Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tunable Electrochemical Diverse Sulfurization of Sulfoxonium Ylides with Disulfides

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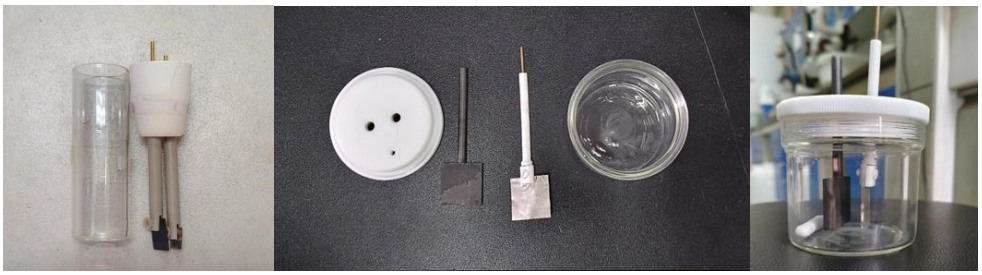
General Remarks

Electrochemical reactions were conducted using an AXIOMET AX-3003P potentiostat in constant current mode using undivided cell equipped with graphite plate (1.0 cm × 1.0 cm × 0.2 cm) as the anode and platinum plate (1.0 cm × 1.0 cm × 0.01 cm) as the cathode under air. Graphite plates are commercially available from Bei Jing Jinglong Special Carbon Technology Co., Ltd. Platinum electrodes are commercially available from Tian Jin Aida (China). Chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H-NMR. TLC: Macherey-Nagel, TLC plates Alugram®Sil G/UV254. Detection under UV light at 254 nm. Chromatography separations were carried out on silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China). High resolution mass spectrometry (HRMS) was measured on Thermo-DFS mass spectrometer (Q Exactive Focus). NMR spectra were recorded on *J*EOL 400 NMR (^{1}H 400 MHz; ^{13}C 100 MHz) in DMSO or $CDCl_3$. If not otherwise specified, chemical shifts (δ) are given in ppm. All sulfides were purchased from TCI, Meryer or Macklin.

The devices of electrochemical reaction

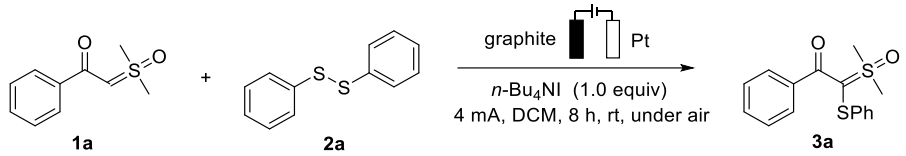


(a) (b)

Figure S1. (a) Equipment of standard reaction; (b) Equipment of gram-scale reaction.

Optimization Studies

Table S1. Optimization of Electrochemical Reaction Conditions[a]

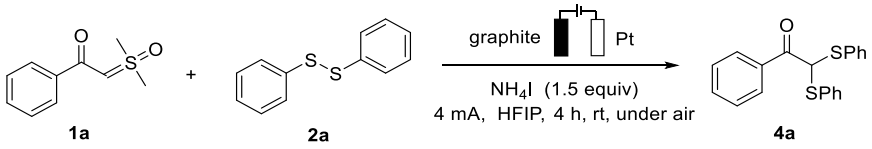


1a 2a 3a

Entry	Deviation from standard conditions	Yield (%)[b]
1	**None**	**82**
2	No current	NR
3	No *n*-Bu$_4$NI	NR
4	*n*-Bu$_4$NBF$_4$ instead of *n*-Bu$_4$NI	Messy
5	*n*-Bu$_4$NPF$_6$ instead of *n*-Bu$_4$NI	31
6	*n*-Bu$_4$NHSO$_4$ instead of *n*-Bu$_4$NI	Messy
7	2 mA	37
8	MeOH as solvent	17
9	MeCN as solvent	60
10	DCM/HFIP (20:1) as solvent	50
11	Graphite instead of Pt	45

[a] Reaction conditions: Undivided cell, graphite anode (1.5 cm × 1.0 cm × 0.2 cm), Pt cathode (1.5 cm × 1.0 cm × 0.01 cm), **1a** (0.5 mmol), **2a** (0.6 mmol), *n*-Bu$_4$NI (0.5 mmol), DCM (6 mL), constant current = 4.0 mA, 8.0 h (2.4 *F*), RT, under air. [b] Yields of isolated products.

Table S2. Optimization of Electrochemical Reaction Conditions[a]



1a 2a 4a

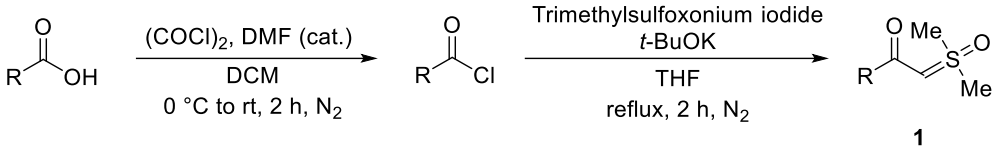
Entry	Deviation from standard conditions	Yield (%)[b]
1	**None**	**73**

2	No current	NR
3	No NH_4I	NR
4	1.0 equiv NH_4I	36
5	2 h	59
6	*n*-Bu_4NI instead of NH_4I	53
7	*n*-Bu_4NPF_6 instead of *n*-Bu_4NI	53
8	*n*-Bu_4NHSO_4 instead of *n*-Bu_4NI	50
9	DCM/HFIP (20:1) instead of HFIP	Trace
10	DCM/HFIP (1:1) instead of HFIP	25
11	MeOH instead of HFIP	NR

[a] Reaction conditions: Undivided cell, graphite anode (1.5 cm × 1.0 cm × 0.2 cm), Pt cathode (1.5 cm × 1.0 cm × 0.01 cm), **1a** (0.5 mmol), **2a** (0.6 mmol), NH_4I (0.75 mmol), HFIP (6 mL), constant current = 4.0 mA, 4.0 h (1.2 *F*), RT, under air. [b] Yields of isolated products.

General Procedure

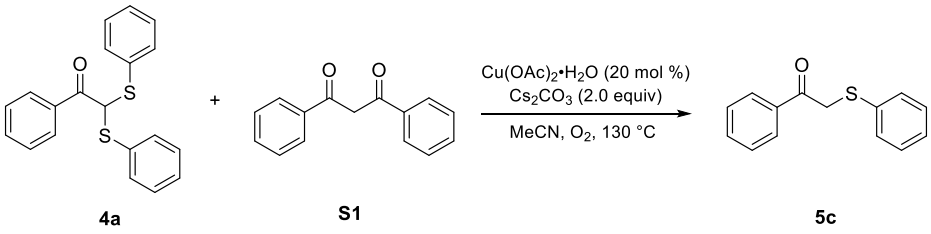
The substrates **1a-1z**[1] were synthesized according to previously described methods as follows.



To a solution of carboxylic acid compound (5.0 mmol, 1.0 equiv) in DCM (30 mL) at 0 °C under N_2 was added dropwise of $(COCl)_2$ (10 mmol, 2.0 equiv) followed by a catalytic amount of dry DMF. The reaction was allowed to stir at room temperature until completion. The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

To a solution of potassium *tert*-butoxide (15 mmol, 3.0 equiv) in anhydrous THF (25 mL) under argon atmosphere, trimethylsulfoxonium iodide (10 mmol; 2.0 equiv) was added. After refluxing at 80 °C for 2 h, the reaction mixture were cooled at 0 °C, followed by slow addition of the crude acid chloride diluted with anhydrous THF. After that, the reaction mixture temperature was naturally increased to room time and stirred overnight. The solvent was then removed on a rotary evaporator. The resulting mixture was added to 60 mL H_2O and extracted with CH_2Cl_2: *i*-PrOH(3:1) mixture (160 mL). After washing with water for three times, the organic phase was dried over Na_2SO_4 and concentrated in vacuo to afford the corresponding sulfoxonium ylides **1a-1z**.

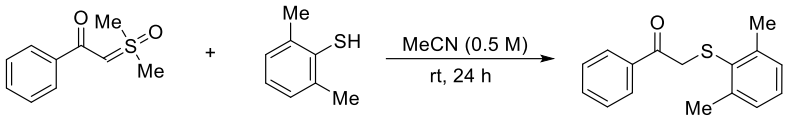
Preparation of **5c** with **4a** and 1,3-diphenylpropane-1,3-dione (**S1**) [2]



To a solution of compound **4a** (2.0 mmol, 673 mg) in 1,3-diphenylpropane-1,3-dione (**S1**) (2.0 mmol, 448 mg), was added Cs_2CO_3 (4.0 mmol, 1.3 g) and $Cu(OAc)_2$ (0.4 mmol, 79.9 mg). The solution was stirred for 24 h at 130 °C. Upon completion, the solvent was removed directly under reduced pressure to afford the crude product, which was further purified by flash column chromatography (PE/EtOAc: 15/1) to give a

yellow liquid **5c** (410 mg, 90%).

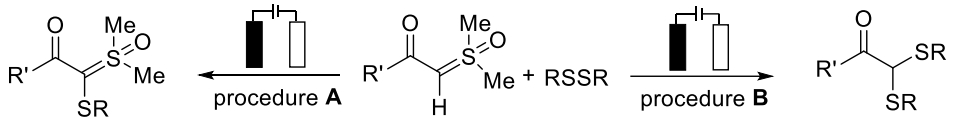
Preparation of **5d** with **1a** and 2,6-dimethylbenzenethiol (**2f**)[3]



1a **2f** **5d**

To a solution of compound **1a** (5.0 mmol, 981 mg) in MeCN (5 mL) was added 2,6-dimethylbenzenethiol (**2f**) (5.0 mmol, 0.67 mL). The reaction mixture was stirred for 24 h at room temperature. Then, the crude compound was purified by flash column chromatography (PE/EA: 15/1) to give a yellow liquid **5d** (833 mg, 65%).

General Procedure for Electrochemical Reactions



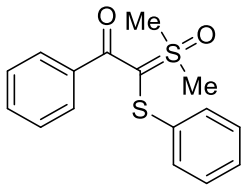
3 **1** **2** **4**

Procedure **A**: In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **1** (0.5 mmol), **2** (0.6 mmol), *n*-Bu_4NI (0.5 mmol, 185 mg) and DCM (6 mL) were added. The cell was equipped with graphite (1.5 cm × 1.0 cm × 0.2 cm) as the anode and platinum plate (1.5 cm × 1.0 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 8 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography afford the desired products **3a**-**3z**.

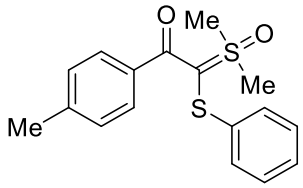
Procedure **B**: In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **1** (0.5 mmol), **2** (0.6 mmol), NH_4I (0.75 mmol, 0.109 mg) and HFIP (6 mL) were added. The cell was equipped with graphite (1.5 cm × 1.0 cm × 0.2 cm) as the anode and platinum plate (1.5 cm × 1.0 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 4 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography afford the desired products **4a-4l**. Notely,

products of **4m**, **4n**, **4o**, and **4p** need to undergo a room-temperature reaction for 4 h.

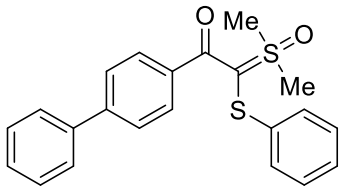
Characterization Data of Products 3a-3z-2、4a-4q、5a-5d and 6-12.



2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenyl-2-(phenylthio)ethan-1-one (3a): Compound **3a** (121 mg, 80%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 90–92 ℃ ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.47 (d, J = 6.9 Hz, 2H), 7.35 – 7.21 (m, 7H), 7.07 (dd, J = 7.2, 7.2 Hz, 1H), 3.73 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.2, 141.8, 140.8, 130.1, 129.6, 127.9, 127.7, 125.6, 124.2, 76.7, 42.0, 41.6. HR-MS (ESI) *m/z* calcd for $C_{16}H_{17}O_2S_2$ $[M+H]^+$ 305.0664, found 305.0665.

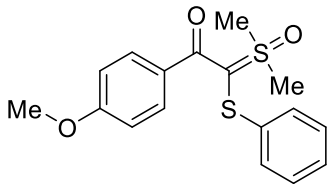


2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)-1-(*p*-tolyl)ethan-1-one (3b): Compound **3b** (92 mg, 58%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as white solid. m.p. 125–127 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.42 (d, J = 7.9 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.21 (m, 2H), 7.11 (dd, J = 7.2, 7.2 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 3.72 (s, 3H), 3.65 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.0, 141.9, 139.8, 137.9, 129.6, 128.5, 127.9, 125.5, 124.2, 76.5, 42.1, 41.8, 21.4. HR-MS (ESI) *m/z* calcd for $C_{17}H_{19}O_2S_2$ $[M+H]^+$ 319.0821, found 319.0820.

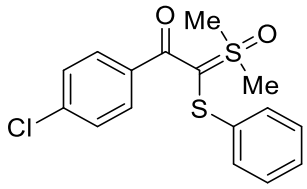


1-([1,1'-Biphenyl]-4-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)ethan-1-on (3c): Compound **3c** (143 mg, 75%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (d, J = 7.3 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.43 (dd, J = 8.3, 6.8 Hz, 2H), 7.36 – 7.25 (m, 5H),

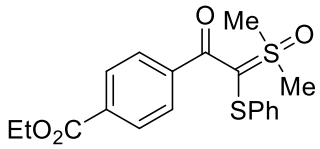
7.15 – 7.11 (m, 1H), 3.75 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D_6) δ 188.7, 141.9, 141.8, 140.0, 139.8, 129.7, 129.5, 128.7, 128.3, 127.3, 126.3, 125.7, 124.3, 76.9, 42.1, 41.7. HR-MS(ESI) *m/z* calcd for $C_{22}H_{21}O_2S_2$ $[M+H]^+$ 381.0970, found 381.0977.



2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-methoxyphenyl)-2-(phenylthio)ethan-1-one (3d): Compound **3d** (102 mg, 61%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 80–82 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.56 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 2H), 7.12 (dd, *J* = 7.2, 7.2 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.71 (d, *J* = 2.2 Hz, 6H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.1, 161.1, 142.0, 132.7, 130.0, 129.6, 125.6, 124.2, 113.2, 76.1, 55.7, 42.1, 41.8. HR-MS(ESI) *m/z* calcd for $C_{17}H_{19}O_3S_2$ $[M+H]^+$ 335.0770, found 335.0771.

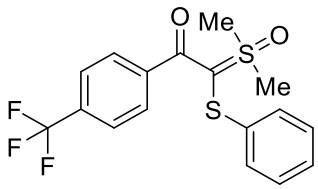


1-(4-Chlorophenyl)-2-(dimethyl(oxo)- λ^6-sulfaneylidene)-2-(phenylthio)ethan-1-one (3e): Compound **3e** (122 mg, 72%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.49 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.08 (dd, *J* = 8.0, 8.0, 1H), 3.70 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.8, 141.5, 139.6, 134.7, 129.7, 129.6, 128.1, 125.7, 124.2, 77.1, 41.9, 41.5. HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClO_2S_2$ $[M+H]^+$ 339.0275, found 339.0273.

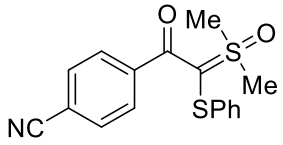


Ethyl 4-(2-(dimethyl(oxo)- λ^6-sulfaneylidene)-2-(phenylthio)acetyl)benzoate (3f): Compound **3f** (134 mg, 71%) (PE/EA = 1/2) was prepared using the general procedure

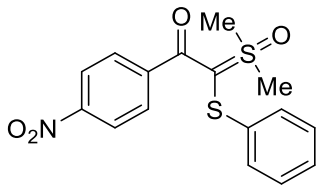
A and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.94 (d, J = 7.3 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.43 – 7.21 (m, 5H), 4.40 – 4.35 (m, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-D_6) δ 188.5, 166.0, 145.7, 141.5, 131.0, 129.7, 129.0, 127.9, 125.8, 124.4, 77.6, 61.5, 42.0, 41.6, 14.8. HR-MS (ESI) *m/z* calcd for $C_{19}H_{21}O_4S_2$ $[M+H]^+$ 377.0876, found 377.0868.



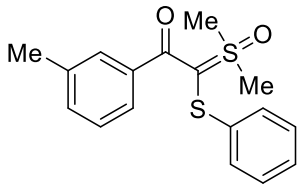
2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)-1-(4-(trifluoromethyl)phenyl) ethan-1-one (3g): Compound **3g** (150 mg, 81%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 80–82 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.63 (d, J = 2.4 Hz, 4H), 7.32 – 7.27 (m, 2H), 7.24 – 7.21 (m, 2H), 7.15 – 7.10 (m, 1H), 3.78 (d, J = 2.4 Hz, 3H), 3.68 (d, J = 2.5 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.9, 145.1, 141.3, 129.9 (q, $^{2}J_{C\text{-}F}$ = 31.6 Hz), 129.7, 128.3, 125.8, 125.1 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.5 (d, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 124.2, 123.2, 77.5, 41.9, 41.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.8 (s). HR-MS (ESI) *m/z* calcd for $C_{17}H_{16}F_3O_2S_2$ $[M+H]^+$ 373.0538, found 373.0535.



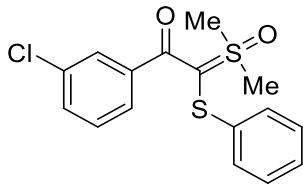
4-(2-(Dimethyl(oxo)- λ^6-sulfaneylidene)-2-(phenylthio)acetyl)benzonitrile (3h): Compound **3h** (135 mg, 82%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.75 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.21 (dd, J = 8.4, 1.0 Hz, 2H), 7.18 – 7.08 (m, 1H), 3.76 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, DMSO-D_6) δ 187.5, 145.6, 141.2, 132.2, 129.7, 128.4, 125.9, 124.4, 119.1, 112.4, 77.8, 41.9, 41.5. HR-MS (ESI) *m/z* calcd for $C_{17}H_{16}NO_2S_2$ $[M+H]^+$ 330.0617, found 330.0611.



2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-nitrophenyl)-2-(phenylthio)ethan-1-one (3i): Compound **3i** (129 mg, 74%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.13 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.22 – 7.20 (m, 2H), 7.13 (dd, J = 7.6, 6.8 Hz, 1H) 3.79 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.3, 148.1, 147.5, 141.1, 129.7, 128.7, 125.9, 124.3, 123.4, 77.8, 41.8, 41.3. HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}NO_4S_2$ $[M+H]^+$ 350.0515, found 350.0516.

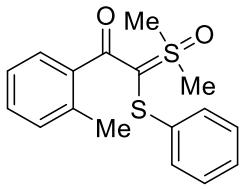


2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)-1-(*m*-tolyl)ethan-1-one (3j): Compound **3j** (105 mg, 66%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as colorless liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.31 (dd, J = 8.0, 7.6 Hz, 2H), 7.25 – 7.21 (m, 4H), 7.15 – 7.09 (m, 3H), 3.72 (s, 3H), 3.65 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.5, 141.9, 140.9, 136.9, 130.7, 129.5, 128.4, 127.8, 125.6, 124.8, 124.3, 76.7, 41.9, 41.6, 21.4. HR-MS (ESI) *m/z* calcd for $C_{17}H_{19}O_2S_2$ $[M+H]^+$ 319.0821, found 319.0818.

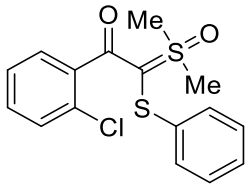


1-(3-Chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)ethan-1-one (3k): Compound **3k** (96 mg, 57%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.45 – 7.36 (m, 3H), 7.33 – 7.28 (m, 3H), 7.23 (d, J = 7.7 Hz, 2H), 7.13 (dd, J = 7.6, 7.2 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.3, 142.9, 141.4, 132.6, 130.1, 129.8, 129.6, 127.5, 126.2, 125.7, 124.3, 77.3, 41.8, 41.5. HR-MS (ESI)

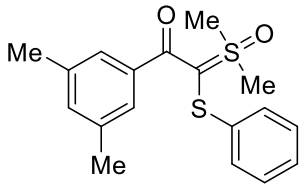
m/z calcd for $C_{16}H_{16}ClO_2S_2$ $[M+H]^+$ 339.0275, found 339.0271.



2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)-1-(*o*-tolyl)ethan-1-one (3l): Compound **3l** (115 mg, 75%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.26 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.06 (m, 3H), 6.97 (d, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 3.65 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.5, 142.2, 141.5, 134.2, 130.3, 129.4, 128.3, 125.9, 125.5, 125.1, 124.3, 77.5, 42.0, 41.4, 19.3. HR-MS (ESI) *m/z* calcd for $C_{17}H_{19}O_2S_2$ $[M+H]^+$ 319.0821, found 319.0820.

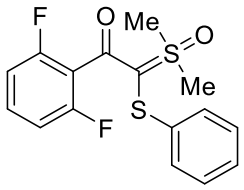


1-(2-Chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)ethan-1-one (3m): Compound **3m** (128 mg, 76%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 115–117 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.21 – 7.07 (m, 5H), 3.77 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 187.7, 141.5, 141.0, 130.0, 129.9, 129.5, 129.4, 127.7, 126.9, 125.6, 124.4, 77.5, 41.8, 41.2. HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClO_2S_2$ $[M+H]^+$ 339.0274, found 339.0279.

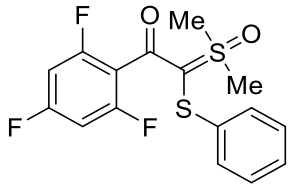


2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(3,5-dimethylphenyl)-2-(phenylthio)ethan-1-one (3n): Compound **3n** (99 mg, 60%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 2H), 7.15 – 7.11 (m, 1H), 7.02 (s, 2H), 6.95 (s, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 2.12 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.8, 142.1,

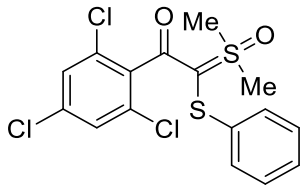
140.9, 136.8, 131.4, 129.5, 125.61, 125.58, 124.4, 76.7, 41.9, 41.6, 21.3. HR-MS (ESI) *m/z* calcd for $C_{18}H_{21}O_2S_2$ $[M+H]^+$ 333.0977, found 333.0975.



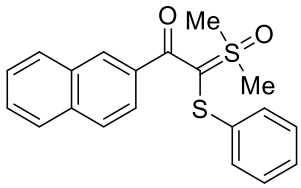
1-(2,6-Difluorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)ethan-1-one (3o): Compound **3o** (139 mg, 82%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 123–125 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.34 – 7.16 (m, 5H), 7.14 – 6.99 (m, 2H), 6.94 (d, J = 9.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 180.8, 159.2 (d, $^1J_{C\text{-}F}$ = 246.7 Hz), 158.7 (d, $^1J_{C\text{-}F}$ = 246.1 Hz), 140.3, 130.7 (d, $^2J_{C\text{-}F}$ = 39.5 Hz), 129.4, 125.8, 124.5, 119.8 (t, $^2J_{C\text{-}F}$ = 24.1 Hz), 112.0 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 79.9, 41.7, 41.3. ^{19}F NMR (376 MHz, DMSO-d_6) δ -113.7 (s), -114.4 (s). HR-MS (ESI) *m/z* calcd for $C_{16}H_{15}F_2O_2S_2$ $[M+H]^+$ 341.0476, found 341.0476.



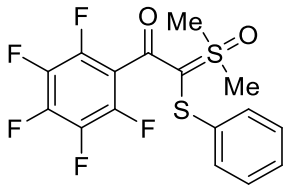
2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)-1-(2,4,6-trifluorophenyl)ethan-1-one (3p): Compound **3p** (133 mg, 74%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.25 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.4 Hz, 2H), 7.05 – 7.00 (m, 1H), 3.74 (d, J = 29.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 179.8, 162.1 (d, $^1J_{C\text{-}F}$ = 248.7 Hz), 159.2 (d, $^1J_{C\text{-}F}$ = 233.3 Hz), 140.2, 129.4, 125.9, 124.5, 116.6 (d, $^2J_{C\text{-}F}$ = 24.2 Hz) 101.0 (m), 79.8, 41.6, 41.3. ^{19}F NMR (376 MHz, DMSO-d_6) δ -108.0 (m), -110.6 (s), -111.6(s). HR-MS (ESI) *m/z* calcd for $C_{16}H_{14}F_3O_2S_2$ $[M+H]^+$ 359.0382, found 359.0383.



2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)-1-(2,4,6-trichlorophenyl) ethan-1-one (3q): Compound **3q** (173 mg, 85%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as white solid. m.p. 80–82 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.56 (d, *J* = 41.8 Hz, 2H), 7.26 – 7.22 (m, 4H), 7.13 – 7.07 (m, 1H), 3.77 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 183.2, 139.9, 139.2, 133.6, 132.8, 132.2, 129.3, 128.5, 128.1, 125.9, 125.2, 78.7, 41.6, 40.9. HR-MS (ESI) *m/z* calcd for $C_{16}H_{14}Cl_3O_2S_2$ $[M+H]^+$ 406.9495, found 406.9498.

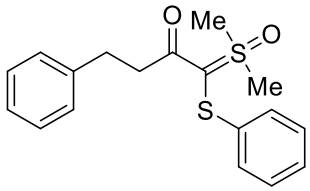


2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(naphthalen-2-yl)-2-(phenylthio)ethan-1-one (3r): Compound **3r** (110 mg, 62%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.02 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.34 – 7.23 (m, 4H), 7.13 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.2, 141.8, 138.3, 133.9, 132.4, 129.58, 129.59, 128.9, 128.0, 127.4, 127.3, 126.9, 125.7, 125.5, 124.3, 77.1, 42.0, 41.6. HR-MS (ESI) *m/z* calcd for $C_{20}H_{19}O_2S_2$ $[M+H]^+$ 355.0821, found 355.0817.



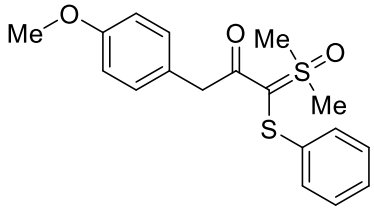
2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(perfluorophenyl)-2-(phenylthio)ethan-1-one (3s): Compound **3s** (136 mg, 69%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 116–118 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.30 – 7.24 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.13 (dd, *J* = 7.6, 7.2 Hz,

1H), 3.81 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.4, 144.5 (d, $^{1}J_{C-F}$ = 253.8 Hz), 139.6, 137.1 (d, $^{1}J_{C-F}$ = 249.4 Hz), 129.5, 126.2, 124.8, 117.1 (t, $^{2}J_{C-F}$ = 21.8 Hz), 81.4, 41.4, 41.0. ^{19}F NMR (376 MHz, DMSO-d_6) δ -141.9 (d, J = 30.8 Hz), -143.6 (d, J = 20.7 Hz), -154.6 (t, J = 21.8 Hz), -161.7 (m). HR-MS (ESI) *m/z* calcd for $C_{16}H_{12}F_5O_2S_2$ $[M+H]^+$ 395.0193, found 395.0192.

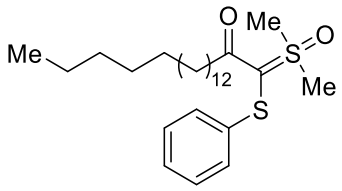


1-(Dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenyl-1-(phenylthio)butan-2-one (3t)

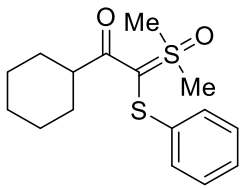
Compound **3t** (121 mg, 73%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.27 (d, J = 7.5 Hz, 2H), 7.19 (dd, J = 7.4, 2.2 Hz, 4H), 7.15 – 7.06 (m, 4H), 3.63 (s, 3H), 3.56 (s, 3H), 2.86 (ddd, J = 14.6, 9.4, 5.9 Hz, 1H), 2.78 – 2.72 (m, 2H), 2.60 – 2.51 (m, 1H). ^{13}C NMR (100 MHz, DMSO-D_6) δ = 192.7, 142.4, 141.2, 129.6, 128.8, 128.7, 126.2, 125.6, 124.2, 75.1, 42.2, 41.8, 31.3. HR-MS (ESI) m/z calcd for $C_{18}H_{20}O_2S_2$ $[M^+H]^+$ 333.0977, found 333.0962.



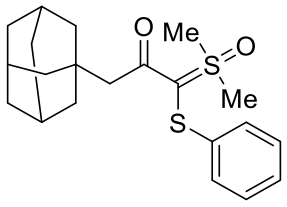
1-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-(4-methoxyphenyl)-1-(phenylthio)propan-2-one (3u): Compound **3u** (145 mg, 83%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 7.17 – 7.12 (m, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.77 – 6.73 (m, 2H), 3.68 (s, 3H), 3.61 (s, 3H), 3.55 (s, 3H), 3.38 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.7, 158.1, 141.2, 130.8, 129.6, 129.2, 125.7, 124.2, 113.9, 75.4, 55.5, 43.1, 42.1, 41.7. HR-MS (ESI) *m/z* calcd for $C_{18}H_{21}O_3S_2$ $[M+H]^+$ 349.0927, found 349.0930.



1-(Dimethyl(oxo)-λ^6-sulfaneylidene)-1-(phenylthio)nonadecan-2-one (3v): Compound **3v** (119 mg, 50%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as yellow solid. m.p. 75–77 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 – 7.25 (m, 2H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.12 (dd, 1H), 3.53 (s, 3H), 3.48 (s, 3H), 2.75 – 2.40 (m, 2H), 1.60 – 1.52 (m, 2H), 1.25 – 1.21 (m, 28H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 140.7, 129.2, 125.5, 124.3, 74.8, 43.2, 42.9, 41.1, 37.8, 32.0, 29.80, 29.76, 29.60, 29.57, 29.5, 25.5, 22.8, 14.2. HR-MS (ESI) *m/z* calcd for $C_{27}H_{47}O_2S_2$ $[M+H]^+$ 467.3012, found 467.3003.

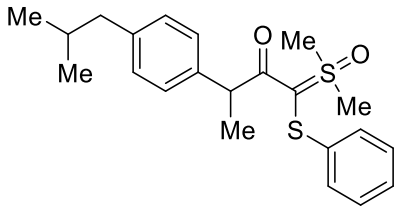


1-Cyclohexyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-2-(phenylthio)ethan-1-one (3w): Compound **3w** (78 mg, 50%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.33 – 7.28 (m, 2H), 7.24 – 7.20 (m, 2H), 7.15 – 7.10 (m, 1H), 3.59 (s, 3H), 3.52 (s, 3H), 2.90 (tt, *J* = 11.2, 3.6 Hz, 1H), 1.70 – 1.52 (m, 4H), 1.37 – 0.97 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 197.1, 141.8, 129.6, 125.6, 124.2, 74.2, 44.3, 42.2, 41.8, 30.1, 29.2, 26.1, 26.1, 25.9. HR-MS (ESI) *m/z* calcd for $C_{16}H_{23}O_2S_2$ $[M+H]^+$ 311.1134, found 311.1132.

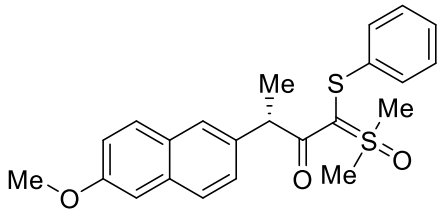


3-(Adamantan-1-yl)-1-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(phenylthio)propan-2-one (3x): Compound **3x** (150 mg, 80%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.33 – 7.28 (m, 2H), 7.22 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 3.61 (s, 3H), 3.53 (s, 3H),

2.57 (d, J = 12.9 Hz, 1H), 1.88 – 1.81 (m, 4H), 1.66 – 1.59 (m, 6H), 1.58 – 1.49 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.0, 141.7, 129.5, 125.6, 124.3, 77.2, 49.8, 42.9, 42.5, 42.1, 33.9, 28.7. HR-MS (ESI) *m/z* calcd for $C_{21}H_{29}O_2S_2$ $[M+H]^+$ 377.1603, found 377.1606.

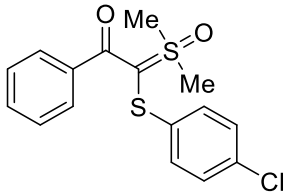


1-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-(4-isobutylphenyl)-1-(phenylthio)butan-2-one (3y): Compound **3y** (157 mg, 81%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as white solid. m.p. 97–99 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.38 – 7.33 (m, 1H), 7.30 – 7.26 (m, 1H), 7.18 (dd, J = 7.2, 7.6 Hz, 2H), 7.09 (dd, J = 7.6, 7.6 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.81 (d, J = 7.9 Hz, 1H), 4.39 (q, J = 7.1 Hz, 1H), 3.59 (d, J = 3.6 Hz, 3H), 3.53 (s, 3H), 2.34 (dd, J = 7.2 Hz, 7.2 Hz, 2H), 1.83 – 1.68 (m, 1H), 1.23 (d, J = 7.2 Hz, 3H), 0.85 (d, J = 6.5 Hz, 3H), 0.81 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.6, 141.3, 140.4, 139.2, 129.5, 128.9, 127.9, 125.5, 124.2, 75.3, 44.8, 44.6, 42.1, 41.8, 30.1, 22.8, 20.0. HR-MS (ESI) *m/z* calcd for $C_{22}H_{29}O_2S_2$ $[M+H]^+$ 389.1603, found 389.1607.

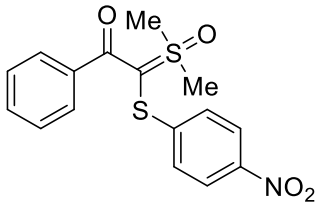


(*S*)-1-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-(6-methoxynaphthalen-2-yl)-1-(phenylthio)butan-2-one (3z): Compound **3z** (170 mg, 83%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as white solid. m.p. 110–112 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 (d, J = 8.9 Hz, 0.5H), 7.73 – 7.67 (m, 1H), 7.51 (d, J = 8.6 Hz, 0.5H), 7.46 – 7.42 (m, 1H), 7.40 – 7.30 (m, 3H), 7.25 (d, J = 2.6 Hz, 0.5H), 7.21 – 7.10 (m, 2H), 7.06 – 6.91 (m, 2.7H), 4.68 – 4.46 (m, 1H), 3.84 (d, J = 9.2 Hz, 3H), 3.61 (s, 3H), 3.54 (d, J = 8.0 Hz, 3H), 1.33 (dd, J = 41.8, 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-D_6) δ 194.5, 157.4, 141.3, 138.8, 133.5, 129.7, 129.2, 128.9, 127.4,

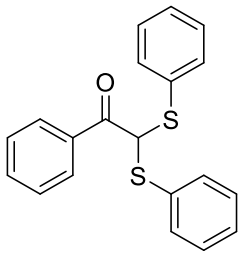
127.0, 126.3, 125.5, 124.3, 118.8, 106.1, 75.4, 55.6, 44.9, 42.0, 19.8. HR-MS (ESI) *m/z* calcd for $C_{23}H_{25}O_3S_2$ $[M+H]^+$ 413.1240, found 413.1242.



2-((4-Chlorophenyl)thio)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (3z-1): Compound **3z-1** (150 mg, 89%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.47 – 7.43 (m, 2H), 7.39 – 7.28 (m, 3H), 7.29 – 7.23 (m, 4H), 3.75 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.2, 141.1, 140.8, 130.2, 130.1, 129.5, 128.0, 127.6, 126.0, 76.5, 42.0, 41.6. HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}ClO_2S_2$ $[M+H]^+$ 339.0275, found 339.0276.

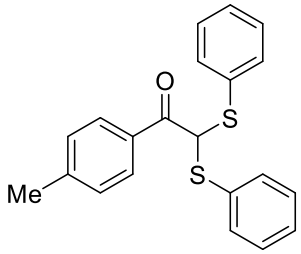


2-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-((4-nitrophenyl)thio)-1-phenylethan-1-one (3z-2): Compound **3z-2** (122 mg, 70%) (PE/EA = 1/2) was prepared using the general procedure A and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.16 – 8.12 (m, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.46 – 7.42 (m, 2H), 7.39 – 7.28 (m, 1H), 7.29 – 7.24 (m, 2H), 3.81 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.1, 152.2, 145.4, 140.6, 130.3, 128.1, 127.5, 124.8, 124.7, 75.0, 42.1, 41.6. HR-MS (ESI) *m/z* calcd for $C_{16}H_{16}NO_4S_2$ $[M+H]^+$ 350.0515, found 350.0518.

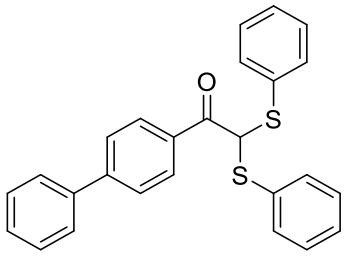


1-Phenyl-2,2-bis(phenylthio)ethan-1-one (4a): Compound **4a** (122 mg, 73%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as a yellow solid. ^{1}H

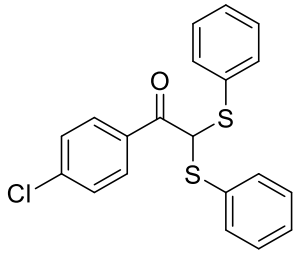
NMR (400 MHz, DMSO-d_6) δ = 8.05 (d, J = 7.1 Hz, 2H), 7.68 (dd, J = 7.2, 8.0 Hz, 1H), 7.53 (dd, J = 7.6, 8.0 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.36 – 7.35 (m, 6H), 6.67 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.3, 134.3, 133.8, 133.1, 131.5, 129.1, 129.0, 128.8, 128.4, 59.8. Analytical data for compound **4a** is consistent with literature report.[4]



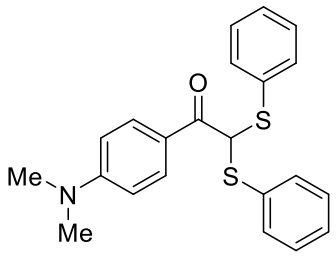
2,2-Bis(phenylthio)-1-(*p*-tolyl)ethan-1-one (4b): Compound **4b** (96 mg, 55%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.97 (d, J = 8.2 Hz, 2H), 7.42 (dd, J = 6.6, 3.0 Hz, 4H), 7.36 – 7.31 (m, 8H), 6.62 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.4, 144.9, 133.6, 132.2, 132.1, 129.9, 129.7, 129.5, 128.9, 60.3, 21.8. Analytical data for compound **4b** is consistent with literature report.[4]



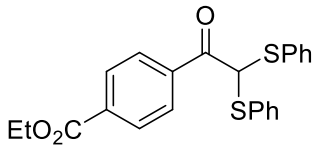
1-([1,1'-Biphenyl]-4-yl)-2,2-bis(phenylthio)ethan-1-one (4c): Compound **4c** (99 mg, 48%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.16 (s, 2H), 7.84 – 7.75 (m, 4H), 7.51 (dd, J = 6.4, 6.8 Hz, 2H), 7.47 – 7.43 (m, 5H), 7.37 – 7.34 (m, 6H), 6.71 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.3, 145.6, 139.3, 133.7, 132.1, 130.3, 129.6, 129.6, 129.2, 129.1, 128.9, 127.6, 127.4, 60.4. Analytical data for compound **4c** is consistent with literature report.[4]



1-(4-Chlorophenyl)-2,2-bis(phenylthio)ethan-1-one (4d): Compound **4d** (107 mg, 58%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.08 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.39 – 7.33 (m, 6H), 6.69 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.8, 139.3, 133.7, 133.5, 131.8, 131.5, 129.6, 129.4, 129.0, 60.5. Analytical data for compound **4d** is consistent with literature report.[4]

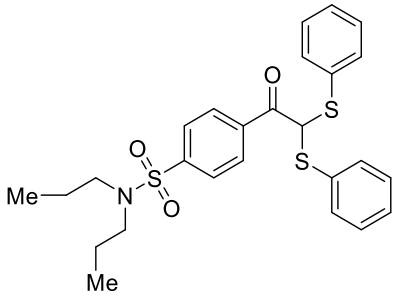


1-(4-(Dimethylamino)phenyl)-2,2-bis(phenylthio)ethan-1-one (4e): Compound **4e** (68 mg, 36%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow solid. m.p. 103–105 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.91 (d, J = 9.1 Hz, 2H), 7.47 – 7.38 (m, 4H), 7.35 – 7.31 (m, 6H), 6.70 (d, J = 9.1 Hz, 2H), 6.43 (s, 1H), 3.02 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.3, 154.1, 133.2, 132.9, 131.8, 129.5, 128.6, 121.4, 111.2, 60.0, 40.1. HR-MS (ESI) *m/z* calcd for $C_{22}H_{22}NOS_2$ $[M+H]^+$ 380.1137, found 380.1134.

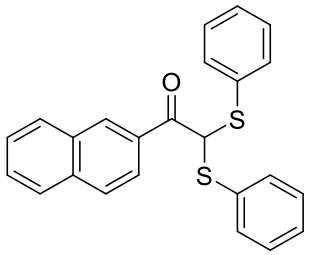


Ethyl 4-(2,2-bis(phenylthio)acetyl)benzoate (4f): Compound **4f** (43 mg, 21%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.16 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 5.7 Hz, 2H), 7.42–7.36 (m, 10H), 6.74 – 6.72 (m, 1H), 4.36 (q, J = 7.0 Hz, 2H), 1.34 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-D_6) δ 191.6, 165.6, 138.5, 134.6, 133.9,

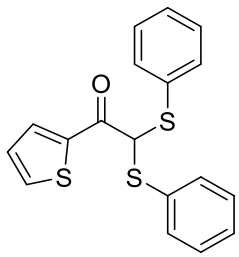
131.8, 130.4, 130.0, 129.8, 129.2, 61.9, 61.0, 14.8. HR-MS (ESI) *m/z* calcd for $C_{23}H_{21}O_3S_2$ $[M+H]^+$ 409.0927, found 409.0921.



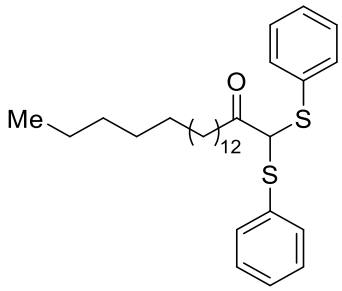
4-(2,2-Bis(phenylthio)acetyl)-*N*,*N*-dipropylbenzenesulfonamide (4g): Compound **4g** (157 mg, 63%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.21 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.39 – 7.36 (m, 6H), 6.77 (s, 1H), 3.11 – 3.05 (m, 4H), 1.52 – 1.44 (m, 4H), 0.81 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.1, 144.2, 137.9, 133.8, 131.6, 130.5, 129.6, 129.1, 127.5, 60.9, 50.1, 22.1, 11.5. HR-MS (ESI) *m/z* calcd for $C_{26}H_{29}NNaO_3S_3$ $[M+Na]^+$ 522.1207, found 522.1200.



