Supporting Information

Synthesis of N-arylsulfonamides via Fe-promoted reaction of sulfonyl halides with nitroarenes in an aqueous medium

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A. Experimental Procedures

I. General Methods

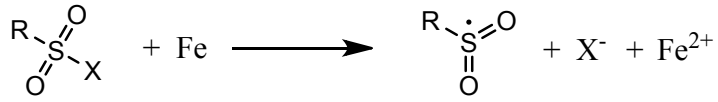
Commercially available reagents were of reagent grade (AR grade) and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silicycle silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). High-resolution mass spectra (HRMS) were obtained with a Q-TOFPremier (ESI).

II. General Procedure for Synthesis of N-arylsulfonamides

A mixture of nitroarenes (0.25 mmol) and sulfonyl chlorides (0.5 mmol) and H_2O (1 mL) was stirred at 60 ºC for 36h in air balloon. After cooling to room temperature, water (10 mL) was added and the aqueous phase was extracted by EtOAc (3×10 mL). The combined organic phases were dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product.

B. Plausible Mechanism

a Reduction of sulfonyl halide by Fe

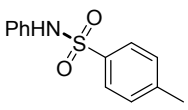


b Reaction sulfonyl radical with nitrosoarene and reduction

Firstly, sulfochloride or sulfofluoride was activated by Fe dust to produce sulfonyl radical. Then, the sulfonyl radical reacted with nitrosoarene originated from the reducing of nitroarene by Fe dust to form the N-S bond. Finally, The generated N-S compound is further reduced by Fe dust and deoxygenated by sulfochloride to produce N-arylsulfonamide.

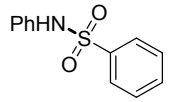
C. Characterization Data for Compounds 3aa-3ax, 3ba-3ja.

4-methyl-N-phenylbenzenesulfonamide (3aa)[1]



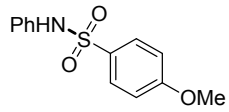
White solid (56.2 mg, 91% yield), m.p.: 104-105 °C. R_f = 0.32 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 4H), 7.11 (d, *J* = 7.7 Hz, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.99, 136.70, 136.09, 129.76, 129.39, 127.39, 125.30, 121.52, 21.65.

_N_-phenylbenzenesulfonamide (3ab)[1]



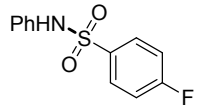
White solid (43.1 mg, 74% yield), m.p.: 105-106 °C. R_f = 0.37 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 2H), 7.57 – 7.50 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.15 – 7.09 (m, 1H), 7.09 – 7.04 (m, 2H), 6.75 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.11, 136.42, 133.16, 129.49, 129.16, 127.35, 125.70, 121.98.

4-methoxy-N-phenylbenzenesulfonamide (3ac)[1]



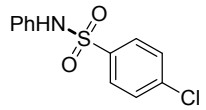
White solid (38.8 mg, 59% yield), m.p.: 108-109 °C. R_f = 0.19 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (td, *J* = 8.1, 7.5, 3.6 Hz, 2H), 7.22 (q, *J* = 6.7, 5.4 Hz, 2H), 7.13 – 6.98 (m, 4H), 6.91 – 6.81 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.20, 136.74, 130.62, 129.55, 129.41, 125.36, 121.64, 114.30, 55.70.

4-fluoro-N-phenylbenzenesulfonamide (3ad)[1]



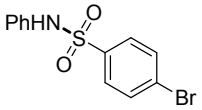
White solid (36.4 mg, 58% yield), m.p.: 109-110 °C. R_f = 0.37 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 8.9, 5.0 Hz, 2H), 7.28-7.23 (m, 2H), 7.18 – 7.03 (m, 5H), 6.61 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63, 164.09, 136.24, 135.02, 134.98, 130.18, 130.09, 129.55, 125.86, 121.99, 116.56, 116.34.

4-chloro-N-phenylbenzenesulfonamide (3ae) [1]



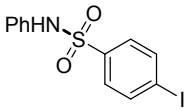
White solid (47.4 mg, 71% yield), m.p.: 104-105 °C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 14.7, 8.1 Hz, 3H), 7.14 (q, *J* = 7.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.72, 137.43, 136.14, 129.57, 129.48, 128.81, 125.88, 121.95.

4-bromo-N-phenylbenzenesulfonamide (3af) [1]



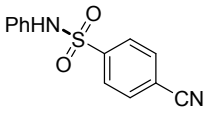
White solid (51.3 mg, 66% yield), m.p.: 116-117 °C. R_f = 0.26 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 4H), 7.27 – 7.23 (m, 2H), 7.19 – 7.13 (m, 1H), 7.09 – 7.04 (m, 2H), 6.65 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.98, 136.08, 132.47, 129.59, 128.88, 128.27, 125.92, 121.99.

4-iodo-N-phenylbenzenesulfonamide (3ag)



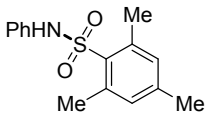
White solid (68.2 mg, 76% yield), m.p.: 65-68 °C. R_f = 0.40 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.17 – 7.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.72, 138.42, 136.08, 129.60, 128.69, 125.95, 122.01, 100.79. HRMS (ESI): m/z calcd for $C_{12}H_{10}INO_2S$ $[M + H]^+$: 359.9555; found, 359.9553.

4-cyano-N-phenylbenzenesulfonamide *(3ah)*[2]



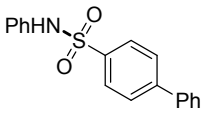
White solid (43.2 mg, 67% yield), m.p.: 110-111 °C. R_f = 0.19 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.72 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.16, 135.54, 132.99, 129.74, 127.98, 126.45, 122.36, 117.31, 116.83.

2,4,6-trimethyl-N-phenylbenzenesulfonamide (3ai)[1]



White solid (40.6 mg, 59% yield), m.p.: 97-98 °C. R_f = 0.25 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.3 Hz, 2H), 6.91 (s, 2H), 6.74 (s, 1H), 2.60 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.77, 139.43, 136.58, 133.49, 132.19, 129.42, 125.33, 121.50, 23.16, 21.10.

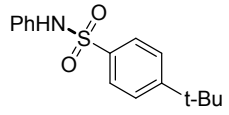
***N*-phenyl-[1,1'-biphenyl]-4-sulfonamide (3aj)[3]**



White solid (58.7 mg, 76% yield), m.p.: 117-118 °C. R_f = 0.20 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.42 (dt, *J* = 13.9, 6.9 Hz, 3H), 7.24 (dd, *J* = 8.6, 6.8 Hz, 3H), 7.17 – 7.06 (m, 3H). ^{13}C NMR (101

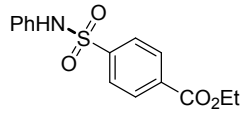
MHz, $CDCl_3$) δ 145.96, 139.19, 137.64, 136.57, 129.49, 129.13, 128.64, 127.89, 127.73, 127.39, 125.53, 121.72.

4-(tert-butyl)-N-phenylbenzenesulfonamide (3ak)[4]



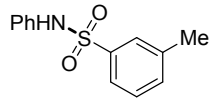
White solid (46.2 mg, 64% yield), m.p.: 65-68 °C. R_f = 0.49 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.71 (m, 2H), 7.46 – 7.40 (m, 2H), 7.26 – 7.20 (m, 3H), 7.13 – 7.07 (m, 3H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.92, 136.78, 136.22, 129.40, 127.20, 126.17, 125.20, 121.33, 35.26, 31.14.

Ethyl 4-(N-phenylsulfamoyl)benzoate (3al)



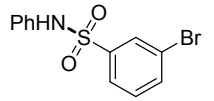
White solid (56.4 mg, 74% yield), m.p.: 121-123°C. R_f = 0.19 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 3H), 7.16 – 7.06 (m, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.24, 142.78, 136.03, 134.55, 130.30, 129.57, 127.37, 125.99, 122.12, 61.90, 14.34. HRMS (ESI): m/z calcd for $C_{15}H_{15}NO_4S$ $[M + H]^+$: 306.0800; found, 306.0802.

3-methyl-N-phenylbenzenesulfonamide (3am)



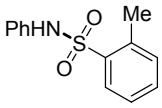
White solid (41.4 mg, 67% yield), m.p.: 101-102 °C. R_f = 0.21 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.56 (m, 2H), 7.31 (d, *J* = 6.8 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.14 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.38, 138.92, 136.60, 133.94, 129.40, 128.98, 127.71, 125.42, 124.51, 121.67, 21.41. HRMS (ESI): m/z calcd for $C_{13}H_{13}NO_2S$ $[M + H]^+$: 248.0745; found, 248.0746.

3-bromo-N-phenylbenzenesulfonamide (3an)[5]



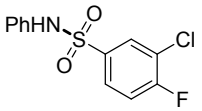
White solid (58.3 mg, 75% yield), m.p.: 98-100 °C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.46 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 3H), 7.16 – 7.08 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.38, 137.15, 136.04, 129.48, 129.46, 125.80, 121.83, 121.45, 120.78, 118.87.

2-methyl-N-phenylbenzenesulfonamide (3ao)[4]



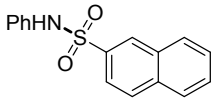
White solid (53.1 mg, 86% yield), m.p.: 65-68 °C. R_f = 0.48 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 7.09 – 7.00 (m, 3H), 6.82 (s, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.47, 137.28, 136.49, 133.29, 132.73, 130.15, 129.48, 126.43, 125.17, 120.78, 20.56.

3-chloro-4-fluoro-N-phenylbenzenesulfonamide (3ap)



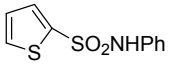
White solid (59.1 mg, 83% yield), m.p.: 112-114 °C. R_f = 0.53 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 6.6, 2.3 Hz, 1H), 7.66 (ddd, *J* = 8.6, 4.3, 2.3 Hz, 1H), 7.31 – 7.08 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.14, 159.58, 135.99, 135.95, 135.83, 130.32, 129.67, 127.92, 127.84, 126.20, 122.65, 122.47, 122.17, 117.57, 117.35. The proton and carbon NMR data for this compound were consistent with literature data. HRMS (ESI): m/z calcd for $C_{12}H_9ClFNO_2S$ $[M + H]^+$: 286.0105; found, 286.0107.

***N*-phenylnaphthalene-2-sulfonamide (3aq)**[12]



White solid (44.6 mg, 63% yield), m.p.: 131-133 °C. R_f = 0.19 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.93 – 7.72 (m, 4H), 7.59 (dt, *J* = 20.6, 7.2 Hz, 2H), 7.24 – 7.01 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.46, 136.01, 135.03, 132.13, 129.55, 129.47, 129.44, 129.06, 127.99, 127.65, 125.58, 122.39, 121.83.

***N*-phenylthiophene-2-sulfonamide (3ar)**[1]



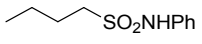
White solid (52.0 mg, 87% yield), m.p.: 80-82 °C. R_f = 0.21 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 4.1 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.18 – 7.12 (m, 3H), 6.98 (dd, *J* = 4.8, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.34, 136.27, 133.05, 132.59, 129.47, 127.45, 125.87, 121.94.

***N*-phenylmethanesulfonamide (3as)**[7]

MsNHPh

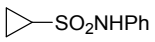
White solid (23.5 mg, 55% yield), m.p.: 99-100 °C. R_f = 0.32 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.17 (m, 3H), 6.89 (s, 1H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.84, 129.85, 125.58, 120.90, 39.42.

***N*-phenylbutane-1-sulfonamide (3at)**



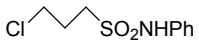
White solid (46.9 mg, 88% yield), m.p.: 108-110°C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.23 – 7.15 (m, 3H), 6.37 (s, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 1.84 – 1.75 (m, 2H), 1.41 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.97, 129.81, 125.23, 120.50, 51.41, 25.58, 21.54, 13.64. HRMS (ESI): m/z calcd for $C_{10}H_{15}NO_2S$ $[M + H]^+$: 214.0902; found, 214.0904.

_N_-phenylcyclopropanesulfonamide (3au)



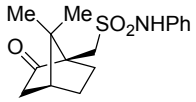
White solid (38.9 mg, 79% yield), m.p.: 115-117 °C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 2H), 7.16 (dt, *J* = 27.4, 4.9 Hz, 3H), 6.48 (s, 1H), 2.41 (dq, *J* = 8.7, 3.9 Hz, 1H), 1.10 (d, *J* = 5.1 Hz, 2H), 0.97 – 0.83 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.87, 129.63, 125.64, 121.96, 29.96, 5.76. HRMS (ESI): m/z calcd for $C_9H_{11}NO_2S$ $[M + H]^+$: 198.0589; found, 198.0587.

3-chloro-N-phenylpropane-1-sulfonamide (3av)



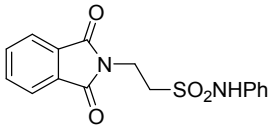
White solid (39.0 mg, 67% yield), m.p.: 65-68 °C. R_f = 0.22 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.20 (m, 3H), 6.50 (s, 1H), 3.64 (t, *J* = 5.5 Hz, 2H), 3.28 (t, *J* = 6.5 Hz, 2H), 2.30 (dd, *J* = 8.9, 5.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.55, 129.84, 125.54, 120.82, 48.99, 42.67, 26.73. HRMS (ESI): m/z calcd for $C_9H_{12}ClNO_2S$ $[M + H]^+$: 234.0356; found, 234.0359.

1-((1R,4S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-N-phenylmethanesulfonamide (3aw)



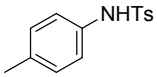
White solid (49.9 mg, 65% yield), m.p.: 112-114°C. R_f = 0.35 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.28 – 7.18 (m, 4H), 7.15 – 7.09 (m, 1H), 3.30 (d, *J* = 15.3 Hz, 1H), 2.80 (d, *J* = 15.2 Hz, 1H), 2.38 (ddd, *J* = 18.8, 4.9, 2.7 Hz, 1H), 2.07 (td, *J* = 10.6, 4.7 Hz, 3H), 2.02 – 1.91 (m, 2H), 1.41 (ddd, *J* = 12.6, 8.8, 3.6 Hz, 1H), 0.89 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.61, 137.73, 129.55, 125.67, 122.33, 59.87, 49.27, 49.13, 43.23, 42.93, 27.79, 27.20, 20.01, 19.47. HRMS (ESI): m/z calcd for $C_{16}H_{21}NO_3S$ $[M + H]^+$: 307.1242; found, 307.1241.

2-(1,3-dioxoisoindolin-2-yl)-N-phenylethanesulfonamide (3ax)[8]



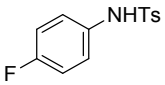
White solid (59.4 mg, 72% yield), m.p.: 141-143 °C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.33 (d, *J* = 4.3 Hz, 4H), 7.19 (s, 1H), 7.17 – 7.12 (m, 1H), 4.09 (t, *J* = 6.0 Hz, 2H), 3.46 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.52, 136.71, 134.55, 131.86, 129.94, 125.33, 123.85, 120.22, 47.91, 32.76.

4-methyl-N-(p-tolyl)benzenesulfonamide (3ba)[1]



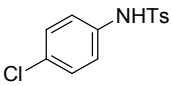
White solid (60.7 mg, 93% yield), m.p.: 117-118 °C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.93 (m, 5H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.82, 136.11, 135.35, 133.89, 129.92, 129.70, 127.39, 122.27, 21.66, 20.96.

_N_-(4-fluorophenyl)-4-methylbenzenesulfonamide (3ca)[4]



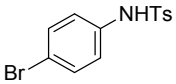
Yellow oil (43.7 mg, 66% yield). R_f = 0.20 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.17 (s, 1H), 7.05 (dd, *J* = 7.6, 4.8 Hz, 2H), 6.94 – 6.89 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.92, 159.48, 144.16, 135.70, 132.45, 132.42, 129.82, 127.39, 124.67, 124.59, 116.44, 116.31, 116.08, 115.93, 21.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.26.

_N_-(4-chlorophenyl)-4-methylbenzenesulfonamide (3da)[1]



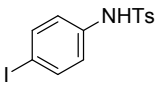
White solid (51.3 mg, 73% yield), m.p.: 118-119 °C. R_f = 0.21 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.32 (s, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.33, 135.67, 135.25, 130.92, 129.91, 129.51, 127.37, 122.94, 21.70.

_N_-(4-bromophenyl)-4-methylbenzenesulfonamide (3ea)[9]



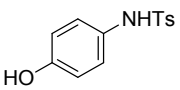
Pale yellow solid (59.9 mg, 74% yield), m.p.: 146-148 °C. R_f = 0.22 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.06 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.35, 135.77, 135.73, 132.48, 132.16, 129.93, 127.36, 123.18, 21.71.

_N_-(4-iodophenyl)-4-methylbenzenesulfonamide (3fa)[10]



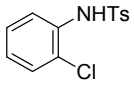
White solid (62.5 mg, 67% yield), m.p.: 96-98 °C. R_f = 0.41 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.37, 138.39, 136.56, 135.69, 129.94, 127.36, 123.09, 89.20, 21.72.

_N_-(4-hydroxyphenyl)-4-methylbenzenesulfonamide (3ga)[11]



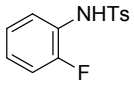
White solid (51.9 mg, 79% yield), m.p.: 147-149 °C. R_f = 0.15 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.95 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.48, 143.94, 135.77, 129.71, 128.66, 127.41, 125.94, 116.10, 21.67.

N-(2-chlorophenyl)-4-methylbenzenesulfonamide (3ha)[4]



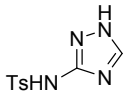
White solid (45.7 mg, 65% yield), m.p.: 65-68 °C. R_f = 0.39 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.3 Hz, 3H), 7.26 – 7.19 (m, 4H), 7.03 (td, *J* = 7.7, 1.6 Hz, 1H), 6.97 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.36, 136.05, 133.65, 129.81, 129.49, 128.02, 127.41, 125.96, 125.17, 122.47, 21.71.

N-(2-fluorophenyl)-4-methylbenzenesulfonamide (3ia)[12]



White solid (51.7 mg, 78% yield), m.p.: 104-106 °C. R_f = 0.23 (petroleum:EtOAc = 4:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.58 (td, *J* = 7.9, 2.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.02 (m, 2H), 6.94 (m, 1H), 6.88 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.24, 152.81, 144.28, 135.90, 129.78, 127.29, 126.24, 126.16, 124.85, 124.81, 124.68, 123.37, 115.62, 115.42, 21.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.60.

4-methyl-N-(1H-1,2,4-triazol-3-yl)benzenesulfonamide (3ja)



White solid (42.2 mg, 71% yield), m.p.: 112-114 °C. R_f = 0.21 (petroleum:EtOAc = 2:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 9.2, 3.0 Hz, 2H), 7.47 – 7.28 (m, 3H), 6.24 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.04, 151.31, 146.77, 133.71, 130.34, 128.29, 21.93. HRMS (ESI): m/z calcd for $C_9H_{10}N_4O_2S$ $[M + H]^+$: 238.0524; found, 238.0526.

