Electrochemical Intramolecular Aromatic C−H Thiolation for the Synthesis of Benzothiazoles

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General information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. **1l-1m**[1], **5a-5l**[2] were prepared according to reported procedures. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anode electrode is graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). Gas chromatographic analyses were performed on SHIMADZU GC-2014 gas chromatography instrument with a FID detector and biphenyl was added as internal standard. GC-MS spectra were recorded on Varian GC MS 3900-2100T or SHIMADZU GC MS-2010. ^{1}H and ^{13}C NMR data were recorded with Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively.

Caution! Acetonitrile can be metabolised to produce hydrogen cyanide. Aryl isothiocyanates are strong irritative to respiratory tract, skin and eyes. Appropriate protective measures should be taken to avoid direct contaction during operation.

Experimental procedure

General procedure for the reaction between aryl isothiocyanates and amines: In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, aryl isothiocyanates (0.50 mmol), amines (1.0 mmol), $^{n}Bu_4NBF_4$ (987 mg, 3.0 mmol) and CH_3CN/H_2O (9 mL/1 mL) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 10 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA (J_{anode} ≈ 11 mA/cm^2) under 70 °C for 4 h (2.1 F). When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl ether = 5:1).

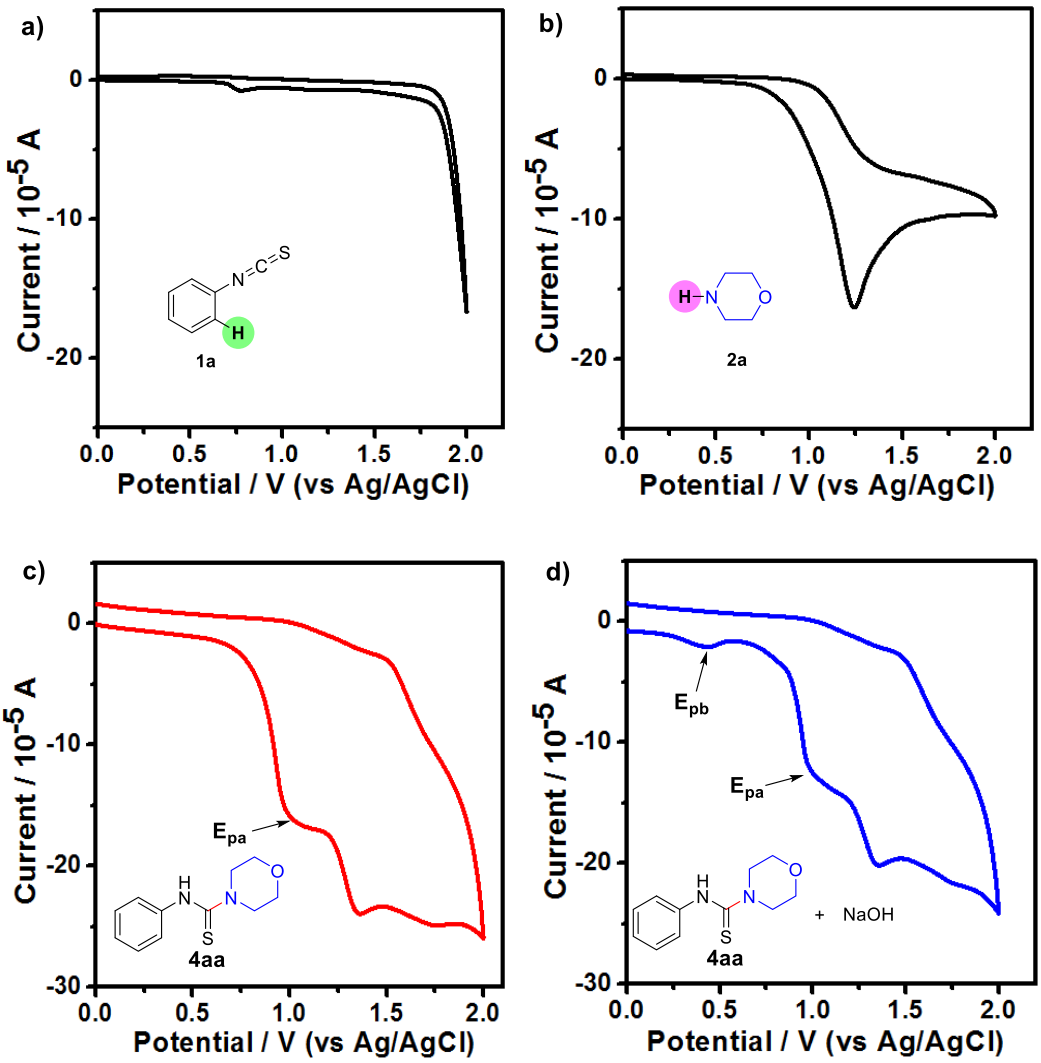
General procedure for the reaction of *N*-aryl thioamides: In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, thioamide (0.50 mmol), PhCOONa (1.0 mmol), $^{n}Bu_4NBF_4$ (987 mg, 3.0 mmol) and CH_3CN/H_2O (9 mL/1 mL) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 10 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA (J_{anode} ≈ 11 mA/cm^2) under 70 °C for 4 h (2.1 F). When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl ether = 50:1).

Procedure for gram scale synthesis: In an oven-dried undivided three-necked bottle (100 mL) equipped with a stir bar, phenyl isothiocyanate (5 mmol), morpholine (10 mmol), $^{n}Bu_4NBF_4$ (9.87 g, 30 mmol) and CH_3CN/H_2O (90 mL/10 mL) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 20 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and was then charged with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA (J_{anode} ≈ 6 mA/cm^2) under 70 °C

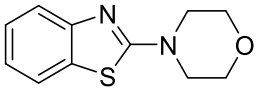
for 36 h (1.9 F). When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (100 mL x 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl ether = 5:1).

Procedure for cyclic voltammetry (CV): Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 9 mL of acetonitrile and 1 mL of water containing 0.2 M $^{n}Bu_4NBF_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 2.0 V.

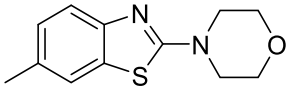
Figure S1 Cyclic voltammogram.



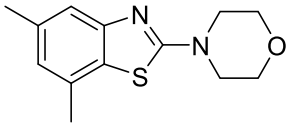
Detail descriptions for products



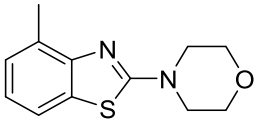
4-(Benzo[d]thiazol-2-yl)morpholine (3aa):[3] white solid was obtained in 92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.14 – 7.05 (m, 1H), 3.82 (t, 4H), 3.61 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.91, 152.35, 130.44, 126.00, 121.58, 120.69, 119.18, 66.12, 48.35.



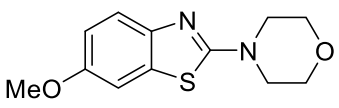
4-(6-Methylbenzo[d]thiazol-2-yl)morpholine (3ba):[4] white solid was obtained in 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 1H), 7.40 (s, 1H), 7.13 – 7.08 (m, 1H), 3.80 (t, 4H), 3.57 (t, 4H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.36, 150.15, 131.30, 130.49, 127.16, 120.71, 118.78, 66.10, 48.33, 21.15.



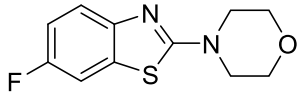
4-(5,7-Dimethylbenzo[d]thiazol-2-yl)morpholine (3ca): white solid was obtained in 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.74 (s, 1H), 3.81 (t, 4H), 3.59 (t, 4H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.82, 152.37, 135.94, 130.09, 127.55, 123.51, 117.13, 66.11, 48.33, 21.34, 21.09. HRMS (EI) calculated for $C_{13}H_{16}N_2OS$ $[M+H]^+$: 249.1056; found: 249.1042.



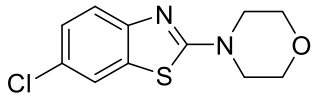
4-(4-Methylbenzo[d]thiazol-2-yl)morpholine (3da): white solid was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 3.79 (t, 4H), 3.58 (t, 4H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.89, 151.43, 130.27, 129.09, 126.61, 121.38, 118.06, 66.15, 48.31, 18.16. HRMS (EI) calculated for $C_{12}H_{14}N_2OS$ $[M+H]^+$: 235.0900; found: 235.0888.



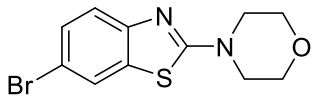
4-(6-Methoxybenzo[d]thiazol-2-yl)morpholine (3ea):[3] white solid was obtained in 76% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 2.6 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.85 – 3.78 (m, 7H), 3.56 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 155.05, 146.48, 131.45, 119.63, 113.63, 105.06, 66.12, 55.73, 48.37.



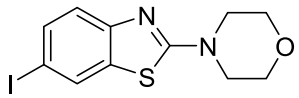
4-(6-Fluorobenzo[d]thiazol-2-yl)morpholine (3fa):[3] white solid was obtained in 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (q, *J* = 8.8, 4.7 Hz, 1H), 7.32 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.07 – 6.99 (m, 1H), 3.82 (t, 4H), 3.58 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.51, 158.11 (d, $J_{C\text{-}F}$ = 241.4 Hz), 148.79 (d, $J_{C\text{-}F}$ = 2.0 Hz), 131.16 (d, $J_{C\text{-}F}$ = 11.1 Hz), 119.65 (d, $J_{C\text{-}F}$ = 8.1 Hz), 113.71 (d, $J_{C\text{-}F}$ = 24.3 Hz), 107.44(d, $J_{C\text{-}F}$ = 27.3 Hz), 66.10, 48.33. ^{19}F NMR (377 MHz, $CDCl_3$) δ -120.91.



4-(6-Chlorobenzo[d]thiazol-2-yl)morpholine (3ga):[3] white solid was obtained in 95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.29 – 7.22 (m, 1H), 3.83 (t, 4H), 3.60 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.98, 151.06, 131.67, 126.67, 126.51, 120.40, 119.84, 66.12, 48.36.

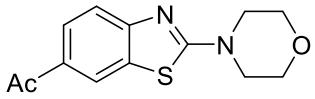


4-(6-Bromobenzo[d]thiazol-2-yl)morpholine (3ha):[3] white solid was obtained in 92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.44 – 7.36 (m, 2H), 3.83 (t, 4H), 3.61 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.97, 151.45, 132.17, 129.28, 123.21, 120.33, 113.91, 66.13, 48.37.

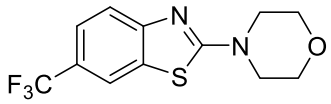


4-(6-Iodobenzo[d]thiazol-2-yl)morpholine (3ia): white solid was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.6 Hz, 1H), 7.58 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 3.83 (t, 4H), 3.62 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.91, 152.02, 135.02,

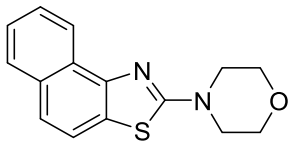
132.67, 128.94, 120.90, 83.66, 66.15, 48.40. HRMS (EI) calculated for $C_{11}H_{11}IN_2OS$ $[M+H]^+$: 349.9710; found: 349.9687.



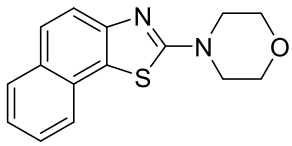
1-(2-Morpholinobenzo[d]thiazol-6-yl)ethan-1-one (3ja): white solid was obtained in 99% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.7 Hz, 1H), 7.93 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 3.85 (t, 4H), 3.69 (t, 4H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.76, 171.19, 156.50, 130.87, 130.82, 127.28, 121.57, 118.44, 66.15, 48.44, 26.54. HRMS (EI) calculated for $C_{13}H_{14}N_2O_2S$ $[M+H]^+$: 263.0849; found: 263.0834.



4-(6-(Trifluoromethyl)benzo[d]thiazol-2-yl)morpholine (3ka):[5] white solid was obtained in 99% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.51 (m, 1H), 3.84 (t, 4H), 3.66 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.53, 155.11, 130.67, 123.78 (q, J_{C-F} = 272.3 Hz), 123.51 (q, J_{C-F} = 32.7 Hz), 123.41 (q, J_{C-F} = 3.8 Hz), 118.98, 118.26 (q, J_{C-F} = 4.0 Hz), 66.17, 48.47. ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.89.

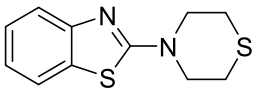


4-(Naphtho[1,2-d]thiazol-2-yl)morpholine (3la):[4] white solid was obtained in 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.46 (t, *J* = 7.1 Hz, 1H), 3.80 (t, 4H), 3.62 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.37, 148.15, 132.03, 127.82, 126.91, 125.76, 125.31, 125.14, 123.79, 121.72, 118.55, 66.12, 48.37.

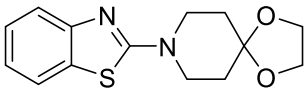


4-(Naphtho[2,1-d]thiazol-2-yl)morpholine (3ma): white solid was obtained in 93% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.67 (m, 3H), 7.53 – 7.45 (m, 1H), 7.43 – 7.33 (m, 1H), 3.82 (t, 4H), 3.61 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.26, 150.17,

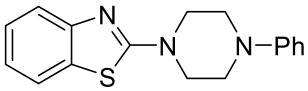
129.39, 128.84, 127.94, 126.74, 126.57, 125.09, 123.96, 123.65, 119.66, 66.08, 48.39. HRMS (EI) calculated for $C_{15}H_{14}N_2OS$ $[M+H]^+$: 271.0900; found: 271.0886.



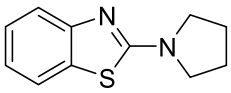
2-Thiomorpholinobenzo[d]thiazole (3ab):[6] white solid was obtained in 93% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.12 – 7.03 (m, 1H), 4.00 – 3.90 (m, 4H), 2.77 – 2.69 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.97, 152.51, 130.54, 125.99, 121.43, 120.61, 119.00, 51.11, 26.47.



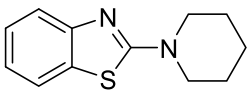
8-(Benzo[d]thiazol-2-yl)-1,4-dioxa-8-azaspiro[4.5]decane (3ac):[4] white solid was obtained in 99% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 1H), 7.59 – 7.54 (m, 1H), 7.34 – 7.28 (m, 1H), 7.12 – 7.05 (m, 1H), 4.02 (s, 4H), 3.82 – 3.72 (m, 4H), 1.91 – 1.79 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.28, 152.88, 130.96, 126.00, 121.35, 120.69, 118.94, 106.91, 64.54, 46.81, 34.41.



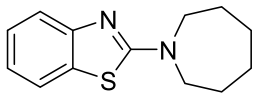
2-(4-Phenylpiperazin-1-yl)benzo[d]thiazole (3ad):[4] white solid was obtained in 99% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.13 – 7.07 (m, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 3.80 (t, 4H), 3.33 (t, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.69, 152.58, 150.93, 130.70, 129.26, 126.06, 121.57, 120.73, 120.68, 119.17, 116.86, 49.13, 48.30.



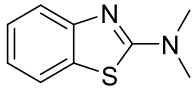
2-(Pyrrolidin-1-yl)benzo[d]thiazole (3ae):[7] white solid was obtained in 79% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.24 (m, 1H), 7.10 – 6.98 (m, 1H), 3.63 – 3.50 (m, 4H), 2.10 – 1.99 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.24, 153.19, 130.60, 125.80, 120.59, 120.54, 118.52, 49.38, 25.56.



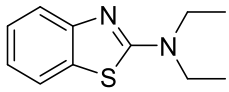
2-(Piperidin-1-yl)benzo[d]thiazole (3af):[7] white solid was obtained in 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.09 – 7.00 (m, 1H), 3.67 – 3.52 (m, 4H), 1.78 – 1.61 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.79, 152.83, 130.53, 125.77, 120.94, 120.48, 118.64, 49.52, 25.21, 24.15.



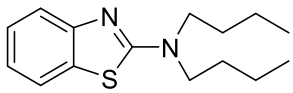
2-(Azepan-1-yl)benzo[d]thiazole (3ag): white solid was obtained in 86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 2H), 7.29 – 7.22 (m, 1H), 7.05 – 6.98 (m, 1H), 3.74 – 3.55 (m, 4H), 1.91 – 1.76 (m, 4H), 1.65 – 1.52 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.92, 153.17, 130.40, 125.68, 120.46, 120.38, 118.33, 50.63, 27.77, 27.42. HRMS (EI) calculated for $C_{13}H_{16}N_2S$ $[M+H]^+$: 233.1107; found: 233.1098.



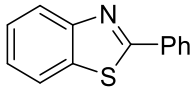
***N,N*-Dimethylbenzo[d]thiazol-2-amine (3ah):**[8] white solid was obtained in 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 3.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.66, 153.11, 130.98, 125.82, 120.77, 120.52, 118.61, 40.08.



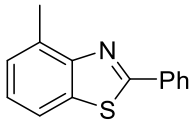
***N,N*-Diethylbenzo[d]thiazol-2-amine[7] (3ai):** white solid was obtained in 87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.10 (s, 1H), 3.71 (q, *J* = 7.1 Hz, 4H), 1.26 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.32, 139.61, 128.42, 125.91, 125.63, 45.51, 12.51.



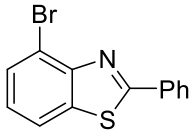
***N,N*-Dibutylbenzo[d]thiazol-2-amine (3aj):**[9] white solid was obtained in 86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.34 – 7.28 (m, 1H), 7.10 – 7.02 (m, 1H), 3.53 (t, 4H), 1.78 – 1.67 (m, 4H), 1.49 – 1.38 (m, 4H), 1.02 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.71, 153.16, 130.52, 125.58, 120.45, 120.27, 118.37, 50.82, 29.49, 19.99, 13.80.



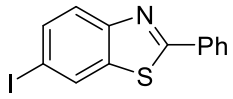
2-Phenylbenzo[d]thiazole (6a):[10] white solid was obtained in 91% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 3H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.41 (m, 4H), 7.36 – 7.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 153.94, 134.87, 133.40, 130.81, 128.85, 127.38, 126.16, 125.03, 123.05, 121.47.



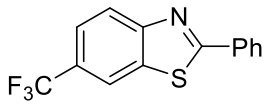
4-Methyl-2-phenylbenzo[d]thiazole (6b):[10] white solid was obtained in 92% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.05 (m, 2H), 7.71 – 7.65 (m, 1H), 7.48 – 7.40 (m, 3H), 7.26 – 7.19 (m, 2H), 2.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.47, 153.44, 134.90, 133.86, 133.25, 130.62, 128.86, 127.42, 126.69, 124.98, 118.90, 18.38.



4-Bromo-2-phenylbenzo[d]thiazole (6c):[10] white solid was obtained in 98% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.81 – 7.74 (m, 1H), 7.68 – 7.60 (m, 1H), 7.51 – 7.41 (m, 3H), 7.17 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.45, 152.13, 135.75, 133.06, 131.24, 129.65, 128.90, 127.64, 125.84, 120.69, 116.77.

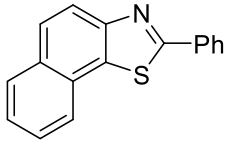


6-Iodo-2-phenylbenzo[d]thiazole (6d):[10] white solid was obtained in 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.2 Hz, 1H), 8.14 – 8.07 (m, 2H), 7.86 – 7.77 (m, 2H), 7.57 – 7.51 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.50, 153.45, 137.07, 135.41, 133.03, 131.32, 130.07, 129.09, 127.56, 124.63, 89.44.

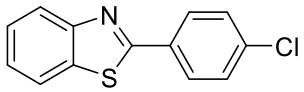


2-Phenyl-5-(trifluoromethyl)benzo[d]thiazole (6e):[10] white solid was obtained in 33% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 8.10 – 8.04 (m, 2H), 7.71 (m, *J* = 8.6, 1.4 Hz, 1H), 7.55 – 7.46 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.07,

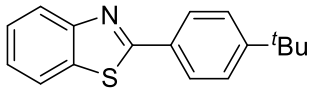
155.99, 135.02, 132.92, 131.63, 129.11, 127.69, 127.01, 124.30 (q, J_{C-F} = 208.8 Hz), 123.27, 122.79, 119.25 (q, J_{C-F} = 4.0 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.35.



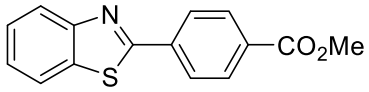
2-Phenylnaphtho[2,1-d]thiazole (6f):[10] white solid was obtained in 97% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.2 Hz, 1H), 8.22 – 8.11 (m, 2H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.59 – 7.52 (m, 1H), 7.52 – 7.41 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.96, 150.34, 133.89, 131.96, 131.59, 130.51, 128.95, 128.68, 128.01, 127.24, 126.87, 126.05, 125.82, 123.96, 118.89.



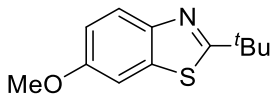
2-(4-Chlorophenyl)benzo[d]thiazole (6g):[10] white solid was obtained in 86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.34 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.53, 153.95, 136.93, 134.95, 131.98, 129.18, 128.61, 126.41, 125.34, 123.20, 121.58.



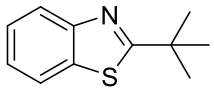
2-(4-(*tert*-Butyl)phenyl)benzo[d]thiazole (6h):[10] white solid was obtained in 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.98 (m, 3H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.44 (m, 3H), 7.42 – 7.33 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.12, 154.49, 154.13, 134.91, 130.82, 127.29, 126.19, 125.95, 124.96, 123.02, 121.54, 34.95, 31.15.



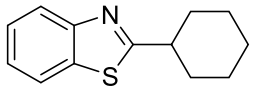
Methyl 4-(benzo[d]thiazol-2-yl)benzoate (6i):[10] white solid was obtained in 92% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.11 (m, 4H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.44 – 7.37 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.46, 166.30, 153.97, 137.31, 135.15, 131.87, 130.15, 127.30, 126.51, 125.61, 123.49, 121.64, 52.30.



2-(*tert*-Butyl)-6-methoxybenzo[d]thiazole (6j):[10] white solid was obtained in 95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.04 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.85 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.20, 157.09, 147.57, 136.10, 123.00, 114.76, 104.04, 55.68, 38.08, 30.66.



2-(*tert*-Butyl)benzo[d]thiazole (6k):[10] colorless oil was obtained in 59% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.40 (m, 1H), 7.37 – 7.28 (m, 1H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.82, 153.15, 134.87, 125.68, 124.46, 122.58, 121.39, 38.25, 30.69.



2-Cyclohexylbenzo[d]thiazole (6l):[10] colorless oil was obtained in 20% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.38 – 7.28 (m, 1H), 3.10 (tt, *J* = 11.7, 3.6 Hz, 1H), 2.27 – 2.14 (m, 2H), 1.89 (dt, *J* = 12.8, 3.2 Hz, 2H), 1.81 – 1.72 (m, 1H), 1.67 (dd, *J* = 12.3, 3.1 Hz, 1H), 1.61 (dd, *J* = 12.4, 3.1 Hz, 1H), 1.48 (dt, *J* = 12.3, 3.3 Hz, 1H), 1.41 (dt, *J* = 12.5, 3.0 Hz, 1H), 1.37 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.60, 153.02, 134.46, 125.75, 124.45, 122.48, 121.51, 43.39, 33.39, 26.02, 25.73.

