

## Supporting Information

### One-step construction of thioureas and oxazolidinethiones from amines and carbon disulfide *via* a cascade reaction sequence

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## General information and materials:

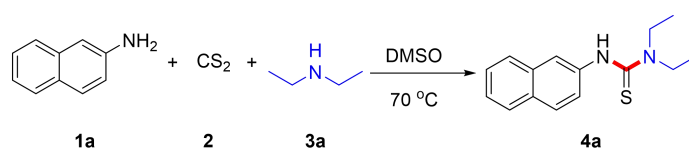
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade. Column chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on a Bruker DRX400 (400 MHz), DRX500 (500 MHz) and DRX600 (600 MHz) spectrometer in CDCl<sub>3</sub> (δ = 7.26 ppm for <sup>1</sup>H, δ = 77.00 ppm for <sup>13</sup>C) and in DMSO-*d*<sub>6</sub> (δ = 2.50 ppm for <sup>1</sup>H, δ = 39.43 ppm for <sup>13</sup>C). Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). High resolution mass spectra were recorded on a LTQ Orbitrap mass spectrometer coupled to an Acceka HPLC-System (HPLC column: *Hypersyl GOLD*, 50 mm × 1 mm, 1.9 μm). Chemical yields refer to isolated pure substances.

## General procedure for the synthesis of products 4 and 6:

A mixture of amine **1** (0.2 mmol), carbon disulfide **2** (0.24 mmol), amine **3** (0.24 mmol) or amine **5** (0.2 mmol), carbon disulfide **2** (0.24 mmol) in DMSO (2 mL) was added in a 5 mL glass tube, which was stirred at 70 °C for 1–12 h. When the reaction was completed, it was mixed with water and ethyl acetate. The reaction mixture was extracted three times with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrate was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (eluting with petroleum ether-ethyl acetate) to provide the desired products **4** or **6**.

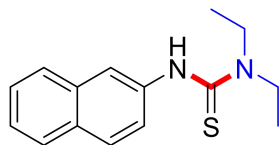
## Optimization with different amounts of reactants.<sup>a</sup>



Entry	Carbon Disulfide Amount	Diethyl Amine Amount	Reaction Time (h)	Yield (%) <sup>b</sup>
1	2.0 equiv.	2.0 equiv.	1.5	89
2	1.5 equiv.	1.5 equiv.	1	92
<b>3</b>	<b>1.2 equiv.</b>	<b>1.2 equiv.</b>	<b>1</b>	<b>95</b>
4	1.2 equiv.	1.0 equiv.	1.5	88
5	1.0 equiv.	1.0 equiv.	7	84

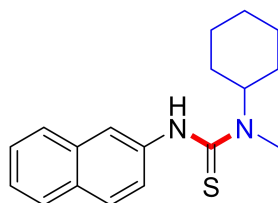
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2** (equiv.), **3a** (equiv.) in DMSO (2 mL) at 70 °C. <sup>b</sup>Yield refers to isolated products after column chromatography.

## Characterization of products 4 and 6



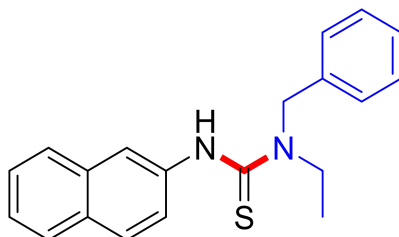
### 1,1-Diethyl-3-(naphthalen-2-yl)thiourea (4a)

Light yellow oil;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.15 (brs, 1H), 7.86 (t,  $J = 9.1$  Hz, 2H), 7.81 (d,  $J = 8.8$  Hz, 1H), 7.71 (s, 1H), 7.56 – 7.54 (m, 1H), 7.49 – 7.43 (m, 2H), 3.79 (q,  $J = 6.9$  Hz, 4H), 1.21 (t,  $J = 7.0$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.65, 138.72, 132.89, 130.57, 127.27, 127.13, 126.93, 126.68, 125.87, 125.10, 122.85, 44.75, 12.65 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{18}\text{N}_2\text{S}$ : 259.12687, found:259.12604.



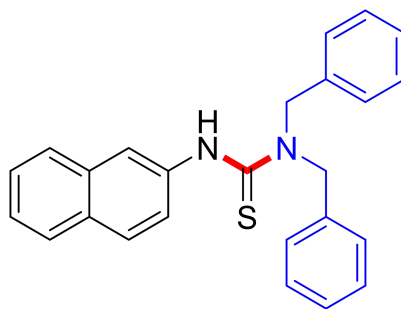
### 1-Cyclohexyl-1-methyl-3-(naphthalen-2-yl)thiourea (4b)

White solid; mp 138–139°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.19 (brs, 1H), 7.87 – 7.79 (m, 3H), 7.70 (d,  $J = 1.7$  Hz, 1H), 7.56 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.47 – 7.44 (m, 2H), 5.01 (s, 1H), 3.10 (s, 3H), 1.76 (dd,  $J = 32.2, 11.9$  Hz, 4H), 1.62 (d,  $J = 12.6$  Hz, 1H), 1.50 (qd,  $J = 12.2, 3.3$  Hz, 2H), 1.33 (dtd,  $J = 12.9, 9.9, 3.2$  Hz, 2H), 1.13 (qt,  $J = 12.9, 3.5$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.02, 138.86, 132.93, 130.42, 127.27, 127.08, 126.74, 126.35, 125.89, 124.98, 121.94, 58.62, 32.33, 29.15, 25.23, 24.87 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{18}\text{H}_{22}\text{N}_2\text{S}$ : 299.15817, found:299.15738.



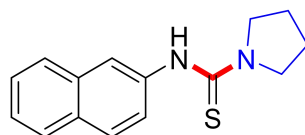
### 1-Benzyl-1-ethyl-3-(naphthalen-2-yl)thiourea (4c)

Light yellow oil;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.43 (brs, 1H), 7.88 – 7.82 (m, 3H), 7.74 (s, 1H), 7.57 (dd,  $J = 8.6, 1.1$  Hz, 1H), 7.50 – 7.44 (m, 2H), 7.41 – 7.38 (m, 4H), 7.29 (t,  $J = 6.2$  Hz, 1H), 5.18 (s, 2H), 3.76 (d,  $J = 6.8$  Hz, 2H), 1.18 (t,  $J = 6.9$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.21, 138.67, 137.50, 132.85, 130.62, 128.30, 127.25, 127.13, 127.05, 126.96, 126.78, 126.70, 125.88, 125.13, 122.81, 53.12, 44.43, 12.30 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{20}\text{H}_{20}\text{N}_2\text{S}$ : 321.14252, found:321.14169.



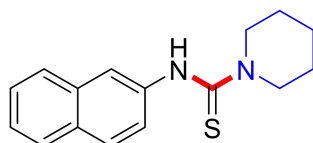
**1,1-Dibenzyl-3-(naphthalen-2-yl)thiourea (4d)**

White solid; mp 120–121°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.67 (brs, 1H), 7.88 – 7.82 (m, 3H), 7.71 (d,  $J = 1.8$  Hz, 1H), 7.52 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 (t,  $J = 7.5$  Hz, 4H), 7.35 – 7.29 (m, 6H), 5.11 (s, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  182.59, 138.56, 136.82, 132.84, 130.66, 128.47, 127.30, 127.19, 127.13, 126.99, 126.97, 126.45, 125.99, 125.26, 122.65, 52.81 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{25}\text{H}_{22}\text{N}_2\text{S}$ : 383.15817, found: 383.15723.



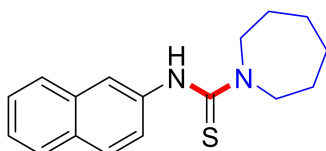
***N*-(naphthalen-2-yl)pyrrolidine-1-carbothioamide (4e)**

White solid; mp 124–125°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.13 (brs, 1H), 7.87 (d,  $J = 7.8$  Hz, 1H), 7.84 – 7.81 (m, 3H), 7.65 (dd,  $J = 8.7, 2.0$  Hz, 1H), 7.49 – 7.43 (m, 2H), 3.67 (s, 4H), 1.94 (s, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  177.60, 138.31, 132.83, 130.38, 127.23, 127.07, 126.72, 126.01, 125.84, 124.93, 121.82, 49.12, 24.84 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{16}\text{N}_2\text{S}$ : 257.11122, found: 257.11041.



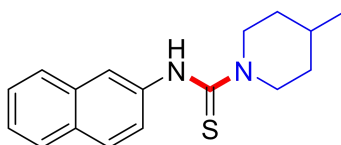
***N*-(naphthalen-2-yl)piperidine-1-carbothioamide (4f)**

White solid; mp 138–139°C;  $R_f = 0.4$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.44 (brs, 1H), 7.86 – 7.79 (m, 3H), 7.67 (d,  $J = 1.8$  Hz, 1H), 7.52 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.45 (dtd,  $J = 14.6, 6.9, 1.3$  Hz, 2H), 3.91 – 3.89 (m, 4H), 1.66 – 1.63 (m, 2H), 1.58 (t,  $J = 7.4$  Hz, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.78, 138.95, 132.98, 130.23, 127.27, 127.04, 126.88, 125.92, 125.65, 124.86, 120.95, 49.19, 25.41, 23.82 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{16}\text{H}_{18}\text{N}_2\text{S}$ : 271.12687, found: 271.12604.



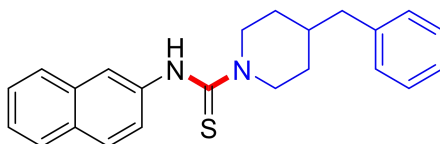
***N*-(naphthalen-2-yl)azepane-1-carbothioamide (4g)**

White solid; mp 140–141°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.18 (brs, 1H), 7.85 (t,  $J = 9.1$  Hz, 2H), 7.81 (d,  $J = 8.7$  Hz, 1H), 7.70 (s, 1H), 7.55 (dd,  $J = 8.7, 1.5$  Hz, 1H), 7.46 (dt,  $J = 15.0, 6.8$  Hz, 2H), 3.91 (s, 4H), 1.79 (s, 4H), 1.56 (s, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.66, 138.79, 132.87, 130.46, 127.21, 127.04, 126.65, 126.61, 125.80, 124.96, 122.34, 50.64, 26.83, 26.14 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$ : 285.14252, found: 285.14163.



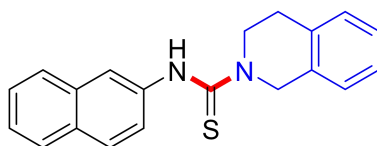
**4-Methyl-*N*-(naphthalen-2-yl)piperidine-1-carbothioamide (4h)**

White solid; mp 127–128°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.45 (brs, 1H), 7.86 – 7.79 (m, 3H), 7.67 (d,  $J = 1.8$  Hz, 1H), 7.52 (dd,  $J = 8.7, 2.1$  Hz, 1H), 7.45 (dtd,  $J = 14.6, 6.9, 1.3$  Hz, 2H), 4.74 (d,  $J = 13.0$  Hz, 2H), 3.11 – 3.05 (m, 2H), 1.69 (d,  $J = 9.8$  Hz, 3H), 1.16 (qd,  $J = 13.6, 3.3$  Hz, 2H), 0.94 (d,  $J = 6.1$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.79, 138.93, 132.97, 130.24, 127.27, 127.04, 126.88, 125.92, 125.64, 124.87, 120.96, 48.44, 33.57, 30.21, 21.36 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$ : 285.14252, found: 285.14188.



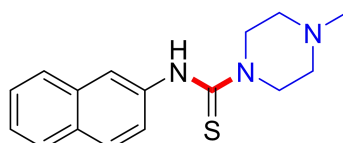
**4-Benzyl-*N*-(naphthalen-2-yl)piperidine-1-carbothioamide (4i)**

White solid; mp 133–134°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.45 (brs, 1H), 7.86 – 7.78 (m, 3H), 7.66 (d,  $J = 1.8$  Hz, 1H), 7.52 (dd,  $J = 8.8, 2.1$  Hz, 1H), 7.44 (dtd,  $J = 14.7, 6.9, 1.3$  Hz, 2H), 7.30 (dd,  $J = 9.6, 5.4$  Hz, 2H), 7.21 – 7.18 (m, 3H), 4.75 (d,  $J = 13.0$  Hz, 2H), 3.04 (td,  $J = 13.3, 2.0$  Hz, 2H), 2.56 (d,  $J = 7.1$  Hz, 2H), 1.87 (ddt,  $J = 14.8, 7.6, 3.7$  Hz, 1H), 1.64 (d,  $J = 11.0$  Hz, 2H), 1.27 – 1.19 (m, 2H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.75, 139.94, 138.91, 132.96, 130.24, 128.94, 128.09, 127.27, 127.04, 126.88, 125.92, 125.76, 125.65, 124.88, 120.98, 48.30, 41.80, 37.19, 31.46 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{23}\text{H}_{24}\text{N}_2\text{S}$ : 361.17382, found: 361.17282.



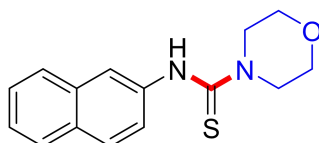
#### ***N*-(naphthalen-2-yl)-3,4-dihydroisoquinoline-2(1*H*)-carbothioamide (4j)**

White solid; mp 169–170°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.57 (brs, 1H), 7.87–7.81 (m, 3H), 7.72 (s, 1H), 7.57 (dd,  $J = 8.7, 1.8$  Hz, 1H), 7.49–7.43 (m, 2H), 7.27–7.20 (m, 4H), 5.08 (s, 2H), 4.11 (t,  $J = 5.8$  Hz, 2H), 2.98 (t,  $J = 5.8$  Hz, 2H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.01, 138.65, 134.96, 133.43, 132.95, 130.44, 128.05, 127.30, 127.11, 126.94, 126.63, 126.18, 125.96, 125.04, 121.68, 50.01, 45.94, 28.10 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+ \text{C}_{20}\text{H}_{18}\text{N}_2\text{S}$ : 319.12687, found: 319.12619.



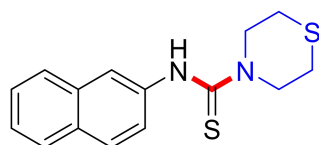
#### **4-Methyl-*N*-(naphthalen-2-yl)piperazine-1-carbothioamide (4k)**

Light yellow oil;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.55 (brs, 1H), 7.86–7.80 (m, 3H), 7.68 (s, 1H), 7.52 (dd,  $J = 8.7, 1.6$  Hz, 1H), 7.45 (dt,  $J = 20.7, 6.9$  Hz, 2H), 3.92 (s, 4H), 2.40–2.39 (m, 4H), 2.22 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.51, 138.69, 132.94, 130.31, 127.26, 127.05, 126.95, 125.94, 125.55, 124.94, 121.15, 54.16, 47.88, 45.26 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+ \text{C}_{16}\text{H}_{19}\text{N}_3\text{S}$ : 286.13777, found: 286.13702.



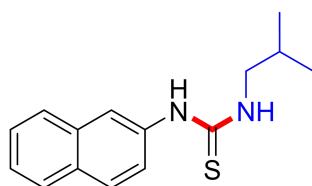
#### ***N*-(naphthalen-2-yl)morpholine-4-carbothioamide (4l)**

White solid; mp 153–154°C;  $R_f = 0.3$  (30% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.60 (brs, 1H), 7.87–7.81 (m, 3H), 7.70 (s, 1H), 7.54 (dd,  $J = 8.7, 1.9$  Hz, 1H), 7.45 (dd,  $J = 16.5, 7.8$  Hz, 2H), 3.93–3.92 (m, 4H), 3.69–3.67 (m, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.81, 138.60, 132.95, 130.39, 127.31, 127.12, 127.03, 126.00, 125.61, 125.05, 121.32, 65.70, 48.43 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+ \text{C}_{15}\text{H}_{16}\text{N}_2\text{OS}$ : 273.10613, found: 273.10532.



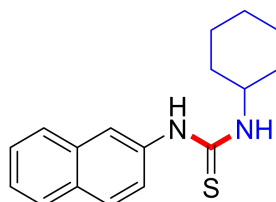
#### ***N*-(naphthalen-2-yl)thiomorpholine-4-carbothioamide (4m)**

White solid; mp 141–142°C;  $R_f = 0.3$  (30% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.56 (brs, 1H), 7.87–7.81 (m, 3H), 7.69 (s, 1H), 7.52 (dd,  $J = 8.7, 1.6$  Hz, 1H), 7.46 (dt,  $J = 14.9, 6.8$  Hz, 2H), 4.24–4.23 (m,  $J = 4.4$  Hz, 4H), 2.73–2.71 (m, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  181.22, 138.62, 132.93, 130.48, 127.30, 127.12, 126.95, 126.03, 125.98, 125.10, 121.81, 50.93, 26.29 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+ \text{C}_{15}\text{H}_{16}\text{N}_2\text{S}_2$ : 289.08329, found: 289.08252.



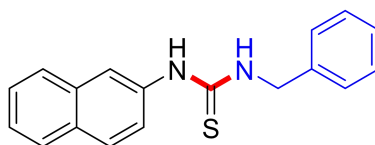
#### 1-Isobutyl-3-(naphthalen-2-yl)thiourea (4n)

White solid; mp 127–128°C;  $R_f = 0.5$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.69 (brs, 1H), 8.01 (brs, 1H), 7.90 – 7.82 (m, 4H), 7.56 (d,  $J = 8.4$  Hz, 1H), 7.45 (dt,  $J = 14.7, 7.1$  Hz, 2H), 3.36 (s, 2H), 1.99 – 1.91 (m, 1H), 0.93 (d,  $J = 6.7$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.72, 136.96, 133.09, 130.11, 127.83, 127.26, 127.11, 126.08, 124.80, 123.31, 119.07, 51.22, 27.39, 20.05 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{18}\text{N}_2\text{S}$ : 259.12687, found: 259.12628.



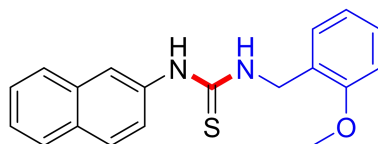
#### 1-Cyclohexyl-3-(naphthalen-2-yl)thiourea (4o)

White solid; mp 140–141°C;  $R_f = 0.4$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.55 (brs, 1H), 8.02 (brs, 1H), 7.85 – 7.80 (m, 3H), 7.76 (d,  $J = 5.0$  Hz, 1H), 7.55 (dd,  $J = 8.7, 1.4$  Hz, 1H), 7.48 – 7.45 (m, 1H), 7.42 (t,  $J = 7.2$  Hz, 1H), 4.14 (s, 1H), 1.95 – 1.93 (m, 2H), 1.70 (dd,  $J = 9.4, 3.5$  Hz, 2H), 1.57 (d,  $J = 13.0$  Hz, 1H), 1.27 (ddd,  $J = 24.4, 16.8, 7.3$  Hz, 4H), 1.18 (dd,  $J = 17.1, 6.3$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.28, 137.13, 133.06, 130.01, 127.67, 127.24, 127.08, 126.06, 124.72, 123.21, 118.76, 52.06, 31.71, 25.03, 24.38 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$ : 285.14252, found: 285.14160.



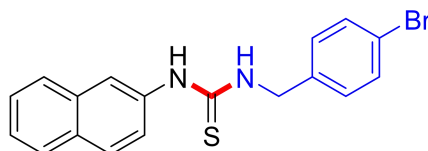
#### 1-Benzyl-3-(naphthalen-2-yl)thiourea (4p)

White solid; mp 145–146°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.83 (brs, 1H), 8.31 (brs, 1H), 7.98 (s, 1H), 7.87 (d,  $J = 8.5$  Hz, 2H), 7.83 (d,  $J = 8.1$  Hz, 1H), 7.54 (dd,  $J = 8.8, 2.0$  Hz, 1H), 7.48 (t,  $J = 6.9$  Hz, 1H), 7.44 (t,  $J = 6.9$  Hz, 1H), 7.38 – 7.34 (m, 4H), 7.27 (t,  $J = 6.5$  Hz, 1H), 4.78 (d,  $J = 5.1$  Hz, 2H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.92, 138.85, 136.70, 133.08, 130.27, 128.14, 127.97, 127.32, 127.29, 127.20, 126.75, 126.15, 124.98, 123.57, 119.77, 47.15 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{18}\text{H}_{16}\text{N}_2\text{S}$ : 293.11122, found: 293.11050.



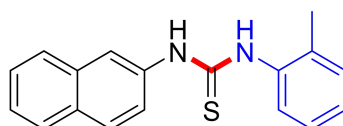
**1-(2-Methoxybenzyl)-3-(naphthalen-2-yl)thiourea (4q)**

White solid; mp 133–134°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.85 (brs, 1H), 8.06 (d,  $J = 24.9$  Hz, 2H), 7.84 (dd,  $J = 21.0, 8.3$  Hz, 3H), 7.56 (dd,  $J = 8.8, 1.9$  Hz, 1H), 7.46 (dt,  $J = 28.0, 6.9$  Hz, 2H), 7.29 – 7.26 (m, 2H), 7.02 – 7.01 (m, 1H), 6.95 (t,  $J = 7.4$  Hz, 1H), 4.71 (d,  $J = 4.1$  Hz, 2H), 3.83 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.83, 156.72, 136.90, 133.08, 130.19, 128.27, 128.21, 127.90, 127.29, 127.15, 126.14, 126.05, 124.89, 123.38, 120.03, 119.29, 110.45, 55.24, 42.74 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{19}\text{H}_{18}\text{N}_2\text{OS}$ : 323.12178, found: 323.12100.



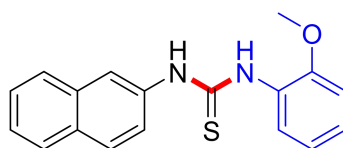
**1-(4-Bromobenzyl)-3-(naphthalen-2-yl)thiourea (4r)**

White solid; mp 122–123°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.88 (brs, 1H), 8.35 (brs, 1H), 7.95 (s, 1H), 7.86 (dd,  $J = 15.0, 8.3$  Hz, 3H), 7.55 – 7.43 (m, 5H), 7.32 (d,  $J = 8.2$  Hz, 2H), 4.74 (d,  $J = 5.0$  Hz, 2H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.98, 138.51, 136.52, 133.08, 130.94, 130.33, 129.50, 128.04, 127.29, 127.24, 126.16, 125.05, 123.62, 120.04, 119.65, 46.43 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{18}\text{H}_{15}\text{BrN}_2\text{S}$ : 371.02173, found: 371.02121.



**1-(Naphthalen-2-yl)-3-(o-tolyl)thiourea (4s)**

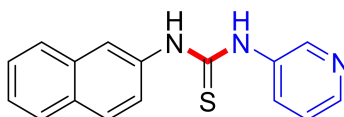
White solid; mp 153–154°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.88 (brs, 1H), 9.47 (brs, 1H), 8.01 (s, 1H), 7.86 (t,  $J = 9.2$  Hz, 3H), 7.63 (dd,  $J = 8.7, 1.8$  Hz, 1H), 7.47 (dt,  $J = 20.1, 6.8$  Hz, 2H), 7.30 (d,  $J = 7.3$  Hz, 1H), 7.26 (d,  $J = 7.2$  Hz, 1H), 7.22 – 7.16 (m, 2H), 2.30 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.49, 137.67, 137.03, 134.72, 133.00, 130.35, 130.21, 127.88, 127.68, 127.28, 127.22, 126.37, 126.09, 125.98, 125.02, 123.95, 120.31, 17.77 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{18}\text{H}_{16}\text{N}_2\text{S}$ : 293.11122, found: 293.11047.





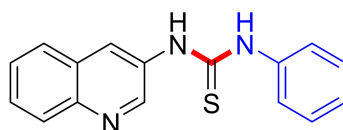
### 1-(2-Methoxyphenyl)-3-(naphthalen-2-yl)thiourea (4t)

White solid; mp 120–121°C;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.14 (s, 1H), 9.29 (s, 1H), 8.10 (s, 1H), 7.94 (d,  $J = 7.7$  Hz, 1H), 7.87 (t,  $J = 10.1$  Hz, 3H), 7.65 (dd,  $J = 11.8, 4.4$  Hz, 1H), 7.47 (dt,  $J = 14.5, 7.0$  Hz, 2H), 7.17 (t,  $J = 7.7$  Hz, 1H), 7.07 (d,  $J = 8.1$  Hz, 1H), 6.95 (t,  $J = 7.6$  Hz, 1H), 3.85 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.41, 151.76, 136.90, 132.98, 130.36, 127.70, 127.55, 127.31, 127.23, 126.15, 125.74, 125.64, 125.07, 123.82, 120.04, 119.70, 111.36, 55.60 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{18}\text{H}_{16}\text{N}_2\text{OS}$ : 309.09833, found: 309.10541



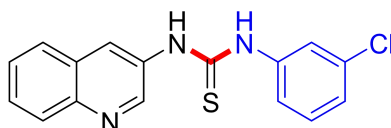
### 1-(Naphthalen-2-yl)-3-(pyridin-3-yl)thiourea (4u)

White solid; mp 123–124°C;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.25 (brs, 1H), 9.96 (brs, 1H), 8.65 (d,  $J = 2.1$  Hz, 1H), 8.34 (d,  $J = 3.9$  Hz, 1H), 8.00 – 7.97 (m, 2H), 7.90 – 7.86 (m, 3H), 7.61 (dd,  $J = 8.7, 1.8$  Hz, 1H), 7.48 (dt,  $J = 21.0, 6.9$  Hz, 2H), 7.38 (dd,  $J = 8.1, 4.7$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.40, 145.44, 145.22, 136.63, 136.29, 133.07, 131.45, 130.56, 127.98, 127.38, 127.35, 126.27, 125.30, 123.82, 123.05, 120.56 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{16}\text{H}_{13}\text{N}_3\text{S}$ : 280.09082, found: 280.09000.



### 1-Phenyl-3-(quinolin-3-yl)thiourea (4v)

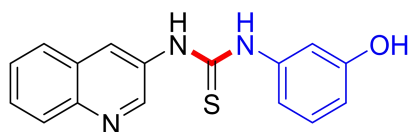
Light yellow oil;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.13 (brs, 1H), 10.08 (brs, 1H), 8.95 (d,  $J = 2.3$  Hz, 1H), 8.38 (d,  $J = 1.8$  Hz, 1H), 7.96 (dd,  $J = 21.3, 8.2$  Hz, 2H), 7.70 (t,  $J = 7.1$  Hz, 1H), 7.59 (t,  $J = 7.2$  Hz, 1H), 7.52 (d,  $J = 7.8$  Hz, 2H), 7.37 (t,  $J = 7.8$  Hz, 2H), 7.17 (t,  $J = 7.3$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.35, 148.69, 144.56, 138.99, 133.38, 128.46, 128.35, 127.72, 127.55, 127.46, 126.71, 124.69, 123.75 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{16}\text{H}_{13}\text{N}_3\text{S}$ : 280.09082, found: 280.09030.



### 1-(3-Chlorophenyl)-3-(quinolin-3-yl)thiourea (4w)

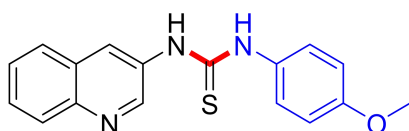
White solid; mp 137–138°C;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.24 (brs, 1H), 10.23 (brs, 1H), 8.95 (d,  $J = 2.4$  Hz, 1H), 8.38 (d,  $J = 1.9$  Hz, 1H), 7.99 (d,  $J = 8.4$  Hz, 1H), 7.95 (d,  $J = 8.0$  Hz, 1H), 7.72 – 7.69 (m, 2H), 7.59 (t,  $J = 7.3$  Hz, 1H), 7.45 (d,  $J = 8.5$  Hz, 1H), 7.39 (t,  $J = 8.0$  Hz, 1H), 7.22 (d,  $J = 7.9$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.48,

148.69, 144.72, 140.66, 133.12, 132.55, 130.04, 128.54, 128.41, 128.05, 127.63, 127.49, 126.80, 124.31, 123.17, 122.10 ppm; HRMS: calc. for  $[M+H]^+C_{16}H_{12}N_3S$ : 314.05185, found:314.05118.



