Supporting Information

Alkyldisulfanium Salt-Mediated Difunctionalization of Alkenes with *NH*-Sulfoximines

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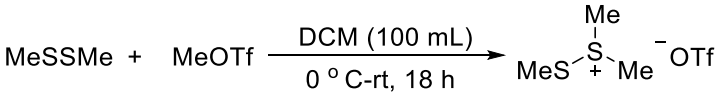
Table of Content

1. General Information

All chemicals and solvents were acquired from commercial sources and utilized directly without additional purification, unless stated otherwise. Nuclear magnetic resonance (NMR) spectra for ^{1}H, ^{13}C, ^{31}P, and ^{19}F were collected using instruments operating at 400 MHz, 100 MHz, 162 MHz, and 376 MHz, respectively. Chemical shifts are expressed in parts per million (ppm) relative to $CDCl_3$, with reference values of δ_H = 7.26 ppm and δ_C = 77.0 ppm. Spectral data are denoted with standard abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and doublet of doublets (dd). Reaction progress was monitored by thin-layer chromatography (TLC) employing silica gel GF254-coated plates. Mass spectrometry analyses were conducted on an electrospray ionization time-of-flight (ESI-TOF) instrument. Melting points were determined using a melting point device and are reported without adjustment.

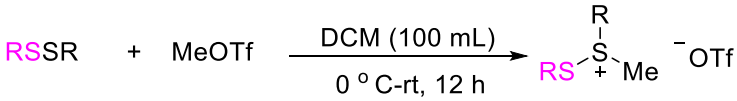
2. Experimental Section

General procedure for the synthesis of DMTSM



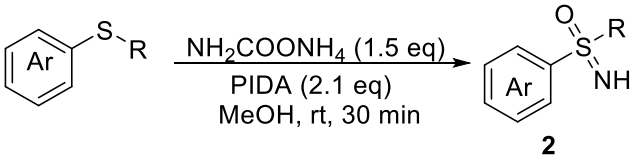
Dimethyl(methylthio)sulfoniumtrifluoromethanesulfonate (DMTSM) was prepared according to Xie's work.[1] At 0 ℃ (in an ice bath), to a solution of methyl trifluoromethanesulfonate (0.12 mol, 13.58 mL, 1.2 equiv) in CH_2Cl_2 (100 mL), Me_2S_2 (0.1 mol, 8.85 mL, 1.0 equiv) was added dropwise over 30 min. The mixture was stirred for 1 h at that temperature, following by 18 h at room temperature.1 Upon completion, the white solid was collected by filtration and washed with fresh distilled Et_2O under nitrogen atmosphere, affording dimethyl(methylthio)sulfonium trifluoromethanesulfonate as a white solid (23.13 g, 90% yield).

General procedure for the synthesis of alkyldisulfanium salt



Alkyldisulfanium salt was synthesized using a method analogous to that of DMTSM. At 0 ℃ (in an ice bath), to a solution of methyl trifluoromethanesulfonate (0.12 mol, 1.2 equiv) in CH_2Cl_2 (100 mL), RSSR (0.1 mol, 1.0 equiv) was added dropwise over 30 min. The mixture was stirred for 1 hour at 0 ℃ and then allowed to stand at room temperature for 12 hours. Upon completion of the reaction, the solvent was evaporated at 30 ℃ under vacuum to yield the residue product, which was not further purified for the subsequent step.

General procedure for the synthesis of *NH*-sulfoximine 2

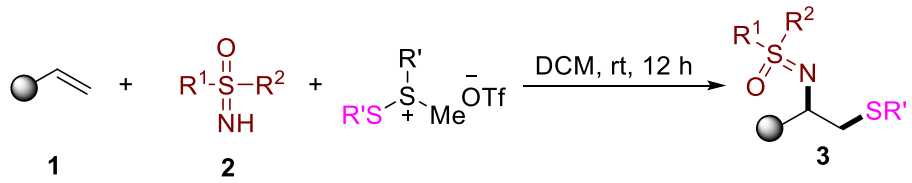


2

NH-sulfoximine was prepared according to the previous work from Luisi and co-workers.[2] To a flask containing a stirrer bar was added successively, sulfide (1 equiv.), ammonium carbamate (1.5 equiv.) and then MeOH (0.5 M). PIDA (2.1 equiv.) was added in one portion and the reaction was stirred at 20 ℃ for 30 min (open flask to the

atmosphere). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel to obtain *NH*-sulfoximine.

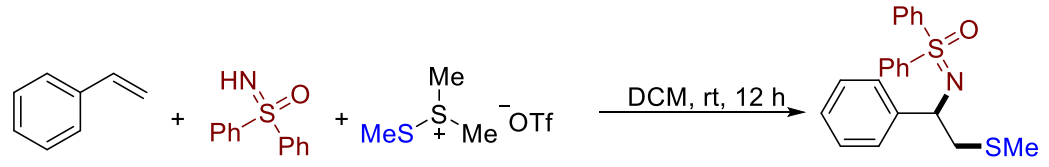
General Procedure for the Synthesis of alkyl sulfoximines 3



1 2 3

To a 10 mL round-bottom flask equipped with a stirring bar was added alkene **1** (0.3 mmol, 1 eq), *NH*-sulfoximine **2** (0.45 mmol, 1.5 eq) and alkyldisulfanium salt (0.36 mmol, 1.2 eq) in DCM (3 mL). The reaction mixture was stirred at room temperature for about 12 h. After completion, H_2O (10 mL) was added to the mixture, followed by extraction with DCM three times (10 mL × 3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was further purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 10:1-6:1) to afford the purified product **3**.

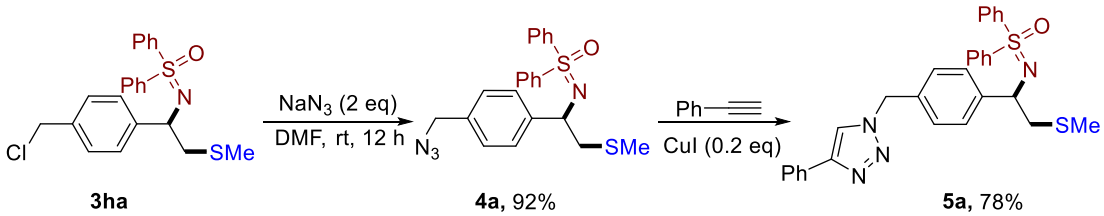
Gram-scale synthesis of 3aa



1a, 5 mmol **2a** **3aa**, 1.45 g, 79% yield

To a 100 mL round-bottom flask equipped with a stirring bar was added styrene **1a** (0.5208 g, 5 mmol), **2a** (1.6296 g, 7.5 mmol) and DMTSM (1.5498 g, 6 mmol) in DCM (30 mL). The reaction mixture was stirred at room temperature for about 12 h. After completion, H_2O (30 mL) was added to the mixture, followed by extraction with DCM three times (30 mL × 3). The combined organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was further purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 10:1-6:1) to afford 1.45 g of **3aa** in 79% yield.

Synthesis of 5a using 3ia as the starting material

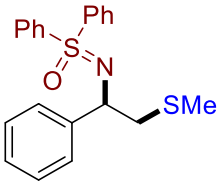


3ha **4a**, 92% **5a**, 78%

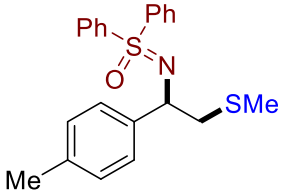
To a solution of **3ha** (174.0 mg, 0.5 mmol, 1.0 equiv) in DMF (5 mL) was added NaN_3 (65.0 mg, 1 mmol, 2 equiv). The reaction mixture was stirred at room temperature for about 12 h. After completion, 10 mL of H_2O was added to the mixture, followed by extraction with DCM three times (10 mL × 3). The organic phase was then dried with anhydrous sodium sulfate, concentrated under vacuum to obtain the residue **4a** without further purification for the next step. (Note: the azido compounds have a certain explosive nature, and explosion-proof measures should be taken when using them). To a solution of the obtained **4a** and phenylacetylene (51.1 mg, 0.5 mmol) in 1,4-dioxane (5 mL) was added CuI (19.0 mg, 0.1 mmol), the reaction mixture was stirred at 80 ℃ for about 6 h. After completion, the reaction was

allowed to cool to room temperature, then, H_2O (5 mL) was added to the mixture, which was further extracted with DCM for three times (10 mL× 3). The organic phase was then dried with anhydrous sodium sulfate, concentrated under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA 4:1- 2:1) to afford 204.4 mg of colorless liquid product **5a** in 78% isolated yield based on **3ha**.

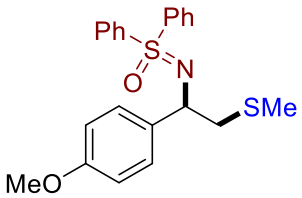
3. Characterization Data of Products



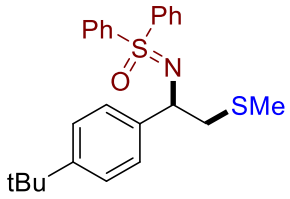
((2-(methylthio)-1-phenylethyl)imino)diphenyl-l6-sulfanone **(3aa):** TLC (PE/EtOAc, 6:1), R_f = 0.61; Colorless liquid (91.5 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.44 - 7.34 (m, 4H), 7.31 - 7.25 (m, 4H), 7.22 - 7.12 (m, 3H), 4.23 (t, *J* = 6.9 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.84 - 2.79 (m, 1H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.9, 140.7, 132.5, 132.5, 129.1, 129.1, 129.0, 128.7, 128.2, 127.1, 58.9, 45.8, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{22}NOS_2$: 368.1137; found: 368.1139.



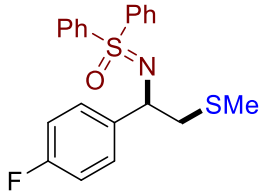
((2-(methylthio)-1-(p-tolyl)ethyl)imino)diphenyl-l6-sulfanone **(3ba):** TLC (PE/EtOAc, 6:1), R_f = 0.63; Colorless liquid (91.6 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.45 -7.37 (m, 4H), 7.33 - 7.29 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 4.20 (t, *J* = 6.9 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.84 - 2.79 (m, 1H), 2.25 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.0, 140.8, 136.6, 132.5, 132.5, 129.2, 129.1, 129.1, 129.0, 128.8, 127.0, 58.7, 45.9, 21.3, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NOS_2$: 382.1294; found: 382.1295.



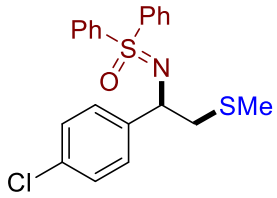
((1-(4-methoxyphenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3ca):** TLC (PE/EtOAc, 6:1), R_f = 0.41; Colorless liquid (87.1 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.43 - 7.37 (m, 4H), 7.33 - 7.29 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.20 (t, *J* = 6.9 Hz, 1H), 3.72 (s, 3H), 3.03 - 2.98 (m, 1H), 2.83 - 2.78 (m, 1H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 141.0, 140.8, 137.1, 132.5, 132.5, 129.2, 129.1, 129.1, 128.8, 128.1, 113.7, 58.4, 55.3, 45.9, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NO_2S_2$: 398.1243; found: 398.1242.



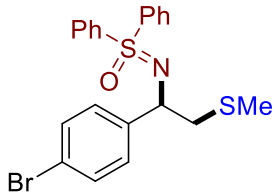
((1-(4-(tert-butyl)phenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3da):** TLC (PE/EtOAc, 6:1), R_f = 0.41; Colorless liquid (90.2 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.42 - 7.33 (m, 4H), 7.30 - 7.26 (m, 2H), 7.22 - 7.18 (m, 4H), 4.23 (t, *J* = 6.9 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.84 - 2.79 (m, 1H), 1.87 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 141.7, 141.0, 140.8, 132.5, 132.4, 129.1, 129.0, 129.0, 128.8, 126.7, 125.1, 58.5, 45.8, 34.5, 31.5, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{30}NOS_2$: 424.1763; found: 424.1766.



((1-(4-fluorophenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3ea):** TLC (PE/EtOAc, 6:1), R_f = 0.50; Colorless liquid (89.1 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.46 - 7.38 (m, 4H), 7.33 - 7.29 (m, 2H), 7.26 - 7.23 (m, 2H), 6.91 - 6.87 (m, 2H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.02 - 2.97 (m, 1H), 2.8 - 2.76 (m, 1H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 245.6 Hz), 140.9, 140.6, 140.5, 132.6 (d, J_{C-F} = 3.8 Hz), 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 115.0 (d, J_{C-F} = 21.3 Hz), 58.2, 45.9, 16.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.92. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}FNOS_2$: 386.1043; found: 386.1045.

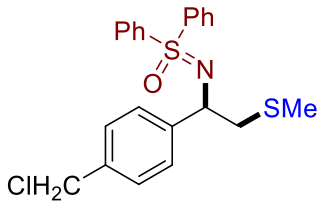


((1-(4-chlorophenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3fa):** TLC (PE/EtOAc, 6:1), R_f = 0.61; Colorless liquid (88.0 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.45 - 7.39 (m, 4H), 7.34 - 7.30 (m, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.20 (t, *J* = 6.9 Hz, 1H), 3.01 - 2.96 (m, 1H), 2.80 - 2.75 (m, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.9, 140.5, 132.7, 132.7, 132.6, 129.3, 129.2, 128.9, 128.8, 128.5, 128.4, 58.3, 45.7, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}ClNOS_2$: 402.0748; found: 402.0751.

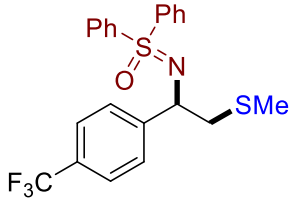


((1-(4-bromophenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3ga):** TLC (PE/EtOAc, 6:1), R_f = 0.59; Colorless liquid (96.4 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.45 - 7.37 (m, 4H), 7.34 - 7.30 (m, 4H), 7.17 (d, *J* = 8.5 Hz, 2H), 4.19 (t, *J* = 6.9 Hz, 1H), 3.00 - 2.96 (m, 1H), 2.80 - 2.75 (m, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

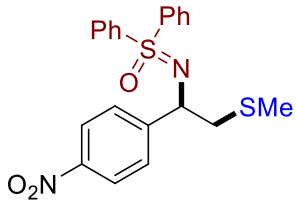
143.9, 140.8, 140.4, 132.7, 132.6, 131.3, 129.2, 129.2, 128.9, 128.9, 128.6, 120.9, 58.3, 45.6, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}BrNOS_2$: 446.0242; found: 446.0243.



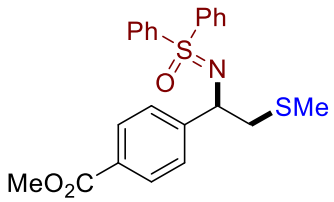
((1-(4-(chloromethyl)phenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3ha)** **:** TLC (PE/EtOAc, 6:1), R_f = 0.43; Colorless liquid (83.6 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.45 - 7.36 (m, 4H), 7.33 - 7.27 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 4.24 (t, *J* = 6.9 Hz, 1H), 3.03 - 2.98 (m, 1H), 2.83 - 2.78 (m, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 140.9, 140.6, 136.2, 132.6, 132.6, 129.2, 129.2, 128.9, 128.8, 128.6, 127.5, 58.6, 46.4, 45.7, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{23}ClNOS_2$: 416.0904; found: 416.0902.



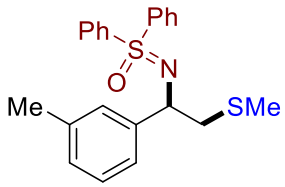
((2-(methylthio)-1-(4-(trifluoromethyl)phenyl)ethyl)imino)diphenyl-l6-sulfanone **(3ia)** **:** TLC (PE/EtOAc, 6:1), R_f = 0.66; Colorless liquid (94.1 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.48 - 7.39 (m, 8H), 7.34 - 730 (m, 2H), 4.29 (t, *J* = 6.8 Hz, 1H), 3.03 - 2.98 (m, 1H), 2.83 - 2.78 (m, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 140.8, 140.4, 132.8, 132.7, 129.4, 129.3, 129.3 (q, $J_{C\text{-}F}$ = 32.3 Hz), 129.2, 128.8, 128.8, 125.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.4 (q, $J_{C\text{-}F}$ = 273.0 Hz), 58.4, 45.6, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{21}F_3NOS_2$: 436.1011; found: 436.1007.



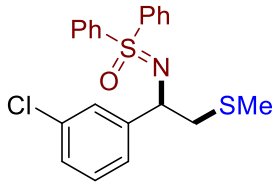
((2-(methylthio)-1-(4-nitrophenyl)ethyl)imino)diphenyl-l6-sulfanone **(3ja)**: TLC (PE/EtOAc, 6:1), R_f = 0.47; Colorless liquid (63.1 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.51 - 7.41 (m, 6H), 7.36 - 7.33 (m, 2H), 4.32 (t, *J* = 6.8 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.83 - 2.78 (m, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 147.1, 140.7, 140.1, 132.9, 132.9, 129.4, 129.3, 128.8, 128.7, 128.1, 123.6, 58.3, 45.5, 16.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}N_2O_3S_2$: 413.0988; found: 413.0990.



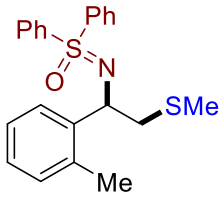
Methyl-4-(2-(methylthio)-1-((oxodiphenyl-l6-sulfaneylidene)amino)ethyl)benzoate **(3ka)**：TLC (PE/EtOAc, 6:1), R_f = 0.32; Colorless liquid (86.8 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.46 - 7.38 (m, 4H), 7.34 - 7.26 (m, 4H), 6.93 (d, *J* = 8.3 Hz, 2H), 4.24 (t, *J* = 6.8 Hz, 1H), 3.02 - 2.97 (m, 1H), 2.81 - 2.77 (m, 1H), 2.21 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 149.7, 142.4, 140.8, 140.6, 132.6, 132.6, 129.2, 129.2, 129.0, 128.8, 128.1, 121.3, 58.4, 45.9, 21.3, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{24}NO_3S_2$: 426.1192; found: 426.1197.



((2-(methylthio)-1-(m-tolyl)ethyl)imino)diphenyl-l6-sulfanone **(3la)**：TLC (PE/EtOAc, 6:1), R_f = 0.61; Colorless liquid (88.1 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.45 - 7.37 (m, 4H), 7.33 - 7.29 (m, 2H), 7.12 - 7.06 (m, 3H), 6.96 (d, *J* = 6.5 Hz, 1H), 4.20 (t, *J* = 6.9 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.85 - 2.80 (m, 1H), 2.24 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.0, 140.7, 137.7, 132.5, 132.5, 129.2, 129.1, 129.1, 128.8, 128.2, 127.9, 127.8, 124.2, 58.9, 45.7, 21.6, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NOS_2$: 382.1294; found: 382.1295.

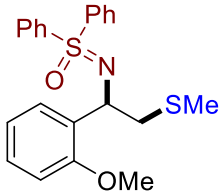


((1-(3-chlorophenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone **(3ma)**：TLC (PE/EtOAc, 6:1), R_f = 0.59; Colorless liquid (88.0 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.47 - 7.37 (m, 4H), 7.34 - 7.31 (m, 2H), 7.27 (s, 1H), 7.18 - 7.08 (m, 3H), 4.20 (t, *J* = 6.8 Hz, 1H), 3.01 - 2.96 (m, 1H), 2.81 - 2.76 (m, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 140.8, 140.5, 134.1, 132.7, 132.7, 129.5, 129.3, 129.2, 128.9, 128.8, 127.4, 127.3, 125.4, 58.4, 45.6, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}ClNOS_2$: 402.0748; found: 402.0751.

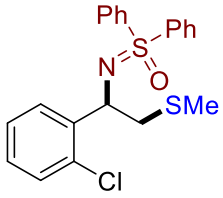


((2-(methylthio)-1-(o-tolyl)ethyl)imino)diphenyl-l6-sulfanone **(3na)**：TLC (PE/EtOAc, 6:1), R_f = 0.50; Colorless liquid (87.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.46 - 7.37 (m, 4H), 7.35 - 7.26 (m, 4H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 4.1 Hz,

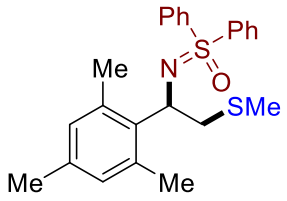
1H), 4.24 (t, *J* = 6.9 Hz, 1H), 3.05 - 3.00 (m, 1H), 2.85 - 2.80 (m, 1H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 141.0, 140.7, 132.6, 132.5, 129.2, 129.1, 129.1, 128.8, 128.3, 127.2, 59.0, 45.8, 29.8, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NOS_2$: 382.1294; found: 382.1298.



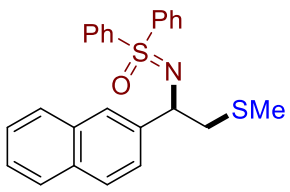
***((1-(2-methoxyphenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone* (3oa):** TLC (PE/EtOAc, 6:1), R_f = 0.41; Colorless liquid (89.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.43 - 7.34 (m, 4H), 7.31 - 7.27 (m, 2H), 7.13 - 7.09 (m, 1H), 6.94 - 6.90 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.81 - 4.78 (m, 1H), 3.51 (s, 3H), 2.94 - 2.82 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 141.5, 140.8, 133.2, 132.3, 132.3, 129.0, 129.0, 128.9, 128.9, 128.2, 127.9, 120.8, 110.2, 55.2, 51.1, 44.4, 16.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NO_2S_2$: 398.1243; found: 398.1243.



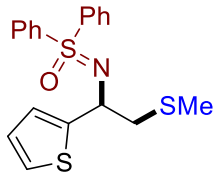
***((1-(2,6-dichlorophenyl)-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone* (3pa):** TLC (PE/EtOAc, 300:1), R_f = 0.58; Colorless liquid (90.4 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.5 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.54 - 7.45 (m, 4H), 7.42 - 7.38 (m, 2H), 7.31 - 7.26 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.16 - 7.13 (m, 1H), 4.90 - 4.81 (m, 1H), 3.00 - 2.88 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.0, 140.2, 132.6, 132.6, 132.1, 129.5, 129.2, 129.1, 129.0, 128.9, 128.2, 127.1, 54.3, 44.5, 16.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{22}ClNOS_2$: 402.0748; found: 402.0745.



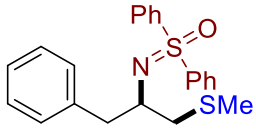
***((1-mesityl-2-(methylthio)ethyl)imino)diphenyl-l6-sulfanone* (3qa):** TLC (PE/EtOAc, 6:1), R_f = 0.65; Colorless liquid (87.2 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.44 - 7.33 (m, 4H), 7.26 - 7.23 (m, 2H), 6.76 (s, 1H), 6.52 (s, 1H), 4.74 (t, *J* = 7.5 Hz, 1H), 3.16 - 3.11 (m, 1H), 3.02 - 2.88 (m, 1H), 2.67 (s, 3H), 2.14 (s, 3H), 1.91 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.0, 137.4, 137.1, 136.0, 135.4, 132.4, 132.3, 131.3, 129.1, 129.0, 128.9, 128.69, 54.0, 42.2, 21.4, 20.9, 20.8, 16.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{28}NOS_2$: 410.1607; found: 410.1609.



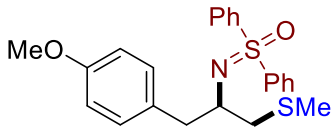
***((2-(methylthio)-1-(naphthalen-2-yl)ethyl)imino)diphenyl-l6-sulfanone* (3ra):** TLC (PE/EtOAc, 6:1), R_f = 0.54; Colorless liquid (91.5 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.70 - 7.65 (m, 1H), 7.60 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 - 7.33 (m, 6H), 7.28 - 7.24 (m, 2H), 4.41 (t, *J* = 6.9 Hz, 1H), 3.12 -3.05 (m, 1H), 2.95 - 2.90 (m, 1H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 140.9, 140.7, 133.4, 133.0, 132.6, 132.5, 129.2, 129.1, 129.0, 128.8, 128.1, 127.8, 125.9, 125.8, 125.6, 125.5, 59.2, 45.6, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{24}NOS_2$: 418.1294; found: 418.1292.



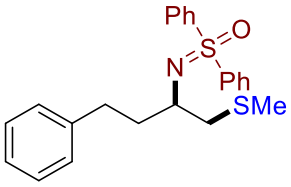
***((2-(methylthio)-1-(thiophen-2-yl)ethyl)imino)diphenyl-l6-sulfanone* (3sa):** TLC (PE/EtOAc, 6:1), R_f = 0.57; Colorless liquid (79.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.41 - 7.30 (m, 4H), 7.28 - 7.24 (m, 2H), 7.07 (d, *J* = 5.0 Hz, 1H), 6.77 - 6.75 (m, 1H), 6.72 - 6.69 (m, 1H), 4.48 (t, *J* = 6.6 Hz, 1H), 3.01 - 2.96 (m, 1H), 2.85 - 2.80 (m, 1H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 140.6, 140.5, 132.7, 132.6, 129.2, 129.2, 129.0, 128.7, 126.5, 124.1, 123.6, 54.9, 46.3, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{20}NOS_3$: 374.0702; found: 374.0705.



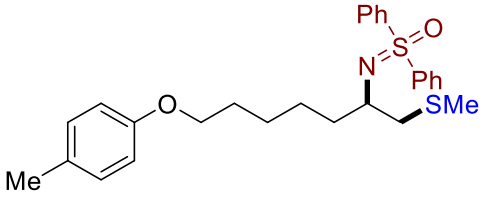
***((1-(methylthio)-3-phenylpropan-2-yl)imino)diphenyl-l6-sulfanone* (3ta):** TLC (PE/EtOAc, 6:1), R_f = 0.50; Colorless liquid (72.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.90 (m, 4H), 7.49 - 7.37 (m, 6H), 7.25 - 7.17 (m, 5H), 3.32 - 3.19 (m, 2H), 3.11 - 3.02 (m, 1H), 2.97 - 2.92 (m, 1H), 2.77 - 2.71 (m, 1H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.7, 140.0, 132.6, 132.5, 129.5, 129.3, 129.3, 128.8, 128.7, 128.3, 126.3, 51.4, 47.1, 38.8, 14.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NOS_2$: 382.1294; found: 382.1298.



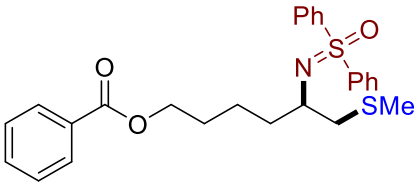
***((1-(4-methoxyphenyl)-3-(methylthio)propan-2-yl)imino)diphenyl-l6-sulfanone* (3ua):** TLC (PE/EtOAc, 6:1), R_f = 0.48; Colorless liquid (76.6 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.89 (m, 4H), 7.45 - 7.36 (m, 6H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 3.71 (s, 3H), 3.26 - 3.14 (m, 2H), 3.06 - 3.02 (m, 1H), 2.94 - 2.84 (m, 1H), 2.72 - 2.67 (m, 1H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 141.0, 140.7, 132.5, 132.5, 132.0, 130.4, 129.3, 129.2, 128.8, 128.7, 113.7, 55.3, 51.6, 47.0, 37.9, 14.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{26}NO_2S_2$: 412.1399; found: 412.1394.



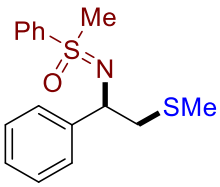
((1-(methylthio)-4-phenylbutan-2-yl)imino)diphenyl-l6-sulfanone **(3va):** TLC (PE/EtOAc, 6:1), R_f = 0.50; Colorless liquid (85.4 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 7.86 (m, 4H), 7.47 - 7.33 (m, 6H), 7.25 - 7.10 (m, 5H), 3.25 - 3.21 (m, 1H), 3.08 - 3.03 (m, 1H), 2.88 - 2.77 (m, 1H), 2.74 - 2.56 (m, 2H), 2.30 - 2.15 (m, 1H), 1.95 (s, 3H), 1.83 - 1.67 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 140.9, 140.8, 132.5, 129.2, 129.2, 128.9, 128.7, 128.6, 128.4, 128.4, 125.8, 48.9, 47.6, 33.6, 33.1, 13.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{26}NOS_2$: 396.1450; found: 396.1447.



((1-(methylthio)-7-(p-tolyloxy)heptan-2-yl)imino)diphenyl-l6-sulfanone **(3wa):** TLC (PE/EtOAc, 6:1), R_f = 0.59; Colorless liquid (103.8 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 - 7.90 (m, 5H), 7.43 - 7.39 (m, 7H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 3.87 - 3.82 (m, 2H), 3.22 - 3.18 (m, 1H), 3.05 - 3.00 (m, 1H), 2.74 - 2.63 (m, 1H), 2.20 (s, 3H), 1.96 (s, 3H), 1.93 - 1.90 (m, 2H), 1.75 - 1.68 (m, 2H), 1.51 - 1.39 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 140.9, 140.8, 132.5, 130.0, 129.8, 129.3, 129.2, 128.9, 128.9, 128.8, 128.7, 114.5, 68.1, 49.6, 47.8, 32.0, 29.4, 26.8, 26.2, 20.6, 13.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{34}NO_2S_2$: 468.2025; found: 468.2027.

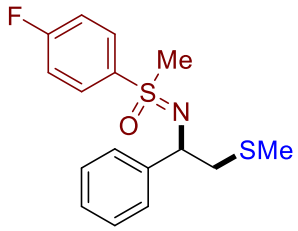


6-(methylthio)-5-((oxodiphenyl-l6-sulfaneylidene)amino)hexyl benzoate **(3xa):** TLC (PE/EtOAc, 6:1), R_f = 0.31; Colorless liquid (92.6 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.92 - 7.89(m, 4H), 7.49 - 7.32 (m, 9H), 4.26 (t, *J* = 6.5 Hz, 2H), 3.25 - 3.20 (m, 1H), 3.05 - 3.00 (m, 1H), 2.75 - 2.61 (m, 1H), 1.96 (s, 3H), 1.74 - 1.70 (m, 2H), 1.66 - 1.2 (m, 2H), 1.54 - 1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 140.9, 140.7, 132.9, 132.5, 132.5, 130.6, 129.7, 129.3, 128.7, 128.7, 128.4, 65.1, 49.5, 47.8, 31.6, 28.8, 23.6, 13.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{30}NO_3S_2$: 468.1662; found: 468.1666.

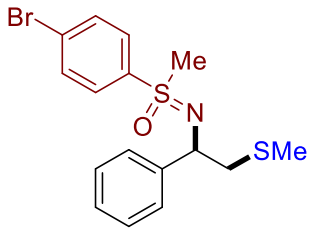


Methyl((-2-(methylthio)-1-phenylethyl)imino)(phenyl)-l6-sulfanone **(3ab):** TLC (PE/EtOAc, 6:1), R_f = 0.28; Colorless liquid (71.5 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.63 - 7.48 (m, 2H), 7.39 - 7.35 (m, 2H), 7.39 - 7.35 (m, 1H), 7.25 - 7.14 (m, 3H), 4.24 (t, *J* = 6.9 Hz, 1H), 3.12 - 3.05 (m, 3H), 3.04 - 2.99 (m, 0.5H), 2.96 - 2.85 (m, 1H), 2.78 -

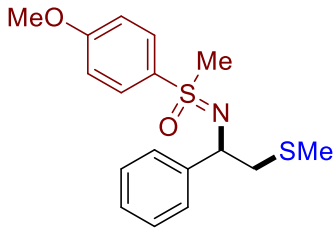
2.73 (m, 0.5H), 1.93 - 1.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 132.9, 129.4, 129.2, 128.8, 128.8, 128.4, 128.2, 127.3, 127.3, 127.1, 127.0, 58.7, 45.4, 45.0, 16.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{20}NOS_2$: 306.0981; found: 306.0980.



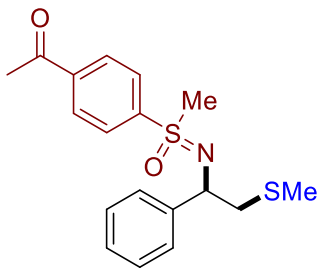
(4-fluorophenyl)(methyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone **(3ac)** : TLC (PE/EtOAc, 3:1), R_f = 0.37; Colorless liquid (62.1 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 8.01 (m, 1H), 7.64 - 7.60 (m, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.28 - 7.24 (m, 1H), 7.22 - 7.16 (m, 4H), 6.99 - 6.95 (m, 1H), 4.21 - 4.17 (m, 1H), 3.07 - 3.00 (m, 3H), 2.98 - 2.63 (m, 2H), 1.91 - 1.90 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, J_{C-F} = 255.9 Hz), 165.5 (d, J_{C-F} = 255.9 Hz), 145.0, 131.7 (d, J_{C-F} = 9.4 Hz), 131.5 (d, J_{C-F} = 9.4 Hz), 128.5, 128.3, 127.3, 127.3, 127.2, 126.9, 116.6 (d, J_{C-F} = 22.4 Hz), 116.3 (d, J_{C-F} = 22.4 Hz), 58.9, 58.6, 45.7, 45.6, 45.6, 45.0, 16.5, 16.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.35, -105.70. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}FNOS_2$: 324.0887; found: 324.0889.



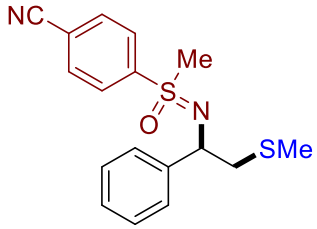
(4-bromophenyl)(methyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone **(3ad)** : TLC (PE/EtOAc, 1:1), R_f = 0.86; Colorless liquid (87.6 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.37 - 7.32 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.18 - 7.00 (m, 4H), 4.10 - 4.04 (m, 1H), 2.95 - 2.89 (m, 3H), 2.88 - 2.82 (m, 0.4H), 2.79 - 2.71 (m, 1H), 2.60 - 2.56 (m, 0.6H), 1.81 - 1.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.8, 139.2, 138.8, 132.6, 132.3, 130.5, 130.3, 128.4, 128.3, 128.0, 127.3, 127.2, 127.2, 126.8, 58.9, 58.6, 45.5, 45.5, 44.9, 16.5, 16.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}BrNOS_2$: 384.0086; found: 384.0089.



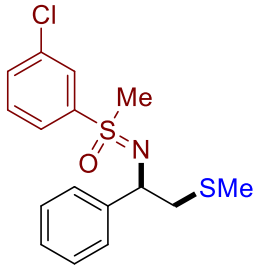
(4-methoxyphenyl)(methyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone **(3ae)** : TLC (PE/EtOAc, 2:1), R_f = 0.25; Colorless liquid (62.4 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.28 - 7.16 (m, 4H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 4.19 - 4.16 (m, 1H), 3.84 - 3.77 (m, 3H), 3.04 - 2.98 (m, 3H), 2.94 - 2.61 (m, 2H), 1.88 - 1.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.0, 130.9, 128.4, 128.3, 127.3, 127.2, 127.1, 127.0, 114.6, 114.4, 58.8, 55.8, 45.8, 45.8, 45.6, 45.1, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{22}NO_2S_2$: 336.1086; found: 336.1084.



