

Supporting Information

Facile Synthesis of 2-Sulfonylbenzothiazoles *via* Cascade SO₂-NCS Addition and S-C(sp²) Coupling

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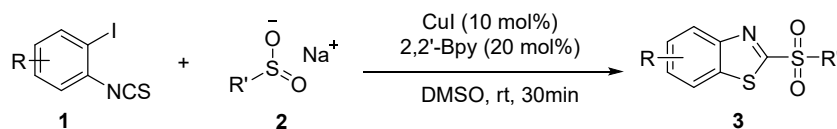
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1. Experimental Section

1.1 General information

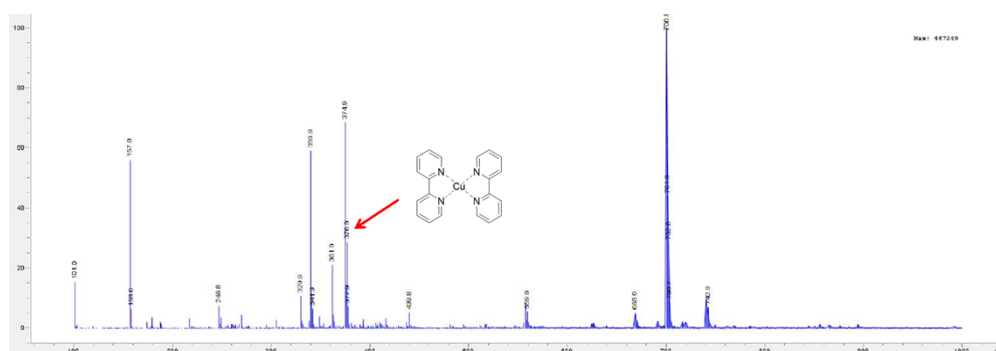
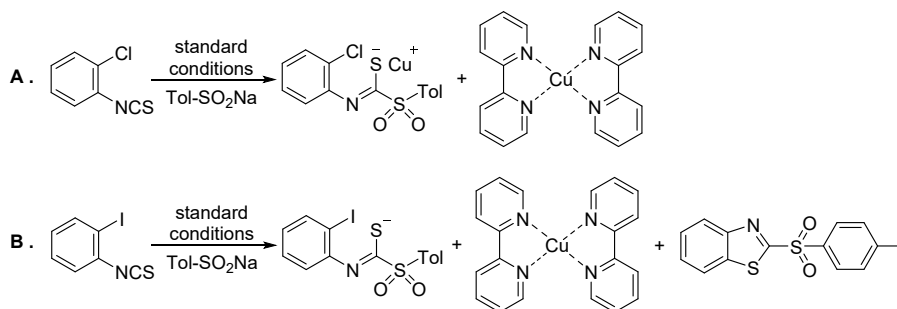
Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. All reactions were performed in oven-dried glassware with magnetic stirring. Reactions were monitored by LC/MS or thin layer chromatography (TLC). NMR spectra were recorded on Bruker 300 instruments and calibrated using residual undeuterated solvents. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Flash column chromatography was performed using Qingdao Haiyang silica (silica gel for thin-layer chromatography, HG/T2354-2010). High-resolution mass spectra (HRMS) were obtained on an Agilent 6545 Q-TOF HPLC and mass spectrometry. The melting point (MP) was measured by Mettler Toledo MP90 melting point system.

1.2 General procedure for synthesis of compounds 3

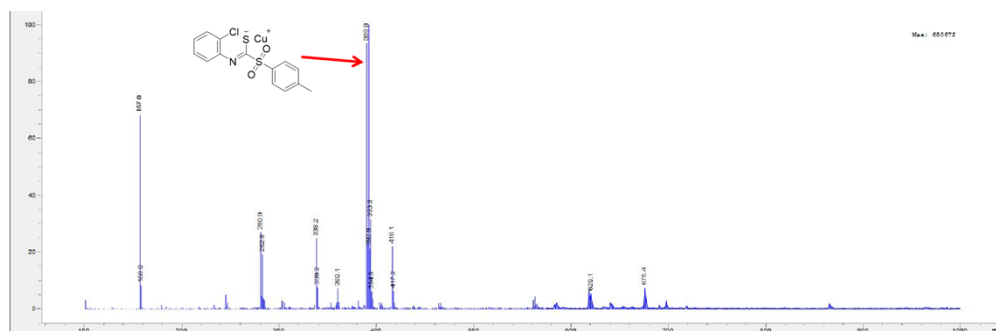


In a reaction flask, **1** (0.20 mmol, 1 equiv.) and **2** (0.40 mmol, 2 equiv.), CuI (10 mol%), 2,2'-Bpy (20 mol%) and DMSO (2 mL) were added. The mixture was stirred for about 30 min at room temperature. The reaction was monitored by thin layer chromatography (TLC) until the substrates disappeared completely. The reaction mixture was added diluted hydrochloric acid (10%, 5 mL) and ethyl acetate (10 mL). The separated organic layer was washed saturated aqueous brine (10 mL × 5), and dried over anhydrous Na₂SO₄. After the solvent was evaporated by a rotary evaporator, the concentrated crude products are generally of high-purity as evidenced by the NMR spectroscopy. (The few low-pure products were further isolated and purified by column chromatography (ethyl acetate and petroleum ether, 1:7) to obtain the pure **3**.)

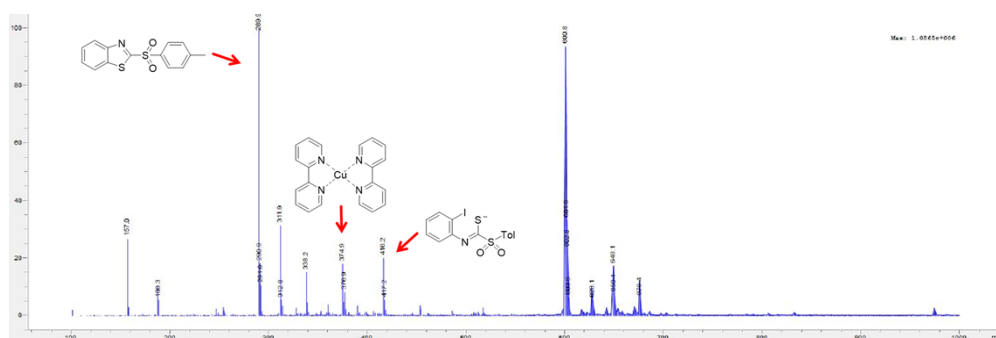
1.3 LC-MS monitoring experiments



A-1: Reaction mixture of 2-Cl-PhNCS (5 min)

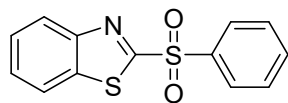


A-2: Reaction mixture of 2-Cl-PhNCS (10 min)



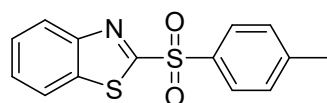
B: Reaction mixture of 2-I-PhNCS (5 min)

2. Characterization data of products 3



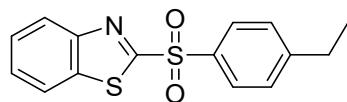
2-(phenylsulfonyl)benzo[d]thiazole (3aa)¹

White solid; mp: 166.4 – 167.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 51.7 mg, yield 94%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.22 – 8.10 (m, 3H), 7.96 (dd, J = 6.9, 2.0 Hz, 1H), 7.70 – 7.50 (m, 5H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.26, 152.92, 138.47, 137.07, 134.62, 129.58, 128.98, 127.94, 127.56, 125.58, 122.25. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₃H₁₀NO₂S₂ 276.0148; Found: 276.0151.



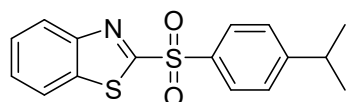
2-tosylbenzo[d]thiazole (3ab)¹

White solid; mp: 146.2 – 147.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 57.2 mg, yield 99%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.13 (dd, J = 6.8, 1.7 Hz, 1H), 8.04 (d, J = 8.3 Hz, 2H), 7.94 (dd, J = 7.2, 2.3 Hz, 1H), 7.61 – 7.47 (m, 2H), 7.36 (d, J = 8.1 Hz, 2H), 2.41 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.63, 152.86, 146.01, 136.99, 135.40, 130.25, 129.00, 127.86, 127.51, 125.46, 122.25, 21.79. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₄H₁₂NO₂S₂ 290.0304; Found: 290.0301.



2-((4-ethylphenyl)sulfonyl)benzo[d]thiazole (3ac)

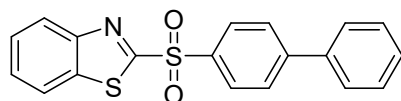
White solid; mp: 104.9 – 105.7 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 58.2 mg, yield 96%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.15 (dd, J = 7.1, 1.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.98 – 7.91 (m, 1H), 7.55 (m, 2H), 7.40 (d, J = 8.5 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.68, 152.91, 151.99, 137.04, 135.59, 129.13, 129.11, 127.82, 127.48, 125.52, 122.23, 29.01, 15.00. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₅H₁₄NO₂S₂ 304.0460; Found: 304.0458.



2-((4-isopropylphenyl)sulfonyl)benzo[d]thiazole (3ad)²

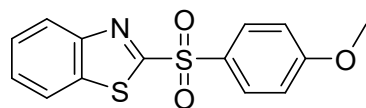
White solid; mp: 133.4 – 134.8 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 57.1 mg, yield 90%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.16 (dd, J = 7.6, 1.2 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.95 (dd, J = 7.9, 1.4 Hz, 1H), 7.62 – 7.48 (m, 2H), 7.42 (d, J = 8.5 Hz, 2H), 3.02 – 2.92 (m, 1H), 1.25 (d, J = 7.0 Hz, 6H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.70, 156.49, 152.95, 137.07, 135.72, 129.16, 127.79, 127.74,

127.46, 125.54, 122.21, 34.37, 23.53. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{16}H_{16}NO_2S_2$ 318.0617; Found: 318.0619.



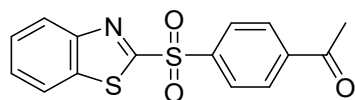
2-((1,1'-biphenyl)-4-ylsulfonyl)benzo[d]thiazole (3ae)²

White solid; mp: 187.4 – 189.0 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 67.4 mg, yield 96%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.25 – 8.16 (m, 3H), 7.99 – 7.94 (m, 1H), 7.77 (d, J = 8.5 Hz, 2H), 7.60 – 7.42 (m, 7H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.45, 152.97, 147.62, 138.93, 137.09, 136.87, 129.53, 129.13, 128.88, 128.18, 127.91, 127.55, 127.44, 125.58, 122.25. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{19}H_{14}NO_2S_2$ 352.0460; Found: 352.0457.



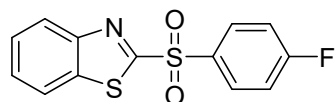
2-((4-methoxyphenyl)sulfonyl)benzo[d]thiazole (3af)¹

White solid; mp: 117.3 – 118.6 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 50.6 mg, yield 83%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.17 – 8.04 (m, 3H), 7.97 – 7.91 (m, 1H), 7.52 (qd, J = 7.3, 1.5 Hz, 2H), 7.07 – 6.99 (m, 2H), 3.86 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 168.02, 164.60, 152.86, 138.38, 136.92, 131.33, 129.58, 127.76, 125.42, 122.23, 114.88, 55.83. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{14}H_{12}NO_3S_2$ 306.0253; Found: 306.0255.



1-(4-(benzo[d]thiazol-2-ylsulfonyl)phenyl)ethan-1-one (3ag)³

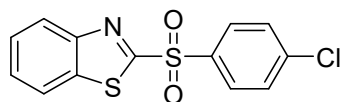
White solid; mp: 163.7 – 165.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 60.2 mg, yield 95%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.27 (d, J = 8.5 Hz, 2H), 8.14 (t, J = 8.5 Hz, 3H), 8.01 – 7.94 (m, 1H), 7.58 (tt, J = 7.3, 5.6 Hz, 2H), 2.65 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 196.60, 166.43, 152.94, 142.18, 141.33, 137.09, 129.38, 129.20, 128.19, 127.74, 125.65, 122.30, 26.98. HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{15}H_{12}NO_3S_2$ 318.0253; Found: 318.0256.



2-((4-fluorophenyl)sulfonyl)benzo[d]thiazole (3ah)²

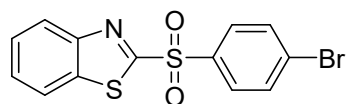
White solid; mp: 153.2 – 155.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 55.1 mg, yield 94%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.24 – 8.12 (m, 3H), 8.00 – 7.93 (m, 1H), 7.62 – 7.50 (m, 2H), 7.30 – 7.23 (m, 2H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.05, 166.4 (d, J = 256.5 Hz), 152.88, 136.97, 134.47, 132.00 (d, J = 9.75 Hz),

127.84 (d, $J = 29.25$ Hz), 125.53, 122.28, 117.15, 116.85. ^{19}F NMR (282 MHz, Chloroform-*d*) δ -101.41. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{FNO}_2\text{S}_2$ 294.0053; Found:294.0056.



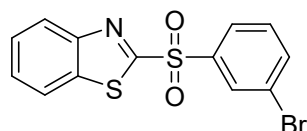
2-((4-chlorophenyl)sulfonyl)benzo[d]thiazole (3ai)²

White solid; mp: 155.7 – 157.1 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 57.5 mg, yield 93%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.21 – 8.05 (m, 3H), 8.02 – 7.93 (m, 1H), 7.64 – 7.50 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.80, 152.90, 141.58, 137.01, 136.90, 130.44, 129.93, 128.09, 127.68, 125.58, 122.29. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{ClNO}_2\text{S}_2$ 309.9758; Found: 309.9760.



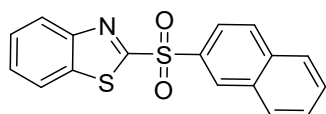
2-((4-bromophenyl)sulfonyl)benzo[d]thiazole (3aj)²

White solid; mp: 161.6 – 162.4 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 62.8 mg, yield 89%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.20 – 8.11 (m, 1H), 8.06 – 7.92 (m, 3H), 7.72 (d, $J = 8.6$ Hz, 2H), 7.63 – 7.52 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.75, 152.92, 137.47, 137.02, 132.92, 130.45, 130.28, 128.08, 127.67, 125.61, 122.27. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{BrNO}_2\text{S}_2$ 353.9253; Found: 353.9255.



2-((3-bromophenyl)sulfonyl)benzo[d]thiazole (3ak)²

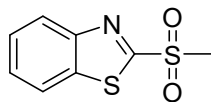
White solid; mp: 170.2 – 171.8 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 49.4 mg, yield 70%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.18 (dd, $J = 7.3$, 1.8 Hz, 1H), 8.11 (d, $J = 7.9$ Hz, 1H), 8.02 – 7.96 (m, 1H), 7.79 (d, $J = 8.3$ Hz, 1H), 7.62 – 7.54 (m, 2H), 7.47 (t, $J = 7.9$ Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.45, 152.93, 140.32, 137.66, 137.11, 131.70, 131.03, 128.15, 127.72, 127.57, 125.69, 123.47, 122.29. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{BrNO}_2\text{S}_2$ 353.9253; Found: 353.9249.



2-((naphthalen-2-yl)sulfonyl)benzo[d]thiazole (3al)²

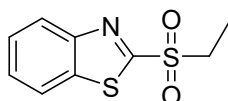
White solid; mp: 158.6 – 159.9 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 60.5 mg, yield 93%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.16 – 7.87 (m,

6H), 7.70 – 7.49 (m, 4H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.36, 152.93, 137.07, 135.68, 135.24, 132.20, 131.16, 129.92, 129.72, 128.04, 127.90, 127.54, 125.56, 123.16, 122.23. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₂NO₂S₂ 326.0304; Found: 326.0307.



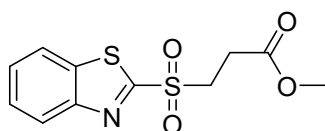
2-(methylsulfonyl)benzo[*d*]thiazole (3am)¹

White solid; mp: 185.3 – 186.9 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 6:1); 42.2 mg, yield 99%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.24 – 8.16 (m, 1H), 8.04 – 7.98 (m, 1H), 7.68 – 7.56 (m, 2H), 3.42 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 166.36, 152.42, 136.59, 128.16, 127.76, 125.38, 122.44, 42.49. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₈H₈NO₂S₂ 213.9991; Found: 213.9992.



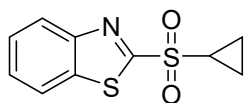
2-(ethylsulfonyl)benzo[*d*]thiazole (3an)⁴

White solid; mp: 91.9 – 93.4 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 6:1); 44.5 mg, yield 98%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 9.5 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.61 – 7.50 (m, 2H), 3.47 (q, *J* = 7.4 Hz, 2H), 1.36 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 165.32, 152.76, 136.77, 128.06, 127.69, 125.46, 122.37, 49.35, 7.18. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₉H₁₀NO₂S₂ 228.0147; Found: 228.0149.



methyl 3-(benzo[*d*]thiazol-2-ylsulfonyl)propanoate (3ao)⁵

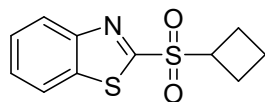
Colorless oily liquid. *R_f* = 0.5 (petroleum ether/ethyl acetate 6:1); 52.5 mg, yield 92%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.25 – 8.19 (m, 1H), 8.06 – 7.99 (m, 1H), 7.69 – 7.57 (m, 2H), 3.89 – 3.82 (m, 2H), 3.67 (s, 3H), 3.01 – 2.93 (m, 2H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 170.10, 165.04, 152.61, 136.77, 128.26, 127.82, 125.52, 122.41, 52.48, 50.28, 27.57. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₁H₁₂NO₄S₂ 286.0202; Found: 286.0219.



2-(cyclopropylsulfonyl)benzo[*d*]thiazole (3ap)

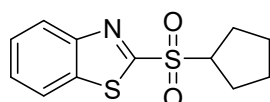
White solid; mp: 118.8 – 119.6 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 6:1); 46.9 mg, yield 98%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 7.2, 1.6 Hz, 1H),

8.07 – 7.95 (m, 1H), 7.67 – 7.54(m, 2H), 2.89 (tt, $J = 7.9, 4.7$ Hz, 1H), 1.59 – 1.49 (m, 2H), 1.25 – 1.17 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.22, 152.76, 136.68, 127.96, 127.62, 125.46, 122.32, 31.70, 6.66. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_{10}\text{NO}_2\text{S}_2$ 240.0147; Found: 240.0149.



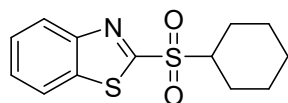
2-(cyclobutylsulfonyl)benzo[*d*]thiazole (3aq)

White solid; mp: 101.2 – 102.3 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 6:1); 49.1 mg, yield 97%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.21 (dd, $J = 6.8, 1.4$ Hz, 1H), 8.01 (dd, $J = 7.0, 1.8$ Hz, 1H), 7.67 – 7.54(m, 2H), 4.33 (p, $J = 8.1$ Hz, 1H), 2.84 – 2.66 (m, 2H), 2.44 – 2.28 (m, 2H), 2.19 – 2.02 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 164.95, 152.85, 136.80, 127.96, 127.61, 125.45, 122.32, 56.06, 22.72, 17.37. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_2\text{S}_2$ 254.0304; Found: 254.0307.



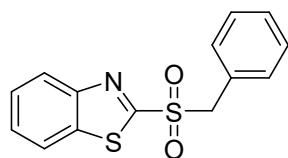
2-(cyclopentylsulfonyl)benzo[*d*]thiazole (3ar)⁶

White solid; mp: 113.4 – 114.9 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 6:1); 51.8 mg, yield 97%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.22 (dd, $J = 7.6, 2.1$ Hz, 1H), 8.06 – 7.98 (m, 1H), 7.67 – 7.54(m, 2H), 4.04 (tt, $J = 9.1, 6.7$ Hz, 1H), 2.26 (dq, $J = 13.4, 7.1$ Hz, 2H), 2.11 – 1.97 (m, 2H), 1.83 (dd, $J = 10.1, 5.4$ Hz, 2H), 1.75 – 1.60 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.93, 152.87, 136.78, 127.96, 127.61, 125.43, 122.34, 63.29, 27.13, 26.03. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_2\text{S}_2$ 268.0460; Found: 268.0462.



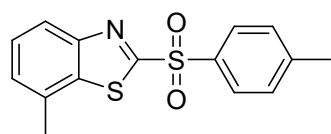
2-(cyclohexylsulfonyl)benzo[*d*]thiazole (3as)⁶

White solid; mp: 116.3 – 118.1 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 6:1); 53.4 mg, yield 95%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.24 (dd, $J = 7.7, 2.1$ Hz, 1H), 8.08 – 7.98 (m, 1H), 7.67 – 7.54(m, 2H), 3.48 (tt, $J = 12.2, 3.5$ Hz, 1H), 2.19 (d, $J = 12.8$ Hz, 2H), 1.91 (d, $J = 13.3$ Hz, 2H), 1.75 – 1.58 (m, 3H), 1.37 – 1.17 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.04, 152.97, 136.98, 127.96, 127.61, 125.51, 122.31, 63.04, 25.11, 25.02, 24.98. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_2\text{S}_2$ 282.0617; Found: 282.0619.



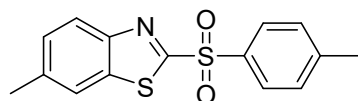
2-(benzylsulfonyl)benzo[d]thiazole (3at)⁶

White solid; mp: 109.7 – 110.9 °C. R_f = 0.5 (petroleum ether/ethyl acetate 15:1); 46.8 mg, yield 81%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.26 (d, J = 6.5 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.70 – 7.54 (m, 2H), 7.38 – 7.27 (m, 5H), 4.77 (s, 2H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 165.16, 152.57, 137.08, 131.15, 129.27, 128.94, 128.05, 127.70, 126.32, 125.51, 122.32, 121.39, 61.06. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₄H₁₂NO₂S₂ 290.0304; Found: 290.0307.



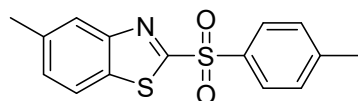
7-methyl-2-tosylbenzo[d]thiazole (3ba)

White solid; mp: 148.3 – 149.7 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 56.4 mg, yield 93%. ¹H NMR (300 MHz, Chloroform-*d*) δ 7.93 (dd, J = 16.8, 8.3 Hz, 3H), 7.40 (t, J = 7.8 Hz, 1H), 7.26 (dd, J = 18.0, 7.7 Hz, 3H), 2.51 (s, 3H), 2.35 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.03, 152.80, 145.89, 137.77, 135.54, 132.45, 130.22, 128.99, 127.76, 127.71, 122.93, 21.78, 21.24. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₅H₁₄NO₂S₂ 304.0460; Found: 304.0463.



6-methyl-2-tosylbenzo[d]thiazole (3bb)¹

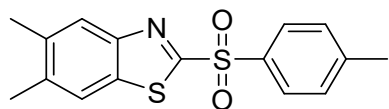
White solid; mp: 142.8 – 144.1 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 59.4 mg, yield 98%. ¹H NMR (300 MHz, Chloroform-*d*) δ 7.94 (s, 2H), 7.81 (s, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.30 – 7.20 (m, 3H), 2.38 (s, 3H), 2.31 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.47, 153.31, 145.88, 137.88, 135.54, 134.07, 130.20, 129.69, 128.93, 125.11, 121.66, 21.77, 21.53. HRMS (ESI) m/z : [M + H]⁺ Calcd for C₁₅H₁₄NO₂S₂ 304.0460; Found: 304.0461.



5-methyl-2-tosylbenzo[d]thiazole (3bc)

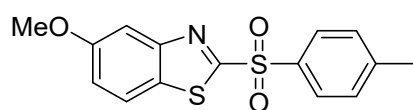
White solid; mp: 144.2 – 145.2 °C. R_f = 0.5 (petroleum ether/ethyl acetate 7:1); 59.4 mg, yield 98%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.01 (t, J = 8.3 Hz, 3H), 7.70 (s, 1H), 7.35 (d, J = 8.5 Hz, 3H), 2.49 (s, 3H), 2.41 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 166.31, 151.05, 145.85, 138.58, 137.28, 135.60, 130.20, 129.33, 128.91, 124.91, 121.66, 21.81, 21.77. HRMS (ESI) m/z : [M + H]⁺ Calcd for

C₁₅H₁₄NO₂S₂ 304.0460; Found: 304.0462.



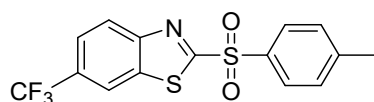
5,6-dimethyl-2-tosylbenzo[d]thiazole (3bd)

White solid; mp: 177.1 – 178.6 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 7:1); 61.5 mg, yield 97%. ¹H NMR (300 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.61 (s, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 2.35 – 2.30 (m, 9H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 166.10, 151.79, 145.67, 138.11, 137.25, 135.78, 134.72, 130.14, 128.90, 125.24, 121.72, 21.76, 20.49, 20.30. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₆NO₂S₂ 318.0617; Found: 318.0619.



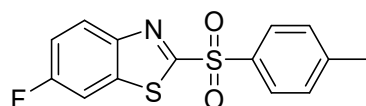
5-methoxy-2-tosylbenzo[d]thiazole (3be)

White solid; mp: 148.1 – 149.3 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 7:1); 61.9 mg, yield 97%. ¹H NMR (300 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 16.9, 8.1 Hz, 3H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 18.1, 7.6 Hz, 3H), 2.51 (s, 3H), 2.35 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.03, 152.80, 145.89, 137.77, 135.54, 132.45, 130.22, 128.99, 127.76, 127.71, 122.93, 21.78, 21.24. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₄NO₃S₂ 320.0410; Found: 320.0411.



2-tosyl-6-(trifluoromethyl)benzo[d]thiazole (3bf)¹

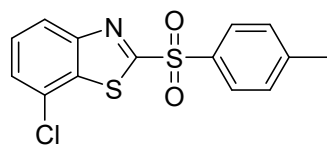
White solid; mp: 142.5 – 144.1 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 7:1); 58.5 mg, yield 82%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.31 – 8.20 (m, 2H), 8.09 – 8.02 (m, 2H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 171.06, 154.66, 146.50, 136.91, 134.74, 130.40, 129.80 (q, *J* = 33Hz), 129.20, 126.05, 124.39 (q, *J* = 3Hz), 123.62 (q, *J* = 271.5Hz), 120.18 (q, *J* = 3.75Hz), 21.83. ¹⁹F NMR (282 MHz, Chloroform-*d*) δ -61.30. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₁F₃NO₂S₂ 358.0178; Found: 358.0181.



6-fluoro-2-tosylbenzo[d]thiazole (3bg)¹

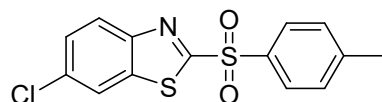
White solid; mp: 171.9 – 172.8 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 7:1); 58.3 mg, yield 95%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.16 – 7.94 (m, 3H), 7.63 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.43 – 7.28 (m, 3H), 2.44 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.38, 161.77 (d, *J* = 249.75Hz), 149.58, 146.11, 138.23 (d, *J* =

11.25Hz), 135.27, 130.29, 129.03, 126.89 (d, $J = 9.75\text{Hz}$), 116.87 (d, $J = 24.75\text{Hz}$), 108.25 (d, $J = 26.25\text{Hz}$), 21.79. ^{19}F NMR (282 MHz, Chloroform-*d*) δ -110.47. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{FNO}_2\text{S}_2$ 308.0210; Found: 308.0213.



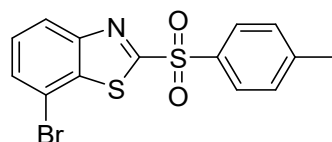
7-chloro-2-tosylbenzo[d]thiazole (3bh)

White solid; mp: 182.6 – 184.4 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 27.1 mg, yield 42%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.11 – 7.96 (m, 3H), 7.57 – 7.46 (m, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.62, 153.30, 146.28, 137.41, 135.06, 130.34, 129.12, 128.42, 127.34, 127.24, 123.82, 21.81. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{ClNO}_2\text{S}_2$ 323.9914; Found: 323.9917.



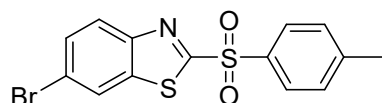
6-chloro-2-tosylbenzo[d]thiazole (3bi)¹

White solid; mp: 184.7 – 186.1 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 59.4 mg, yield 92%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.04 (dd, $J = 8.6, 3.2$ Hz, 3H), 7.93 (d, $J = 2.1$ Hz, 1H), 7.52 (dd, $J = 8.8, 2.1$ Hz, 1H), 7.39 (d, $J = 8.1$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.23, 151.38, 146.21, 138.06, 135.13, 134.08, 130.31, 129.07, 128.58, 126.26, 121.77, 21.81. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{ClNO}_2\text{S}_2$ 323.9914; Found: 323.9915.



7-bromo-2-tosylbenzo[d]thiazole (3bk)

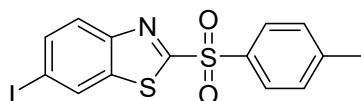
White solid; mp: 161.7 – 162.9 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 29.4 mg, yield 40%. ^1H NMR (300 MHz, Chloroform-*d*) δ 8.11 (d, $J = 8.3$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 7.7$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.42 (s, 1H), 7.40 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.06, 152.46, 146.24, 140.12, 135.09, 130.41, 130.33, 129.13, 128.61, 124.34, 114.23, 21.82. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{BrNO}_2\text{S}_2$ 367.9409; Found: 367.9411.



6-bromo-2-tosylbenzo[d]thiazole (3bl)¹

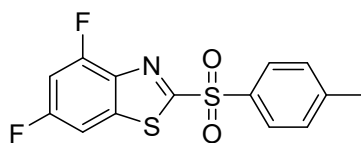
White solid; mp: 185.2 – 186.6 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate 7:1); 67.5

mg, yield 92%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.17 – 7.83 (m, 4H), 7.64 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 168.24, 151.67, 146.24, 138.42, 135.09, 131.23, 130.33, 129.06, 126.49, 124.76, 121.88, 21.82. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₁BrNO₂S₂ 367.9409; Found: 367.9412.



