Supporting Information

Sulfide Synthesis through Copper-Catalyzed C-S Bonds Formation under Biomolecule-Compatible Conditions

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I. General information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

NMR spectrum:

^{1}H and ^{13}C NMR spectra were collected on 400 MHz NMR spectrometers (Bruker AVANCE) using $CDCl_3$ or DMSO-d_6. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

Mass spectroscopy:

Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

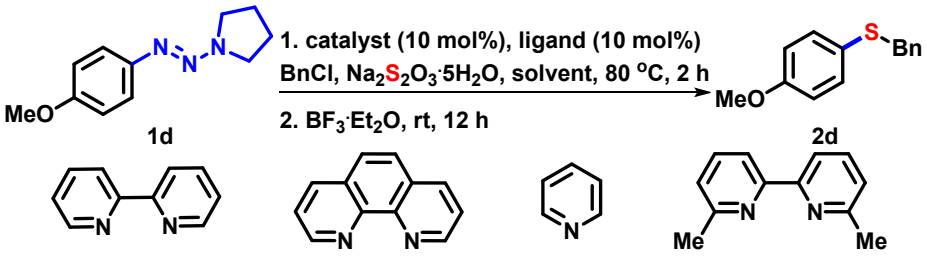
Chromatography:

Column chromatography was performed with silica gel (200-300 mesh ASTM).

IR:

TENSOR (27) Series FT-IR Spectrometers.

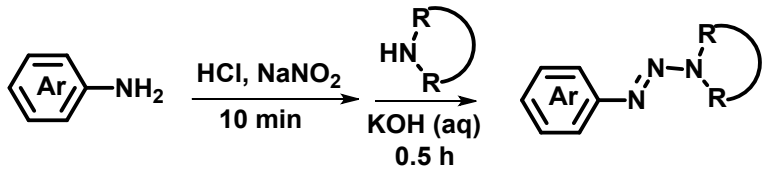
II. Optimization of Reaction Conditions



entry	catalyst	ligand	promoter	solvent	yield (%)[b]
1	$Pd_2(dba)_3$	L1	$BF_3{\cdot}Et_2O$	DMSO (2 mL)	33
2	$FeCl_3$	L1	$BF_3{\cdot}Et_2O$	MeOH/H_2O	42
3	$Cu(acac)_2$	L1	$BF_3{\cdot}Et_2O$	MeOH/H_2O	59
4	$CuSO_4{\cdot}5H_2O$	L1	$BF_3{\cdot}Et_2O$	MeOH/H_2O	65
5	-	-	$BF_3{\cdot}Et_2O$	MeOH/H_2O	20
6	$CuSO_4{\cdot}5H_2O$	L1	-	MeOH/H_2O	NR
7	$CuSO_4{\cdot}5H_2O$	-	$BF_3{\cdot}Et_2O$	MeOH/H_2O	46
8	$CuSO_4{\cdot}5H_2O$	L2	$BF_3{\cdot}Et_2O$	MeOH/H_2O	62
9	$CuSO_4{\cdot}5H_2O$	L3	$BF_3{\cdot}Et_2O$	MeOH/H_2O	37
10	$CuSO_4{\cdot}5H_2O$	L4	$BF_3{\cdot}Et_2O$	MeOH/H_2O	23
11	$CuSO_4{\cdot}5H_2O$	L1	$BF_3{\cdot}Et_2O$	MeOH/H_2O	66[c]
12	$CuSO_4{\cdot}5H_2O$	L1	$BF_3{\cdot}Et_2O$	MeOH/H_2O	54[d]
13	$CuSO_4{\cdot}5H_2O$	L1	$BF_3{\cdot}Et_2O$	H_2O (2 mL)	55
14	$CuSO_4{\cdot}5H_2O$	L1	$BF_3{\cdot}Et_2O$	H_2O (2 mL)	55[e]
15	***$CuSO_4{\cdot}5H_2O$***	***L1***	***$BF_3{\cdot}Et_2O$***	***H_2O (1 mL)***	***88***
16	$CuSO_4{\cdot}5H_2O$	L1	$BF_3{\cdot}Et_2O$	-	Trace
17	$CuSO_4{\cdot}5H_2O$	L1	HBF_4	H_2O (1 mL)	82

[a]Reaction conditions: catalyst (10 mol%), ligand (10 mol%), BnCl (1 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (1 mmol), MeOH/H_2O = 1/1 (2 mL), 80 °C, 2 h, then 1d (0.2 mmol), BF3·Et_2O (0.2 mmol) was added, and stirred at room temperature. [b]Isolated yields. [c]MeOH/H_2O = 1/2 (2 mL). [d]MeOH/H_2O = 2/1 (2 mL). [e]TBAB (0.2 mmol) was added.

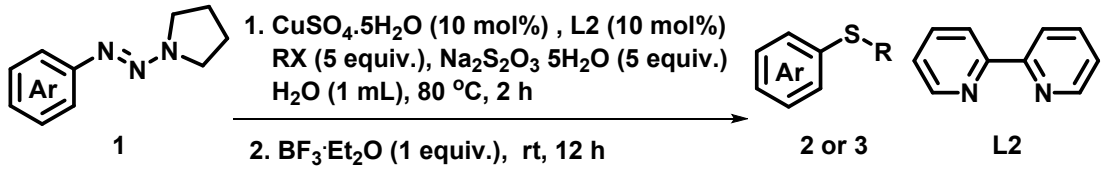
III. The Synthetic Procedure for Substrates



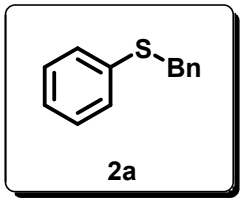
1-Aryltriazenes were prepared by a modification of the literature procedure.[1] A solution of arylamine (10 mmol) in concentrated HCl (2 mL) was cooled in an ice bath while a solution of $NaNO_2$ (10 mmol) in water (1 mL) was added dropwise. The resulting solution of the diazonium salt was stirred under ice bath for 10 min and then added all at once to a chilled solution of secondary amine (11 mmol) in 1 M KOH (10 mL). The reaction mixture was stirred for 30 min with cooling and the resulting precipitate isolated by filtration. The damp solid was recrystallized from EtOH and dried under reduced pressure or by column chromatography.

1. Margaret, L. G.; David, H. B.; Willard, M. W. *J. Org. Chem.* **1993**, *58*, 2104-2109.

IV. The Synthetic Procedure and Data for 2a-2y and 3a-3r .

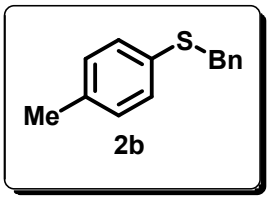


A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), RX (1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1** (0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, and $BF_3 \cdot Et_2O$ (0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature, some substrate need elevate temperature after added $BF_3 \cdot Et_2O$. When the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1 to ethyl acetate) to afford the desired product **2** or **3**.



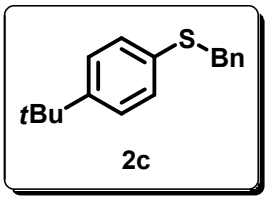
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1a** (35 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(phenyl)sulfane (**2a**): (38.8 mg, 97%), colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.13-7.24 (m, 9 H), 7.08-7.11 (m, 1 H), 4.03 (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.4, 136.3, 129.8, 128.8, 128.7, 128.4,

127.1, 126.3, 39.0; IR (neat): ν = 1582, 1477, 1230, 1068, 1025, 827, 737, 690; MS: 200.



2b

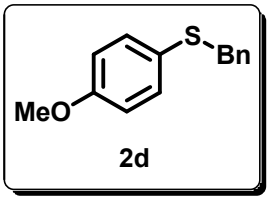
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1b** (37.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(*p*-tolyl)sulfane (**2b**): (35.1 mg, 82%), colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.19 (m, 5 H), 7.14 (d, J = 8 Hz, 2 H), 6.98 (d, J = 8 Hz, 2 H), 3.98 (s, 2 H), 2.22 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 136.6, 132.5, 130.7, 129.6, 128.9, 128.5, 127.1, 39.8, 21,1; IR (neat): ν = 2970, 2914, 1489, 1451, 1395, 1237, 1066, 800, 711, 694; MS m/z: 214.



2c

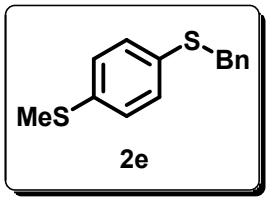
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1c** (46.2 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under

vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(4-tert-butylphenyl)sulfane (**2c**): (40.4 mg, 79%). colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19-7.22 (m, 9 H), 4.03 (s, 2 H), 1.22 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 137.7, 132.9, 129.9, 128.8, 128.5, 127.1, 39.4, 34.5, 31,3; IR (neat): ν = 2960, 2902, 1600, 1493, 1453, 1396, 1363, 1268, 1119, 1069, 823, 764, 697; MS m/z: 256.



2d

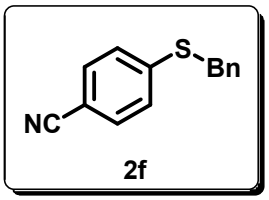
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, and $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product benzyl(4-methoxyphenyl)sulfane (**2d**): (40.5 mg, 88%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13-7.16 (m, 5 H), 7.08-7.11 (m, 2 H), 6.69 (d, J = 8.4 Hz, 2 H), 3.89 (s, 2 H), 3.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 138.2, 134.1, 128.9, 128.6, 128.4, 127.0, 126.1, 114.5, 55.3, 41.3; IR (neat): ν = 2960, 2917, 2835, 1593, 1491, 1453, 1285, 1241, 1176, 1026, 811, 696; MS m/z: 230.



2e

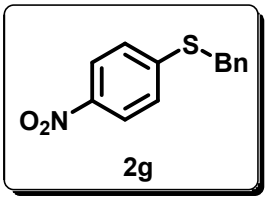
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to

room temperature, **1e** (44.2 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product benzyl(4-(methylthio)phenyl)sulfane (**2e**): (29.0 mg, 59%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.18 (m, 7 H), 7.04-7.13 (m, 2 H), 3.98 (s, 2 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6, 137.1, 132.5, 131.2, 128.8, 128.5, 127.2, 127.0, 39.7, 15.9; IR (neat): ν = 2918, 2851, 1493, 1474, 1390, 1260, 1238, 1102, 1005, 804, 695; HRMS (FAB): Calcd for $C_{14}H_{15}S_2$: 246.0537, Found 246.0539.

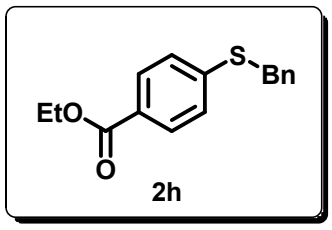


2f

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1f** (40.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was allowed to 50 ^{o}C for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product 4-(benzylthio)benzonitrile (**2f**): (25.2 mg, 56%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J = 8.8 Hz, 2 H), 7.19-7.42 (m, 7 H), 4.13 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 135.7, 132.2, 128.8, 128.7, 127.7, 127.3, 118.8, 108.6, 37.1; IR (neat): ν = 2923, 2853, 2222, 1903, 1739, 1590, 1483, 1453, 1398, 1086, 818, 780, 718, 698; MS m/z: 225.

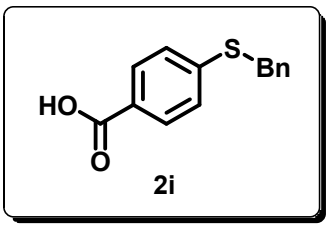


A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1g** (44.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was allowed to 80 ^oC for 6 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to afford the desired product benzyl(4-nitrophenyl)sulfane (**2g**): (33.8 mg, 69%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.01-8.03 (m, 2 H), 7.18-7.32 (m, 7 H), 4.17 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 145.5, 135.5, 128.9, 128.7, 127.8, 1265.7, 123.9, 37.1; IR (neat): ν = 2962, 1572, 1507, 1451, 1334, 1179, 837, 739, 717, 697; MS m/z: 245.



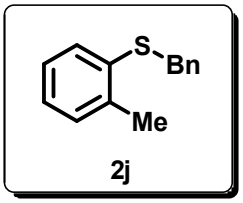
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1h** (49.4 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to afford the desired product ethyl 4-(benzylthio)benzoate (**2h**): (39.2 mg, 72%), yellow solid. ^1H NMR

(400 MHz, $CDCl_3$) δ: 7.84 (d, J = 8.0 Hz, 2 H), 7.18-7.29 (m, 7 H), 4.27 (q, J = 7.2 Hz, 2 H), 4.12 (s, 2 H), 1.30 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 143.5, 136.4, 129.9, 128.8, 128.7, 127.5, 127.1, 66.9, 37.4, 14.3; IR (neat): v = 2098, 1711, 1593, 1271, 1179, 1107, 1017, 758, 693; MS m/z: 272.



2i

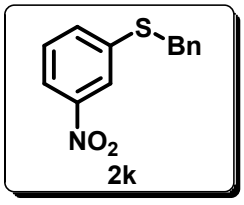
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1i** (43.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was allowed to 80 ^{o}C for 6 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 1:1 to ethyl acetate) to afford the desired product 4-(benzylthio)benzoic acid (**2i**): (34.6 mg, 71%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.87 (br, 1 H), 7.83 (d, J = 8.4 Hz, 2 H), 7.41-7.43 (m, 4 H), 7.30-7.34 (m, 2 H), 7.26 (t, J = 7.2 Hz, 1 H), 4.35 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.4, 143.5, 137.0, 130.2, 129.3, 128.9, 127.9, 127.7, 126.9, 35.8; IR (neat): v = 3060, 3027, 2972, 2911, 1677, 1591, 1493, 1452, 1321, 1293, 1118, 919, 759, 694; MS m/z: 244.



2j

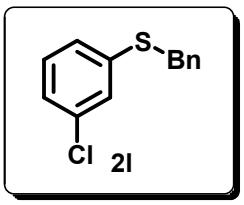
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature,

1j (37.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(o-tolyl)sulfane (**2j**): (30.0 mg, 70%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14-7.21 (m, 6 H), 7.01-7.06 (m, 3 H), 3.99 (s, 2 H), 2.24 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, 137.3, 135.8, 130.1, 129.0, 128.9, 128.5, 127.2, 126.4, 126.1, 38.3, 20.3; IR (neat): ν = 2920, 1587, 1493, 1452, 1238, 743, 696; MS m/z: 214.

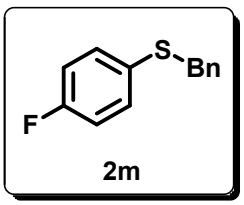


2k

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1k** (44.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to afford the desired product benzyl(3-nitrophenyl)sulfane (**2k**): (33.3 mg, 68%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (t, J = 1.6 Hz, 1 H), 7.91 (dd, J_1 = 1.6 Hz, J_2 = 8 Hz, 1 H), 7.47 (d, J = 7.6 Hz, 1 H), 7.32 (t, J = 8 Hz 1 H), 7.18-7.27 (m, 5 H), 4.13 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 139.4, 136.0, 134.6, 129.5, 128.9, 128.8, 128.6, 127.7, 123.1, 120.8, 38.2; IR (neat): ν = 1593, 1574, 1516, 1344, 724; HRMS (FAB): Calcd for $C_{13}H_{11}NO_2S$: 245.0511, Found : 245.0509.

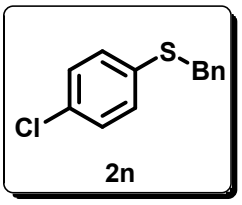


A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1l** (41.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(3-chlorophenyl)sulfane (**2l**): (40.7 mg, 87%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.17-7.23 (m, 6 H), 7.07-7.08 (m, 3 H), 4.04 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6, 136.8, 134.6, 129.8, 129.0, 128.8, 128.6, 127.4, 127.3, 126.3, 38.7; IR (neat): ν = 1588, 1488, 1445, 1255, 943, 880, 784, 743; HRMS (FAB): Calcd for $C_{13}H_{11}ClS$: 234.0270, Found 234.0271.



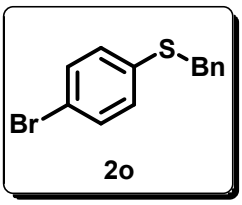
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1m** (38.6 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum

ether/ethyl acetate 200:1) to afford the desired product benzyl(4-fluorophenyl)sulfane (**2m**): (35.3 mg, 81%), colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11-7.19 (m, 7 H), 6.82-6.87 (m, 2 H), 3.94 (s, 2 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -114.7 (s, 1 F); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.1 (d, $J_{C\text{-}F}$ = 245 Hz), 137.5, 133.4 (d, $J_{C\text{-}F}$ = 8 Hz), 130.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.9, 128.5, 127.2, 115.9 (d, $J_{C\text{-}F}$ = 21 Hz), 40.5; IR (neat): ν = 1592, 1487, 1397, 1227, 1158, 1091, 820, 694; MS: 218.



2n

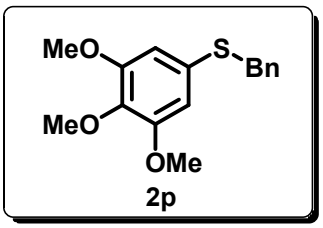
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1n** (41.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(4-chlorophenyl)sulfane (**2n**): (34.2 mg, 73%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14-7.22 (m, 5 H), 7.12 (s, 4H), 3.99 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 134.7, 132.5, 131.4, 129.4, 129.1, 129.0, 128.8, 127.3, 39.3; IR (neat): ν = 2902, 1452, 1393, 1229, 1068, 893, 810; MS m/z: 234.



2o

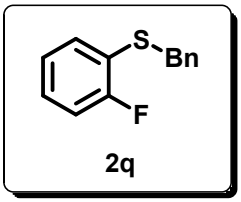
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1o** (50.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was

stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(4-bromophenyl)sulfane: (**2o**) (42.4 mg, 76%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (d, J = 8.4 Hz, 2 H), 7.12-7.21 (m, 5 H), 7.06 (d, J = 8.4 Hz, 2 H), 4.00 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1, 135.5, 131.9, 131.5, 128.8, 128.6, 127.4, 120.3, 39.1; IR (neat): ν = 2970, 1492, 1384, 1230, 1069, 1004, 807, 763, 695; MS m/z: 279.



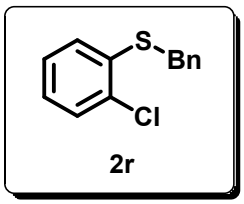
2p

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1p** (53.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product benzyl(3,4,5-trimethoxyphenyl)sulfane (**2p**): (56.8 mg, 98%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18-7.22 (m, 5 H), 6.43 (s, 2 H), 3.98 (s, 2 H), 3.74 (s, 3 H), 3.68(s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.1, 137.9, 137.4, 130.4, 130.0, 128.5, 127.2, 108.6, 60.9, 56.1, 40.4; IR (neat): ν = 2935, 2831, 1577, 1496, 1451, 1306, 1330, 1123, 1004, 879, 796 698; HRMS (FAB): Calcd for $C_{16}H_{18}O_3S$: 290.0977, Found 290.0979.



2q

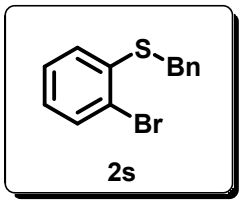
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1q** (38.6 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(2-fluorophenyl)sulfane (**2q**): (28.3 mg, 65%) colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.30 (m, 3 H), 7.22-7.24 (m, 2 H), 7.15-7.19 (m, 2 H), 7.02-7.09 (m, 2 H), 4.07 (s, 2 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -109.1 (s, 1 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.6 (d, $J_{C\text{-}F}$ = 244 Hz), 137.1, 132.9 (d, $J_{C\text{-}F}$ = 1.8 Hz), 128.7, 128.6 (d, $J_{C\text{-}F}$ = 38 Hz), 127.2, 124.6 (d, $J_{C\text{-}F}$ = 4 Hz), 122.7 (d, $J_{C\text{-}F}$ = 17 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22 Hz), 38.3 (d, $J_{C\text{-}F}$ = 3 Hz); IR (neat): ν = 2922, 1523, 1493,1471, 745; MS m/z: 218.



2r

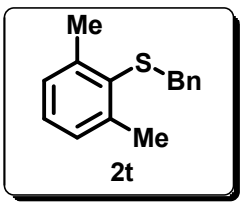
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1r** (41.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(2-chlorophenyl)sulfane

(**2r**): (30.0 mg, 64%), white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18-7.30 (m, 7 H), 7.02-7.17 (m, 2 H), 4.07 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.3, 135.8 133.7, 129.7, 129.3, 128.9, 128.6 127.4, 127.1, 126.9, 37.5; IR (neat): ν = 2924, 1523, 1493, 743; MS m/z: 234.



2s

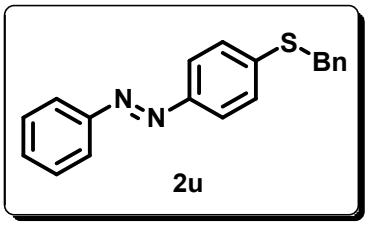
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1s** (50.6 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(2-bromophenyl)sulfane (**2s**): (40.7 mg, 73%) white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.58 (m, 1 H), 7.38-7.40 (m, 2 H), 7.31-7.35 (m, 2 H), 7.27-7.30 (m, 1 H), 7.23-7.26 (m, 2 H), 7.02-7.07 (m, 1 H), 4.18 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, 136.1, 132.9, 129.0, 128.8, 127.7, 127.5, 126.9, 123.6, 37.9; IR (neat): ν = 2923, 1575, 1493, 743; MS m/z: 279.



2t

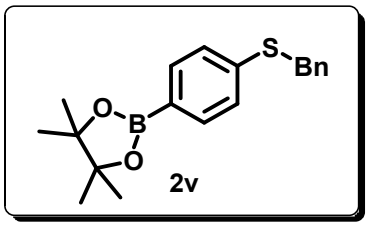
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1t** (40.6 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was

allowed to 50 °C for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product benzyl(2,6-dimethylphenyl)sulfane (**2t**): (22.3 mg, 49%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14-7.19 (m, 3 H), 7.03-7.05 (m, 1 H), 6.99-7.01 (m, 4 H), 3.72 (s, 2 H), 2.32 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.6, 138.4, 132.8, 128.6, 128.5, 128.3, 128.0, 126.9, 39.8, 21.8; IR (neat): ν = 3058, 3027, 2921, 1600, 1493, 1455, 1375, 1232, 767, 696; MS m/z: 228.

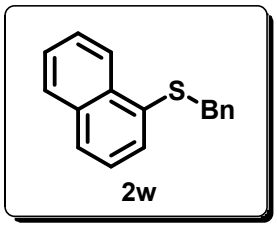


2u

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1u** (55.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product (*E*)-1-(4-(benzylthio)phenyl)-2-phenyldiazene (**2u**): (45.0 mg, 74%), red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J = 7.2 Hz, 2 H), 7.73 (d, J = 8.4 Hz, 2 H), 7.35-7.42 (m, 3 H), 7.21-7.30 (m, 4 H), 7.12-7.19 (m, 3 H) , 4.10 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.7, 150.6, 141.1, 136.7, 131.0, 129.2, 128.9, 128.7, 128.6, 128.5, 127.5, 123.4, 122.9, 38.0; IR (neat): ν = 2970, 2904, 1582, 1496, 1400, 828, 766, 715, 685; HRMS (FAB): Calcd for $C_{19}H_{16}N_2S$: 304.1034, Found 304.1036.

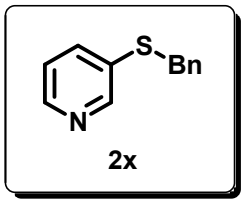


A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1v** (60.2 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 2-(4-(benzylthio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2v**): (42.4 mg, 65%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 8 Hz, 2 H), 7.32 (t, J = 7.2 Hz, 3 H), 7.28 (s, 3 H), 7.23 (s, 1 H), 4.17 (s, 2 H), 1.33 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 137.0, 135.1, 128.8, 128.6, 127.4, 127.3, 83.8, 37.8, 24.9; IR (neat): ν = 2976, 2930, 2903, 2251, 1596, 1361, 1130, 1050, 909, 733; MS m/z: 326.



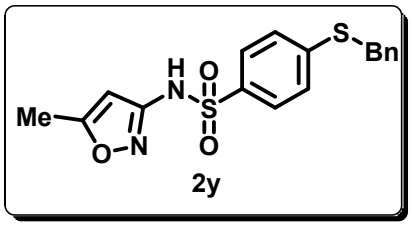
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1w** (45.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was allowed to 50 ^oC for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired

product benzyl(naphthalen-1-yl)sulfane (**2w**): (42.0 mg, 84%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, J = 7.2 Hz, 1 H), 7.90 (d, J = 7.2 Hz, 1 H), 7.80 (d, J = 8.4 Hz, 1 H), 7.52-7.61 (m, 3 H), 7.40-7.42 (m, 1 H), 7.28-7.32 (m, 5 H), 4.21 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 133.9, 133.4, 133.0, 128.6, 128.5, 127.7, 127.2, 126.5, 126.3, 125.6, 125.1, 39.4; IR (neat): ν = 2974, 2902, 1493, 1458, 1378, 1231, 1054, 773, 729, 679; MS m/z: 250.



2x

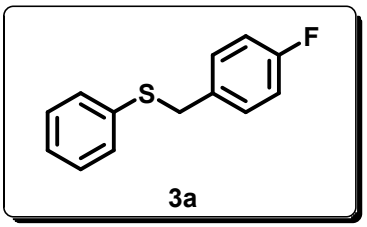
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1x** (35.2 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was allowed to 80 ^{o}C for 6 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 3-(benzylthio)pyridine (**2x**): (22.5 mg, 56%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (d, J = 2 Hz, 1 H), 8.35 (dd, J_1 = 1.2 Hz, J_2 = 4.8 Hz, 1 H), 7.47-7.50 (m, 1 H), 7.16-7.21 (m, 5 H), 7.08 (dd, J_1 = 4.7 Hz, J_2 = 7.6 Hz, 1 H), 4.03 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 147.6, 138.2, 136.8, 133.0, 128.8, 128.6, 127.5, 123.5, 39.2; IR (neat): ν = 2972, 2883, 1379, 1088, 1046, 881; MS m/z: 201.



2y

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), BnCl (126 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was

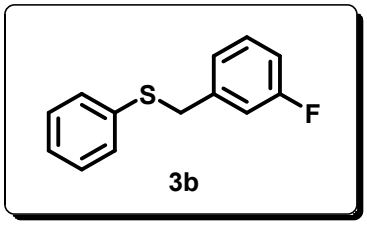
heated at 80 °C for 2 h. After cooled to room temperature, **1y** (67.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at 80 °C for 6 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 2:1-1:2) to afford the desired product 4-(Benzylthio)-N-(5-methylisoxazol-3-yl)benzenesulfonamide (**2y**): (46.8 mg, 65%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.39 (br, 1 H), 7.72 (d, J = 8.0 Hz, 2 H), 7.51 (d, J = 8.0 Hz, 2 H), 7.40-7.42 (m, 2 H), 7.30-7.34 (m, 2 H), 7.23-7.27 (m, 1 H), 6.13 (s, 1 H), 4.36 (s, 2 H), 2.29 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 157.4, 144.3, 135.6, 127.3, 127.1, 126.6, 95.4, 35.1, 12.0; IR (neat): ν = 3088, 2903, 2853, 1614, 1463, 1464, 1400, 1343, 1261, 1170, 1076, 1032, 930, 816, 799, 758, 719, 682; MS m/z: 360.



3a

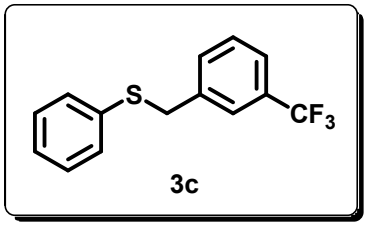
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-4-fluorobenzene (144 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1a** (35.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product (4-fluorobenzyl)(phenyl)sulfane (**3a**): (31.0 mg, 71%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13-7.22 (m, 7 H), 6.88 (t, J = 8.7 Hz, 2 H), 3.99 (s, 2 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.4 (s, 1 F); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 244 Hz), 135.9, 133.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8 Hz), 130.2, 128.9, 126.6, 115.3 (d, $J_{C\text{-}F}$ = 21 Hz), 38.4; IR (neat): v = 3063, 2920, 2853 1688, 1597, 1500, 1478 ,1224, 1153, 1068, 1012, 834, 756, 730, 687; MS: 218.



3b

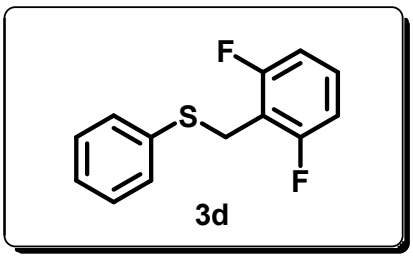
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-3-fluorobenzene (144 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1a** (35.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product (3-fluorobenzyl)(phenyl)sulfane (**3b**): (36.2 mg, 83%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.19-7.23 (m, 3 H), 7.16-7.18 (m, 2 H), 7.11-7.14 (m, 1 H), 6.91-6.97 (m, 2 H), 6.84-6.86 (m, 1 H), 4.00 (s, 2 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -113.2 (s, 1 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 244 Hz), 140.2 (d, $J_{C\text{-}F}$ = 7.4 Hz), 135.7, 130.2, 129.9 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.0, 126.7, 124.4 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22 Hz), 114.1 (d, $J_{C\text{-}F}$ = 21 Hz), 38.7 (d, $J_{C\text{-}F}$ = 1.7 Hz); IR (neat): v = 3059, 2926, 1587, 1484, 1587, 1484, 1444, 1256, 1137, 1071, 943, 784 ,687; HRMS (FAB): Calcd for $C_{13}H_{11}FS$: 218.0565, Found 218.564.



3c

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-3-

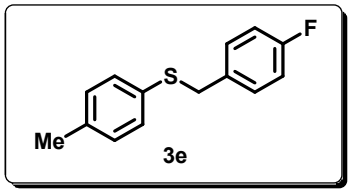
(trifluoromethyl)benzene (194 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1a** (35.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product phenyl(3-(trifluoromethyl)benzyl)sulfane (**3c**): (38.6 mg, 72%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.42 (m, 3 H), 7.31 (t, J = 1.8 Hz, 1 H), 7.14-7.22 (m, 5 H), 4.05 (s, 2 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.5 (s, 3 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.1, 132.2, 130.7, 129.0, 128.9, 127.0, 125.6 (q, J_{C-F} = 38 Hz), 125.4, 124.0 (q, J_{C-F} = 38 Hz), 122.6, 39.0; IR (neat): ν = 3026, 1585, 1479, 1449, 1329, 1163, 1120, 1071, 906, 802, 739 ,697; MS: 268.



3d

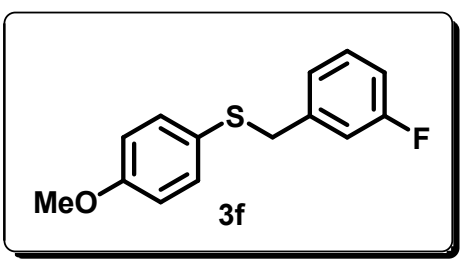
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 2-(chloromethyl)-1,3-difluorobenzene (162 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1a** (35.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product (2,6-difluorobenzyl)(phenyl)sulfane (**3d**): (39.6 mg, 84%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (dd, J_1 = 0.5 Hz, J_2 = 8 Hz, 2 H), 7.15-7.20 (m, 3 H),

7.07-7.09 (m, 1 H), 6.74 (t, J = 8 Hz, 2 H), 4.04 (s, 2 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -114.6 (s, 2 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (dd, $J_{C\text{-}F1}$ = 248 Hz, $J_{C\text{-}F2}$ = 7.7 Hz), 135.0, 131.8, 128.9, 128.8, 128.8 (t, $J_{C\text{-}F}$ = 10.1 Hz), 127.3, 114.4 (t, $J_{C\text{-}F}$ = 19 Hz), 111.2 (dd, $J_{C\text{-}F1}$ = 37.8 Hz, $J_{C\text{-}F2}$ = 6.2 Hz), 26.8 (t, $J_{C\text{-}F}$ = 2.5 Hz); IR (neat): v = 3072, 2945, 1624, 1590, 1469, 1439, 1272, 1237, 1171, 995, 785, 737, 691; HRMS (FAB): Calcd for $C_{13}H_{10}F_2S$: 236.0471, Found 236.0474.



3e

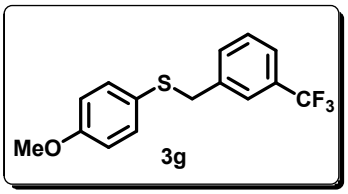
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-4-fluorobenzene (144 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1b** (37.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product (4-fluorobenzyl)(*p*-tolyl)sulfane (**3e**): (32.9 mg, 71%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11-7.14 (m, 4 H), 6.99 (d, J = 8 Hz, 2 H), 6.85-6.90 (m, 2 H), 3.95 (s, 2 H), 2.24 (s, 3 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.6 (s, 1 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 244 Hz), 136.9, 136.6 (d, $J_{C\text{-}F}$ = 3 Hz), 131.9, 131.1, 130.4 (d, $J_{C\text{-}F}$ = 8 Hz), 129.7, 115.3 (d, $J_{C\text{-}F}$ = 21 Hz), 39.1, 21.1; IR (neat): v = 2949, 2844, 1714, 1602, 1511, 1433, 1246, 1166, 1026, 829; MS m/z: 232.



3f

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-3-

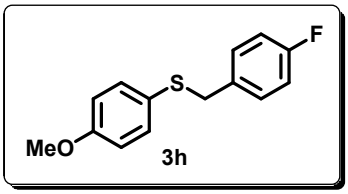
fluorobenzene (144 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product (3-fluorobenzyl)(4-methoxyphenyl)sulfane (**3f**): (44.6 mg, 90%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16-7.18 (m, 2 H), 6.81-6.87 (m, 4 H), 6.70-6.73 (m, 2 H), 3.87 (s, 2 H), 3.71 (s, 3 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -113.4 (s, 1 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 244 Hz), 159.4, 140.8 (d, $J_{C\text{-}F}$ = 7.3 Hz), 134.4, 129.7 (d, $J_{C\text{-}F}$ = 8.2 Hz), 125.4, 124.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22 Hz), 114.5, 113.9 (d, $J_{C\text{-}F}$ = 21 Hz), 55.3, 40.9 (d, $J_{C\text{-}F}$ = 1.7 Hz); IR (neat): ν = 2983, 2898, 1592, 1493, 1331, 1256, 1247, 1171, 1130, 1074, 910, 736; HRMS (FAB): Calcd for $C_{14}H_{13}FOS$: 248.0671, Found 248.0672.



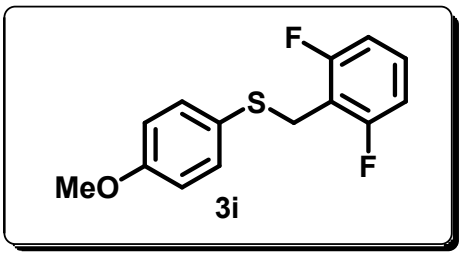
3g

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-3-(trifluoromethyl)benzene (194 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography

(petroleum ether/ethyl acetate 100:1) to afford the desired product (4-methoxyphenyl)(3-(trifluoromethyl)benzyl)sulfane (**3g**): (47.1 mg, 79%) white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.47 (m, 1 H), 7.34-7.36 (m, 3 H), 7.20-7.22 (m, 2 H), 6.77-6.80 (m, 2 H), 3.98 (s, 2 H), 3.78 (s, 3 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.6 (s, 3 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 139.3, 134.9, 132.2, 128.8, 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.8, 123.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 114.6, 55.3, 41.0; IR (neat): ν = 2973, 2286, 1592, 1331, 1089, 1048, 881; HRMS (FAB): Calcd for $C_{15}H_{13}F_3OS$: 298.0639, Found 298.0637.

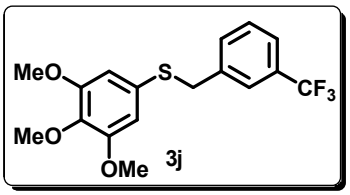


A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-4-fluorobenzene (144 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product (4-fluorobenzyl)(4-methoxyphenyl)sulfane (**3h**): (32.2 mg, 65%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14-7.18 (m, 2 H), 7.03-7.06 (m, 2 H), 6.83-6.87 (m, 2 H), 6.70-6.72 (m, 2 H), 3.86 (s, 2 H), 3.70 (s, 3 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.7 (d, J = 4.5 Hz, 1 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 244 Hz), 159.4, 134.4, 134.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 125.6, 115.2 (d, $J_{C\text{-}F}$ = 11.3 Hz), 114.5, 55.3, 40.5; IR (neat): ν = 2965, 2919, 1896, 1594, 1508, 1492, 1332, 1285, 1177, 1155, 1027, 812, 756; HRMS (FAB): Calcd for $C_{14}H_{13}FOS$: 248.0671, Found 248.0673.



3i

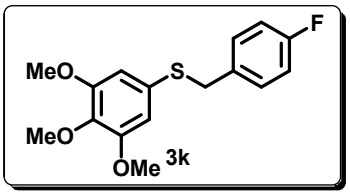
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 2-(chloromethyl)-1,3-difluorobenzene (162 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product (2,6-difluorobenzyl)(4-methoxyphenyl)sulfane (**3i**): (38.8 mg, 73%), white solid. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.21-7.23 (m, 2 H), 7.08-7.18 (m, 1 H), 6.69-6.74 (m, 4 H), 3.93 (s, 2 H), 3.71 (s, 3 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -114.9 (s, 2 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (dd, $J_{C\text{-}F1}$ = 248 Hz, $J_{C\text{-}F2}$ = 7.9 Hz), 159.8, 135.6, 131.9, 128.7, 128.6, 128.5, 124.9, 114.4, 111.1 (dd, $J_{C\text{-}F1}$ = 16.5 Hz, $J_{C\text{-}F2}$ = 6.3 Hz), 55.3, 28.3; IR (neat): ν = 2964, 2839, 2228, 1624, 1589, 1492, 1467, 1272, 1239, 1176, 1023, 996, 826, 784, 736; HRMS (FAB): Calcd for $C_{14}H_{12}F_2OS$: 266.0577, Found 266.0576.



3j

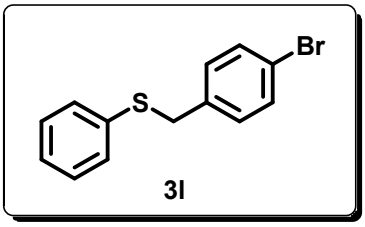
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-3-(trifluoromethyl)benzene (194 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1p** (53.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added.

The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product (3-(trifluoromethyl)benzyl)(3,4,5-trimethoxyphenyl)sulfane (**3j**): (52.2 mg, 73%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.49 (m, 1 H), 7.43 (s, 1 H), 7.38-7.40 (m, 2 H), 6.48 (s, 2 H), 4.05 (s, 2 H), 3.80 (s, 3 H), 3.73 (s, 6 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.6 (s, 3 F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 139.1, 137.8, 132.31, 132.30, 130.8, 130.5, 129.2, 129.0, 125.7 (q, J_{C-F} = 3.8 Hz), 129.9 (q, J_{C-F} = 3.8 Hz), 109.4, 60.9, 56.0, 40.2; IR (neat): ν = 2985, 2941, 2905, 2254, 1736, 1580, 1498, 1374, 1237, 1125, 1045, 917, 731; HRMS (FAB): Calcd for $C_{17}H_{17}F_3O_3S$: 358.0850, Found 358.0847.