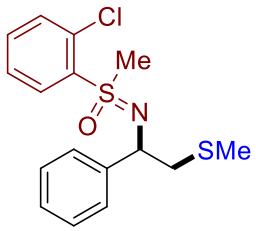
***(4-acetylphenyl)(methyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone* (3af):** TLC (PE/EtOAc, 3:1), R_f = 0.36; Colorless liquid (69.8 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.02 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.32 - 7.12 (m, 5H), 4.24 - 4.10 (m, 1H), 3.07 - 3.01 (m, 3H), 2.98 - 2.93 (m, 0.4H), 2.88 - 2.80 (m, 1H), 2.68 - 2.64 (m, 0.6H), 2.61 - 2.54 (m, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 144.9, 144.0, 143.6, 140.5, 140.2, 129.3, 129.2, 129.0, 128.9, 128.5, 128.3, 127.4, 127.2, 126.9, 59.0, 58.6, 45.5, 45.4, 45.3, 44.9, 27.1, 27.0, 16.5, 16.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{22}NOS_2$: 348.1086; found: 348.1087.



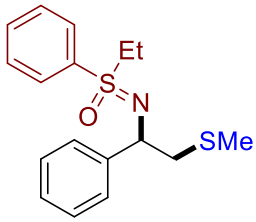
***4-(S-methyl-N-(2-(methylthio)-1-phenylethyl)sulfonimidoyl)benzonitrile* (3ag):** TLC (PE/EtOAc, 2:1), R_f = 0.34; Colorless liquid (62.5 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.29 - 7.18 (m, 2H), 7.12 (s, 2H), 4.29 - 4.06 (m, 1H), 3.09 - 3.03 (m, 3H), 3.00 - 2.95 (m, 0.5H), 2.91 - 2.79 (m, 1H), 2.71 - 2.66 (m, 0.5H), 1.93 - 1.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.6, 143.3, 133.1, 132.7, 129.6, 129.2, 128.5, 128.4, 127.5, 127.4, 127.2, 126.8, 117.5, 116.9, 116.3, 59.1, 58.4, 45.5, 45.4, 45.1, 44.7, 16.5, 16.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{19}N_2OS_2$: 331.0933; found: 331.0936.



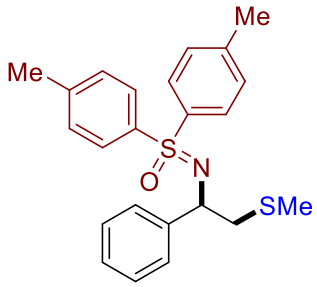
***(3-chlorophenyl)(methyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone* (3ah)** : TLC (PE/EtOAc, 6:1), R_f = 0.64; Colorless liquid (71.4 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.43 - 7.40 (m, 1H), 7.34 - 7.07 (m, 6H), 4.16 - 4.05 (m, 1H), 3.01 - 2.97 (m, 3H), 2.94 - 2.69 (m, 0.4H), 2.84 - 2.73 (m, 1H), 2.65 - 2.61 (m, 0.6H), 1.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 143.5, 141.6, 135.6, 135.3, 133.3, 132.9, 130.7, 130.3, 129.1, 128.9, 128.5, 128.3, 127.3, 127.2, 127.1, 126.8, 126.7, 58.8, 58.5, 45.5, 45.5, 45.4, 44.7, 16.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}ClNOS_2$: 340.0591; found: 340.0591.



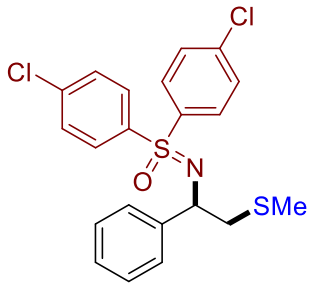
(2-chlorophenyl)(methyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone (3ai): TLC (PE/EtOAc, 6:1), R_f = 0.65; Colorless liquid (57.1 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 5.5 Hz, 2H), 7.42 - 7.35 (m, 1H), 7.28 - 7.19 (m, 4H), 7.15 - 7.12 (m, 1H), 4.09 - 3.95 (m, 1H), 3.22 (s, 3H), 2.86 - 2.67 (m, 2H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.3, 134.2, 132.8, 132.3, 132.1, 128.3, 127.6, 127.3, 127.3, 59.6, 44.2, 43.6, 16.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}ClNOS_2$: 340.0591; found: 340.0594.



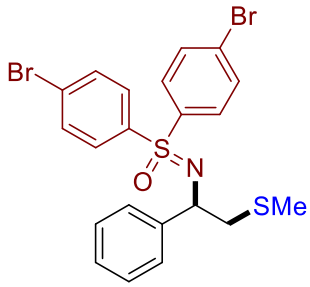
***Ethyl(((methylthio)-1-phenylethyl)imino)(phenyl)-l6-sulfanone (3aj)*:** TLC (PE/EtOAc, 6:1), R_f = 0.59; Colorless liquid (60.4 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.54 - 7.36(m, 3H), 7.29 - 7.06 (m, 6H), 4.17 - 4.12 (m, 1H), 3.19 - 2.99 (m, 2H), 2.94 - 2.89 (m, 1H), 2.84 - 2.77 (m, 1H), 2.66 - 2.61 (m, 1H), 1.82 - 1.80 (m, 3H), 1.13 - 1.00 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.3, 137.9, 137.5, 133.0, 132.8, 129.7, 129.6, 129.3, 129.0, 128.3, 128.2, 127.3, 127.1, 127.0, 126.9, 58.5, 58.5, 51.3, 51.1, 45.6, 45.1, 16.5, 7.8, 7.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{22}NOS_2$: 320.1137; found: 320.1139.



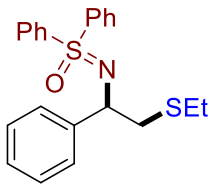
***((2-(methylthio)-1-phenylethyl)imino)di-p-tolyl-l6-sulfanone* (3ak):** TLC (PE/EtOAc, 6:1), R_f = 0.51; Colorless liquid (93.8 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.24 - 7.16 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.84 - 2.79 (m, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 143.2, 129.8, 129.8, 129.0, 128.8, 128.3, 127.2, 127.1, 59.0, 53.6, 45.8, 21.6, 21.6, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{26}NOS_2$: 396.1450; found: 396.1454.



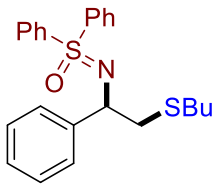
Bis(4-chlorophenyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone **(3al):** TLC (PE/EtOAc, 6:1), R_f = 0.64; Colorless liquid (100.8 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.30 - 7.15 (m, 7H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.03 - 2.98 (m, 1H), 2.82 - 2.77 (m, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 139.5, 139.4, 139.4, 138.9, 130.4, 130.3, 129.6, 129.5, 128.4, 127.4, 127.0, 59.0, 45.8, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{20}Cl_2NOS_2$: 436.0358; found: 436.0356.



Bis(4-bromophenyl)((2-(methylthio)-1-phenylethyl)imino)-l6-sulfanone **(3am):** TLC (PE/EtOAc, 300:1), R_f = 0.63; Colorless liquid (118.2 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.26 - 7.13 (m, 5H), 4.21 (t, *J* = 6.9 Hz, 1H), 3.02 - 2.97 (m, 1H), 2.81 - 2.76 (m, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 139.9, 139.4, 132.6, 132.4, 130.5, 130.4, 128.4, 128.1, 128.0, 127.3, 127.0, 58.9, 45.8, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{20}Br_2NOS_2$: 523.9348; found: 523.9351.

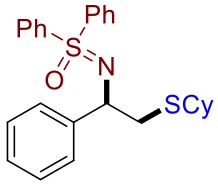


((2-(ethylthio)-1-phenylethyl)imino)diphenyl-l6-sulfanone **(3ao):** TLC (PE/EtOAc, 6:1), R_f = 0.60; Colorless liquid (59.5 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.46 - 7.38 (m, 4H), 7.33 - 7.27 (m, 4H), 7.24 - 7.12 (m, 5H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.06 - 3.01 (m, 1H), 2.90 - 2.85 (m, 1H), 2.31 (q, *J* = 7.3 Hz, 2H), 1.10 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 132.6, 132.6, 129.2, 129.1, 129.1, 128.9, 128.3, 127.2, 59.4, 43.0, 26.8, 14.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}NOS_2$: 382.1294; found: 382.1291.

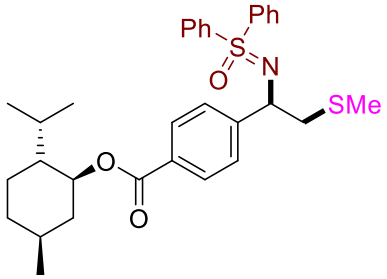


((2-(butylthio)-1-phenylethyl)imino)diphenyl-l6-sulfanone **(3ap):** TLC (PE/EtOAc, 6:1), R_f = 0.57; Colorless liquid (62.7 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* =

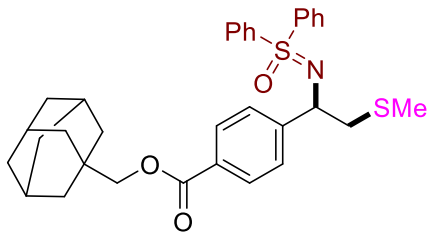
7.8 Hz, 2H), 7.52 - 7.44 (m, 4H), 7.39 - 7.34 (m, 4H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.24 - 7.19 (m, 1H), 4.27 (t, *J* = 7.0 Hz, 1H), 3.11 - 3.06 (m, 1H), 2.94 - 2.89 (m, 1H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.50 - 1.43 (m, 2H), 1.34 - 1.27 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 141.0, 140.7, 132.6, 132.5, 129.2, 129.1, 129.1, 128.9, 128.3, 127.2, 127.1, 59.5, 43.4, 32.7, 31.9, 22.1, 13.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{28}NOS_2$: 410.1607; found: 410.1609.



***((2-(cyclohexylthio)-1-phenylethyl)imino)diphenyl-l6-sulfanone* (3aq):** TLC (PE/EtOAc, 6:1), R_f = 0.60; Colorless liquid (62.7 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.46 - 7.38 (m, 4H), 7.33 - 7.27 (m, 4H), 7.23 - 7.19 (m, 2H), 7.18 - 7.11 (m, 1H), 4.20 (t, *J* = 7.0 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.92 - 2.87 (m, 1H), 2.36- 2.31 (m, 1H), 1.84 - 1.78 (m, 2H), 1.63 (s, 2H), 1.21 - 1.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 141.0, 140.7, 132.5, 132.5, 129.2, 129.1, 129.1, 128.9, 128.2, 127.2, 127.1, 59.9, 44.1, 41.3, 33.9, 33.8, 29.8, 26.4, 26.3, 26.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{30}NOS_2$: 436.1763; found: 436.1767.

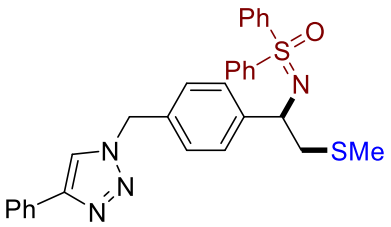


***2-isopropyl-5-methylcyclohexyl 4-(-2-(methylthio)-1-((oxodiphenyl-l6-sulfaneylidene)amino) ethyl) benzoate* (3ya):** TLC (PE/EtOAc, 6:1), R_f = 0.57; Colorless liquid (107.2 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.81 - 7.77 (m, 2H), 7.47 - 7.29 (m, 8H), 4.88 - 4.82 (m, 1H), 4.28 (t, *J* = 6.8 Hz, 1H), 3.04 - 2.99 (m, 1H), 2.86 - 2.75 (m, 1H), 2.06 - 2.03 (m, 1H), 1.92 - 1.84 (m, 4H), 1.69 - 1.59 (m, 3H), 1.47 - 1.44 (m, 2H), 1.11 - 0.96 (m, 2H), 0.86 (s, 3H), 0.84 (s, 3H), 0.73 - 0.71 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 149.9, 140.8, 140.7, 132.7, 129.7, 129.3, 129.2, 128.9, 128.8, 128.8, 127.1, 74.7, 58.7, 47.4, 45.6, 45.5, 41.1, 34.5, 31.6, 26.6, 26.5, 23.7, 23.6, 22.2, 21.0, 20.9, 16.6, 16.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{32}H_{40}NO_3S_2$: 550.2444; found: 550.2449.



***Adamantan-1-ylmethyl-4-(2-(methylthio)-1-((oxodiphenyl-l6-sulfaneylidene)amino)ethyl)benzoate*(3 za):** TLC (PE/EtOAc, 6:1), R_f = 0.47; Colorless liquid (104.1 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.91 (m, 4H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.49 - 7.36 (m, 6H), 7.34 - 7.30 (m, 2H), 4.28 (t, *J* = 6.8 Hz, 1H), 3.90 - 3.77 (m, 2H), 3.04 - 2.99 (m, 1H), 2.85 - 2.80 (m, 1H), 1.99 - 1.92 (m, 3H), 1.89 (s, 3H), 1.72 - 1.63 (m, 5H), 1.61 - 1.58 (m, 4H), 1.55 - 1.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8,

150.0, 140.8, 140.5, 132.7, 129.7, 129.5, 129.3, 129.2, 128.9, 128.8, 127.2, 74.5, 58.7, 45.6, 39.6, 37.2, 33.7, 28.2, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{38}NO_3S_2$: 560.2288; found: 560.2291.



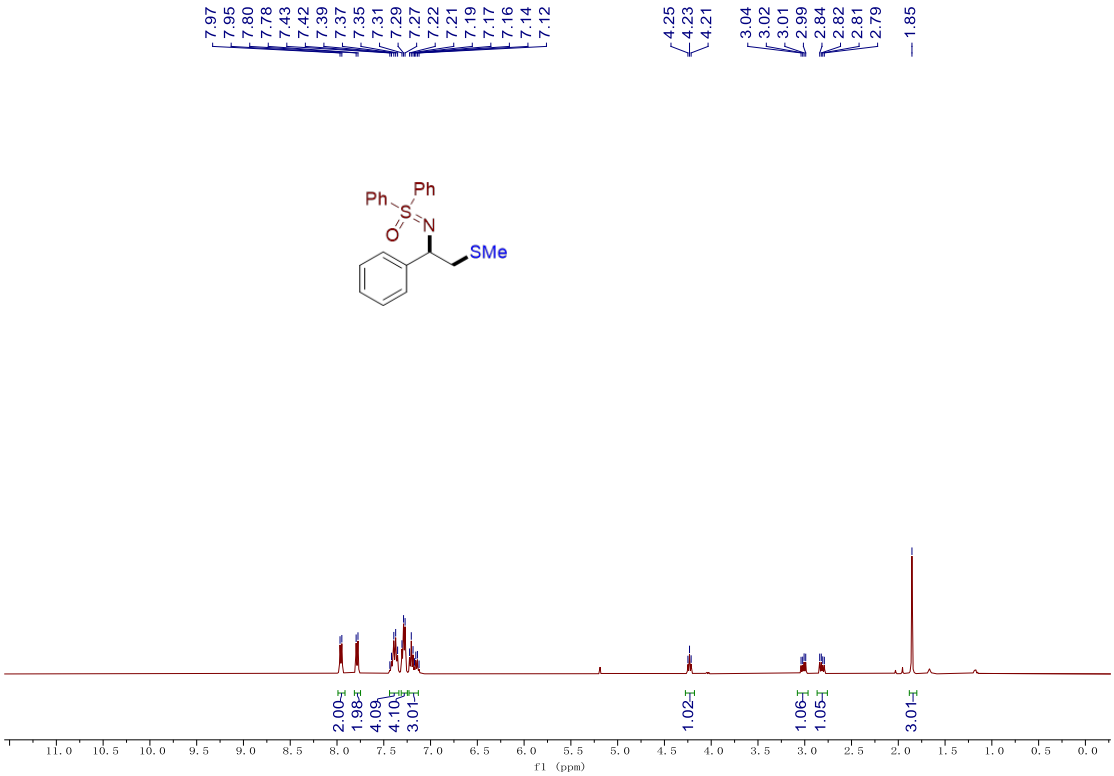
***((2-(methylthio)-1-(4-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)phenyl)ethyl)imino)diphenyl-l6-sulfanone (5a)*:** TLC (PE/EtOAc, 6:1), R_f = 0.26; Colorless liquid (204.6 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.70 (s, 1H), 7.54 - 7.31 (m, 11H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.55 (s, 2H), 4.32 (t, *J* = 6.8 Hz, 1H), 3.10 - 3.05 (m, 1H), 2.85 - 2.89 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 145.7, 140.9, 140.5, 133.4, 132.7, 132.6, 130.7, 129.3, 129.2, 129.0, 128.9, 128.8, 128.3, 128.0, 128.0, 125.8, 119.7, 58.4, 54.2, 45.7, 16.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{29}N_4OS_2$: 525.1777; found: 525.1773.

4. References

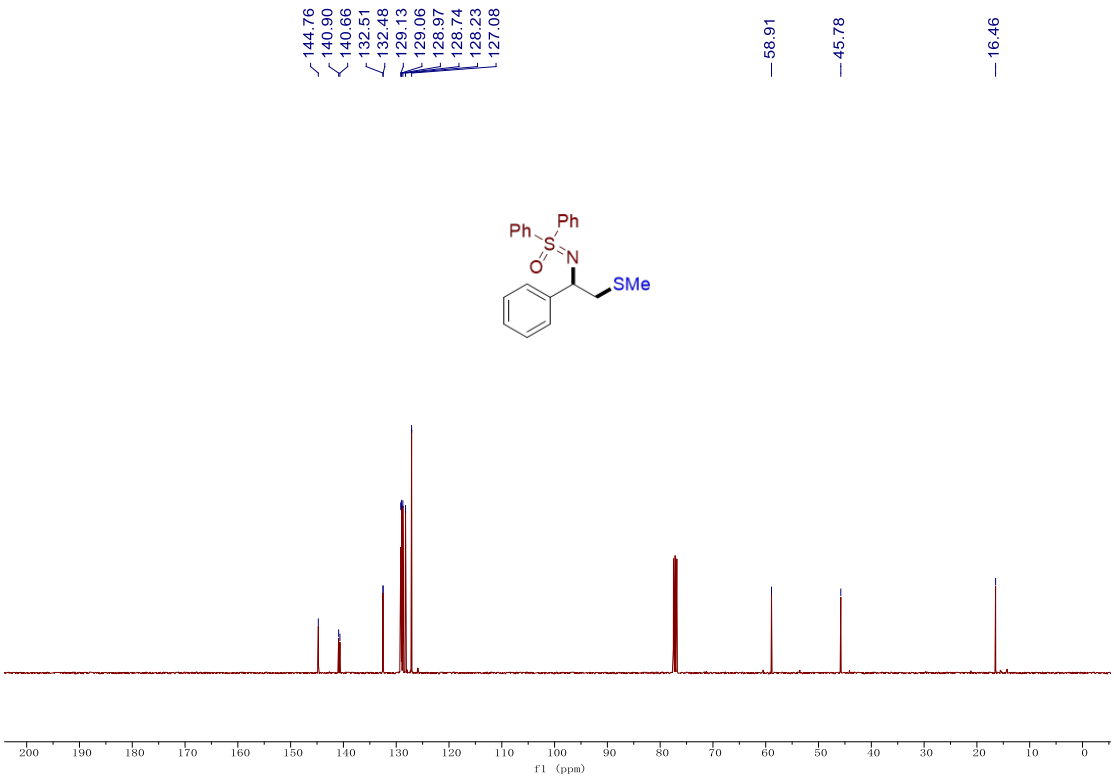
[1] M. Tang, Y.-X. Wang, S. Huang, L.-G. Xie, *Org. Chem. Front.* **2023**, *10*, 2416-2421.

[2] A. Tota, M. Zenzola, S. J. Chawner, S. S. John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull, R. Luisi, *Chem. Commun.* **2017**, *53*, 348-351.

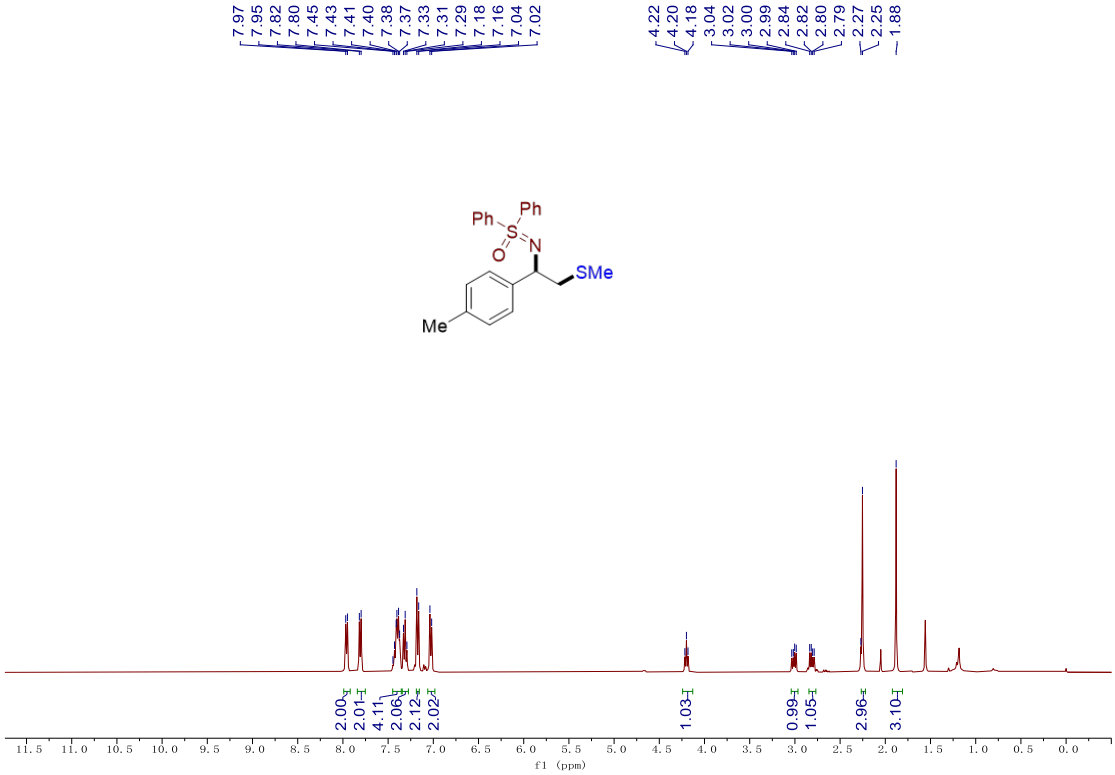
5. NMR Spectra of Products



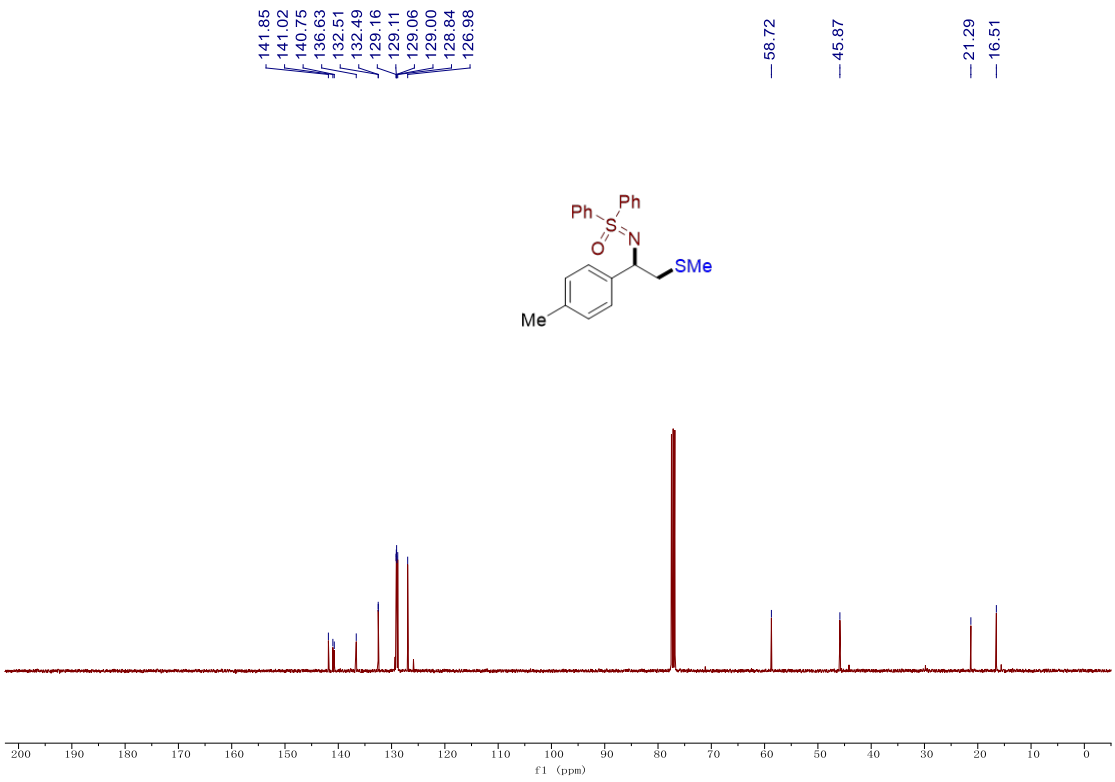
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**



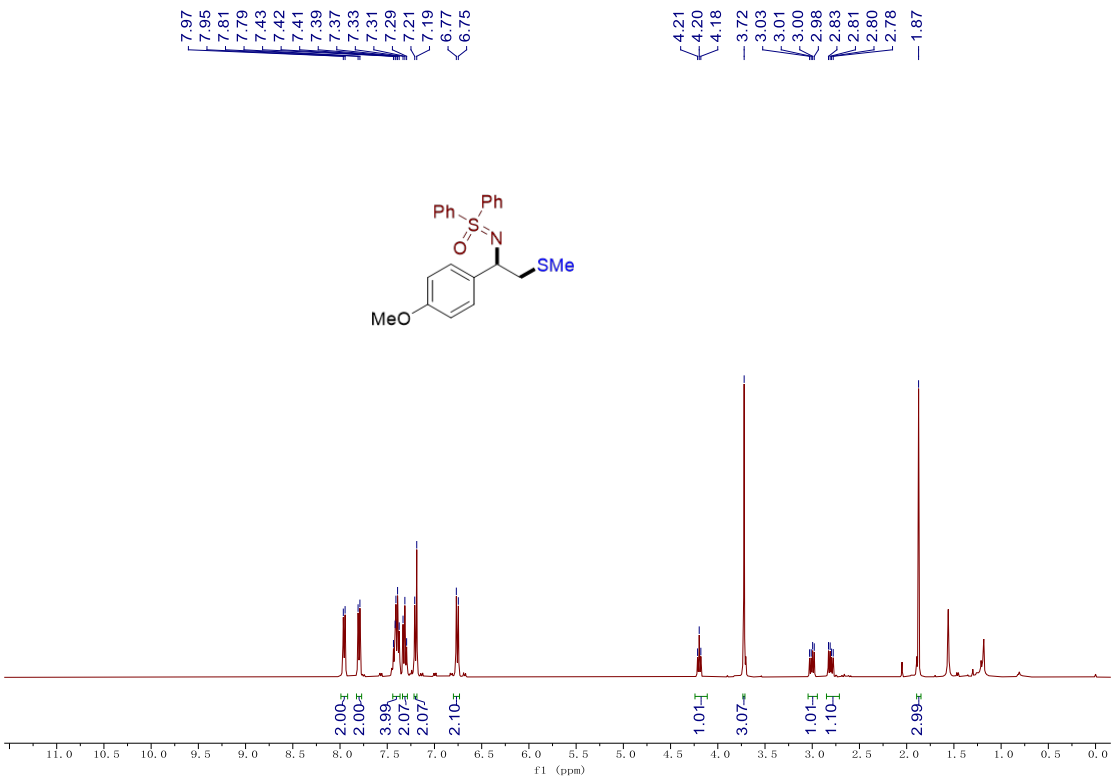
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aa**



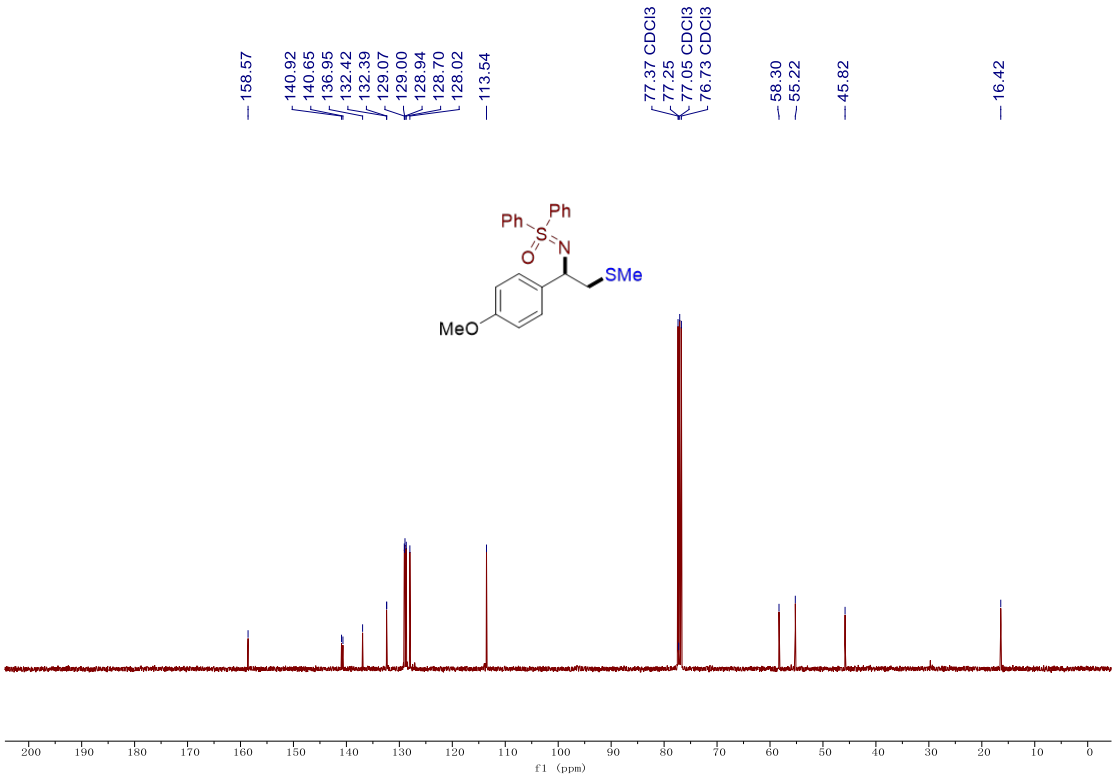
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba**



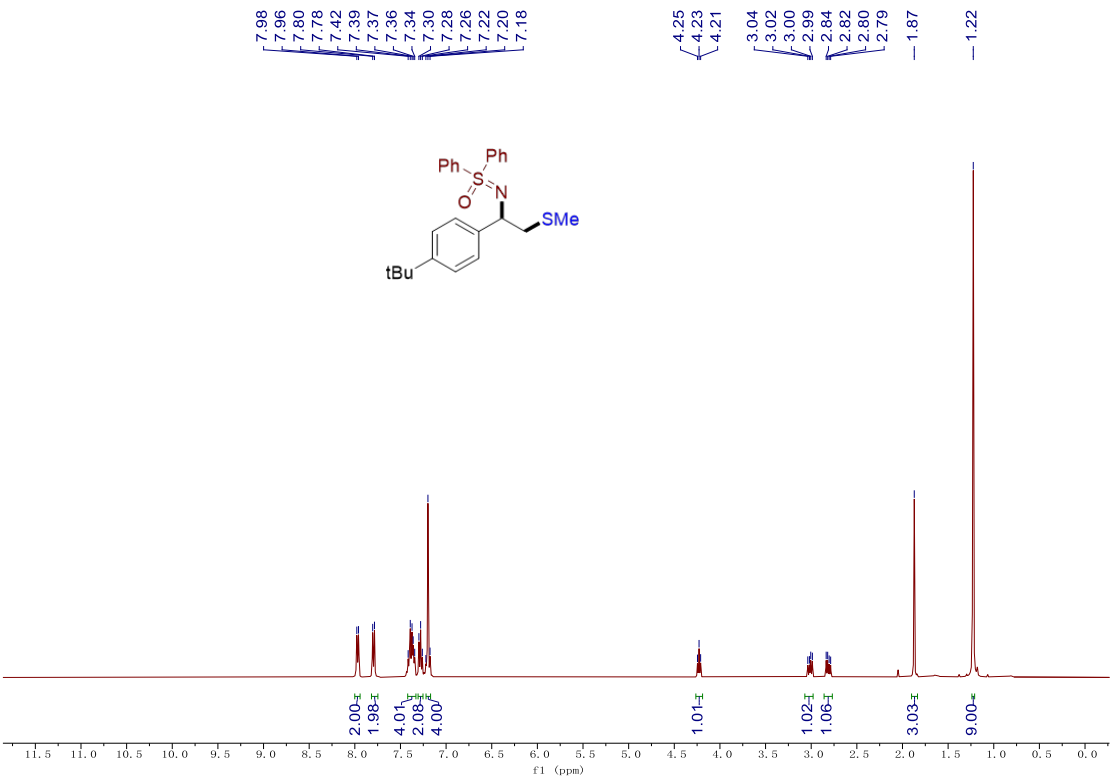
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ba**



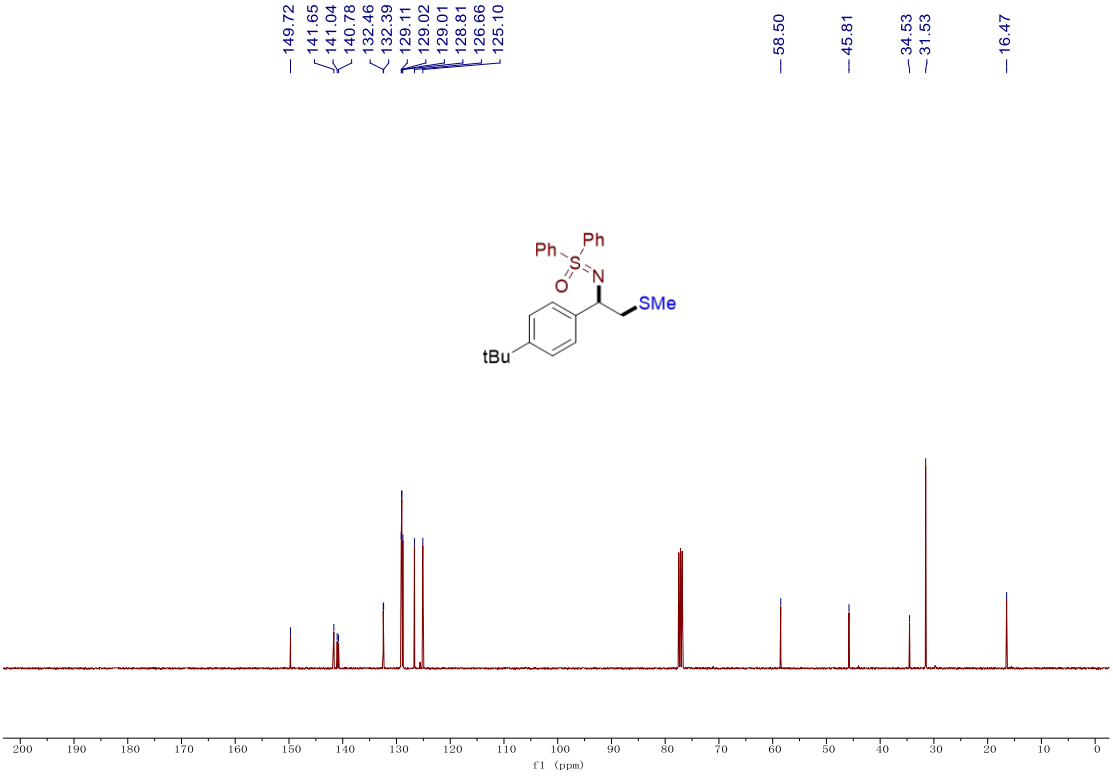
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ca**



