Assembly of (Hetero)aryl Thioethers via Simple Nucleophilic Aromatic Substitution and Cu-Catalyzed Coupling Reaction with (Hetero)aryl Chlorides and Bromides under Mild Conditions

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Supporting Information

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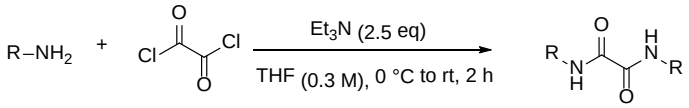
1. General information and materials

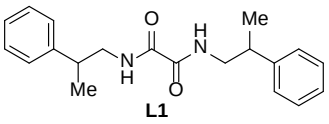
Reagent: All the reactions were carried out under inert atmosphere. All the solvents used for the reactions were dried according to standard procedures. All glassware was oven dried before use. All commercial materials were used as received unless otherwise noted. CuCl (99.999%, Aladdin), Cu_2O (99.9%, Alfa), *t*-BuOK (>97.0%(T),TCI), K_2CO_3 (>99.0%(T), TCI) were used. Anhydrous DMAc, DMF, DMSO, MeCN and dioxane were purchased from J&K. All the reactions were monitored by thin layer chromatography (TLC, Silica gel Merck 60 F_{254}); The spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel (particle size 40-63 μm, 230-400 mesh SiliaFlash® P60 (Silicycle Inc.)).

Instruments: NMR spectra were recorded on Bruker Ultrashield™ 400 MHz or Agilent 500 MHz. For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), t (triplet), td (triple doublet), q (quartet), m (multiplet), as well as br (broad); High resolution ESI mass experiments were operated on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument.

2. General procedure for the preparation of ligands

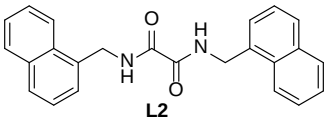


In an oven-dried round-bottom flask was charged with corresponding amine (2.0 eq.) in THF (0.3 M) was added Et_3N (2.5 eq.), oxalyl chloride (1.0 eq.) was then added to the solution slowly at 0 ^oC. After the resulting mixture was stirred at room temperature for 2 h, it was concentrated in vacuo to remove the solvent. Water was added to the resulting residue to dissolve $Et_3N{\cdot}HCl$ salt. The slurry was filtered and the solid on filter paper was washed with water and cold diethyl ether or methanol 2-3 times. These solids were dried in vacuo to afford the corresponding oxalamide. It was pure enough to be used.



L1

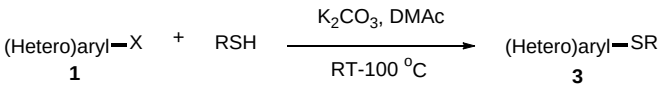
L1 was prepared from 1-phenylpropan-2-amine and oxalyl chloride as white solid in 84% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (t, J = 6.0 Hz, 2H), 7.33–7.25 (m, 4H), 7.21 (d, J = 7.9 Hz, 6H), 3.28 (h, J = 6.7, 6.3 Hz, 4H), 3.01 (h, J = 7.2 Hz, 2H), 1.15 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.3, 144.8, 128.8, 127.5, 126.8, 46.1, 39.1, 19.7; HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}N_2O_2$ [M + H]$^+$ 325.4240 found 325.4239.



L2

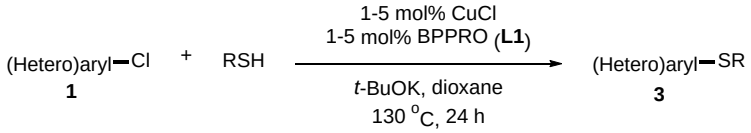
L2 was prepared from naphthalen-1-ylmethanamine and oxalyl chloride as white solid in 91% yield. ^{1}H NMR (500 MHz, DMSO-*d6*) δ 9.39 (t, J = 5.8 Hz, 2H), 8.17 (d, J = 7.8 Hz, 2H), 7.93 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.53 (p, J = 6.4 Hz, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.40 (d, J = 6.9 Hz, 2H), 4.80 (d, J = 6.2 Hz, 4H); ^{13}C NMR (126 MHz, DMSO-*d6*) δ 160.6, 134.2, 133.7, 131.2, 129.0, 128.1, 126.7, 126.3, 125.9, 125.8, 123.9, 40.9.[1]

3. General procedure for the (hetero)aryl thioethers formation

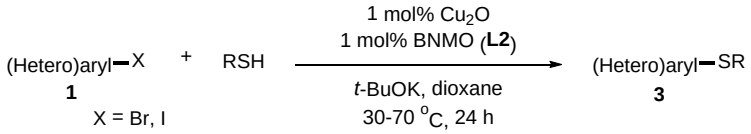


The (hetero)aryl halides (0.5 mmol), K_2CO_3 (1.0 mmol, 138.2 mg), were placed into a Schlenk tube (4 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with nitrogen three times, then thiols (1.2 mmol) and DMAc (0.5 mL) were added (in some case, 1 eq of 18-crown-6 was added) under a positive nitrogen pressure (Note: for liquid substrates, they were added slowly after the tube was backfilled with nitrogen); The reaction mixture was heated at RT-100 °C for 12 h under vigorous stirring. The cooled solution was diluted with ethyl acetate and washed with brine. The organic phase was dried over Na_2SO_4 and concentrated in

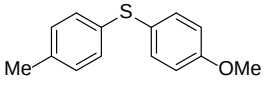
vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding (hetero)aryl thioethers.



The (hetero)aryl chlorides (1.0 mmol), *t*-BuOK (2.0 mmol, 224.4 g), **L1** (0.01 -0.05mmol, 3.55-17.75 mg) and CuCl (0.01-0.05 mmol, 1.0-4.95 mg) were placed into a Schlenk tube (10.0 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with nitrogen three times, then thiols (1.5 mmol) and Dioxane (5.0 mL) were added under a positive nitrogen pressure (Note: for liquid substrates, they were added after the tube was backfilled with nitrogen); The reaction mixture was heated at 130 °C for 24 h under vigorous stirring. The cooled solution was diluted with ethyl acetate and washed with brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding (hetero)aryl thioethers.

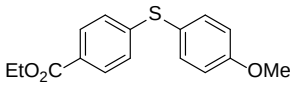


The (hetero)aryl halides (1.0 mmol), *t*-BuOK (1.7 mmol, 190.7 mg), ligand **L2** (0.01 mmol, 4.0 mg), Cu_2O (0.01 mmol, 1.43 mg) were placed into a Schlenk tube (8 mL) with a magnetic stir bar. The reaction vessel was evacuated and backfilled with nitrogen three times, then thiols (1.2 mmol) and Dioxane (1.0 mL) were added under a positive nitrogen pressure (Note: for liquid substrates, they were added after the tube was backfilled with nitrogen); The reaction mixture was heated at 30-70 °C for 24 h under vigorous stirring. The cooled solution was diluted with ethyl acetate and washed with brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford the corresponding product.



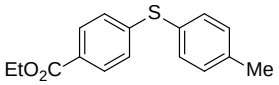
3a

3a: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 136.1, 134.4, 129.8, 129.4, 125.7, 114.9, 55.4, 21.0.[2]



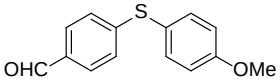
3b

3b: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 160.6, 146.2, 136.7, 129.9, 127.0, 125.8, 121.6, 115.3, 60.9, 55.4, 14.3.[3]



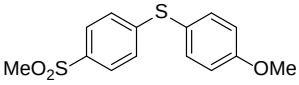
3c

3c: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 145.2, 139.2, 134.3, 130.5, 130.0, 128.3, 127.4, 126.7, 60.9, 21.3, 14.3.[4]



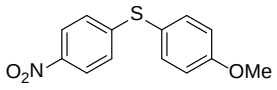
3d

3d: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 160.9, 149.1, 137.1, 133.2, 130.1, 125.8, 120.7, 115.5, 55.4.[5]



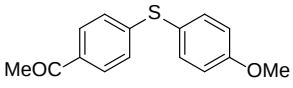
3e

3e: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 161.0, 148.4, 137.1, 136.6, 127.7, 126.1, 120.5, 115.6, 55.5, 44.7; HRMS (ESI) *m/z* calcd. for $C_{14}H_{14}O_3S_2$ $[M + Na]^+$ 317.0384 found 317.0277.



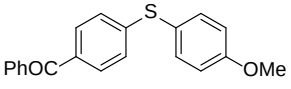
3f

3f: light yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 9.1 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 9.1 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 150.1, 145.0, 137.2, 125.5, 124.0, 120.1, 115.7, 55.5.[6]



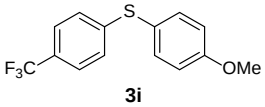
3g

3g: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 160.7, 146.9, 136.8, 133.8, 128.8, 125.7, 121.3, 115.4, 55.4, 26.4.[7]



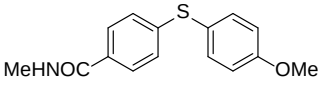
3h

3h: pale red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8, 160.7, 146.3, 137.8, 136.9, 134.1, 132.2, 130.7, 129.9, 128.3, 125.7, 121.5, 115.4, 55.5.[8]



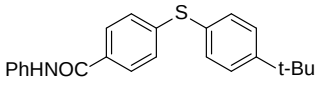
3i

3i: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 144.8, 136.7, 127.1 (q, *J* = 32.6 Hz), 126.3, 125.6 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271.7 Hz), 121.6, 115.4, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 (s).[9]



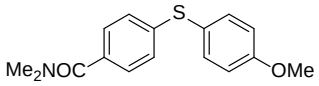
3j

3j: white solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.36 (d, J = 4.4 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 2.74 (d, J = 4.5 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.4, 160.6, 142.7, 136.7, 132.1, 128.3, 126.5, 121.7, 116.0, 55.8, 26.7; HRMS (EI) *m/z* calcd. for $C_{15}H_{15}NO_2S$ $[M]^+$ 273.0823 found 273.0822.



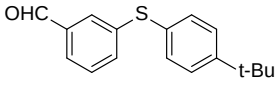
3k

3k: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.42 (s, 4H), 7.36 (t, J = 8.0 Hz, 2H), 7.25 (d, J = 9.4 Hz, 2H), 7.14 (t, J = 7.9 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 152.2, 143.7, 137.9, 133.6, 131.8, 129.1, 128.7, 127.8, 127.6, 126.8, 124.6, 120.2, 34.8, 31.3; HRMS (ESI) *m/z* calcd. for $C_{23}H_{23}NOS$ $[M + H]^+$ 362.1500 found 362.1581.



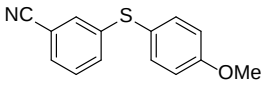
3l

3l: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.1 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 2.95 (d, J = 36.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 159.3, 140.4, 135.1, 132.1, 126.8, 125.9, 121.8, 114.17, 54.4, 38.6, 34.4; HRMS (ESI) *m/z* calcd. for $C_{16}H_{17}NO_2S$ $[M + H]^+$ 288.0980 found 288.1053.



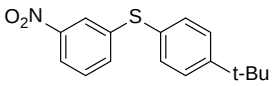
3m

3m: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.74 (t, J = 1.8 Hz, 1H), 7.68 (dt, J = 7.5, 1.4 Hz, 1H), 7.48 (dt, J = 7.8, 1.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 1.7 Hz, 4H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 151.7, 140.0, 139.5, 137.0, 134.7, 132.7, 130.0, 129.6, 127.3, 126.7, 34.7, 31.2; HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}OS$ $[M + H]^+$ 293.1078 found 293.0971.



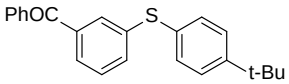
3n

3n: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.9 Hz, 2H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.33–7.27 (m, 2H), 7.25 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 142.1, 136.7, 130.9, 129.6, 129.3, 128.6, 121.2, 118.5, 115.6, 113.1, 55.4.[8]



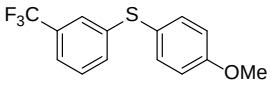
3o

3o: light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.9 Hz, 1H), 7.98 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.48–7.45 (m, 1H), 7.43 (s, 4H), 7.39 (t, *J* = 8.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 148.7, 141.3, 133.8, 133.6, 129.6, 128.2, 127.0, 122.7, 120.6, 34.8, 31.2; HRMS (EI) *m/z* calcd. for $C_{16}H_{17}NO_2S$ $[M]^+$ 287.0980 found 287.0987.



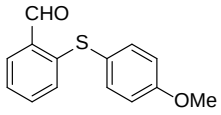
3p

3p: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.66 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 3H), 7.38 (d, *J* = 3.5 Hz, 5H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 151.4, 138.3, 138.3, 137.2, 132.9, 132.6, 132.5, 130.6, 130.1, 130.1, 129.0, 128.3, 127.8, 126.6, 34.7, 31.3; HRMS (EI) *m/z* calcd. for $C_{23}H_{22}OS$ $[M]^+$ 346.1391 found 346.1392.



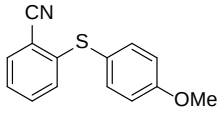
3r

3r: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.9 Hz, 2H), 7.37 (s, 1H), 7.33 (d, *J* = 5.3 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 139.8, 135.2, 130.3 (q, *J* = 32.3 Hz), 129.3 (q, *J* = 1.4 Hz), 128.2, 122.8 (q, *J* = 272.7 Hz), 122.8 (q, *J* = 3.9 Hz), 121.3, 121.1 (q, *J* = 3.8 Hz), 114.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s).[10]



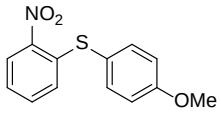
3s

3s: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 8.5 Hz, 1H), 7.23 (t, *J* = 9.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 160.6, 144.1, 136.7, 133.9, 132.8, 132.5, 128.0, 125.1, 122.1, 115.5, 55.4.[11]



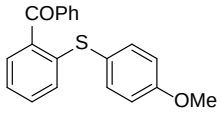
3t

3t: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 144.6, 136.8, 133.4, 132.8, 127.8, 125.5, 120.8, 117.0, 115.5, 110.8, 55.4.[6]



3u

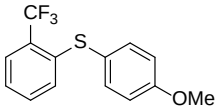
3u: light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 9.5 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.18 (t, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2, 144.6, 140.7, 137.7, 133.4, 127.9, 125.8, 124.7, 121.2, 115.7, 55.5.[12]



3v

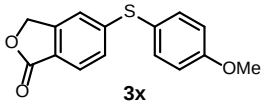
3v: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.42–7.36 (m, 3H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 160.2, 140.2, 137.5, 137.0, 136.3, 133.0,

131.0, 130.2, 130.0, 129.2, 128.4, 124.7, 123.8, 115.1, 55.4; HRMS (ESI) *m/z* calcd. for $C_{20}H_{16}O_2S$ $[M + H]^+$ 321.0871 found 321.0944.



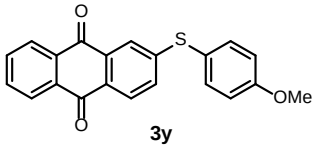
3w

3w: pink solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 139.2, 136.8, 131.9, 129.6, 127.5 (q, *J* = 30.5 Hz), 126.5 (q, *J* = 5.6 Hz), 125.1, 124.0 (q, *J* = 273.8 Hz), 122.3, 115.3, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.2 (s).[13]



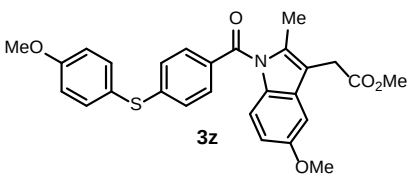
3x

3x: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.02 (s, 1H), 6.98 (d, *J* = 8.7 Hz, 2H), 5.17 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 161.0, 149.1, 147.4, 137.1, 126.6, 125.7, 122.4, 120.7, 118.5, 115.6, 69.1, 55.4.[14]



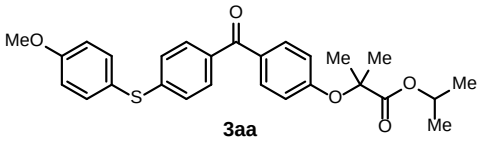
3y

3y: light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31–8.20 (m, 2H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.92 (s, 1H), 7.82–7.71 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 10.0 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.9, 181.4, 160.0, 148.4, 136.1, 133.2, 132.9, 132.6, 132.5, 132.3, 129.5, 129.1, 126.8, 126.2, 126.1, 122.6, 119.2, 114.6, 54.4; HRMS (ESI) *m/z* calcd. for $C_{21}H_{14}O_3S$ $[M + H]^+$ 347.0664 found 347.0737.



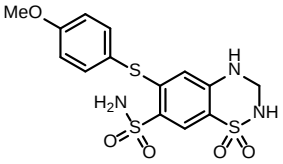
3z

3z: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.67 (dd, *J* = 9.0, 1.7 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 3.66 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 168.8, 160.8, 155.8, 147.0, 136.9, 136.0, 131.6, 131.0, 130.5, 125.8, 121.0, 115.4, 114.9, 111.9, 111.5, 110.9, 101.1, 55.7, 55.4, 52.1, 30.2, 13.2; HRMS (ESI) *m/z* calcd. for $C_{27}H_{25}NO_5S$ $[M + H]^+$ 476.1453 found 476.1534.



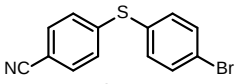
3aa

3aa: pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.07 (hept, *J* = 6.1 Hz, 1H), 3.82 (s, 3H), 1.64 (s, 6H), 1.18 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 172.1, 159.6, 158.4, 144.5, 135.7, 133.6, 130.8, 129.7, 129.4, 124.7, 120.6, 116.2, 114.3, 78.3, 68.2, 54.4, 24.3, 20.5; HRMS (ESI) *m/z* calcd. for $C_{27}H_{28}O_5S$ $[M + H]^+$ 465.1657 found 465.1729.



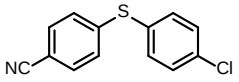
3ab

3ab: pale yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.93 (s, 1H), 7.75 (t, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.40 (s, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.12 (s, 1H), 4.57 (dd, *J* = 8.1, 2.4 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.1, 146.1, 144.6, 137.8, 127.6, 125.2, 121.0, 117.3, 116.3, 113.5, 55.8, 54.6; HRMS (EI) *m/z* calcd. for $C_{14}H_{15}N_3O_5S_3$ $[M]^+$ 401.0174 found 401.0177.



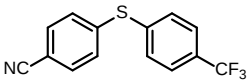
3ac

3ac: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 135.7, 133.1, 132.5, 130.3, 127.7, 123.8, 118.6, 109.2.[18]



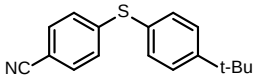
3ad

3ad: colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.41 (q, *J* = 8.8 Hz, 4H), 7.17 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 144.9, 135.7, 135.6, 132.5, 130.1, 129.5, 127.5, 118.6, 109.1.[19]



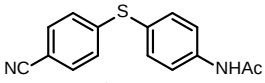
3ae

3ae: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 136.5, 131.7, 131.6, 129.6 (q, *J* = 33.0 Hz), 128.5, 125.5 (q, *J* = 3.8 Hz), 122.7 (q, *J* = 272.3 Hz), 117.4, 109.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s); HRMS (ESI) *m/z* calcd. for $C_{14}H_8F_3NS$ $[M + H]^+$ Exact 280.0330 found 280.0403.



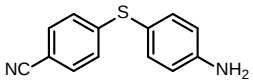
3af

3af: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9.0 Hz, 6H), 7.14 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 146.4, 134.5, 132.3, 127.0, 126.9, 126.8, 118.9, 108.3, 34.8, 31.2.[16]



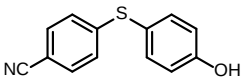
3ag

3ag: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 4H), 7.09 (d, *J* = 8.6 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 146.6, 139.6, 135.8, 132.3, 126.6, 124.7, 121.0, 118.9, 108.1, 24.6; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}N_2OS$ $[M + H]^+$ Exact 269.0670 found 269.0731.



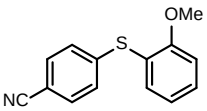
3ah

3ah: yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 148.2, 137.2, 132.1, 125.7, 119.1, 116.6, 116.1, 107.6; HRMS (ESI) *m/z* calcd. for $C_{13}H_{10}N_2S$ $[M + H]^+$ 227.0565 found 227.0638



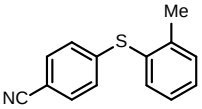
3ai

3ai: white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 147.6, 137.8, 133.1, 126.0, 119.3, 117.7, 117.5, 107.5; HRMS (ESI) *m/z* calcd. for $C_{13}H_9NOS$ $[M + H]^+$ 228.0405 found 228.0478.



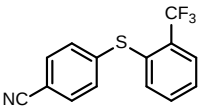
3aj

3aj: white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 12.6, 8.1 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 145.1, 136.6, 132.2, 131.7, 126.8, 121.6, 119.0, 118.0, 111.7, 108.2, 55.9.[6]



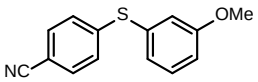
3ak

3ak: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.37 (d, *J* = 6.6 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 145.6, 142.5, 136.4, 132.4, 131.3, 130.3, 129.2, 127.4, 126.4, 118.9, 108.2, 20.7. [9]



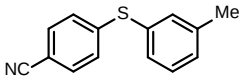
3al

3al: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.3 Hz, 1H), 7.61–7.44 (m, 5H), 7.17 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.22, 137.41, 132.88, 132.79 (q, *J* = 30.4 Hz), 132.5, 130.7, 129.4, 128.5, 127.5 (q, *J* = 5.5 Hz), 123.3 (q, *J* = 273.9 Hz), 118.5, 109.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.5 (s); HRMS (ESI) *m/z* calcd. for $C_{14}H_8F_3NS$ $[M + H]^+$ Exact 280.0330 found 280.0403.



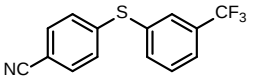
3am

3am: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 7.03 (s, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 145.5, 132.4, 131.9, 130.7, 127.5, 126.4, 119.4, 118.8, 115.2, 108.8, 55.4.[6]



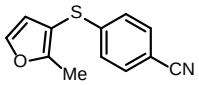
3an

3an: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.36–7.29 (m, 3H), 7.26–7.22 (m, 1H), 7.15 (d, *J* = 8.7 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 139.9, 135.1, 132.3, 131.6, 130.3, 130.3, 129.7, 127.2, 118.9, 108.5, 21.3.[6]



3ao

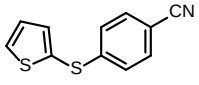
3ao: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.58–7.50 (m, 3H), 7.25 (d, *J* = 8.3 Hz, 2H); 13C NMR (101 MHz, $CDCl_3$) δ 142.5, 135.7 (q, *J* = 1.3 Hz), 132.3, 131.7, 131.3 (q, *J* = 32.7 Hz), 129.3, 129.1 (q, *J* = 3.8 Hz), 127.5, 124.7 (q, *J* = 3.8 Hz), 122.4 (q, *J* = 272.8 Hz), 117.5, 108.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s).[6]



3ap

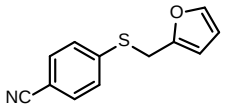
3ap: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.43 (s, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.37 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl3)

δ 156.9, 144.7, 140.9, 131.3, 124.5, 117.9, 114.2, 107.1, 104.5, 10.8; HRMS (ESI) *m/z* calcd. for $C_{12}H_9NOS$ $[M + H]^+$ 216.0405 found 216.0479.



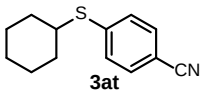
3ar

3ar: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 5.4 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.17–7.15 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 137.8, 132.9, 132.4, 128.5, 127.3, 125.8, 118.7, 108.8; HRMS (ESI) *m/z* calcd. for $C_{11}H_7NS_2$ $[M + H]^+$ 218.0020 found 218.0093.



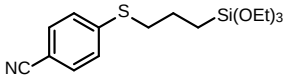
3as

3as: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.34 (d, *J* = 4.0 Hz, 2H), 6.31–6.28 (m, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 4.19 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 143.5, 142.5, 132.2, 127.9, 118.7, 110.7, 109.0, 108.4, 29.6; HRMS (ESI) *m/z* calcd. for $C_{12}H_9NOS$ $[M + H]^+$ 216.0405 found 216.0478.



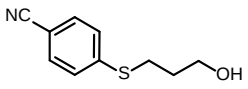
3at

3at: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 3.29 (t, *J* = 10.2 Hz, 1H), 2.02 (d, *J* = 10.8 Hz, 2H), 1.80 (d, *J* = 12.2 Hz, 2H), 1.65 (d, *J* = 13.0 Hz, 1H), 1.37 (tq, *J* = 23.2, 11.3, 10.9 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 131.2, 127.5, 117.9, 107.4, 43.9, 31.9, 24.8, 24.6.[17]



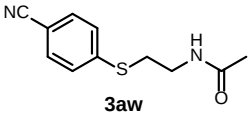
3au

3au: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 3.02 (t, *J* = 7.4 Hz, 2H), 1.82 (dt, *J* = 15.8, 7.8 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.85–0.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 132.2, 126.8, 119.0, 107.9, 58.5, 34.5, 22.5, 18.3, 9.9; HRMS (EI) *m/z* calcd. for $C_{16}H_{25}NO_3SSi$ $[M]^+$ 339.1324 found 339.1326.



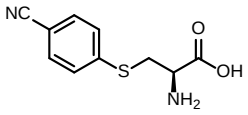
3av

3av: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 3.78 (t, *J* = 5.9 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.94 (p, *J* = 6.9 Hz, 2H), 1.73 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 132.2, 126.8, 118.9, 108.0, 60.9, 31.2, 28.3; HRMS (EI) *m/z* calcd. for $C_{10}H_{11}NOS$ $[M]^+$ 193.0561 found 193.0554.



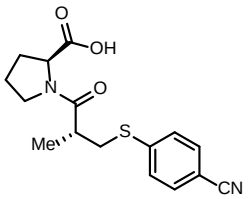
3aw

3aw: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.39 (s, 2H), 6.11 (s, 1H), 3.47 (q, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 6.8 Hz, 2H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 143.5, 132.4, 127.0, 118.8, 108.4, 38.6, 31.2, 23.1; HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}N_2OS$ $[M + H]^+$ 221.0670 found 221.0744.



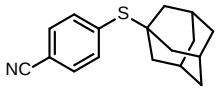
3ax

3ax: white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.08 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 5.36–5.25 (m, 1H), 3.78–3.59 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.1, 167.7, 136.9, 131.5, 130.2, 129.4, 78.8, 35.7.



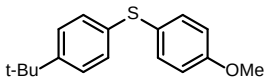
3ay

3ay: yellow solid, slightly impure with captopril; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.52 (dd, *J* = 7.8, 4.1 Hz, 1H), 3.65–3.29 (m, 2H), 3.11–2.77 (m, 2H), 2.35–1.86 (m, 5H), 1.30 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 174.4, 144.2, 132.3, 127.1, 118.7, 108.5, 59.2, 47.3, 38.0, 35.1, 28.5, 24.7, 17.3; HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}N_2O_3S$ $[M + H]^+$ 319.1038 found 319.1120.



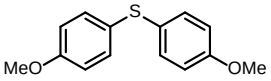
3az

3az: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 4H), 2.04 (s, 3H), 1.82 (d, *J* = 2.9 Hz, 6H), 1.67 (d, *J* = 12.7 Hz, 3H), 1.60 (d, *J* = 12.9 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 137.6, 131.7, 118.6, 112.1, 49.6, 43.7, 36.0, 30.0.



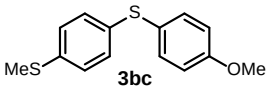
3ba

3ba: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.2, 134.8, 134.7, 128.6, 126.0, 125.1, 114.9, 55.4, 34.5, 31.3.[18]



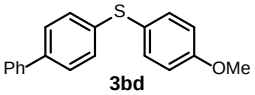
3bb

3bb: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 3.80 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 132.7, 128.5, 114.6, 55.4.[19]



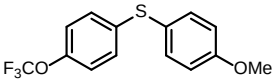
3bc

3bc: pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 2H), 7.14 (s, 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 136.4, 134.8, 134.7, 129.5, 127.4, 125.0, 115.0, 55.4, 16.1.[20]



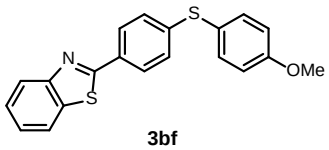
3bd

3bd: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.49–7.38 (m, 6H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 140.5, 138.7, 137.8, 135.5, 128.8, 128.5, 127.6, 127.3, 126.9, 124.1, 115.0, 55.4.[15]



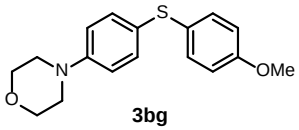
3be

3be: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 147.2 (q, *J* = 2.0 Hz), 137.8, 135.8, 129.0, 123.5, 121.6, 120.5 (q, *J* = 257.1 Hz), 115.2, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.1 (s).[22]



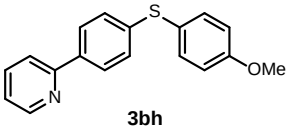
3bf

3bf: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 160.4, 154.1, 143.6, 136.4, 132.2, 130.6, 128.9, 127.9, 127.1, 126.3, 125.1, 123.0, 121.6, 115.3, 55.3.[23]



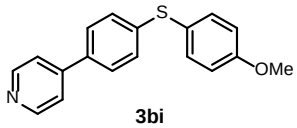
3bg

3bg: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 8.9, 2.4 Hz, 4H), 6.83 (dd, *J* = 8.9, 1.2 Hz, 4H), 3.86–3.82 (m, 4H), 3.78 (s, 3H), 3.17–3.11 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 150.4, 132.7, 132.4, 127.7, 126.0, 116.1, 114.7, 66.8, 55.4, 48.9; HRMS (ESI) *m/z* calcd. for $C_{17}H_{19}NO_2S$ $[M + H]^+$ 302.1136 found 302.1209.



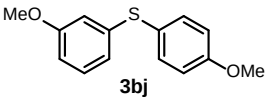
3bh

3bh: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.3 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.28–7.16 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 156.6, 149.4, 140.3, 137.0, 136.5, 135.6, 128.0, 127.4, 123.6, 122.0, 120.3, 115.1, 55.4; HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}NOS$ $[M + H]^+$ 294.0874 found 294.0947.



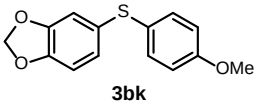
3bi

3bi: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.9 Hz, 2H), 7.48 (t, *J* = 9.0 Hz, 4H), 7.44 (d, *J* = 4.7 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 150.2, 147.6, 141.0, 136.2, 135.0, 127.8, 127.4, 122.9, 121.2, 115.2, 55.4; HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}NOS$ $[M + H]^+$ 294.0874 found 294.0947.



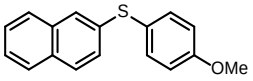
3bj

3bj: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.9 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.72–6.65 (m, 2H), 3.83 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 159.9, 140.2, 135.7, 129.7, 123.7, 120.2, 115.0, 113.3, 111.3, 55.4, 55.2.[24]



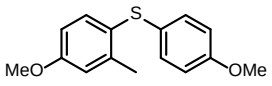
3bk

3bk: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.83 (s, 1H), 6.77 (s, 1H), 6.73 (d, *J* = 8.1 Hz, 1H), 5.94 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 148.2, 146.9, 133.5, 129.6, 126.6, 124.3, 114.8, 111.2, 108.8, 101.3, 55.4; HRMS (EI) *m/z* calcd. for $C_{14}H_{12}O_3S$ $[M]^+$ 260.0507 found 260.0508.



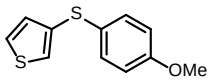
3bl

3bl: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.64 (s, 1H), 7.49 (d, *J* = 8.9 Hz, 2H), 7.48–7.40 (m, 2H), 7.33 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 135.9, 135.2, 133.8, 131.7, 128.6, 127.7, 127.2, 126.7, 126.5, 126.4, 125.6, 124.4, 115.0, 55.4.[25]



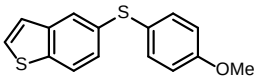
3bm

3bm: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 3H), 6.69 (dd, *J* = 8.5, 2.8 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 158.4, 141.8, 134.8, 131.0, 127.7, 125.5, 116.3, 114.7, 112.0, 55.3, 55.3, 21.0.[20]



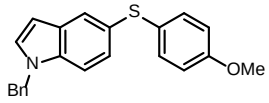
3bn

3bn: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 3H), 7.13 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.95 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 132.8, 132.4, 129.7, 126.4, 126.3, 124.4, 114.8, 55.4.[10]



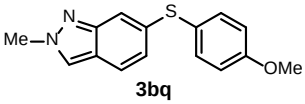
3bo

3bo: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 3.5 Hz, 2H), 7.93 (d, *J* = 9.1 Hz, 1H), 7.56–7.49 (m, 4H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 145.2, 143.9, 143.7, 143.4, 141.3, 137.0, 129.5, 129.2, 124.4, 121.2, 115.6, 55.4; HRMS (EI) *m/z* calcd. for $C_{15}H_{12}OS_2$ $[M]^+$ 272.0330 found 272.0333.



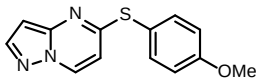
3bp

3bp: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.34–7.23 (m, 5H), 7.20 (s, 2H), 7.16–7.05 (m, 3H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.48 (s, 1H), 5.29 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 137.2, 135.6, 132.1, 129.5, 129.1, 128.8, 128.7, 127.7, 126.8, 125.9, 125.8, 124.9, 114.6, 110.5, 101.7, 55.3, 50.2; HRMS (EI) *m/z* calcd. for $C_{22}H_{19}NOS$ $[M]^+$ 345.1187 found 345.1188



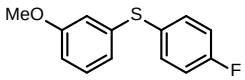
3bq

3bq: white solid; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 1H), 4.09 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.3, 148.2, 146.9, 133.5, 129.6, 126.6, 124.3, 114.8, 111.2, 108.8, 101.3, 55.4, 40.4; HRMS (ESI) *m/z* calcd. for $C_{15}H_{14}N_2OS$ $[M + H]^+$ 271.0827 found 271.0933.



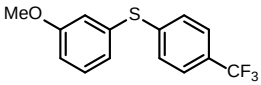
3br

3br: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.4 Hz, 1H), 8.00 (d, *J* = 2.2 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 6.33 (d, *J* = 7.4 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 161.2, 145.3, 137.4, 134.3, 119.3, 115.4, 105.5, 95.3, 55.5; HRMS (ESI) *m/z* calcd. for $C_{13}H_{11}N_3OS$ $[M + H]^+$ 258.0623 found 258.0696.



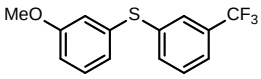
3bs

3bs: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.8, 5.4 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.80–6.72 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.1 Hz), 160.1, 138.1, 134.5 (d, *J* = 8.2 Hz), 129.9, 129.7, 121.9, 116.4 (d, *J* = 22.0 Hz), 115.0, 112.3, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7 (ddd, *J* = 13.8, 8.6, 5.2 Hz).[9]



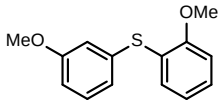
3bt

3bt: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 3H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 160.3, 142.5, 133.7, 130.4, 128.5, 128.1 (q, *J* = 32.8 Hz), 125.8 (q, *J* = 3.8 Hz), 125.5, 124.1 (q, *J* = 271.8 Hz), 118.4, 114.4, 55.4;^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 (s). [26]



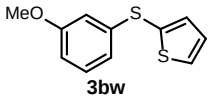
3bu

3bu: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.41–7.34 (m, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.94 (s, 1H), 6.86 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 138.1, 134.8, 133.1 (q, *J* = 1.5 Hz), 131.5 (q, *J* = 32.4 Hz), 130.3, 129.5, 126.5 (q, *J* = 3.8 Hz), 124.4, 123.7 (q, *J* = 272.7 Hz), 123.4 (q, *J* = 3.8 Hz), 117.3, 114.0, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s).[27]



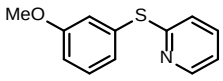
3bv

3bv: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 6.91 (dd, *J* = 8.0, 3.6 Hz, 2H), 6.87 (d, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 157.5, 135.9, 132.1, 129.9, 128.6, 127.7, 123.4, 121.3, 116.2, 112.9, 110.9, 55.9, 55.3; HRMS (EI) *m/z* calcd. for $C_{14}H_{14}O_2S$ $[M]^+$ 246.0715 found 246.0716



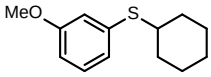
3bw

3bw: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 5.4 Hz, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 4.9 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.75–6.68 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 140.1, 136.3, 131.5, 130.7, 129.8, 127.9, 119.2, 112.5, 111.7, 55.2.[28]



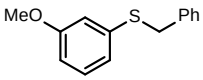
3bx

3bx: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.4 Hz, 1H), 7.46 (t, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.14 (s, 1H), 7.03–6.97 (m, 1H), 6.94 (t, *J* = 8.4 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 160.3, 149.5, 136.8, 132.1, 130.4, 127.0, 121.6, 119.9, 119.7, 115.2, 55.4.[29]



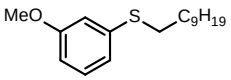
3by

3by: pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 7.00–6.91 (m, 2H), 6.75 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.80 (s, 3H), 3.13 (t, *J* = 10.2 Hz, 1H), 2.00 (d, *J* = 11.1 Hz, 2H), 1.77 (d, *J* = 9.0 Hz, 2H), 1.61 (d, *J* = 10.6 Hz, 1H), 1.33 (dp, *J* = 27.7, 9.8, 9.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 136.6, 129.5, 123.7, 116.9, 112.2, 55.2, 46.4, 33.3, 26.0, 25.8; HRMS (ESI) *m/z* calcd. for $C_{13}H_{18}OS$ $[M + H]^+$ 223.1078 found 223.1151.



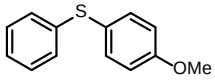
3bz

3bz: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 22.2, 6.5 Hz, 5H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.84 (s, 1H), 6.74 (dd, *J* = 9.0, 1.6 Hz, 1H), 4.14 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 137.8, 137.4, 129.7, 128.9, 128.5, 127.2, 121.7, 114.8, 112.2, 55.2, 38.8; HRMS (ESI) *m/z* calcd. for $C_{14}H_{14}OS$ $[M + H]^+$ 231.0765 found 231.0838.



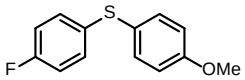
3ca

3ca: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.87–6.85 (m, 1H), 6.70 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.80 (s, 3H), 2.94–2.89 (m, 2H), 1.66 (p, *J* = 7.4 Hz, 2H), 1.42 (p, *J* = 7.3 Hz, 2H), 1.26 (s, 12H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 138.5, 129.6, 120.8, 114.0, 111.2, 55.2, 33.3, 31.9, 29.53, 29.50, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1; HRMS (EI) *m/z* calcd. for $C_{17}H_{28}OS$ $[M]^+$ 280.1861 found 280.1863.



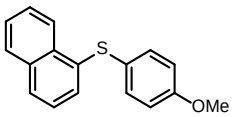
3cb

3cb: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.9 Hz, 2H), 7.25–7.20 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, CDCl3) δ 159.8, 138.6, 135.4, 128.9, 128.2, 125.8, 124.3, 115.0, 55.4.[30]



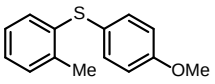
3cd

3cd: pale yellow oil;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.9 Hz, 2H), 7.20 (dd, *J* = 8.9, 5.2 Hz, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 246.0 Hz), 159.7, 134.5, 133.1 (d, *J* = 3.3 Hz), 131.0 (d, *J* = 7.9 Hz), 125.2, 116.1 (d, *J* = 21.9 Hz), 115.0, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.07–-116.2 (m).[21]



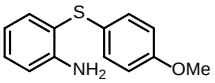
3ce

3ce: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.52 (p, *J* = 6.6, 6.1 Hz, 2H), 7.34 (d, *J* = 11.3 Hz, 4H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 134.6, 134.0, 133.9, 132.2, 128.50, 128.45, 127.4, 126.5, 126.3, 125.7, 125.1, 124.9, 115.0, 55.4. [9]



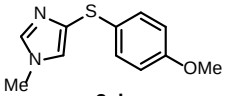
3cf

3cf: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.09 (t, *J* = 6.6 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 137.1, 136.9, 134.7, 130.2, 128.9, 126.5, 126.1, 124.3, 115.0, 55.4, 20.3.[21]



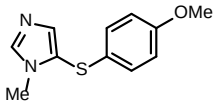
3cg

3cg: brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 1H), 7.22–7.15 (m, 1H), 7.13 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.79–6.70 (m, 2H), 4.27 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 148.1, 136.4, 130.4, 129.6, 126.8, 118.7, 116.7, 115.4, 114.8, 55.4.[31]



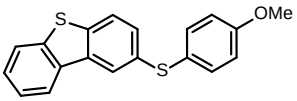
3ch

3ch: brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.00 (s, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 138.8, 133.5, 131.4, 127.6, 123.8, 114.5, 55.3, 33.6; HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}N_2OS$ $[M + H]^+$ 221.0670 found 221.0746.



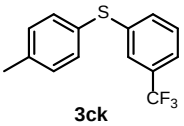
3ci

3ci: brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.40 (s, 1H), 7.09 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 137.3, 132.7, 131.7, 129.6, 126.2, 114.9, 55.4, 31.7; HRMS (ESI) *m/z* calcd. for $C_{11}H_{12}N_2OS$ $[M + H]^+$ 221.0670 found 221.0746.



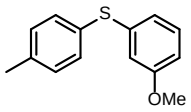
3cj

3cj: yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 5.5 Hz, 2H), 7.83 (d, *J* = 9.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.49–7.40 (m, 4H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 139.9, 137.7, 136.3, 134.8, 134.3, 134.0, 128.4, 127.0, 125.5, 124.5, 123.3, 122.9, 122.6, 121.7, 115.1, 55.4; HRMS (EI) *m/z* calcd. for $C_{19}H_{14}OS_2$ $[M]^+$ 322.0486 found 322.0488.



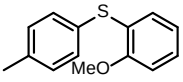
3ck

3ck: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.40 (d, J = 6.4 Hz, 1H), 7.35 (dd, J = 11.4, 7.2 Hz, 4H), 7.20 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 138.8, 133.5, 131.6 (q, *J* = 1.5 Hz), 131.3 (q, *J* = 32.4 Hz), 130.5, 129.3, 129.1, 125.0 (q, *J* = 3.9 Hz), 123.8 (q, *J* = 272.6 Hz), 122.6 (q, *J* = 3.8 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s).[32]



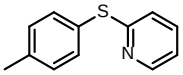
3cl

3cl: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.1 Hz, 2H), 7.20–7.12 (m, 3H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.81–6.78 (m, 1H), 6.73 (dd, *J* = 8.6, 2.8 Hz, 1H), 3.75 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 138.6, 137.8, 132.6, 130.7, 130.1, 129.8, 121.7, 114.8, 112.0, 55.3, 21.2.[33]



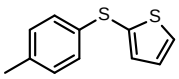
3cm

3cm: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 3H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 137.7, 133.0, 130.1, 129.9, 129.8, 127.4, 125.7, 121.2, 110.6, 55.9, 21.2; HRMS (ESI) *m/z* calcd. for $C_{17}H_{17}NS_2$ $[M + H]^+$ 300.0802 found 300.0875.



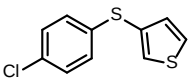
3cn

3cn: pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.46–7.39 (m, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.00–6.94 (m, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 149.5, 139.5, 136.6, 135.3, 130.5, 127.2, 120.8, 119.6, 21.3.[34]



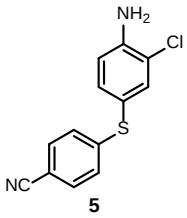
3co

3co: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 5.4, 1.3 Hz, 1H), 7.28 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.06 (dd, *J* = 5.4, 3.6 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 135.3, 134.8, 132.4, 130.8, 129.8, 128.0, 127.8, 21.0.[14]



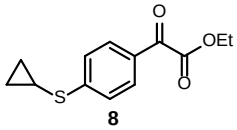
3cp

3cp: yellow oil;[1]H NMR (500 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.04 (dd, *J* = 4.9, 1.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 132.0, 131.2, 129.5, 129.3, 129.1, 128.8, 127.1.[35]



5

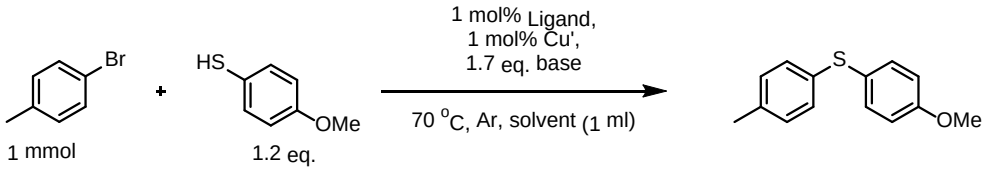
5: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.43 (m, 3H), 7.23 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.35 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 144.6, 136.5, 135.4, 132.3, 125.9, 119.6, 118.9, 117.5, 116.5, 108.1.[36]

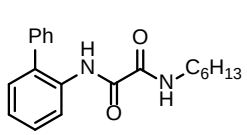


8

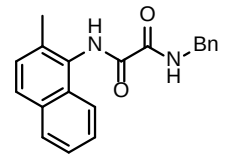
8: yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.20 (ddd, *J* = 11.7, 7.4, 4.4 Hz, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.20–1.14 (m, 2H), 0.73 (q, *J* = 5.6, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.4, 163.9, 149.8, 130.3, 128.7, 125.2, 62.3, 14.1, 11.0, 8.6.[37]

Condition screening for Cu-catalyzed arylation of thiol

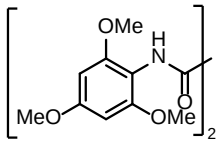




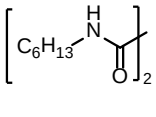
L1



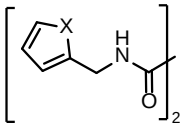
L2



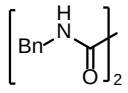
L3



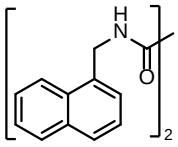
L4 (DBO)



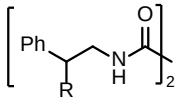
L5 (BTMO): X = S
L6 (BMFO): X = O



L7

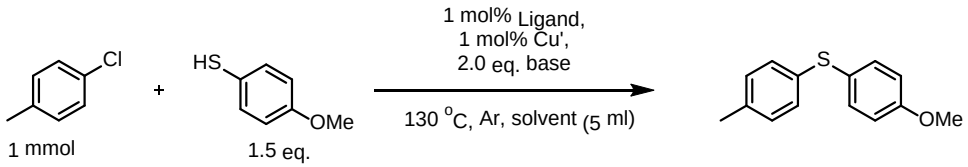


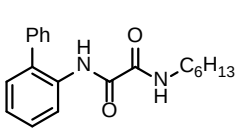
L8 (BNMO)



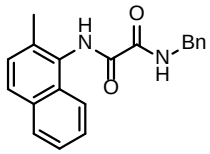
L9 (DPEO): R = H
L10 (BPPRO): R = Me

Entry	Catalyst	Ligand	Base	Solvent	NMR Yield
1	CuI	**L1**	t-BuOK	Dioxane	36%
2	CuI	**L2**	t-BuOK	Dioxane	80%
3	CuI	**L3**	t-BuOK	Dioxane	22%
4	CuI	**L4**	t-BuOK	Dioxane	58%
5	CuI	**L5**	t-BuOK	Dioxane	60%
6	CuI	**L6**	t-BuOK	Dioxane	49%
7	CuI	**L7**	t-BuOK	Dioxane	72%
8	CuI	**L2**	t-BuONa	Dioxane	21%
9	CuI	**L2**	K_2CO_3	Dioxane	NR
10	CuI	**L2**	KOH	Dioxane	18%
11	CuI	**L2**	K_3PO_4	Dioxane	NR
12	CuI	**L2**	t-BuOLi	Dioxane	15%
13	CuI	**L2**	t-BuOK	DMSO	32%
14	CuI	**L2**	t-BuOK	DME	46%
15	CuI	**L2**	t-BuOK	THF	43%
16	CuI	**L2**	t-BuOK	DMF	NR
17	CuI	**L8**	t-BuOK	Dioxane	86%
18	CuCl	**L8**	t-BuOK	Dioxane	83%
19	CuBr	**L8**	t-BuOK	Dioxane	85%
20	Cu_2O	**L8**	t-BuOK	Dioxane	94%

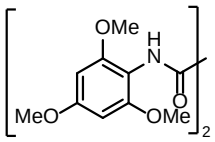




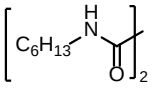
L1



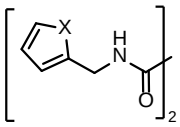
L2



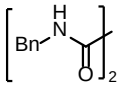
L3



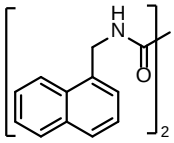
L4 (DBO)



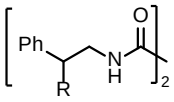
L5 (BTMO): X = S
L6 (BMFO): X = O



L7



L8 (BNMO)



L9 (DPEO): R = H
L10 (BPPRO): R = Me

Entry	Catalyst	Ligand	Base	Solvent (1 ml)	NMR Yield
1	CuI	**L1**	t-BuOK	Dioxane	15%
2	CuI	**L2**	t-BuOK	Dioxane	27%
3	CuI	**L3**	t-BuOK	Dioxane	30%
4	CuI	**L4**	t-BuOK	Dioxane	38%
5	CuI	**L8**	t-BuOK	Dioxane	45%
6	CuI	**L9**	t-BuOK	Dioxane	51%
7	CuI	**L10**	t-BuOK	Dioxane	57%
8	CuI	**L10**	K_2CO_3	Dioxane	NR
9	CuI	**L10**	KOH	Dioxane	trace
10	CuI	**L10**	K_3PO_4	Dioxane	NR
11	CuI	**L10**	t-BuONa	Dioxane	13%
12	Cu_2O	**L10**	t-BuOK	Dioxane	52%
13	CuCl	**L10**	t-BuOK	Dioxane	62%
14	CuCl	**L10**	t-BuOK	Toluene	20%
15	CuCl	**L10**	t-BuOK	DME	50%
16	CuCl	**L10**	t-BuOK	THF	50%
17	CuCl	**L10**	t-BuOK	2-MeTHF	37%
18	CuCl	**L10**	t-BuOK	Cyclopentyl methyl ether	25%
19	CuCl	**L10**	t-BuOK	Dioxane (3 ml)	76%
20	CuCl	**L10**	t-BuOK	Dioxane (5 ml)	90%

4. References

[1] Chen, Zhixiang; Jiang, Yongwen; Zhang, Li; Guo, Yinlong; Ma, Dawei, *Journal of the American Chemical Society*, **2019**, *141*, 354-3549

[2] Xu, Yuenian; Liu, Yong; Zhang, Yan; Yang, Kefang; Wang, Yan; Peng, Jiajian; Shao, Xinxin; Bai, Ying, *Journal of Organic Chemistry*, **2023**, *88*, 2773-2783

[3] Dutta, Soumya; Saha, Amit, *Organic and Biomolecular Chemistry*, **2019**, *17*, 9360-9366

[4] Wang, Rongkang; Chen, Fangming; Jiang, Lvqi; Yi, Wenbin, *Advanced Synthesis and Catalysis*, **2021**, *363*, 1904-1911

[5] Zhu, Yuan-Yuan; Lan, Guangxu; Fan, Yingjie; Veroneau, Samuel S.; Song, Yang; Micheroni, Daniel; Lin, Wenbin, *Angewandte Chemie - International Edition*, **2018**, *57*, 14090-14094; *Angew. Chem.*, **2018**, *130*, 14286-14290

[6] Jiang, Min; Li, Haifang; Yang, Haijun; Fu, Hua, *Angewandte Chemie - International Edition*, **2017**, *56*, 874-879; *Angew. Chem.*, **2017**, *129*, 892-897

[7] Swan, Charlie; Maggi, Lorenzo; Park, Mahri; Taylor, Sophie; Shepherd, William; Ball, Liam T., *Synthesis*, **2022**, *54*, 3399-3408

[8] Arisawa, Mieko; Suzuki, Takaaki; Ishikawa, Tomofumi; Yamaguchi, Masahiko, *Journal of the American Chemical Society*, **2008**, *130*, 12214-12215

[9] Qiao, Zongjun; Ge, Nanyang; Jiang, Xuefeng, *Chemical Communications*, **2015**, *51*, 10295-10298

[10] Zhou, Jing-Ya; Zhu, Yong-Ming, *European Journal of Organic Chemistry*, **2021**, *2021*, 2452-2461

[11] Manna, Sudipta Kumar; Manda, Srinivas Lavanya Kumar; Panda, Gautam, *Tetrahedron Letters*, **2014**, *55*, 5759-5763

[12] Li, Minghao; Hoover, Jessica M., *Chemical Communications*, **2016**, *52*, 8733-8736

[13] Graßl, Simon; Hamze, Clémence; Koller, Thaddäus J.; Knochel, Paul, *Chemistry - A European Journal*, **2019**, *25*, 3752-3755

[14] Deng, Guo-Jun; Huang, Huawen; Mao, Guojiang; Zhao, Feng; Zhong, Shuai; Zhou, Zhiwei, *Organic Letters*, **2022**, *24*, 1865-1870

[15] Yao, Fang; Zhang, Rongli; Wu, Yichao; Cai, Mingzhong, J*ournal of Chemical Research*, **2015**, *39*, 612-616

[16] Wu, Jiang-Ping; Saha, Anjan K.; Haddad, Nizar; Busacca, Carl A.; Lorenz, Jon C.; Lee, Heewon; Senanayake, Chris H., A*dvanced Synthesis and Catalysis*, **2016**, *358*, 1924-1928

[17] Delcaillau, Tristan; Bismuto, Alessandro; Lian, Zhong; Morandi, Bill, *Angewandte Chemie - International Edition*, **2020**, *59*, 2110-2114; *Angew. Chem.* **2020**, *132*, 2126-2131

[18] Lai, Chih-Shin; Kao, Hsin-Lun; Wang, Yan-Jhang; Lee, Chin-Fa, *Tetrahedron Letters*, **2012**, *53*, 4365-4367

[19] Jang, Yujin; Kim, Kyoung Tae; Jeon, Heung Bae, *Journal of Organic Chemistry*, **2013**, *78*, 6328-6331

[20] Chen, Bin; Lei, Tao; Li, Xu-Bing; Nan, Xiao-Lei; Tung, Chen-Ho; Wang, Jing-Hao; Wu, Hao-Lin; Wu, Li-Zhu, *Organic Letters*, **2020**, *22*, 3804-3809

[21] Wang, Ting-Ting; Yang, Fu-Lai; Tian, Shi-Kai, *Advanced Synthesis and Catalysis*, **2015**, *357*, 928-932

[22] Chen, Bin; Chen, Ya-Jing; Cheng, Yuan-Yuan; Lei, Tao; Liang, Ge; Tung, Chen-Ho; Wang, Jing-Hao; Wu, Li-Zhu; Ye, Chen; Zhou, Chao, *Organic Letters*, **2021**, *23*, 8082-8087

[23] Katla, Ramesh; Katla, Rakhi, *New Journal of Chemistry*, **2022**, *46*, 13918-13923

[24] Fernandez-Rodriguez, Manuel A.; Hartwig, John F., *Journal of Organic Chemistry*, **2009**, *74*, 1664-1672

[25] Wang, Changliu; Zhang, Zhenming; Tu, Yongliang; Li, Ying; Wu, Jiale; Zhao, Junfeng, *Journal of Organic Chemistry*, **2018**, *83*, 2389-2394.

[26] EAST CHINA NORMAL UNIVERSITY - CN107857717, **2018**, A, Paragraph 0228

[27] EAST CHINA NORMAL UNIVERSITY - CN107857717, **2018**, A, Paragraph 0240

[28] Reeves, Jonathan T.; Camara, Kaddy; Han, Zhengxu S.; Xu, Yibo; Lee, Heewon; Busacca, Carl A.; Senanayake, Chris H, *Organic Letters*, **2014**, *16*, 1196-1199.

[29] Platon, Mélanie; Wijaya, Novi; Rampazzi, Vincent; Cui, Luchao; Rousselin, Yoann; Saeys, Mark; Hierso, Jean-Cyrille, *Chemistry - A European Journal*, **2014**, *20*, 12584-12594.

[30] Reddy, Vutukuri Prakash; Kumar, Akkilagunta Vijay; Swapna, Kokkirala; Rao, Kakulapati Rama, *Organic Letters*, **2009**, *11*, 1697-1700.

[31] Matsuzawa, Tsubasa; Hosoya, Takamitsu; Yoshida, Suguru, *Organic Letters*, **2021**, *23*, 2347-2352.

[32] Liu, Xing; Cao, Qiang; Xu, Wan; Zeng, Meng-Tian; Dong, Zhi-Bing, *European Journal of Organic Chemistry*, **2017**, *2017*, 5795-5799.

[33] Qiao, Zongjun; Jiang, Xuefeng, *Organic Letters*, **2016**, *18*, 1550-1553.

[34] Pan, Lei; Cooke, Maria Victoria; Spencer, Amara; Laulhé, Sébastien, *Advanced Synthesis and Catalysis*, **2022**, *364*, 420-425.

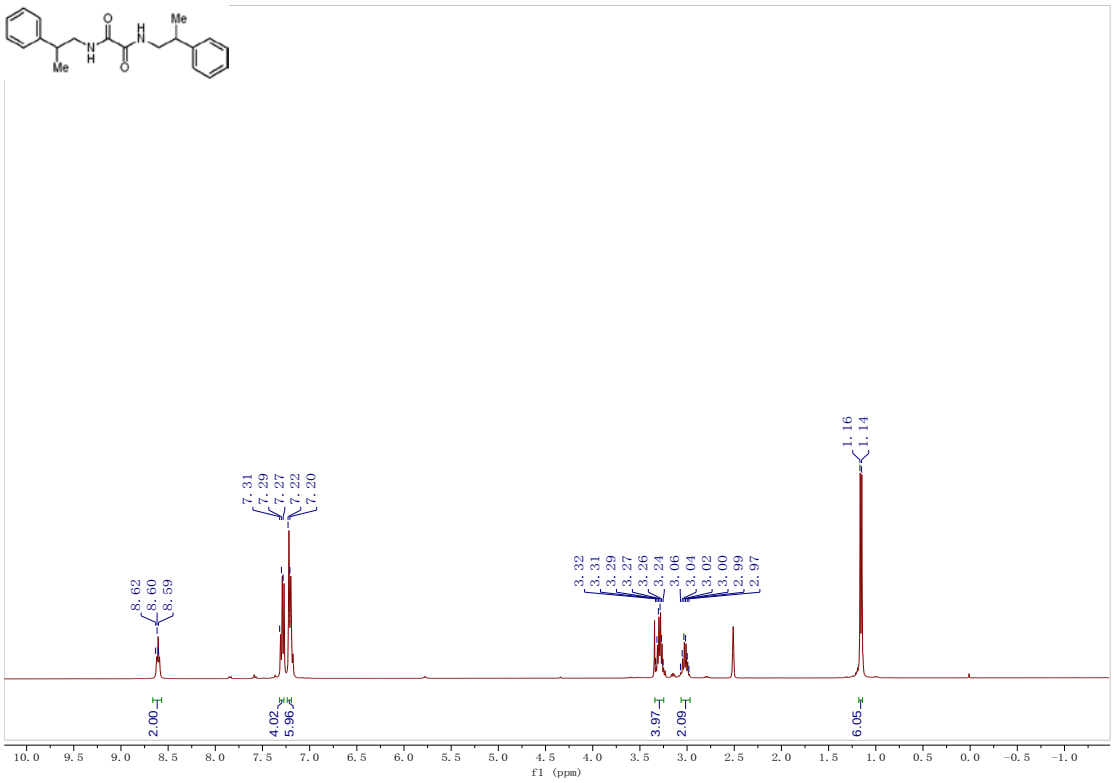
[35] Lam, Long Yin; Ma, Cong, *Organic Letters*, **2021**, *23*, 6164-6168.

[36] Patel, Bharti; Firkin, Catherine R.; Snape, Evan W.; Jenkin, Shelley L.; Brown, David; Chaffey, Julian G. K.; Hopes, Philip A.; Reens, Carl D.; Butters, Mike; Moseley, Jonathan D, *Organic Process Research and Development*. **2012**, *16*, 447-460.

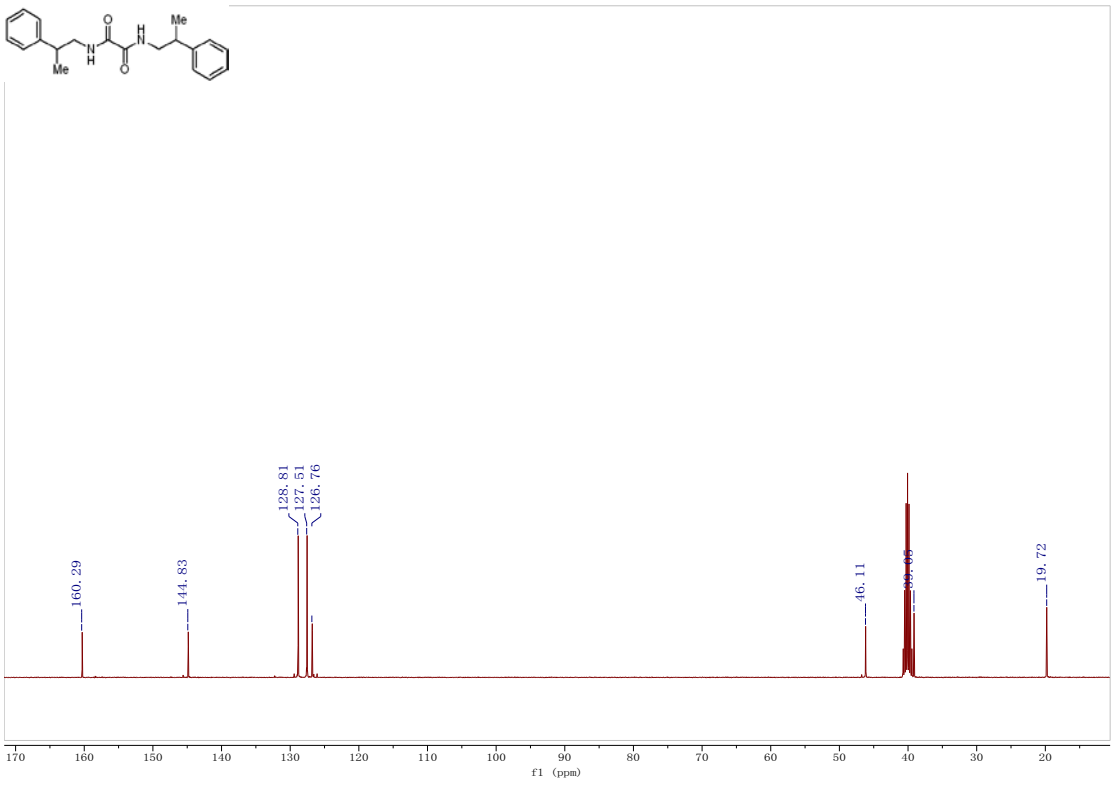
[37] Magnus, Nicholas A.; Braden, Timothy M.; Buser, Jonas Y.; Debaillie, Amy C.; Heath, Perry C.; Ley, Christopher P.; Remacle, Jacob R.; Varie, David L.; Wilson, Thomas M.; *Organic Process Research and Development*, **2012**, *16*, 830-835.

5. Copies of ^{1}H and ^{13}C spectrum of ligands and (hetero)aryl thioethers.

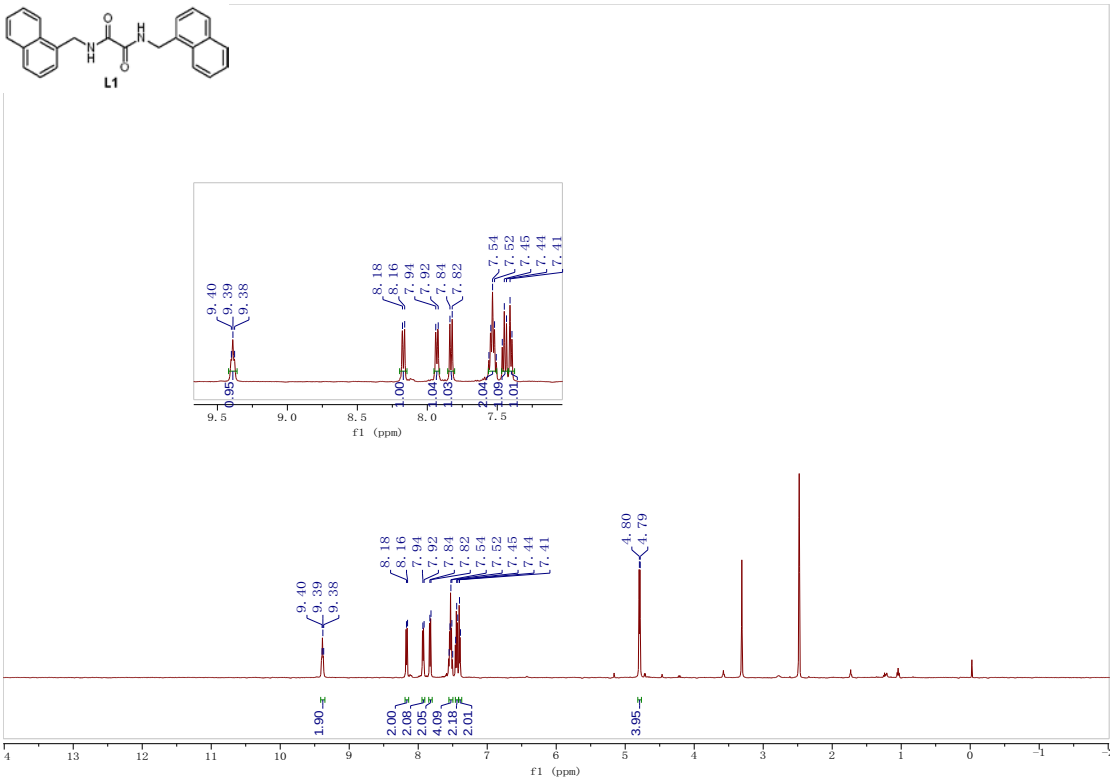
^{1}H NMR Spectrum of **L1** (500 MHz, DMSO-*d6*)



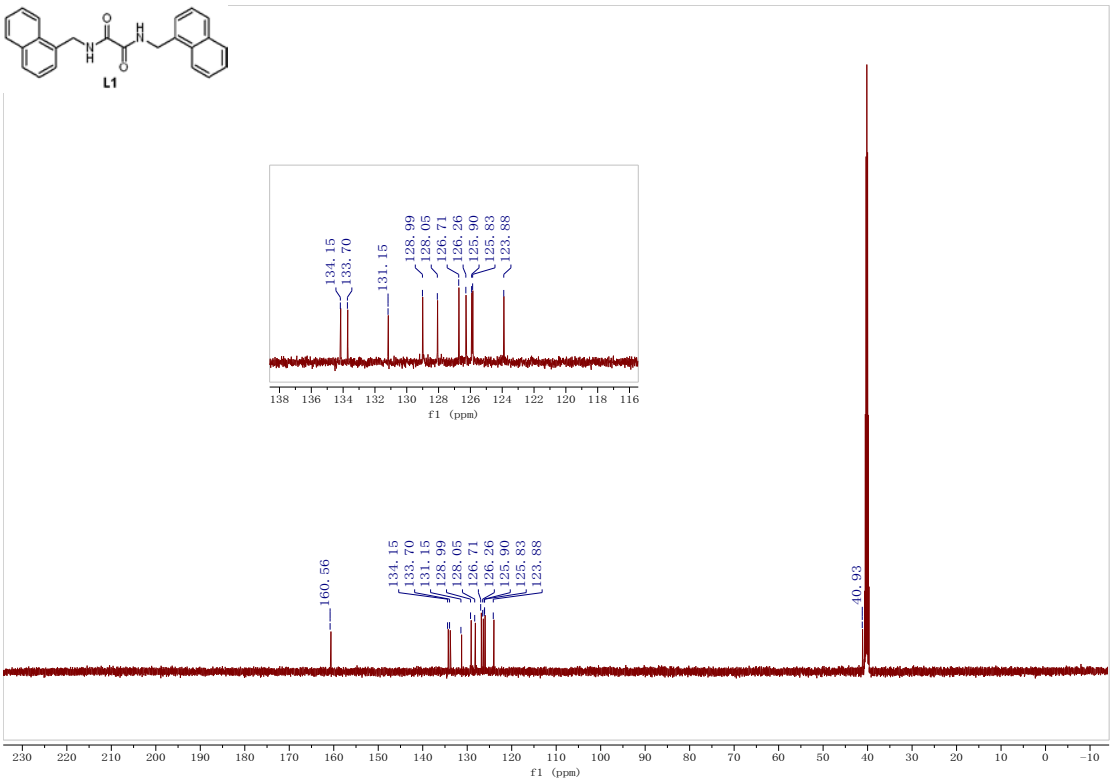
^{13}C NMR Spectrum of **L1** (126 MHz, DMSO-*d6*)



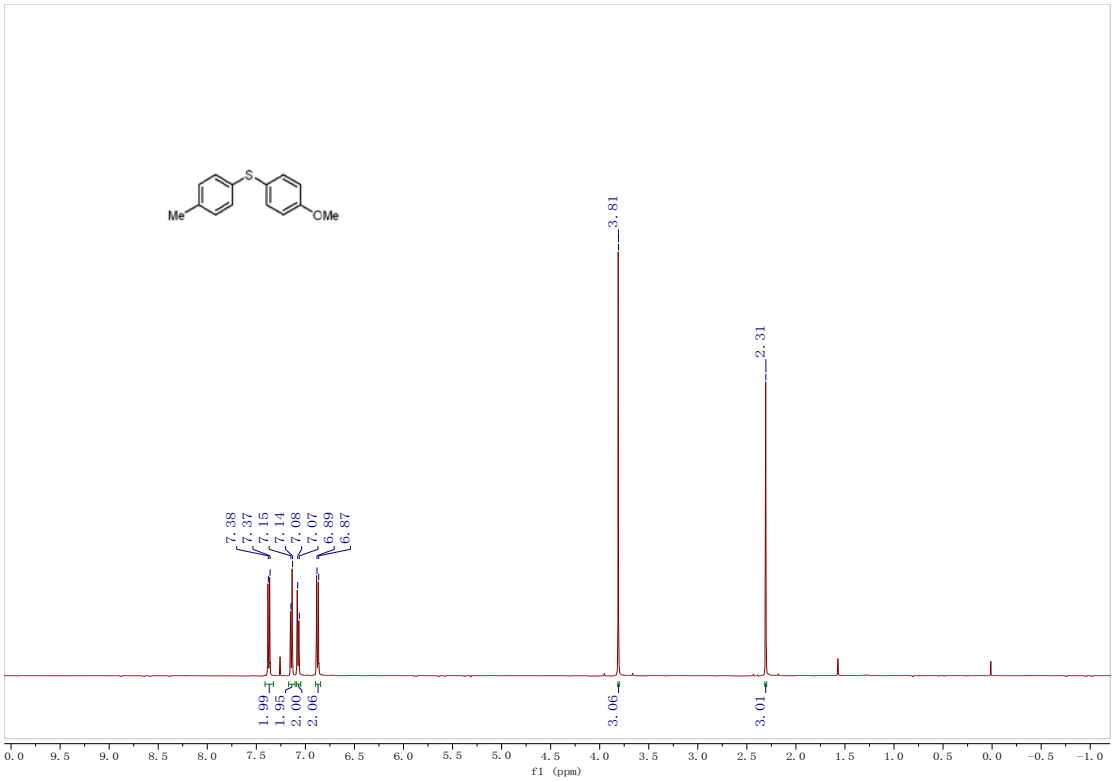
^{1}H NMR Spectrum of **L2** (500 MHz, DMSO-*d6*)



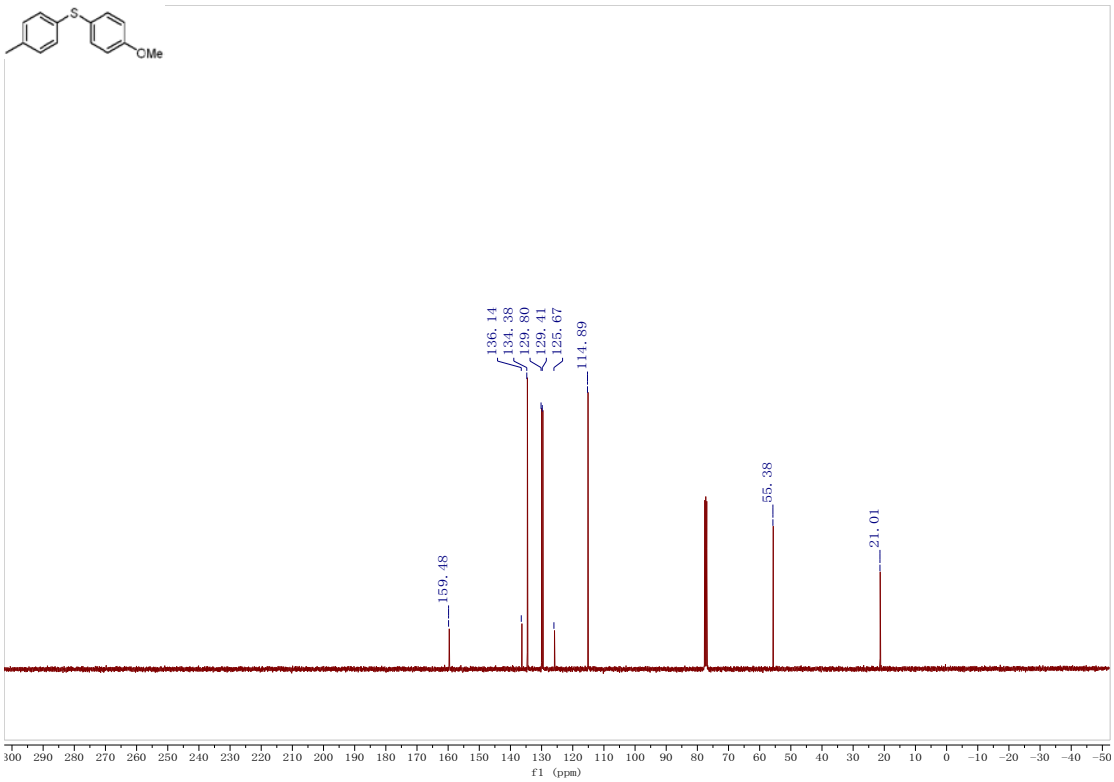
^{13}C NMR Spectrum of **L2** (126 MHz, DMSO-*d6*)



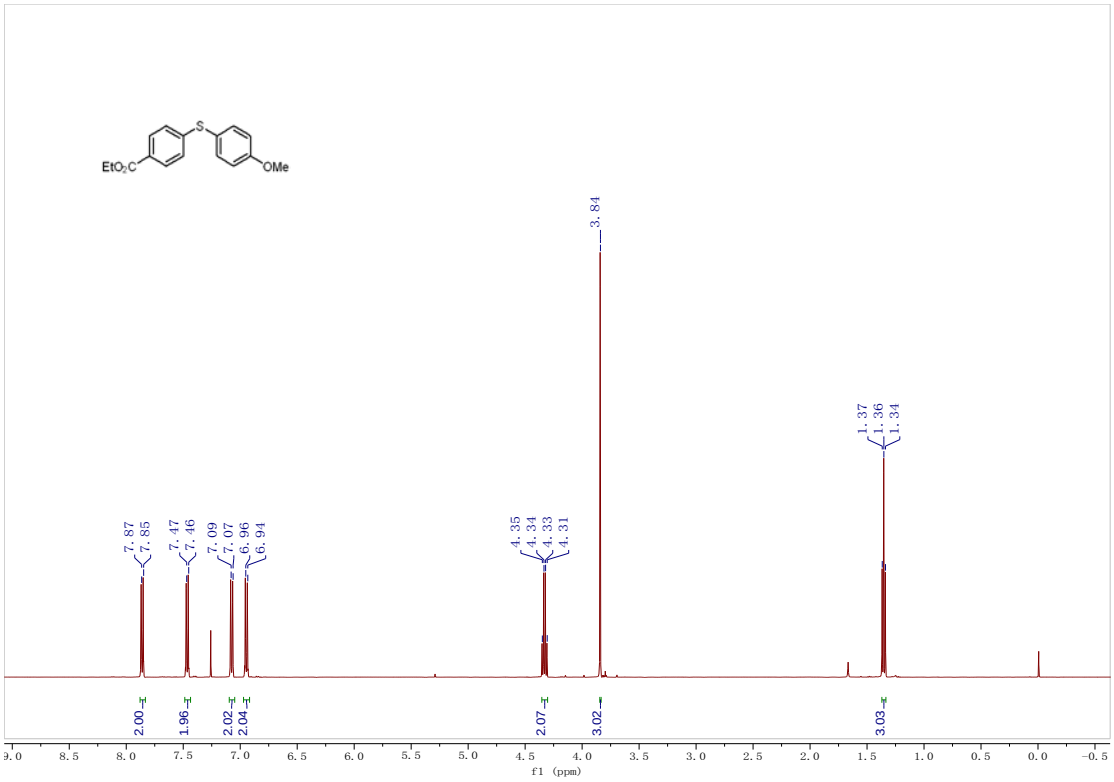
^{1}H NMR Spectrum of **3a** (500 MHz, $CDCl_3$)