6-iodo-2-tosylbenzo[*d*]thiazole (3bm)

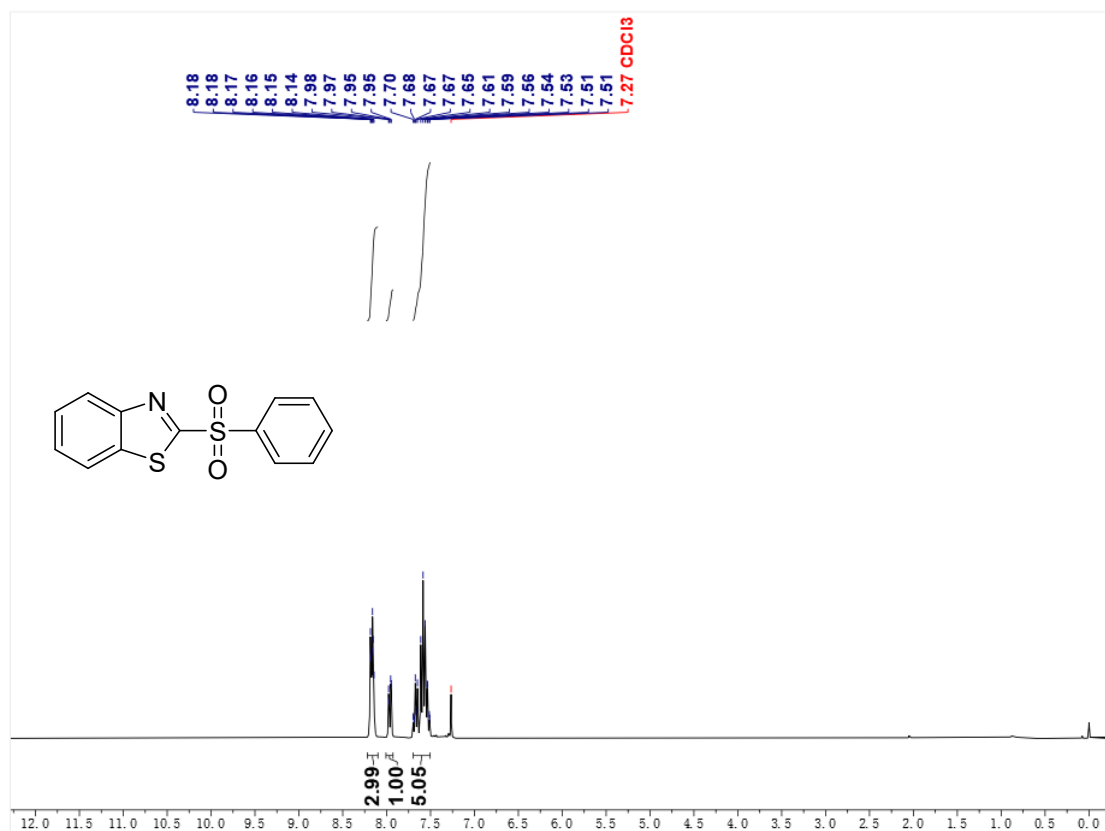
White solid; mp: 174.6 – 176.1 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 7:1); 69.7 mg, yield 84%. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 0.7 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 168.15, 152.15, 146.21, 138.76, 136.75, 135.10, 130.75, 130.32, 129.07, 126.71, 93.01, 21.82. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₁INO₂S₂ 415.9270; Found: 415.9272.



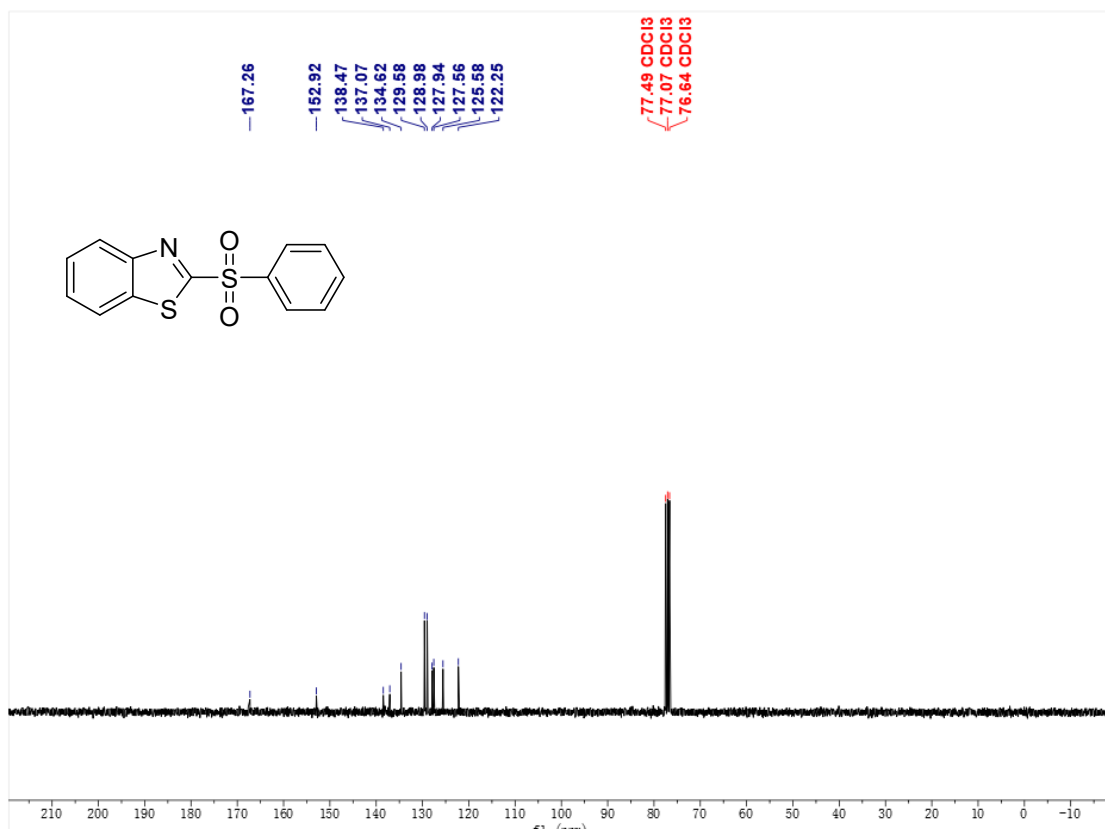
4,6-difluoro-2-tosylbenzo[*d*]thiazole (3bn)¹

White solid; mp: 164.8 – 165.6 °C. *R_f* = 0.5 (petroleum ether/ethyl acetate 7:1); 61.8 mg, yield 95%. ¹H NMR (300 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 17.7, 7.7 Hz, 3H), 6.99 (m, 1H), 2.37 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 167.94 (d, *J* = 3Hz) 163.44 (d, *J* = 10.5Hz), 160.09 (d, *J* = 10.5Hz), 156.46 (d, *J* = 13.5Hz), 154.95 (d, *J* = 13.5Hz), 146.37, 139.78 – 139.10 (m), 134.85, 130.34, 129.18, 104.44 – 103.51(m), 21.82. ¹⁹F NMR (282 MHz, Chloroform-*d*) δ -106.58, -113.19. HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₀F₂NO₂S₂ 326.0116; Found: 326.0119.

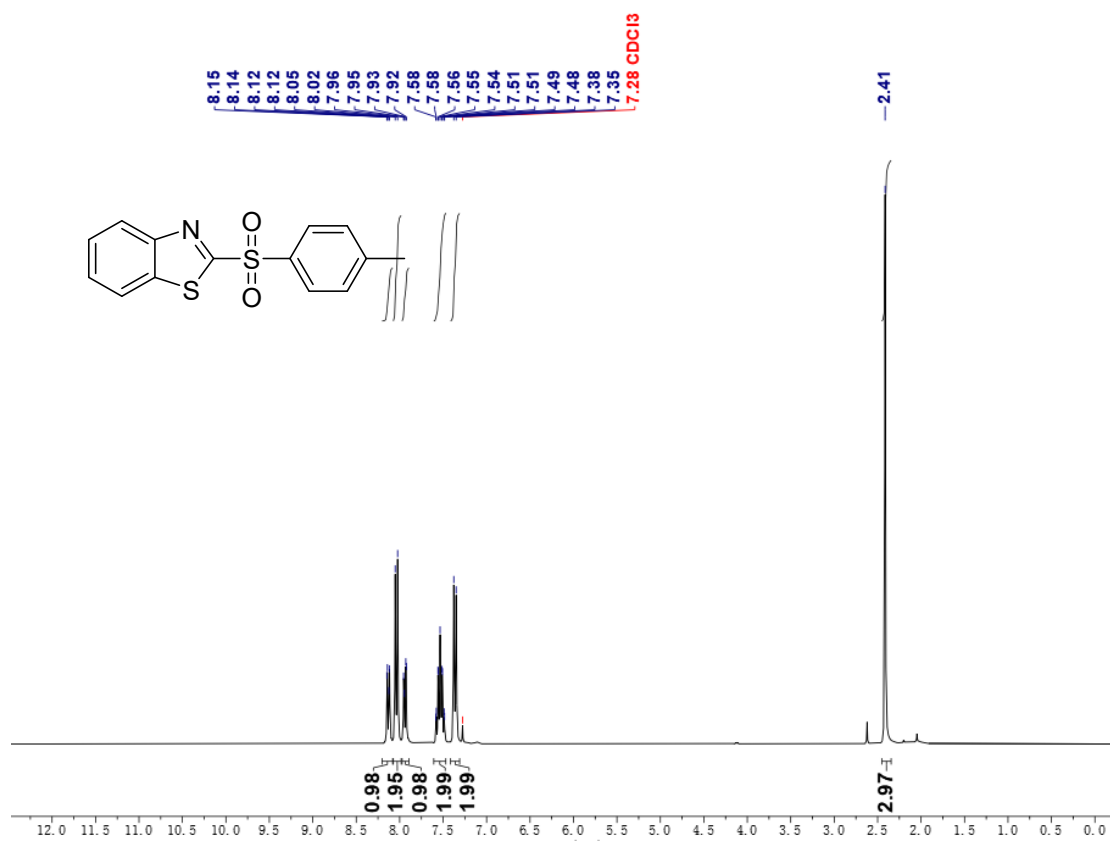
3. Copies of NMR spectra of products 3



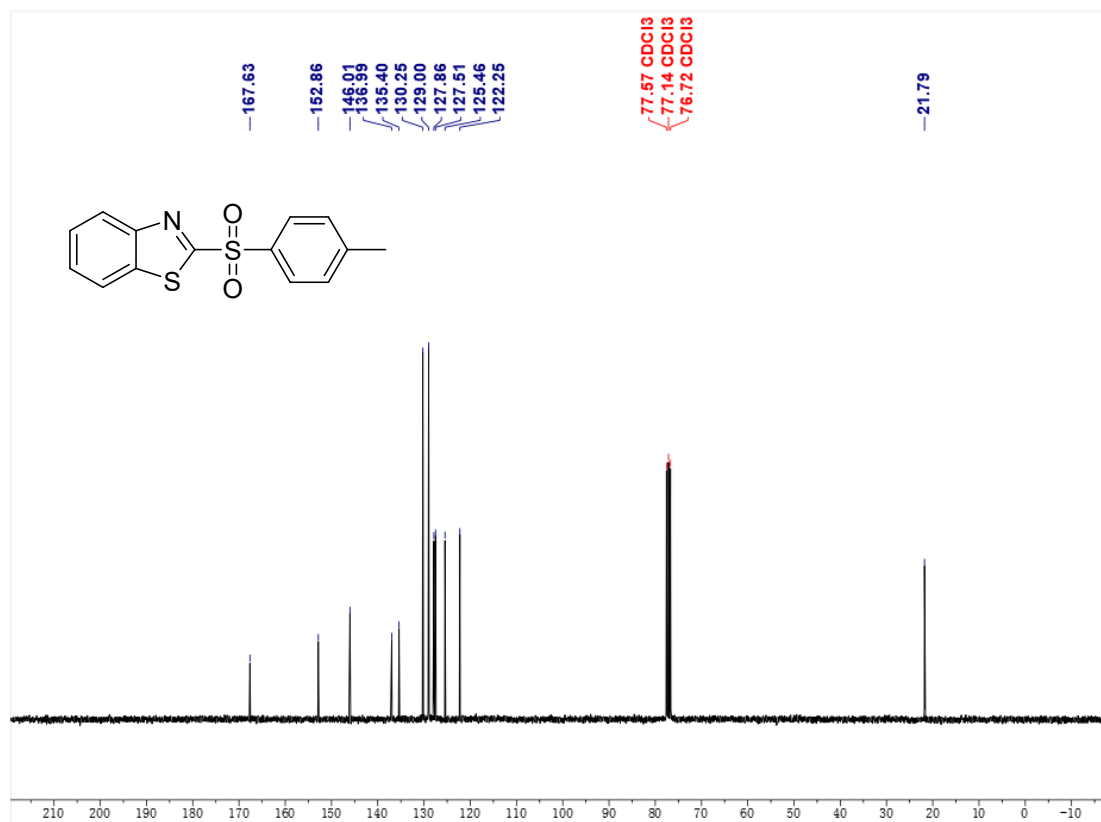
¹H NMR (300 MHz, CDCl₃) of 3aa.



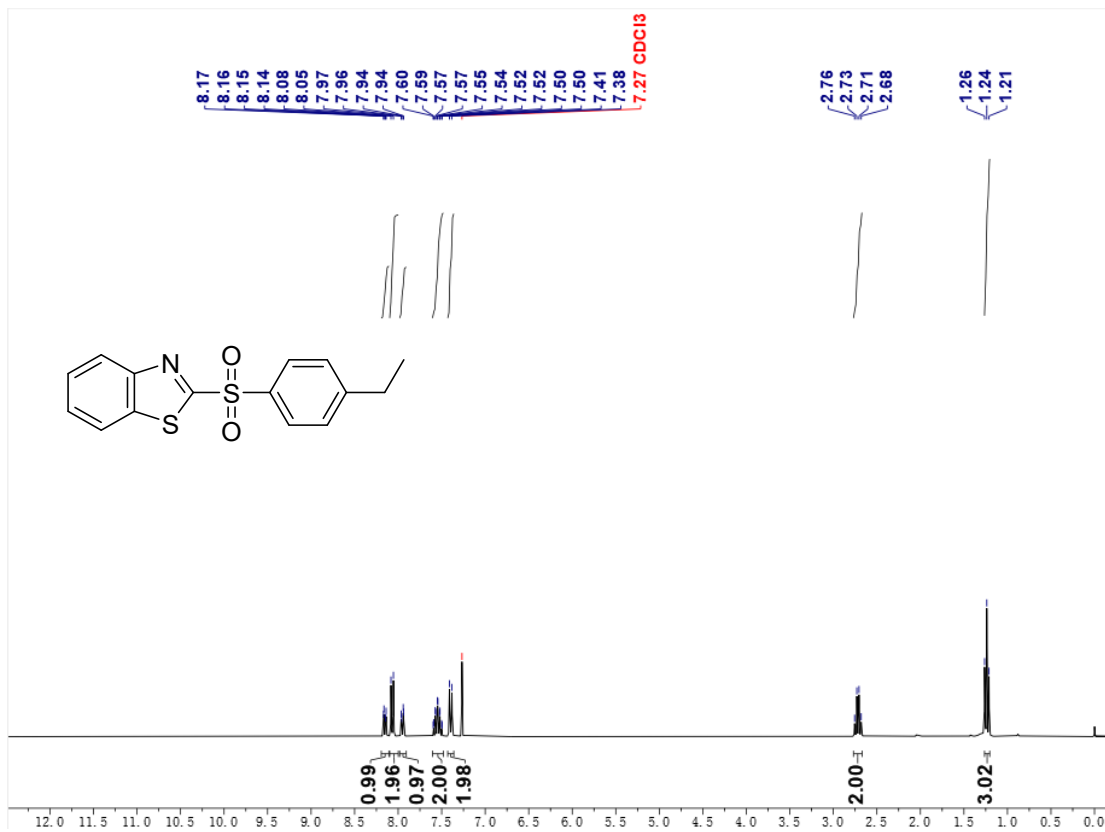
¹³C NMR (75 MHz, CDCl₃) of 3aa.



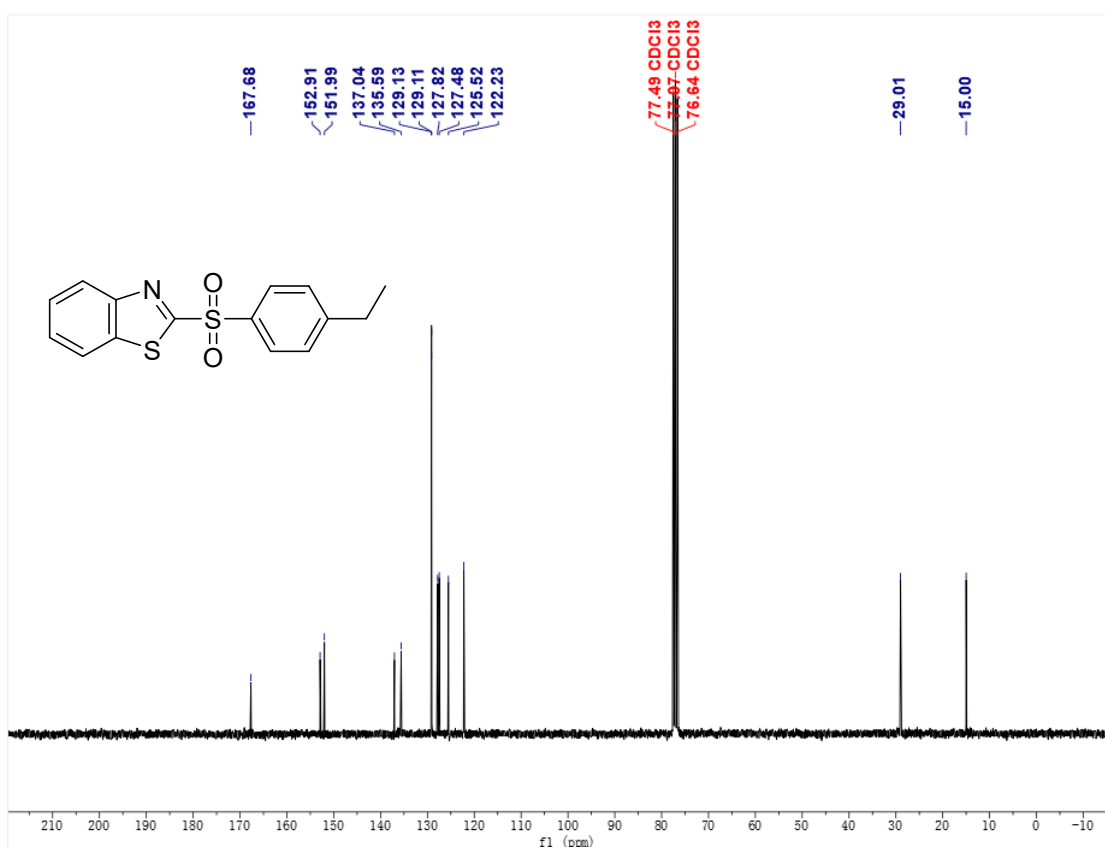
¹H NMR (300 MHz, CDCl₃) of **3ab**.



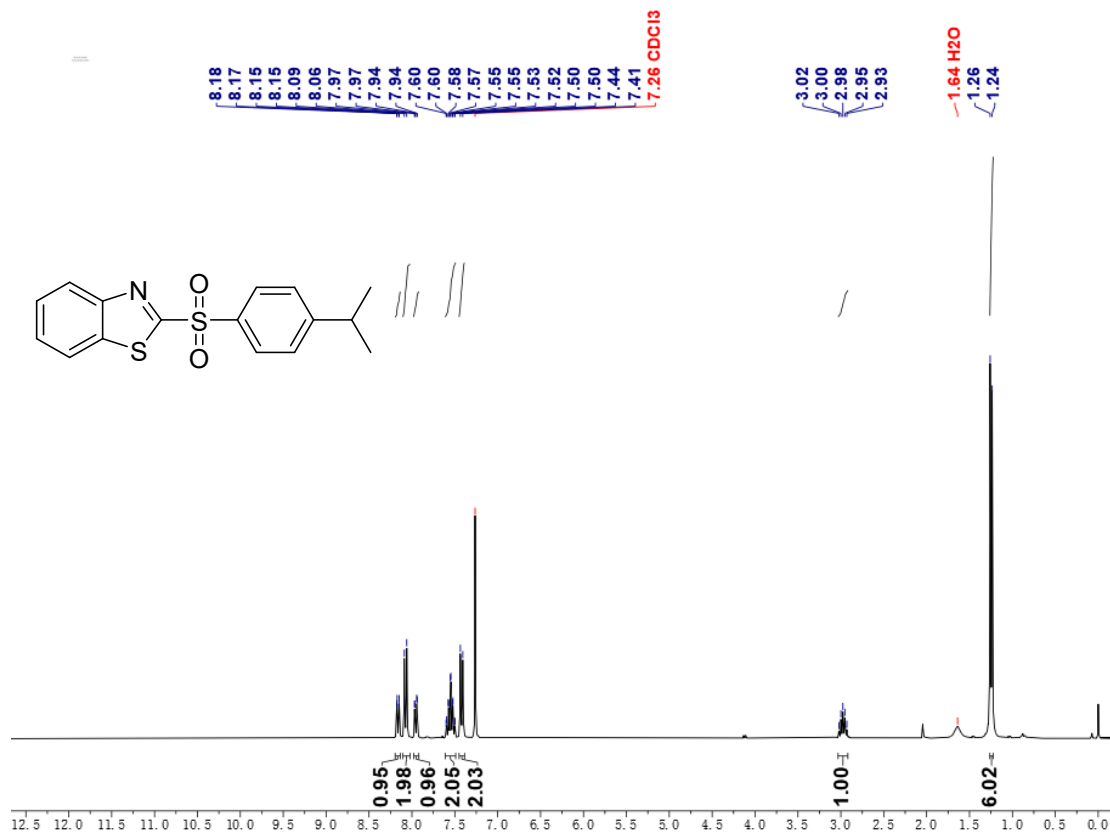
¹³C NMR (75 MHz, CDCl₃) of **3ab**.



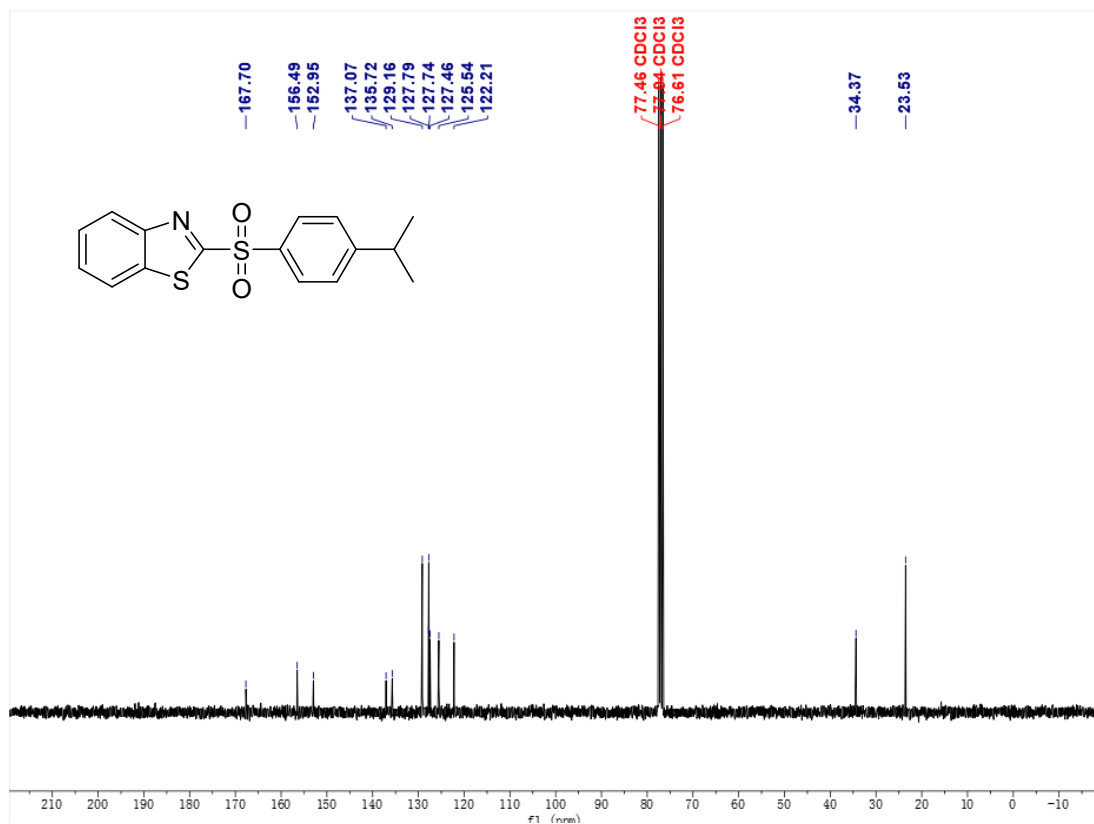
¹H NMR (300 MHz, CDCl₃) of 3ac.



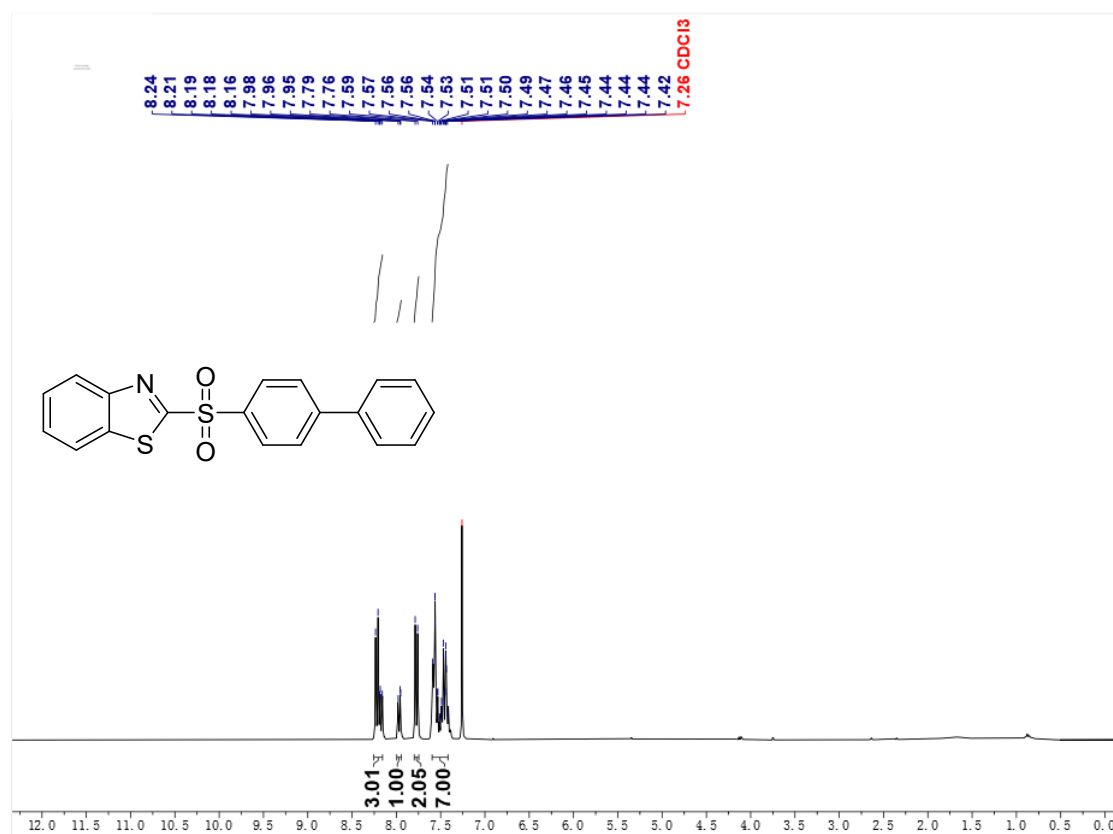
¹³C NMR (75 MHz, CDCl₃) of 3ac.



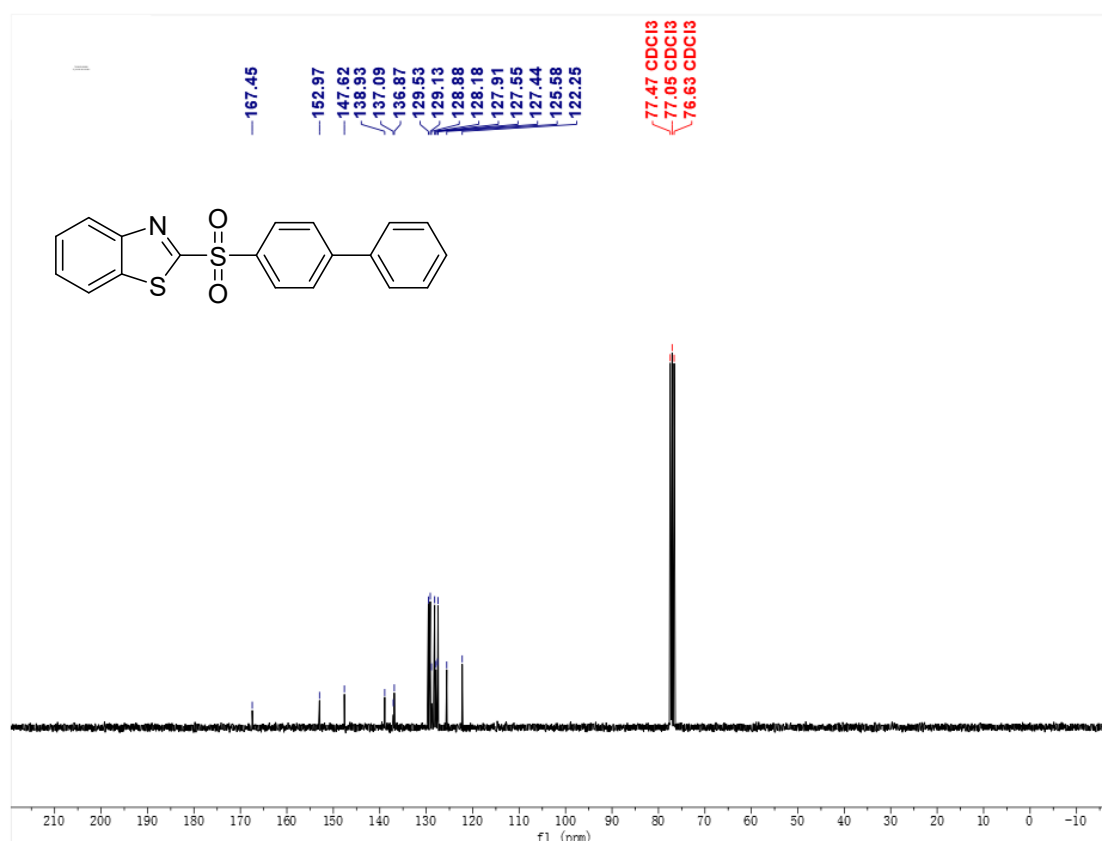
¹H NMR (300 MHz, CDCl₃) of **3ad**.