References

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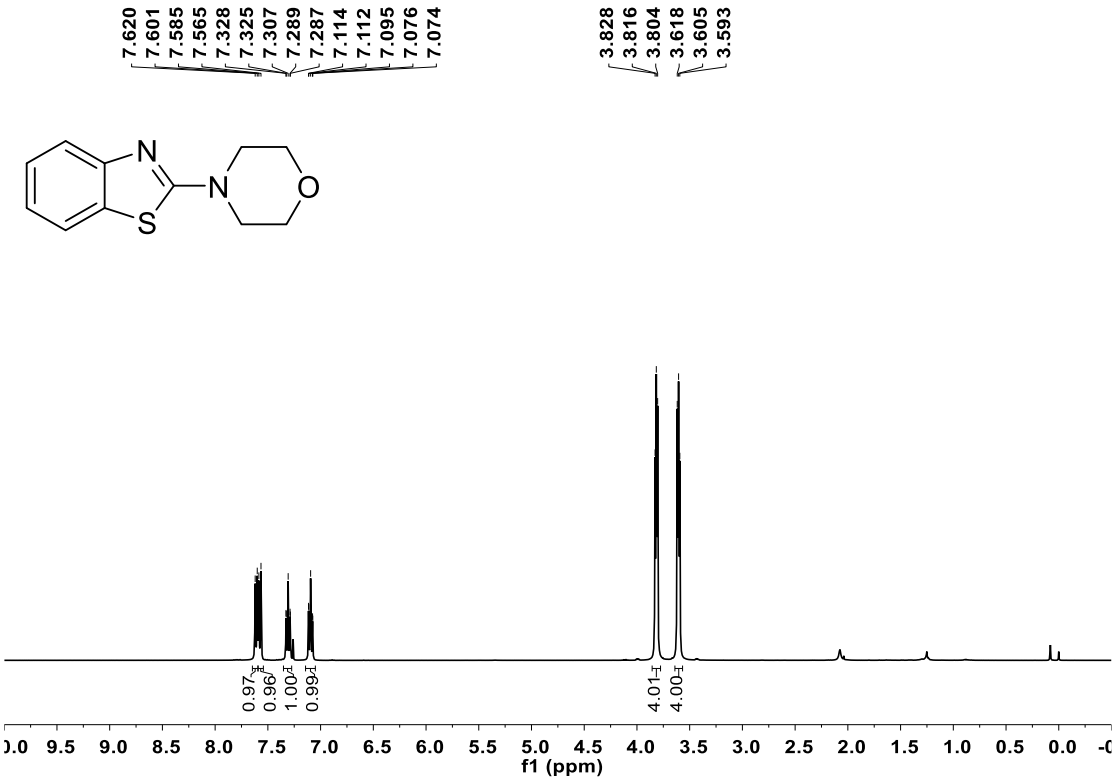
Copies of product NMR Spectra

3aa

^{1}H NMR



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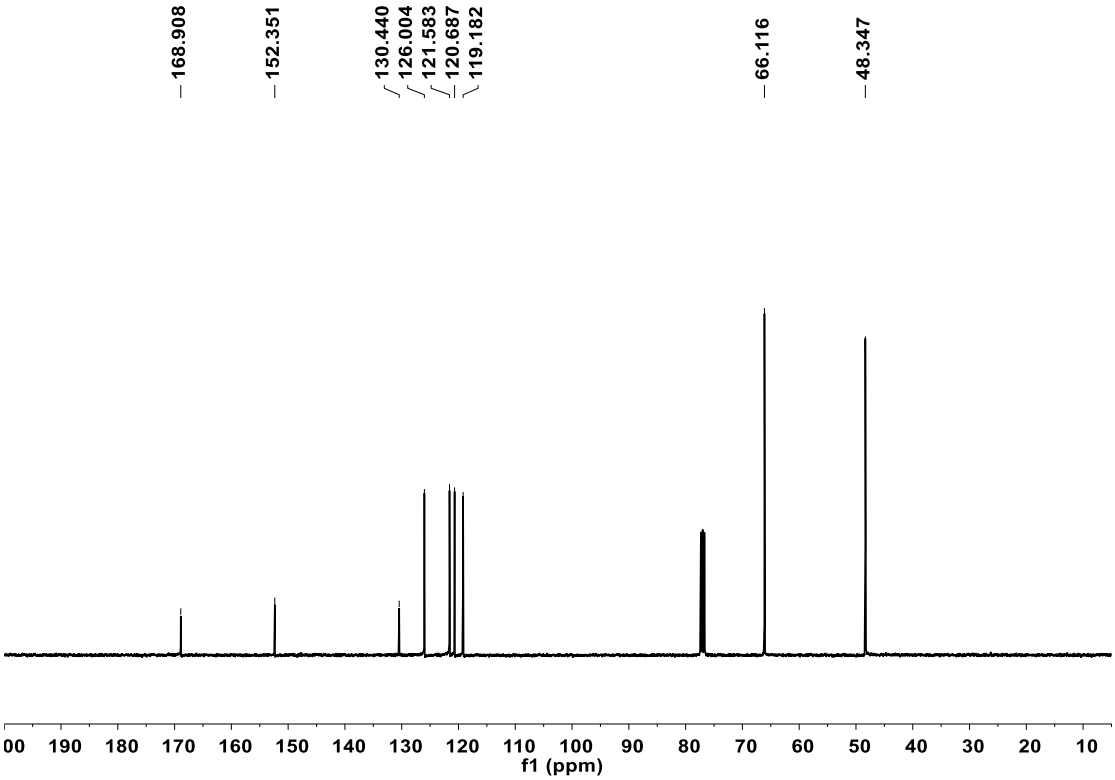

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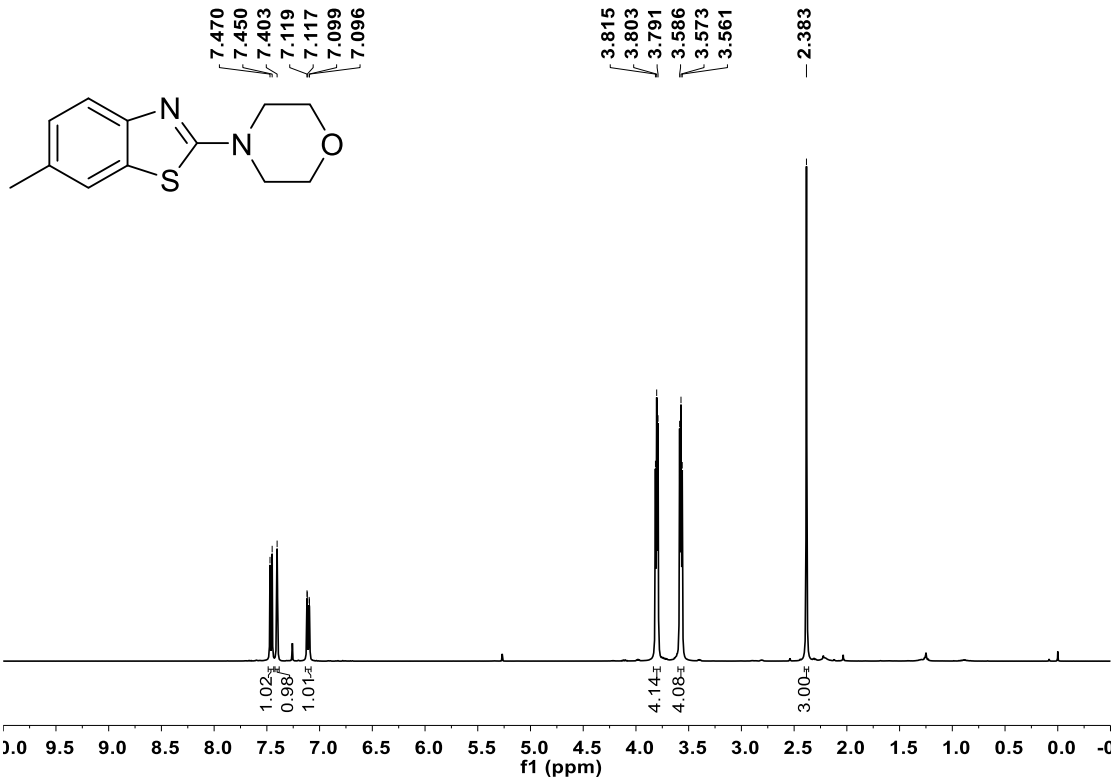

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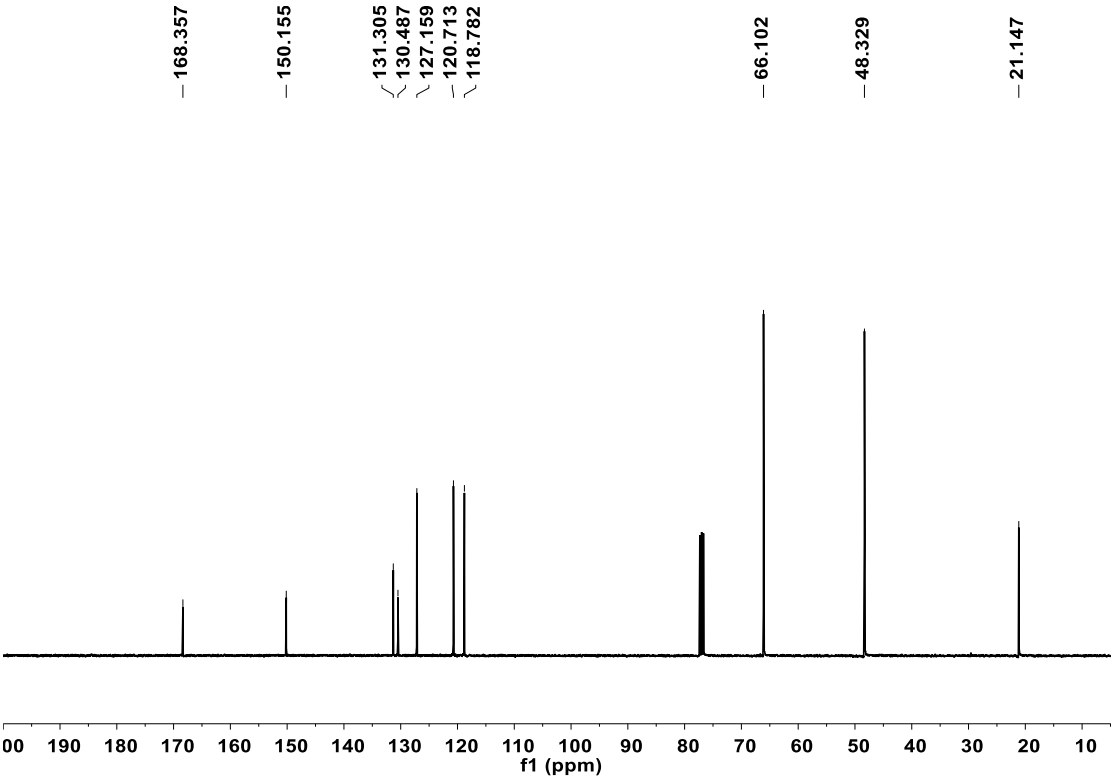

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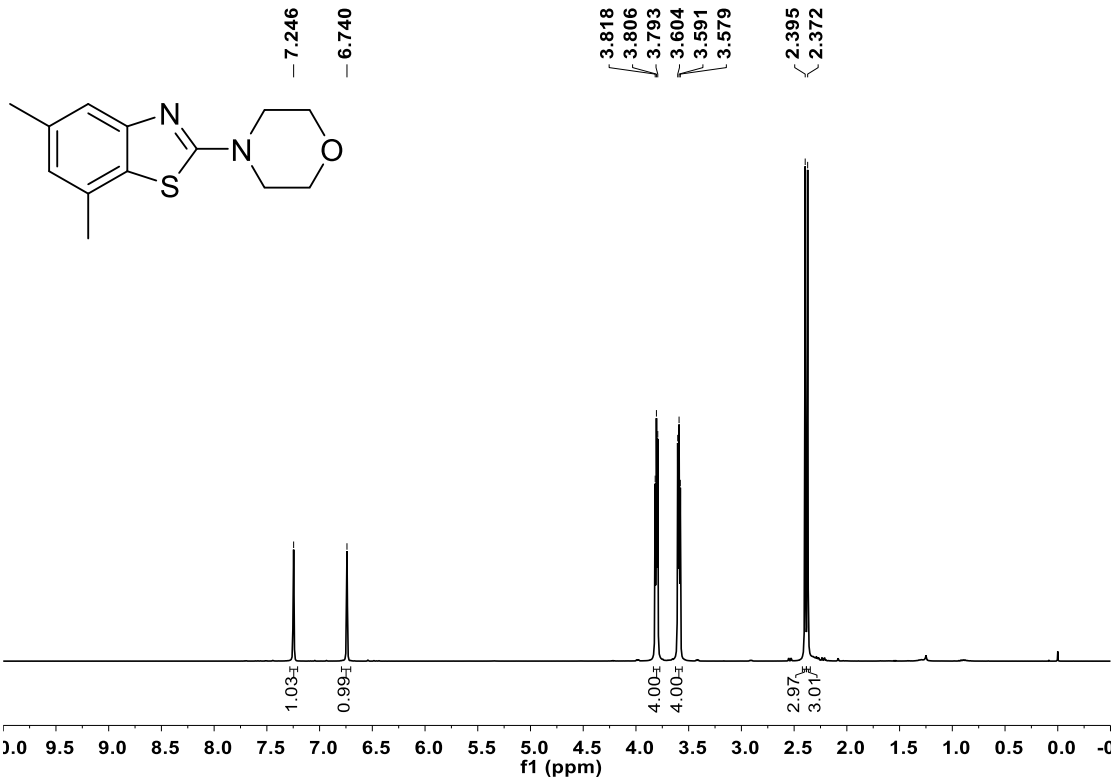

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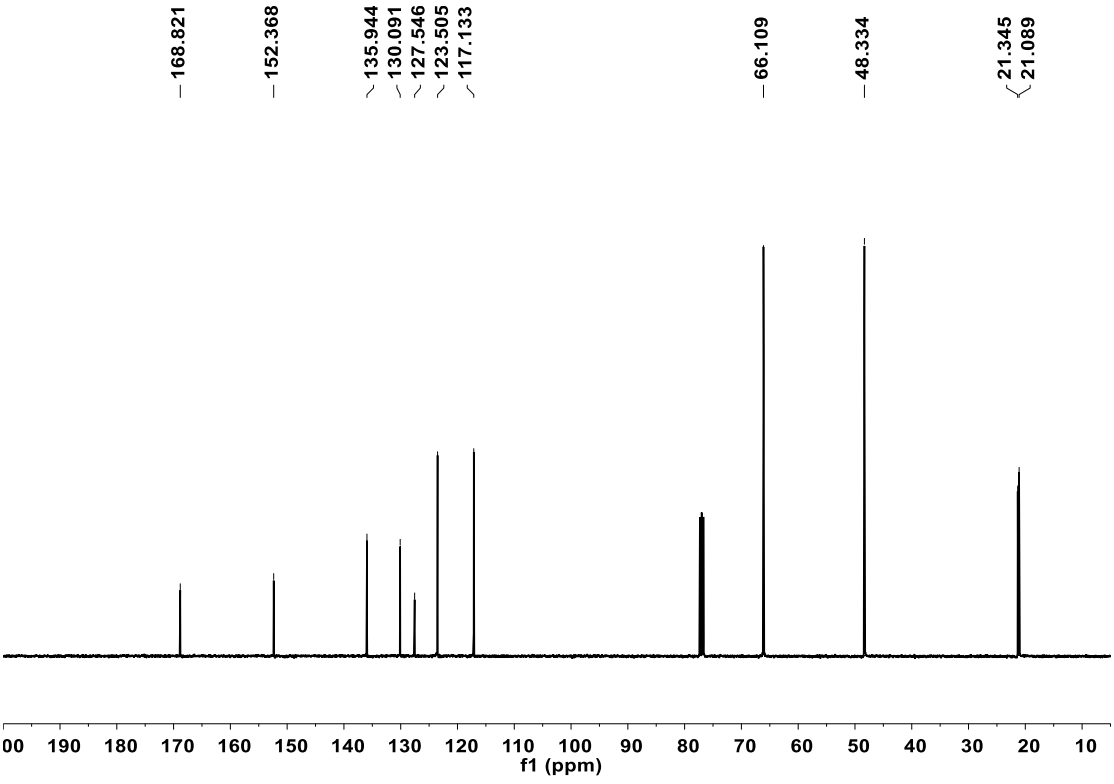

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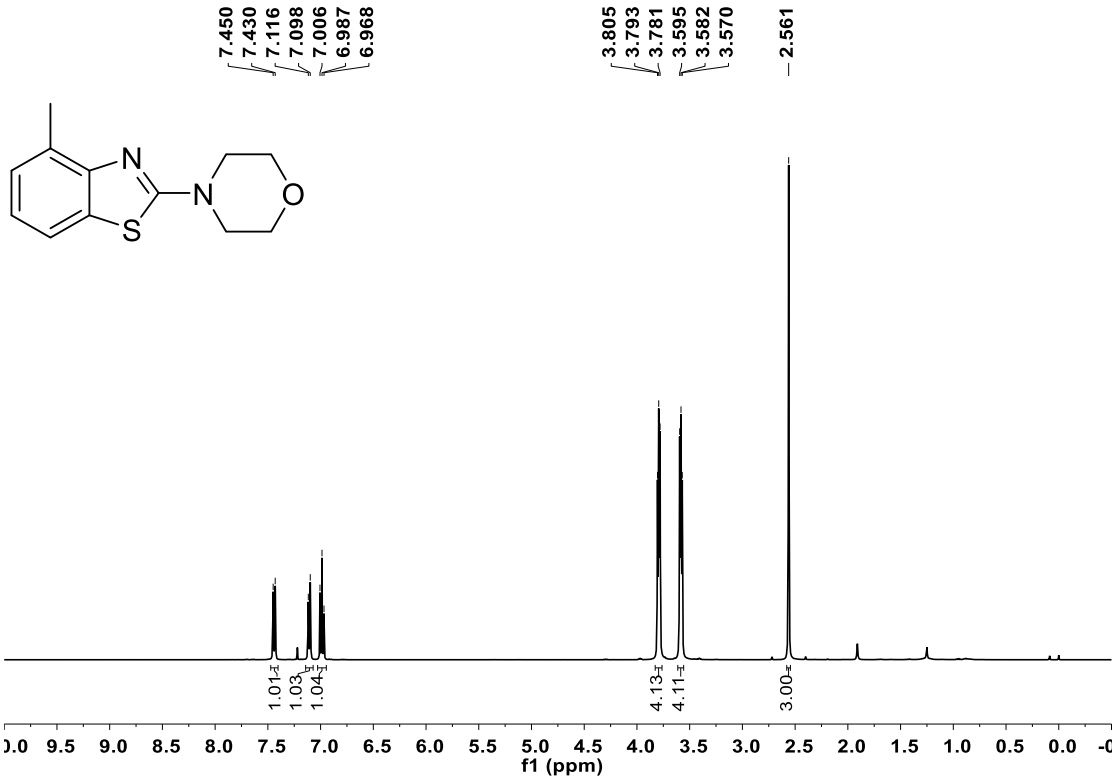

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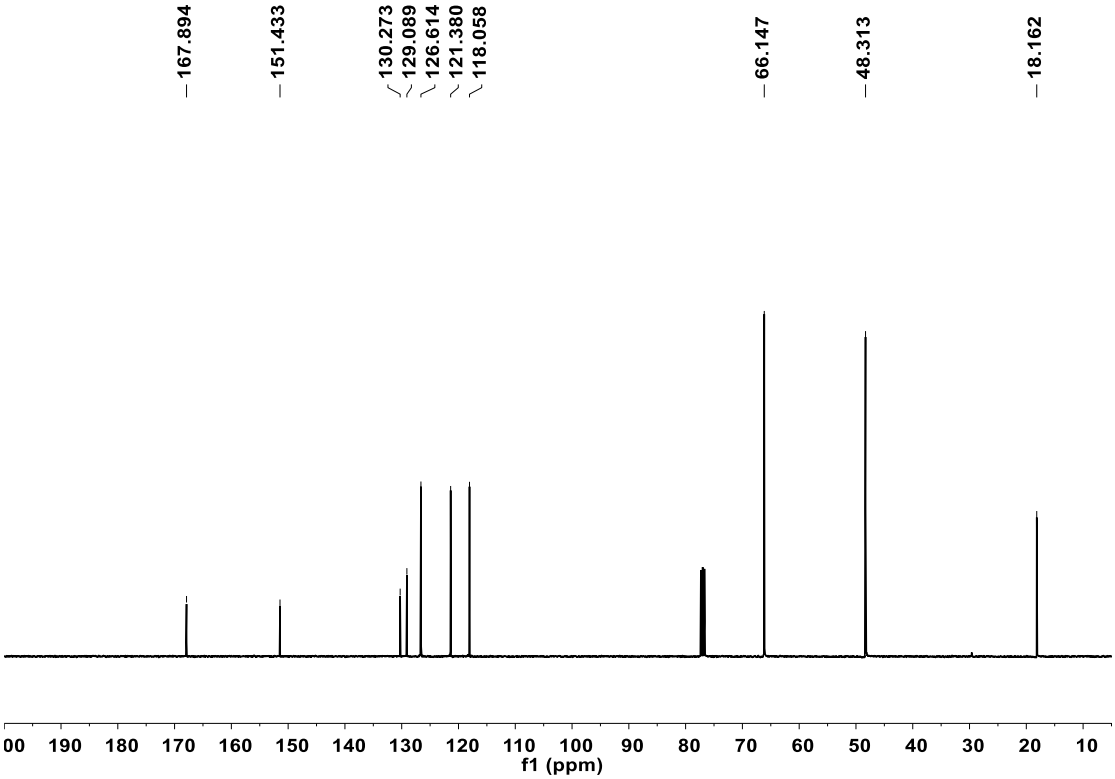

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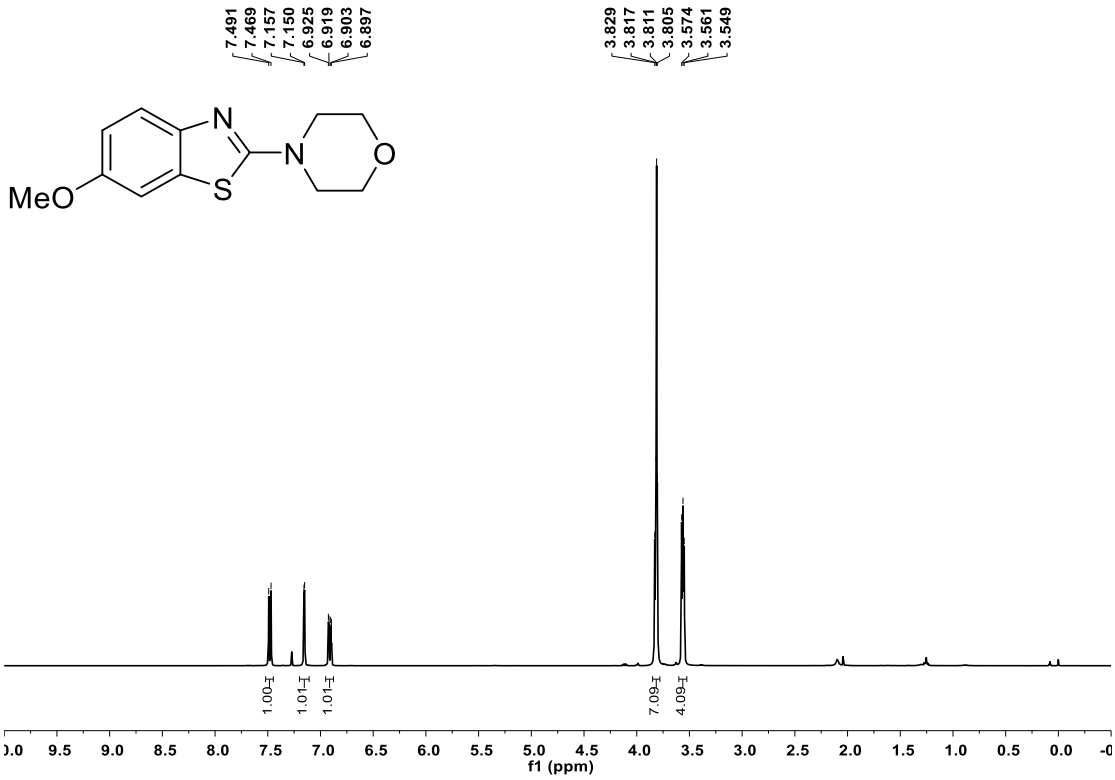

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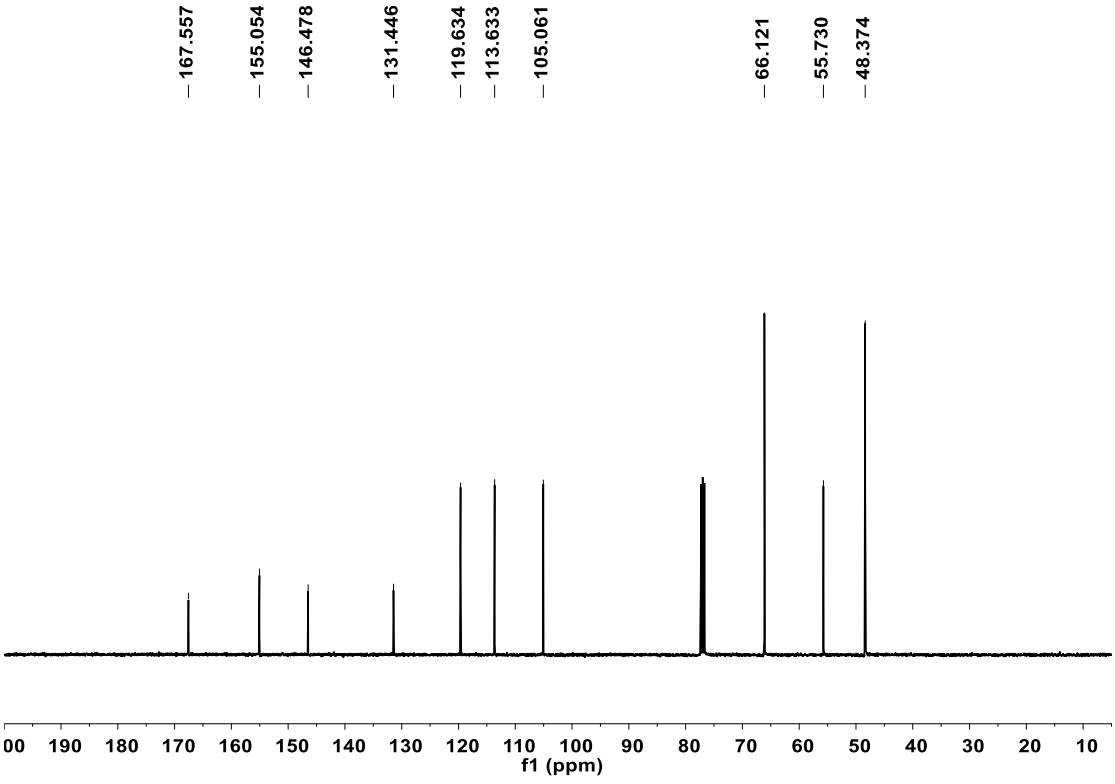

