Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electro-oxidative three-component cascade cyclization of isocyanides with elemental sulfur and amines for the synthesis of 2-aminobenzothiazoles

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General information

All glassware was oven dried at 110 ℃ for hours and cooled down under vacuum. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is DCRegulated power supply (HY3005B) (made in China). 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 ℃). GC-MS spectra were recorded on SHIMADZU GCMS-QP2020NX. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. 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 (77.16 ppm, chloroform), respectively. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

Experimental procedure

General procedure for the synthesis of 2-aminobenzothiazoles: In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, isocyanides (0.20 mmol), S_8 (1.5 equiv., 0.30 mmol, 32 g/mol), amines (2.0 equiv., 0.40 mmol), $^nBu_4NBF_4$ (65.9 mg, 0.20 mmol) and DMF (3 mL) were combined and added. The bottle was equipped with a carbon plate (100 mm×10 mm×2 mm, about 15 mm immersion depth in solution) as the anode and a nickel plate (100 mm×10 mm×2 mm, about 15 mm immersion depth in solution) as the cathode, which was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 3 h. When the reaction finished, the reaction mixture was extracted with EtOAc (20 mL×3) and H_2O (20 mL×3). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The pure product was obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

Procedure for gram scale synthesis: In an oven-dried beaker without spout (150 mL) equipped with a stir bar, 2-isocyanonaphthalene (0.726 g, 5.0 mmol), S_8 (0.240 g, 7.5 mmol), amines (0.730 g, 10.0 mmol), $^nBu_4NBF_4$ (1.645 g, 5.0 mmol) and DMF (75 mL) were combined and added to a bottle. The bottle was equipped with a carbon felt electrode (4.0 cm×4.0 cm×3 mm) as the anode and a Ni plate (4.0 cm×4.0 cm×3 mm) as the cathode and was then charged with argon. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under room temperature for 18.75 h. When the reaction was finished, the reaction mixture was extracted with EtOAc (100 mL ×3) and H_2O (100 mL×3). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

Figure S1. Pictures of the gram scale synthesis.

General procedure for cyclic voltammetry (CV): Cyclic voltammetry was performed on a "computer-controlled CH InstrumentElectrochemical Analyzer [CHI760E]" in a three-electrode cell connected to a schlenk line under argon at room temperature. The working electrode was a glassy carbon electrode (length: 80 mm, diameter: 3 mm), the counter electrode was a platinum wire (length: 37 mm, diameter: 0.5 mm, surface area: 0.59 cm^2). The electrode was polished with figure-eightS34motions on a cloth polishing pad in a water-alumina slurry. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from the reaction by a salt bridge. 6 mL DMF containing 0.1 M $^{n}Bu_4NBF_4$ were poured into the electrochemical cell in all experiments. For the cyclic voltammetric measurement, IUPAC convention was followed. The starting point for the CV curve was at 0.0 volt and measured in the positive direction. For the CV experiments, the initial potential was 0.0 V, the switching potential was +2.0 V and the scan rate was 100 mV/s. All solutions used for the voltametric experiments were deoxygenated by purging with high purity argon gas up to 5 mins and measurements were performed in open air at room temperature (25 ± 2 ºC).

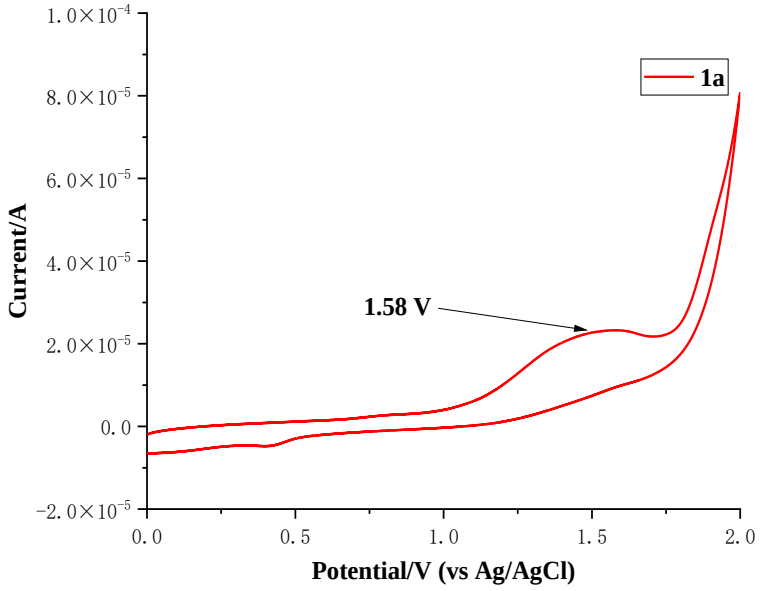


Figure S2: Cyclic voltammograms of **1a** (2-isocyanonaphthalene) following IUPAC convention. A three-electrode configuration having a glassy carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in 0.1 M $^{n}Bu_4NBF_4$ in DMF (6 mL) was used. Scan rate: 0.1 V/s.

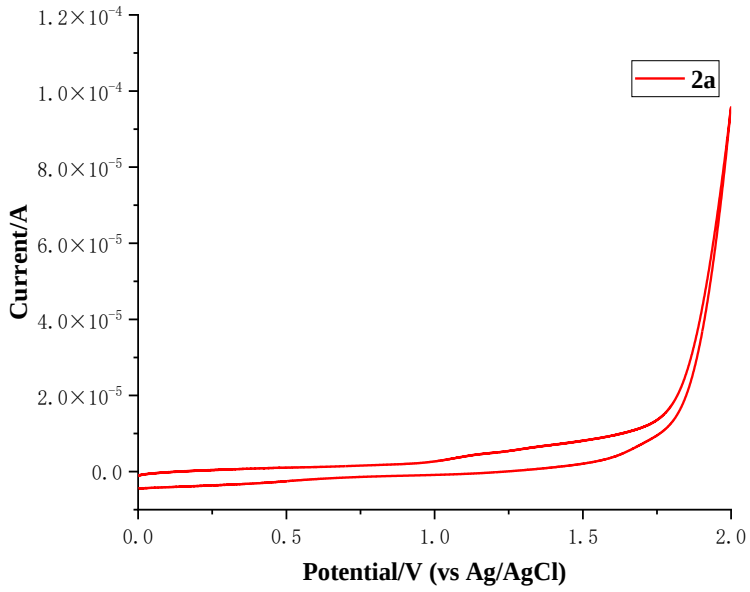


Figure S3: Cyclic voltammograms of **2a** (elemental sulfur) following IUPAC convention. A three-electrode configuration having a glassy carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in 0.1 M $^{n}Bu_4NBF_4$ in DMF (6 mL) was used. Scan rate: 0.1 V/s.

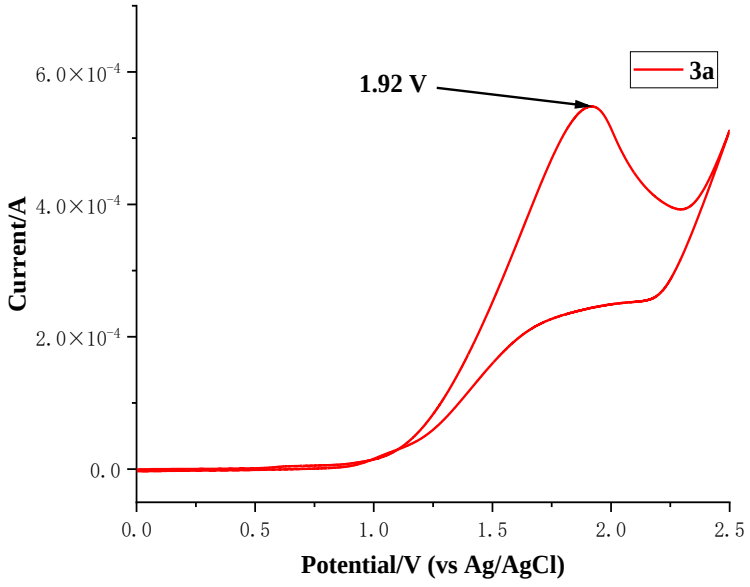


Figure S4: Cyclic voltammograms of **3a** (diethylamine) following IUPAC convention. A three-electrode configuration having a glassy carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in 0.1 M $^{n}Bu_4NBF_4$ in DMF (6 mL) was used. Scan rate: 0.1 V/s.

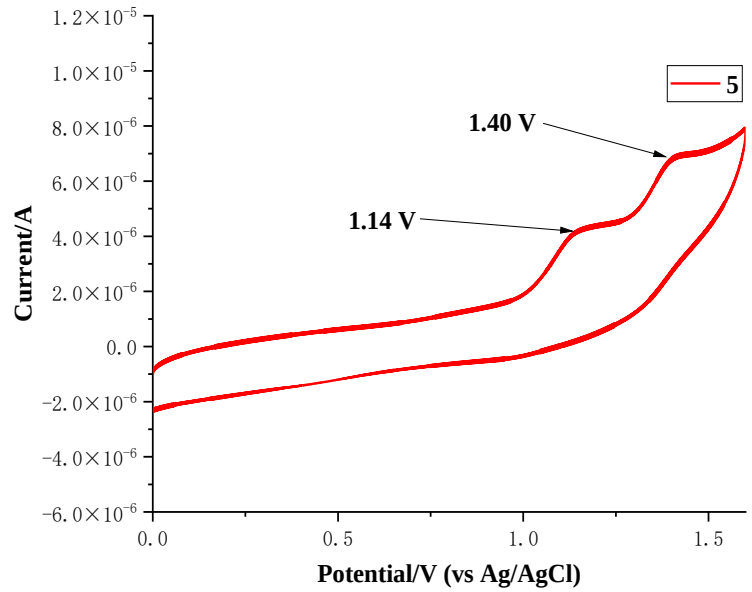


Figure S5: Cyclic voltammograms of **5** (2-isothiocyanatonaphthalene) following IUPAC convention. A three-electrode configuration having a glassy carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in 0.1 M $^{n}Bu_4NBF_4$ in DMF (6 mL) was used. Scan rate: 0.1 V/s.

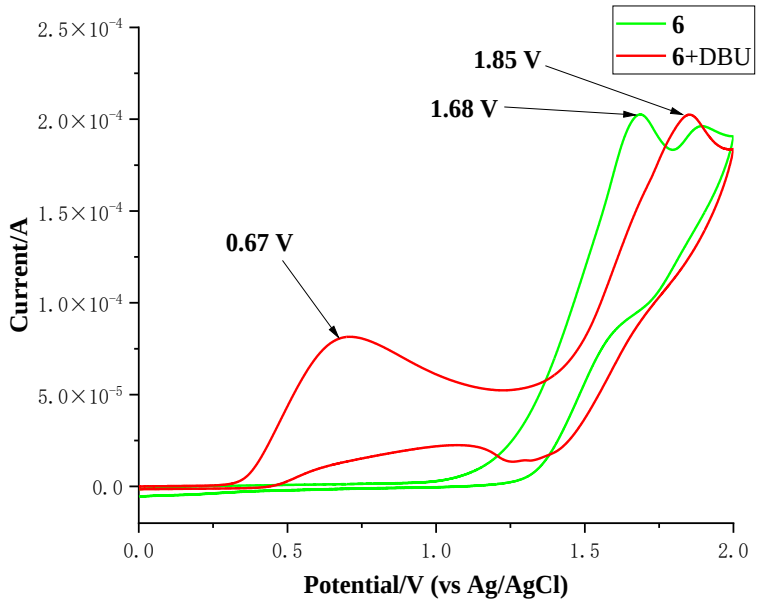
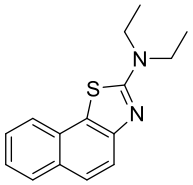
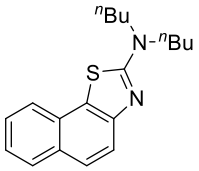


Figure S6: Cyclic voltammograms of **6** (1,1-diethyl-3-(naphthalen-2-yl)thiourea) following IUPAC convention. A three-electrode configuration having a glassy carbon as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in 0.1 M $^{n}Bu_4NBF_4$ in DMF (6 mL) was used. Scan rate: 0.1 V/s.

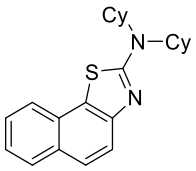
Detail descriptions for products



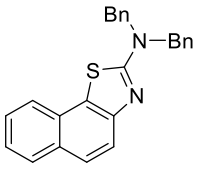
***N,N*-diethylnaphtho[2,1-d]thiazol-2-amine (4aaa):** yellow solid was obtained in 96% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.74–7.68 (m, 3H), 7.48–7.42 (m, 1H), 7.36–7.30 (m, 1H), 3.59 (q, *J* = 7.2 Hz, 4H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.77, 151.18, 129.18, 128.95, 128.25, 126.52 (2C), 124.72, 123.74, 123.52, 119.60, 45.55, 12.88. HRMS (ESI-TOF) calculated for $C_{15}H_{17}N_2S$ $[M+H]^+$: 257.1107; found: 257.1110.



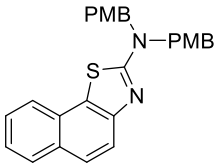
***N,N*-dibutylnaphtho[2,1-d]thiazol-2-amine (4aab):** yellow liquid was obtained in 95% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 1H), 7.76–7.68 (m, 3H), 7.50–7.43 (m, 1H), 7.37–7.31 (m, 1H), 3.55 (t, *J* = 7.8 Hz, 4H), 1.77–1.66 (m, 4H), 1.47–1.36 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.42, 151.19, 129.20, 128.98, 128.27, 126.52, 126.50, 124.75, 123.78, 123.51, 119.67, 51.26, 29.68, 20.31, 14.08. HRMS (ESI-TOF) calculated for $C_{19}H_{25}N_2S$ $[M+H]^+$: 313.1733; found: 313.1730.



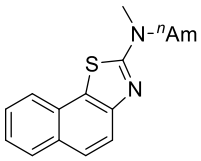
***N,N*-dicyclohexylnaphtho[2,1-d]thiazol-2-amine (4aac):** yellow liquid was obtained in 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.75–7.66 (m, 3H), 7.48–7.42 (m, 1H), 7.35–7.30 (m, 1H), 3.62–3.51 (m, 2H), 2.25–2.12 (m, 4H), 1.93–1.84 (m, 4H), 1.81–1.74 (m, 4H), 1.73–1.67 (m, 2H), 1.47–1.33 (m, 4H), 1.31–1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.63, 151.13, 129.17, 128.96, 128.17, 126.37, 126.20, 123.94, 123.91, 123.29, 119.86, 60.73, 30.52, 26.53, 25.58. HRMS (ESI-TOF) calculated for $C_{23}H_{29}N_2S$ $[M+H]^+$: 365.2046; found: 365.2048.



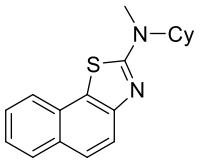
***N,N*-dibenzylnaphtho[2,1-d]thiazol-2-amine (4aad):** yellow liquid was obtained in 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.78–7.72 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.47–7.42 (m, 1H), 7.37–7.25 (m, 11H), 4.78 (s, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 169.56, 150.89, 136.37, 129.50, 129.01, 128.87, 128.25, 127.91, 127.84, 126.82, 126.68, 125.34, 123.88, 123.83, 119.85, 53.52. HRMS (ESI) calculated for $C_{25}H_{21}N_2S$ $[M+H]^+$: 381.1420; found: 381.1416.



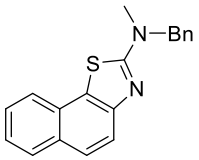
***N,N*-bis(4-methoxybenzyl)naphtho[2,1-d]thiazol-2-amine (4aae):** brown solid was obtained in 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.78–7.72 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.47–7.42 (m, 1H), 7.37–7.32 (m, 1H), 7.25–7.19 (m, 4H), 6.88–6.82 (m, 4H), 4.68 (s, 4H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.45, 159.24, 150.85, 129.42, 129.29, 128.96, 128.31, 128.20, 126.74, 126.62, 125.15, 123.77, 119.76, 114.15, 55.32, 52.74. HRMS (ESI) calculated for $C_{27}H_{25}N_2O_2S$ $[M+H]^+$: 441.1631; found: 441.1630.



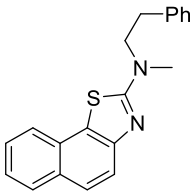
***N*-methyl-*N*-pentylnaphtho[2,1-d]thiazol-2-amine (4aaf):** brown liquid was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.77–7.69 (m, 3H), 7.50–7.45 (m, 1H), 7.38–7.32 (m, 1H), 3.58–3.50 (m, 2H), 3.22 (s, 3H), 1.78–1.66 (m, 2H), 1.44–1.31 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.84, 151.17, 129.26, 129.00, 128.28, 126.64, 126.58, 125.05, 123.79, 123.64, 119.69, 53.87, 38.06, 29.10, 26.95, 22.63, 14.17.HRMS (ESI) calculated for $C_{17}H_{21}N_2S$ $[M+H]^+$: 285.1420; found: 285.1422.



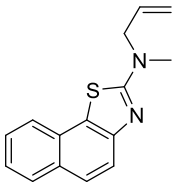
***N*-cyclohexyl-*N*-methylnaphtho[2,1-d]thiazol-2-amine (4aag):** yellow liquid was obtained in 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.76–7.69 (m, 3H), 7.49–7.43 (m, 1H), 7.37–7.31 (m, 1H), 4.04–3.91 (m, 1H), 3.09 (s, 3H), 1.96–1.82 (m, 4H), 1.76–1.67 (m, 1H), 1.59–1.39 (m, 4H), 1.21–1.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.13, 150.99, 129.21, 128.97, 128.25, 126.57, 126.53, 124.49, 123.72, 123.55, 119.65, 60.67, 32.32, 30.10, 25.89, 25.60. HRMS (ESI) calculated for $C_{18}H_{21}N_2S$ $[M+H]^+$: 297.1420; found: 297.1423.



***N*-benzyl-*N*-methylnaphtho[2,1-d]thiazol-2-amine (4aah):** yellow solid was obtained in 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.1 Hz, 1H), 7.78–7.73 (m, 2H), 7.73–7.69 (m, 1H), 7.49–7.43 (m, 1H), 7.38–7.25 (m, 6H), 4.78 (s, 2H), 3.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.26, 151.02, 136.46, 129.35, 128.98, 128.85, 128.23, 127.80, 127.64, 126.77, 126.68, 126.64, 125.31, 123.79, 119.75, 56.60, 37.99. HRMS (ESI) calculated for $C_{19}H_{17}N_2S$ $[M+H]^+$: 305.1107; found: 305.1111.

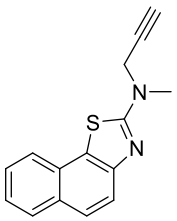


***N*-methyl-*N*-phenethylnaphtho[2,1-d]thiazol-2-amine (4aai):** yellow liquid was obtained in 66% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.78–7.69 (m, 3H), 7.50–7.43 (m, 1H), 7.38–7.33 (m, 1H), 7.31–7.26 (m, 2H), 7.26–7.17 (m, 3H), 3.75 (t, *J* = 7.4 Hz, 2H), 3.09 (s, 3H), 3.00 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.24, 151.13, 138.74, 129.26, 128.98, 128.96, 128.73, 128.24, 126.68, 126.63, 126.60, 125.21, 123.79, 123.71, 119.74, 55.50, 38.90, 33.54. HRMS (ESI-TOF) calculated for $C_{20}H_{19}N_2S$ $[M+H]^+$: 319.1263; found: 319.1268.

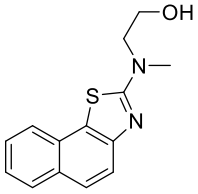


***N*-allyl-*N*-methylnaphtho[2,1-d]thiazol-2-amine (4aaj):** yellow liquid was obtained in 56% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.77–7.70 (m, 3H), 7.52–

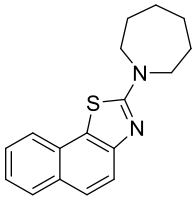
7.46 (m, 1H), 7.40–7.35 (m, 1H), 5.99–5.85 (m, 1H), 5.35–5.22 (m, 2H), 4.26–4.17 (m, 2H), 3.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.75, 150.90, 132.01, 129.24, 128.92, 128.16, 126.64, 126.55, 125.21, 123.72, 123.70, 119.64, 118.09, 55.55, 37.80. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2S$ $[M+H]^+$: 255.0950; found: 255.0953.



***N*-methyl-*N*-(prop-2-yn-1-yl)naphtho[2,1-d]thiazol-2-amine (4aak):** yellow solid was obtained in 50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.80–7.73 (m, 3H), 7.54–7.47 (m, 1H), 7.43–7.36 (m, 1H), 4.47 (d, *J* = 2.4 Hz, 2H), 3.27 (s, 3H), 2.32 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.55, 150.70, 129.54, 129.04, 128.22, 126.89, 126.74, 125.92, 124.09, 123.91, 119.98, 77.98, 73.10, 41.71, 38.10. HRMS (ESI-TOF) calculated for $C_{15}H_{13}N_2S$ $[M+H]^+$: 253.0794; found: 253.0796.

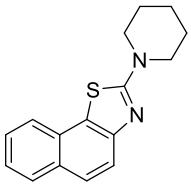


2-(methyl(naphtho[2,1-d]thiazol-2-yl)amino)ethan-1-ol (4aal): white solid was obtained in 52% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.68 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.53–7.46 (m, 1H), 7.42–7.34 (m, 1H), 3.97 (t, *J* = 5.4 Hz, 2H), 3.83 (t, *J* = 4.8 Hz, 2H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.07, 150.21, 129.42, 129.05, 128.17, 126.94, 126.77, 125.17, 123.99, 123.72, 119.52, 61.98, 56.22, 40.74. HRMS (ESI-TOF) calculated for $C_{14}H_{15}N_2OS$ $[M+H]^+$: 259.0900; found: 259.0902.

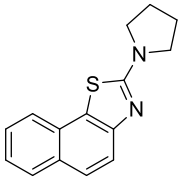


2-(azepan-1-yl)naphtho[2,1-d]thiazole (4aam): brown solid was obtained in 89% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.81 (m, 1H), 7.75–7.67 (m, 3H), 7.50–7.42 (m, 1H), 7.39–7.30 (m, 1H), 3.76–3.63 (m, 4H), 1.94–1.80 (m, 4H), 1.68–1.55 (m, 4H). ^{13}C NMR (100 MHz,

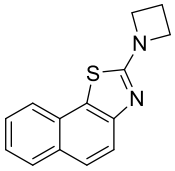
$CDCl_3$) δ 168.52, 151.23, 129.15, 128.96, 128.27, 126.55, 126.52, 124.64, 123.73, 123.50, 119.62, 50.93, 27.98, 27.74. HRMS (ESI-TOF) calculated for $C_{17}H_{19}N_2S$ $[M+H]^+$: 283.1263; found: 283.1260.



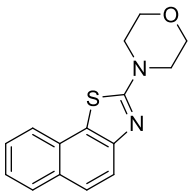
2-(piperidin-1-yl)naphtho[2,1-d]thiazole (4aan): brown solid was obtained in 84% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.76–7.68 (m, 3H), 7.50–7.43 (m, 1H), 7.38–7.31 (m, 1H), 3.62 (t, *J* = 5.0 Hz, 4H), 1.75–1.62 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.45, 150.80, 129.35, 128.97, 128.19, 126.64, 126.58, 124.99, 123.78, 123.74, 119.67, 49.75, 25.35, 24.29. HRMS (ESI-TOF) calculated for $C_{16}H_{17}N_2S$ $[M+H]^+$: 269.1107; found: 269.1112.



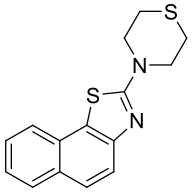
2-(pyrrolidin-1-yl)naphtho[2,1-d]thiazole (4aao): brown solid was obtained in 76% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.78–7.71 (m, 3H), 7.51–7.45 (m, 1H), 7.38–7.32 (m, 1H), 3.64–3.55 (m, 4H), 2.11–2.02 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 151.22, 129.16, 128.97, 128.32, 126.68, 126.56, 124.97, 123.78, 123.59, 119.67, 49.69, 25.81. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2S$ $[M+H]^+$: 255.0950; found: 255.0951.



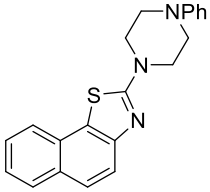
2-(azetidin-1-yl)naphtho[2,1-d]thiazole (4aap): yellow solid was obtained in 68% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.78–7.70 (m, 3H), 7.52–7.46 (m, 1H), 7.41–7.35 (m, 1H), 4.25 (t, *J* = 7.6 Hz, 4H), 2.53 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.98, 150.88, 129.48, 129.02, 128.34, 126.81, 126.70, 126.09, 123.99, 123.95, 119.80, 53.37, 17.58. HRMS (ESI-TOF) calculated for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.0794; found: 241.0792.



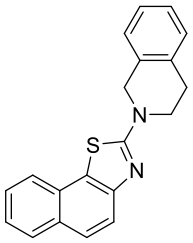
4-(naphtho[2,1-d]thiazol-2-yl)morpholine (4aaq): white solid was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.80–7.70 (m, 3H), 7.55–7.47 (m, 1H), 7.43–7.36 (m, 1H), 3.92–3.81 (m, 4H), 3.70–3.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.50, 150.40, 129.63, 129.06, 128.16, 126.97, 126.79, 125.31, 124.19, 123.87, 119.88, 66.34, 48.65. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2OS$ $[M+H]^+$: 271.0900; found: 271.0903.



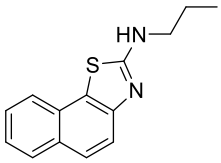
2-thiomorpholinonaphtho[2,1-d]thiazole (4aar): brown solid was obtained in 63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.78–7.68 (m, 3H), 7.54–7.46 (m, 1H), 7.43–7.35 (m, 1H), 4.06–3.98 (m, 4H), 2.84–2.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.62, 150.56, 129.56, 129.07, 128.16, 126.94, 126.79, 125.27, 124.10, 123.81, 119.79, 51.40, 26.70. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2S_2$ $[M+H]^+$: 287.0671; found: 287.0677.



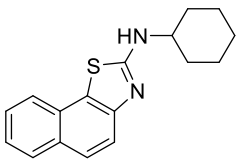
2-(4-phenylpiperazin-1-yl)naphtho[2,1-d]thiazole (4aas): yellow solid was obtained in 42% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.80–7.72 (m, 3H), 7.55–7.49 (m, 1H), 7.44–7.38 (m, 1H), 7.35–7.28 (m, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 3.90–3.81 (m, 4H), 3.41–3.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.25, 151.11, 150.57, 129.63, 129.44, 129.09, 128.22, 126.97, 126.80, 125.45, 124.15, 123.90, 120.86, 119.87, 117.04, 49.29, 48.58. HRMS (ESI-TOF) calculated for $C_{21}H_{20}N_3S$ $[M+H]^+$: 346.1372; found: 346.1374.



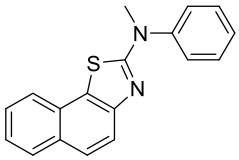
2-(3,4-dihydroisoquinolin-2(1H)-yl)naphtho[2,1-d]thiazole (4aat): white solid was obtained in 52% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 1H), 7.81–7.73 (m, 3H), 7.54–7.47 (m, 1H), 7.42–7.35 (m, 1H), 7.29–7.18 (m, 4H), 4.86 (s, 2H), 3.93 (t, *J* = 6.0 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.59, 150.76, 134.48, 132.67, 129.44, 129.06, 128.72, 128.26, 127.02, 126.89, 126.74, 126.73, 126.57, 125.01, 123.93, 123.84, 119.81, 49.83, 46.37, 28.94. HRMS (ESI-TOF) calculated for $C_{20}H_{17}N_2S$ $[M+H]^+$: 317.1107; found: 317.1106.



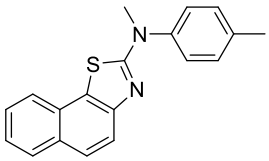
***N*-propylnaphtho[2,1-d]thiazol-2-amine (4aau):** yellow liquid was obtained in 46% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.86–7.77 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 4.19–4.07 (m, 1H), 3.90–3.78 (m, 1H), 2.09–1.94 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.75, 150.52, 130.01, 129.02, 128.22, 127.09, 126.90, 126.87, 124.67, 124.20, 120.32, 53.12, 21.29, 11.68. HRMS (ESI-TOF) calculated for $C_{14}H_{15}N_2S$ $[M+H]^+$: 243.0950; found: 243.0953.



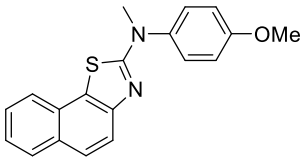
***N*-cyclohexylnaphtho[2,1-d]thiazol-2-amine (4aav):** white solid was obtained in 50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.80 (q, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 6.9 Hz, 1H), 7.38 (t, *J* = 6.9 Hz, 1H), 4.29–4.19 (m, 1H), 2.61–2.43 (m, 2H), 2.04–1.82 (m, 4H), 1.77–1.68 (m, 1H), 1.55–1.38 (m, 2H), 1.31–1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.88, 150.68, 129.90, 128.97, 128.14, 126.72, 126.64, 126.39, 124.45, 124.31, 120.42, 65.44, 30.79, 30.44, 26.11, 25.93, 25.81. HRMS (ESI-TOF) calculated for $C_{17}H_{19}N_2S$ $[M+H]^+$: 283.1263; found: 283.1265.



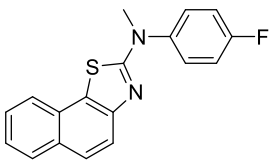
***N*-methyl-*N*-phenylnaphtho[2,1-d]thiazol-2-amine (4aaw):** brown solid was obtained in 82% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.80–7.73 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.53–7.46 (m, 4H), 7.45–7.40 (m, 1H), 7.39–7.33 (m, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.63, 150.47, 146.11, 130.15, 129.71, 128.97, 128.09, 127.51, 126.71, 126.62, 126.01, 125.68, 124.03, 123.94, 119.85, 40.60. HRMS (ESI-TOF) calculated for $C_{18}H_{15}N_2S$ $[M+H]^+$: 291.0950; found: 291.0948.



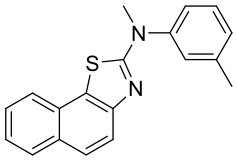
***N*-methyl-*N*-(*p*-tolyl)naphtho[2,1-d]thiazol-2-amine (4aax):** brown liquid was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.80–7.70 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.43–7.37 (m, 1H), 7.35–7.30 (m, 3H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.63 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.94, 150.58, 143.59, 137.60, 130.75, 129.63, 128.93, 128.09, 126.63, 126.55, 126.00, 125.68, 123.91, 123.88, 119.80, 40.57, 21.28. HRMS (ESI-TOF) calculated for $C_{19}H_{17}N_2S$ $[M+H]^+$: 305.1107; found: 305.1114.



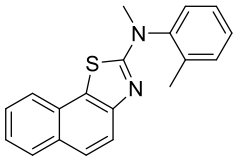
***N*-(4-methoxyphenyl)-*N*-methylnaphtho[2,1-d]thiazol-2-amine (4aay):** black liquid was obtained in 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.79–7.70 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.43–7.38 (m, 1H), 7.37–7.28 (m, 3H), 7.02–6.95 (m, 2H), 3.83 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.50, 158.93, 150.72, 139.03, 129.55, 128.92, 128.09, 127.94, 126.62, 126.54, 125.80, 123.87, 123.86, 119.77, 115.30, 55.59, 40.68. HRMS (ESI-TOF) calculated for $C_{19}H_{17}N_2OS$ $[M+H]^+$: 321.1056; found: 321.1057.



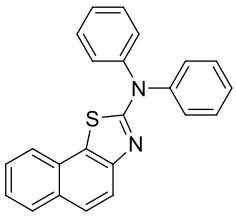
***N*-(4-fluorophenyl)-*N*-methylnaphtho[2,1-d]thiazol-2-amine (4aaz):** black solid was obtained in 62% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.81–7.71 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.48–7.40 (m, 3H), 7.39–7.33 (m, 1H), 7.22–7.13 (m, 2H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.75, 161.55 (d, *J* = 247.8 Hz), 150.55, 142.10 (d, *J* = 3.1 Hz), 129.73, 129.00, 128.32, 128.24, 128.08, 126.76 (d, *J* = 11.7 Hz), 125.84, 124.12, 123.92, 119.88, 117.11 (d, *J* = 22.7 Hz), 40.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.30. HRMS (ESI-TOF) calculated for $C_{18}H_{14}FN_2S$ $[M+H]^+$: 309.0856; found: 309.0859.



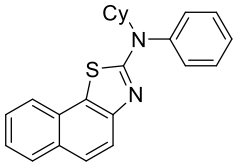
***N*-methyl-*N*-(m-tolyl)naphtho[2,1-d]thiazol-2-amine (4aaaa):** brown liquid was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.80–7.71 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45–7.39 (m, 1H), 7.38–7.32 (m, 2H), 7.27 (s, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 3.66 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.72, 150.48, 146.05, 140.24, 129.91, 129.66, 128.95, 128.35, 128.08, 126.66, 126.58, 125.64, 123.97, 123.92, 122.98, 119.81, 40.57, 21.57. HRMS (ESI-TOF) calculated for $C_{19}H_{17}N_2S$ $[M+H]^+$: 305.1107; found: 305.1112.



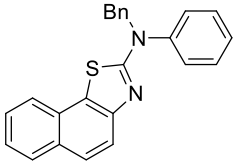
***N*-methyl-N-(o-tolyl)naphtho[2,1-d]thiazol-2-amine (4aaab):** brown liquid was obtained in 79% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 1H), 7.82–7.77 (m, 1H), 7.76–7.71 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.44–7.30 (m, 6H), 3.59 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.22, 150.83, 144.31, 136.83, 132.18, 129.46, 129.12, 128.93, 128.59, 128.14, 128.12, 126.66, 126.55, 126.09, 123.87, 123.84, 119.75, 39.57, 17.59. HRMS (ESI-TOF) calculated for $C_{19}H_{17}N_2S$ $[M+H]^+$: 305.1107; found: 305.1105.



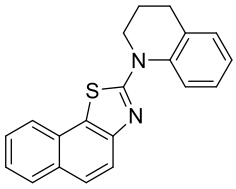
***N,N*-diphenylnaphtho[2,1-d]thiazol-2-amine (4aaac):** colorless liquid was obtained in 60% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 1H), 7.82–7.73 (m, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.54–7.37 (m, 10H), 7.34–7.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.58, 150.07, 144.99, 130.09, 129.85, 129.03, 127.95, 127.06, 126.79, 126.75, 126.61, 126.47, 124.53, 124.15, 120.57. HRMS (ESI-TOF) calculated for $C_{23}H_{17}N_2S$ $[M+H]^+$: 353.1107; found: 353.1108.



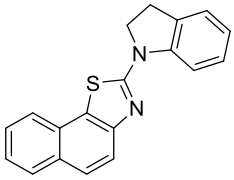
***N*-cyclohexyl-*N*-phenylnaphtho[2,1-d]thiazol-2-amine (4aaad):** yellow solid was obtained in 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.78–7.70 (m, 2H), 7.58–7.47 (m, 4H), 7.41–7.28 (m, 4H), 4.89–4.71 (m, 1H), 2.23–2.08 (m, 2H), 1.88–1.76 (m, 2H), 1.63 (s, 1H), 1.59–1.46 (m, 2H), 1.30–1.18 (m, 2H), 1.08–0.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.83, 150.79, 141.43, 131.29, 130.12, 129.41, 129.10, 128.91, 128.09, 126.47, 126.43, 125.40, 123.89, 123.67, 119.85, 59.08, 31.90, 25.96, 25.58. HRMS (ESI-TOF) calculated for $C_{23}H_{23}N_2S$ $[M+H]^+$: 359.1576; found: 359.1574.



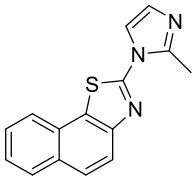
***N*-benzyl-*N*-phenylnaphtho[2,1-d]thiazol-2-amine (4aaae)**, yellow solid was obtained in 55% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.81–7.72 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.46–7.40 (m, 3H), 7.39–7.31 (m, 6H), 7.31–7.20 (m, 3H), 5.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.97, 150.51, 144.59, 137.47, 130.15, 129.73, 128.98, 128.61, 128.34, 128.13, 127.94, 127.56, 127.43, 126.68, 126.62, 125.96, 124.03, 123.95, 120.03, 56.50. HRMS (ESI-TOF) calculated for $C_{24}H_{19}N_2S$ $[M+H]^+$: 367.1263; found: 367.1262.



2-(3,4-dihydroquinolin-1(2H)-yl)naphtho[2,1-d]thiazole (4aaaf): yellow solid was obtained in 72% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.96 (m, 1H), 7.92–7.86 (m, 1H), 7.83–7.70 (m, 3H), 7.53–7.45 (m, 1H), 7.44–7.36 (m, 1H), 7.32–7.24 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14–7.06 (m, 1H), 4.20–4.08 (m, 2H), 2.89–2.78 (m, 2H), 2.18–2.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.93, 149.74, 140.57, 130.77, 130.02, 129.24, 129.03, 128.07, 126.83, 126.78, 126.75, 125.08, 124.31, 124.28, 124.09, 121.20, 120.06, 49.61, 27.56, 23.54. HRMS (ESI-TOF) calculated for $C_{20}H_{17}N_2S$ $[M+H]^+$: 317.1107; found: 317.1111.

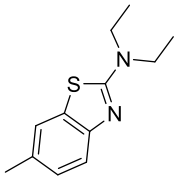


2-(indolin-1-yl)naphtho[2,1-d]thiazole (4aaag): brown liquid was obtained in 69% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.88–7.80 (m, 2H), 7.78–7.70 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 4.16–4.04 (m, 2H), 3.27–3.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.28, 150.27, 143.45, 131.49, 129.67, 129.00, 128.08, 127.74, 126.95, 126.73, 125.14, 124.95, 124.19, 124.03, 122.29, 120.26, 113.42, 51.59, 28.01. HRMS (ESI-TOF) calculated for $C_{19}H_{15}N_2S$ $[M+H]^+$: 303.0950; found: 303.0956.

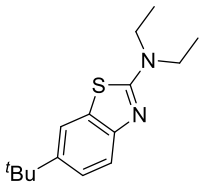


2-(2-methyl-1H-imidazol-1-yl)naphtho[2,1-d]thiazole (4aaah): yellow solid was obtained in 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.92 (m, 2H), 7.92–7.81 (m, 2H), 7.64–7.52 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.94, 148.65, 145.90, 131.07, 129.71, 129.17, 128.92, 127.94, 127.63, 127.43, 126.26, 124.46,

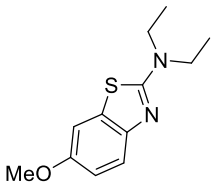
121.34, 119.64, 16.13. HRMS (ESI-TOF) calculated for $C_{15}H_{12}N_3S$ $[M+H]^+$: 266.0746; found: 266.0748.