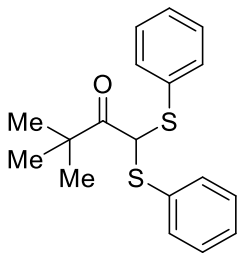
1-(Naphthalen-2-yl)-2,2-bis(phenylthio)ethan-1-one (4h): Compound **4h** (85 mg, 44%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.79 (s, 1H), 8.06 – 7.98 (m, 4H), 7.71 – 7.61 (m, 2H), 7.47 – 7.45 (m, 4H), 7.38 – 7.33 (m, 6H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.8, 135.7, 133.8, 132.6, 132.1, 132.0, 131.6, 130.2, 129.6, 129.0, 128.2, 127.6, 124.9, 60.7. Analytical data for compound **4h** is consistent with literature report.[4]



2,2-Bis(phenylthio)-1-(thiophen-2-yl)ethan-1-one (4i): Compound **4i** (110 mg, 64%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.18 – 8.16 (m, 1H), 8.08 (dd, J = 5.0, 1.3 Hz, 1H), 7.47 – 7.43 (m, 4H), 7.38 – 7.34 (m, 6H), 7.26 – 7.23 (m, 1H), 6.45 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 185.3, 141.3, 137.1, 135.5, 133.5, 132.2, 129.6, 129.4, 129.0, 60.1. Analytical data for compound **4i** is consistent with literature report.[4]

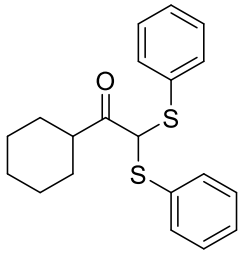


1,1-Bis(phenylthio)nonadecan-2-one (4j): Compound **4j** (112 mg, 45%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow solid. m.p. 65–67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (dd, J = 6.7, 3.0 Hz, 4H), 7.34 – 7.30 (m, 6H), 4.90 (s, 1H), 2.67 (t, J = 7.3 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.26 (d, J = 6.3 Hz, 28H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 133.1, 132.8, 129.3, 128.6, 64.8, 38.8, 32.1, 29.82, 29.79, 29.7, 29.6, 29.50, 29.45, 29.2, 24.1, 22.8, 14.3. HR-MS (ESI) *m/z* calcd for $C_{31}H_{46}NaOS_2$ $[M+Na]^+$ 521.2882, found 521.2875.

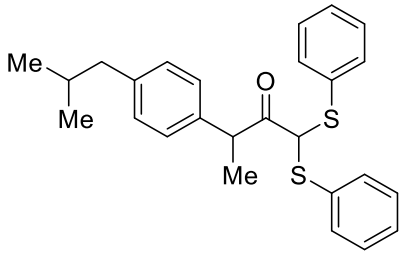


3,3-Dimethyl-1,1-bis(phenylthio)butan-2-one (4k): Compound **4k** (82 mg, 52%)

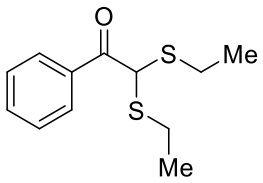
(PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow solid. m.p. 65–67 ℃. as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 – 7.42 (m, 4H), 7.39 – 7.35 (m, 6H), 5.78 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 206.1, 134.0, 132.2, 129.6, 129.1, 58.4, 44.5, 26.8. HR-MS (ESI) *m/z* calcd for $C_{18}H_{20}NaOS_2$ $[M+Na]^+$ 339.0848, found 339.0850.



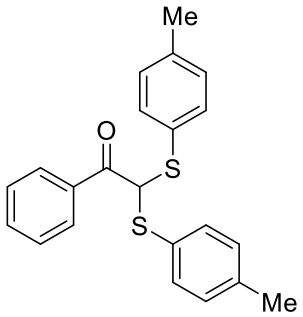
1-Cyclohexyl-2,2-bis(phenylthio)ethan-1-one (4l): Compound **4l** (102 mg, 60%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as white solid. m.p. 65–67 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.46 – 7.42 (m, 4H), 7.39 – 7.33 (m, 6H), 5.84 (s, 1H), 2.86 (tt, *J* = 11.2, 3.5 Hz, 1H), 1.79 – 1.65 (m, 4H), 1.27 – 1.06 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 204.1, 133.0, 132.3, 129.5, 128.7, 61.7, 47.6, 29.0, 25.7, 25.5. HR-MS (ESI) *m/z* calcd for $C_{20}H_{22}NaOS_2$ $[M+Na]^+$ 365.1004, found 365.1007.



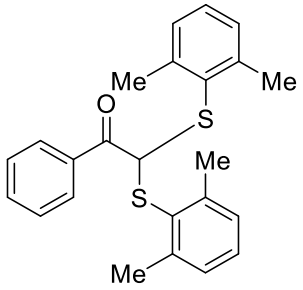
3-(4-Isobutylphenyl)-1,1-bis(phenylthio)butan-2-one (4m): Compound **4m** (105 mg, 50%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.40 – 7.36 (m, 4H), 7.25 – 7.17 (m, 3H), 7.12 – 7.05 (m, 7H), 5.47 (s, 1H), 4.30 (q, *J* = 6.9 Hz, 1H), 2.40 (d, *J* = 7.0 Hz, 2H), 1.85 – 1.75 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 201.3, 140.7, 137.3, 134.1, 132.7, 132.5, 131.6, 129.8, 129.7, 129.5, 129.4, 128.5, 128.3, 62.7, 49.2, 44.8, 30.2, 22.7, 18.9. HR-MS (ESI) *m/z* calcd for $C_{26}H_{28}NaOS_2$ $[M+Na]^+$ 443.1474, found 443.1477.



2,2-Bis(ethylthio)-1-phenylethan-1-one (4n): Compound **4n** (108 mg, 90%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 – 8.00 (m, 2H), 7.60 – 7.55 (m, 1H), 7.47 (dd, *J* = 8.0, 7.6 Hz, 2H), 5.36 (s, 1H), 2.76 (q, *J* = 7.4 Hz, 2H), 2.62 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 134.5, 133.5, 129.0, 128.7, 54.4, 24.3, 14.2. HR-MS (ESI) *m/z* calcd for $C_{12}H_{16}NaOS_2$ $[M+Na]^+$ 263.0535, found 263.0536.

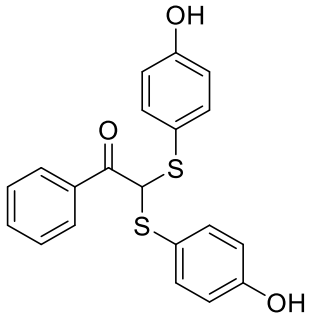


1-Phenyl-2,2-bis(*p*-tolylthio)ethan-1-one (4o): Compound **4o** (91 mg, 50%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.47 – 7.43 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 4H), 7.13 (d, *J* = 7.9 Hz, 4H), 5.66 (s, 1H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 139.3, 134.7, 134.6, 133.6, 130.0, 129.2, 128.7, 128.7, 63.5, 21.4. Analytical data for compound **4o** is consistent with literature report.[4]

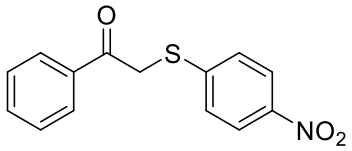


2,2-Bis((2,6-dimethylphenyl)thio)-1-phenylethan-1-one (4p): Compound **4p** (137 mg, 70%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow solid. m.p. 108–110 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.66 – 7.62 (m,

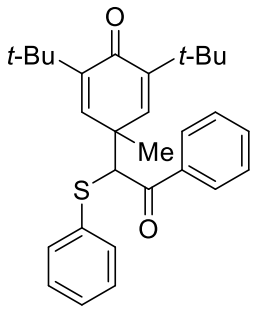
2H), 7.61 – 7.57 (m, 1H), 7.36 (dd, *J* = 7.6, 8.0 Hz, 2H), 7.17 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 4H), 5.03 (s, 1H), 2.22 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.7, 143.6, 134.5, 134.4, 131.4, 130.2, 129.2, 129.0, 128.9, 60.9, 21.8. HR-MS (ESI) *m/z* calcd for $C_{24}H_{24}NaOS_2$ $[M+Na]^+$ 415.1161, found 415.1142.



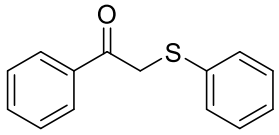
2,2-Bis((4-hydroxyphenyl)thio)-1-phenylethan-1-one (4q): Compound **4q** (81 mg, 44%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.79 (s, 2H), 7.99 – 7.94 (m, 2H), 7.75 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.56 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.25 – 7.20 (m, 4H), 6.76 – 6.70 (m, 4H), 6.10 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.2, 159.0, 137.0, 135.1, 134.1, 129.4, 129.2, 120.2, 116.6, 63.4. Analytical data for compound **4q** is consistent with literature report.[4]



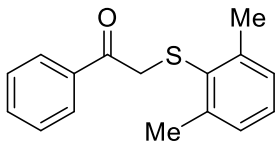
2-((4-Nitrophenyl)thio)-1-phenylethan-1-one (5a): Compound **5a** (20 mg, 14%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. as a yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.13 – 8.07 (m, 4H), 7.71 – 7.66 (m, 1H), 7.59 – 7.52 (m, 4H), 4.98 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.1, 147.2, 145.1, 135.8, 134.4, 129.4, 129.2, 127.1, 124.3, 39.8. Analytical data for compound **5a** is consistent with literature report.[3]



2,6-Di-*tert*-butyl-4-methyl-4-(2-oxo-2-phenyl-1-(phenylthio)ethyl)cyclohexa-2,5-dien-1-one (5b): Compound **5b** (49 mg, 22%) (PE/EA = 15/1) was prepared using the general procedure B and isolated as yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.01 – 7.92 (m, 2H), 7.62 (dd, J = 7.6, 7.2 Hz, 1H), 7.47 (dd, J = 8.0, 7.6 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.21 (m, 3H), 7.02 (d, J = 2.7 Hz, 1H), 6.89 (d, J = 2.9 Hz, 1H), 5.46 (s, 1H), 1.35 (s, 3H), 1.14 (s, 9H), 1.03 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.6, 186.0, 144.9, 143.9, 137.0, 135.2, 134.2, 131.1, 129.7, 129.3, 129.0, 127.8, 58.5, 43.5, 35.0, 29.60, 29.55, 24.0. HR-MS (ESI) *m/z* calcd for $C_{29}H_{34}NaO_2S$ $[M+Na]^+$ 469.2172, found 469.2167.

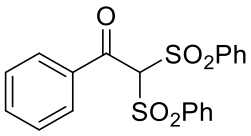


1-Phenyl-2-(phenylthio)ethan-1-one (**5c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.0 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.37 (m, 2H), 7.28 (dd, J = 7.6 Hz, 2H), 7.25 – 7.21 (m, 1H), 4.28 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 135.5, 134.9, 133.6, 130.6, 129.2, 128.82, 128.80, 127.2, 41.3. Analytical data for compound **5c** is consistent with literature report.[3]

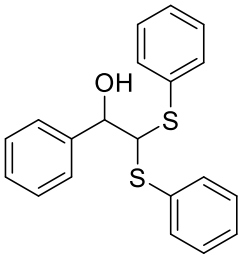


2-((2,6-Dimethylphenyl)thio)-1-phenylethan-1-one (5d): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (d, J = 7.7 Hz, 2H), 7.56 (dd, J = 7.6, 7.2 Hz, 1H), 7.43 (dd, J = 7.6, 7.6 Hz, 2H), 7.15 (dd, J = 8.7, 6.1 Hz, 1H), 7.09 (d, J = 8.1 Hz, 2H), 3.98 (s, 2H), 2.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 143.5, 135.6, 133.4, 132.1, 129.1, 128.8, 128.7, 128.5, 40.9, 22.0. HR-MS (ESI) *m/z* calcd for $C_{16}H_{17}OS$ $[M+H]^+$ 257.0995,

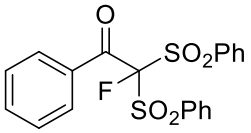
found 257.0998.



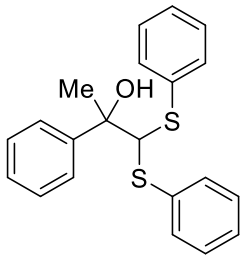
1-Phenyl-2,2-bis(phenylsulfonyl)ethan-1-one (**6**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.4 Hz, 4H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.67 (dd, *J* = 7.5 Hz, 2H), 7.58 (dd, *J* = 11.5, 4.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 7.6 Hz, 4H), 7.42 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.54 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 137.4, 136.3, 135.2, 134.9, 130.5, 129.14, 129.13, 129.10, 86.2. Analytical data for compound **6** is consistent with literature report.[5]



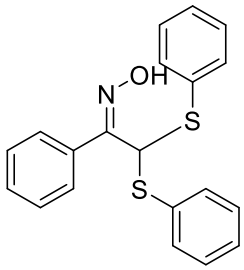
1-Phenyl-2,2-bis(phenylthio)ethan-1-ol (**7**):^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 – 7.26 (m, 15H), 4.93 (d, *J* = 4.7 Hz, 1H), 4.62 (d, *J* = 4.9 Hz, 1H), 3.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 134.1, 133.6, 133.09, 133.07, 129.3, 129.1, 128.3, 128.26, 128.24, 128.1, 126.9, 74.5, 68.5. Analytical data for compound **7** is consistent with literature report.[5]



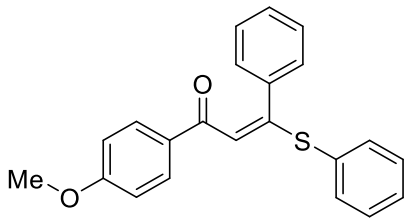
2-Fluoro-1-phenyl-2,2-bis(phenylsulfonyl)ethan-1-one (**8**): ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.98 (d, *J* = 7.9 Hz, 4H), 7.75 – 7.70 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.54 (m, 5H), 7.36 – 7.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 136.0, 134.9, 134.5, 131.5, 130.3, 129.7, 129.6, 129.3, 128.5, 113.1(d, *J* = 282.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -166.8. Analytical data for compound **8** is consistent with literature report.[5]



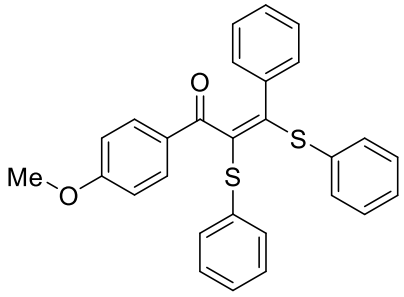
2-Phenyl-1,1-bis(phenylthio)propan-2-ol (**9**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 8.0 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.22 – 7.16 (m, 10H), 4.67 (s, 1H), 3.30 (s, 1H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 135.02, 134.96, 133.3, 133.2, 129.01, 129.00, 128.1, 127.98, 127.95, 127.6, 125.9, 77.8, 76.6, 27.2. Analytical data for compound **9** is consistent with literature report.[5]



(*Z*)-1-Phenyl-2,2-bis(phenylthio)ethan-1-one oxime (**10**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.39 (m, 7H), 7.27 – 7.24 (m, 6H), 6.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 134.5, 133.4, 132.8, 129.7, 129.1, 128.34, 128.25, 128.0, 51.7. HR-MS (ESI) *m/z* calcd for $C_{20}H_{18}NOS_2$ $[M+H]^+$ 352.0824, found 352.0814.



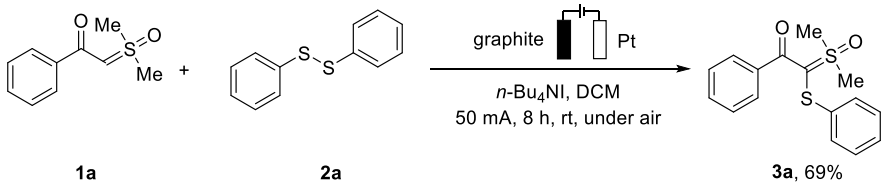
(*E*)-1-(4-Methoxyphenyl)-3-phenyl-3-(phenylthio)prop-2-en-1-one (**11**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.19 (m, 5H), 7.16 – 7.13 (m, 3H), 7.09 – 7.05 (m, 3H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 163.2, 161.0, 139.0, 134.4, 133.0, 131.5, 130.6, 129.1, 128.4, 127.9, 120.1, 113.9, 55.6. Analytical data for compound **11** is consistent with literature report. [6]



(*Z*)-1-(4-Methoxyphenyl)-3-phenyl-2,3-bis(phenylthio)prop-2-en-1-one (**12**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.30 – 7.26 (m, 4H), 7.24 – 7.21 (m, 1H), 7.16 – 7.12 (m, 5H), 7.07 – 7.05 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 163.8, 136.9, 136.8, 136.1, 133.6, 133.4, 131.9, 131.8, 131.5, 129.9, 129.3, 128.8, 128.7, 128.5, 128.3, 128.1, 127.4, 113.9, 55.6. Analytical data for compound **12** is consistent with literature report. [7]

Gram-scale synthesis

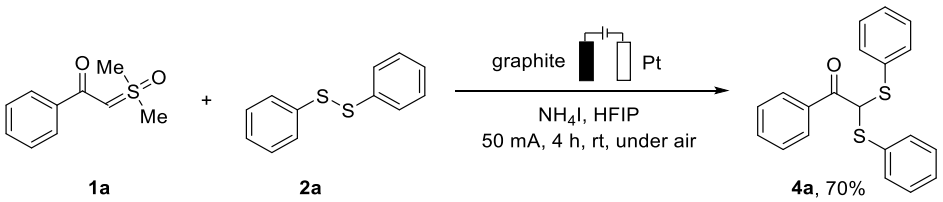
(a) Gram-scale experiments for **3a**:



1a **2a** **3a**, 69%

In an undivided cell (250.0 mL) equipped with a stir bar, a mixture of substrates **1a** (10.0 mmol, 1.96 g), **2a** (12.0 mmol, 2.62 g), *n*-Bu_4NI (10.0 mmol, 3.69 g) and DCM (120.0 mL) were added. The cell was equipped with graphite (3 cm × 3 cm × 0.6 cm) as the anode and platinum plate (3 cm × 3 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA at room temperature for 8 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 1/2) to give as yellow liquid **3a** (2.10 g, 69%).

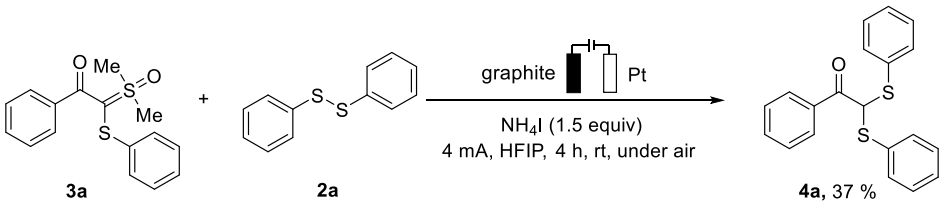
(b) Gram-scale experiments for **4a**:



In an undivided cell (250.0 mL) equipped with a stir bar, a mixture of substrates **1a** (10 .0 mmol, 1.96 g), **2a** (12.0 mmol, 2.62 g), NH_4I (15.0 mmol, 2.17 g) and HFIP (120 mL) were added. The cell was equipped with graphite (3 cm × 3 cm × 0.6 cm) as the anode and platinum plate (3 cm × 3 cm × 0.01 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA at room temperature for 4 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 15/1) to give as yellow liquid **4a** (2.35 g, 70%).

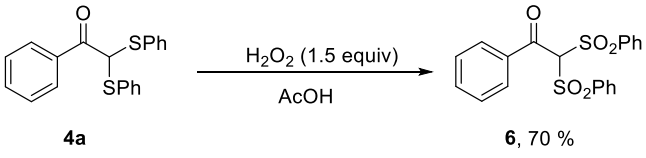
The Synthetic Application of Compound 4a

(a) Procedure for the synthesis of **4a**



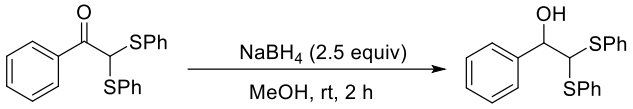
In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **3a** (0.5 mmol, 152 mg), **2a** (0.6 mmol, 131 mg), NH_4I (0.75 mmol, 109 mg) and HFIP (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 4 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 15/1) to give **4a** (62 mg, 37%).

(b) Procedure for the synthesis of 1-phenyl-2,2-bis(phenylsulfonyl)ethan-1-one (**6**)[5]



To a solution of compound **4a** (0.2 mmol, 67.3 mg) in AcOH (2 mL) was added H_2O_2 (0.3 mmol, 30% in H_2O). After stirring for 2 h at room temperature, the reaction mixture was allowed to slowly warm up to 50 °C and stir overnight. After the reaction completed, the mixture was cooled to room temperature, and concentrated in vacuo. The crude compound was purified by flash column chromatography (PE/EA: 1/1) to give as white solid (56.1 mg, 70%).

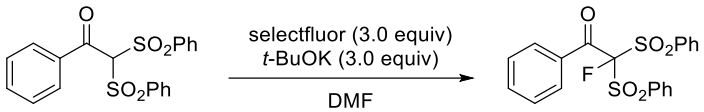
(c) Procedure for the synthesis of 1-phenyl-2,2-bis(phenylthio)ethan-1-ol (**7**) [5]



4a **7**, 80 %

To a solution of compound **4a** (0.2 mmol, 67.3 mg) in MeOH (2 mL) at 0 °C was added $NaBH_4$ (0.5 mmol, 19.4 mg). After stirring for 2 h at room temperature, the resulting mixture was quenched with saturated NH_4Cl (aq.) and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude compound was purified by flash column chromatography (PE/EA: 10/1) to give as colorless liquid (54.1 mg, 80%).

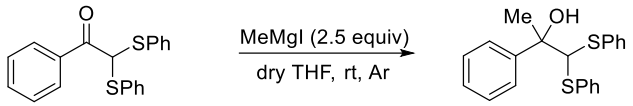
(d) Procedure for the synthesis of 2-fluoro-1-phenyl-2,2-bis(phenylsulfonyl)ethan- 1-one (**8**)[5]



6 **8,** 25 %

To a solution of compound **6** (0.2 mmol, 80 mg) in 2 mL DMF was added *t*-BuOK (0.6 mmol, 67.3 mg). The reaction was stirred at room temperature for 20 min before Selectfluor (0.6 mmol, 213 mg) in 2 mL DMF was added slowly. After stirring for 2 h at room temperature, the resulting mixture was quenched by water and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude compound was purified by flash column chromatography (PE/EA/DCM: 7/1/3) to give as colorless liquid (17.8 mg, 25%).

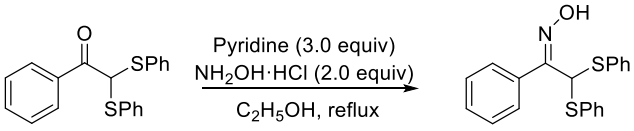
(e) Procedure for the synthesis of 2-phenyl-1,1-bis(phenylthio)propan-2-ol (**9**)[5]



4a **9**, 75 %

To a solution of compound **4a** (0.5 mmol, 168 mg) in dry THF (5 mL) was added methylmagnesium iodide (1.25 mmol, 208 mg) at 0 ℃ under argon atmosphere. After stirring for 5 h at room temperature, the resulting mixture was quenched with saturated NH_4Cl (aq) and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude compound was purified by flash column chromatography (PE/EA: 10/1) to give as colorless liquid (132 mg, 75%).

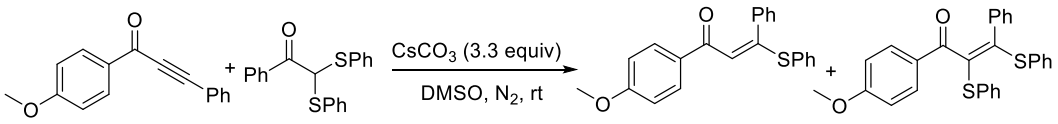
(f) Procedure for the synthesis of (*Z*)-1-phenyl-2,2-bis(phenylthio)ethan-1-one oxime (**10**)[8]



4a **10**, 38 %

To a solution of compound **4a** (0.2 mmol, 67.3mg) in C_2H_5OH (10 mL) was added $NH_2Cl{\cdot}H_2O$ (0.4 mmol, 27.8 mg) and Pyridine (0.6 mmol, 47.5 mg). The reaction mixture were refluxed at 80 °C for 2 h. After completion of the reaction as indicated by thin-layer chromatography (TLC), the solvent was evaporated. The reaction was quenched with water (10 mL) and extracted with EtOAc (2 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude compound was purified by flash column chromatography (PE/EtOAc: 1/3) to give as yellow liquid (26.7 mg, 38%).

(g) Procedure for the synthesis of (*E*)-1-(4-methoxyphenyl)-3-phenyl- 3-(phenylthio)prop-2-en-1-one (**11**) and (*Z*)-1-(4-methoxyphenyl)-3-phenyl-2,3-bis(phenylthio)prop-2-en-1-one (**12**)[9]

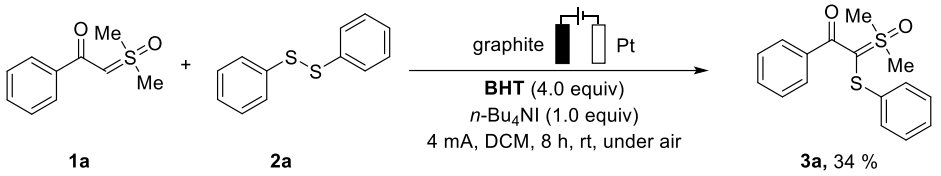


S2 **4a** **11**, 16 % **12**, 14 %

To a solution of compound **4a** (0.3 mmol, 101 mg) in DMSO (2 mL) was added $CsCO_3$ (1.0 mmol, 195 mg) and 1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one **S2** (0.3 mmol, 70.8 mg) under nitrogen atmosphere. After stirring for 2 h at room temperature, the resulting mixture was quenched by water and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The crude compound was purified by flash column chromatography (PE/EA/DCM: 10/1/3) to give a yellow liquid **11** (16.7 mg, 16%) and a yellow liquid **12** (19.0 mg, 14%).

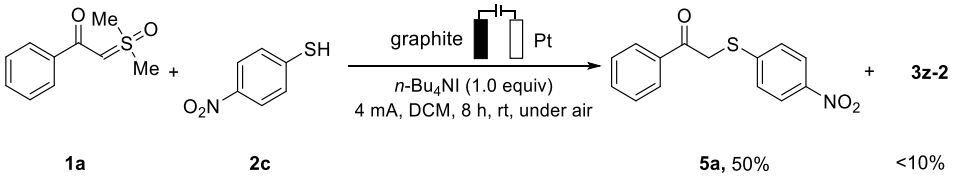
Control Experiments and Mechanism Studies

(a) Radical scavenger experiments with BHT



In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **1a** (0.5 mmol, 98 mg), BHT (4.0 mmol, 440 mg), **2a** (0.6 mmol, 131 mg), *n*-Bu_4NI (0.5 mmol, 185 mg) and DCM (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 8 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 1/3) to give as yellow liquid **3a** (52 mg, 34%).

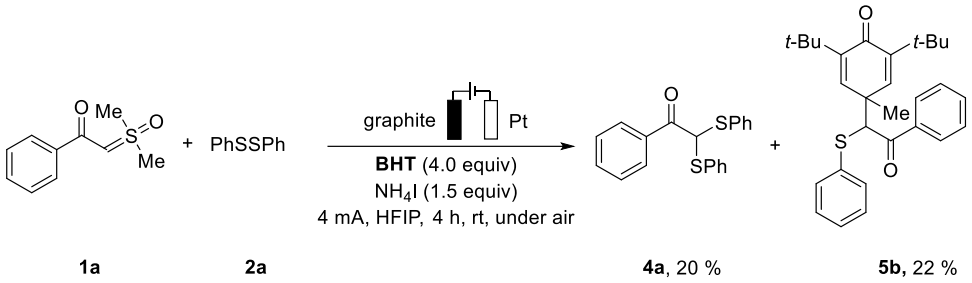
(b) Reactions of **1a** and **2c** under standard condition A



In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **1a** (0.5 mmol, 98 mg), **2c** (0.6 mmol, 93 mg), *n*-Bu_4NI (0.5 mmol, 185 mg) and DCM (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 8 h. Upon completion, the solvent was further removed

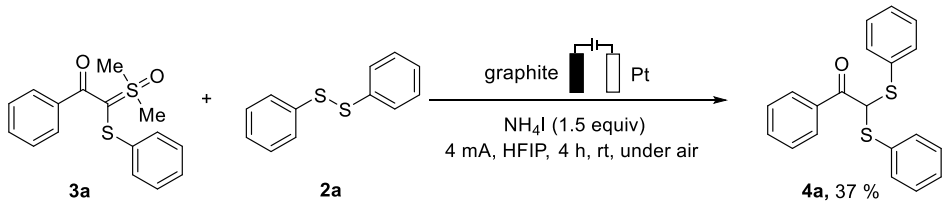
directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 1/1) to give as yellow liquid **5a** (68 mg, 50 %).

(c) Radical scavenger experiments with BHT under condition B



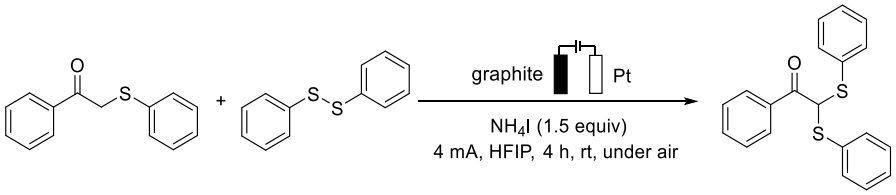
In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **1a** (0.5 mmol, 98 mg), BHT (4.0 mmol, 440 mg), **2a** (0.6 mmol, 131 mg), NH_4I (0.75 mmol, 109 mg) and HFIP (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 4 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 15/1) to give **4a** (34 mg, 20%) and yellow liquid **5b** (50 mg, 22%).

(d) Reactions of **3a** and **2a** under standard condition B



In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **3a** (0.5 mmol, 152 mg), **2a** (0.6 mmol, 131 mg), NH_4I (0.75 mmol, 109 mg) and HFIP (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 4 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 15/1) to give **4a** (62 mg, 37%).

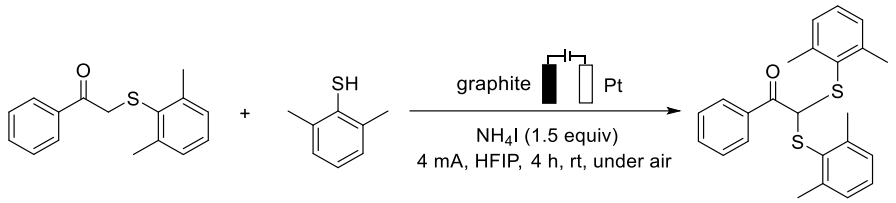
(e) Reactions of **5c** and **2a** under standard condition B



5c **2a** **4a**, 61 %

In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **5c** (0.5 mmol, 114 mg), **2a** (0.6 mmol, 131 mg), NH_4I (0.75 mmol, 109 mg) and HFIP (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 4 h. Upon completion, the solvent was further removed directly under reduced pressure to afford the crude product, which was purified by flash column chromatography (PE/EtOAc: 15/1) to give **4a** (102 mg, 61%).

(f) Reactions of **5d** and **2f** under standard condition B

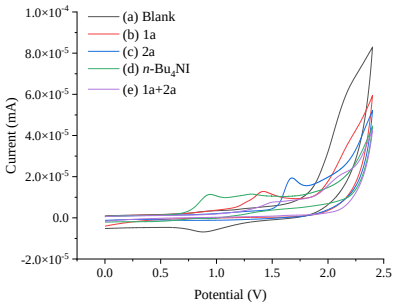


5d **2f** **4p,** no reaction

In an undivided cell (30 mL) equipped with a stirring bar, a mixture of substrates **5d** (0.5 mmol, 128 mg), **2f** (0.6 mmol, 83 mg), NH_4I (0.75 mmol, 109 mg) and HFIP (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 4 mA at room temperature for 4 h. Upon completion, the reaction does not give the expected product.

Cyclic Voltammetry Experiment

Cyclic voltammetry experiments were carried out on an IGS 1230 electrochemical work station (Ingsens instruments, Guangzhou). 0.1 M electrolyte was dissolved in acetonitrile. Working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgCl (3 M KCl). Scan rate: 100 mV/s.



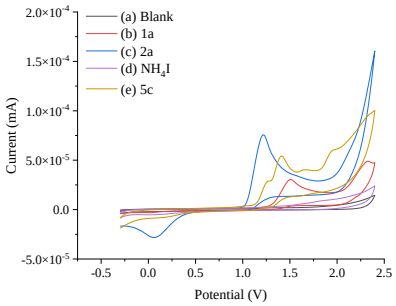


Figure S2-a.

Figure S2-b.

Figure S2-a. Cyclic voltammograms of condition A. Conditions: a glassy carbon working electrode, a Ag/AgCl (3 M KCl) reference electrode, and a platinum wire counter electrode, 0.01 M analyte in 0.1 M *n*-Bu_4NI dissolved in DCM, 100 mV/s scan rate. (a) *n*-Bu_4NPF_6 (1 mM) as blank; (b) **1a** (1 mM); (c) **2a** (1 mM); (d) *n*-Bu_4NI (1 mM) ; (e) **1a** and **2a** (1 mM).

Figure S2-b. Cyclic voltammograms of condition B. Conditions: a glassy carbon working electrode, a Ag/AgCl (3 M KCl) reference electrode, and a platinum wire counter electrode, 0.01 M analyte in 0.1 M *n*-Bu_4NPF_6 dissolved in HFIP, 100 mV/s scan rate. (a) *n*-Bu_4NPF_6 (1 mM) as blank; (b) **1a** (1 mM); (c) **2a** (1 mM); (d) NH_4I (1 mM) (e) **5c** (1 mM).

Crystallographic description of 3s and 4a

(a) Crystal structure determination of 3s

The compound **3s** was crystallized from a mixture of CH_2Cl_2 and *n*-hexane ether. Suitable single crystal was picked from the mother liquor and covered with perfluorinated polyether oil on a microscope slide. Compound **3s** was collected at 180.00 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Data reduction was carried out with the diffractometer's software[10]. The structure was solved by direct methods using Olex2 software[11], and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018[12] using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were

obtained based on F^2. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data has been deposited with the Cambridge Crystallographic Centre and allocated with the deposition numbers: CCDC 2272115. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure determination of 3s

Crystal Data for $C_{16}H_{11}F_5O_2S_2$ (M =394.37 g/mol): triclinic, space group P-1 (no. 2), a = 9.0497(5) Å, b = 9.8617(6) Å, c = 17.5484(11) Å, α = 92.637(5)°, β = 91.848(5)°, γ = 95.942(5)°, V = 1554.97(16) Å^3, Z = 4, T = 169.99(10) K, μ(Mo Kα) = 0.406 mm^{-1}, *Dcalc* = 1.685 g/cm^3, 9482 reflections measured (4.158° ≤ 2Θ ≤ 50°), 5463 unique (R_{int} = 0.0548, R_{sigma} = 0.0849) which were used in all calculations. The final R_1 was 0.0684 (I > 2σ(I)) and wR_2 was 0.1752 (all data).

Table S3 Crystal data and structure refinement for 3s.

Identification code	**3s**
Empirical formula	$C_{16}H_{11}F_5O_2S_2$
Formula weight	394.37
Temperature/K	169.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.0497(5)
b/Å	9.8617(6)
c/Å	17.5484(11)
α/°	92.637(5)
β/°	91.848(5)
γ/°	95.942(5)
Volume/Å^3	1554.97(16)
Z	4
ρ_{calc}g/cm^3	1.685
μ/mm^{-1}	0.406
F(000)	800.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.158 to 50
Index ranges	$-10 \le h \le 9$, $-10 \le k \le 11$, $-18 \le l \le 20$
Reflections collected	9482
Independent reflections	5463 [R_{int} = 0.0548, R_{sigma} = 0.0849]
Data/restraints/parameters	5463/0/455
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0684, wR_2 = 0.1653
Final R indexes [all data]	R_1 = 0.0839, wR_2 = 0.1752
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.47

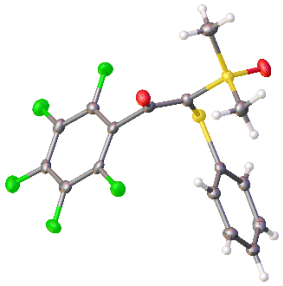


Figure S3. X-ray structure of **3s**. Ellipsoids show 30% probability levels. H atoms are omitted for clarity.

Table S4. Bond lengths [Å] and angles [°] of **3s**

S1-O2	1.440(4)	C23-C24	1.406(7)	C11-C12-C13	119.2(5)
S1-C8	1.722(5)	C27-C28	1.390(7)	C14-C13-C12	120.4(5)
S1-C9	1.759(5)	C27-C32	1.403(7)	C15-C14-C13	119.8(5)
S1-C10	1.764(5)	C28-C29	1.384(7)	C14-C15-C16	121.0(5)
S2-C8	1.736(5)	C29-C30	1.380(7)	C15-C16-C11	119.3(5)
S2-C11	1.786(5)	C30-C31	1.389(8)	C24-S3-C27	105.1(2)
F1-C2	1.345(6)	C31-C32	1.371(7)	O4-S4-C24	112.3(2)
F2-C3	1.341(6)			O4-S4-C25	110.5(3)
F3-C4	1.337(5)			O4-S4-C26	111.3(3)
F4-C5	1.335(6)			C24-S4-C25	109.6(3)
F5-C6	1.356(5)	O2-S1-C8	112.5(2)	C24-S4-C26	109.4(3)
O1-C7	1.246(6)	O2-S1-C9	110.6(3)	C25-S4-C26	103.3(3)
C1-C2	1.390(7)	O2-S1-C10	110.9(3)	F8-C17-C18	120.6(5)
C1-C6	1.369(7)	C8-S1-C9	109.2(2)	F8-C17-C22	119.5(5)
C1-C7	1.520(6)	C8-S1-C10	109.0(3)	C18-C17-C22	119.8(5)
C2-C3	1.378(7)	C9-S1-C10	104.3(3)	F7-C18-C17	120.1(5)
C3-C4	1.374(7)	C8-S2-C11	105.3(2)	F7-C18-C19	119.9(5)
C4-C5	1.373(7)	C2-C1-C7	121.6(4)	C17-C18-C19	120.0(5)
C5-C6	1.383(7)	C6-C1-C2	117.0(4)	F6-C19-C18	119.6(5)
C7-C8	1.403(7)	C6-C1-C7	121.4(4)	F6-C19-C20	120.6(5)

C11-C12	1.390(7)	F1-C2-C1	120.2(4)	C18-C19-C20	119.8(5)
C11-C16	1.387(7)	F1-C2-C3	118.2(5)	F10-C20-C19	118.3(5)
C12-C13	1.395(7)	C3-C2-C1	121.6(5)	F10-C20-C21	120.3(5)
C13-C14	1.381(8)	F2-C3-C2	120.8(5)	C19-C20-C21	121.4(5)
C14-C15	1.372(8)	F2-C3-C4	119.4(4)	C20-C21-C23	122.3(5)
C15-C16	1.386(8)	C4-C3-C2	119.7(5)	C22-C21-C20	117.4(5)
S3-C24	1.735(5)	F3-C4-C3	119.9(5)	C22-C21-C23	120.1(4)
S3-C27	1.782(5)	F3-C4-C5	120.0(5)	F9-C22-C17	118.6(5)
S4-O4	1.440(4)	C5-C4-C3	120.1(5)	F9-C22-C21	119.9(5)
S4-C24	1.721(5)	F4-C5-C4	120.2(5)	C21-C22-C17	121.5(5)
S4-C25	1.758(6)	F4-C5-C6	120.7(5)	O3-C23-C21	118.3(4)
S4-C26	1.759(5)	C4-C5-C6	119.0(5)	O3-C23-C24	124.0(5)
F6-C19	1.346(6)	F5-C6-C1	119.7(4)	C24-C23-C21	117.6(4)
F7-C18	1.342(6)	F5-C6-C5	117.7(4)	S4-C24-S3	116.9(3)
F8-C17	1.339(6)	C1-C6-C5	122.6(5)	C23-C24-S3	126.1(4)
F9-C22	1.338(6)	O1-C7-C1	117.8(4)	C23-C24-S4	116.8(4)
O3-C23	1.247(6)	O1-C7-C8	124.7(4)	C28-C27-S3	123.3(4)
C17-C18	1.360(8)	C8-C7-C1	117.4(4)	C28-C27-C32	119.4(5)
C17-C22	1.394(7)	S1-C8-S2	116.3(3)	C32-C27-S3	117.3(4)
C18-C19	1.377(8)	C7-C8-S1	116.8(3)	C29-C28-C27	119.7(4)
C19-C20	1.382(7)	C7-C8-S2	126.8(4)	C30-C29-C28	121.1(5)
C20-C21	1.385(7)	C12-C11-S2	122.3(4)	C29-C30-C31	118.8(5)
C21-C22	1.379(7)	C16-C11-S2	117.3(4)	C32-C31-C30	121.3(5)
C21-C23	1.515(7)	C16-C11-C12	120.3(5)	C31-C32-C27	119.7(5)

(b) Crystal structure determination of 4a

The compound **4a** was crystallized from a mixture of CH_2Cl_2 and *n*-hexane ether. Suitable single crystal was picked from the mother liquor and covered with perfluorinated polyether oil on a microscope slide. Compound **4a** was collected at 180.00 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Data reduction was carried out with the diffractometer's software[10]. The structure was solved by direct methods using Olex2 software[11] , and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2018[12] using a full-matrix least squares procedure based on F^2. The weighted *R* factor, *wR* and goodness-of-fit *S* values were obtained based on F^2. The hydrogen atom positions were fixed geometrically at the

calculated distances and allowed to ride on their parent atoms. Crystallographic data has been deposited with the Cambridge Crystallographic Centre and allocated with the deposition numbers: CCDC 2272099. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal structure determination of 4a

Crystal Data for $C_{20}H_{16}OS_2$ (*M* =336.45 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 10.0077(5) Å, *b* = 11.6105(5) Å, *c* = 14.5031(7) Å, *β* = 99.121(4)°, *V* = 1663.87(14) Å^3, *Z* = 4, *T* = 169.98(10) K, μ(Mo Kα) = 0.321 mm^{-1}, *Dcalc* = 1.343 g/cm^3, 7621 reflections measured (4.516° ≤ 2Θ ≤ 49.998°), 2934 unique (R_{int} = 0.0190, R_{sigma} = 0.0248) which were used in all calculations. The final R_1 was 0.0305 (I > 2σ(I)) and wR_2 was 0.0752 (all data).

Table S5 Crystal data and structure refinement for 4a.

Identification code	**4a**
Empirical formula	$C_{20}H_{16}OS_2$
Formula weight	336.45
Temperature/K	169.98(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.0077(5)
b/Å	11.6105(5)
c/Å	14.5031(7)
α/°	90
β/°	99.121(4)
γ/°	90
Volume/Å^3	1663.87(14)
Z	4
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	0.321
F(000)	704.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.516 to 49.998

Index ranges	$-11 \leq h \leq 9, -13 \leq k \leq 11, -16 \leq l \leq 17$
Reflections collected	7621
Independent reflections	2934 [R_{int} = 0.0190, R_{sigma} = 0.0248]
Data/restraints/parameters	2934/0/208
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0722
Final R indexes [all data]	R_1 = 0.0361, wR_2 = 0.0752
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.20

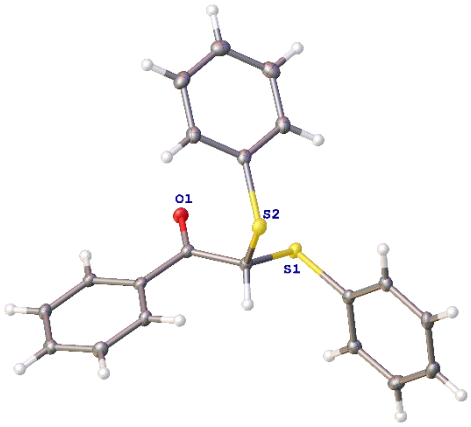


Figure S4. X-ray structure of **4a**. Ellipsoids show 30% probability levels. H atoms are omitted for clarity.