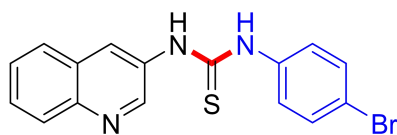
#### 1-(3-Hydroxyphenyl)-3-(quinolin-3-yl)thiourea (4x)

White solid; mp 150–151°C;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.07 (brs, 1H), 10.02 (brs, 1H), 9.53 (brs, 1H), 8.95 (s, 1H), 8.36 (s, 1H), 7.97 – 7.93 (m, 2H), 7.63 (d,  $J = 42.9$  Hz, 2H), 7.15 – 6.90 (m, 3H), 6.57 (s, 1H) ppm;  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  180.03, 157.47, 148.78, 144.56, 139.87, 133.50, 129.26, 128.37, 128.35, 127.71, 127.55, 127.47, 126.71, 114.07, 111.87, 110.46 ppm; HRMS: calc. for  $[M+H]^+C_{16}H_{13}N_3OS$ : 296.08573, found:296.08493.



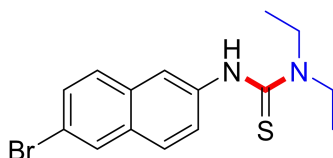
#### 1-(4-Methoxyphenyl)-3-(quinolin-3-yl)thiourea (4y)

Light yellow oil;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1H$  NMR (600 MHz, DMSO- $d_6$ )  $\delta$  9.95 (brs, 1H), 9.92 (brs, 1H), 8.94 (d,  $J = 2.3$  Hz, 1H), 8.36 (s, 1H), 7.97 (d,  $J = 8.4$  Hz, 1H), 7.93 (d,  $J = 8.0$  Hz, 1H), 7.69 (t,  $J = 7.2$  Hz, 1H), 7.58 (t,  $J = 7.3$  Hz, 1H), 7.37 (d,  $J = 8.8$  Hz, 2H), 6.94 (d,  $J = 8.9$  Hz, 2H), 3.76 (s, 3H) ppm;  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  180.58, 156.75, 148.82, 144.55, 133.52, 131.65, 128.37, 128.30, 127.71, 127.54, 127.47, 126.68, 126.06, 113.77, 55.16 ppm; HRMS: calc. for  $[M+H]^+C_{17}H_{15}N_3OS$ : 310.10138, found:310.10074.



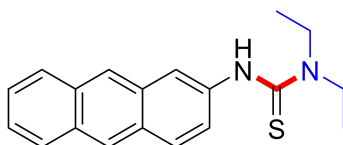
#### 1-(4-Bromophenyl)-3-(quinolin-3-yl)thiourea (4z)

White solid; mp  $> 340^\circ C$ ;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1H$  NMR (600 MHz, DMSO- $d_6$ )  $\delta$  10.18 (brs, 1H), 10.17 (brs, 1H), 8.94 (d,  $J = 2.3$  Hz, 1H), 8.37 (s, 1H), 7.99 (d,  $J = 8.4$  Hz, 1H), 7.94 (d,  $J = 8.0$  Hz, 1H), 7.70 (t,  $J = 7.2$  Hz, 1H), 7.59 (t,  $J = 7.5$  Hz, 1H), 7.55 (d,  $J = 8.8$  Hz, 2H), 7.50 (d,  $J = 8.7$  Hz, 2H) ppm;  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  180.39, 148.66, 144.67, 138.48, 133.20, 131.26, 128.46, 128.39, 127.88, 127.59, 127.46, 126.76, 125.71, 116.74 ppm; HRMS: calc. for  $[M+H]^+C_{16}H_{12}BrN_3S$ : 358.00133, found:358.00070.



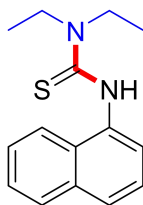
### 3-(6-Bromonaphthalen-2-yl)-1,1-diethylthiourea (4aa)

White solid; mp 132–133°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.17 (brs, 1H), 8.15 (s, 1H), 7.81 (dd,  $J = 17.3, 8.8$  Hz, 2H), 7.73 (s, 1H), 7.59 (t,  $J = 8.5$  Hz, 2H), 3.78 (q,  $J = 6.7$  Hz, 4H), 1.20 (t,  $J = 7.0$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.60, 139.31, 131.62, 131.39, 129.30, 129.10, 128.73, 127.88, 125.89, 122.53, 117.97, 44.76, 12.58 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{17}\text{BrN}_2\text{S}$ : 337.03738, found: 337.03632.



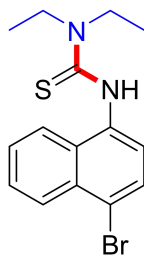
### 3-(Anthracen-2-yl)-1,1-diethylthiourea (4ab)

Yellow solid; mp 65–66°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.26 (brs, 1H), 8.50 (d,  $J = 12.9$  Hz, 2H), 8.08 – 8.02 (m, 2H), 7.96 (d,  $J = 9.0$  Hz, 1H), 7.83 (s, 1H), 7.62 (dd,  $J = 9.0, 1.8$  Hz, 1H), 7.49 – 7.46 (m, 2H), 3.81 (dd,  $J = 13.7, 6.7$  Hz, 4H), 1.23 (t,  $J = 7.0$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.62, 138.31, 131.24, 131.18, 130.72, 129.17, 127.88, 127.62, 127.32, 126.63, 125.49, 125.36, 124.97, 124.87, 121.30, 44.78, 12.61 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{19}\text{H}_{20}\text{N}_2\text{S}$ : 309.14252, found: 309.14151.



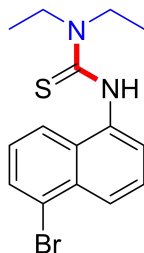
### 1,1-Diethyl-3-(naphthalen-1-yl)thiourea (4ac)

White solid; mp 60–61°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.16 (brs, 1H), 7.95 – 7.93 (m, 1H), 7.84 – 7.79 (m, 2H), 7.51 (dt,  $J = 9.2, 6.3$  Hz, 3H), 7.32 (d,  $J = 7.2$  Hz, 1H), 3.83 (dd,  $J = 13.3, 6.4$  Hz, 4H), 1.26 (t,  $J = 6.9$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.59, 137.47, 133.64, 131.11, 127.76, 126.50, 126.29, 125.60, 125.58, 125.31, 123.63, 44.72, 12.74 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{18}\text{N}_2\text{S}$ : 259.12687, found: 259.12604.



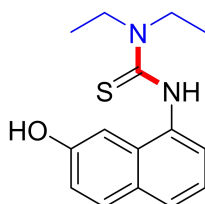
### 3-(4-Bromonaphthalen-1-yl)-1,1-diethylthiourea (4ad)

White solid; mp 163–164°C;  $R_f = 0.3$  (30% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.20 (brs, 1H), 8.14 (d,  $J = 8.4$  Hz, 1H), 7.86 (dd,  $J = 16.0, 8.1$  Hz, 2H), 7.68 (t,  $J = 7.3$  Hz, 1H), 7.62 (t,  $J = 7.4$  Hz, 1H), 7.25 (d,  $J = 7.9$  Hz, 1H), 3.82 (d,  $J = 6.8$  Hz, 4H), 1.25 (t,  $J = 6.9$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.54, 137.92, 132.45, 131.44, 129.41, 127.48, 127.34, 126.64, 126.39, 124.51, 119.46, 44.81, 12.71 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{17}\text{BrN}_2\text{S}$ : 337.03738, found: 337.03668.



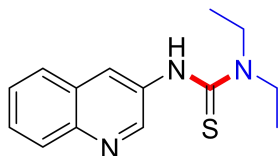
### 3-(5-Bromonaphthalen-1-yl)-1,1-diethylthiourea (4ae)

White solid; mp 135–136°C;  $R_f = 0.3$  (30% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.24 (brs, 1H), 8.08 (d,  $J = 8.5$  Hz, 1H), 7.87 (dd,  $J = 12.8, 7.9$  Hz, 2H), 7.68 – 7.65 (m, 1H), 7.44 (t,  $J = 7.7$  Hz, 2H), 3.82 – 3.79 (m, 4H), 1.26 (t,  $J = 6.9$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.62, 138.18, 132.64, 131.69, 129.83, 127.59, 127.11, 126.26, 124.81, 124.13, 121.71, 44.74, 12.72 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{17}\text{BrN}_2\text{S}$ : 337.03738, found: 337.03662.



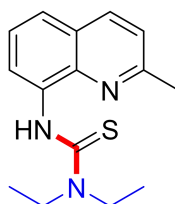
### 1,1-Diethyl-3-(7-hydroxynaphthalen-1-yl)thiourea (4af)

White solid; mp 162–163°C;  $R_f = 0.3$  (50% EtOAc in petroleum ether);  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.75 (brs, 1H), 9.00 (brs, 1H), 7.77 (d,  $J = 8.6$  Hz, 1H), 7.69 (d,  $J = 8.0$  Hz, 1H), 7.24 (t,  $J = 7.6$  Hz, 1H), 7.19 (d,  $J = 7.1$  Hz, 1H), 7.05 (d,  $J = 8.2$  Hz, 2H), 3.81 (d,  $J = 6.8$  Hz, 4H), 1.25 (t,  $J = 6.9$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.45, 155.16, 135.82, 132.86, 129.39, 128.43, 126.88, 126.12, 121.82, 118.31, 104.96, 44.60, 12.78 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{18}\text{N}_2\text{OS}$ : 275.12178, found: 275.12091.



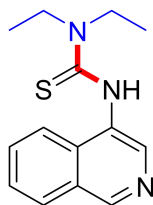
#### 1,1-Diethyl-3-(quinolin-3-yl)thiourea (4ag)

White solid; mp 103–104°C;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.32 (brs, 1H), 8.89 (d,  $J = 2.2$  Hz, 1H), 8.09 (s, 1H), 7.96 (dd,  $J = 20.9, 8.2$  Hz, 2H), 7.69 (t,  $J = 7.3$  Hz, 1H), 7.57 (t,  $J = 7.4$  Hz, 1H), 3.81 – 3.78 (m, 4H), 1.22 (t,  $J = 7.0$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  179.85, 150.99, 144.57, 134.87, 129.70, 128.31, 127.49, 127.40, 126.45, 44.91, 12.54 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{14}\text{H}_{17}\text{N}_3\text{S}$ : 260.12212, found: 260.12164.



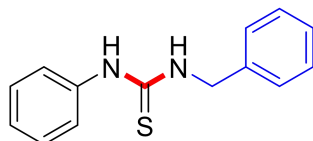
#### 1,1-Diethyl-3-(2-methylquinolin-8-yl)thiourea (4ah)

Light red oil;  $R_f = 0.3$  (50% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.21 (brs, 1H), 9.15 (d,  $J = 7.7$  Hz, 1H), 8.27 (d,  $J = 8.4$  Hz, 1H), 7.57 (d,  $J = 8.0$  Hz, 1H), 7.48 (t,  $J = 8.1$  Hz, 2H), 3.85 (q,  $J = 6.9$  Hz, 4H), 2.67 (s, 3H), 1.34 (t,  $J = 6.8$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  176.43, 156.98, 138.00, 136.76, 134.99, 125.63, 125.26, 122.55, 120.85, 116.69, 44.85, 24.68, 12.38 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{19}\text{N}_3\text{S}$ : 274.13777, found: 274.13705.



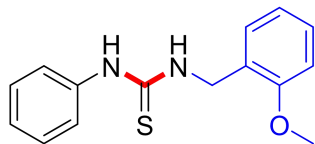
#### 1,1-Diethyl-3-(isoquinolin-4-yl)thiourea (4ai)

White solid; mp 111–112°C;  $R_f = 0.3$  (67% EtOAc in petroleum ether);  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.22 (brs, 1H), 9.21 (brs, 1H), 8.30 (s, 1H), 8.15 (d,  $J = 8.1$  Hz, 1H), 7.78 (d,  $J = 6.1$  Hz, 2H), 7.67 (t,  $J = 7.0$  Hz, 1H), 3.83 (dd,  $J = 13.1, 6.3$  Hz, 4H), 1.26 (t,  $J = 6.8$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.79, 150.22, 142.79, 133.82, 132.45, 130.08, 128.47, 127.41, 127.09, 122.75, 44.83, 12.66 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{14}\text{H}_{17}\text{N}_3\text{S}$ : 260.12212, found: 260.12152.



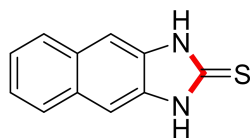
#### 1-Benzyl-3-phenylthiourea (4aj)

White solid; mp 139–140°C;  $R_f = 0.4$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.61 (brs, 1H), 8.16 (brs, 1H), 7.42 (d,  $J = 7.8$  Hz, 2H), 7.33 (dd,  $J = 11.2, 6.0$  Hz, 6H), 7.25 (dd,  $J = 6.0, 3.0$  Hz, 1H), 7.12 (t,  $J = 7.3$  Hz, 1H), 4.74 (d,  $J = 5.3$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.72, 139.07, 138.85, 128.47, 128.13, 127.30, 126.73, 124.13, 123.17, 47.06 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}$ : 243.09557, found: 243.09508.



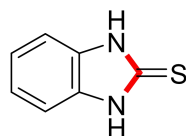
#### 1-(2-Methoxybenzyl)-3-phenylthiourea (4ak)

White solid; mp 111–112°C;  $R_f = 0.4$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.66 (brs, 1H), 7.94 (brs, 1H), 7.47 (d,  $J = 7.8$  Hz, 2H), 7.33 (t,  $J = 7.8$  Hz, 2H), 7.26 (dd,  $J = 13.4, 7.0$  Hz, 2H), 7.11 (t,  $J = 7.4$  Hz, 1H), 7.01 (d,  $J = 8.0$  Hz, 1H), 6.94 (t,  $J = 7.3$  Hz, 1H), 4.69 (d,  $J = 4.1$  Hz, 2H), 3.82 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  180.61, 156.71, 139.19, 128.42, 128.25, 128.20, 126.04, 124.01, 122.92, 120.01, 110.44, 55.22, 42.67 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{15}\text{H}_{16}\text{N}_2\text{OS}$ : 273.10613, found: 273.10541.



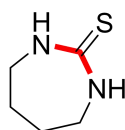
#### 1,3-Dihydro-2H-naphtho[2,3-d]imidazole-2-thione (6a)

White solid; mp 110–111°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.65 (brs, 2H), 7.93 (dd,  $J = 6.2, 3.3$  Hz, 2H), 7.56 (s, 2H), 7.37 (dd,  $J = 6.3, 3.2$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  172.02, 132.75, 129.61, 127.34, 124.01, 104.60 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_{11}\text{H}_8\text{N}_2\text{S}$ : 201.04862, found: 201.04810.



#### 1,3-Dihydro-2H-benzo[d]imidazole-2-thione (6b)

White solid; mp 310–311°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  12.52 (brs, 2H), 7.15 – 7.10 (m, 4H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ )  $\delta$  168.06, 132.12, 122.15, 109.32 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_7\text{H}_6\text{N}_2\text{S}$ : 151.03297, found: 151.03246.



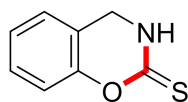
### 1,3-Diazepane-2-thione (6c)

White solid; mp 169–170°C;  $R_f = 0.4$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.77 (brs, 2H), 3.05 (s, 4H), 1.57 (s, 4H) ppm;  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  187.82, 44.66, 27.01 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_5\text{H}_{10}\text{N}_2\text{S}$ : 131.06427, found: 131.06387.



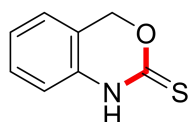
### 3,4-Dihydroquinazoline-2(1H)-thione (6d)

White solid; mp 215–216°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  10.36 (brs, 1H), 8.59 (brs, 1H), 7.15 (t,  $J = 7.5$  Hz, 1H), 7.08 (d,  $J = 7.3$  Hz, 1H), 6.94 (dd,  $J = 15.3$ , 7.7 Hz, 2H), 4.35 (s, 2H) ppm;  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  175.72, 135.12, 127.88, 125.80, 122.74, 117.31, 113.78, 42.68 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_8\text{H}_8\text{N}_2\text{S}$ : 165.04862, found: 165.04813.



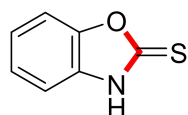
### 3,4-Dihydro-2H-benzo[e][1,3]oxazine-2-thione (6e)

White solid; mp 175–176°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.32 (brs, 1H), 7.33 (t,  $J = 7.6$  Hz, 1H), 7.26 (d,  $J = 7.4$  Hz, 1H), 7.19 (t,  $J = 7.4$  Hz, 1H), 7.10 (d,  $J = 8.1$  Hz, 1H), 4.42 (s, 2H) ppm;  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  181.82, 148.17, 128.83, 126.39, 124.97, 116.91, 115.26, 41.33 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_8\text{H}_7\text{NOS}$ : 166.03263, found: 166.03209.



### 1,4-Dihydro-2H-benzo[d][1,3]oxazine-2-thione (6f)

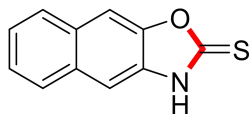
White solid; mp 104–105°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  12.15 (brs, 1H), 7.31 (t,  $J = 7.6$  Hz, 1H), 7.23 (d,  $J = 7.2$  Hz, 1H), 7.13 (t,  $J = 7.3$  Hz, 1H), 7.01 (d,  $J = 7.8$  Hz, 1H), 5.35 (s, 2H) ppm;  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  184.61, 133.28, 128.95, 124.48, 124.23, 118.60, 113.67, 68.35 ppm; HRMS: calc. for  $[\text{M}+\text{H}]^+\text{C}_8\text{H}_7\text{NOS}$ : 166.03263, found: 166.03218.



### Benzo[d]oxazole-2(3H)-thione (6g)

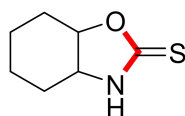
White solid; mp 184–185°C;  $R_f = 0.3$  (25% EtOAc in petroleum ether);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  13.87 (brs, 1H), 7.47 (d,  $J = 7.7$  Hz, 1H), 7.28 – 7.20 (m, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ )

$\delta$  180.01, 148.00, 131.06, 124.98, 123.61, 110.33, 109.82 ppm; HRMS: calc. for  $[M+H]^+C_7H_5NOS$ : 152.01698, found: 152.01645.



**Naphtho[2,3-*d*]oxazole-2(3*H*)-thione (6h)**

White solid; mp 236–237°C;  $R_f$  = 0.3 (25% EtOAc in petroleum ether);  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  14.03 (brs, 1H), 8.03 – 7.98 (m, 1H), 7.98 (s, 2H), 7.69 (s, 1H), 7.49 (p,  $J$  = 6.4 Hz, 2H) ppm;  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  181.56, 147.28, 130.95, 130.78, 129.81, 127.91, 127.59, 125.42, 125.12, 106.06, 105.64 ppm; HRMS: calc. for  $[M+H]^+C_{11}H_7NOS$ : 202.03263, found: 202.03210.

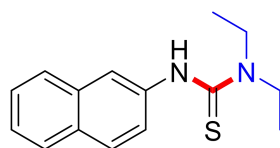


**Hexahydrobenzo[*d*]oxazole-2(3*H*)-thione (6i)**

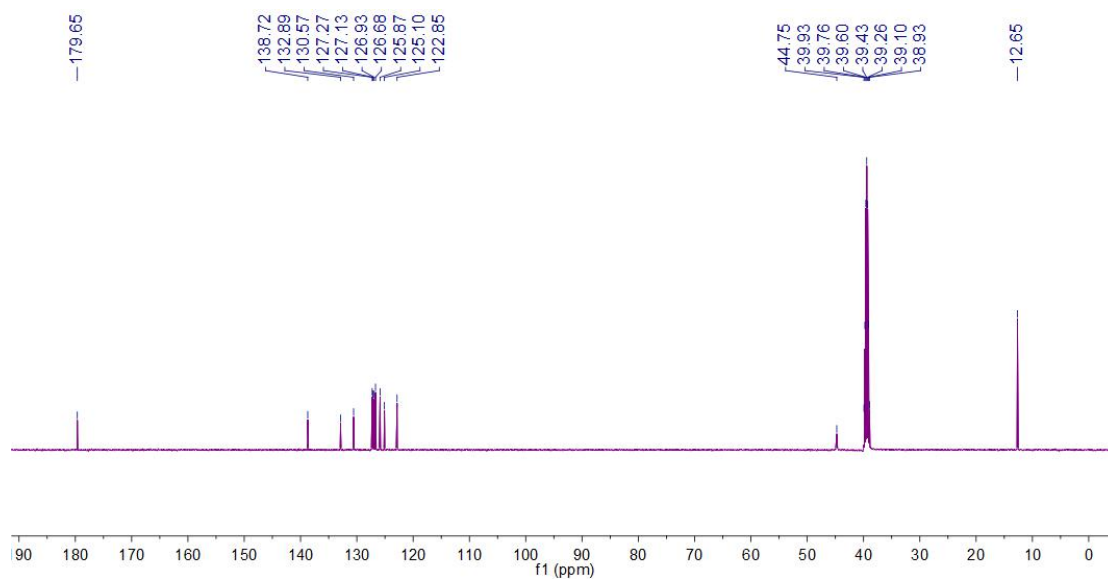
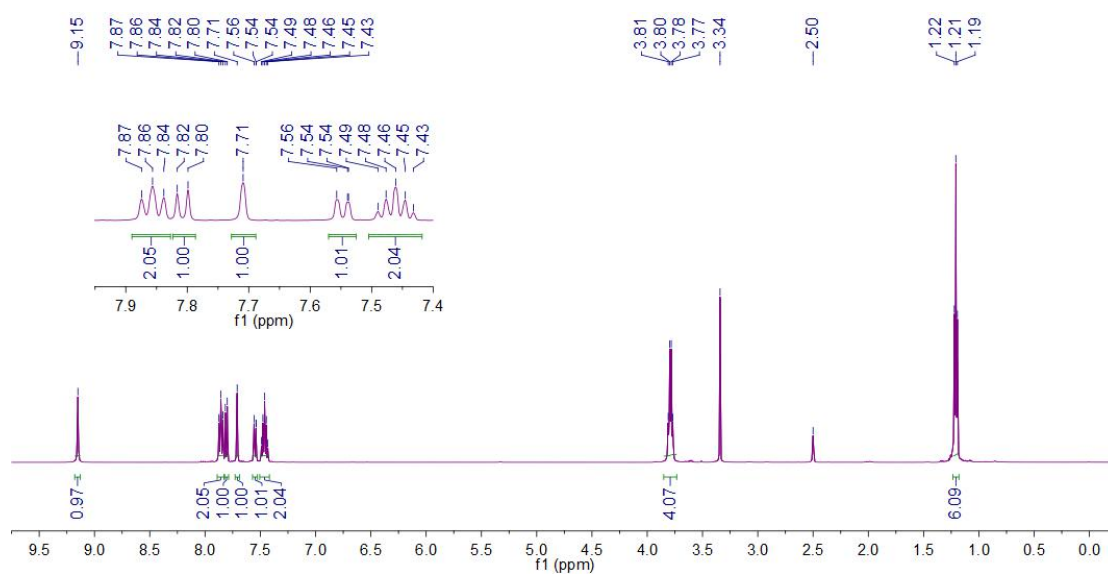
White solid; mp 140–141°C;  $R_f$  = 0.3 (25% EtOAc in petroleum ether);  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.10 (brs, 1H), 3.97 (t,  $J$  = 12.0 Hz, 1H), 3.38 – 3.32 (m, 1H), 2.12 (d,  $J$  = 10.6 Hz, 1H), 1.95 (d,  $J$  = 11.3 Hz, 1H), 1.79 (d,  $J$  = 11.8 Hz, 1H), 1.65 (dd,  $J$  = 25.8, 13.8 Hz, 2H), 1.33 (ddd,  $J$  = 30.4, 22.8, 12.4 Hz, 3H) ppm;  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$  190.44, 87.04, 61.89, 27.83, 27.79, 23.01, 22.78 ppm; HRMS: calc. for  $[M+H]^+C_7H_{11}NOS$ : 158.06393, found: 158.06343.

