

## **Supporting Information**

### **Nickel-Catalyzed Reductive Cyclization of Alkyl Dihalides**

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## I. Experimental Section

### Part 1. General Information

For product purification by flash column chromatography, silica gel (300–400 mesh) and petroleum ether (bp 60–90 °C) were used. All solvents were purified and dried by standard techniques and distilled prior to use. Organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub>, unless otherwise noted. Experiments were conducted under an argon or nitrogen atmosphere in oven-dried or flame-dried glassware with magnetic stirring, unless otherwise specified. NMR spectra were measured on 500 MHz instruments at room temperature. Reference peaks for chloroform in <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 and IonSpec 4.7 TESLA FTMS. Low resolution mass spectra were recorded on GCMS-QP2010 SE (SHIMADZU). Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China). The following chemicals were purchased and used as received: Zn (99.9%, powder), NiI<sub>2</sub> (99.5%, Alaf Aesar), Ni(cod)<sub>2</sub> (99%, Stream), NiCl<sub>2</sub> (99.5%, Alaf Aesar), NiBr<sub>2</sub> (99.5%, Alaf Aesar), Ni(acac)<sub>2</sub> (99%, Alaf Aesar), **4a–4c** (99.5%, Aldrich), **5a–5c** (99.5%, Aldrich), DMA (99.8%, Super dry, with molecular sieves), DMF (99.8%, Super dry, with molecular sieves), dioxane (99.5%, Super dry, with molecular sieves), THF (99.5%, Super dry, with molecular sieves).

## Part 2. Details of Optimization of Diiodides

*A typical procedure for optimization reactions for cyclization of alkyl diiodide:* To a flame-dried Schlenk tube equipped with a stir bar was loaded **1g** (69.0 mg, 0.15 mmol, 100 mol %), followed by addition of ligand (0.015 mmol, 10 mol %) and zinc powder (29.6 mg, 0.45 mmol, 300 mol %). The tube was moved into a dry glove box, at which point  $\text{NiI}_2$  (4.7 mg, 0.015 mmol, 10 mol %) was added. The tube was capped with a rubber septum, and it was moved out of the glove box. Solvent (1 mL) was then added via syringe. After the reaction mixture was allowed to stir for 16 hours under  $\text{N}_2$  atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.

**Table S1.** Ligand screening for intramolecular cyclization of **1g**.

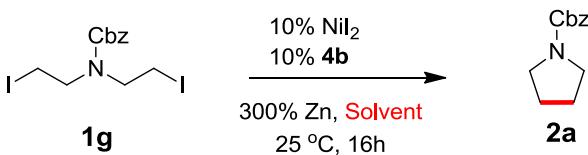
<b>1g</b>		<b>2a</b>
Entry	Ligand	Yield (%) <sup>a</sup>
1	<b>4b</b>	54
2	<b>4c</b>	29
3	<b>5a</b>	42
4	<b>5b</b>	40
5	<b>5c</b>	52
6	<b>6</b>	29
7	<b>7</b>	46

<sup>a</sup> Isolated yield.

**Table S2.** Catalyst screening for intramolecular cyclization of **1g**.

<b>1g</b>		<b>2a</b>
Entry	Catalyst	Yield ( % ) <sup>a</sup>
1	$\text{Ni}(\text{cod})_2$	27
2	$\text{Ni}(\text{acac})_2$	25
3	$\text{NiBr}_2$	22
4	$\text{NiI}_2$	54
5	$\text{NiCl}_2$	12

<sup>a</sup> Isolated yield.

**Table S3.** Solvent screening for intramolecular cyclization of **1g**.

Entry	Solvent	Yield ( % ) <sup>a</sup>
1	DMA	54
2	DMF	25
3	DMI	trace
4	1,4-Dioxane	ND <sup>b</sup>
5	DMA/1,4-Dioxane(9/1)	49
6	DMA/1,4-Dioxane(8/2)	45
7	<b>DMA/1,4-Dioxane(7/3)</b>	<b>93</b>
8	DMA/1,4-Dioxane(6/4)	50

<sup>a</sup> Isolated yield. <sup>b</sup> Not detected.

### Part 3. Preparation of Dihalides

**General Procedure A for the Synthesis of Alkyl dihalides.** To the solution of the corresponding dialcohols (10 mmol) in DCM was added imidazole (1.36 g, 20.0 mmol), PPh<sub>3</sub> (5.24 g, 20.0 mmol). I<sub>2</sub> (5.06 g, 20.0 mmol) or Br<sub>2</sub> (3.20 g, 20.0 mmol) were added over 20 minutes at 0 °C. The reaction mixture was allowed to stir overnight at room temperature. The suspension was washed with brine, and Na<sub>2</sub>SO<sub>3</sub> (saturated). The organic phase was dried (over MgSO<sub>4</sub>) and filtered, at which point silica gel was added. The mixture was concentrated under reduced pressure, and the residue was loaded onto a silica column. Flash chromatography afforded alkyl dihalides.

**General Procedure B for the Synthesis of Alkyl dihalides.** To the solution of the HBr (48% aq, 20.0 mL) was added corresponding dialcohols (10.0 mmol). The reaction mixture was allowed to reflux overnight. The suspension was washed with DCM. The organic phase was dried (over MgSO<sub>4</sub>) and filtered, at which point silica gel was added. The mixture was concentrated under reduced pressure, and the residue was loaded onto a silica column. Flash chromatography afforded alkyl dihalides.

The starting materials **1d**,<sup>1</sup> **1e**,<sup>1</sup> **1f**,<sup>2</sup> **1i**,<sup>3</sup> **1s**,<sup>4</sup> **1p**,<sup>4</sup> **1s**,<sup>5</sup> **1t**,<sup>6</sup> were synthesized by the methods

of reported literature.

**Benzyl bis(2-bromoethyl)carbamate (1a).** According to *the general procedure A*, this compound was obtained in 70% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.33 (m, 5H), 5.18 (s, 2H), 3.75 (dt,  $J$  = 3.0, 6.5 Hz, 4H), 3.56 (t,  $J$  = 7.0 Hz, 2H), 3.45 (t,  $J$  = 7.0 Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.5, 136.1, 128.6, 128.2, 127.9, 67.6, 50.9, 50.4, 29.5, 29.4. HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{15}\text{Br}_2\text{NO}_2$  [M] $^+$  362.9467, found 362.9470.

**Phenyl bis(2-bromoethyl)carbamate (1b).** According to *the general procedure A*, this compound was obtained in 75% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.38 (m, 2H), 7.27-7.23 (m, 1H), 7.16-7.13 (m, 2H), 3.93 (t,  $J$  = 7.0 Hz, 2H), 3.82 (t,  $J$  = 6.5 Hz, 2H), 3.62 (t,  $J$  = 6.5 Hz, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.1, 150.8, 129.4, 125.7, 121.5, 51.0, 50.8, 29.3, 29.2. HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{13}\text{Br}_2\text{NO}_2$  [M] $^+$  348.9311, found 348.9313.

**Methyl bis(2-bromoethyl)carbamate (1c).** According to *the general procedure A*, this compound was obtained in 67% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.74 (s, 3H), 3.73-3.68 (m, 4H), 3.55 (t,  $J$  = 6.8 Hz, 2H), 3.45 (t,  $J$  = 6.8 Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.2, 53.0, 50.9, 50.4, 29.5, 29.2. HRMS (ESI): calcd for  $\text{C}_6\text{H}_{11}\text{Br}_2\text{NO}_2$  [M] $^+$  286.9150, found 286.9156.

**Benzyl bis(2-iodoethyl)carbamate (1g).** According to *the general procedure A*, this compound was obtained in 80% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.33 (m, 5H), 5.18 (s, 2H), 3.71-3.67 (m, 4H), 3.31 (t,  $J$  = 7.5 Hz, 2H), 3.22 (t,  $J$  = 7.5 Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.4, 136.1, 128.6, 128.2, 127.9, 67.6, 51.2, 50.8, 1.5, 1.47. HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{15}\text{I}_2\text{NO}_2$  [M] $^+$  458.9119, found 458.9192.

**Phenyl bis(2-iodoethyl)carbamate (1h).** According to *the general Procedure A*, this compound was obtained in 50% yield. White solid. M.P. 105-107 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.38 (m, 2H), 7.27-7.23 (m, 1H), 7.16-7.14 (m, 2H), 3.86 (t,  $J$  = 7.5 Hz, 2H), 3.76 (t,  $J$  = 7.0 Hz, 2H), 3.38 (dt,  $J$  = 1.5, 7.5 Hz, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.9, 150.8, 129.4, 125.7, 121.5, 51.2, 51.1, 1.3, 1.2. HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{13}\text{I}_2\text{NO}_2$  [M] $^+$  444.903, found 444.9036.

**1-(1,5-Dibromopentan-3-yl)-4-methoxybenzene (1j).** According to *the general procedure B*, this compound was obtained in 40% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14-7.07 (m, 2H), 6.91-6.82 (m, 2H), 3.80 (d,  $J$  = 2.1 Hz, 3H), 3.28 (ddd,  $J$  = 10.0, 7.0, 5.0 Hz, 2H), 3.15-3.05 (m, 2H), 3.00 (tt,  $J$  = 10, 5.0 Hz, 1H), 2.19-2.06 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 133.2, 128.6, 114.23, 55.2, 41.7, 39.3, 31.5. HRMS (ESI): calcd for  $\text{C}_{12}\text{H}_{16}\text{Br}_2\text{O} [\text{M}]^+$  333.9564, found 333.9568.

**4-(1,5-Dibromopentan-3-yl)-1,1'-biphenyl (1k).** According to *the general procedure B*, this compound was obtained in 43% yield. White solid. M.p. 68-70 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64-7.53 (m, 4H), 7.45 (dd,  $J$  = 10.5, 4.8 Hz, 2H), 7.35 (t,  $J$  = 7.4 Hz, 1H), 7.28 (d,  $J$  = 8.2 Hz, 2H), 3.30-3.35 (m, 2H), 3.21-3.06 (m, 3H), 2.26-2.15 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.7, 140.5, 140.0, 128.8, 128.1, 127.6, 127.3, 127.0, 42.3, 39.2, 31.4. HRMS (ESI): calcd for  $\text{C}_{17}\text{H}_{18}\text{Br}_2 [\text{M}]^+$  379.9775, found 379.9775.

**4-(1,5-Diiodopentan-3-yl)-1,1'-biphenyl (1l).** According to *the general procedure A*, this compound was obtained in 38% yield. Yellow solid. M.p. 70-73 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.58 (dd,  $J$  = 15.2, 7.7 Hz, 4H), 7.45 (t,  $J$  = 7.7 Hz, 2H), 7.36 (t,  $J$  = 7.4 Hz, 1H), 7.28 (d,  $J$  = 8.1 Hz, 2H), 3.08-3.13 (m, 2H), 3.01-2.84 (m, 3H), 2.26-2.10 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.6, 140.3, 139.9, 128.8, 128.1, 127.6, 127.2, 126.9, 46.6, 39.7, 4.3. HRMS (ESI): calcd for  $\text{C}_{17}\text{H}_{18}\text{I}_2 [\text{M}]^+$  475.9495, found 475.9498.

**N-(2-Bromoethyl)-N-(2-bromopropyl)aniline (1m).** According to *the general procedure B*, this compound was obtained in 20% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31-7.26 (m, 2H), 6.80 (t,  $J$  = 7.3 Hz, 1H), 6.70 (d,  $J$  = 8.0 Hz, 2H), 4.39-4.24 (m, 1H), 3.90 (ddd,  $J$  = 15.3, 9.2, 6.1 Hz, 1H), 3.83-3.71 (m, 2H), 3.64 (dd,  $J$  = 15.3, 7.4 Hz, 1H), 3.53-3.41 (m, 2H), 1.74 (d,  $J$  = 6.7 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.0, 129.8, 117.8, 112.3, 60.2, 53.9, 46.7, 28.1, 23.6. HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{15}\text{Br}_2\text{N} [\text{M}]^+$  318.9567, found 318.9571.

**Benzyl (2-bromoethyl)(2-bromopropyl)carbamate (1n).** According to *the general procedure A*, this compound was obtained in 53% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42-7.29 (m, 5H), 5.22-5.11 (m, 2H), 4.46-4.18 (m, 1H), 3.90-3.64

(m, 3H), 3.63-3.37 (m, 3H), 1.60-1.72 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.8, 136.2, 128.6, 128.3, 127.9, 67.6, 57.6, 57.0, 51.2, 50.7, 47.6, 47.2, 29.4, 23.4, 23.3. HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{17}\text{Br}_2\text{NO}_2$   $[\text{M}]^+$  376.962, found 376.9626.

**Benzyl bis(2-bromopropyl)carbamate (1o).** According to *the general procedure A*, this compound was obtained in 37% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.30 (m, 5H), 5.21-5.11 (m, 2H), 4.54-4.38 (m, 1H), 4.35-4.15 (m, 1H), 3.99-3.72 (m, 2H), 3.68-3.38 (m, 2H), 1.68 (d,  $J = 6.7$  Hz, 3H), 1.65-1.59 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.8, 136.1, 128.6, 128.2, 127.8, 67.5, 58.2, 57.1, 48.0, 47.9, 23.5, 23.4. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{19}\text{Br}_2\text{NO}_2$   $[\text{M}]^+$  390.9778, found 390.9783.

**Benzyl (2-bromoethyl)(3-bromopropyl)carbamate (1q).** According to *the general procedure A*, this compound was obtained in 45% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41-7.29 (m, 5H), 5.15 (s, 2H), 3.73-3.62 (m, 2H), 3.33-3.54 (m, 6H), 2.25-2.05 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.3, 128.6, 128.2, 128.0, 67.5, 50.3, 49.6, 47.4, 31.9, 31.4, 30.6, 30.3, 29.1. HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{17}\text{Br}_2\text{NO}_2$   $[\text{M}]^+$  376.962, found 376.9626.

**Benzyl (2-bromopropyl)(3-bromopropyl)carbamate (1r).** According to *the general procedure A*, this compound was obtained in 25% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41-7.28 (m, 5H), 5.20-5.10 (m, 2H), 4.47-4.13 (m, 1H), 3.77-3.28 (m, 6H), 2.20-1.95 (m, 2H), 1.75-1.55 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.3, 155.9, 136.4, 136.3, 128.2, 128.0, 127.9, 67.5, 67.4, 56.8, 56.0, 47.7, 47.5, 47.4, 47.3, 47.2, 46.9, 46.7, 46.4, 46.3, 42.43, 42.42, 42.40, 42.2, 31.7, 31.6, 31.1, 30.9, 30.7, 30.4, 23.5, 23.4. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{19}\text{Br}_2\text{NO}_2$   $[\text{M}]^+$  390.9778, found 390.9783.

