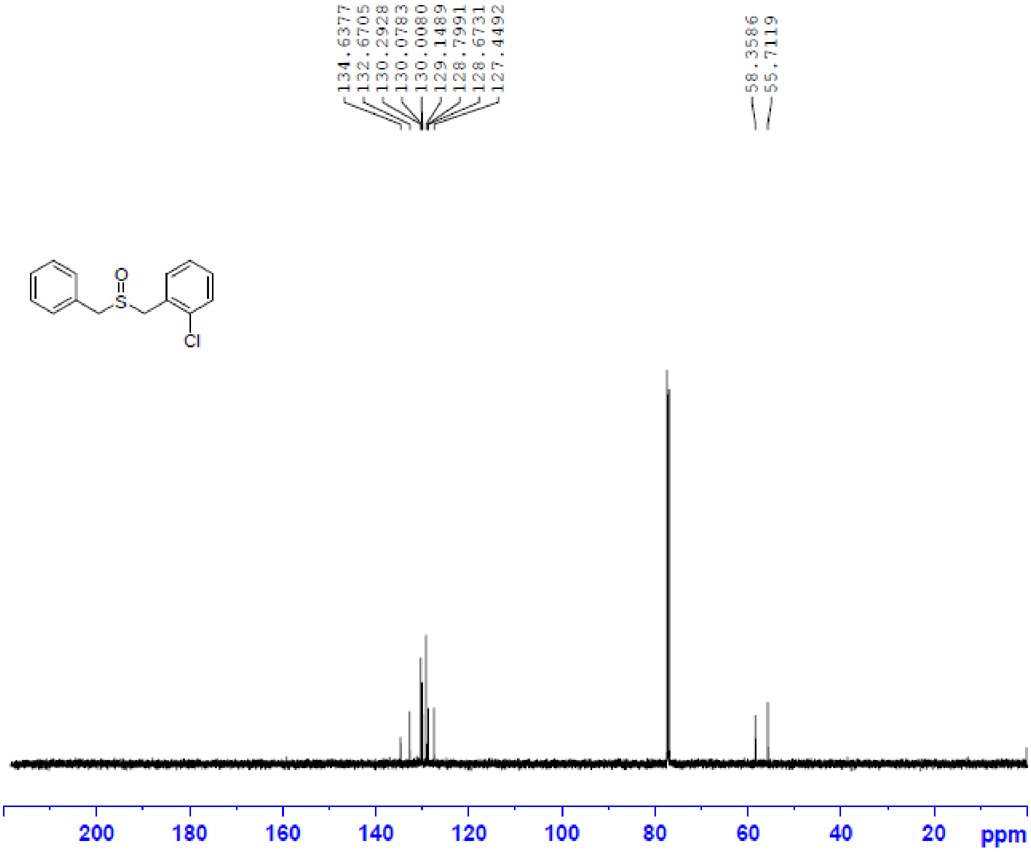
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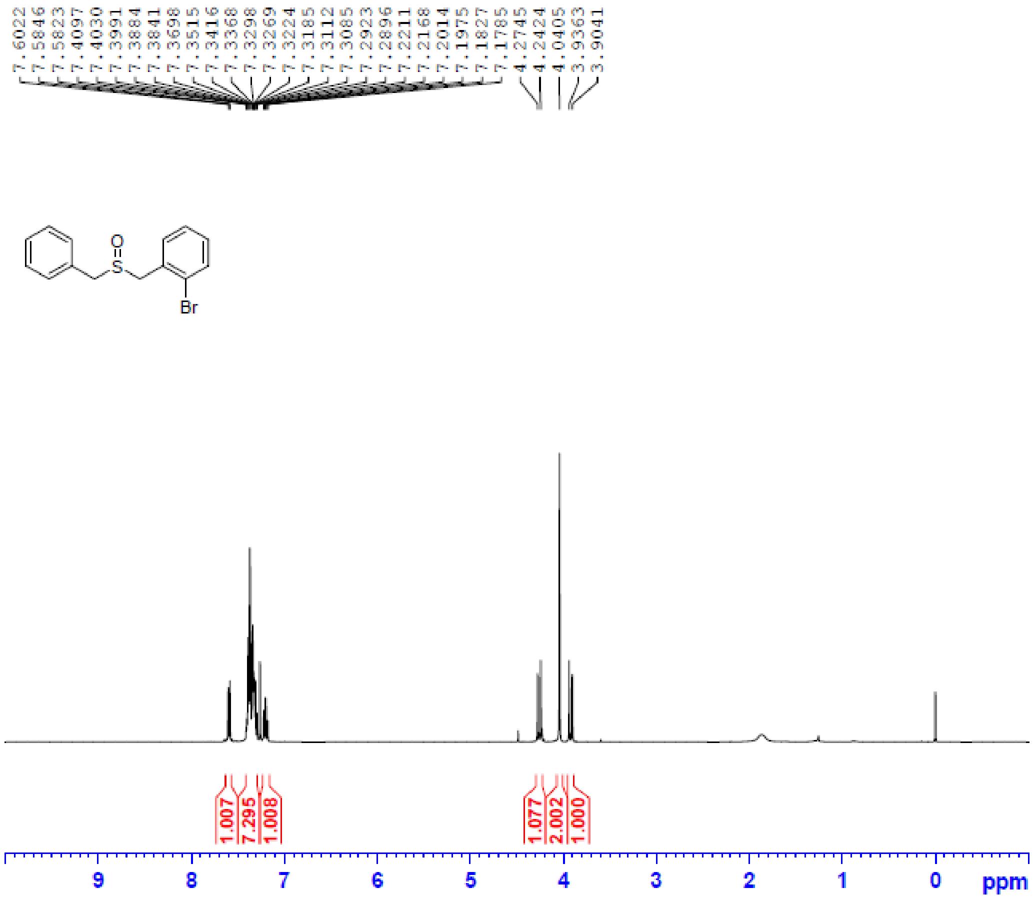
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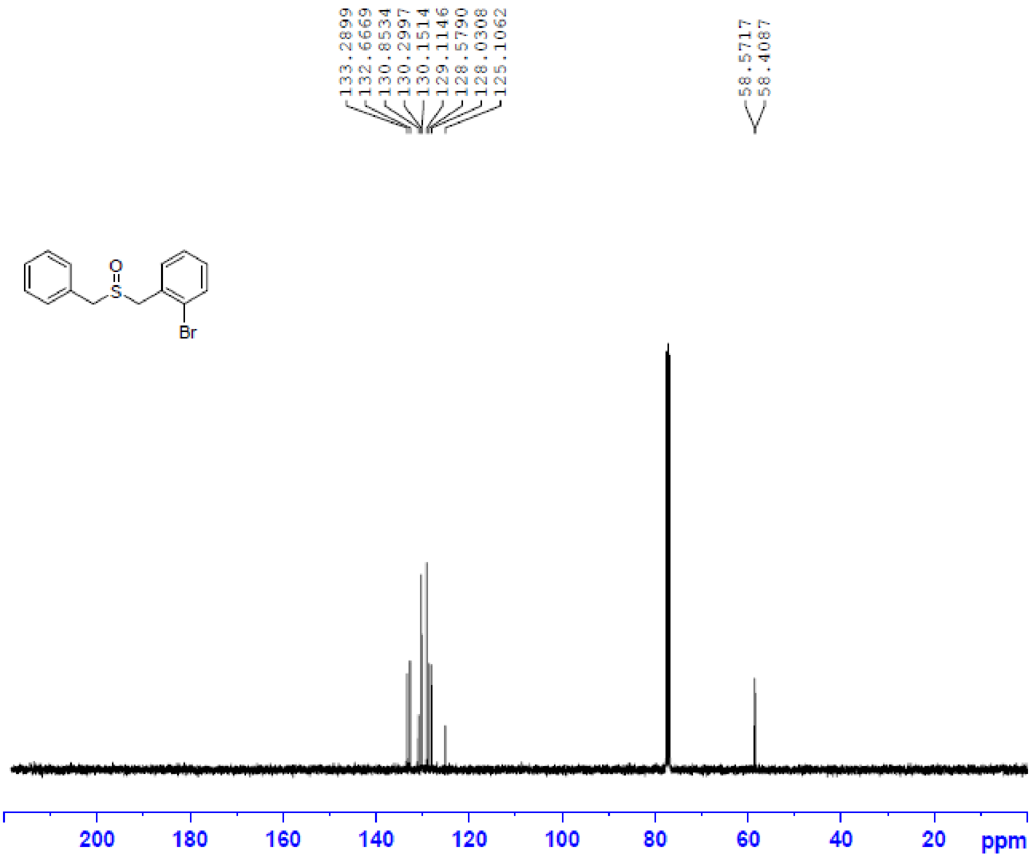
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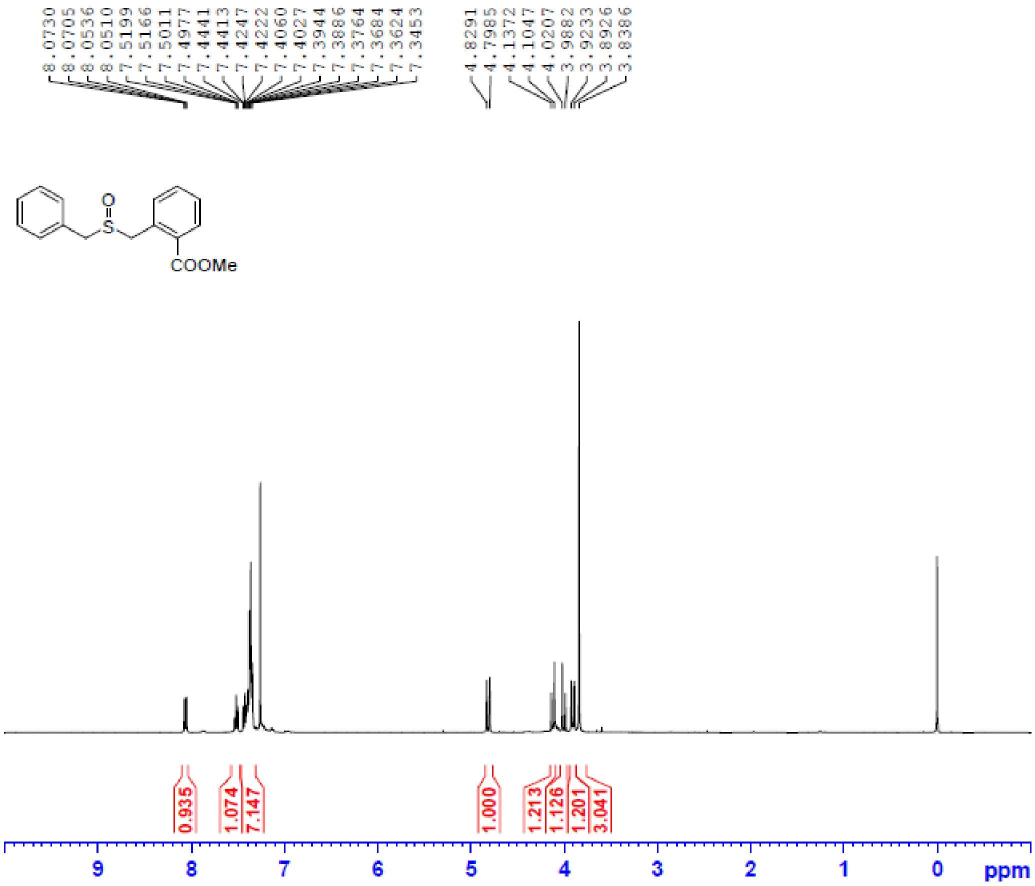
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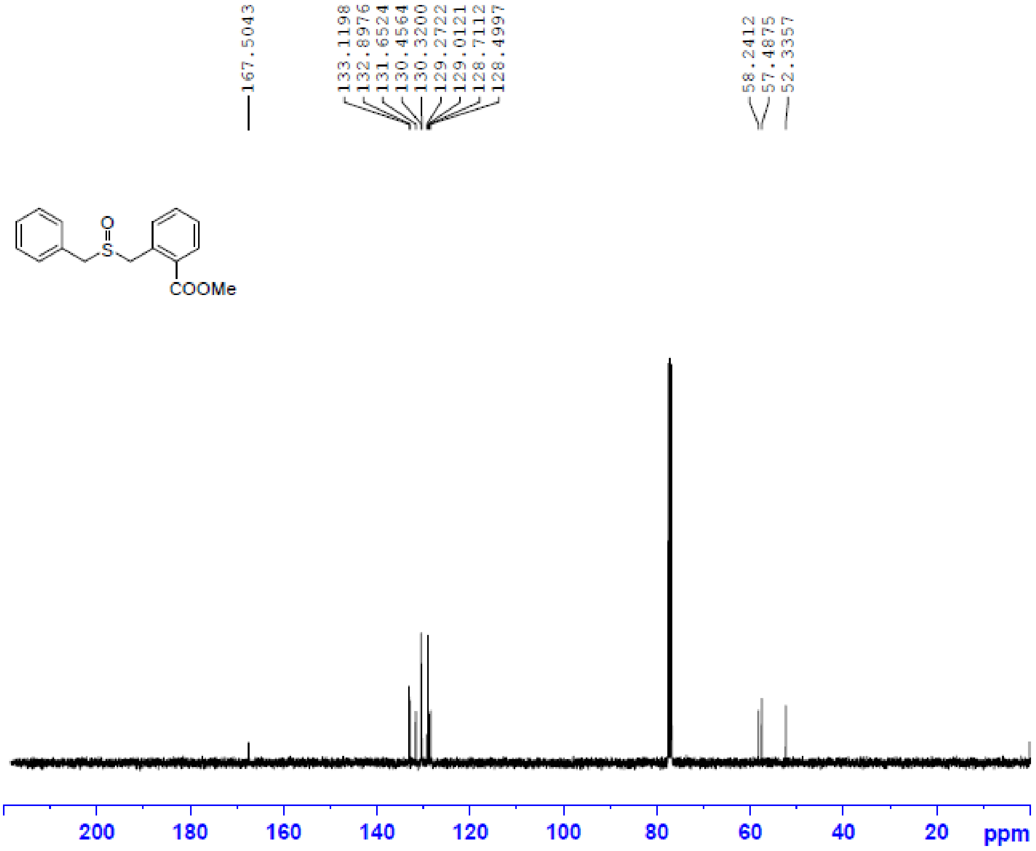
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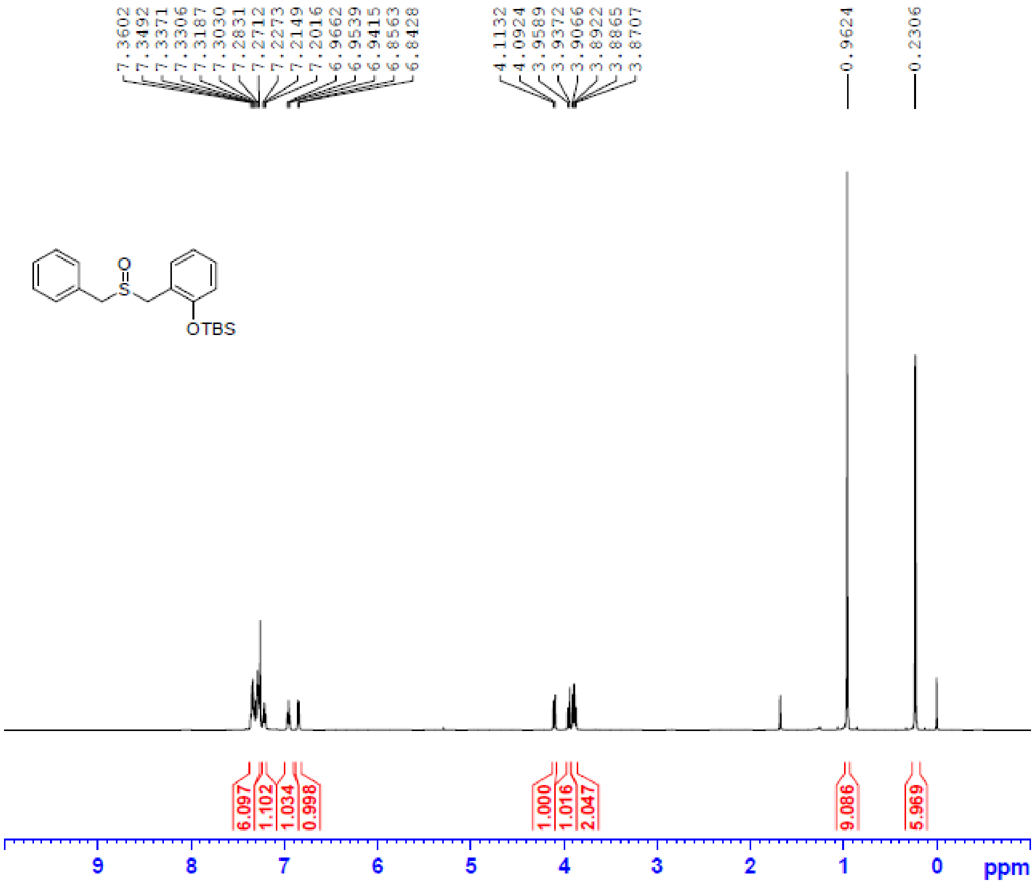
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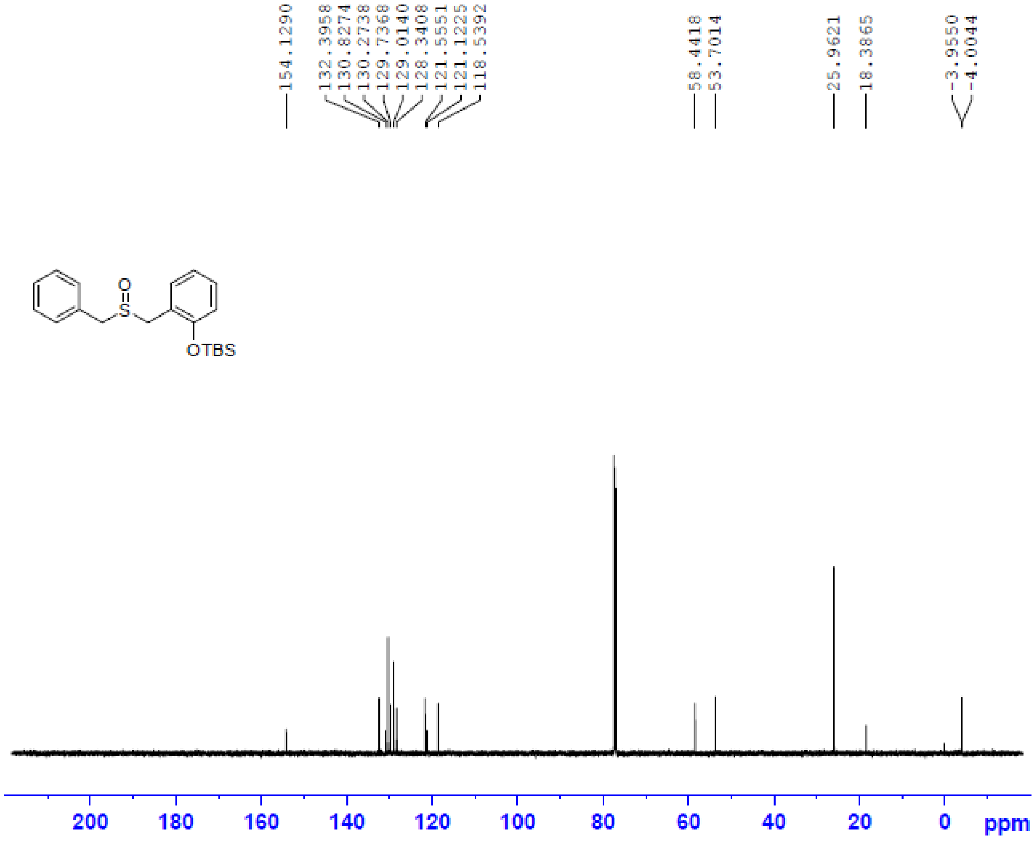
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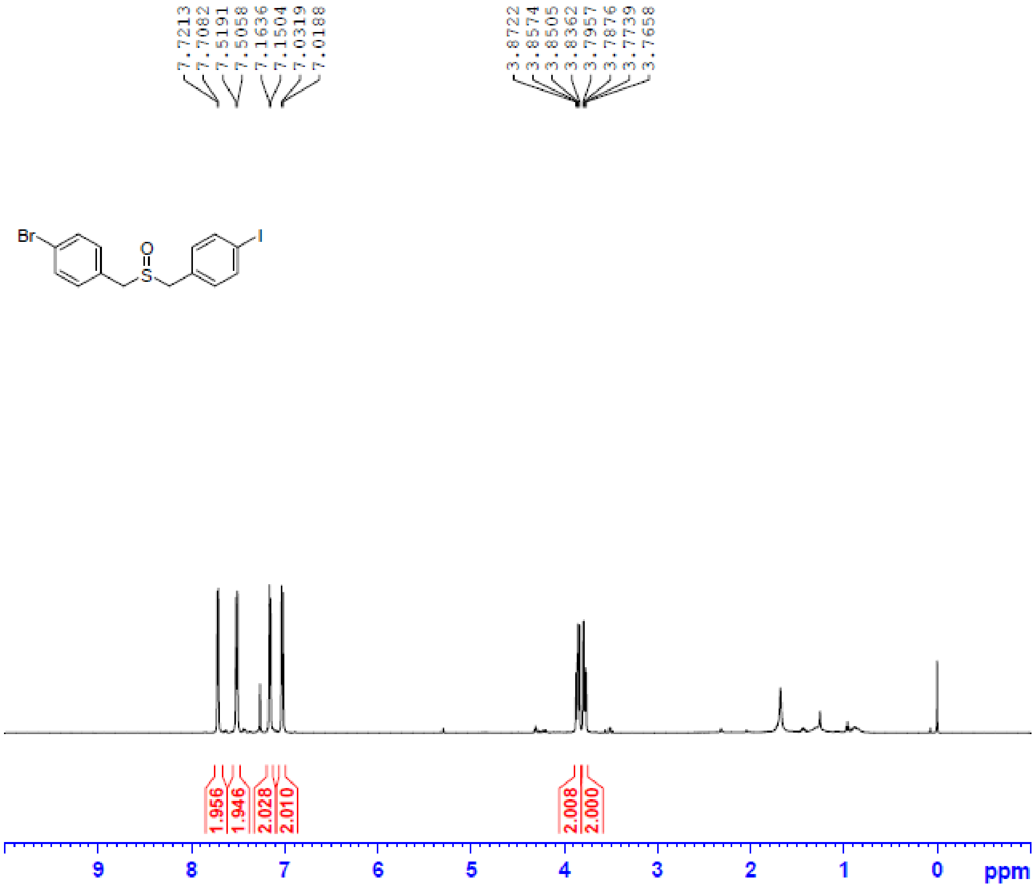
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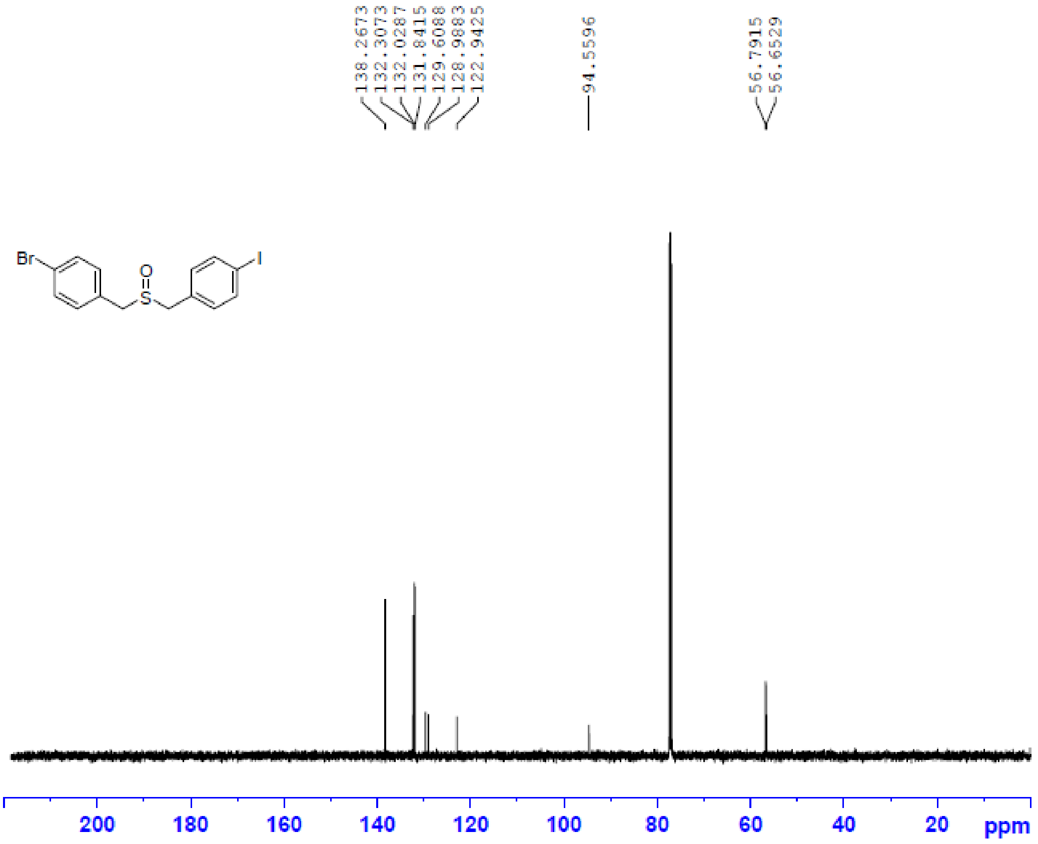
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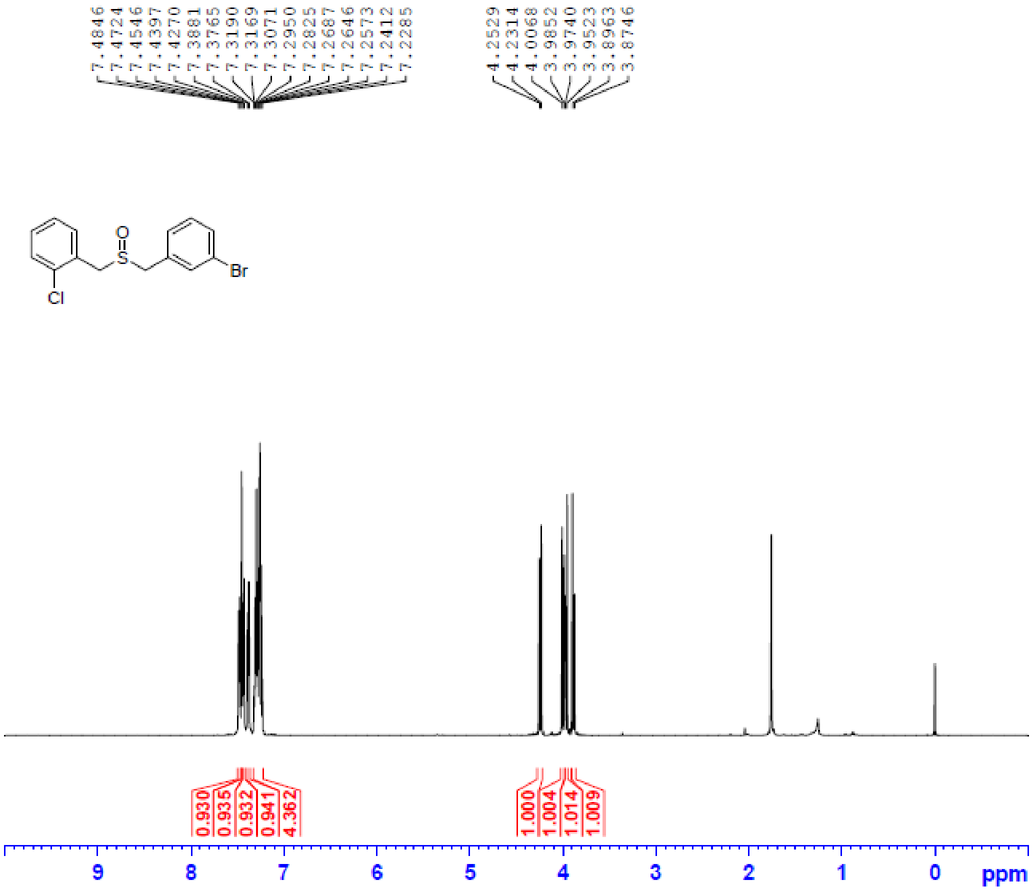
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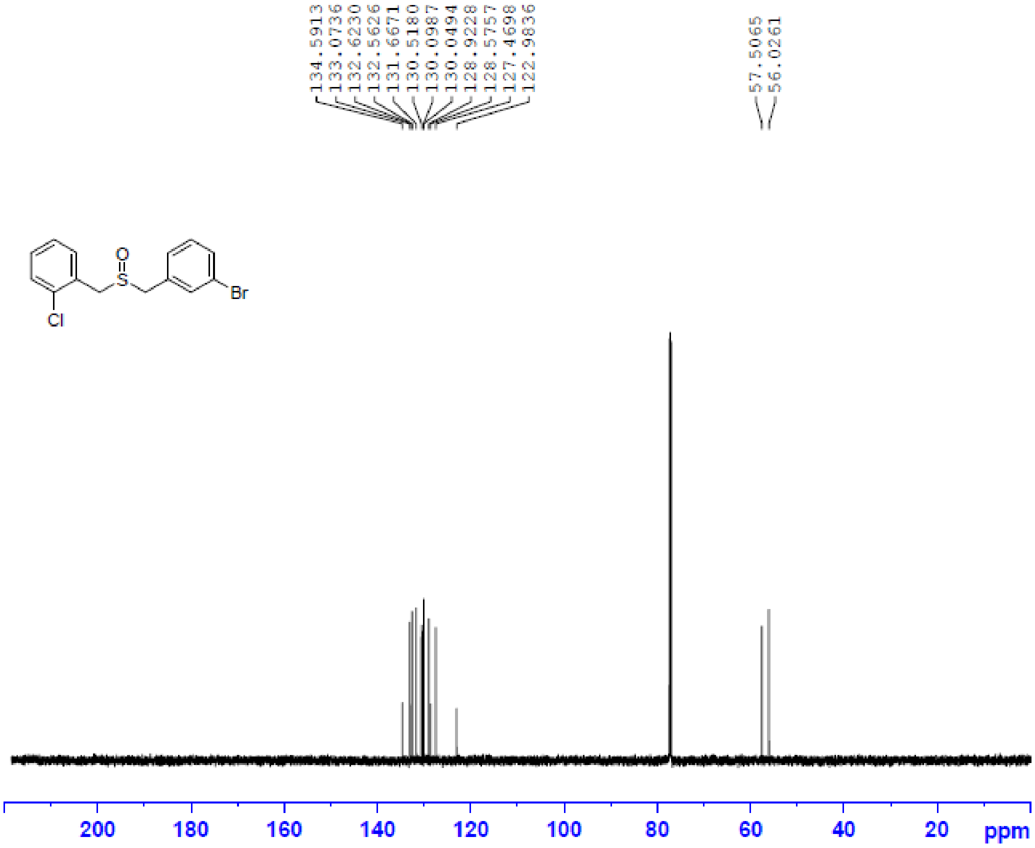
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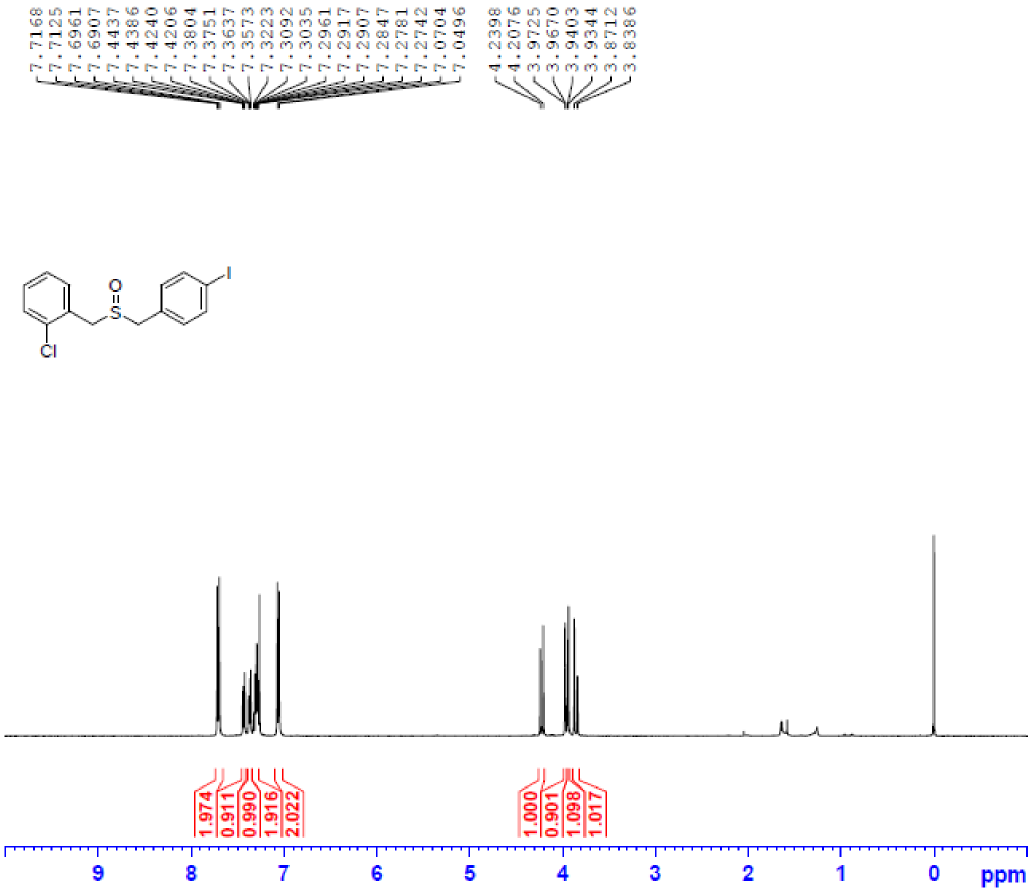
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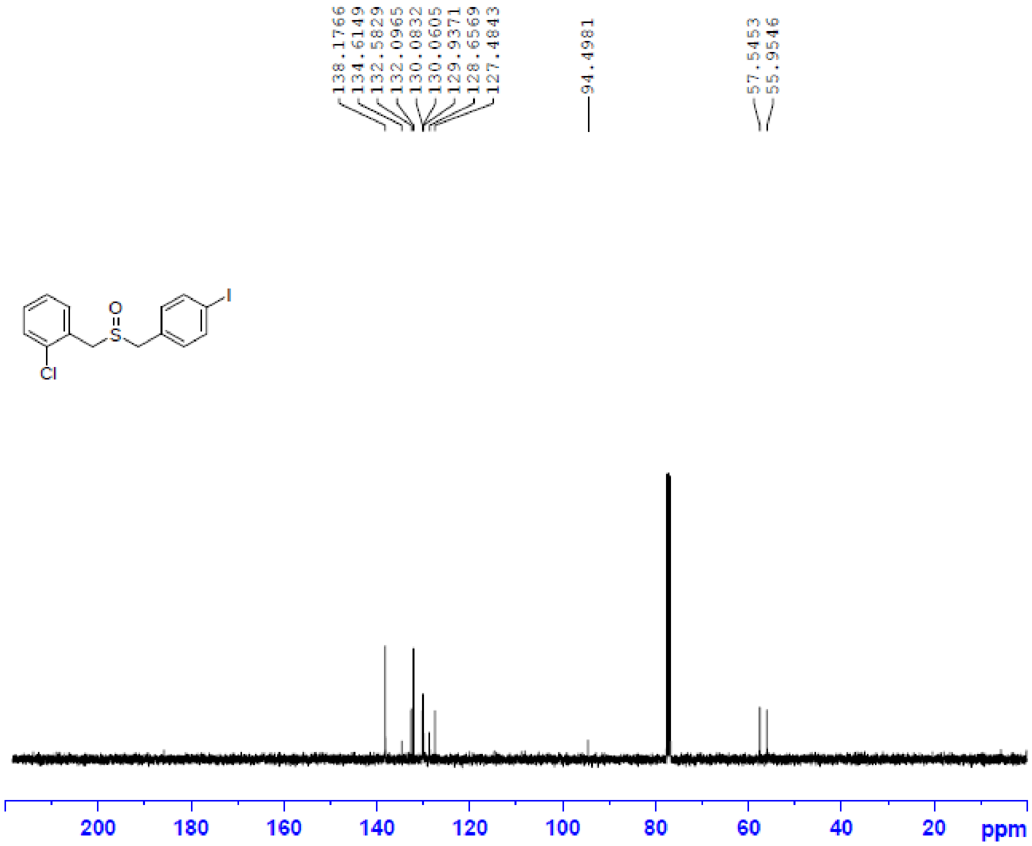
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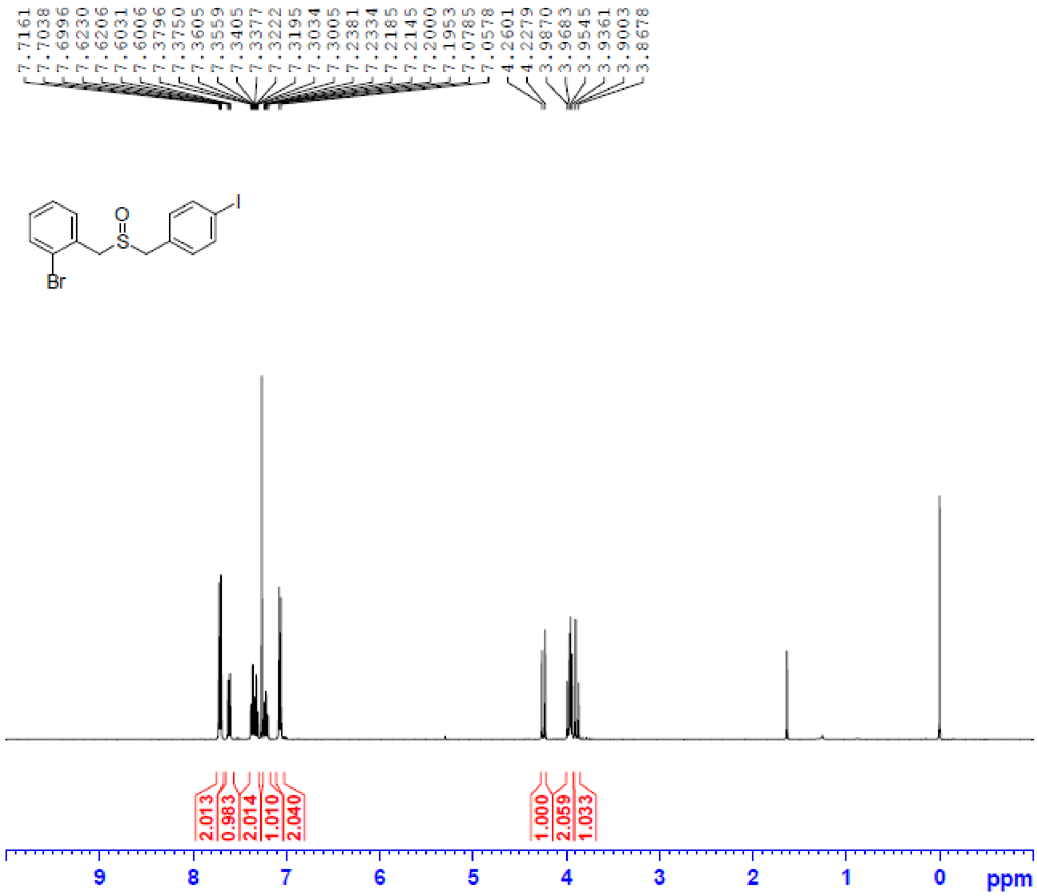
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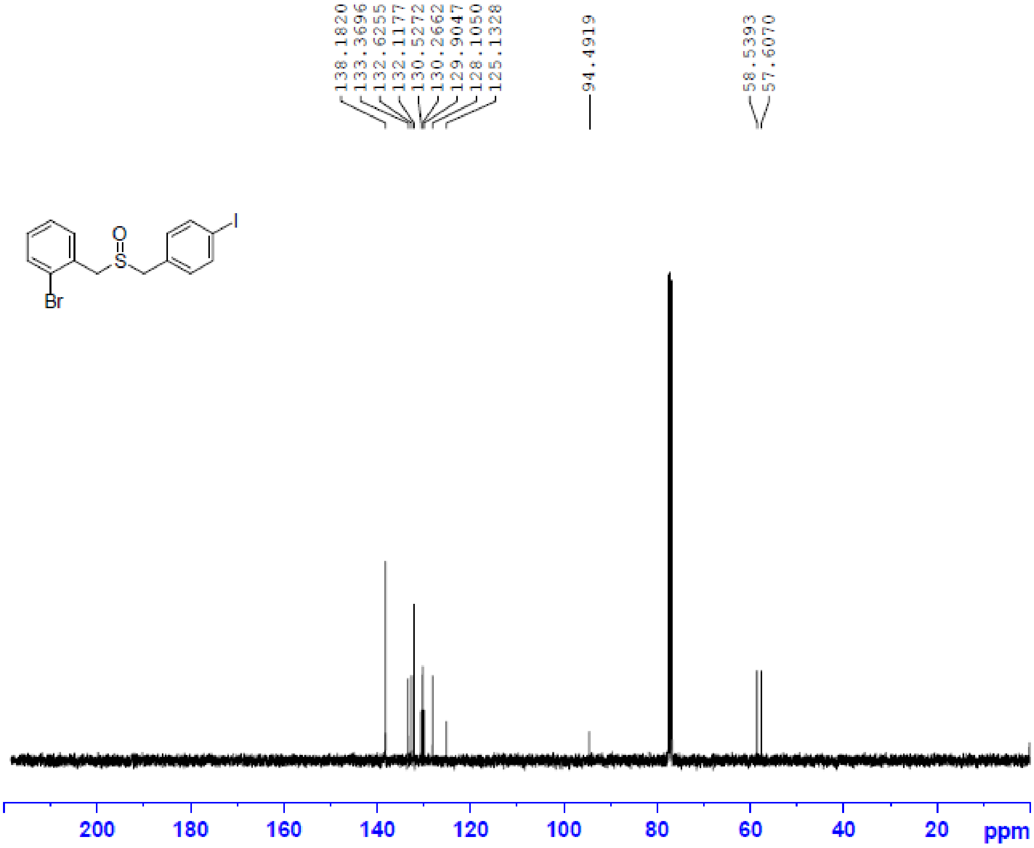
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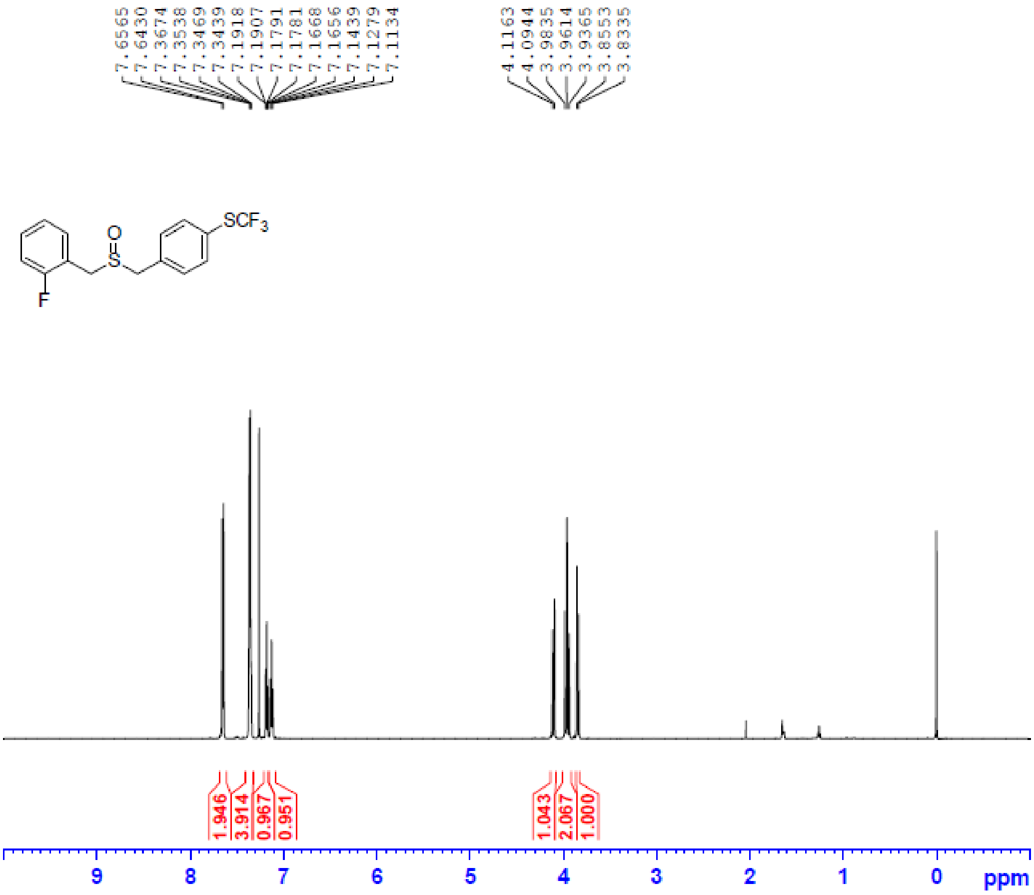
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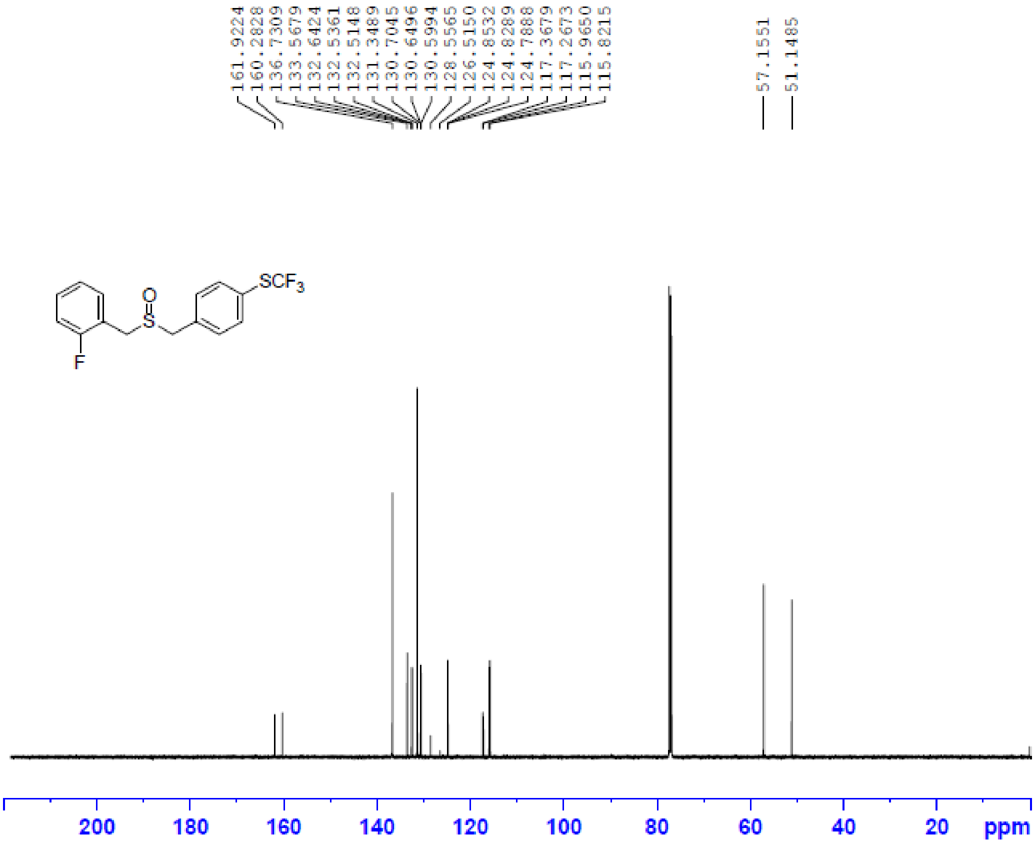
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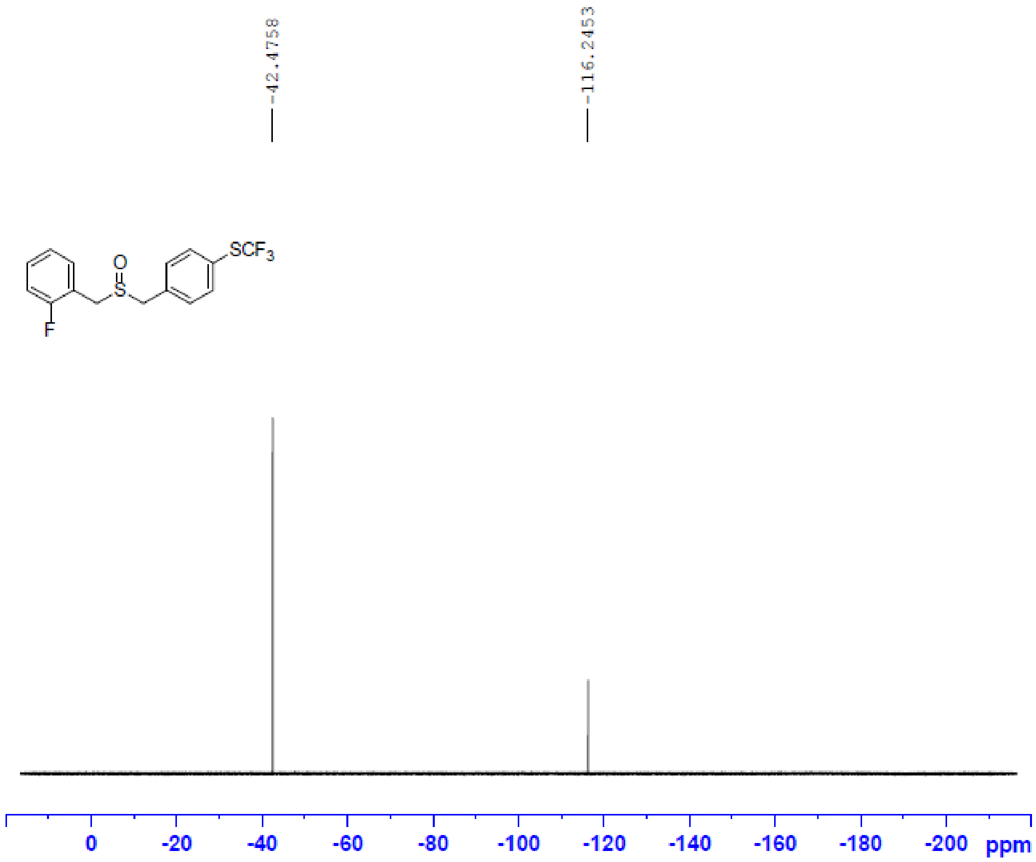
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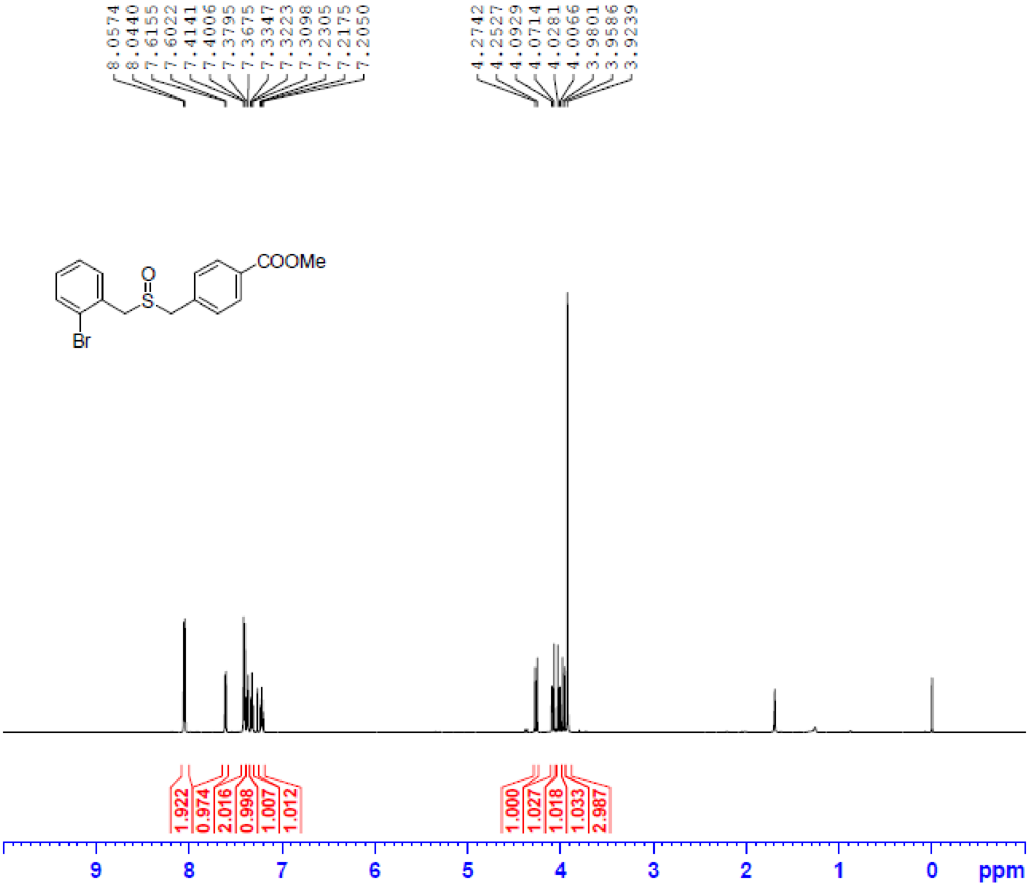
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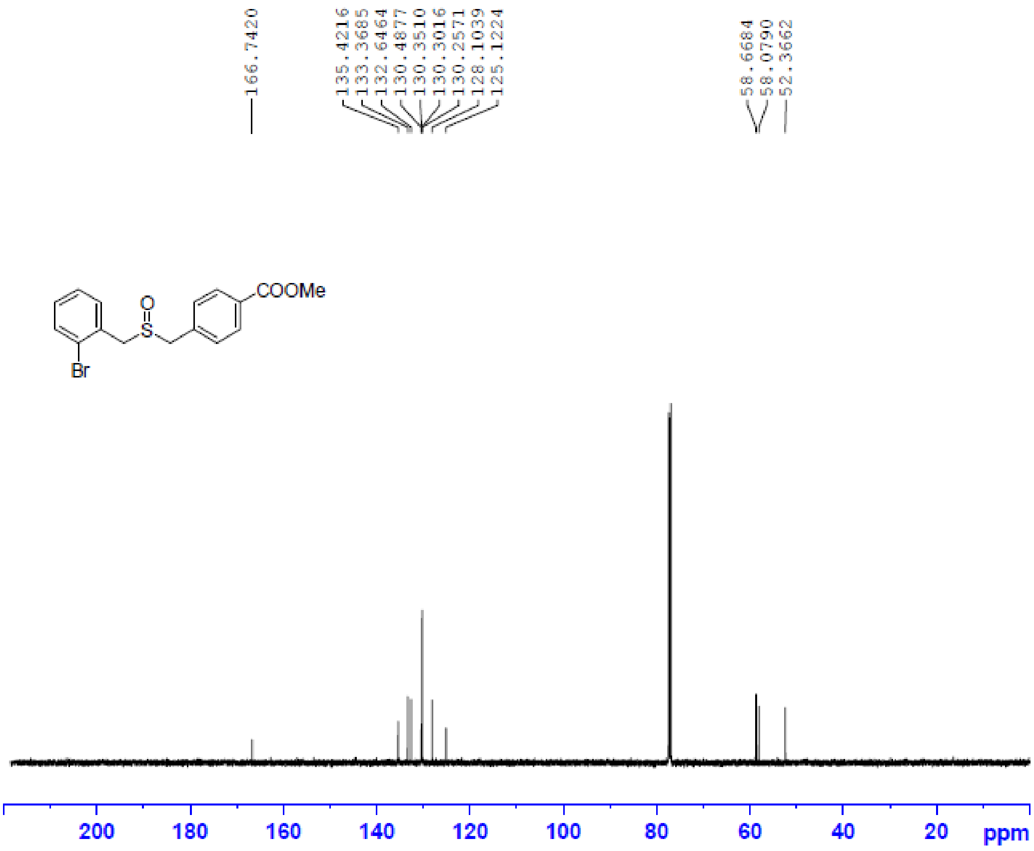
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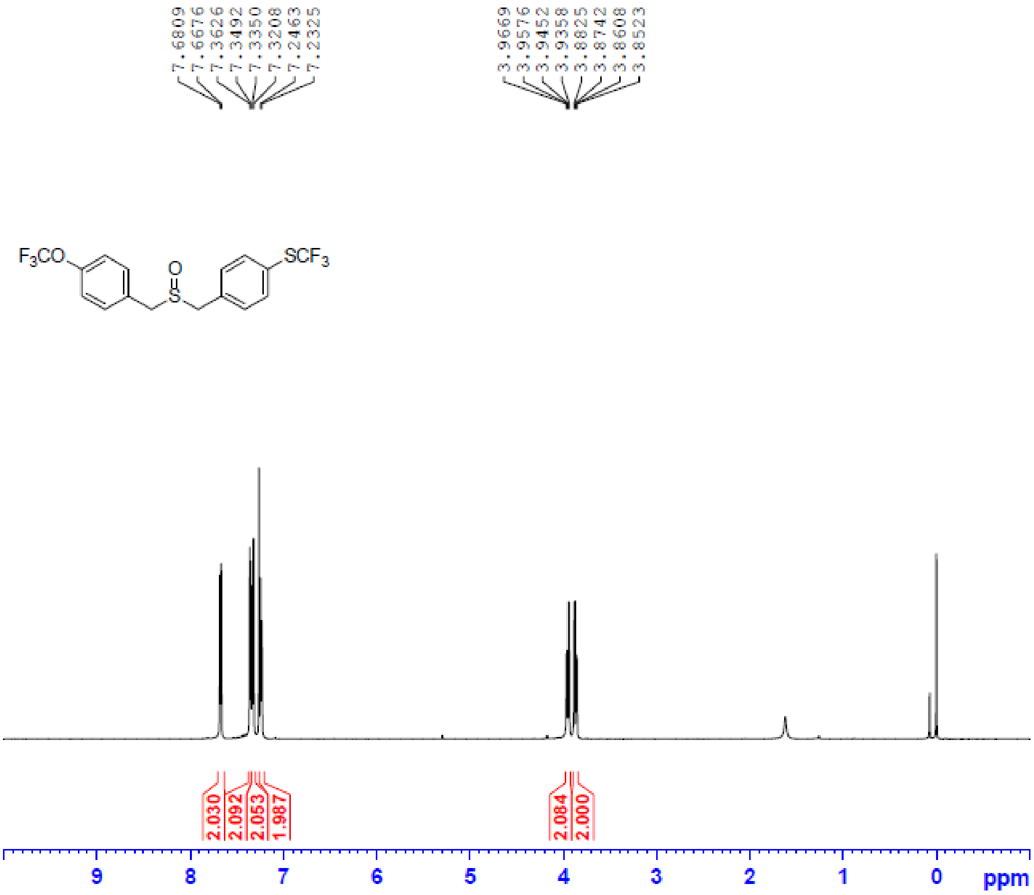