Table S6. Bond lengths [Å] and angles [°] of **4a**

S1-C1	1.7851(16)	C15-C16	1.388(2)	C8-C7-S2	109.37(10)
S1-C7	1.8200(15)	C16-C17	1.381(3)	O1-C8-C7	119.43(14)
S2-C7	1.8302(16)	C17-C18	1.381(3)	O1-C8-C9	122.04(14)
S2-C15	1.7771(17)	C18-C19	1.379(3)	C9-C8-C7	118.52(13)
O1-C8	1.2140(19)	C19-C20	1.380(3)	C10-C9-C8	123.34(14)
C1-C2	1.391(2)			C14-C9-C8	117.49(14)
C1-C6	1.386(2)			C14-C9-C10	119.10(15)
C2-C3	1.386(2)			C11-C10-C9	120.12(15)
C3-C4	1.379(3)	C1-S1-C7	98.76(7)	C12-C11-C10	120.20(15)
C4-C5	1.379(3)	C15-S2-C7	102.50(7)	C11-C12-C13	119.89(15)
C5-C6	1.382(2)	C2-C1-S1	121.42(12)	C14-C13-C12	120.23(15)
C7-C8	1.523(2)	C6-C1-S1	118.83(12)	C13-C14-C9	120.45(15)
C8-C9	1.492(2)	C6-C1-C2	119.72(15)	C16-C15-S2	118.91(13)
C9-C10	1.395(2)	C3-C2-C1	119.65(16)	C16-C15-C20	119.99(16)
C9-C14	1.391(2)	C4-C3-C2	120.32(17)	C20-C15-S2	121.04(13)
C10-C11	1.384(2)	C3-C4-C5	120.01(17)	C17-C16-C15	119.77(17)
C11-C12	1.383(2)	C4-C5-C6	120.18(17)	C18-C17-C16	120.25(18)

C12-C13	1.383(2)	C5-C6-C1	120.09(16)	C19-C18-C17	119.93(18)
C13-C14	1.378(2)	S1-C7-S2	115.66(9)	C18-C19-C20	120.34(18)
C15-C15	1.386(2)	C8-C7-S1	108.74(10)	C19-C20-C15	119.72(17)

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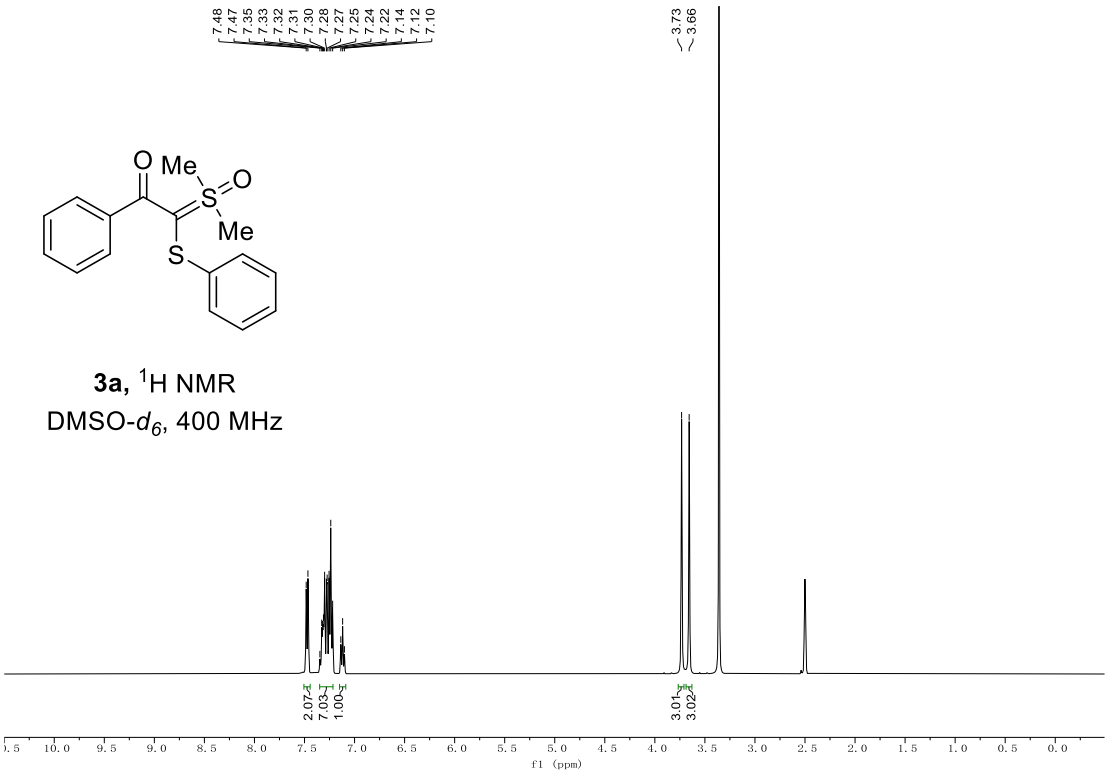
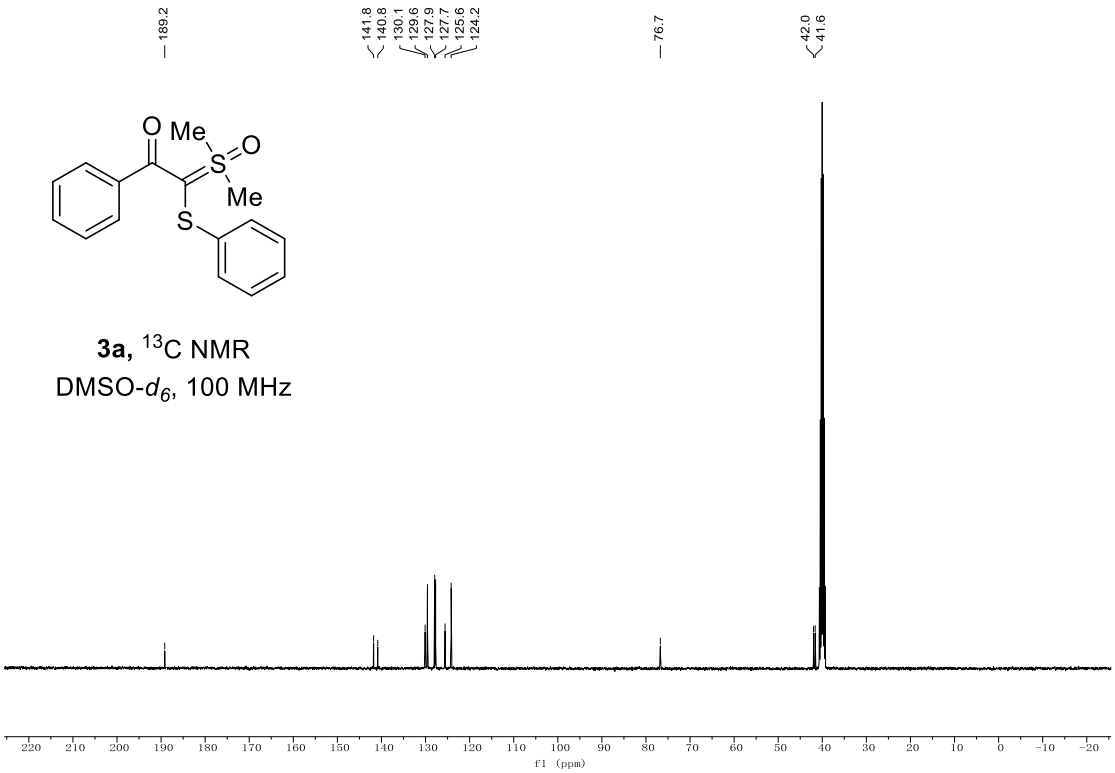
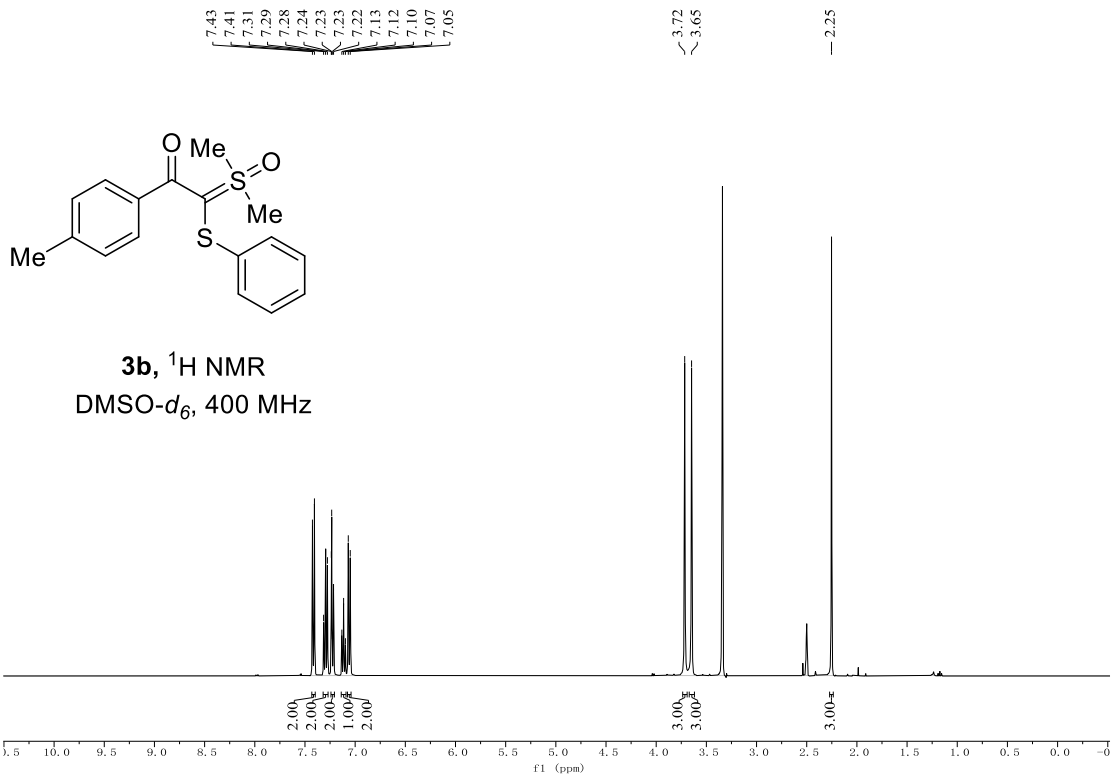
NMR Spectra