D. References

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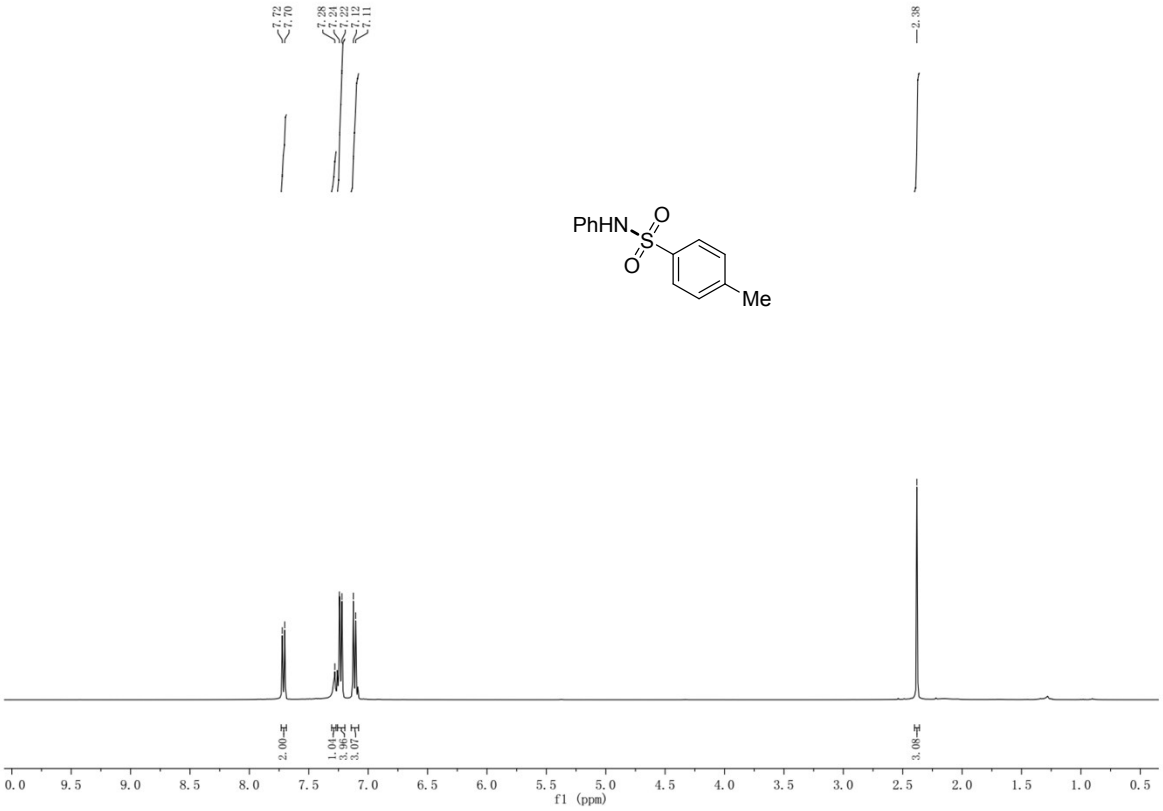
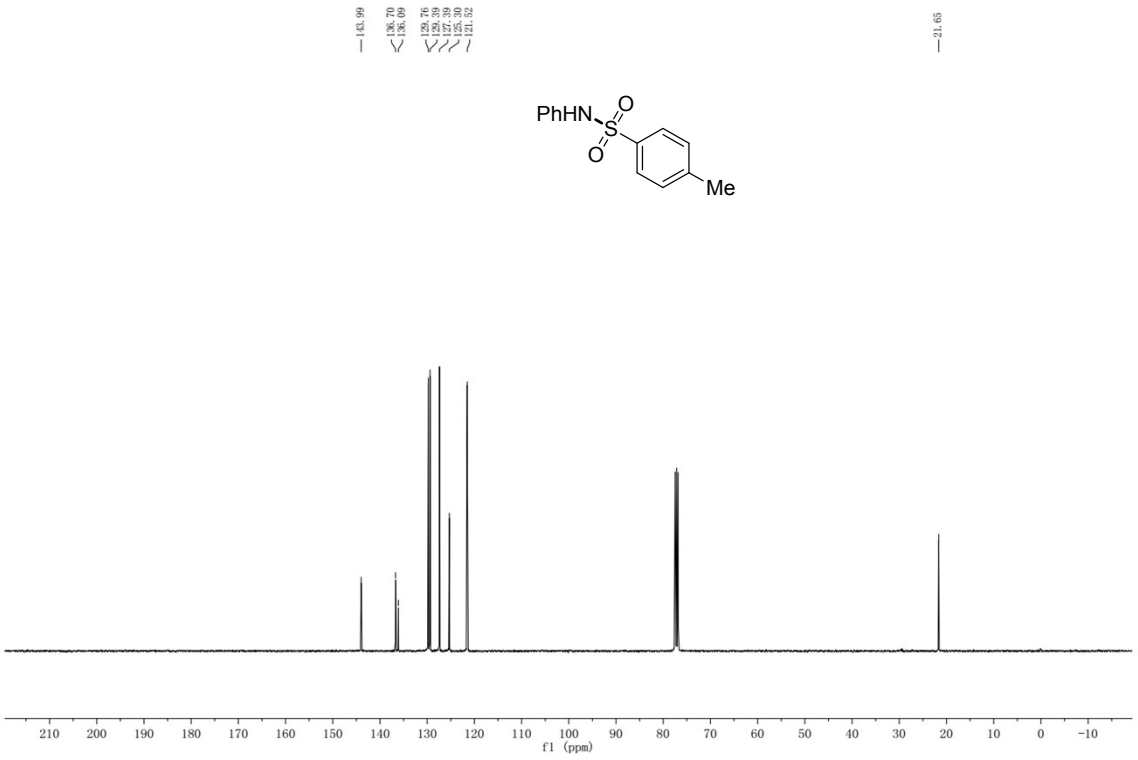
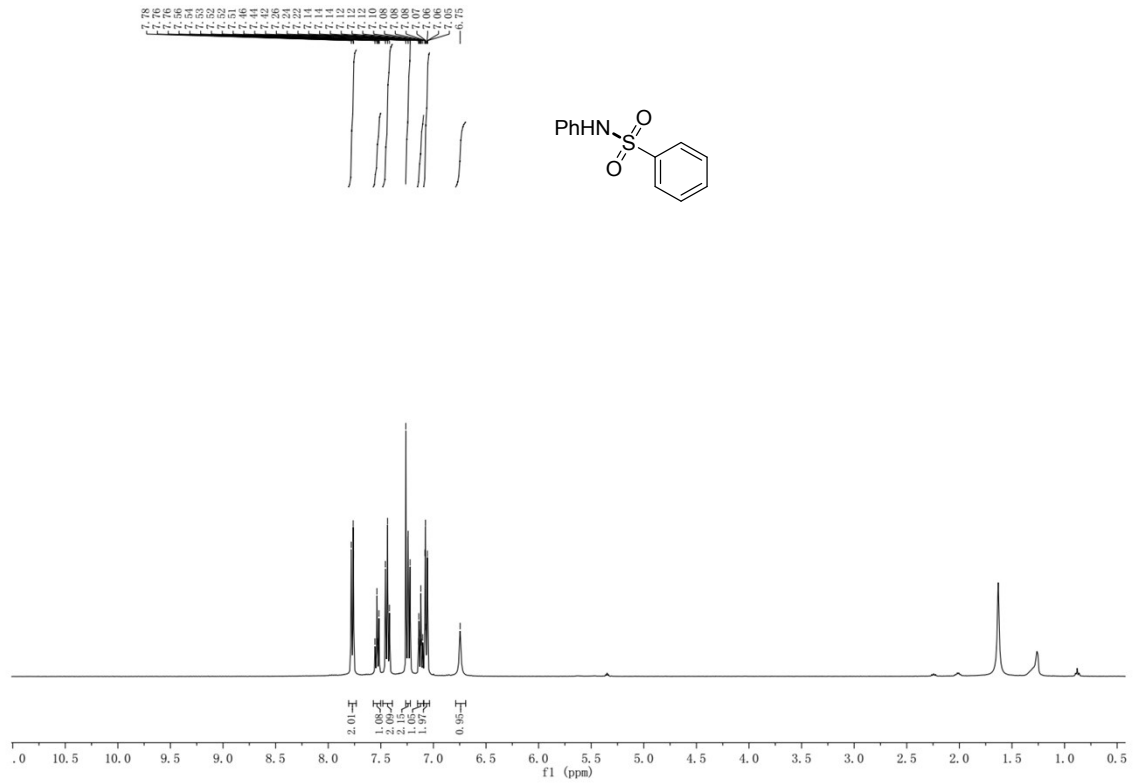
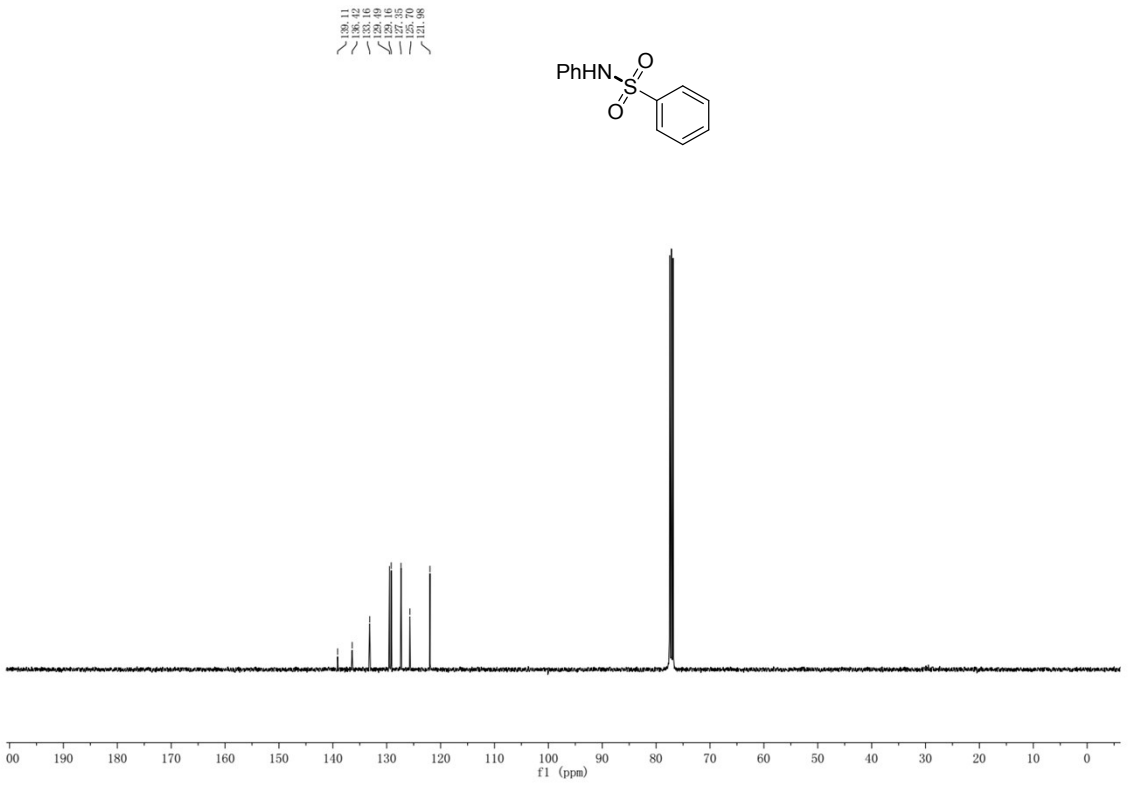
E. NMR Spectra *4-methyl-N-phenylbenzenesulfonamide(**3aa**)*



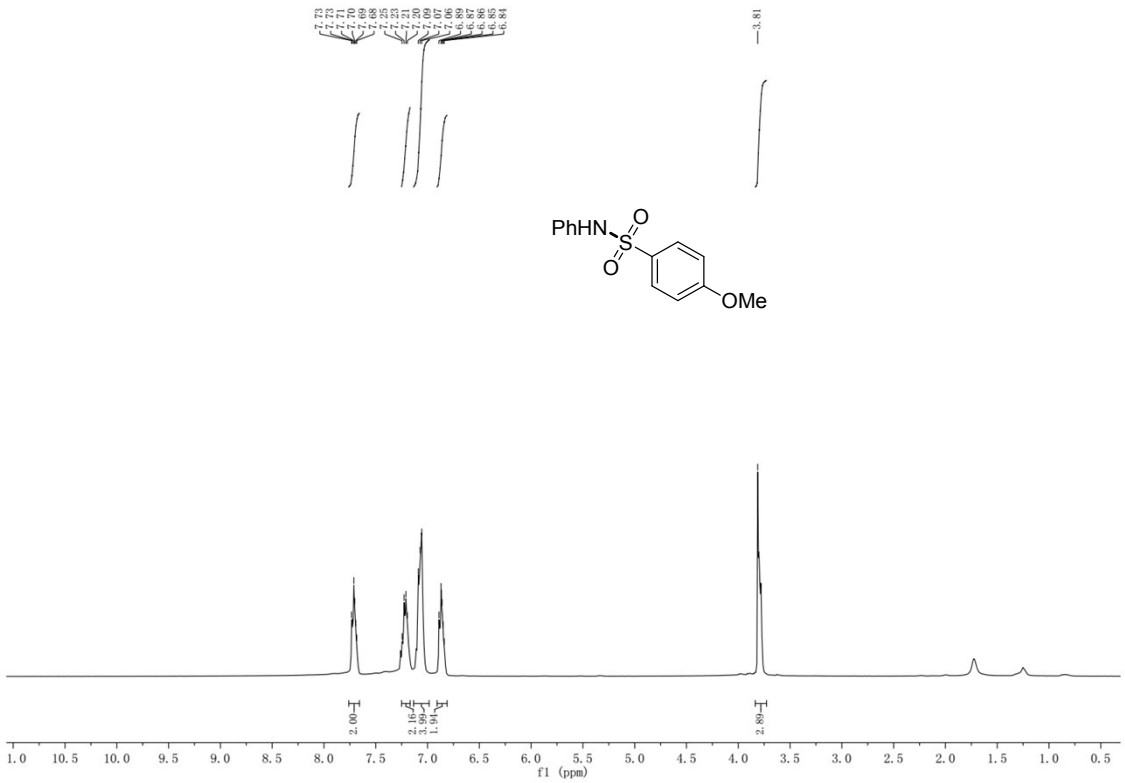


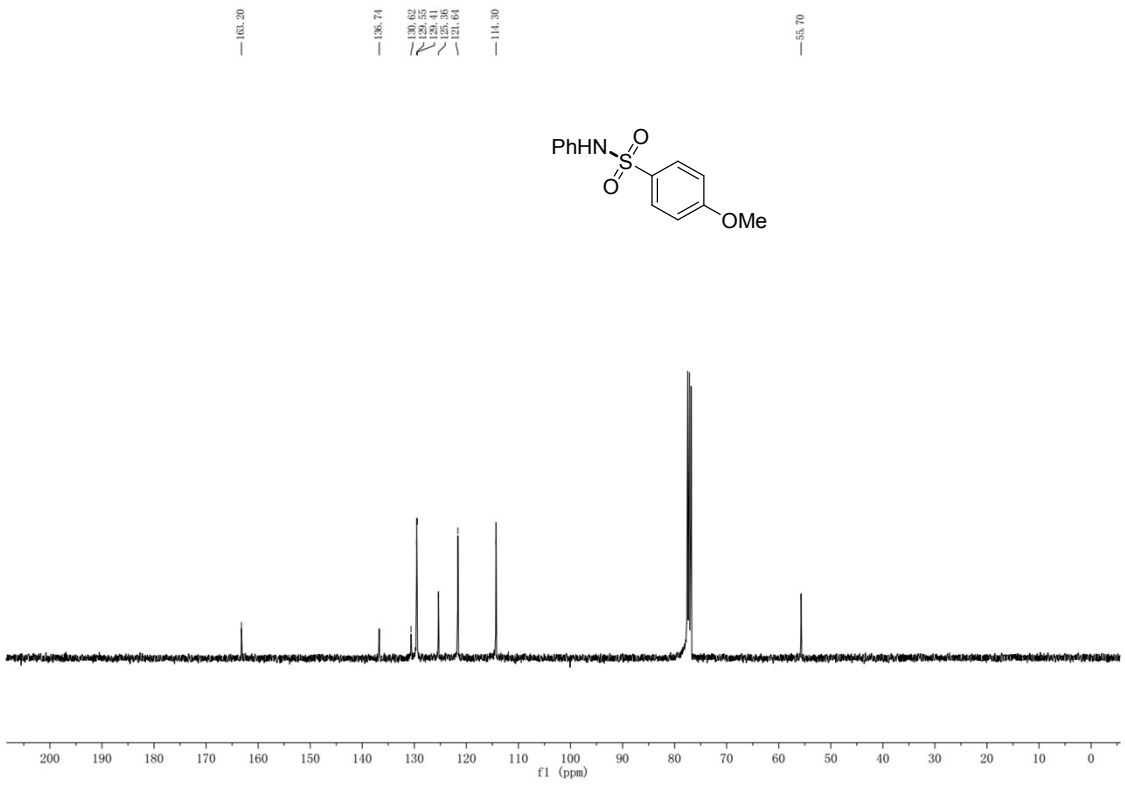
*N-phenylbenzenesulfonamide (**3ab**)*



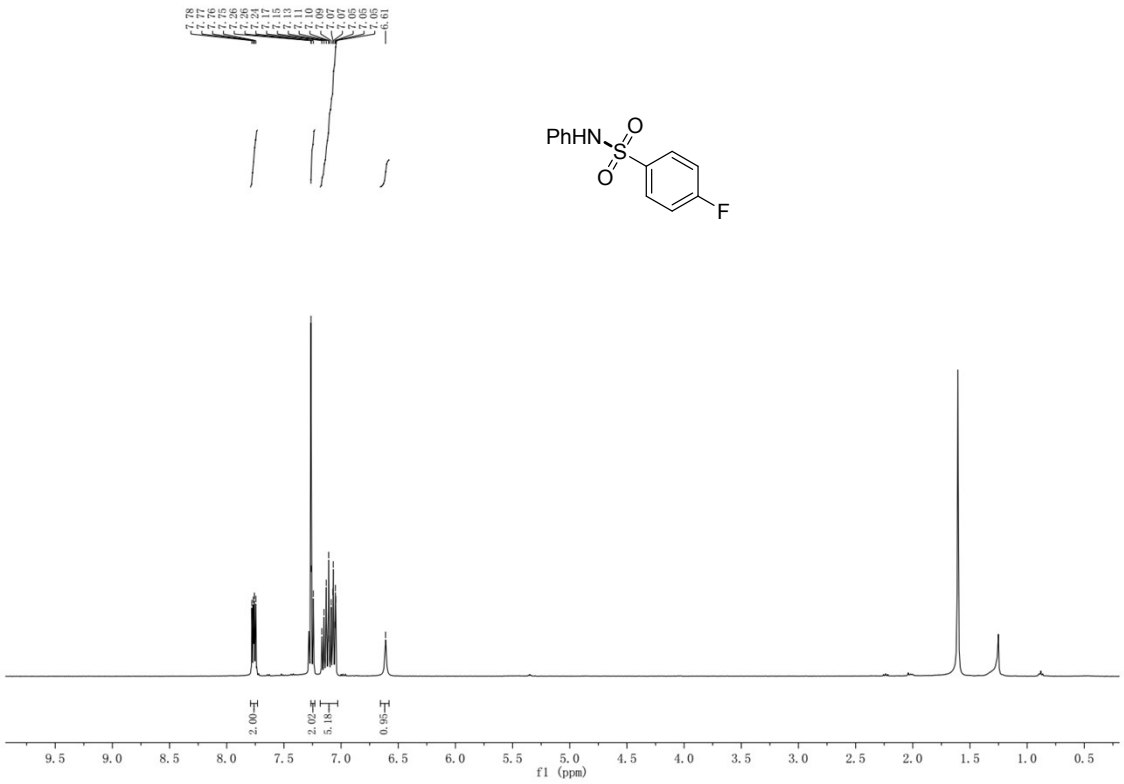


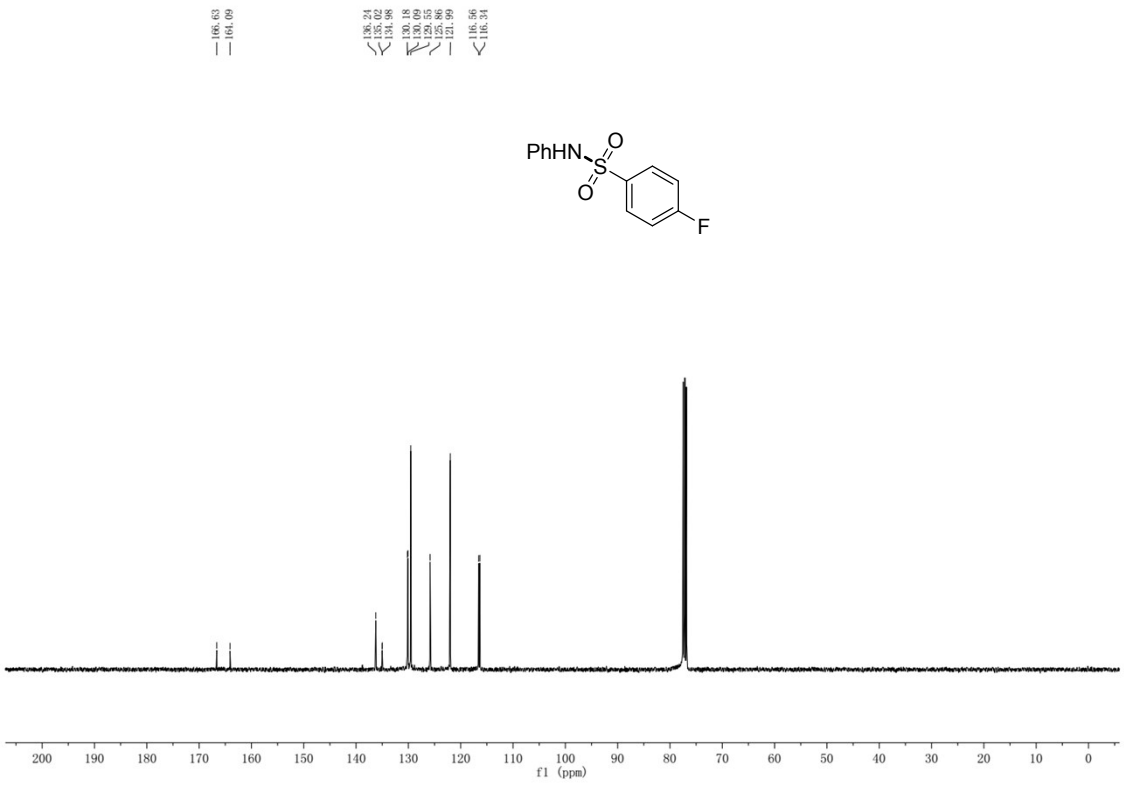
*4-methoxy-N-phenylbenzenesulfonamide (**3ac**)*



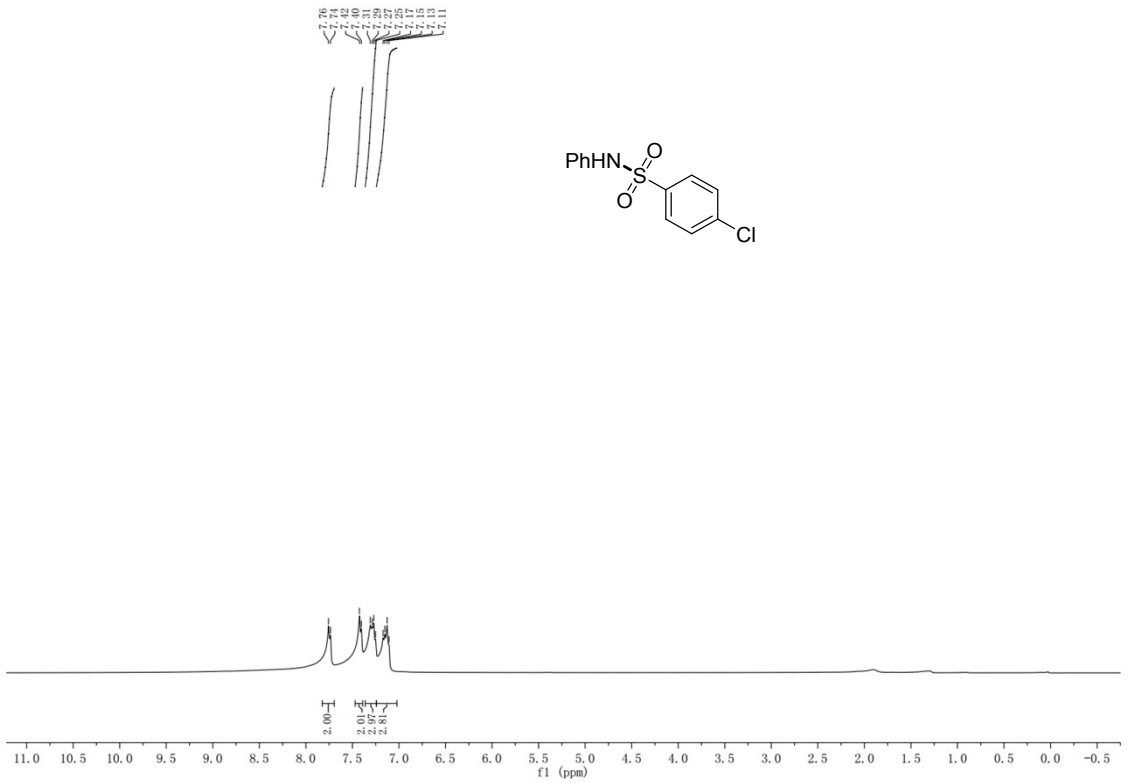


*4-fluoro-N-phenylbenzenesulfonamide (**3ad**)*

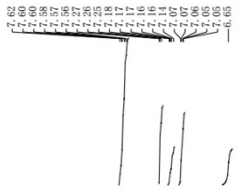


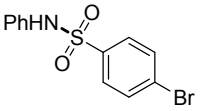


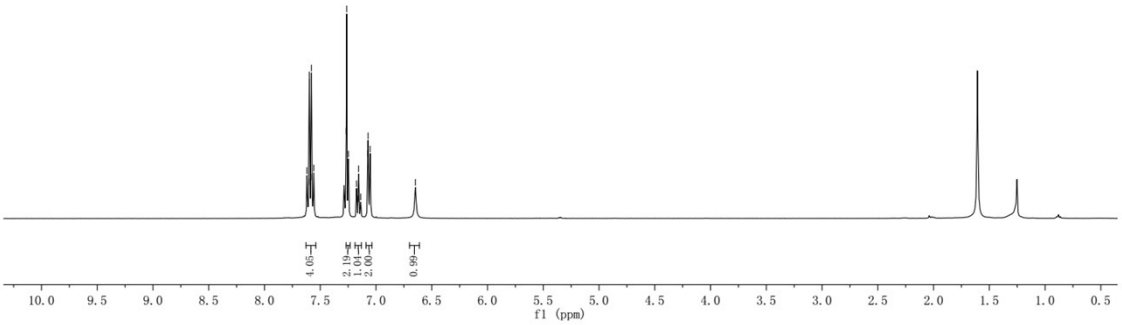
*4-chloro-N-phenylbenzenesulfonamide (**3ae**)*

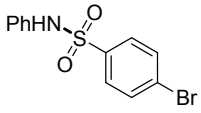


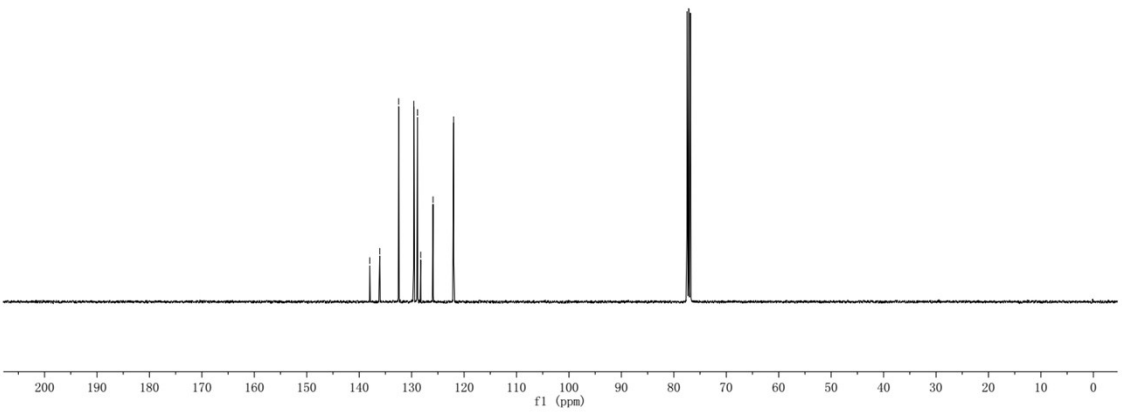
*4-bromo-N-phenylbenzenesulfonamide (**3af**)*



