Support information

Visible Light-Mediated Three-component Functionalization of Olefins with Sulfoxyimidoylsulfonium Salt for the Synthesis of Amino Alcohols and Amino Ethers

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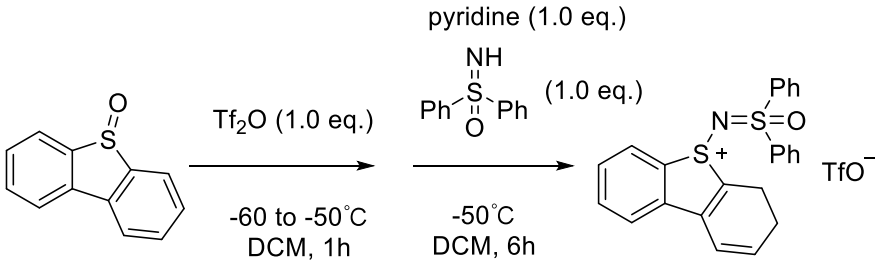
1 General information

Unless otherwise noted, all experiments were carried out in dried glassware under an atmosphere of nitrogen using standard Schlenk techniques. All NMR spectra were recorded on Bruker AV600, and AV400; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS (Me_4Si), using the solvent signals as references and converting the chemical shifts to the TMS(Me_4Si) scale. Coupling constants (*J*) are given in Hz. All high-resolution mass spectra were obtained on ESI(HRMS). Photocatalysis reactions

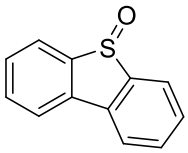
were subjected to irradiation from a blue LED with an input power of 50 W and a maximum wavelength of 455 nm. All solvents were redistilled to give anhydrous dry solvents. All reagents unless otherwise noted were obtained from commercial sources and used without further purification.

2 Experiment Section

2.1 General Procedure for the synthesis of salts 1a

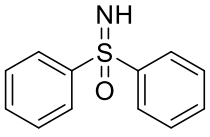


Step 1: Preparation of dibenzothiophene-S-oxide



Dibenzothiophene (1.84 g, 10 mmol, 1.0 eq.) was dissolved in DCM (50 mL) in a 250 mL round bottom flask in an ice bath. m-CPBA (1.72 g, 77% in H_2O, 10 mmol, 1.0 eq.) in water was added in batches over 30 minutes and the resulting white suspension was stirred for a further 3 hours. The reaction was then quenched with saturated aqueous $NaHCO_3$ (50 mL) and the organic layer was extracted with DCM (3 x 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (3 x 20 mL) and saturated NaCl brine (50 mL), dried over anhydrous NaSO4, filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (50% EtOAc/PE) to give (1.42 g, 0.71 mmol, 71%) as a white solid.

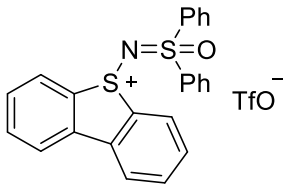
Step 1: Preparation of diphenyl sulfinamide



This experimental synthesis method is modified from the literature[1]. Diphenyl sulfide (1.86 g, 10 mmol, 1.0 eq.) was dissolved in MeOH (100 mL) in a 250 mL round-bottom flask, followed by ammonium carbonate (1.44 g, 15 mmol, 1.5 eq.), then iodobenzeneacetic acid (7.41 g, 23 mmol, 2.3 eq.) and the solution was stirred at room temperature for 45 min. After. After the diphenyl sulfide had disappeared (by TLC thin-plate examination), the solvent was removed under reduced pressure. The crude product was purified by silica

gel column chromatography (1.94 g, 9 mmol, 90%) as a white solid.

Step 2: Preparation of salts 1a

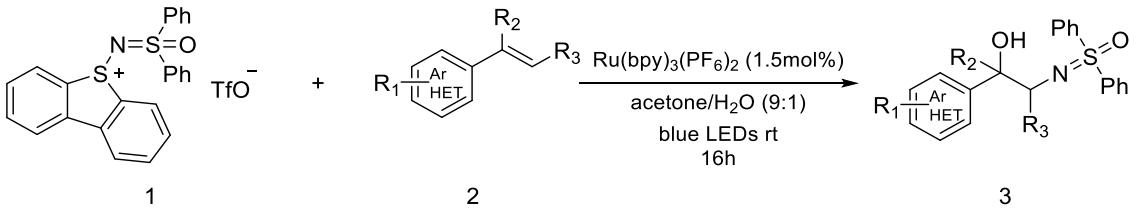


This experimental synthesis method is modified from the literature[2], triflic anhydride (3 mmol, 846 mg, 1.0 eq.) was added dropwise to a stirred solution of dibenzothiophene-S-oxide (3 mmol, 600 mg, 1.0 eq.) in dry DCM (25 mL 0.1 M) at a temperature between -60 °C and -50 °C. After stirring the resulting mixture for an additional 1 hour, a mixture of pyridine (3 mmol, 241 uL, 1.0 eq.) and the corresponding diphenyl sulfinamide (3 mmol, 651 mg, 1.0 eq.) dissolved in 5 mL DCM was then added dropwise and the reaction mixture was stirred at -50°C for a further 6 hours. Then, the cooling system was removed, and the formed solution was allowed reaching room temperature. The aqueous Na_2CO_3 solution was added, and the organic phase was separated and dried with anhydrous $NaSO_4$. The solvent was filtered and evaporated under vacuum to give an amorphous oily residue, which was transferred to an aubergine flask and subsequently stirred with anhydrous ether at -10°C until a solid was precipitated, then washed three times with anhydrous ether and dried under vacuum to give, a beige solid (1.1 g, 2 mmol, 67%).

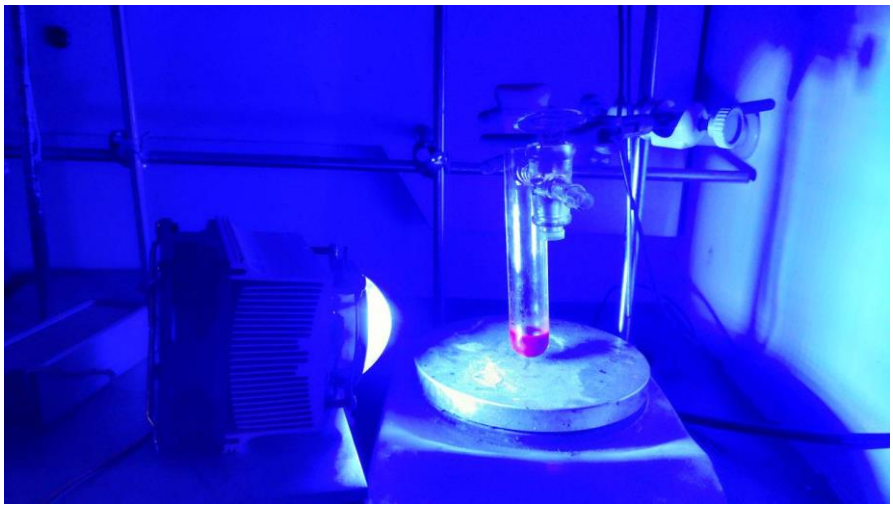
2.2 Preparation of $Ru(bpy)_3(PF_6)_2$

The following experimental steps are based on the literature[3, 4], 2,2'-Bipyridine (941 mg, 3 mmol) and $RuCl_3.2H_2O$ (293 mg, 1.2 mmol) dissolved in ethylene glycol (14 mL) were added to a 50 mL three-necked flask under nitrogen protection, followed by stirring of the reaction solution at 180°C for 3 hours. When the reaction was completed, a solution of KPF6 (808 mg, 4.38 mmol) in H_2O (3.5 mL) was added to the reaction mixture and a red solid precipitated. The red solid was completely dissolved in acetone by filtration of the precipitate under reduced pressure, washed with a small amount of water and ether was added to crystallise the red solid $Ru(bpy)_3(PF_6)_2$ (850 mg, 80%; acetone/ether, 1/1, v/v).

2.3 General Procedure for Amino alcohols

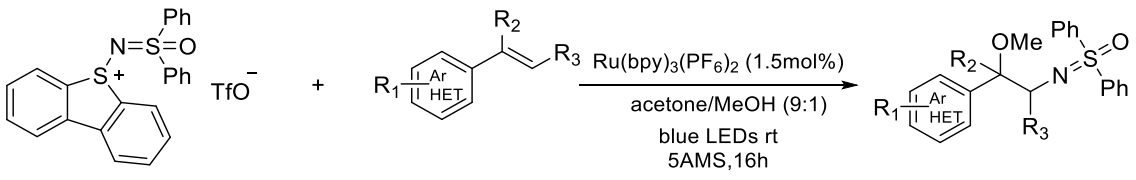


1 2 3



Under a nitrogen atmosphere, a dry schlenk tube was charged with sulfonium salt 1 (0.1 mmol, 55 mg, 1 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.3 mg, 1.5 μmol, 1.5 mol%), styrene compound 2a (0.6 mmol, 6 equiv.) and degassed wet acetone (2 mL, acetone/H_2O, 9/1, v/v). After illumination with a blue LED and magnetic stirring for 16 hours at room temperature, the reaction solution was concentrated and the product purified by column chromatography (SiO_2, EtOAc and PE as eluents).

2.4 General Procedure for Amino ethers



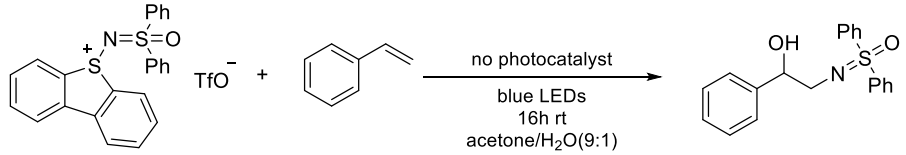
1 2a 3

Under a nitrogen atmosphere, a dry schlenk tube was charged with sulfonium salt 1 (0.1 mmol, 55 mg, 1 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.3 mg, 1.5 μmol, 1.5 mol%), styrene

compound 2a (0.6 mmol, 6 equiv.), 100mg 5A dried molecular sieves, degassed dried acetone (1.8 mL) and degassed dried MeOH (0.2mL). After illumination with a blue LED and magnetic stirring for 16 hours at room temperature, the reaction solution was concentrated and the product purified by column chromatography (SiO_2, EtOAc and PE as eluents).

2.5 Control experiment

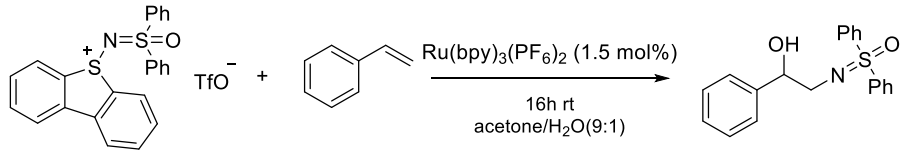
2.5.1 The reaction in the absence of photocatalyst under LED light irradiation



1 2a 3a,0% yield

Under a nitrogen atmosphere, a dry schlenk tube was charged with sulfonium salt 1 (0.1 mmol, 55 mg, 1 equiv.), styrene compound 2a (0.6 mmol, 6 equiv.), and degassed wet acetone (2 mL, acetone/H_2O, 9/1, v/v). After illumination with a blue LED and magnetic stirring for 16 hours at room temperature, no corresponding target product 3a was detected.

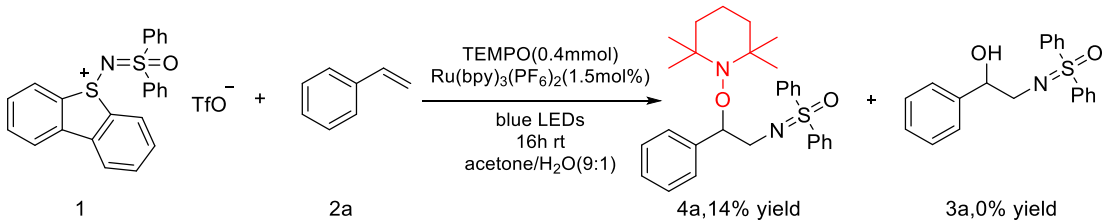
2.5.2 The reaction in the presence of photocatalyst without LED light irradiation



1 2a 3a,0% yield

Under a nitrogen atmosphere, a dry schlenk tube was charged with sulfonium salt 1 (0.1 mmol, 55 mg, 1 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.3 mg, 1.5 μmol, 1.5 mol%), styrene compound 2a (0.6 mmol, 6 equiv.), and degassed wet acetone (2 mL, acetone/H_2O, 9/1, v/v). Without LED irradiation and magnetic stirring for 16 hours at room temperature, no corresponding target product 3a was detected.

2.5.3 TEMPO trap

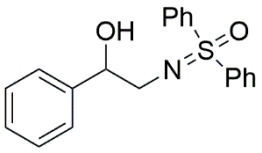


1 2a 4a,14% yield 3a,0% yield

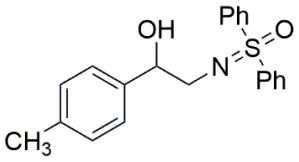
Under a nitrogen atmosphere, a dry schlenk tube was charged with sulfonium salt 1 (0.1 mmol, 55 mg, 1 equiv.), $Ru(bpy)_3(PF_6)_2$ (1.3 mg, 1.5 μmol, 1.5 mol%), styrene compound 2a (0.6 mmol, 6 equiv.), TEMPO (2,2,6,6-tetramethylpiperidine oxide)

(0.4mmol, 62.5mg, 4 equiv.), and degassed wet acetone (2 mL, acetone/H_2O, 9/1, v/v). After illumination with a blue LED and magnetic stirring for 16 hours at room temperature, the reaction solution was concentrated and the product purified by column chromatography (SiO_2, EtOAc and PE as eluents).

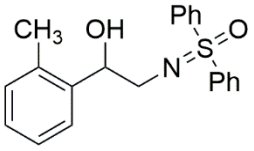
3 Characterization data of products.



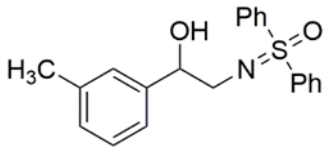
((2-hydroxy-2-phenylethyl)imino)diphenyl-λ^6-sulfanone (3a) was a neutral color and transparent solid (75% yield). R_f=0.3 (pentane/EtOAc, 1.5:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (t, J = 6.9 Hz, 4H), 7.46 – 7.42 (m, 2H), 7.41 – 7.36 (m, 4H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 1H), 4.82 (dd, *J* = 8.8, 3.3 Hz, 1H), 3.52 (s, 1H), 3.30 (dd, *J* = 12.5, 3.3 Hz, 1H), 3.03 (dd, *J* = 12.5, 8.9 Hz, 1H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 142.03 , 140.13 , 132.75 , 129.31 , 128.52 , 128.19 , 127.42 , 126.15 , 74.33 , 52.55 ;**HRMS(ESI)**: $[M+H]^+$ calcd for $C_{20}H_{20}NO_2S$, 338.1216; found: 338.1209.



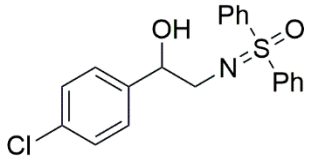
((2-hydroxy-2-(p-tolyl)ethyl)imino)diphenyl-λ^6-sulfanone (3b) was a neutral color and transparent solid (76% yield). R_f = 0.3 (pentane/EtOAc, 1.5:1); ^{1}H NMR 1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, J = 8.1 Hz, 4H), 7.51 – 7.46 (m, 6H), 7.27 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 4.86 (dd, J = 9.0, 3.3 Hz, 1H), 3.57 (s, 1H), 3.34 (dd, J = 12.4, 3.3 Hz, 1H), 3.08 (dd, J = 12.4, 9.0 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.25 , 139.02 , 137.02 , 132.69 , 129.27 , 128.87 , 128.53 , 126.07 , 74.24 , 52.62 , 21.14 . **HRMS(ESI)**: $[M+H]^-$ calcd for $C_{21}H_{22}NO_2S$, 352.1378; found: 352.1356.



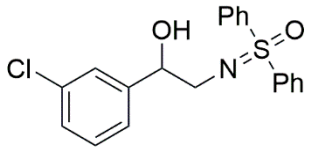
((2-hydroxy-2-(o-tolyl)ethyl)imino)diphenyl-λ^6-sulfanone (3c) was a neutral color and transparent solid (70% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 20.7, 7.9 Hz, 4H), 7.49 – 7.44 (m, 3H), 7.41 (q, *J* = 8.0 Hz, 4H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 5.04 (d, *J* = 8.7 Hz, 1H), 3.26 (d, *J* = 12.6 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.19 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 138.96 , 133.61 , 131.74 , 129.07 , 128.28 , 127.51 , 126.13 , 124.97 , 124.70 , 70.13 , 50.12 , 18.06 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1378; found: 352.1366.



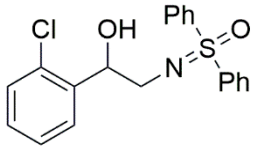
((2-hydroxy-2-(m-tolyl)ethyl)imino)diphenyl-λ^6-sulfanone (3d) was a neutral color and transparent solid (84% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 4H), 7.46 – 7.43 (m, 2H), 7.43 – 7.38 (m, 4H), 7.15 – 7.09 (m, 3H), 7.00 – 6.96 (m, 1H), 4.81 – 4.78 (m, 1H), 3.29 (d, *J* = 12.4 Hz, 1H), 3.02 (t, *J* = 8.0 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.85 , 140.05 , 137.83 , 132.78 , 129.32 , 128.54 , 128.19 , 128.11 , 126.78 , 123.24 , 74.34 , 52.59 , 21.48 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1378; found: 352.1366.



((2-(4-chlorophenyl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3e) was a neutral color and transparent solid (57% yield). R_f = 0.25 (pentane/EtOAc, 1.5:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 7.8, 4.9 Hz, 4H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.40 (q, *J* = 7.1 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 4.78 (dd, *J* = 8.6, 3.3 Hz, 1H), 3.57 (s, 1H), 3.27 (d, *J* = 11.0 Hz, 1H), 2.98 (dd, *J* = 12.5, 8.5 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.63 , 140.13 , 133.00 , 132.77 , 129.34 , 128.47 , 128.29 , 127.55 , 73.70 , 52.44 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{19}ClNO_2S$, 372.0827; found: 372.0815.

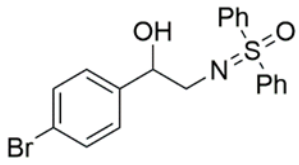


((2-(3-chlorophenyl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3f) was a neutral color and transparent solid (57% yield). R_f = 0.25 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 11.8, 7.5 Hz, 4H), 7.56 – 7.51 (m, 2H), 7.49 (q, *J* = 7.0 Hz, 4H), 7.40 (s, 1H), 7.25 (s, 1H), 7.24 (s, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 4.87 (d, *J* = 8.7 Hz, 1H), 3.66 (s, 1H), 3.37 (dd, *J* = 12.4, 3.4 Hz, 1H), 3.07 (dd, *J* = 12.5, 8.5 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.23 , 140.07 , 134.13 , 132.80 , 129.44 , 129.35 , 128.49 , 127.49 , 126.36 , 124.34 , 73.68 , 52.33 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{19}ClNO_2S$, 372.0827; found: 372.0816.

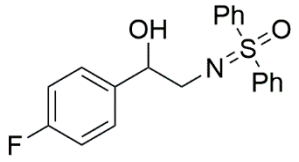


((2-(2-chlorophenyl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3g) was a neutral color and transparent solid (81% yield). R_f = 0.25 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 23.9, 7.6 Hz, 4H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.40 (dt, *J* = 15.2, 7.6 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.19 (dd, *J* = 8.1, 2.8 Hz, 1H), 3.43 (dd, *J* = 12.6, 2.9 Hz, 1H), 2.96 (dd, *J* = 12.5, 8.2 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.06 139.41 , 132.76 , 131.92 , 129.28 , 129.13 , 128.49 ,

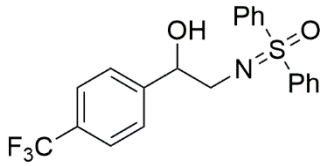
128.39 , 127.74 , 126.81 , 71.02 , 50.38 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{19}ClNO_2S$, 372.0827; found: 372.0820.



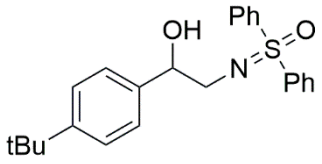
((2-(4-bromophenyl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3h) was a neutral color and transparent solid (72% yield). R_f = 0.3 (pentane/EtOAc, 1.5:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 7.4 Hz, 4H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.41 (q, *J* = 7.5 Hz, 4H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.15 (m, 2H), 4.78 (dd, *J* = 8.6, 3.1 Hz, 1H), 3.62 (s, 1H), 3.28 (dd, *J* = 12.5, 3.0 Hz, 1H), 2.98 (dd, *J* = 12.4, 8.7 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.08 , 139.77 , 132.94 , 131.26 , 129.40 , 128.49 , 127.90 , 121.16 , 73.58 , 52.32 . **HRMS(ESI):** $[M+H]^+$ calcd for $C_{21}H_{19}BrNO_2S$, 416.0322; found: 416.0323.