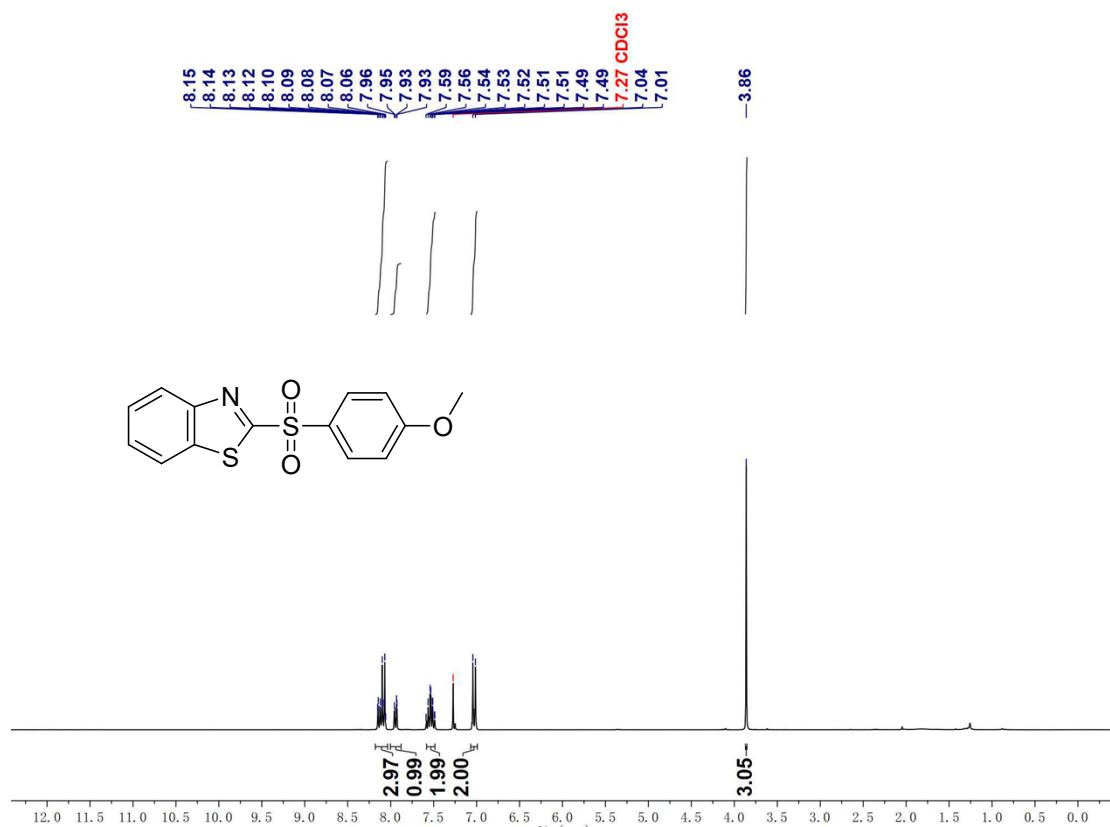
¹³C NMR (75 MHz, CDCl₃) of **3ad**.



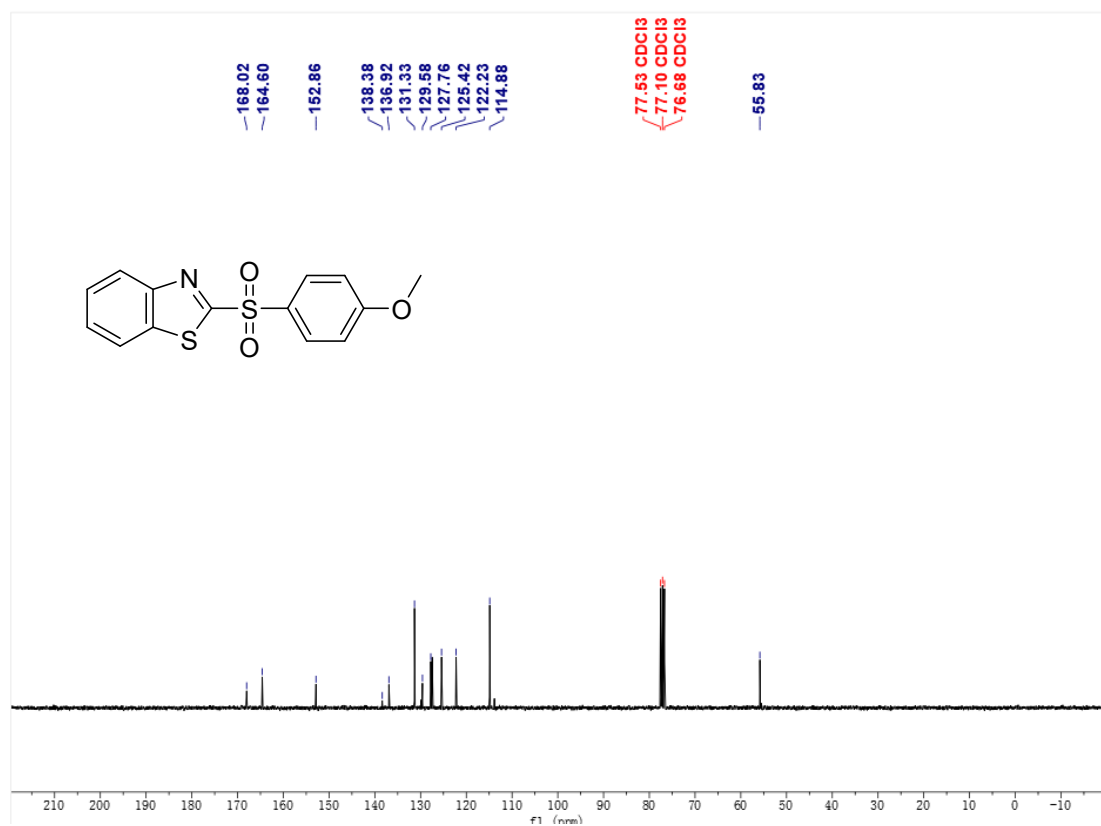
¹H NMR (300 MHz, CDCl₃) of 3ae.



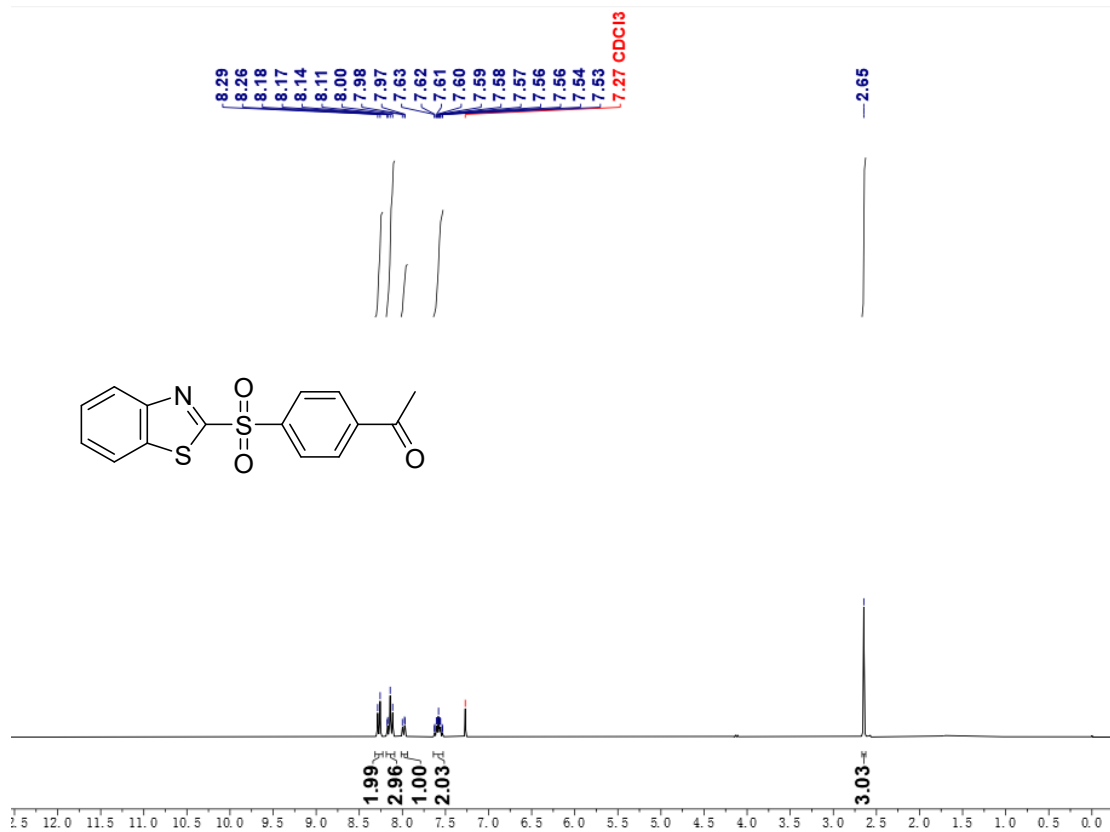
¹³C NMR (75 MHz, CDCl₃) of 3ae.



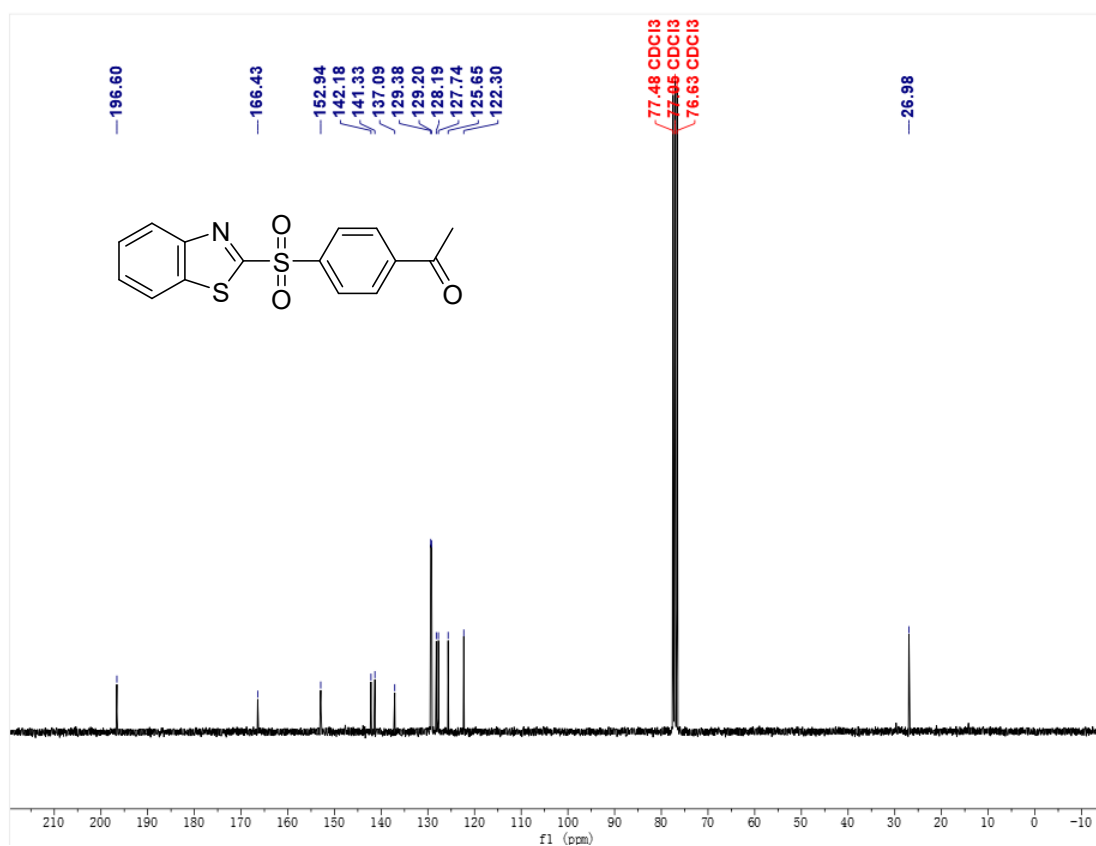
¹H NMR (300 MHz, CDCl₃) of 3af.



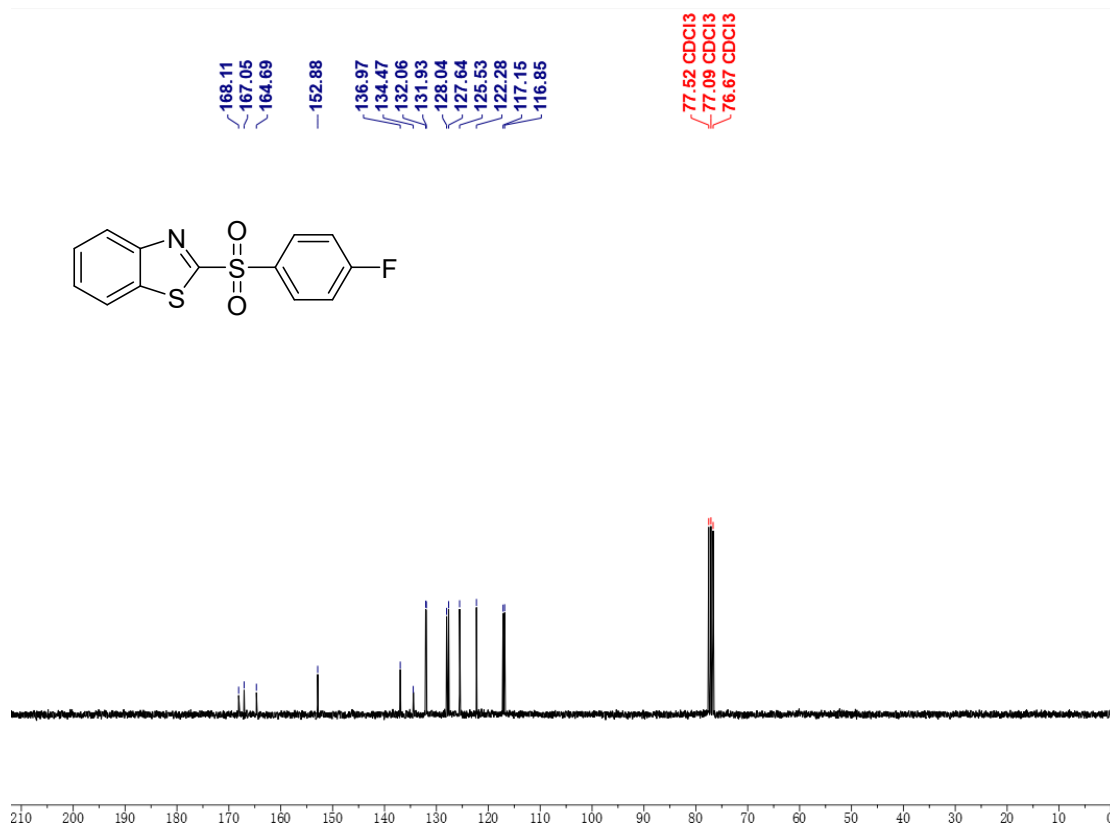
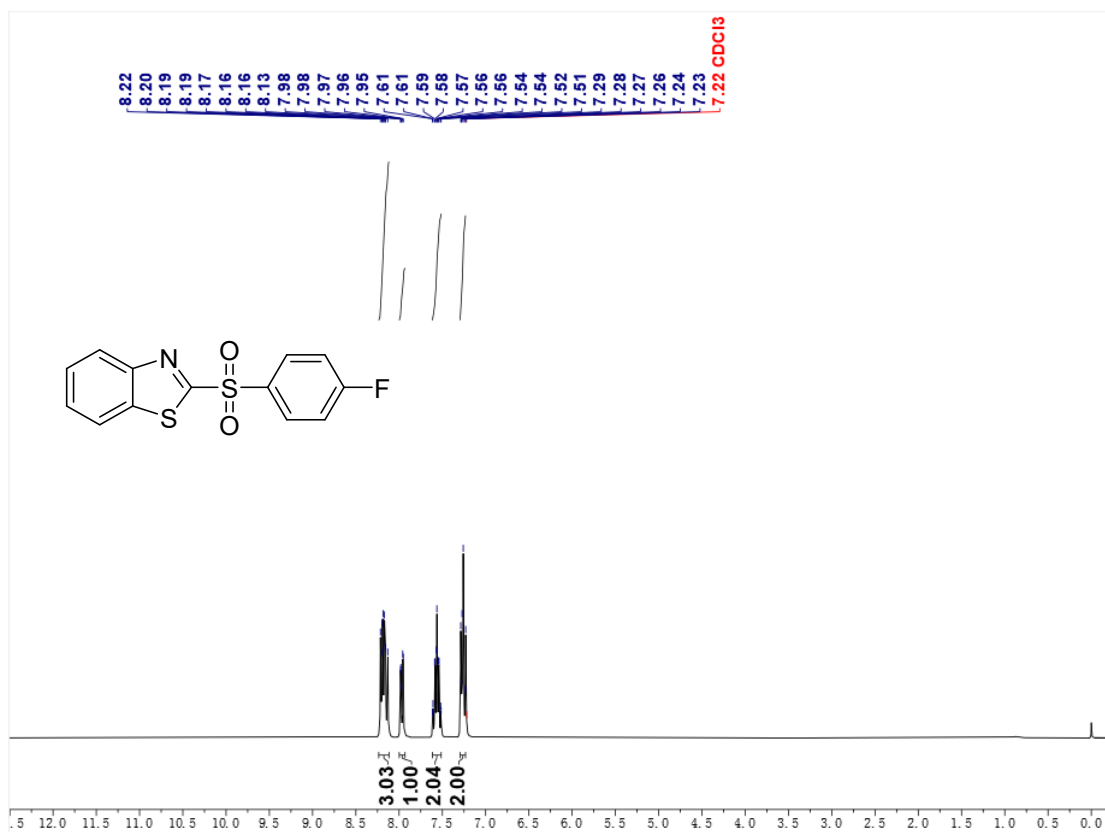
¹³C NMR (75 MHz, CDCl₃) of 3af.

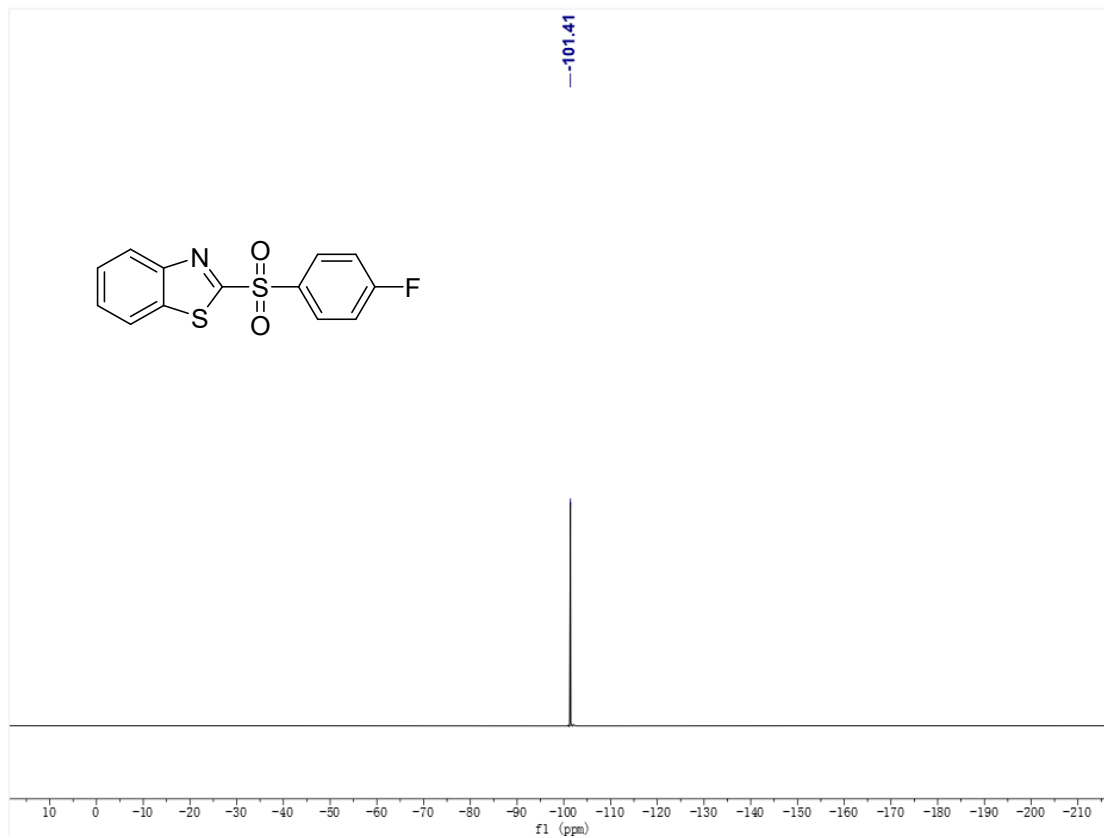


¹H NMR (300 MHz, CDCl₃) of **3ag**.

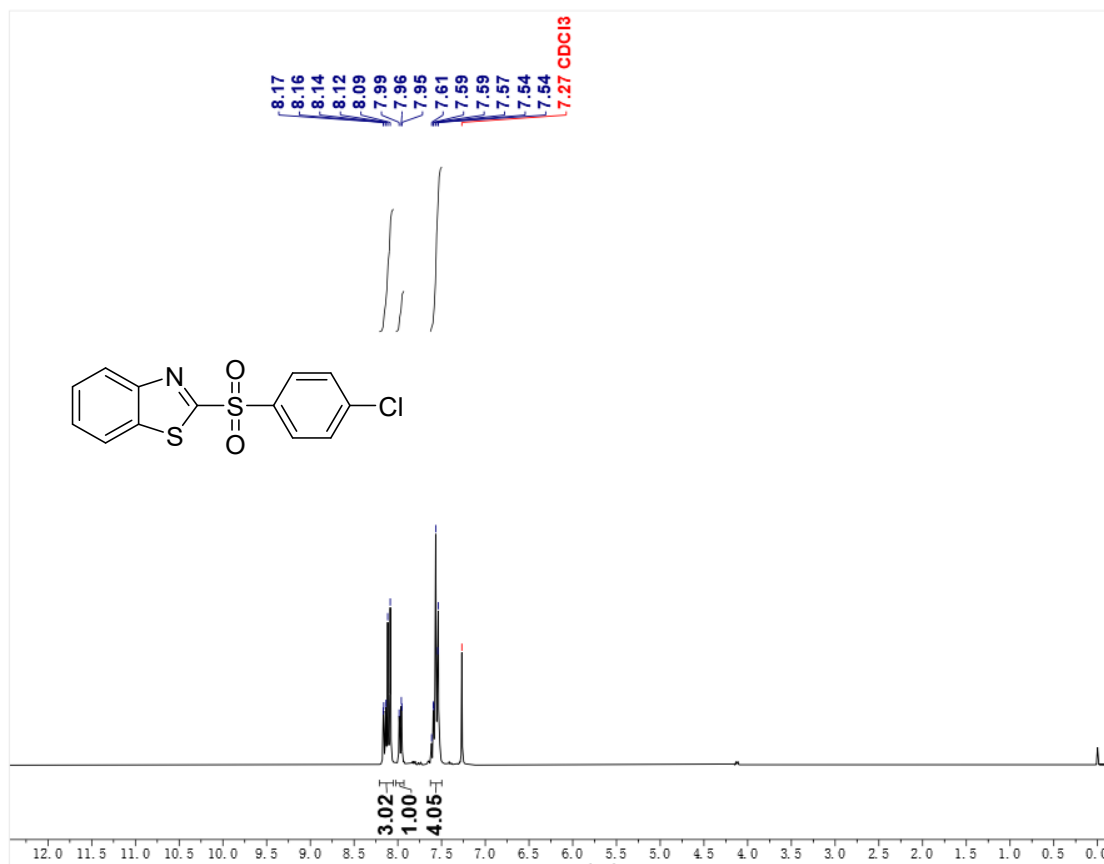


¹³C NMR (75 MHz, CDCl₃) of **3ag**.

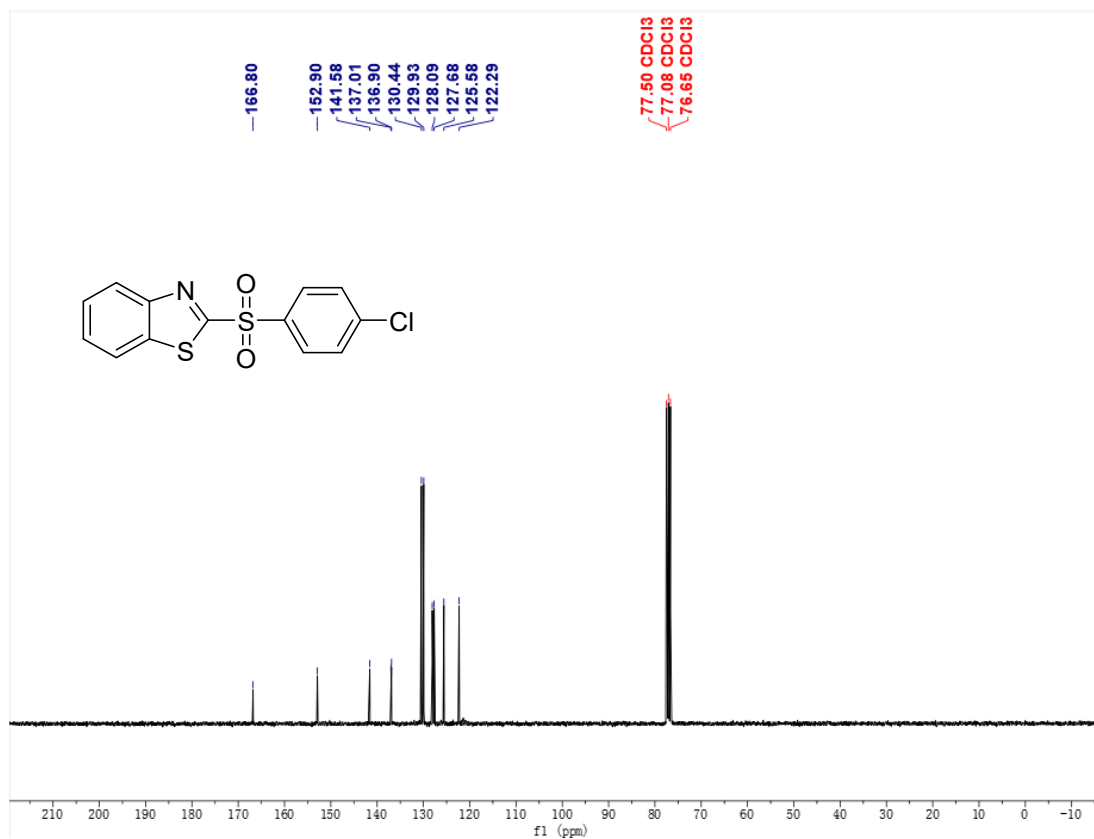




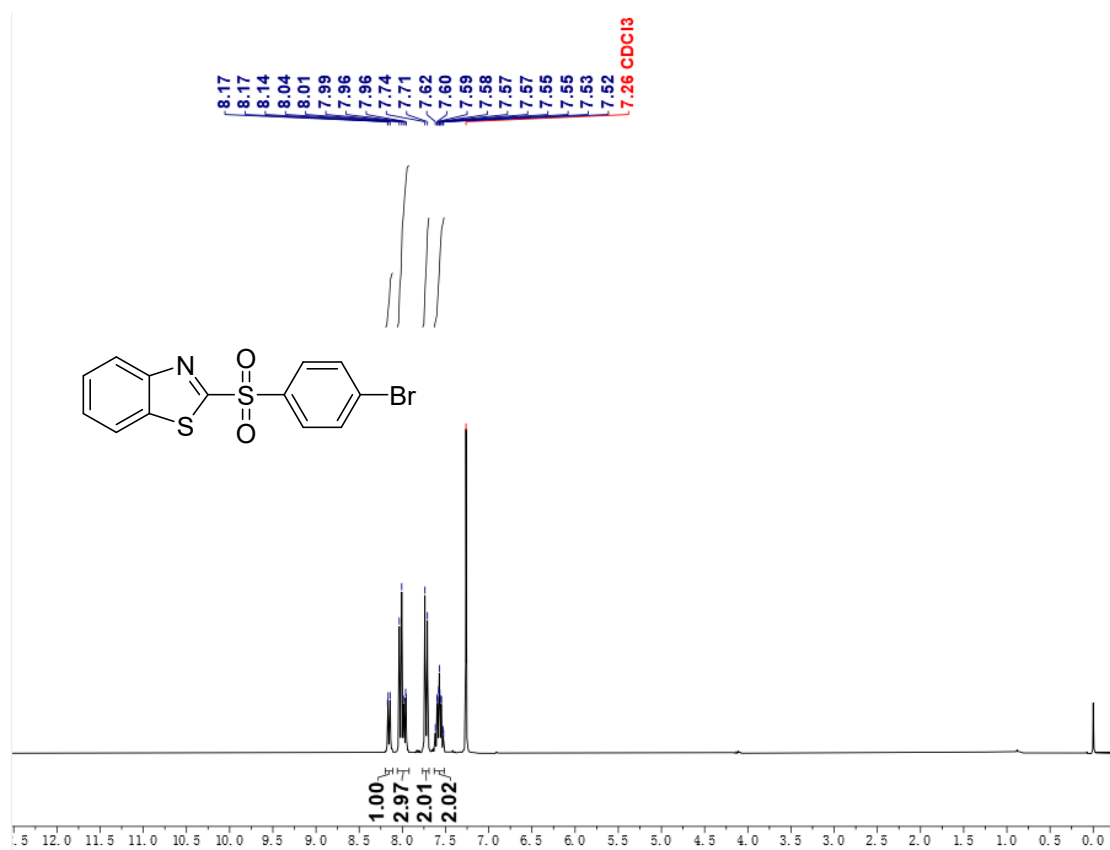
^{19}F NMR (282 MHz, CDCl_3) of **3ah**.