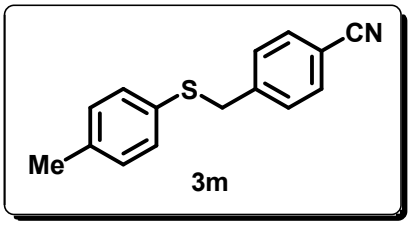
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-4-fluorobenzene (144 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1p** (53.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 50:1) to afford the desired product (4-fluorobenzyl)(3,4,5-trimethoxyphenyl)sulfane (**3k**): (32.6 mg, 53%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18-7.21 (m, 2 H), 6.94-6.98 (m, 2 H), 6.49 (s, 2 H), 4.01 (s, 2 H), 3.81 (s, 3 H), 3.76 (s, 6 H); ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.3 (s, 1 F); ^{13}C NMR (100

MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 244 Hz), 153.2, 137.4, 133.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.0, 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 108.7, 60.9, 56.1, 39.7; IR (neat): v = 2985, 2903, 1738, 1580, 1499, 1405, 1331, 1244, 1168, 1128, 1048, 912, 734; HRMS (FAB): Calcd for $C_{16}H_{17}FO_3S$: 308.0882, Found 308.0880.



3l

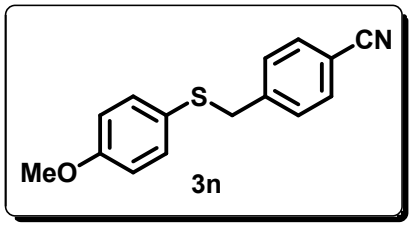
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-bromo-4-(chloromethyl)benzene (205 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1a** (35.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 200:1) to afford the desired product (4-bromobenzyl)(phenyl)sulfane (**3l**): (27.3 mg, 49%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (d, J = 8.4 Hz, 2 H), 7.16-7.22 (m, 4 H), 7.11-7.13 (m, 1 H), 7.06 (d, J = 8.4 Hz, 2 H), 3.96 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 135.6, 131.6, 130.5, 130.3, 128.9, 126.7, 121.0, 38.6; IR (neat): v = 3063, 2921, 1587, 1483, 827, 731, 687; MS: 279.



3m

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 4-(chloromethyl)benzonitrile (151 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1b** (37.8 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room

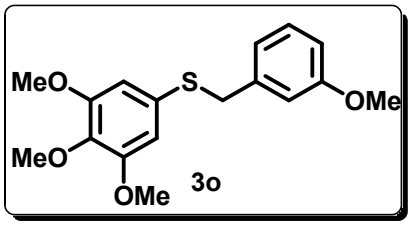
temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 4-(*p*-tolylthiomethyl)benzonitrile (**3m**): (38.2 mg, 80%) white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 4.04 (s, 2 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 137.6, 132.2, 131.7, 130.8 129.8, 129.5, 118.8, 110.8, 39.9, 21.1; IR (neat): ν = 2970, 2937, 2227, 1724, 1602, 1488, 1175, 1017, 846, 811, 682; MS m/z: 239.



3n

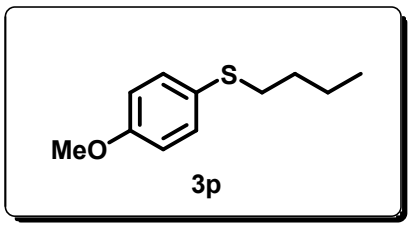
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 4-(chloromethyl)benzonitrile (151 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product 4-((4-methoxyphenylthio)methyl)benzonitrile (**3n**): (33.7 mg, 66%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.4 Hz, 2 H), 6.18-6.20 (m, 4 H), 6.78 (d, J = 8.8 Hz, 2 H), 3.95 (s, 2 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.0, 134.9, 132.1, 129.6, 124.4, 118.9, 114.6, 110.7, 55.3, 41.2; IR (neat): ν = 2958, 2921, 2225, 1735, 1605, 1503, 1413, 1249, 1177, 1076, 834, 734; HRMS (FAB): Calcd for

$C_{15}H_{13}NOS$: 255.0718, Found 255.0716.



3o

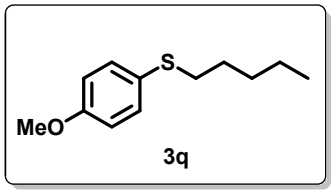
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-(chloromethyl)-3-methoxybenzene (156 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1p** (53.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 40:1) to afford the desired product (3-methoxybenzyl)(3,4,5-trimethoxyphenyl)sulfane (**3o**): (48.0 mg, 75%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (t, J = 8.4 Hz, 2 H), 6.77-6.86 (m, 2 H), 6.52 (s, 2 H), 4.03 (s, 2 H), 3.81 (s, 3 H), 3.76 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 153.1, 139.4, 137.2, 130.5, 129.5, 121.3, 114.3, 112.9, 108.4, 60.9, 56.1, 55.2, 40.3; IR (neat): ν = 2970, 2939, 2252, 1769, 1581, 1496, 1231, 1128, 1047, 908, 730; HRMS (FAB): Calcd for $C_{17}H_{20}O_4S$: 320.1082, Found 320.1083.



3p

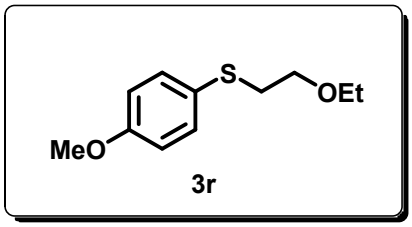
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-bromobutane (137 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 °C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room

temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product butyl(4-methoxyphenyl)sulfane (**3p**): (23.9 mg, 61%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J = 8.0 Hz, 2 H), δ:6.77 (d, J = 8.0 Hz, 2 H), 3.72 (s, 3 H), 2.74 (t, J = 8.0 Hz, 2 H), 1.46-1.53 (m, 2 H), 1.30-1.39 (m, 2 H), 0.82 (t, J = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 132.9, 127.0, 114.5, 55.3, 35.5, 31.5, 21.8, 13.6; IR (neat): ν = 2957, 1593, 1493, 1286, 1245, 1034, 826, 730; MS m/z: 196.



3q

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-bromopentane (151 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^{o}C for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product (4-methoxyphenyl)(pentyl)sulfane (**3q**): (20.2 mg, 45%), colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J = 8.0 Hz, 2 H), δ:6.76 (d, J = 8.0 Hz, 2 H), 3.72 (s, 3 H), 2.74 (t, J = 8.0 Hz, 2 H), 1.47-1.53 (m, 2 H), 1.18-1.32 (m, 4 H), 0.81 (t, J = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.7, 132.9, 127.0, 114.5, 55.3, 35.8, 30.9, 29.0, 22.2, 13.9; IR (neat): ν = 2927, 1593, 1493, 1462, 1284, 1243, 1033, 822; MS m/z: 210.

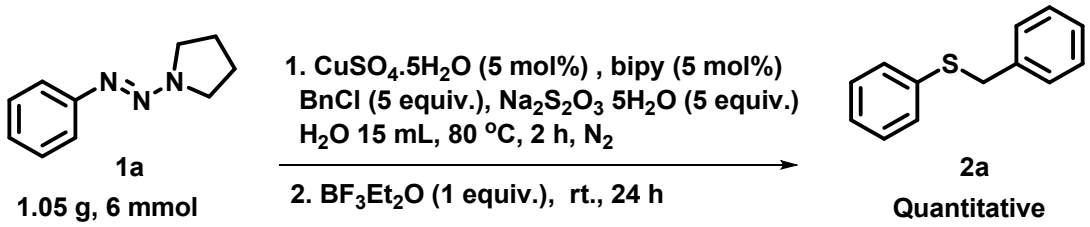


3r

A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), **L2** (3.1 mg, 10 mol%), 1-bromo-2-ethoxyethane (153 mg, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) in a Schlenk tube was heated at 80 ^oC for 2 h. After cooled to room temperature, **1d** (41.0 mg, 0.2 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (25 μL, 0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (5 mL) was added at room temperature, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) to afford the desired product (2-ethoxyethyl)(4-methoxyphenyl)sulfane (**3r**): (28.8 mg, 68%), colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.31 (m, 2 H), 6.75-6.78 (m, 2 H), 3.72 (s, 3 H), 3.48 (t, J = 8.0 Hz, 2 H), 3.41 (q, J = 8.0 Hz, 2 H), 2.92 (t, J = 8.0 Hz, 2 H), 1.12 (t, J = 8.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 133.4, 126.0, 114.6, 69.3, 66.3, 55.3, 35.2, 15.1; IR (neat): ν = 2856, 1592, 1492 , 1284, 1243, 1173, 1102, 1030, 825; MS m/z: 212.

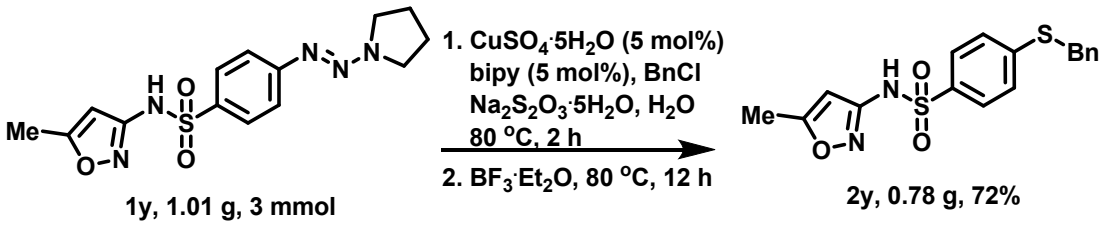
V. Gram scale Experiments

a) Gram scale for synthesis of benzyl(phenyl)sulfane



A mixture of $CuSO_4.5H_2O$ (74 mg, 5 mol%), bipy (47 mg, 5 mol%), BnCl (30 mmol, 5 equiv.) and $Na_2S_2O_3.5H_2O$ (7.44 g, 30 mmol, 5 equiv.) in H_2O (15 mL) was heated at 80 ^oC for 2 h under an atmosphere of N_2. After cooled to room temperature, **1a** (1.05 g, 6 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3.Et_2O$ (6 mmol, 1 equiv.) was added. The mixture was stirred at room temperature 24 h. After the reaction was complete, EtOAc (20 mL) was added, extracted the product with EtOAc (50 mL x 3). The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 20:1) afforded substrate **2a** as a colorless oil (quantitative yield).

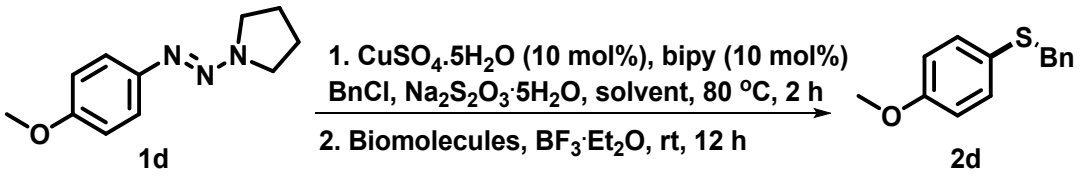
b) Gram scale for synthesis of 4-(benzylthio)-N-(5-methylisoxazol-3-yl) benzenesulfonamide



A mixture of $CuSO_4.5H_2O$ (37 mg, 5 mol%), bipy (23 mg, 5 mol%), BnCl (15 mmol, 5 equiv.) and $Na_2S_2O_3.5H_2O$ (3.70 g, 15 mmol, 5 equiv.) in H_2O (6 mL) was heated at 80 ^oC for 2 h. After cooled to room temperature, **1y** (1.01 g, 3 mmol, 1 equiv.) was added to the solution, stirred for 15 min at room temperature, then $BF_3.Et_2O$ (3 mmol,

1 equiv.) was added. The mixture was stirred at room temperature, and stirred at 80 ^{o}C for 12 h. After the reaction was complete, EtOAc (20 mL) was added, extracted the product with EtOAc (30 mL x 3). The combined organic extracts were washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 1:1-1:2) afforded substrate **2y** as a white solid (0.78 g, 72%).

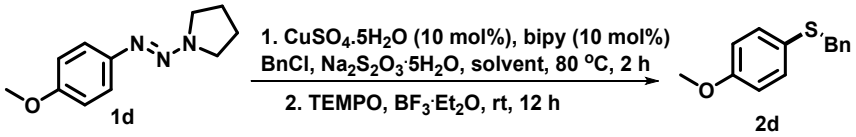
VI. Sulfuration in neutral aqueous conditions and in the presence of biomolecules



1d 2d

A mixture of $CuSO_4{\cdot}5H_2O$ (5.0 mg, 10 mol%), bipy (3.1 mg, 10 mol%), BnCl (0.126 g, 1 mmol, 5 equiv.) and $Na_2S_2O_3{\cdot}5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) or pH 7.4 10X PBS (1 mL) was heated at 80 °C for 2 h. After cooled to room temperature, **1d** (0.2 mmol, 1 equiv.) and bimolecules (0.2 mmol, 1 equiv.) were added to the mixture, stirred for 15 min at room temperature, then $BF_3{\cdot}Et_2O$ (0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature. When the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product **2 d**.

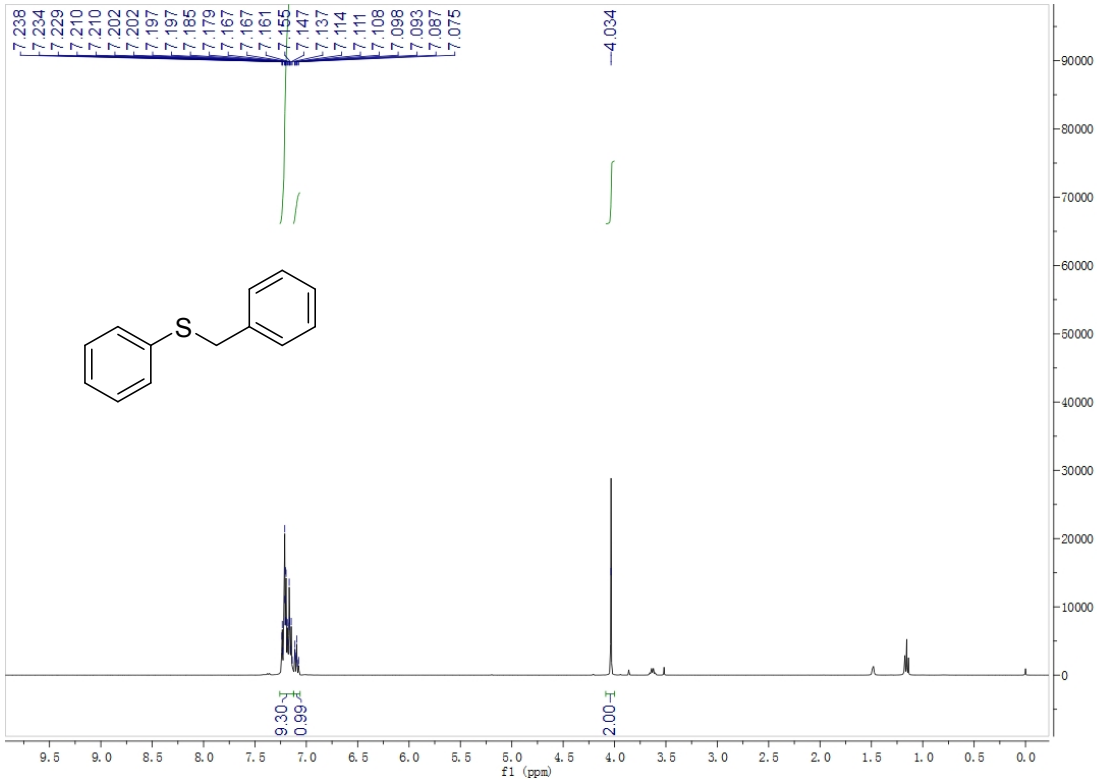
VII. Mechanism Study



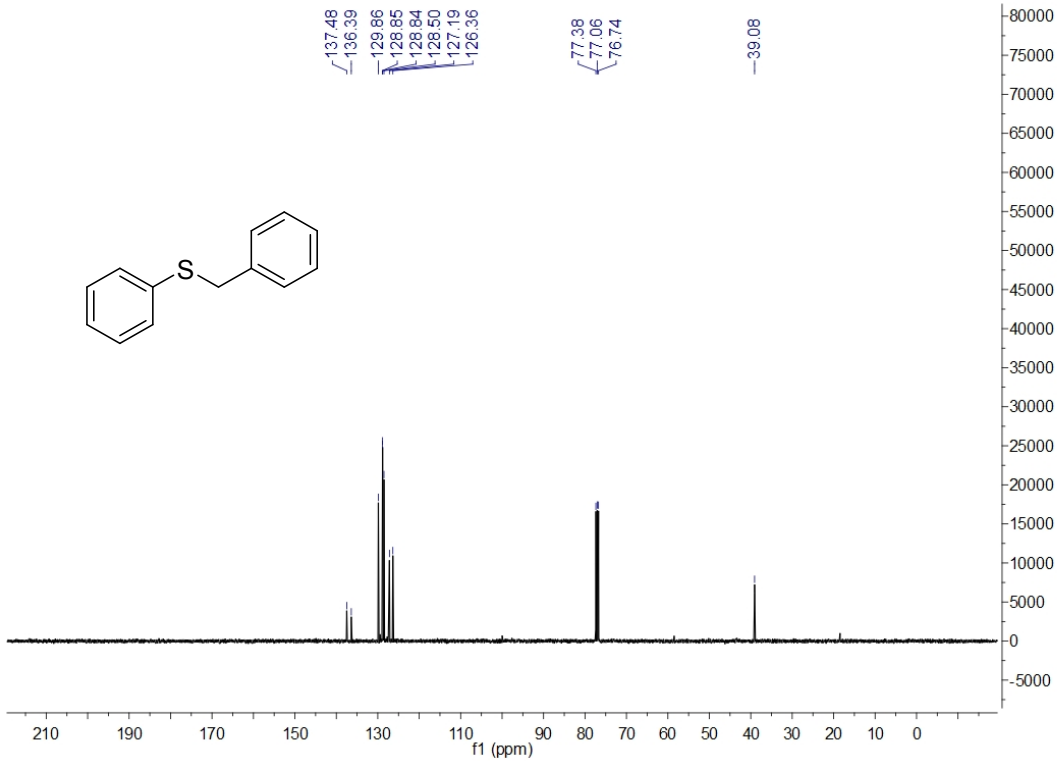
A mixture of $CuSO_4 \cdot 5H_2O$ (5.0 mg, 10 mol%), bipy (3.1 mg, 10 mol%), BnCl (0.126 g, 1 mmol, 5 equiv.) and $Na_2S_2O_3 \cdot 5H_2O$ (248 mg, 1 mmol, 5 equiv.) in H_2O (1 mL) was heated at 80 °C for 2 h. After cooled to room temperature, **1d** (0.2 mmol, 1 equiv.) and TEMPO (0.2 mmol, 2 equiv.) were added to the mixture, stirred for 15 min at room temperature, then $BF_3 \cdot Et_2O$ (0.2 mmol, 1 equiv.) was added. The mixture was stirred at room temperature. When the reaction was complete, EtOAc (5 mL) was added, the combined mixture was dried over anhydrous $MgSO_4$, then filtrated through celite, washed with EtOAc (5 mL x 3), the mixture was evaporated under vacuum and purified by flash column chromatography (petroleum ether/ethyl acetate 100:1) to afford the desired product benzyl(4-methoxyphenyl)sulfane **2d** in 16% yield.

VIII. Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR.