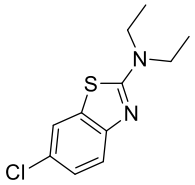
***N,N*-diethyl-6-methylbenzo[d]thiazol-2-amine (4baa):** green liquid was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 1H), 7.37 (s, 1H), 7.11–7.03 (m, 1H), 3.55 (q, *J* = 7.0 Hz, 4H), 2.37 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.93, 151.22, 130.75, 130.42, 127.02, 120.71, 118.22, 45.38, 21.30, 13.02. HRMS (ESI-TOF) calculated for $C_{12}H_{17}N_2S$ $[M+H]^+$: 221.1107; found: 221.1112.



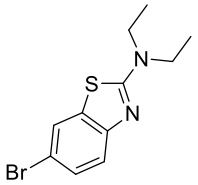
6-(tert-butyl)-*N,N*-diethylbenzo[d]thiazol-2-amine (4caa): yellow liquid was obtained in 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.56 (q, *J* = 7.2 Hz, 4H), 1.34 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.19, 151.15, 144.08, 130.61, 123.53, 118.02, 117.12, 45.47, 34.75, 31.83, 13.03. HRMS (ESI-TOF) calculated for $C_{12}H_{17}N_2S$ $[M+H]^+$: 263.1576; found: 263.1574.



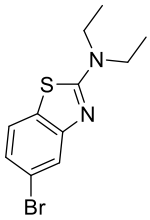
***N,N*-diethyl-6-methoxybenzo[d]thiazol-2-amine (4daa):** brown liquid was obtained in 72% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 2.6 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.81 (s, 3H), 3.54 (q, *J* = 7.2 Hz, 4H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.06, 154.56, 147.63, 131.58, 118.90, 113.30, 105.34, 56.00, 45.32, 13.01. HRMS (ESI-TOF) calculated for $C_{12}H_{17}N_2OS$ $[M+H]^+$: 237.1056; found: 237.1059.



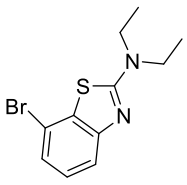
6-chloro-*N,N*-diethylbenzo[d]thiazol-2-amine (4eaa): yellow liquid was obtained in 66% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.50 (m, 1H), 7.44–7.38 (m, 1H), 7.24–7.17 (m, 1H), 3.56 (q, *J* = 7.0 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.57, 152.07, 131.95, 126.32, 125.79, 120.29, 119.23, 45.61, 12.97. HRMS (ESI-TOF) calculated for $C_{11}H_{14}ClN_2S$ $[M+H]^+$: 241.0561; found: 241.0566.



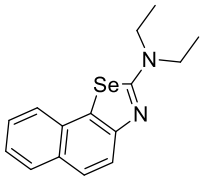
6-bromo-*N,N*-diethylbenzo[d]thiazol-2-amine (4faa): yellow liquid was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.8 Hz, 1H), 7.40–7.32 (m, 2H), 3.55 (q, *J* = 7.2 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.54, 152.43, 132.46, 129.05, 123.05, 119.71, 112.91, 45.60, 12.96. HRMS (ESI-TOF) calculated for $C_{11}H_{14}BrN_2S$ $[M+H]^+$: 285.0056; found: 285.0059.



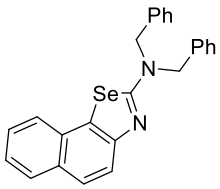
5-bromo-*N,N*-diethylbenzo[d]thiazol-2-amine (4haa): yellow liquid was obtained in 48% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (p, *J* = 4.2 Hz, 1H), 7.16–7.10 (m, 2H), 3.57 (q, *J* = 7.2 Hz, 4H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.60, 153.55, 133.37, 127.11, 123.49, 117.19, 113.07, 45.61, 12.96. HRMS (ESI-TOF) calculated for $C_{11}H_{14}BrN_2S$ $[M+H]^+$: 285.0056; found: 285.0060.



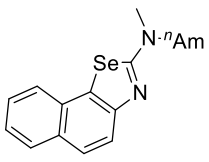
7-bromo-*N,N*-diethylbenzo[d]thiazol-2-amine (4haa'): yellow liquid was obtained in 12% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.56 (q, *J* = 7.2 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.31, 154.85, 129.60, 123.54, 121.57 (2C), 119.47, 45.69, 12.96. HRMS (ESI-TOF) calculated for $C_{11}H_{14}BrN_2S$ $[M+H]^+$: 285.0056; found: 285.0059.



***N,N*-diethylnaphtho[2,1-d][1,3]selenazol-2-amine (4aba):** yellow solid was obtained in 87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 1H), 7.74–7.68 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.45–7.39 (m, 1H), 7.34–7.27 (m, 1H), 3.51 (q, *J* = 7.2 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.23, 152.92, 130.75, 129.10, 129.06, 128.77, 126.66, 126.55, 125.82, 123.54, 120.69, 46.62, 12.95. HRMS (ESI-TOF) calculated for $C_{15}H_{17}N_2Se$ $[M+H]^+$: 305.0551; found: 305.0550.

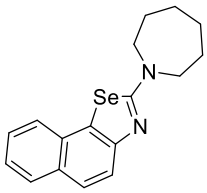


***N,N*-dibenzylnaphtho[2,1-d][1,3]selenazol-2-amine (4abd):** white solid was obtained in 58% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.78–7.72 (m, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.46–7.40 (m, 1H), 7.37–7.25 (m, 11H), 4.75 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.40, 152.56, 136.27, 130.77, 130.00, 129.48, 128.90, 128.88, 127.97, 127.90, 126.96, 126.75, 125.89, 123.95, 121.01, 54.73. HRMS (ESI-TOF) calculated for $C_{25}H_{21}N_2Se$ $[M+H]^+$: 429.0864; found: 429.0866.

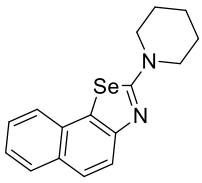


***N*-methyl-*N*-pentylnaphtho[2,1-d][1,3]selenazol-2-amine (4abf):** yellow liquid was obtained in 74% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.6 Hz, 1H), 7.72 (s, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.48–7.41 (m, 1H), 7.37–7.30 (m, 1H), 3.48 (t, *J* = 8.4 Hz, 2H), 3.18 (s, 3H), 1.70

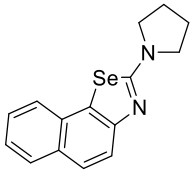
(p, *J* = 7.4 Hz, 2H), 1.40 – 1.31 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.43, 152.93, 130.78, 129.43, 129.19, 128.83, 126.79, 126.63, 125.86, 123.66, 120.80, 55.08, 38.80, 29.09, 27.04, 22.58, 14.14. HRMS (ESI-TOF) calculated for $C_{17}H_{21}N_2Se$ $[M+H]^+$: 333.0864; found: 333.0869.



2-(azepan-1-yl)naphtho[2,1-d][1,3]selenazole (4abm): yellow liquid was obtained in 86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.72 (s, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.47–7.41 (m, 1H), 7.36–7.29 (m, 1H), 3.66 (t, *J* = 5.8 Hz, 4H), 1.91–1.81 (m, 4H), 1.65–1.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.21, 153.03, 130.80, 129.12, 129.00, 128.82, 126.74, 126.59, 125.86, 123.56, 120.76, 52.10, 28.02, 27.71. HRMS (ESI-TOF) calculated for $C_{17}H_{19}N_2Se$ $[M+H]^+$: 331.0708; found: 331.0705.

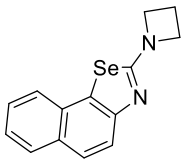


2-(piperidin-1-yl)naphtho[2,1-d][1,3]selenazole (4abn): yellow liquid was obtained in 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.77–7.67 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.50–7.41 (m, 1H), 7.39–7.31 (m, 1H), 3.59 (t, *J* = 5.2 Hz, 4H), 1.78–1.63 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.20, 152.66, 130.72, 129.40, 129.31, 128.83, 126.81, 126.65, 125.89, 123.79, 120.81, 51.06, 25.51, 24.41. HRMS (ESI-TOF) calculated for $C_{16}H_{17}N_2Se$ $[M+H]^+$: 317.0551; found: 317.0555.

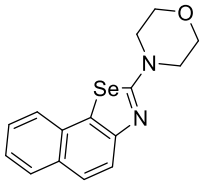


2-(pyrrolidin-1-yl)naphtho[2,1-d][1,3]selenazole (4abo): white solid was obtained in 84% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.79–7.70 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.49–7.41 (m, 1H), 7.37–7.30 (m, 1H), 3.55 (t, *J* = 6.4 Hz, 4H), 2.09–1.99 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.11, 152.95, 130.85, 129.38, 129.09, 128.81, 126.83, 126.61,

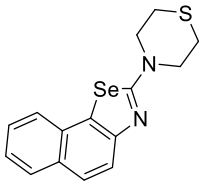
125.87, 123.62, 120.79, 50.54, 25.73. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2Se$ $[M+H]^+$: 303.0395; found: 303.0392.



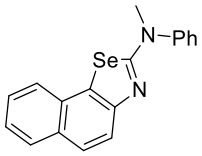
2-(azetidin-1-yl)naphtho[2,1-d][1,3]selenazole (4abp): white solid was obtained in 64% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.78–7.71 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.49–7.43 (m, 1H), 7.39–7.32 (m, 1H), 4.19 (t, *J* = 7.6 Hz, 4H), 2.49 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.45, 152.65, 130.89, 130.57, 129.34, 128.86, 126.96, 126.76, 126.04, 123.98, 120.85, 53.67, 17.32. HRMS (ESI-TOF) calculated for $C_{14}H_{13}N_2Se$ $[M+H]^+$: 289.0238; found: 289.0240.



4-(naphtho[2,1-d][1,3]selenazol-2-yl)morpholine (4abq): white solid was obtained in 71% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.77–7.70 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50–7.44 (m, 1H), 7.40–7.34 (m, 1H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.60 (t, *J* = 4.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.47, 152.14, 130.62, 129.83, 129.53, 128.89, 127.06, 126.82, 125.94, 124.19, 121.00, 66.37, 49.77. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2OSe$ $[M+H]^+$: 319.0344; found: 319.0345.



4-(naphtho[2,1-d][1,3]selenazol-2-yl)thiomorpholine (4abr): white solid was obtained in 68% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.76–7.67 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.50–7.43 (m, 1H), 7.40–7.34 (m, 1H), 4.02–3.91 (m, 4H), 2.81–2.72 (m, 4H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.40, 152.32, 130.63, 129.86, 129.48, 128.89, 127.03, 126.81, 125.87, 124.11, 120.92, 52.71, 26.85. HRMS (ESI-TOF) calculated for $C_{15}H_{15}N_2SSe$ $[M+H]^+$: 335.0116; found: 335.0114.

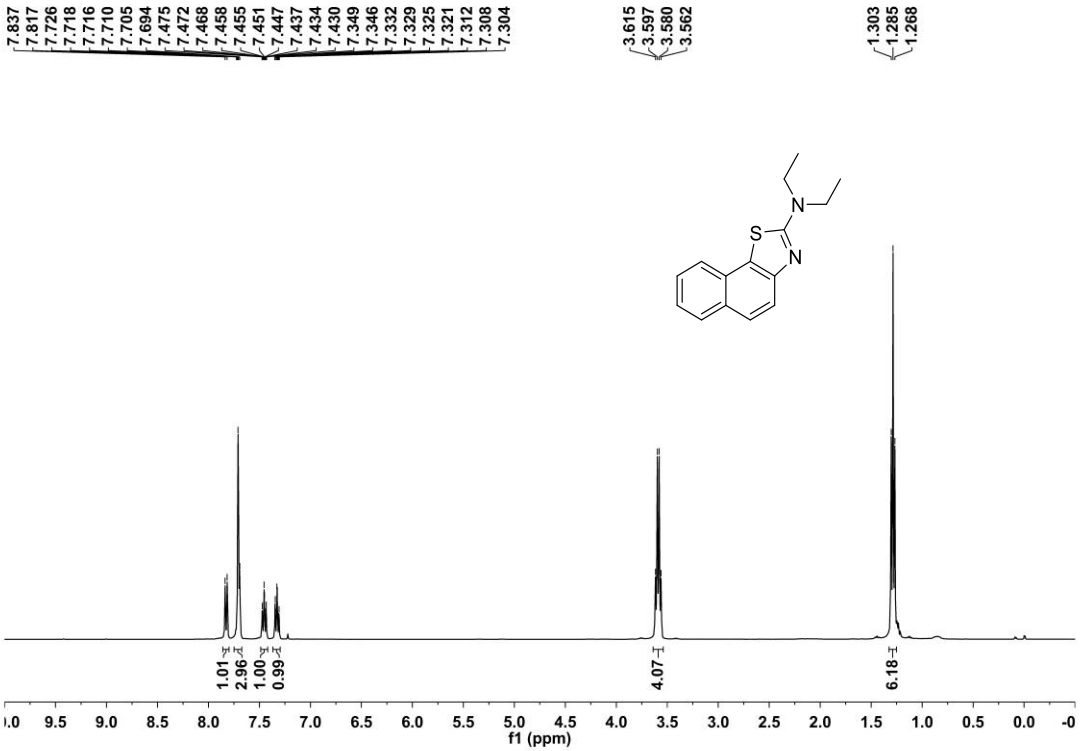


***N*-methyl-*N*-phenylnaphtho[2,1-d][1,3]selenazol-2-amine (4abw):** yellow solid was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.69 (m, 3H), 7.45 (d, *J* = 4.8 Hz, 4H), 7.41–7.28 (m, 4H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.65, 152.38, 147.20, 130.59, 130.22, 129.94, 129.70, 128.80, 127.73, 126.81, 126.64, 125.98, 125.95, 124.01, 120.96, 40.50. HRMS (ESI-TOF) calculated for $C_{18}H_{15}N_2Se$ $[M+H]^+$: 339.0395; found: 339.0398.

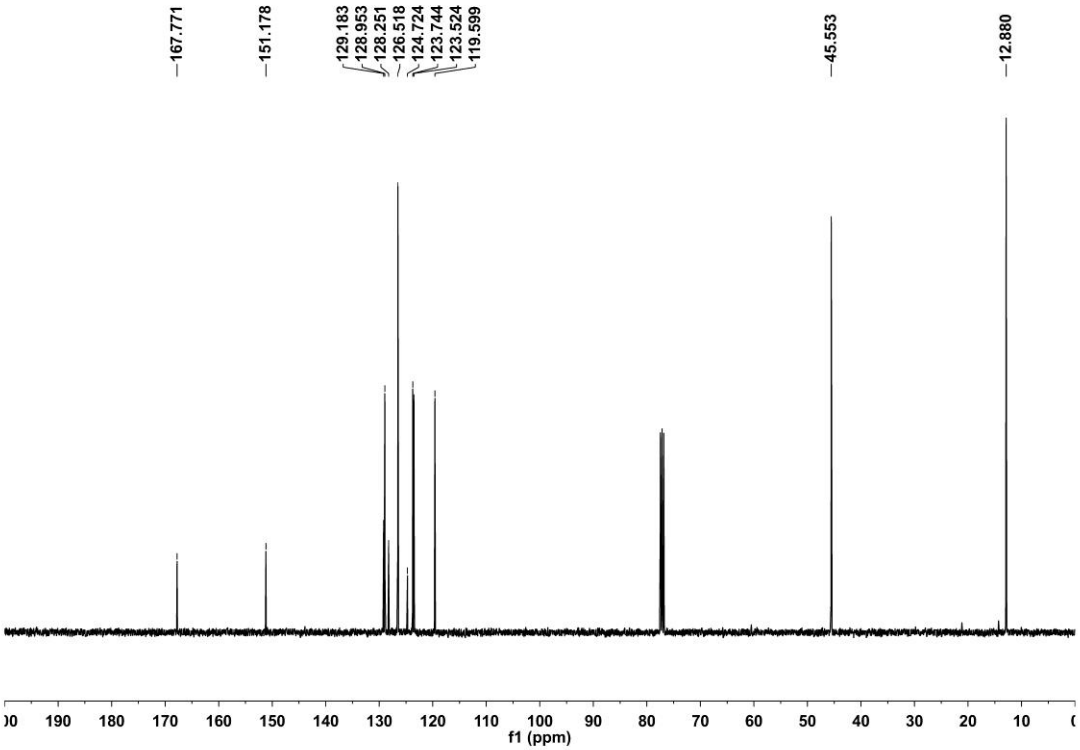
Copies of product NMR Spectra

4aaa

^{1}H NMR

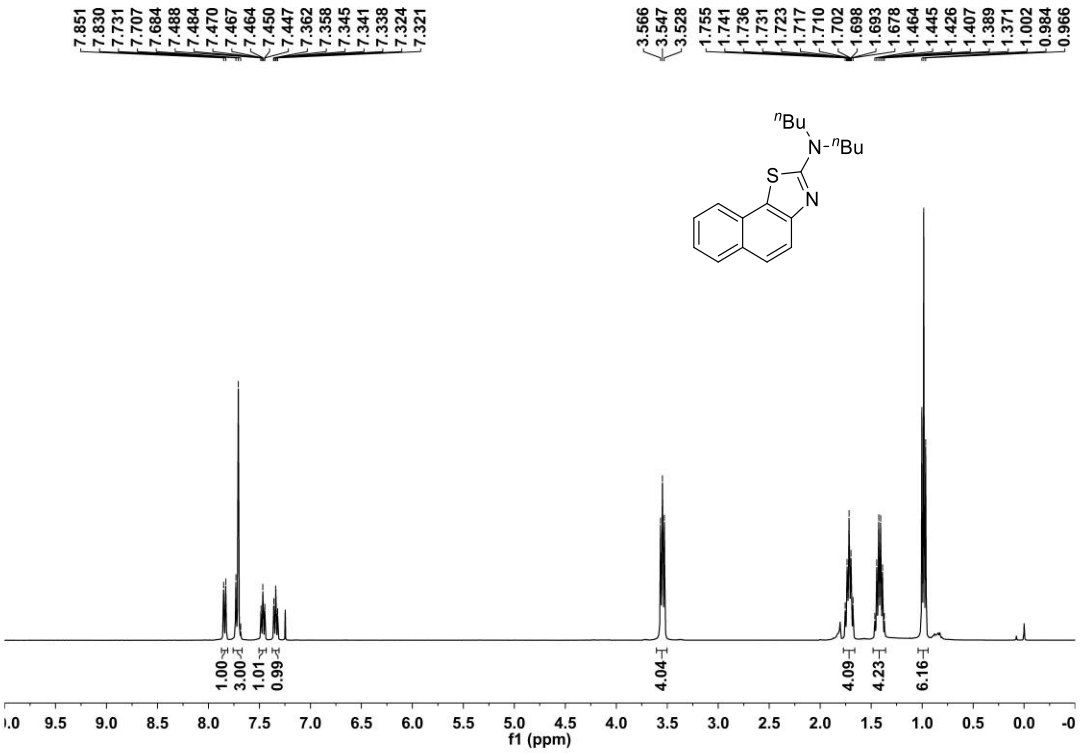


^{13}C NMR

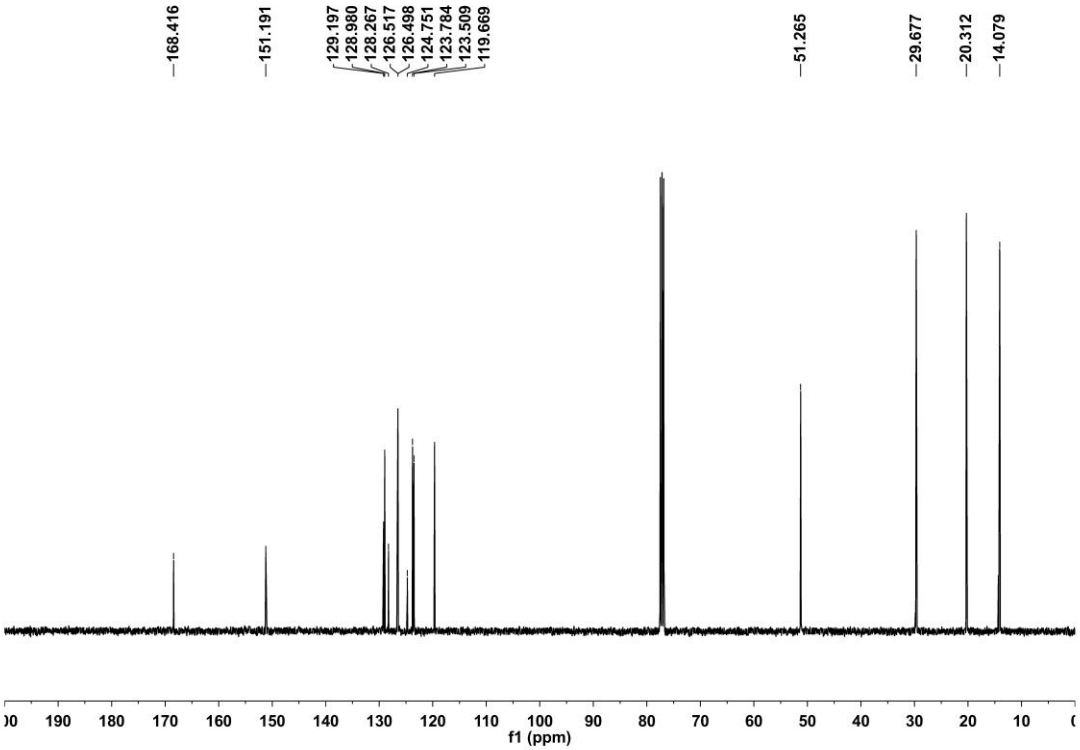


4aab

^{1}H NMR



^{13}C NMR



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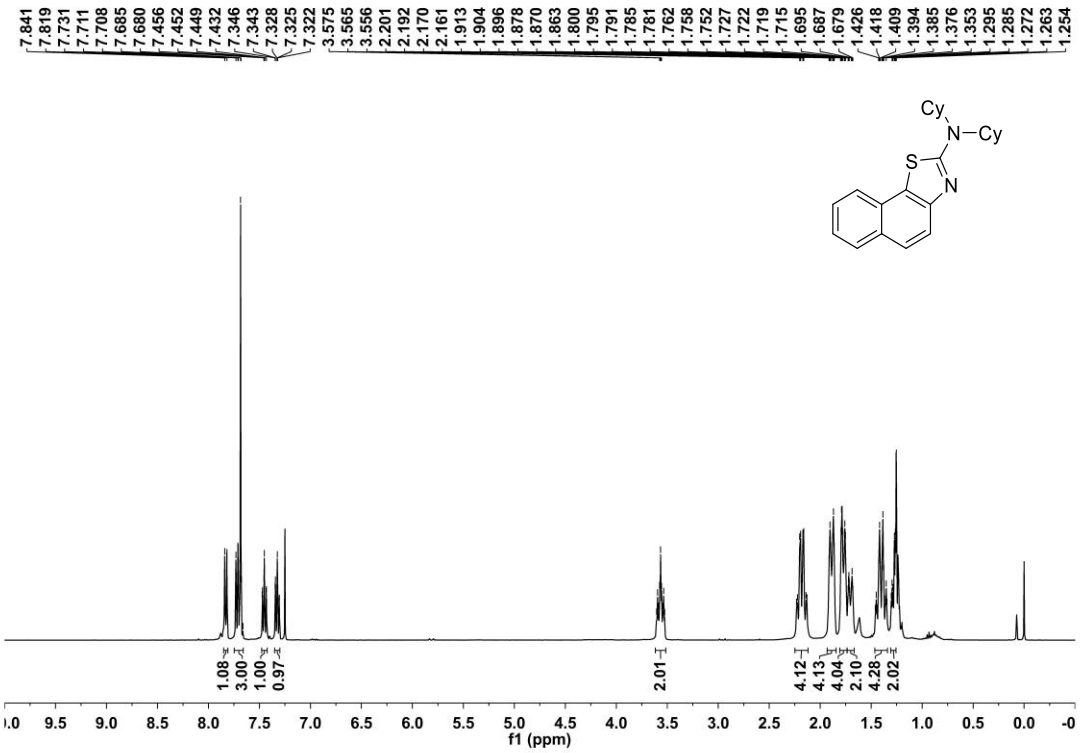

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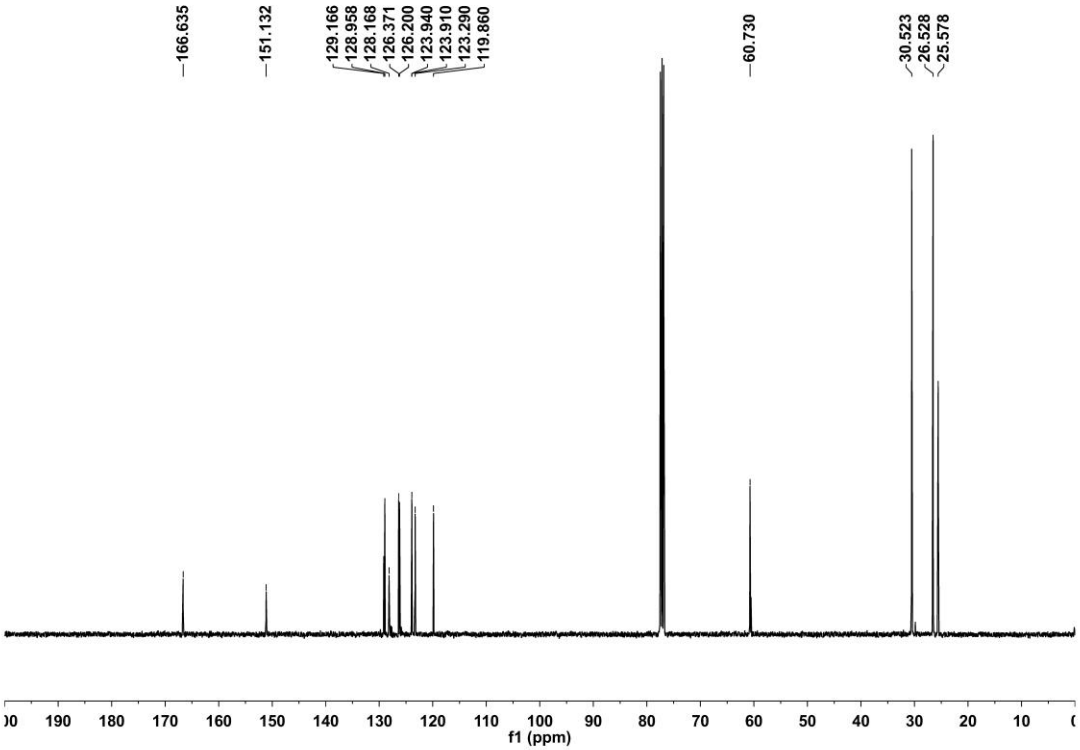

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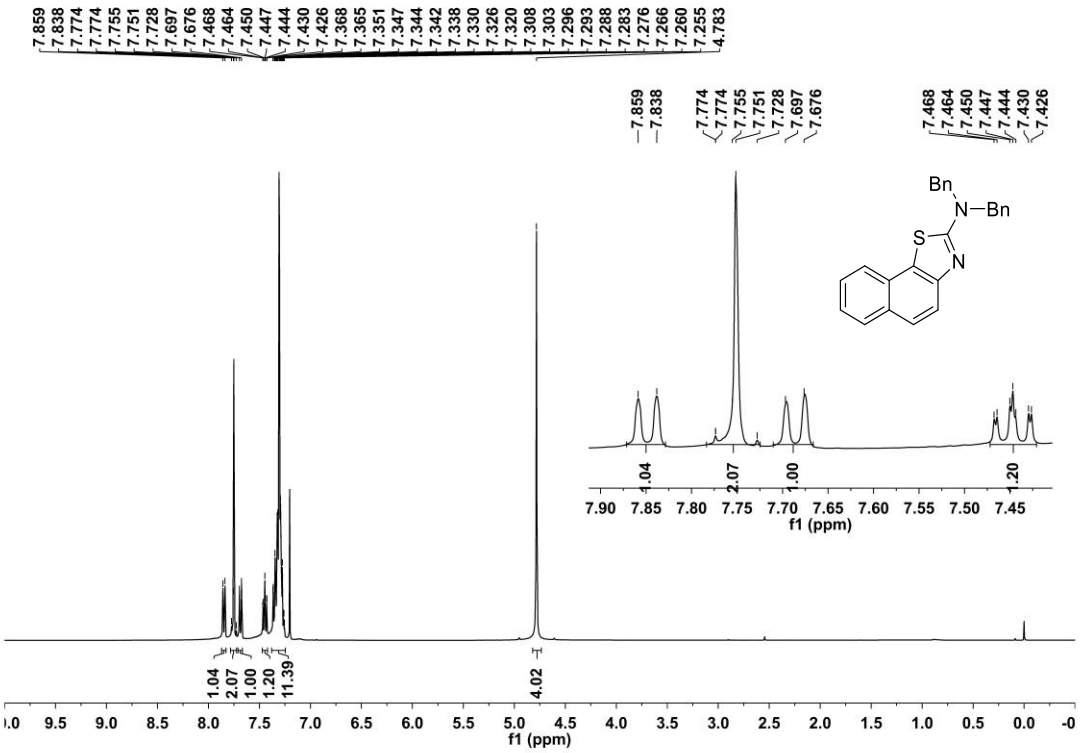
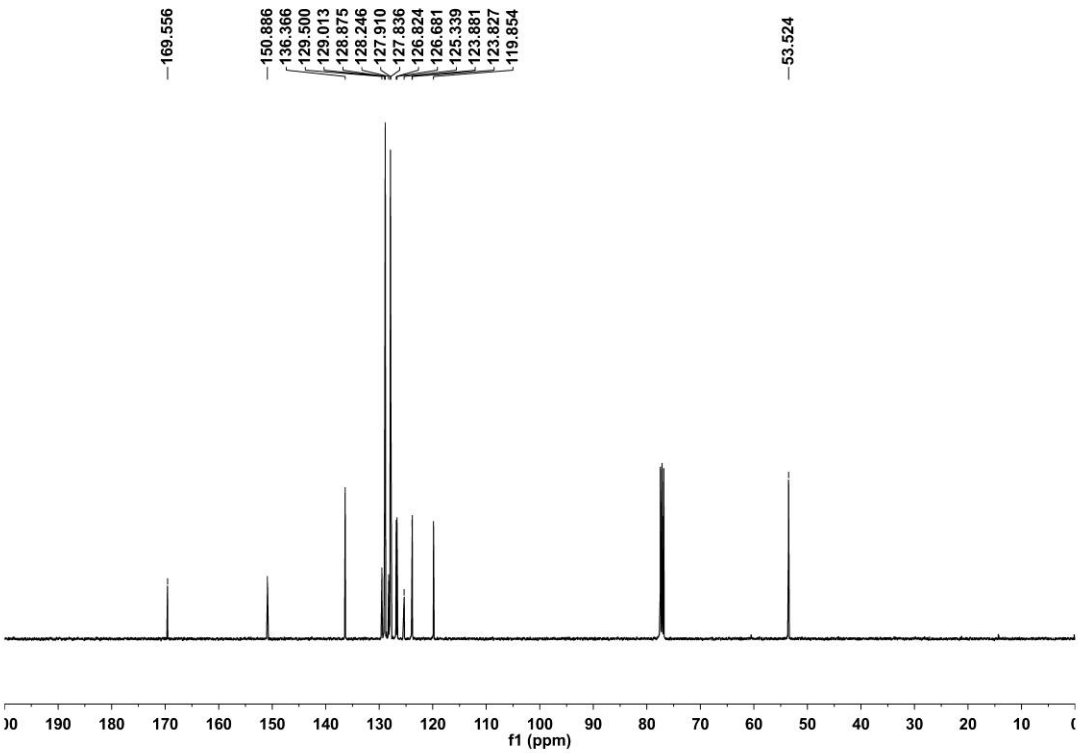


^{13}C NMR



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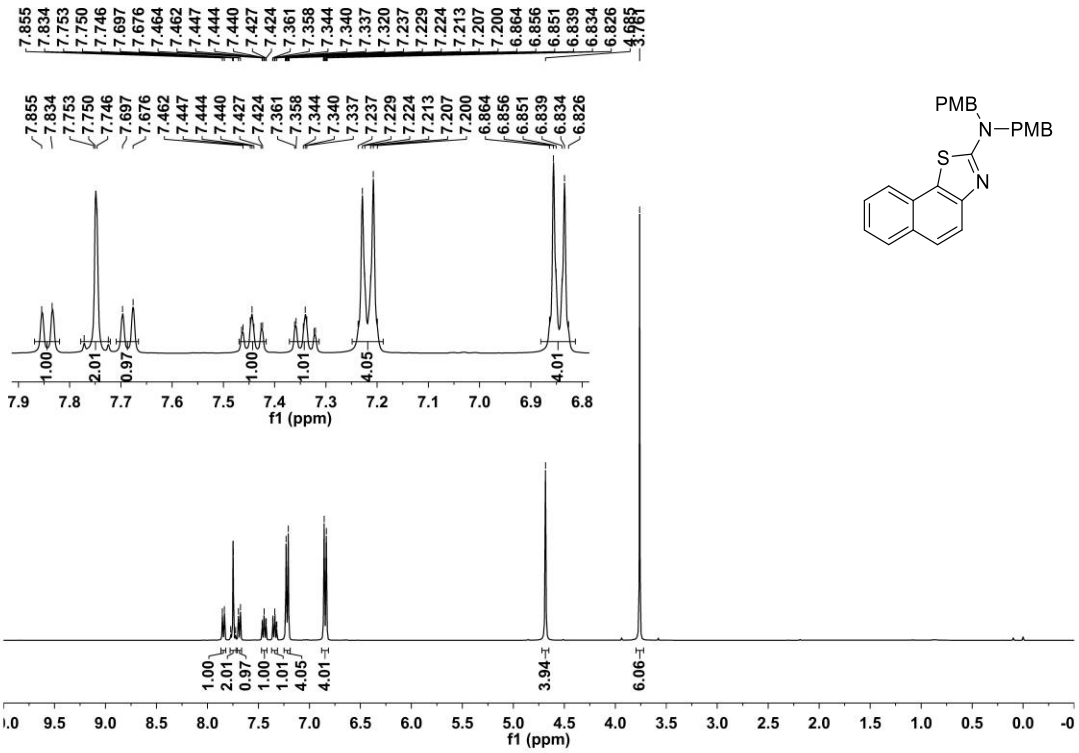

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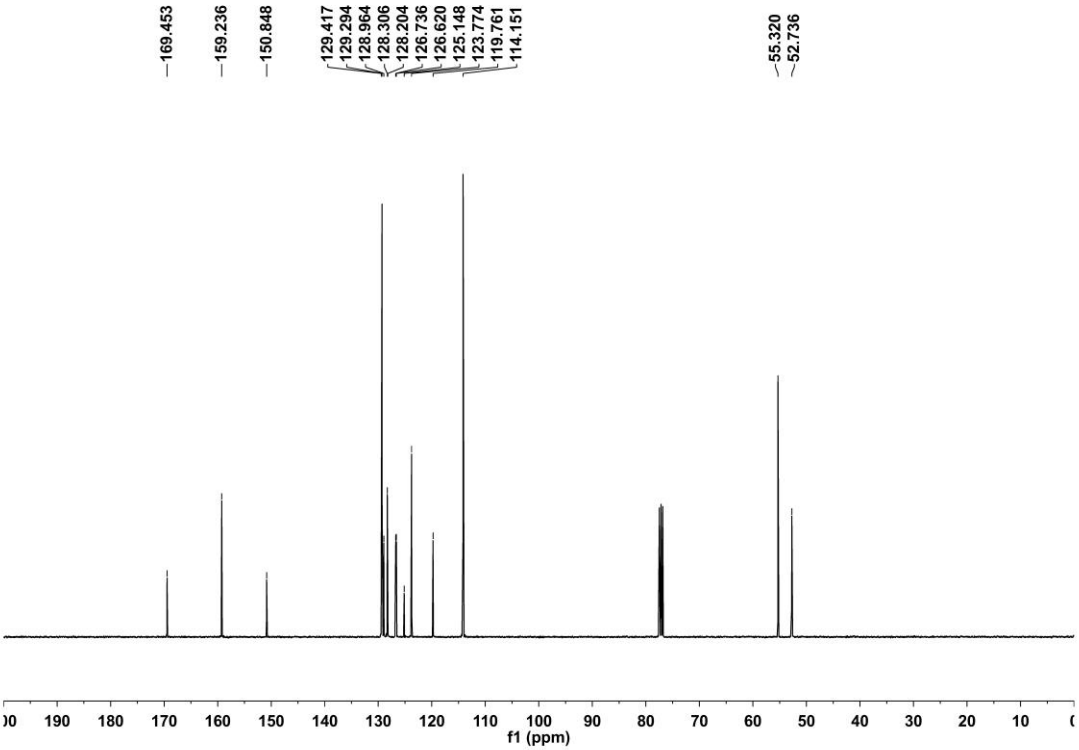