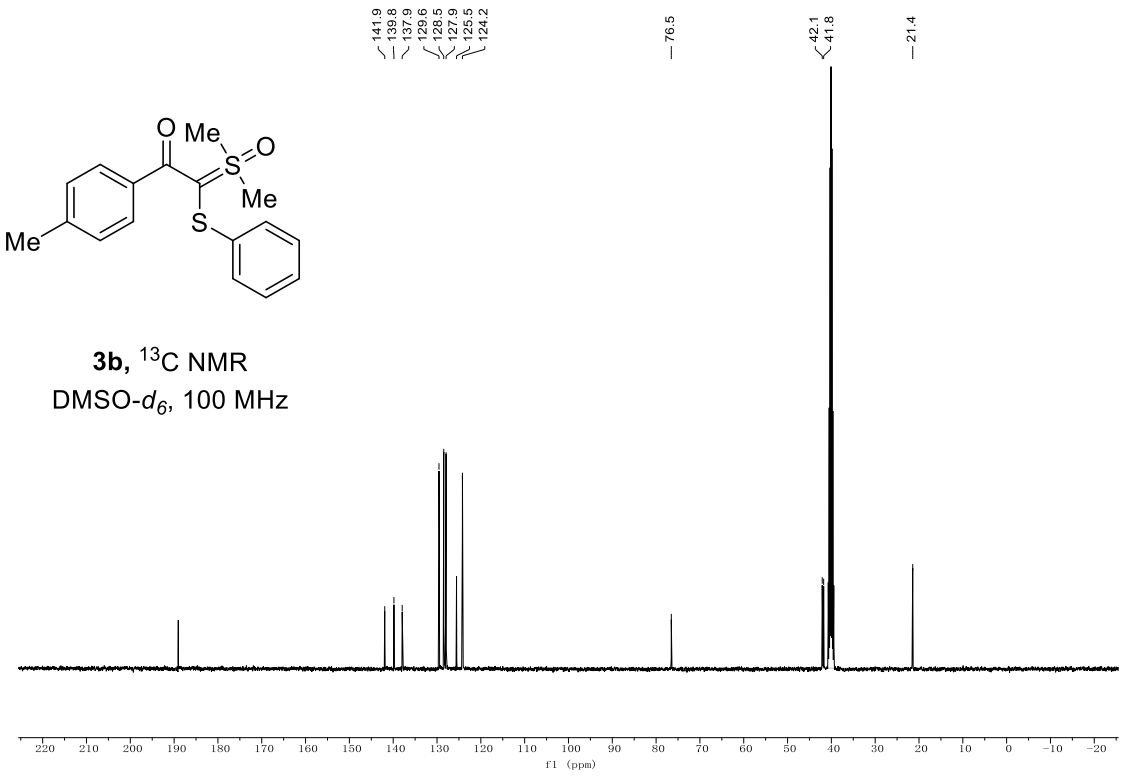
3a, ^{1}H NMR
DMSO-d_6, 400 MHz



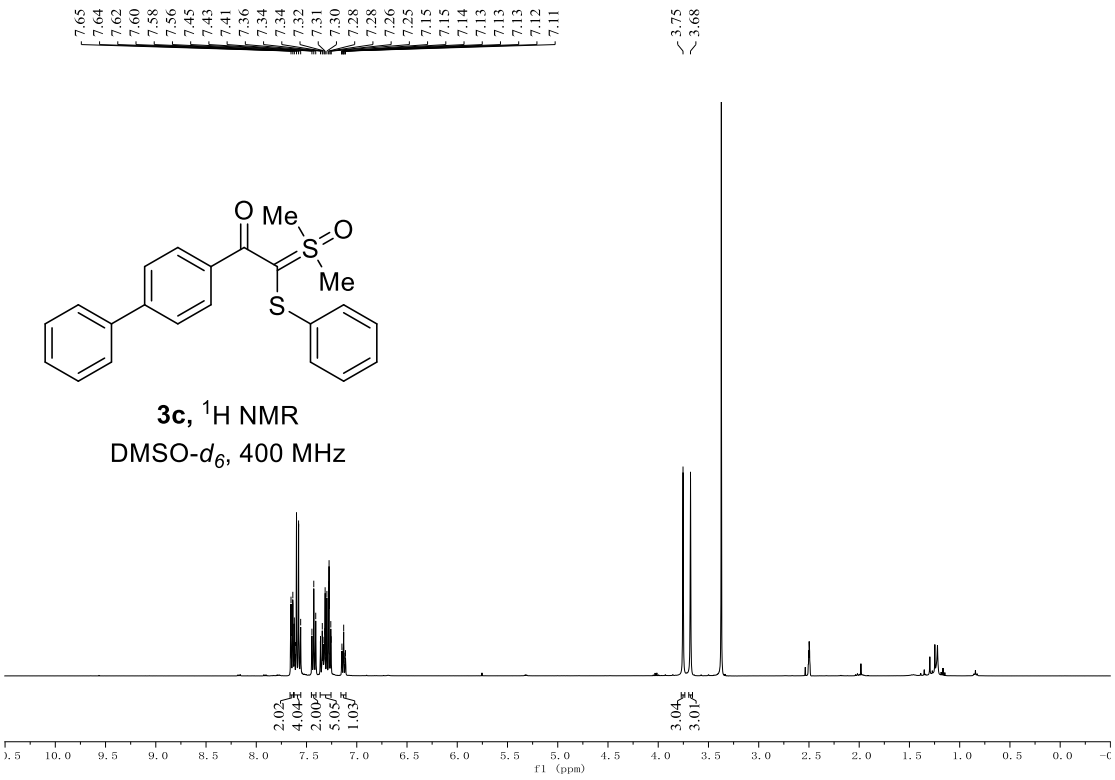
3a, ^{13}C NMR
DMSO-d_6, 100 MHz



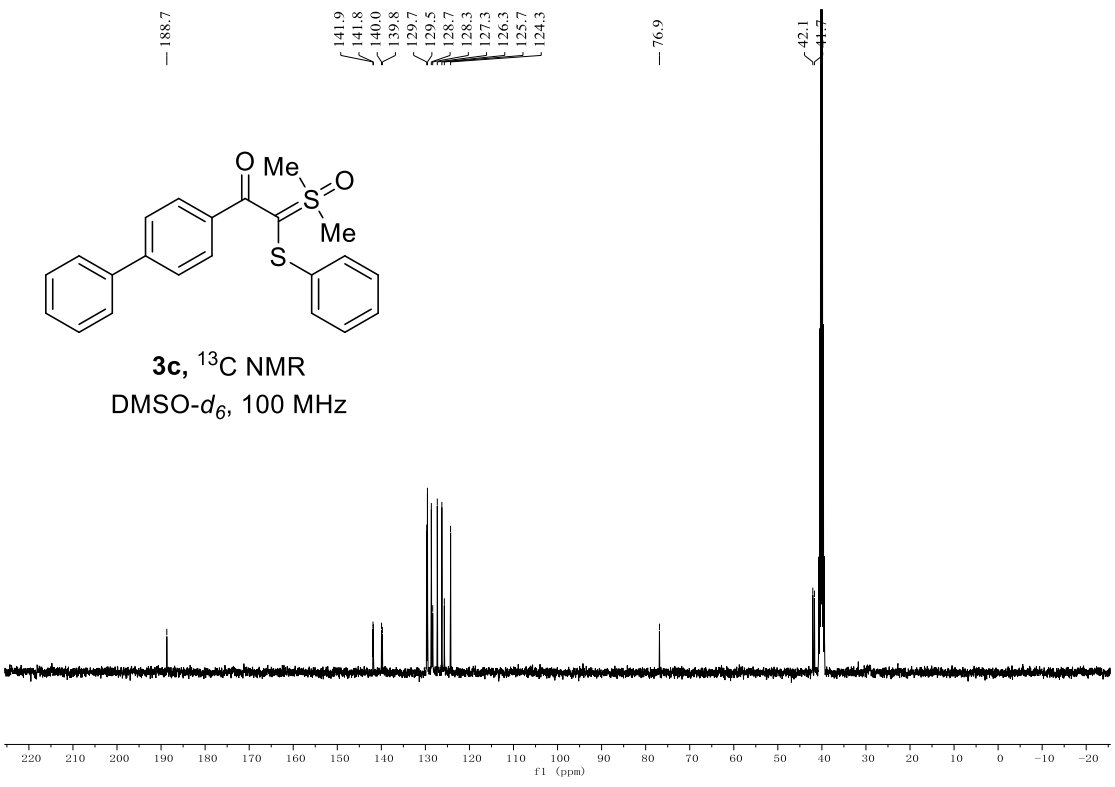
3b, ^{1}H NMR
DMSO-d_6, 400 MHz



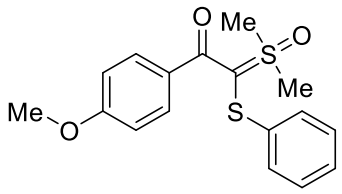
3b, ^{13}C NMR
DMSO-d_6, 100 MHz



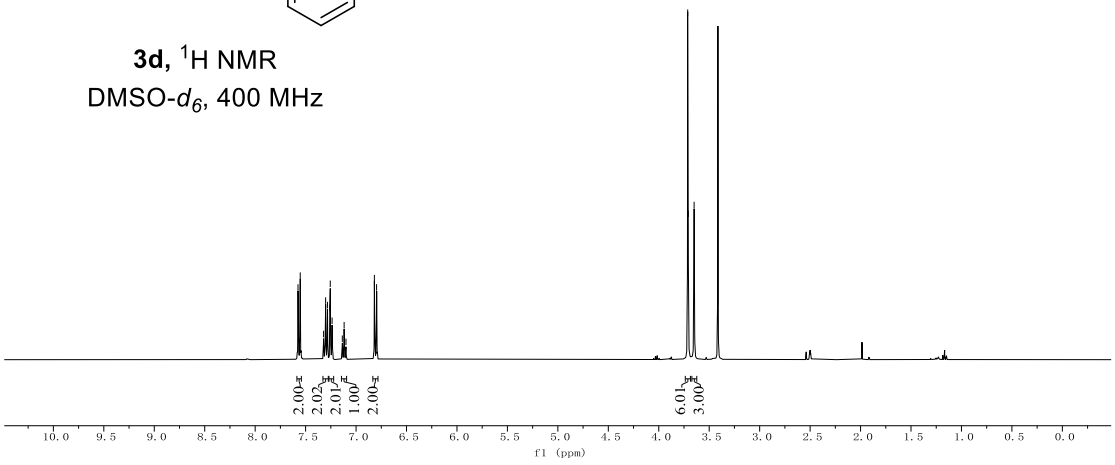
3c, ^{1}H NMR
DMSO-d_6, 400 MHz

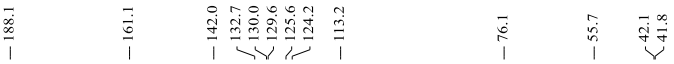


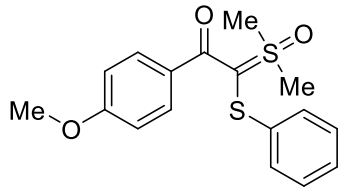
3c, ^{13}C NMR
DMSO-d_6, 100 MHz



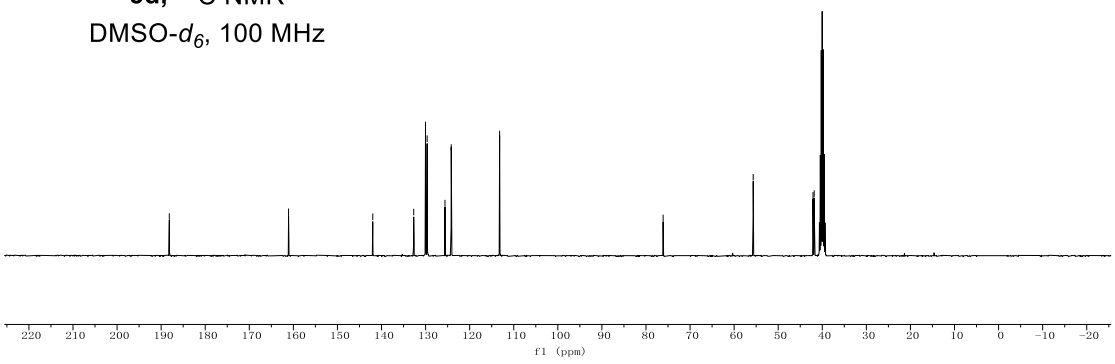
3d, ^{1}H NMR
DMSO-d_6, 400 MHz

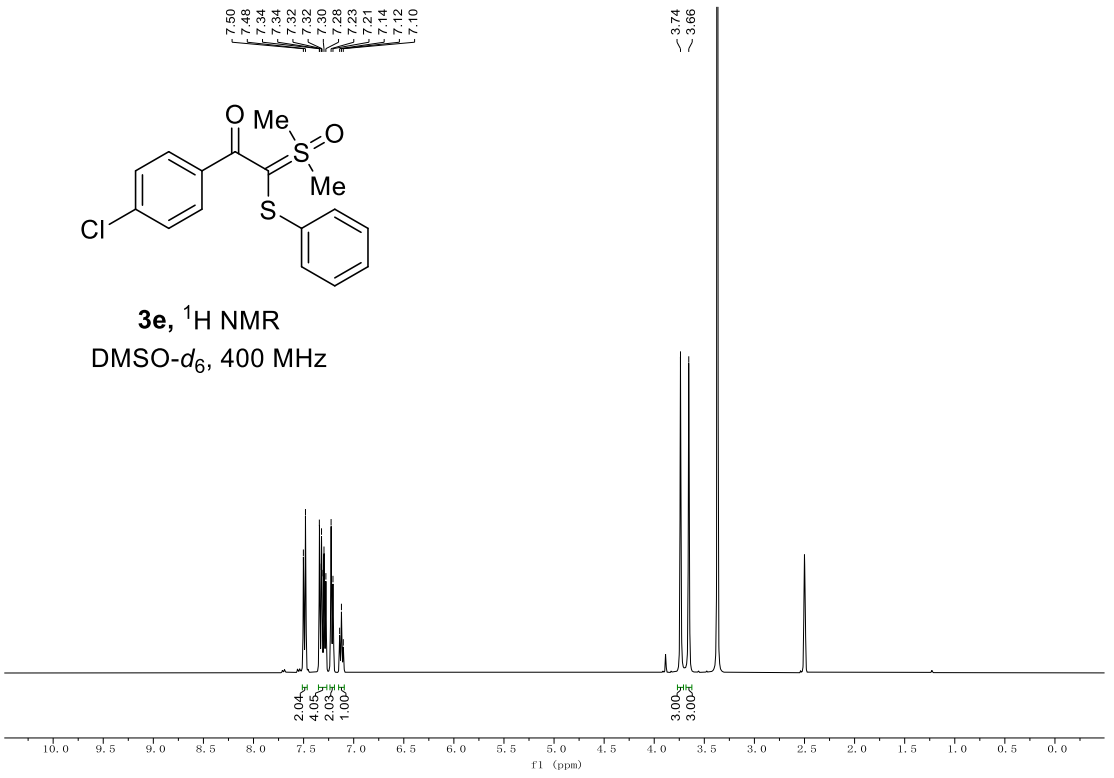




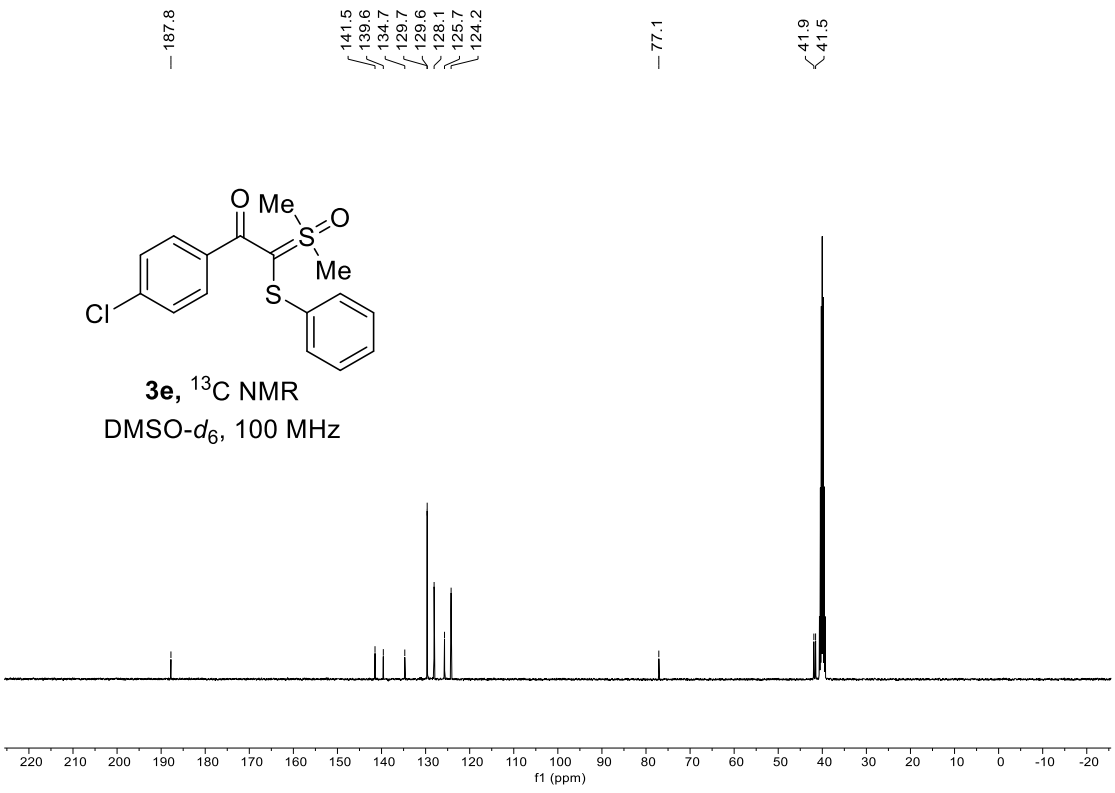


3d, ^{13}C NMR
DMSO-d_6, 100 MHz

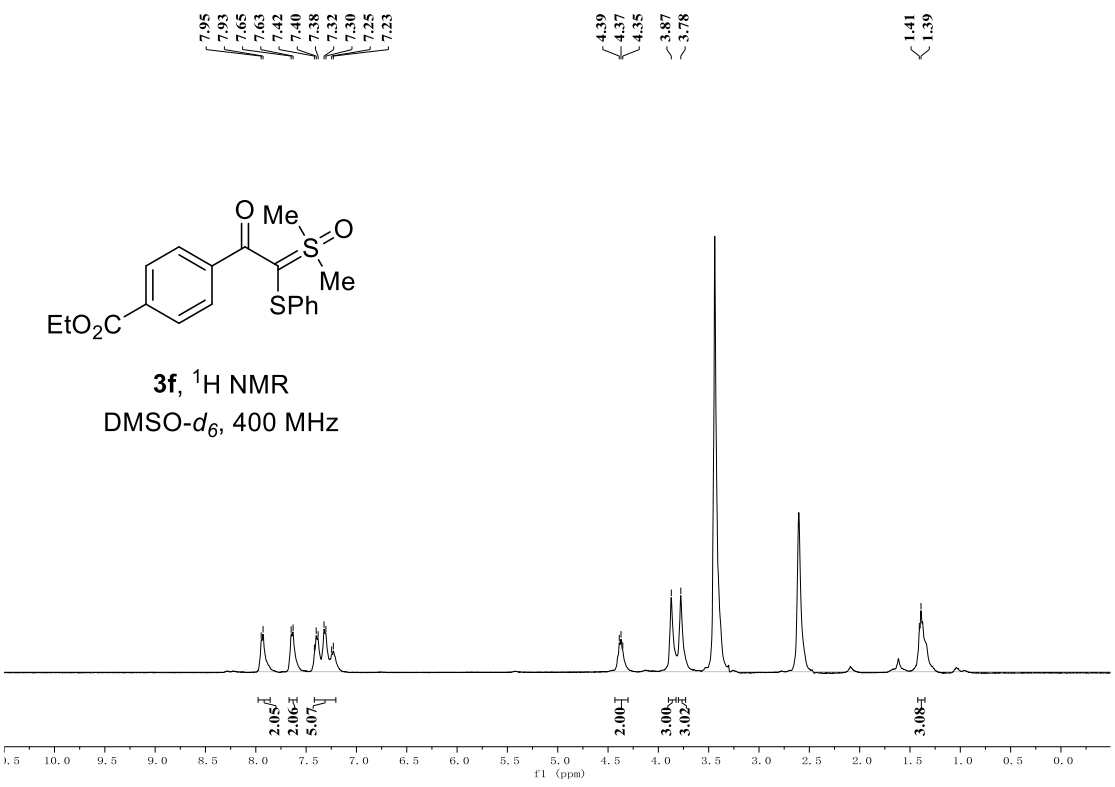




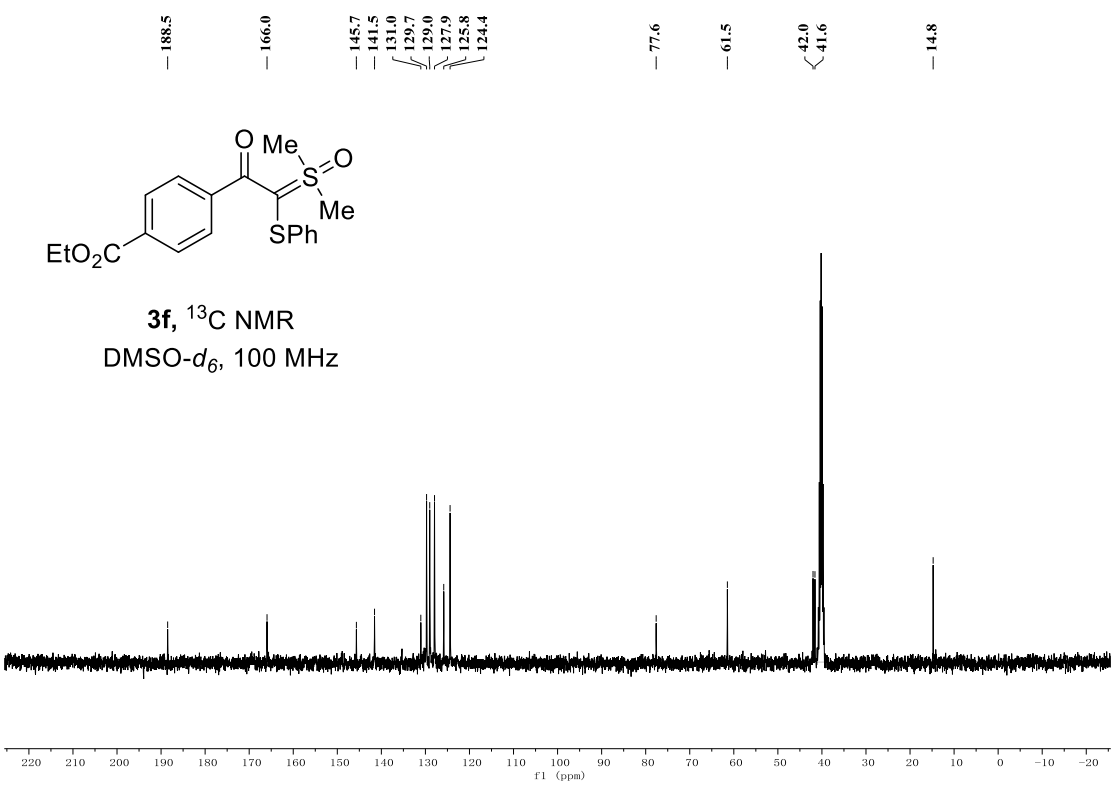
3e, ^{1}H NMR
DMSO-d_6, 400 MHz



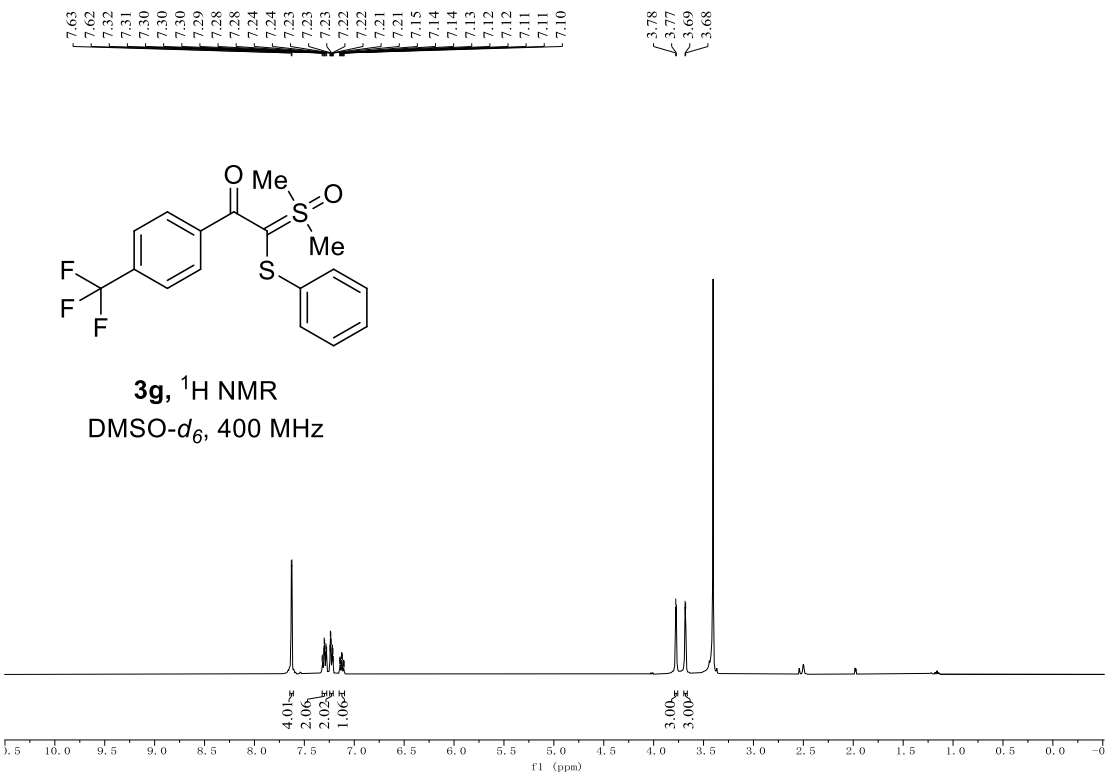
3e, ^{13}C NMR
DMSO-d_6, 100 MHz



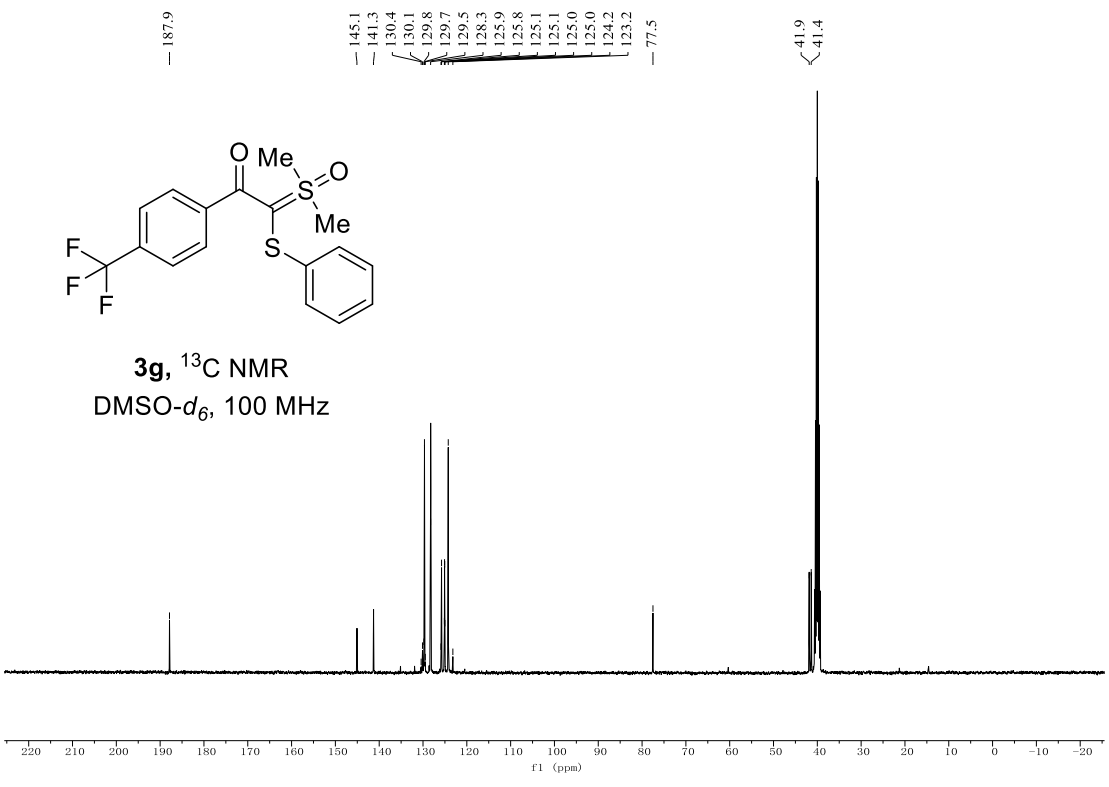
3f, ^{1}H NMR
DMSO-d_6, 400 MHz



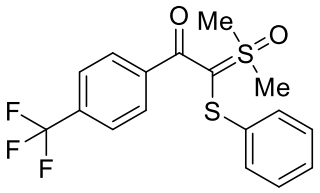
3f, ^{13}C NMR
DMSO-d_6, 100 MHz



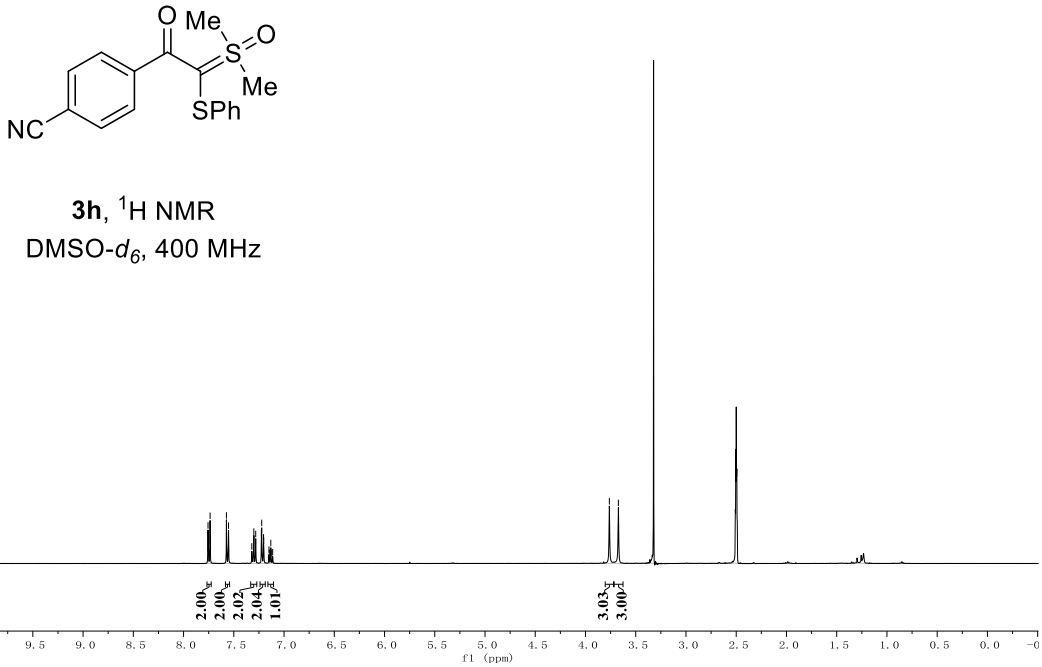
3g, ^{1}H NMR
DMSO-d_6, 400 MHz



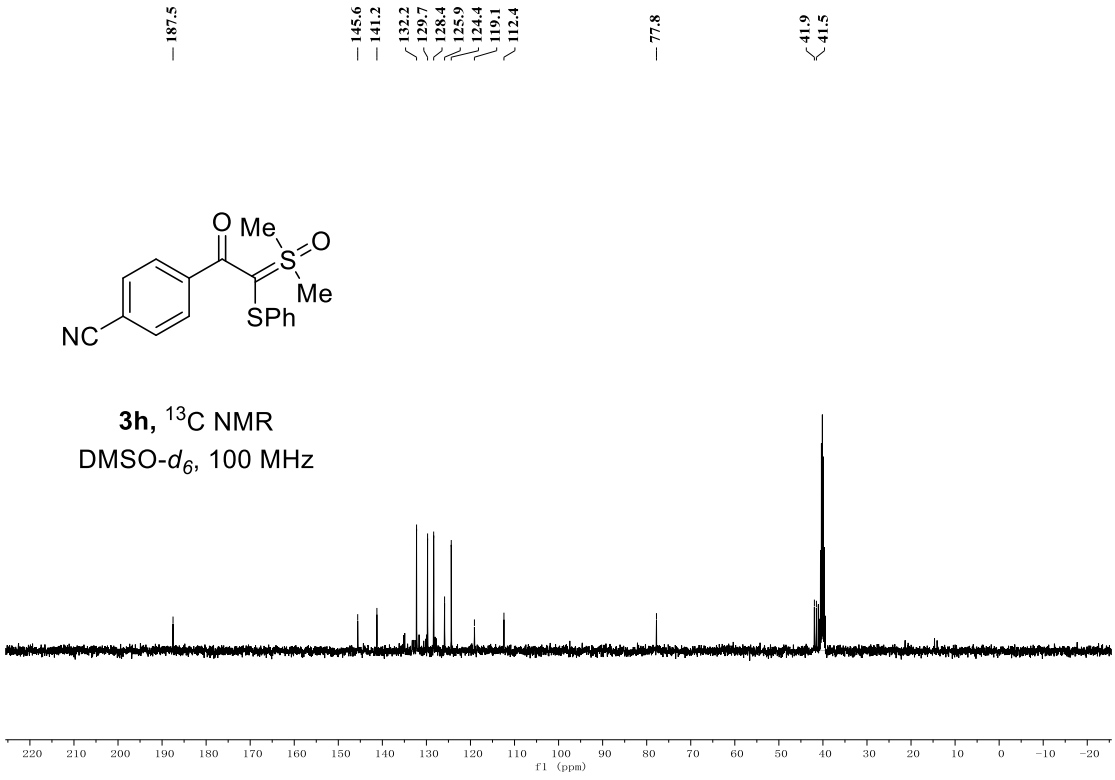
3g, ^{13}C NMR
DMSO-d_6, 100 MHz



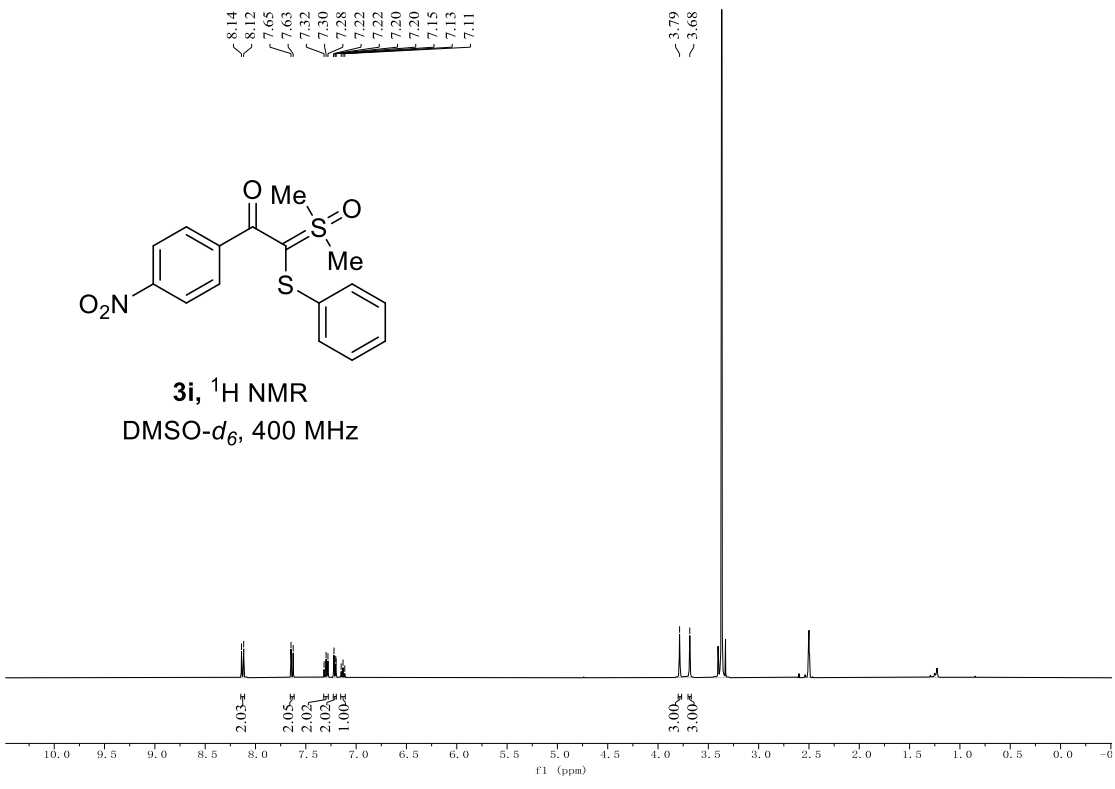
3g, ^{19}F NMR
DMSO-d_6, 376 MHz



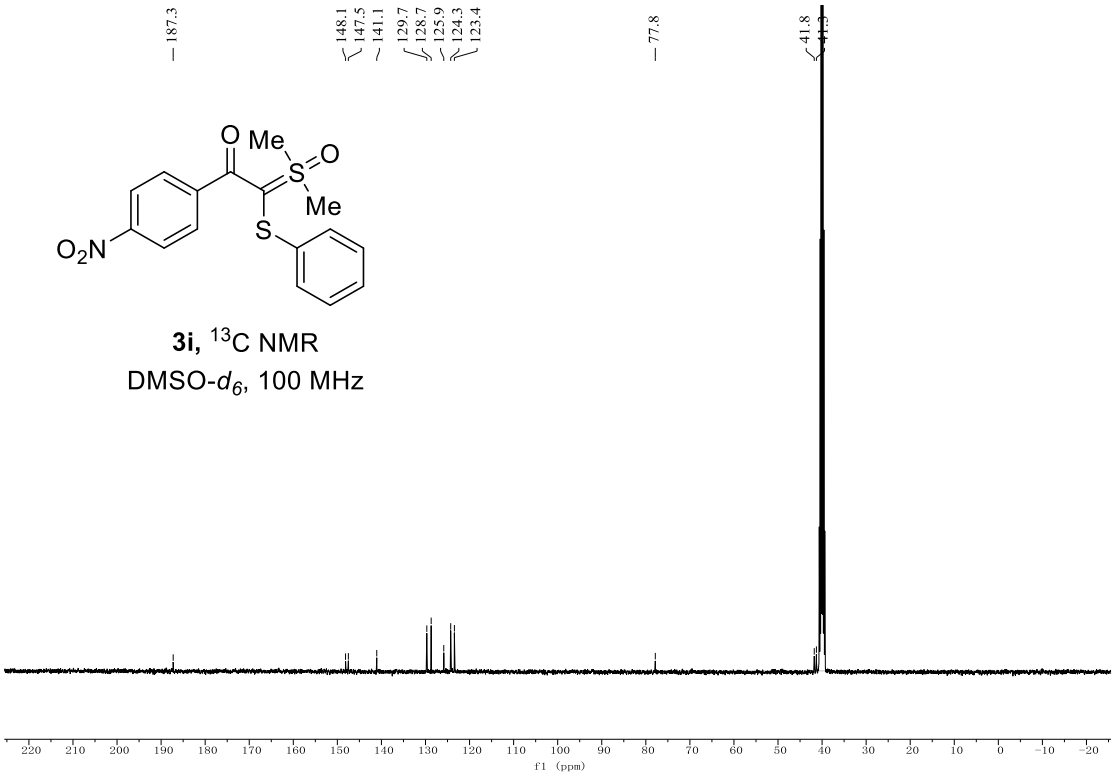
3h, ^{1}H NMR
DMSO-d_6, 400 MHz



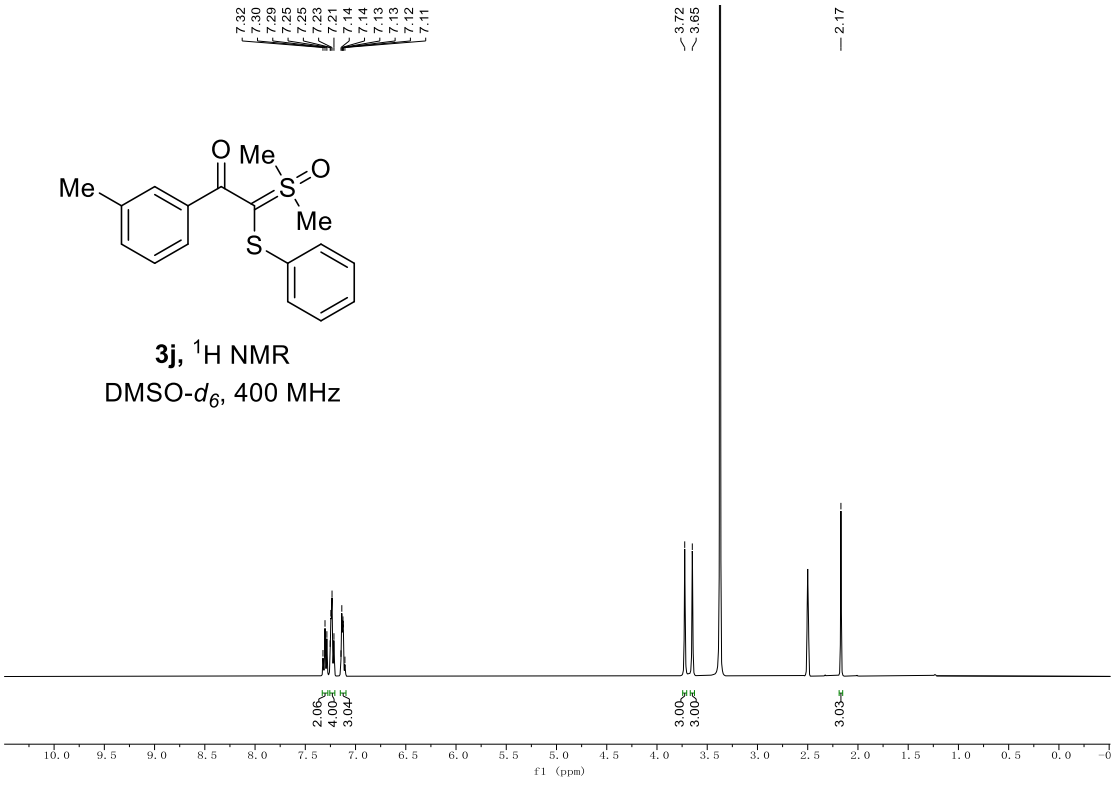
3h, ^{13}C NMR
DMSO-d_6, 100 MHz



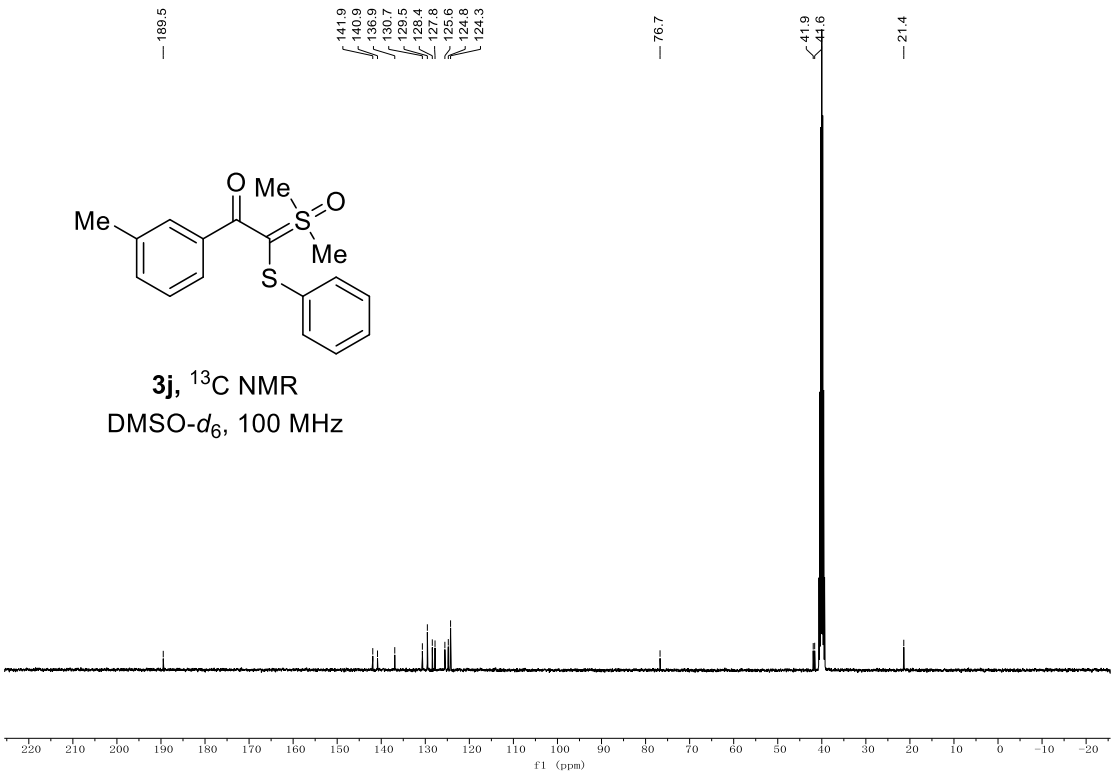
3i, ^{1}H NMR
DMSO-d_6, 400 MHz



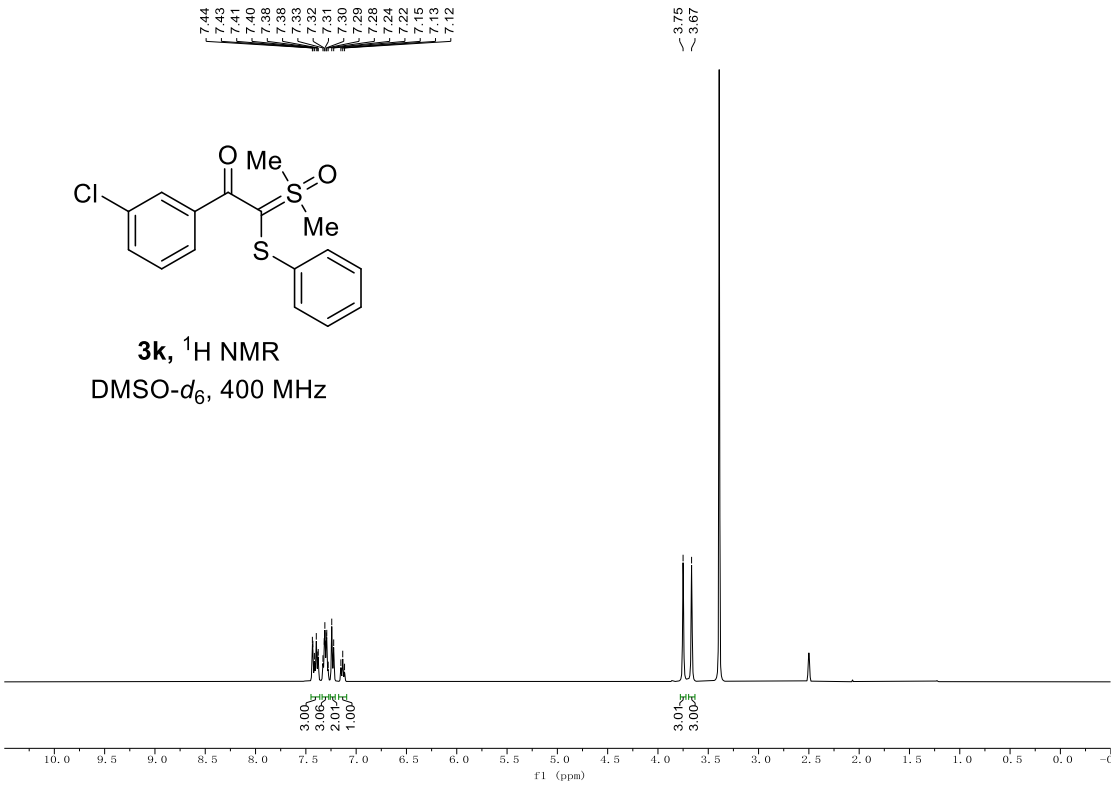
3i, ^{13}C NMR
DMSO-d_6, 100 MHz



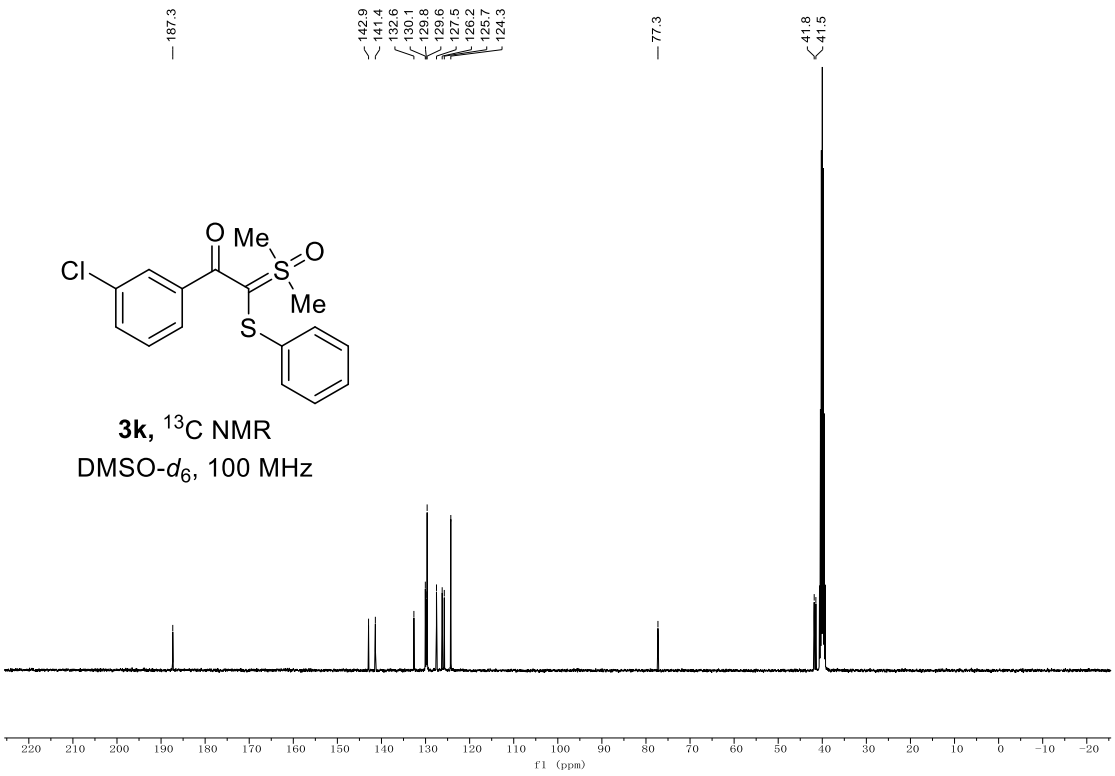
3j, ^{1}H NMR
DMSO-d_6, 400 MHz



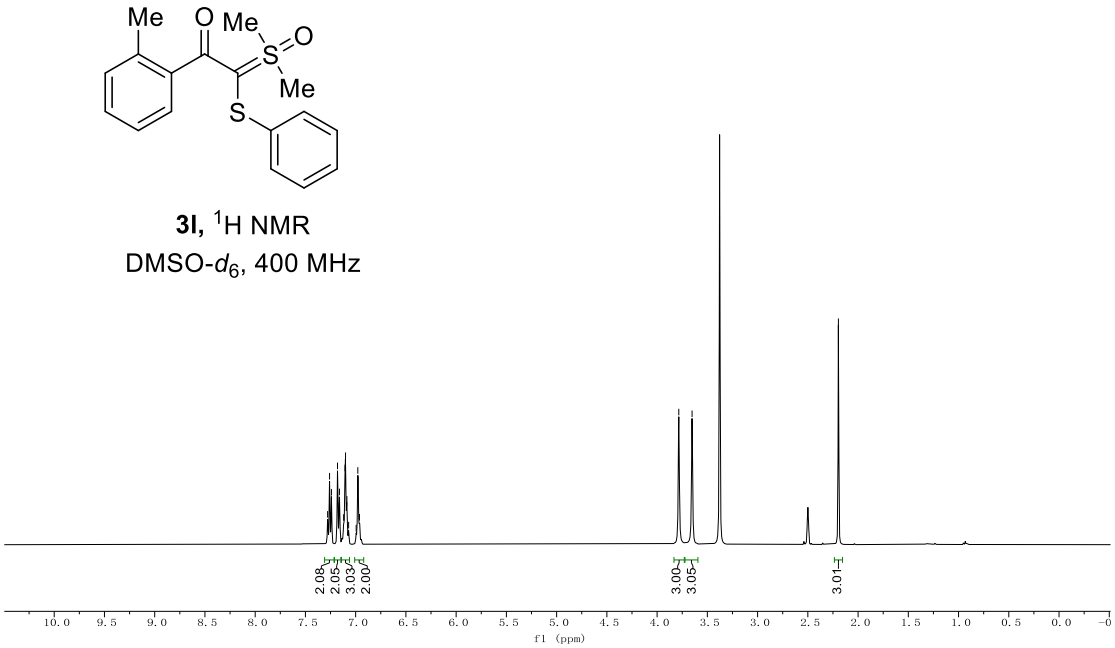
3j, ^{13}C NMR
DMSO-d_6, 100 MHz



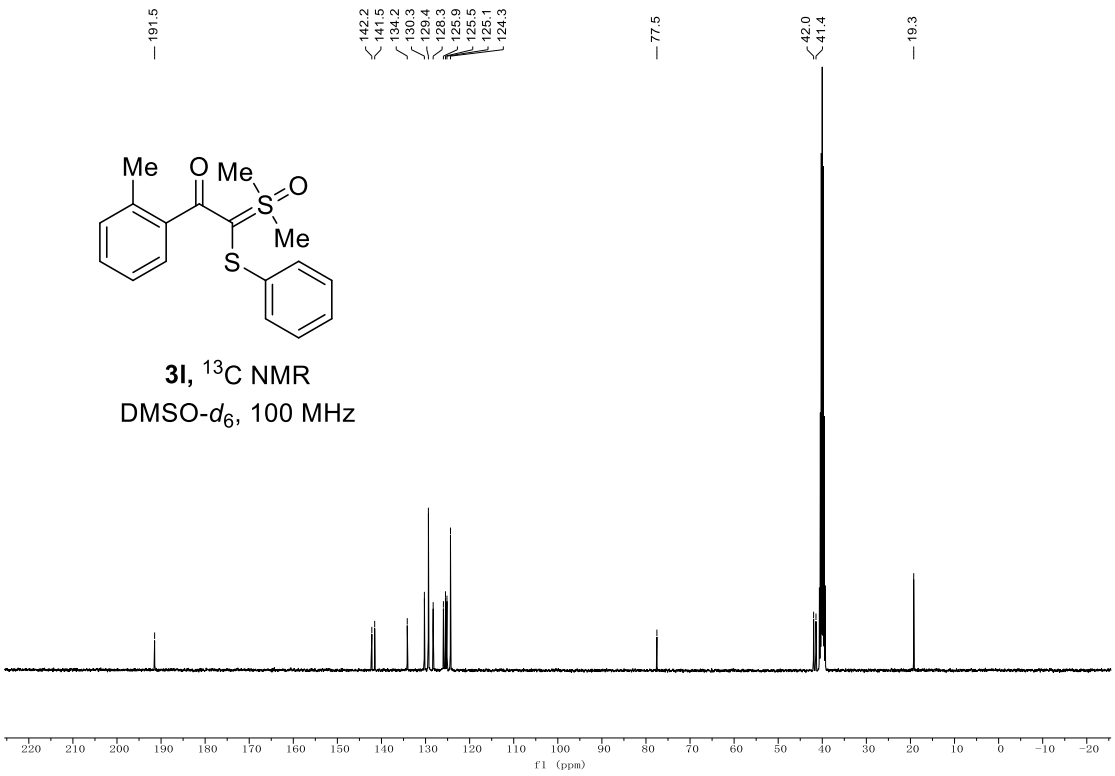
3k, ^{1}H NMR
DMSO-d_6, 400 MHz



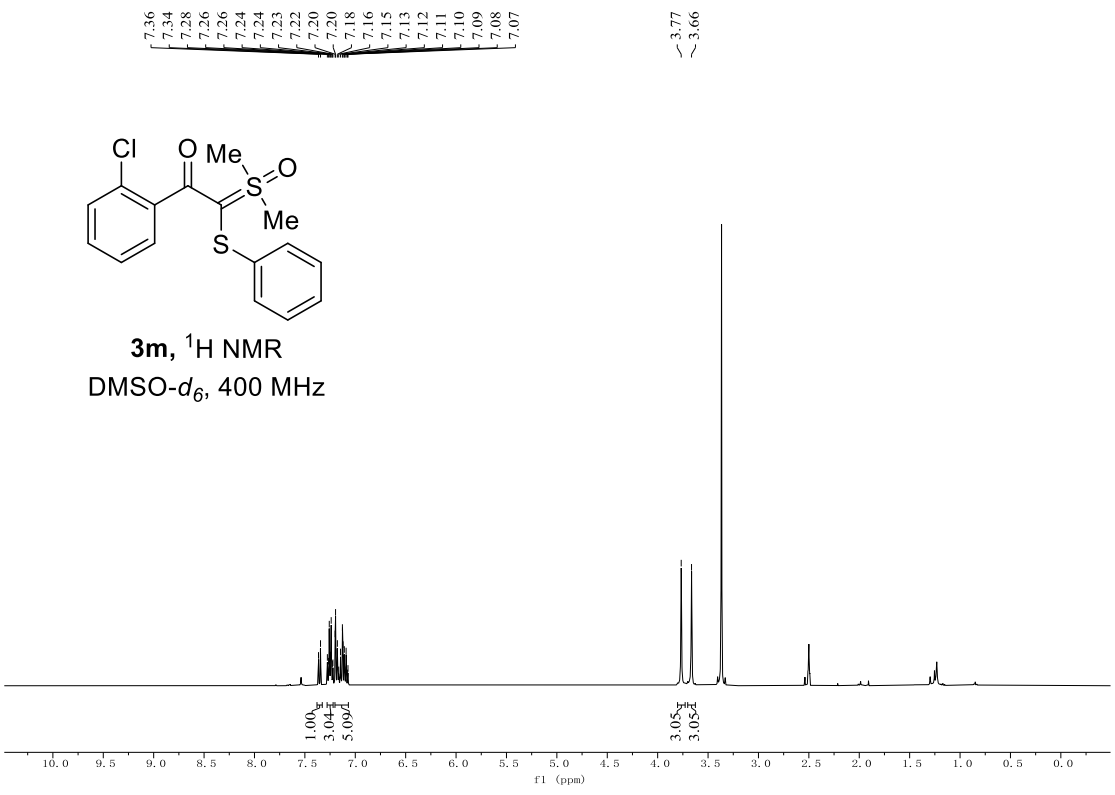
3k, ^{13}C NMR
DMSO-d_6, 100 MHz



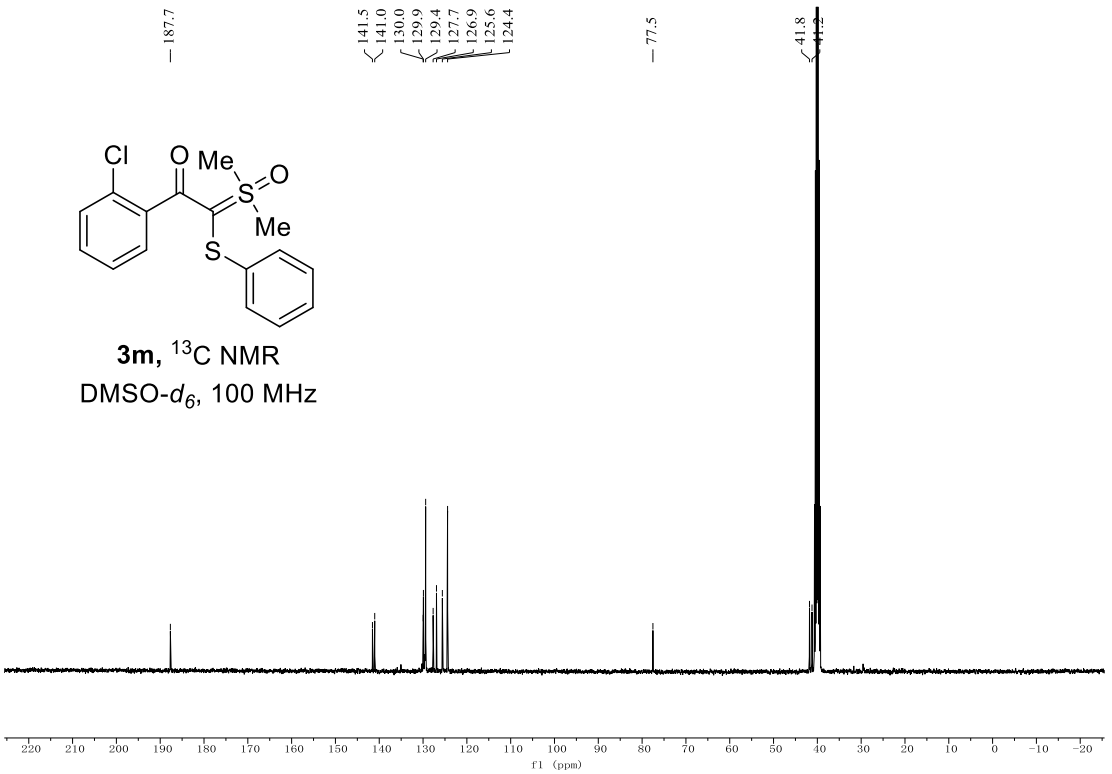
3l, ^{1}H NMR
DMSO-d_6, 400 MHz



3l, ^{13}C NMR
DMSO-d_6, 100 MHz

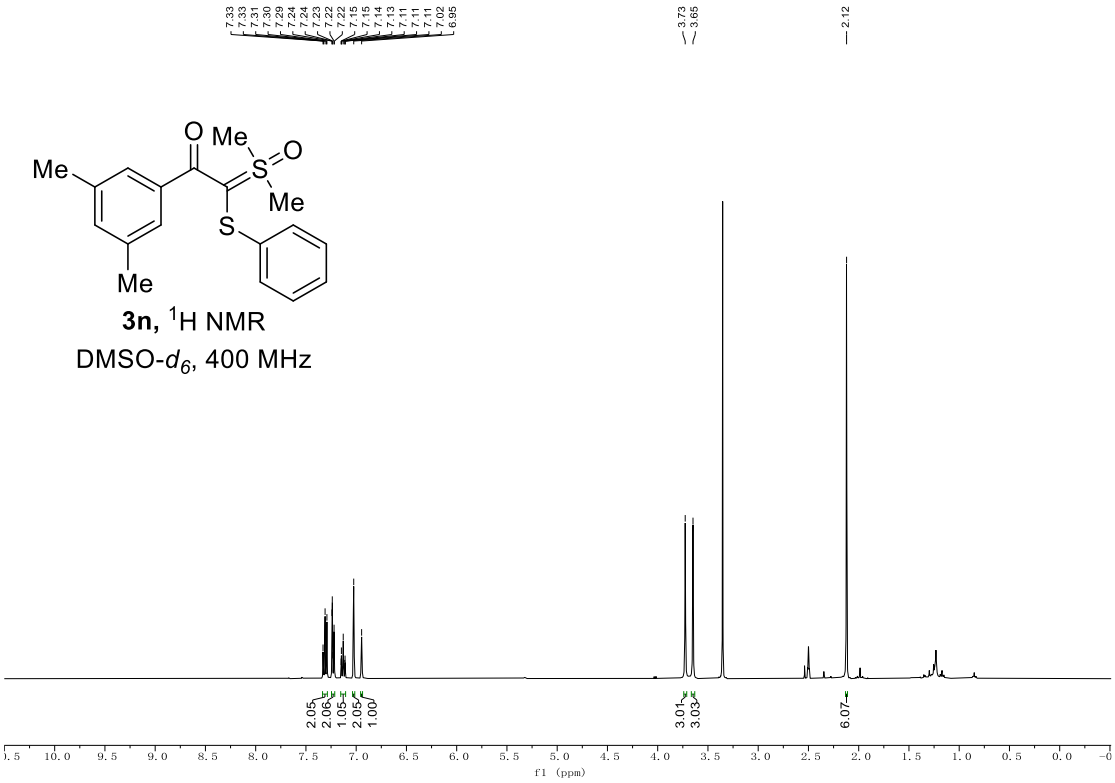


3m, ^{1}H NMR
DMSO-d_6, 400 MHz



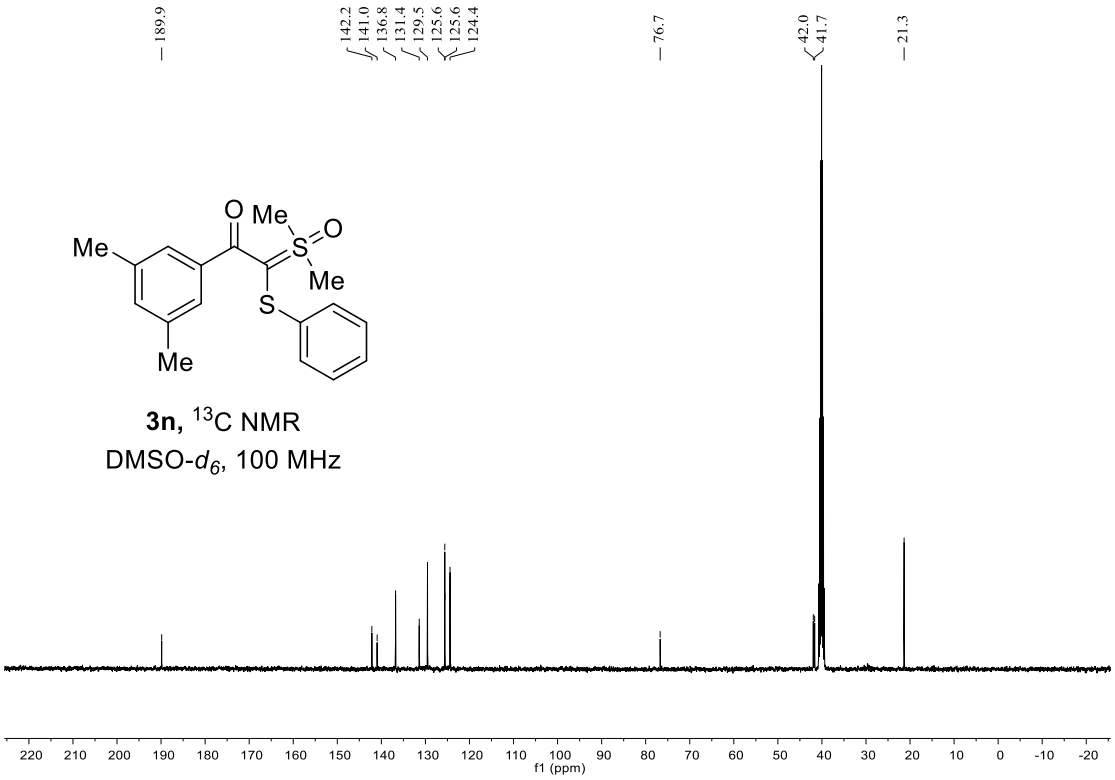
3m, ^{13}C NMR

DMSO-d_6, 100 MHz

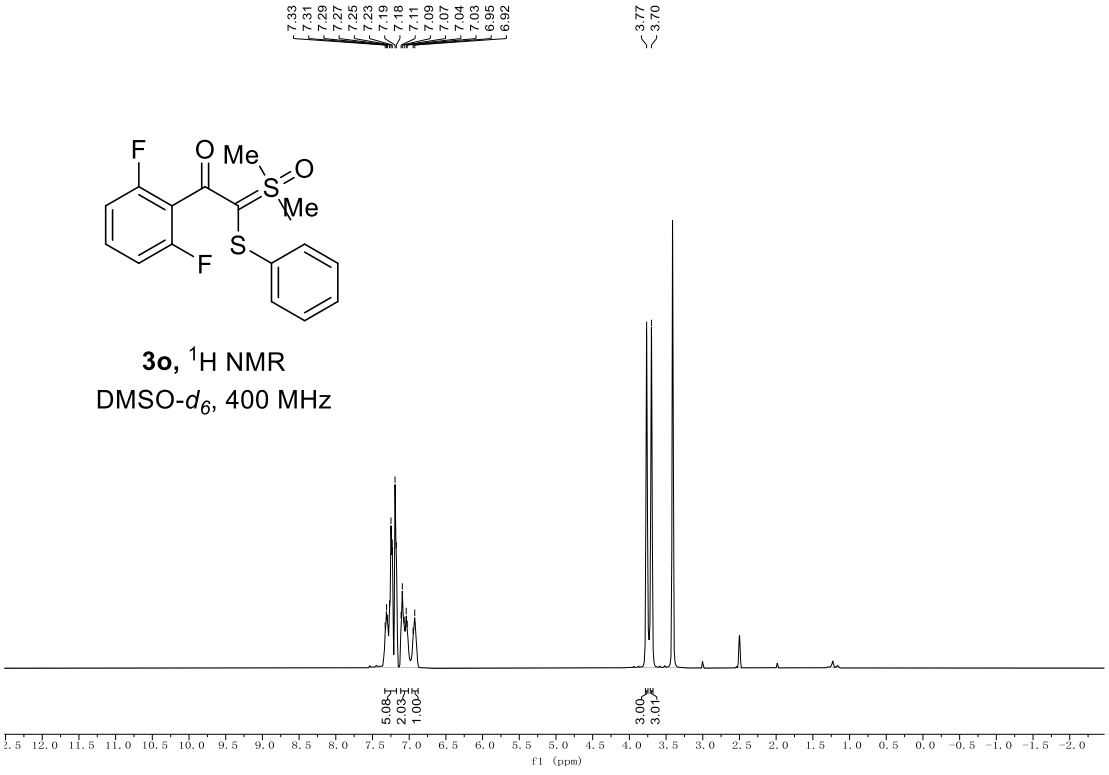


3n, ^{1}H NMR

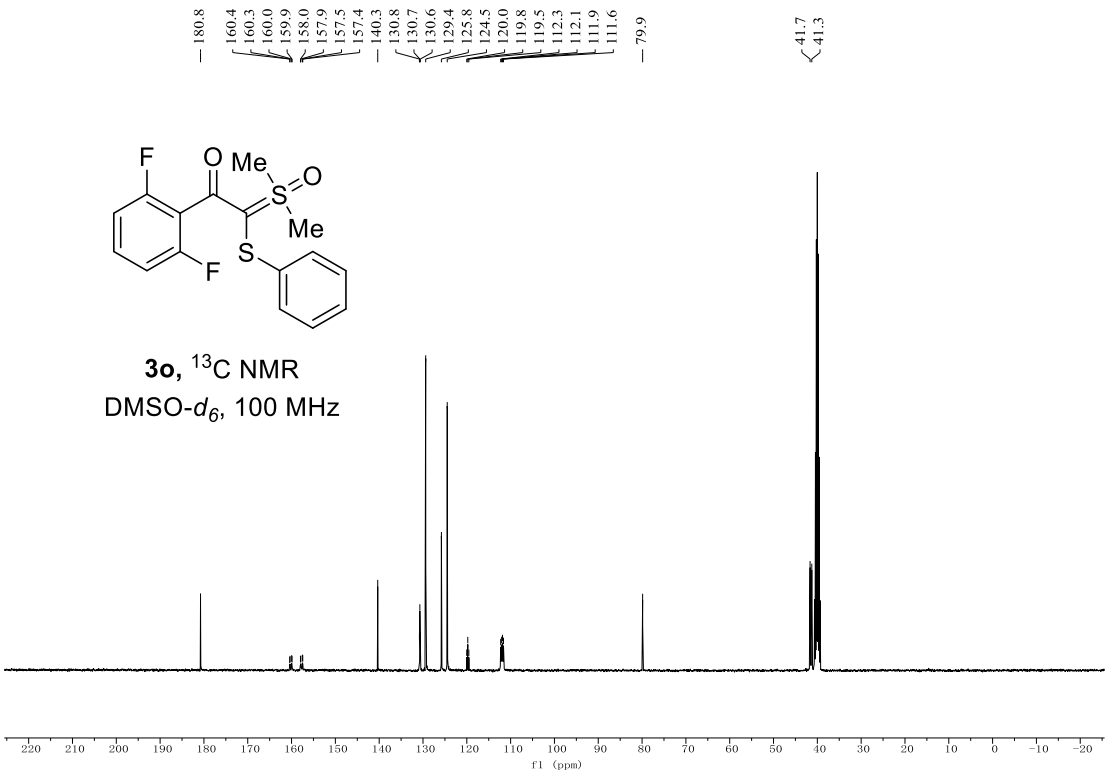
DMSO-d_6, 400 MHz



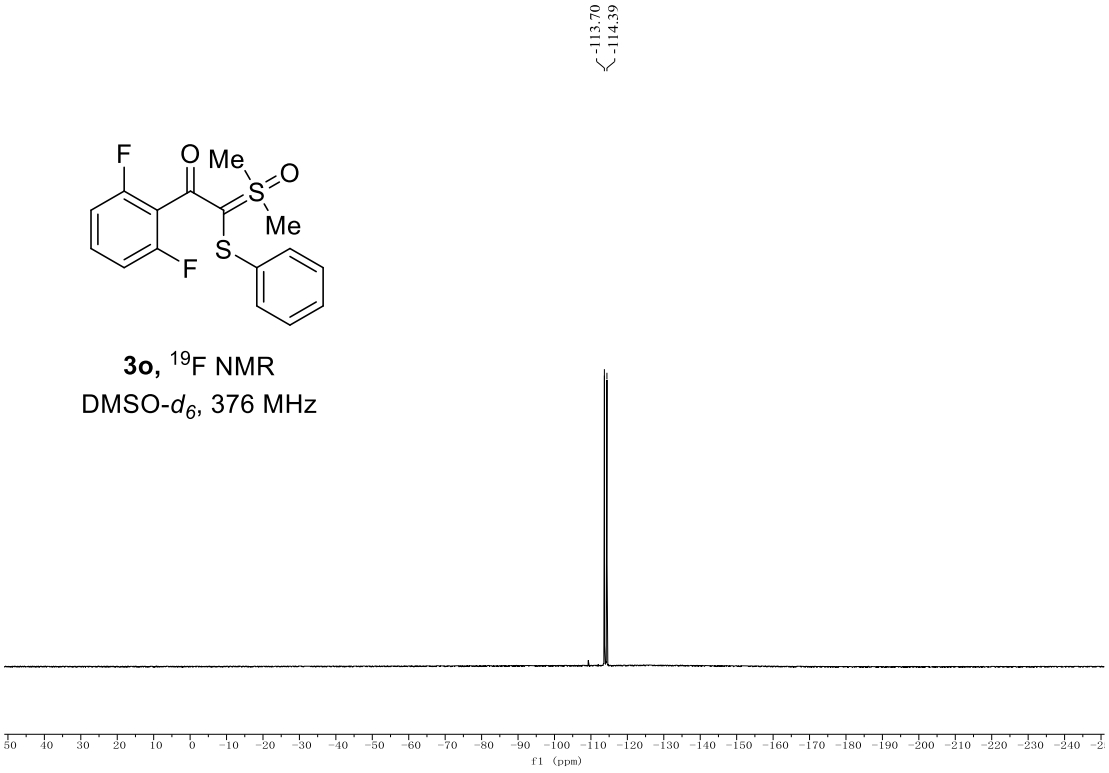
3n, ^{13}C NMR
DMSO-d_6, 100 MHz



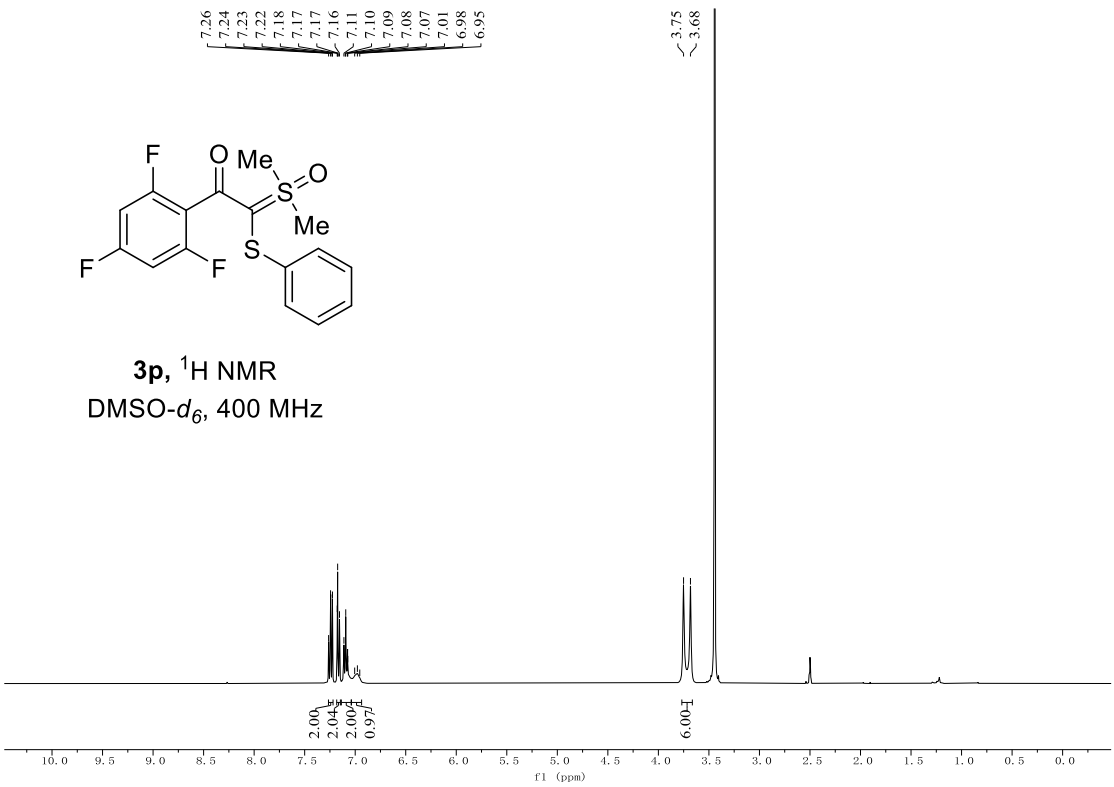
3o, ^{1}H NMR
DMSO-d_6, 400 MHz