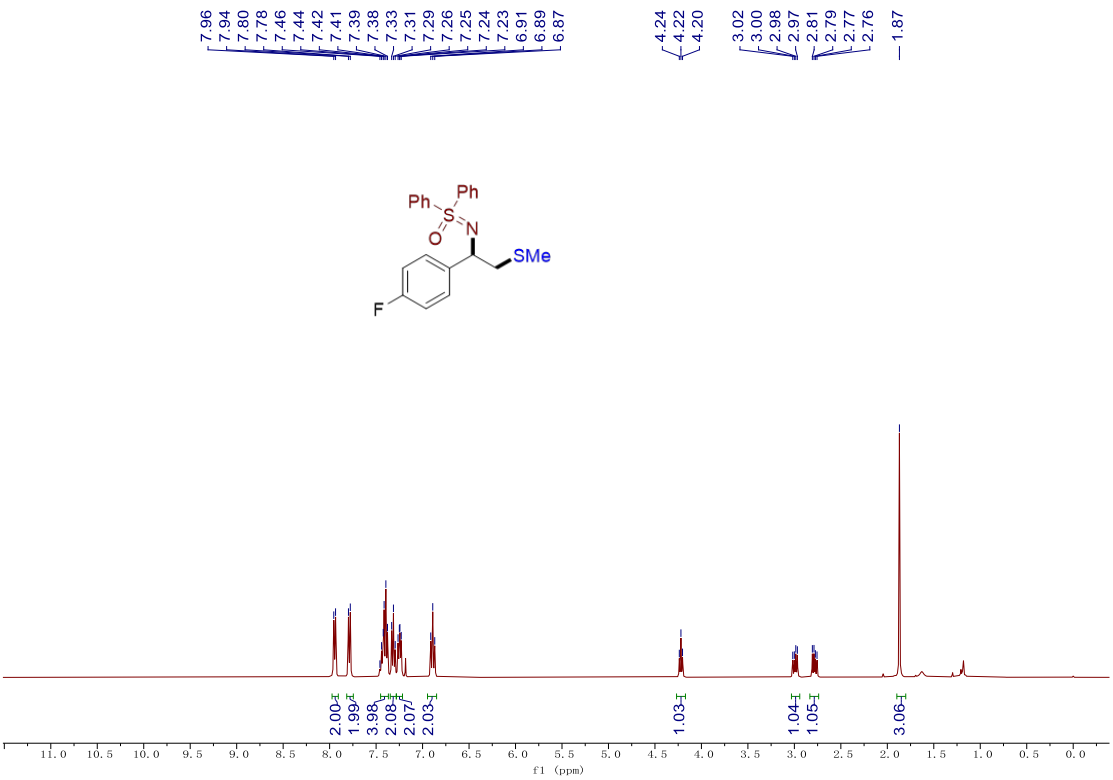
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ca**



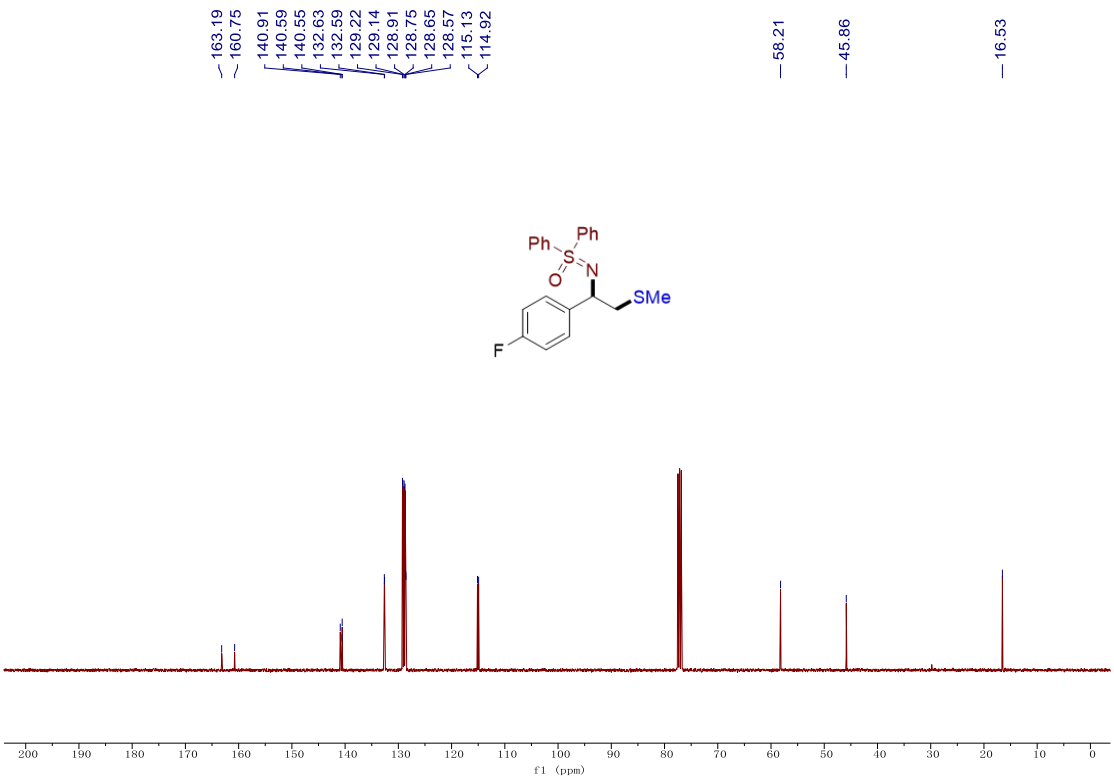
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3da**



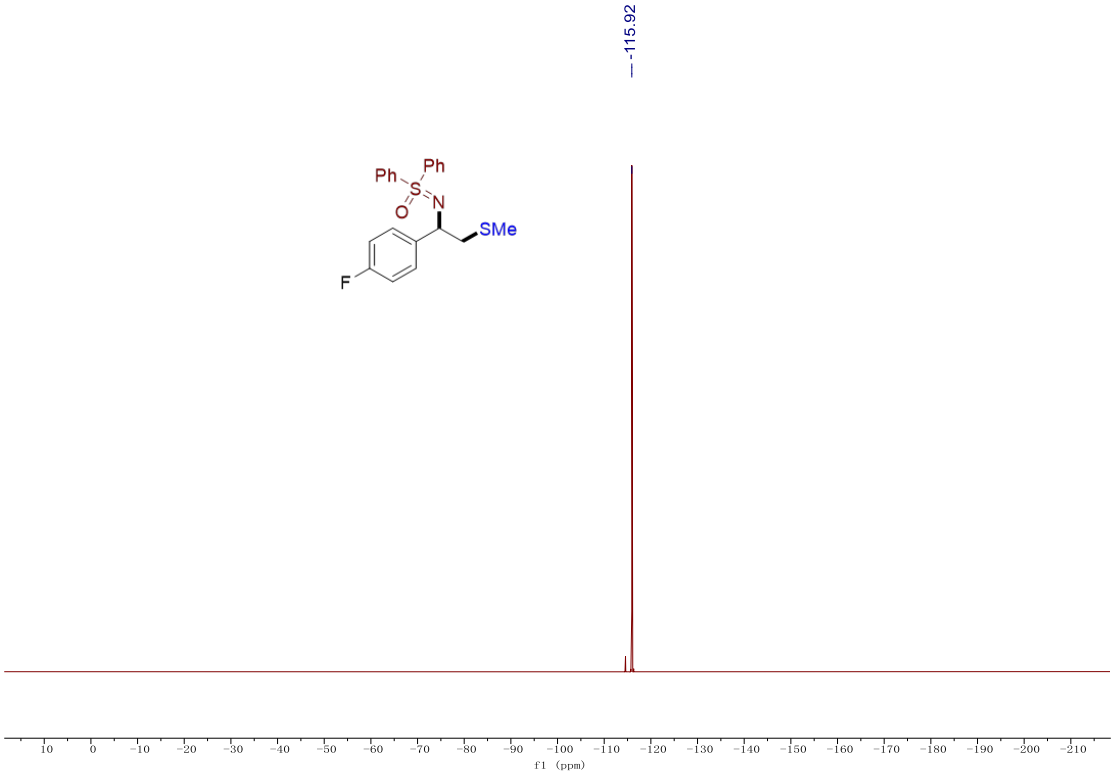
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3da**



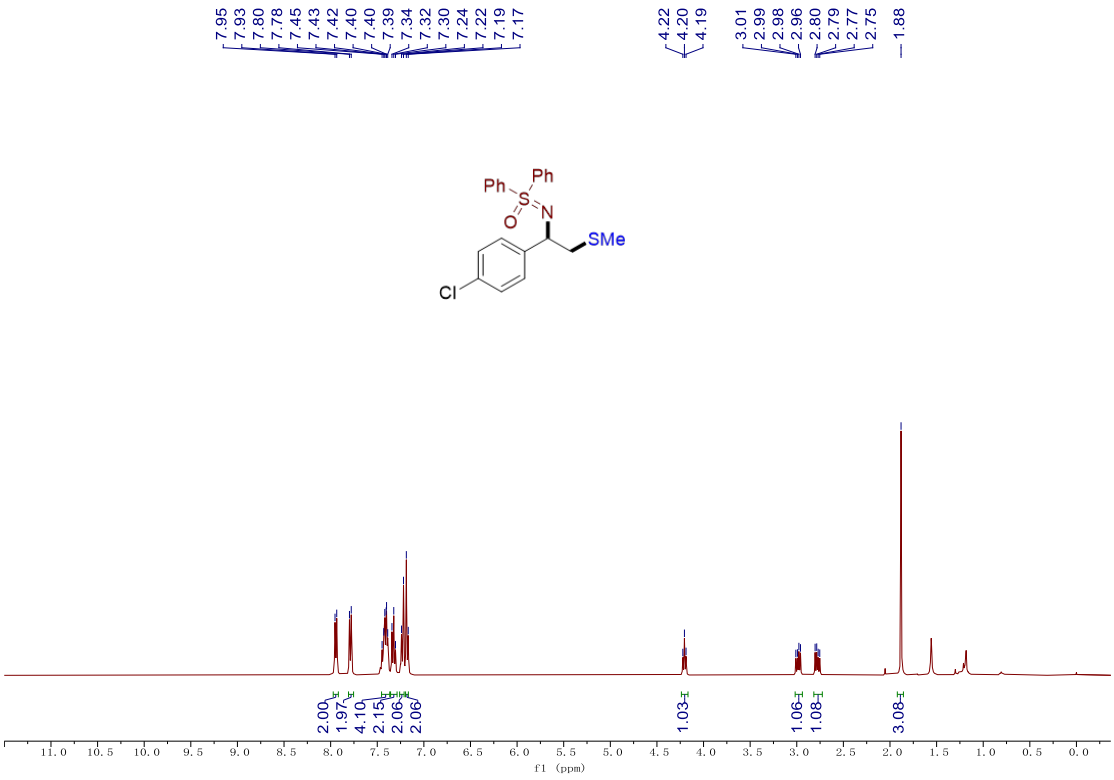
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ea**



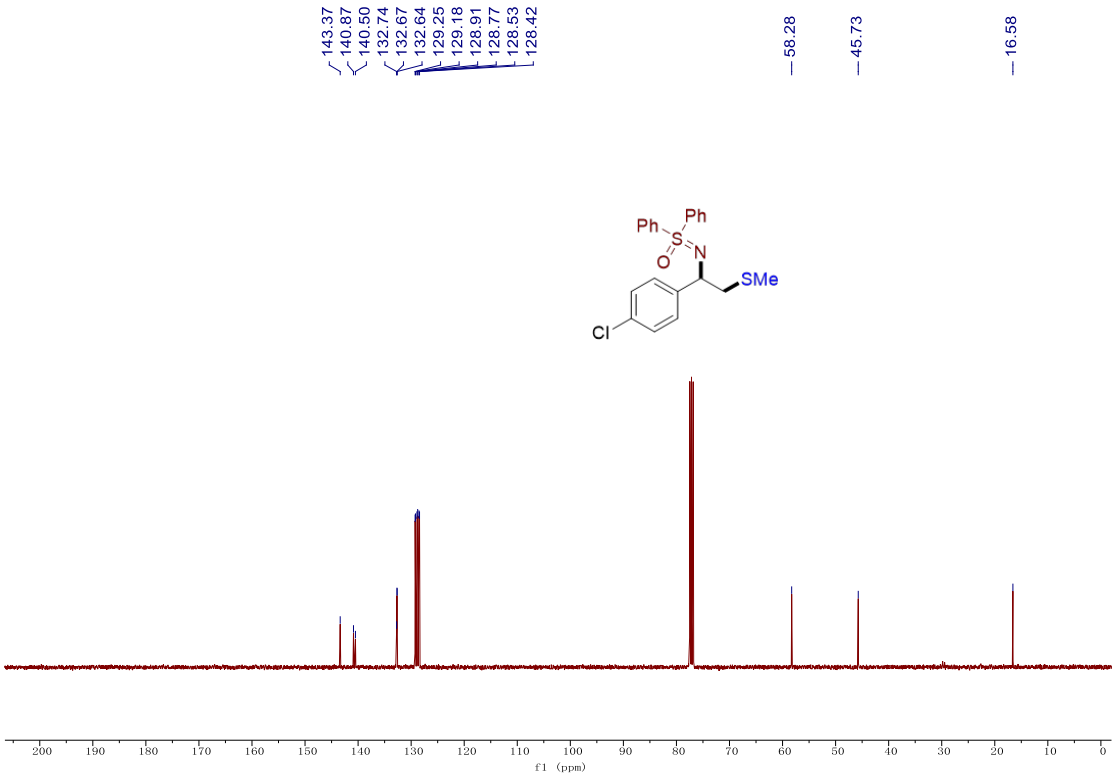
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ea**



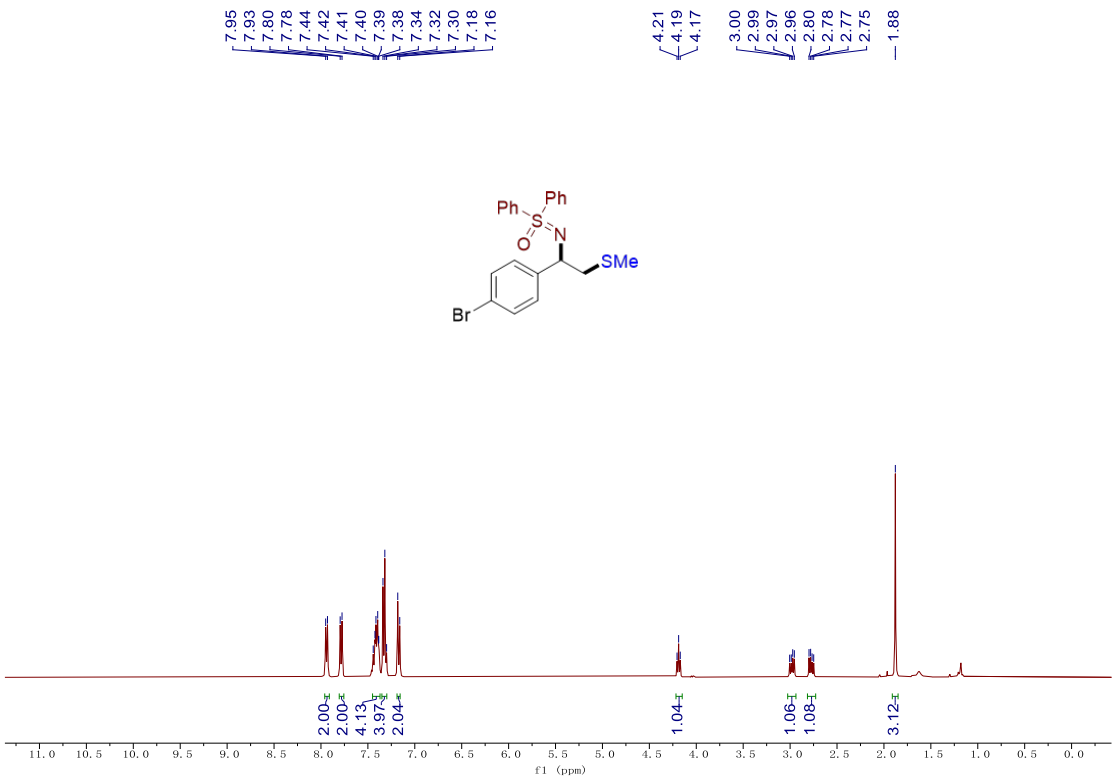
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ea**



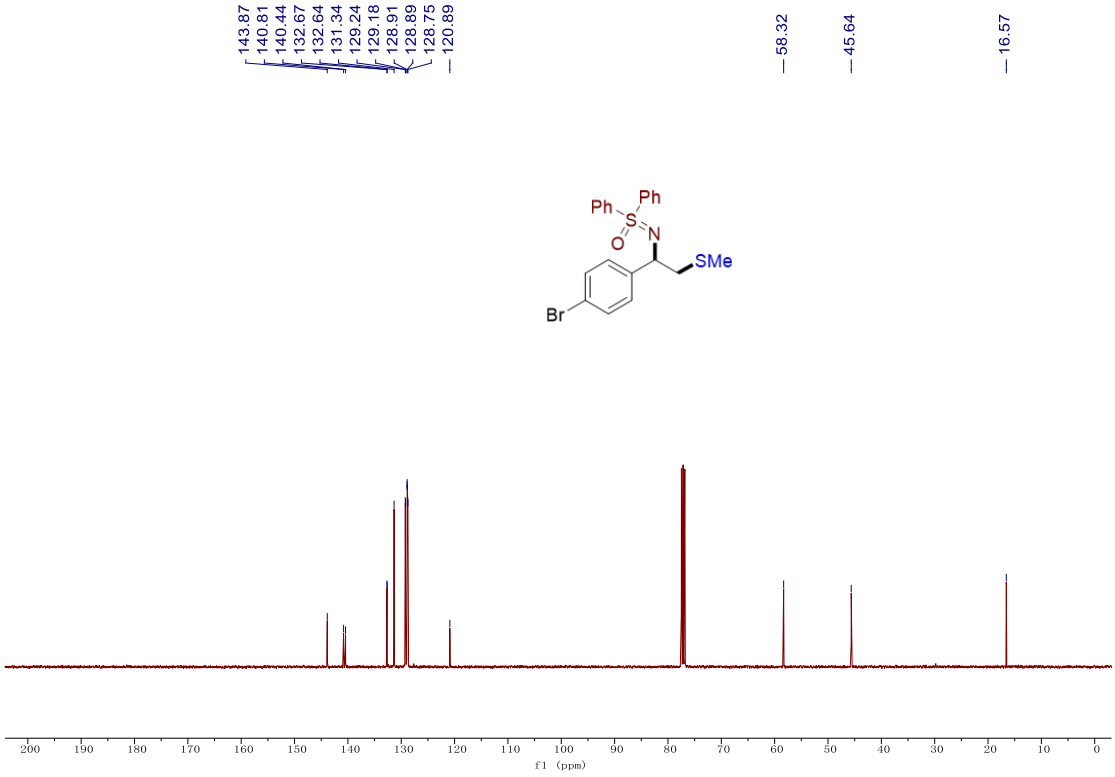
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3fa**



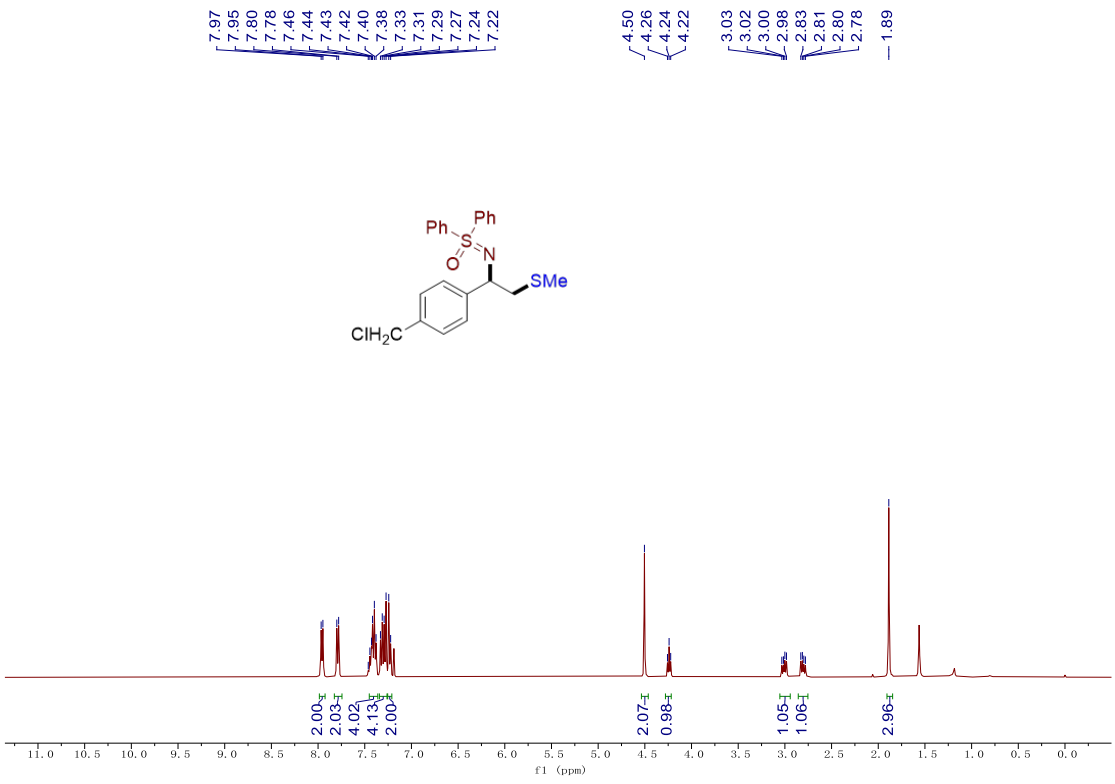
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3fa**



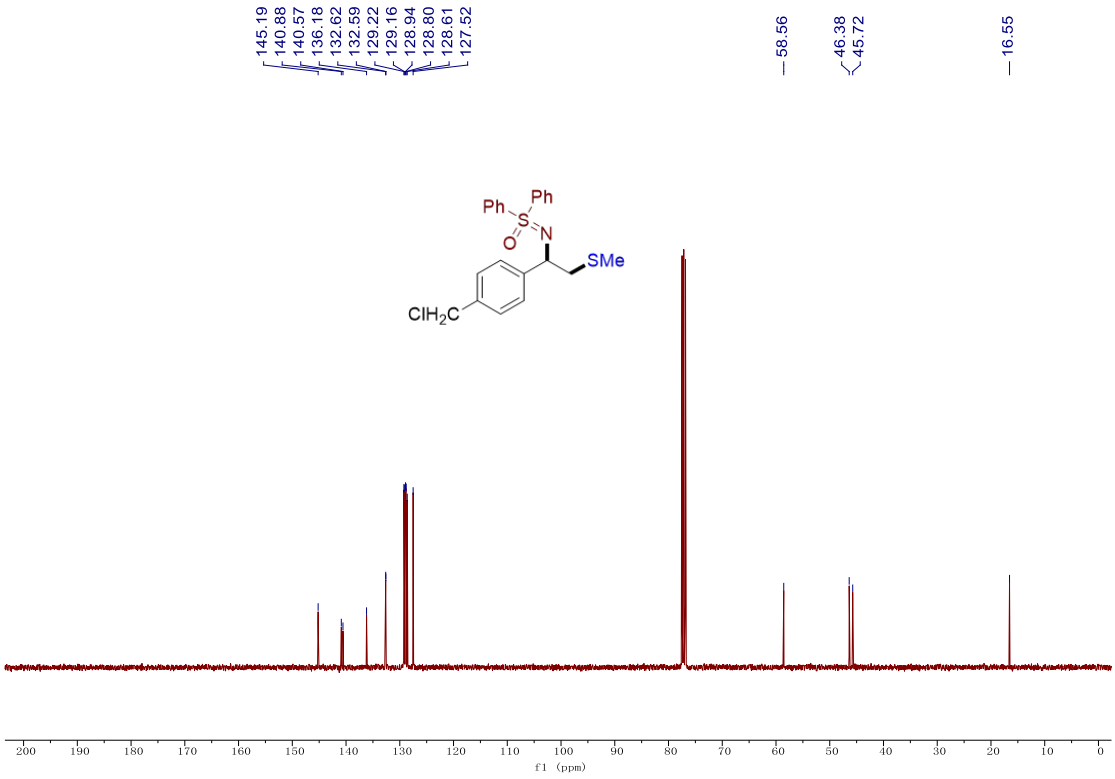
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ga**



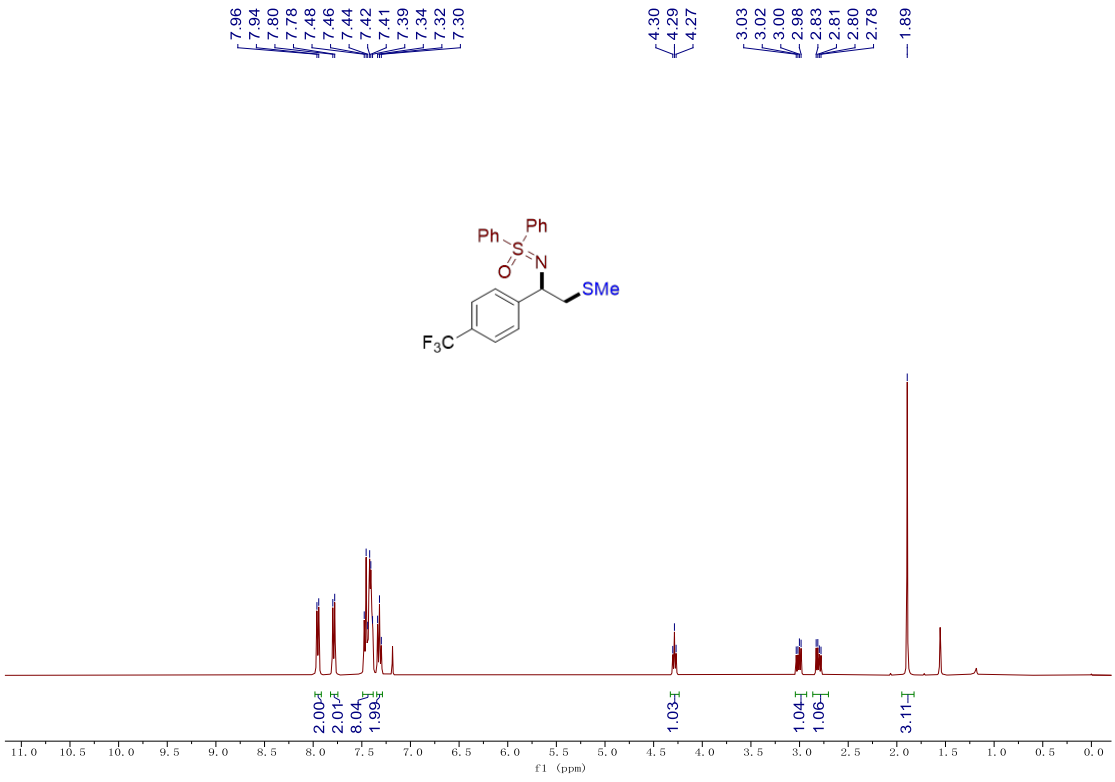
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ga**



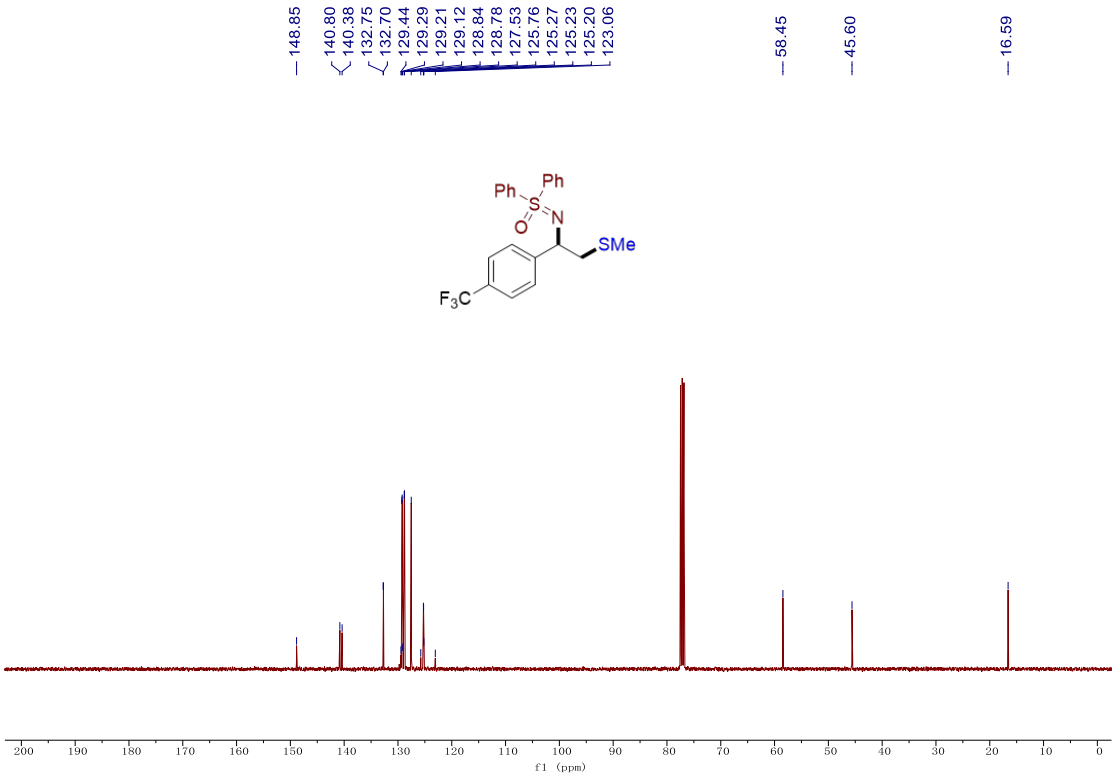
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ha**



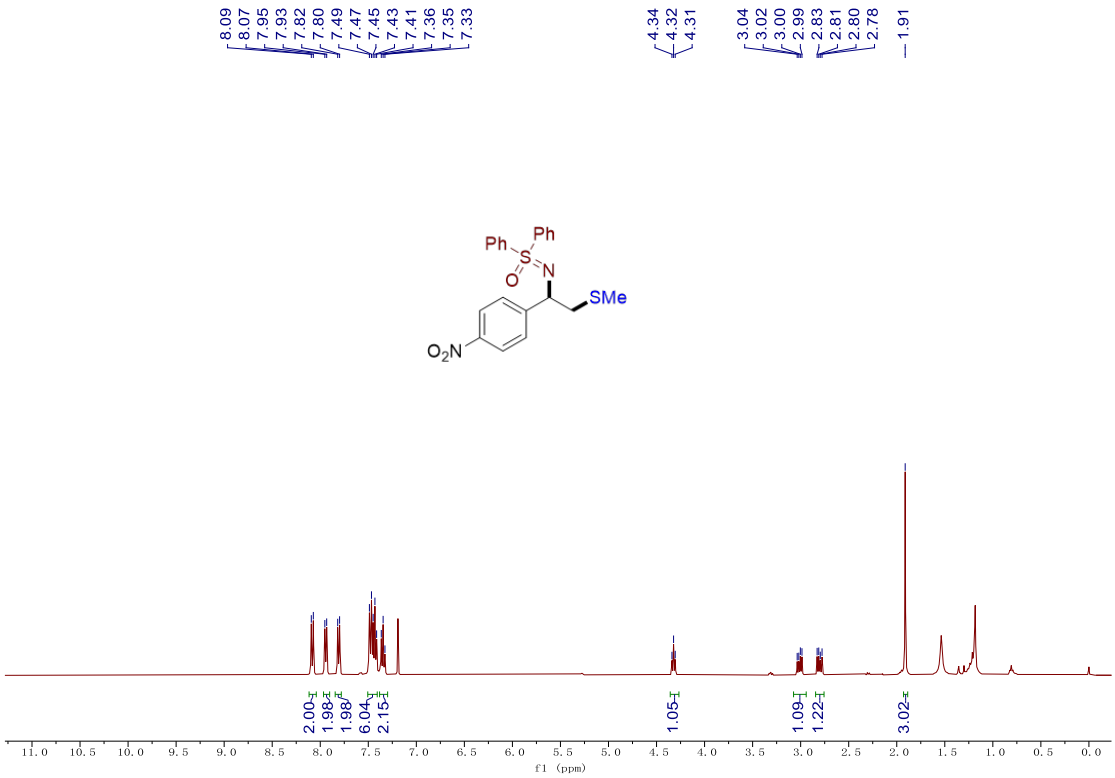
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ha**



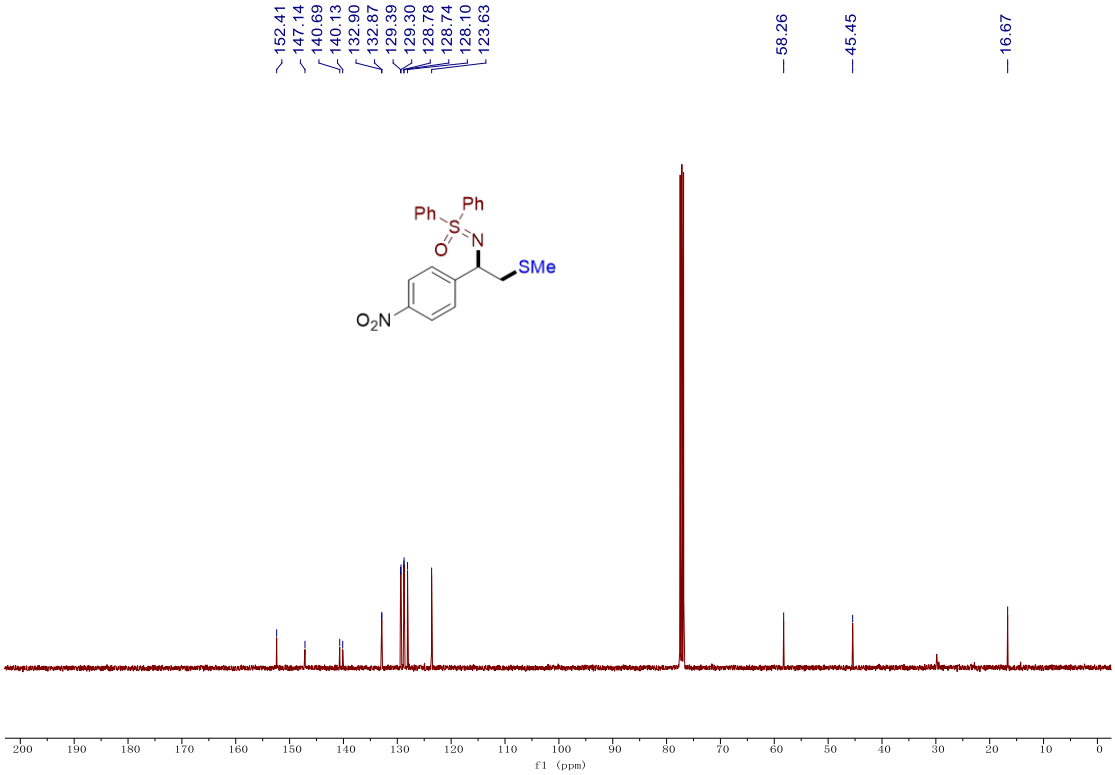
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ia**