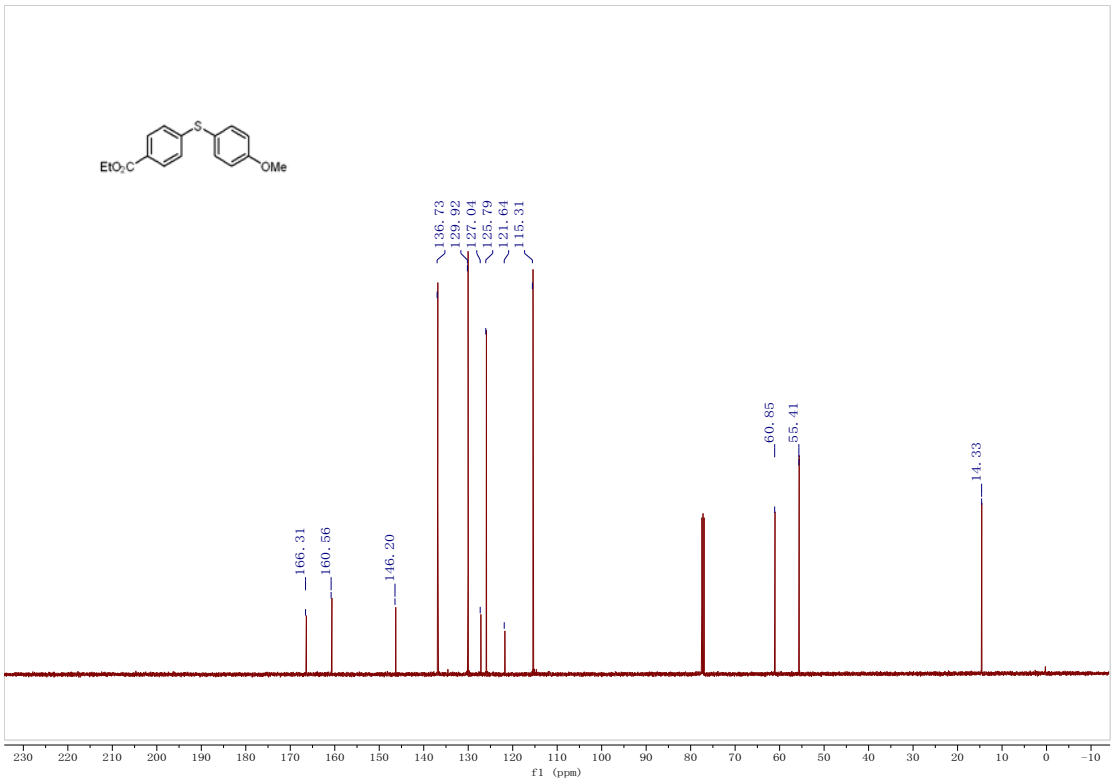
^{13}C NMR Spectrum of **3a** (126 MHz, $CDCl_3$)



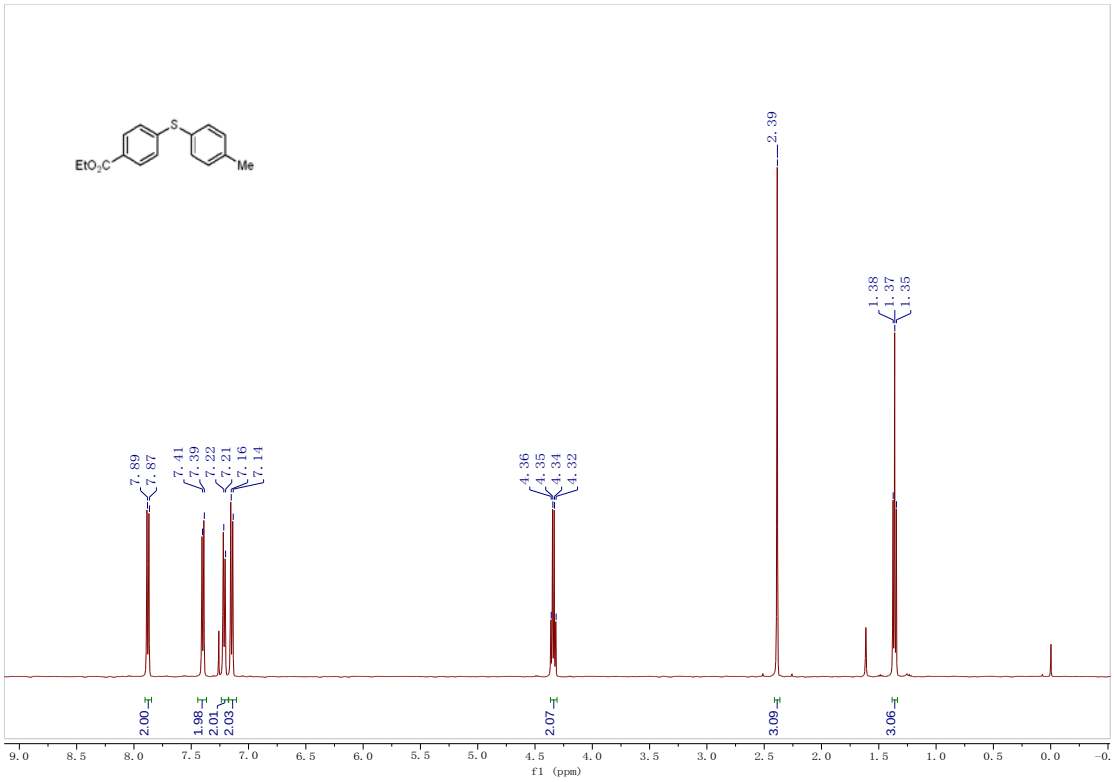
^{1}H NMR Spectrum of **3b** (500 MHz, $CDCl_3$)



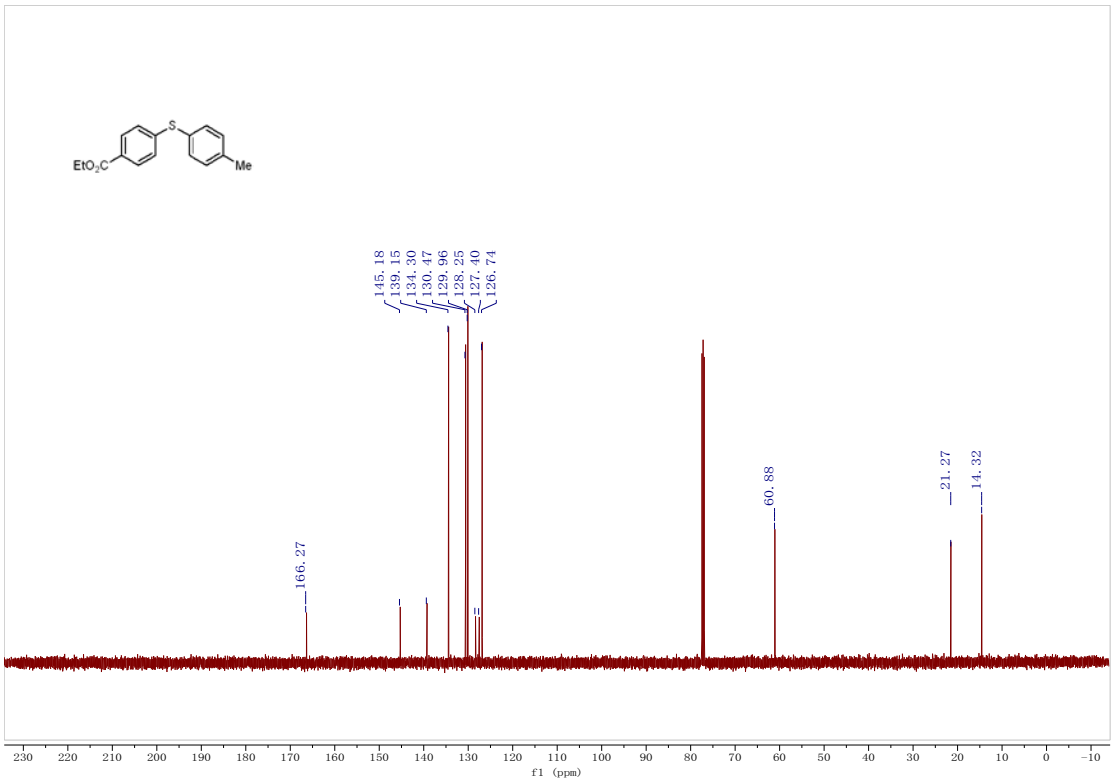
^{13}C NMR Spectrum of **3b** (126 MHz, $CDCl_3$)



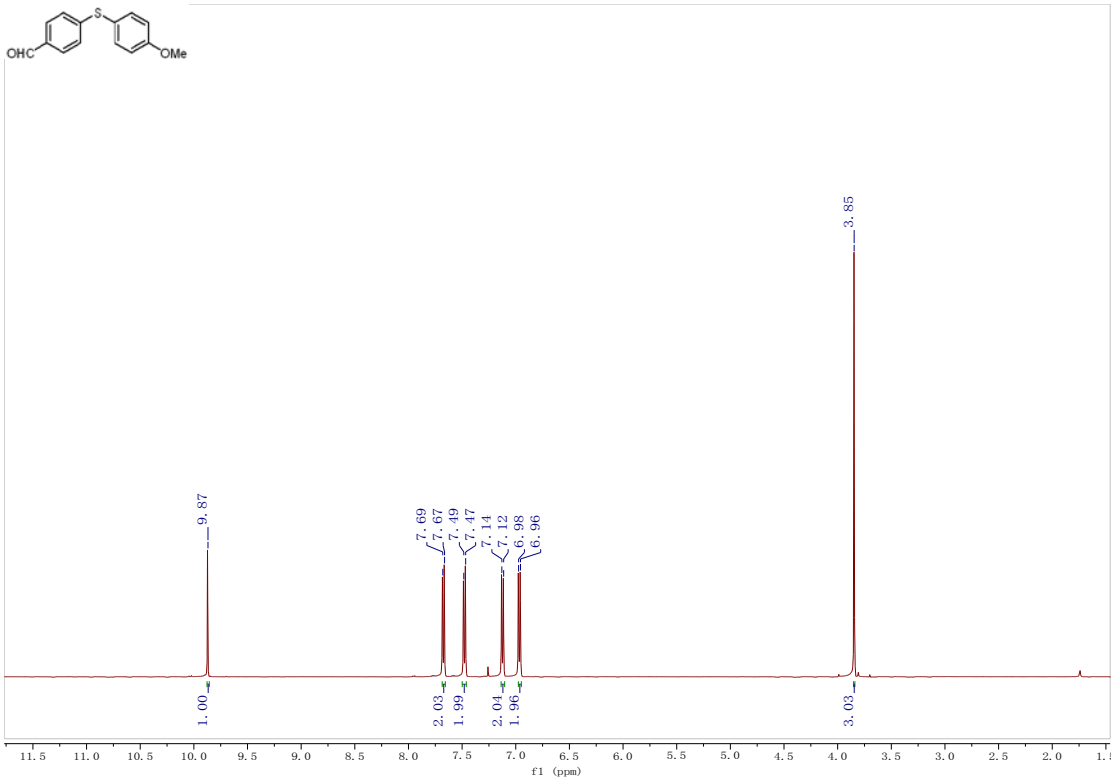
^{1}H NMR Spectrum of **3c** (500 MHz, $CDCl_3$)



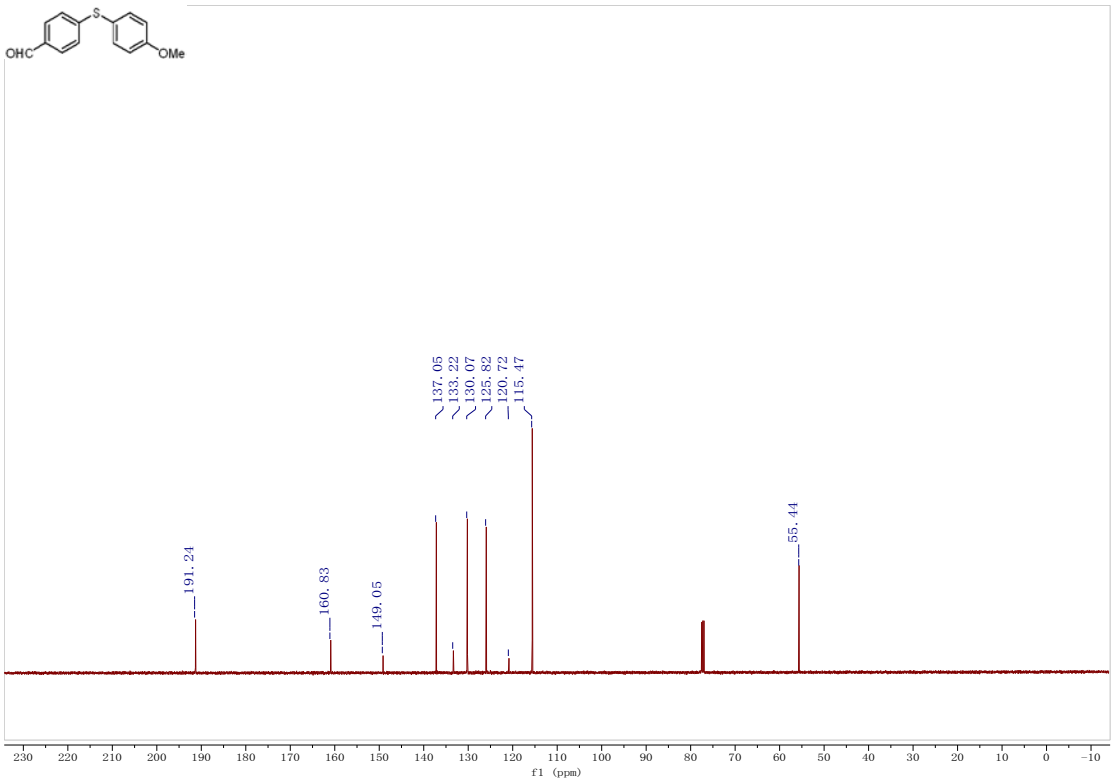
^{13}C NMR Spectrum of **3c** (126 MHz, $CDCl_3$)



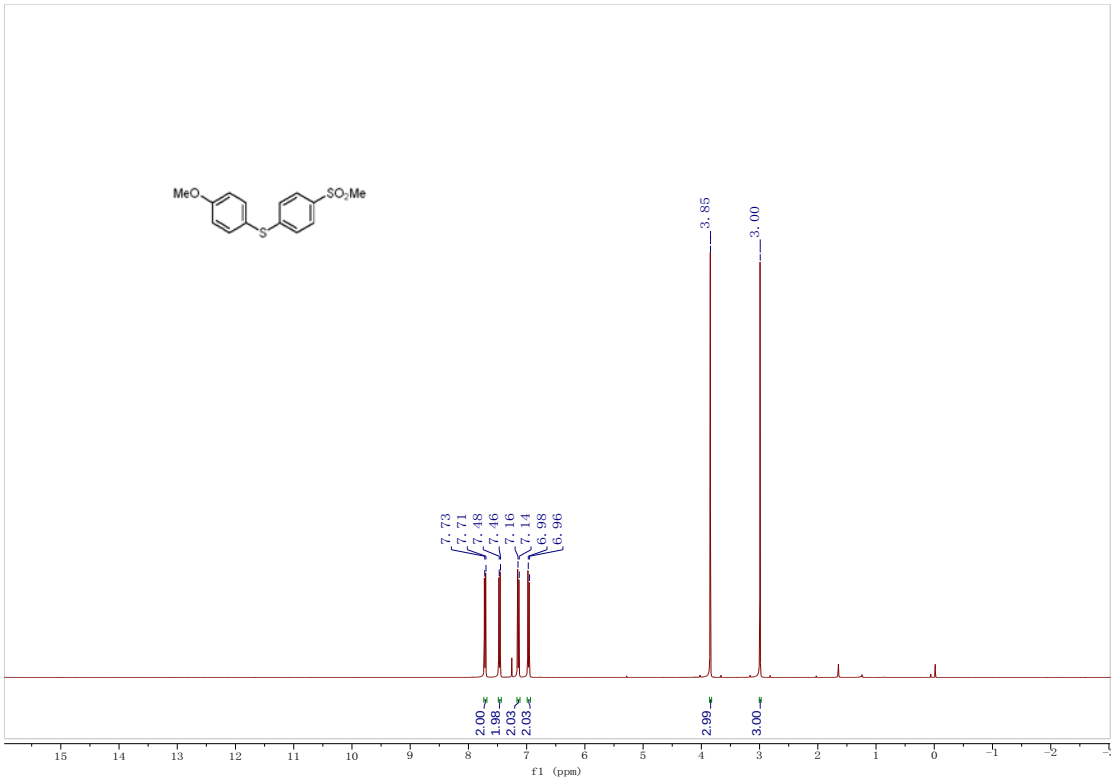
^{1}H NMR Spectrum of **3d** (500 MHz, $CDCl_3$)



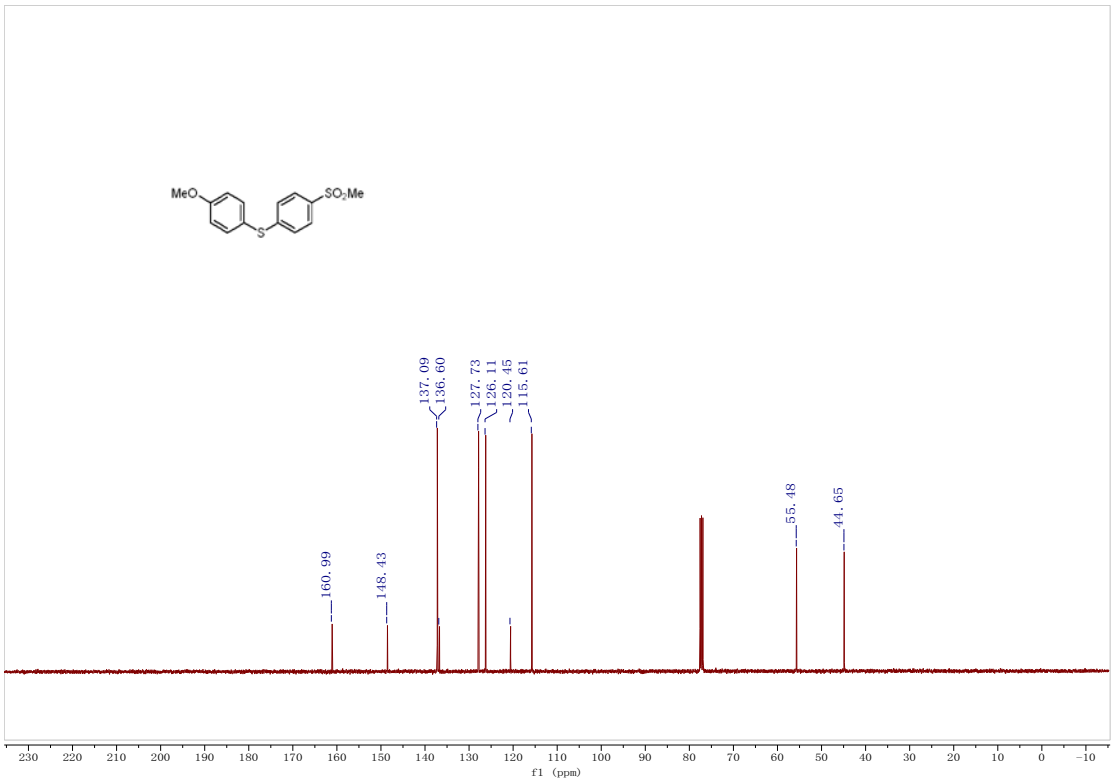
^{13}C NMR Spectrum of **3d** (126 MHz, $CDCl_3$)



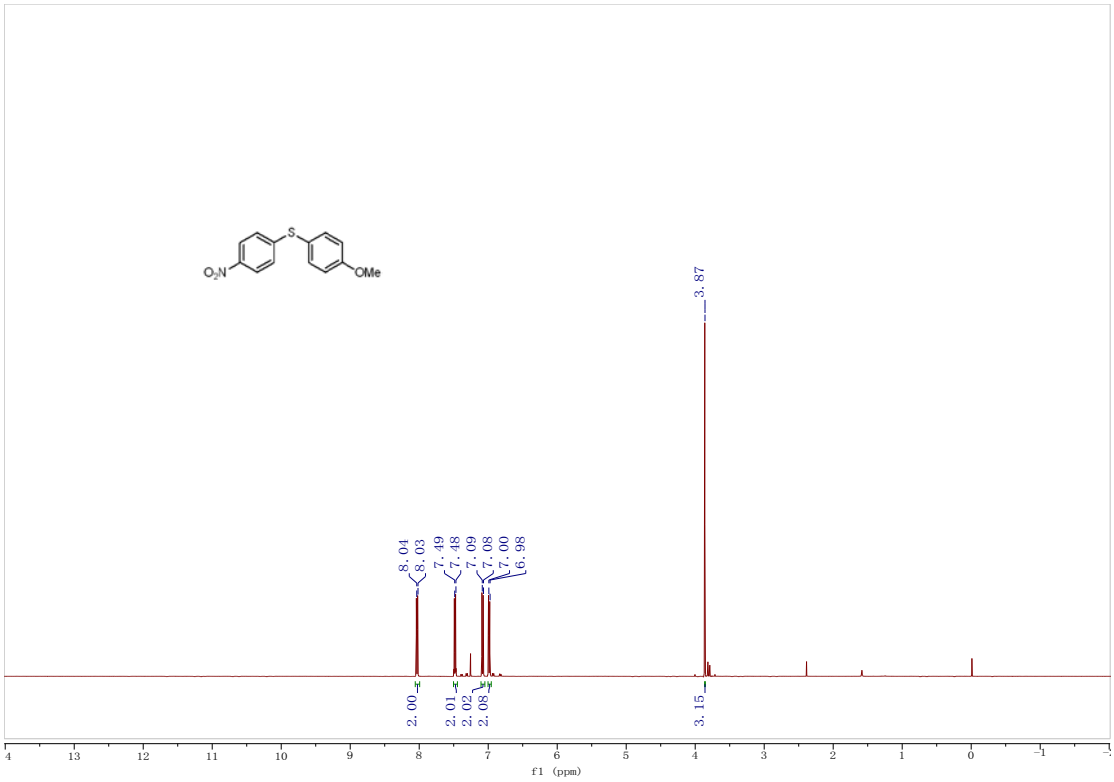
^{1}H NMR Spectrum of **3e** (400 MHz, $CDCl_3$)



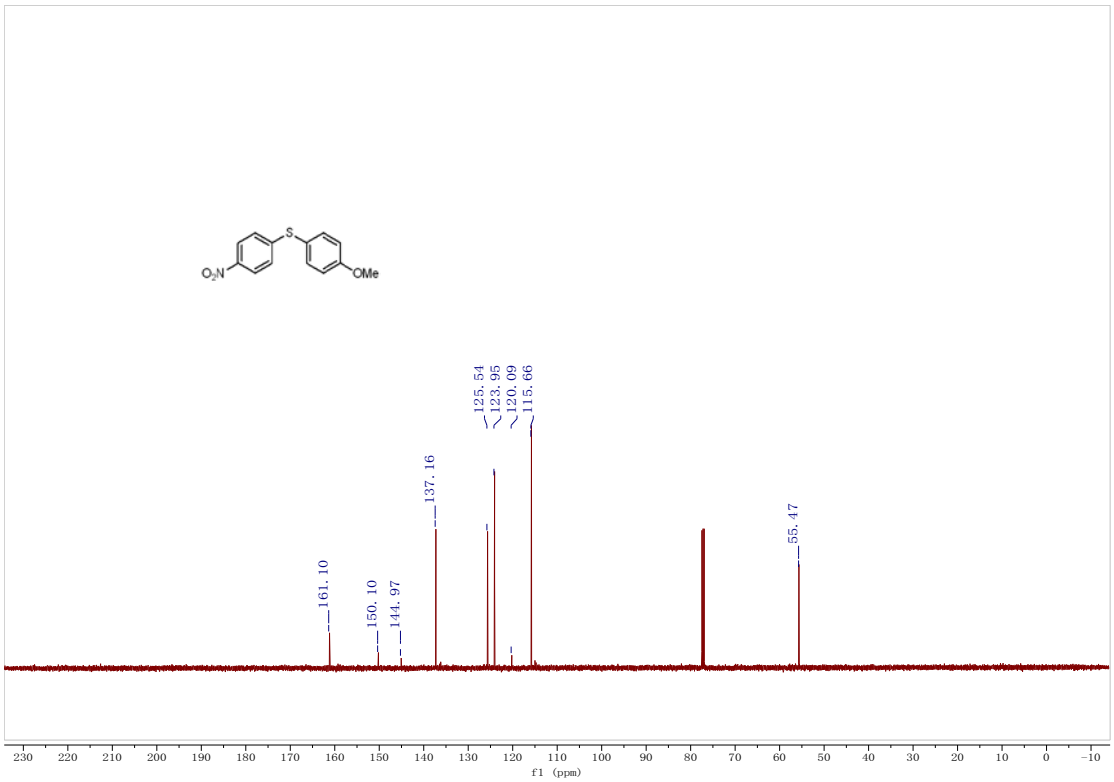
^{13}C NMR Spectrum of **3e** (400 MHz, $CDCl_3$)



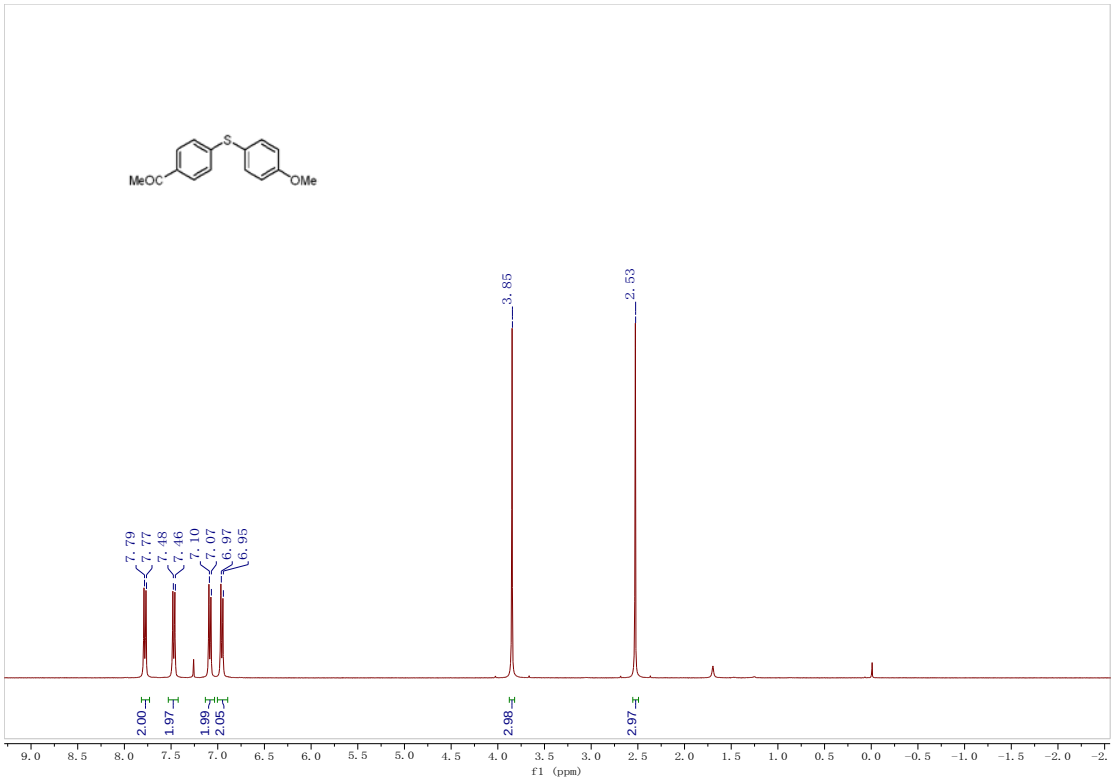
^{1}H NMR Spectrum of **3f** (500 MHz, $CDCl_3$)



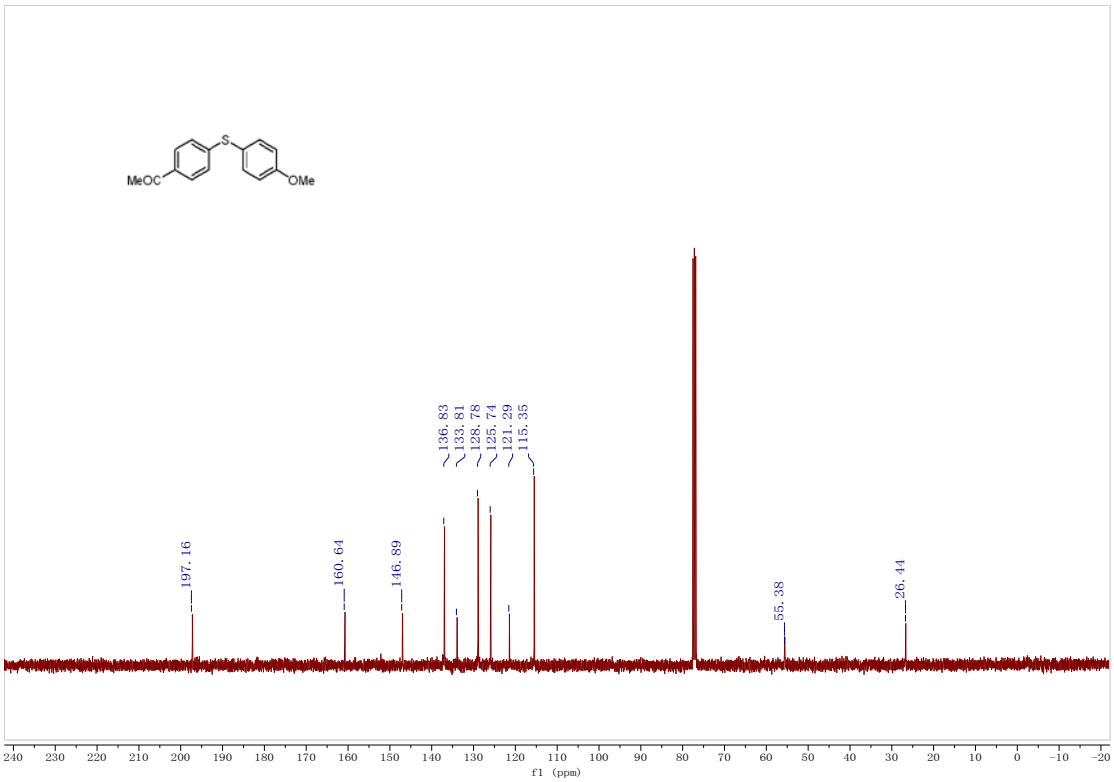
^{13}C NMR Spectrum of **3f** (126 MHz, $CDCl_3$)



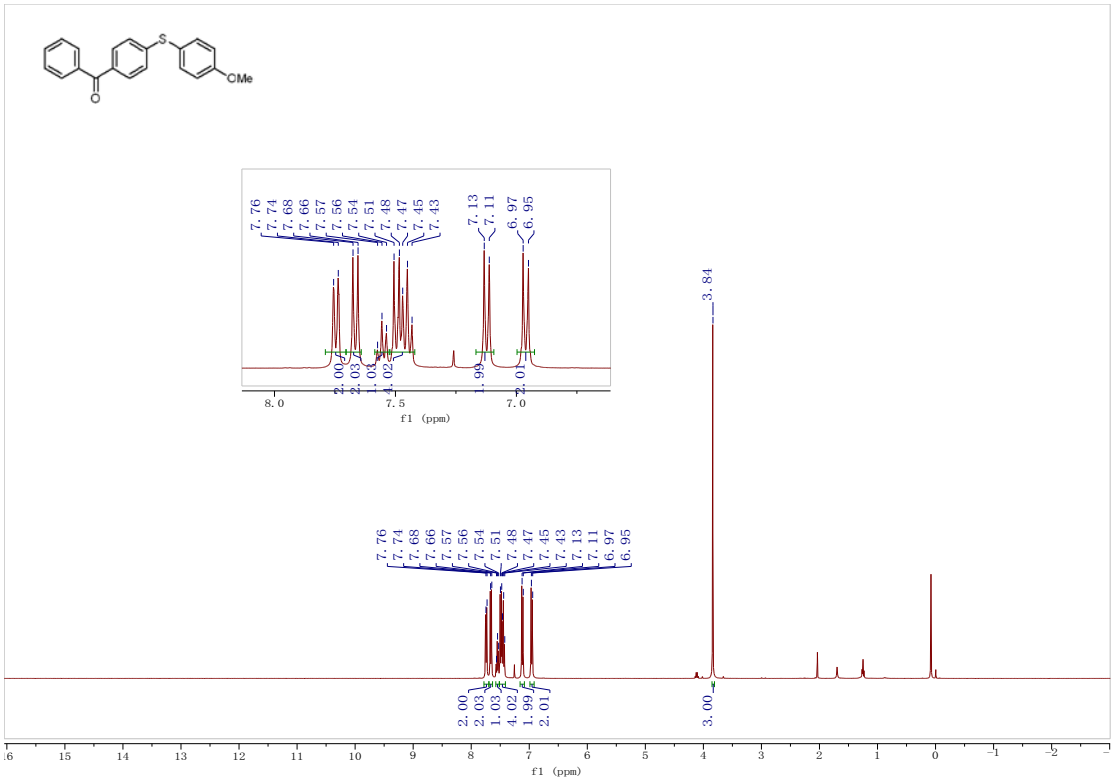
^{1}H NMR Spectrum of **3g** (400 MHz, $CDCl_3$)



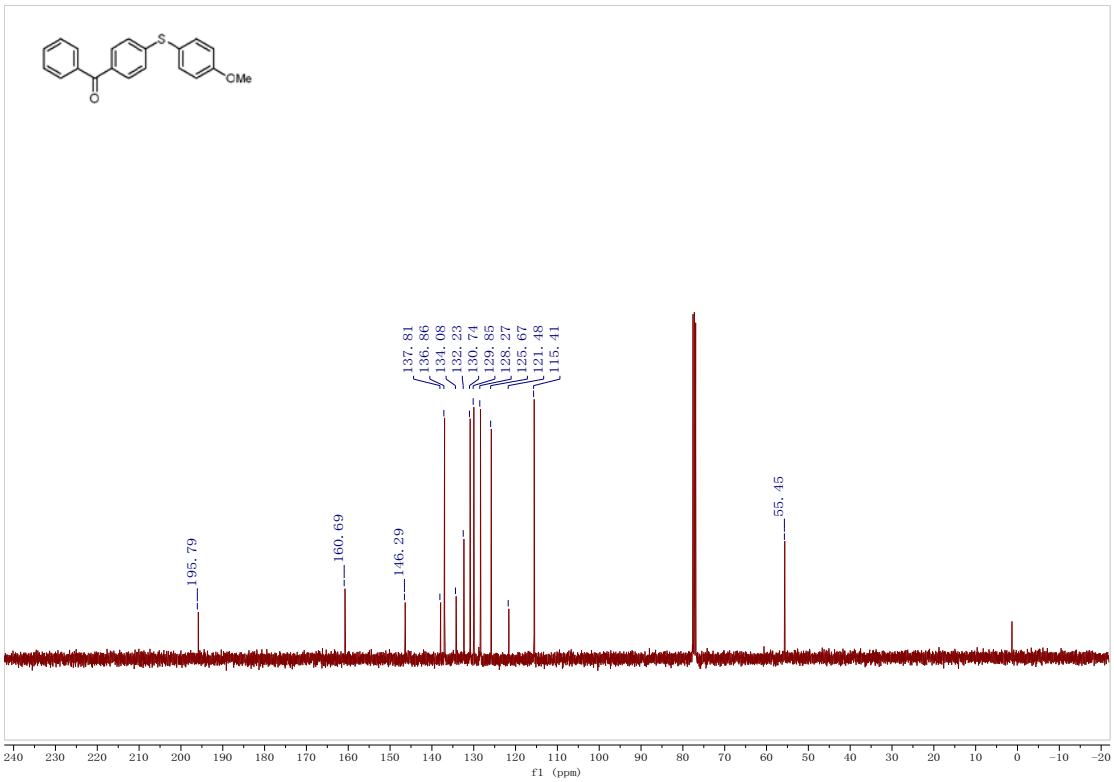
^{13}C NMR Spectrum of **3g** (101 MHz, $CDCl_3$)



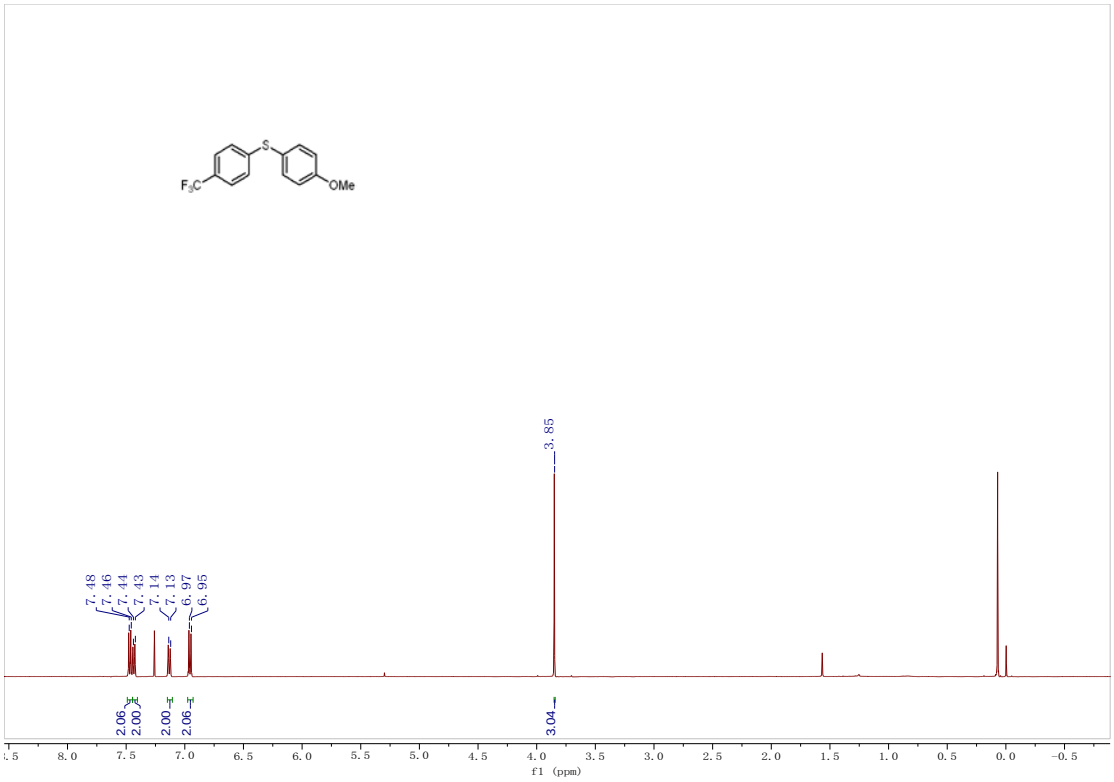
^{1}H NMR Spectrum of **3h** (400 MHz, $CDCl_3$)



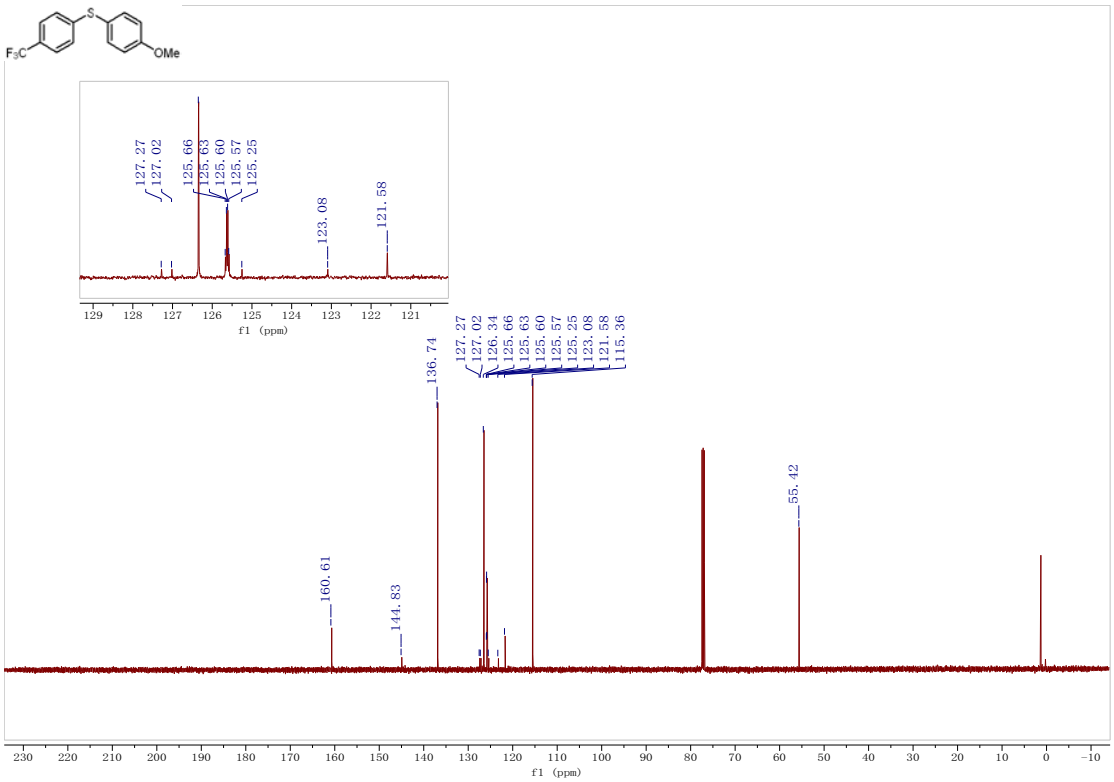
^{13}C NMR Spectrum of **3h** (101 MHz, $CDCl_3$)



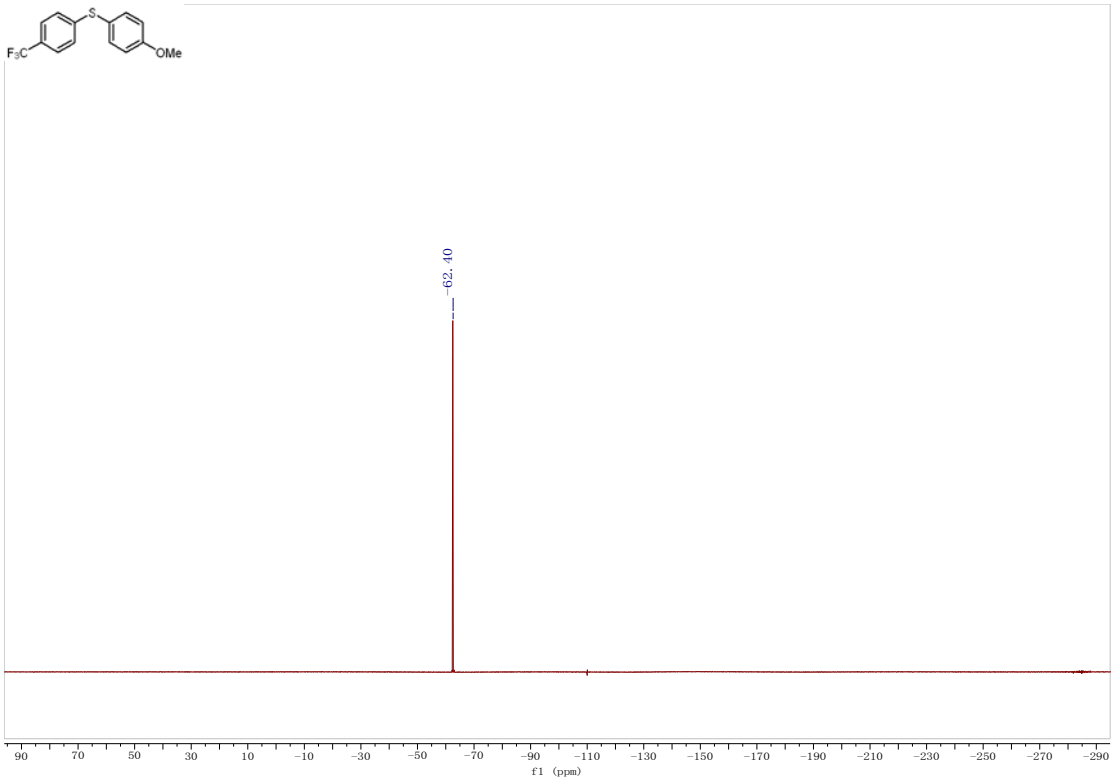
^{1}H NMR Spectrum of **3i** (500 MHz, $CDCl_3$)



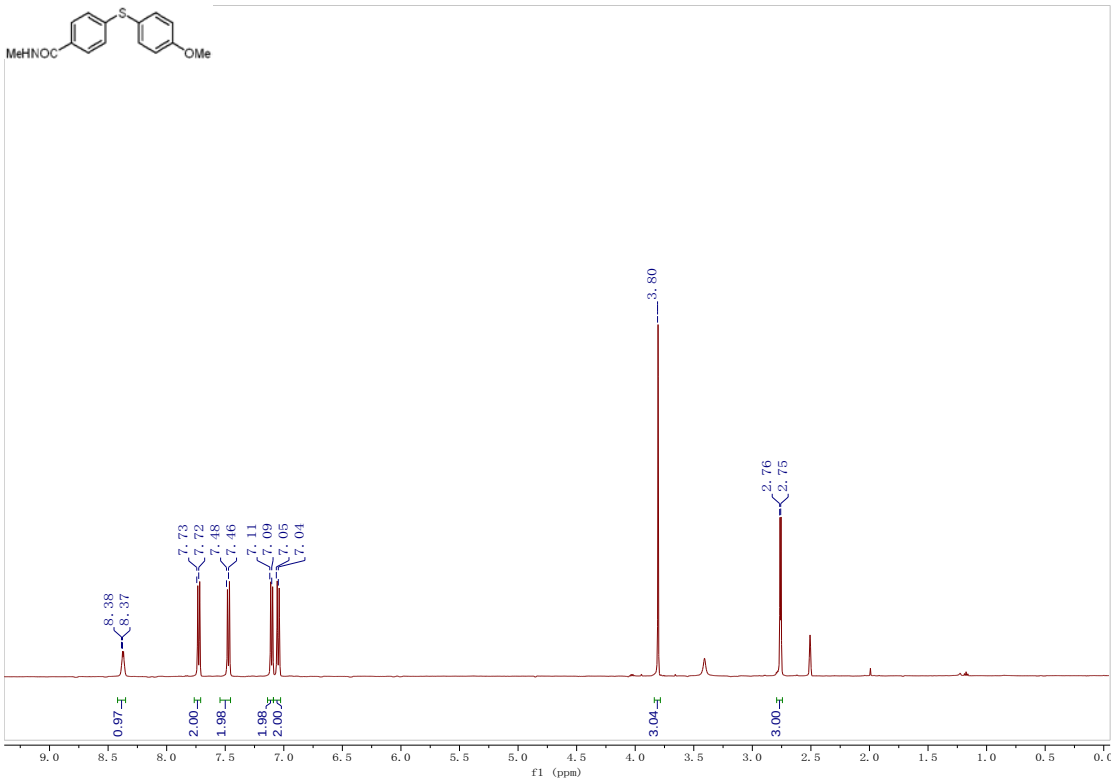
^{13}C NMR Spectrum of **3i** (126 MHz, $CDCl_3$)



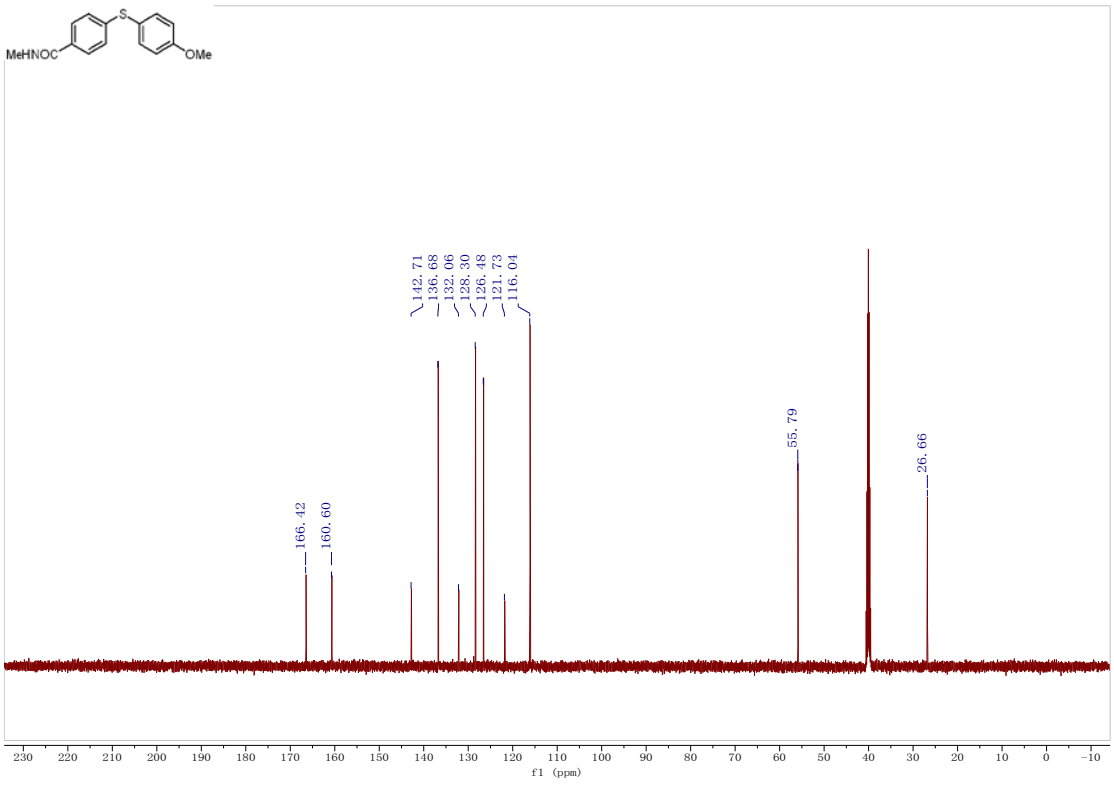
^{13}F NMR Spectrum of **3i** (376 MHz, DMSO-*d6*)



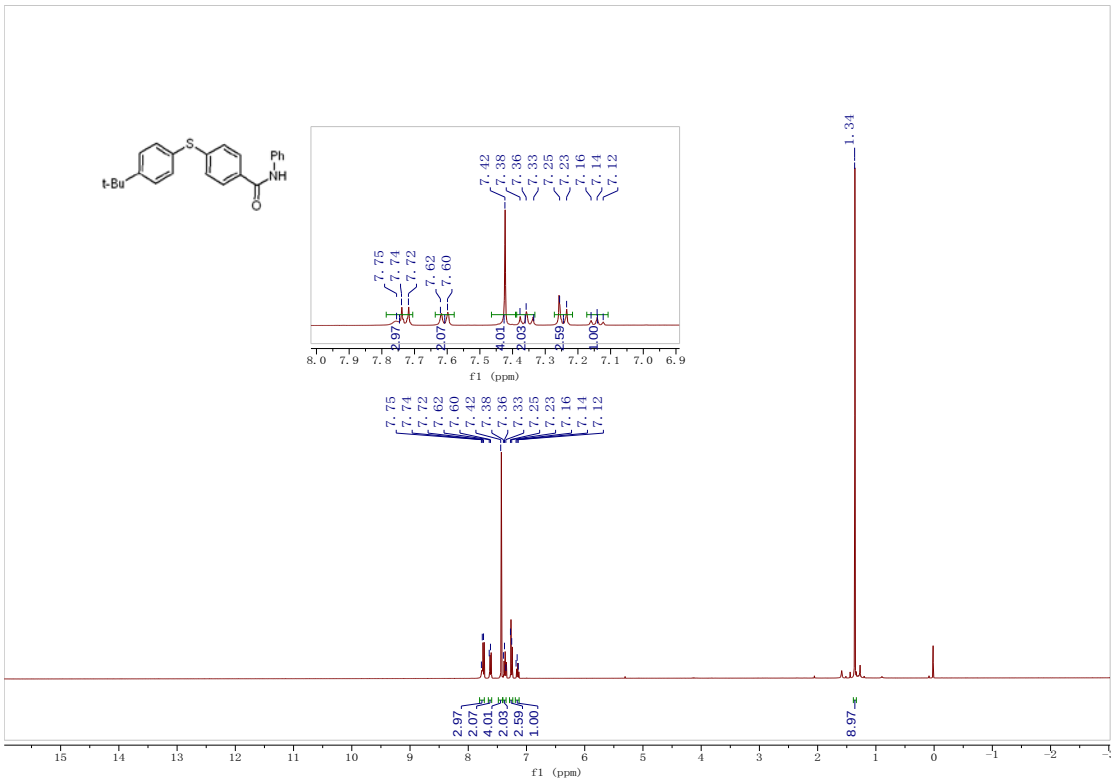
^{1}H NMR Spectrum of **3j** (500 MHz, DMSO-*d6*)



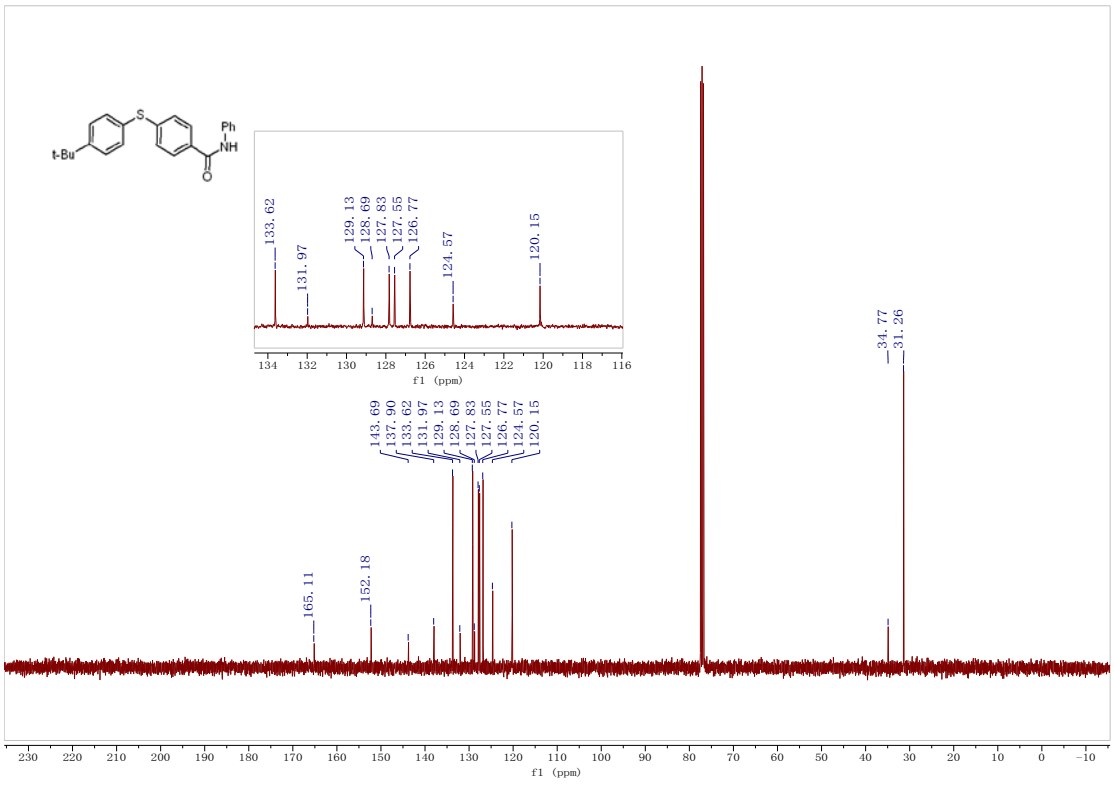
^{13}C NMR Spectrum of **3j** (126 MHz, DMSO-*d6*)



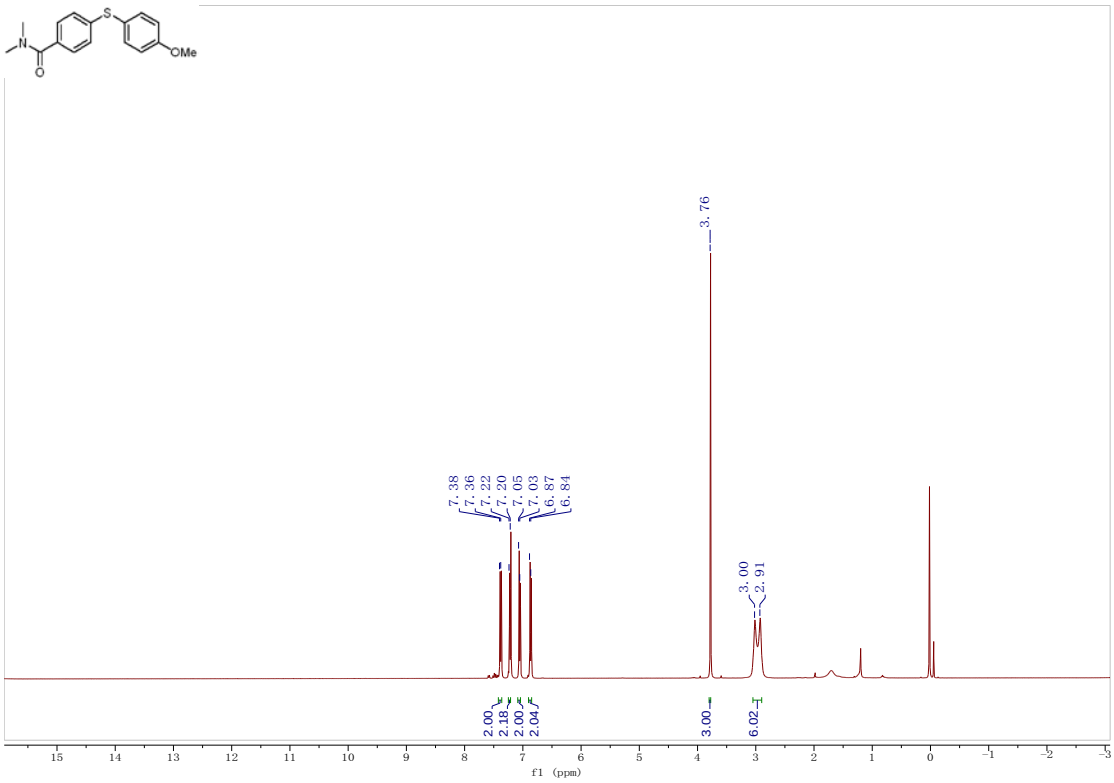
^{1}H NMR Spectrum of **3k** (400 MHz, $CDCl_3$)



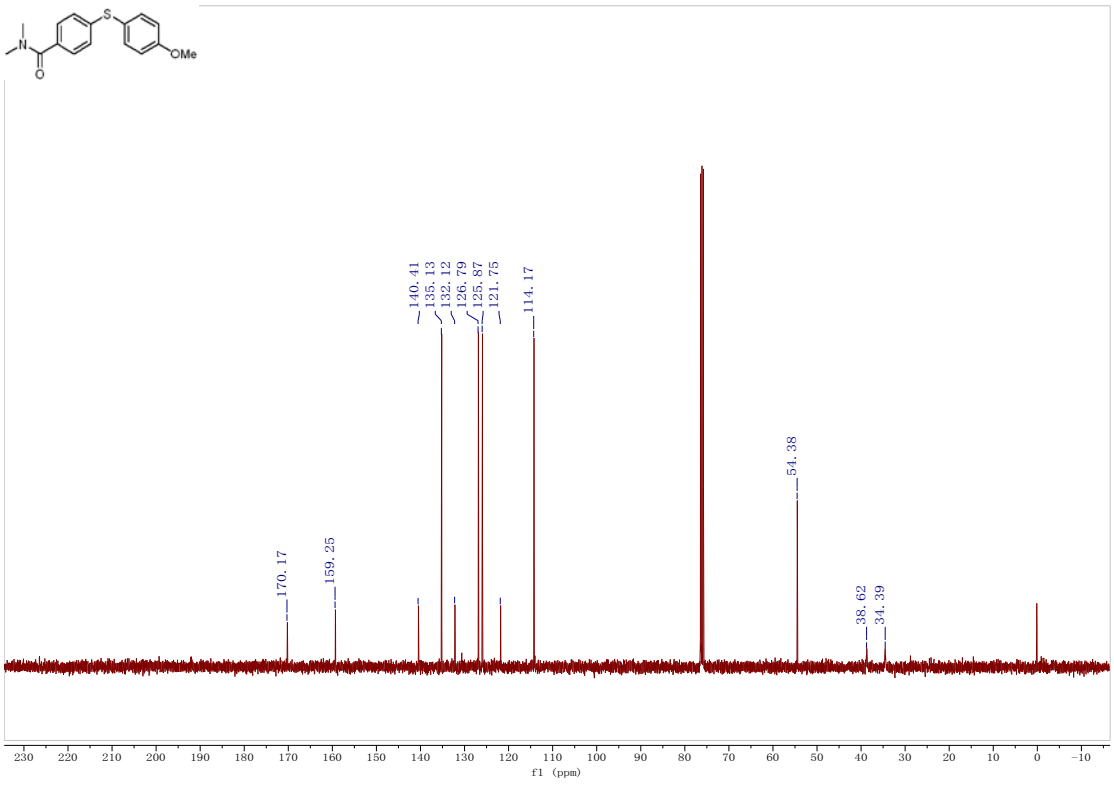
^{13}C NMR Spectrum of **3k** (101 MHz, $CDCl_3$)



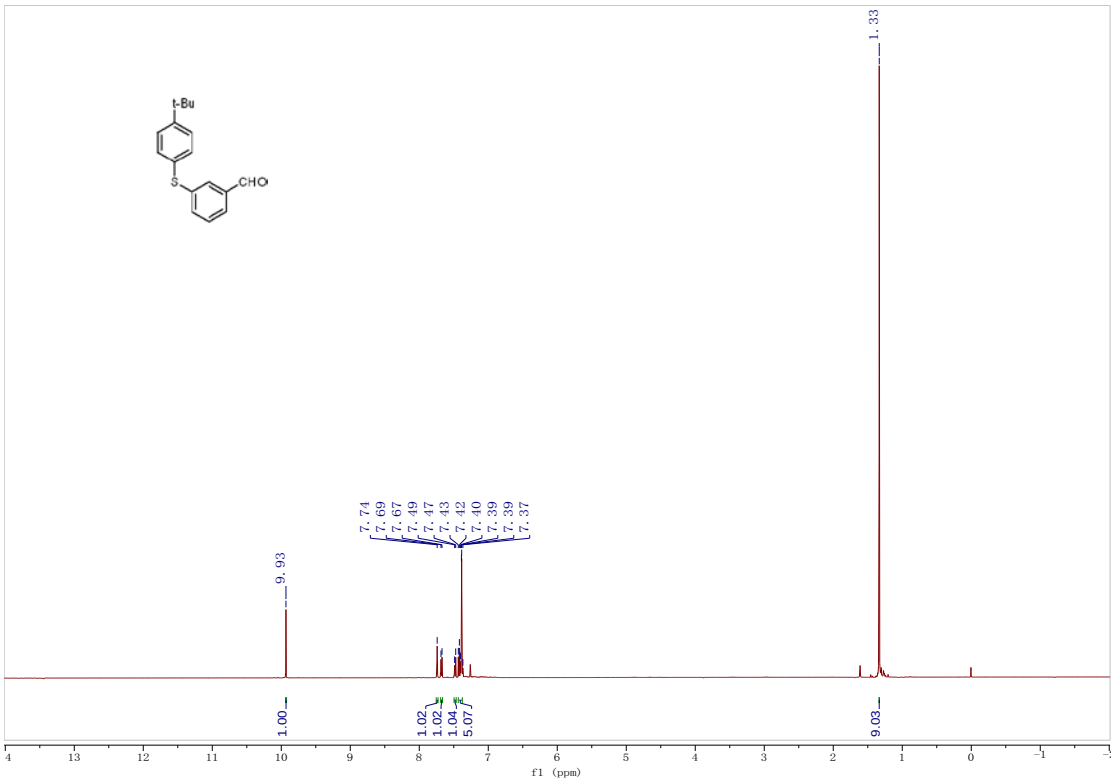
^{1}H NMR Spectrum of **3l** (400 MHz, $CDCl_3$)



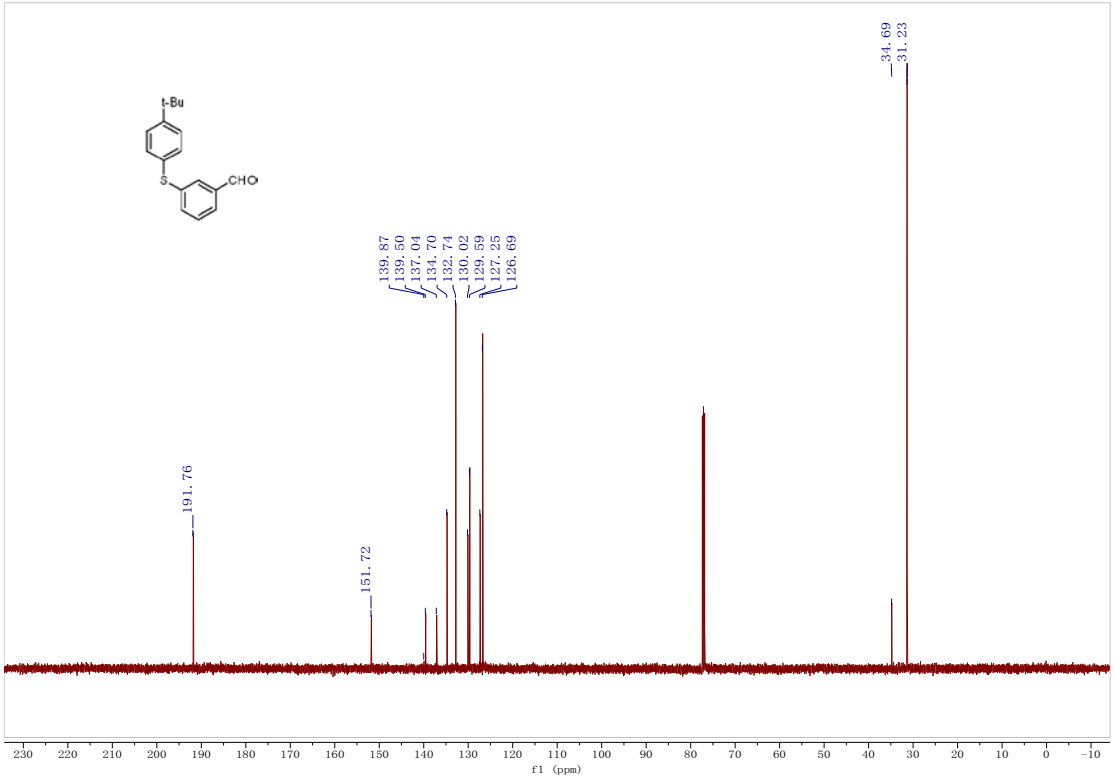
^{13}C NMR Spectrum of **3l** (101 MHz, $CDCl_3$)



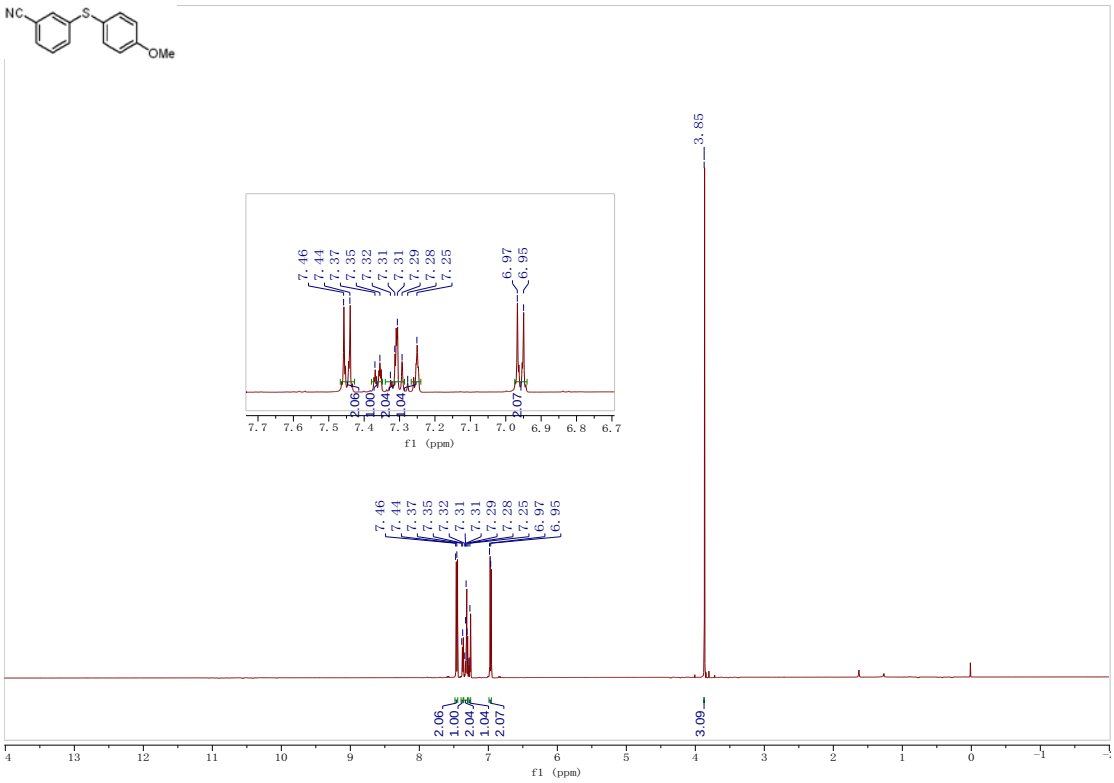
^{1}H NMR Spectrum of **3m** (500 MHz, $CDCl_3$)



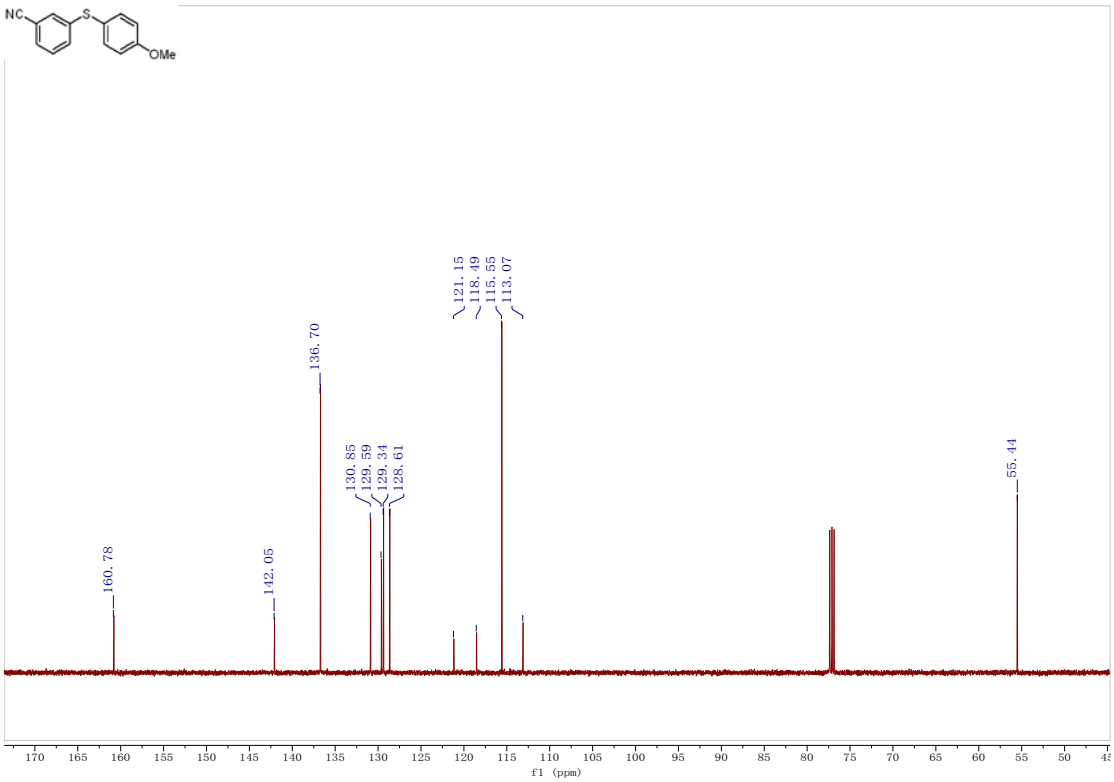
^{13}C NMR Spectrum of **3m** (126 MHz, $CDCl_3$)



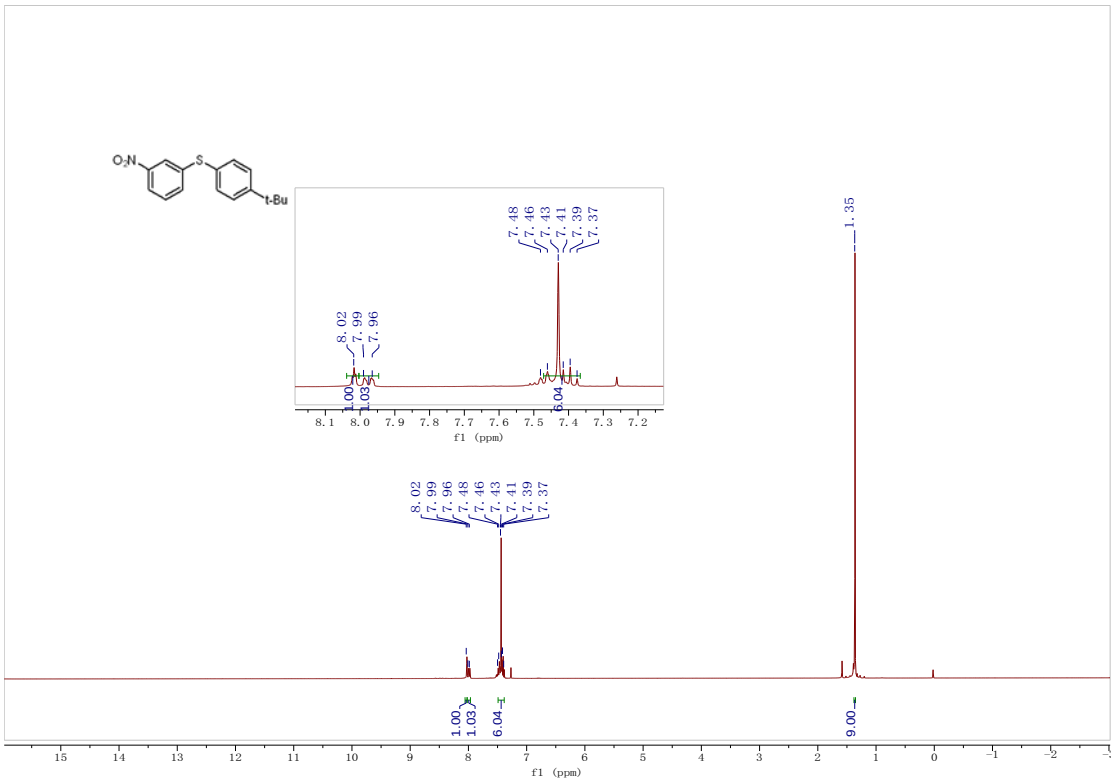
^{1}H NMR Spectrum of **3n** (500 MHz, $CDCl_3$)



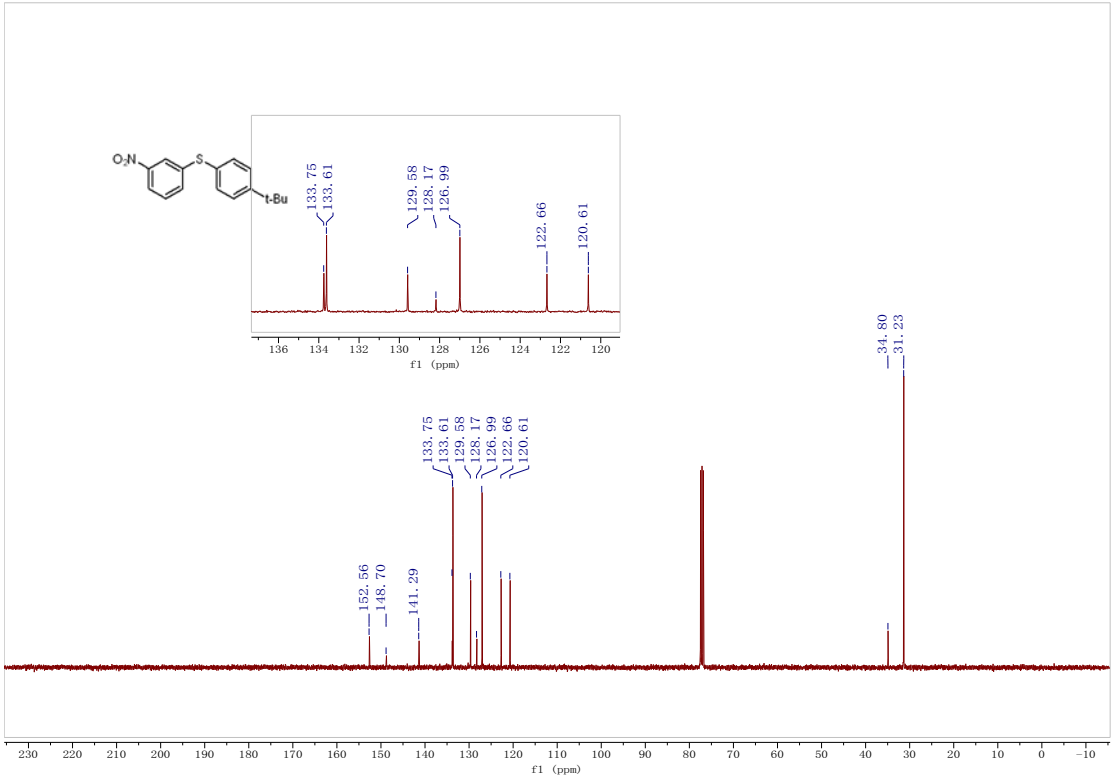
^{13}C NMR Spectrum of **3n** (126 MHz, $CDCl_3$)