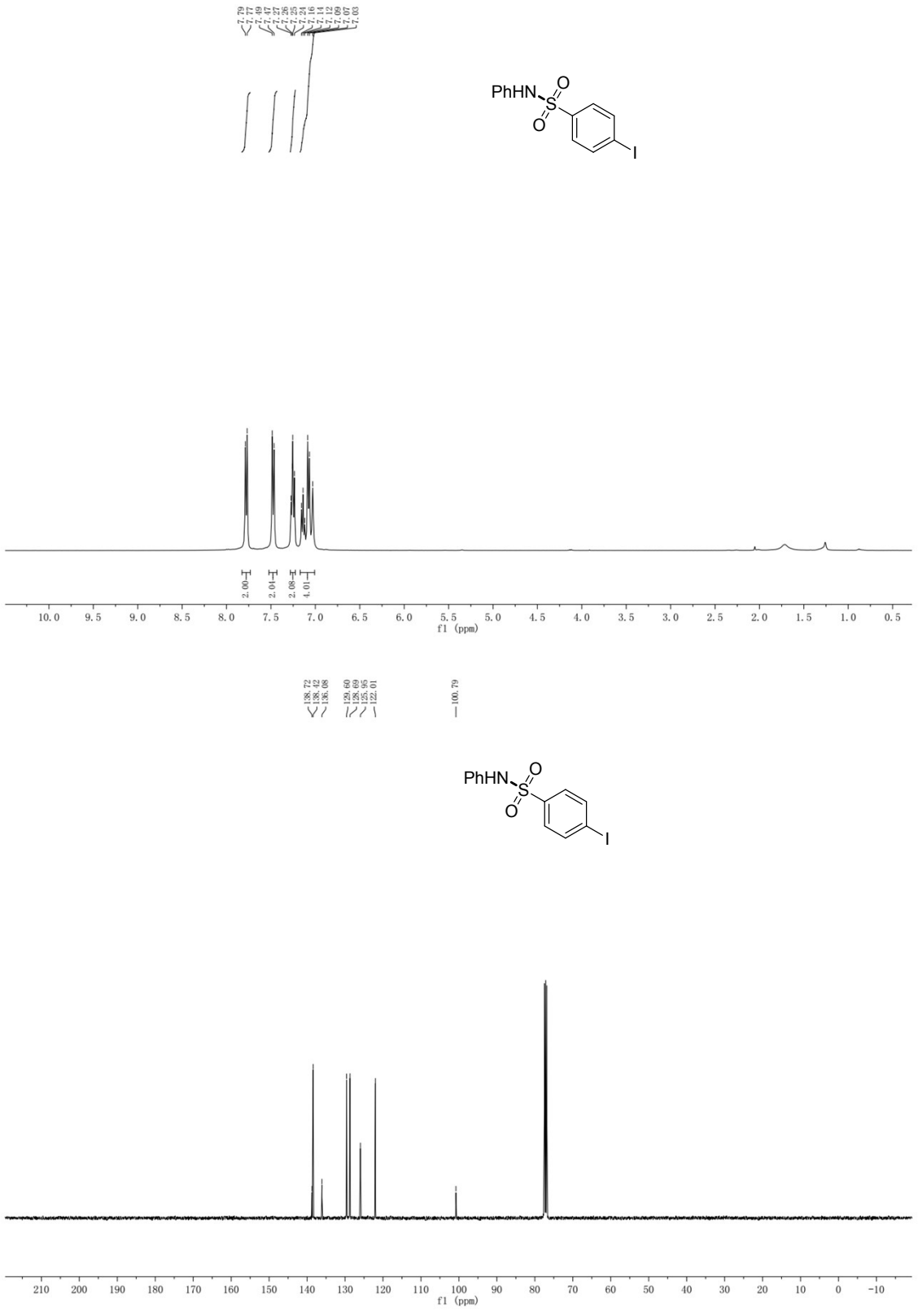




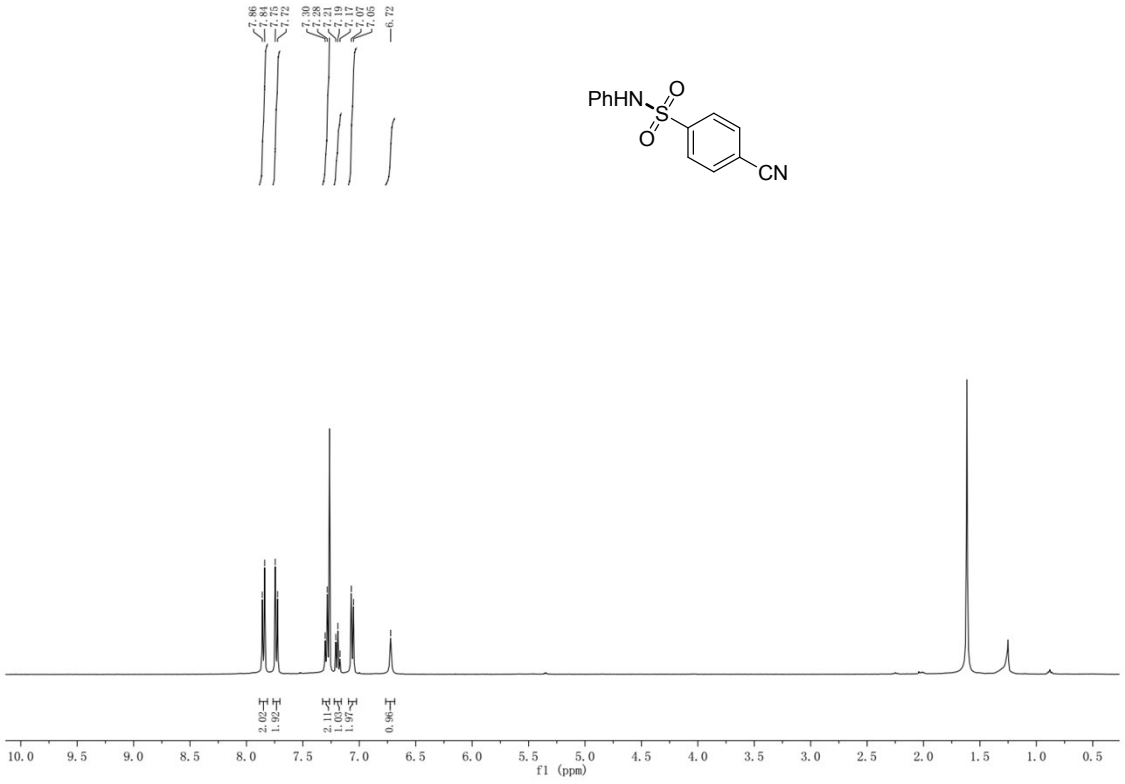


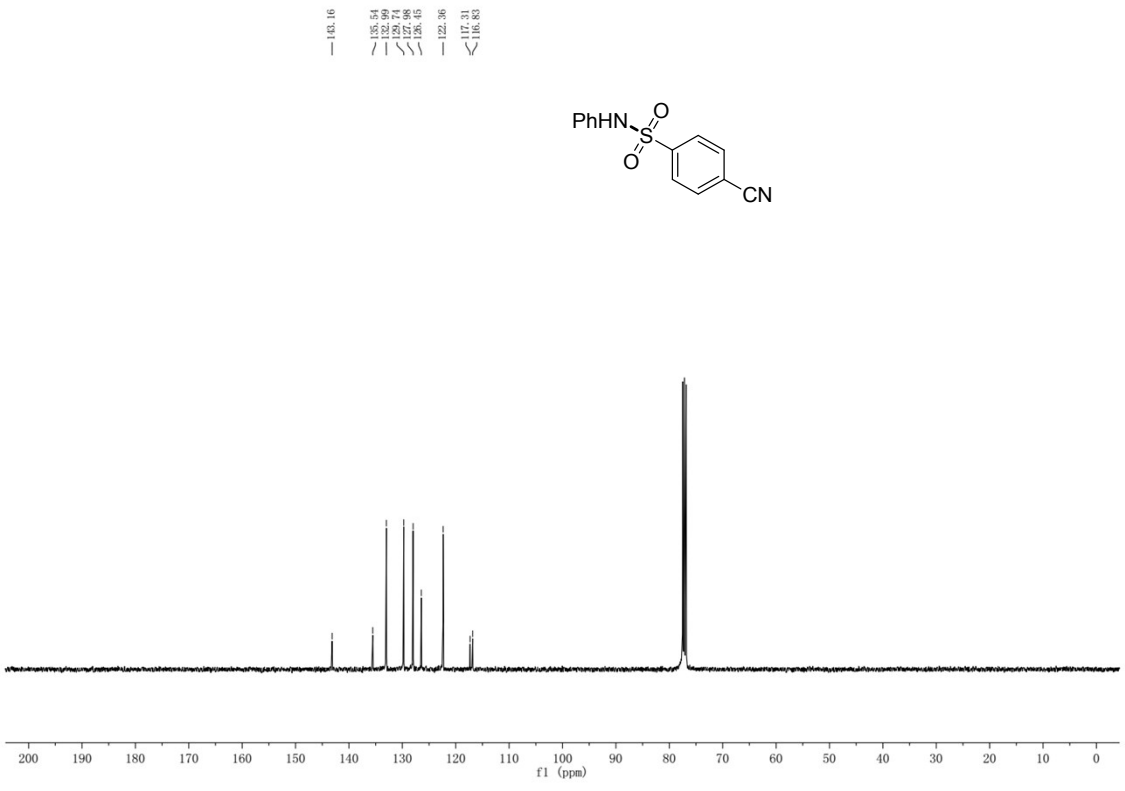


*4-iodo-N-phenylbenzenesulfonamide (**3ag**)*

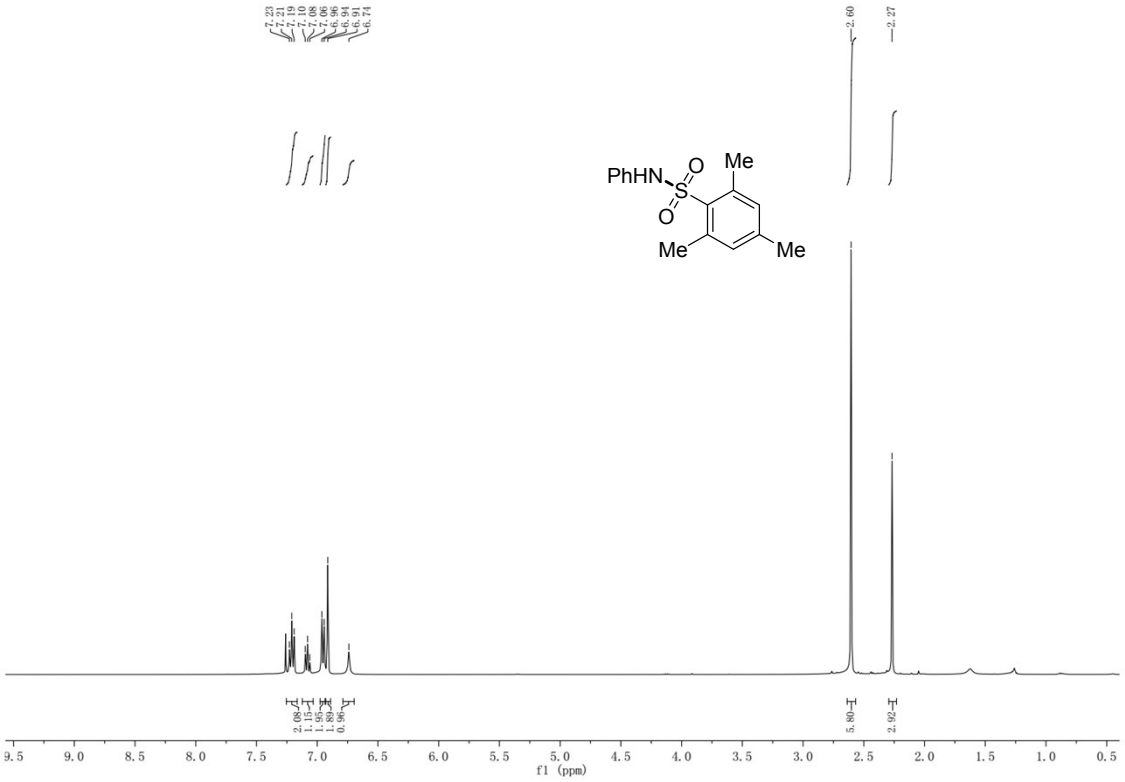


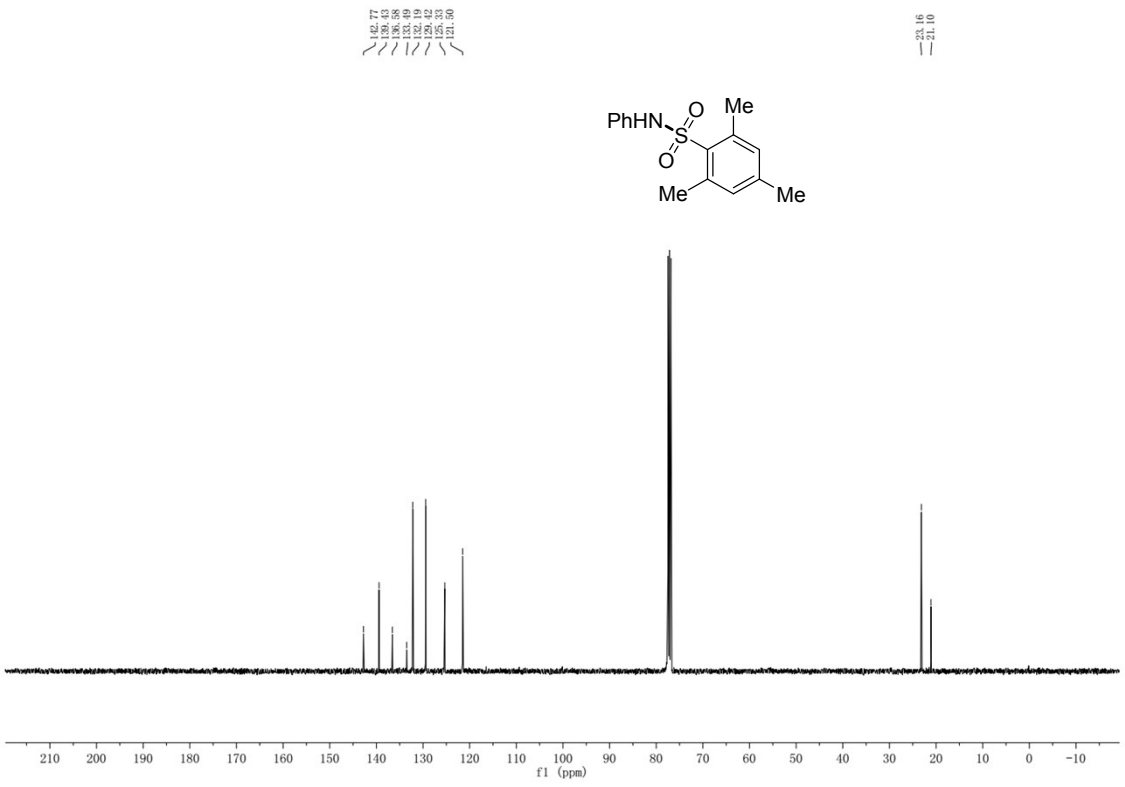
*4-cyano-N-phenylbenzenesulfonamide (**3ah**)*



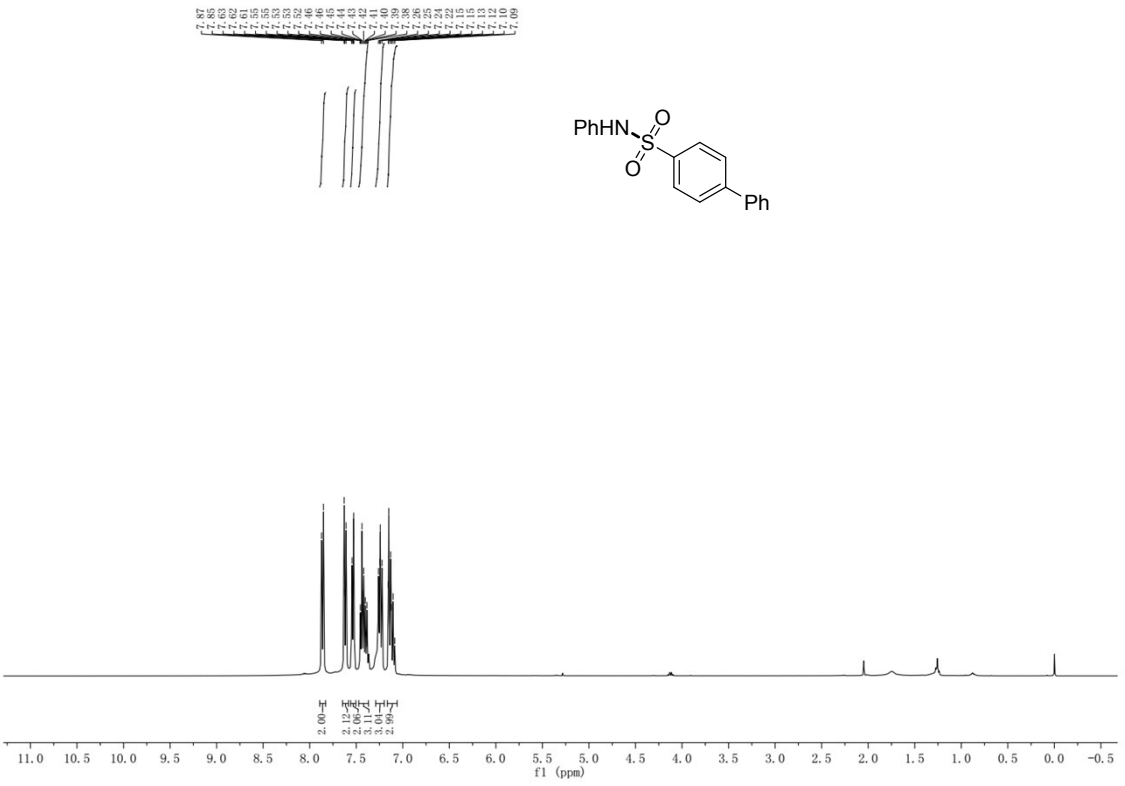


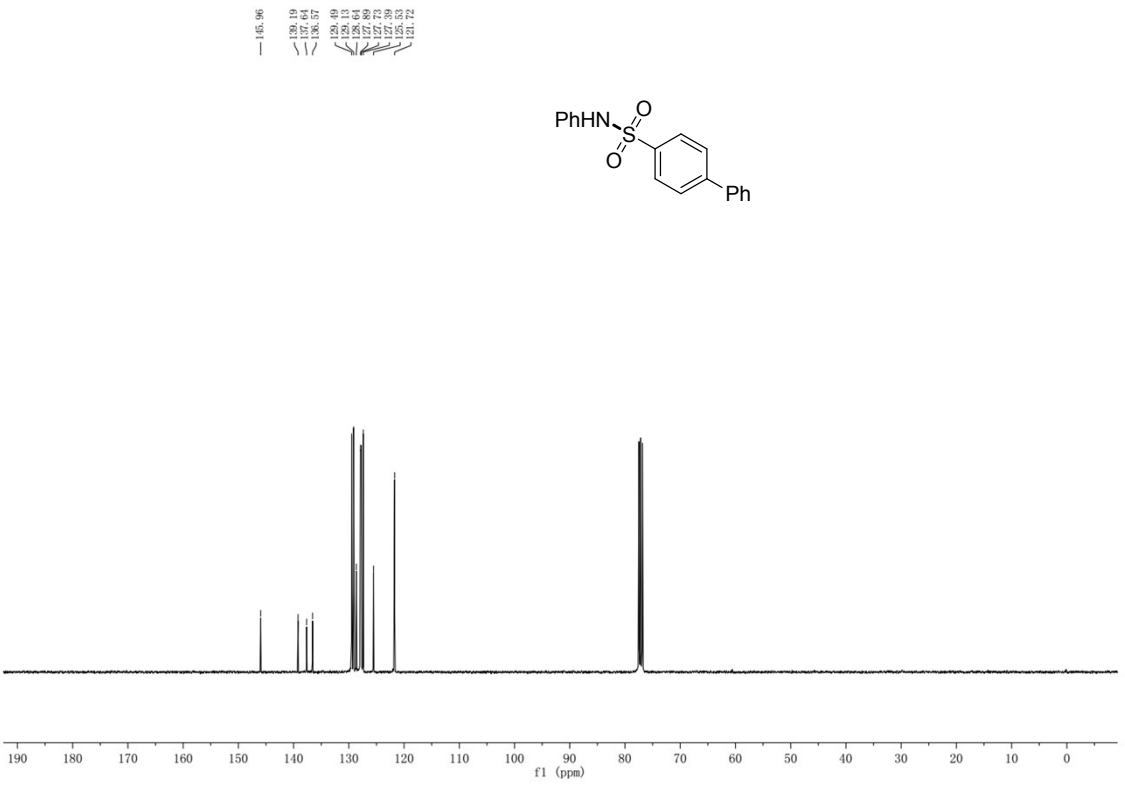
*2,4,6-trimethyl-N-phenylbenzenesulfonamide (**3ai**)*