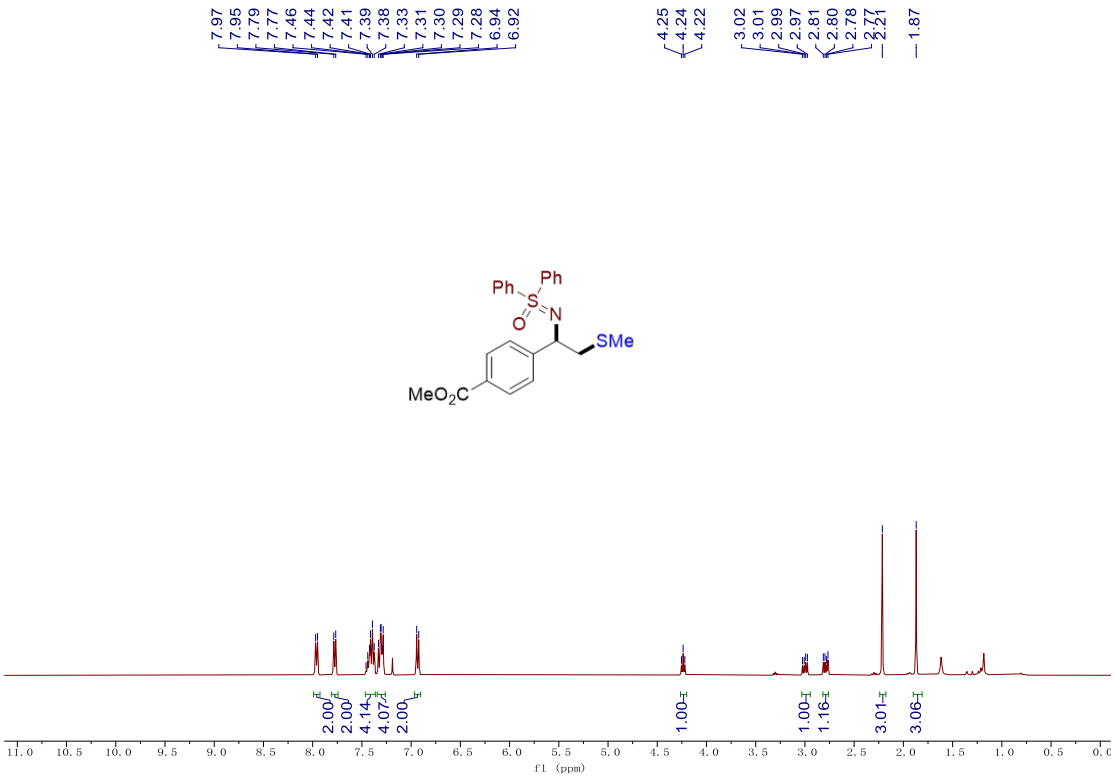
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ia**



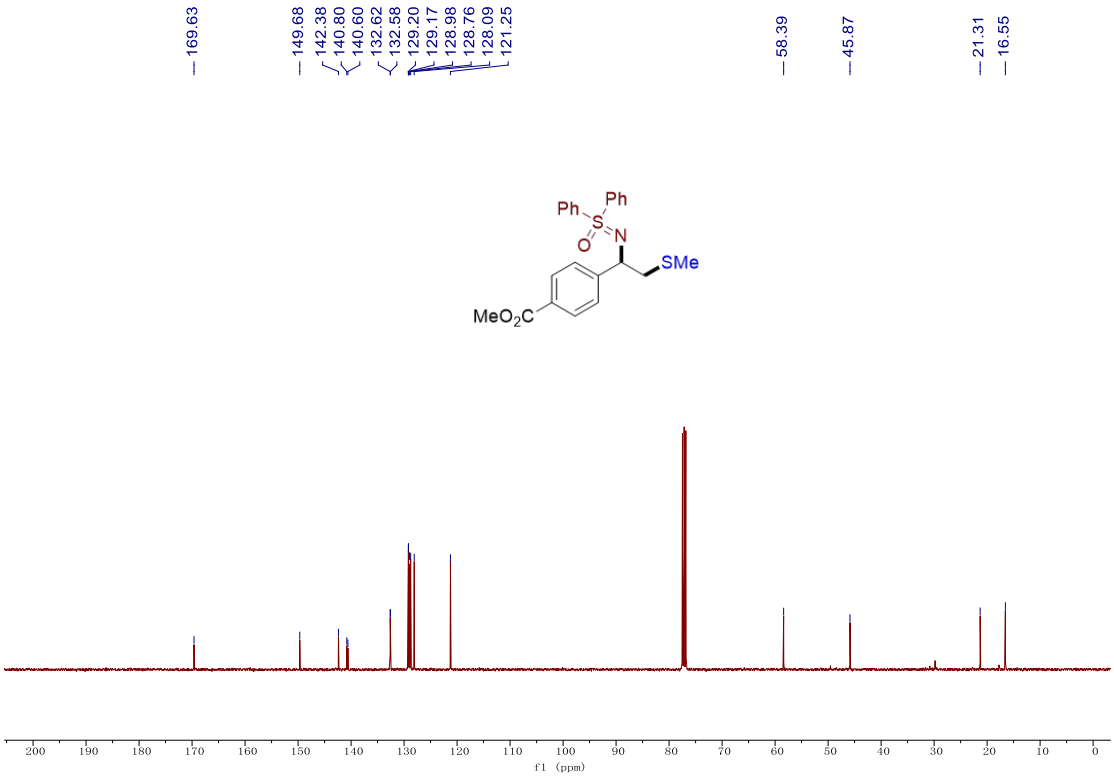
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ja**



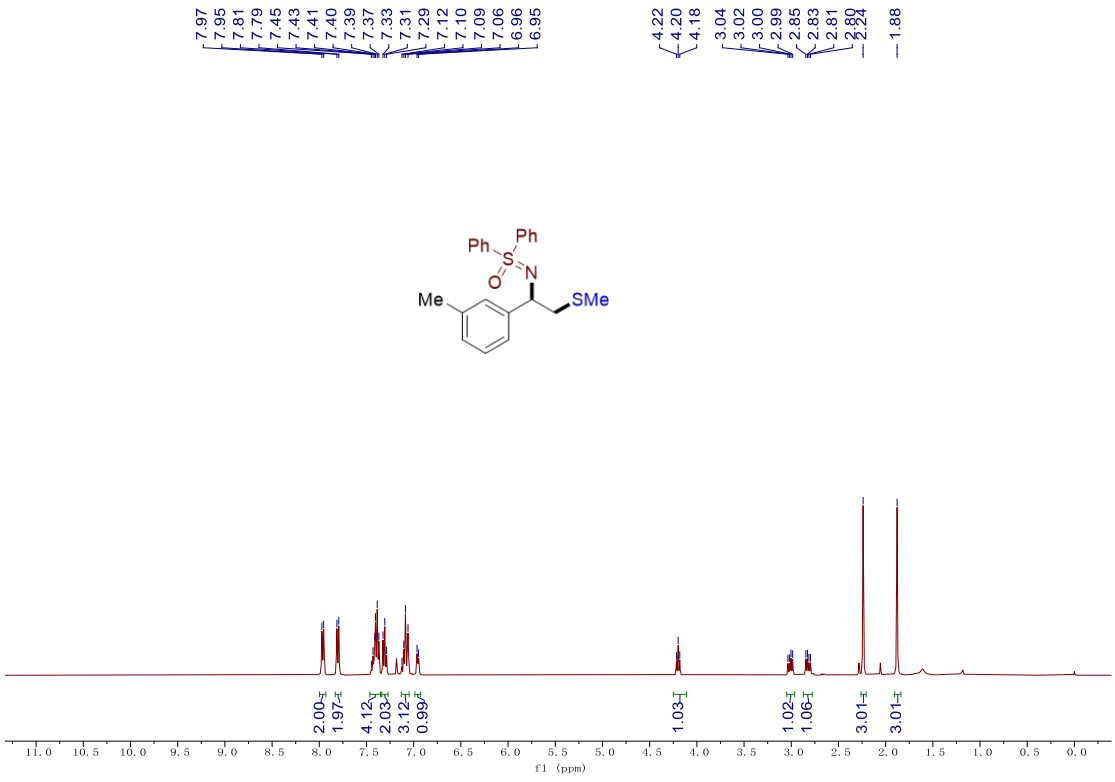
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ja**



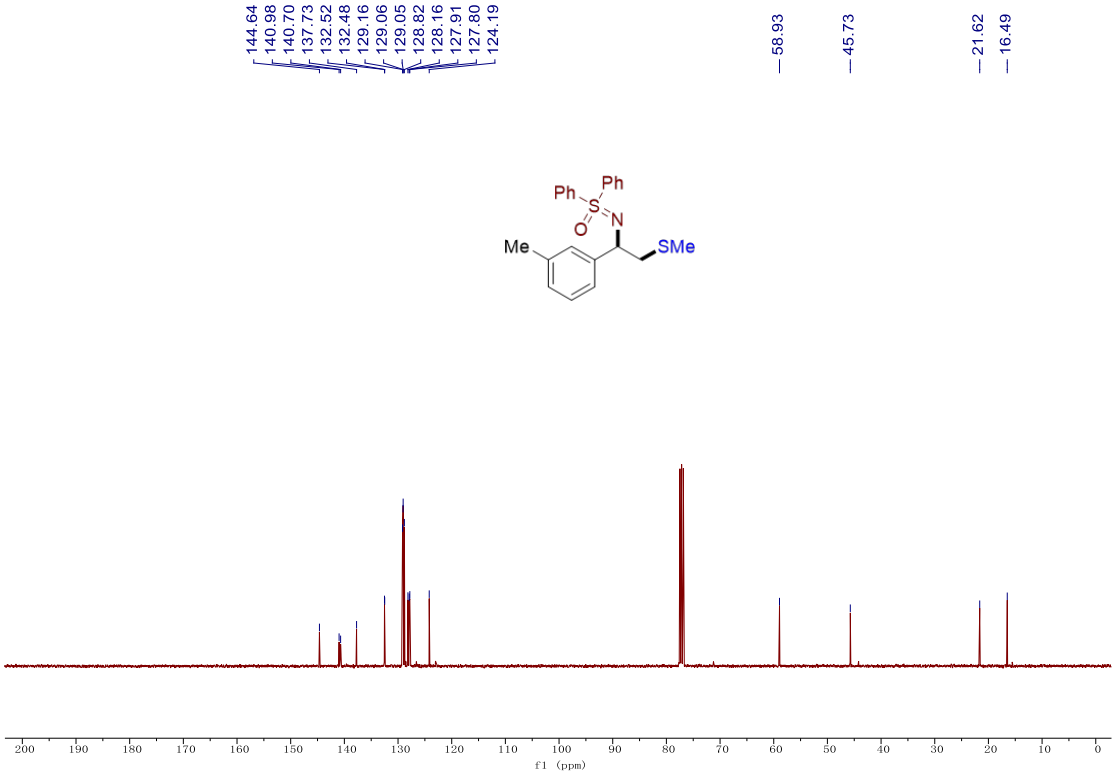
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ka**



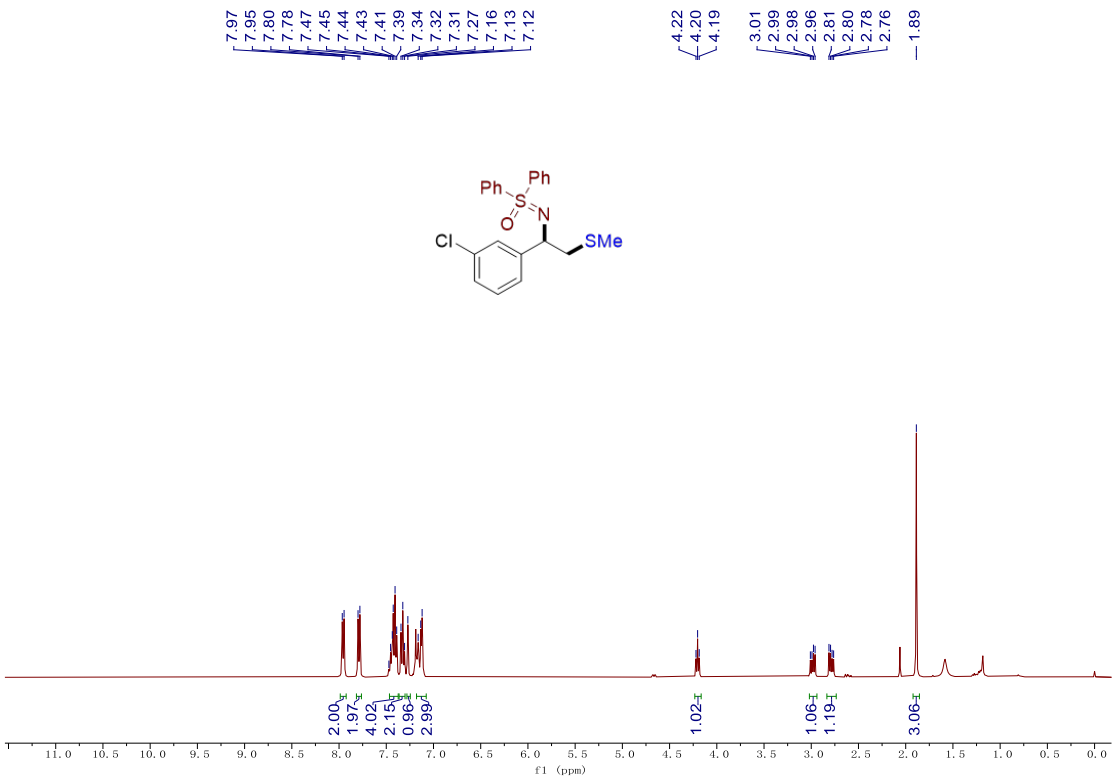
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ka**



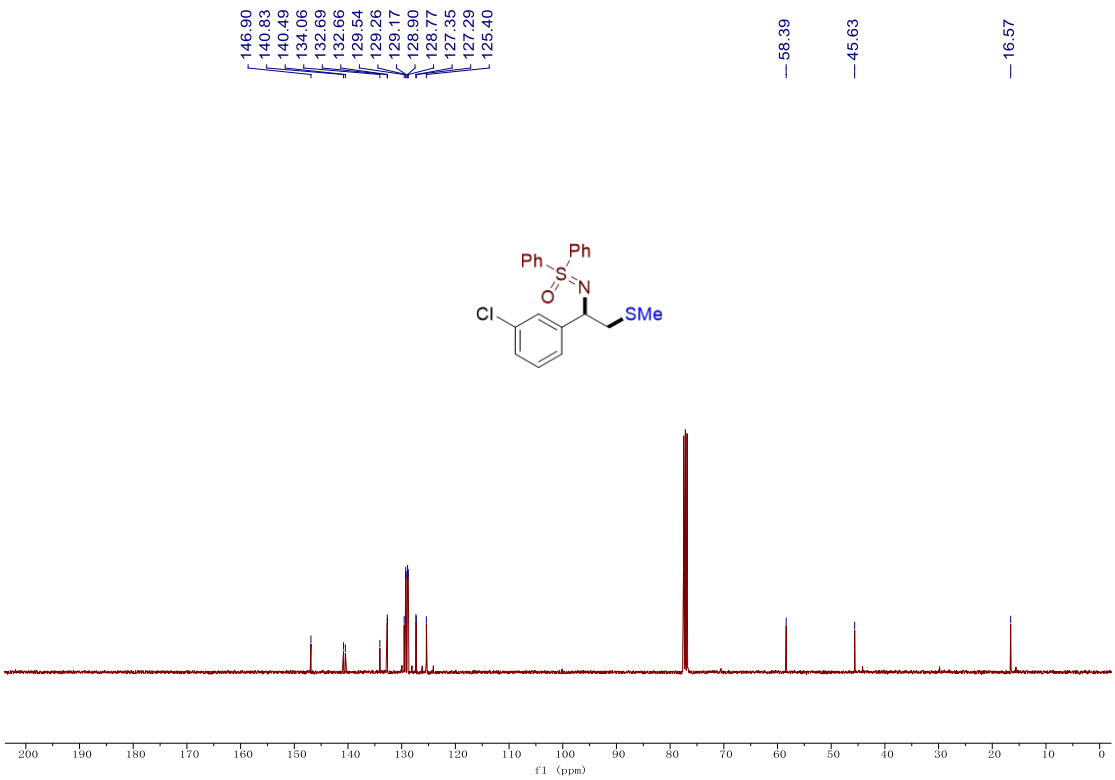
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3la**



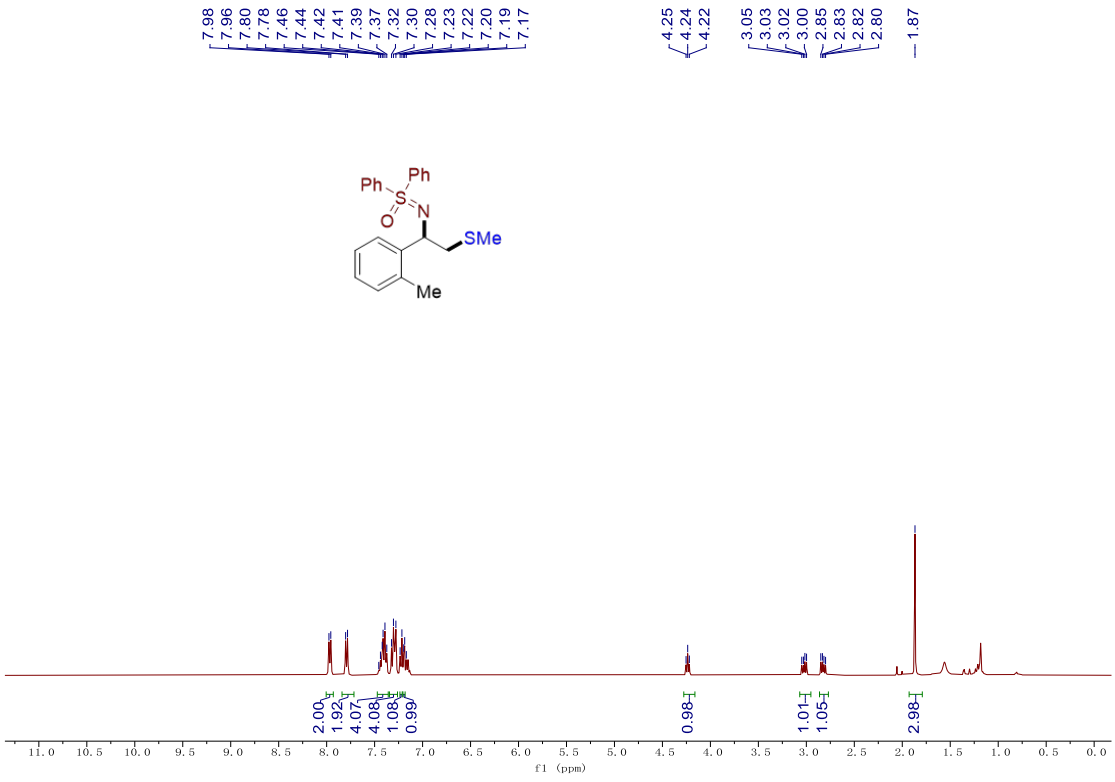
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3la**



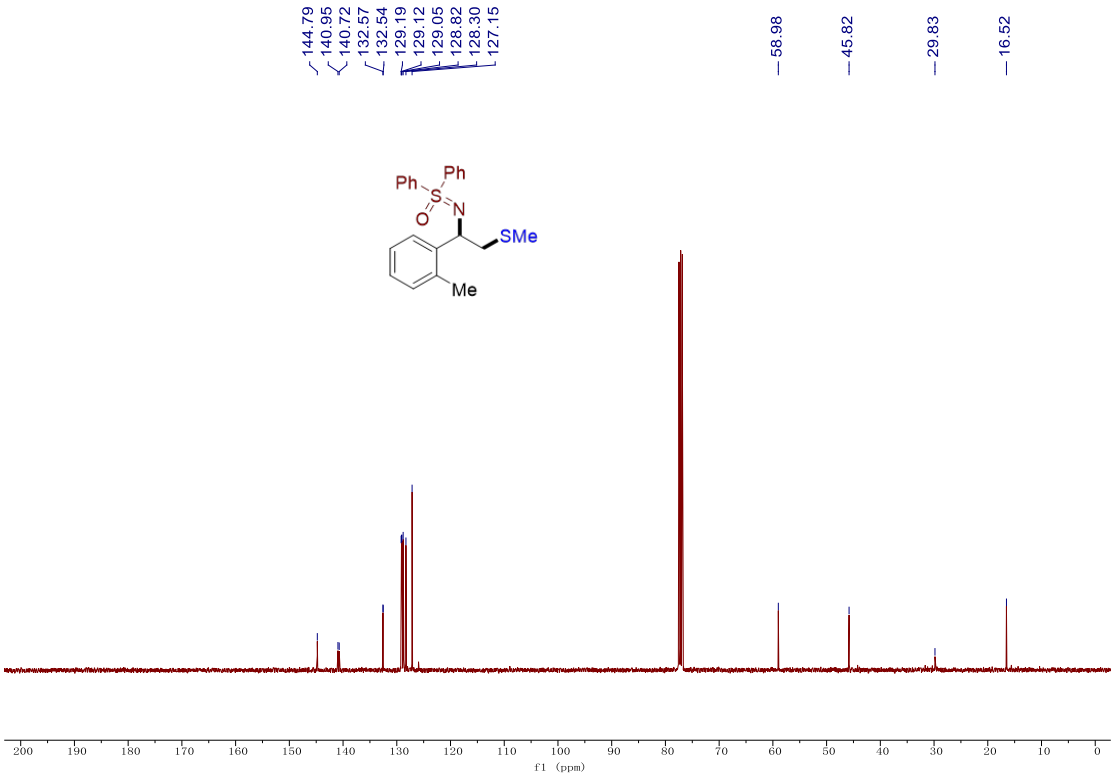
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ma**



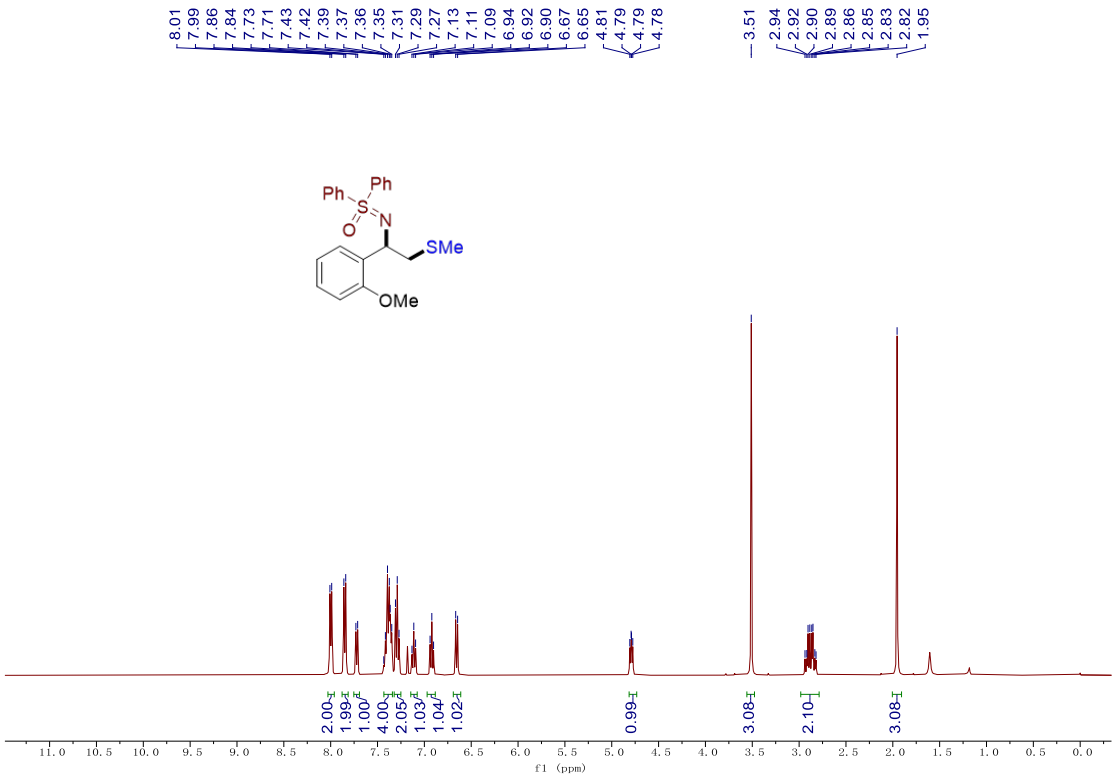
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ma**



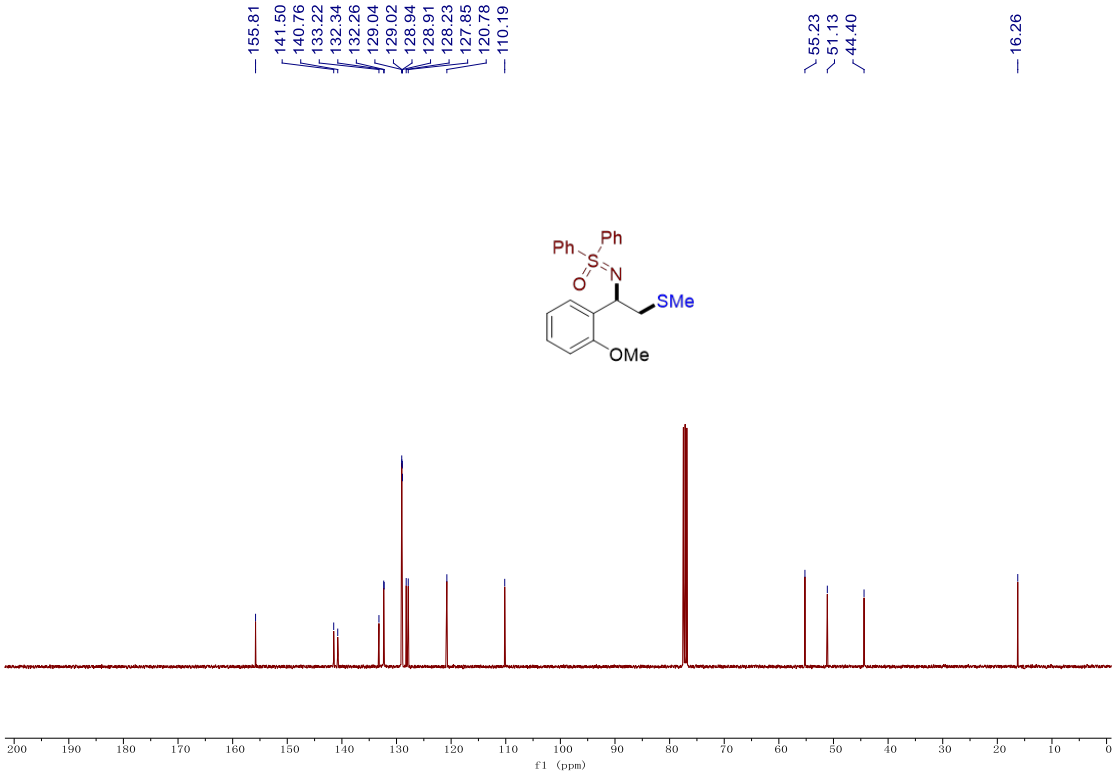
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3na**



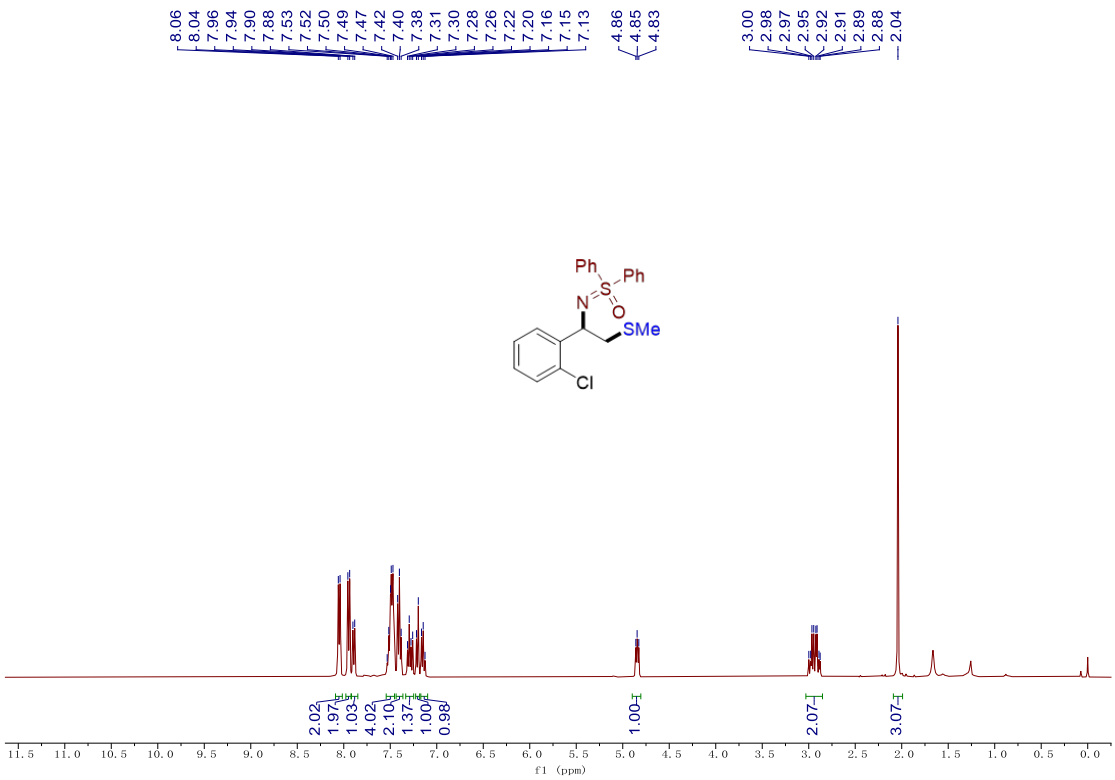
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3na**



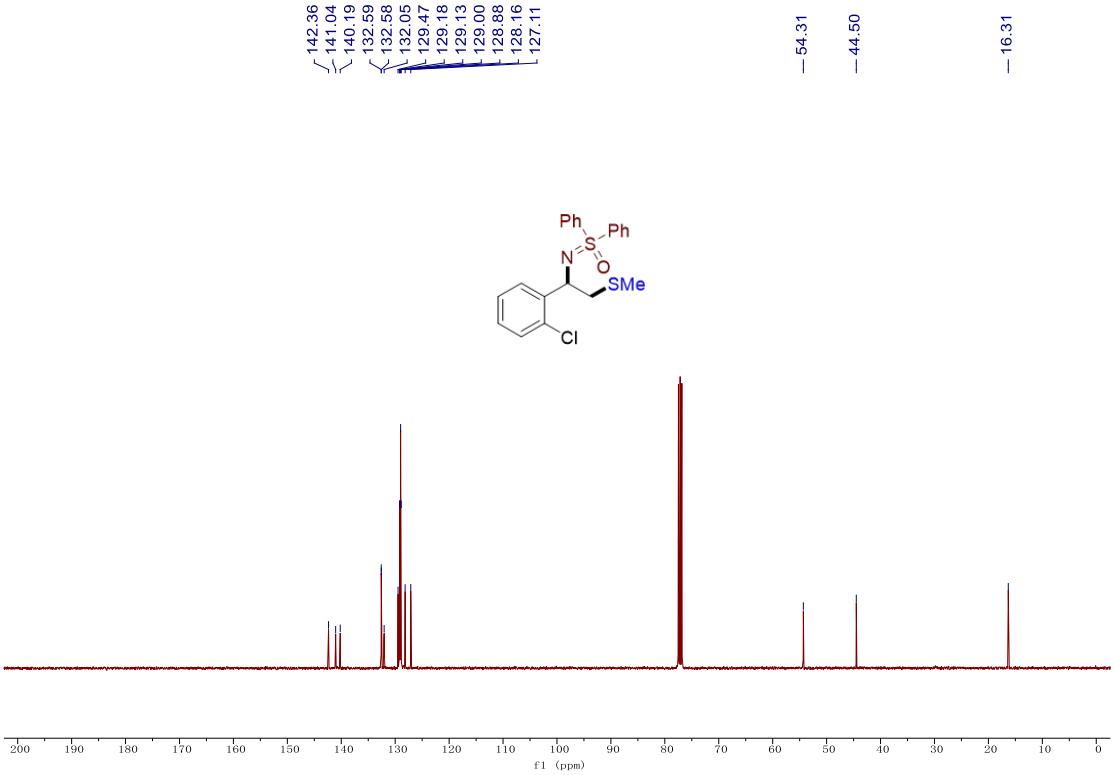
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3oa**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3oa**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3pa**