**Benzyl bis(3-bromopropyl)carbamate (1u).** According to *the general procedure A*, this compound was obtained in 48% yield. Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40-7.29 (m, 5H), 5.13 (s, 2H), 3.1-3.5 (m, 8H), 2.0-2.2 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.1, 136.5, 128.6, 128.1, 67.3, 46.8, 46.2, 31.8, 31.3, 30.7, 30.4. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{19}\text{Br}_2\text{NO}_2$   $[\text{M}]^+$  390.9778, found 390.9783.

## Part 4. Reductive Cyclization

**General procedure C for reductive cyclization.** To a flame-dried Schlenk tube equipped with a stir bar was loaded alkyl dihalides (0.15 mmol, 100 mol%), followed by addition of ligand (0.015 mmol, 10 mol%) and zinc power (29.6 mg, 0.45 mmol, 300 mol%). The tube was moved to a dry glove box, at which point  $\text{NiI}_2$  (4.7 mg, 0.015 mmol, 10 mol%) was added. The tube was capped with a rubber septum, and it was moved out of the glove box. Solvent (1 mL) was then added via syringe. After the reaction mixture was allowed to stir for 16 hours under  $\text{N}_2$  atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of DCM. Flash column chromatography provided the product as a solid or oil.

**Benzyl pyrrolidine-1-carboxylate (2a).** According to *the general procedure C*, this compound was obtained in 83% (from **1a**), 93% (from **1g**) yields, respectively. The data matched those reported in the literature.<sup>7</sup> Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41-7.27 (m, 5H), 5.14 (s, 2H), 3.41 (t,  $J$  = 6.5 Hz, 2H), 3.38 (t,  $J$  = 6.5 Hz, 2H), 2.00-1.79 (m, 4H). GC-MS (EI) m/z: 205 ( $\text{M}^+$ ).

**Phenyl pyrrolidine-1-carboxylate (2b).** According to *the general procedure C*, this compound was obtained in 92% (from **1b**) and 70% (from **1h**) yields, respectively. The data matched those reported in the literature.<sup>8</sup> Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35 (t,  $J$  = 7.9 Hz, 2H), 7.23-7.08 (m, 3H), 3.56 (t,  $J$  = 6.6 Hz, 2H), 3.48 (t,  $J$  = 6.6 Hz, 2H), 2.02-1.86 (m, 4H). GC-MS (EI) m/z: 191 ( $\text{M}^+$ ).

**Methyl pyrrolidine-1-carboxylate (2c).** According to *the general procedure C*, this compound was obtained in 48% yield. The data matched those reported in the literature. Colorless oil.<sup>9</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.66 (s, 3H), 3.25-3.44 (m, 4H), 1.78-1.88 (m, 4H). GC-MS (EI) m/z: 129 ( $\text{M}^+$ )

**1-Phenylpyrrolidine (2d).** According to *the general procedure C*, this compound was obtained in 54% yield. The data matched those reported in the literature.<sup>10</sup> Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.38-7.26 (m, 2H), 6.68-6.75 (m, 1H), 6.67-6.58 (m, 2H), 3.38-3.30 (m, 4H), 2.10-2.00 (m, 4H). GC-MS (EI) m/z: 147 ( $\text{M}^+$ ).

**1-(p-Tolyl)pyrrolidine (2e).** According to *the general procedure C*, this compound was obtained in 50% (from **1e**) and 58% (from **1i**) yields, respectively. The data matched those reported in the literature.<sup>11</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.04 (d, *J* = 8.3 Hz, 2H), 6.51 (d, *J* = 8.3 Hz, 2H), 3.26 (t, *J* = 6.5 Hz, 4H), 2.25 (s, 3H), 2.04-1.94 (m, 4H). GC-MS (EI) m/z: 161 (M<sup>+</sup>).

**1-Cyclopentyl-4-methoxybenzene (2j).** According to *the general procedure C*, this compound was obtained in 42% yield. The data matched those reported in the literature.<sup>12</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.02 -2.87 (m, 1H), 2.14 -1.96 (m, 2H), 1.88-1.75 (m, 2H), 1.74-1.62 (m, 2H), 1.63-1.47 (m, 2H). GC-MS (EI) m/z: 176 (M<sup>+</sup>).

**4-Cyclopentyl-1,1'-biphenyl (2k).** According to *the general procedure C*, this compound was obtained in 52% (from **1k**) and 56% (from **1l**) yields, respectively. The data matched those reported in the literature.<sup>13</sup> White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.61-7.57 (m, 2H), 7.54 (dd, *J* = 8.1, 6.3 Hz, 2H), 7.44 (dd, *J* = 10.5, 4.9 Hz, 2H), 7.36-7.30 (m, 3H), 3.11-2.96 (m, 1H), 2.19-2.09 (m, 2H), 1.90-1.80 (m, 2H), 1.77-1.61 (m, 4H). GC-MS (EI) m/z: 222 (M<sup>+</sup>).

**3-Methyl-1-phenylpyrrolidine (2m).** According to *the general procedure C*, this compound was obtained in 46% yield. The data matched those reported in the literature.<sup>14</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.18 (t, *J* = 8.7 Hz, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 3.60-3.41 (m, 3H), 2.98-3.05 (m, 1H), 2.58-2.46 (m, 1H), 2.30-2.21 (m, 1H), 1.79-1.68 (m, 1H), 1.23 (d, *J* = 6.4 Hz, 3H). GC-MS (EI) m/z: 161 (M<sup>+</sup>).

**Benzyl 3-methylpyrrolidine-1-carboxylate (2n).** According to *the general procedure C*, this compound was obtained in 61% yield. Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44-7.27 (m, 5H), 5.13 (s, 2H), 3.68-3.45 (m, 2H), 3.45-3.28 (m, 1H), 2.99-2.82 (m, 1H), 2.23 (td, *J* = 14.6, 7.3 Hz, 1H), 2.05-1.91 (m, 1H), 1.57-1.39 (m, 1H), 1.05 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  154.8, 137.1, 128.4, 127.8, 127.7, 66.5, 66.4, 53.2, 52.8, 46.0, 45.5, 33.6, 33.5, 32.8, 32.8, 32.6, 17.6. GC-MS (EI) m/z: 219 (M<sup>+</sup>). HRMS (ESI): calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub> [M]<sup>+</sup> 219.1256, found 219.1259.

**Benzyl 3,4-dimethylpyrrolidine-1-carboxylate (2o).** According to *the general procedure C*, this compound was obtained in 71% yield. Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42-7.27 (m, 5H), 5.18-5.09 (m, 2H), 3.61-3.73 (m, 1H), 3.59-3.45 (m, 1H), 3.11 (ddd,  $J$  = 30.0, 10.7, 5.7 Hz, 1H), 2.93 (dd,  $J$  = 21.1, 10.8 Hz, 1H), 2.24 (tq,  $J$  = 12.7, 6.4 Hz, 1H), 1.78-1.65 (m, 1H), 1.01 (dd,  $J$  = 10.2, 6.1 Hz, 3H), 0.93 (dd,  $J$  = 6.6, 3.0 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  155.0, 154.6, 137.1, 128.4, 127.8, 127.76, 127.72, 66.5, 66.4, 53.5, 53.2, 52.4, 51.9, 40.6, 39.8, 36.1, 35.3, 15.5, 13.1, 13.0. GC-MS (EI) m/z: 233 (M<sup>+</sup>). HRMS (ESI): calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub> [M]<sup>+</sup> 233.1405, found 233.1416.

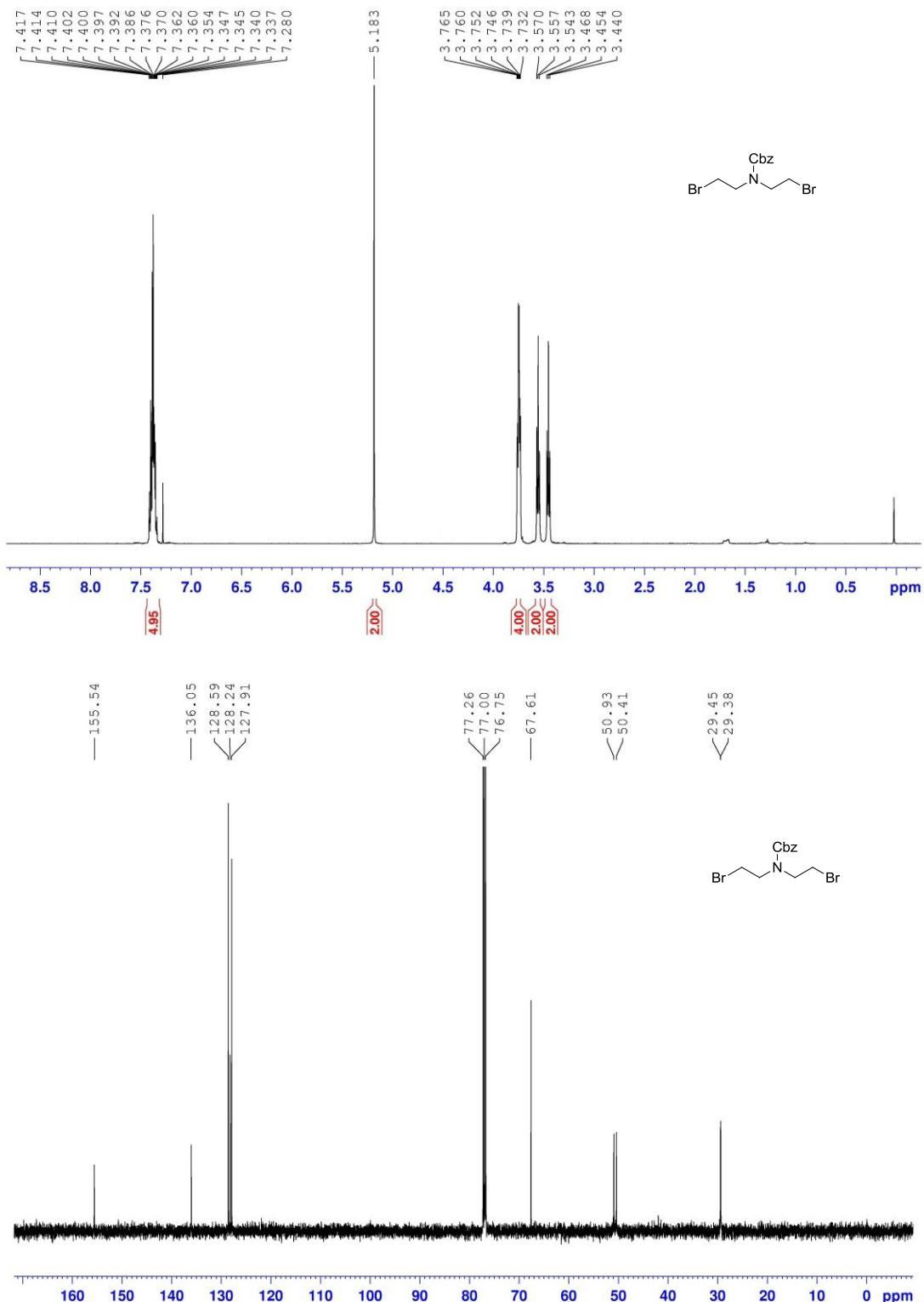
**Benzyl piperidine-1-carboxylate (2q).** According to *the general procedure C*, this compound was obtained in 50% yield. The data matched those reported in the literature.<sup>15</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.41-7.27 (m, 5H), 5.13 (s, 2H), 3.45 (t,  $J$  = 5.7 Hz, 4H), 1.64-1.42 (m, 6H). GC-MS (EI) m/z: 219 (M<sup>+</sup>).

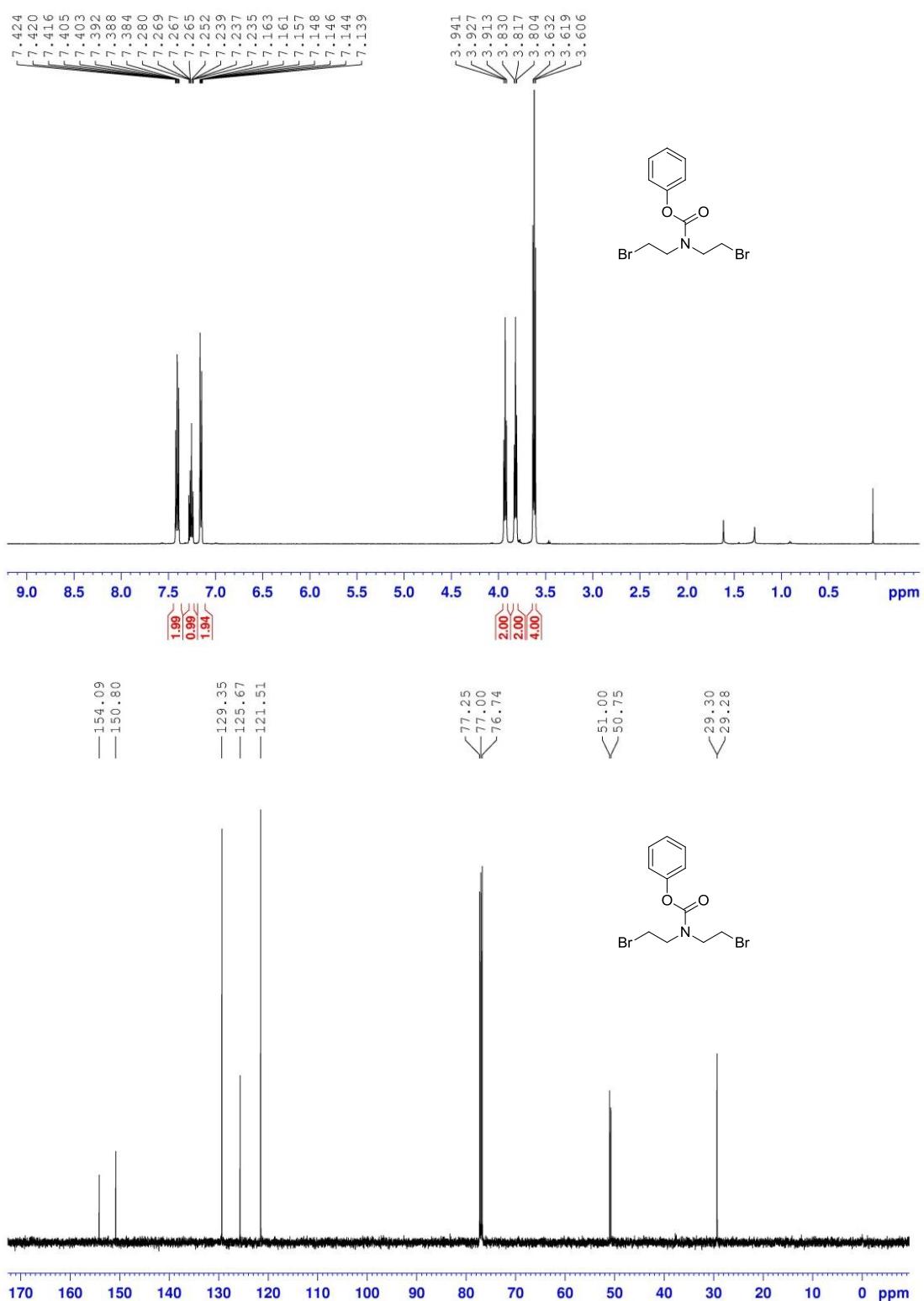
**Benzyl 3-methylpiperidine-1-carboxylate (2r).** According to *the general procedure C*, this compound was obtained in 60% yield. The data matched those reported in the literature.<sup>16</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.41-7.27 (m, 5H), 5.12 (s, 2H), 3.87-4.22 (m, 2H), 2.76 (td,  $J$  = 13.0, 3.0 Hz, 1H), 2.32-2.59 (m, 1H), 1.77-1.84 (m, 1H), 1.40-1.69 (m, 3H), 1.16 – 0.98 (m, 1H), 0.88 (d,  $J$  = 6.4 Hz, 3H). GC-MS (EI) m/z: 233 (M<sup>+</sup>).