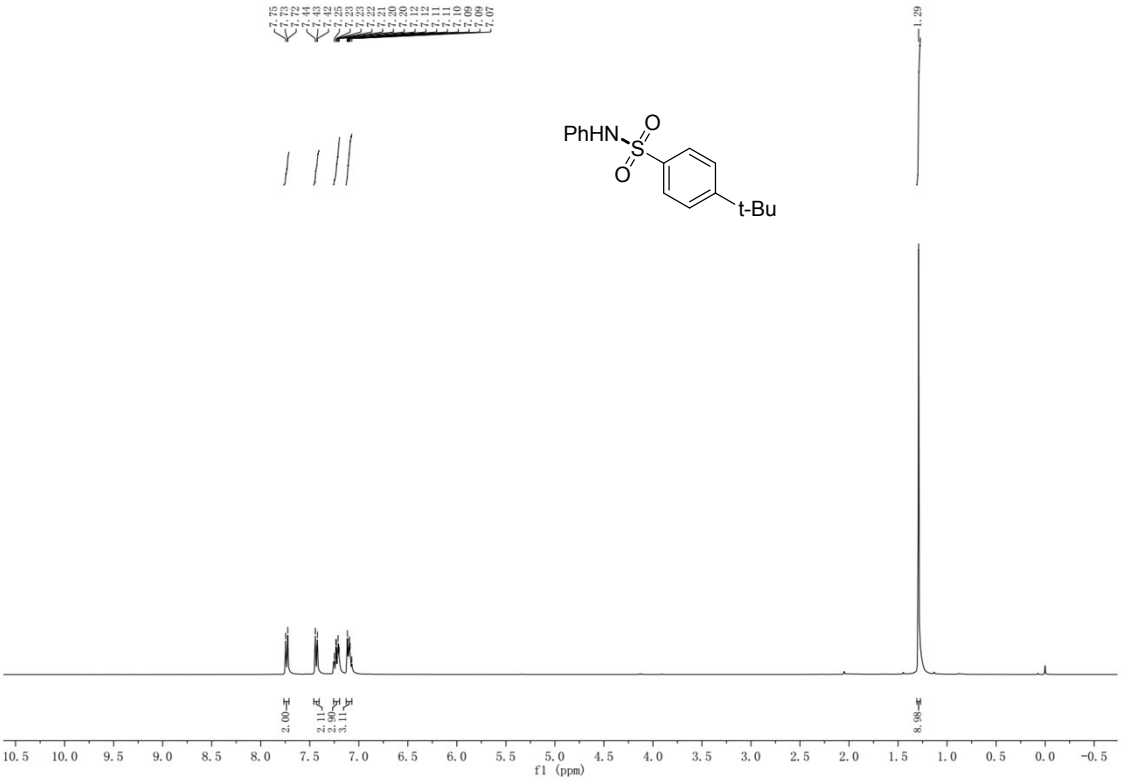


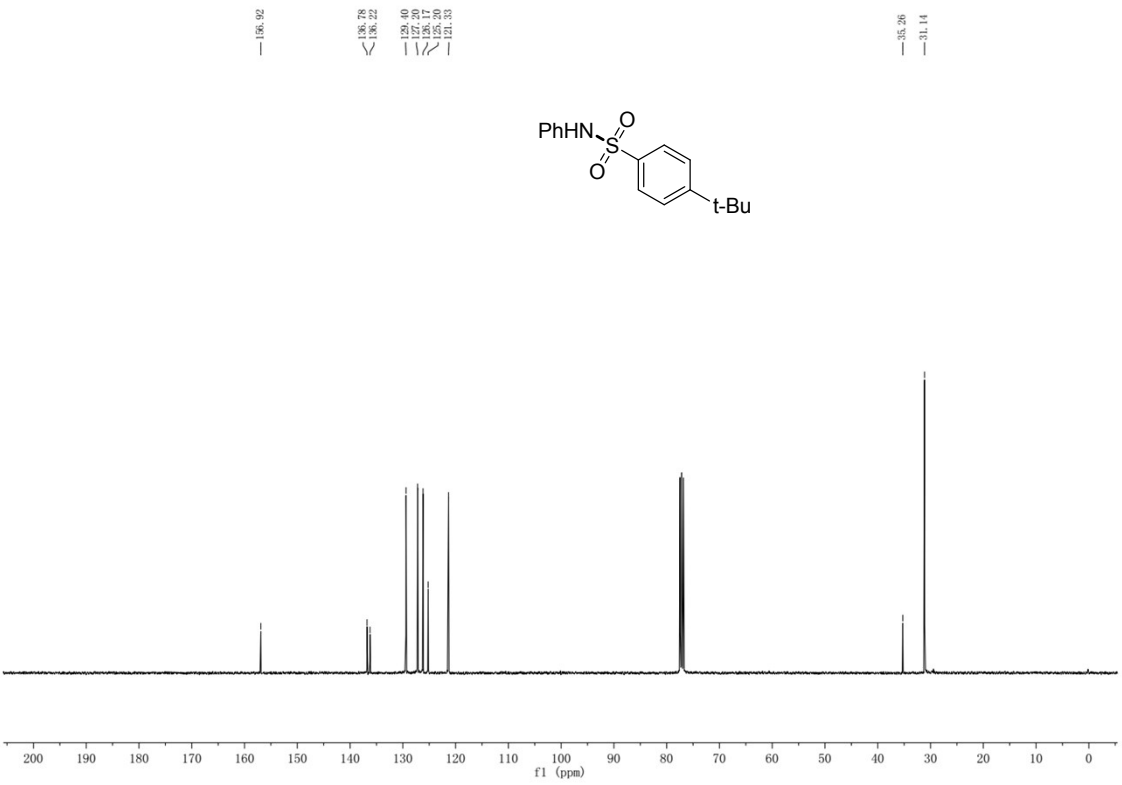
*N-phenyl-[1,1'-biphenyl]-4-sulfonamide (**3aj**)*



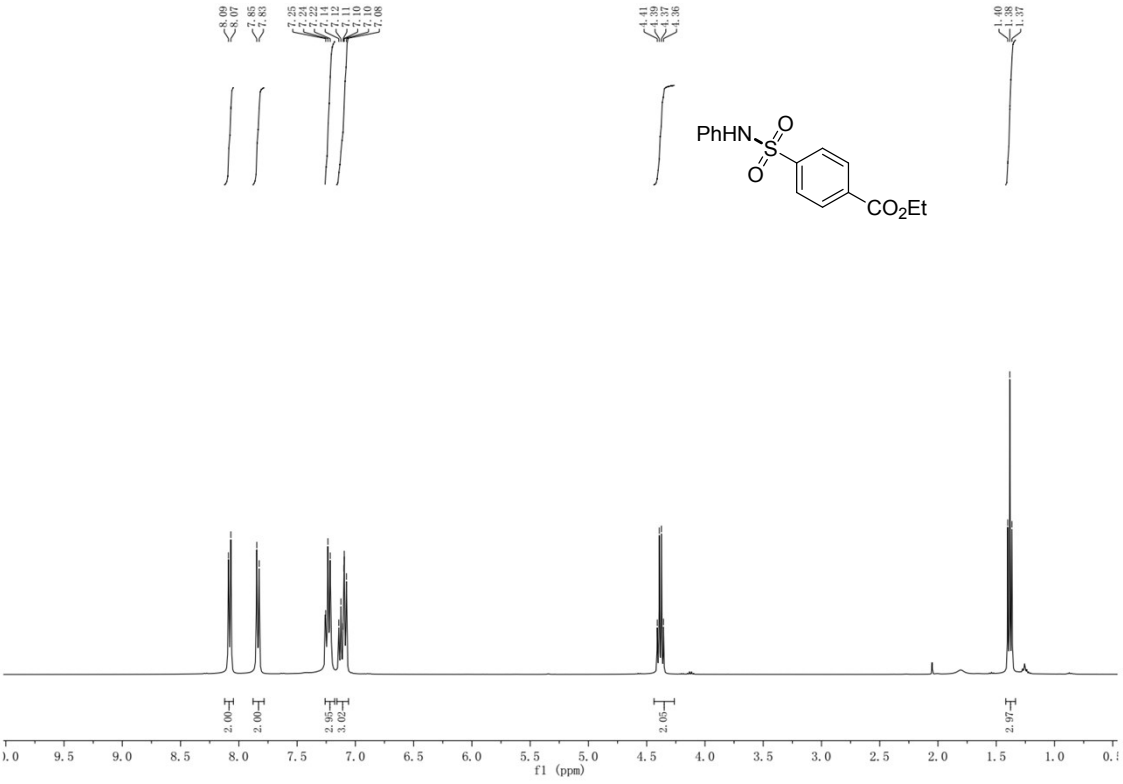


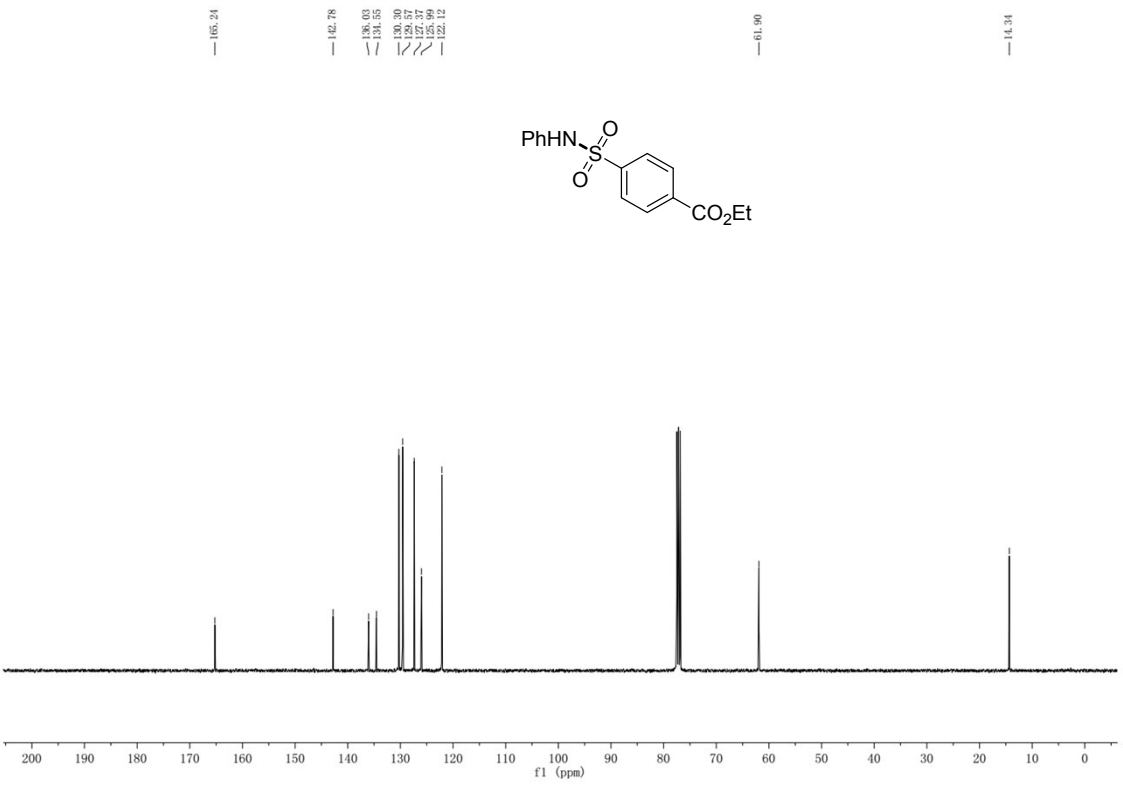
4-(tert-butyl)-N-phenylbenzenesulfonamide ***(3ak)***



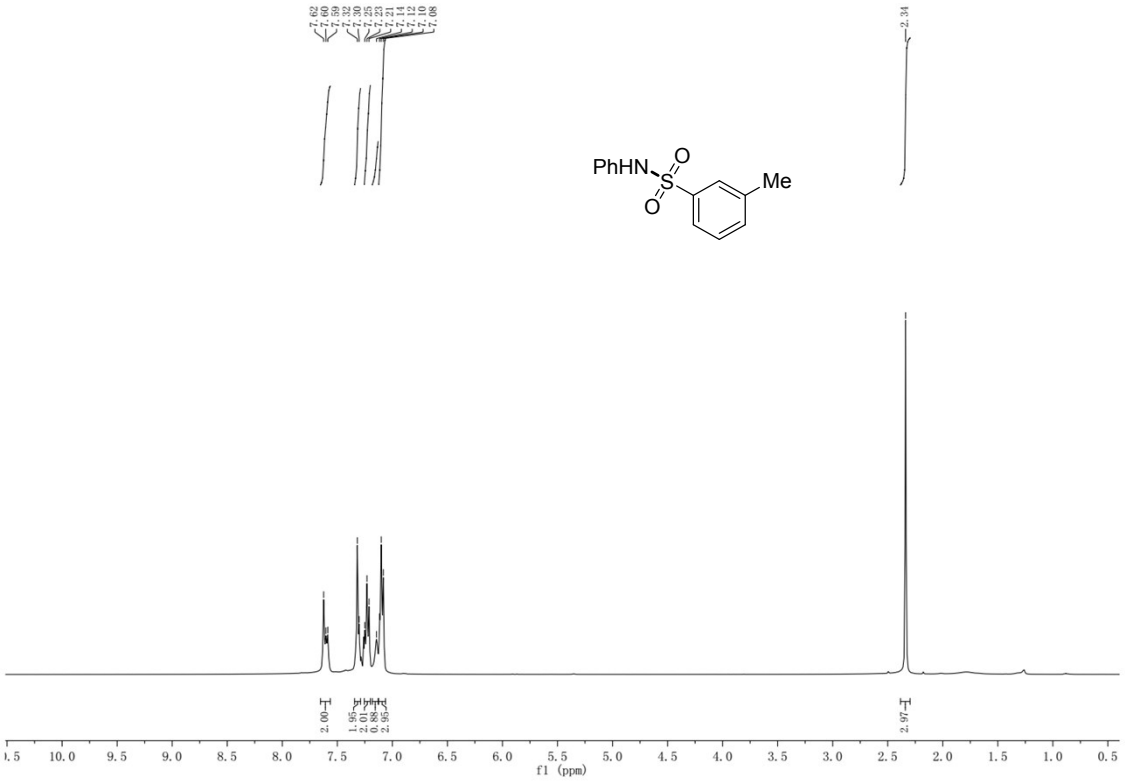


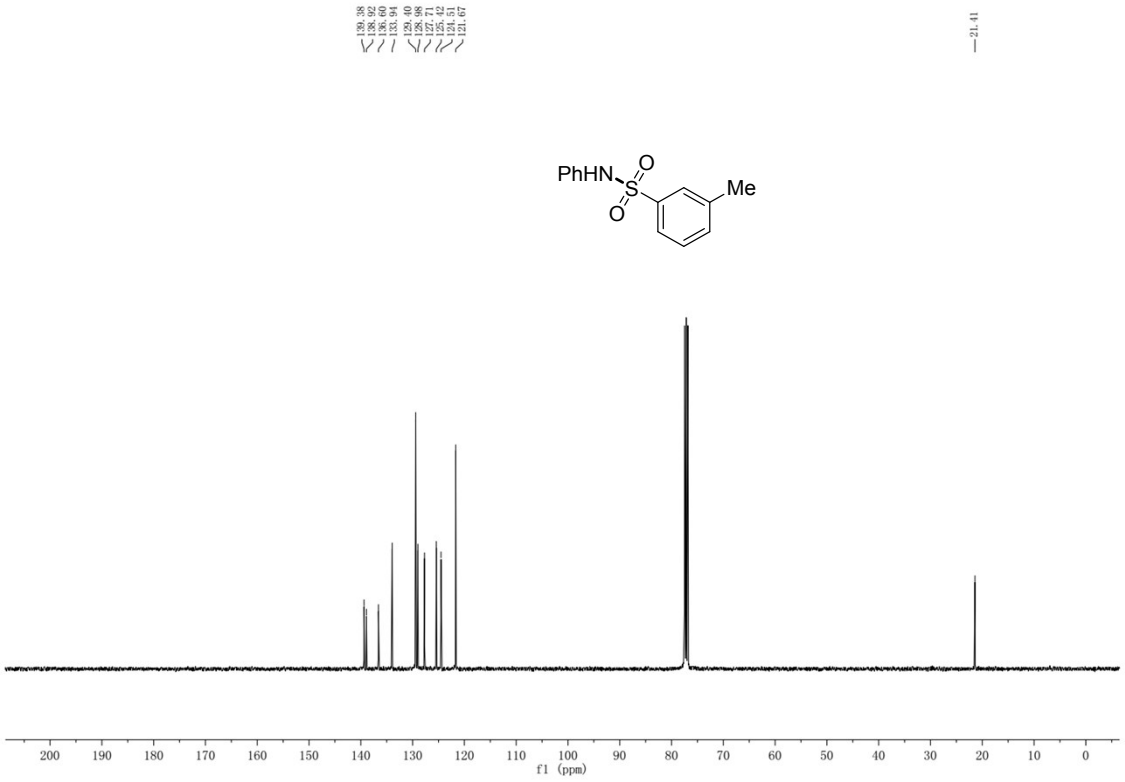
*Ethyl 4-(N-phenylsulfamoyl)benzoate (**3al**)*



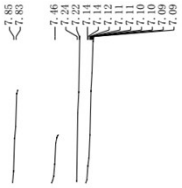


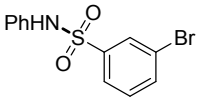
*3-methyl-N-phenylbenzenesulfonamide (**3am**)*

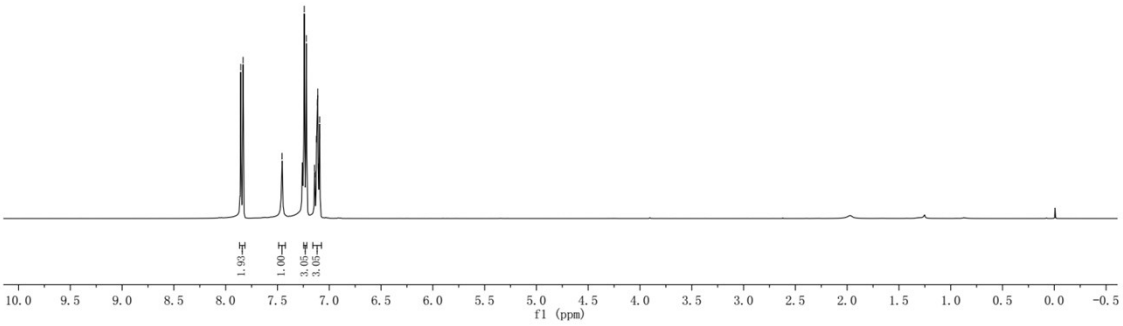


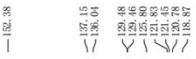


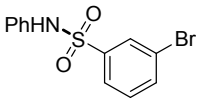
*3-bromo-N-phenylbenzenesulfonamide (**3an**)*

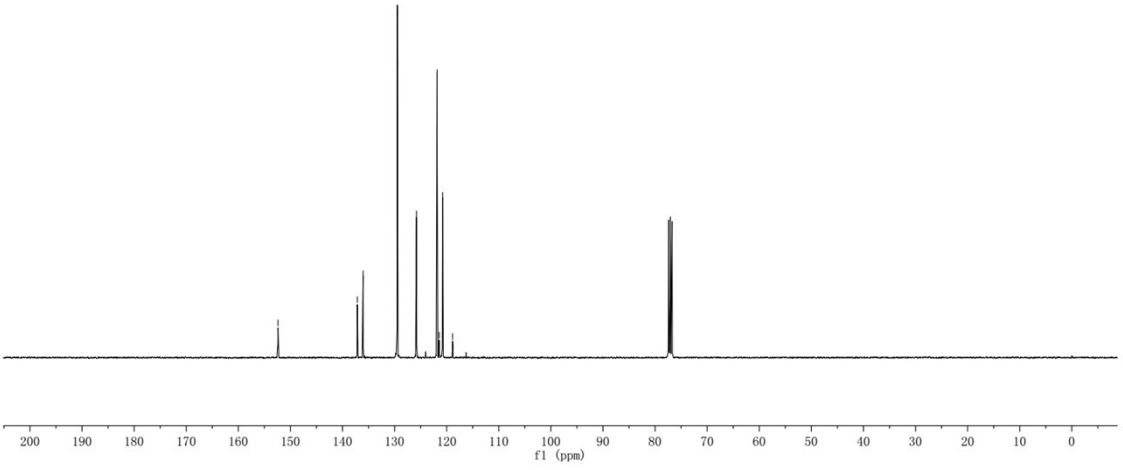




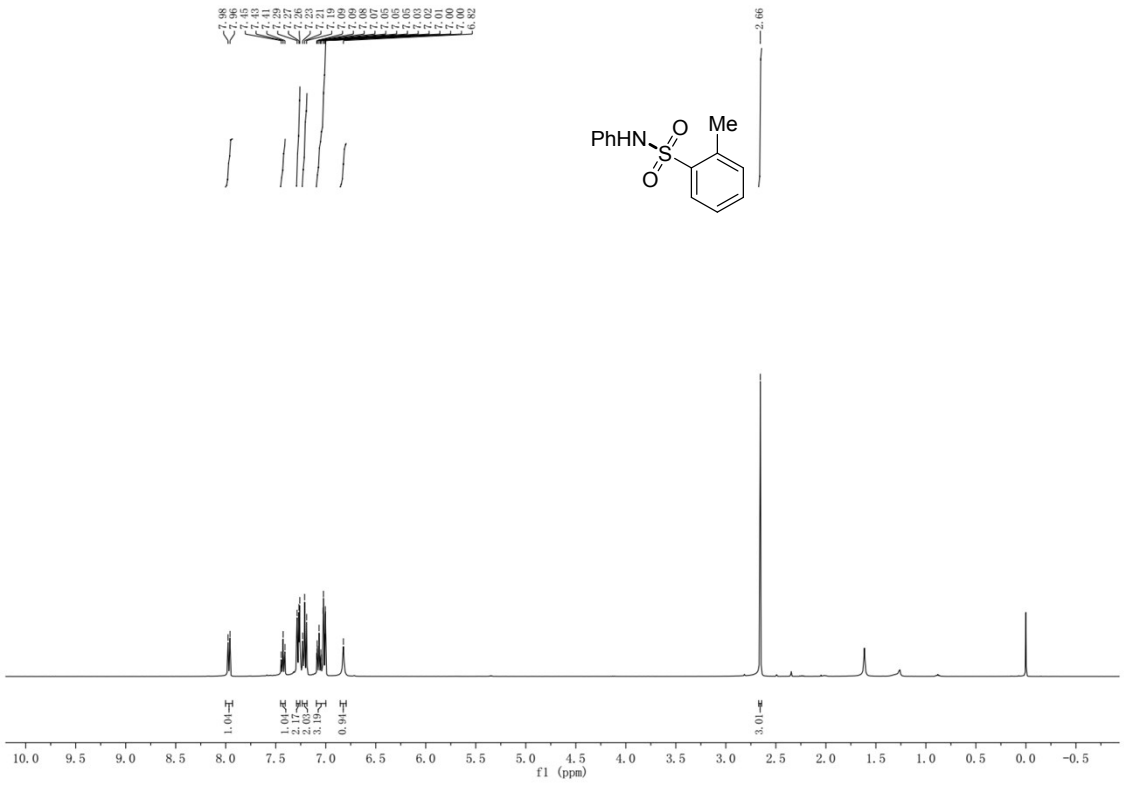


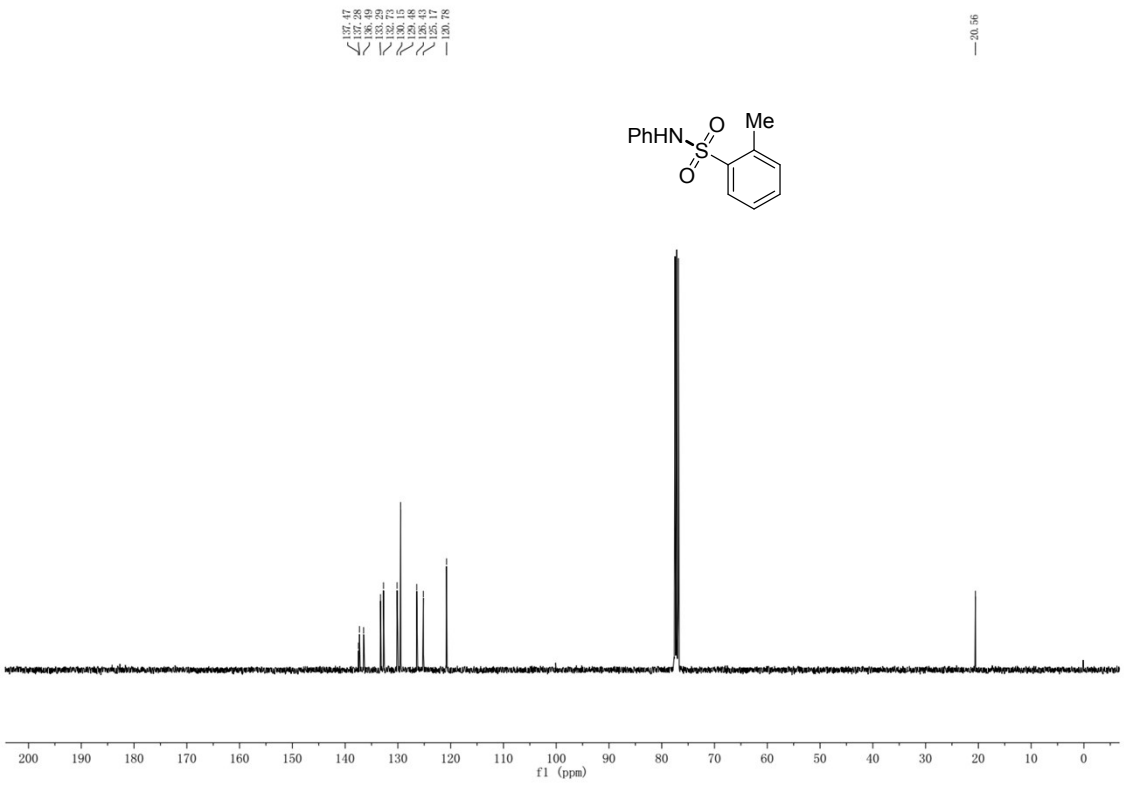




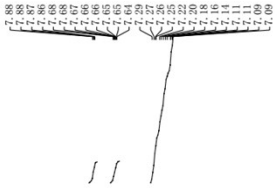


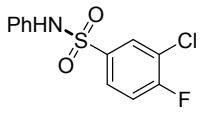
*2-methyl-N-phenylbenzenesulfonamide (**3ao**)*