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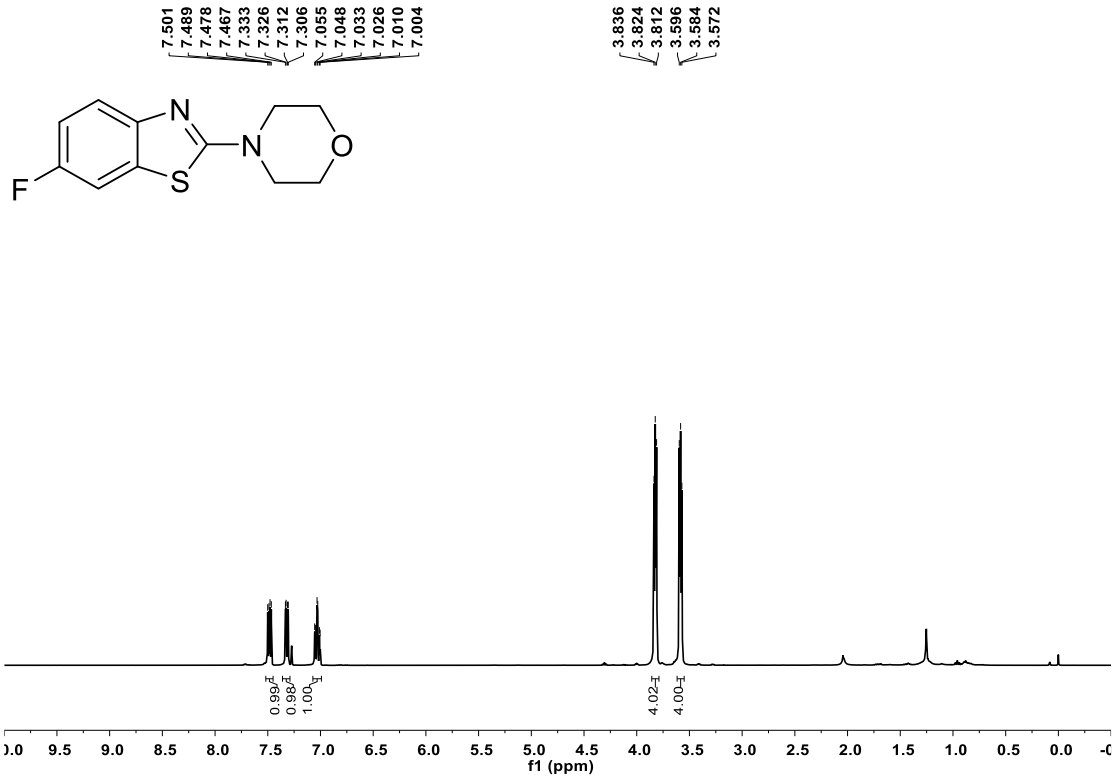

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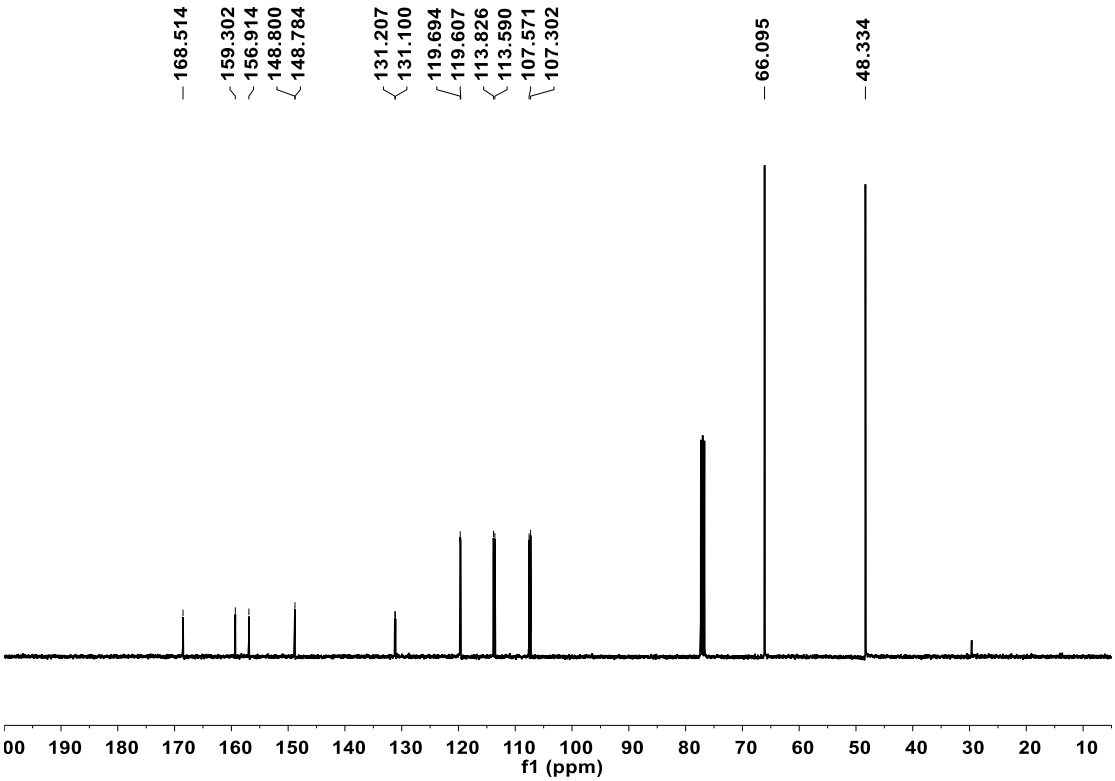

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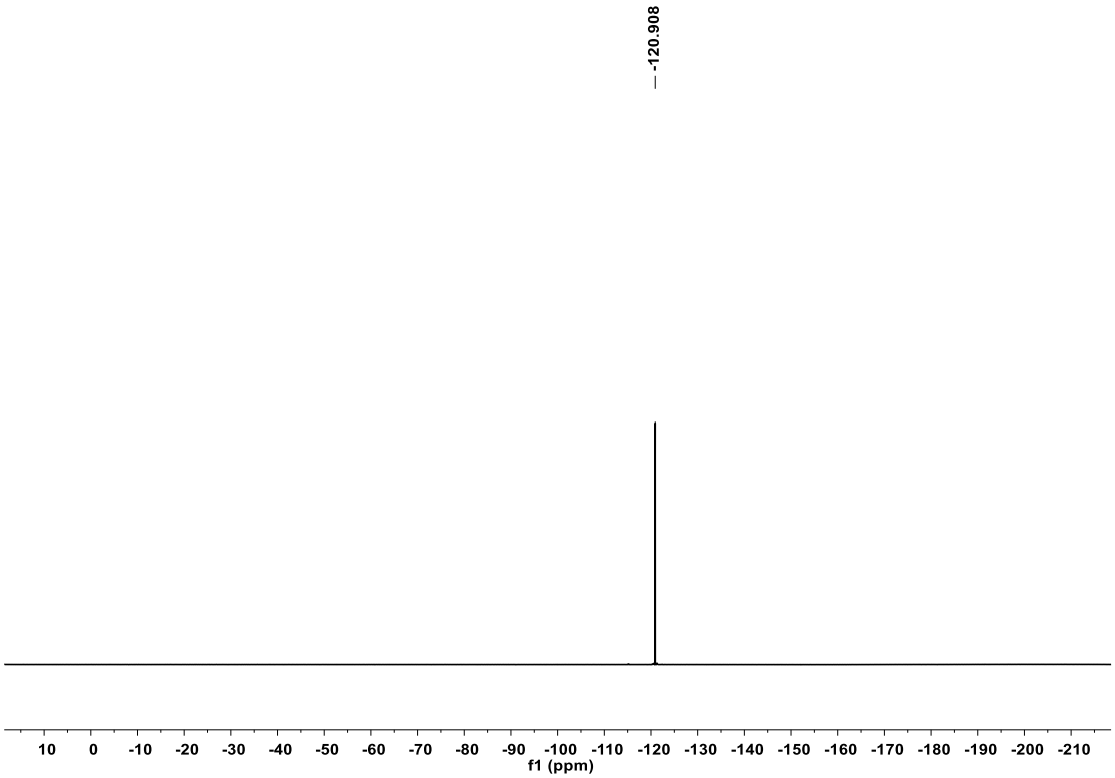
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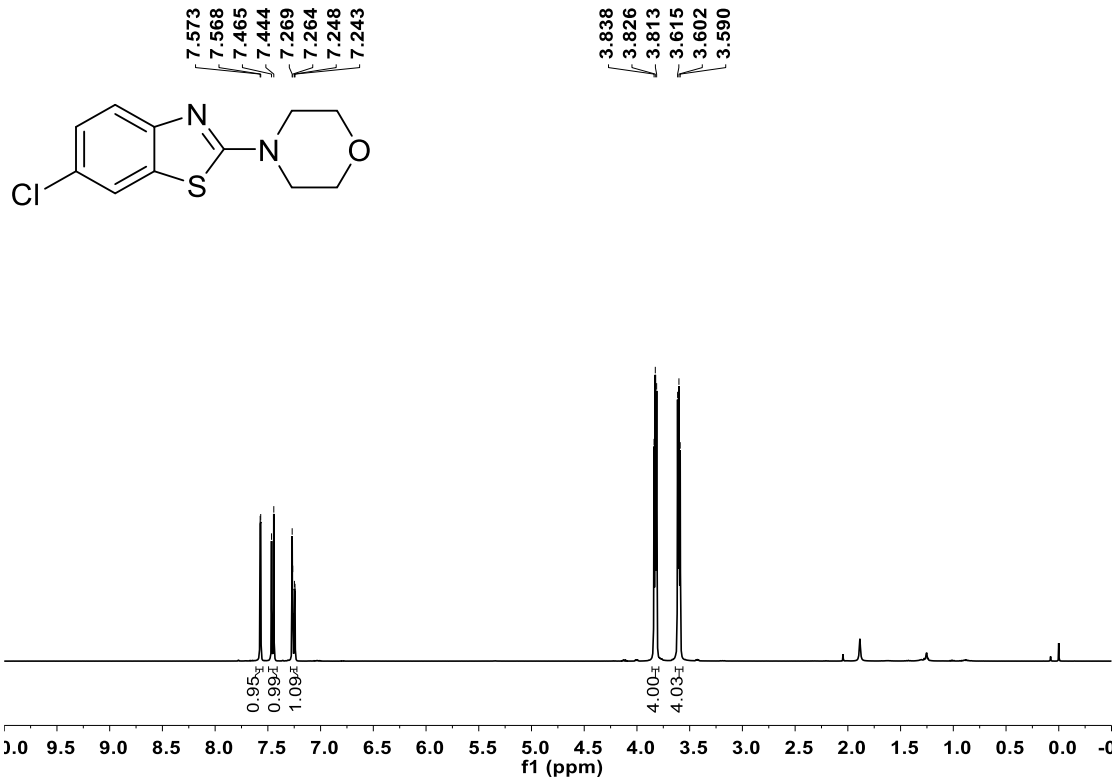
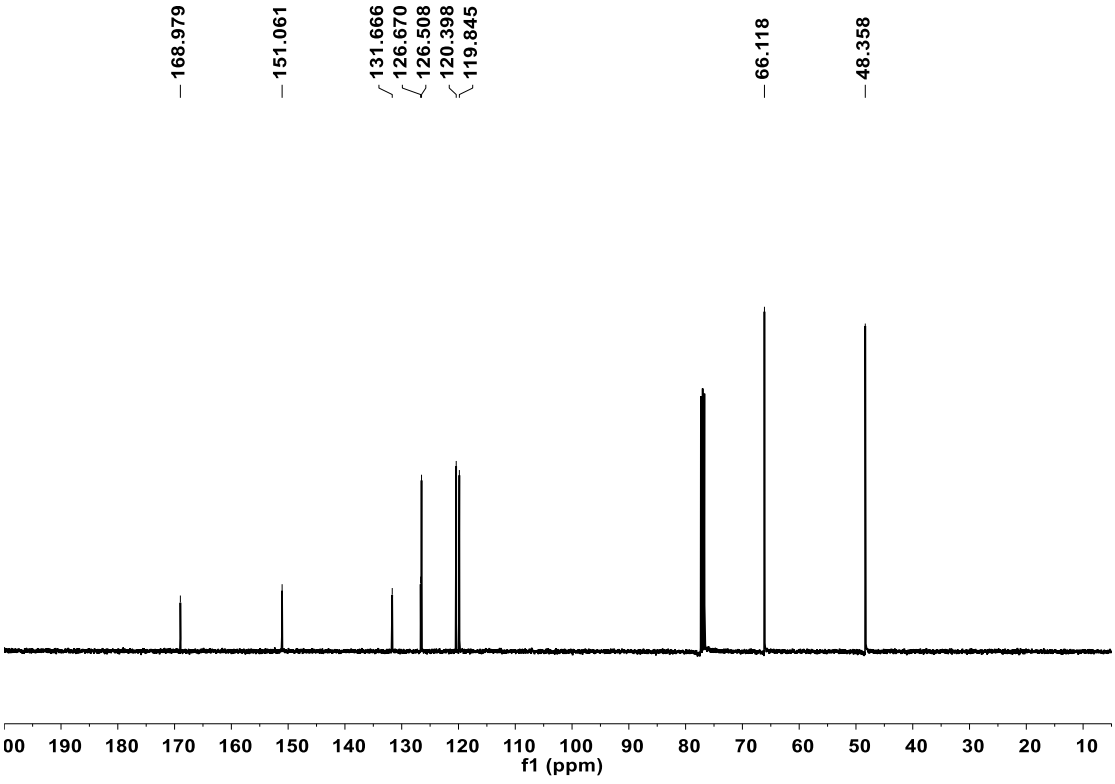
f1 (ppm)