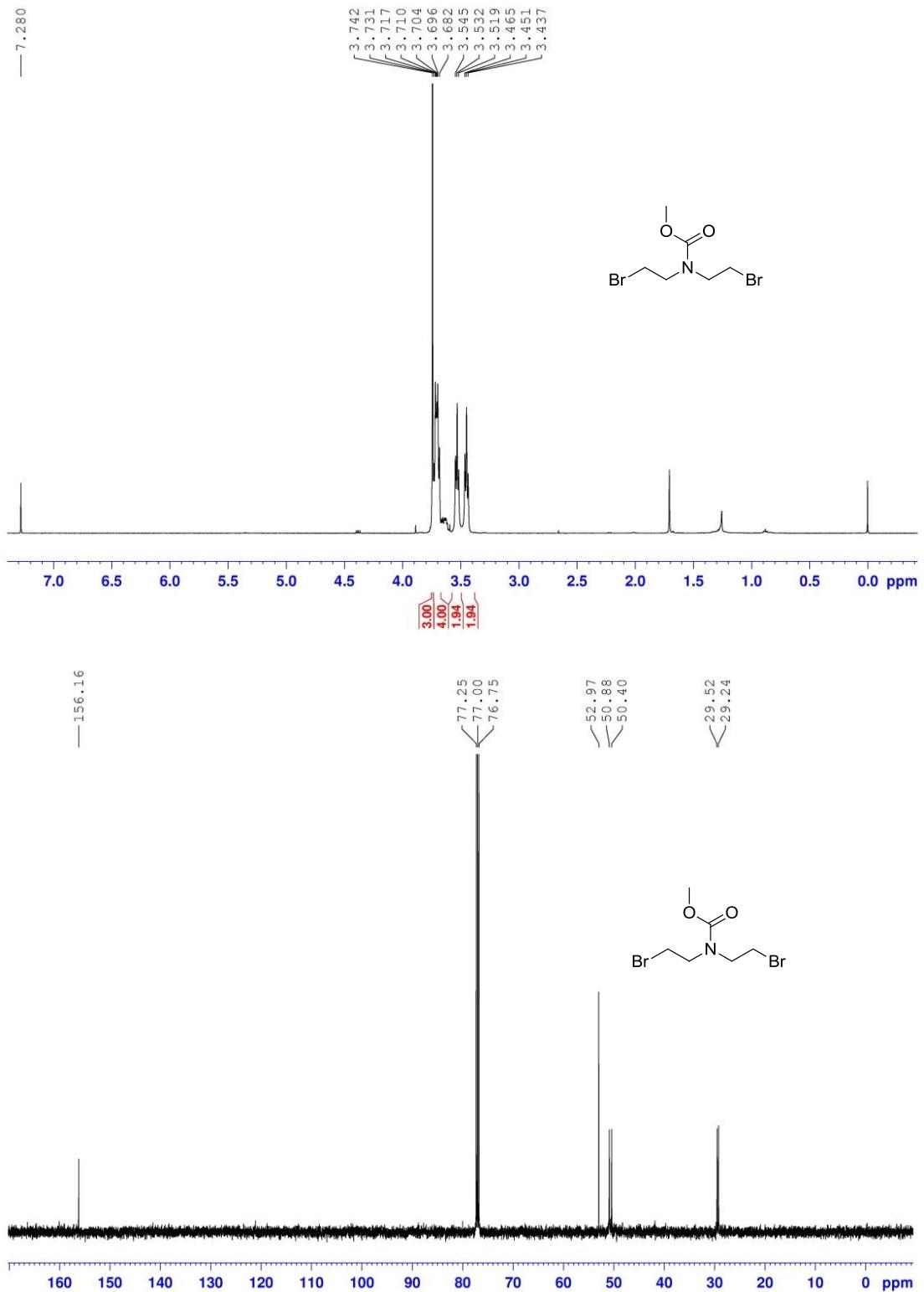
**9,10-Dihydrophenanthrene (2t).** According to *the general procedure C*, this compound was obtained in 66% yield. The data matched those reported in the literature.<sup>17</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (d,  $J$  = 7.7 Hz, 2H), 7.31-7.37 (m, 2H), 7.28-7.22 (m, 4H), 2.89 (s, 4H). GC-MS (EI) m/z: 180 (M<sup>+</sup>).

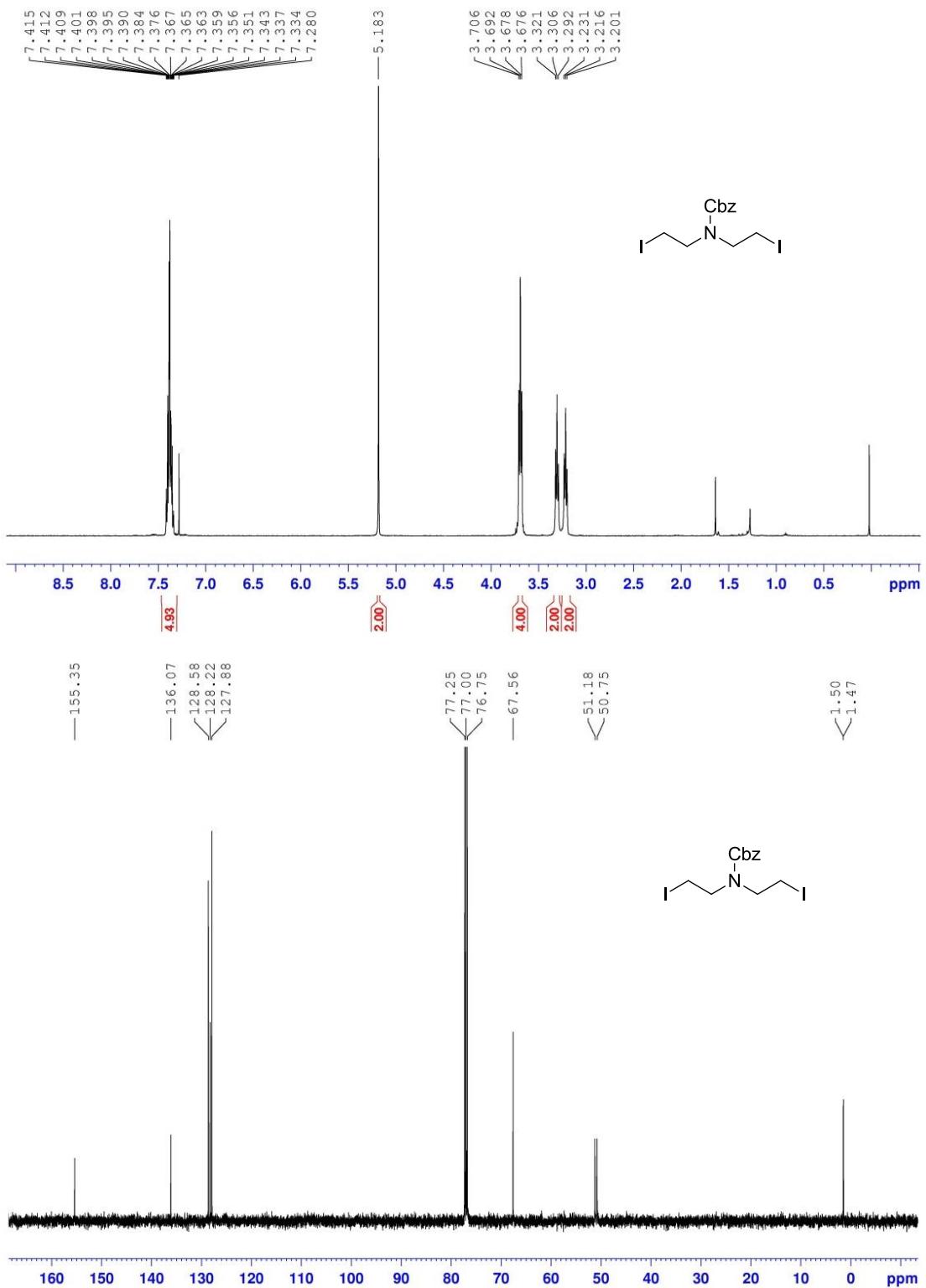
**Benzyl azepane-1-carboxylate (2u).** According to *the general procedure C*, this compound was obtained in 38% yield. The data matched those reported in the literature.<sup>16</sup> Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.41-7.27 (m, 5H), 5.14 (s, 2H), 3.48 (t,  $J$  = 6.0 Hz, 2H), 3.42 (t,  $J$  = 6.0 Hz, 2H), 1.76-1.62 (m, 4H), 1.61-1.52 (m, 4H). GC-MS (EI) m/z: 233 (M<sup>+</sup>).