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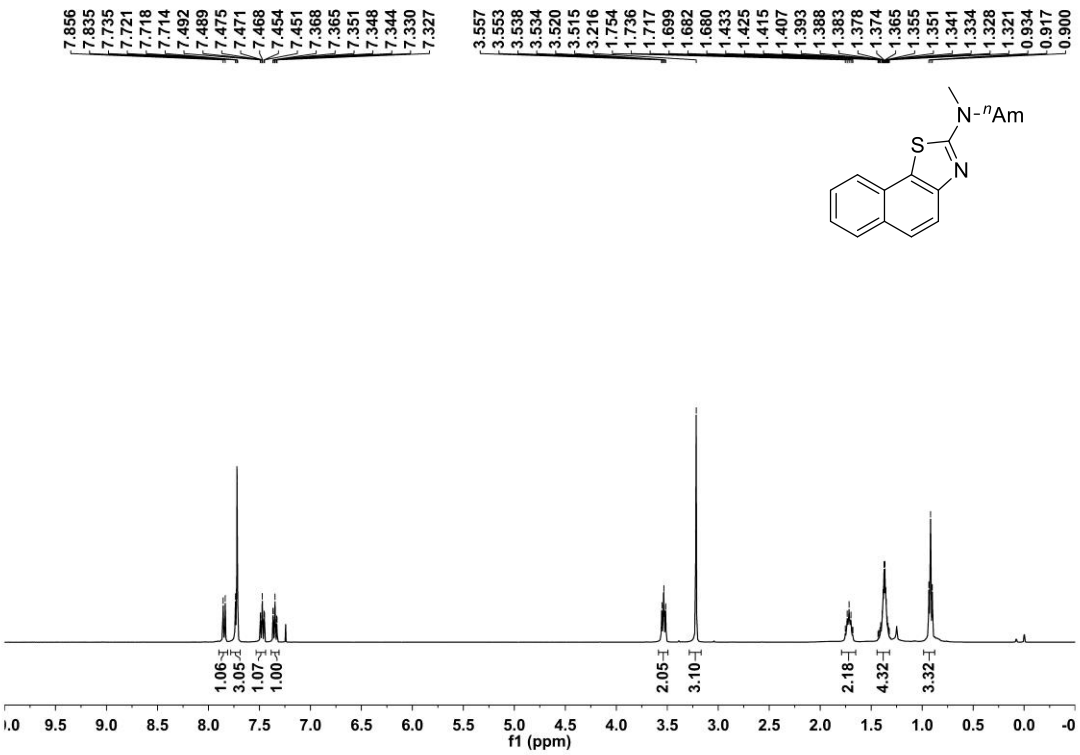
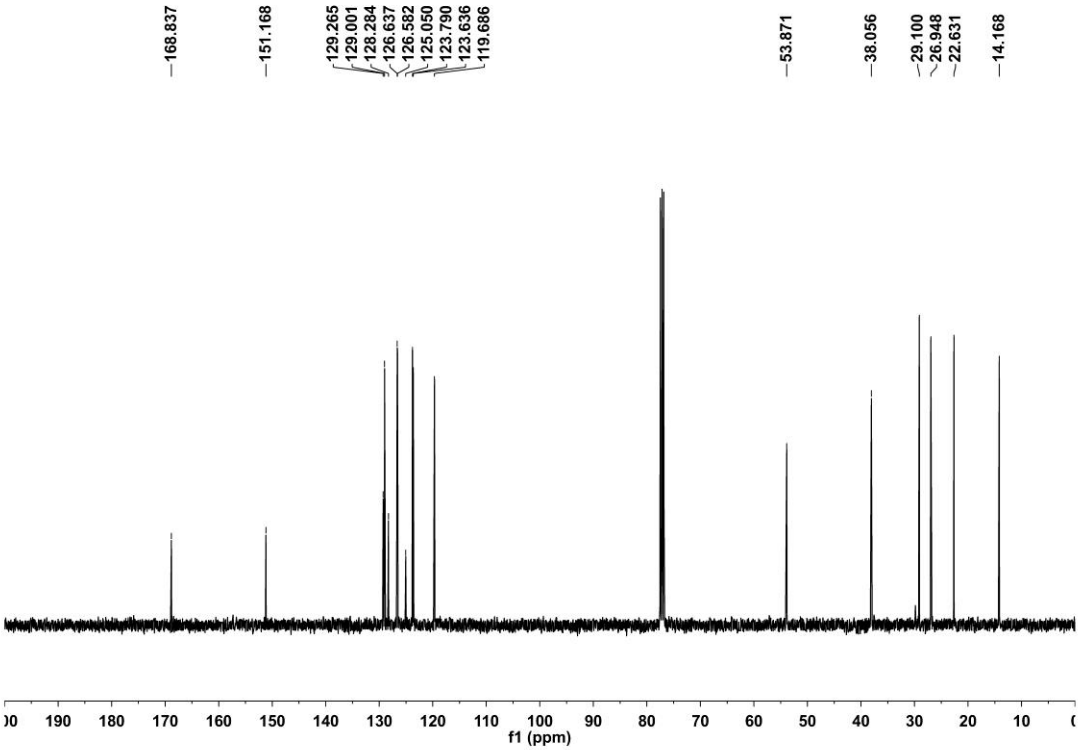


^{13}C NMR



4aag

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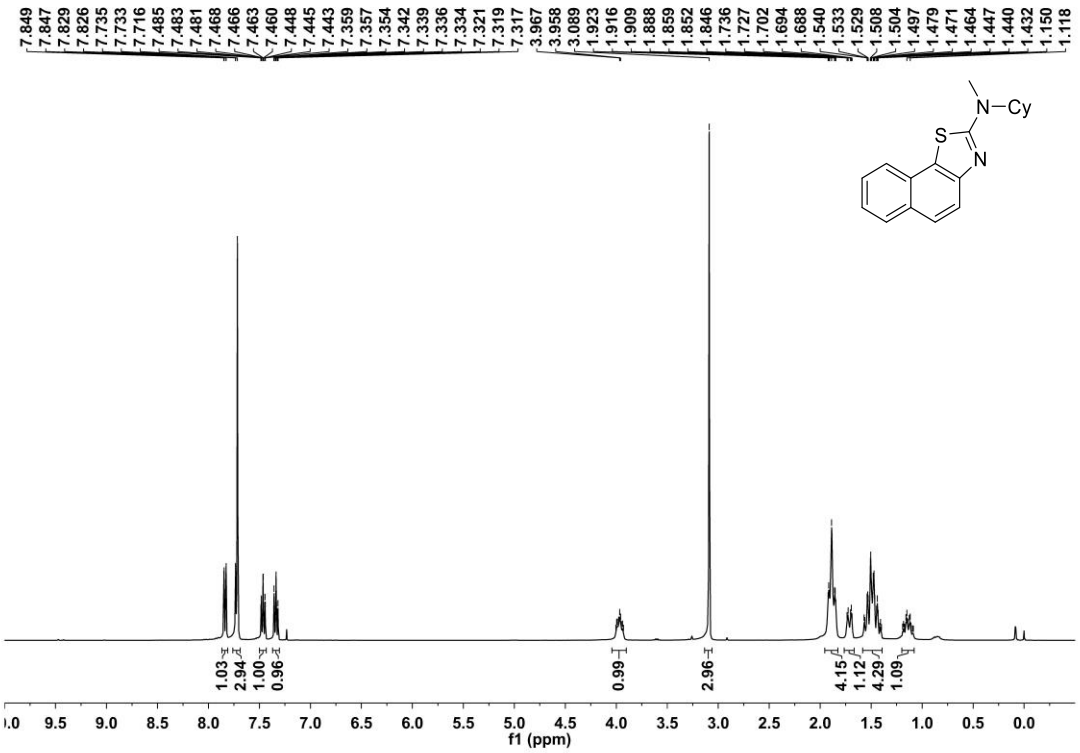

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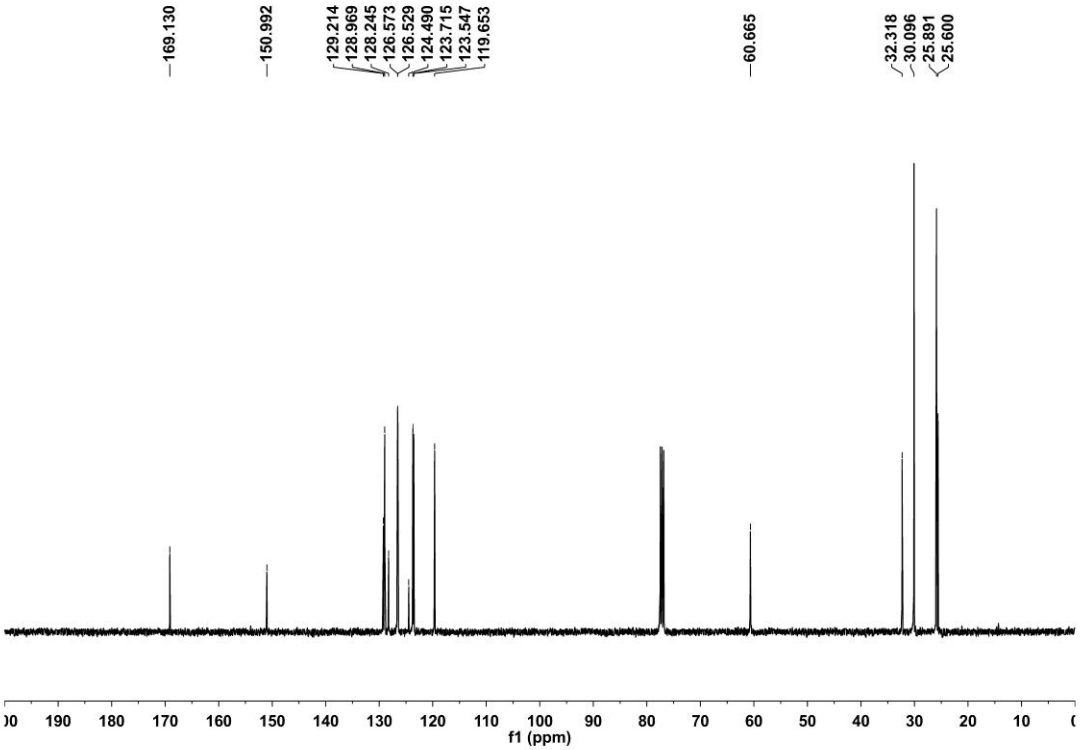
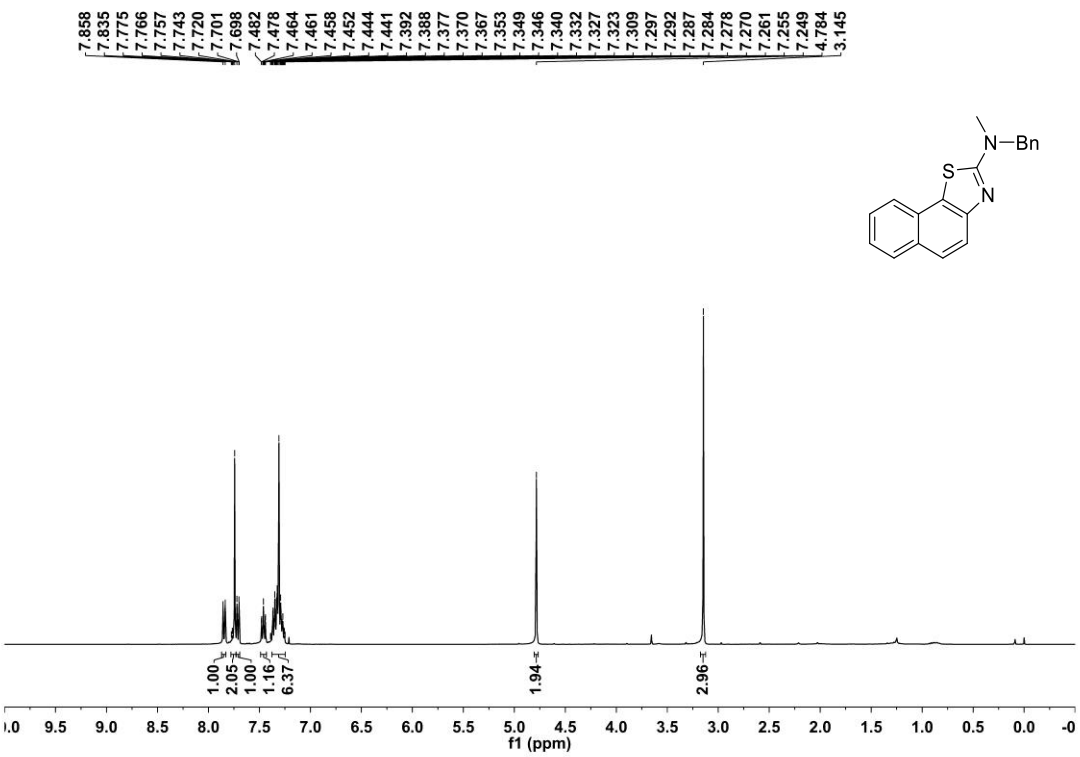


4aah

^{1}H NMR



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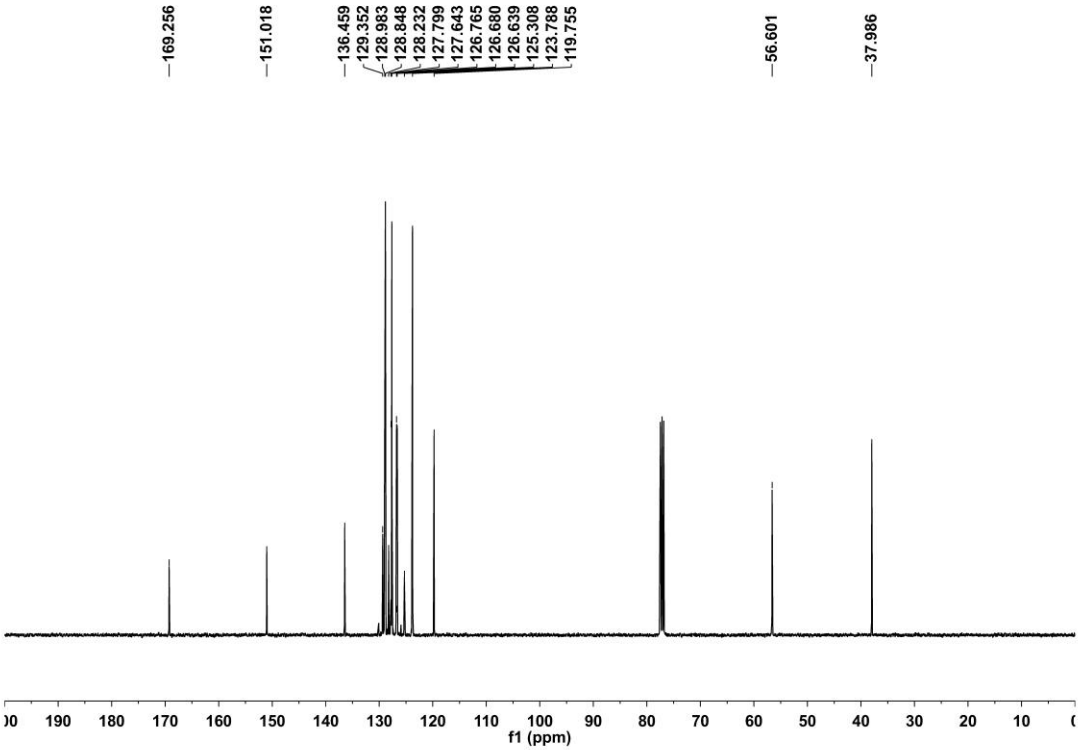

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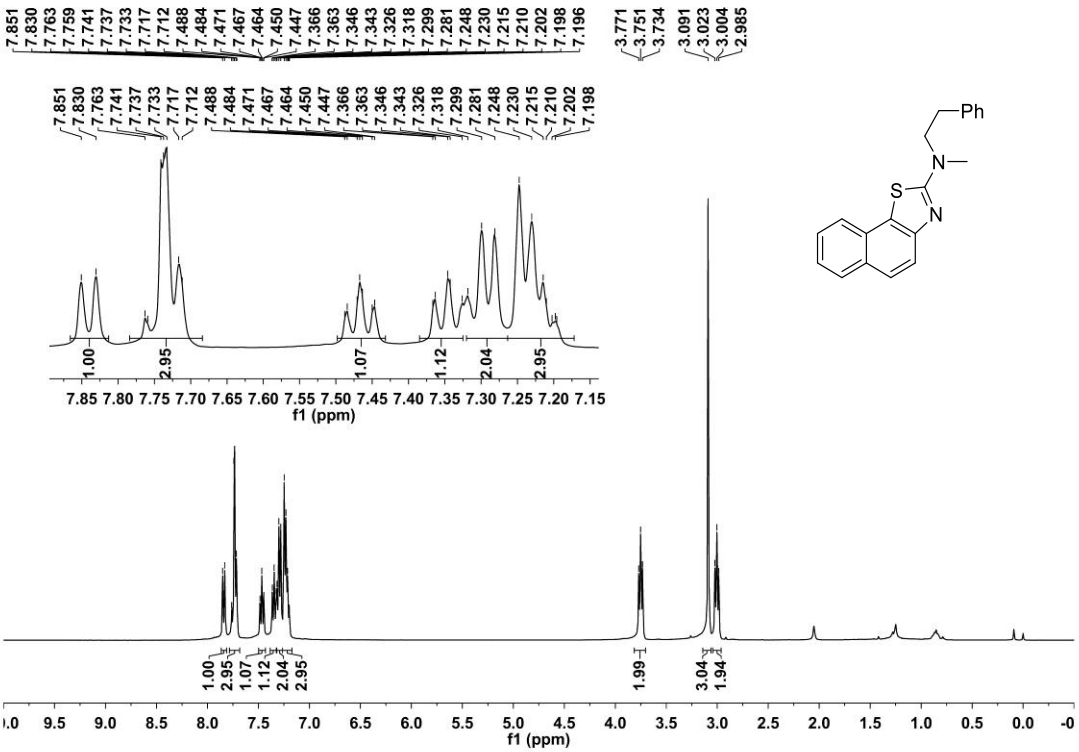

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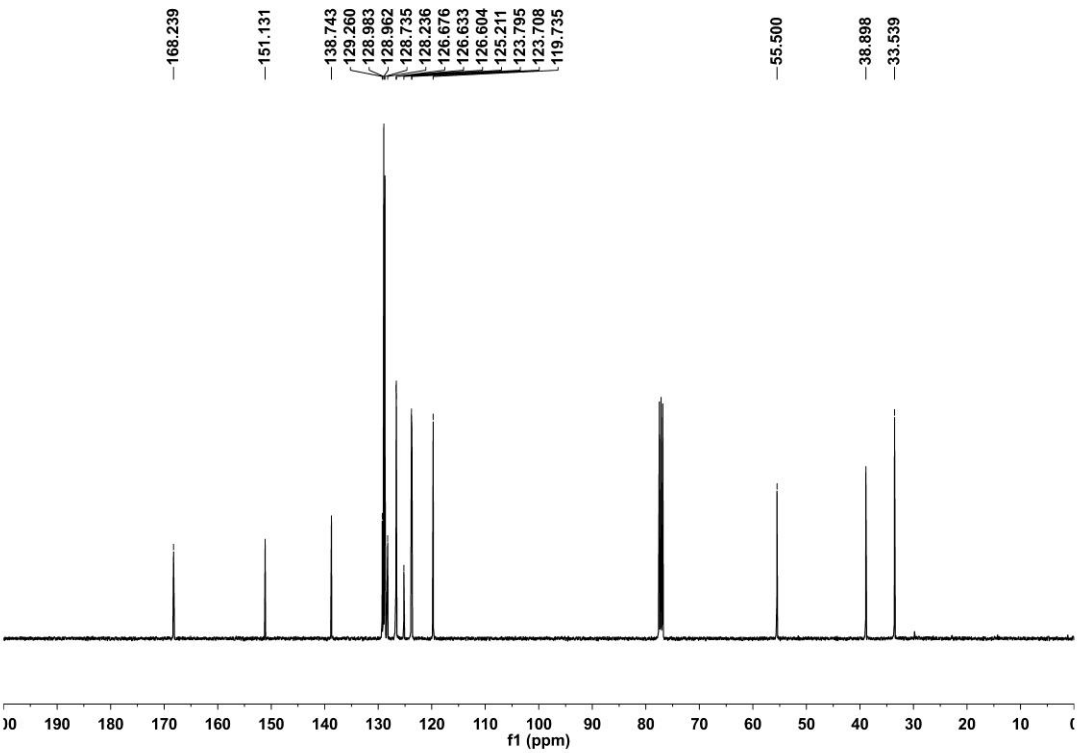

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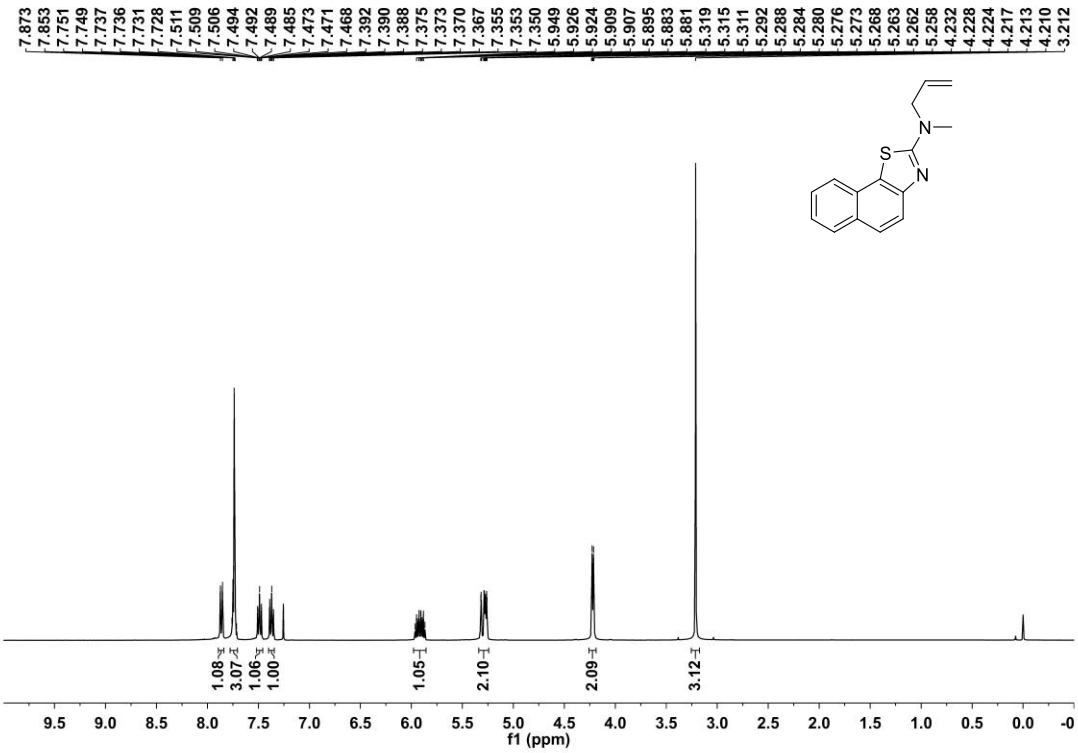

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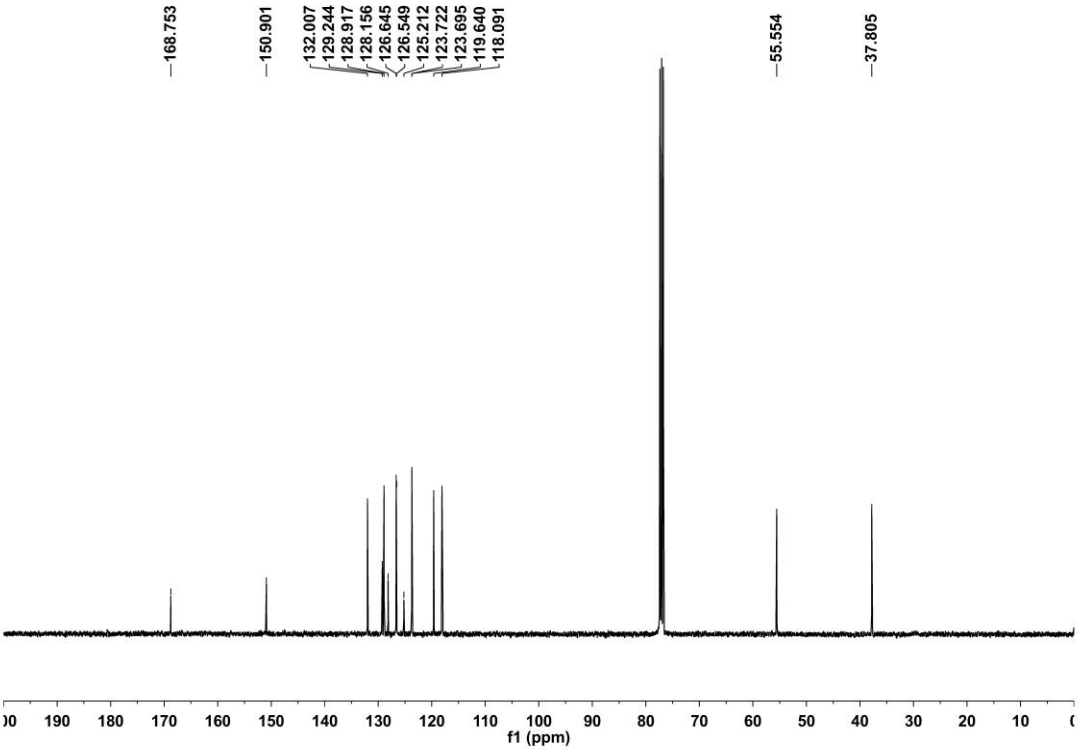

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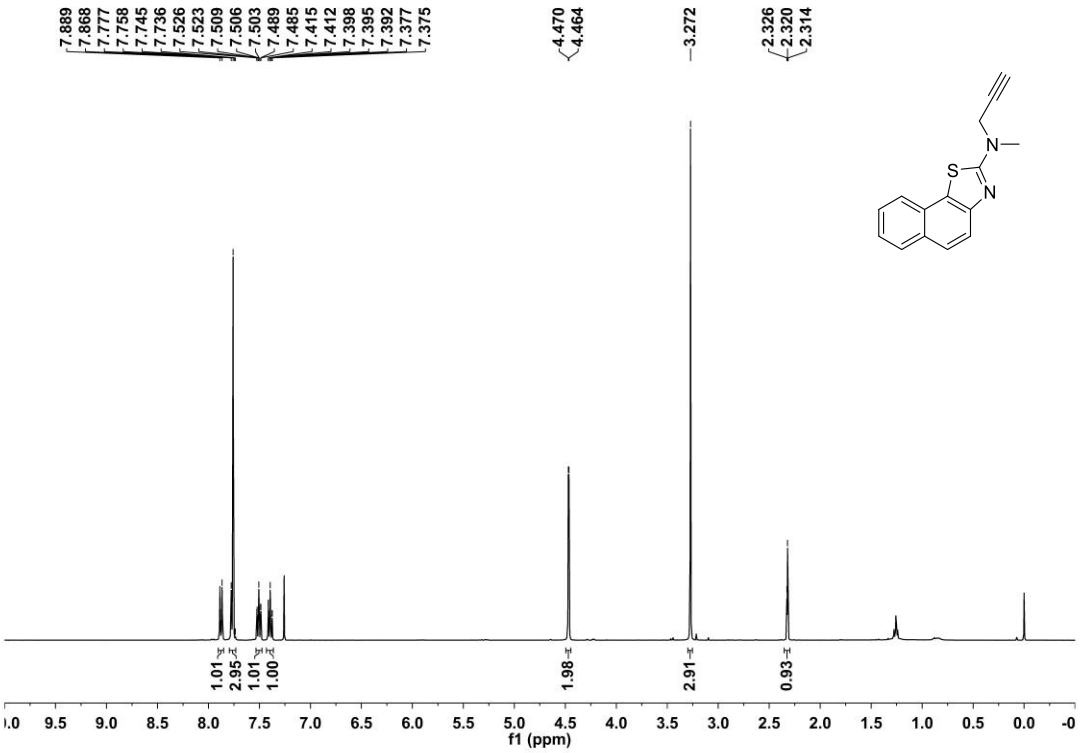

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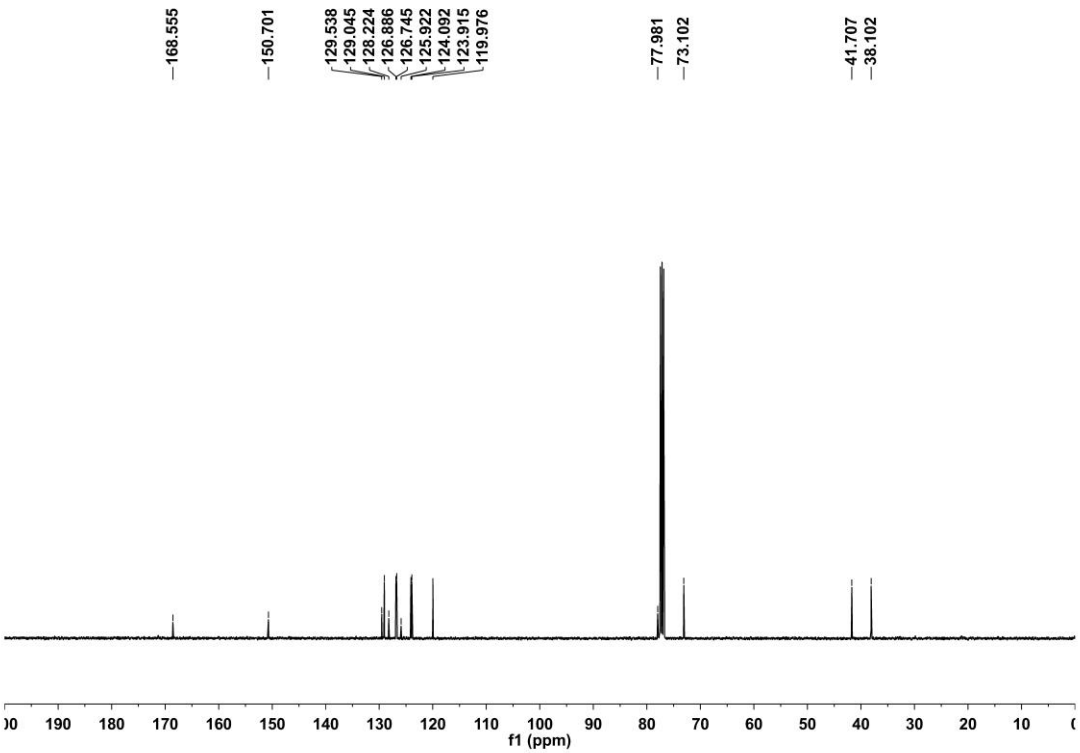

4aal

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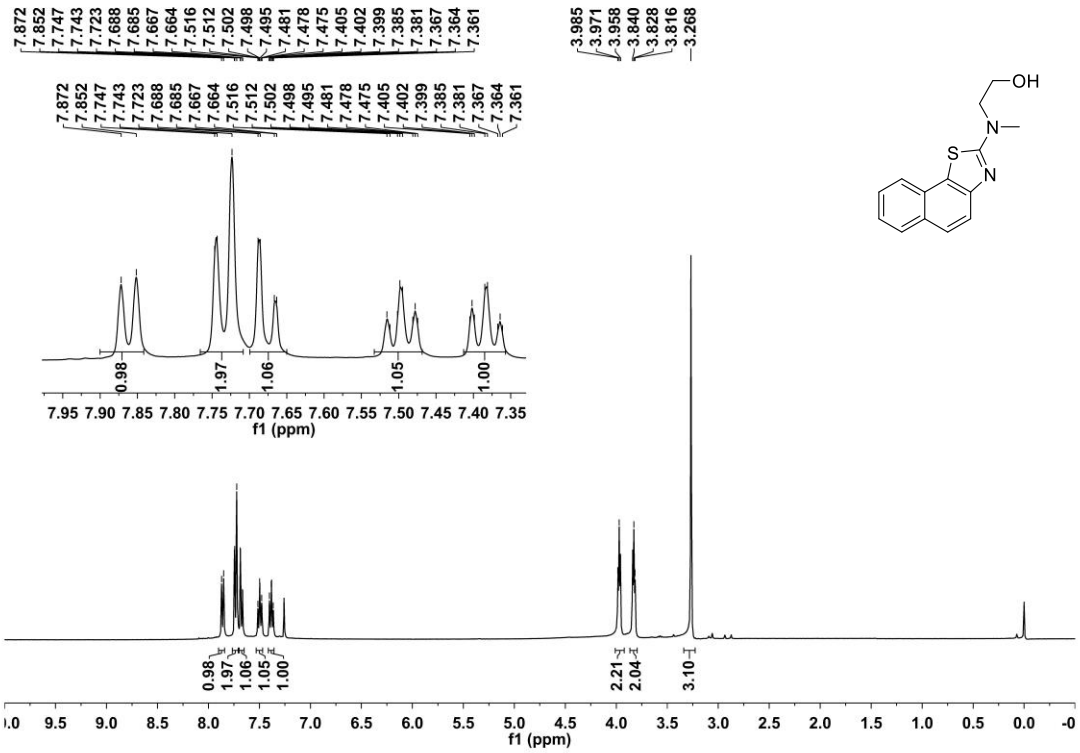
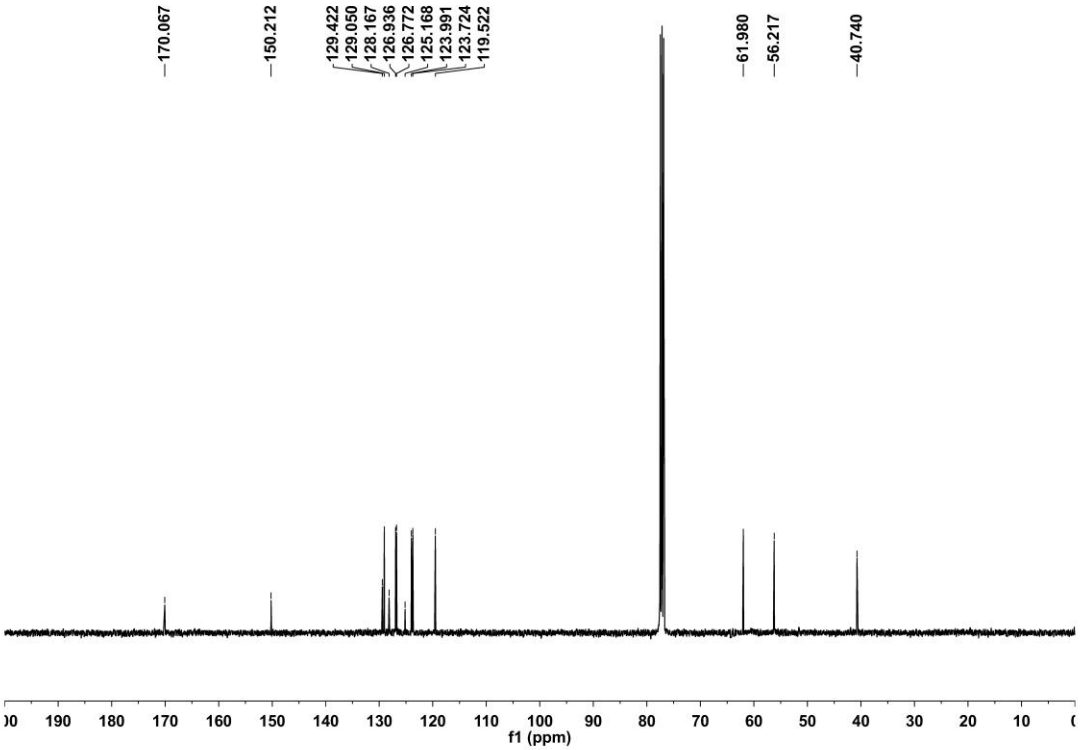


^{13}C NMR



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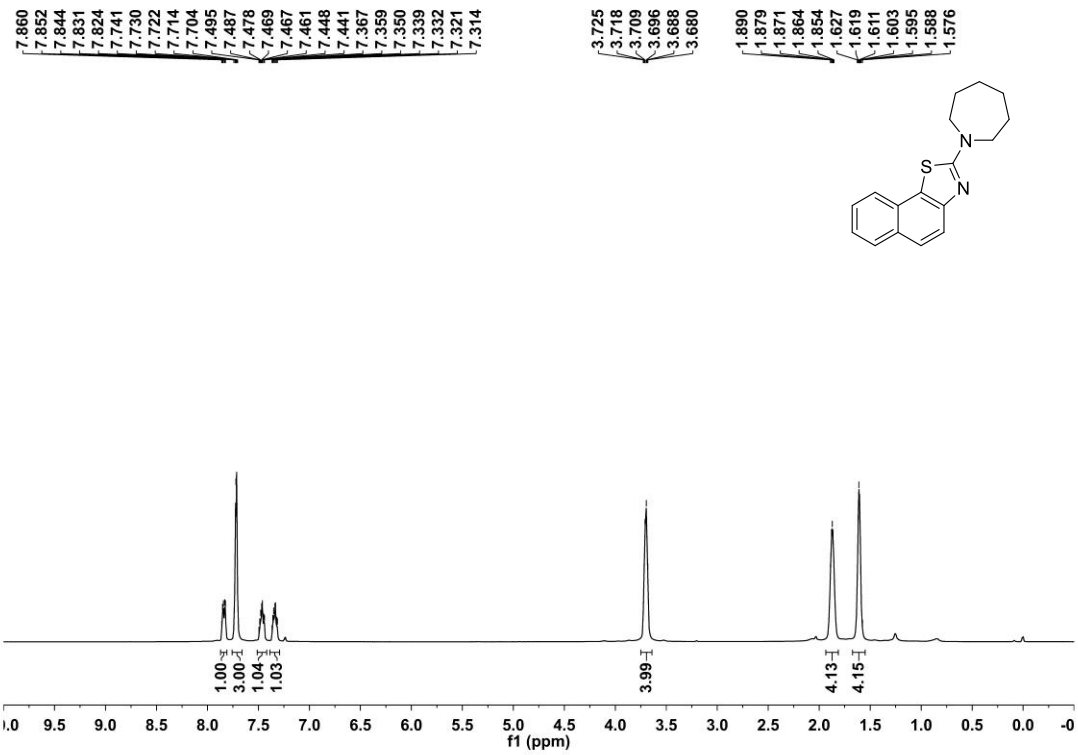

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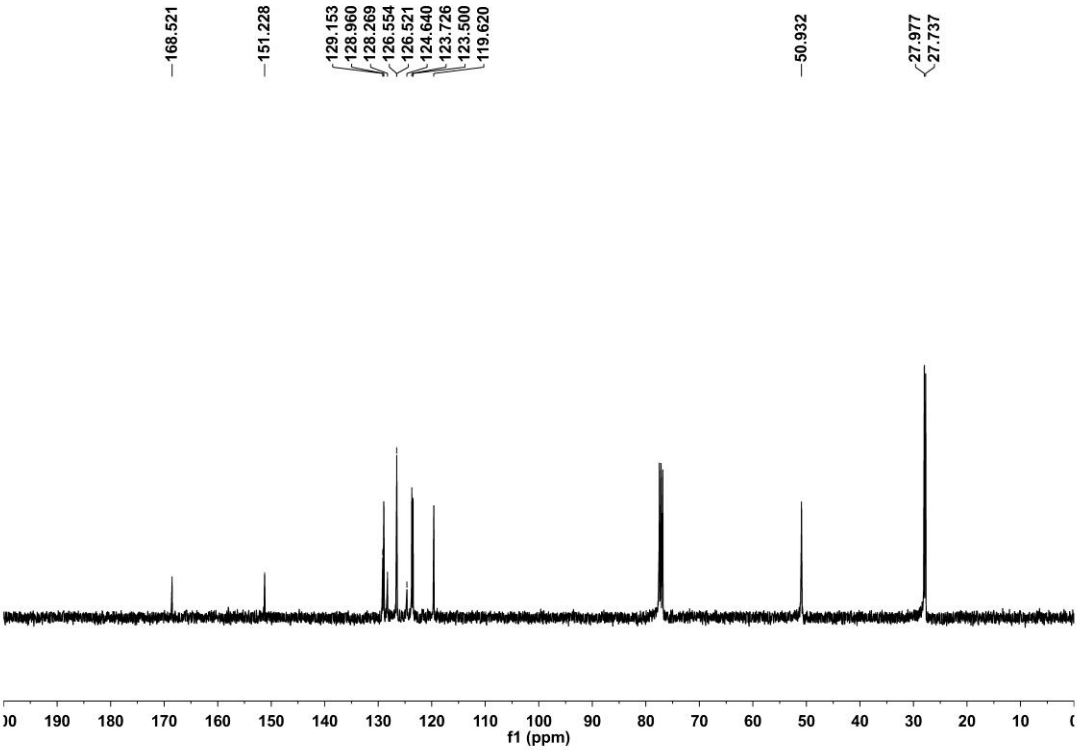