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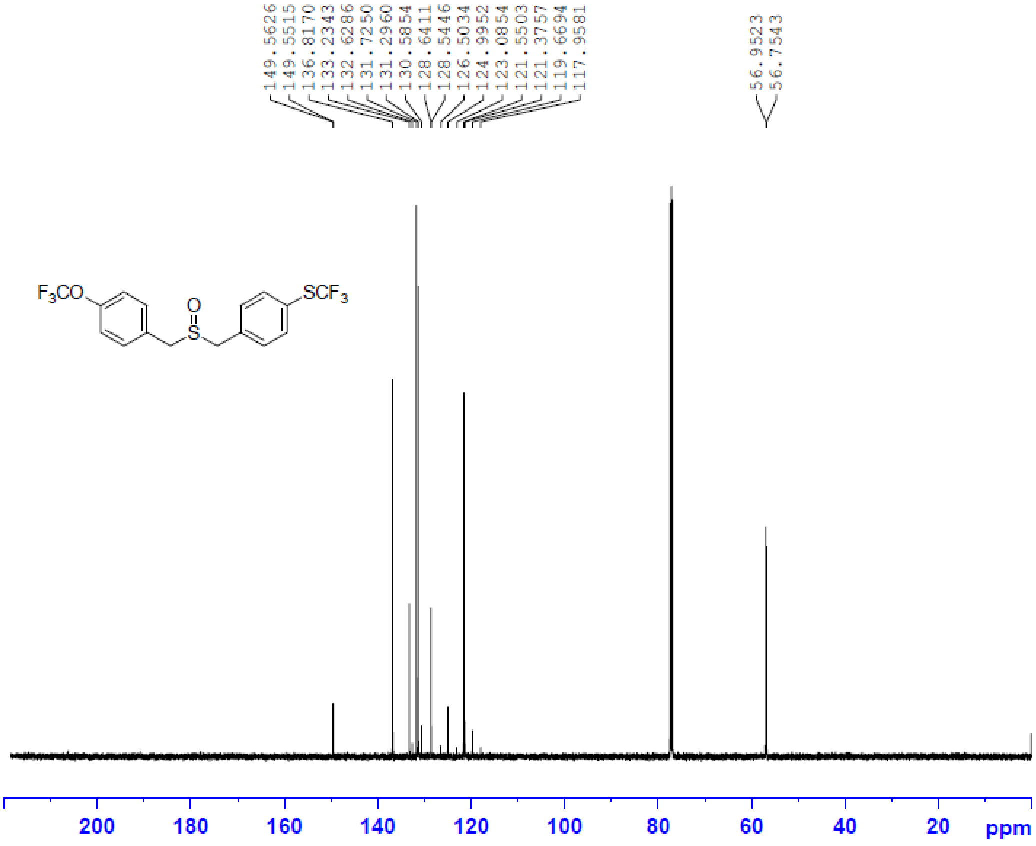
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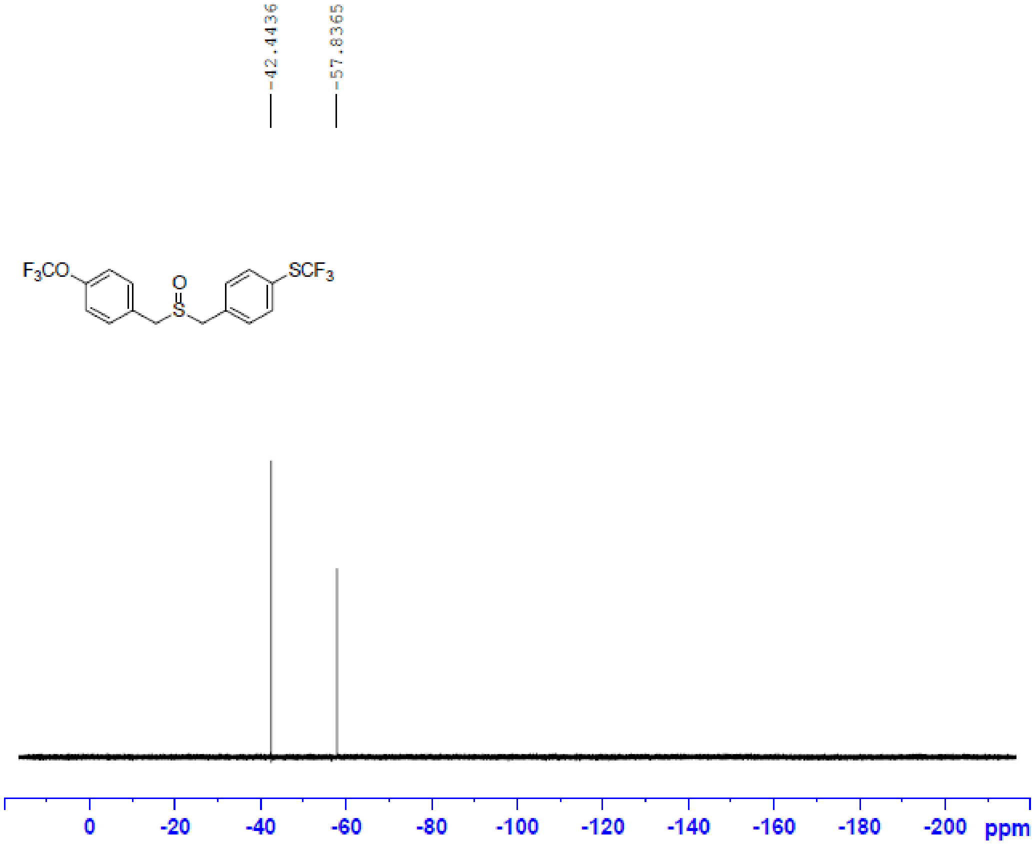
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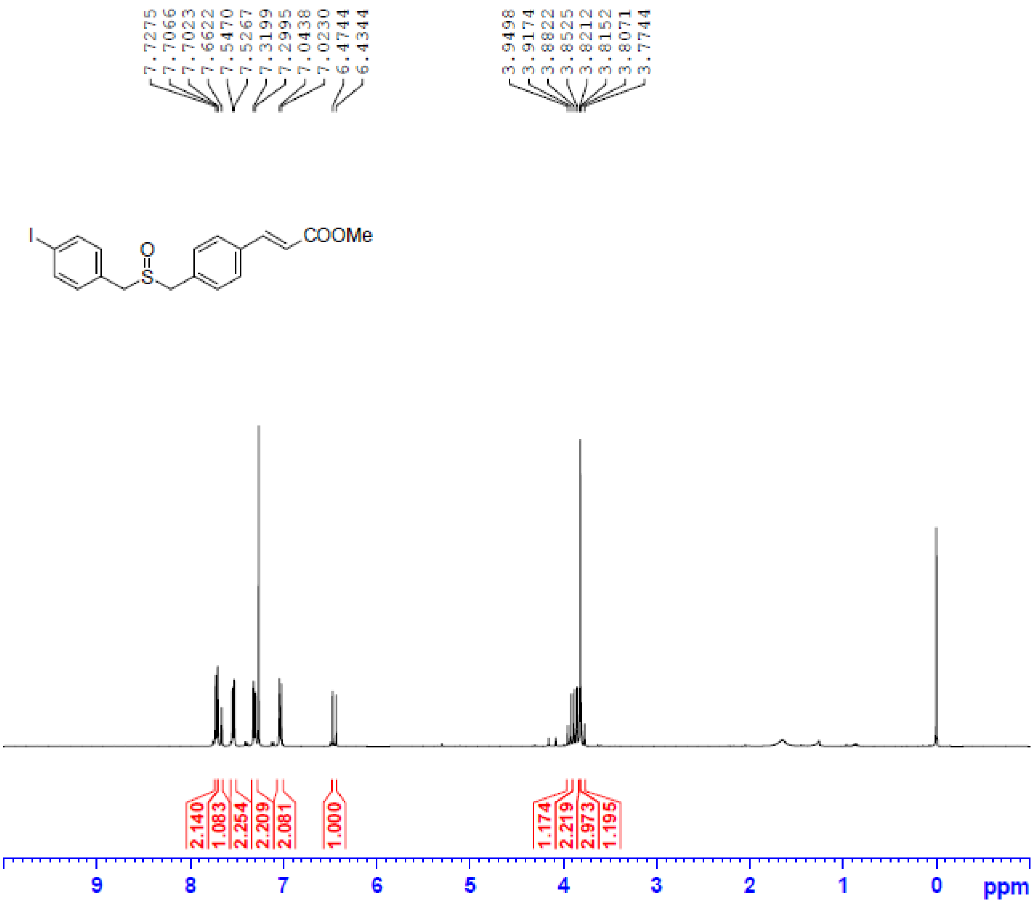
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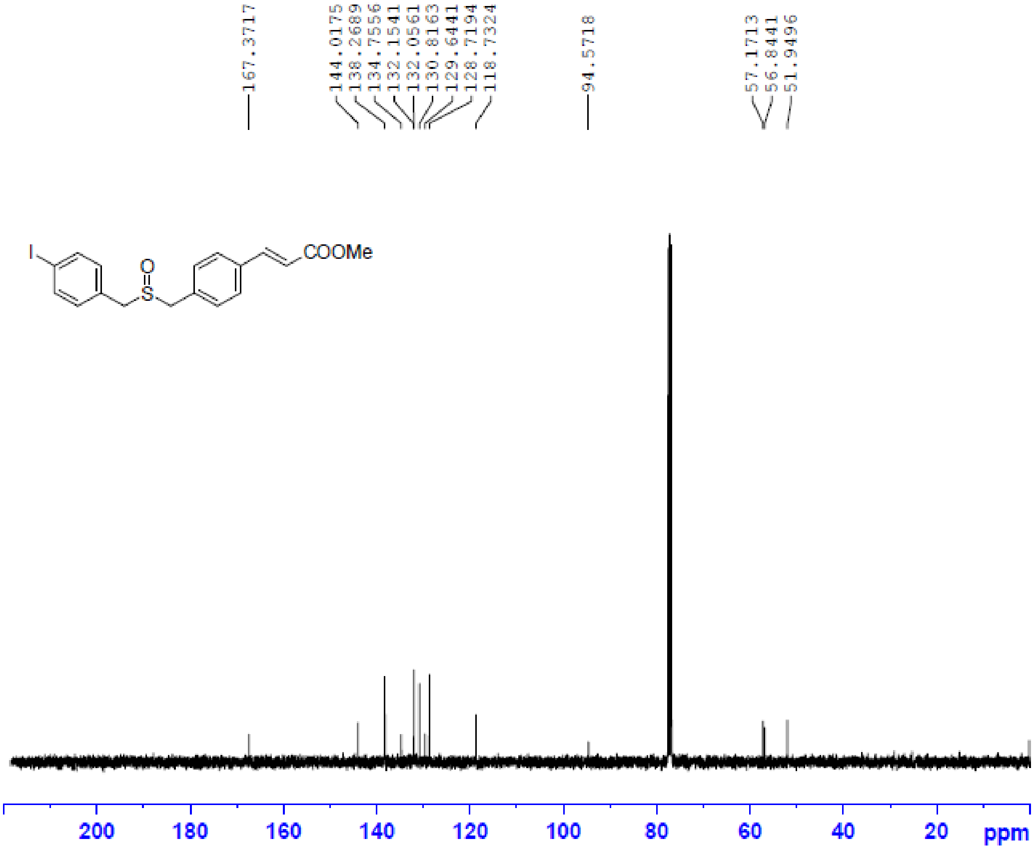
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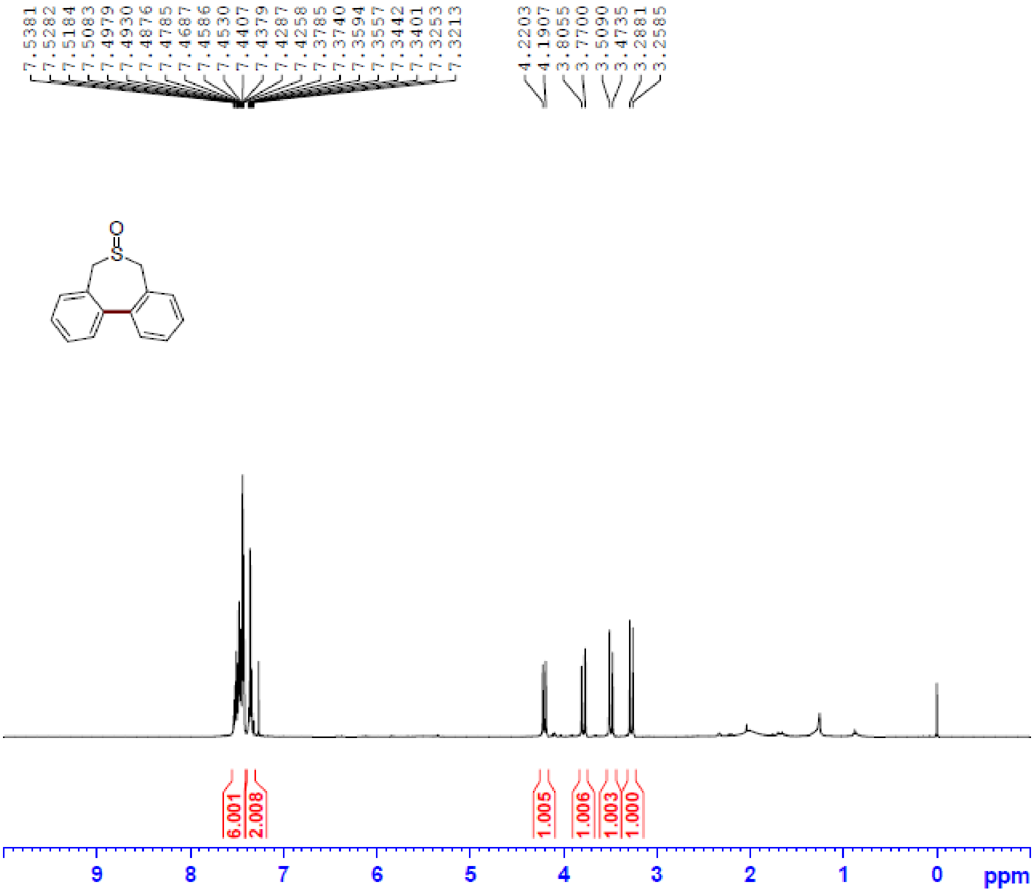
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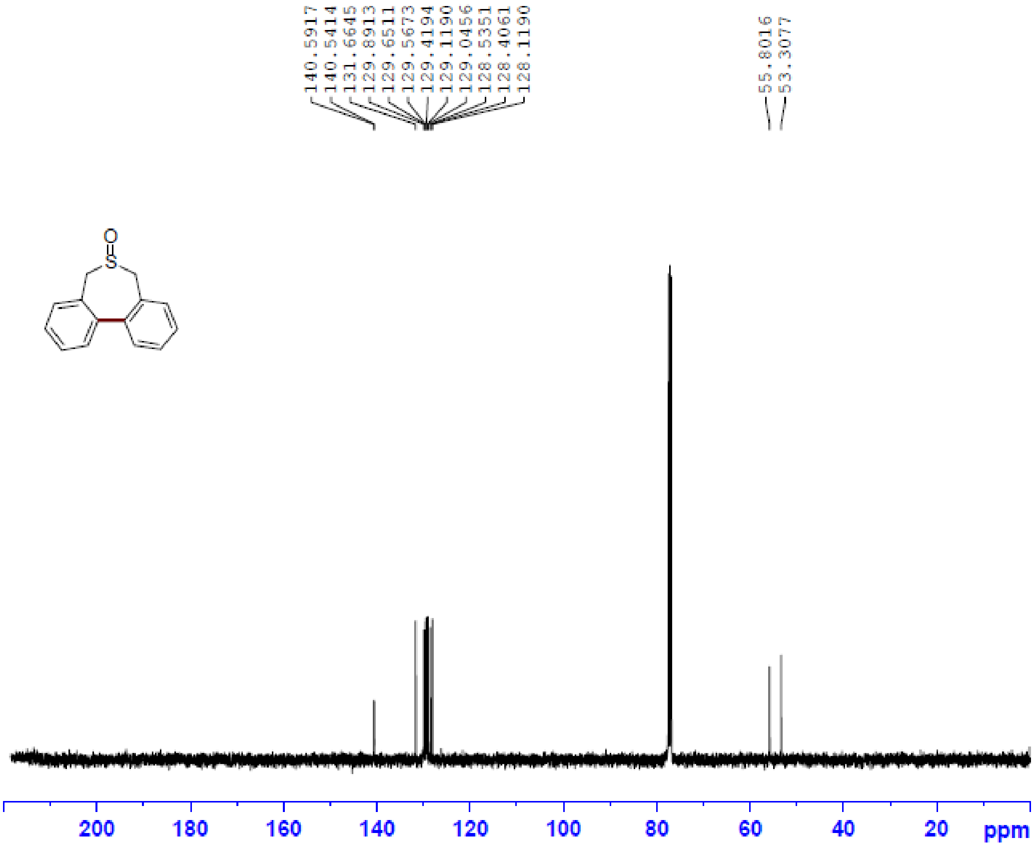
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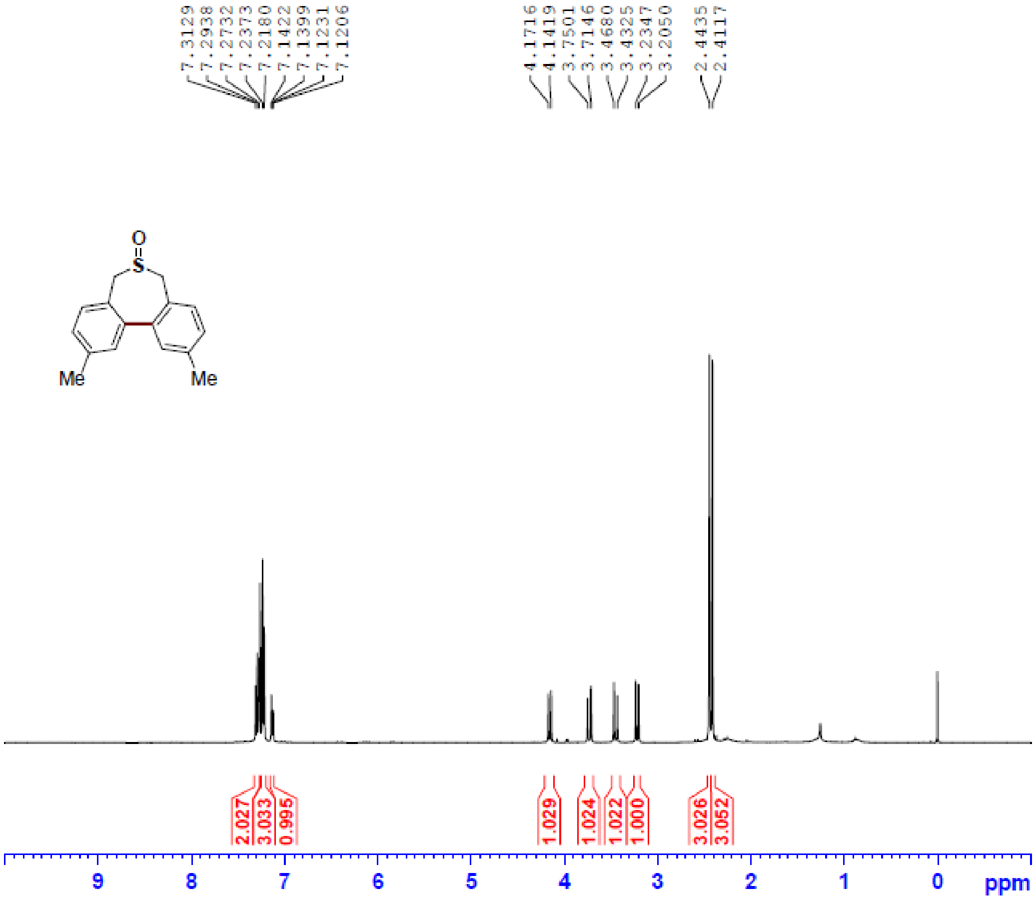
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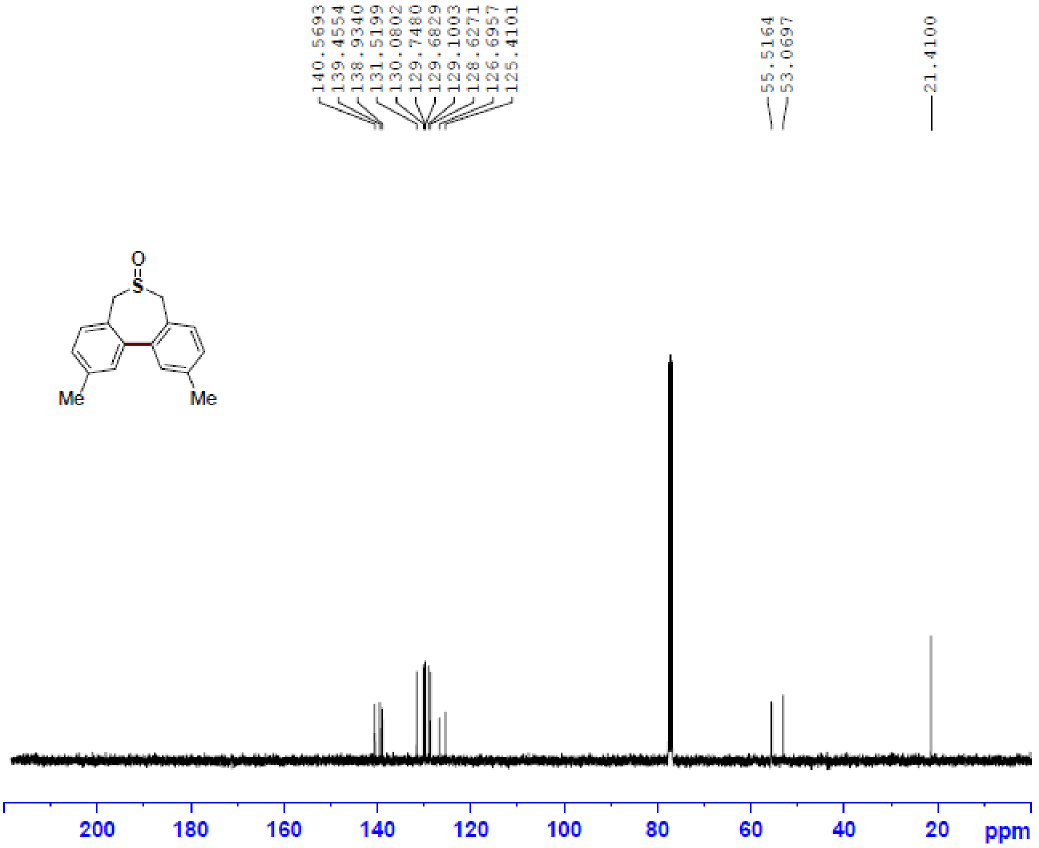
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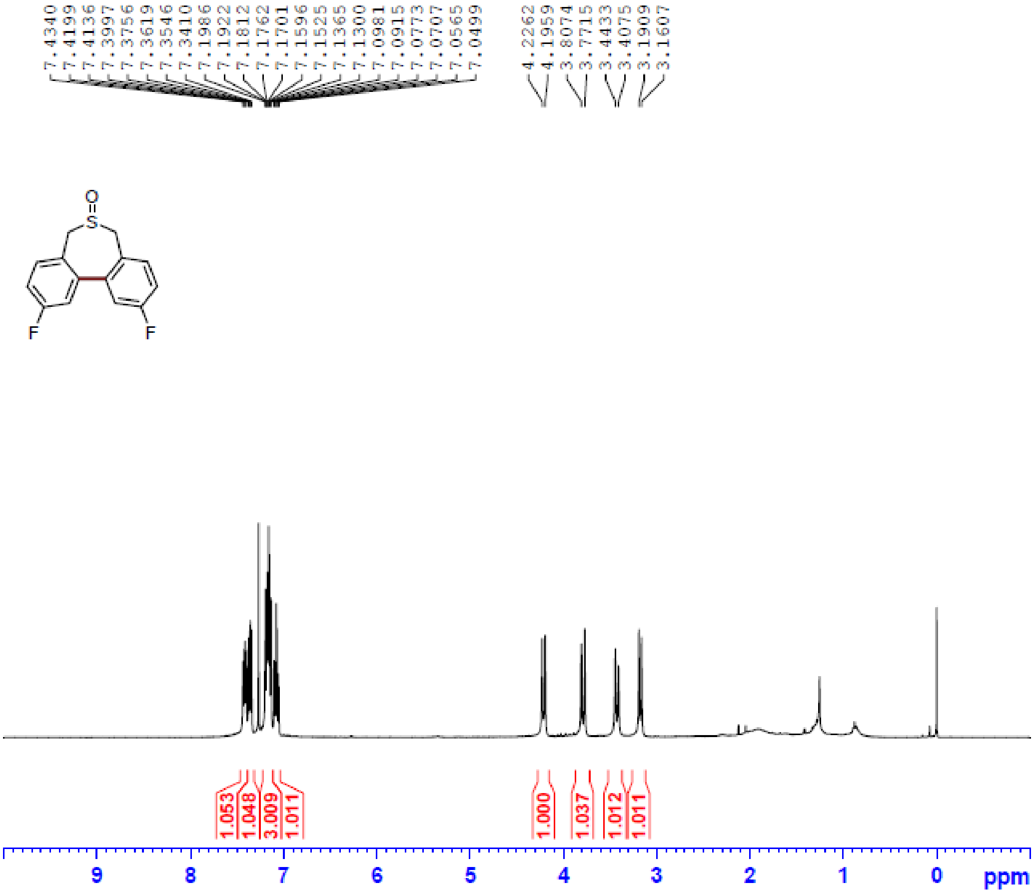

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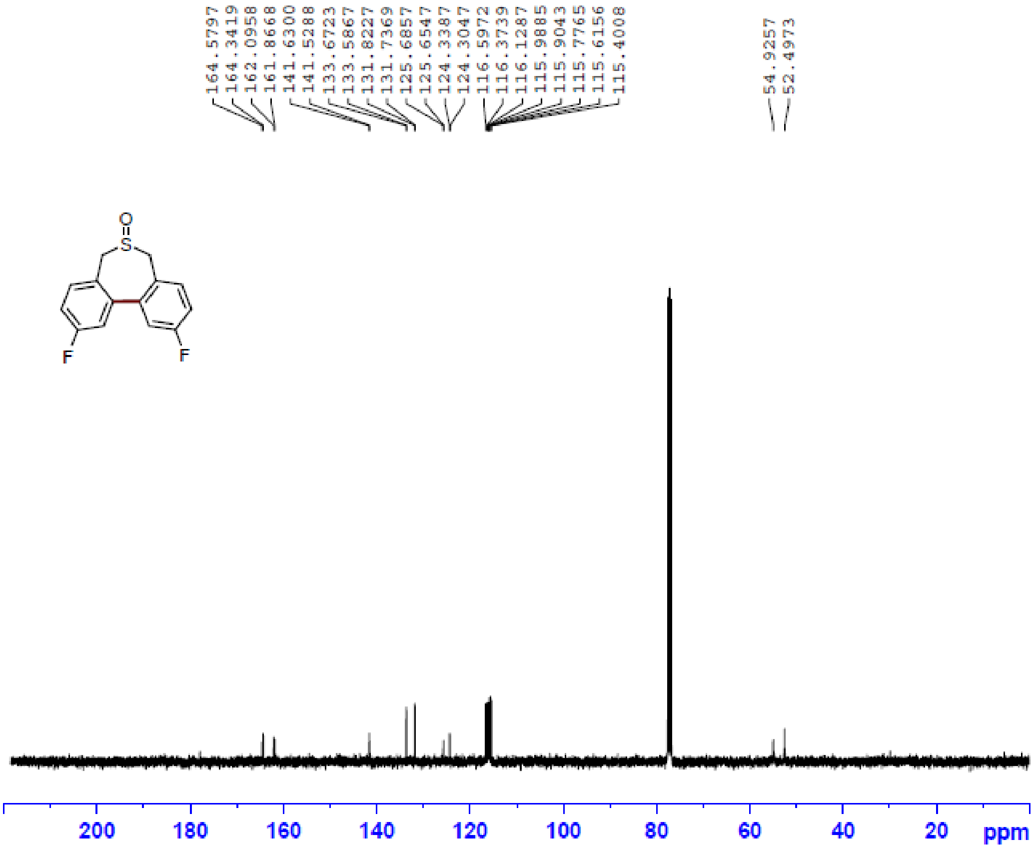

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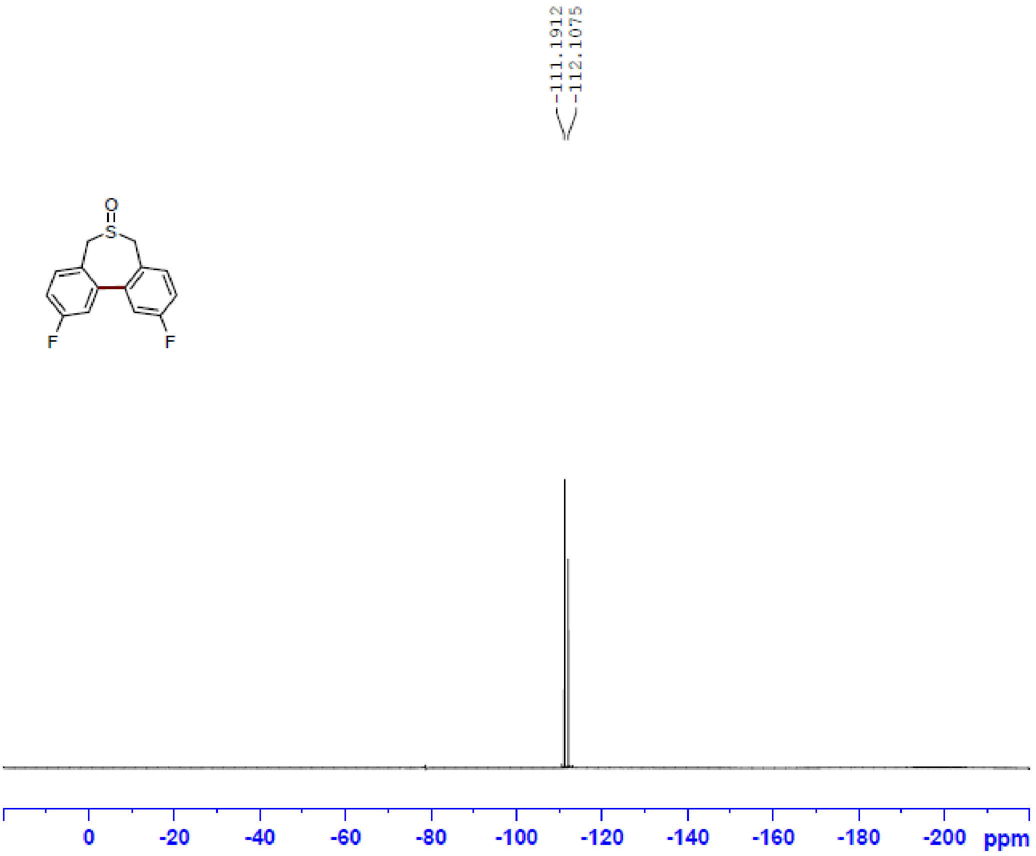
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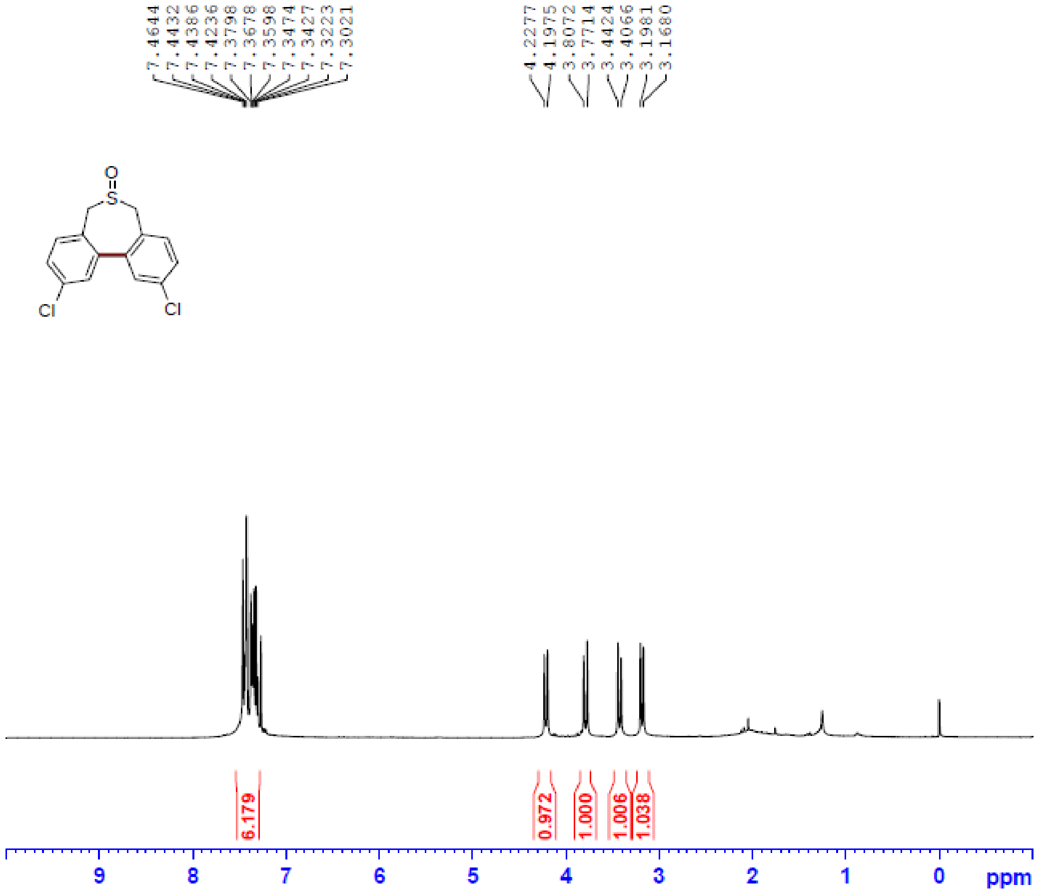
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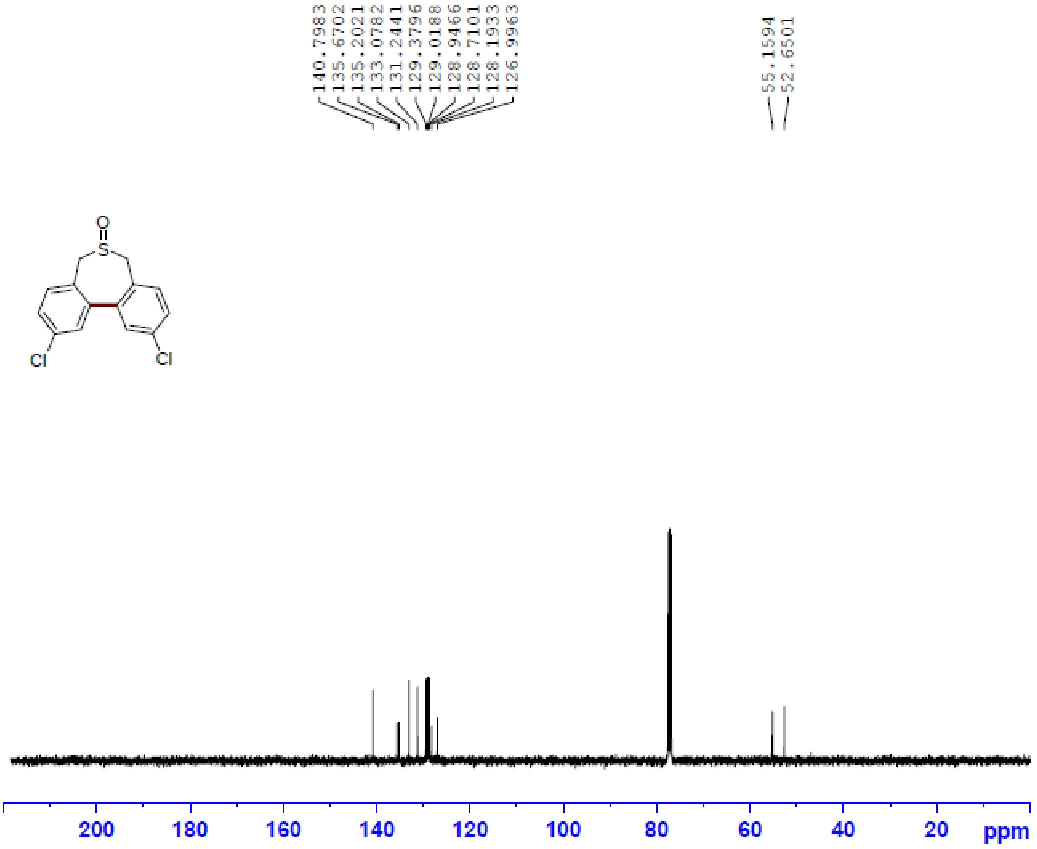
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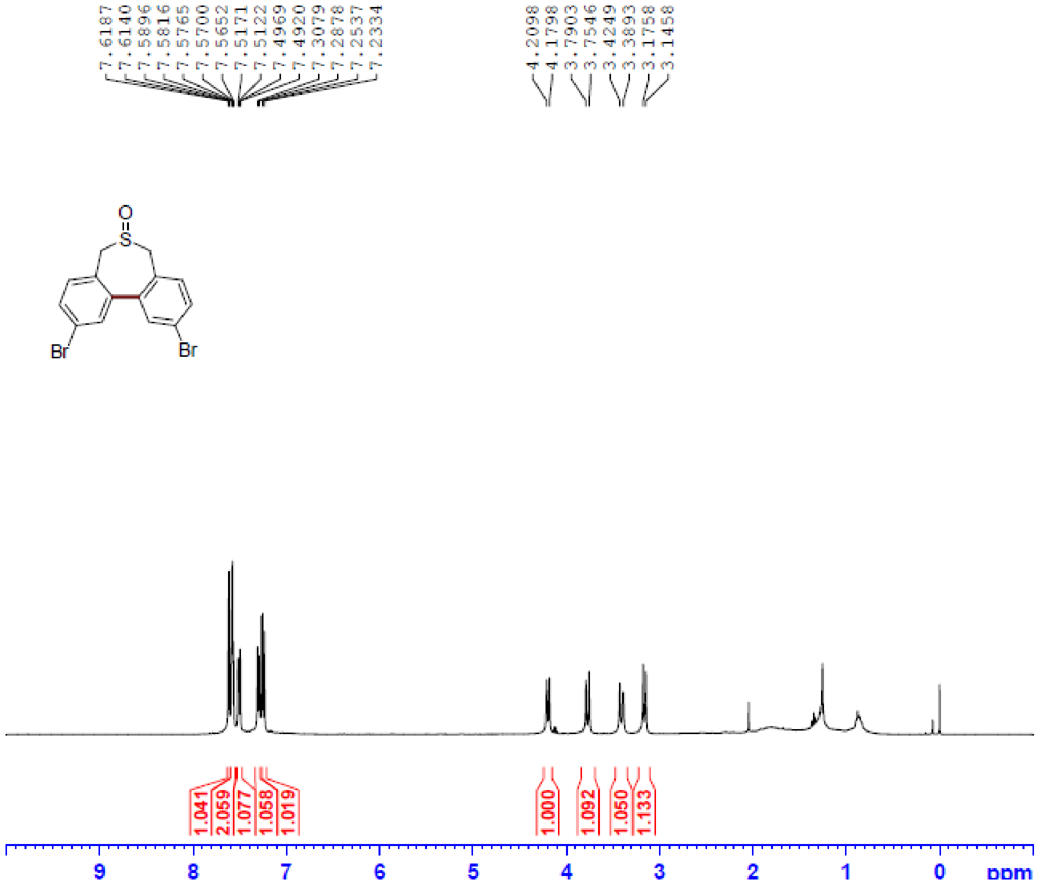
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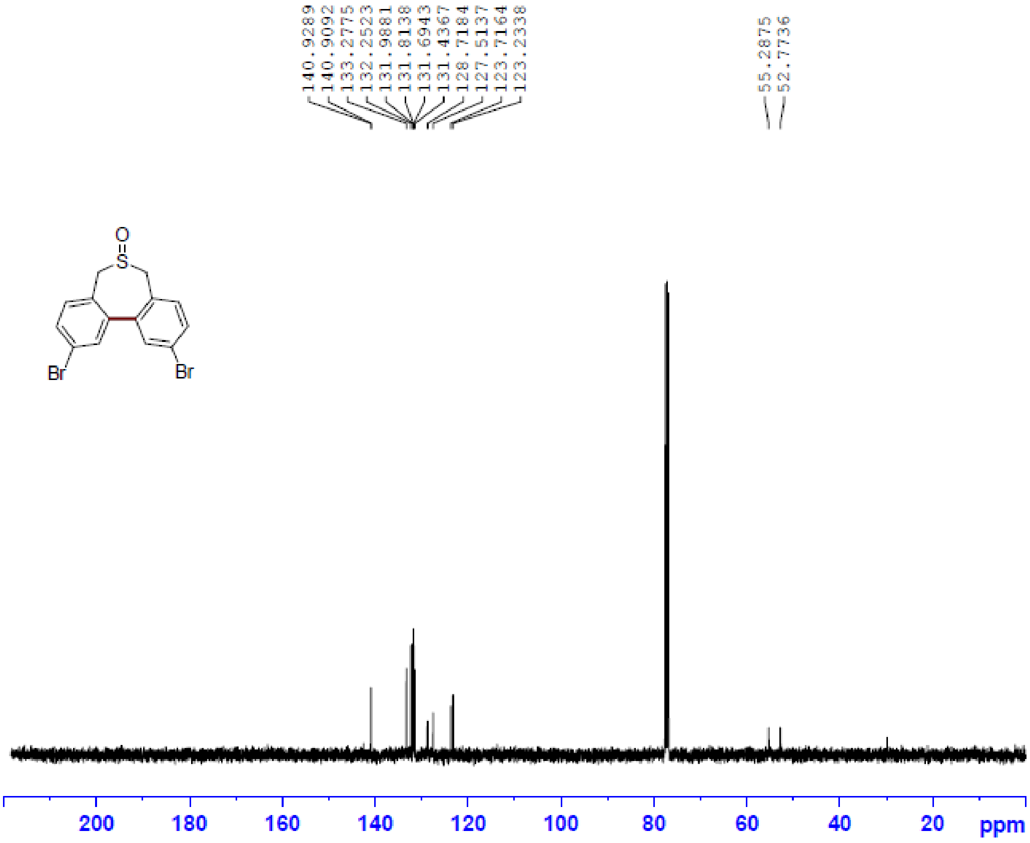
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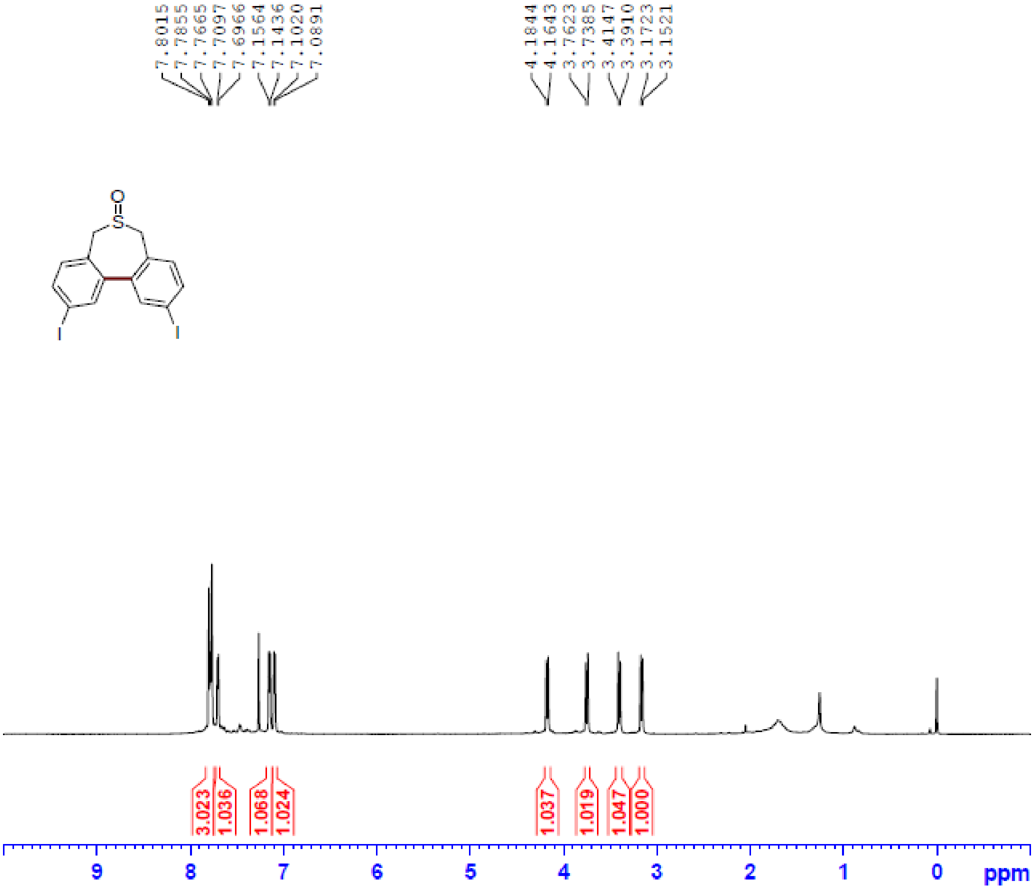
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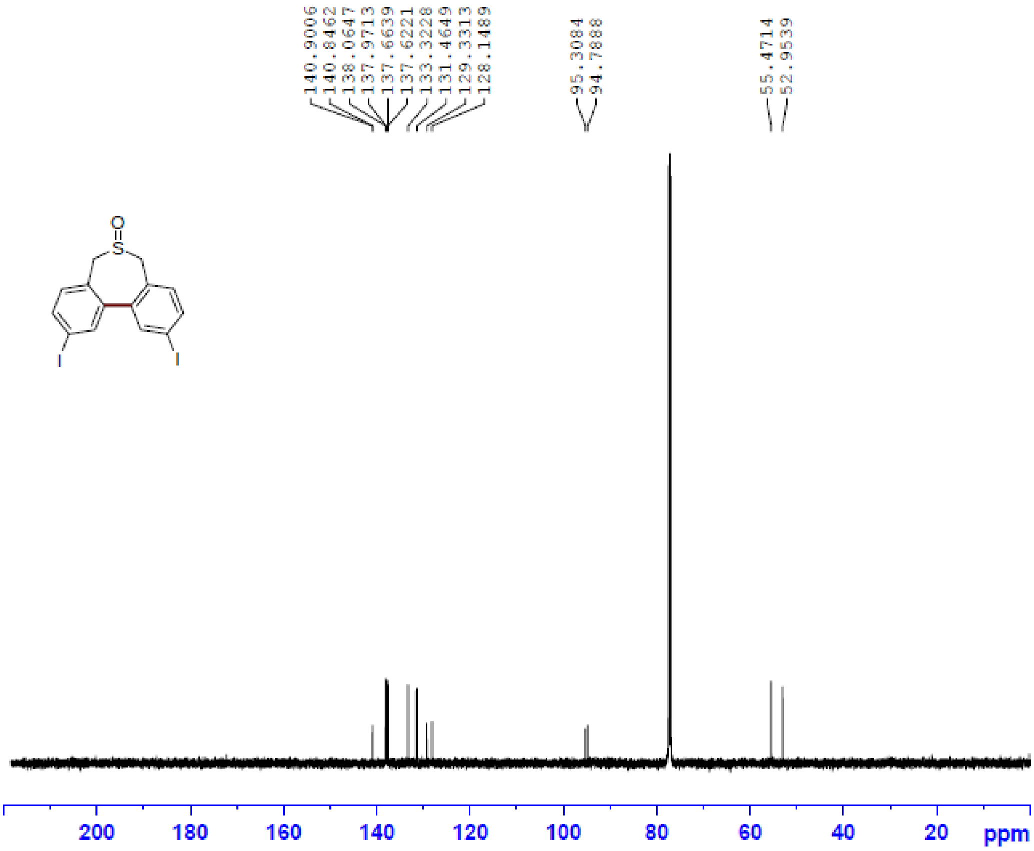
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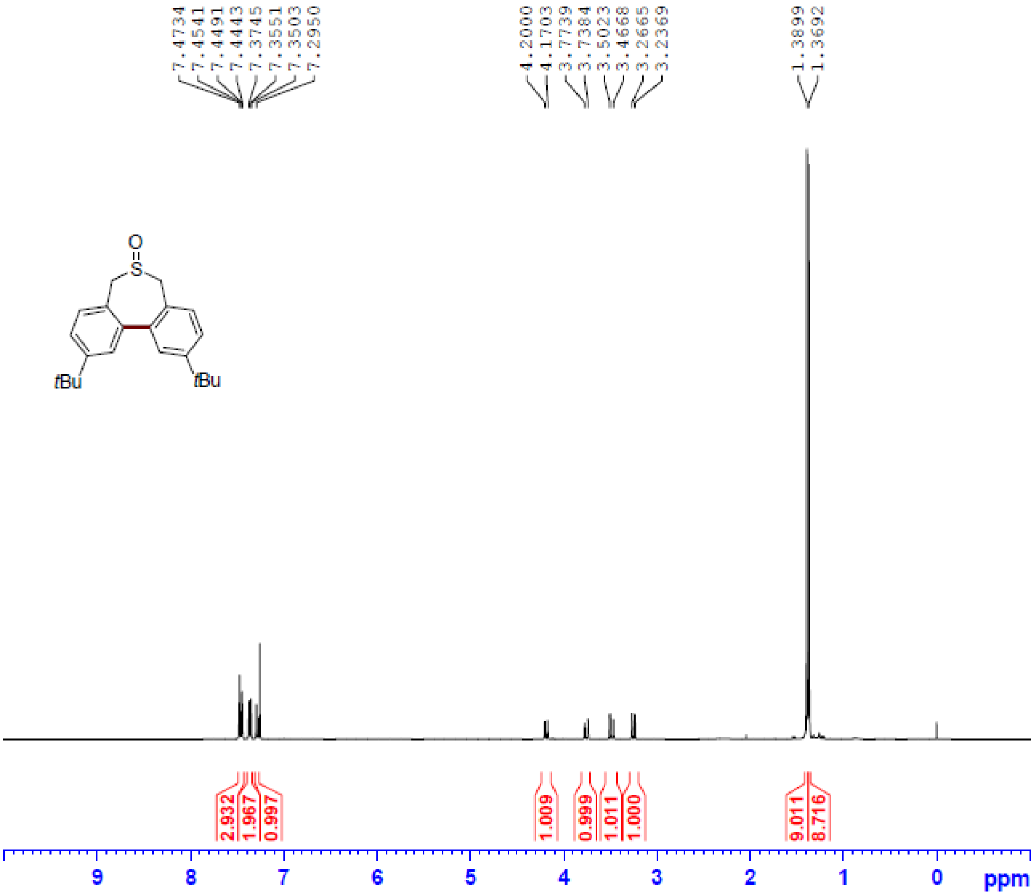
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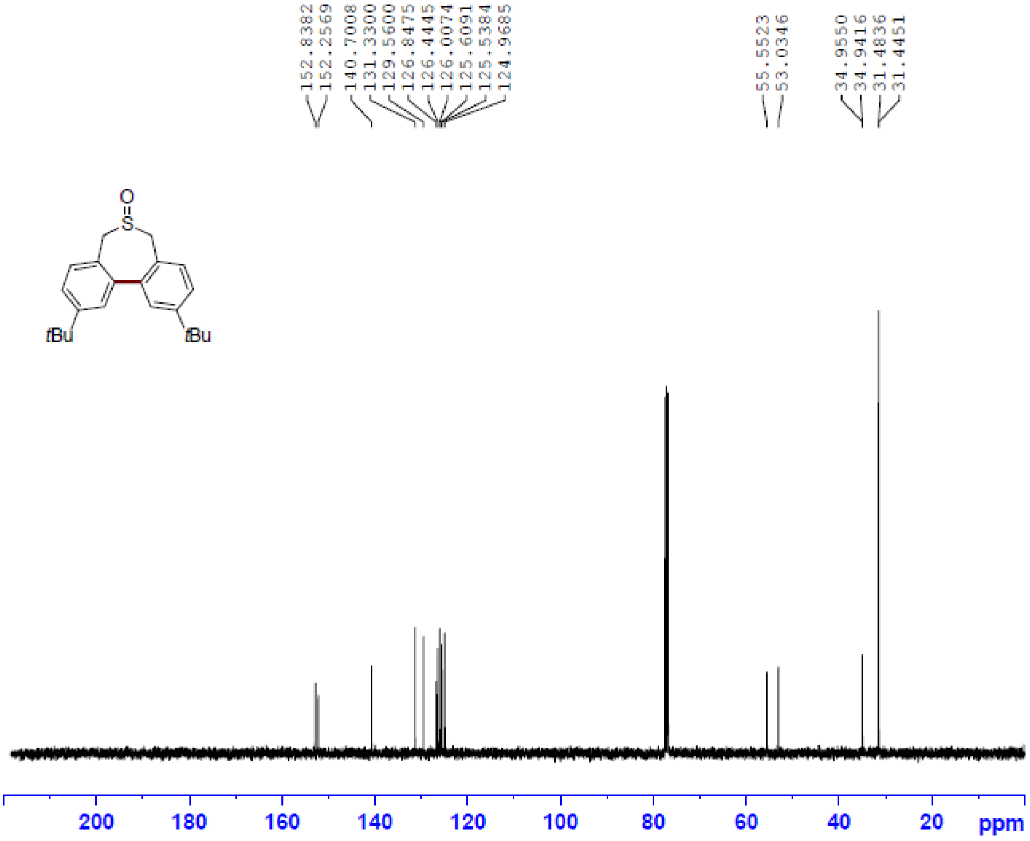
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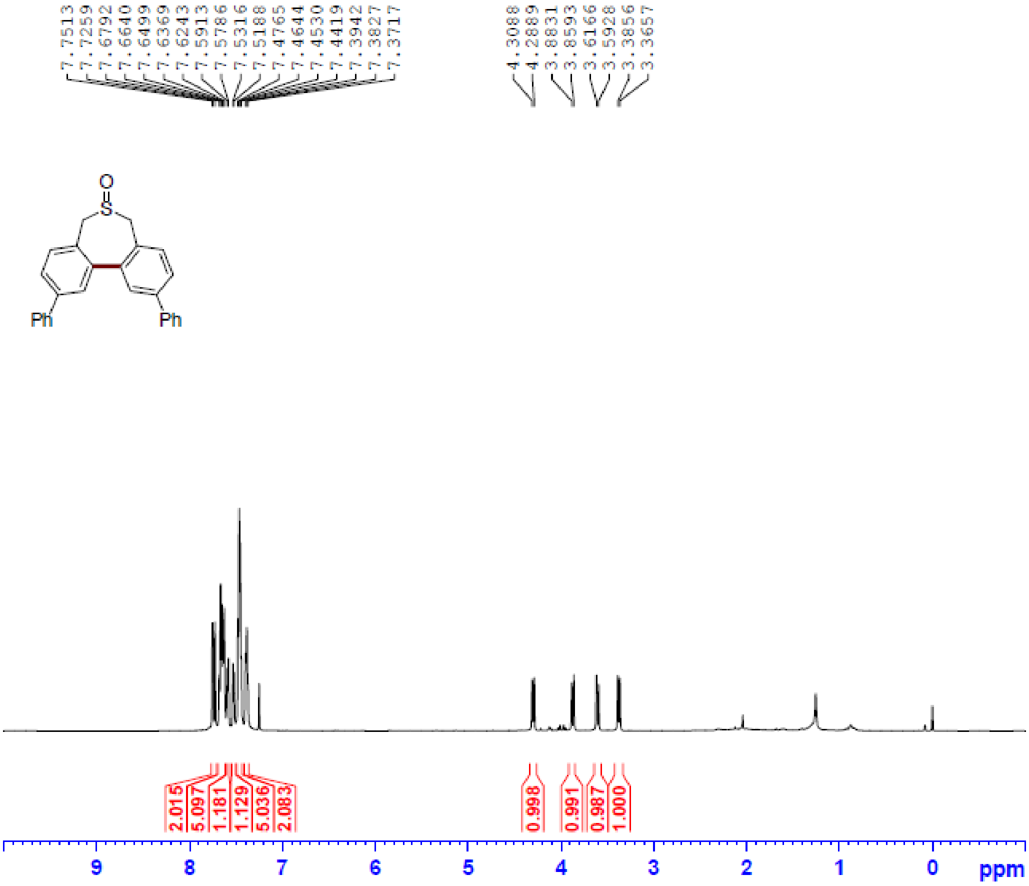
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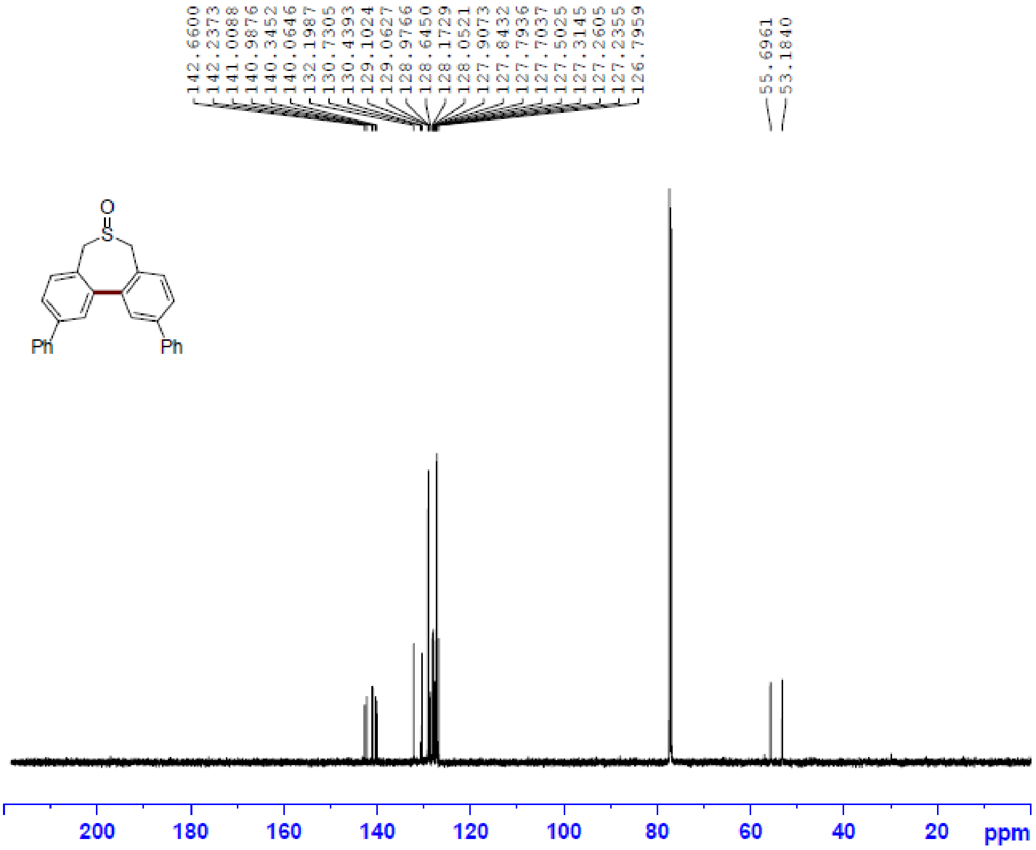