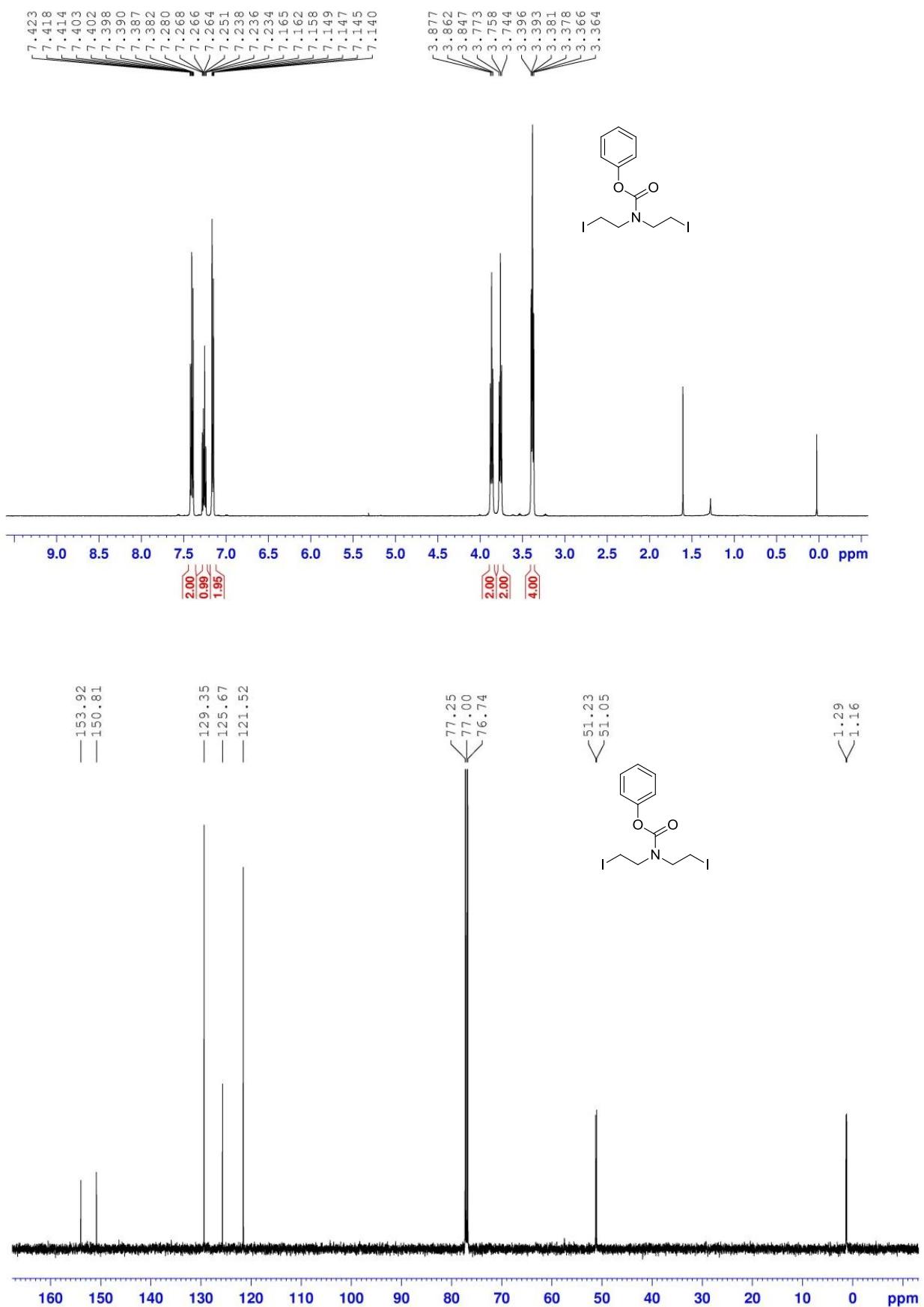
## II. Spectral Data for Compounds

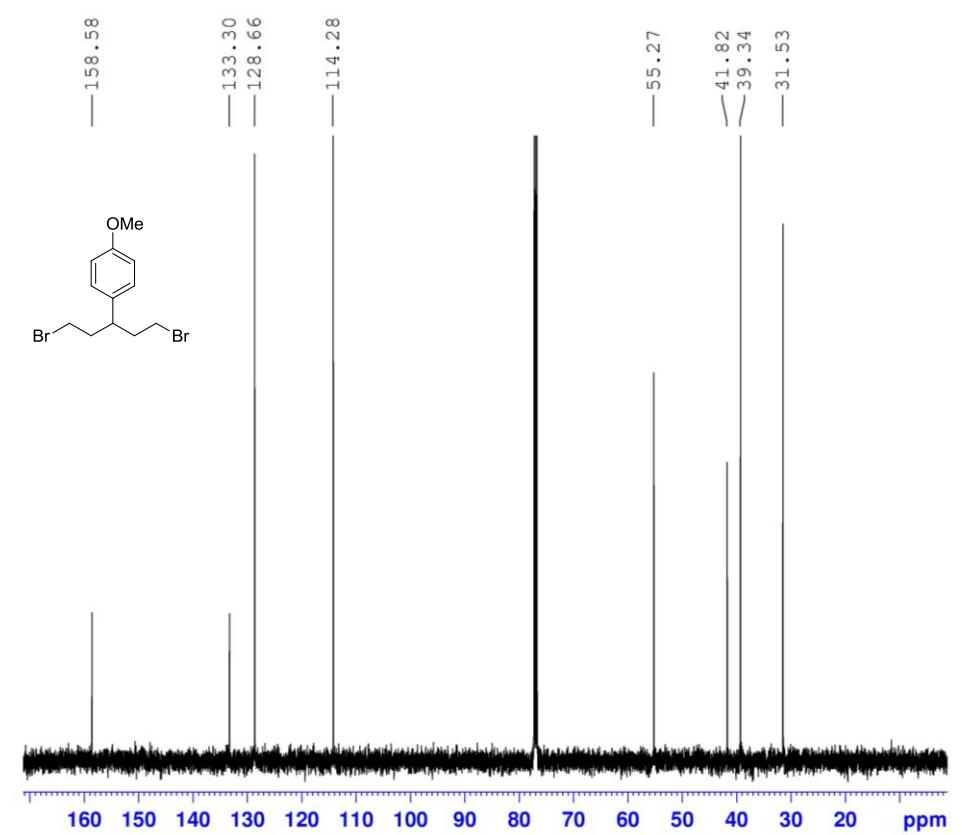
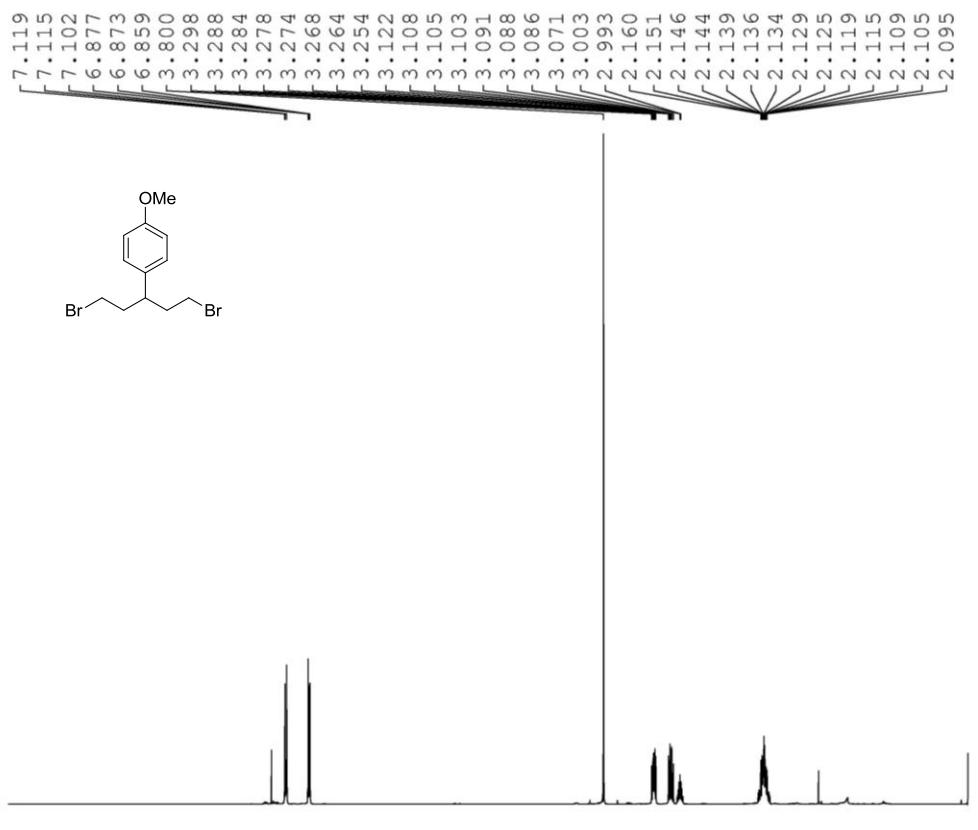


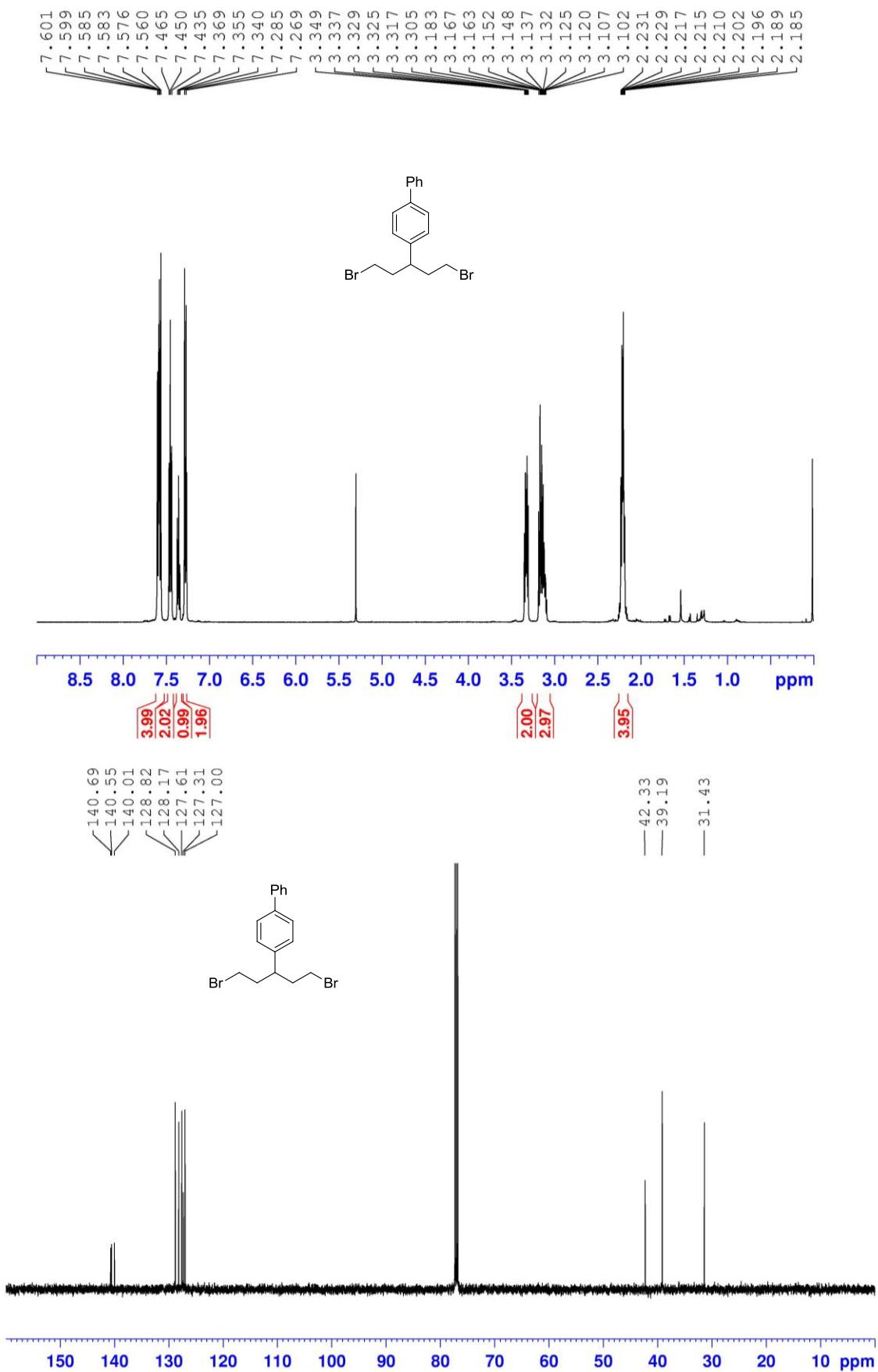


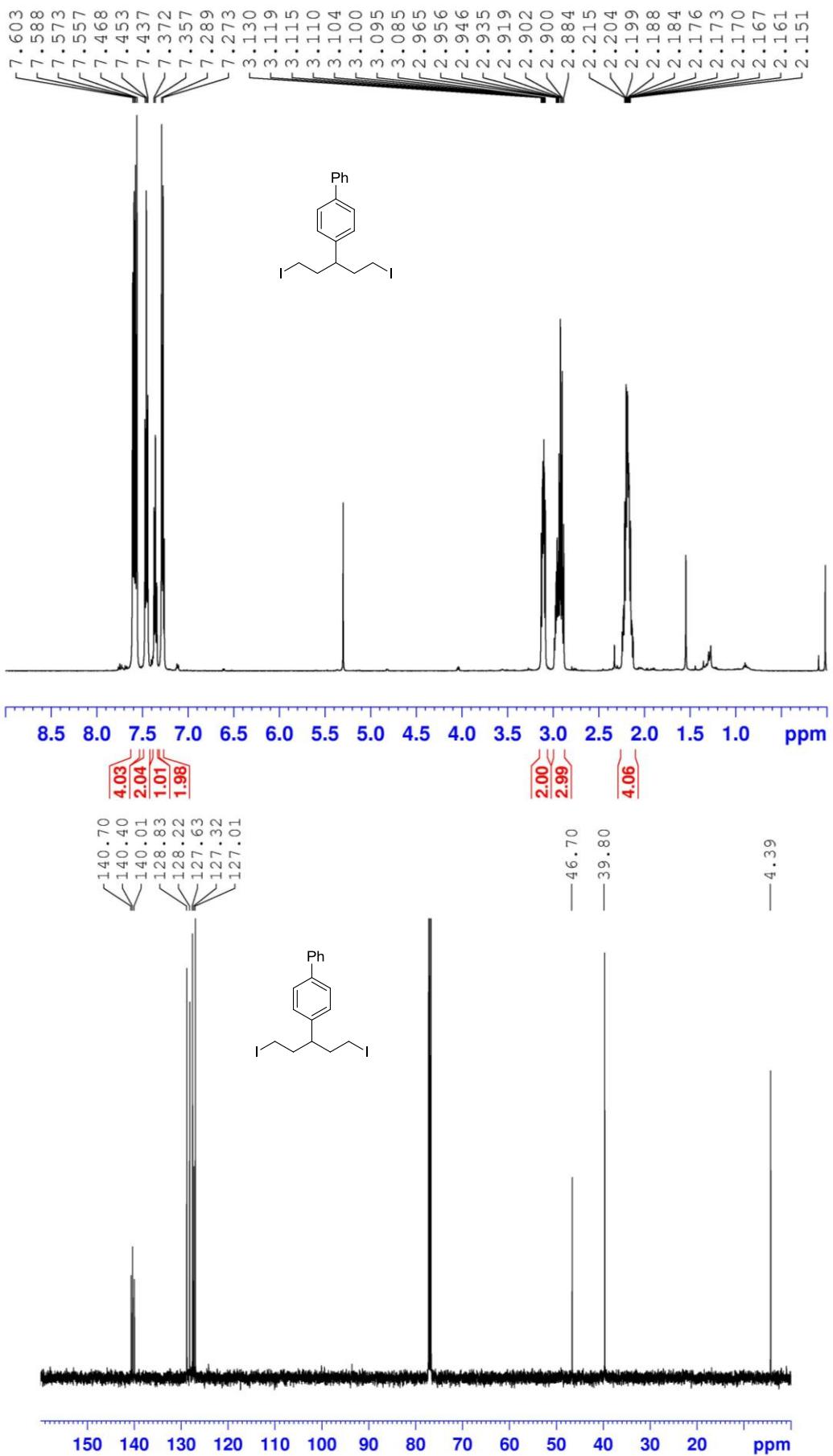


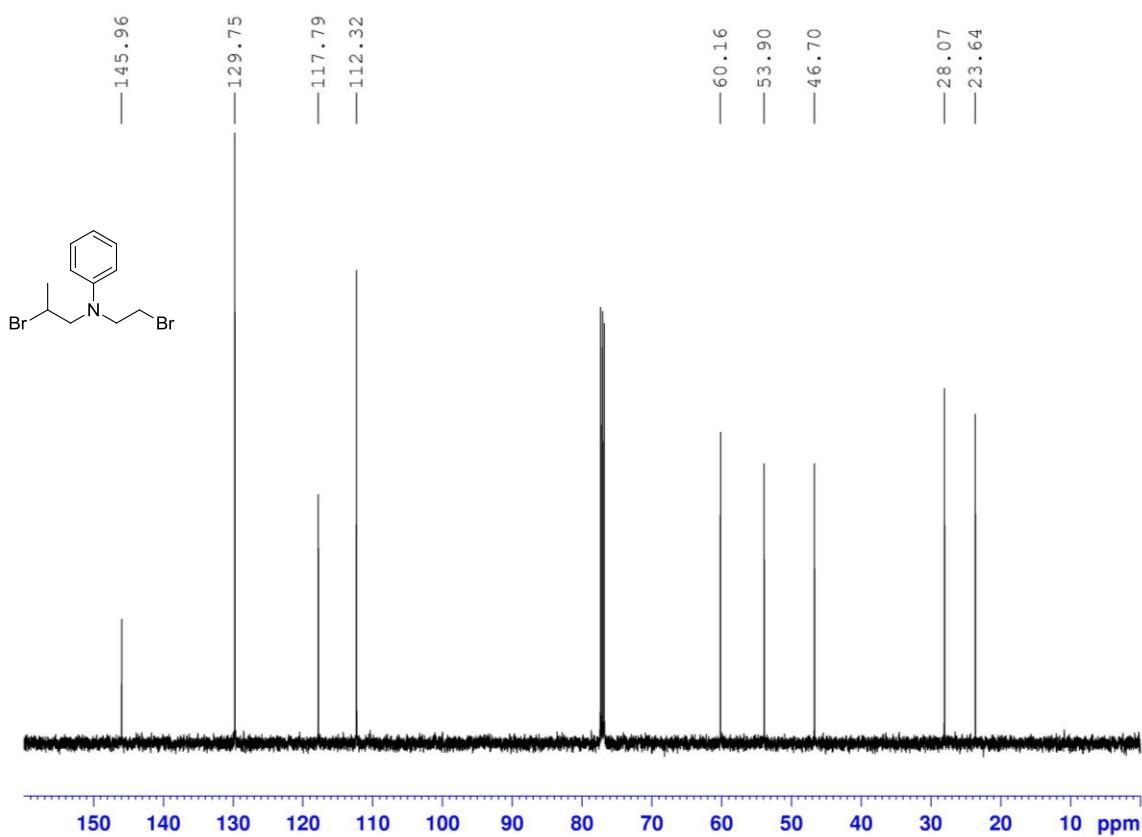
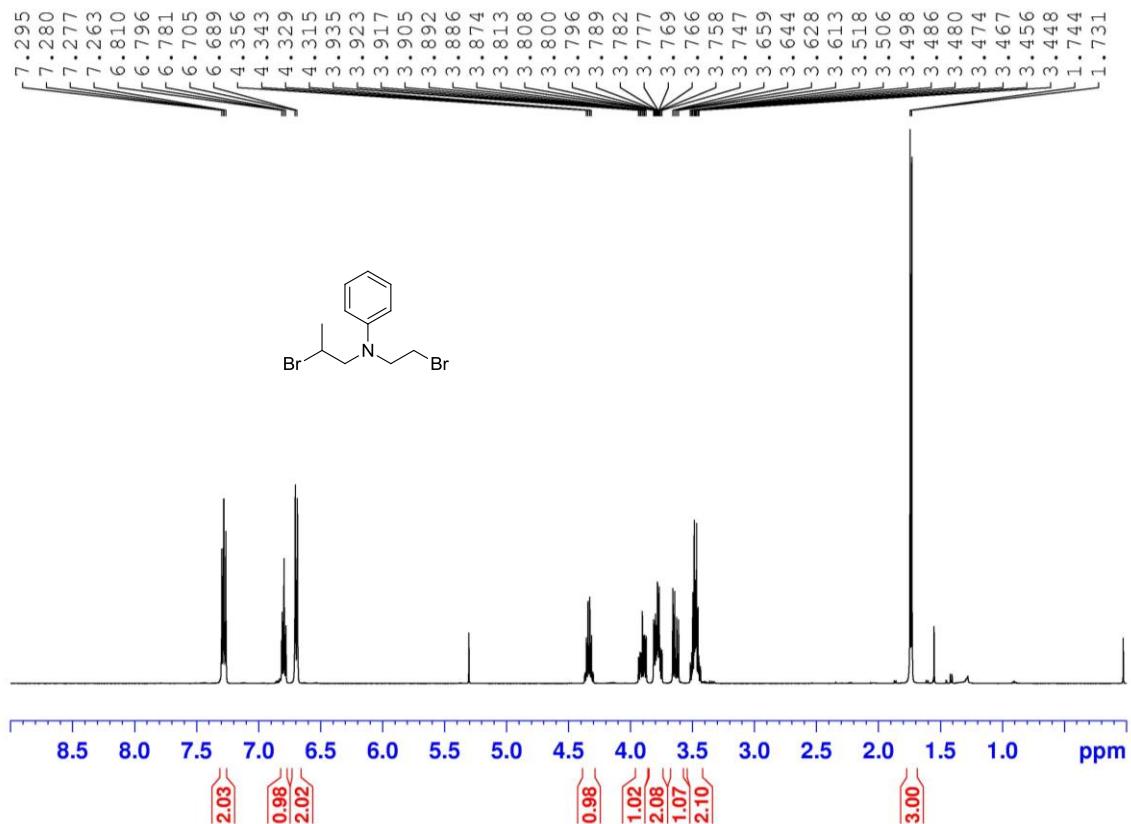