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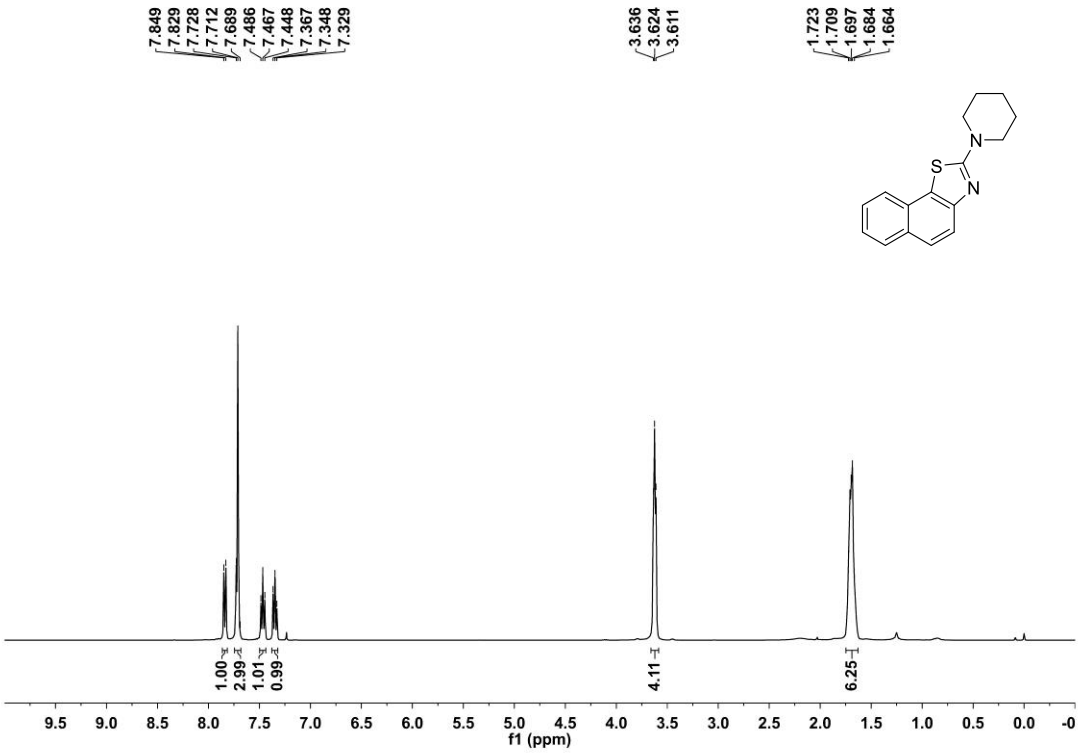

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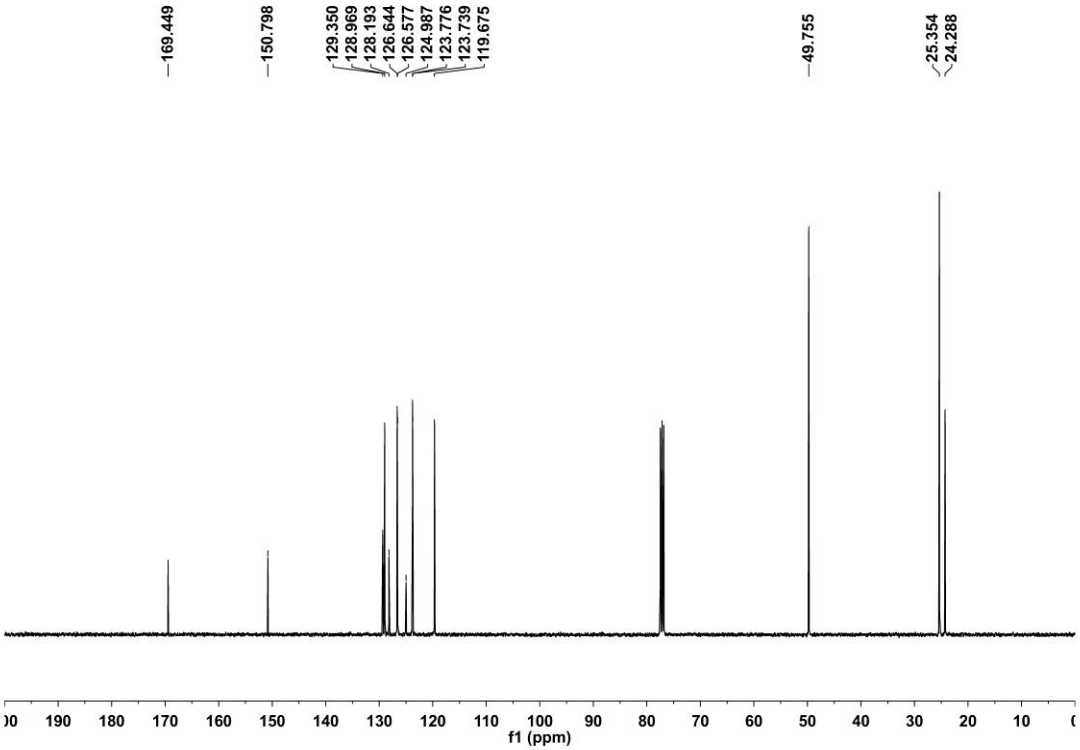

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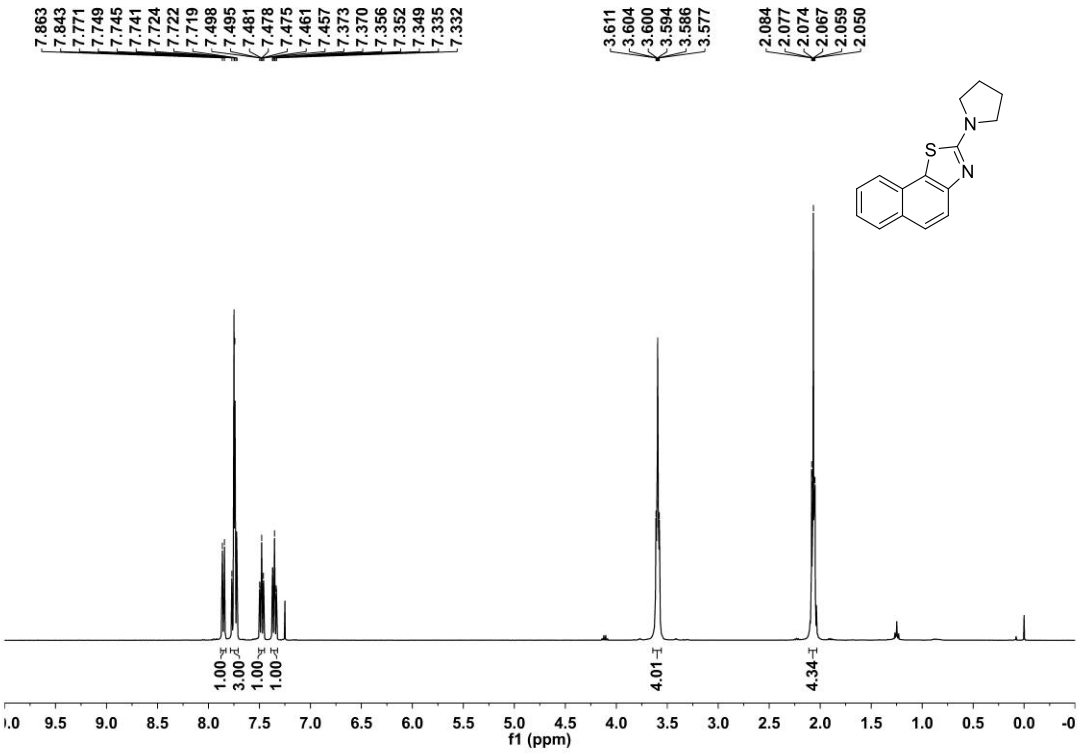

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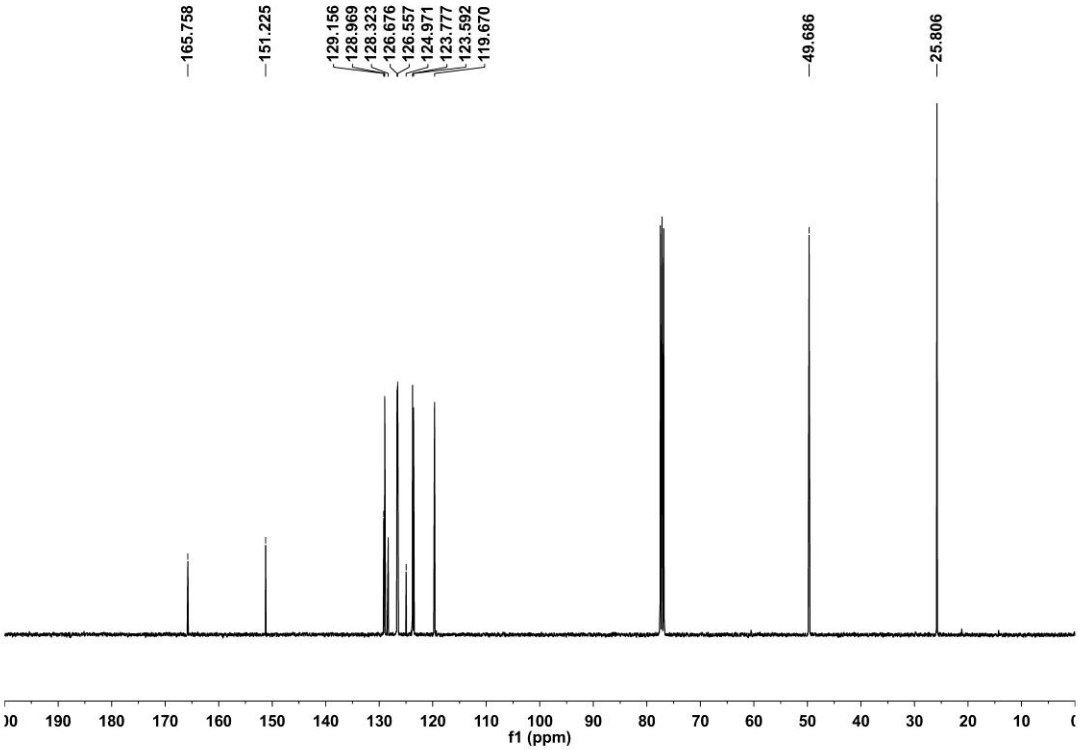

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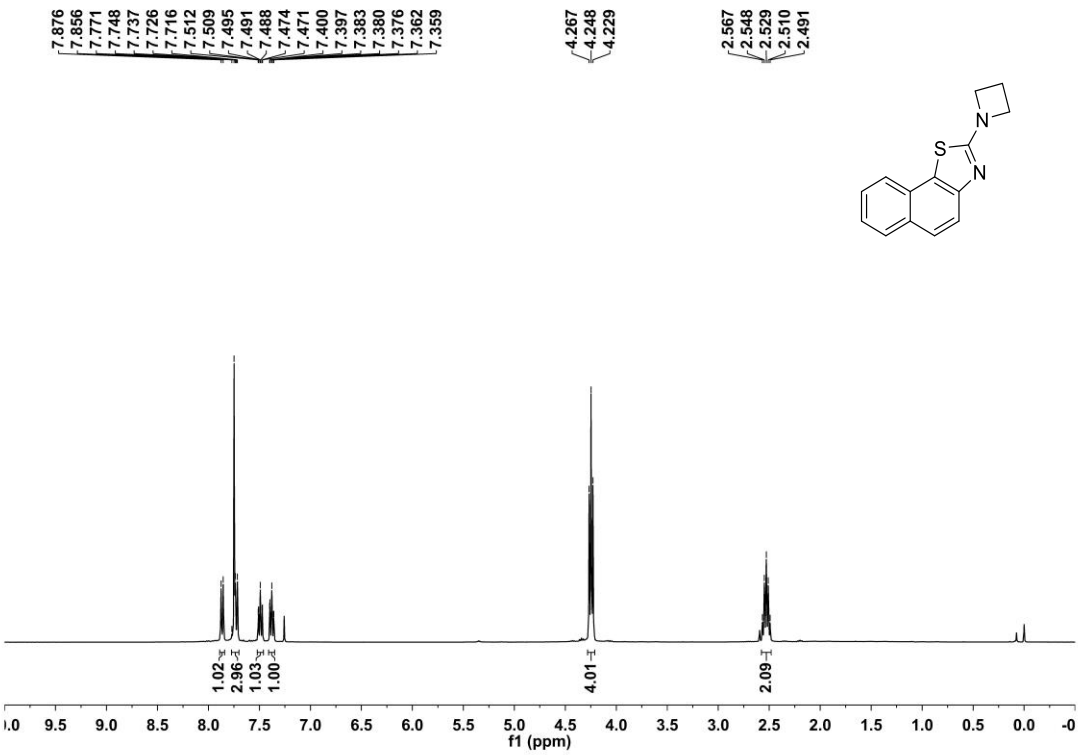

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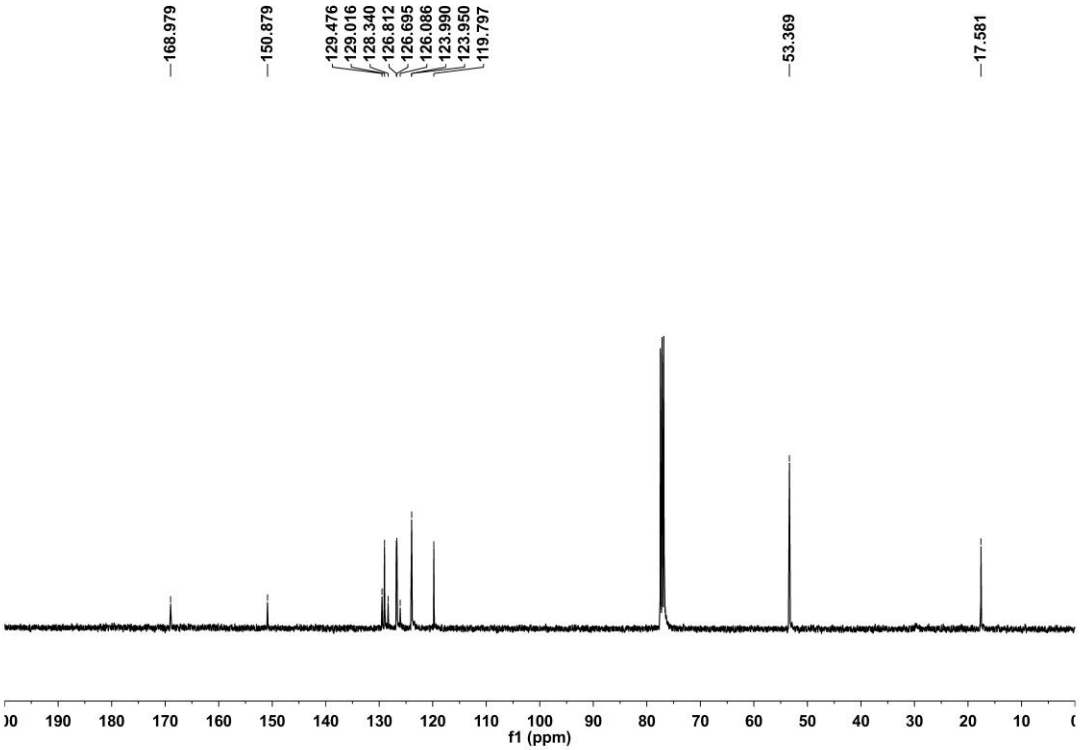
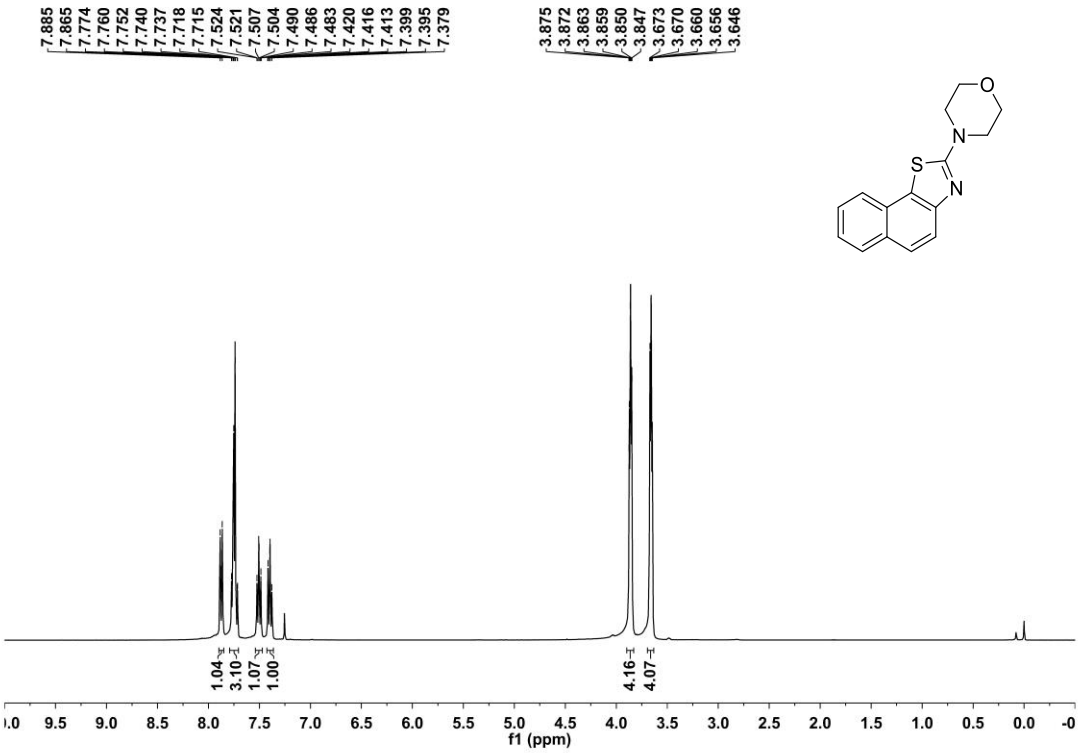


4aaq

^{1}H NMR



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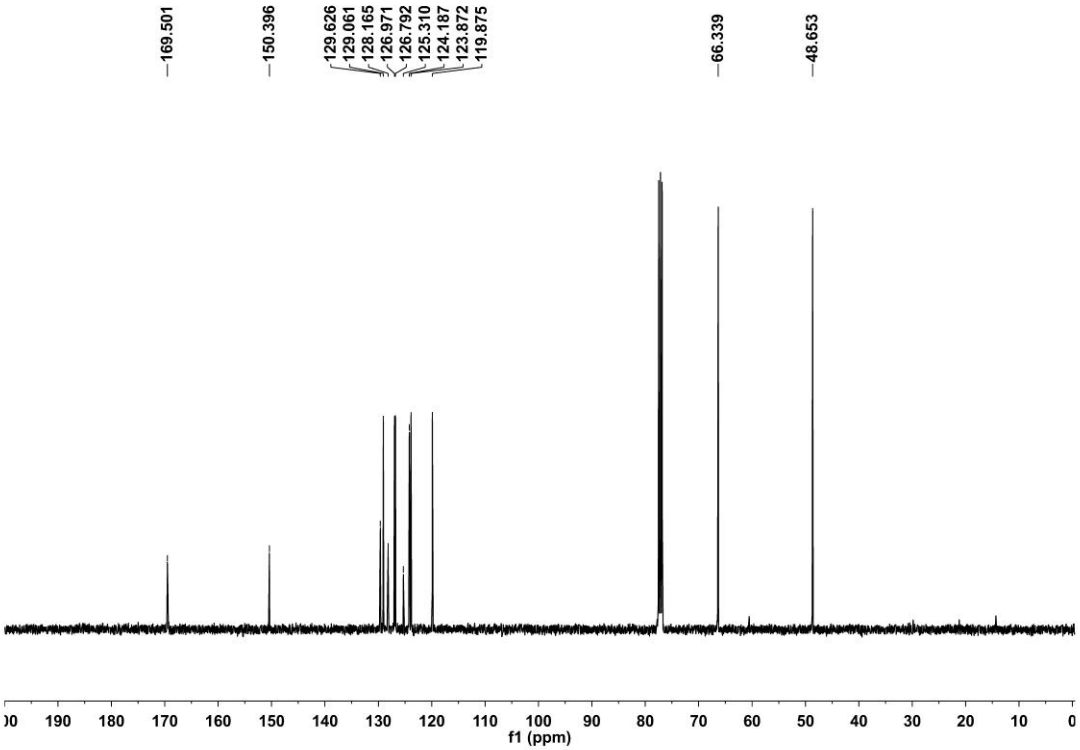

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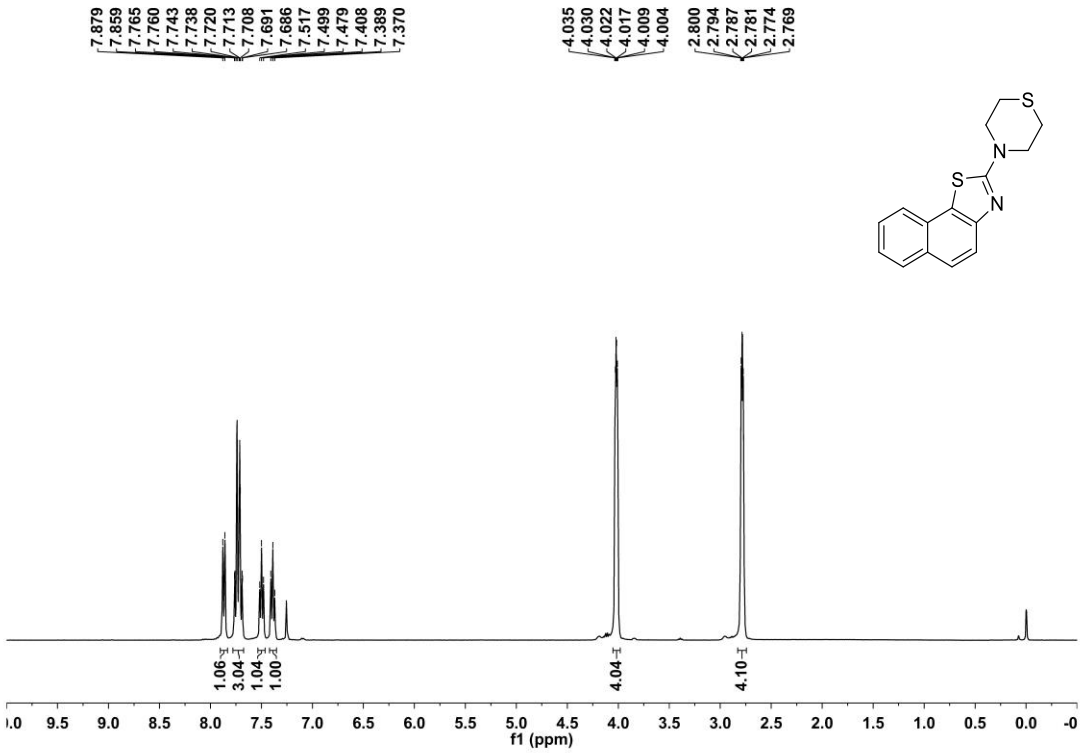

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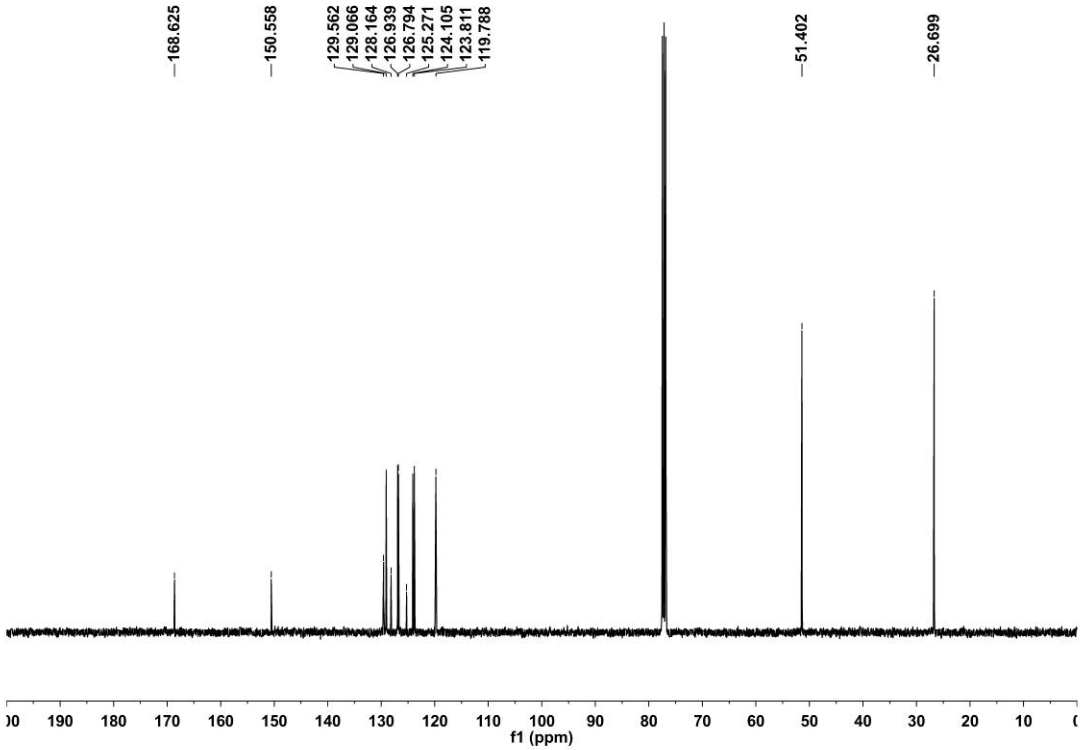

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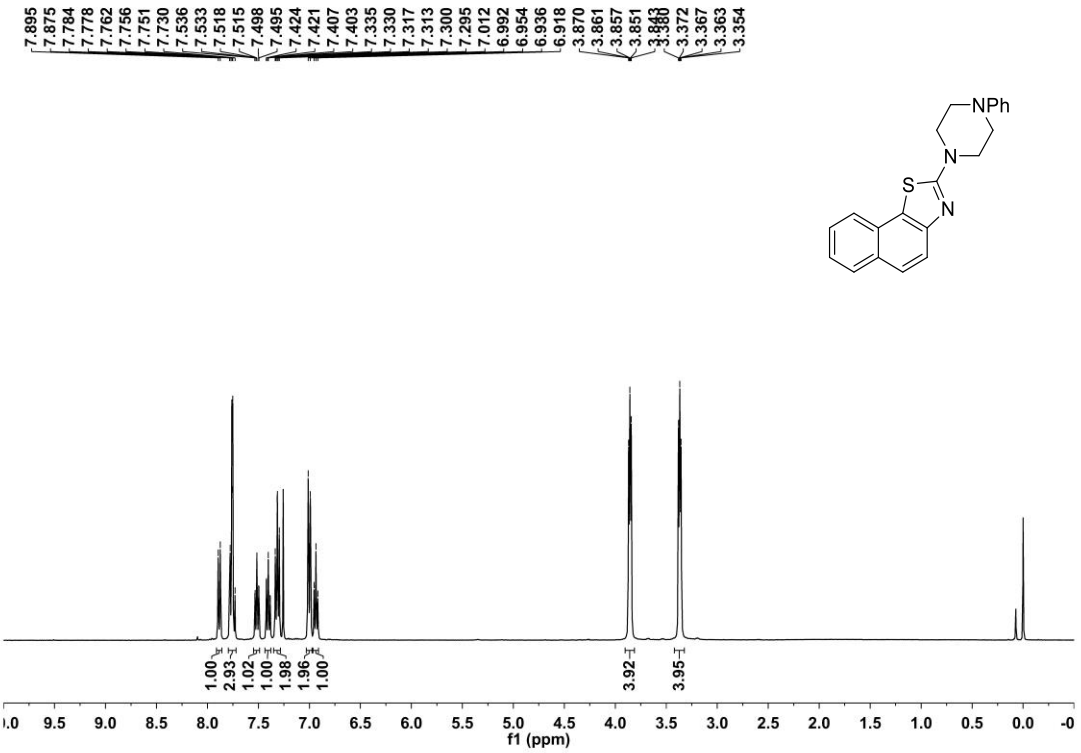

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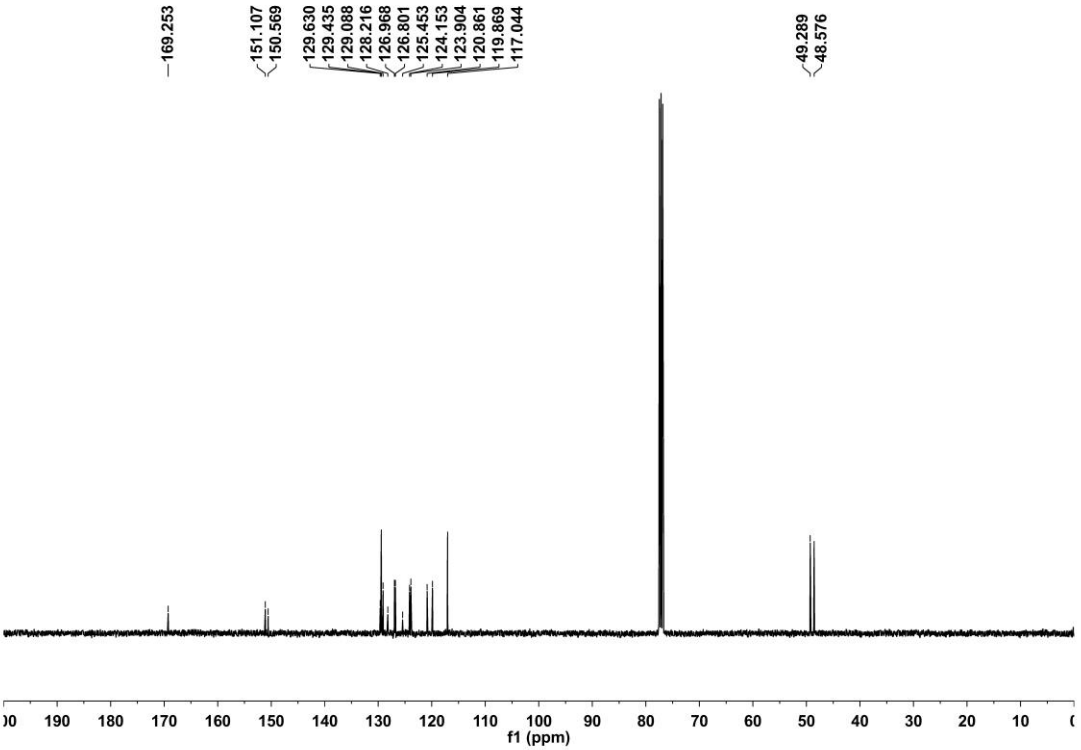

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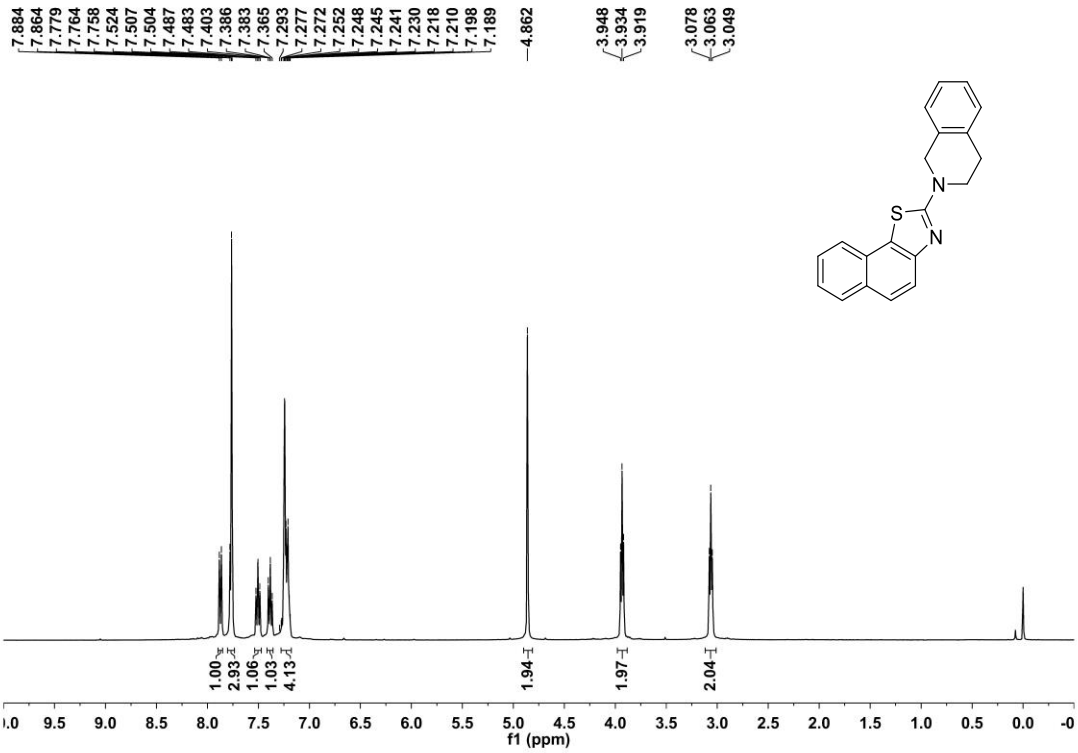

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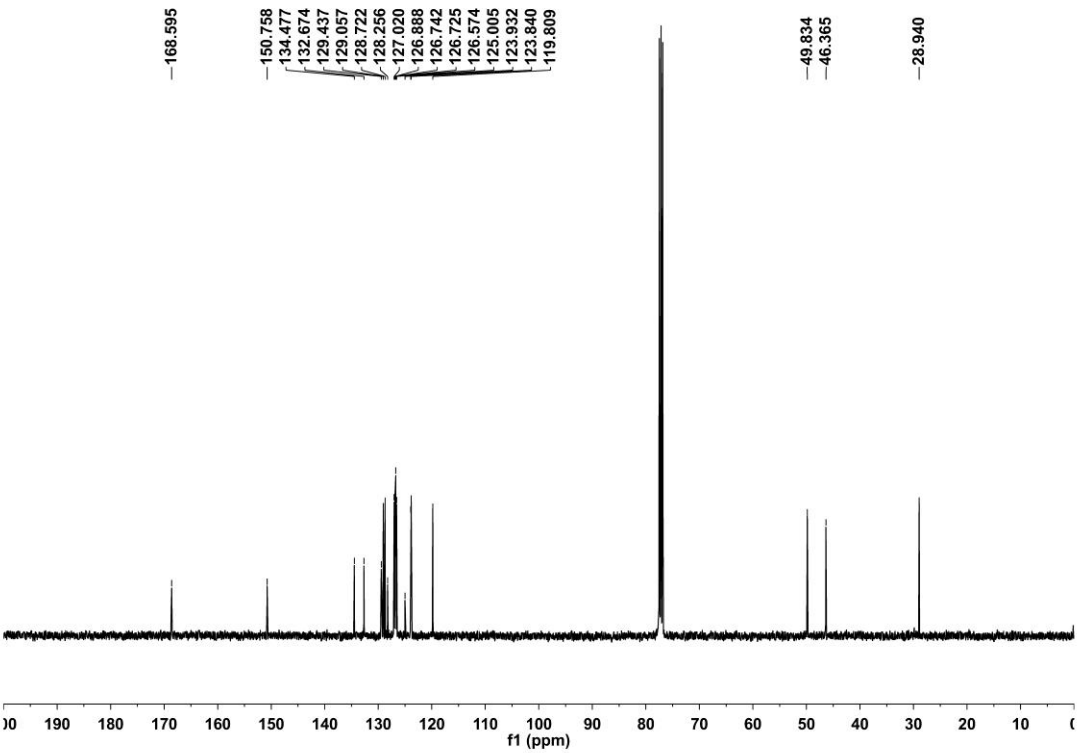

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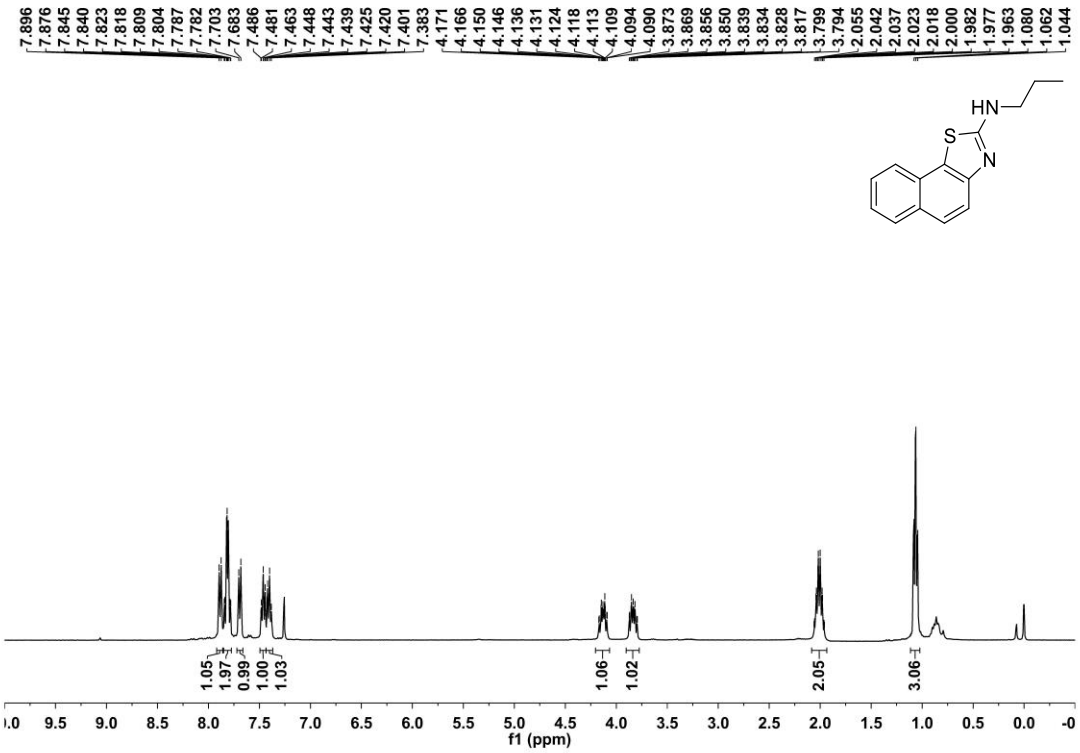

