

## Supporting Information

### CuI nanoparticles as a recyclable heterogeneous catalyst for C-N bond formation reactions

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## **1. Experimental section**

### **General**

Cuprous iodide was purchased from Loba Chemie Pvt. Ltd, India. Silica gel (Merk 60-120 mesh) was used for column chromatography and all other chemicals were purchased from Merck, Sigma Aldrich and Spectrochem, used without further purification. NMR spectra were measured on a Bruker Avance-300 and Avance-600 spectrometer. Mass spectra were recorded on a QTOF Micromass of Waters. The GC analysis was performed on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), an AOC-20i auto-sampler coupled, and a DB-5 MS capillary column ( $30\text{ m} \times 0.25\text{ mm i.d.}$ ,  $0.25\text{ }\mu\text{m}$ ). The initial temperature of the column was held at  $70\text{ }^{\circ}\text{C}$  for 4 min and was programmed to  $230\text{ }^{\circ}\text{C}$  at  $4\text{ }^{\circ}\text{C min}^{-1}$ , then held for 15 min at  $230\text{ }^{\circ}\text{C}$ ; the sample injection volume was  $1\text{ }\mu\text{L}$  in GC grade dichloromethane. Nitrogen was used as the carrier gas at a flow rate of  $1.1\text{ mL min}^{-1}$  onsplit mode (1:50). The IR spectra were recorded on Shimadzu IR Prestige-21 FT-IR spectrophotometer. Atomic Absorption Spectroscopy (AAS) were performed on Shimadzu AA-6300 spectrophotometer.

### **General procedure for the synthesis of CuI nanoparticles**

To a 15 mL reaction tube with magnetic stirrer bar, added benzaldehyde (1 mmol), aniline (1.0 mmol), phenylsilane (1.5 mmol), CuI (5 mol%), and ethanol (3 mL). The reaction mixture was stirred at  $80\text{ }^{\circ}\text{C}$  for 4h. After completion of reaction, catalyst settled down at the bottom was filtered, and washed 5-6 times with ethyl acetate and ethanol. Dried catalyst was kept under nitrogen atmosphere.

**General procedure for reductive amination of carbonyl compounds using CuI/PhSiH<sub>3</sub>**

To a 15 mL reaction tube with magnetic stirrer bar, added CuI (0.03 mmol), carbonyl compound (1 mmol), amines (1.0 mmol), phenylsilane (1.5 mmol) and ethanol (3 mL). The reaction mixture was stirred at 80 °C and monitored by TLC. After completion of reaction, the reaction mixture was filtered, dried under reduced pressure and purified by column chromatography using *n*-hexane/ethyl acetate as eluent. Purified products were characterized by NMR (<sup>1</sup>H and <sup>13</sup>C) and mass spectrometry.

**General procedure for the synthesis of sterically hindered amide using CuI NPs/TBHP/CaCO<sub>3</sub>**

To a 15 mL reaction tube with magnetic stirrer bar, added CuI NPs (5 mol %), aldehyde (0.3 mmol), amine (1.2 mmol), TBHP (1.1 mmol), CaCO<sub>3</sub> (1.1 mmol), and acetonitrile (3 mL). The reaction mixture was stirred at 60 °C for 6 h. After completion of reaction, the reaction mixture was filtered, dried under reduced pressure and purified by column chromatography using *n*-hexane/ethyl acetate as eluent. Purified products were characterized by NMR (<sup>1</sup>H and <sup>13</sup>C) and mass spectrometry.

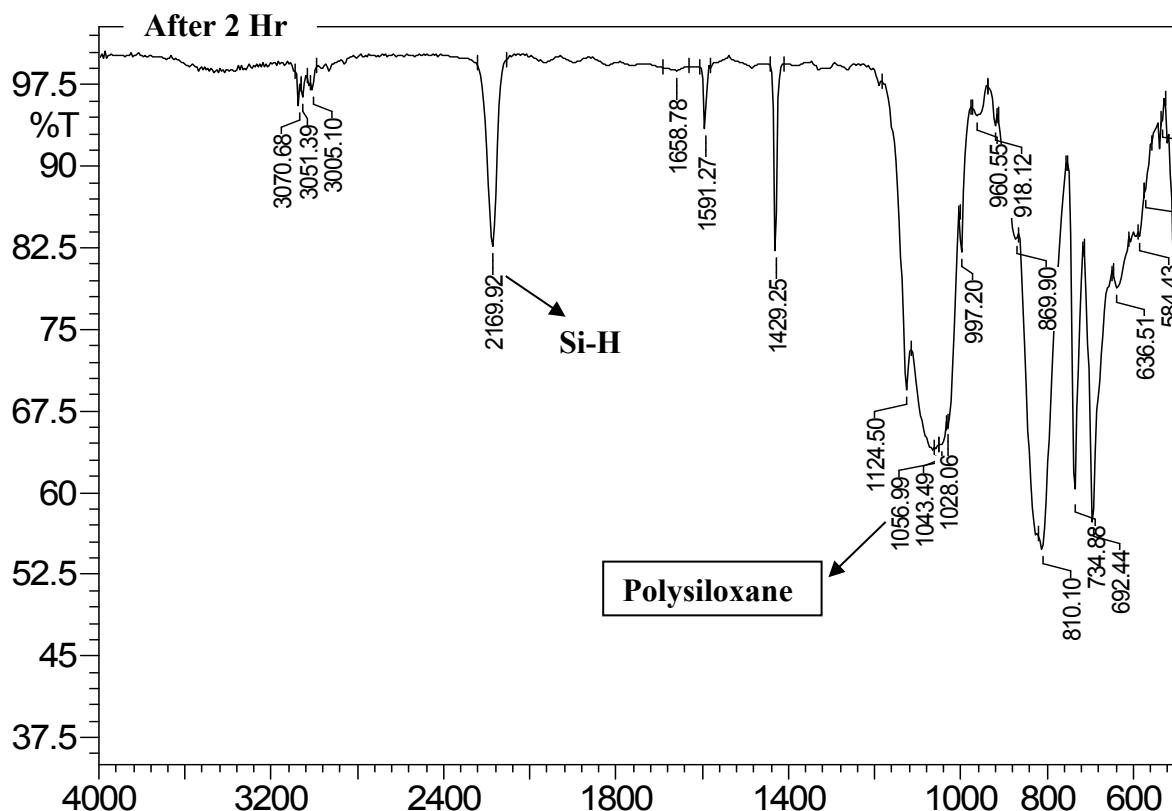
**General procedure for the synthesis of triazole using CuI NPs**