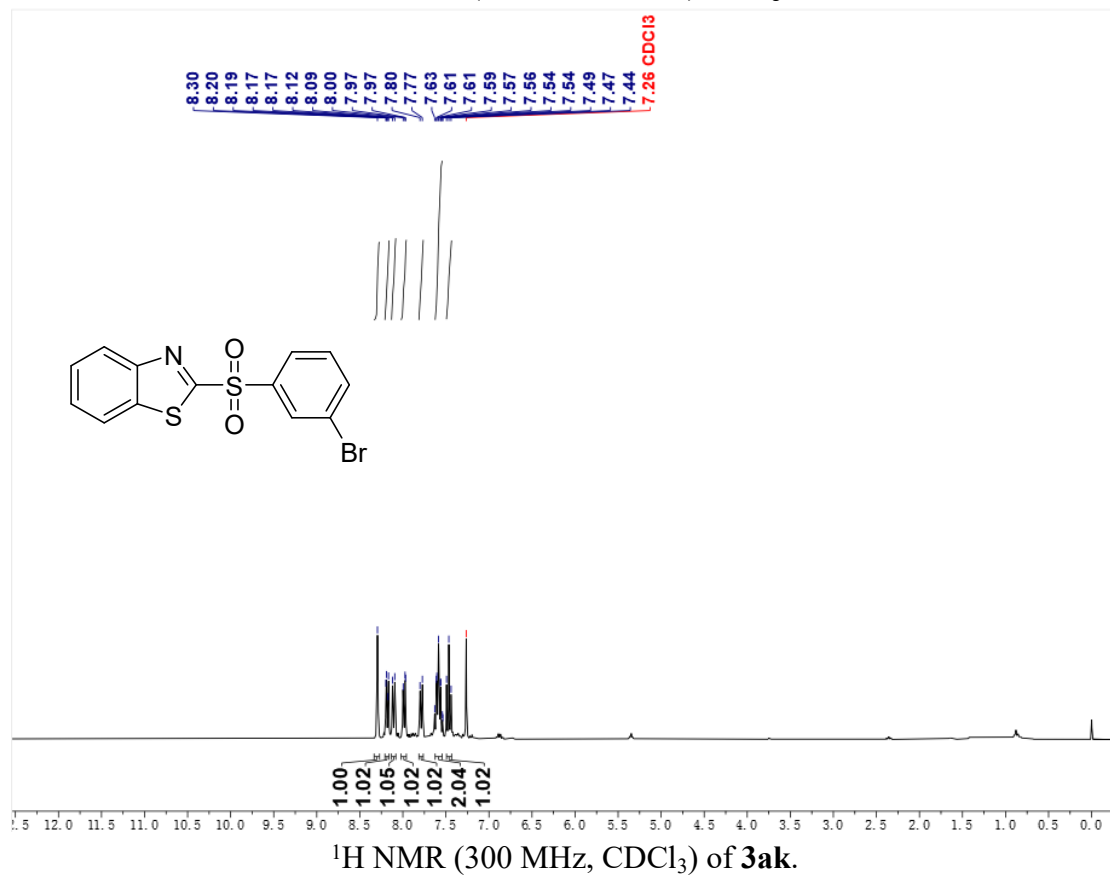
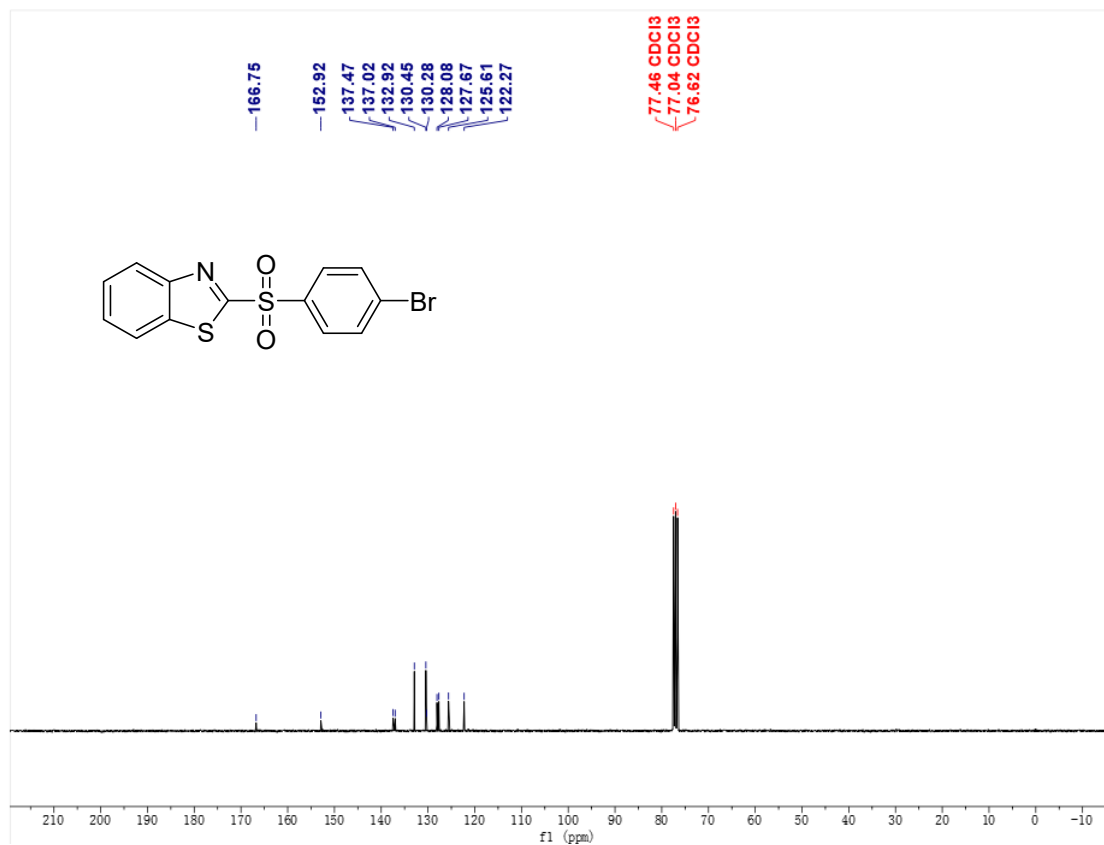
^1H NMR (300 MHz, CDCl_3) of **3ai**.

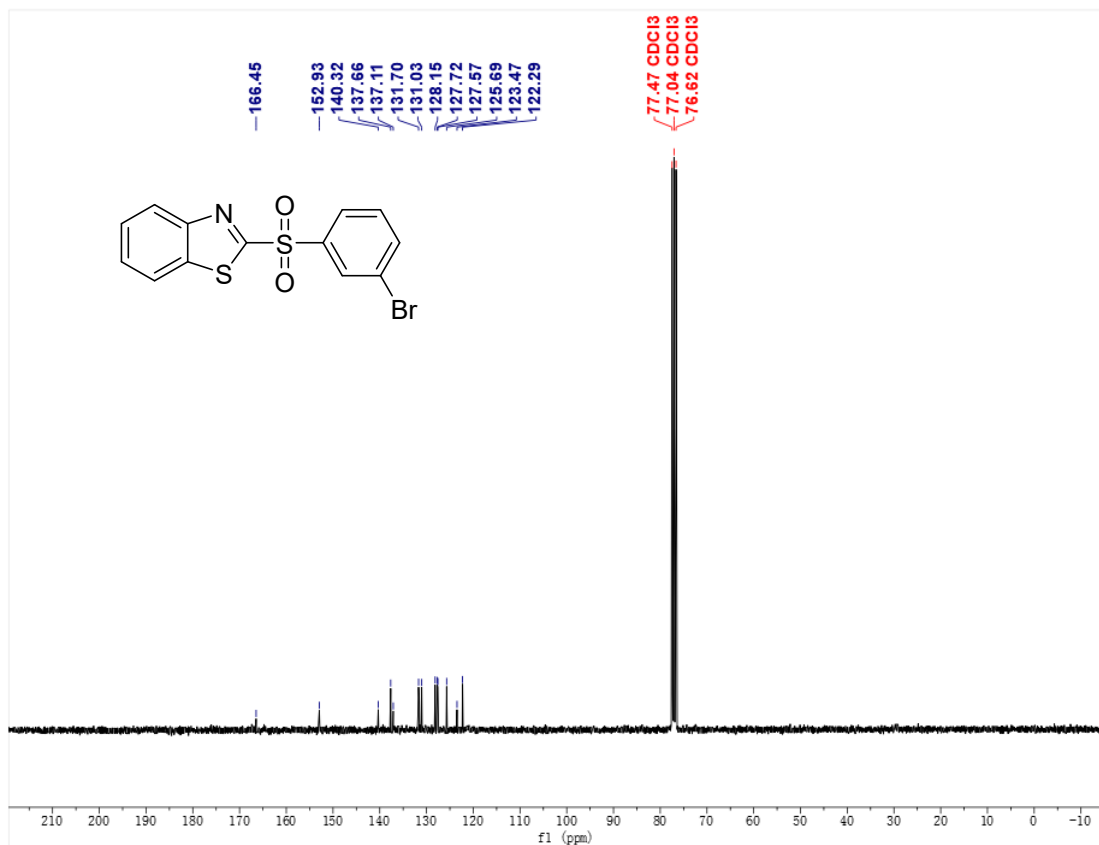


¹³C NMR (75 MHz, CDCl₃) of **3ai**.

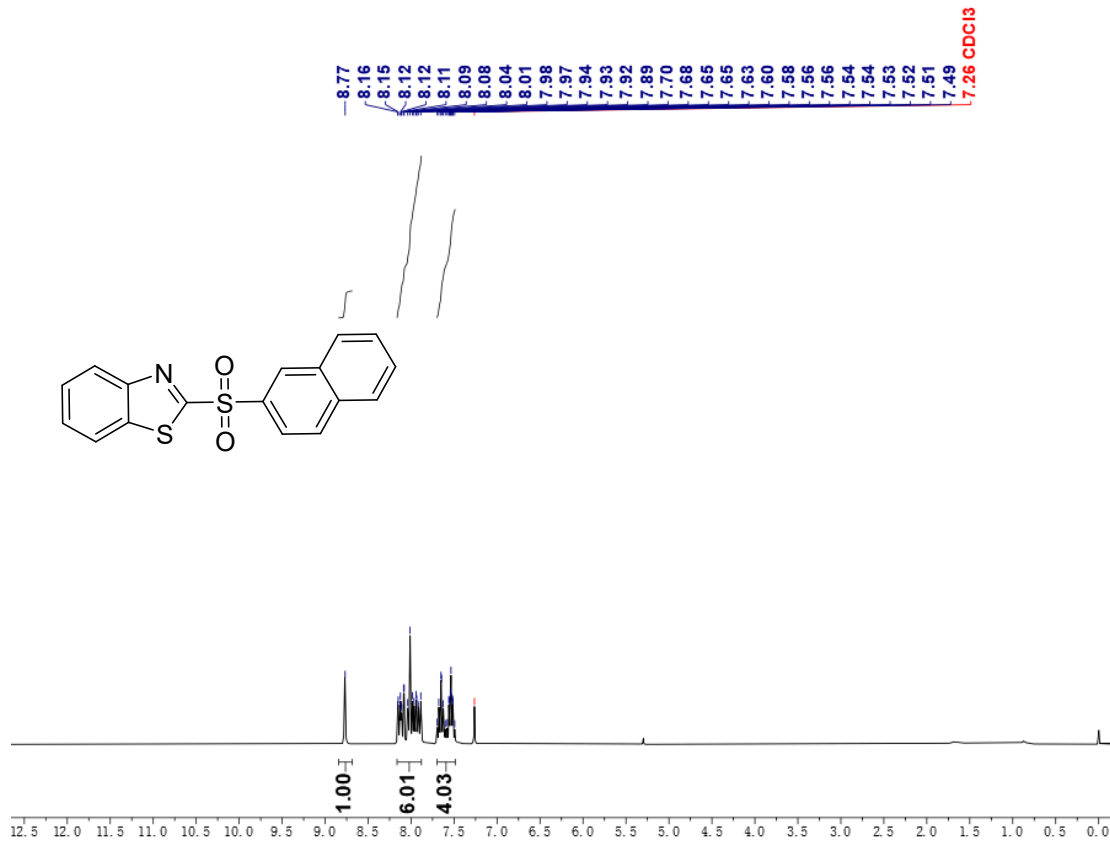


¹H NMR (300 MHz, CDCl₃) of **3aj**.

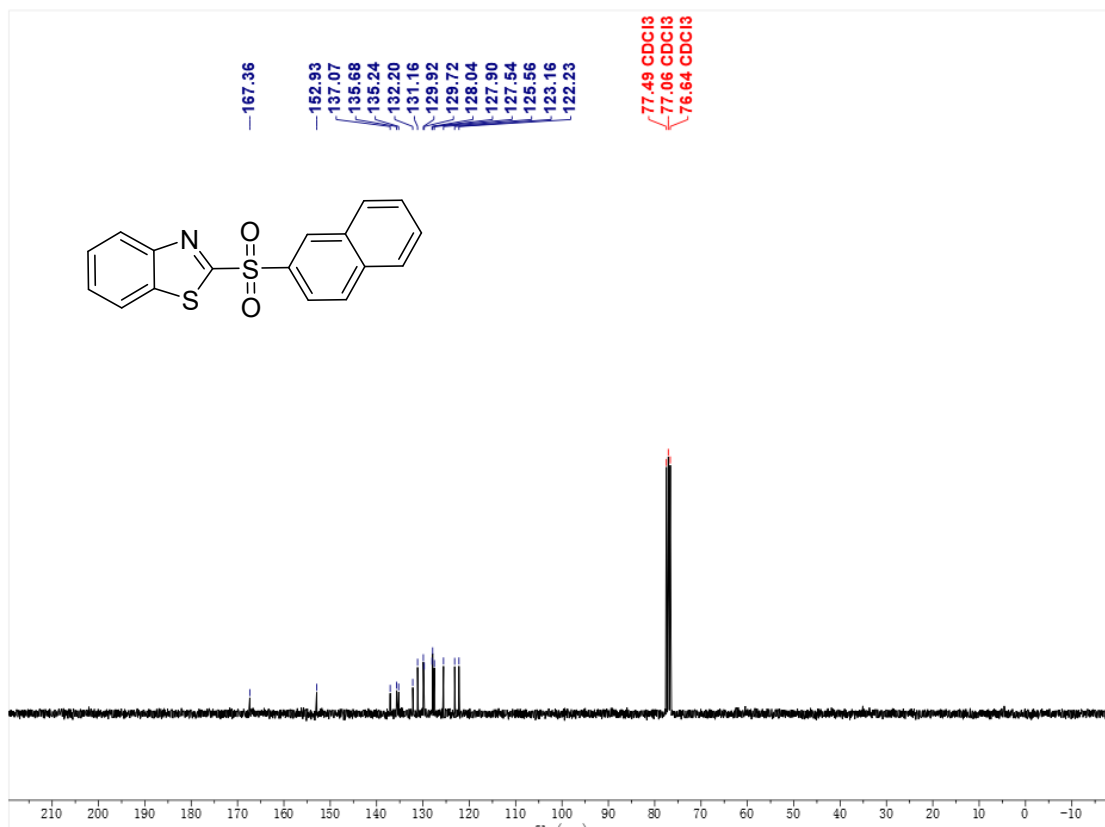




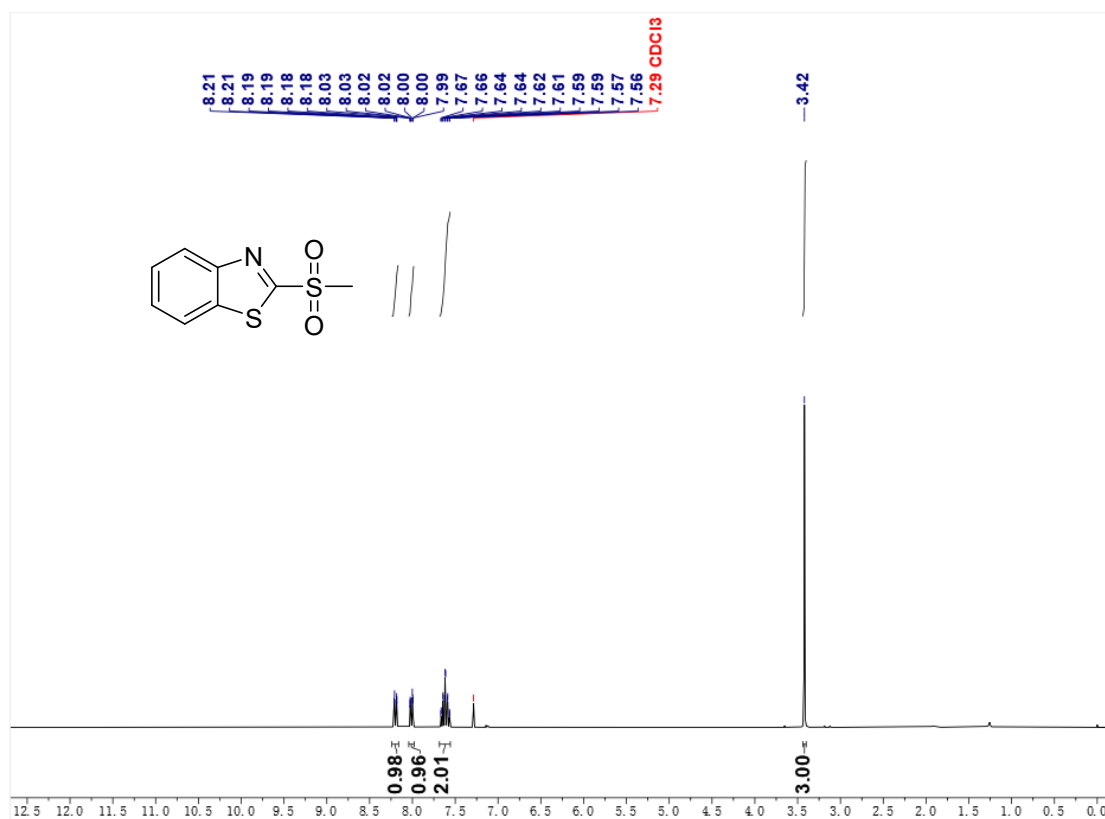
¹³C NMR (75 MHz, CDCl₃) of **3ak**.



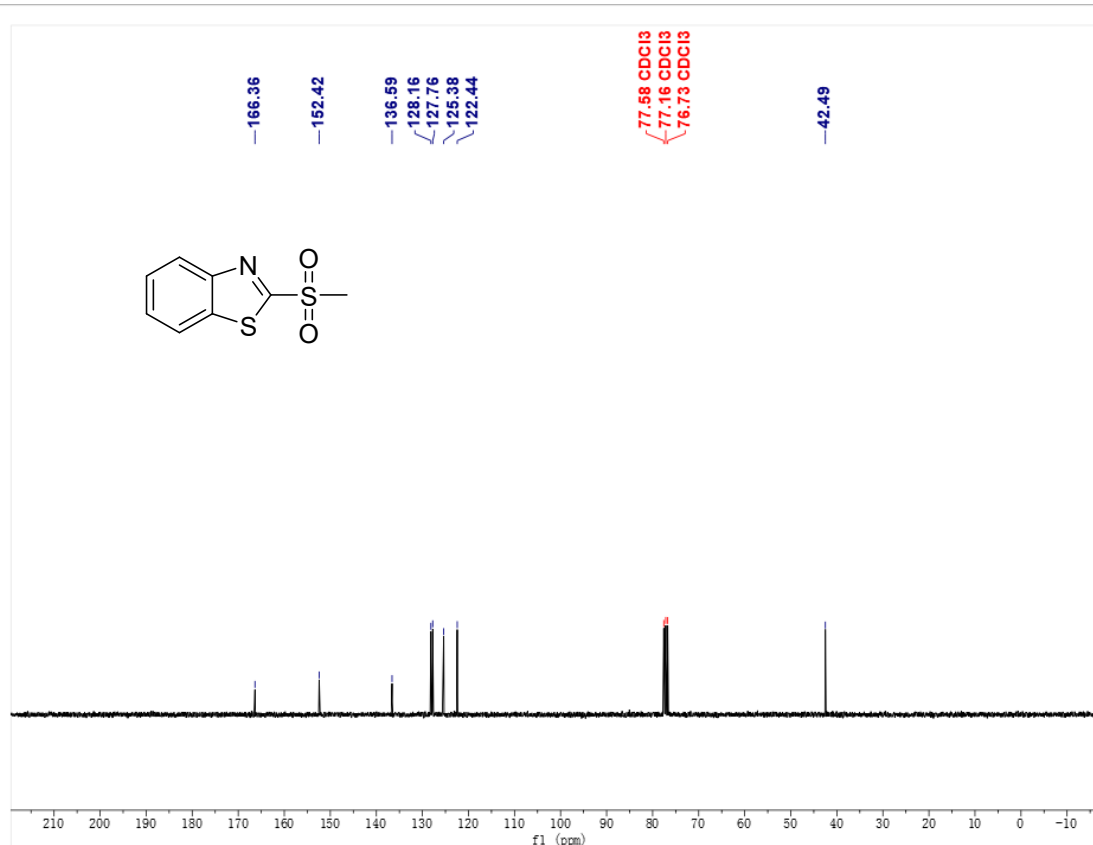
¹H NMR (300 MHz, CDCl₃) of **3al**.



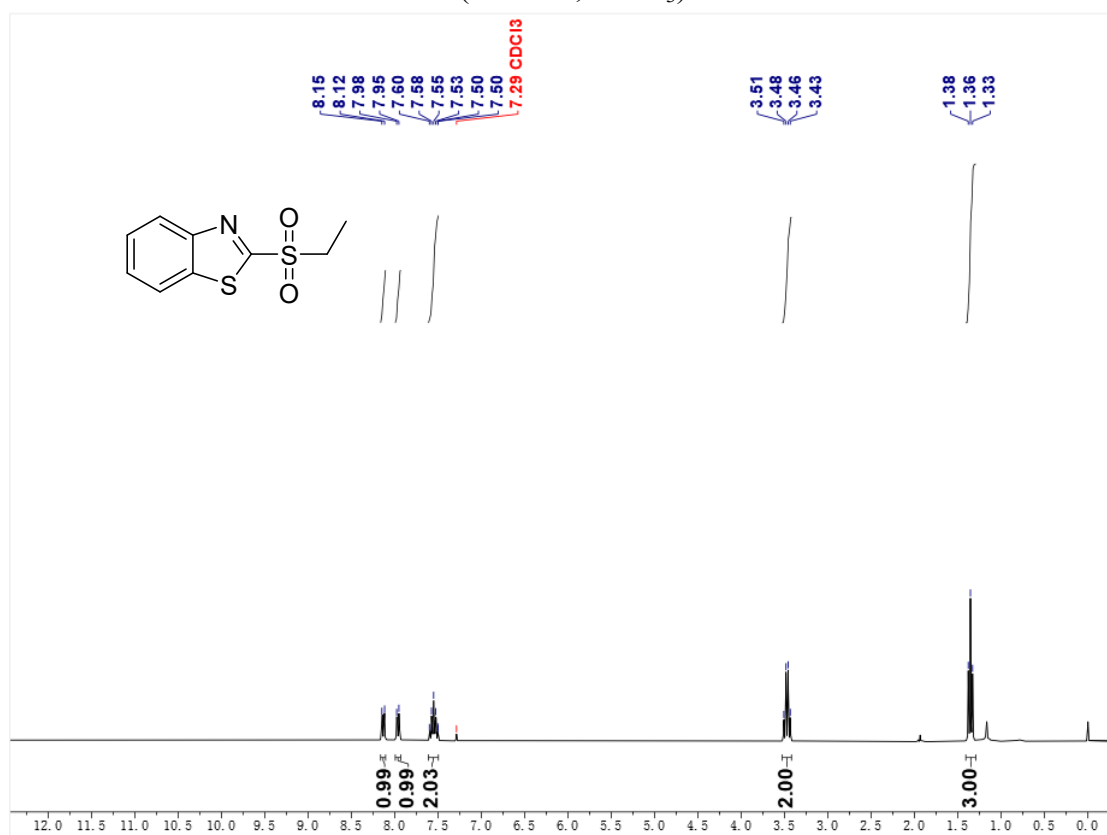
¹³C NMR (75 MHz, CDCl₃) of 3al.



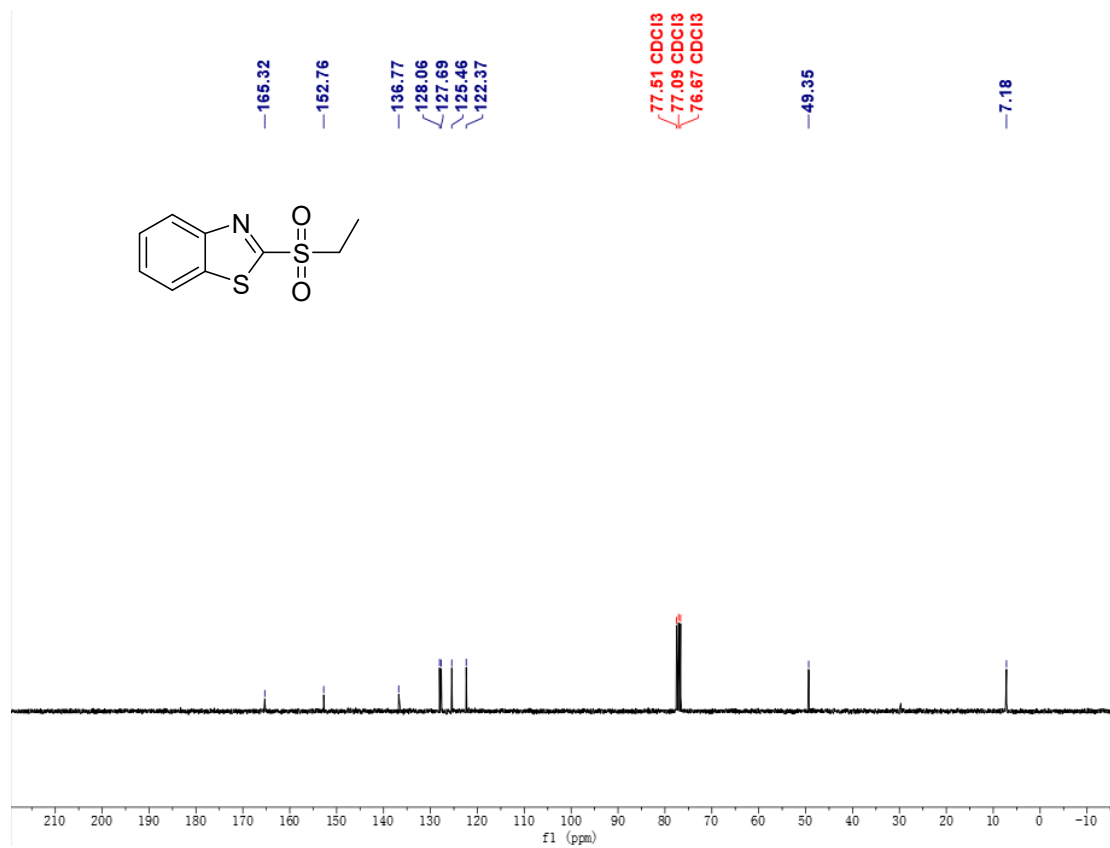
¹H NMR (300 MHz, CDCl₃) of 3am.



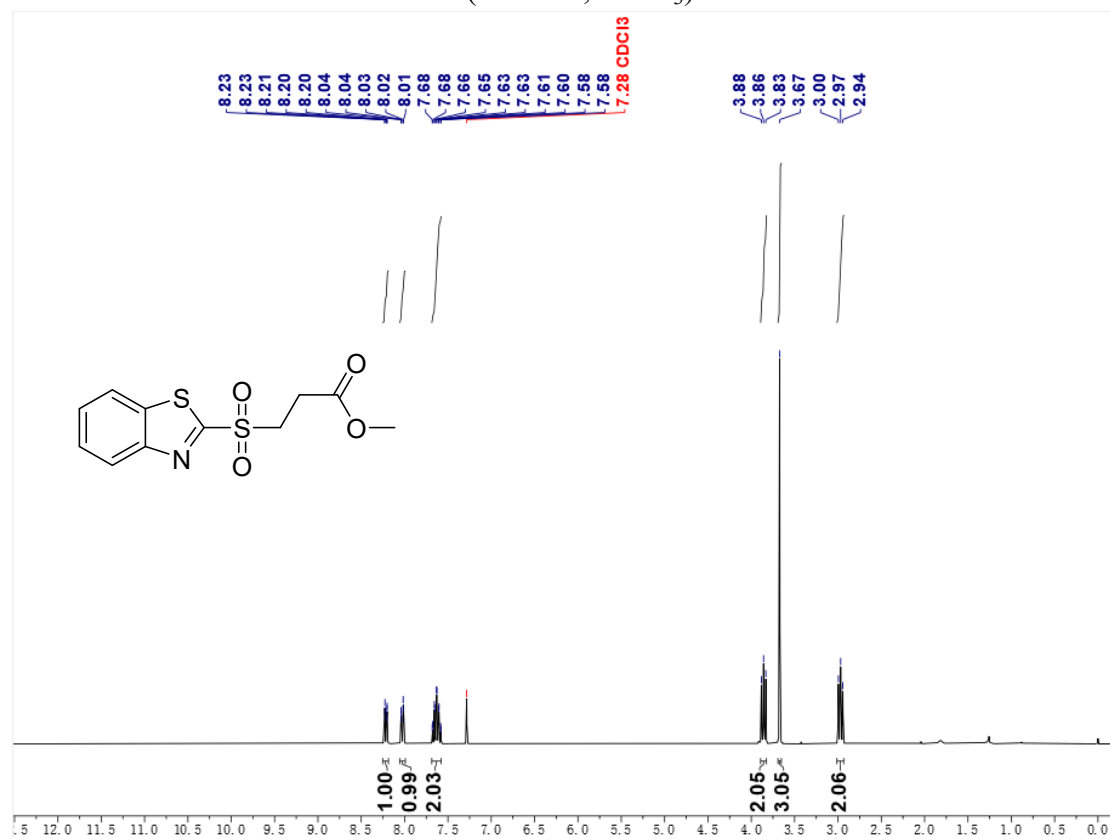
^{13}C NMR (75 MHz, CDCl_3) of **3am**.