3ga

^{1}H NMR

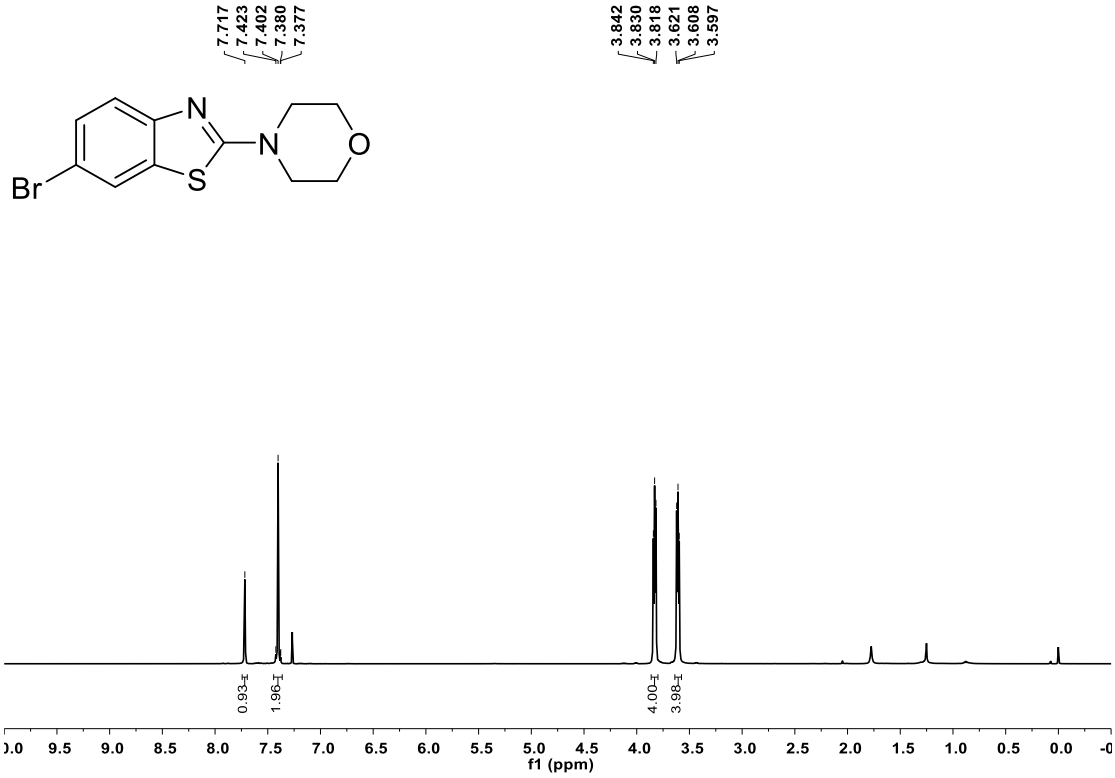


^{13}C NMR

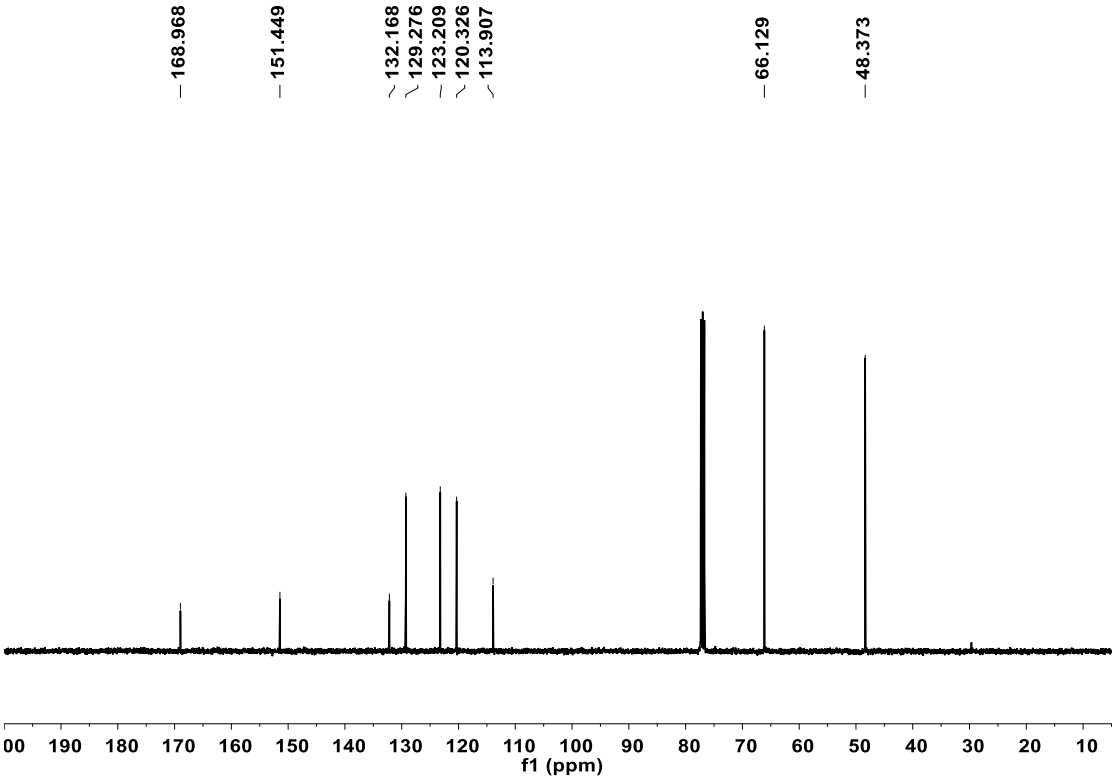


3ha

^{1}H NMR

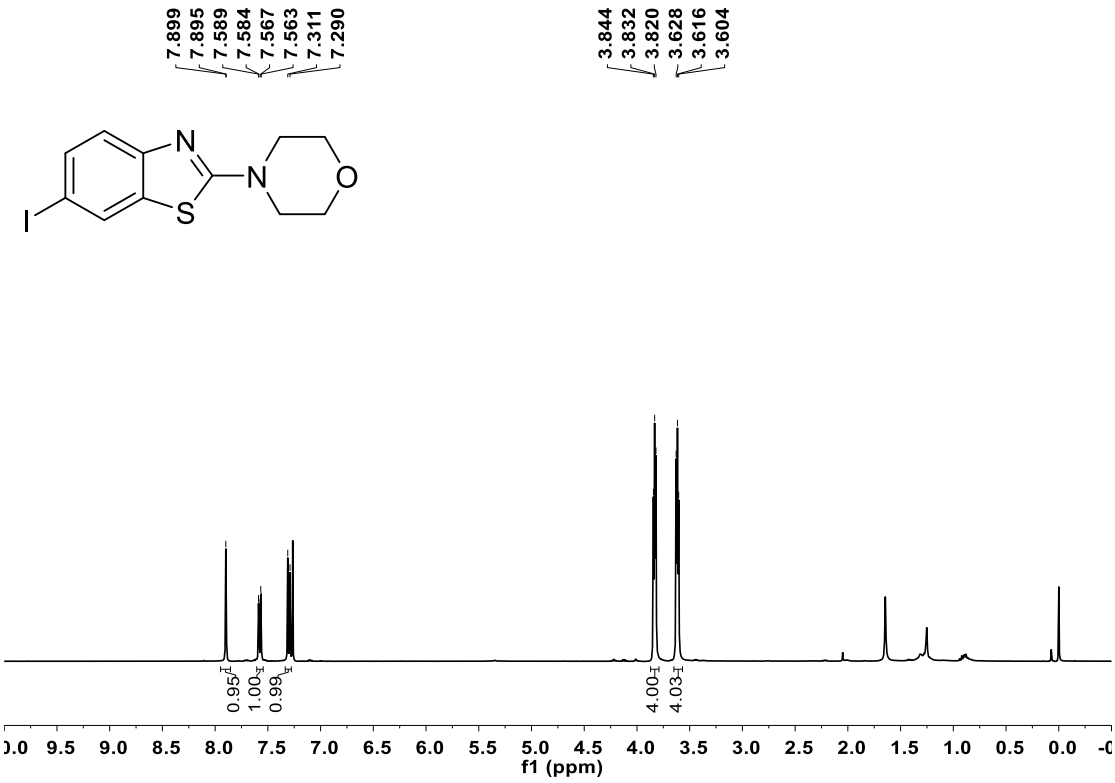


^{13}C NMR

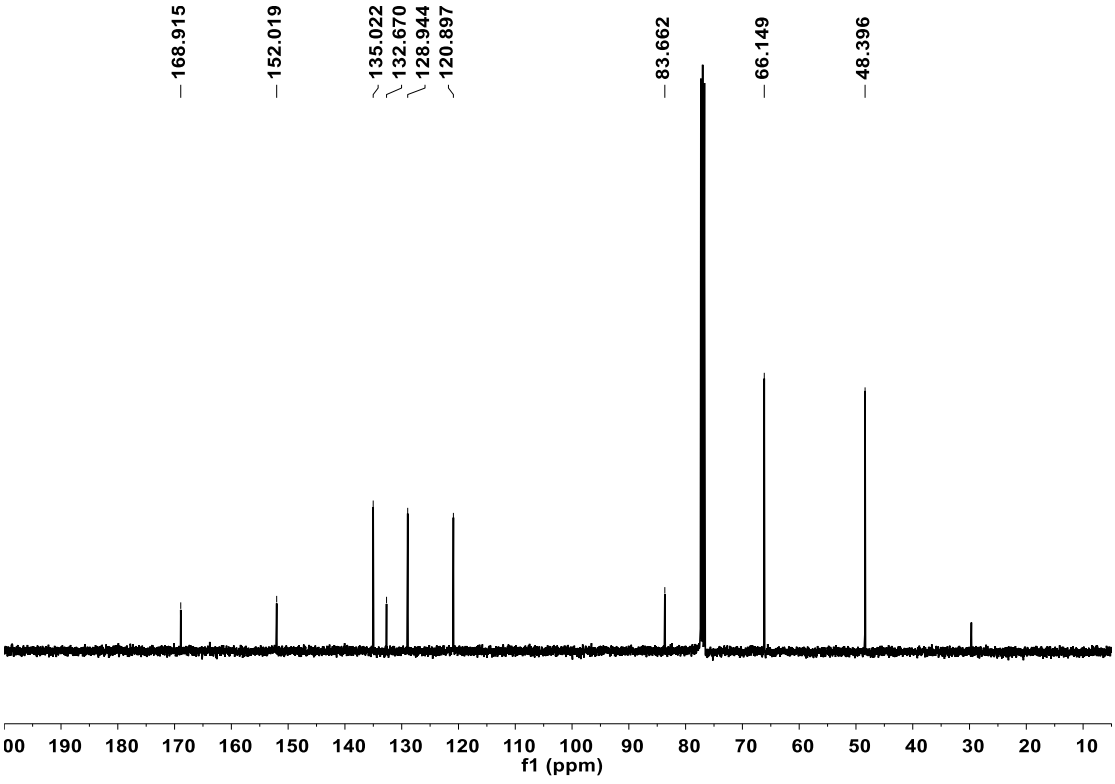


3ia

^{1}H NMR

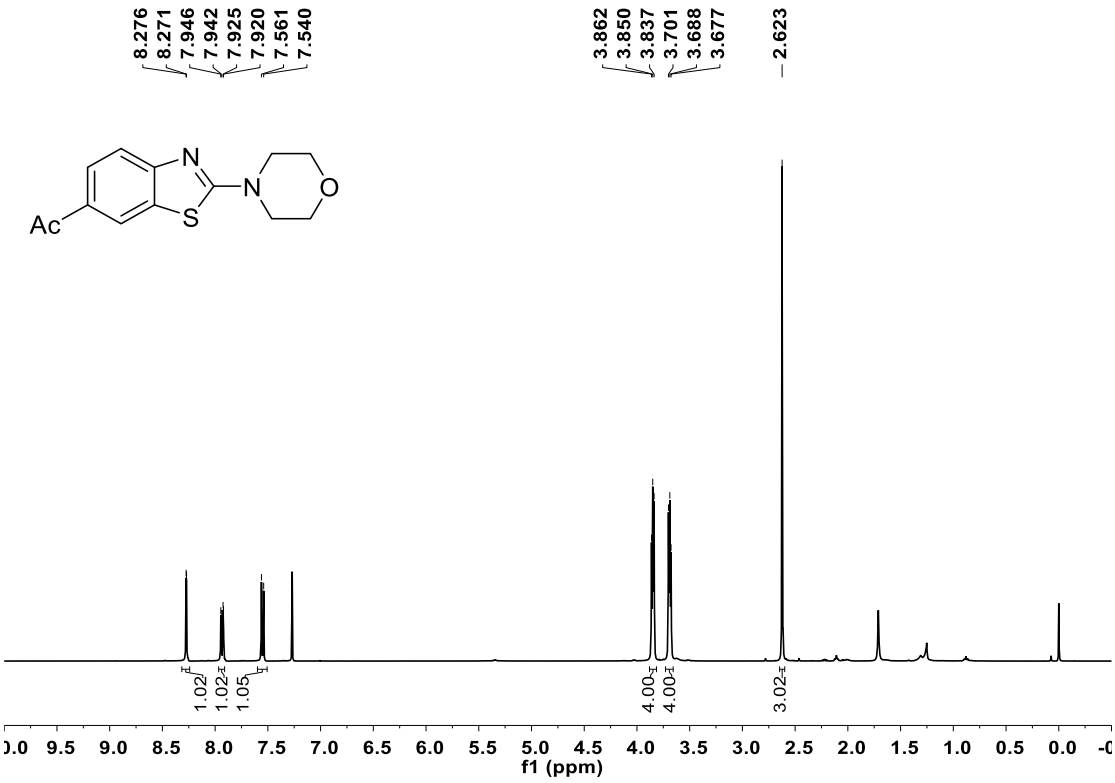


^{13}C NMR

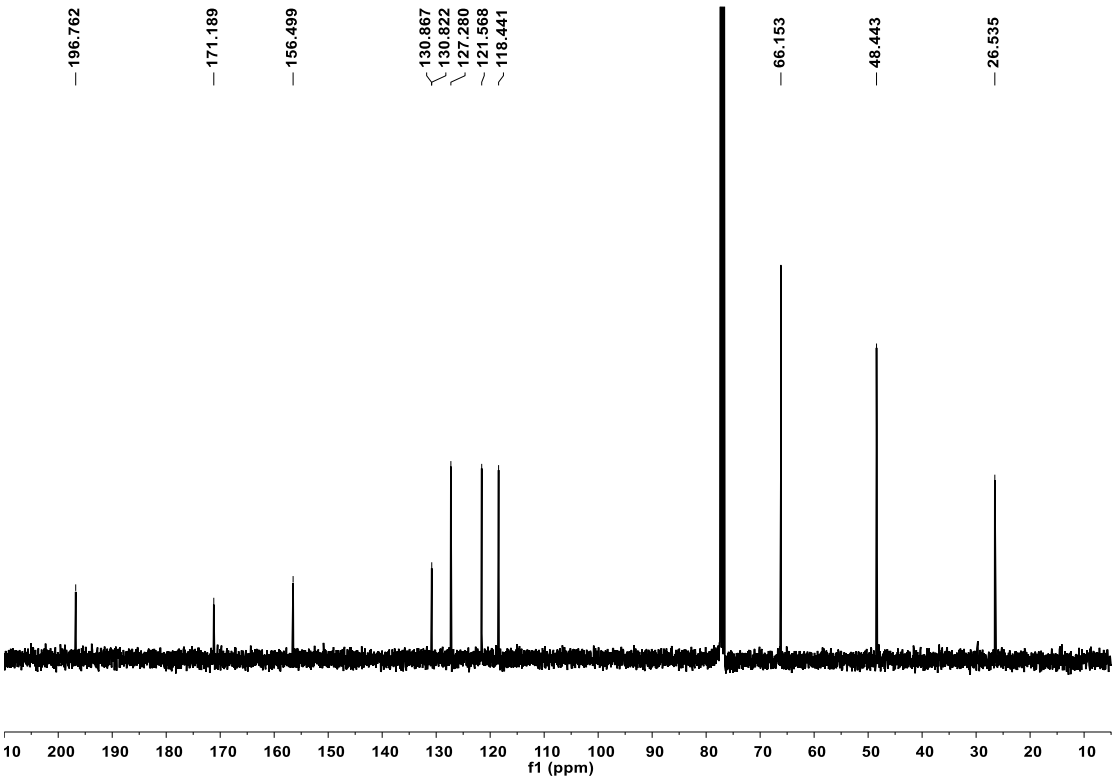


3ja

^{1}H NMR

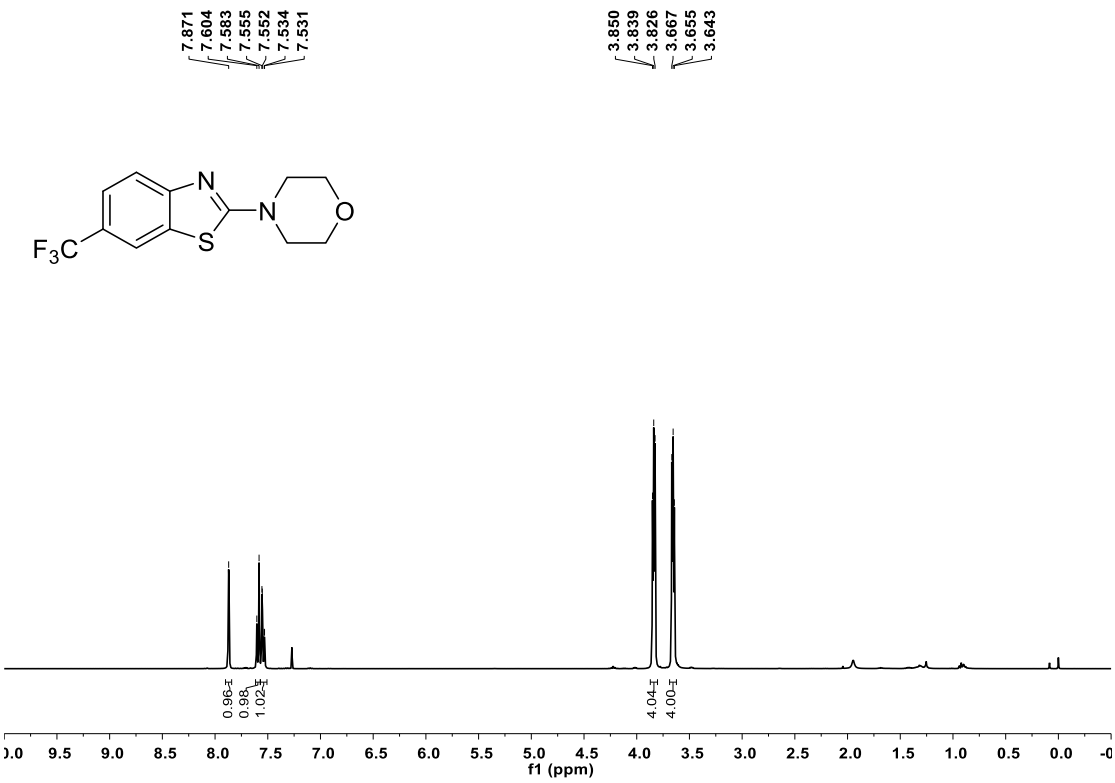


^{13}C NMR

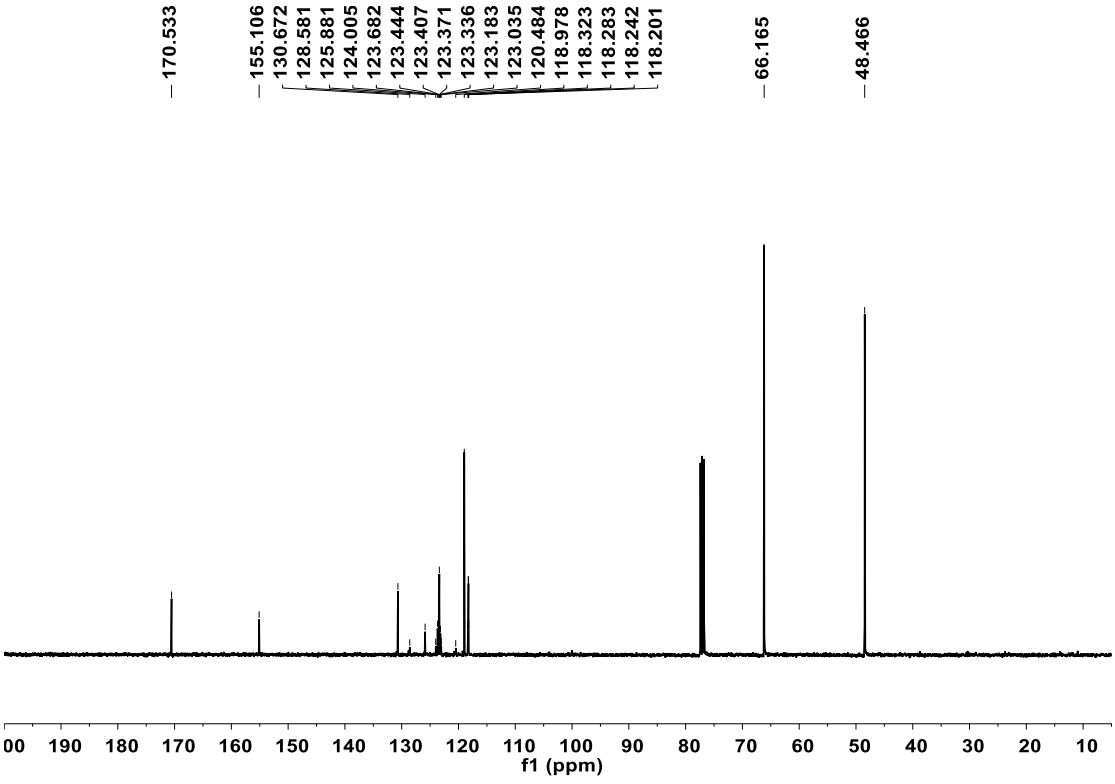


3ka

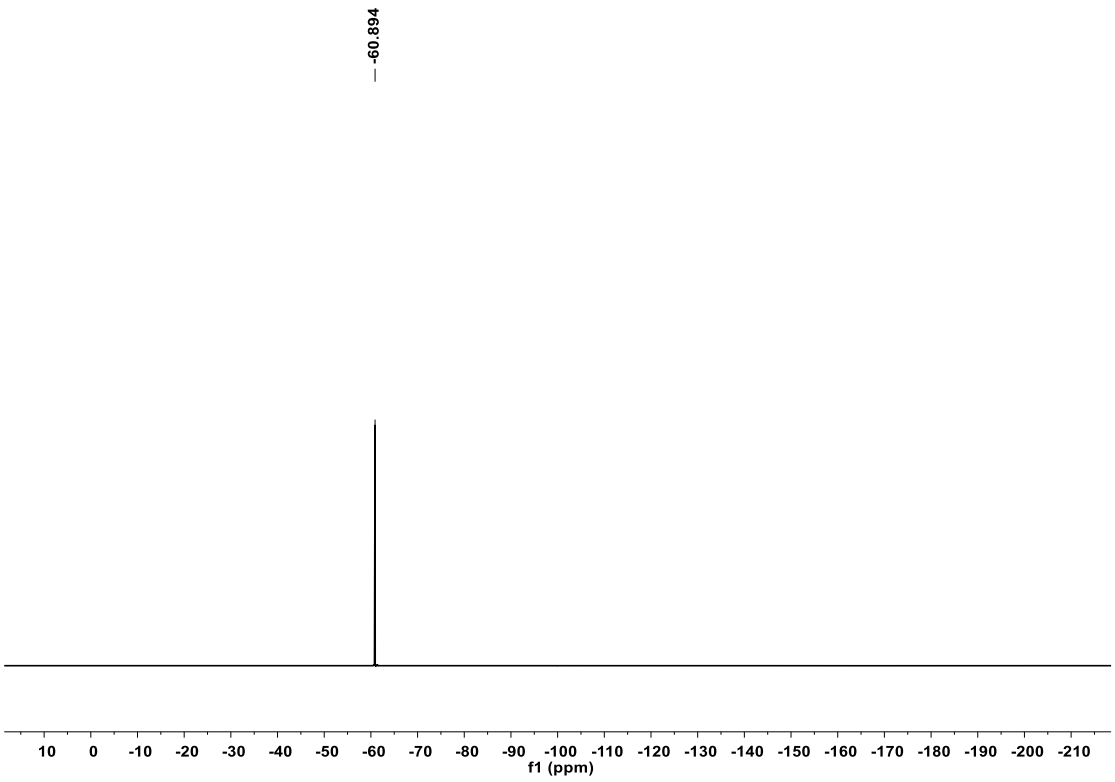
^{1}H NMR



^{13}C NMR

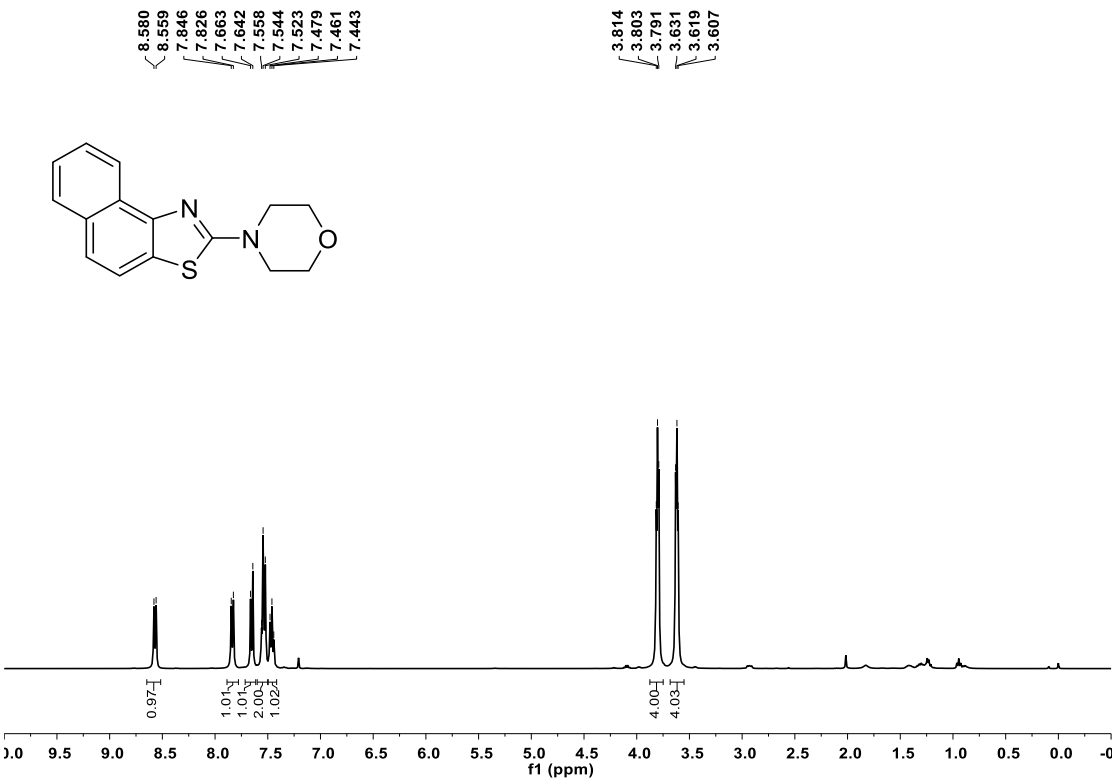


^{19}F NMR

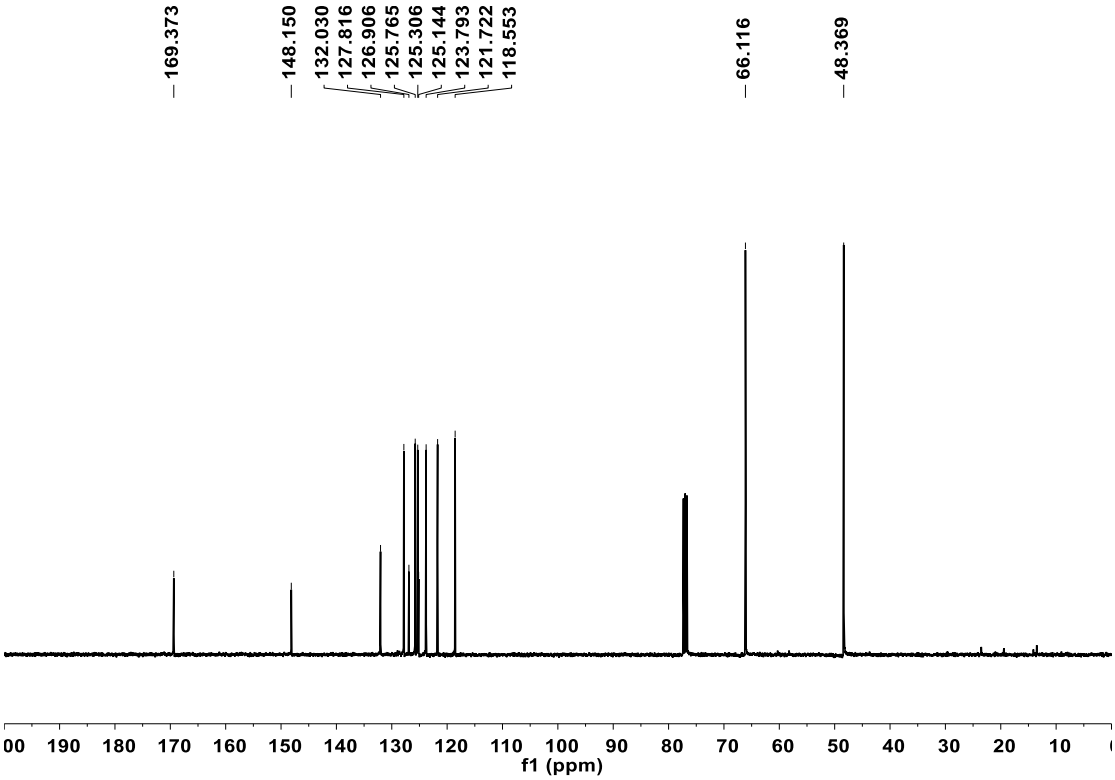

-60.894
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3la

^{1}H NMR



^{13}C NMR



3ma

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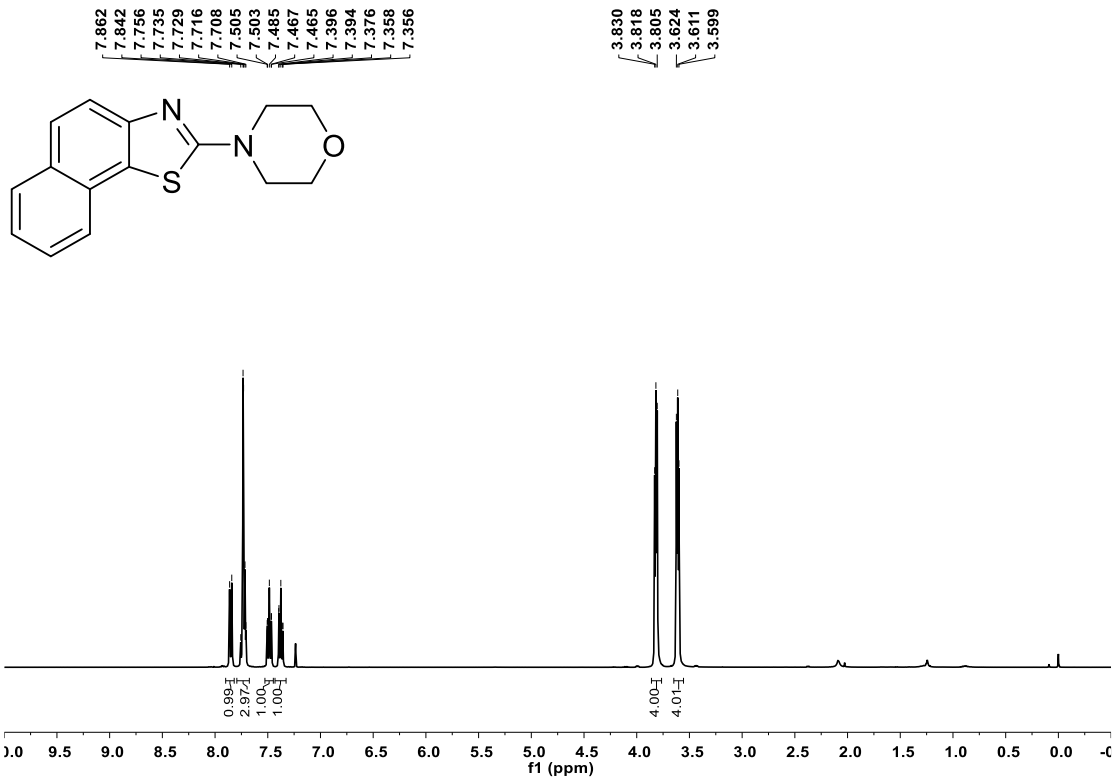
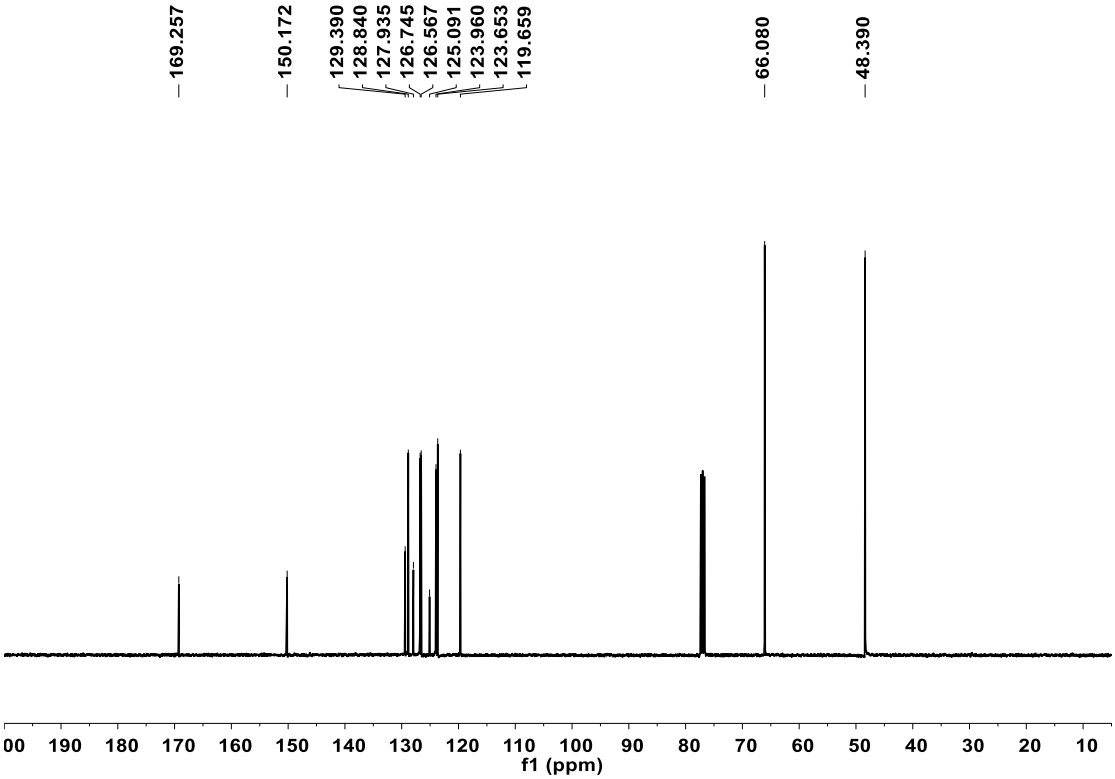
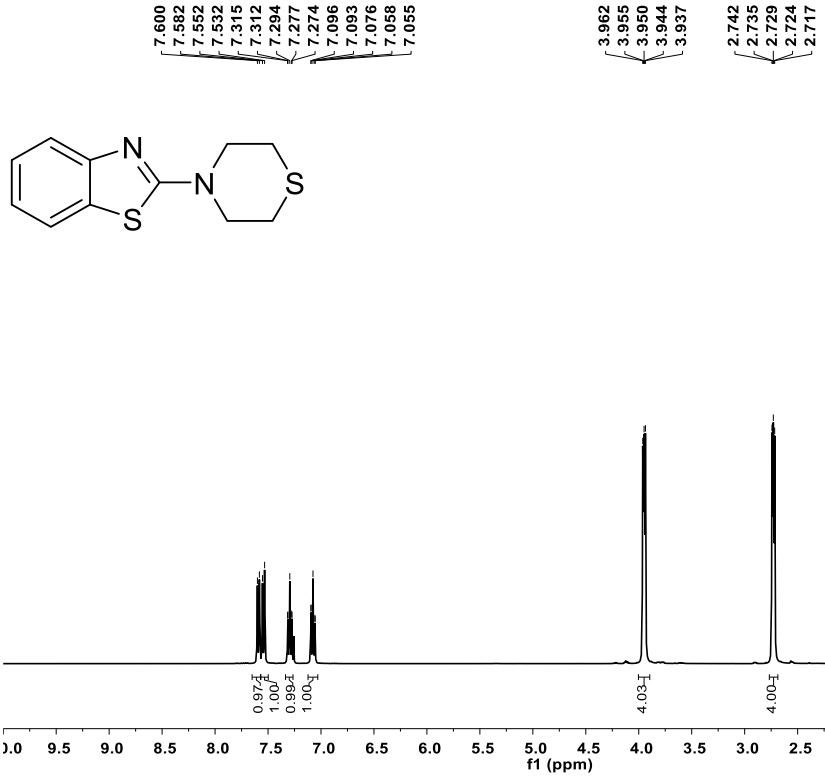