To a 15 mL reaction tube with magnetic stirrer bar, added CuI NPs (5 mol %), 2-nitrobenzylchloride (0.3 mmol), NaN<sub>3</sub> (1.0 mmol), phenylacetylene (1.0 mmol), and ethanol (3 mL). The reaction mixture was stirred at 80 °C for 24 h. After completion of reaction, the reaction mixture was filtered, dried under reduced pressure and purified by column chromatography using *n*-hexane/ethyl acetate as eluent. Purified products were characterized by NMR (<sup>1</sup>H and <sup>13</sup>C) and mass spectrometry.

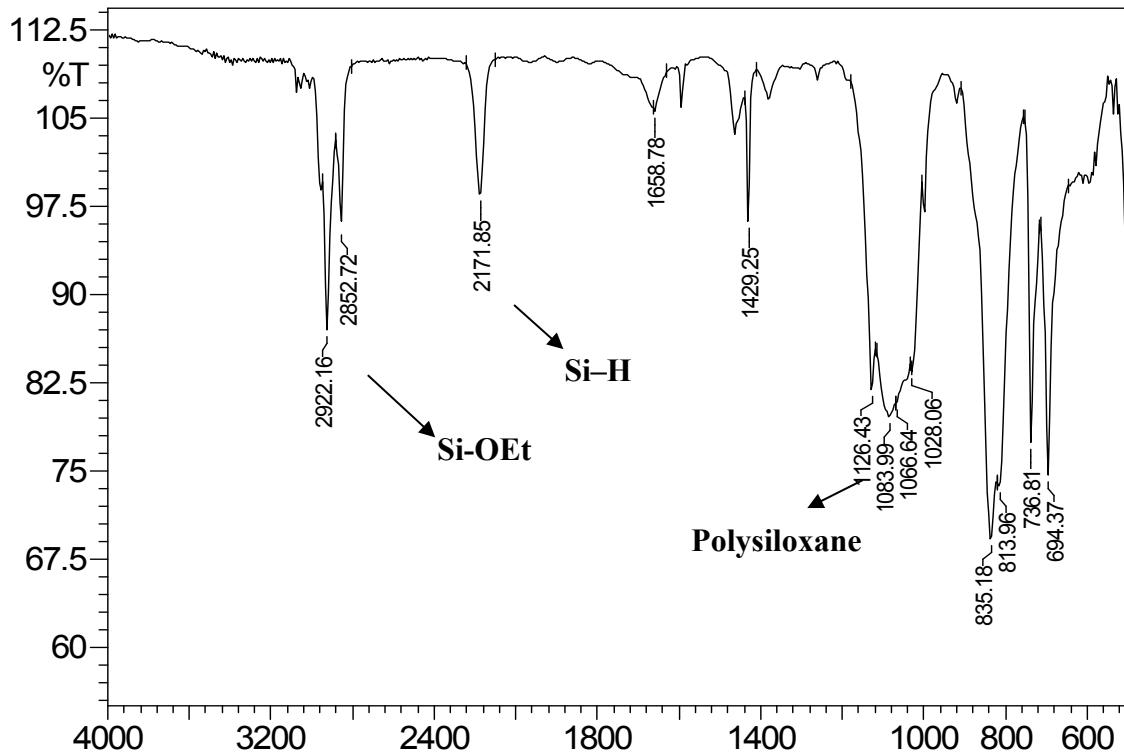
## 2. Mechanistic studies

### Evidences for formation of polysiloxane:

The reaction of phenylsilane (1.5 eq) and CuI (3 mol%) in ethanol at different time interval was analyzed with IR spectroscopy. A new band was observed at  $1066\text{ cm}^{-1}$  and  $1028\text{ cm}^{-1}$  which can be attributed to long chain Si–O–Si stretching frequencies. In case of dry ethanol over a period of 4 h, another new band was appeared at 2922 and  $2852\text{ cm}^{-1}$  corresponding to Si–OC<sub>2</sub>H<sub>5</sub> which confirms the formation of PhSiOEt.