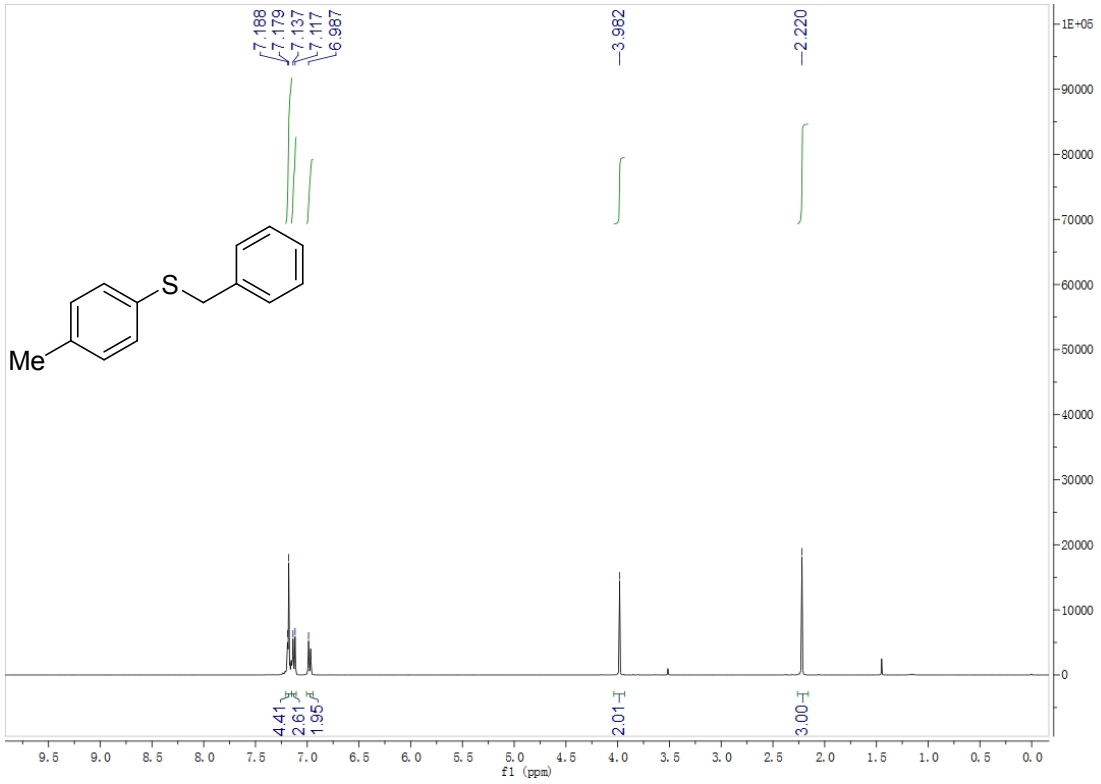
2a ^{1}H NMR



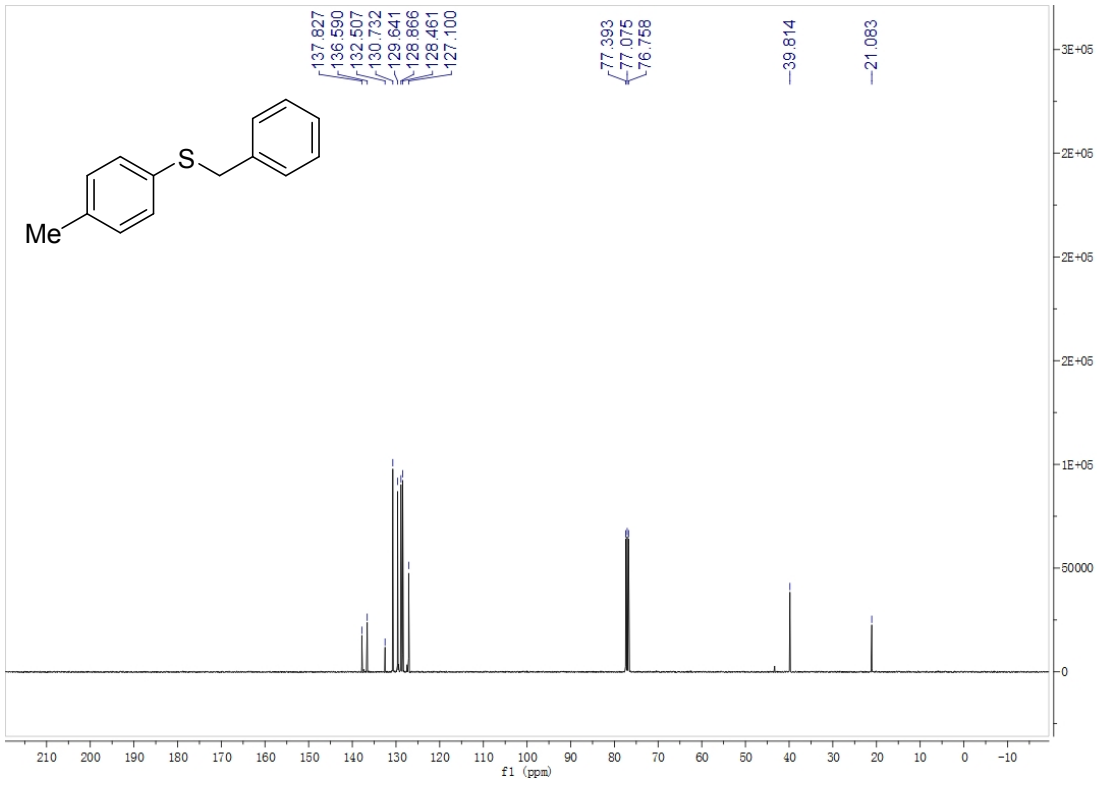
2a ^{13}C NMR



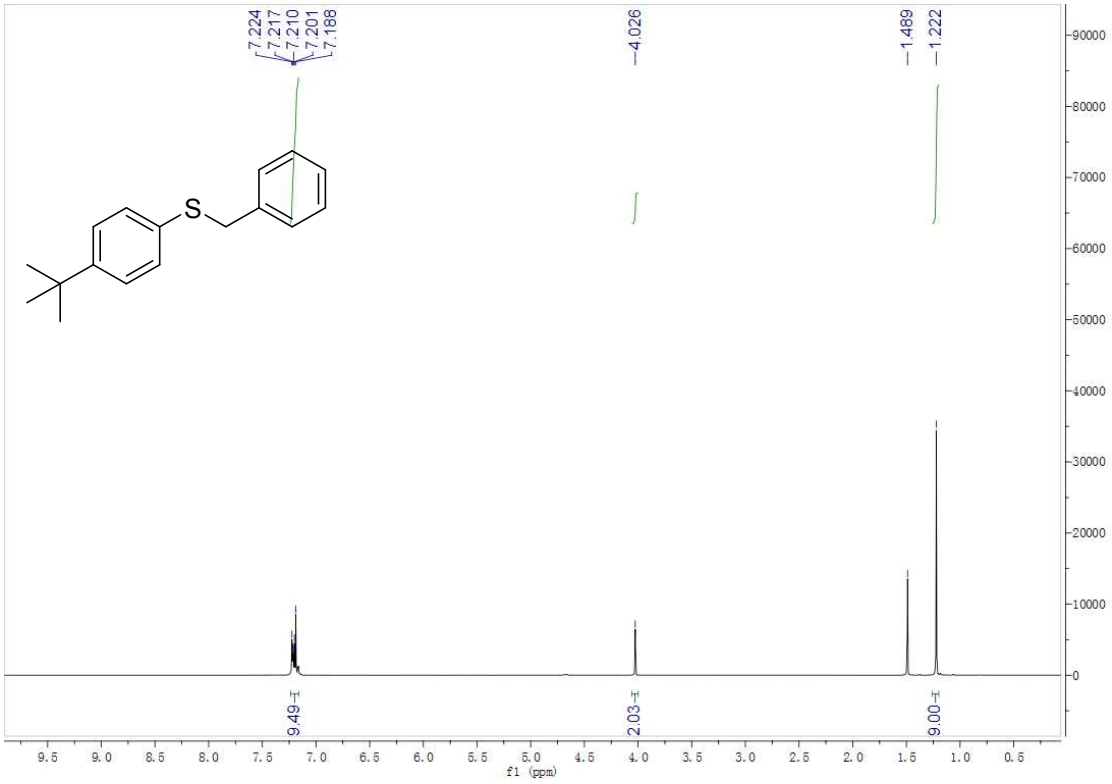
2b ^{1}H NMR



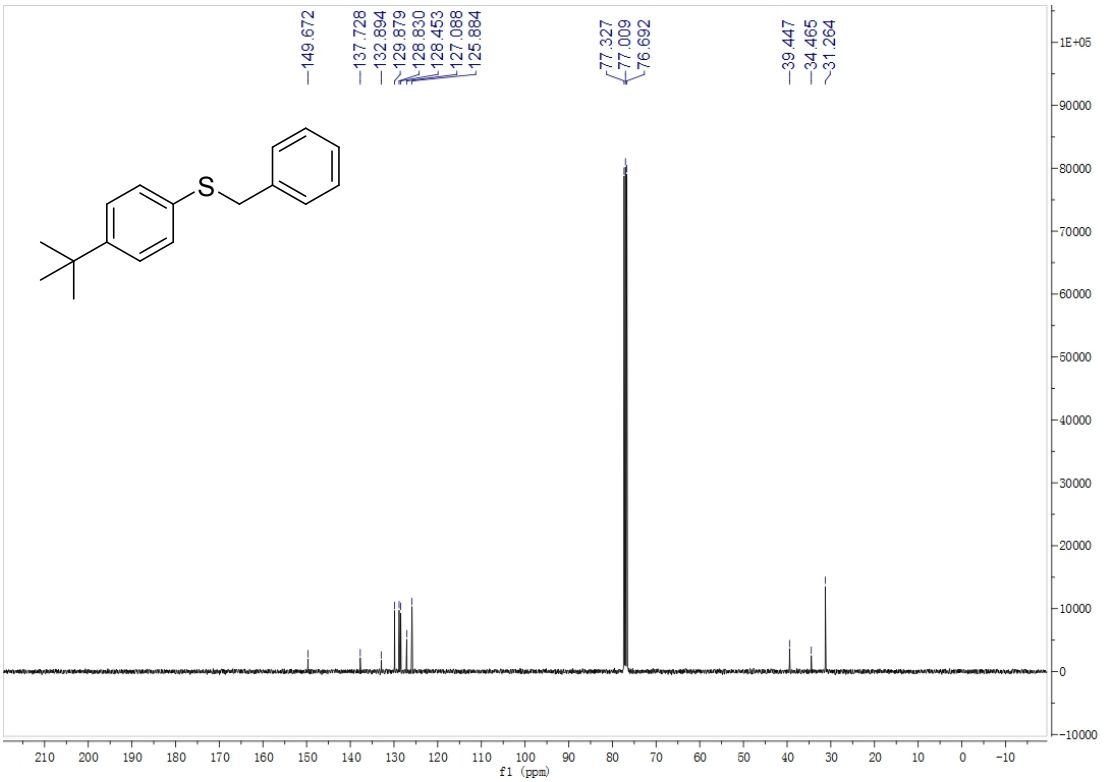
2b ^{13}C NMR



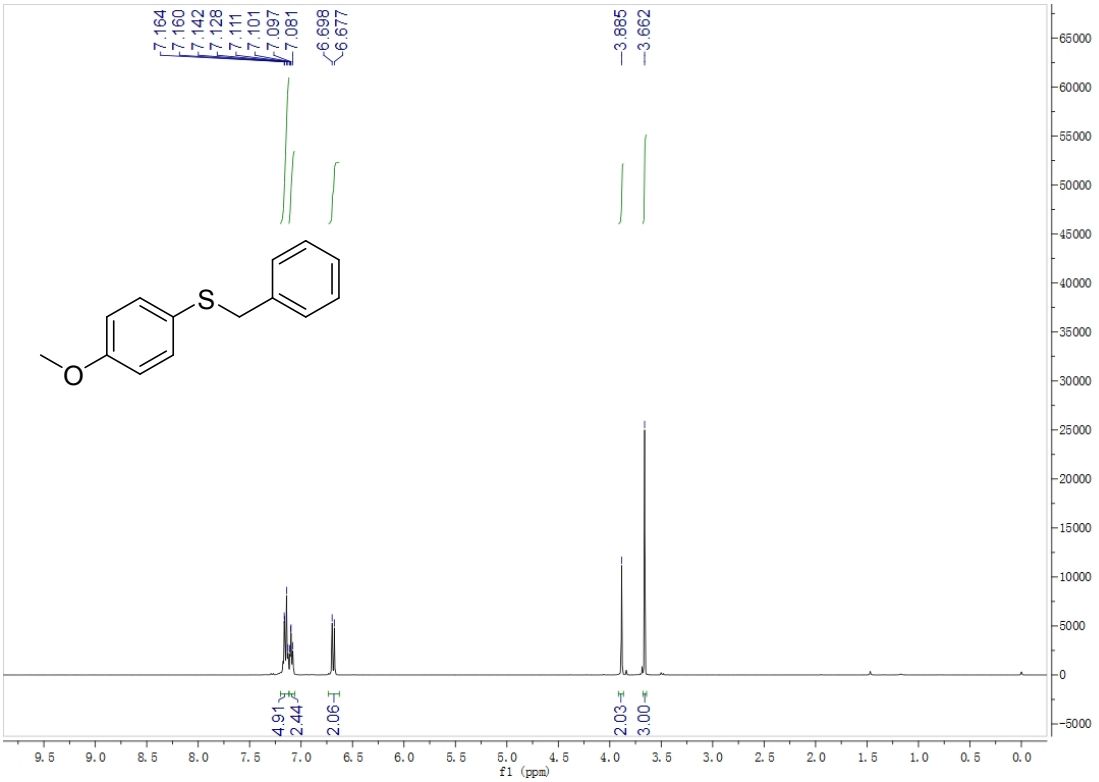
2c ^{1}H NMR



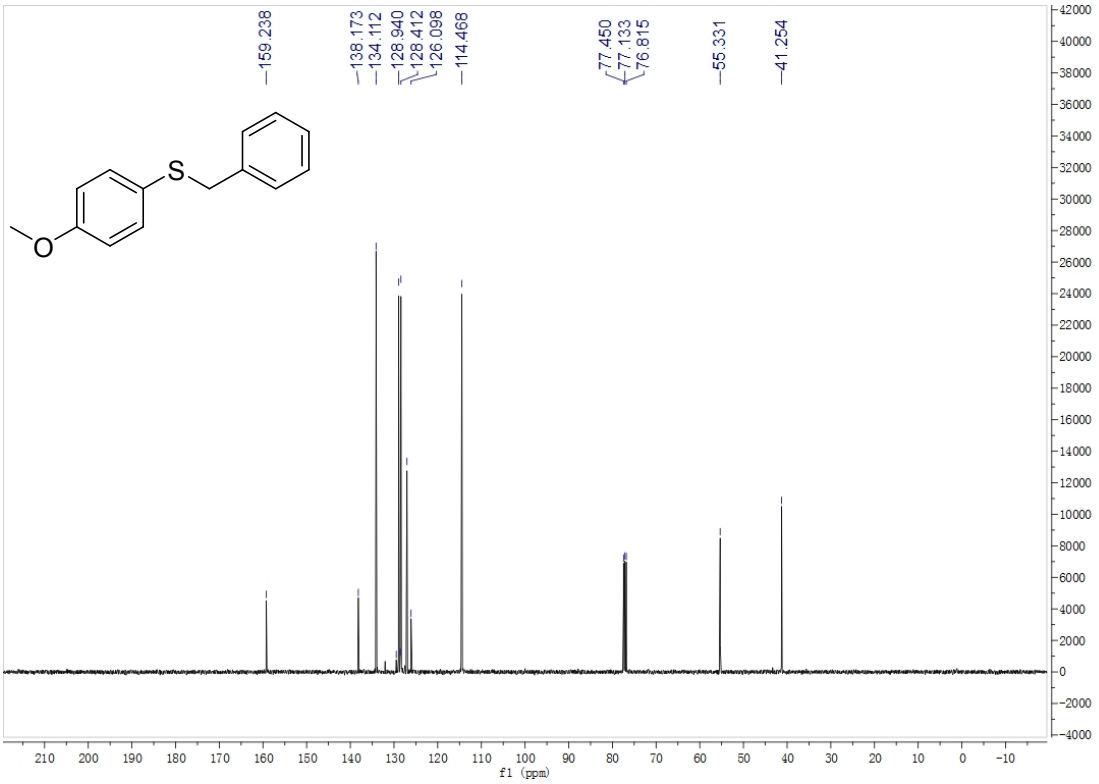
2c ^{13}C NMR



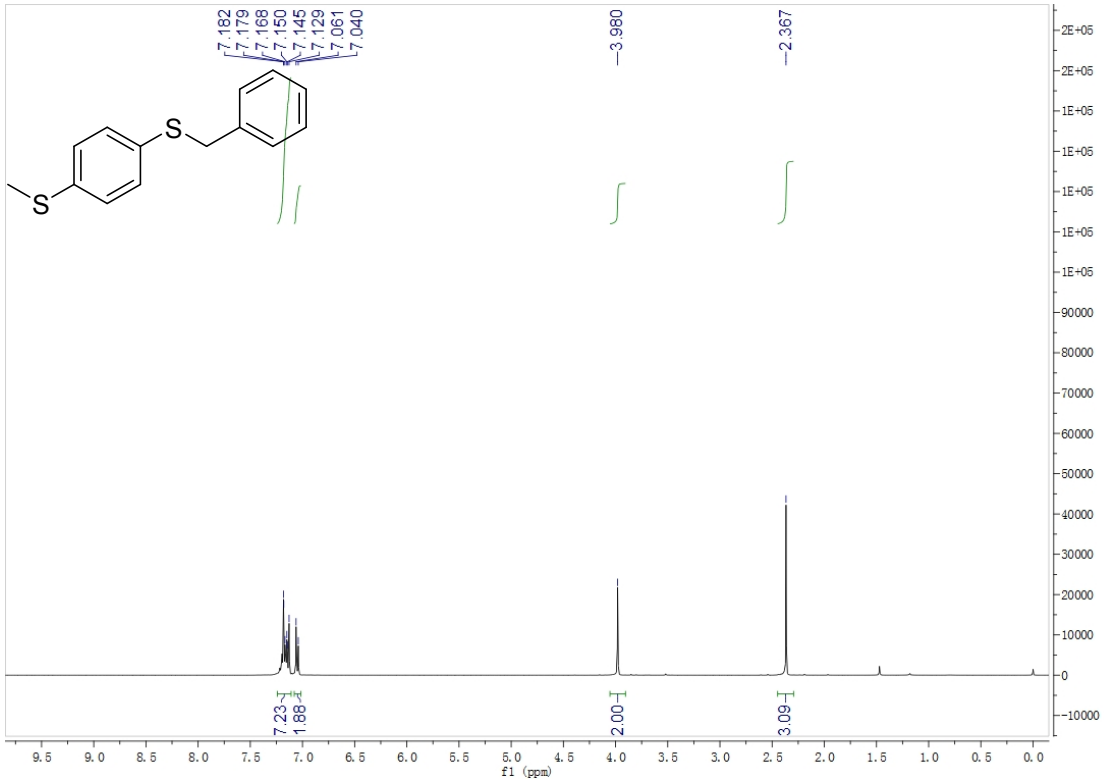
2d ^{1}H NMR



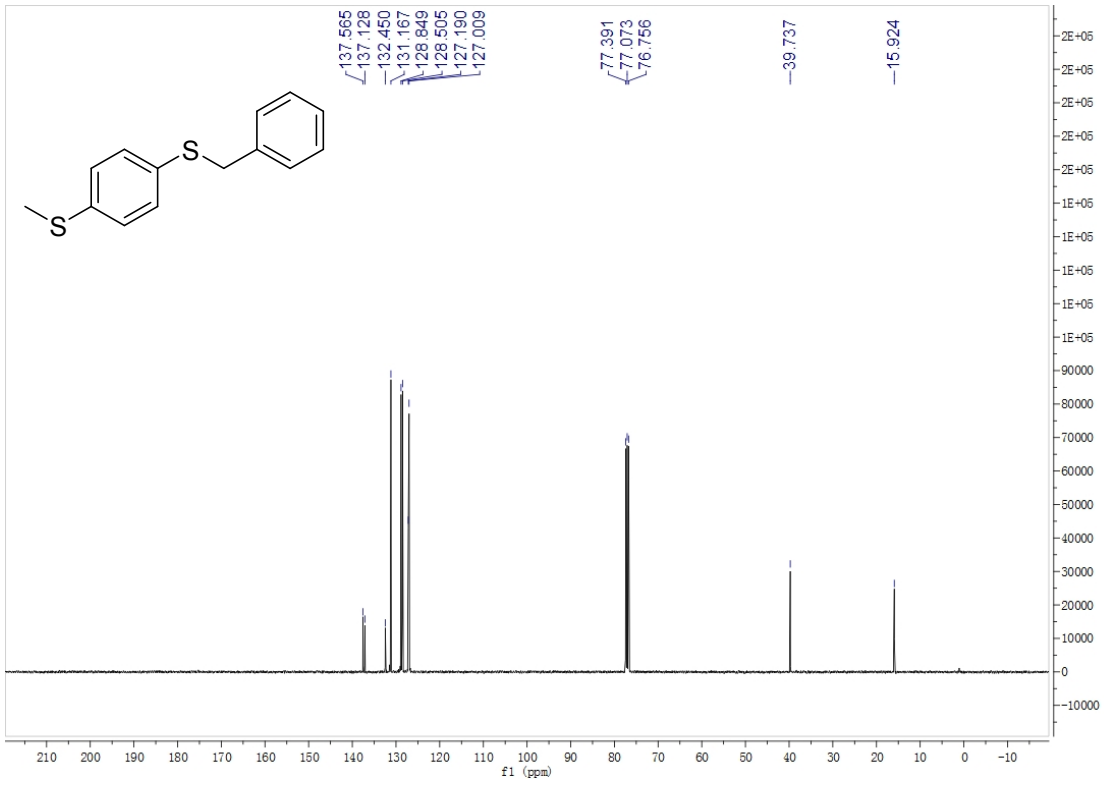
2d ^{13}C NMR



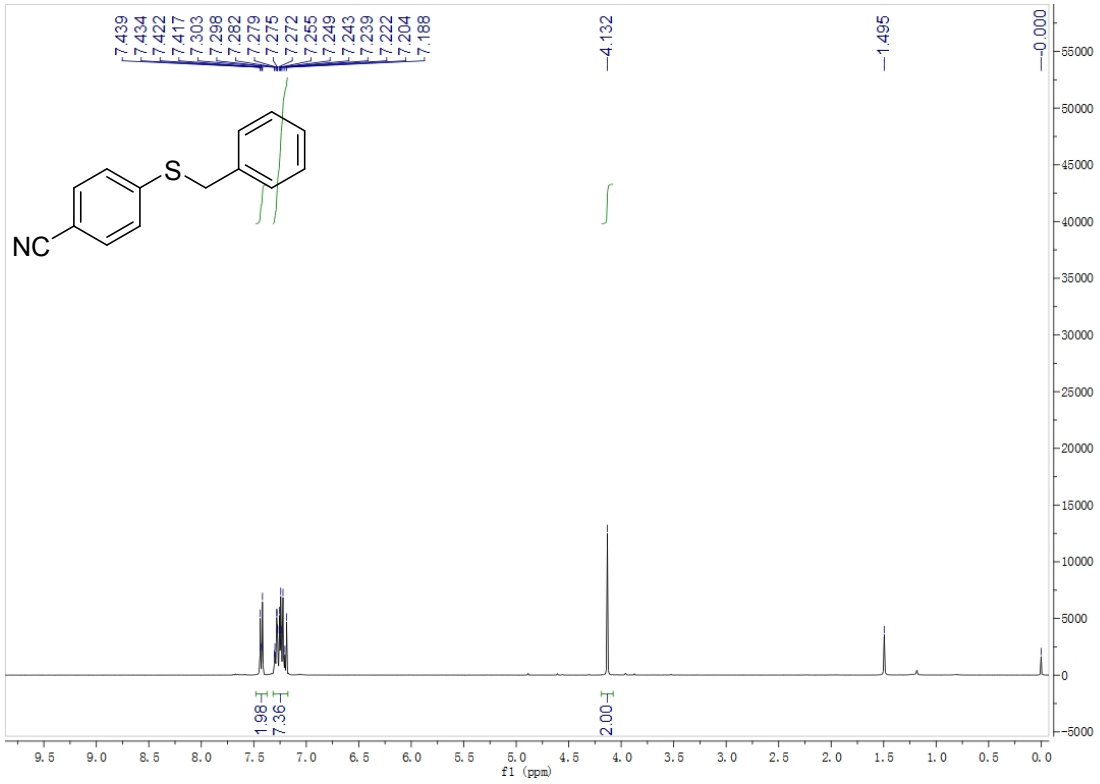
2e ^{1}H NMR



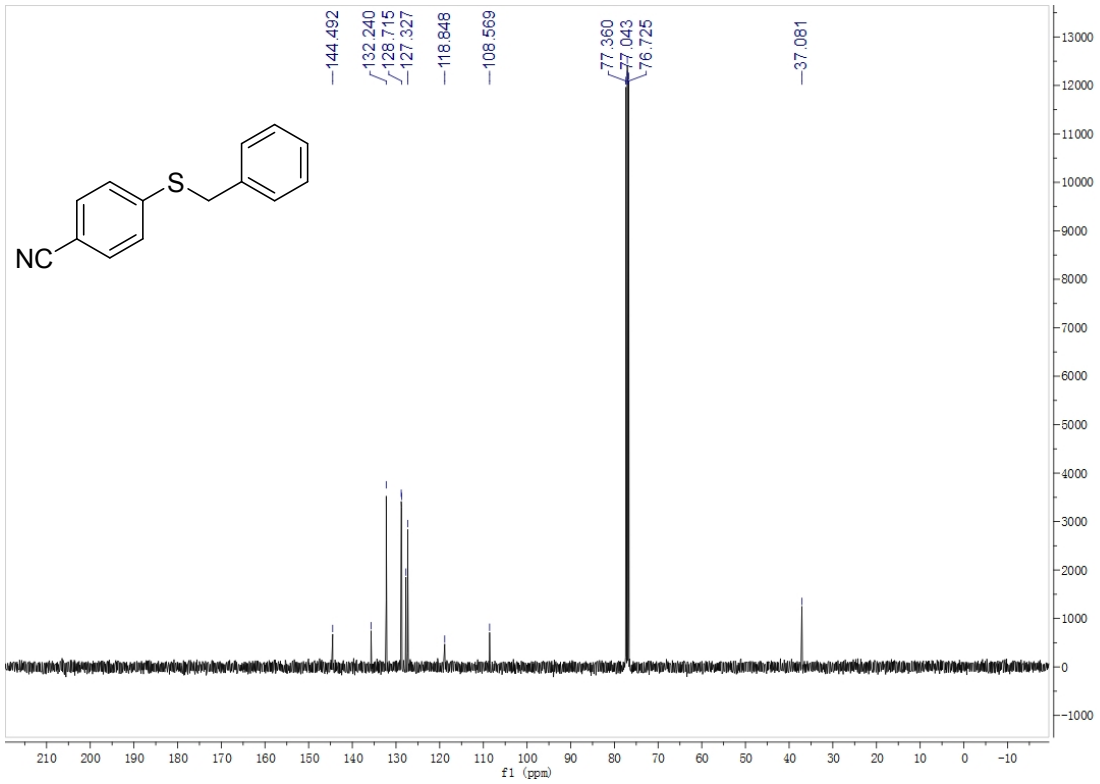
2e ^{13}C NMR



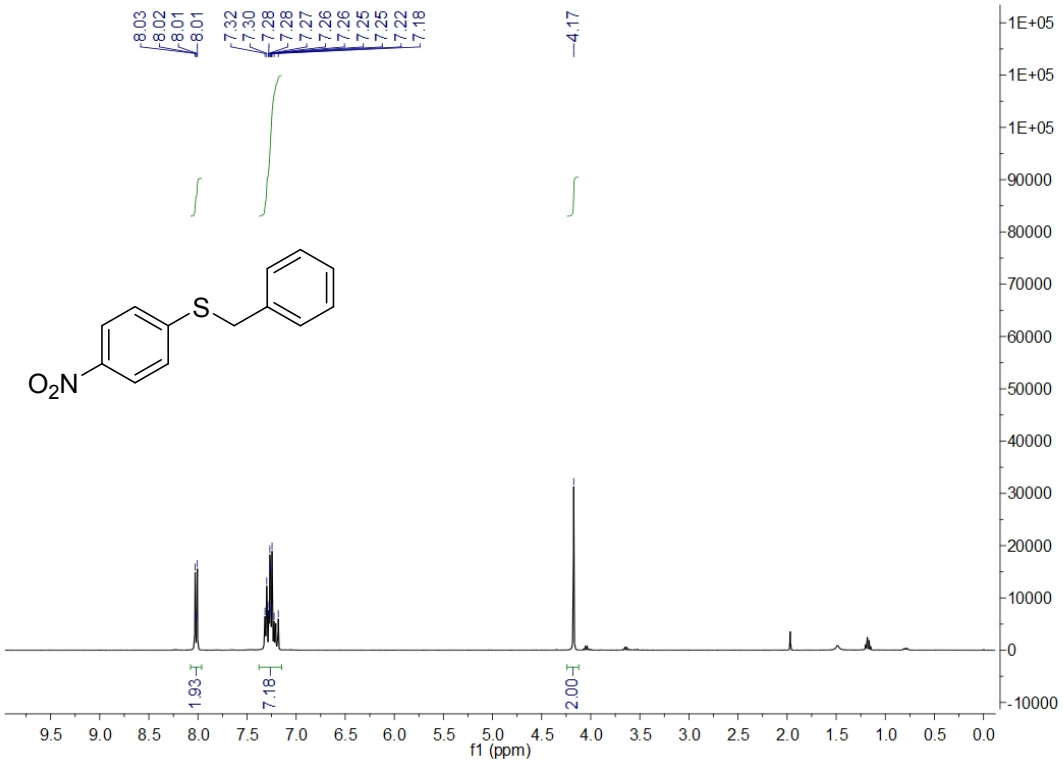
2f ^{1}H NMR



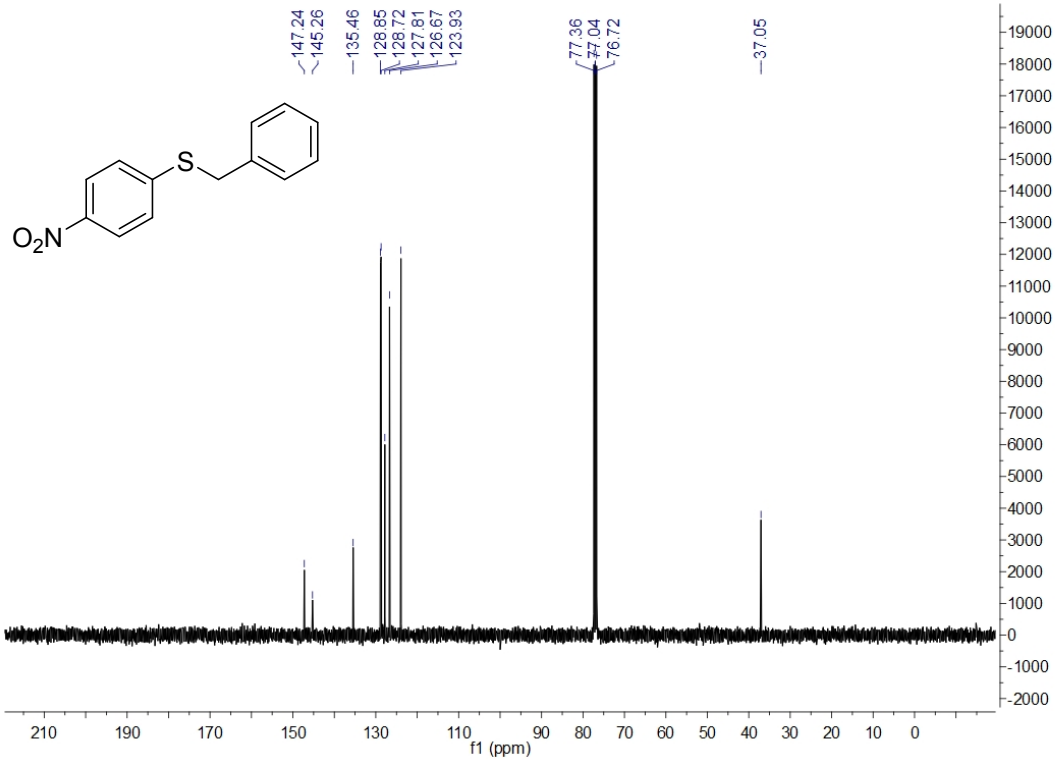
2f^{13}C NMR



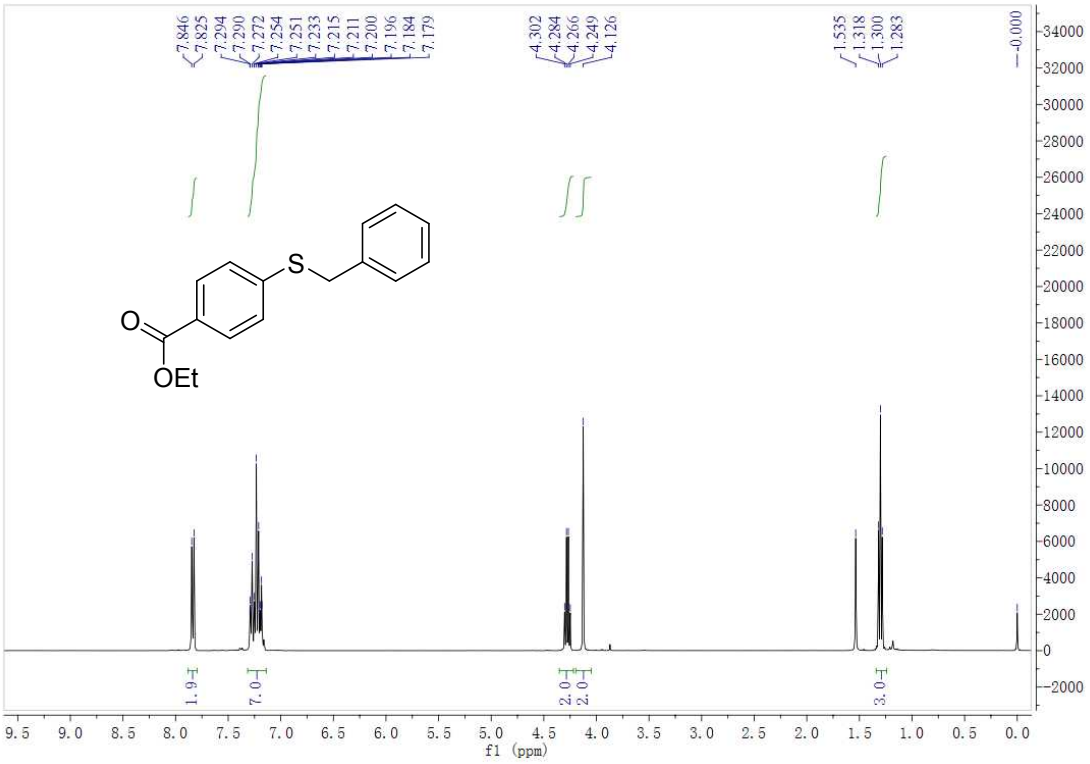
2g ^{1}H NMR



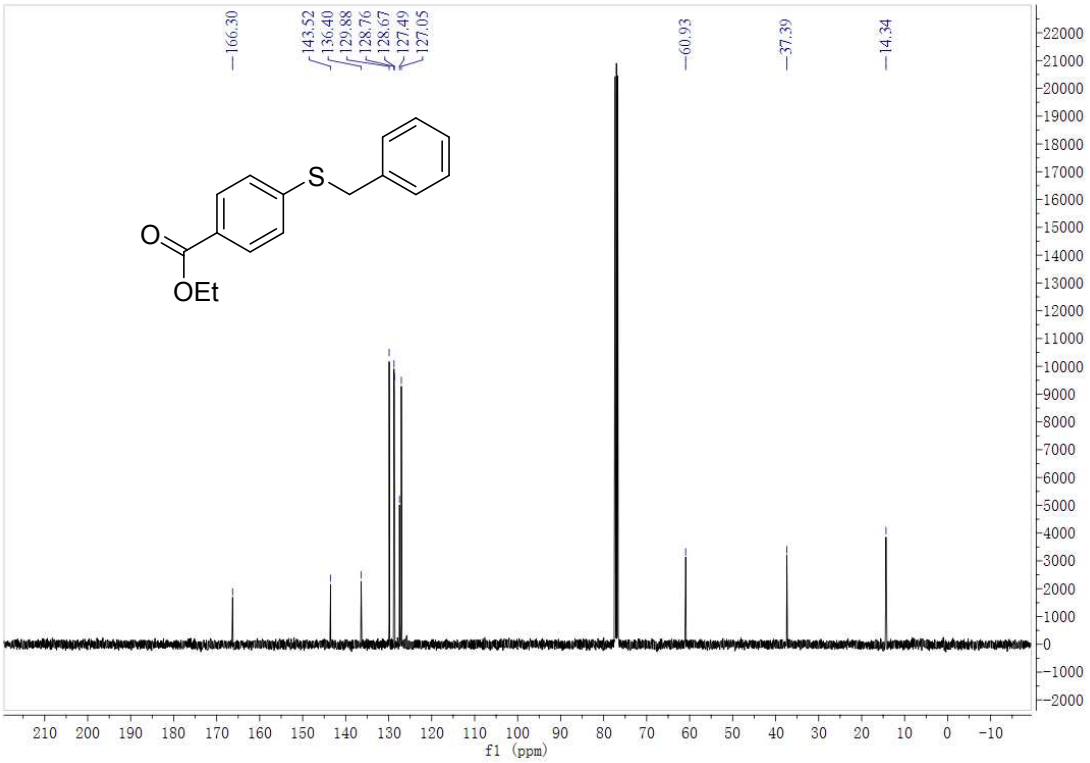
2g ^{13}C NMR



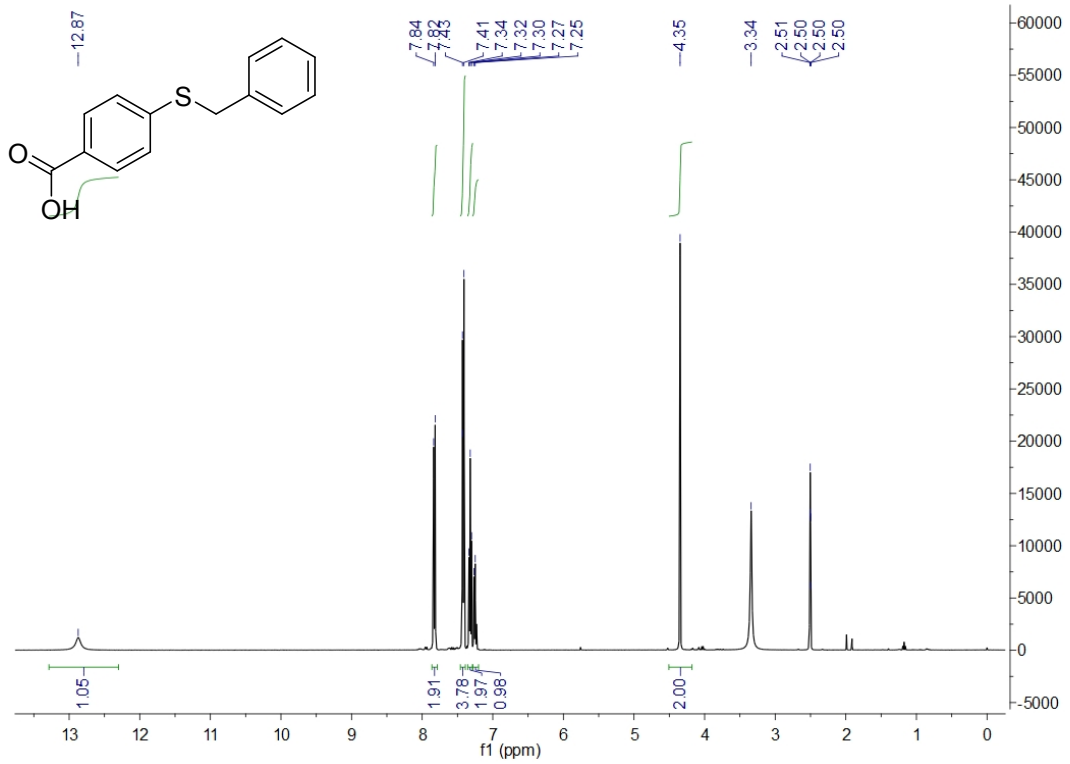
2h ^{1}H NMR



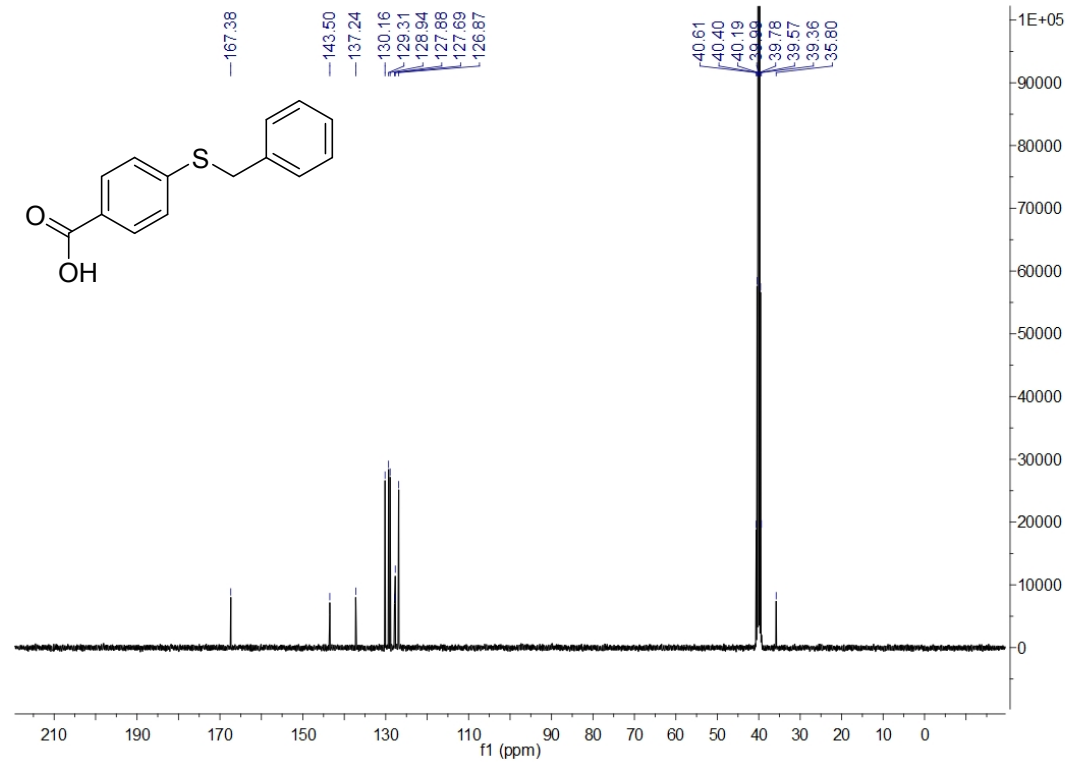
2h^{13}C NMR



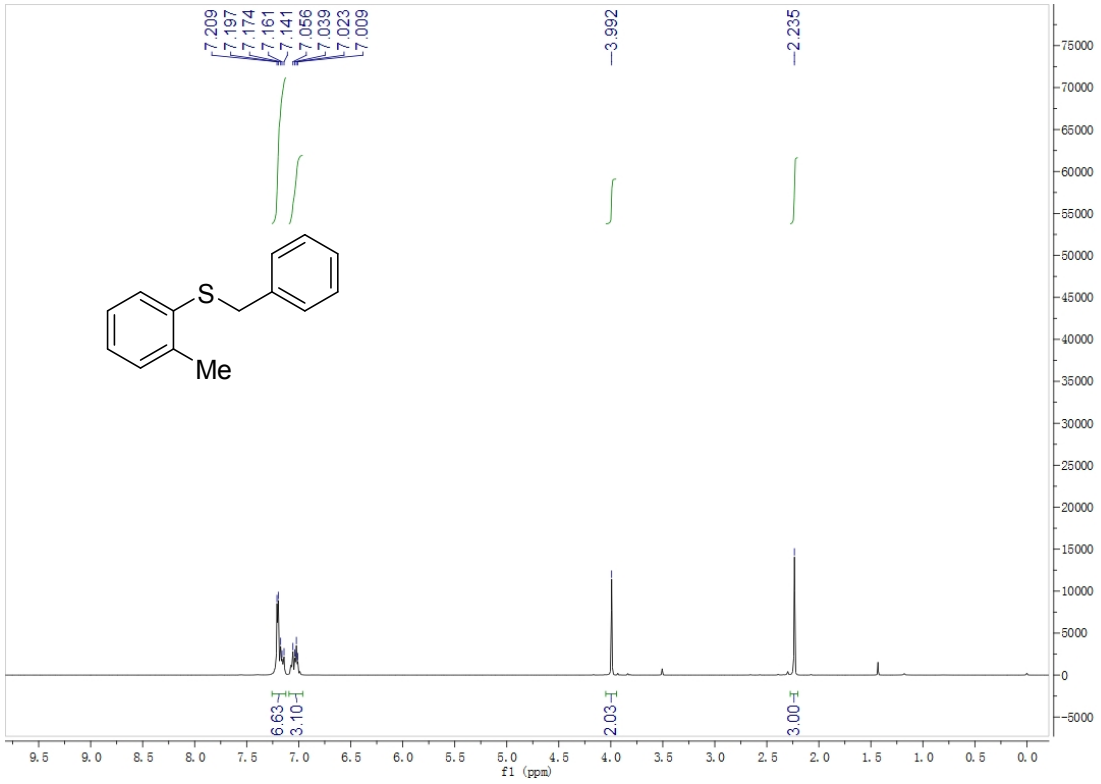
2i ^{1}H NMR



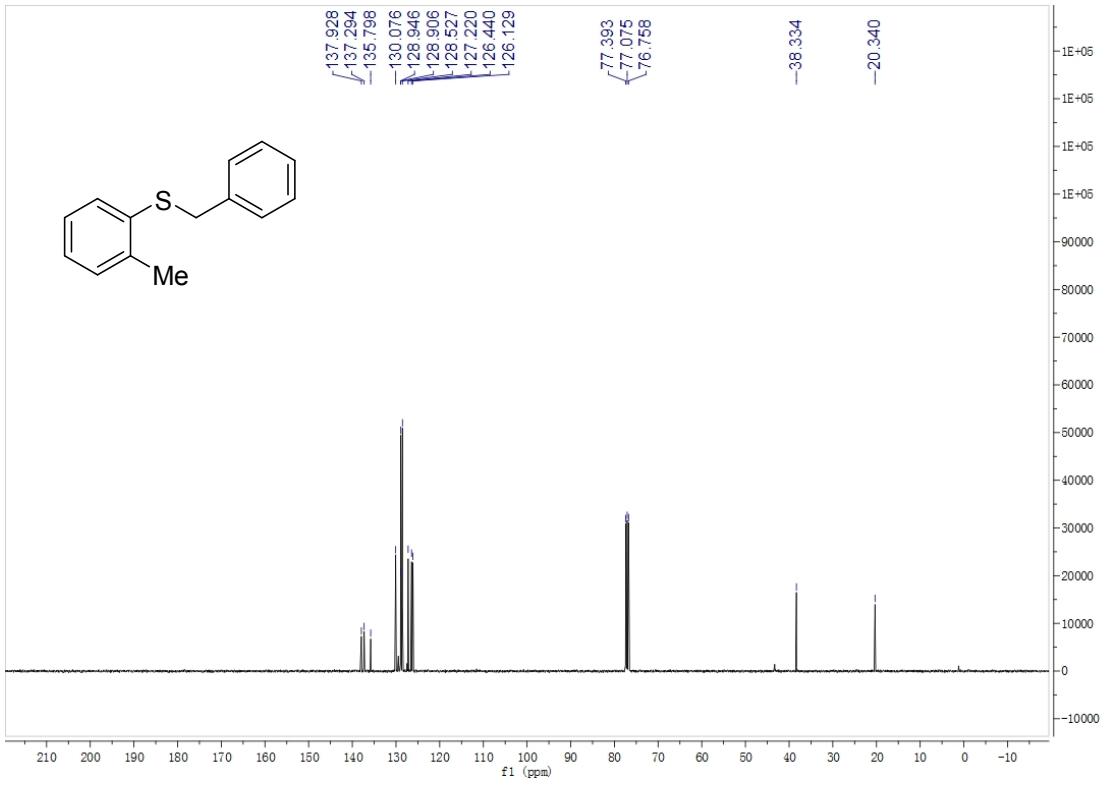