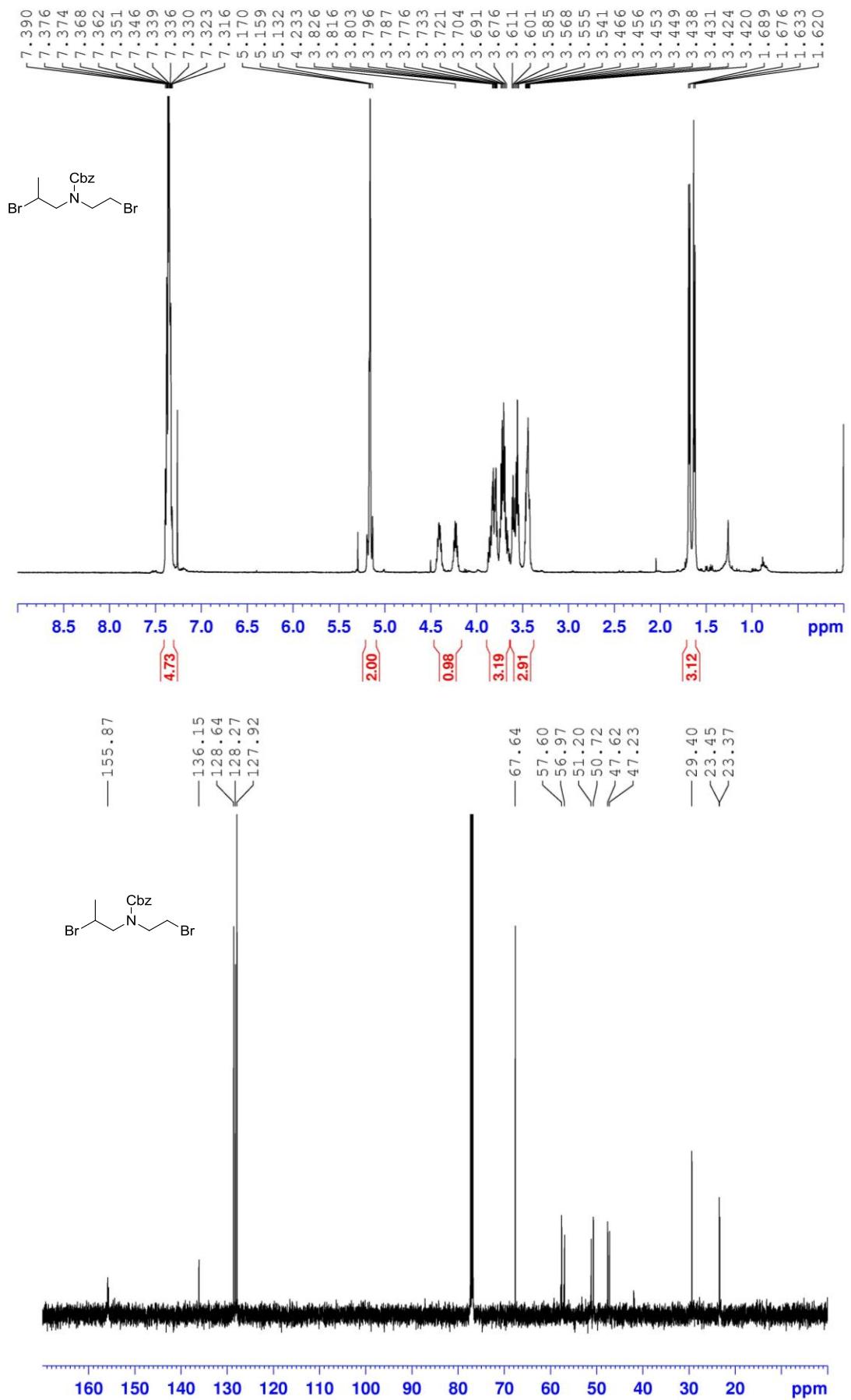


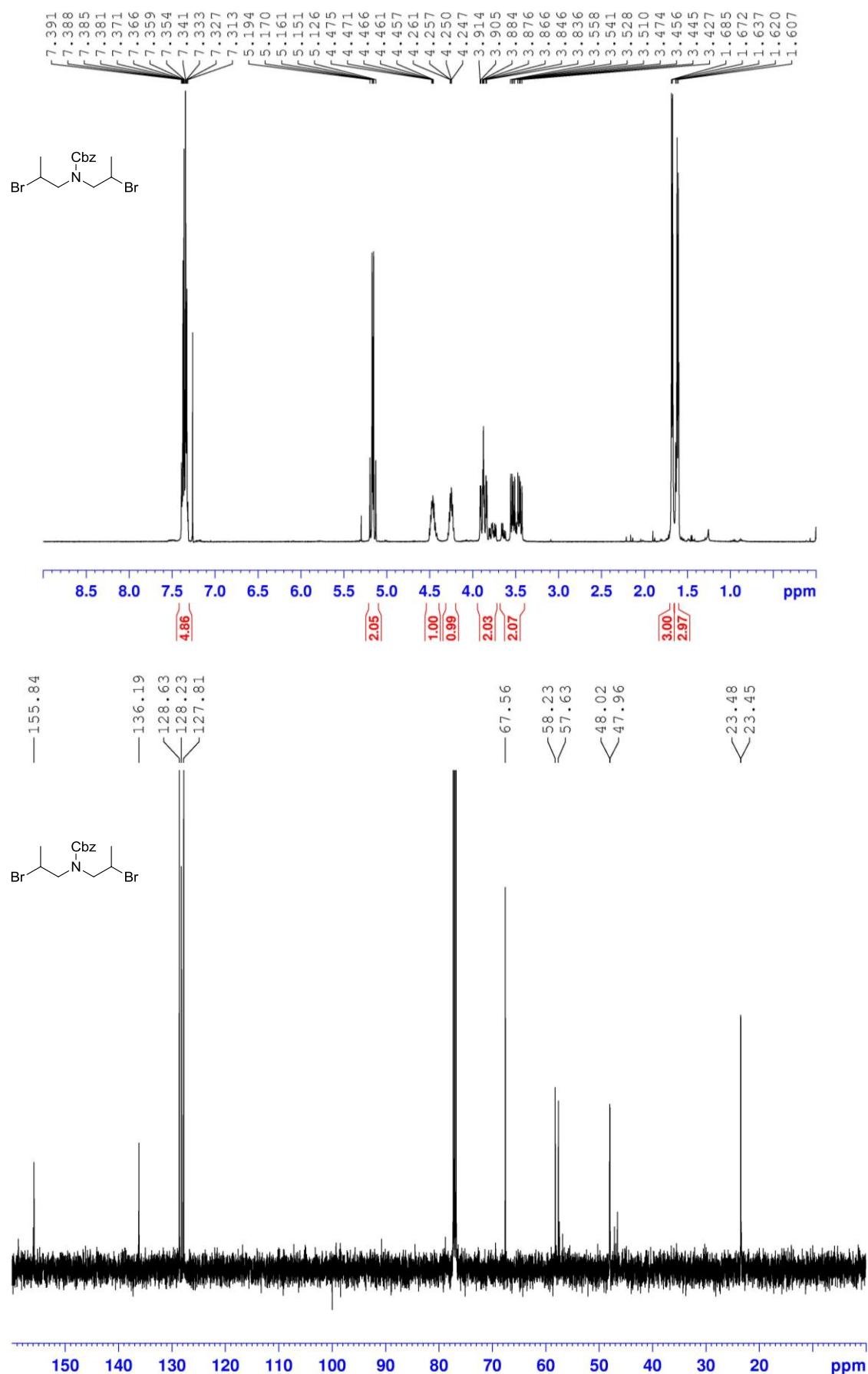


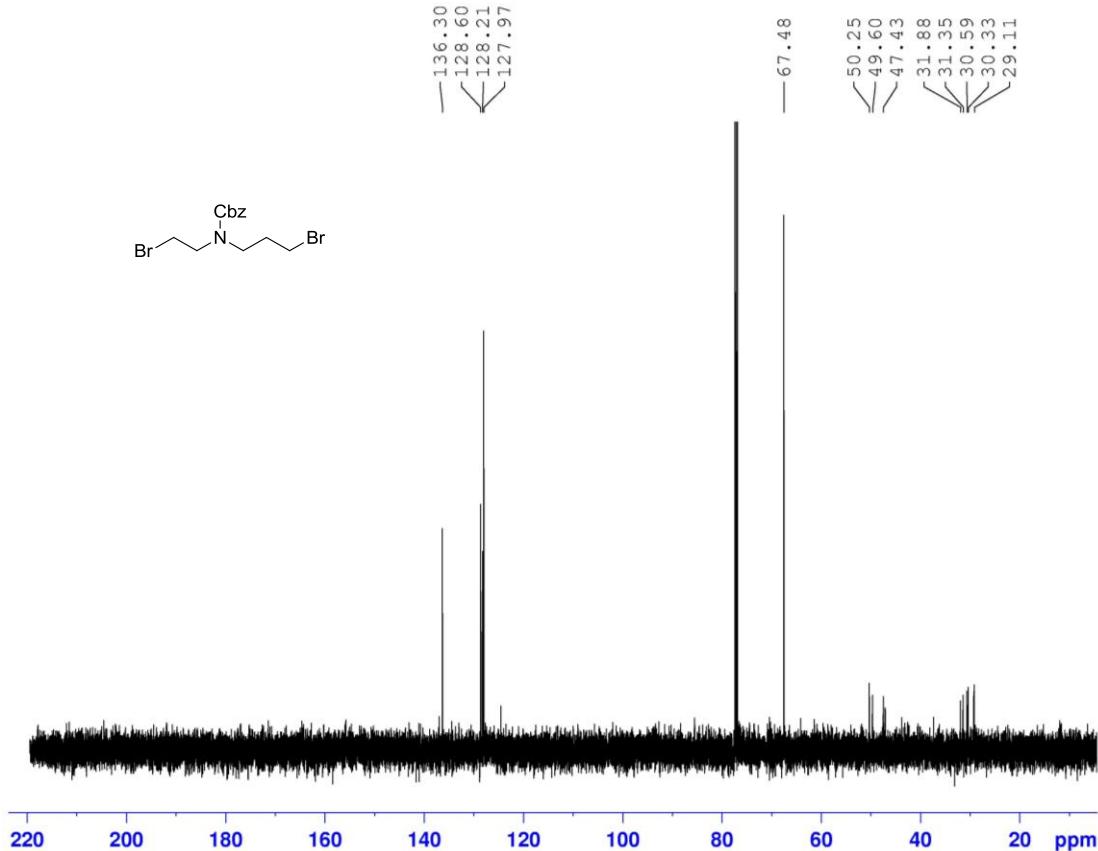
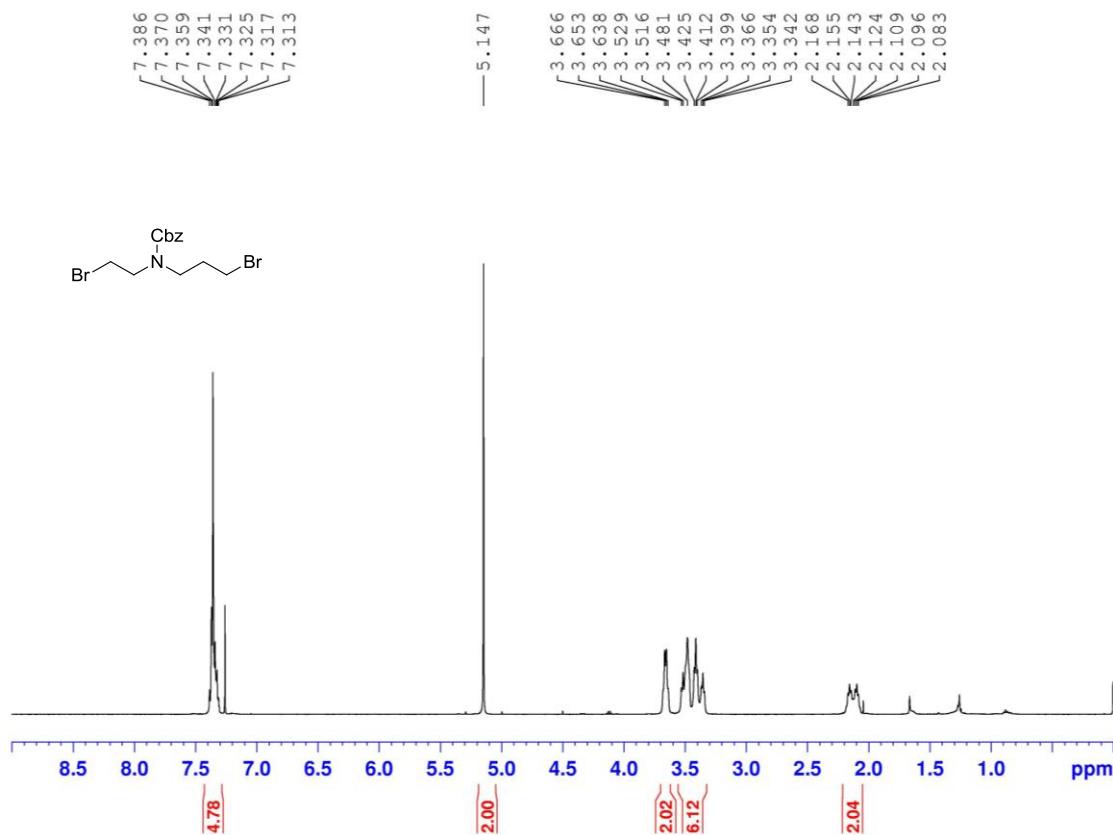