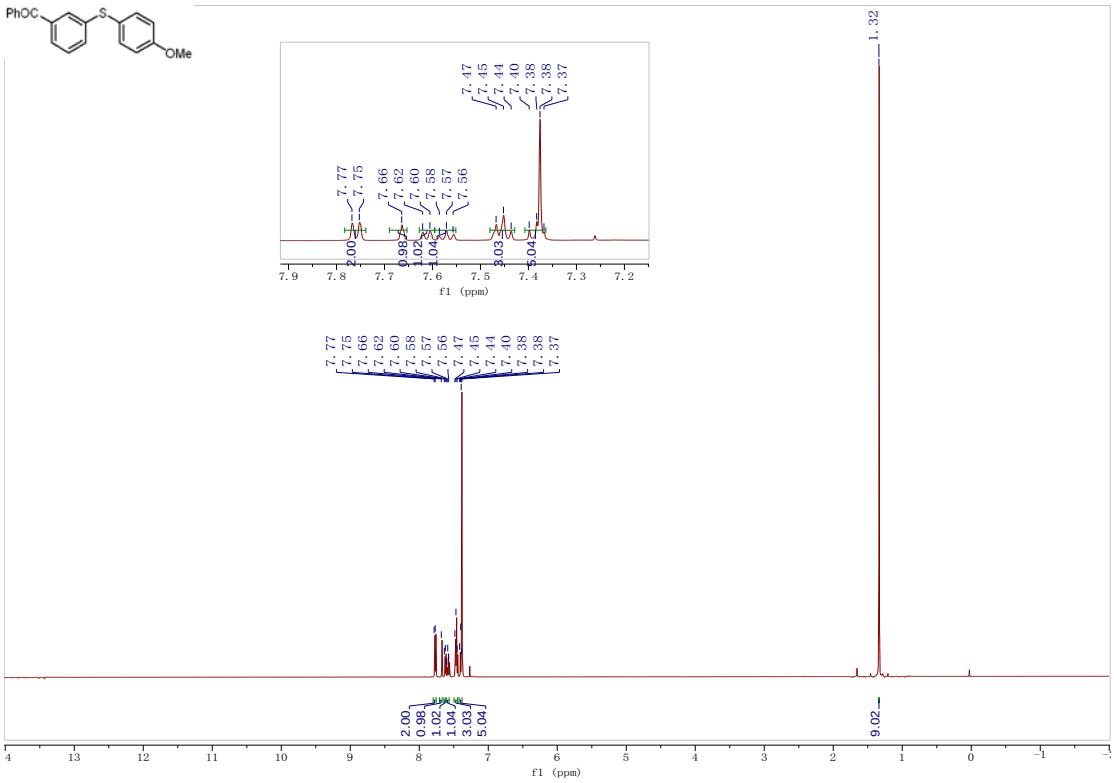
^{1}H NMR Spectrum of **3o** (400 MHz, $CDCl_3$)



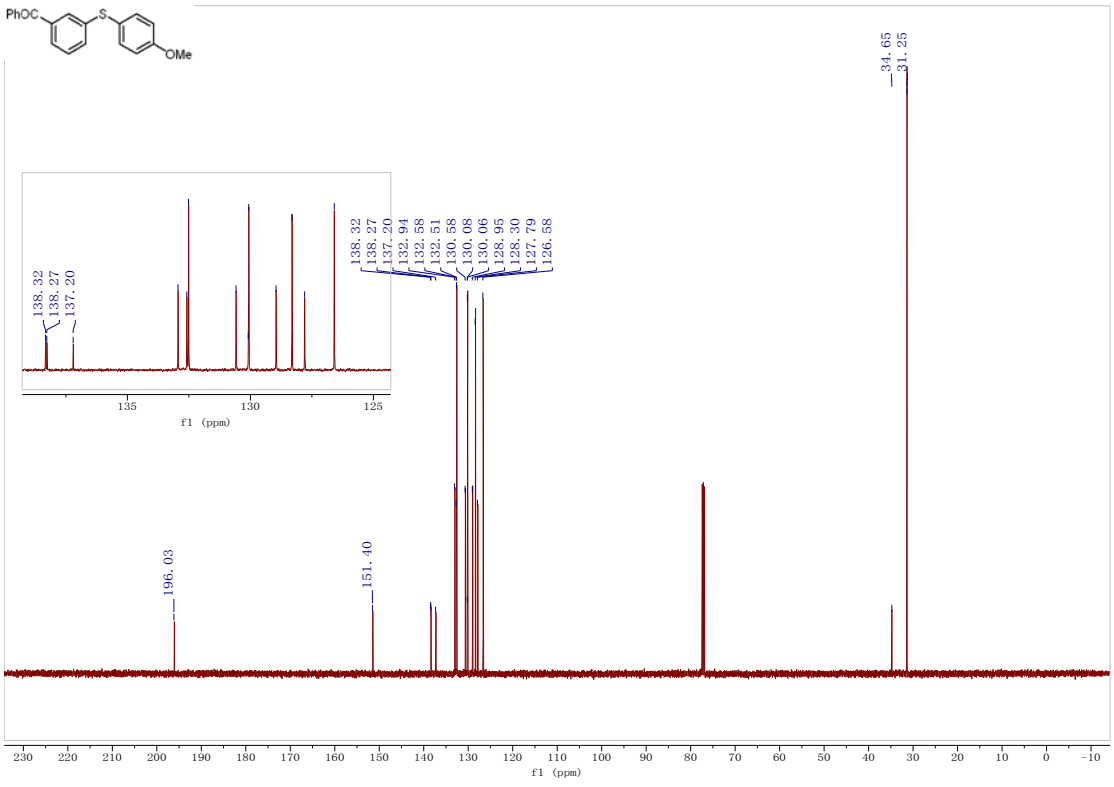
^{13}C NMR Spectrum of **3o** (101 MHz, $CDCl_3$)



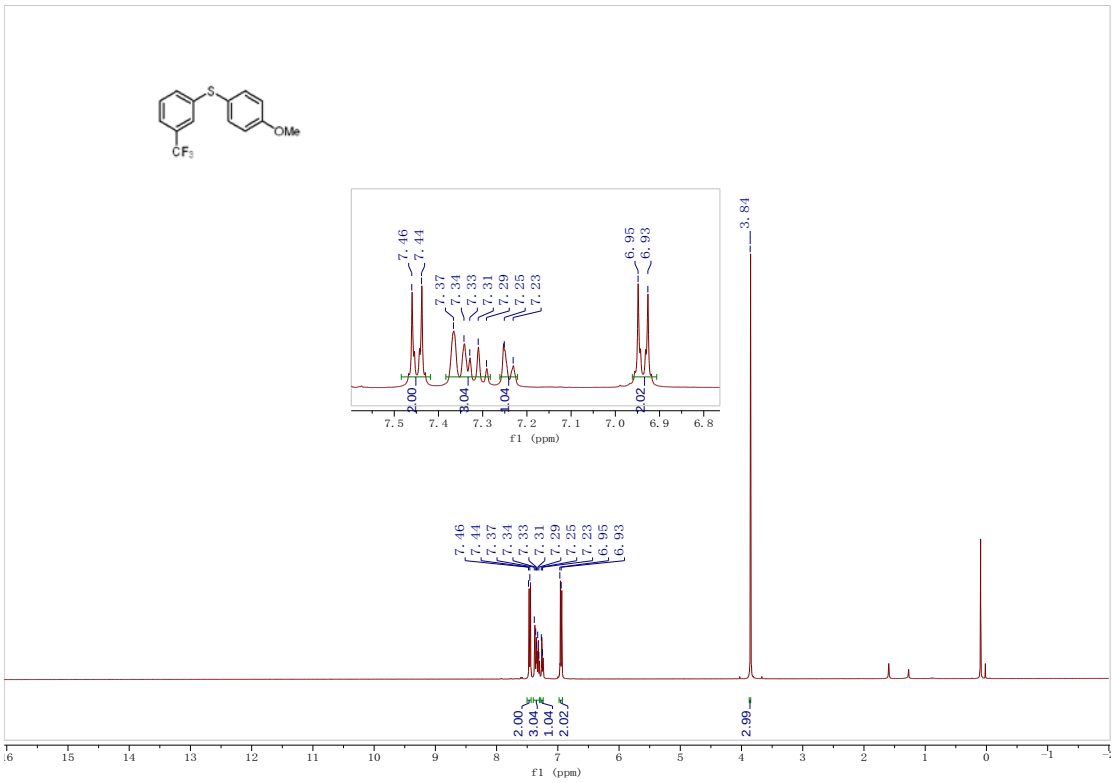
^{1}H NMR Spectrum of **3p** (500 MHz, $CDCl_3$)



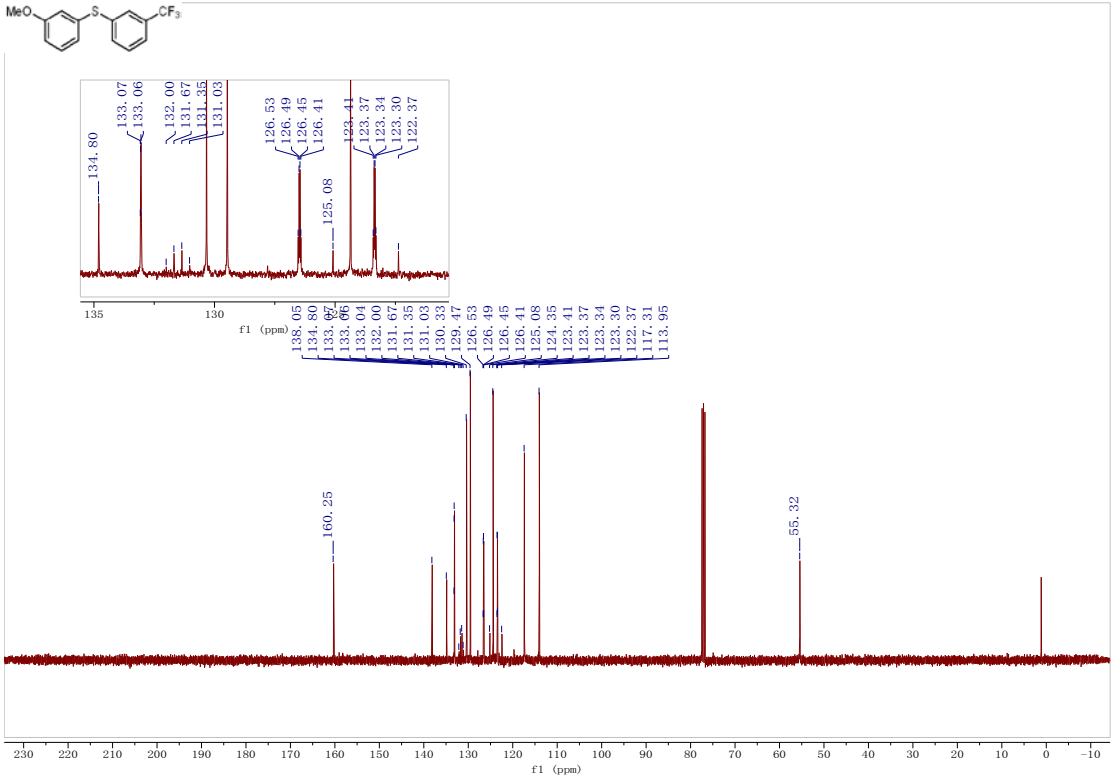
^{13}C NMR Spectrum of **3p** (126 MHz, $CDCl_3$)



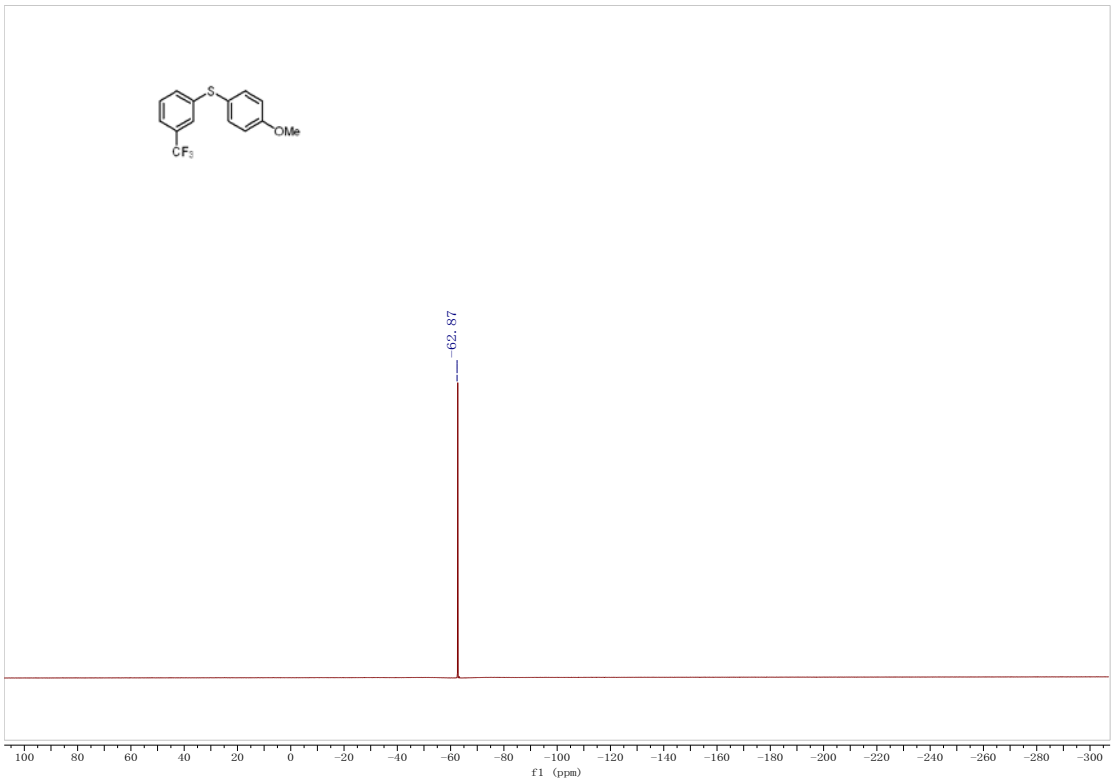
^{1}H NMR Spectrum of **3r** (400 MHz, $CDCl_3$)



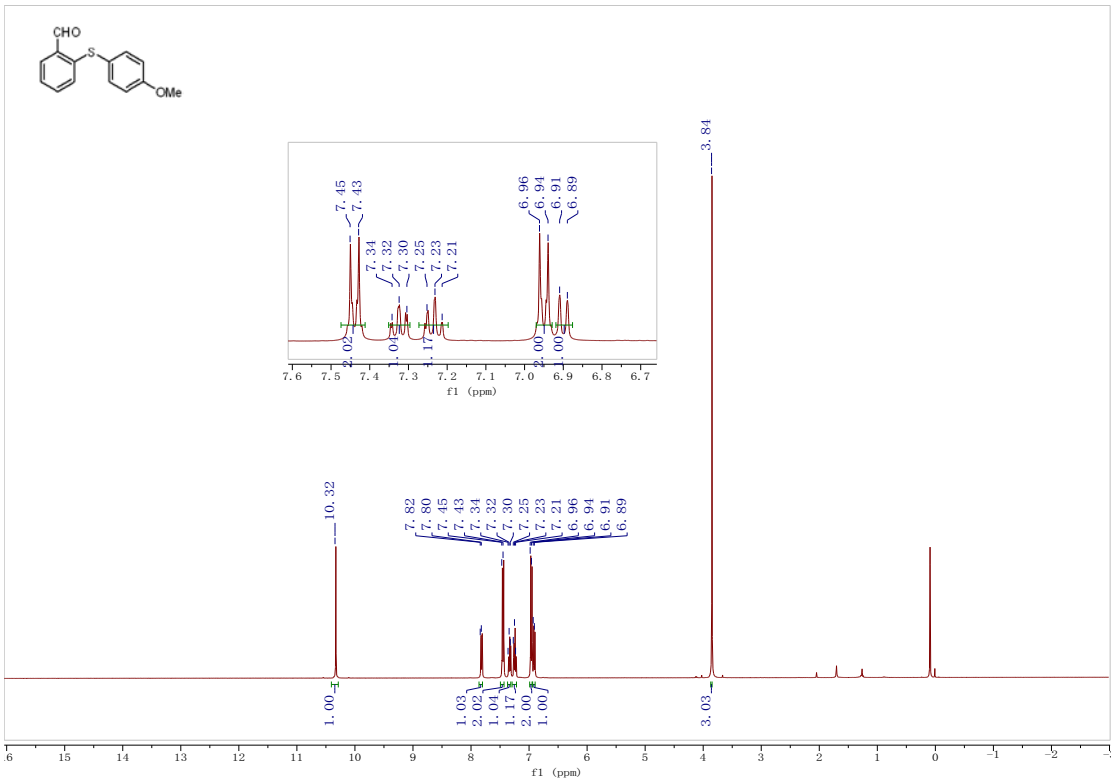
^{13}C NMR Spectrum of **3r** (101 MHz, $CDCl_3$)



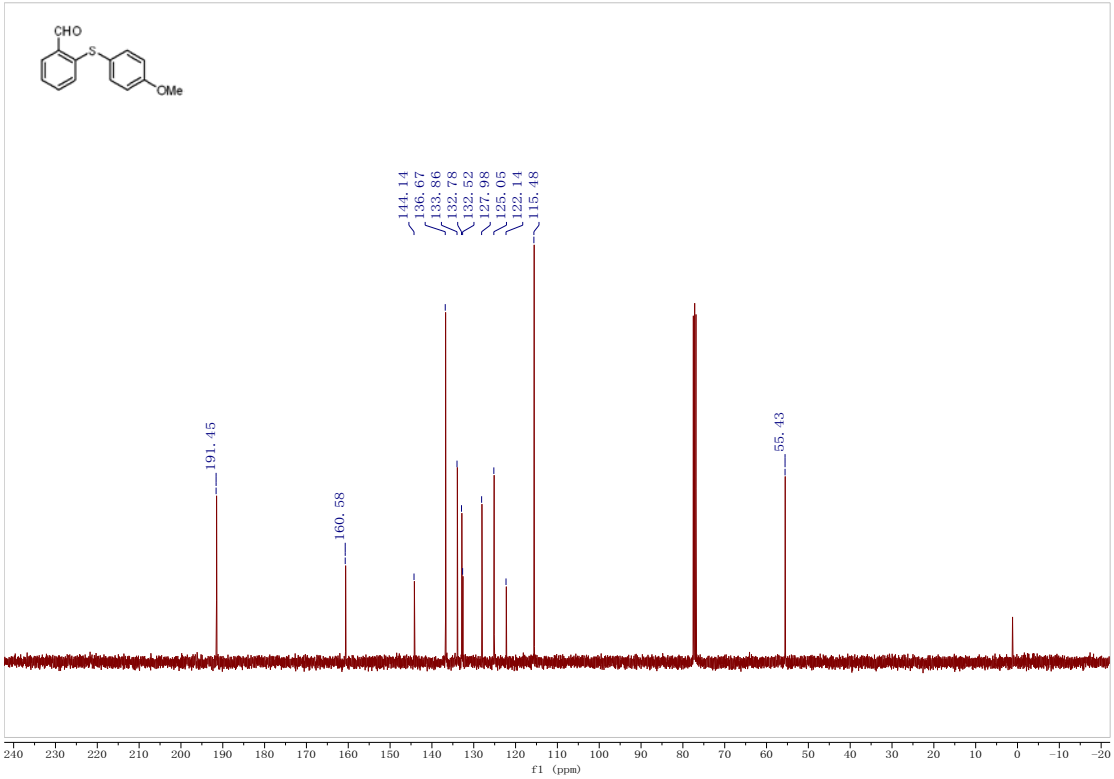
^{19}F NMR Spectrum of **3r** (376 MHz, $CDCl_3$)



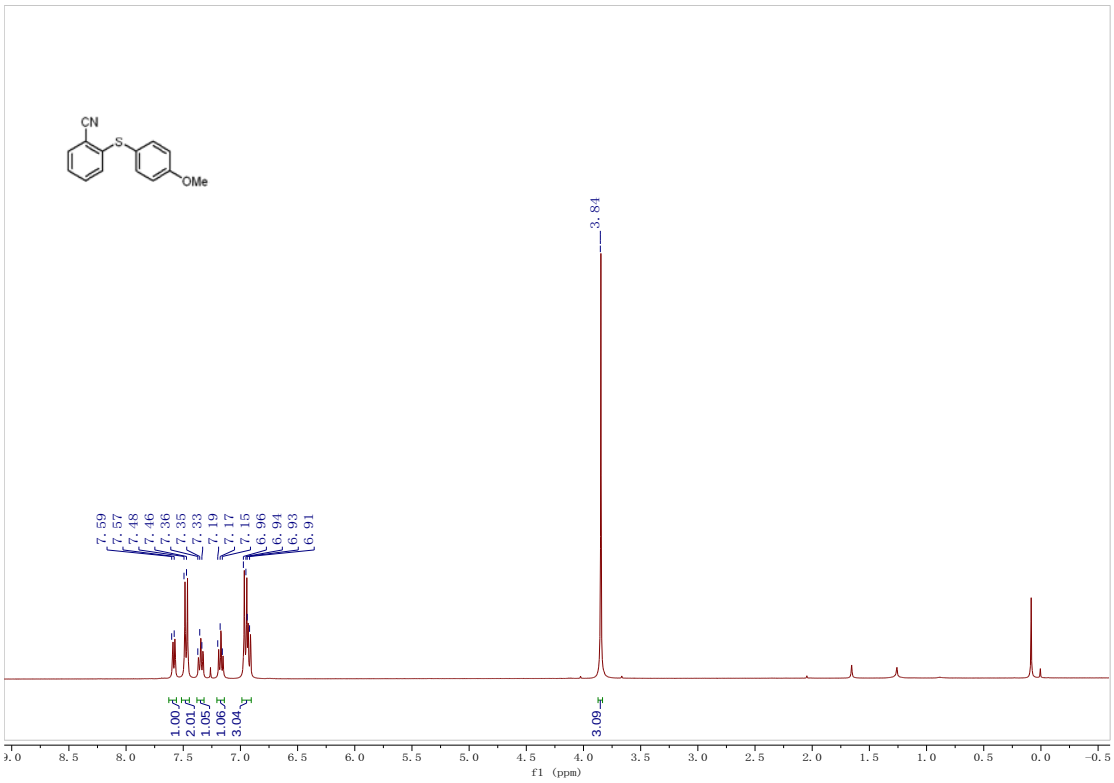
^{1}H NMR Spectrum of **3s** (400 MHz, $CDCl_3$)



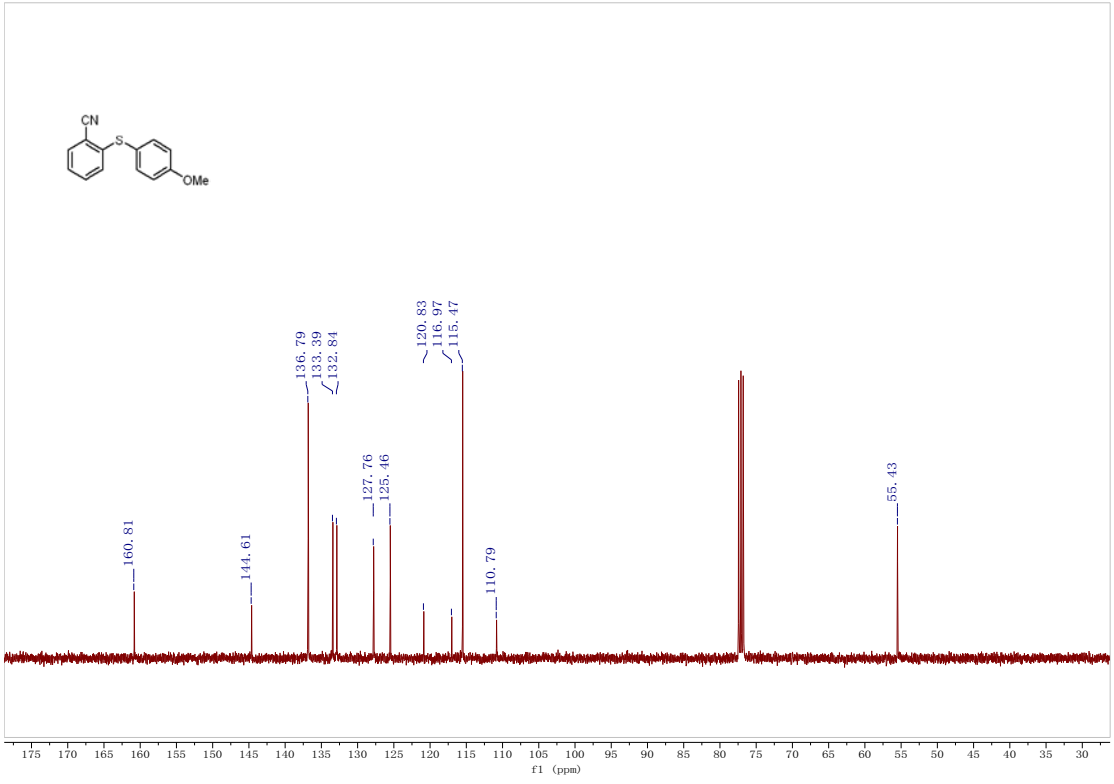
^{13}C NMR Spectrum of **3s** (101 MHz, $CDCl_3$)



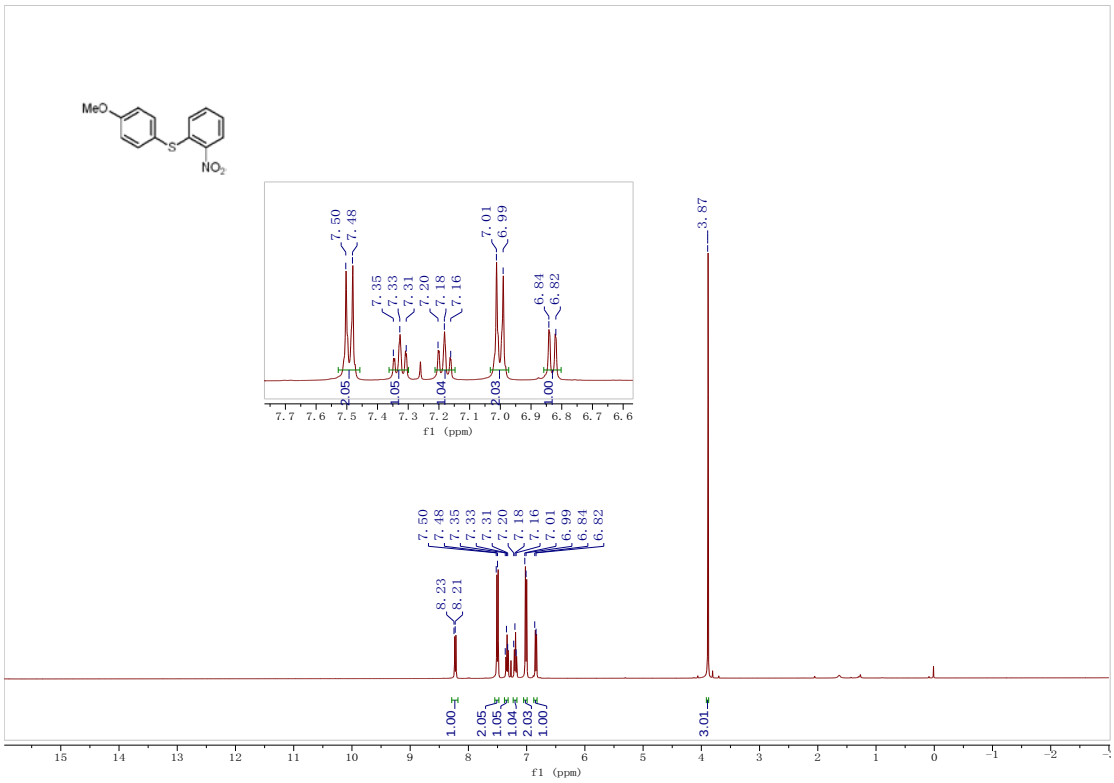
^{1}H NMR Spectrum of **3t** (400 MHz, $CDCl_3$)



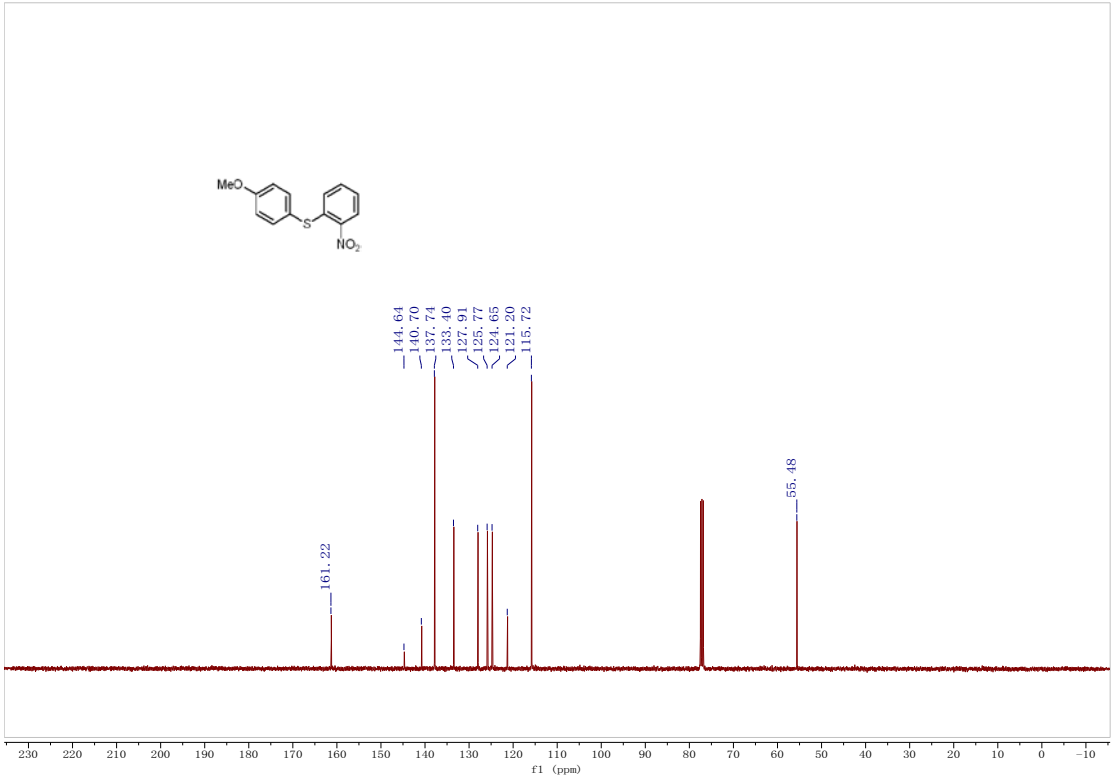
^{13}C NMR Spectrum of **3t** (101 MHz, $CDCl_3$)



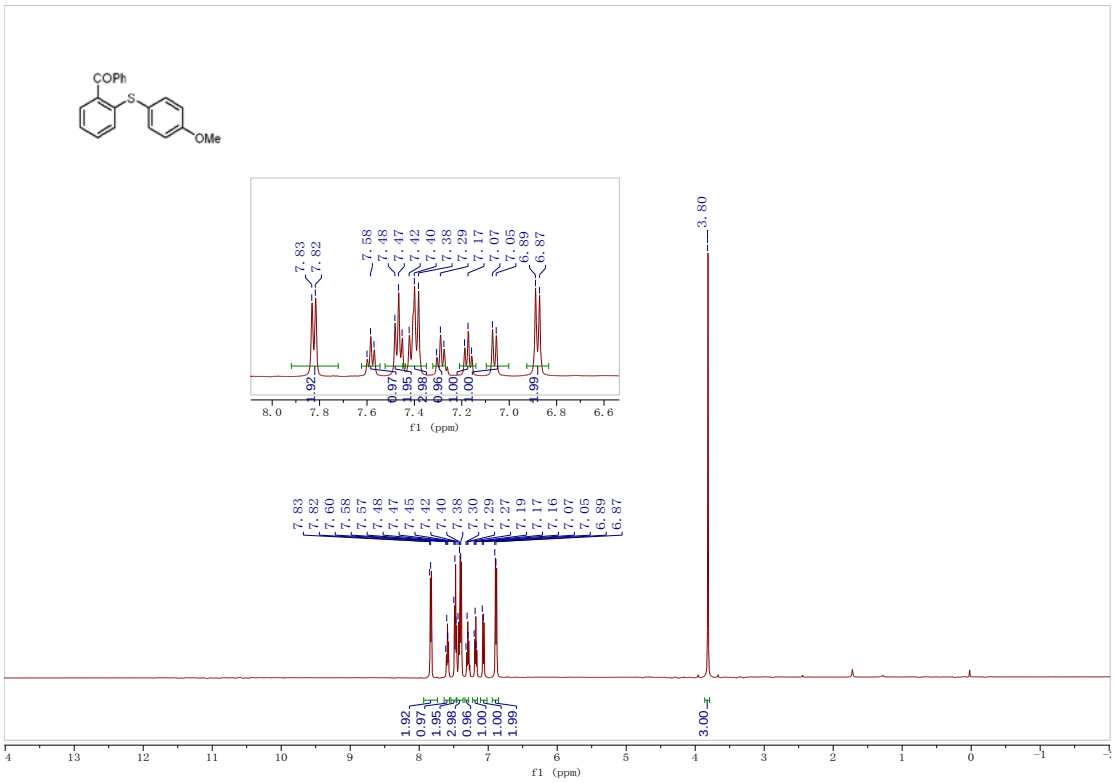
^{1}H NMR Spectrum of **3u** (400 MHz, $CDCl_3$)



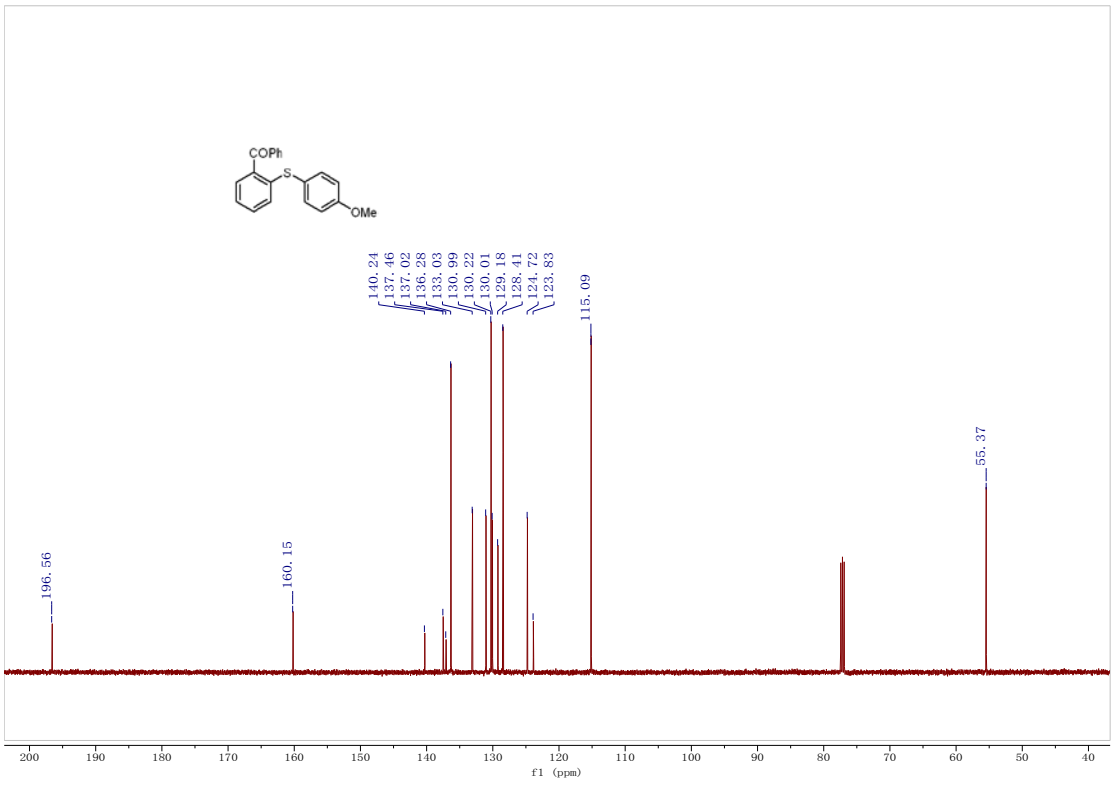
^{13}C NMR Spectrum of **3u** (101 MHz, $CDCl_3$)



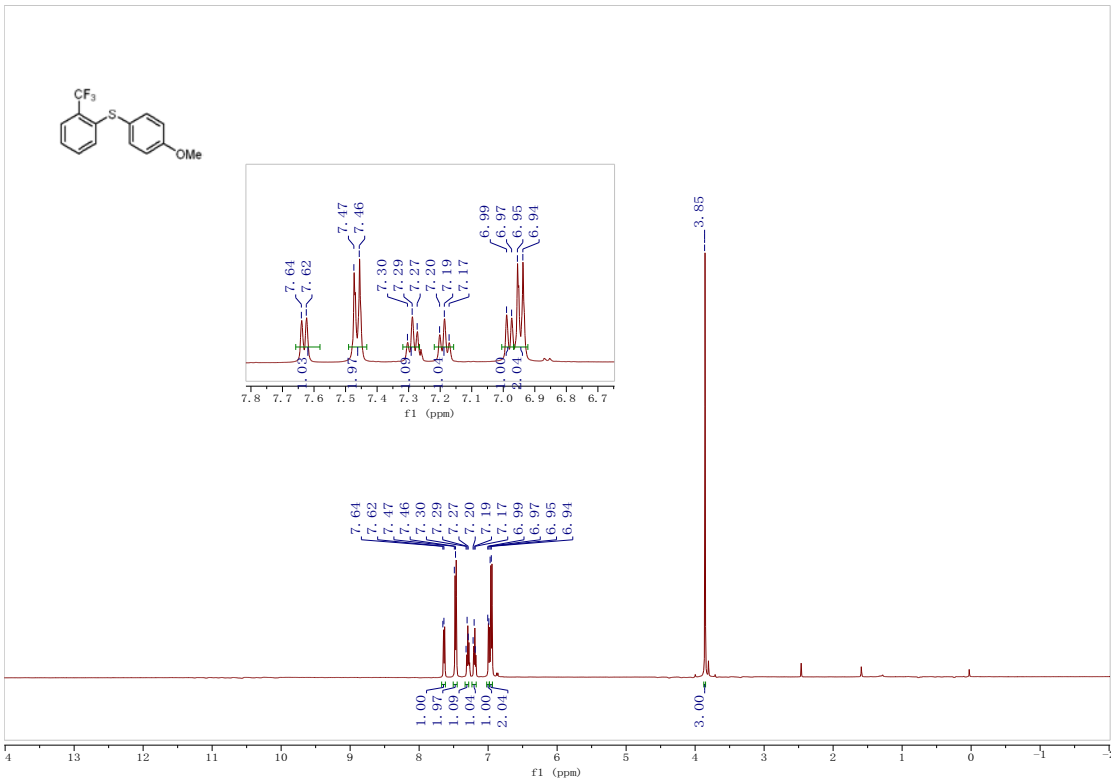
^{1}H NMR Spectrum of **3v** (500 MHz, $CDCl_3$)



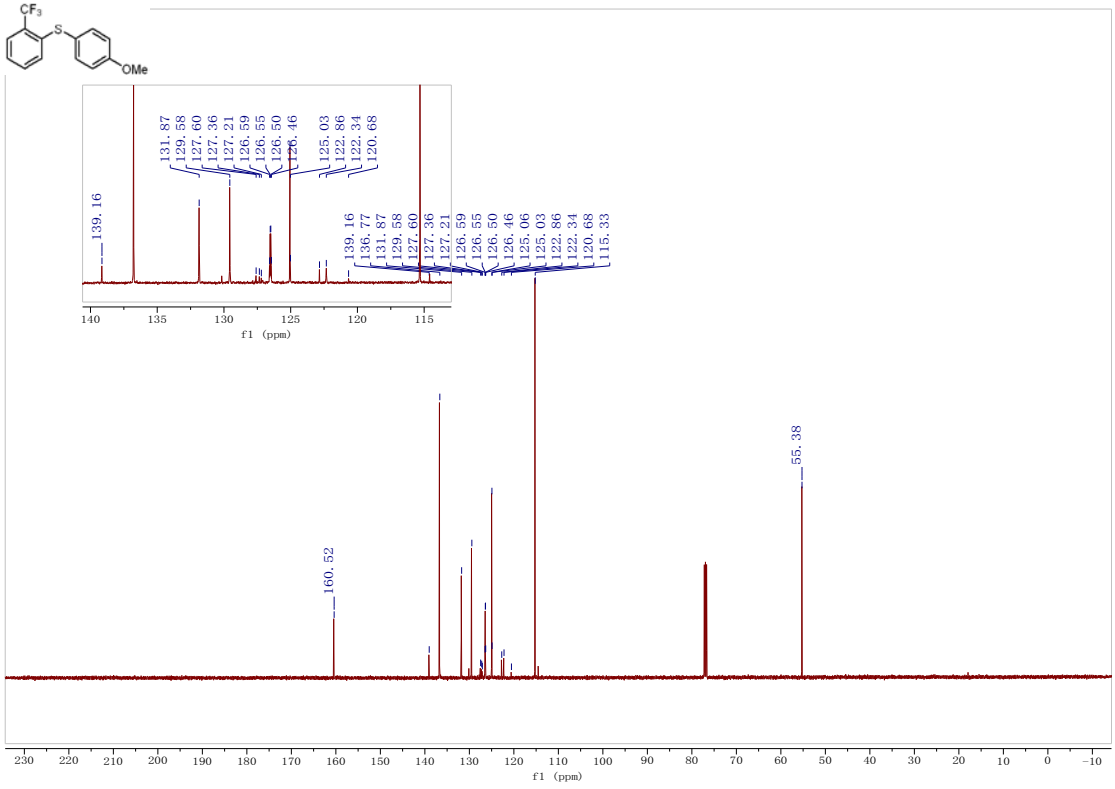
^{13}C NMR Spectrum of **3v** (126 MHz, $CDCl_3$)



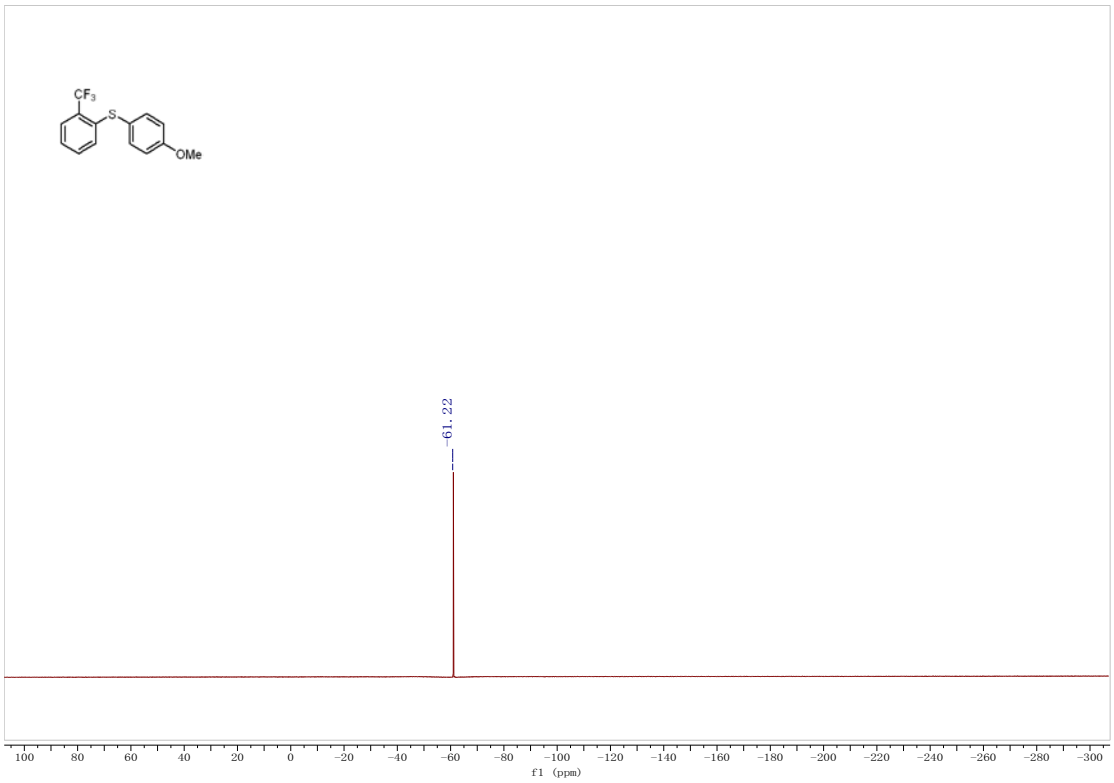
^{1}H NMR Spectrum of **3w** (500 MHz, $CDCl_3$)



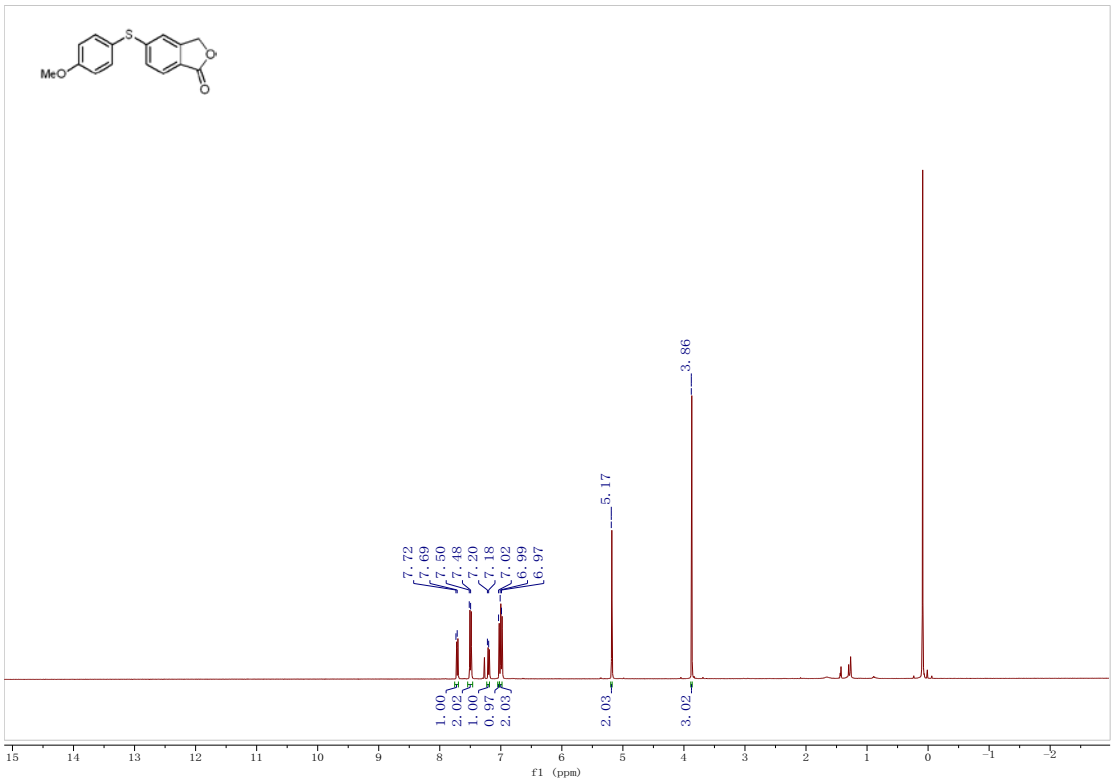
^{13}C NMR Spectrum of **3w** (126 MHz, $CDCl_3$)



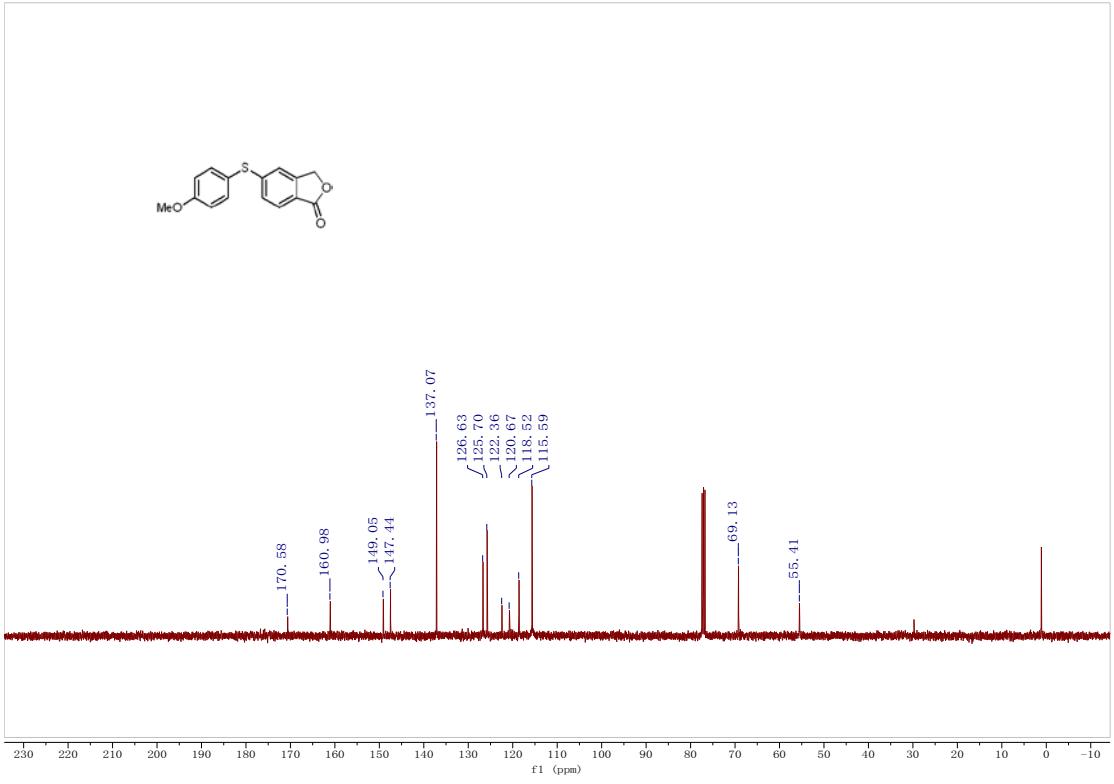
^{19}F NMR Spectrum of **3w** (376 MHz, $CDCl_3$)



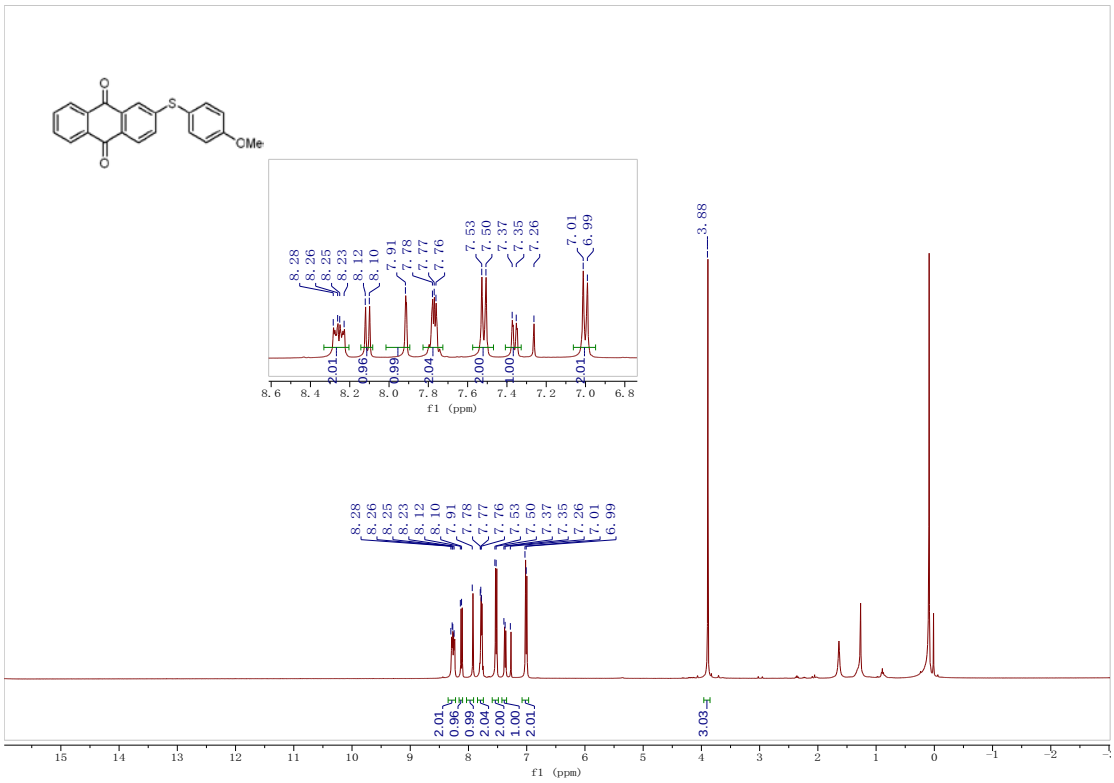
^{1}H NMR Spectrum of **3x** (400 MHz, $CDCl_3$)



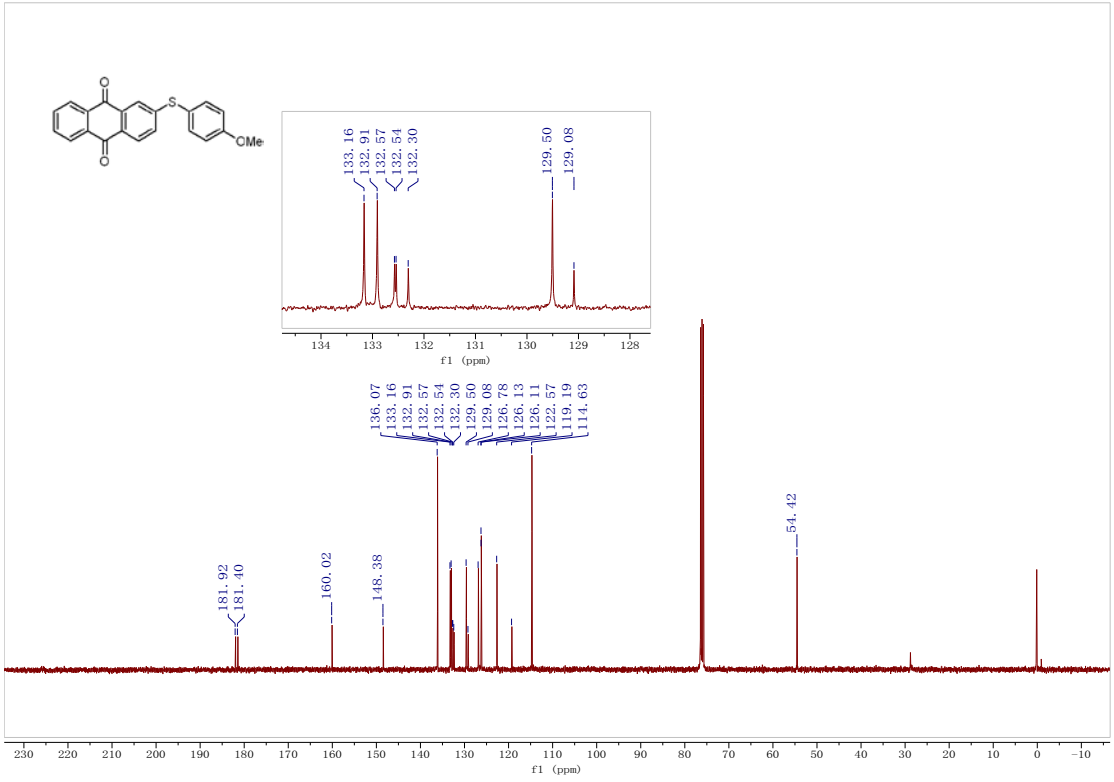
^{13}C NMR Spectrum of **3x** (101 MHz, $CDCl_3$)



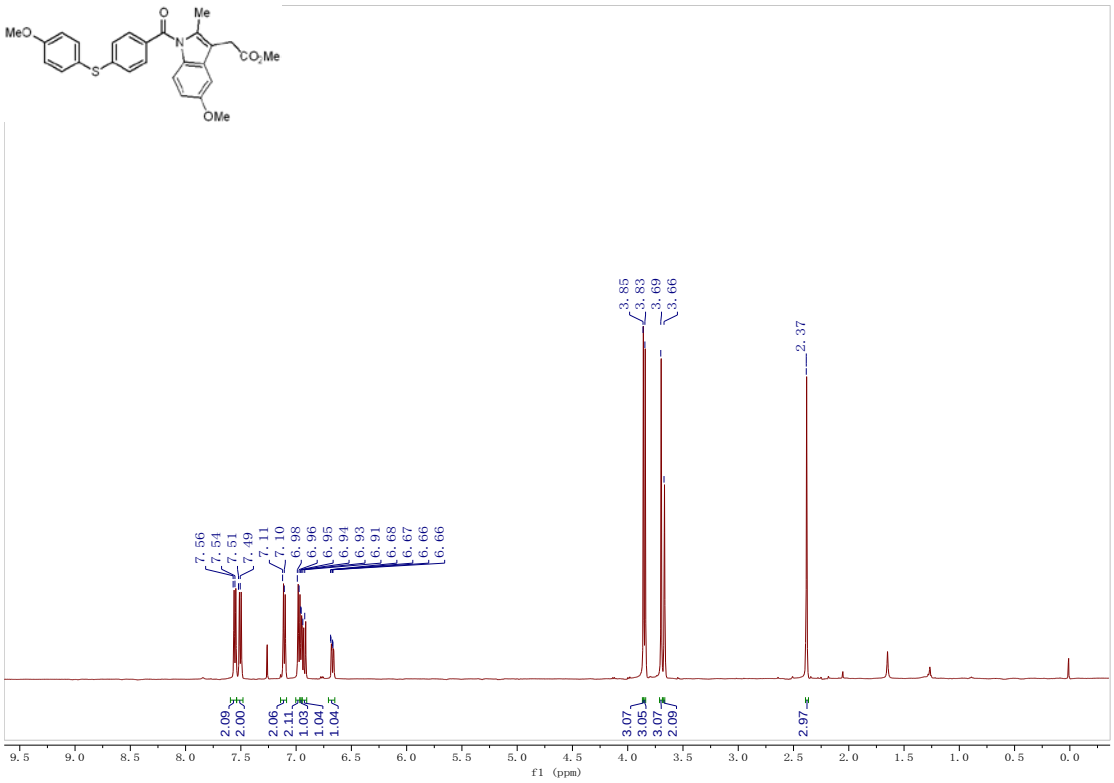
^{1}H NMR Spectrum of **3y** (400 MHz, $CDCl_3$)



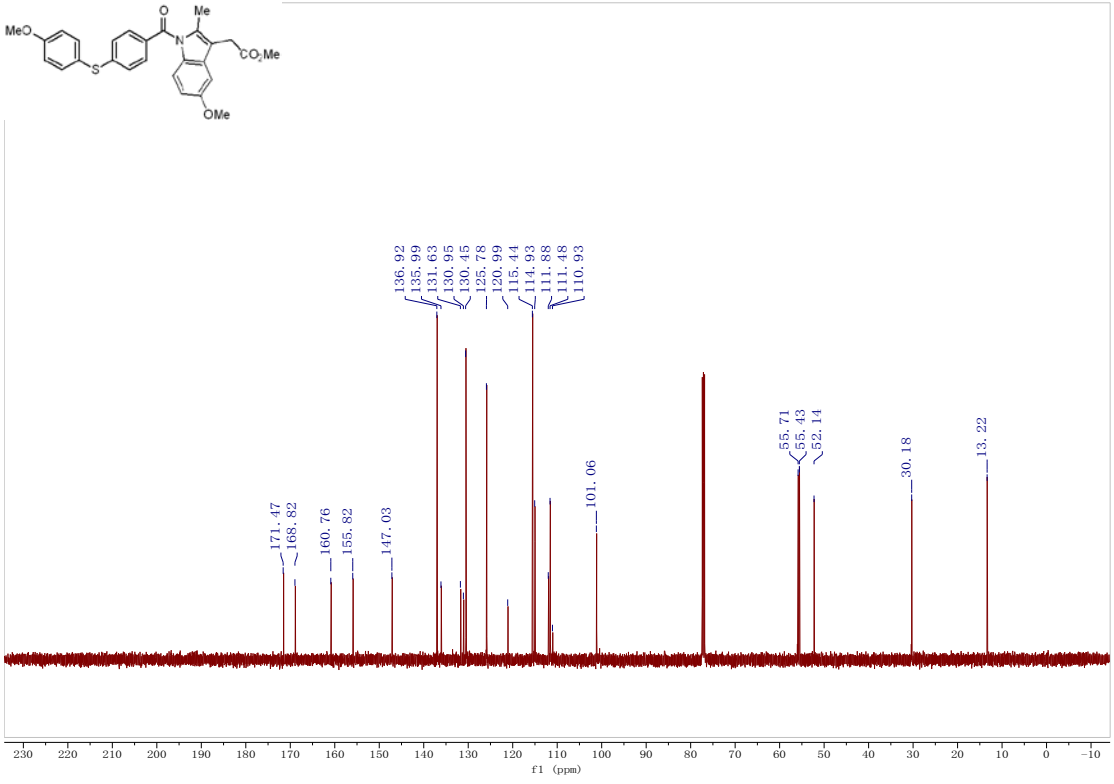
^{13}C NMR Spectrum of **3y** (101 MHz, $CDCl_3$)



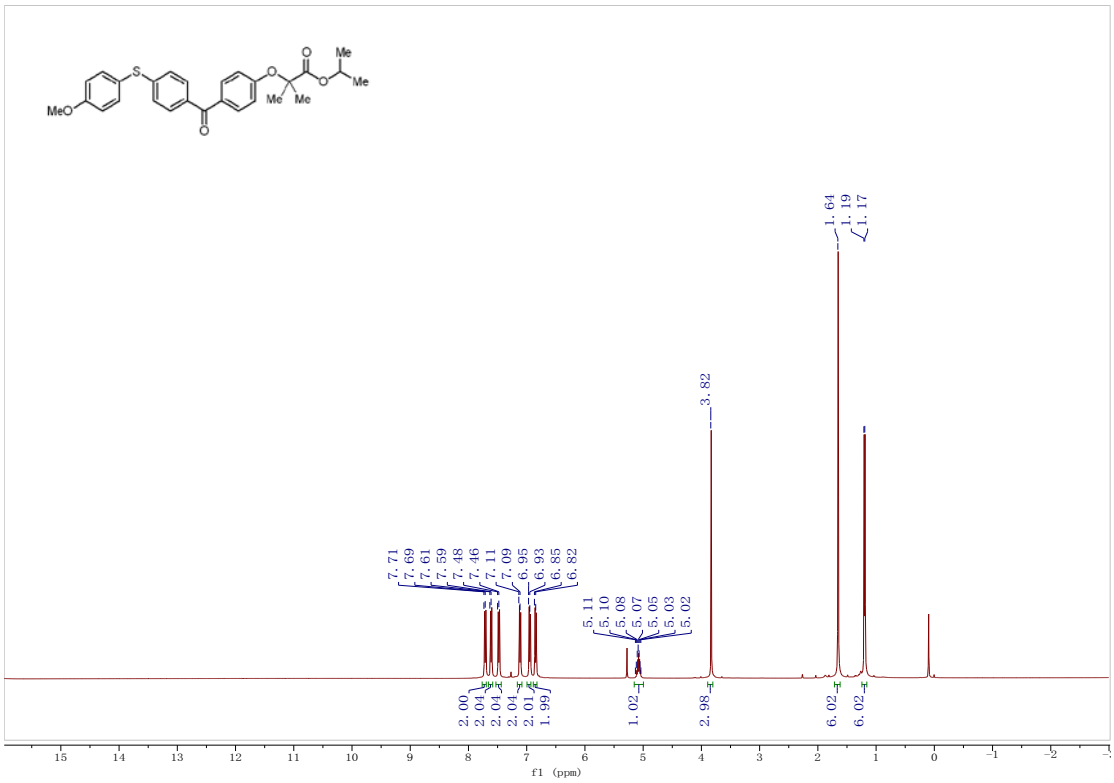
^{1}H NMR Spectrum of **3z** (500 MHz, $CDCl_3$)



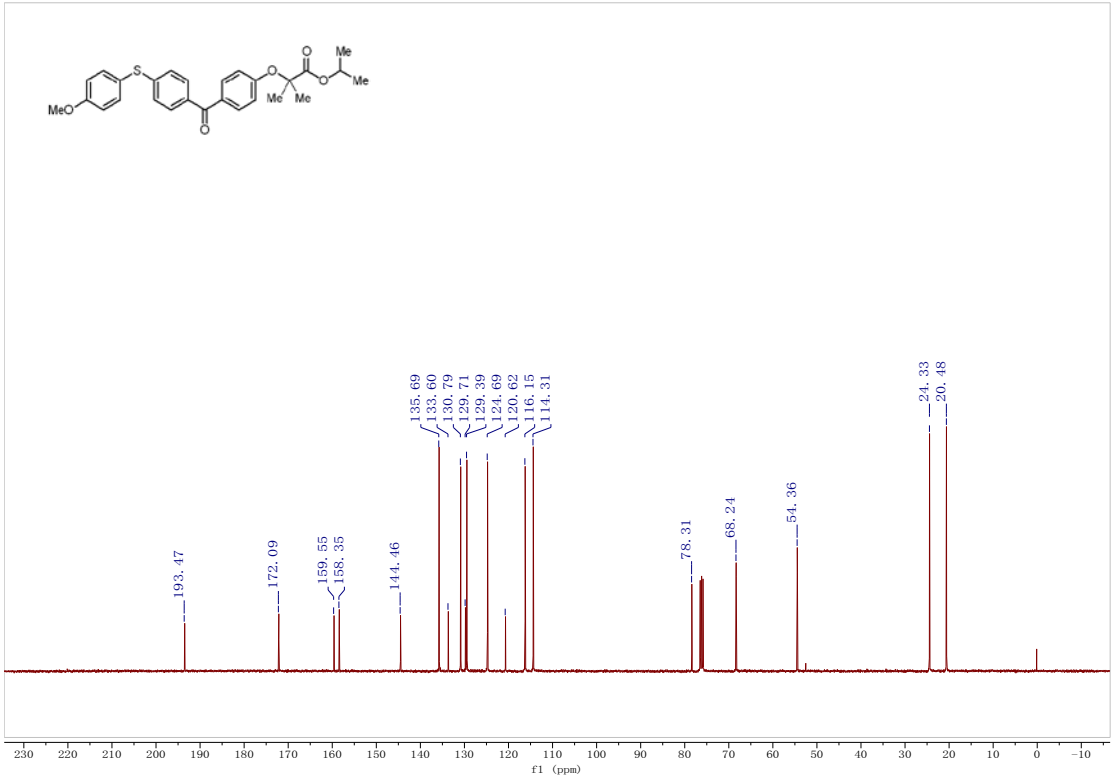
^{13}C NMR Spectrum of **3z** (101 MHz, $CDCl_3$)



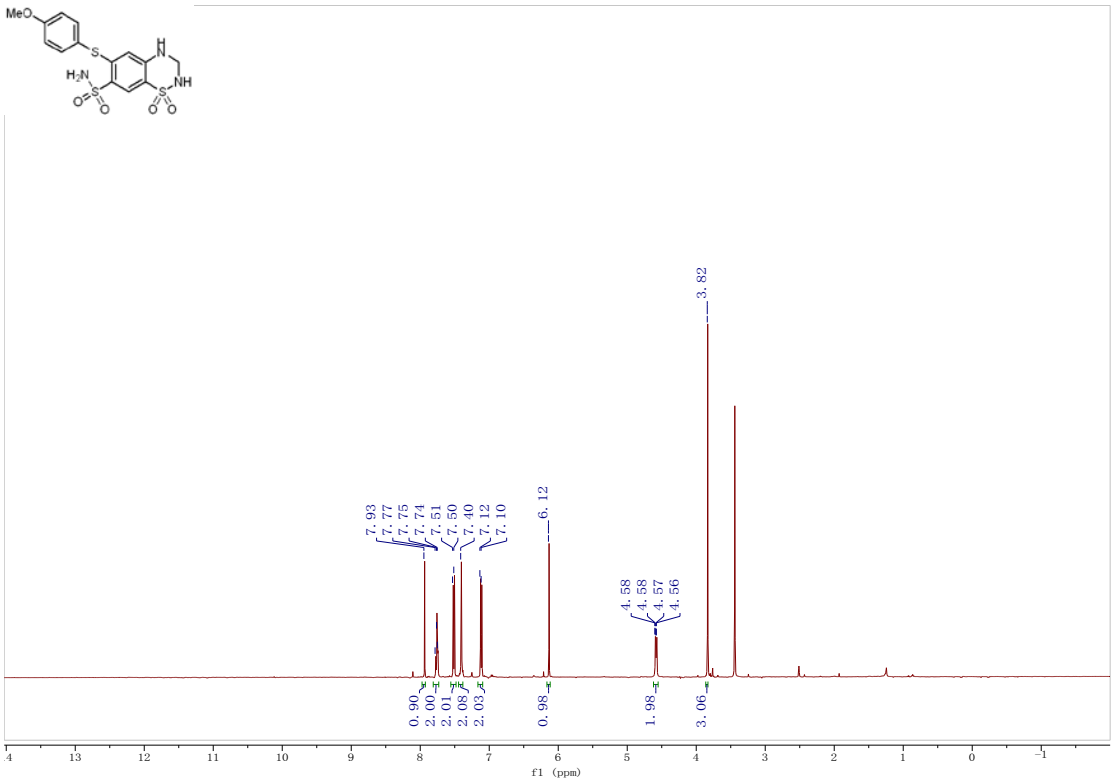
^{1}H NMR Spectrum of **3aa** (400 MHz, $CDCl_3$)



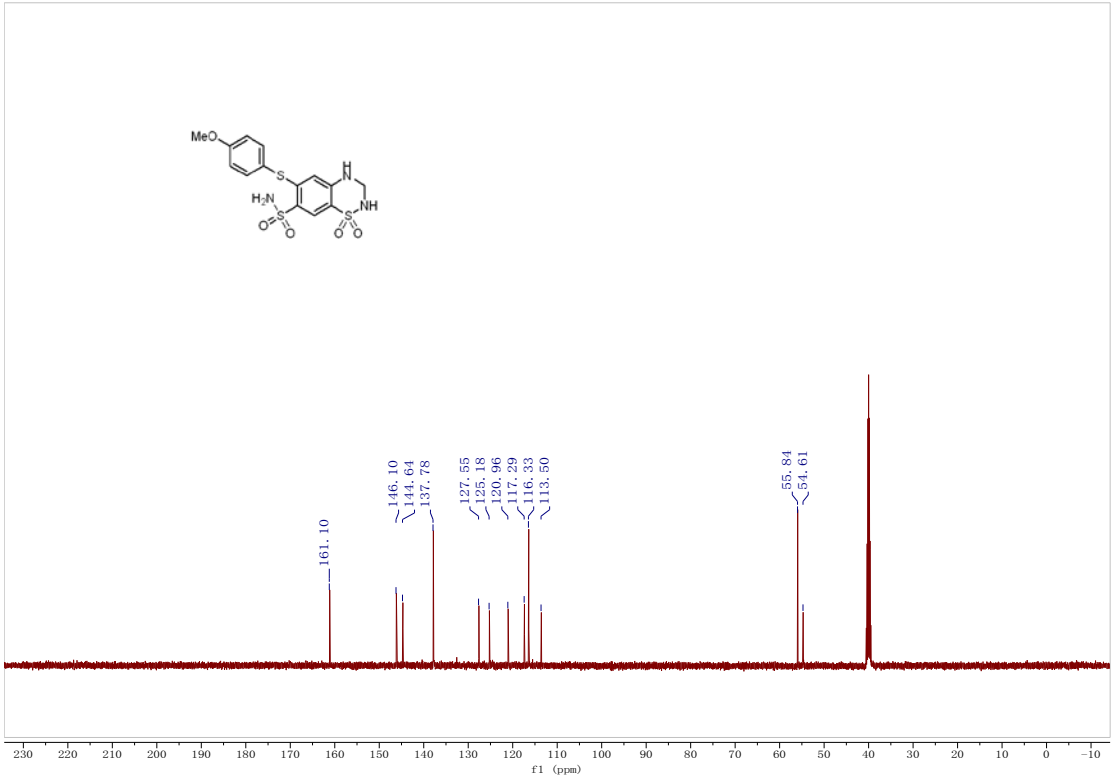
^{13}C NMR Spectrum of **3aa** (101 MHz, $CDCl_3$)



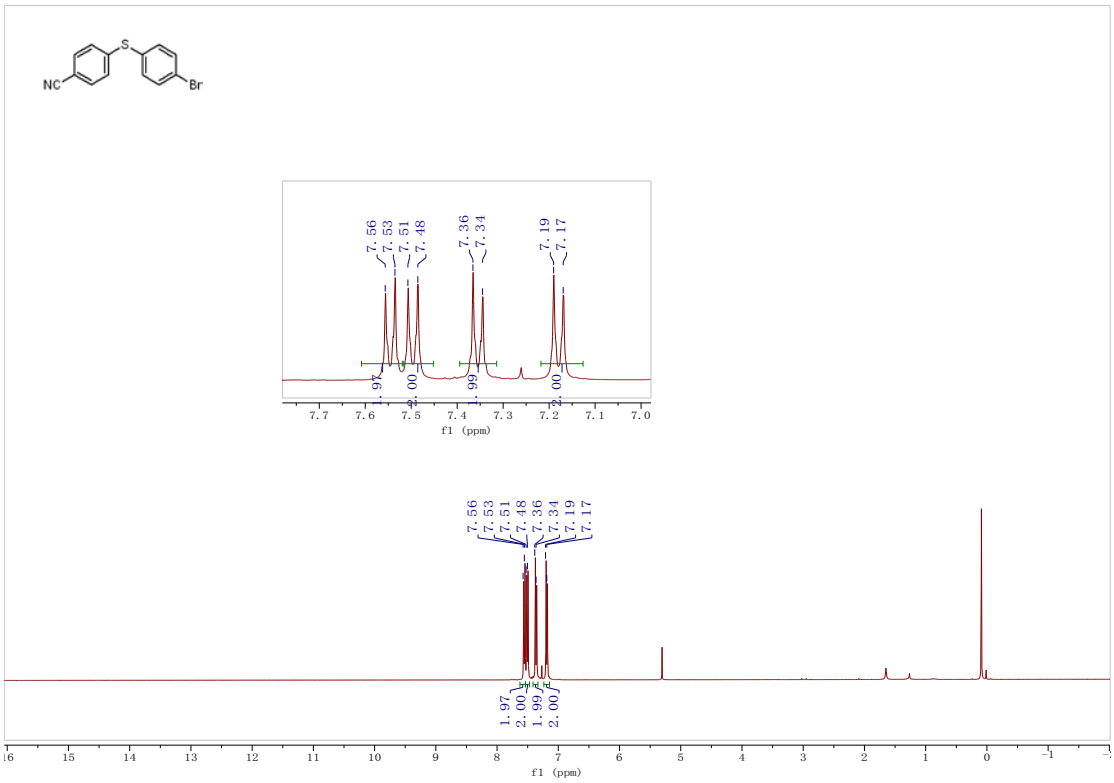
^{1}H NMR Spectrum of **3ab** (500 MHz, DMSO-*d6*)



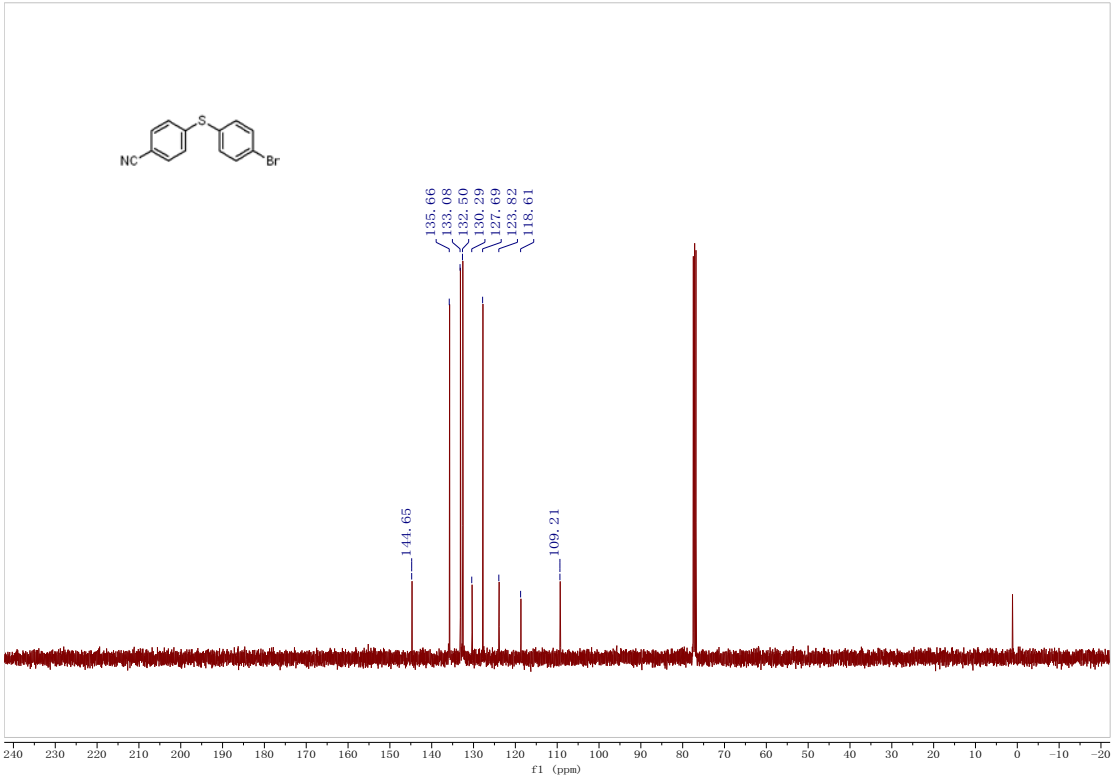
^{13}C NMR Spectrum of **3ab** (101 MHz, DMSO-*d6*)