2i ^{13}C NMR



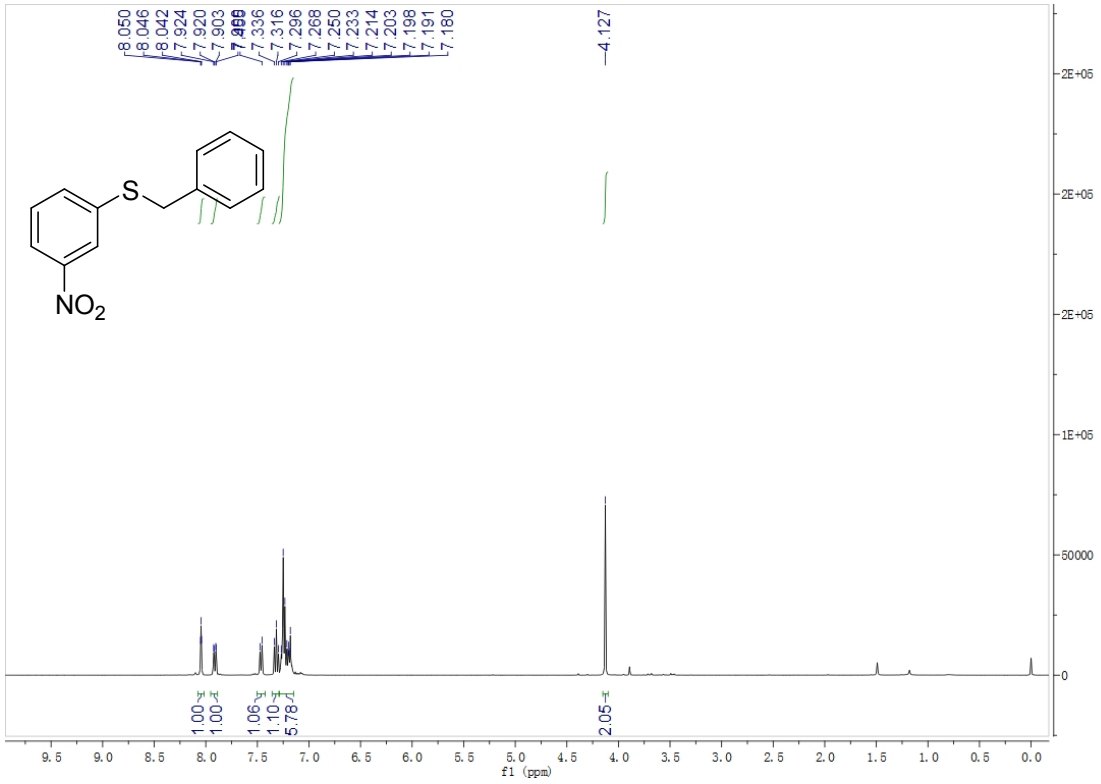
2j ^{13}H NMR



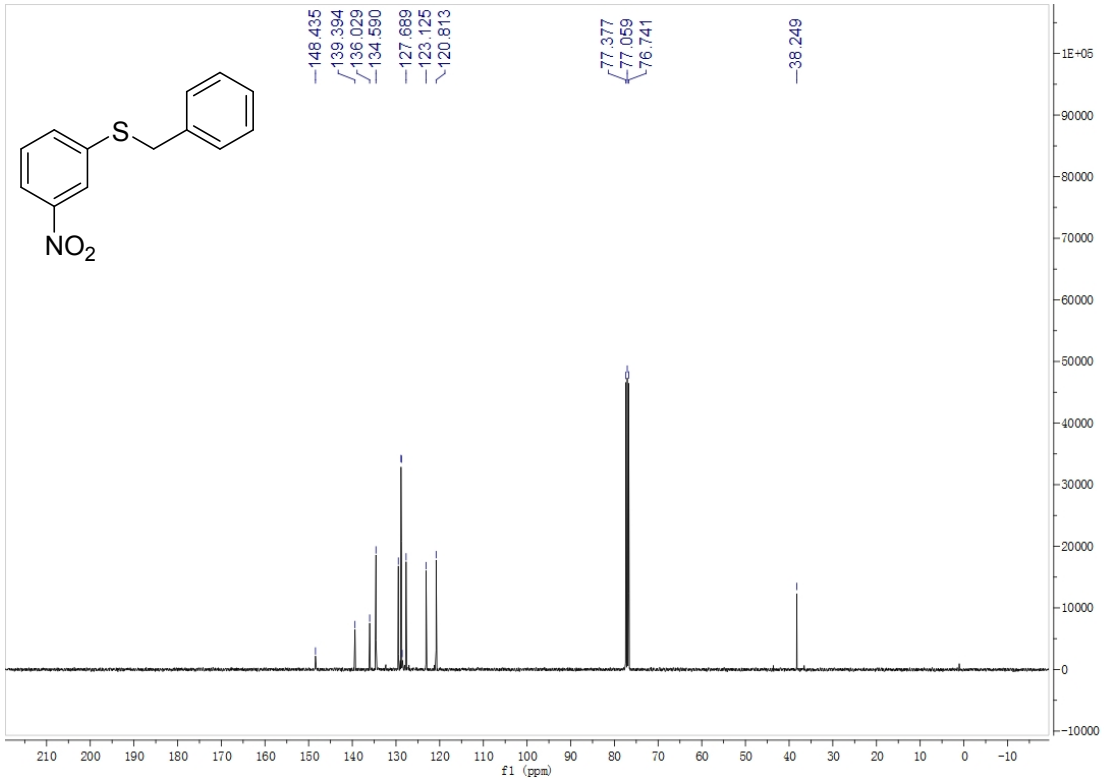
2j ^{13}C NMR



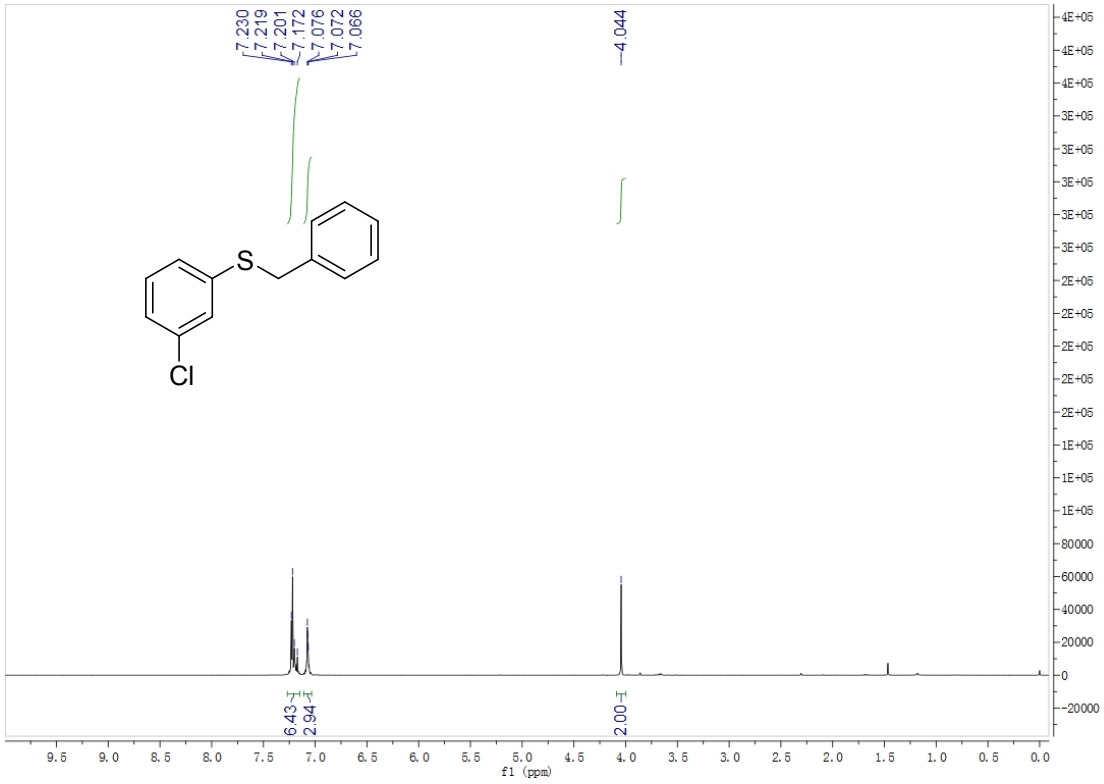
2k ^{1}H NMR



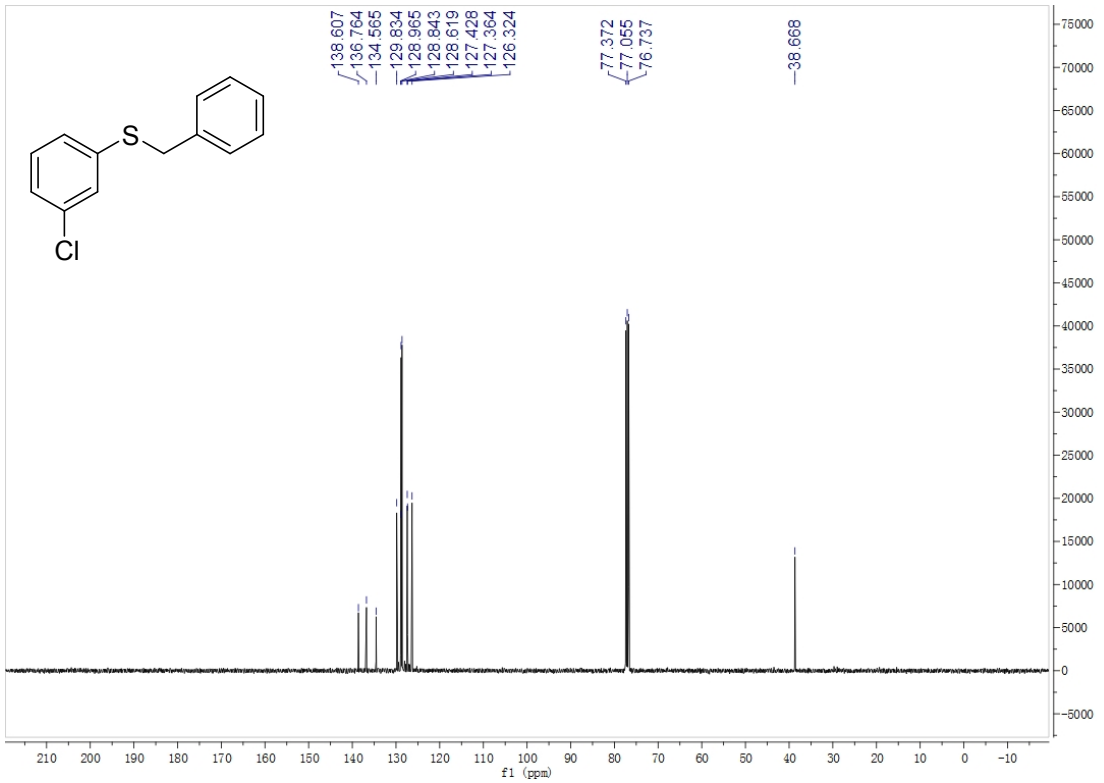
2k ^{13}C NMR



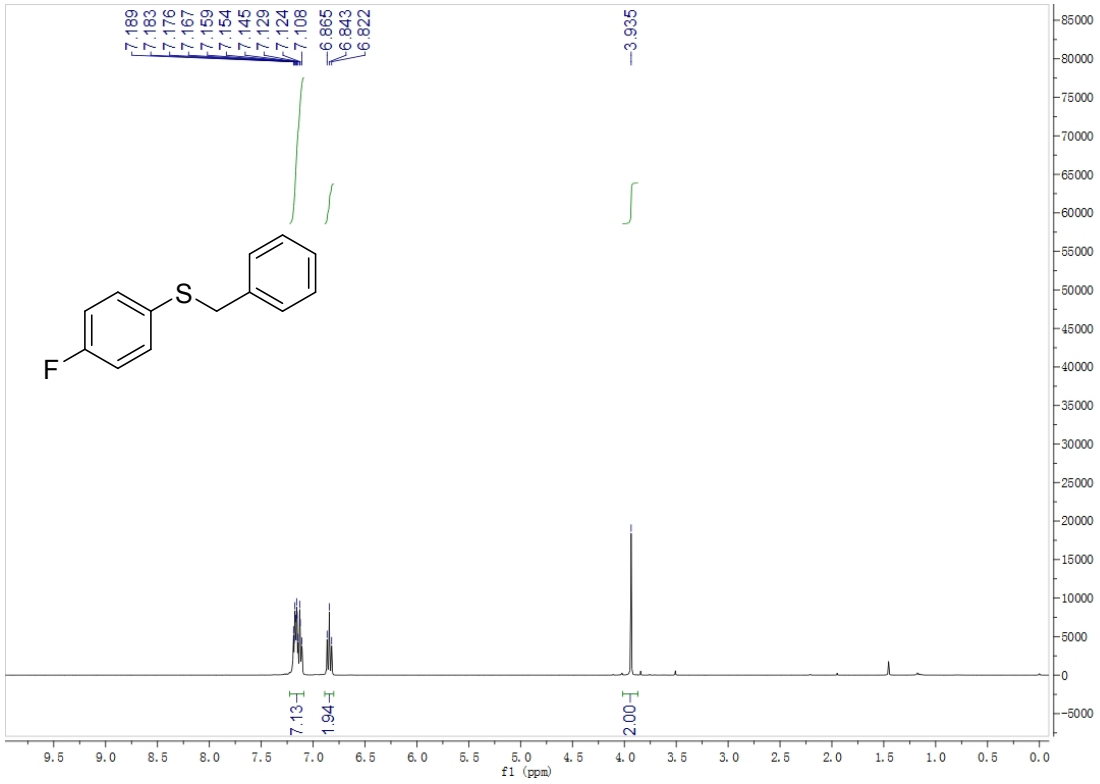
2l ^{1}H NMR



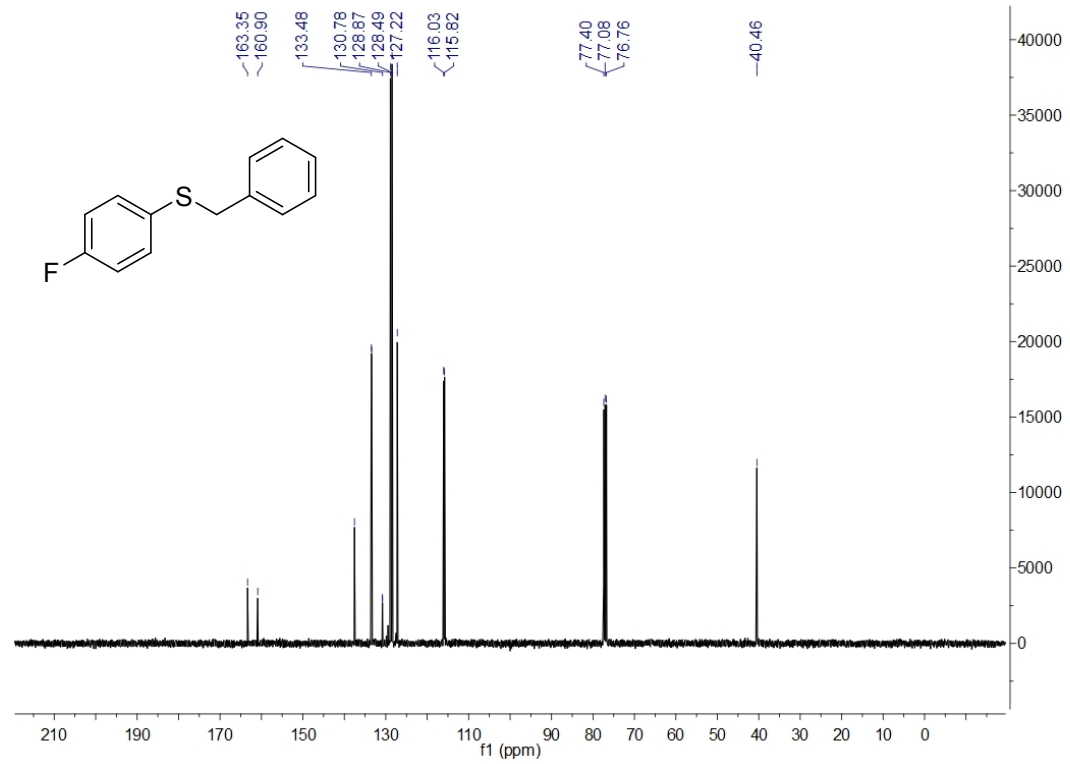
2l^{13}C NMR



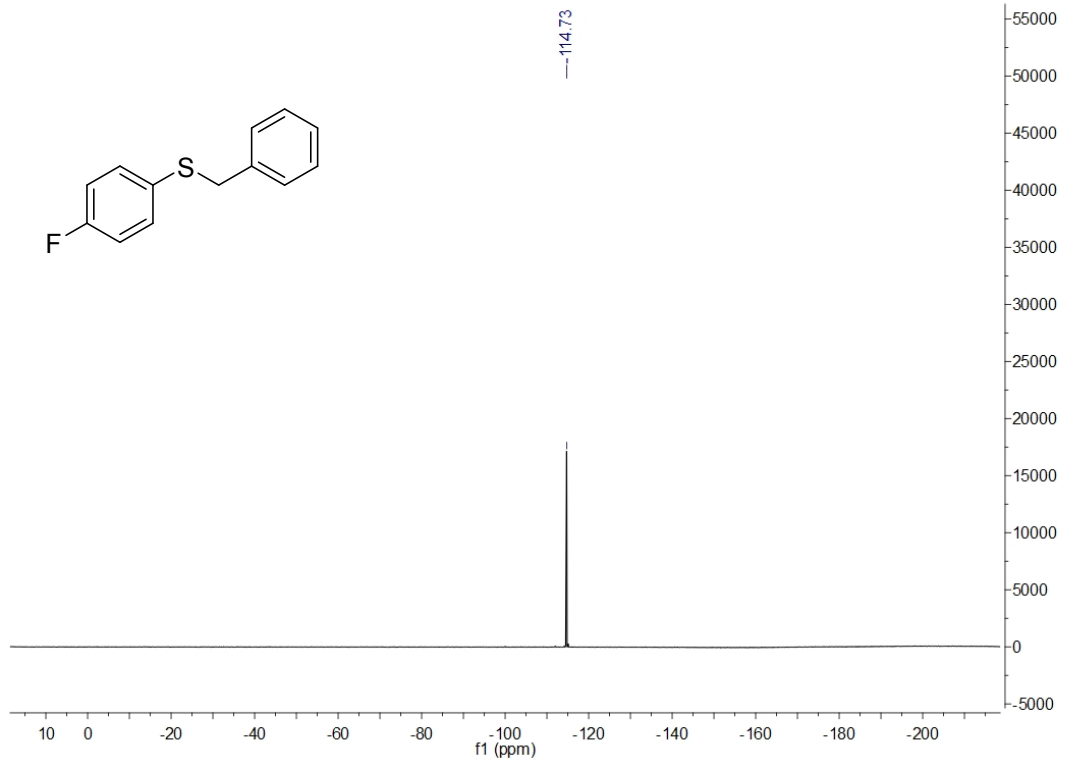
2m ^{1}H NMR



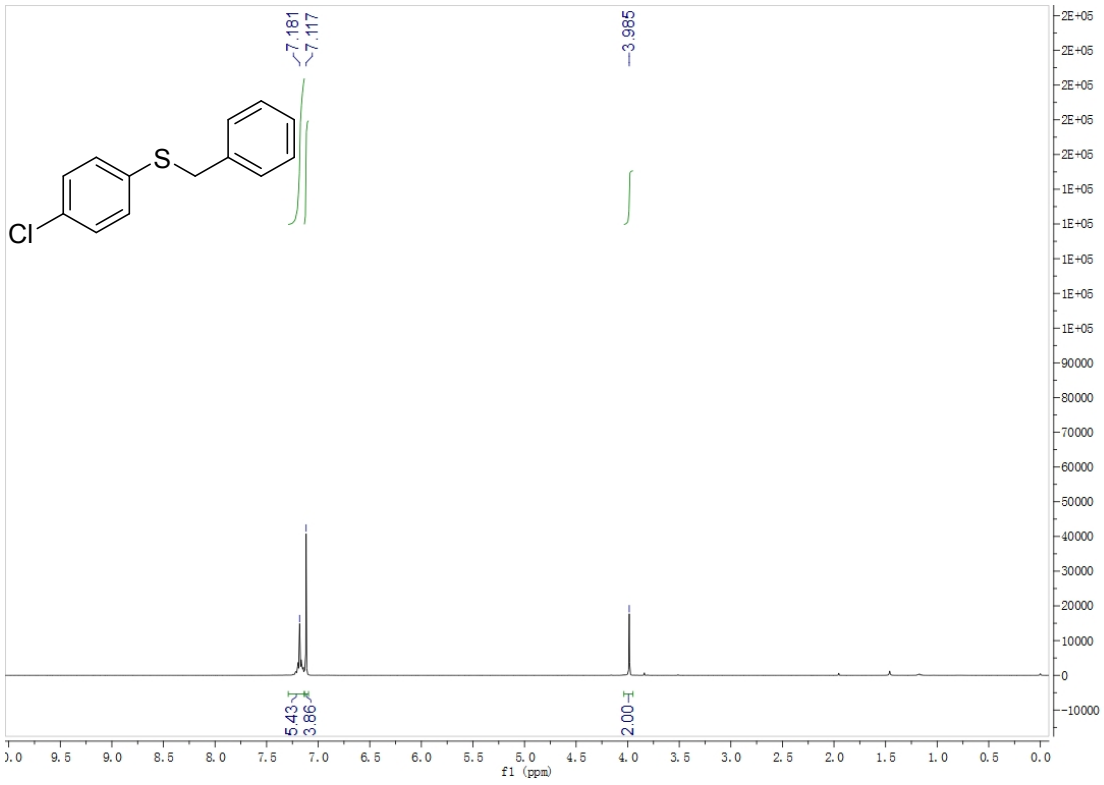
2m ^{13}C NMR



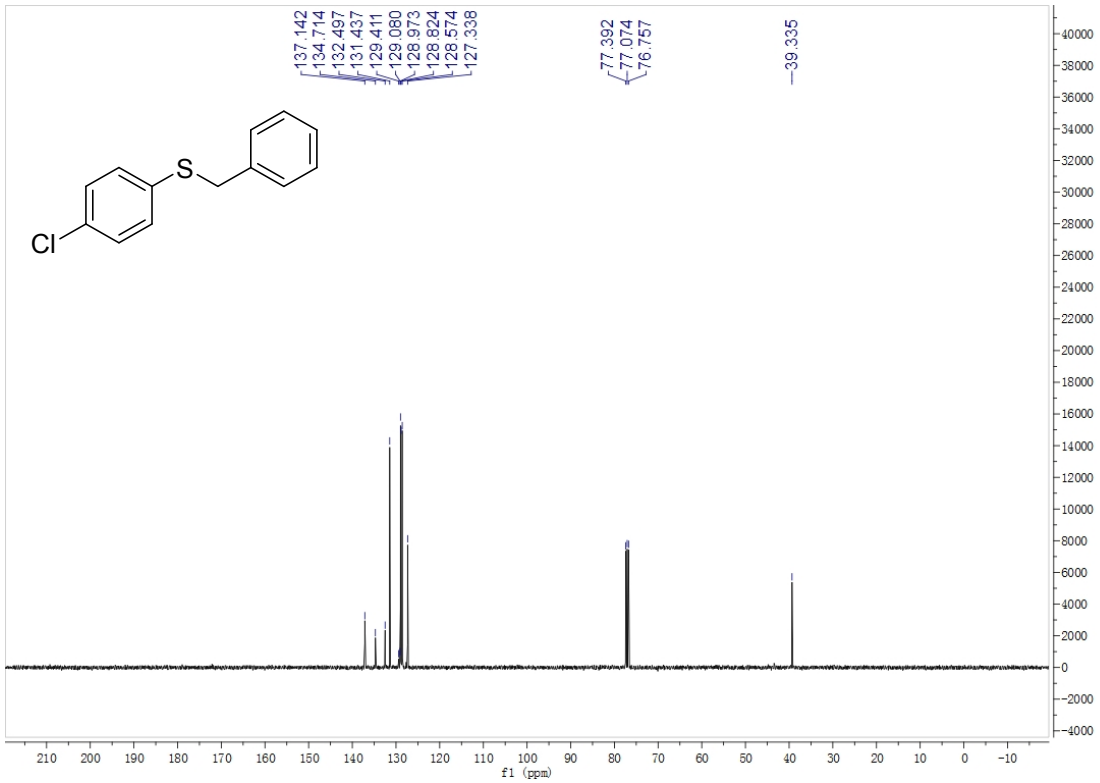
2m ^{19}F NMR



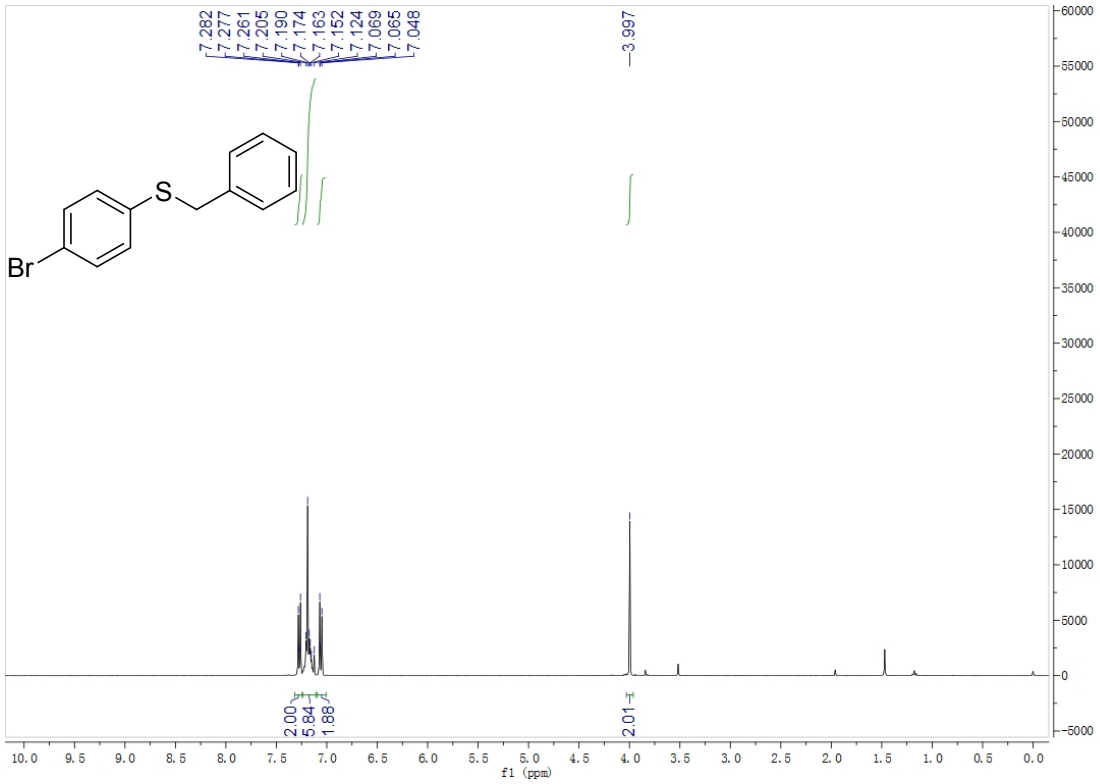
2n ^{1}H NMR



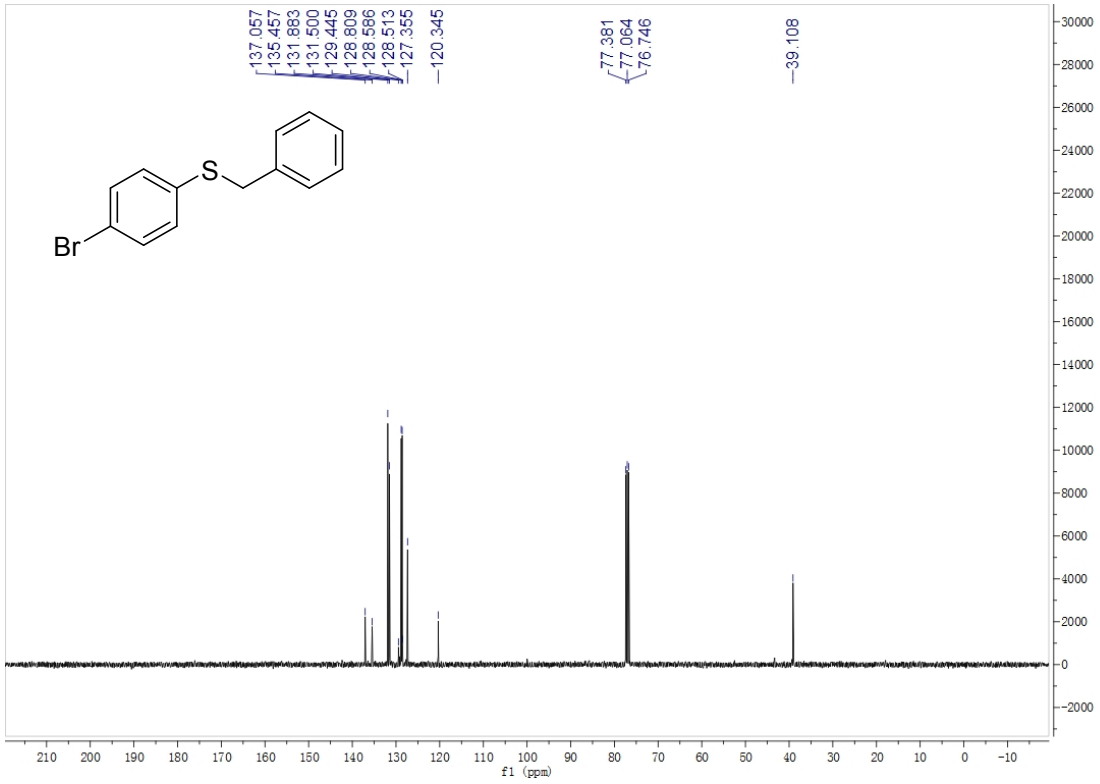
2n ^{13}C NMR



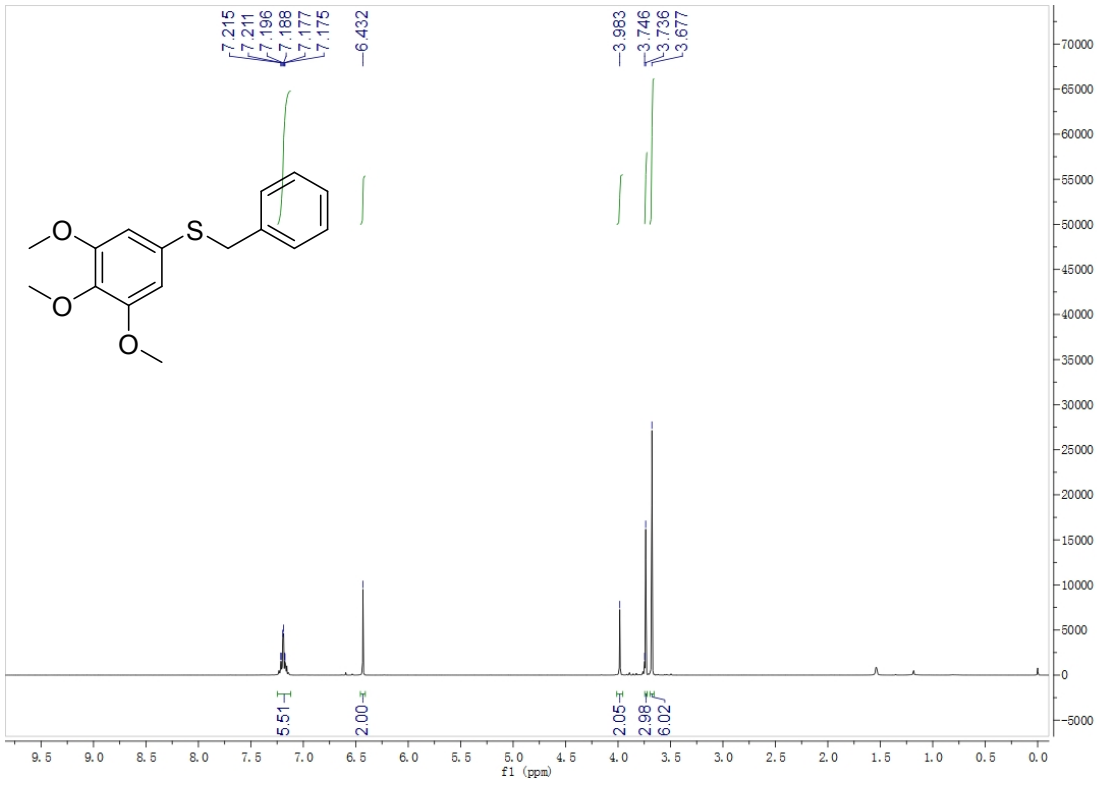
2o ^{1}H NMR



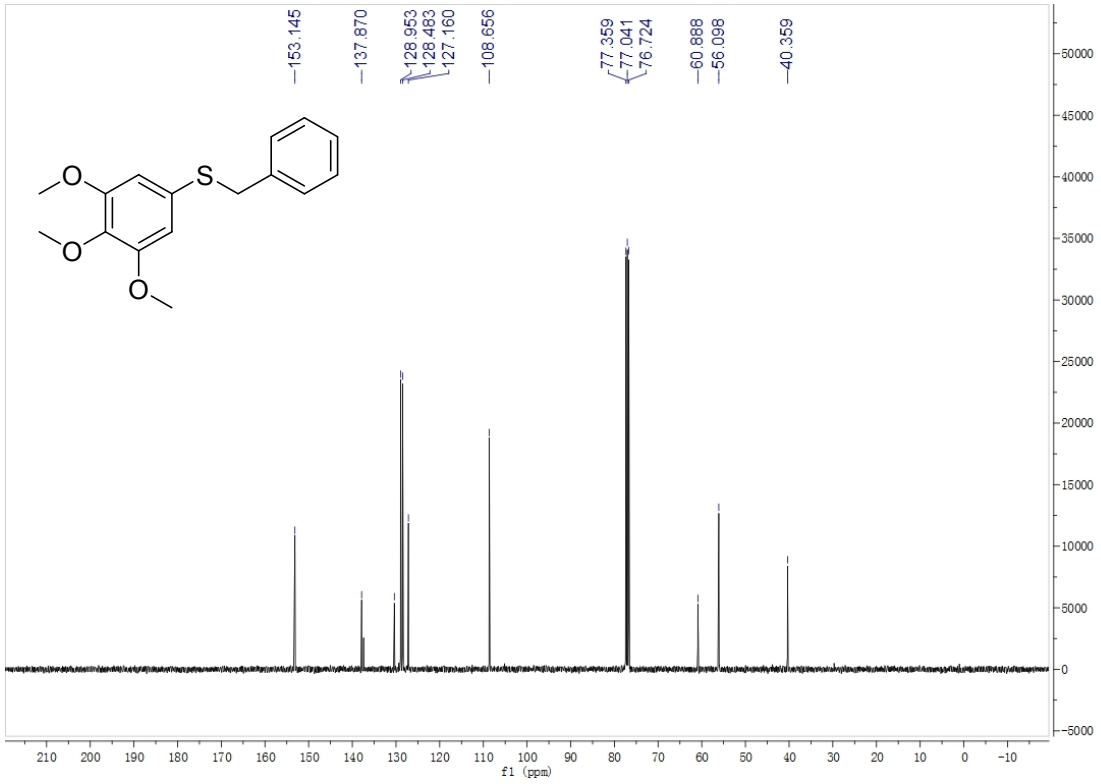
2o ^{13}C NMR



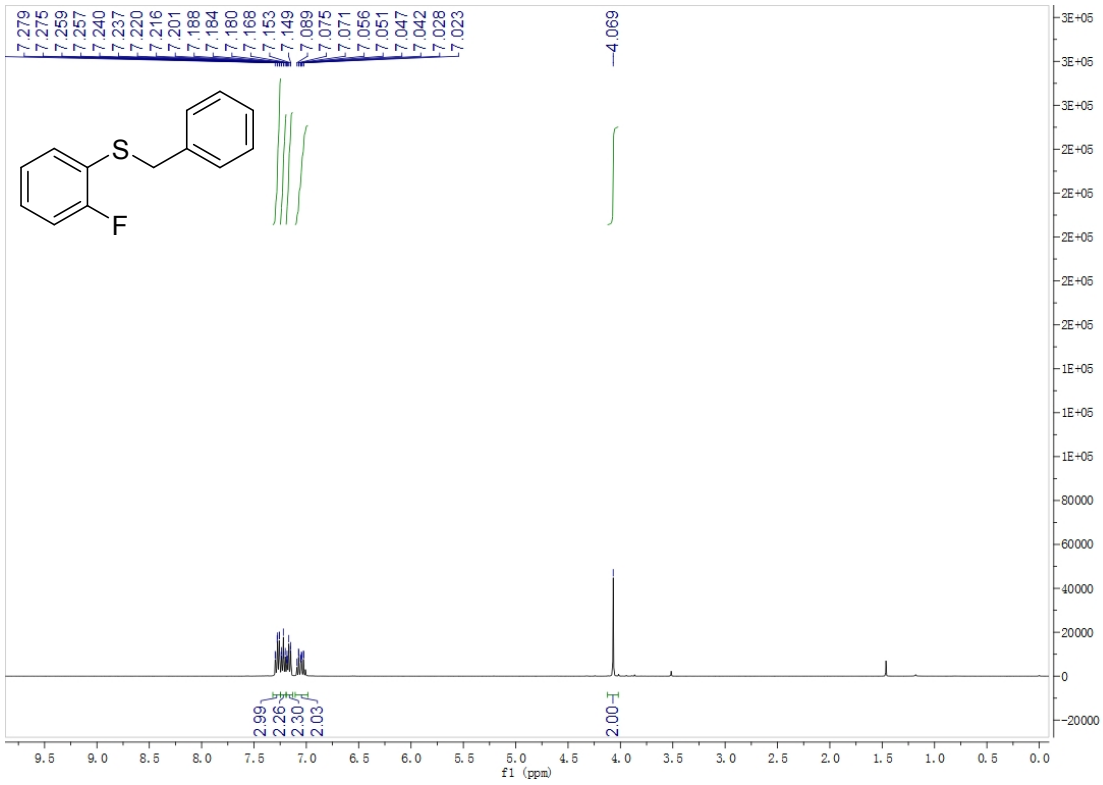
2p^{1}H NMR



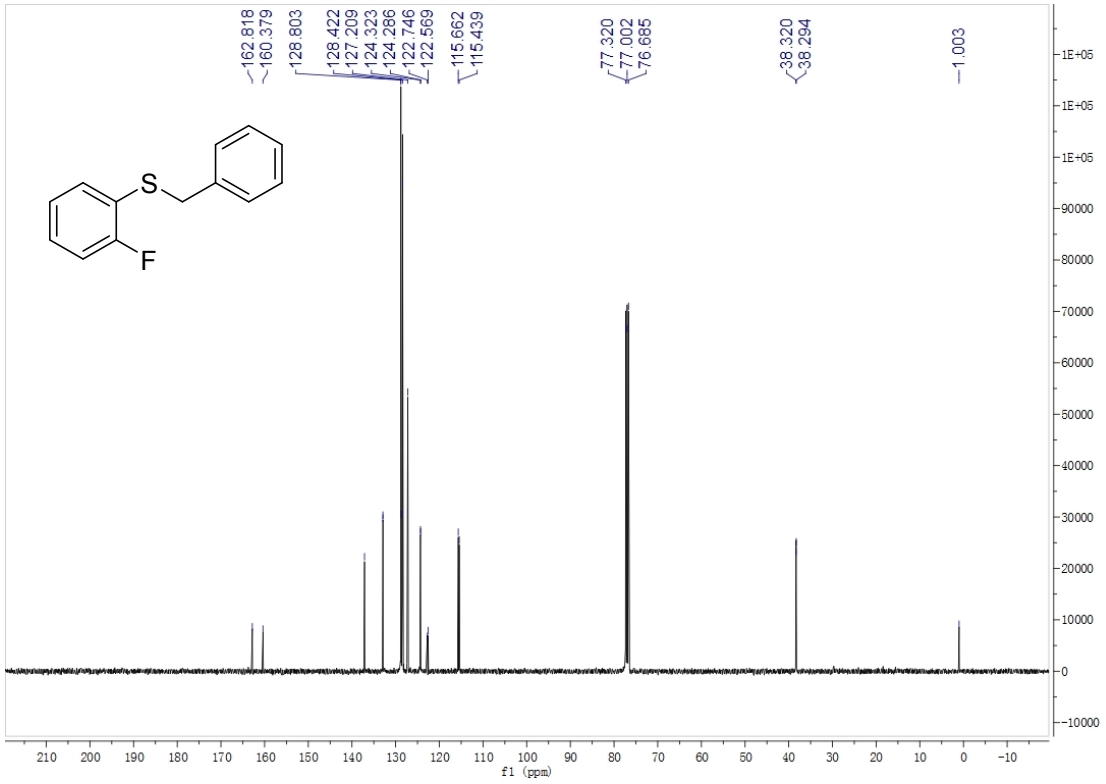
2p ^{13}C NMR



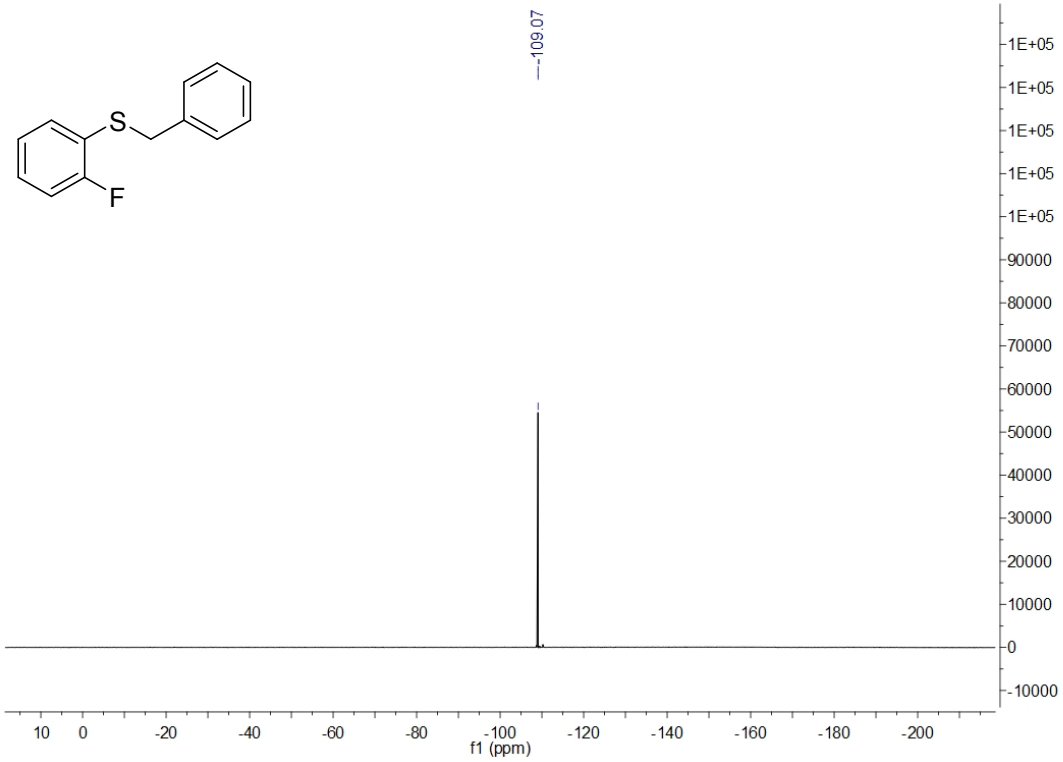
2q ^{1}H NMR



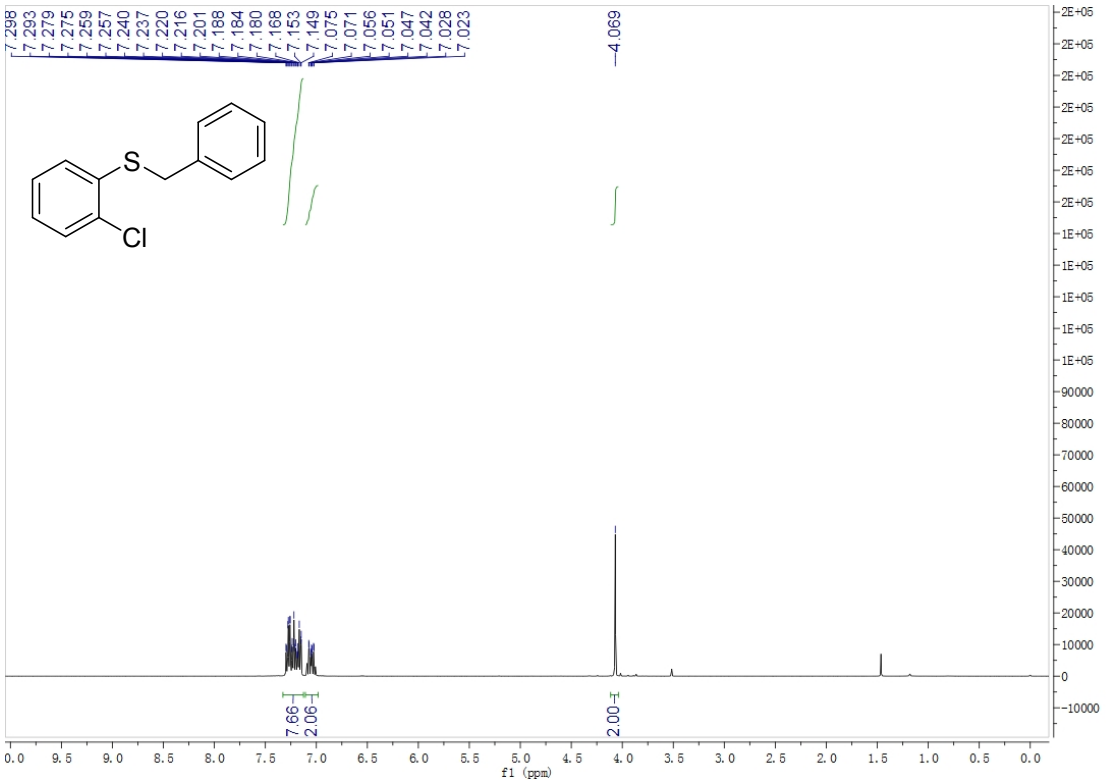
2q ^{13}C NMR