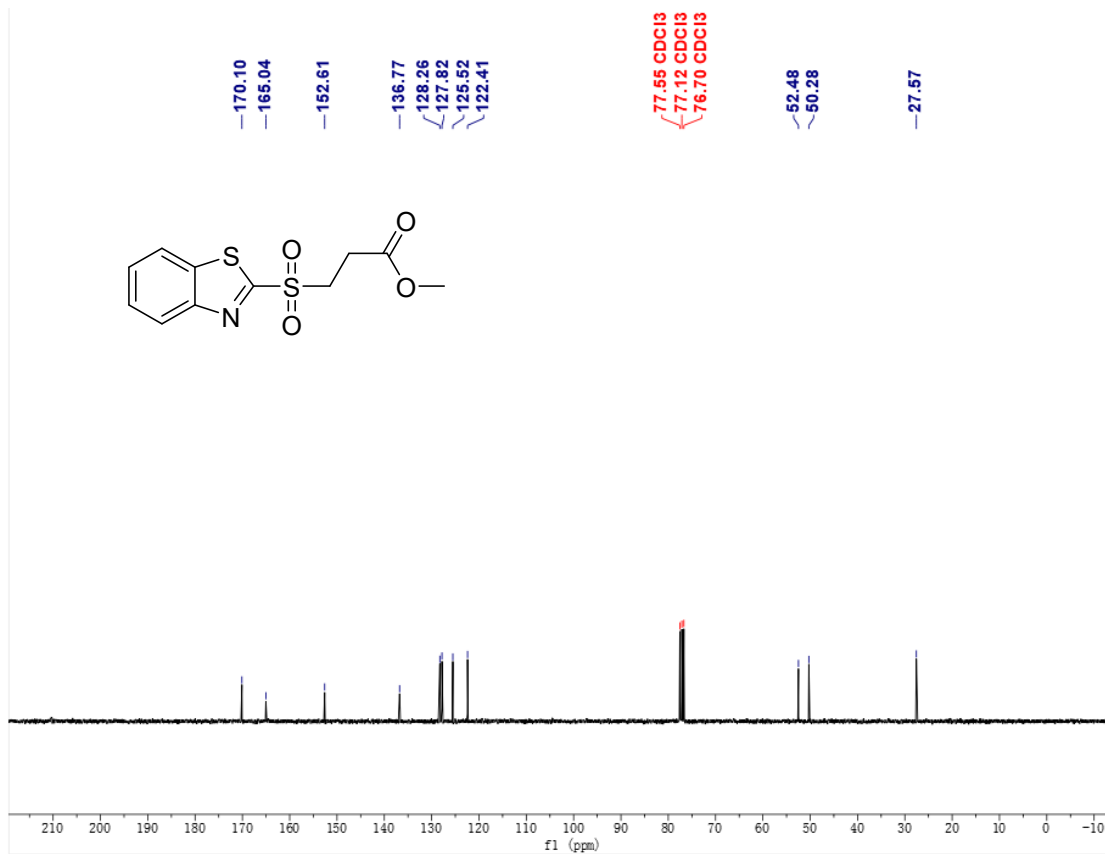
^1H NMR (300 MHz, CDCl_3) of **3an**.



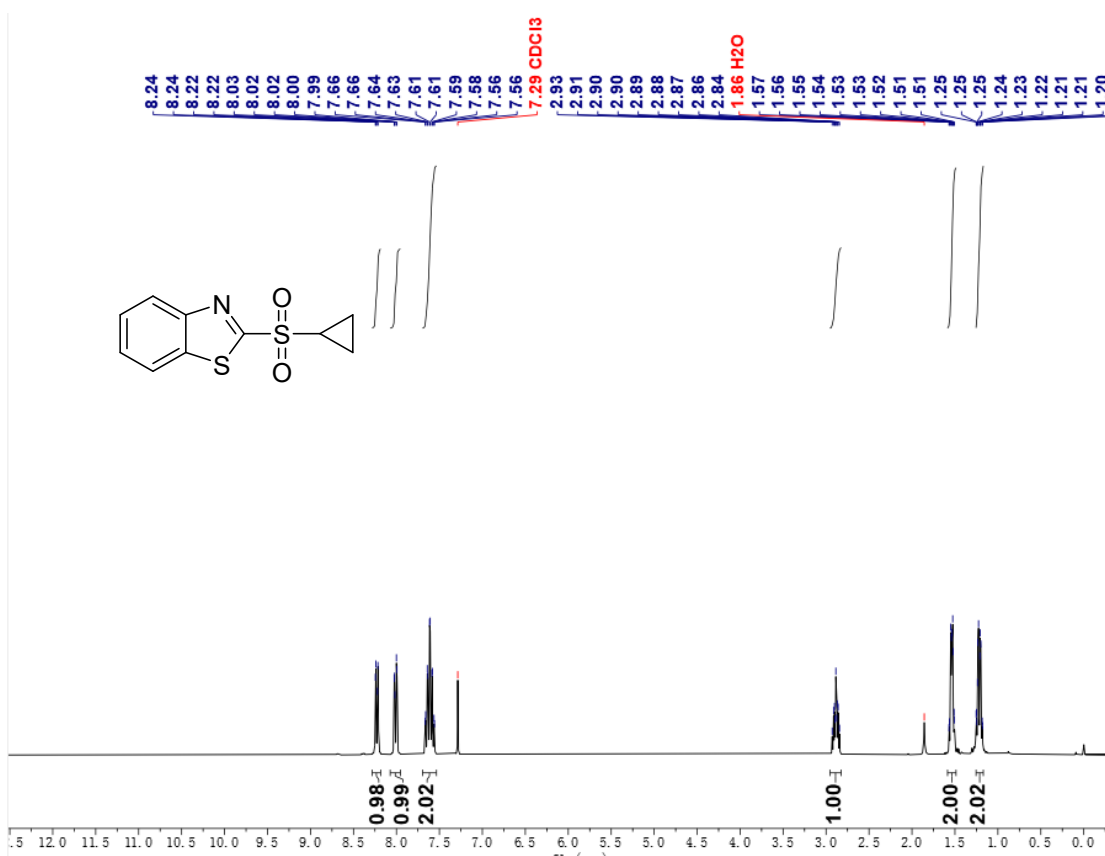
¹³C NMR (75 MHz, CDCl₃) of **3an**.



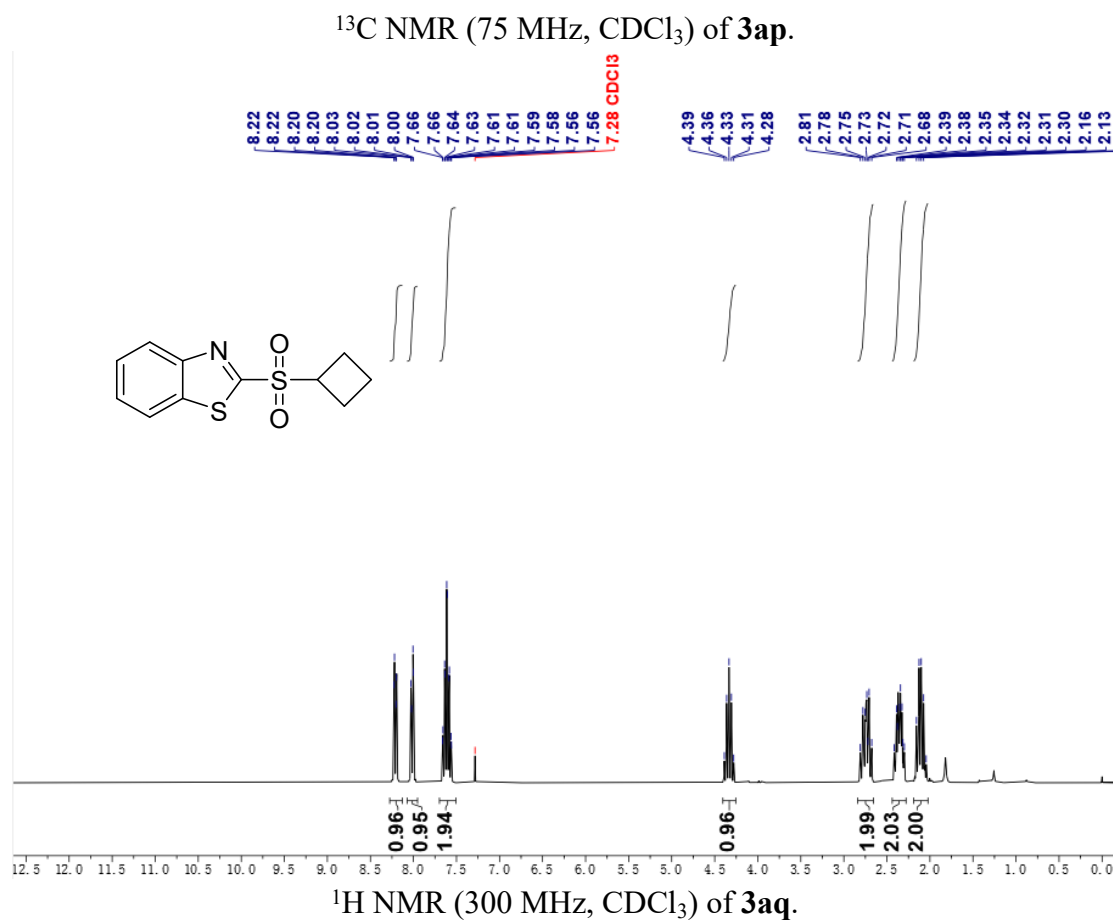
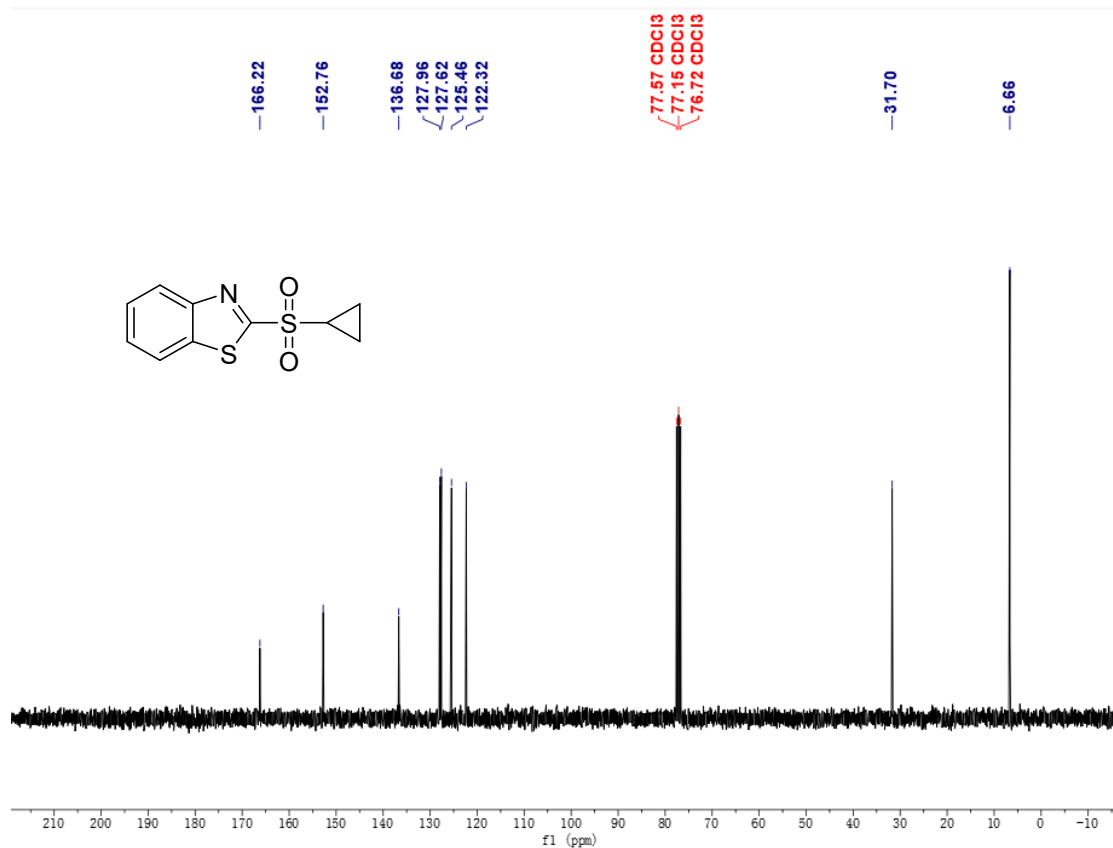
¹H NMR (300 MHz, CDCl₃) of **3ao**.

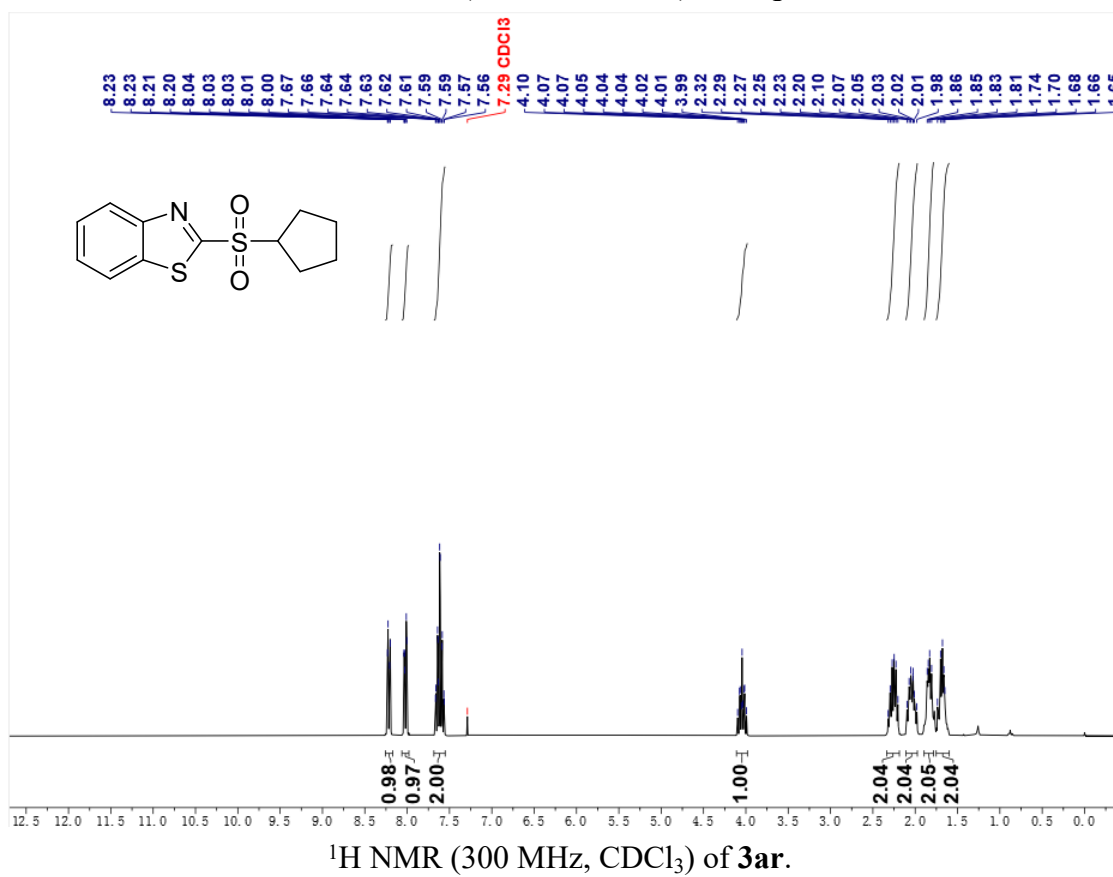
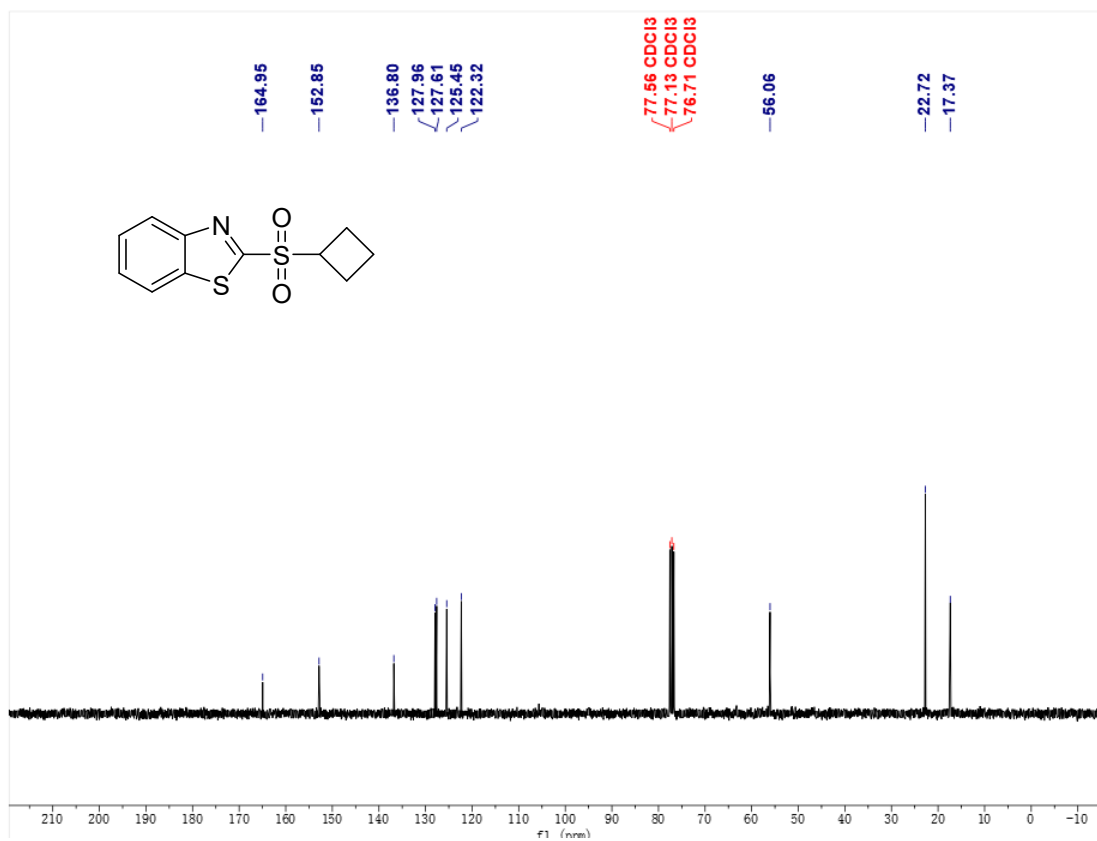


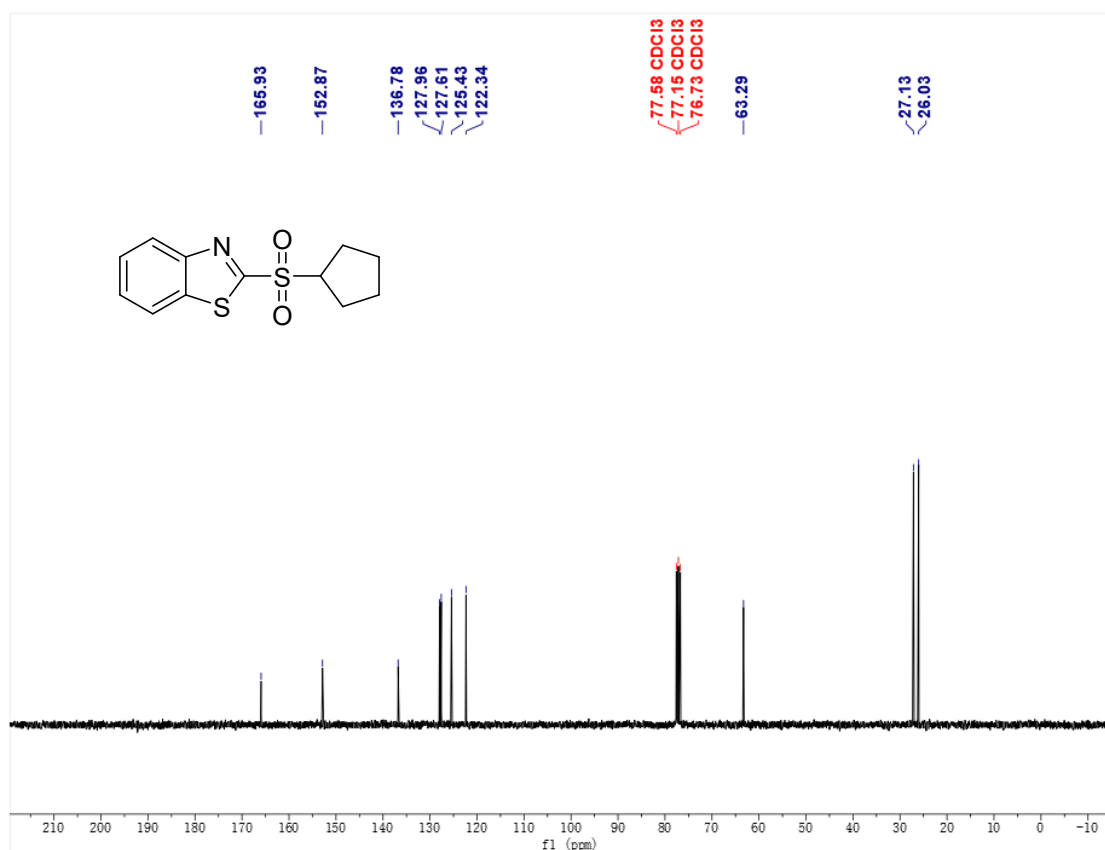
¹³C NMR (75 MHz, CDCl₃) of 3ao.



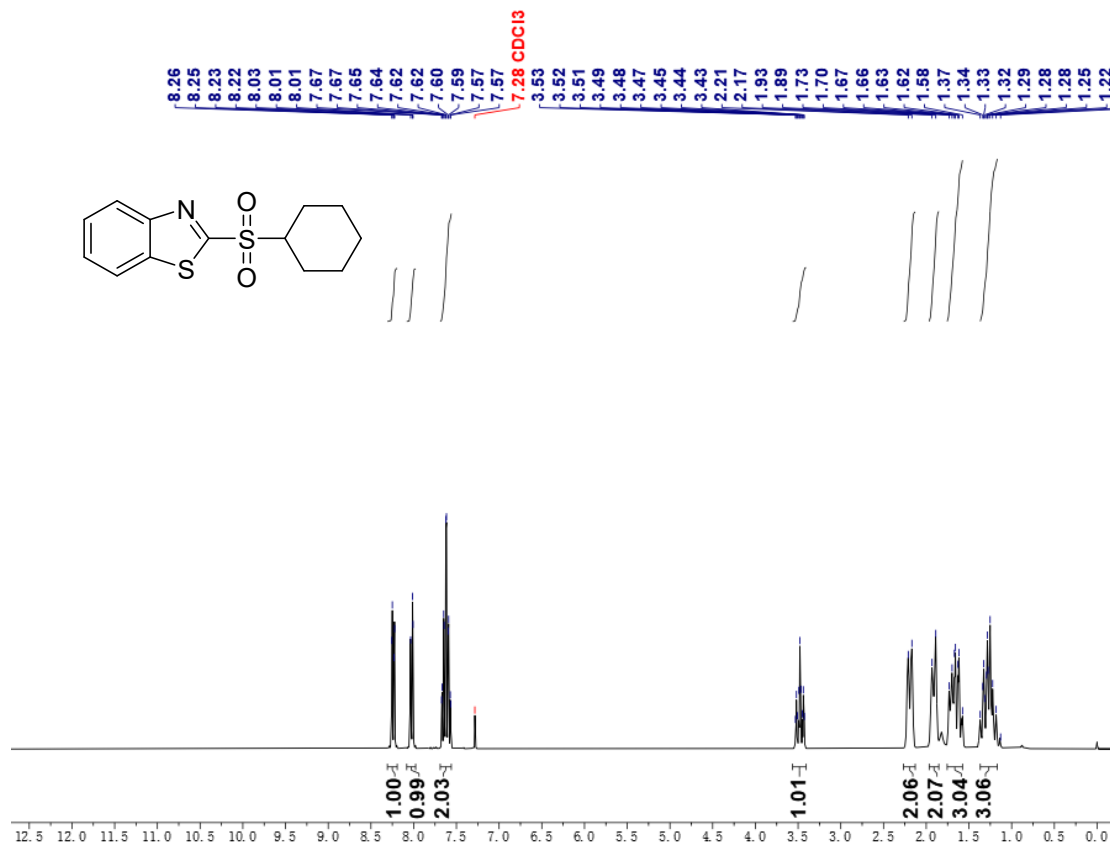
¹H NMR (300 MHz, CDCl₃) of 3ap.



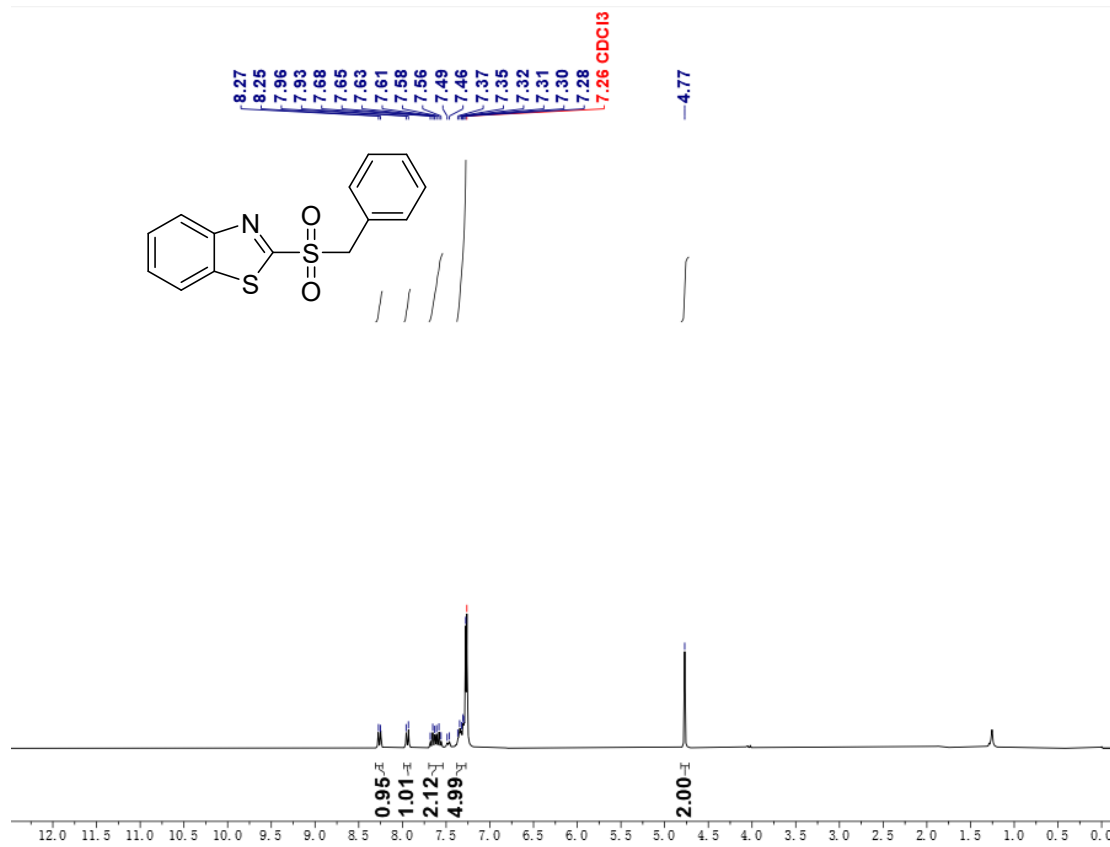
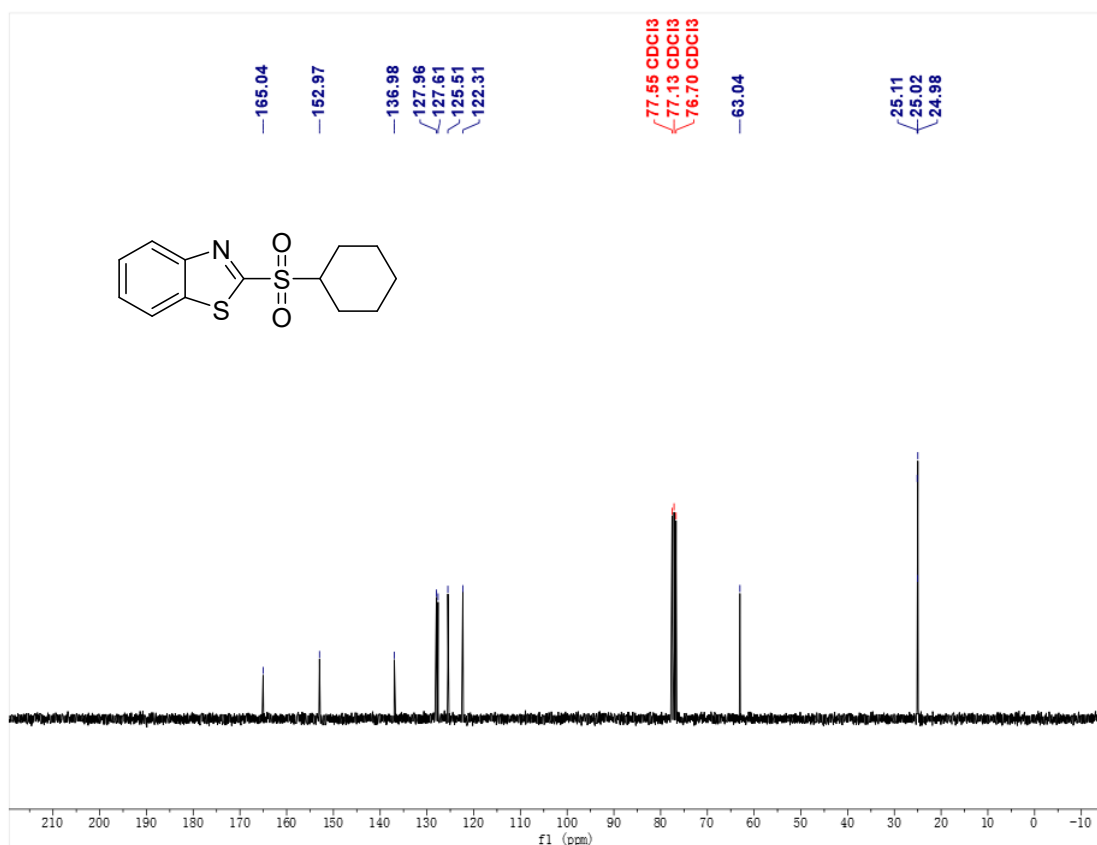


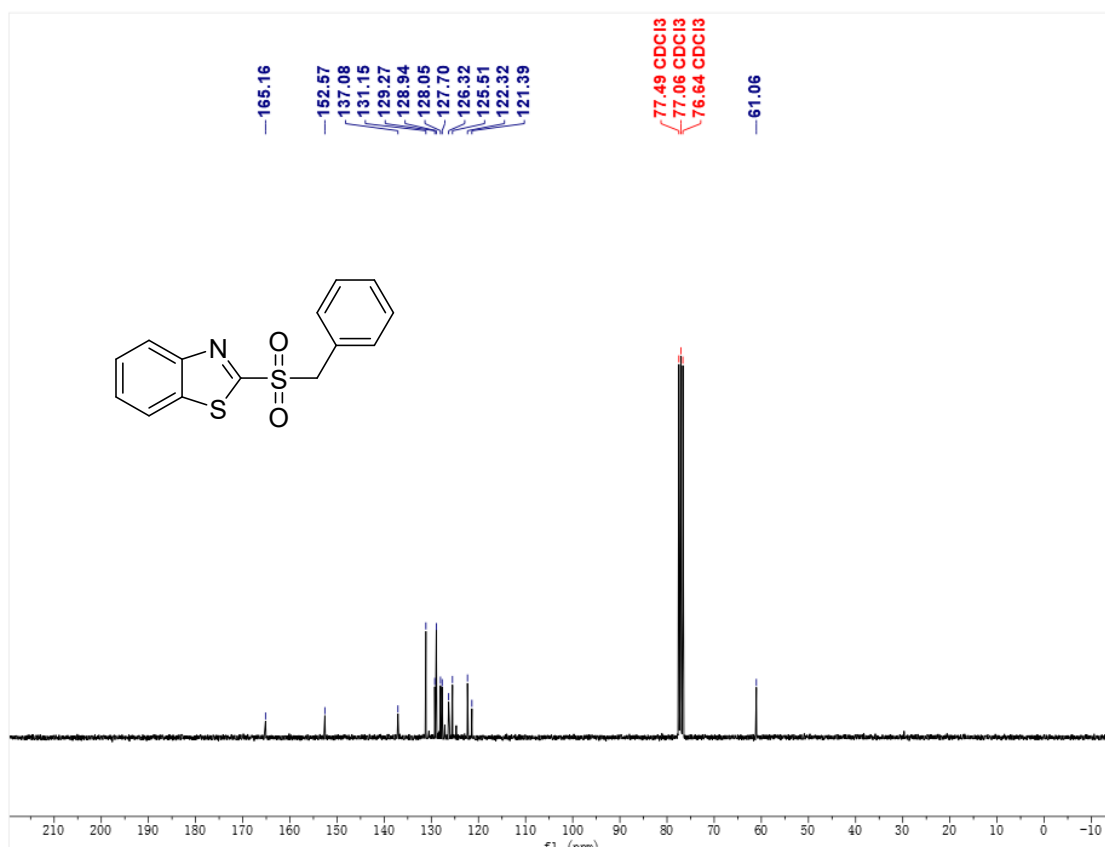


¹³C NMR (75 MHz, CDCl₃) of **3ar**.