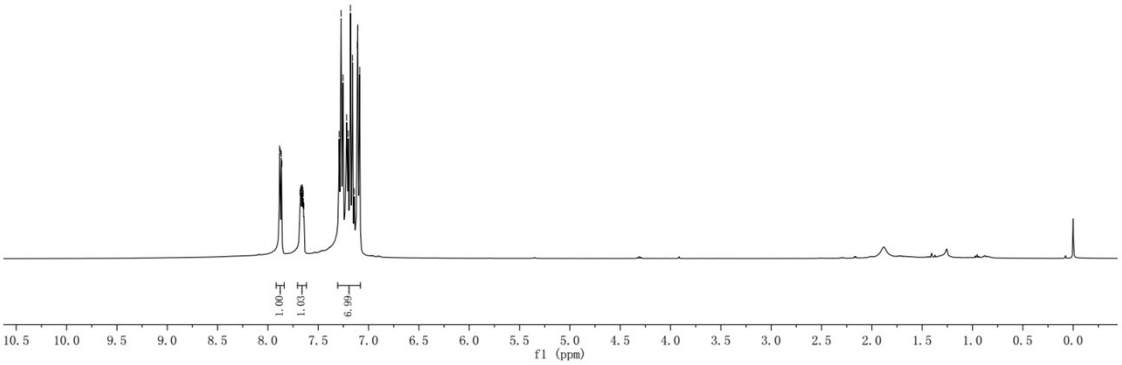


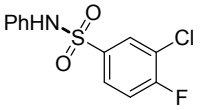


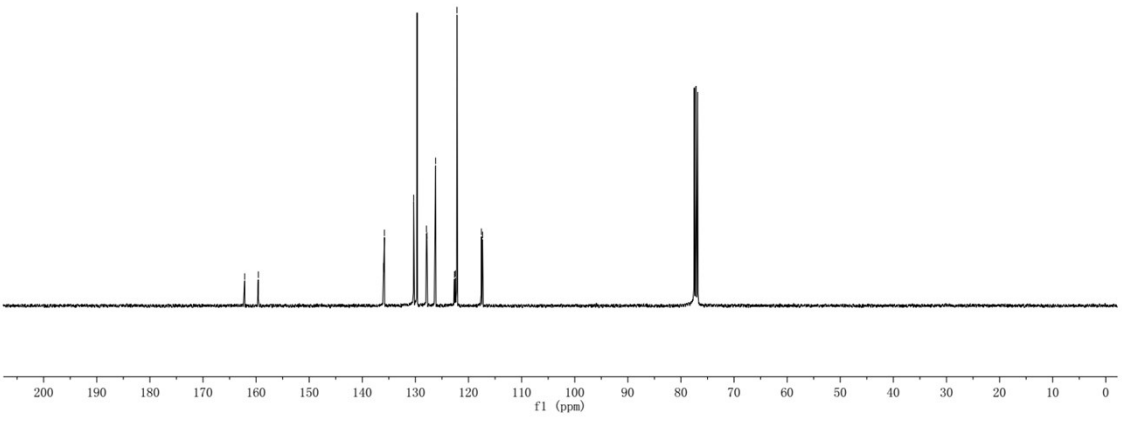
*3-chloro-4-fluoro-N-phenylbenzenesulfonamide (**3ap**)*



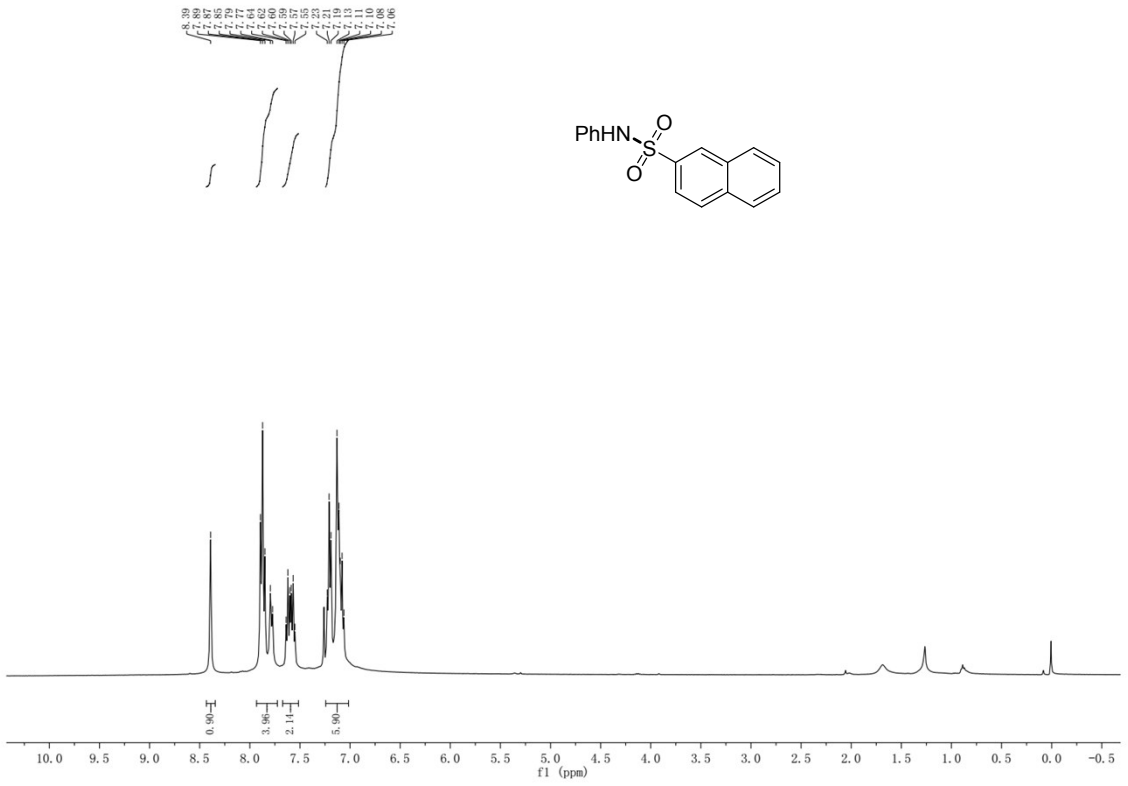


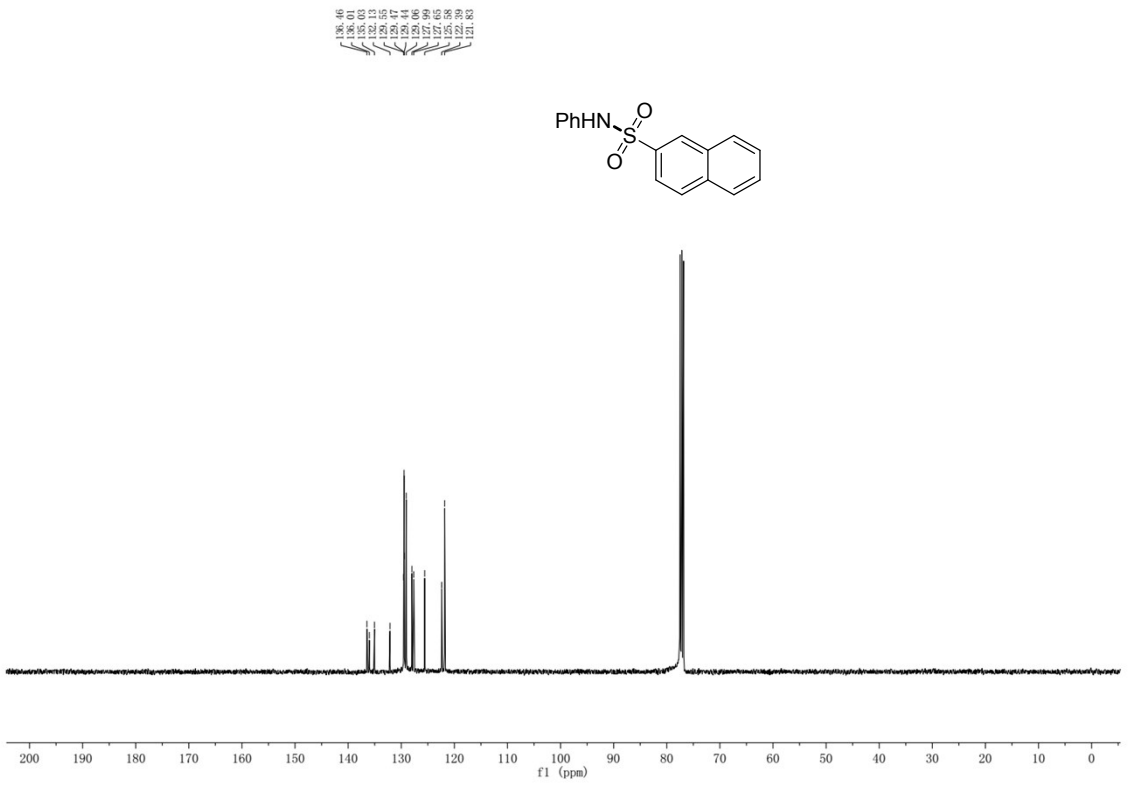




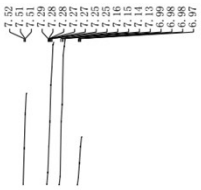


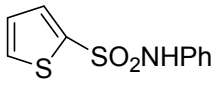
*N-phenylnaphthalene-2-sulfonamide (**3aq**)*

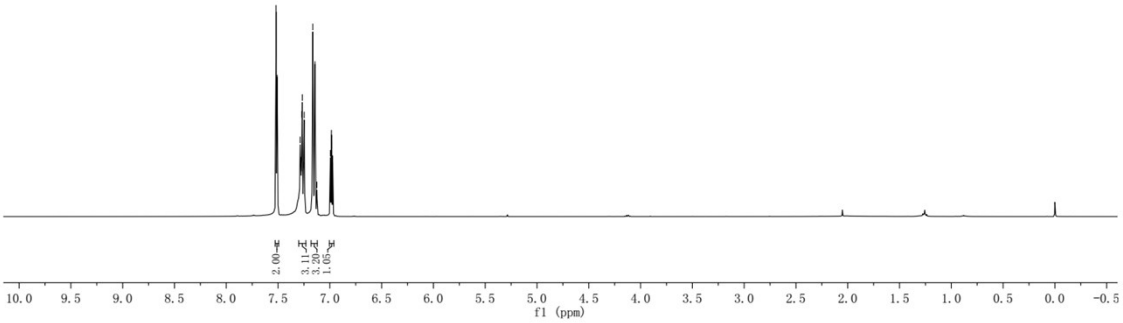


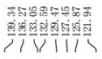


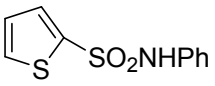
*N-phenylthiophene-2-sulfonamide (**3ar**)*

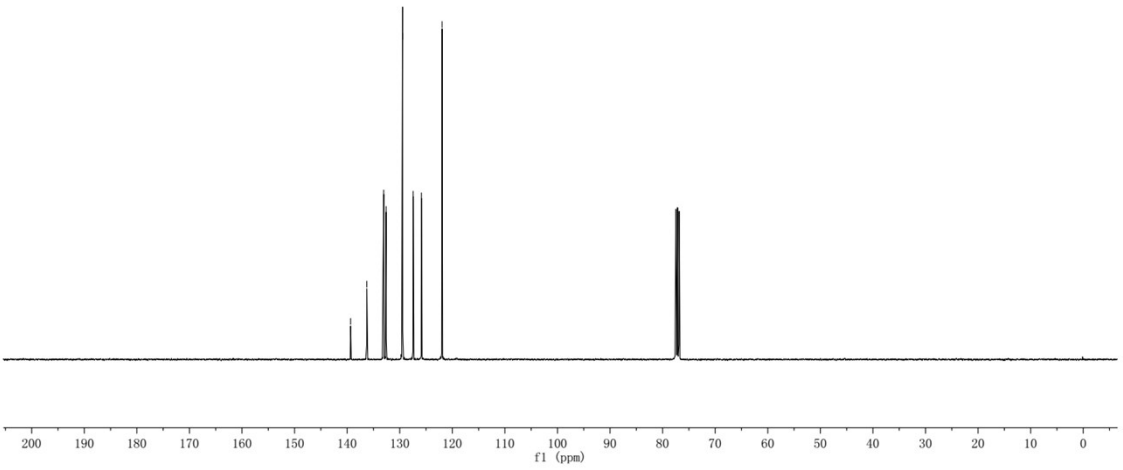




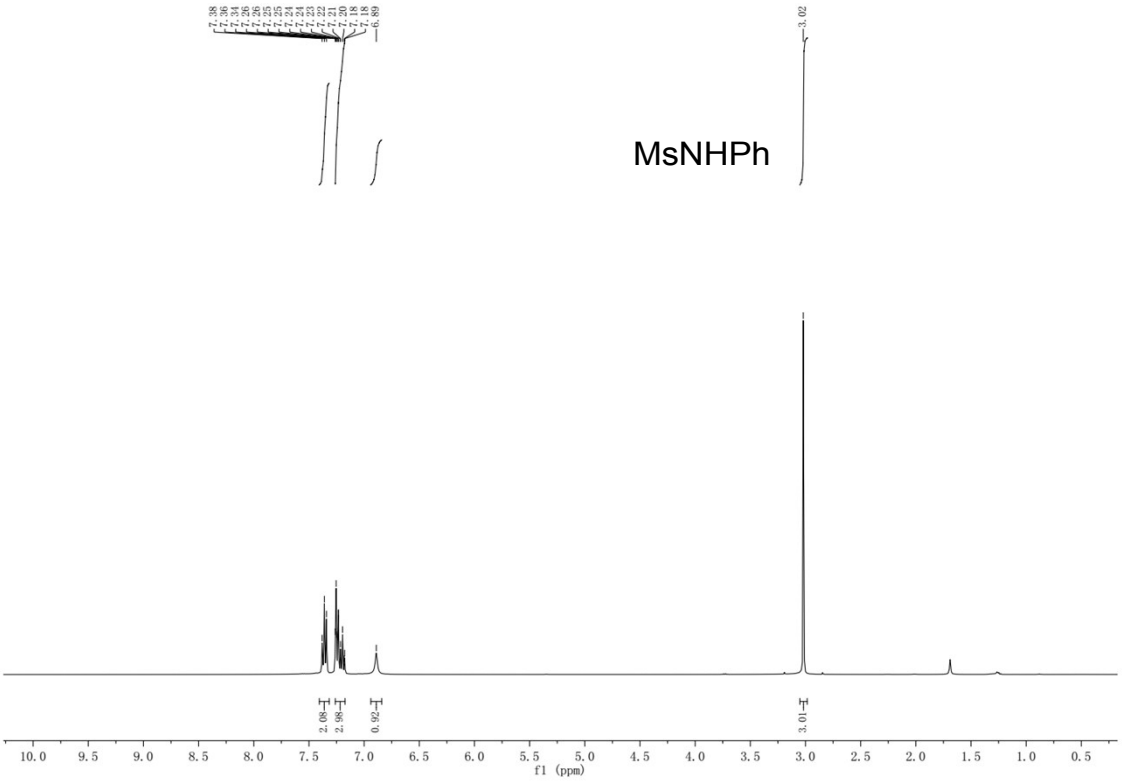


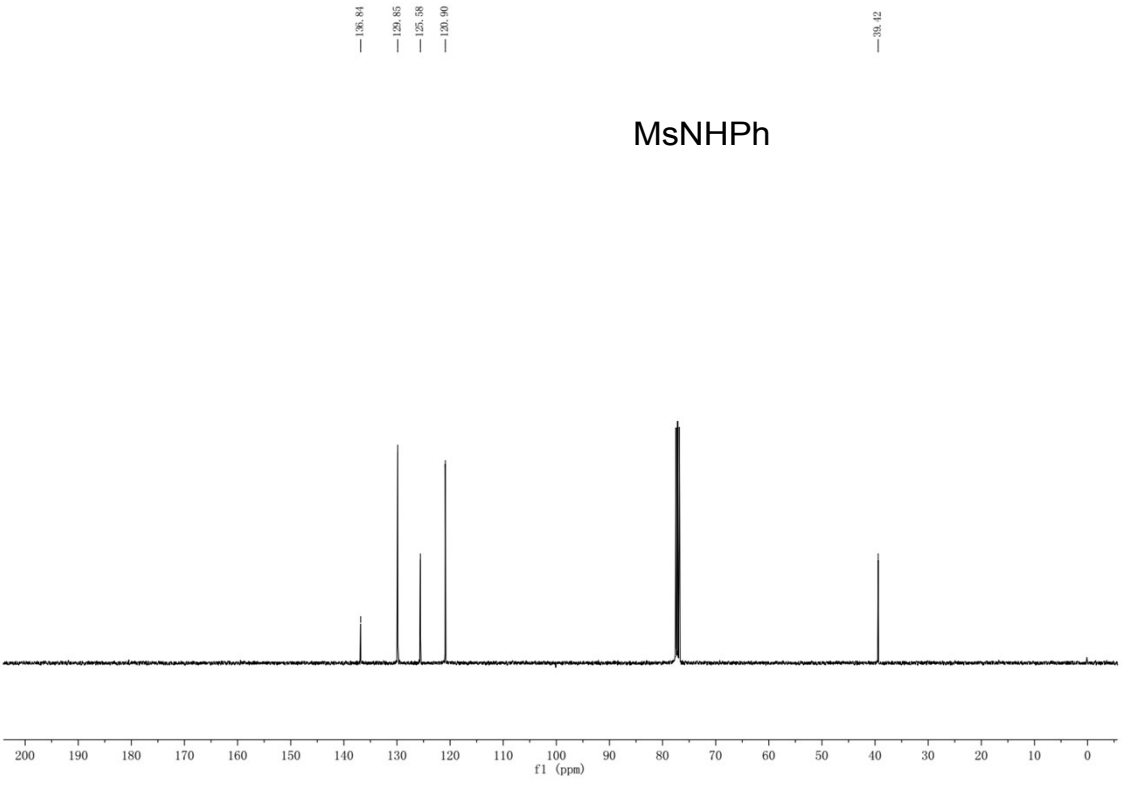




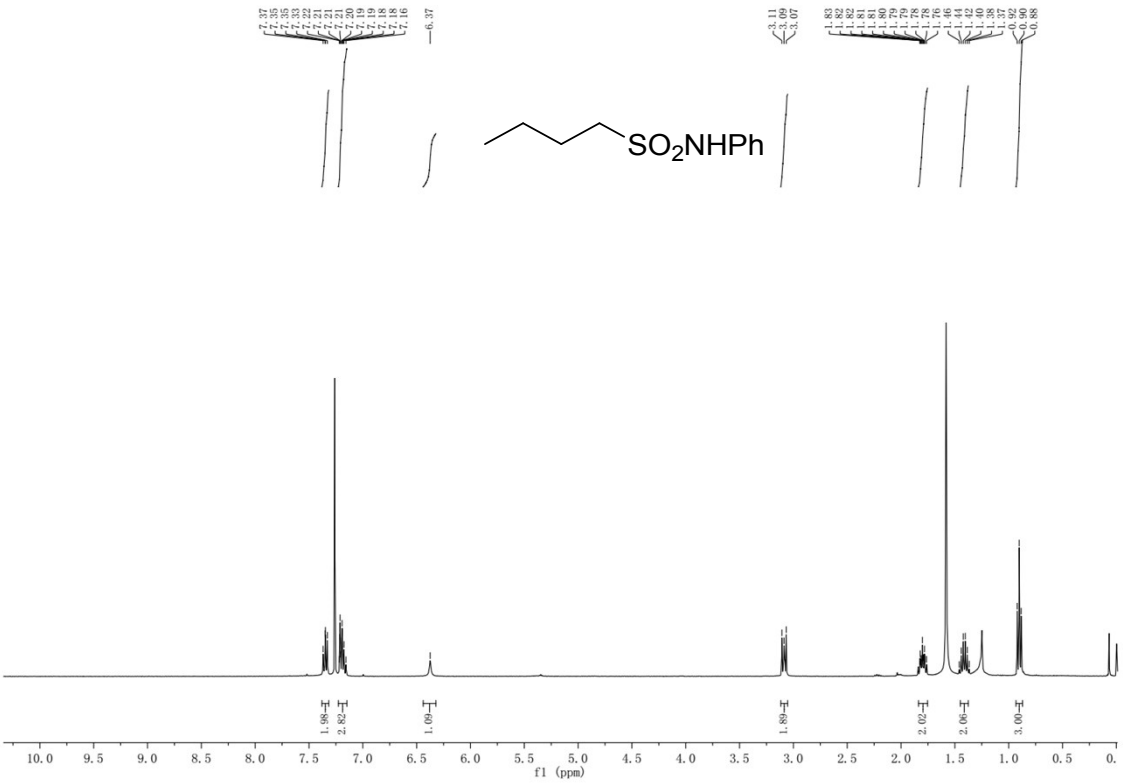


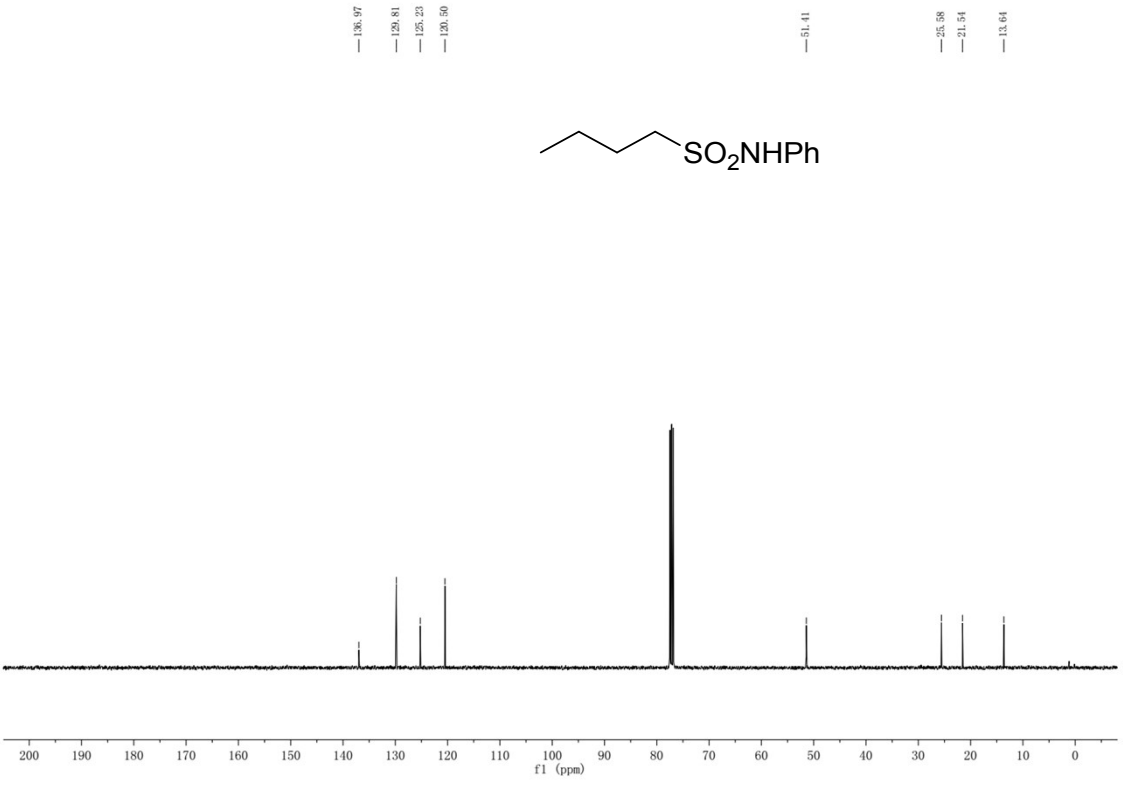
N-phenylmethanesulfonamide(3as)