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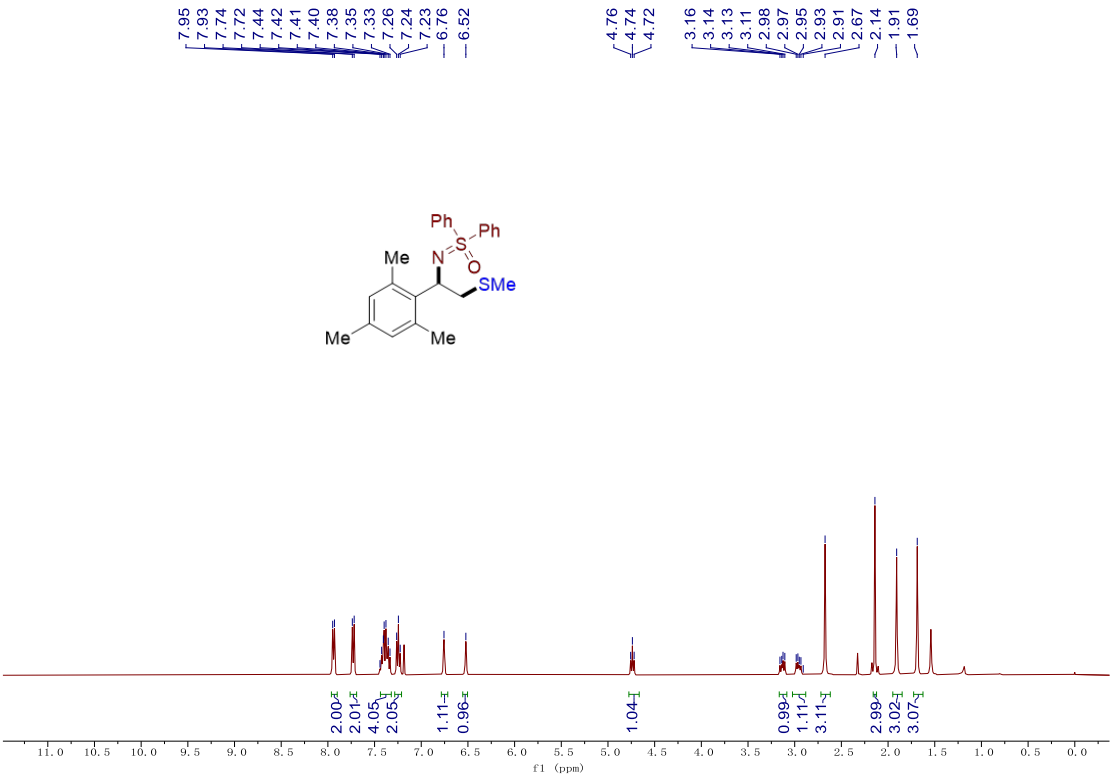
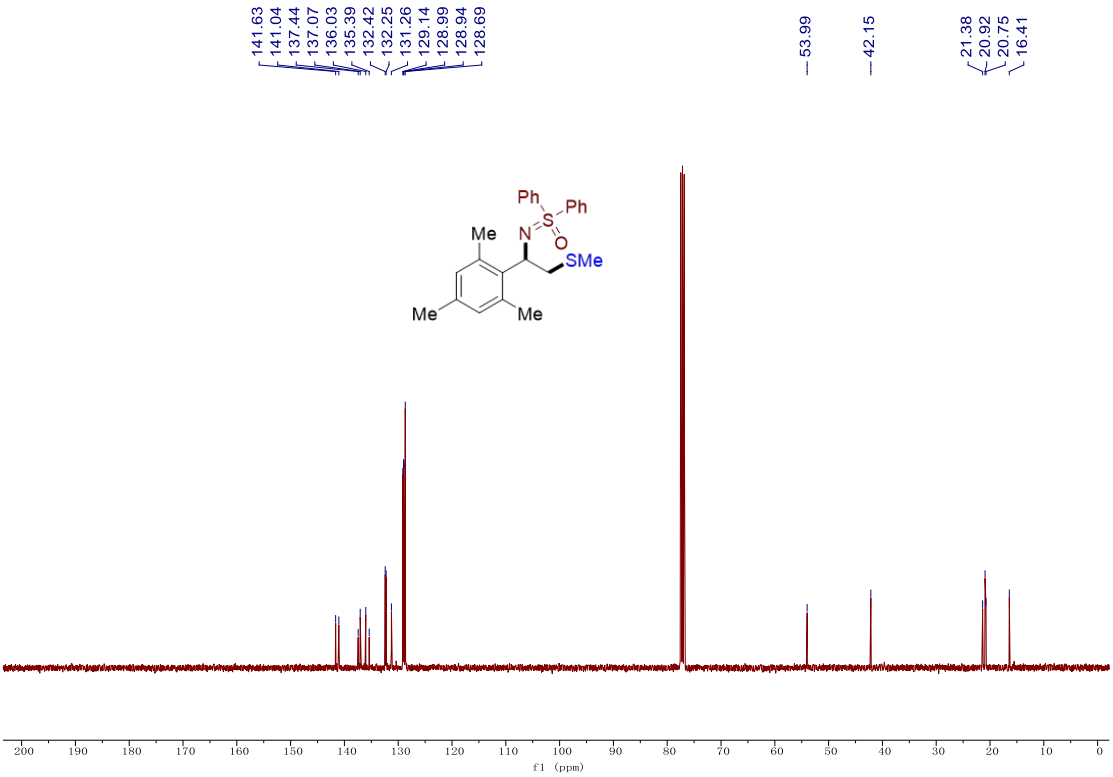


^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3qa**



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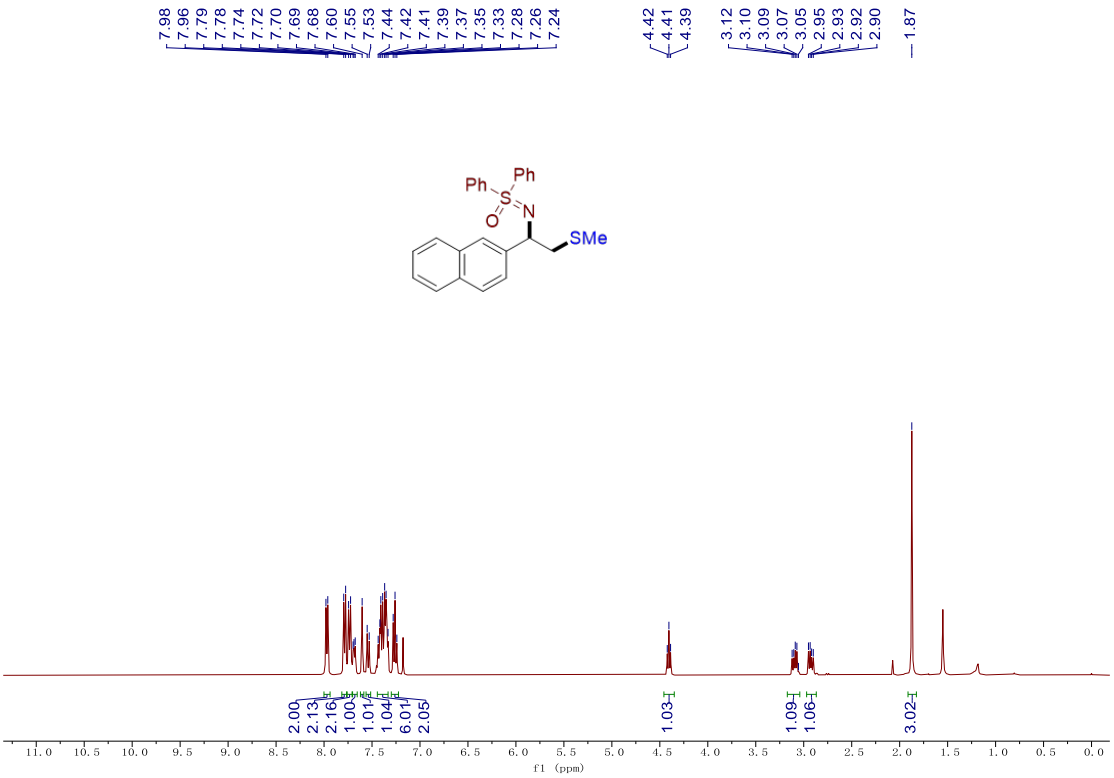

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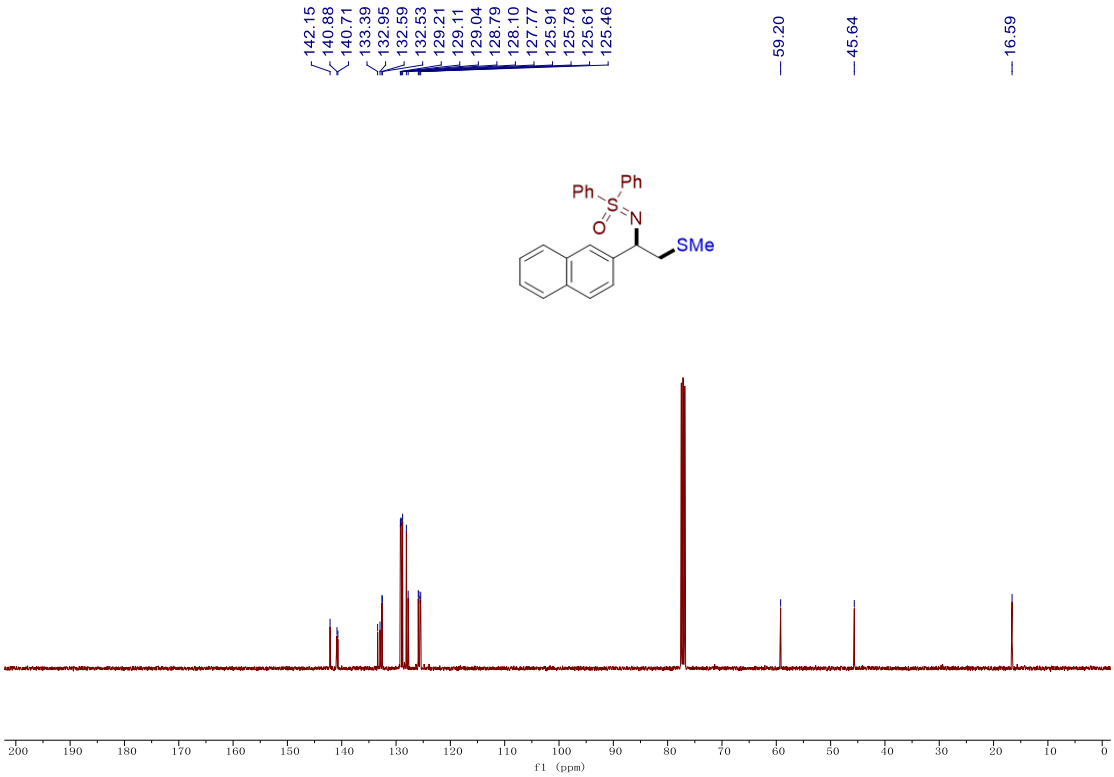
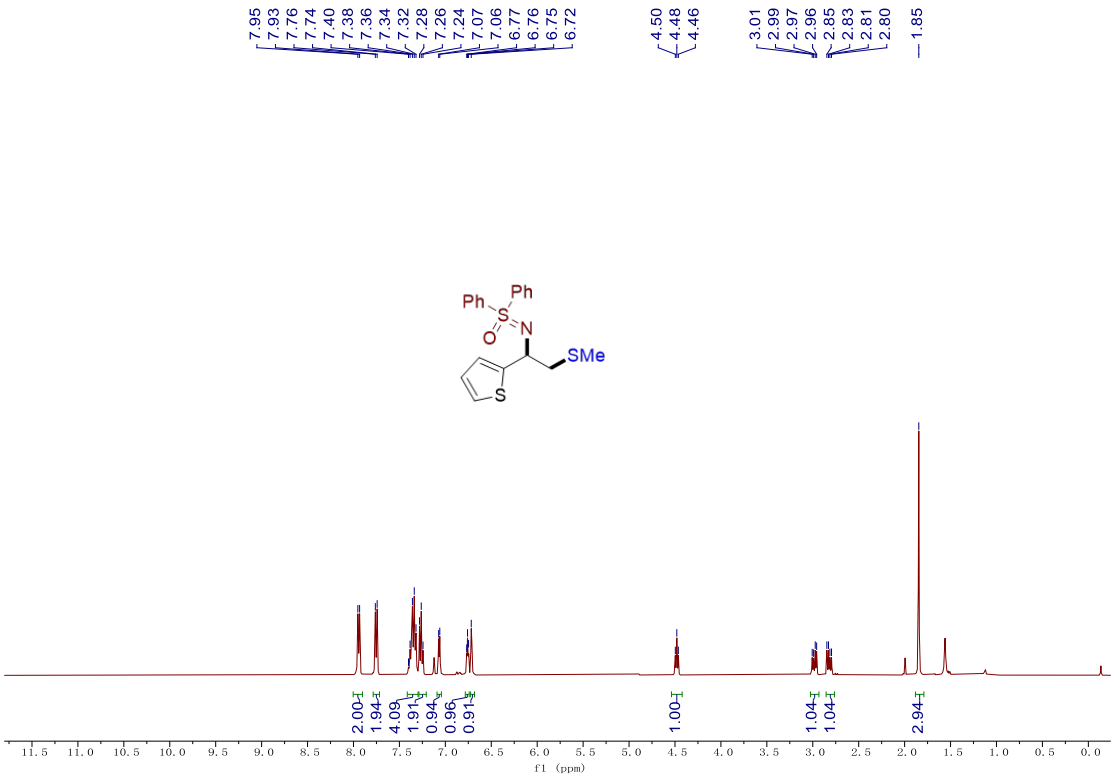
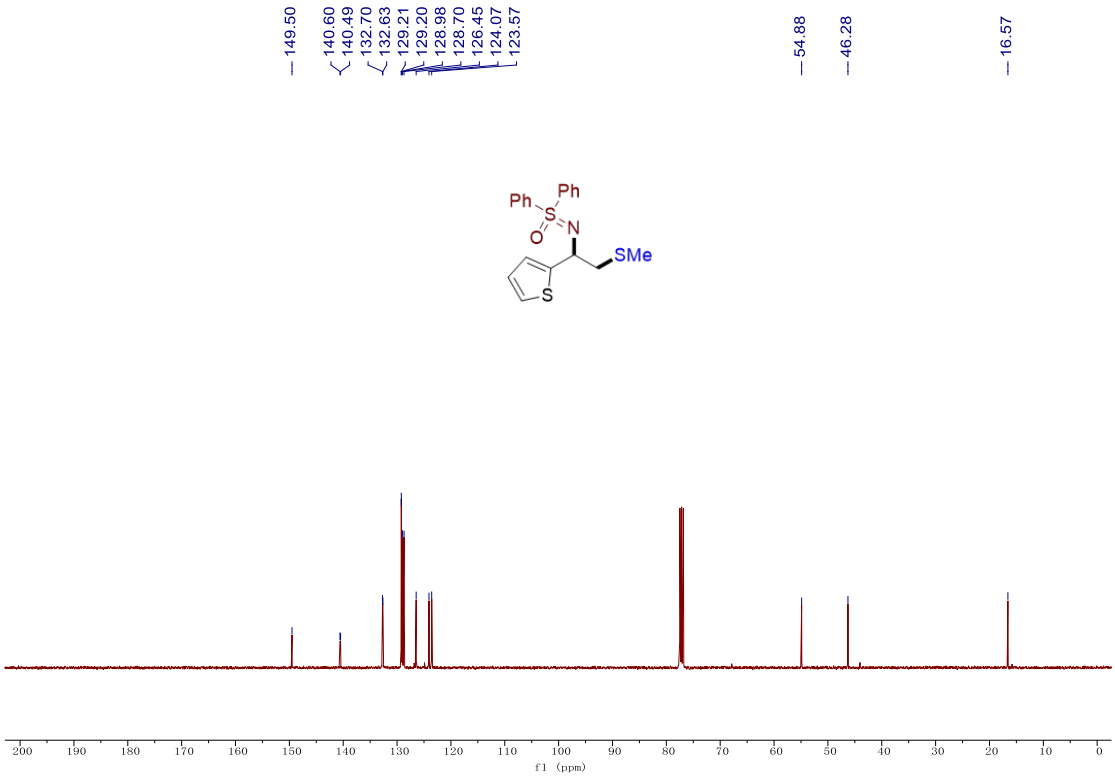


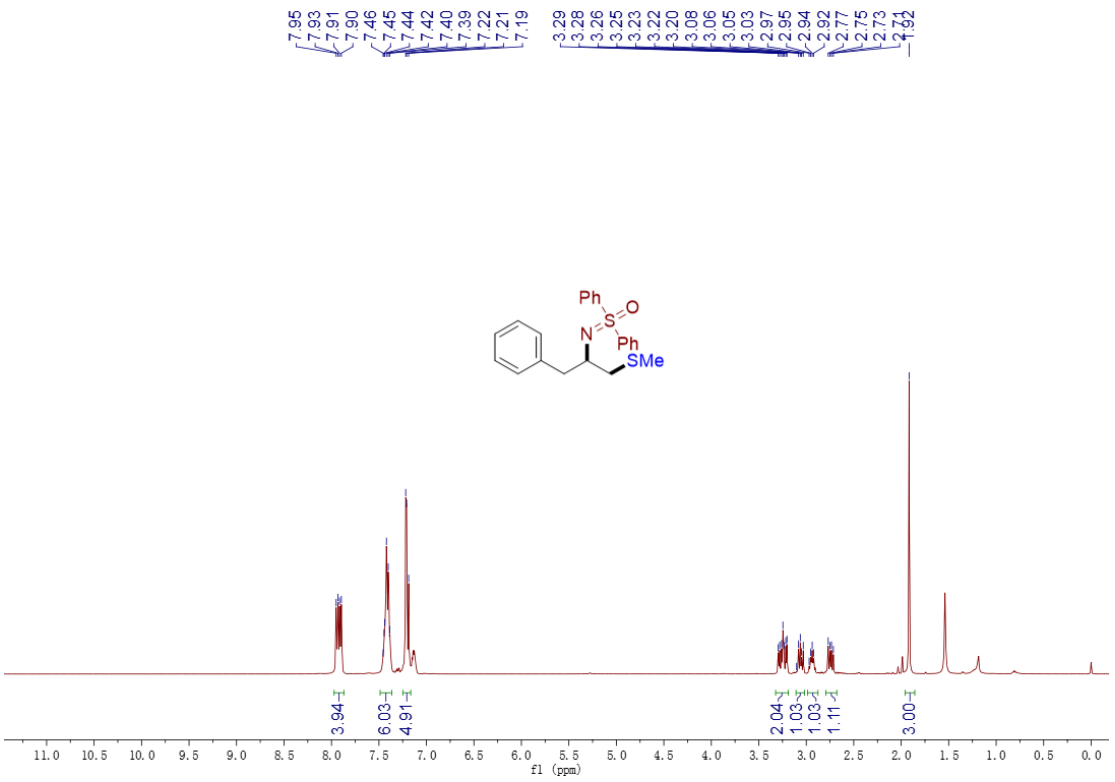
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ra**



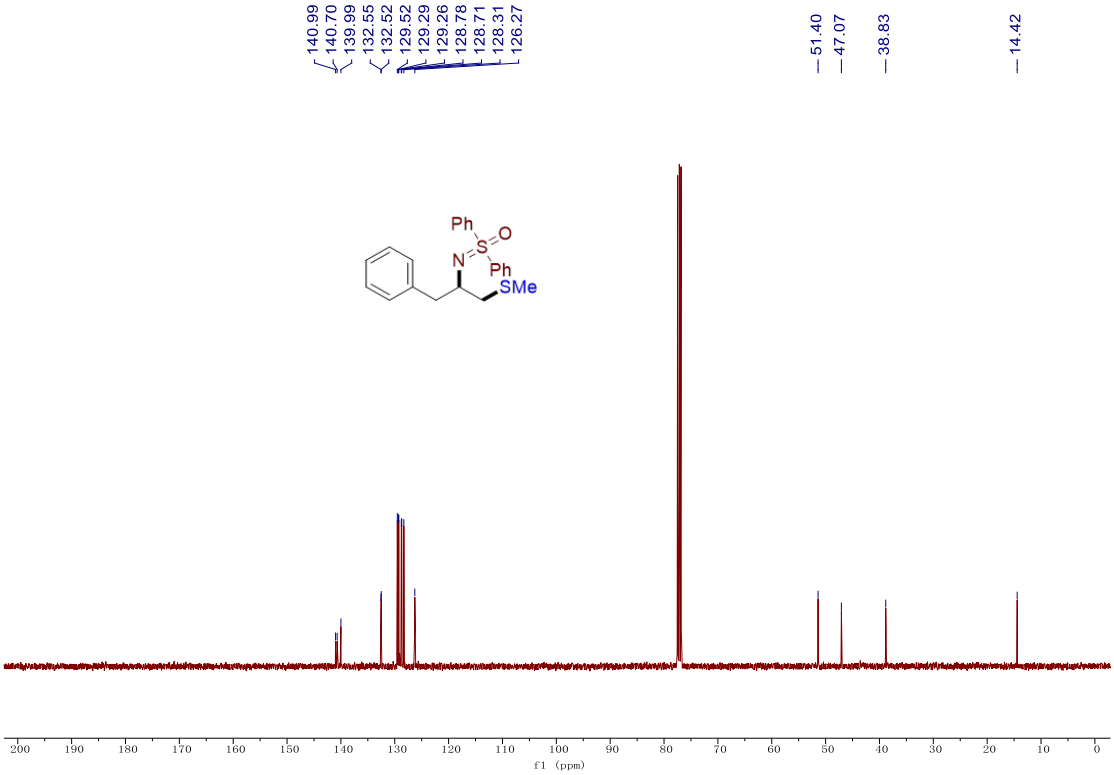
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3sa**



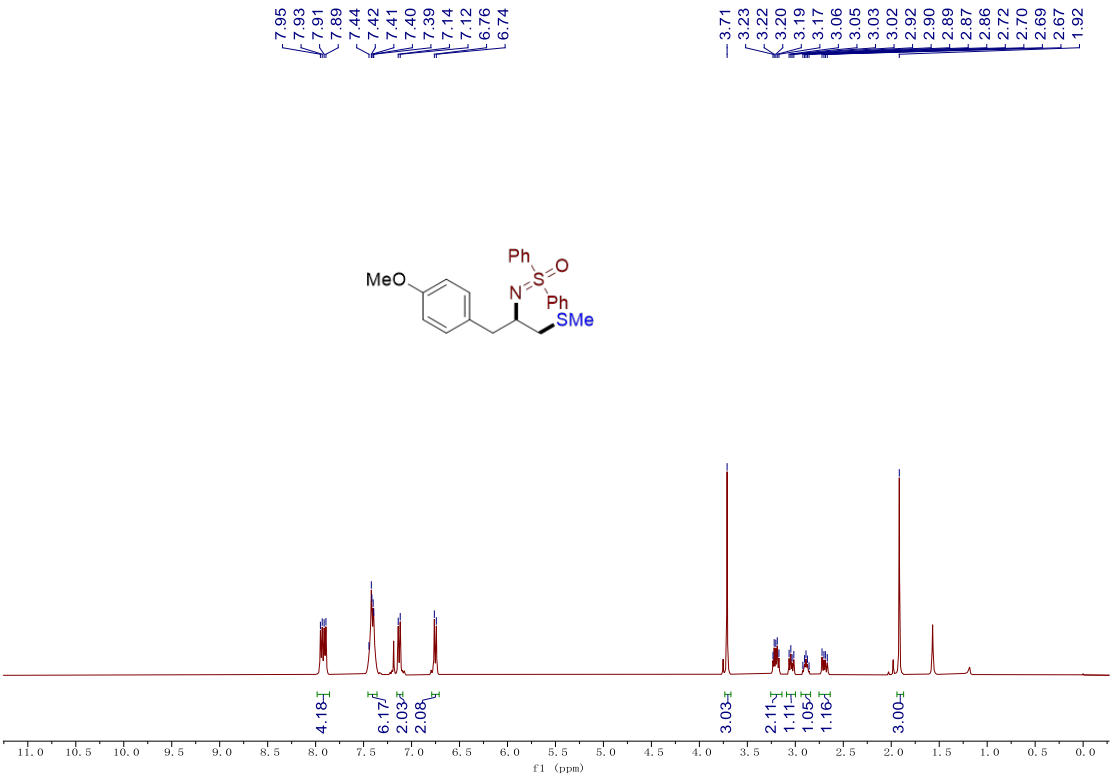
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3sa**



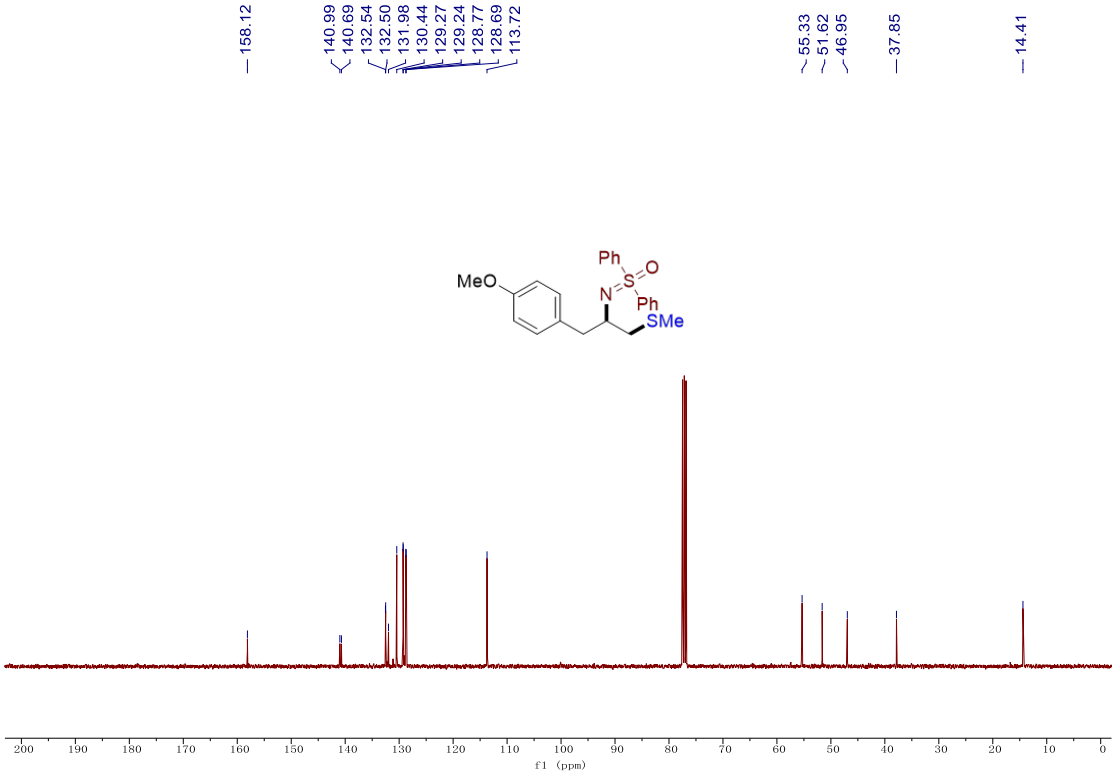
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ta**



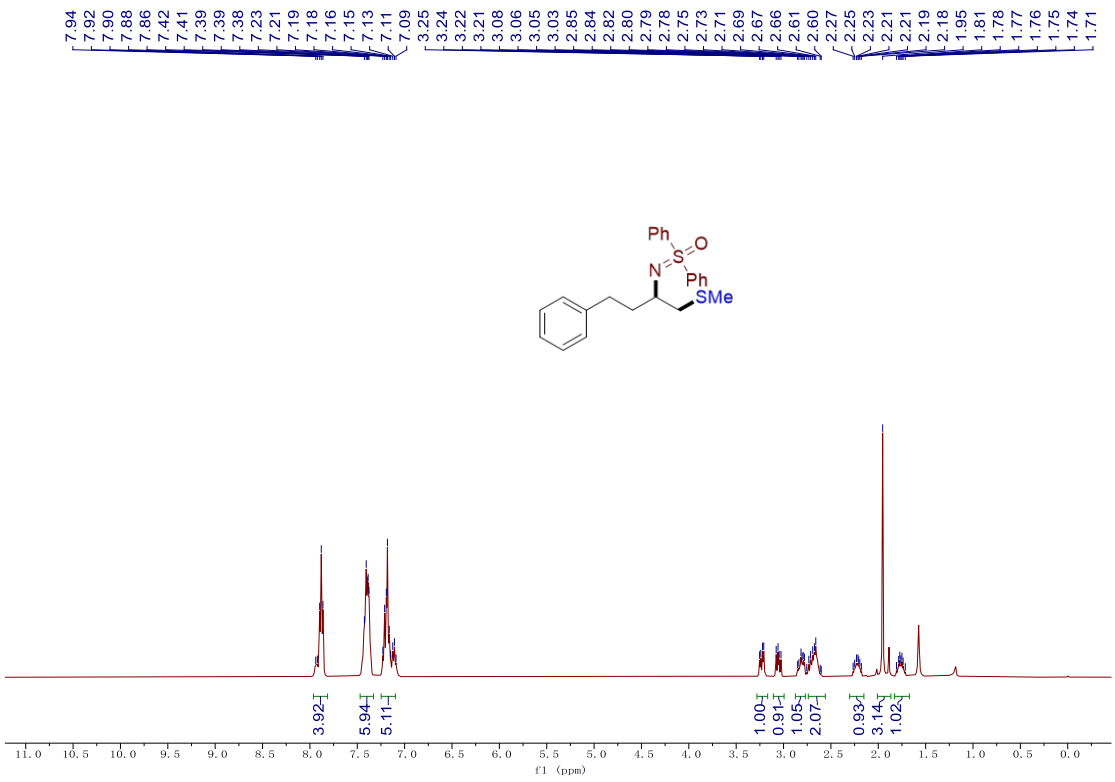
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ta**



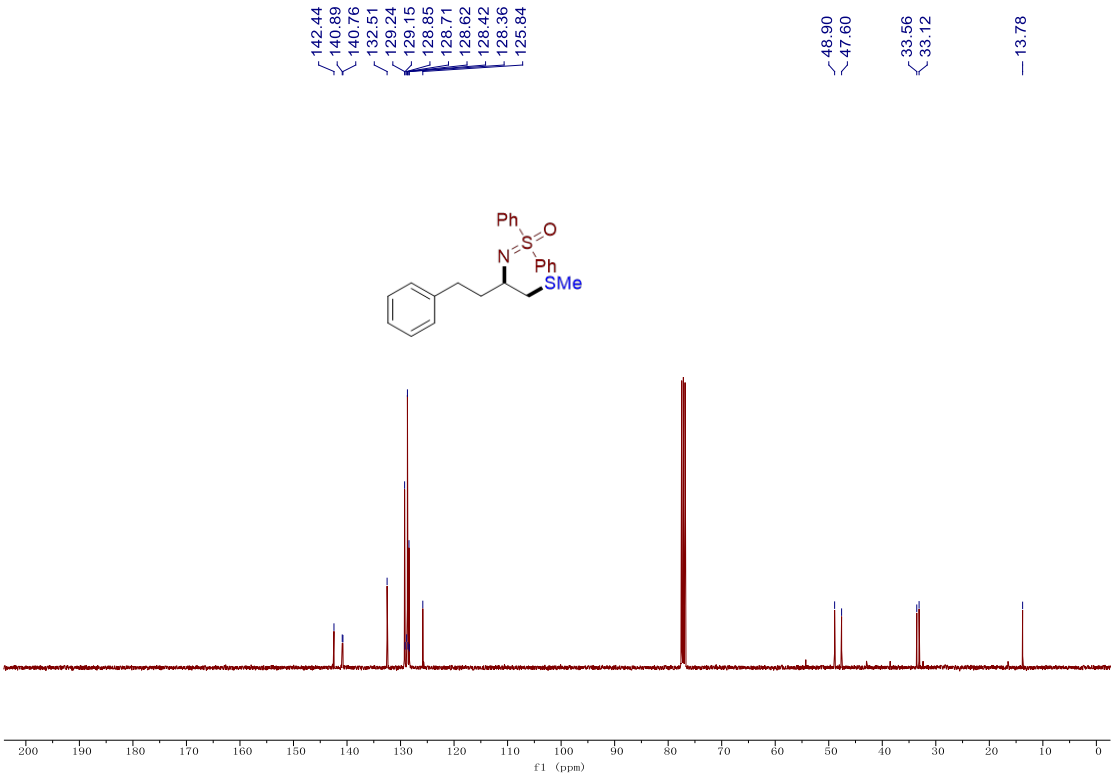
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ua**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ua**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3va**



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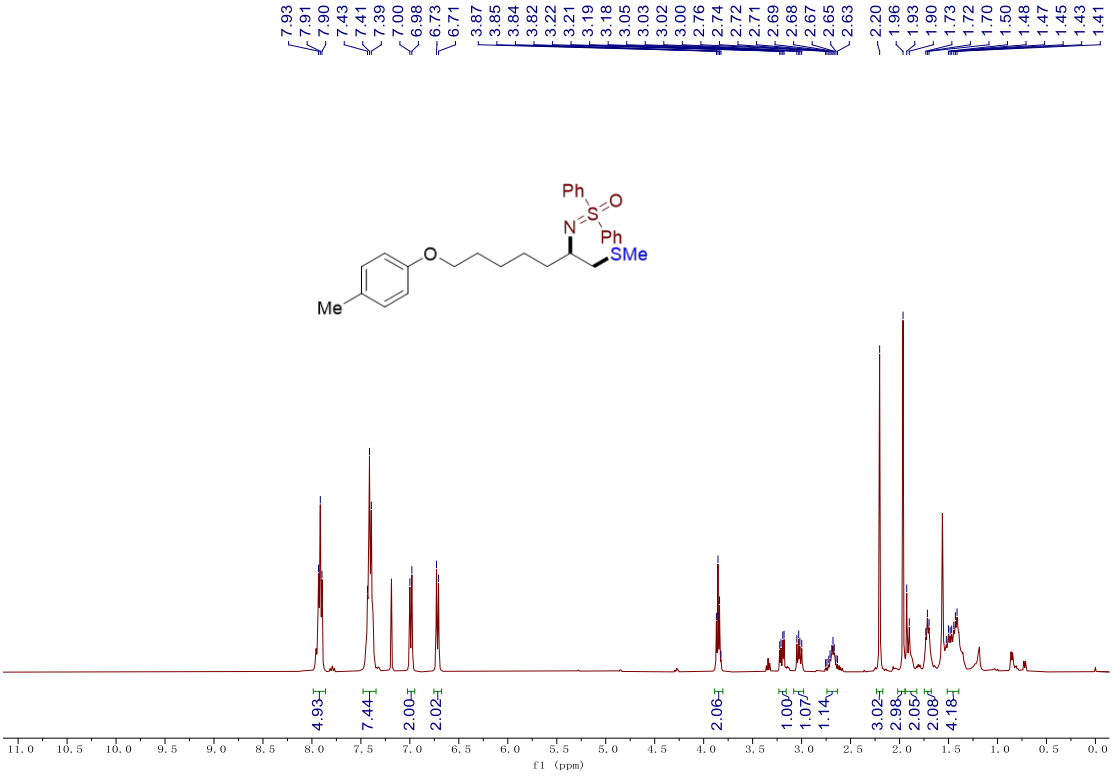
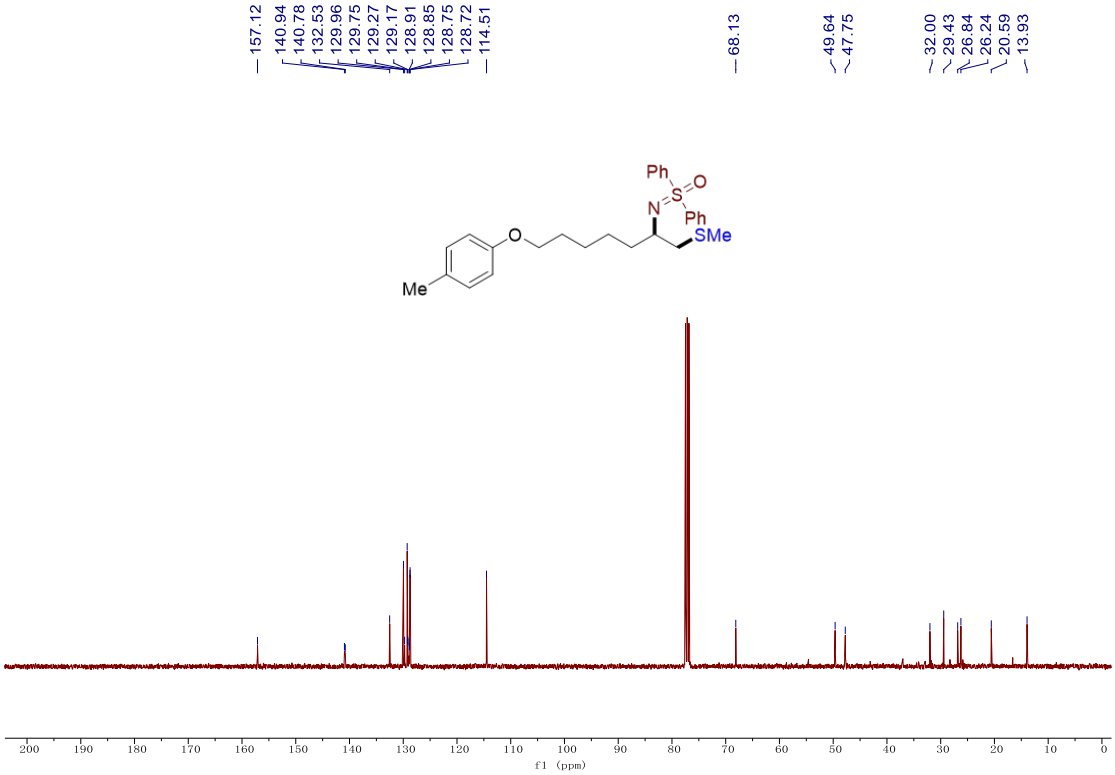
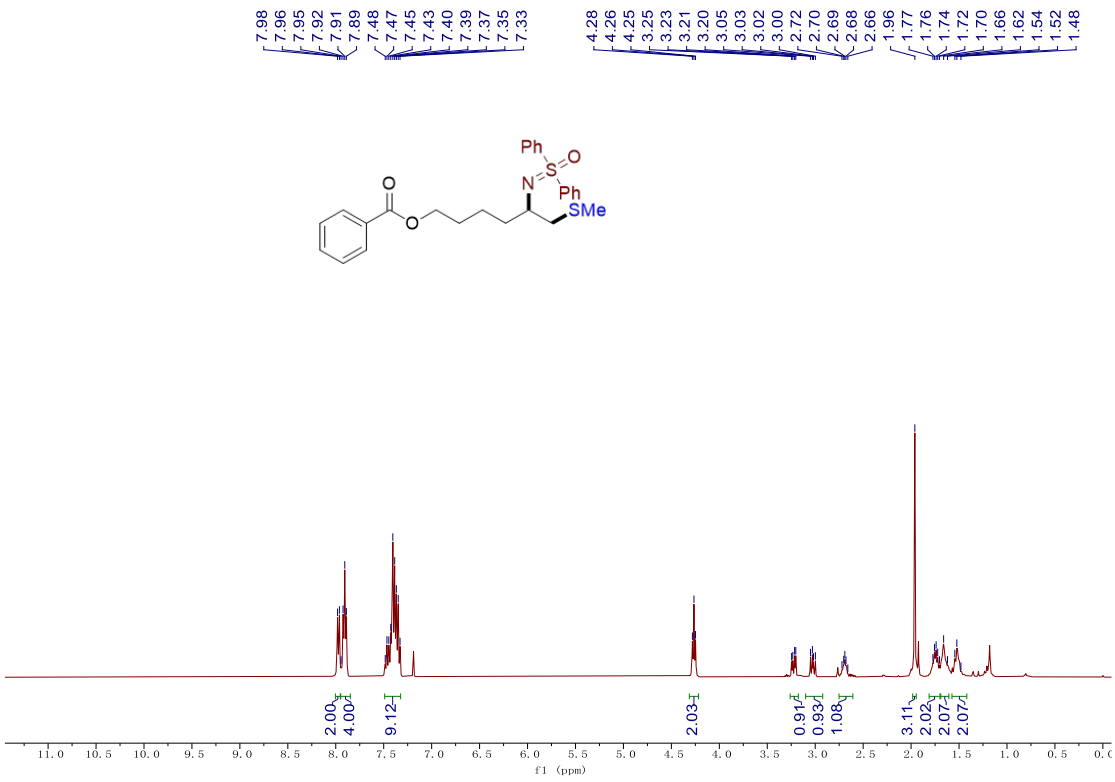