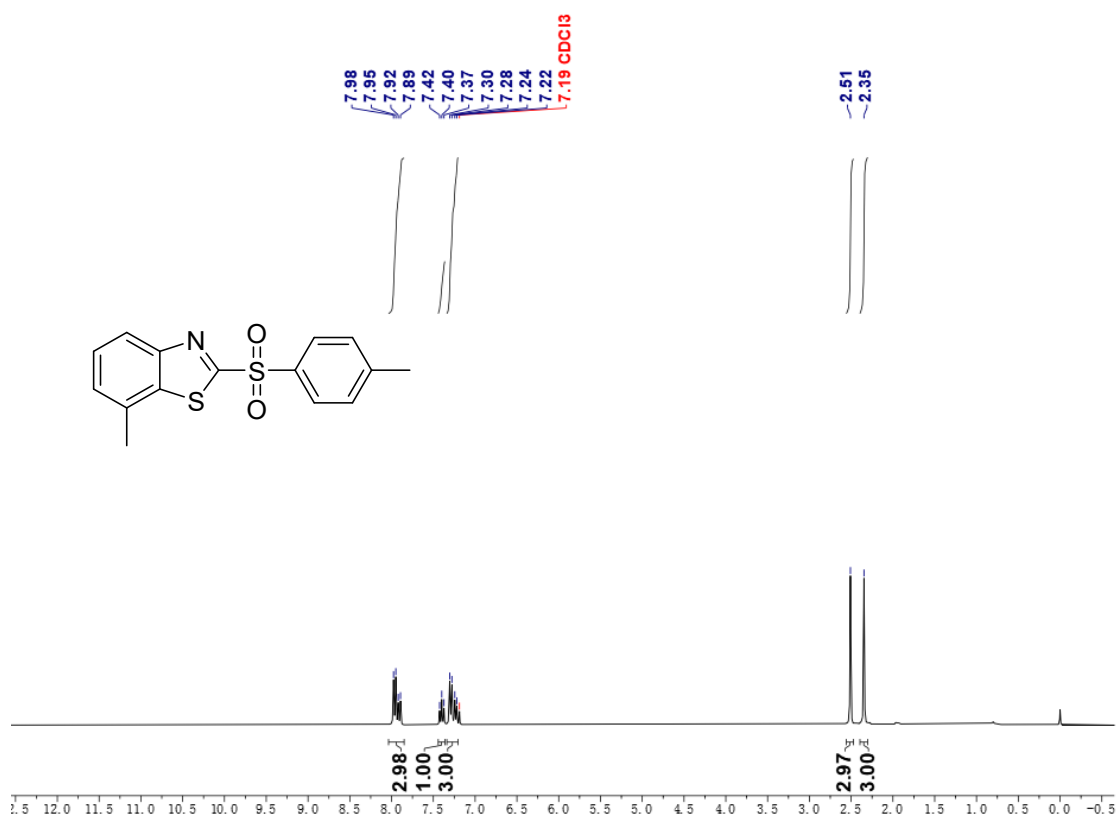


¹H NMR (300 MHz, CDCl₃) of **3as**.

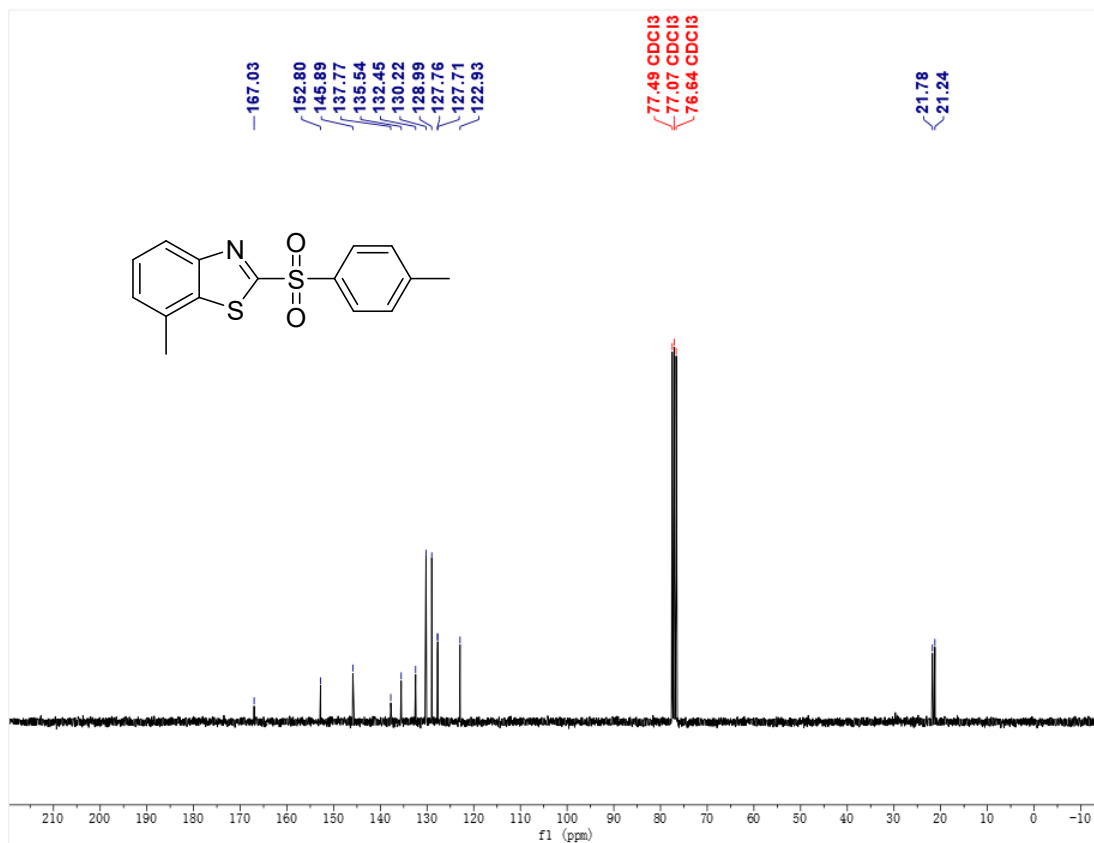




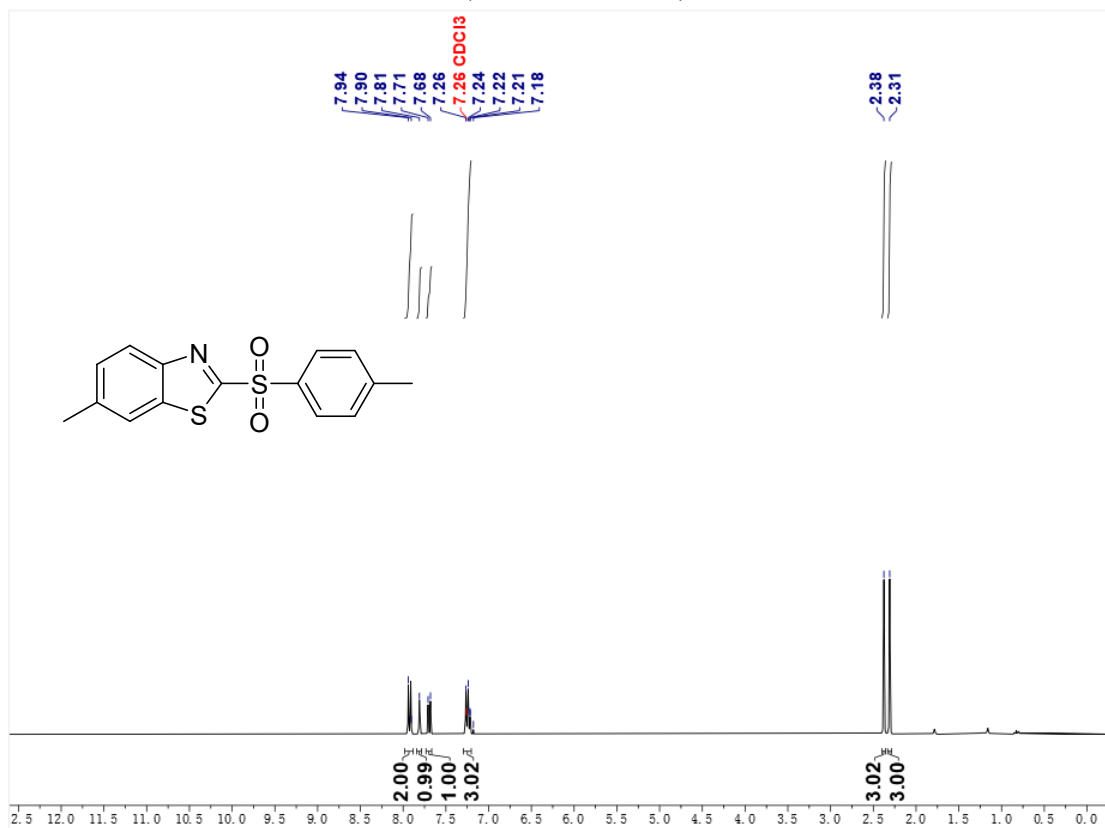
^{13}C NMR (75 MHz, CDCl_3) of 3at.



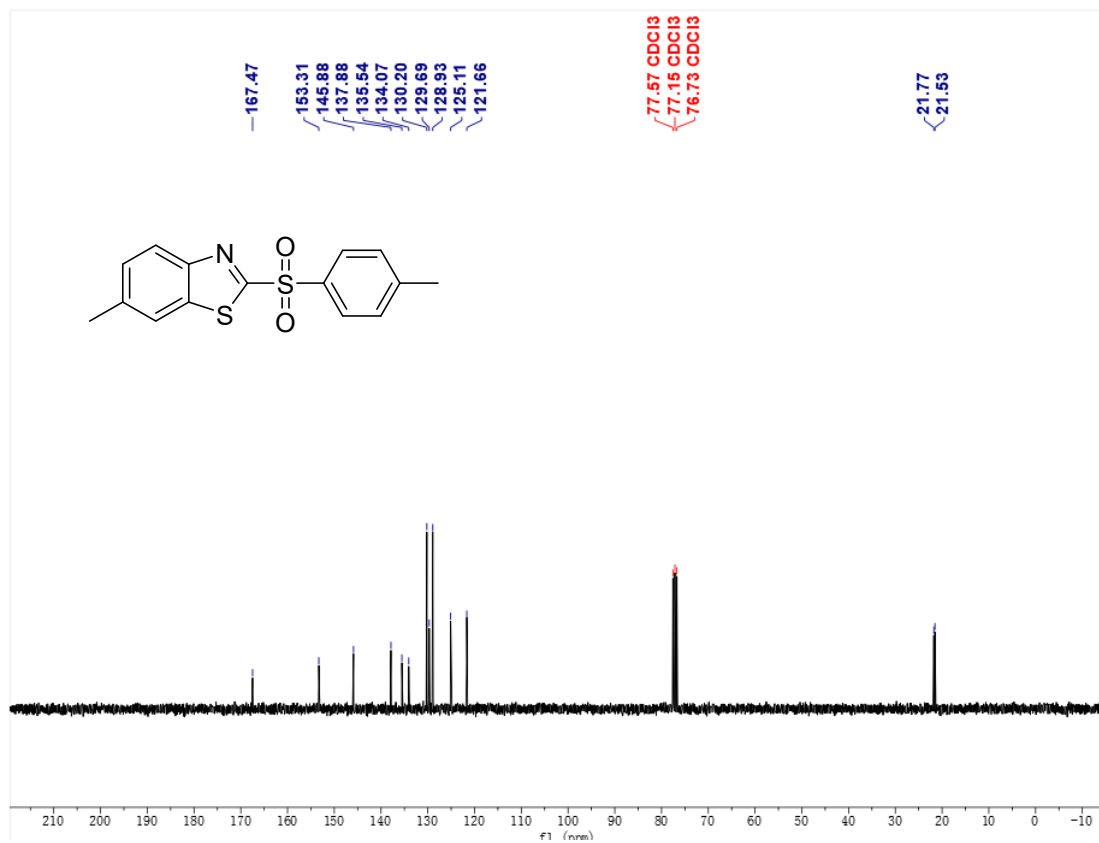
^1H NMR (300 MHz, CDCl_3) of 3ba.



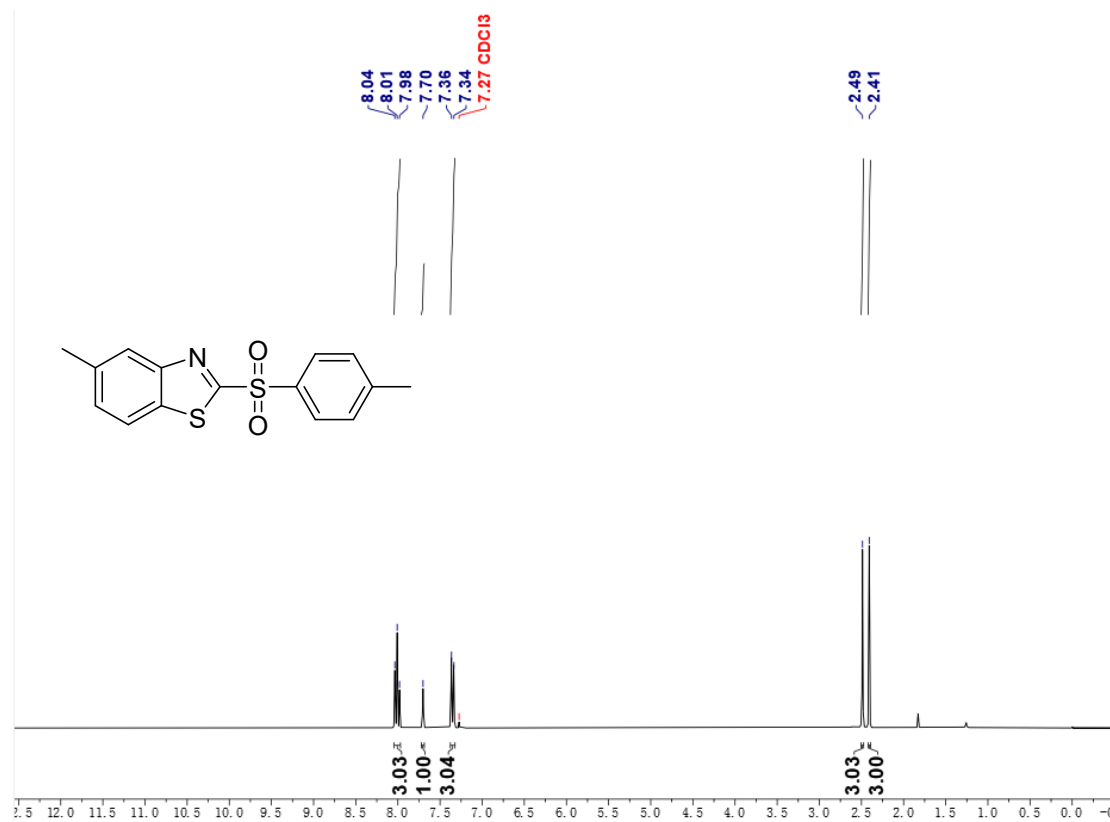
¹³C NMR (75 MHz, CDCl₃) of 3ba.



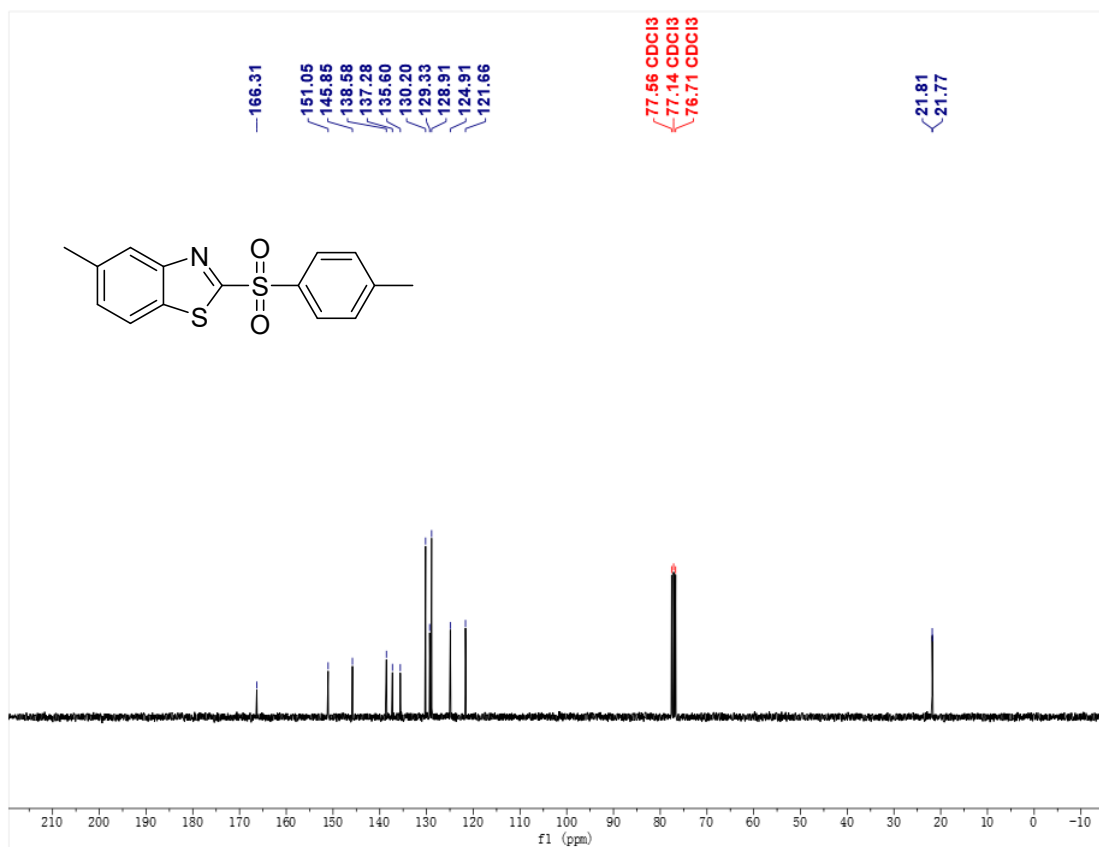
¹H NMR (300 MHz, CDCl₃) of 3bb.



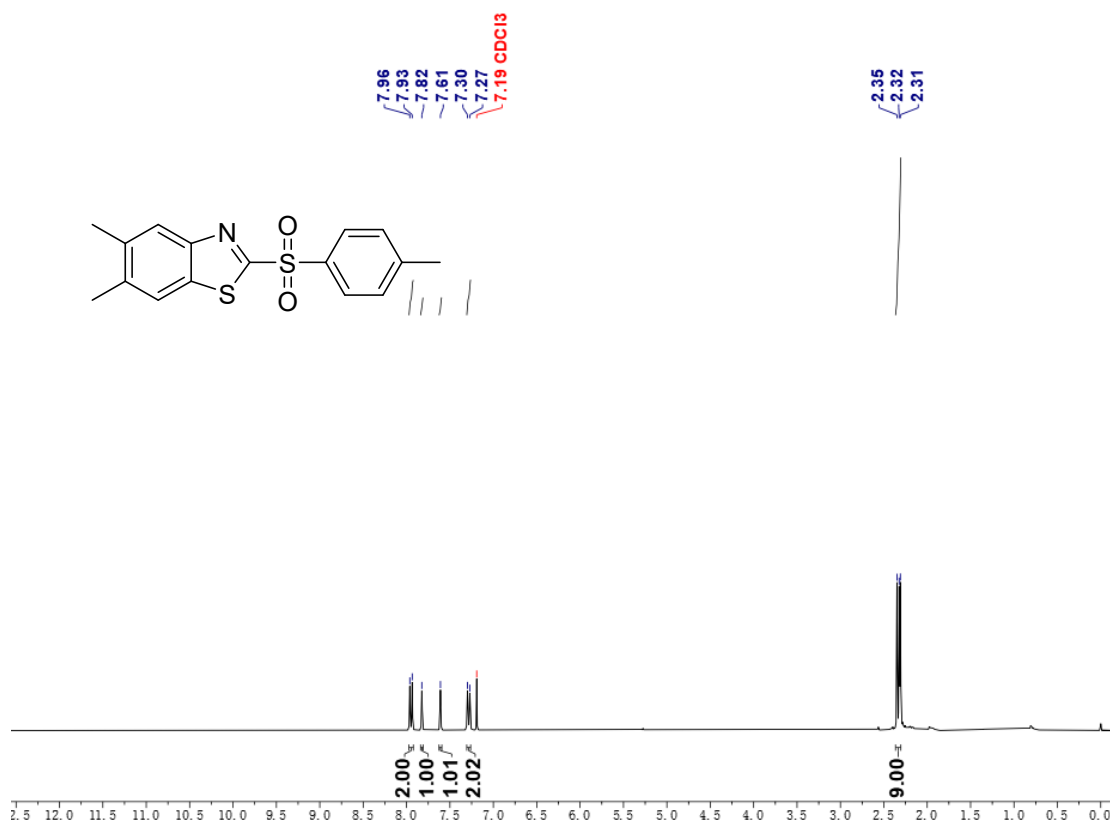
¹³C NMR (75 MHz, CDCl₃) of 3bb.



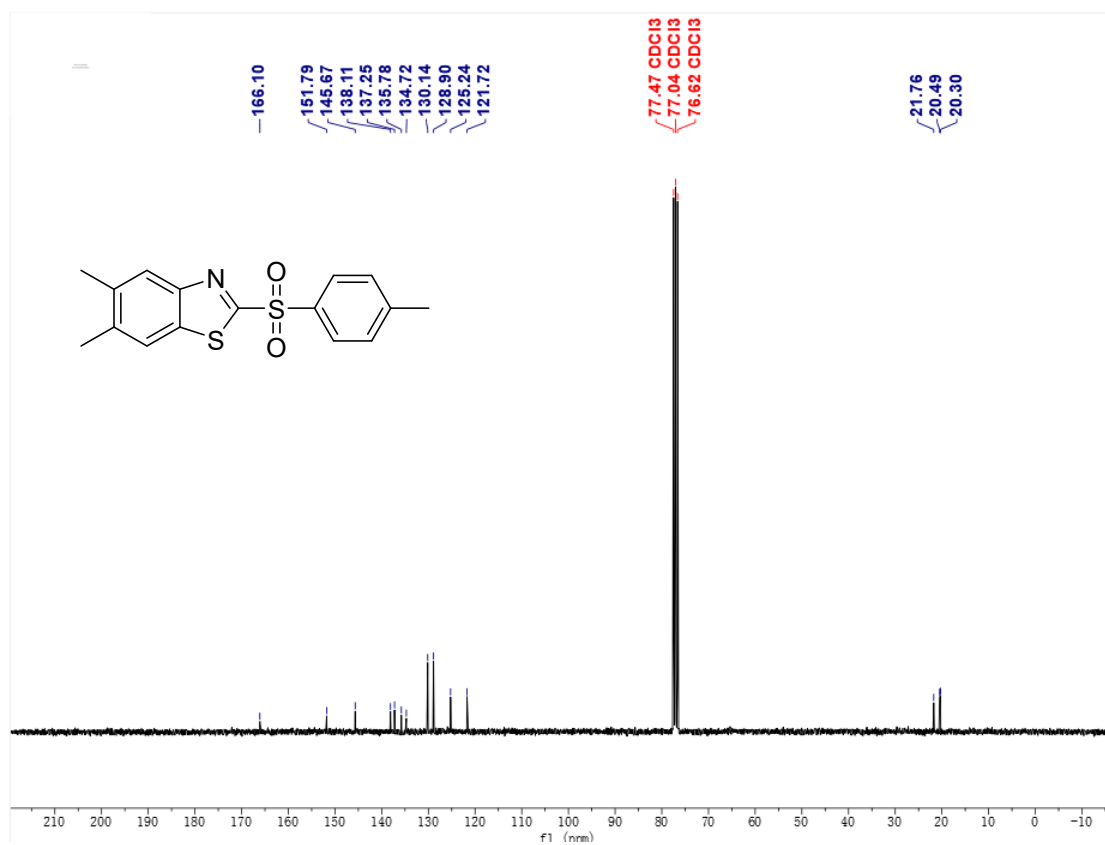
¹H NMR (300 MHz, CDCl₃) of 3bc.



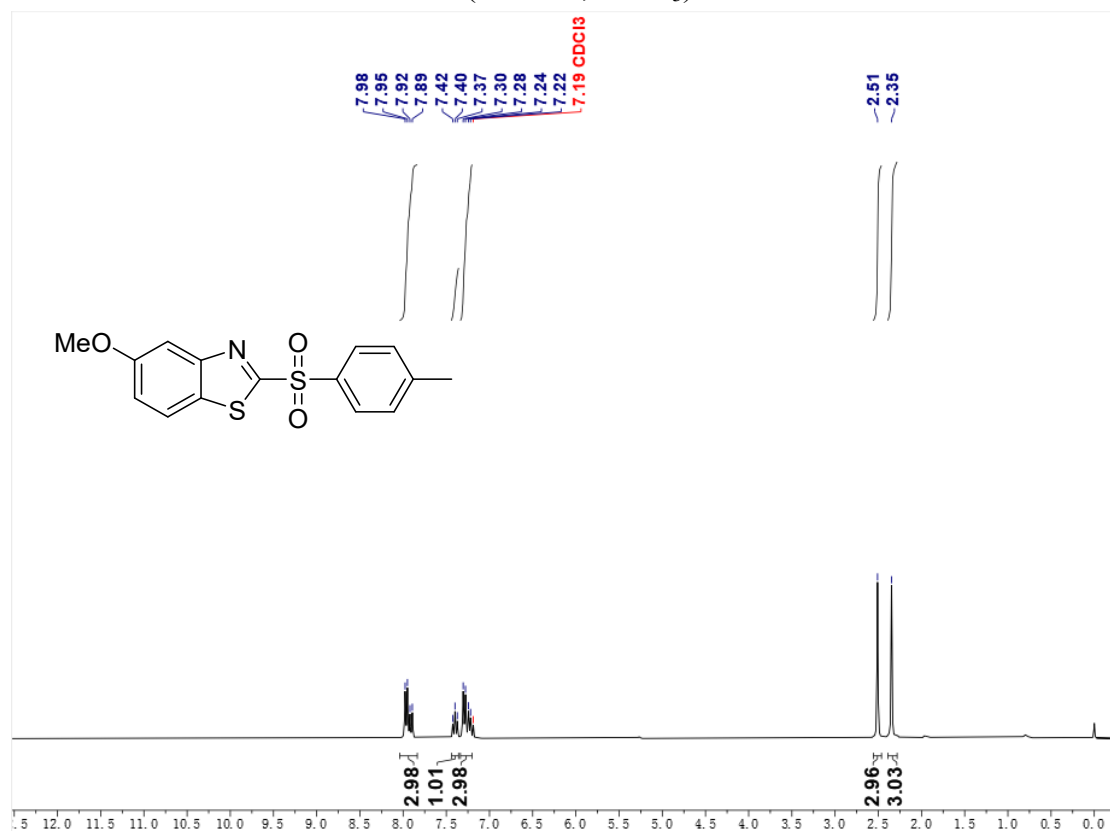
¹³C NMR (75 MHz, CDCl₃) of 3bc.