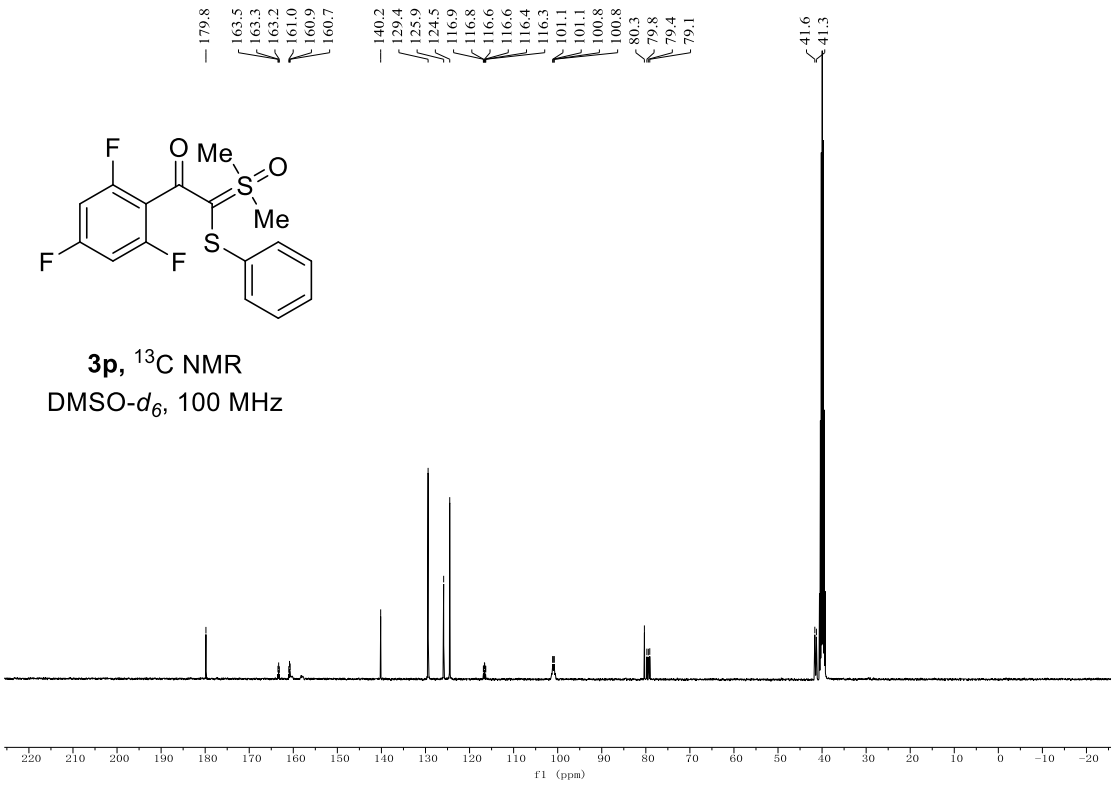
3o, ^{13}C NMR
DMSO-d_6, 100 MHz



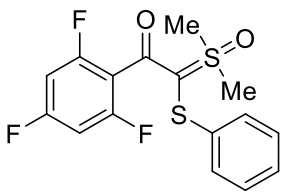
3o, ^{19}F NMR
DMSO-d_6, 376 MHz



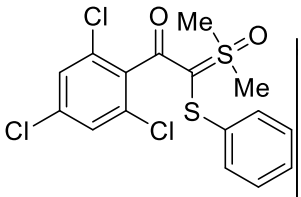
3p, ^{1}H NMR
DMSO-d_6, 400 MHz



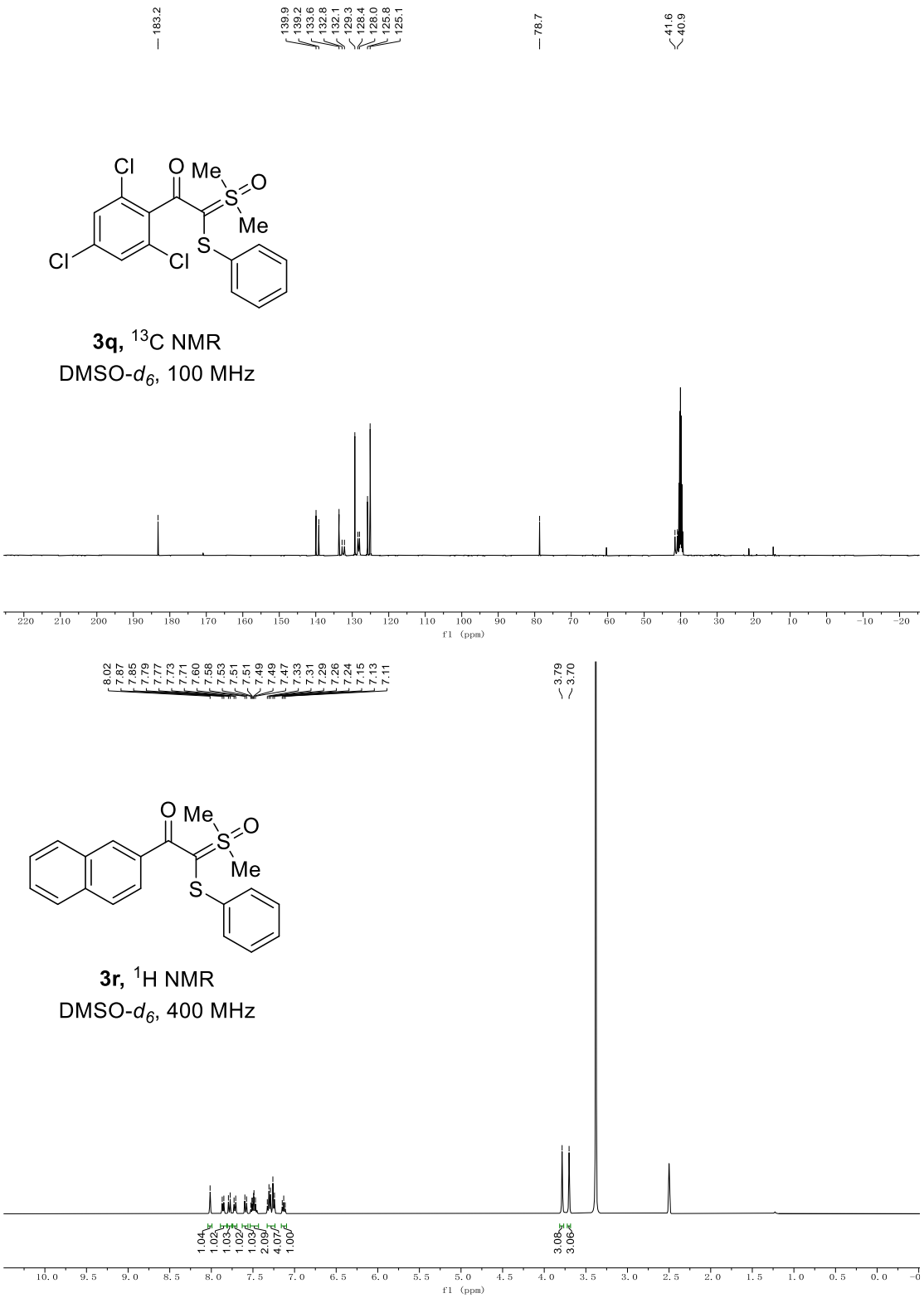
3p, ^{13}C NMR
DMSO-d_6, 100 MHz



3p, ^{19}F NMR
DMSO-d_6, 376 MHz

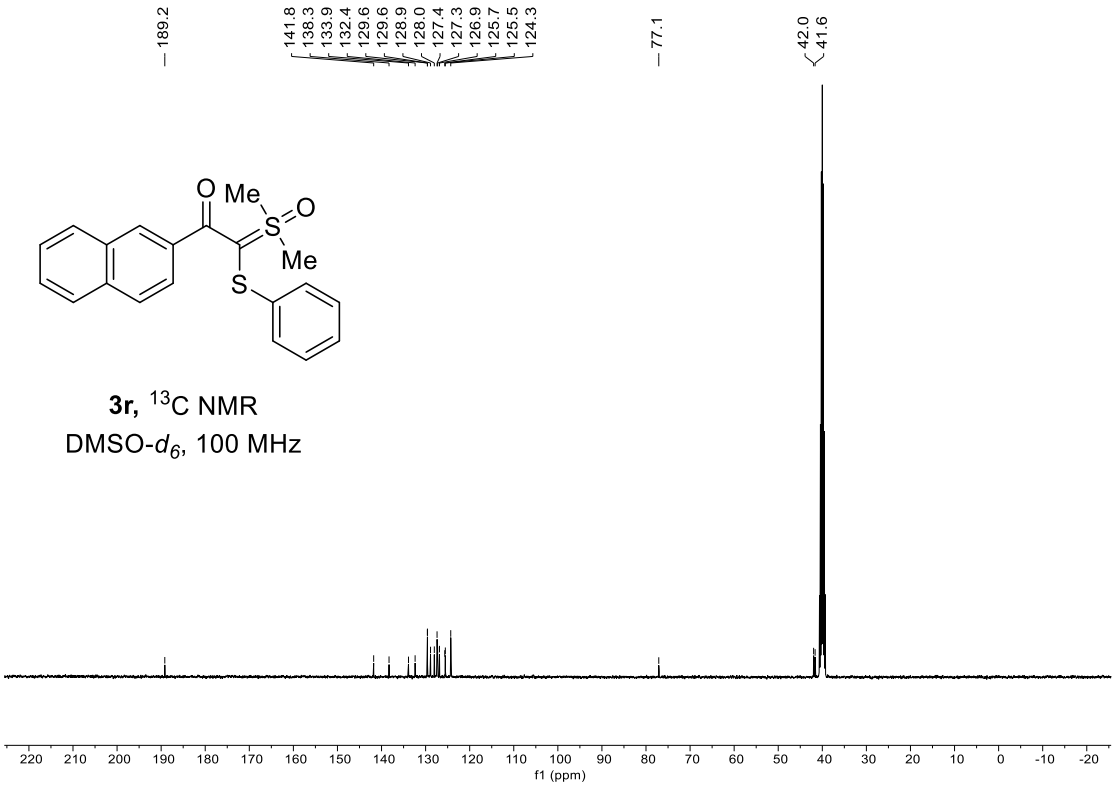


3q, ^{1}H NMR
DMSO-d_6, 400 MHz

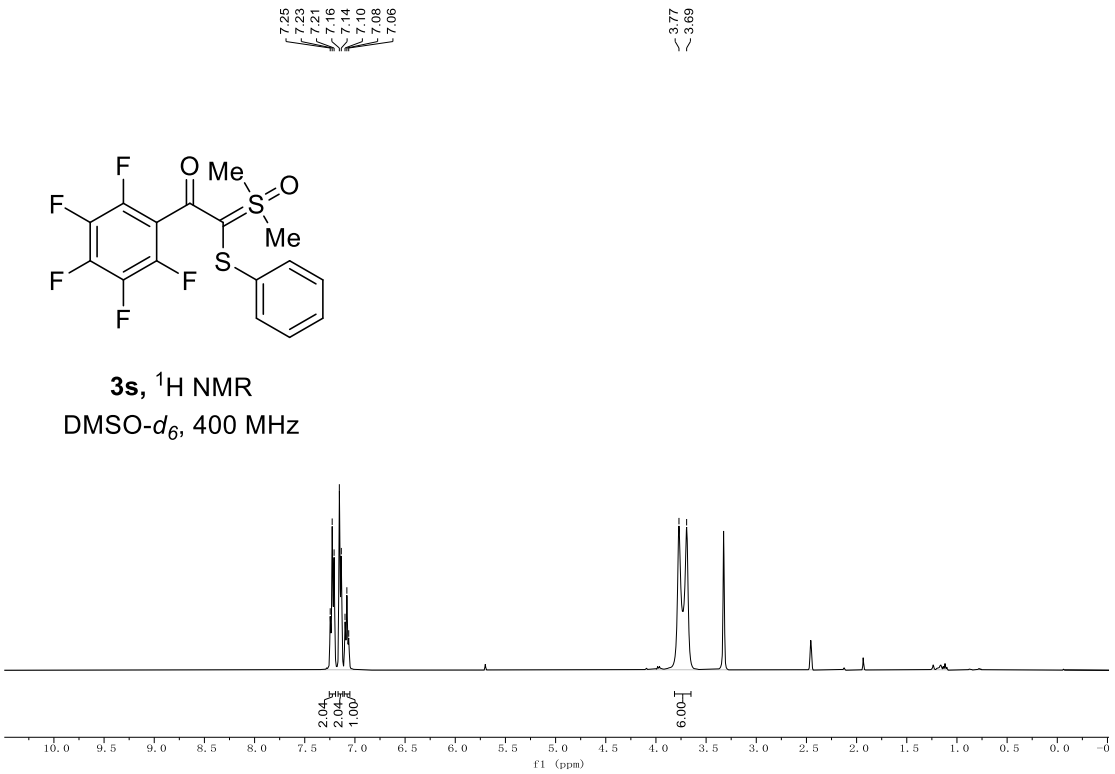


3q, ^{13}C NMR
DMSO-d_6, 100 MHz

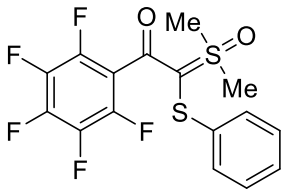
3r, ^{1}H NMR
DMSO-d_6, 400 MHz



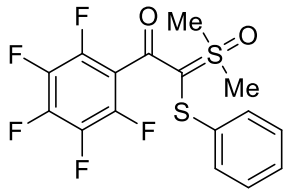
3r, ^{13}C NMR
DMSO-d_6, 100 MHz



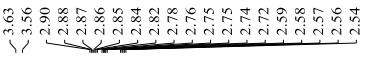
3s, ^{1}H NMR
DMSO-d_6, 400 MHz

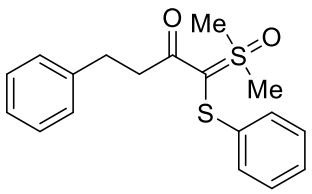


3s, ^{13}C NMR
DMSO-d_6, 100 MHz

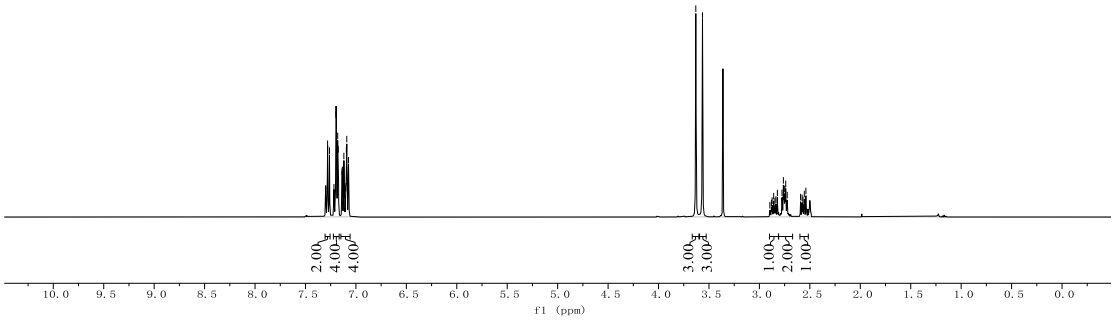


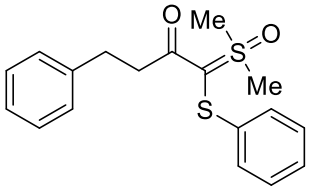
3s, ^{19}F NMR
DMSO-d_6, 376 MHz



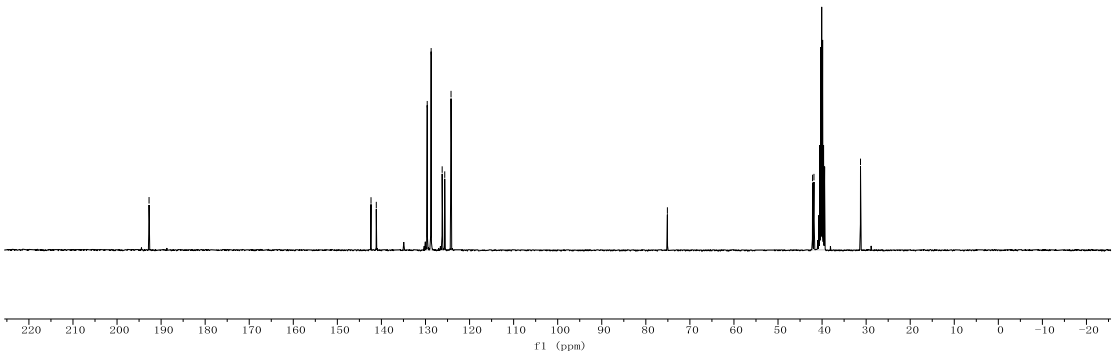


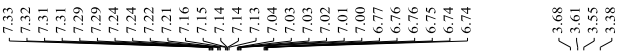
3t, ^{1}H NMR
DMSO-d6, 400 MHz

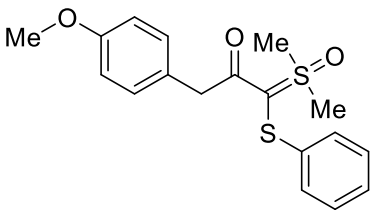




3t, ^{13}C NMR
DMSO-d6, 100 MHz

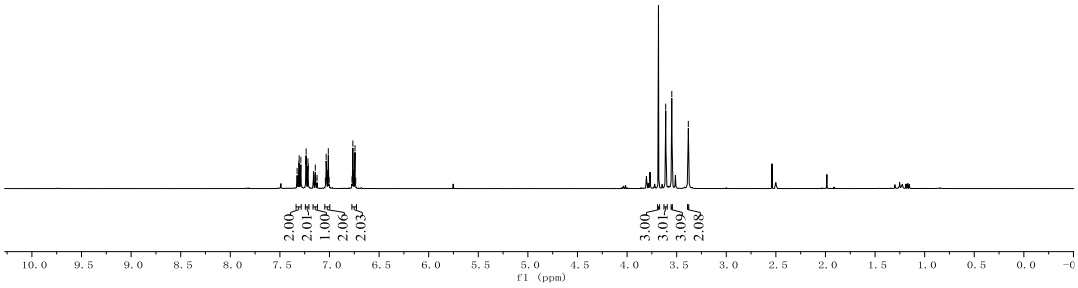


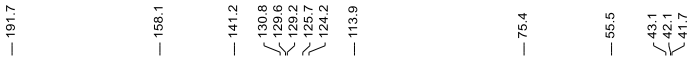


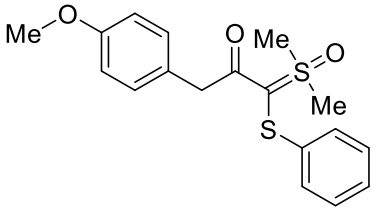


3u, ^{1}H NMR

DMSO-d_6, 400 MHz

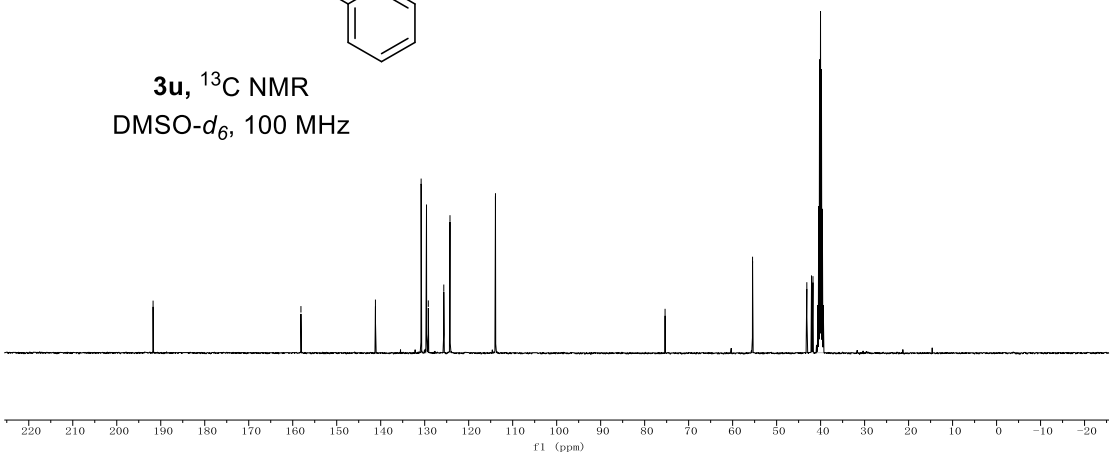


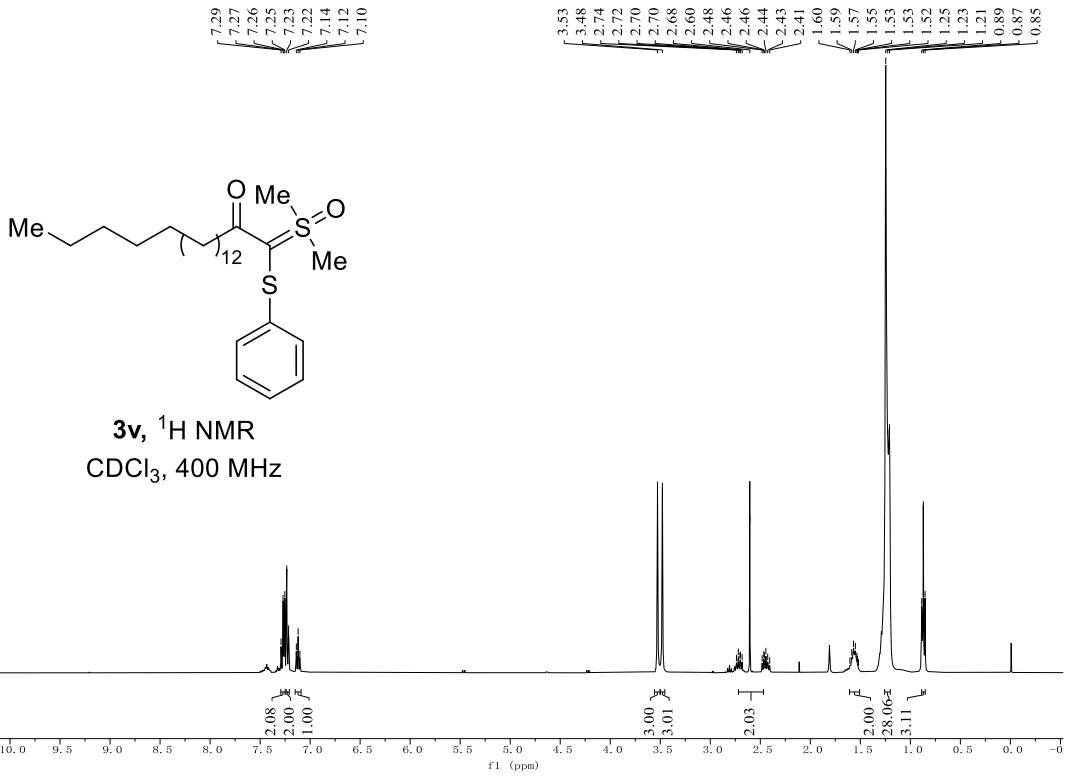




3u, ^{13}C NMR

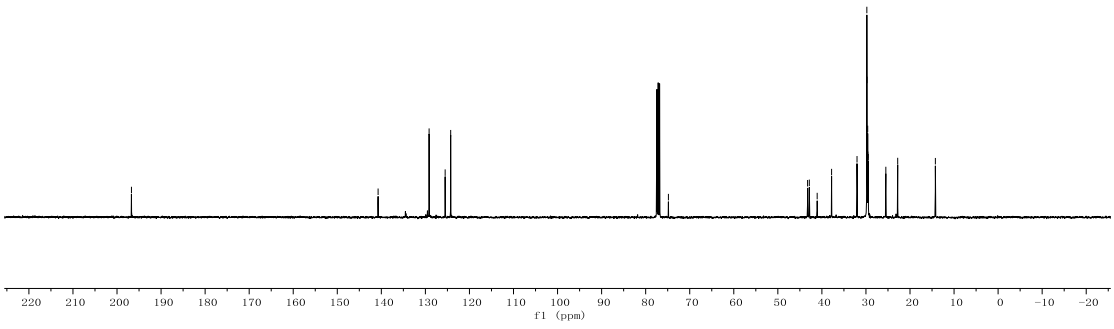
DMSO-d_6, 100 MHz

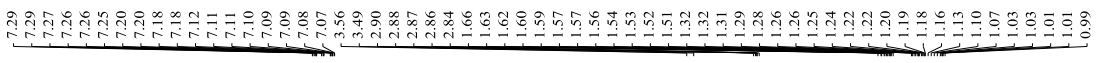


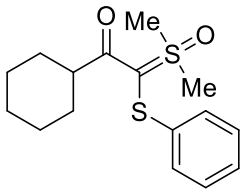


3v, ^{1}H NMR
$CDCl_3$, 400 MHz

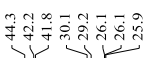
3v, ^{13}C NMR
$CDCl_3$, 100 MHz

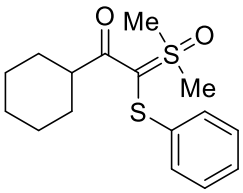




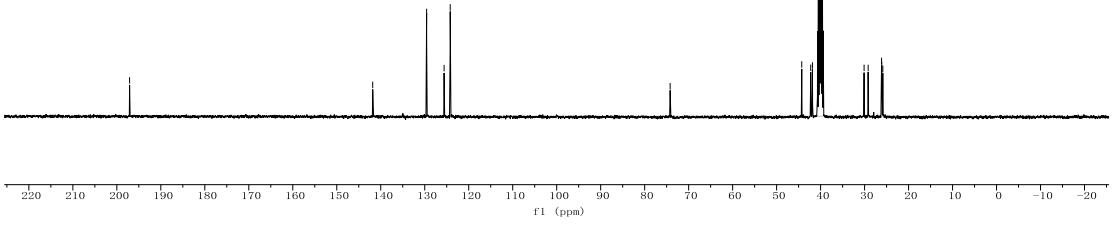


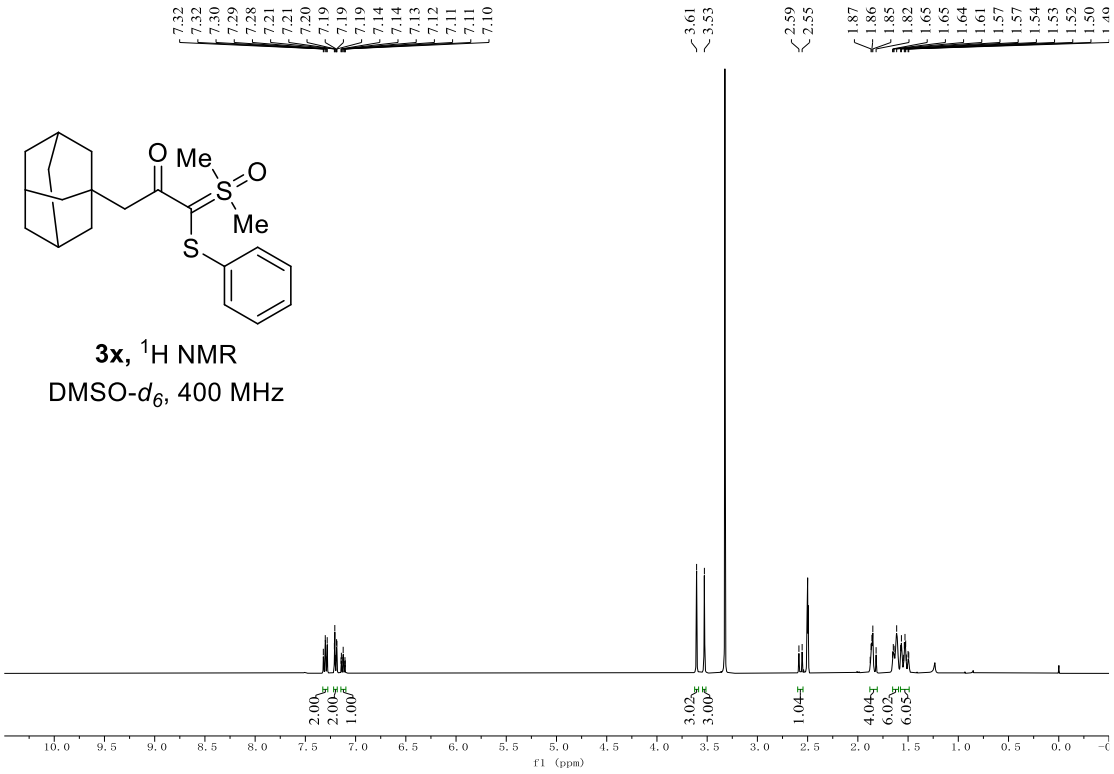
3w, ^{1}H NMR
DMSO-d_6, 400 MHz



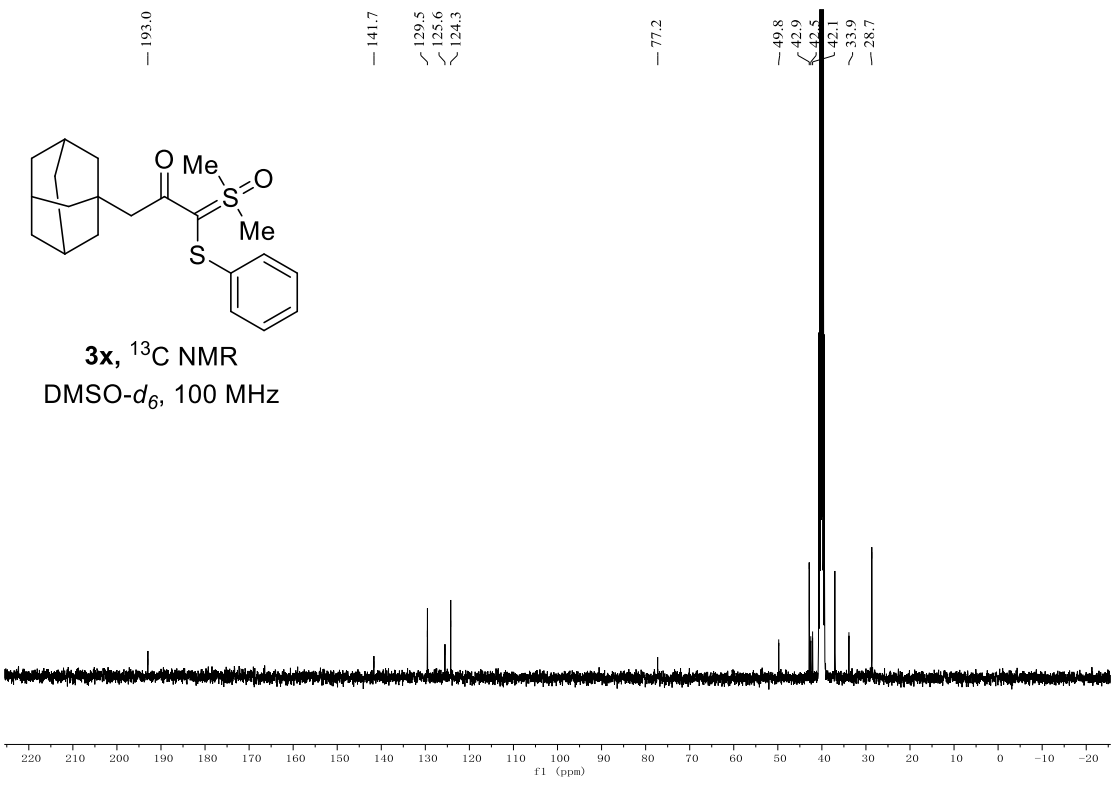


3w, ^{13}C NMR
DMSO-d_6, 100 MHz

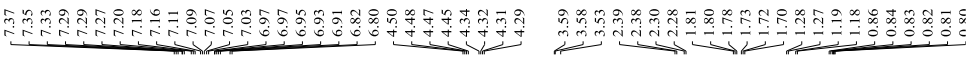


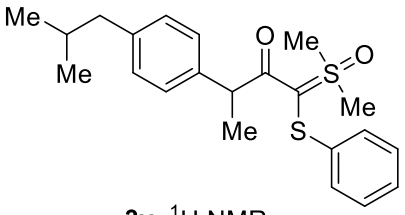


3x, ^{1}H NMR
DMSO-d_6, 400 MHz



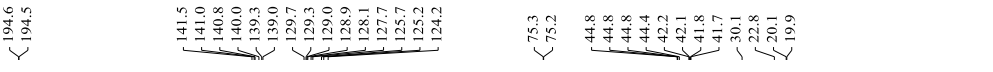
3x, ^{13}C NMR
DMSO-d_6, 100 MHz

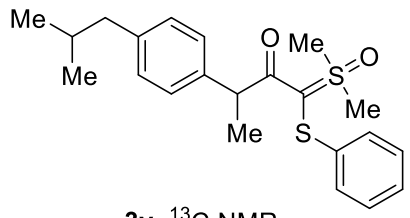




3y, ^{1}H NMR

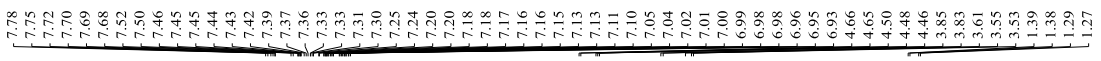
DMSO-d_6, 400 MHz

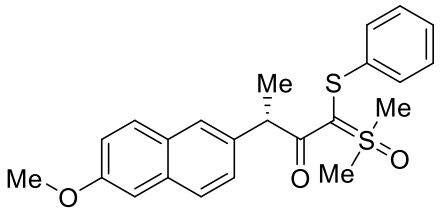




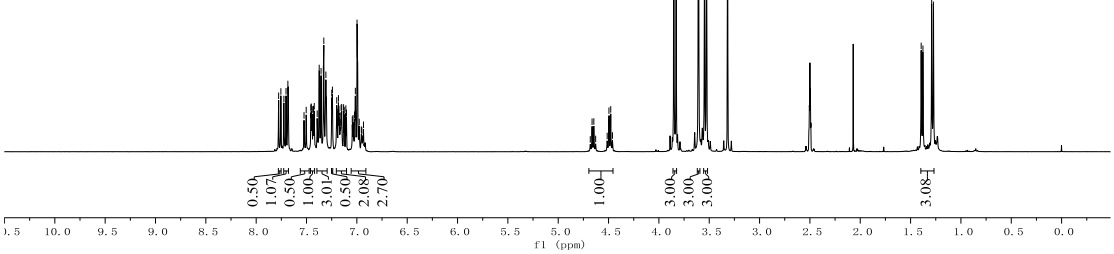
3y, ^{13}C NMR

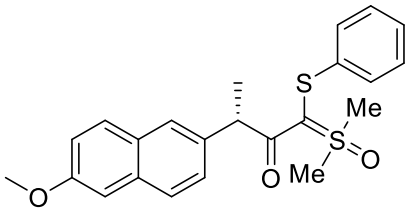
DMSO-d_6, 100 MHz



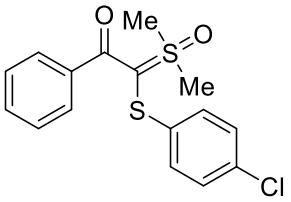


3z, ^{1}H NMR