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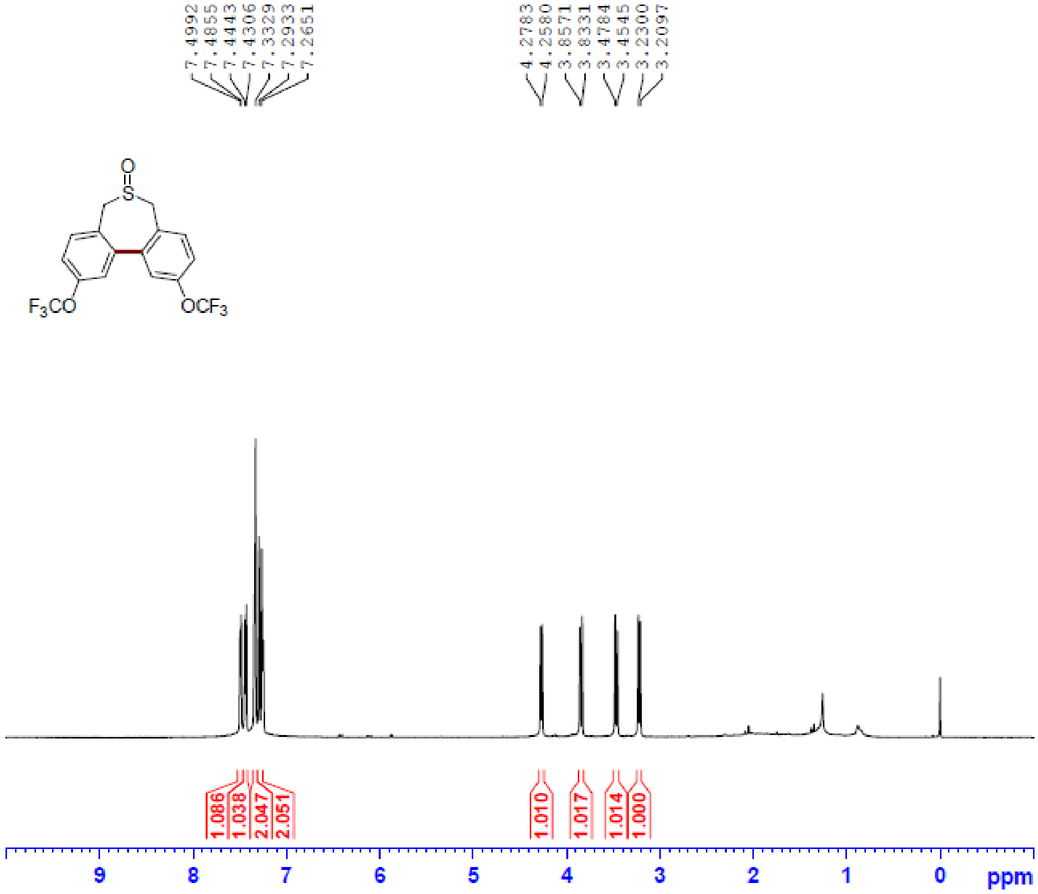
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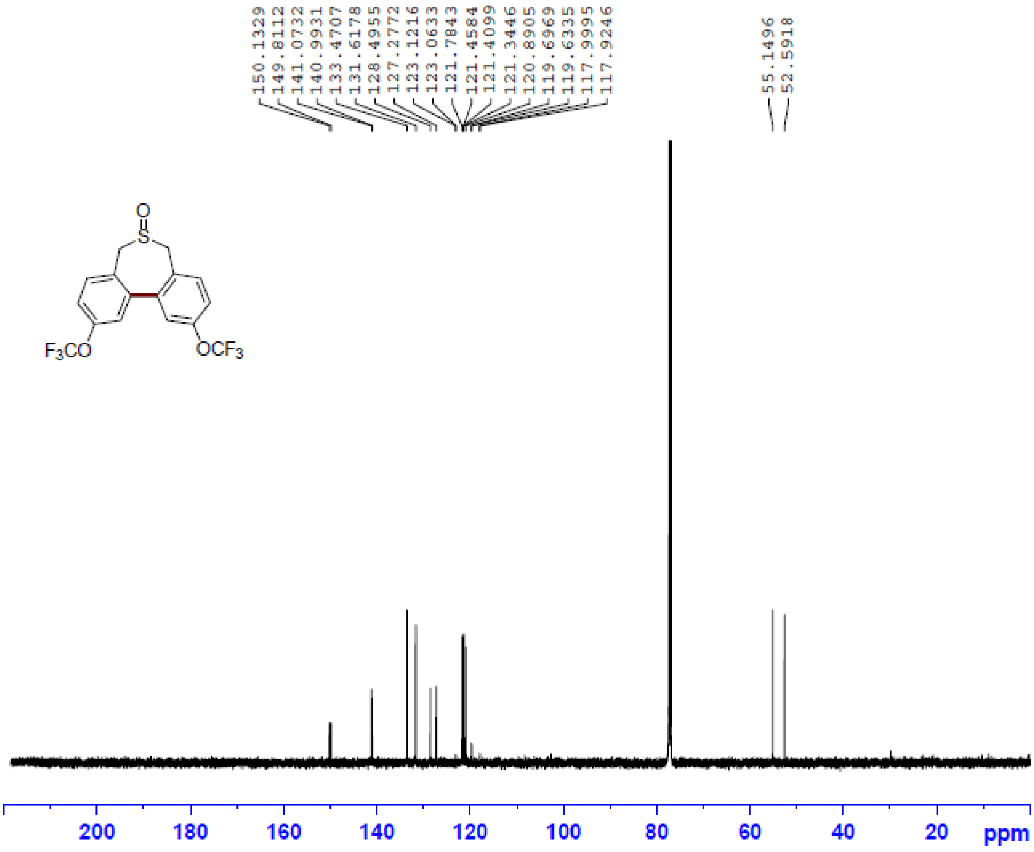
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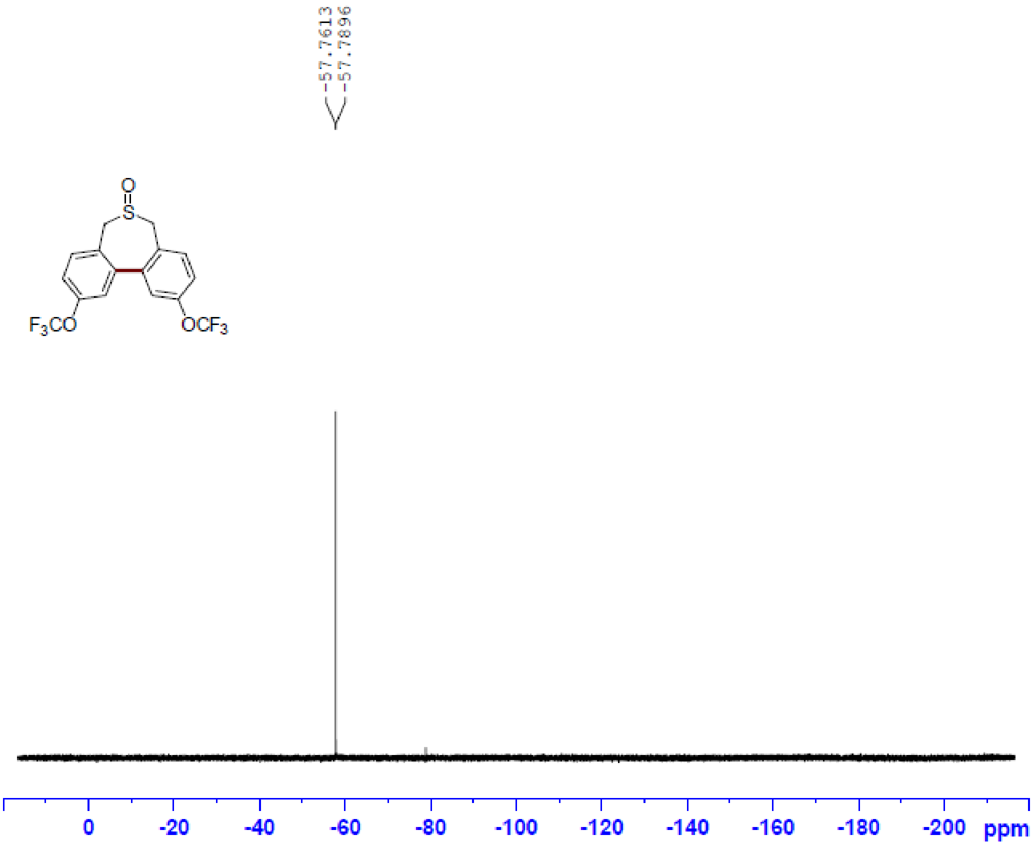
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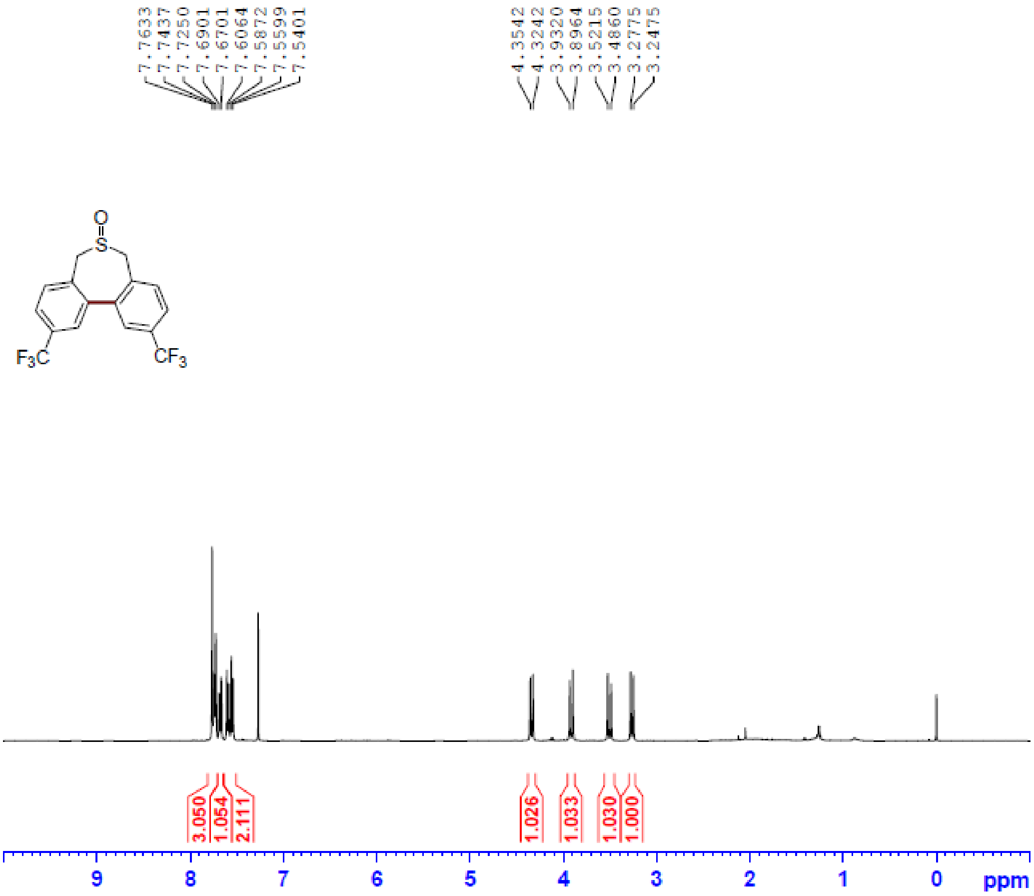
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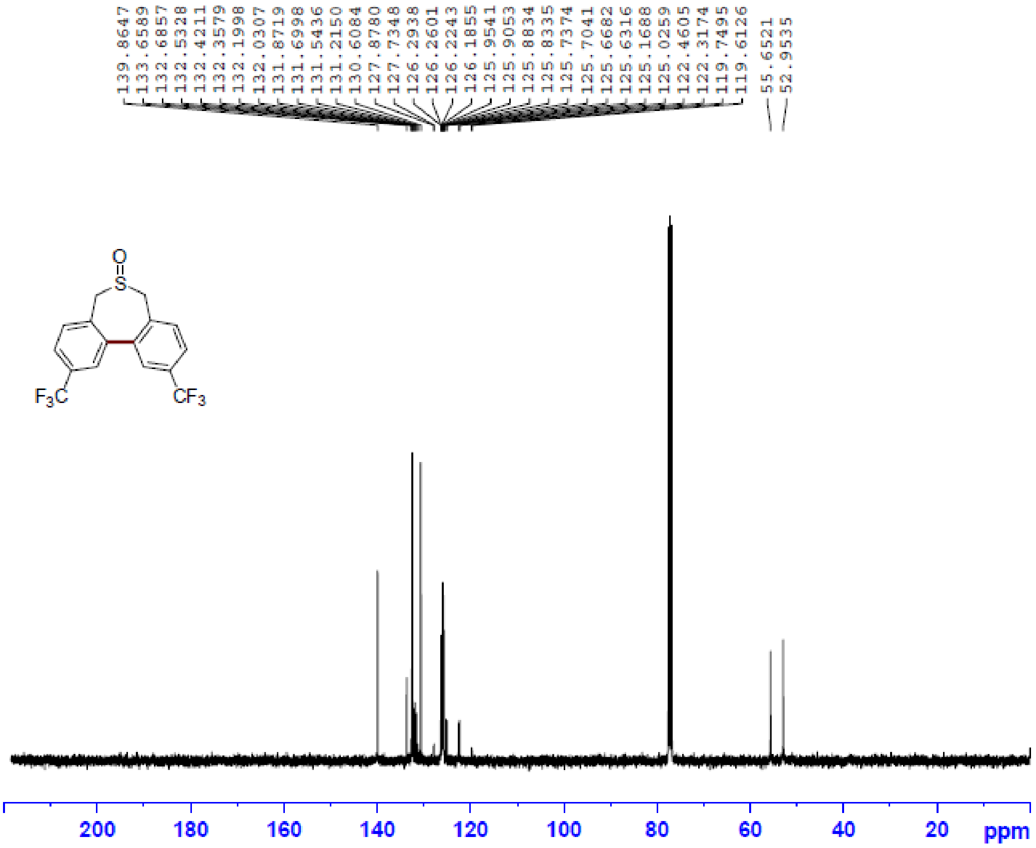
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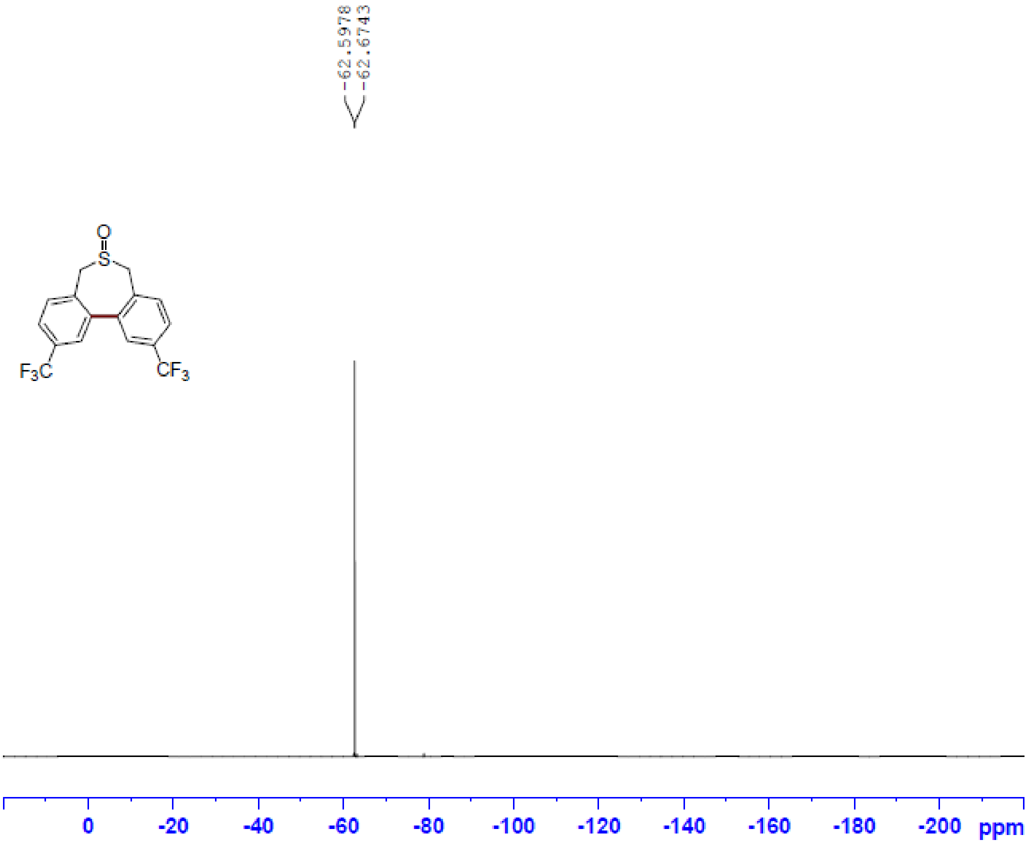
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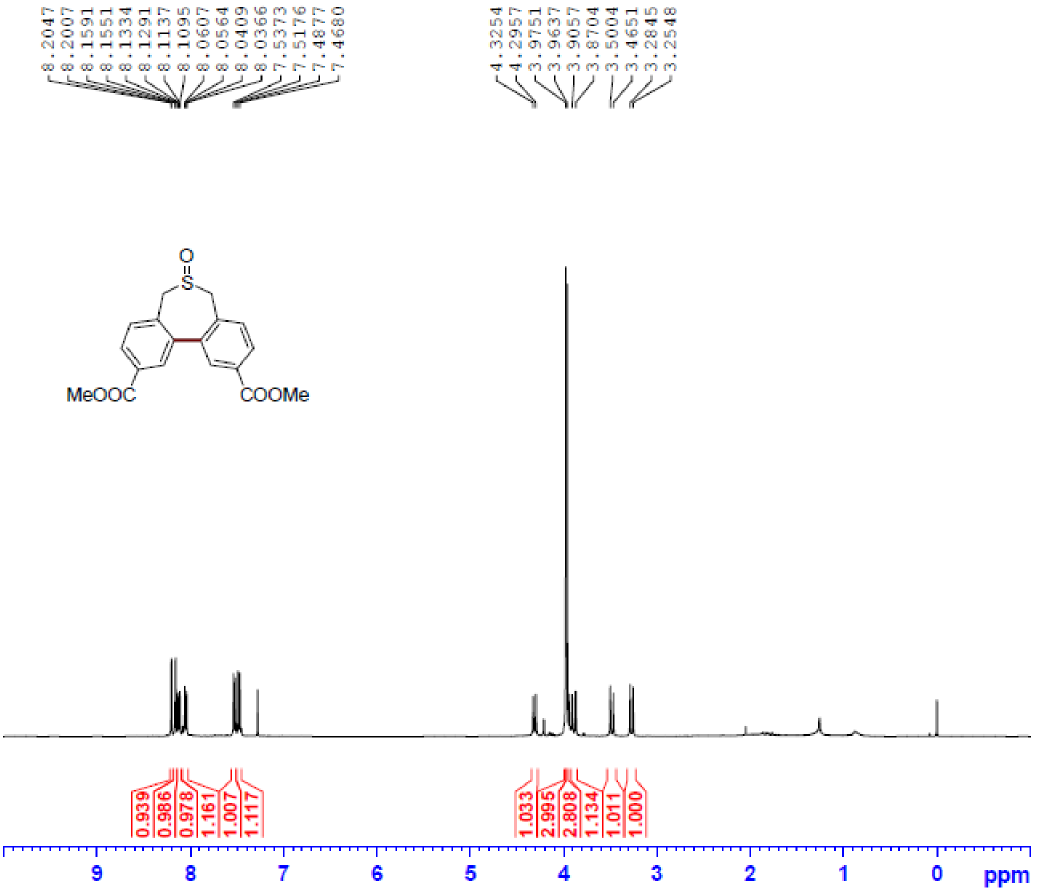
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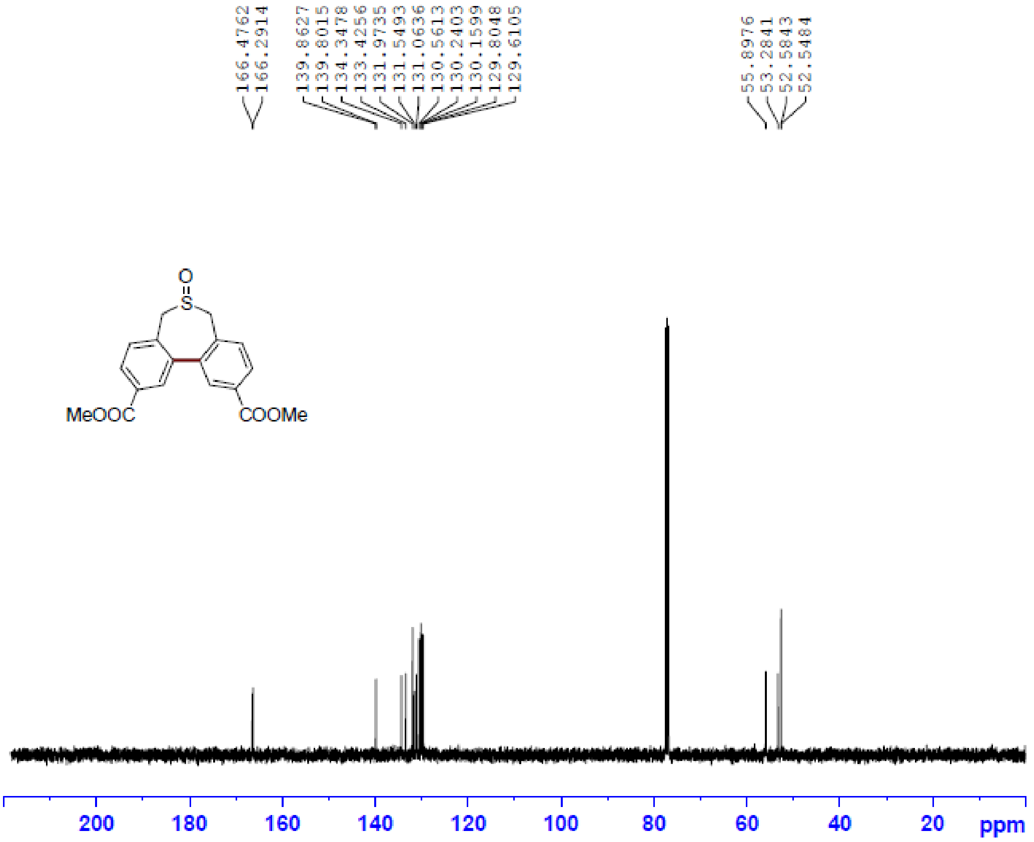
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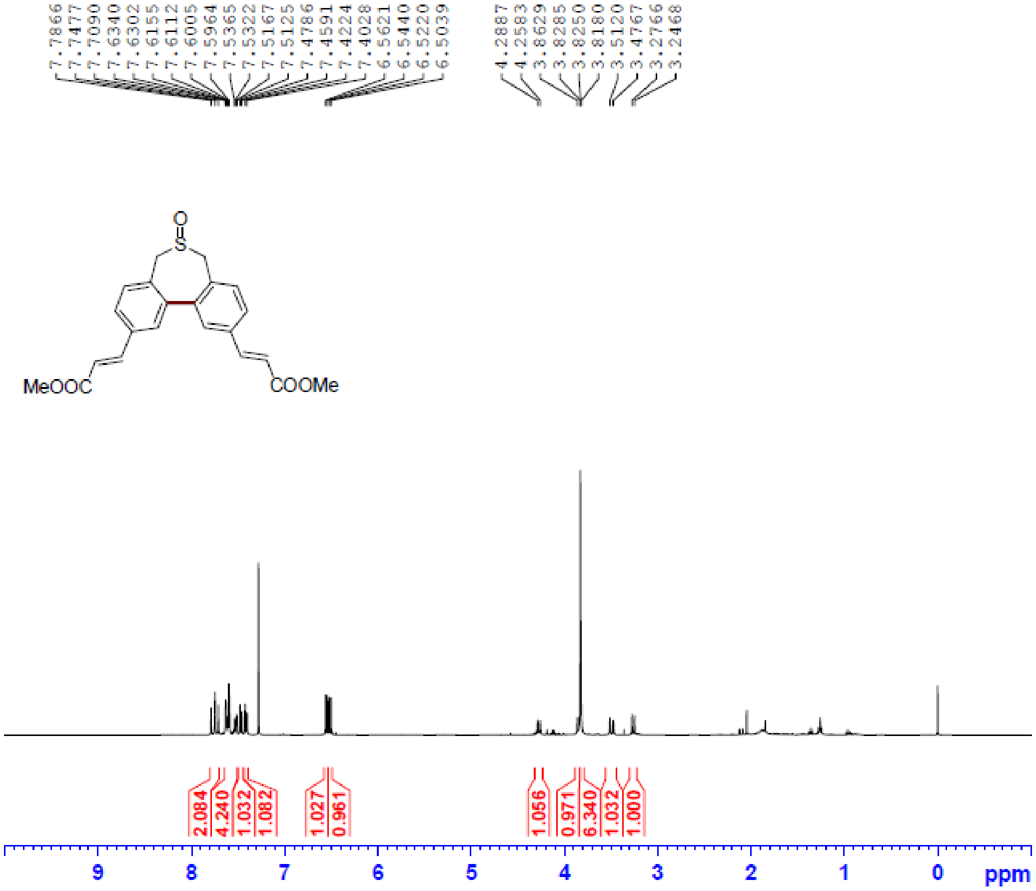
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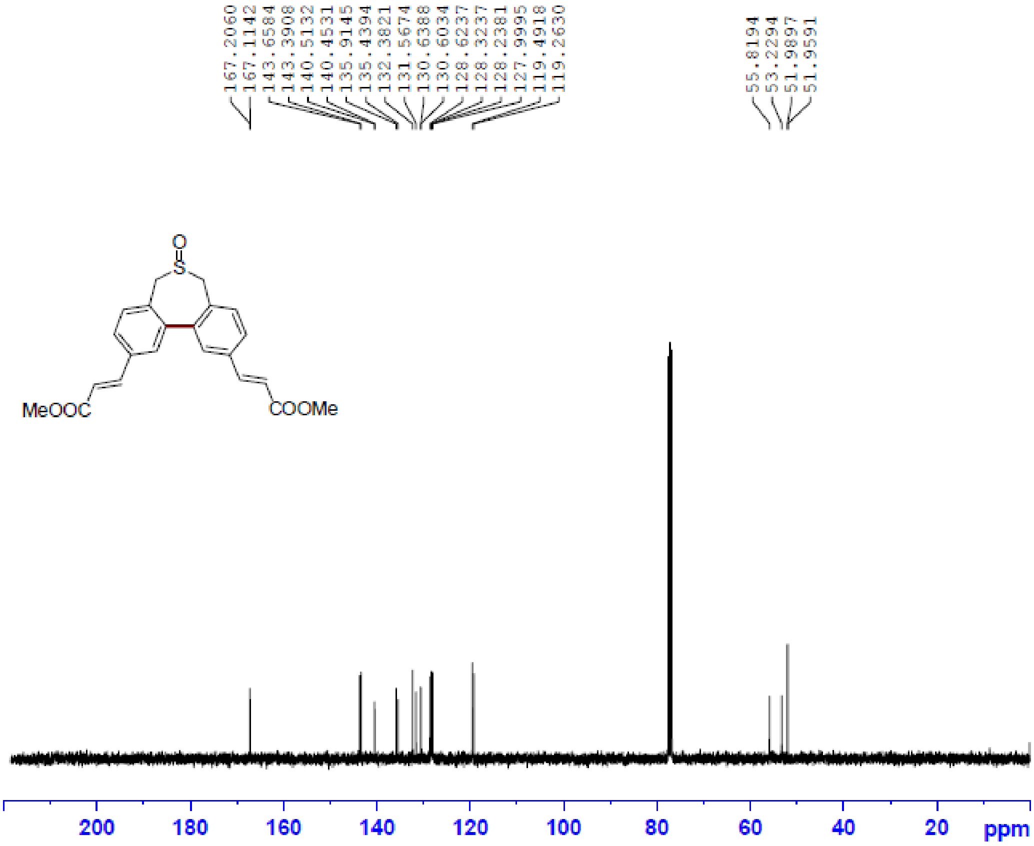

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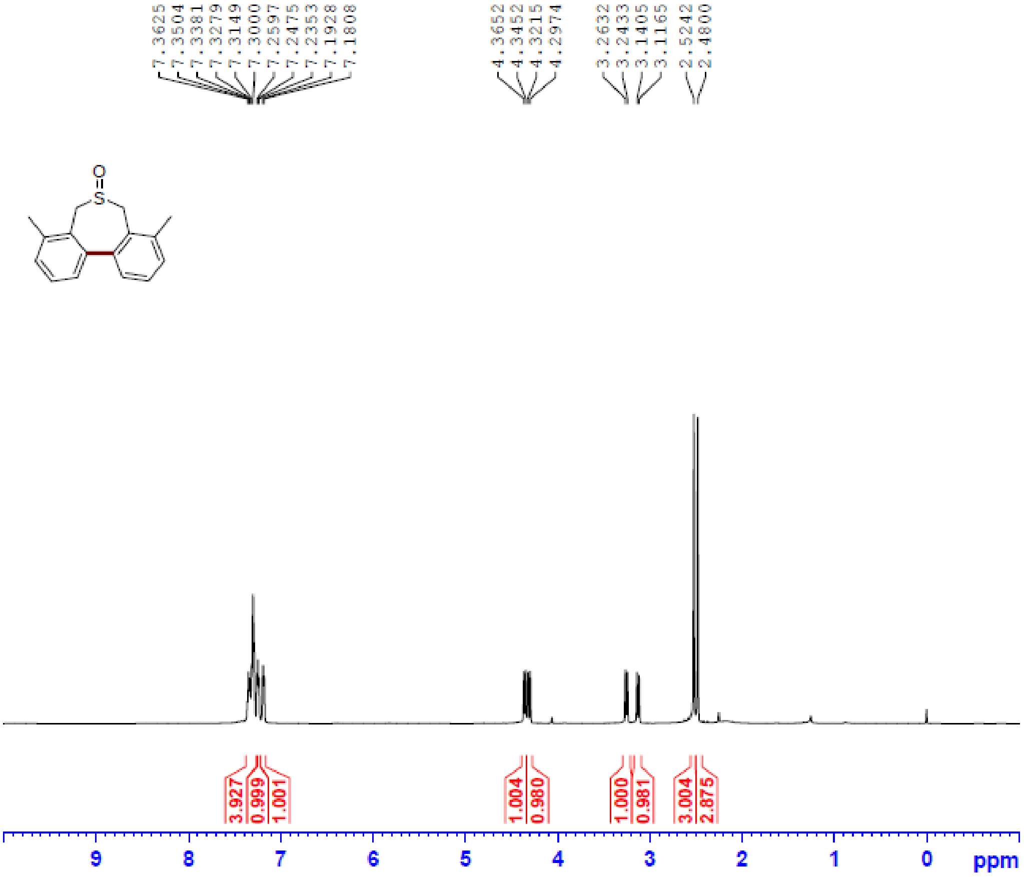

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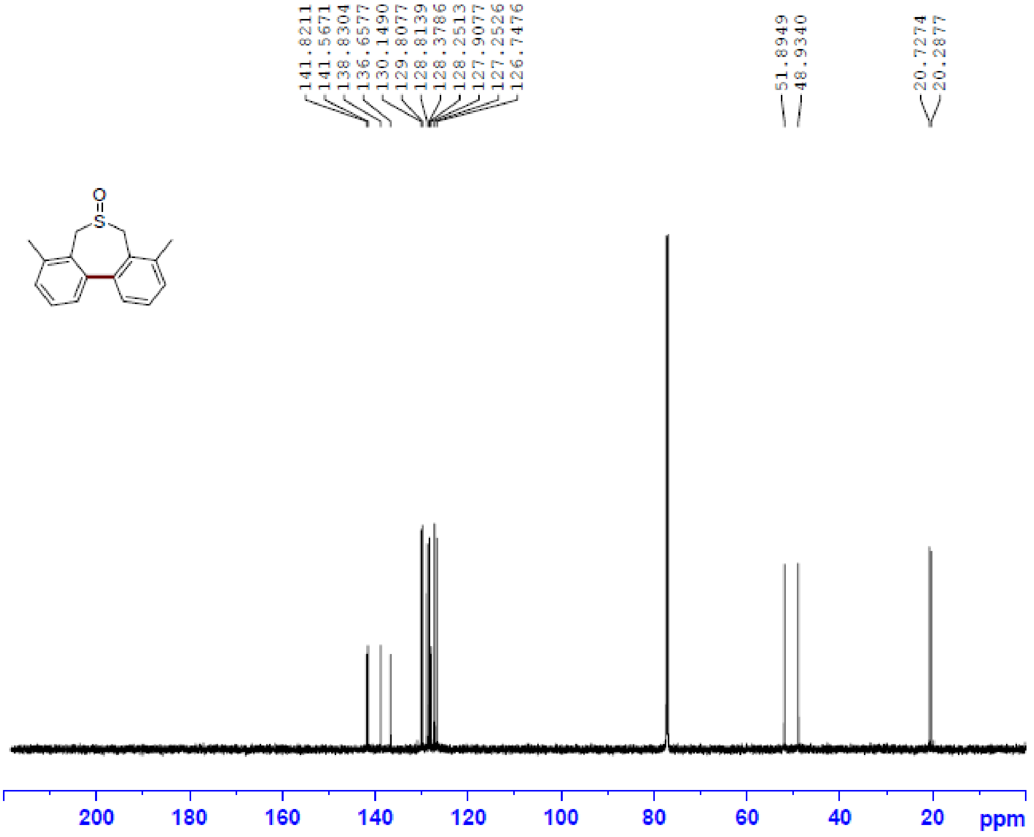
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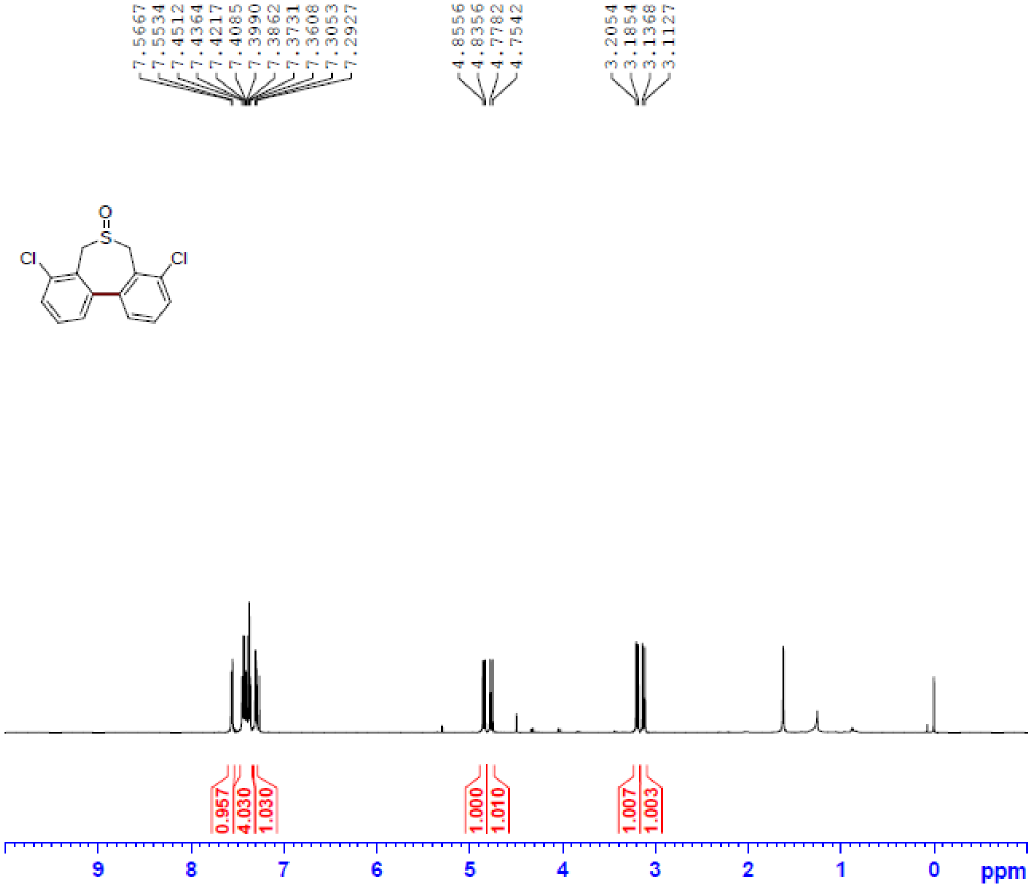
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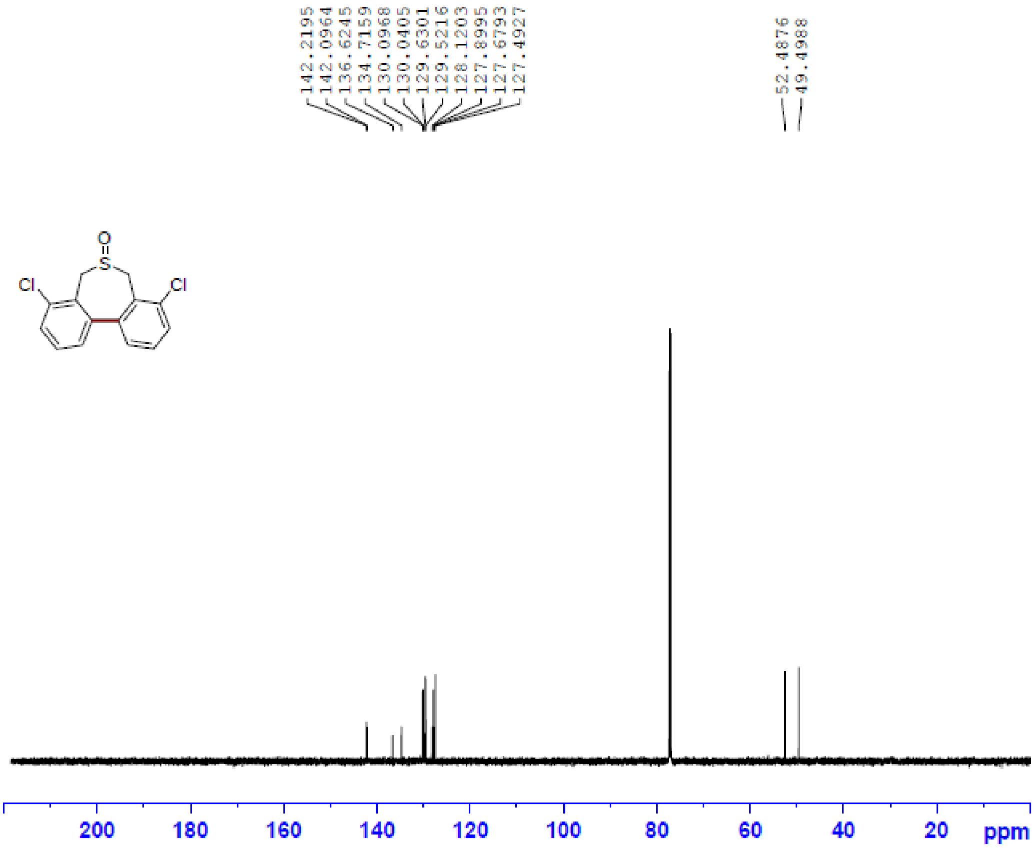
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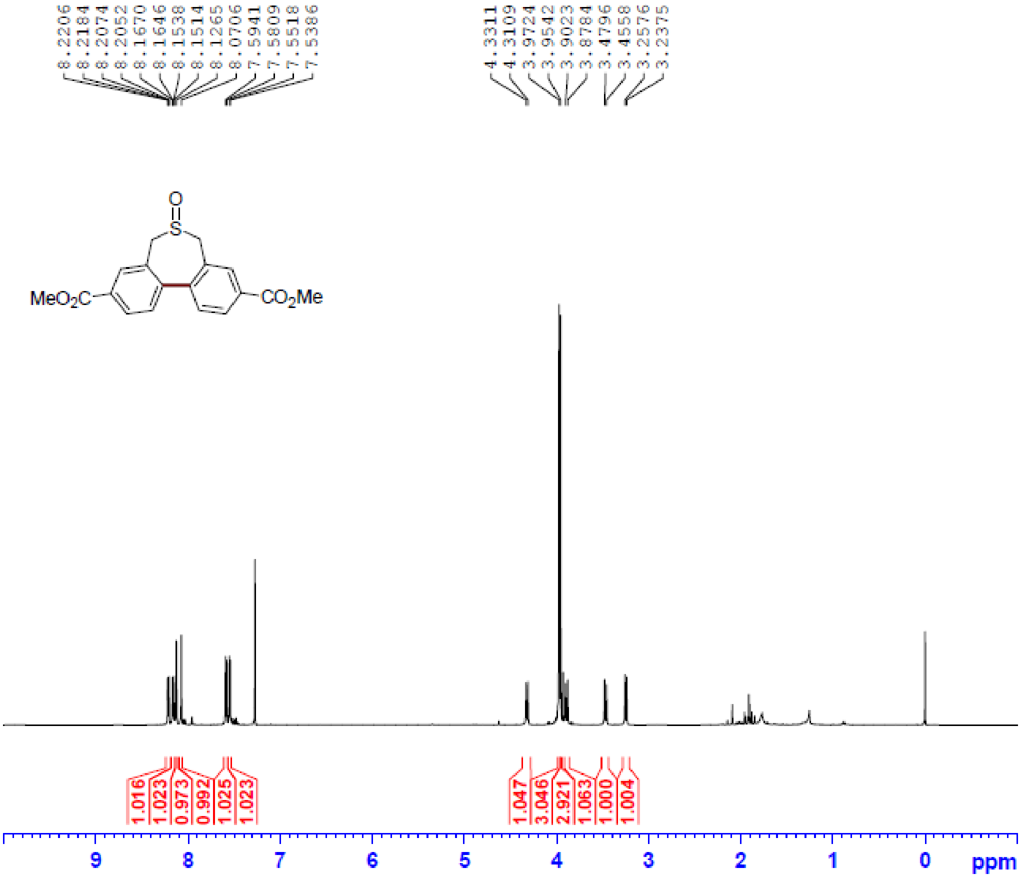
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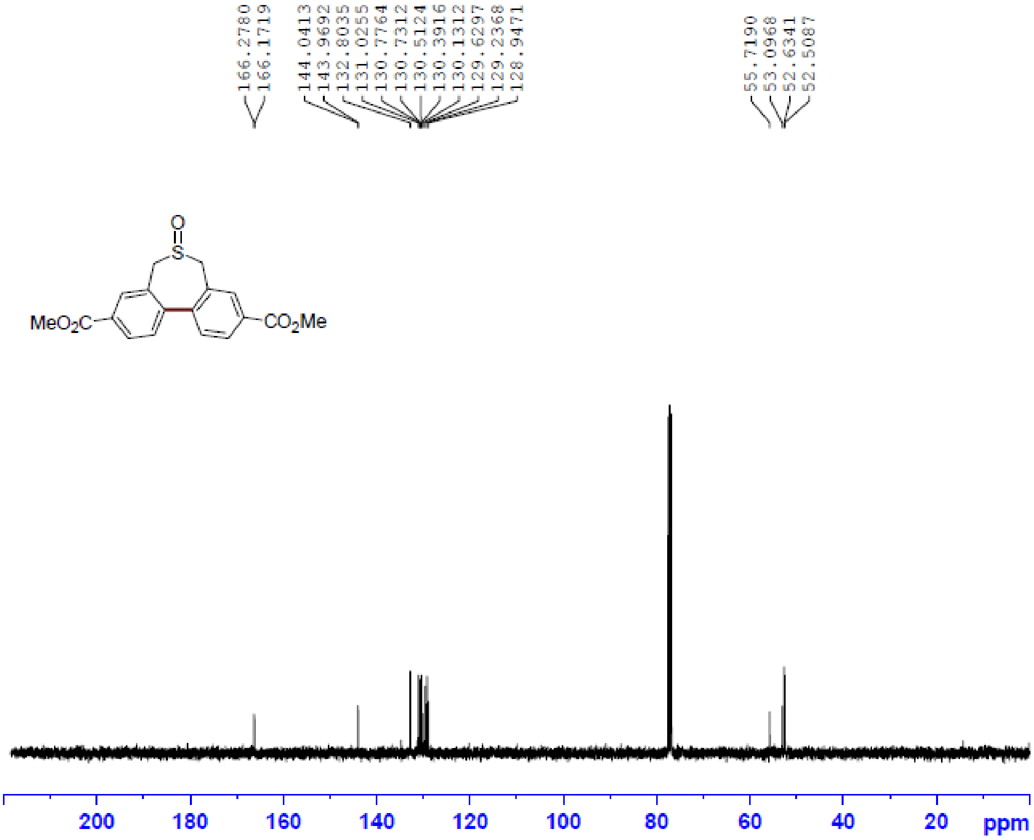
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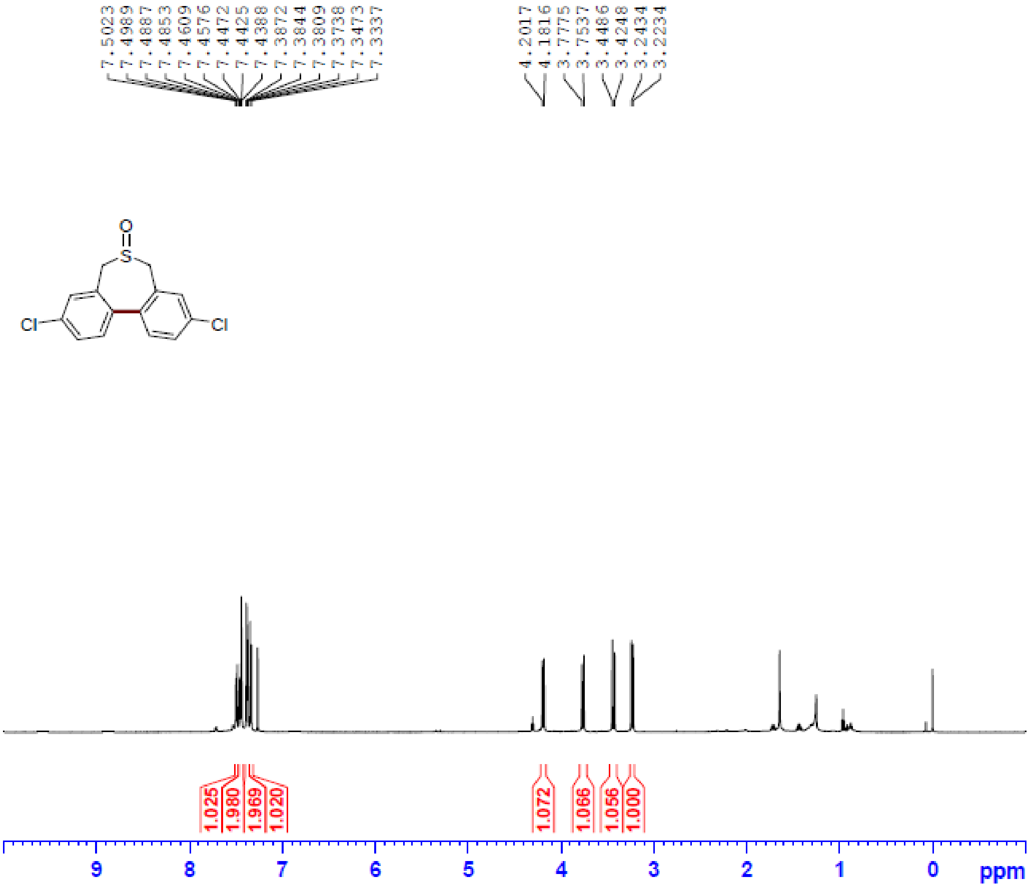
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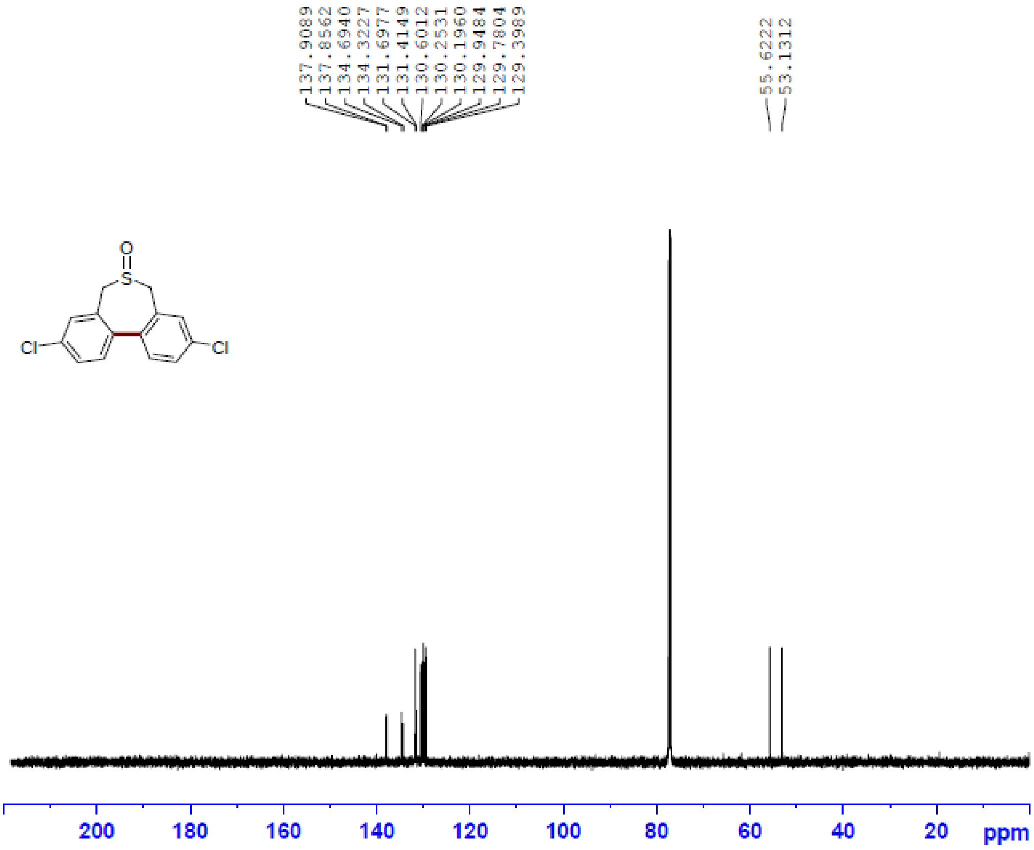
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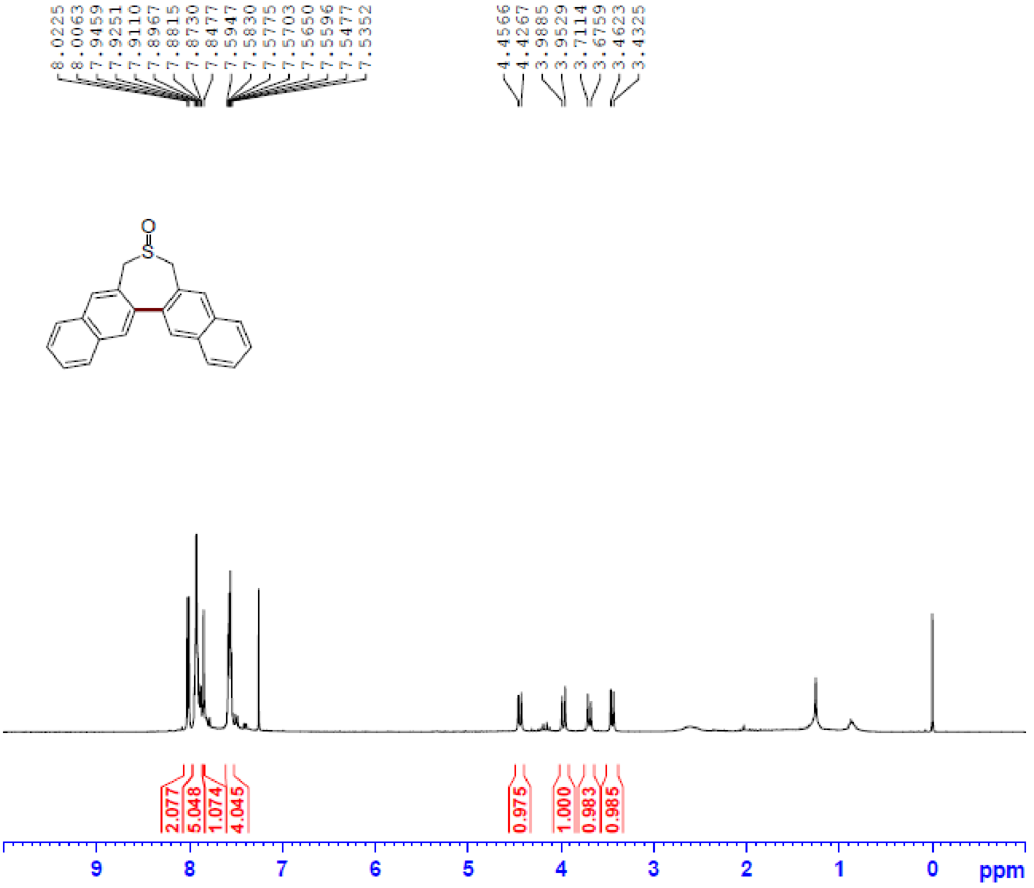
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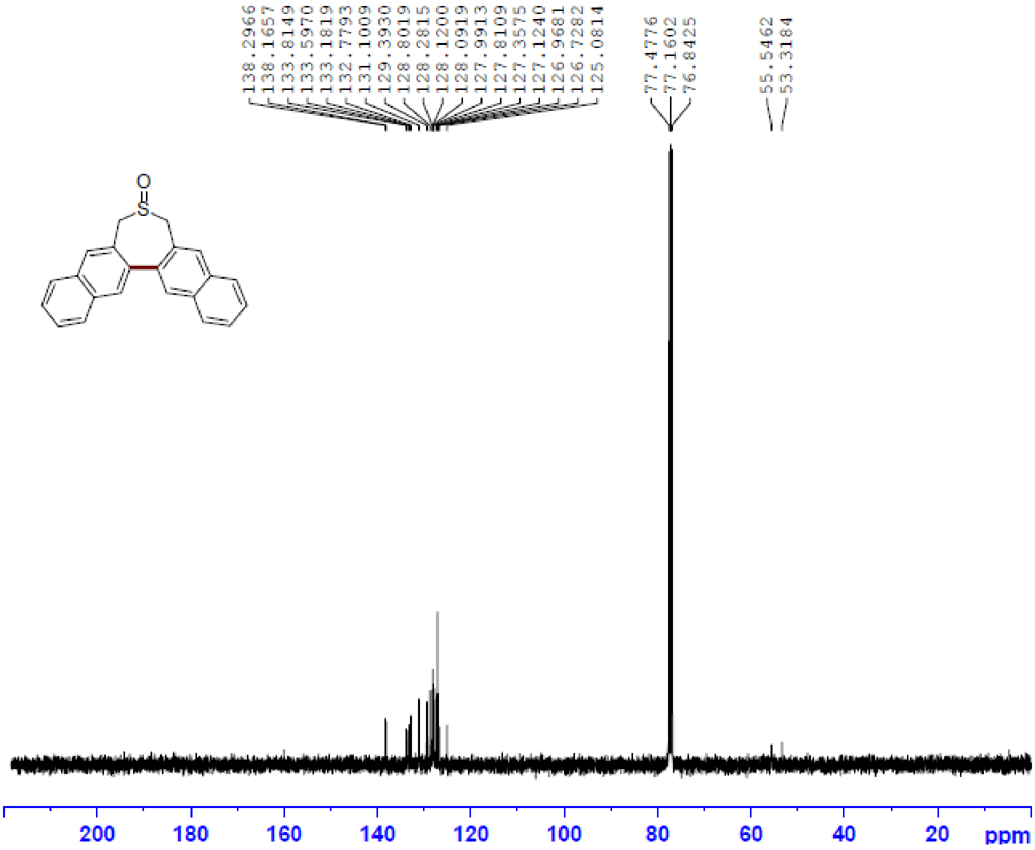
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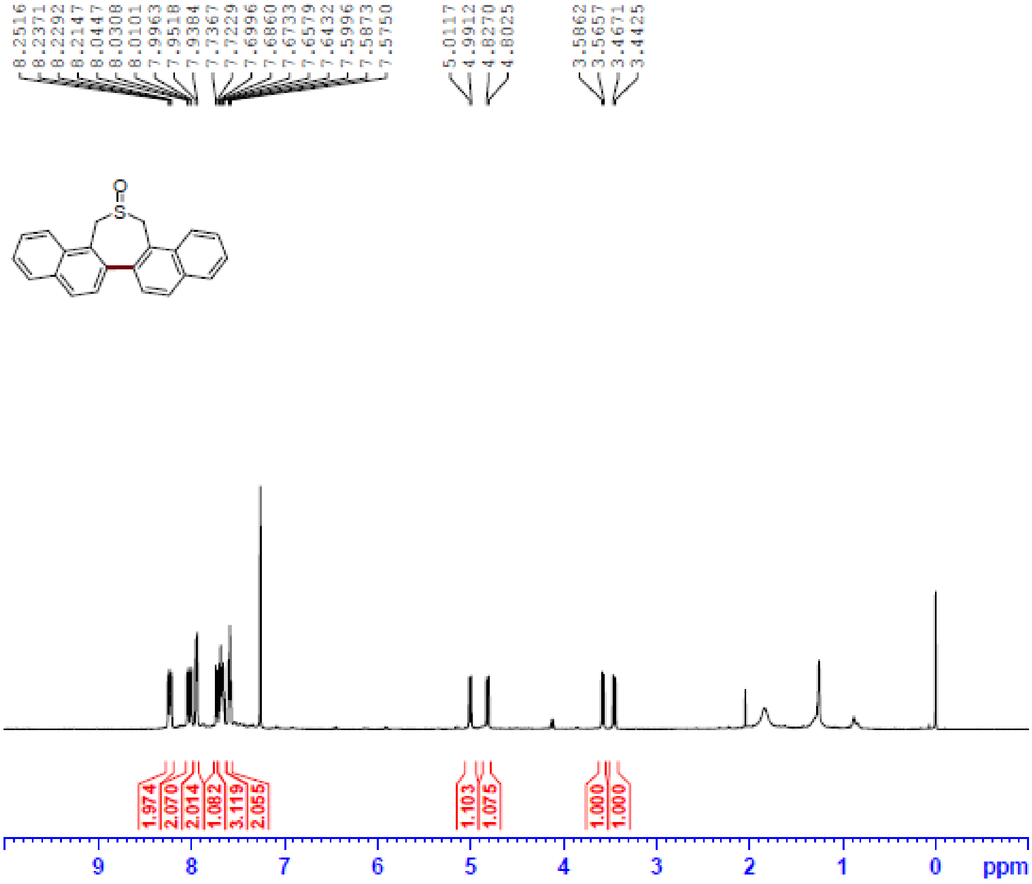