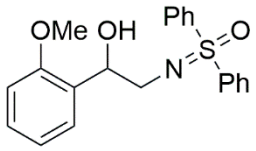
((2-(4-fluorophenyl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3i) was a neutral color and transparent solid (45% yield). R_f = 0.3 (pentane/EtOAc, 1.5:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 8.1 Hz, 4H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.28 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.92 (t, *J* = 8.7 Hz, 2H), 4.81 (dd, *J* = 8.8, 3.1 Hz, 1H), 3.61 (s, 1H), 3.27 (dd, *J* = 12.5, 3.2 Hz, 1H), 3.00 (dd, *J* = 12.5, 8.9 Hz, 1H).**^{13}C NMR** (151 MHz, Chloroform-*d*) δ162.18 (d, J = 244.6 Hz), 139.89 , 137.71 , 132.89 , 129.38 , 128.49 , 127.74 , 114.91 , 73.66 , 52.50 .**^{19}F NMR** (565 MHz, Chloroform-*d*) δ -115.42 .**HRMS(ESI):** $[M+H]^+$ calcd for $C_{21}H_{19}FNO_2S$, 356.1122; found: 356.1117.



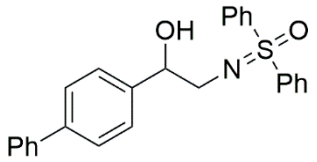
((2-hydroxy-2-(4-(trifluoromethyl)phenyl)ethyl)imino)diphenyl-λ^6-sulfanone (3j) was a neutral color and transparent solid (45% yield). R_f = 0.25 (pentane/EtOAc, 1.5:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 10.6, 7.8 Hz, 4H), 7.56 (t, *J* = 7.5 Hz, 3H), 7.54 – 7.51 (m, 3H), 7.50 – 7.45 (m, 4H), 4.94 (dd, *J* = 8.4, 3.0 Hz, 1H), 3.48 (s, 1H), 3.40 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.08 (dd, *J* = 12.5, 8.6 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 146.16 , 140.04 , 132.83 , 129.38 (dd, *J* = 10.8, 4.3 Hz), 128.43 (t, *J* = 4.9 Hz), 127.97 , 126.43 , 126.05 , 125.09 (q, *J* = 3.7 Hz), 73.75 , 52.42 .**^{19}F NMR** (565 MHz, Chloroform-d) δ -62.39 .**HRMS(ESI):** $[M+H]^+$ calcd for $C_{21}H_{19}F_3NO_2S$, 406.1090; found: 406.1085.



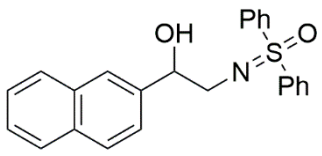
((2-(4-(tert-butyl)phenyl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3k) was a neutral color and transparent solid (50% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.1 Hz, 4H), 7.47 – 7.43 (m, 2H), 7.40 (q, *J* = 8.2, 7.2 Hz, 4H), 7.26 (t, *J* = 5.9 Hz, 4H), 4.83 – 4.78 (m, 1H), 3.31 – 3.27 (m, 1H), 3.04 (dd, *J* = 11.2, 9.2 Hz, 1H), 1.21 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 150.33 , 140.28 , 138.93 , 132.67 , 129.28 , 128.54 , 125.86 , 125.09 , 74.23 , 52.54 , 34.49 , 31.38 . **HRMS(ESI):** $[M+H]^+$ calcd for $C_{24}H_{28}NO_2S$, 394.1842; found: 394.1841.



((2-hydroxy-2-(2-methoxyphenyl)ethyl)imino)diphenyl-λ^6-sulfanone (3l) was a neutral color and transparent solid (74% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 32.9, 7.6 Hz, 4H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 (dd, *J* = 14.9, 7.8 Hz, 4H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.14 (dd, *J* = 7.8, 3.3 Hz, 1H), 3.64 (s, 3H), 3.41 (dd, *J* = 12.3, 3.3 Hz, 1H), 3.00 (dd, *J* = 12.3, 7.9 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 156.25 , 132.68 , 130.27 , 129.23 , 128.62 , 128.12 , 126.99 , 120.51 , 110.05 , 69.46 , 55.12 , 50.35 . **HRMS(ESI):** $[M+H]^+$ calcd for $C_{21}H_{22}NO_3S$, 368.1322; found: 368.1315.

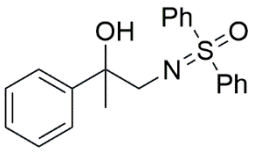


((2-([1,1'-biphenyl]-4-yl)-2-hydroxyethyl)imino)diphenyl-λ^6-sulfanone (3m) was a neutral color and transparent solid (52% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.94 (t, *J* = 6.8 Hz, 4H), 7.55 (dd, *J* = 11.7, 7.9 Hz, 4H), 7.46 (q, *J* = 7.9, 6.8 Hz, 7H), 7.41 (t, *J* = 7.7 Hz, 3H), 4.95 (dd, *J* = 8.7, 3.2 Hz, 1H), 3.68 (s, 1H), 3.42 (dd, *J* = 12.5, 3.3 Hz, 1H), 3.15 (dd, *J* = 12.5, 8.8 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.18 , 141.04 , 140.35 , 140.19 , 132.76 , 129.32 , 128.77 , 128.54 , 127.95 , 127.11 , 126.97 , 126.62 , 74.16 , 52.57 . **HRMS(ESI):** $[M+H]^+$ calcd for $C_{26}H_{24}NO_2S$, 414.1529; found: 414.1526.

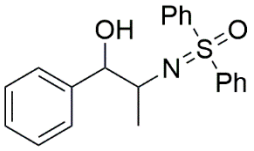


((2-hydroxy-2-(naphthalen-2-yl)ethyl)imino)diphenyl-λ^6-sulfanone (3n) was a neutral color and transparent solid (40% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 12.8, 7.9 Hz, 4H), 7.88 (s, 1H), 7.79 (t, *J*

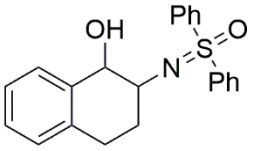
= 7.9 Hz, 3H), 7.49 (d, *J* = 7.8 Hz, 3H), 7.43 (dt, *J* = 13.9, 7.7 Hz, 6H), 5.07 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.47 (dd, *J* = 12.6, 3.3 Hz, 1H), 3.19 (dd, *J* = 12.5, 8.7 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.15 , 139.55 , 133.30 , 132.96 , 132.73 , 129.32 , 128.51 , 127.98 , 127.81 , 127.65 , 125.97 , 125.66 , 124.87 , 124.43 , 74.44 , 52.52 . **HRMS(ESI):** $[M+H]^+$ calcd for $C_{24}H_{22}NO_2S$, 388.1373; found: 388.1372.



((2-hydroxy-2-phenylpropyl)imino)diphenyl-λ^6-sulfanone (3o) was a neutral color and transparent solid (81% yield). R_f = 0.4 (pentane/EtOAc, 8:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.49 (q, *J* = 8.7, 7.8 Hz, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 4.9 Hz, 1H), 3.74 (s, 1H), 3.30 (d, *J* = 11.9 Hz, 1H), 3.21 (d, *J* = 11.9 Hz, 1H), 1.60 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.06 , 140.57 , 132.52 , 129.22 , 128.64 , 128.33 , 127.95 , 126.52 , 125.30 , 74.06 , 55.36 , 27.39 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1373; found: 352.1365.

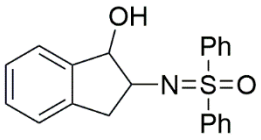


((1-hydroxy-1-phenylpropan-2-yl)imino)diphenyl-λ^6-sulfanone (3p) was a neutral color and transparent solid (70% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR 1H NMR (600 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 7.85 – 7.81 (m, 2H), 7.54 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 7.32 (dt, J = 14.9, 7.5 Hz, 4H), 7.24 (d, J = 7.1 Hz, 1H), 4.81 (d, J = 4.3 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.25 (s, 1H), 1.08 (d, J = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.65 , 132.57 , 132.48 , 129.15 , 128.55 , 127.89 , 127.11 , 126.77 , 78.25 , 56.49 , 18.23 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1373; found: 352.1370.

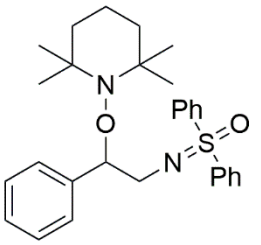


((1-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)imino)diphenyl-λ^6-sulfanone (3q) was a neutral color and transparent solid (75% yield). R_f = 0.3 (pentane/EtOAc, 2:1); ^{1}H NMR (600 MHz, Chloroform-*d*) (major isomer) δ 8.10 (d, *J* = 7.4 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.50 (dt, *J* = 12.8, 7.7 Hz, 6H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 4.72 (d, *J* = 8.3 Hz, 1H), 3.46 (s, 1H), 3.24 (ddd, *J* = 11.7, 8.4, 3.7 Hz, 1H), 2.86 (dd, *J* = 18.8, 2.8 Hz, 1H), 2.81 (dd, *J* = 11.4, 5.6 Hz, 1H), 2.17 (dd, *J* = 5.8, 3.3 Hz, 1H), 2.11 (dd, *J* = 12.2, 6.1 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) (major isomer) δ 137.74 , 135.69 , 132.77 , 132.69 , 129.38 , 129.28 , 128.72 , 128.62 , 127.96 , 127.47 , 126.89 , 126.13 , 74.33 , 59.53 , 30.91 , 28.55. **^{1}H NMR** (600 MHz, Chloroform-d) (minor isomer) δ 8.05 – 7.99 (m, 4H), 7.54 – 7.52 (m, 2H), 7.50 (t, J = 7.4 Hz, 4H), 7.47 – 7.44 (m, 1H), 7.20 – 7.15 (m, 2H), 7.10 – 7.04 (m, 1H), 4.68 (d, J = 3.4 Hz, 1H), 3.57 (dt, J = 9.9, 2.9 Hz, 1H), 3.48 (s, 1H), 3.02 (dt, J = 16.9, 5.0 Hz, 1H), 2.71 (ddd, J = 16.3, 9.7, 5.7 Hz, 1H), 2.27 (dq, J = 13.9, 4.6 Hz, 0H), 1.94

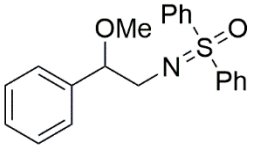
– 1.83 (m, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) (minor isomer) δ 137.03, 136.36, 132.81, 130.12, 129.35, 129.27 , 128.69 , 128.42 , 127.63 , 125.98 , 70.66 , 55.51 , 27.73 , 27.41 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{22}H_{22}NO_2S$, 364.1373; found: 364.1369.



((1-hydroxy-2,3-dihydro-1H-inden-2-yl)imino)diphenyl-λ^6-sulfanone(3r) was a neutral color and transparent solid (57% yield). R_f = 0.3 (pentane/EtOAc, 2:1);^{1}H NMR (600 MHz, Chloroform-*d*) (major isomer) δ 8.01 (dd, J = 15.2, 8.1 Hz, 4H), 7.50 (dp, J = 22.7, 7.5 Hz, 7H), 7.24 – 7.15 (m, 3H), 4.91 (d, J = 5.4 Hz, 1H), 4.00 (q, J = 6.1 Hz, 1H), 3.73 (s, 1H), 3.17 (dd, J = 15.6, 6.1 Hz, 1H), 2.99 (dd, J = 15.6, 6.8 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-d) (major isomer) δ 143.06 , 141.75 , 140.19 , 132.78 , 129.39 , 128.70 , 128.37 , 126.74 , 125.35 , 124.85 , 76.19 , 58.74 , 39.59 .**^{1}H NMR** (600 MHz, Chloroform-*d*) (minor isomer) δ 8.11 (d, J = 7.3 Hz, 2H), 7.95 (d, J = 7.0 Hz, 2H), 7.49 (tt, J = 14.2, 6.7 Hz, 6H), 7.35 (d, J = 7.0 Hz, 1H), 7.18 (dt, J = 14.0, 7.1 Hz, 2H), 7.13 (d, J = 7.0 Hz, 1H), 5.11 (d, J = 7.4 Hz, 1H), 3.73 (s, 1H), 3.61 (q, J = 7.8 Hz, 1H), 3.15 – 3.04 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) (major isomer) δ 142.63, 139.36, 132.79, 129.26, 128.96, 128.38, 127.67, 126.84, 124.29, 123.69, 81.58, 66.75 , 38.66. **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{22}H_{20}NO_2S$, 350.1216; found: 350.1200.

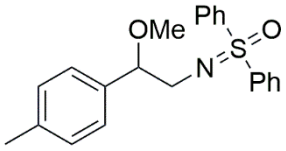


diphenyl((2-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)imino)- λ^6-sulfanone (4a) was a neutral color and transparent solid (14% yield). R_f = 0.4 (pentane/EtOAc, 8:1);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 3H), 7.37 (d, *J* = 4.5 Hz, 6H), 7.30 (dt, *J* = 15.5, 7.4 Hz, 3H), 4.90 (dd, *J* = 9.2, 4.4 Hz, 1H), 3.83 (dd, *J* = 11.7, 4.4 Hz, 1H), 3.14 – 3.04 (m, 1H), 1.25 (s, 12H), 1.13 (s, 2H), 1.00 (s, 2H), 0.67 (s, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 143.58 , 141.10 , 132.14 , 131.94 , 128.90 , 128.45 , 127.57 , 126.96 , 87.88 , 48.08 , 40.46 , 29.70 , 17.18 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{29}H_{37}N_2O_2S$, 477.2577; found: 477.2577.

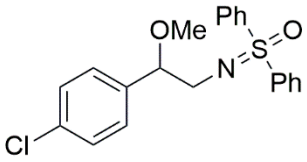


((2-methoxy-2-phenylethyl)imino)diphenyl-l6-sulfanone (3aa) was a neutral color and transparent solid (63% yield). R_f = 0.4 (pentane/EtOAc, 2:1);^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.0 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.39 (m, 5H), 7.38 – 7.34 (m, 5H), 4.45 – 4.39 (m, 1H), 3.39 (dd, *J* = 12.6, 6.8 Hz, 1H), 3.31 (s, 3H), 3.18 (dd, *J* = 12.6, 5.6 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 141.09 , 140.80 , 132.20 , 128.99 , 128.66 ,

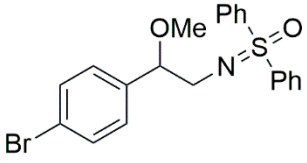
128.16 , 127.60 , 127.29 , 85.16 , 57.13 , 50.21 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S$, 352.1373; found: 352.1365.



((2-methoxy-2-(p-tolyl)ethyl)imino)diphenyl-l6-sulfanone (3ab) was a neutral color and transparent solid (50% yield). R_f = 0.4 (pentane/EtOAc, 2:1);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 4.39 (t, *J* = 6.1 Hz, 1H), 3.37 (dd, *J* = 12.7, 7.0 Hz, 1H), 3.29 (s, 3H), 3.16 (dd, *J* = 12.6, 5.3 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 140.79 , 137.99 , 137.21 , 132.26 , 128.99 , 128.88 , 128.69 , 127.19 , 85.00 , 57.03 , 50.35 , 21.23 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{22}H_{24}NO_2S$, 365.1529; found: 365.1499.



((2-(4-chlorophenyl)-2-methoxyethyl)imino)diphenyl-l6-sulfanone (3ac) was a neutral color and transparent solid (40% yield). R_f = 0.3 (pentane/EtOAc, 2:1);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.31 (q, *J* = 8.4 Hz, 4H), 4.39 (t, *J* = 6.2 Hz, 1H), 3.37 (dd, *J* = 12.6, 6.5 Hz, 1H), 3.29 (s, 3H), 3.14 (dd, *J* = 12.6, 5.9 Hz, 1H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 139.68 , 133.25 , 132.33 , 129.08 , 128.68 , 128.58 , 128.33 , 126.82 , 84.43 , 57.14 , 50.00 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{21}ClNO_2S$, 386.0983; found: 386.0984.



((2-(4-bromophenyl)-2-methoxyethyl)imino)diphenyl-l6-sulfanone (3ad) was a neutral color and transparent solid (40% yield). R_f = 0.3 (pentane/EtOAc, 2:1);^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.23 (m, 2H), 4.39 (t, *J* = 6.1 Hz, 1H), 3.37 (dd, *J* = 12.6, 6.5 Hz, 1H), 3.28 (s, 3H), 3.15 (dd, *J* = 12.6, 5.9 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.12 , 131.30 , 129.14 , 129.11 , 129.04 , 128.59 , 128.55 , 121.42 , 84.31 , 57.15 , 49.91 . **HRMS(ESI)**: $[M+H]^+$ calcd for $C_{21}H_{21}BrNO_2S$, 430.0478; found: 430.0478.

4 Reference

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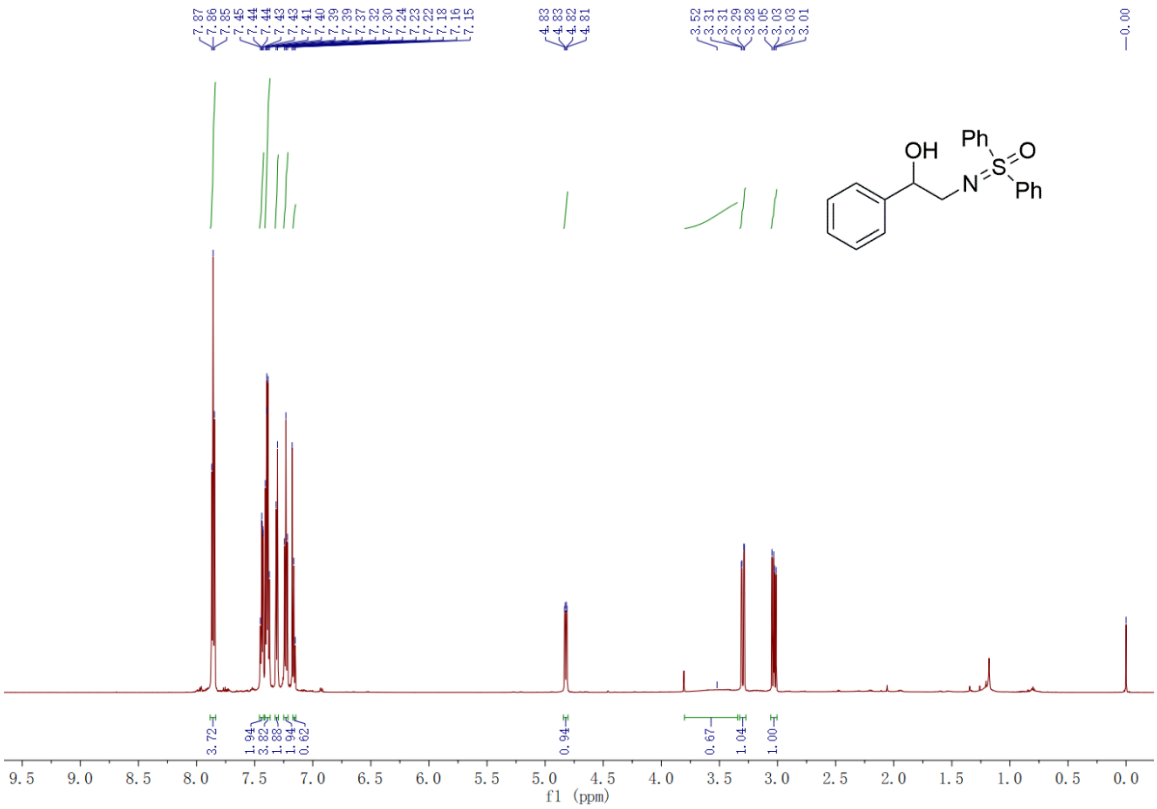
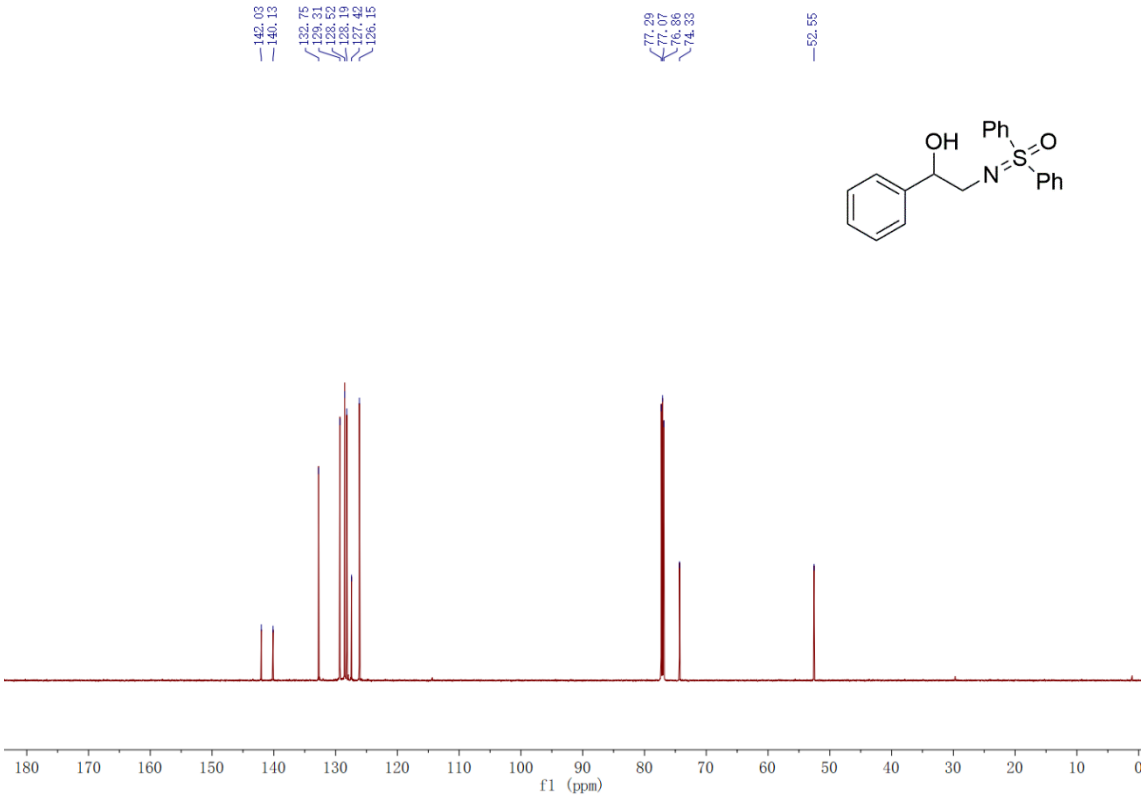
5 NMR spectra