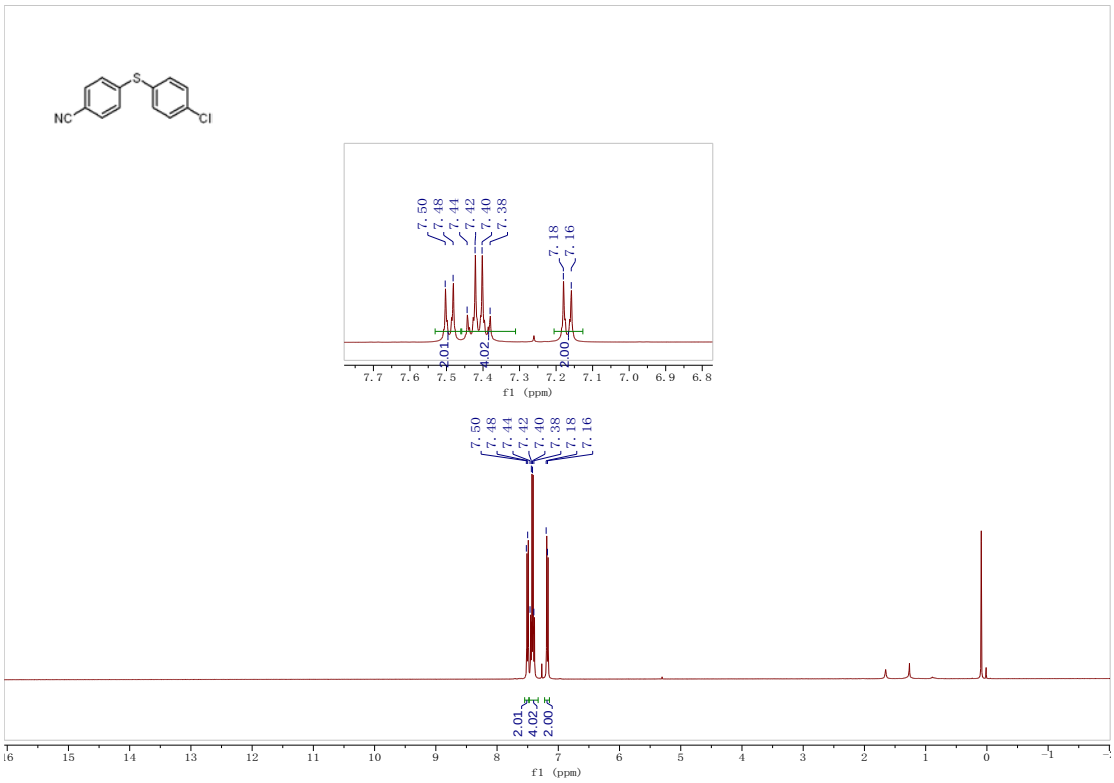
^{1}H NMR Spectrum of **3ac**(400 MHz, $CDCl_3$)



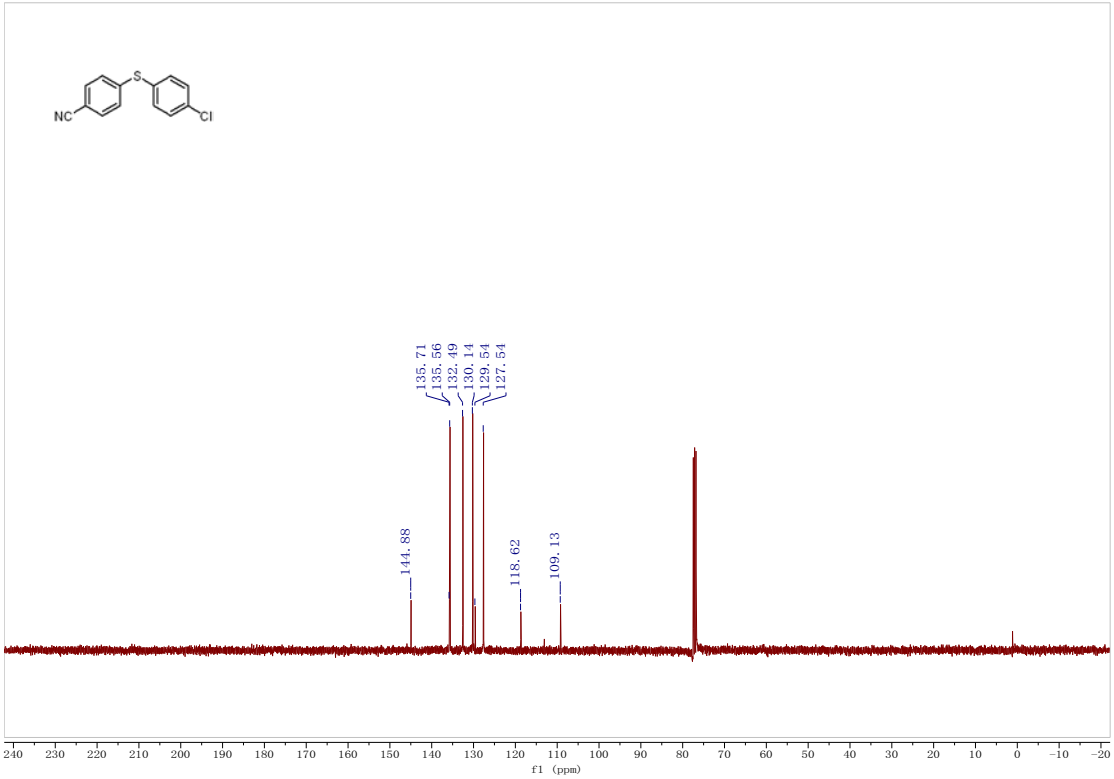
^{13}C NMR Spectrum of **3ac** (101 MHz, $CDCl_3$)



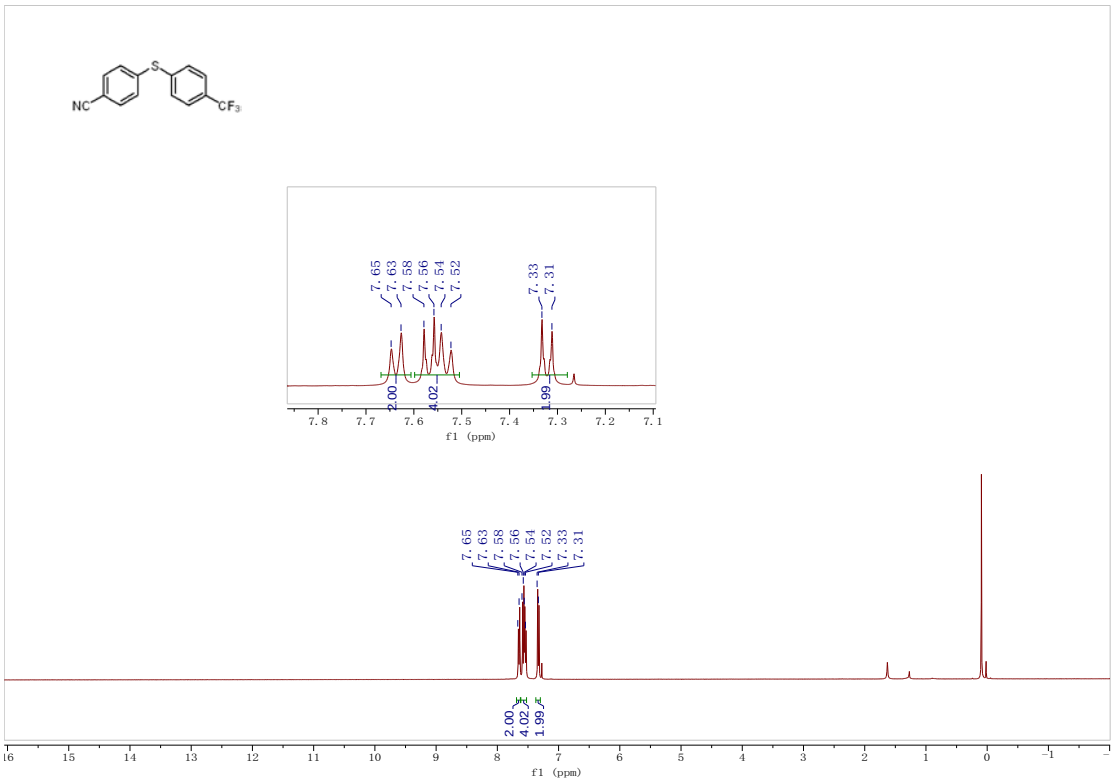
^{1}H NMR Spectrum of **3ad** (400 MHz, $CDCl_3$)



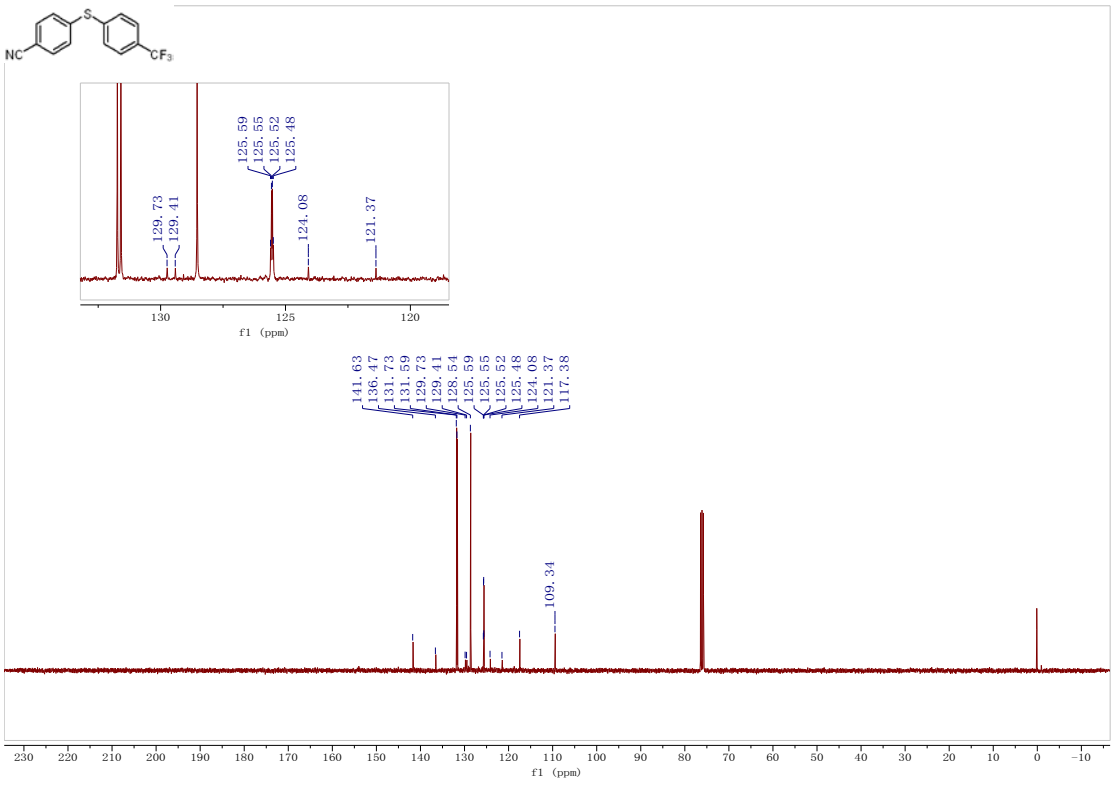
^{13}C NMR Spectrum of **3ad** (101 MHz, $CDCl_3$)



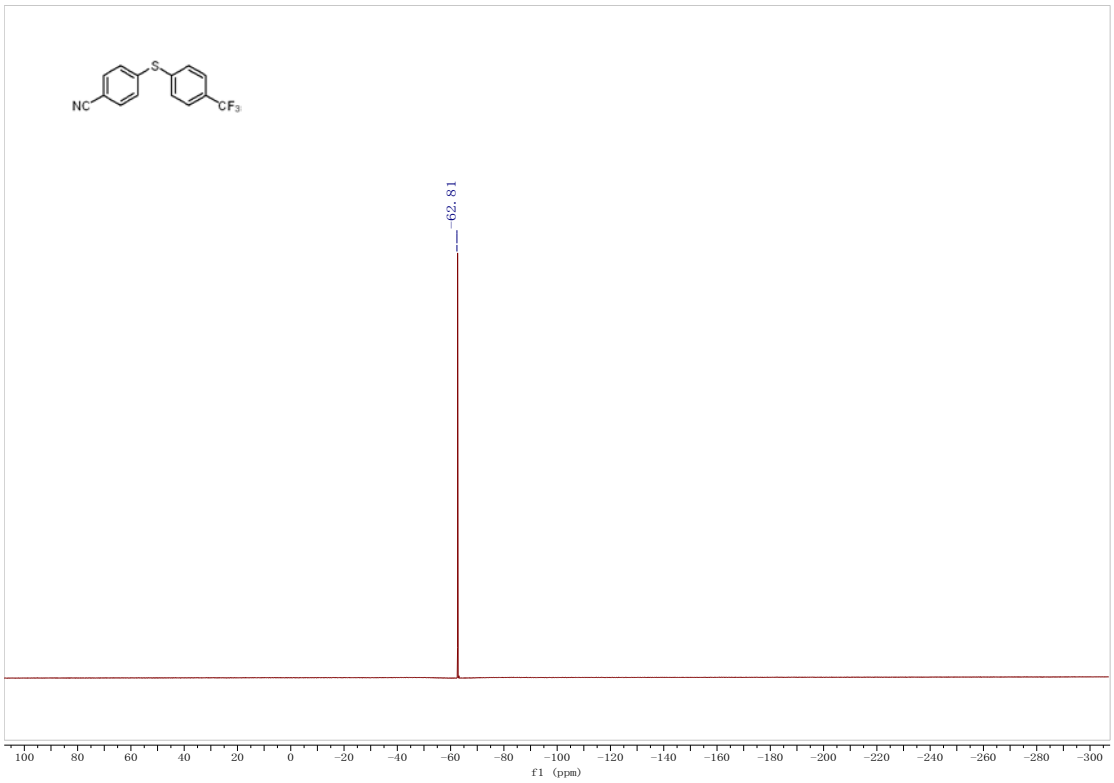
^{1}H NMR Spectrum of **3ae** (400 MHz, $CDCl_3$)



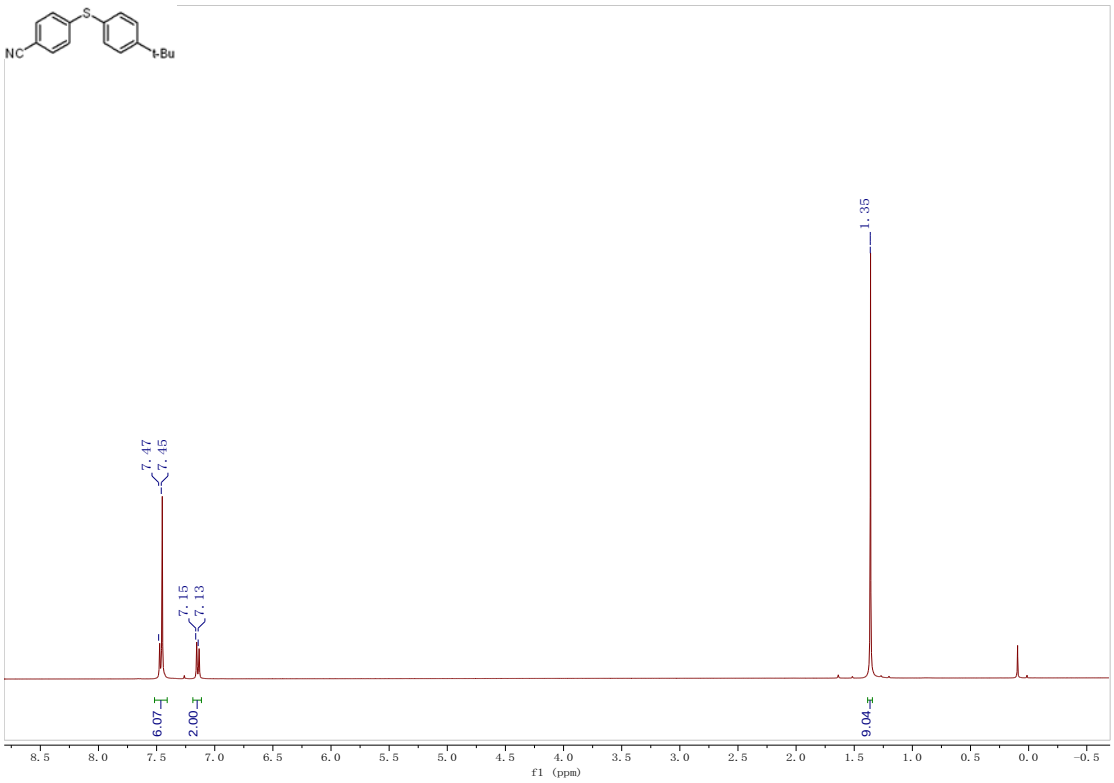
^{13}C NMR Spectrum of **3ae** (101 MHz, $CDCl_3$)



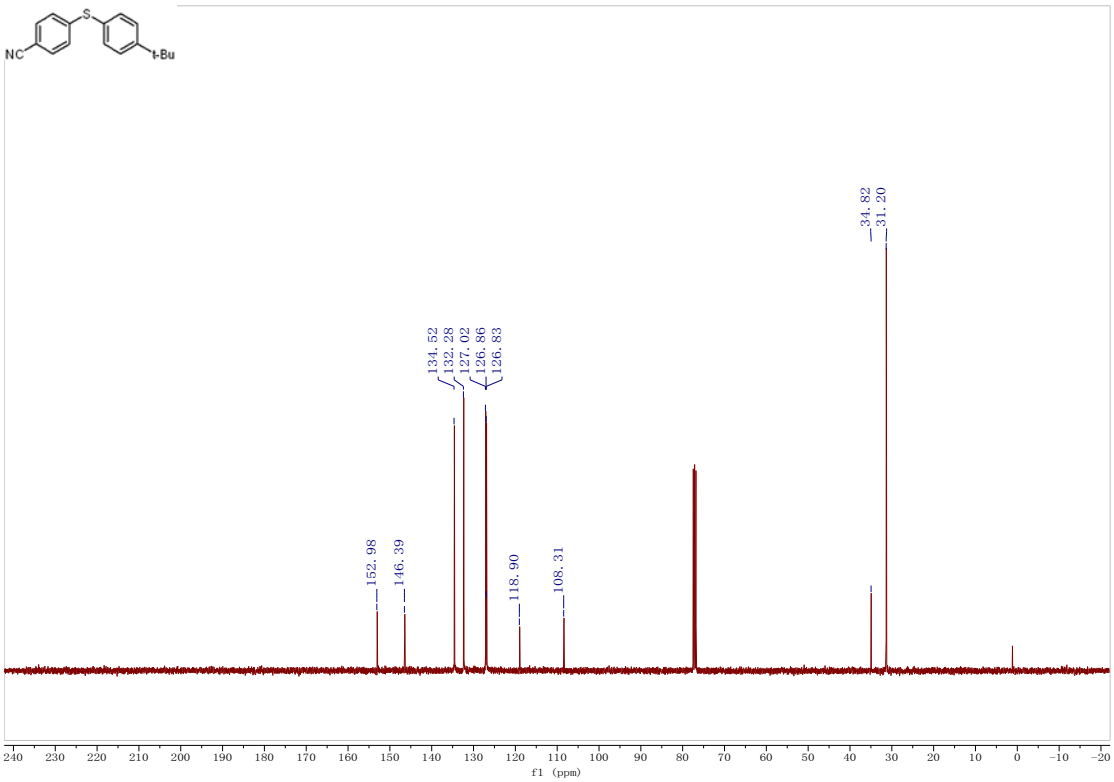
^{19}F NMR Spectrum of **3ae** (376 MHz, $CDCl_3$)



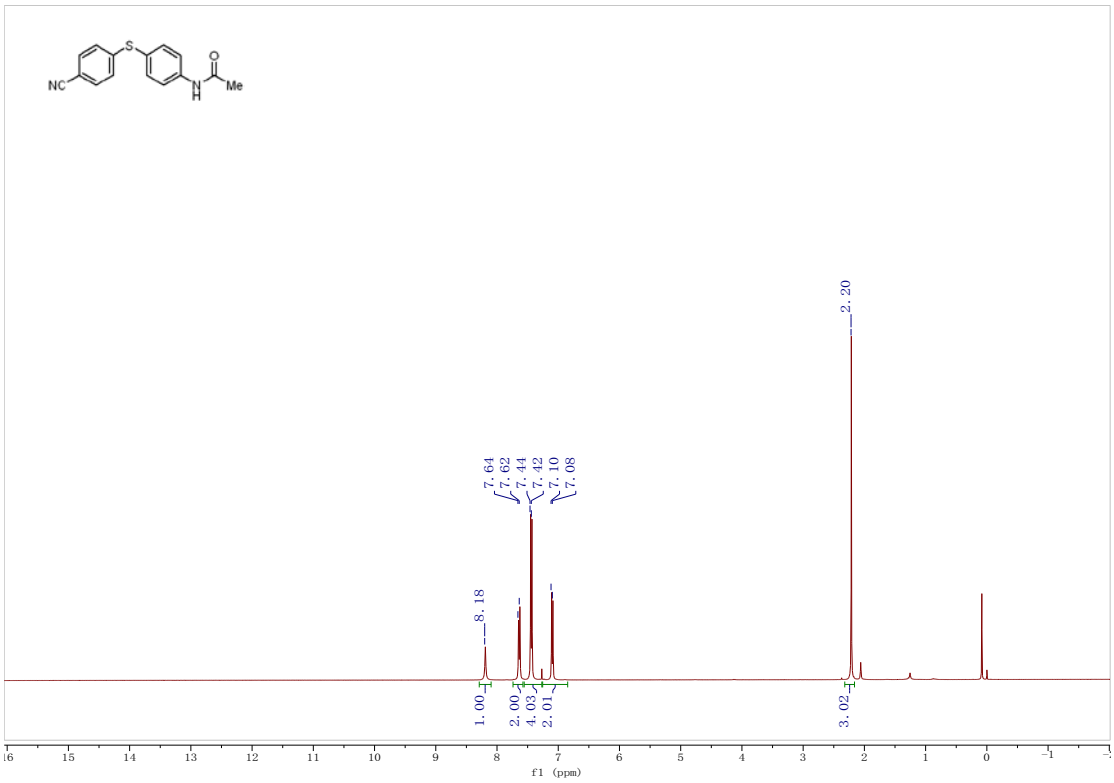
^{1}H NMR Spectrum of **3af** (400 MHz, $CDCl_3$)



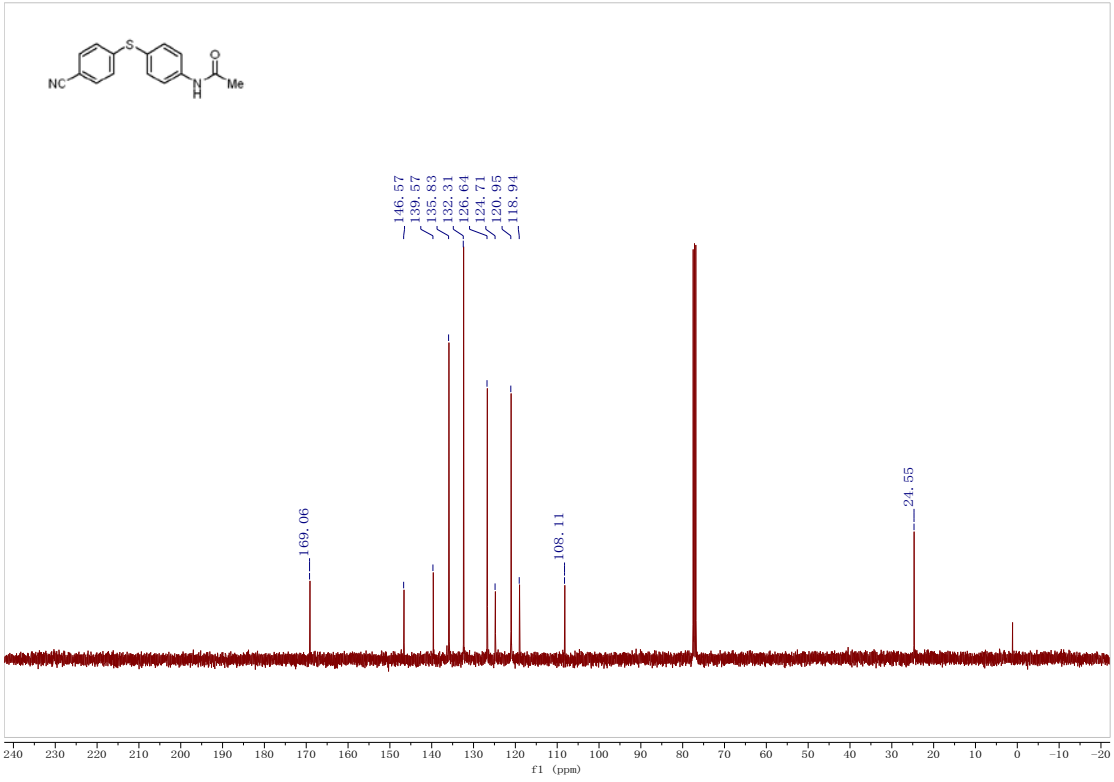
^{13}C NMR Spectrum of **3af** (101 MHz, $CDCl_3$)



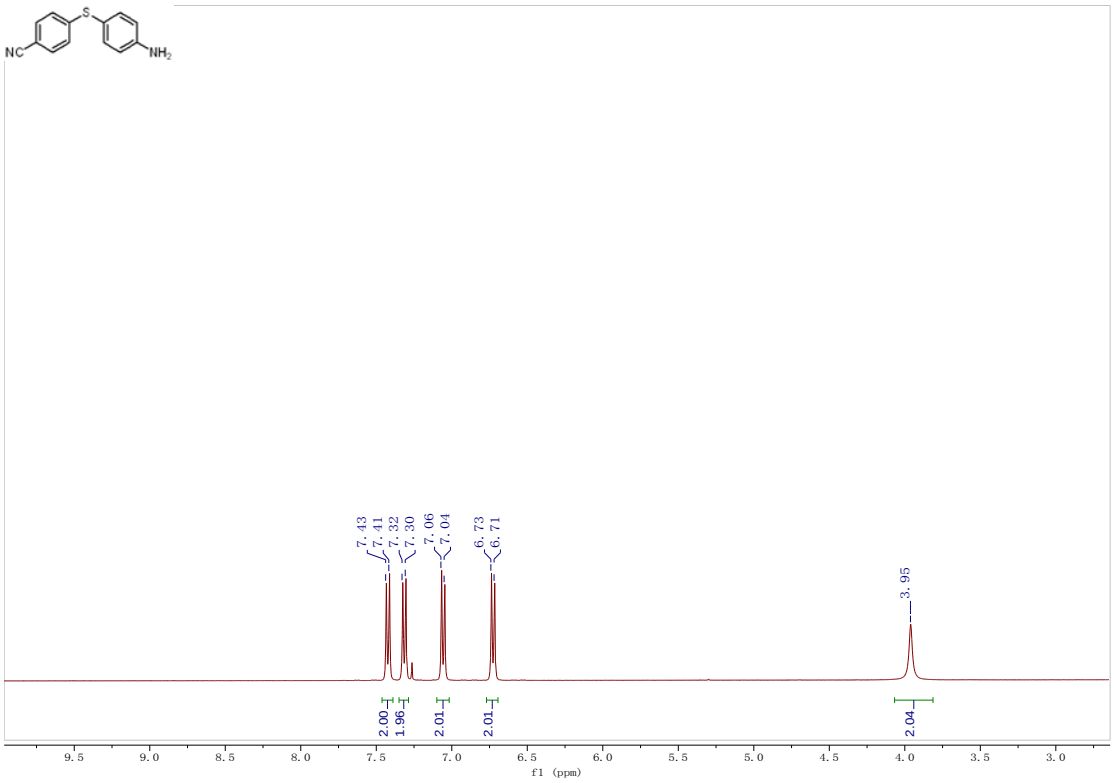
^{1}H NMR Spectrum of **3ag** (400 MHz, $CDCl_3$)



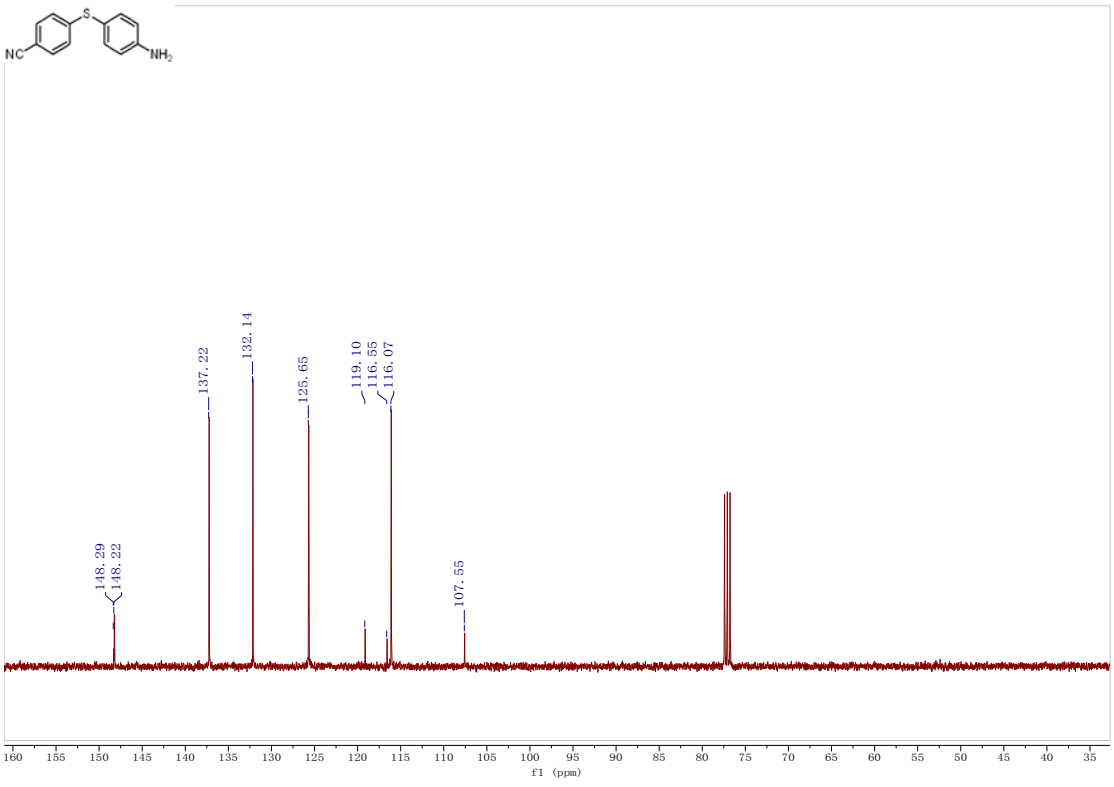
^{13}C NMR Spectrum of **3ag** (101 MHz, $CDCl_3$)



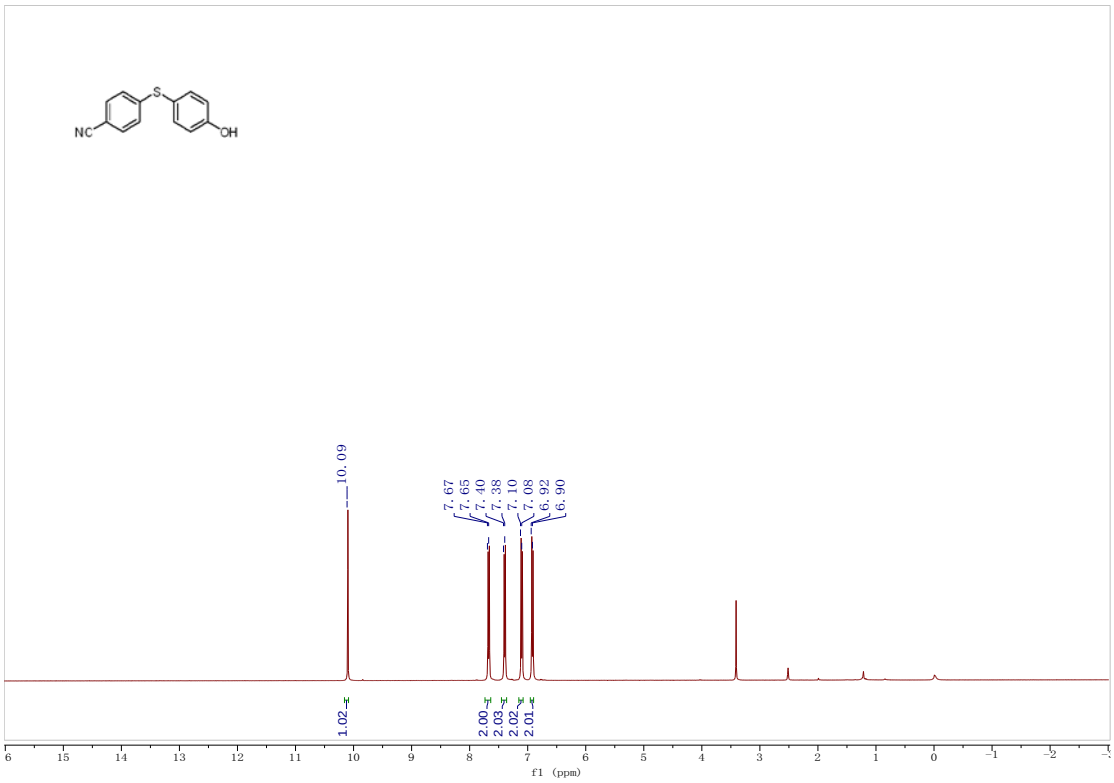
^{1}H NMR Spectrum of **3ah** (400 MHz, $CDCl_3$)



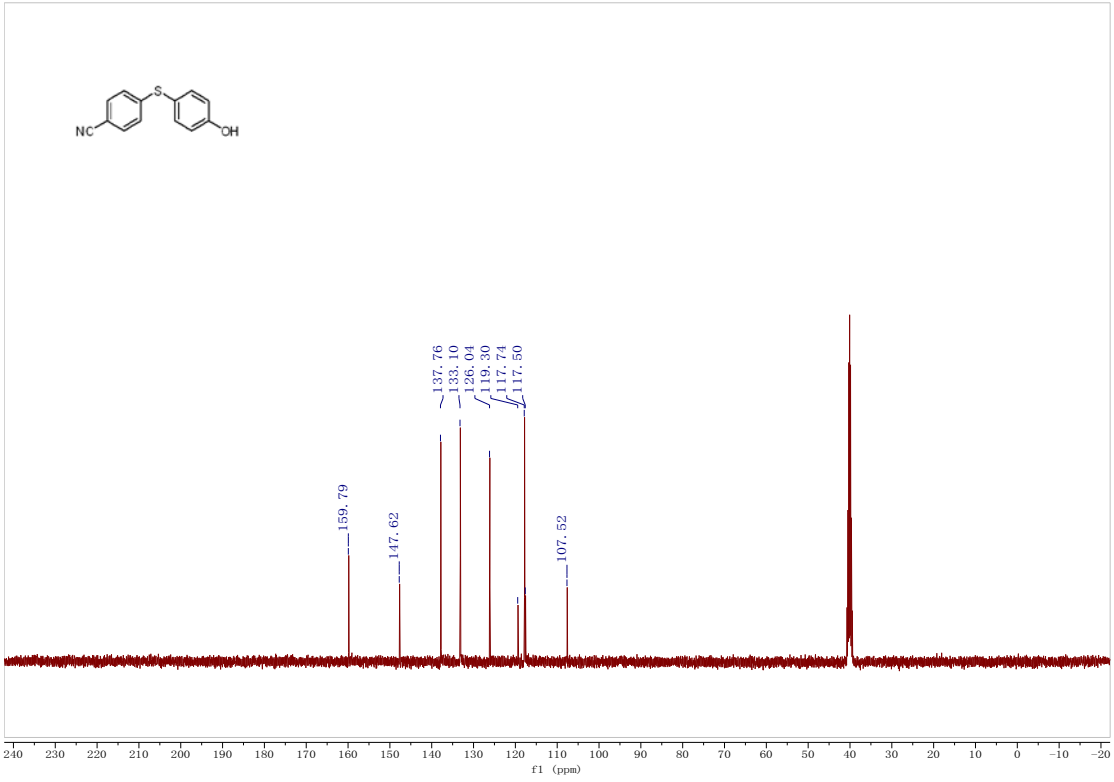
^{13}C NMR Spectrum of **3ah** (101 MHz, $CDCl_3$)



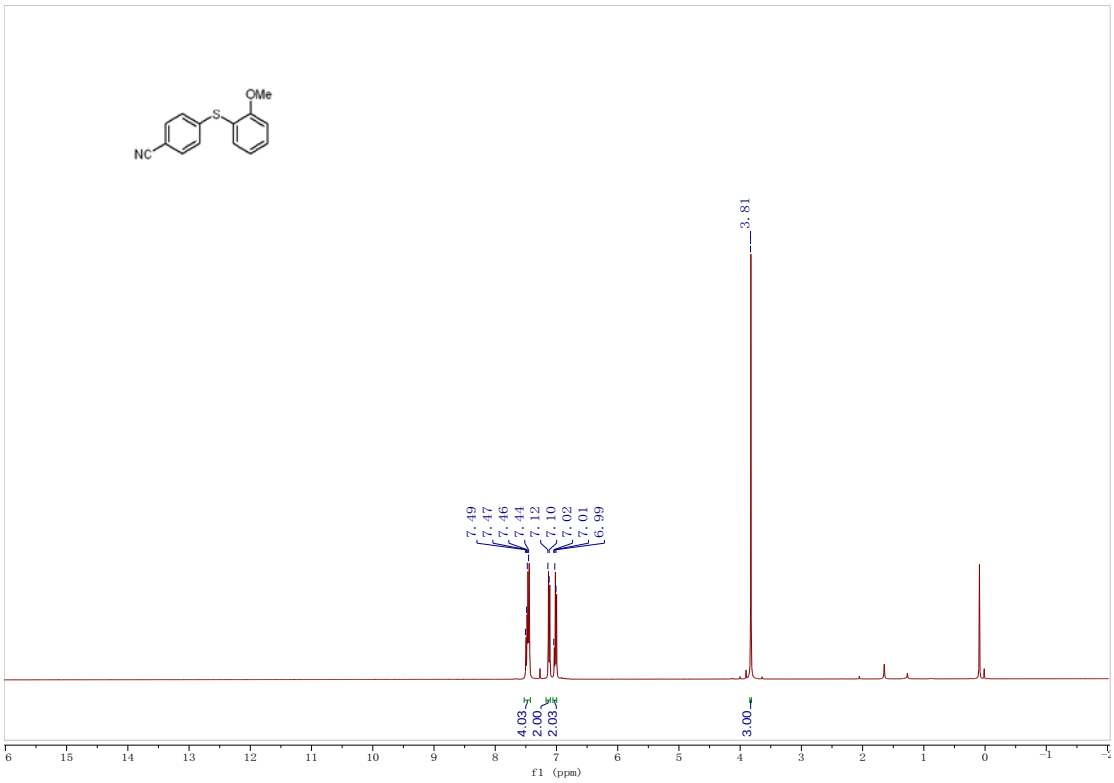
^{1}H NMR Spectrum of **3ai** (400 MHz, DMSO-*d6*)



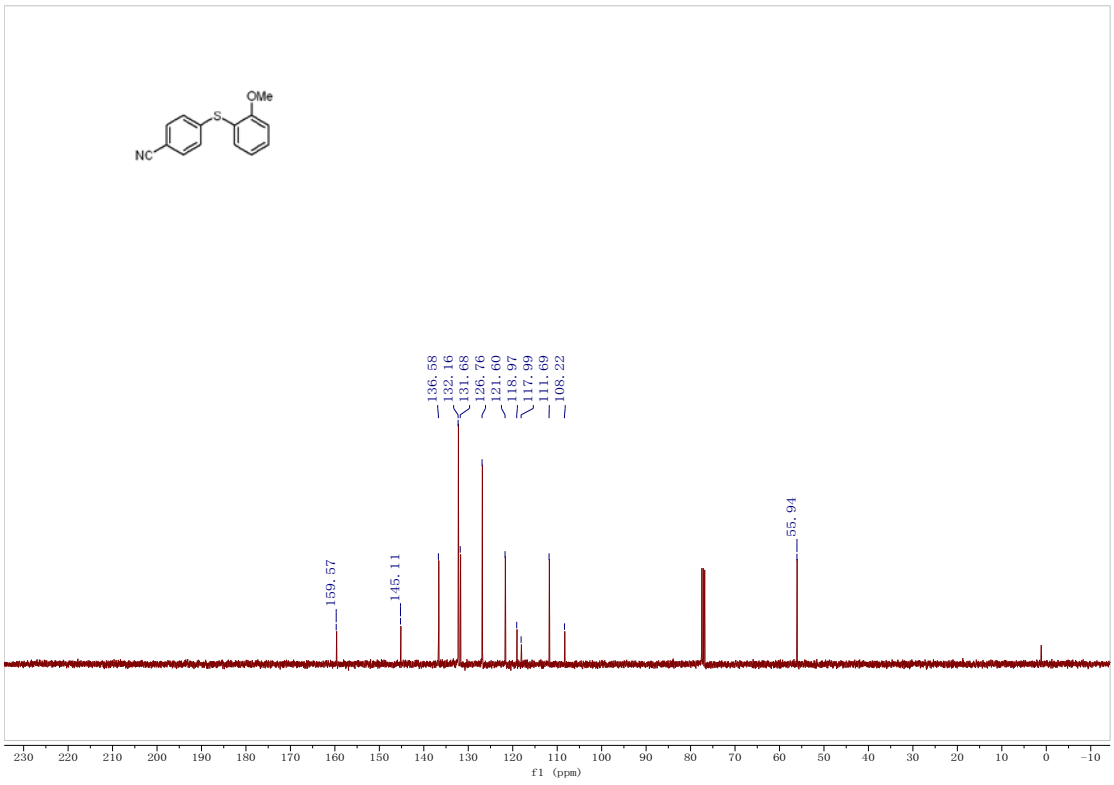
^{13}C NMR Spectrum of **3ai** (101 MHz, DMSO-*d6*)



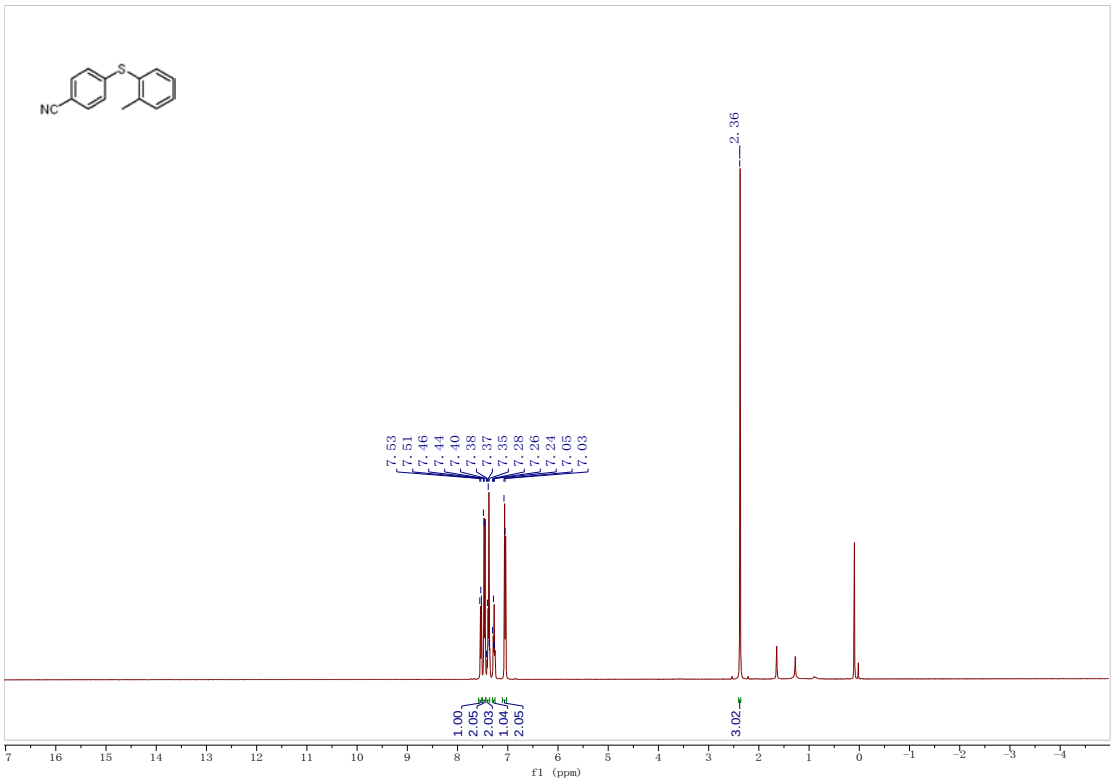
^{1}H NMR Spectrum of **3aj** (400 MHz, $CDCl_3$)



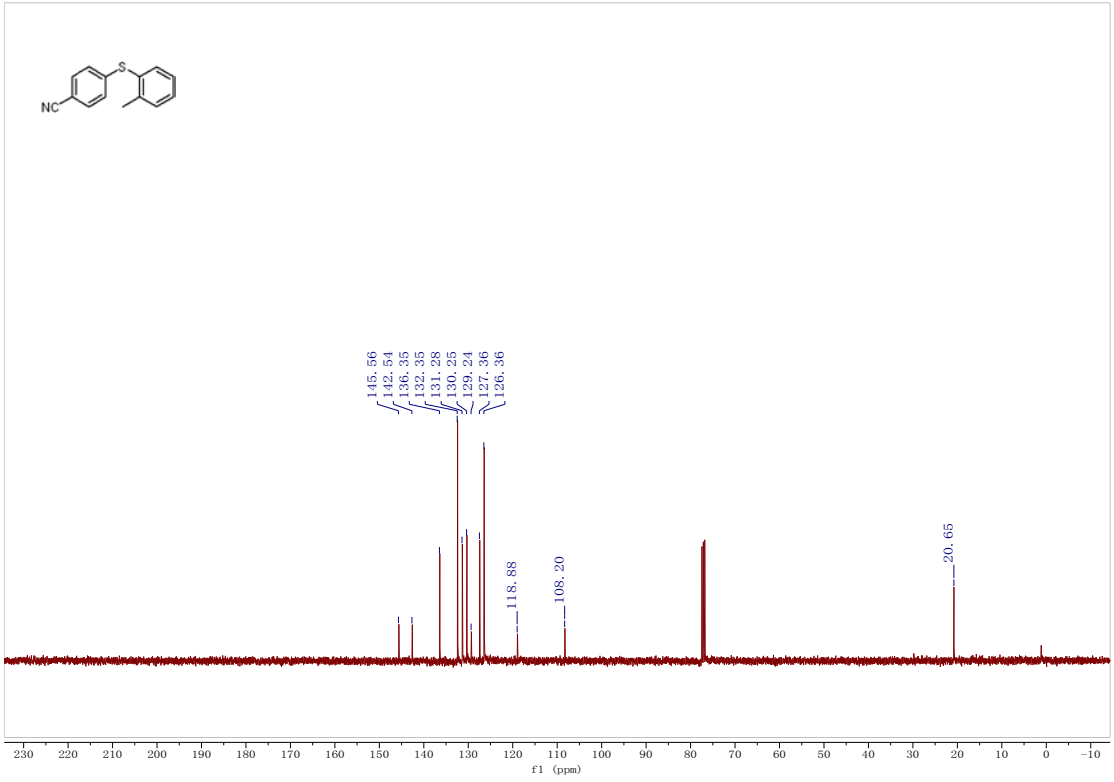
^{13}C NMR Spectrum of **3aj** (101 MHz, $CDCl_3$)



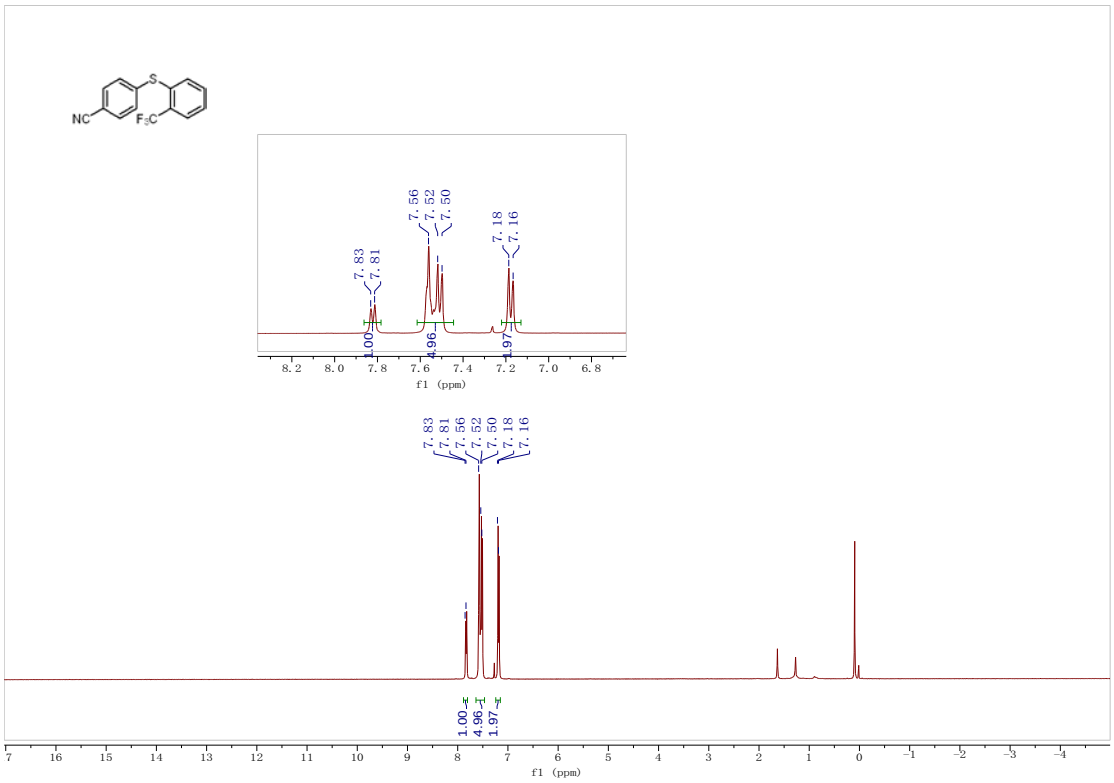
^{1}H NMR Spectrum of **3ak** (400 MHz, $CDCl_3$)



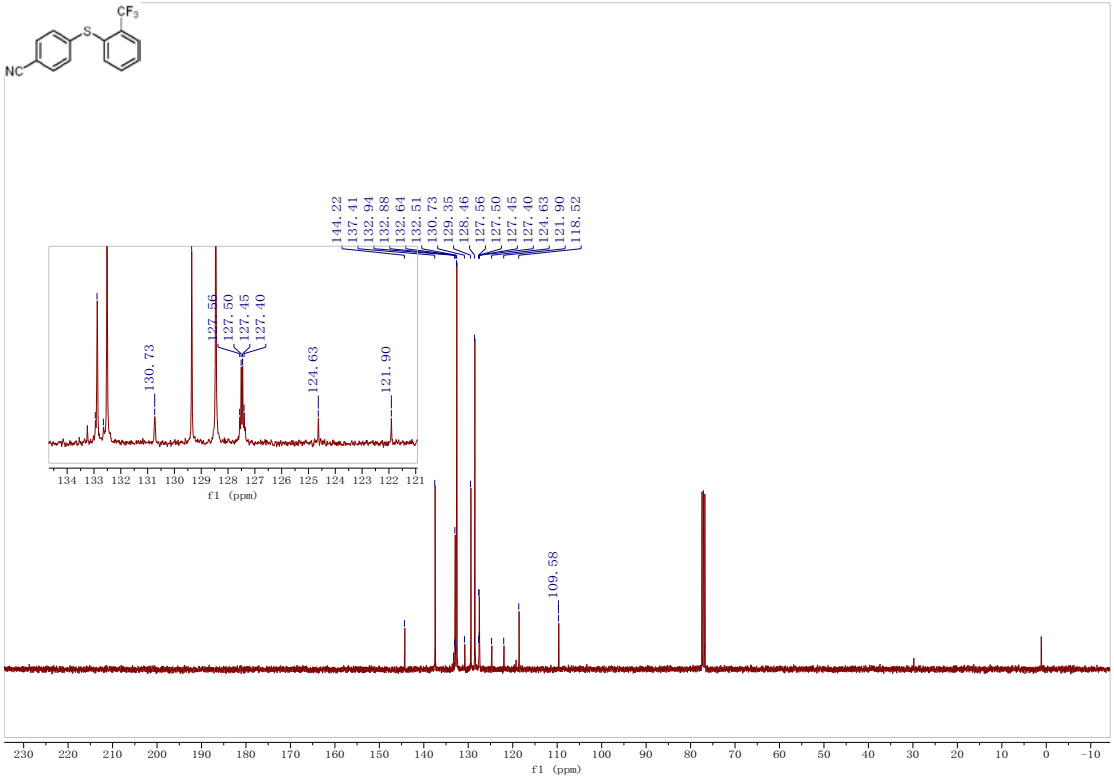
^{13}C NMR Spectrum of **3ak** (101 MHz, $CDCl_3$)



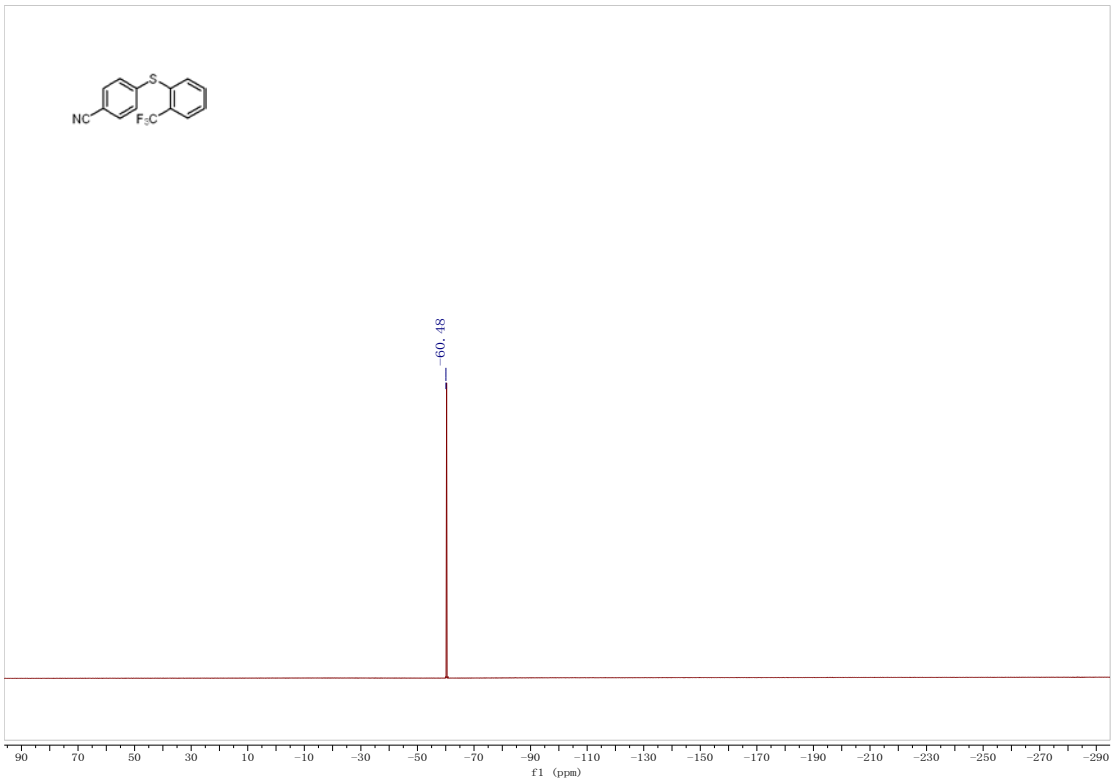
^{1}H NMR Spectrum of **3al** (376 MHz, $CDCl_3$)



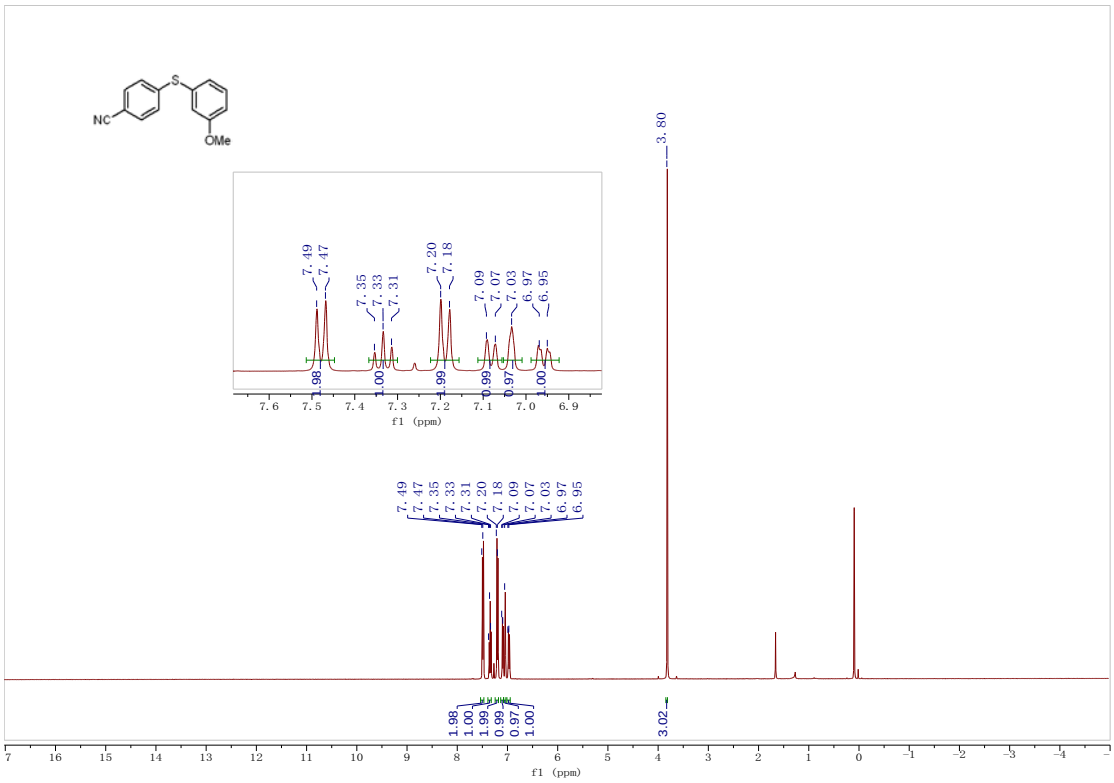
^{13}C NMR Spectrum of **3al** (101 MHz, $CDCl_3$)



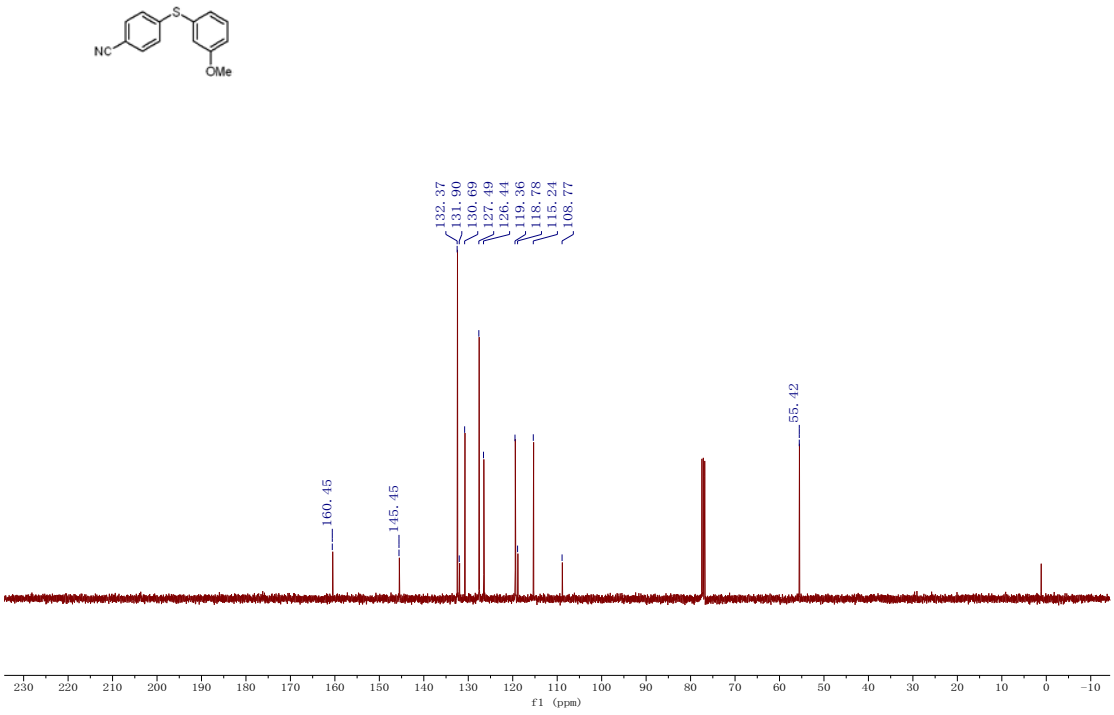
^{19}F NMR Spectrum of **3al** (376 MHz, $CDCl_3$)



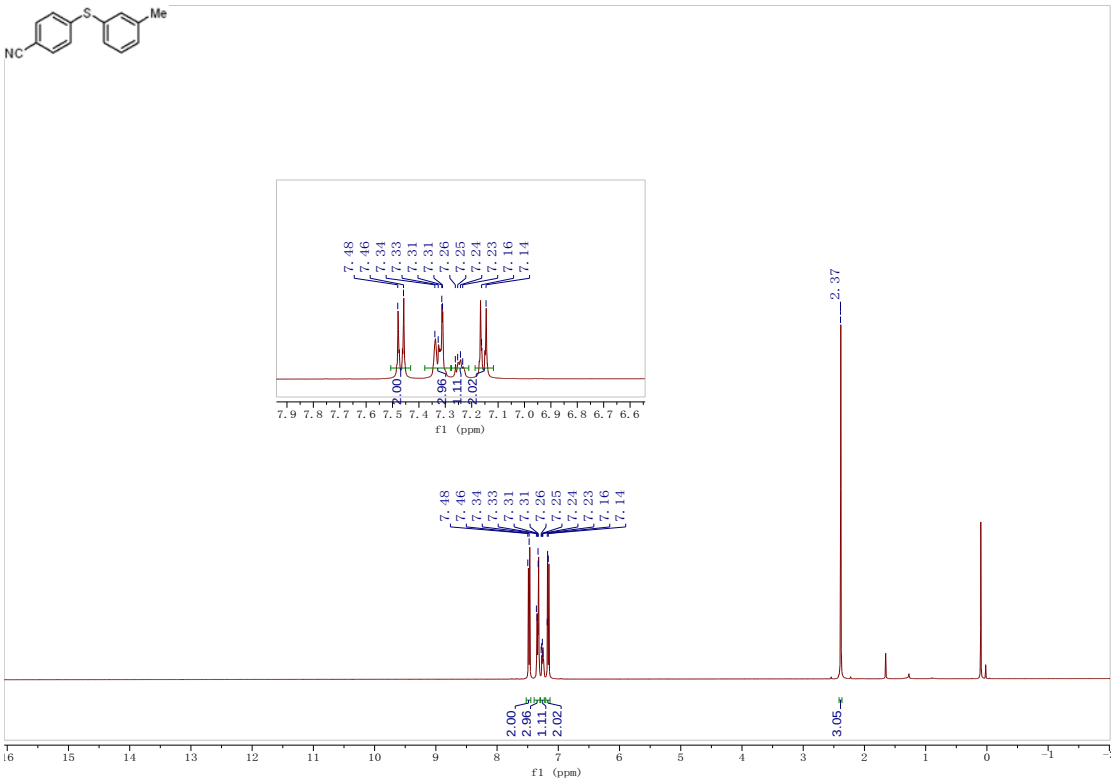
^{1}H NMR Spectrum of **3am** (400 MHz, $CDCl_3$)



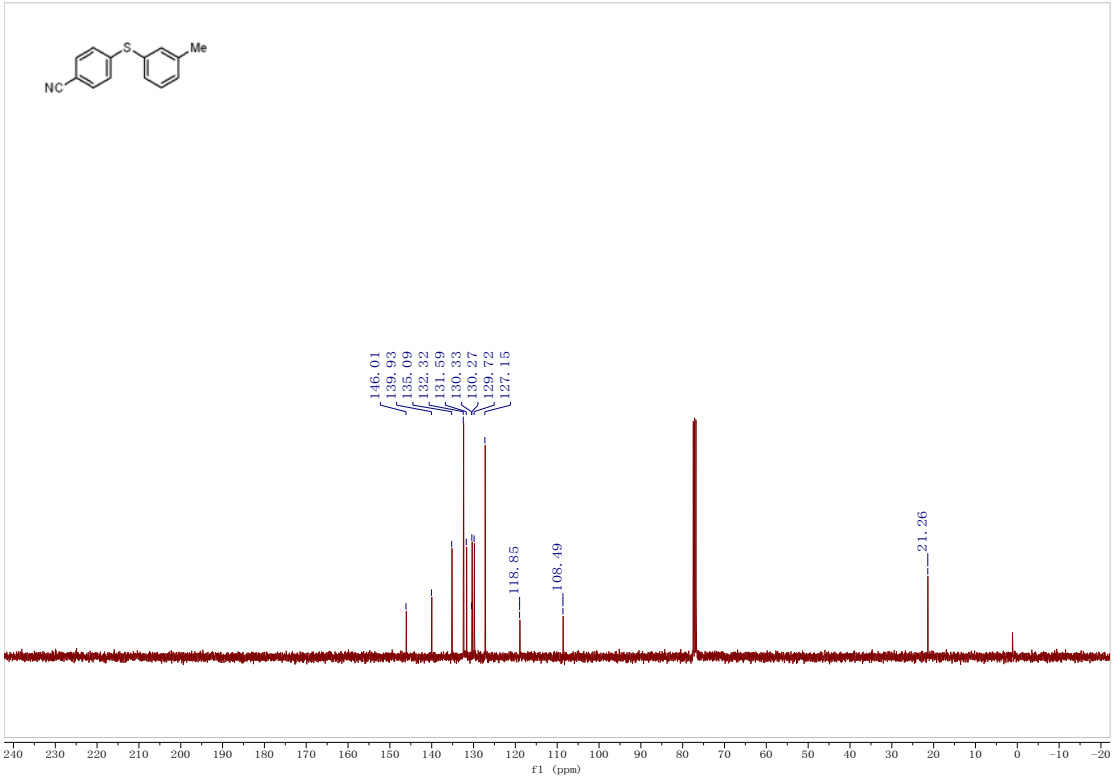
^{13}C NMR Spectrum of **3am** (101 MHz, $CDCl_3$)



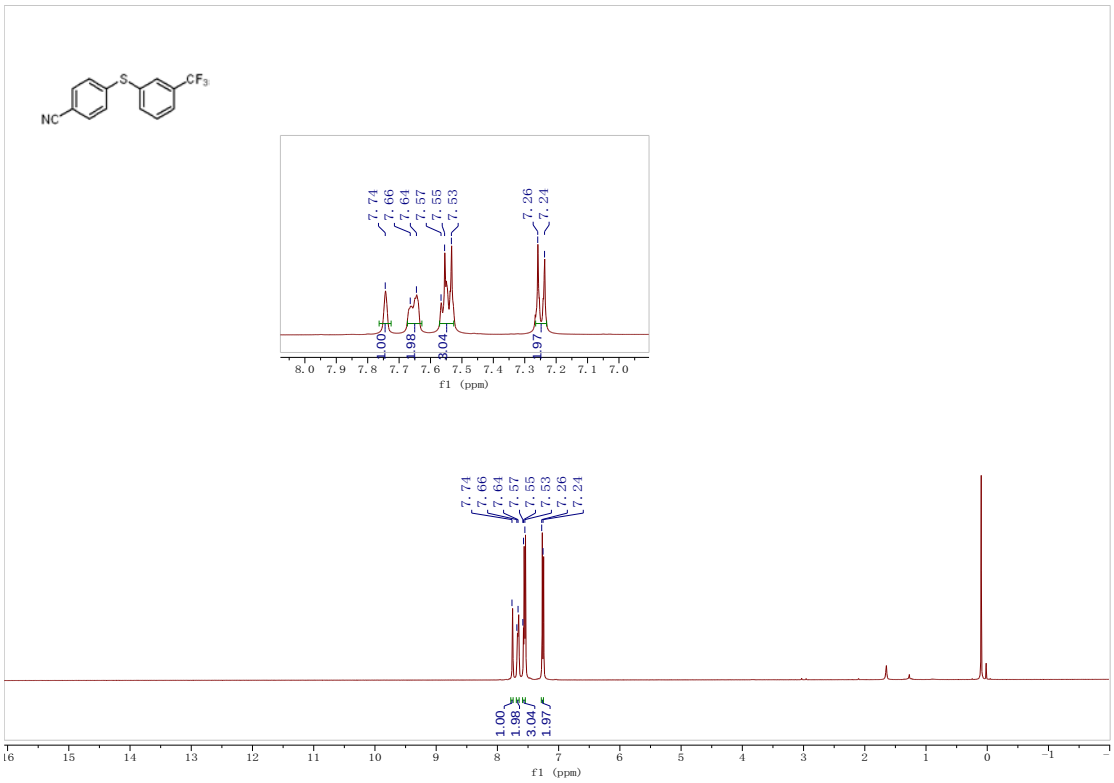
^{1}H NMR Spectrum of **3an** (400 MHz, $CDCl_3$)



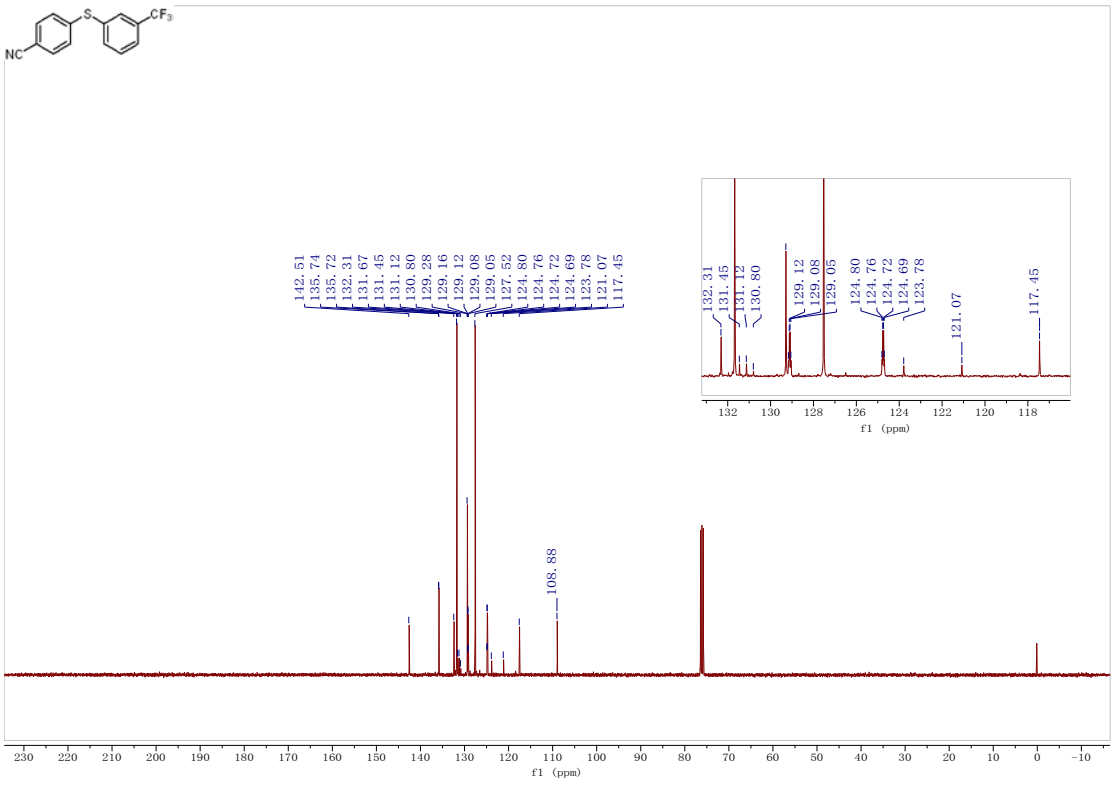
^{13}C NMR Spectrum of **3an** (101 MHz, $CDCl_3$)



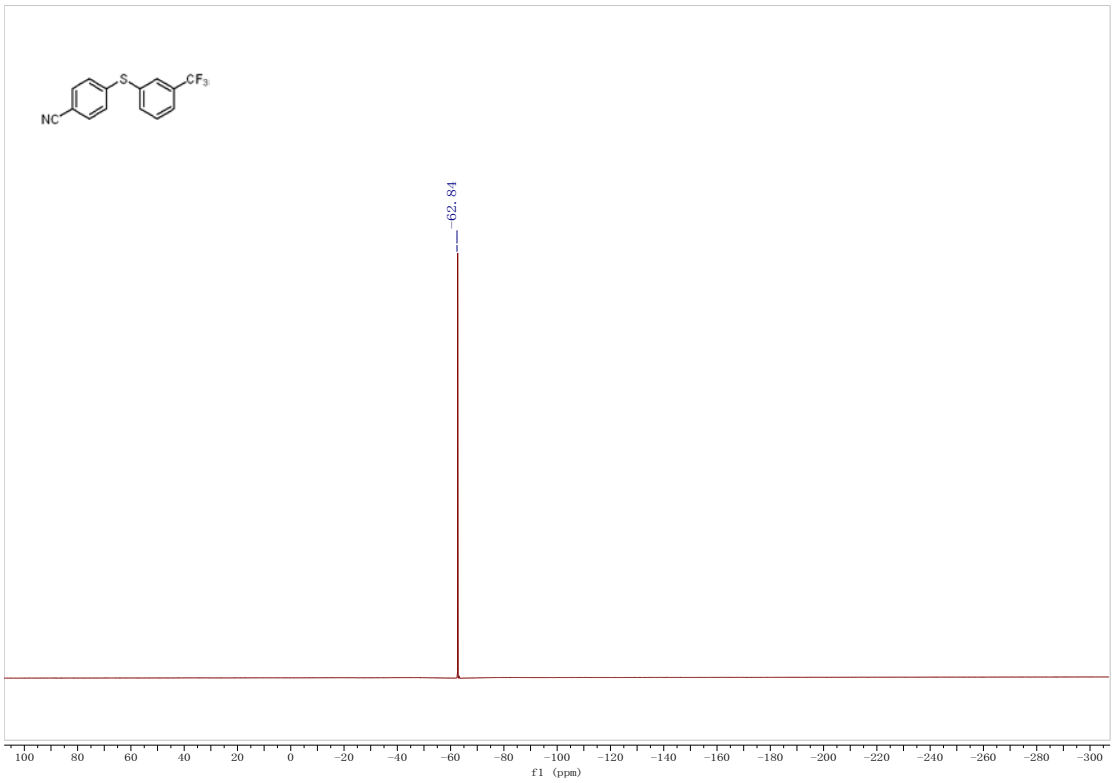
^{1}H NMR Spectrum of **3ao** (400 MHz, $CDCl_3$)



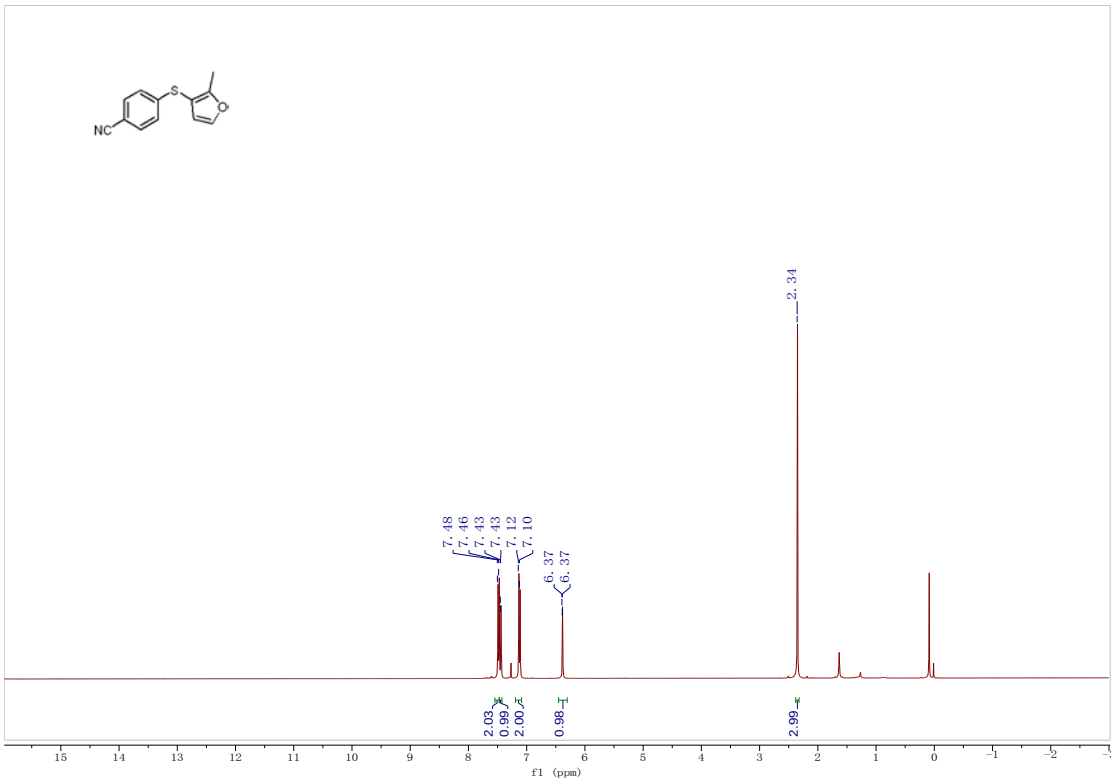
^{13}C NMR Spectrum of **3ao** (101 MHz, $CDCl_3$)