^{13}C NMR

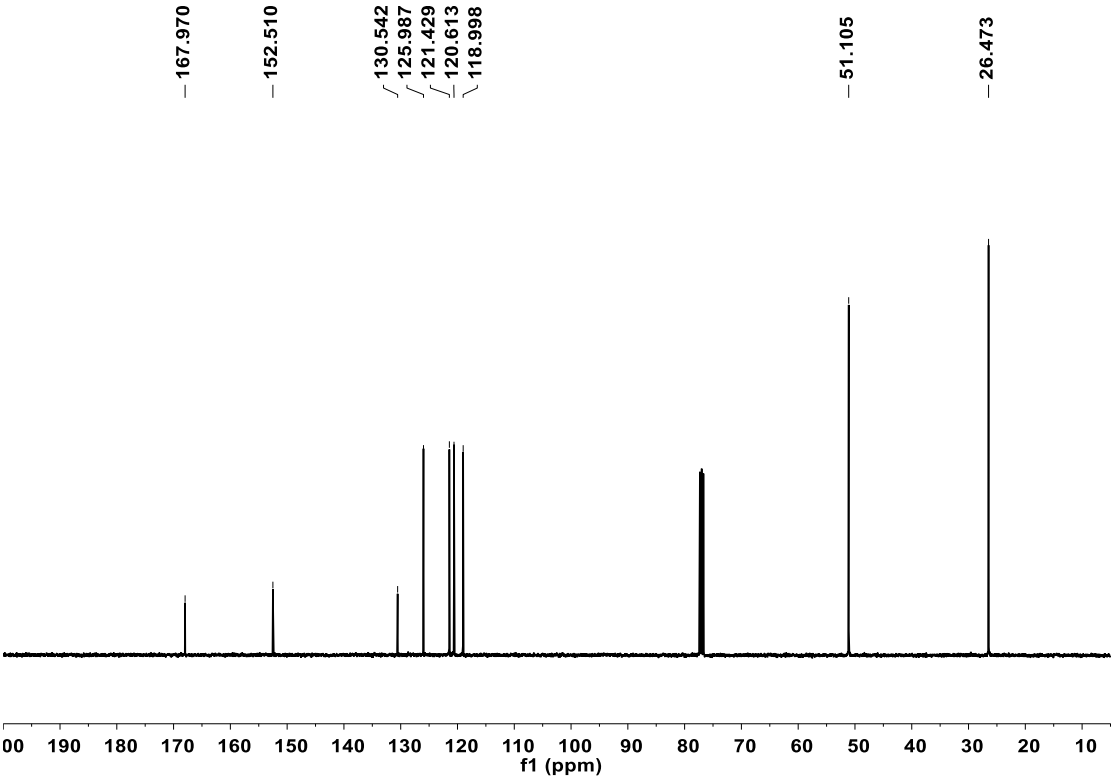


3ab

^{1}H NMR

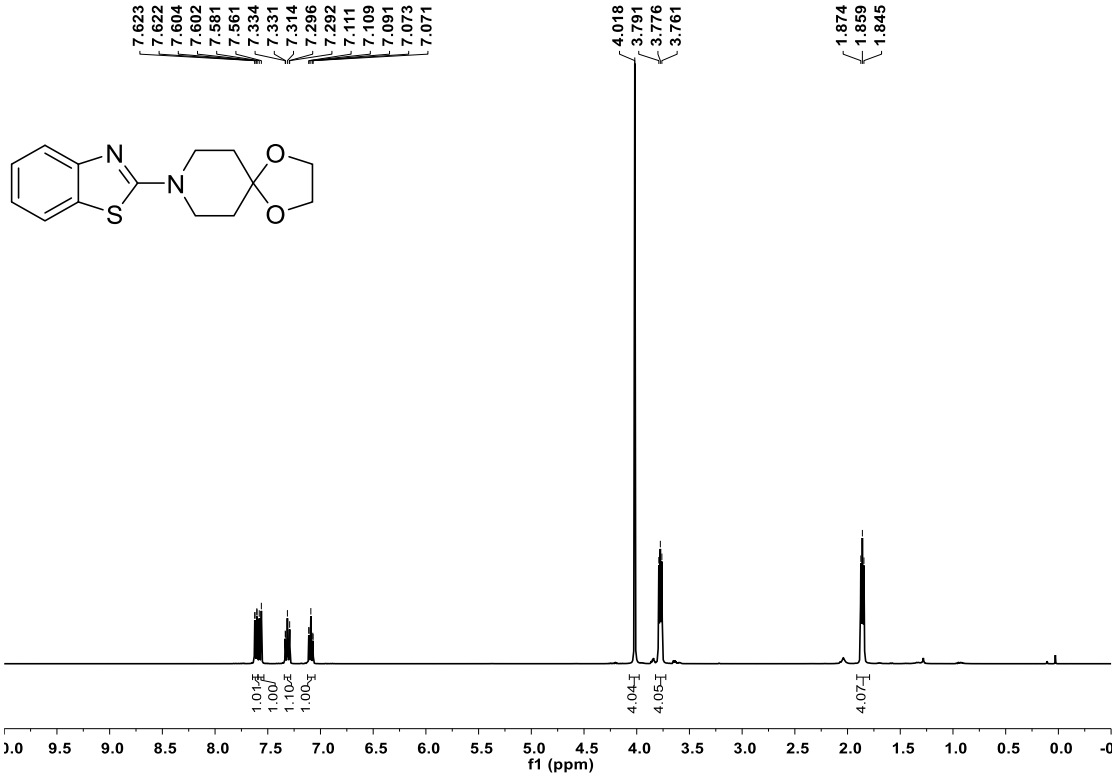


^{13}C NMR

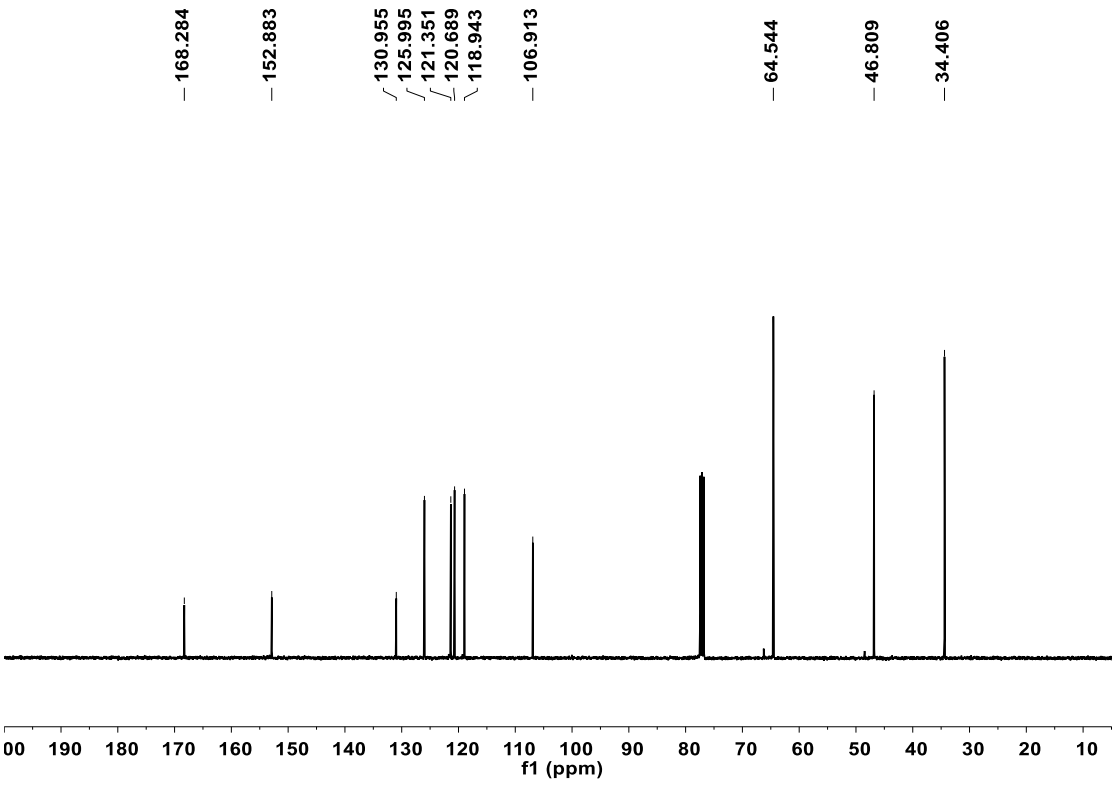


3ac

^{1}H NMR

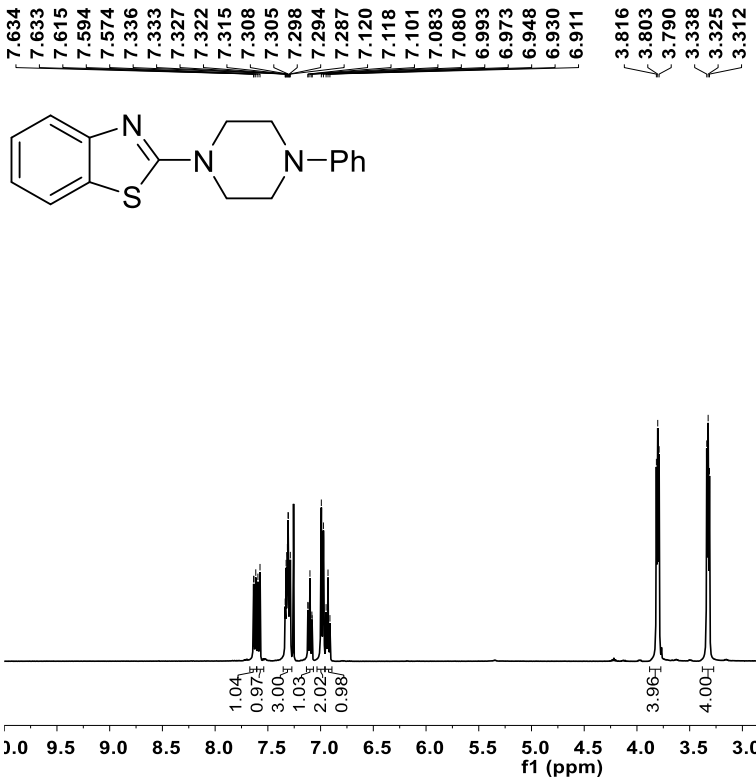


^{13}C NMR

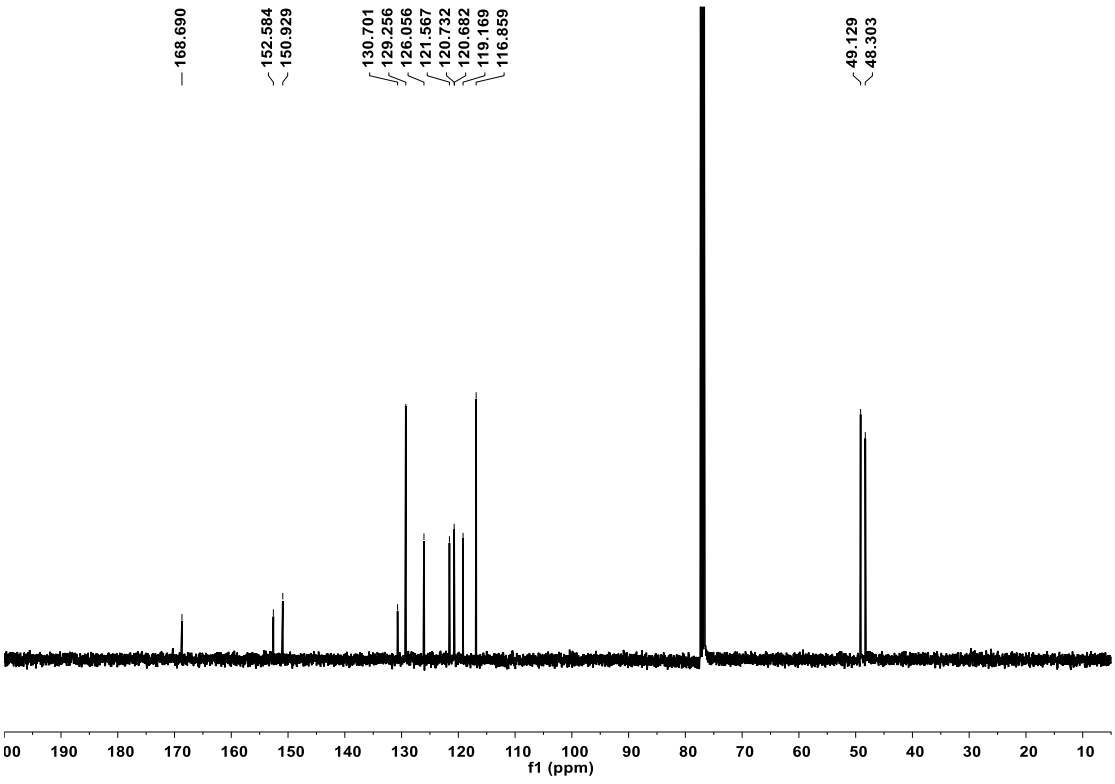


3ad

^{1}H NMR

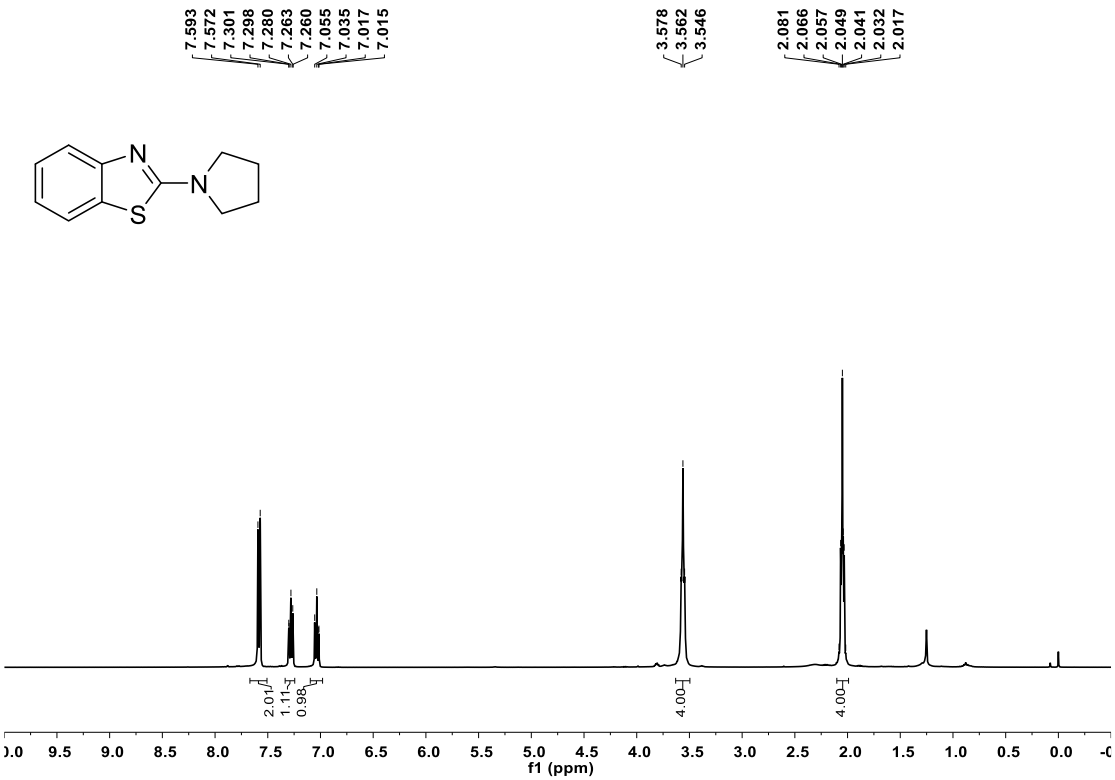


^{13}C NMR

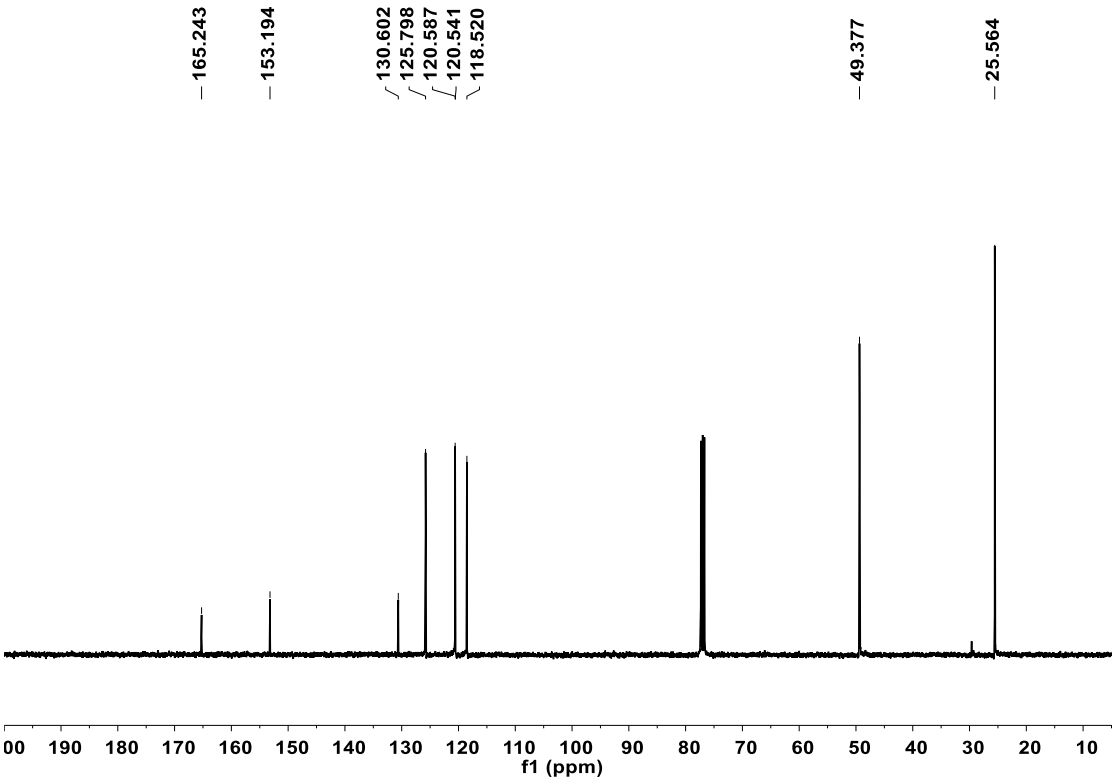


3ae

^{1}H NMR

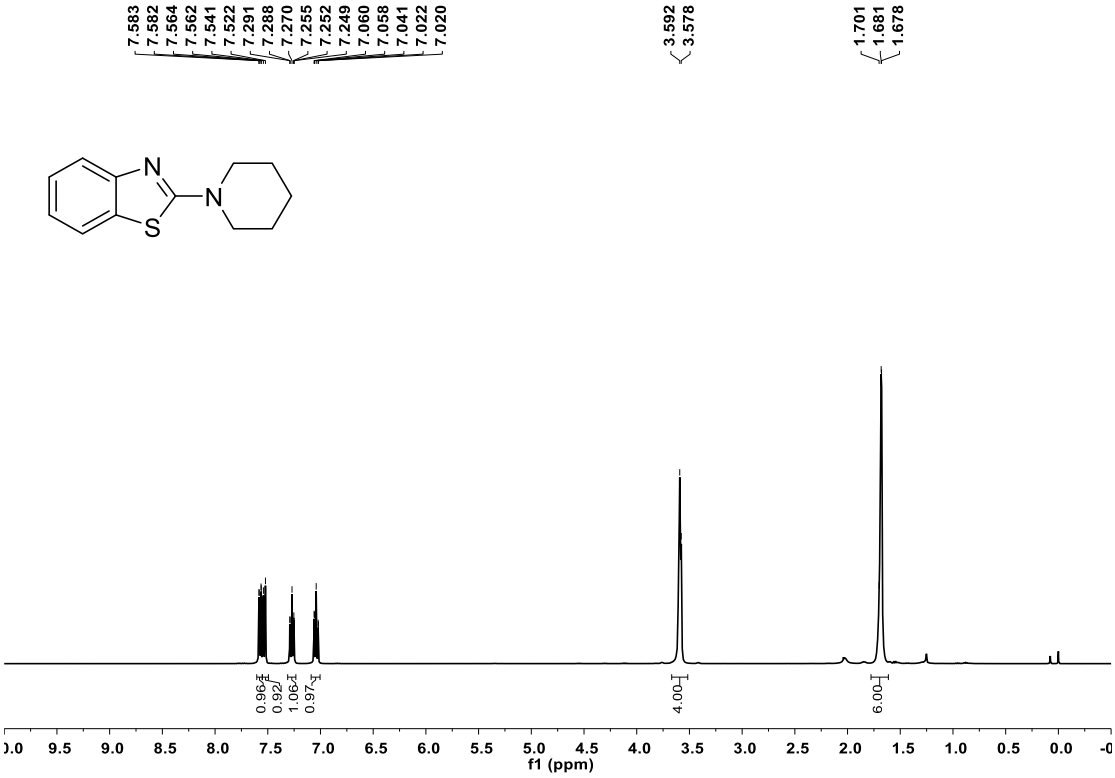