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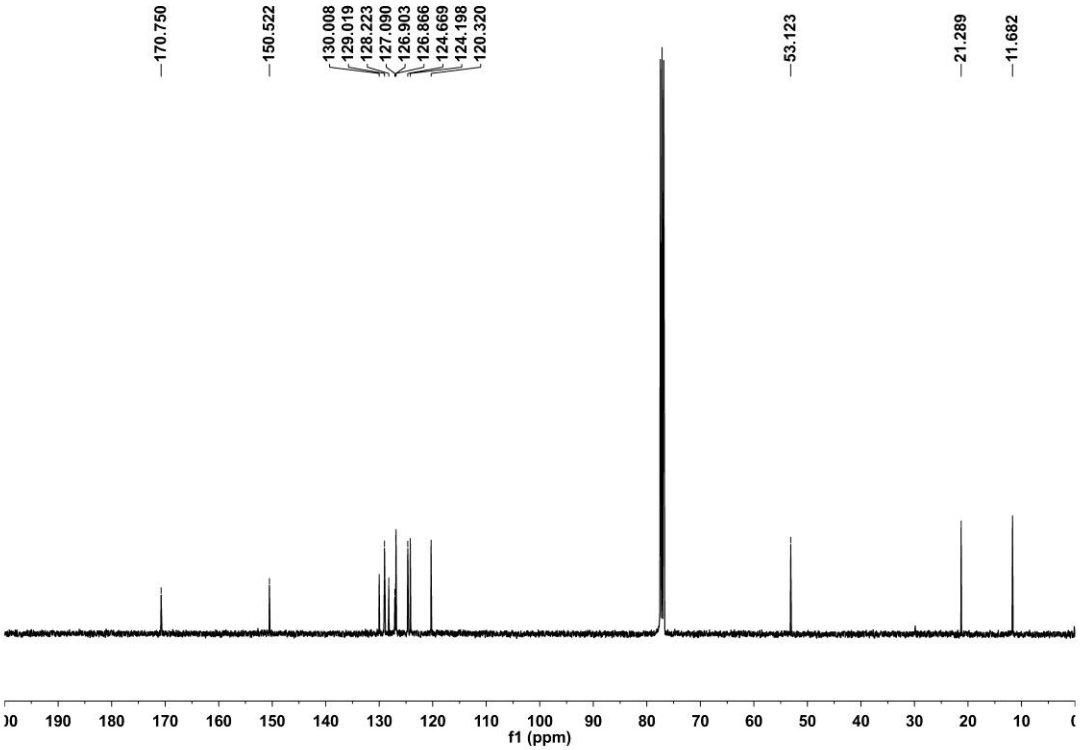

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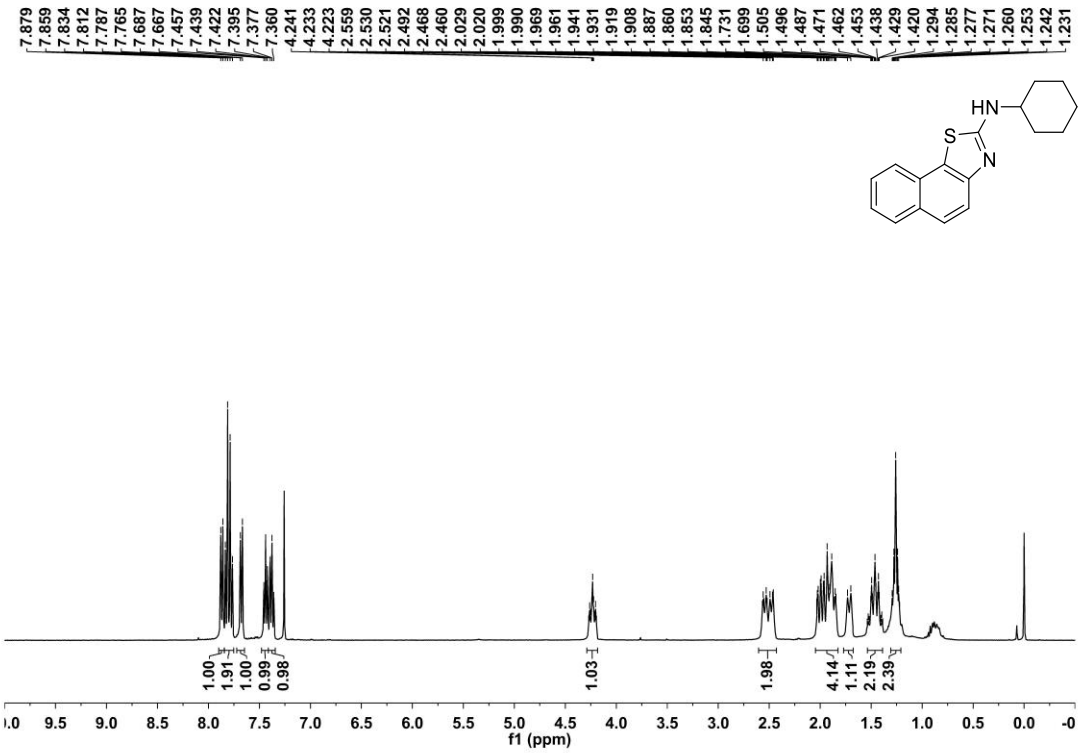

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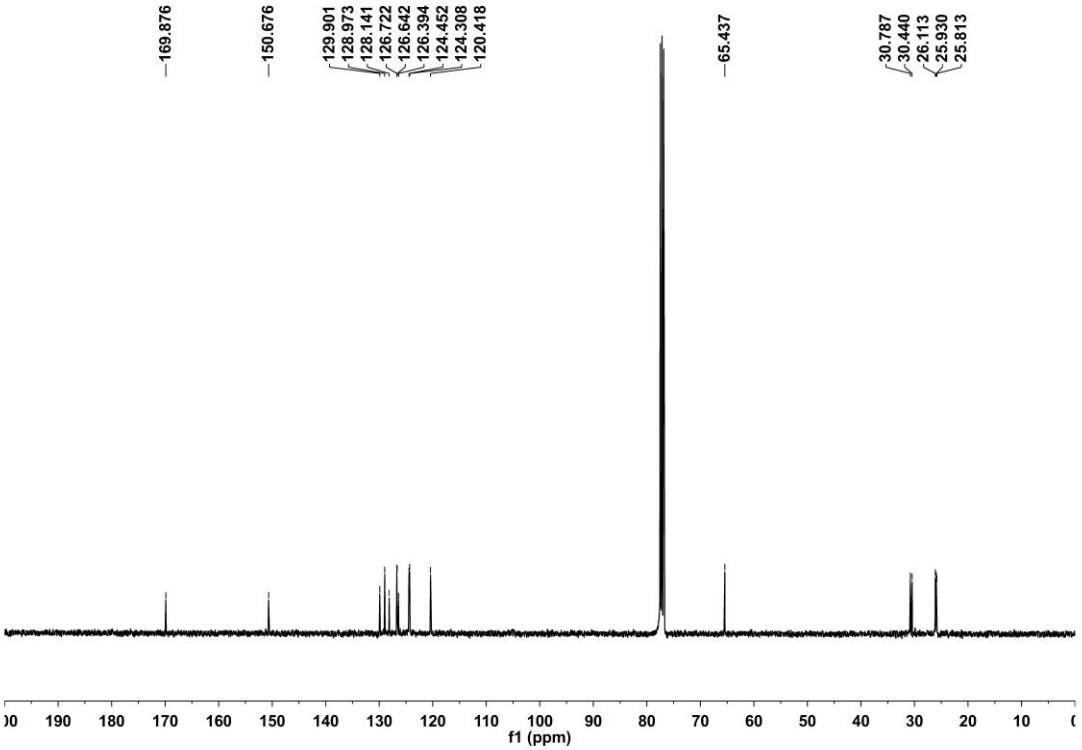

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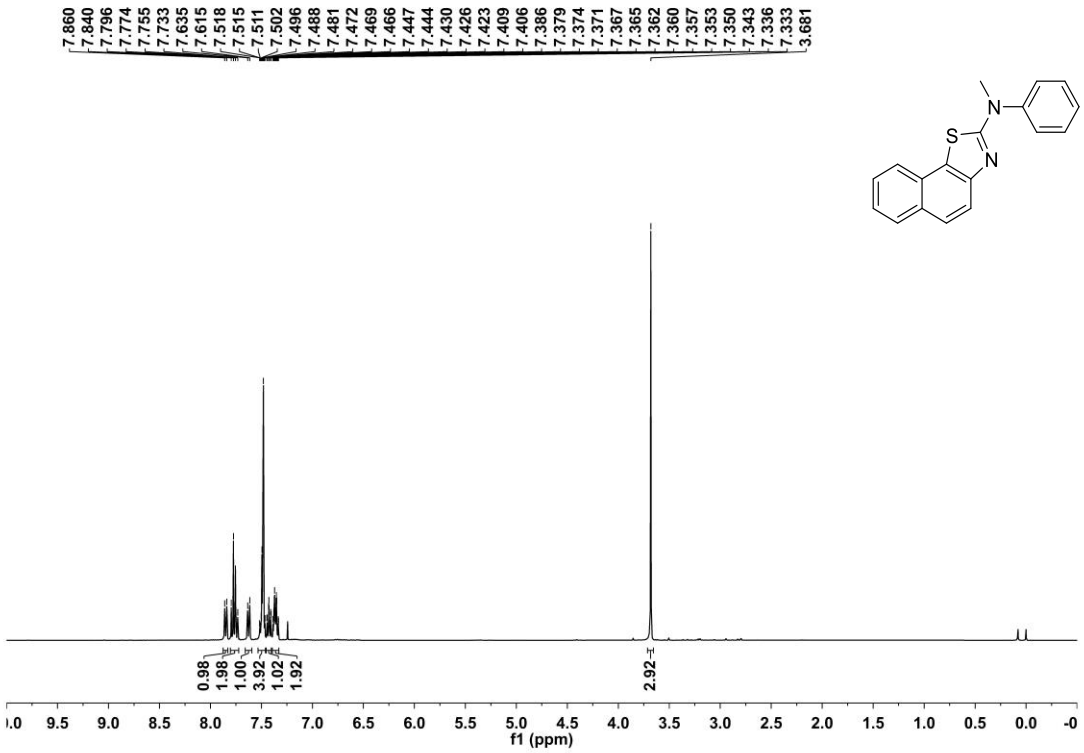

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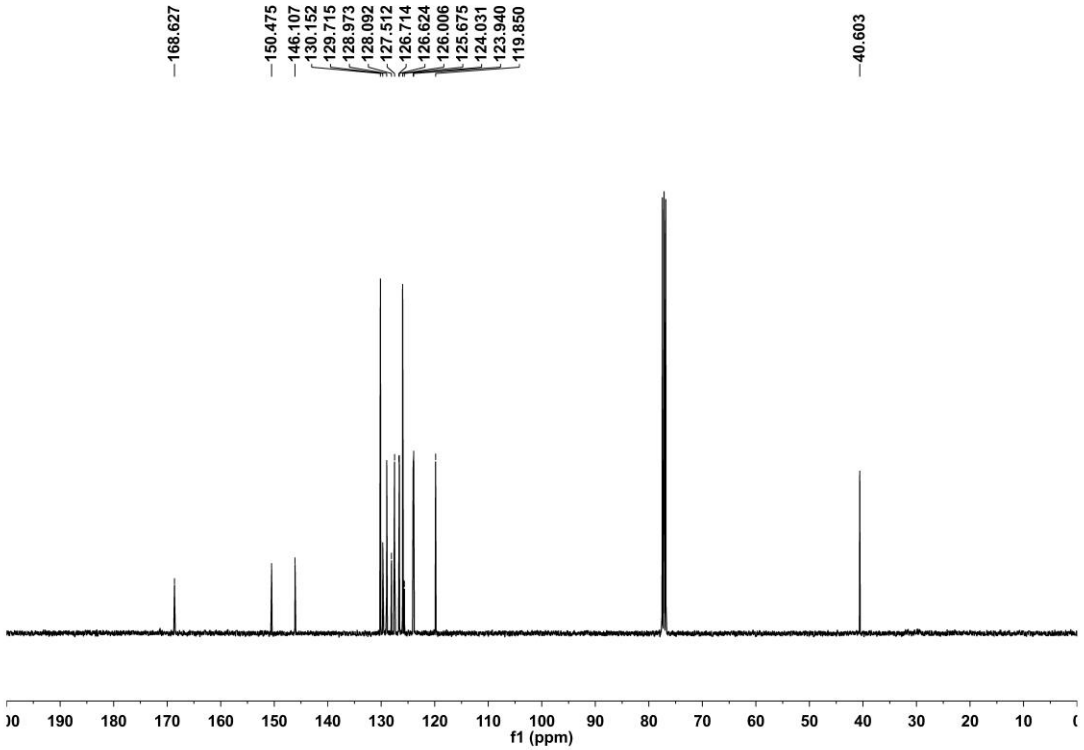

4aax

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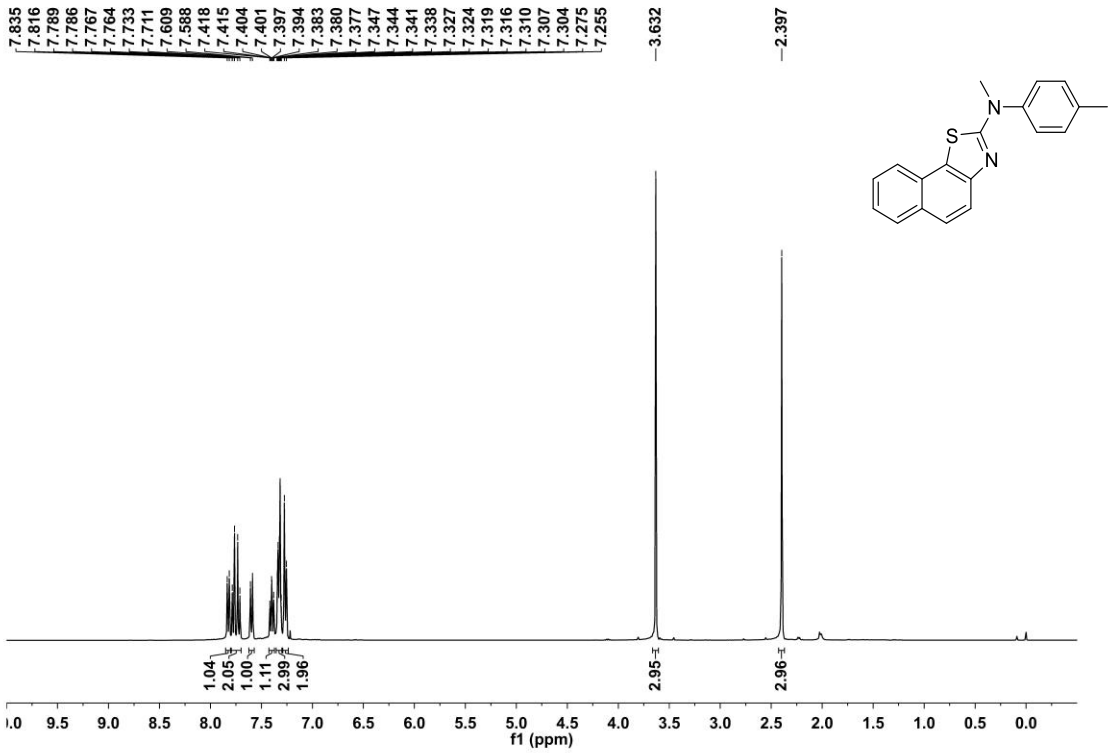

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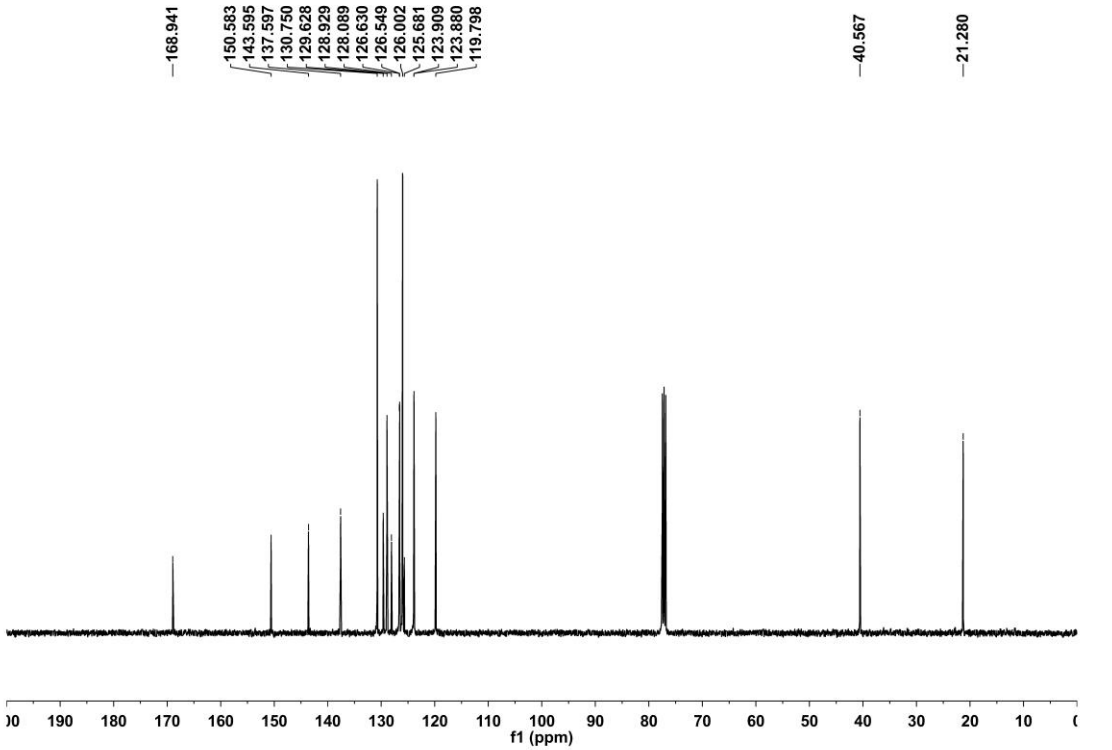
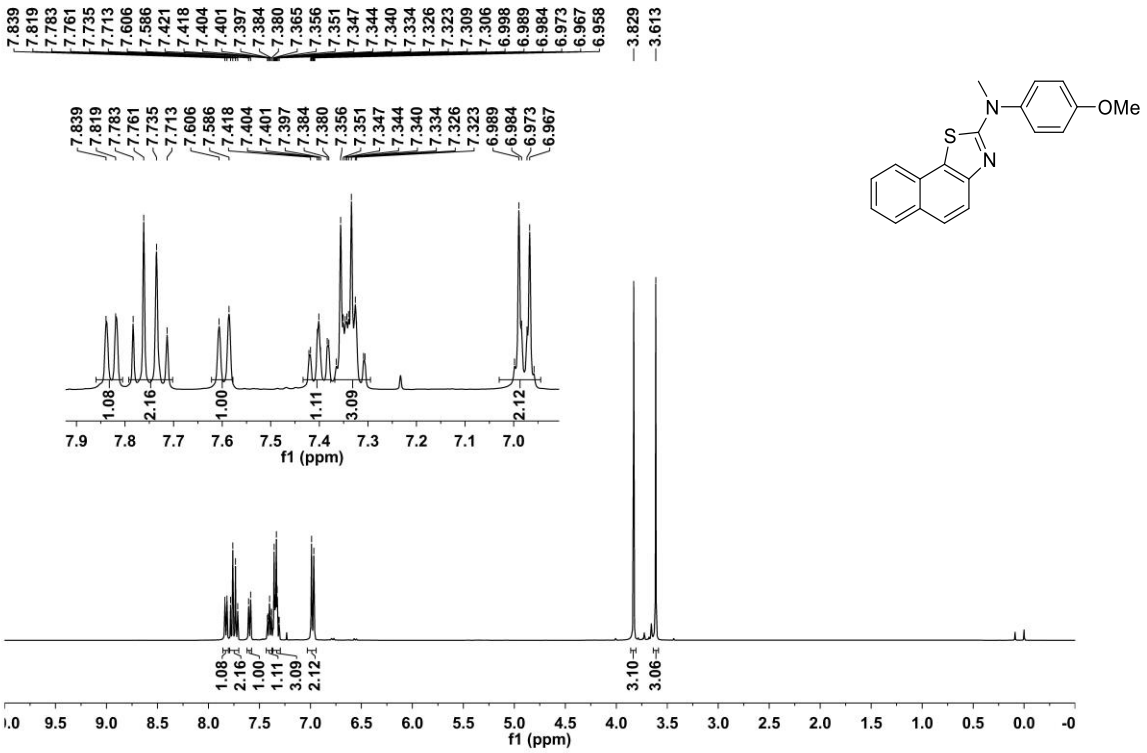


4aay

^{1}H NMR



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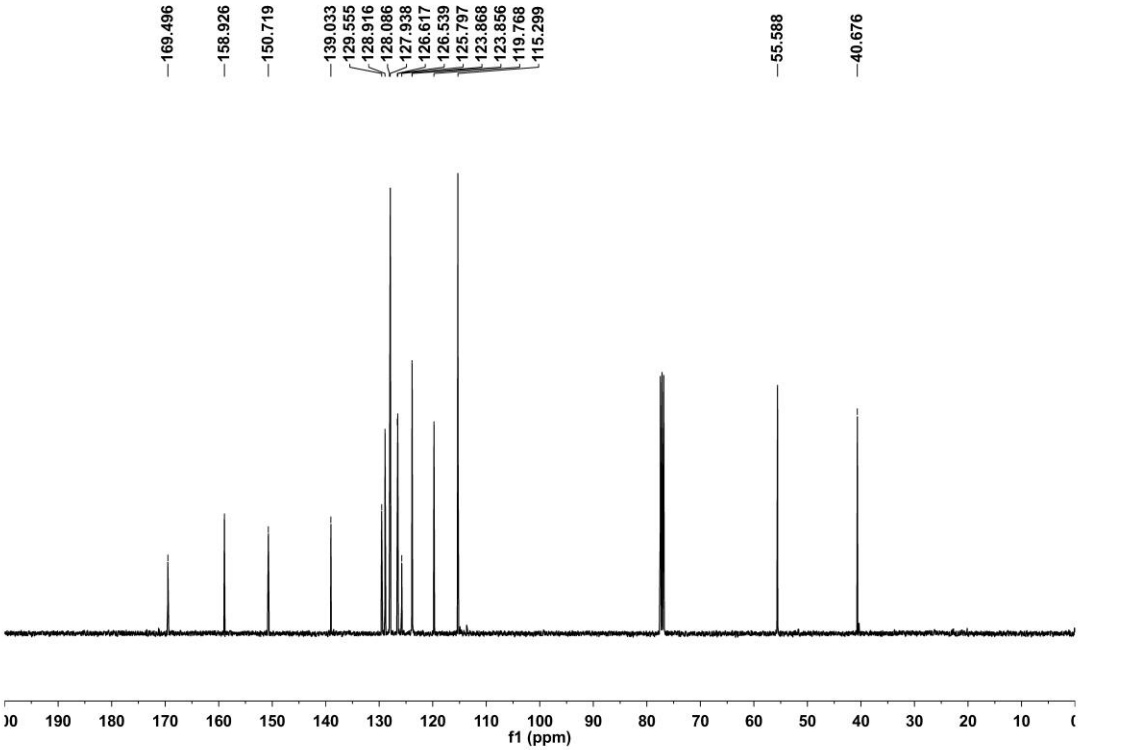

4aaz

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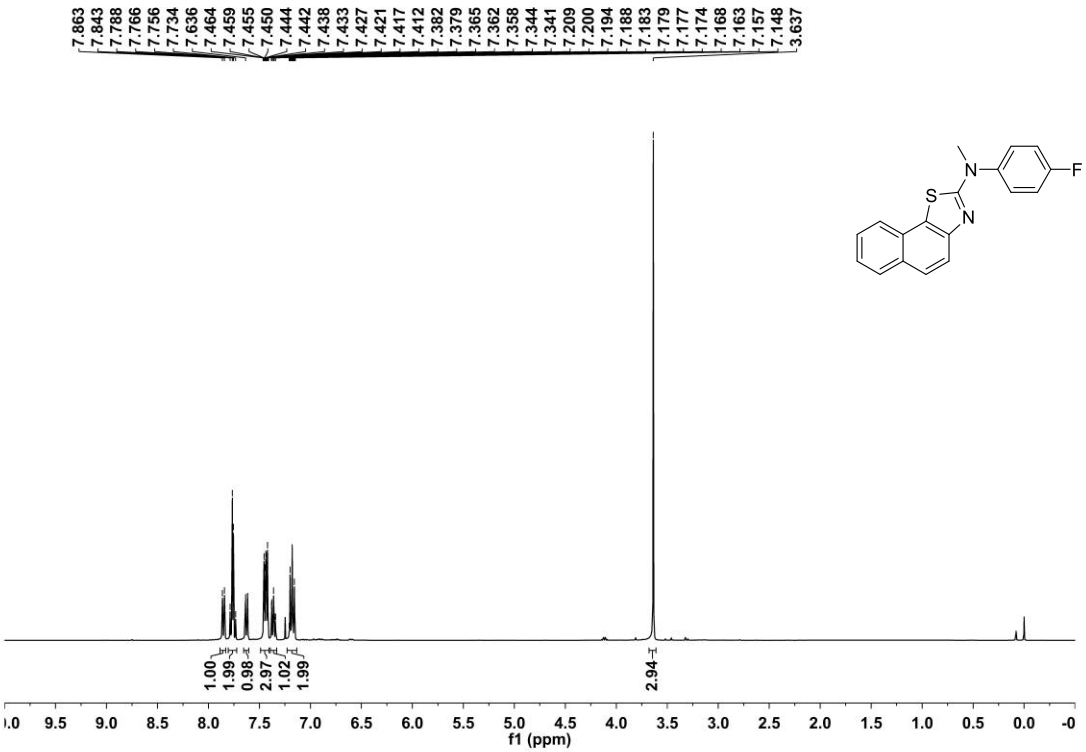

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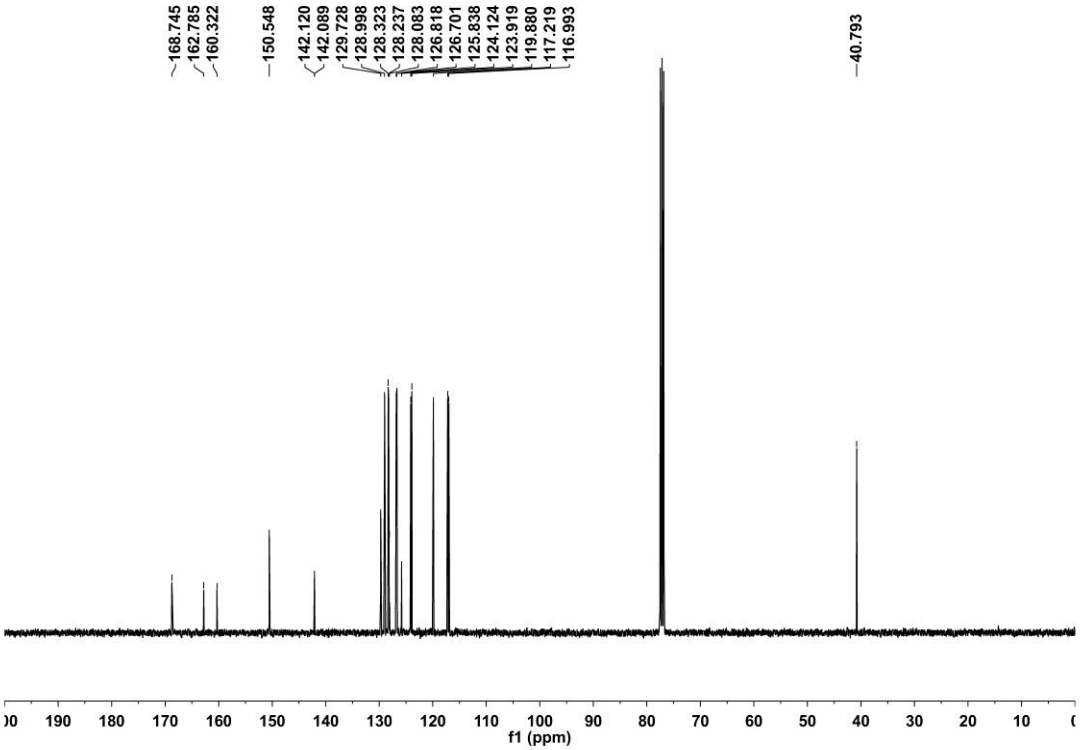

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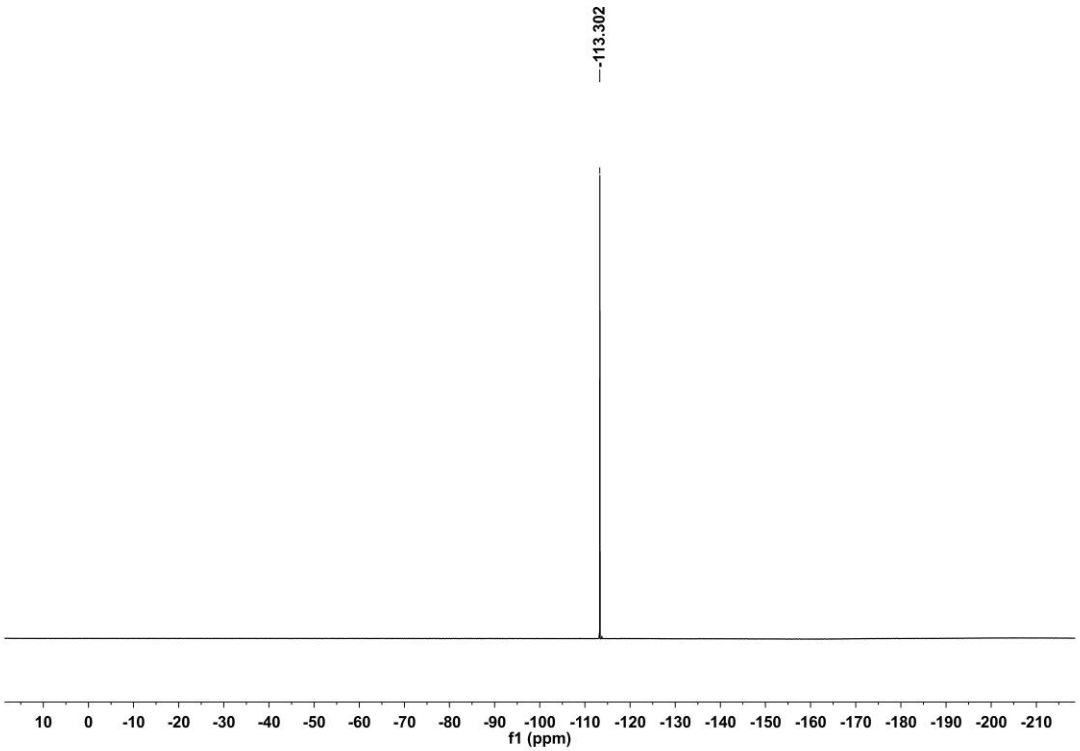
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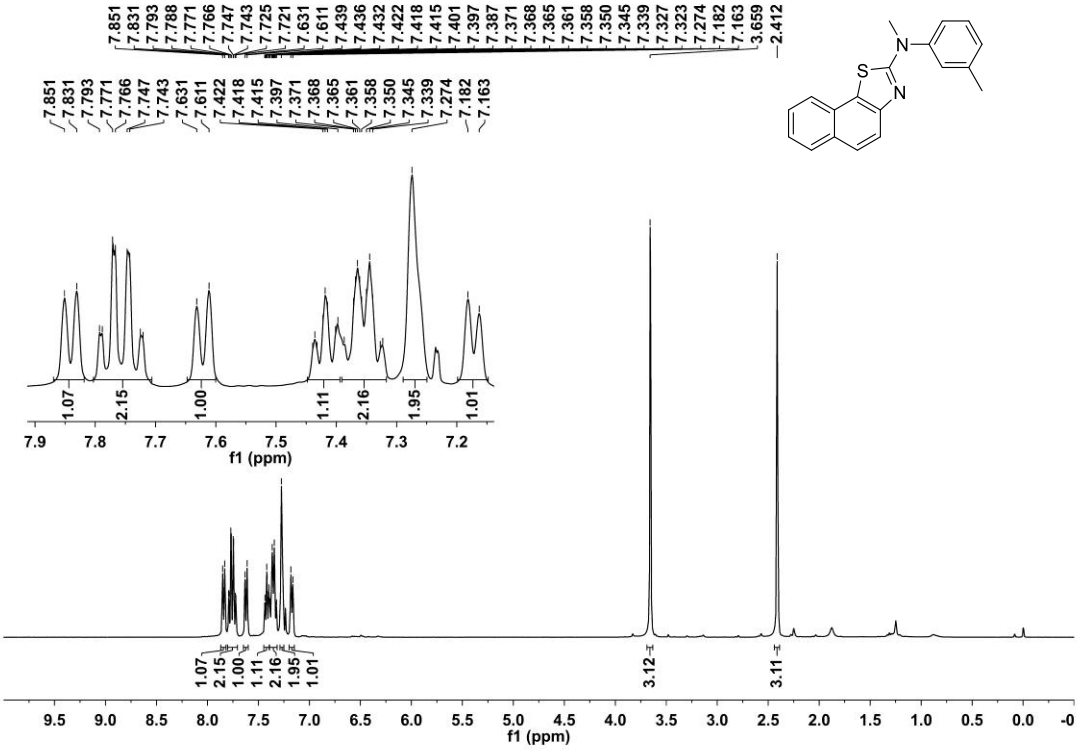
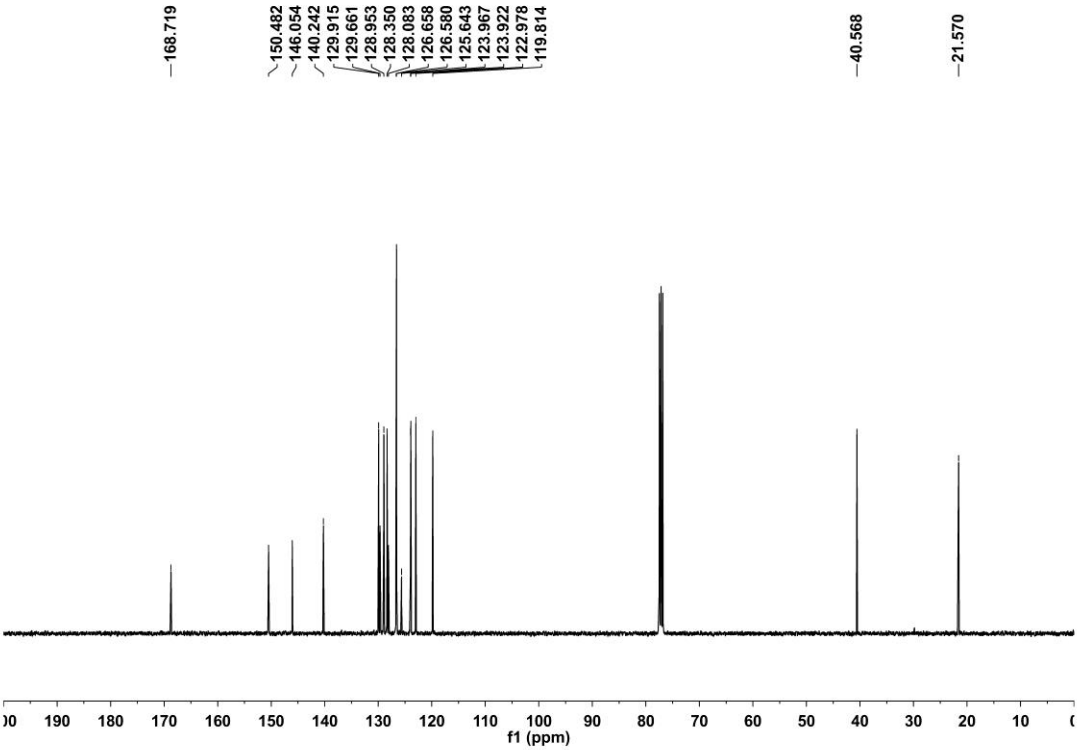
4aaaa

^{1}H NMR



^{13}C NMR



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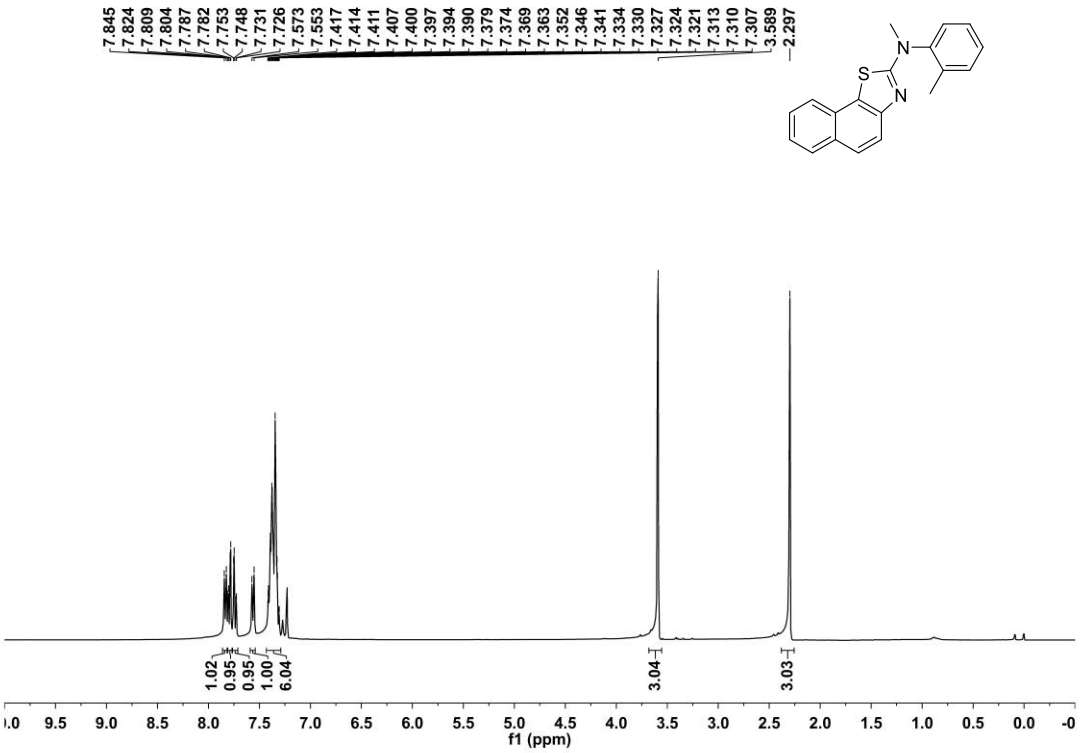