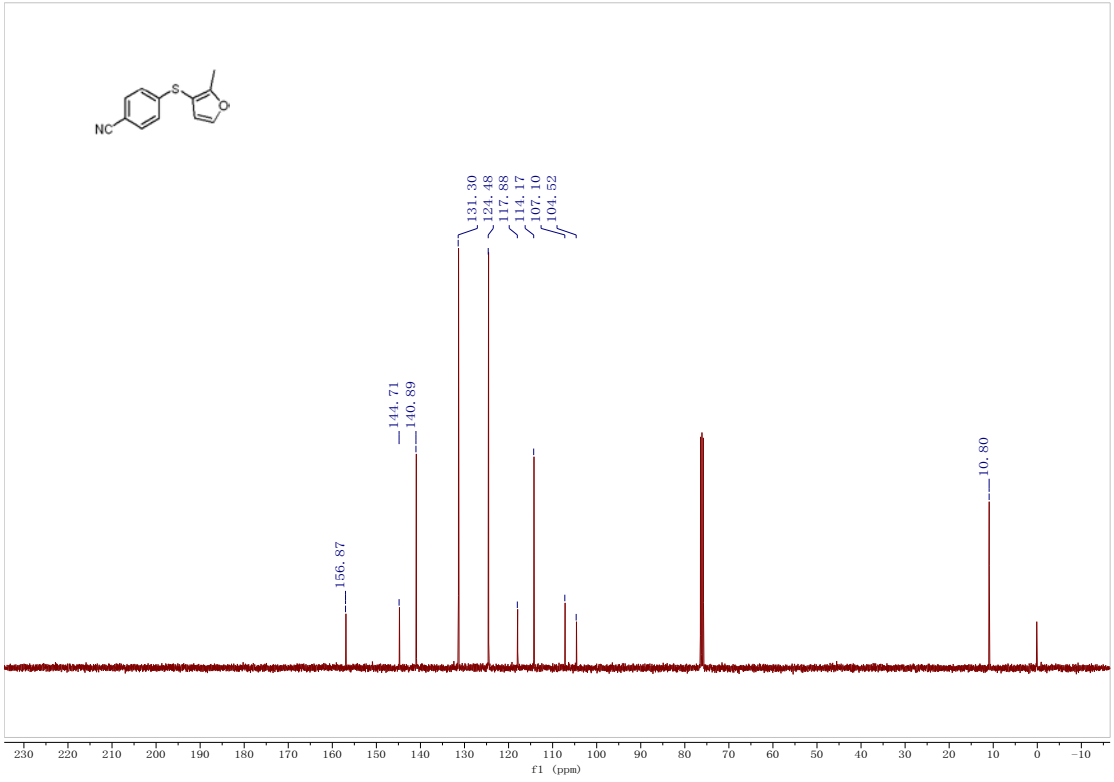
^{19}F NMR Spectrum of **3ao** (376 MHz, $CDCl_3$)



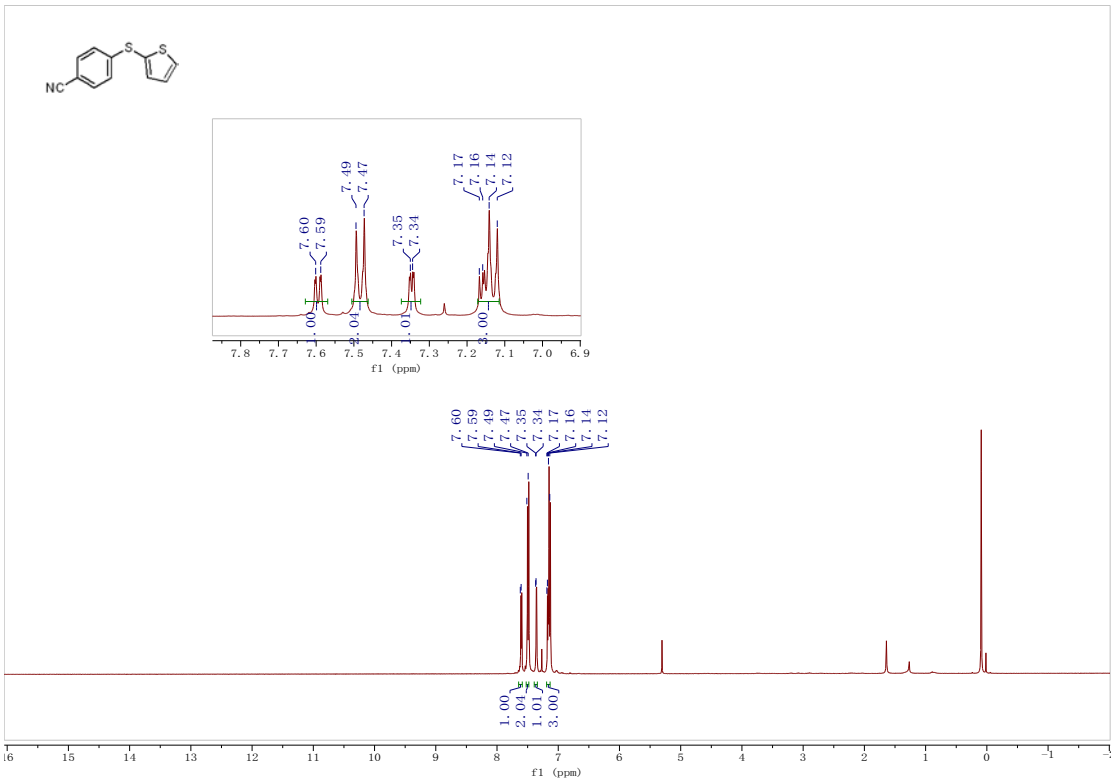
^{1}H NMR Spectrum of **3ap** (400 MHz, $CDCl_3$)



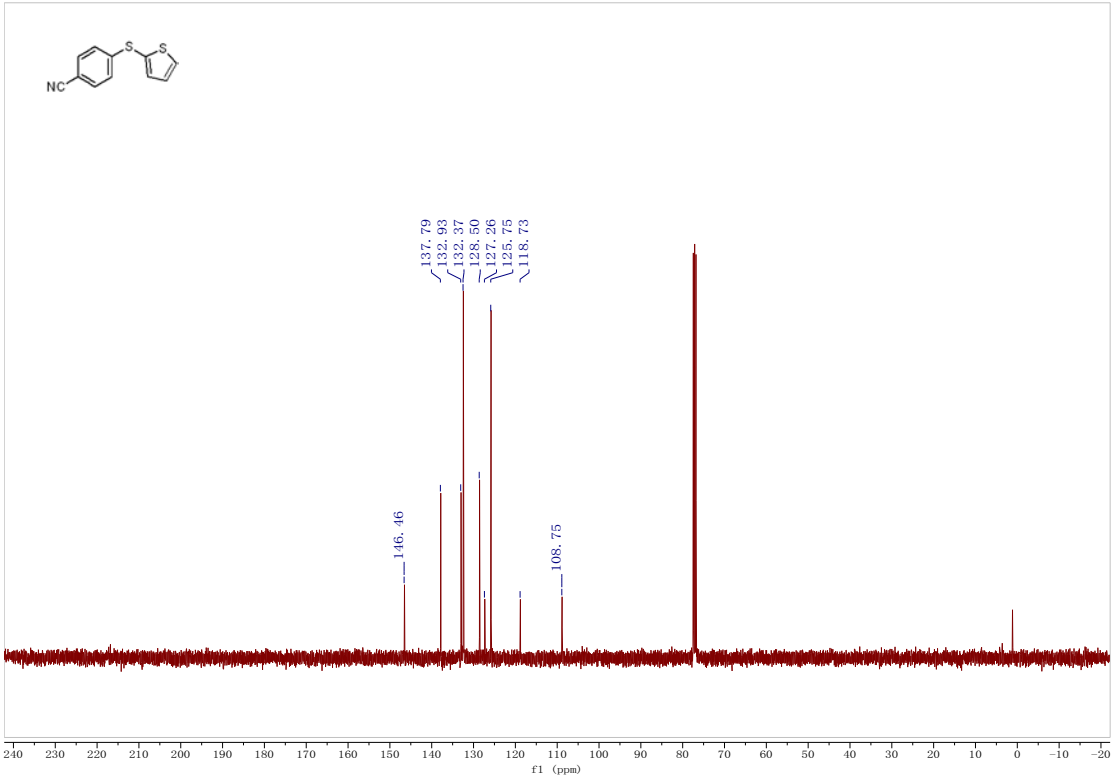
^{13}C NMR Spectrum of **3ap** (101 MHz, $CDCl_3$)



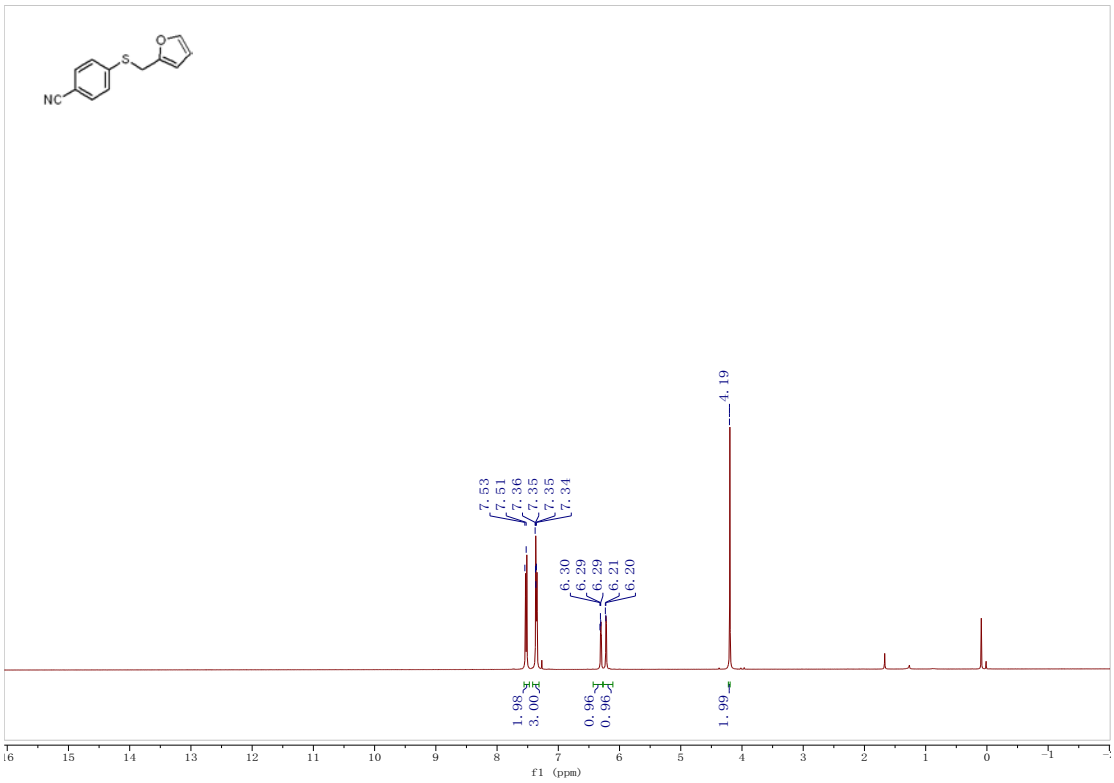
^{1}H NMR Spectrum of **3ar** (400 MHz, $CDCl_3$)



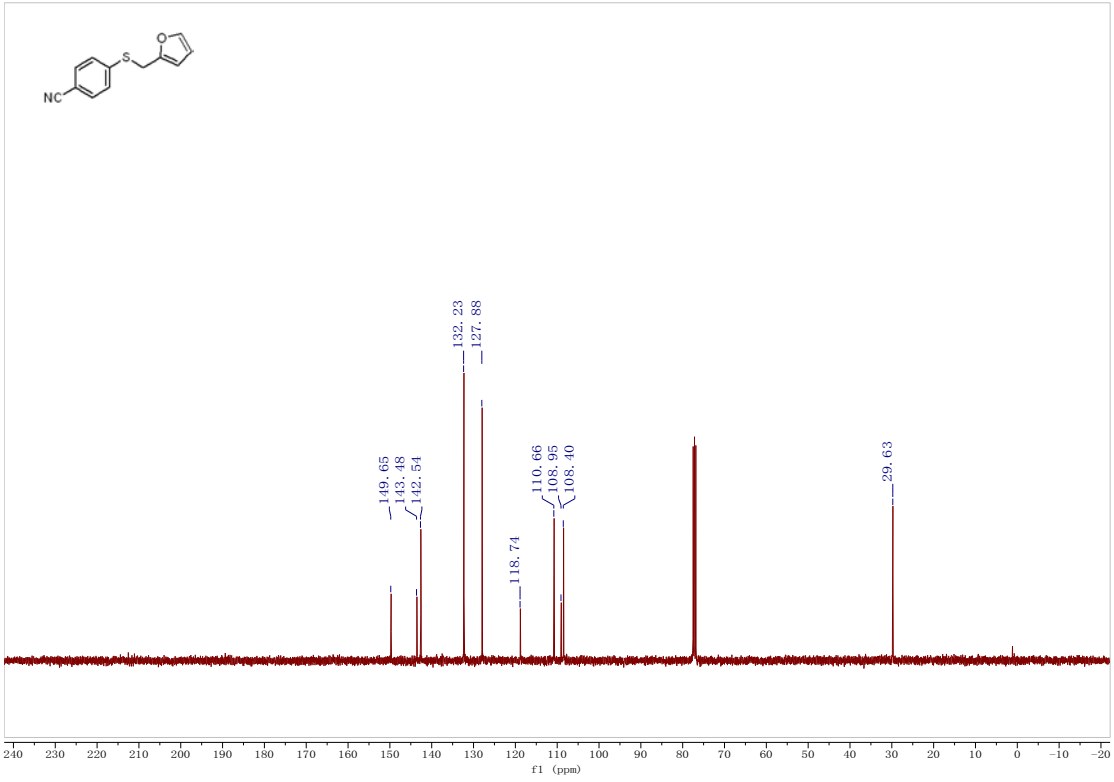
^{13}C NMR Spectrum of **3ar** (101 MHz, $CDCl_3$)



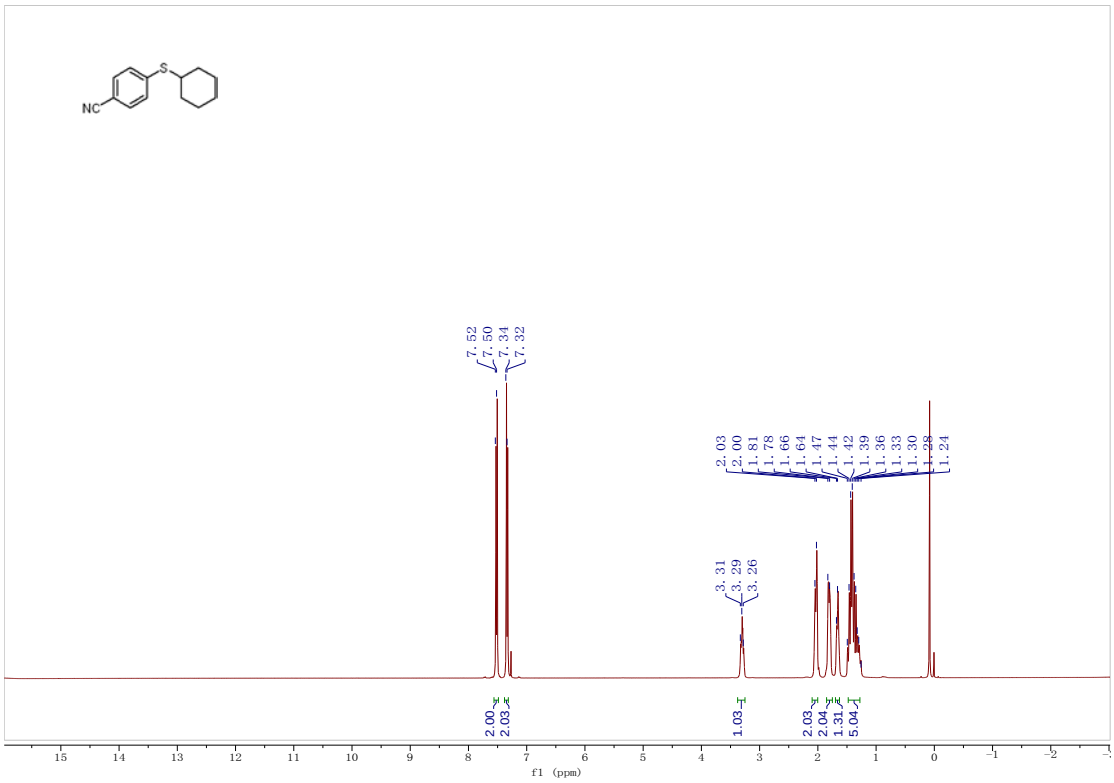
^{1}H NMR Spectrum of **3as** (400 MHz, $CDCl_3$)



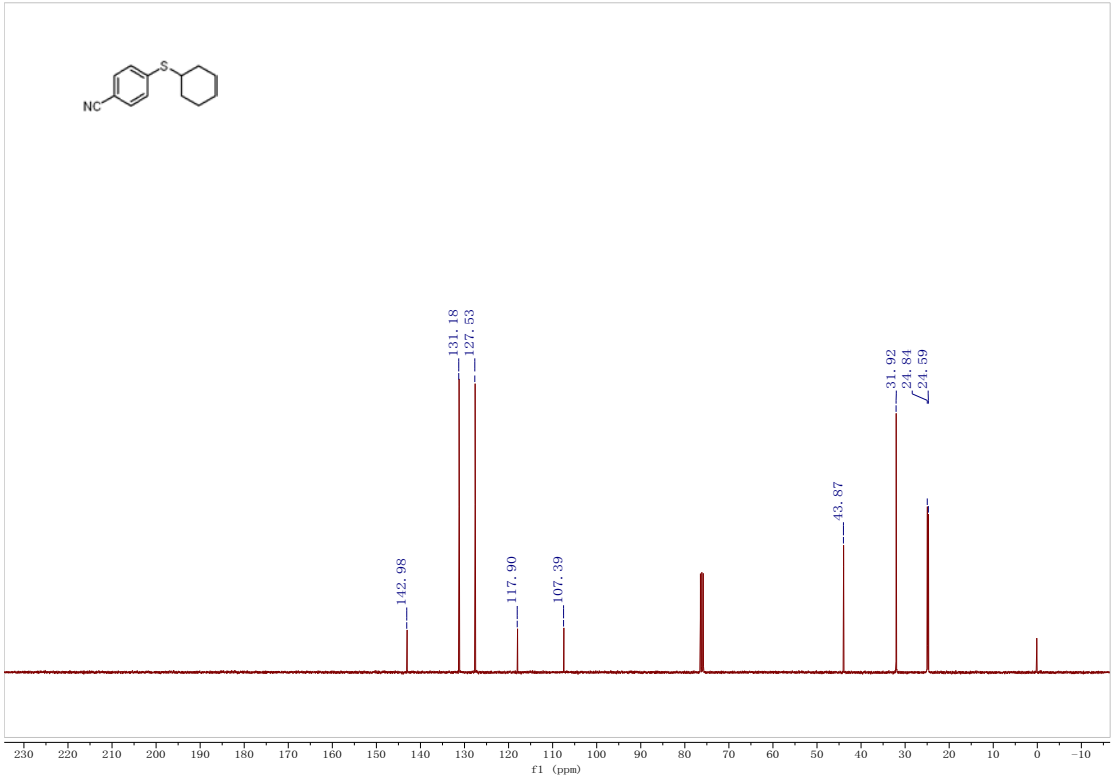
^{13}C NMR Spectrum of **3as** (101 MHz, $CDCl_3$)



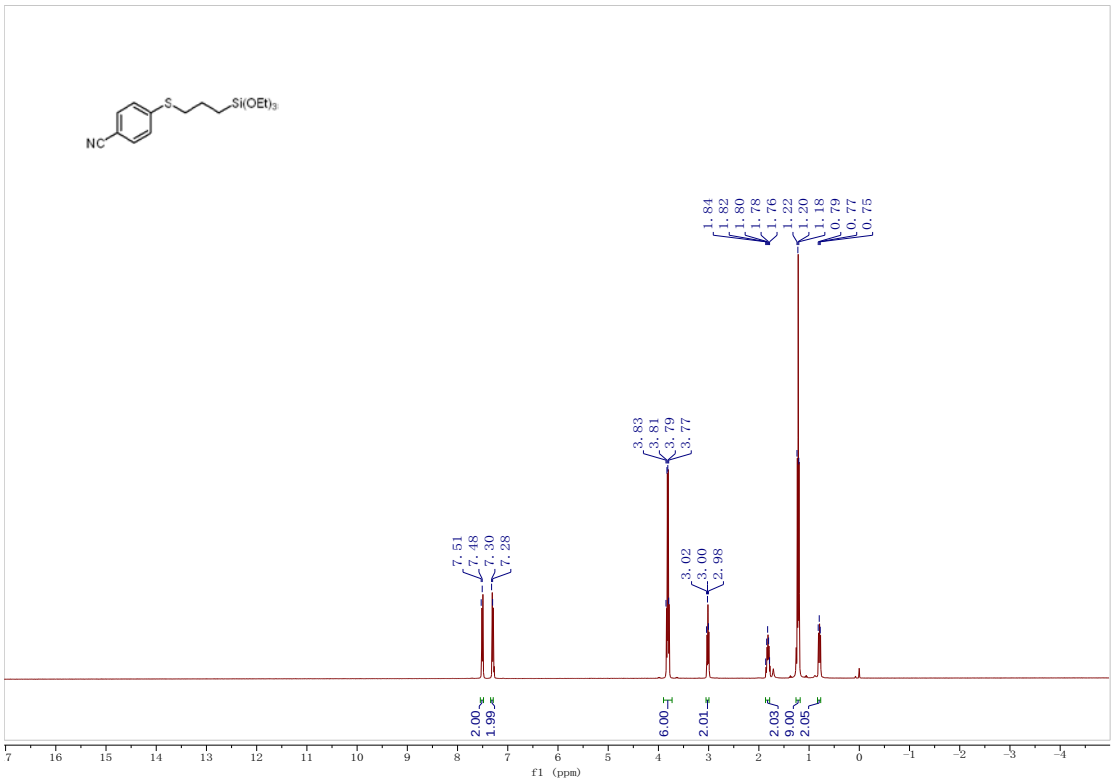
^{1}H NMR Spectrum of **3at** (400 MHz, $CDCl_3$)



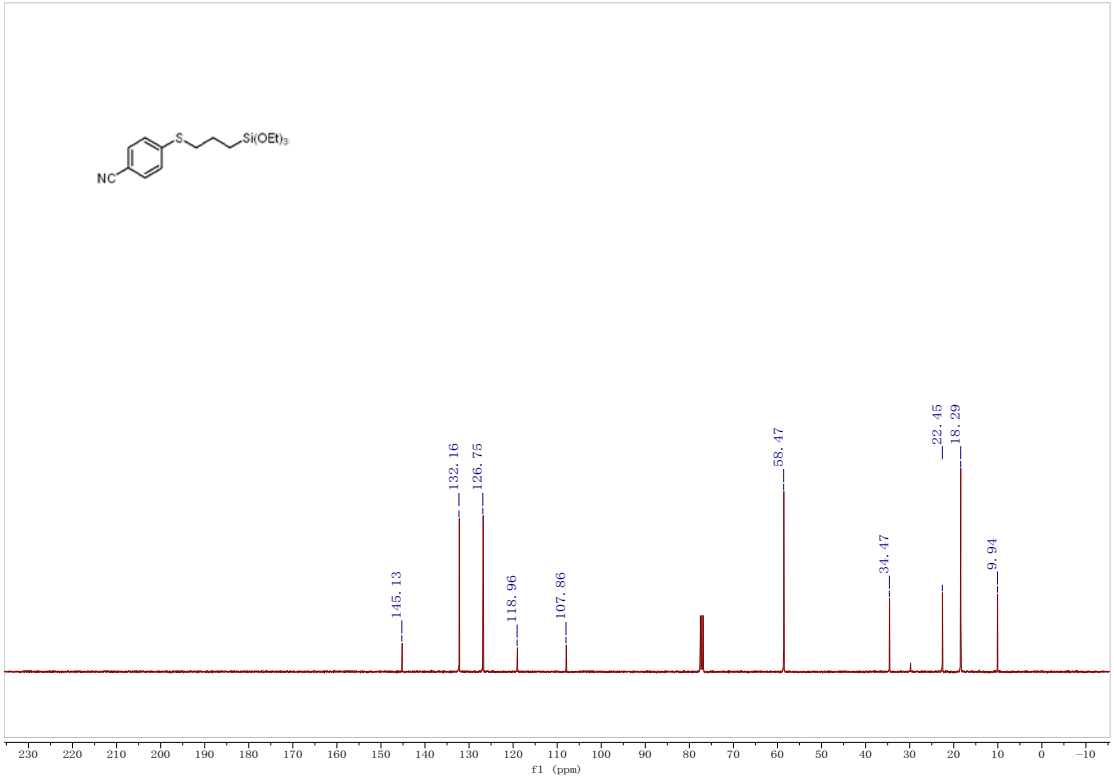
^{13}C NMR Spectrum of **3at** (101 MHz, $CDCl_3$)



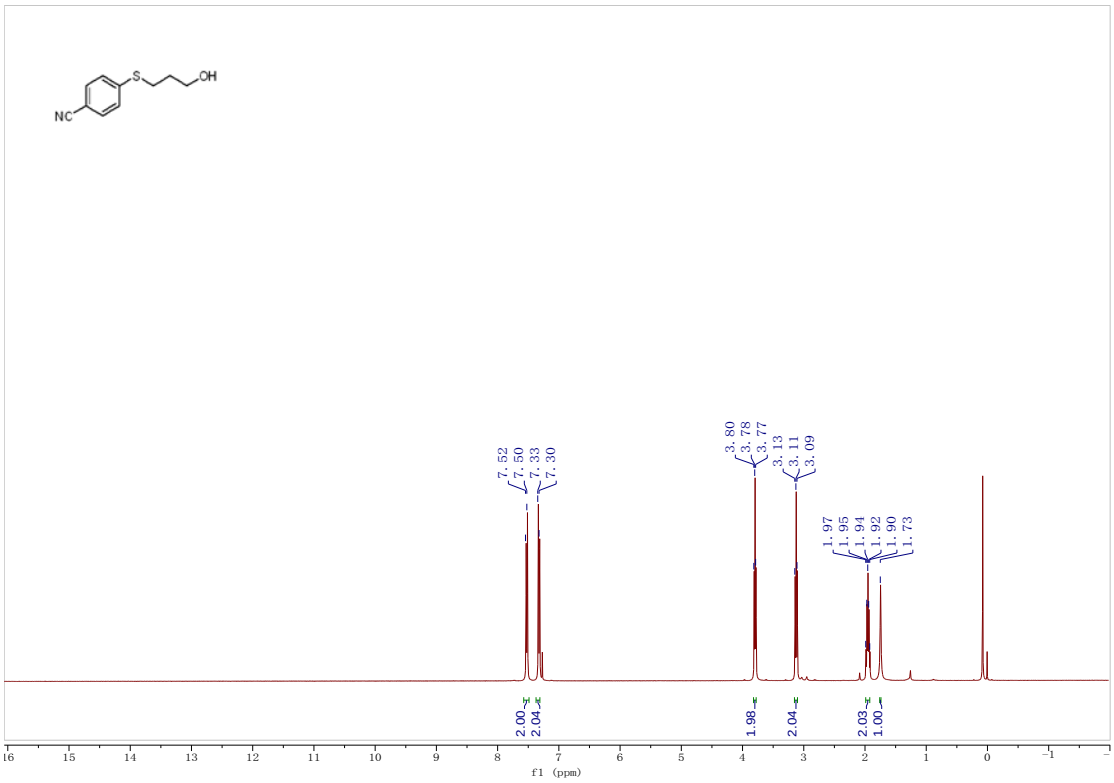
^{1}H NMR Spectrum of **3au** (400 MHz, $CDCl_3$)



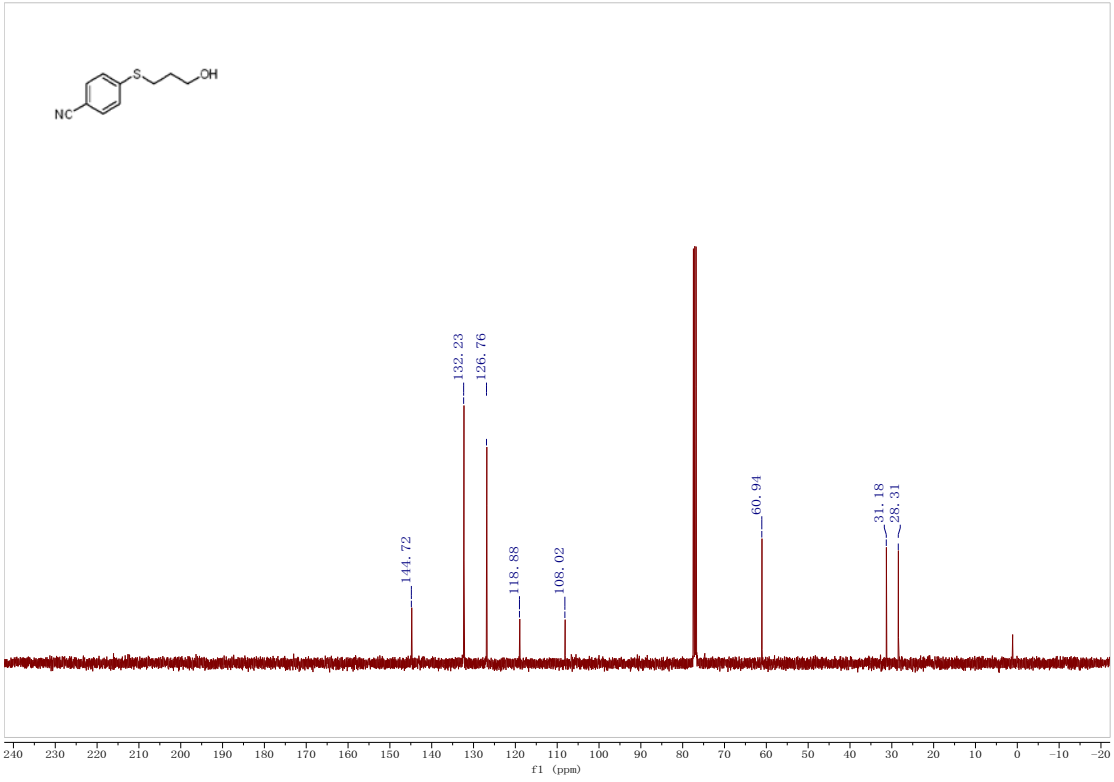
^{13}C NMR Spectrum of **3au** (101 MHz, $CDCl_3$)



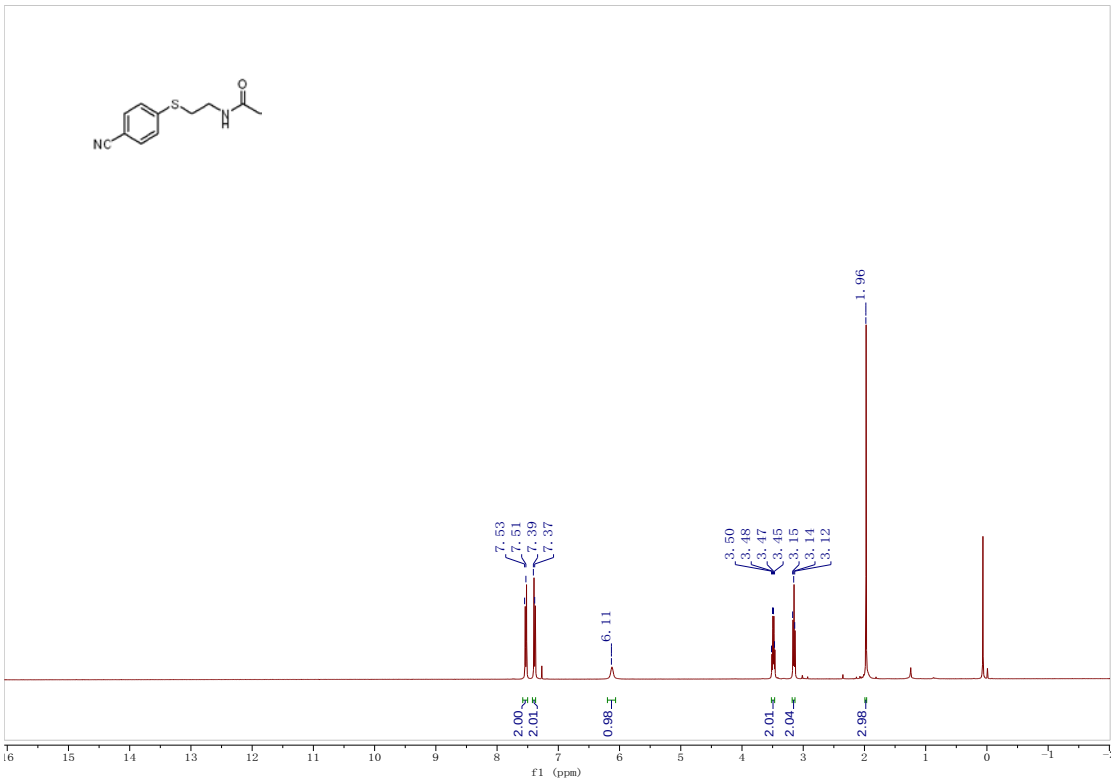
^{1}H NMR Spectrum of **3av** (400 MHz, $CDCl_3$)



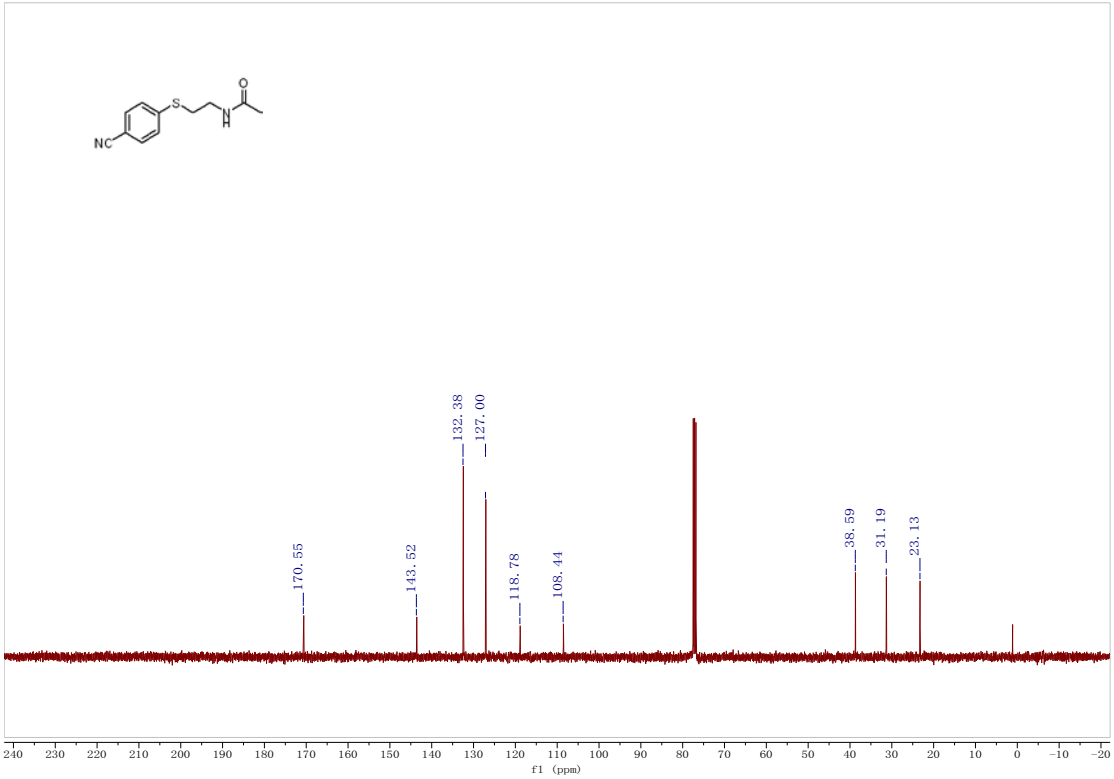
^{13}C NMR Spectrum of **3av** (101 MHz, $CDCl_3$)



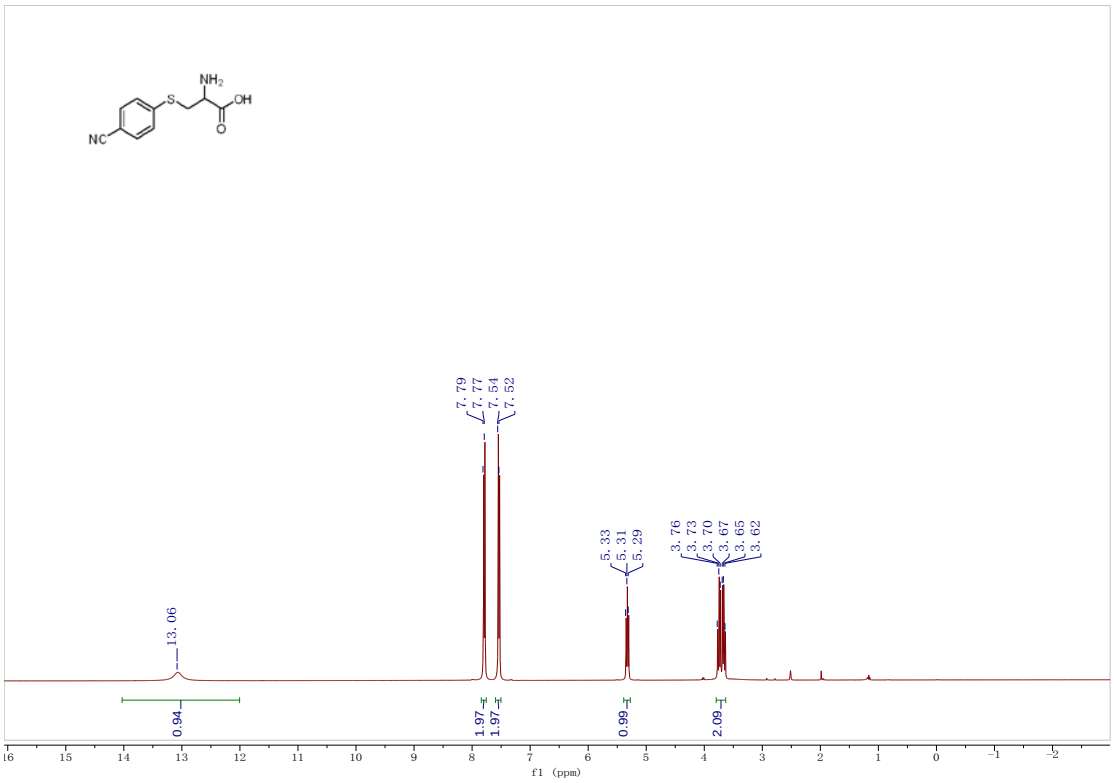
^{1}H NMR Spectrum of **3aw** (400 MHz, $CDCl_3$)



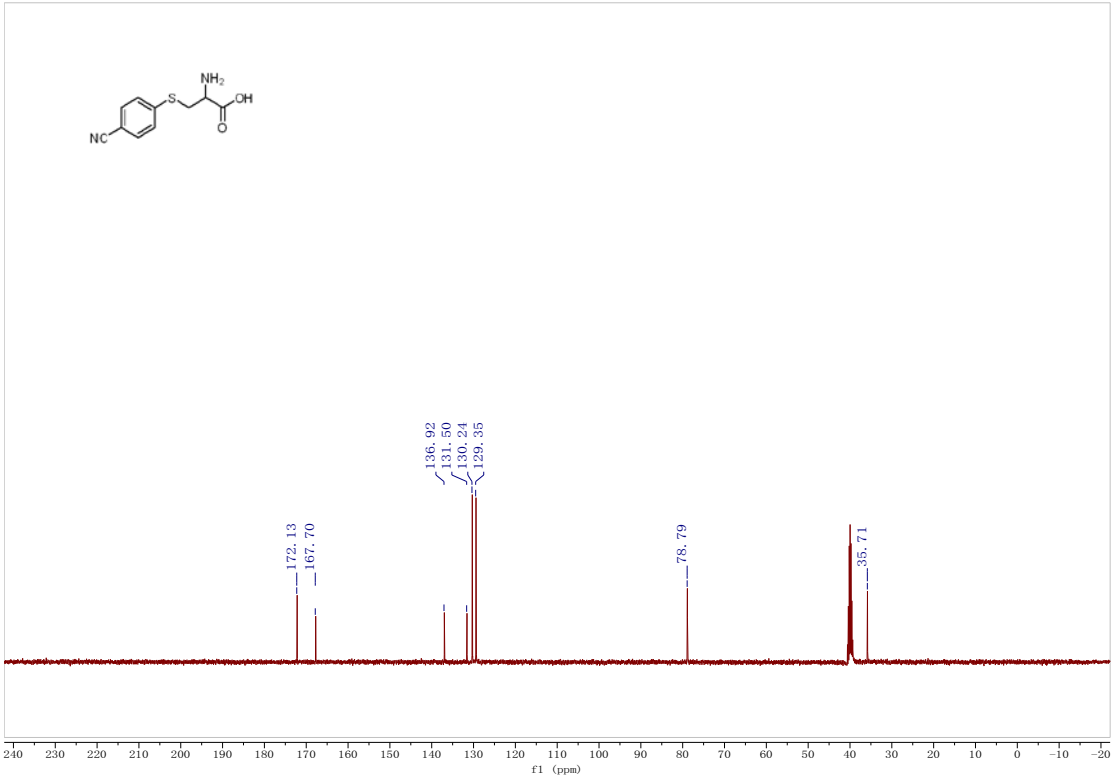
^{13}C NMR Spectrum of **3aw** (101 MHz, $CDCl_3$)



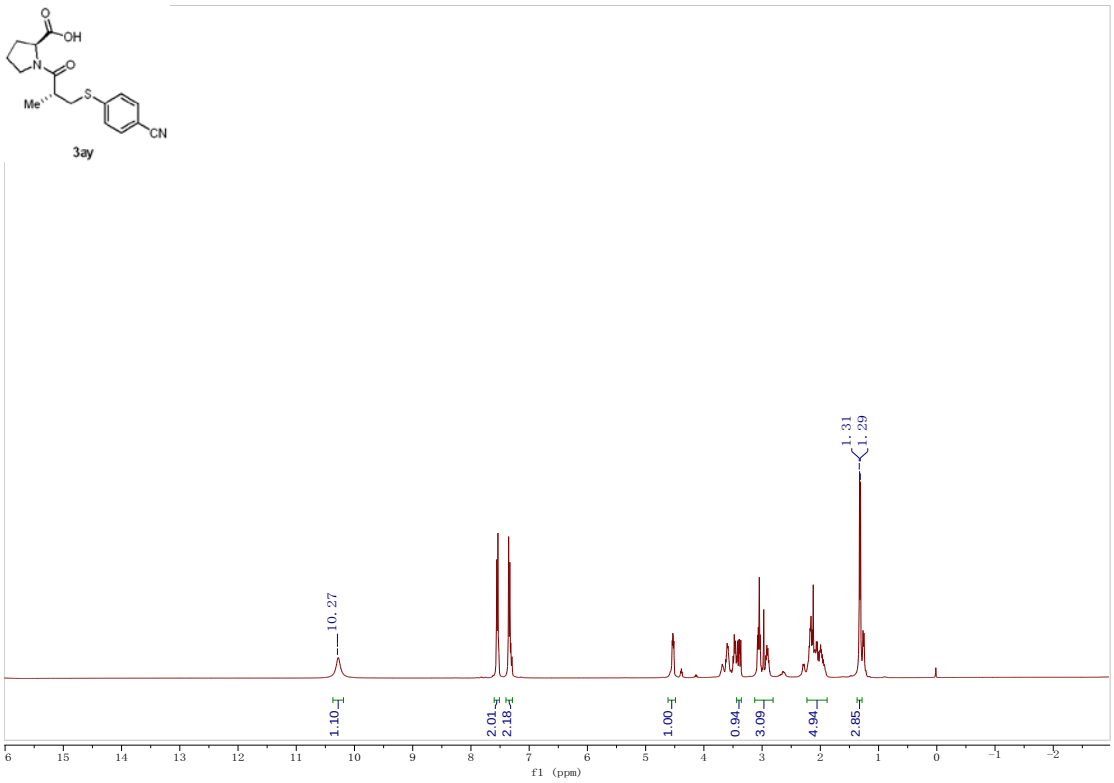
^{1}H NMR Spectrum of **3ax** (400 MHz, DMSO-*d6*)



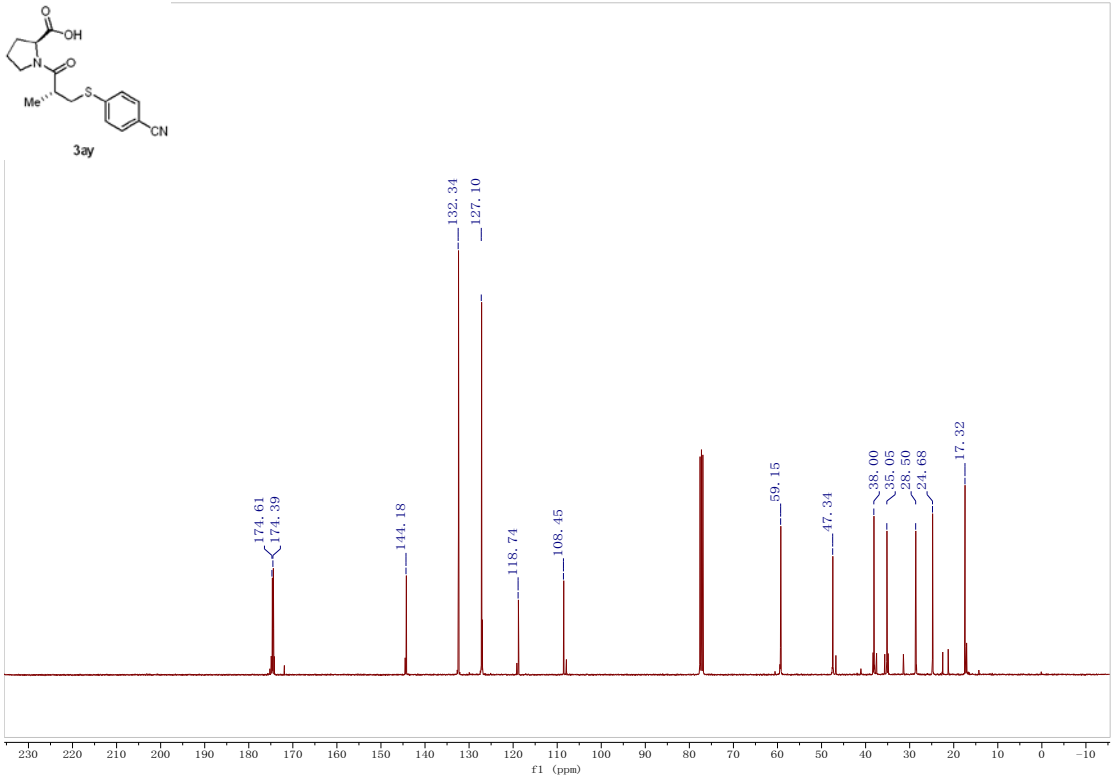
^{13}C NMR Spectrum of **3ax** (101 MHz, DMSO-*d6*)



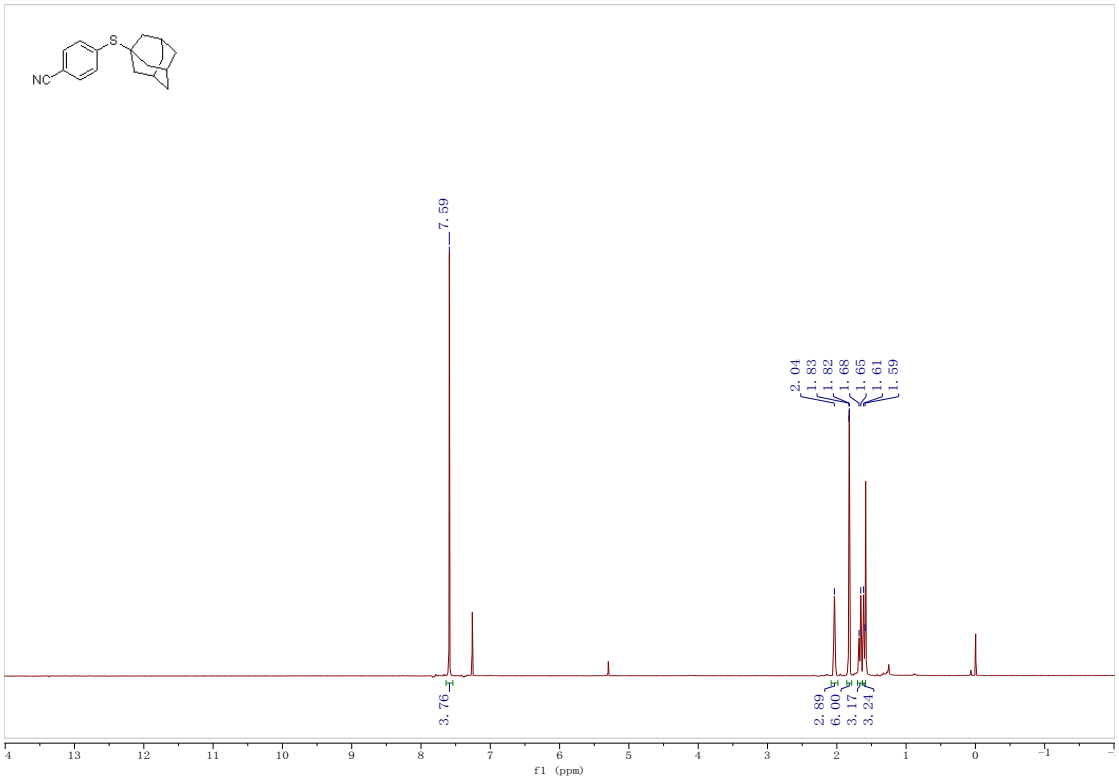
^{1}H NMR Spectrum of **3ay** (500 MHz, DMSO-*d6*)



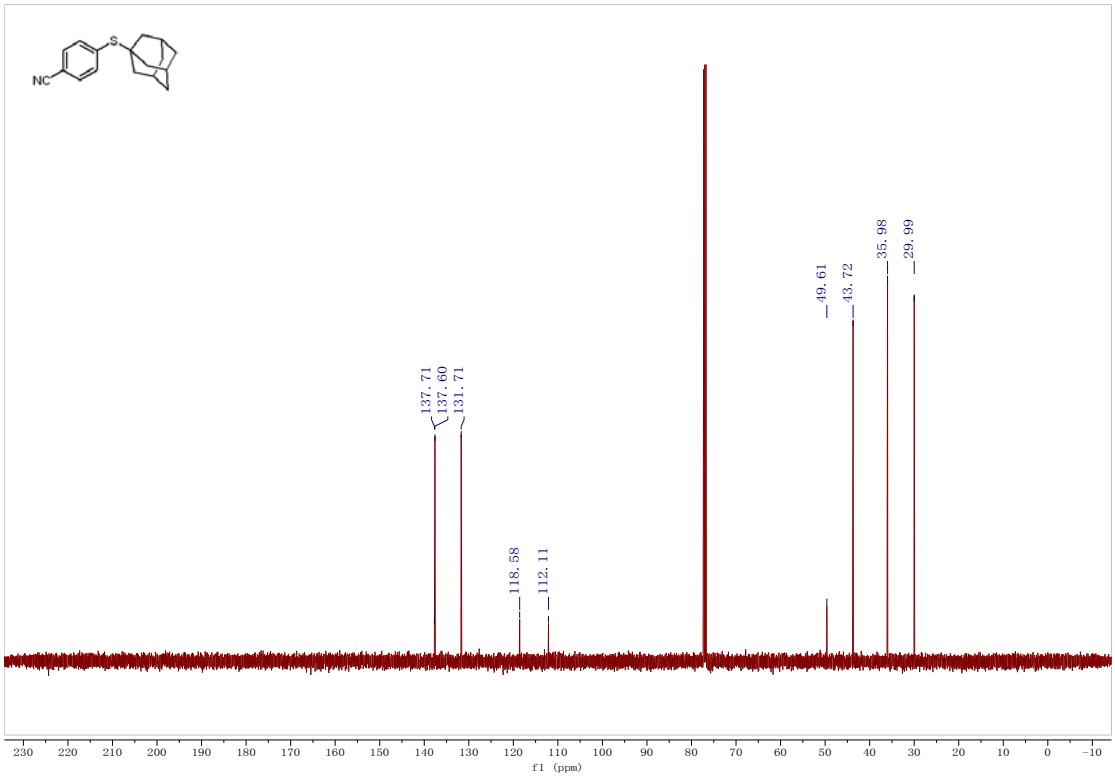
^{13}C NMR Spectrum of **3ay** (126 MHz, DMSO-*d6*)



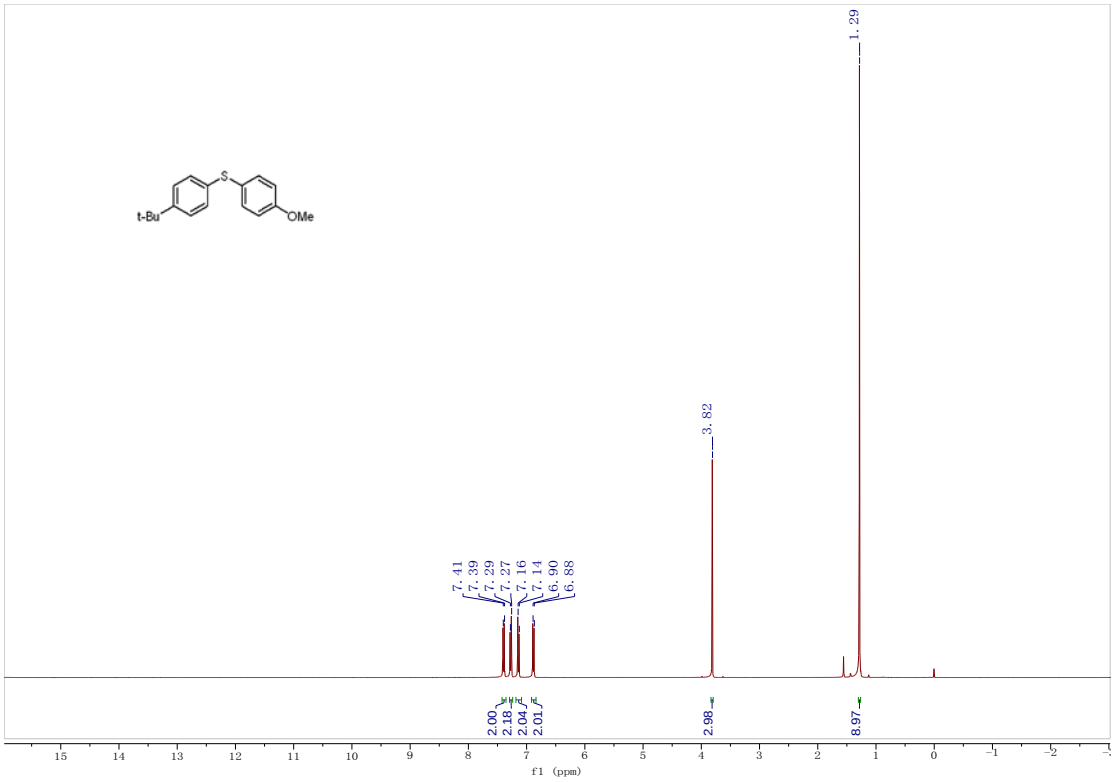
^{1}H NMR Spectrum of **3az** (126 MHz, $CDCl_3$)



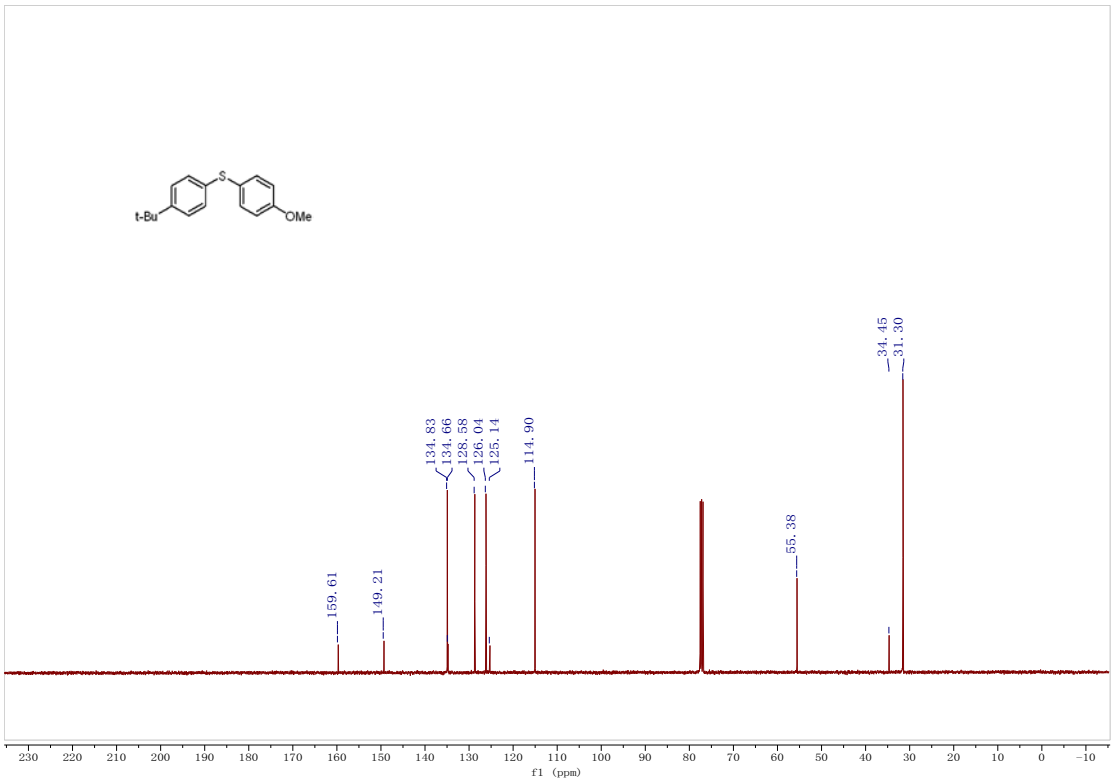
^{13}C NMR Spectrum of **3az** (126 MHz, $CDCl_3$)



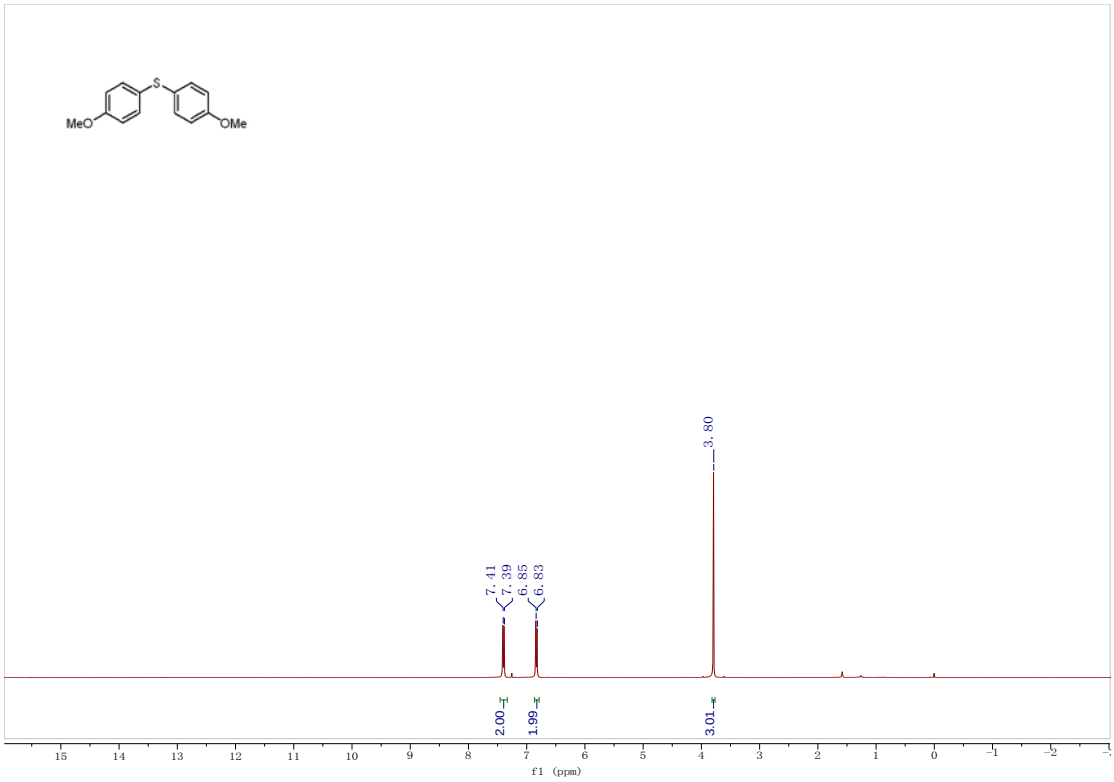
^{1}H NMR Spectrum of **3ba** (400 MHz, $CDCl_3$)



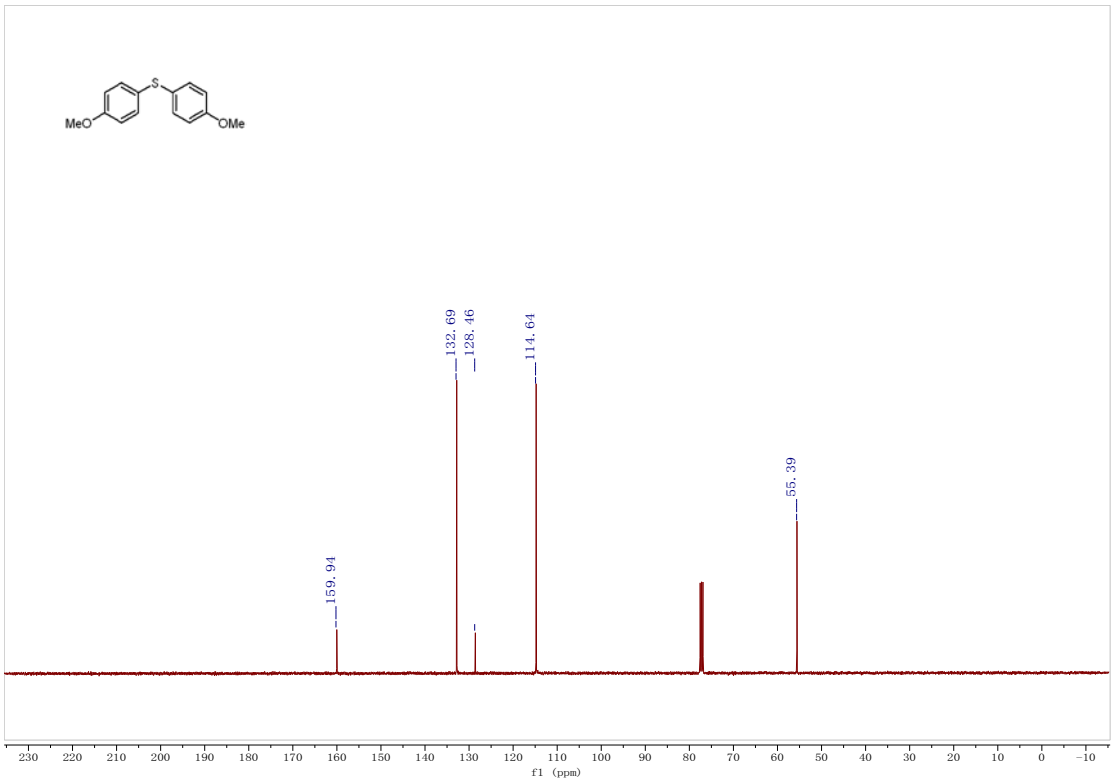
^{13}C NMR Spectrum of **3ba** (101 MHz, $CDCl_3$)



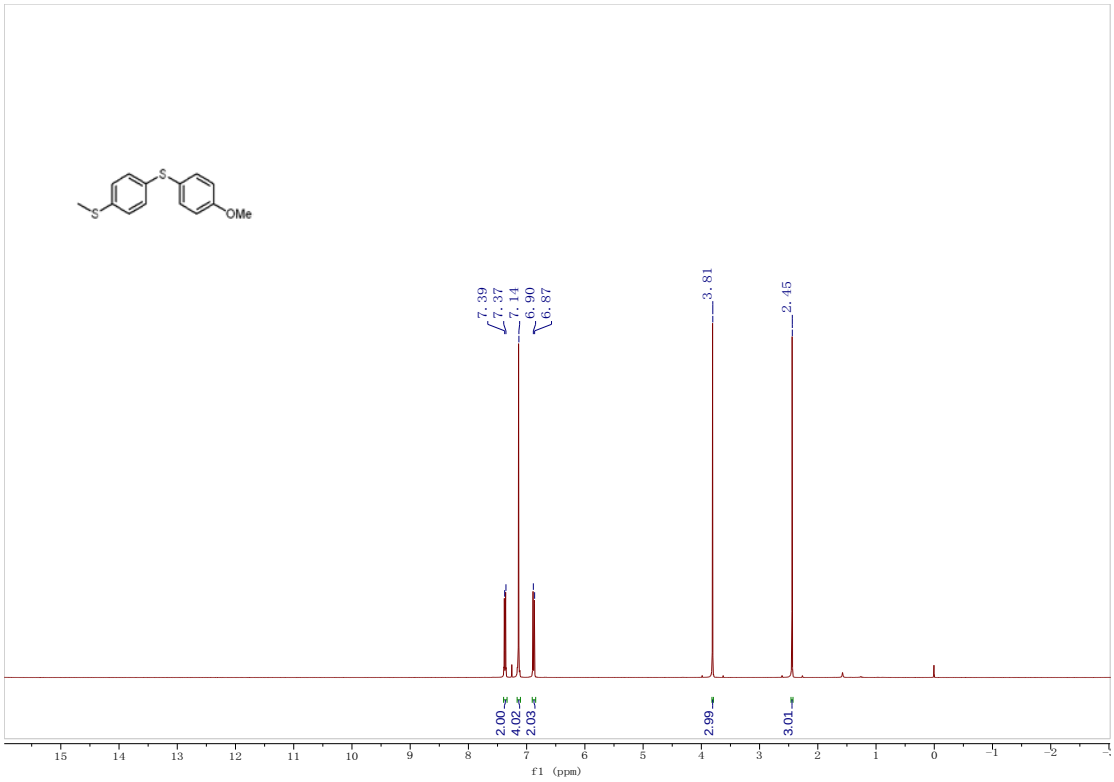
^{1}H NMR Spectrum of **3bb** (400 MHz, $CDCl_3$)



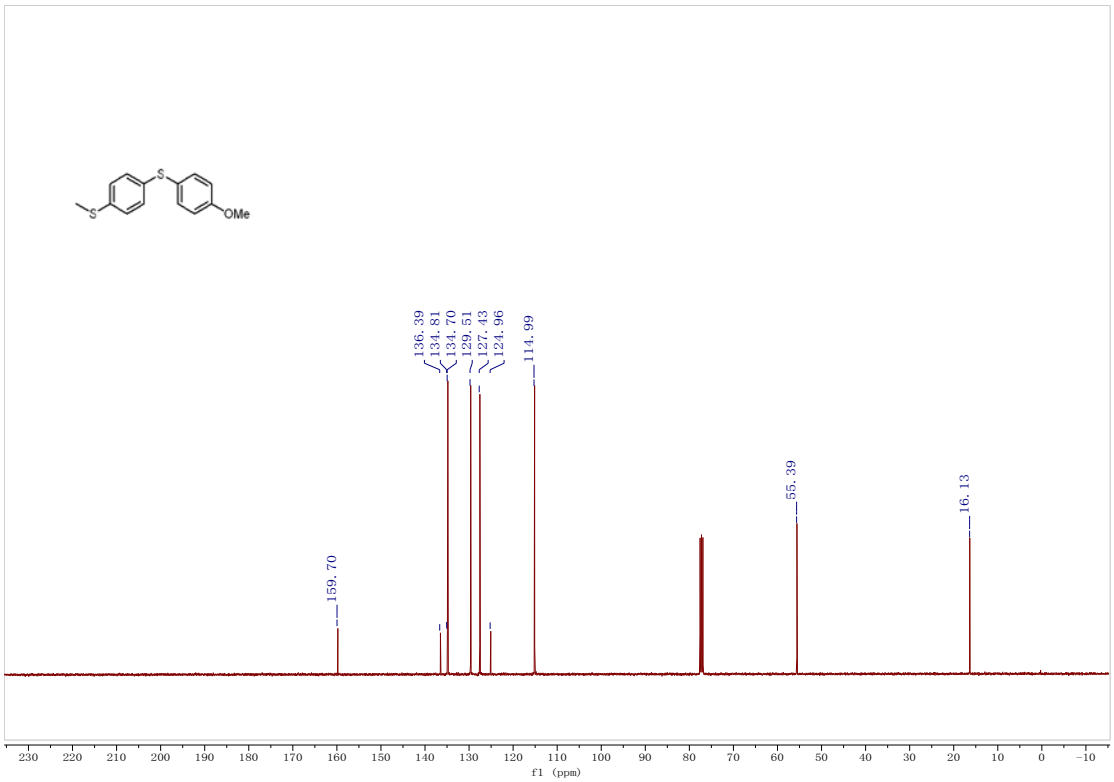
^{13}C NMR Spectrum of **3bb** (101 MHz, $CDCl_3$)



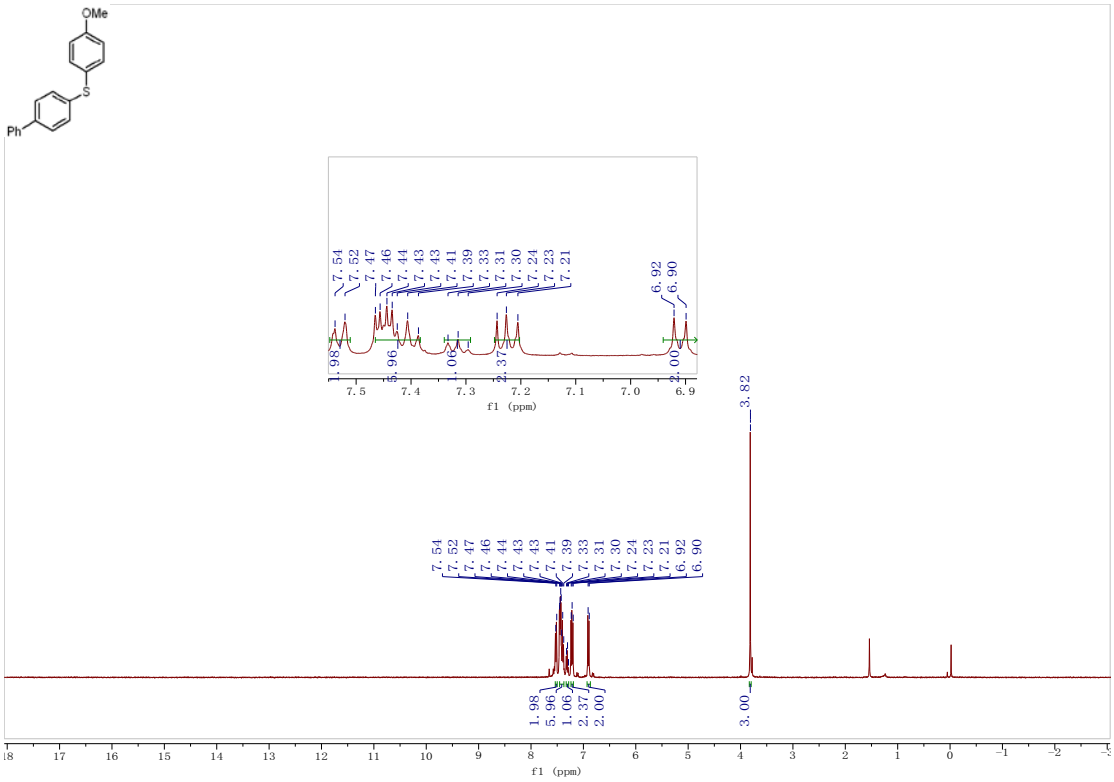
^{1}H NMR Spectrum of **3bc** (400 MHz, $CDCl_3$)



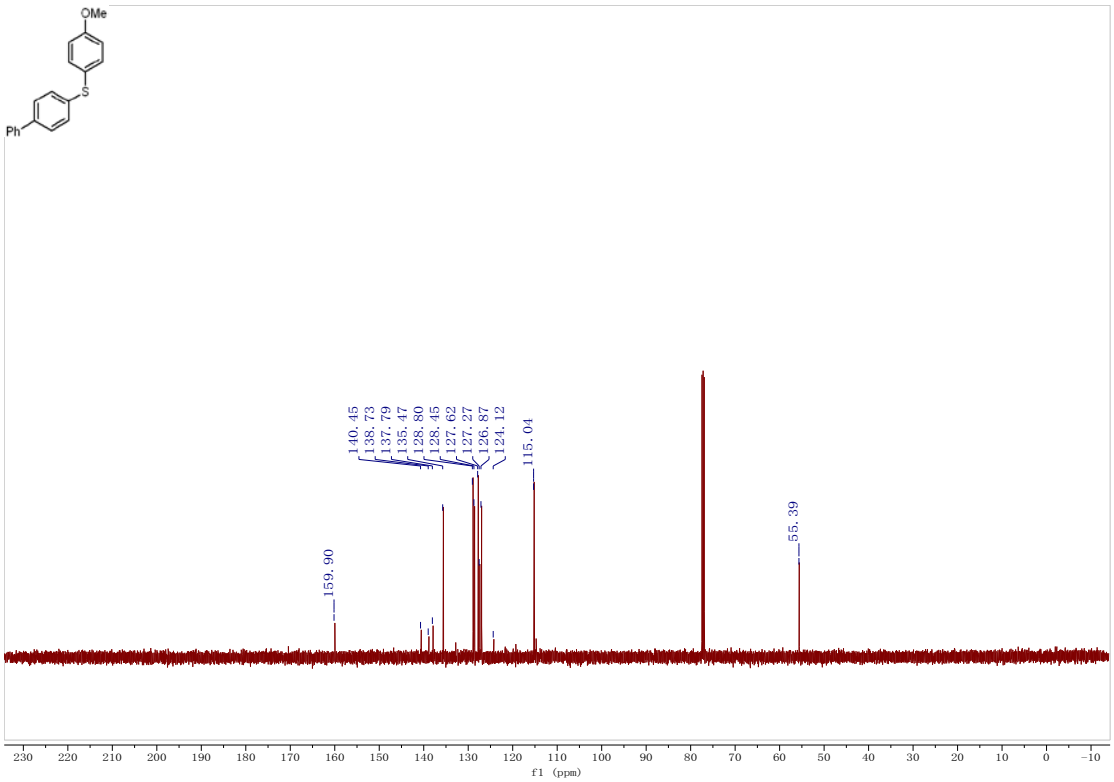
^{13}C NMR Spectrum of **3bc** (101 MHz, $CDCl_3$)



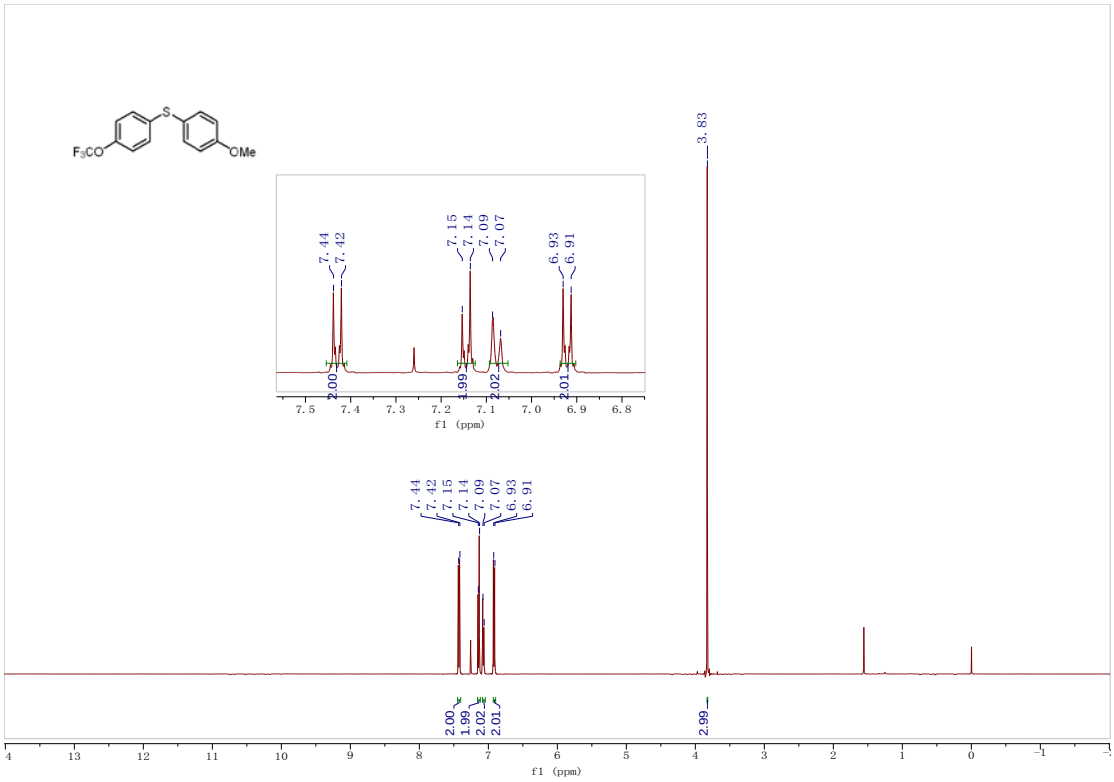
^{1}H NMR Spectrum of **3bd** (400 MHz, $CDCl_3$)