DMSO-d_6, 400 MHz



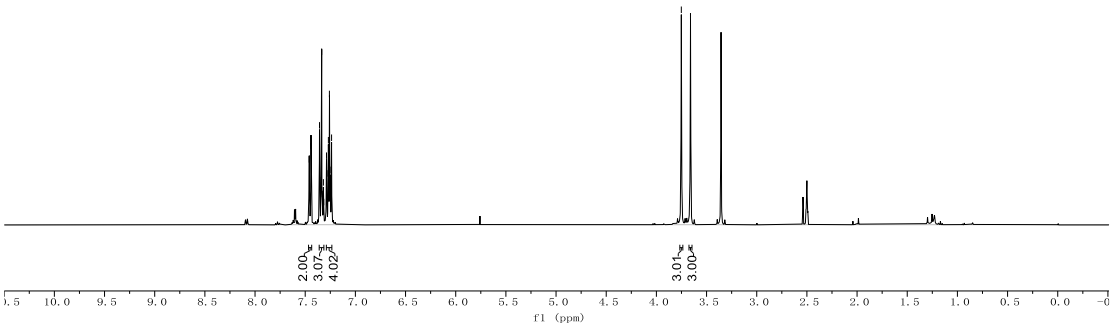


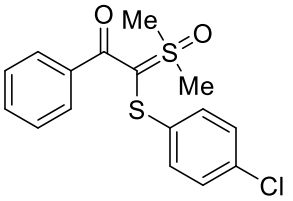
3z, ^{13}C NMR
DMSO-d_6, 100 MHz



3z-1, ^{1}H NMR

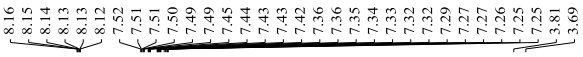
DMSO-d_6, 400 MHz

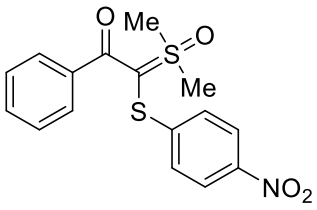




3z-1, ^{13}C NMR

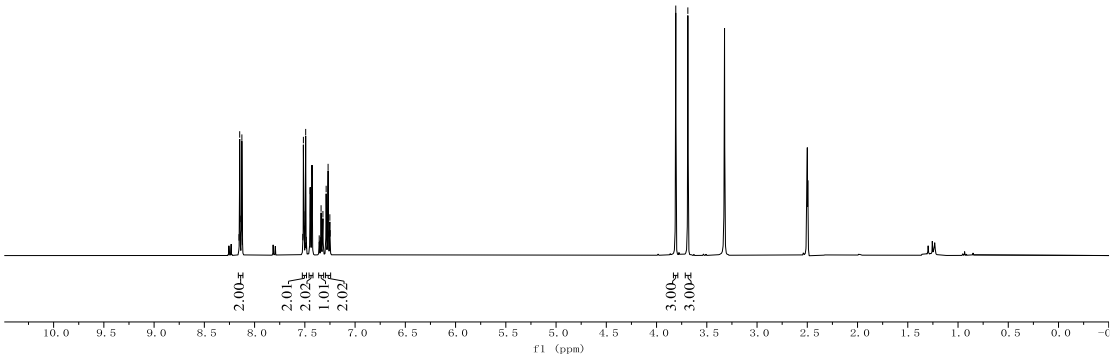
DMSO-d_6, 100 MHz

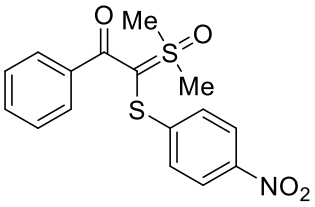




3z-2, ^{1}H NMR

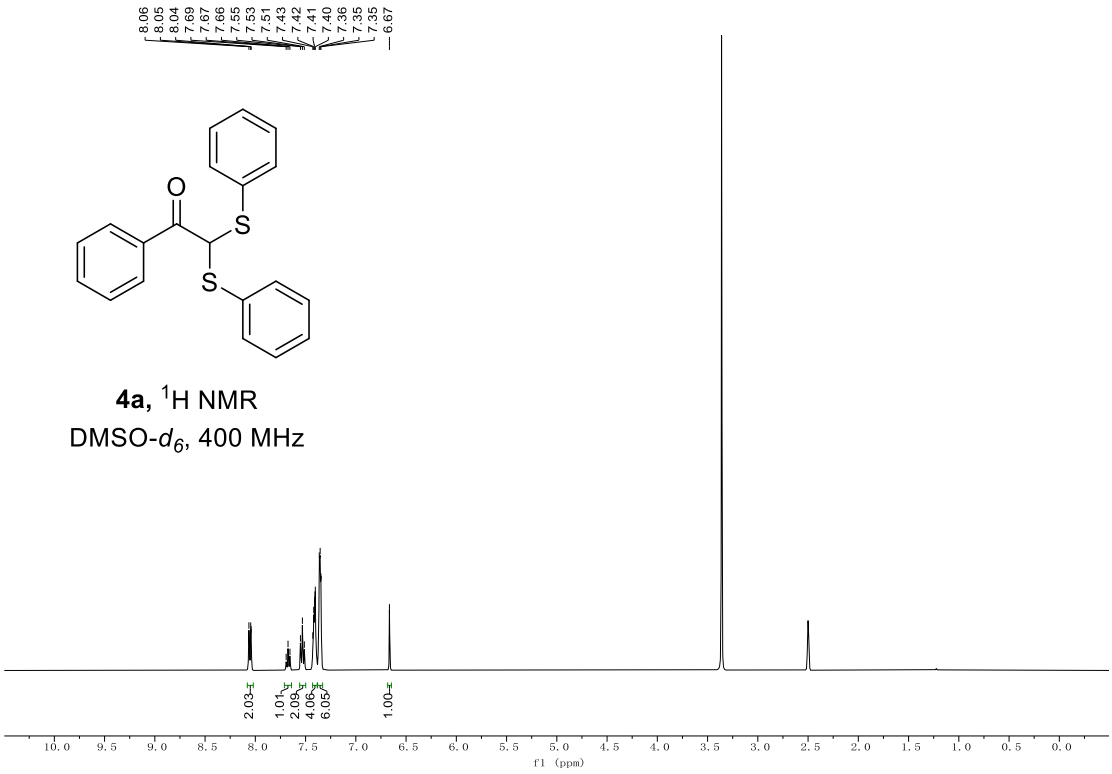
DMSO-d_6, 400 MHz



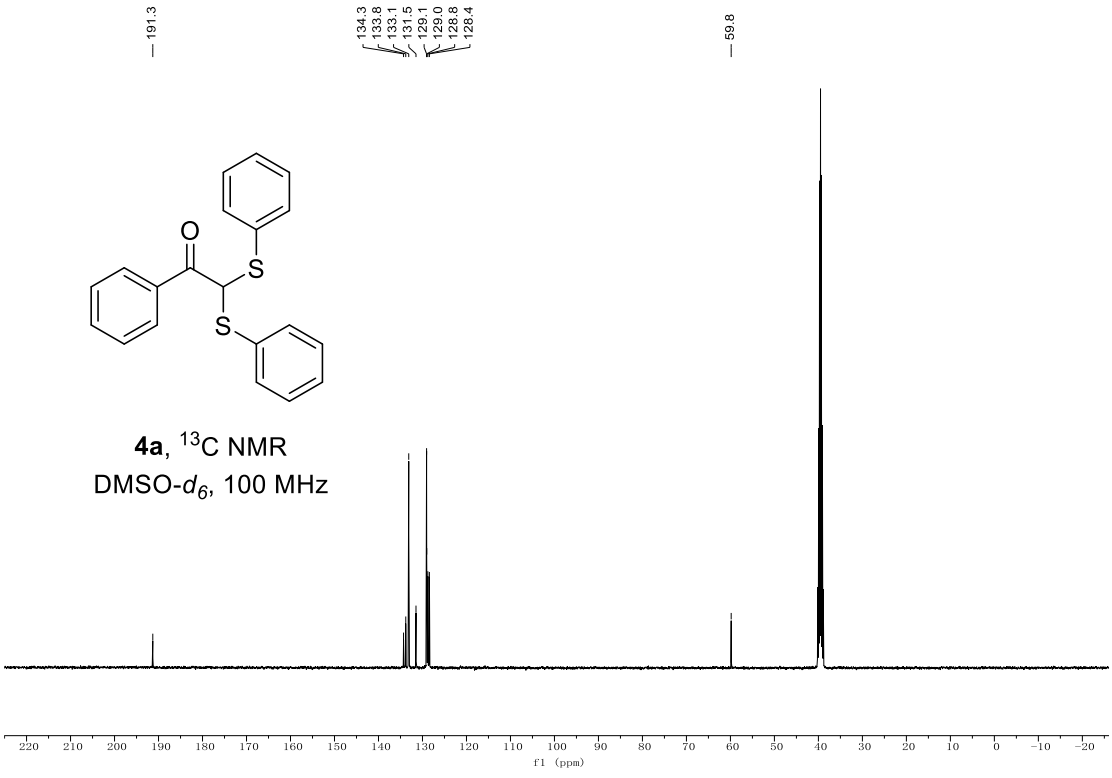


3z-2, ^{13}C NMR

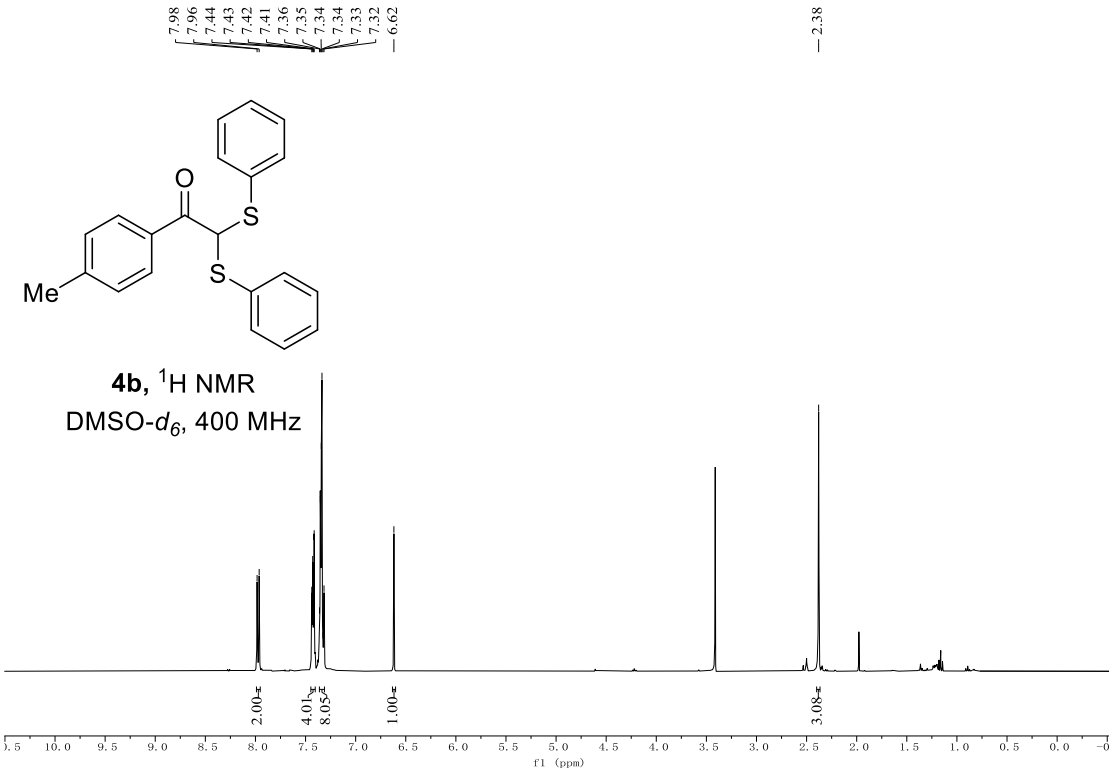
DMSO-d_6, 100 MHz



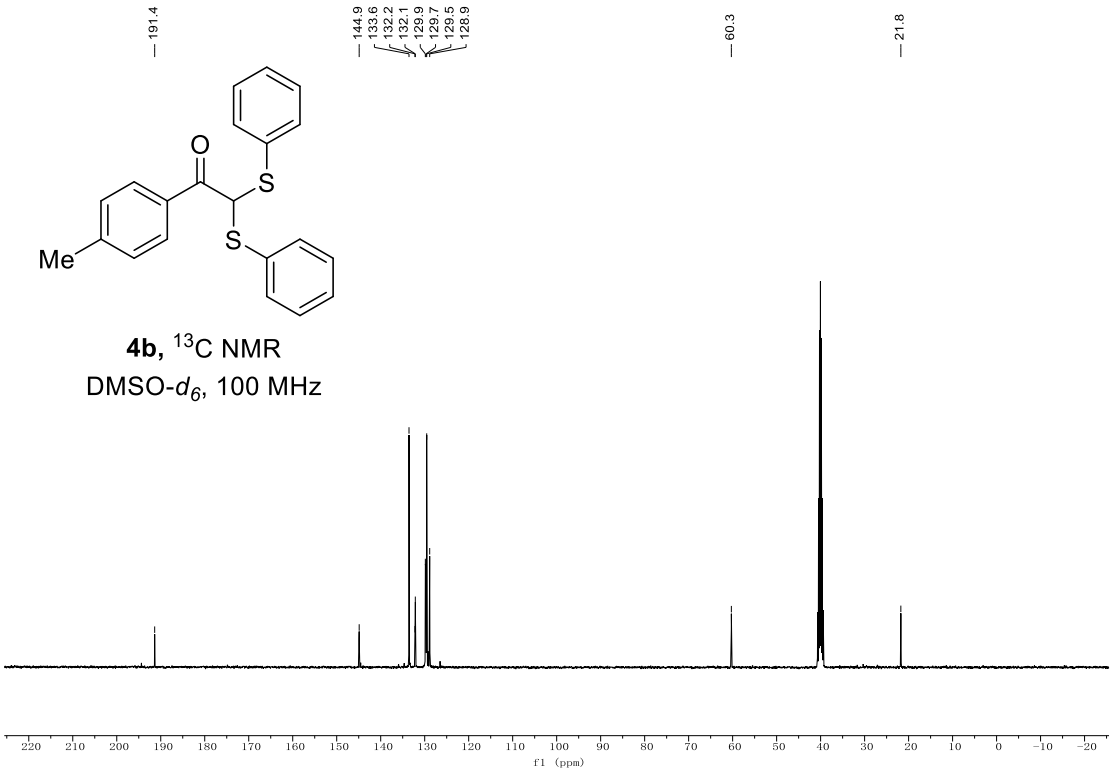
4a, ^{1}H NMR
DMSO-d_6, 400 MHz



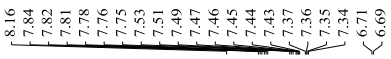
4a, ^{13}C NMR
DMSO-d_6, 100 MHz

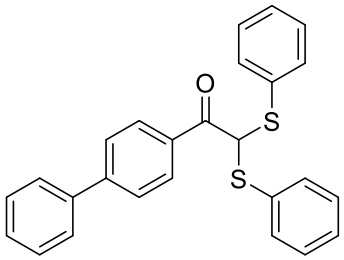


4b, ^{1}H NMR
DMSO-d_6, 400 MHz



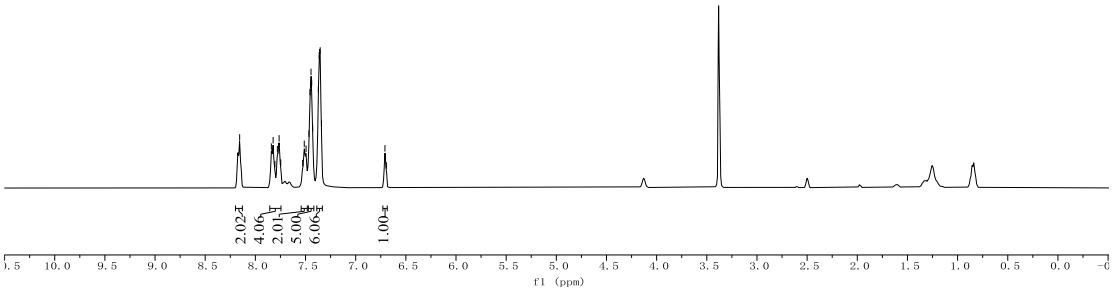
4b, ^{13}C NMR
DMSO-d_6, 100 MHz

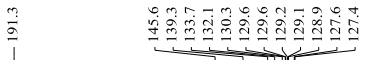


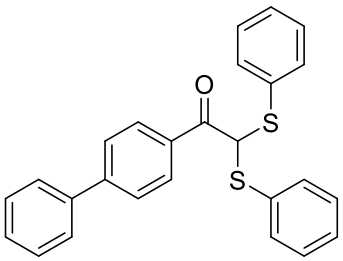


4c, ^{1}H NMR

DMSO-d_6, 400 MHz

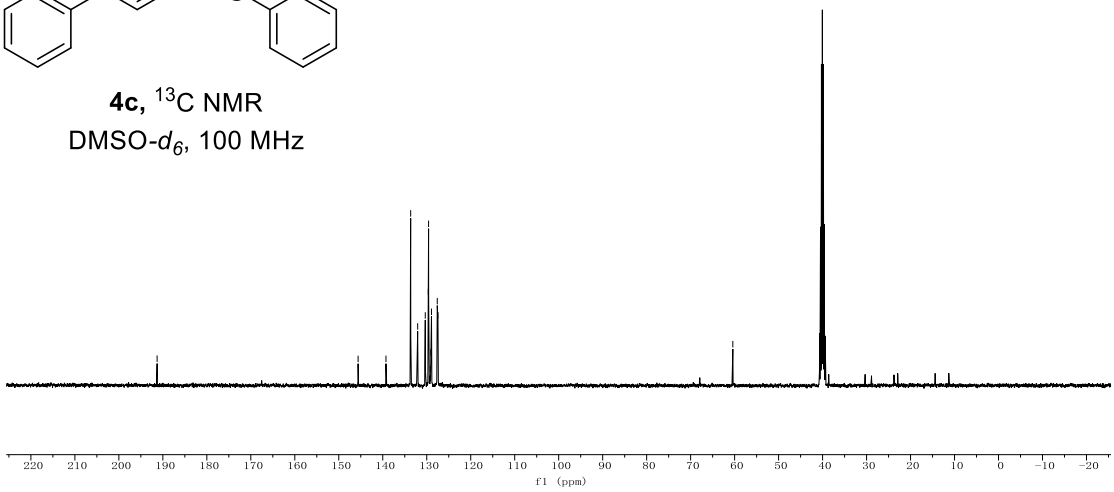


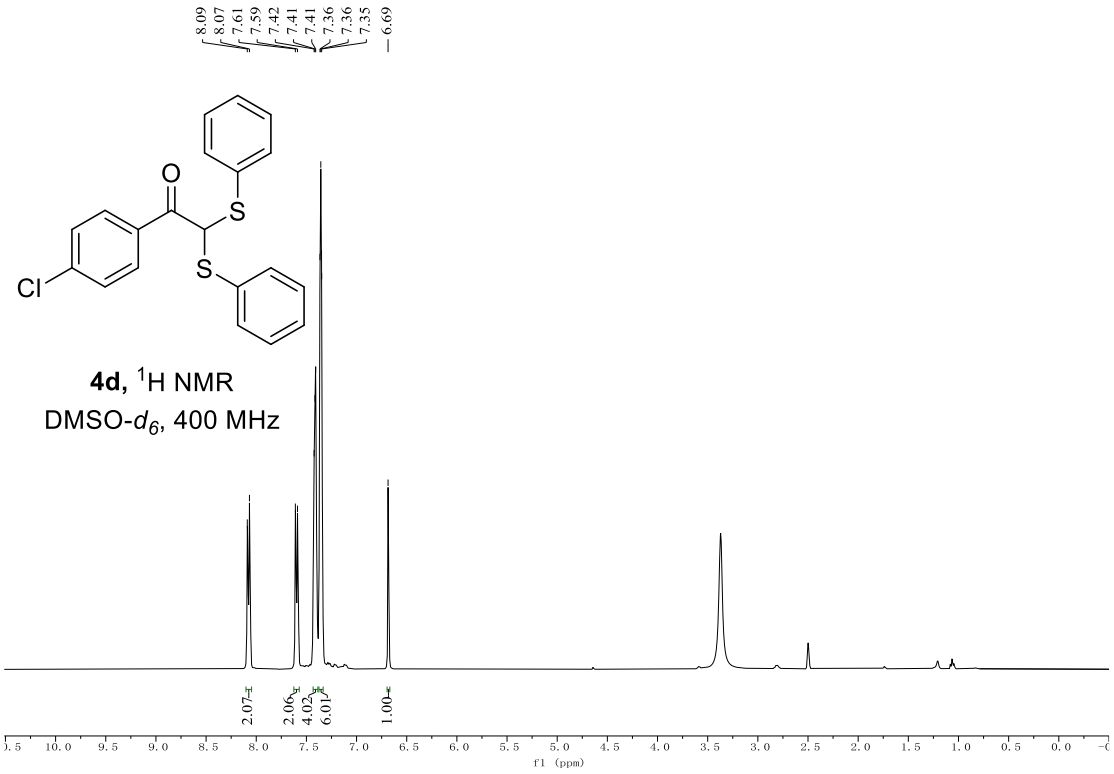


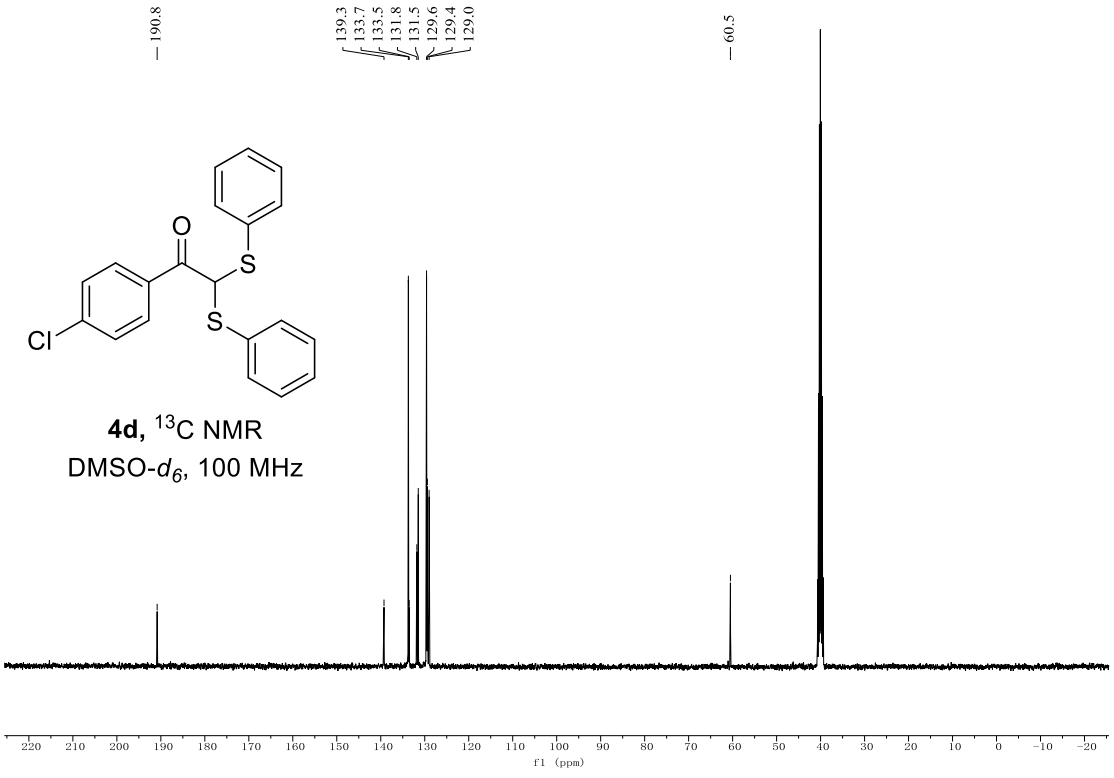


4c, ^{13}C NMR

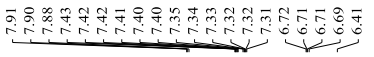
DMSO-d_6, 100 MHz

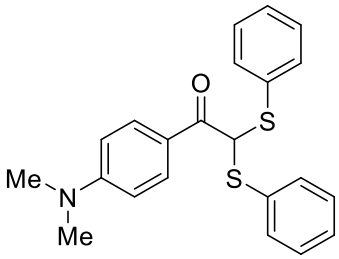



8.09
8.07
7.61
7.59
7.42
7.41
7.41
7.36
7.36
7.35
6.69
O
S
S
Cl
4d, 1H NMR
DMSO-d6, 400 MHz
2.07
2.06
4.02
6.01
1.00
f1 (ppm)


190.8
139.3
133.7
133.5
131.8
131.5
129.6
129.4
129.0
60.5
O
S
S
Cl
4d, 13C NMR
DMSO-d6, 100 MHz
f1 (ppm)

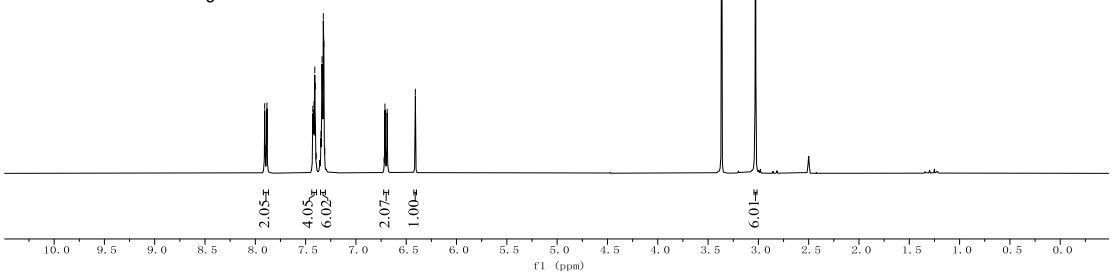
+

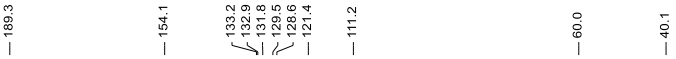


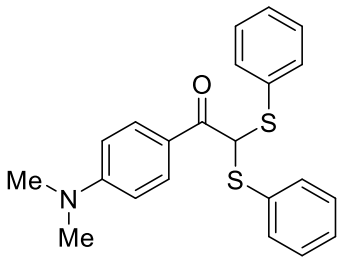


4e, ^{1}H NMR

DMSO-d_6, 400 MHz

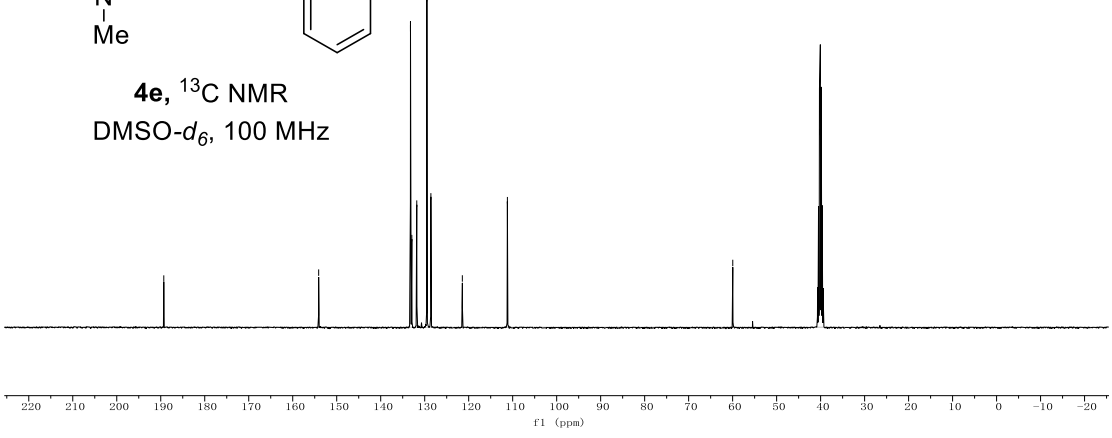


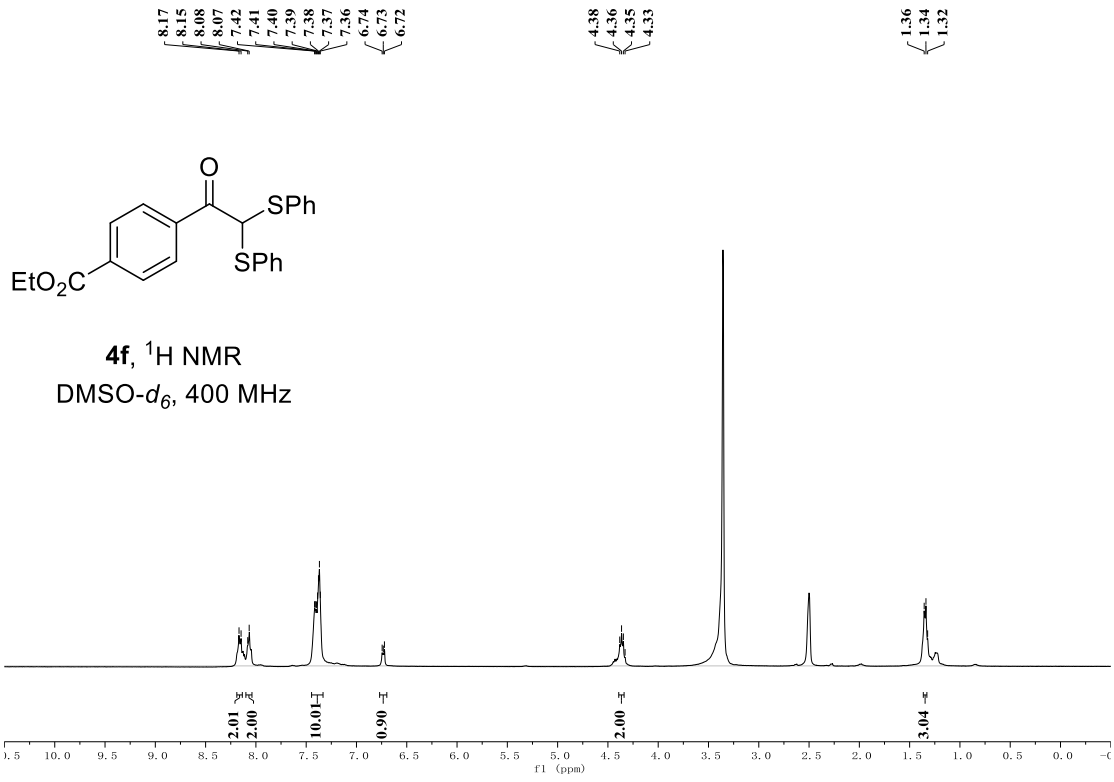




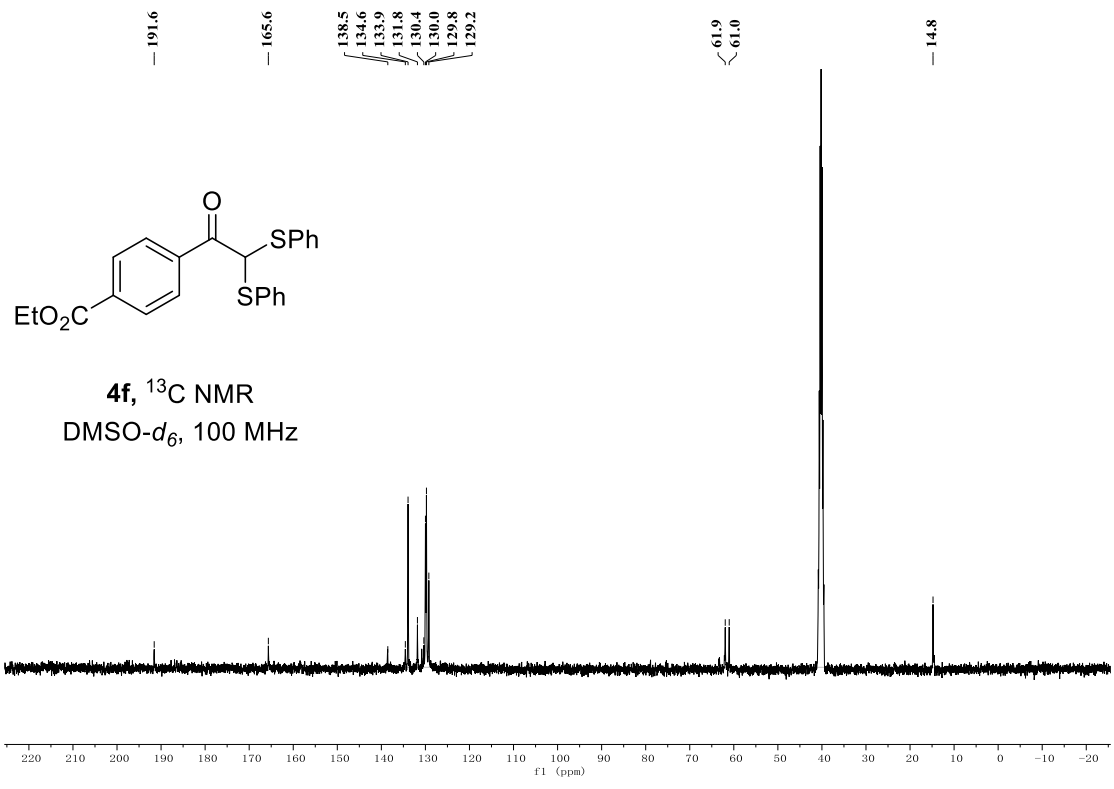
4e, ^{13}C NMR

DMSO-d_6, 100 MHz

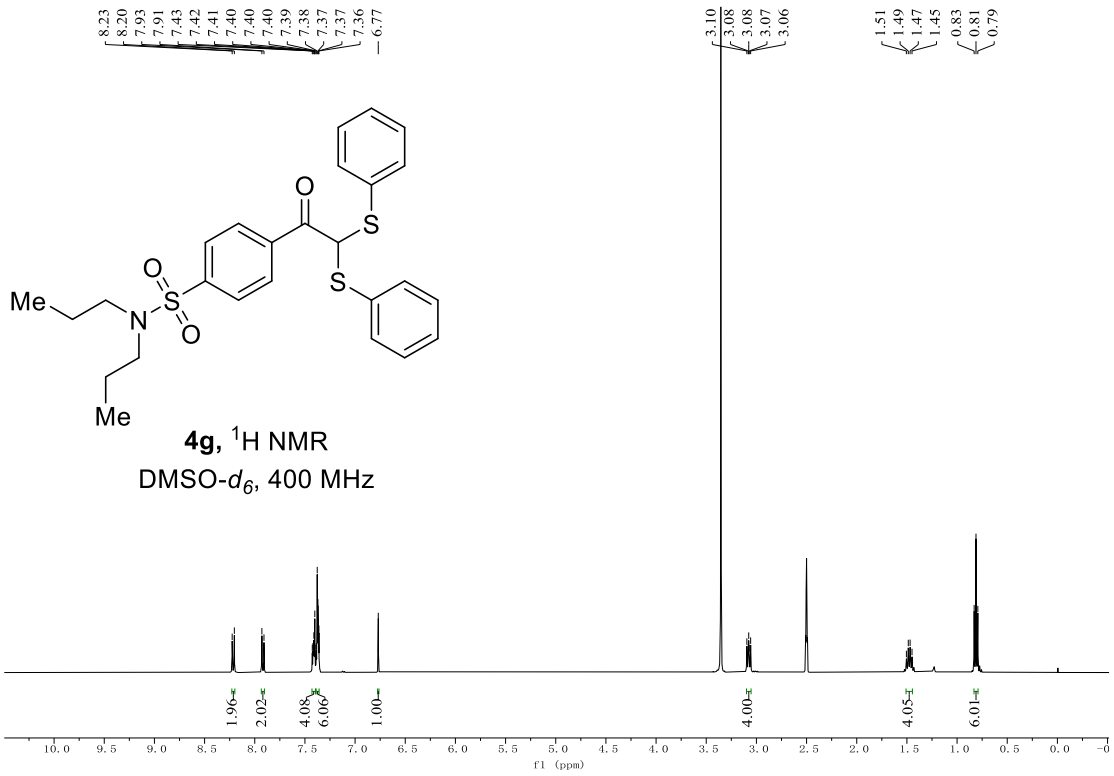




4f, ^{1}H NMR
DMSO-d_6, 400 MHz

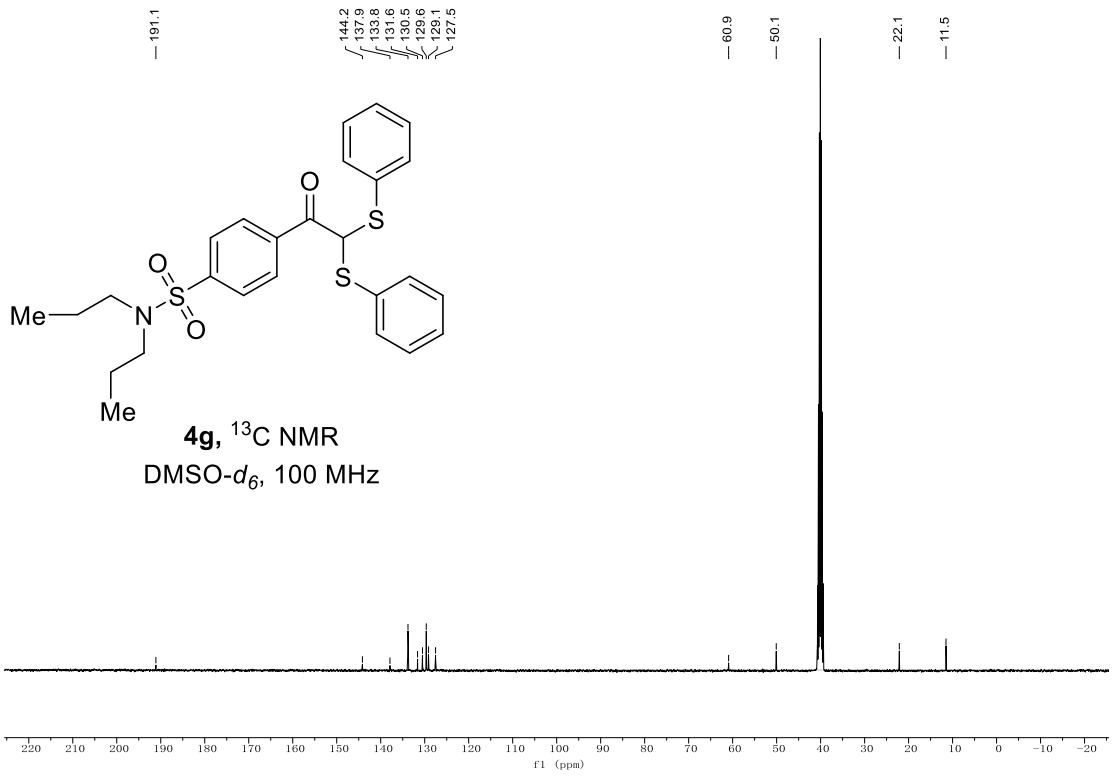


4f, ^{13}C NMR
DMSO-d_6, 100 MHz



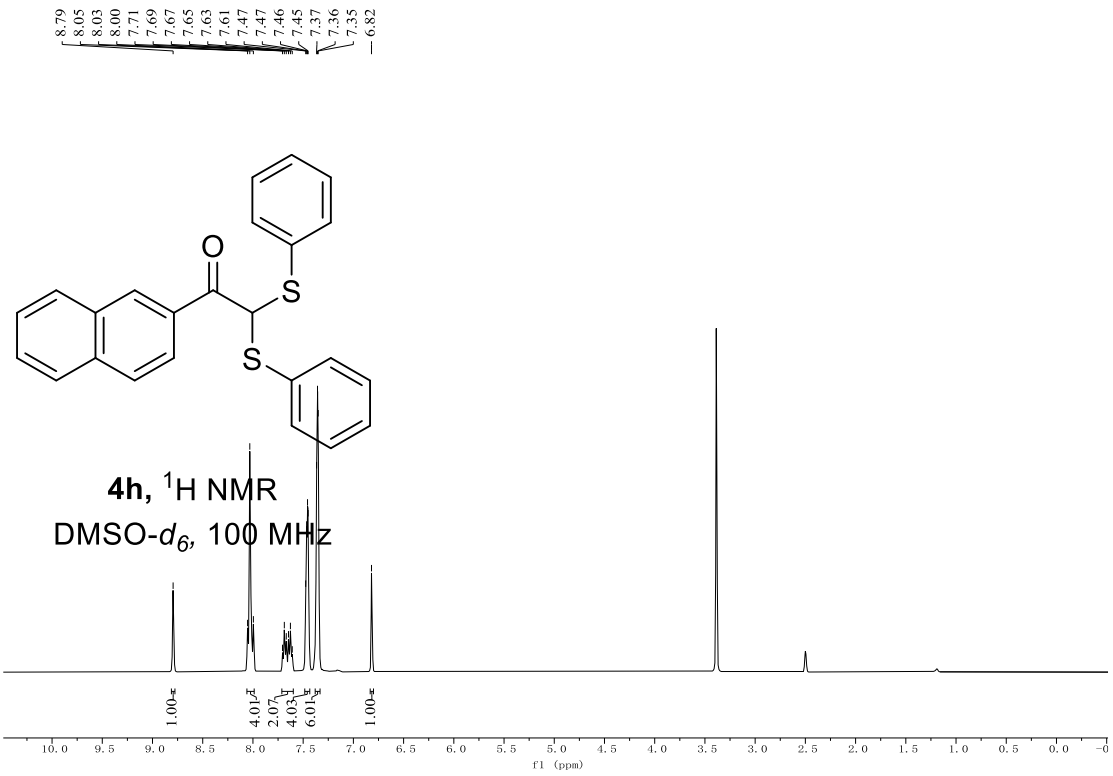
4g, ^{1}H NMR

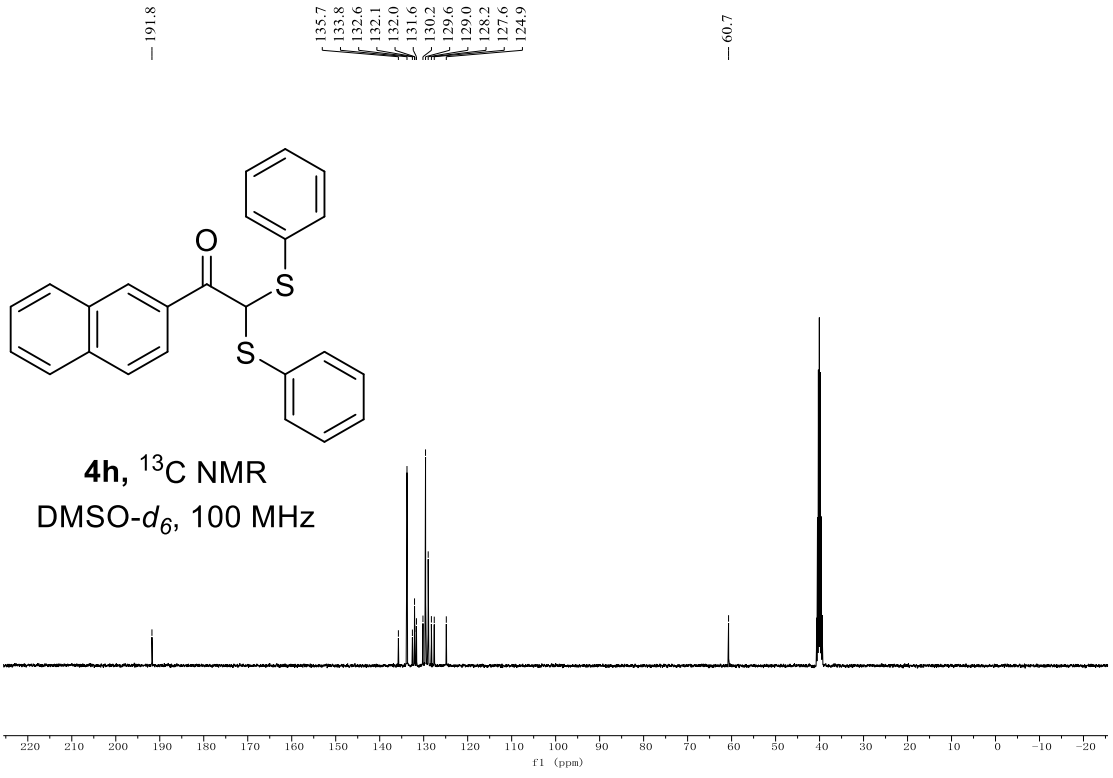
DMSO-d_6, 400 MHz

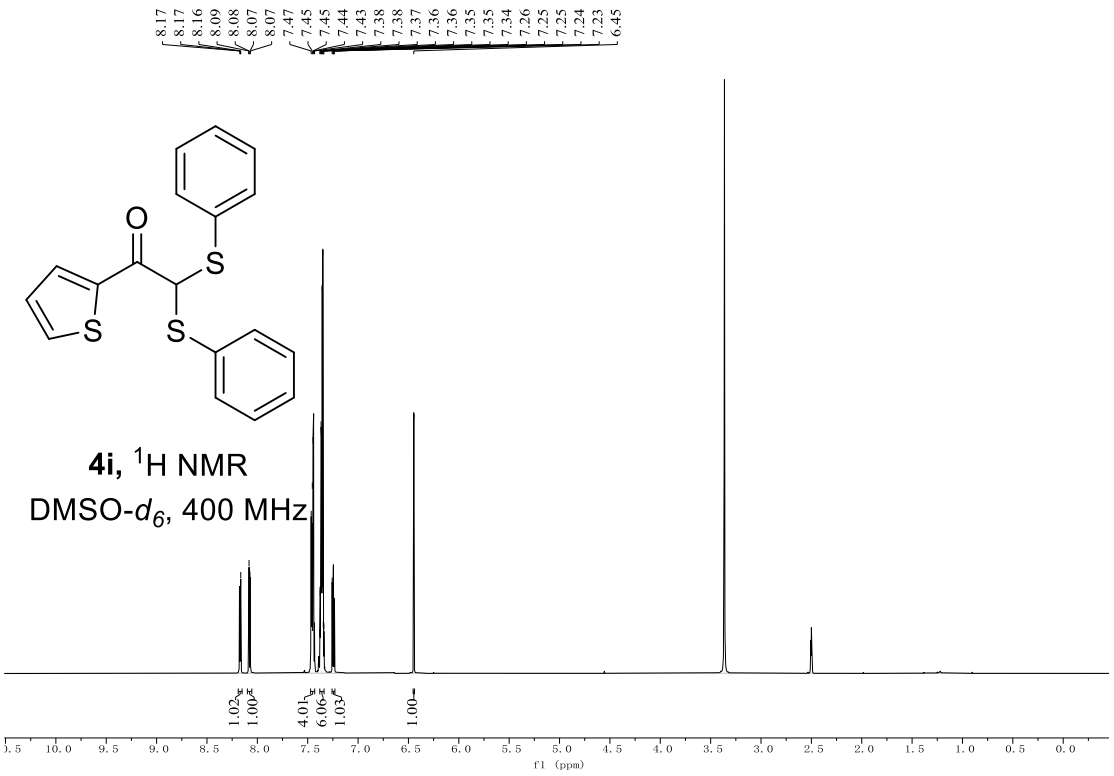


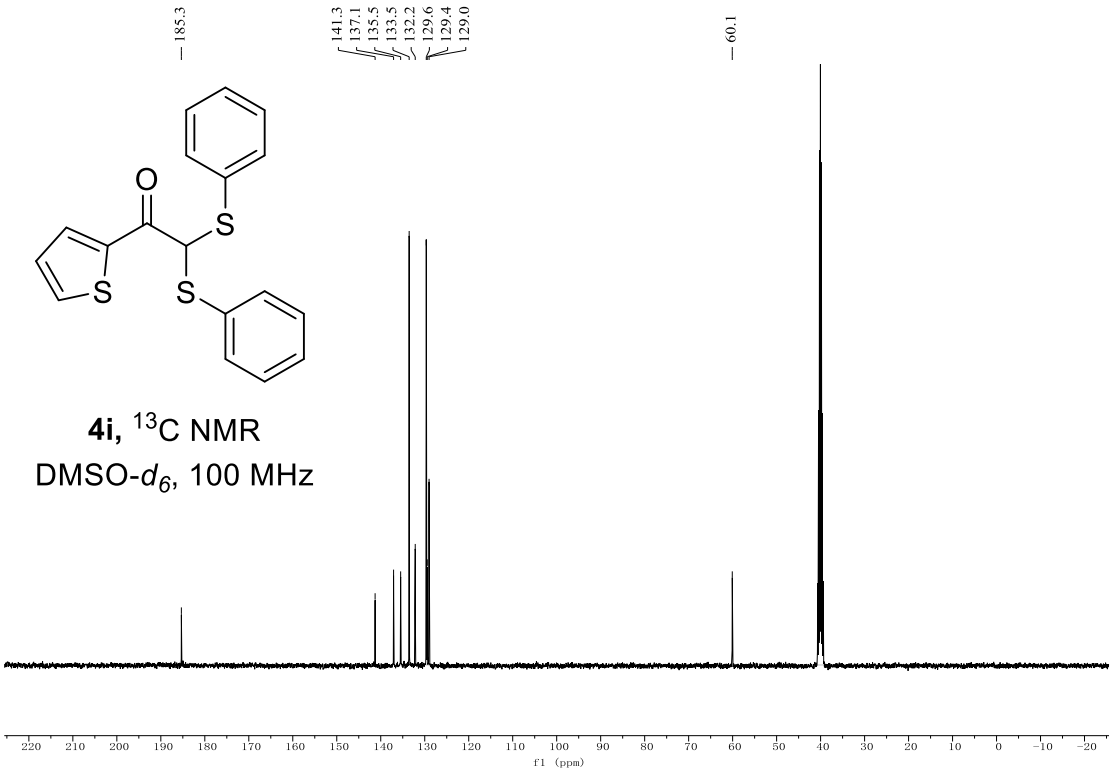
4g, ^{13}C NMR

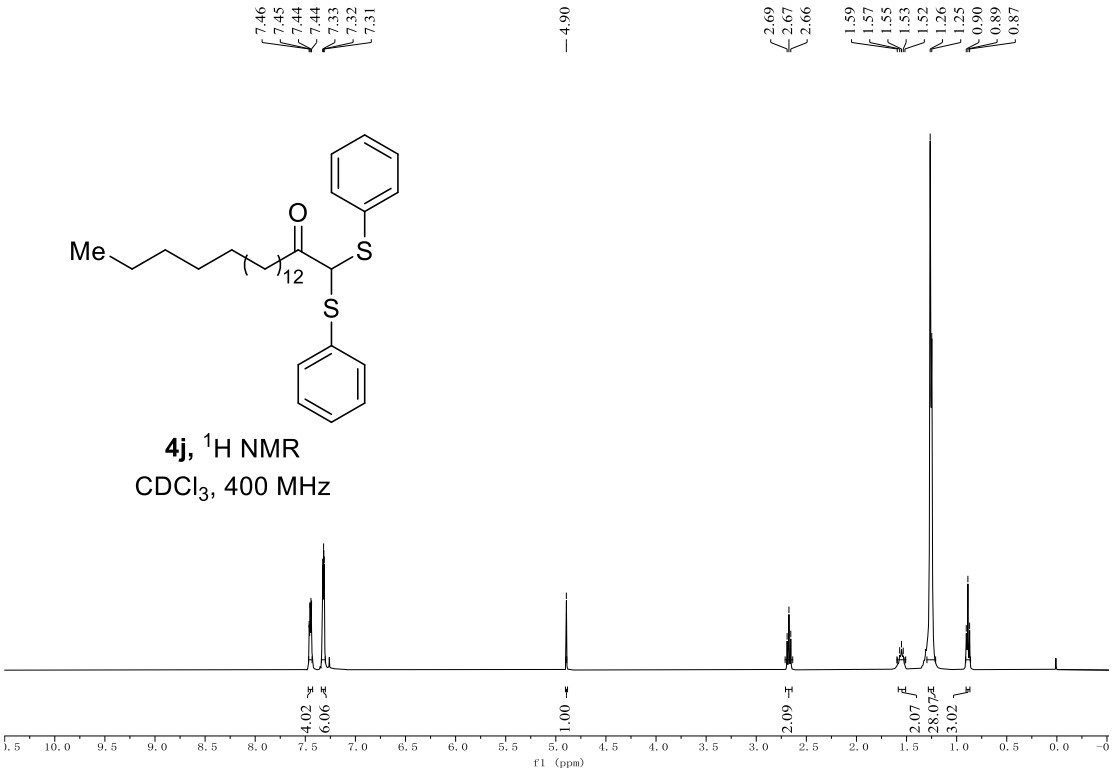
DMSO-d_6, 100 MHz


8.79
8.05
8.03
8.00
7.71
7.69
7.67
7.65
7.63
7.61
7.47
7.47
7.46
7.45
7.37
7.36
7.35
6.82
O
S
S
4h, 1H NMR
DMSO-d6, 100 MHz
1.00
4.01
2.07
4.03
6.01
1.00
f1 (ppm)