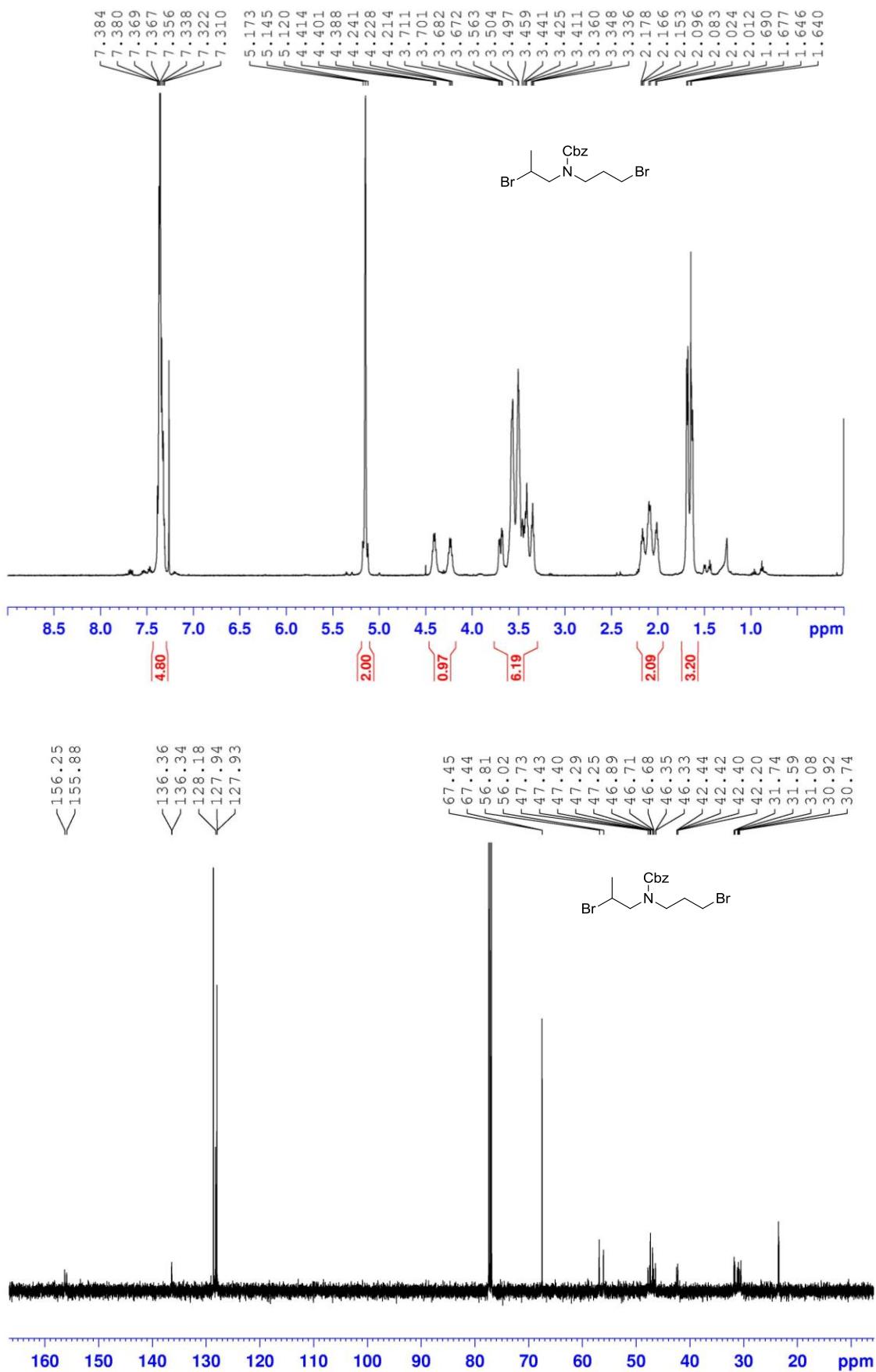


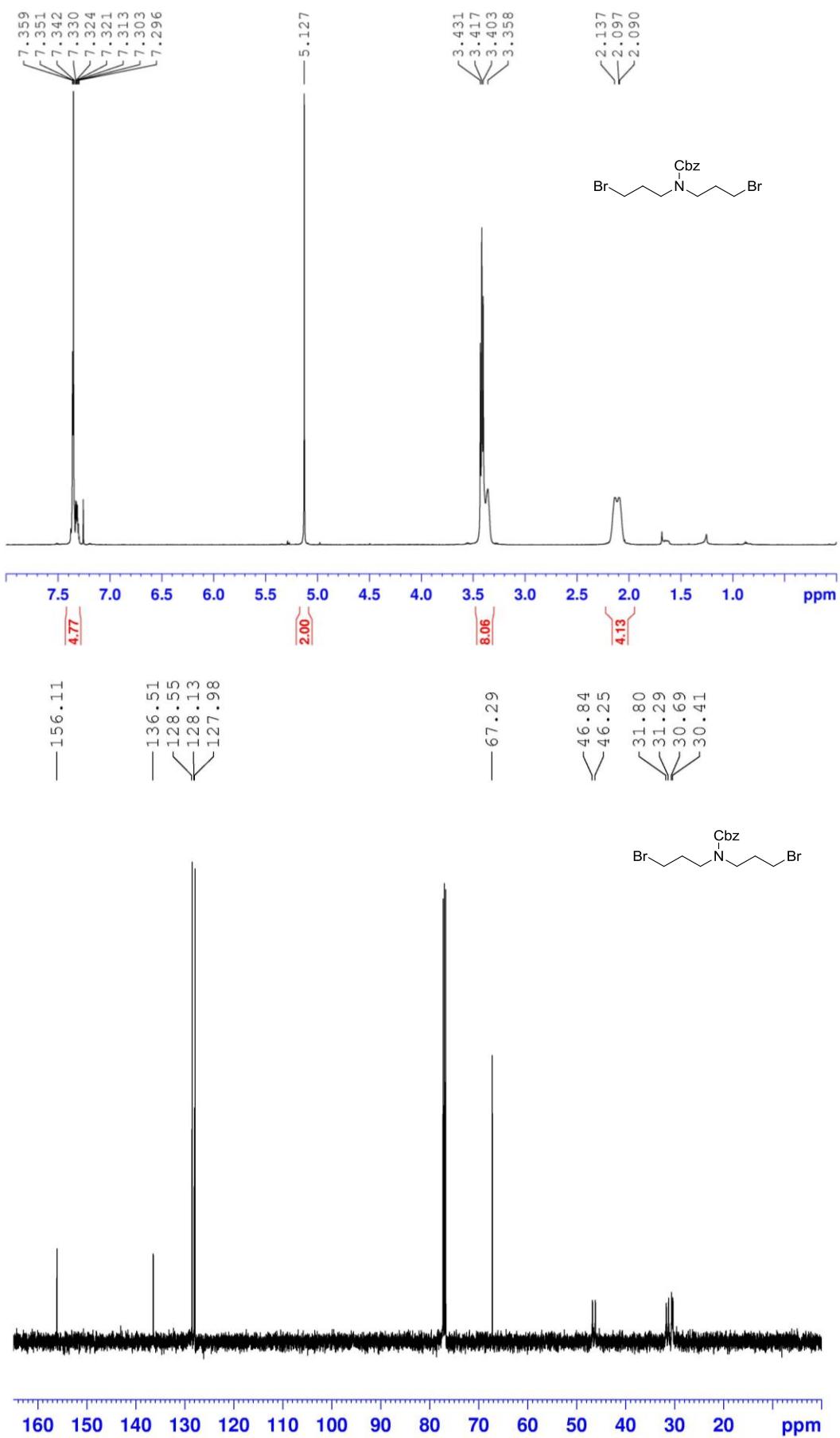


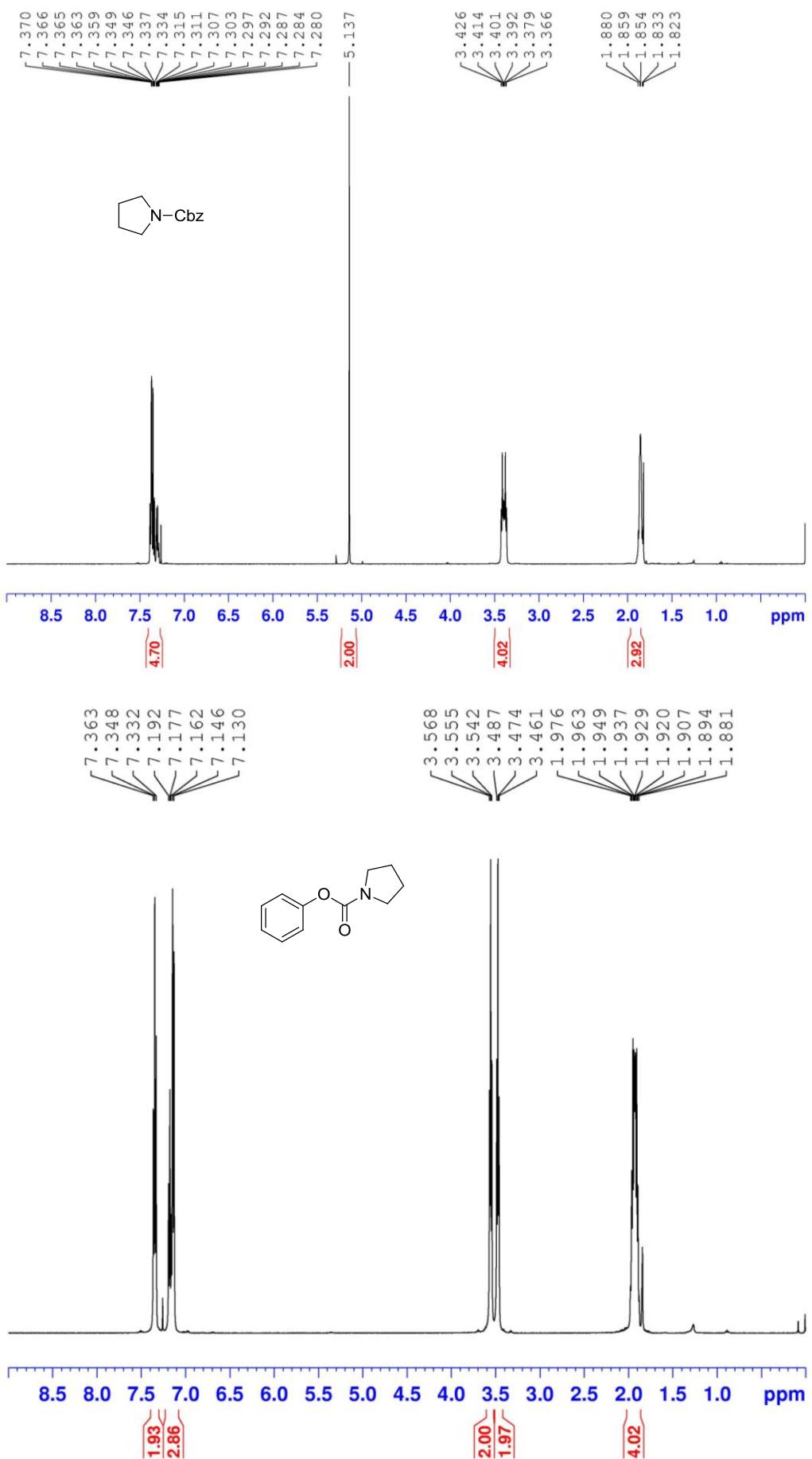


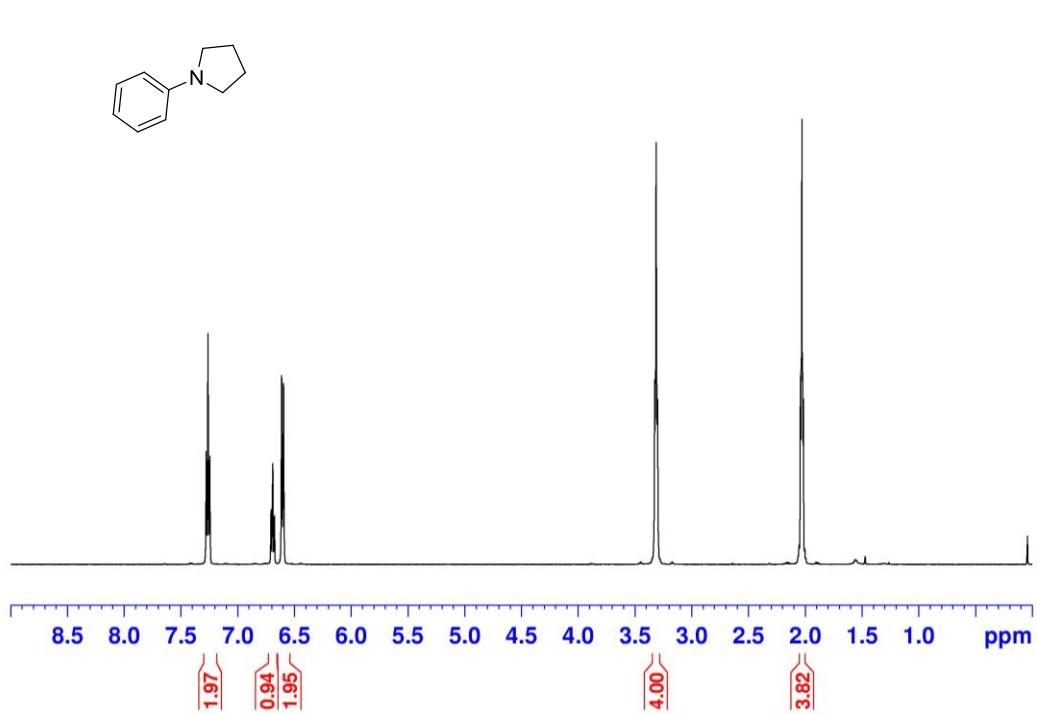
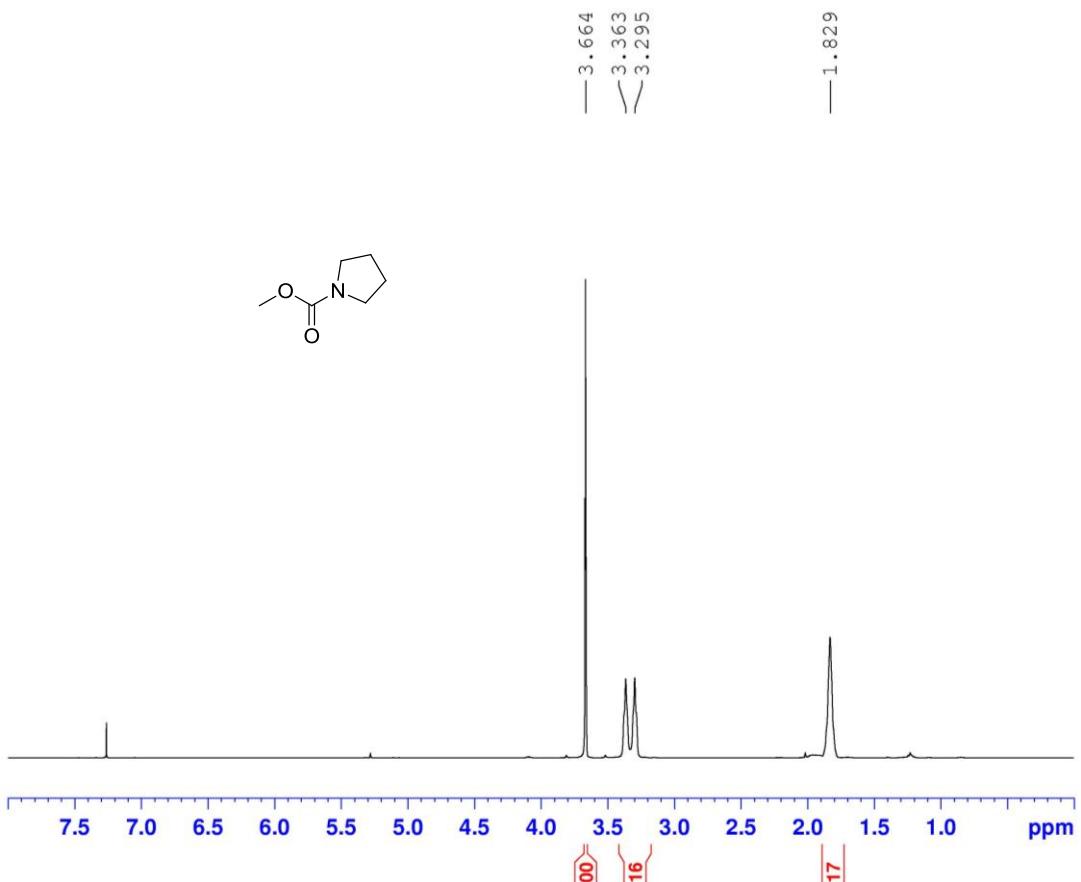


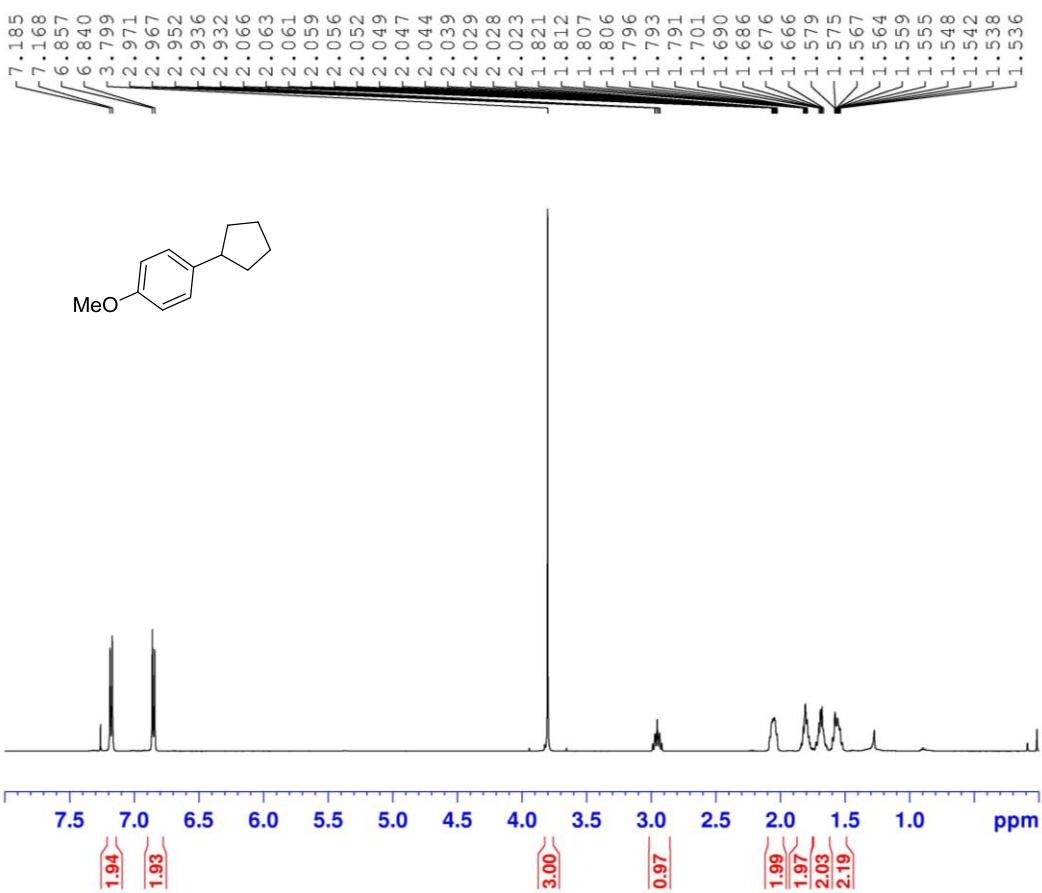