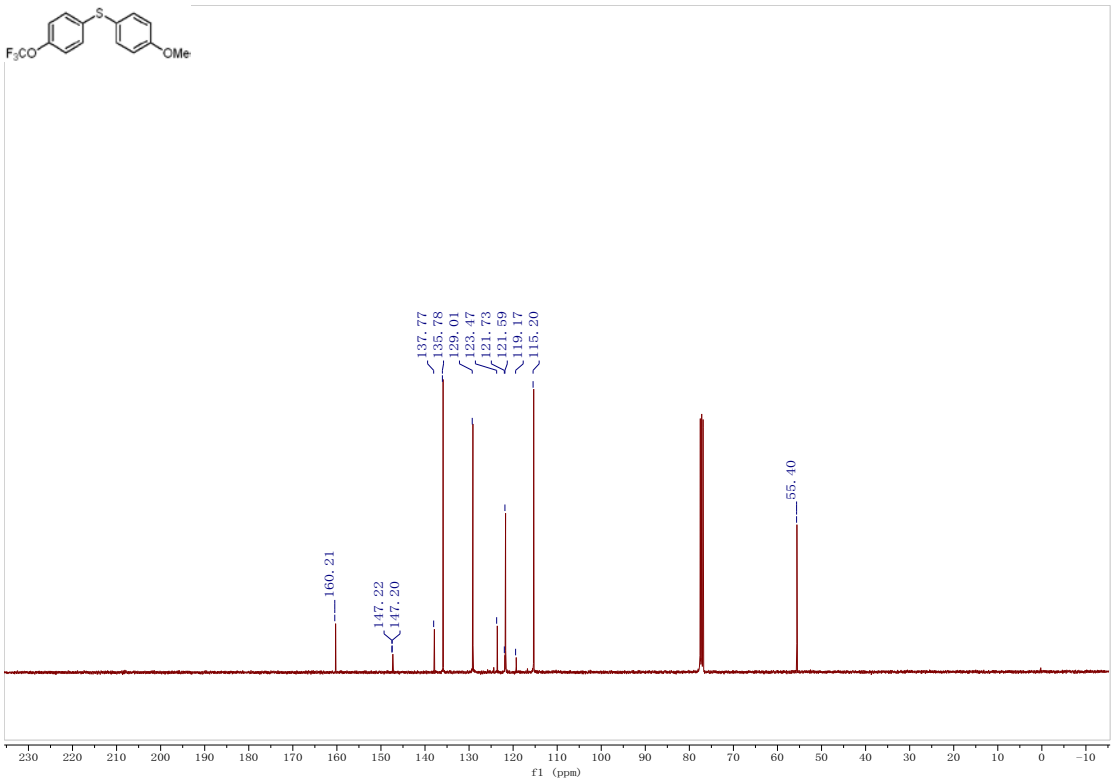
^{13}C NMR Spectrum of **3bd** (101 MHz, $CDCl_3$)



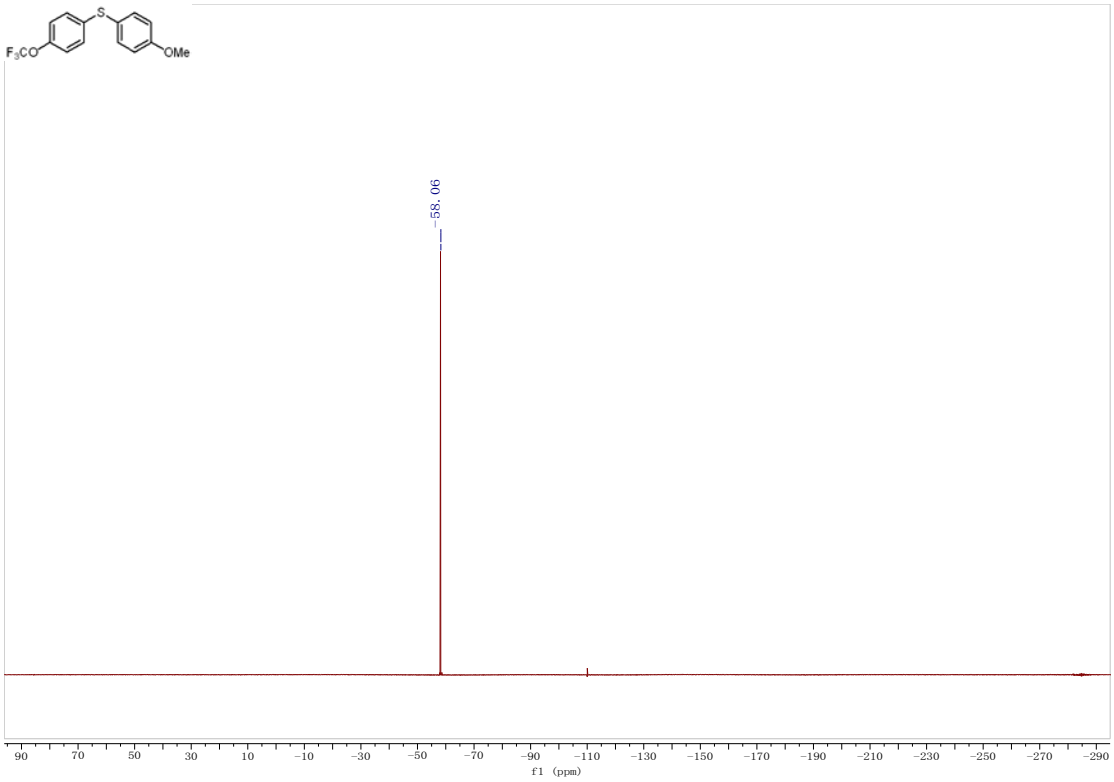
^{1}H NMR Spectrum of **3be** (500 MHz, $CDCl_3$)



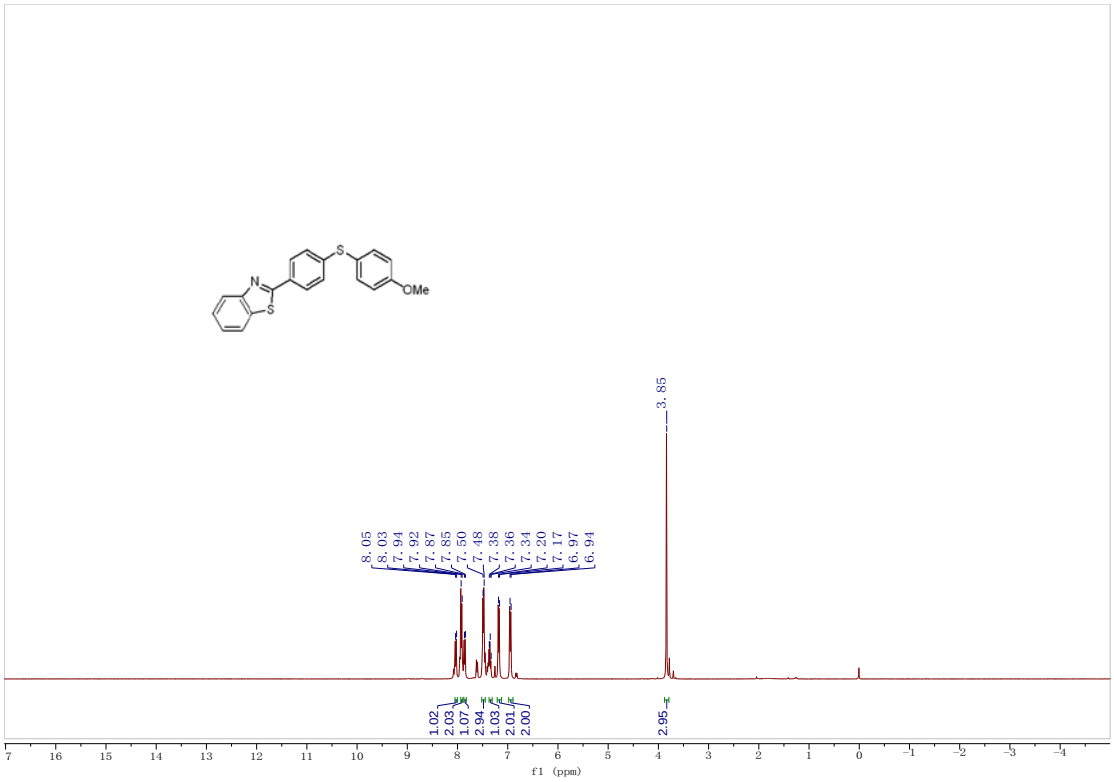
^{13}C NMR Spectrum of **3be** (126 MHz, $CDCl_3$)



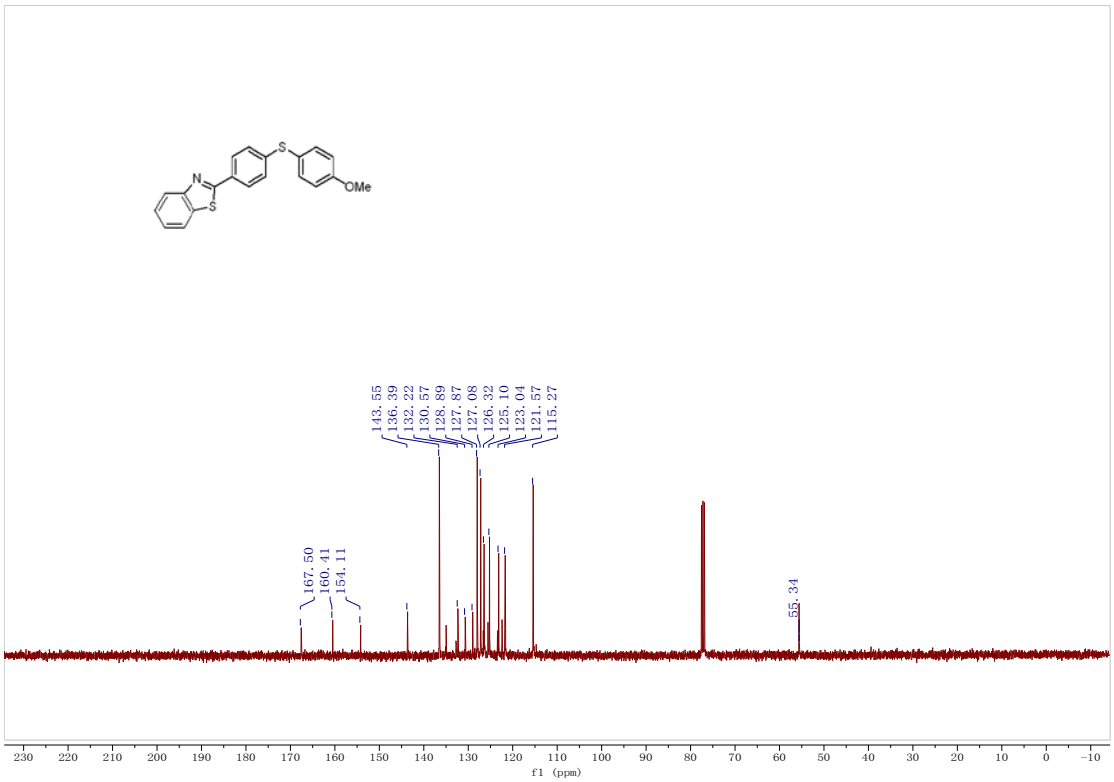
^{13}F NMR Spectrum of **3i** (376 MHz, $CDCl_3$)



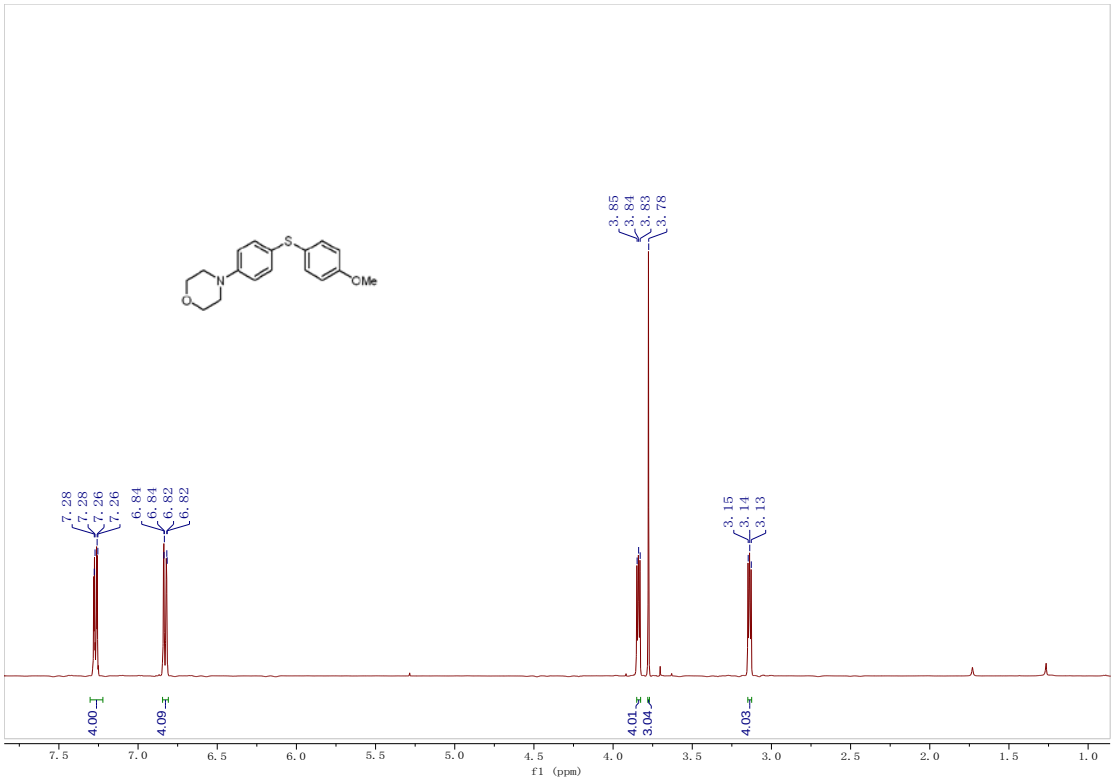
^{1}H NMR Spectrum of **3bf** (400 MHz, $CDCl_3$)



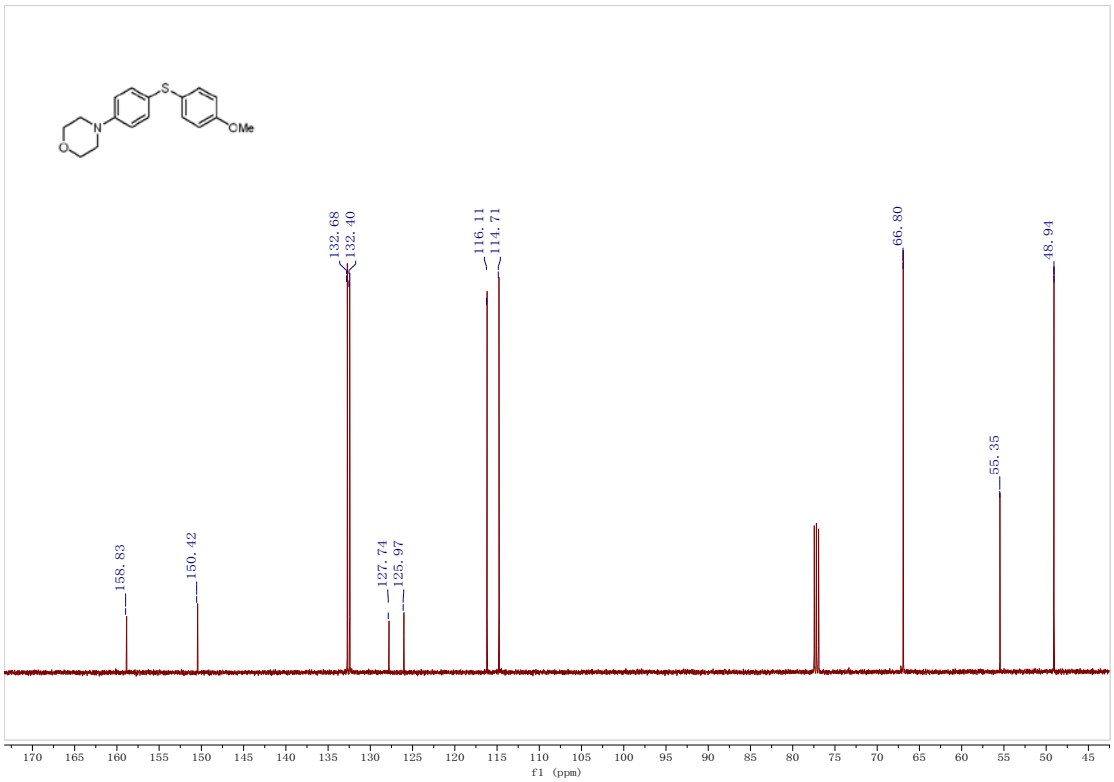
^{13}C NMR Spectrum of **3bf** (101 MHz, $CDCl_3$)



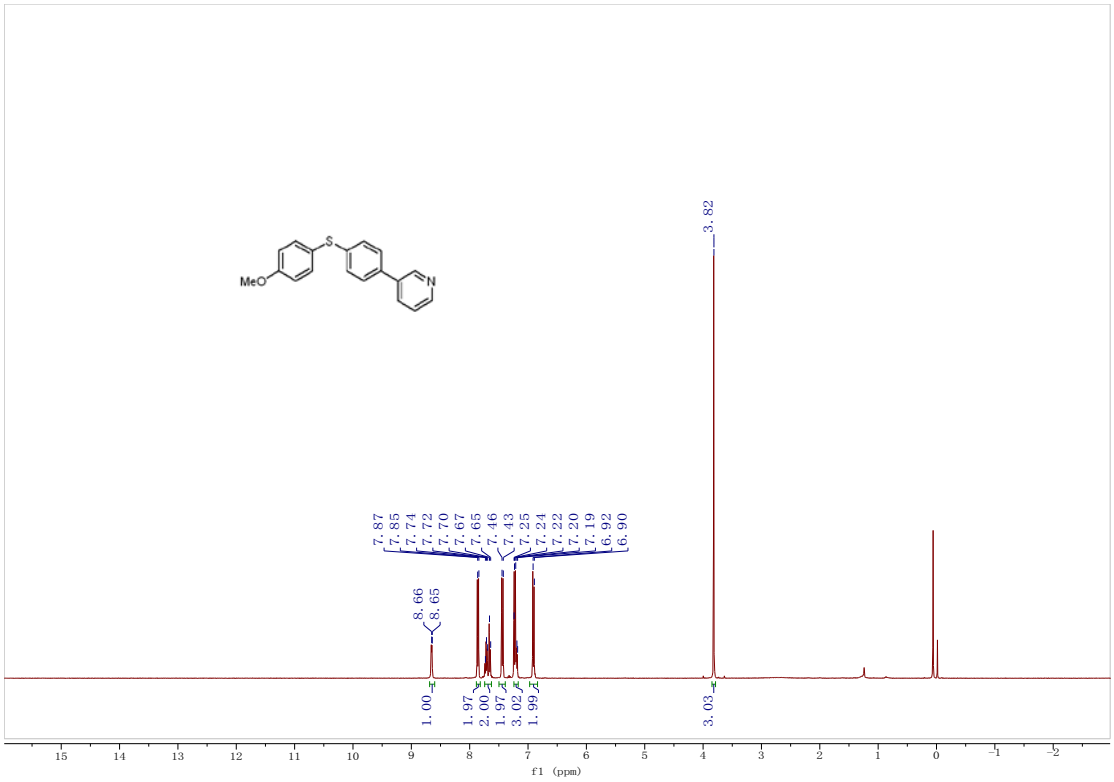
^{1}H NMR Spectrum of **3bg** (500 MHz, $CDCl_3$)



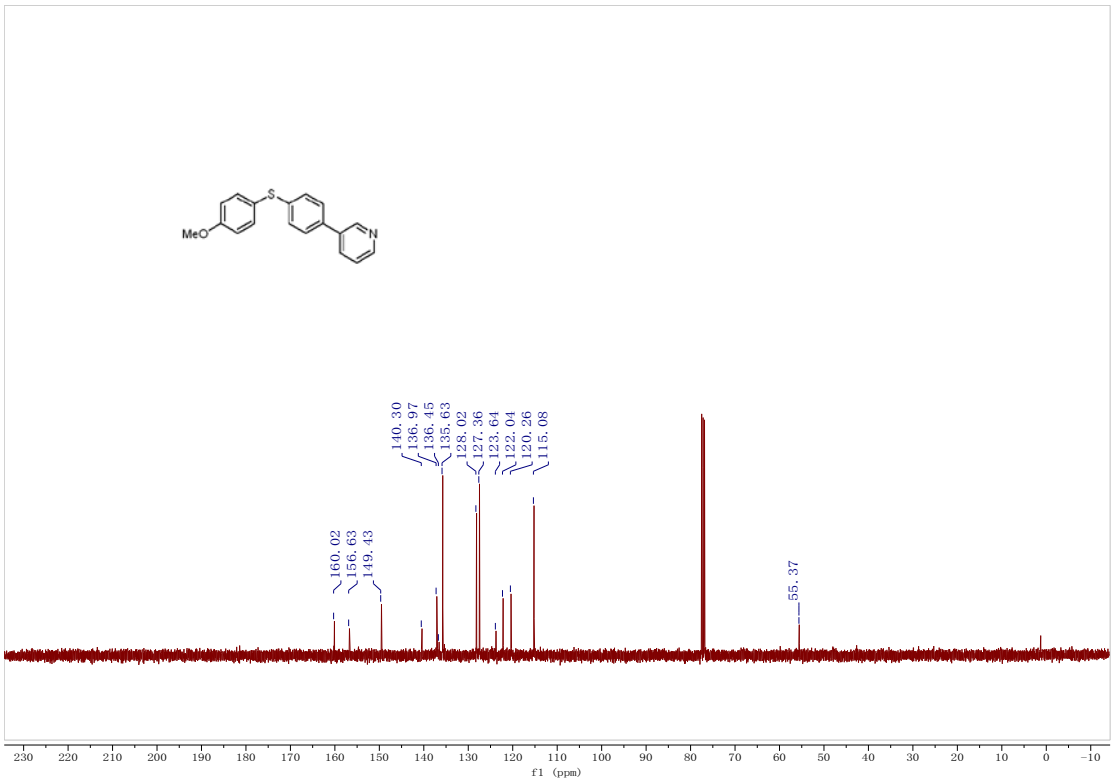
^{13}C NMR Spectrum of **3bg** (126 MHz, $CDCl_3$)



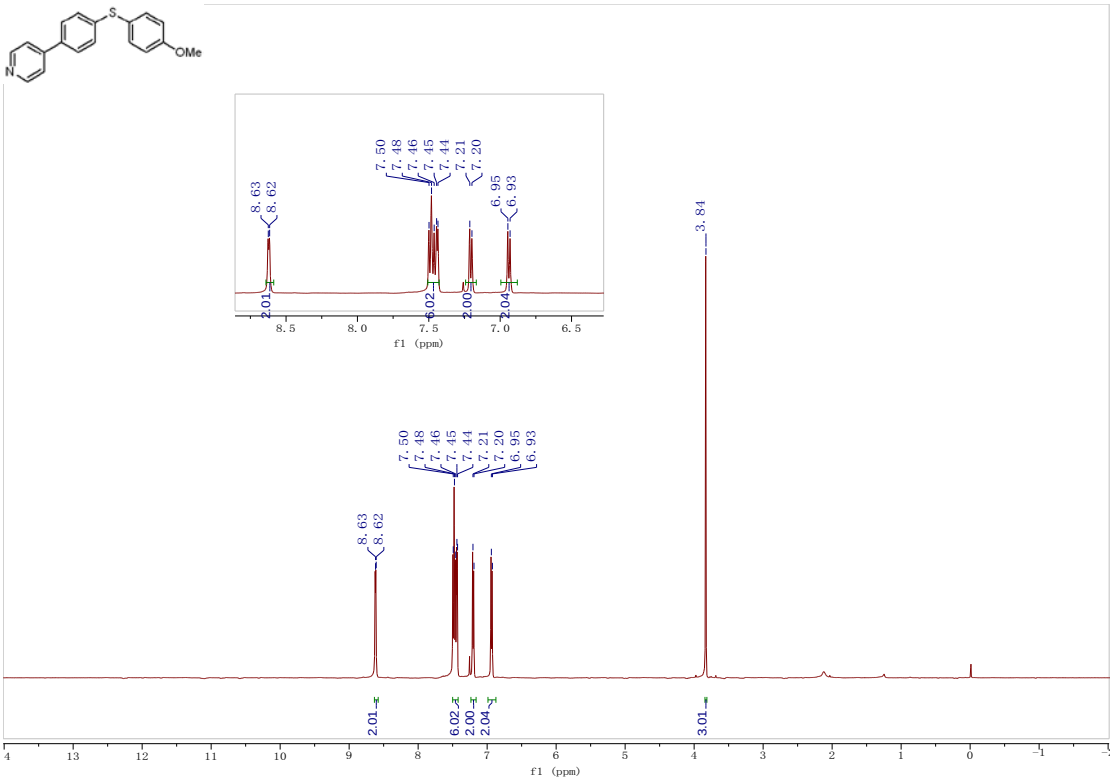
^{1}H NMR Spectrum of **3bh** (400 MHz, $CDCl_3$)



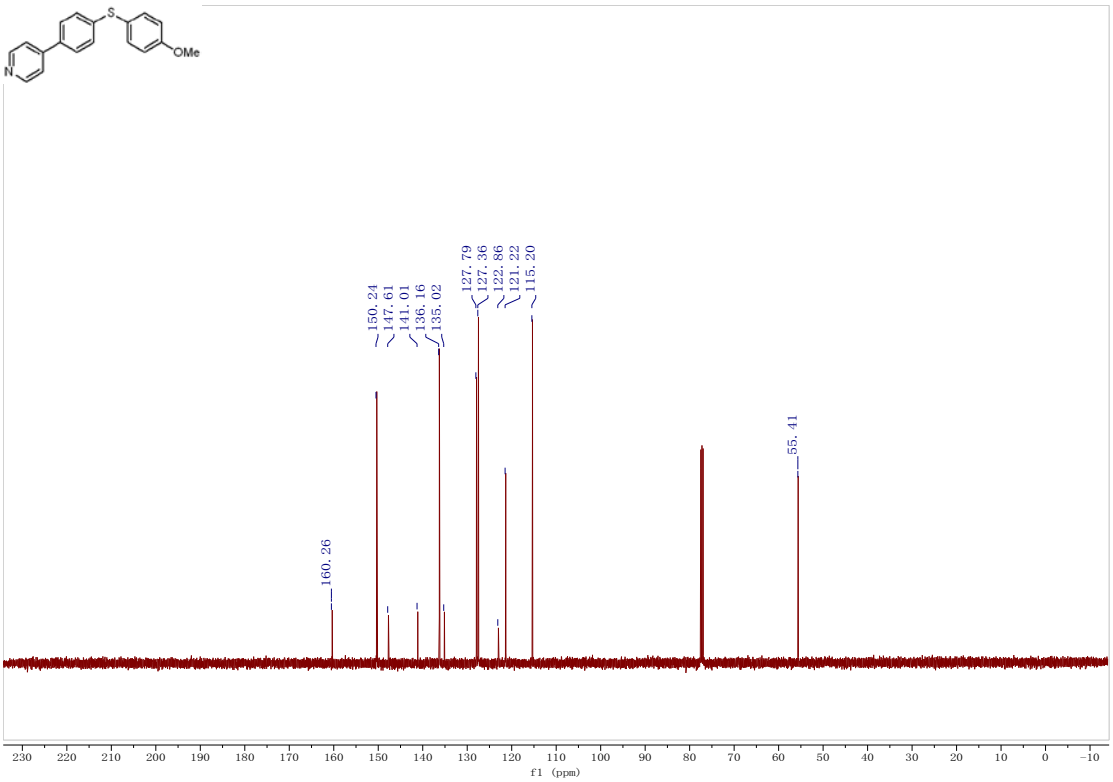
^{13}C NMR Spectrum of **3bh** (101 MHz, $CDCl_3$)



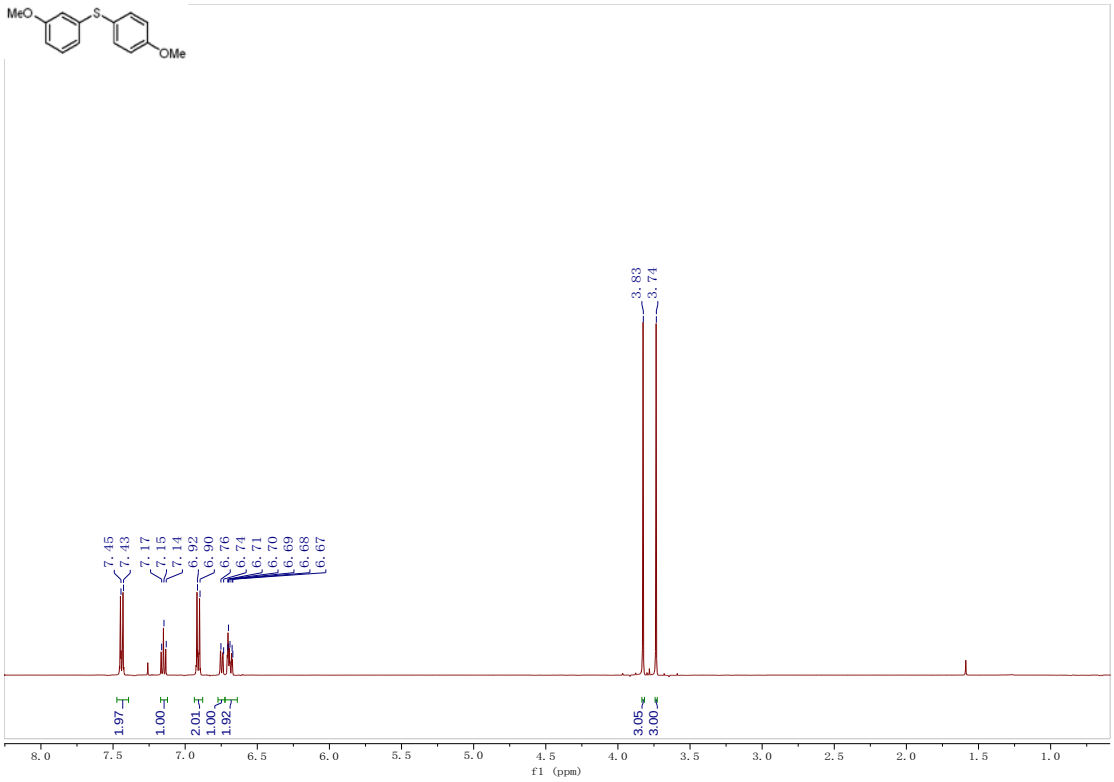
^{1}H NMR Spectrum of **3bi** (500 MHz, $CDCl_3$)



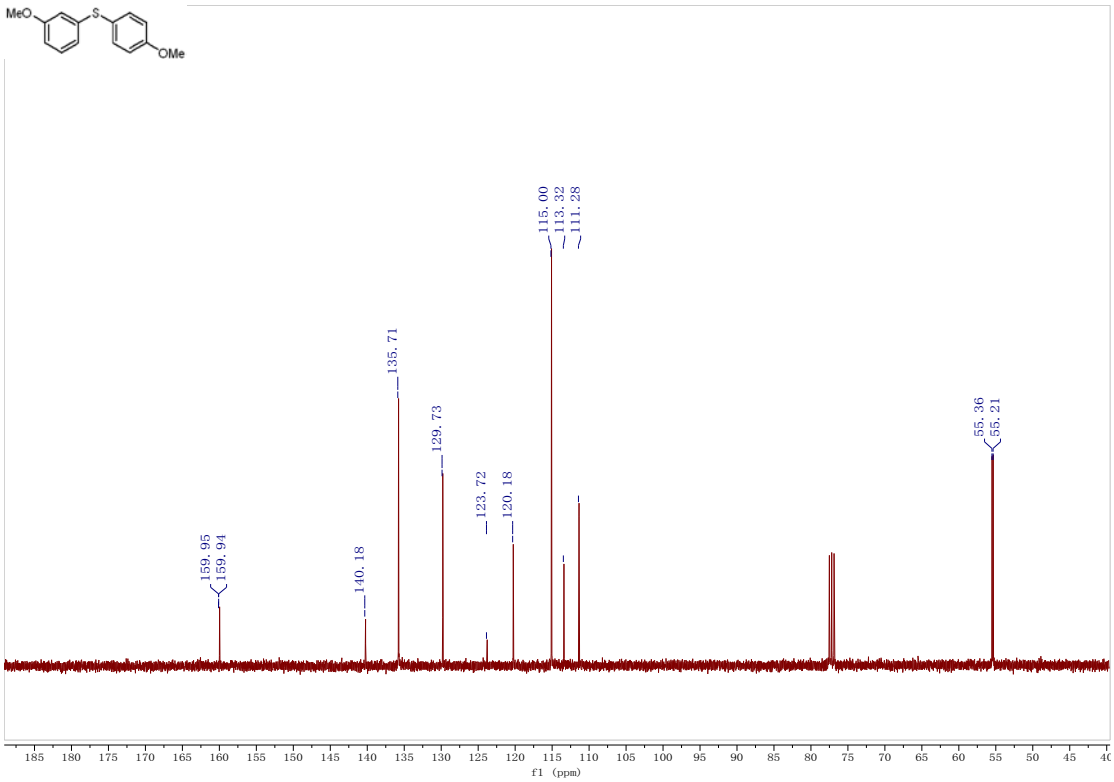
^{13}C NMR Spectrum of **3bi** (126 MHz, $CDCl_3$)



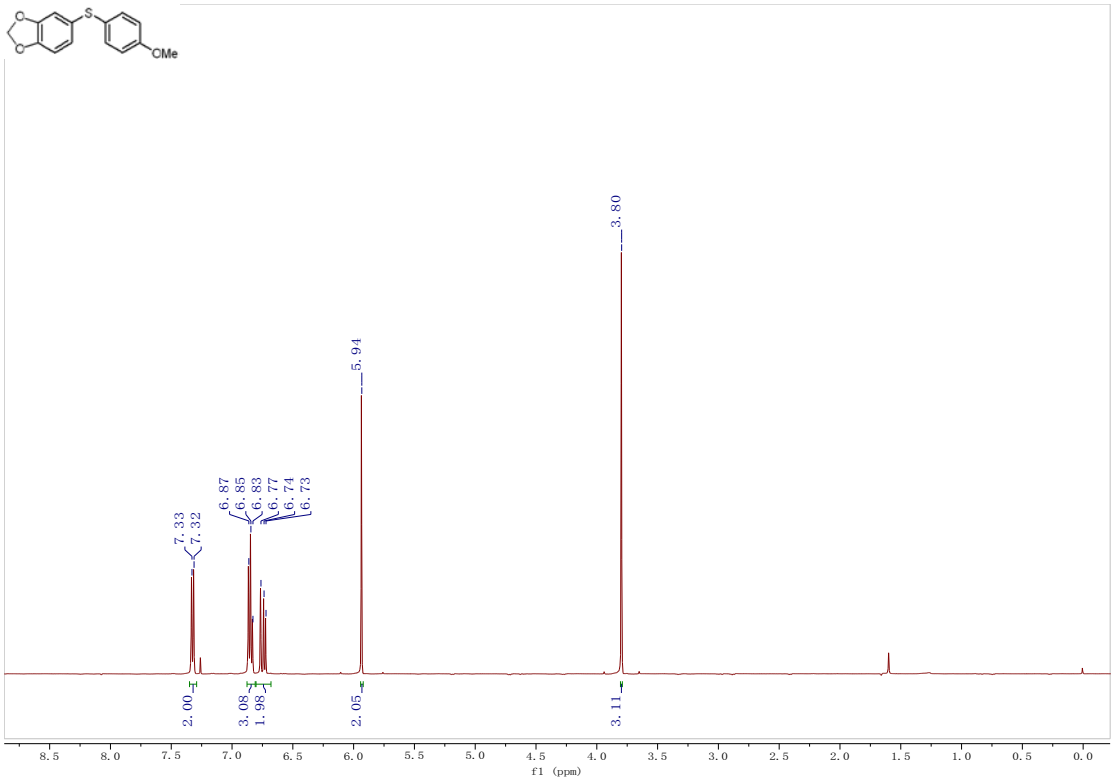
^{1}H NMR Spectrum of **3bj** (500 MHz, $CDCl_3$)



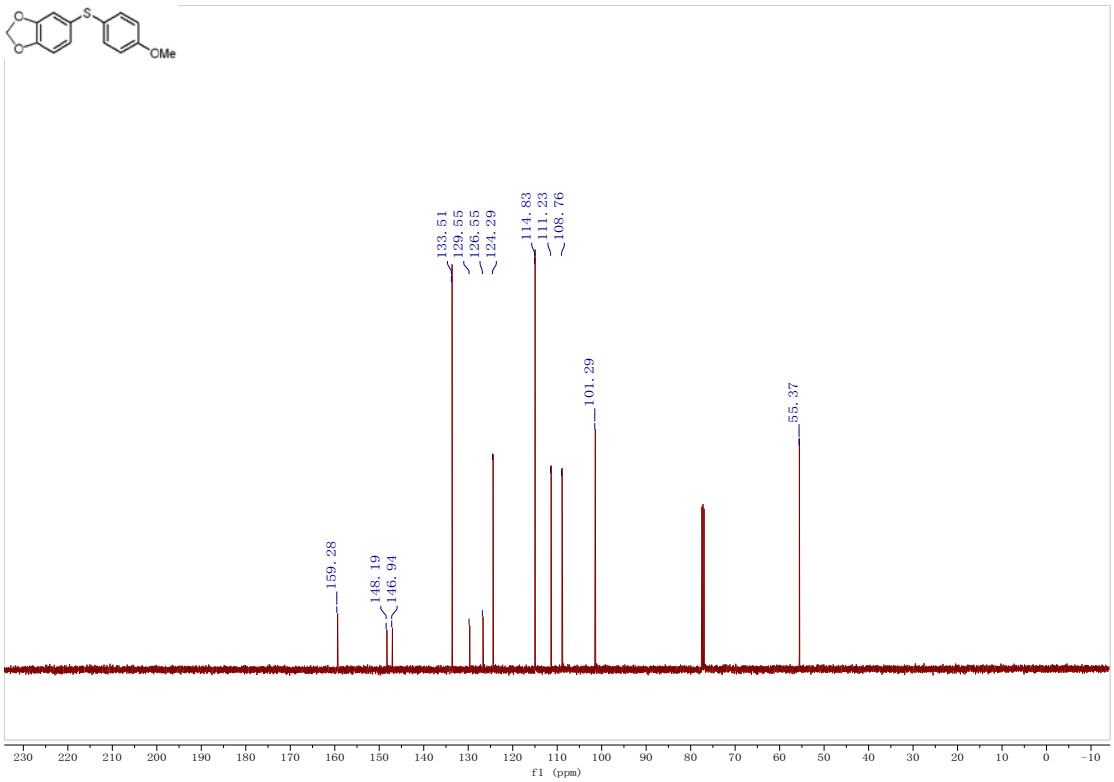
^{13}C NMR Spectrum of **3bj** (101 MHz, $CDCl_3$)



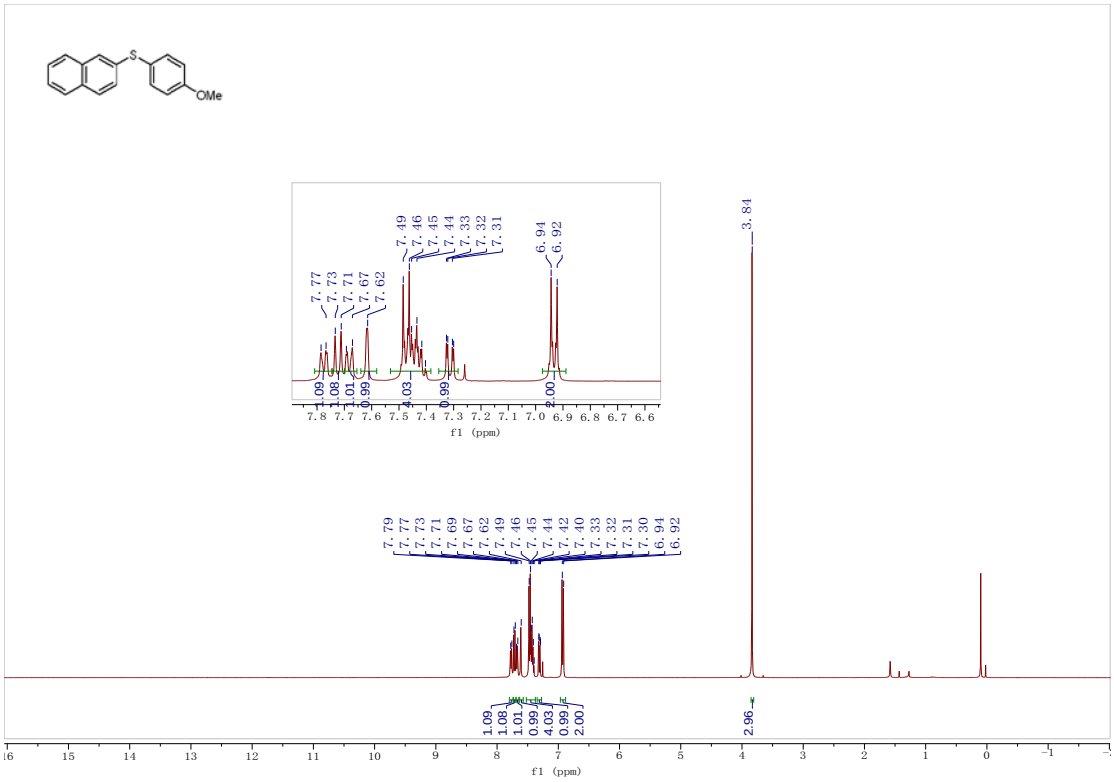
^{1}H NMR Spectrum of **3bk** (500 MHz, $CDCl_3$)



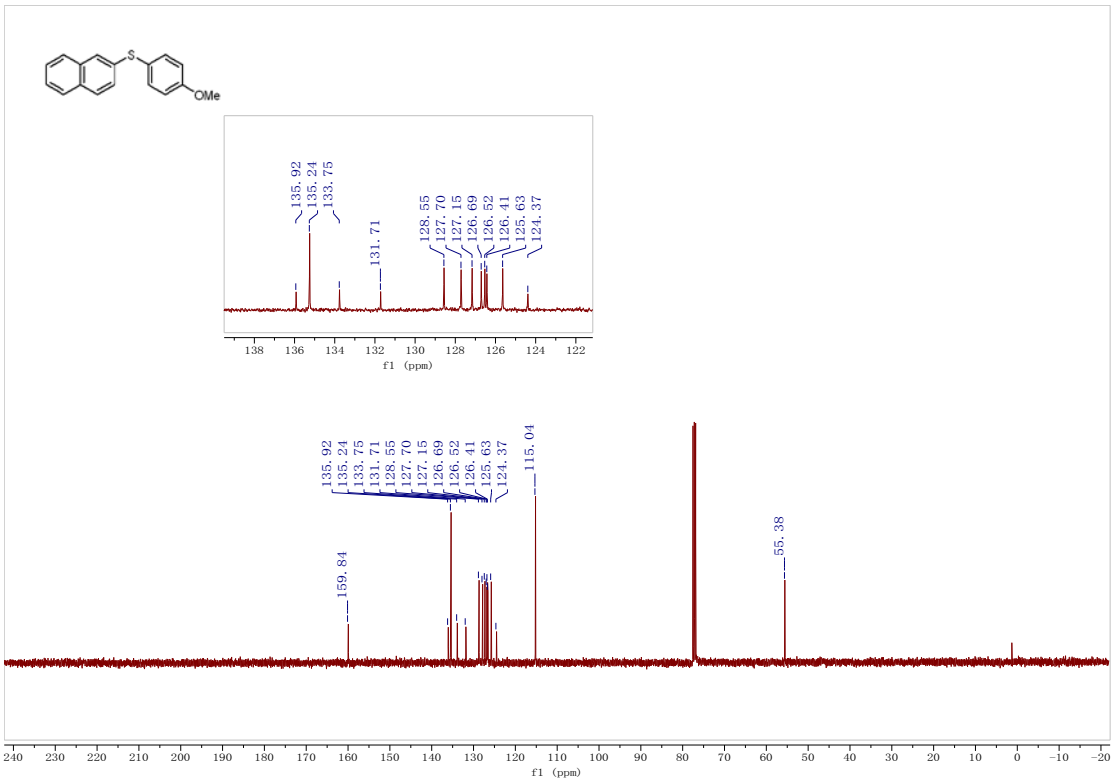
^{13}C NMR Spectrum of **3bk** (126 MHz, $CDCl_3$)



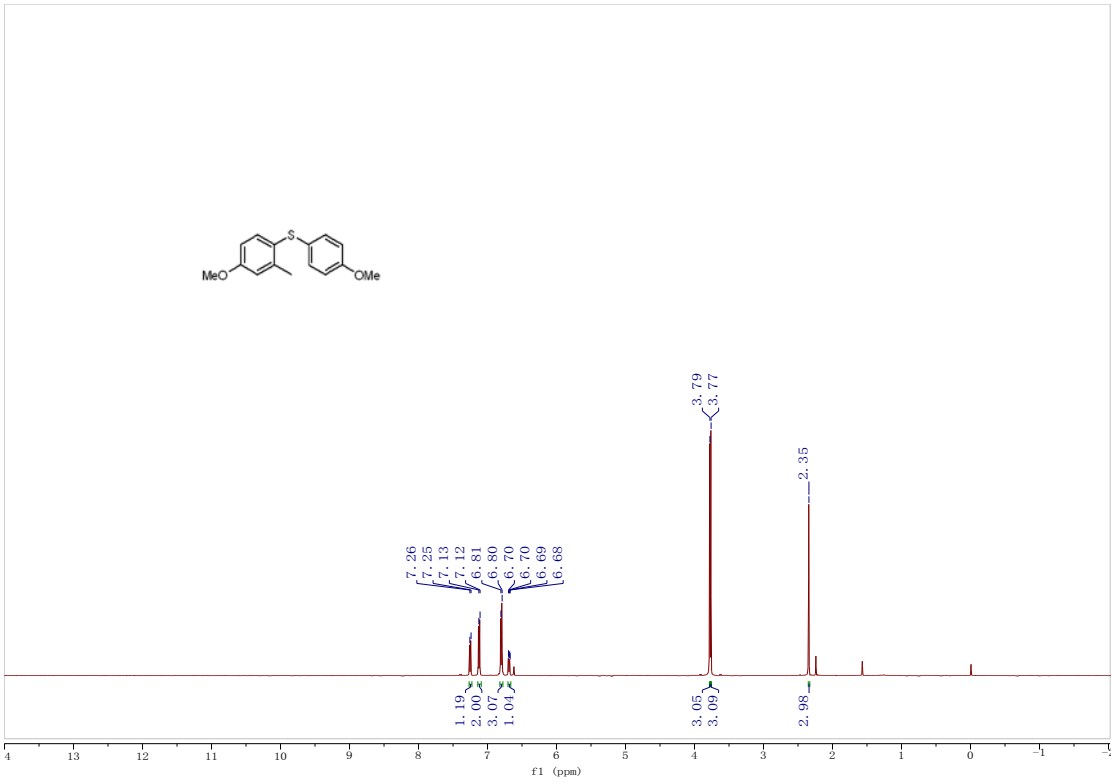
^{1}H NMR Spectrum of **3bl** (400 MHz, $CDCl_3$)



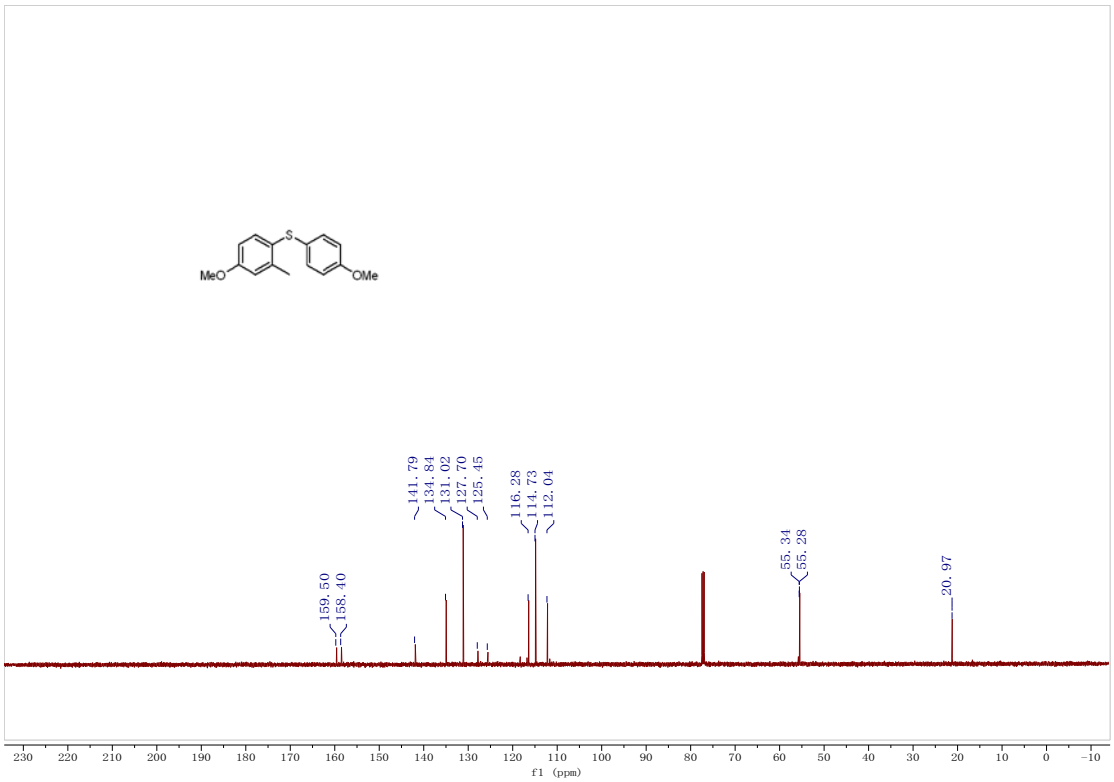
^{13}C NMR Spectrum of **3bl** (101 MHz, $CDCl_3$)



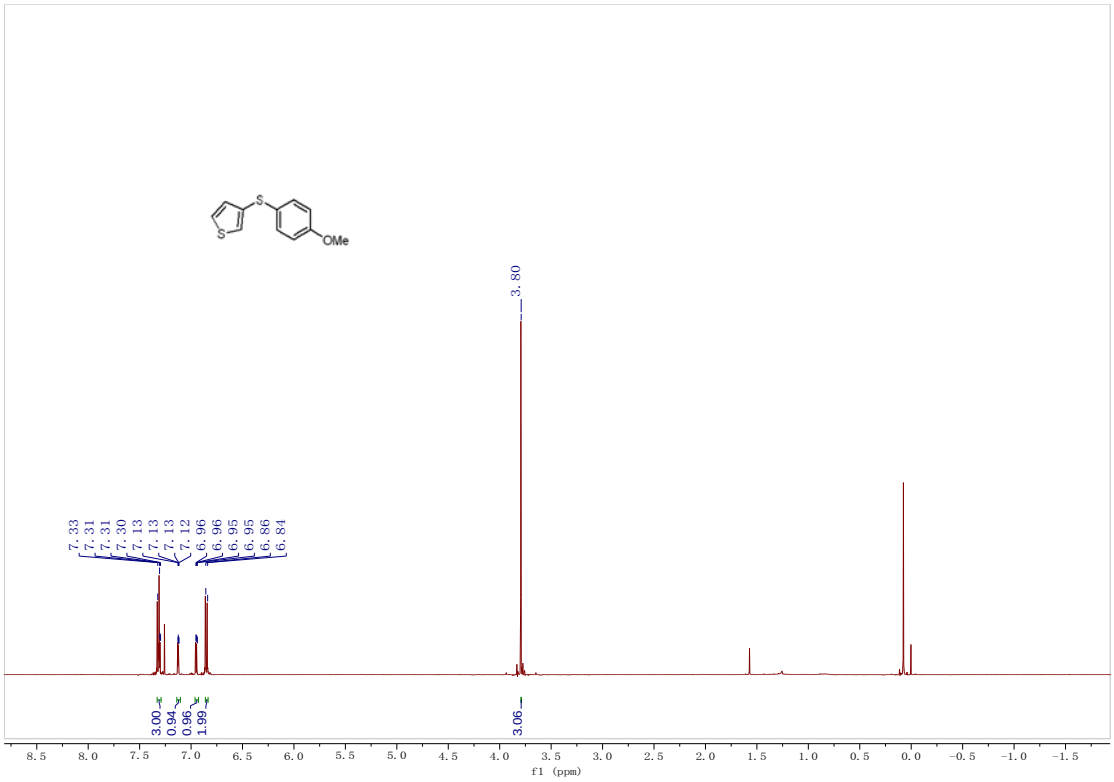
^{1}H NMR Spectrum of **3bm** (500 MHz, $CDCl_3$)



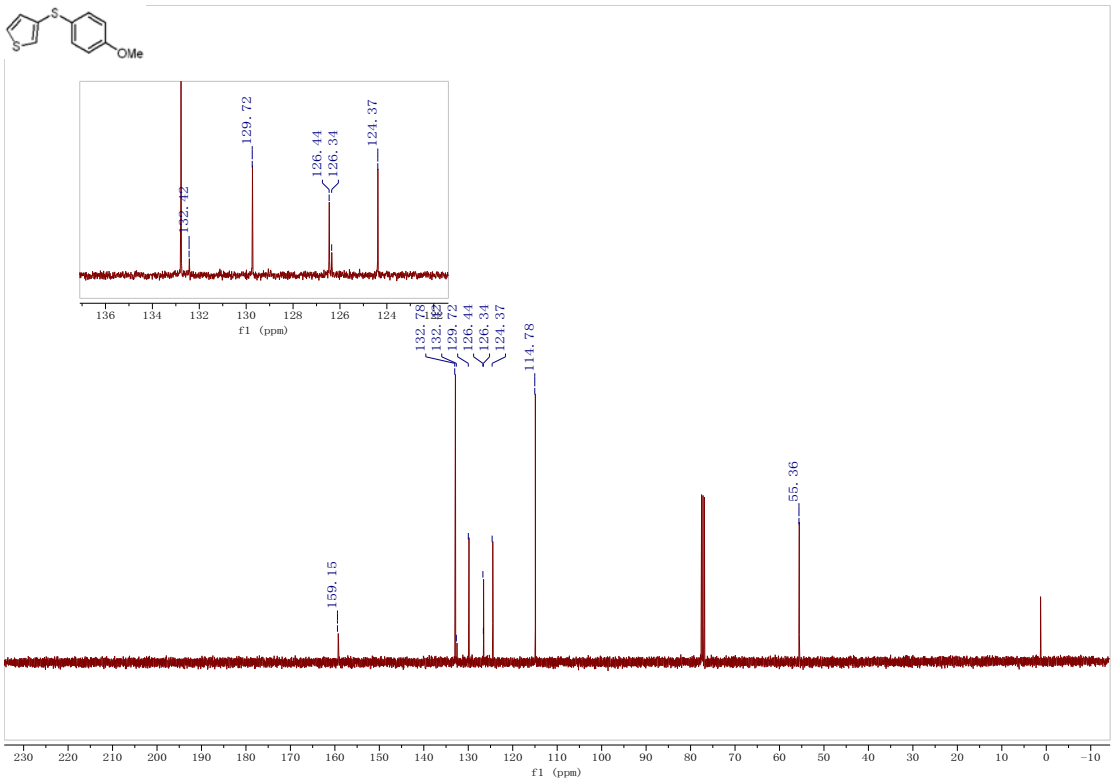
^{13}C NMR Spectrum of **3bm** (126 MHz, $CDCl_3$)



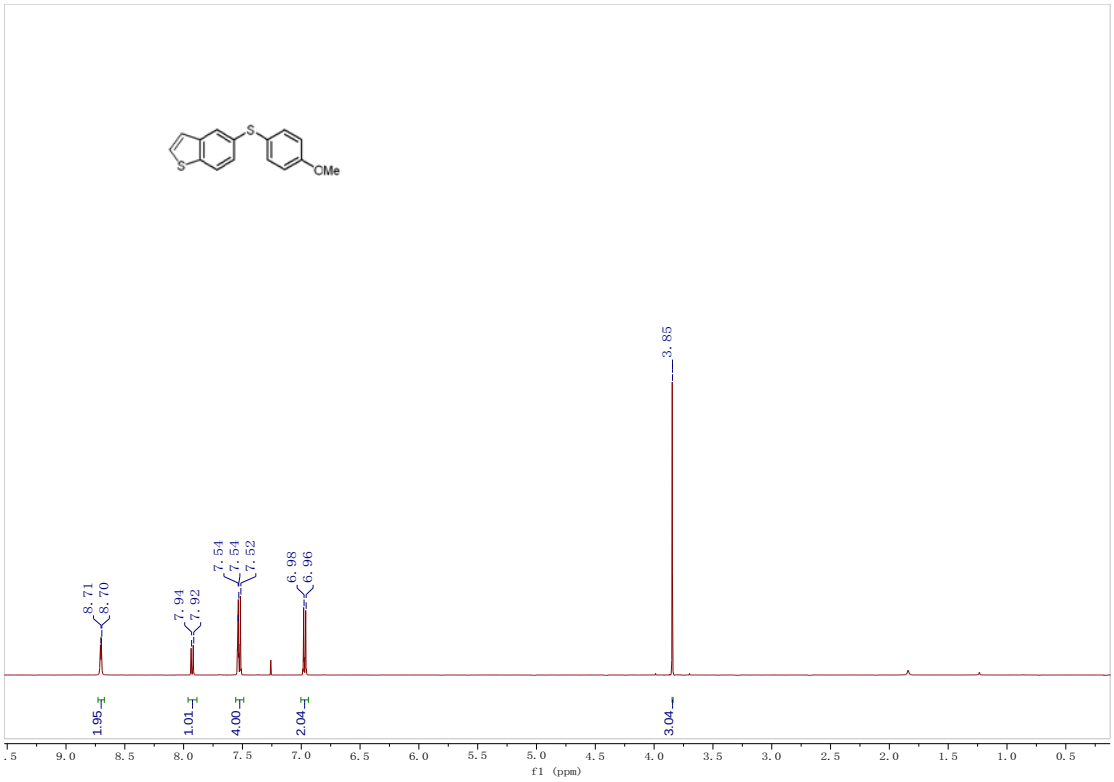
^{1}H NMR Spectrum of **3bn** (500 MHz, $CDCl_3$)



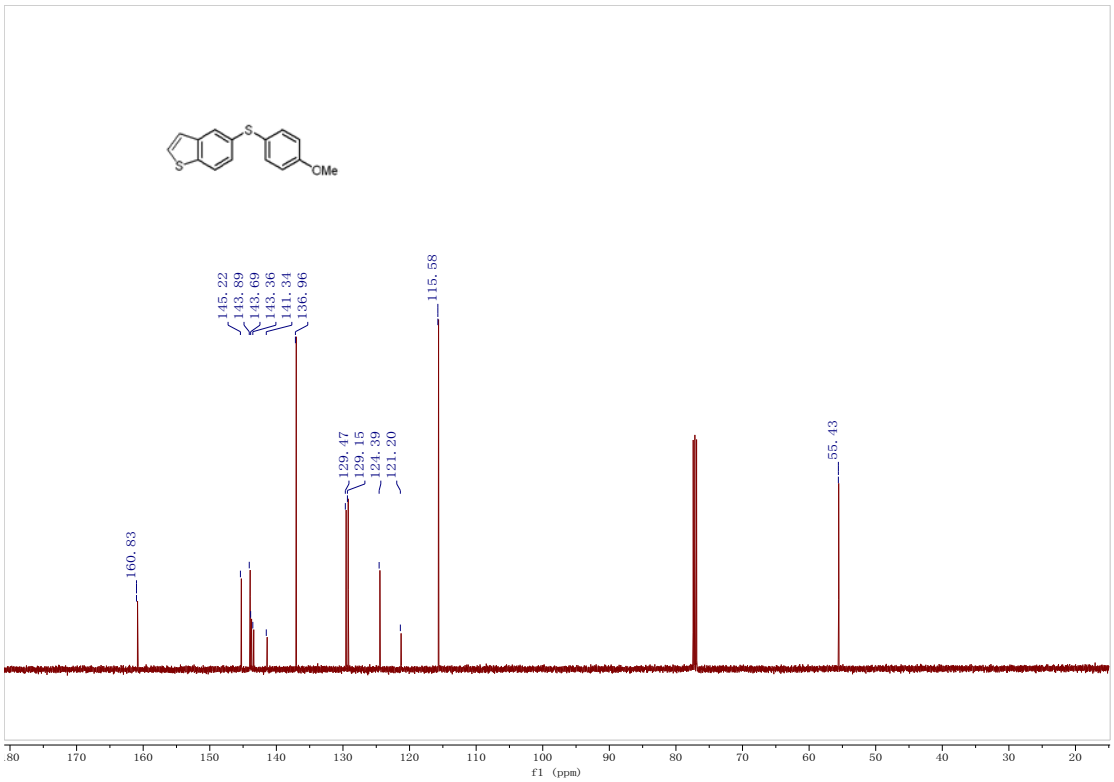
^{13}C NMR Spectrum of **3bn** (101 MHz, $CDCl_3$)



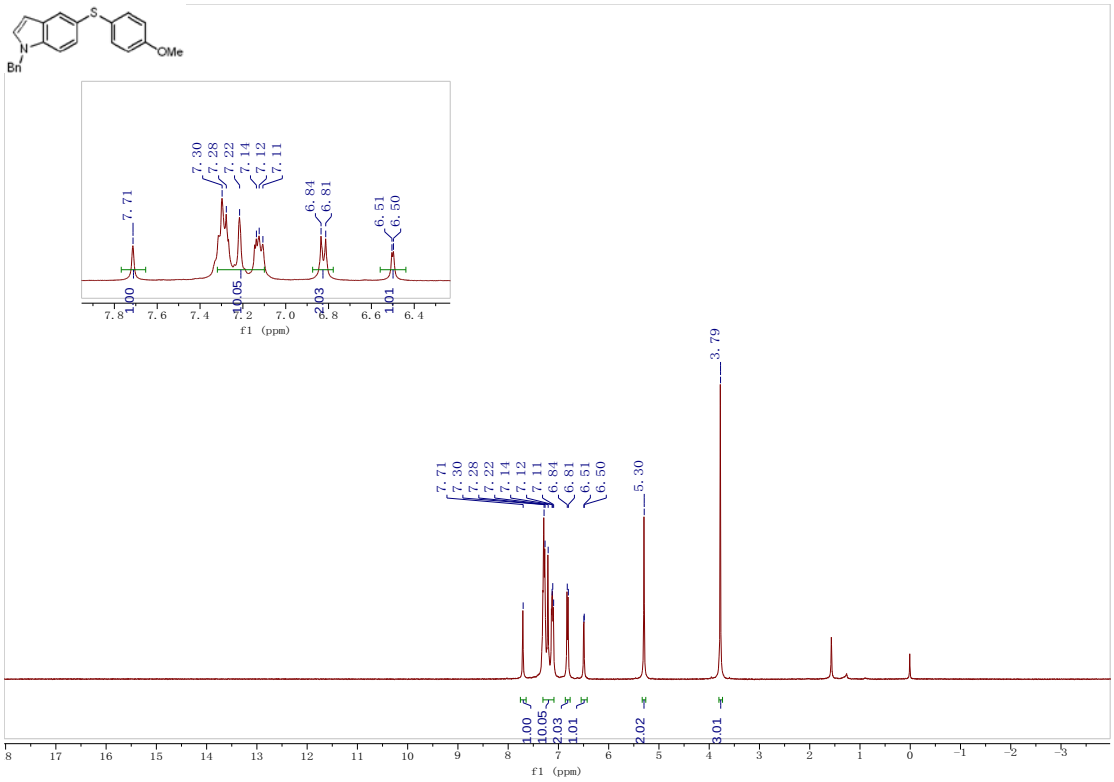
^{1}H NMR Spectrum of **3bo** (500 MHz, $CDCl_3$)



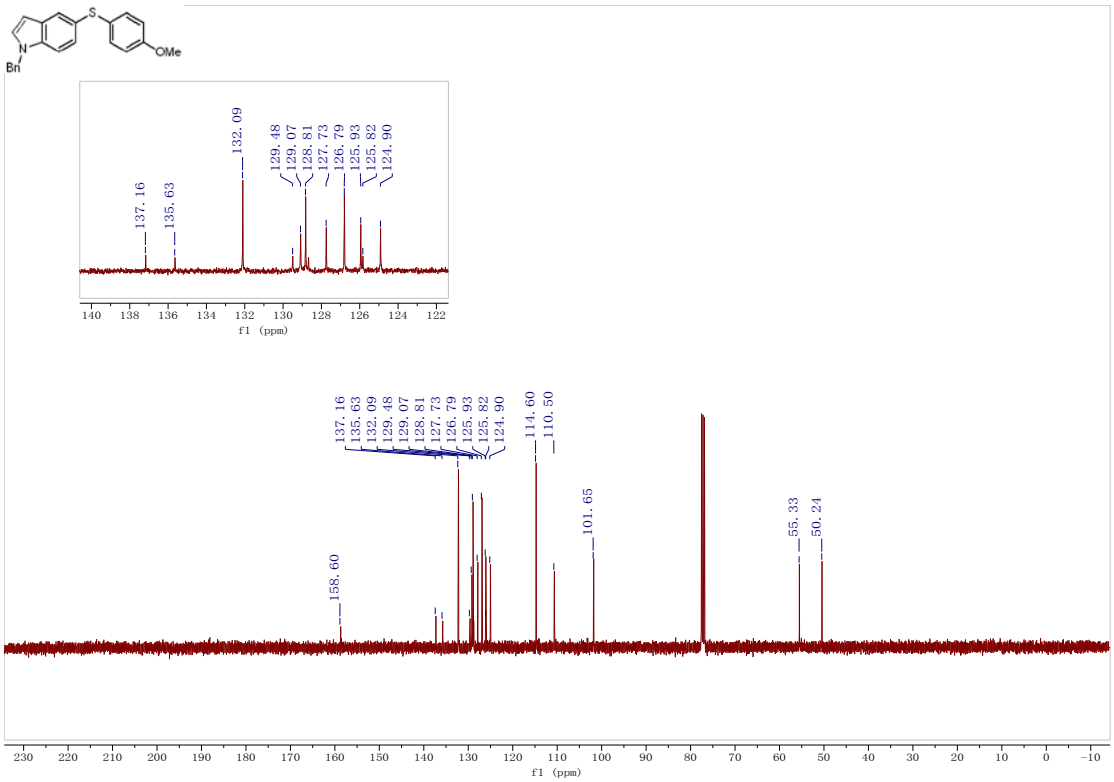
^{13}C NMR Spectrum of **3bo** (126 MHz, $CDCl_3$)



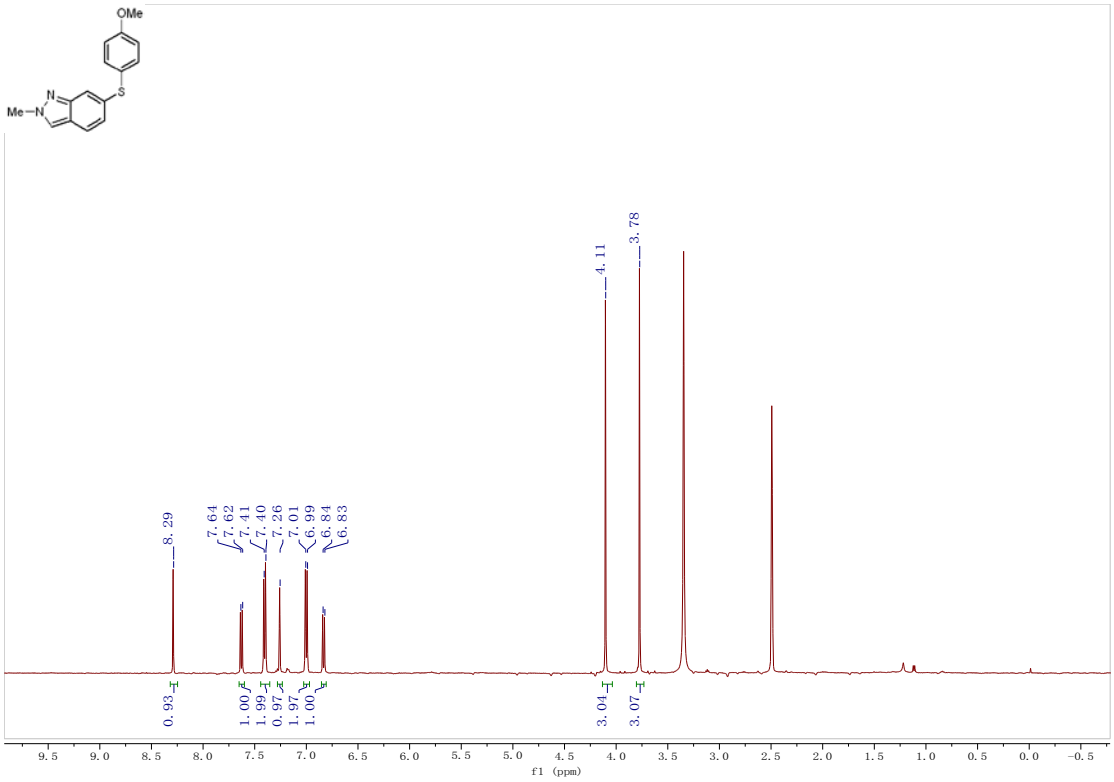
^{1}H NMR Spectrum of **3bp** (500 MHz, $CDCl_3$)



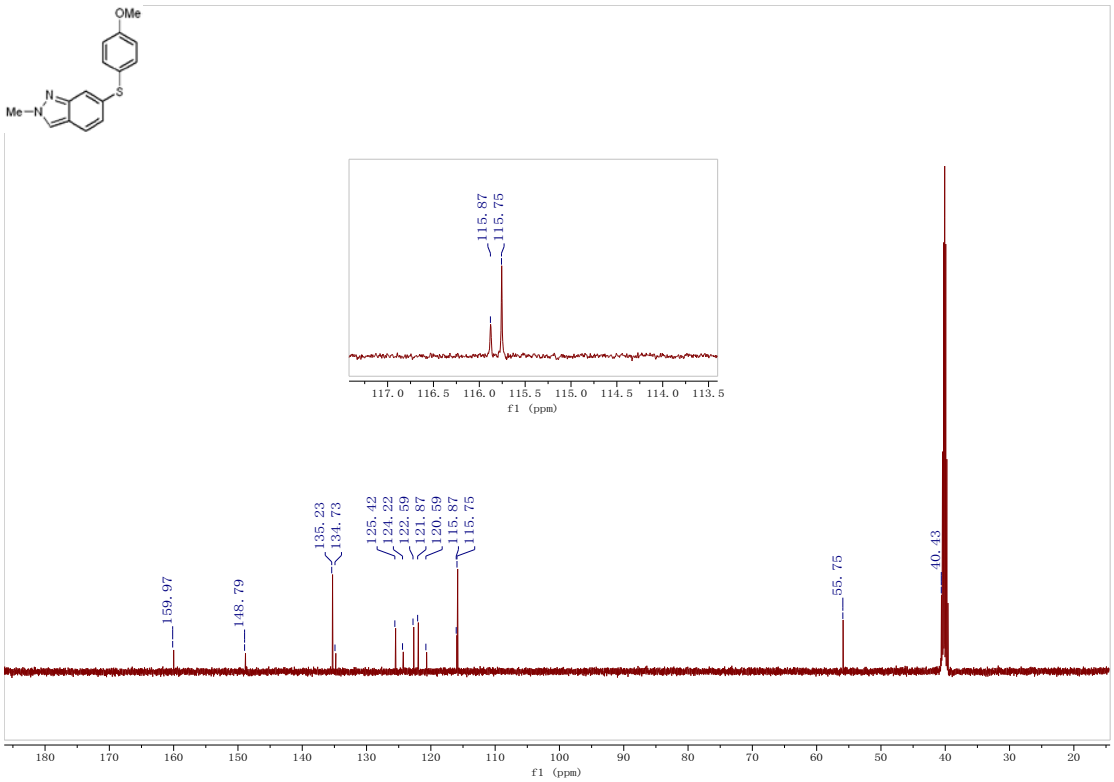
^{13}C NMR Spectrum of **3bp** (101 MHz, $CDCl_3$)



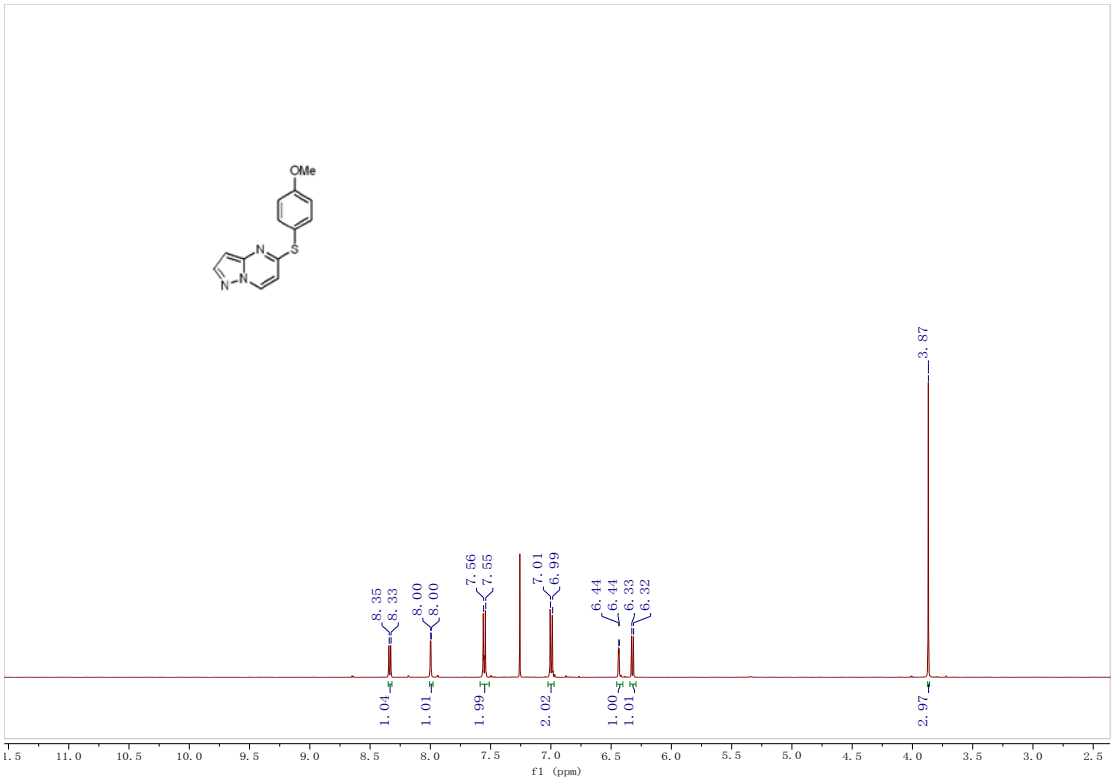
^{1}H NMR Spectrum of **3bq** (500 MHz, DMSO-*d6*)



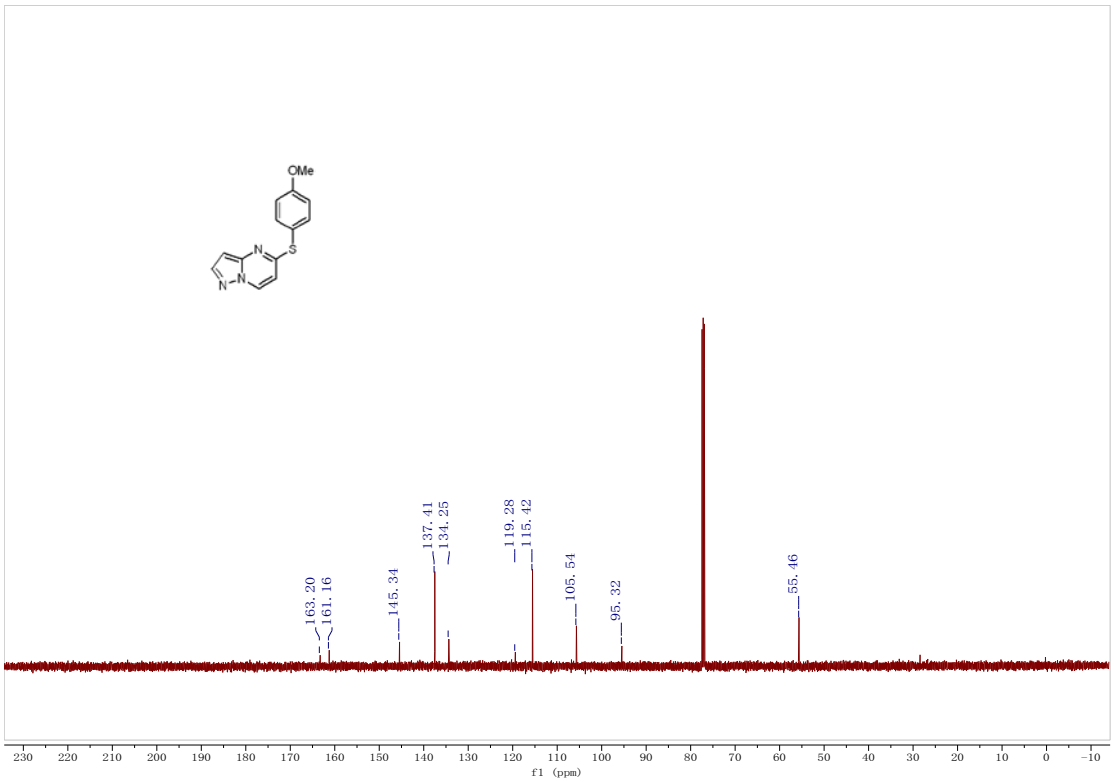
^{13}C NMR Spectrum of **3bq** (126 MHz, DMSO-*d6*)