((2-hydroxy-2-phenylethyl)imino)diphenyl- λ 6-sulfanone (3a)





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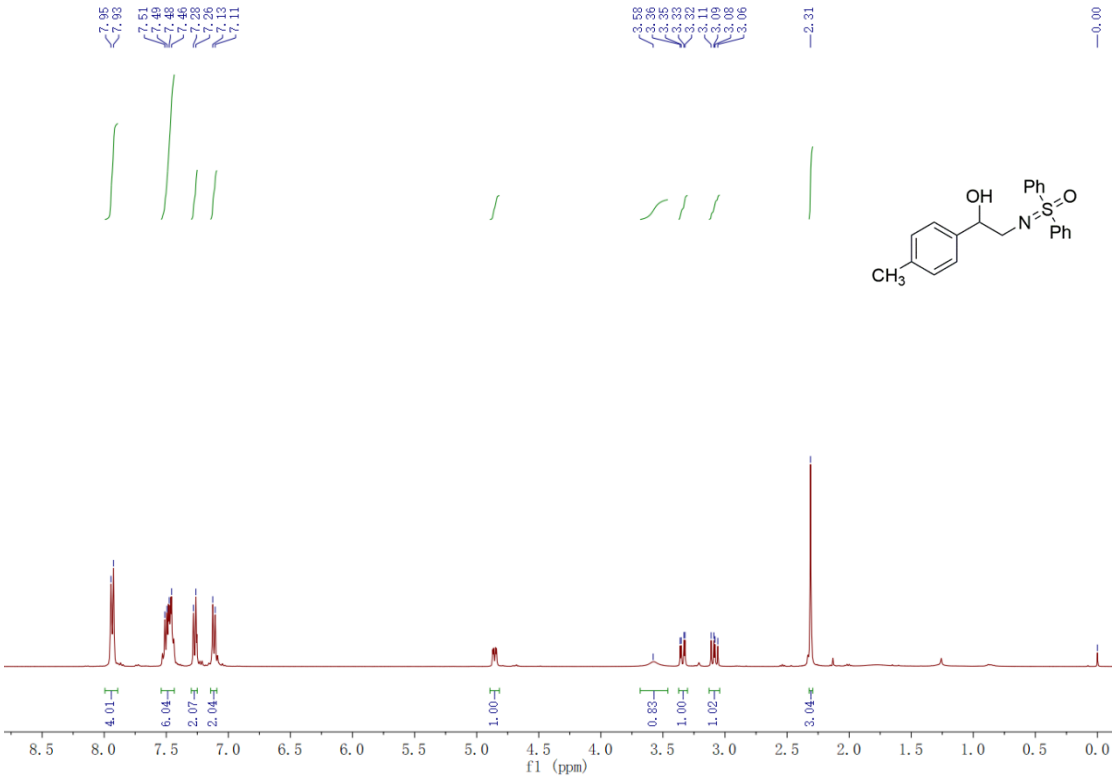

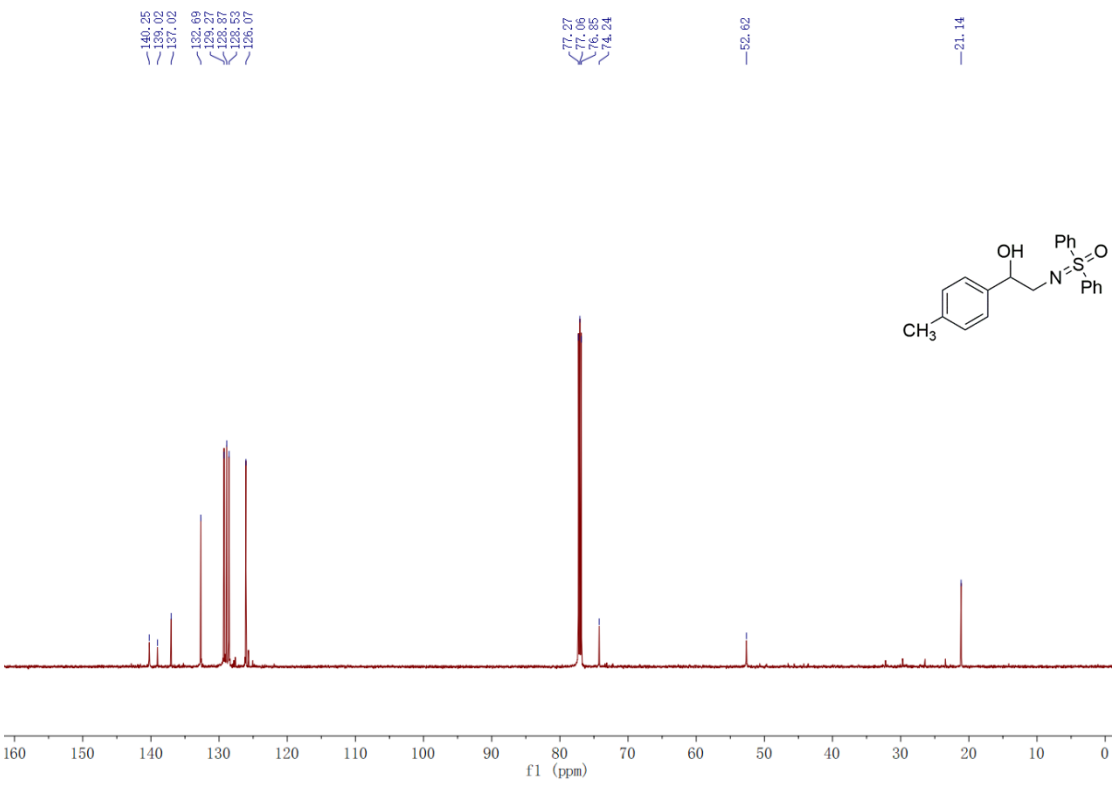

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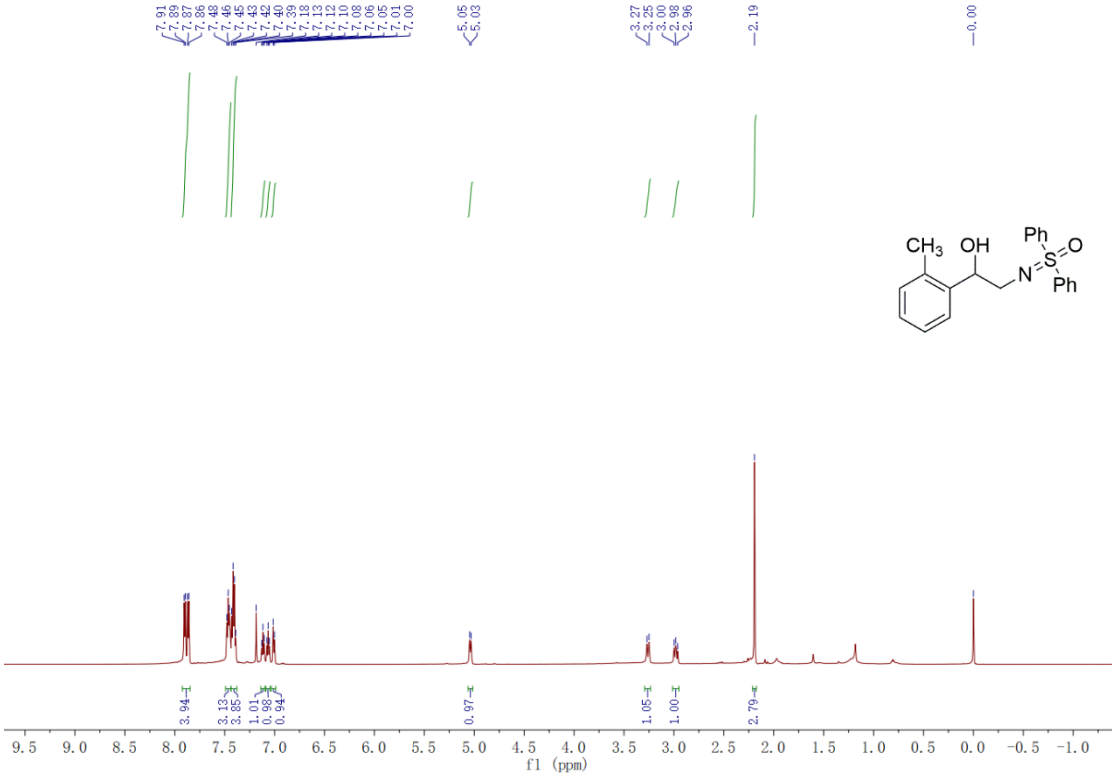

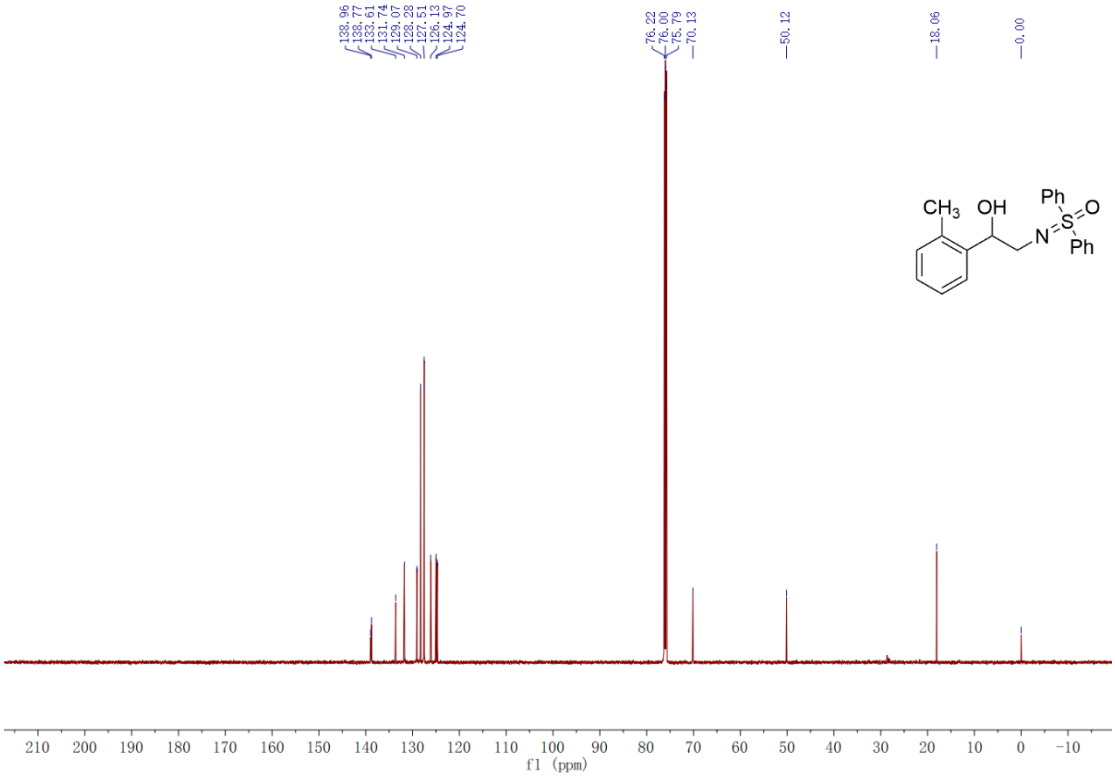

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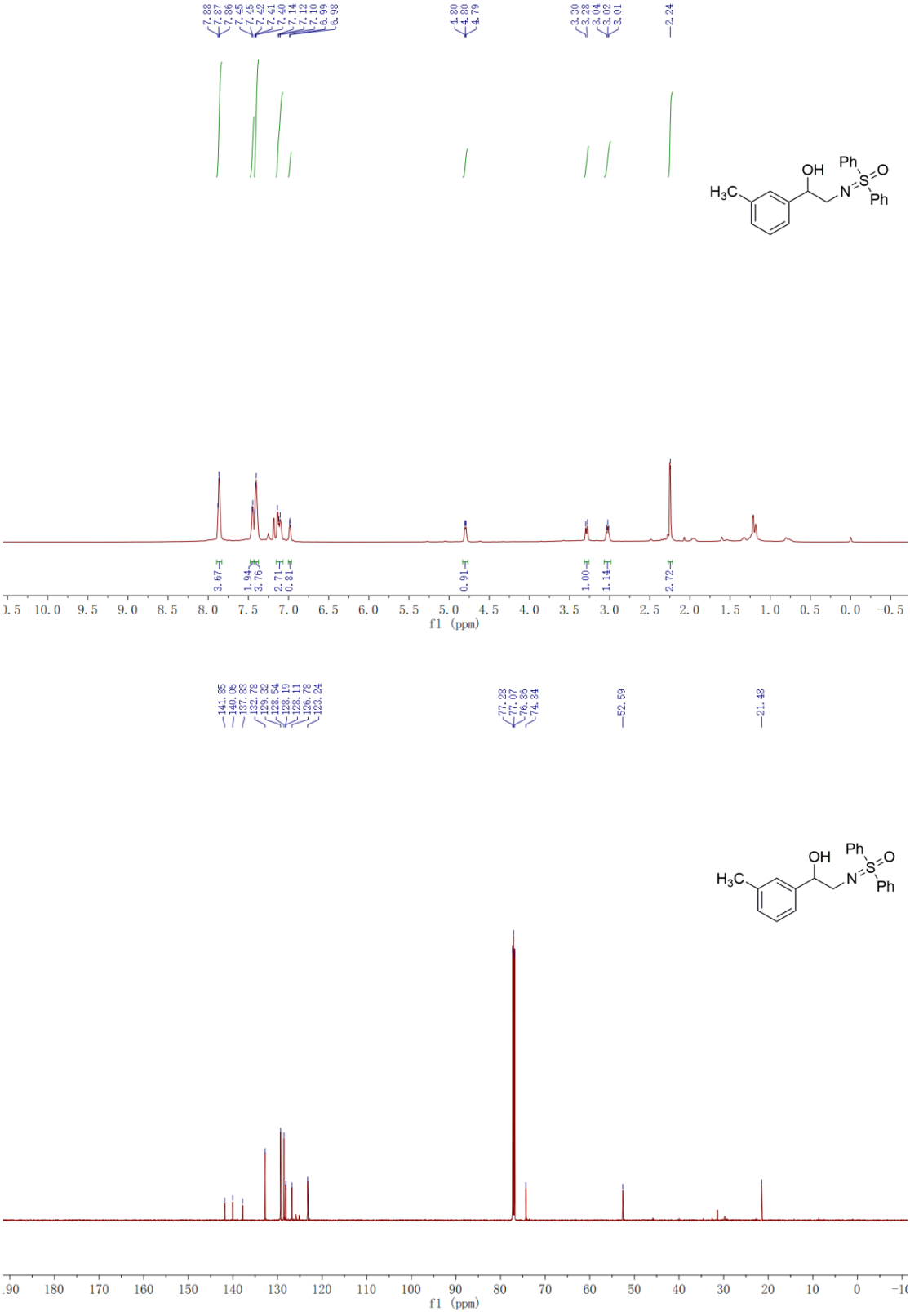

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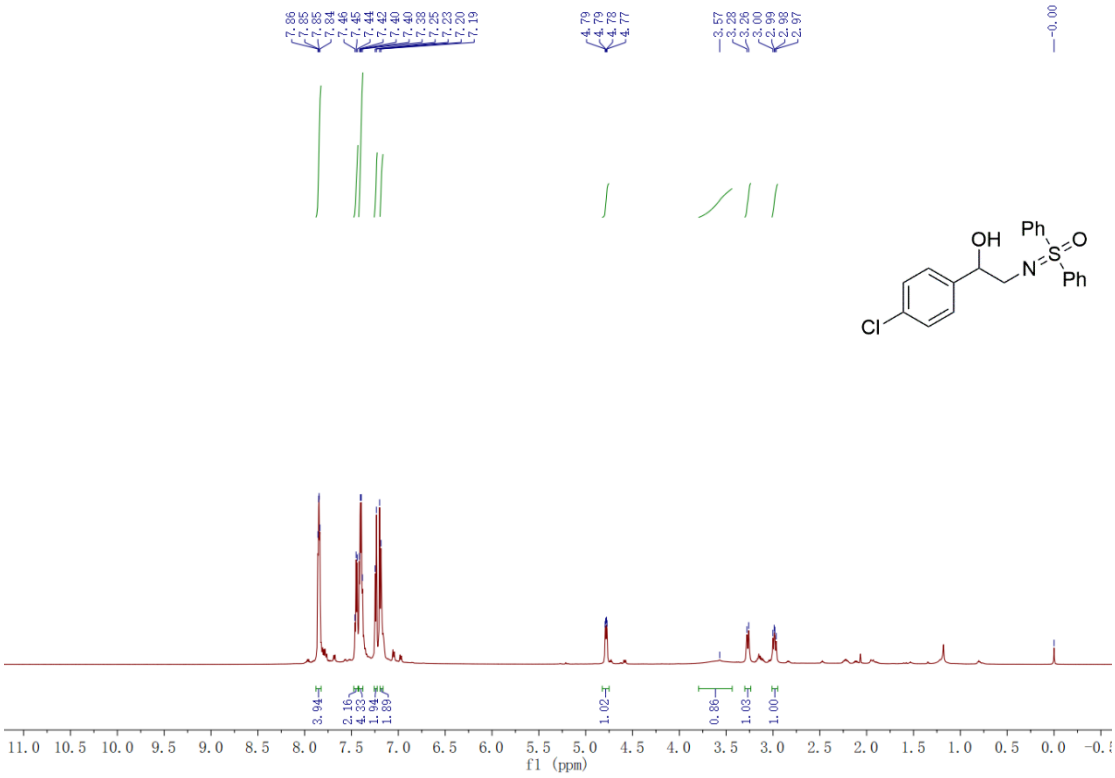