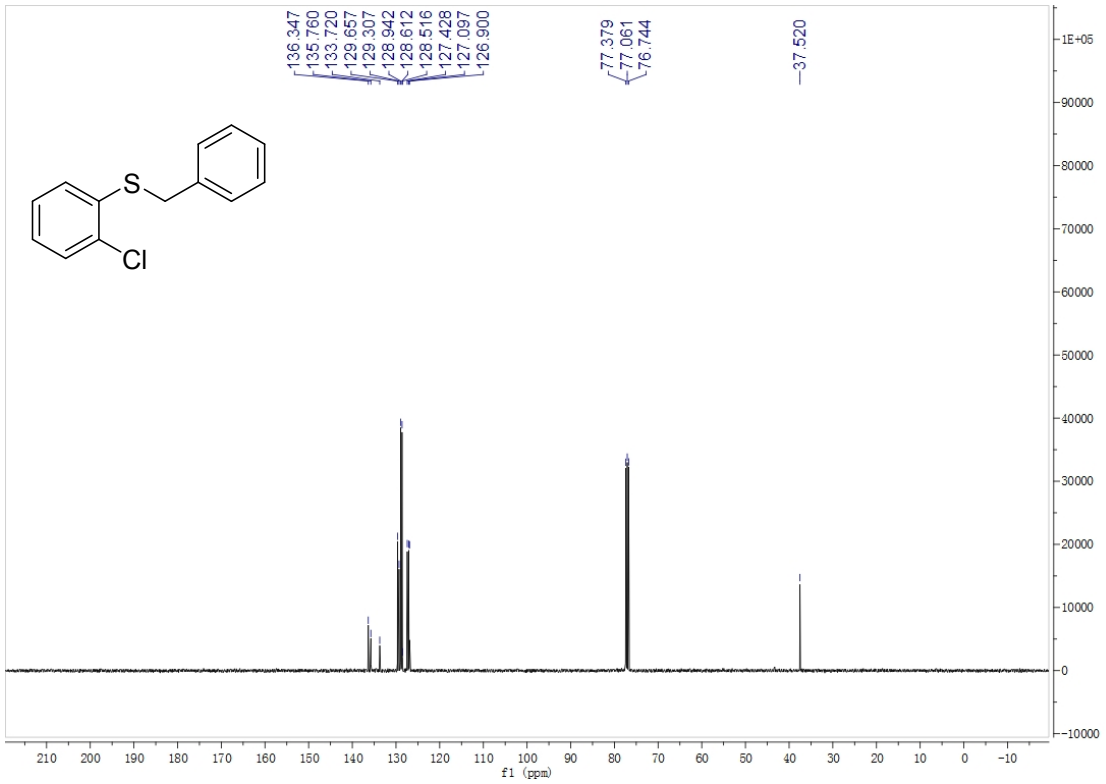
2q ^{19}F NMR



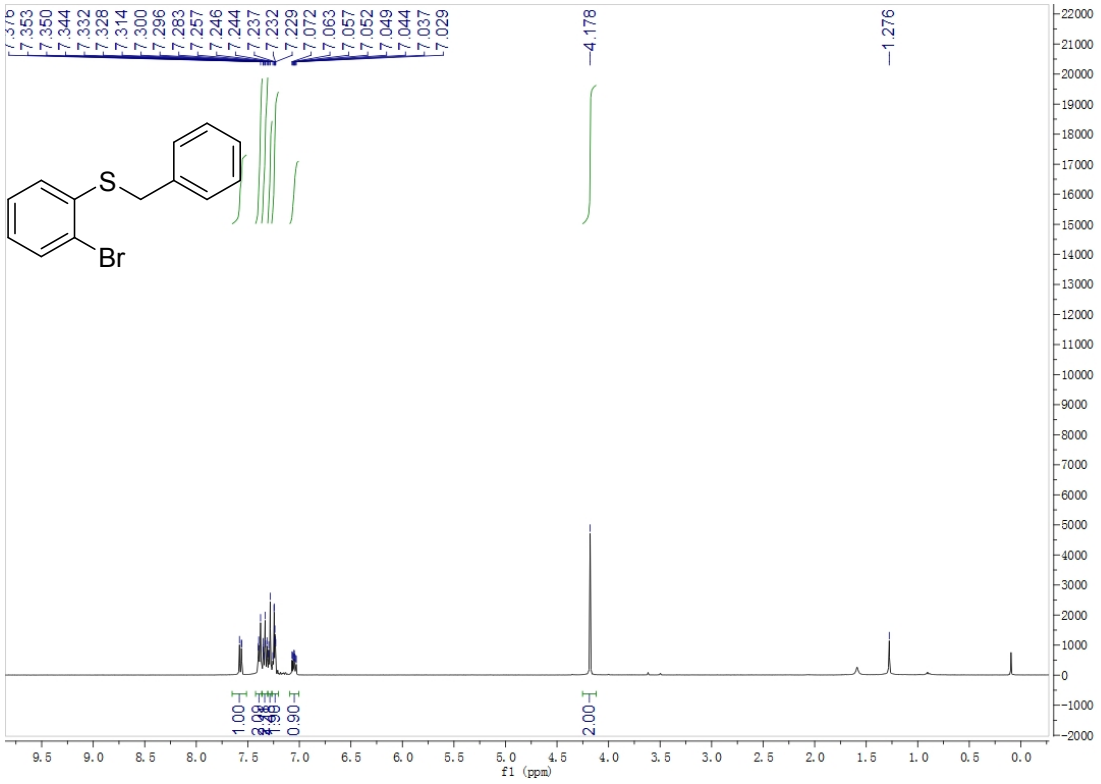
2r ^{1}H NMR



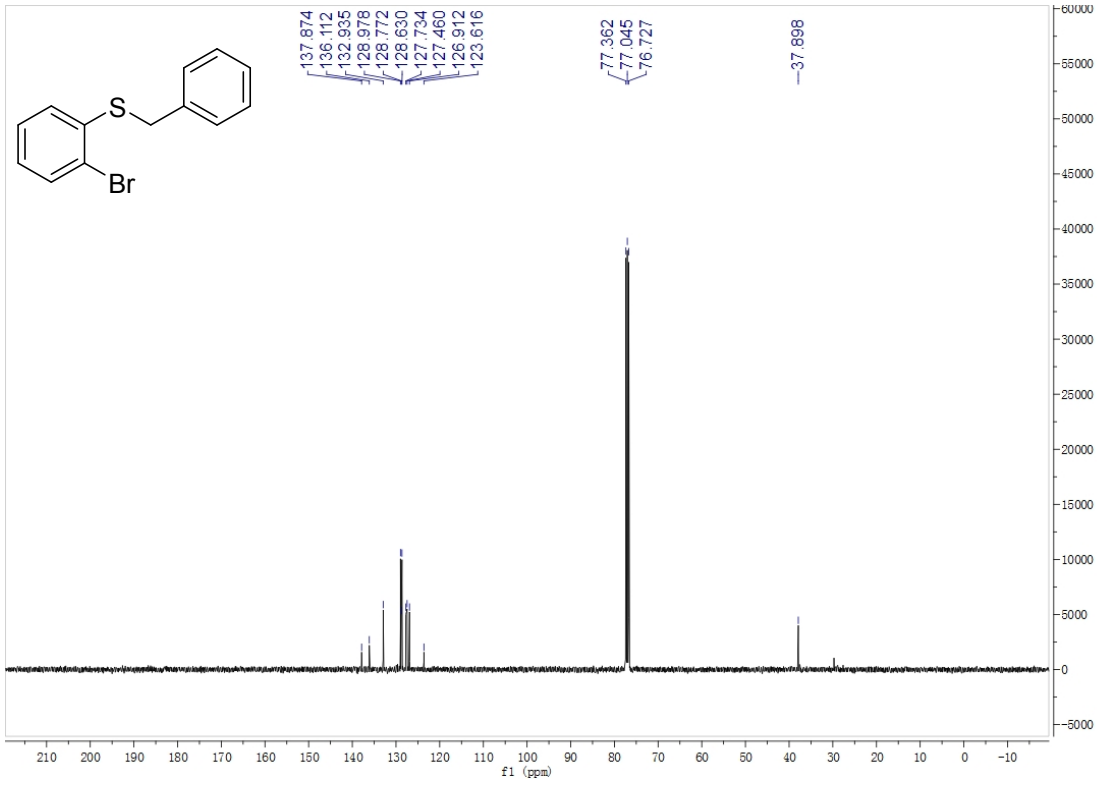
2r ^{13}C NMR



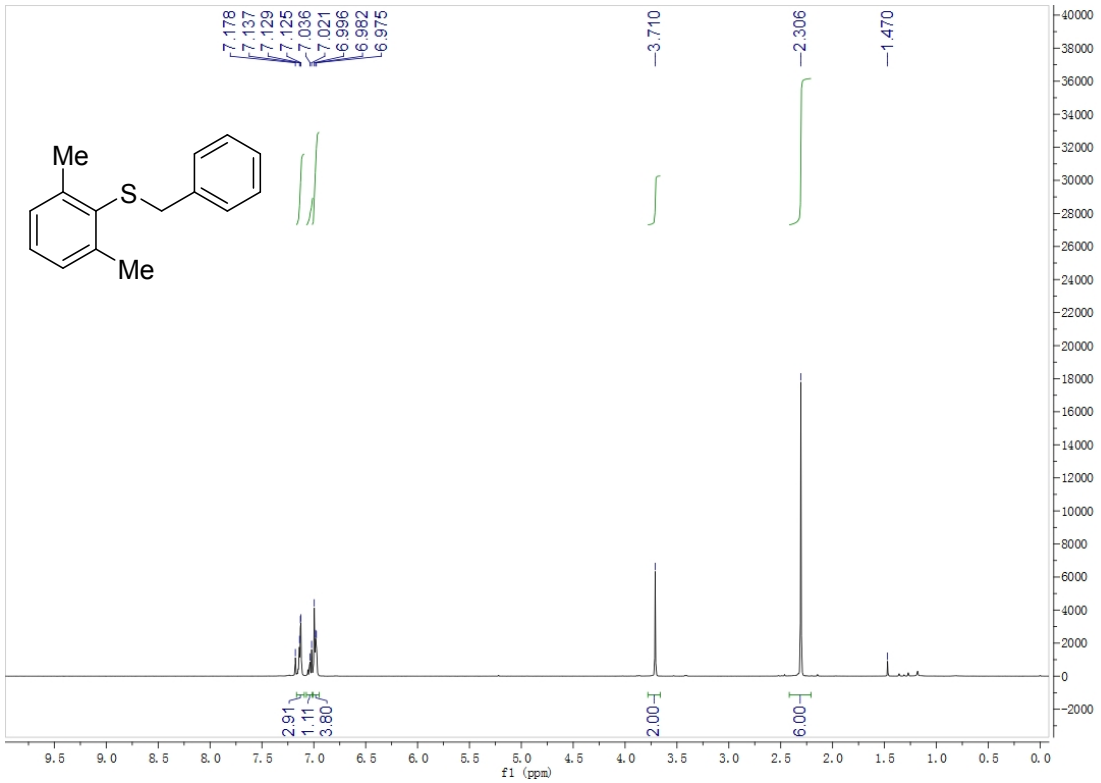
2s ^{1}H NMR



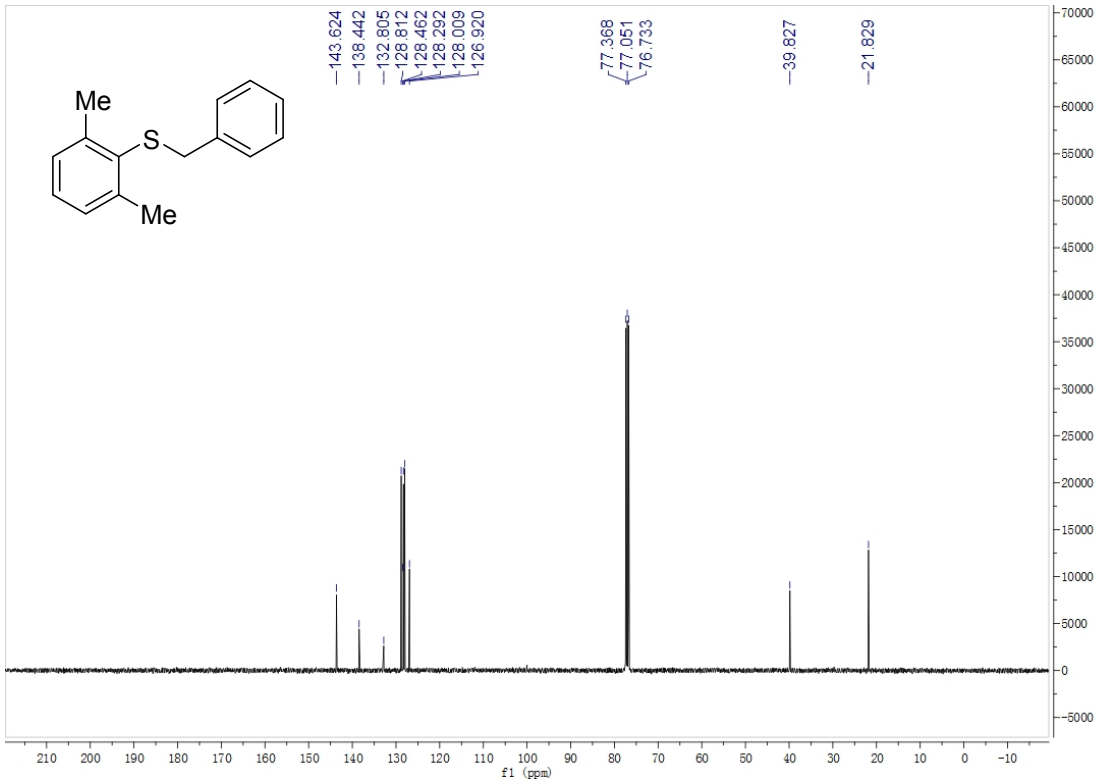
2s ^{13}C NMR



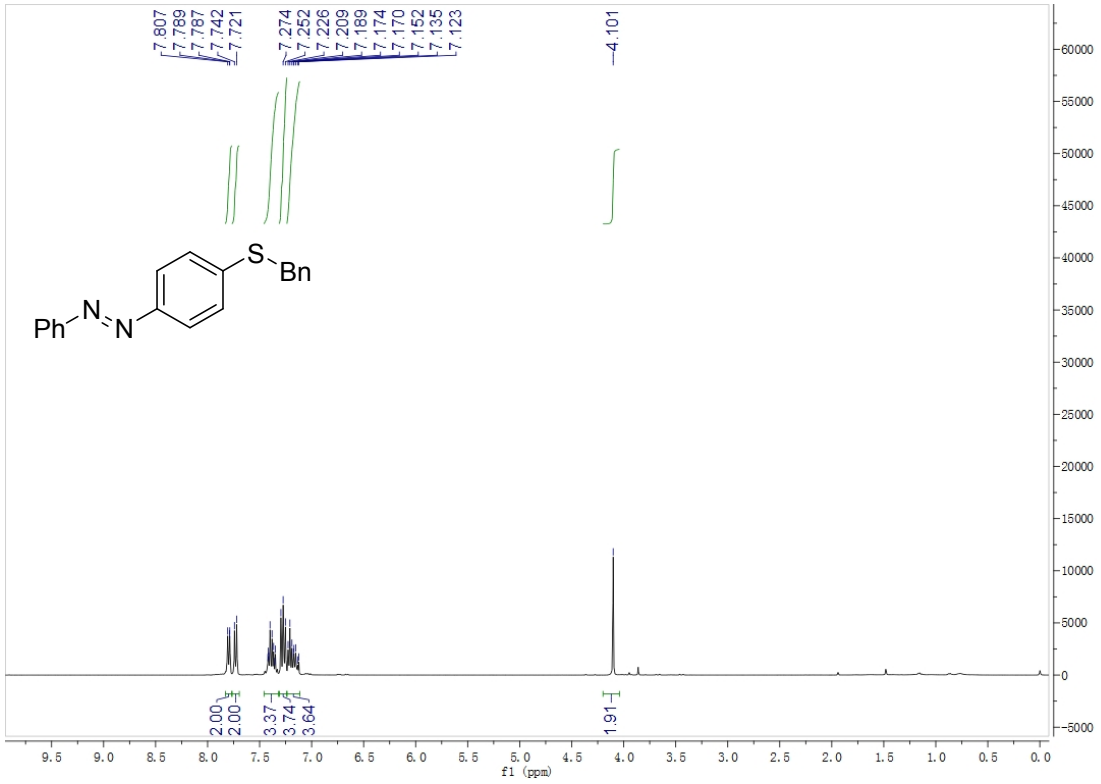
2t ^{1}H NMR



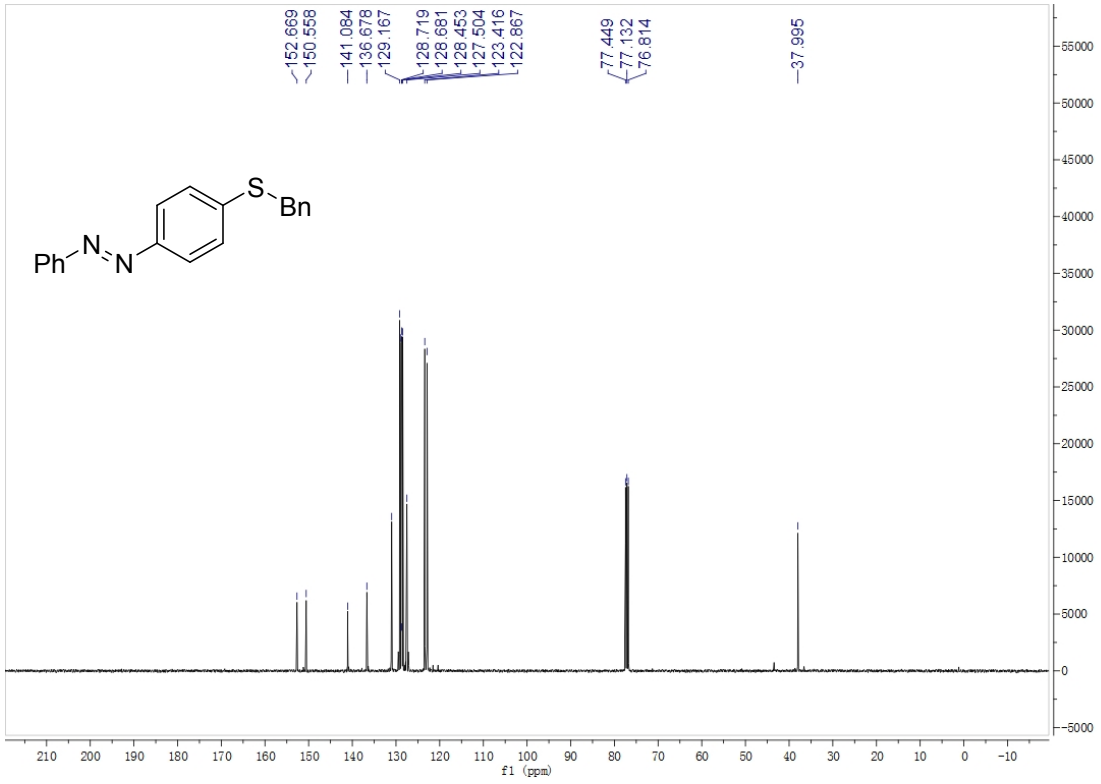
2t ^{13}C NMR



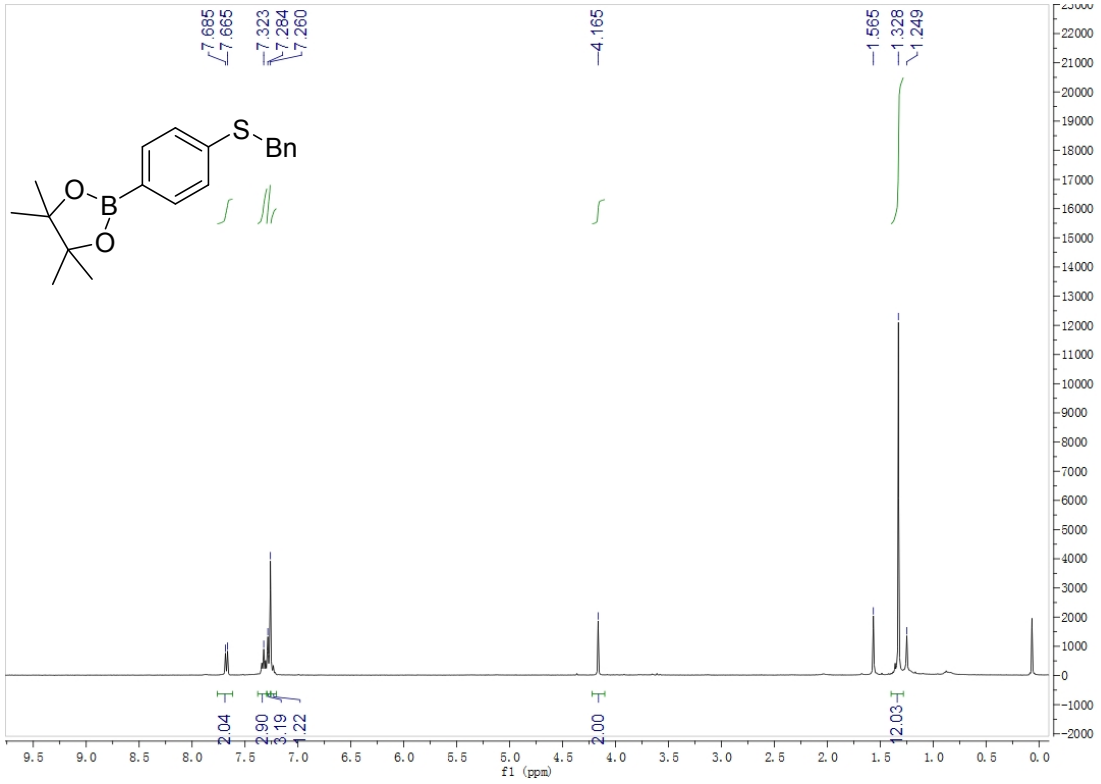
2u ^{1}H NMR



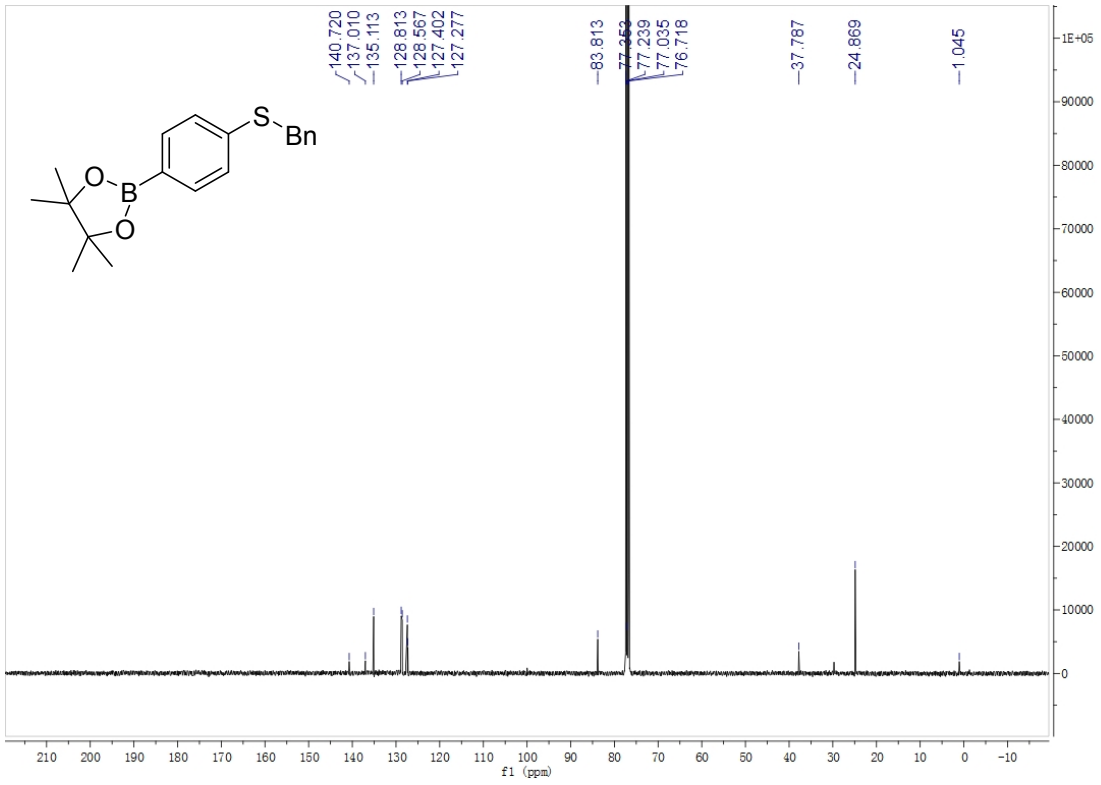
2u ^{13}C NMR



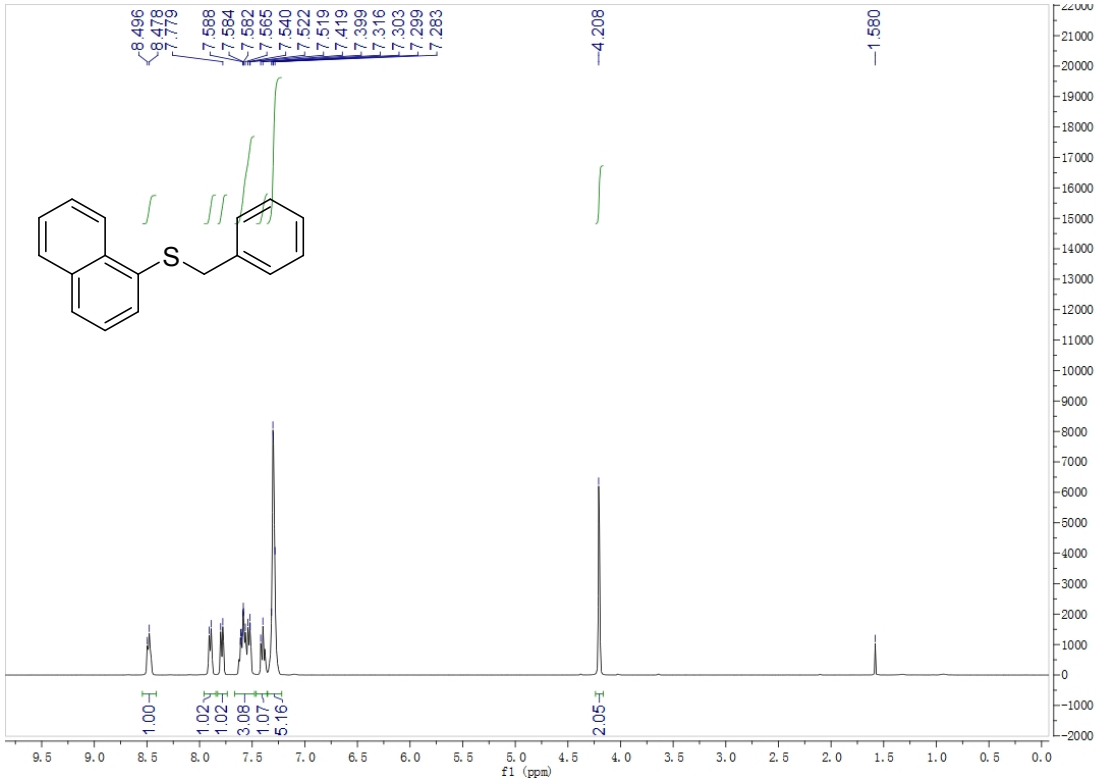
2v ^{1}H NMR



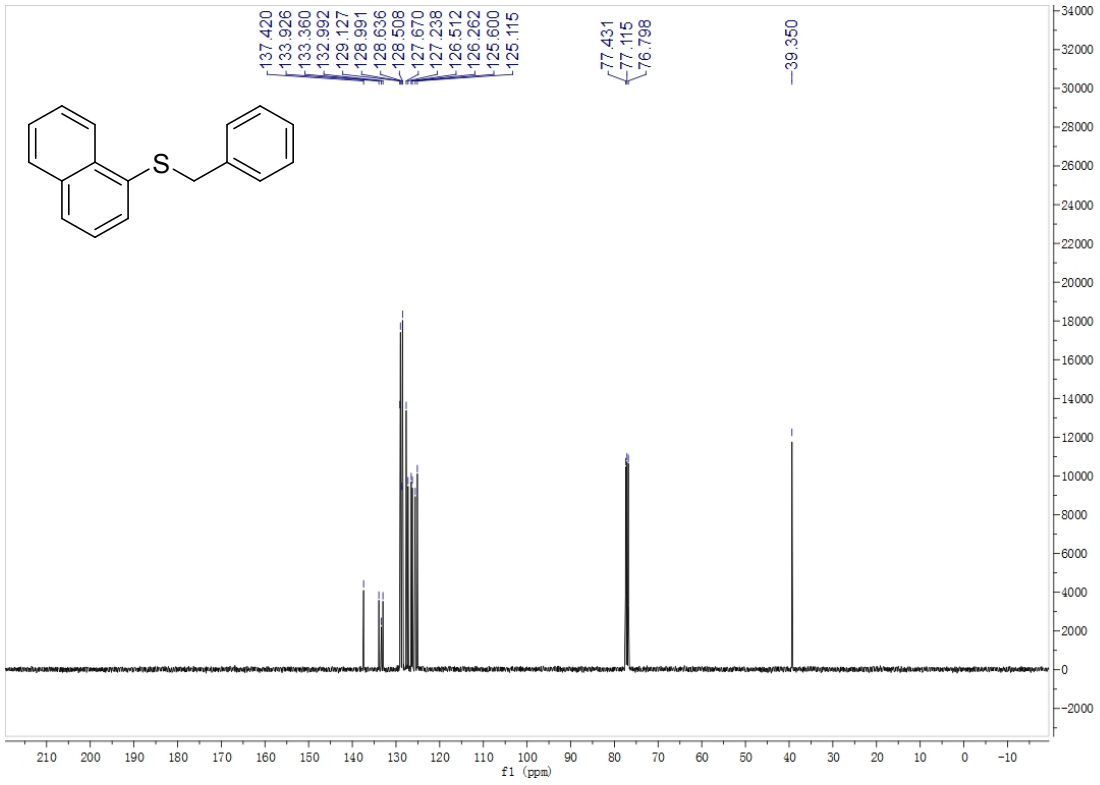
2v ^{13}C NMR



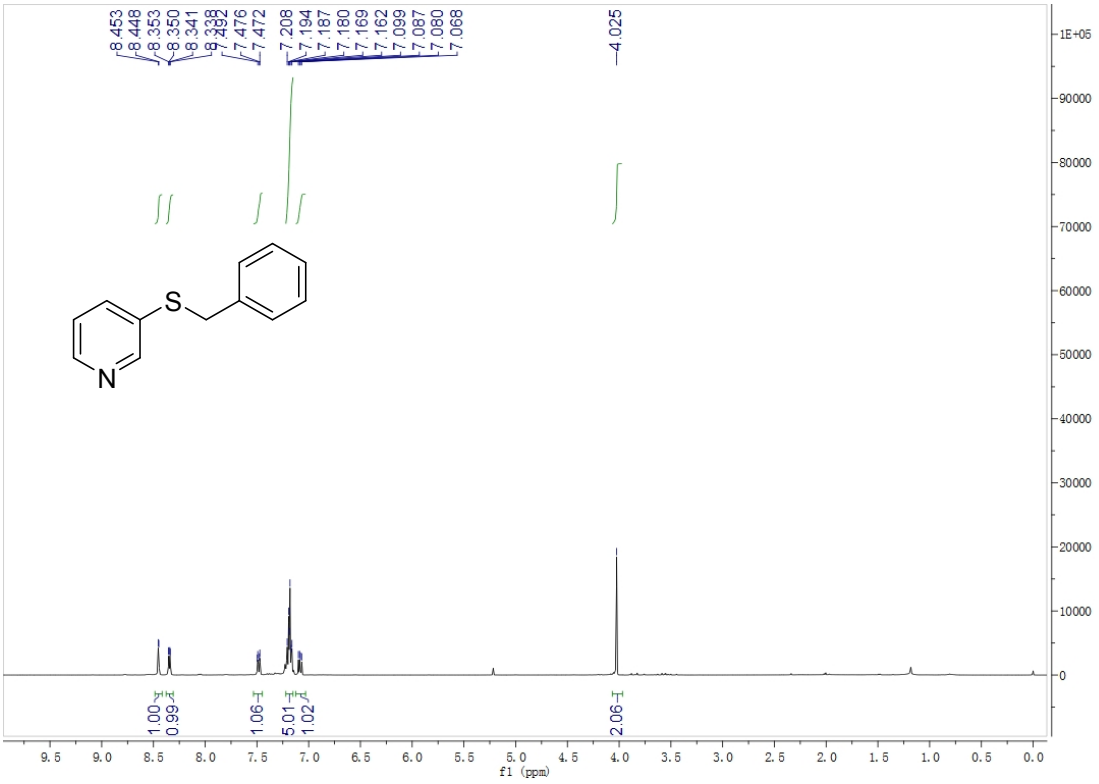
2w ^{1}HNMR



2w ^{13}C NMR



2x ^{1}H NMR



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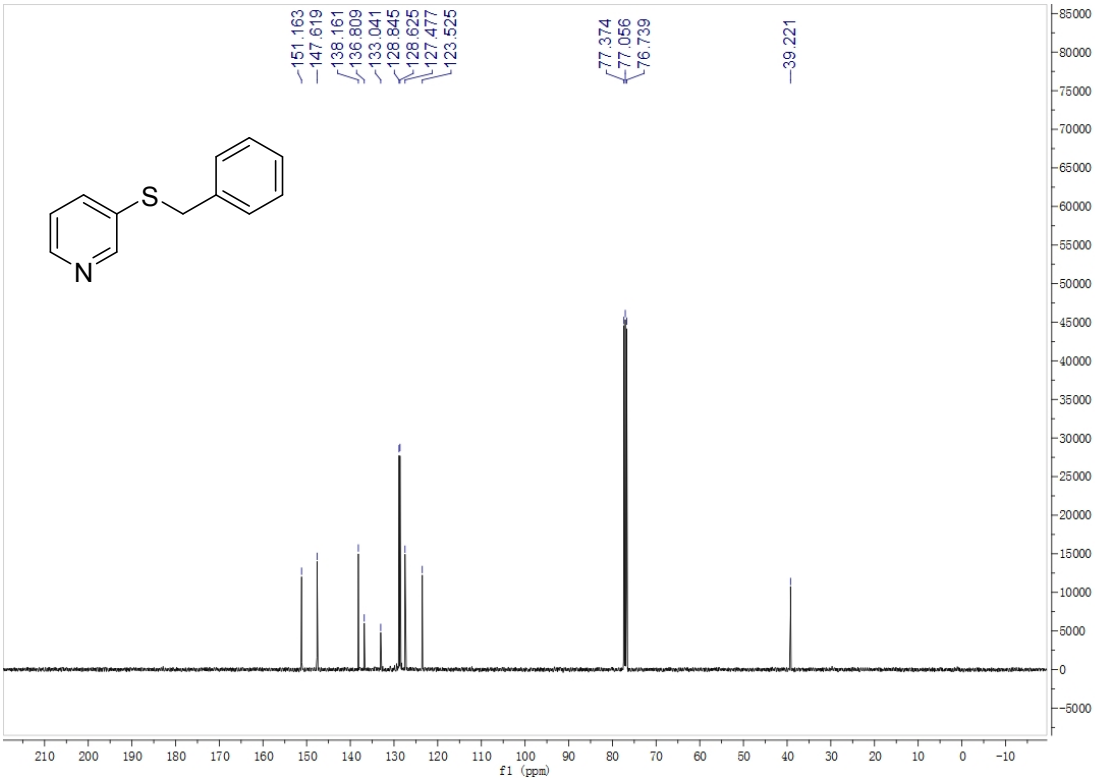
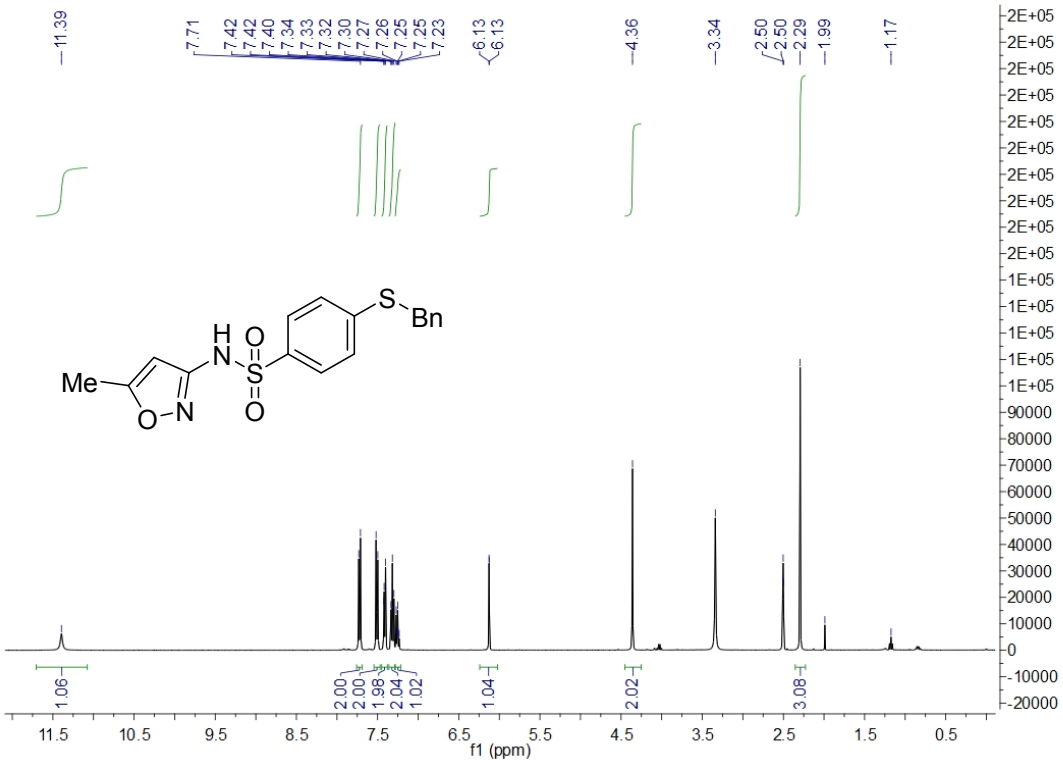
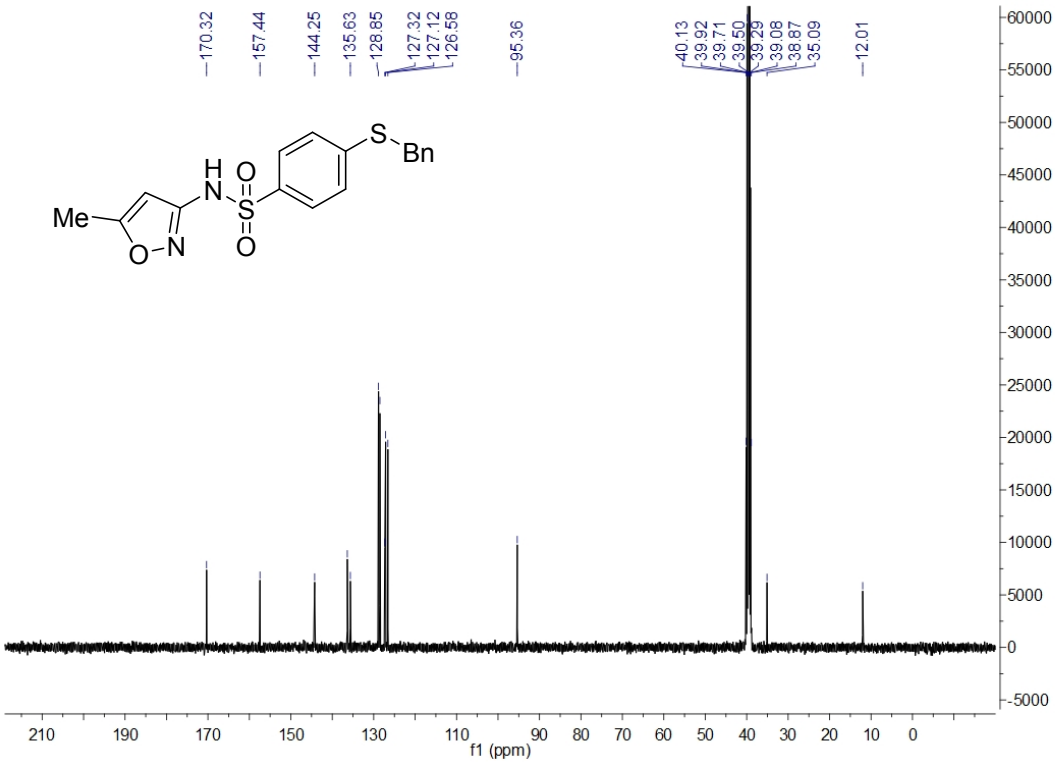


2y ^{1}H NMR



2y ^{13}C NMR



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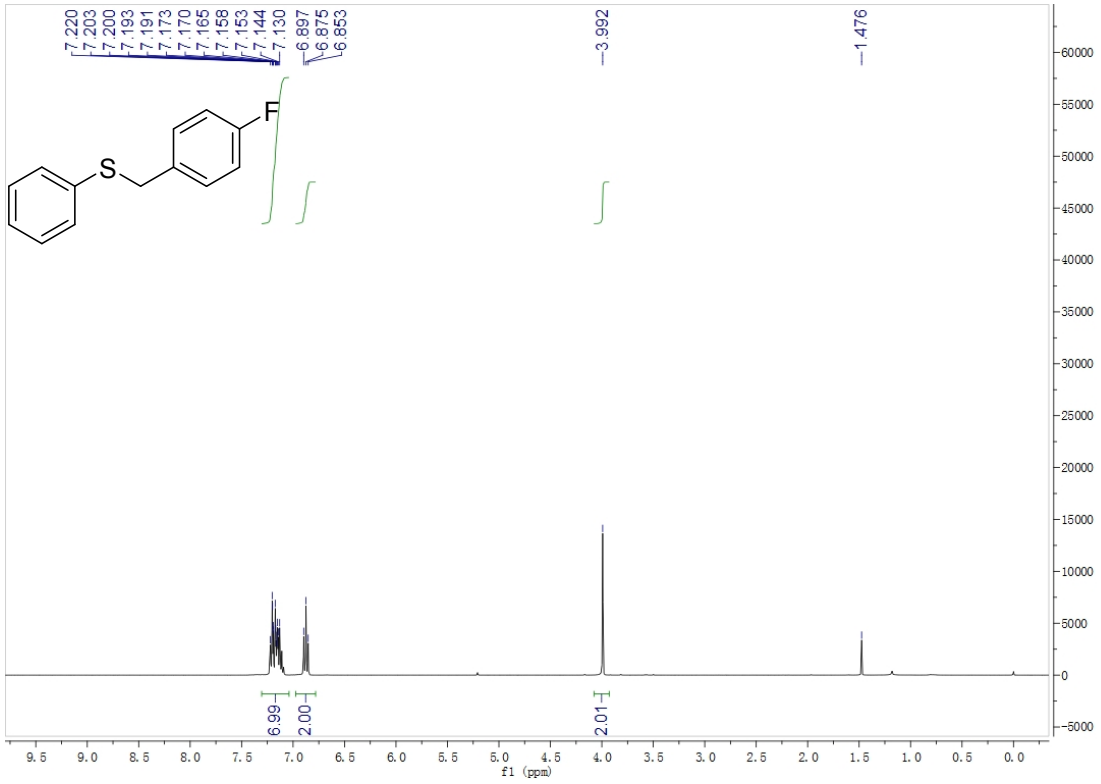