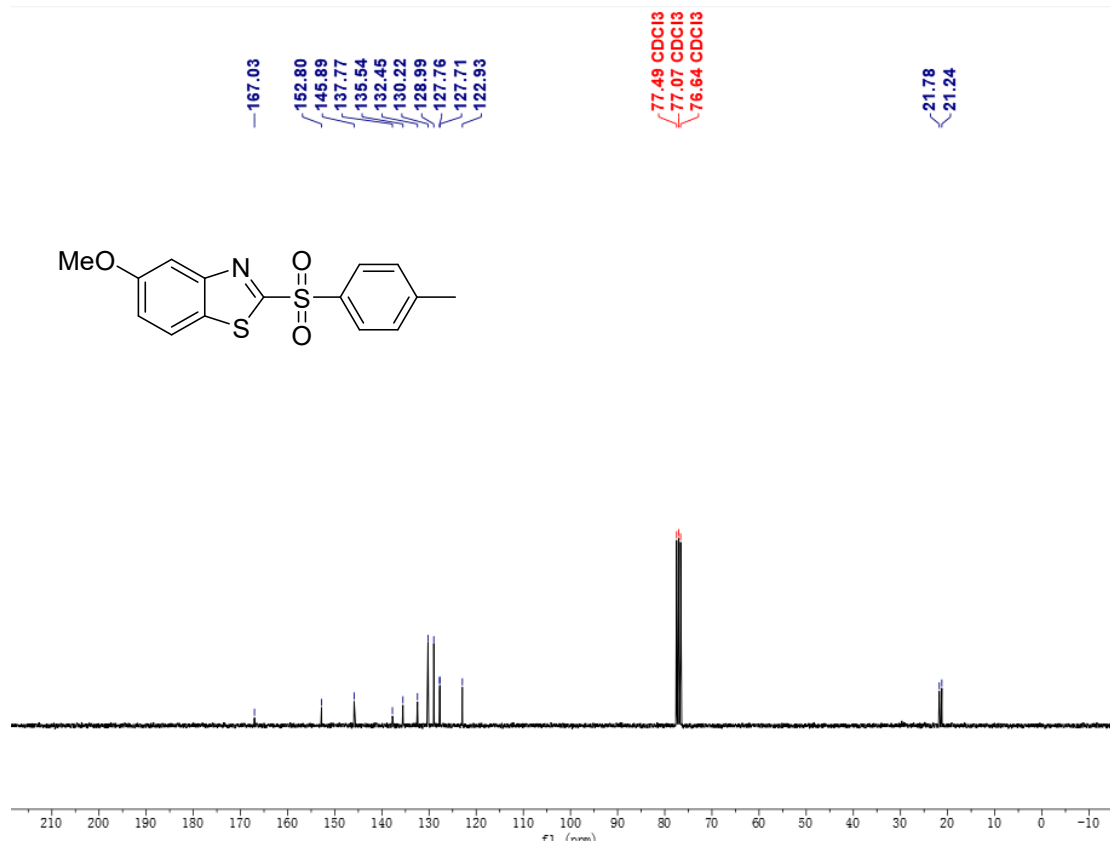
¹H NMR (300 MHz, CDCl₃) of 3bd.



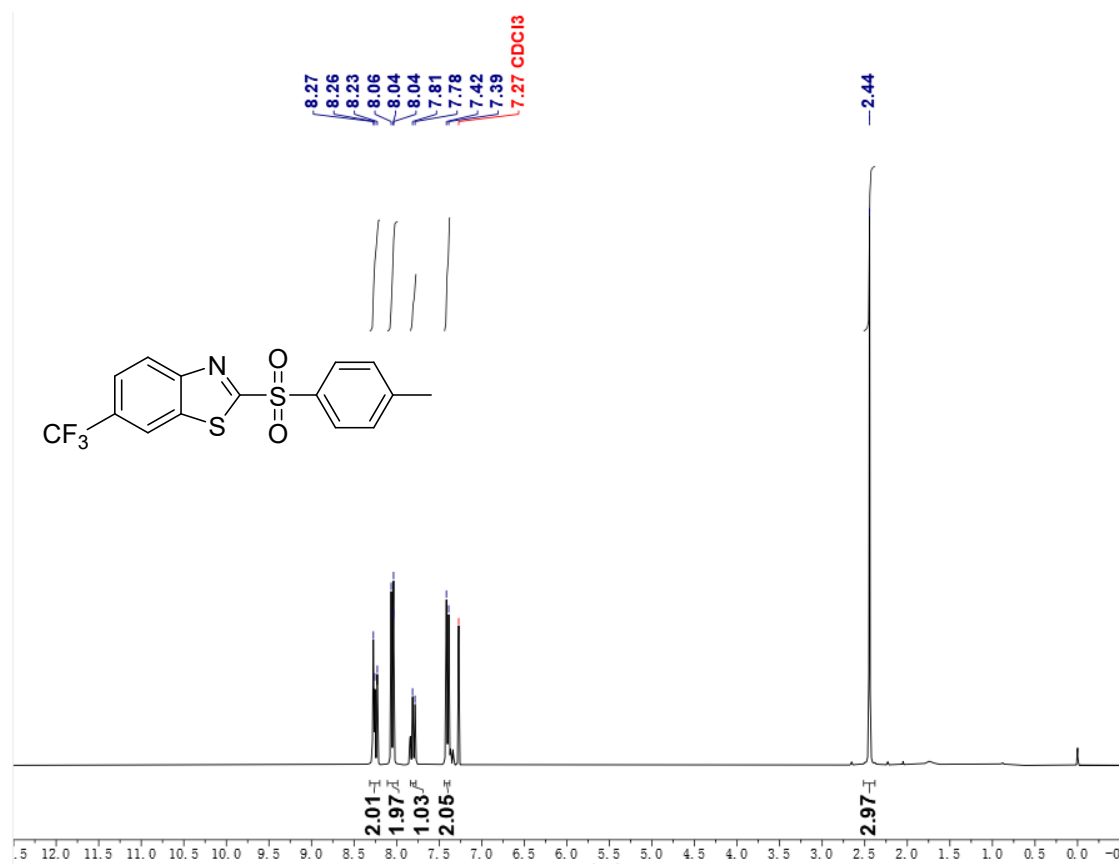
¹³C NMR (75 MHz, CDCl₃) of 3bd.



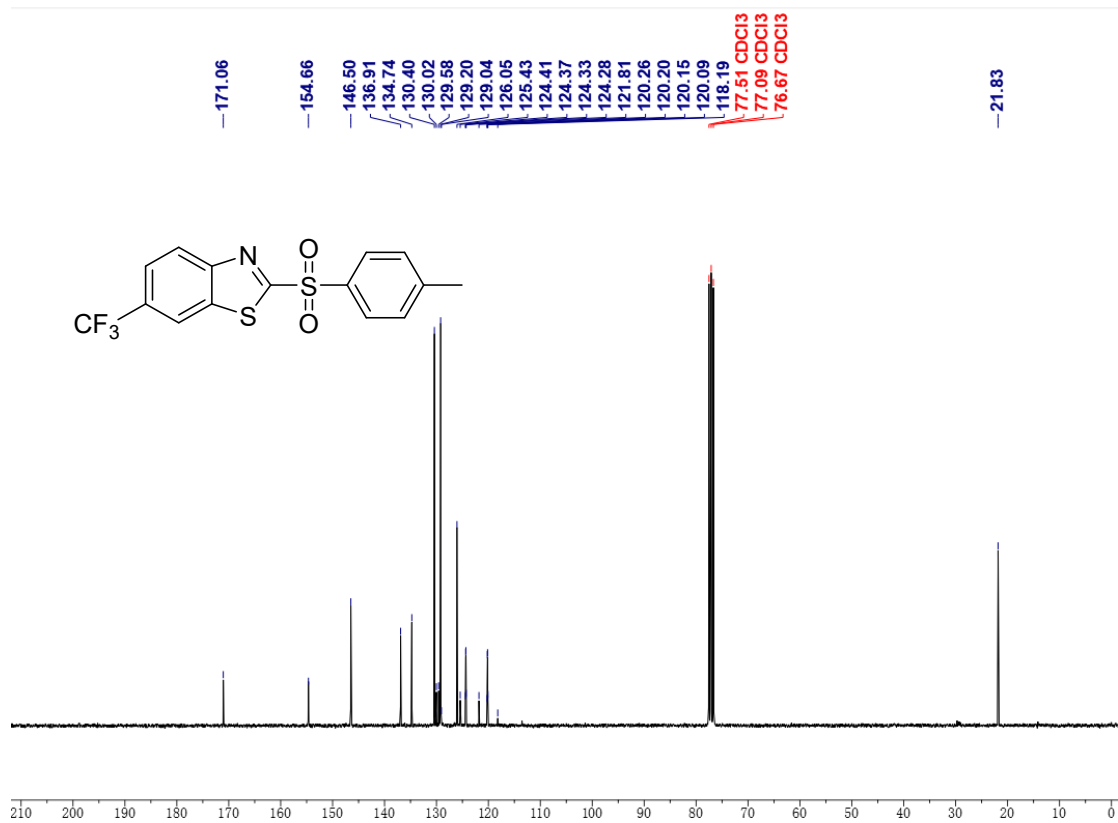
¹H NMR (300 MHz, CDCl₃) of 3be.



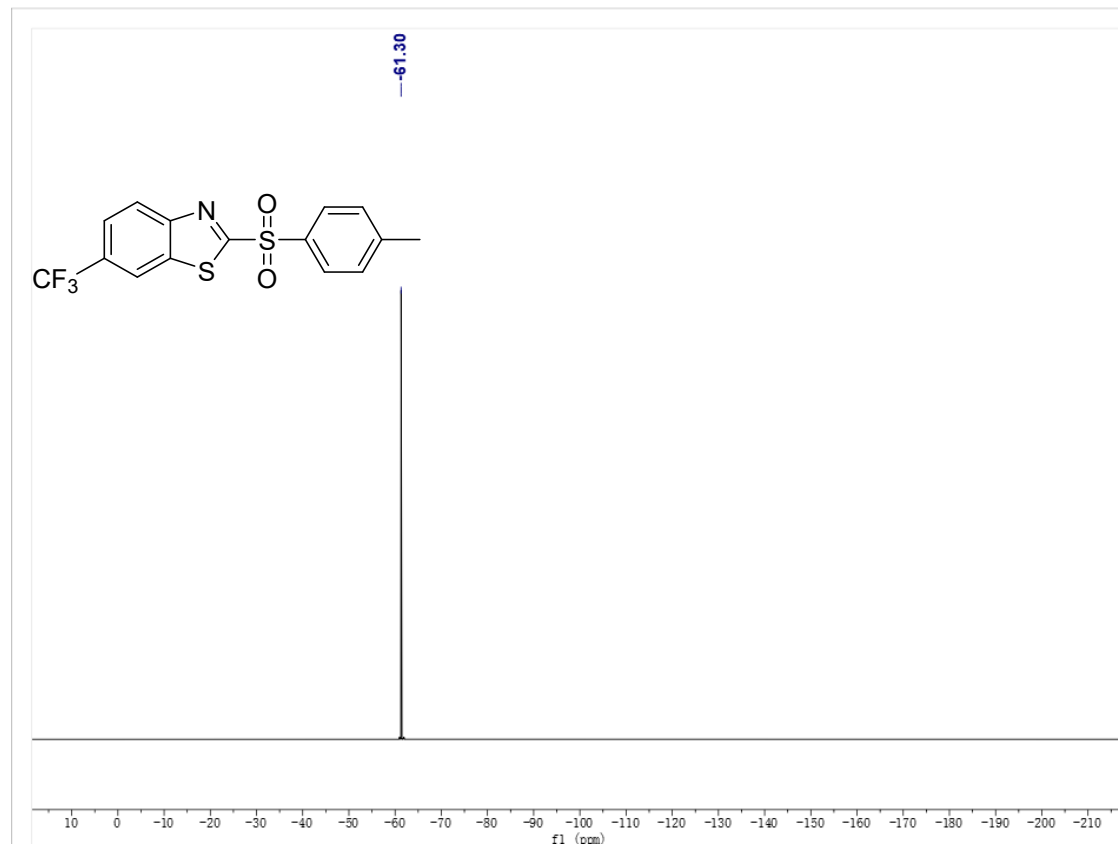
¹³C NMR (75 MHz, CDCl₃) of 3be.



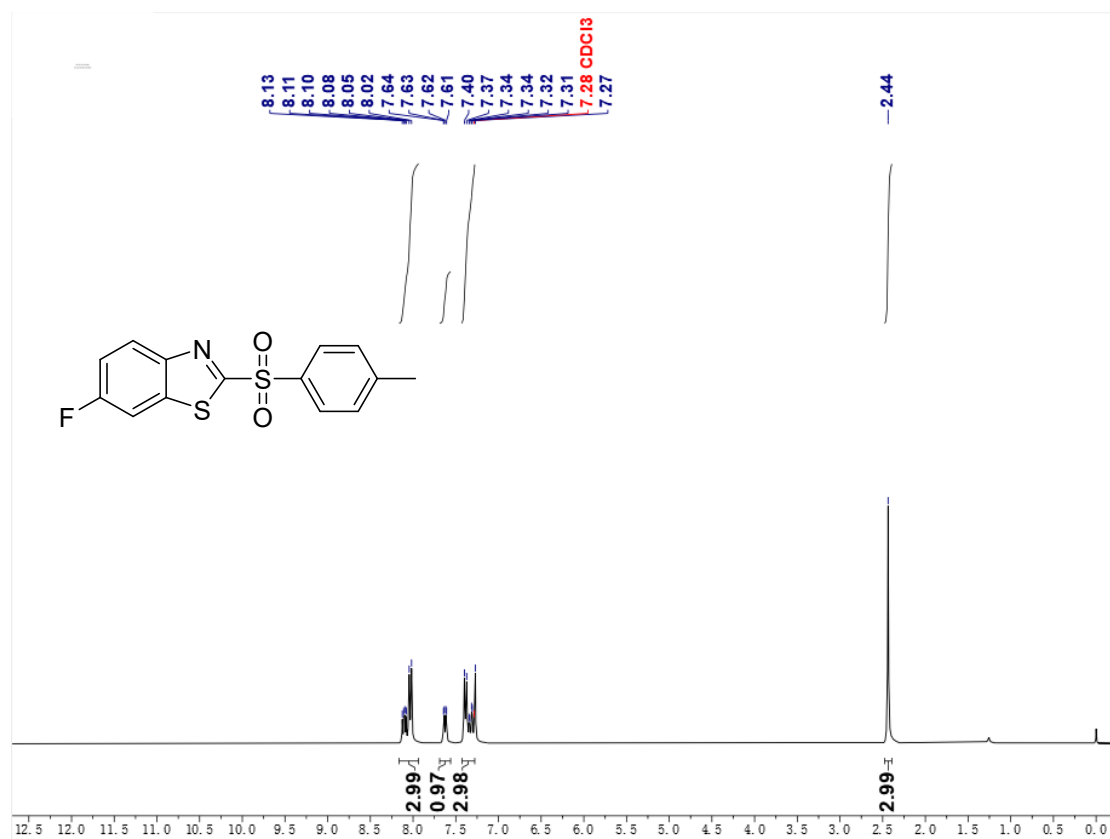
¹H NMR (300 MHz, CDCl₃) of 3bf.



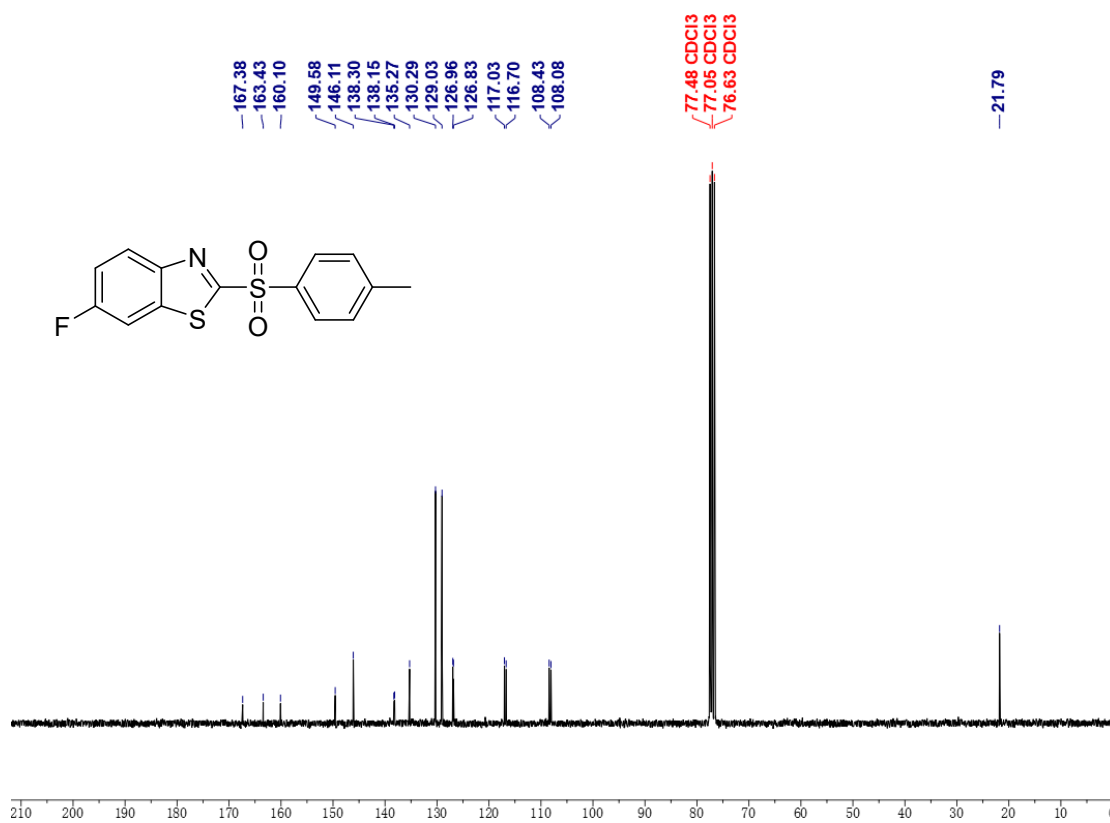
¹³C NMR (75 MHz, CDCl₃) of **3bf**.



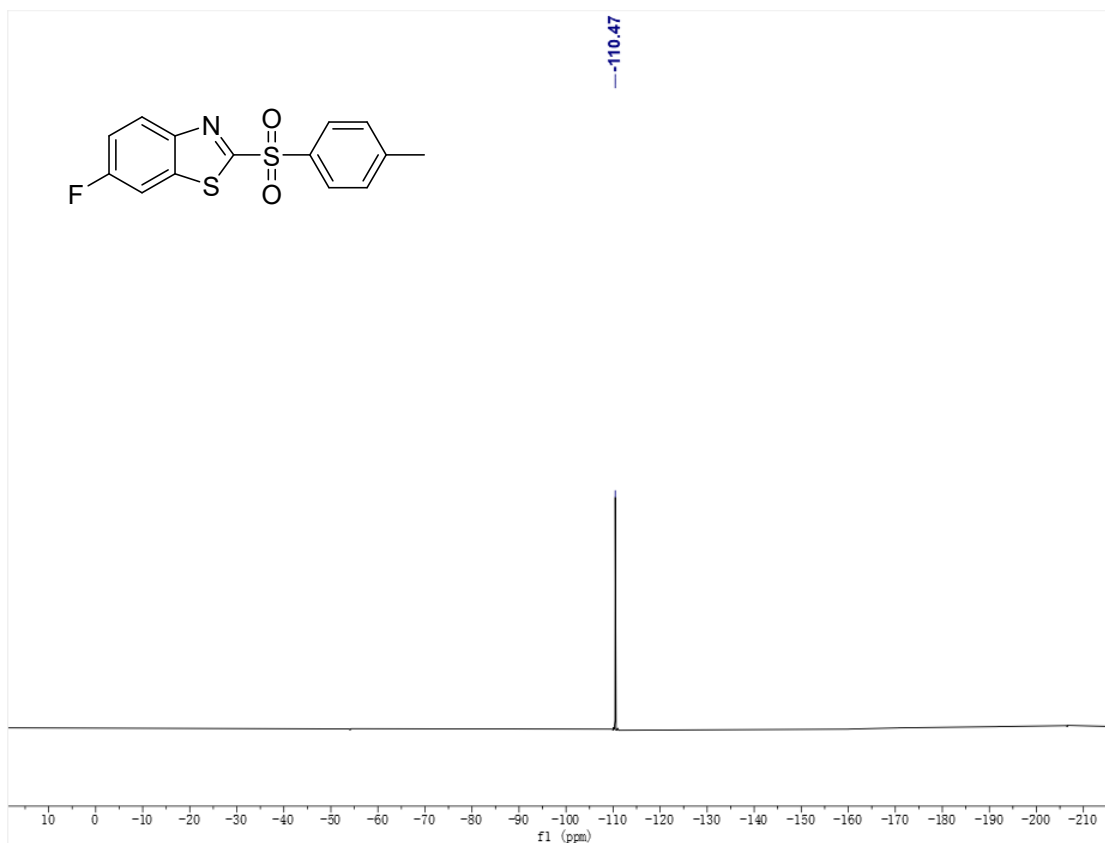
¹⁹F NMR (282 MHz, CDCl₃) of **3bf**.



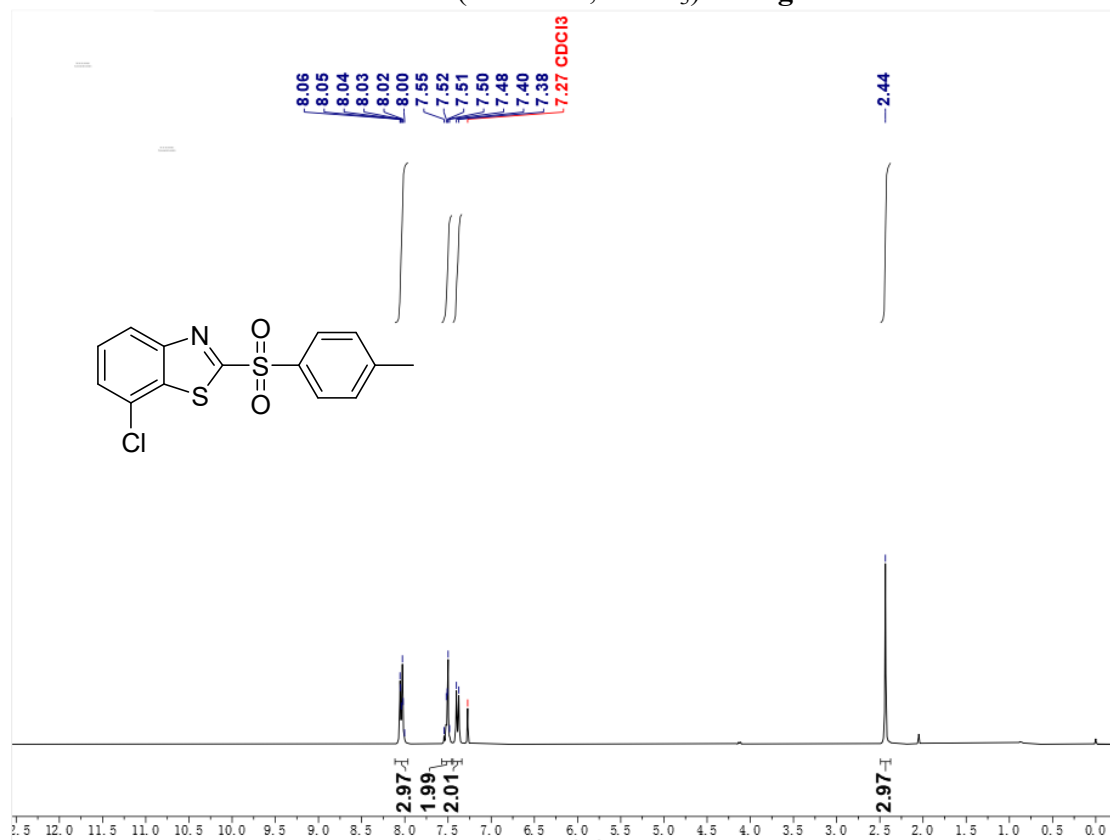
¹H NMR (300 MHz, CDCl₃) of **3bg**.



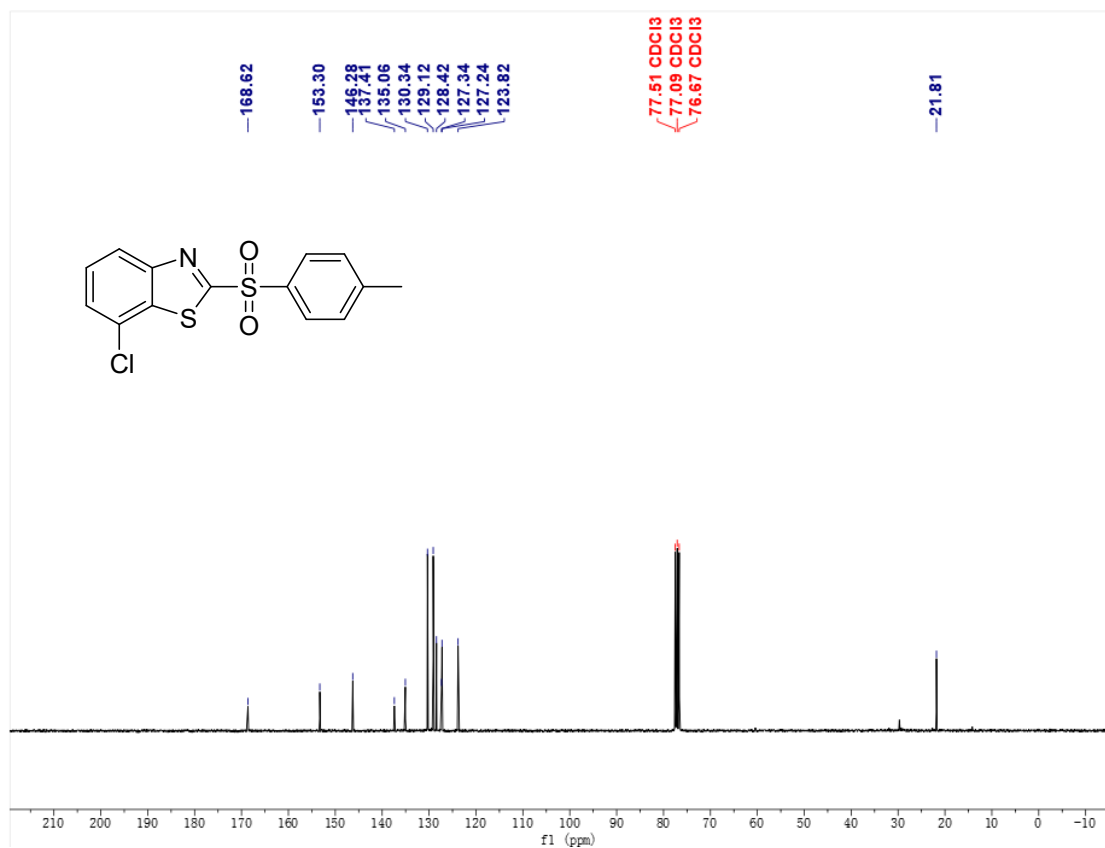
¹³C NMR (75 MHz, CDCl₃) of **3bg**.



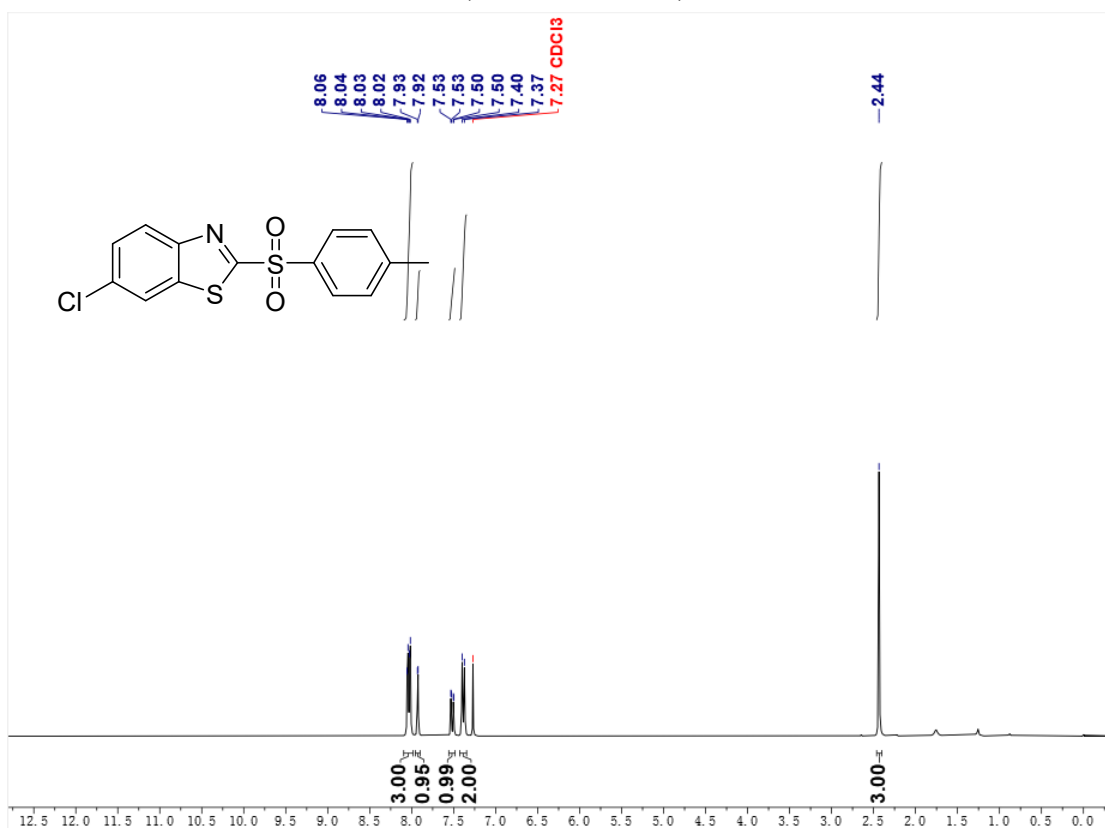
^{19}F NMR (282 MHz, CDCl_3) of **3bg**.