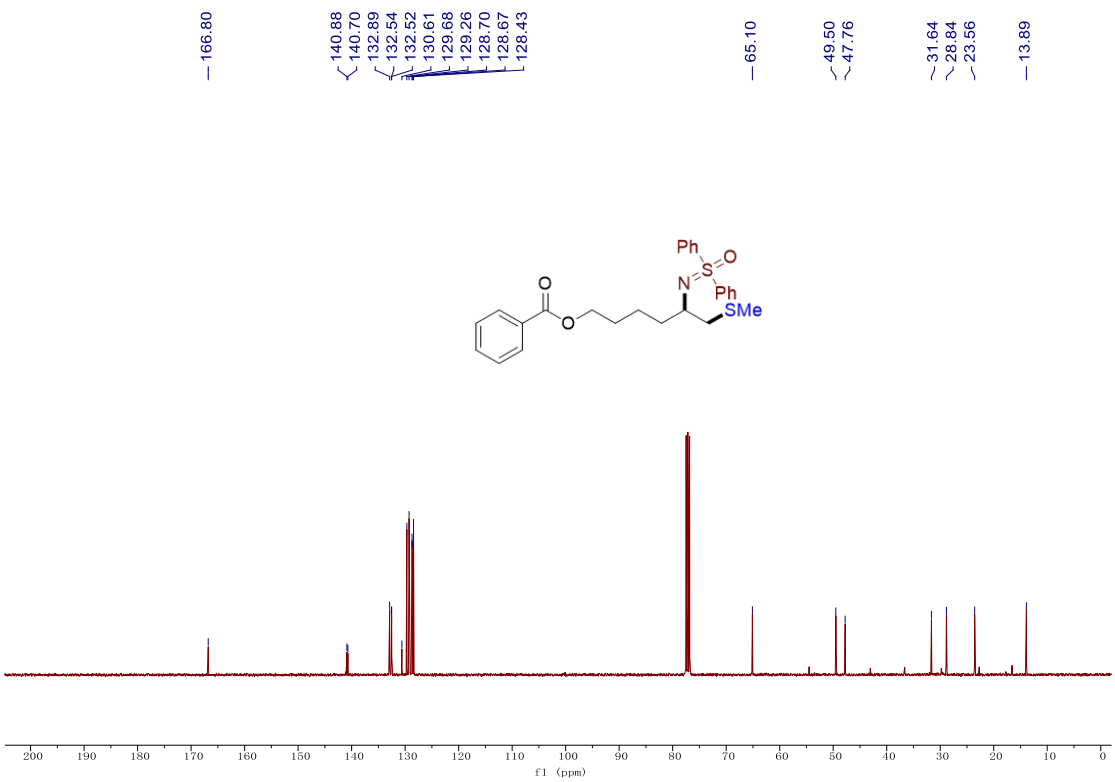
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3wa**



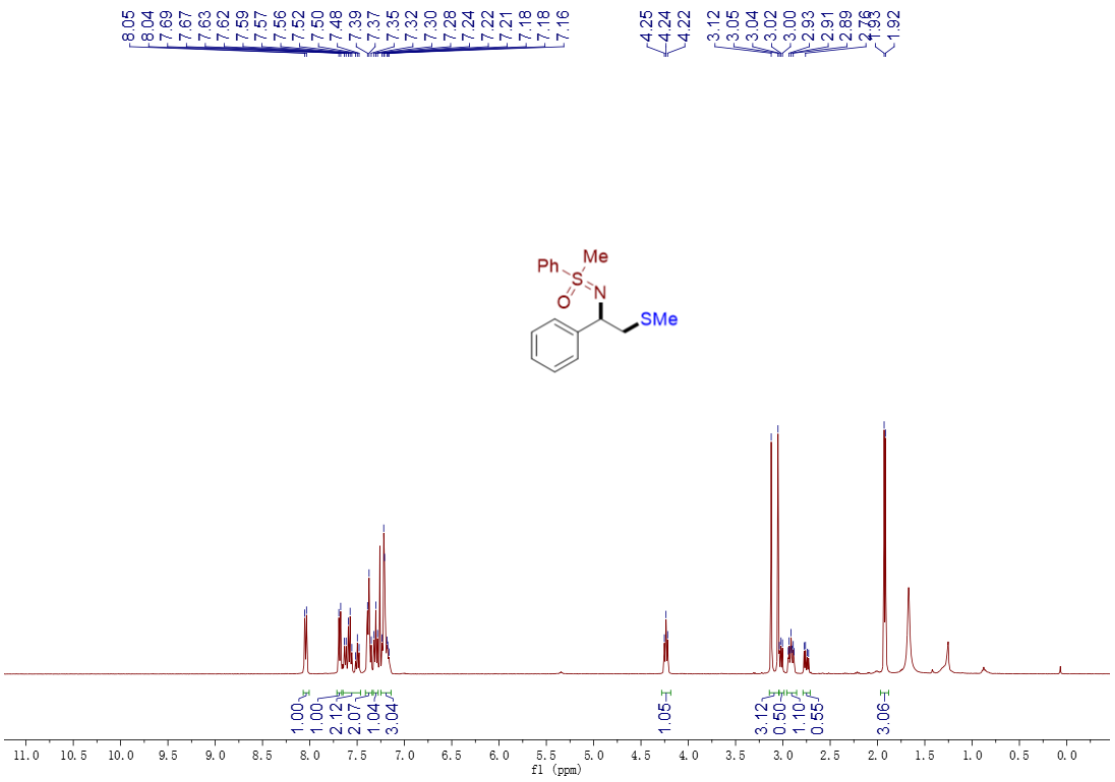
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3wa**



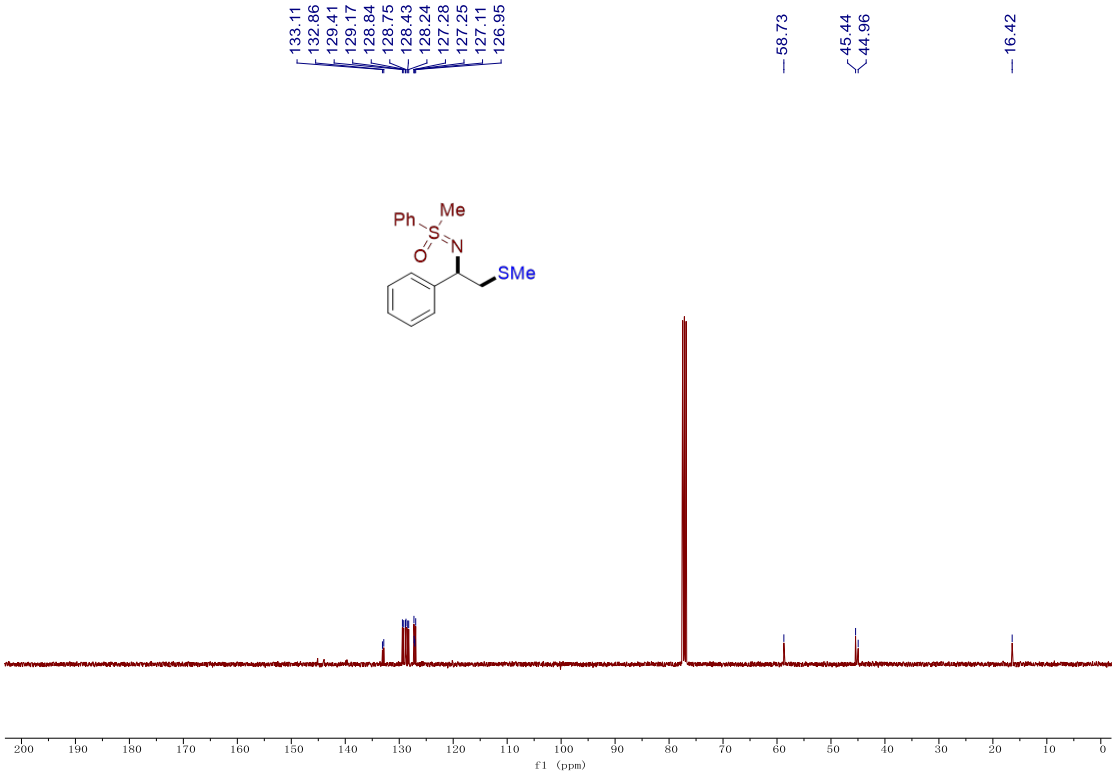
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3xa**



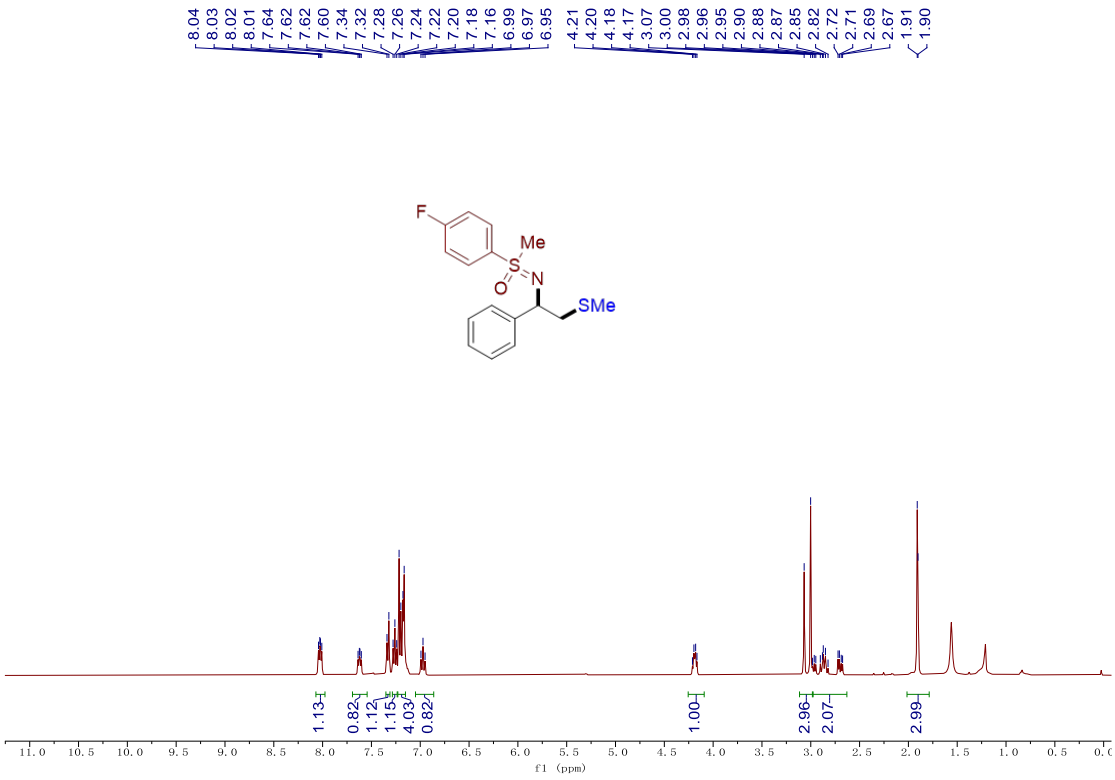
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3xa**



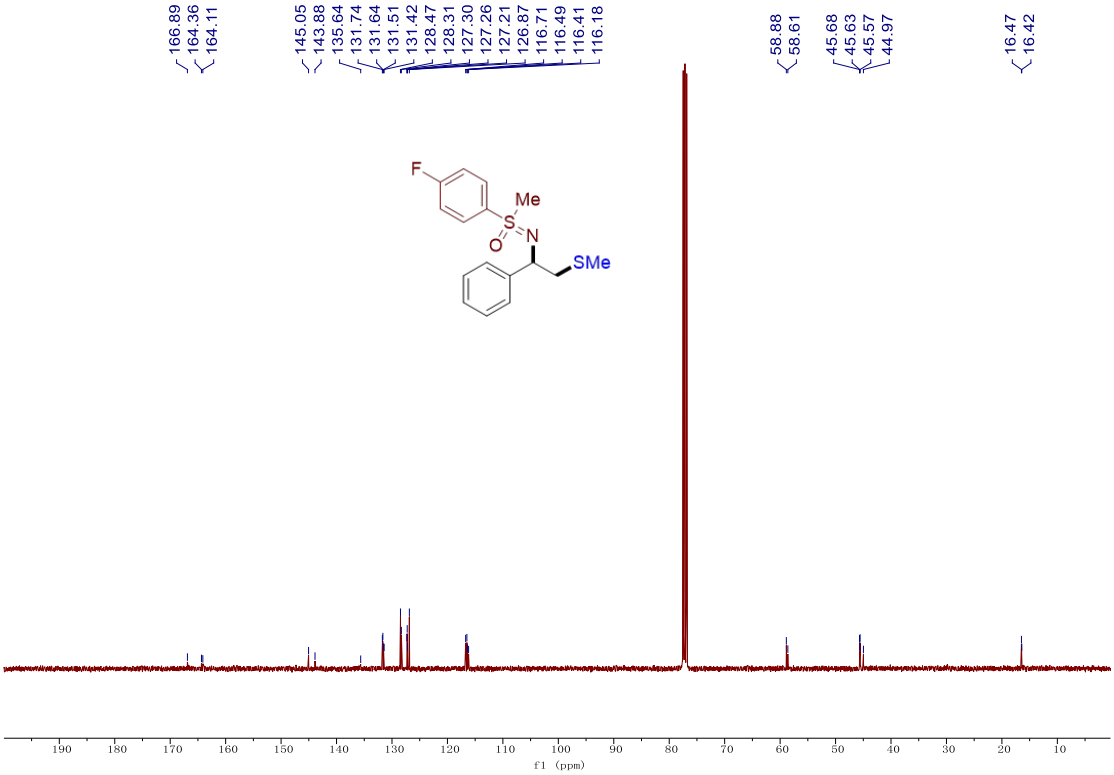
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ab**



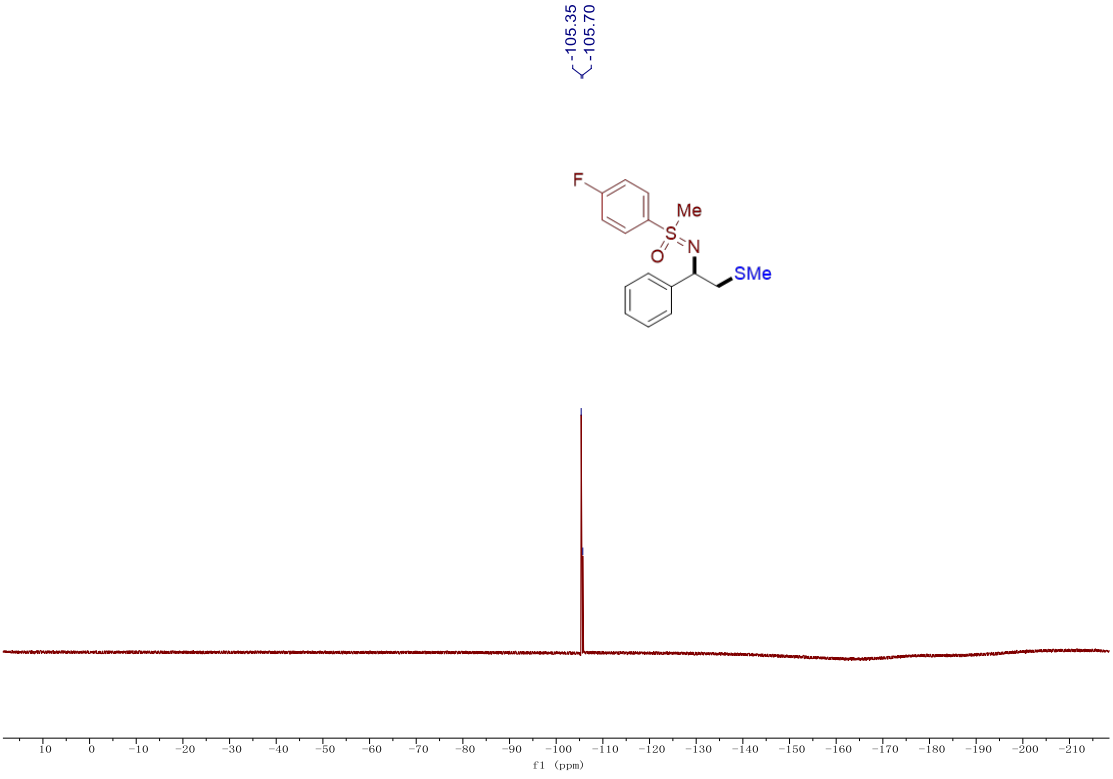
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ab**



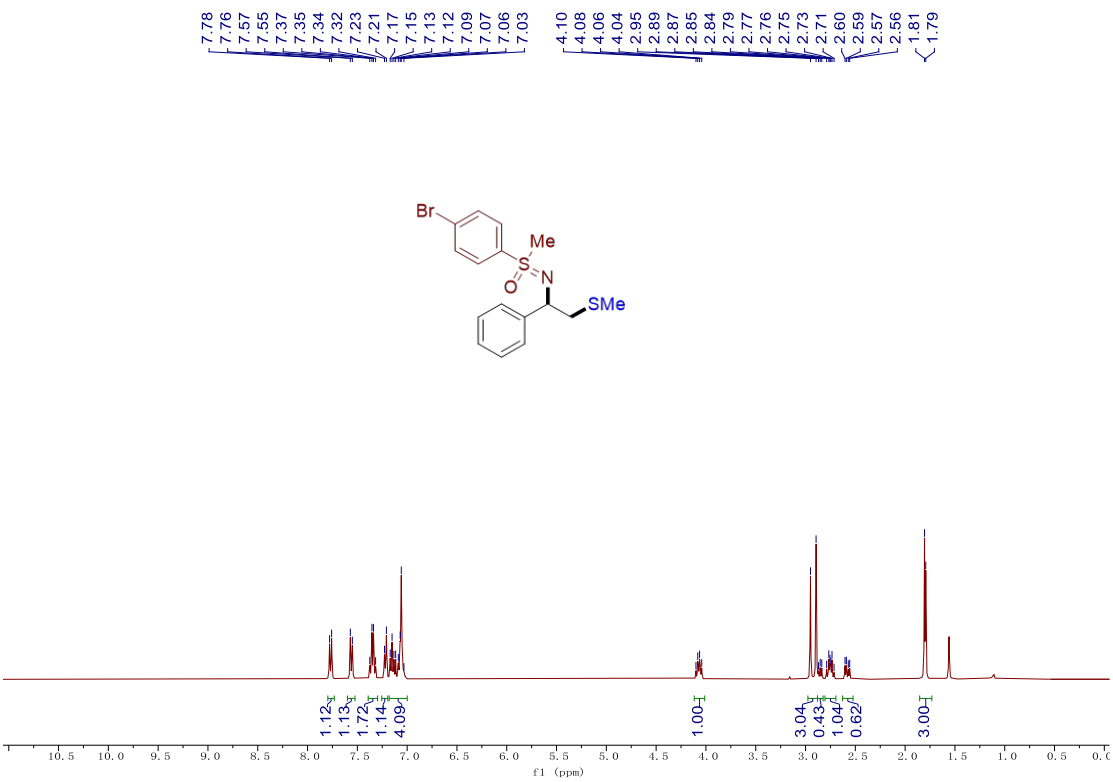
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ac**



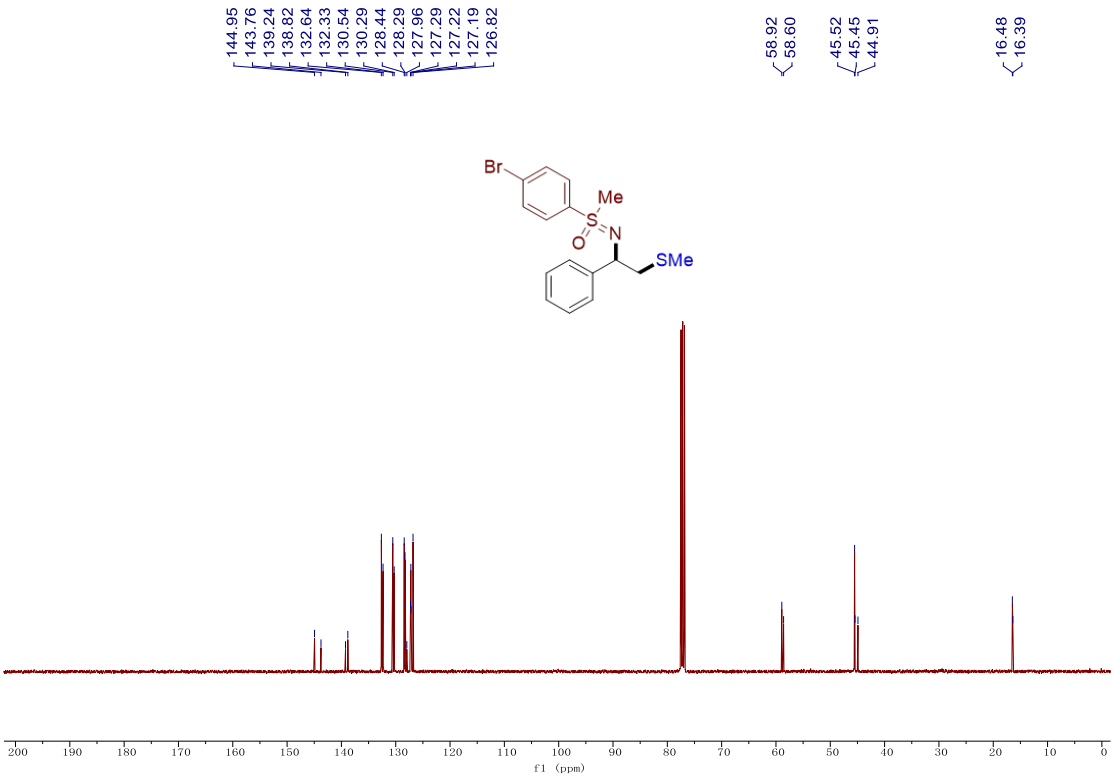
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ac**



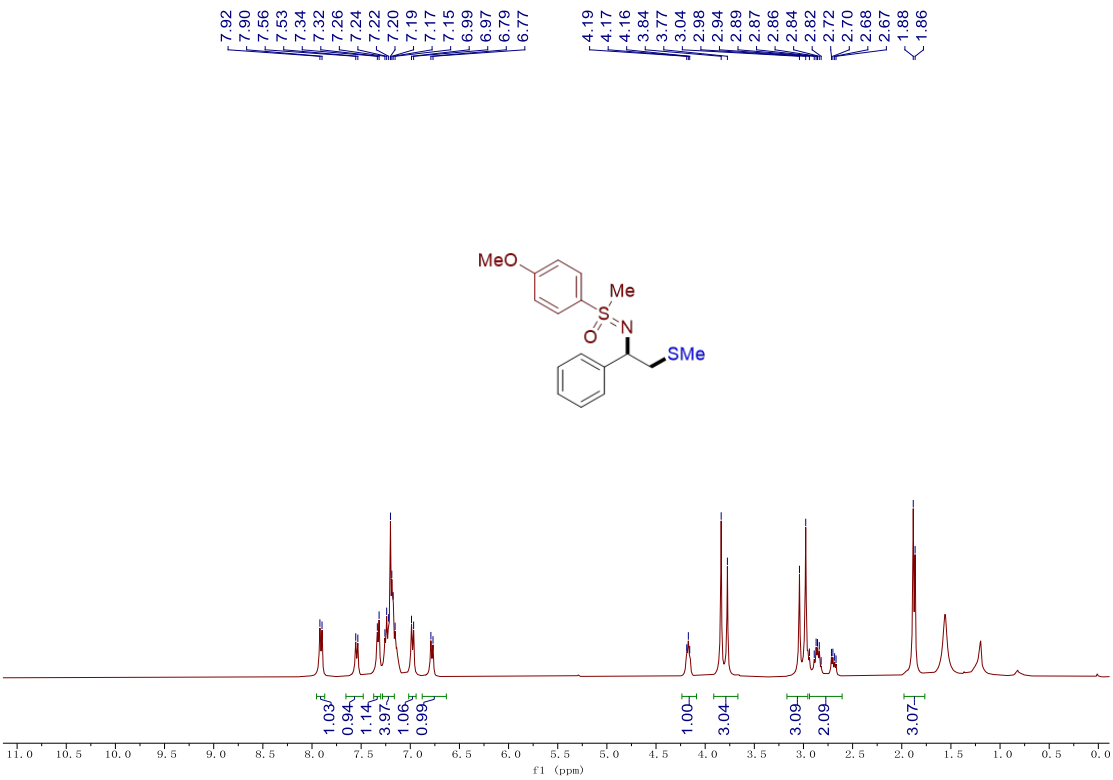
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ac**



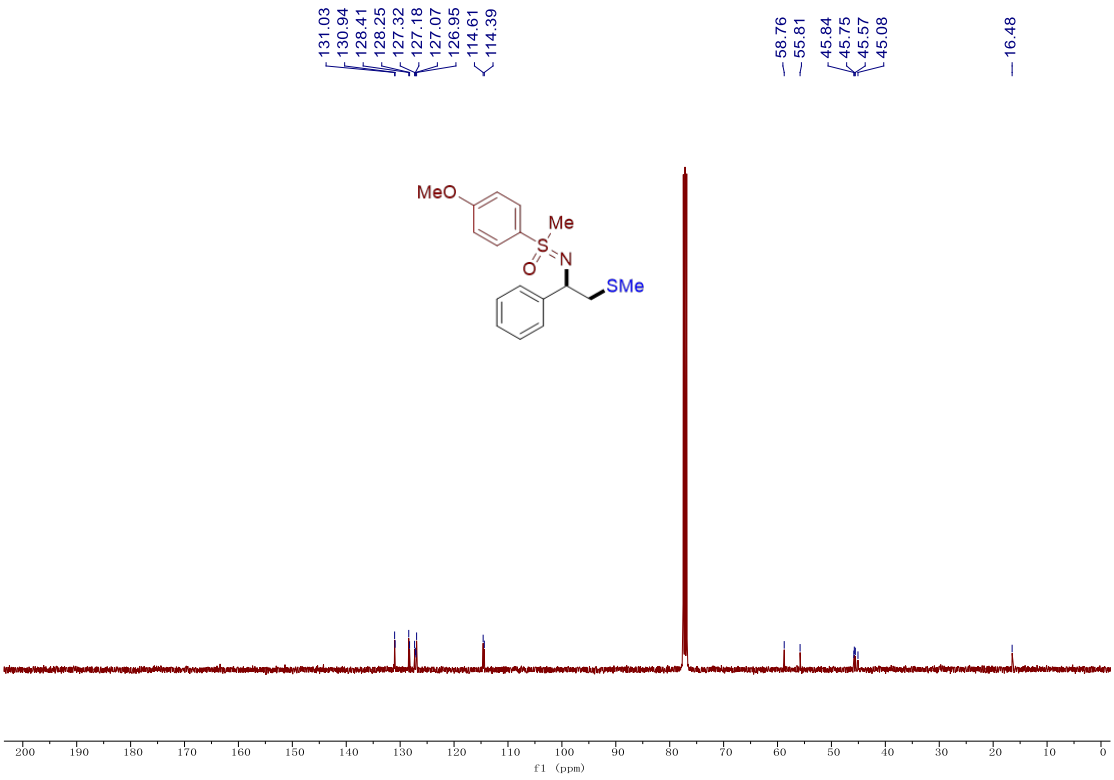
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ad**



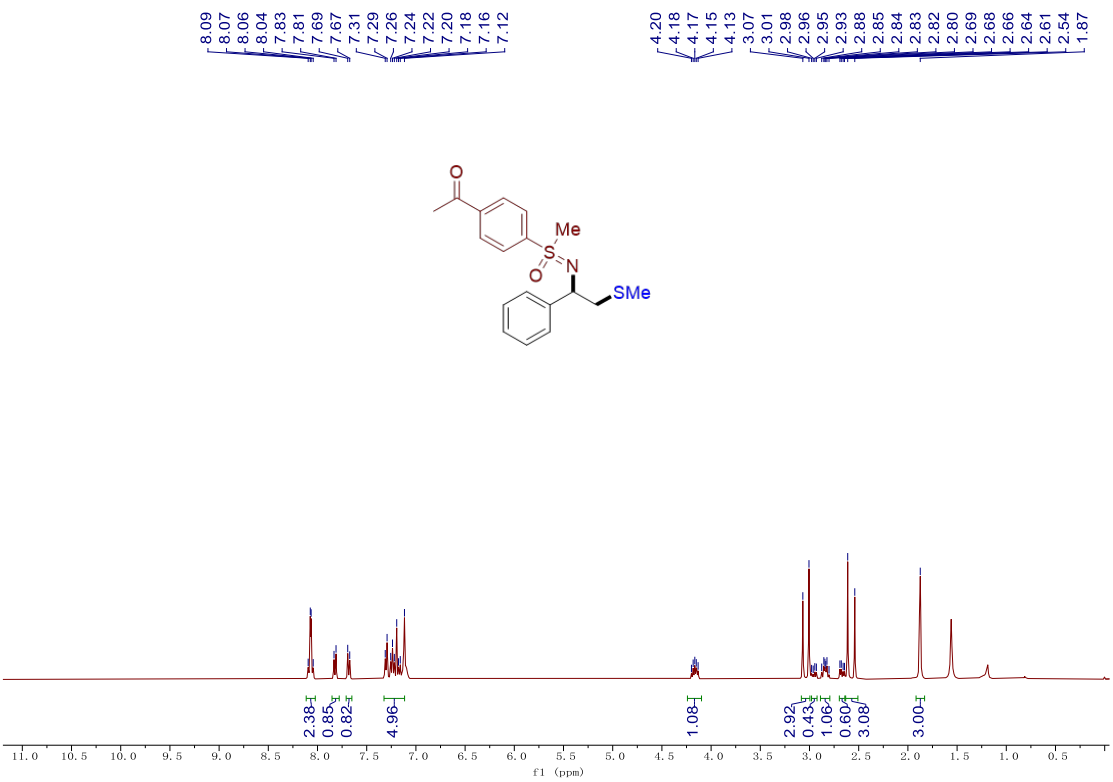
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ad**



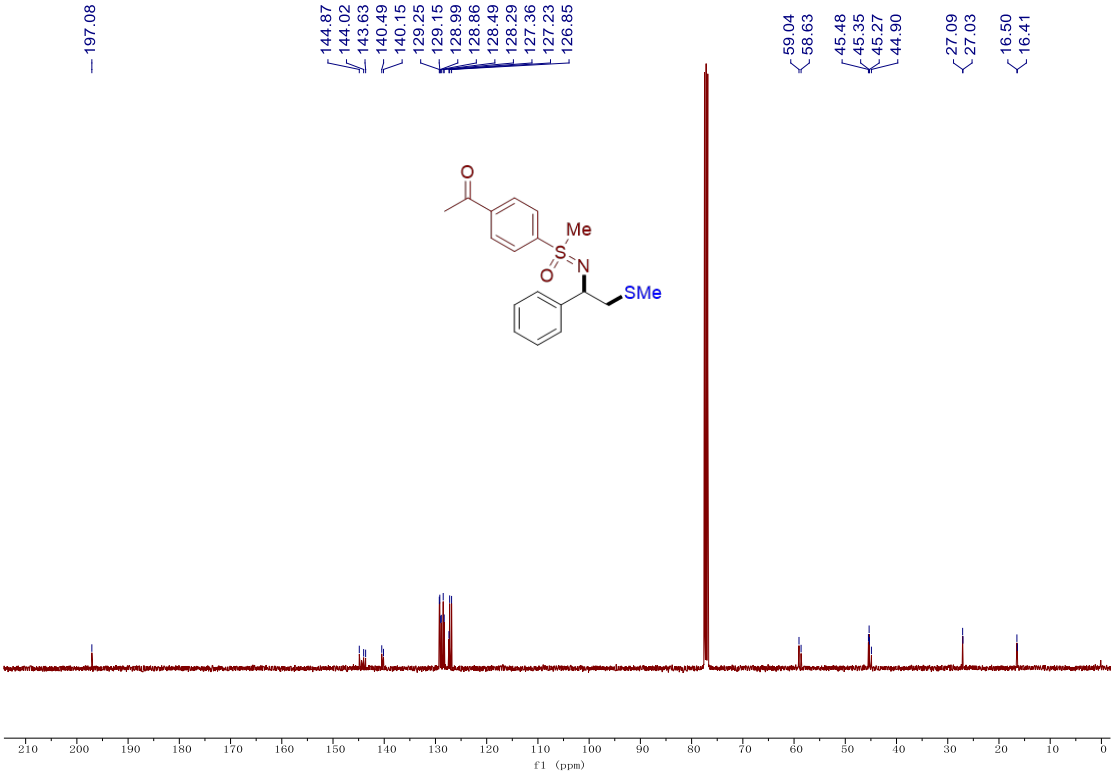
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ae**