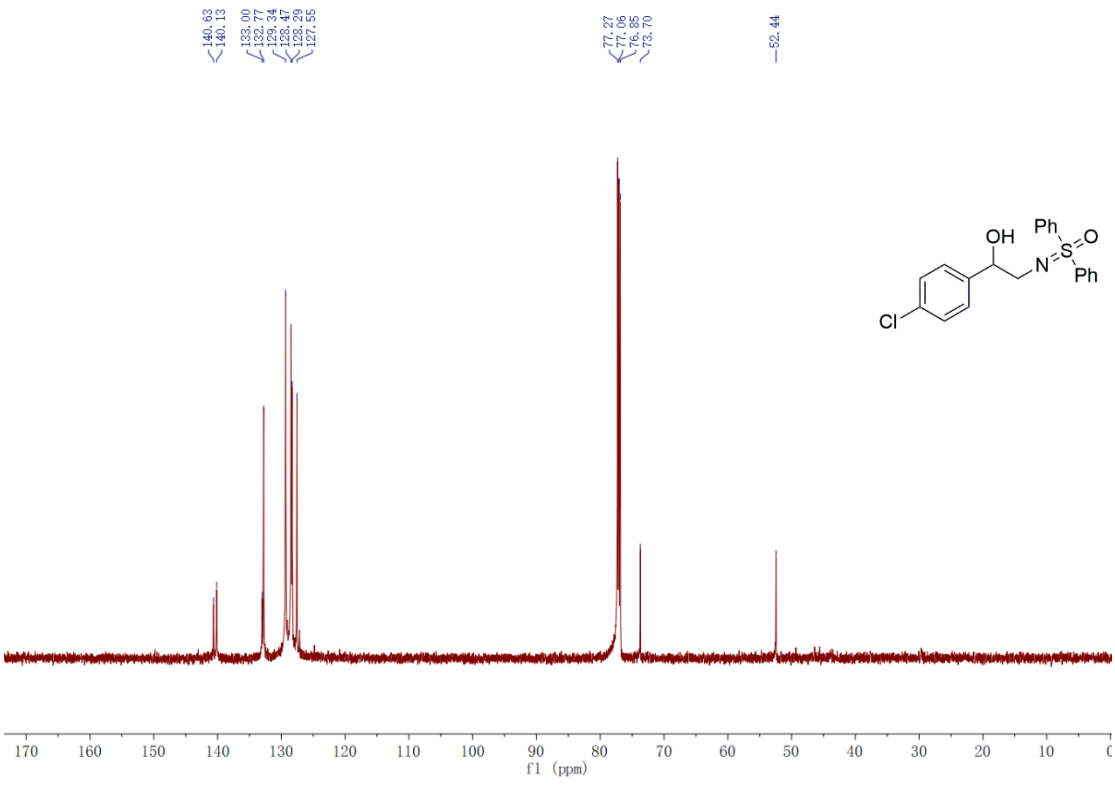

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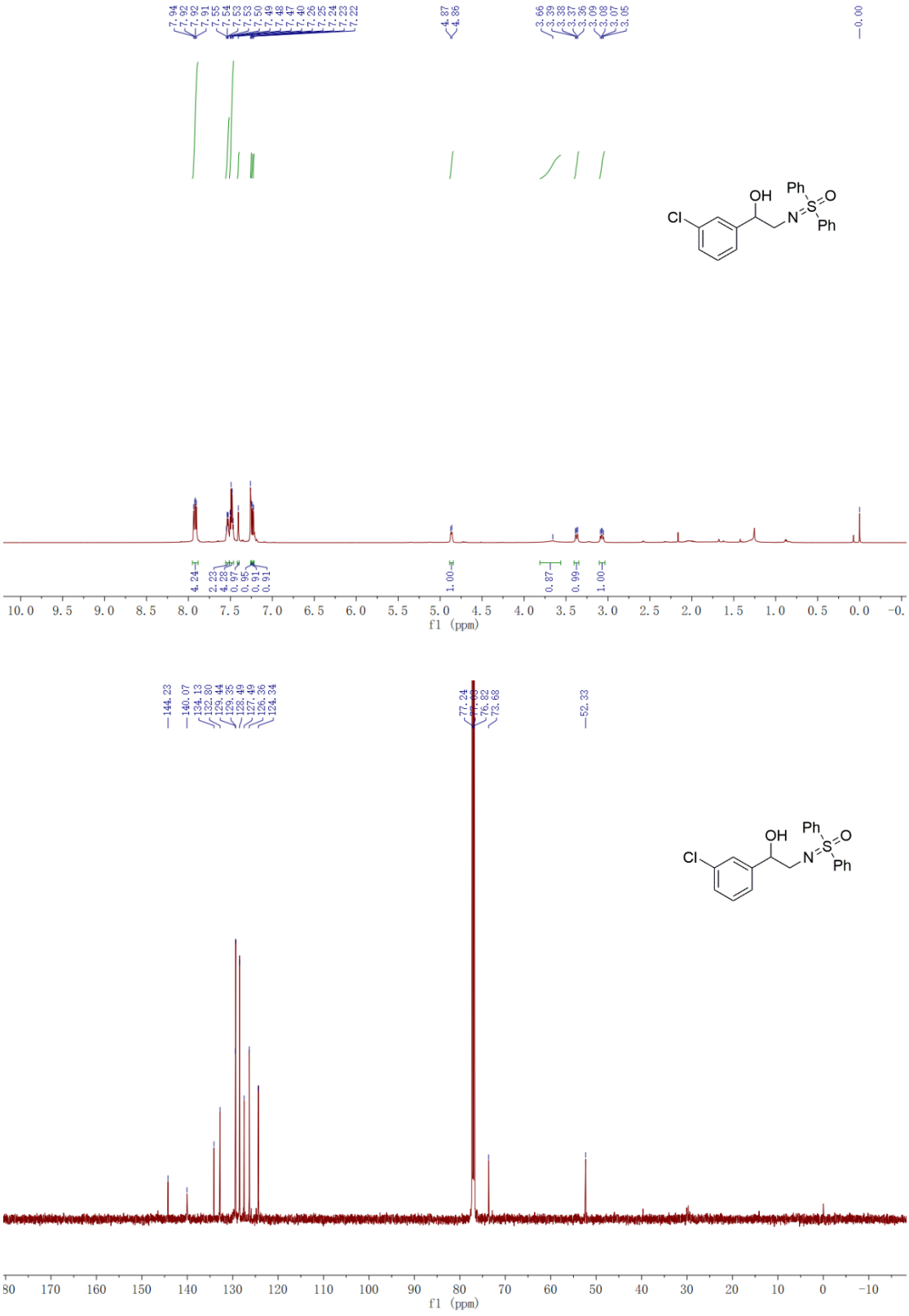

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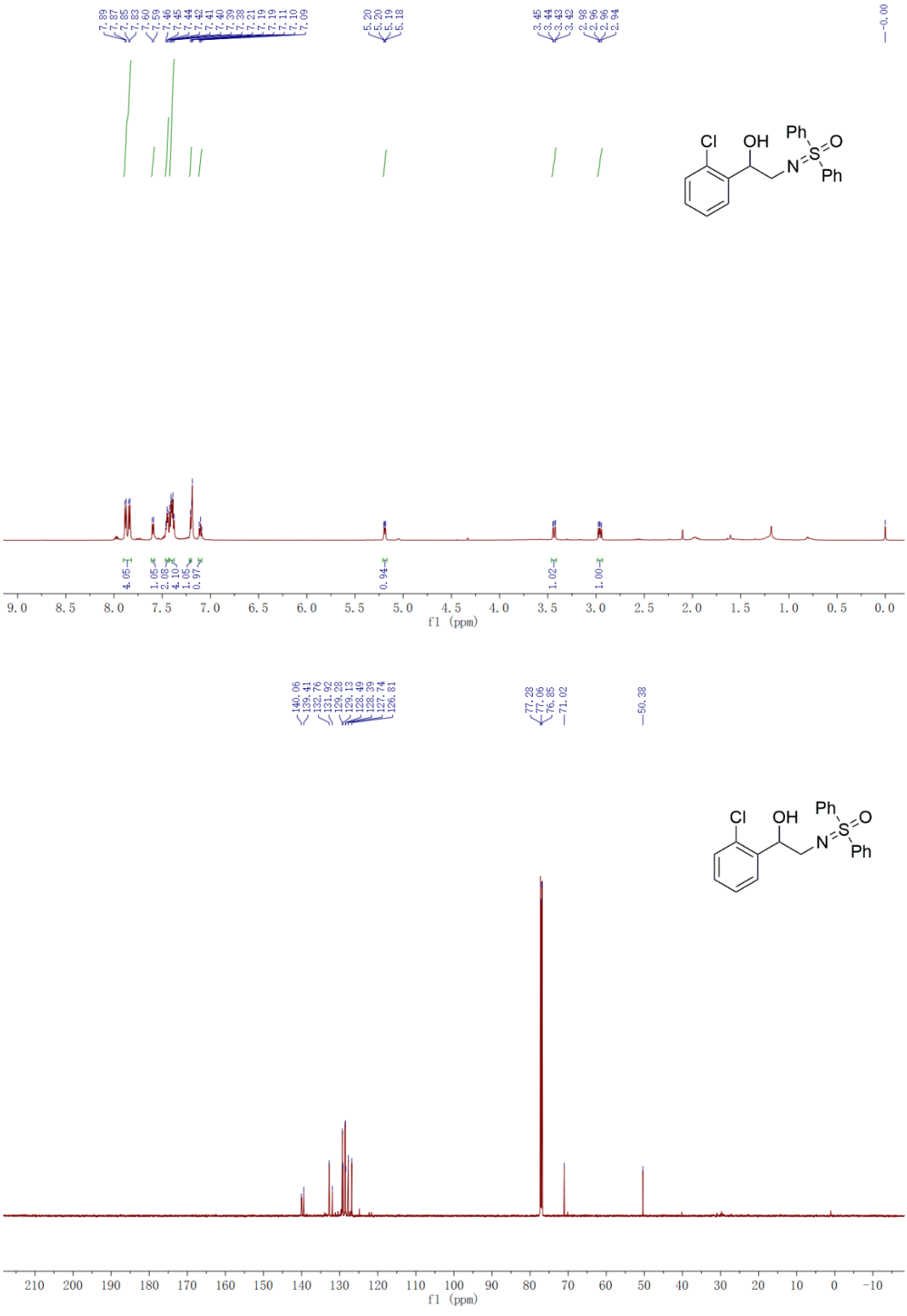

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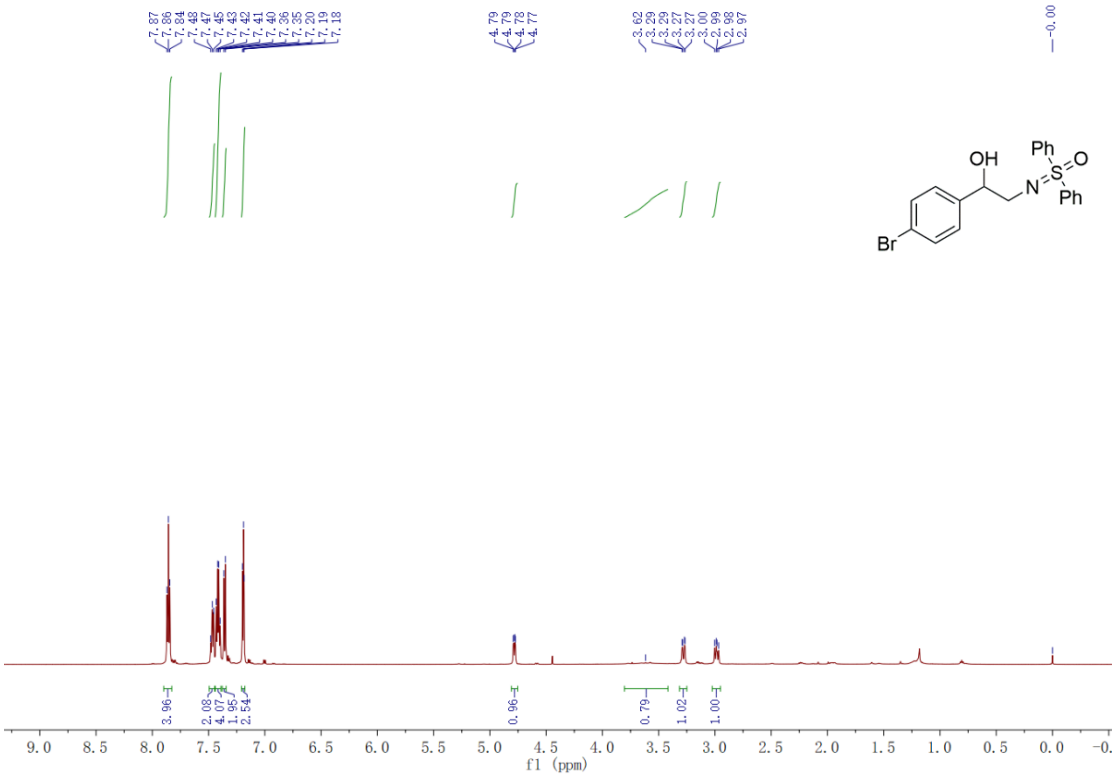

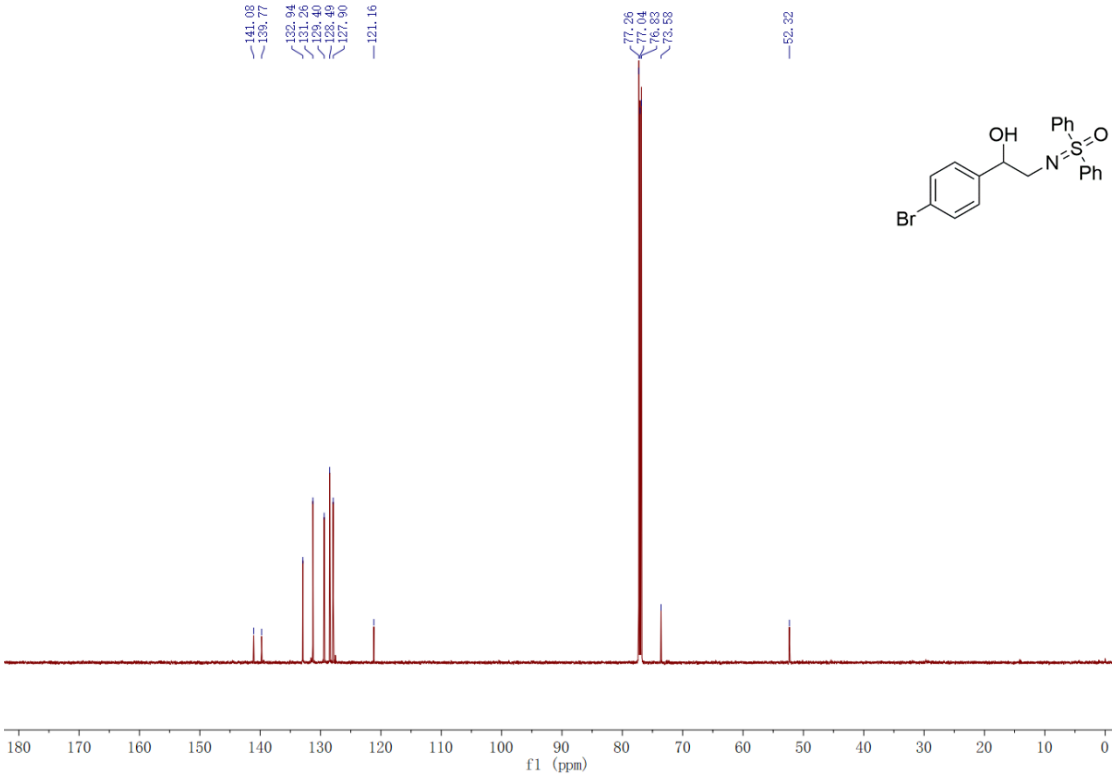

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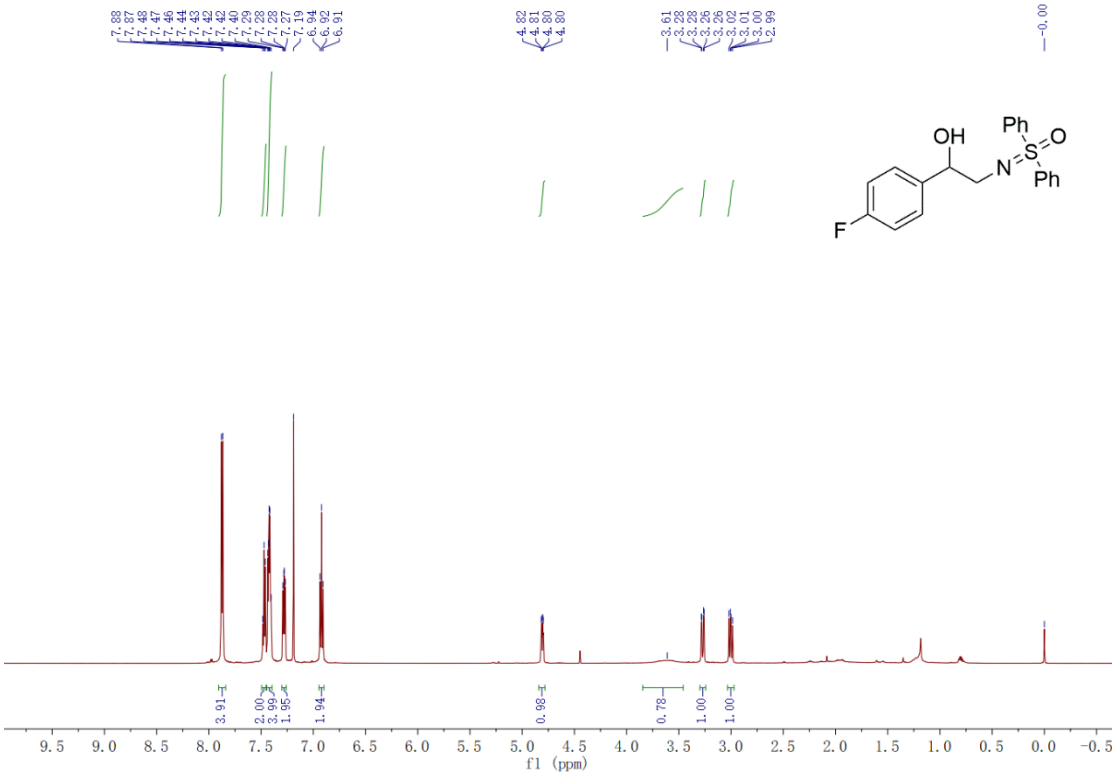