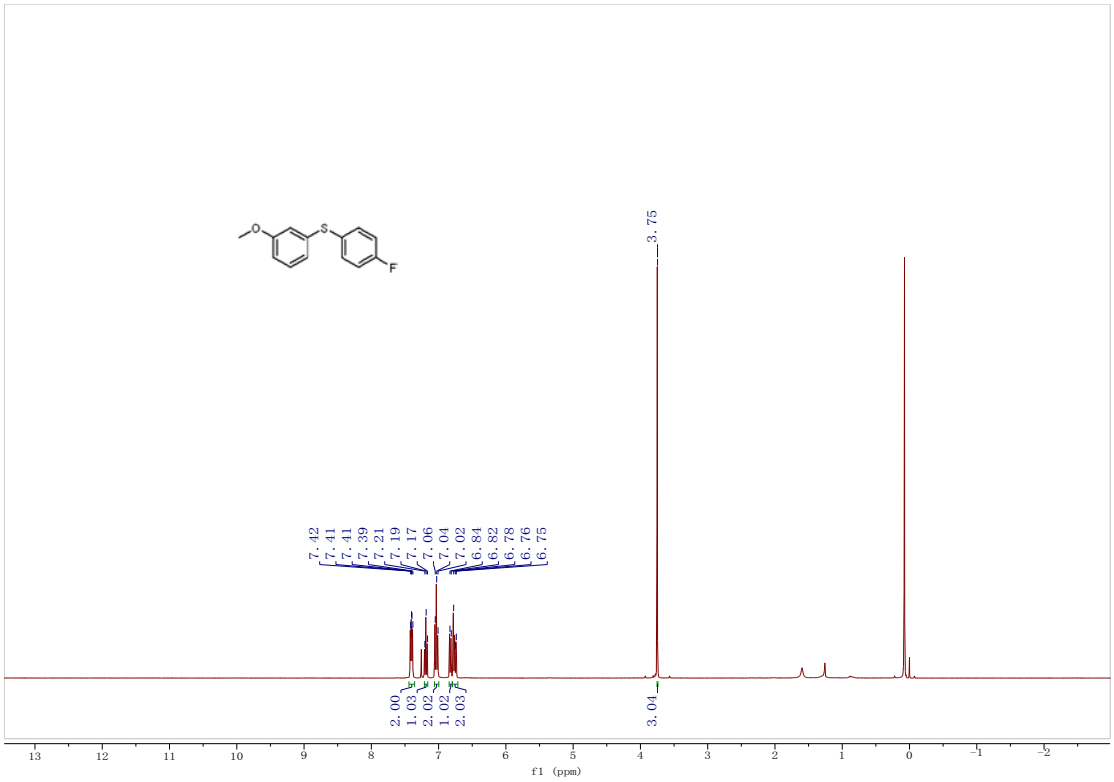
^{1}H NMR Spectrum of **3br** (500 MHz, $CDCl_3$)



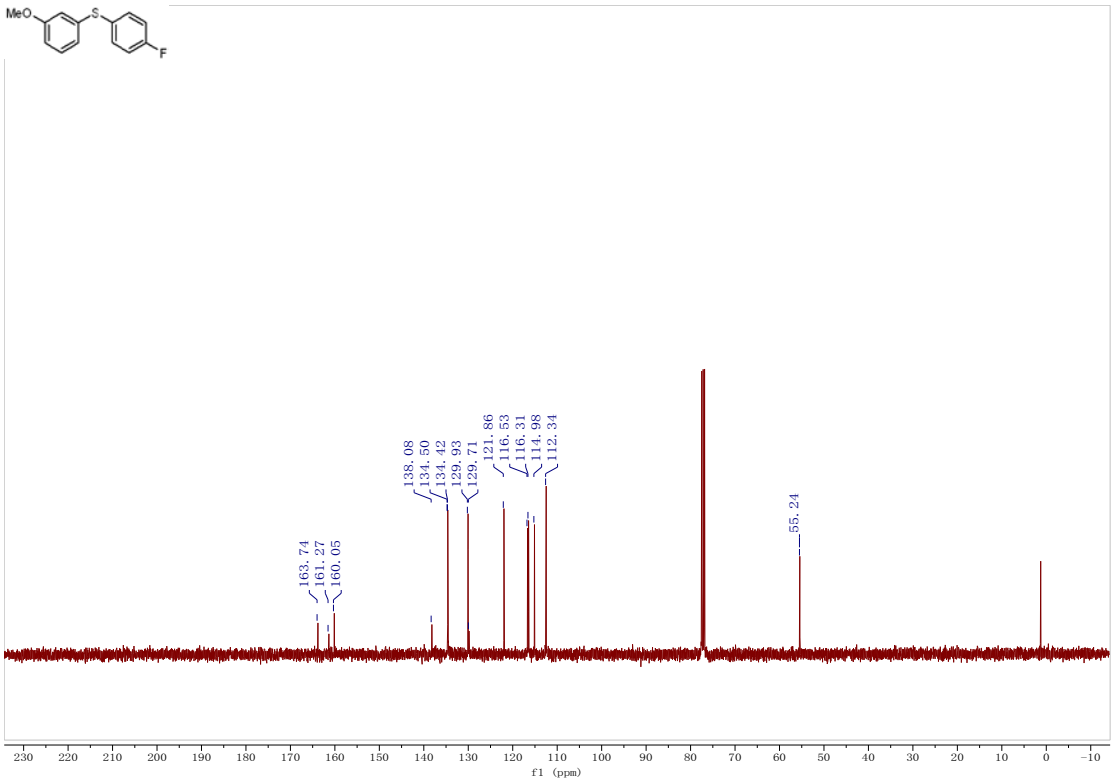
^{13}C NMR Spectrum of **3br** (126 MHz, $CDCl_3$)



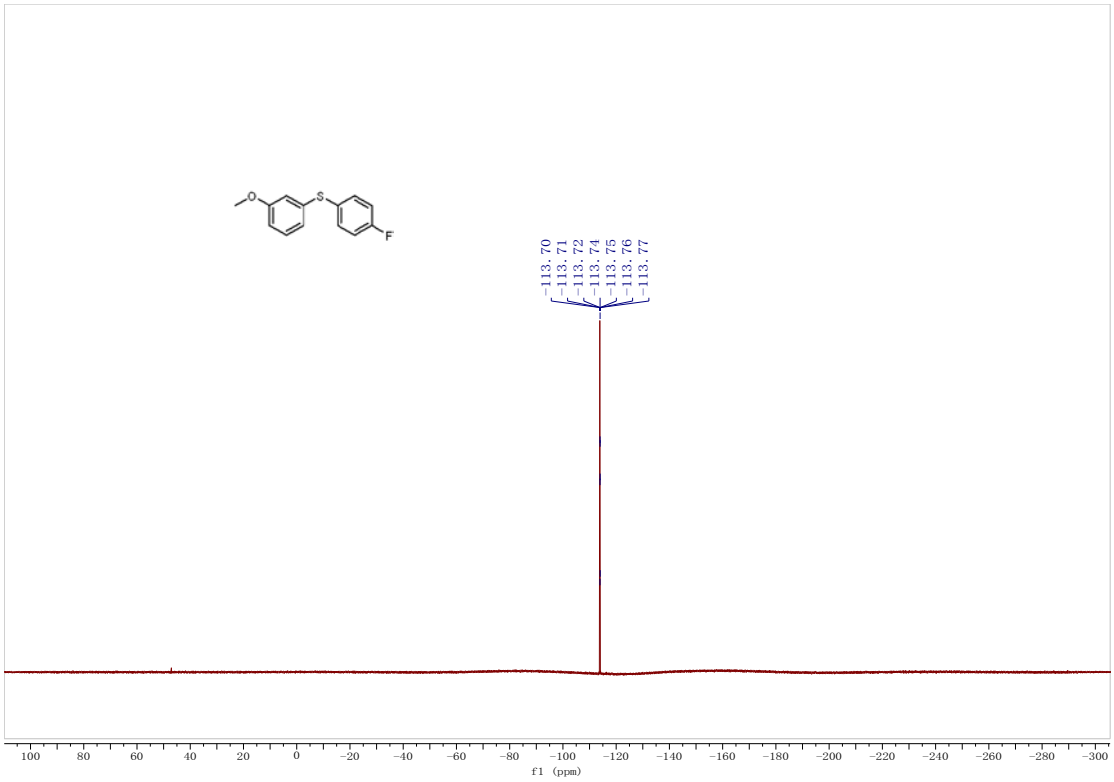
^{1}H NMR Spectrum of **3bs** (400 MHz, $CDCl_3$)



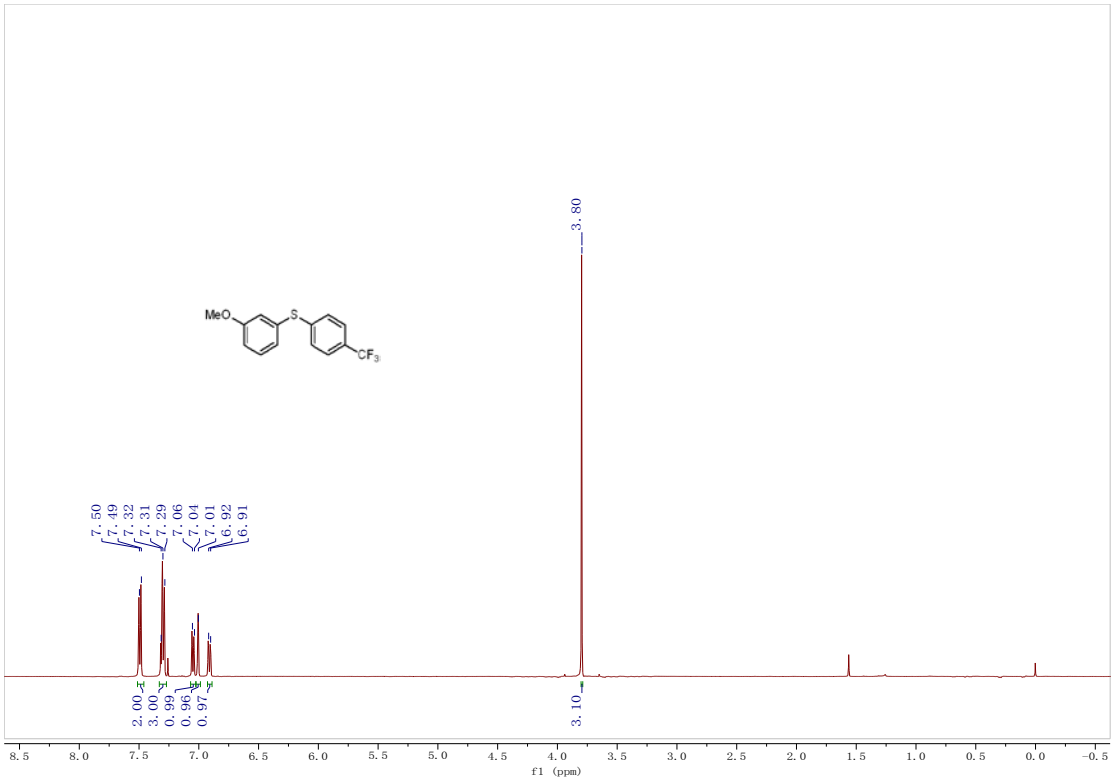
^{13}C NMR Spectrum of **3bs** (101 MHz, $CDCl_3$)



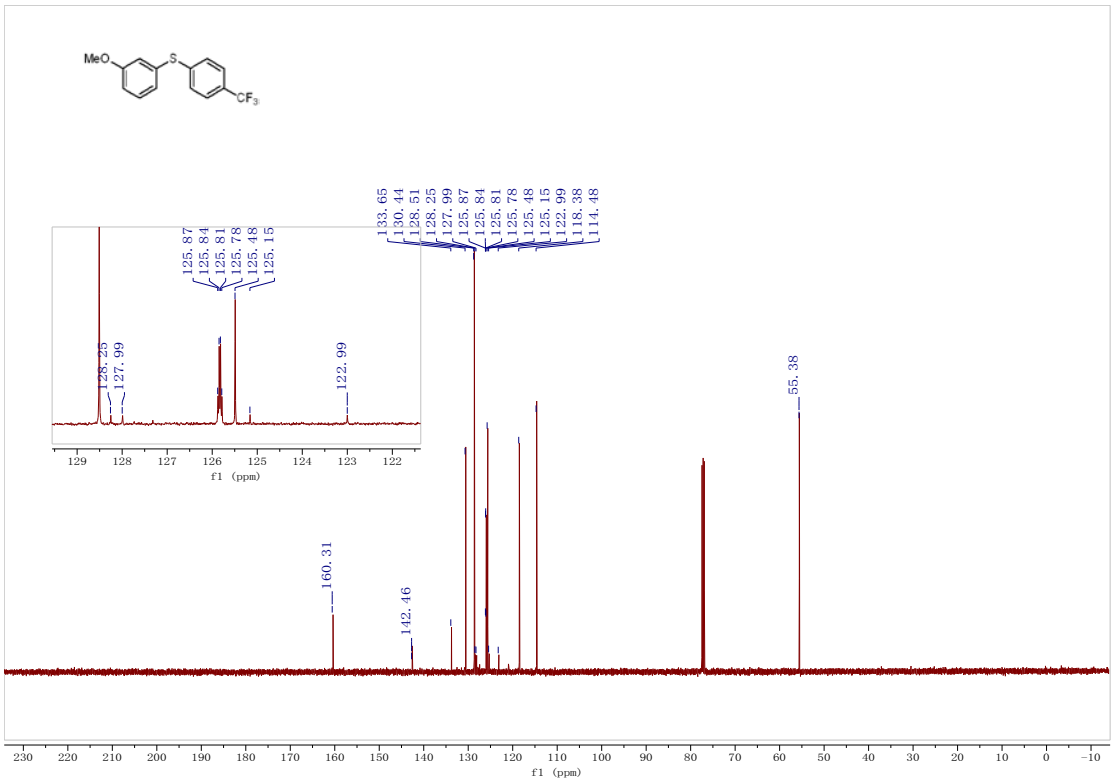
^{19}F NMR Spectrum of **3bs** (376 MHz, $CDCl_3$)



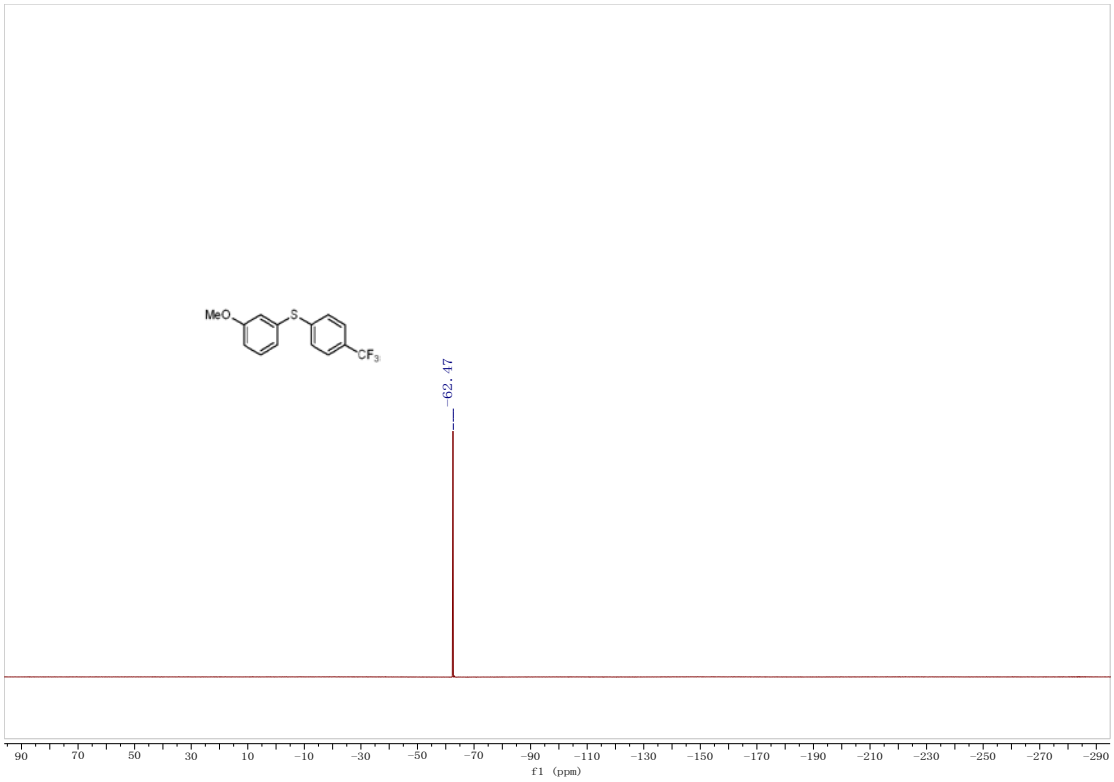
^{1}H NMR Spectrum of **3bt** (500 MHz, $CDCl_3$)



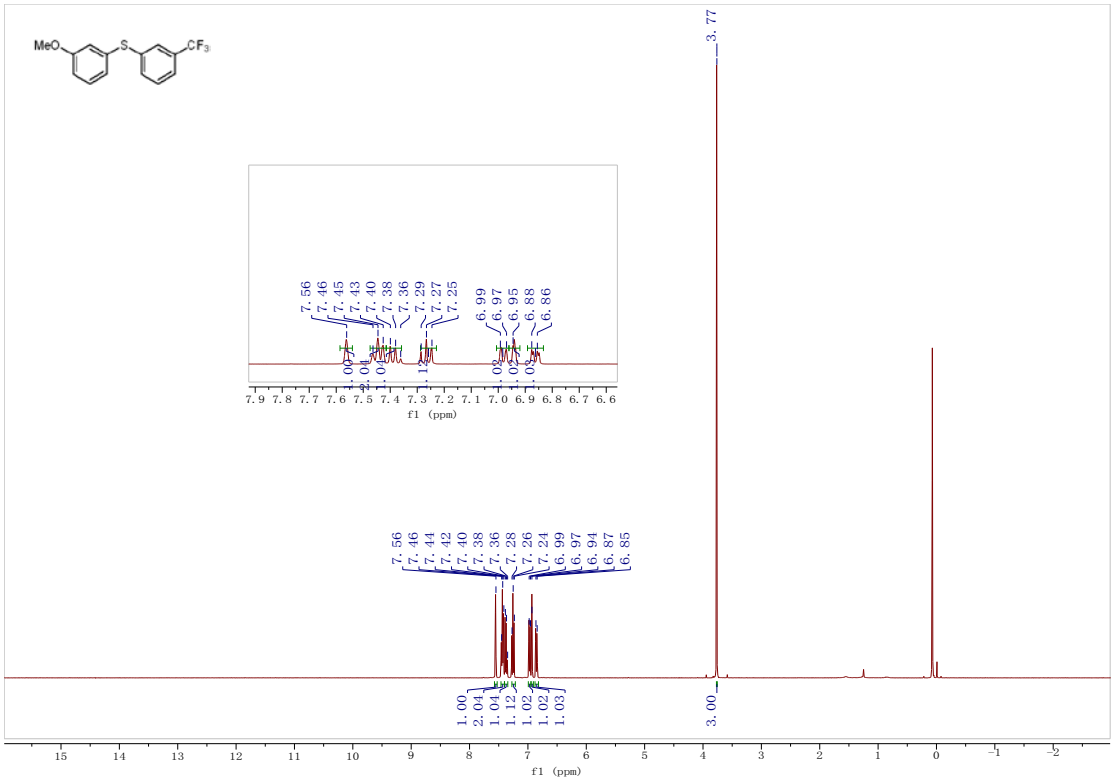
^{13}C NMR Spectrum of **3bt** (126 MHz, $CDCl_3$)



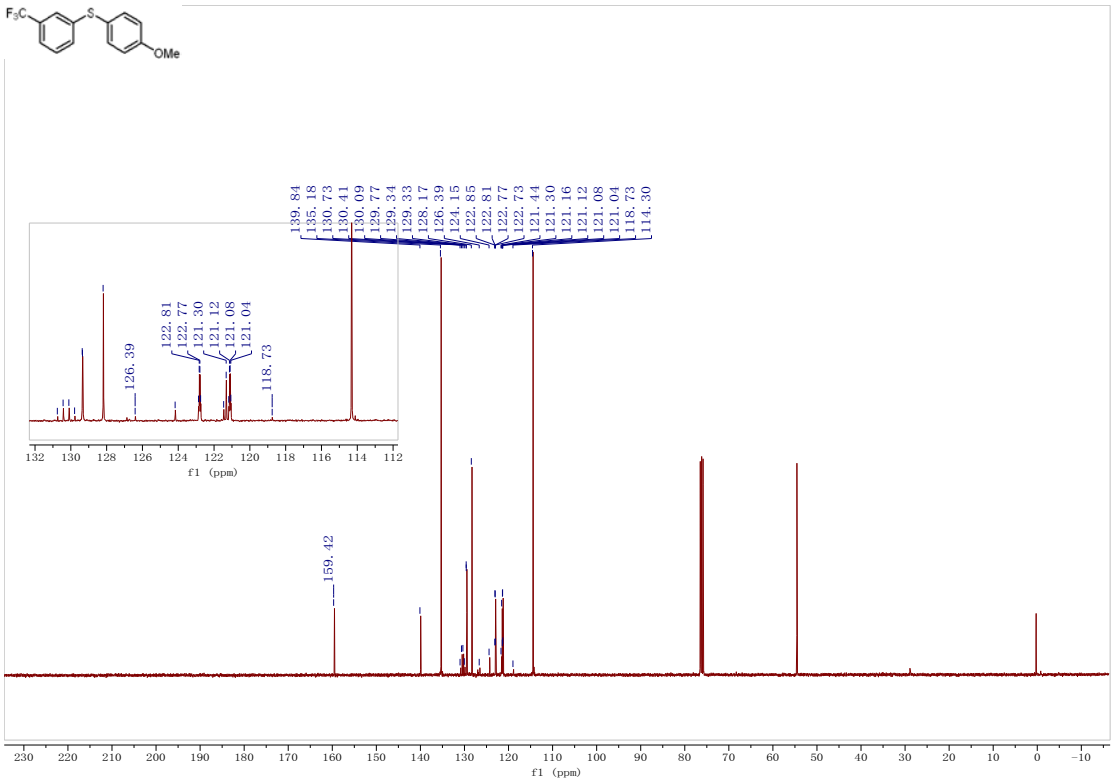
^{19}F NMR Spectrum of **3bt** (376 MHz, $CDCl_3$)



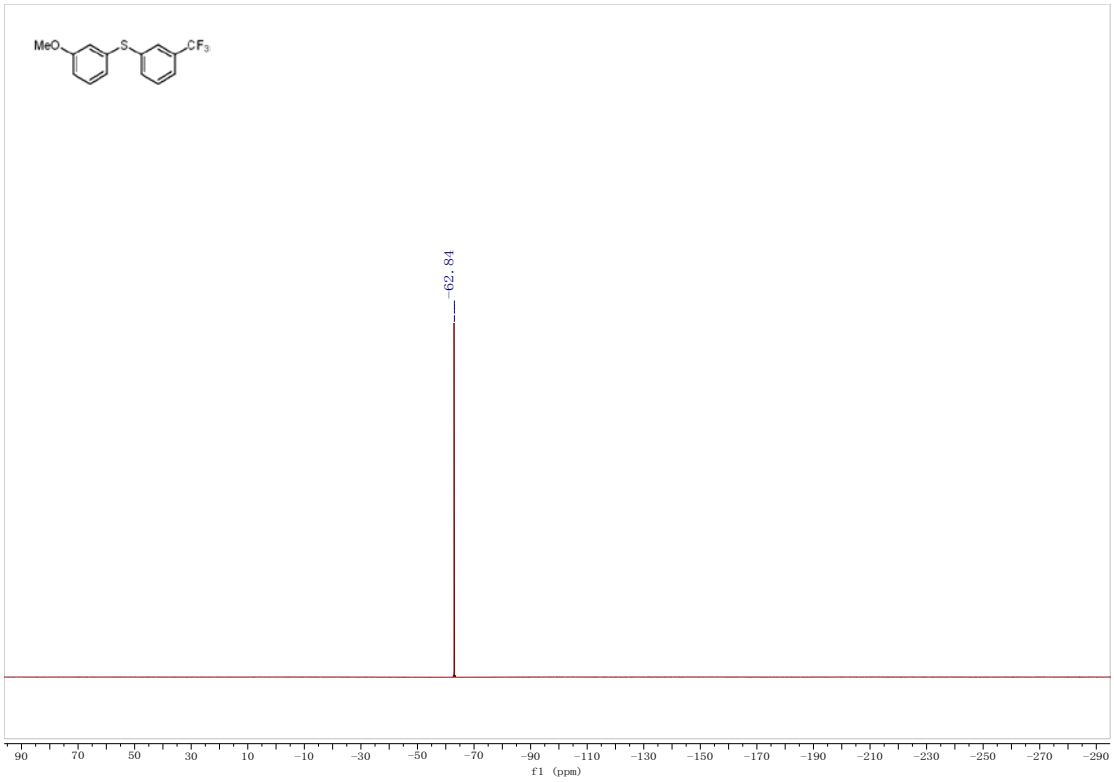
^{1}H NMR Spectrum of **3bu** (400 MHz, $CDCl_3$)



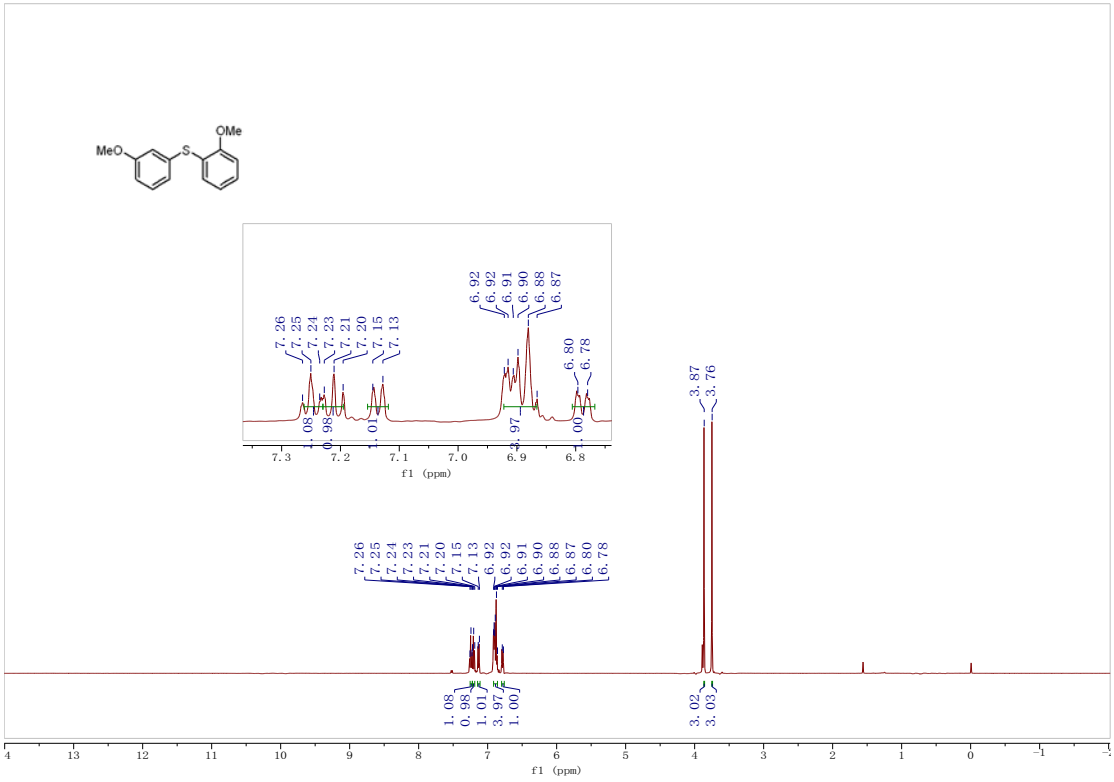
^{13}C NMR Spectrum of **3bu** (101 MHz, $CDCl_3$)



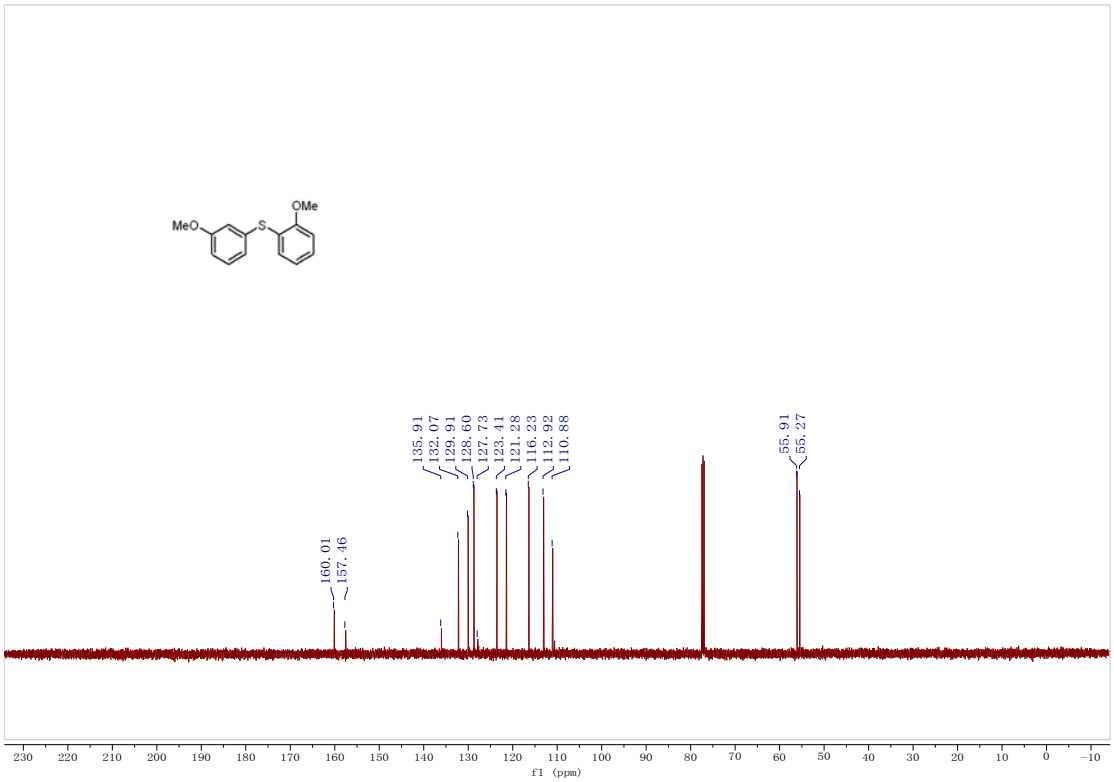
^{19}F NMR Spectrum of **3bu** (376 MHz, $CDCl_3$)



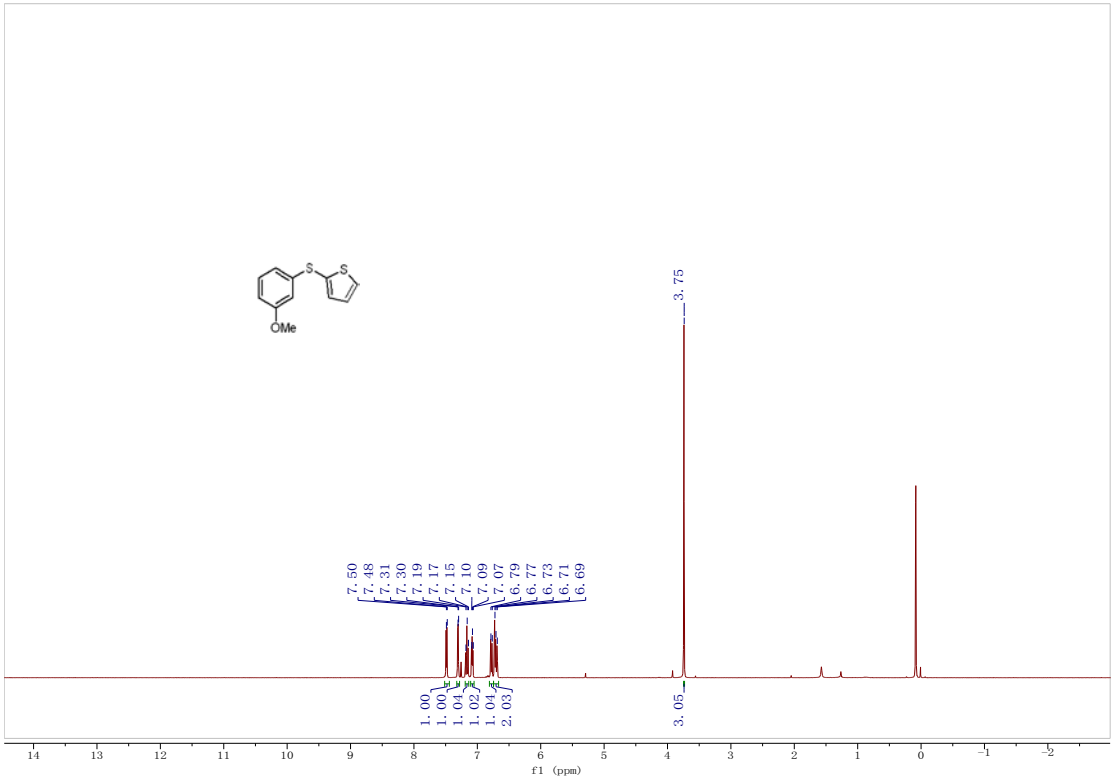
^{1}H NMR Spectrum of **3bv** (500 MHz, $CDCl_3$)



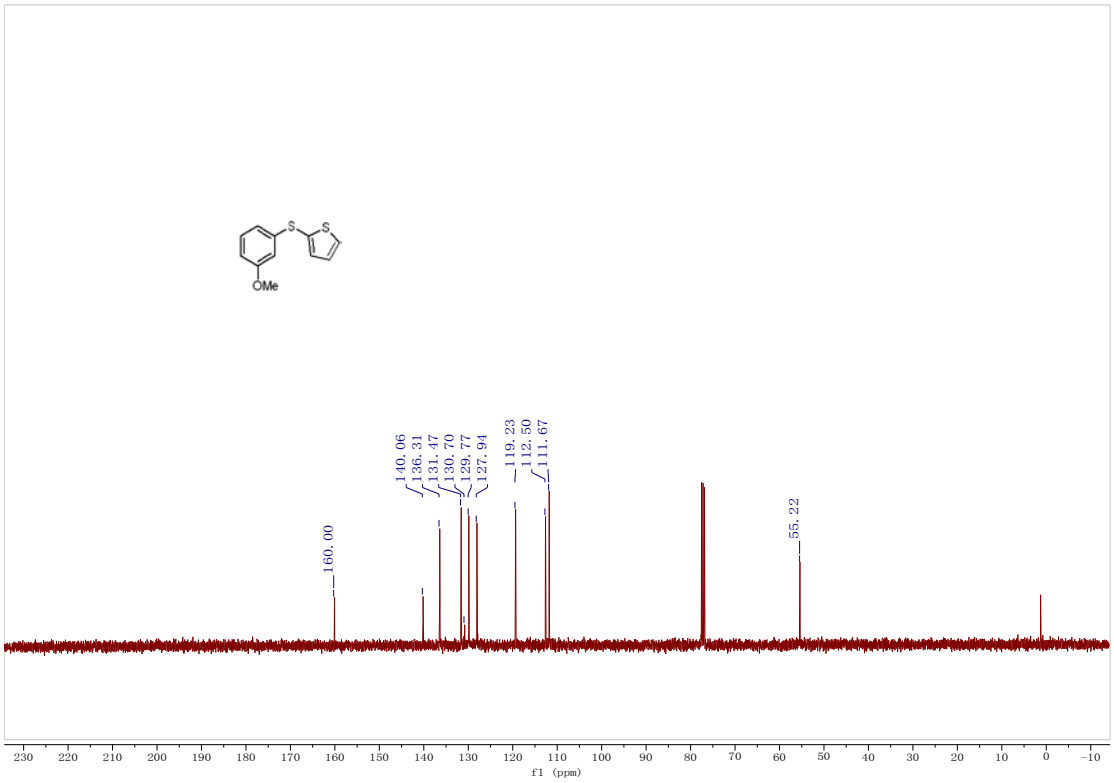
^{13}C NMR Spectrum of **3bv** (126 MHz, $CDCl_3$)



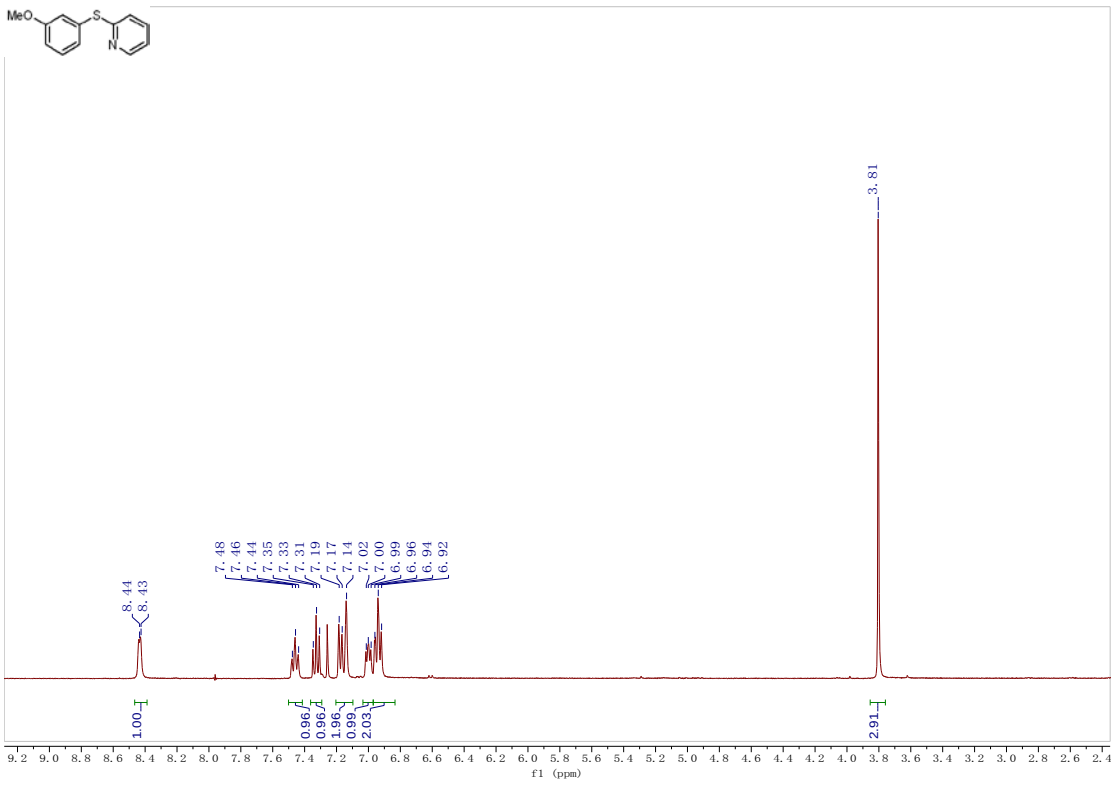
^{1}H NMR Spectrum of **3bw** (400 MHz, $CDCl_3$)



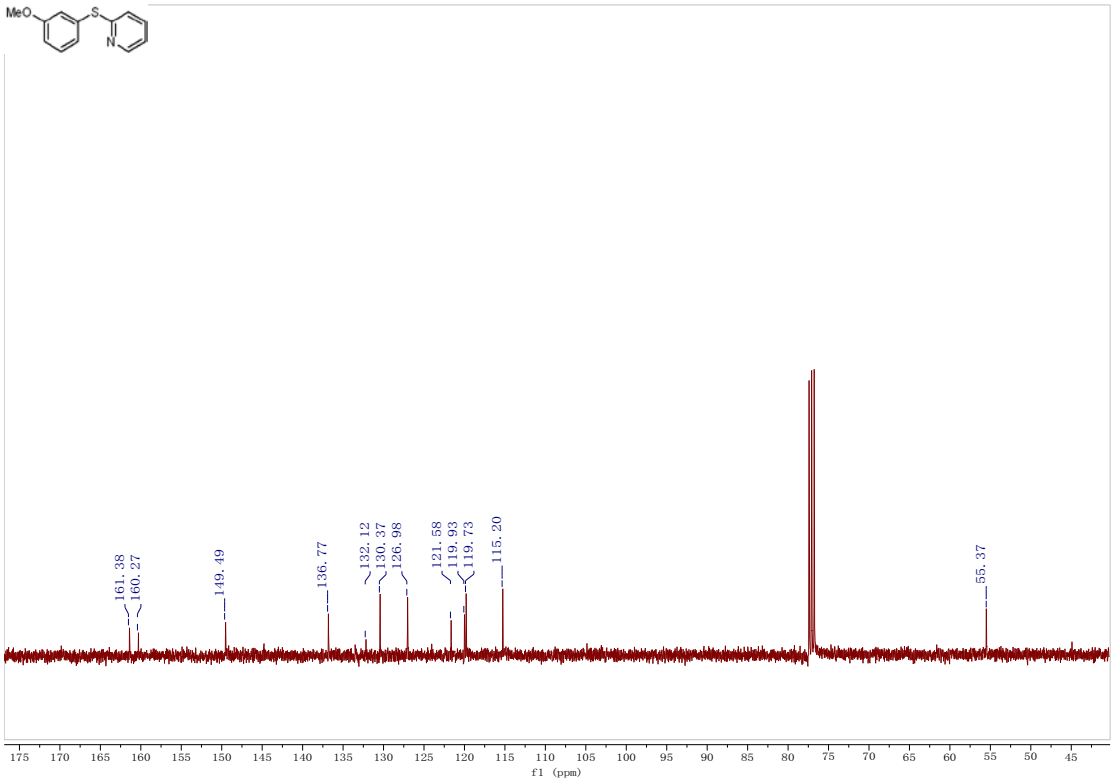
^{13}C NMR Spectrum of **3bw** (101 MHz, $CDCl_3$)



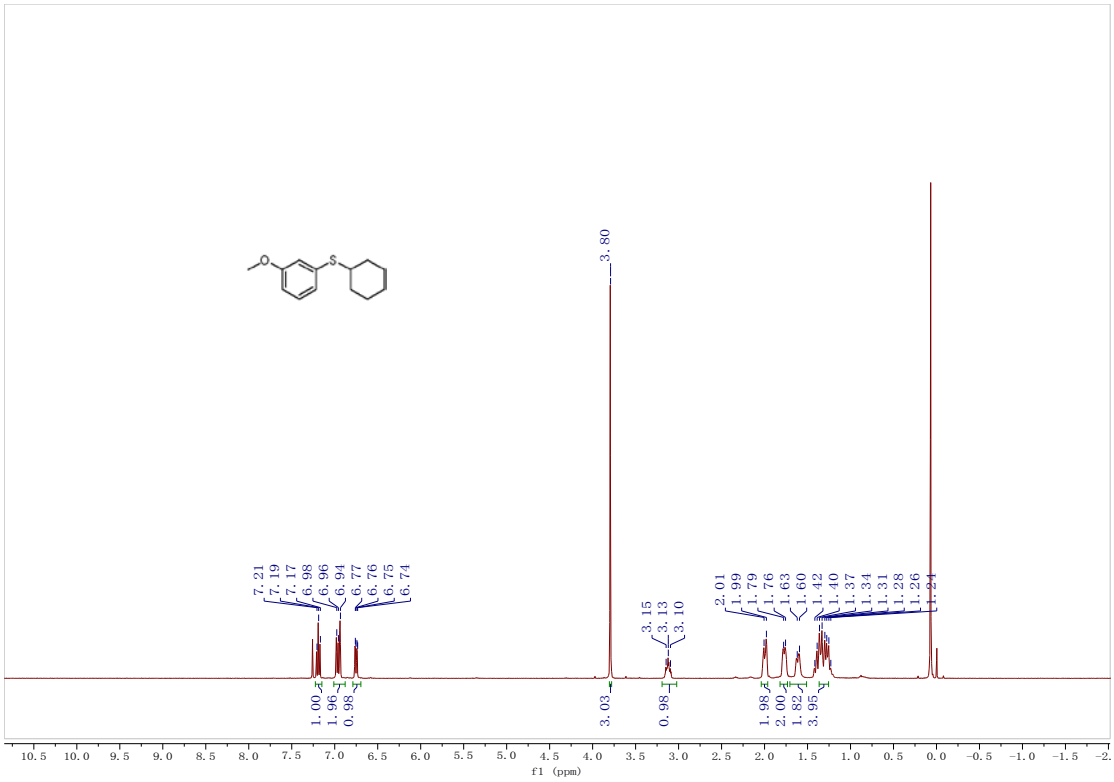
^{1}H NMR Spectrum of **3bx** (400 MHz, $CDCl_3$)



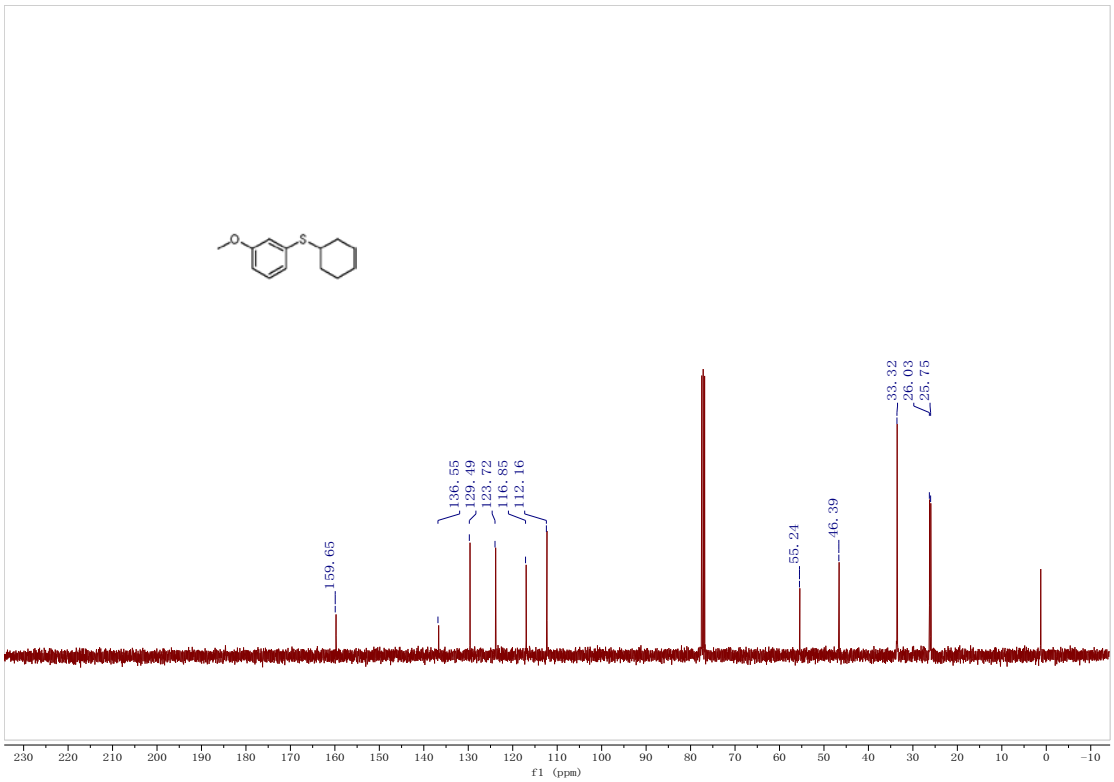
^{13}C NMR Spectrum of **3bx** (101 MHz, $CDCl_3$)



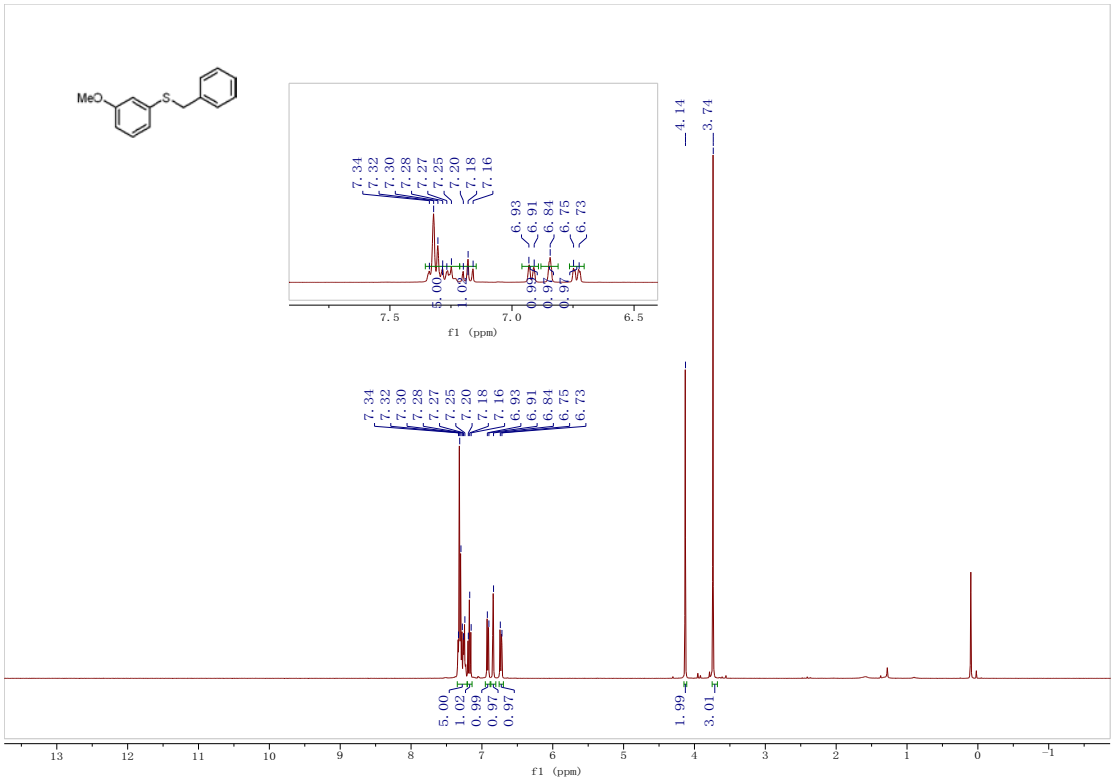
^{1}H NMR Spectrum of **3by** (400 MHz, $CDCl_3$)



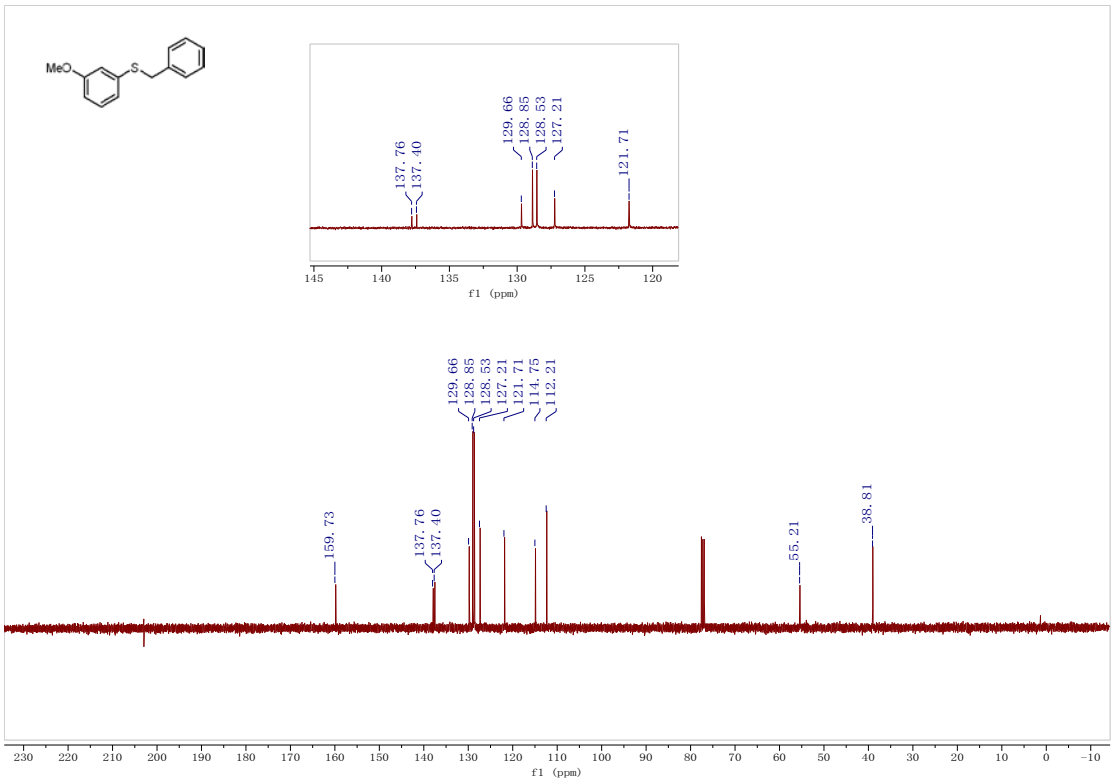
^{13}C NMR Spectrum of **3by** (101 MHz, $CDCl_3$)



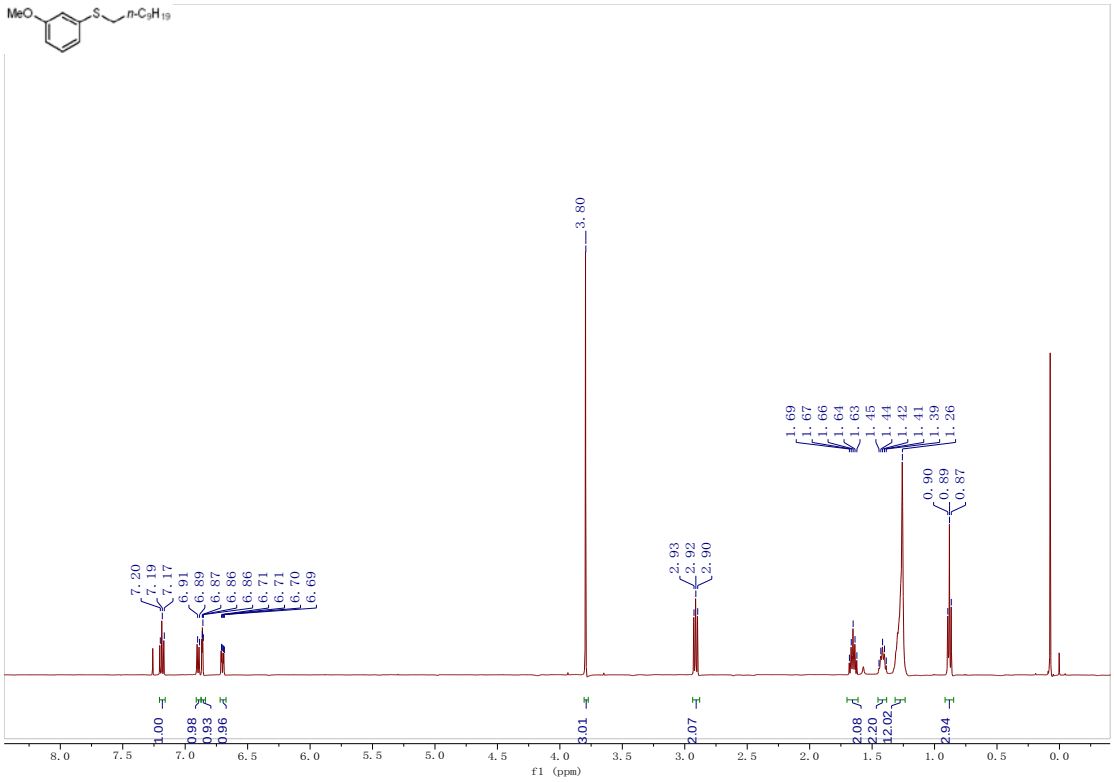
^{1}H NMR Spectrum of **3bz** (400 MHz, $CDCl_3$)



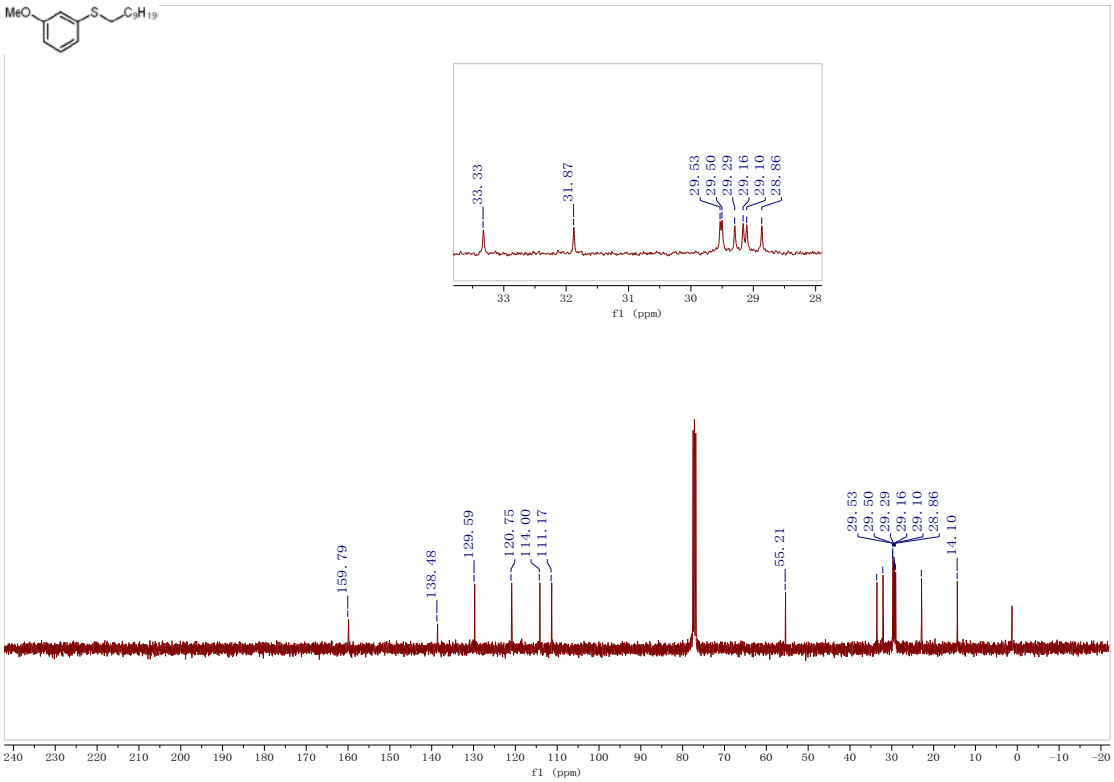
^{13}C NMR Spectrum of **3bz** (101 MHz, $CDCl_3$)



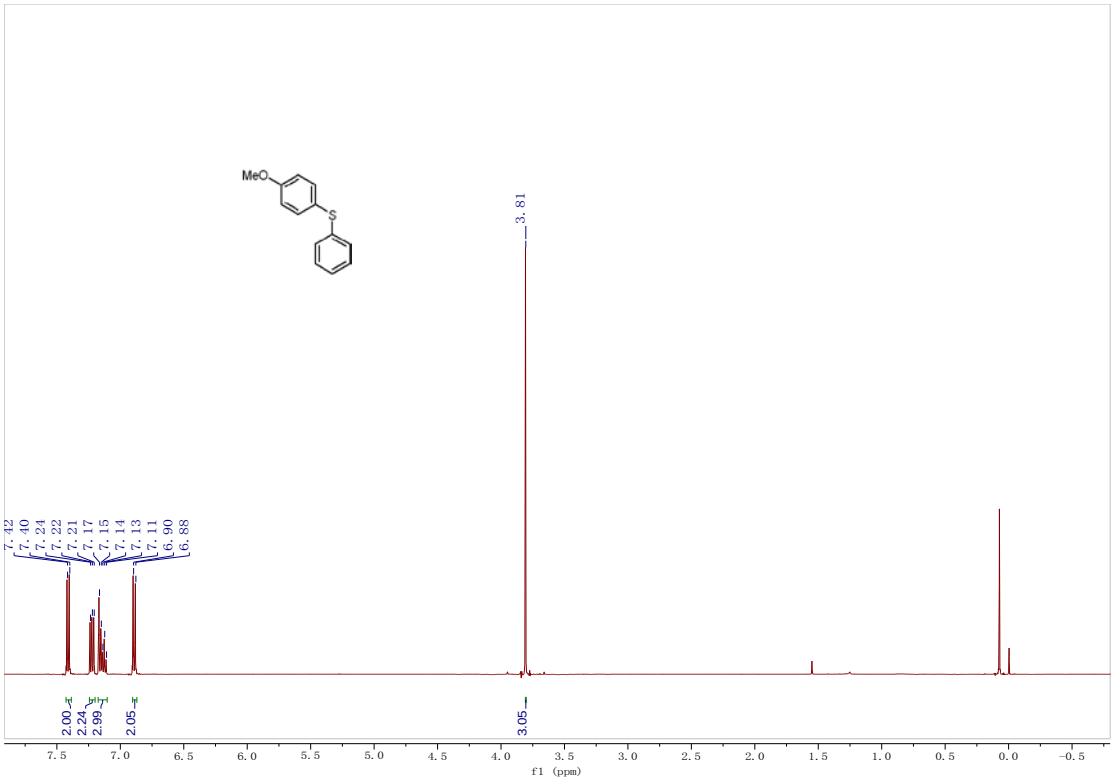
^{1}H NMR Spectrum of **3ca** (500 MHz, $CDCl_3$)



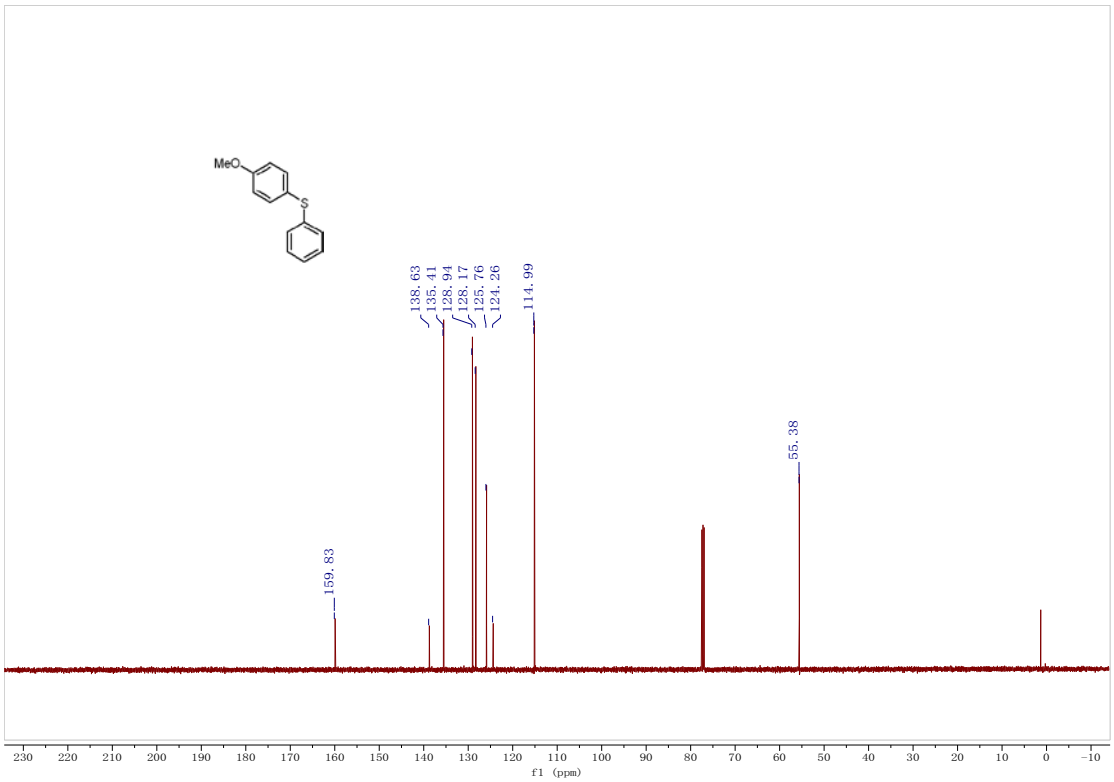
^{13}C NMR Spectrum of **3ca** (101 MHz, $CDCl_3$)



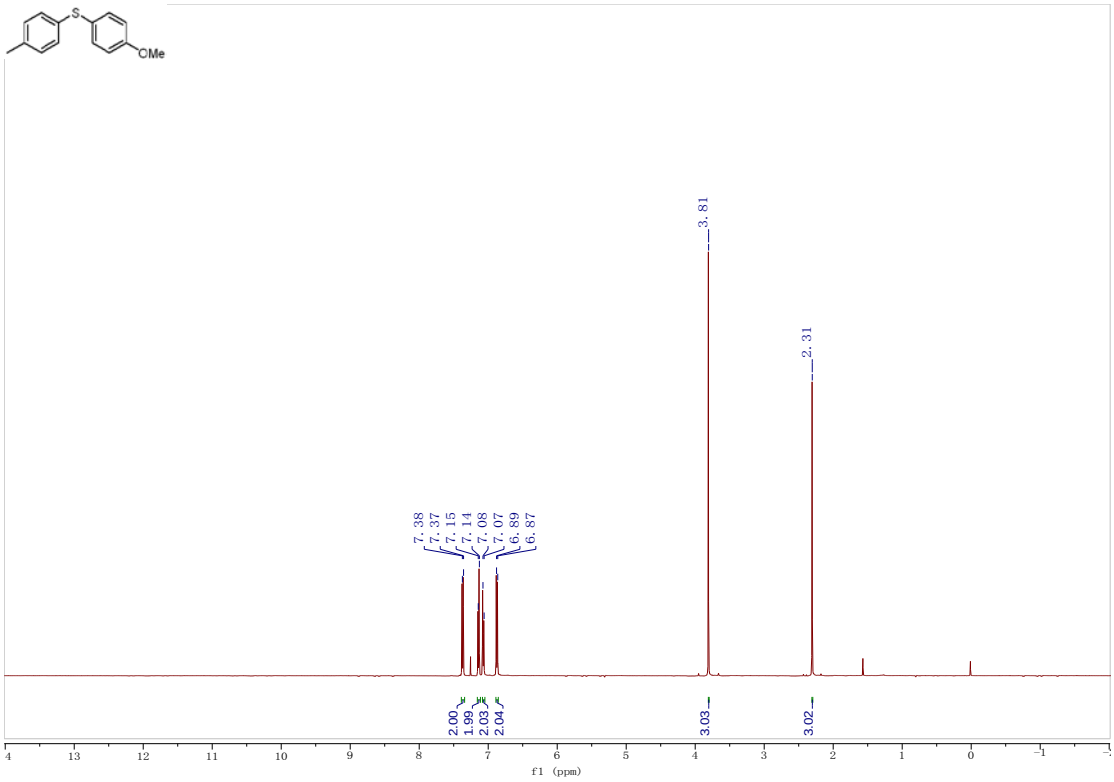
^{1}H NMR Spectrum of **3cb** (500 MHz, $CDCl_3$)



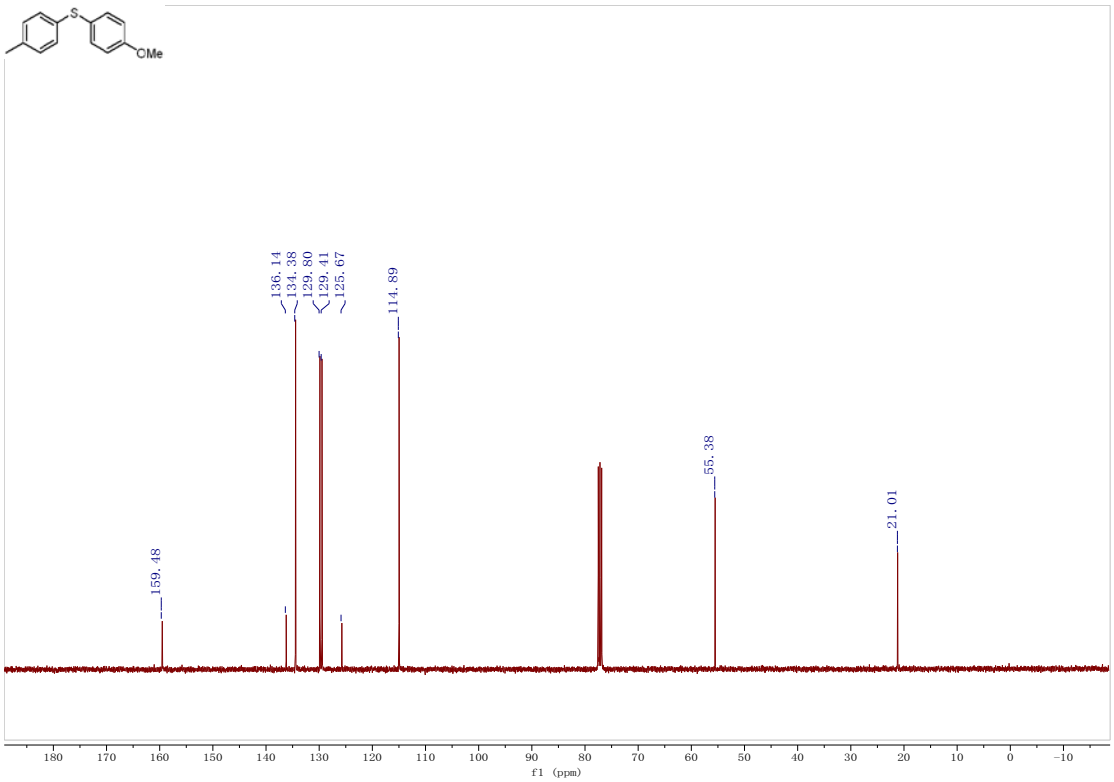
^{13}C NMR Spectrum of **3cb** (126 MHz, $CDCl_3$)



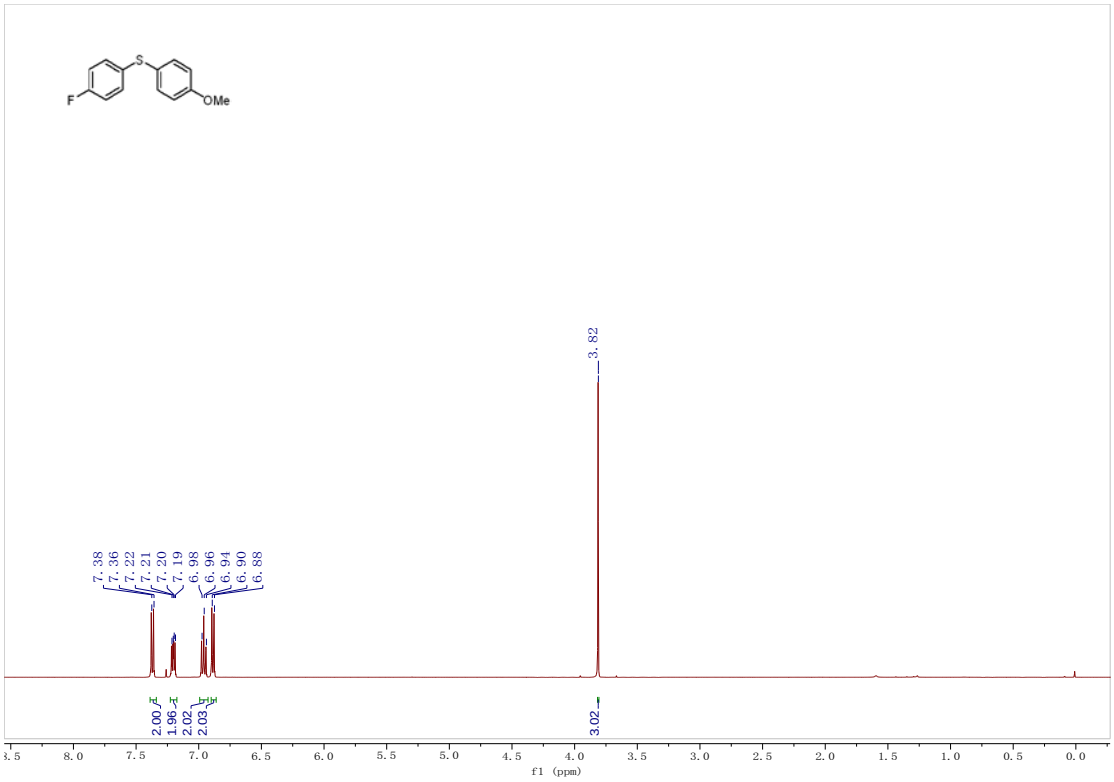
^{1}H NMR Spectrum of **3cc** (500 MHz, $CDCl_3$)



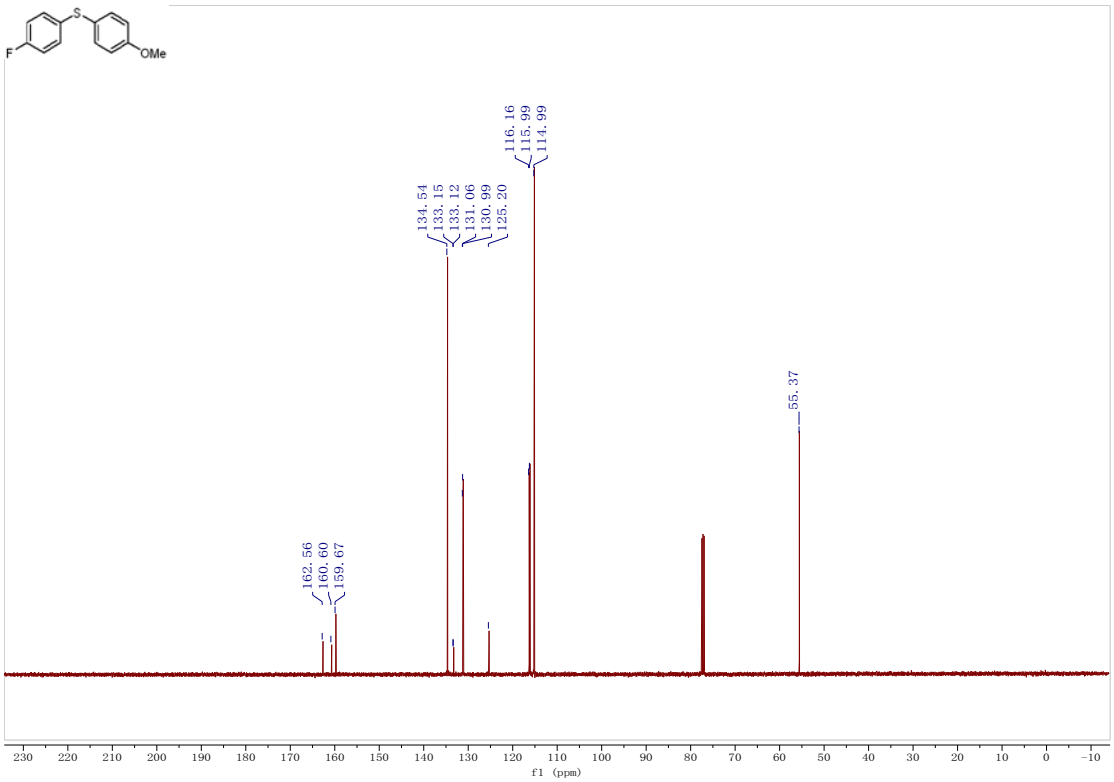
^{13}C NMR Spectrum of **3cc** (126 MHz, $CDCl_3$)



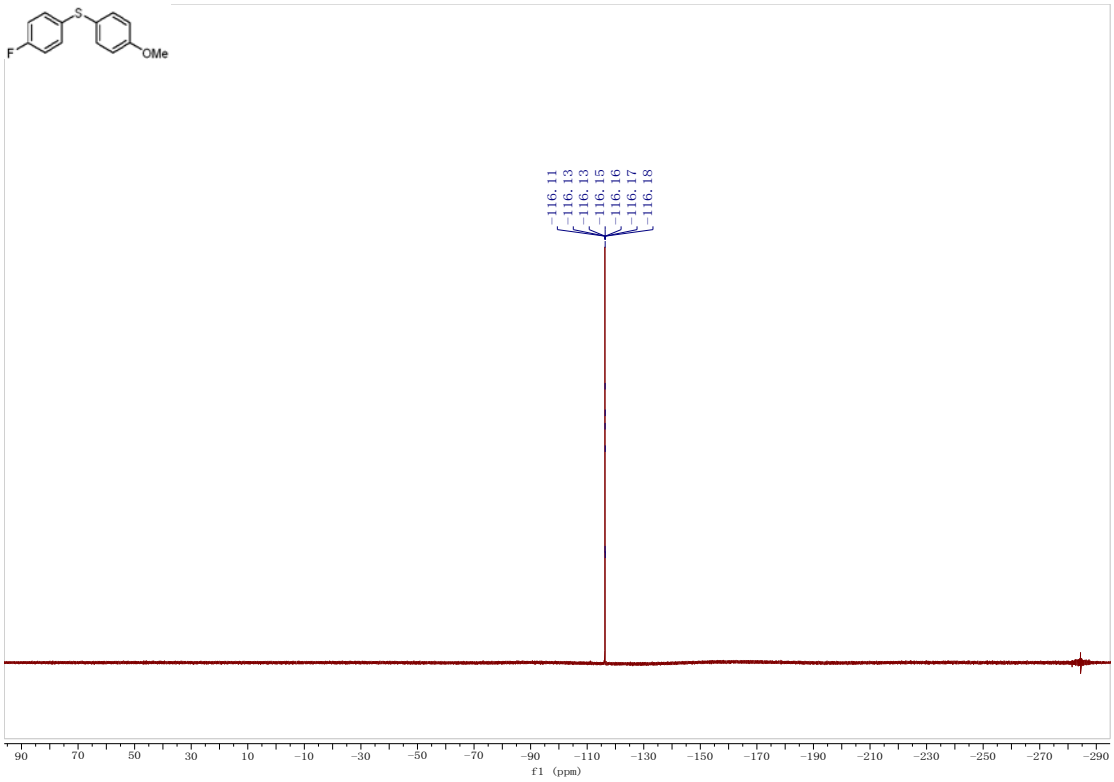
^{1}H NMR Spectrum of **3cd** (500 MHz, $CDCl_3$)