^{13}C NMR

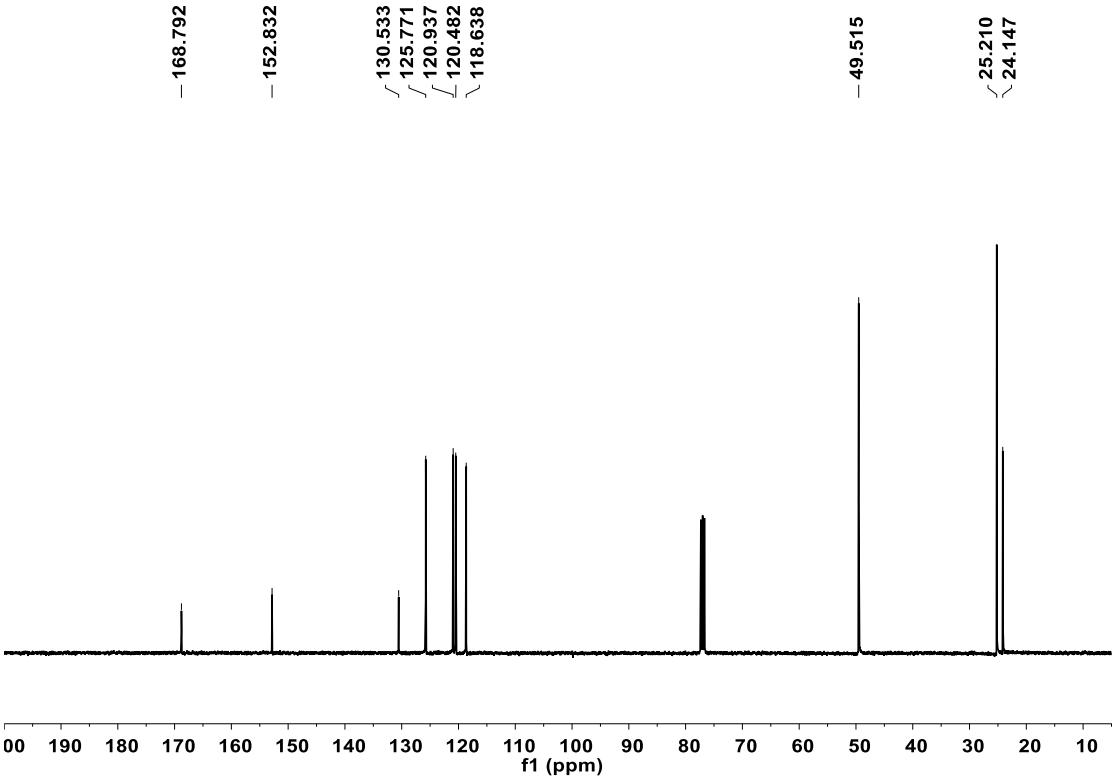


3af

^{1}H NMR

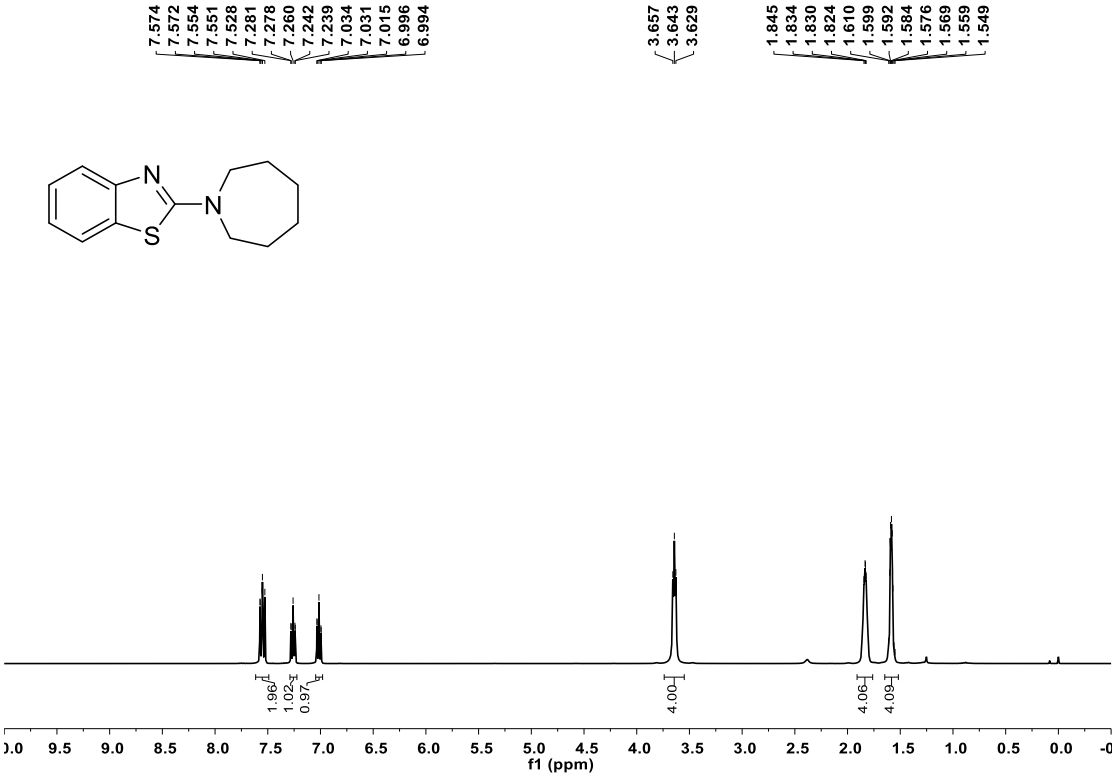


^{13}C NMR

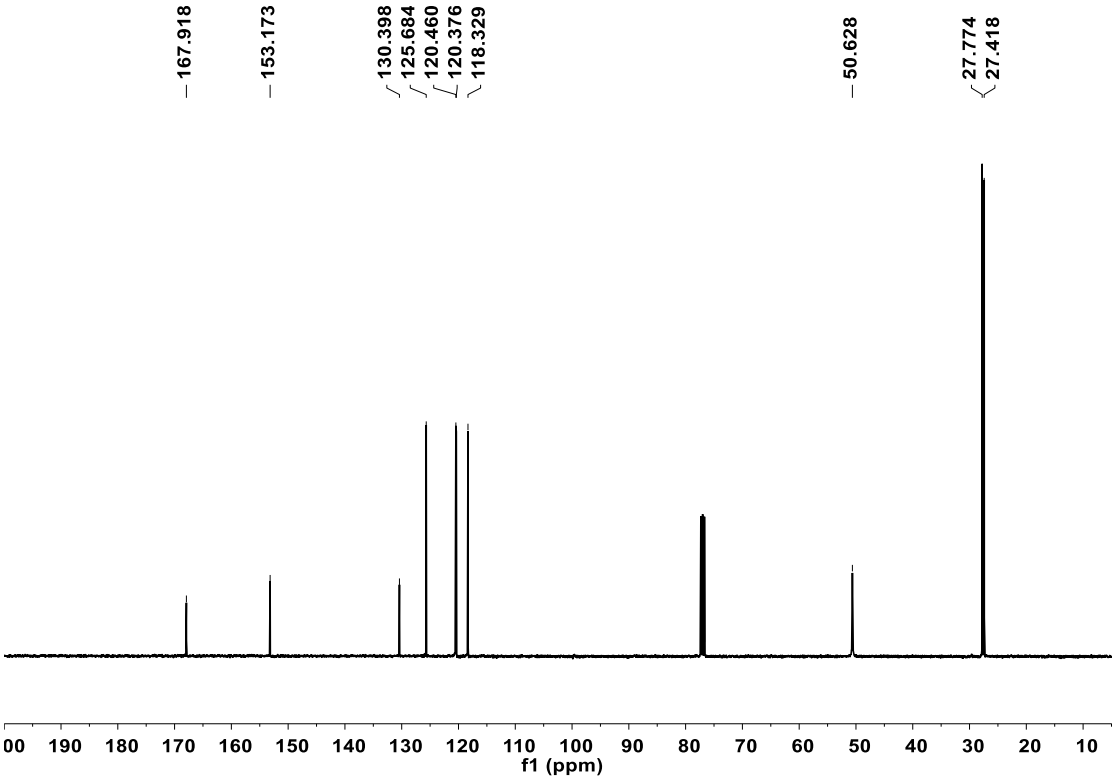


3ag

^{1}H NMR

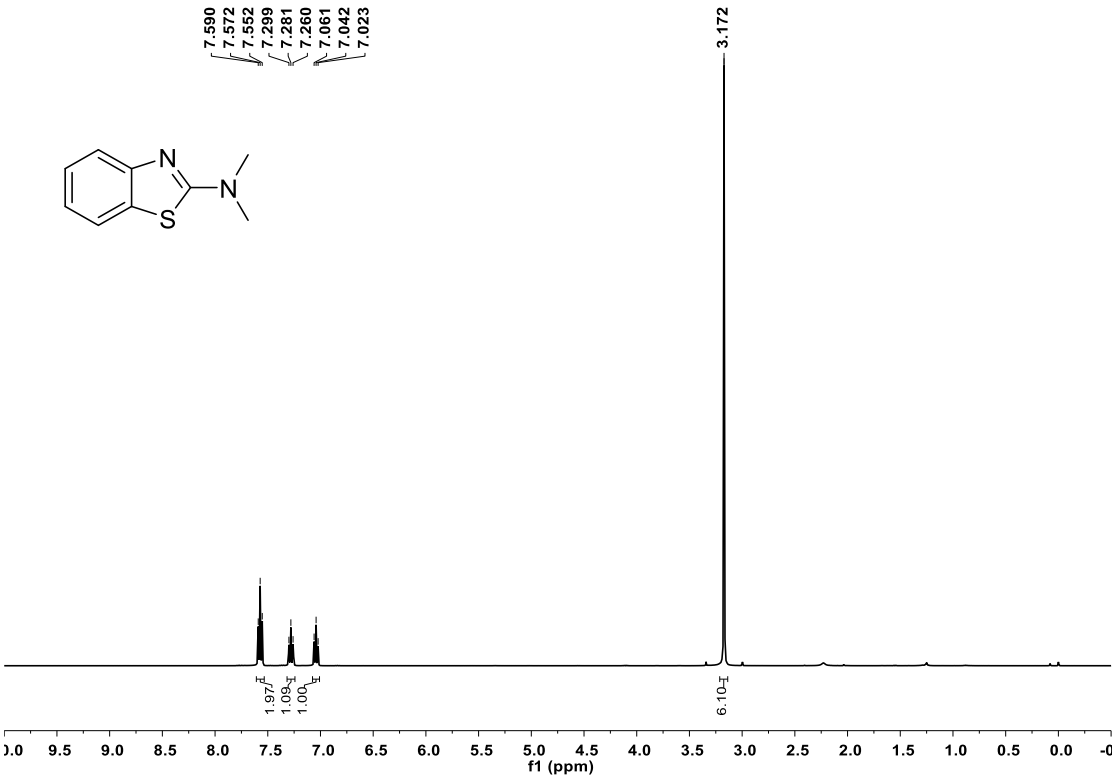


^{13}C NMR



3ah

^{1}H NMR



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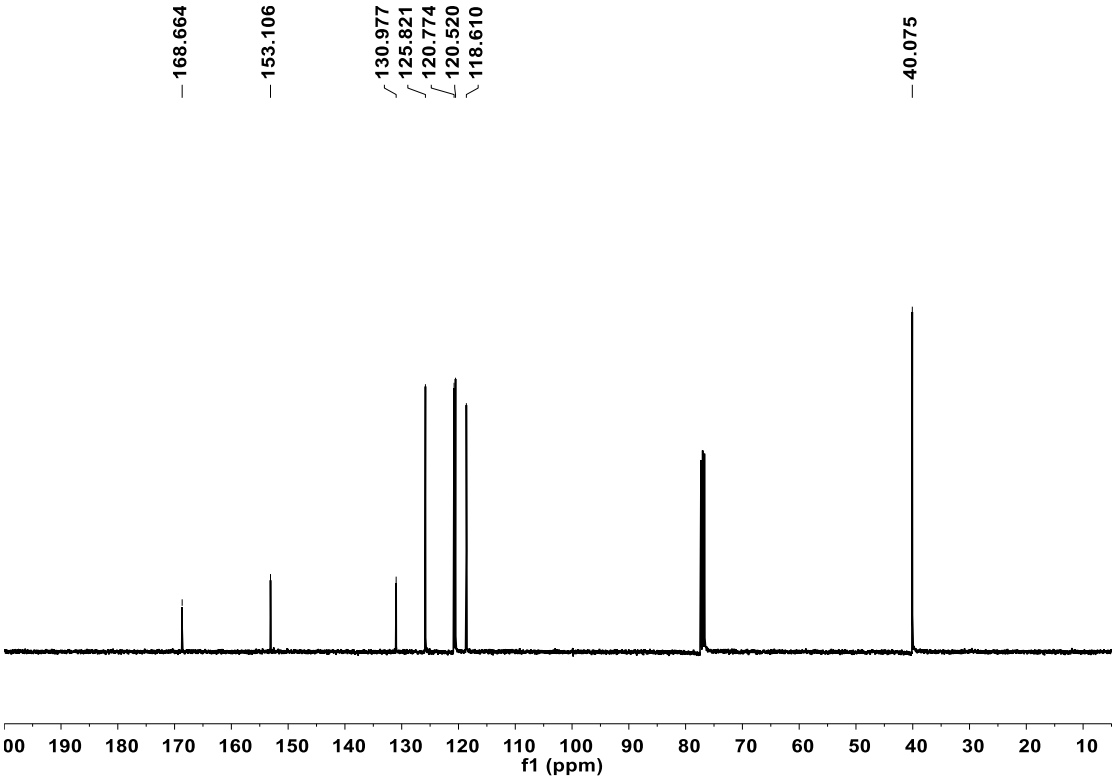
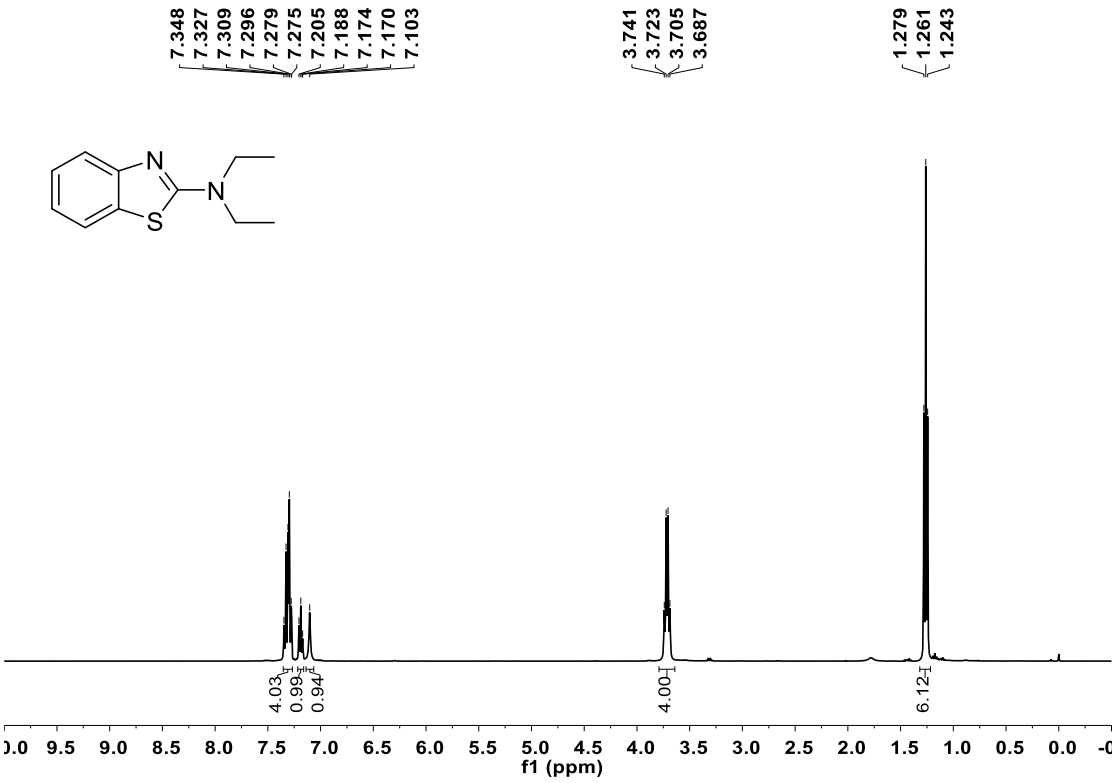
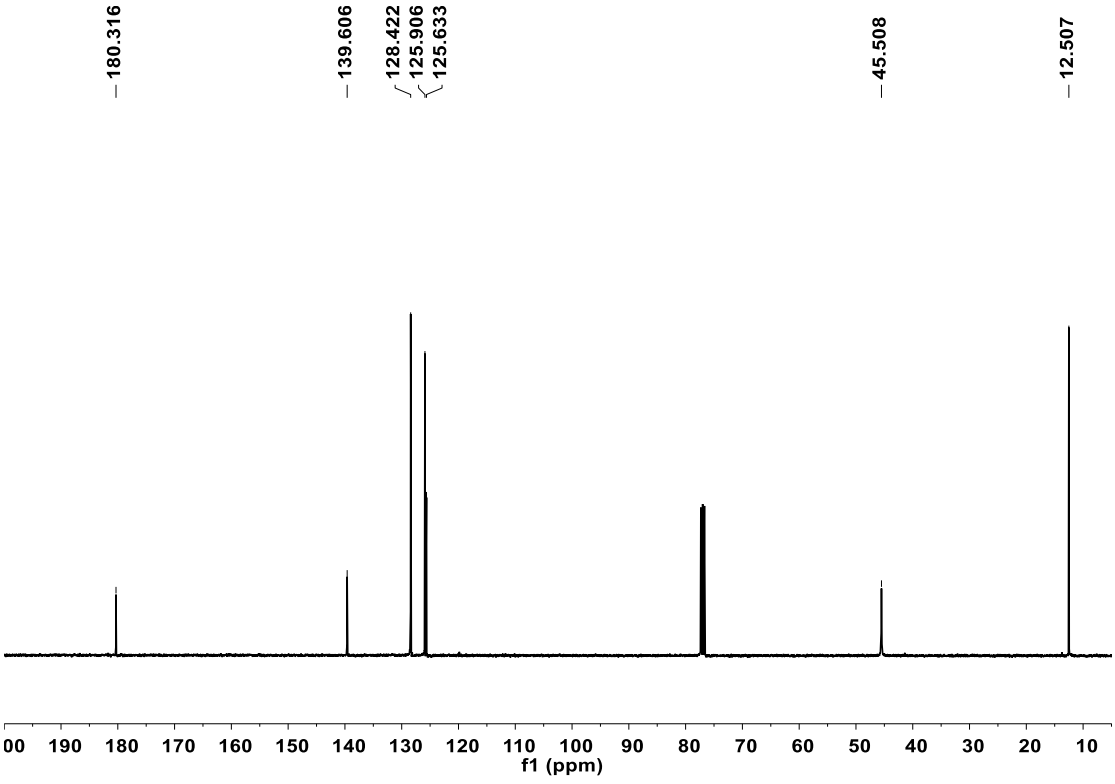