191.8
135.7
133.8
132.6
132.1
132.0
131.6
130.2
129.6
129.0
128.2
127.6
124.9
60.7
O
S
S
4h, 13C NMR
DMSO-d6, 100 MHz
f1 (ppm)

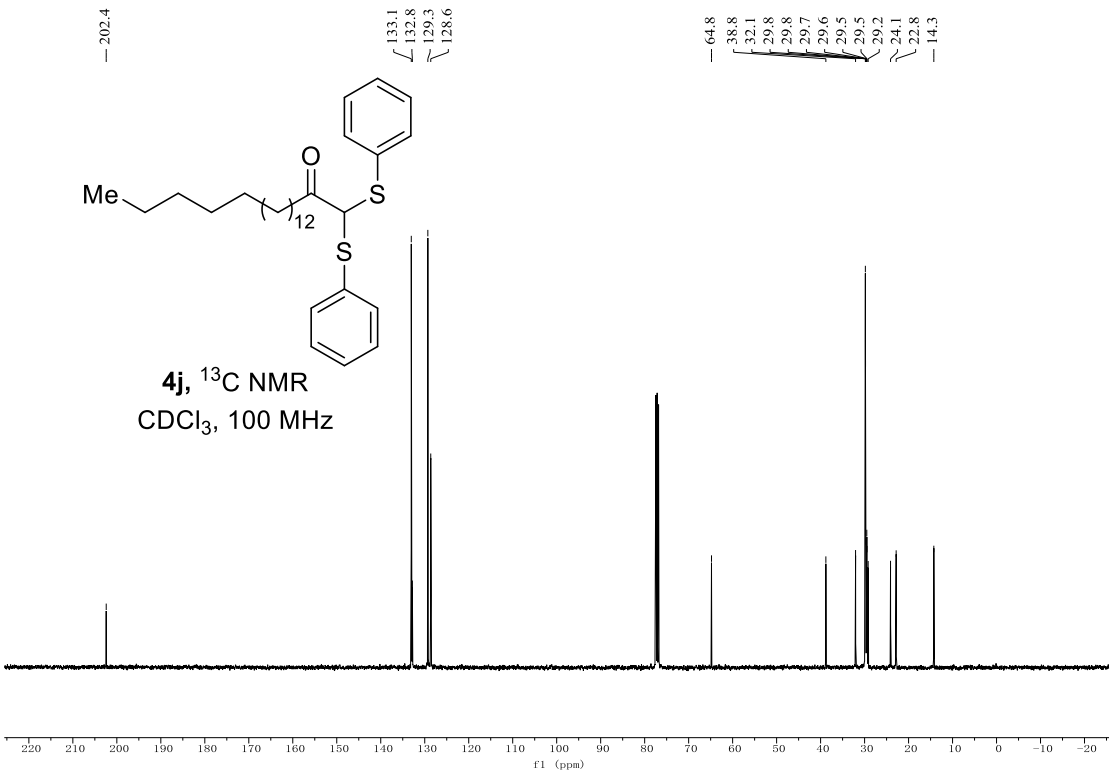

8.17
8.17
8.16
8.09
8.08
8.07
8.07
7.47
7.45
7.45
7.44
7.43
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.26
7.25
7.25
7.24
7.23
6.45
O
S
S
S
4i, 1H NMR
DMSO-d6, 400 MHz
1.02
1.00
4.01
6.06
1.03
1.00
f1 (ppm)


185.3
141.3
137.1
135.5
133.5
132.2
129.6
129.4
129.0
60.1
O
S
S
S
4i, 13C NMR
DMSO-d6, 100 MHz
f1 (ppm)



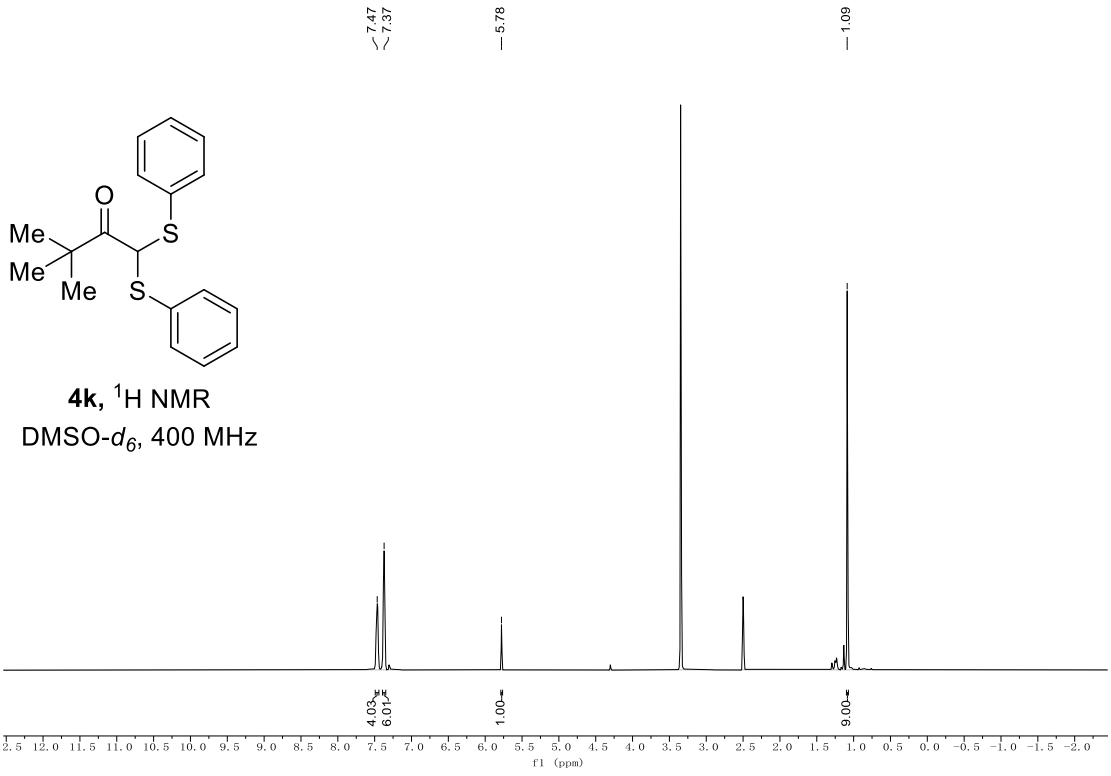
4j, ^{1}H NMR

$CDCl_3$, 400 MHz

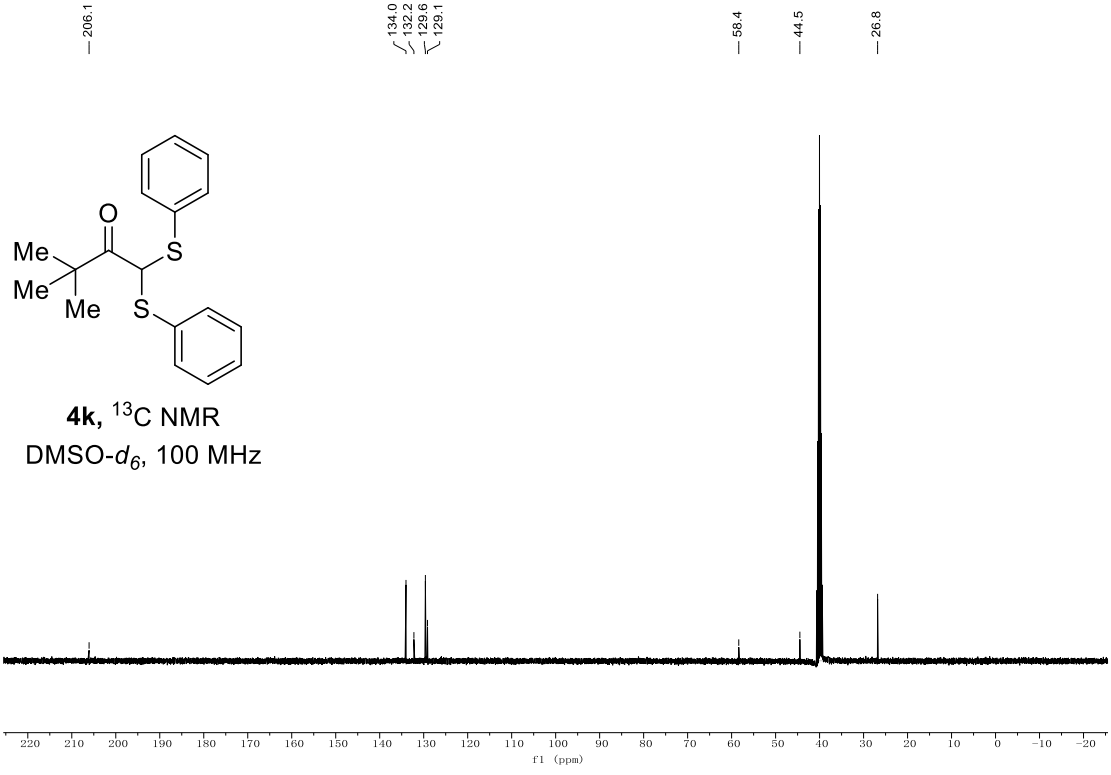


4j, ^{13}C NMR

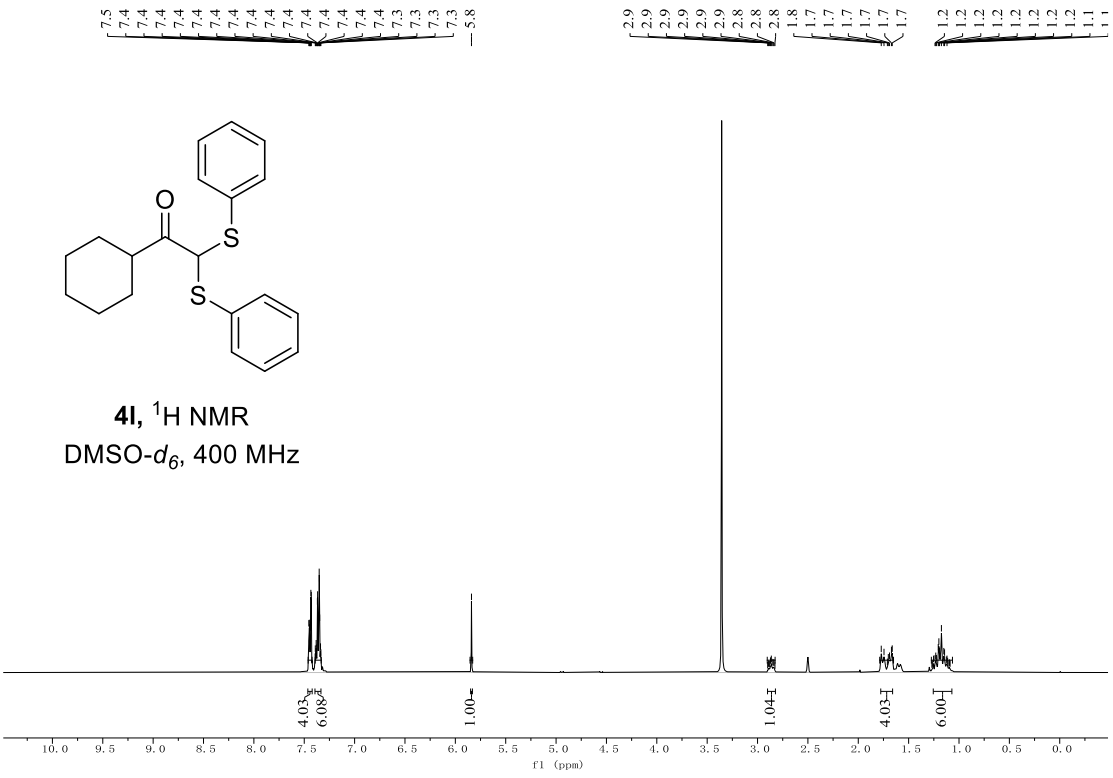
$CDCl_3$, 100 MHz



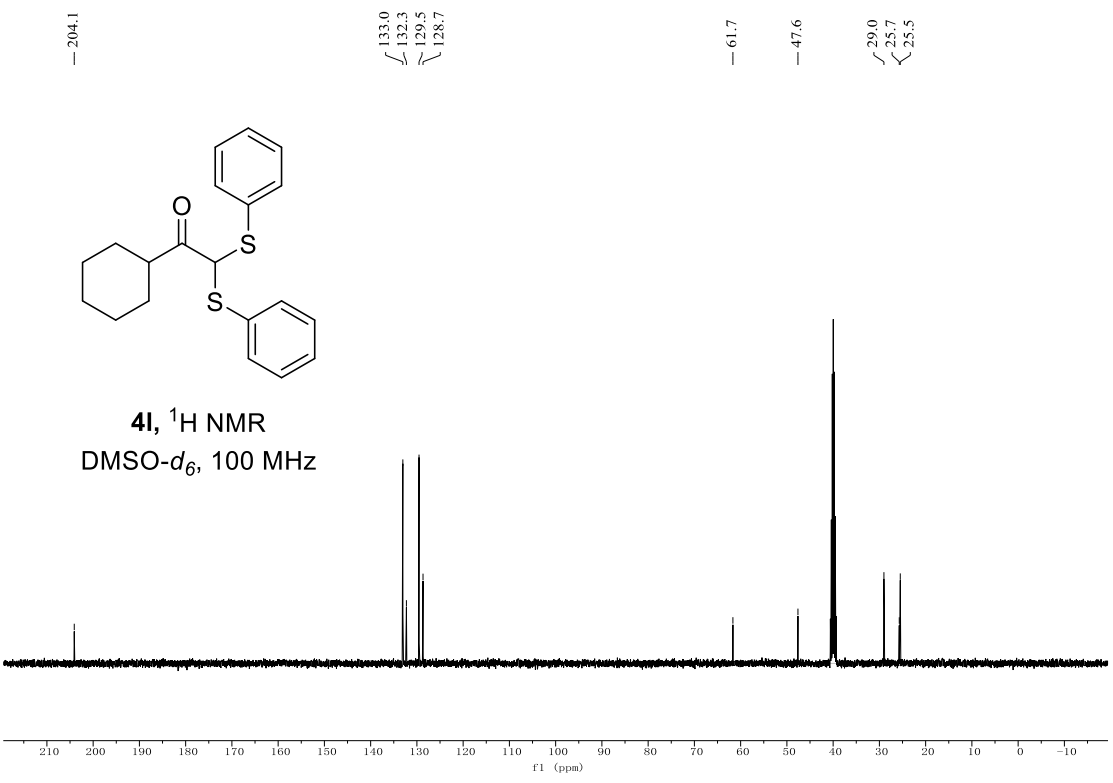
4k, ^{1}H NMR
DMSO-d_6, 400 MHz



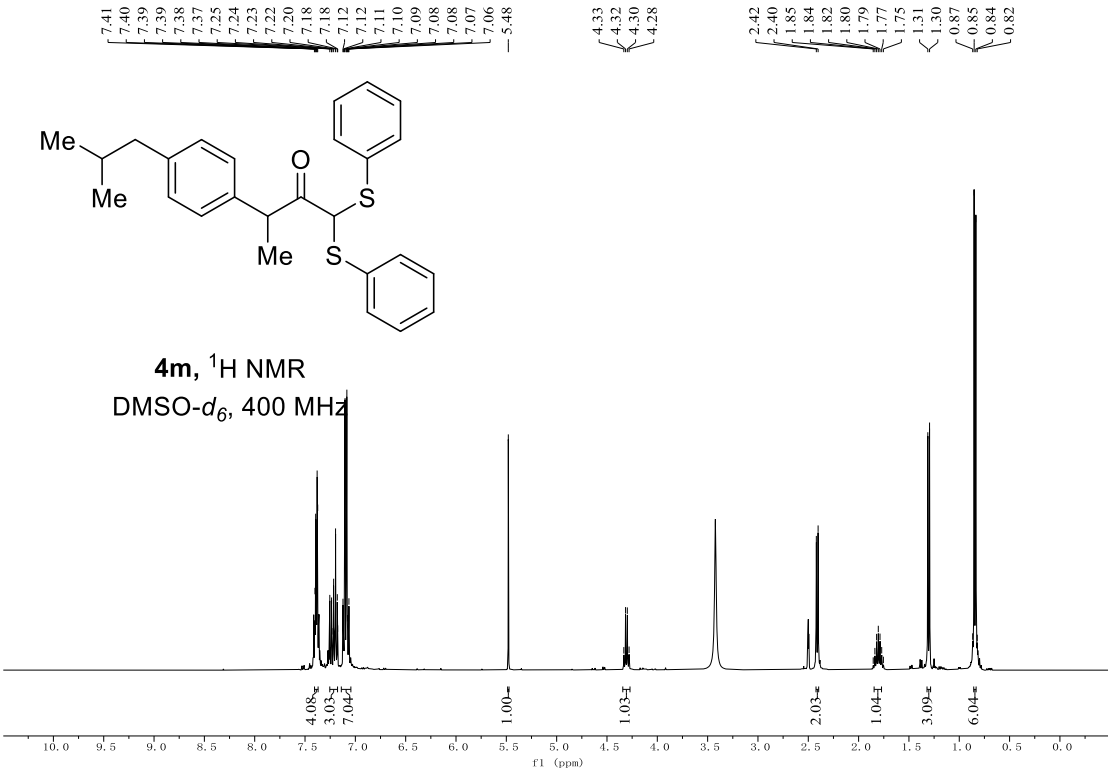
4k, ^{13}C NMR
DMSO-d_6, 100 MHz



4l, ^{1}H NMR
DMSO-d_6, 400 MHz

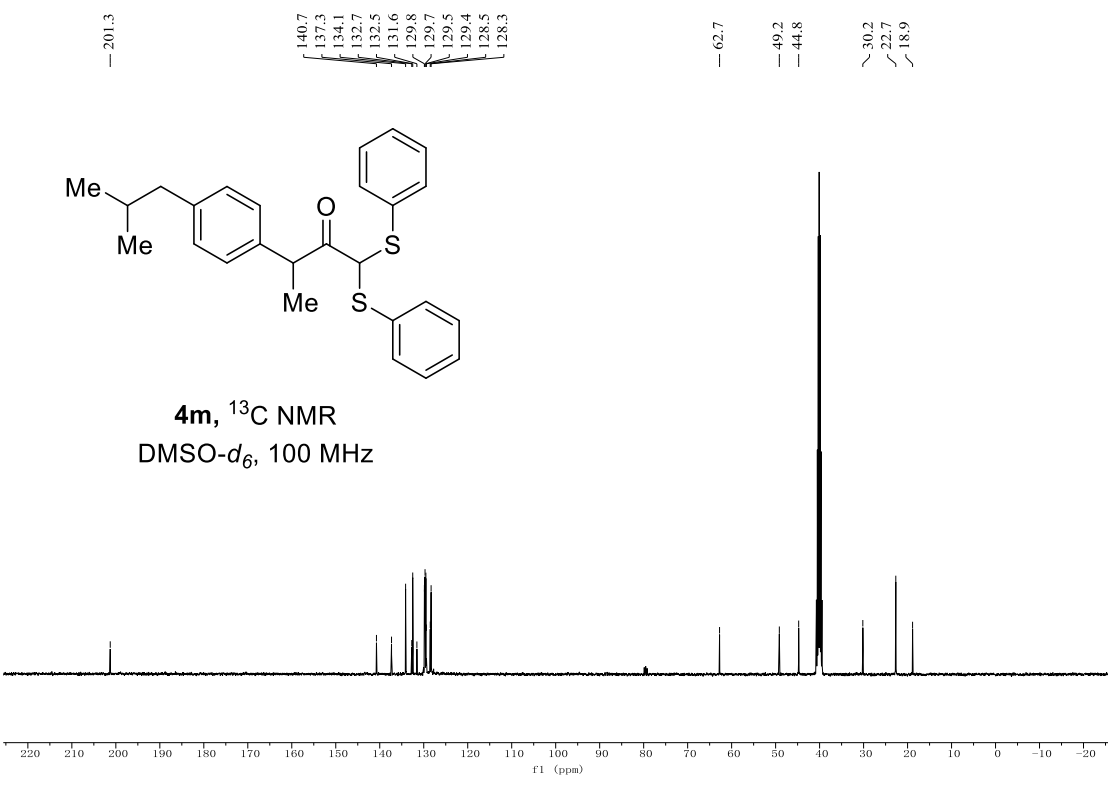


4l, ^{1}H NMR
DMSO-d_6, 100 MHz



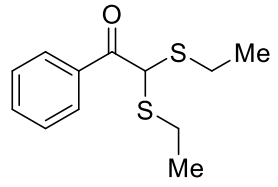
4m, ^{1}H NMR

DMSO-d_6, 400 MHz

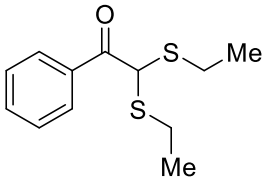


4m, ^{13}C NMR

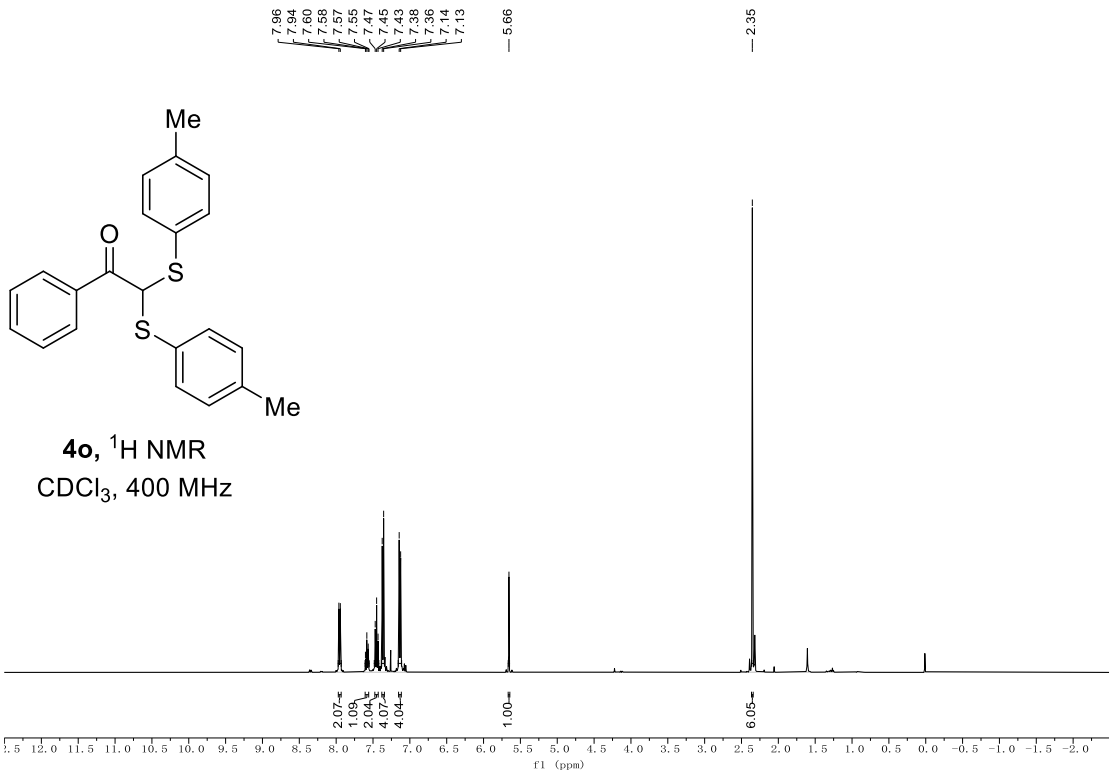
DMSO-d_6, 100 MHz



4n, ^{1}H NMR
$CDCl_3$, 400 MHz

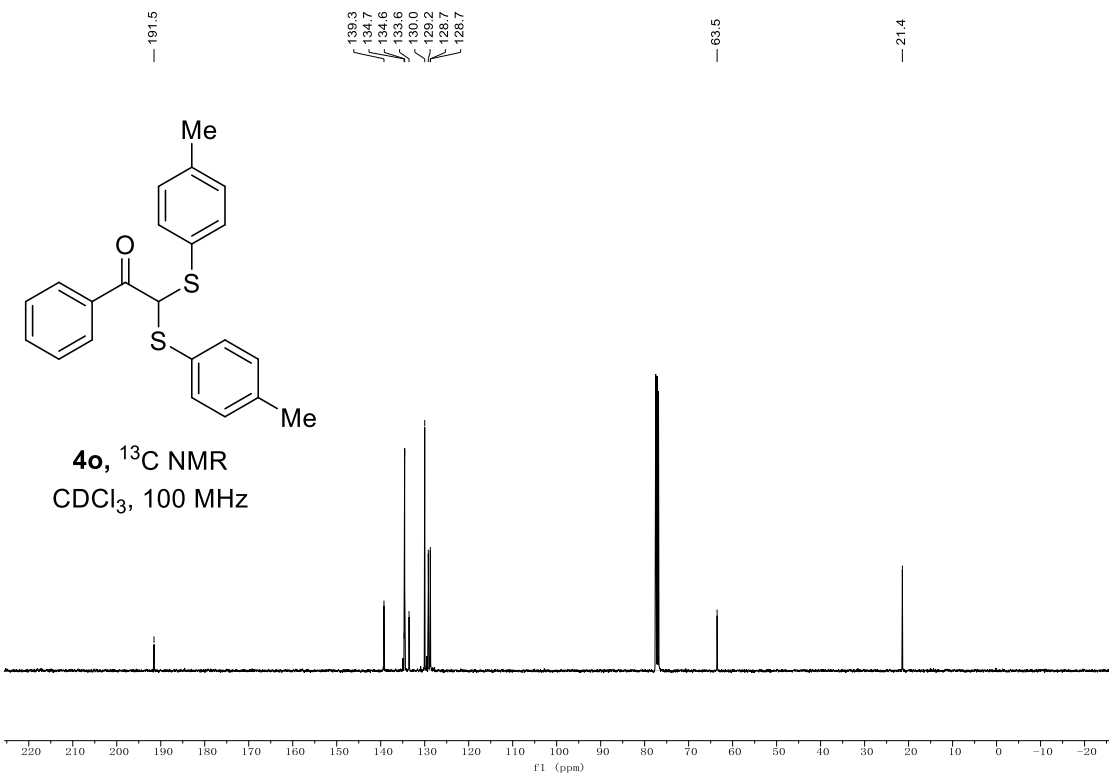


4n, ^{13}C NMR
$CDCl_3$, 100 MHz



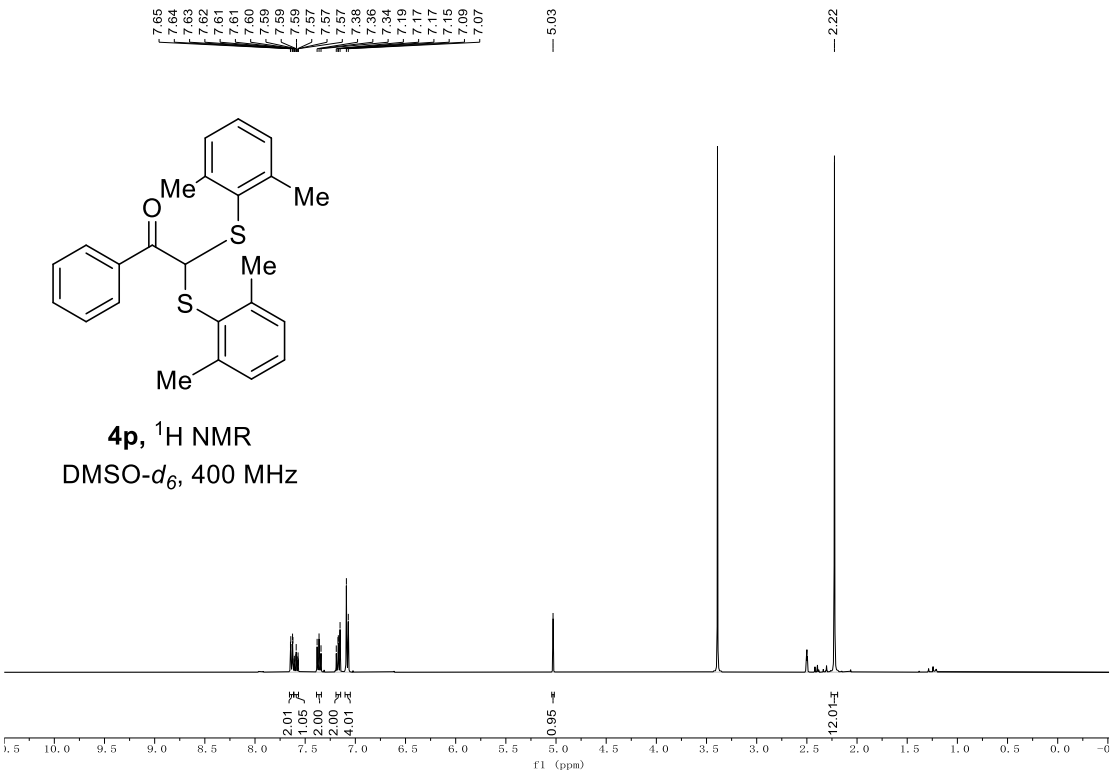
4o, ^{1}H NMR

$CDCl_3$, 400 MHz

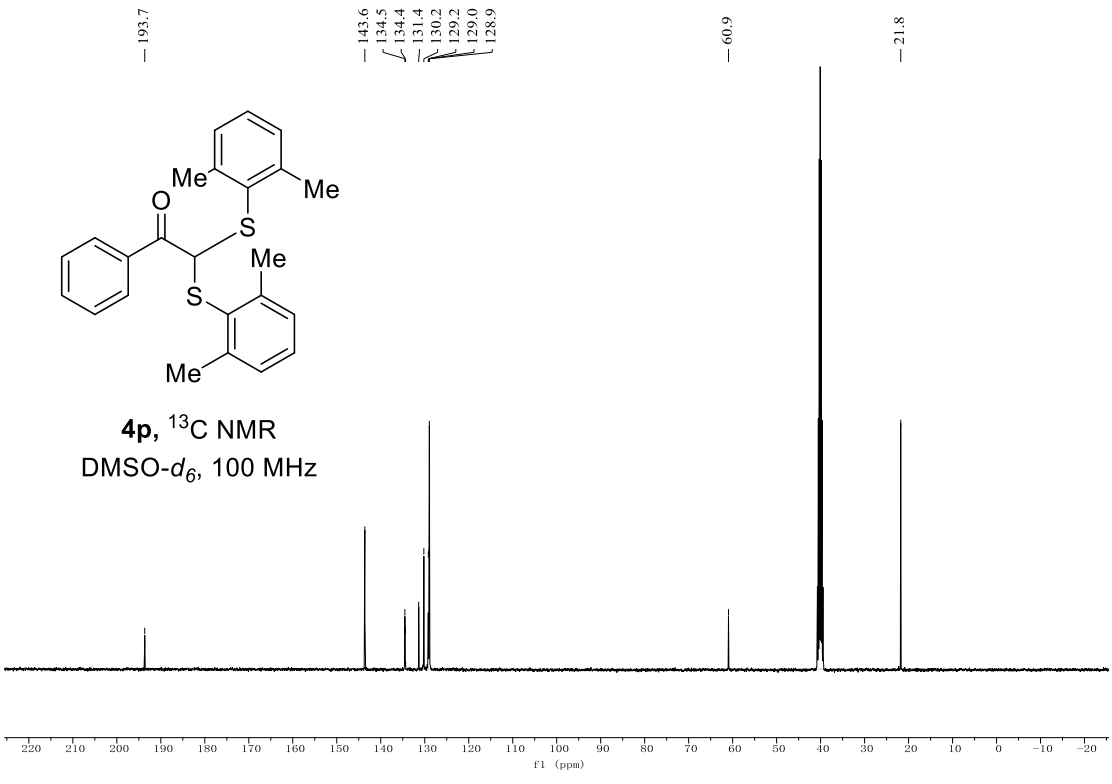


4o, ^{13}C NMR

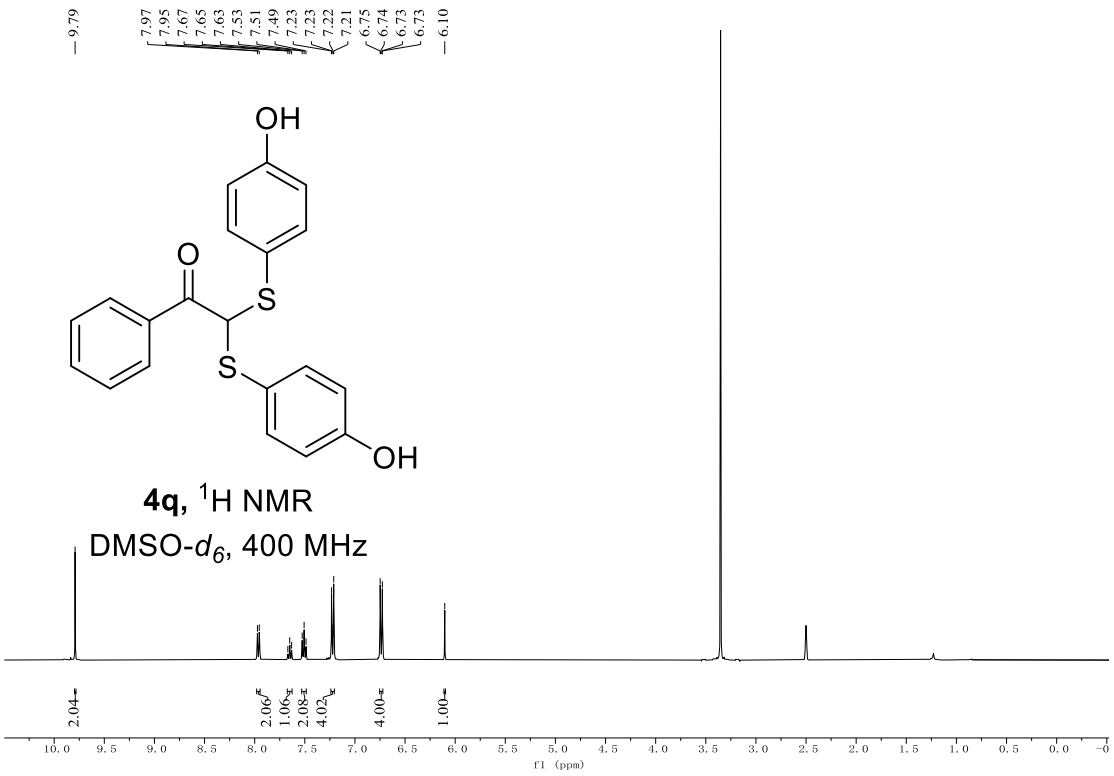
$CDCl_3$, 100 MHz

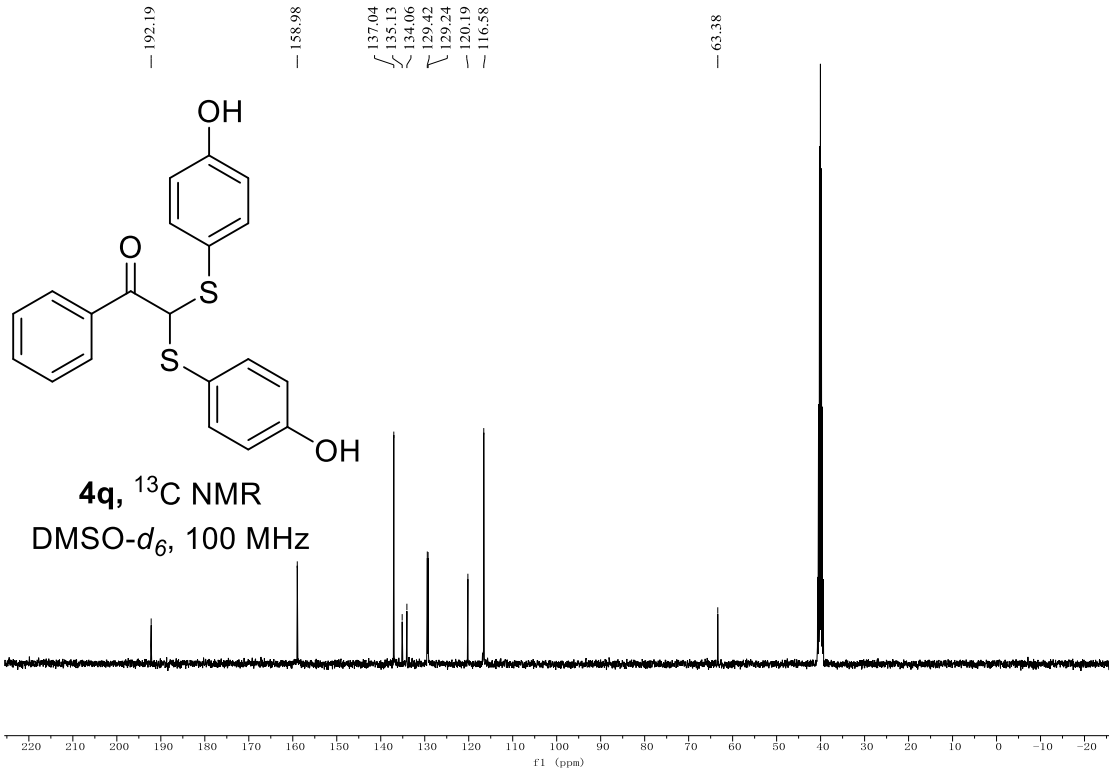


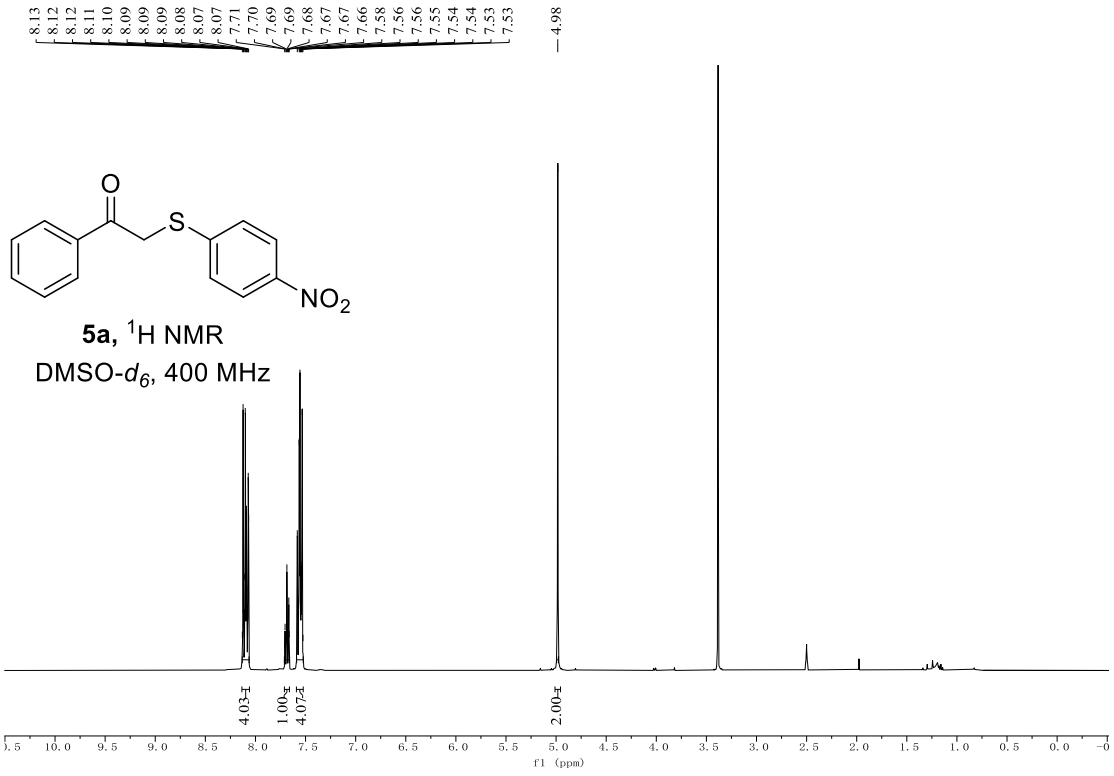
4p, ^{1}H NMR
DMSO-d_6, 400 MHz

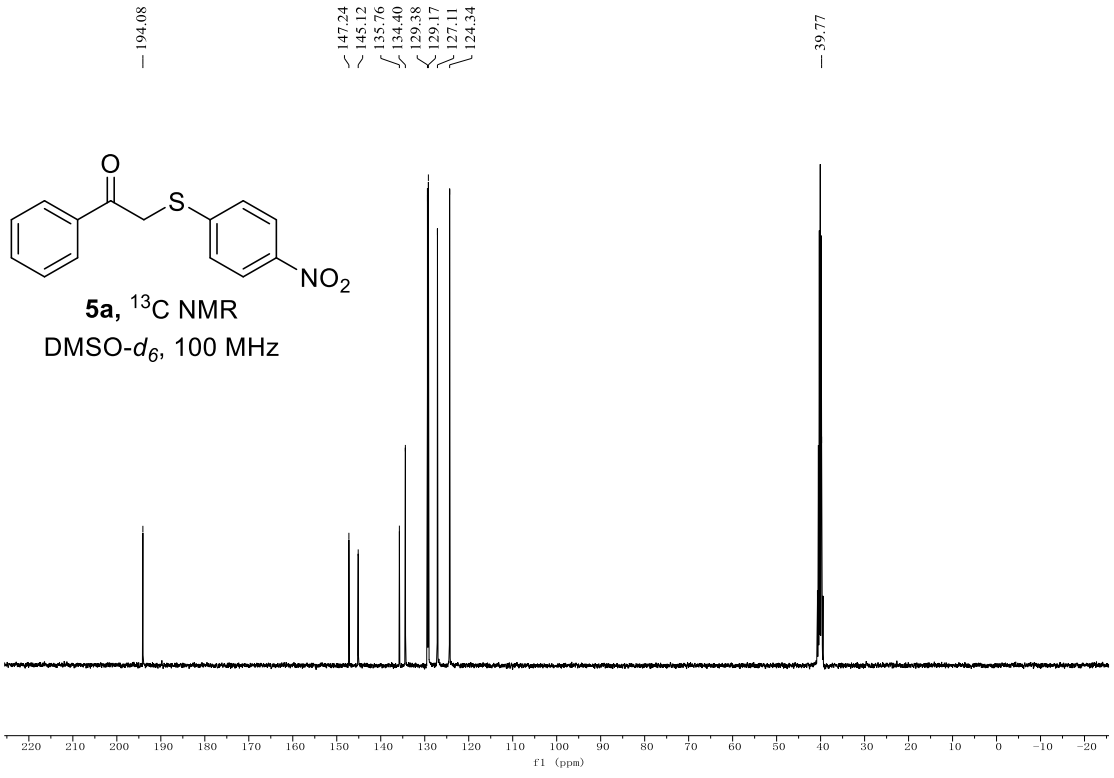


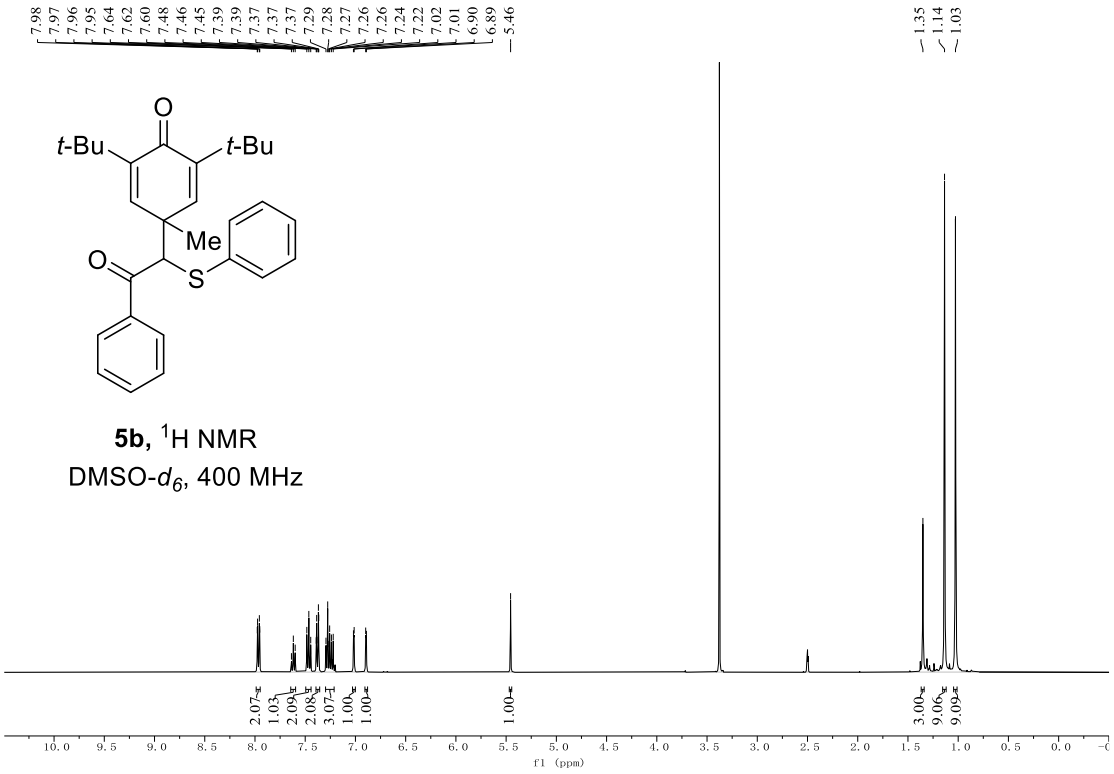
4p, ^{13}C NMR
DMSO-d_6, 100 MHz


9.79
7.97
7.95
7.67
7.65
7.63
7.53
7.51
7.49
7.23
7.23
7.22
7.21
6.75
6.74
6.73
6.73
6.10
OH
O
S
S
OH
4q, 1H NMR
DMSO-d6, 400 MHz
2.04
2.06
1.06
2.08
4.02
4.00
1.00
f1 (ppm)