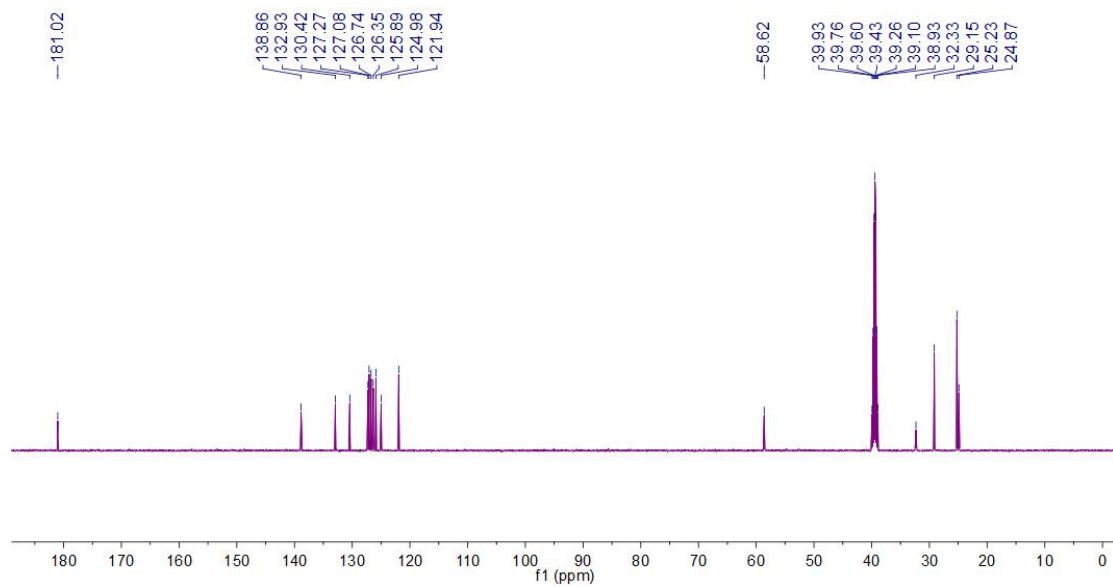
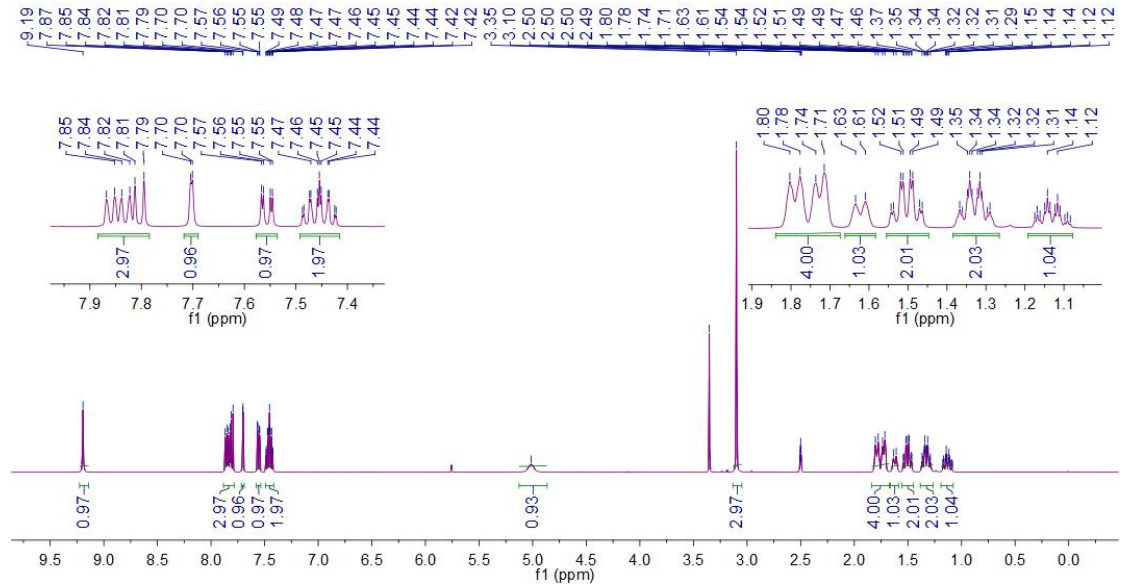
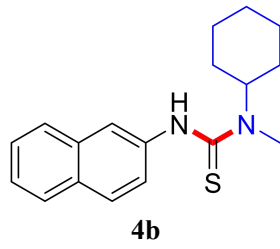


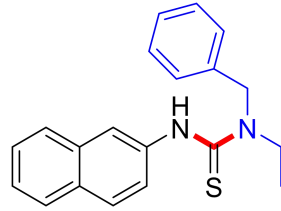
Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of products 4 and 6



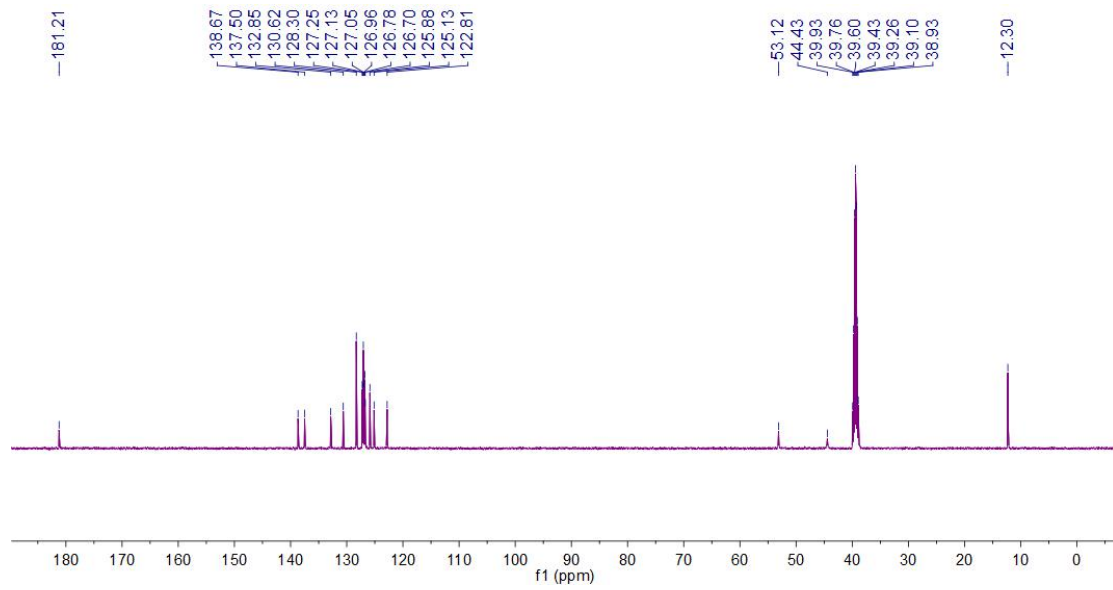
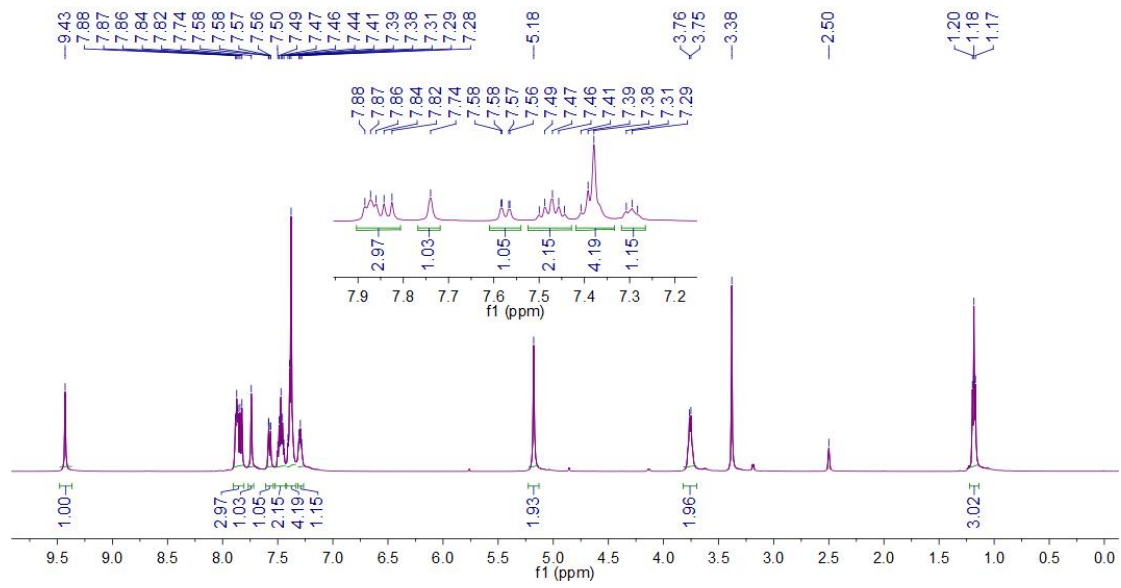
4a

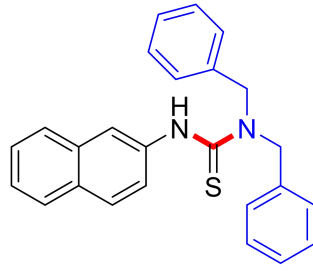




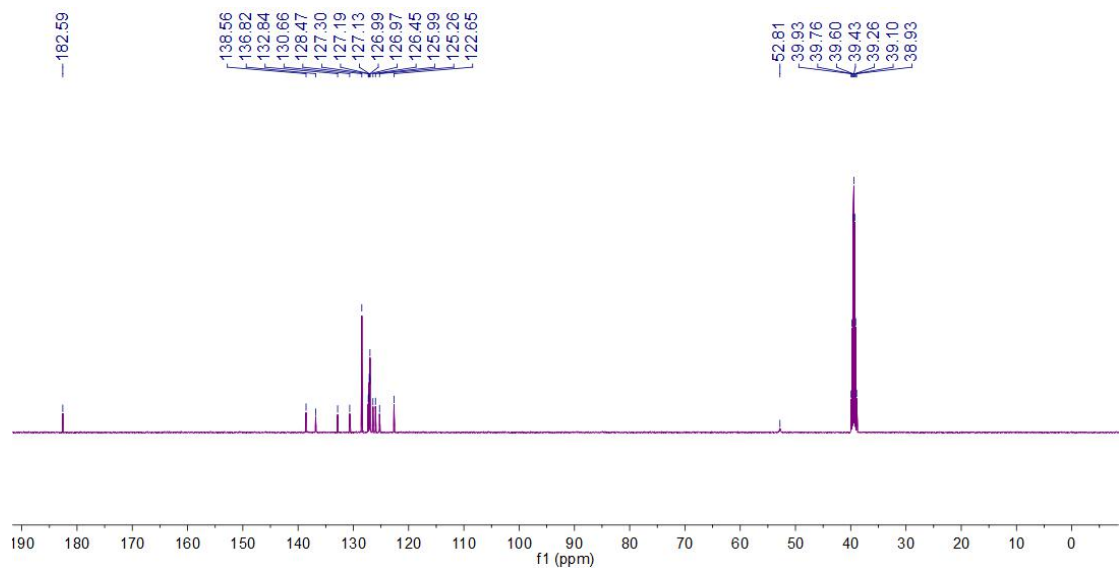
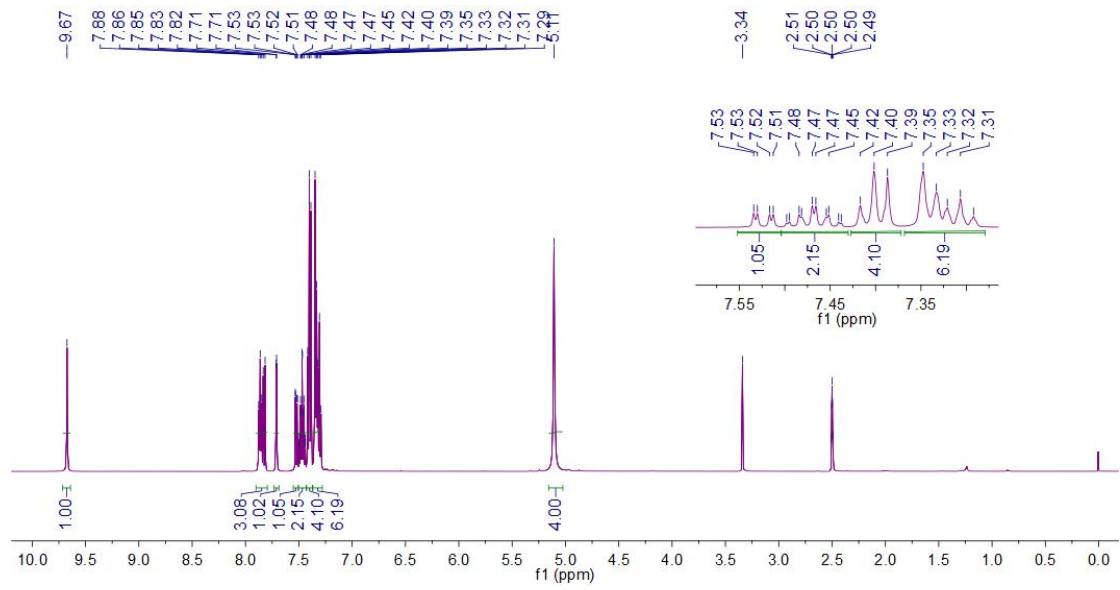


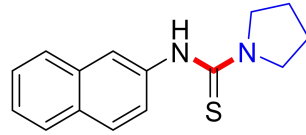
4c



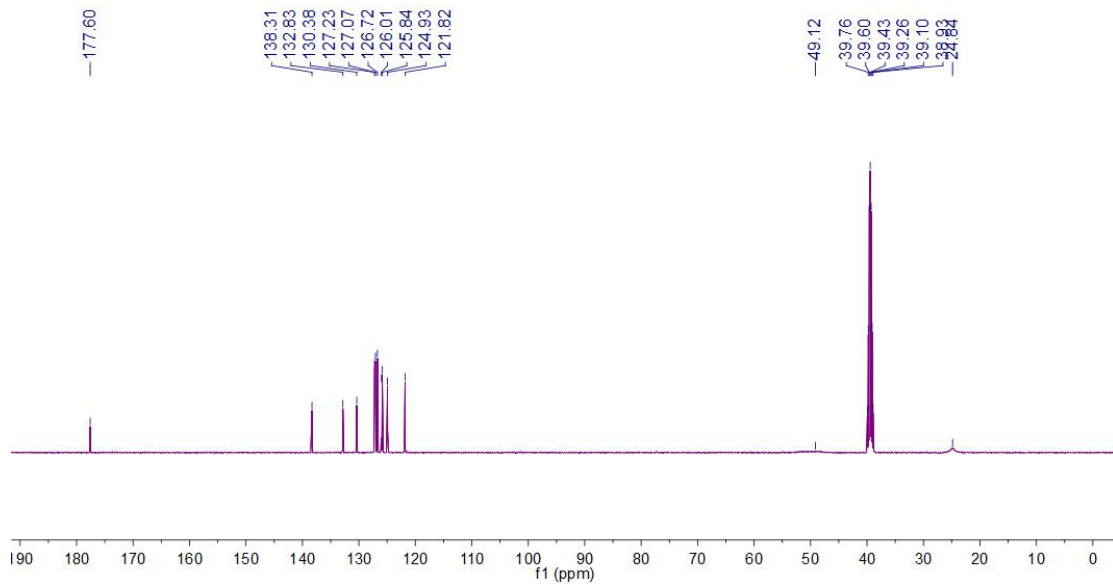
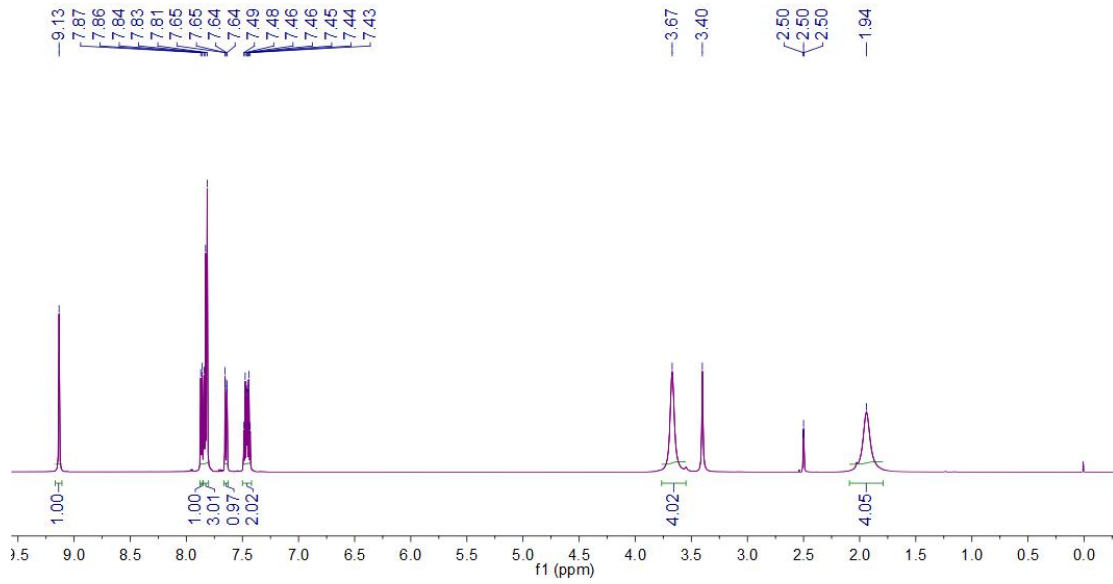


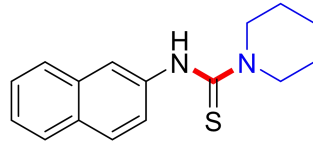
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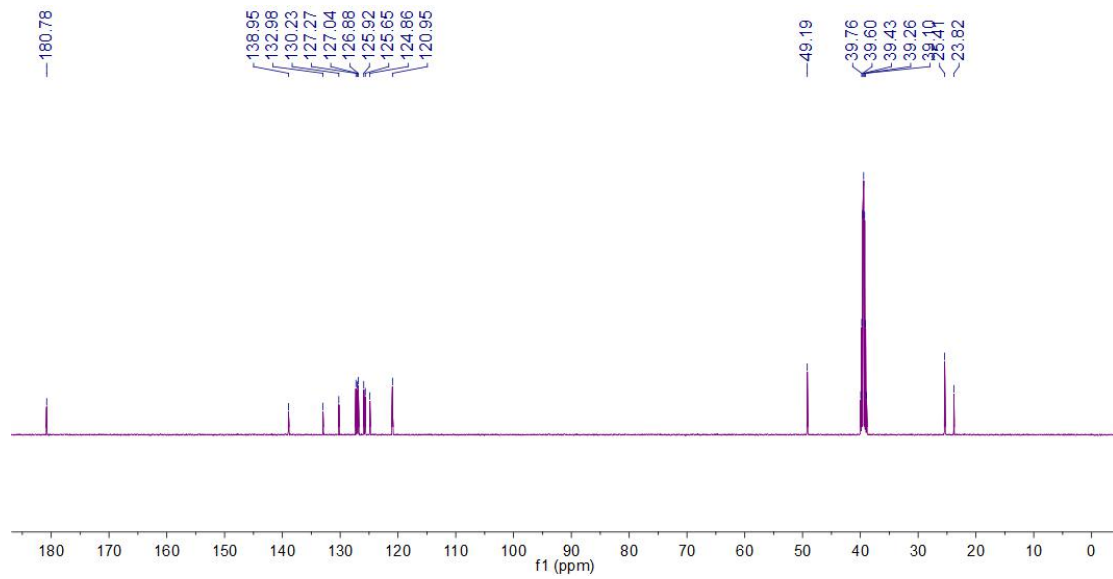
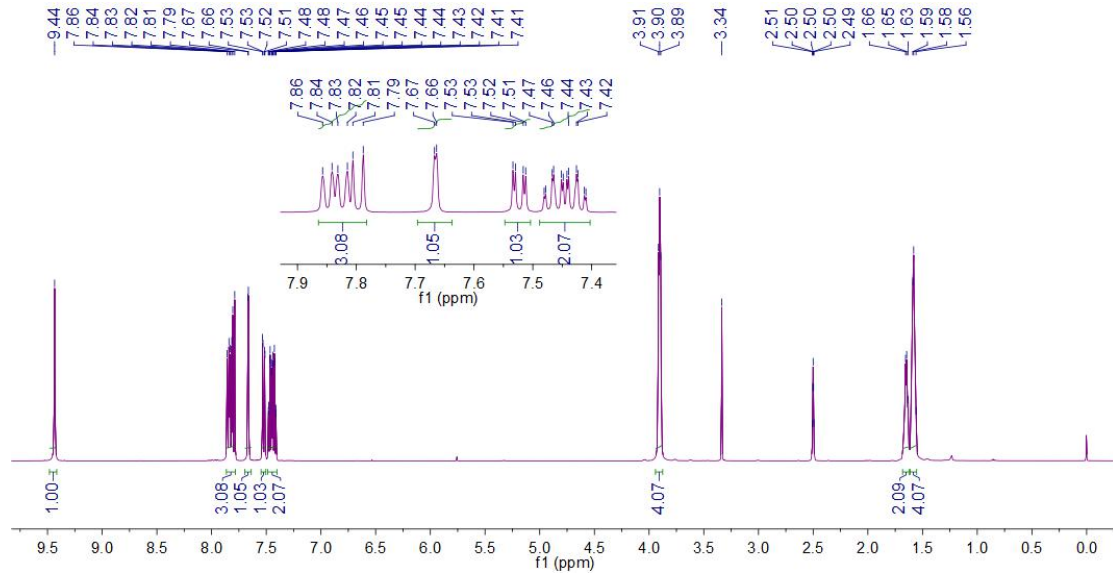


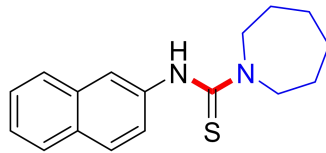
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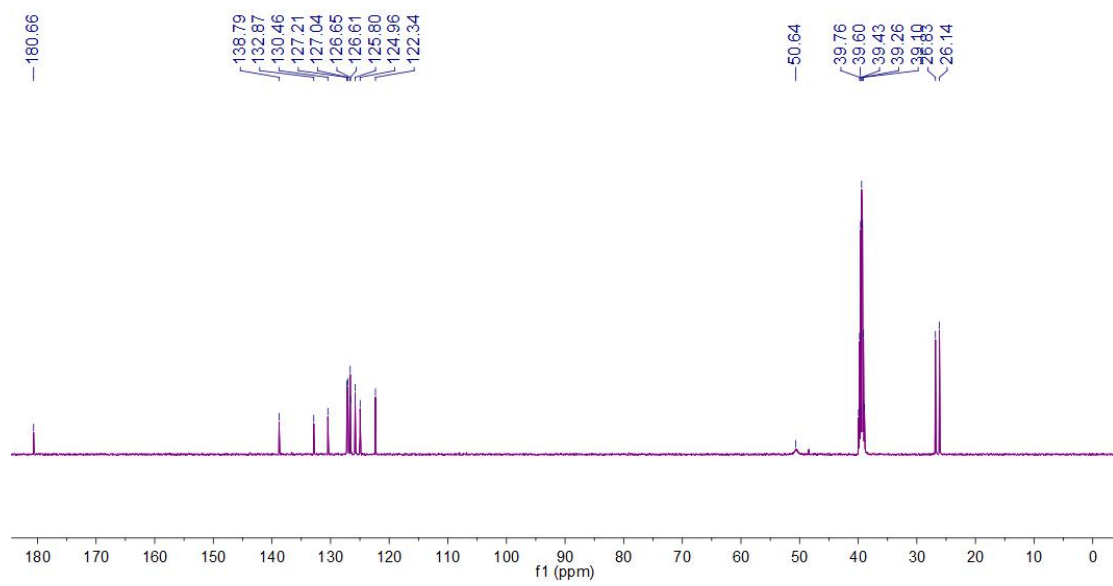
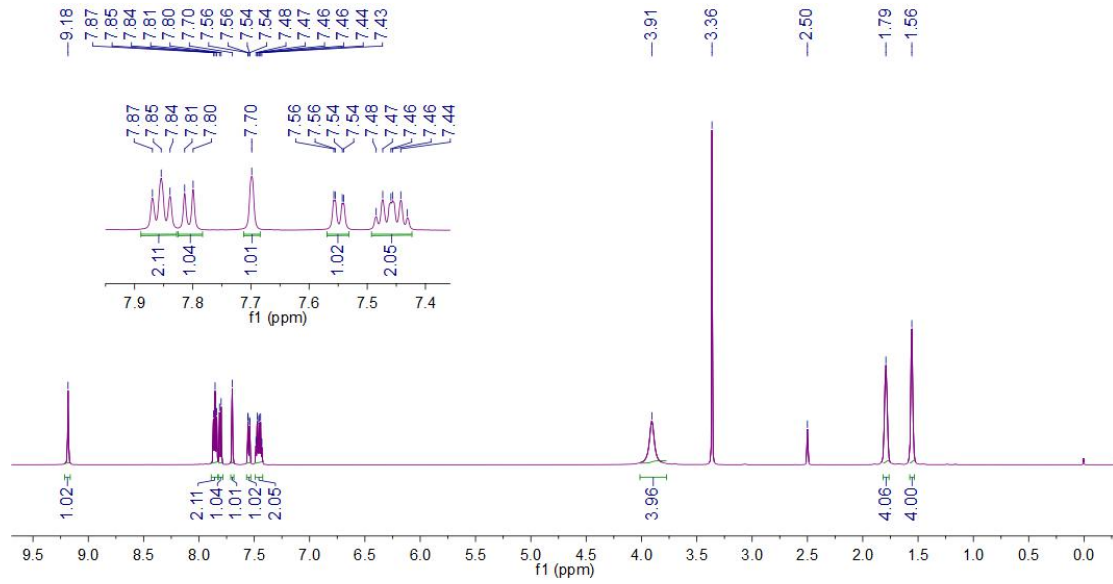


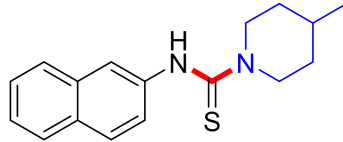
4f



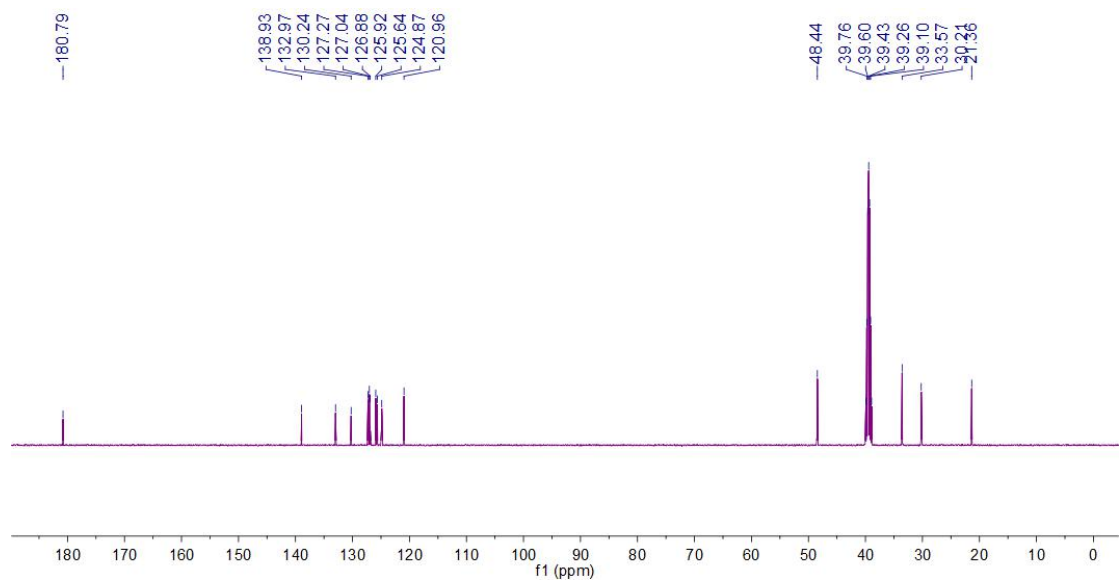
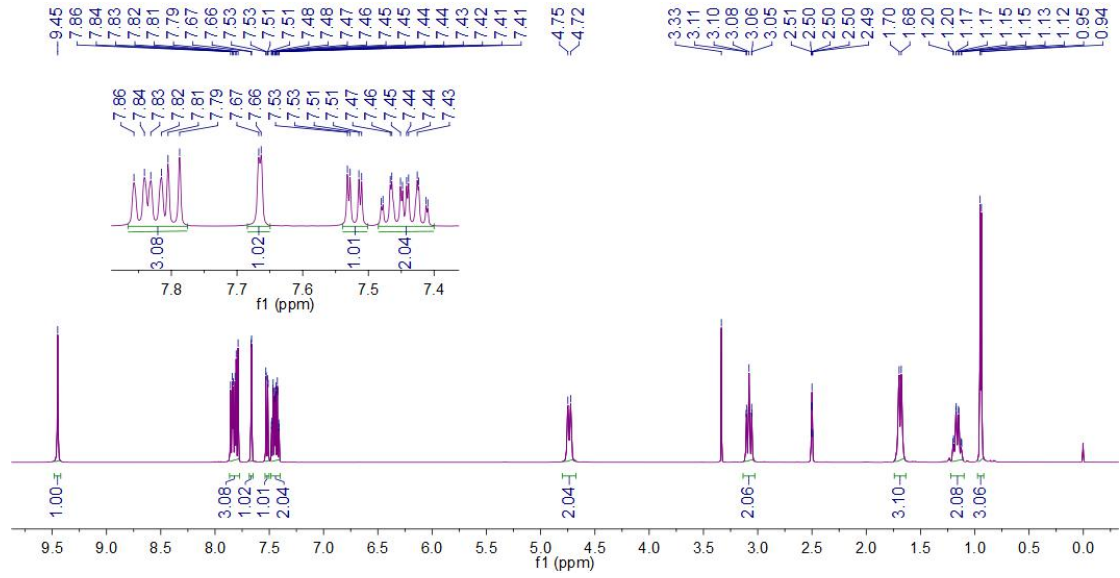