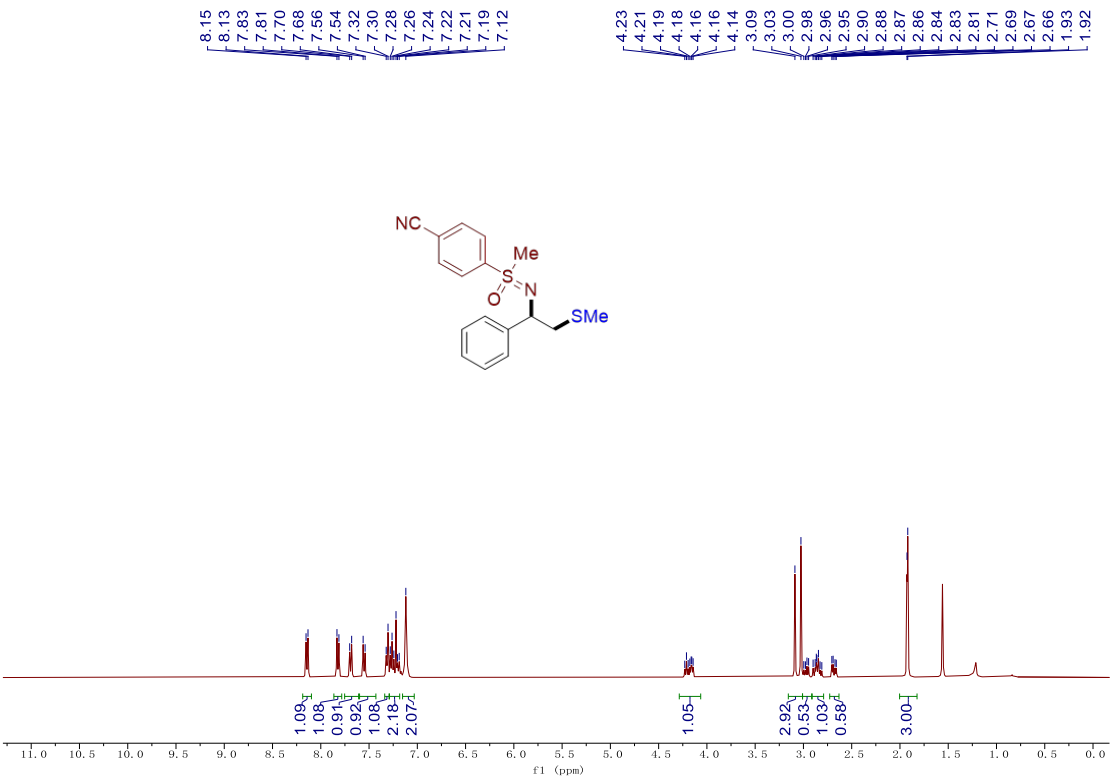
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ae**



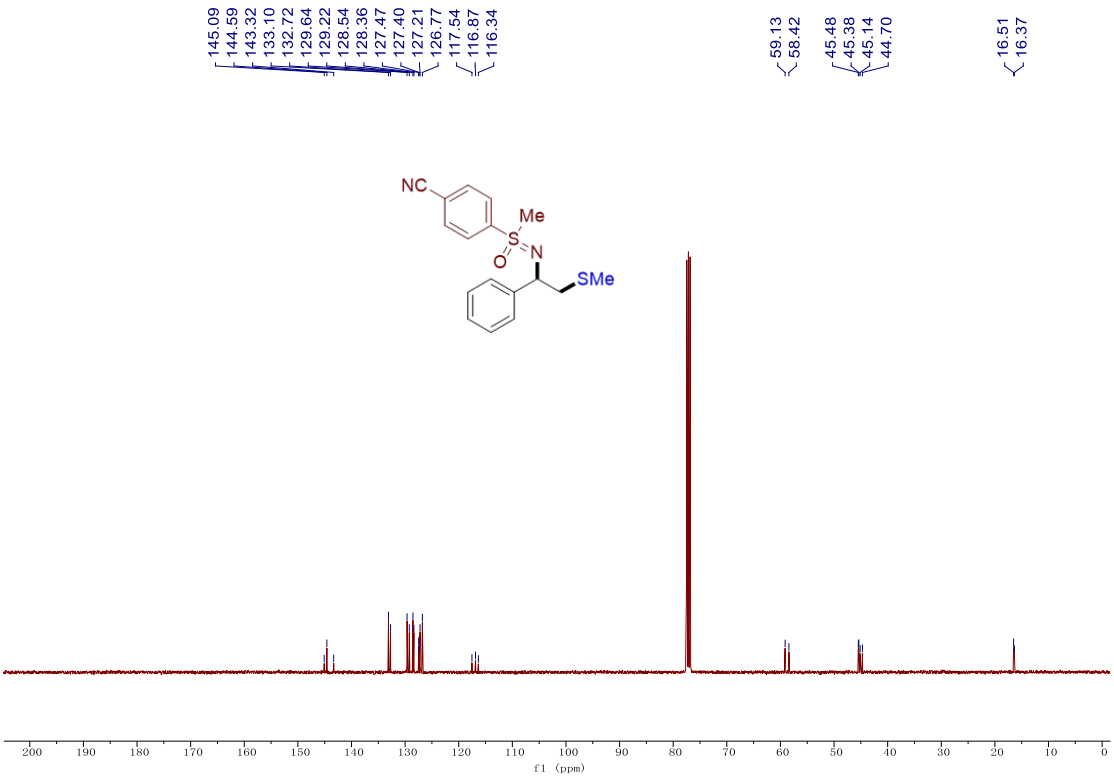
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3af**



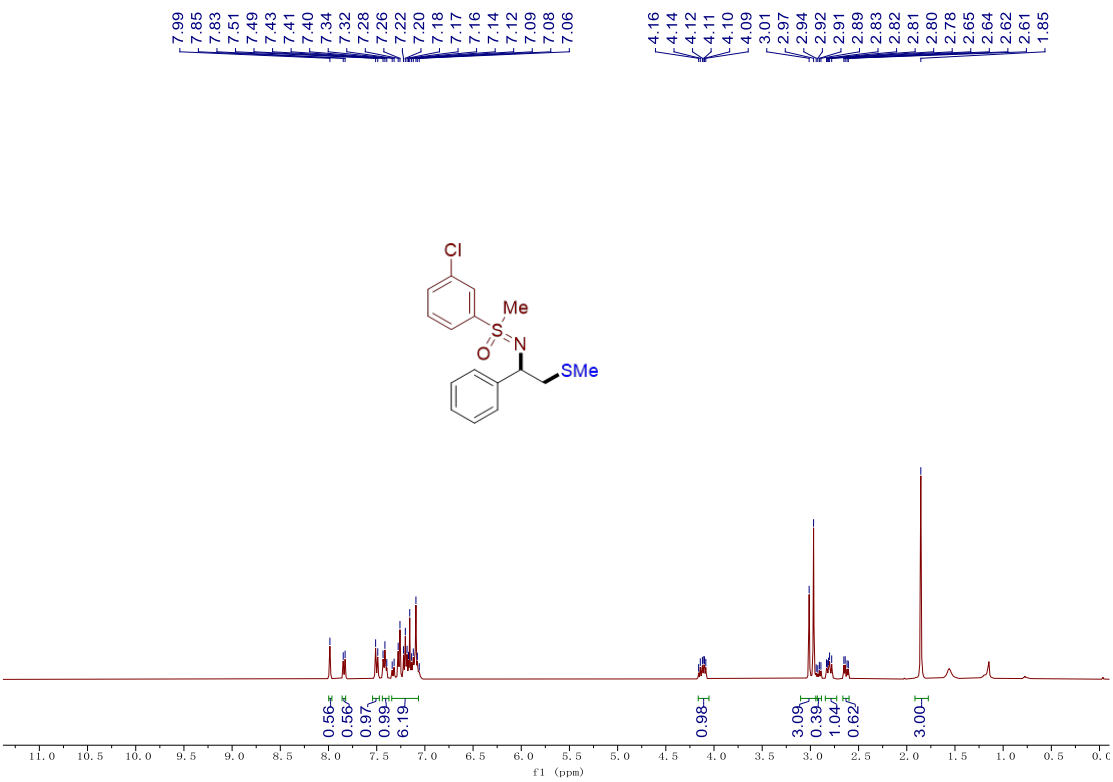
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3af**



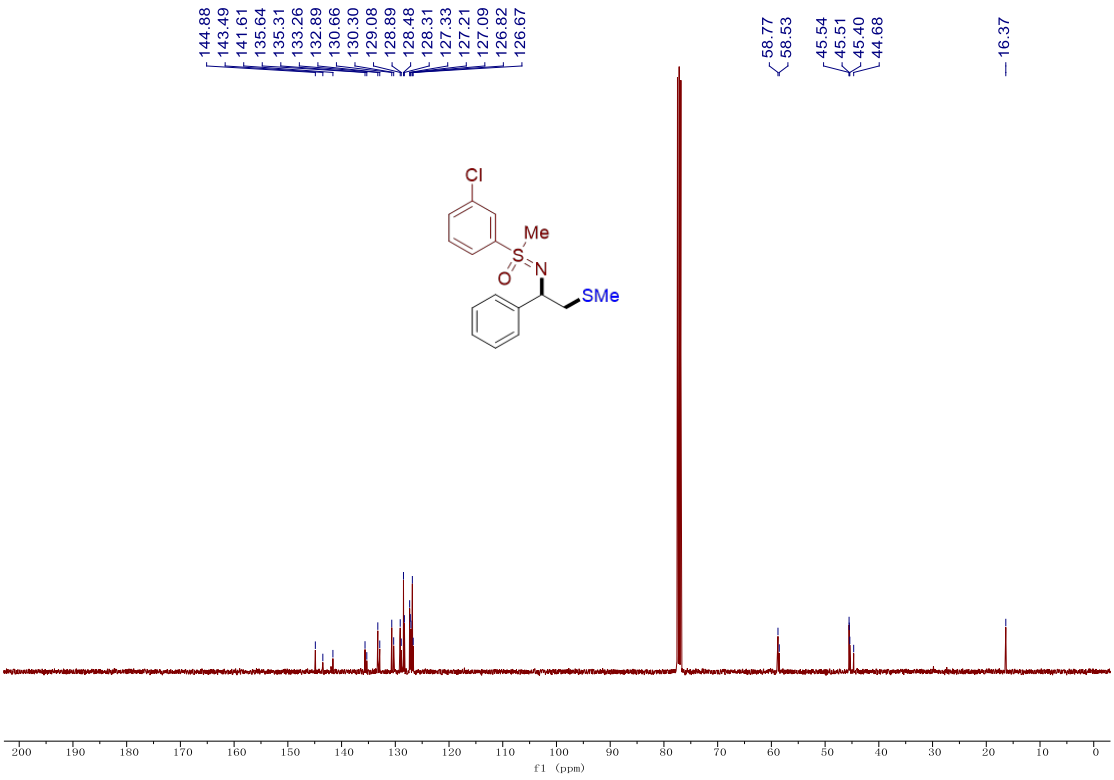
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ag**



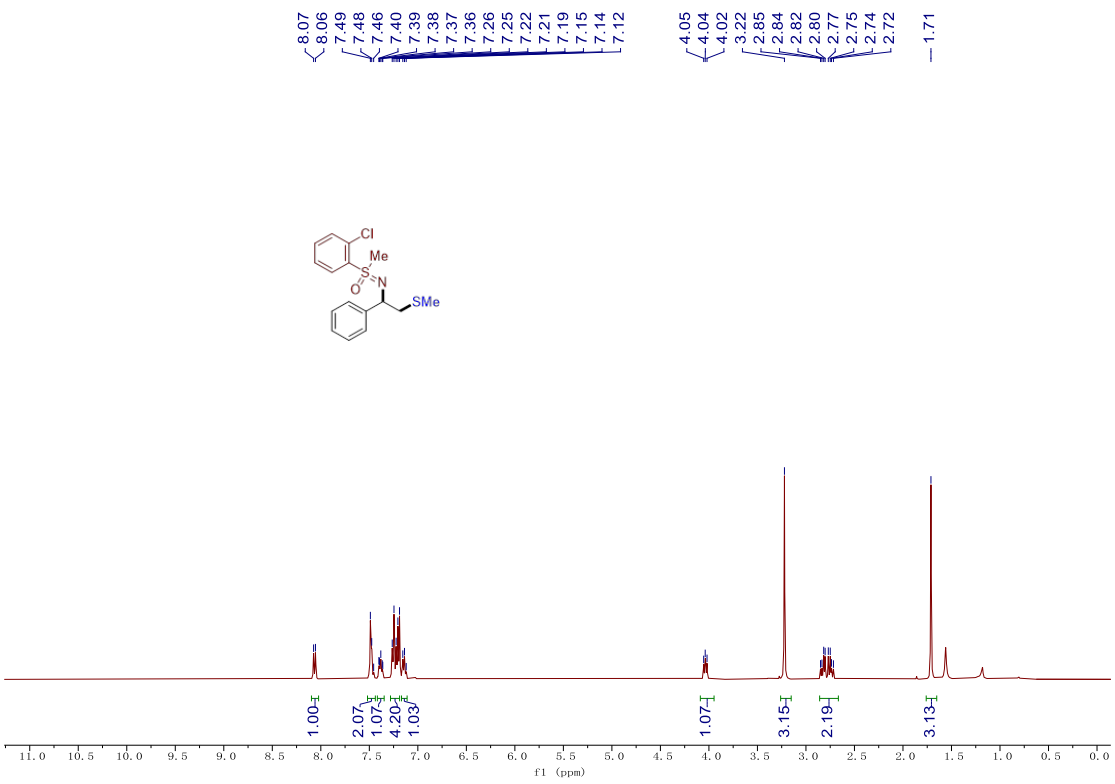
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ag**



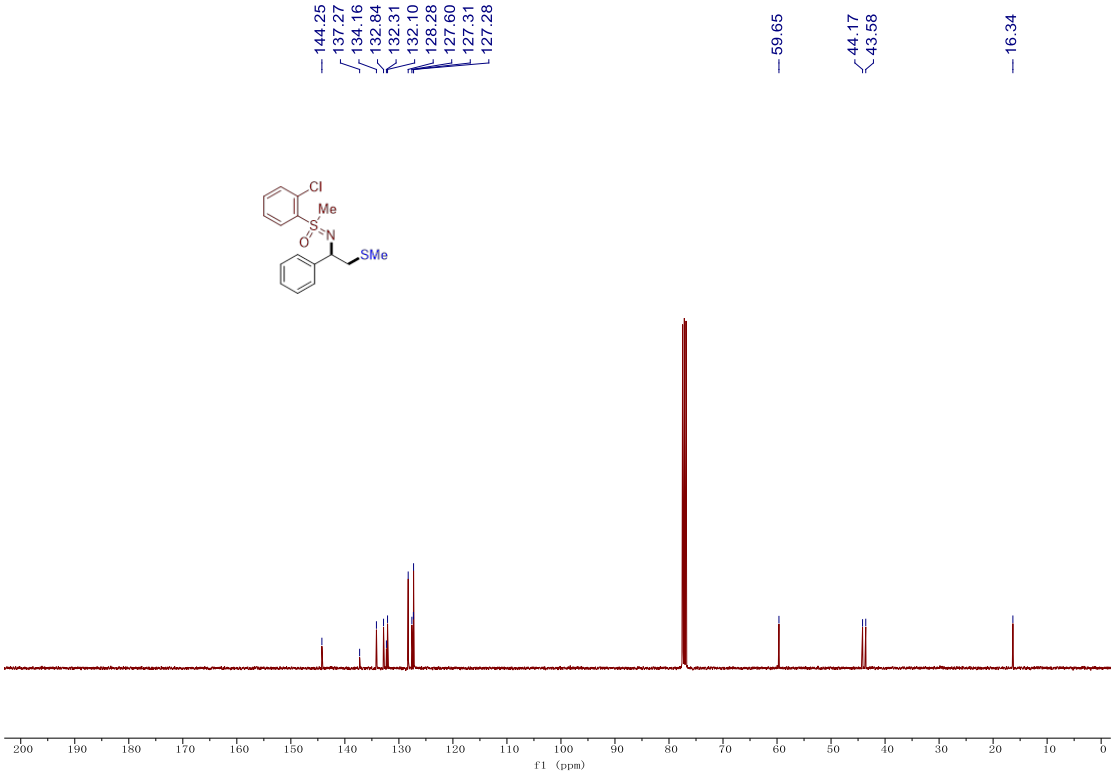
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah**



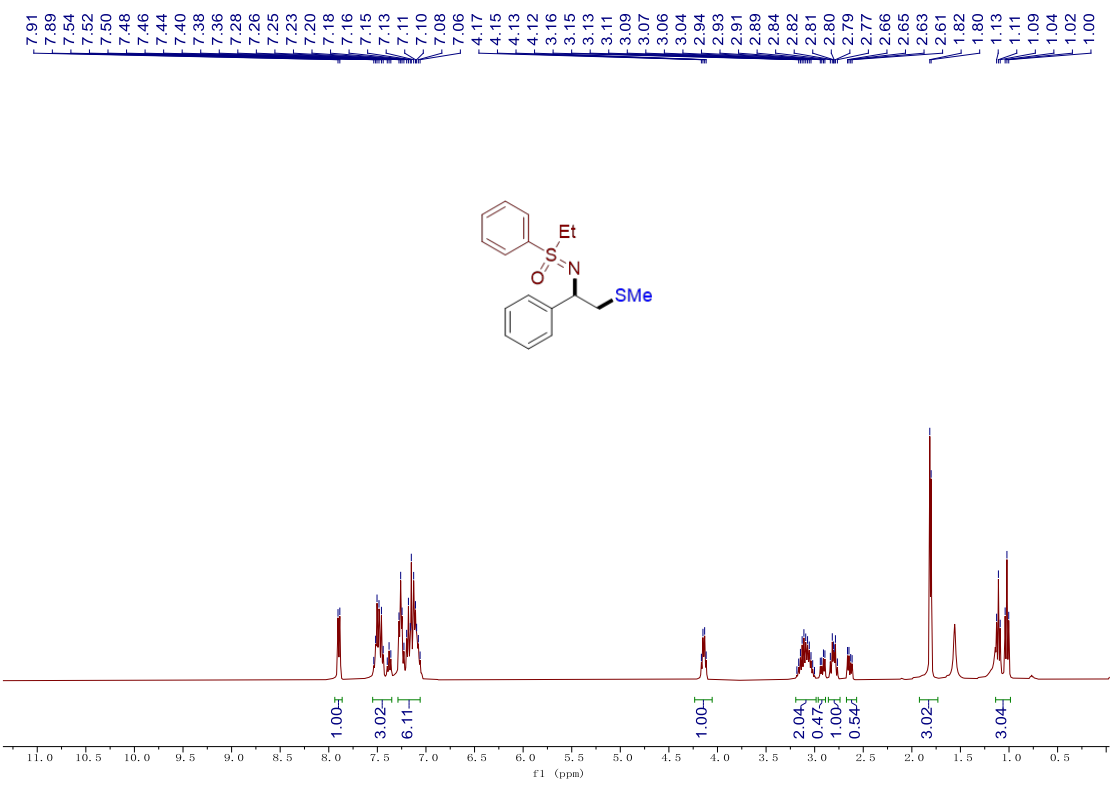
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ah**



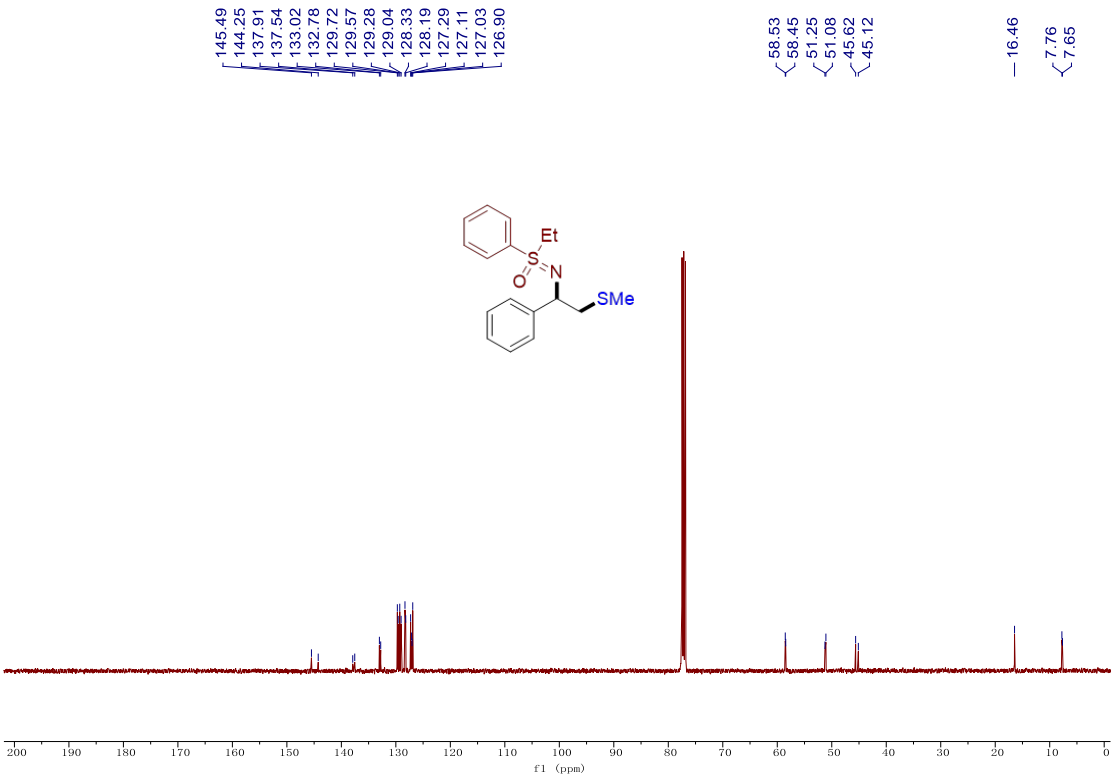
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ai**



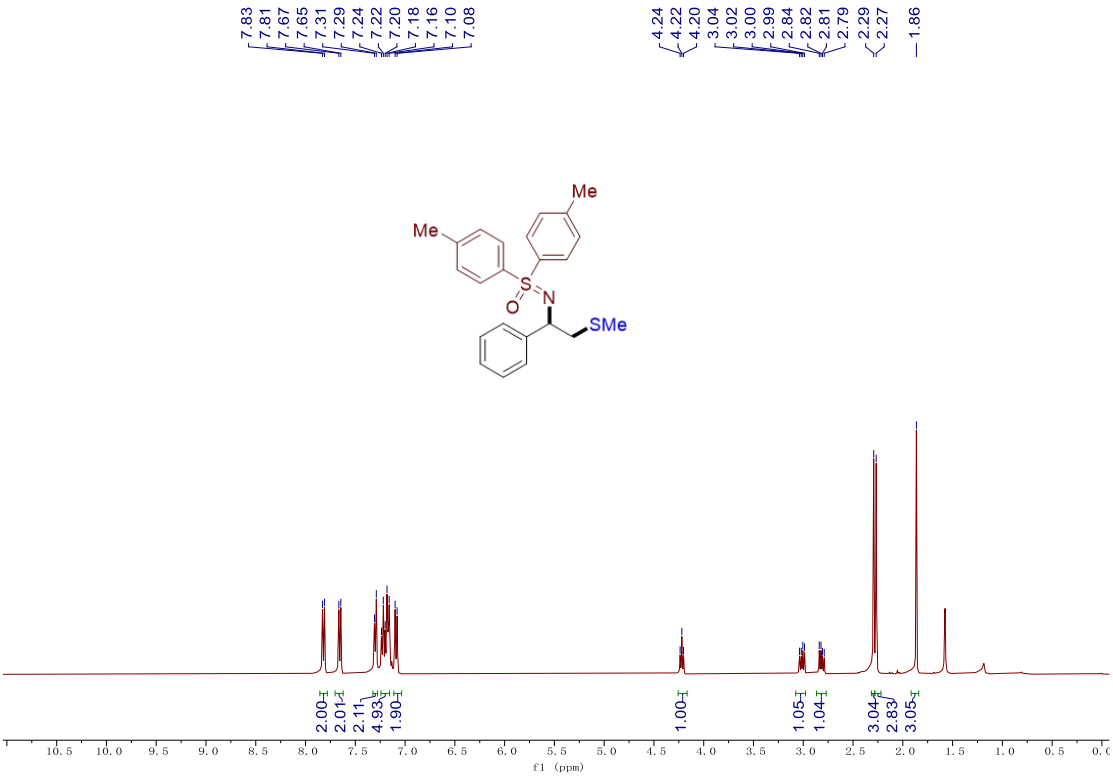
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ai**



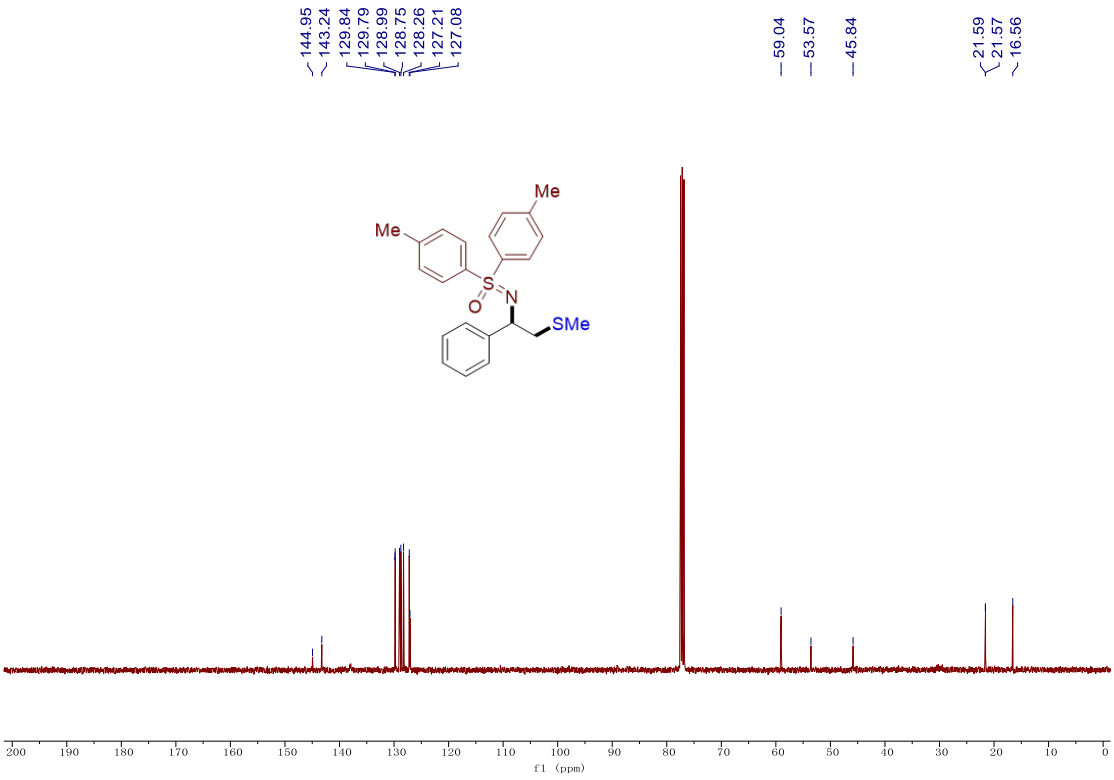
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aj**



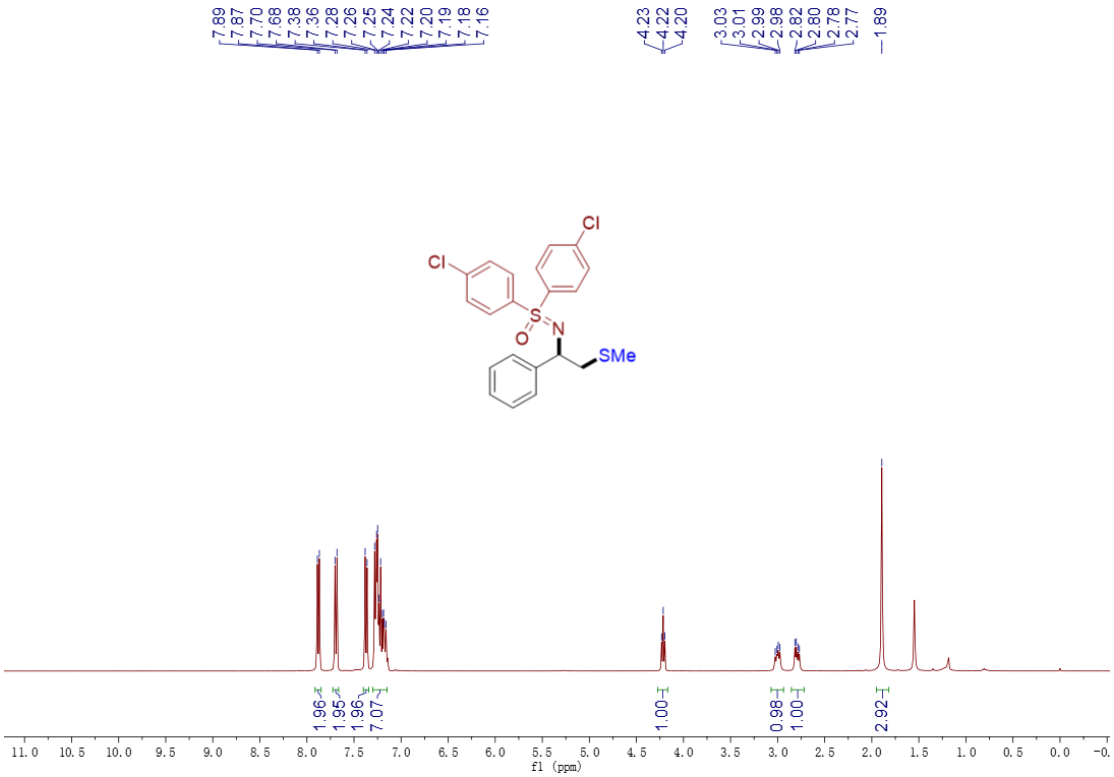
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aj**



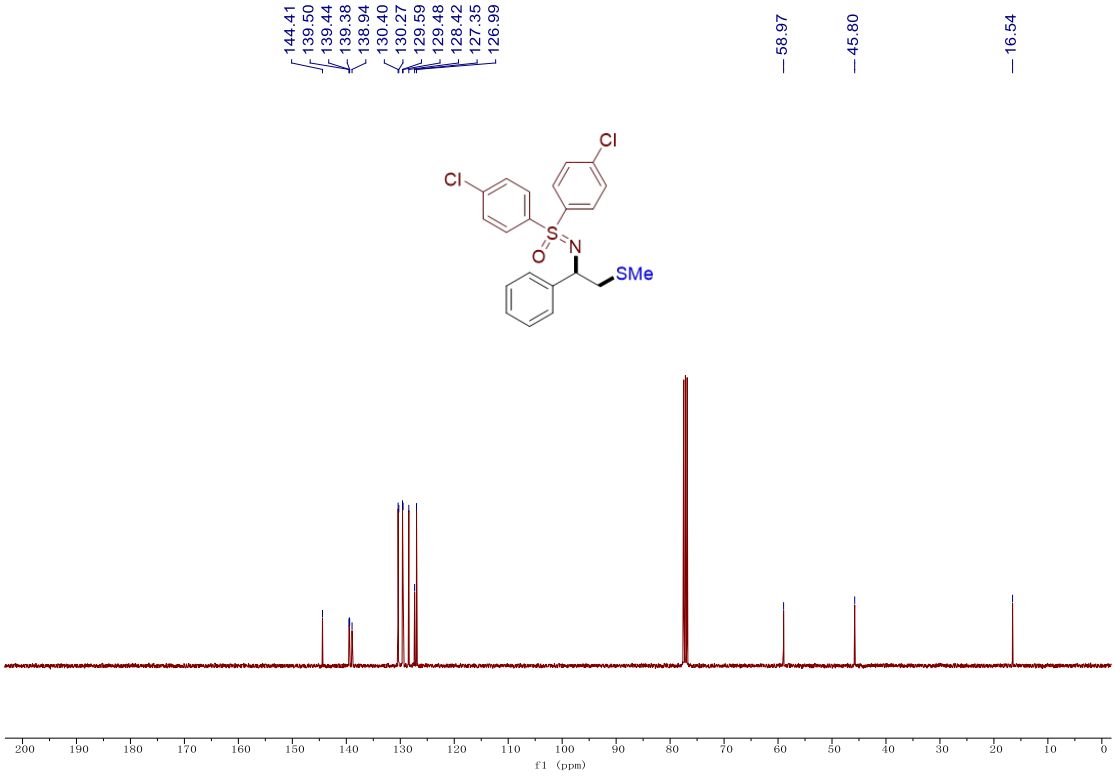
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ak**



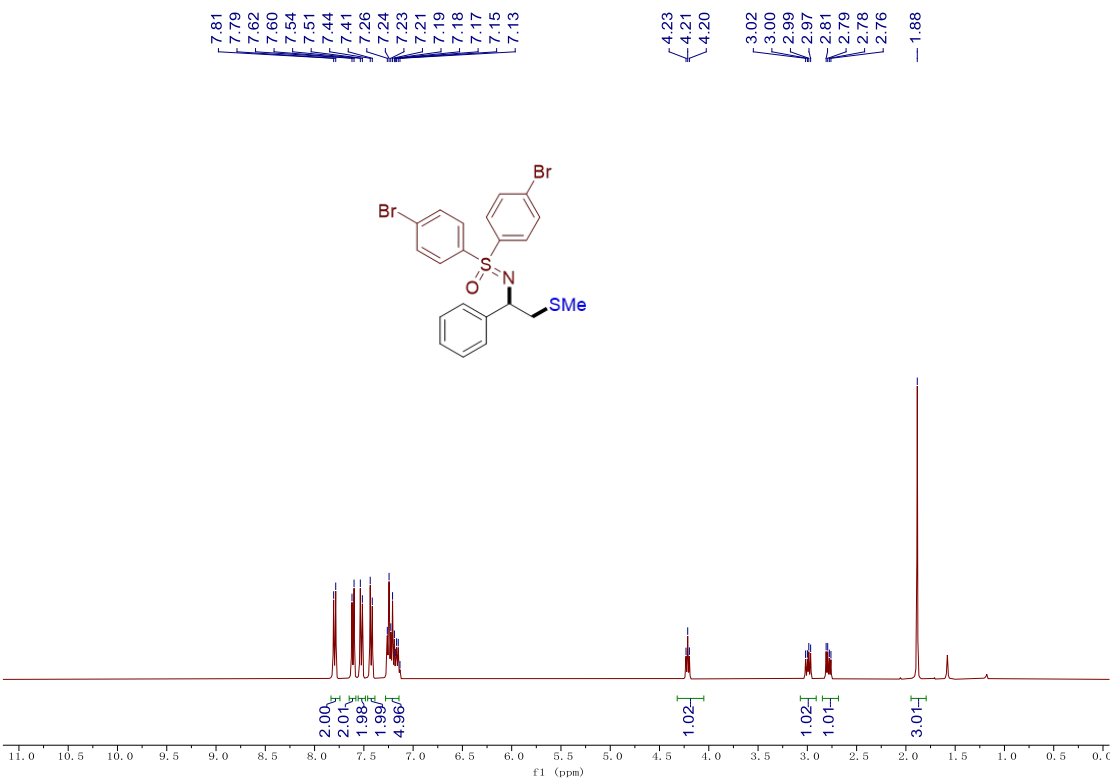
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ak**