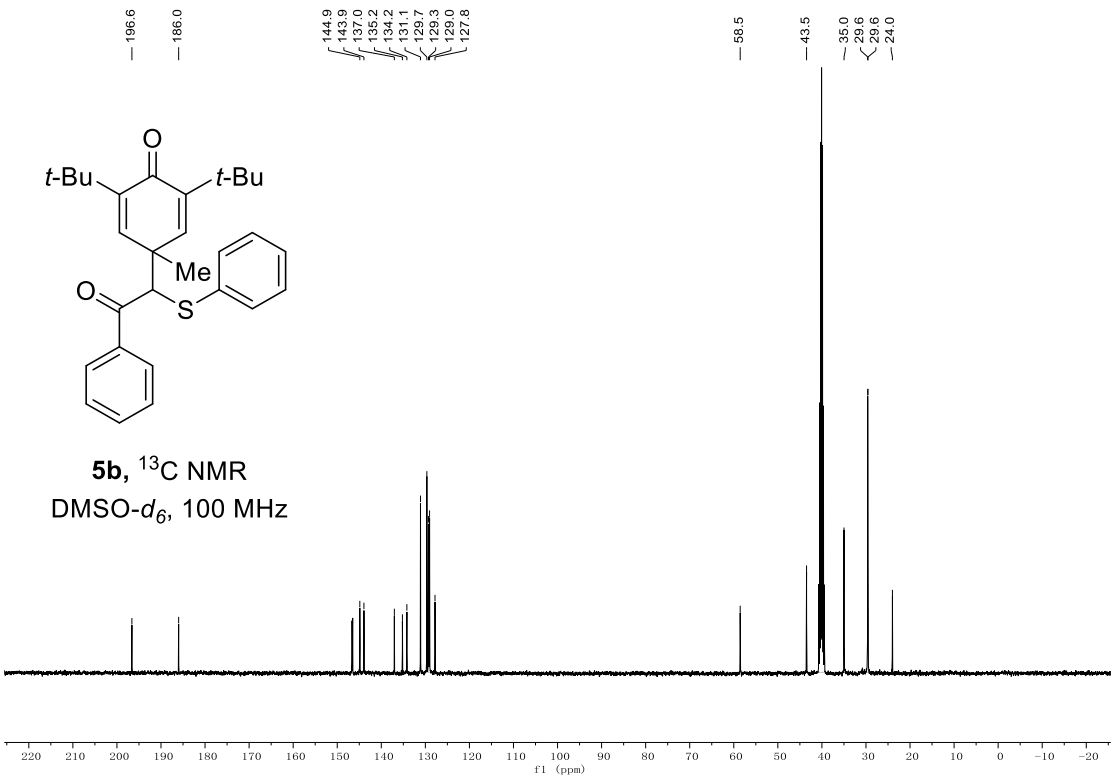

192.19
158.98
137.04
135.13
134.06
129.42
129.24
120.19
116.58
63.38
OH
O
S
S
OH
4q, 13C NMR
DMSO-d6, 100 MHz
f1 (ppm)


8.13
8.12
8.12
8.11
8.10
8.09
8.09
8.09
8.08
8.07
8.07
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.58
7.56
7.56
7.55
7.54
7.54
7.53
7.53
4.98
O
S
NO2
5a, 1H NMR
DMSO-d6, 400 MHz
4.03
1.00
4.07
2.00
f1 (ppm)

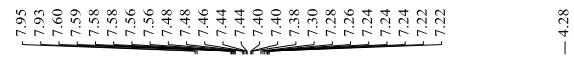

194.08
147.24
145.12
135.76
134.40
129.38
129.17
127.11
124.34
39.77
O
S
NO2
5a, 13C NMR
DMSO-d6, 100 MHz
f1 (ppm)

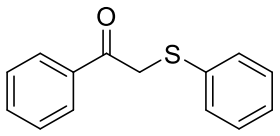


5b, ^{1}H NMR
DMSO-d_6, 400 MHz



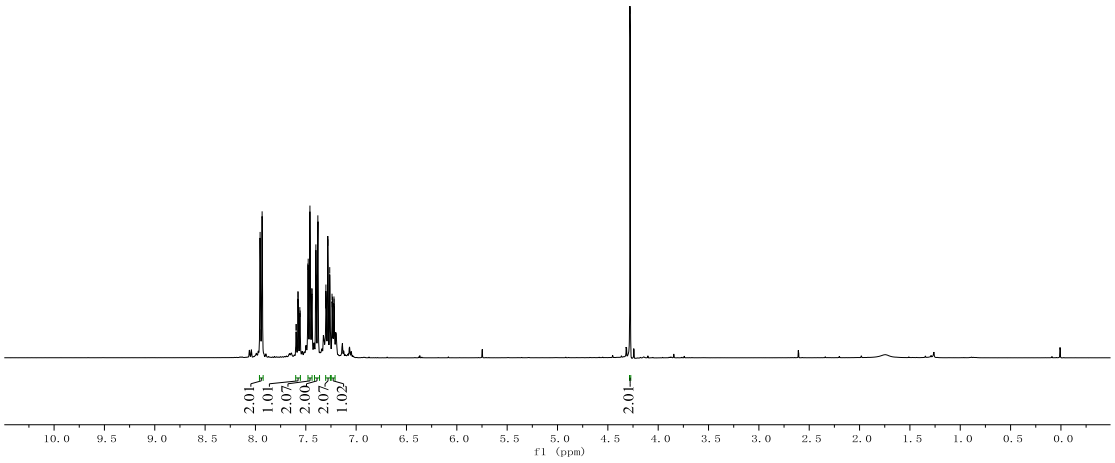
5b, ^{13}C NMR
DMSO-d_6, 100 MHz

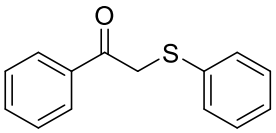




5c, ^{1}H NMR

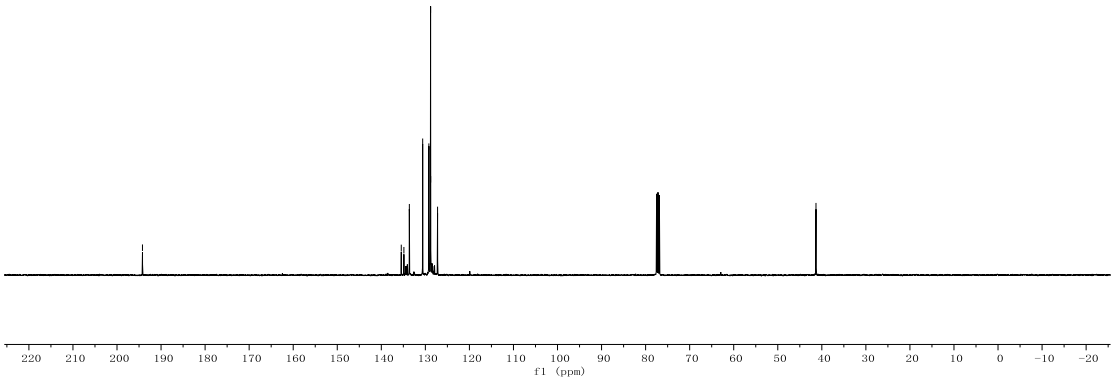
$CDCl_3$, 400 MHz

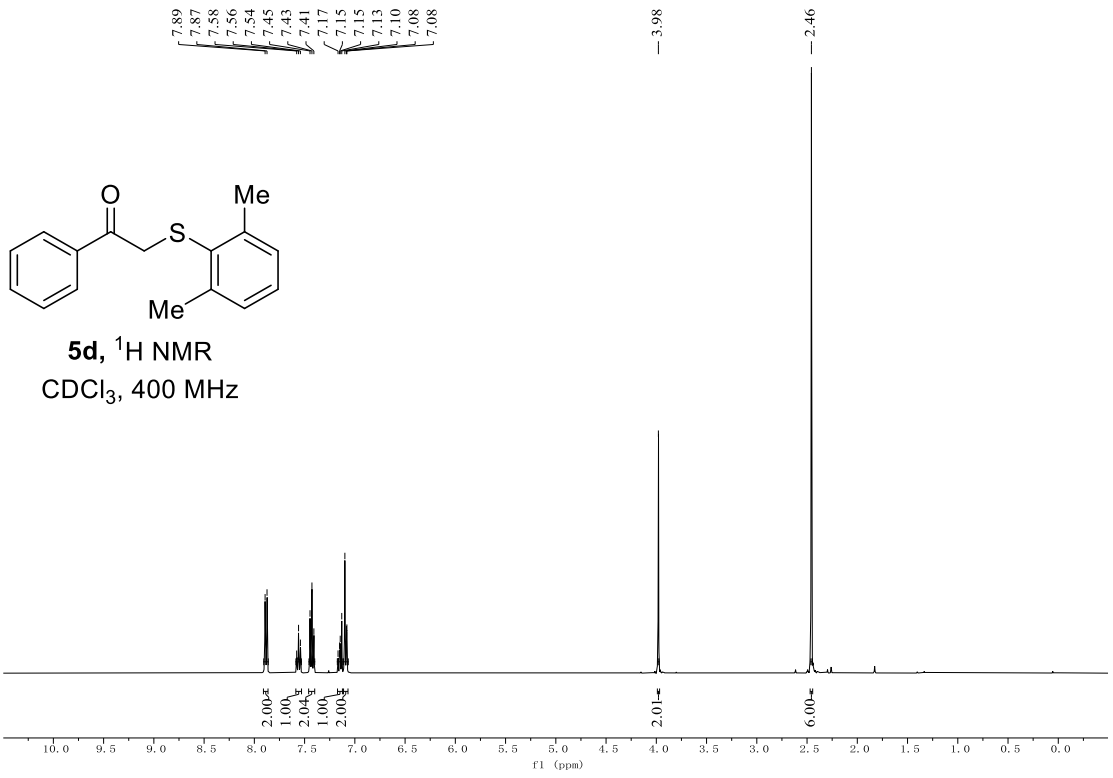




5c, ^{13}C NMR

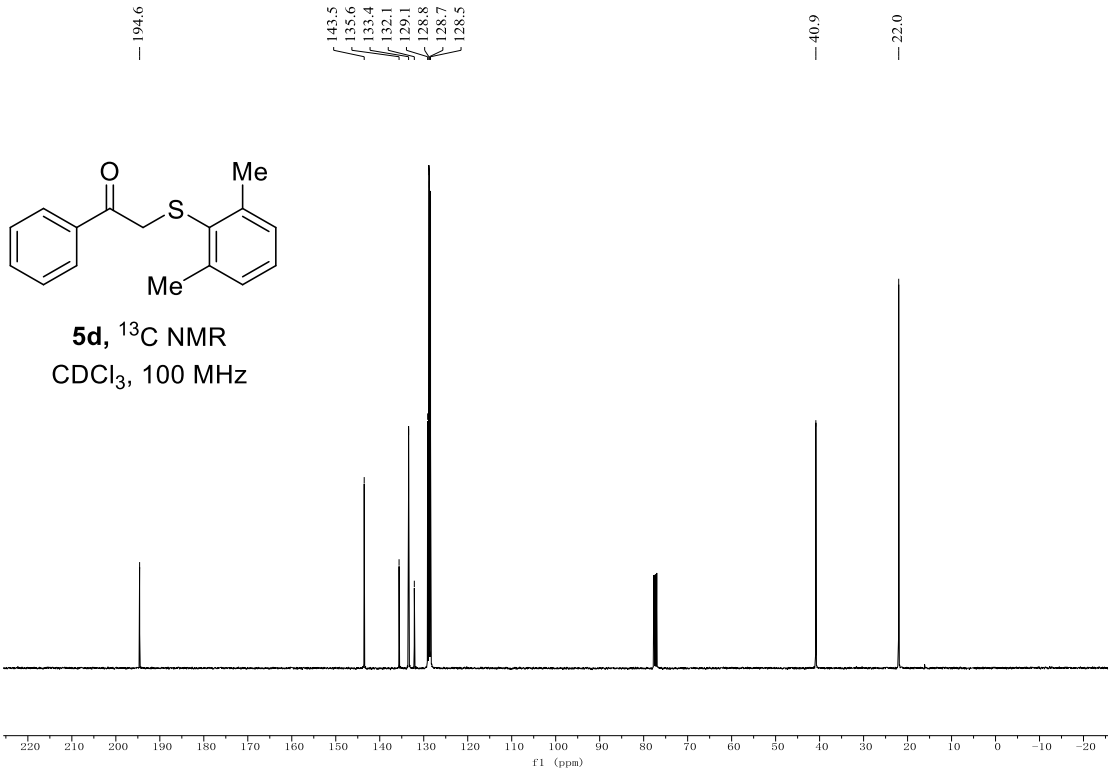
$CDCl_3$, 100 MHz





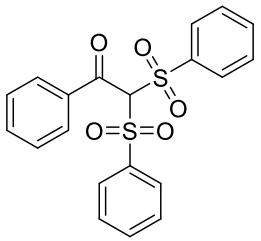
5d, ^{1}H NMR

$CDCl_3$, 400 MHz



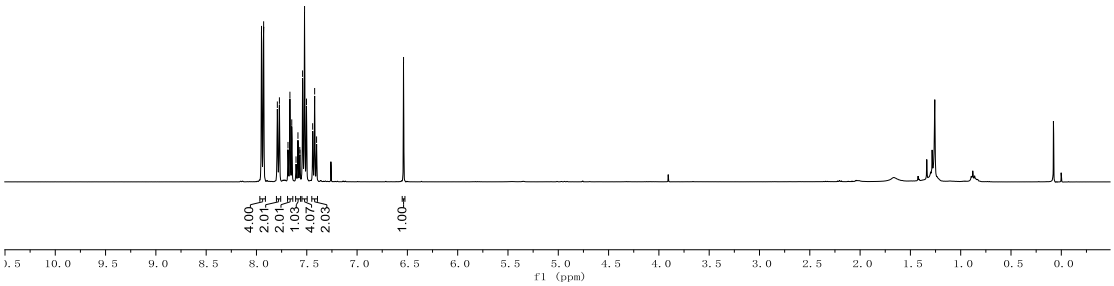
5d, ^{13}C NMR

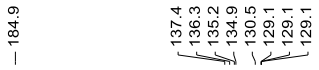
$CDCl_3$, 100 MHz

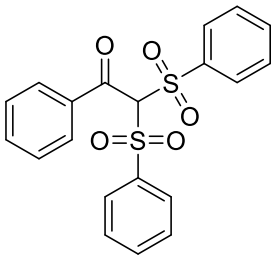


6, ^{1}H NMR

$CDCl_3$, 400 MHz

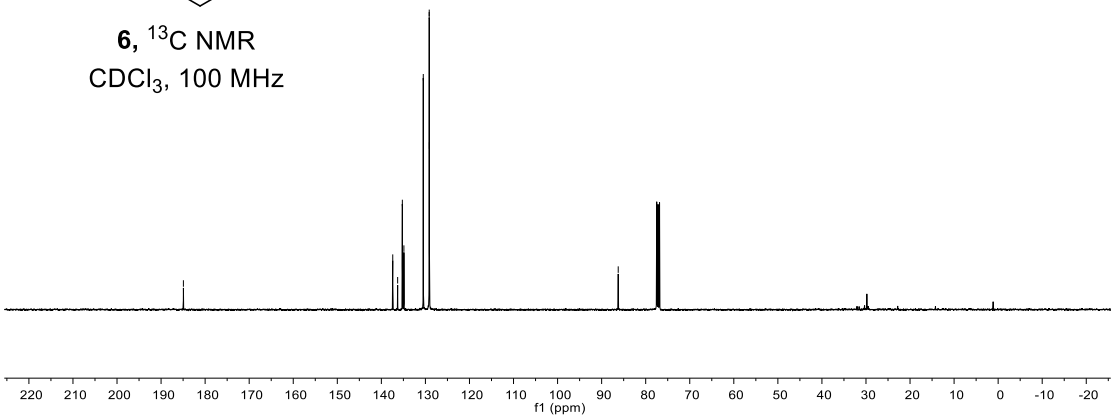


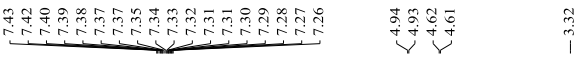


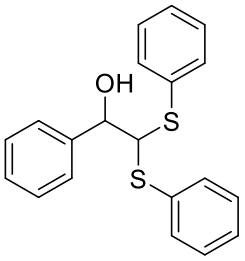


6, ^{13}C NMR

$CDCl_3$, 100 MHz

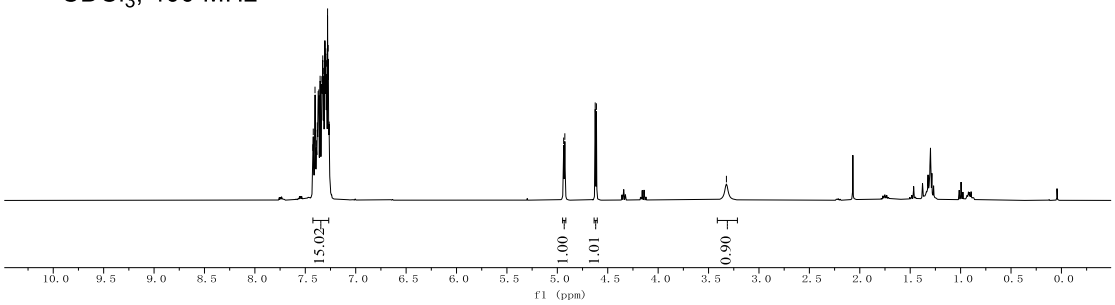


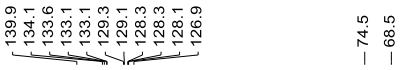


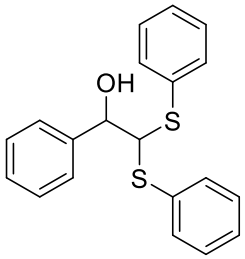


7, ^{1}H NMR

$CDCl_3$, 400 MHz

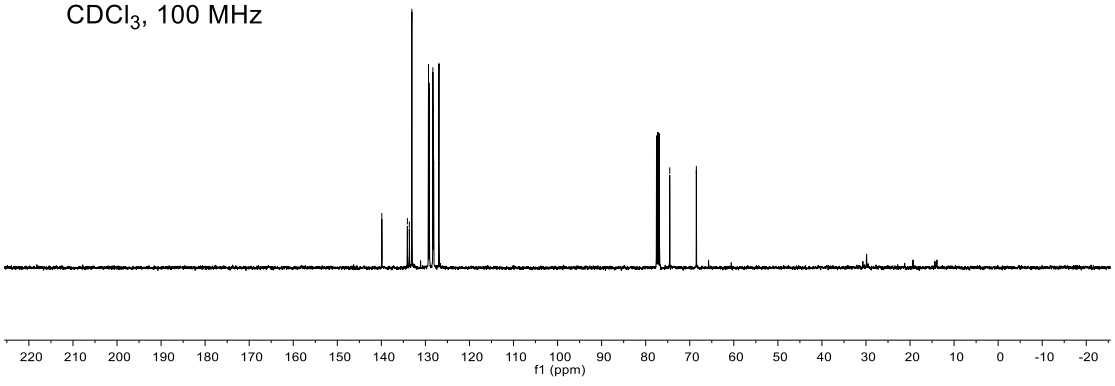


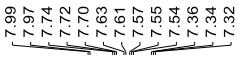


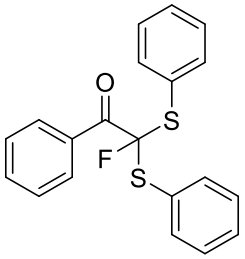


7, ^{13}C NMR

$CDCl_3$, 100 MHz

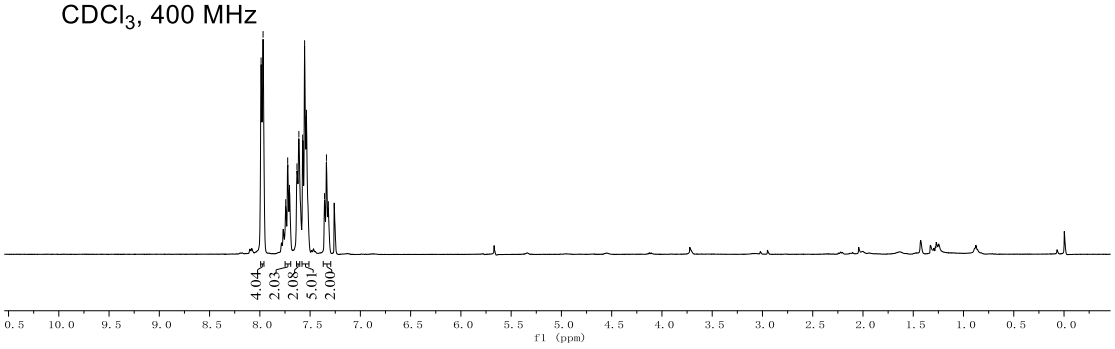


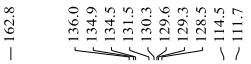


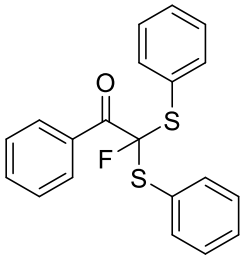


8, ^{1}H NMR

$CDCl_3$, 400 MHz

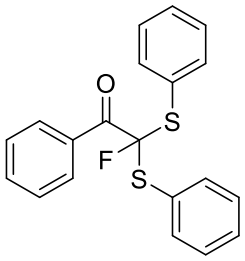






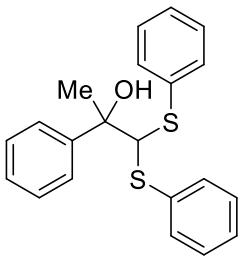
8, ^{13}C NMR

$CDCl_3$, 100 MHz



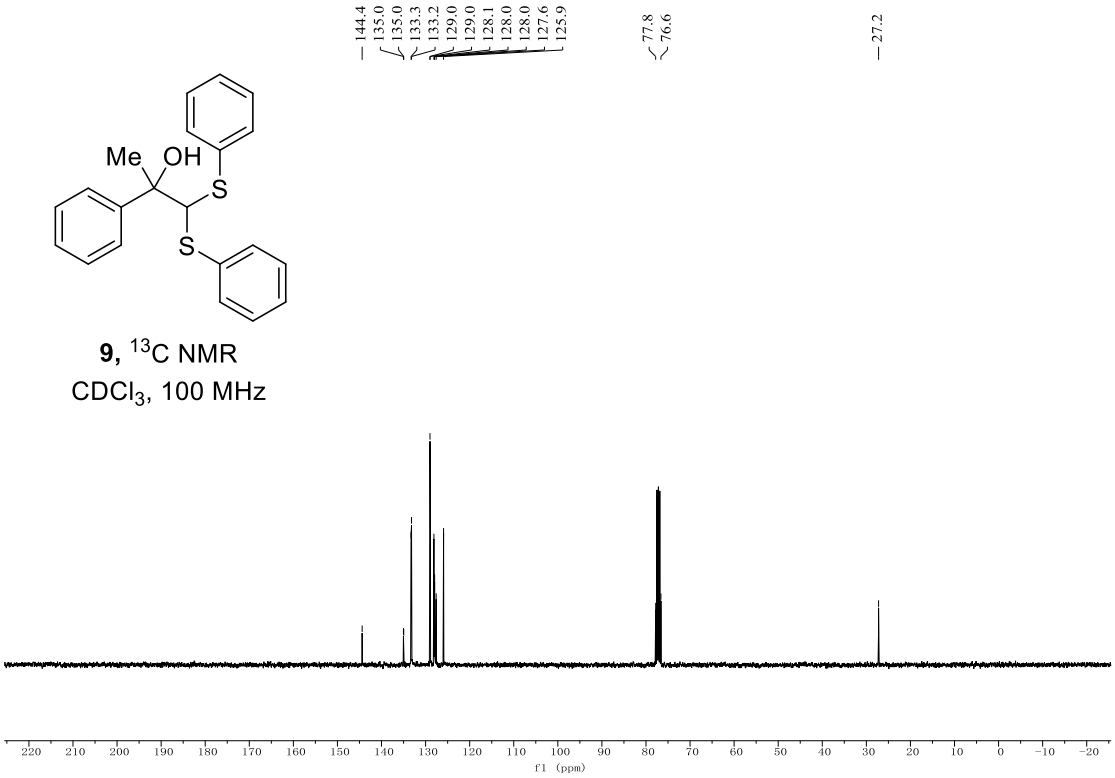
8, ^{19}F NMR

$CDCl_3$, 376 MHz

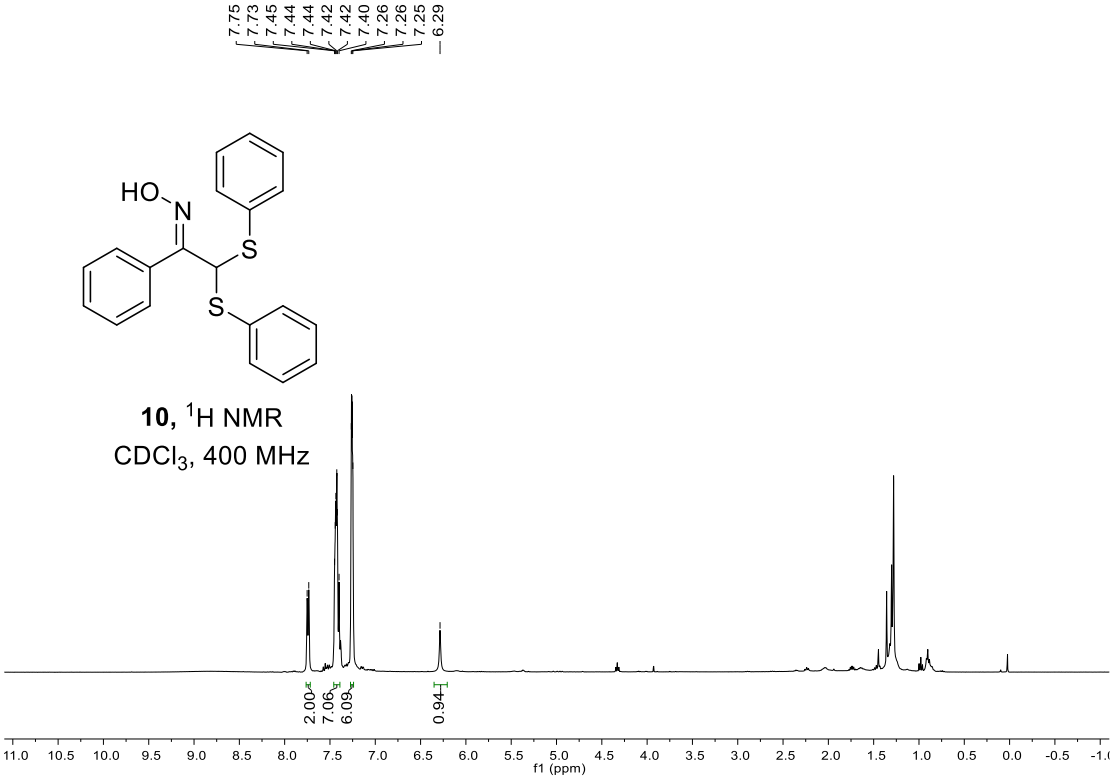


9, ^{1}H NMR

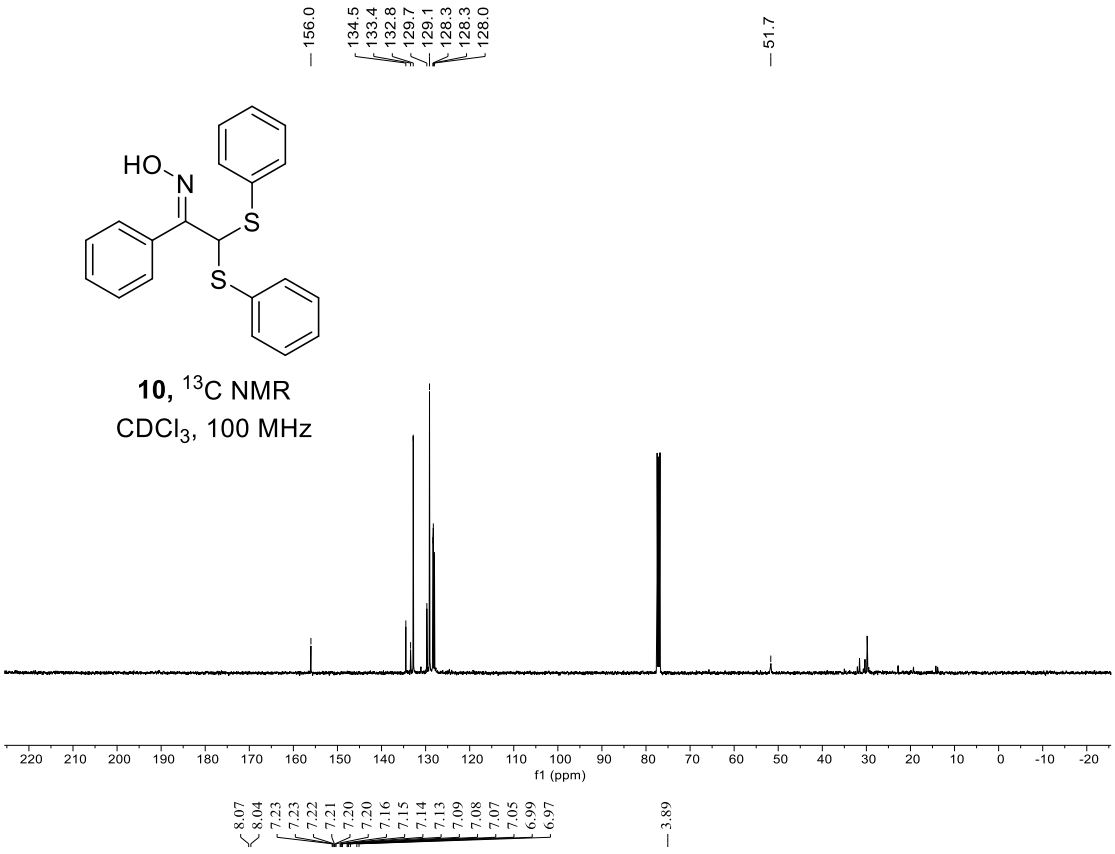
$CDCl_3$, 400 MHz



9, ^{13}C NMR
$CDCl_3$, 100 MHz

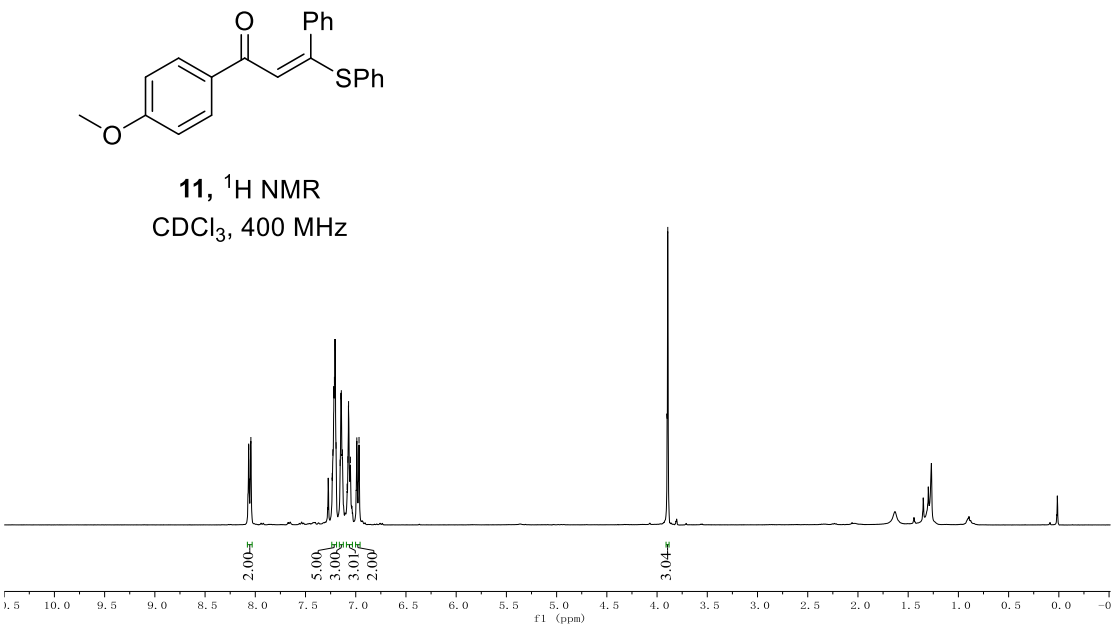


10, ^{1}H NMR
$CDCl_3$, 400 MHz



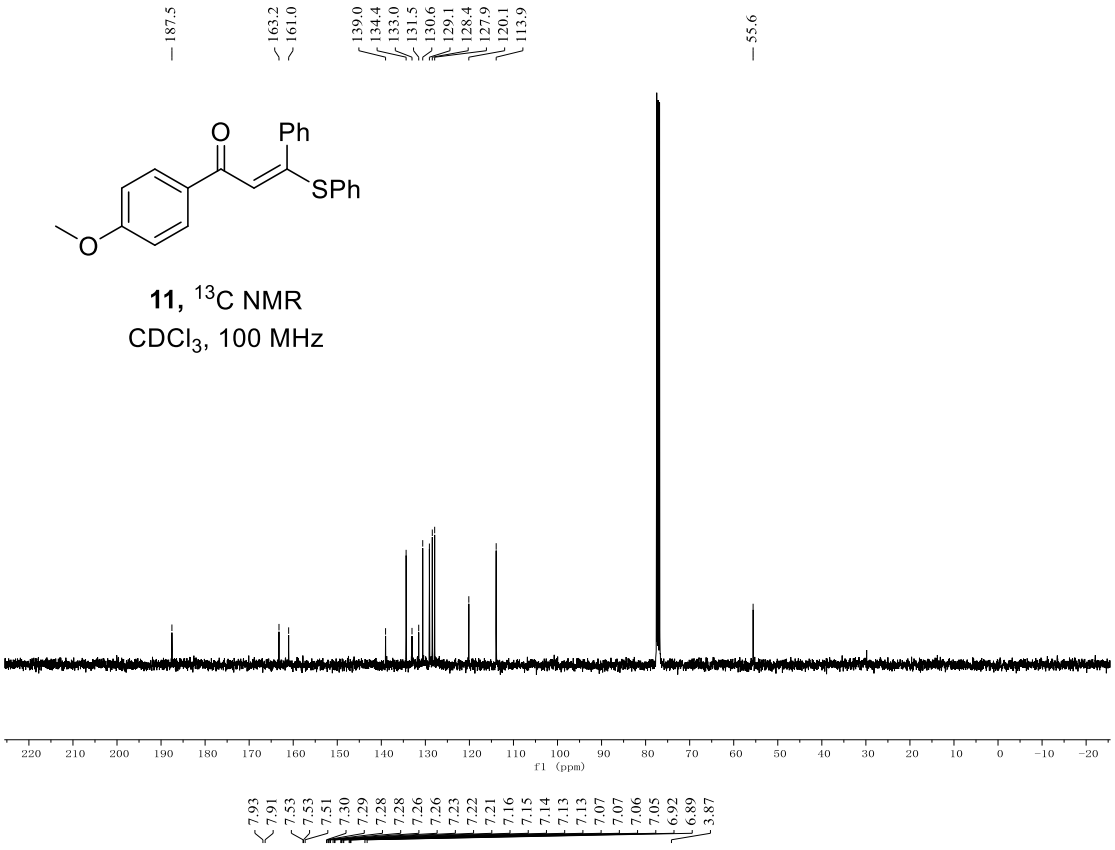
10, ^{13}C NMR

$CDCl_3$, 100 MHz

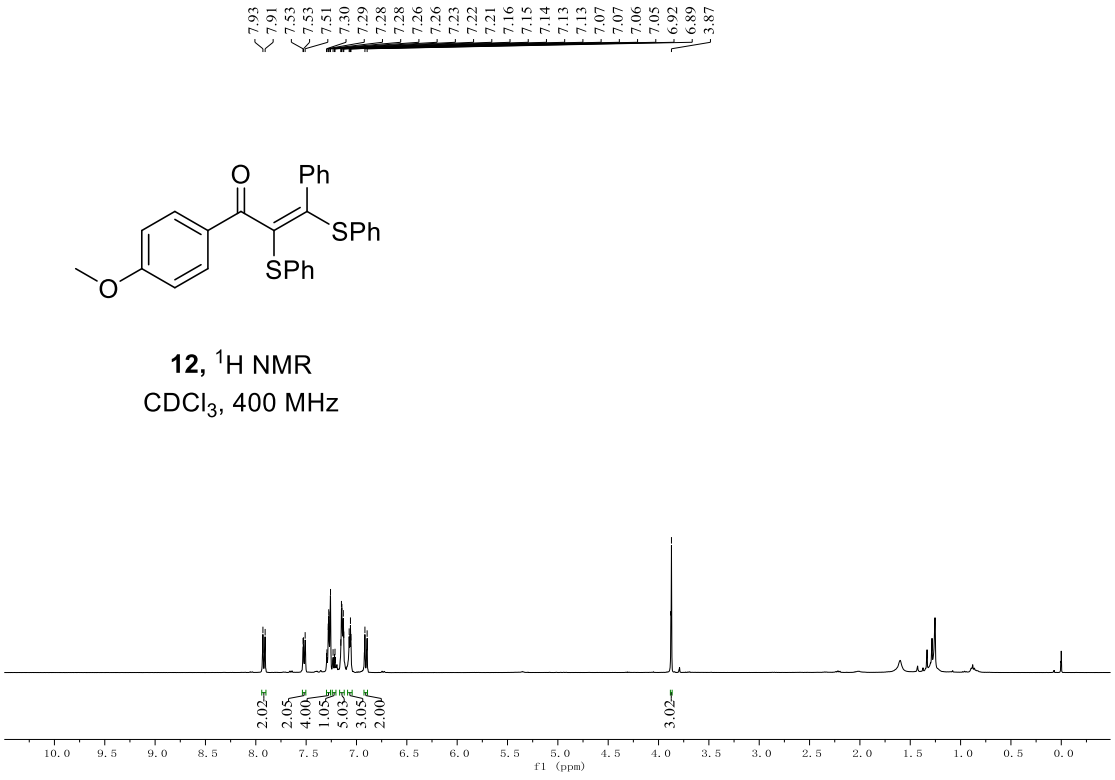


11, ^{1}H NMR

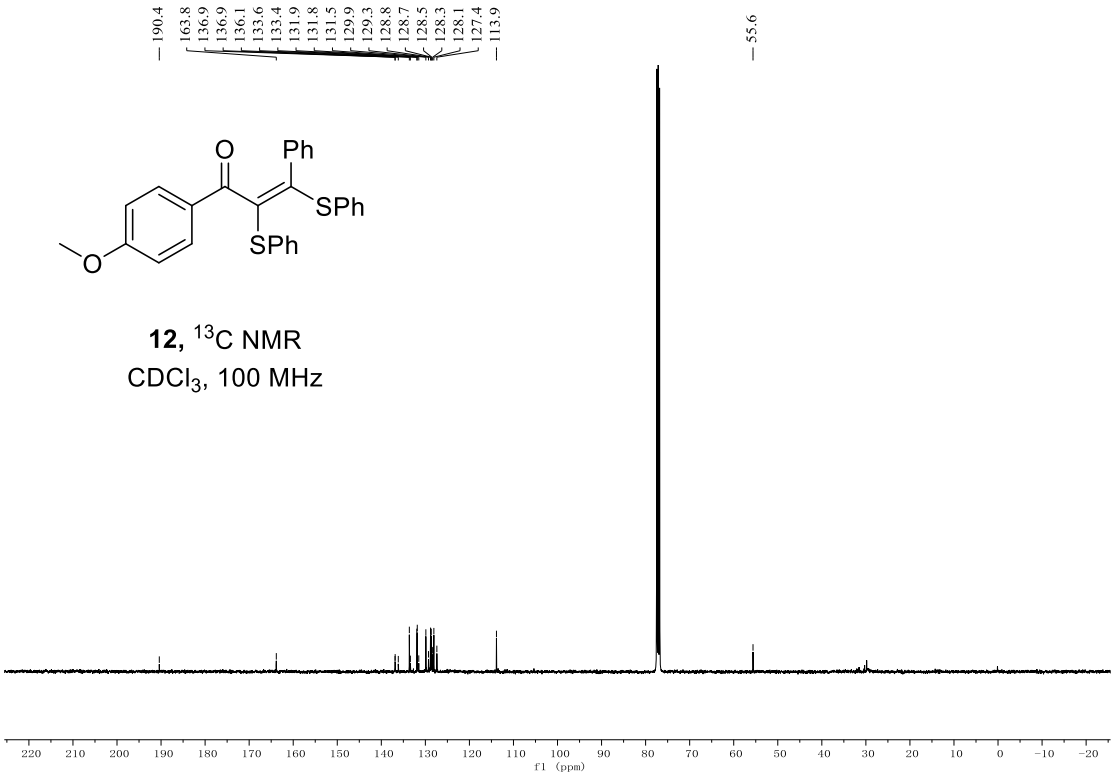
$CDCl_3$, 400 MHz



11, ^{13}C NMR
$CDCl_3$, 100 MHz



12, ^{1}H NMR
$CDCl_3$, 400 MHz



12, ^{13}C NMR

$CDCl_3$, 100 MHz