4g

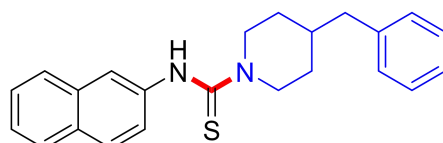




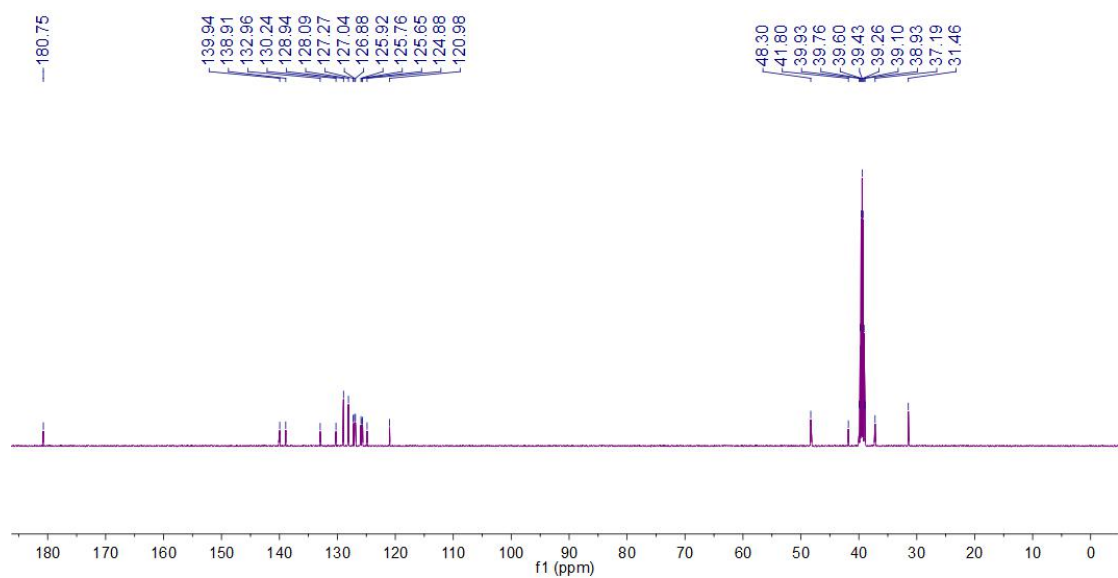
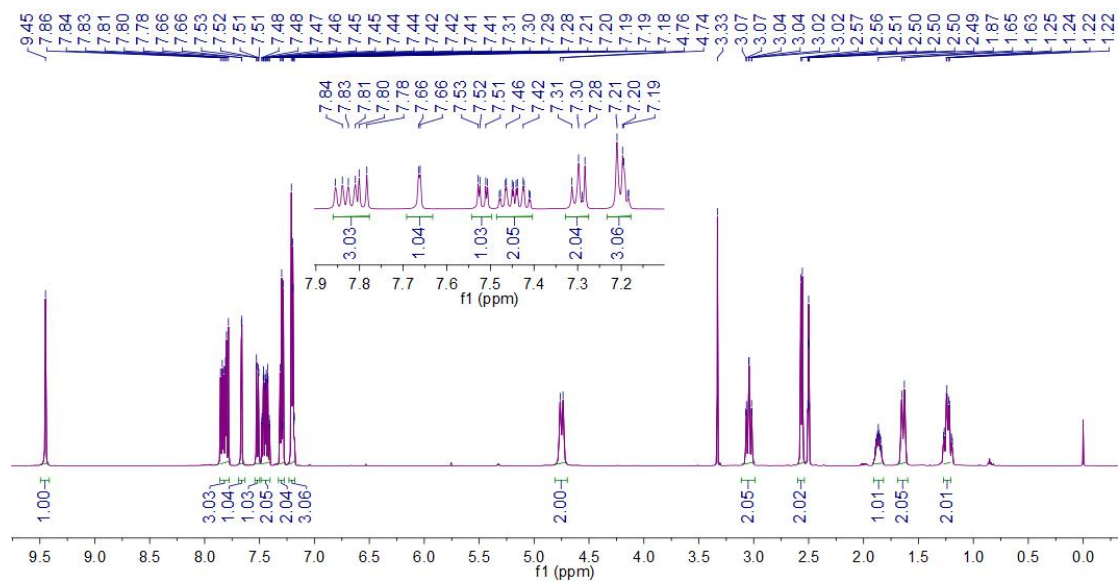
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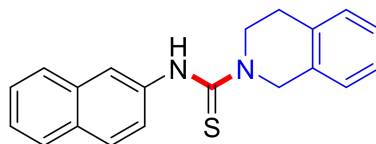




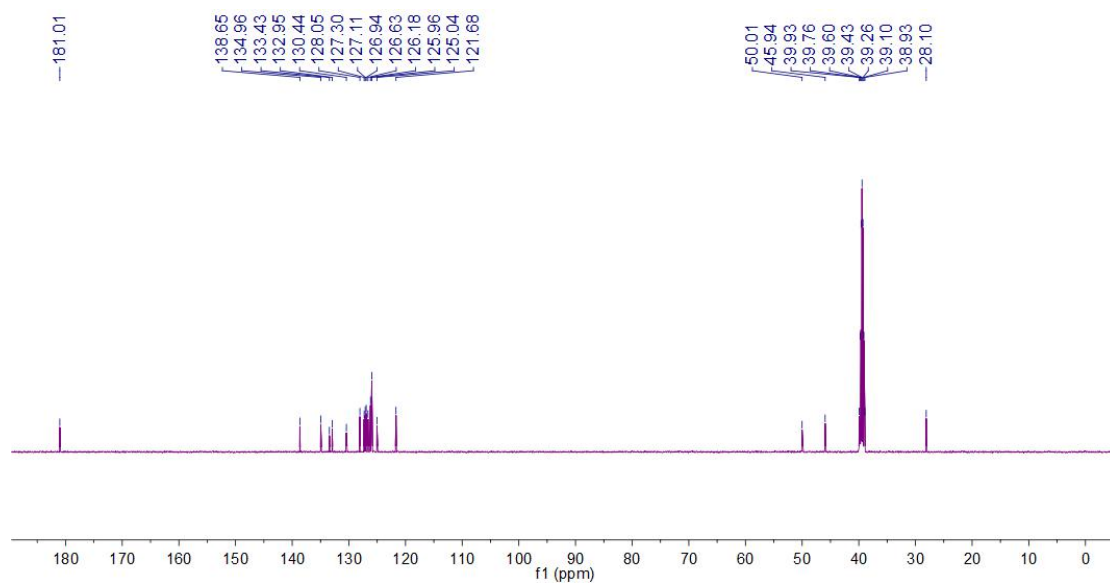
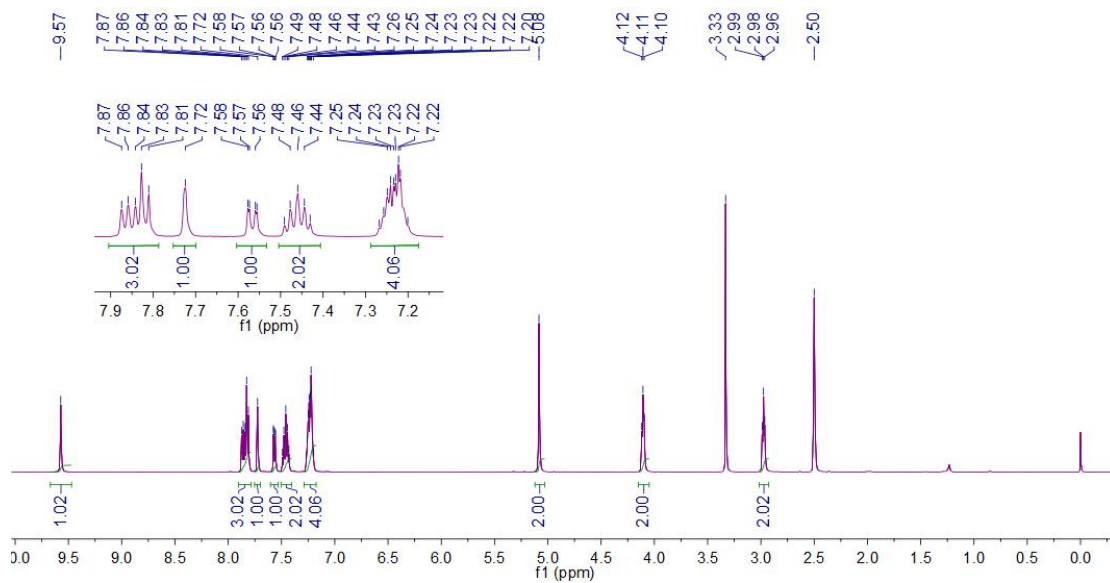


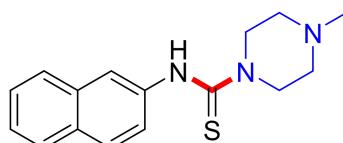
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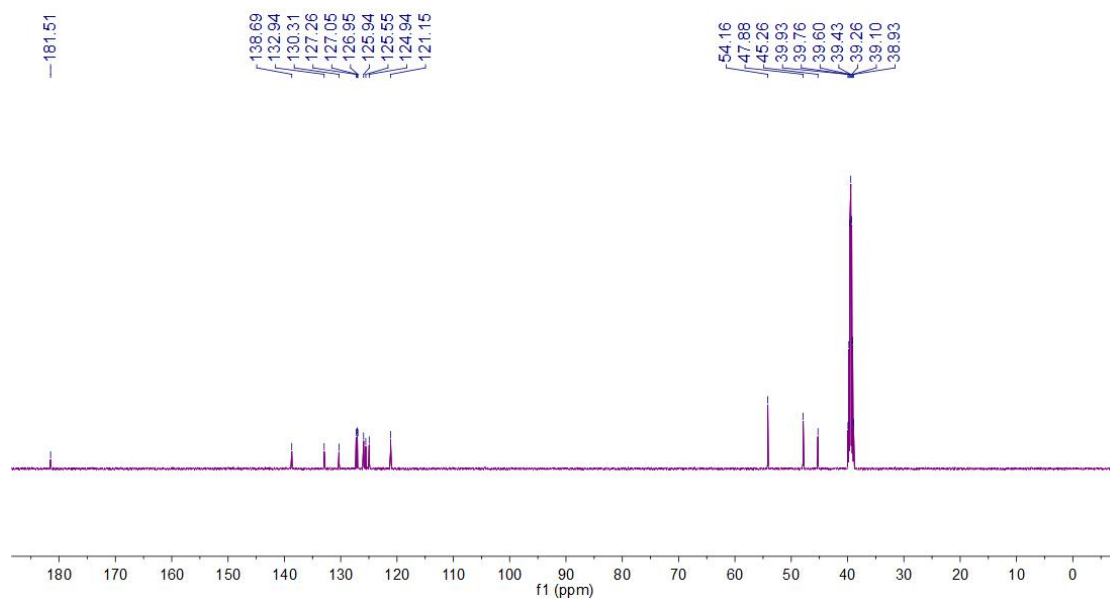
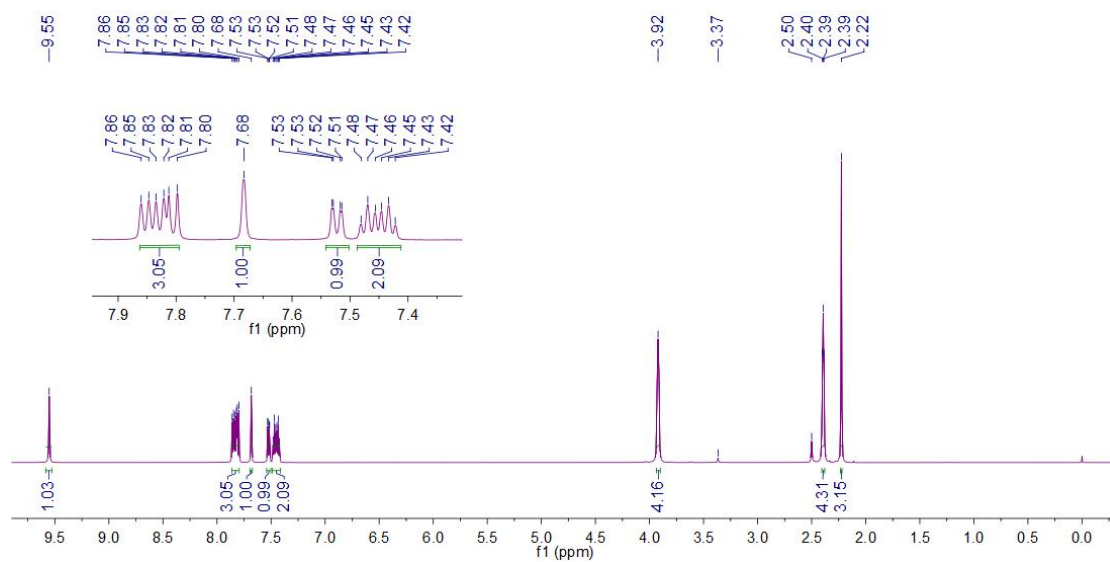


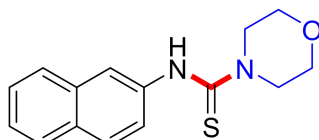
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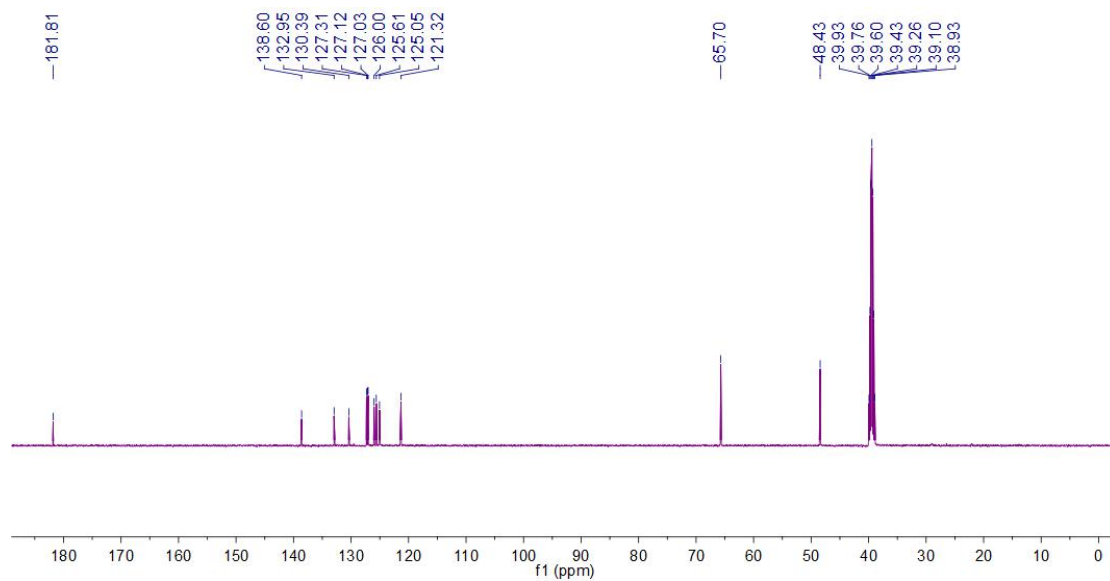
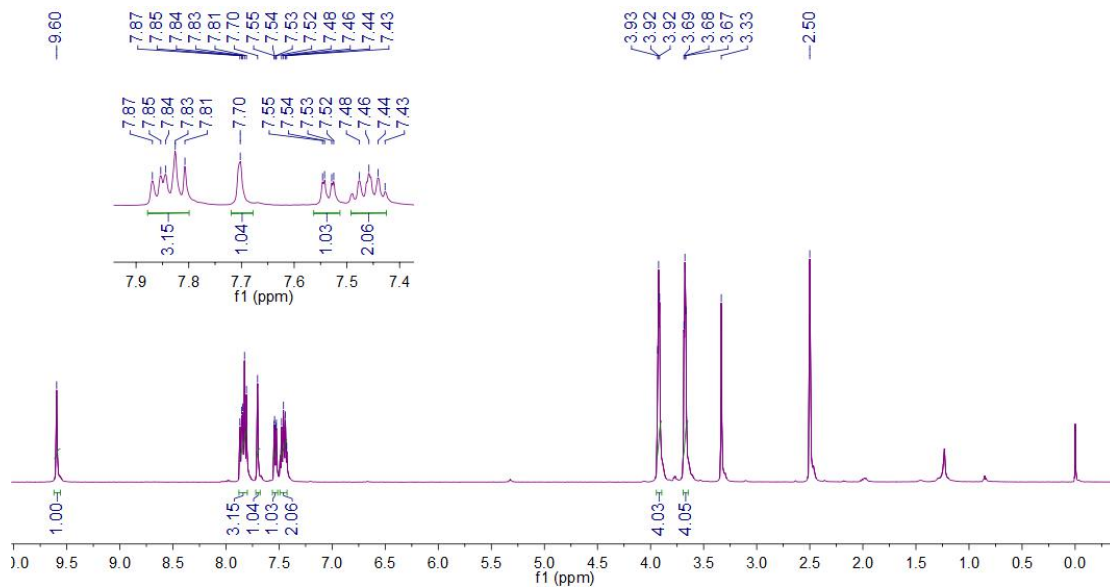


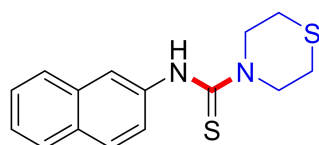
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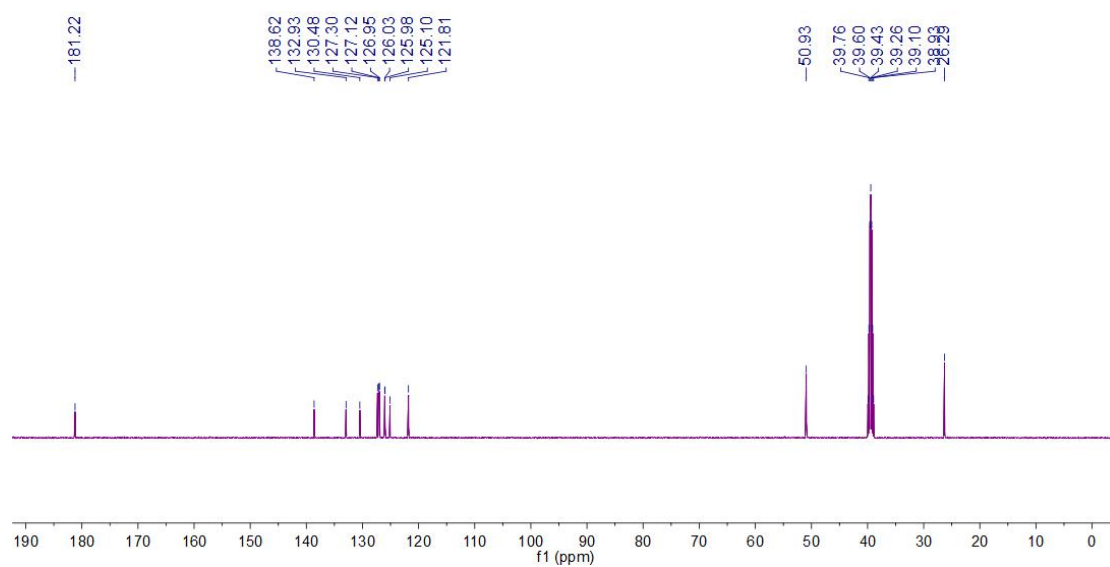
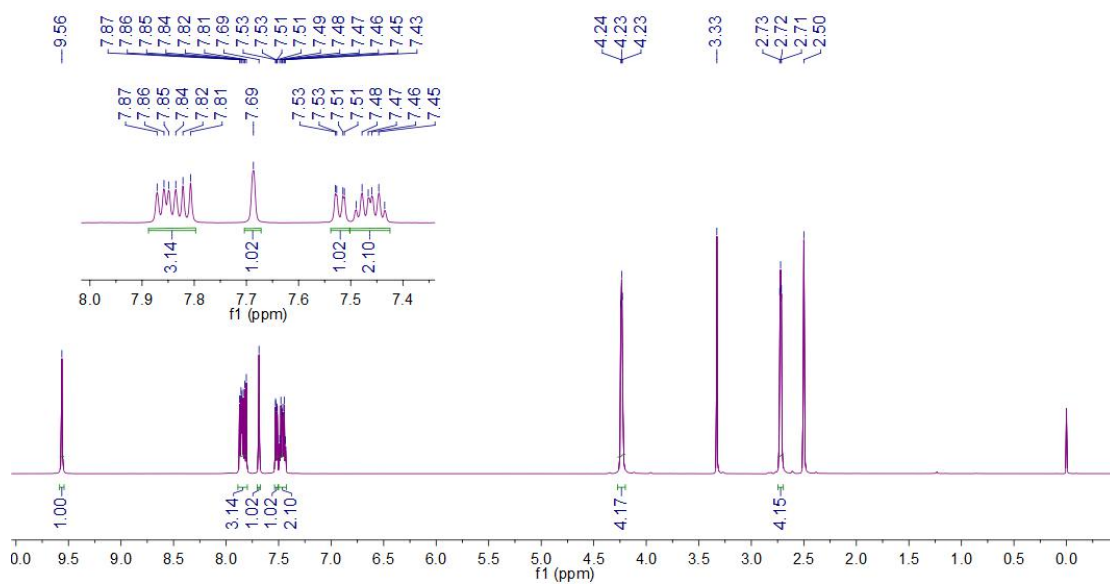


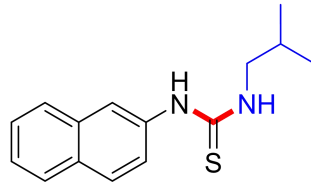
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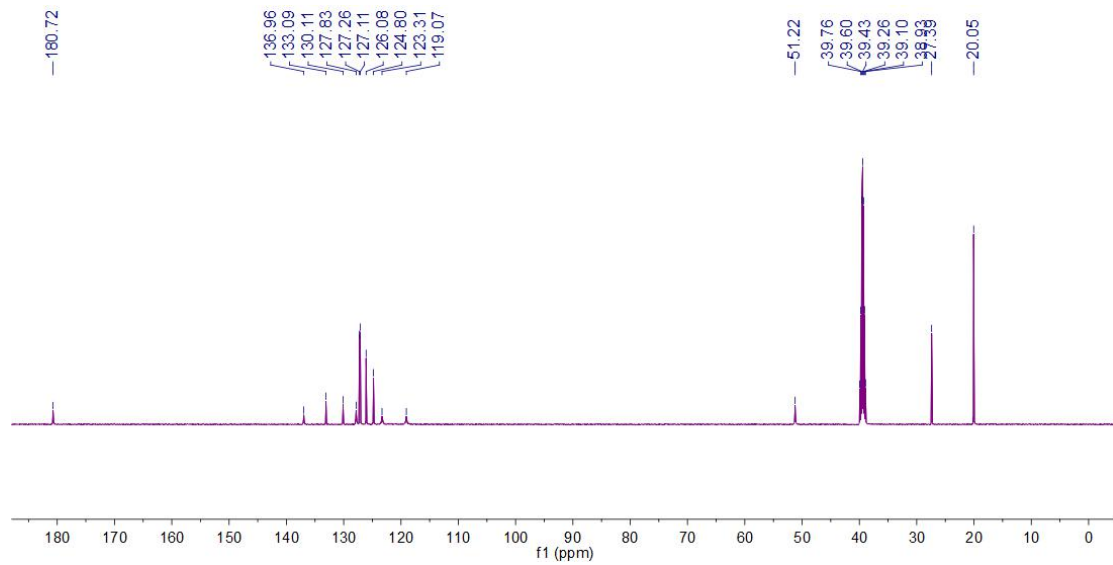
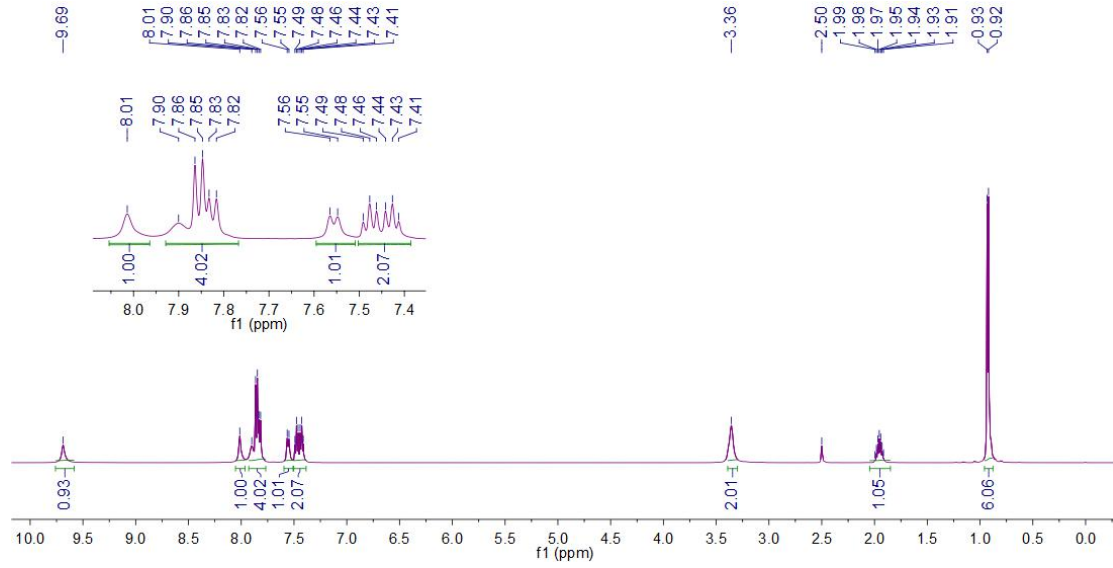


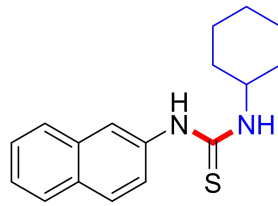
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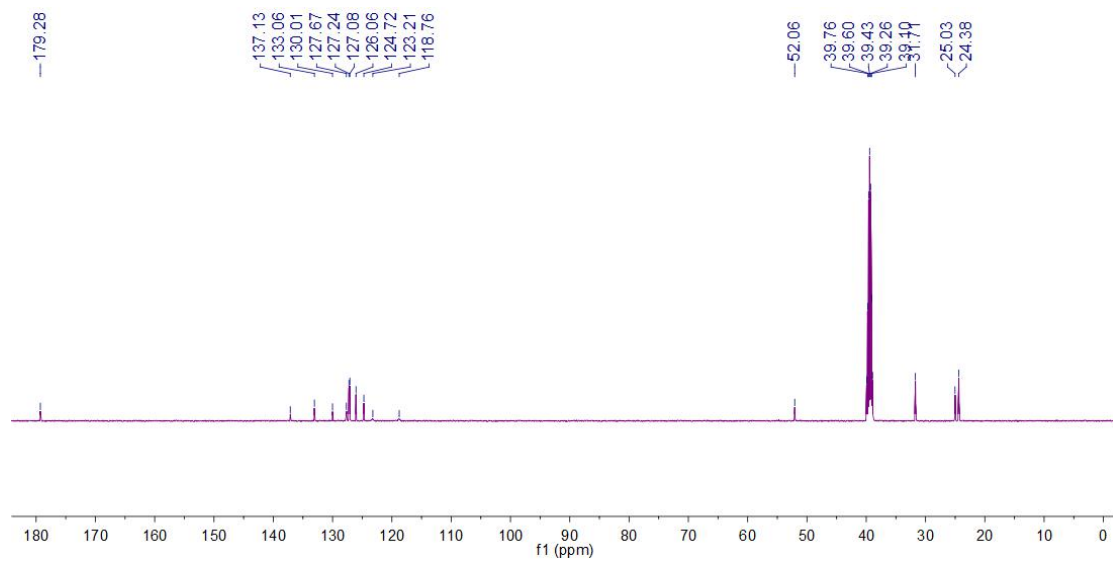
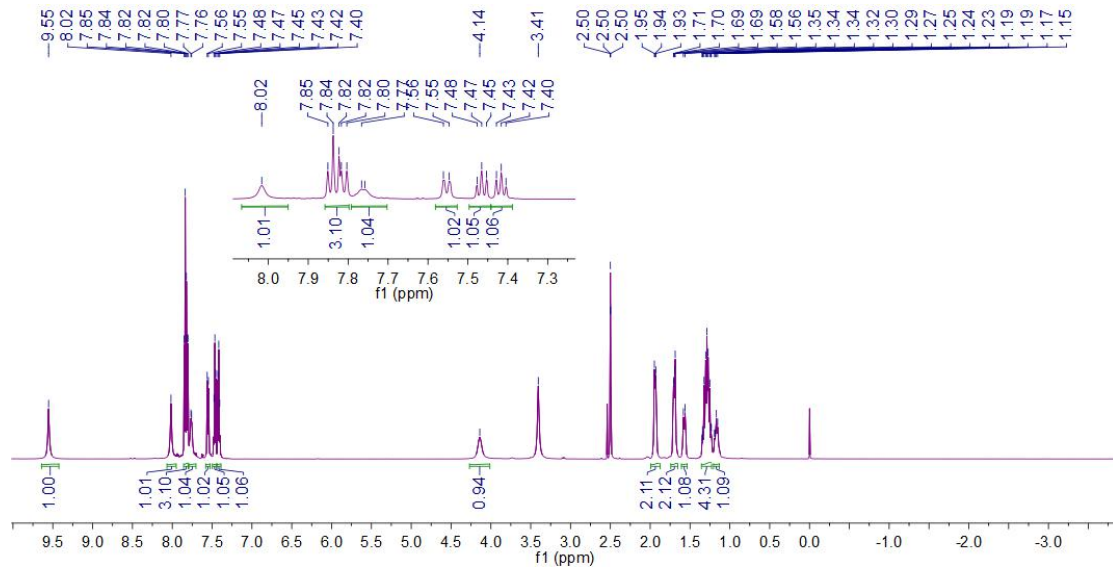