3ai

^{1}H NMR

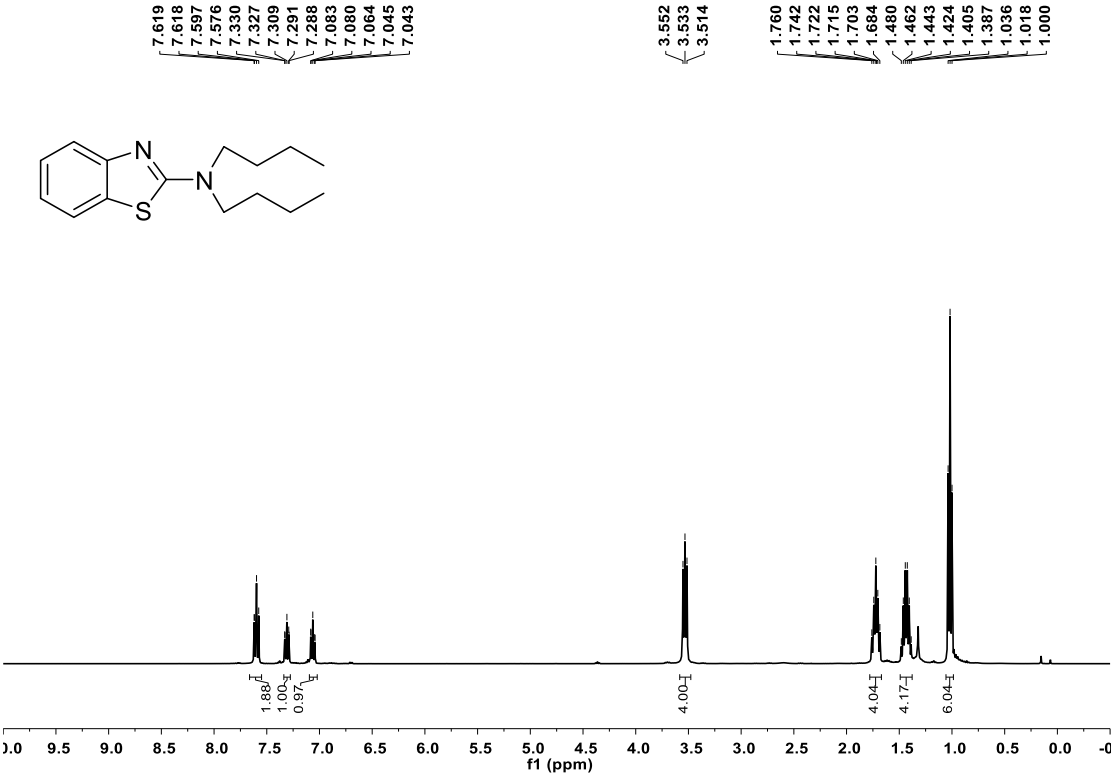


^{13}C NMR

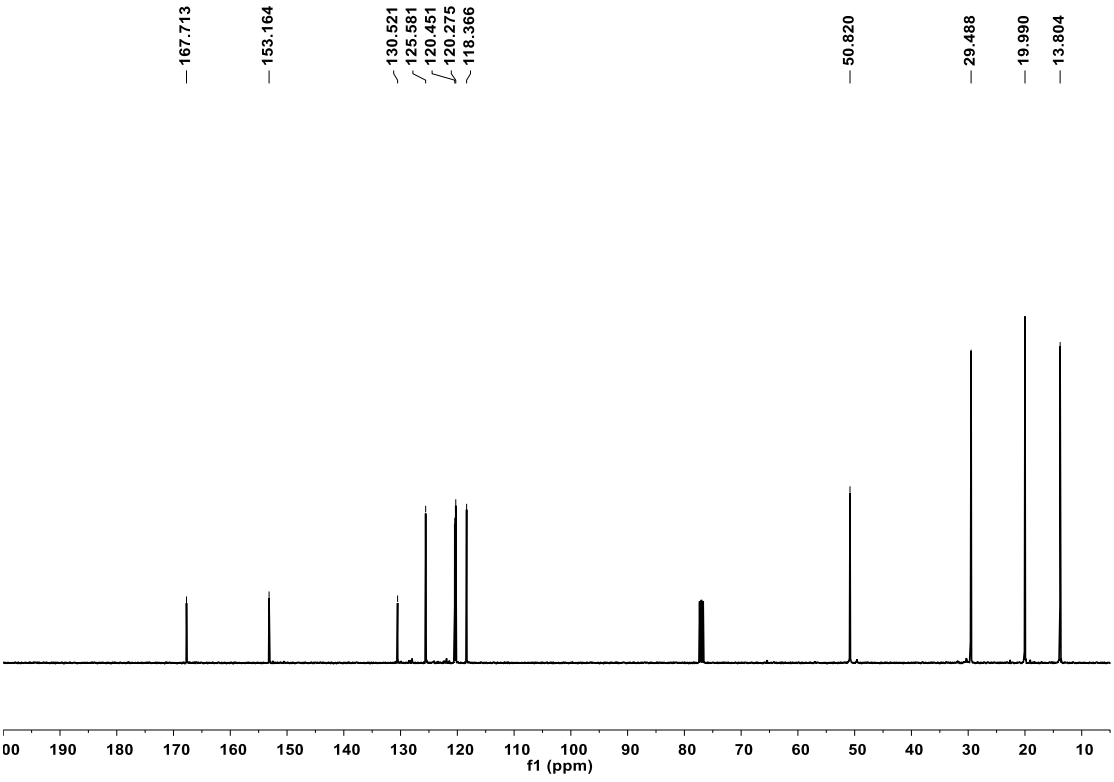


3aj

^{1}H NMR

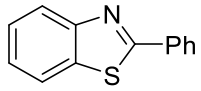


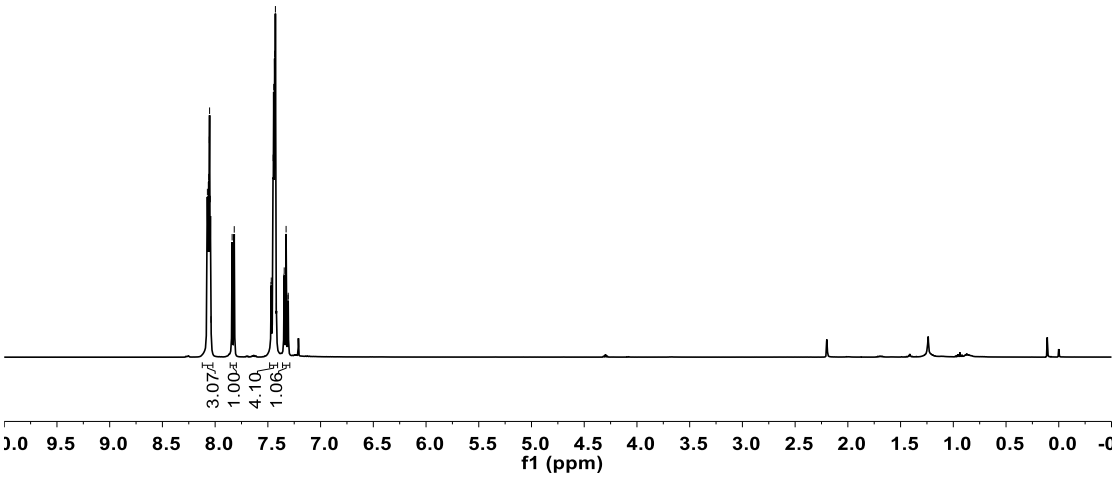
^{13}C NMR



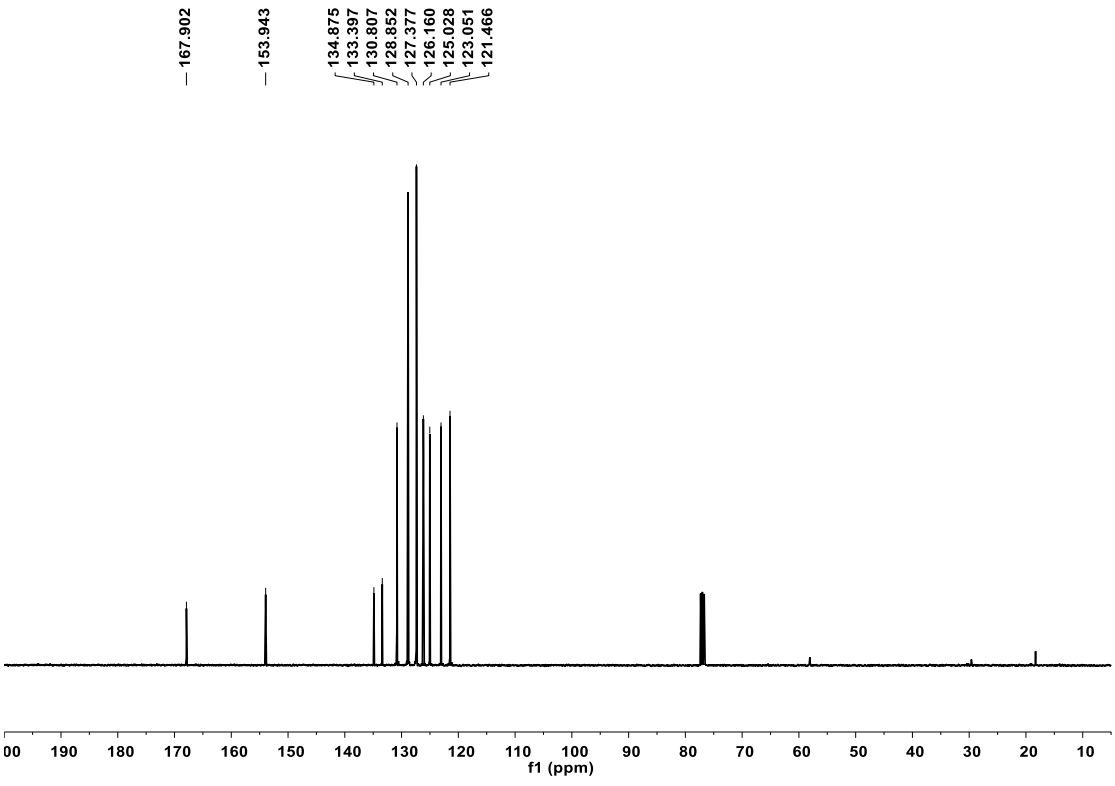
6a

^{1}H NMR



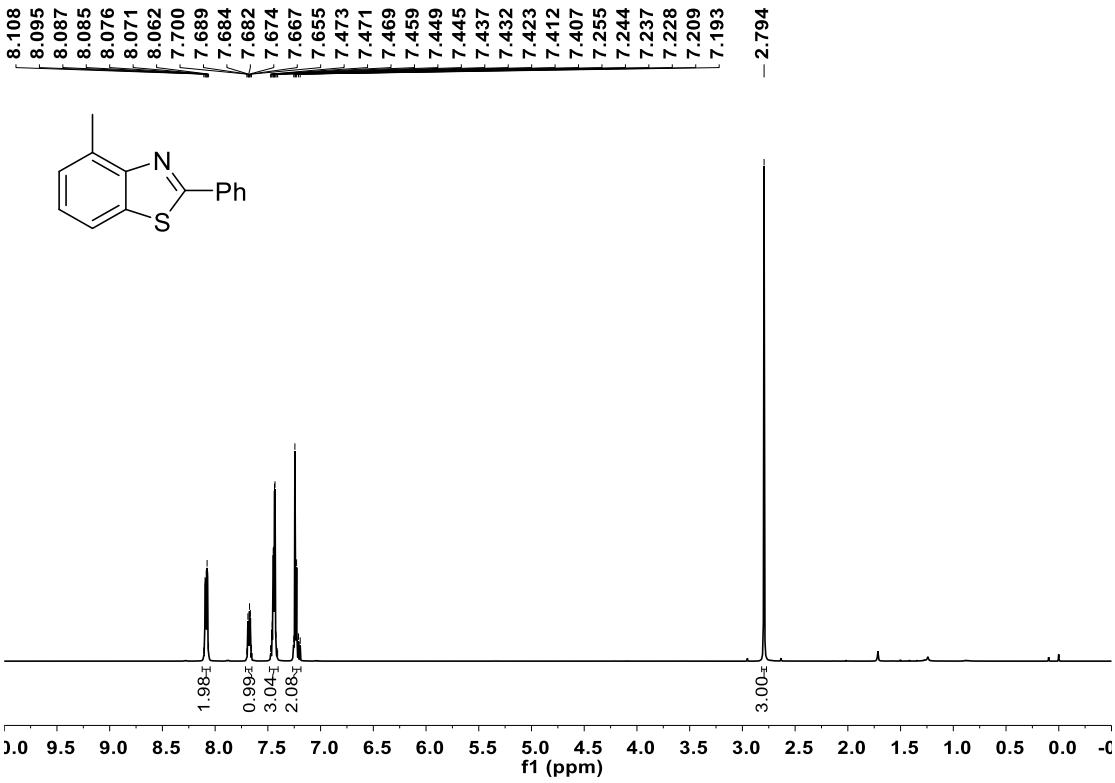


^{13}C NMR

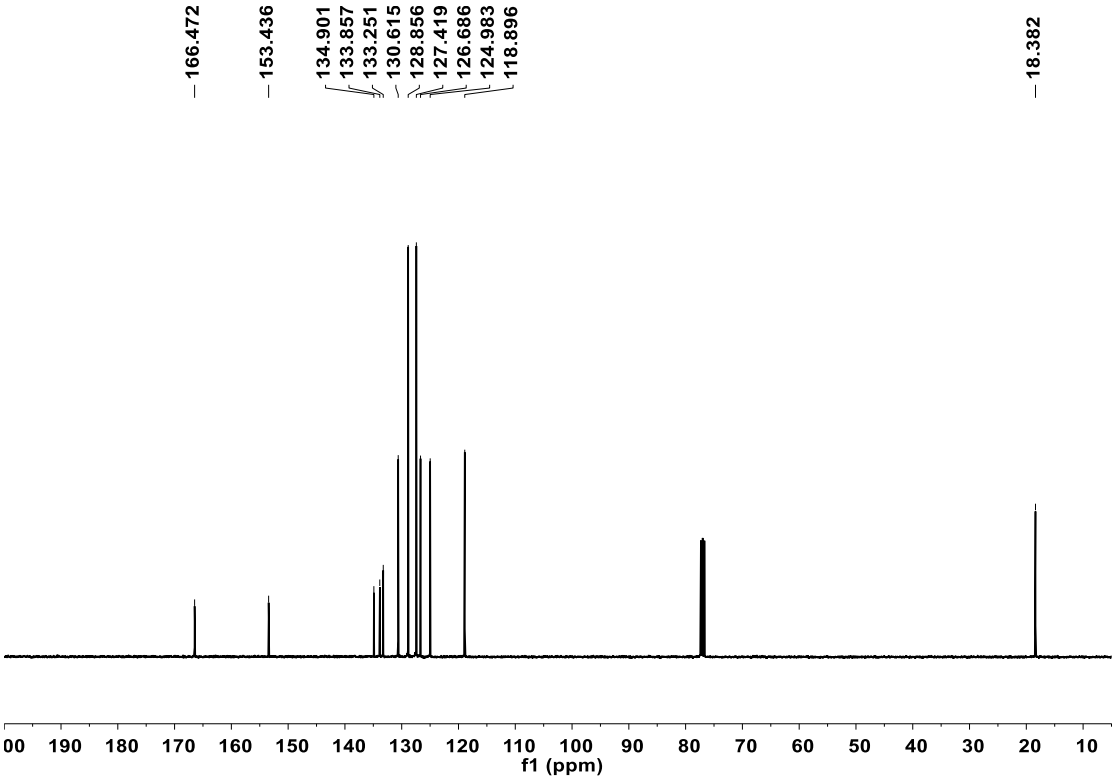


6b

^{1}H NMR

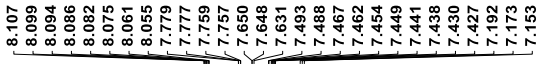


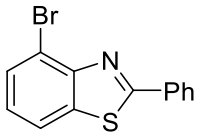
^{13}C NMR

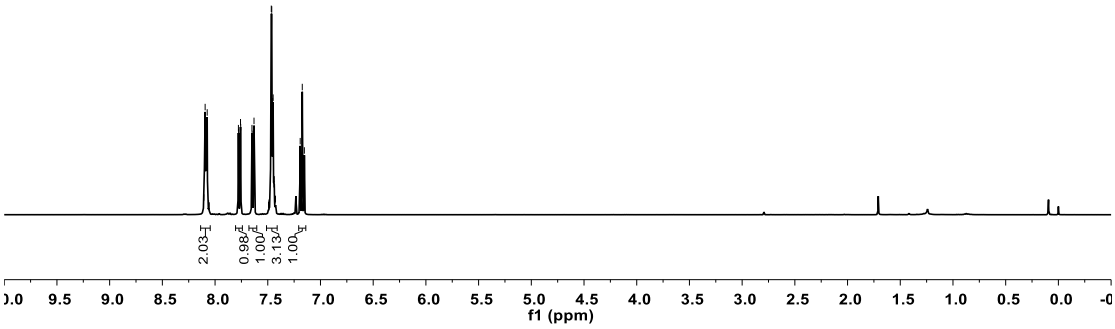


6c

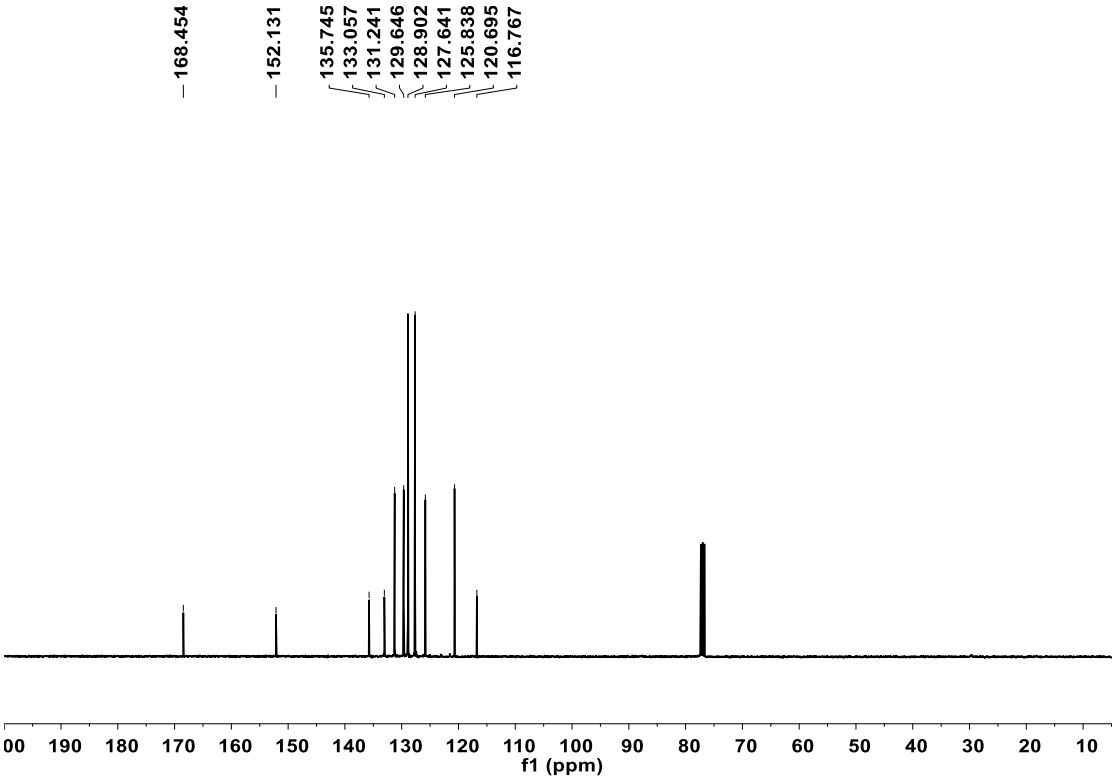
^{1}H NMR





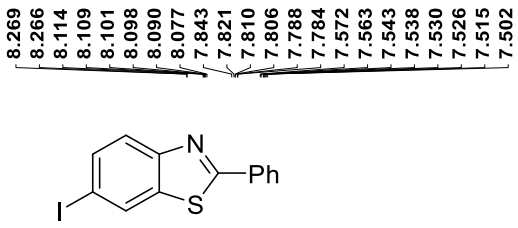


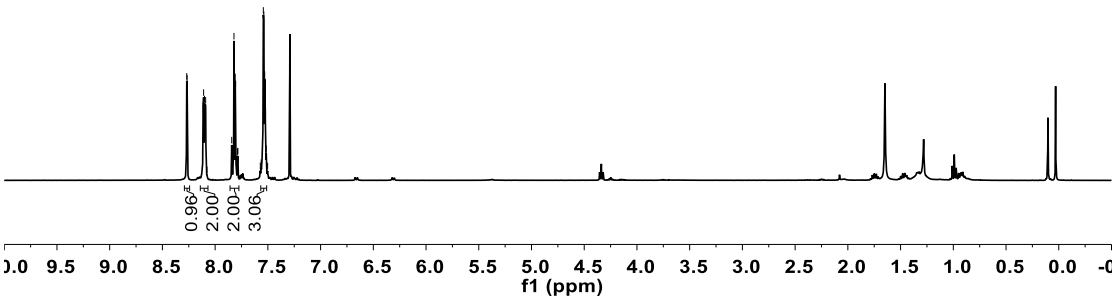
^{13}C NMR



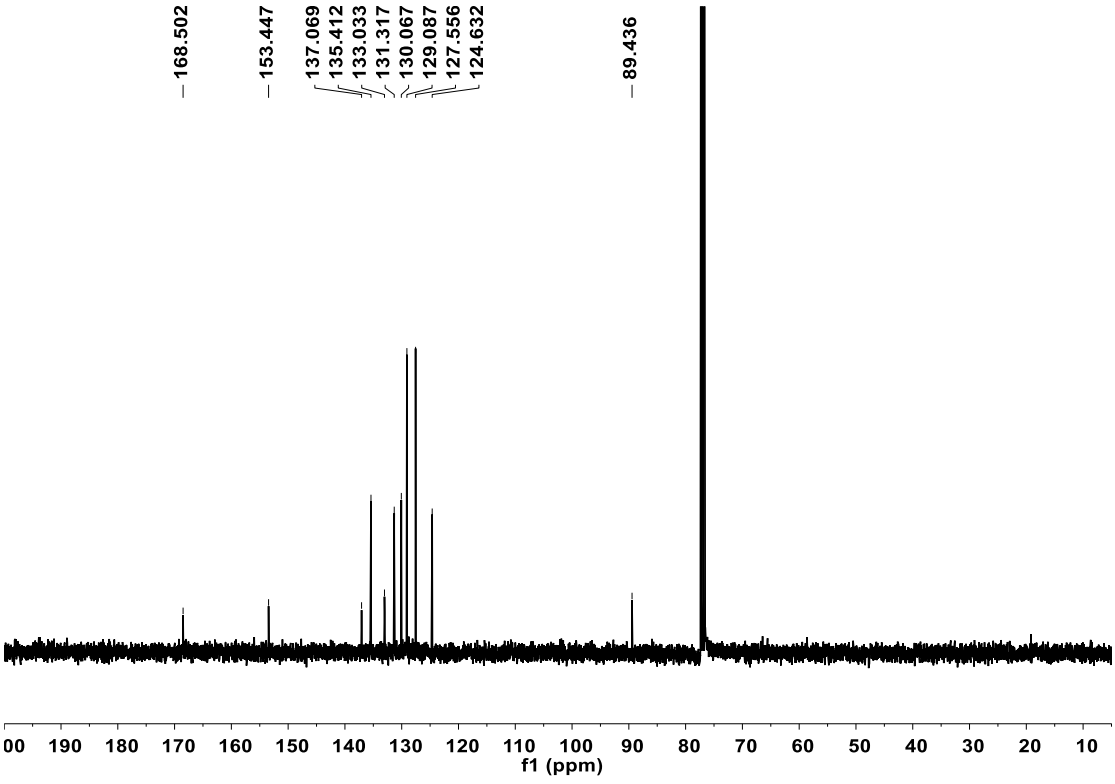
6d

^{1}H NMR



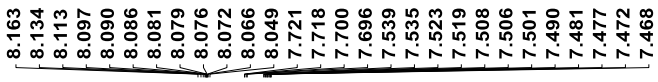


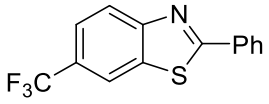
^{13}C NMR

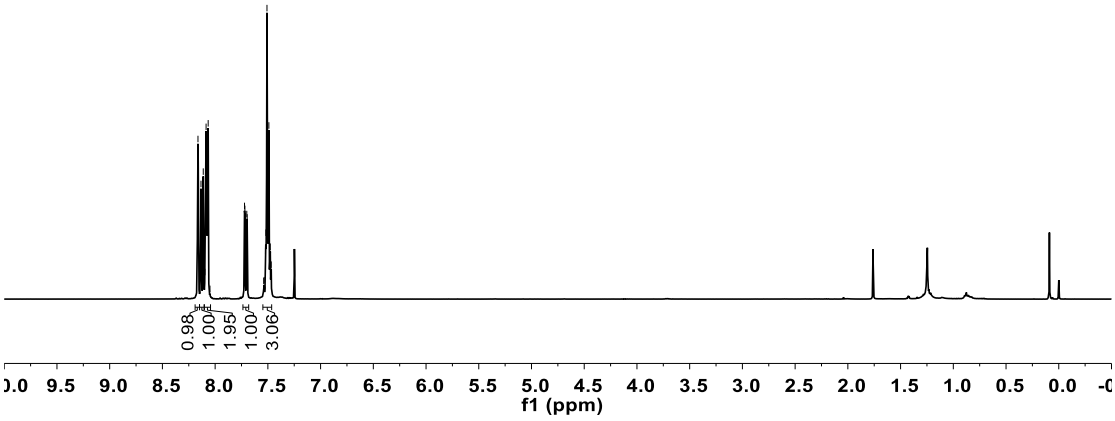


6e

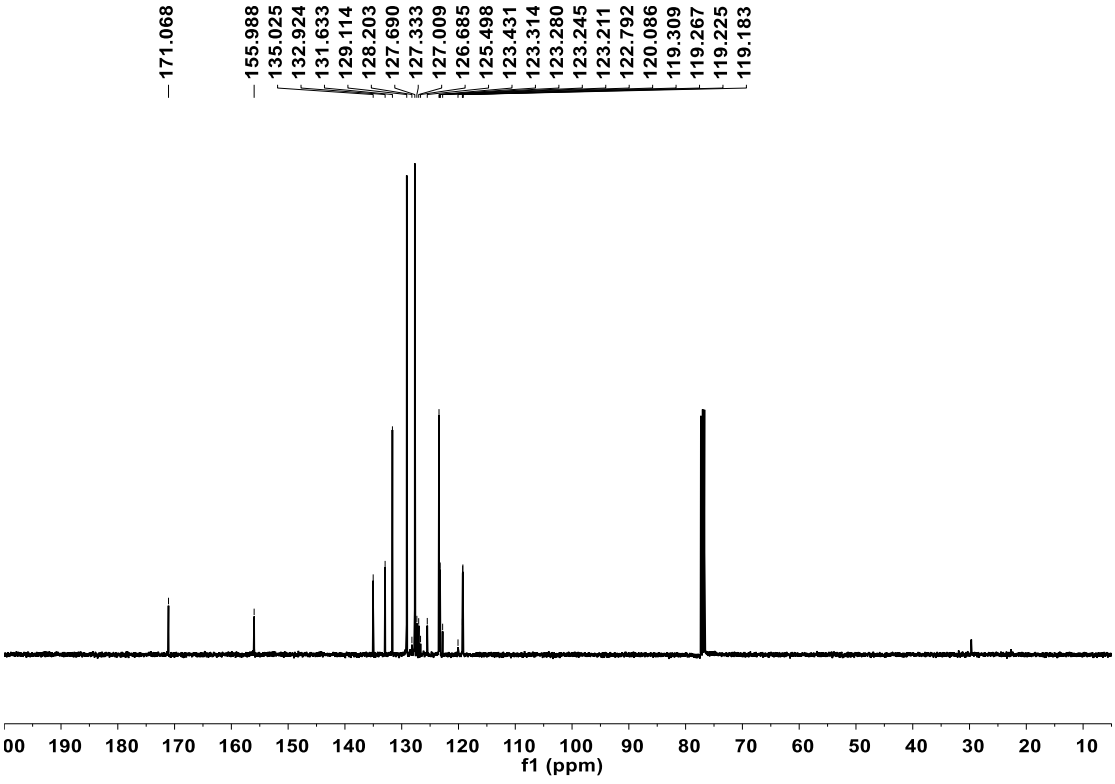