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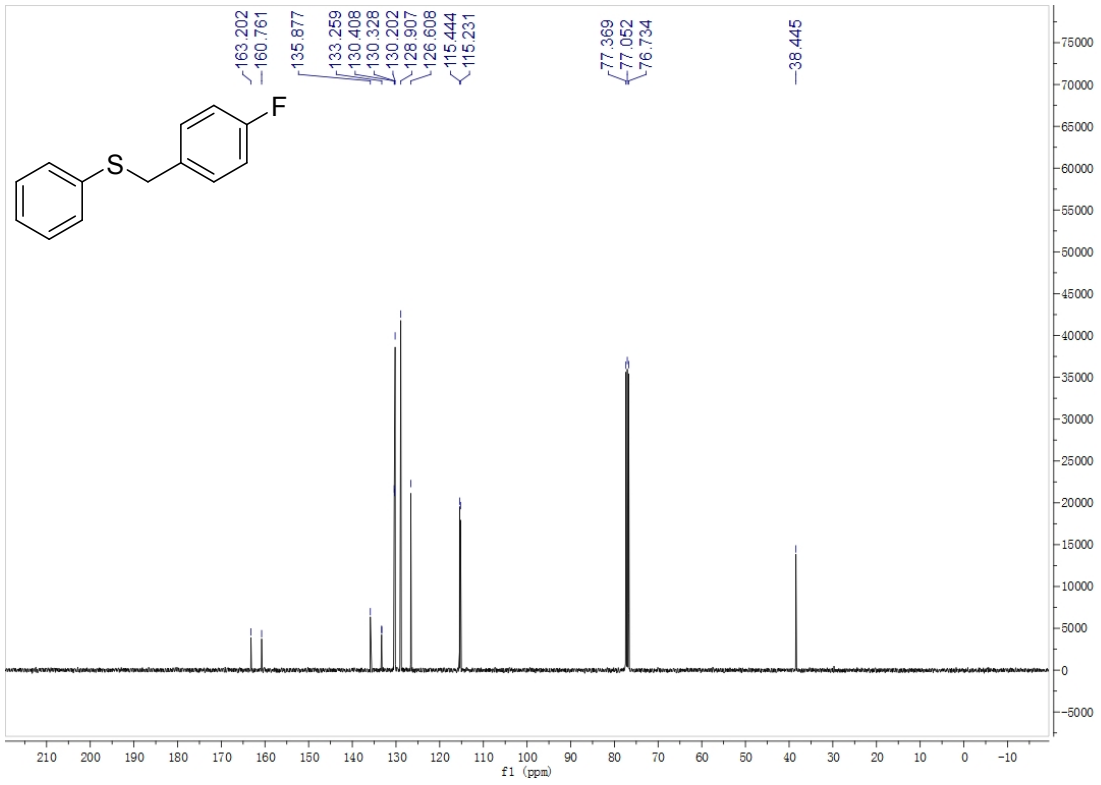
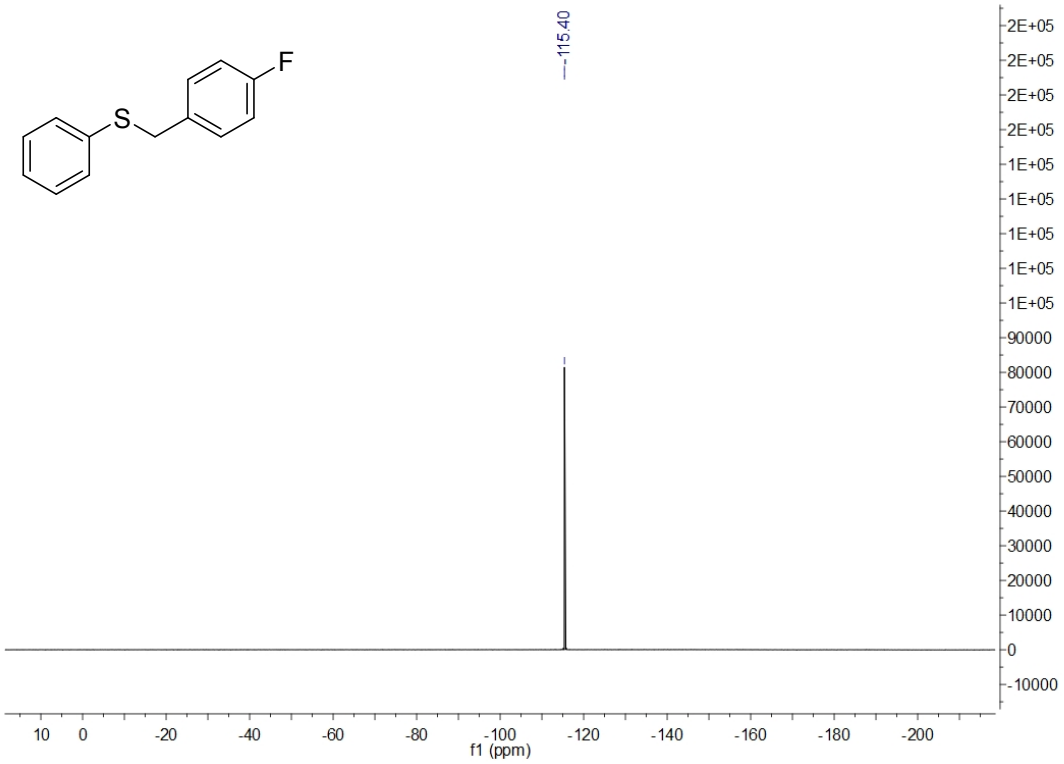
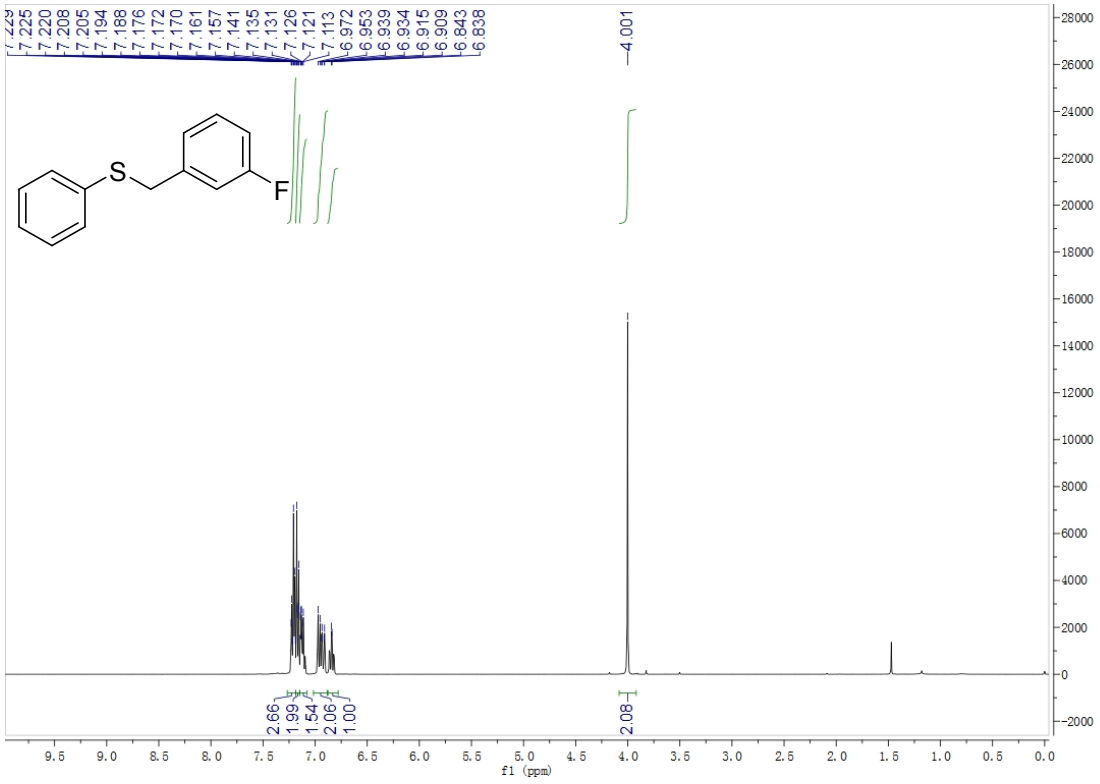


3a ^{19}F NMR



3b ^{1}H NMR



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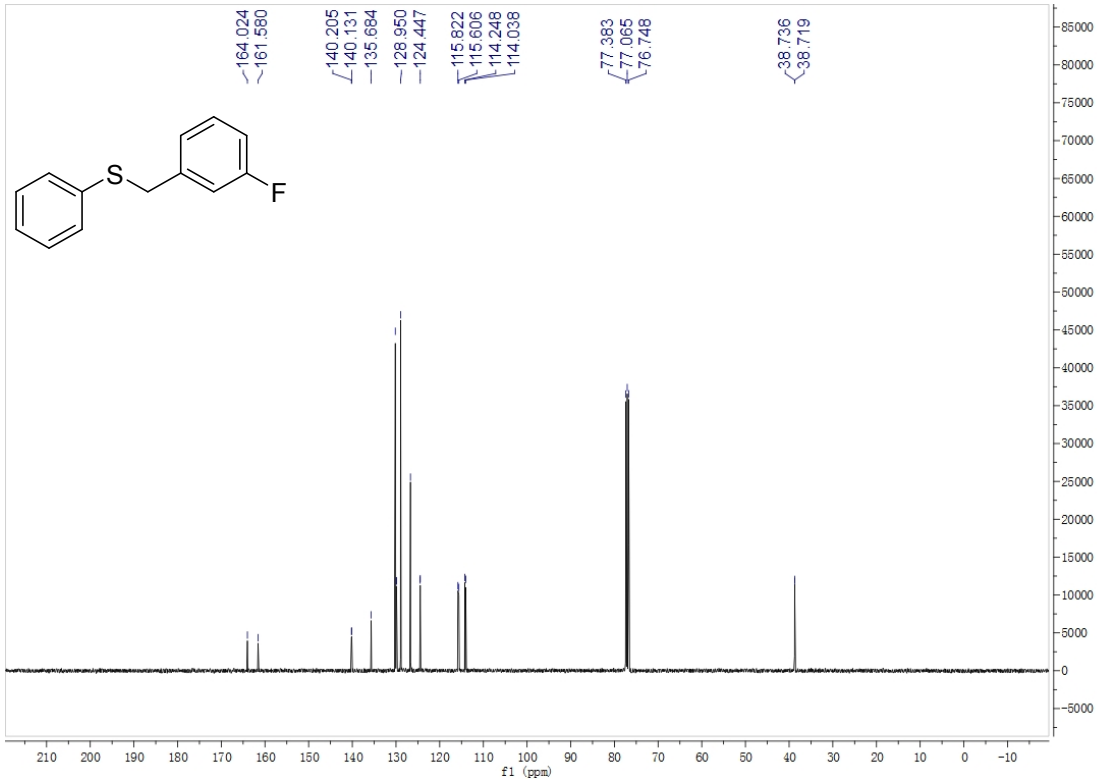

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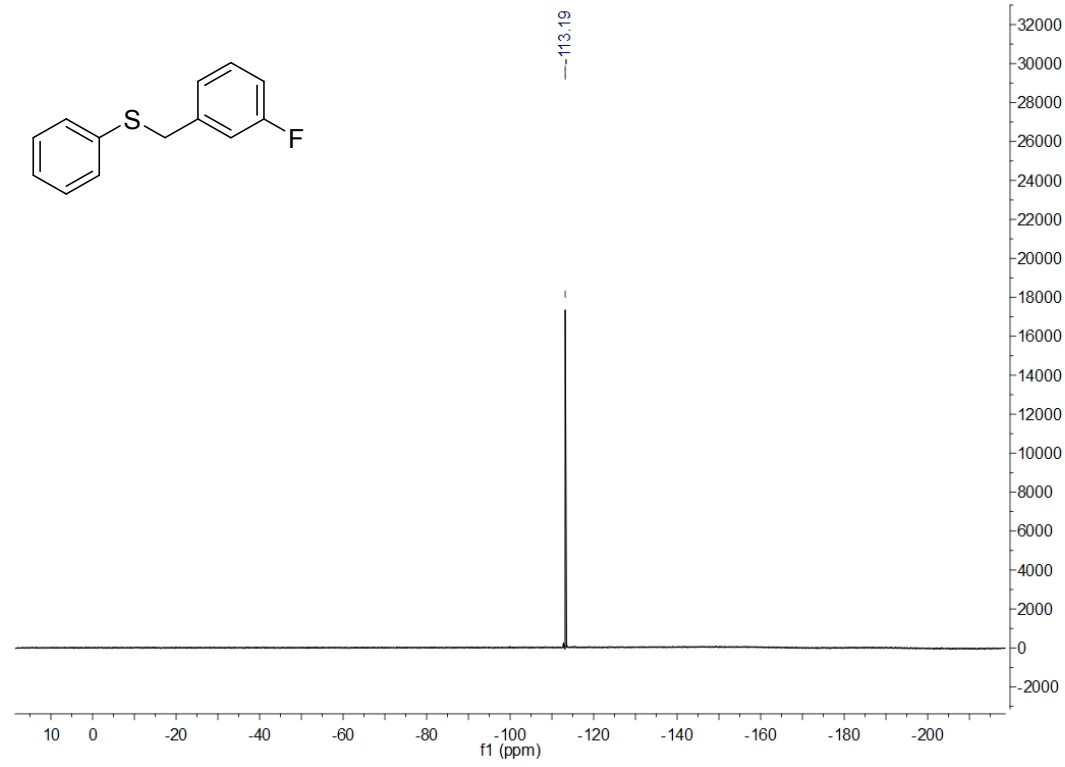
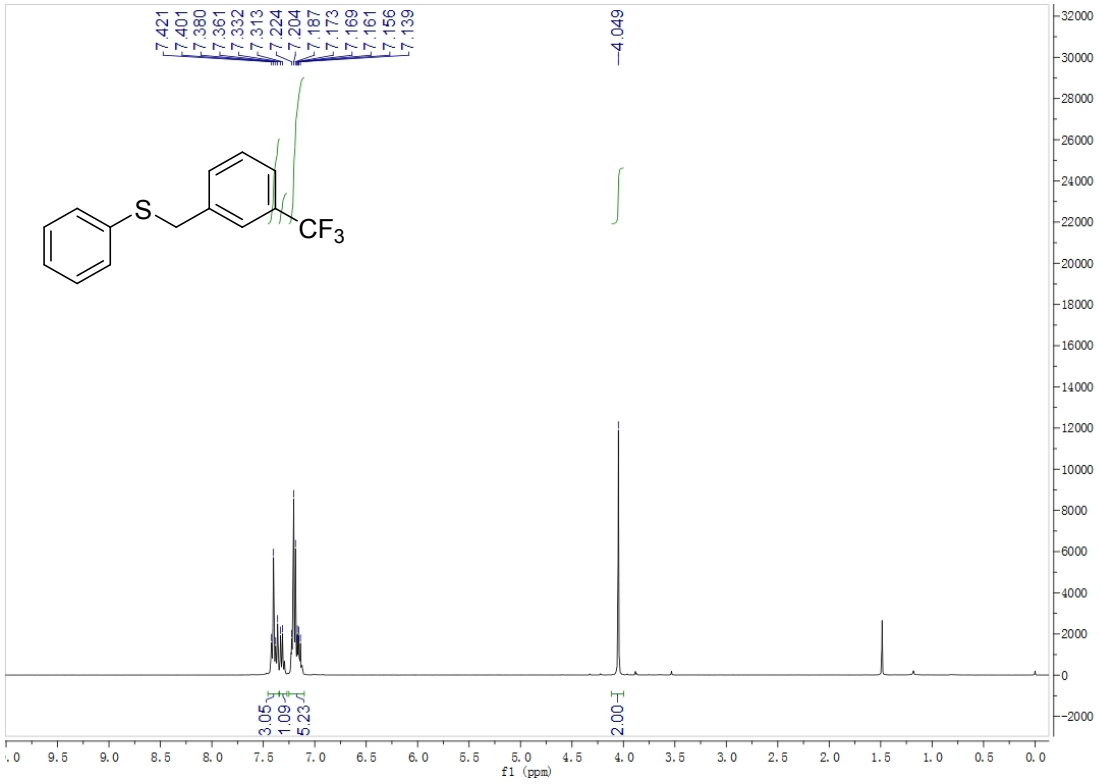
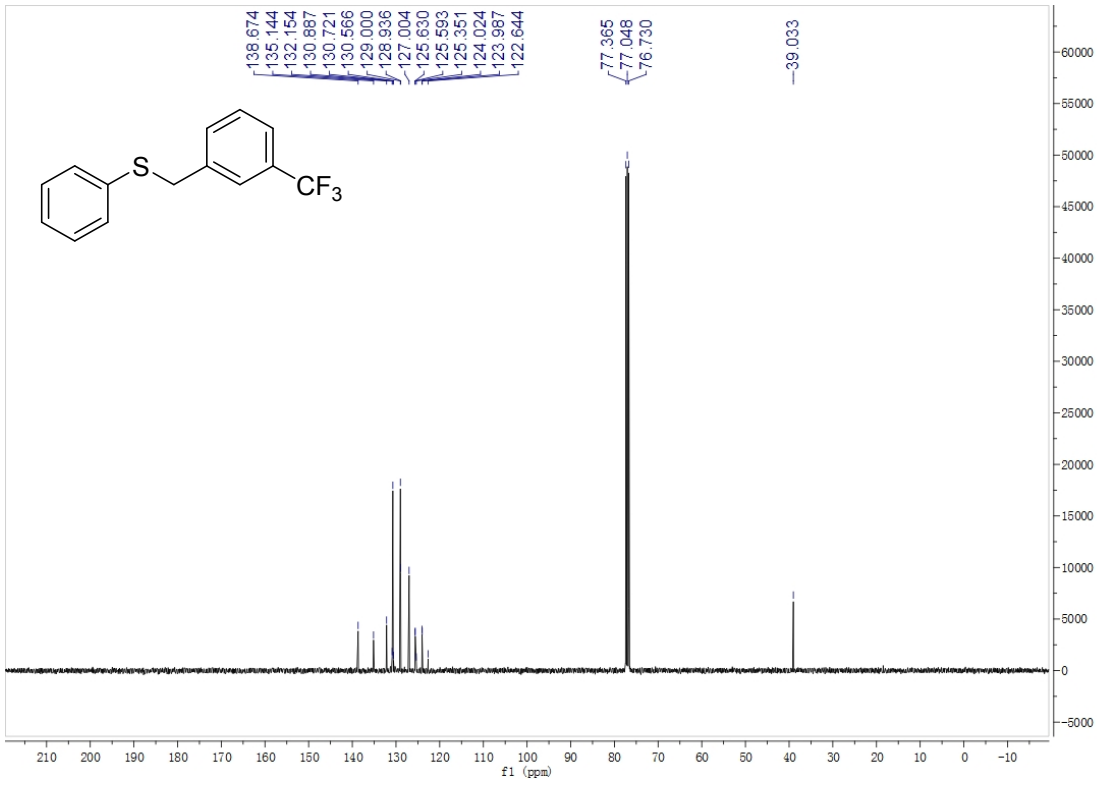


3c ^{1}H NMR



3c ^{13}C NMR



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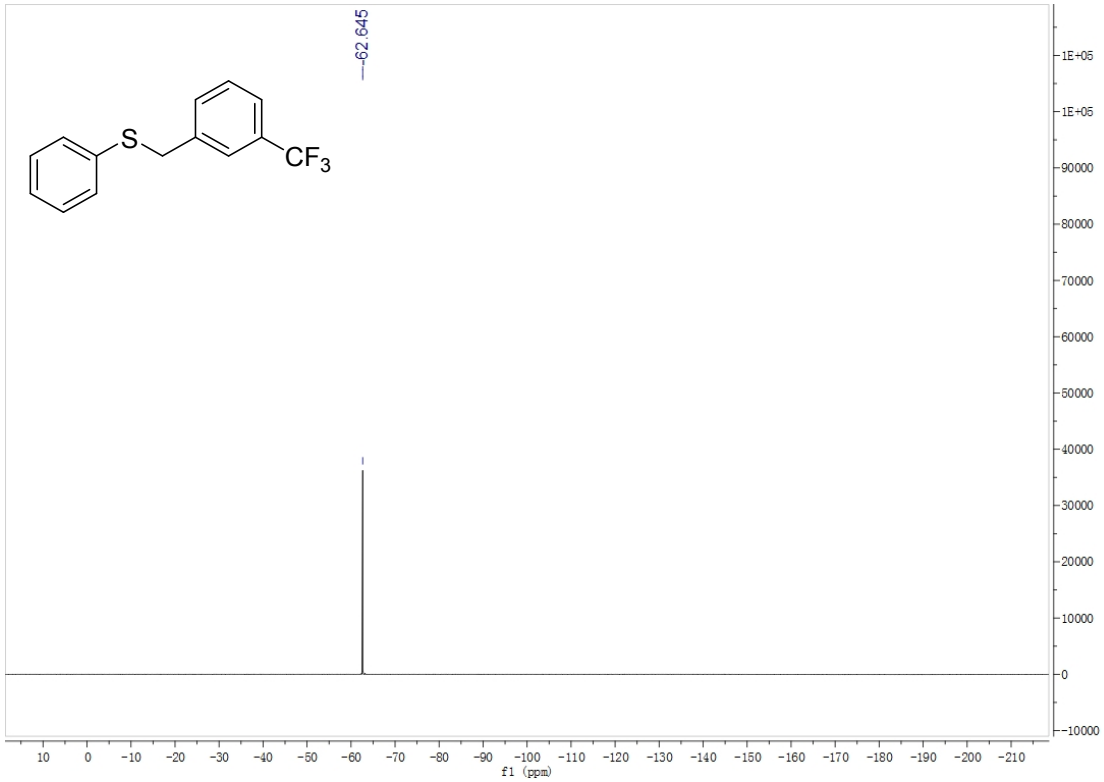
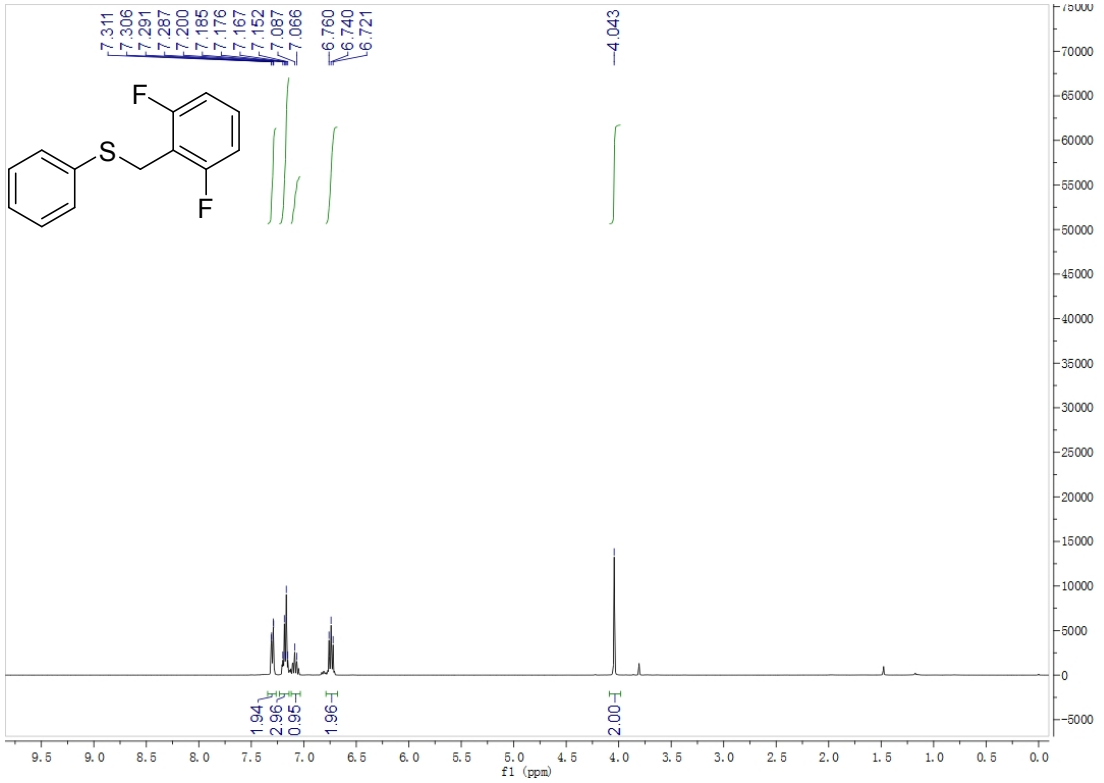
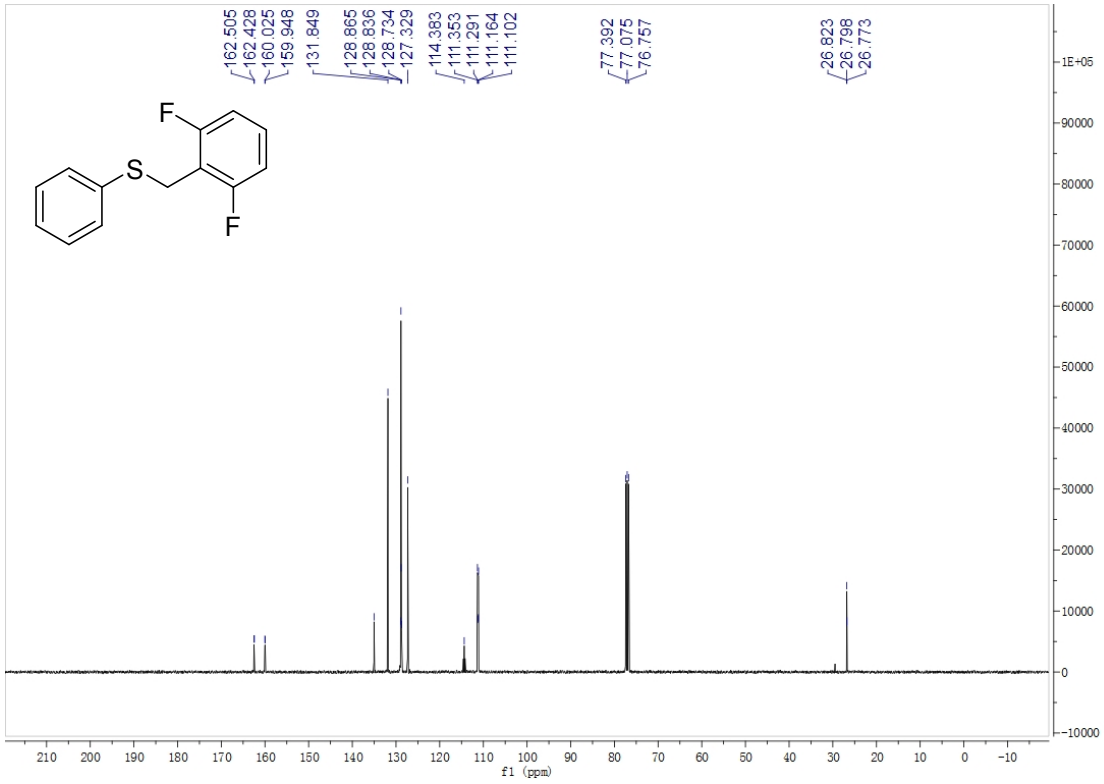


3d ^{1}H NMR



3d ^{13}C NMR



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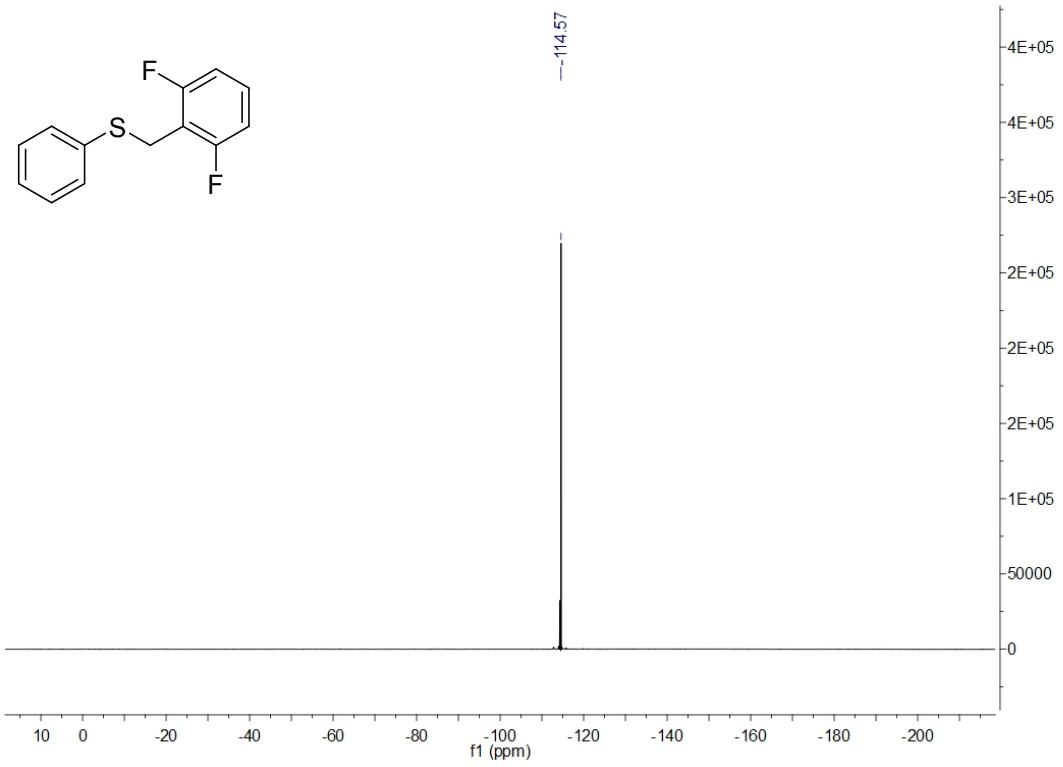
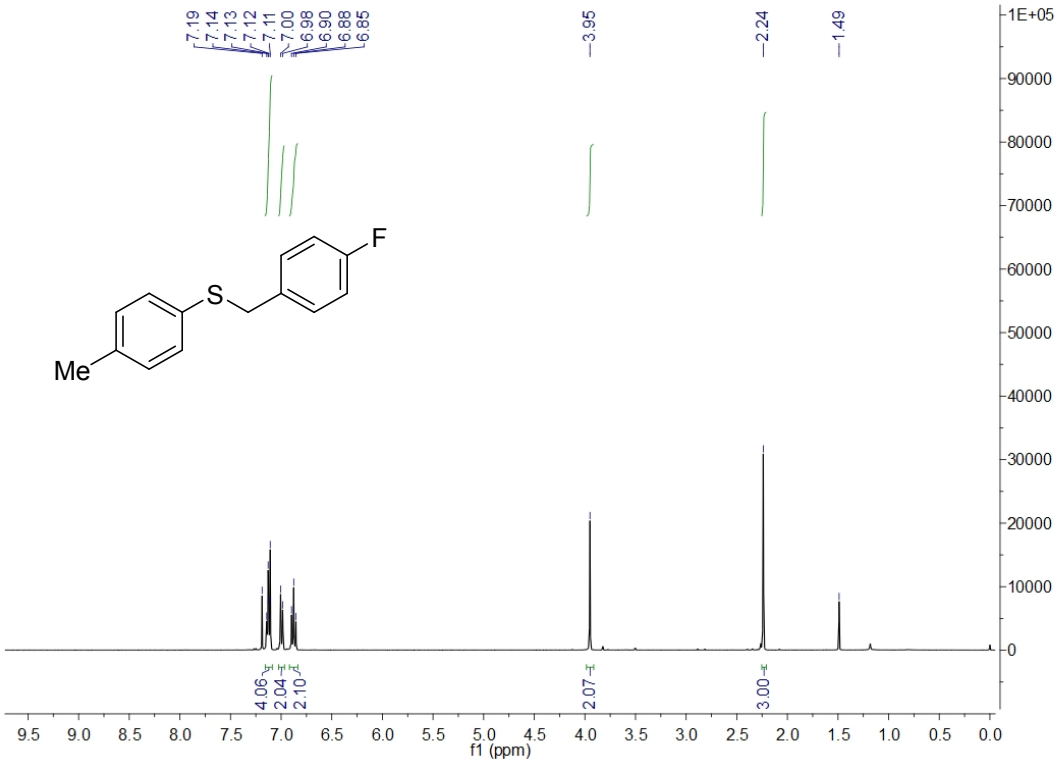


3e ^{1}H NMR



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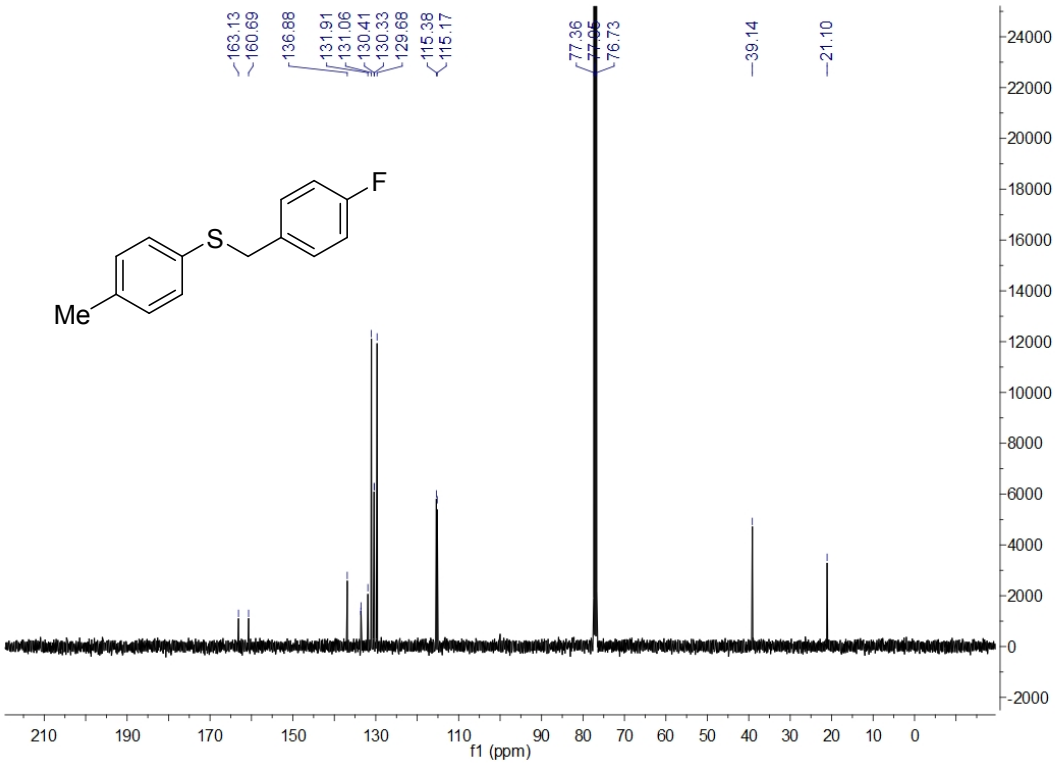
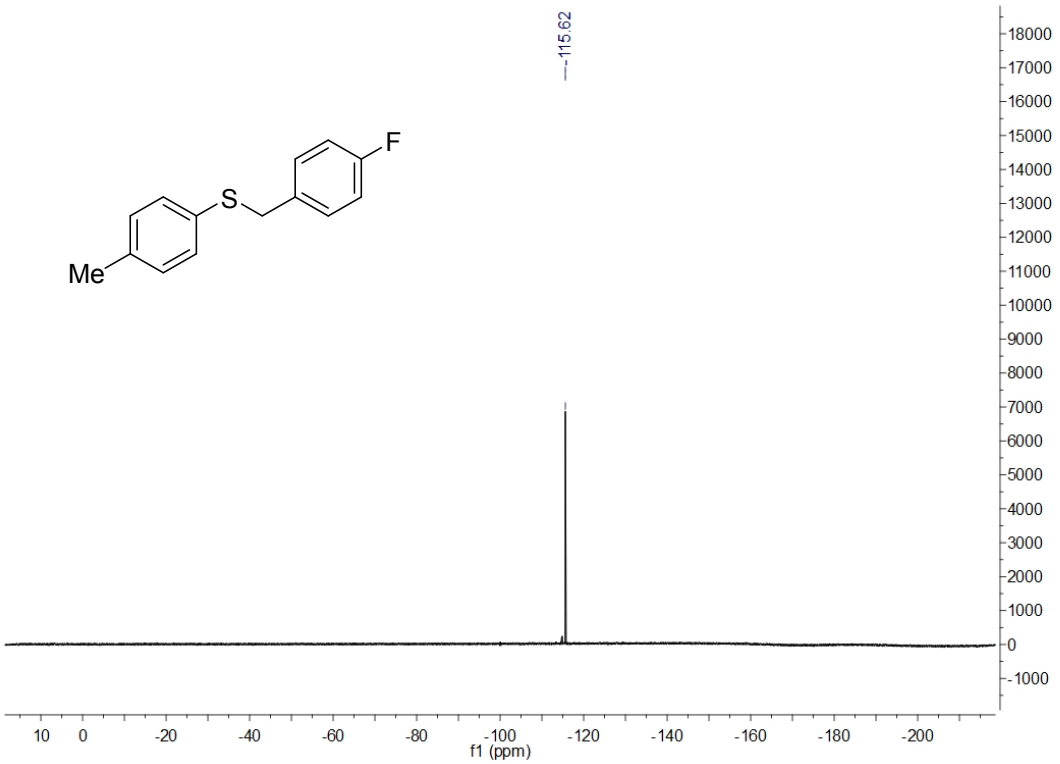
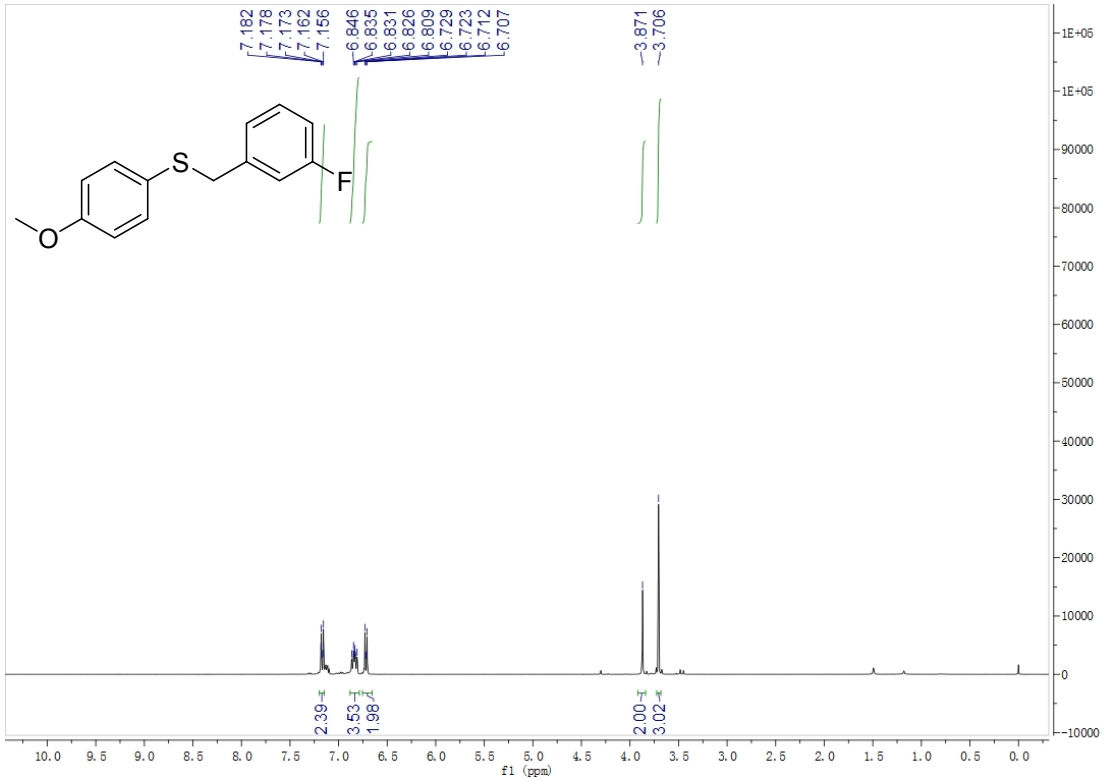