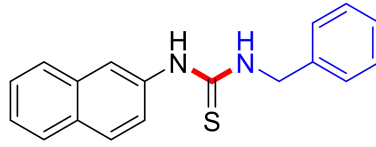
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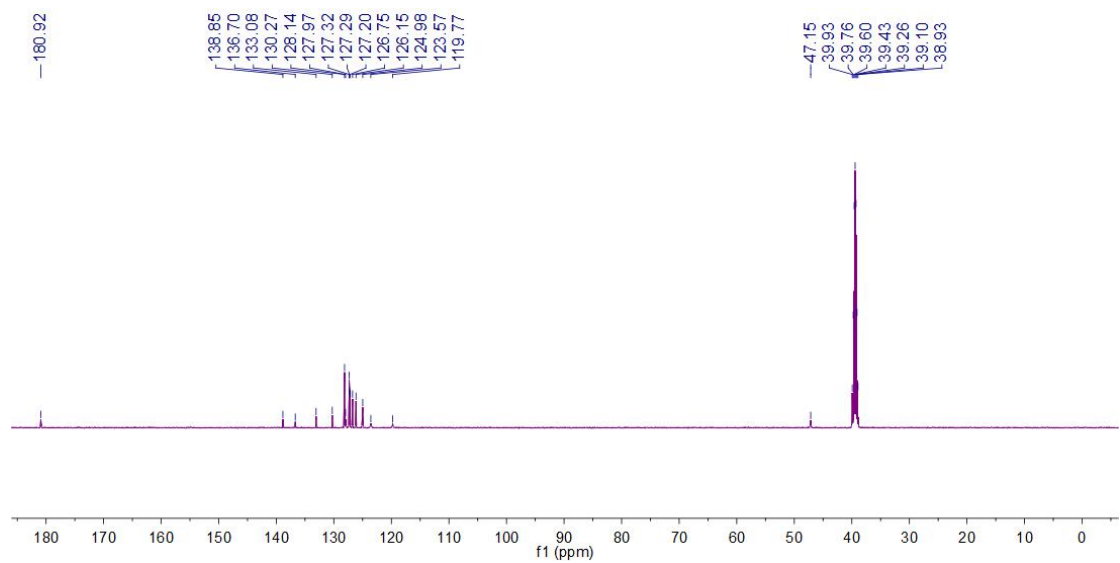
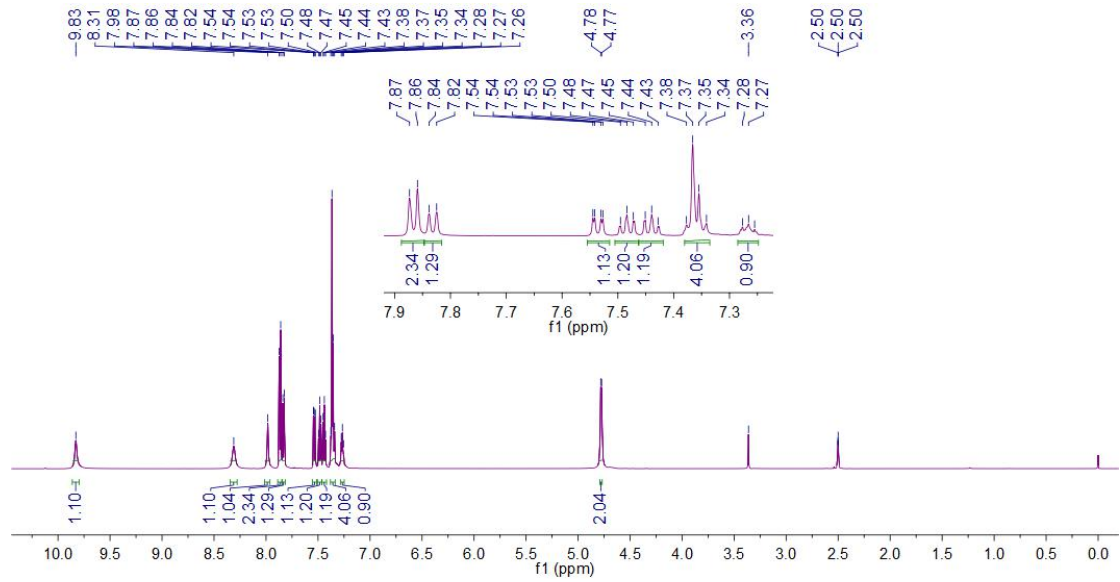


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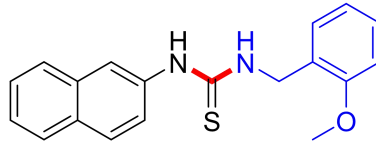




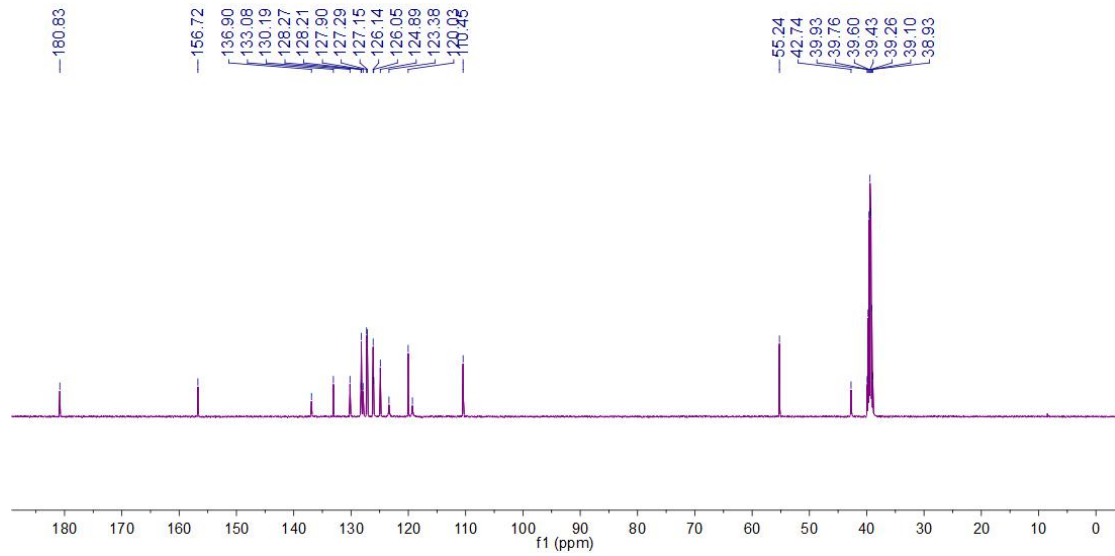
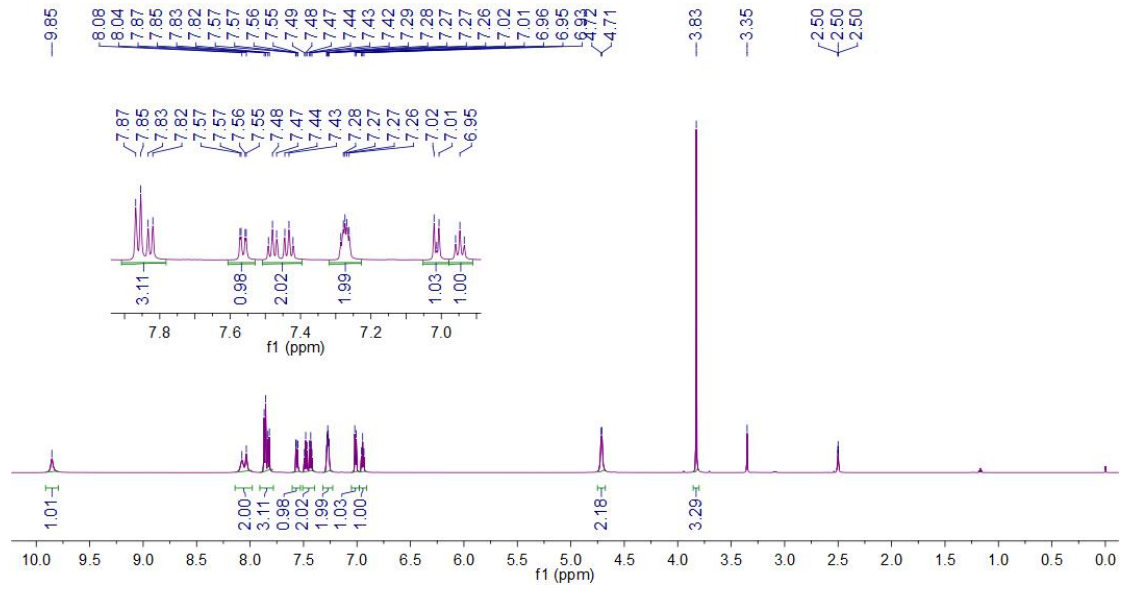
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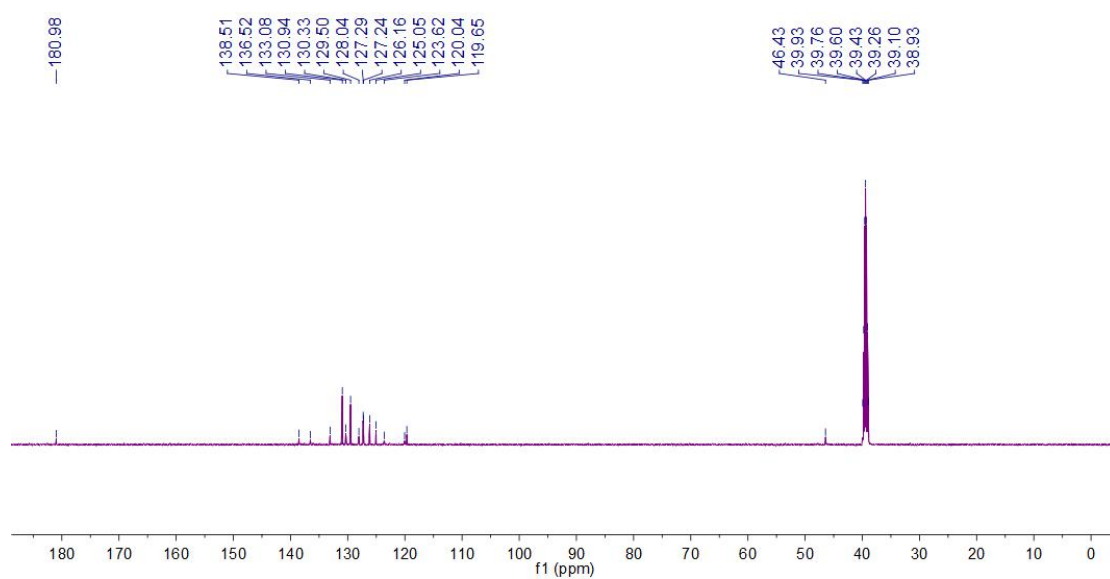
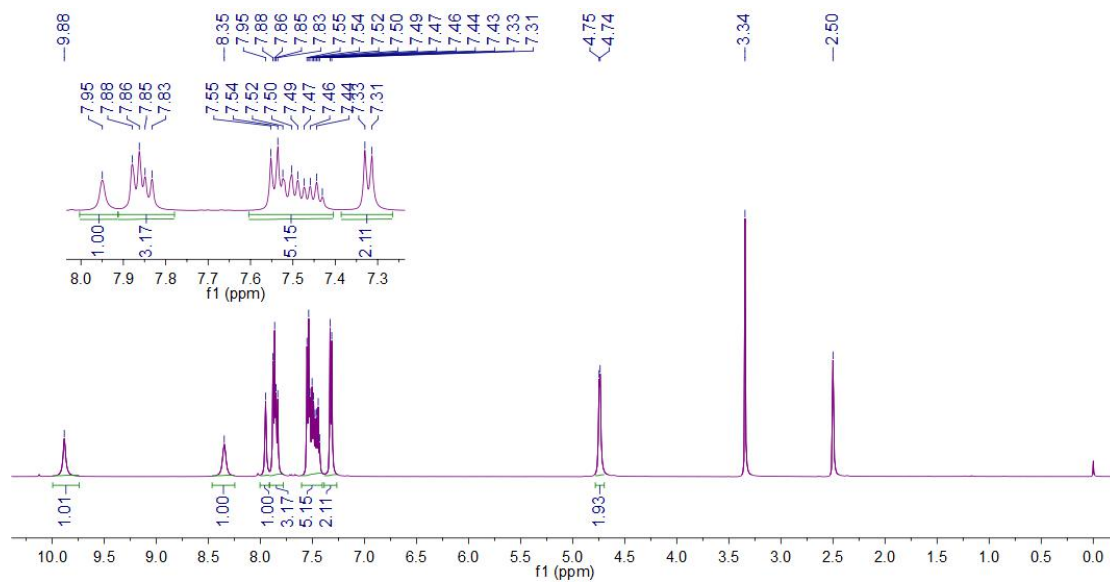
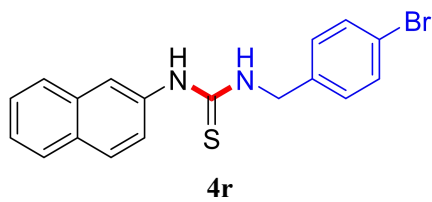


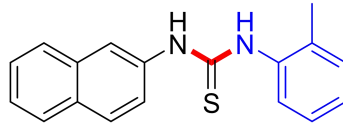




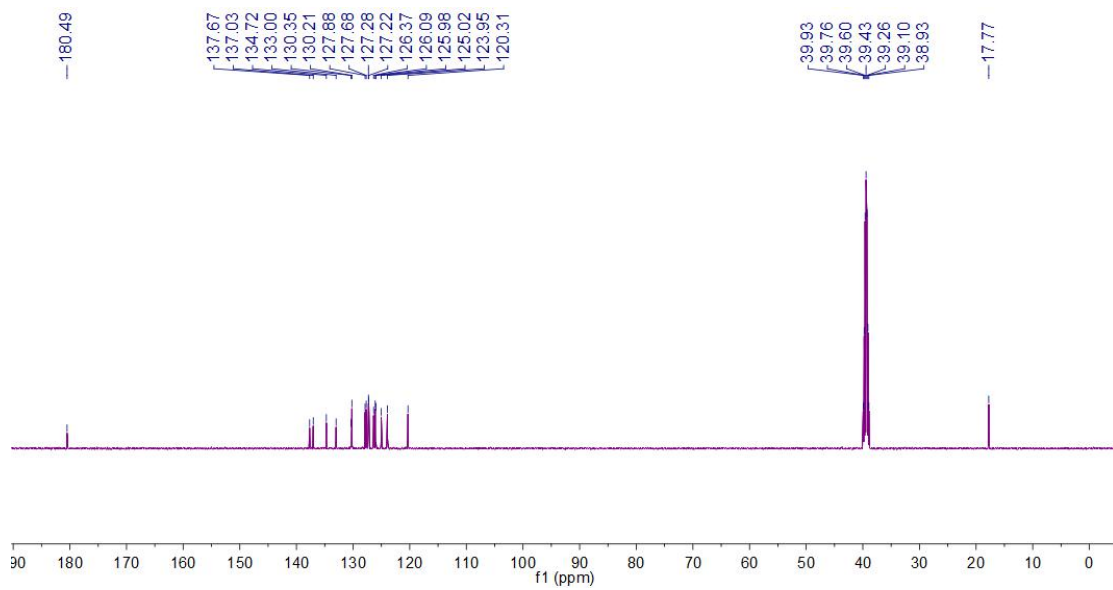
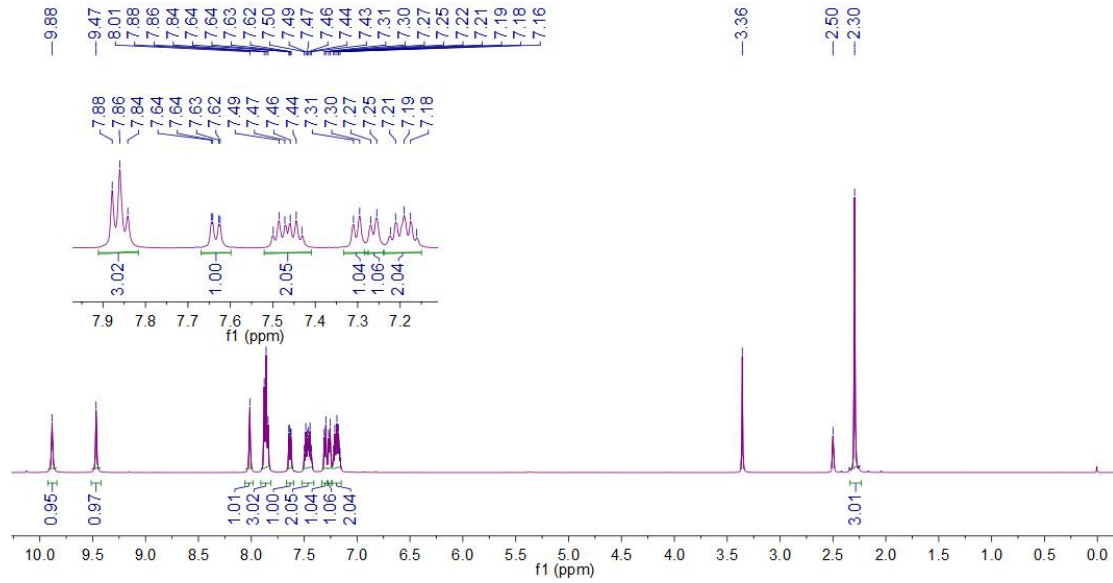
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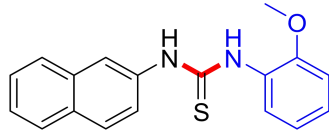




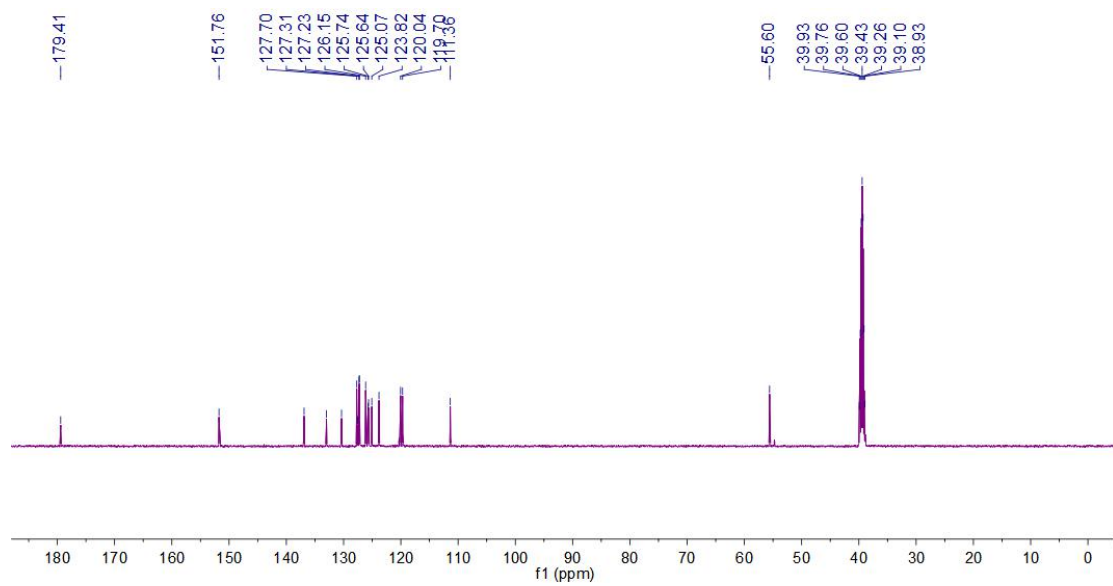
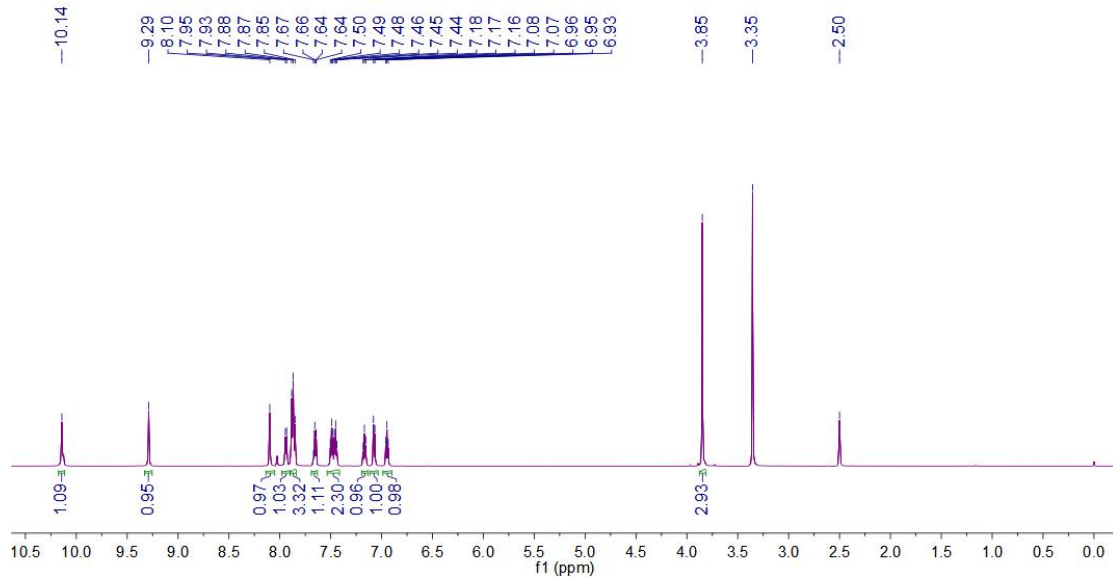


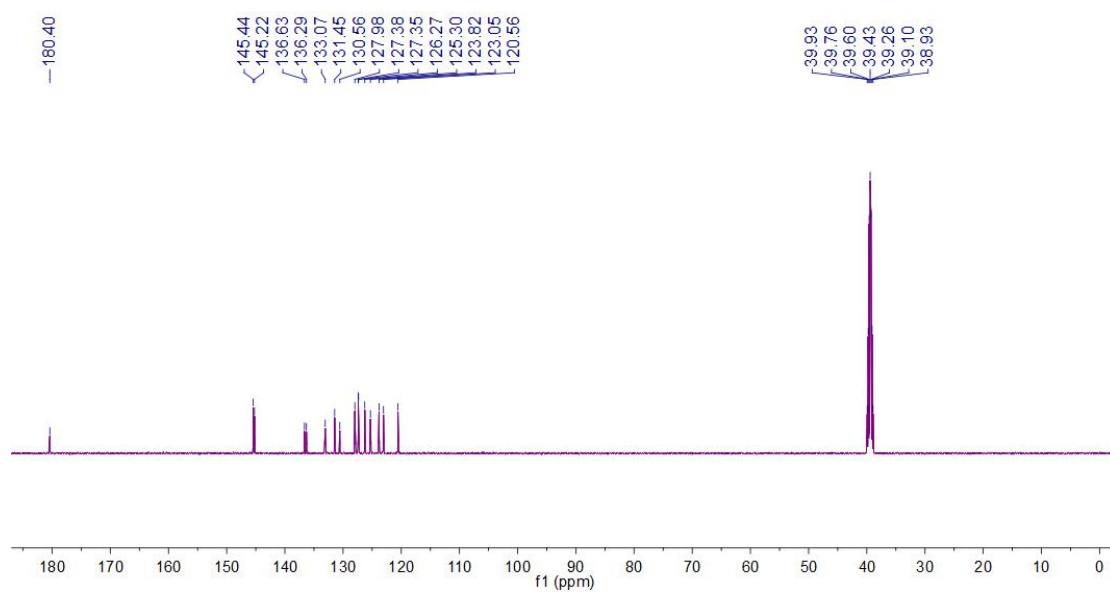
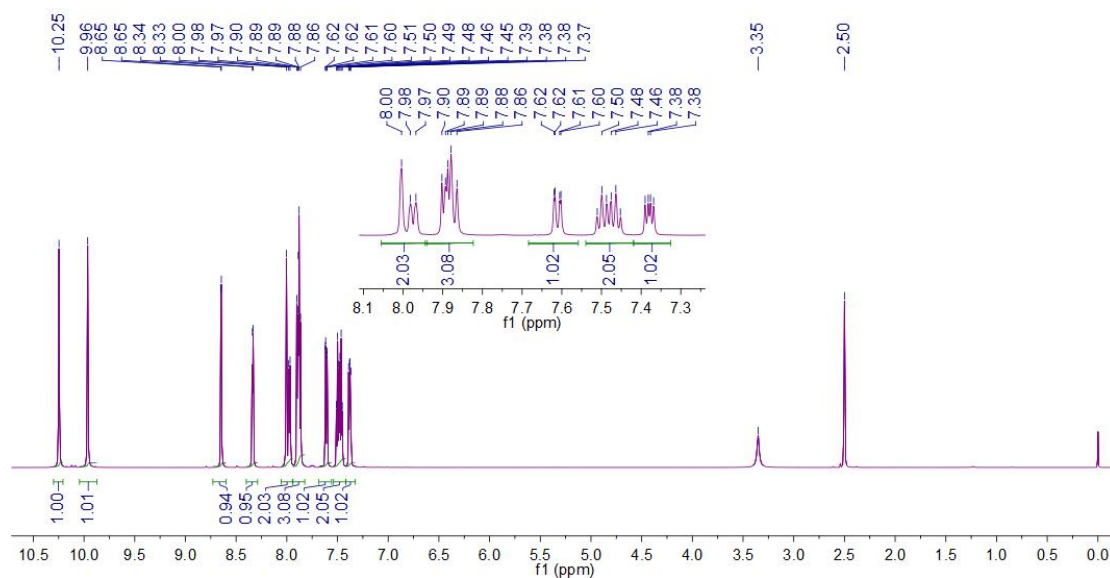
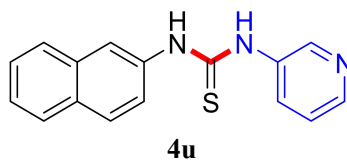
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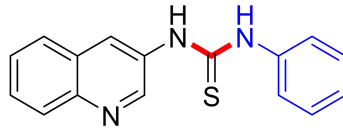