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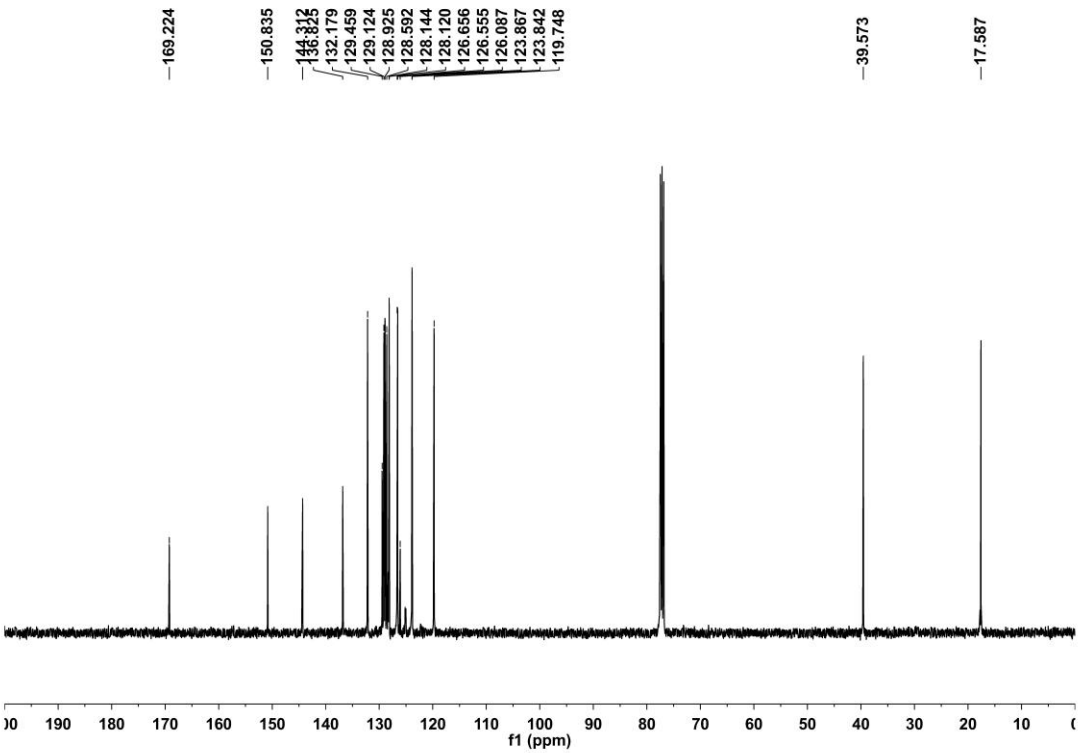

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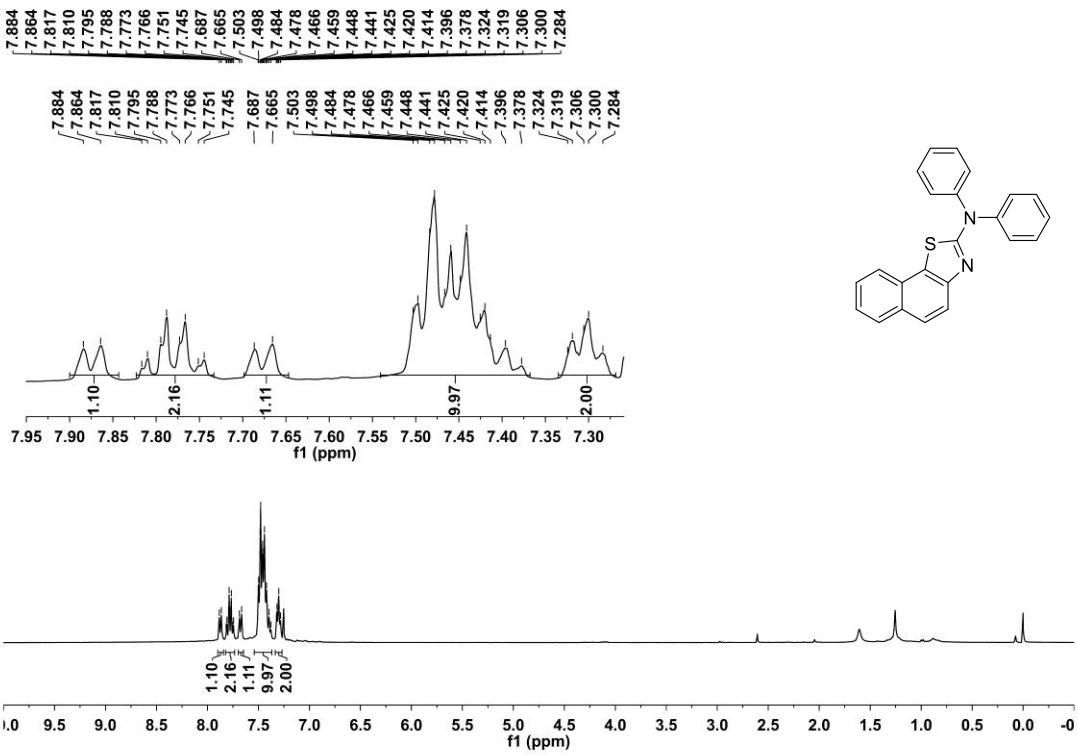

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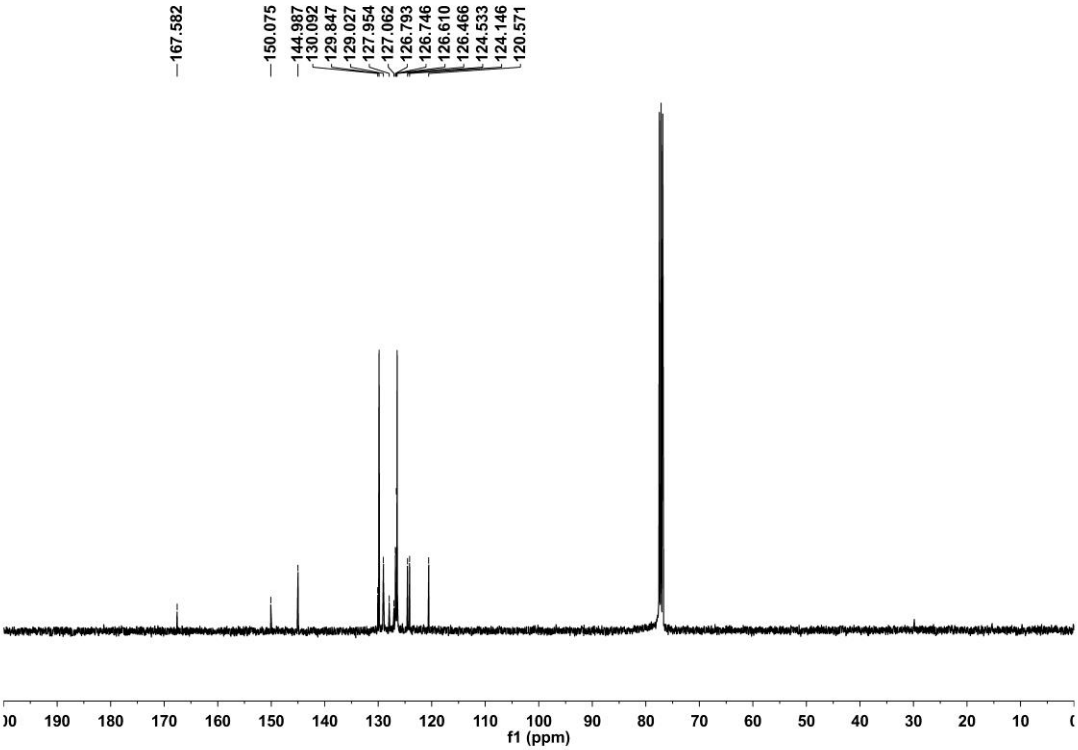

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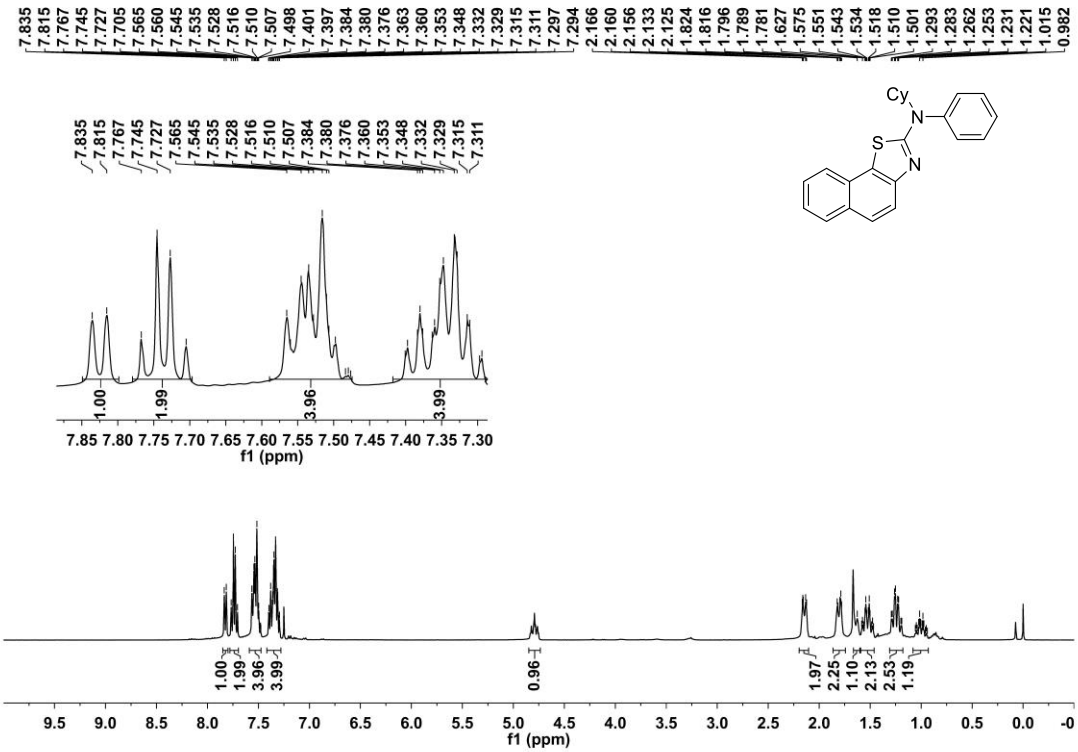

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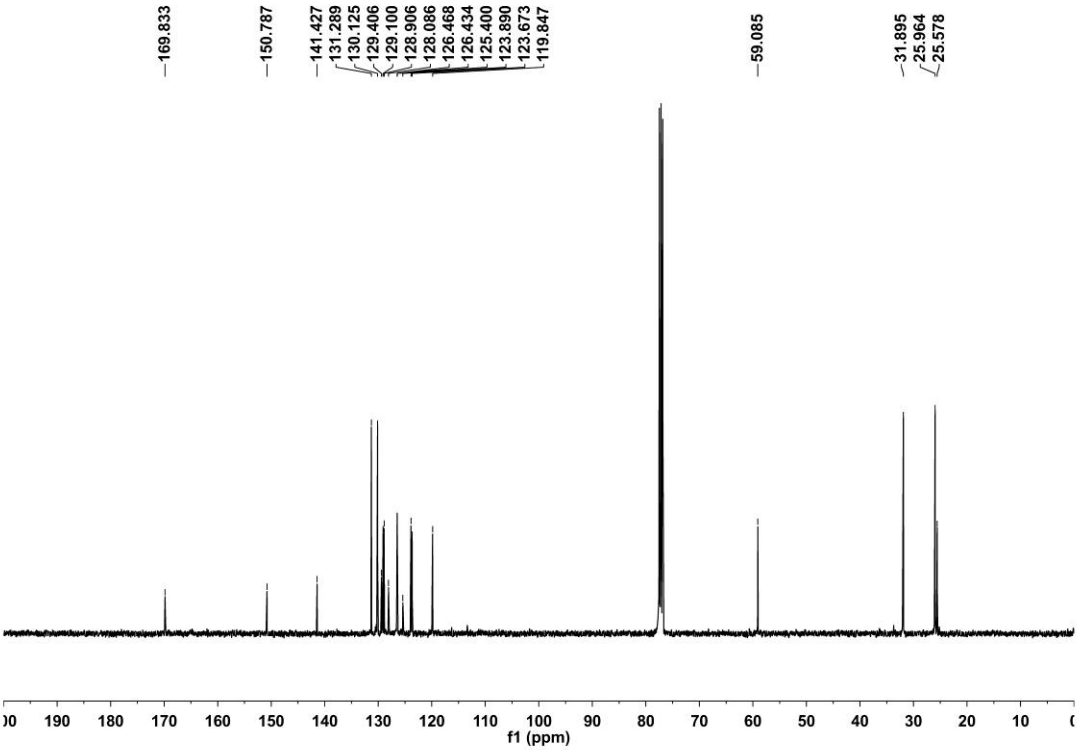

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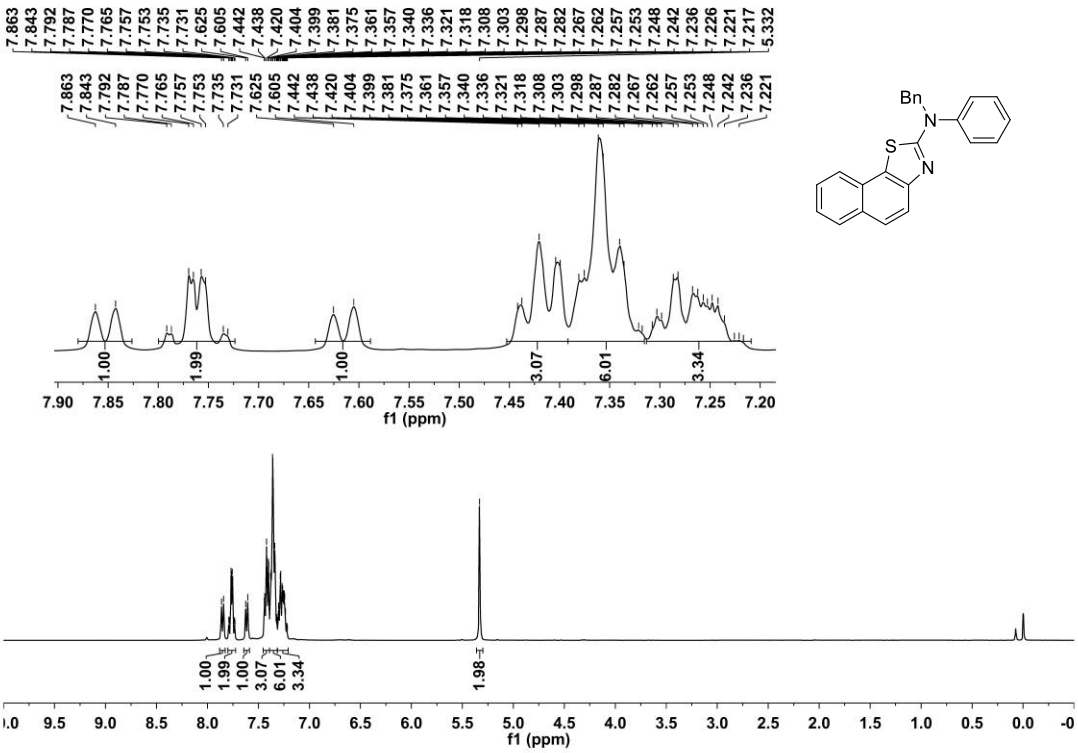

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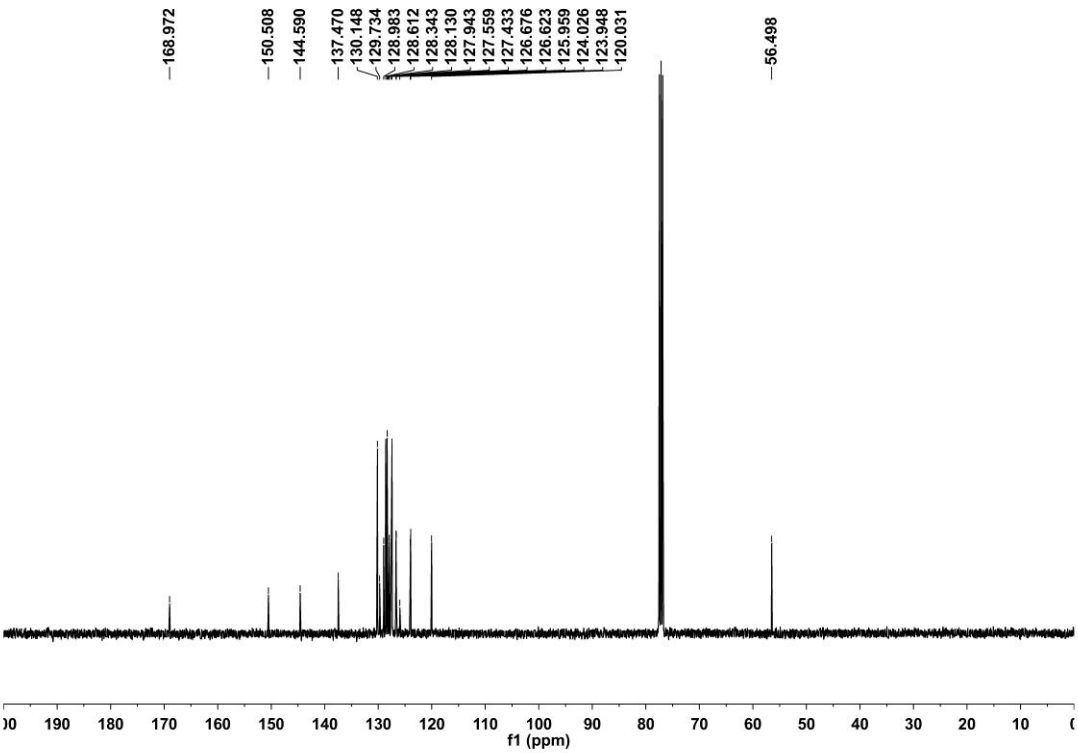

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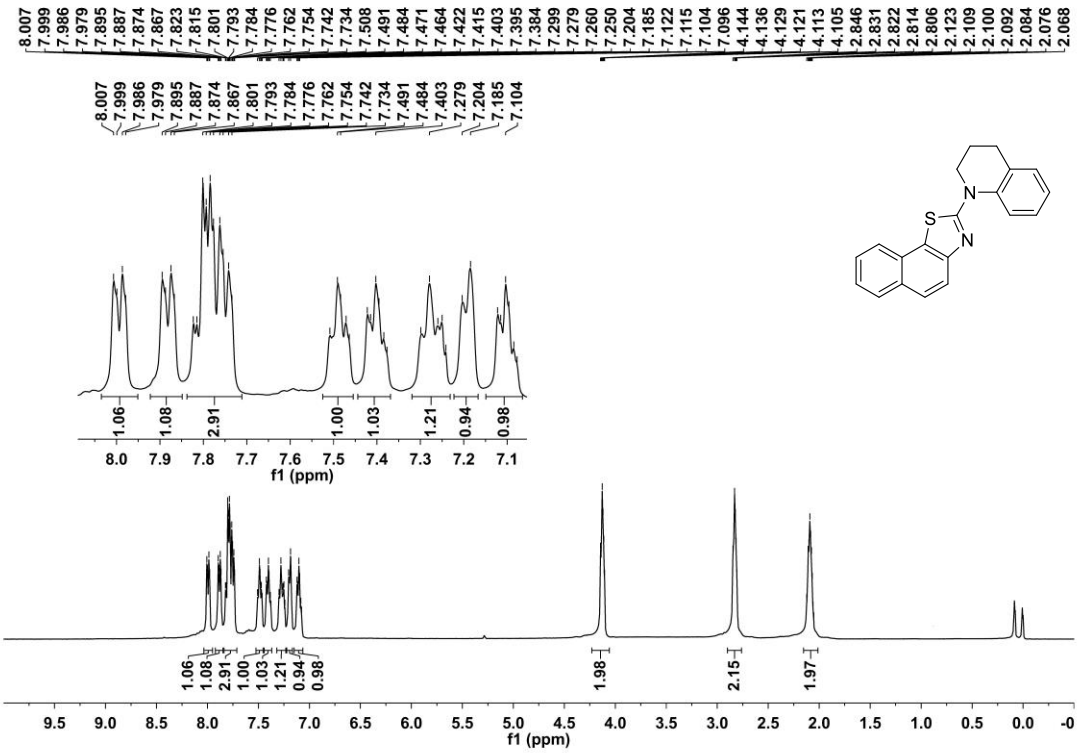

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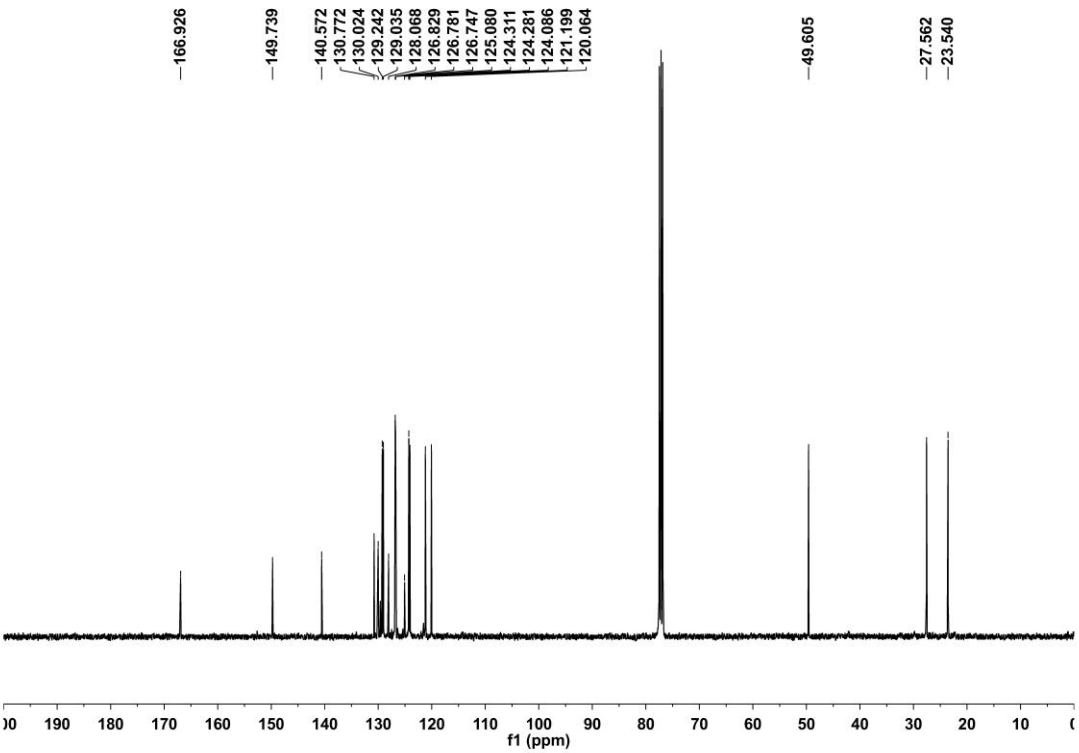

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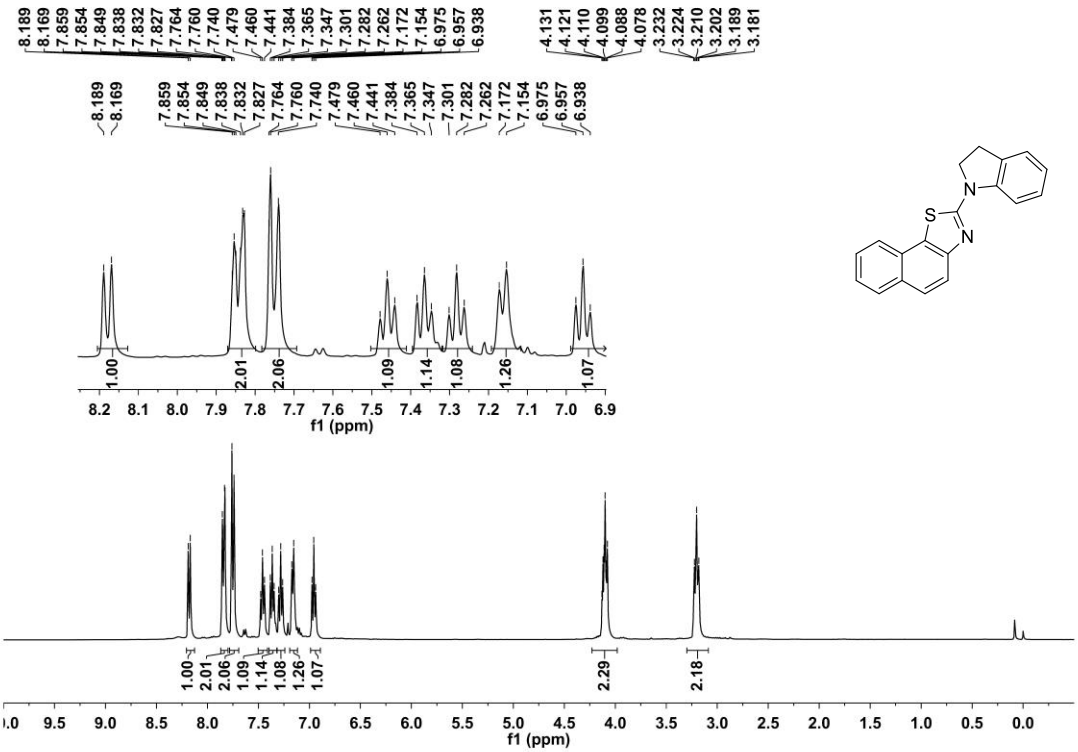

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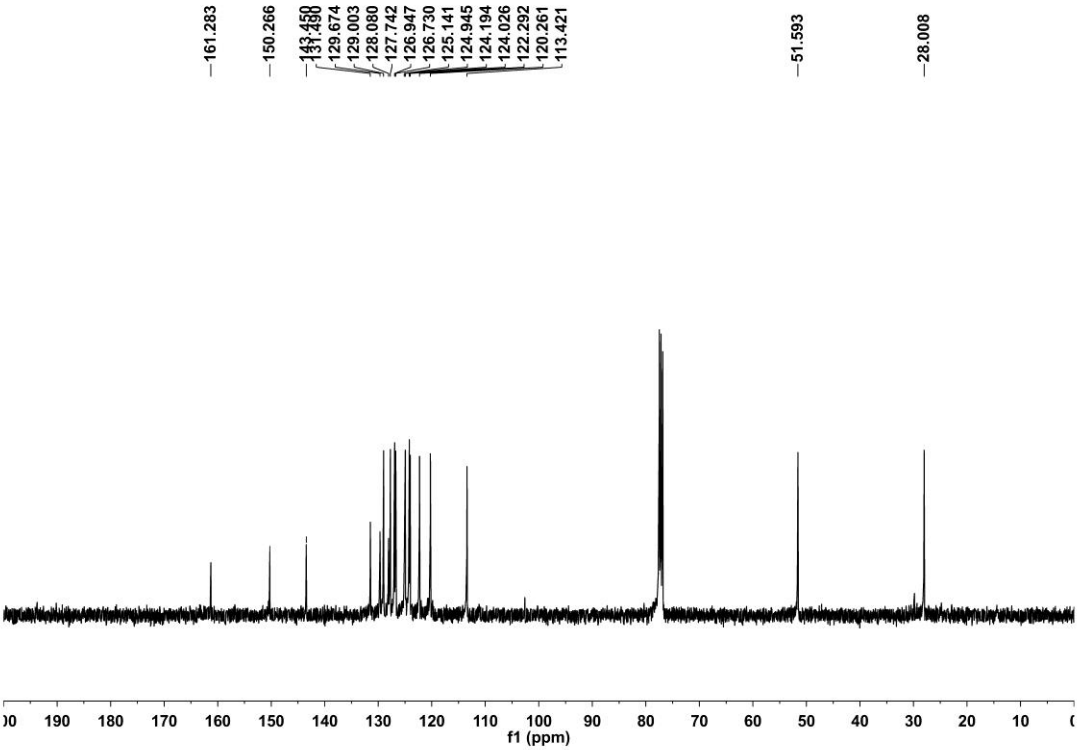

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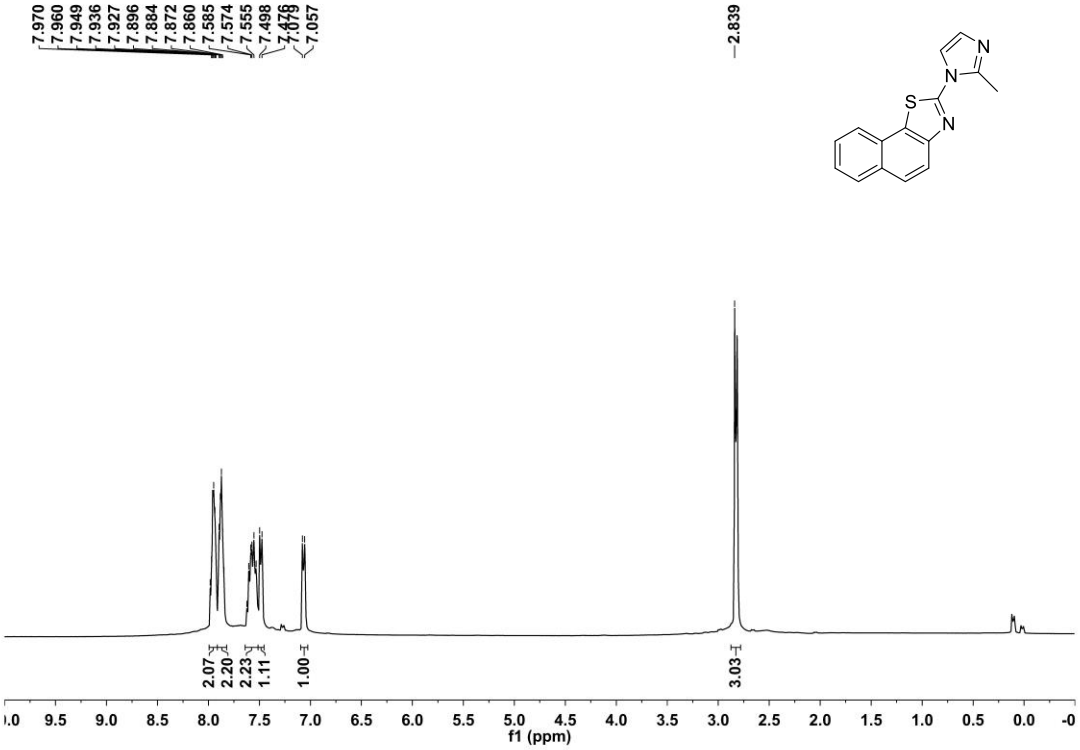

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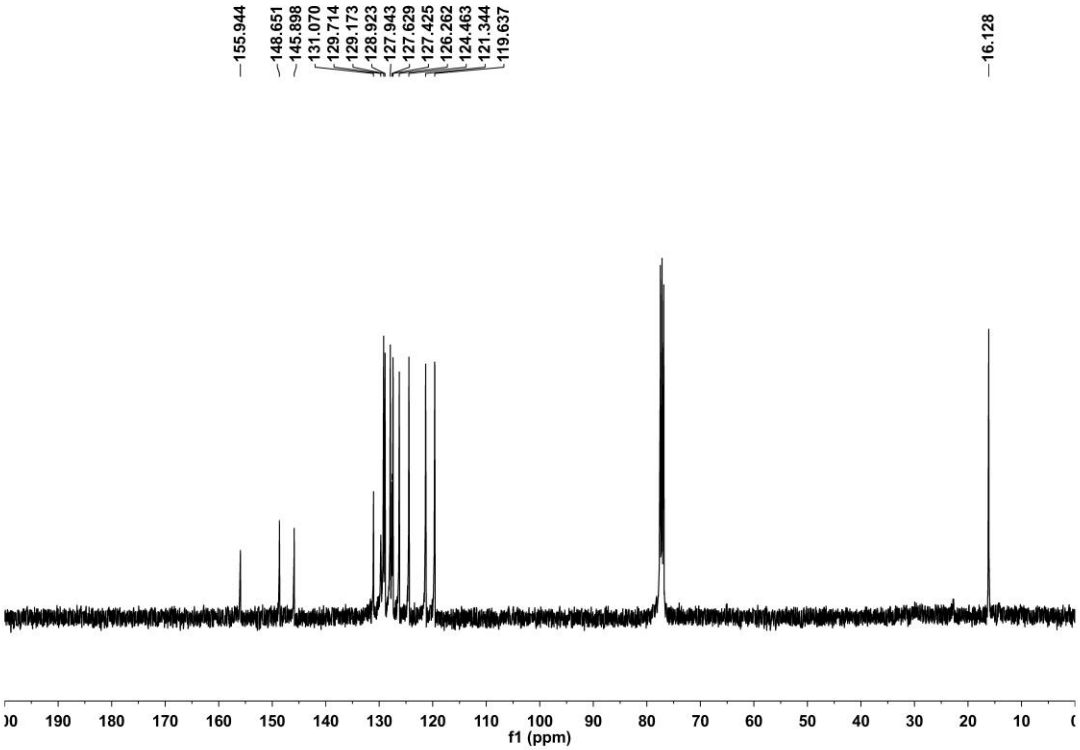

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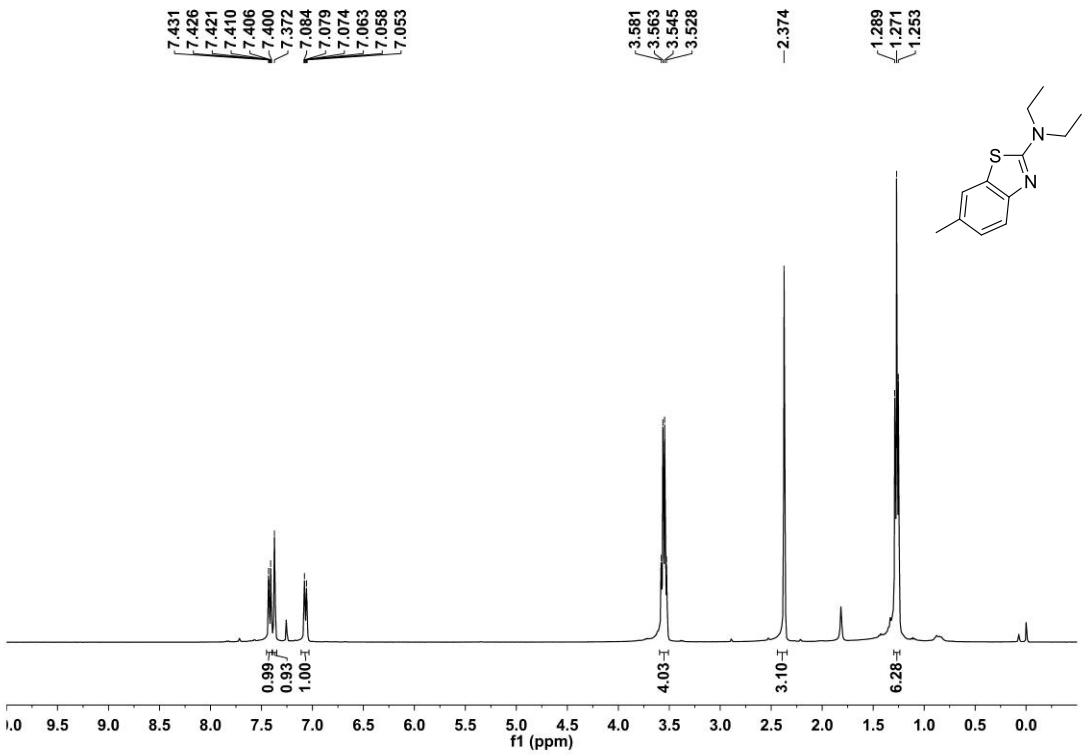

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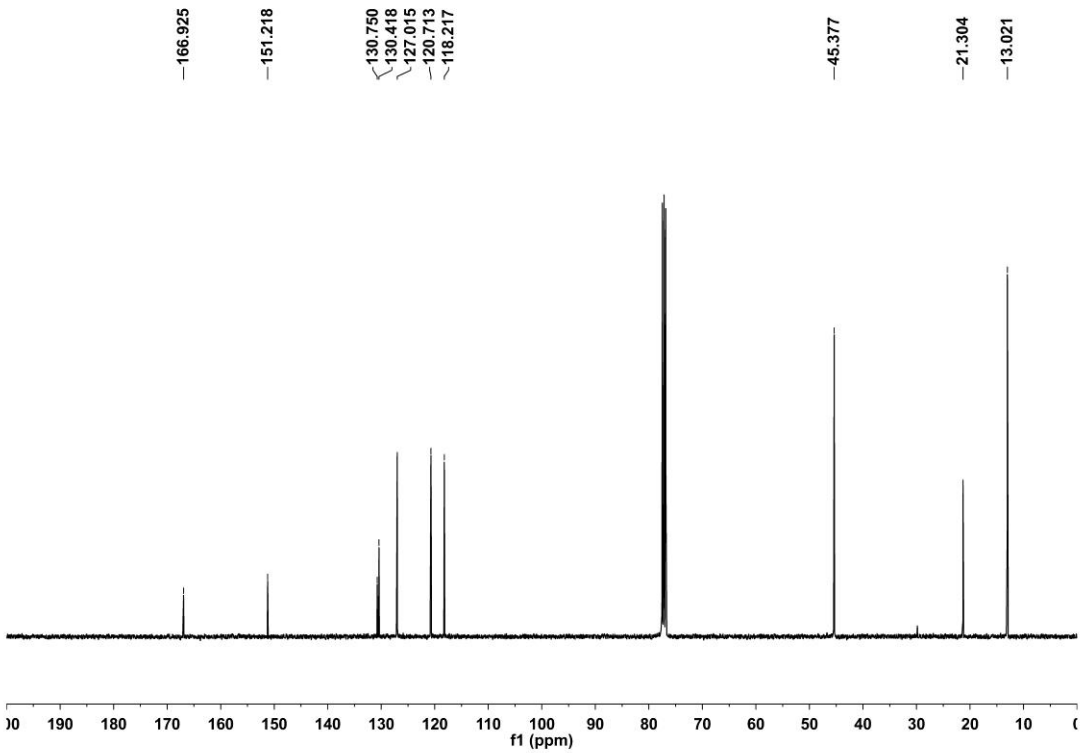

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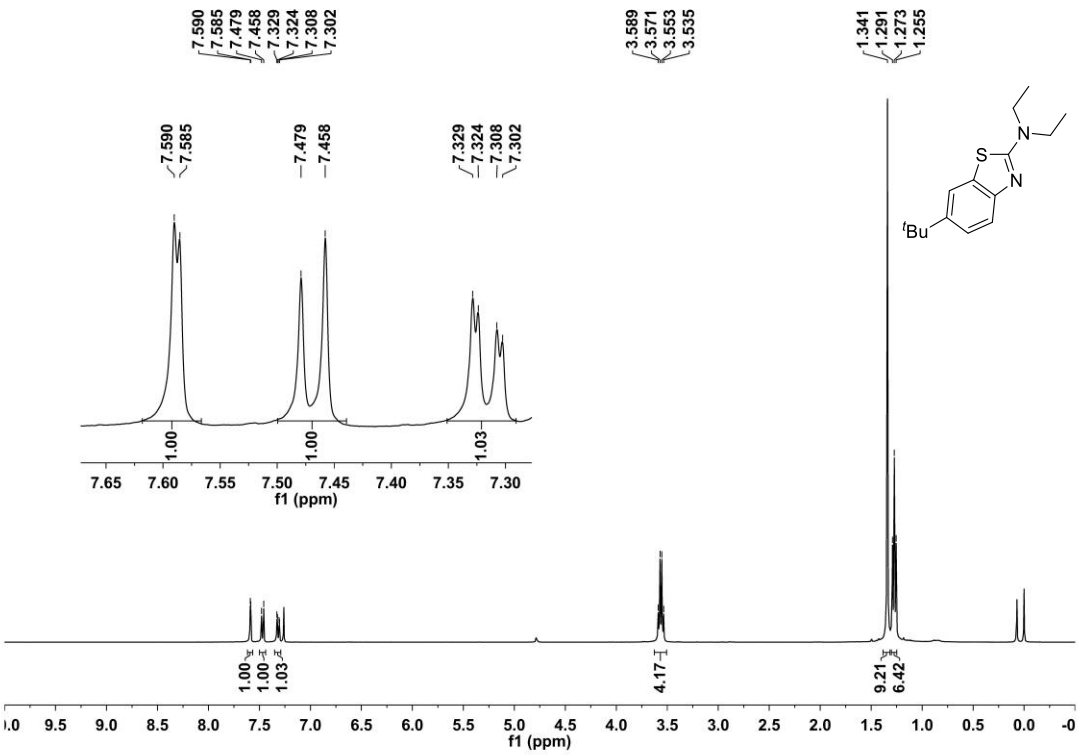