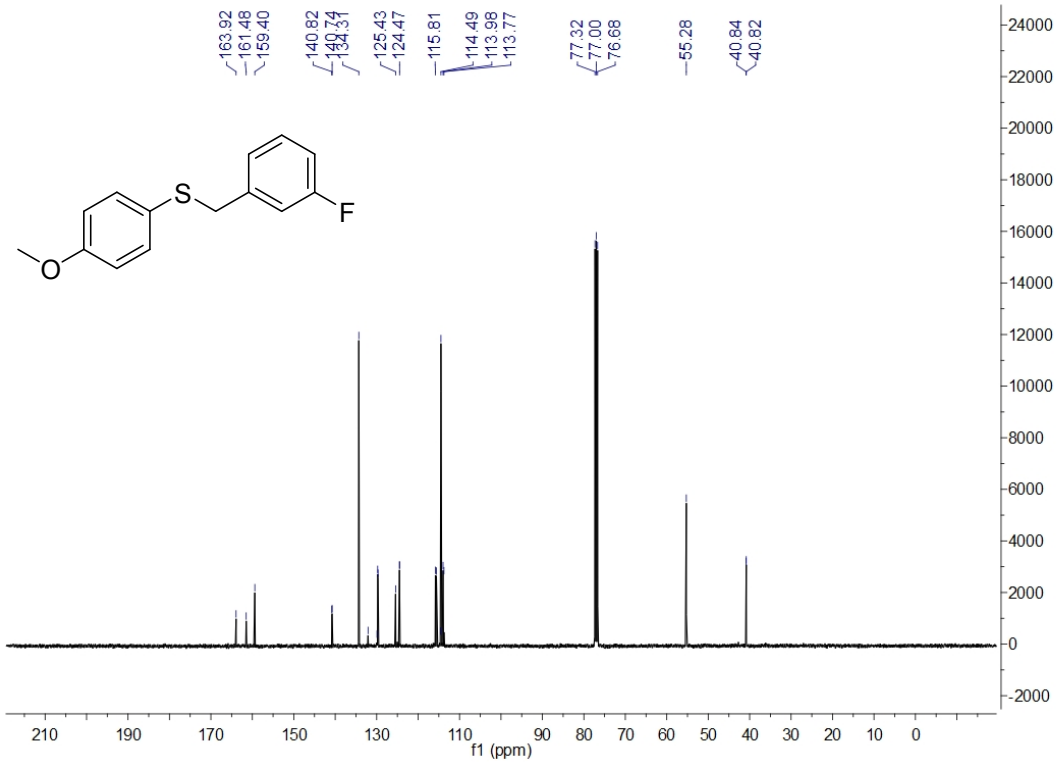
3e ^{19}F NMR


-115.62
F
S
Me
f1 (ppm)

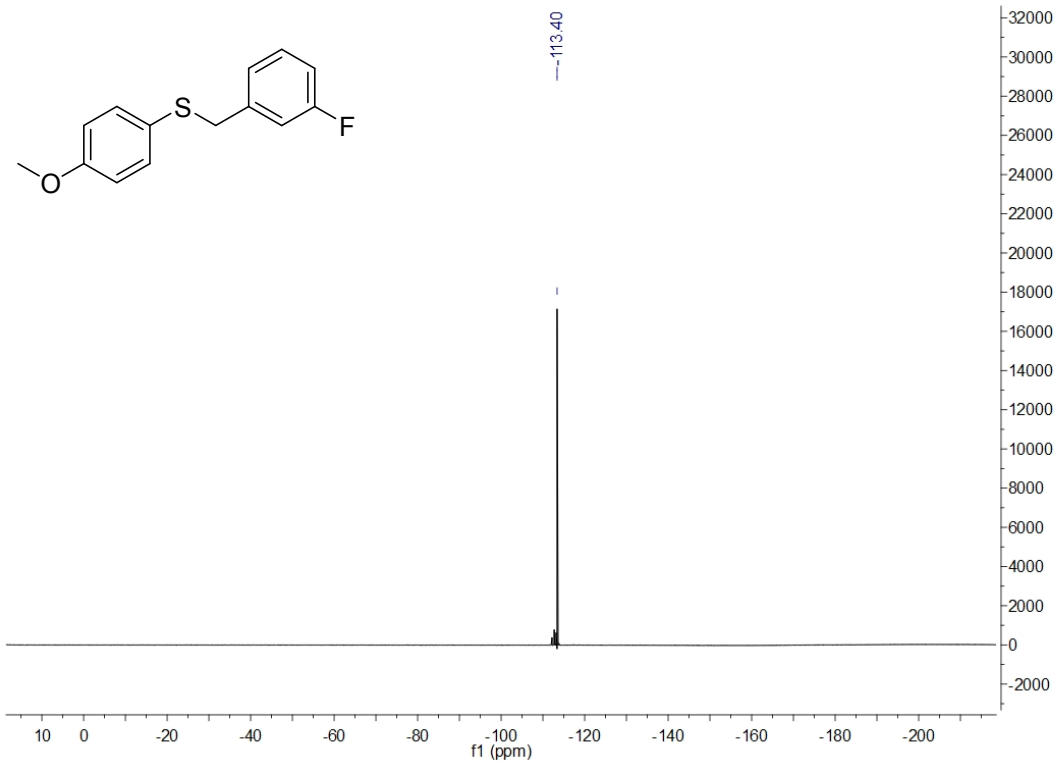
3f ^{1}H NMR


7.182
7.178
7.173
7.162
7.156
6.846
6.835
6.831
6.826
6.809
6.729
6.723
6.712
6.707
3.871
3.706
S
F
O
2.39
3.53
1.98
2.00
3.02
f1 (ppm)

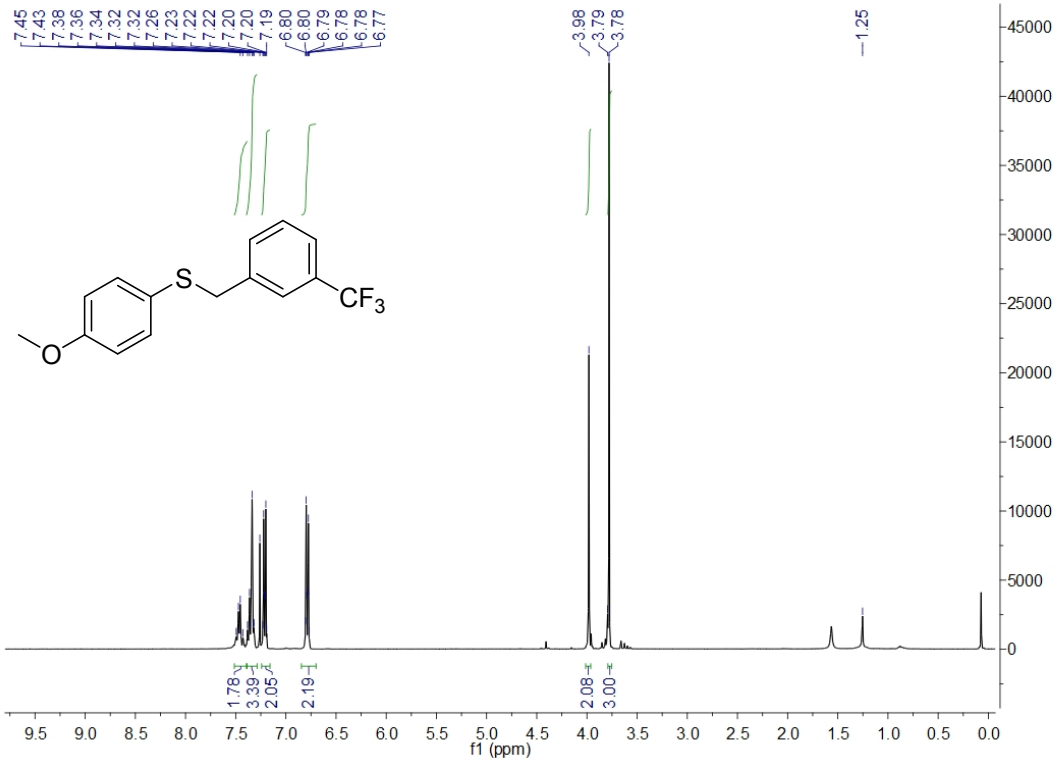
3f ^{13}C NMR



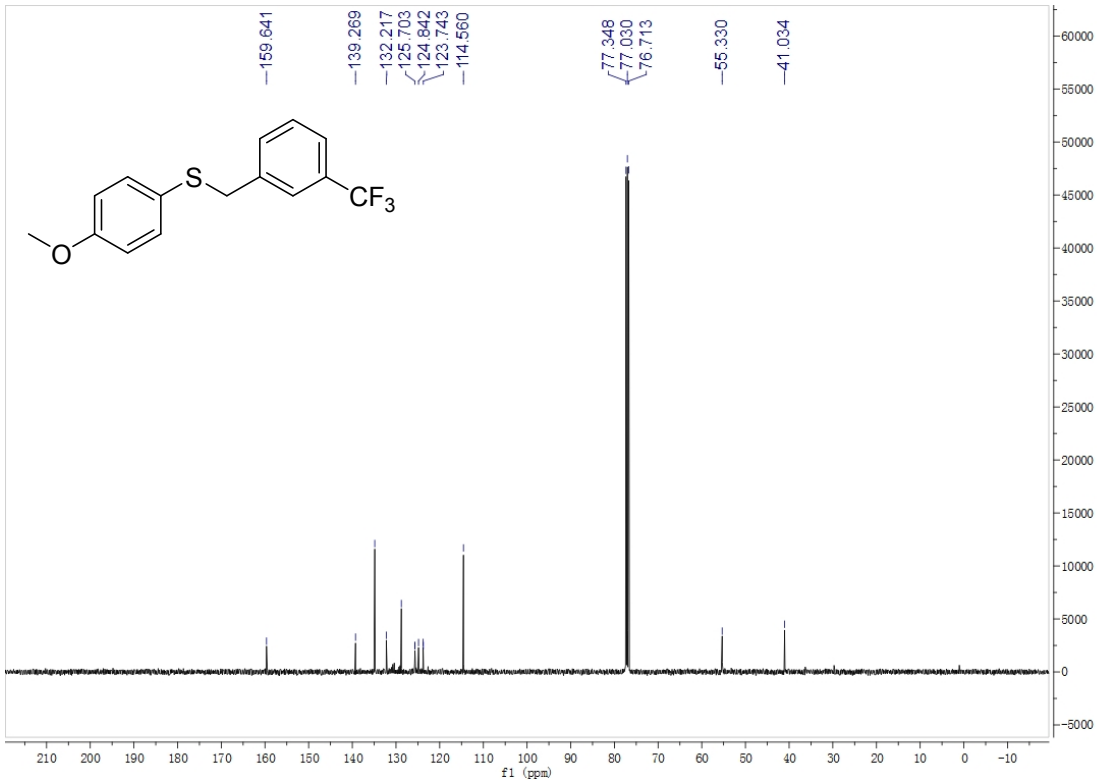
3f ^{19}F NMR



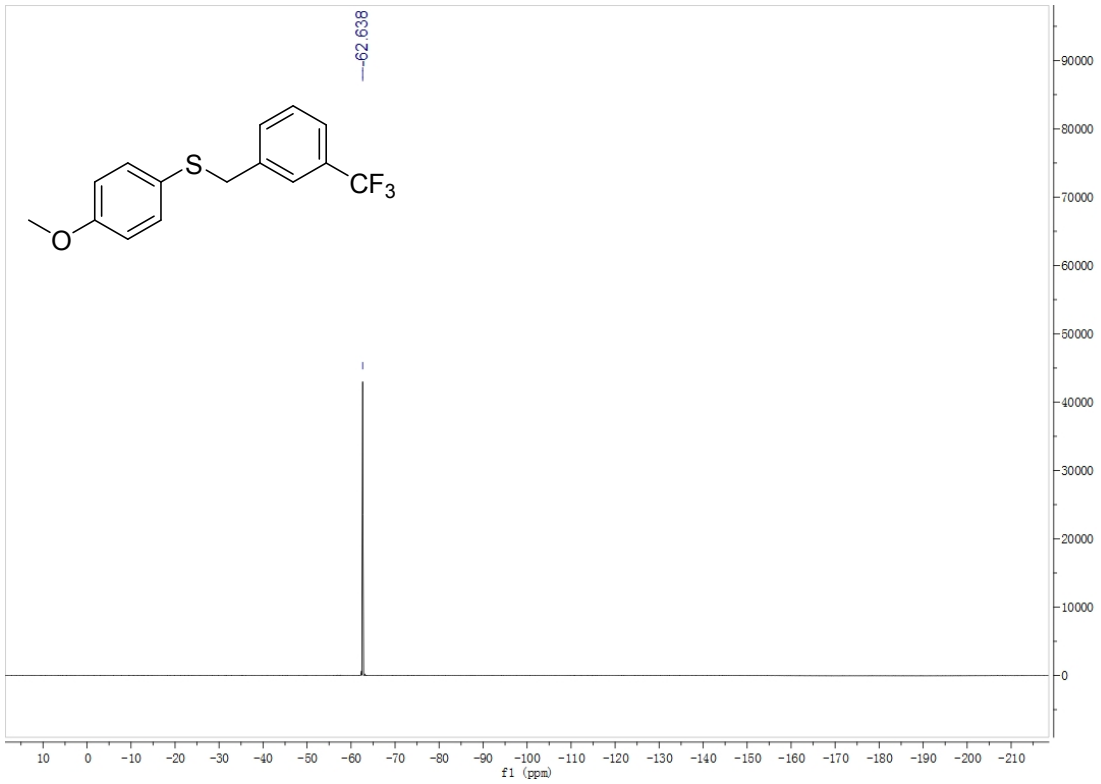
3g ^{1}H NMR



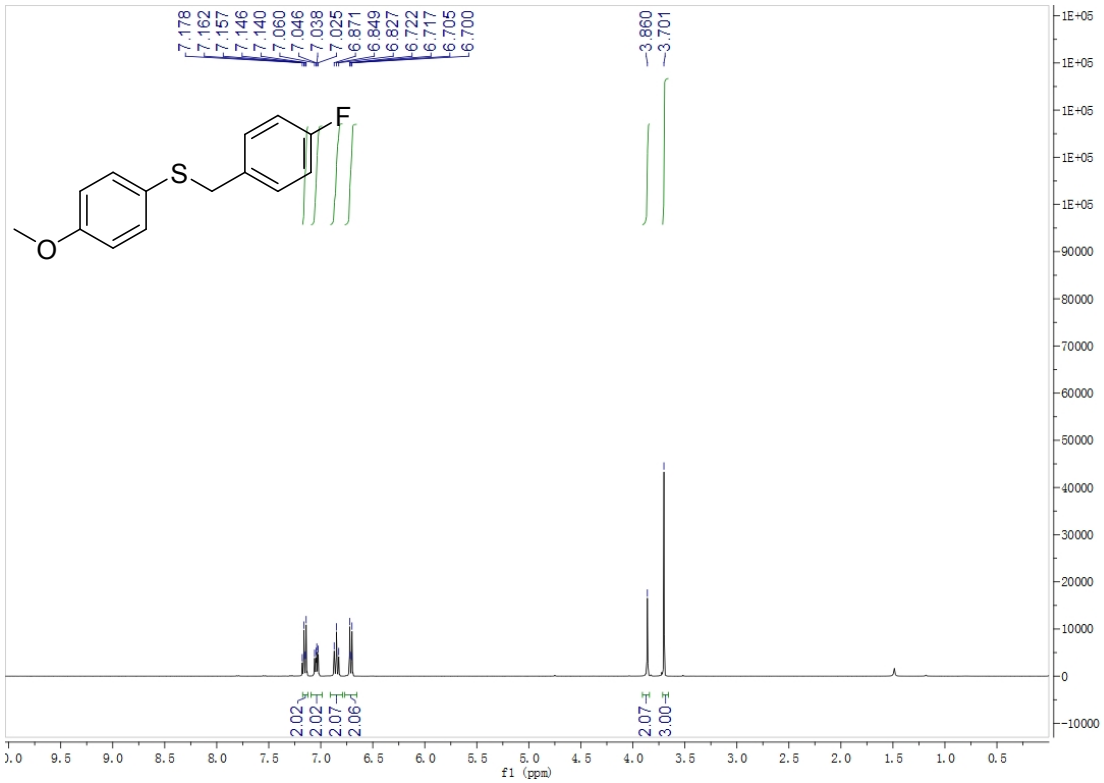
3g ^{13}C NMR



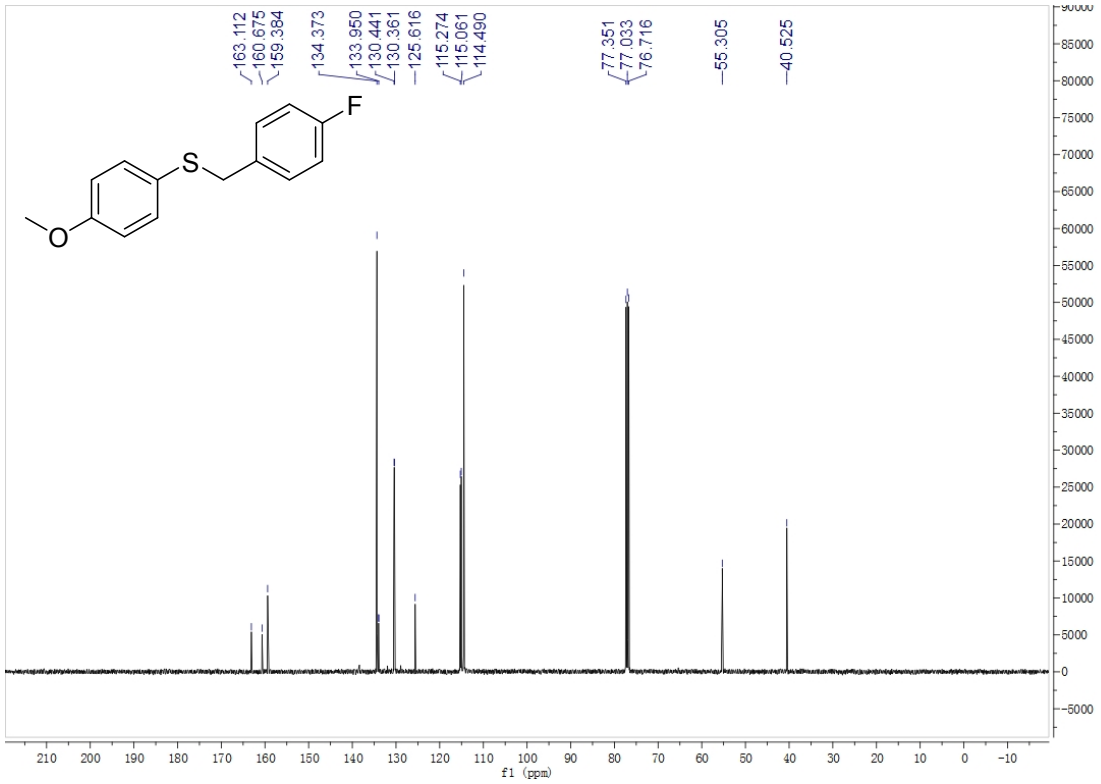
3g ^{19}F NMR



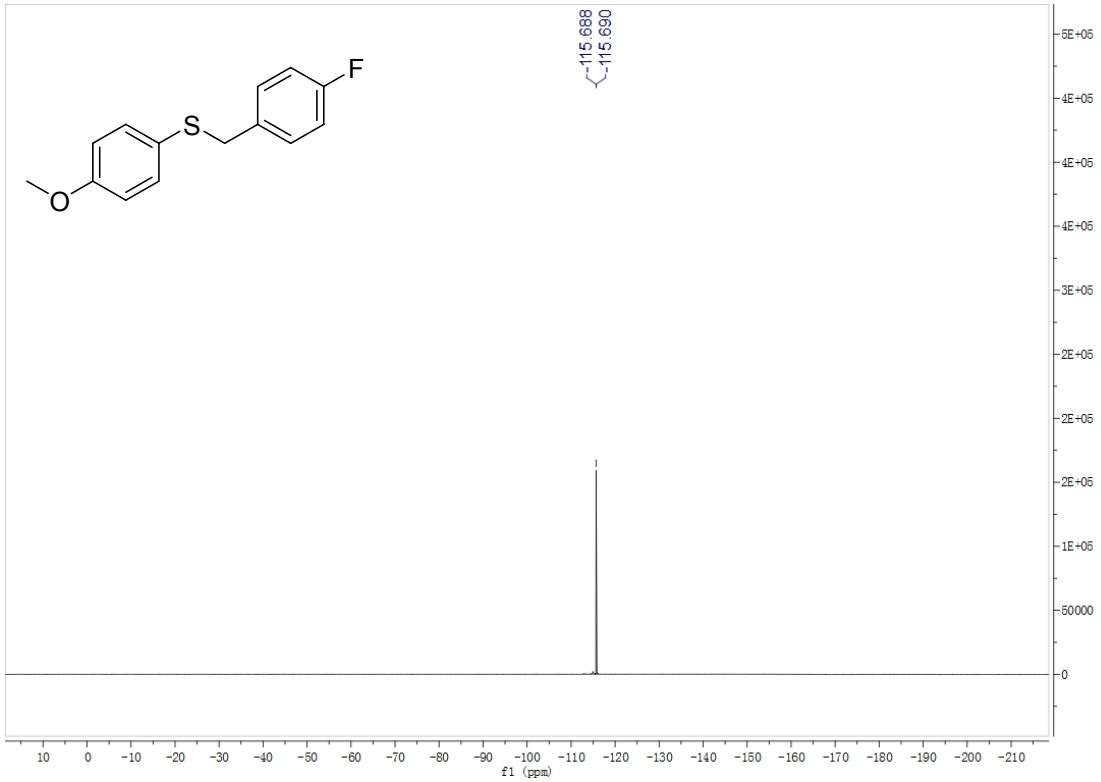
3h ^{1}H NMR



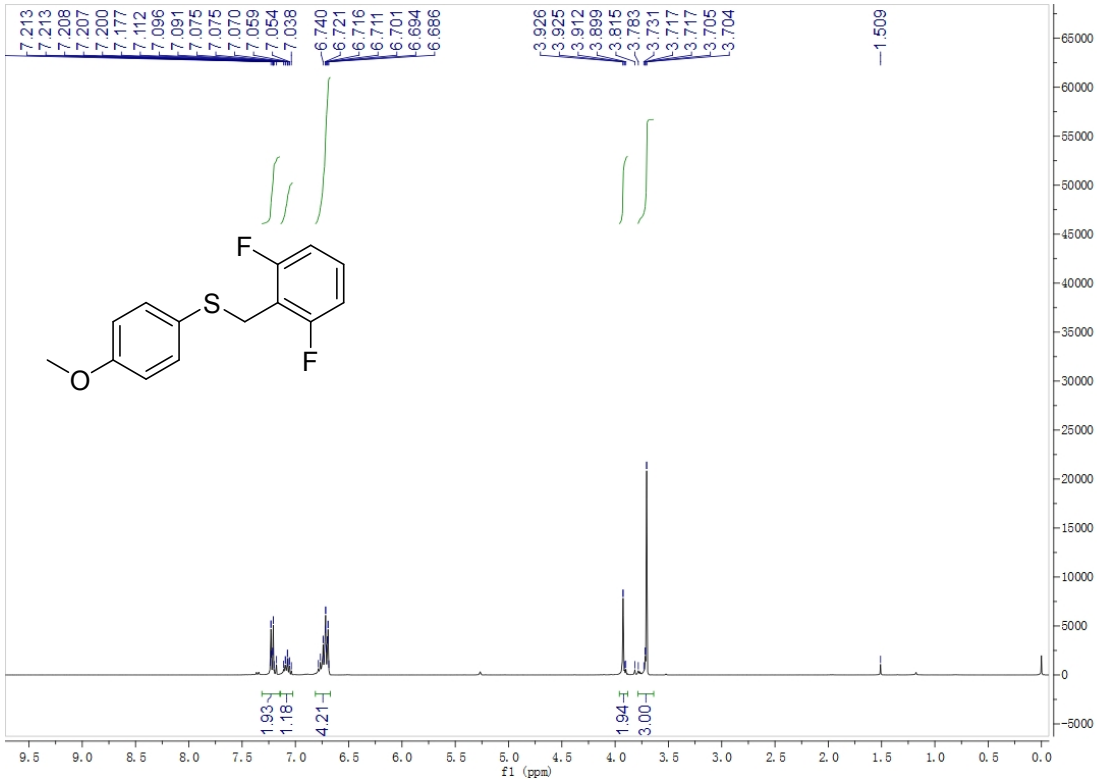
3h ^{13}C NMR


163.112
160.675
159.384
134.373
133.950
130.441
130.361
125.616
115.274
115.061
114.490
77.351
77.033
76.716
55.305
40.525
F
S
O
f1 (ppm)