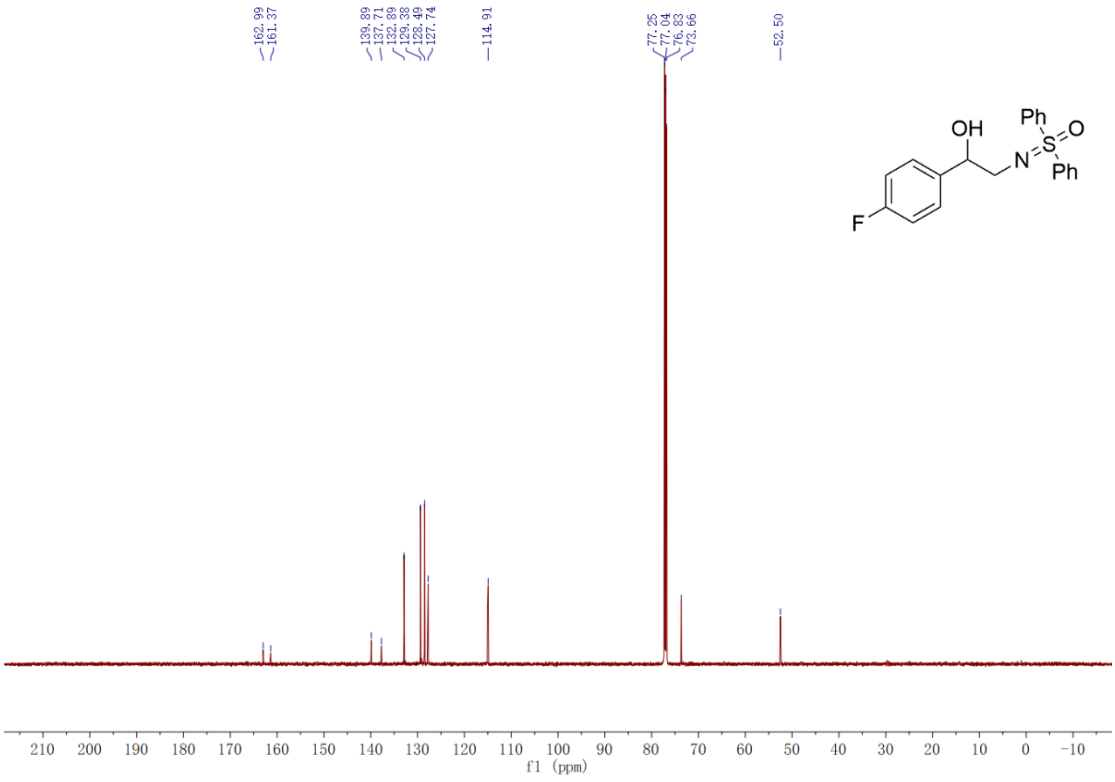

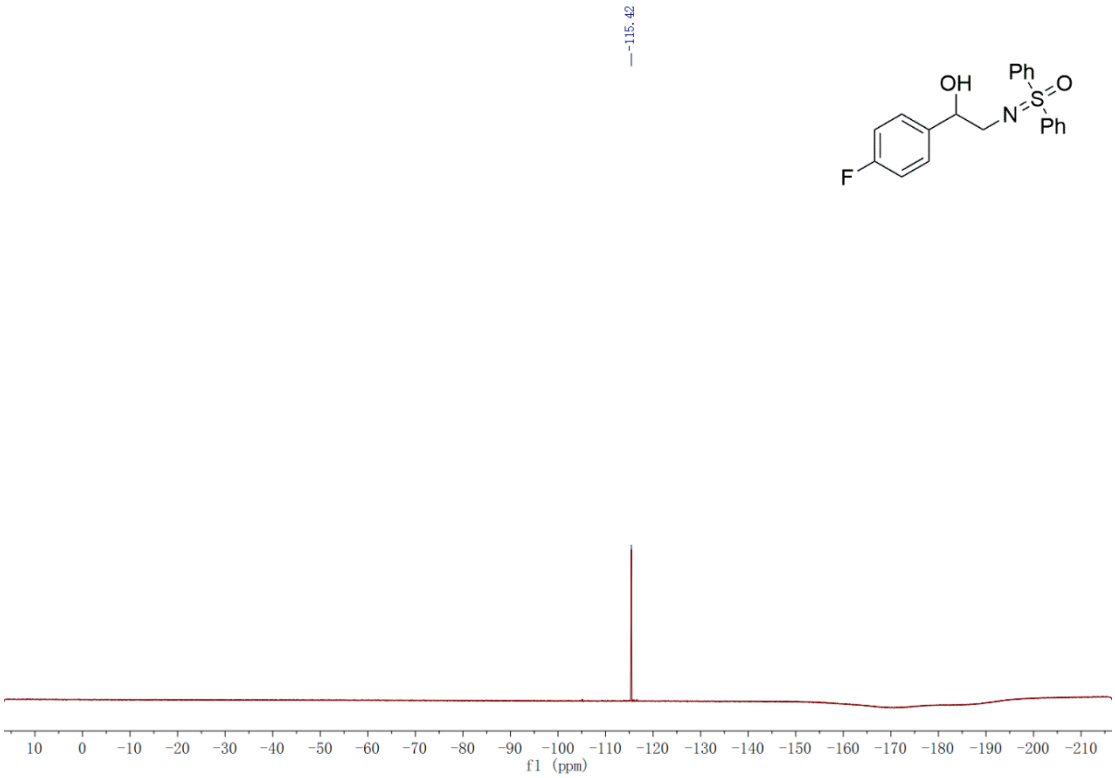

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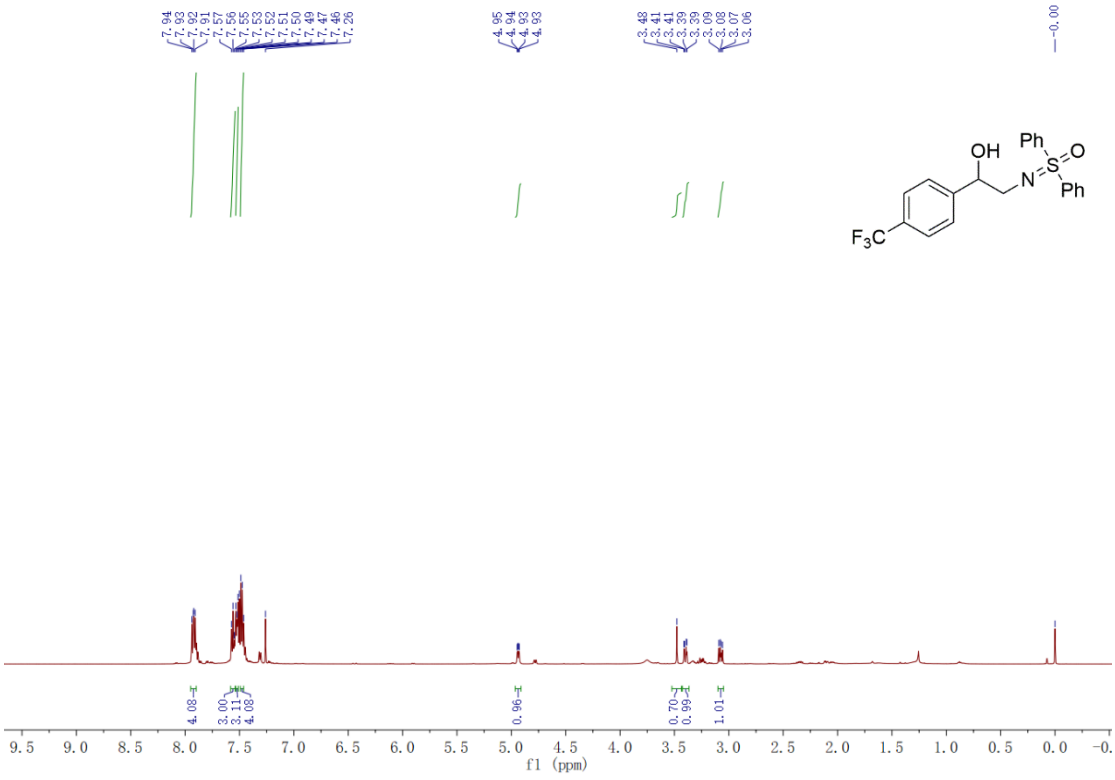

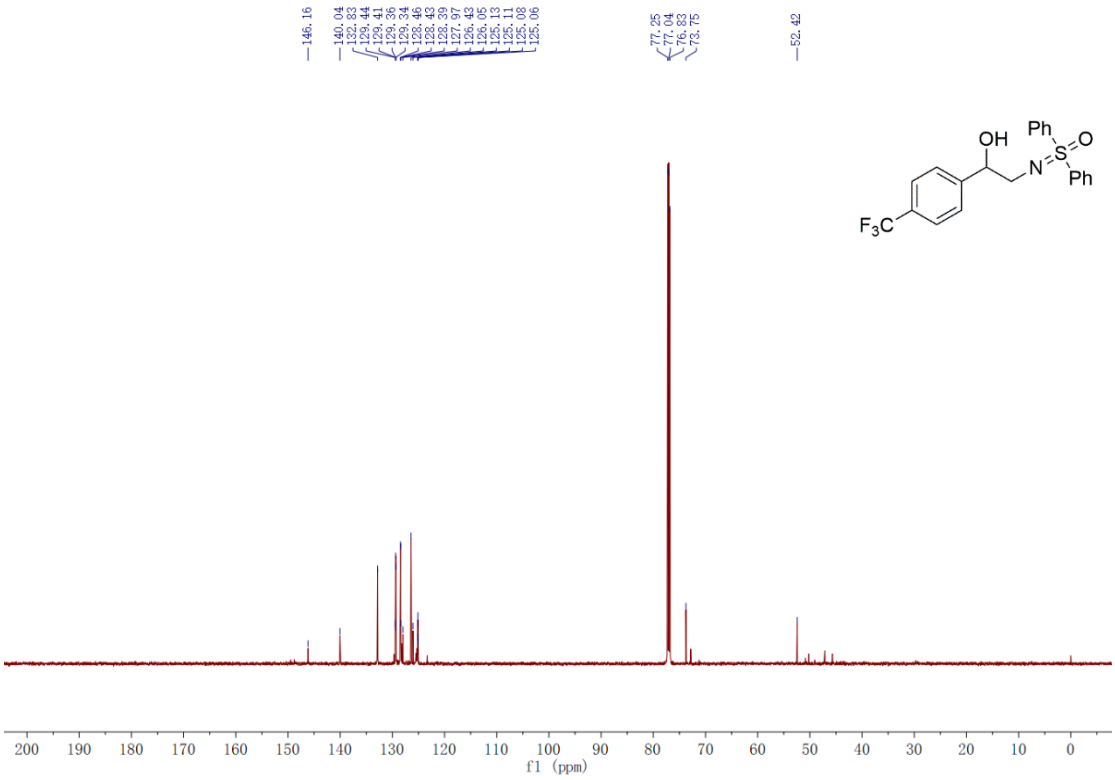
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126.05
125.13
125.11
125.08
125.06
77.25
77.04
76.83
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N
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Ph
F3C
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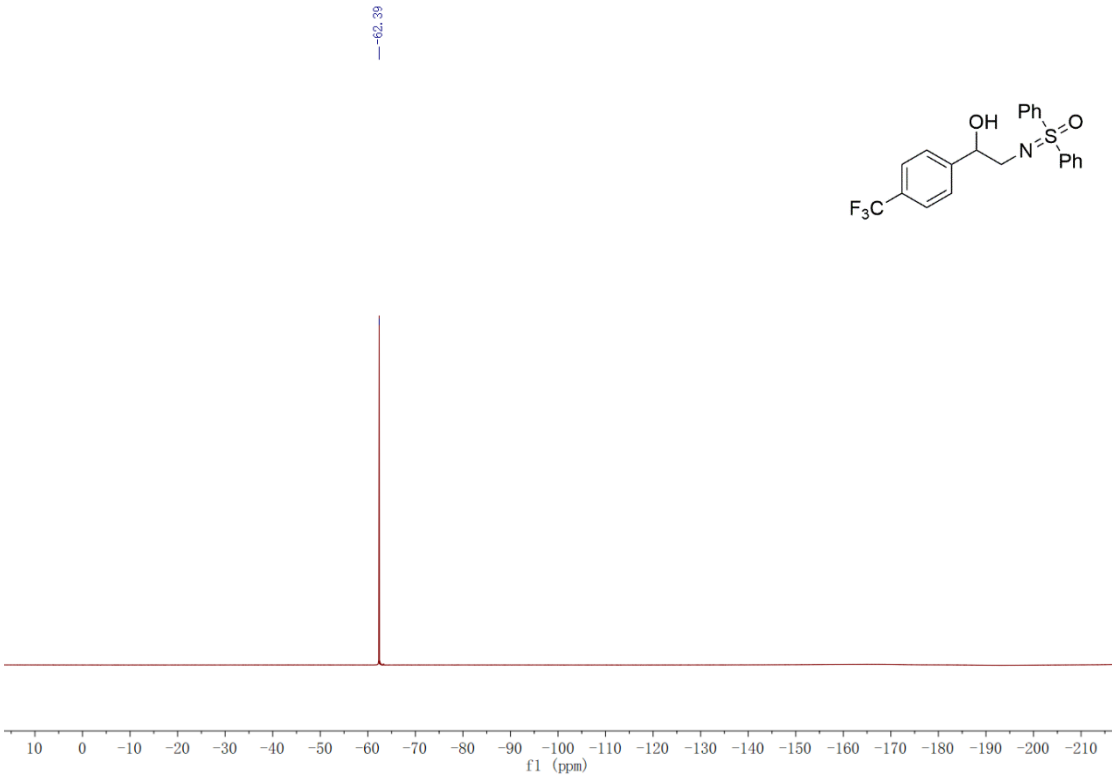
f1 (ppm)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f1 (ppm)

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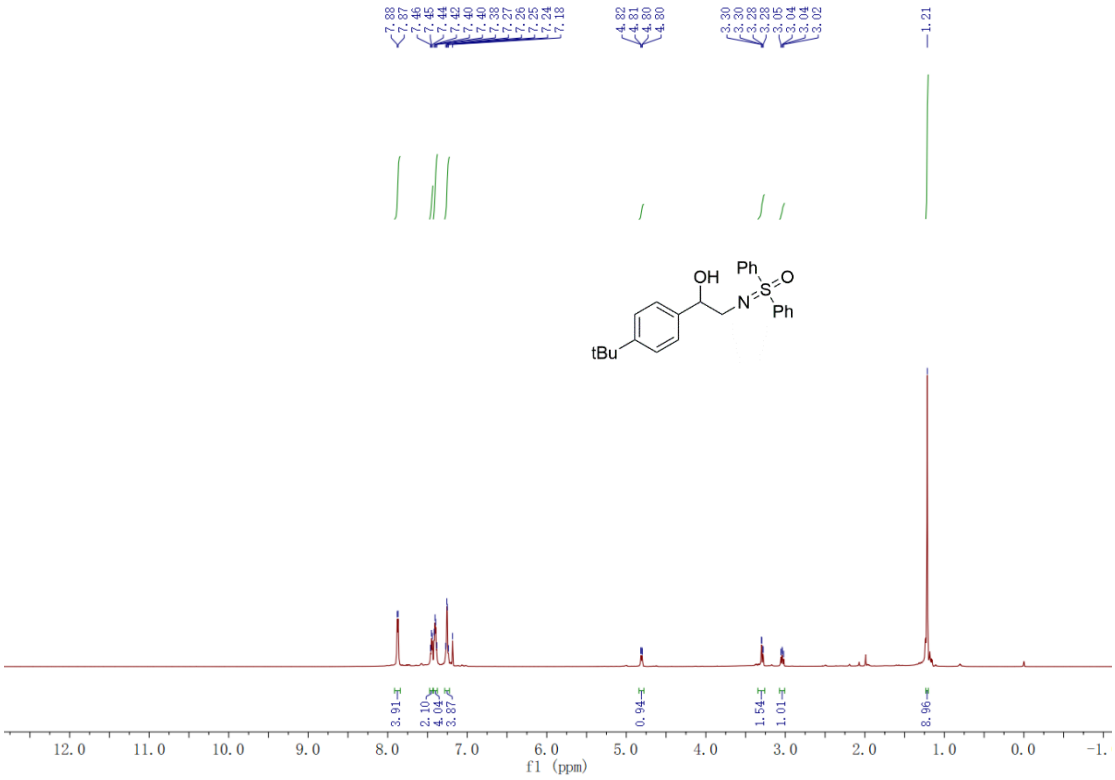

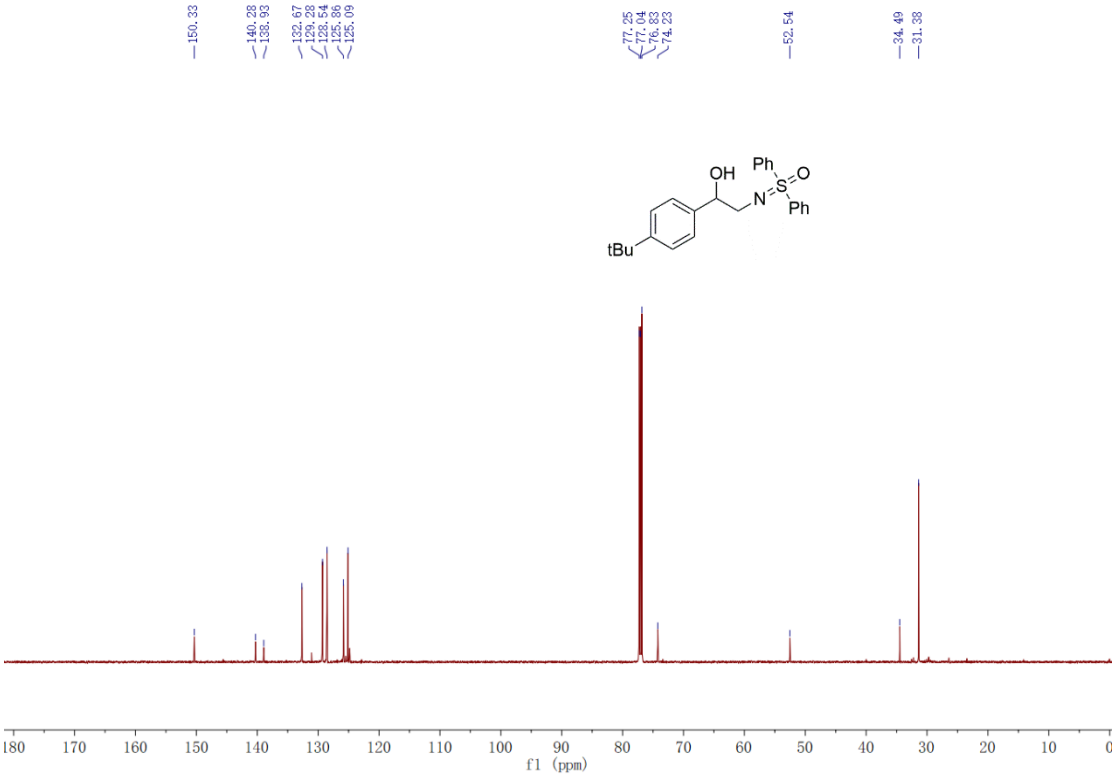

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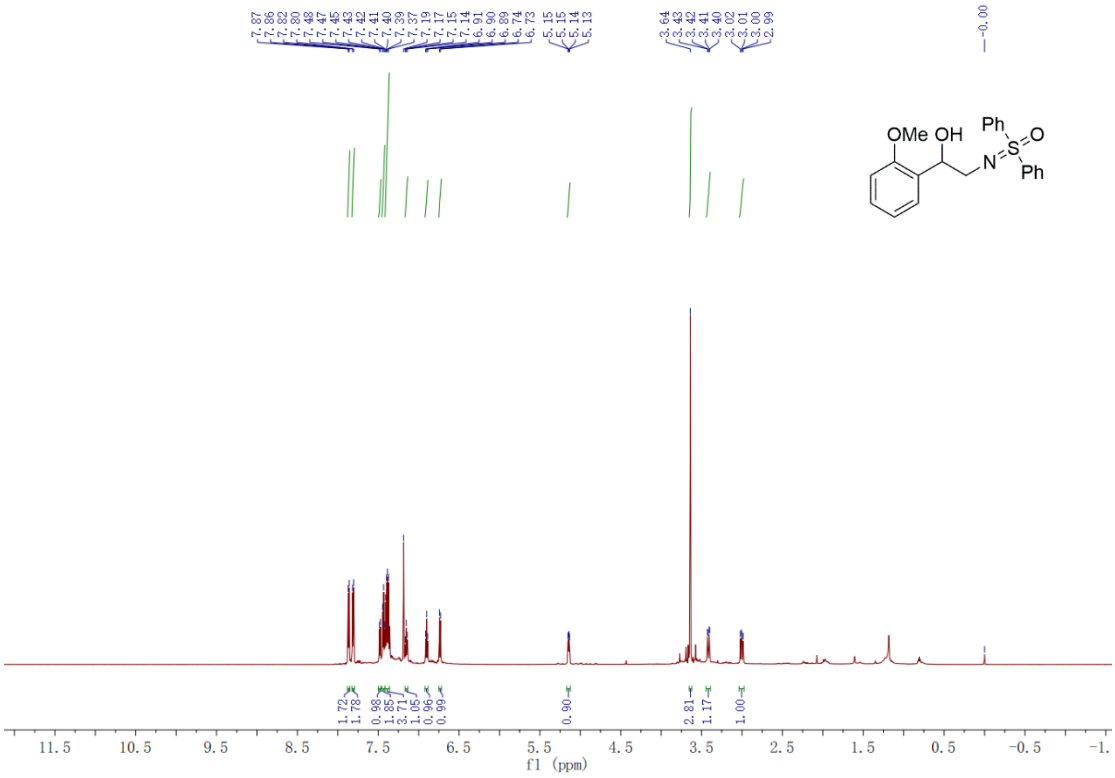