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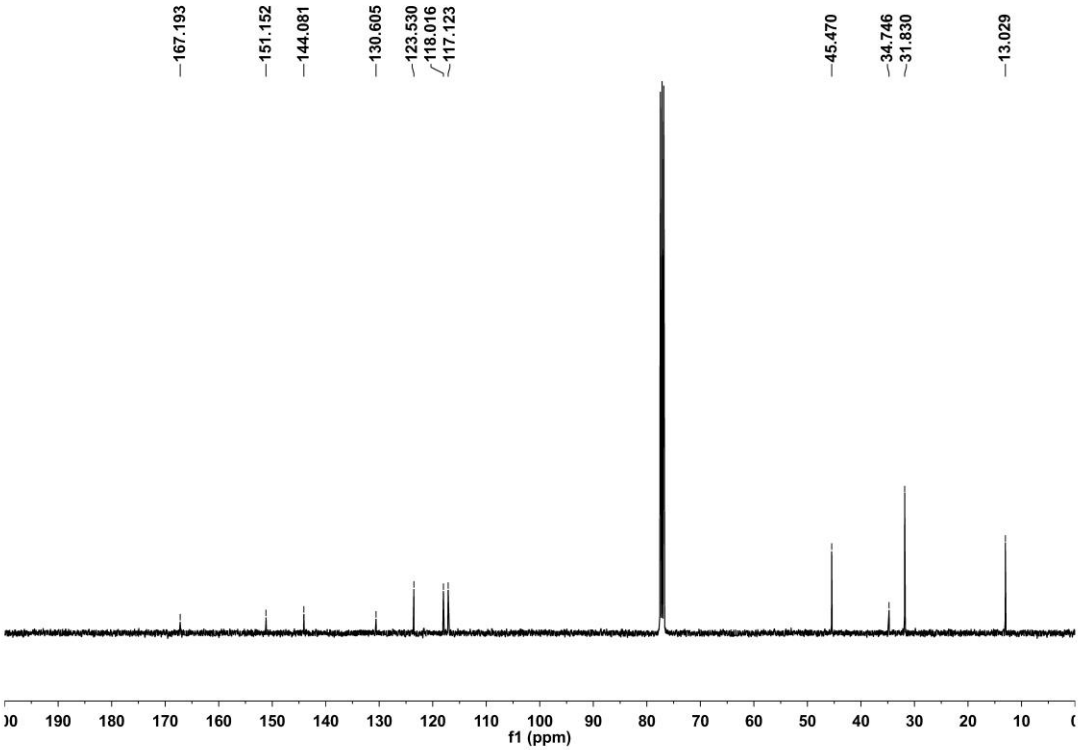

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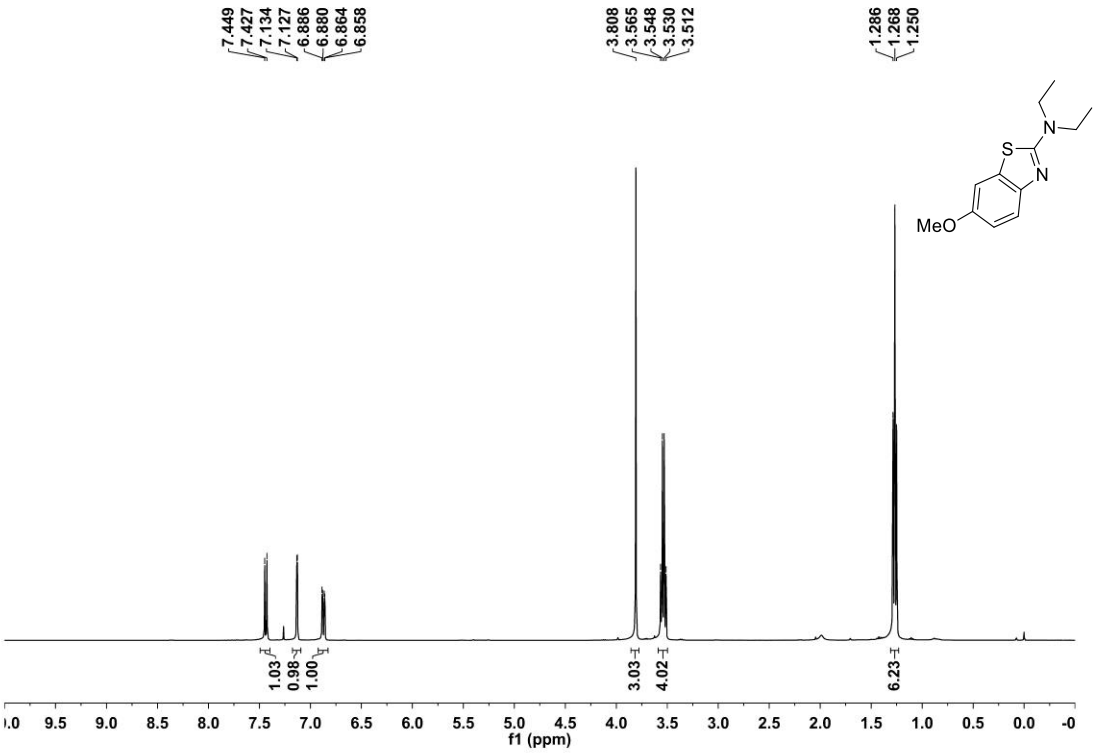

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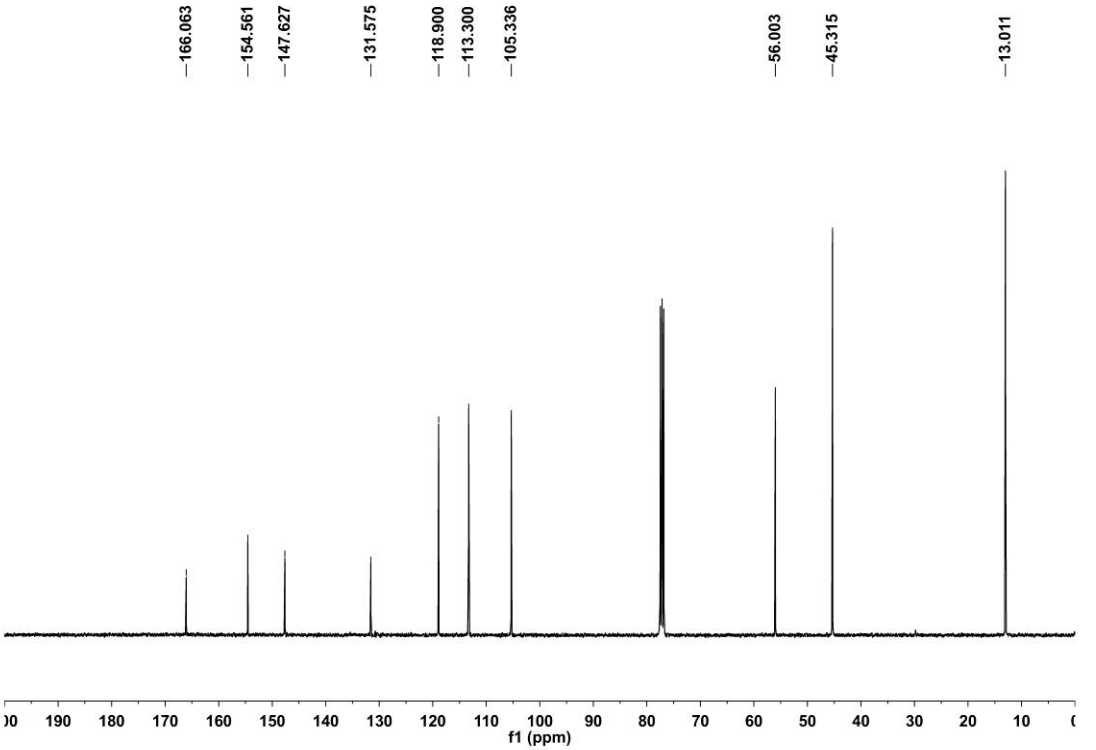

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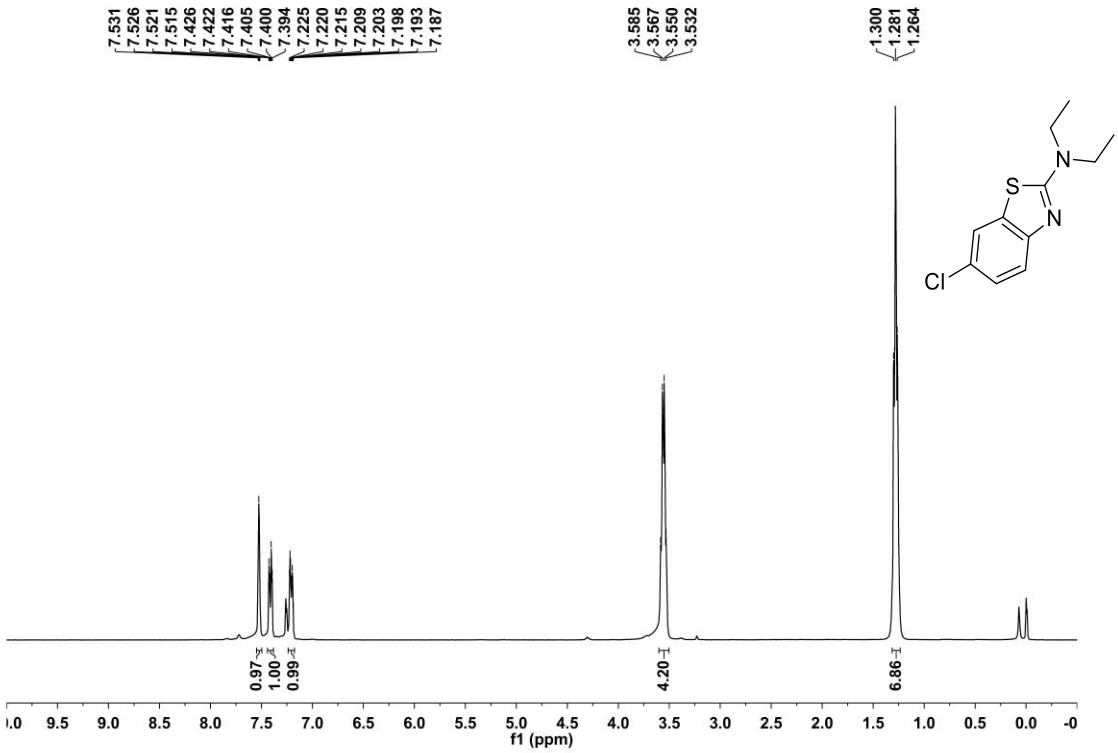

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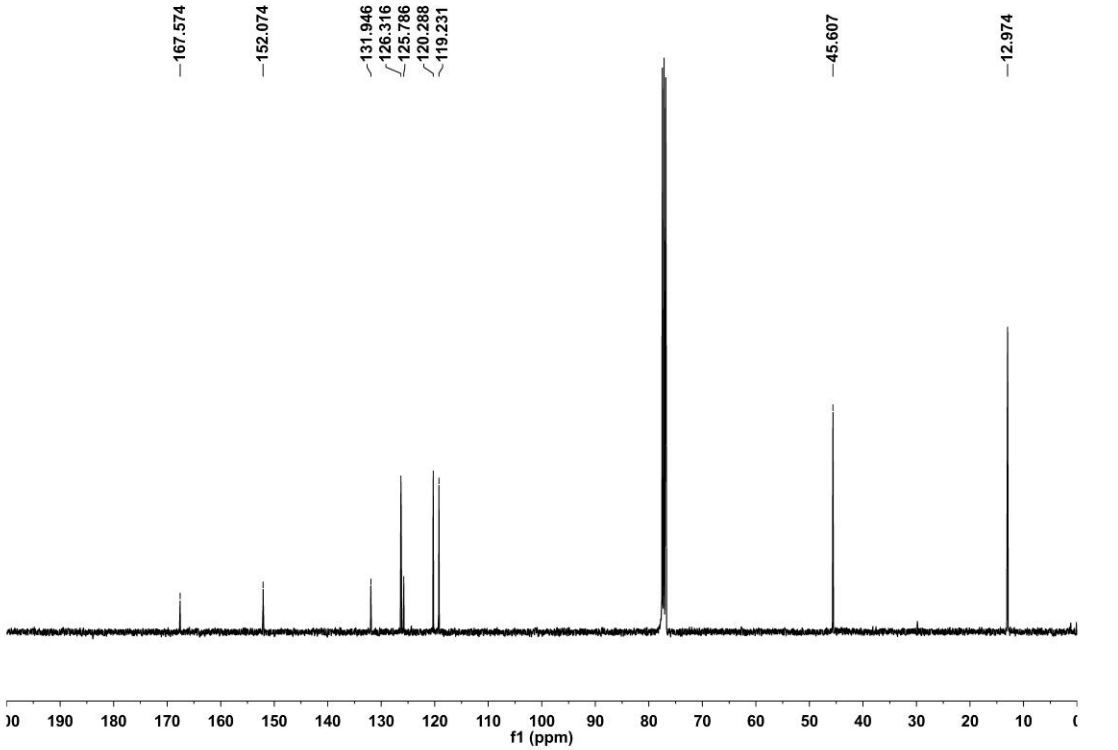

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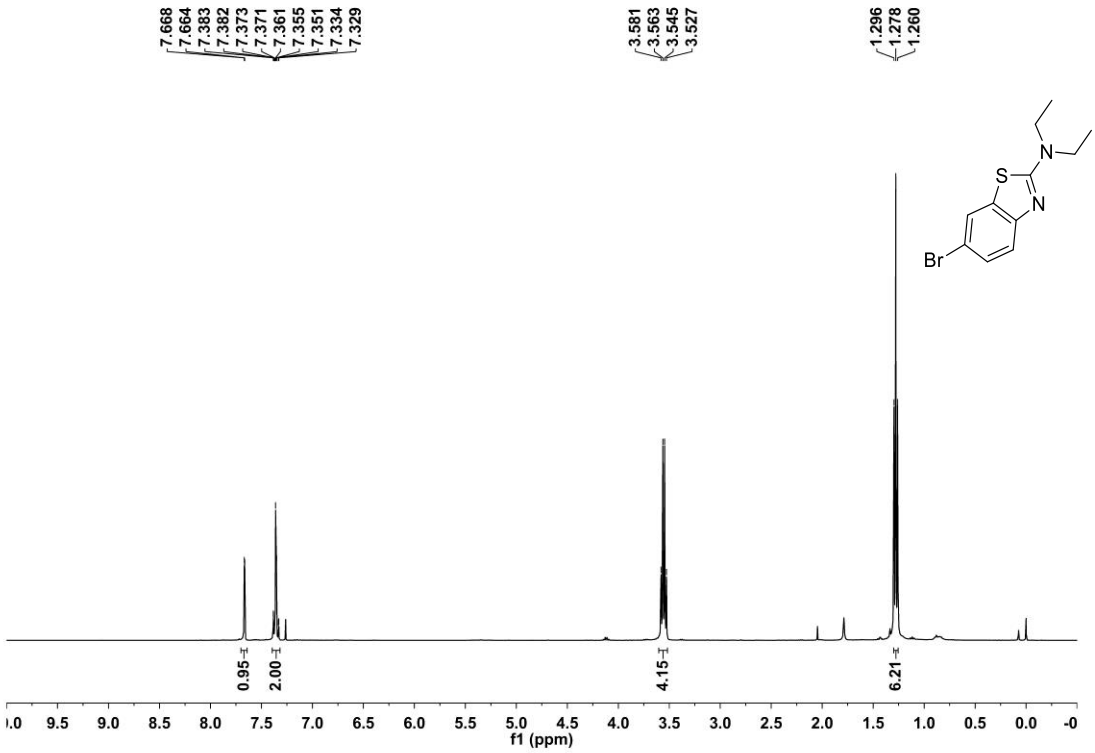

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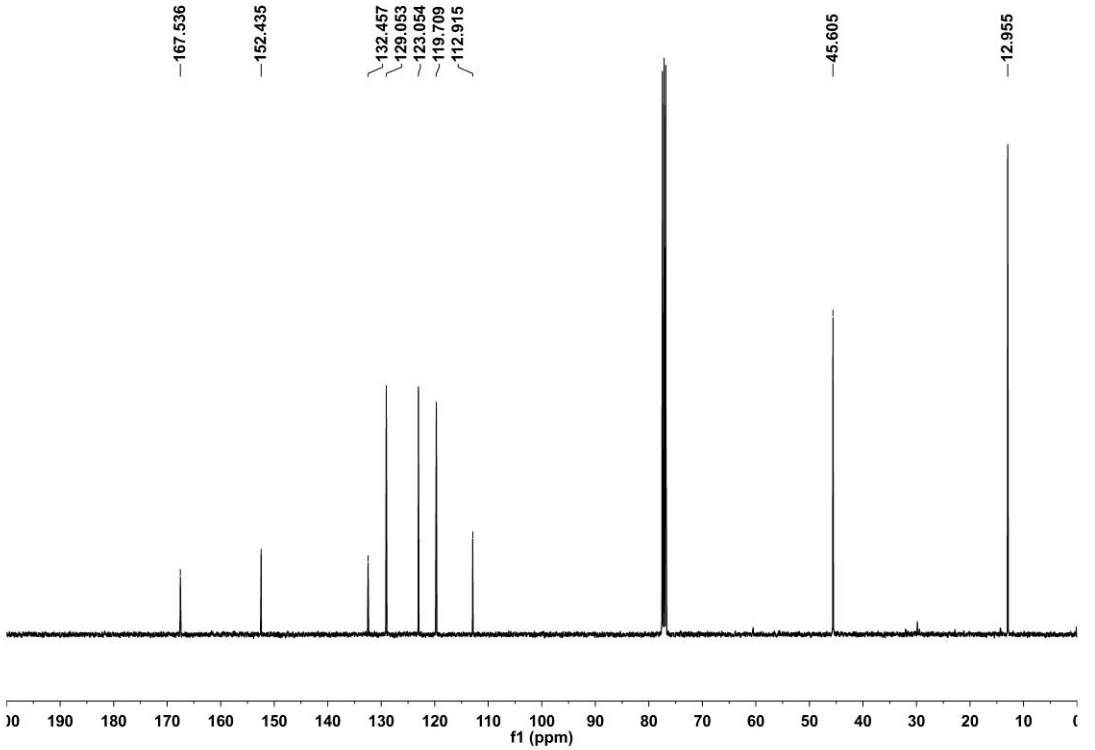
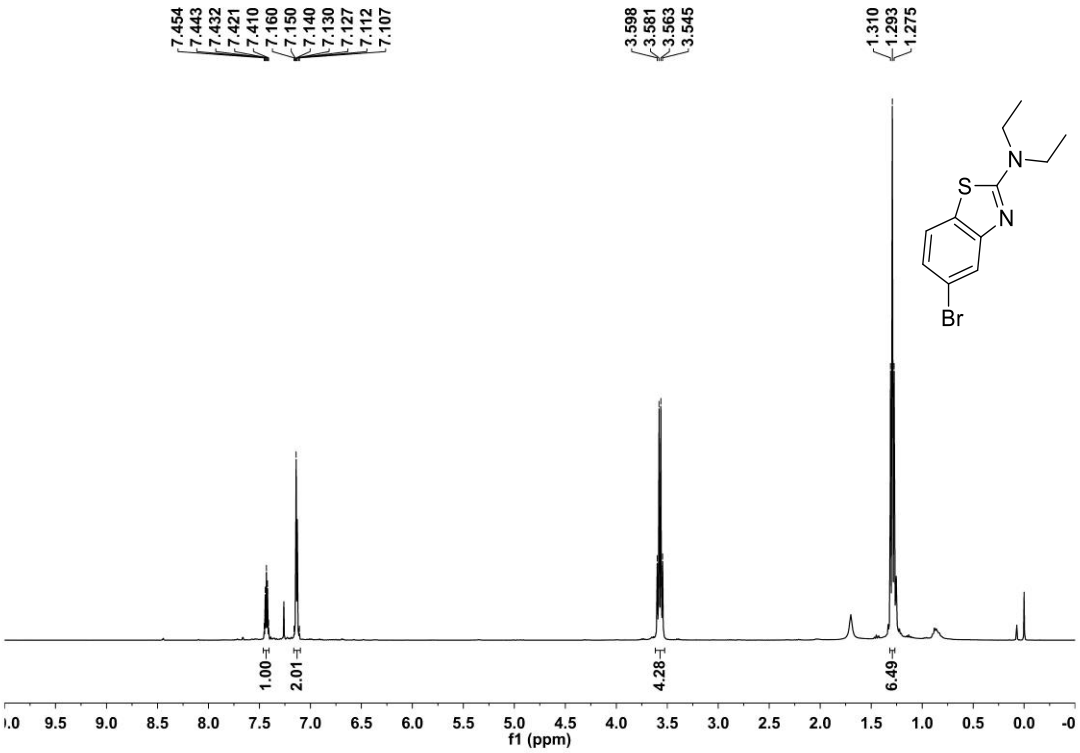


4haa

^{1}H NMR



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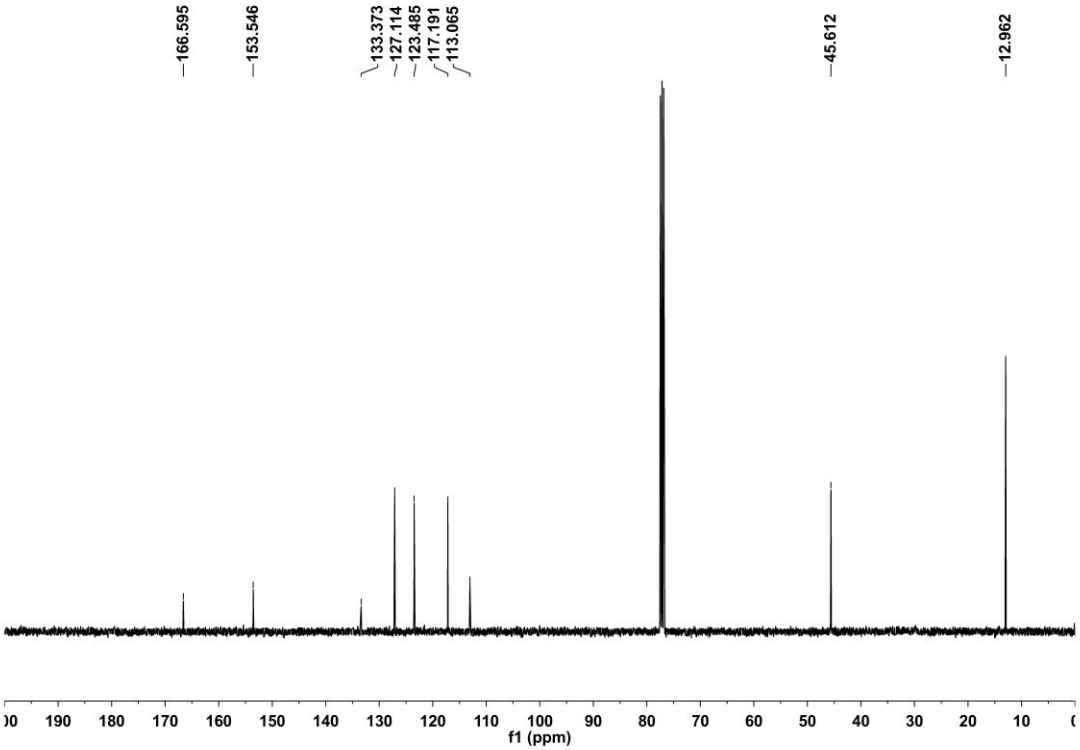

4haa’

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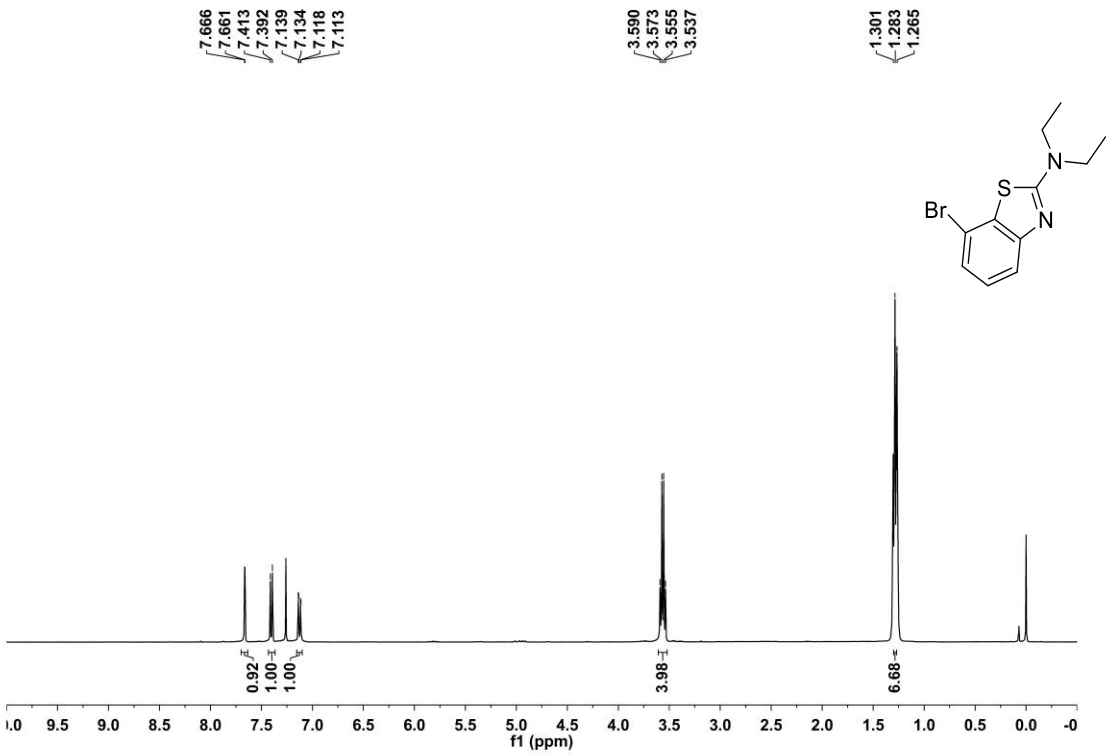

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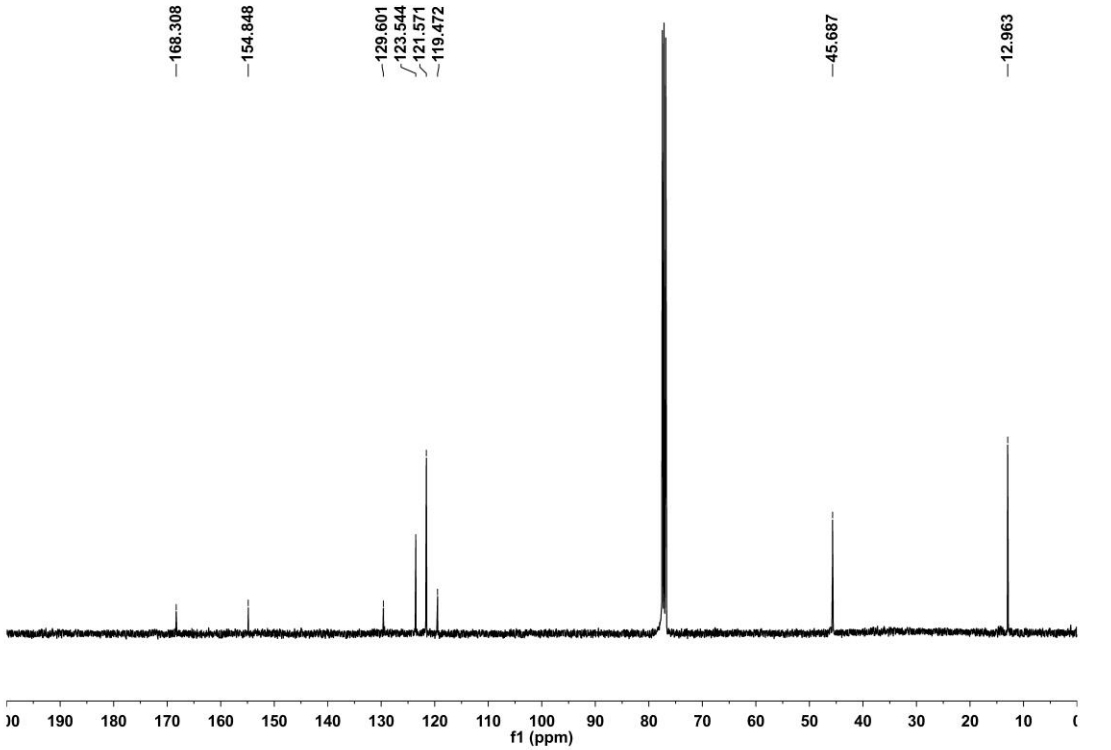

4aba

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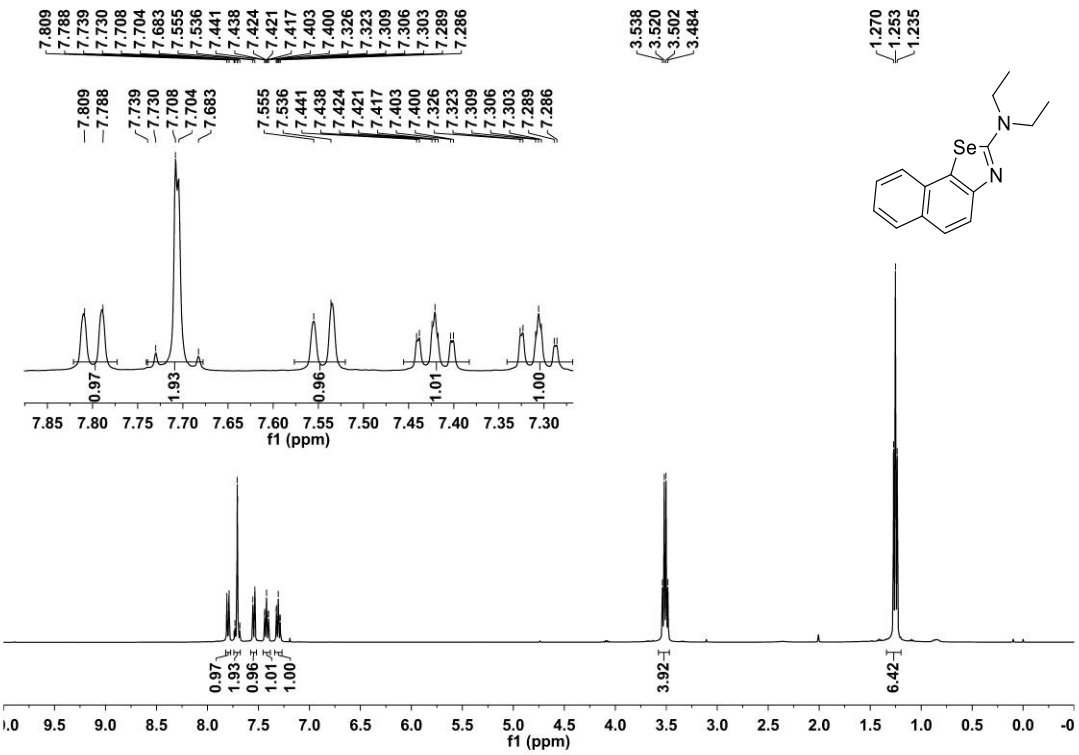

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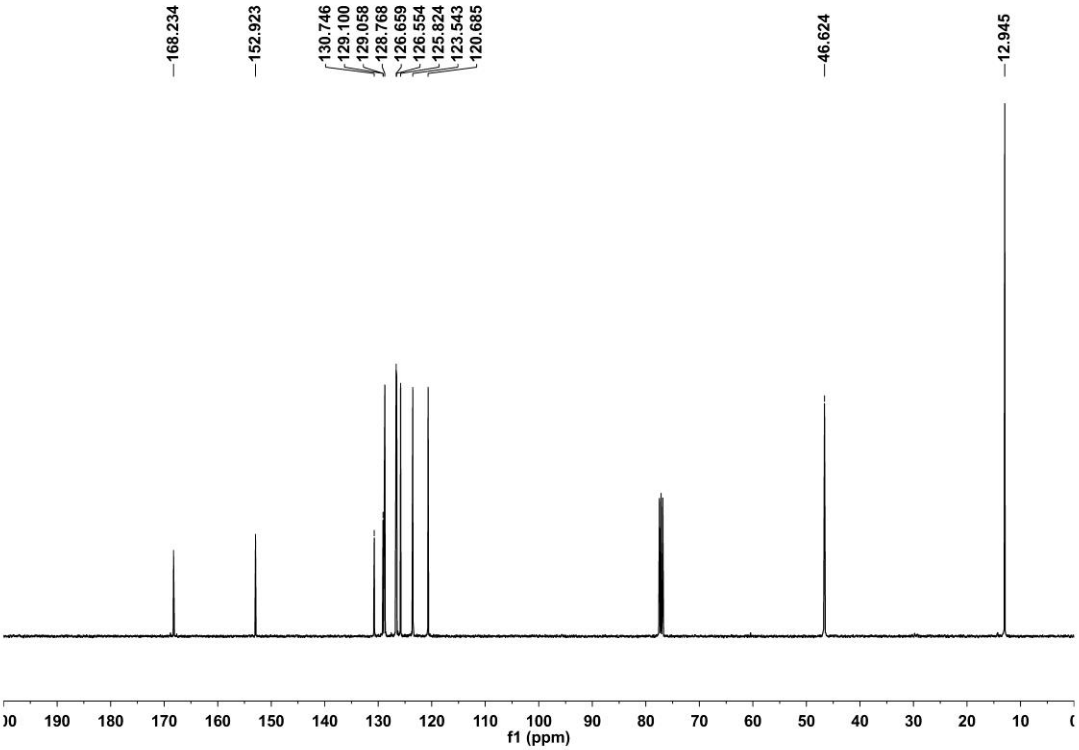

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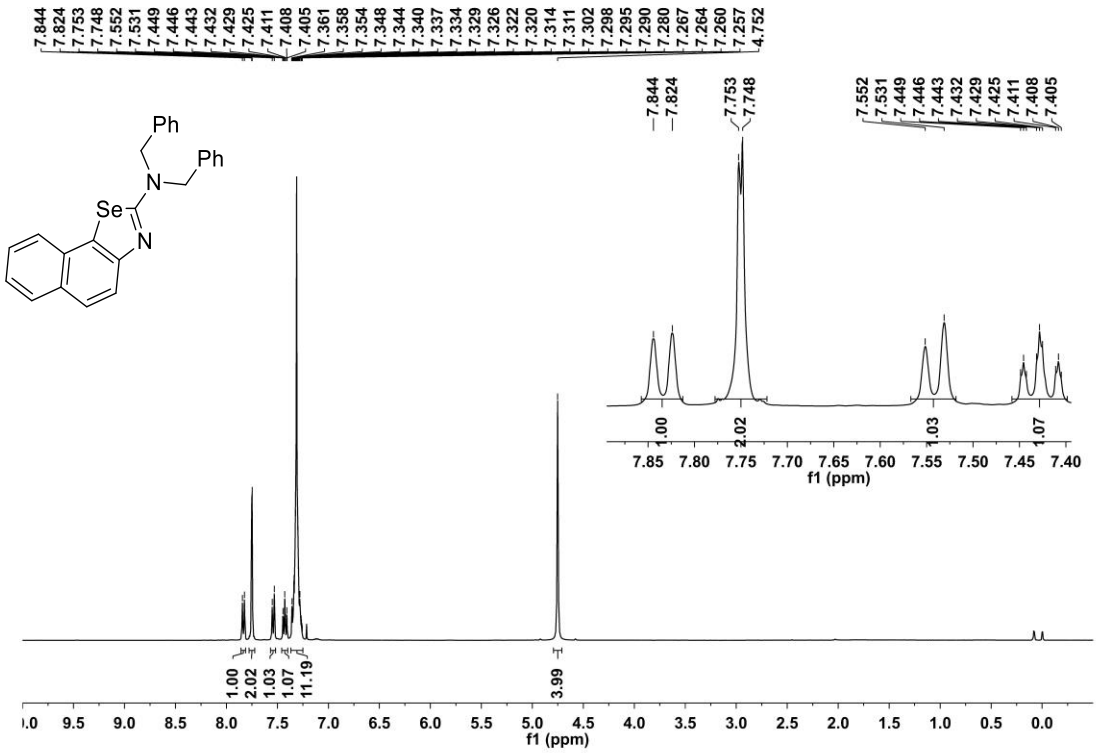

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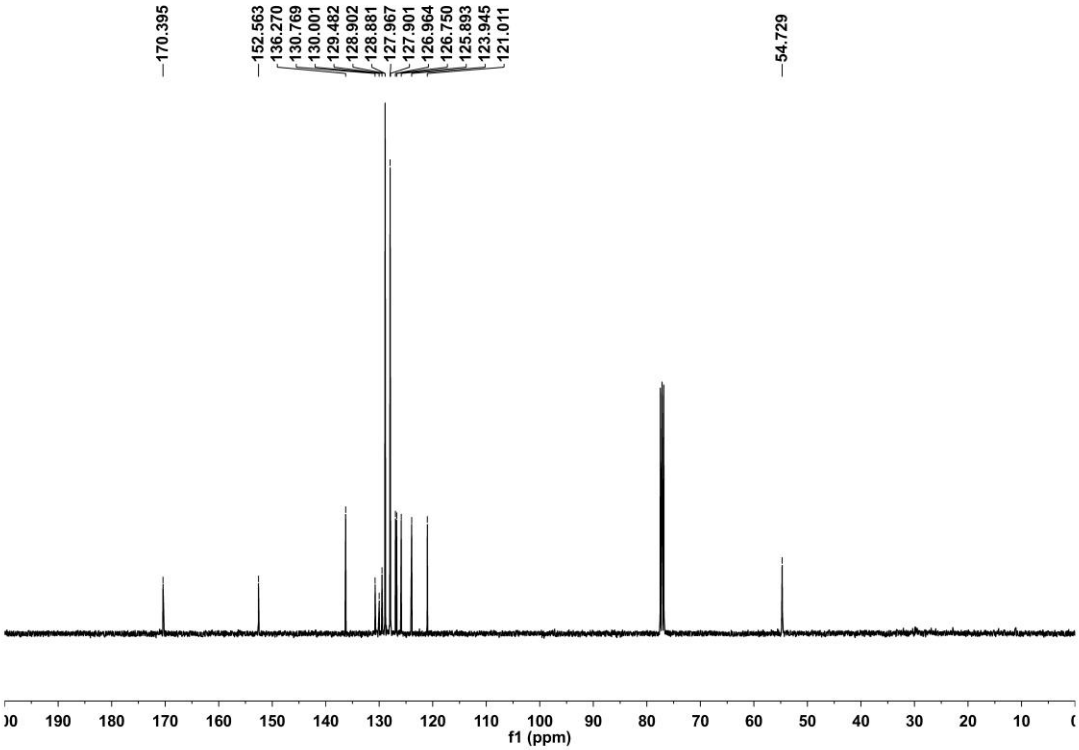