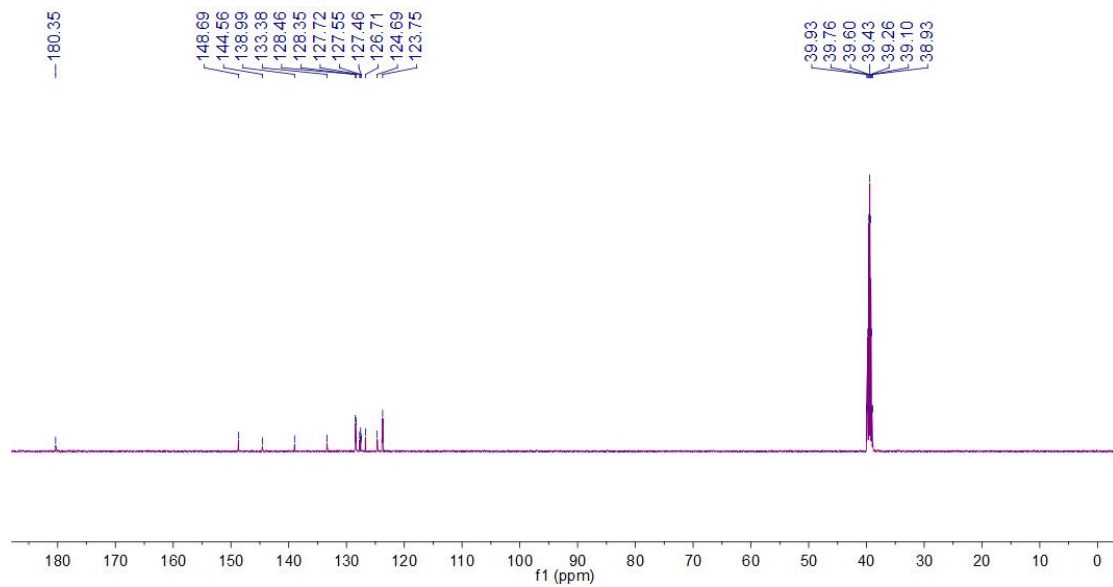
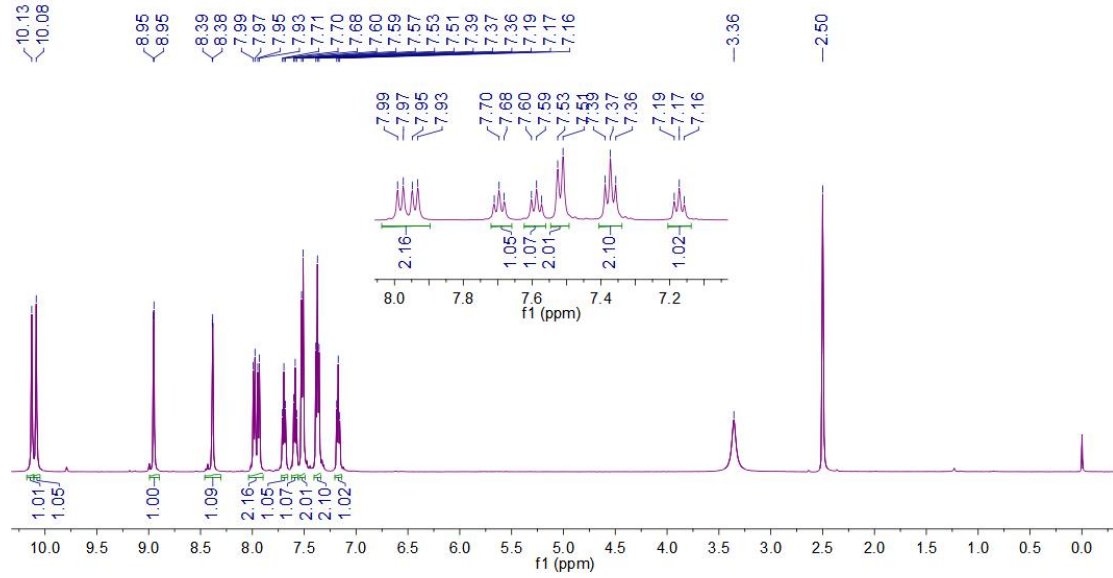
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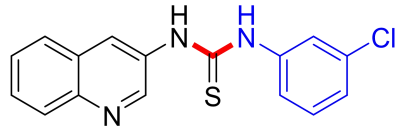




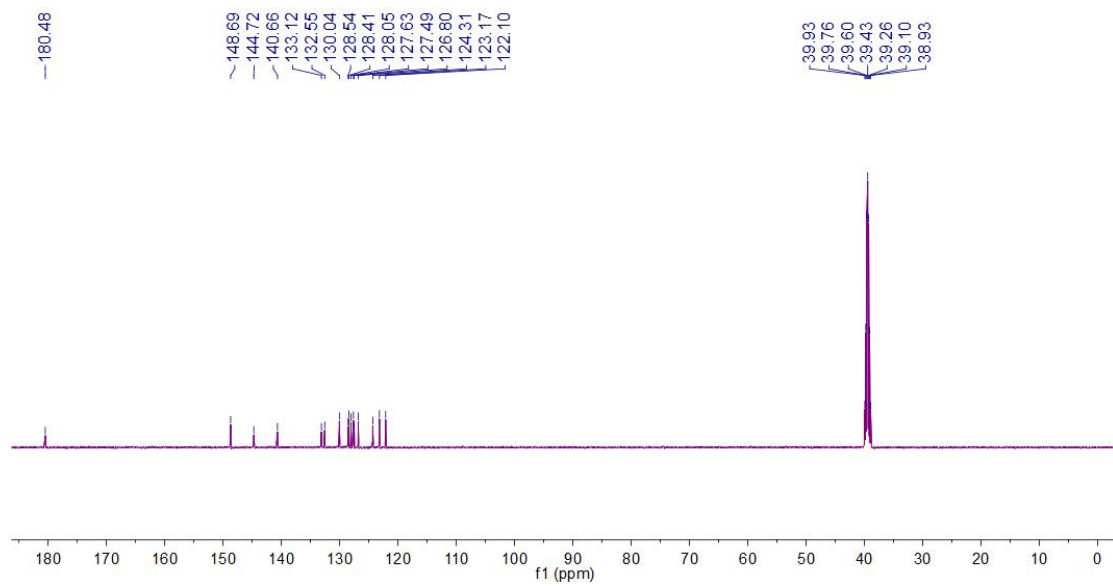
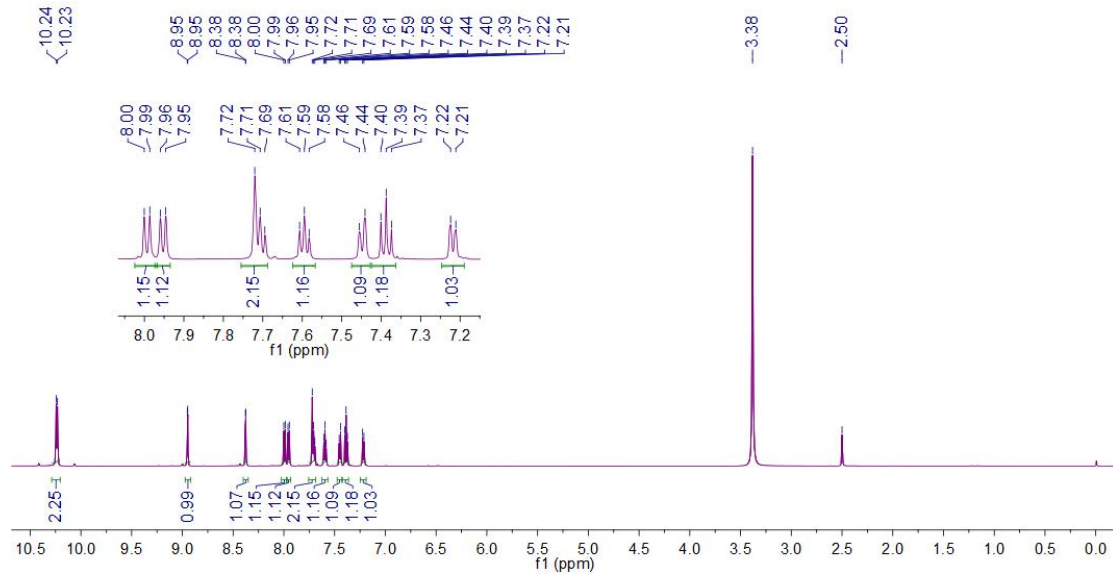


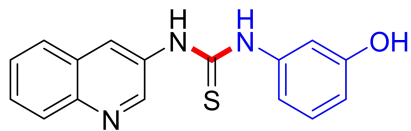
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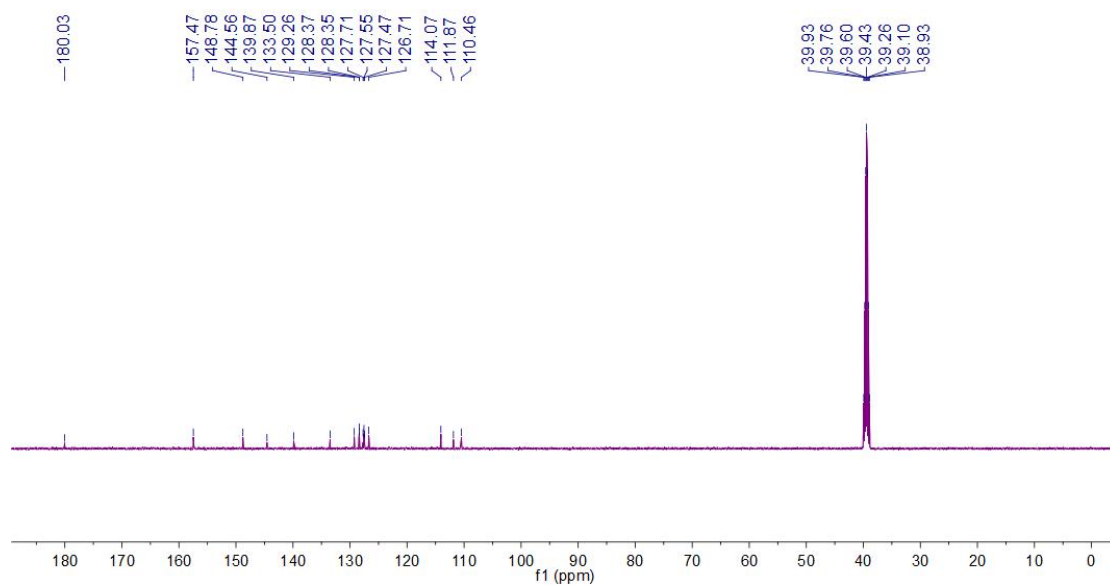
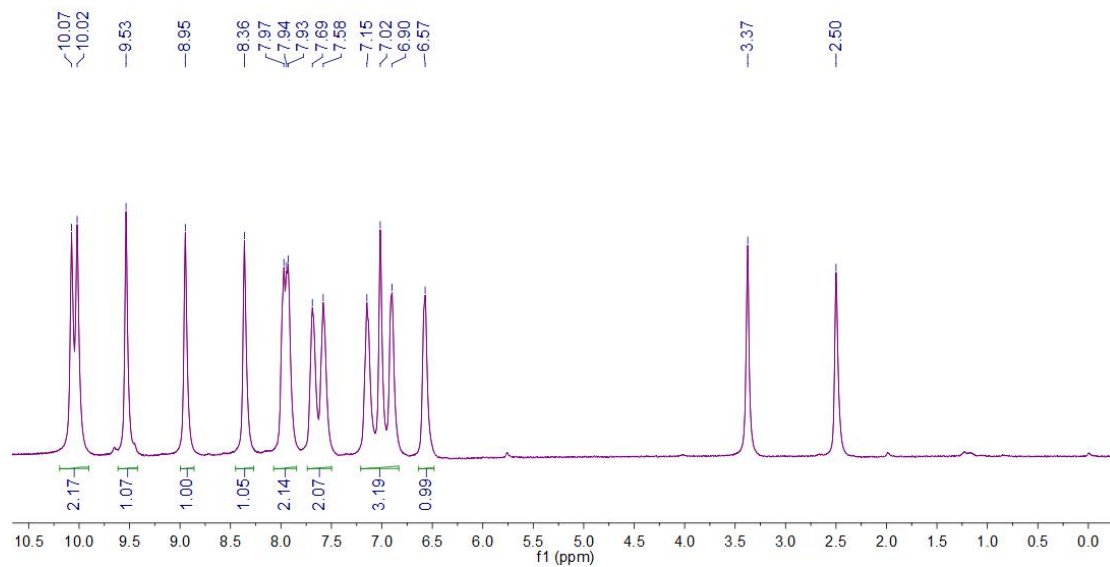


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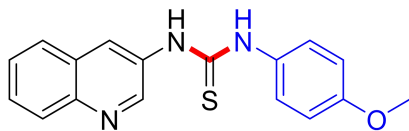




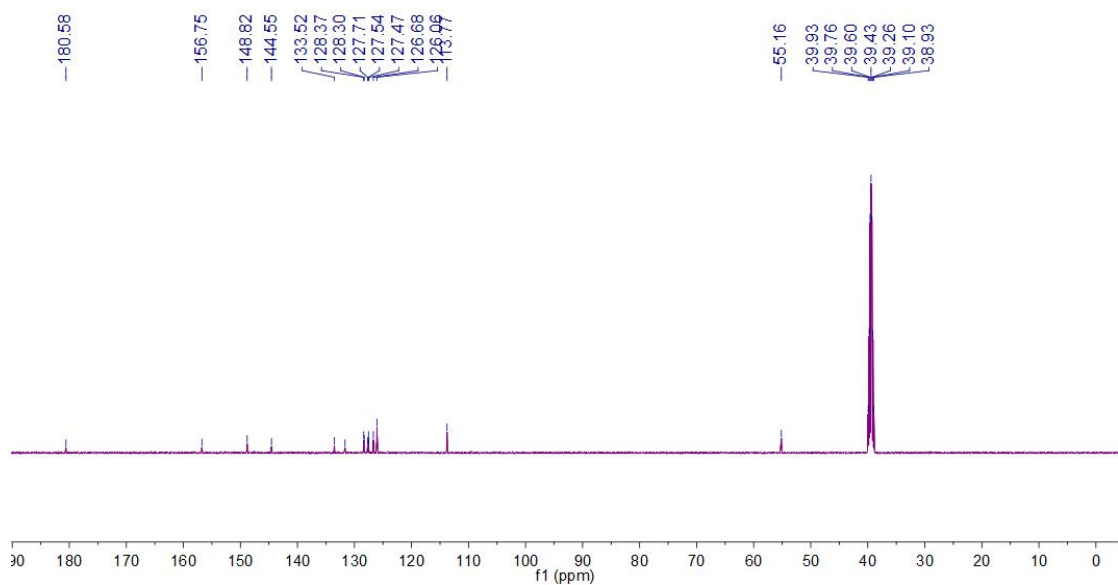
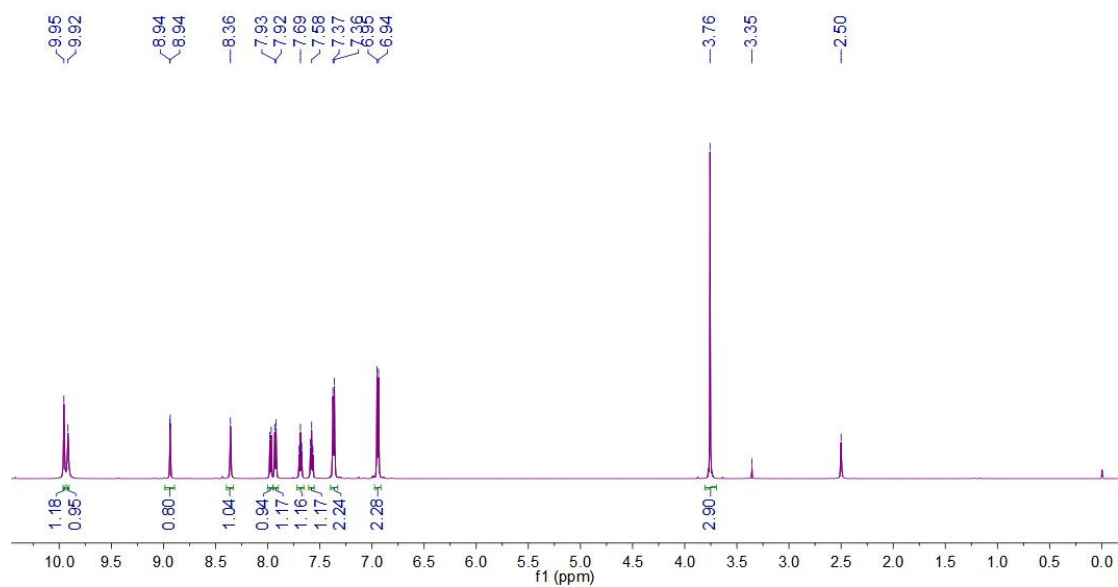
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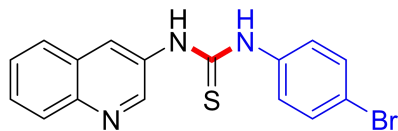




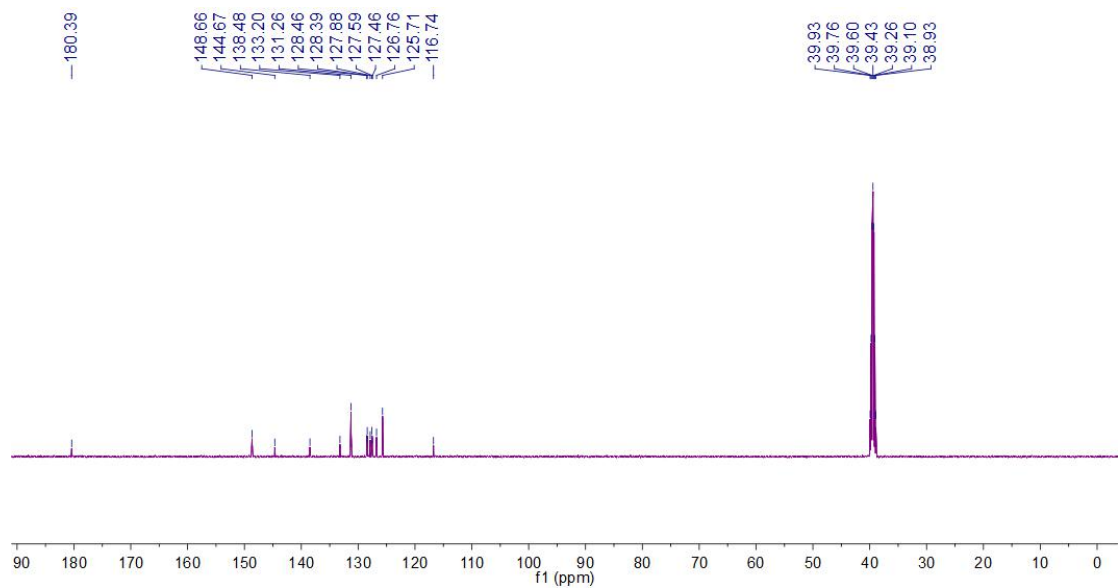
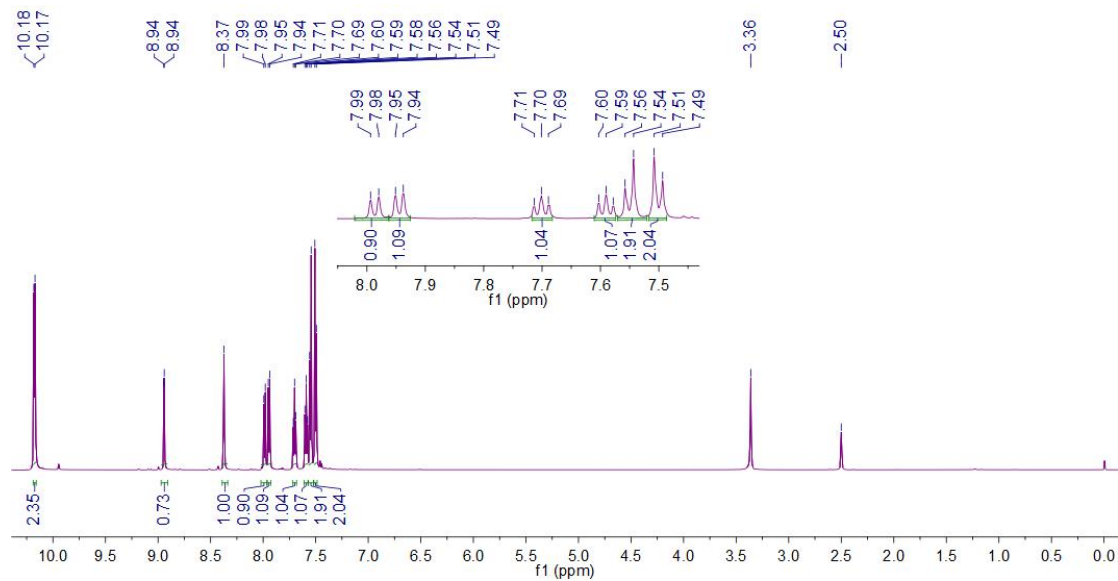


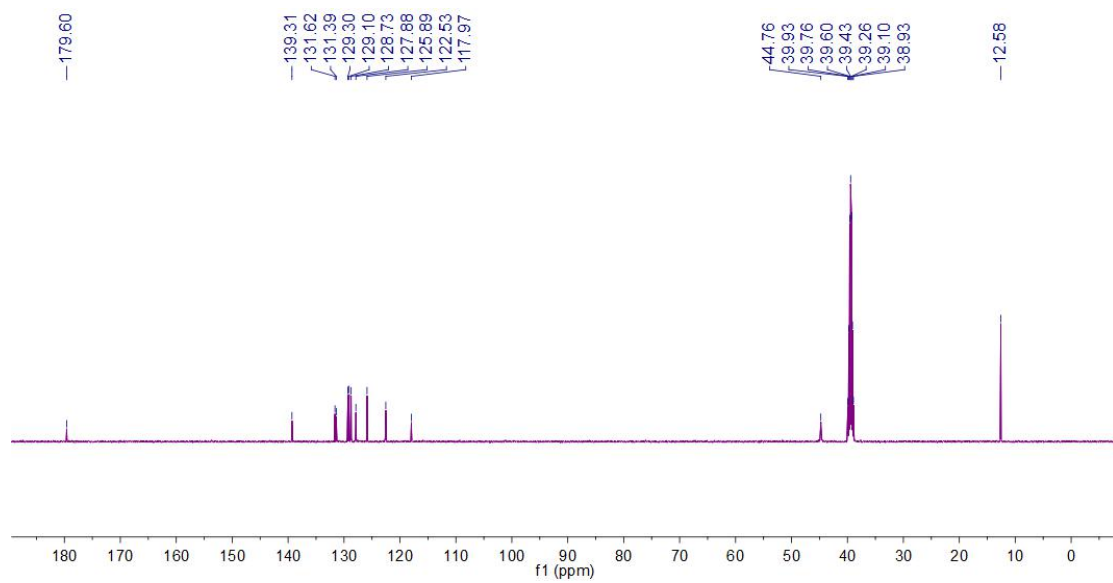
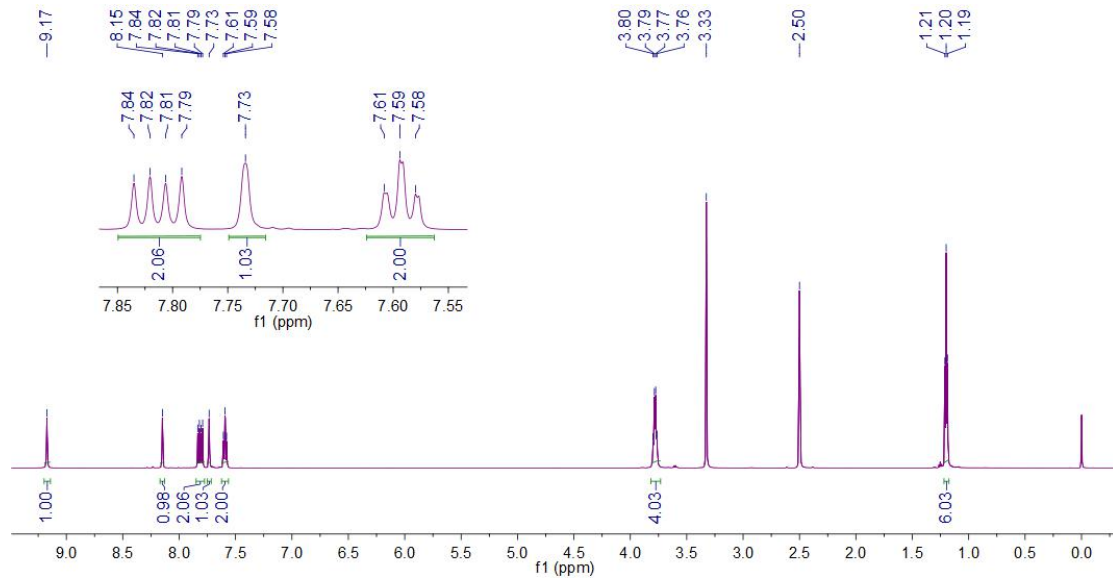
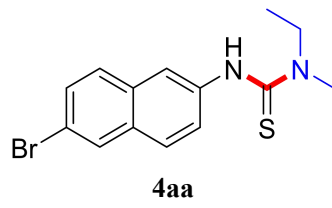
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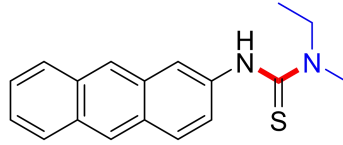