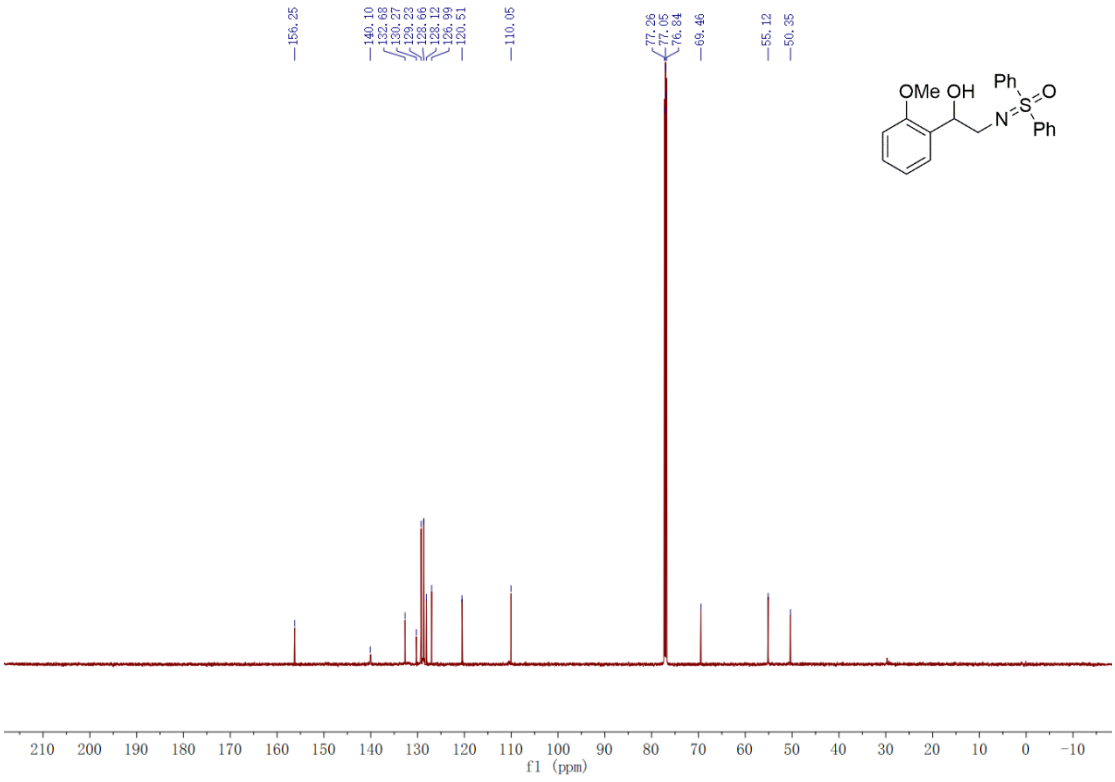

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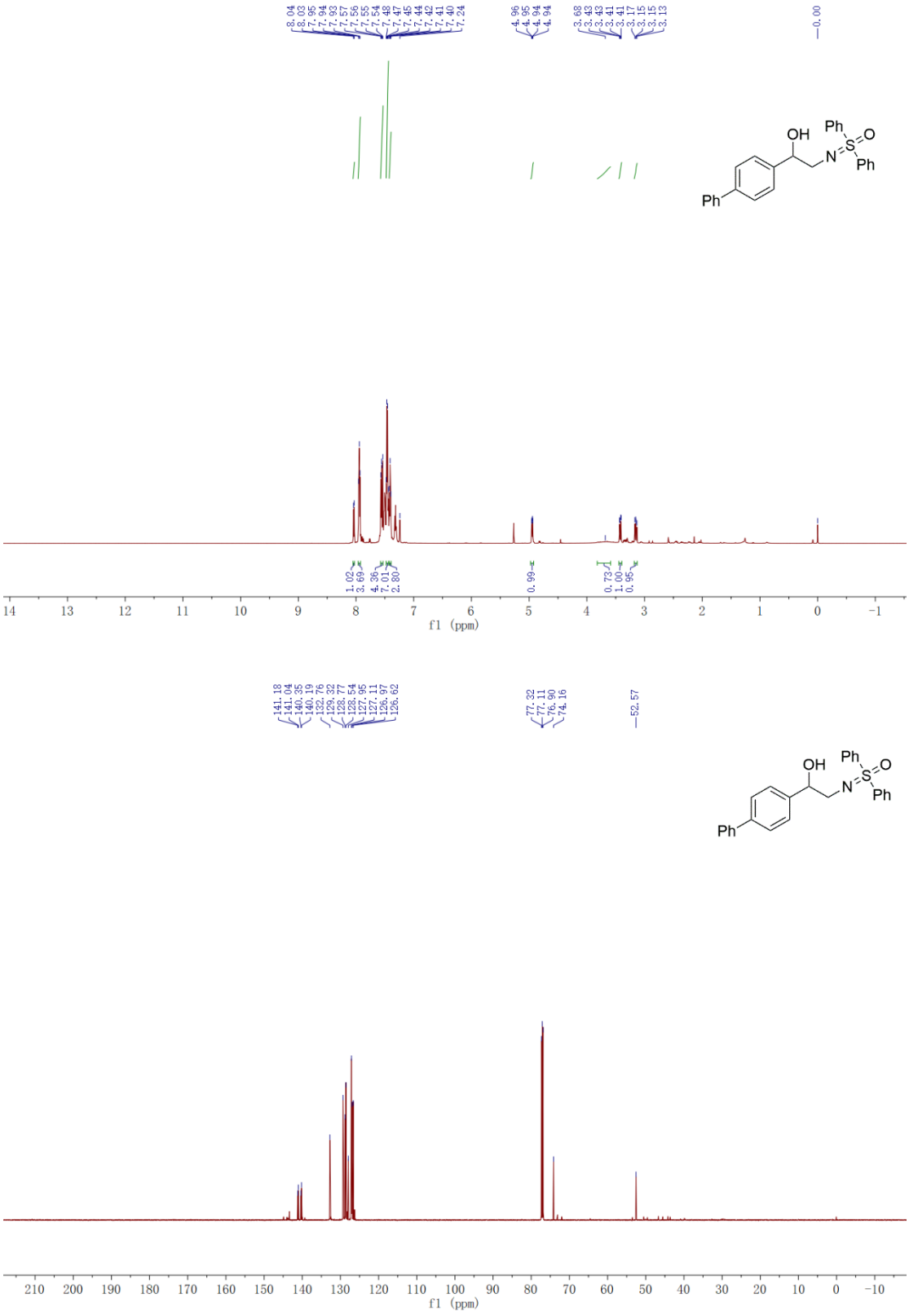

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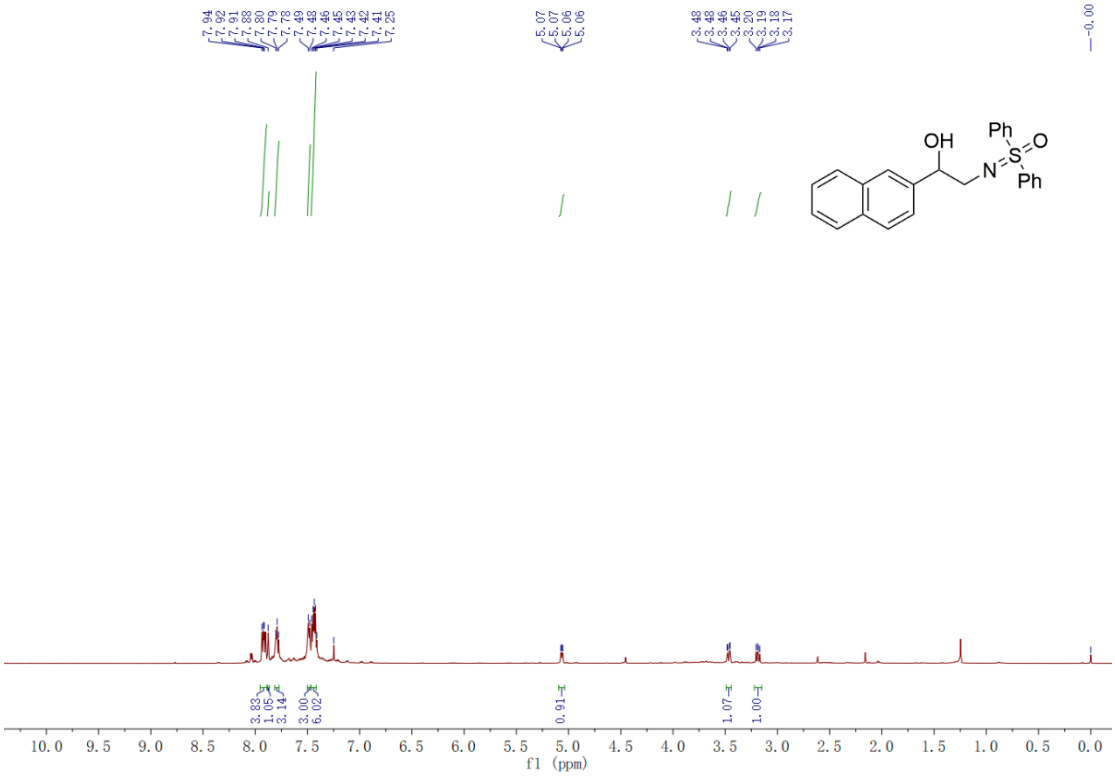
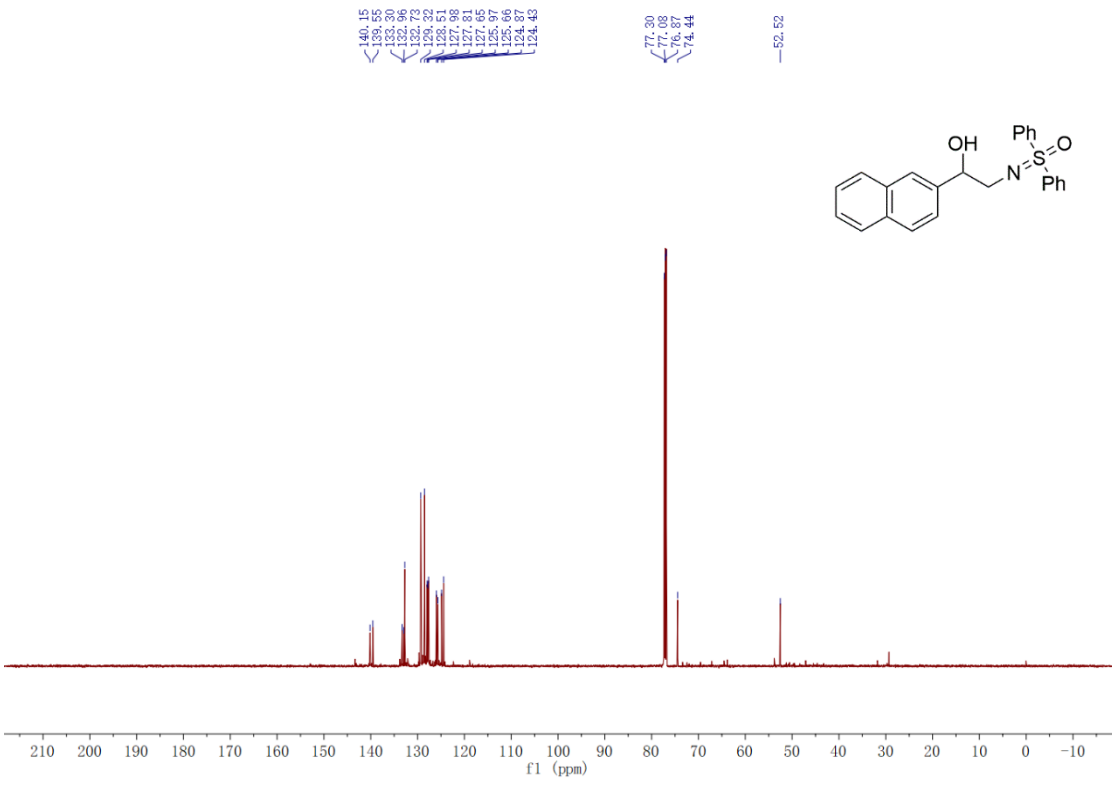
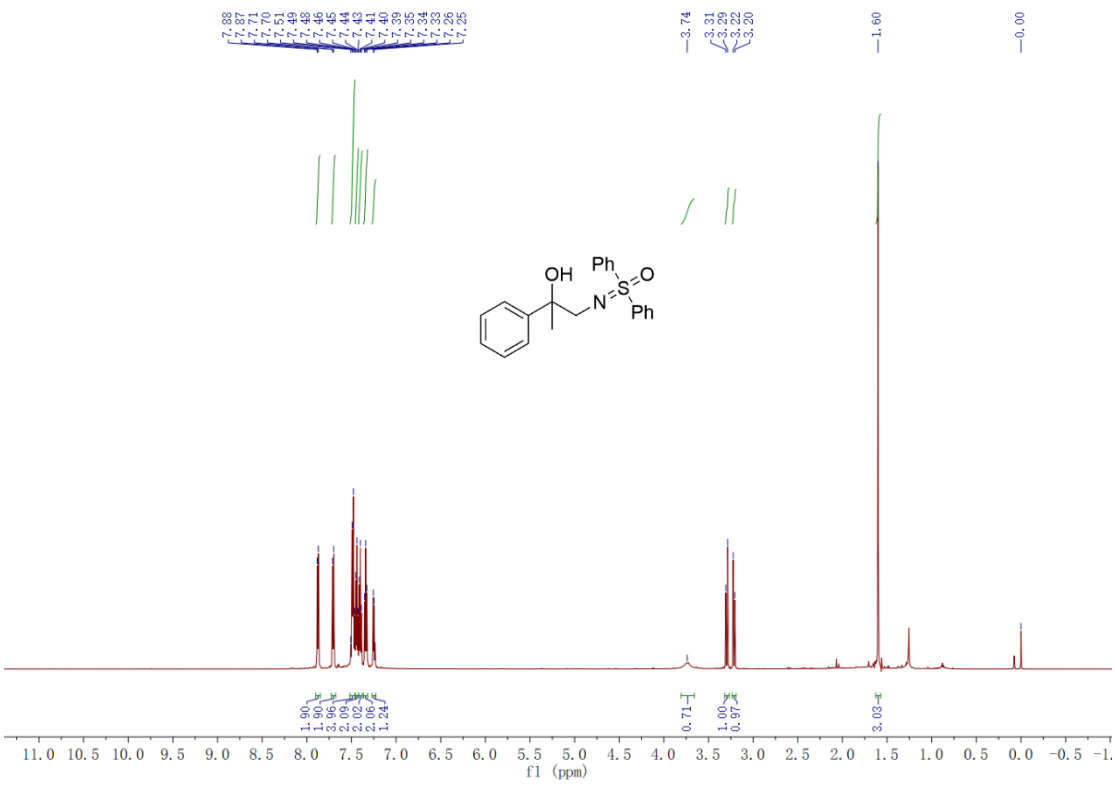
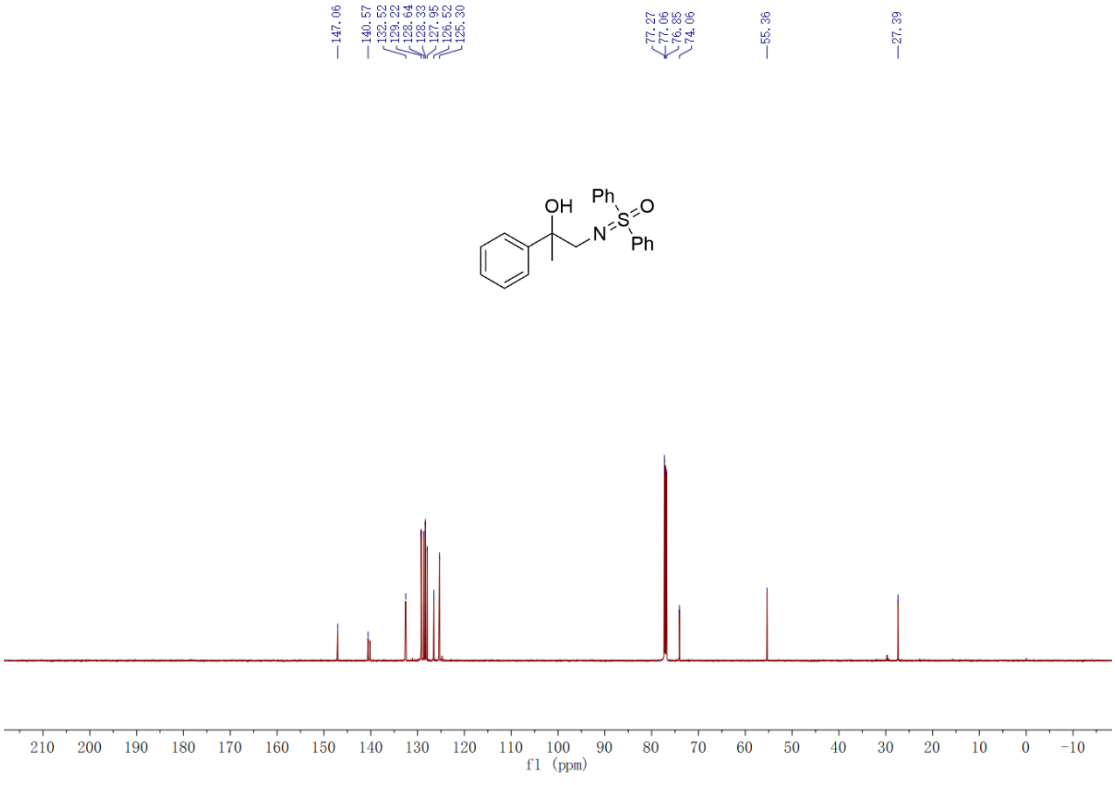


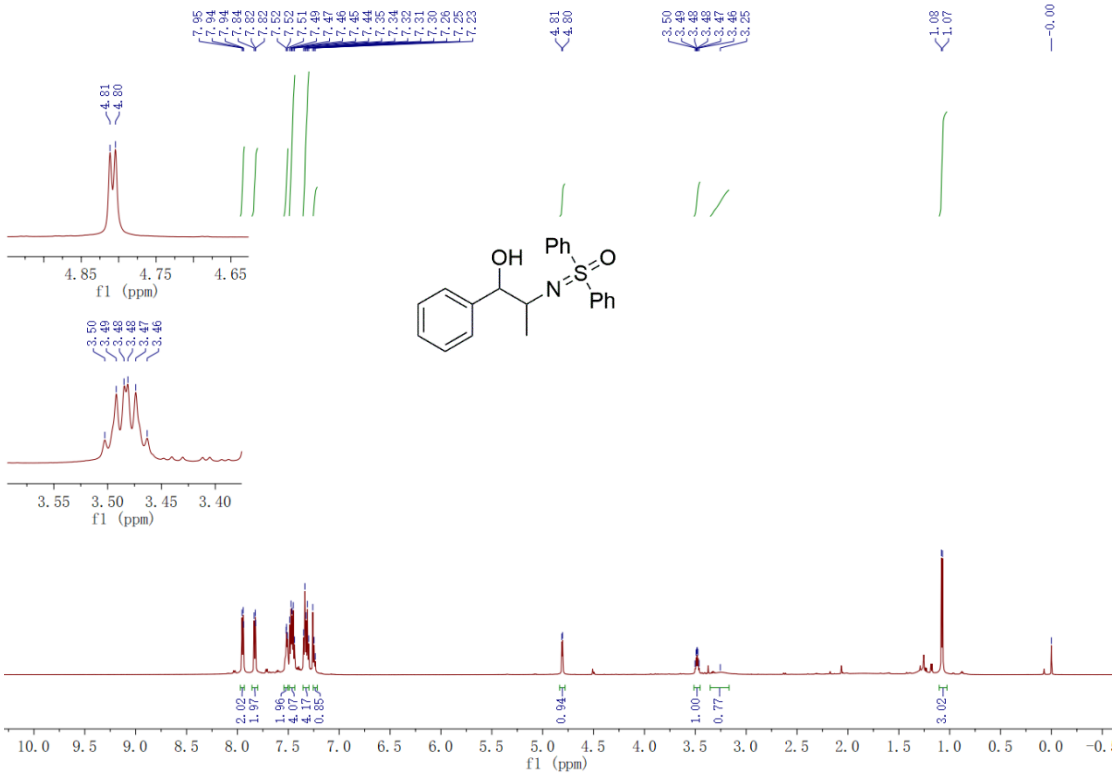


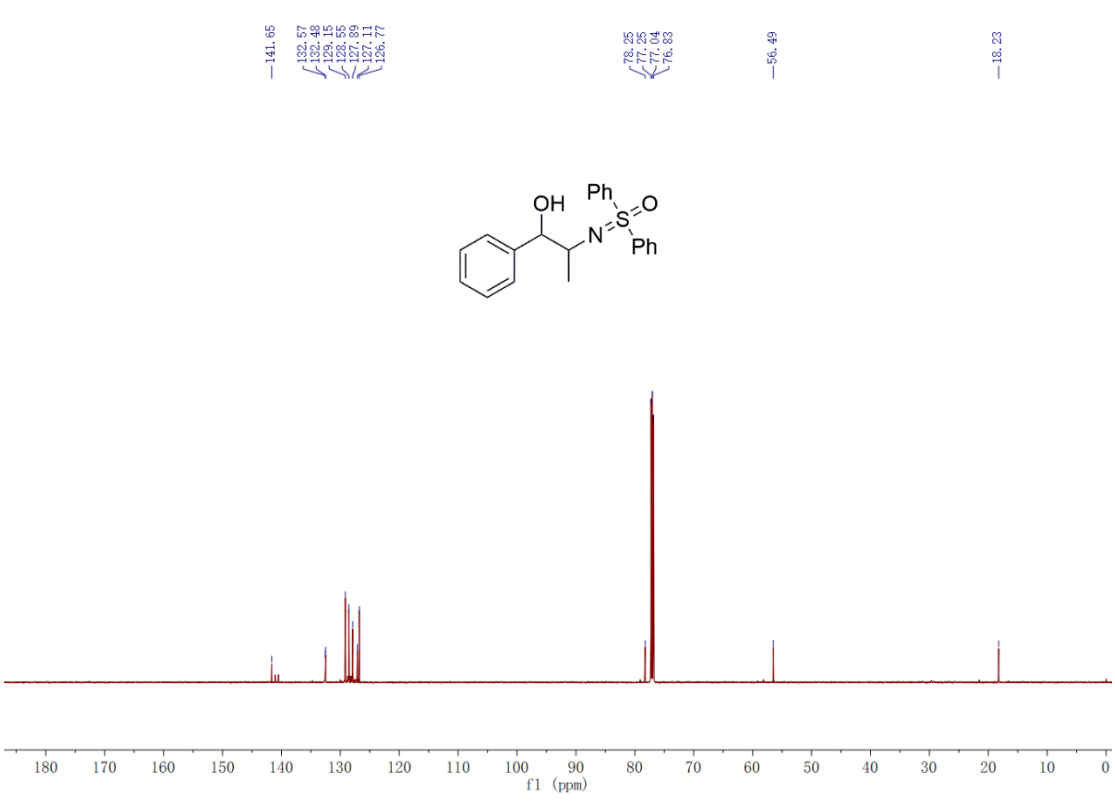
((2-hydroxy-2-phenylpropyl)imino)diphenyl-λ^6-sulfanone (3o)