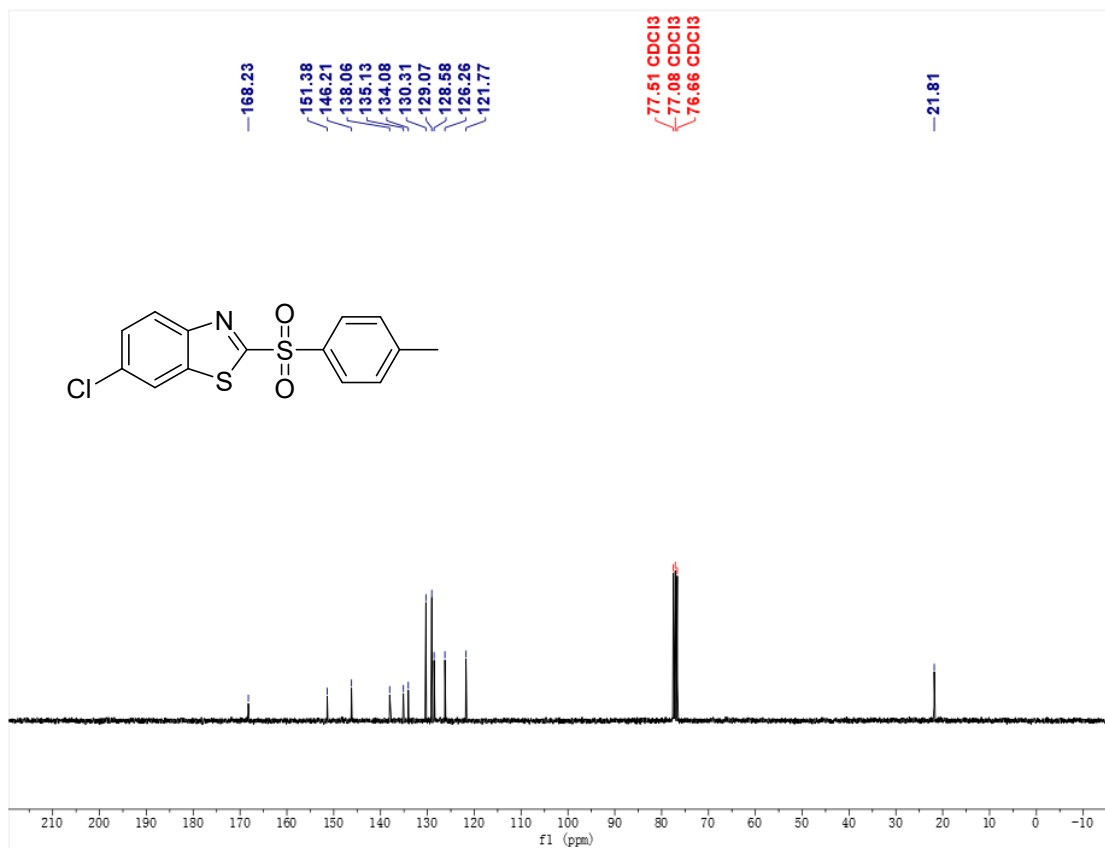
^1H NMR (300 MHz, CDCl_3) of **3bh**.



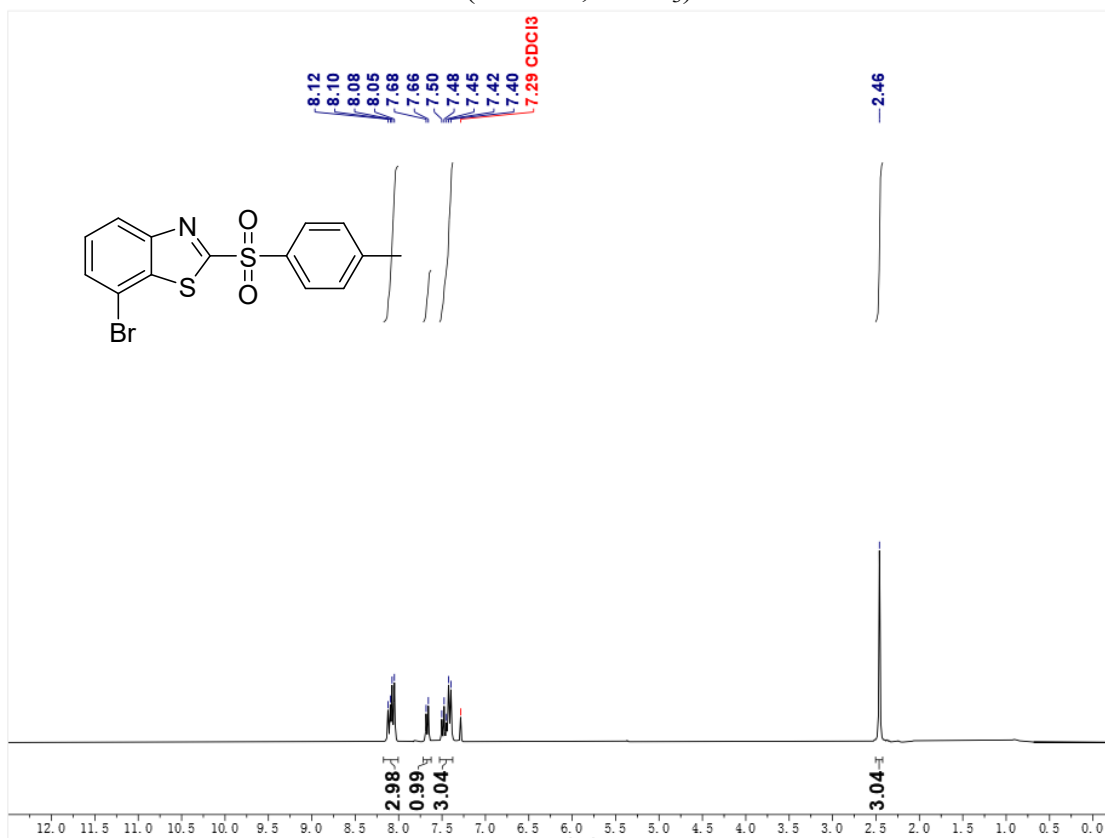
¹³C NMR (75 MHz, CDCl₃) of 3bh.



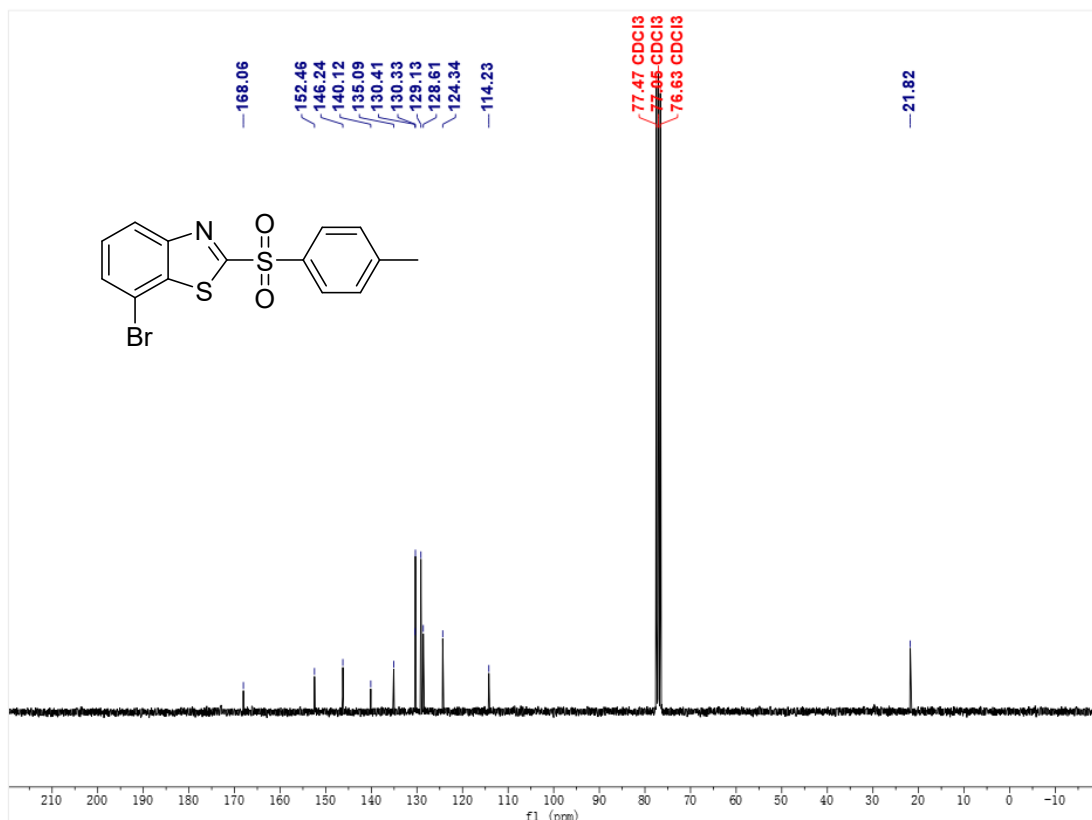
¹H NMR (300 MHz, CDCl₃) of 3bi.



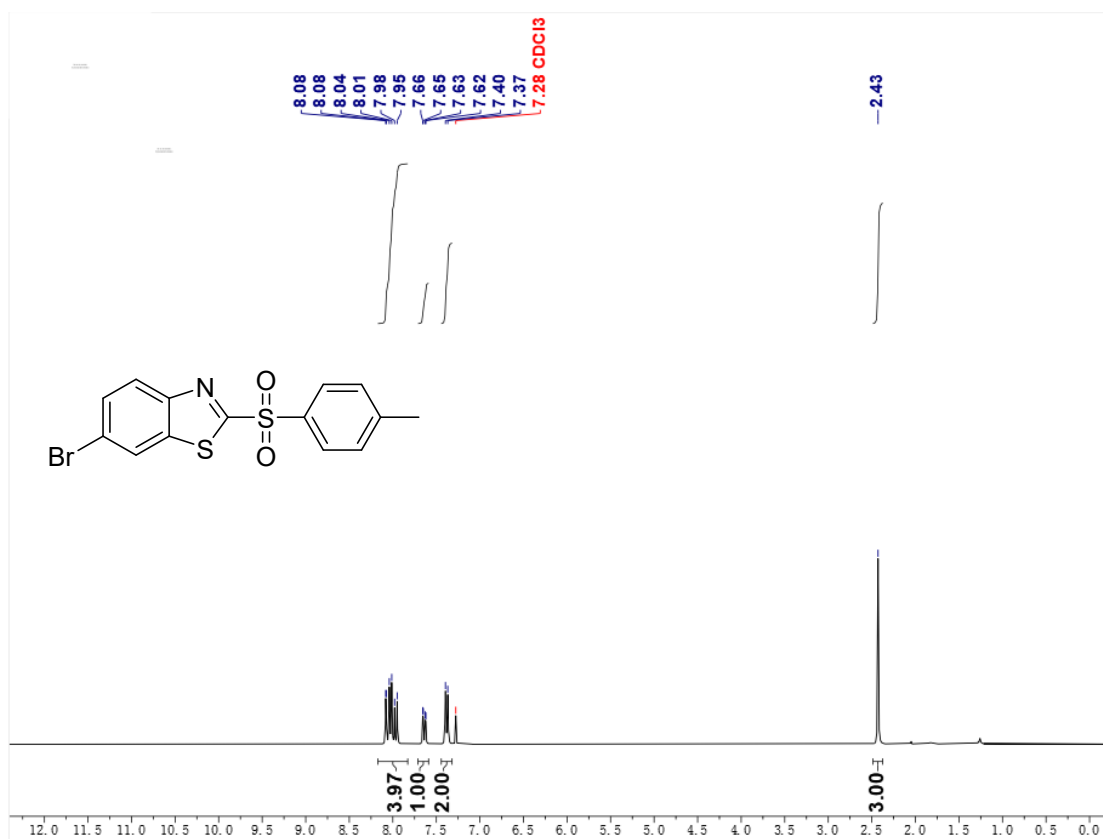
¹³C NMR (75 MHz, CDCl₃) of **3bi**.



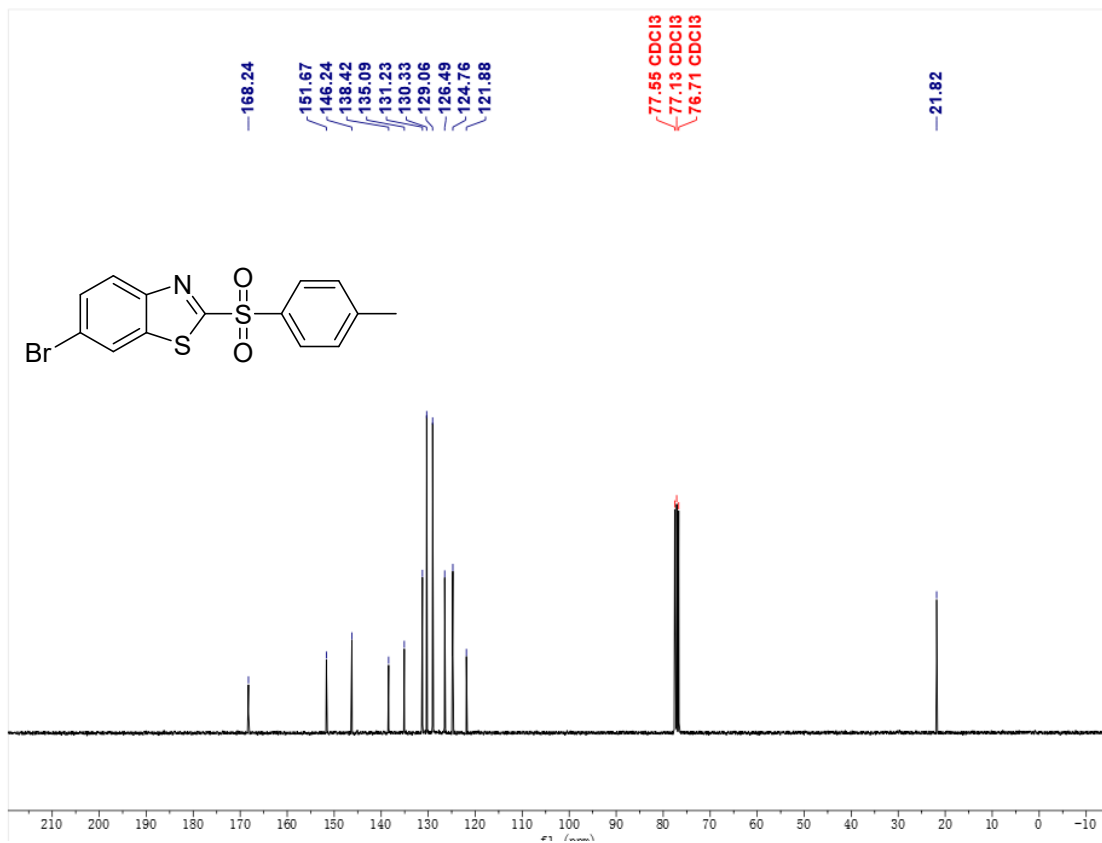
¹H NMR (300 MHz, CDCl₃) of **3bk**.



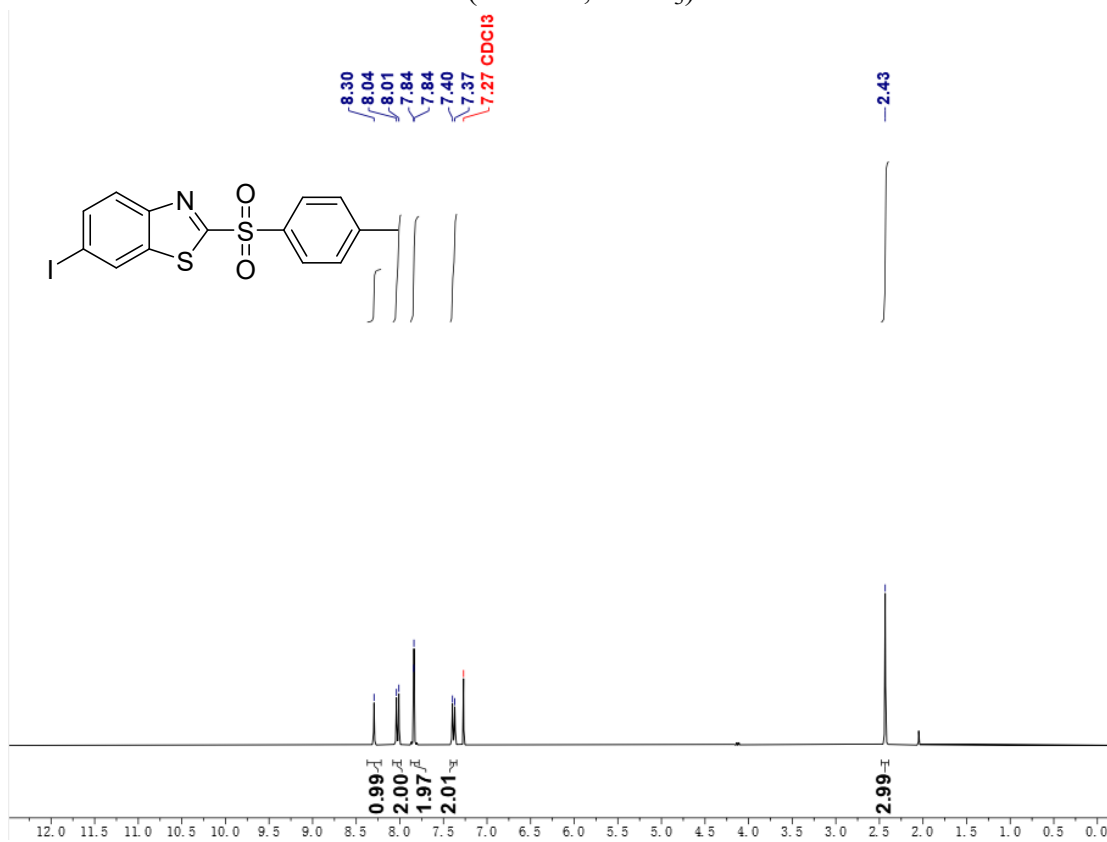
¹³C NMR (75 MHz, CDCl₃) of 3bk.



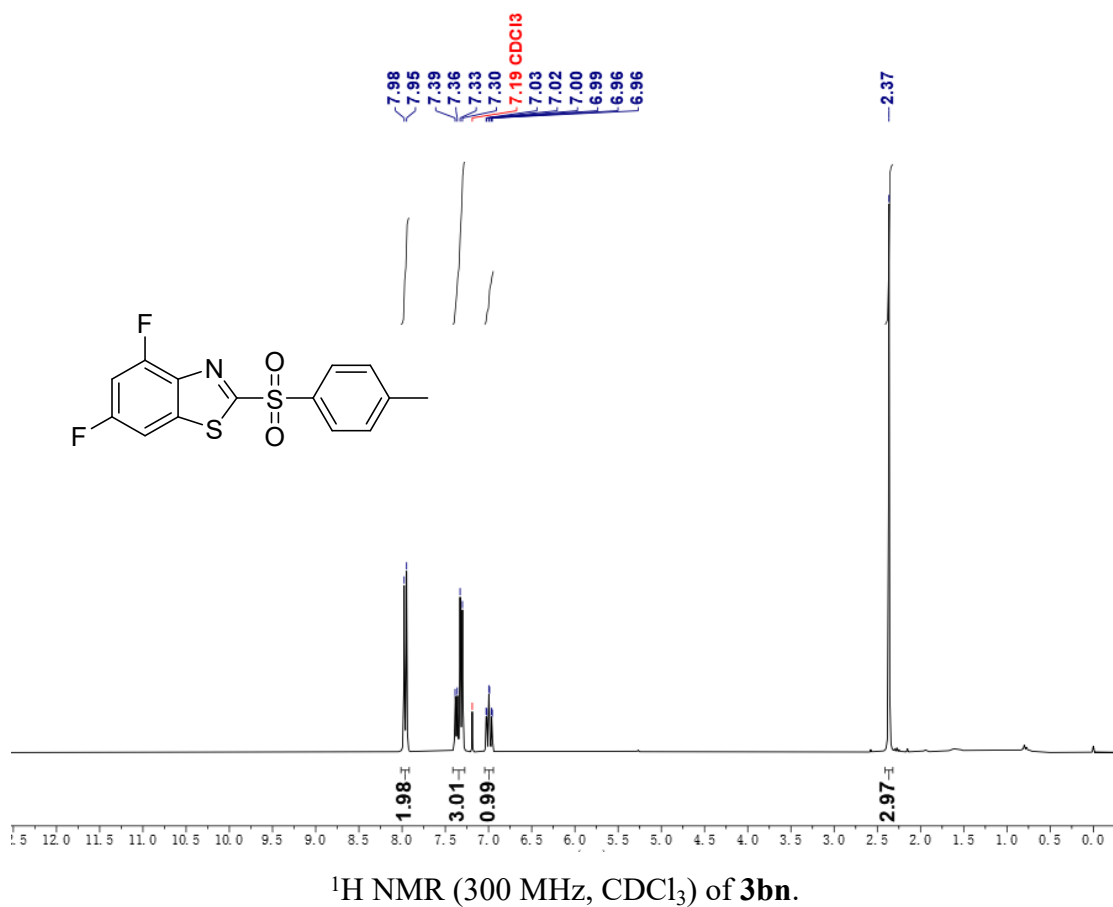
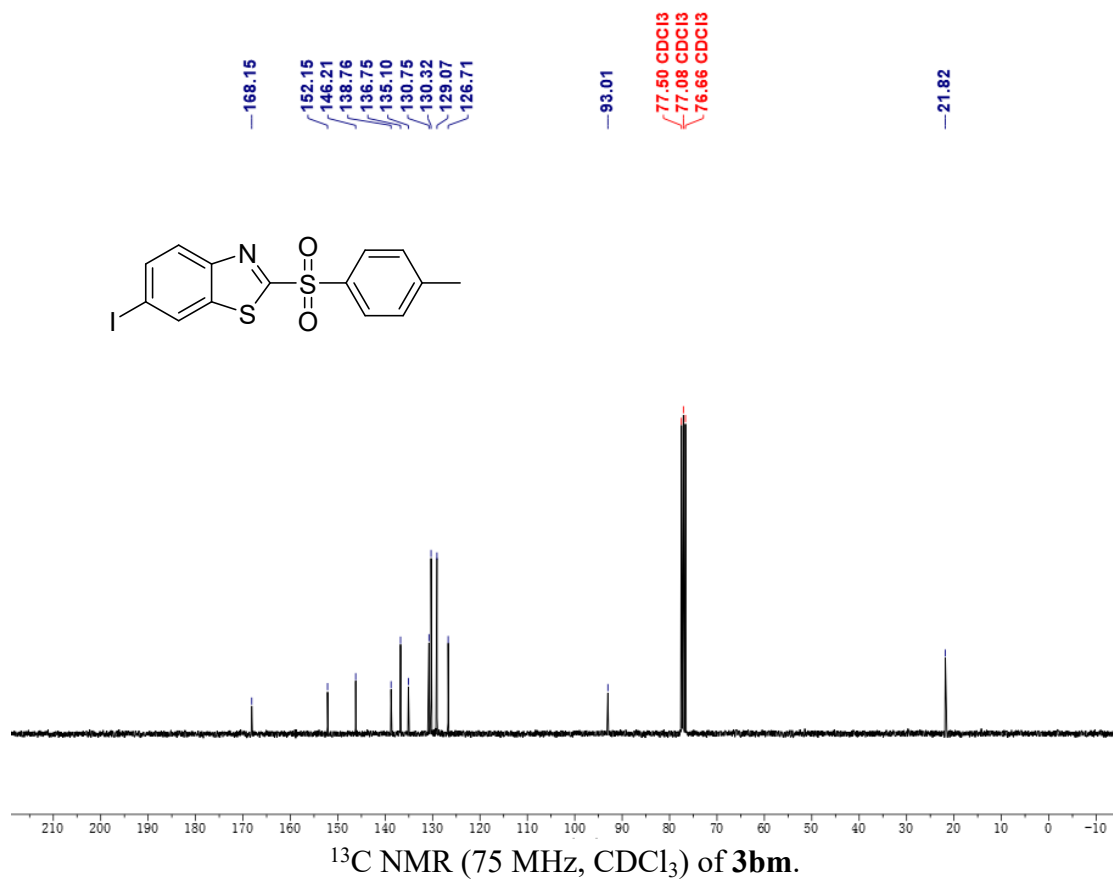
¹H NMR (300 MHz, CDCl₃) of 3bl.

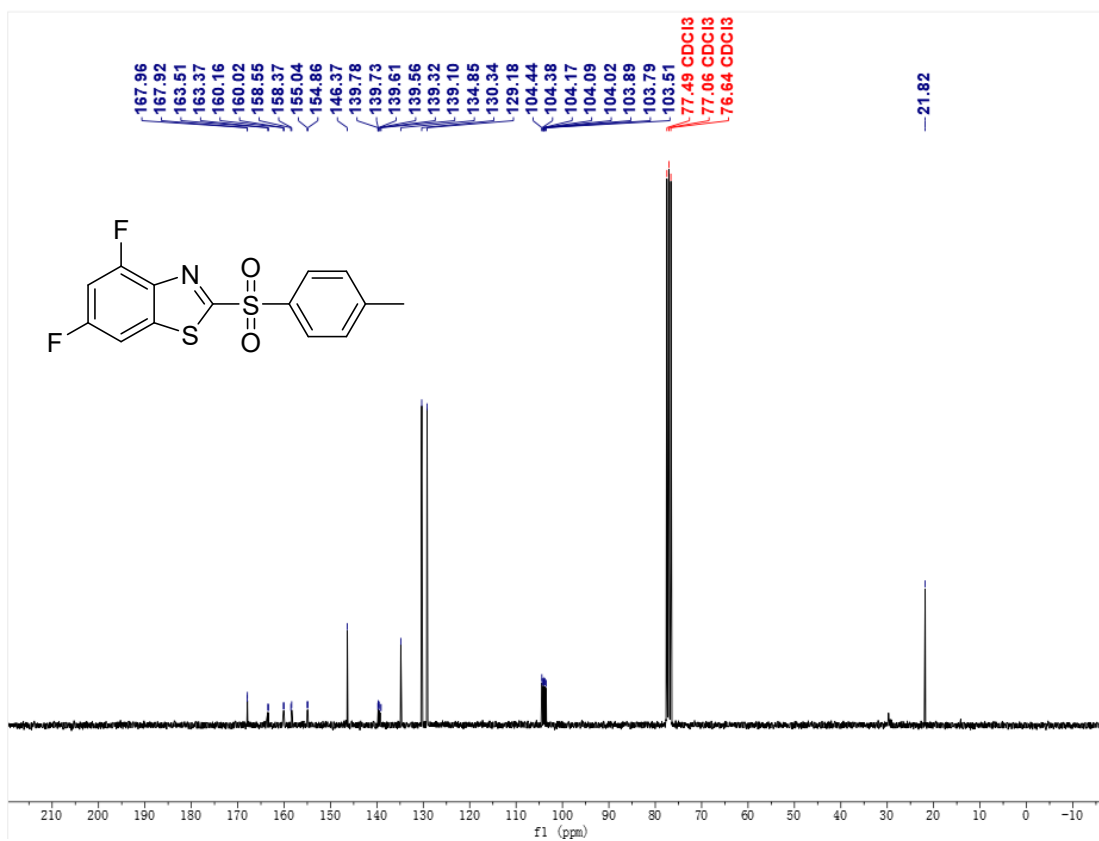


¹³C NMR (75 MHz, CDCl₃) of **3bl**.

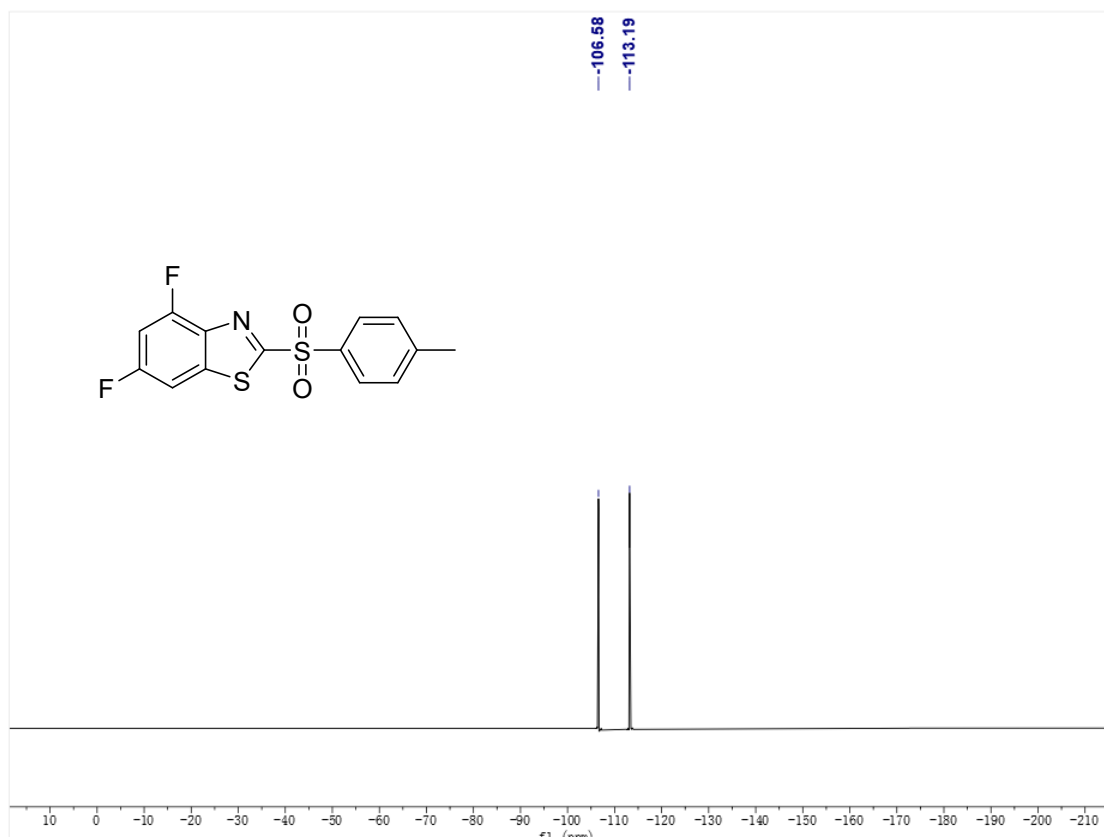


¹H NMR (300 MHz, CDCl₃) of **3bm**.





¹³C NMR (75 MHz, CDCl₃) of 3bn.



¹⁹F NMR (282 MHz, CDCl₃) of 3bn.

4. Reference

- [S1] H. Zhu, Y. Zhang, G. Ren, Y. Wang, J. Meng, Q. Fan, Z. Xie and Z.-G. Le, *Chem. Commun.*, 2023, **59**, 1050-1053.
- [S2] H. Zhu, Y. Zhong, L. Yan, H. Zhang, Y. Shen, Z. Le, Q. Fan and Z. Xie, *Green Chem.*, 2024, **26**, 1387.
- [S3] H. Zhang, H. Zhu, Y. Zhang, G. Ren, W. Fang, Q. Fan and Z. Xie, *Chem. Asian J.*, 2023, **18**, e202300757.
- [S4] H. Motiwala, Y. Kuo, B. Stinger, B. Palfey and B. Martin, *J. Am. Chem. Soc.*, 2020, **142**, 1801–1810.
- [S5] A. F. Xinlan, Loïc R. E. Pantaine, D. C. Blakemore, I. B. Moses, N. W. Sach, A. Shavnya and M. C. Willis, *Angew. Chem. Int. Ed.* 2021, **60**, 22461 – 22468.
- [S6] P. Sandeep, P. Biprajit, P. Hrishikesh, S. Rajat, C. Indranil, *Chem. Commun.*, 2022, **58**, 4857-4860.