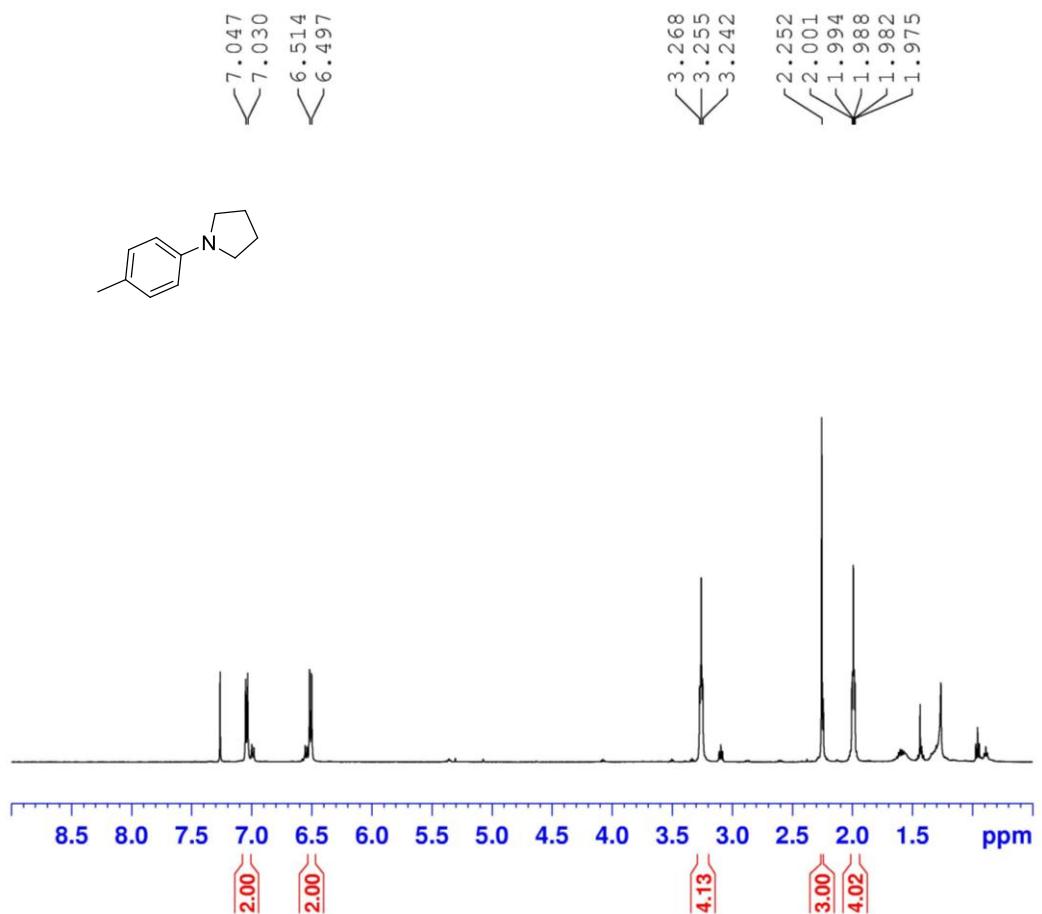


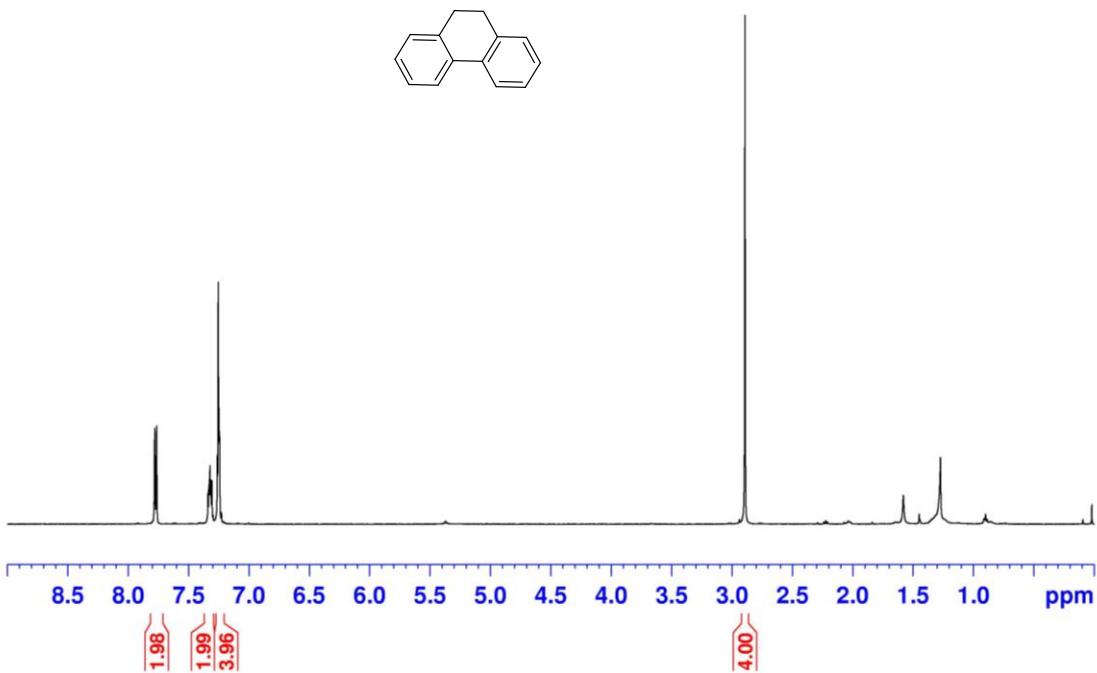
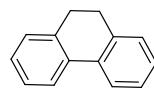
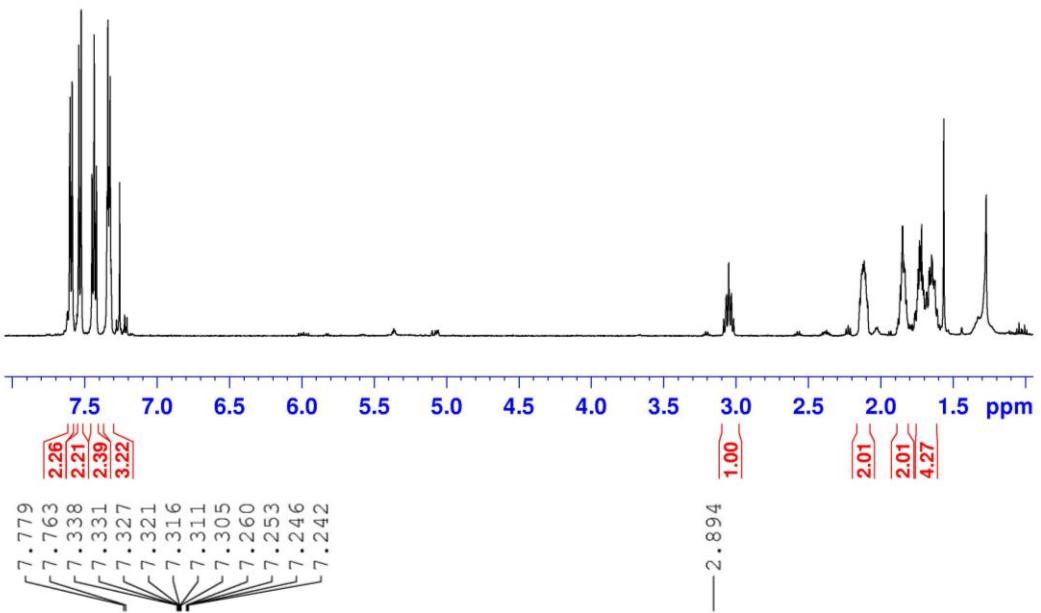
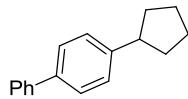
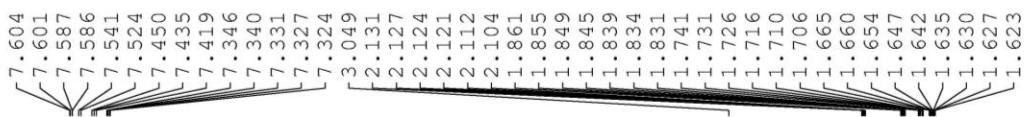