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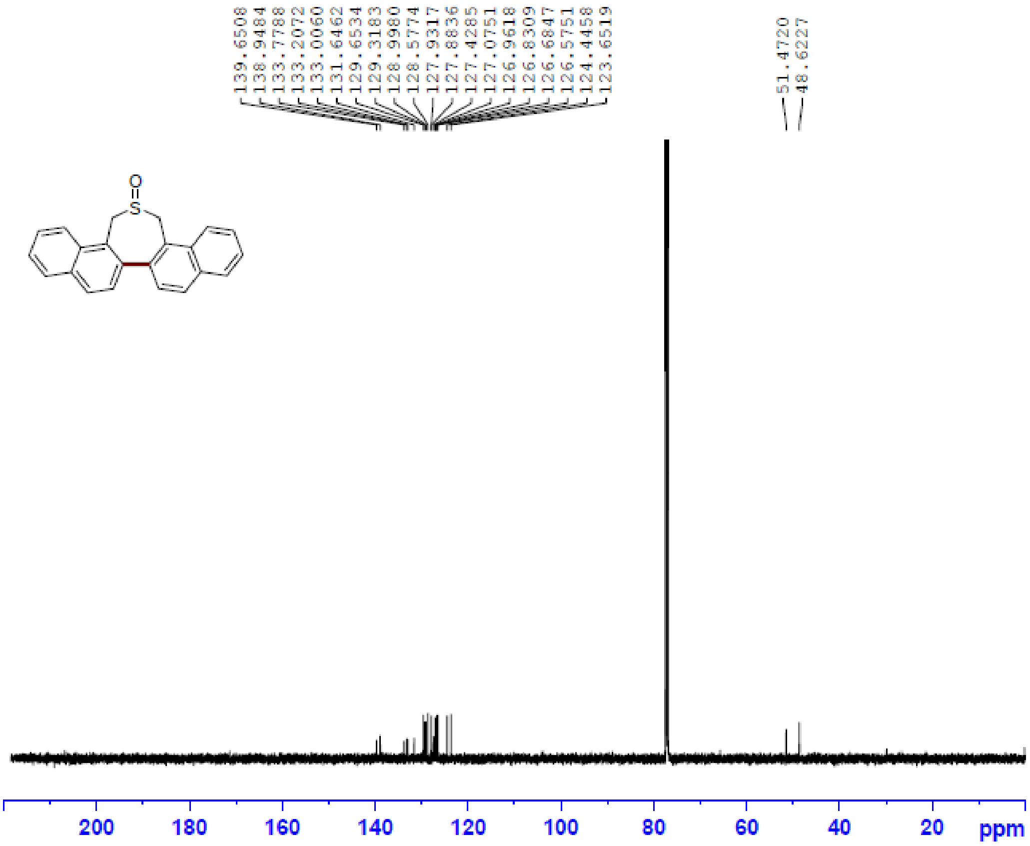
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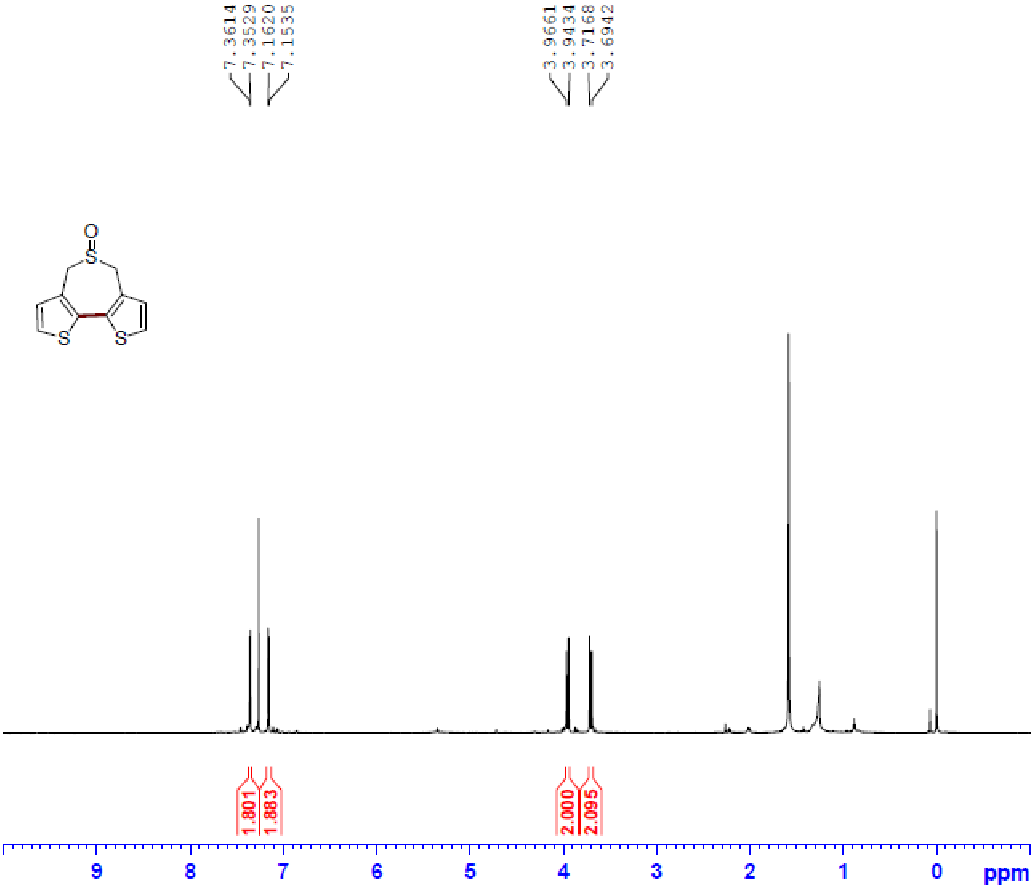
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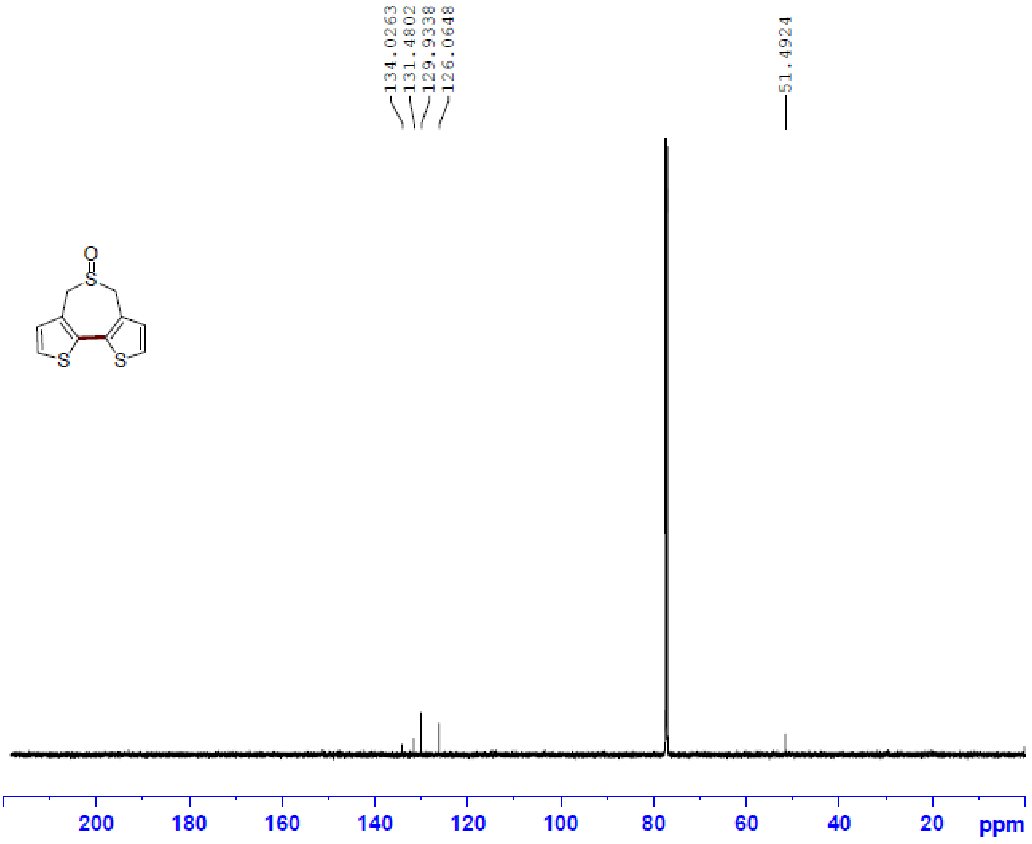
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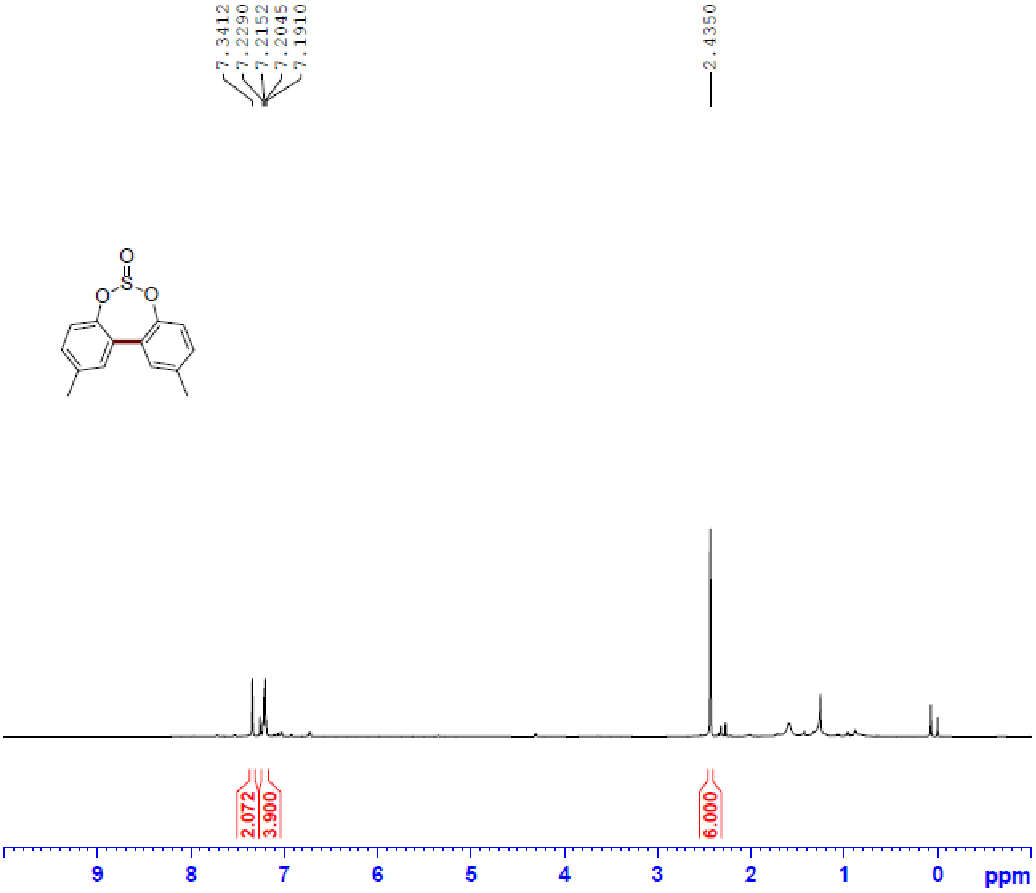
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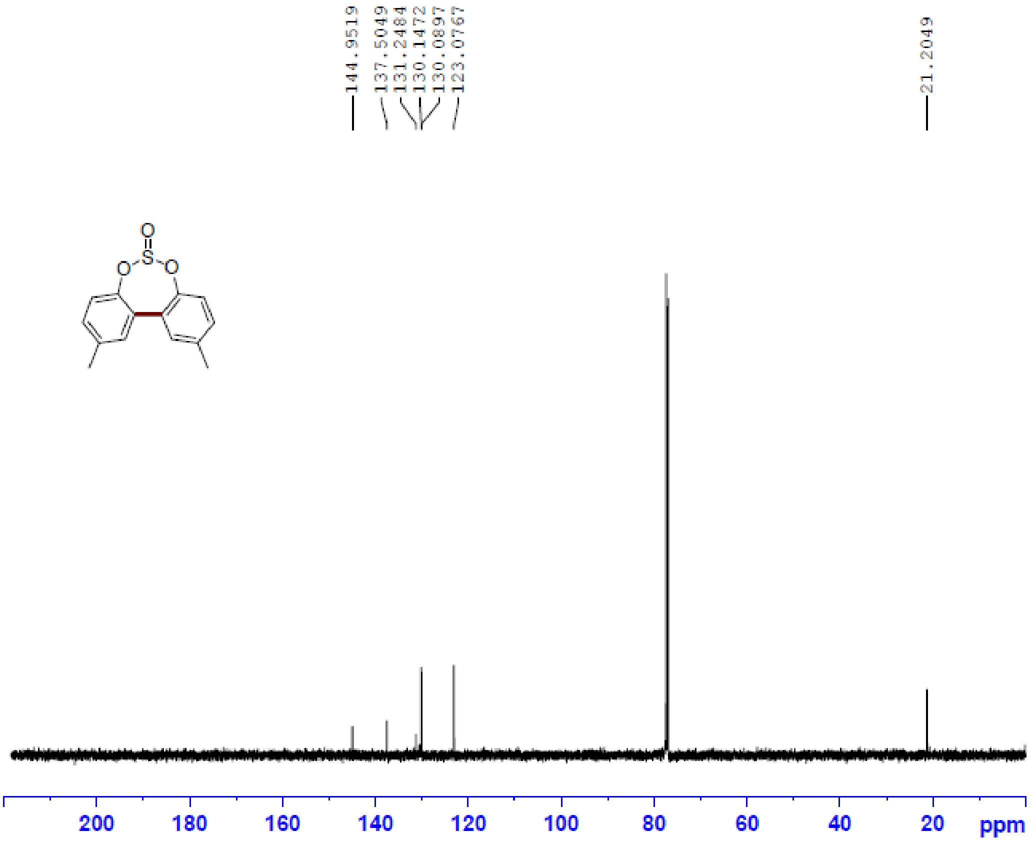
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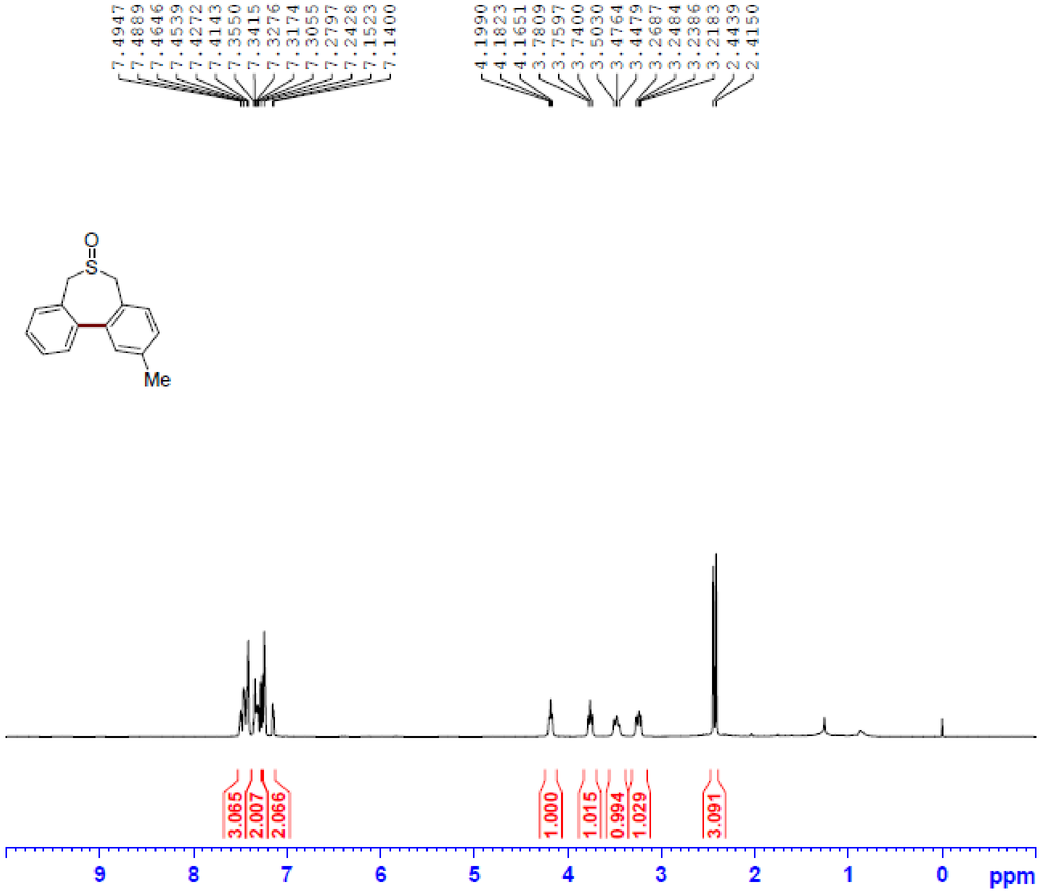
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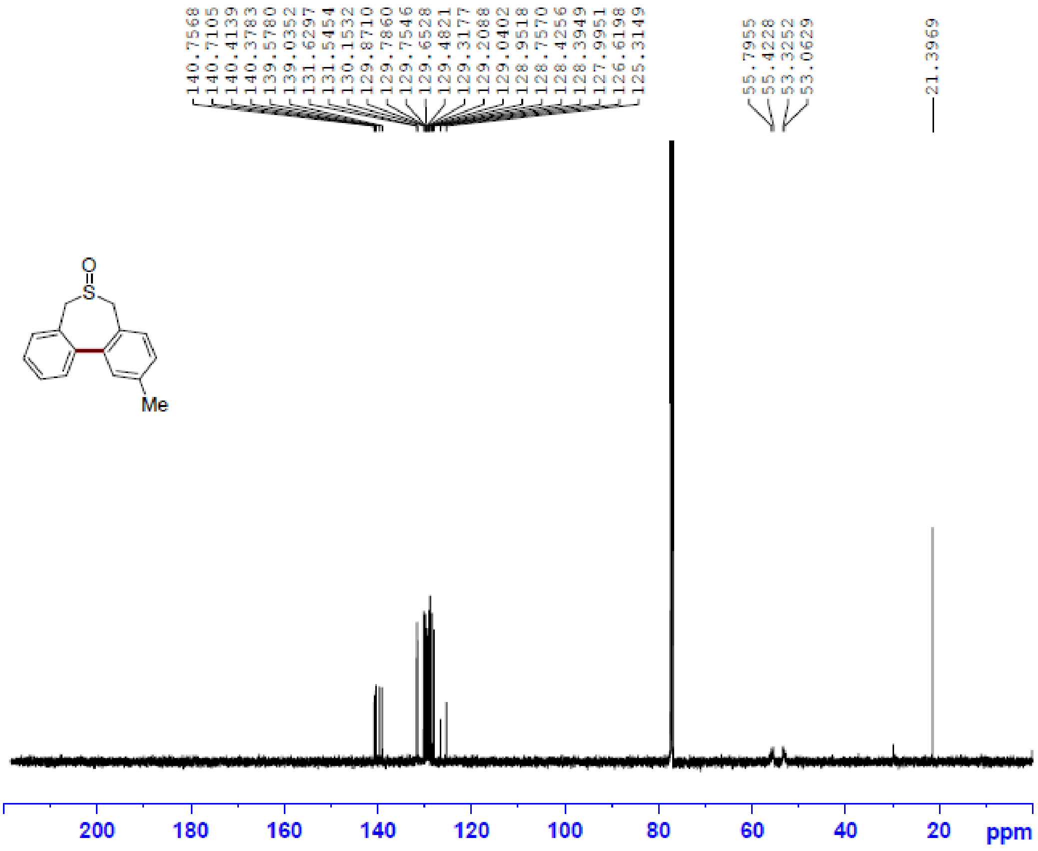
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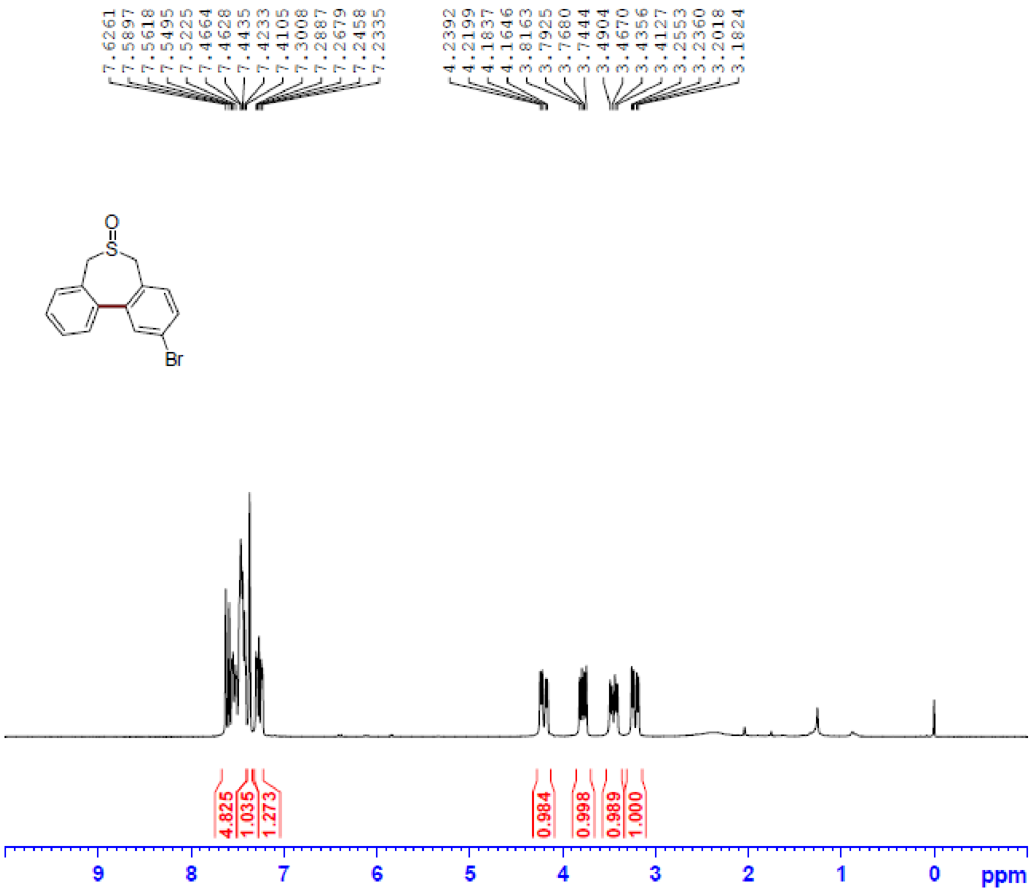
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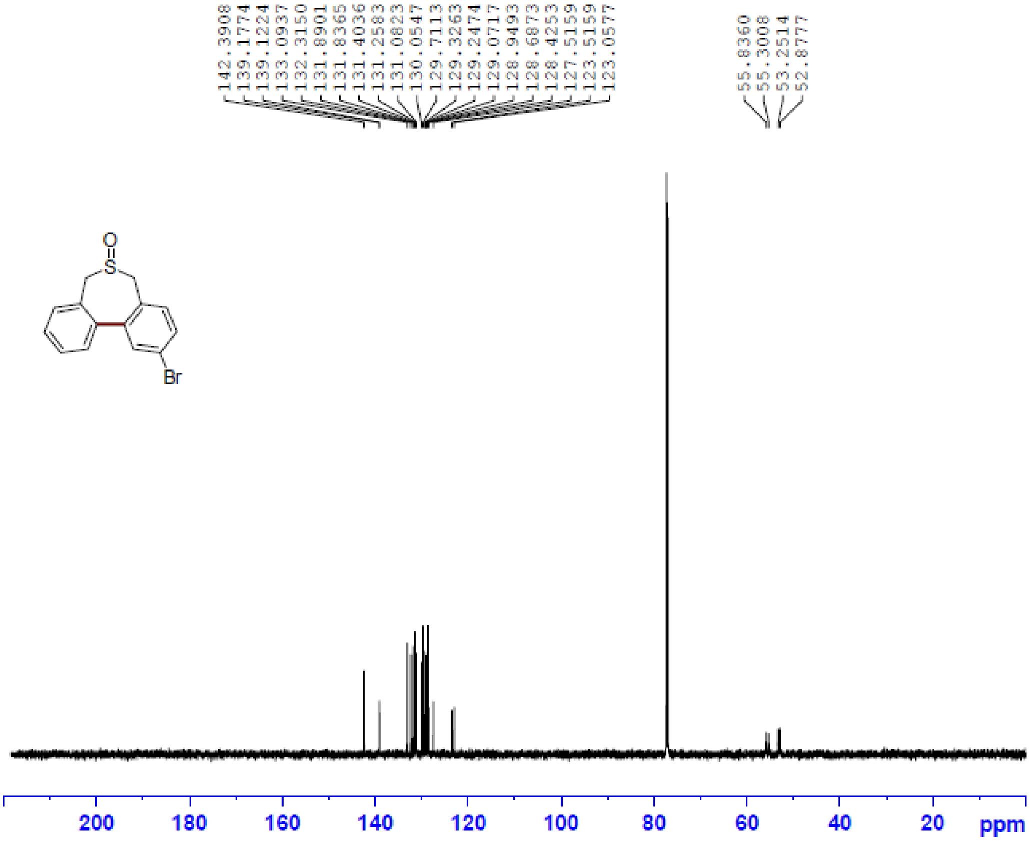
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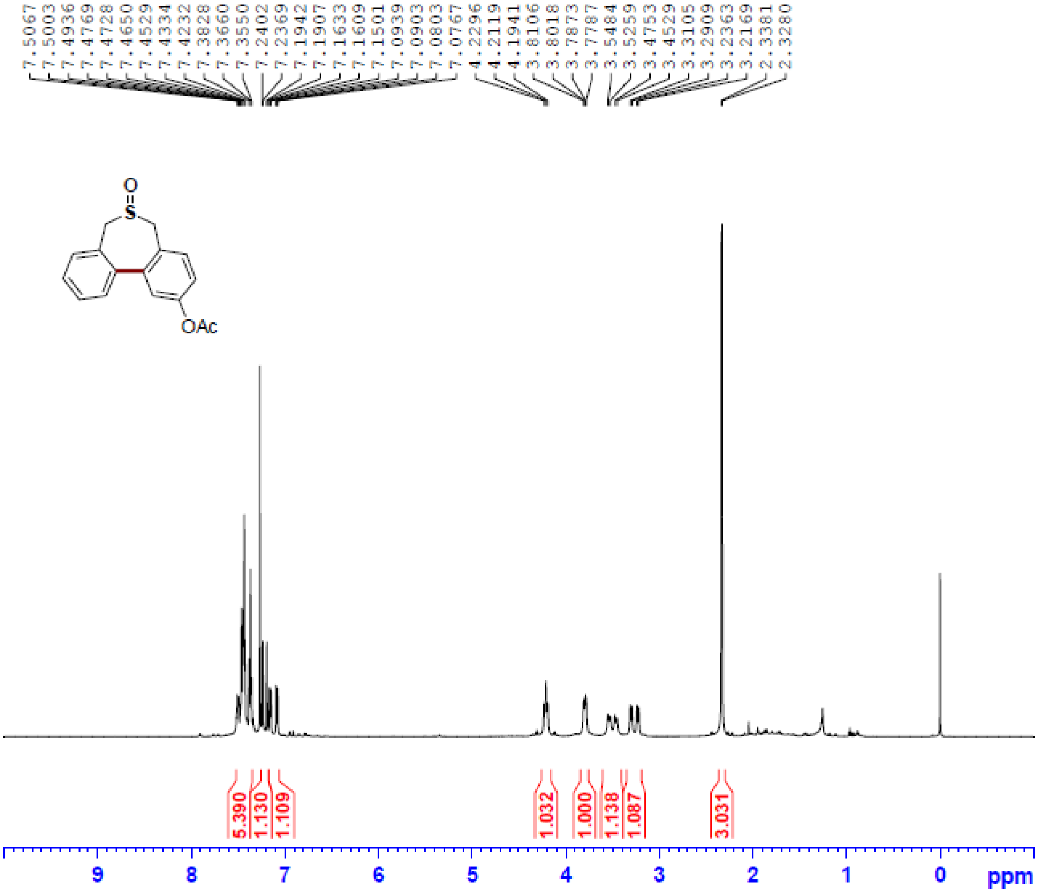
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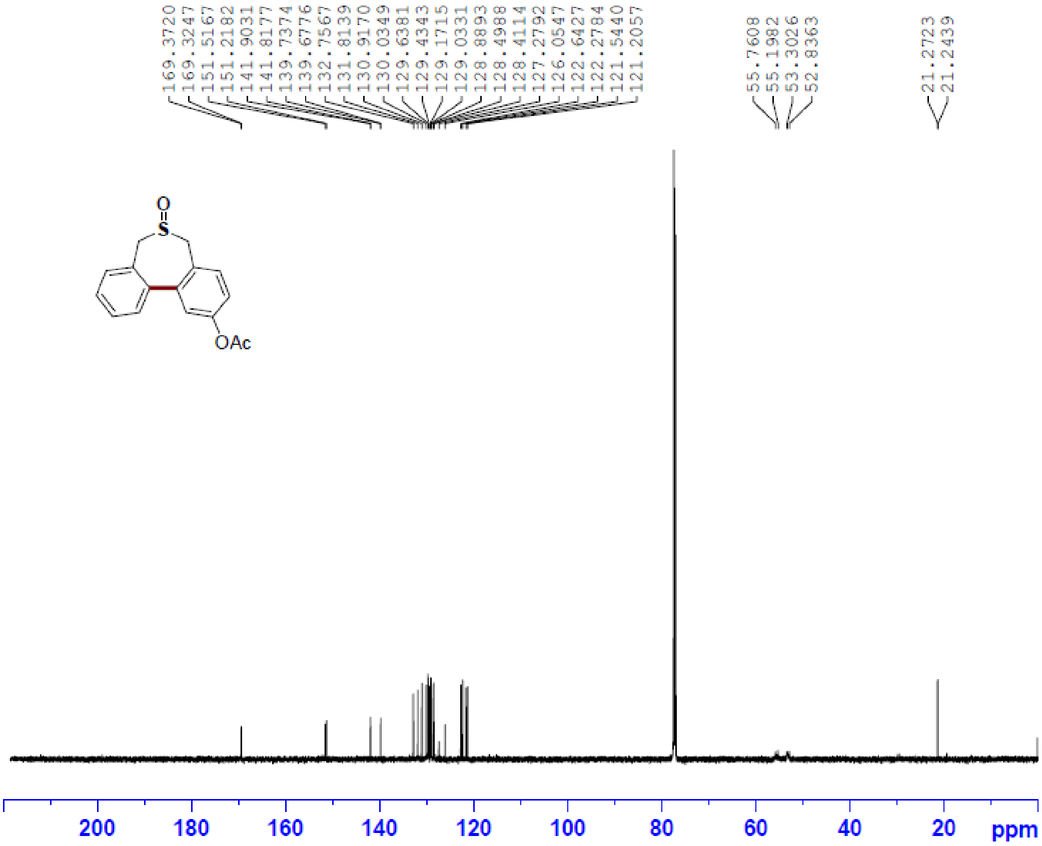
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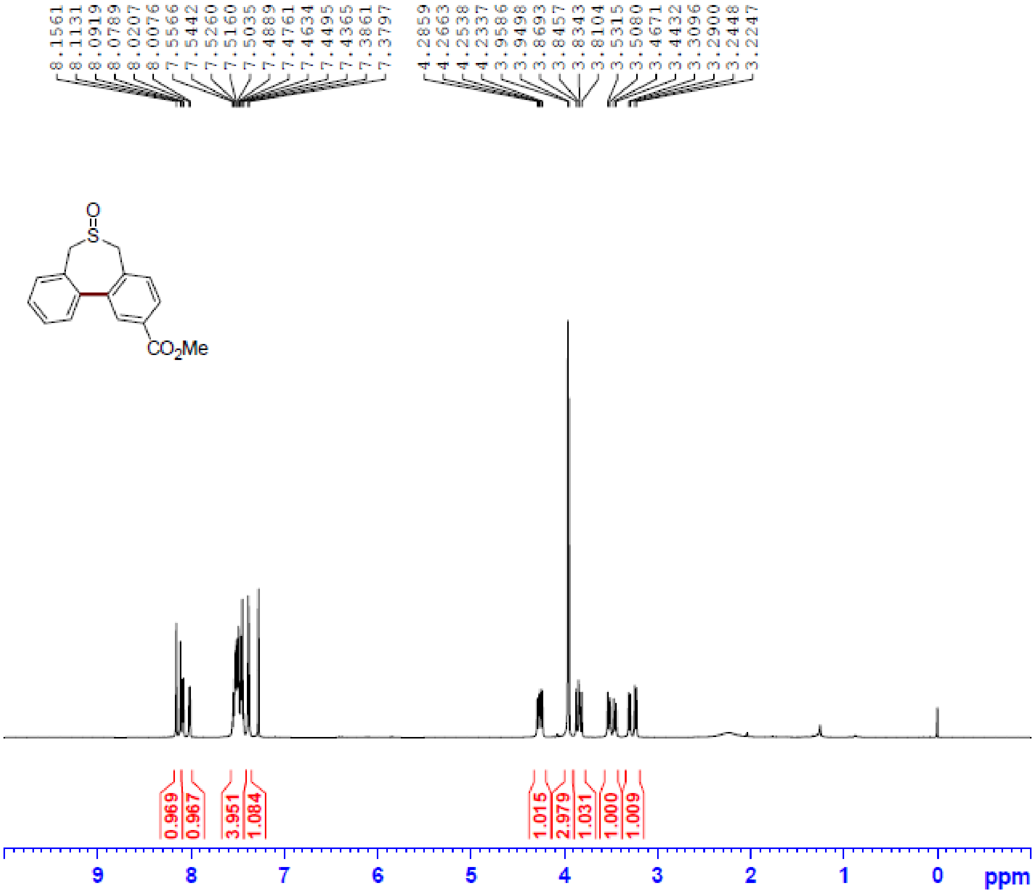
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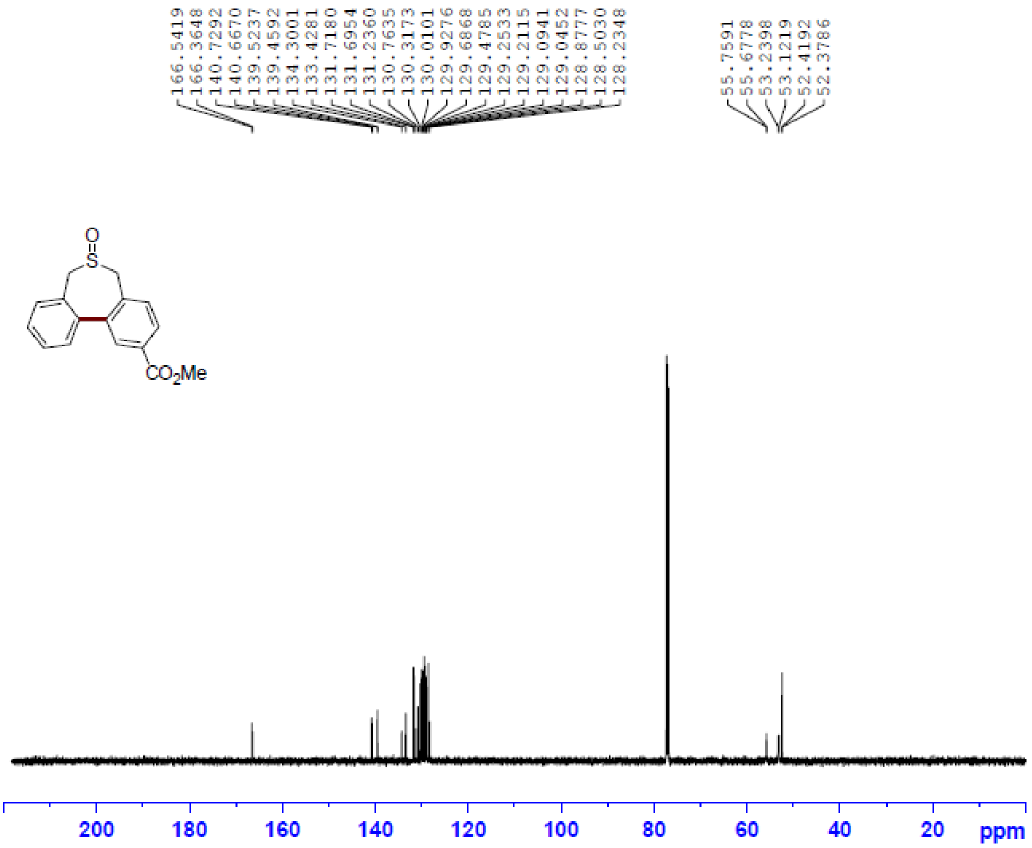
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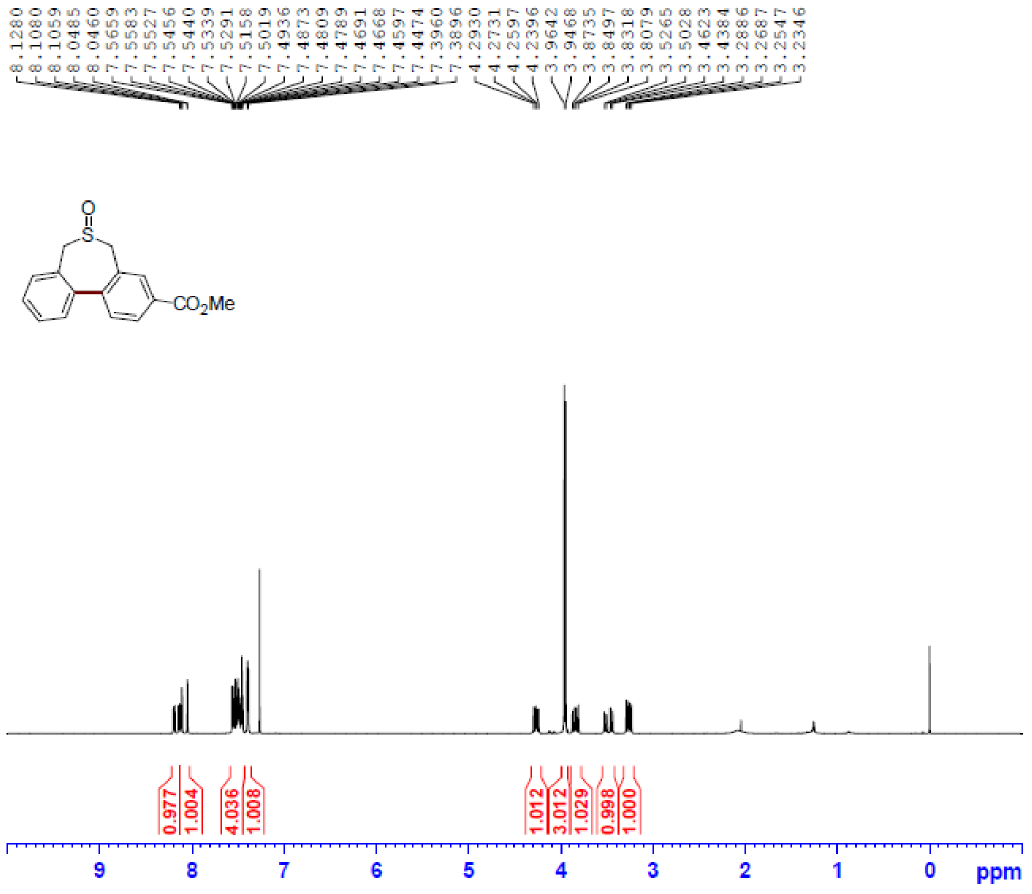
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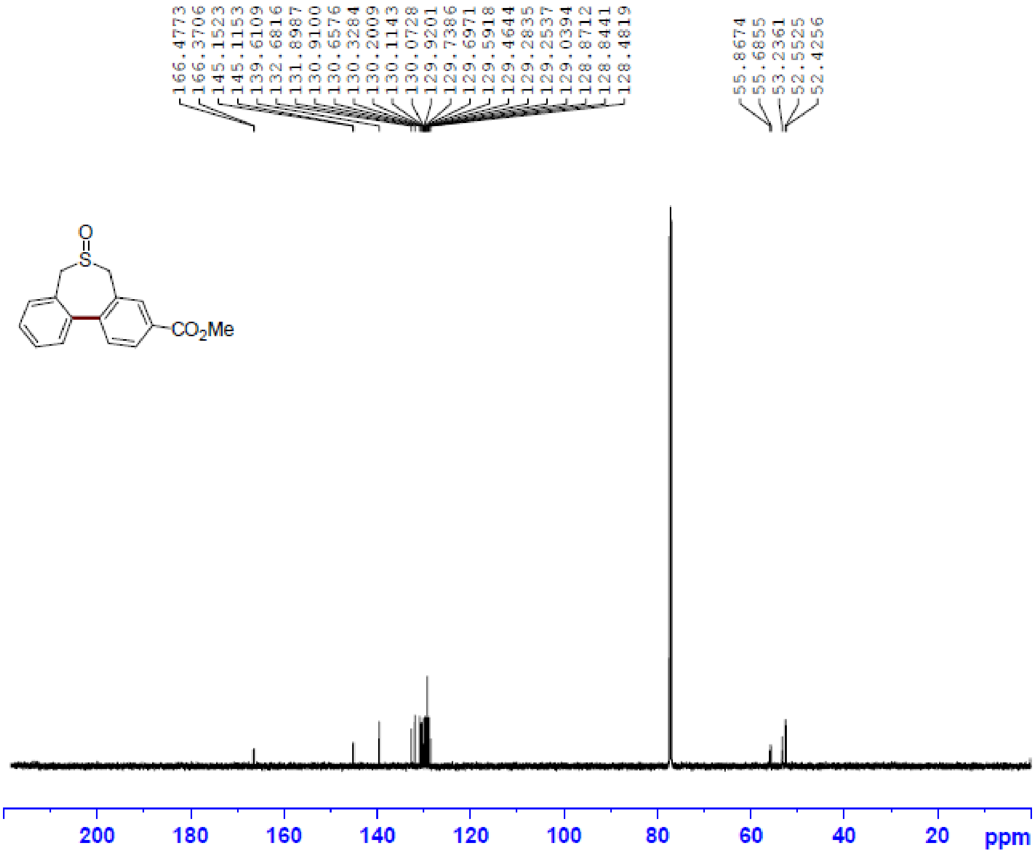
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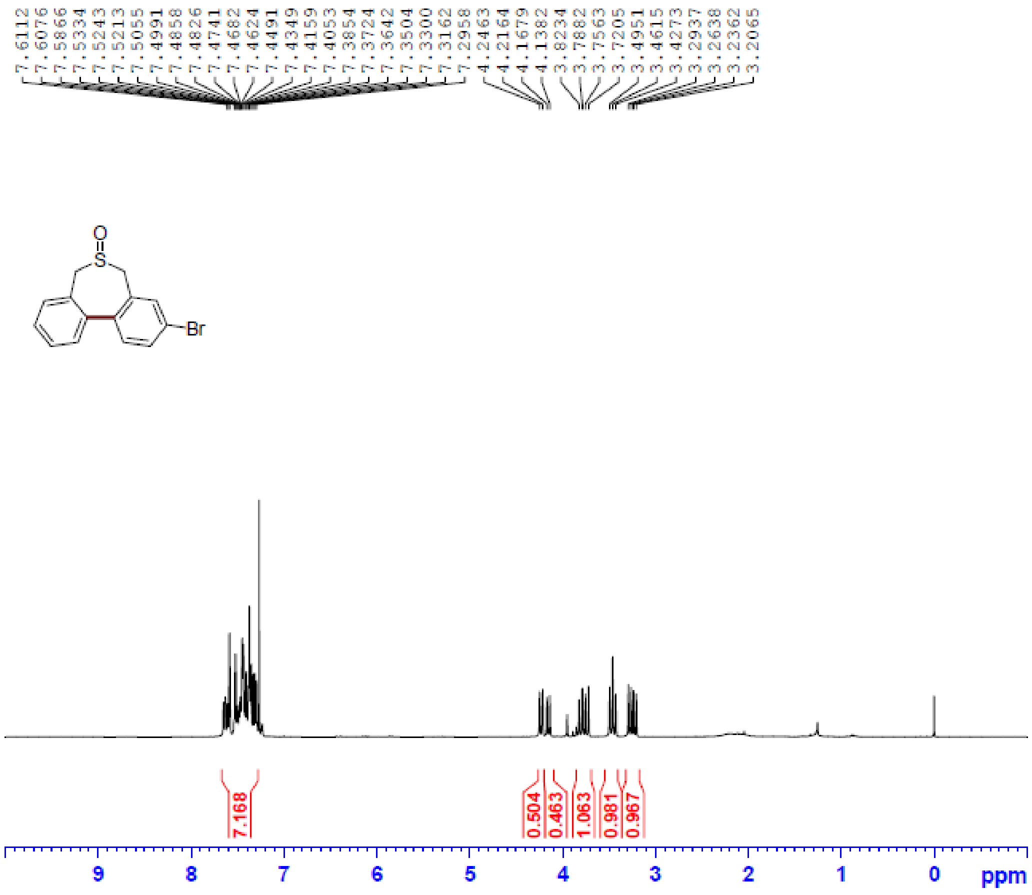
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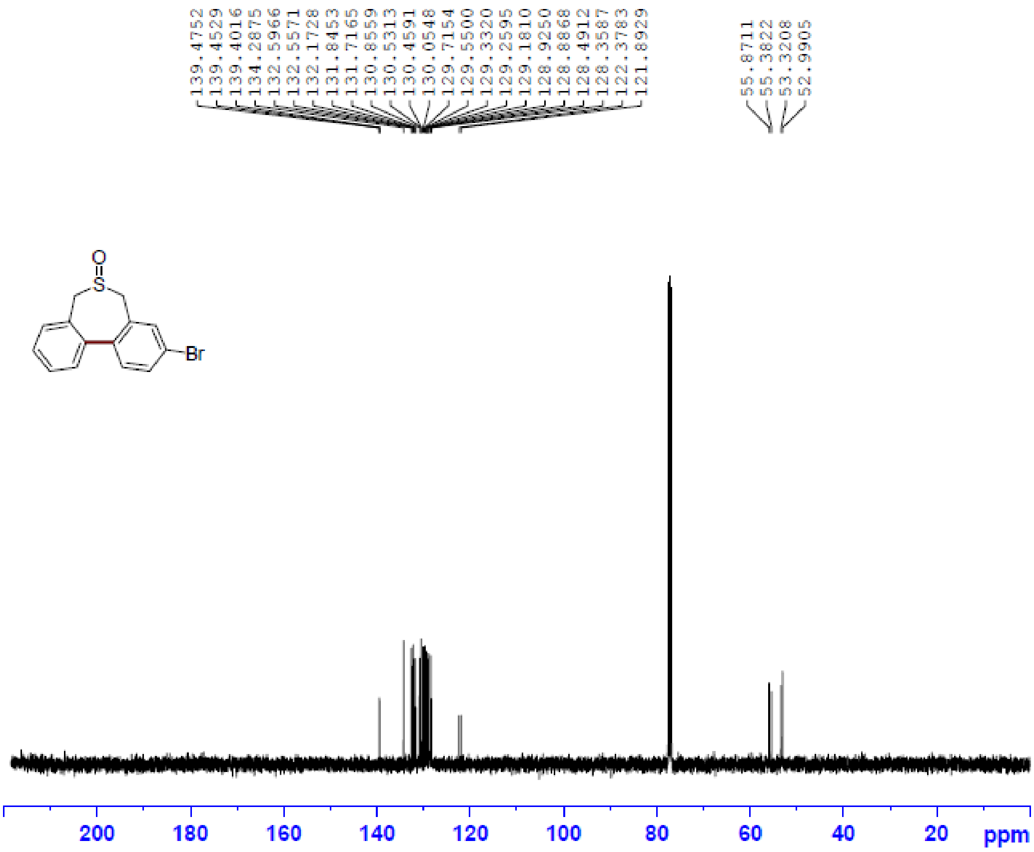
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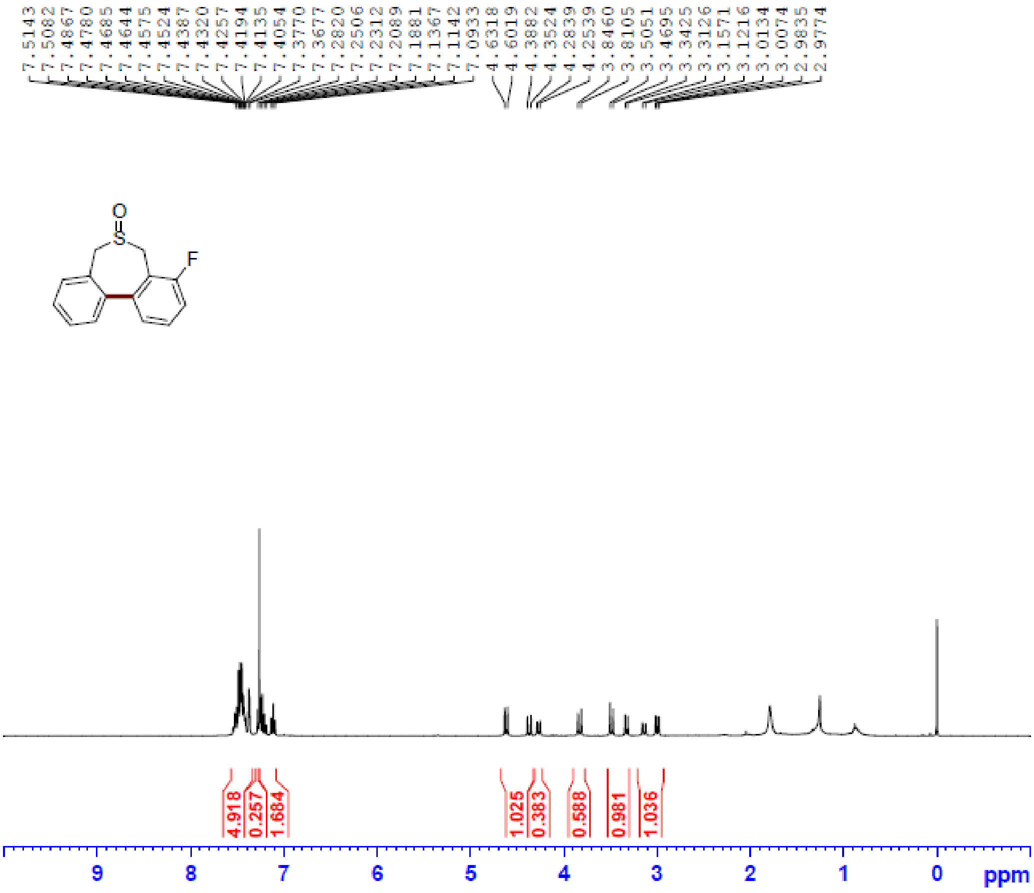
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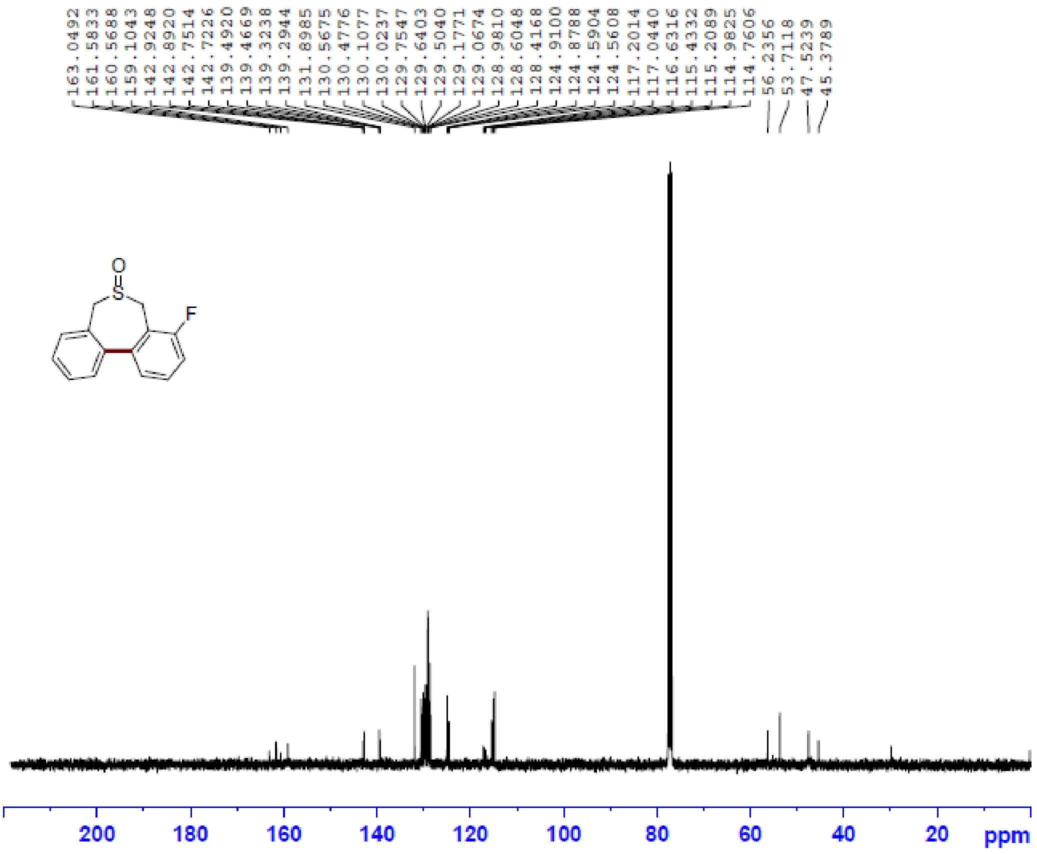

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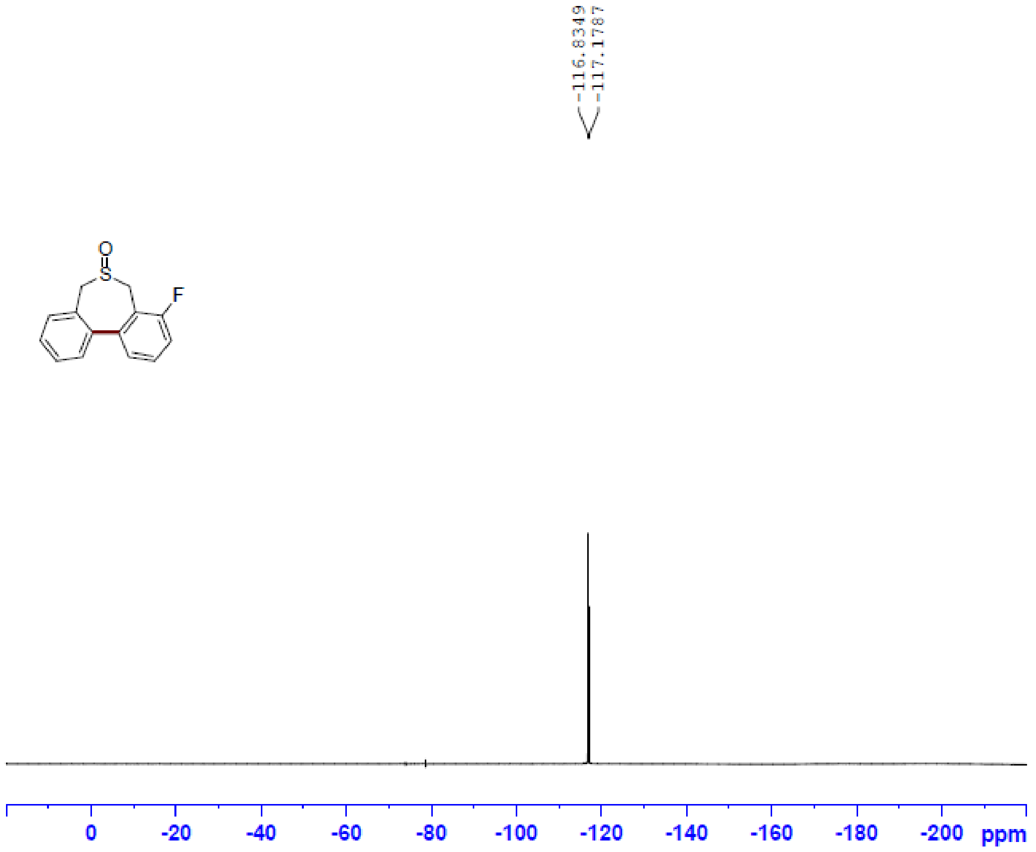

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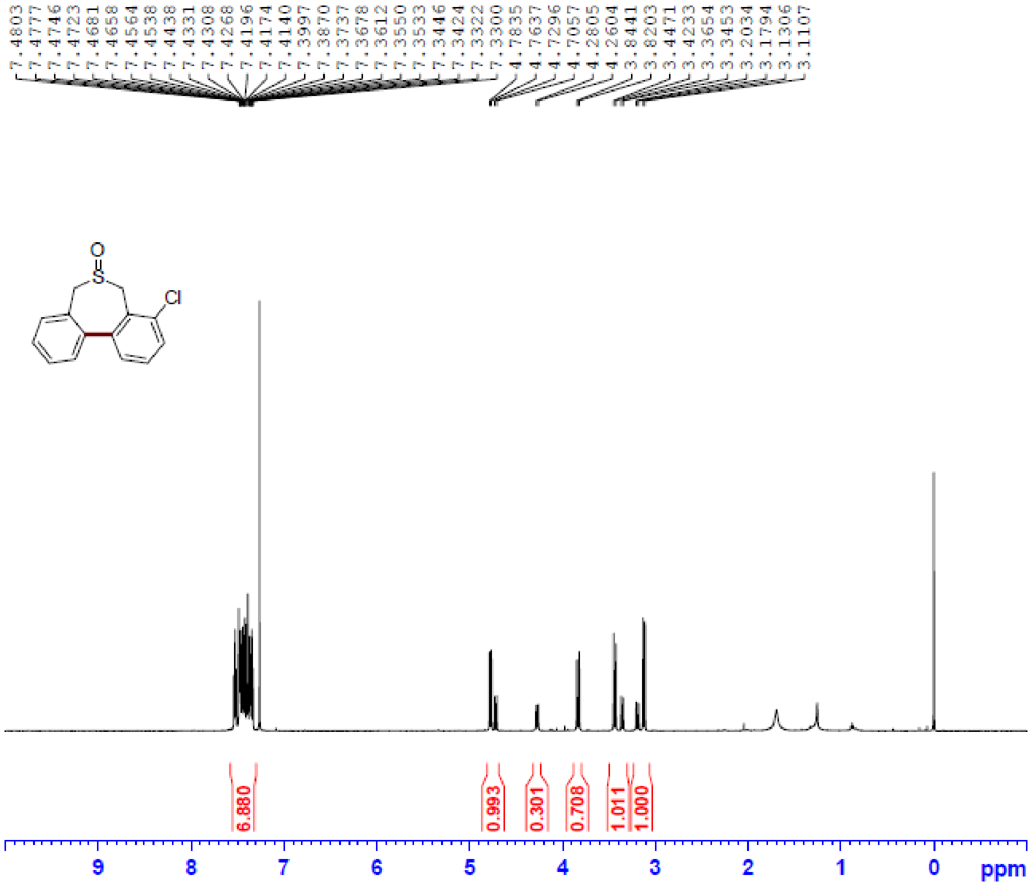