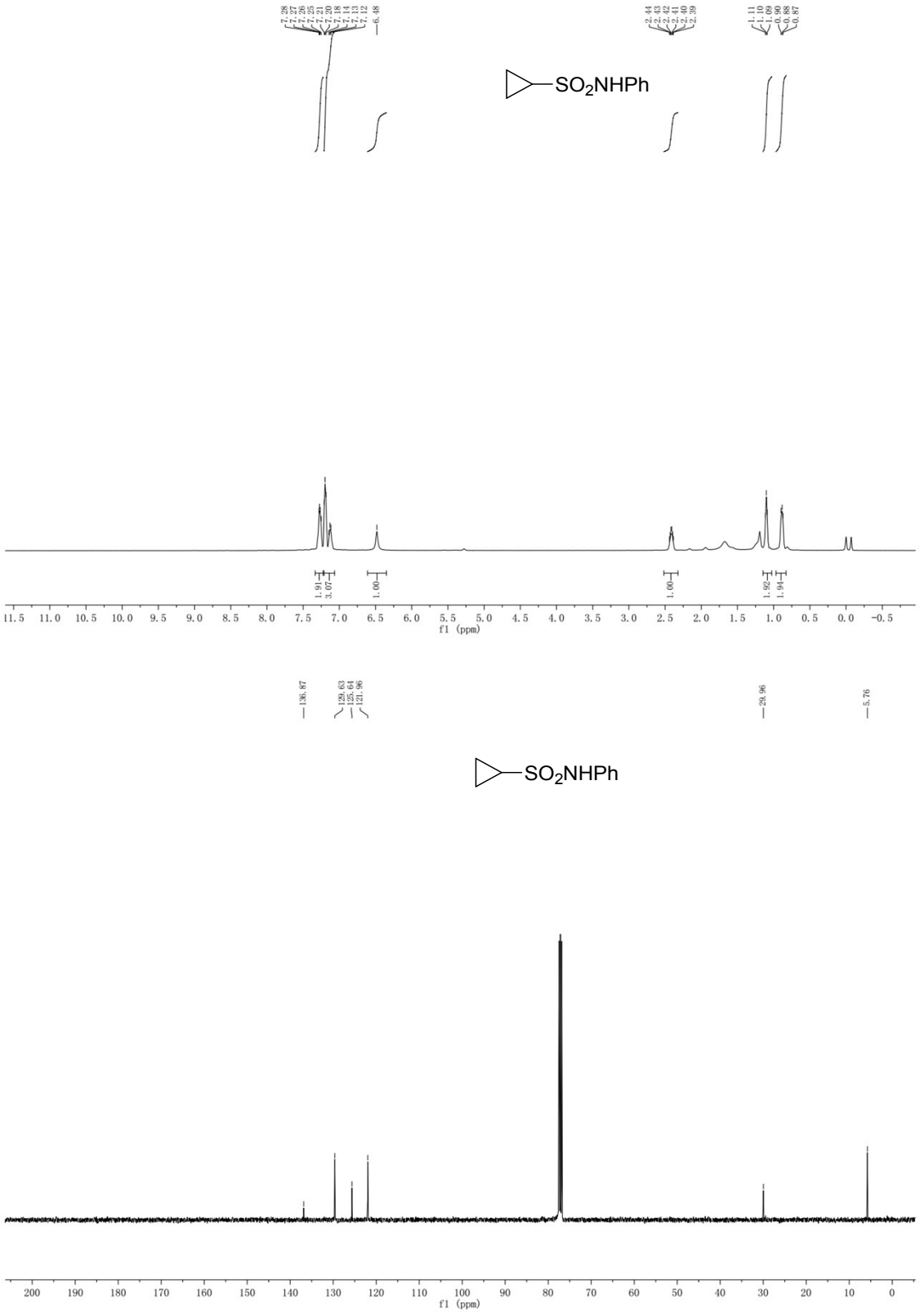


*N-phenylbutane-1-sulfonamide (**3at**)*

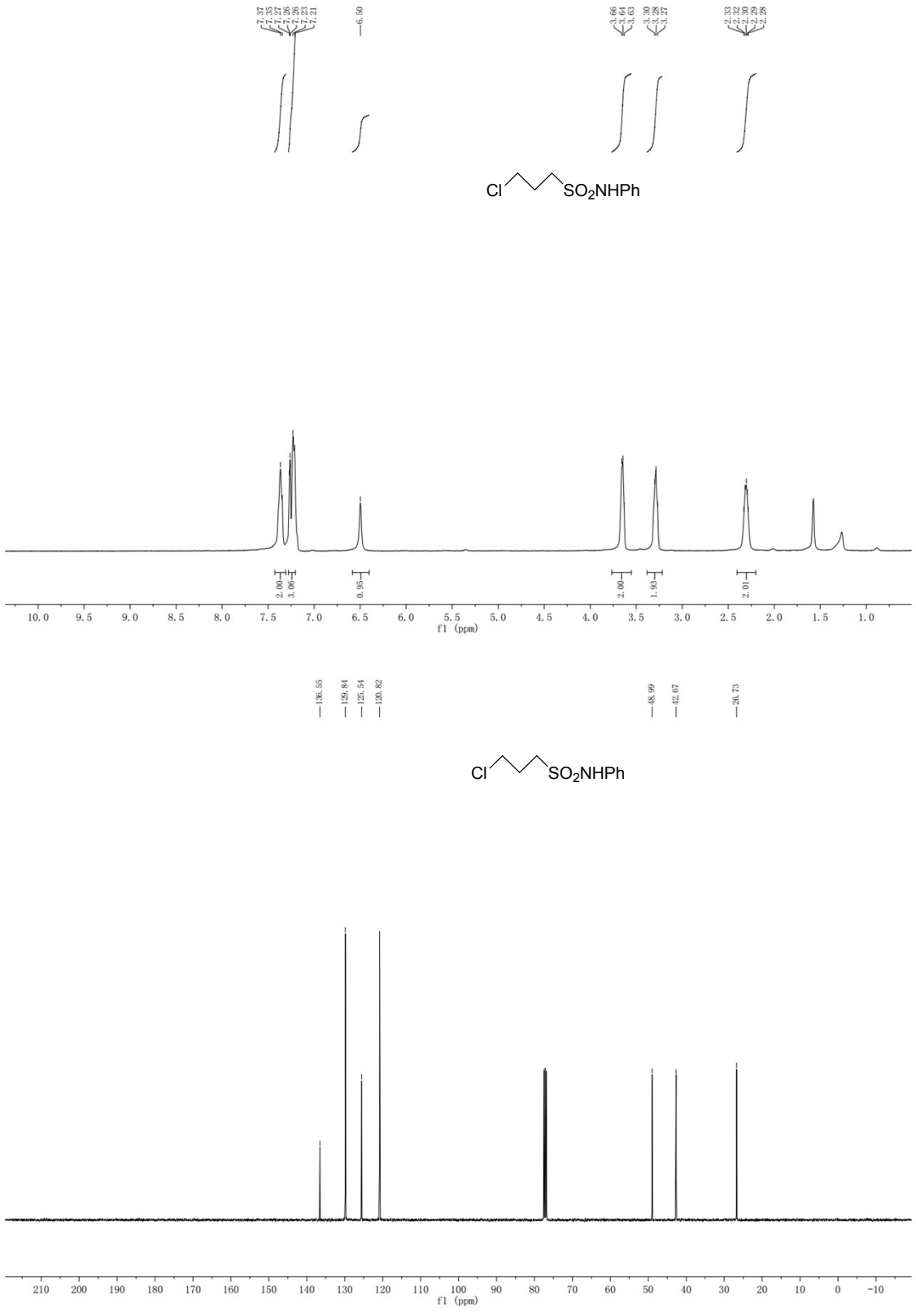




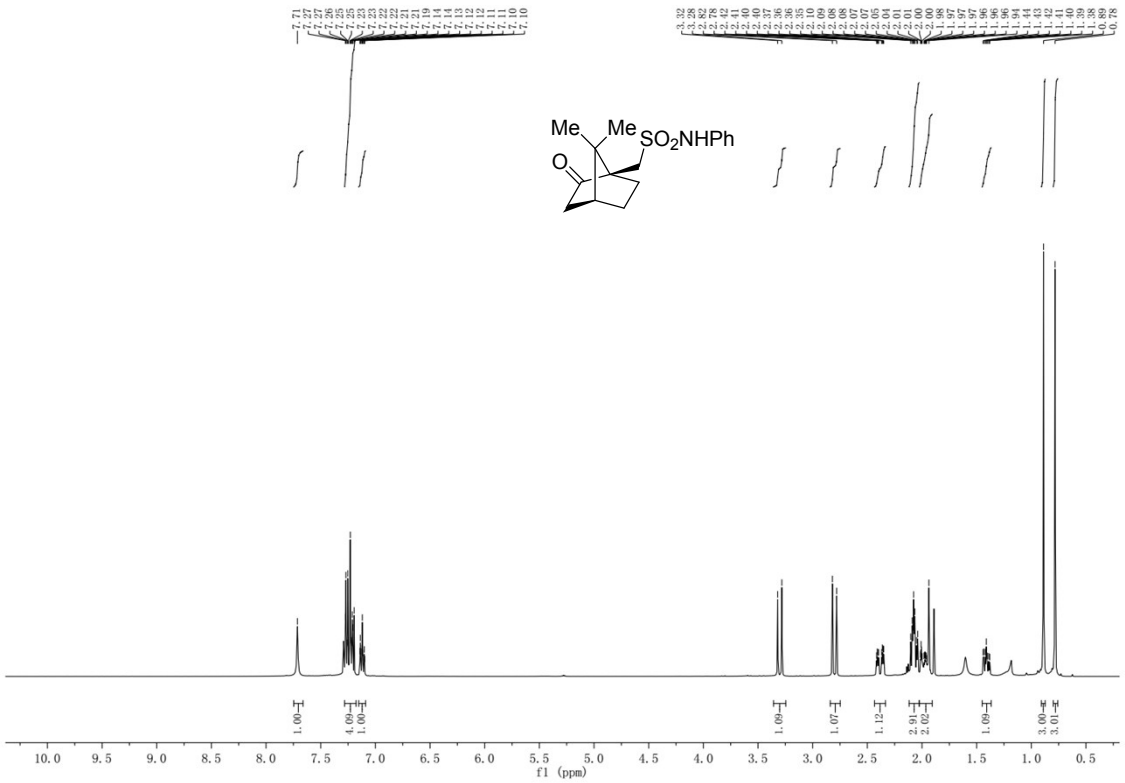
*N-phenylcyclopropanesulfonamide (**3au**)*

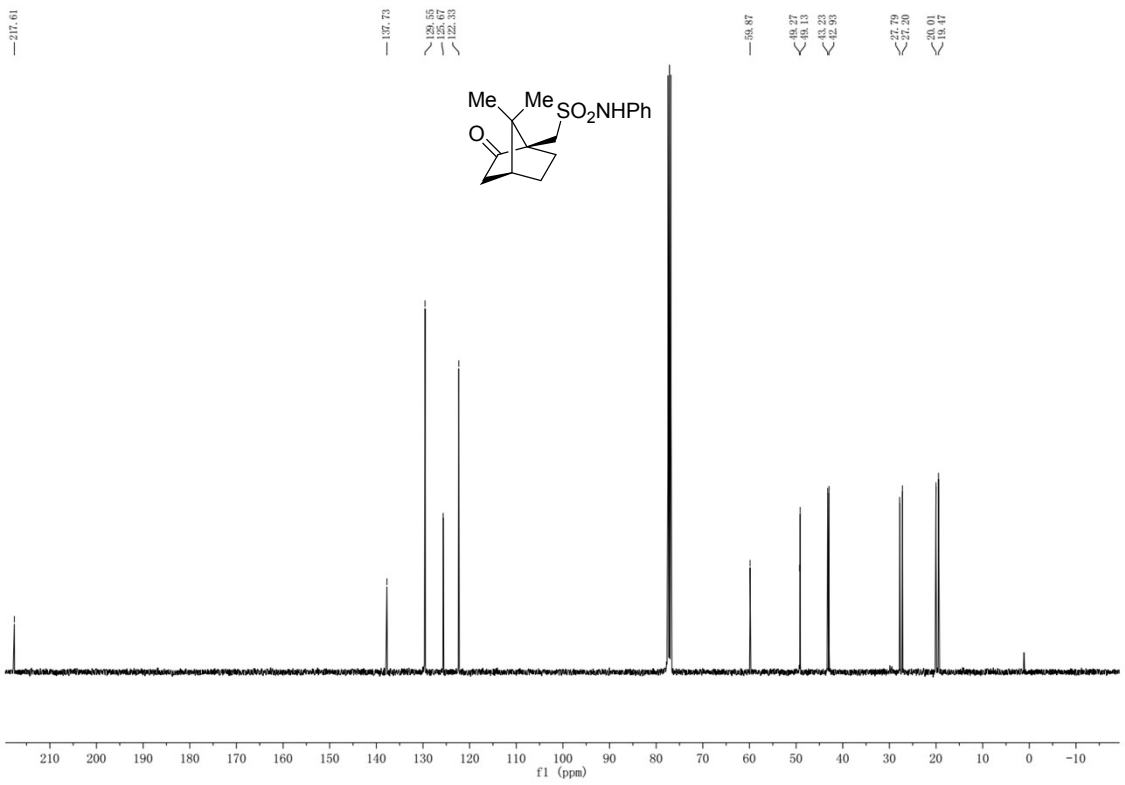


*3-chloro-N-phenylpropane-1-sulfonamide (**3av**)*

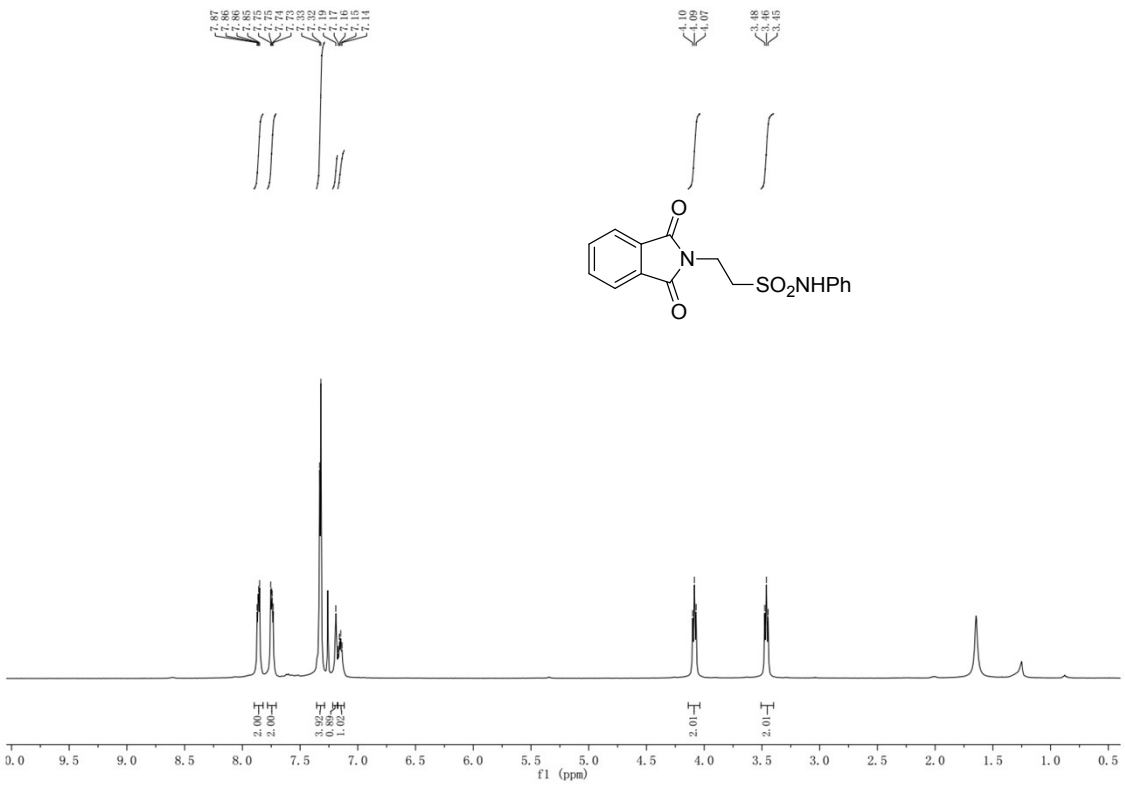


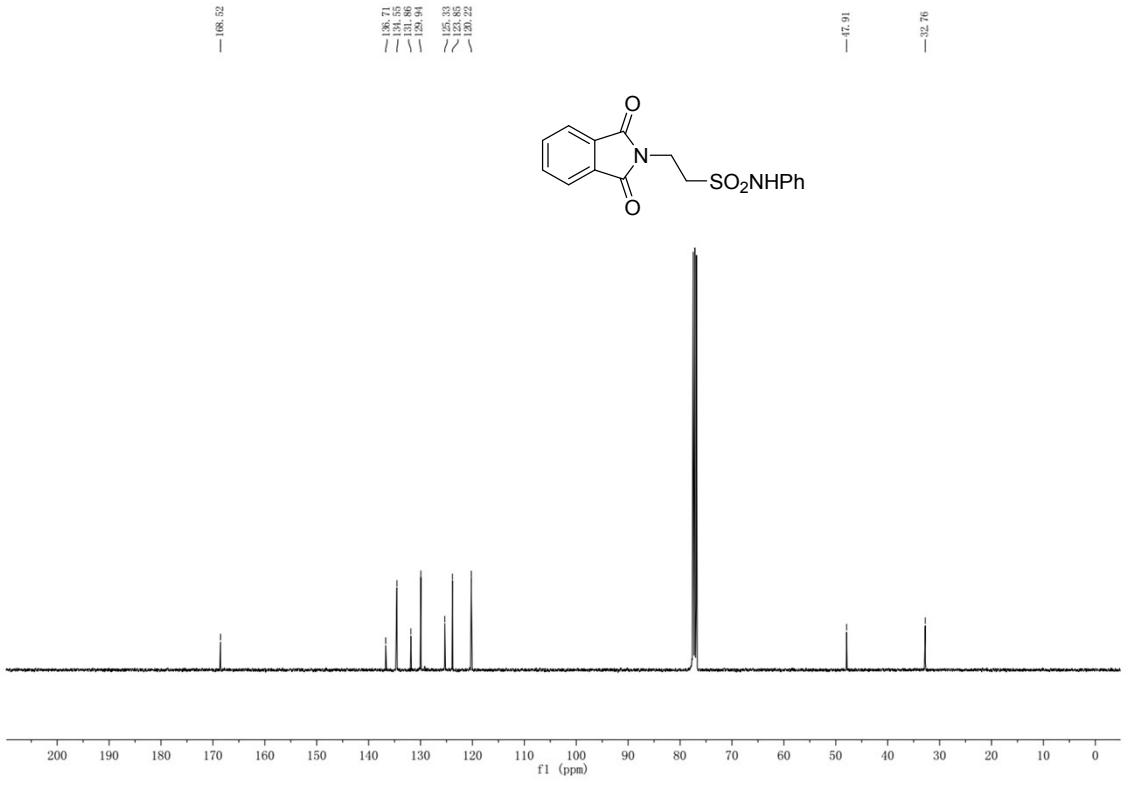
*1-((1R,4S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-N-phenylmethanesulfonamide (**3aw**)*



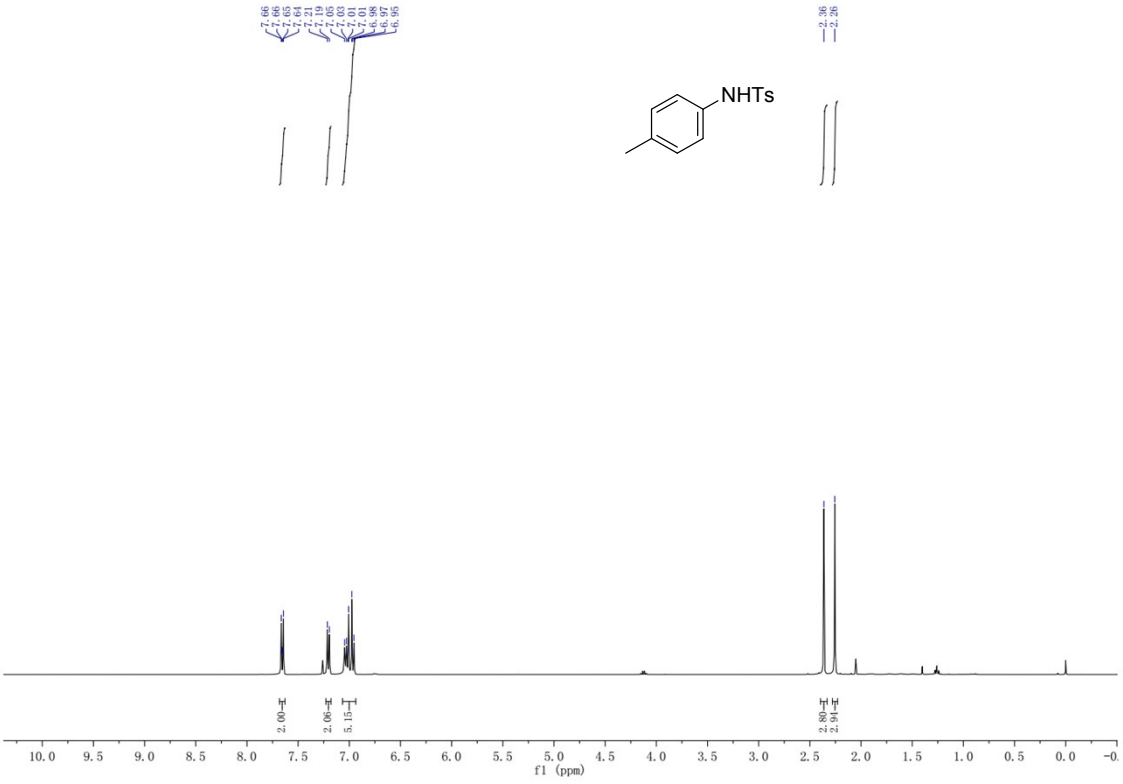


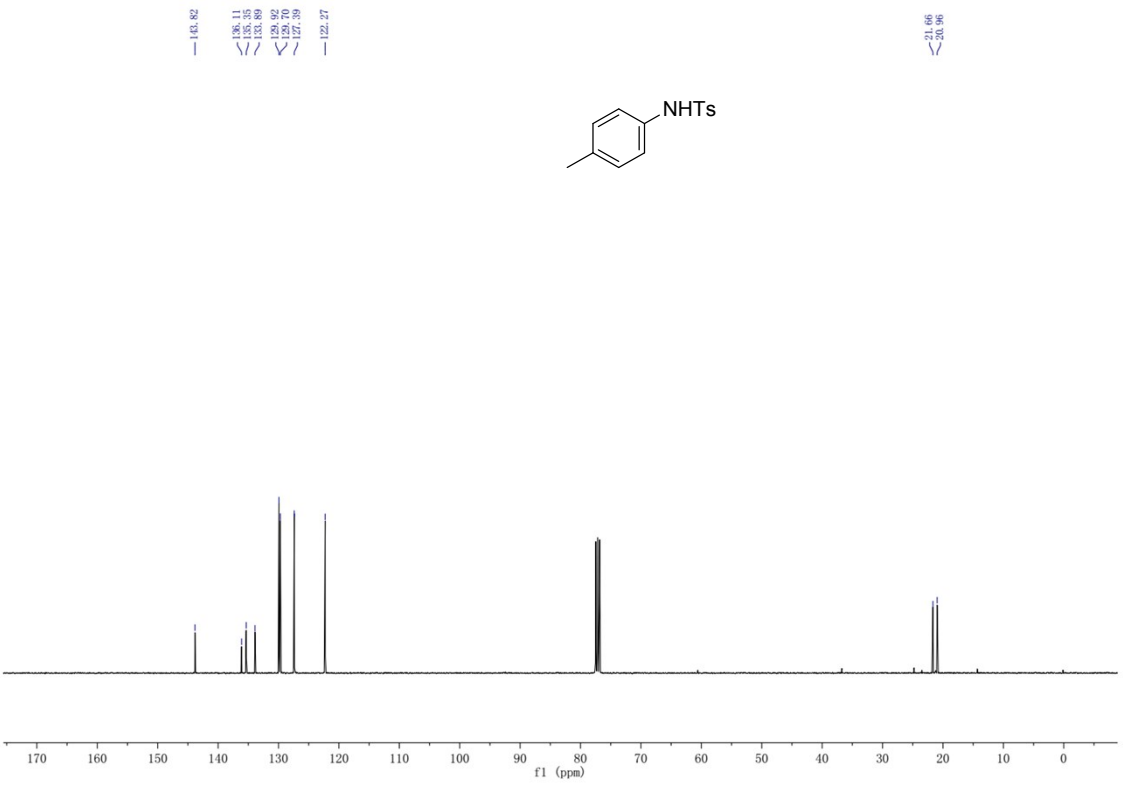
2-(1,3-dioxoisoindolin-2-yl)-N-phenylethanesulfonamide ***(3ax)***