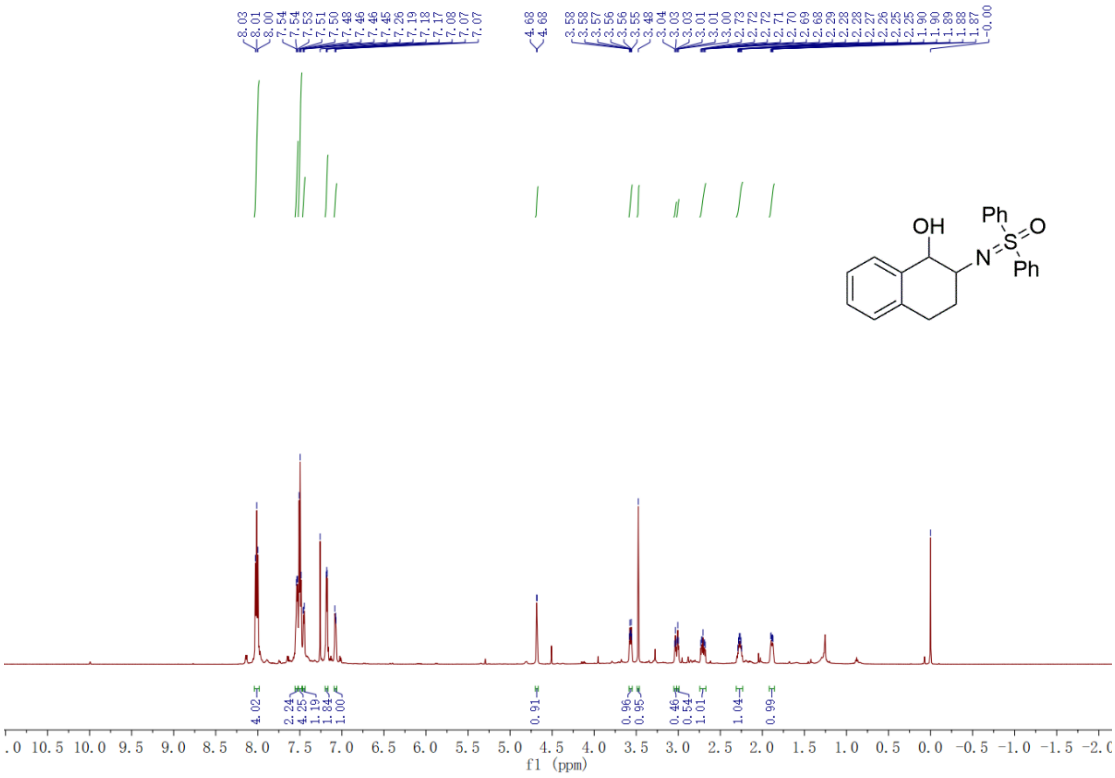


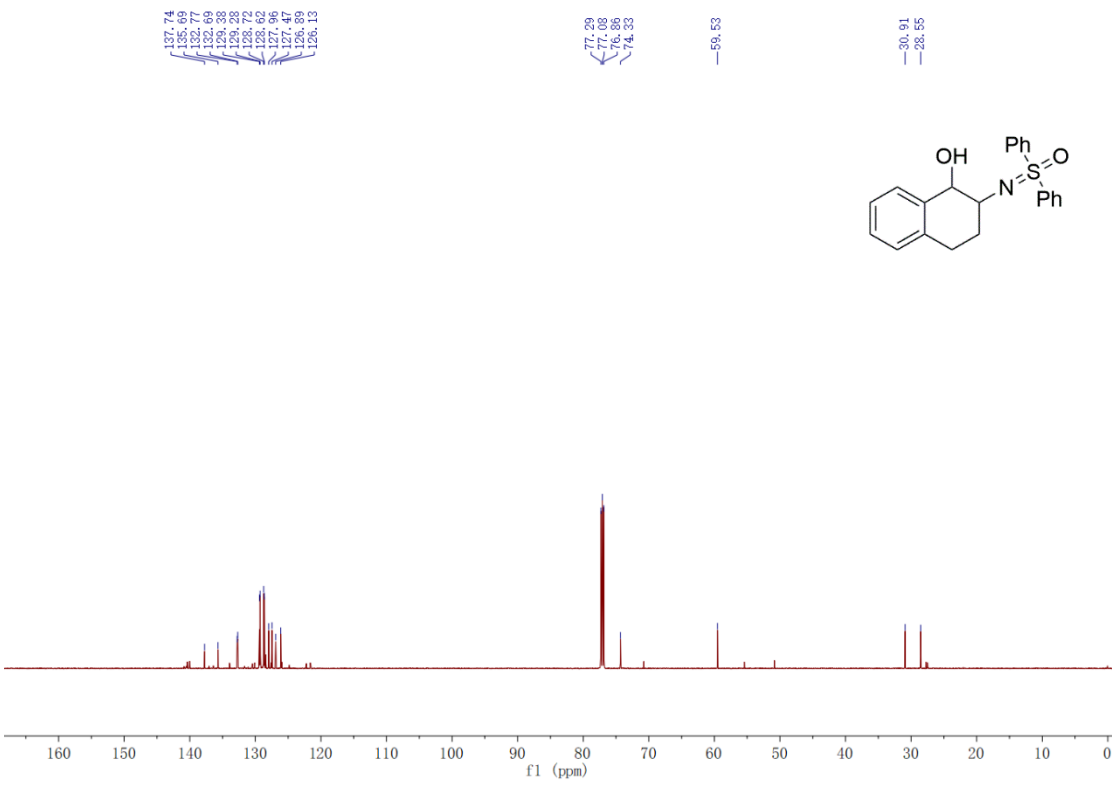
((1-hydroxy-1-phenylpropan-2-yl)imino)diphenyl-λ^6-sulfanone (3p)



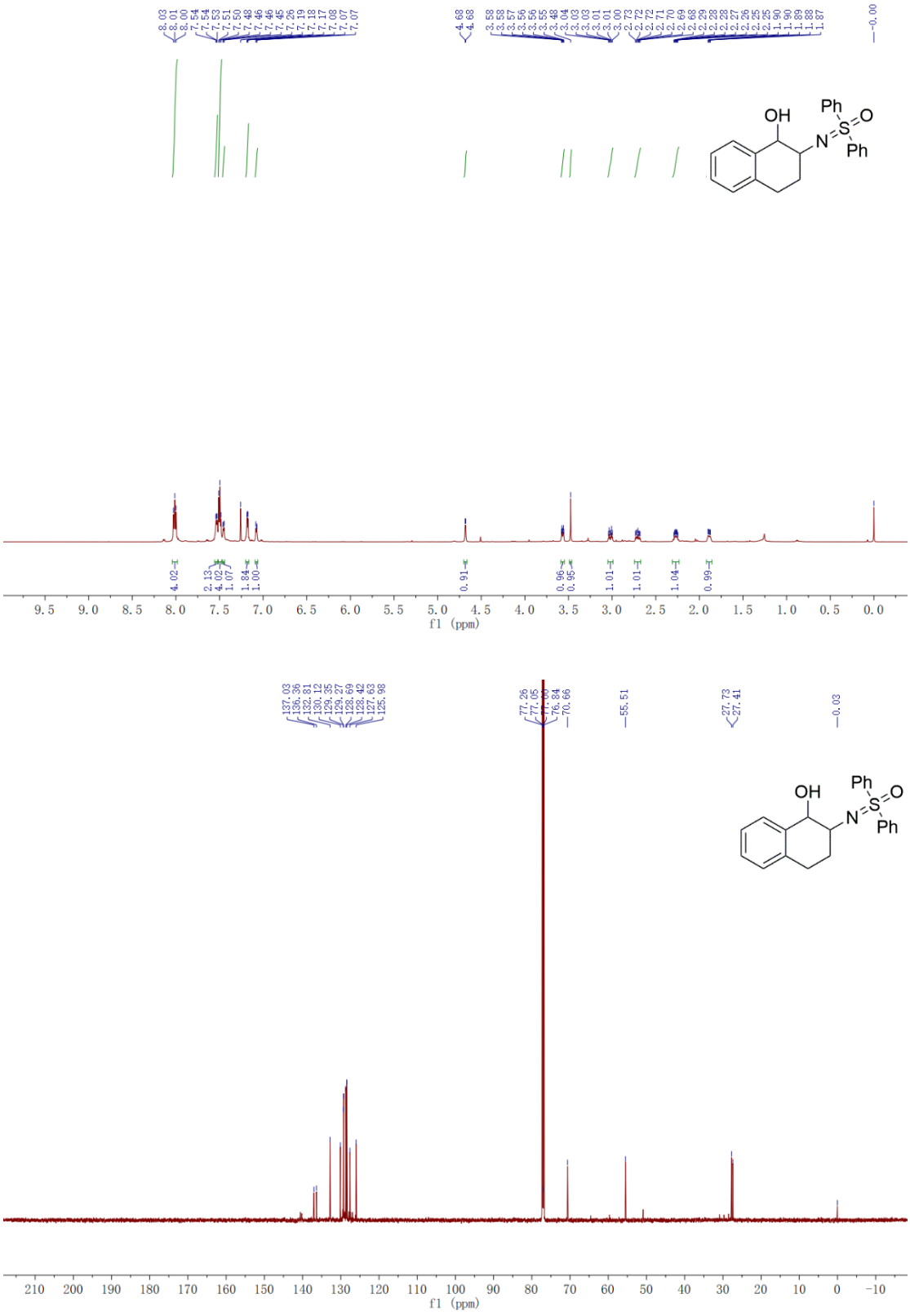


((1-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)imino)diphenyl-λ^6-sulfanone (3q)(major isomer)

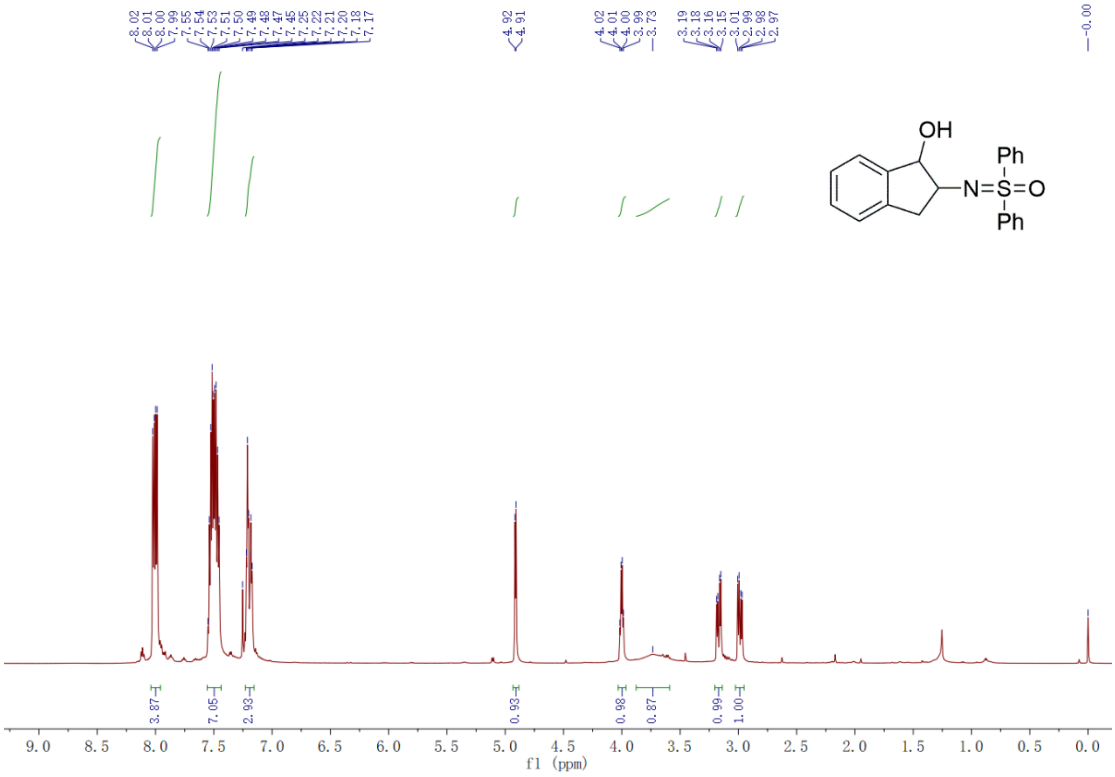


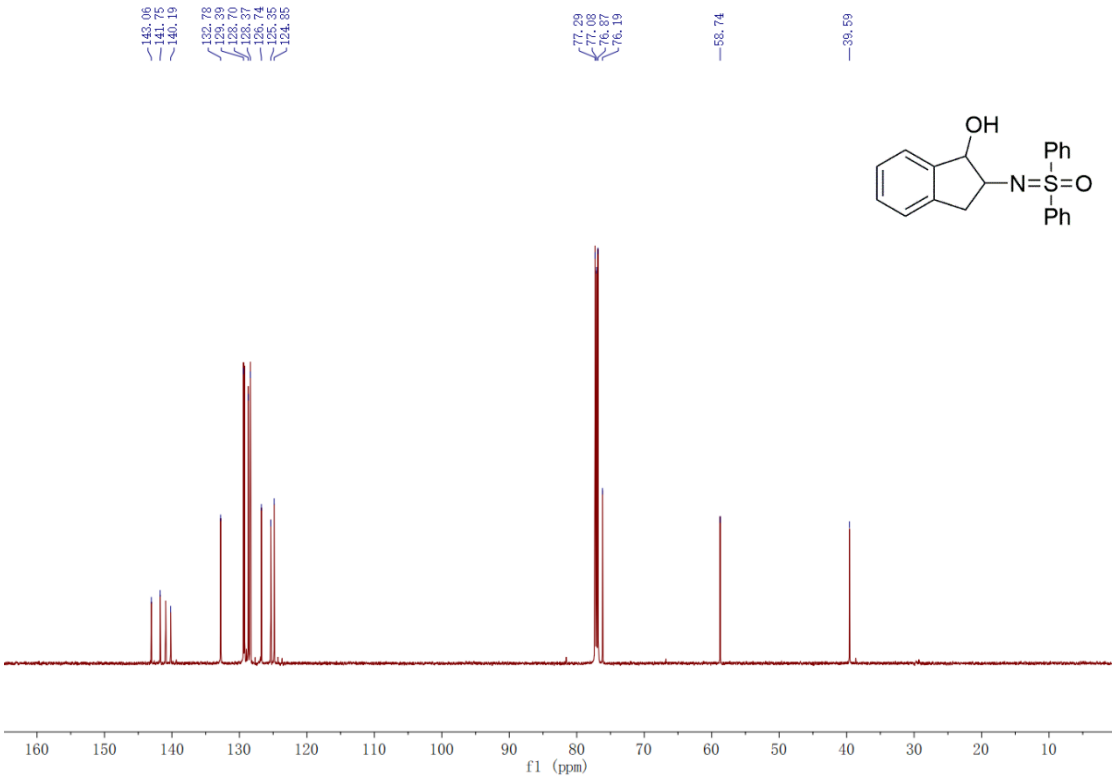


((1-hydroxy-1,2,3,4-tetrahydronaphthalen-2-yl)imino)diphenyl-λ^6-sulfanone (3q)(minor isomer)



((1-hydroxy-2,3-dihydro-1H-inden-2-yl)imino)diphenyl-λ⁶-sulfanone(3r) (major isomer)





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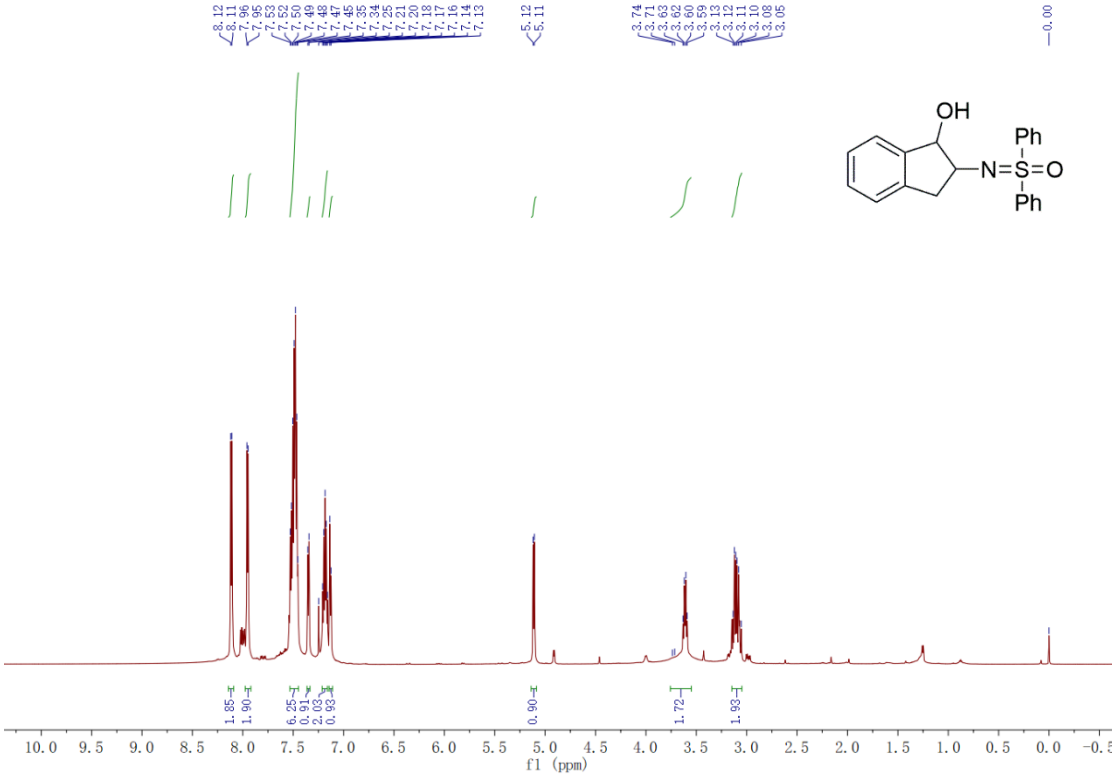