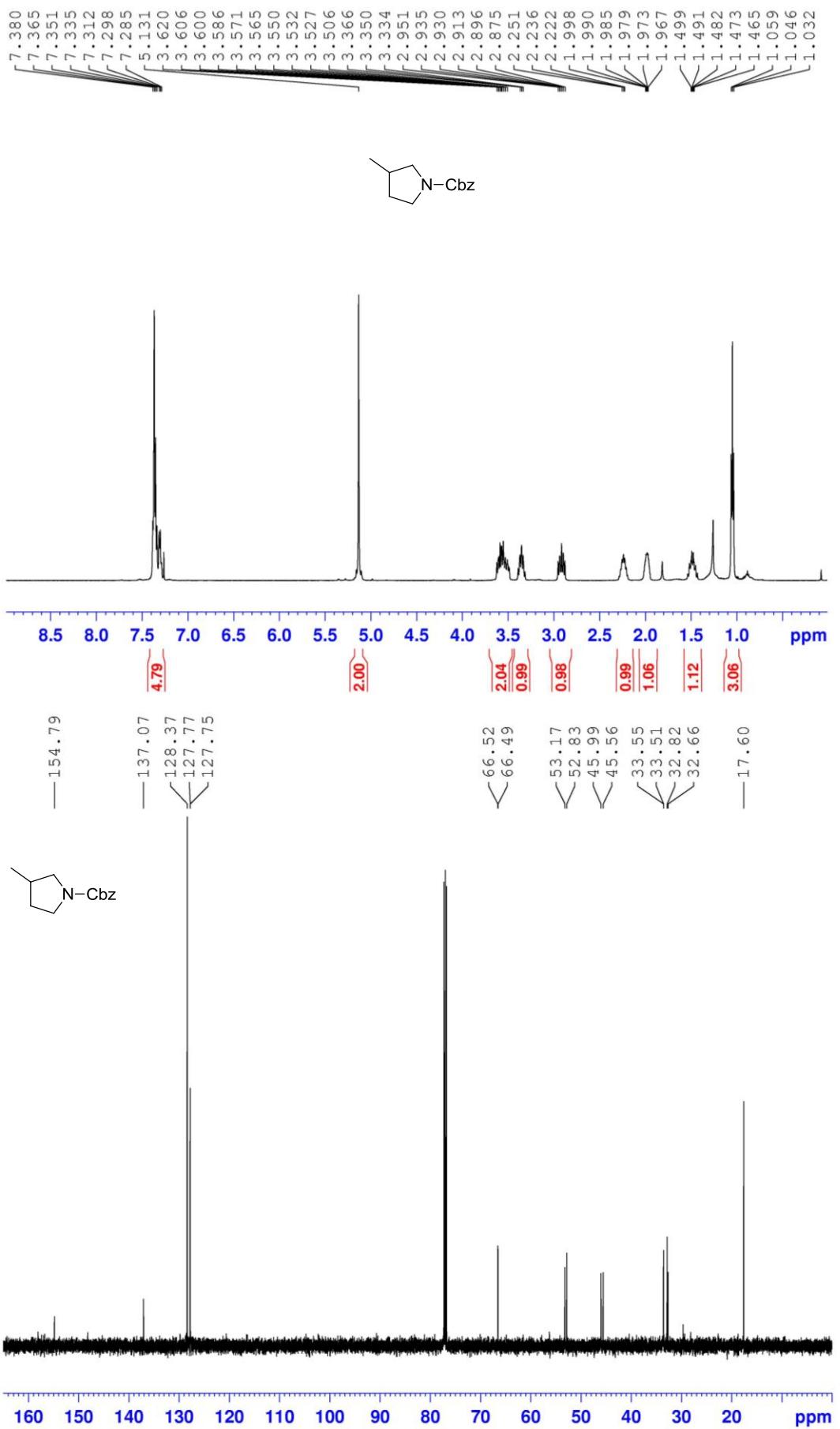


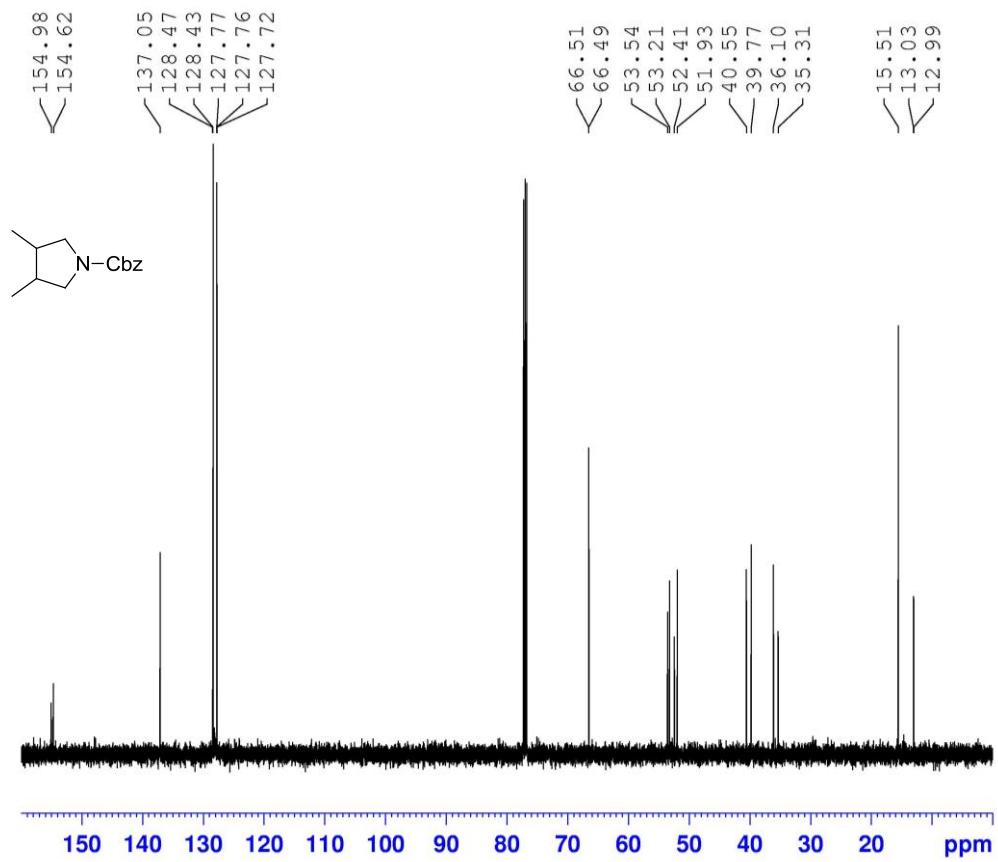
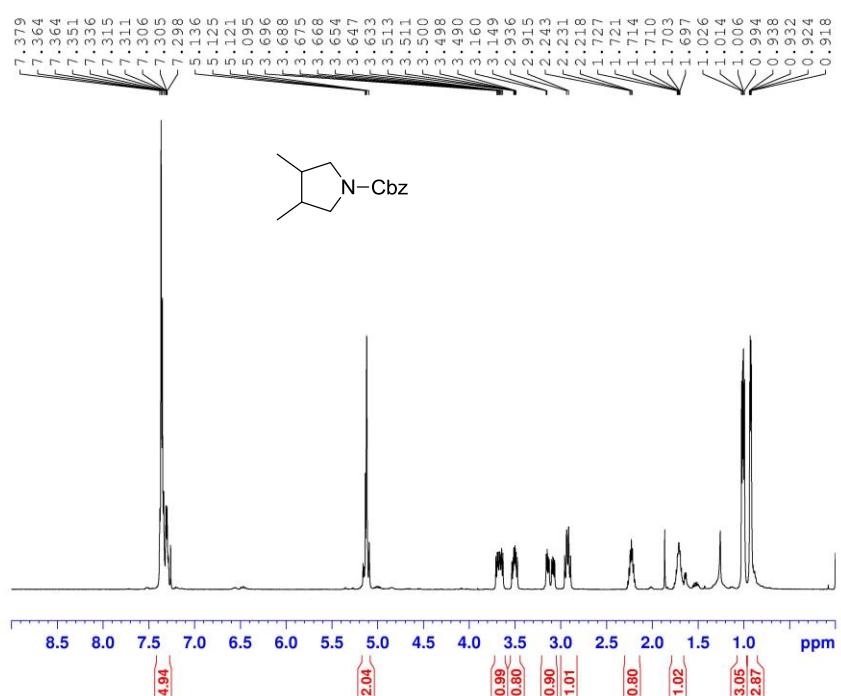


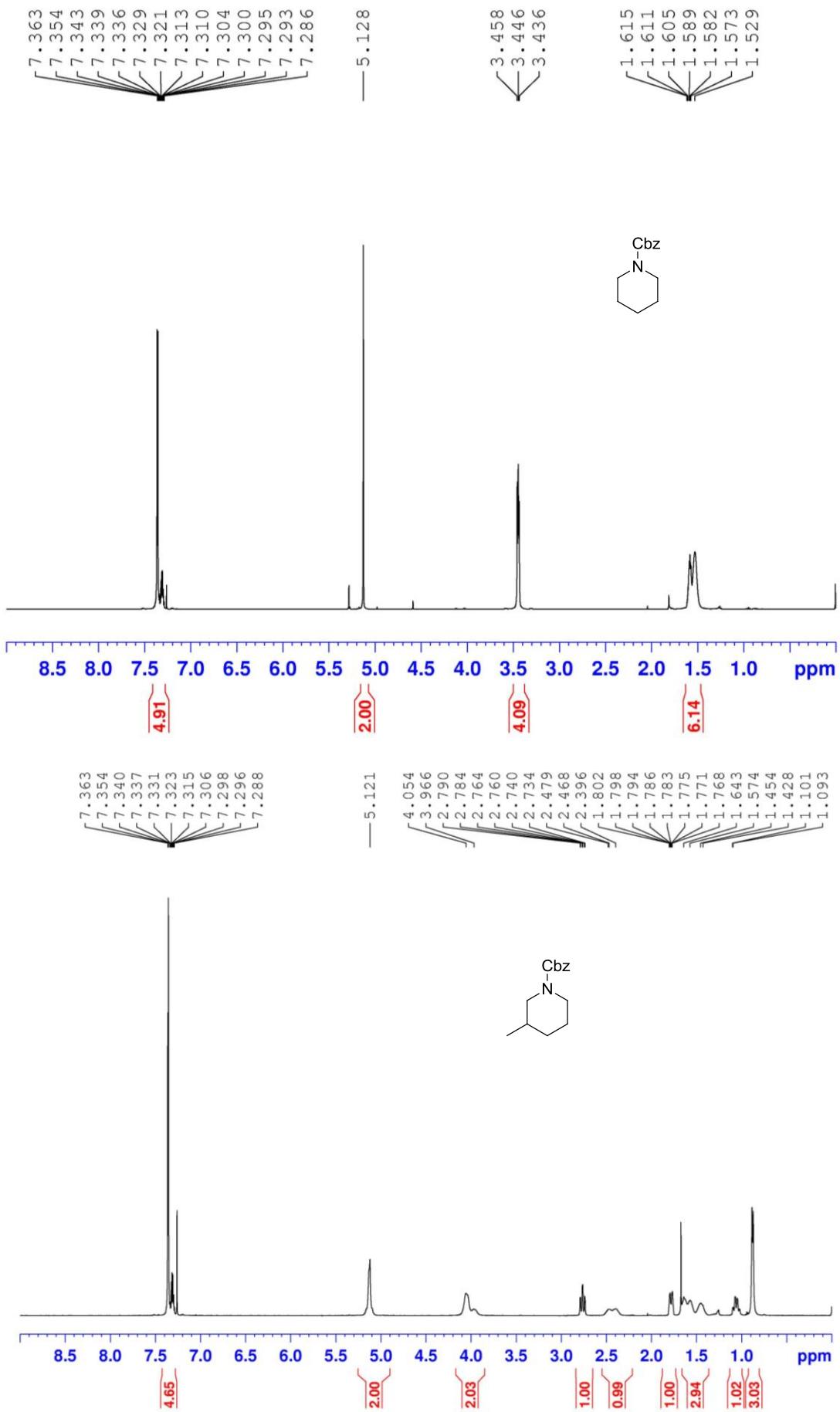


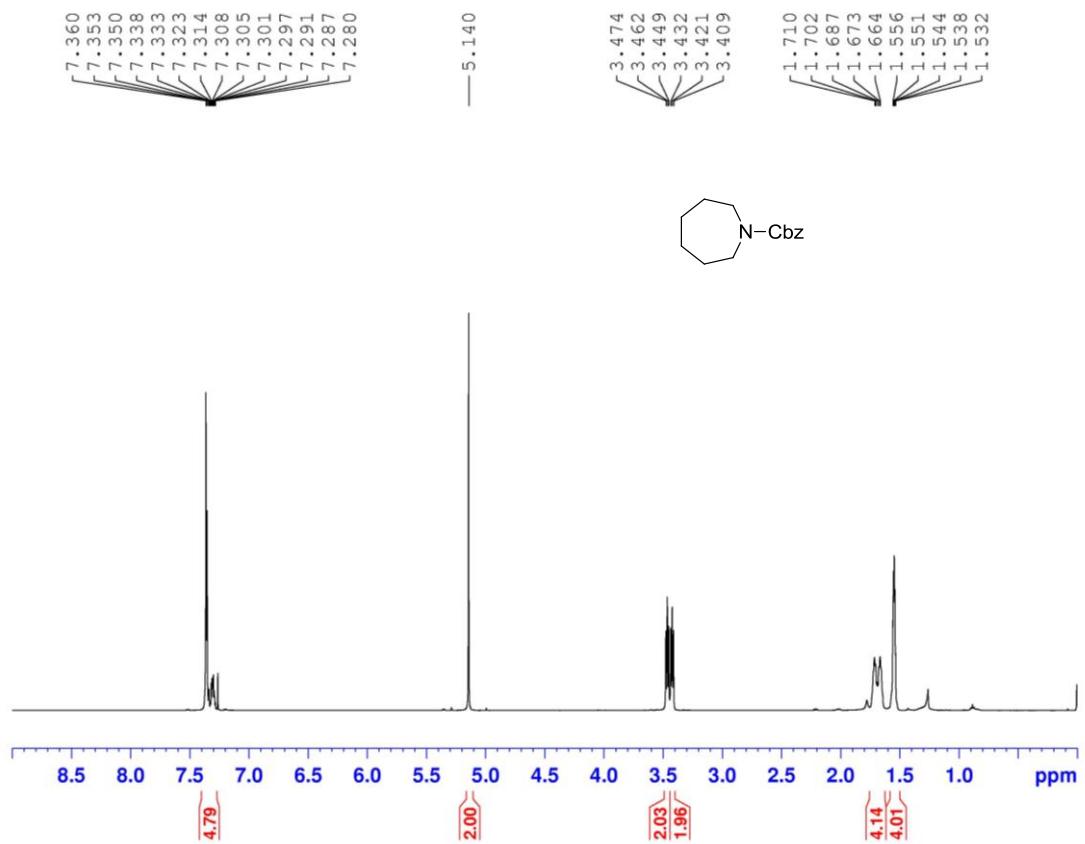












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