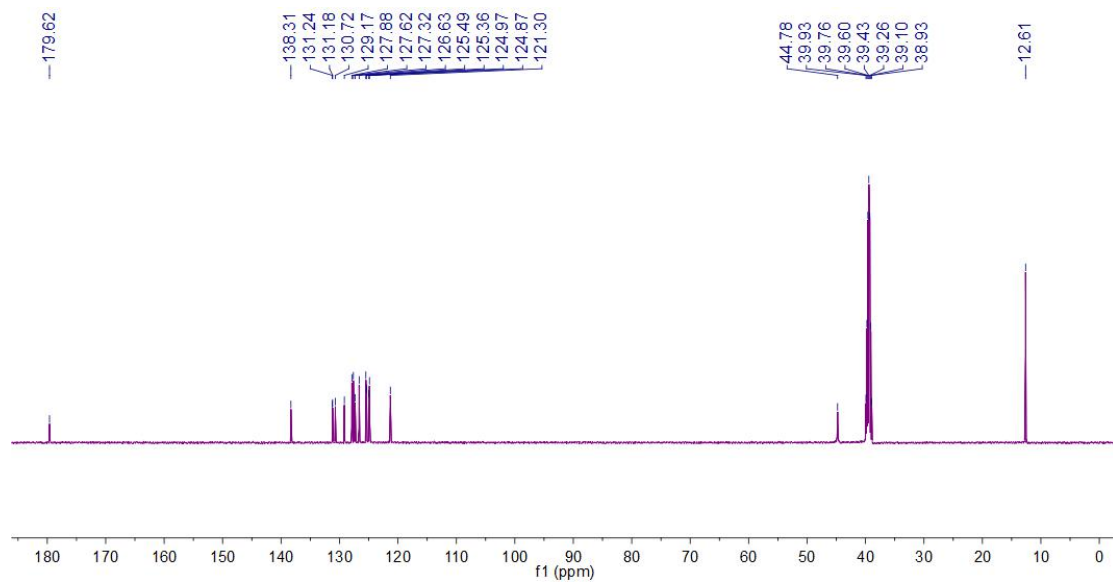
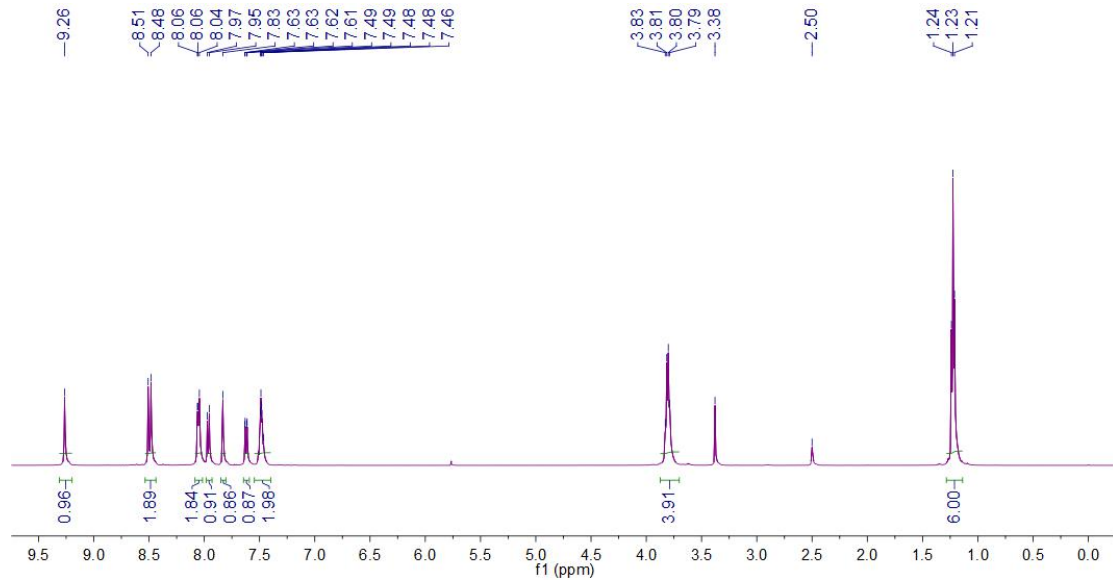
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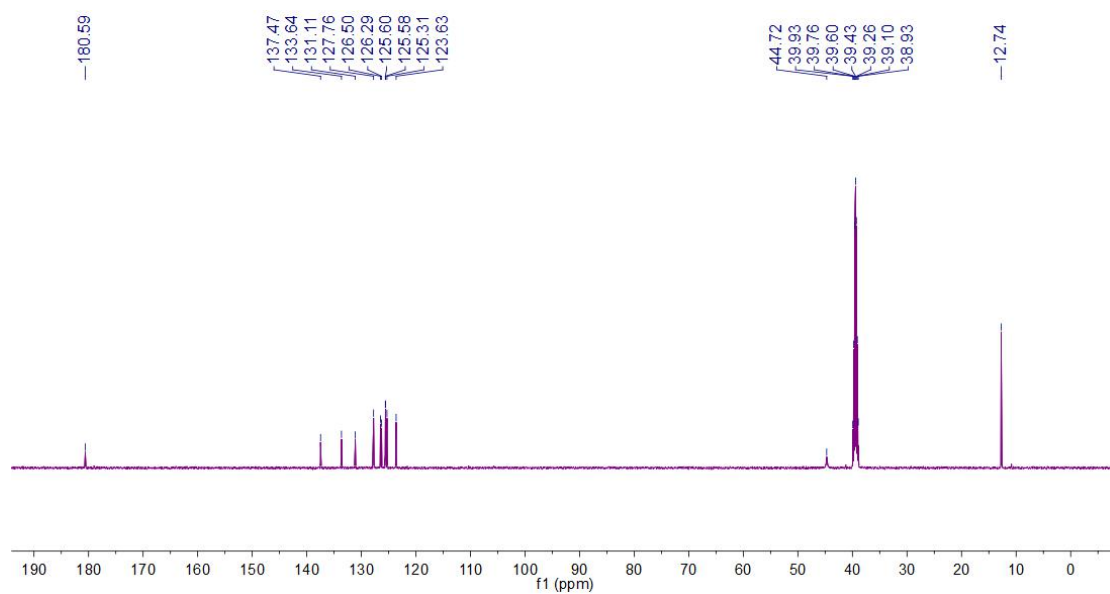
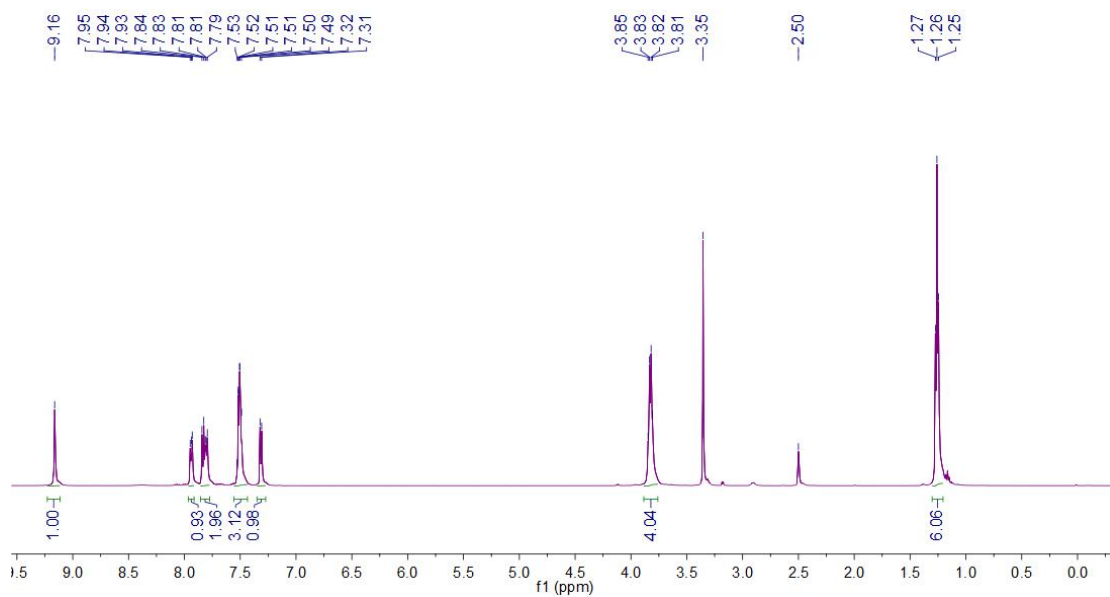
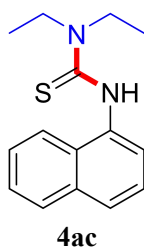


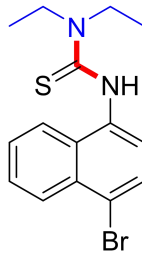




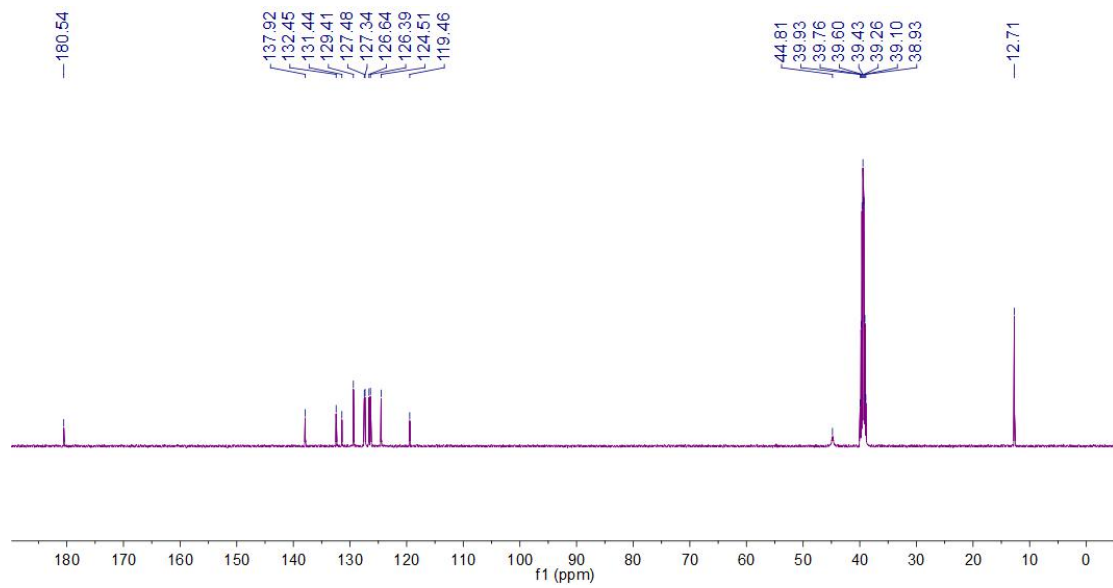
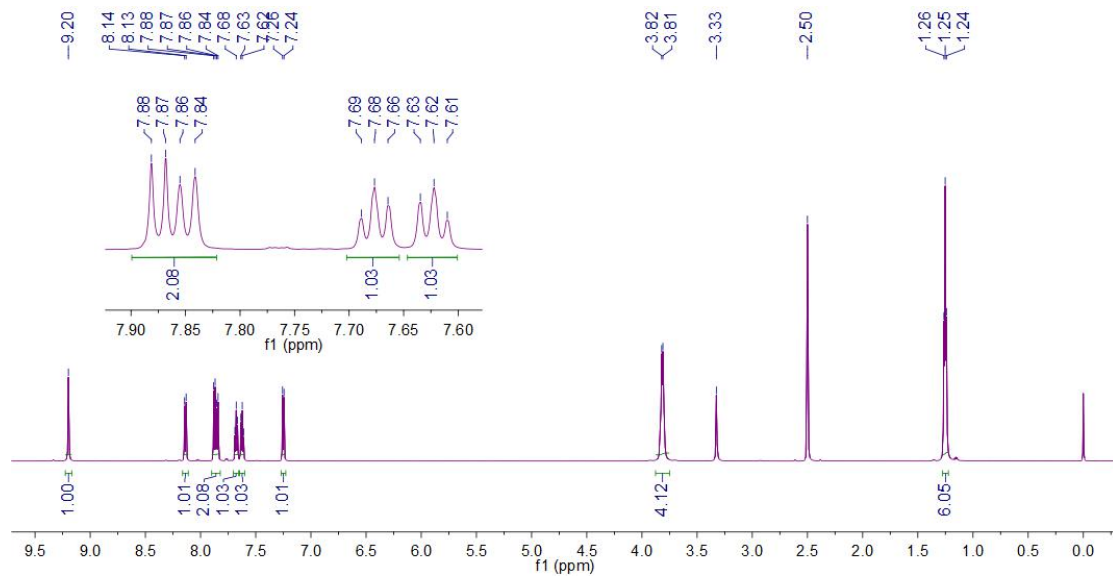
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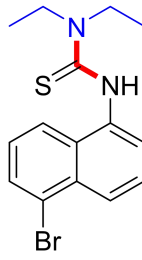




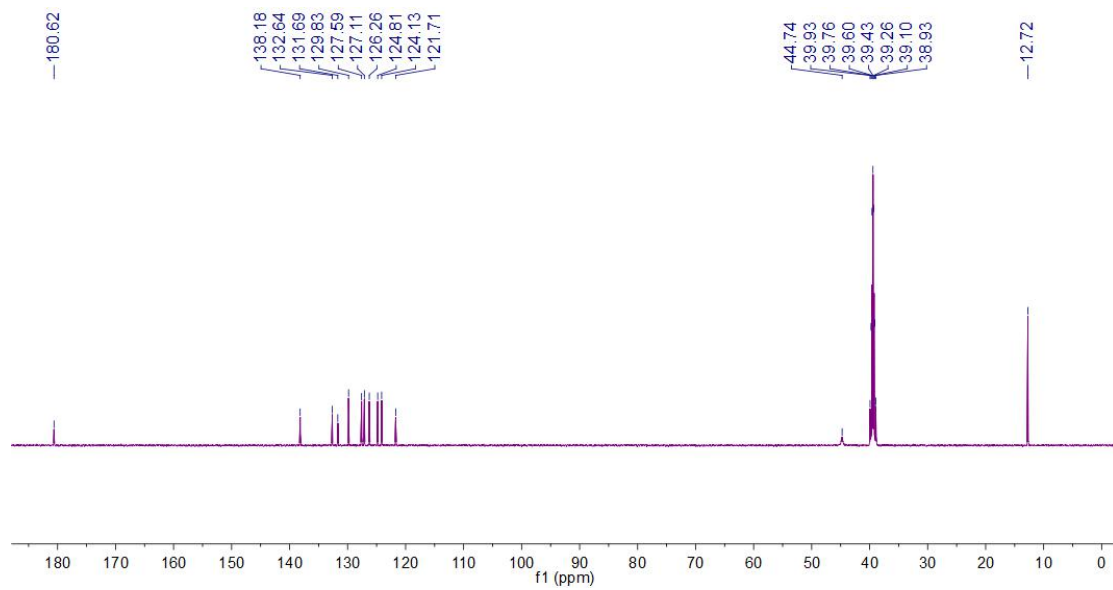
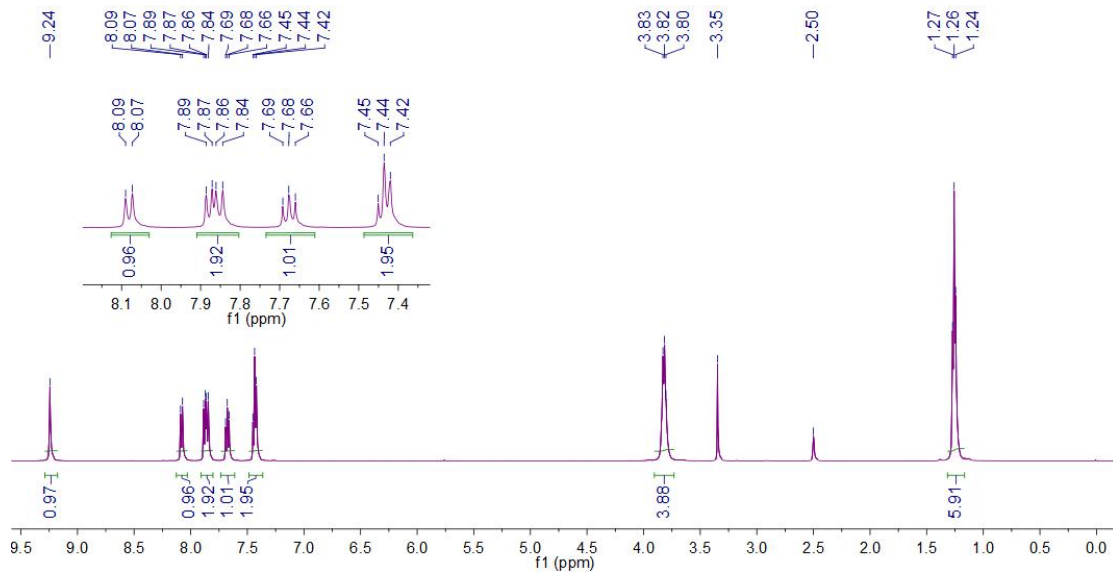


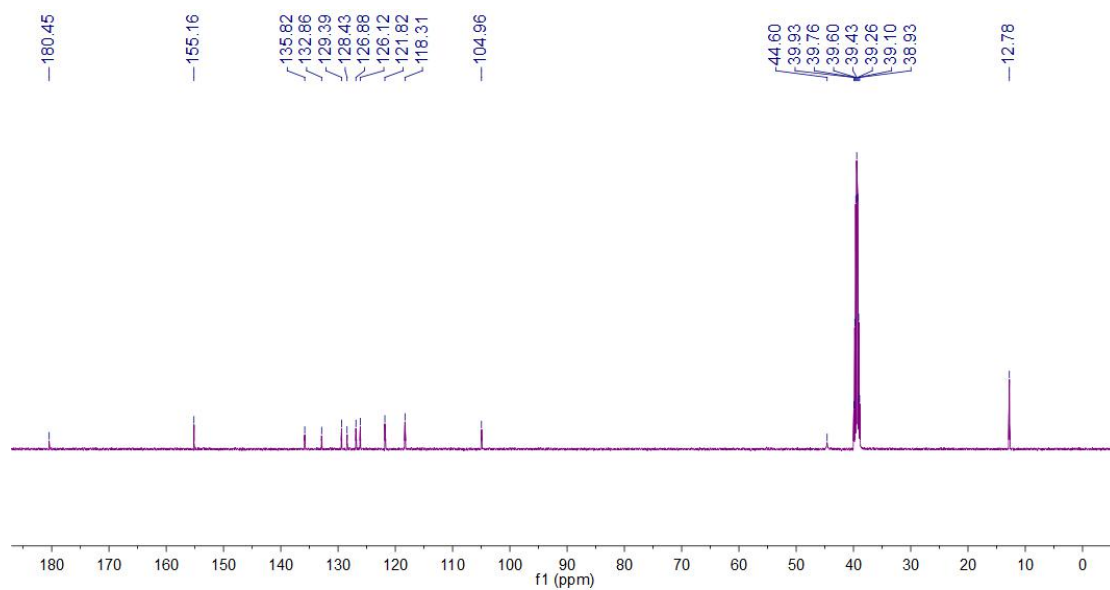
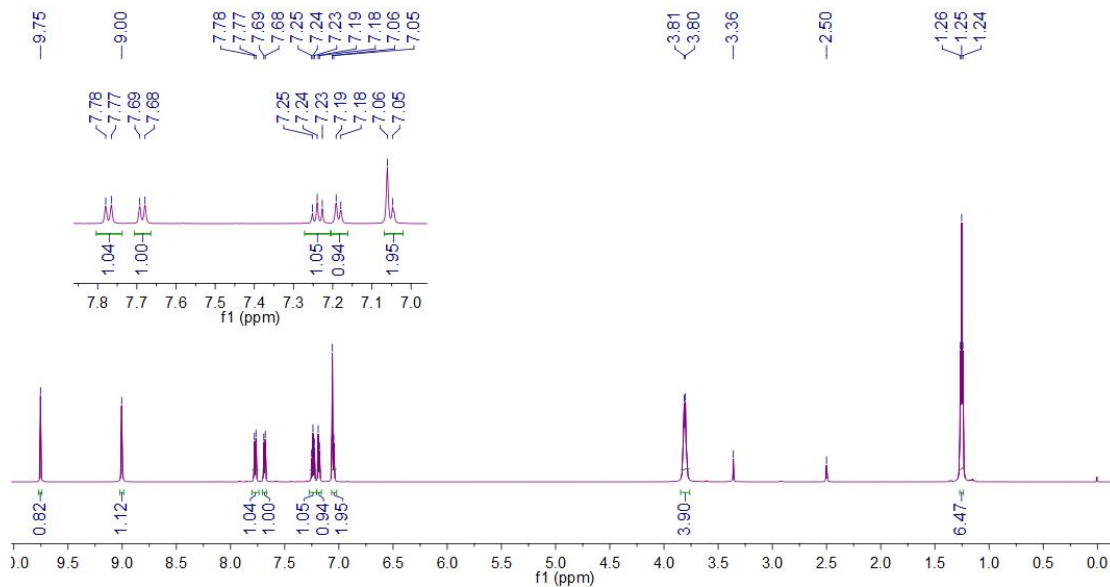
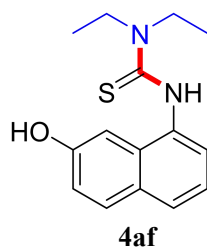
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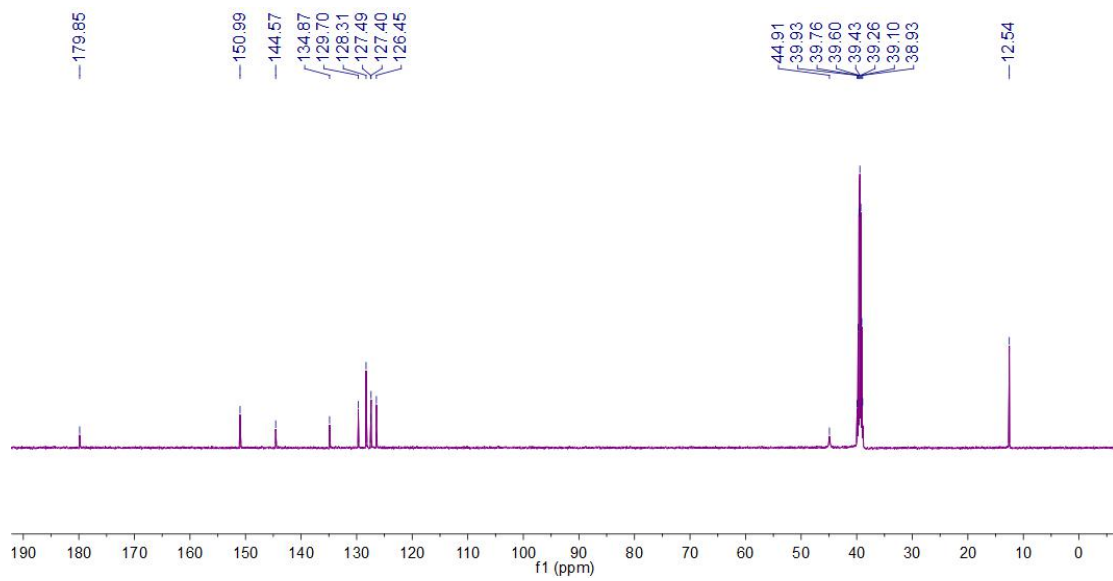
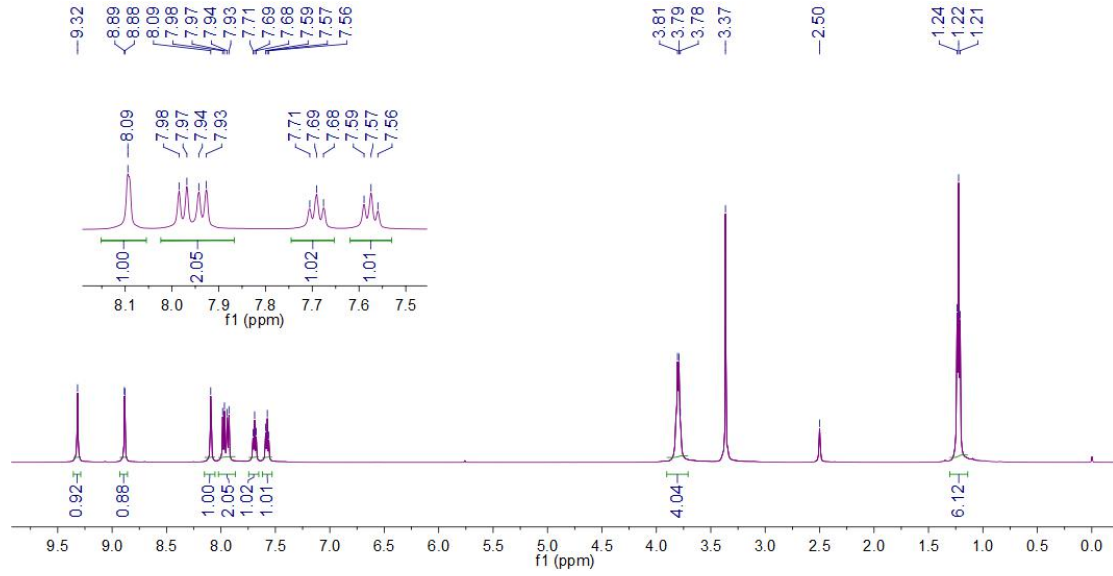
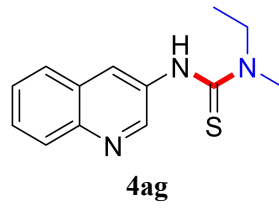


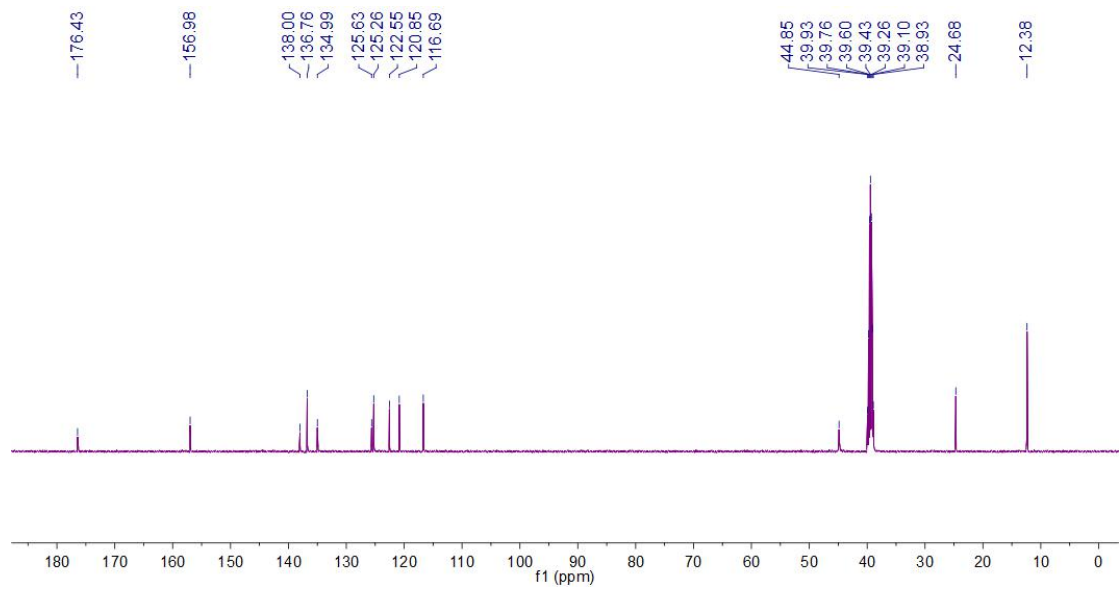
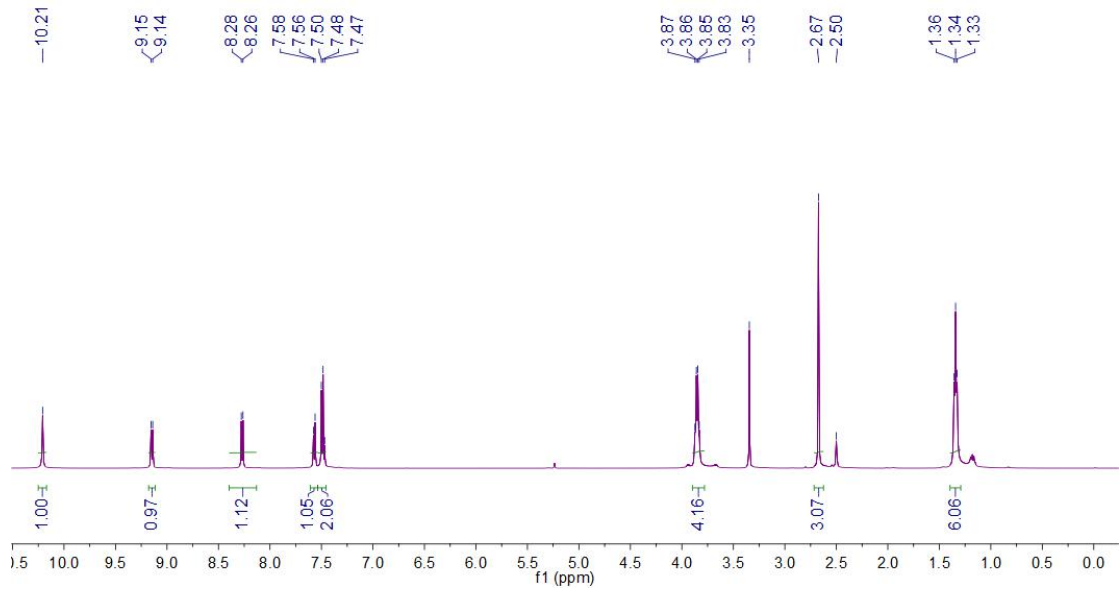
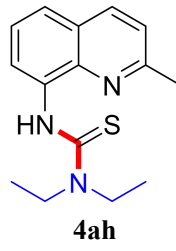
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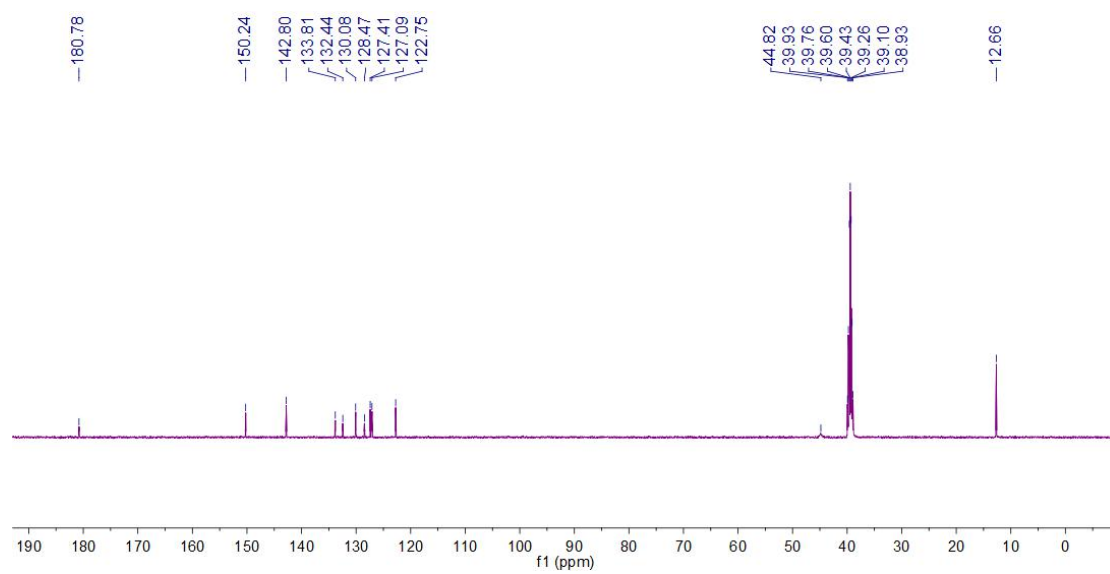
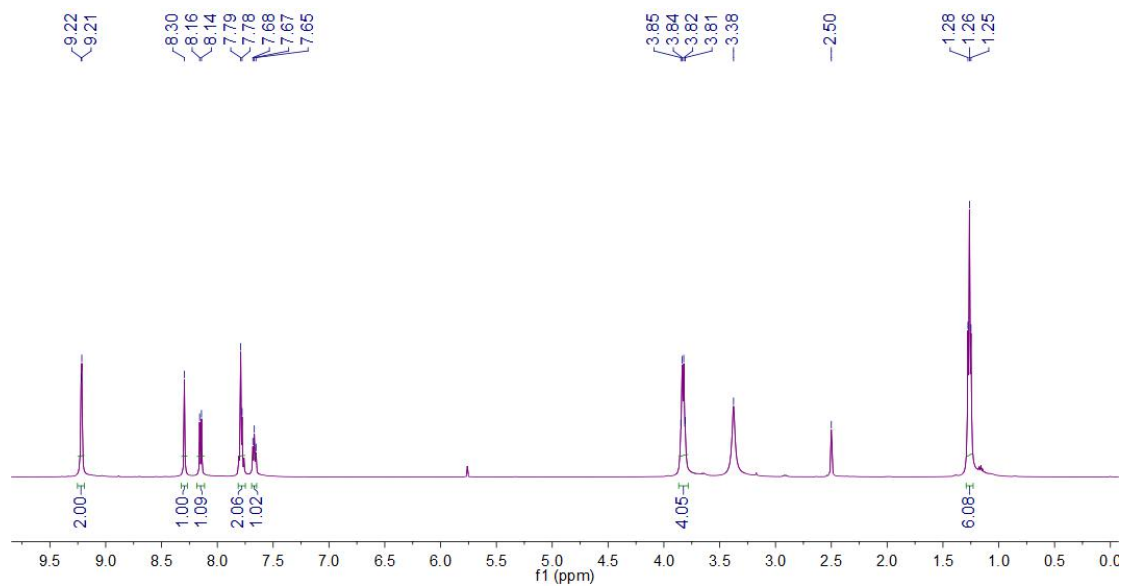
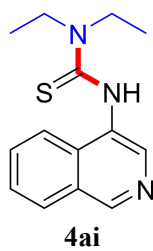