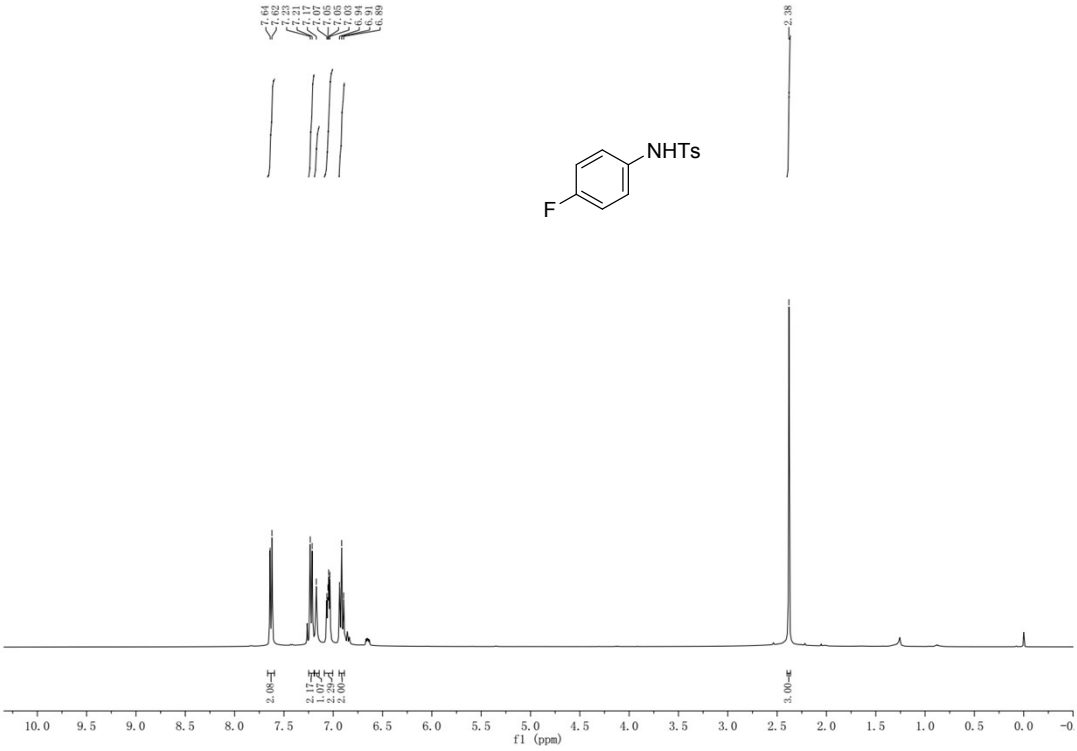


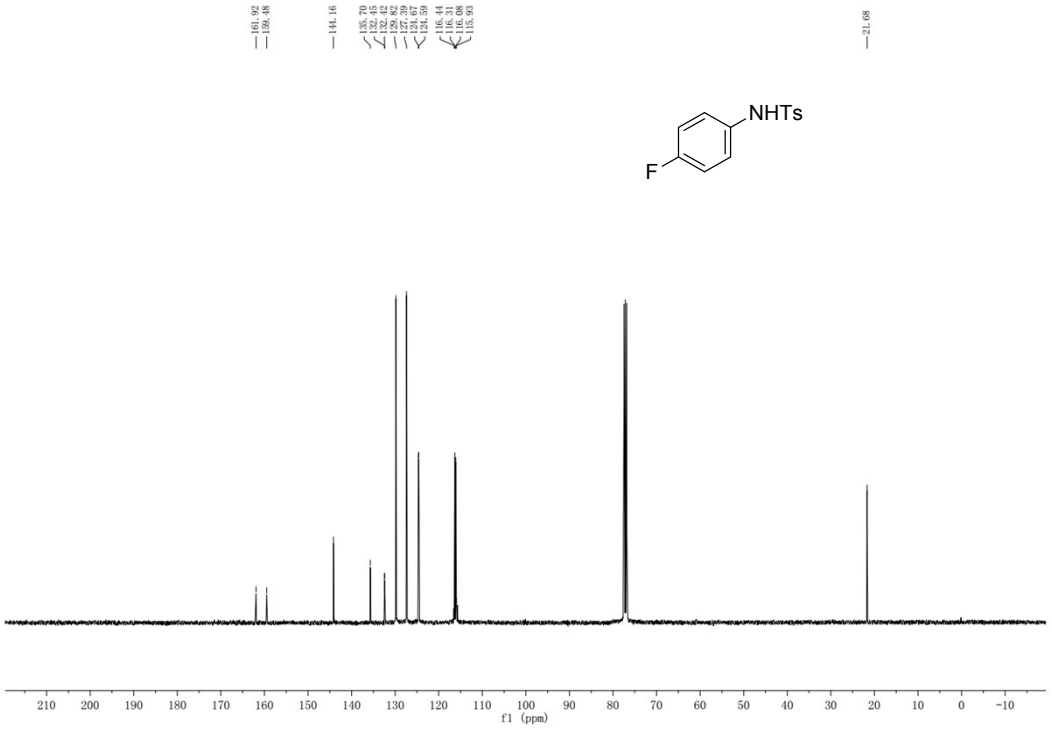
*4-methyl-N-(p-tolyl)benzenesulfonamide (**3ba**)*

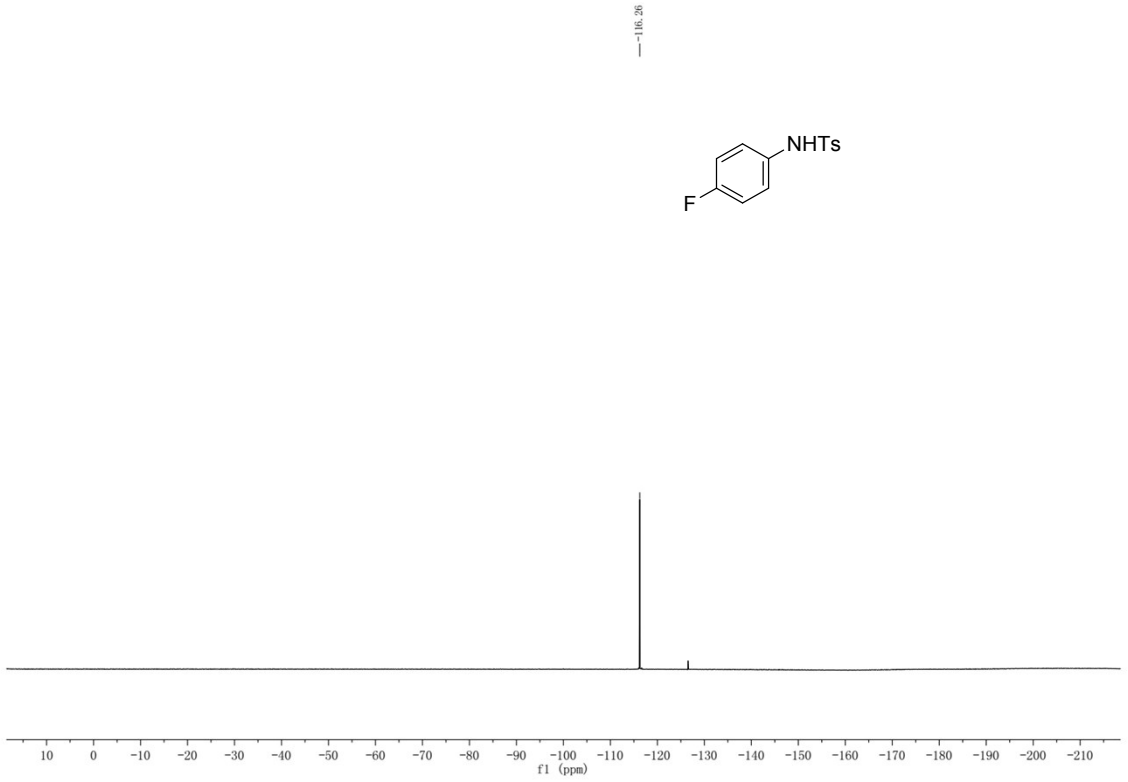

7.66
7.66
7.65
7.64
7.21
7.19
7.05
7.03
7.01
6.98
6.97
6.95
2.36
2.26
NHTs
2.00
2.06
5.15
2.80
2.94
f1 (ppm)


143.82
136.11
135.35
133.89
129.92
129.70
127.39
122.27
21.66
20.96
NHTs
f1 (ppm)

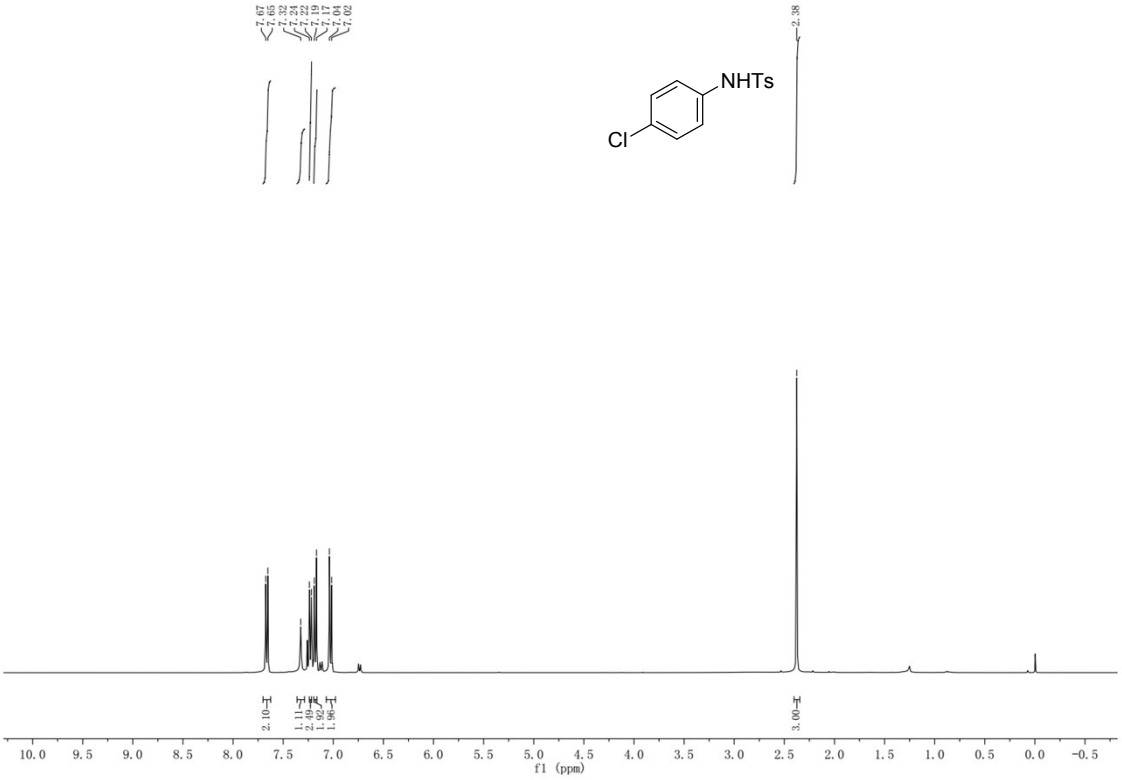
*N-(4-fluorophenyl)-4-methylbenzenesulfonamide(**3ca**)*

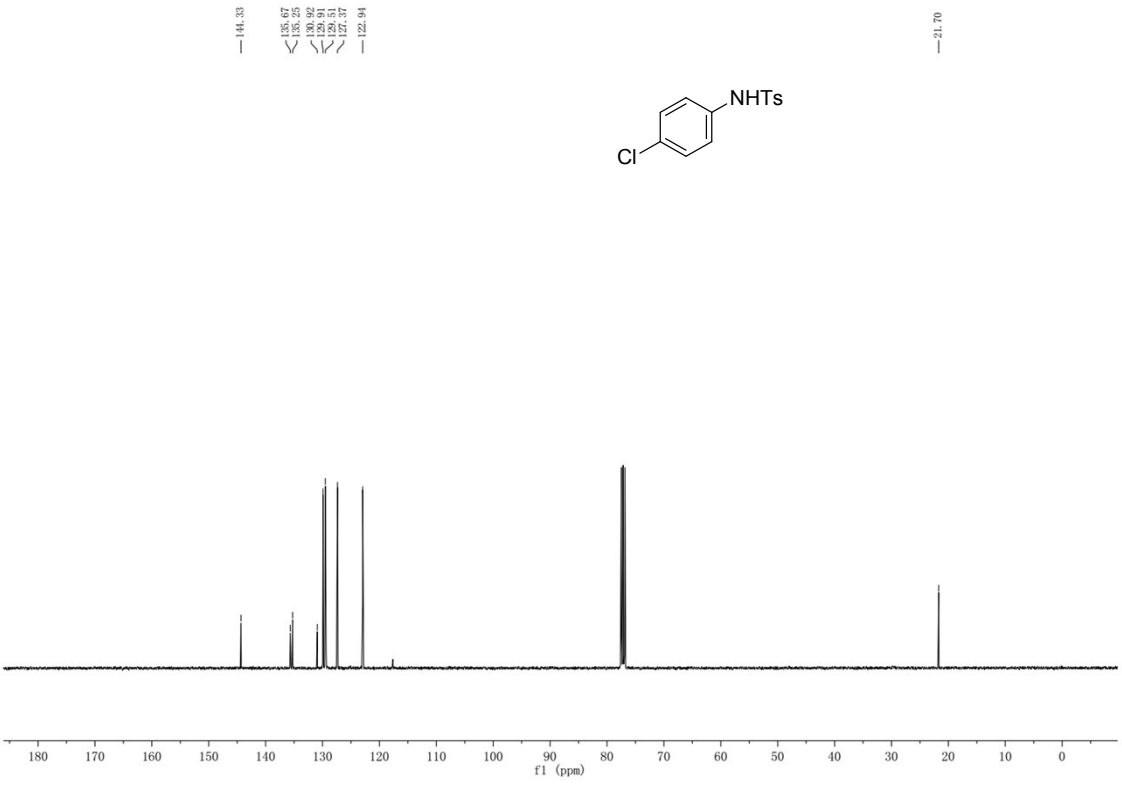



161.92
159.48
144.16
135.70
132.45
132.42
129.82
127.39
124.67
124.59
116.44
116.31
116.08
115.93
21.68
NHTs
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

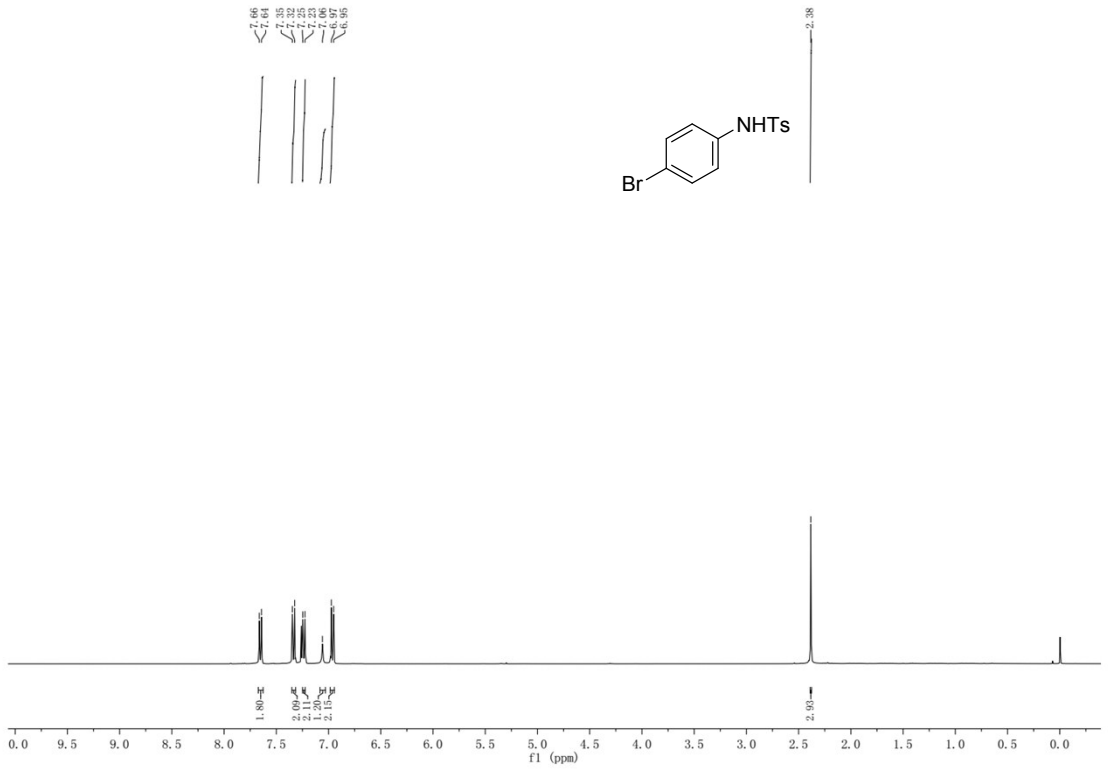

-116.26
NHTs
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

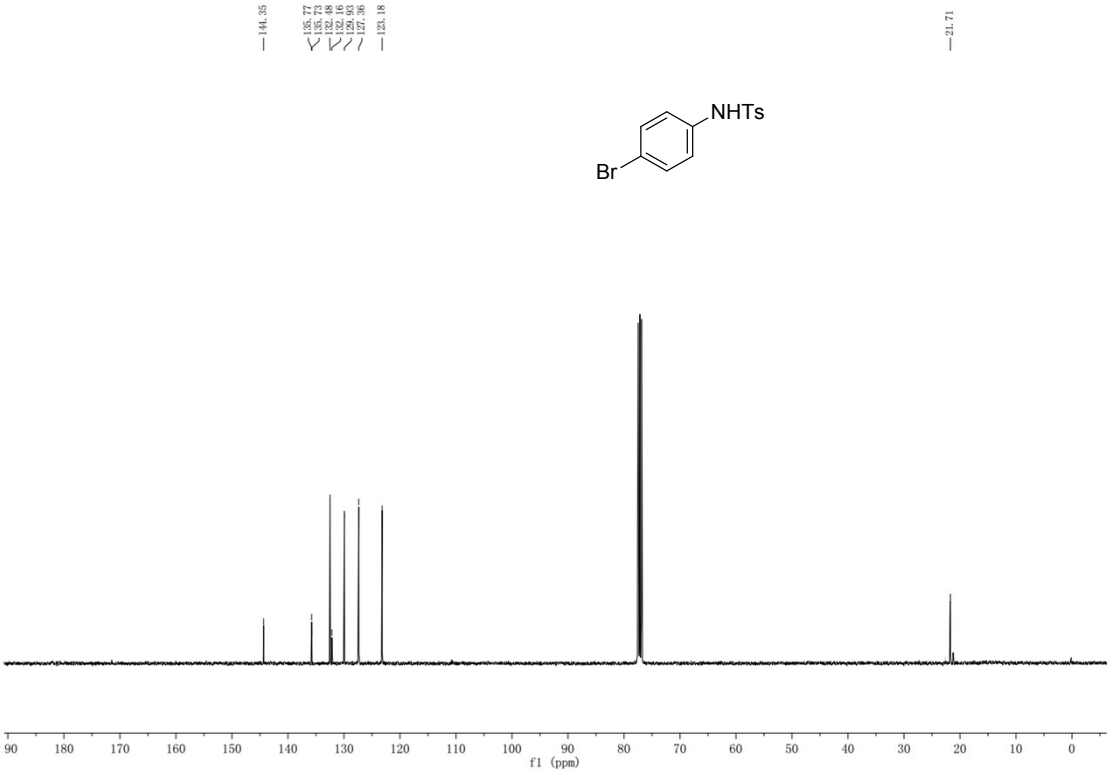
*N-(4-chlorophenyl)-4-methylbenzenesulfonamide (**3da**)*