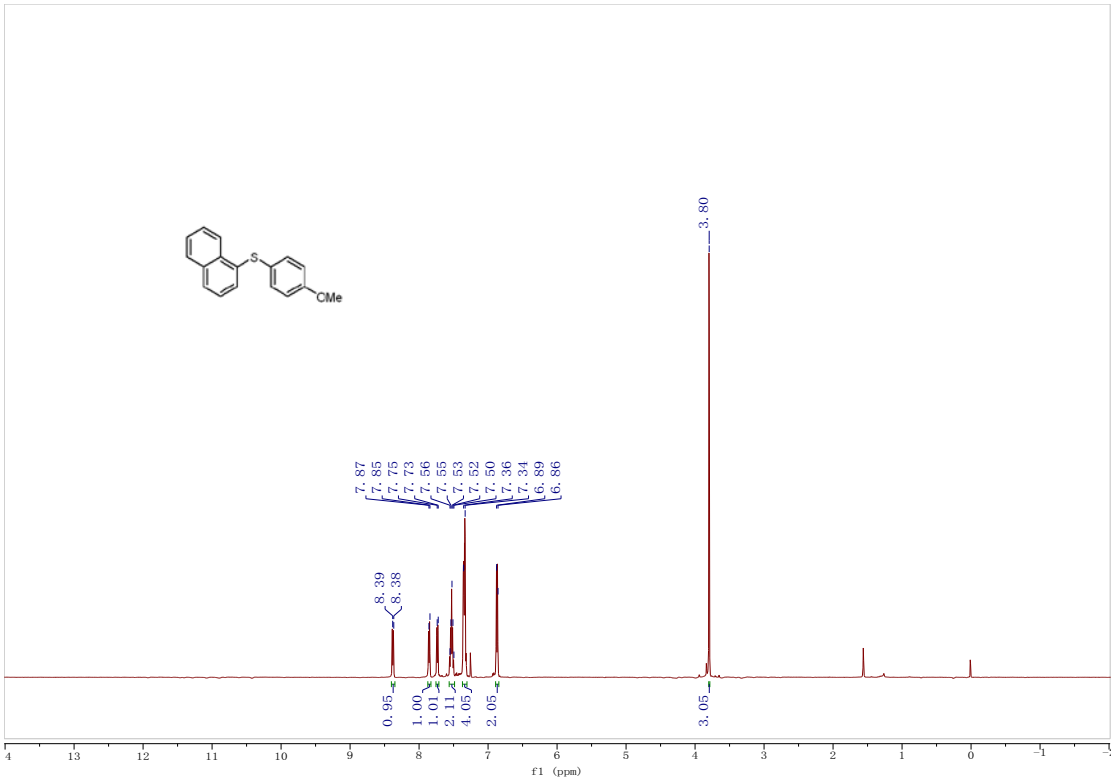
^{13}C NMR Spectrum of **3cd** (126 MHz, $CDCl_3$)



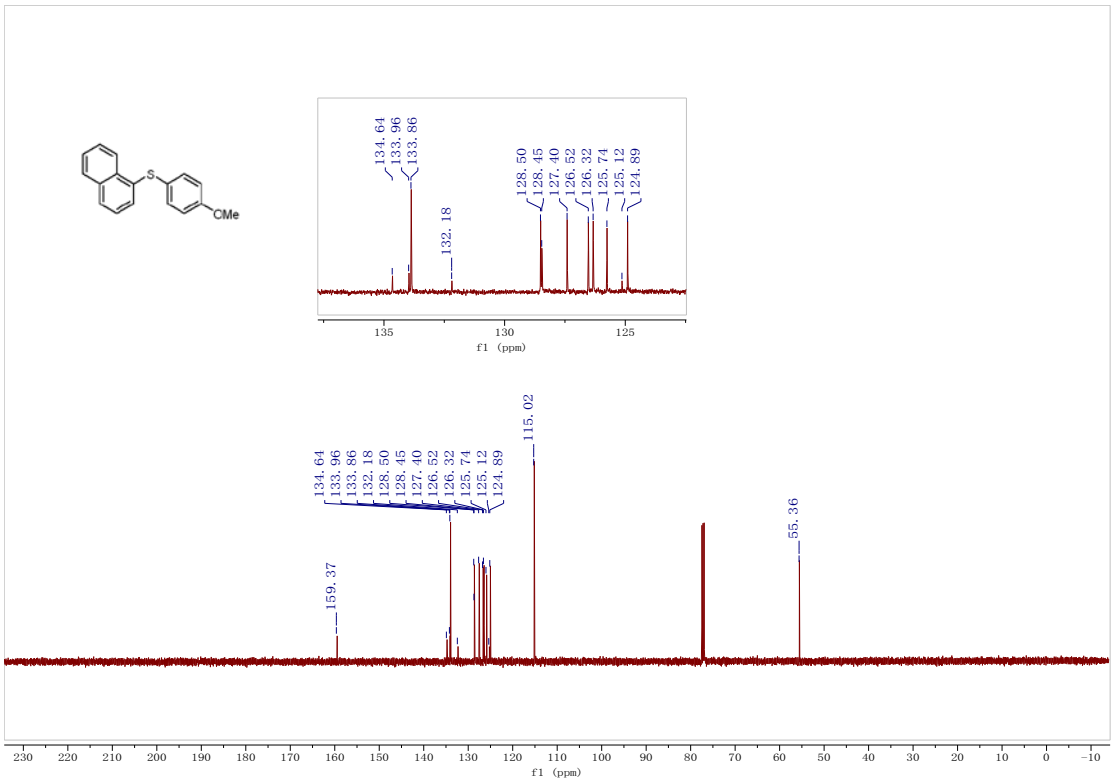
^{19}F NMR Spectrum of **3cd** (376 MHz, $CDCl_3$)



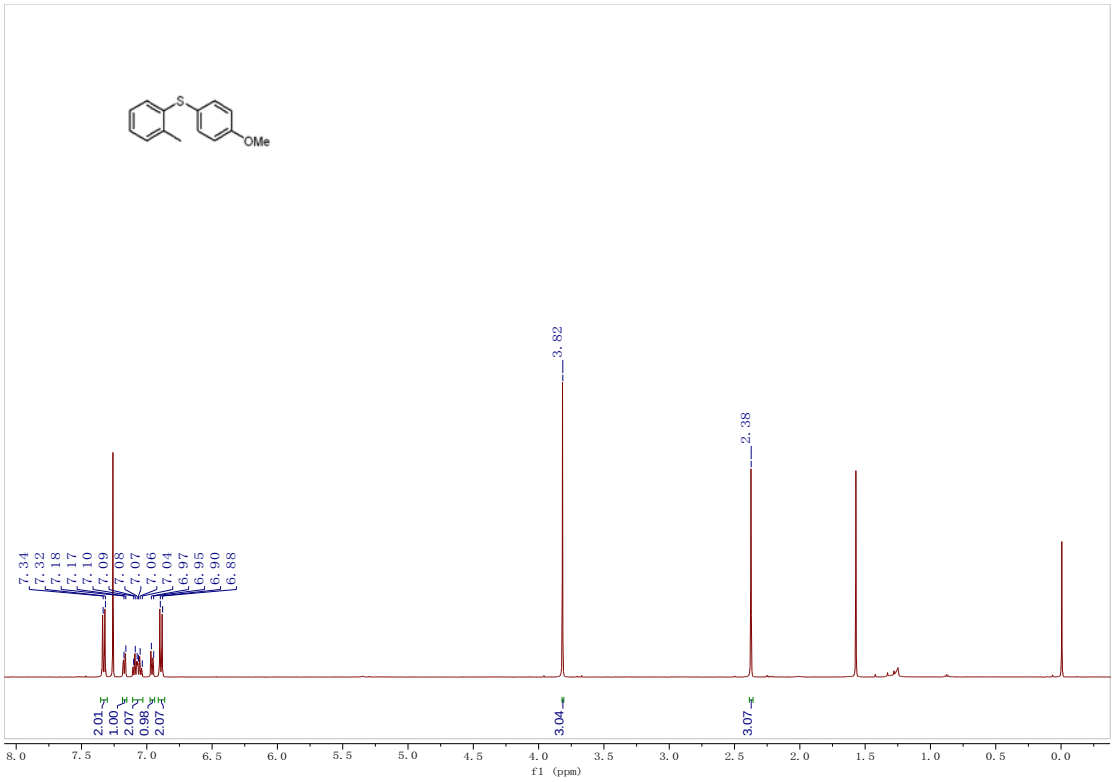
^{1}H NMR Spectrum of **3ce** (500 MHz, $CDCl_3$)



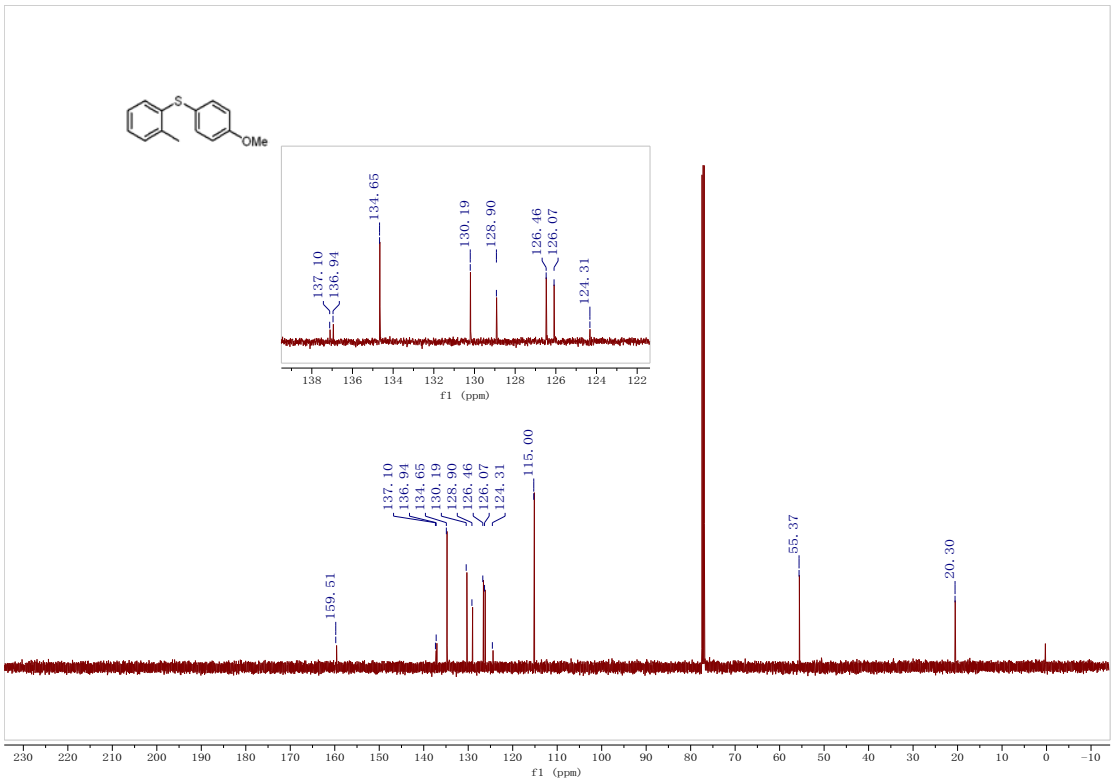
^{13}C NMR Spectrum of **3ce** (126 MHz, $CDCl_3$)



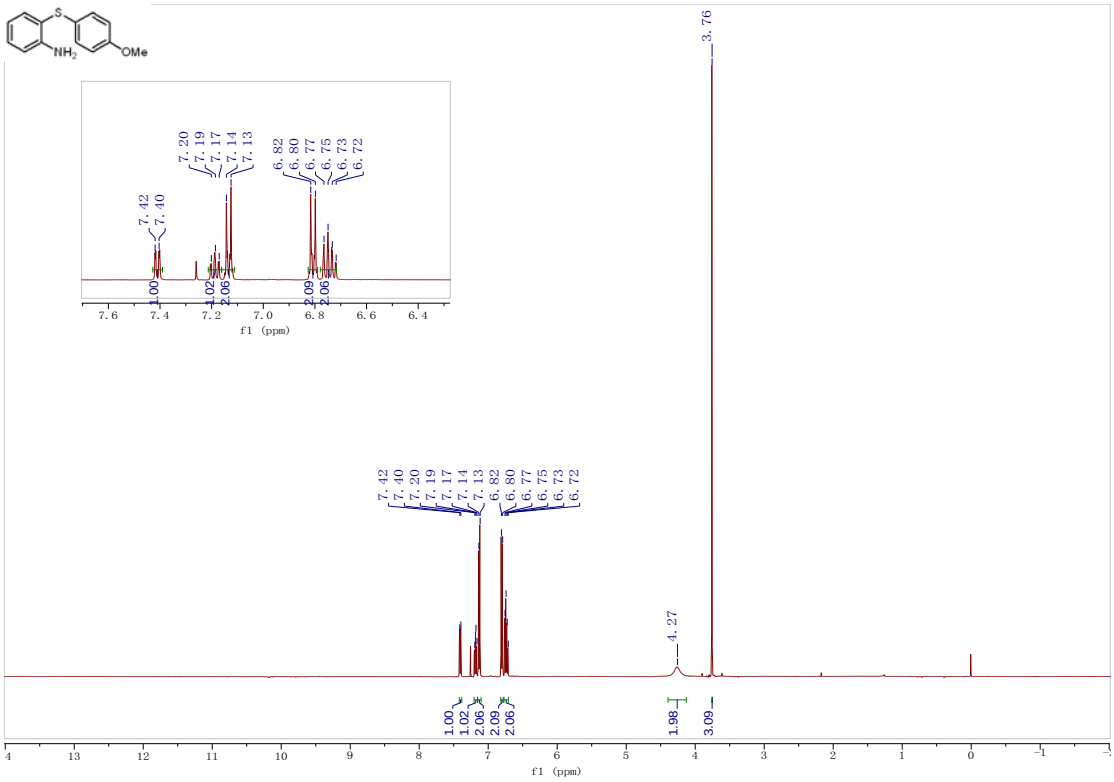
^{1}H NMR Spectrum of **3cf** (500 MHz, $CDCl_3$)



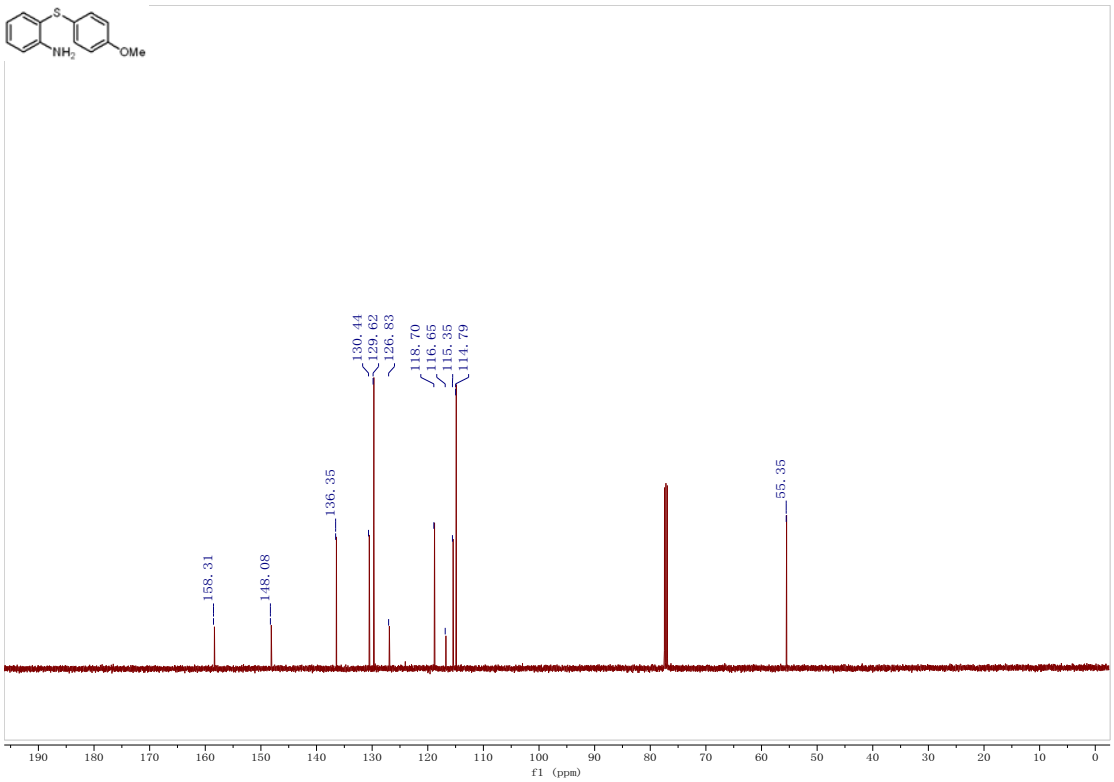
^{13}C NMR Spectrum of **3cf** (126 MHz, $CDCl_3$)



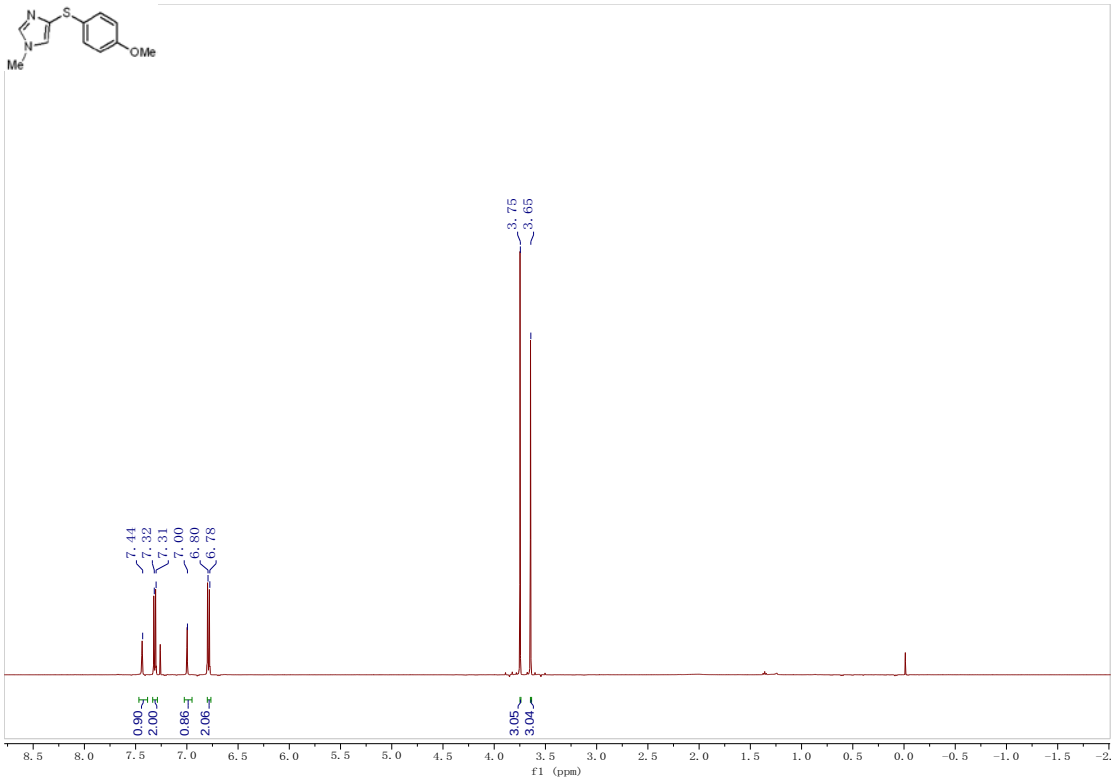
^{1}H NMR Spectrum of **3cg** (500 MHz, $CDCl_3$)



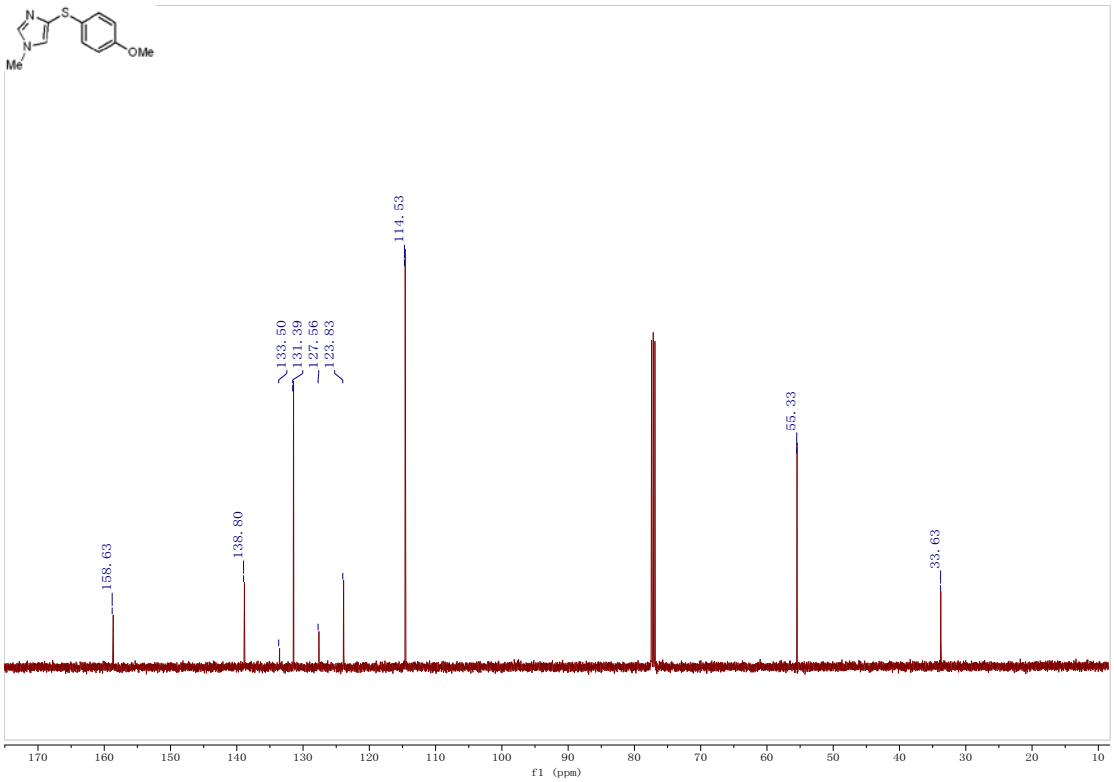
^{13}C NMR Spectrum of **3cg** (126 MHz, $CDCl_3$)



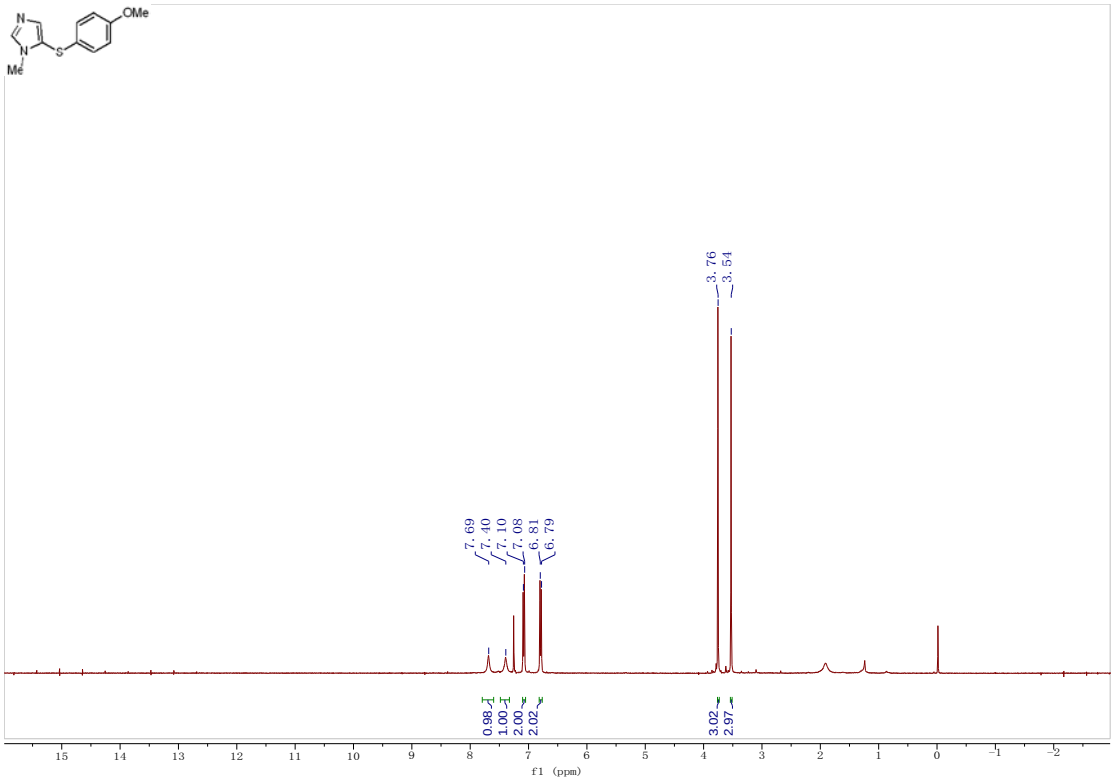
^{1}H NMR Spectrum of **3ch** (500 MHz, $CDCl_3$)



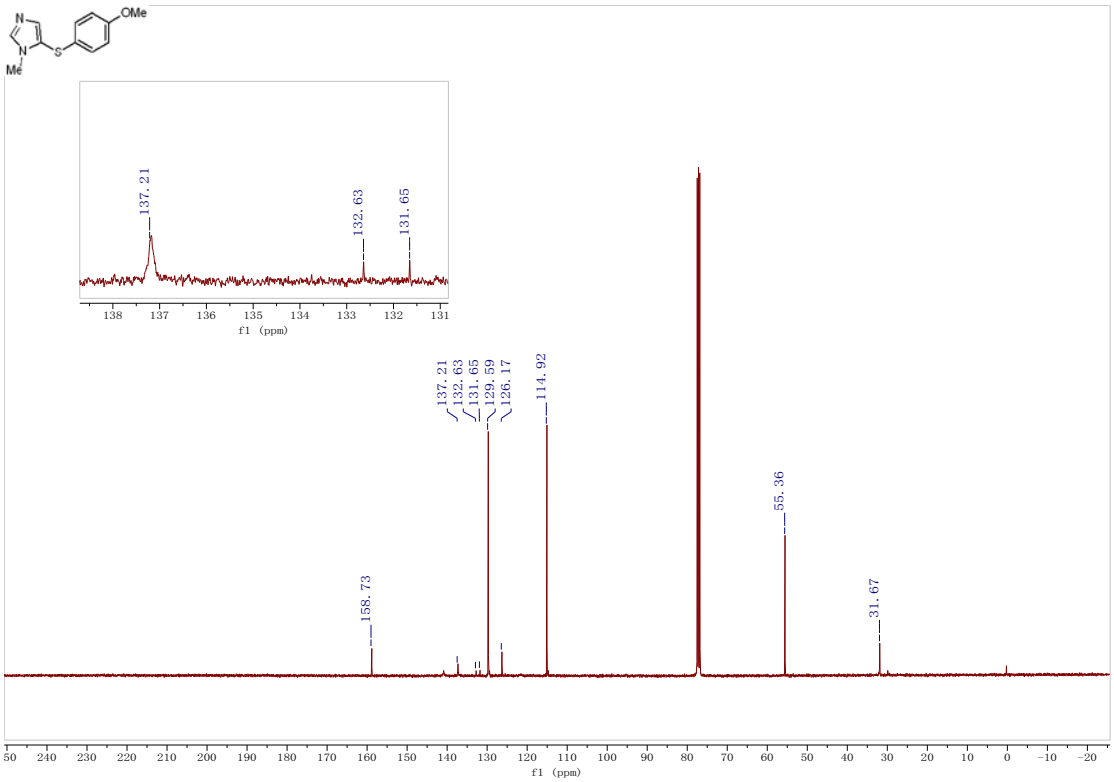
^{13}C NMR Spectrum of **3ch** (126 MHz, $CDCl_3$)



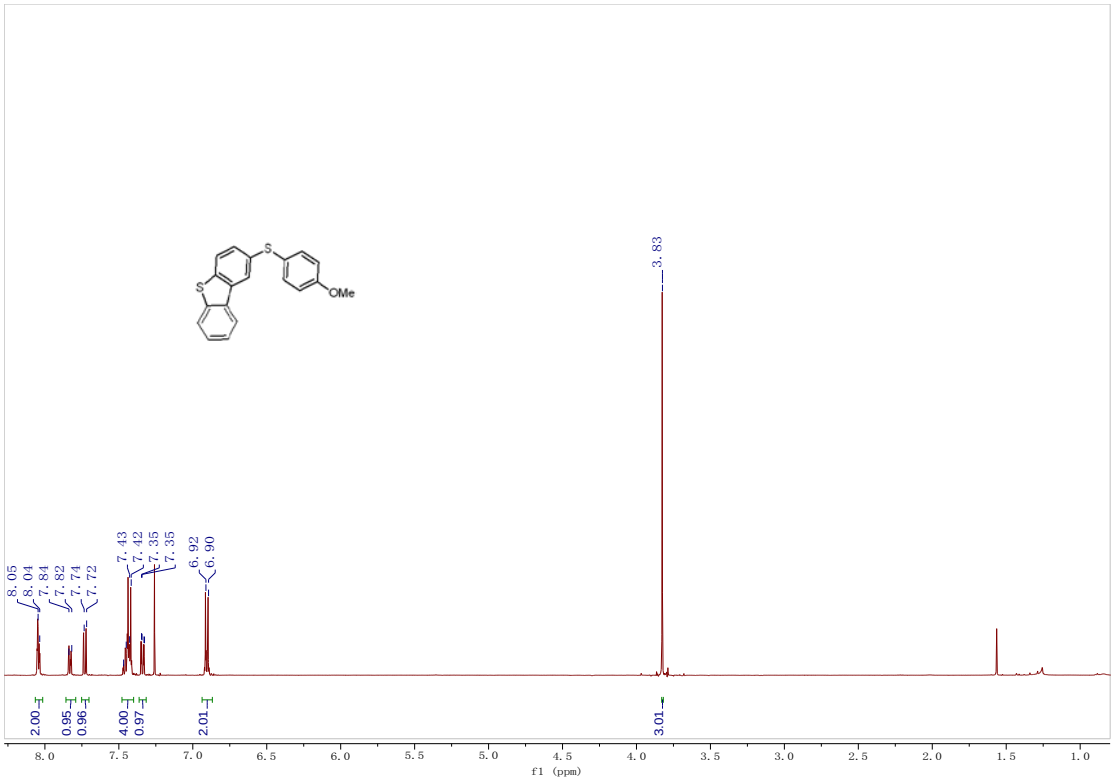
^{1}H NMR Spectrum of **3ci** (500 MHz, DMSO-*d6*)



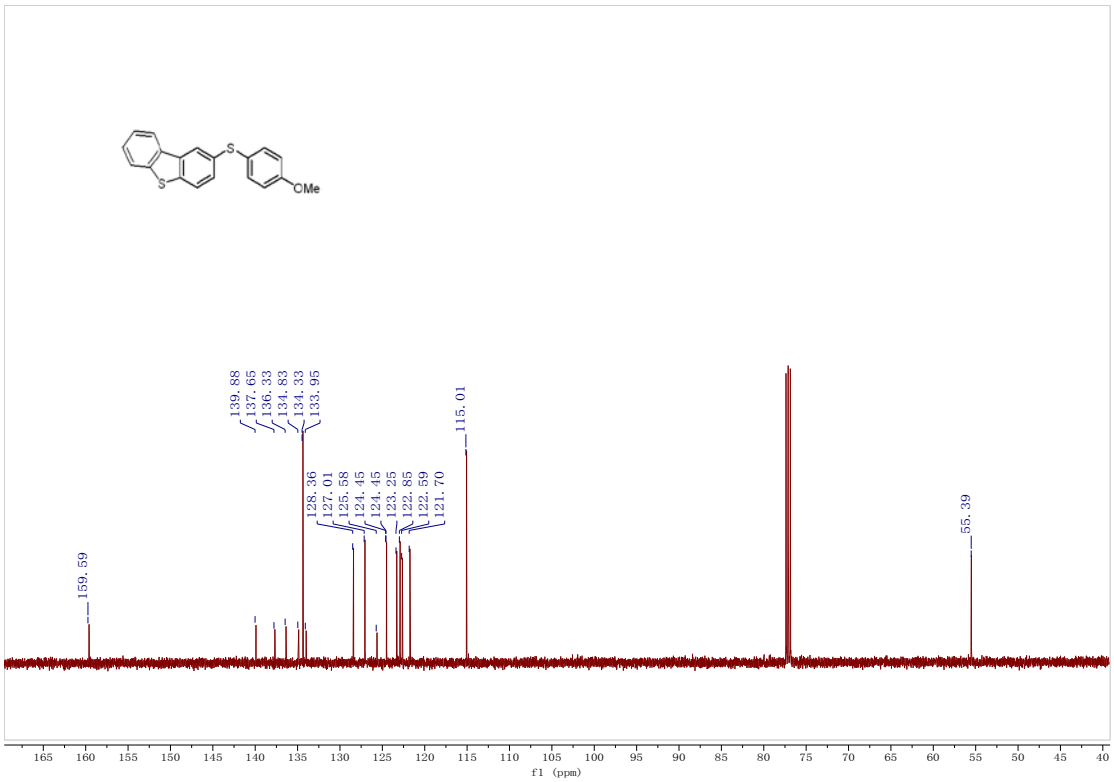
^{13}C NMR Spectrum of **3ci** (101 MHz, DMSO-*d6*)



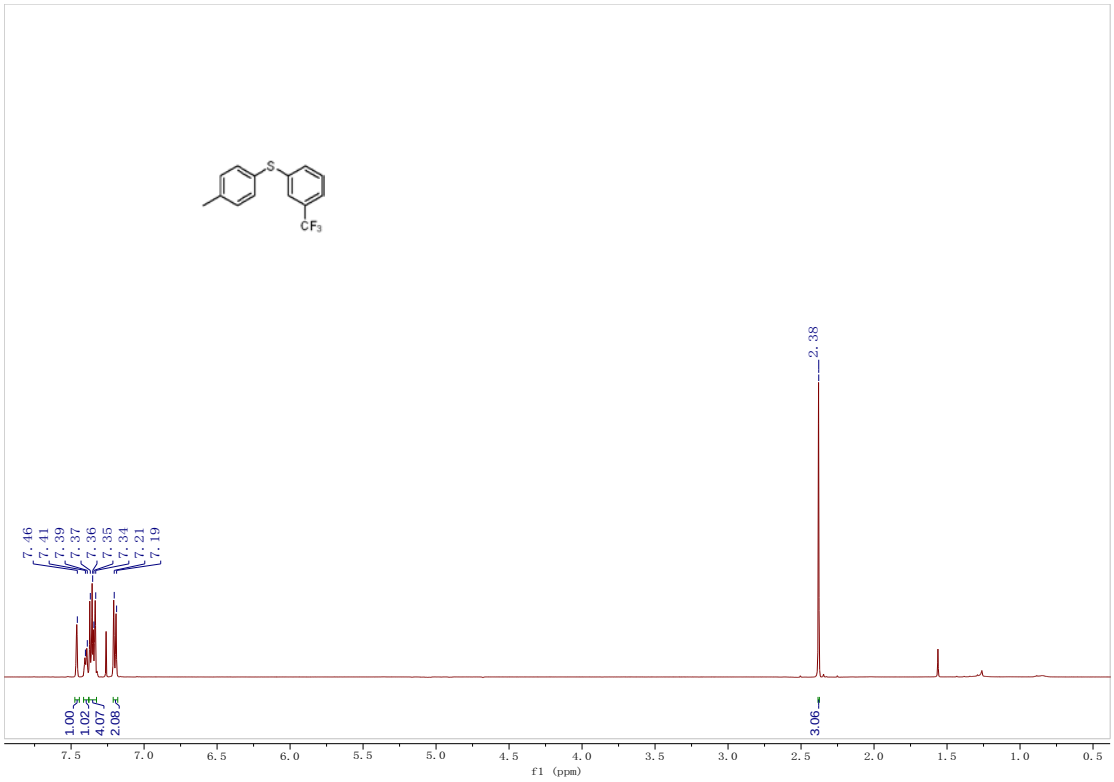
^{1}H NMR Spectrum of **3cj** (500 MHz, $CDCl_3$)



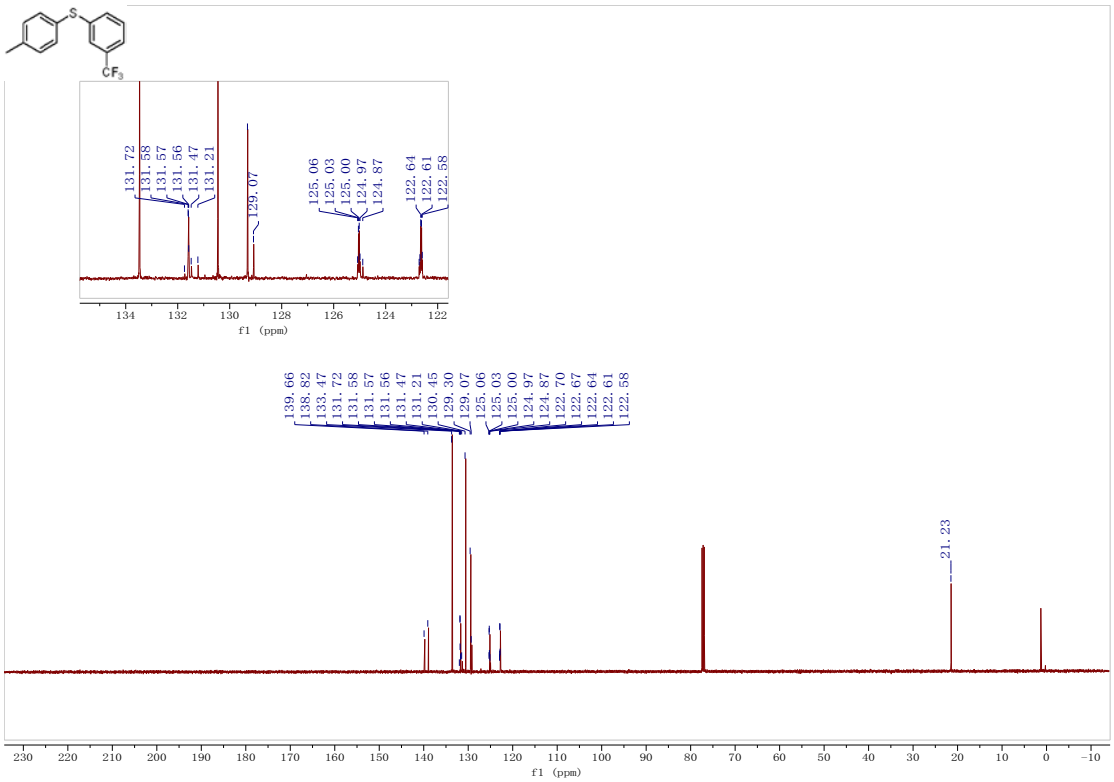
^{13}C NMR Spectrum of **3cj** (126 MHz, $CDCl_3$)



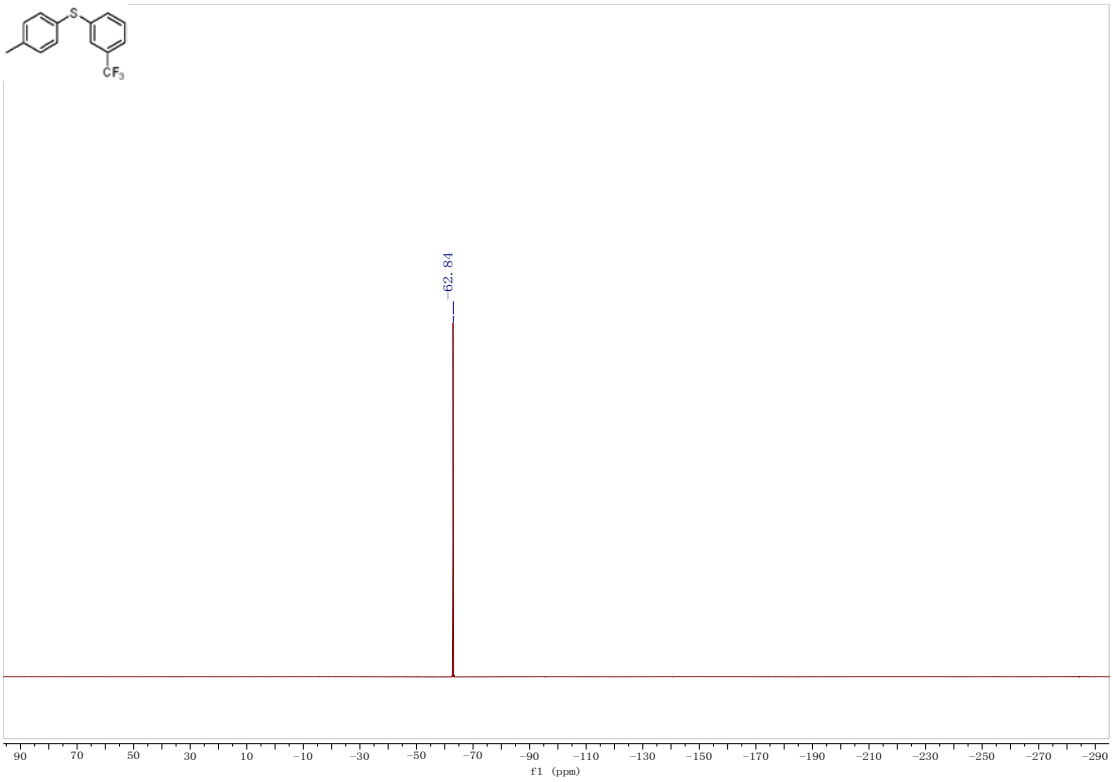
^{1}H NMR Spectrum of **3ck** (500 MHz, $CDCl_3$)



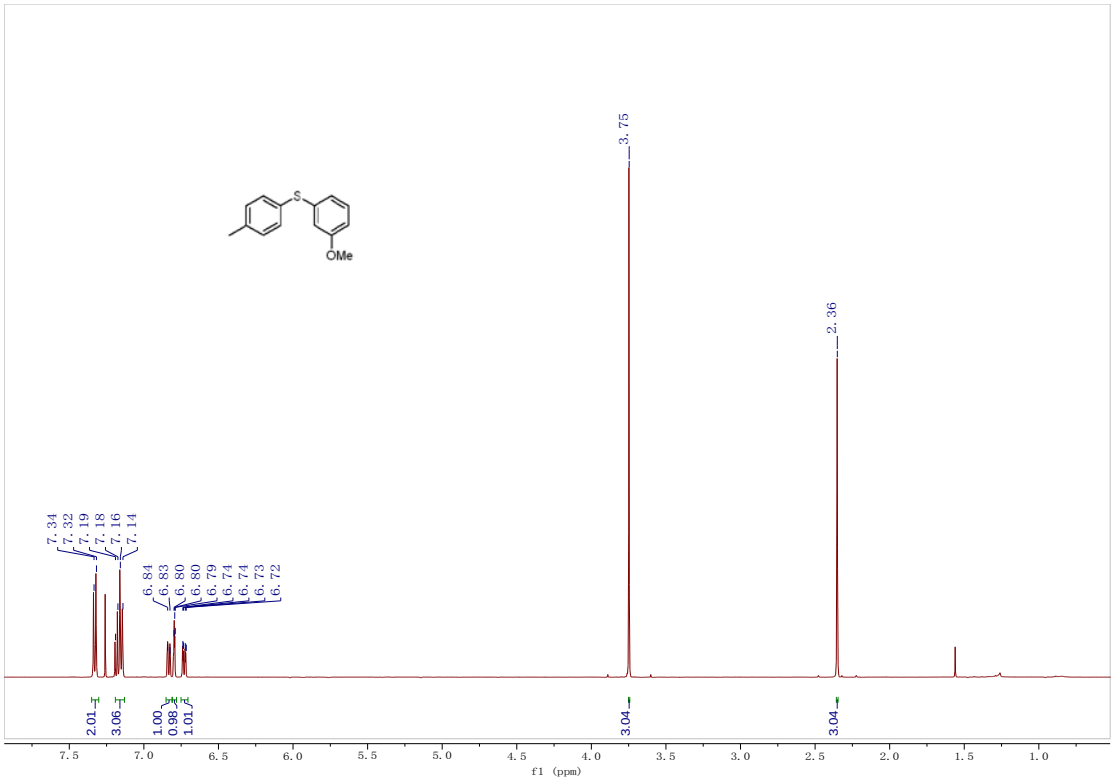
^{13}C NMR Spectrum of **3ck** (126 MHz, $CDCl_3$)



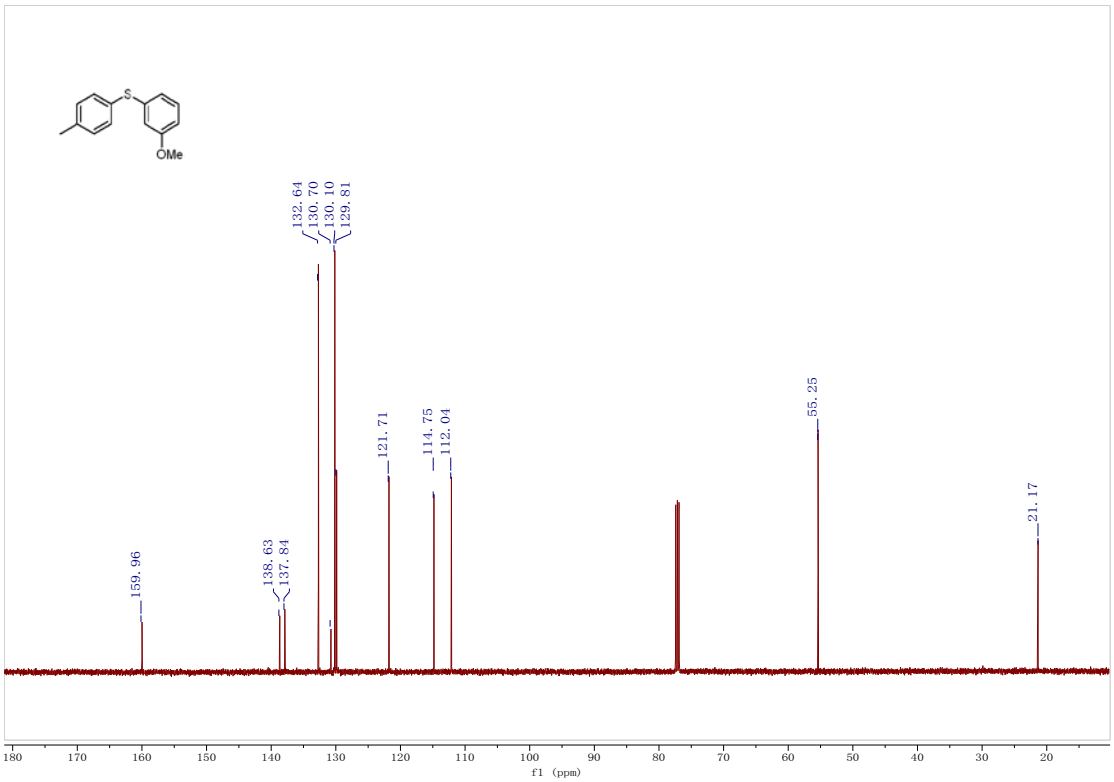
^{19}F NMR Spectrum of **3ck** (376 MHz, $CDCl_3$)



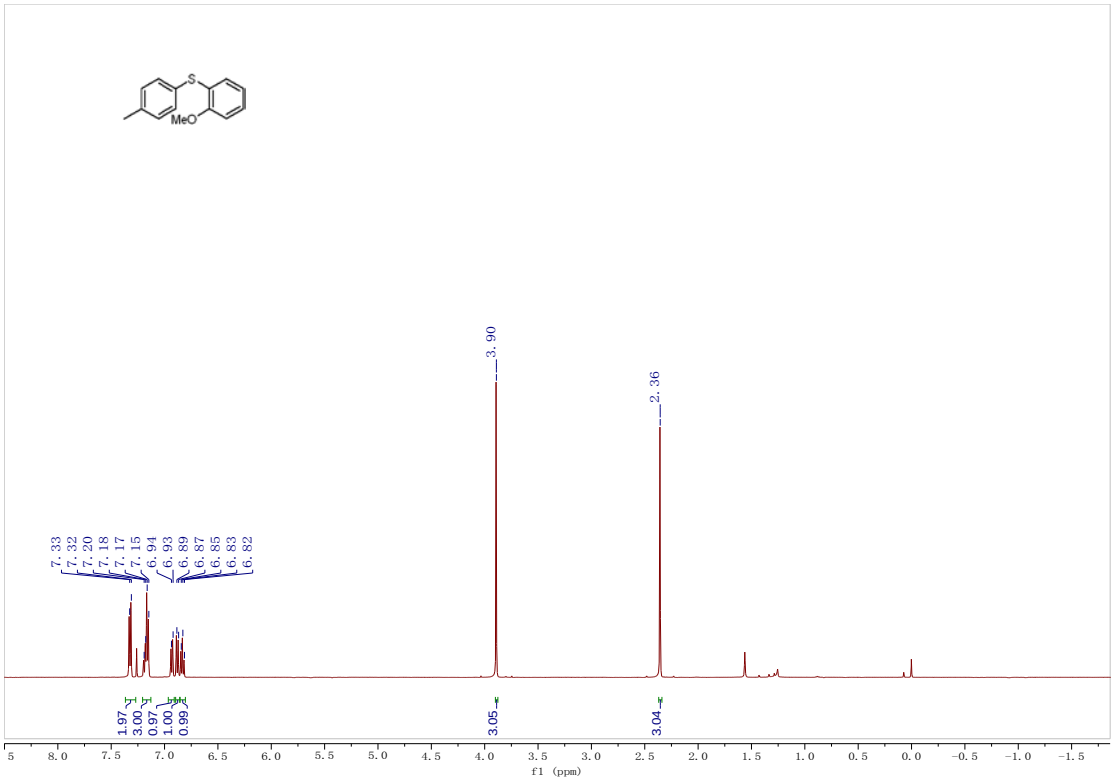
^{1}H NMR Spectrum of **3cl** (500 MHz, $CDCl_3$)



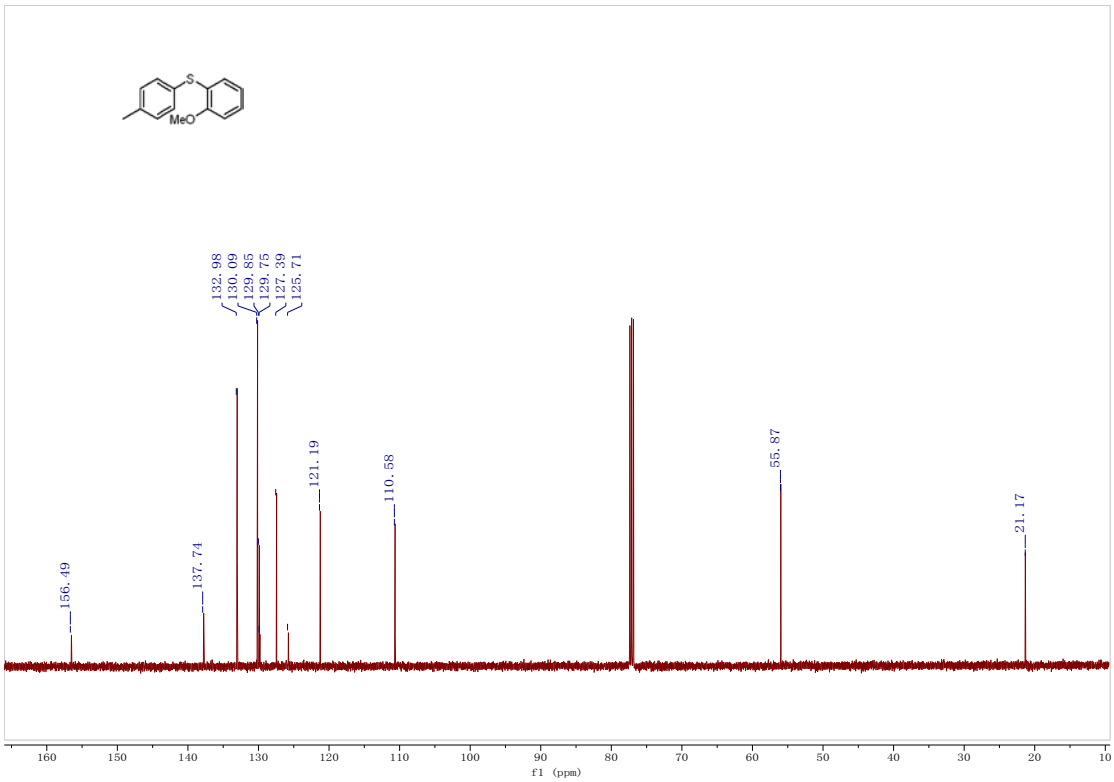
^{13}C NMR Spectrum of **3cl** (126 MHz, $CDCl_3$)



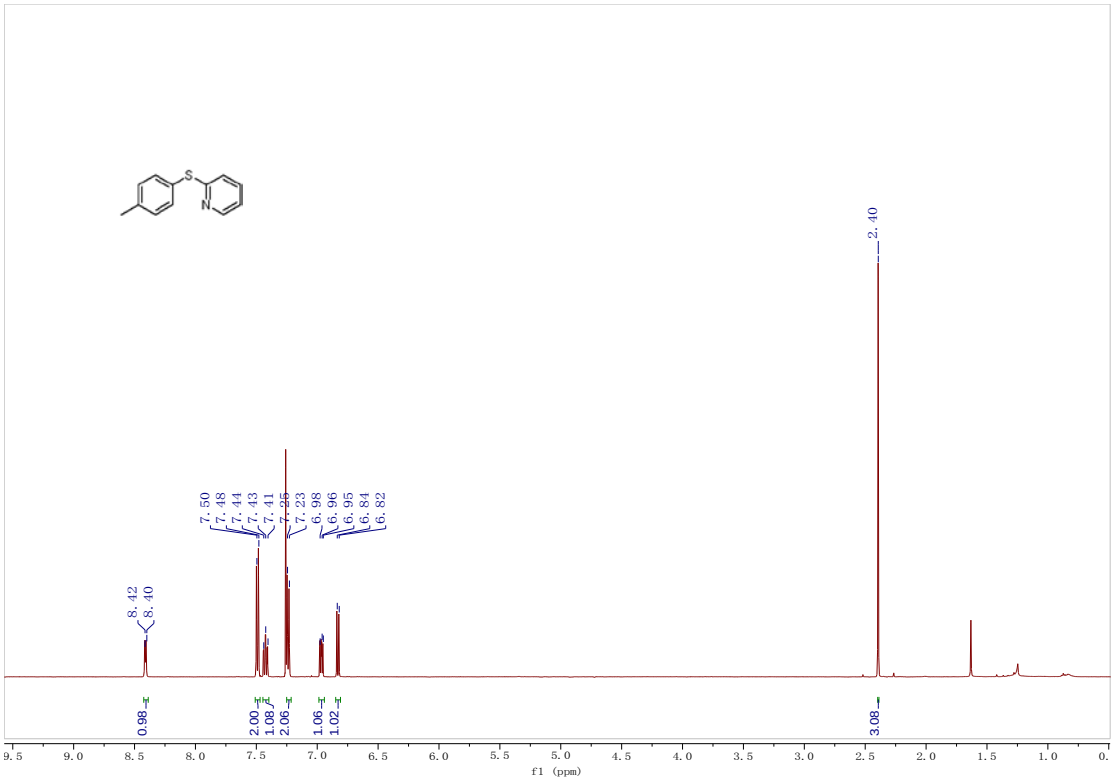
^{1}H NMR Spectrum of **3cm** (500 MHz, $CDCl_3$)



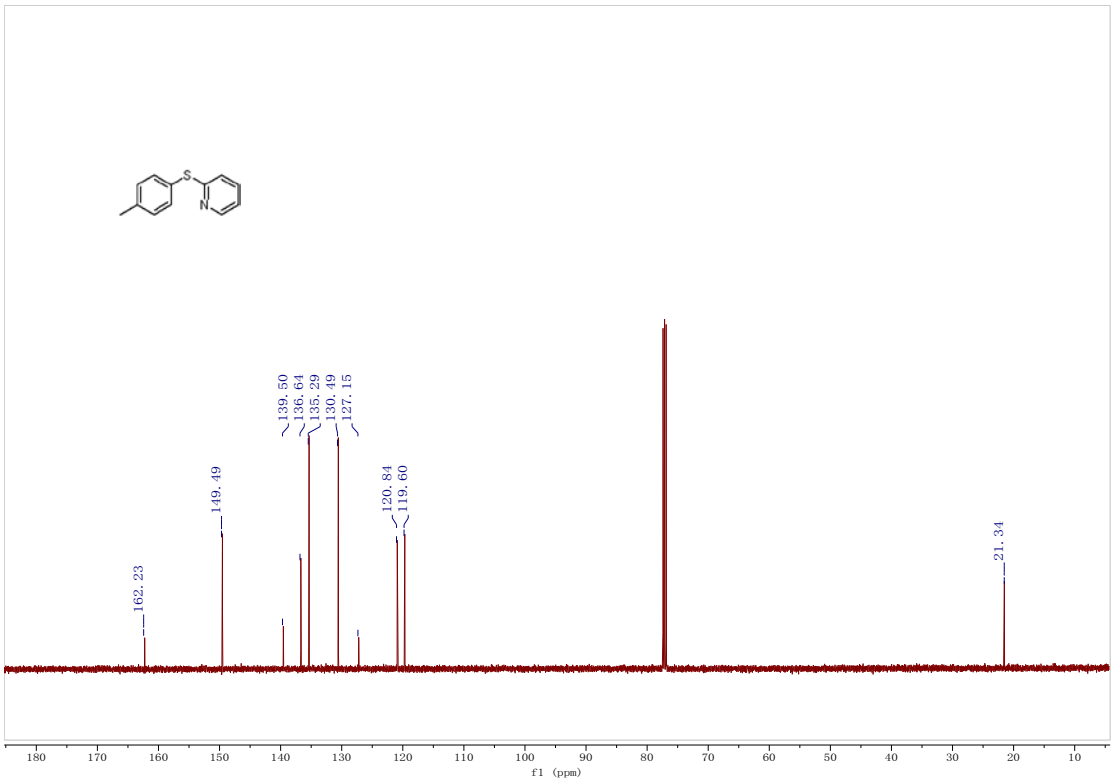
^{13}C NMR Spectrum of **3cm** (126 MHz, $CDCl_3$)



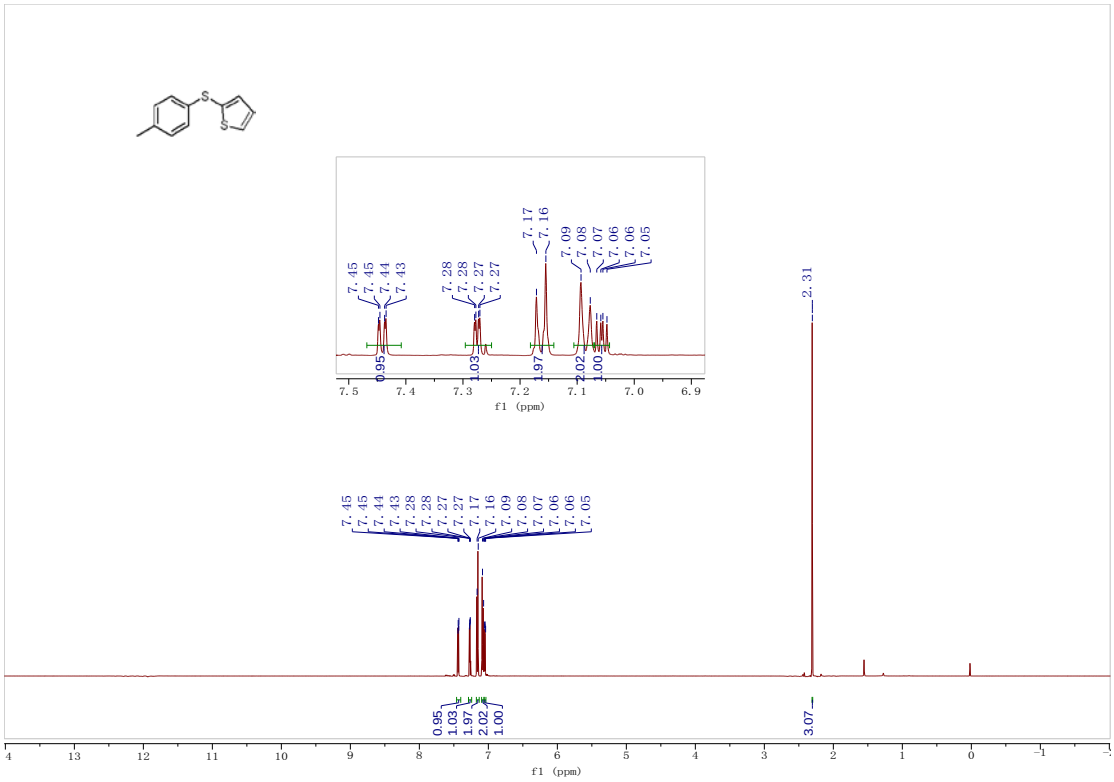
^{1}H NMR Spectrum of **3cn** (500 MHz, $CDCl_3$)



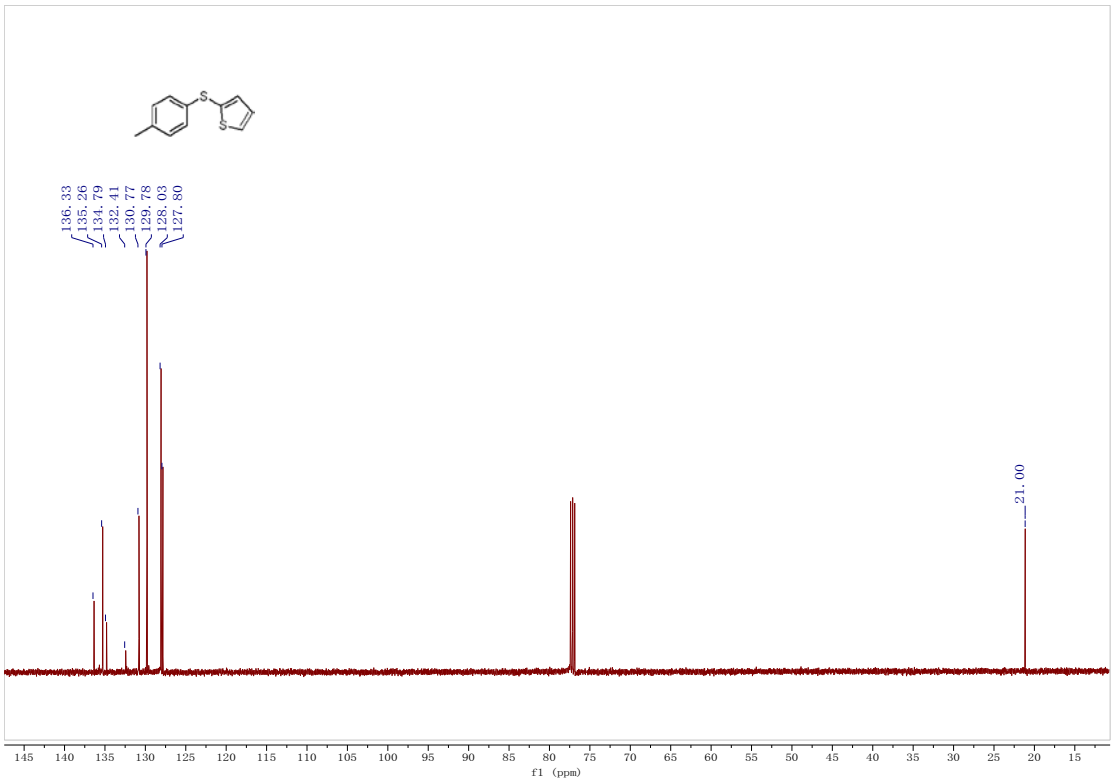
^{13}C NMR Spectrum of **3cn** (126 MHz, $CDCl_3$)



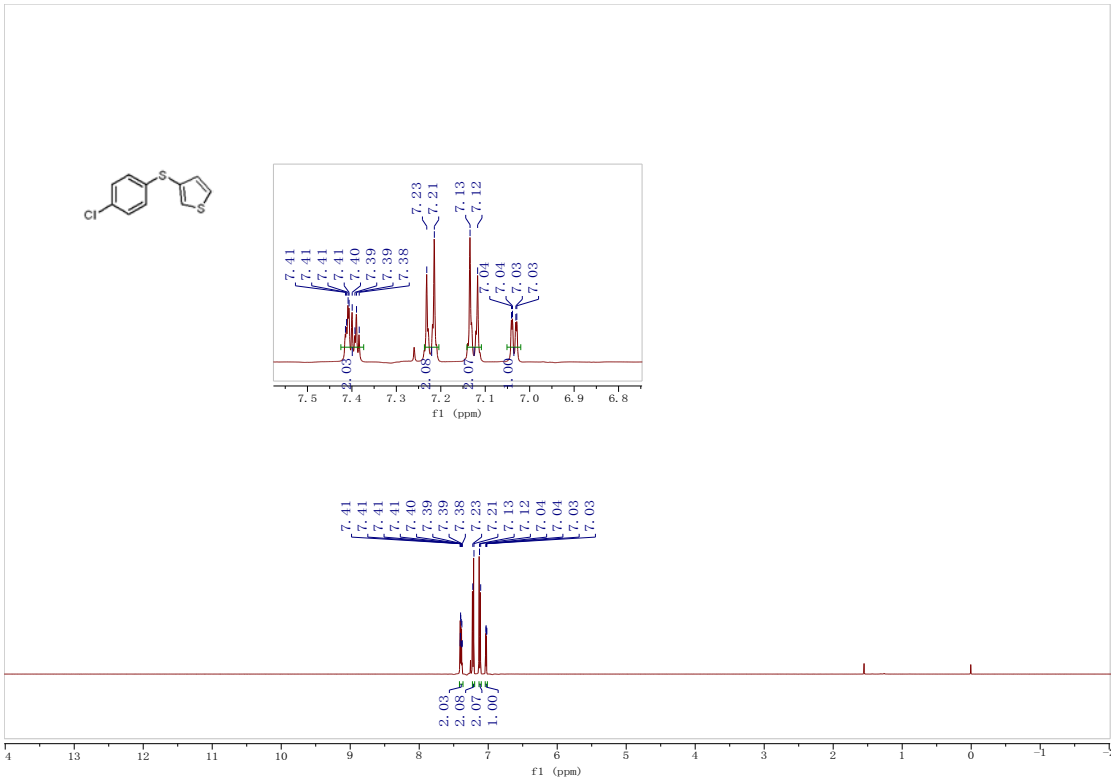
^{1}H NMR Spectrum of **3co** (500 MHz, $CDCl_3$)



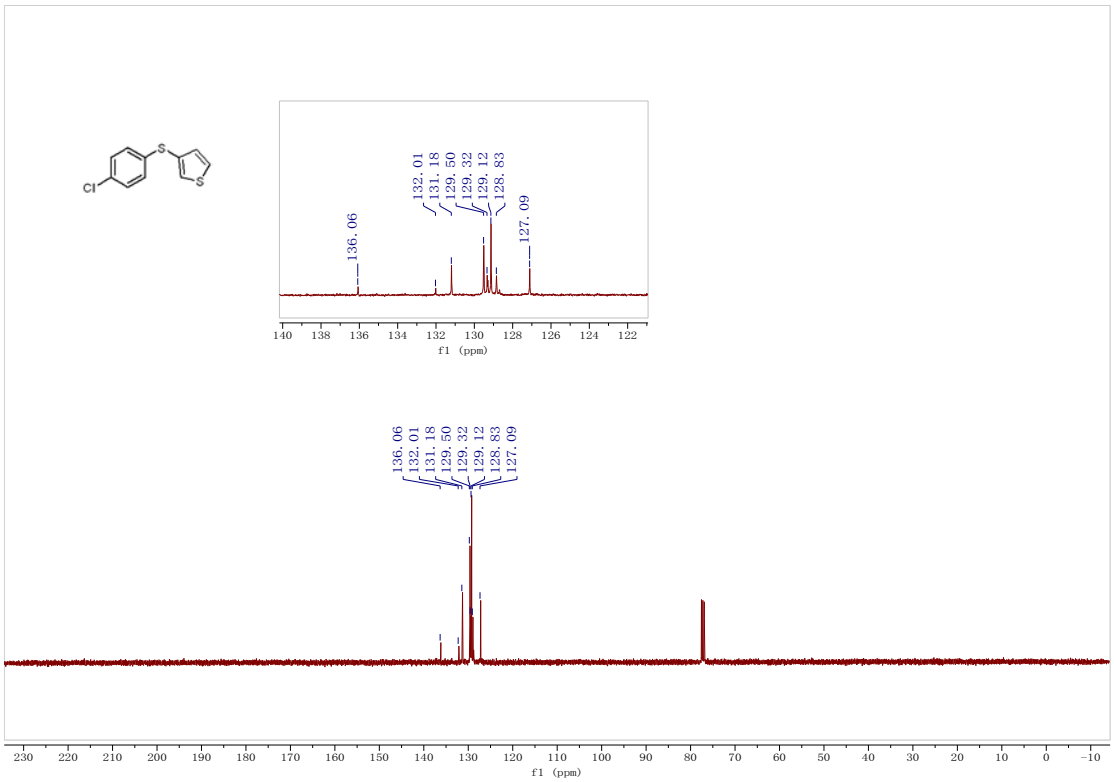
^{13}C NMR Spectrum of **3co** (126 MHz, $CDCl_3$)



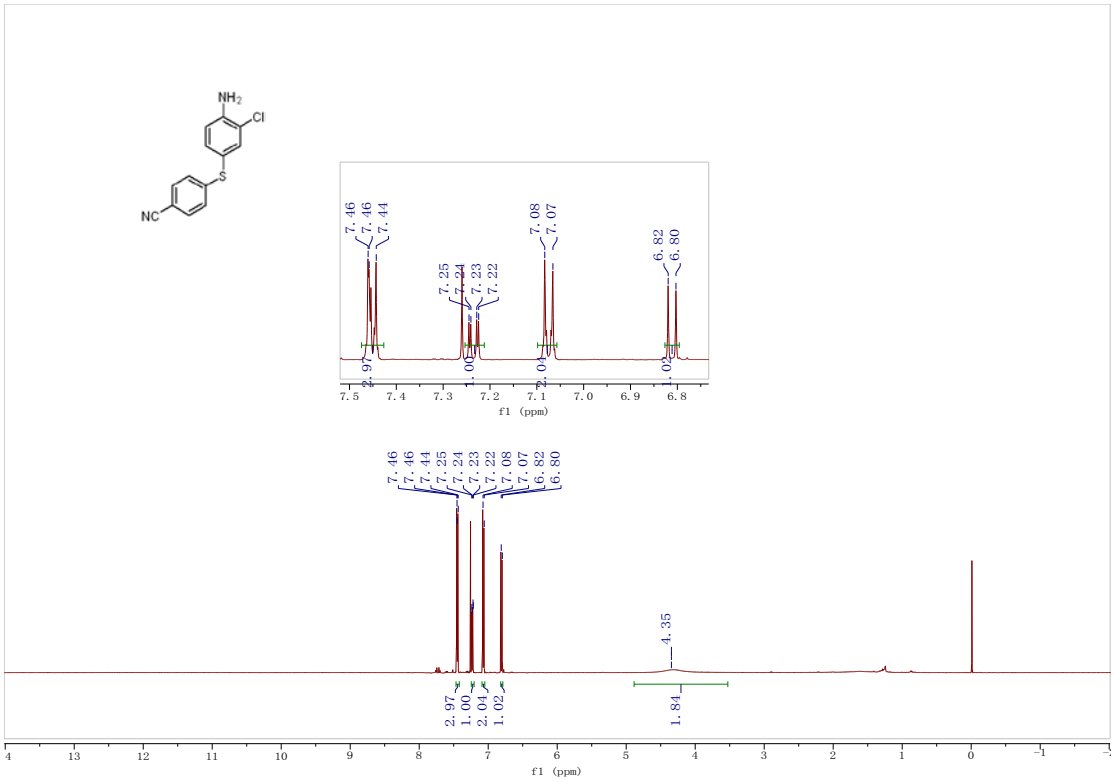
^{1}H NMR Spectrum of **3cp** (500 MHz, $CDCl_3$)



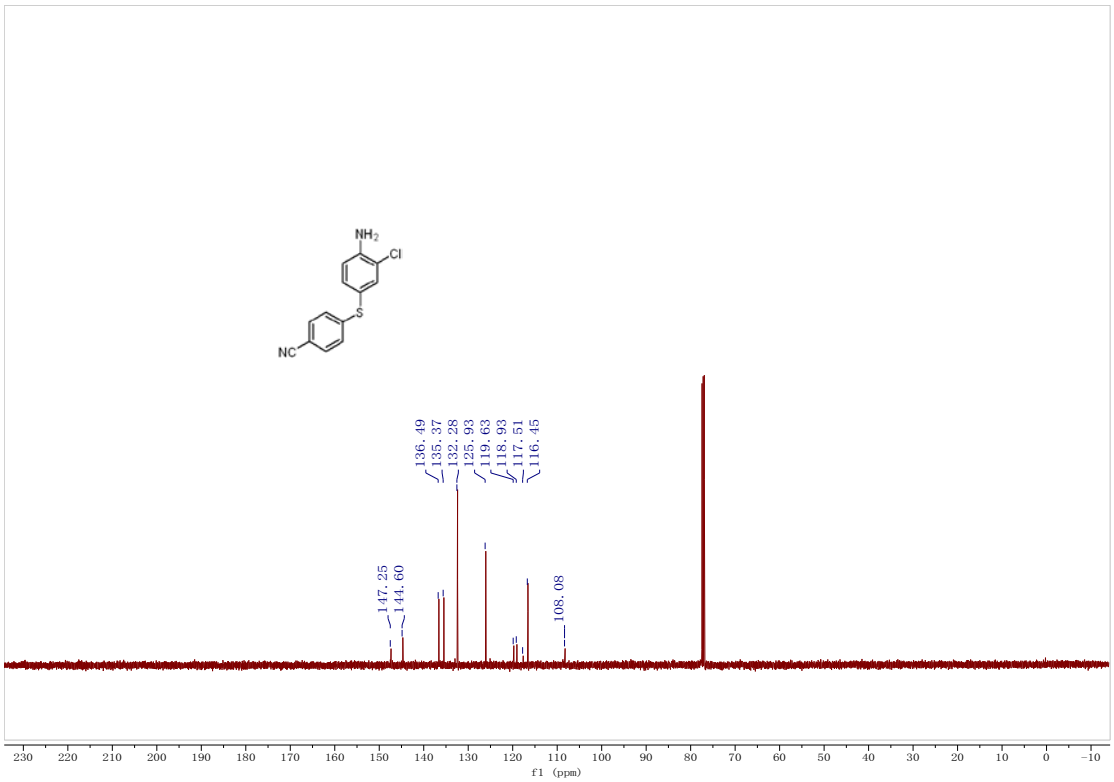
^{13}C NMR Spectrum of **3cp** (101 MHz, $CDCl_3$)



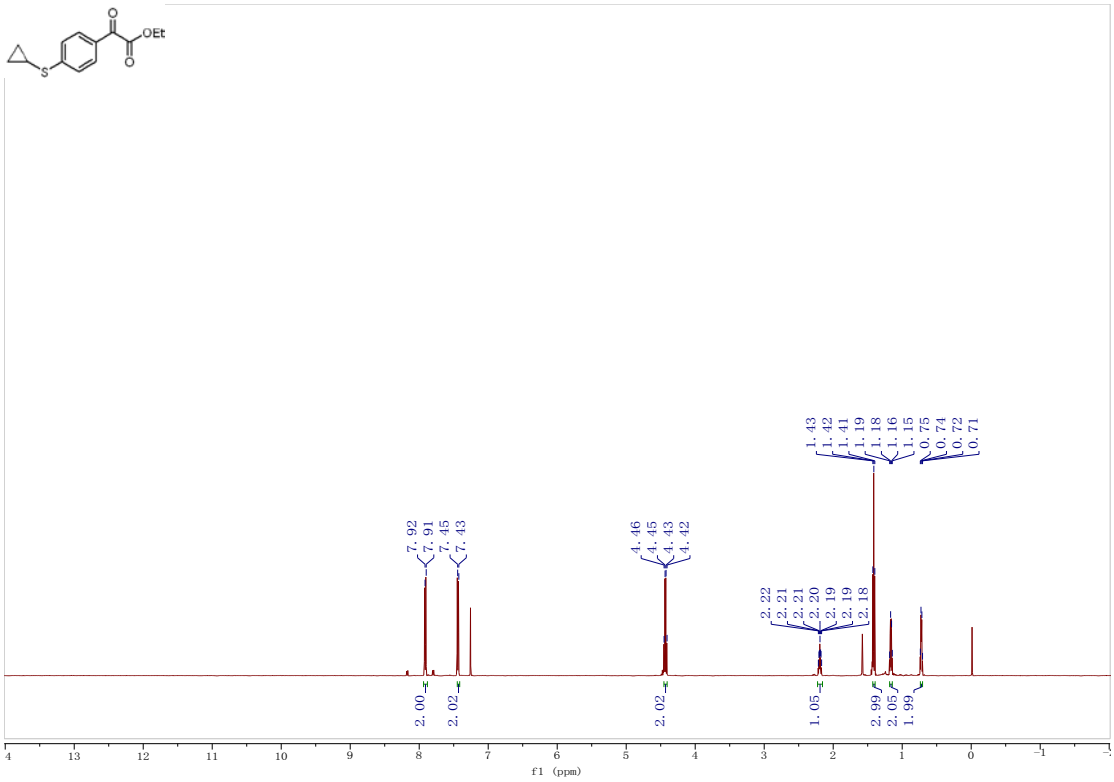
^{1}H NMR Spectrum of **5** (500 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **5** (500 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **8** (500 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **8** (500 MHz, $CDCl_3$)