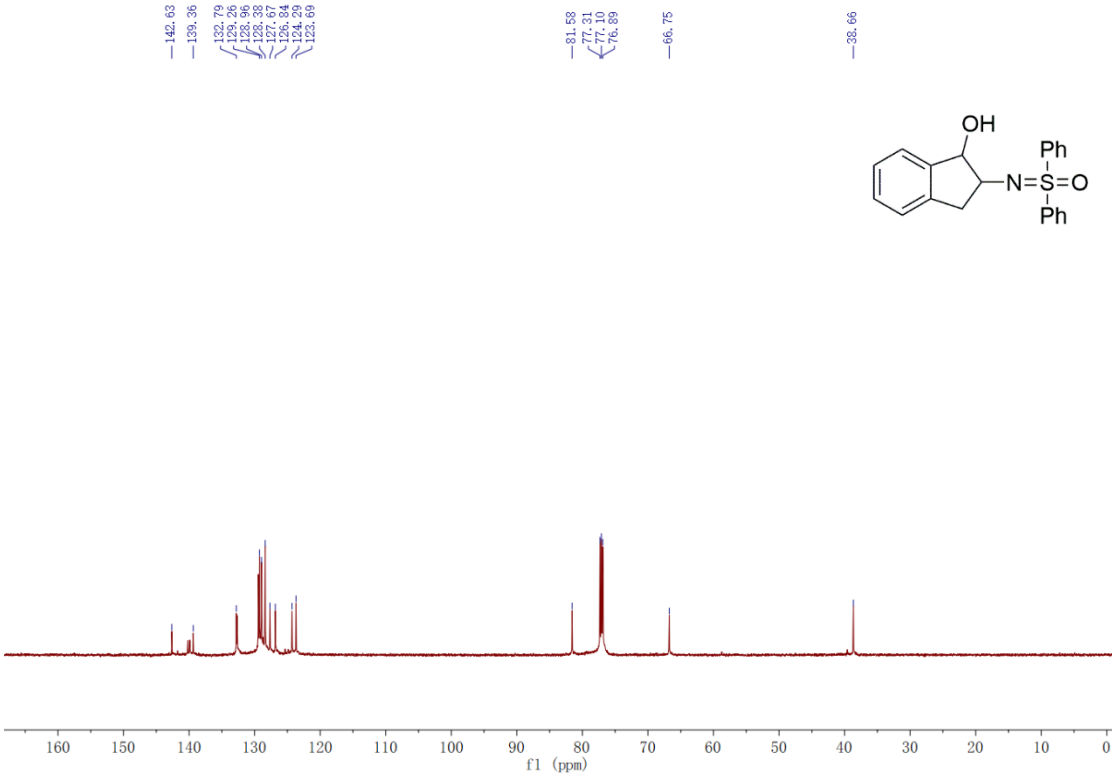

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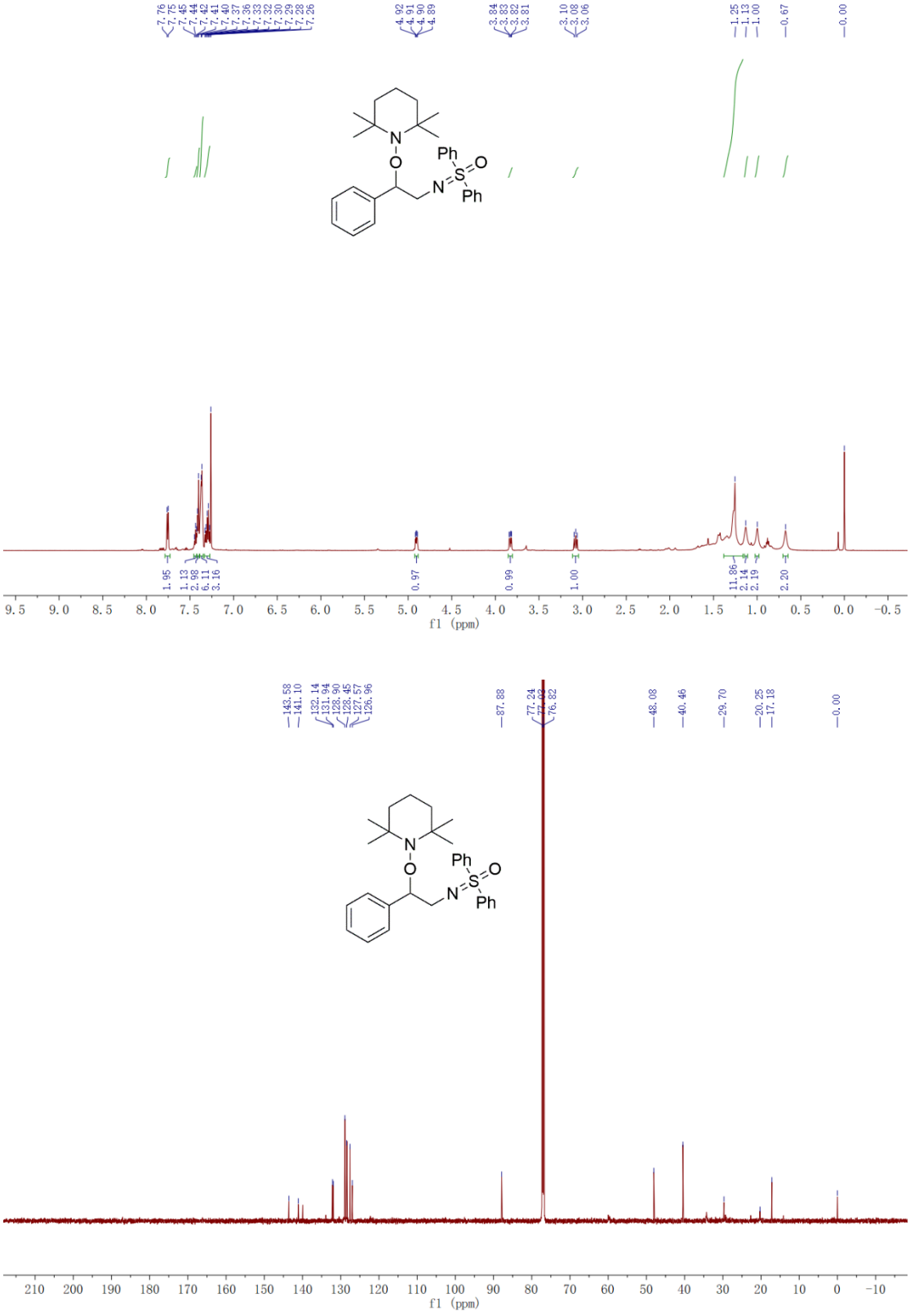
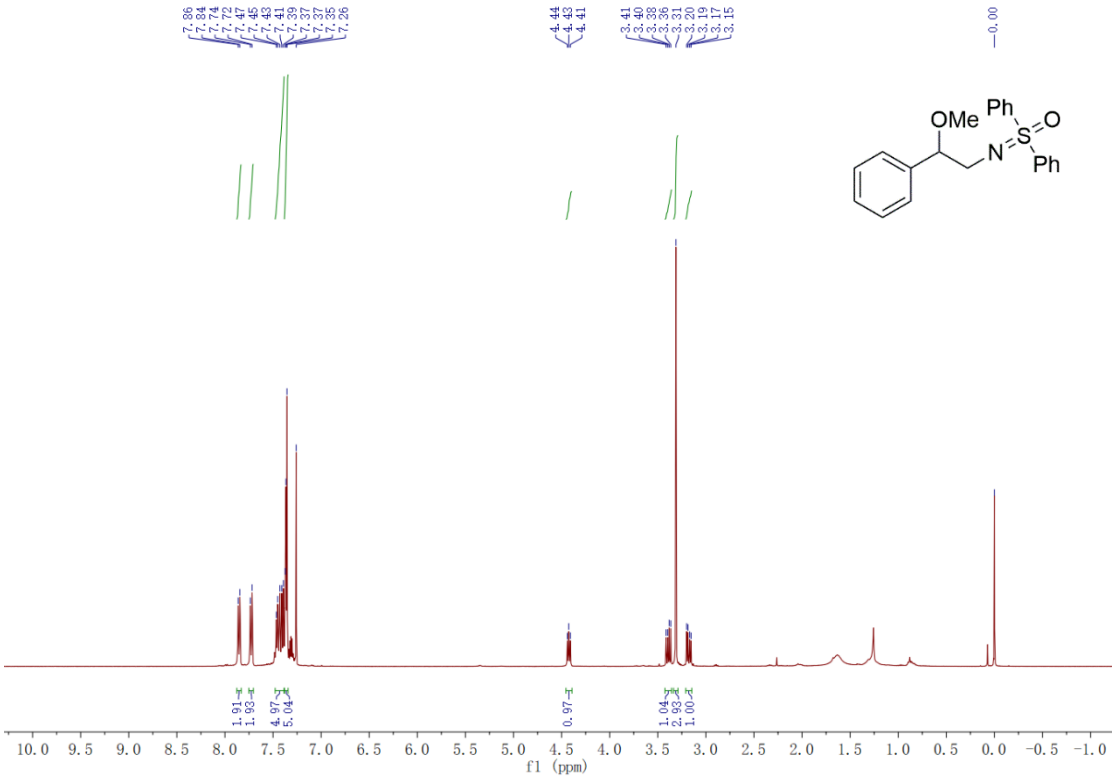
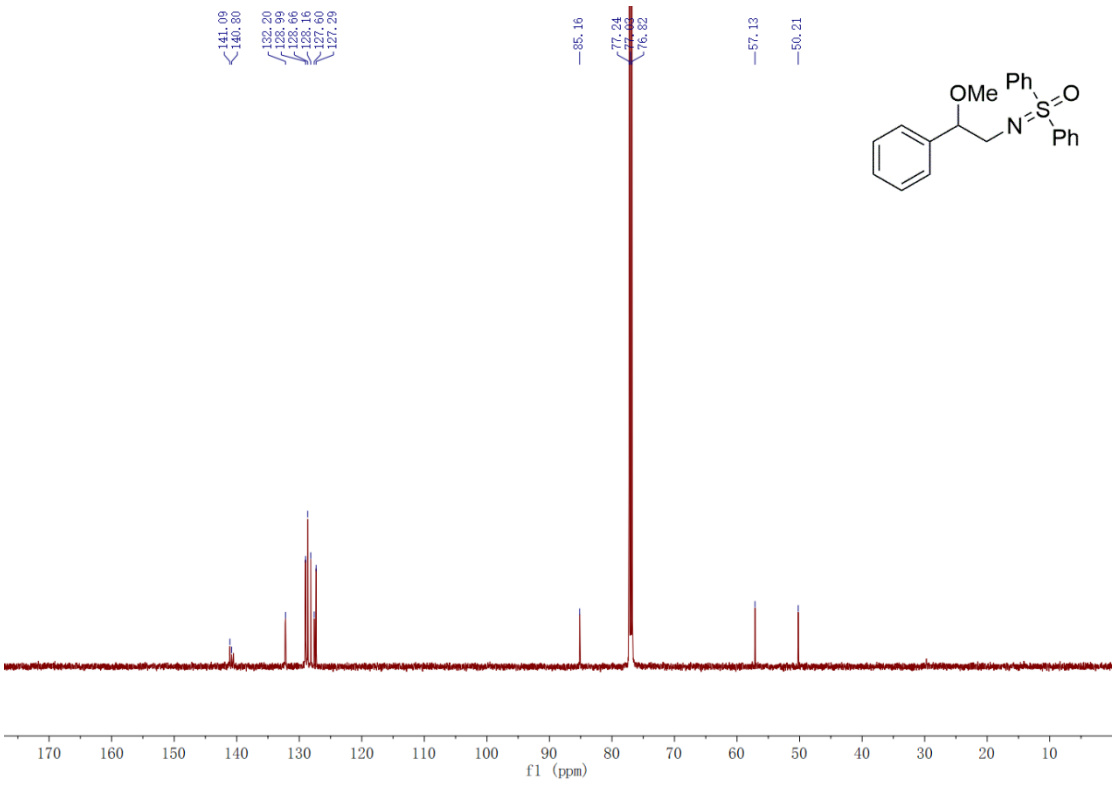


((2-methoxy-2-phenylethyl)imino)diphenyl-l6-sulfanone (3aa)





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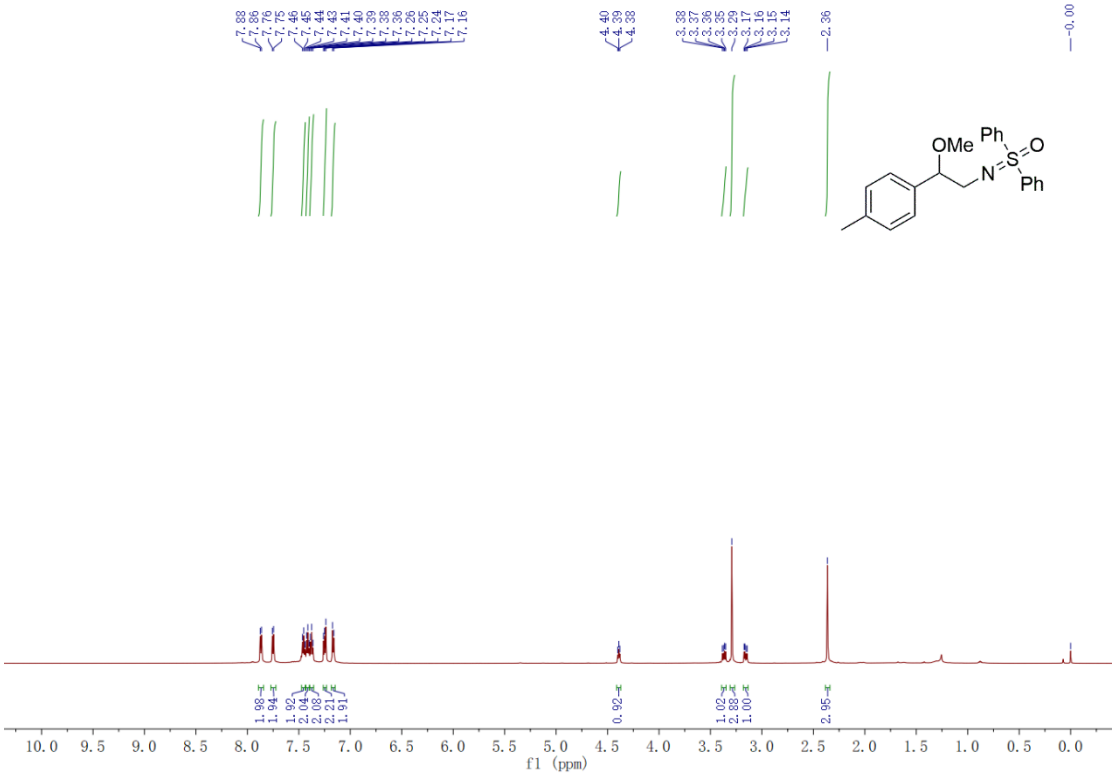

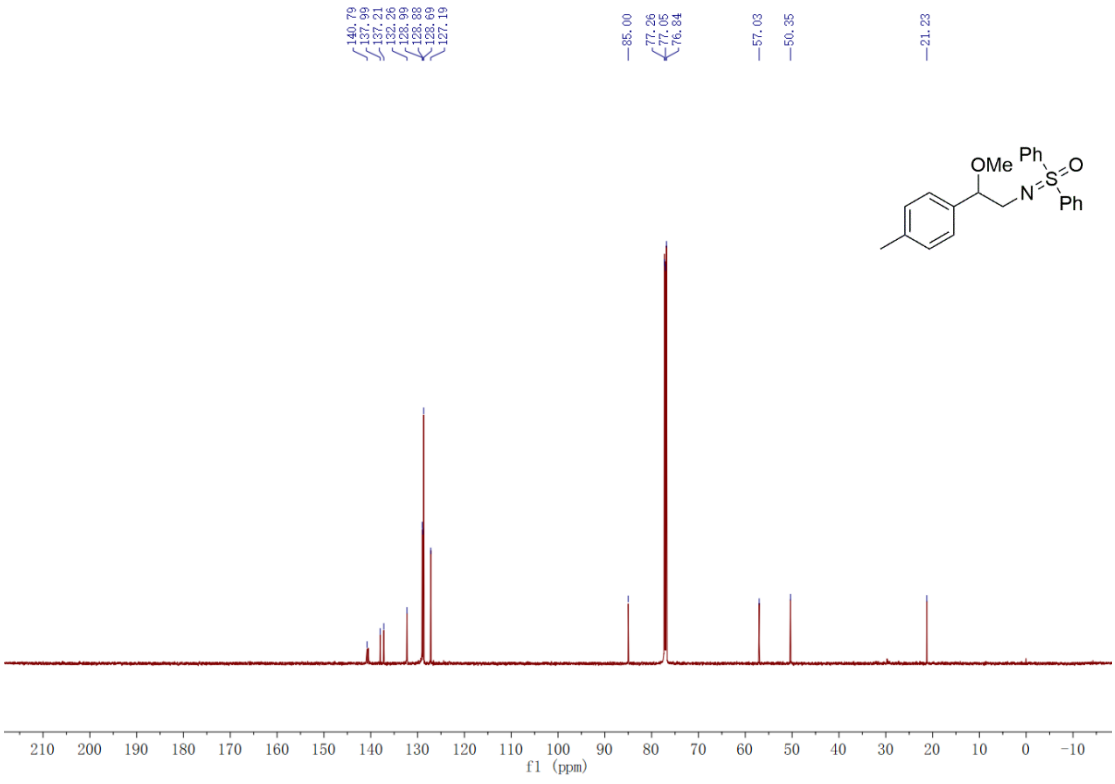

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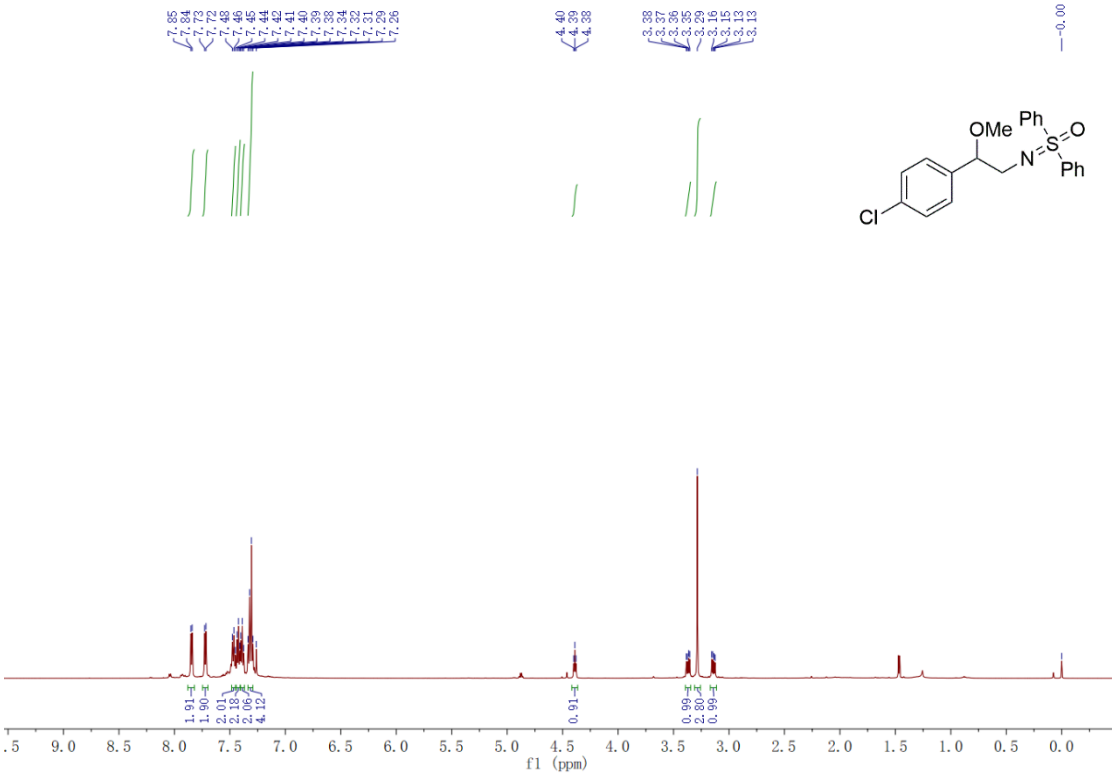

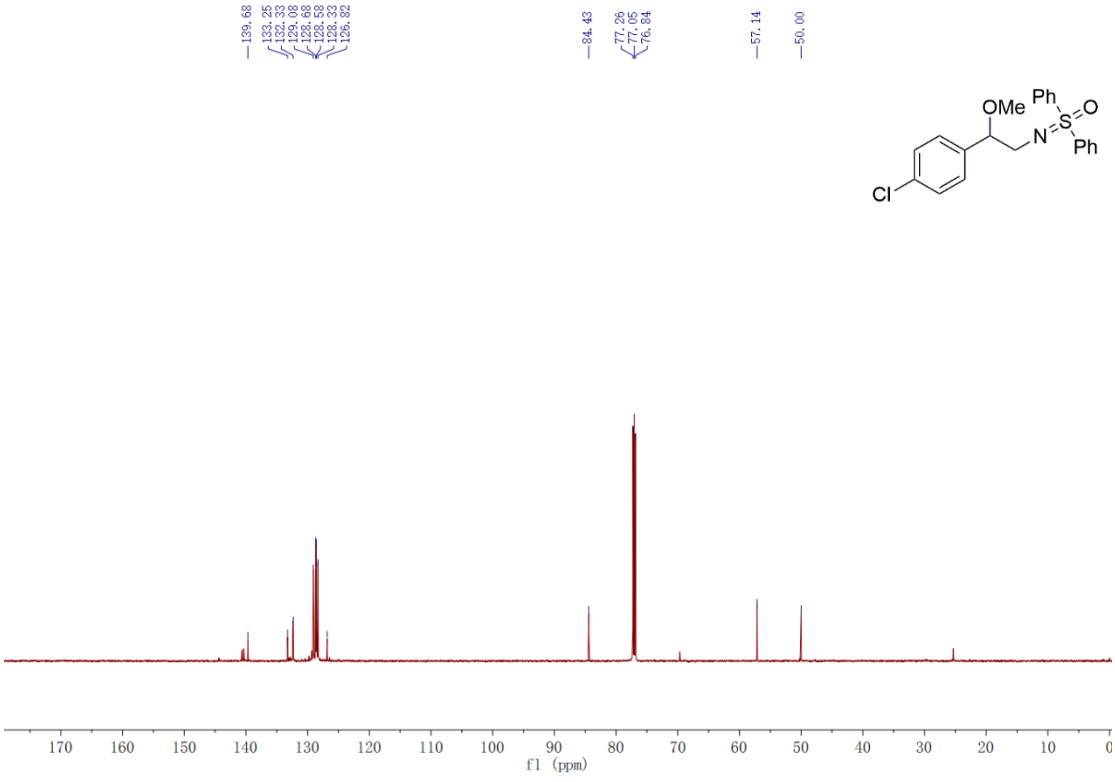

((2-(4-bromophenyl)-2-methoxyethyl)imino)diphenyl-l6-sulfanone (3ad)