^{1}H NMR



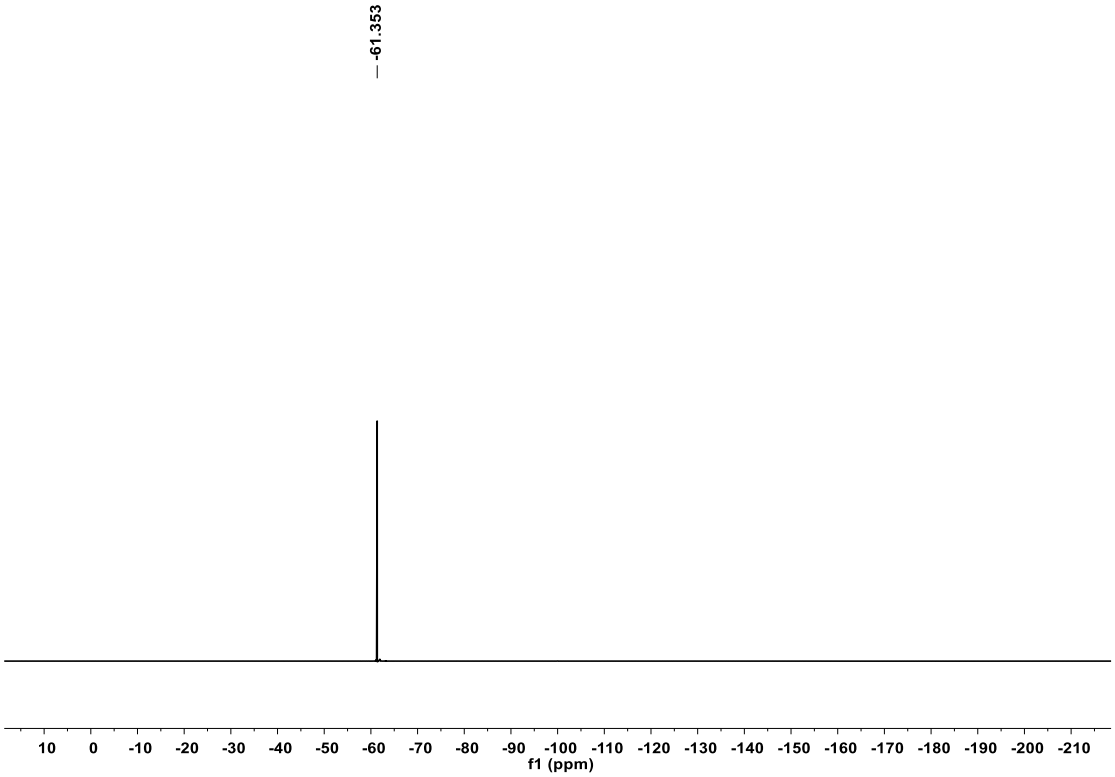




^{13}C NMR

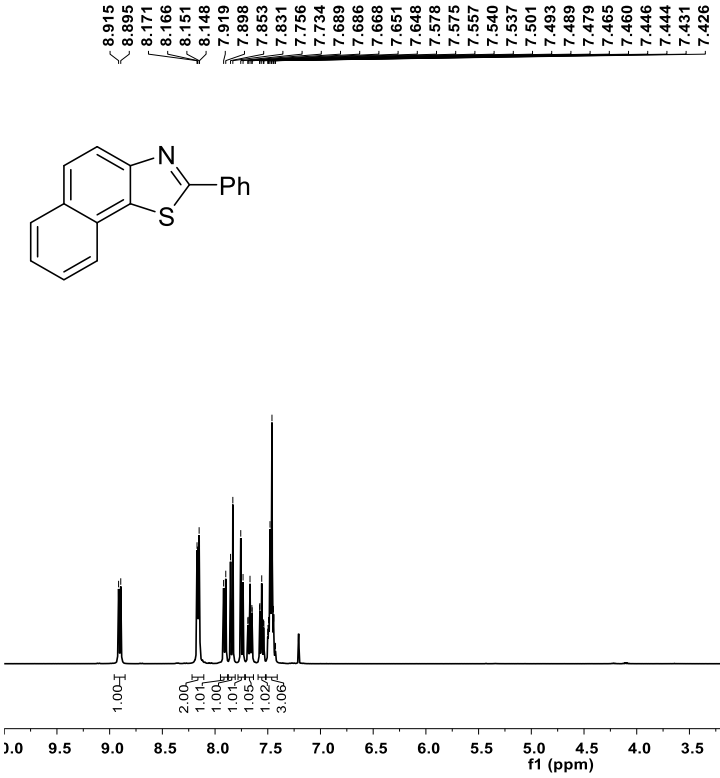


^{19}F NMR

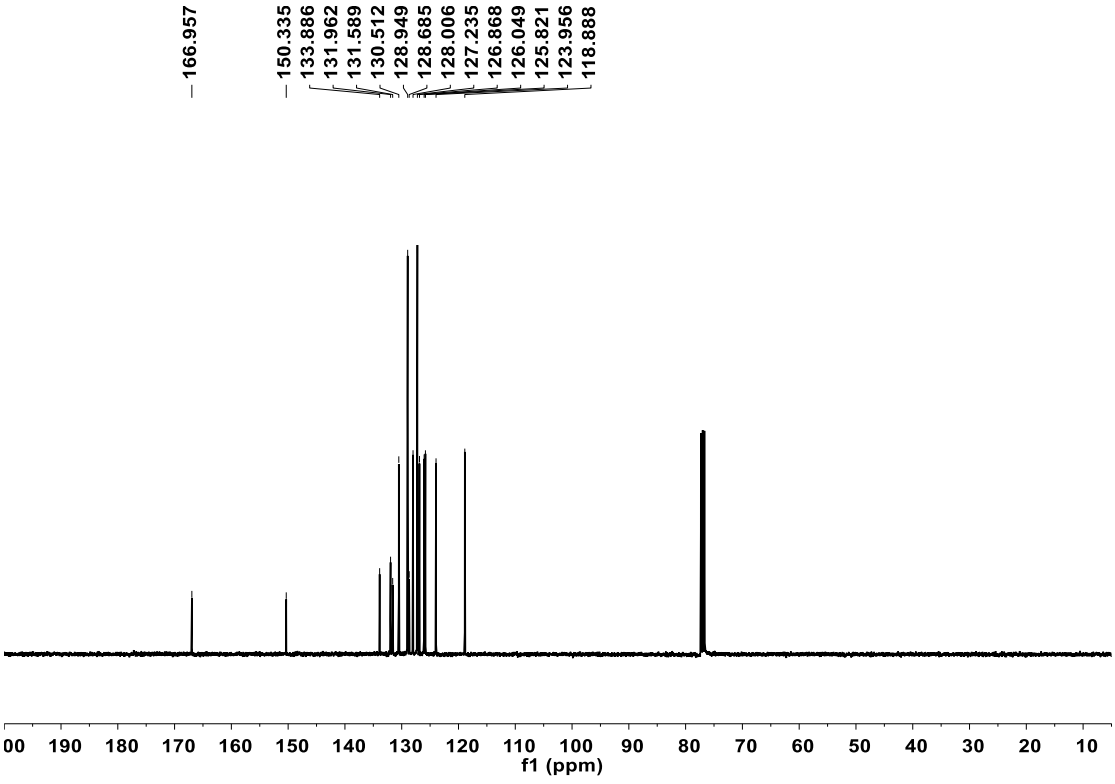

-61.353
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

6f

^{1}H NMR

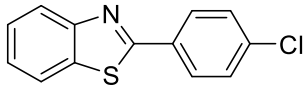


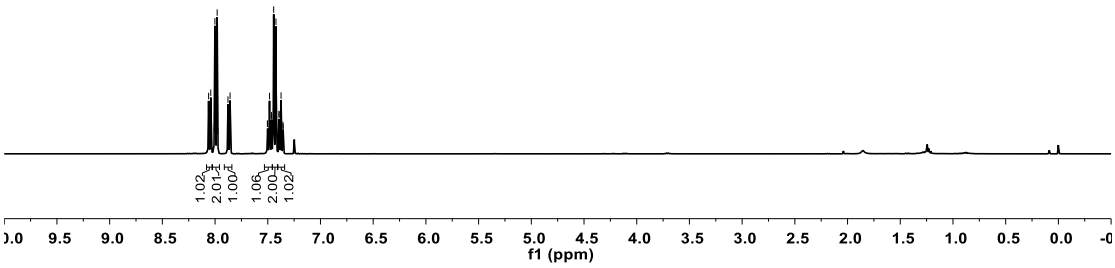
^{13}C NMR



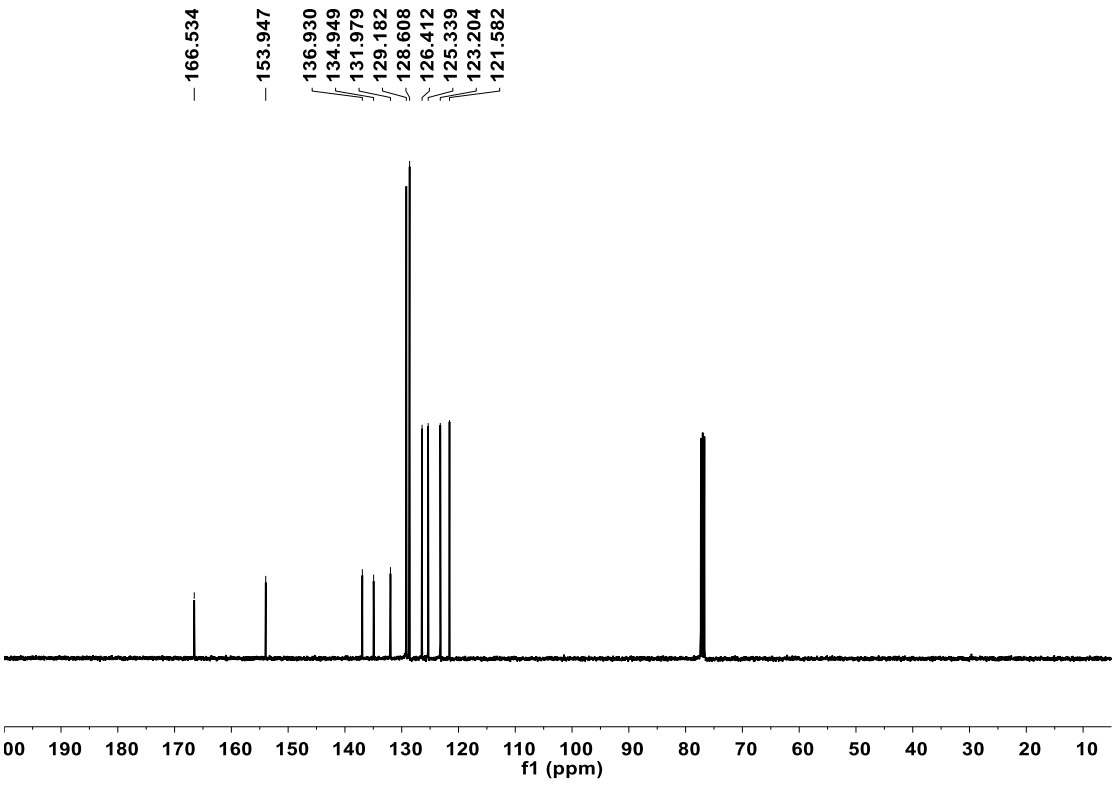
6g

^{1}H NMR



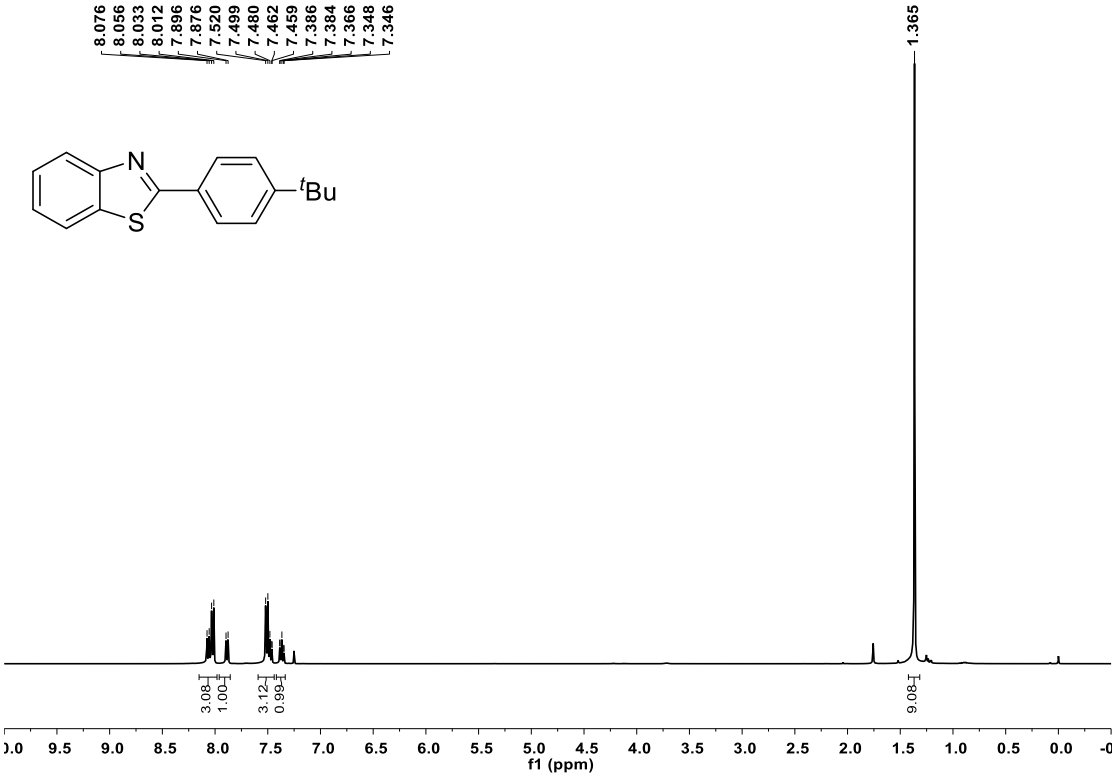


^{13}C NMR

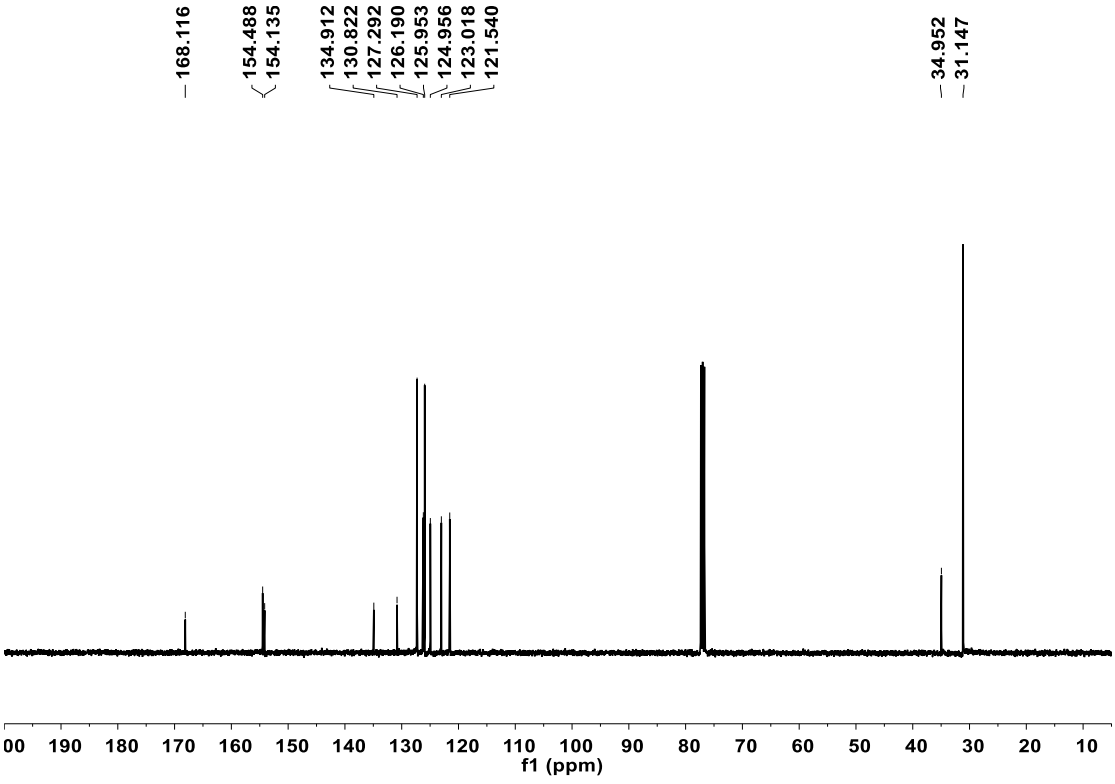


6h

^{1}H NMR

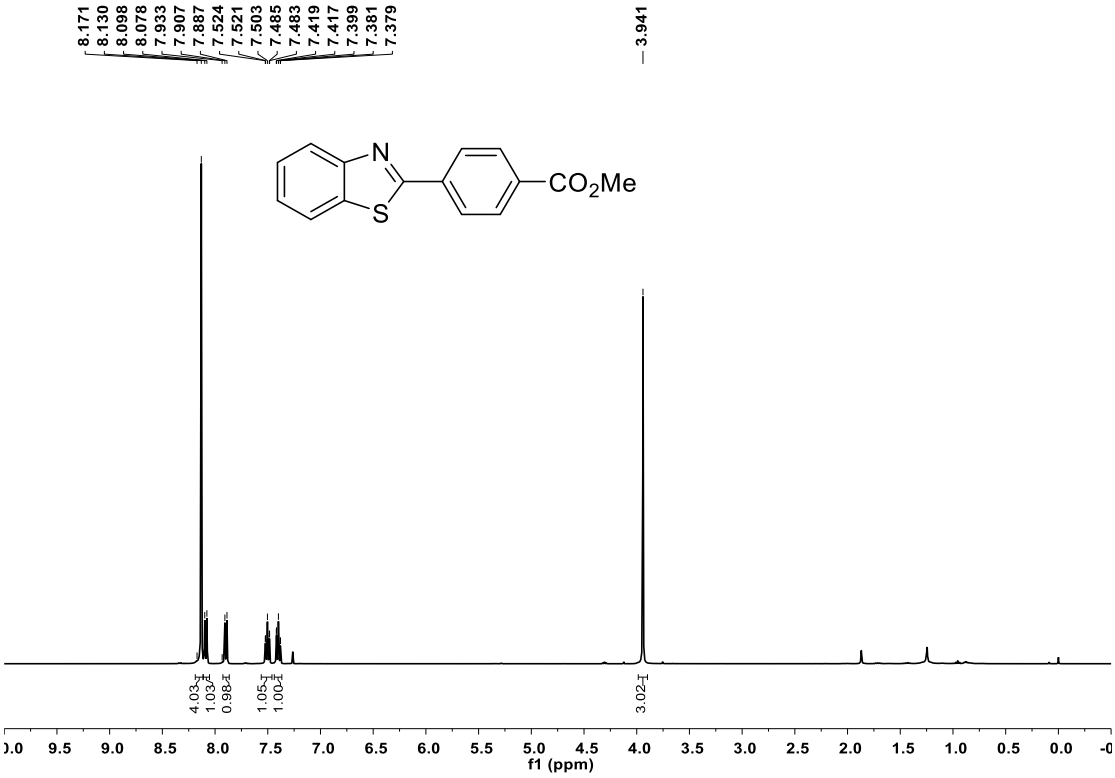


^{13}C NMR

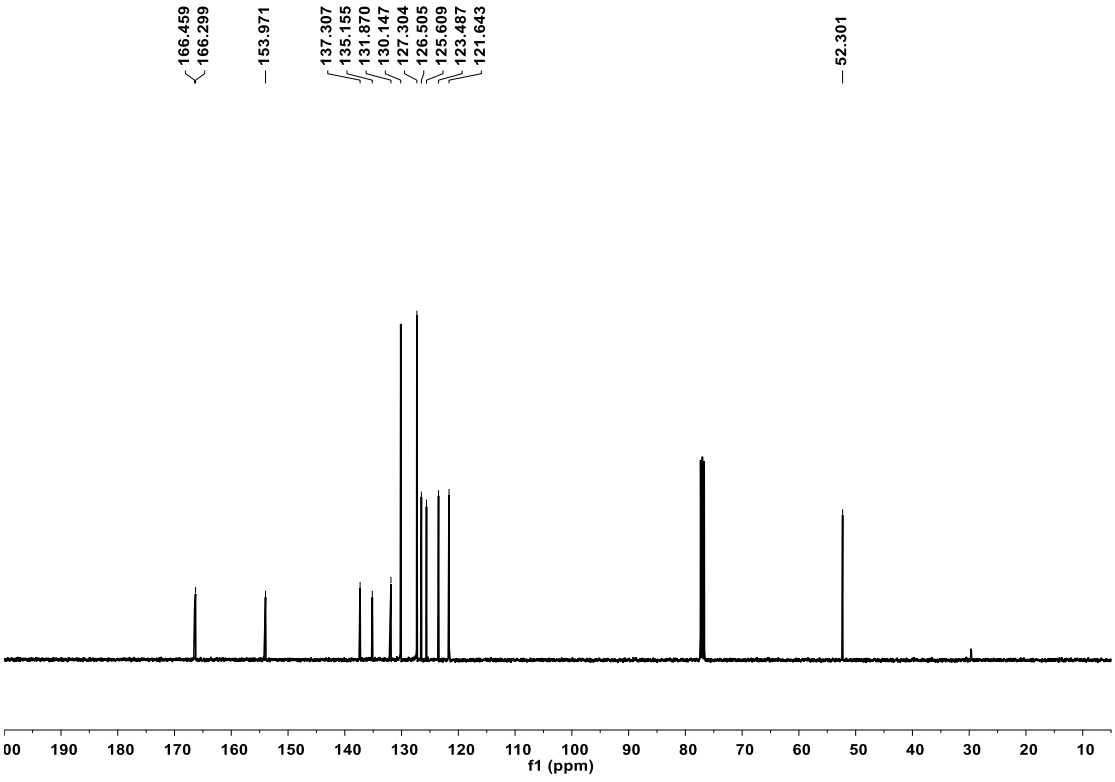


6i

^{1}H NMR

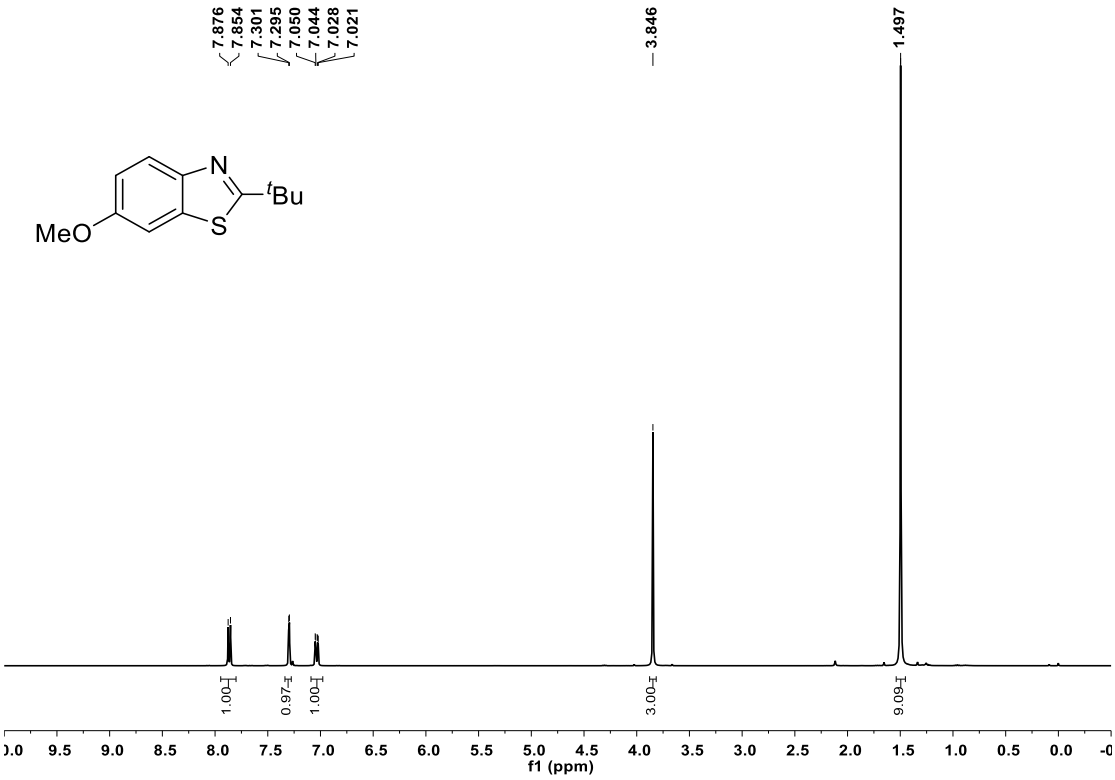


^{13}C NMR

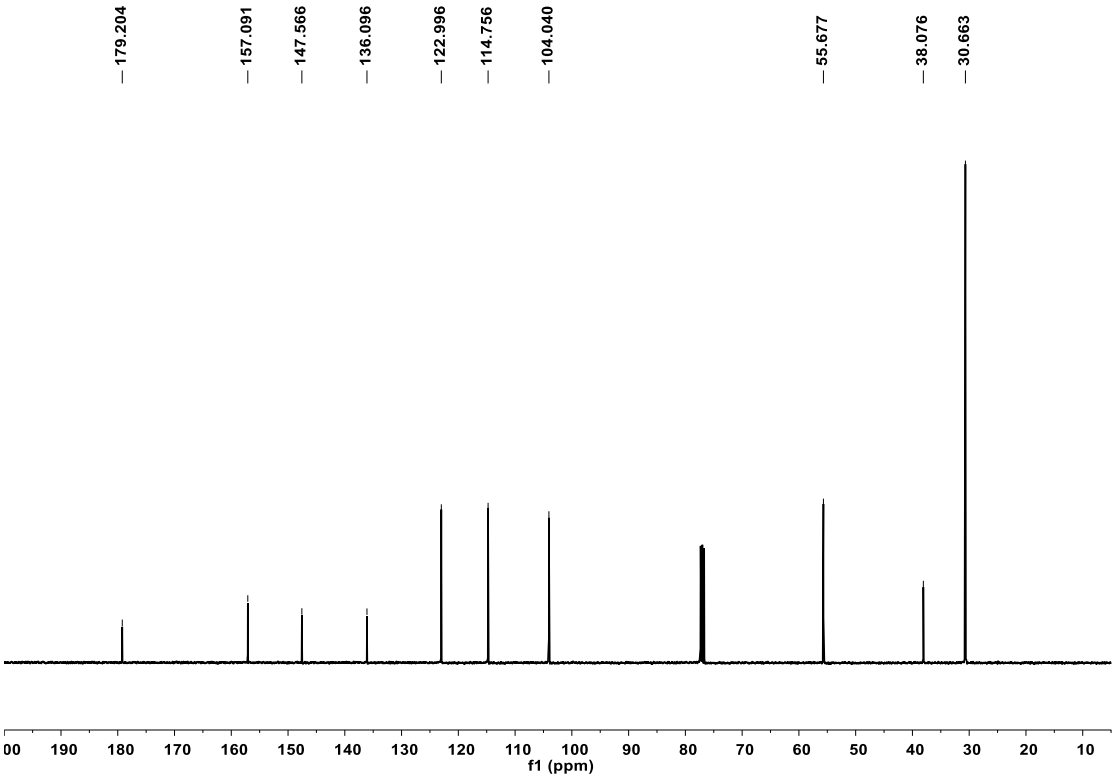


6j

^{1}H NMR

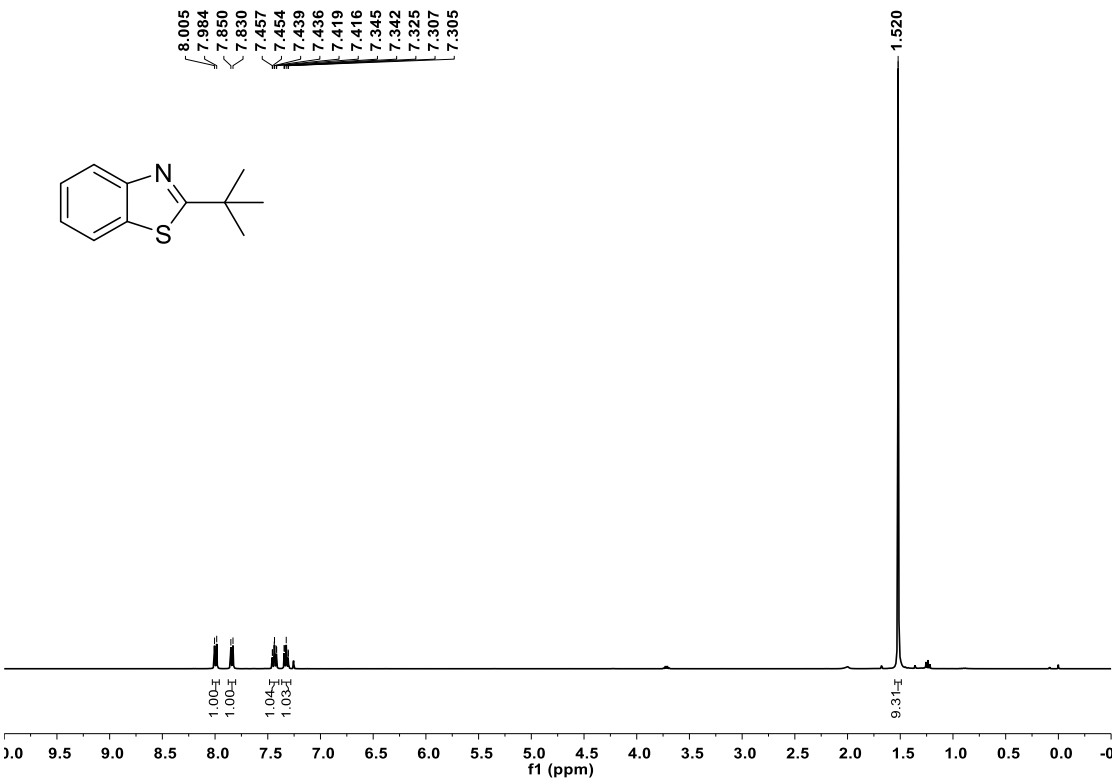


^{13}C NMR

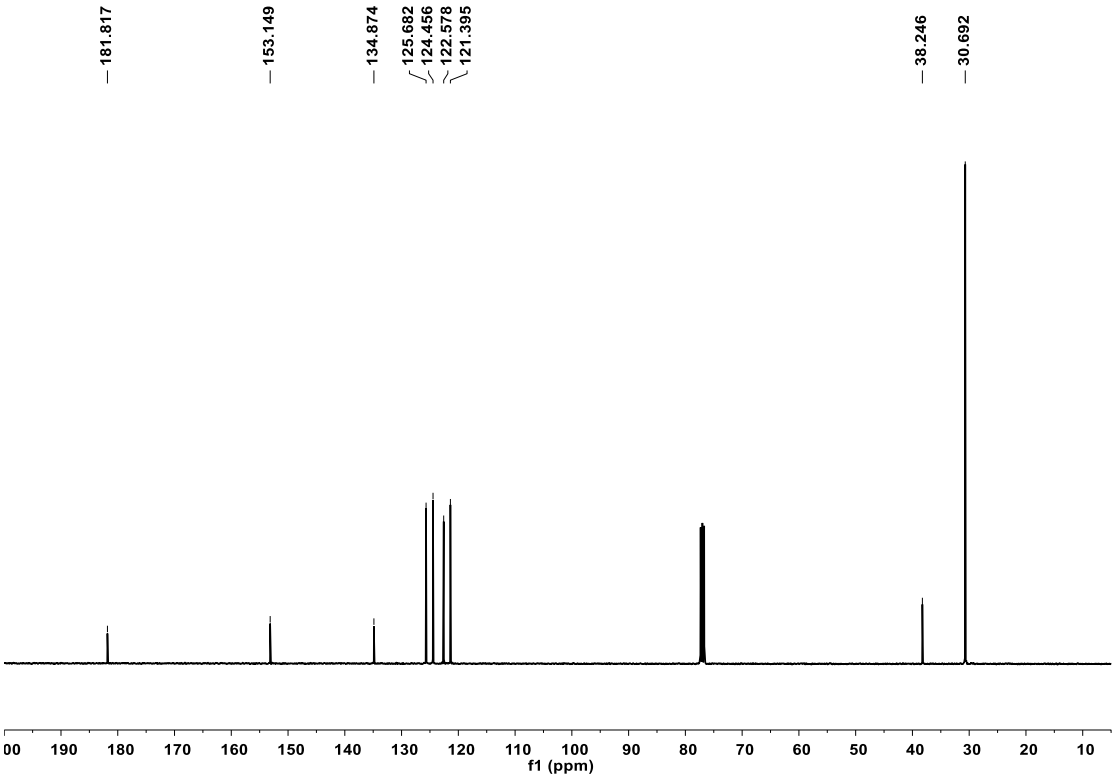


6k

^{1}H NMR

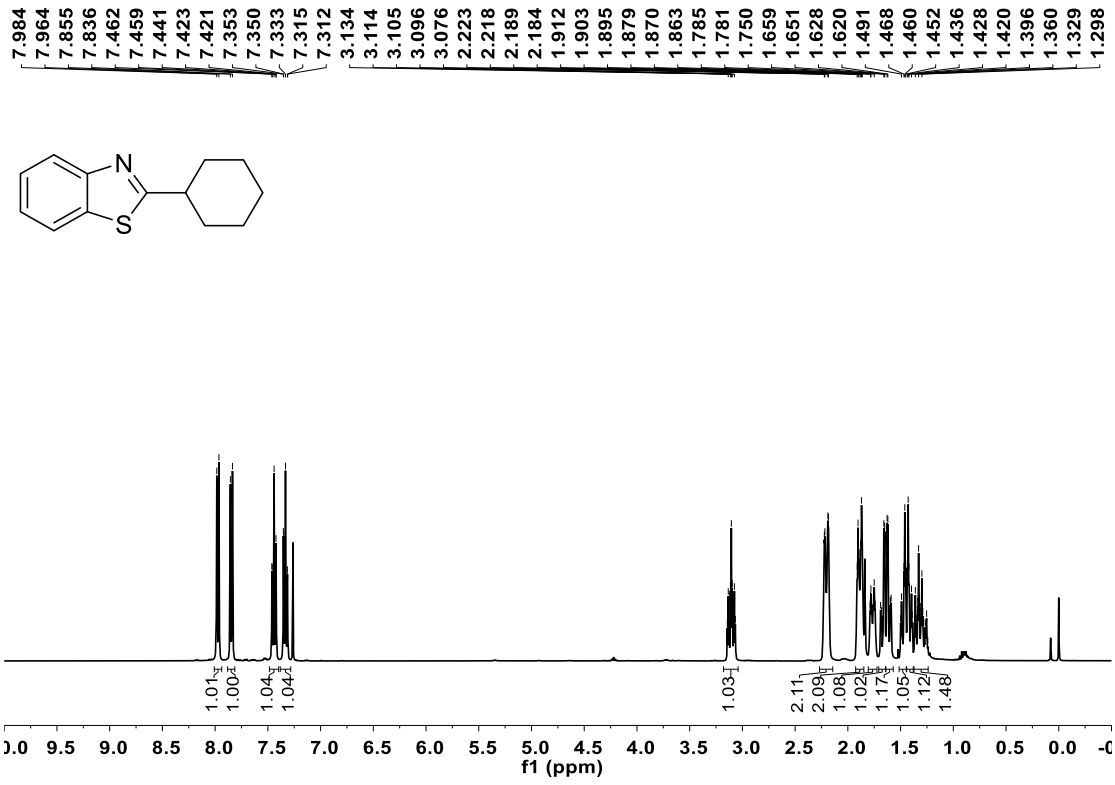


^{13}C NMR



6l

^{1}H NMR



^{13}C NMR