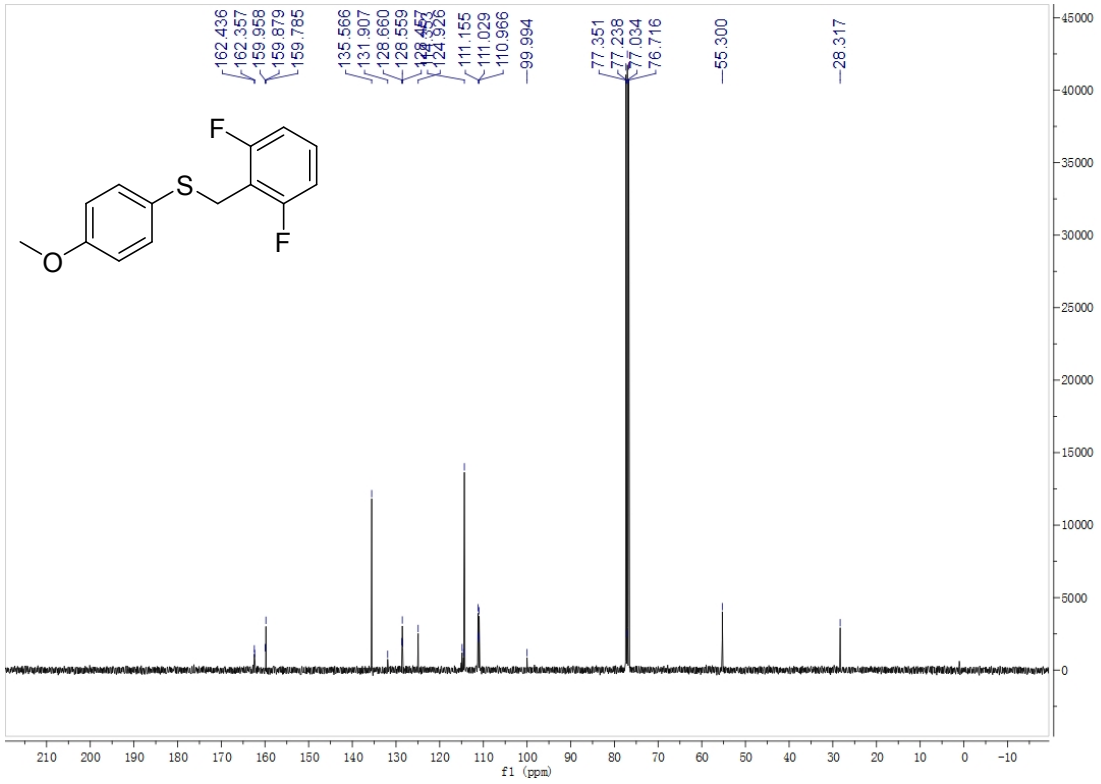
3h ^{19}F NMR



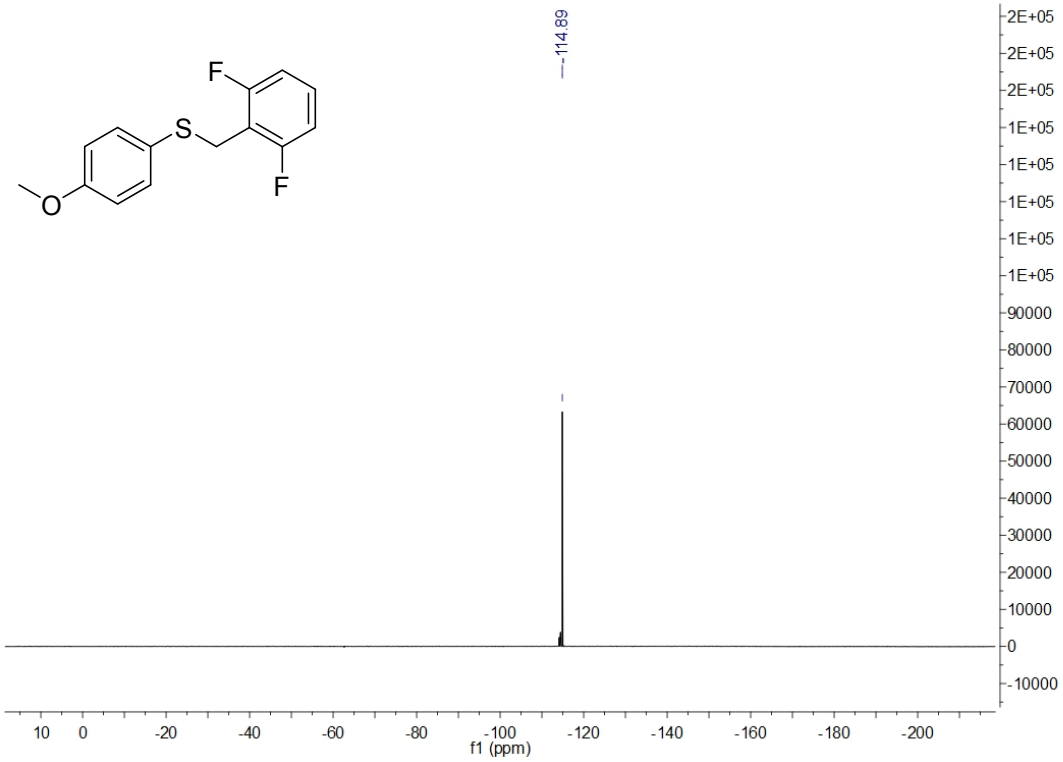
3i ^{1}H NMR



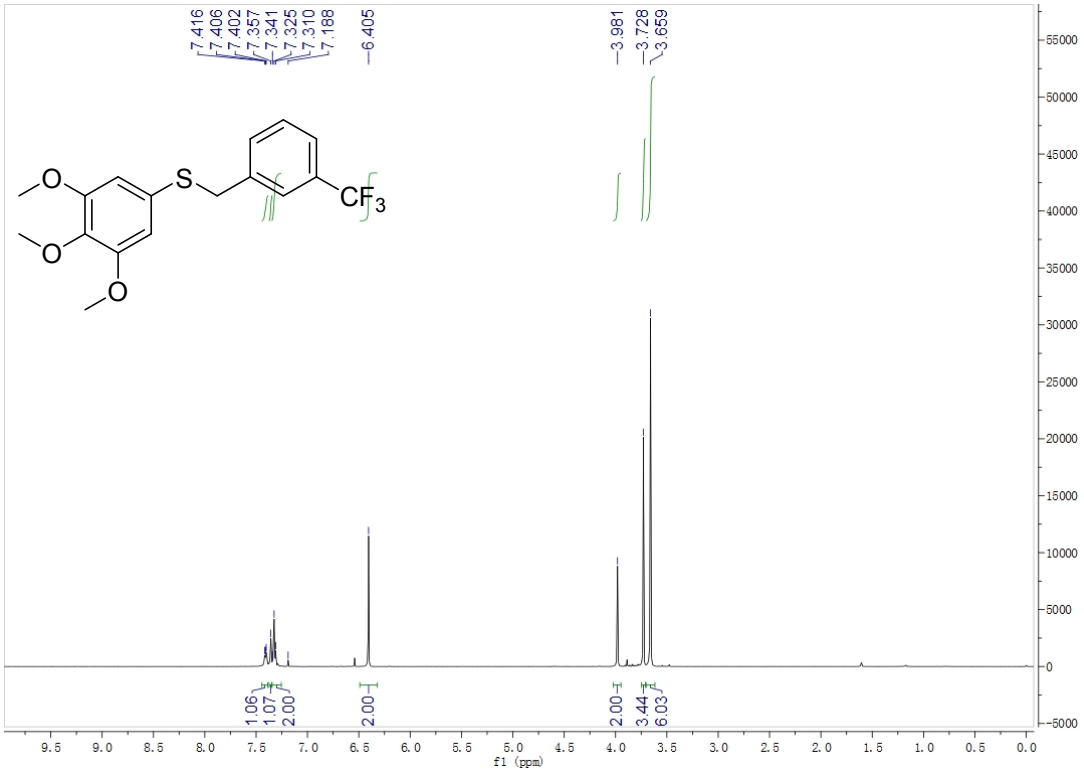
3i ^{13}C NMR



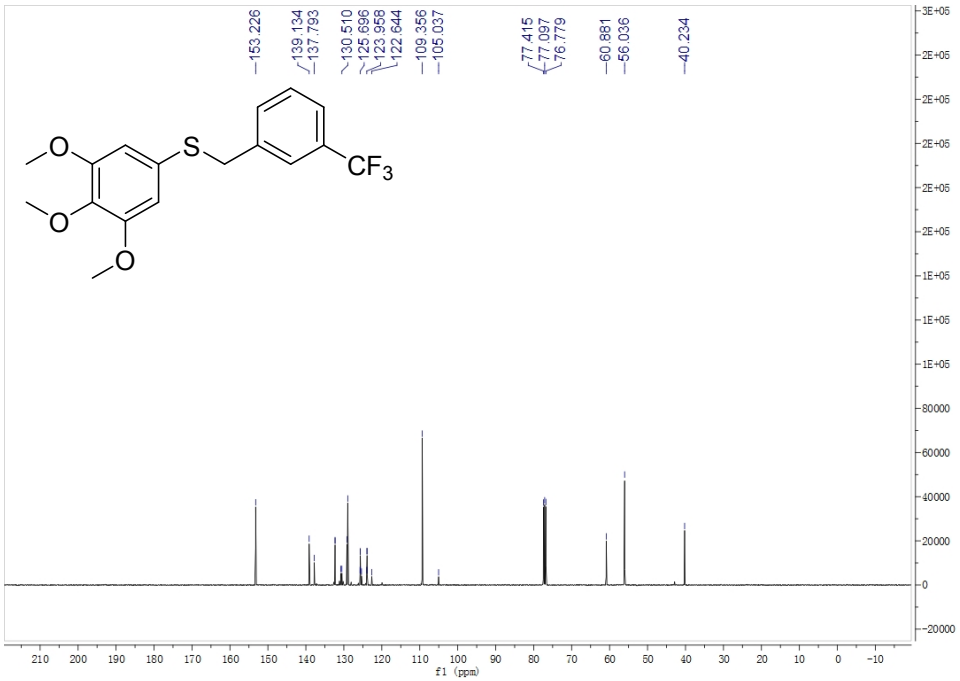
3i ^{19}F NMR



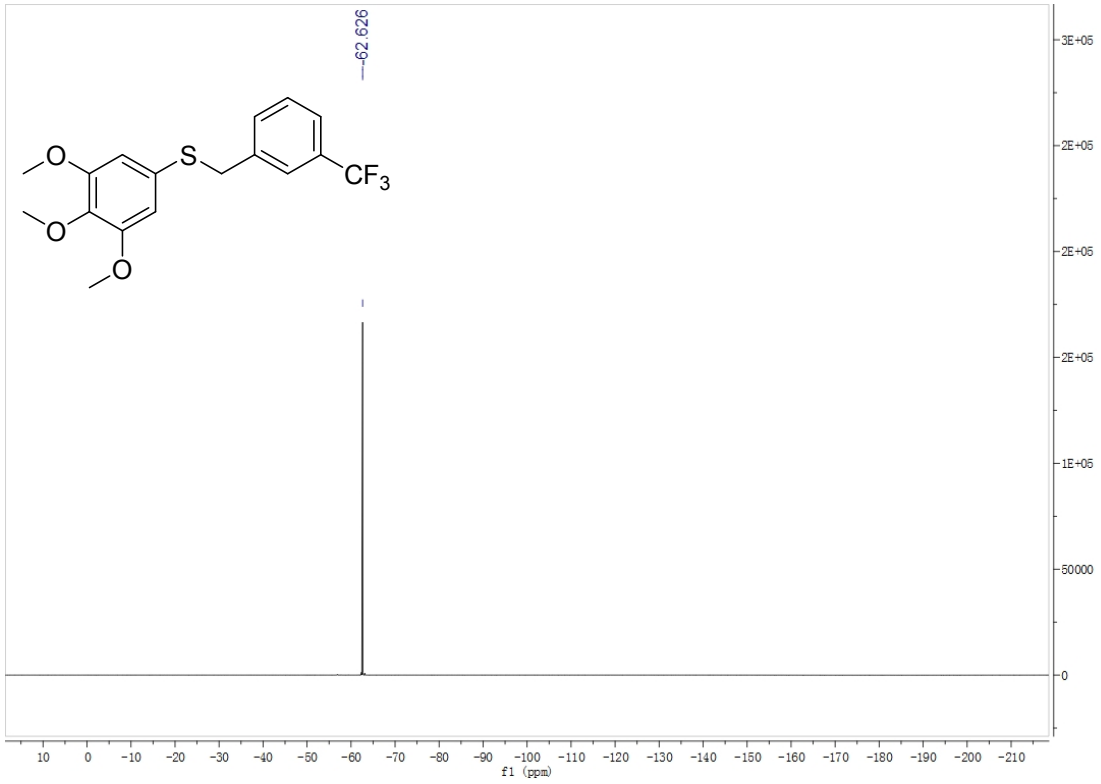
3j ^{1}H NMR



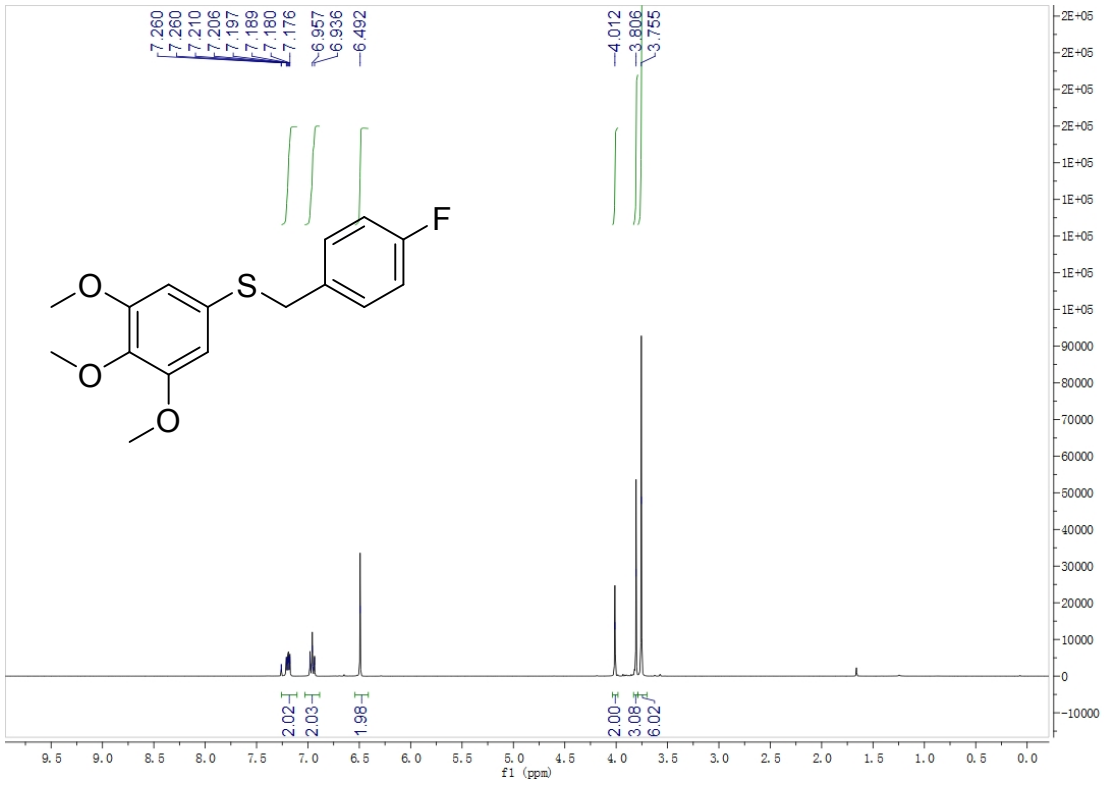
3j ^{13}C NMR



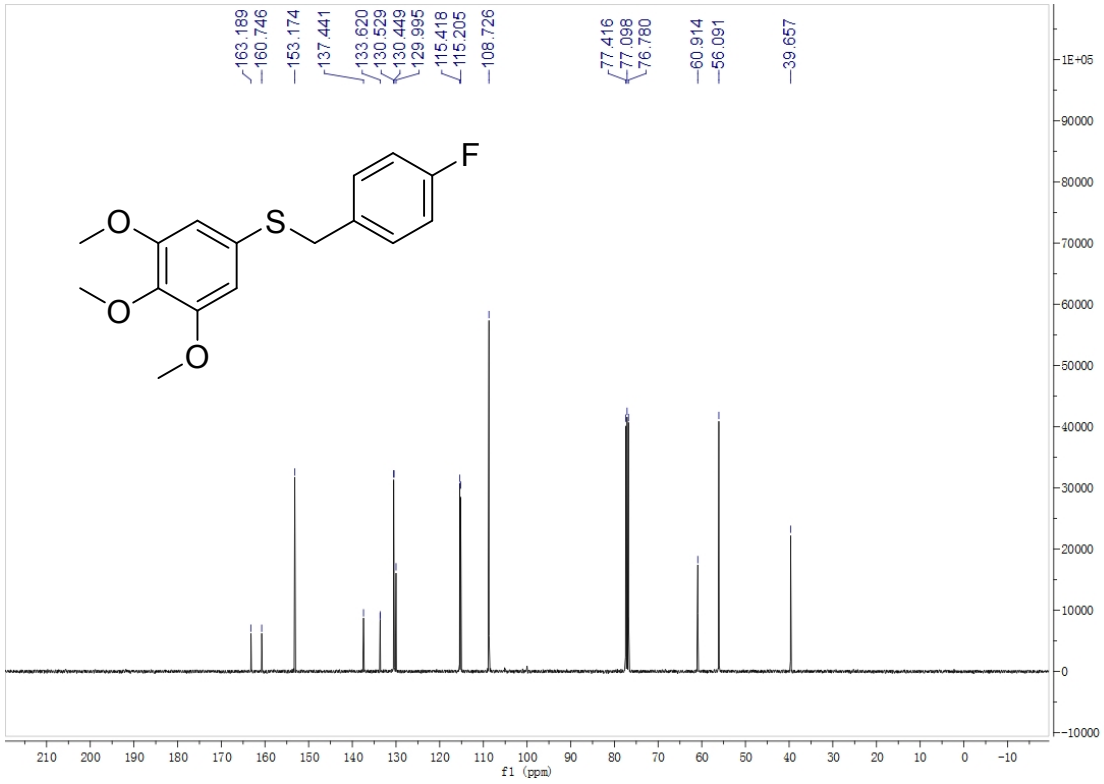
3j ^{19}F NMR



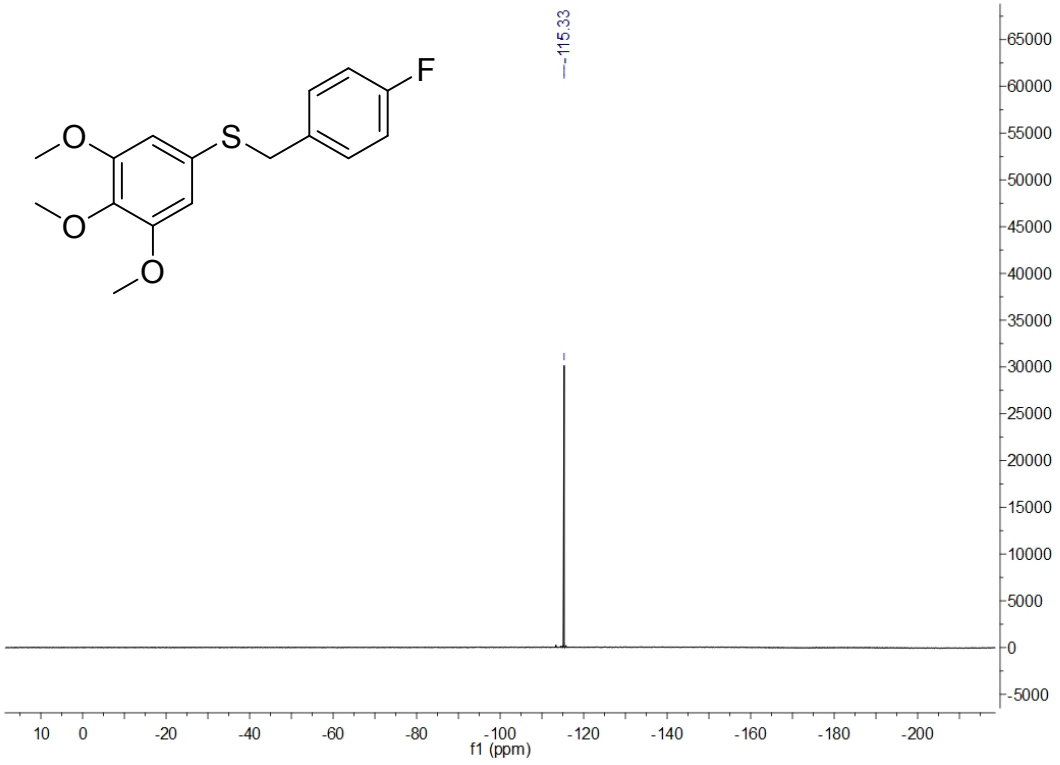
3k ^{1}H NMR



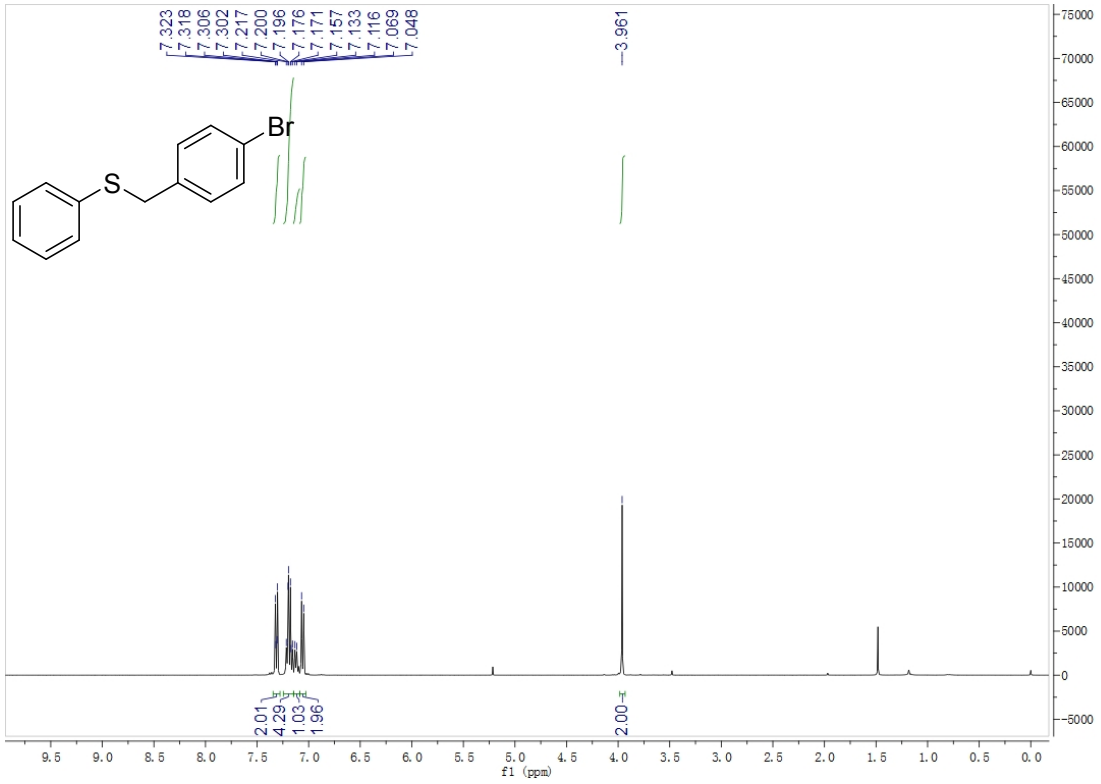
3k ^{13}C NMR



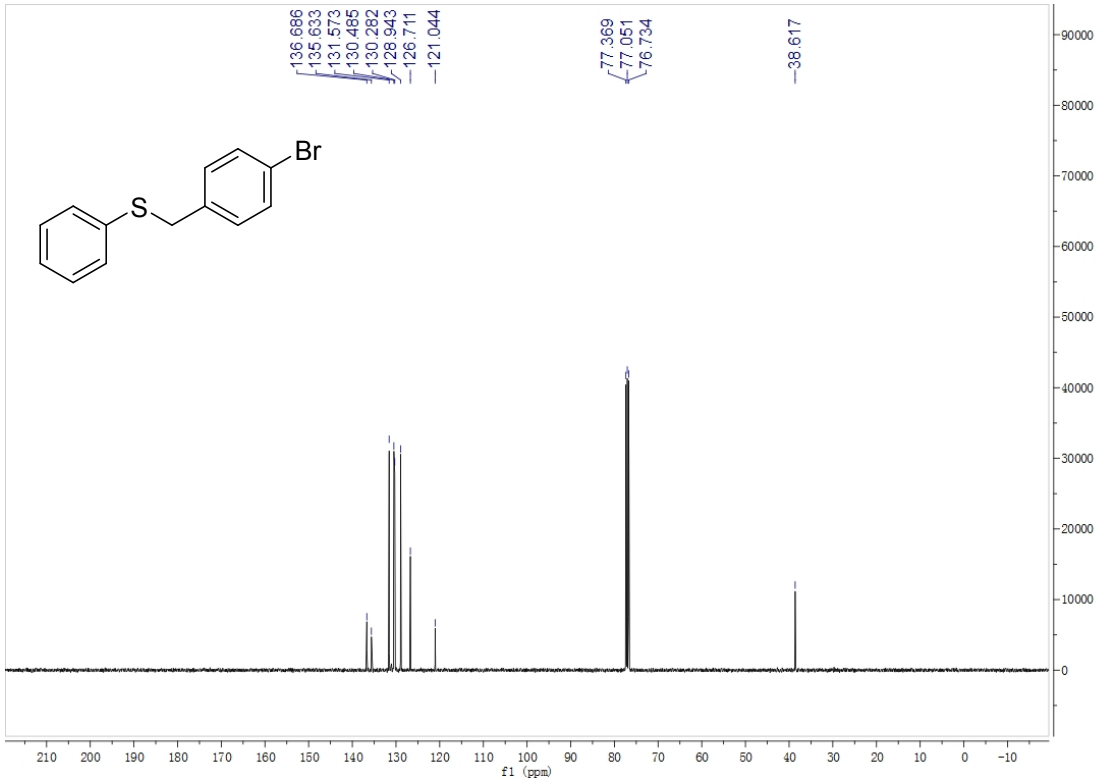
3k ^{19}F NMR



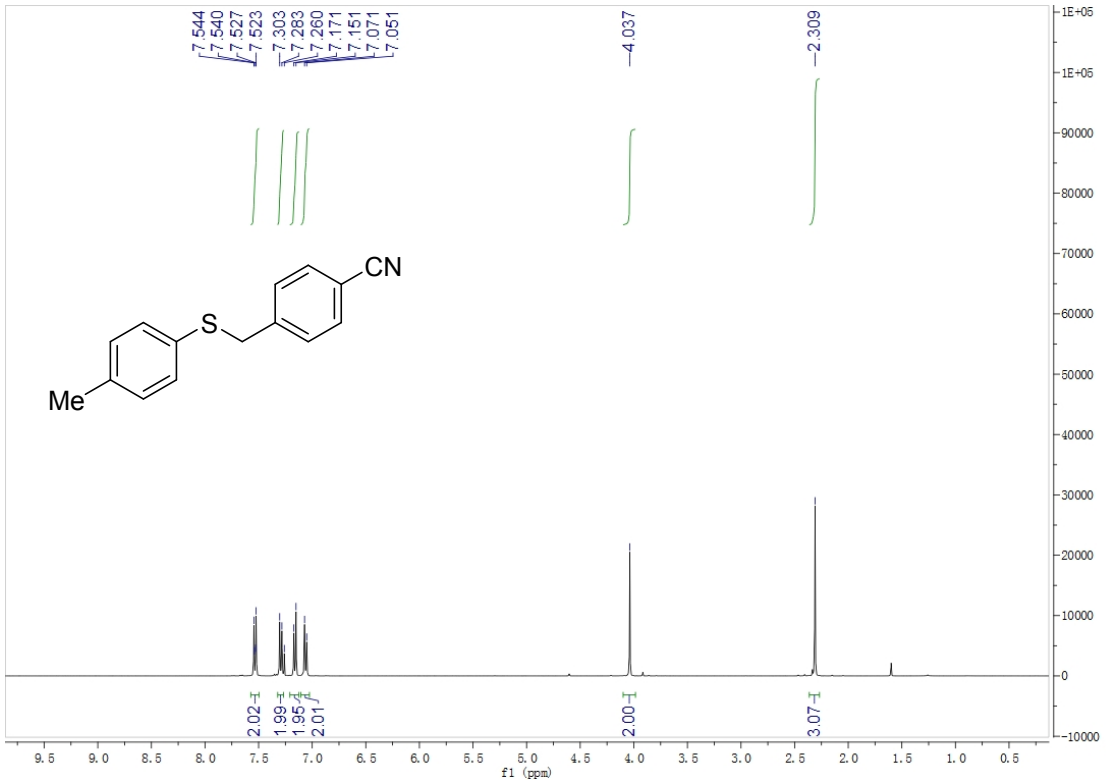
3l ^{1}H NMR



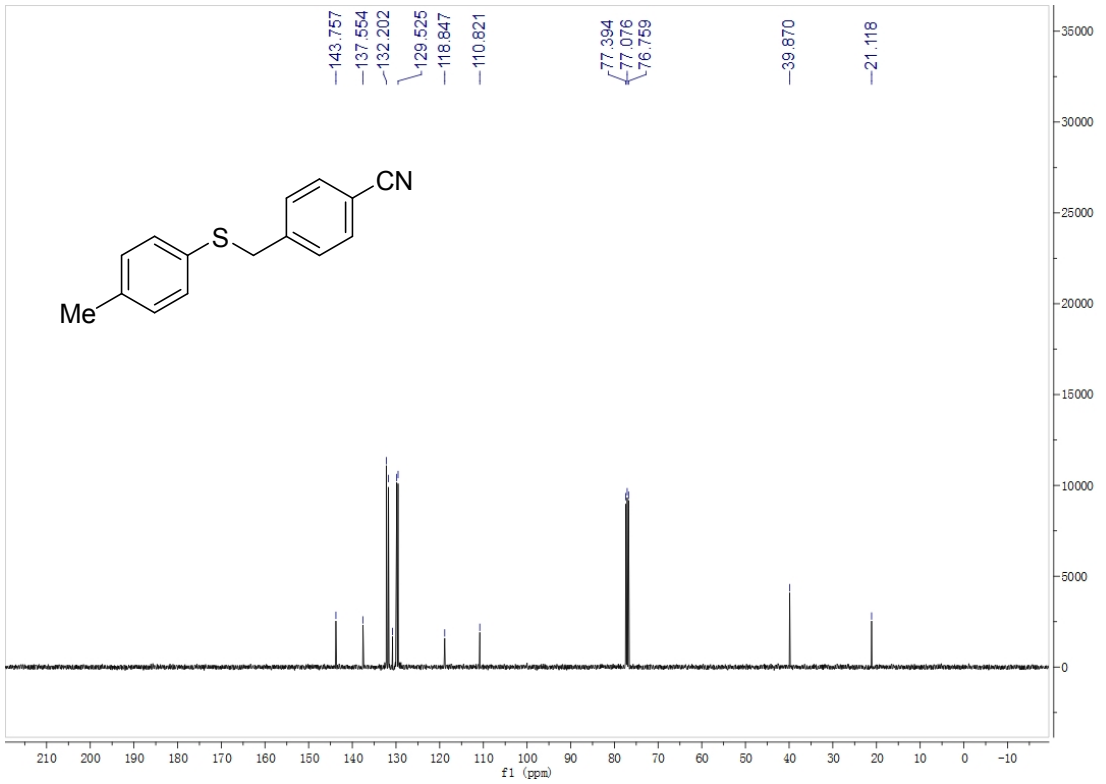
3l ^{13}C NMR



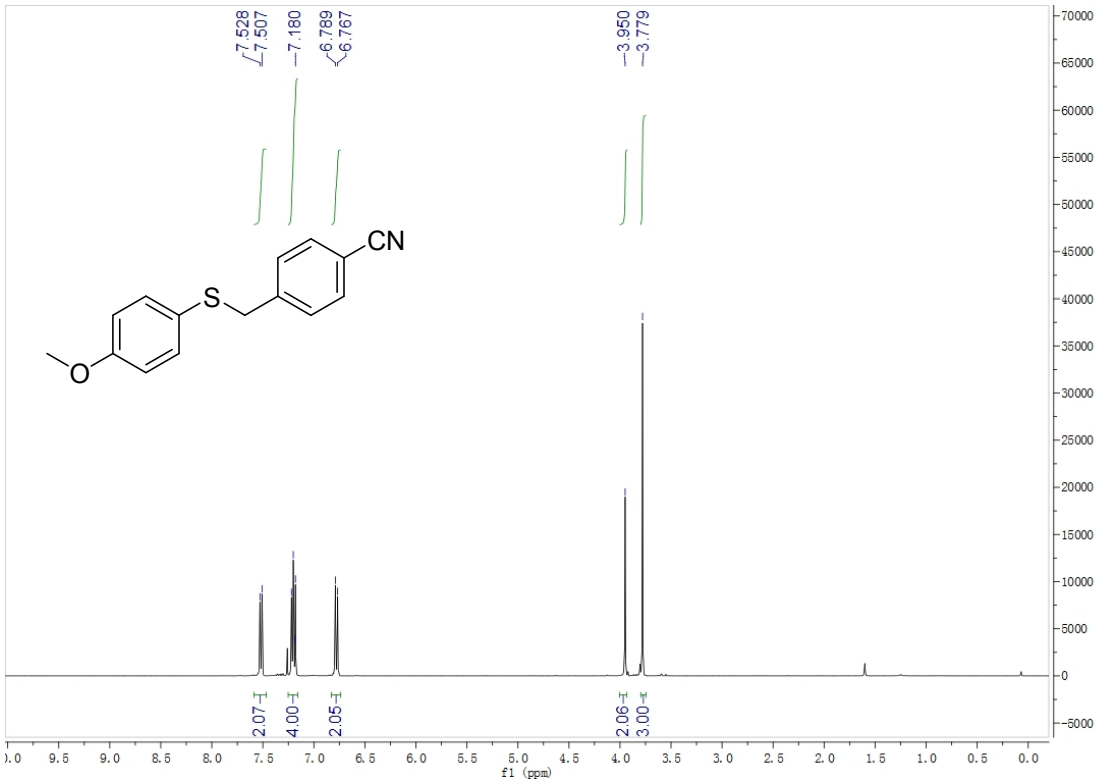
3m ^{1}H NMR



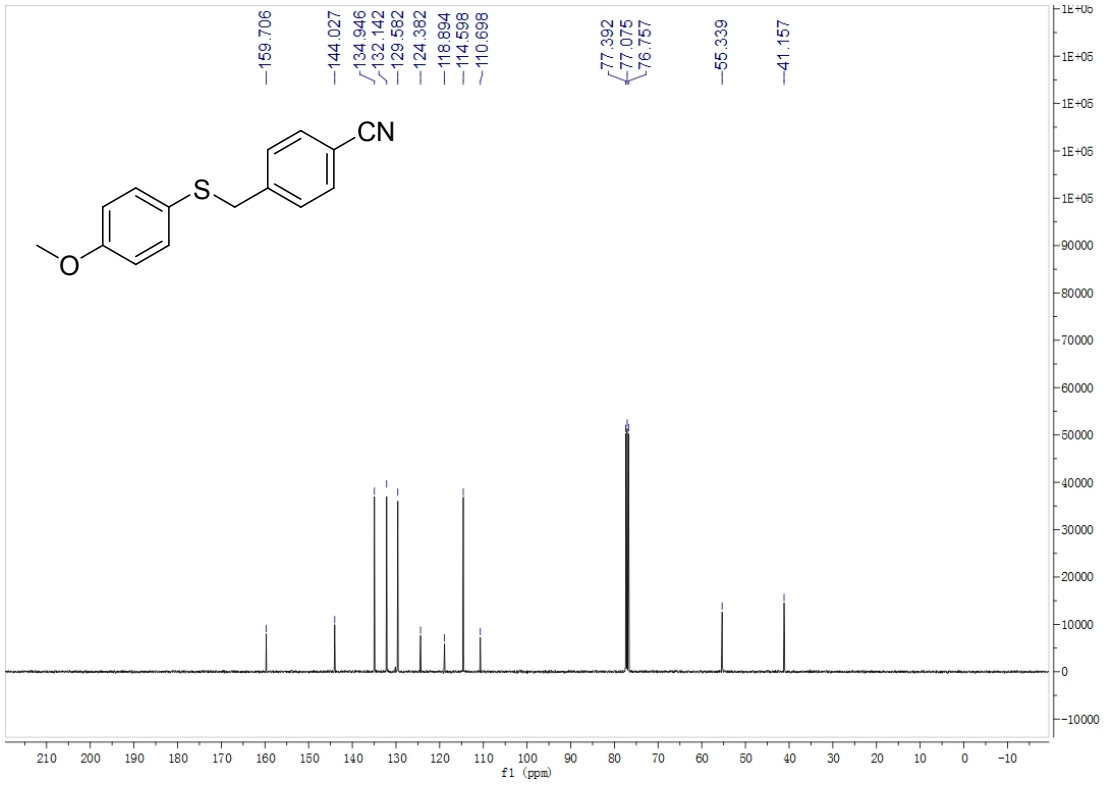
3m ^{13}C NMR



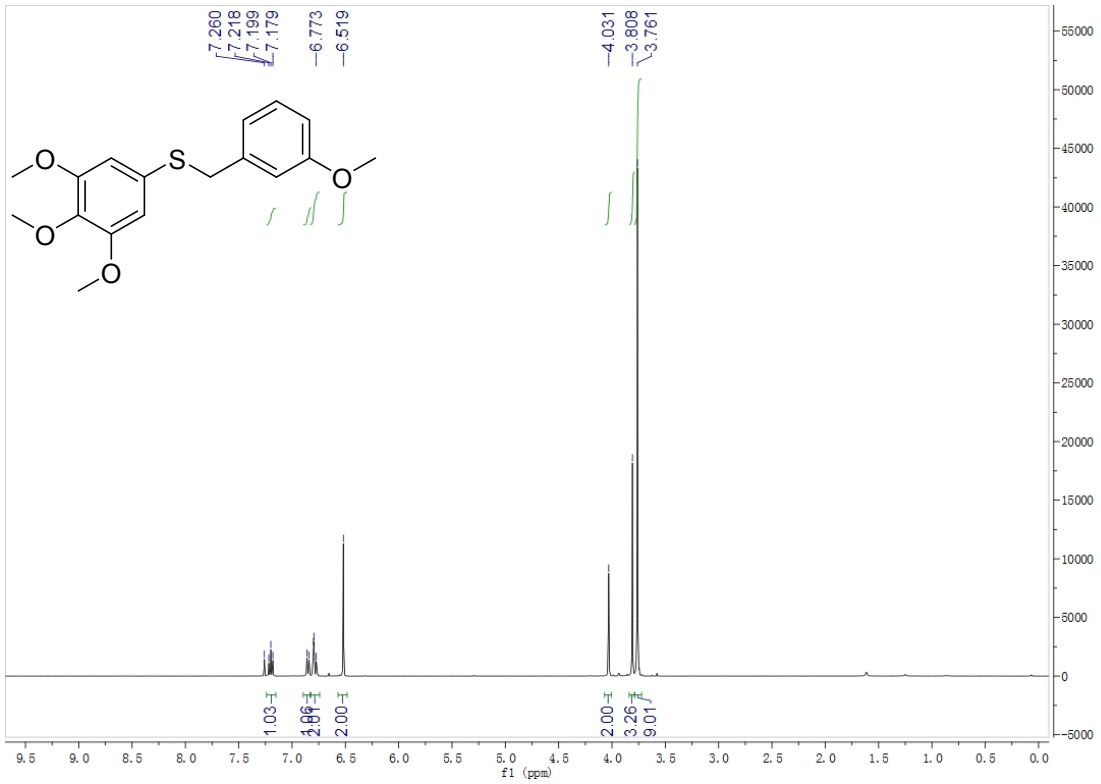
3n ^{1}H NMR



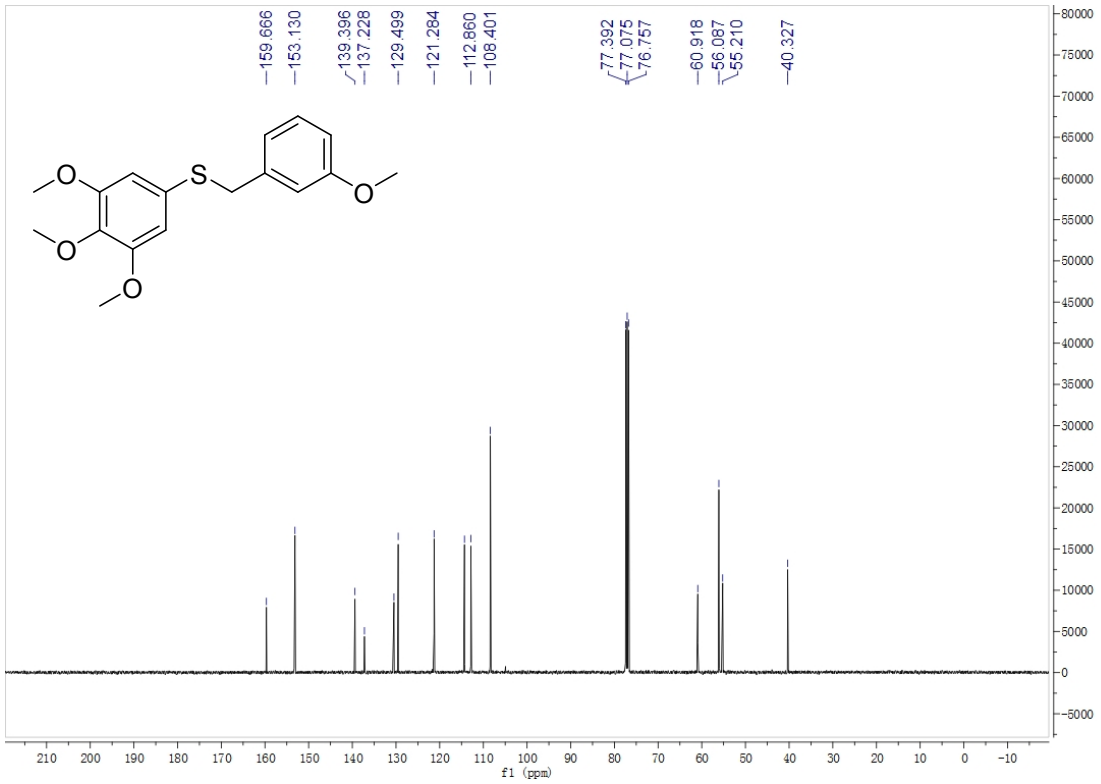
3n ^{13}C NMR



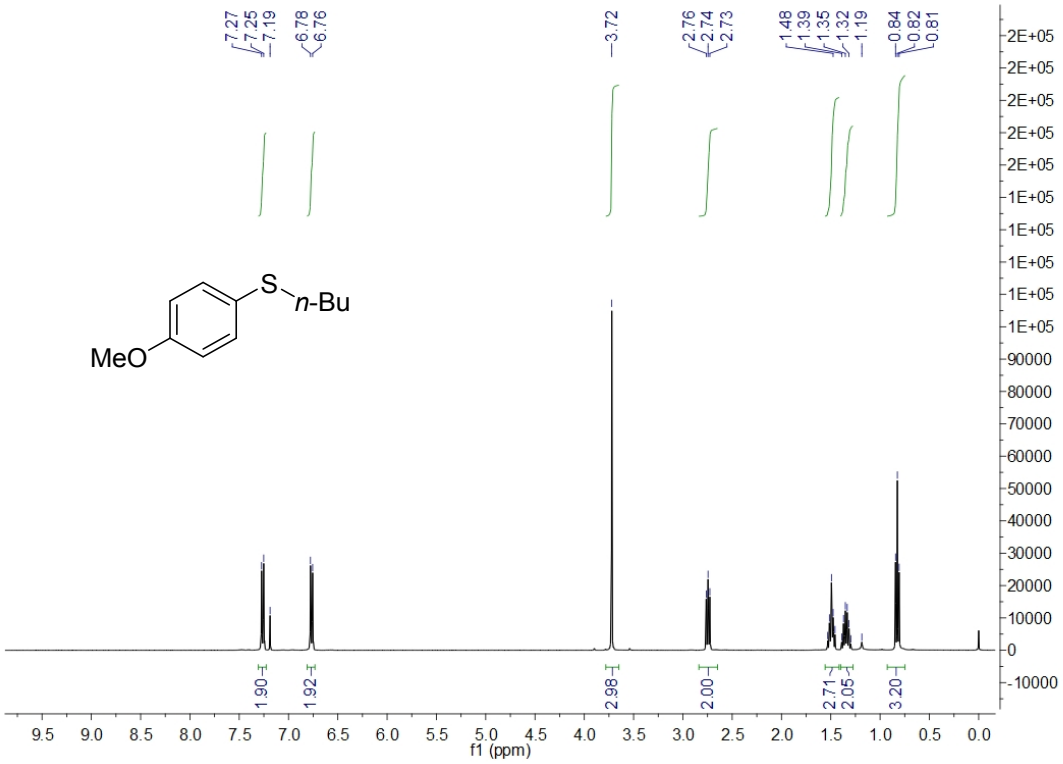
3o ^{1}H NMR



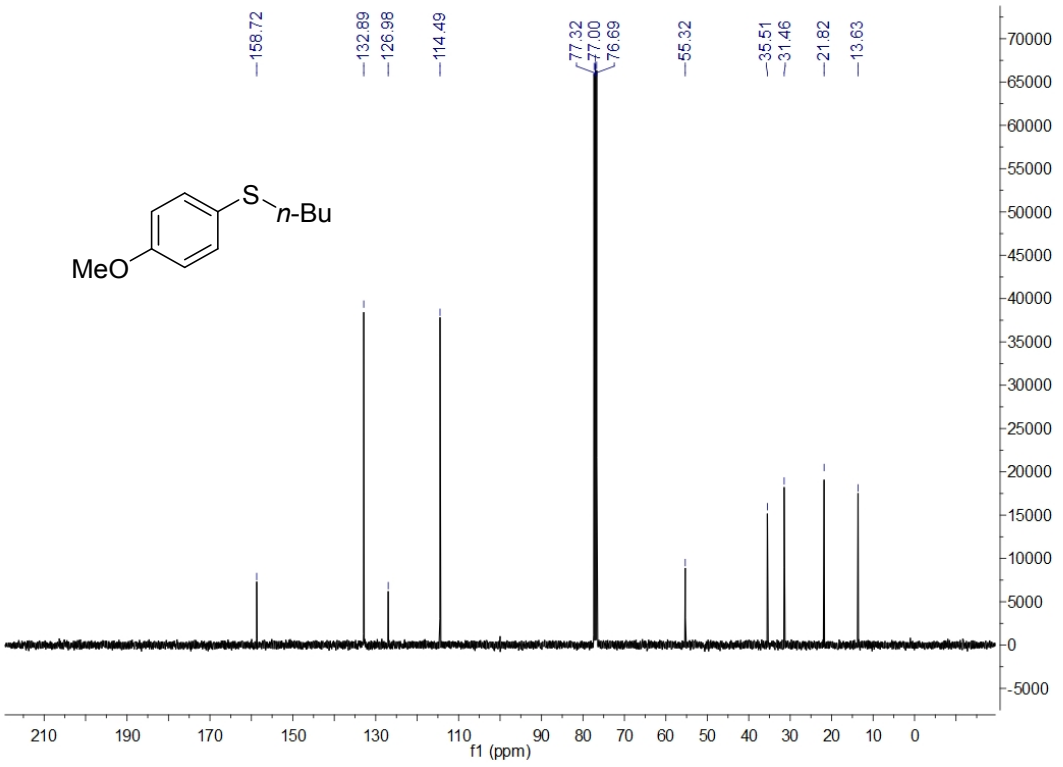
3o ^{13}C NMR



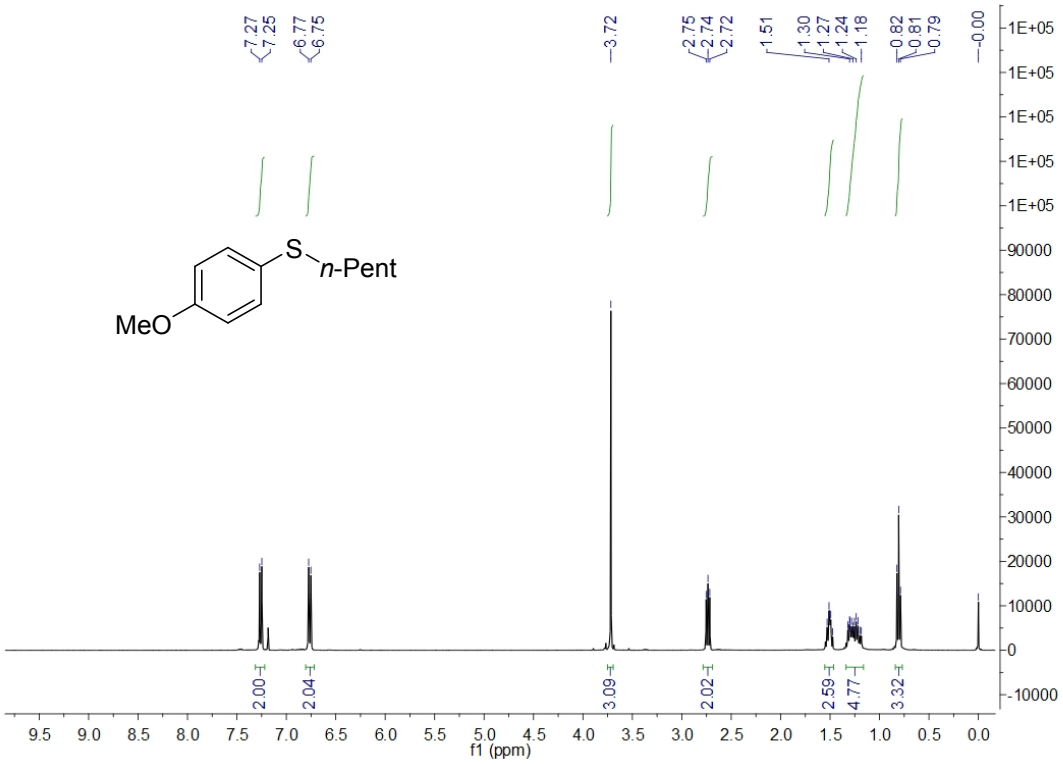
3p ^{1}H NMR



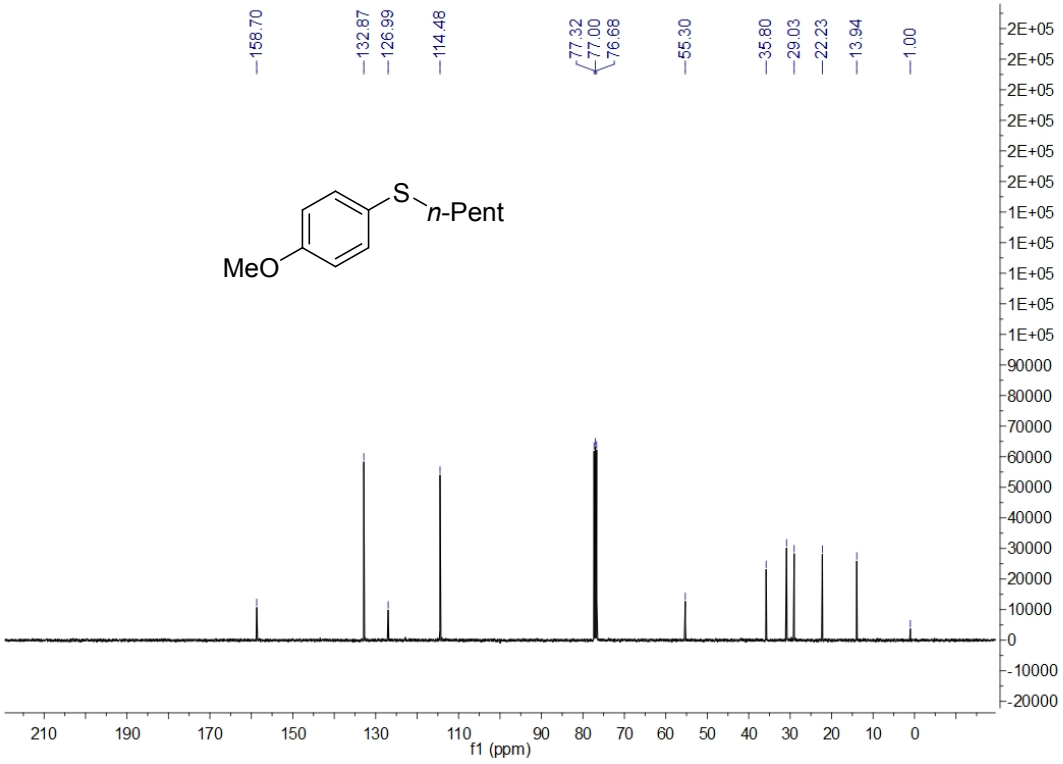
3p ^{13}C NMR



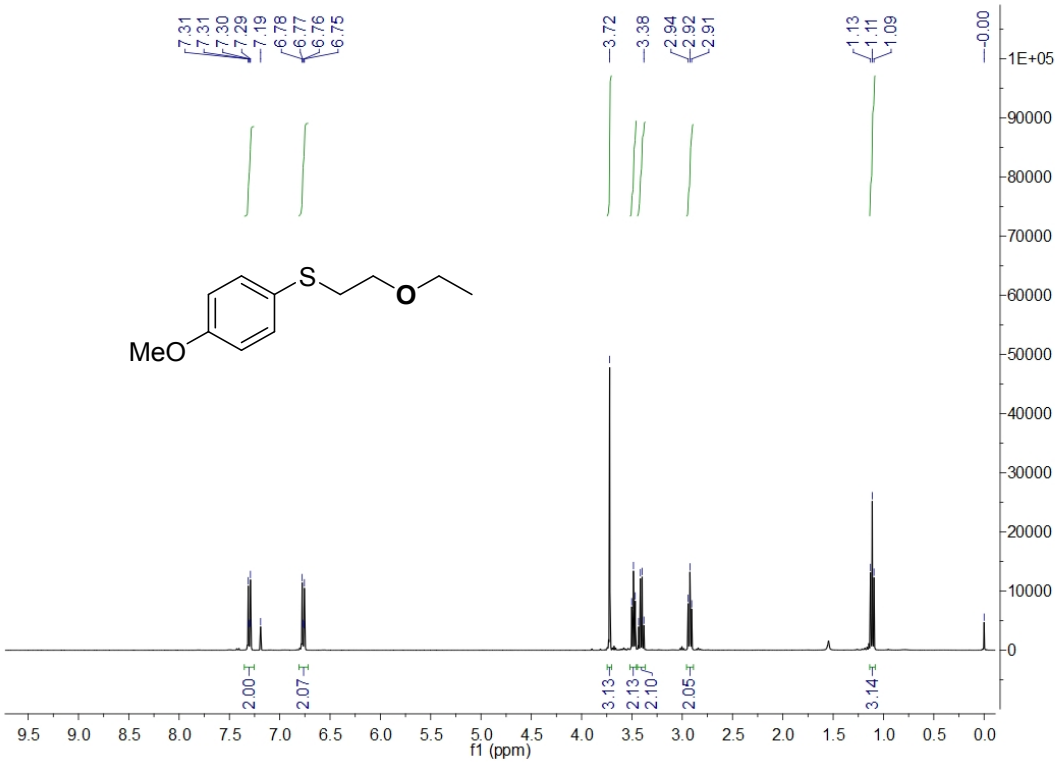
3q ^{1}H NMR



3q ^{13}C NMR



3r ^{1}H NMR



3r ^{13}C NMR