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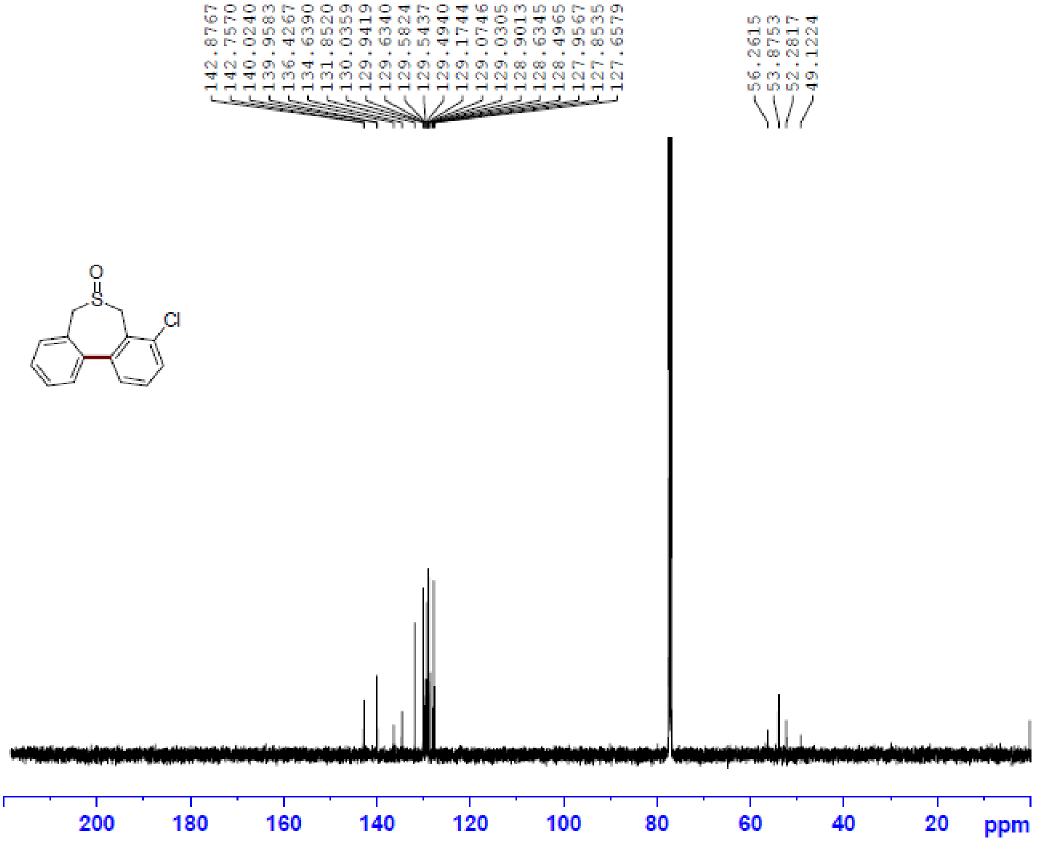
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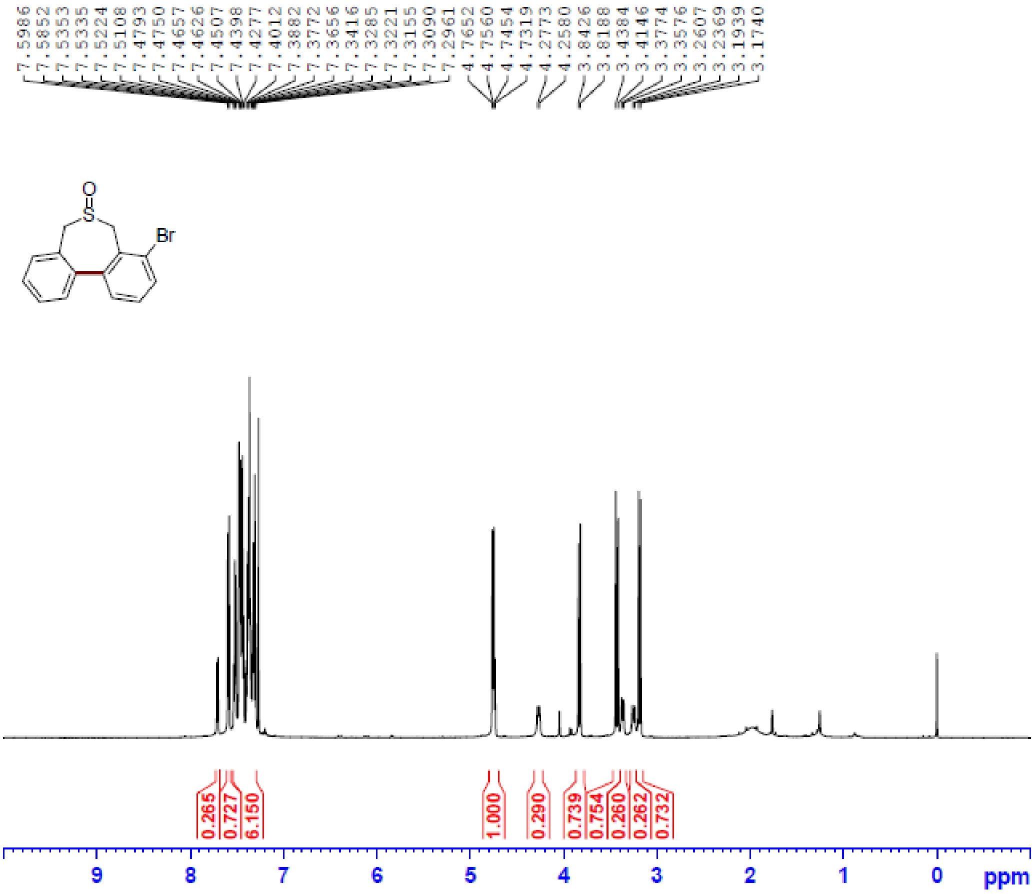
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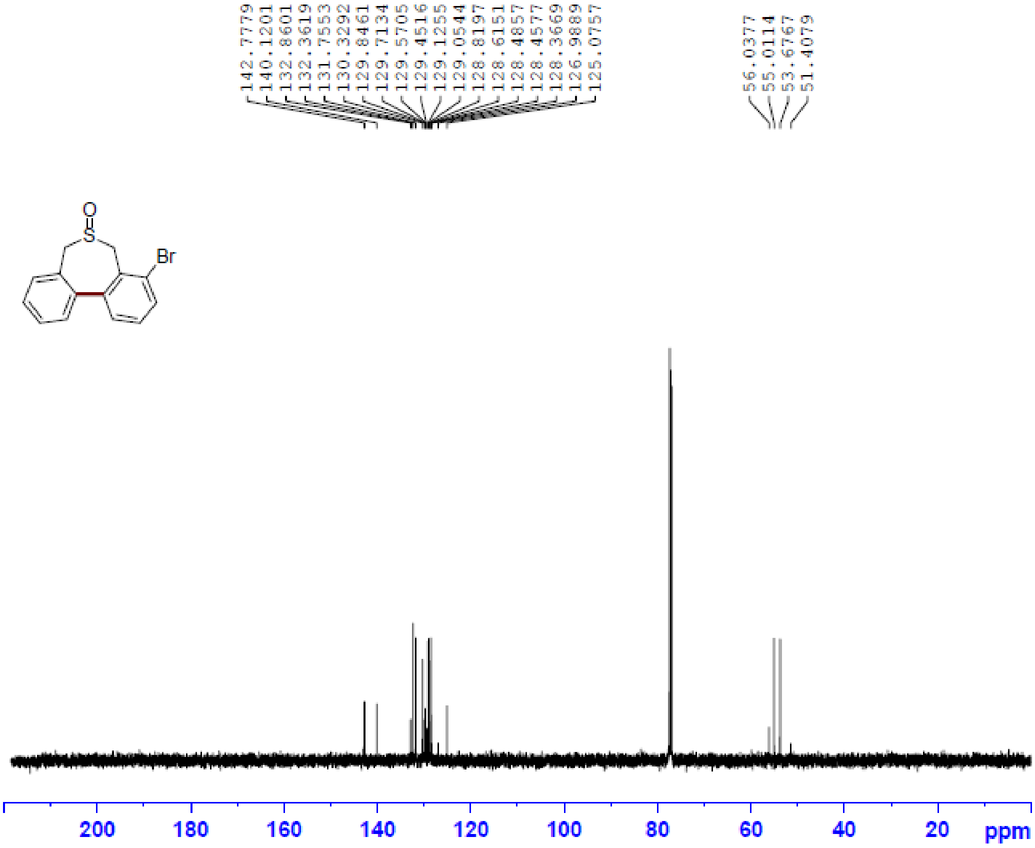
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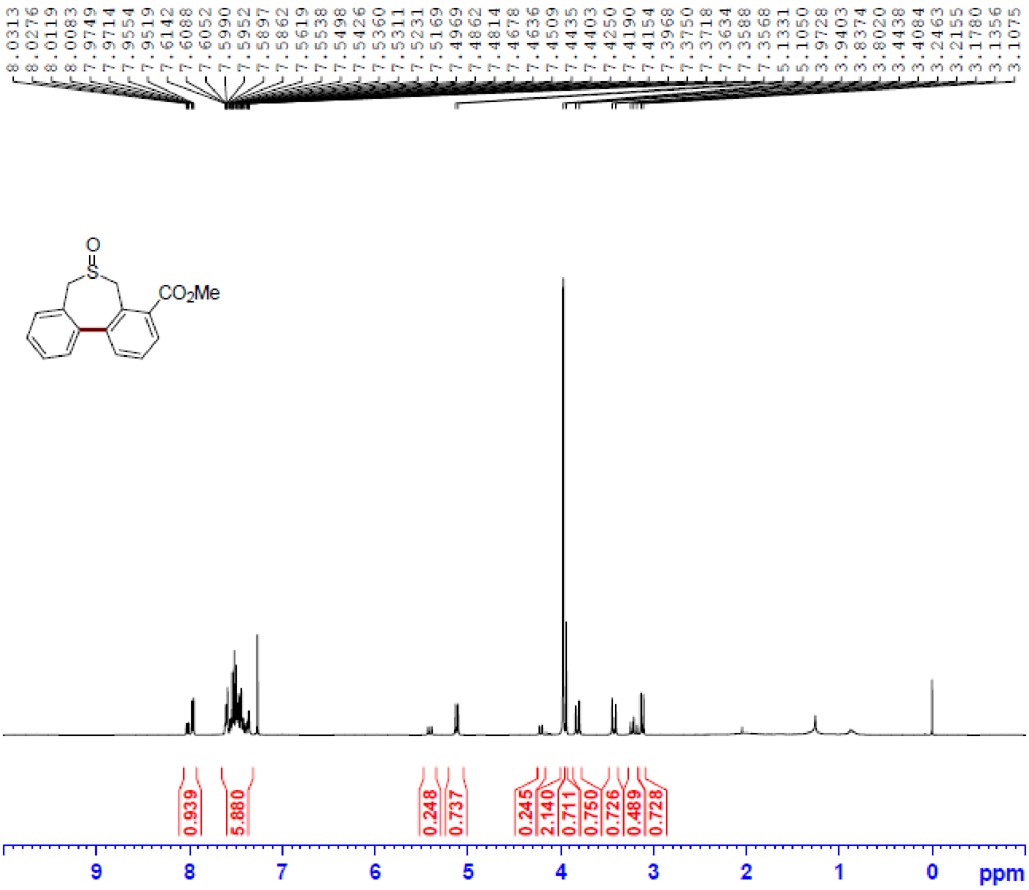
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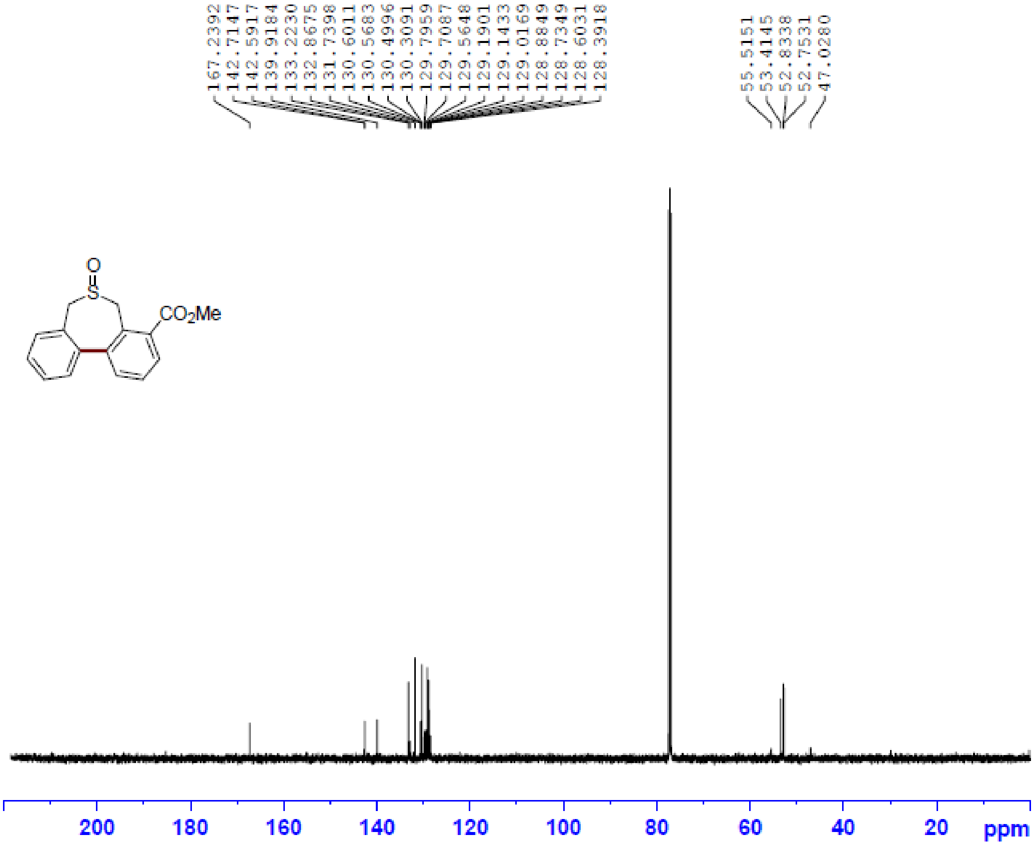
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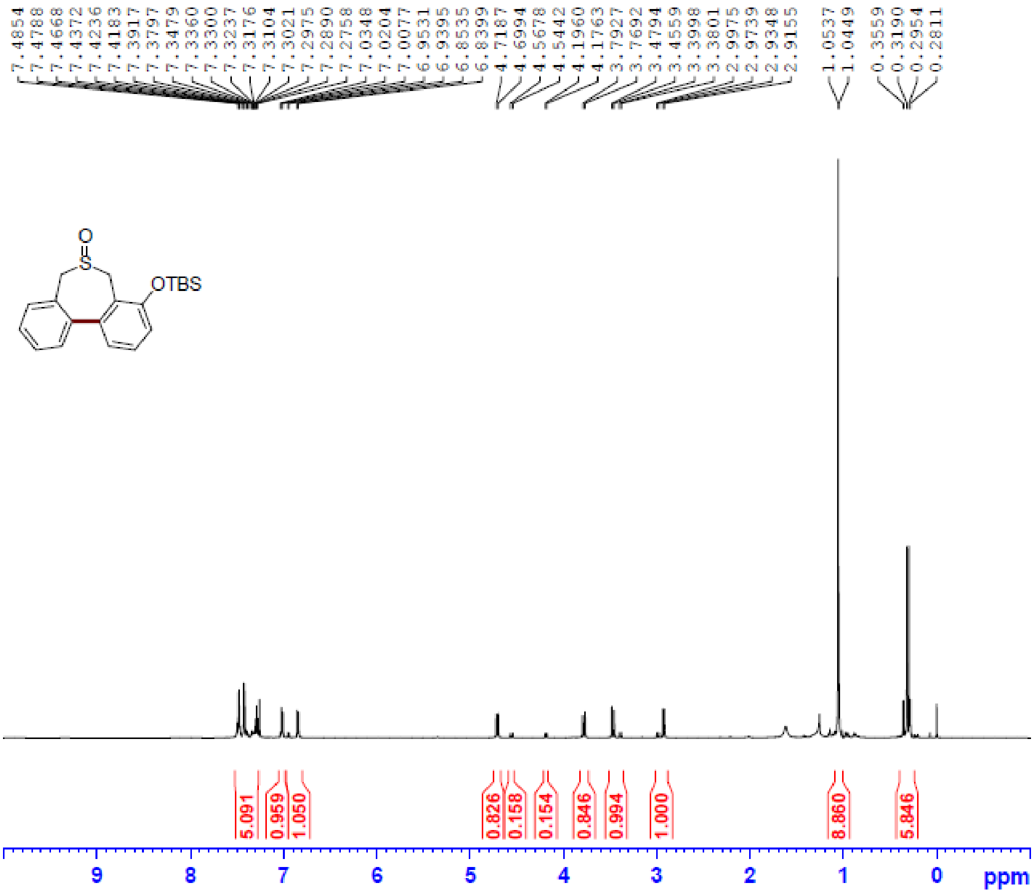
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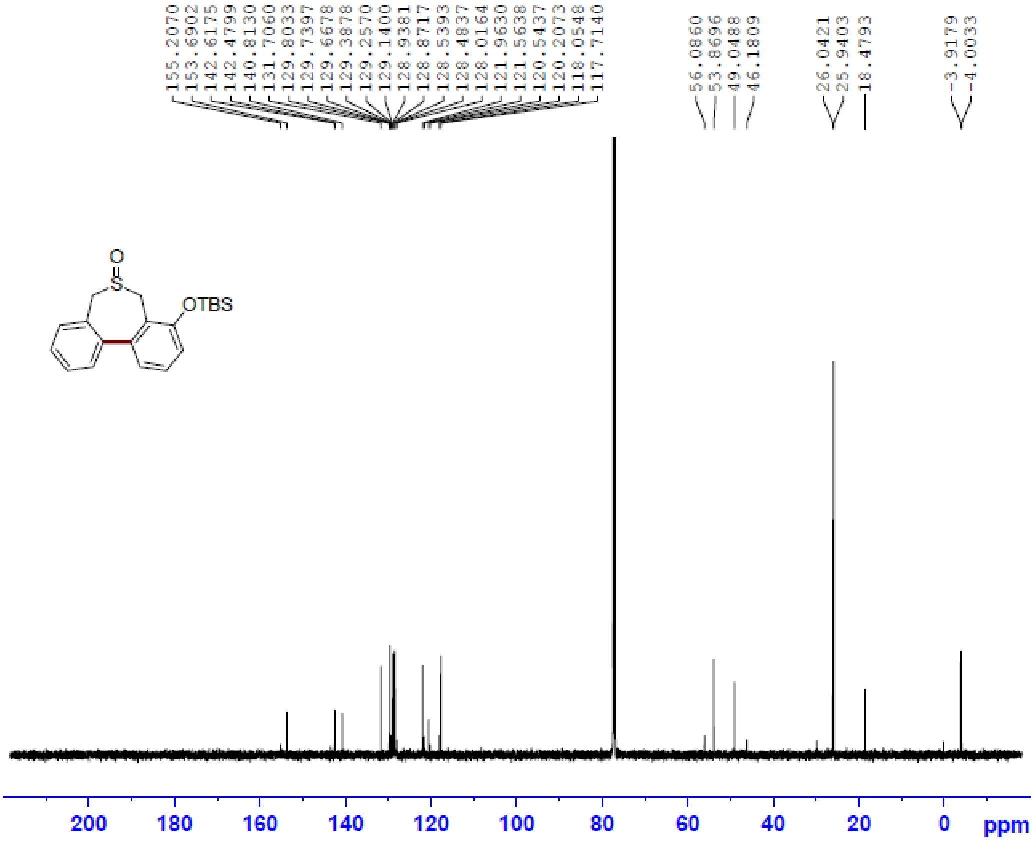
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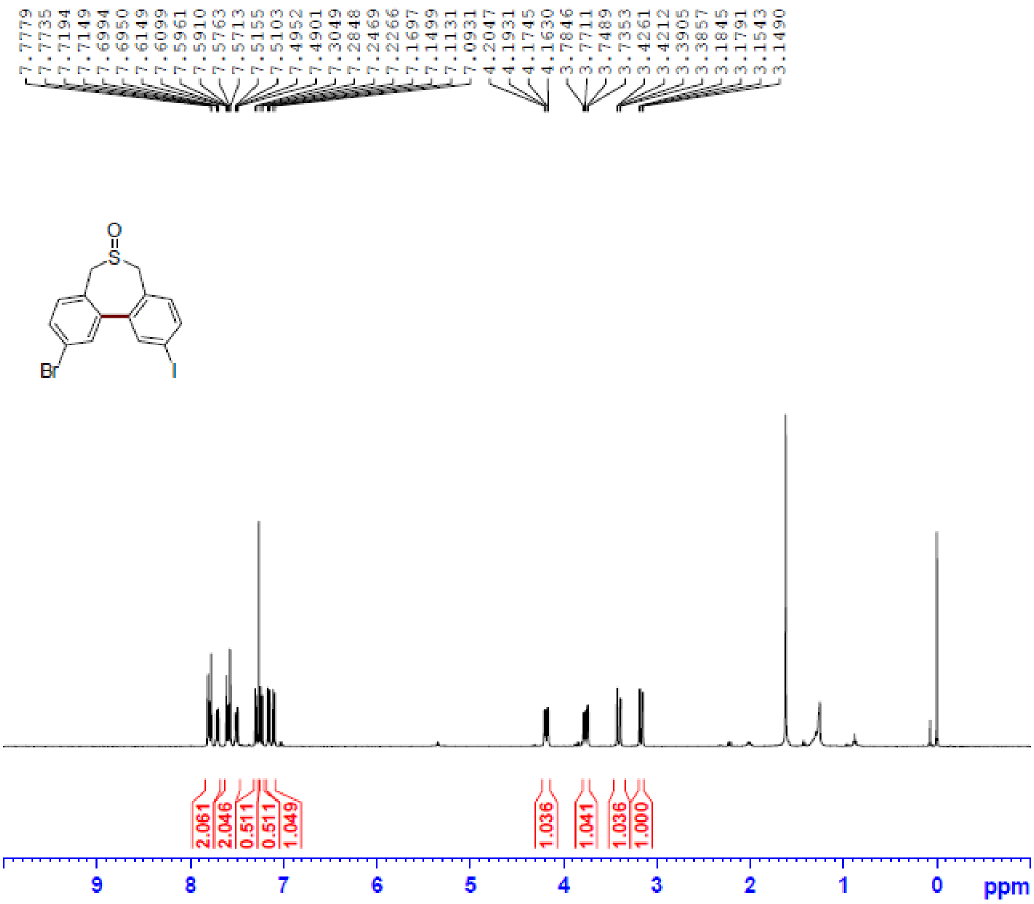
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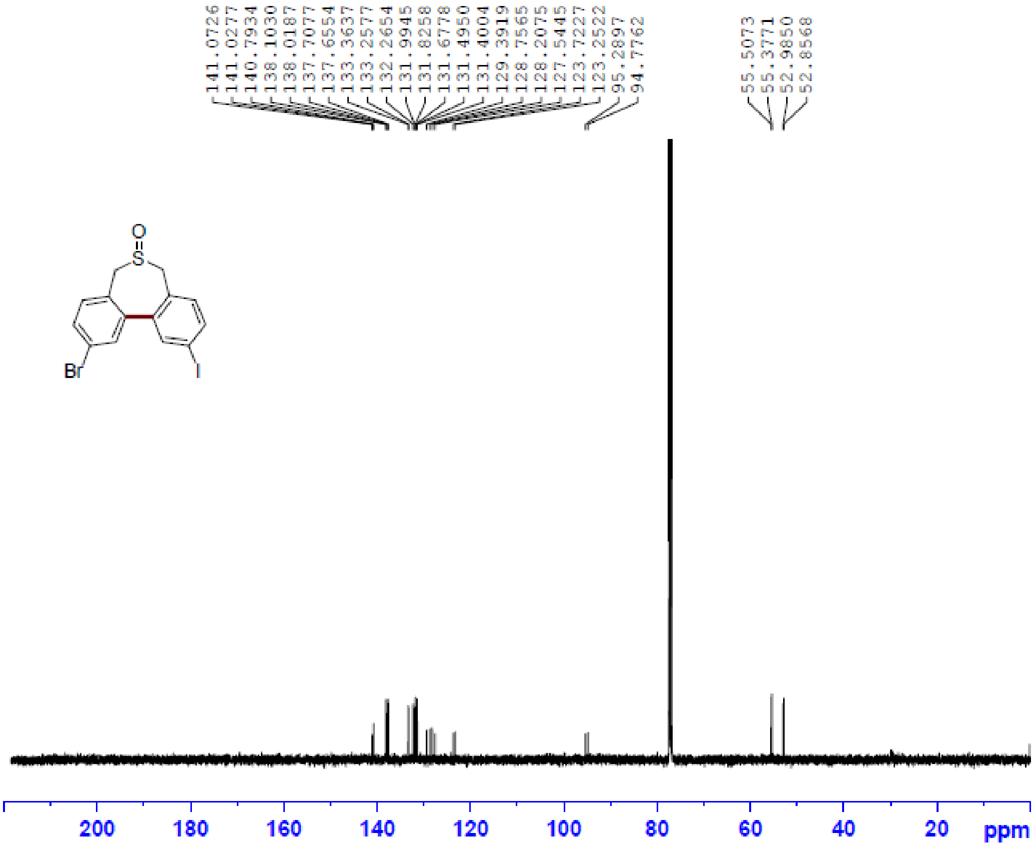
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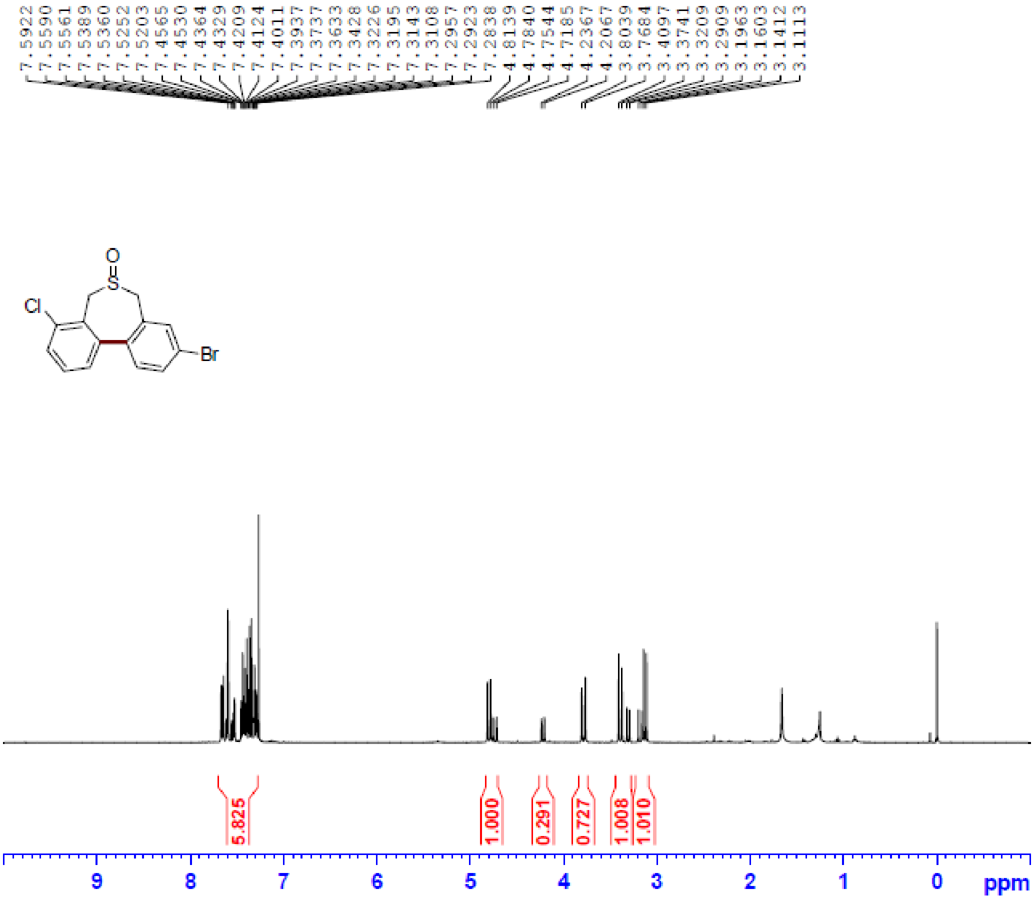
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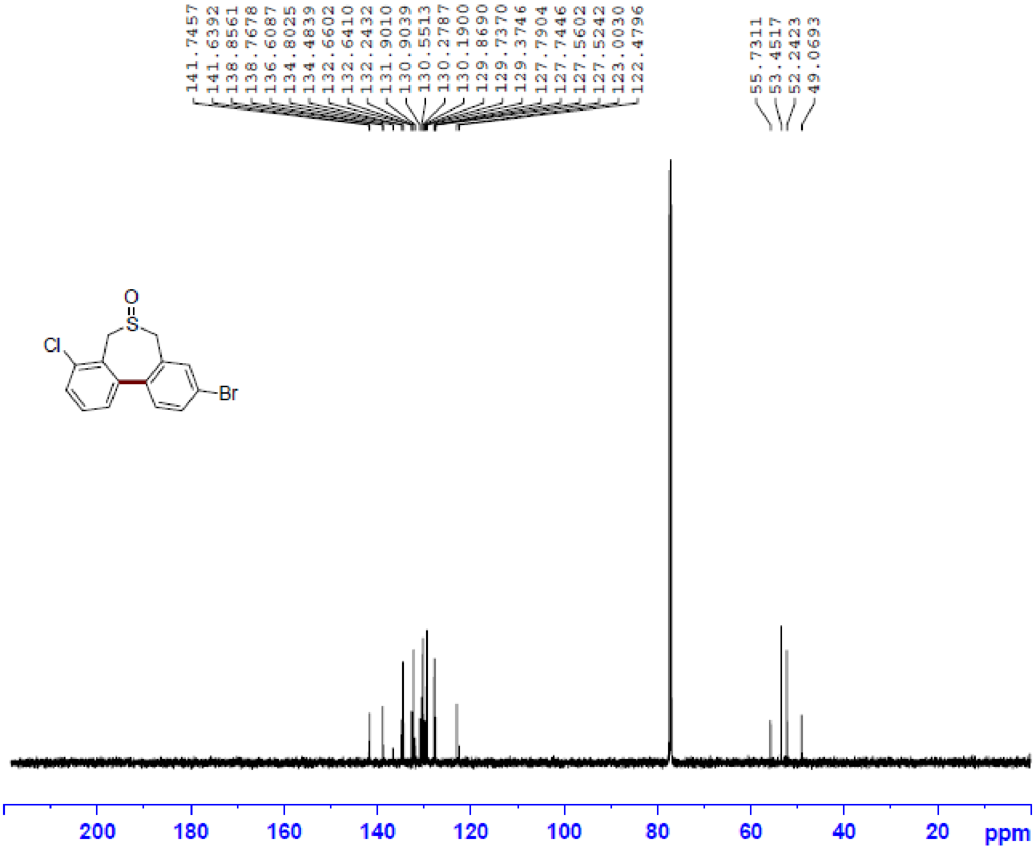
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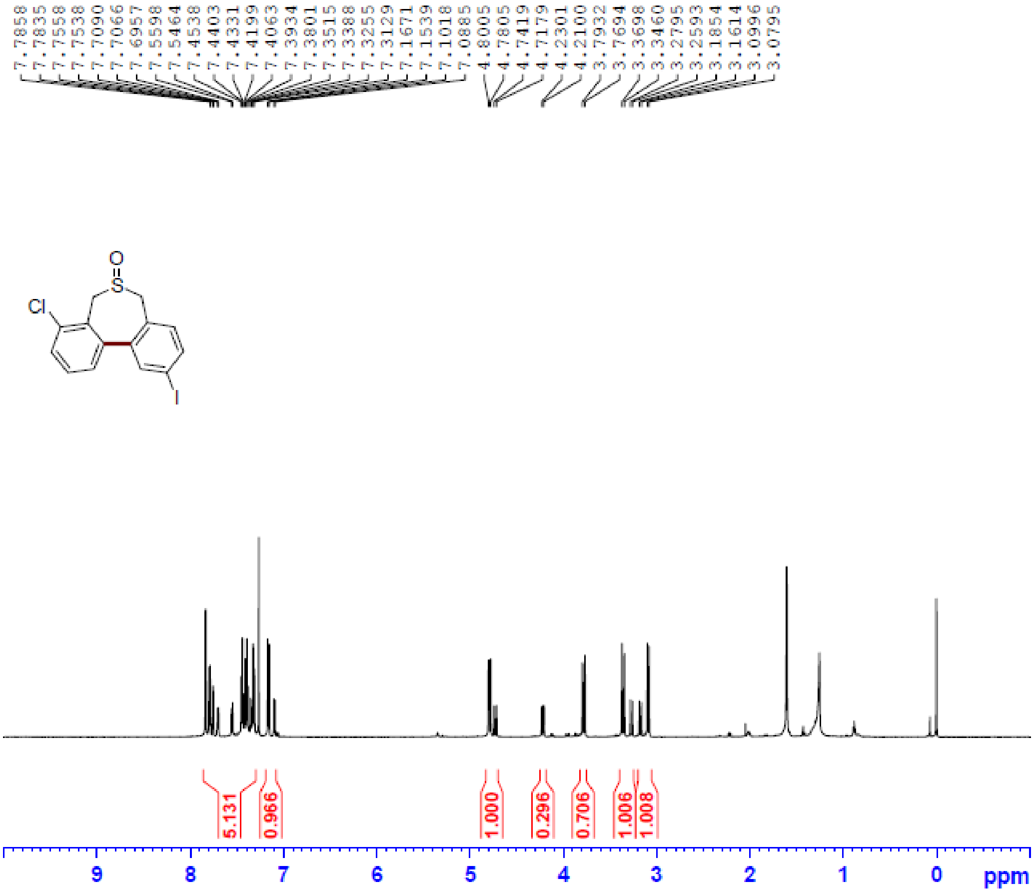
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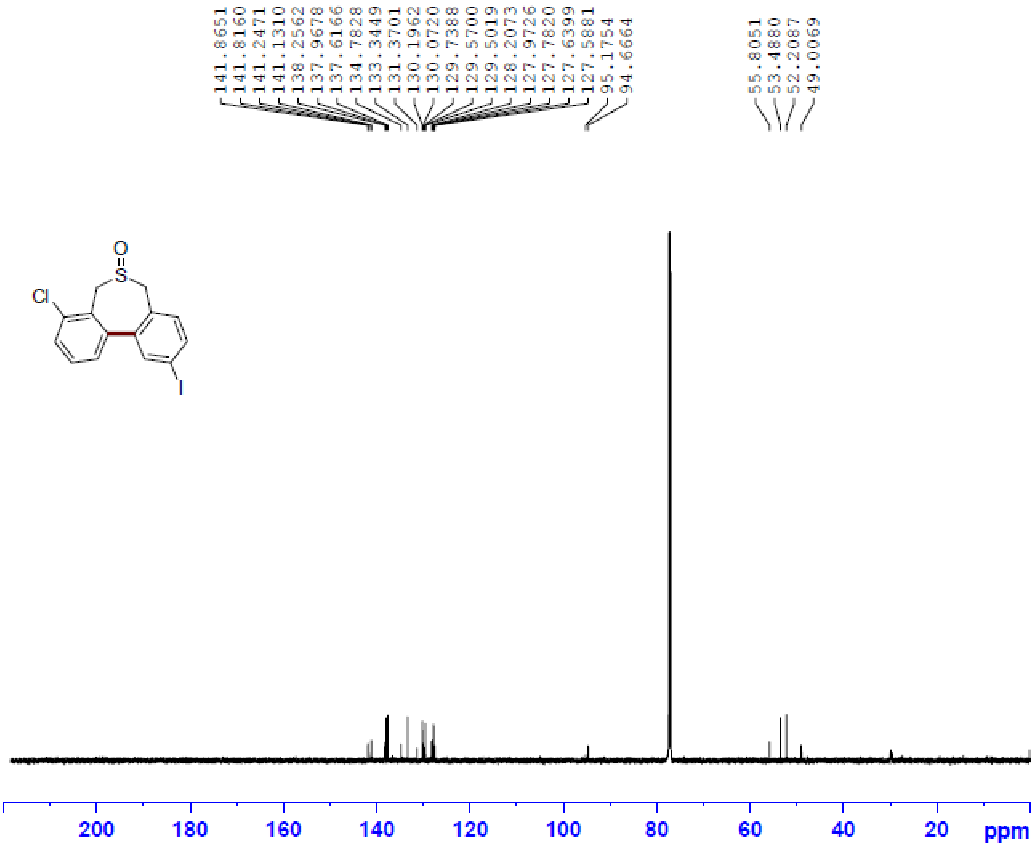
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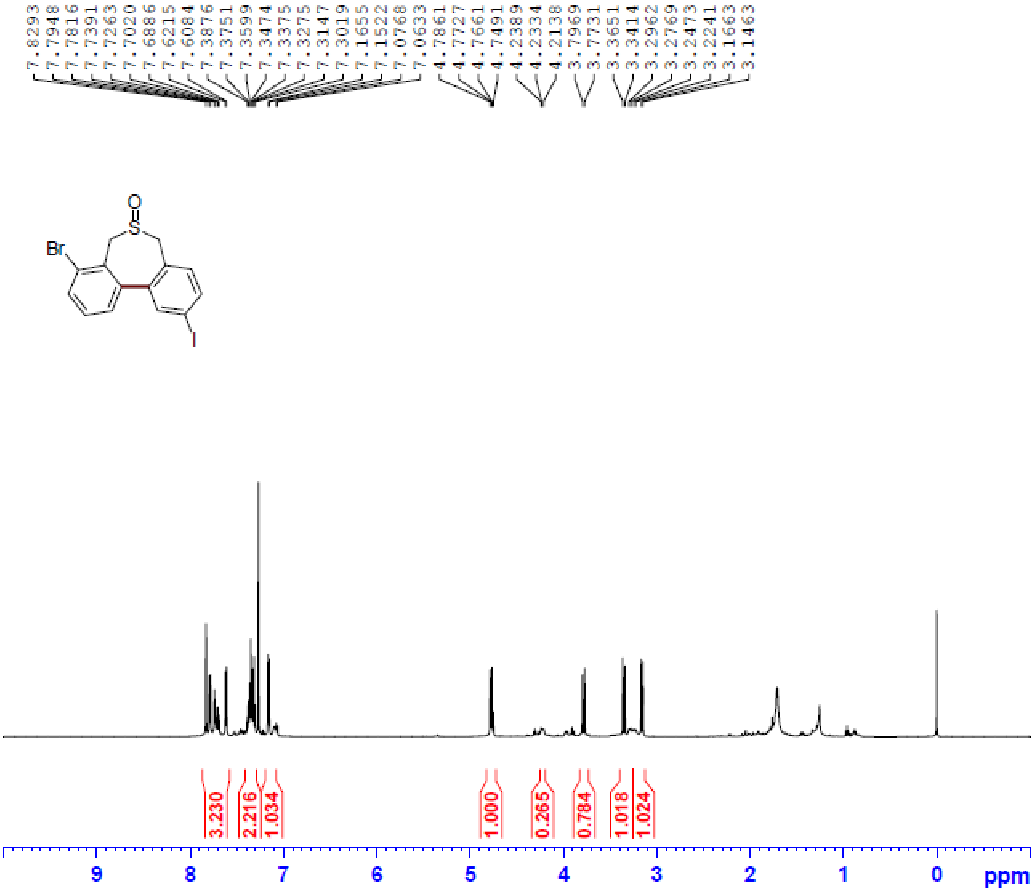
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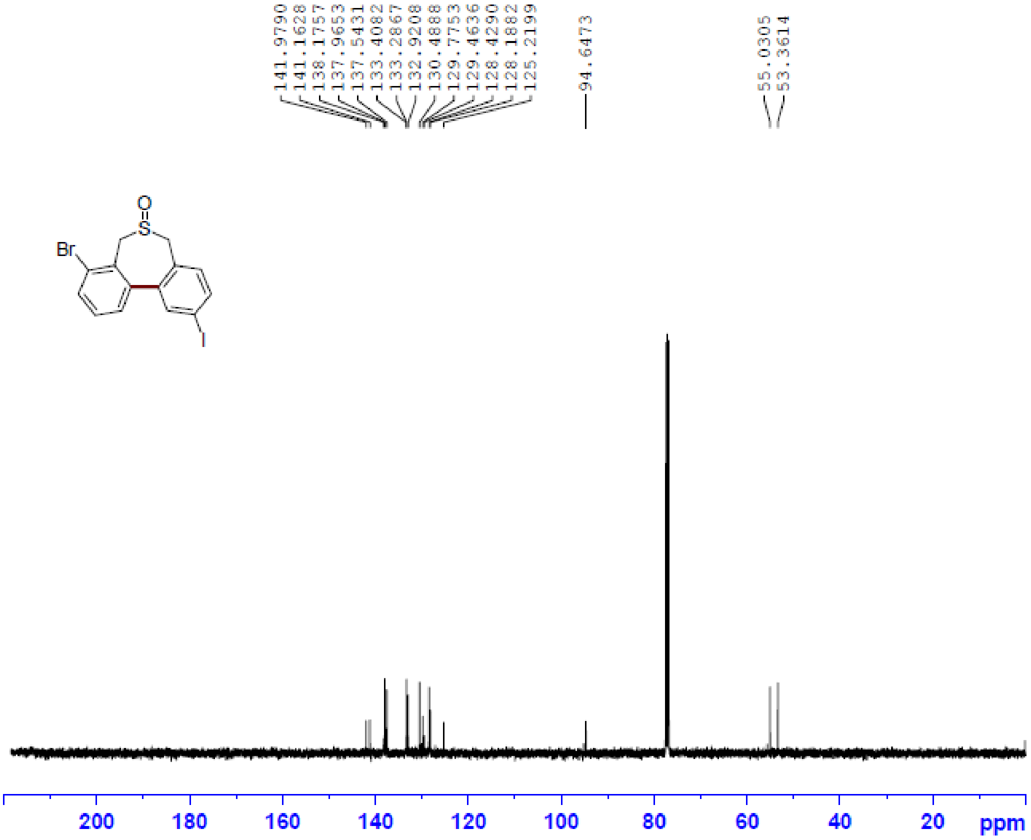
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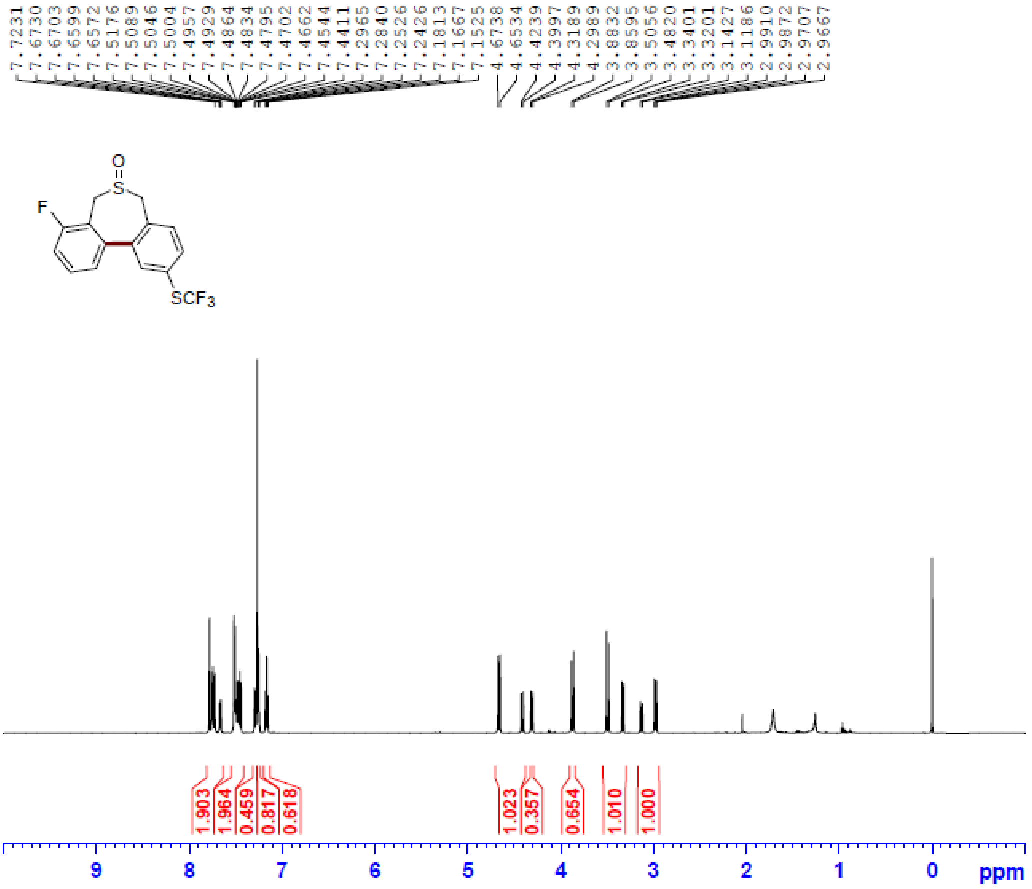
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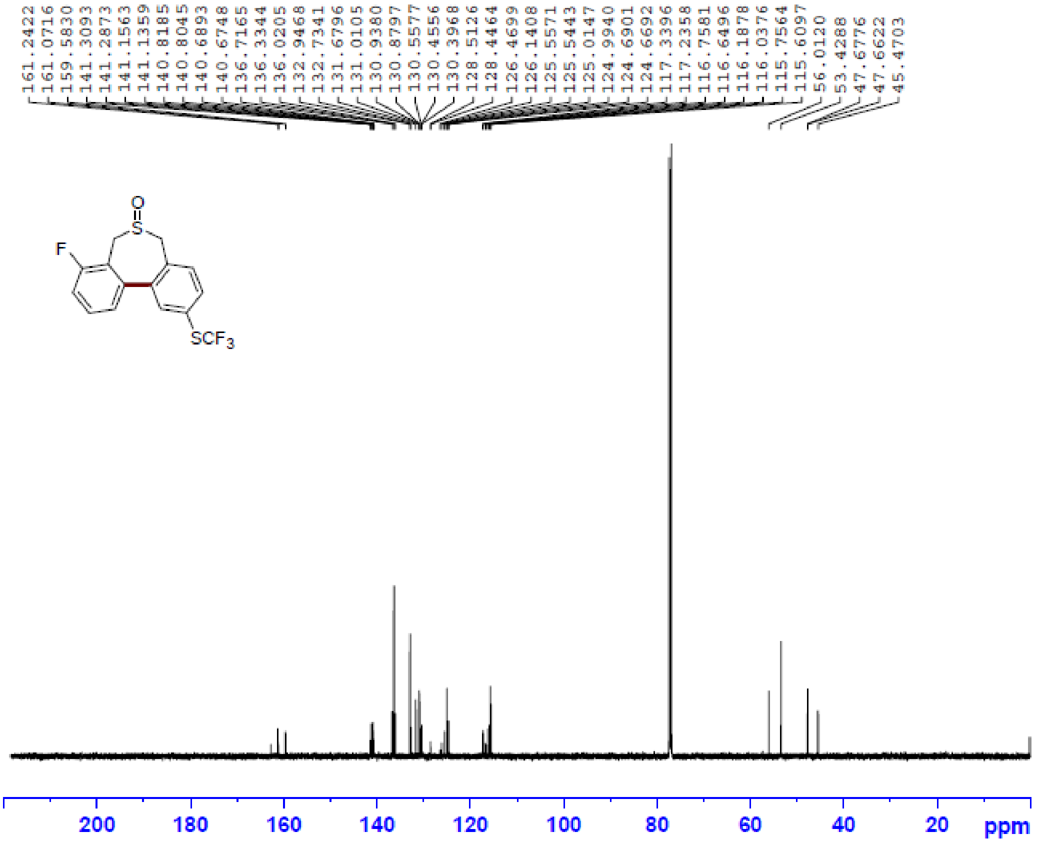
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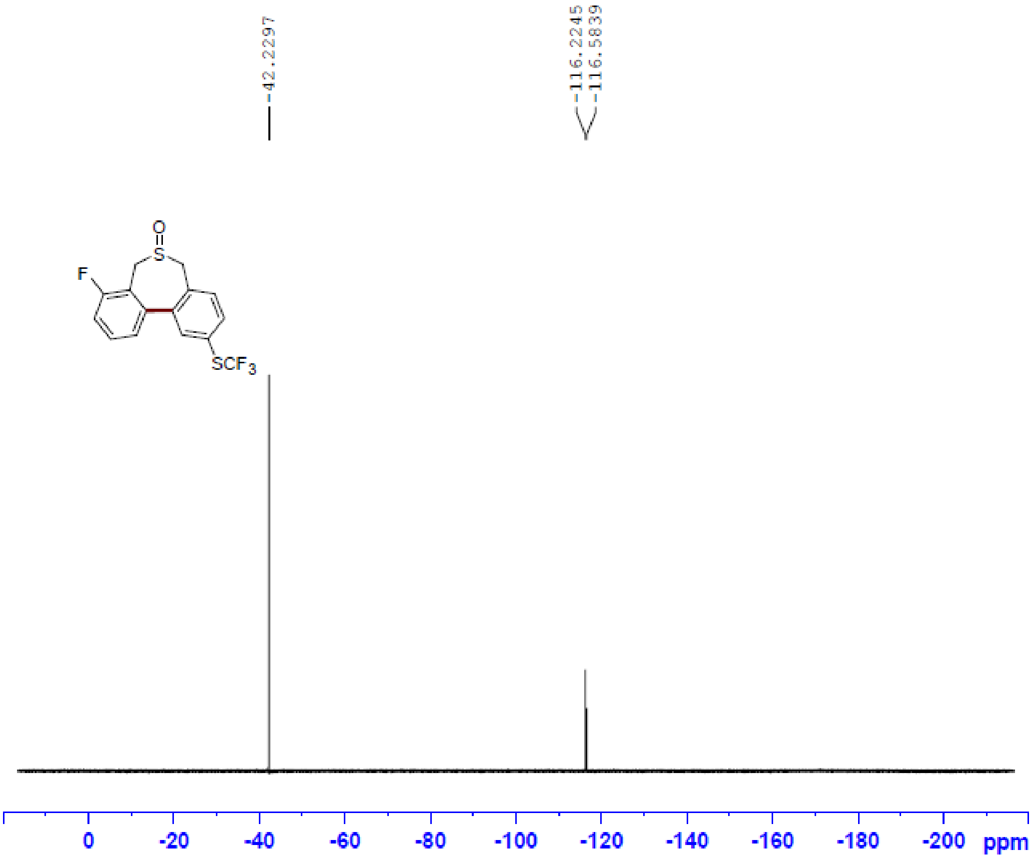
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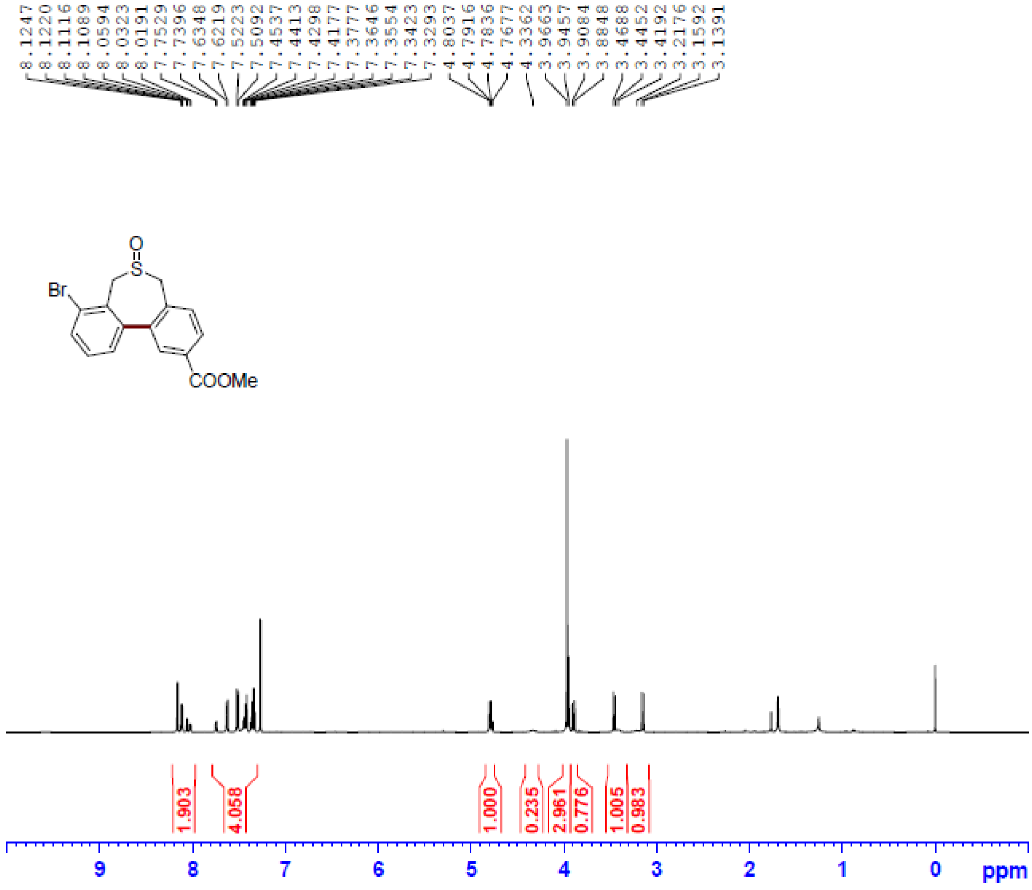
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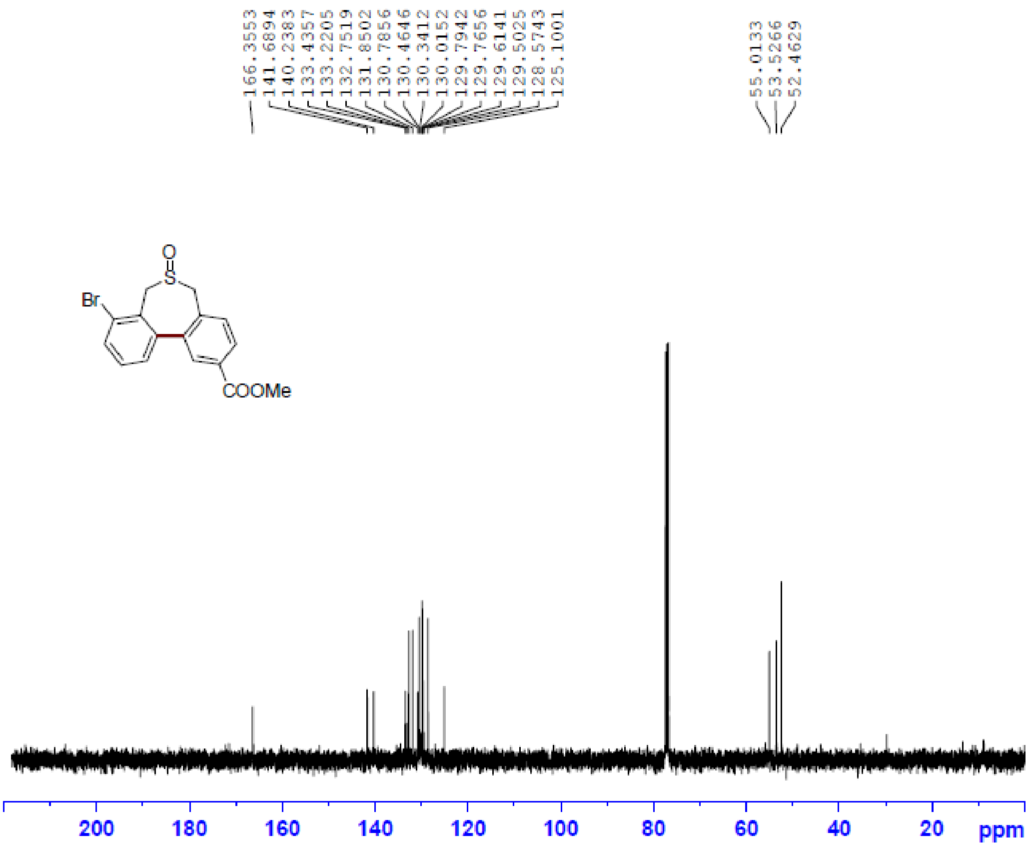