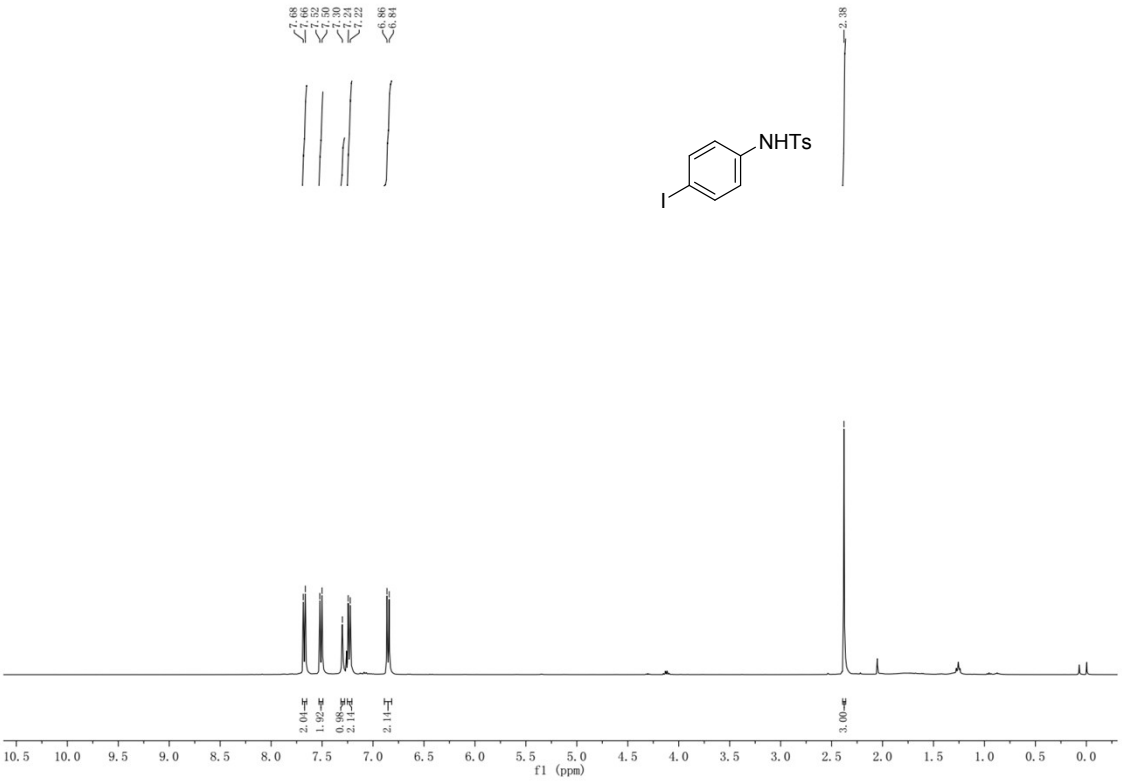


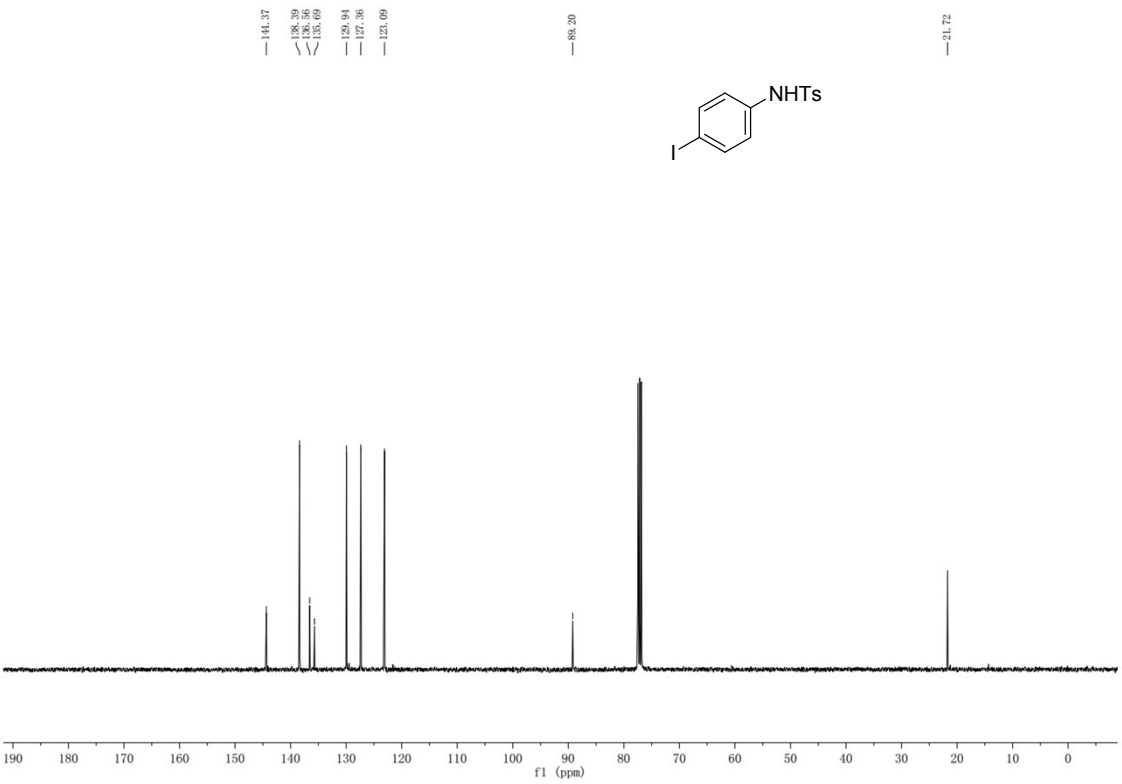
*N-(4-bromophenyl)-4-methylbenzenesulfonamide (**3ea**)*



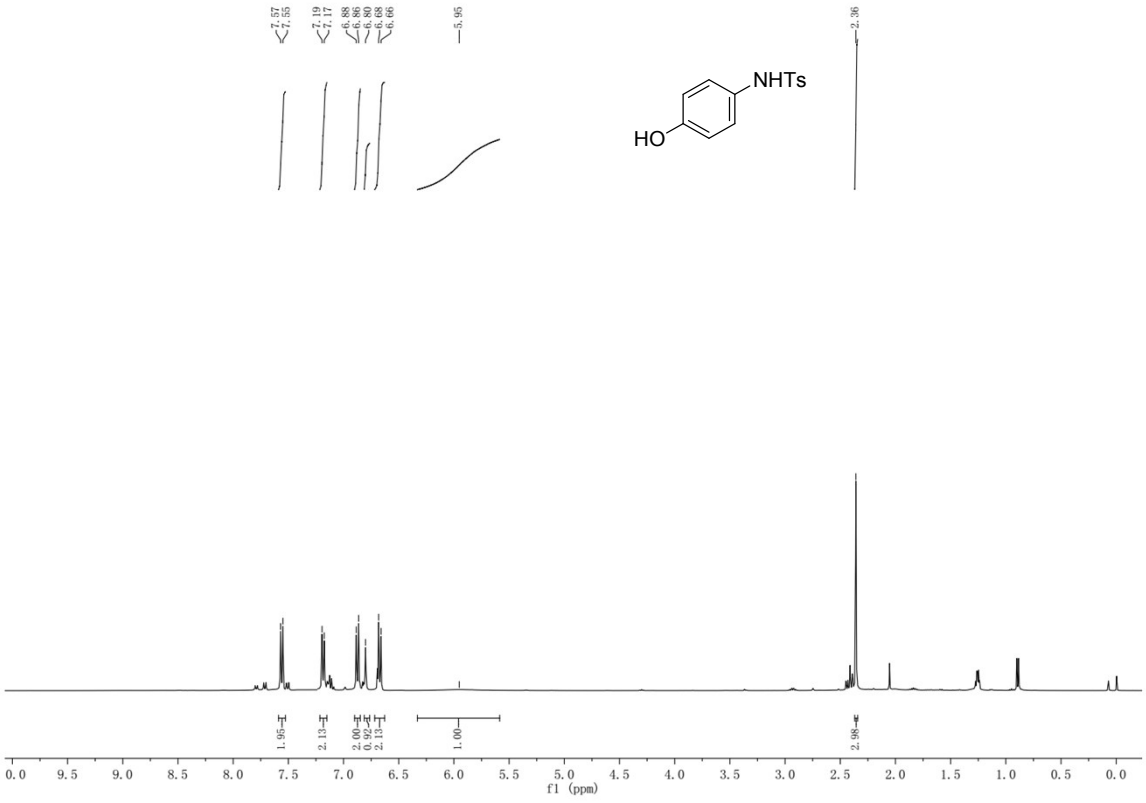


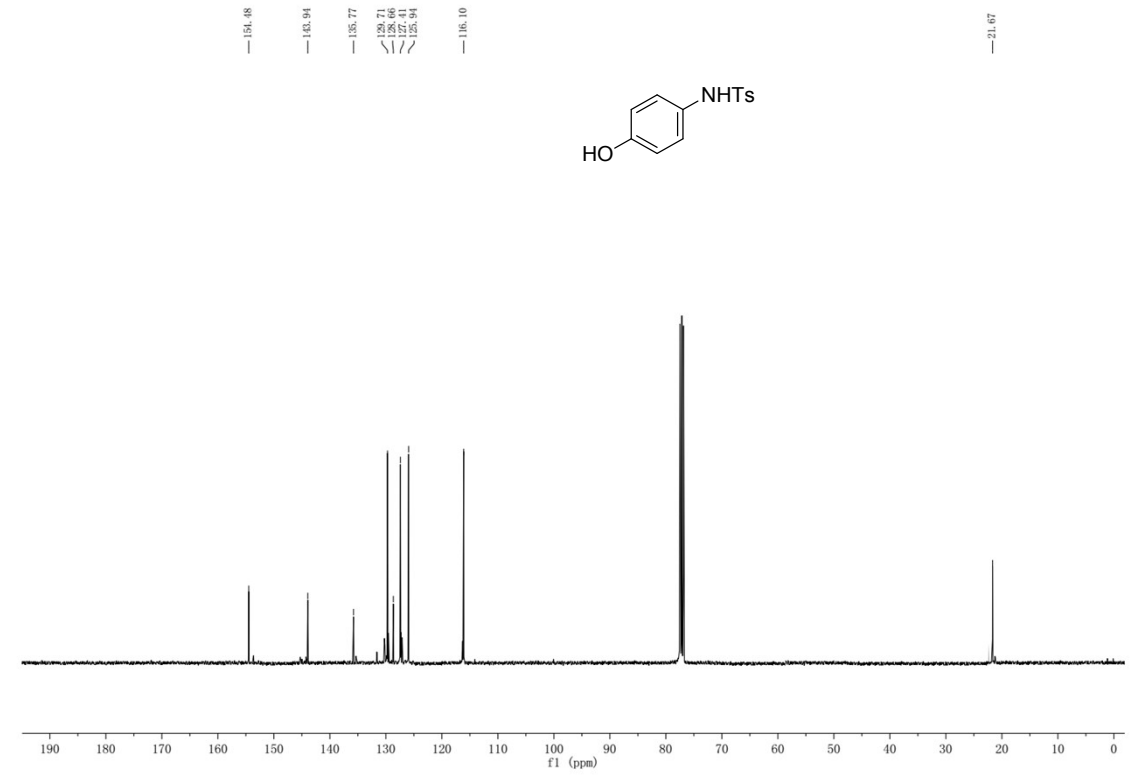
*N-(4-iodophenyl)-4-methylbenzenesulfonamide (**3fa**)*



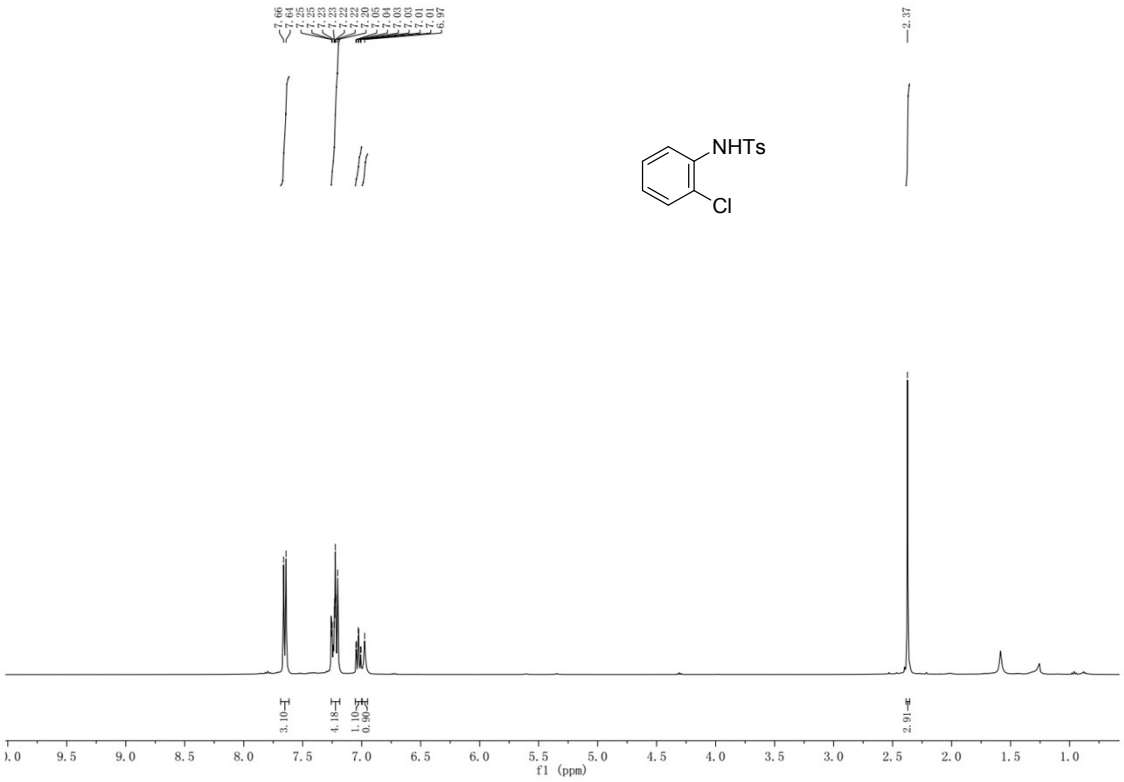


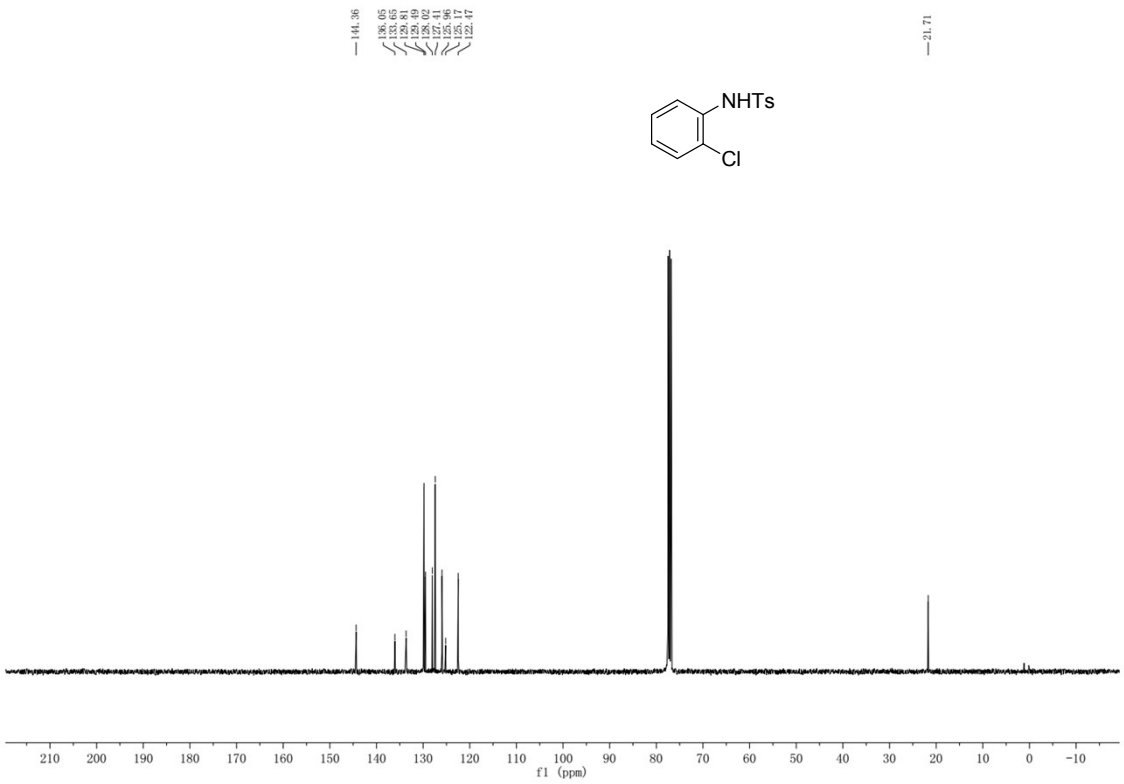
*N-(4-hydroxyphenyl)-4-methylbenzenesulfonamide (**3ga**)*



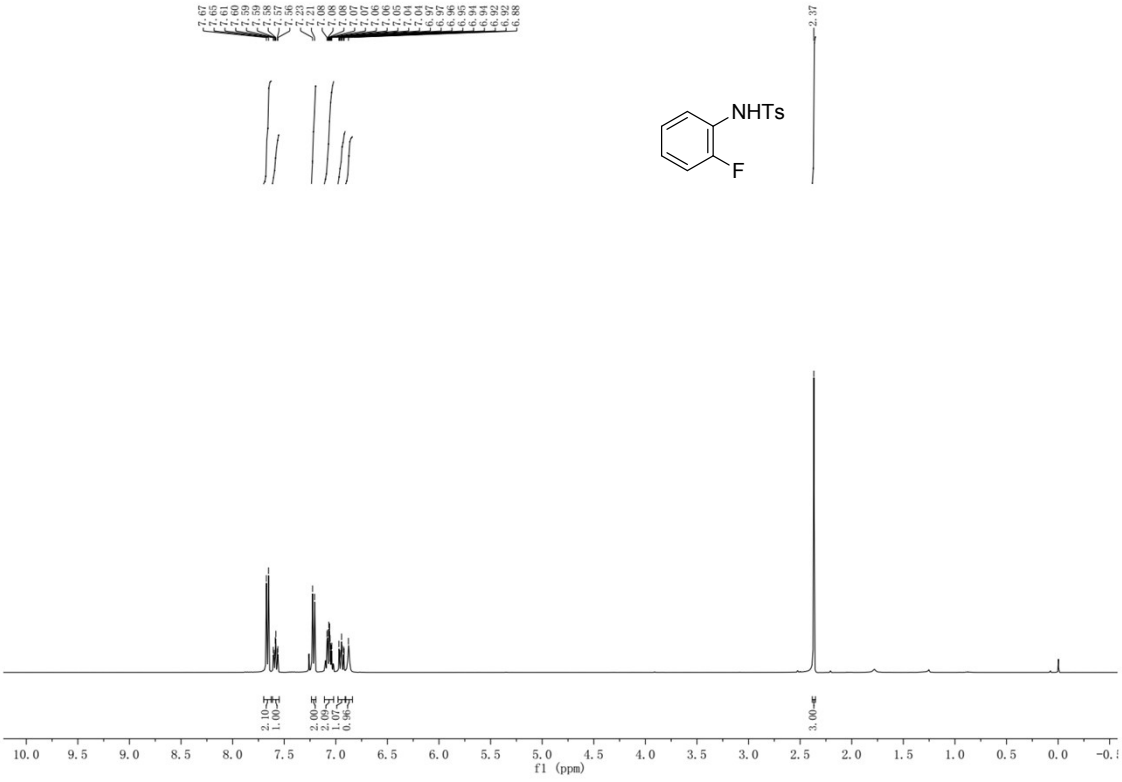


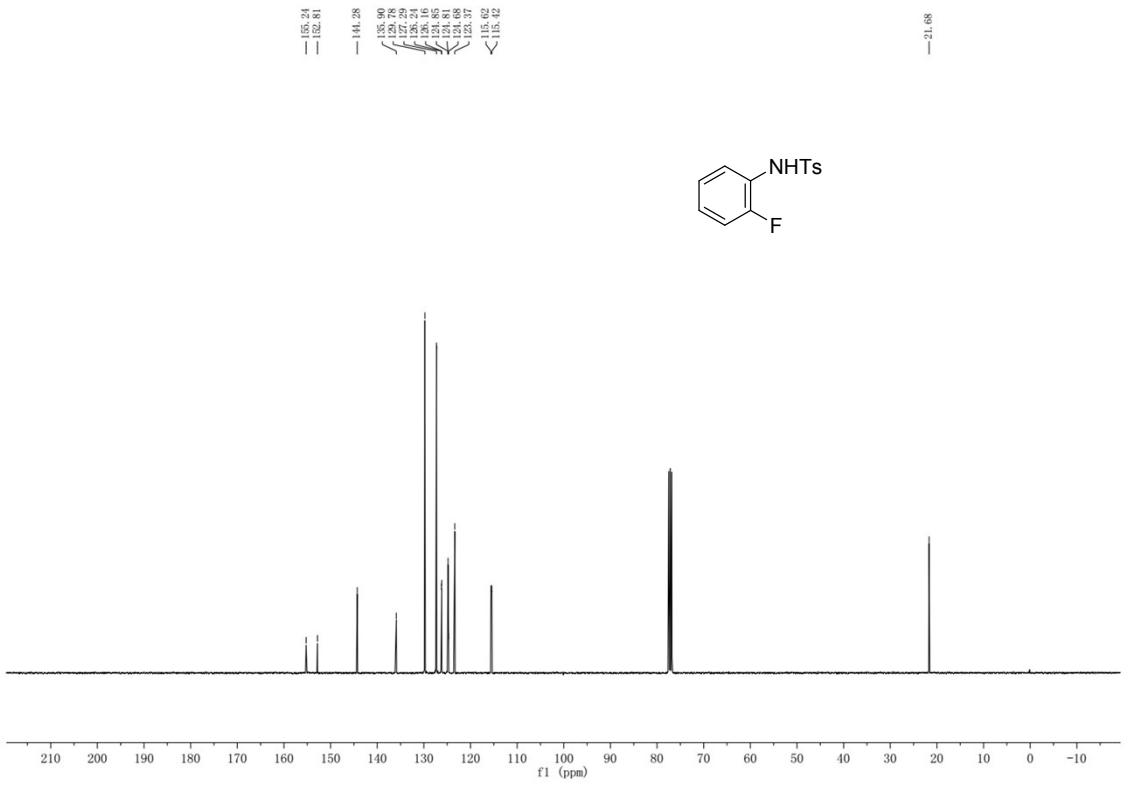
*N-(2-chlorophenyl)-4-methylbenzenesulfonamide (**3ha**)*

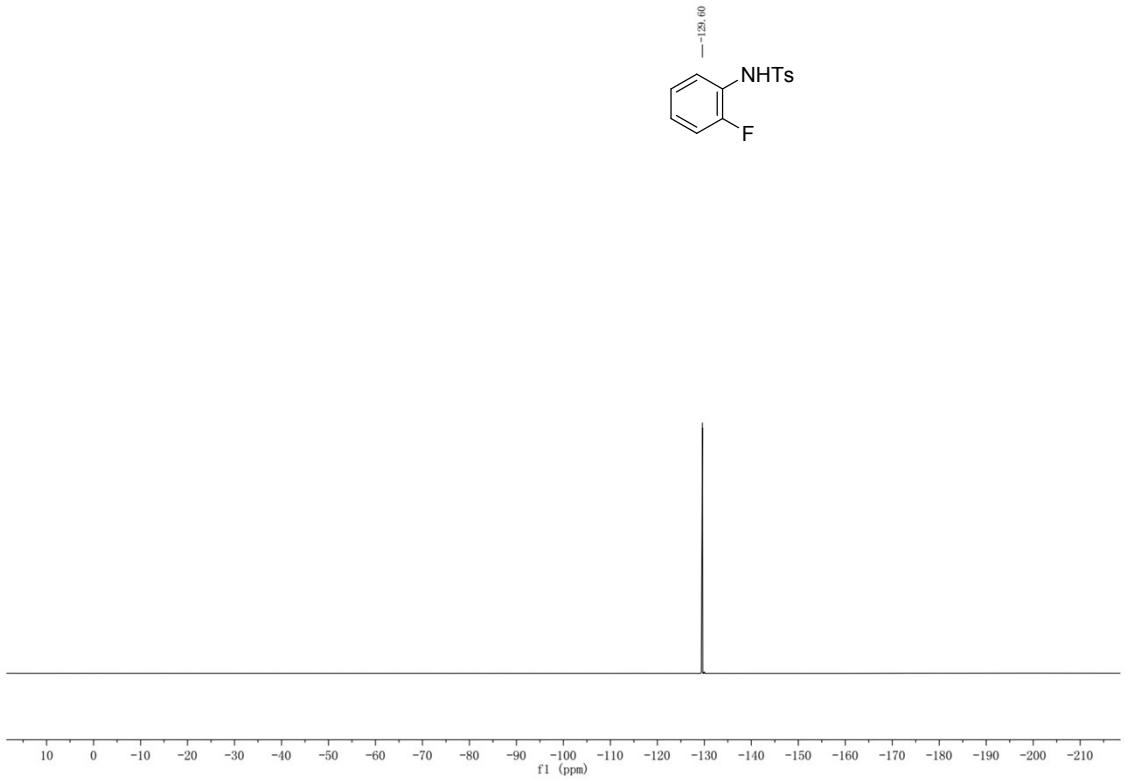




*N-(2-fluorophenyl)-4-methylbenzenesulfonamide(**3la**)*




155.24
152.81
144.28
135.90
129.78
127.29
126.24
126.16
124.85
124.81
124.68
121.57
115.62
115.42
21.68
NHTs
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-129.60
NHTs
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

*4-methyl-N-(1H-1,2,4-triazol-3-yl)benzenesulfonamide (**3ja**)*