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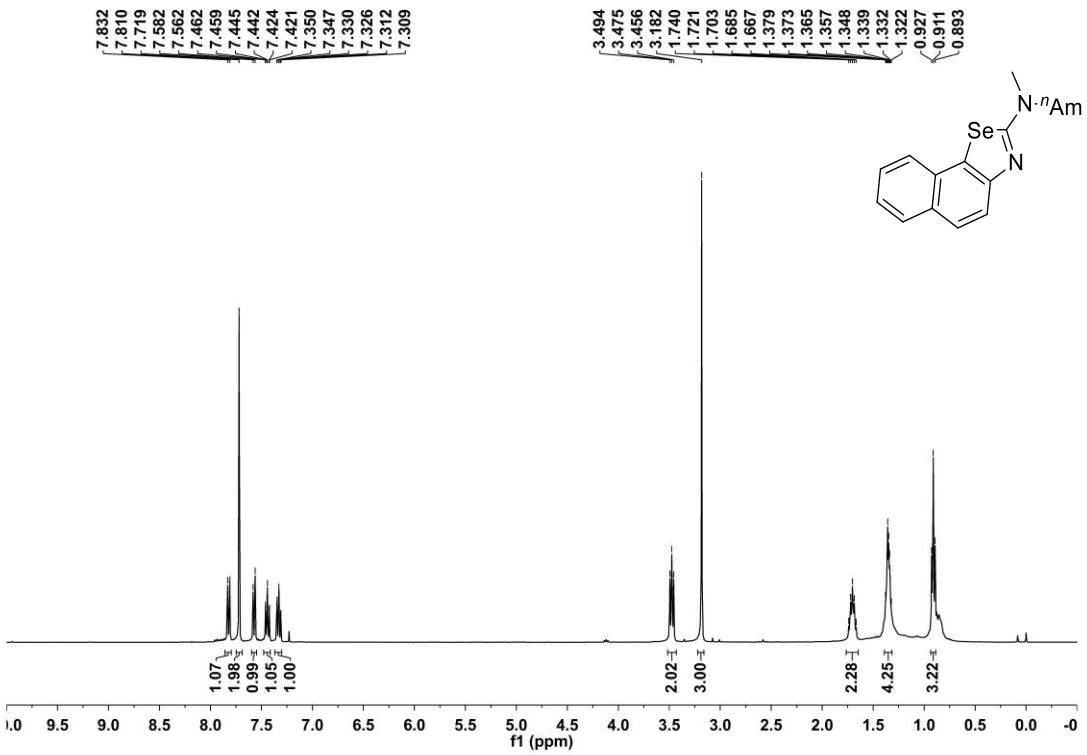

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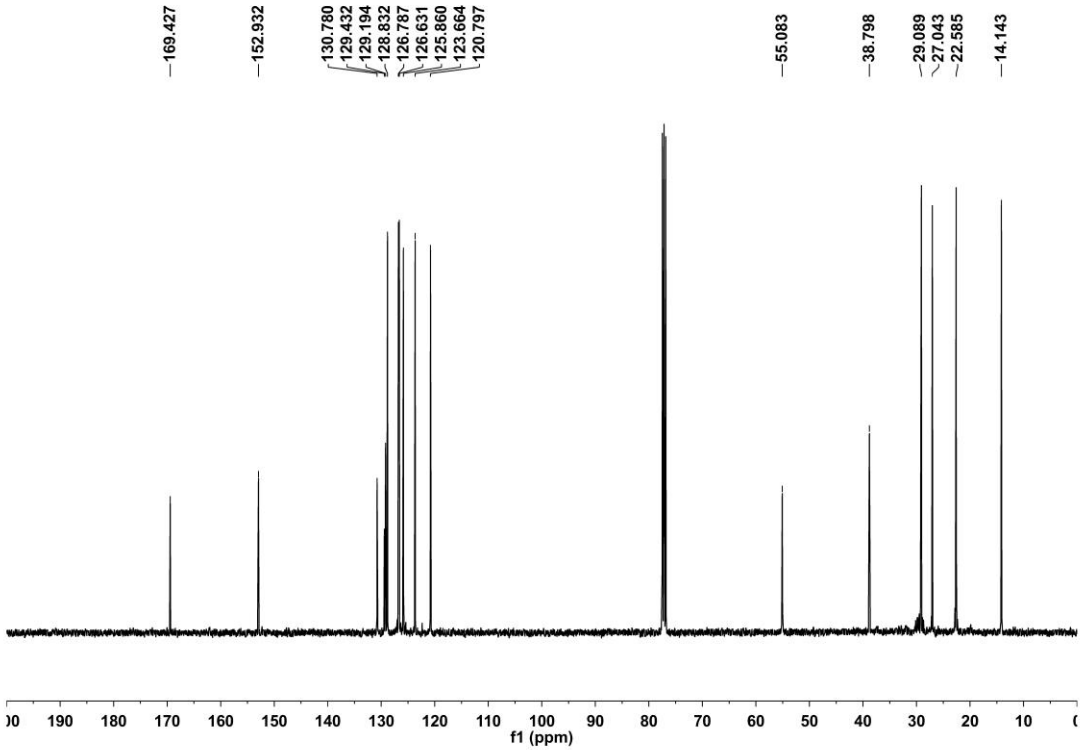

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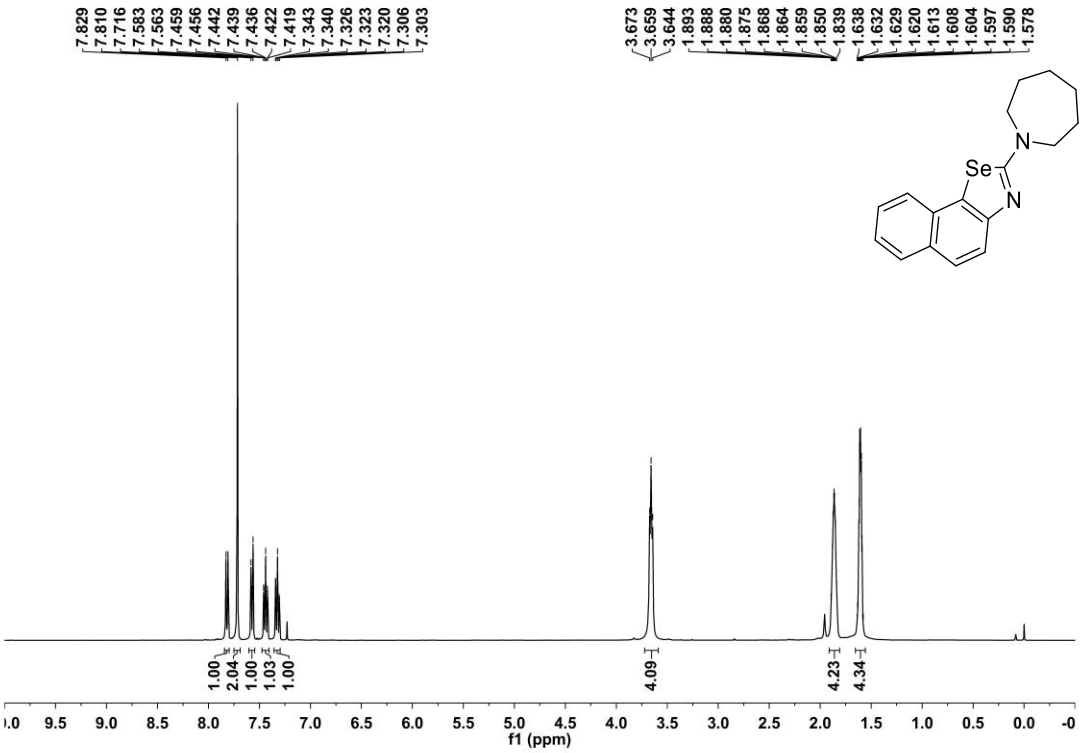

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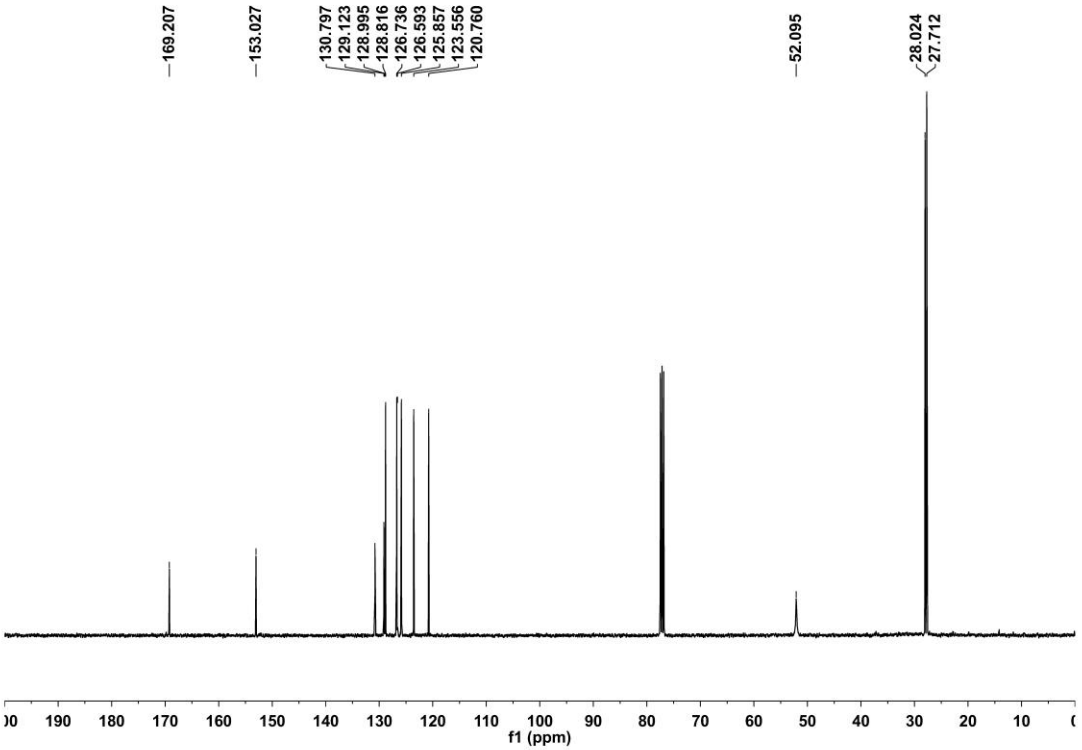

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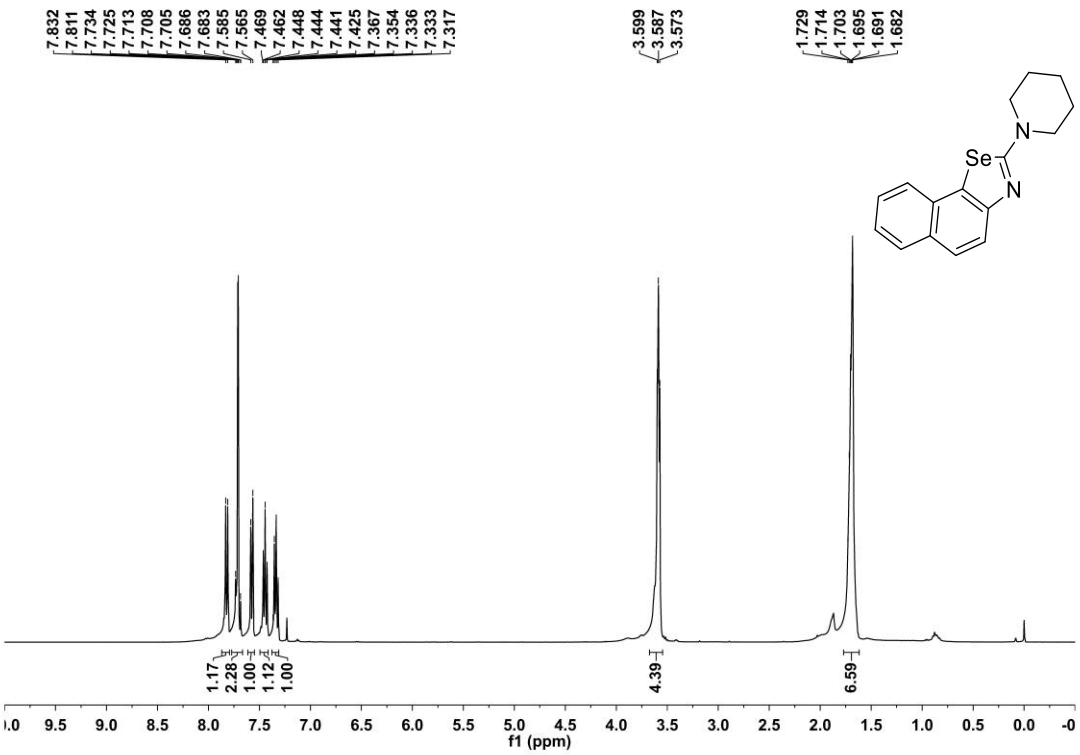

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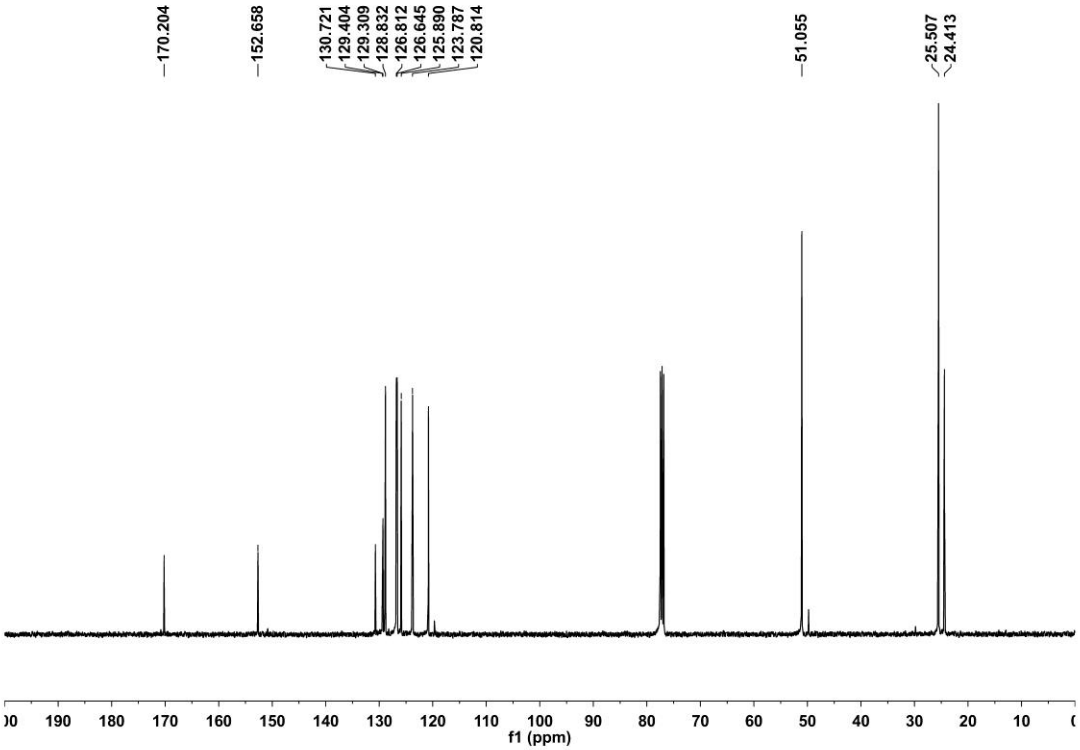
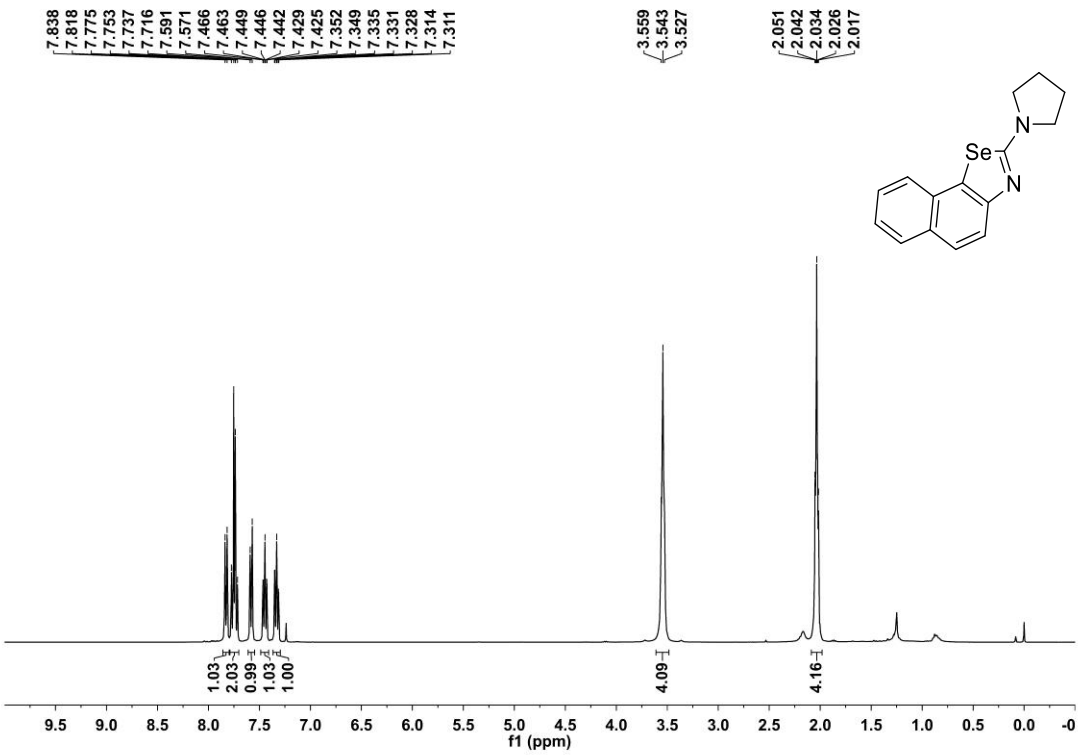


4abo

^{1}H NMR



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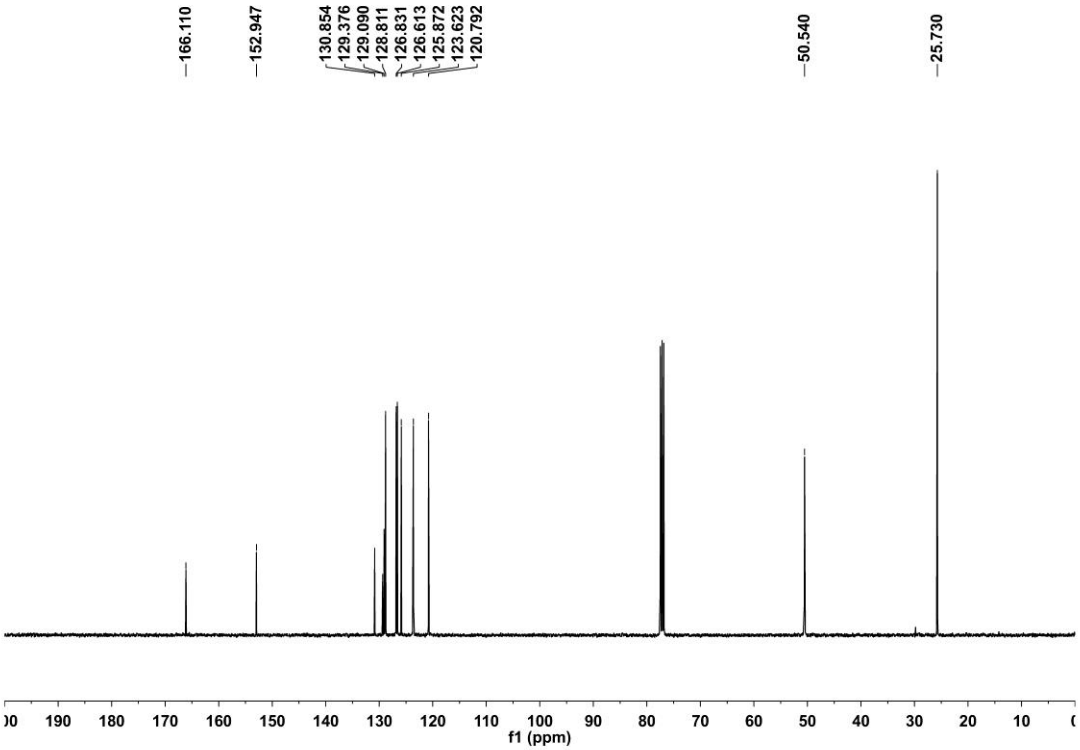
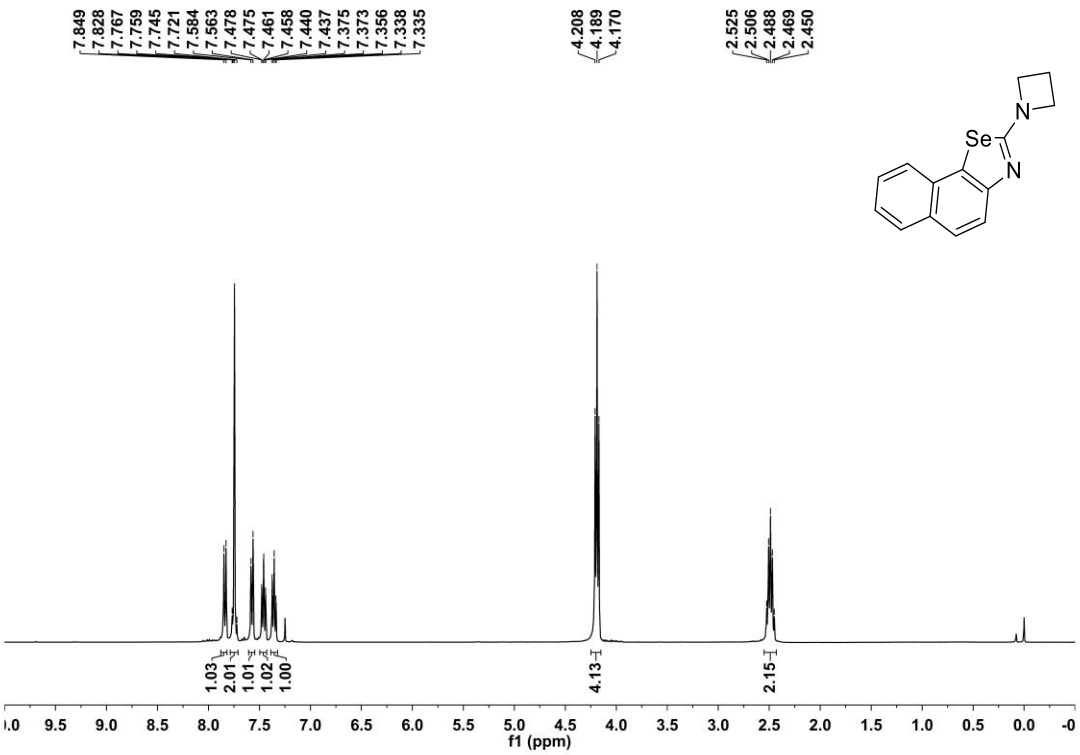


4abp

^{1}H NMR



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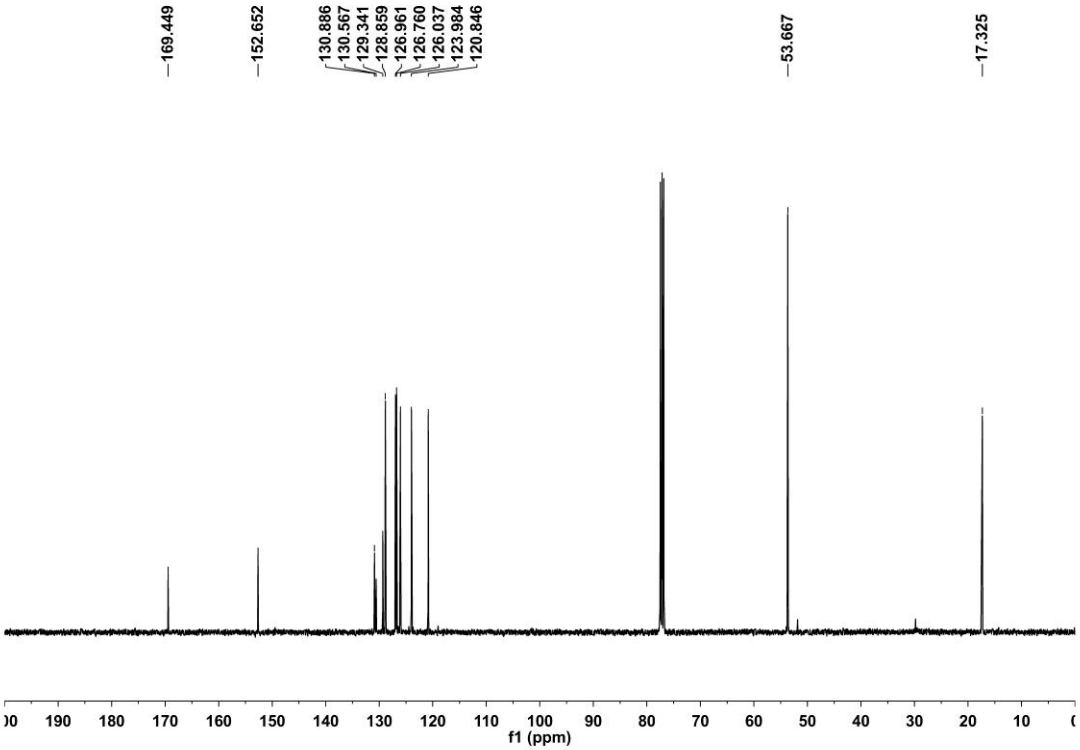
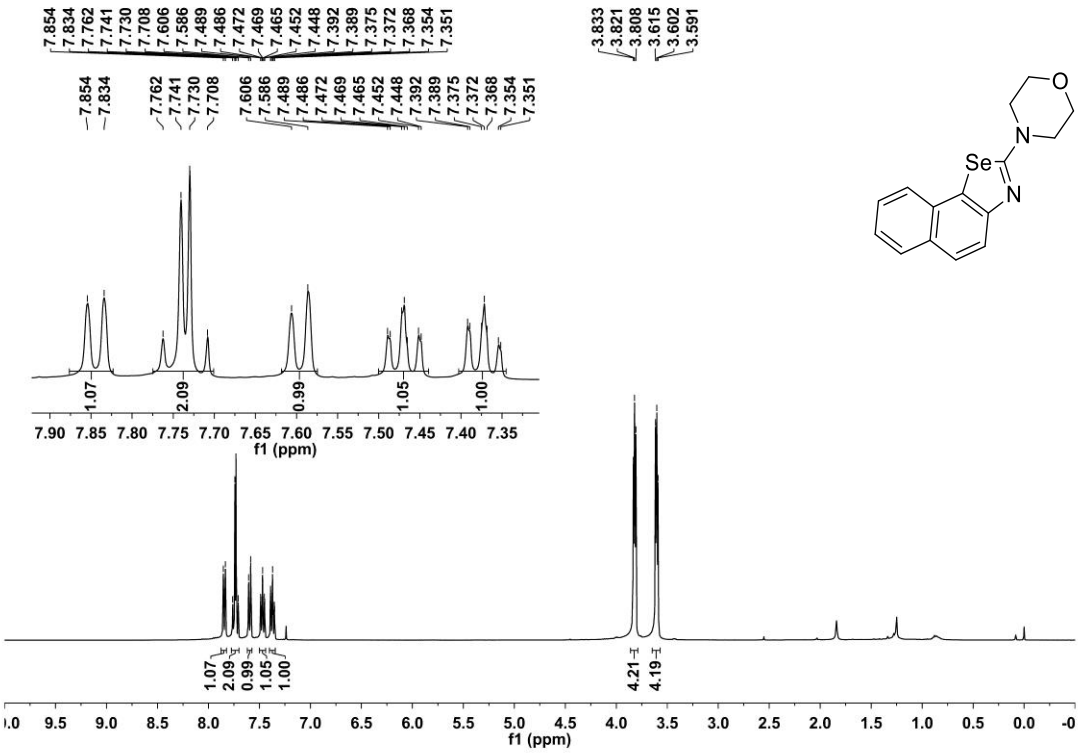


4abq

^{1}H NMR



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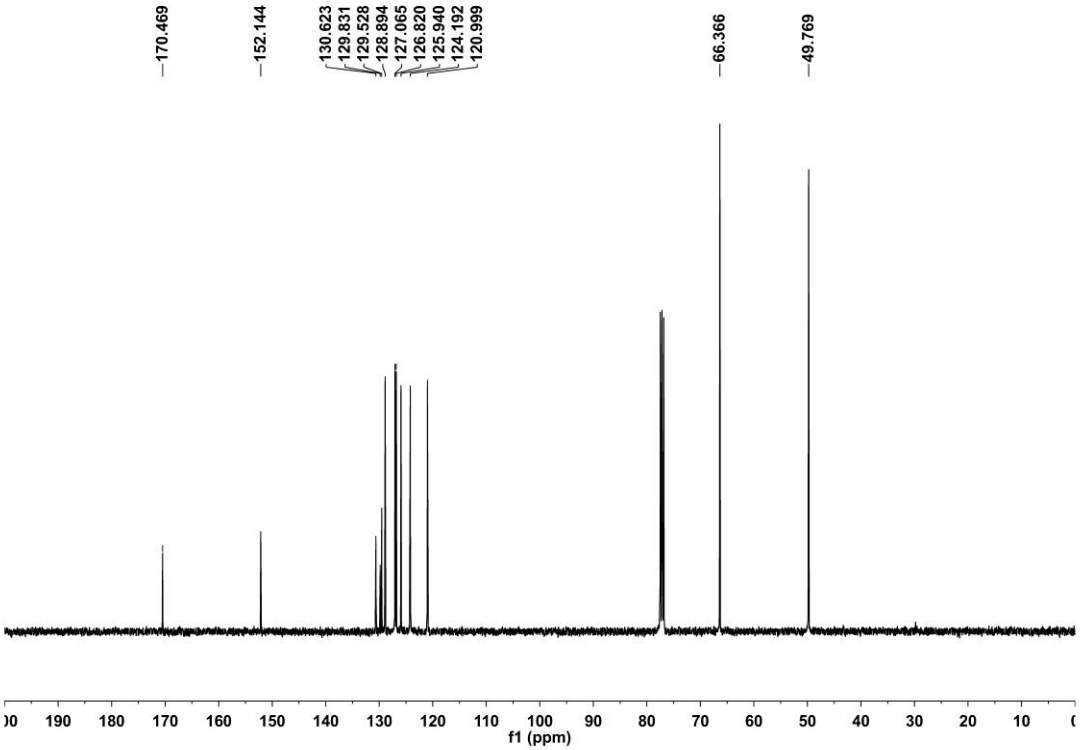

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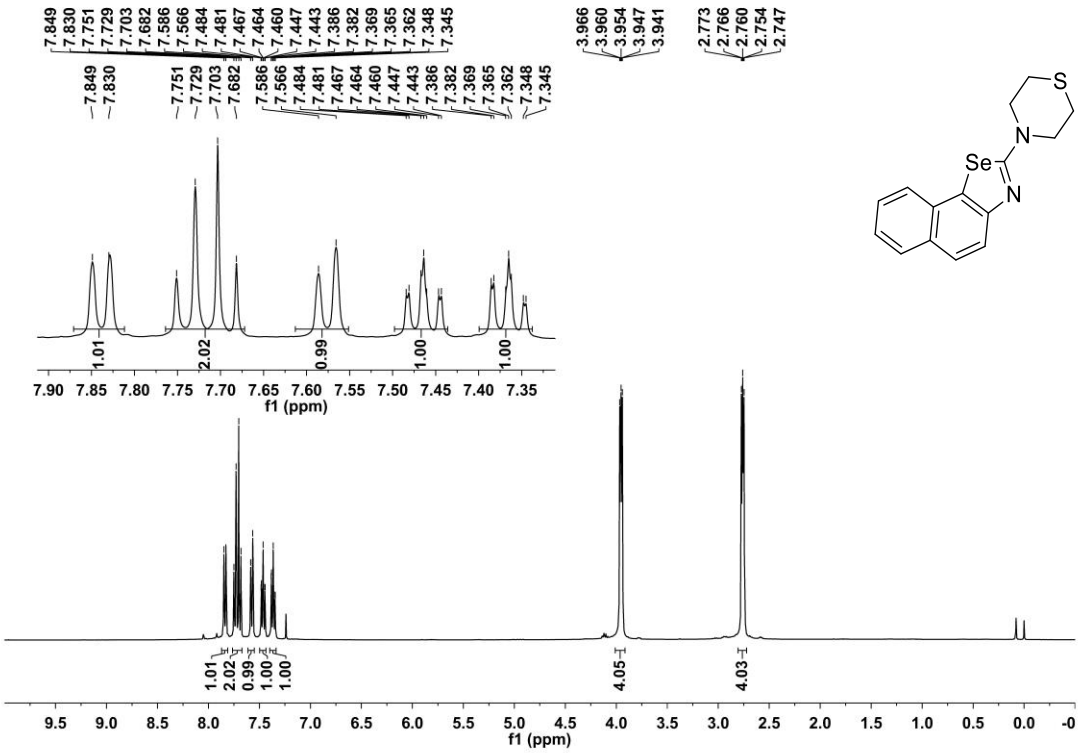

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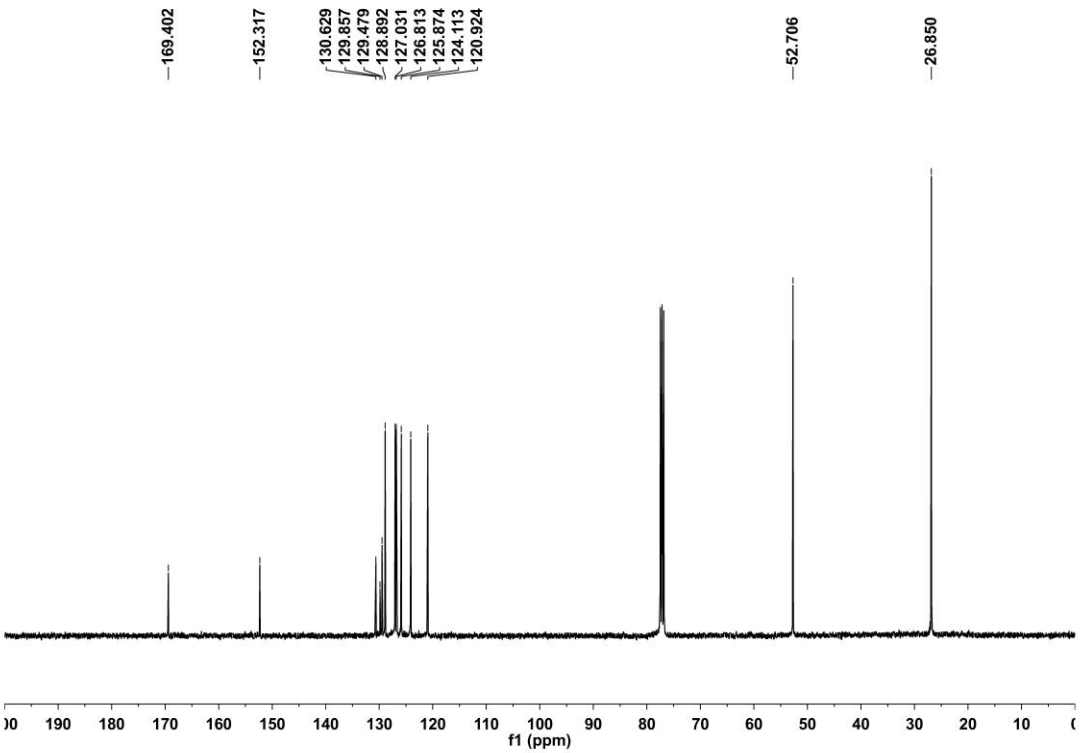

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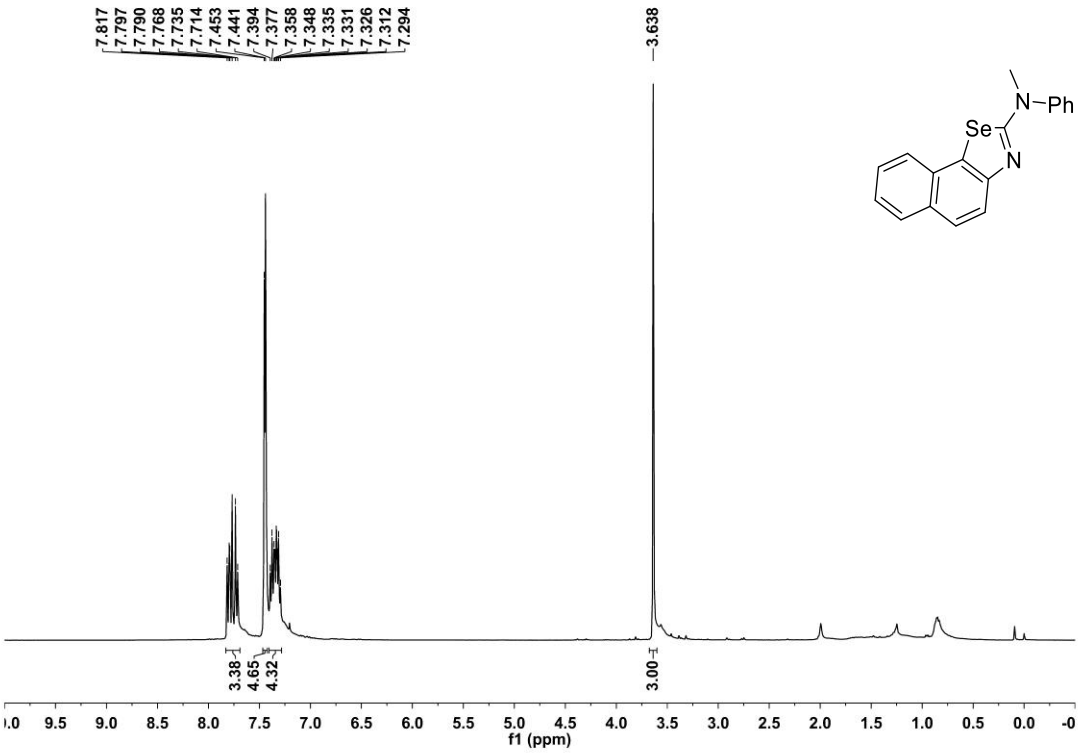

^{13}C NMR