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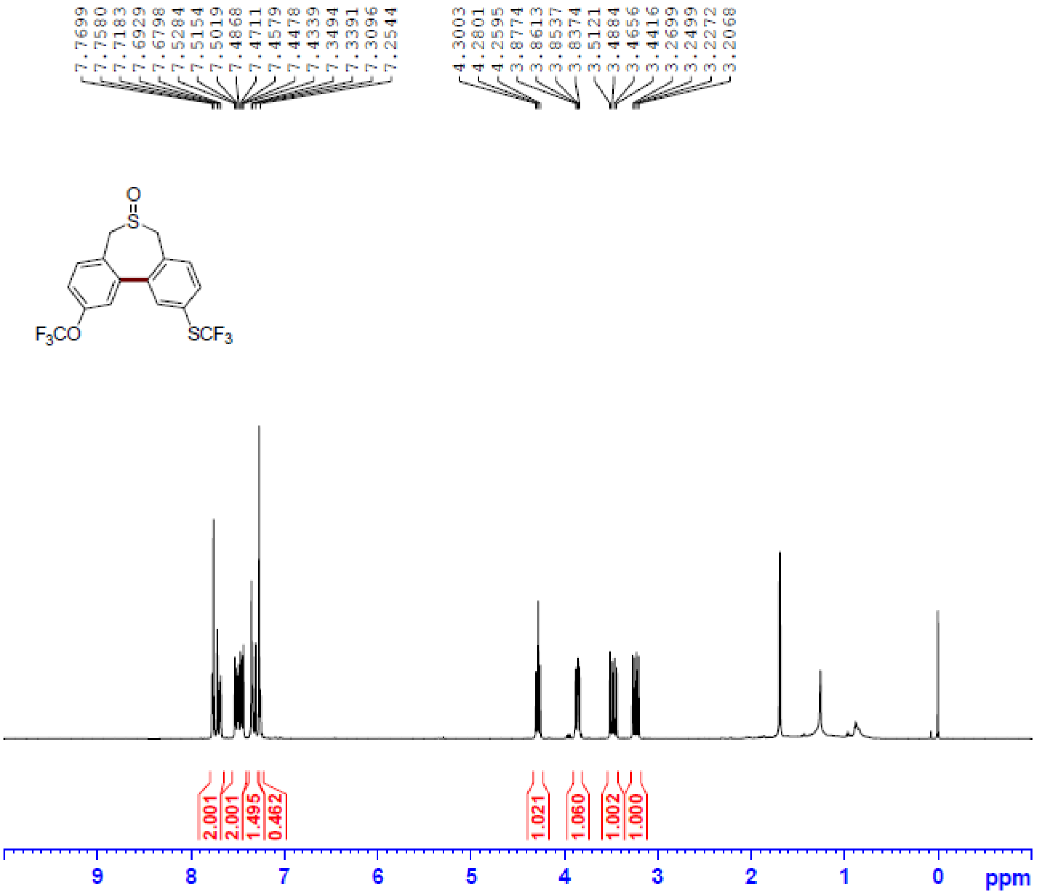
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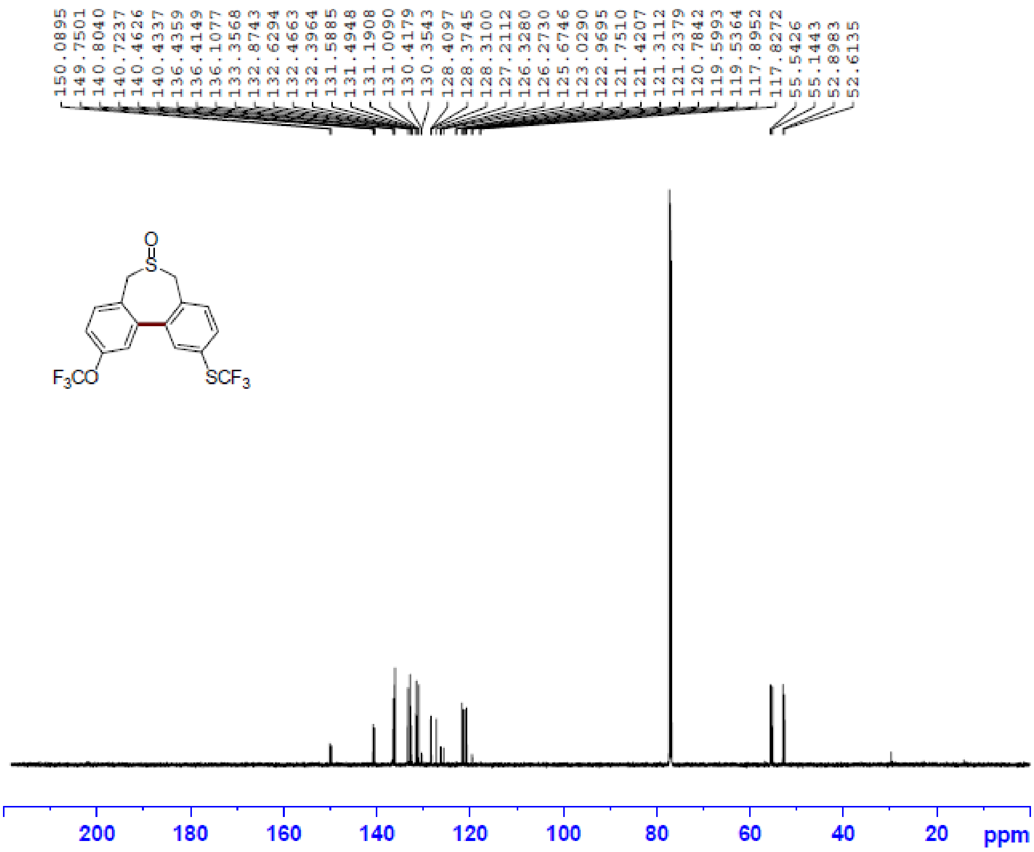
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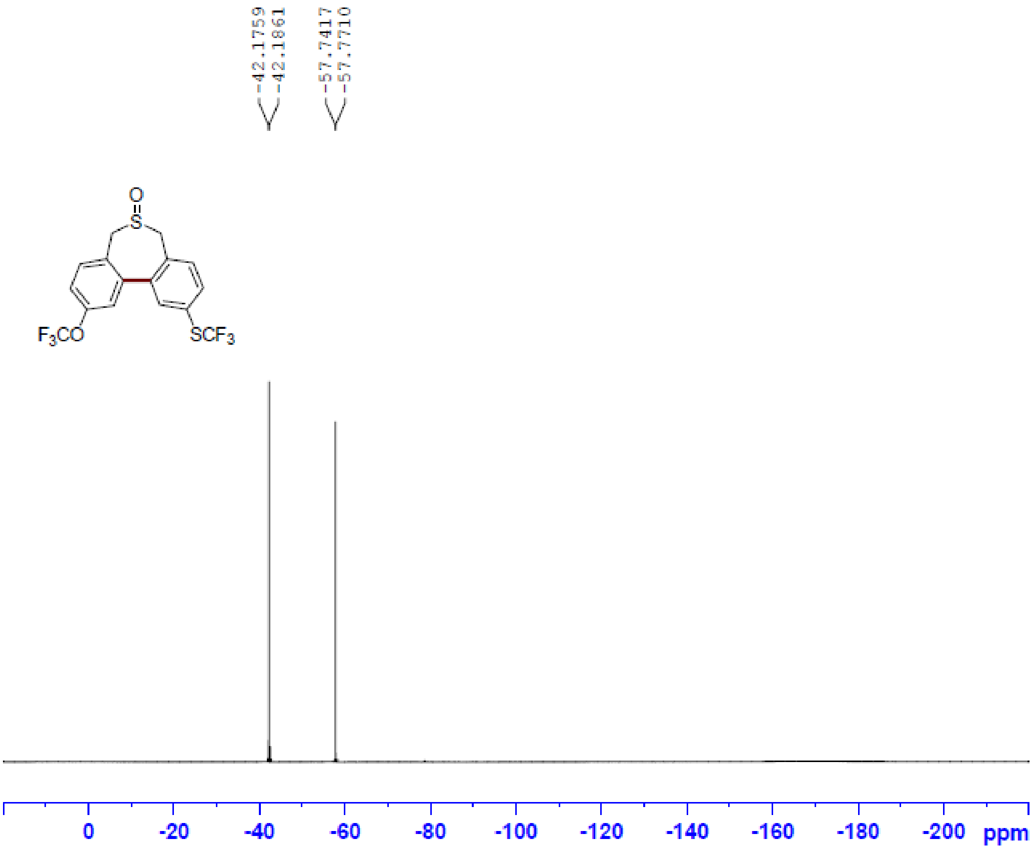
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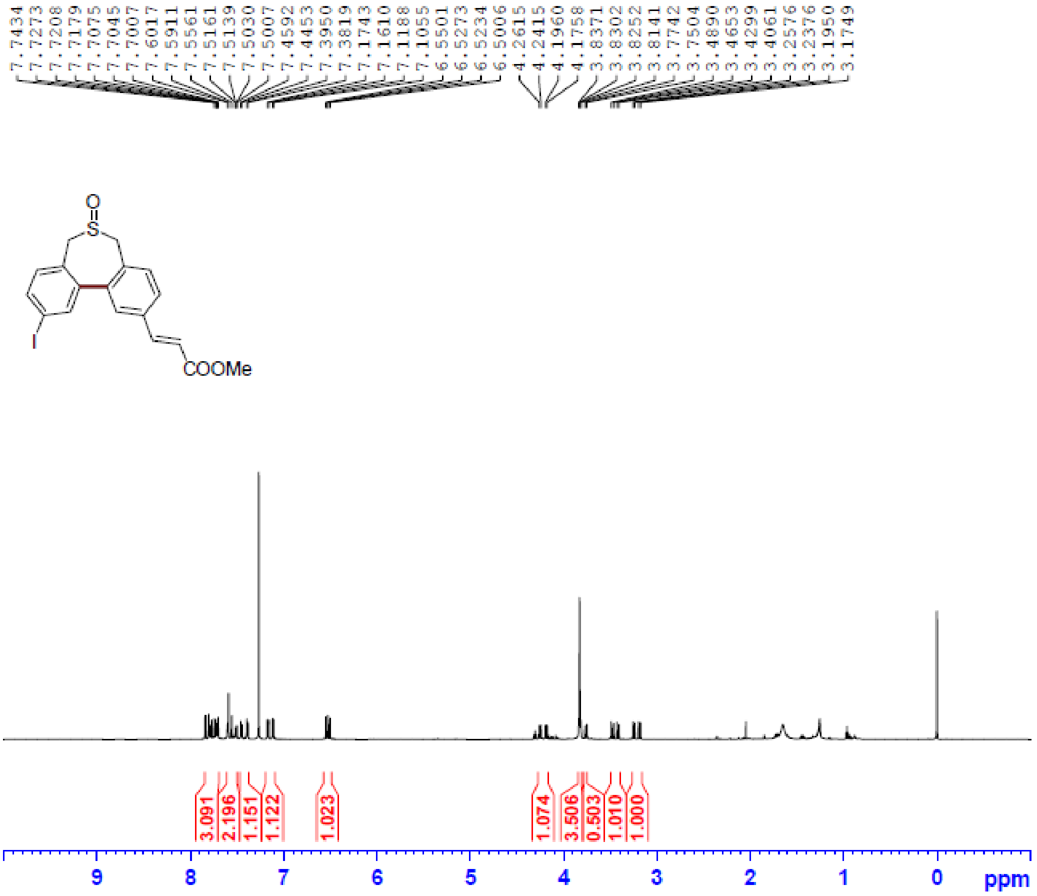
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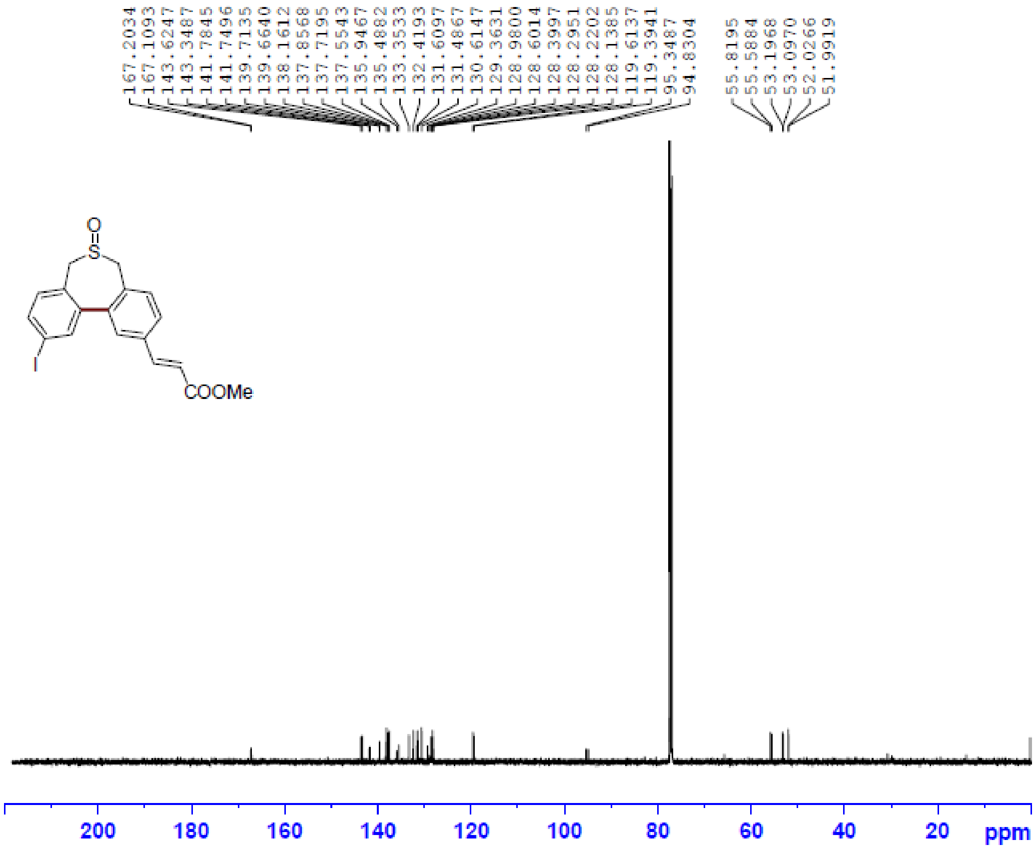
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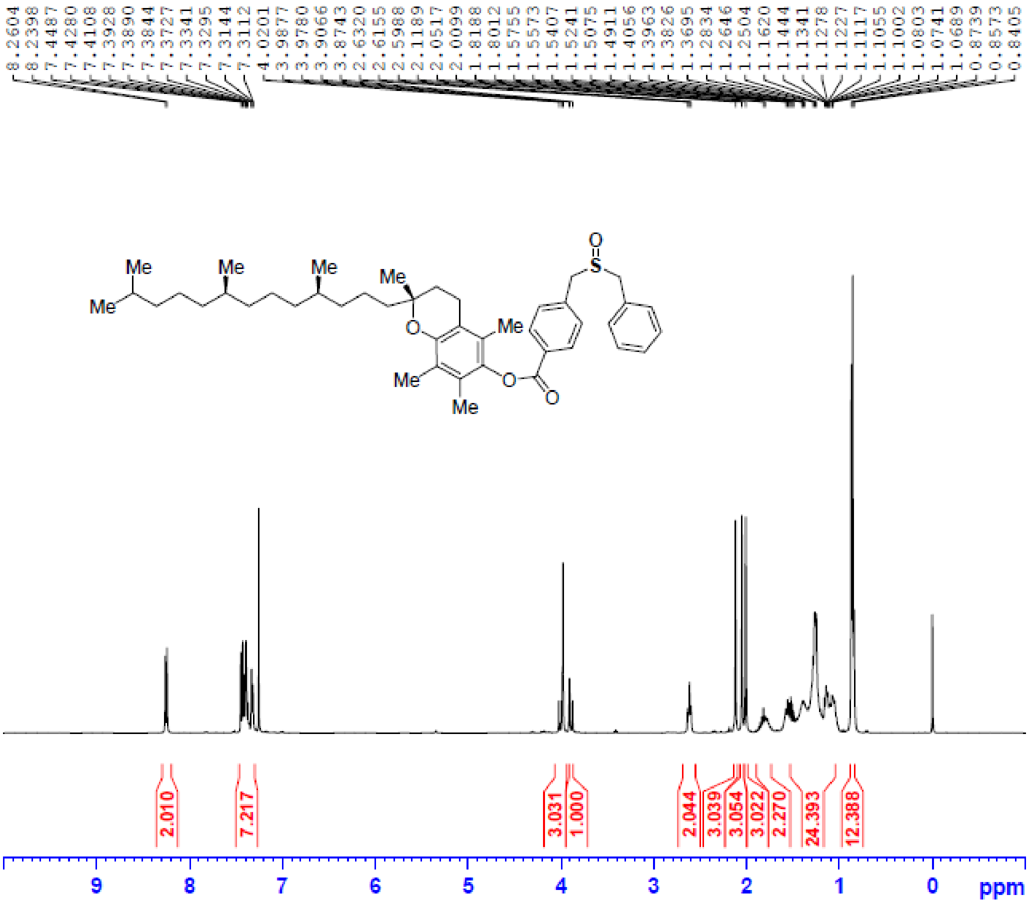
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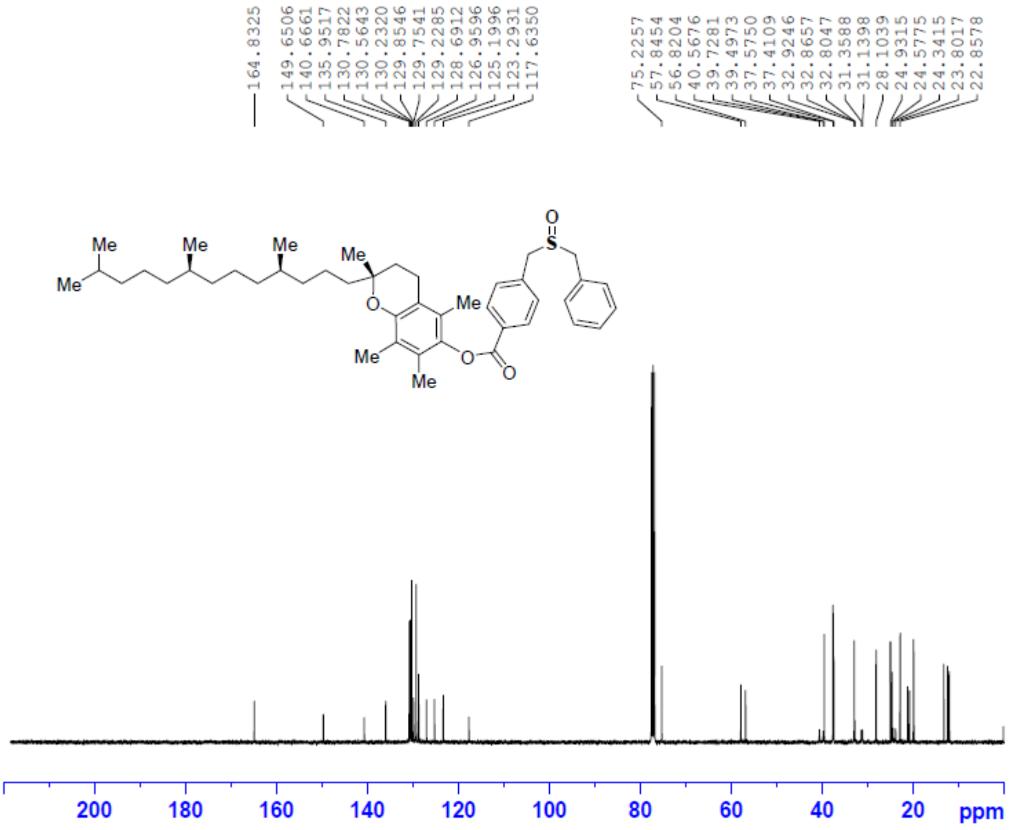
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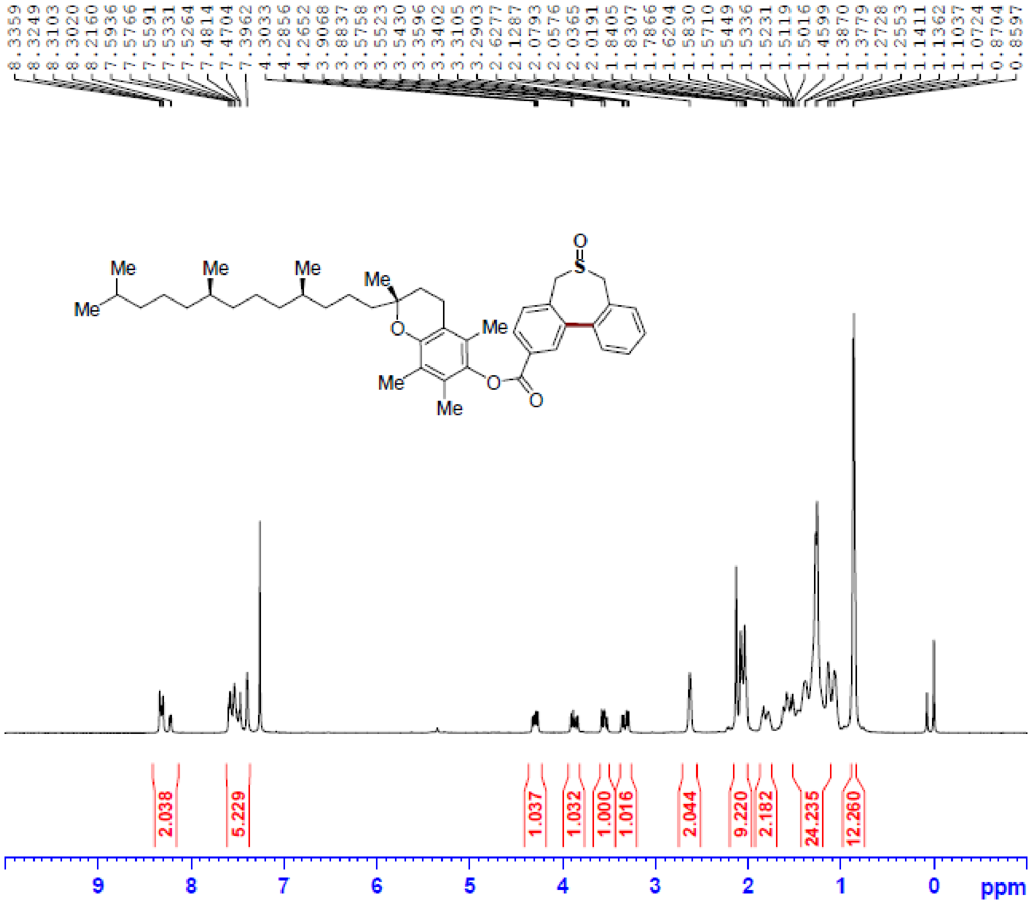
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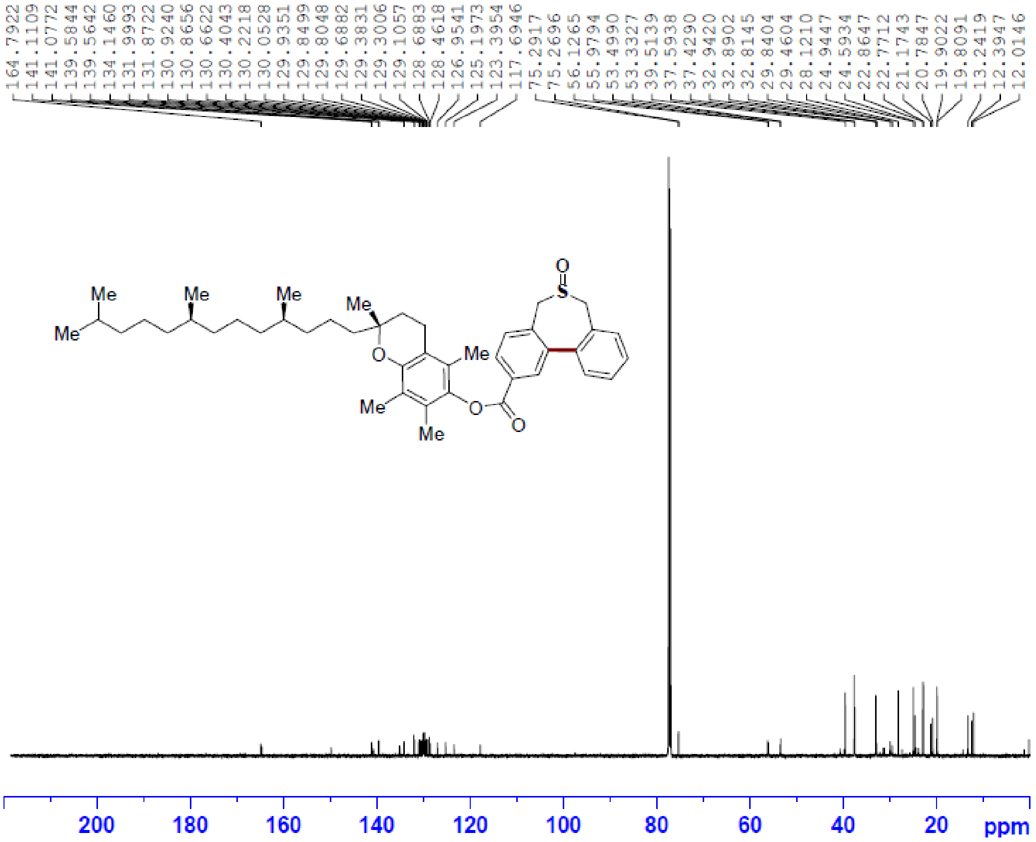
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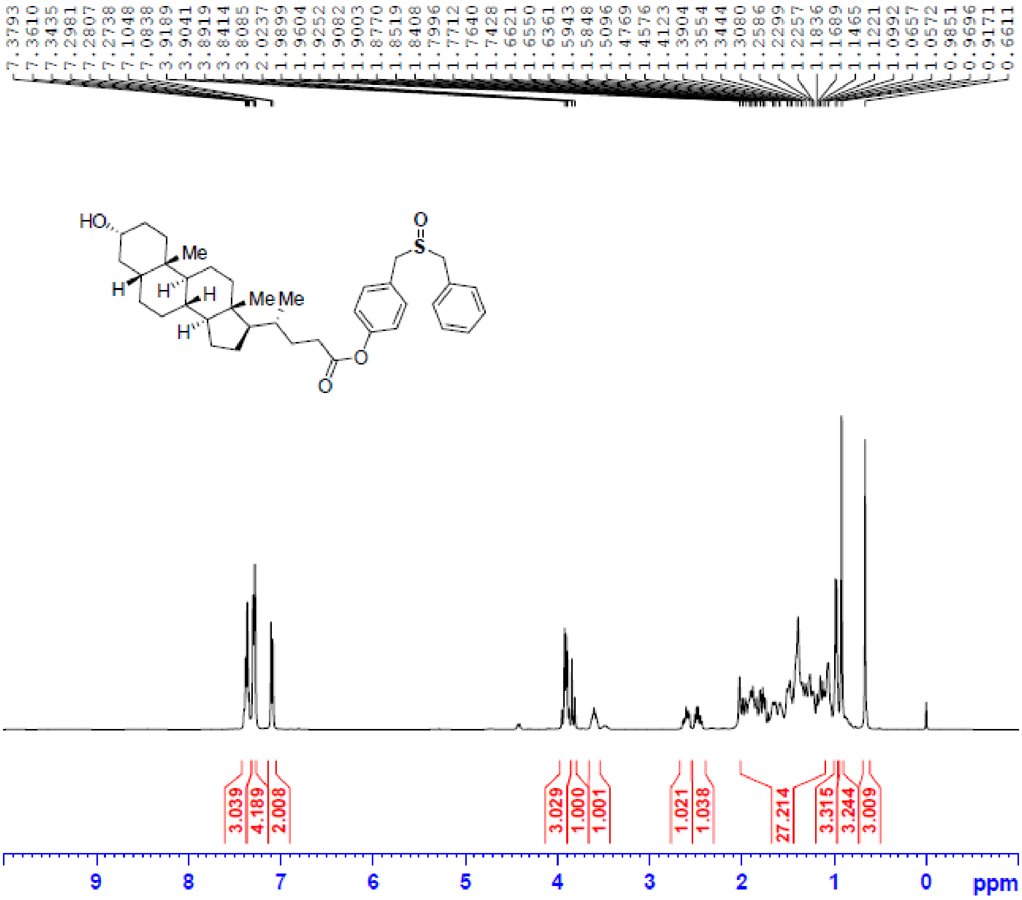
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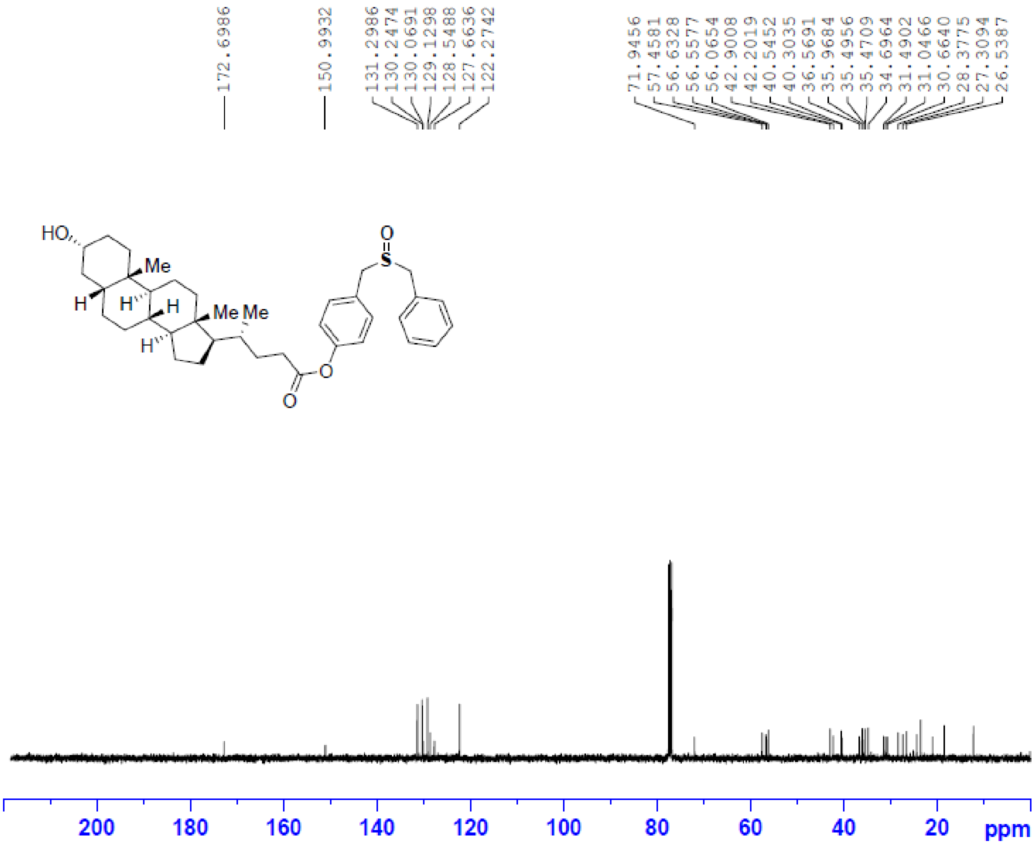
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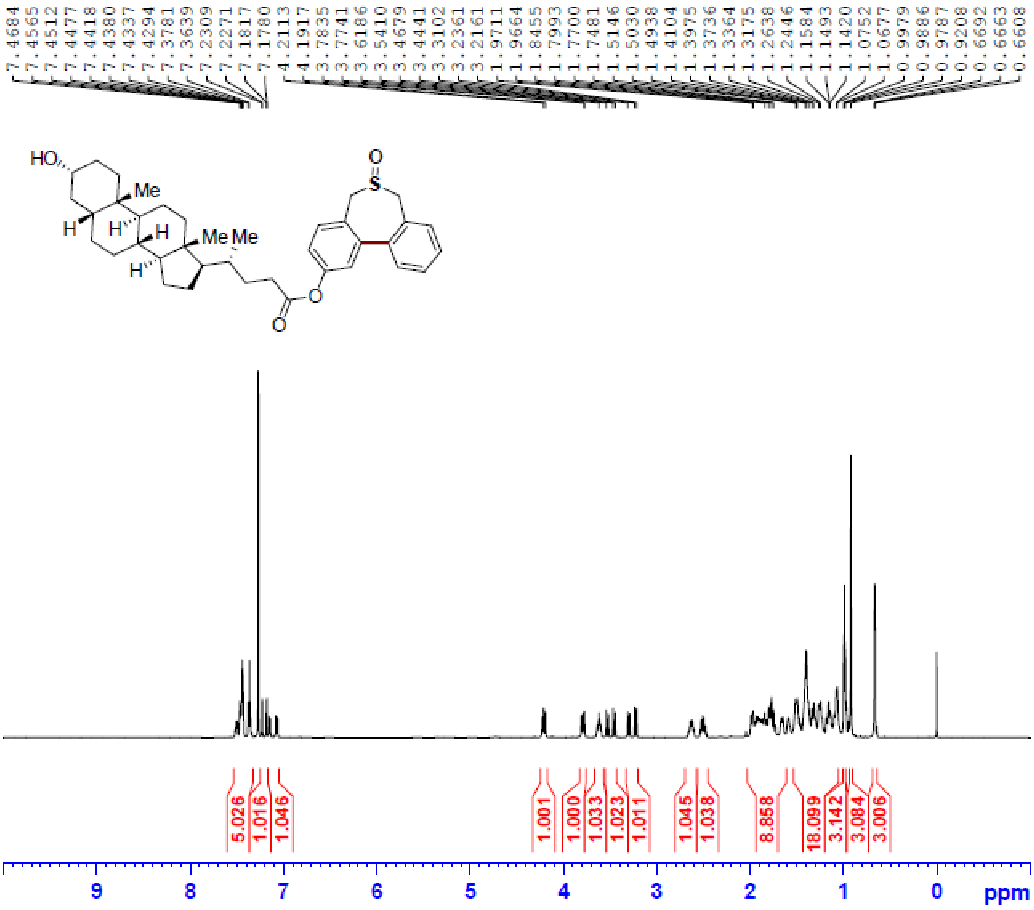
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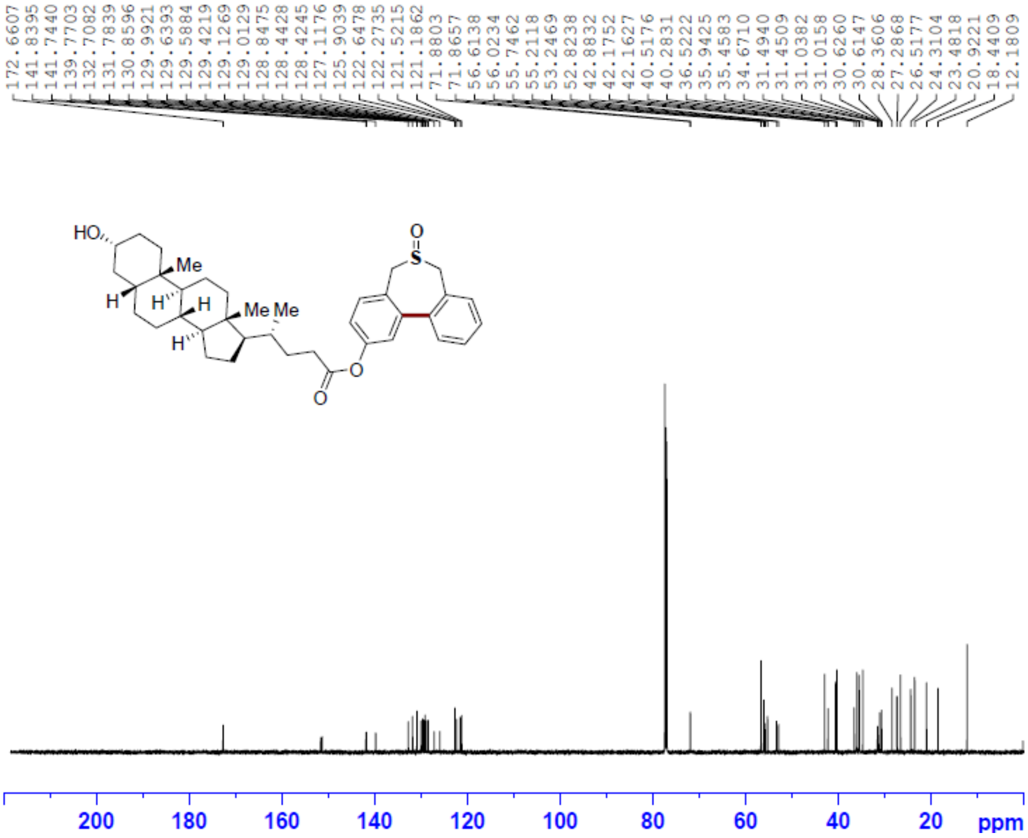
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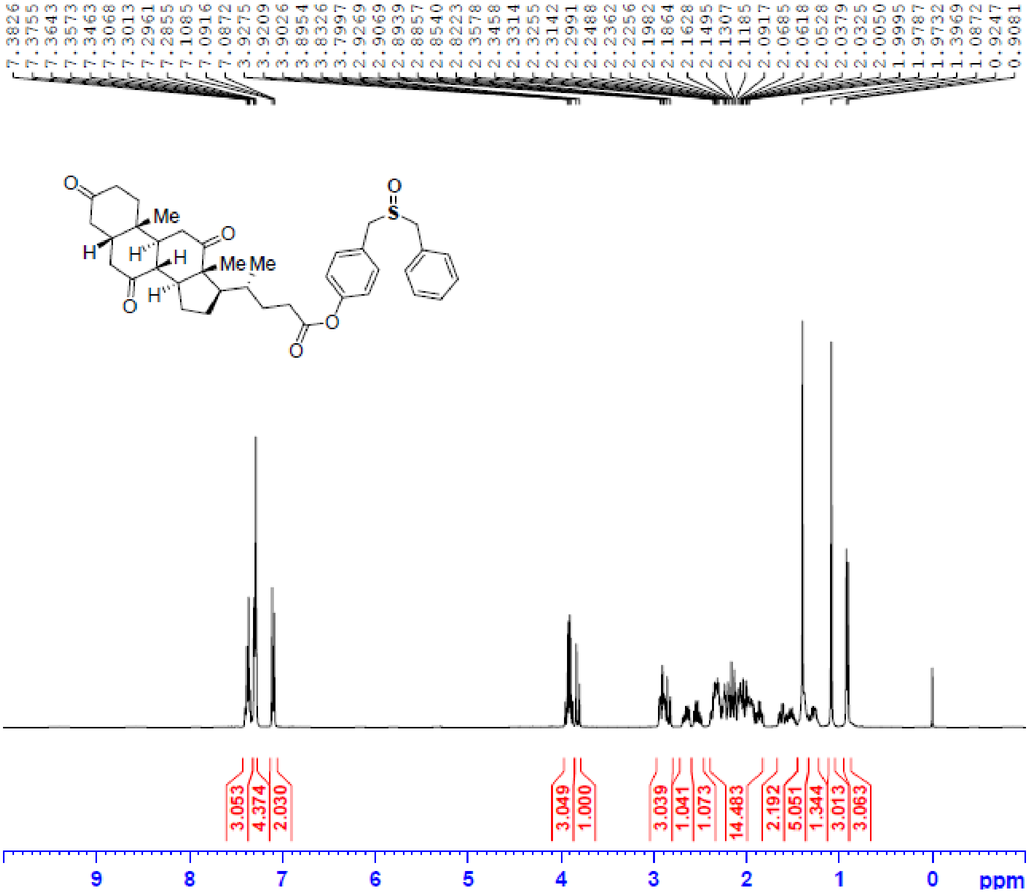
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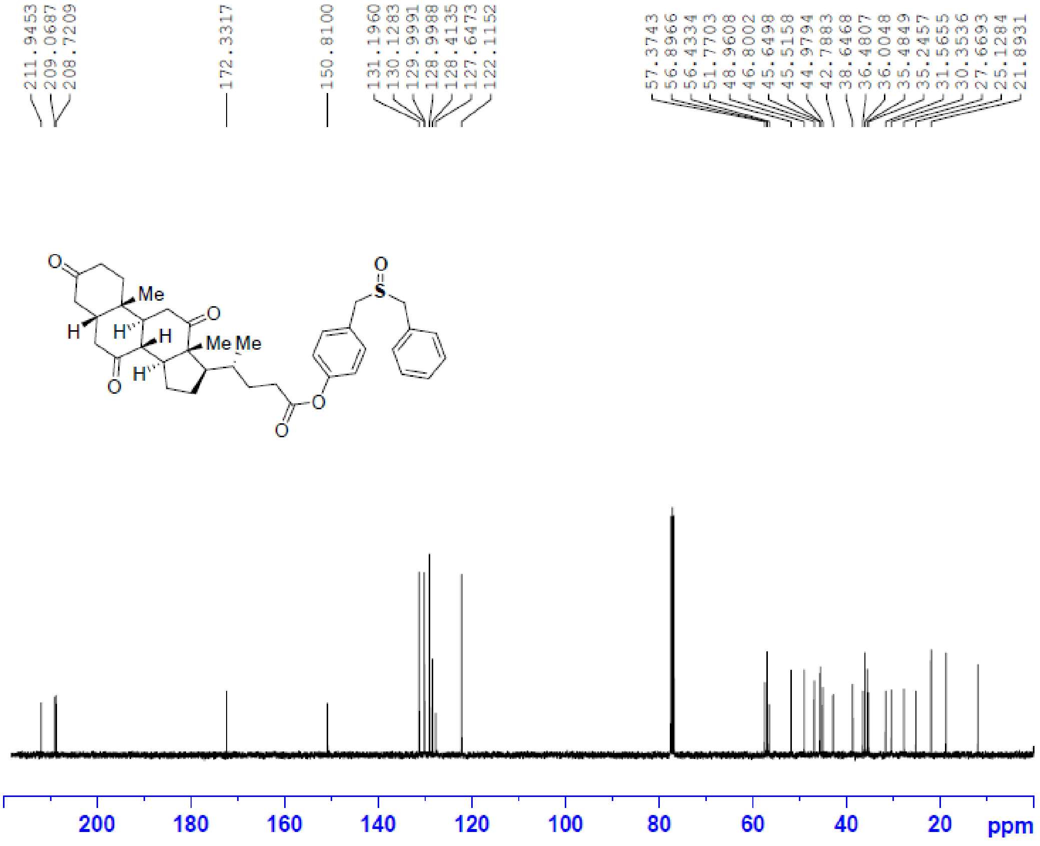
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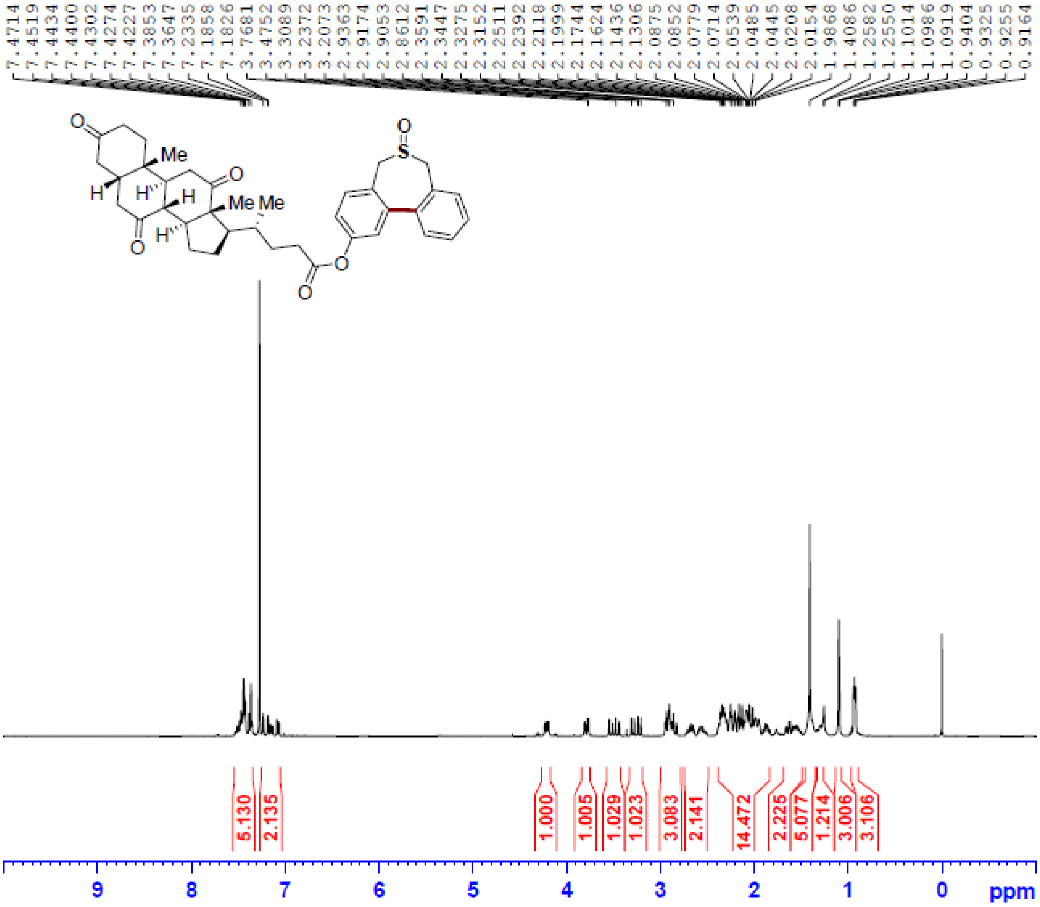
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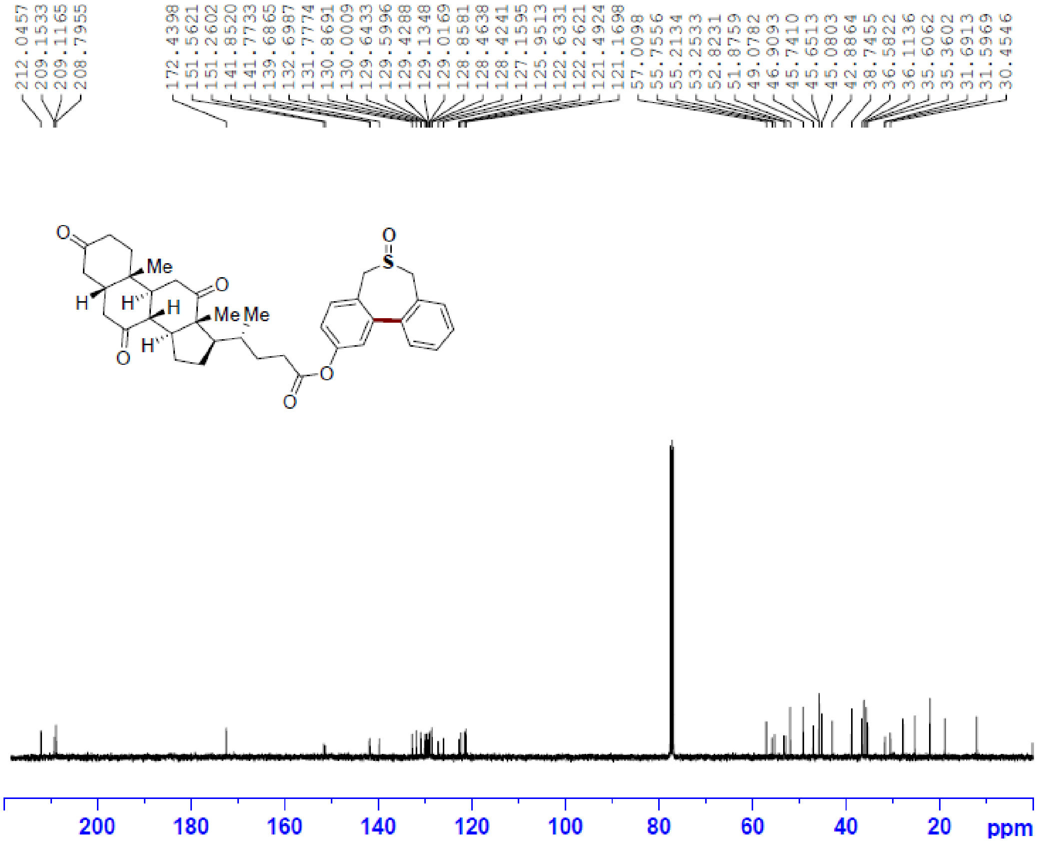
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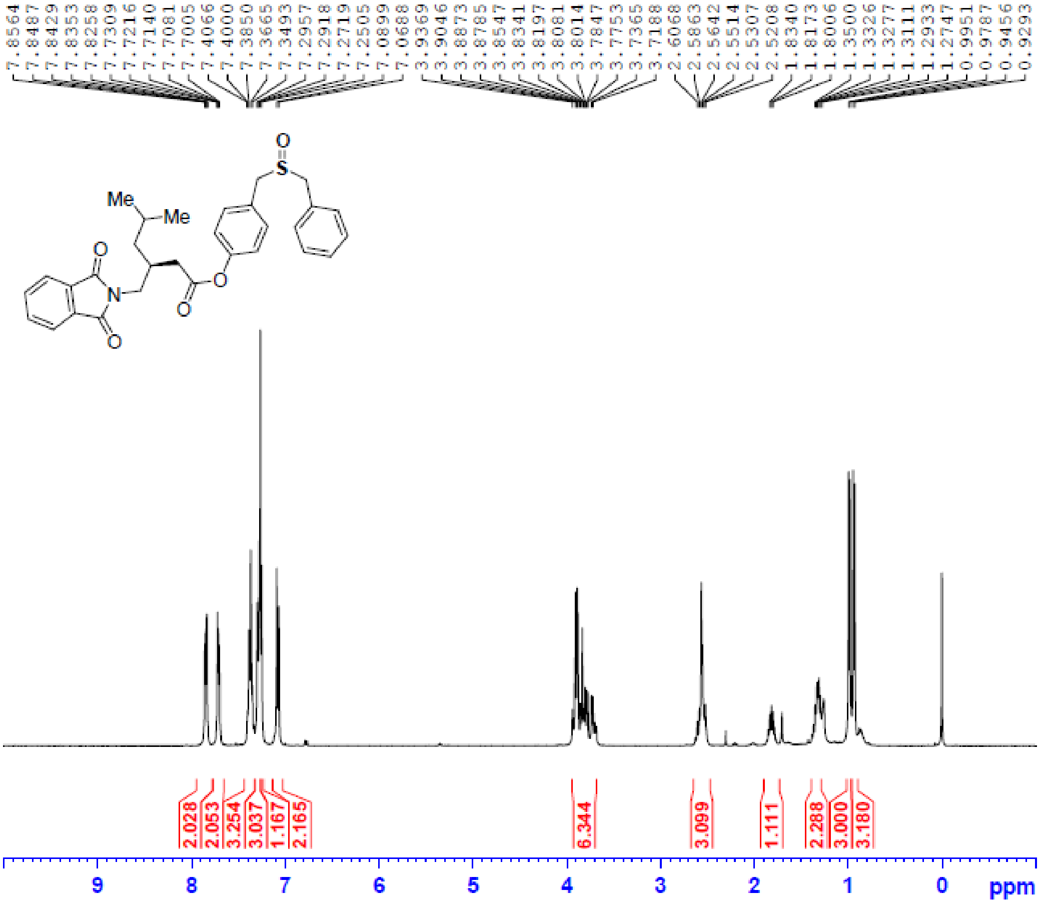
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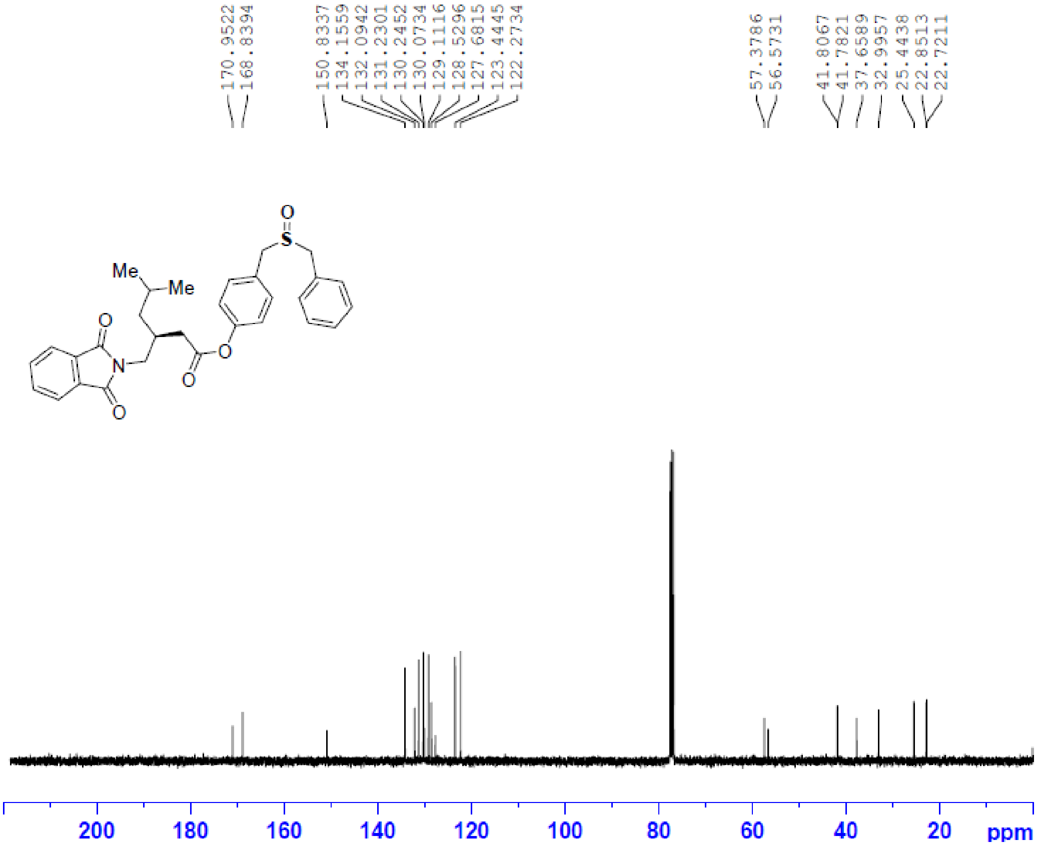
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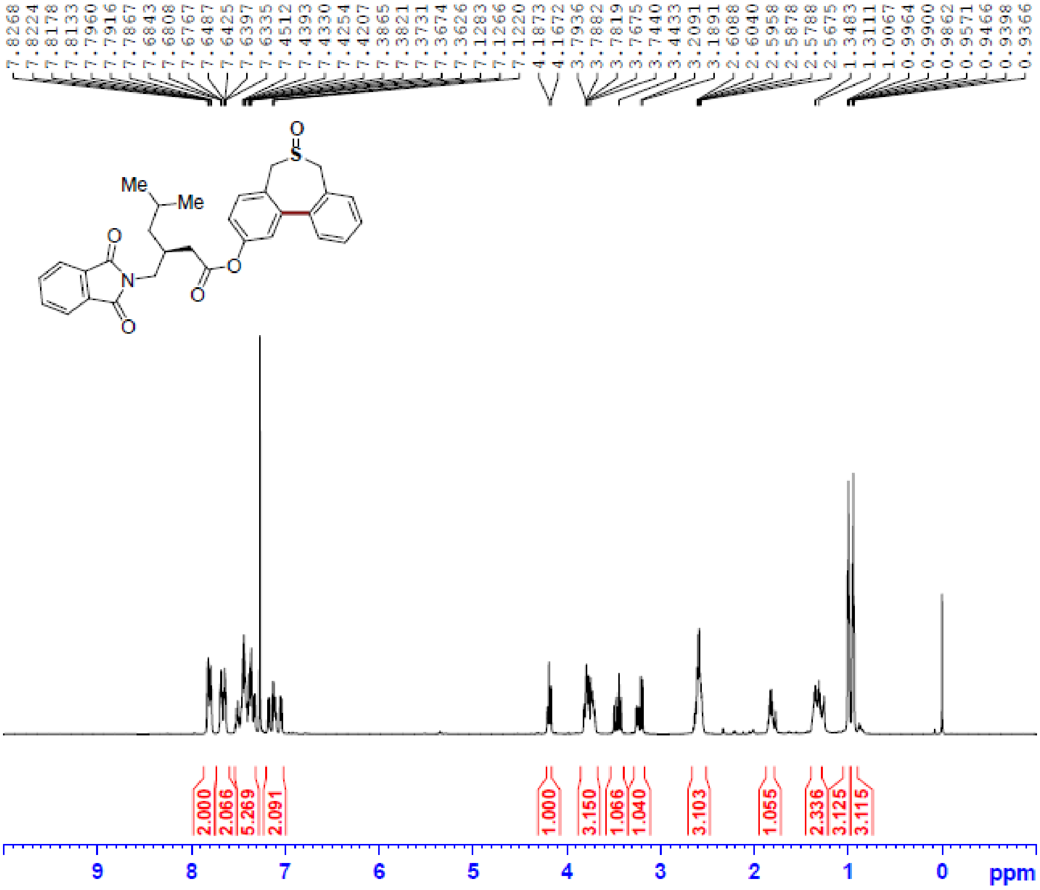
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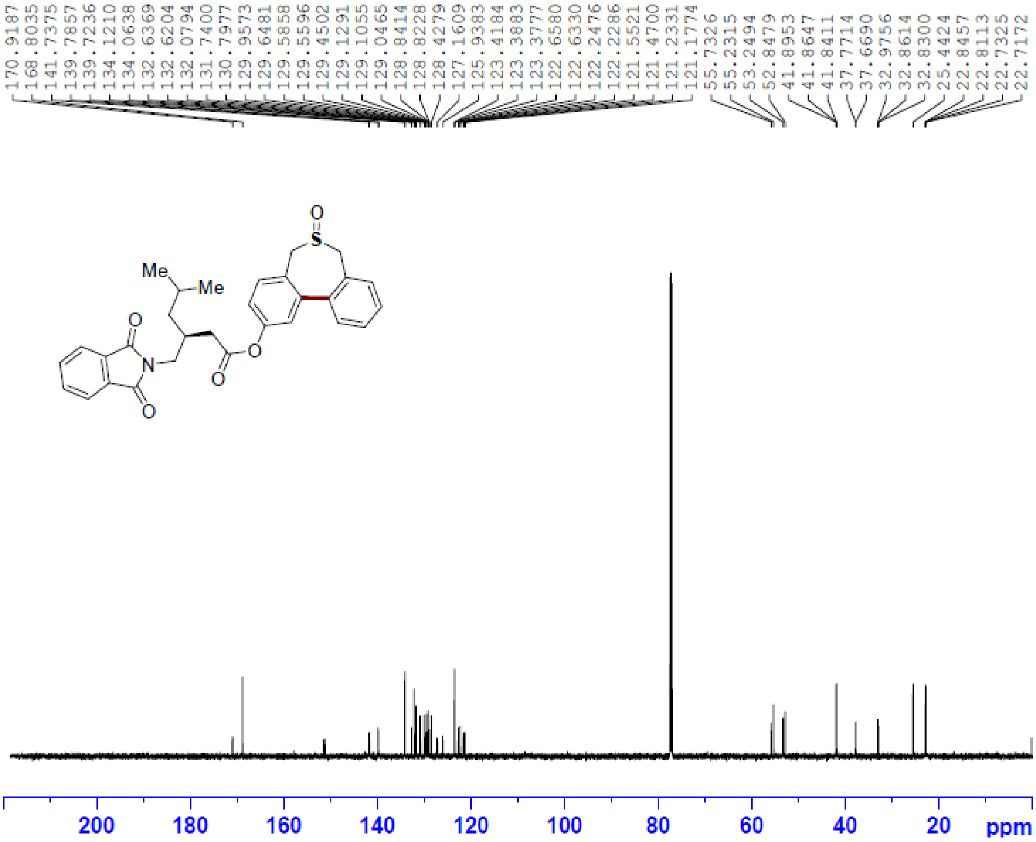