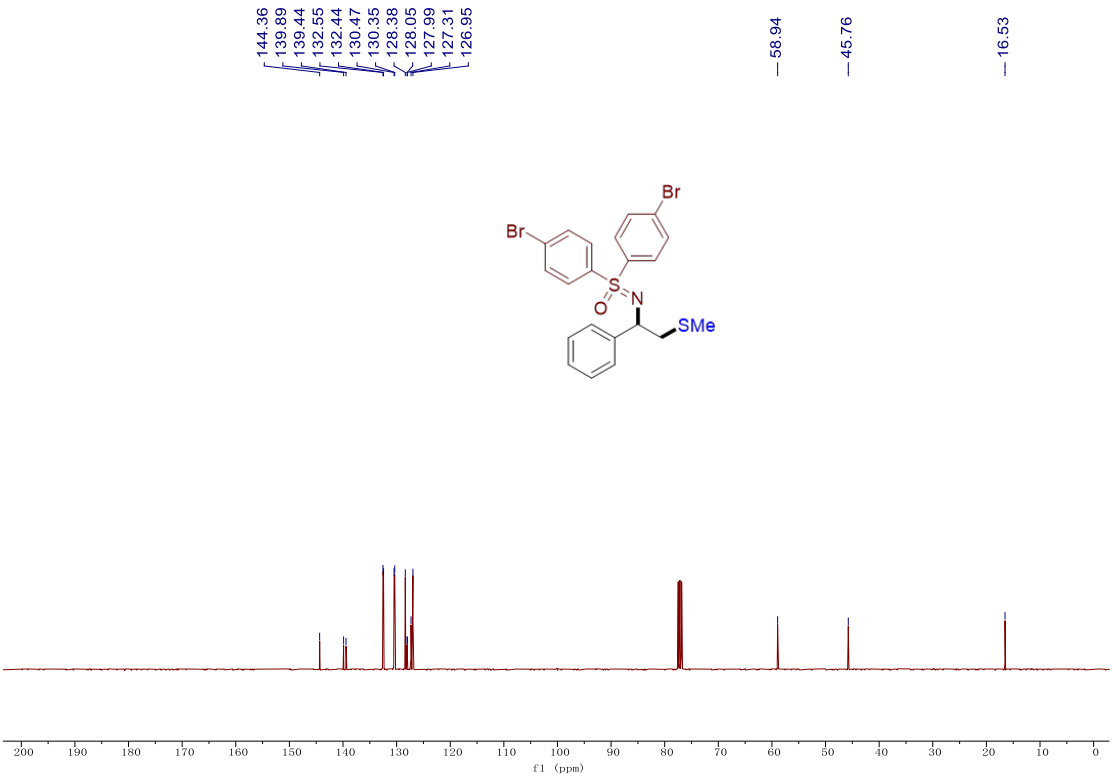
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3al**



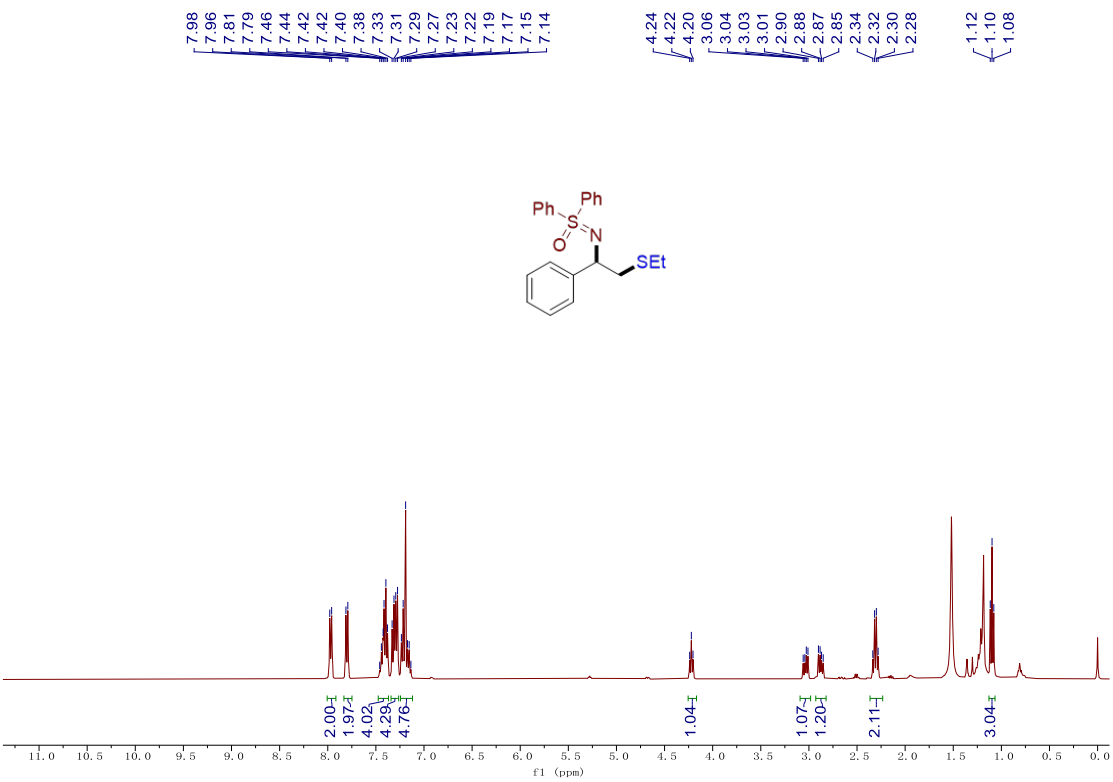
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3al**



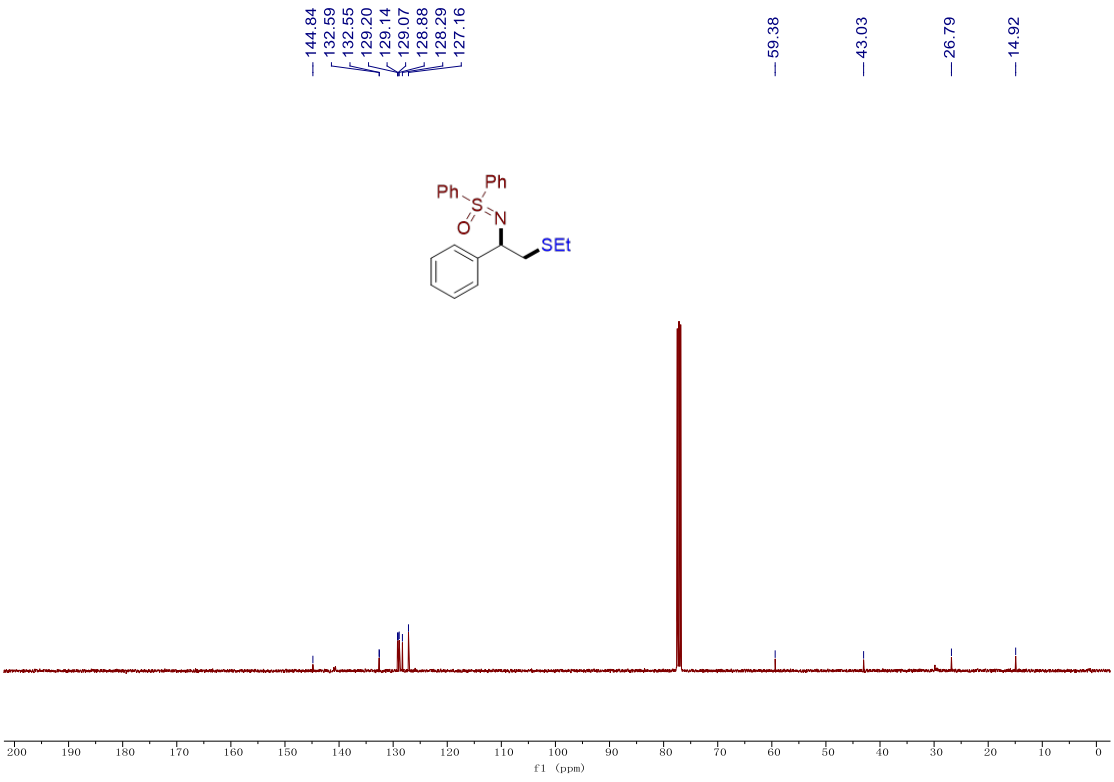
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3am**



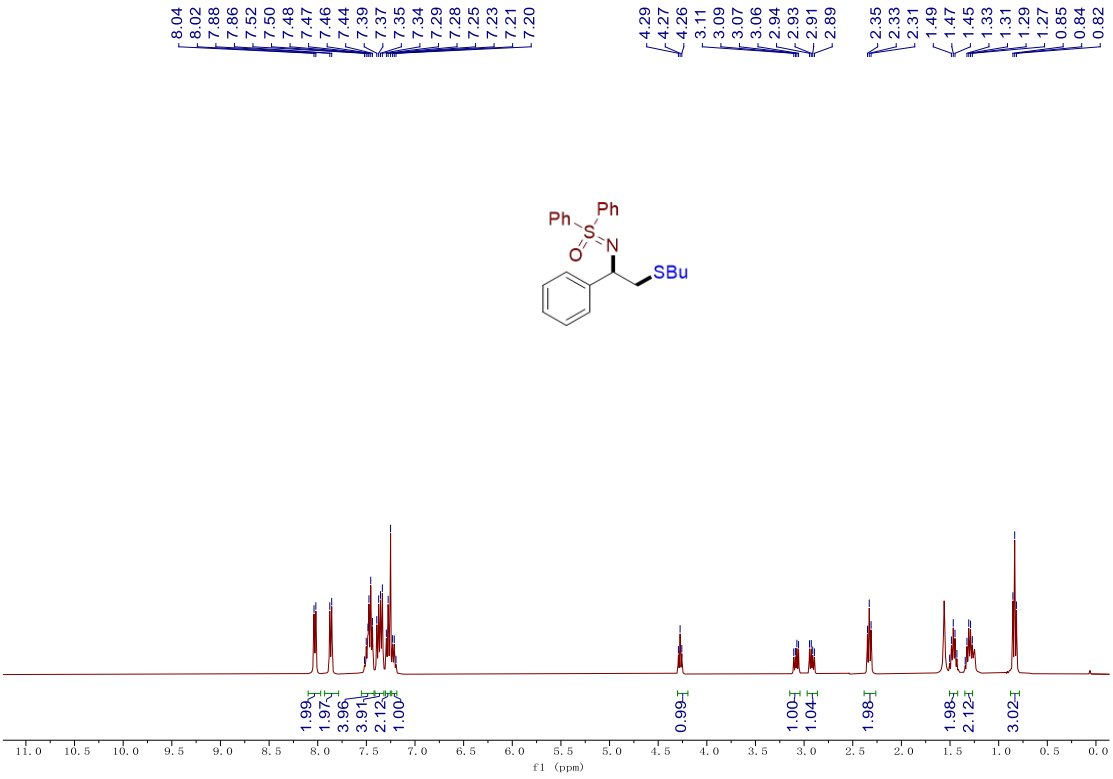
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3am**



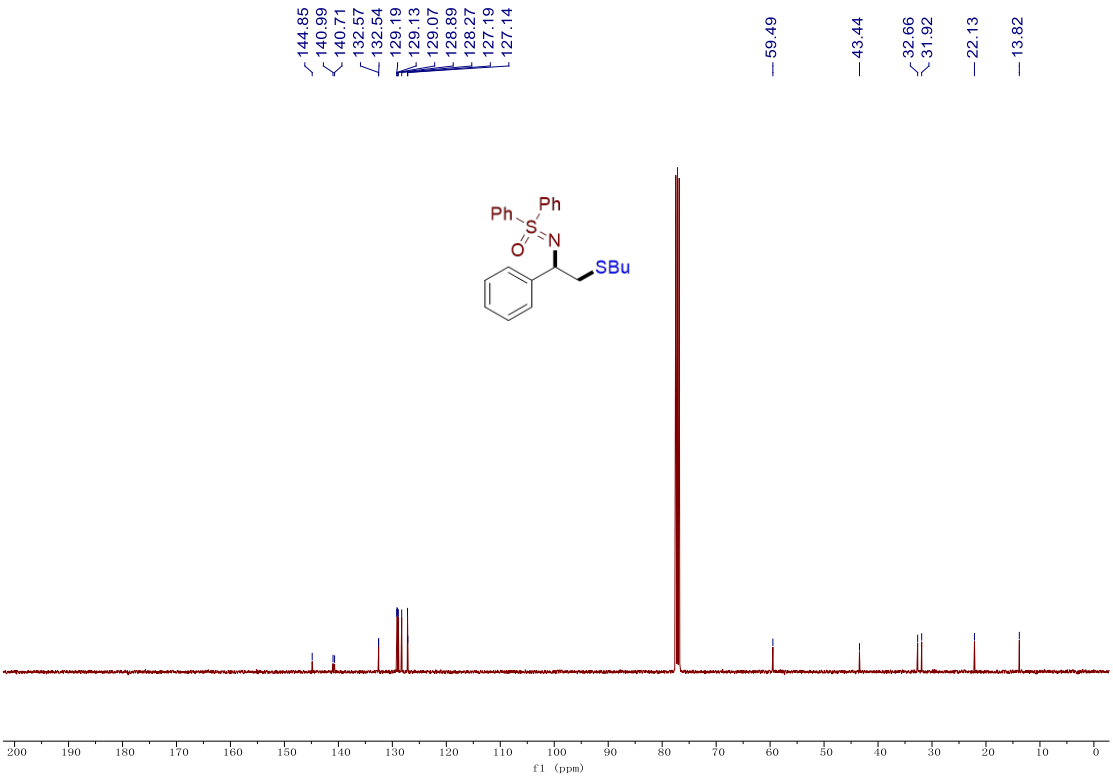
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ao**



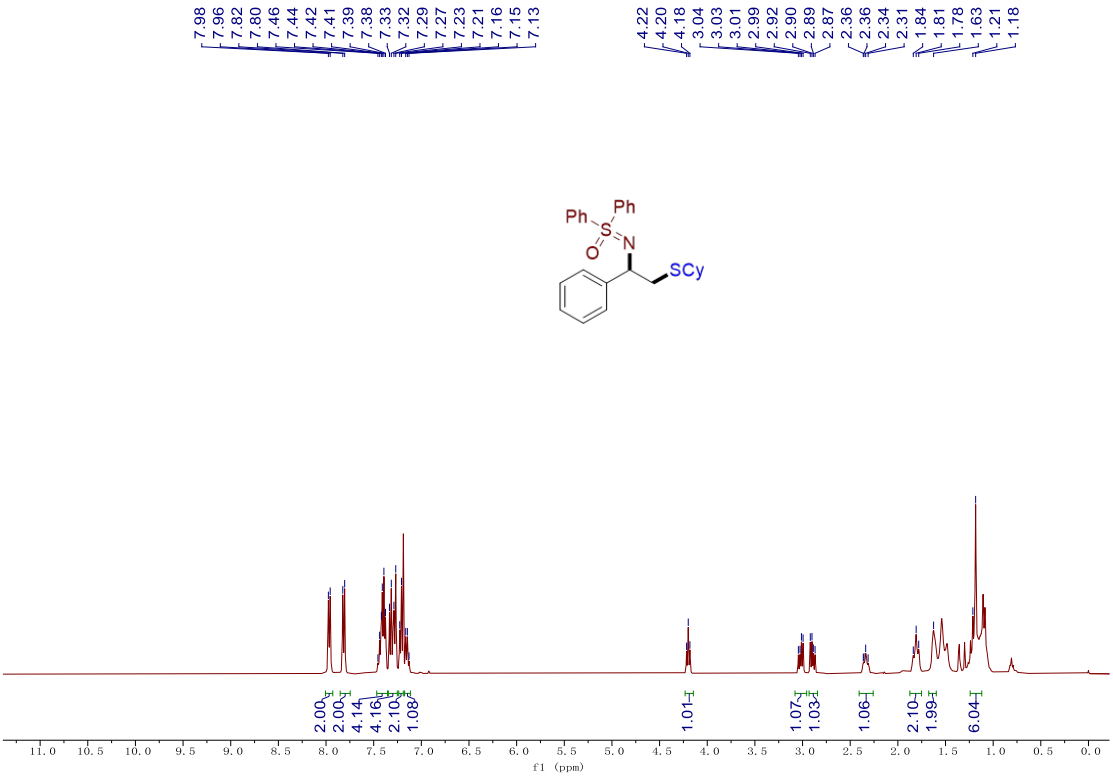
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ao**



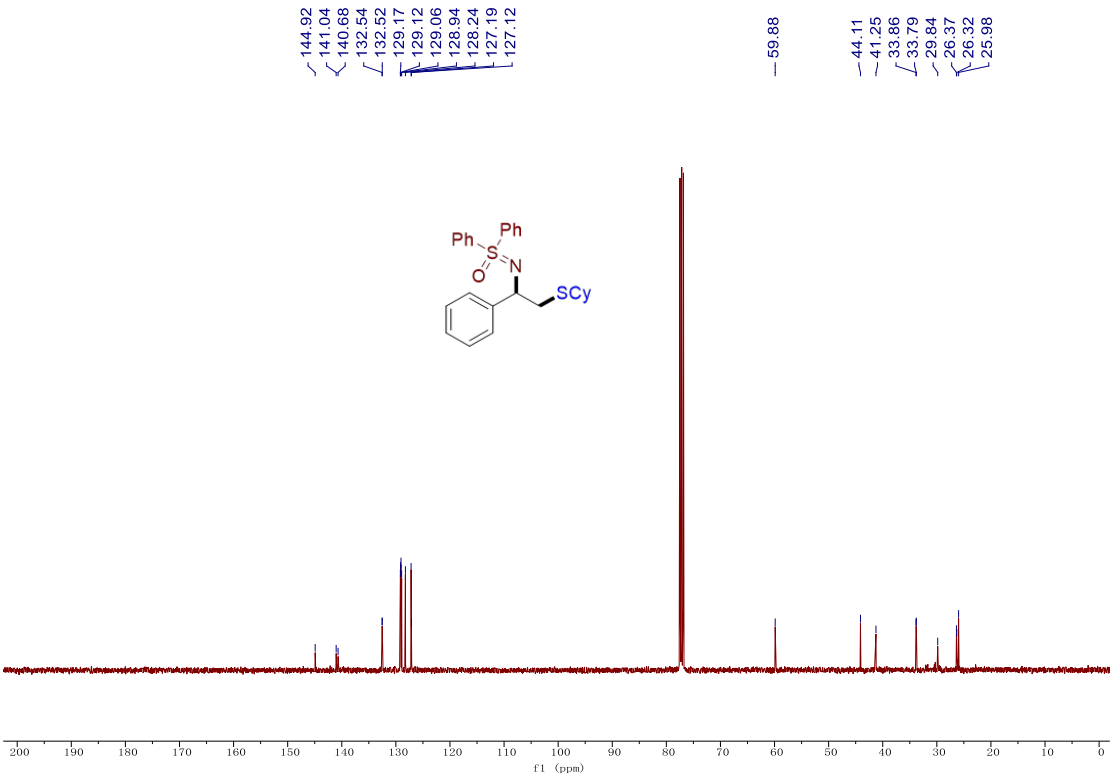
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ap**



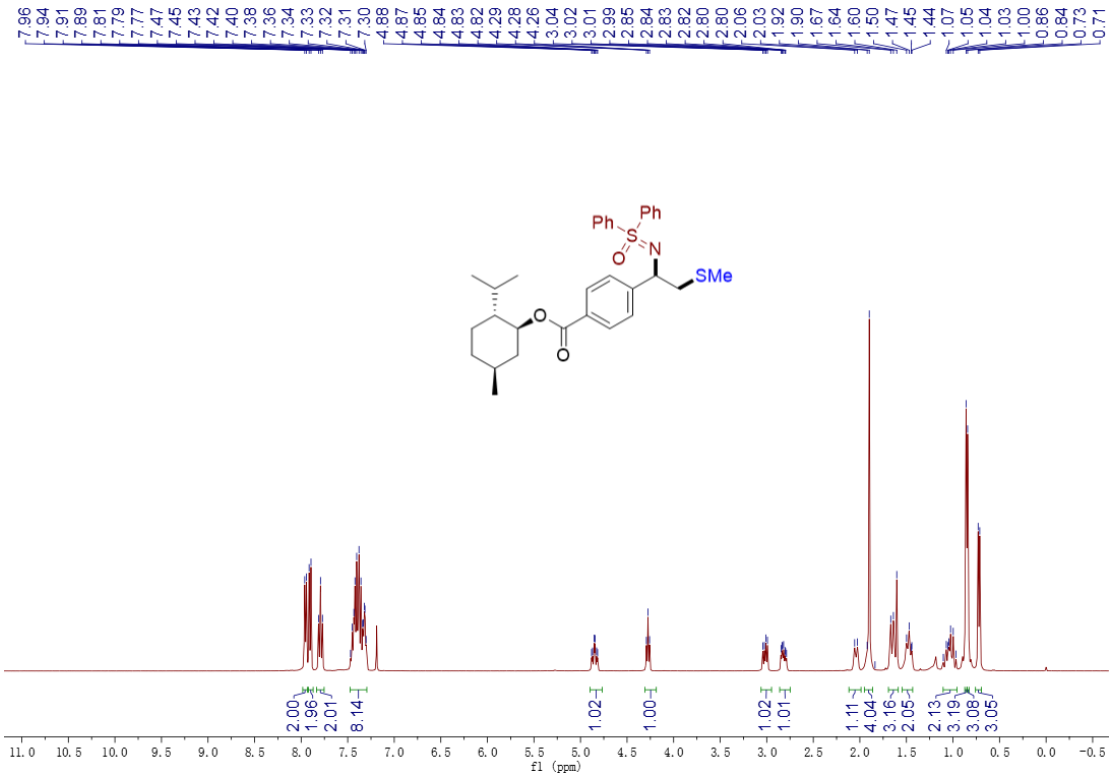
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ap**



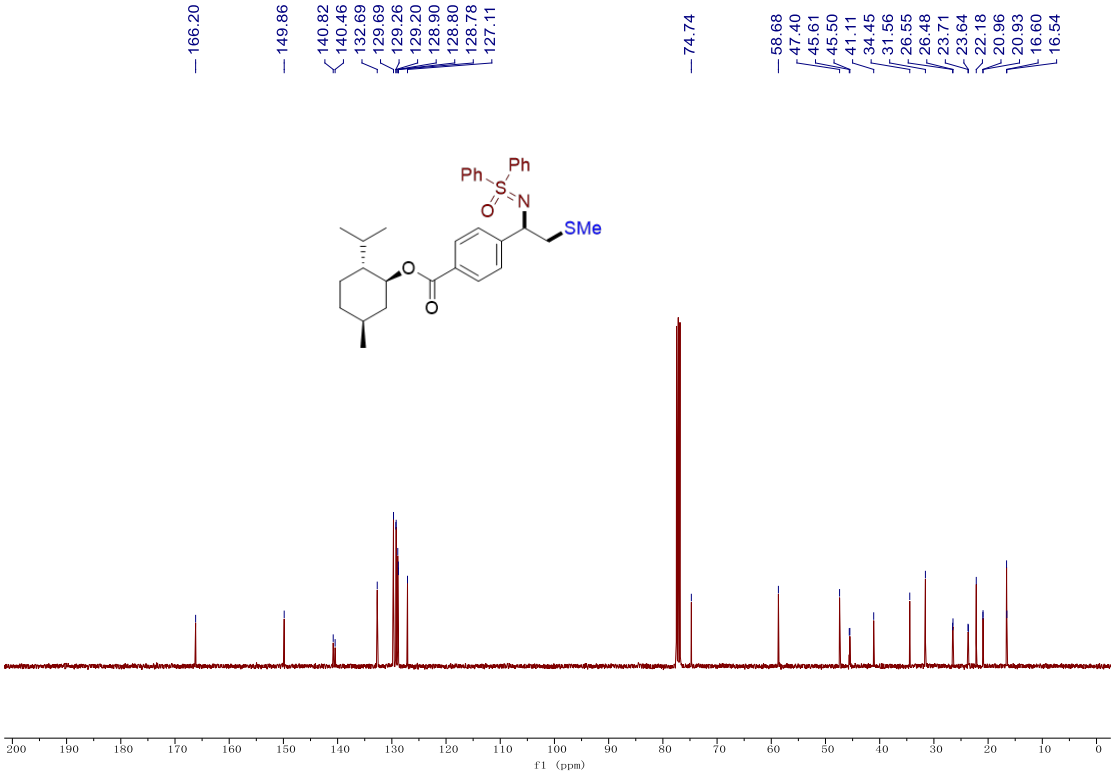
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aq**



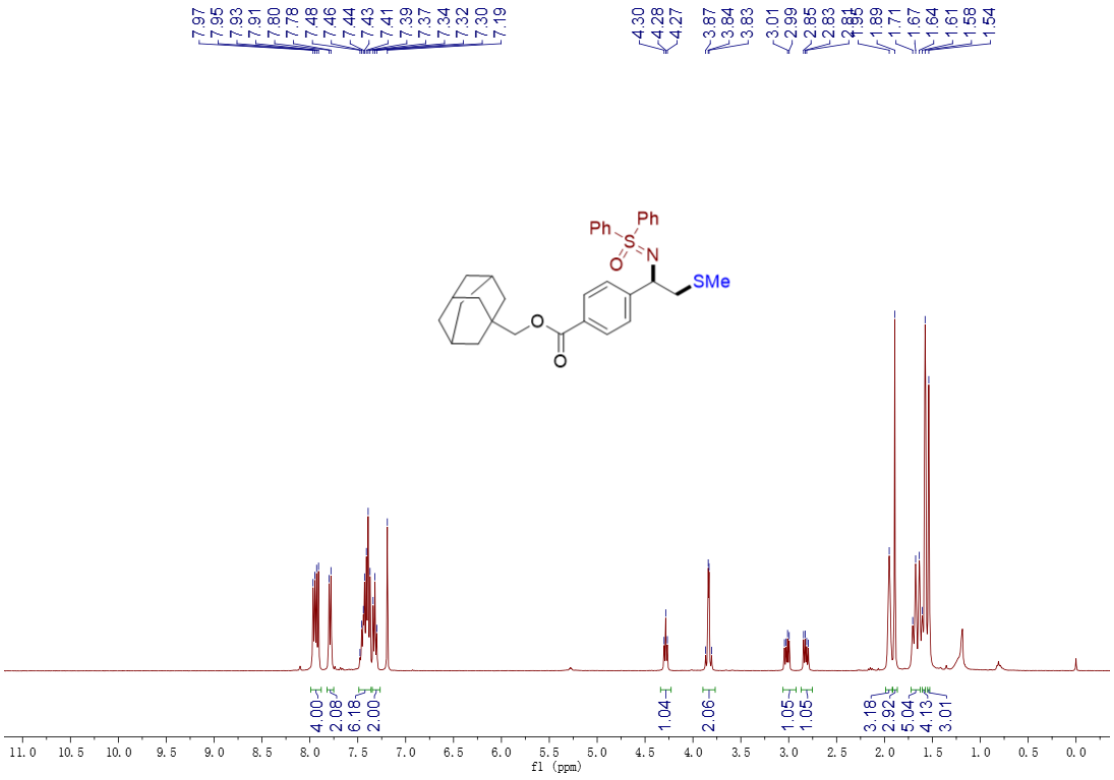
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aq**



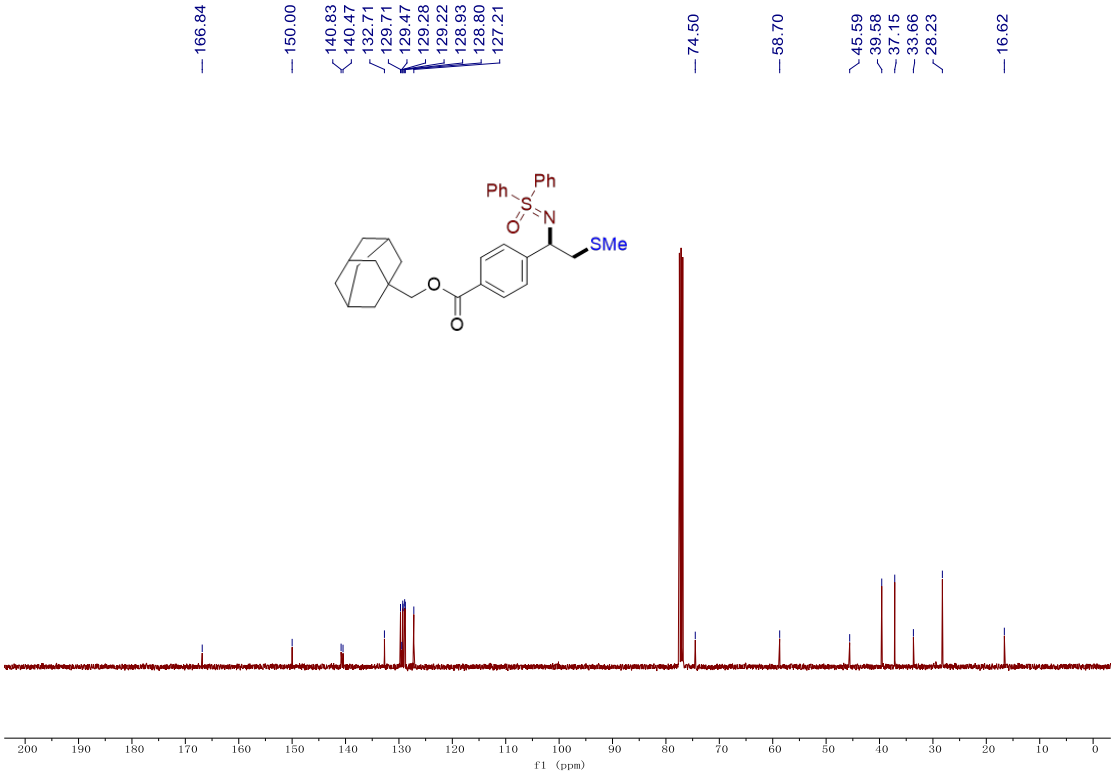
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ya**



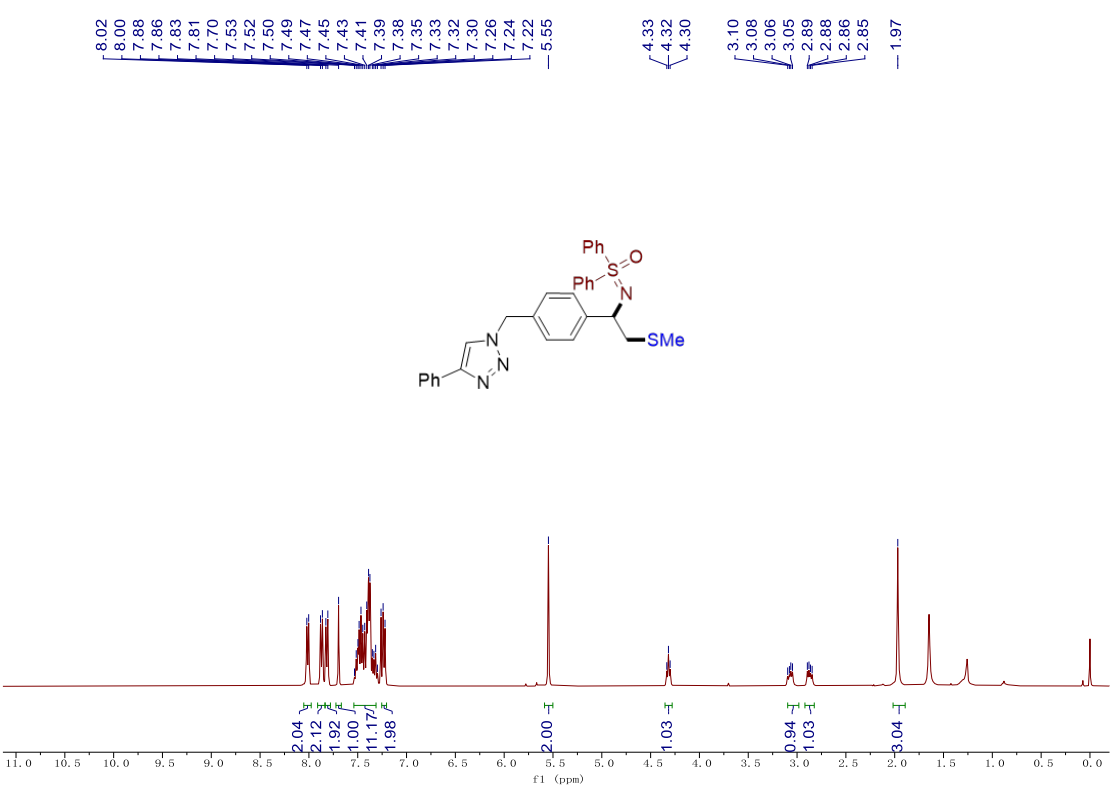
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ya**



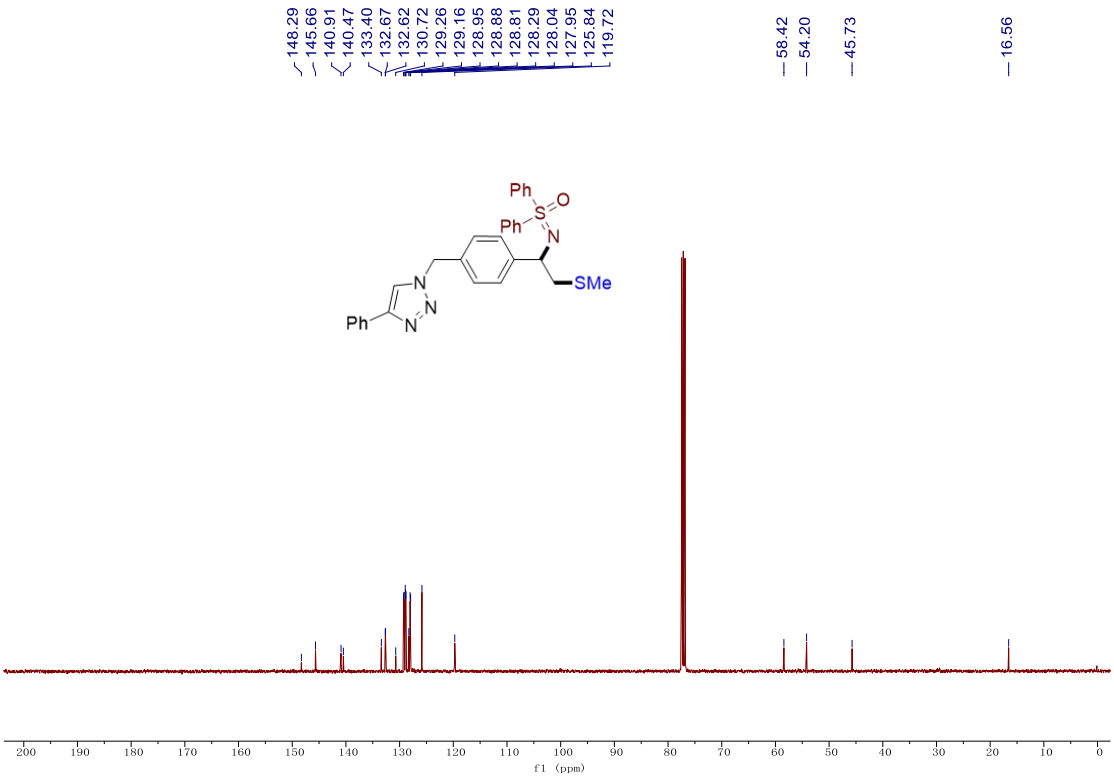
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3za**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3za**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5a**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5a**