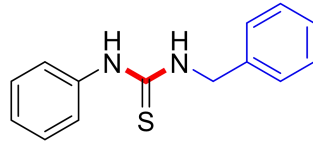




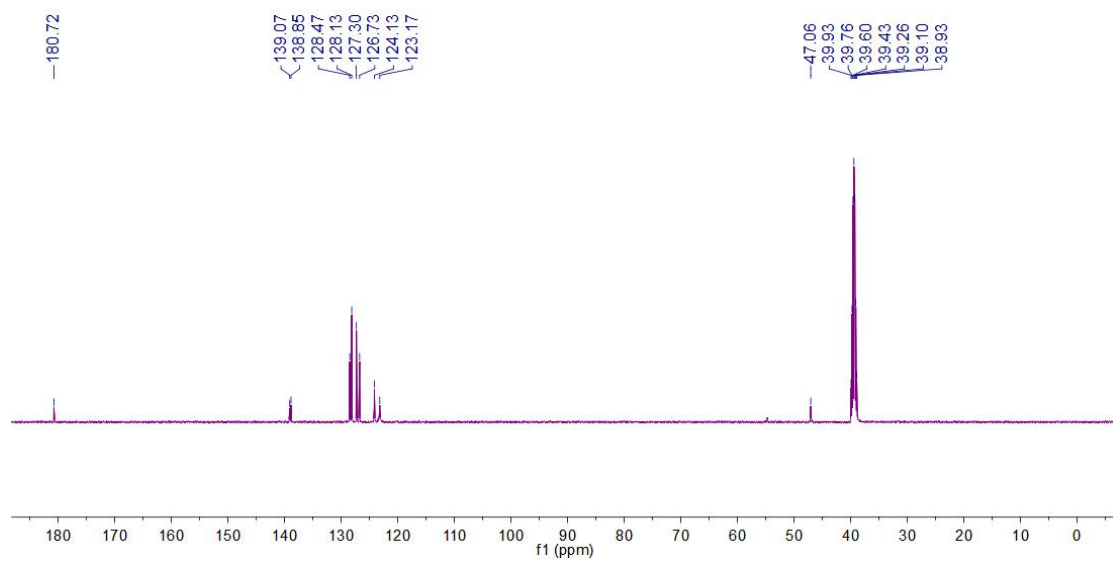
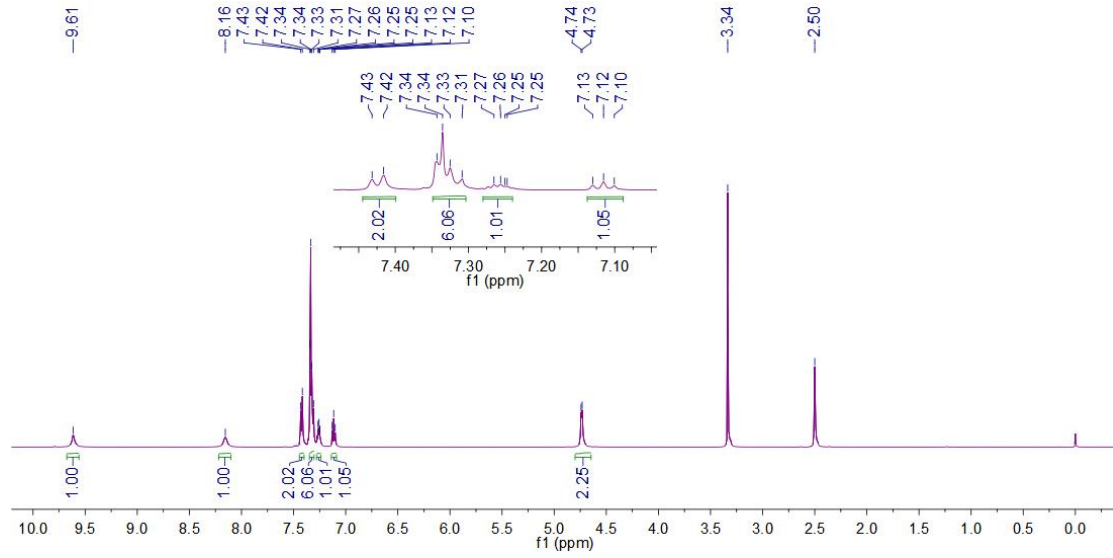


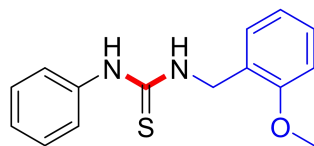




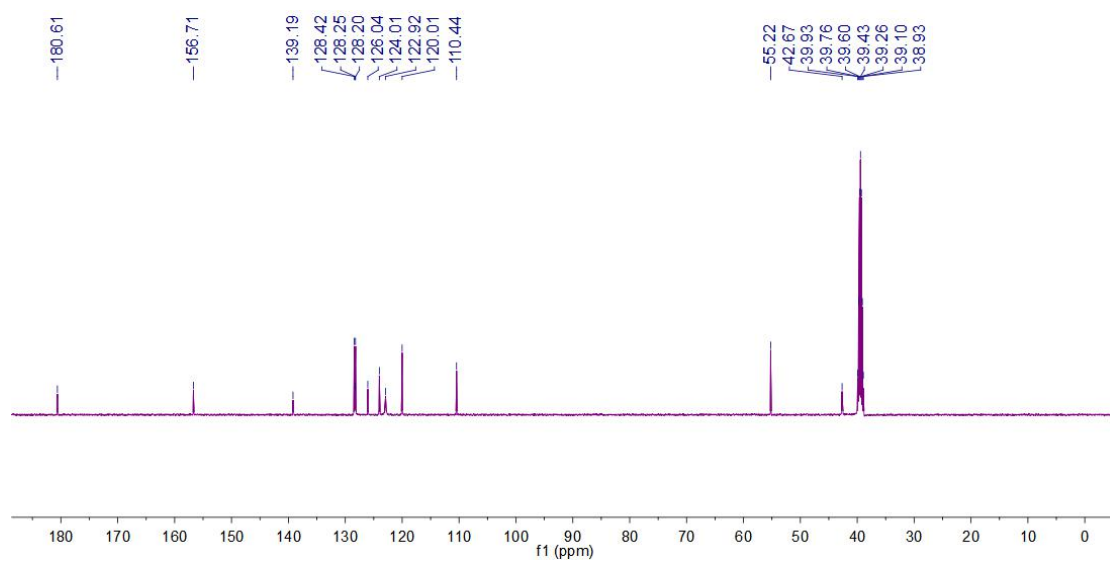
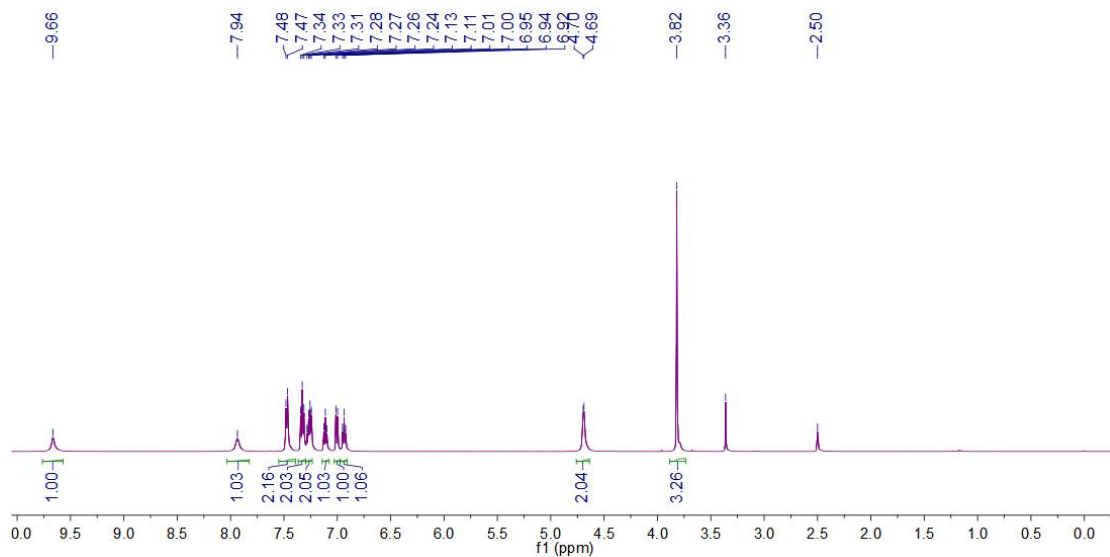


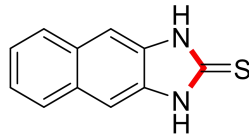
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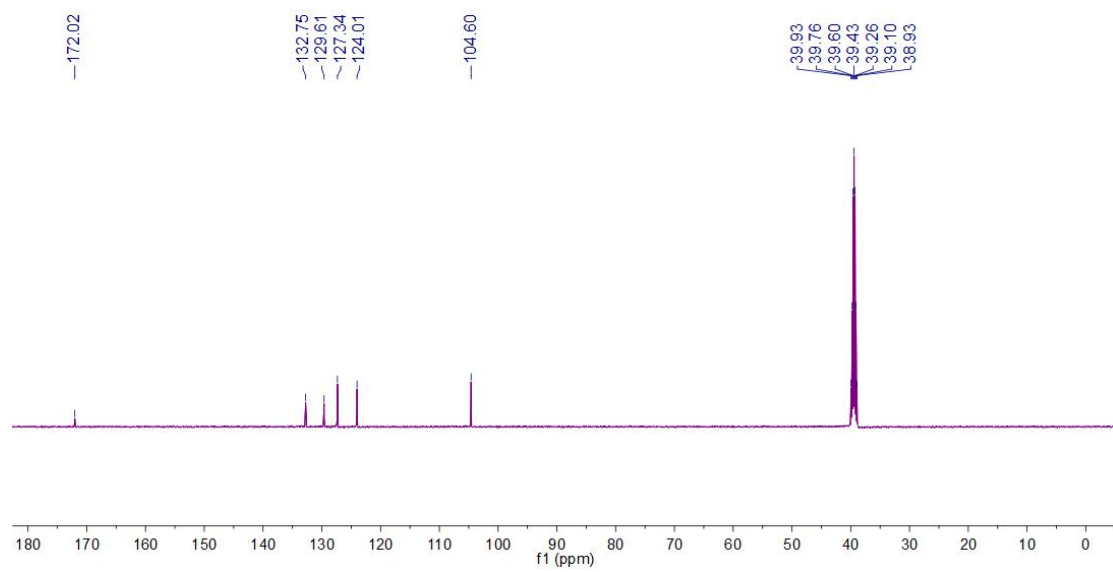
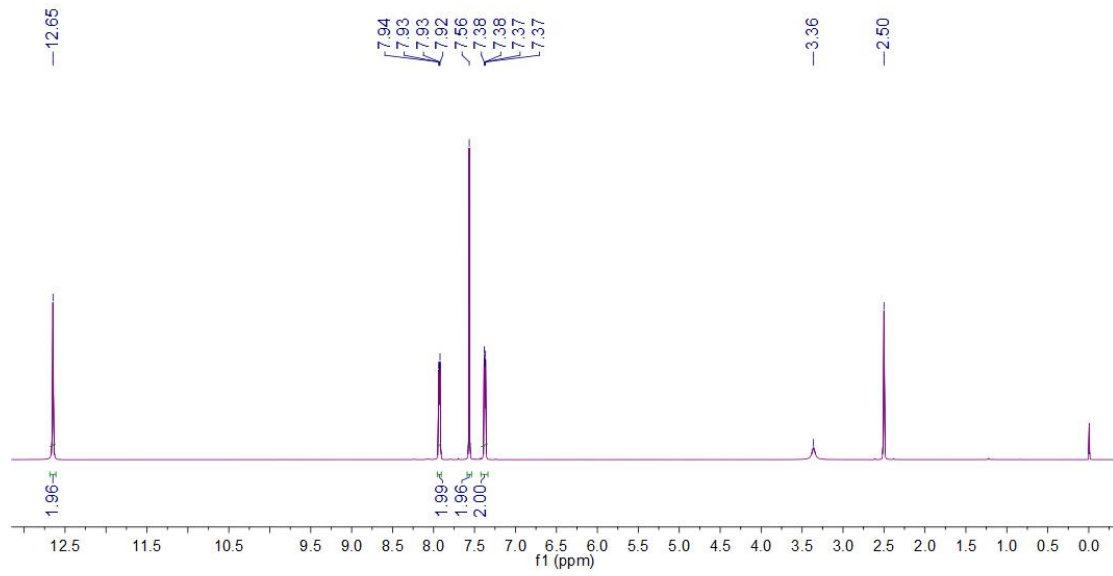


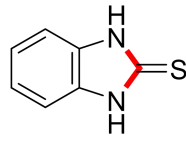
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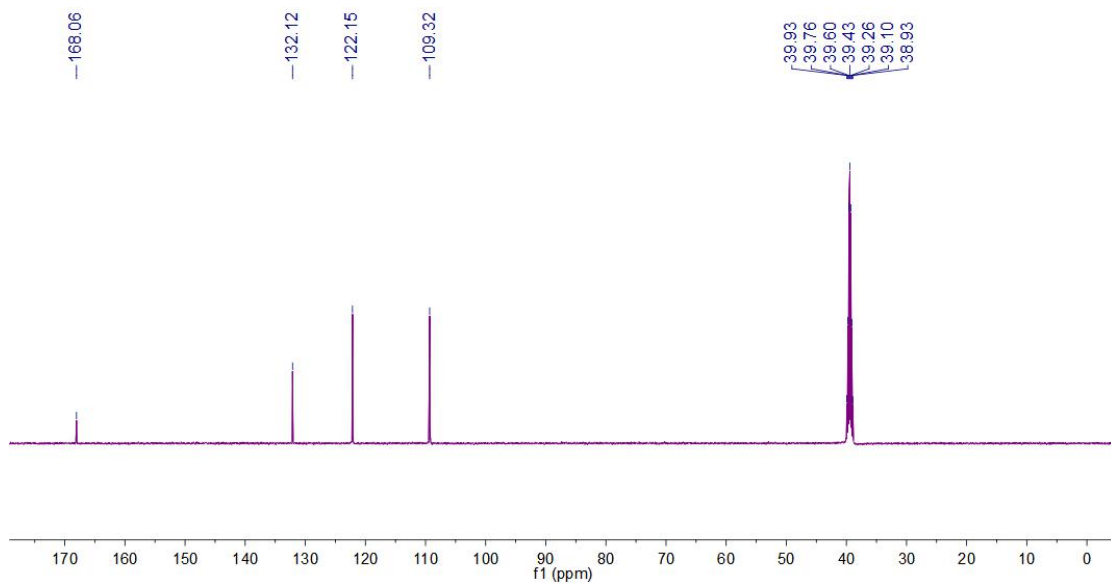
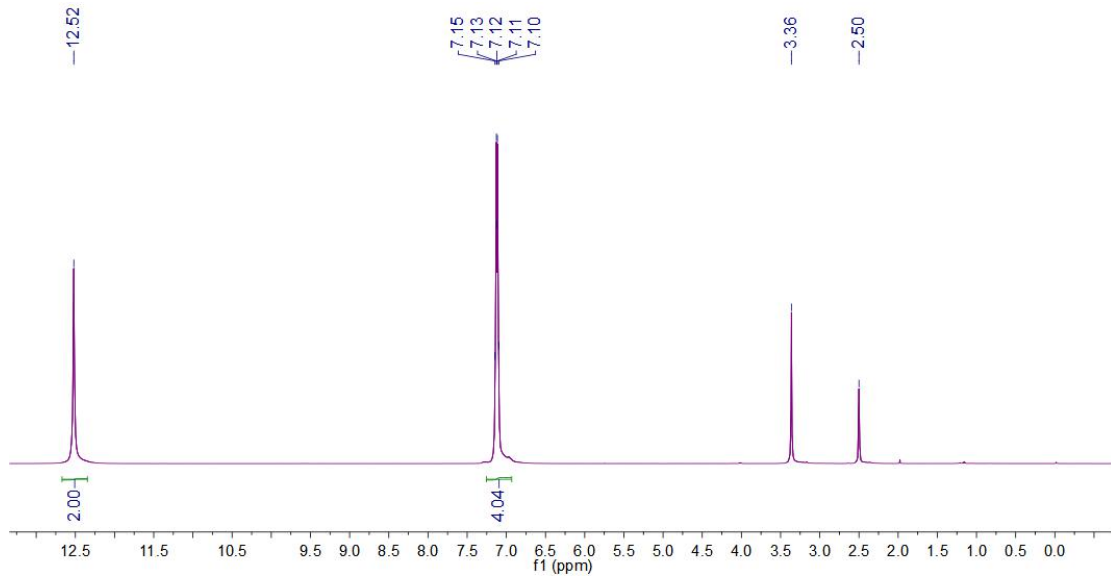


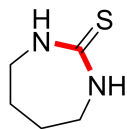
6a



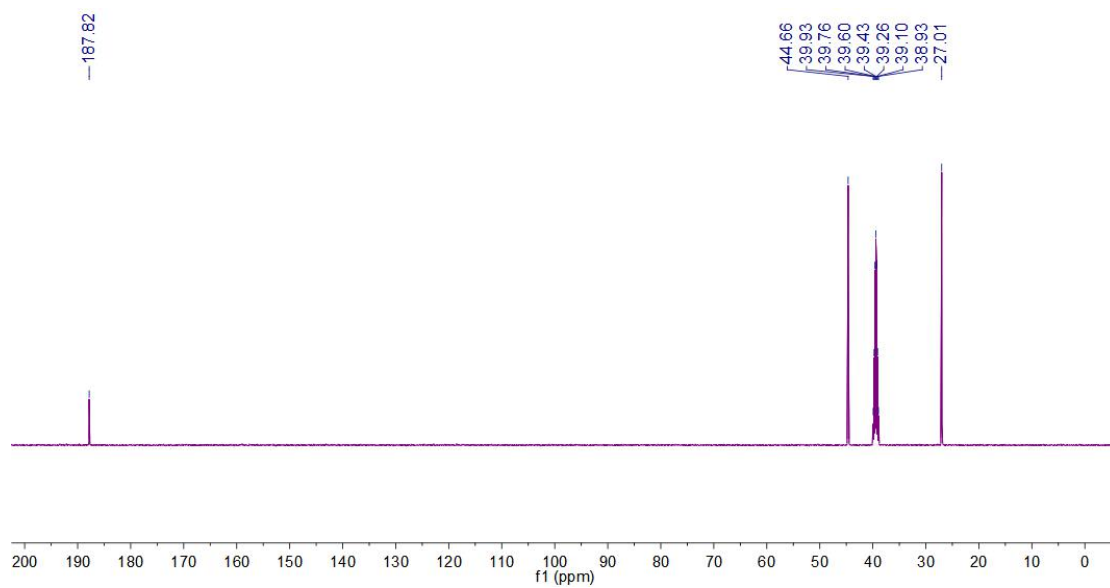
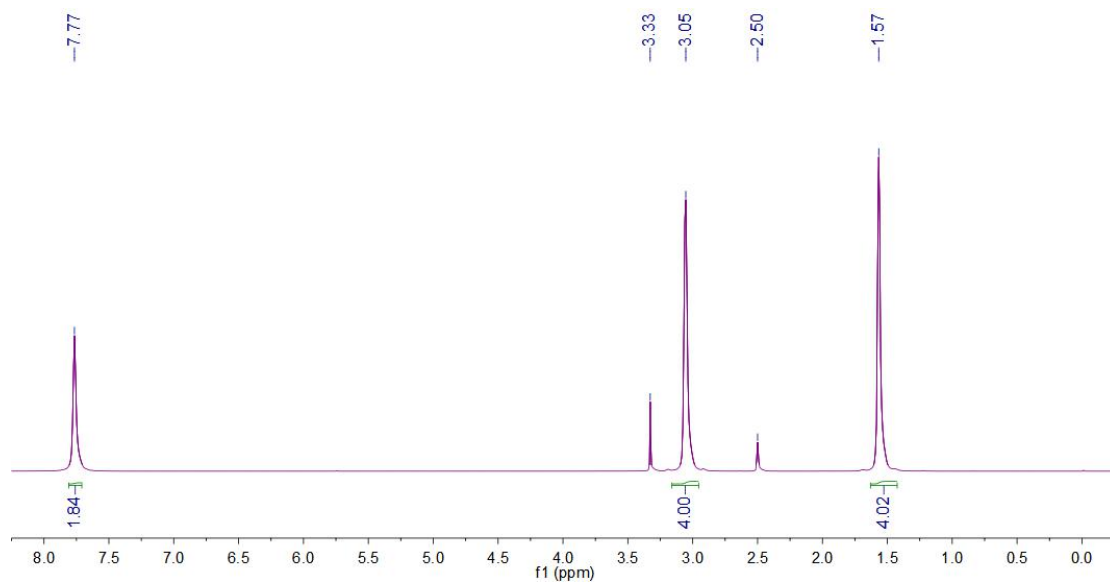


6b

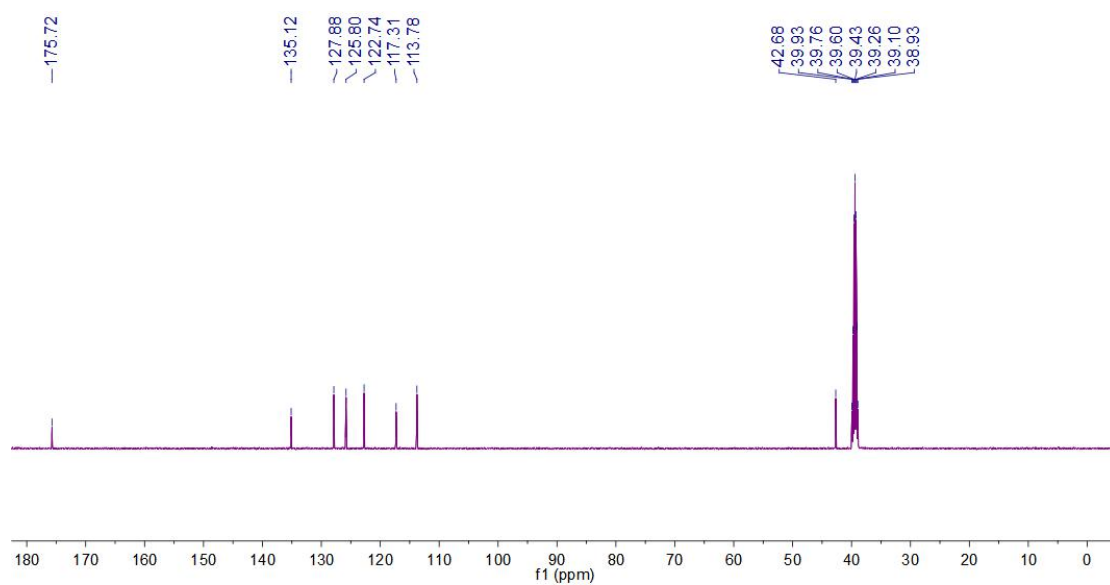
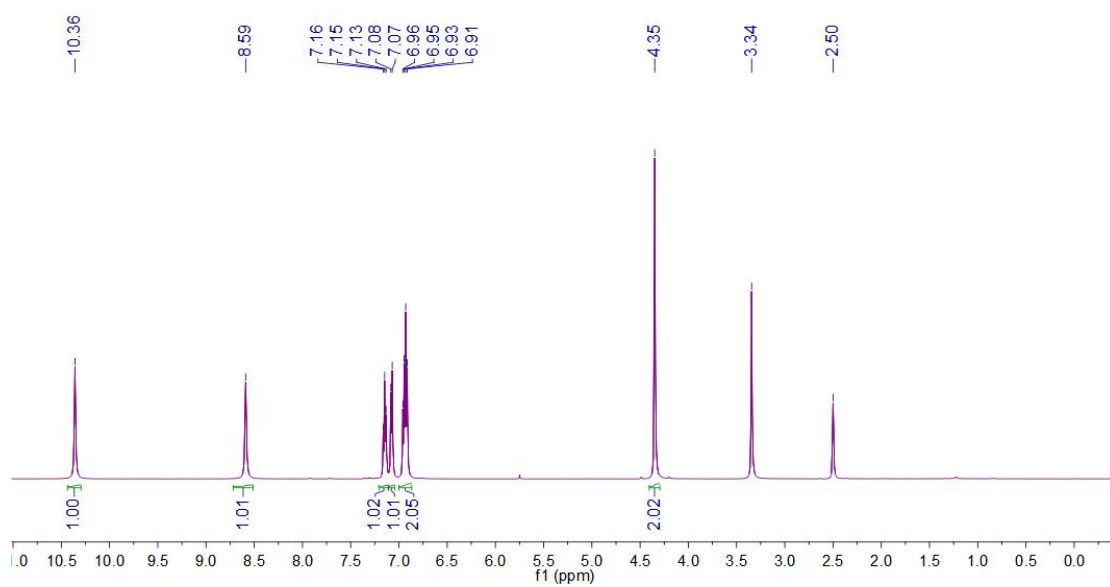
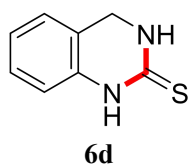


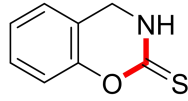


6c









6e