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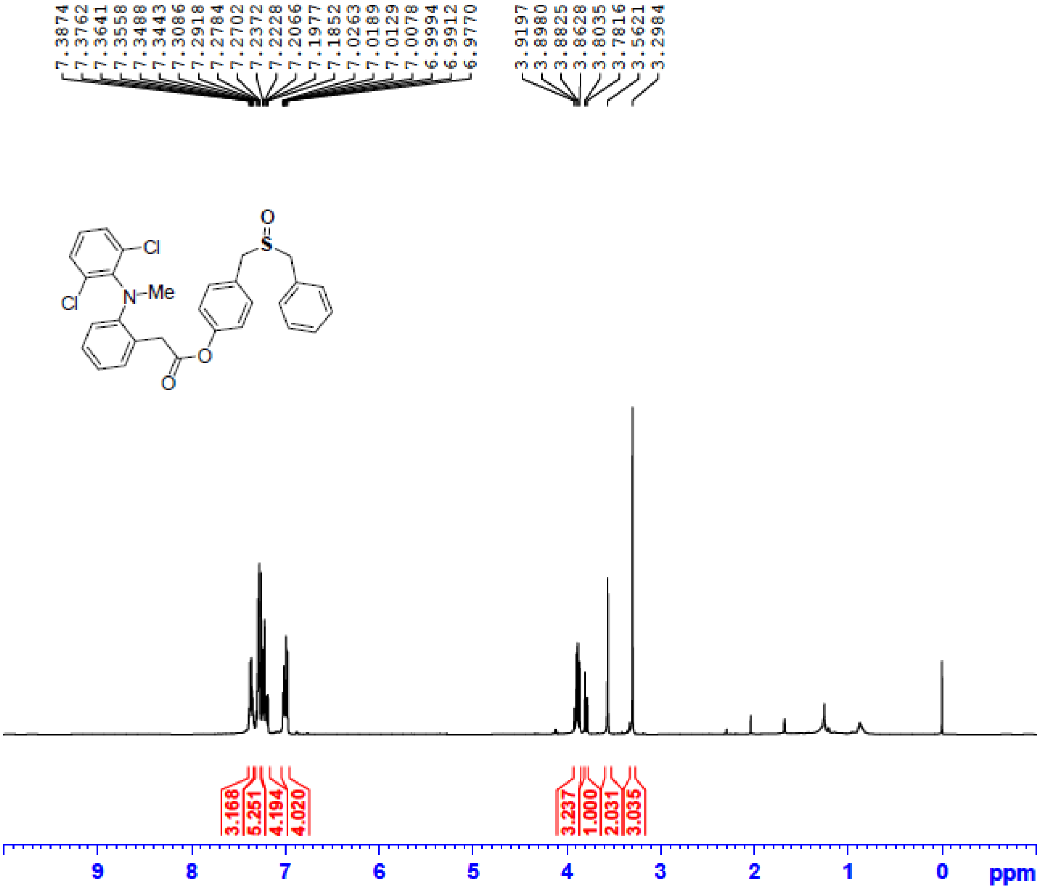
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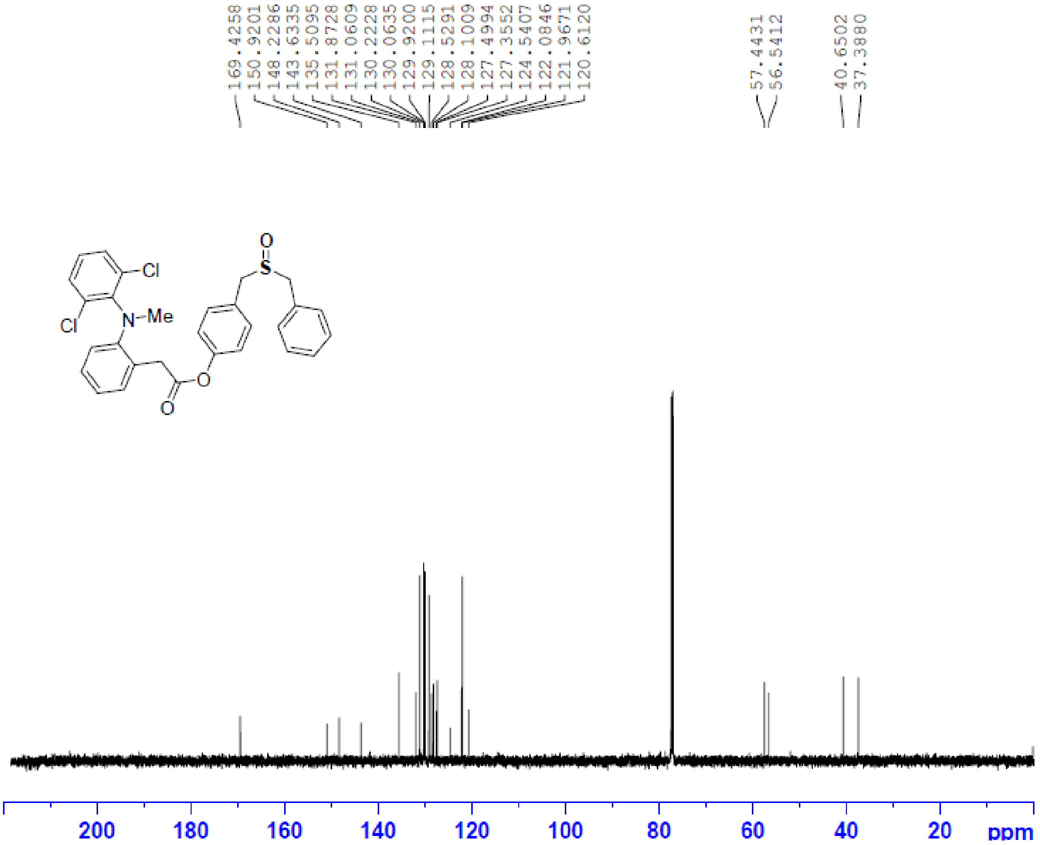
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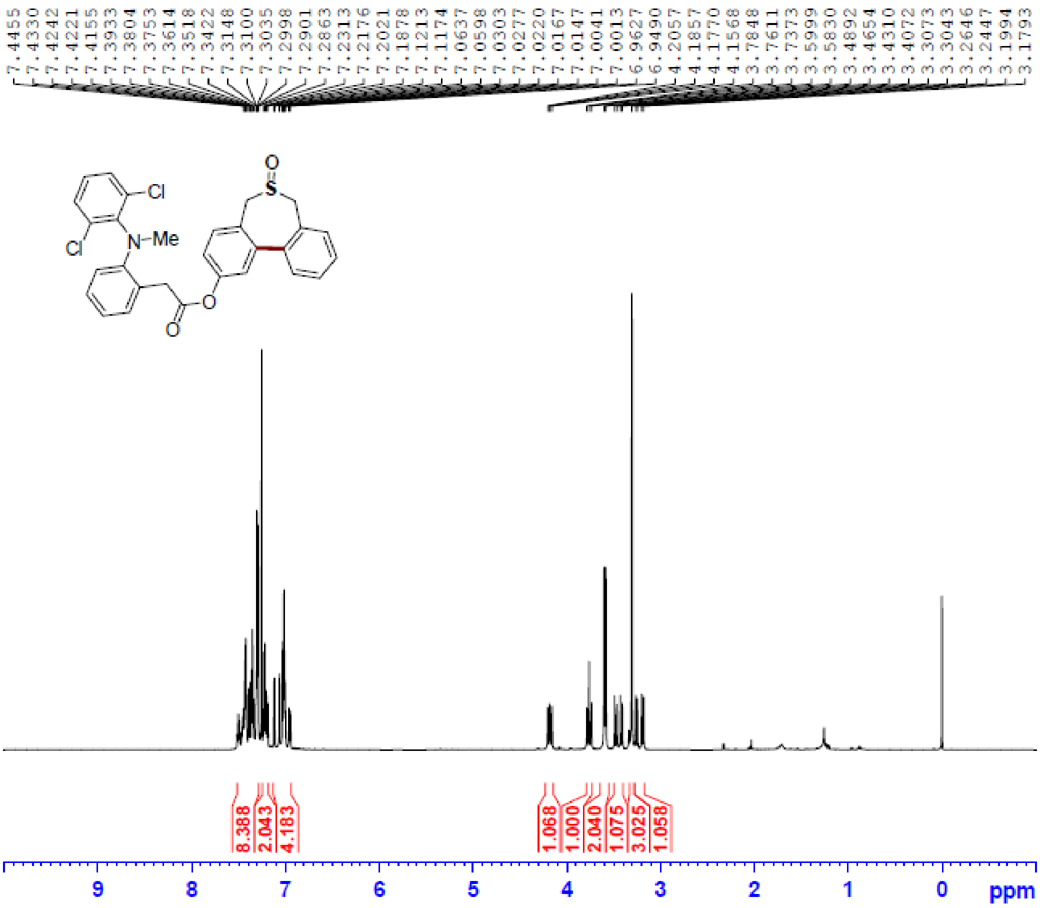
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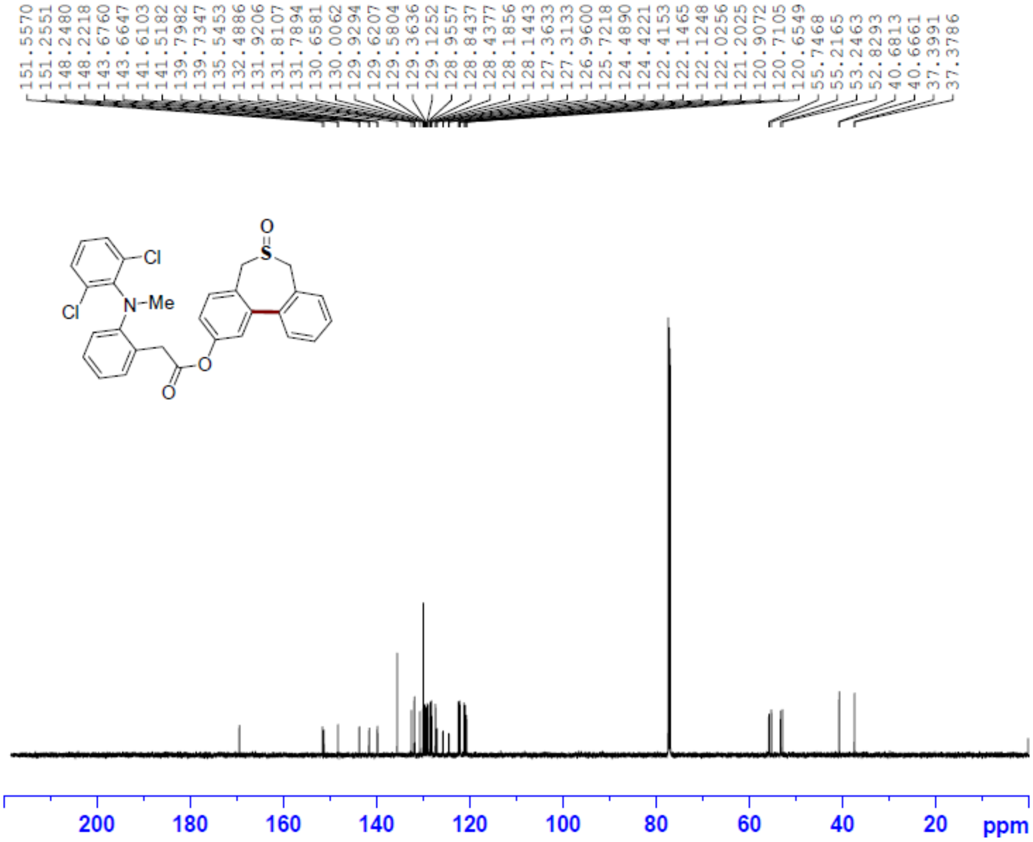
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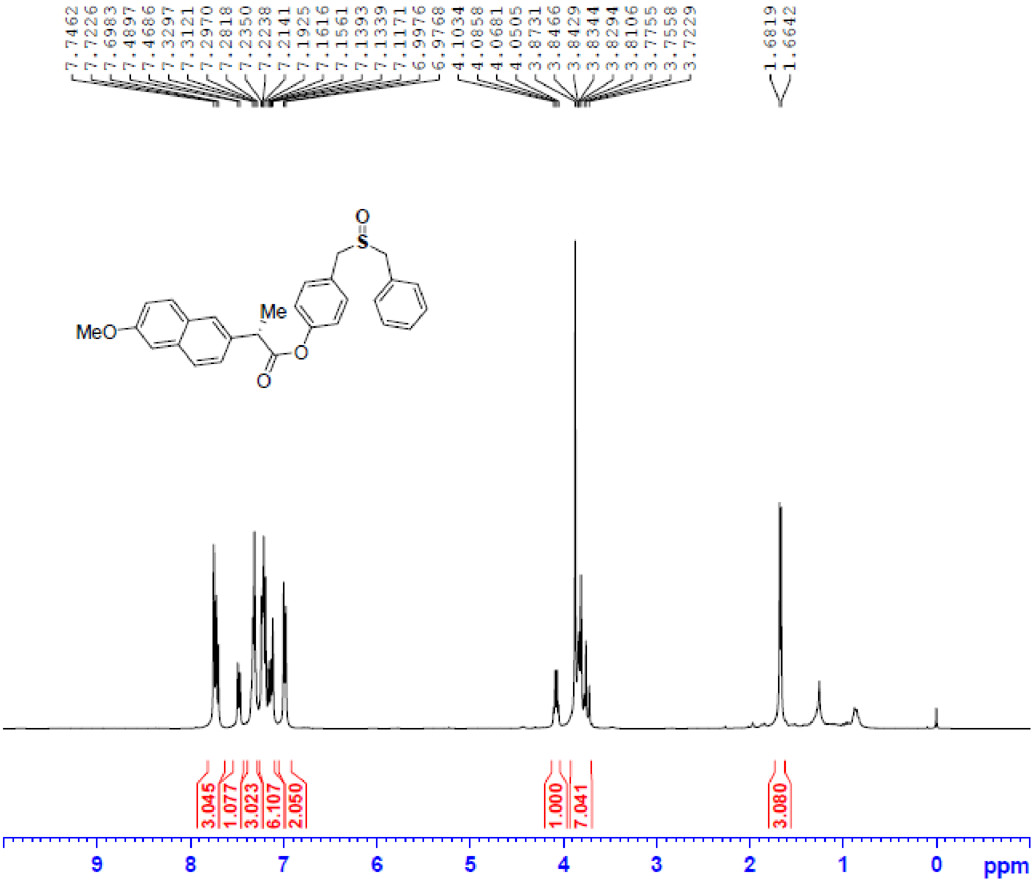
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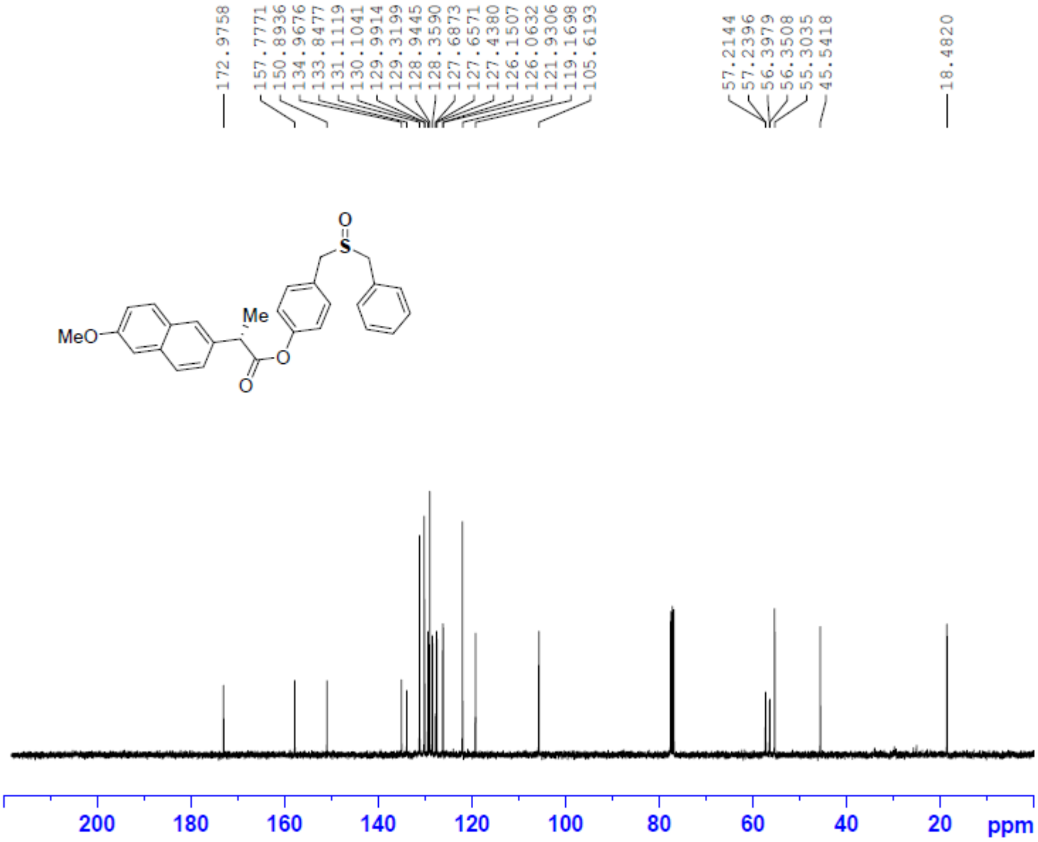
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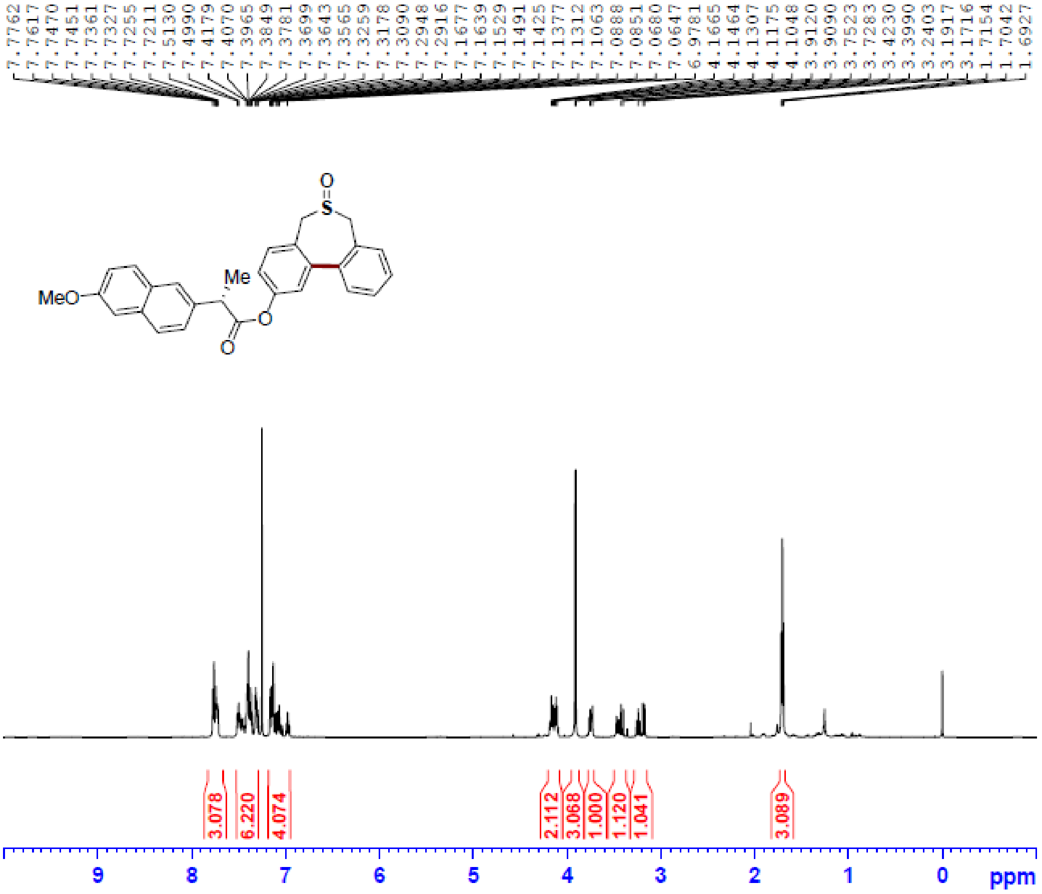
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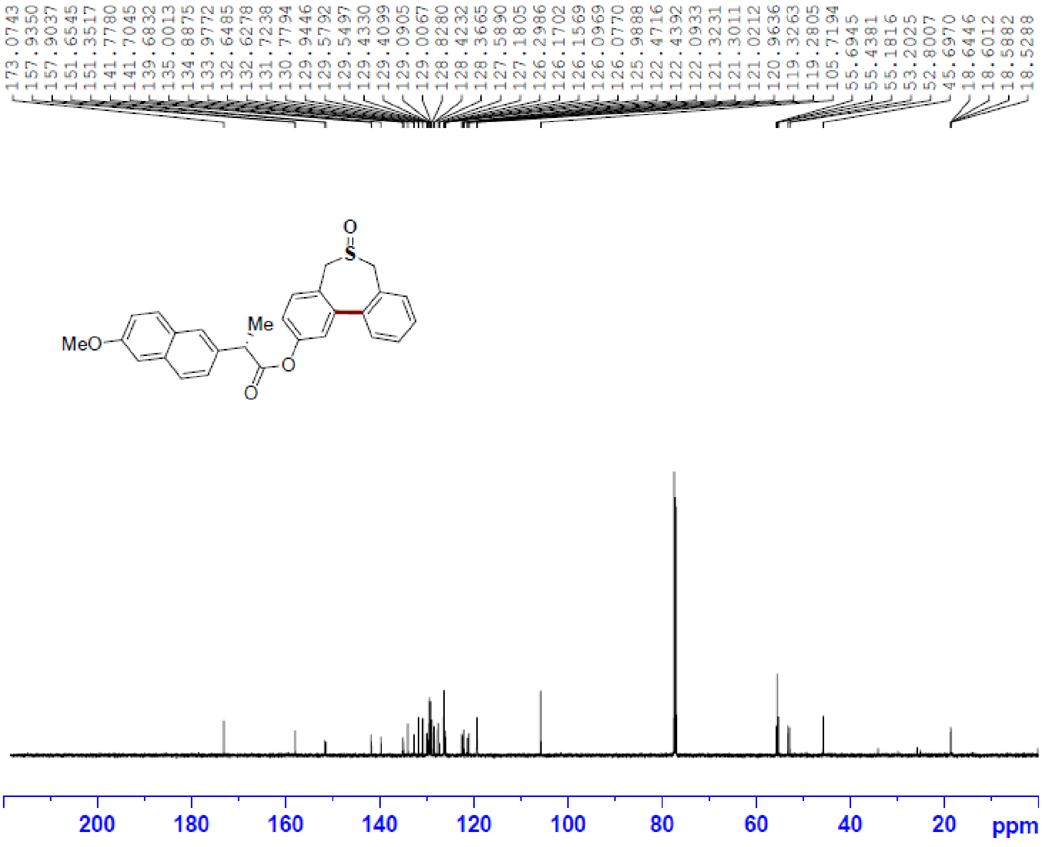
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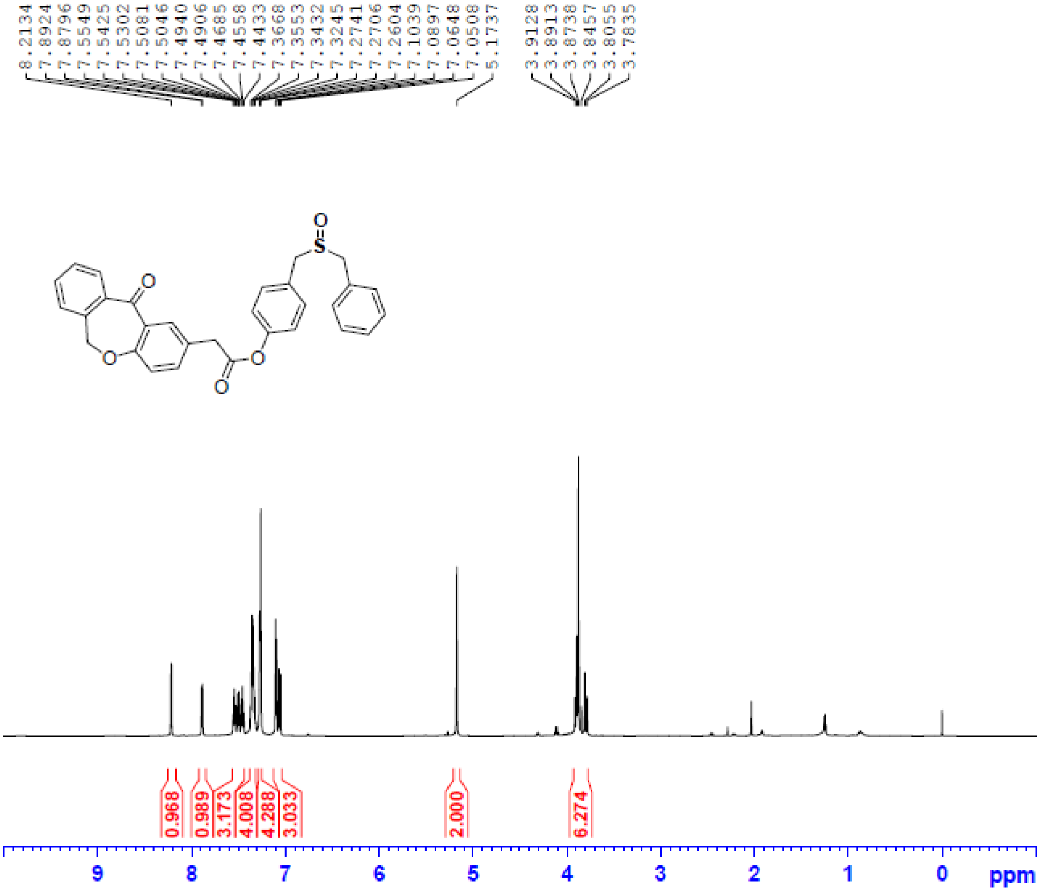
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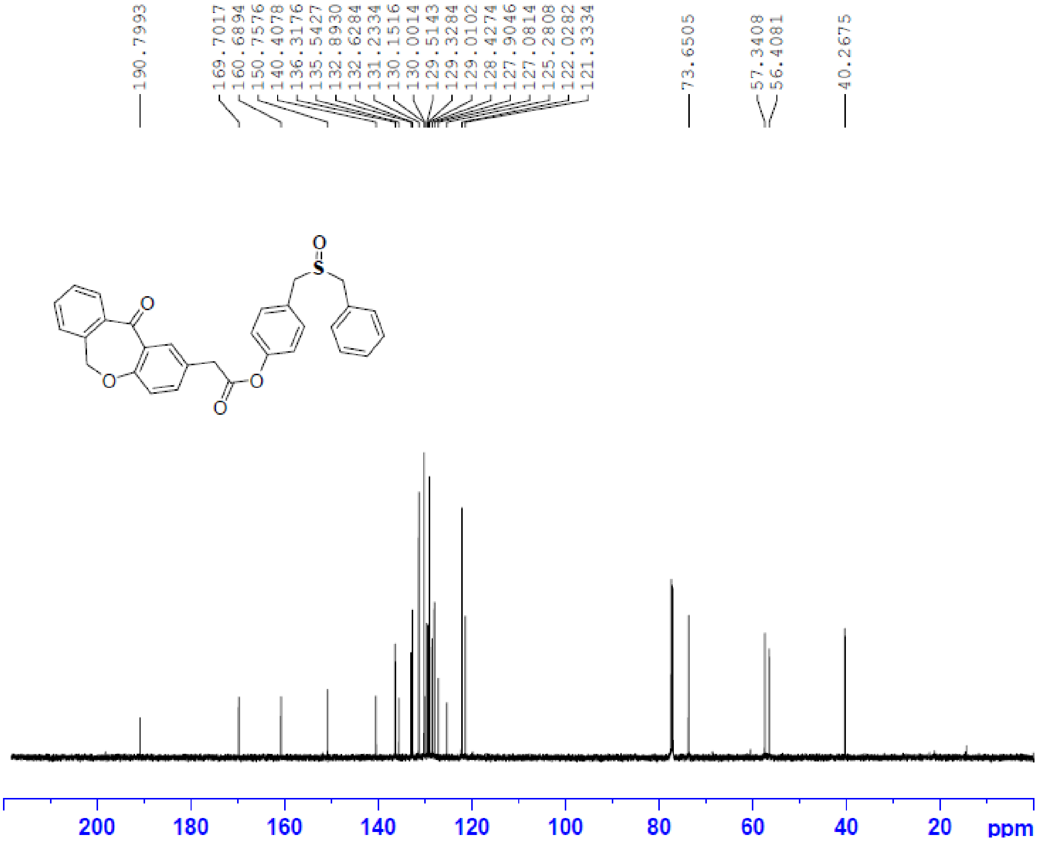
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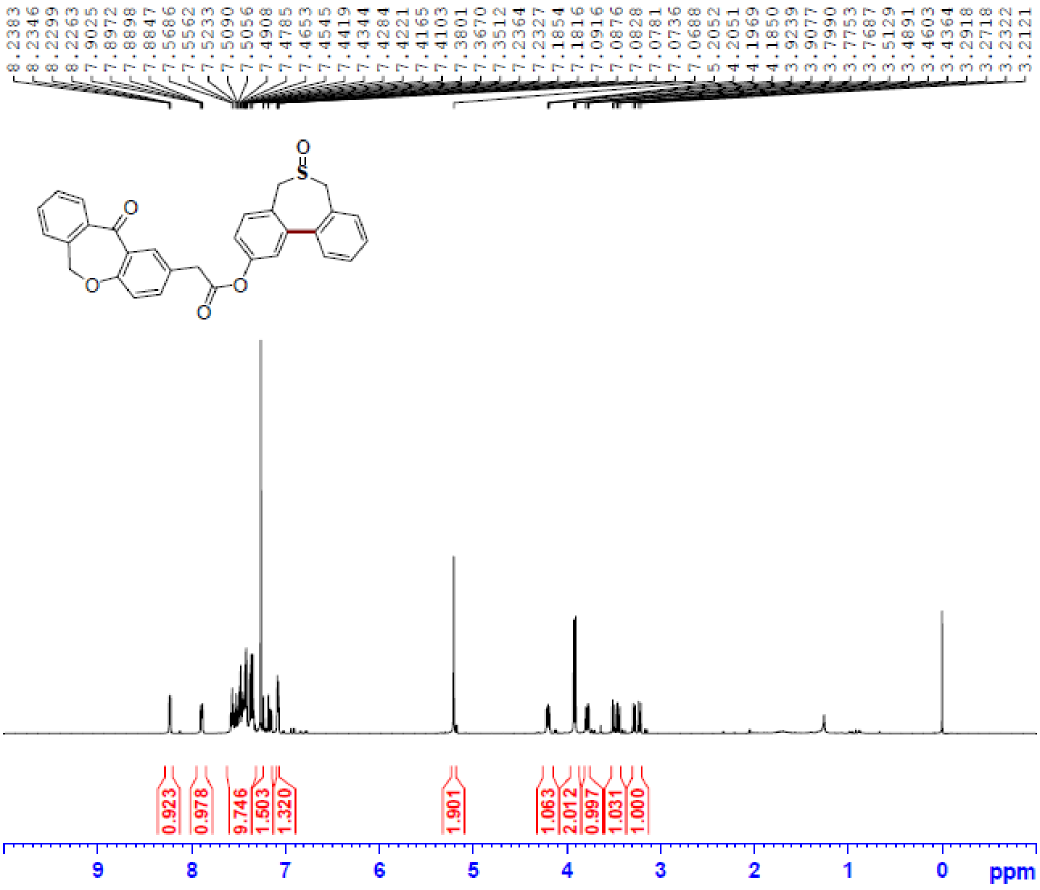
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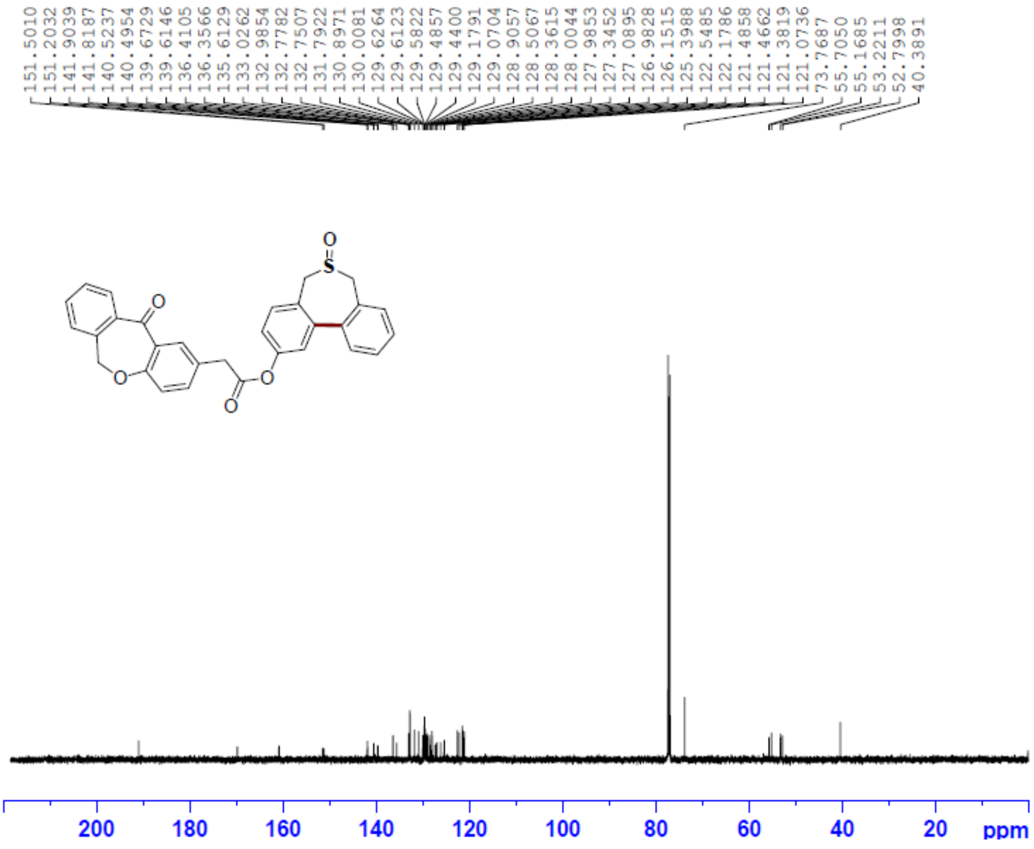
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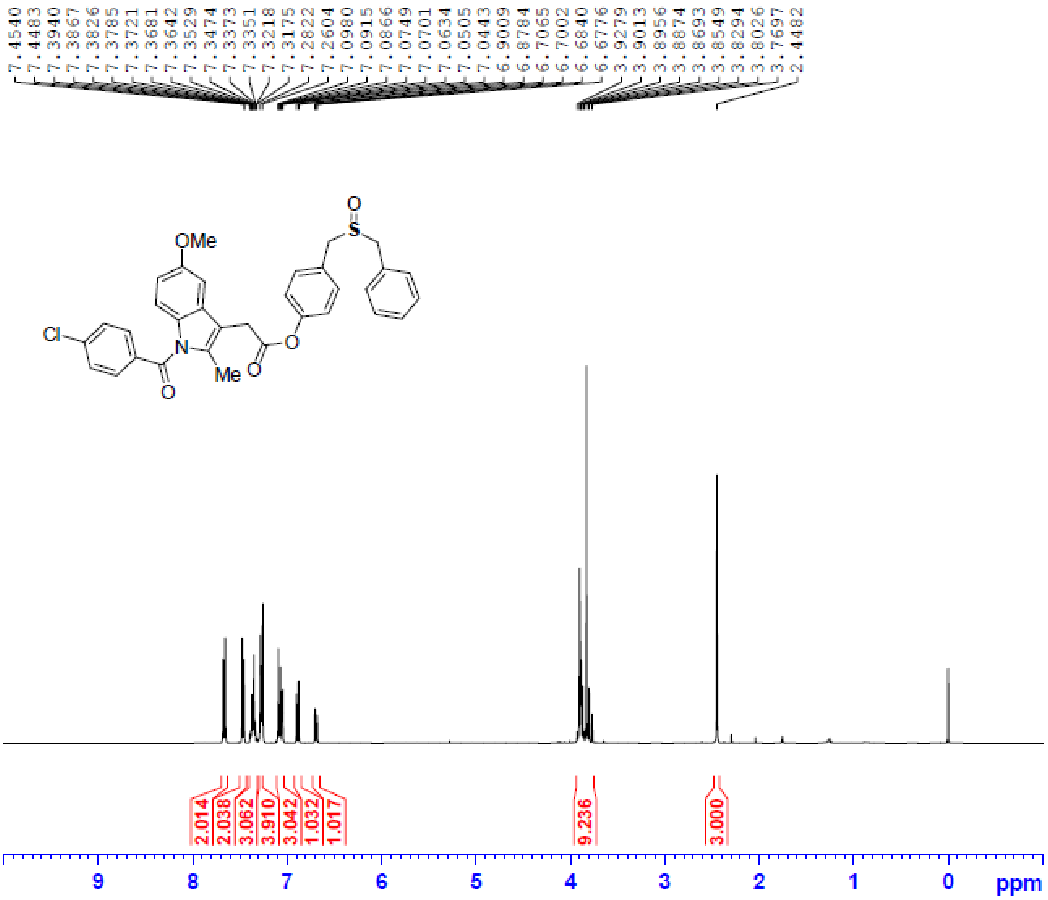
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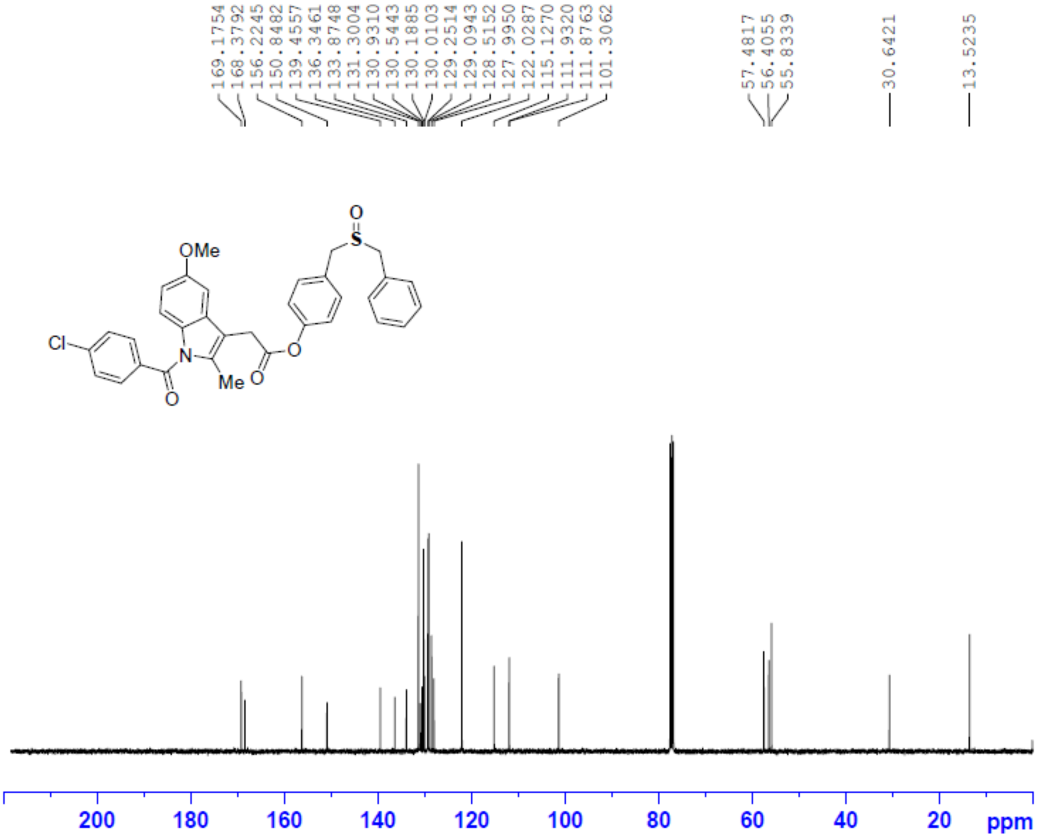
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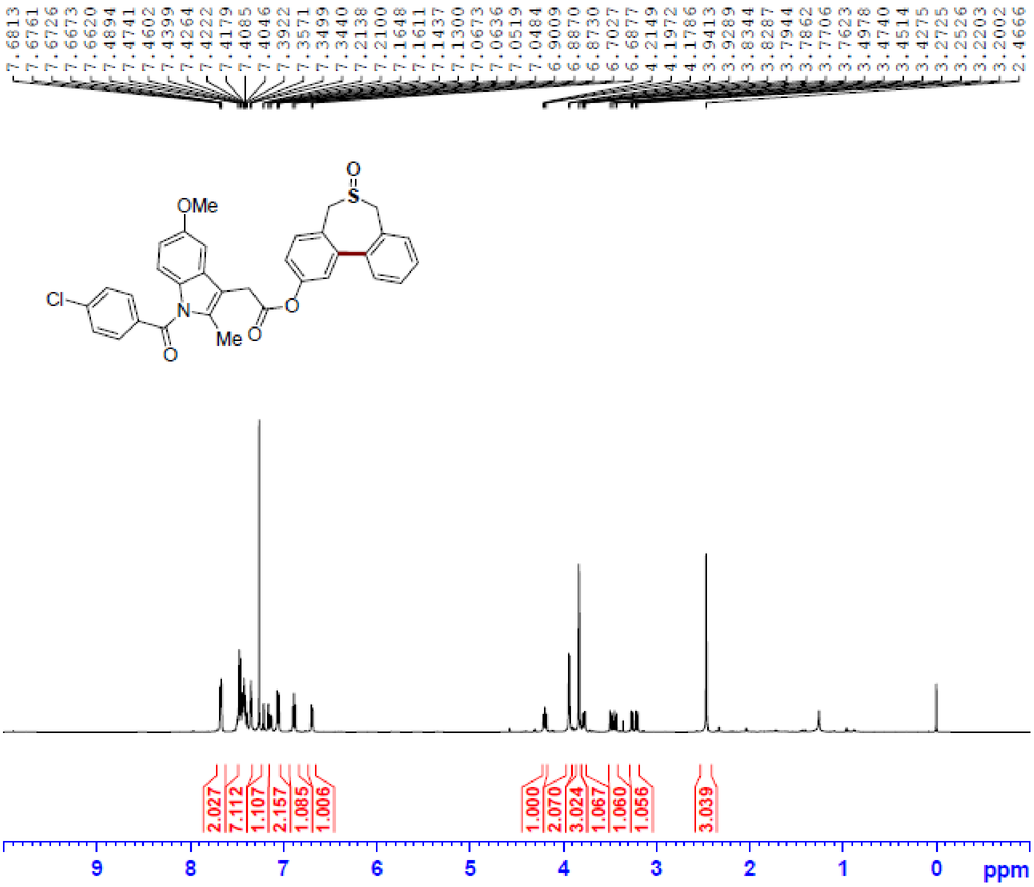
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Cl
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Me
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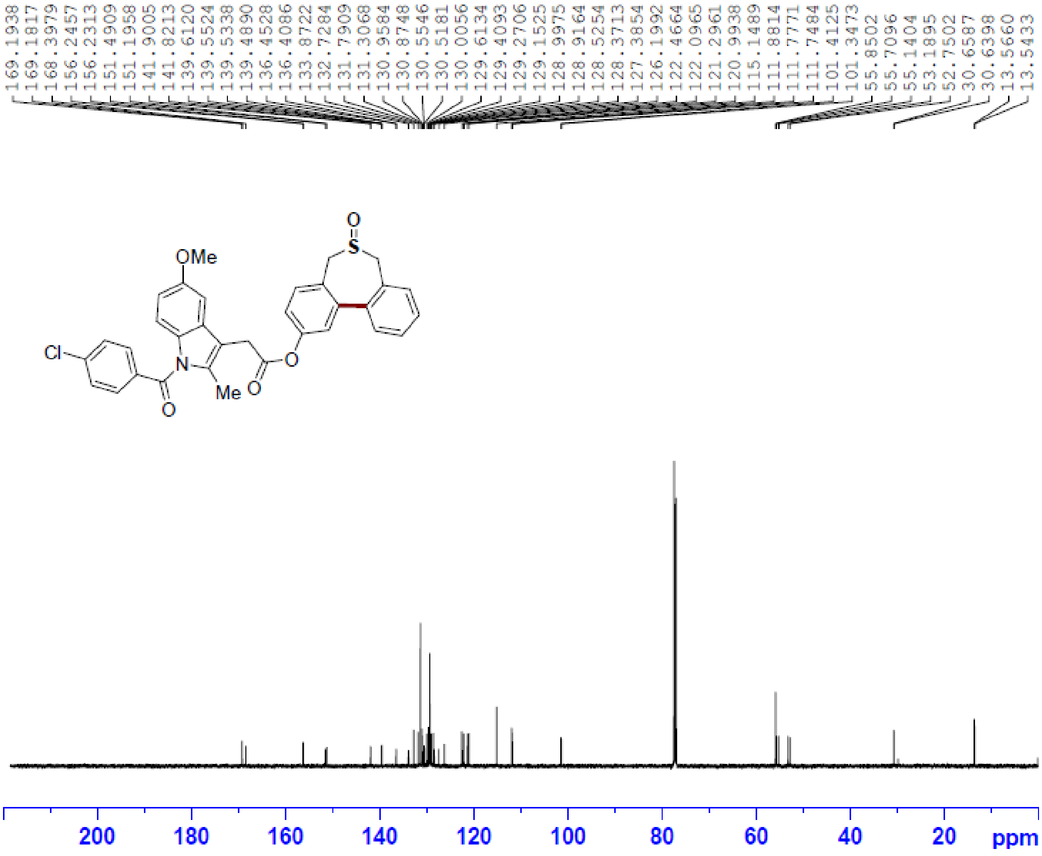
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Me
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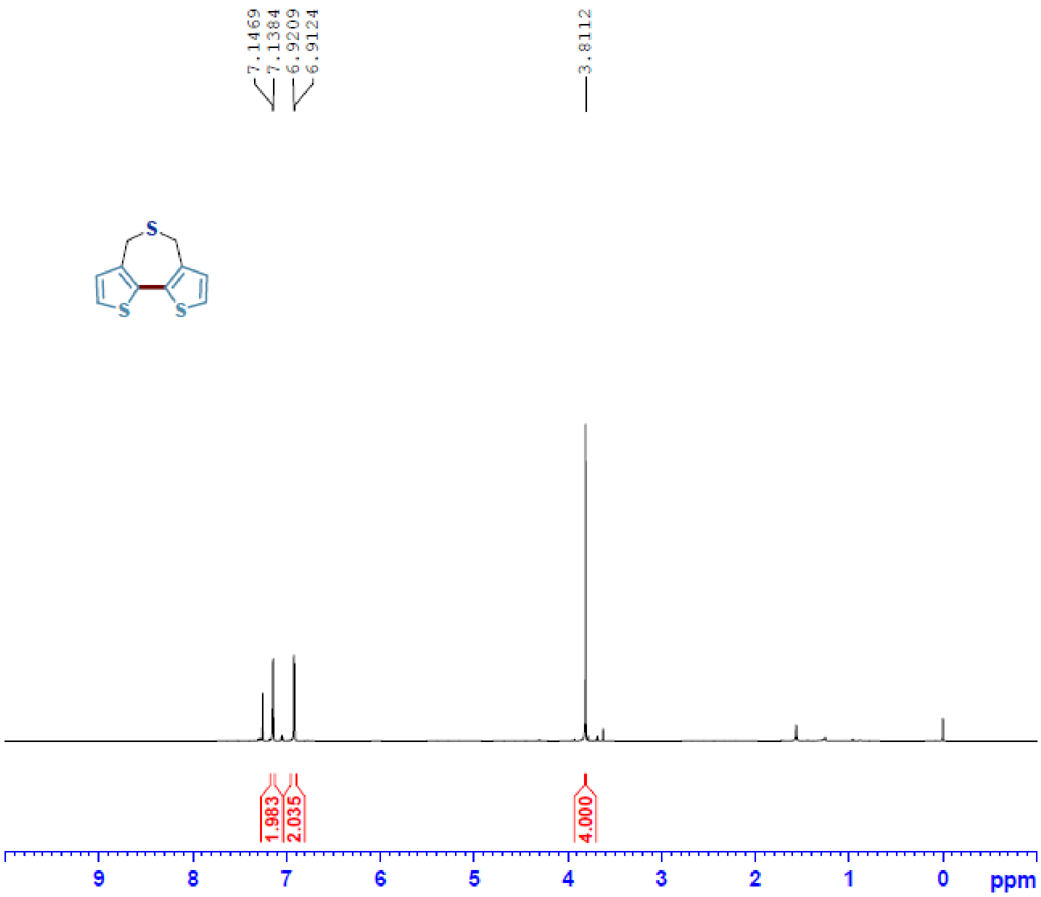
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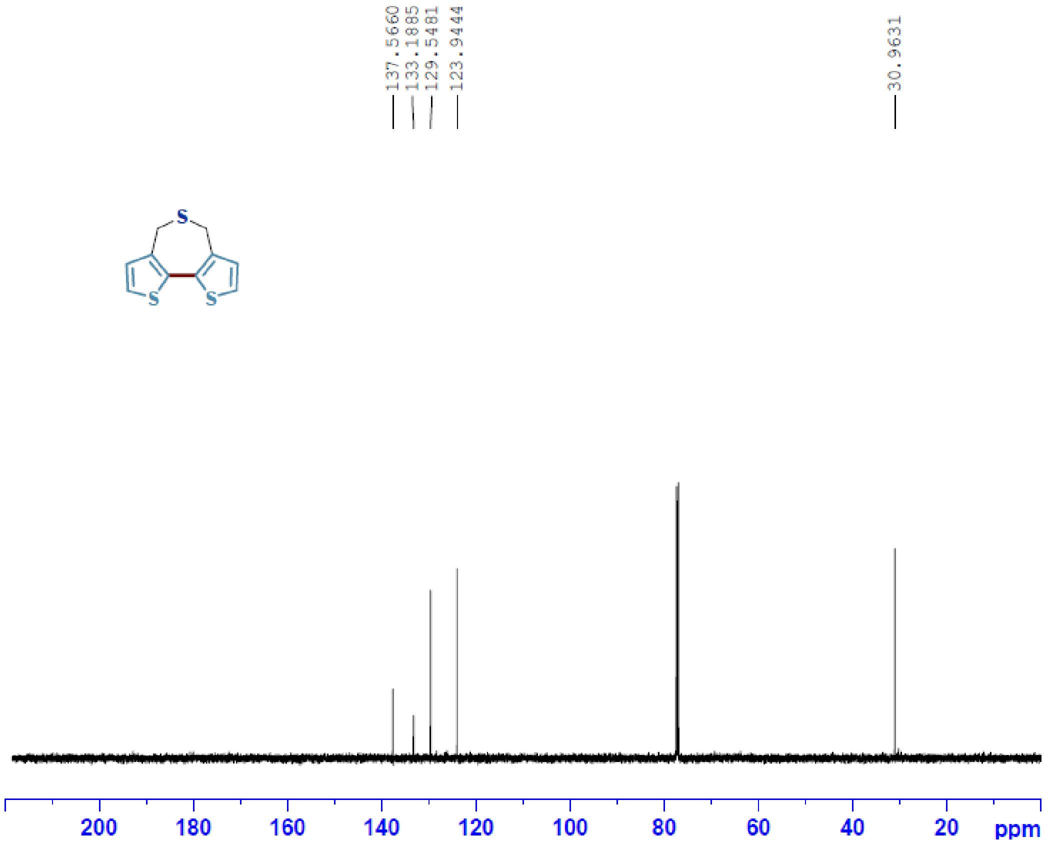
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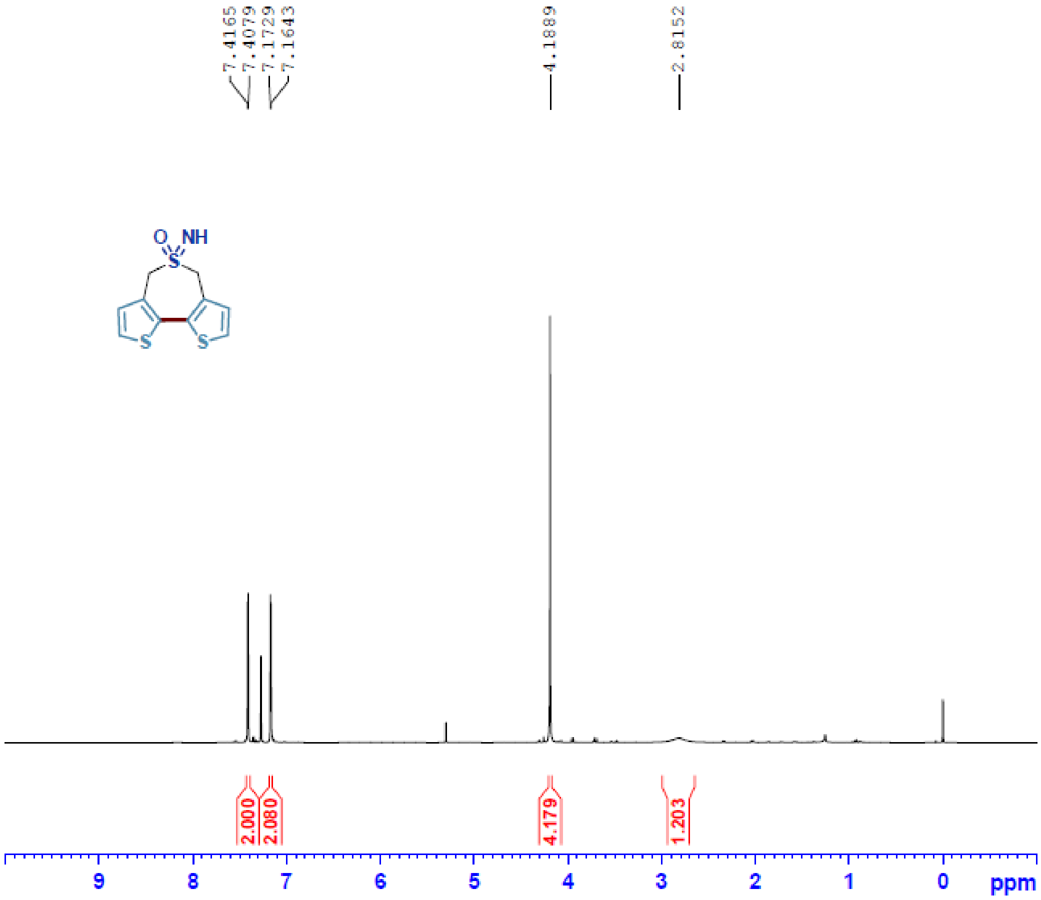
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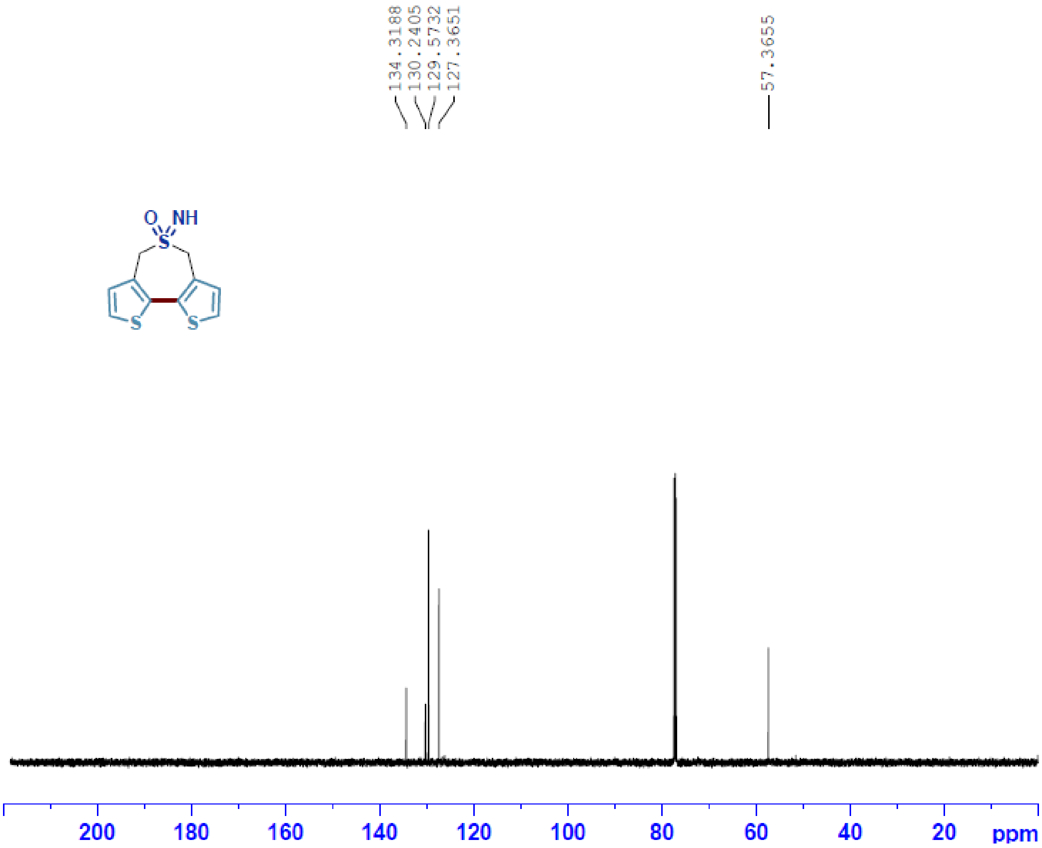
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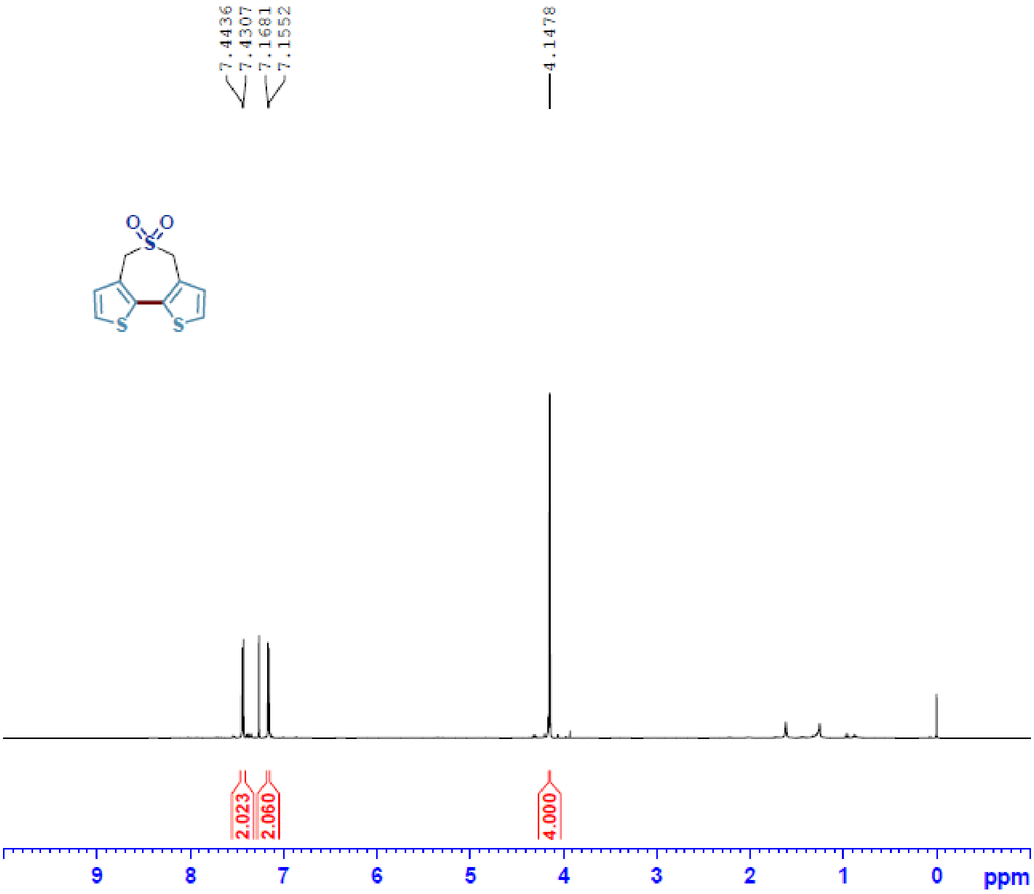
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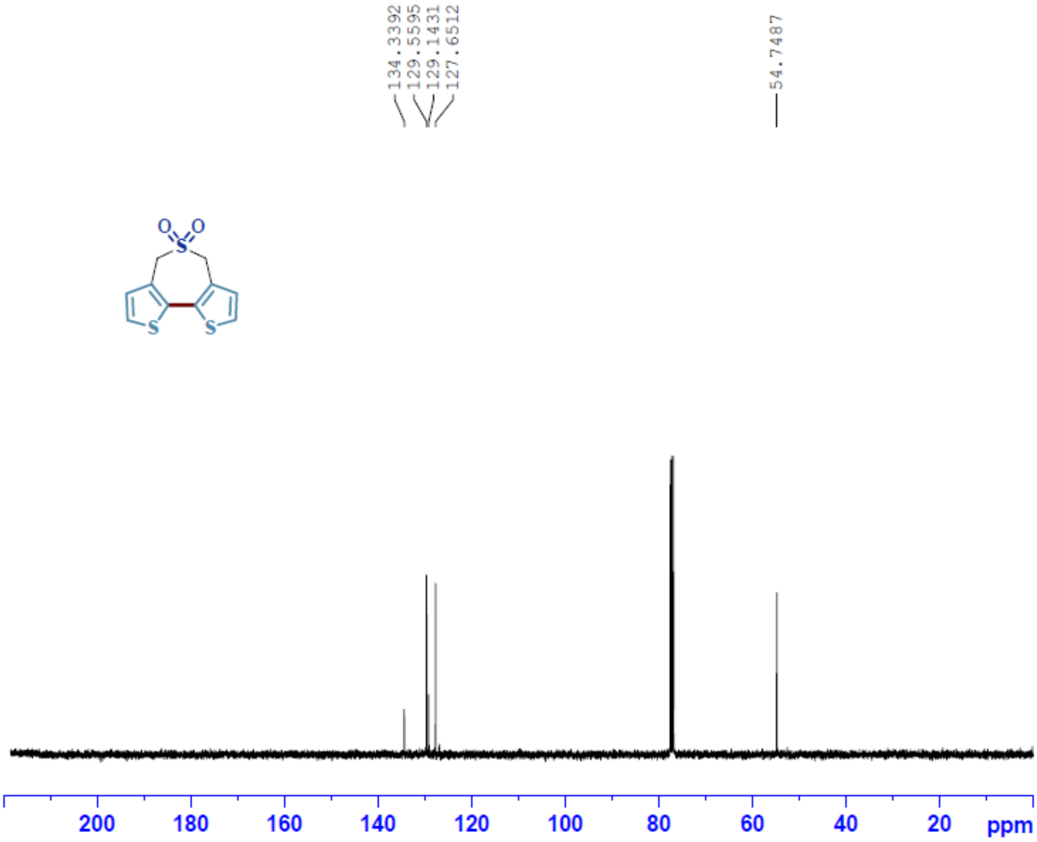
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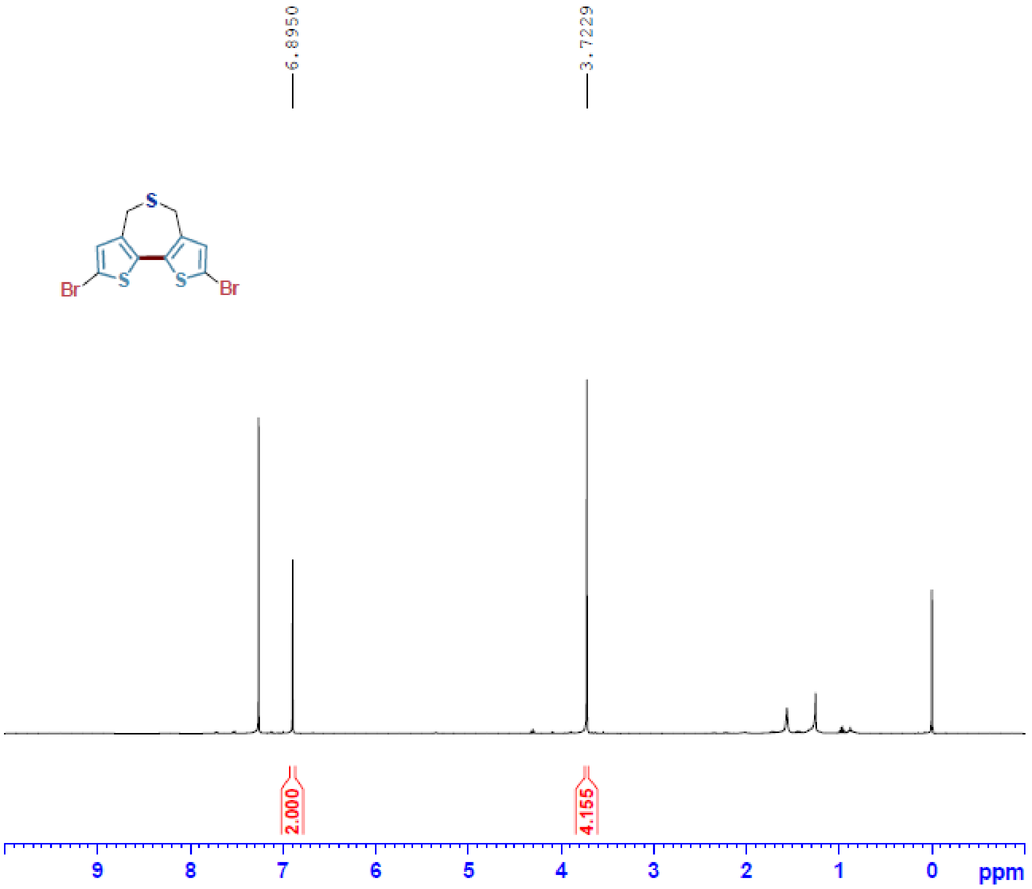
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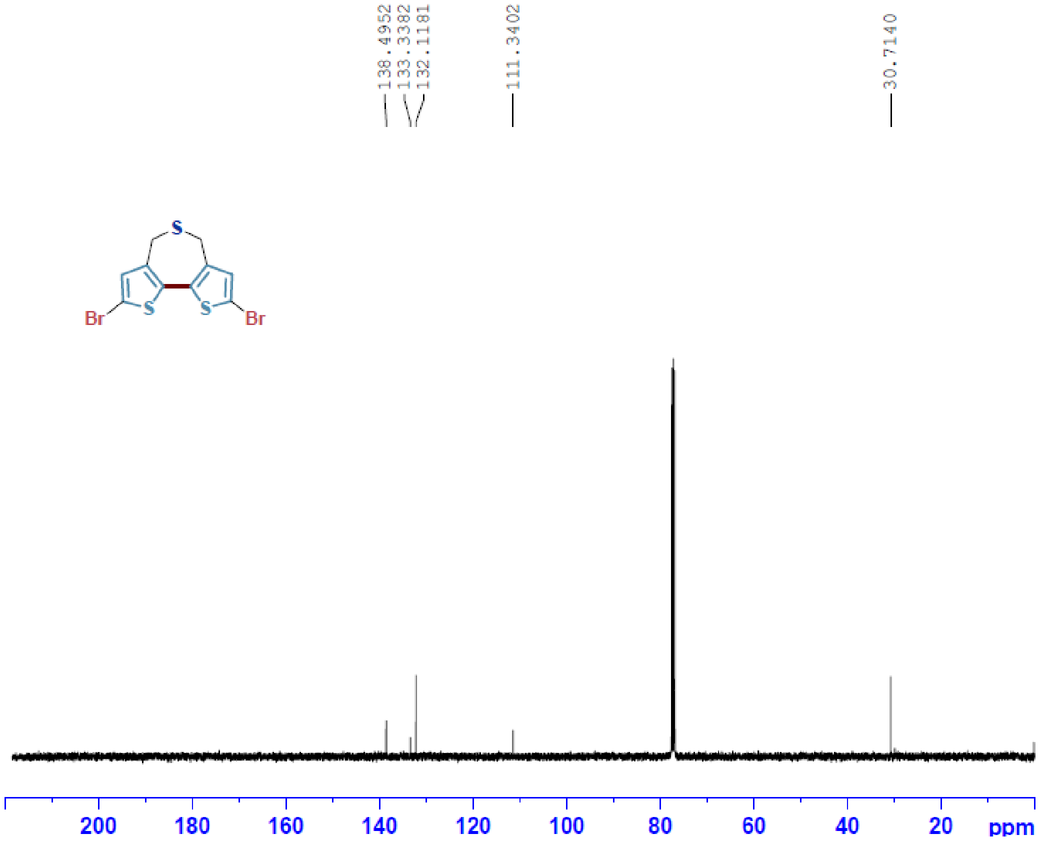
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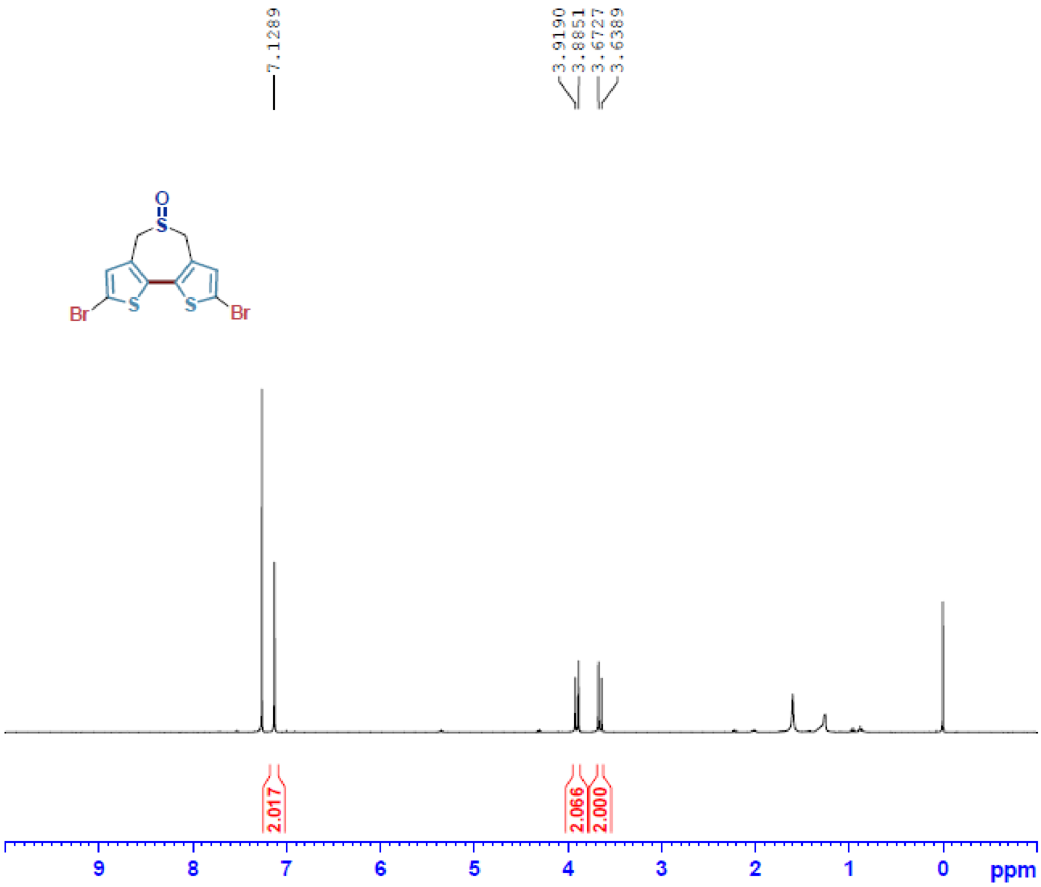
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2.000
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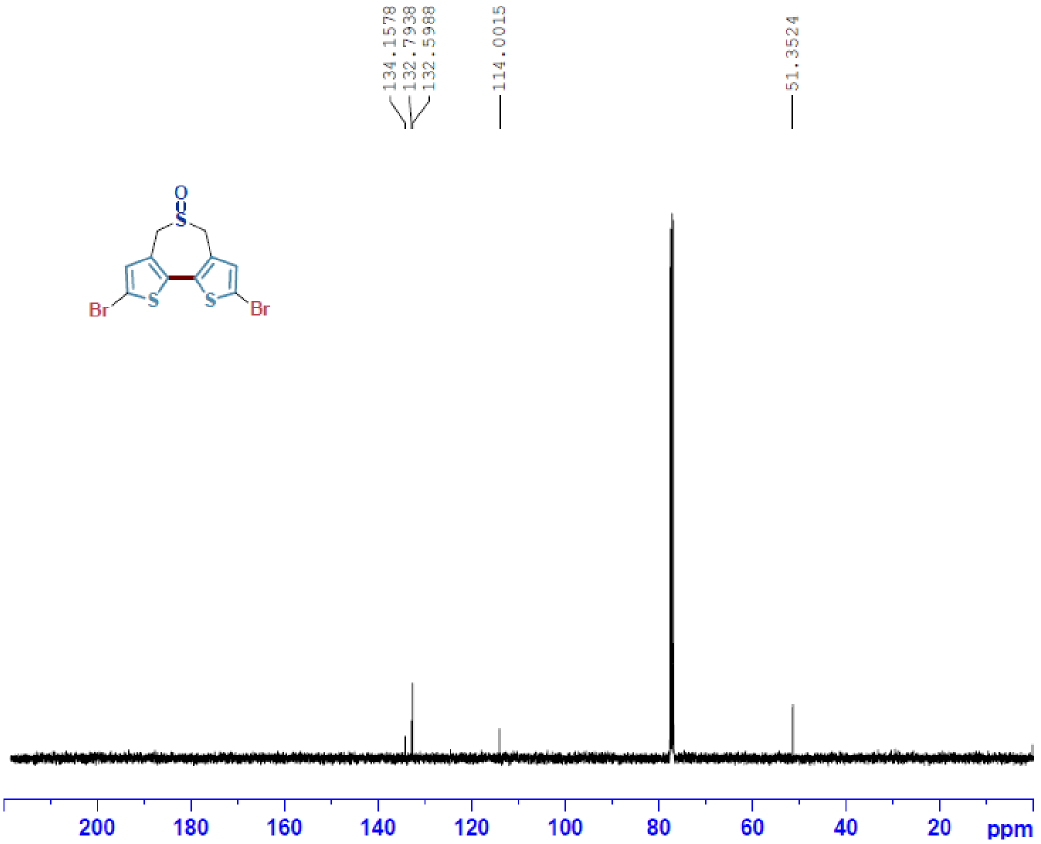
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Br
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60
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20
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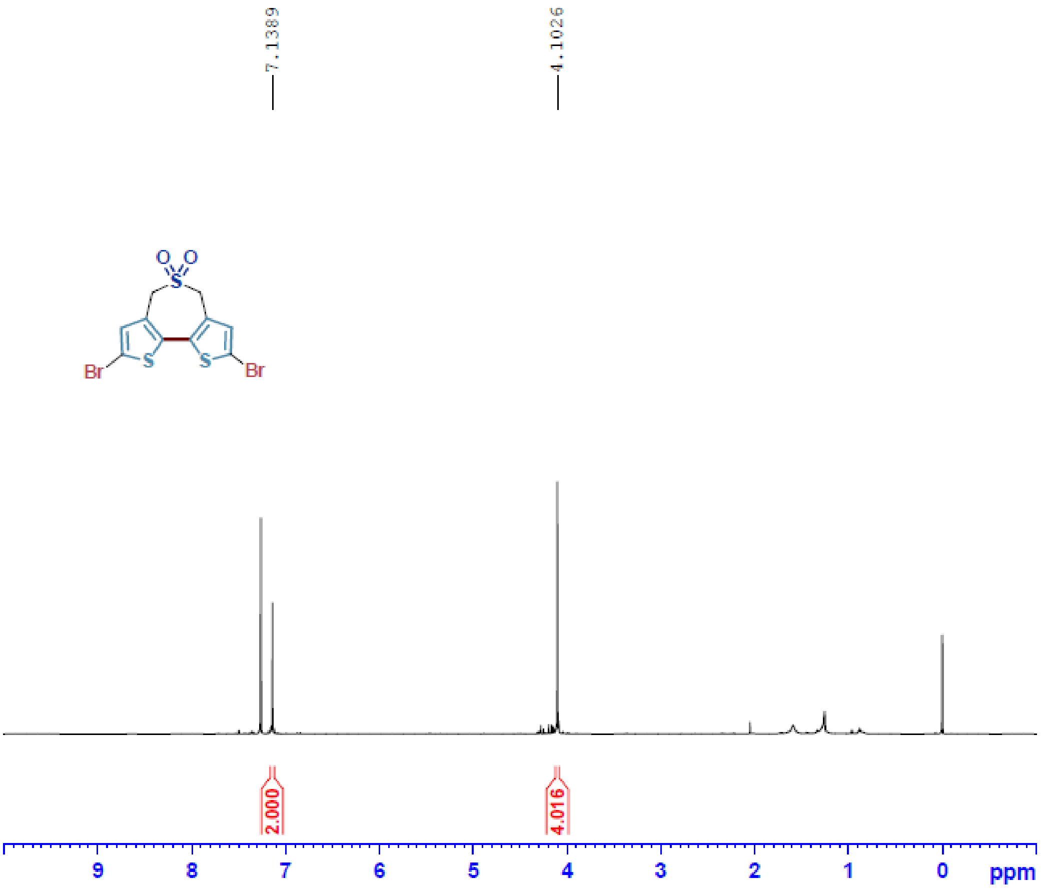
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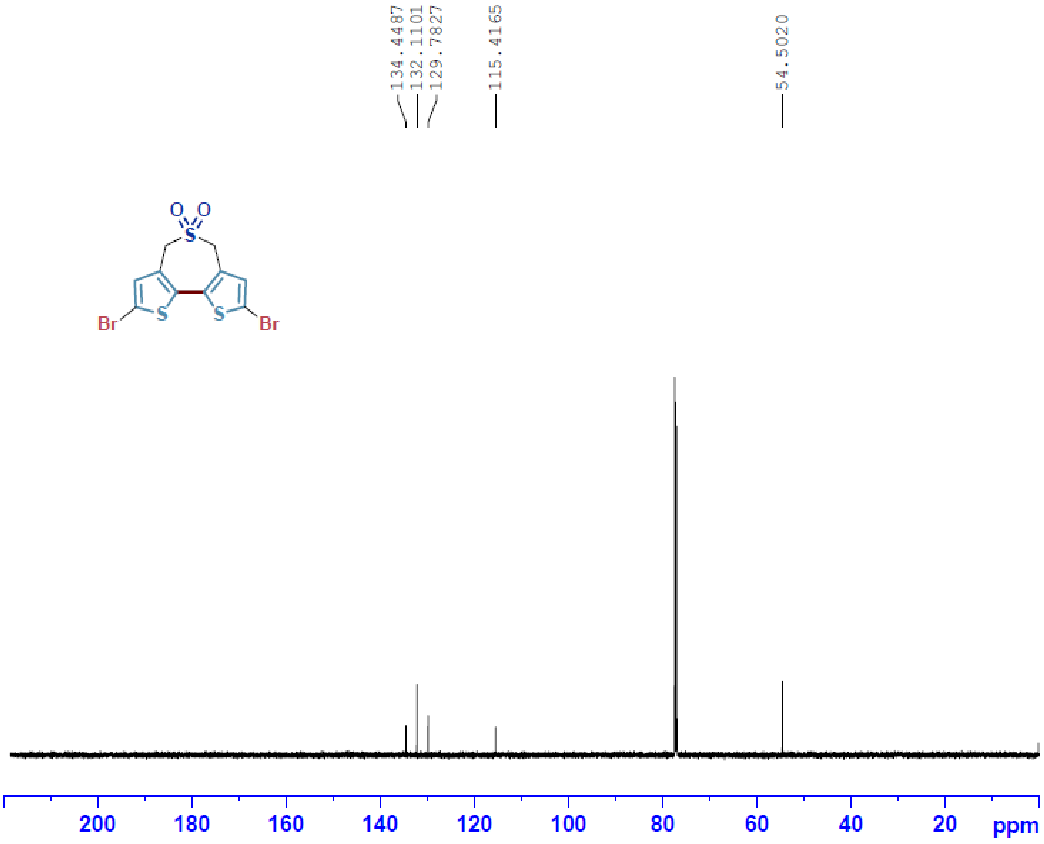
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Br
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Br
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20
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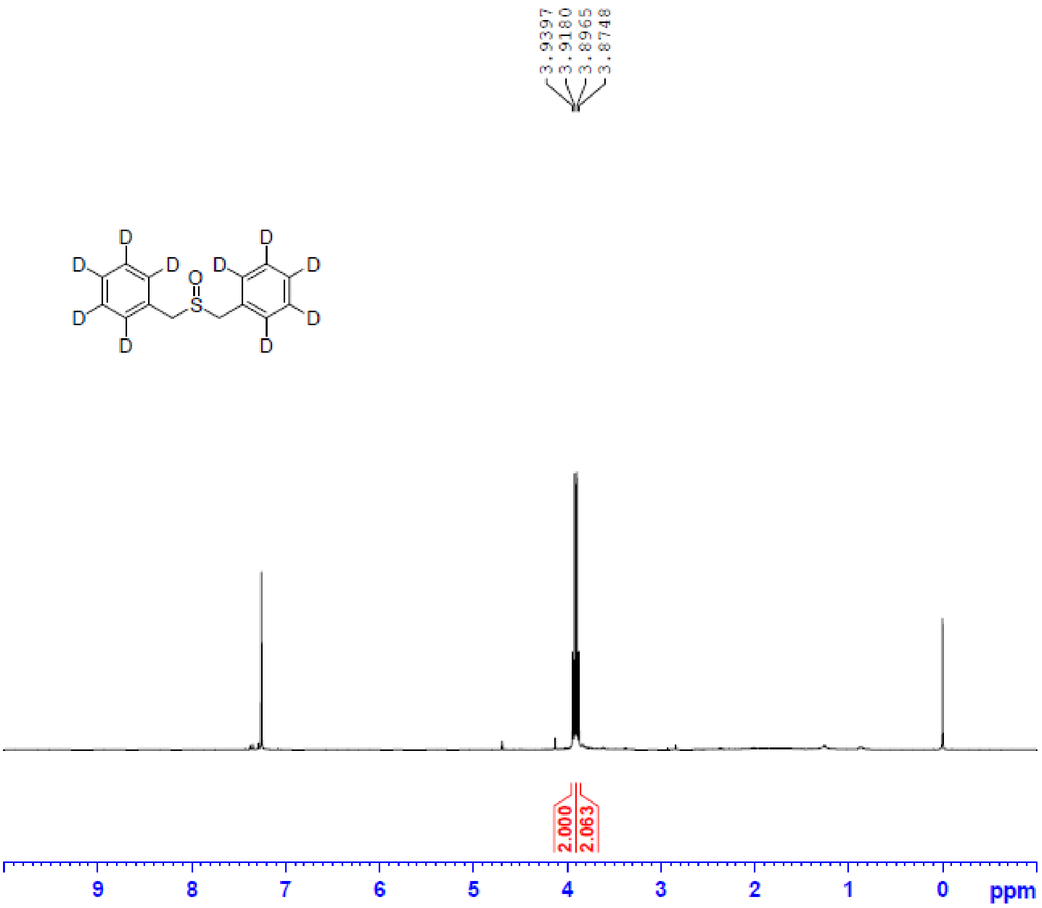
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D
D
D
O
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D
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6
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2
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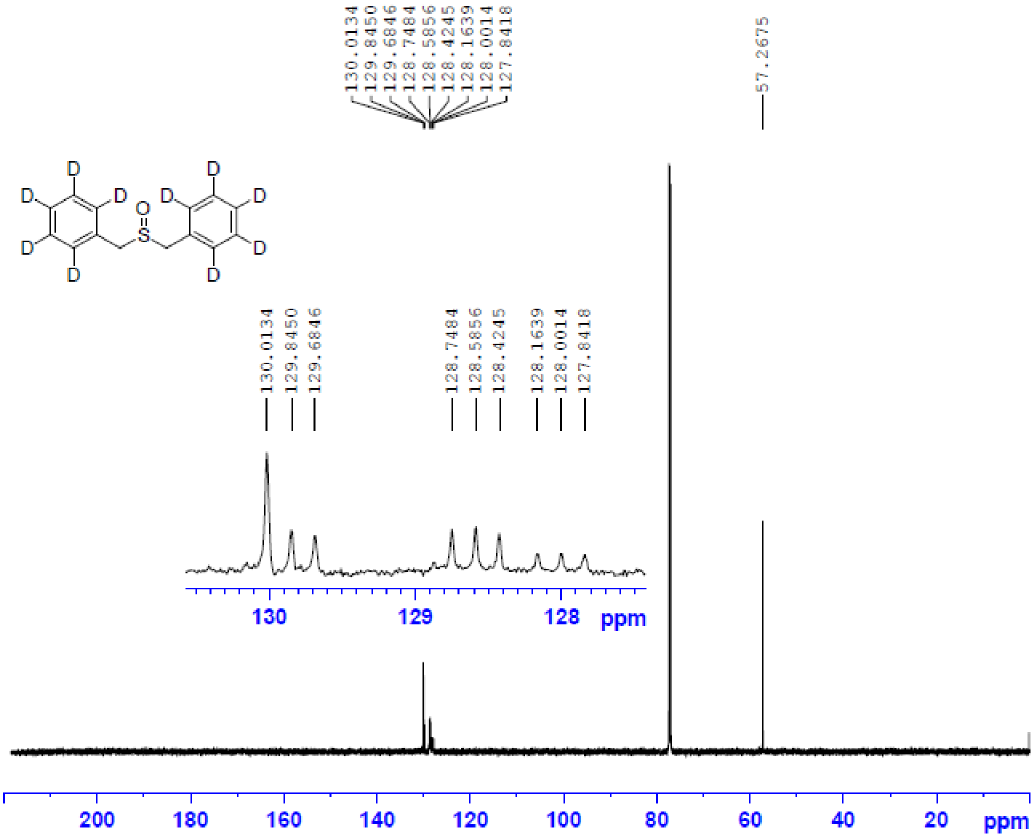
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D
D
D
O
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D
D
D
D
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ppm
200
180
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140
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80
60
40
20
ppm