### After 4 hr



### 3. Catalyst Characterization

**X-ray powder diffraction (XRD):** Powder X-ray diffraction patterns were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K $\alpha$  radiation source. Diffraction patterns in the 2°-80° region were recorded at a rate of 0.5 degrees (2q) per minute.

**Transmission electron microscopy (TEM):** TEM images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon coated Cu grid.

**X-ray photoelectron spectroscopy (XPS):** X-Ray photoelectron spectra were recorded on a PHI 5000 Versa Probe II, X-Ray photoelectron spectrometer and binding energies ( $\pm 0.1$  eV) were determined with respect to the position C 1s peak at 283 eV. Calibration of the binding energy (BE) scale was done by using the C 1s (BE = 284.6 eV) signal.

**Fourier Transformation Infra-red Spectroscopy (FTIR):** The FTIR spectra were recorded on Shimadzu IR Prestige-21 FTIR spectrophotometer.

**CHN analysis experiment :** The CHN analysis experiment of catalyst were recorded on Elementar, vario Macro cube using sulphanilamide as reference compound.

#### 4. $^1\text{H}$ and $^{13}\text{C}$ NMR values of synthesized compounds

**N–benzylaniline (3a):** Brown oil (168 mg, 92% yield),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600MHz)  $\delta$  : 4.35 (s, 2H), 6.66 (d, 2H,  $J = 7.8$  Hz), 6.72 (t, 2H,  $J = 7.32$  Hz), 7.18–7.21 (m, 2H), 7.28 (t, 1H,  $J = 7.14$  Hz), 7.35–7.40 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  : 48.3, 112.8, 117.6, 127.2, 127.5, 128.6, 129.3, 139.4, 148.1; HRESIMS calcd for  $\text{C}_{13}\text{H}_{14}\text{N} [\text{M}+\text{H}]^+$  184.1129, found 184.1109.

**N–(4'–Methoxybenzyl)aniline (3b):** Yellow oil (195 mg, 92% yield),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  : 3.88 (s, 3H), 4.33 (s, 2H), 6.72 (d, 2H,  $J = 7.9$  Hz), 6.83 (t, 1H,  $J = 7.2$  Hz), 6.98 (d, 2H,  $J = 8.46$  Hz), 7.28 (t, 2H,  $J = 7.8$  Hz), 7.38 (d, 2H,  $J = 8.4$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz)  $\delta$  : 47.8, 55.3, 113.0, 114.1, 117.6, 128.9, 129.3, 131.6, 148.3, 159.0; HRESIMS calcd for  $\text{C}_{14}\text{H}_{16}\text{NO} [\text{M}+\text{H}]^+$  214.1232, found 214.1209.

**N–(4'–Methylbenzyl)aniline (3c):** Yellow solid (151 mg, 77% yield), mp. 43-44 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  2.38 (s, 3H), 4.32 (s, 2H), 6.66-6.77 (m, 3H), 7.18-7.31(m, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  21.5, 48.5, 113.2, 117.9, 127.9, 129.6, 129.7, 136.7, 137.2, 148.6; HRESIMS calcd for  $\text{C}_{14}\text{H}_{16}\text{N} [\text{M}+\text{H}]^+$  198.1283, found 198.1268.

**N–(4'–bromobenzyl)aniline (3d):** Greenish oil (224 mg, 86% yield),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  4.30 (s, 2H), 6.61 (d, 2H,  $J = 7.8$  Hz), 6.75 (t, 1H,  $J = 7.3$  Hz), 7.18 (t, 2H,  $J = 7.8$  Hz), 7.25 (d, 2H,  $J = 8.2$  Hz), 7.46 (d, 2H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150

MHz):  $\delta$  47.7, 112.9, 117.8, 120.9, 129.0, 129.3, 131.7, 138.5, 147.8; HRESIMS calcd for C<sub>13</sub>H<sub>13</sub>NBr [M+H]<sup>+</sup> 262.0231, found 262.0215.

**N-(4'-chlorobenzyl)aniline (3e):** Yellow oil (180 mg, 83% yield), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  4.32 (s, 2H), 6.62 (d, 2H,  $J$  = 7.5 Hz), 6.75–6.77 (m, 1H), 7.19–7.21 (m, 2H), 7.31–7.34 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  47.6, 112.9, 117.8, 128.7, 128.7, 129.3, 132.9, 138.0, 147.8; HRESIMS calcd for C<sub>13</sub>H<sub>13</sub>NCl [M+H]<sup>+</sup> 218.0737, found 218.0718.

**N-Benzyl-4-fluoroaniline (3f):** Colorless viscous liquid (184 mg, 92% yield), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  4.30 (s, 2H), 6.57–6.59 (m, 2H), 6.8–6.9 (m, 2H), 7.30–7.32 (m, 1H), 7.36–7.39 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  48.9, 113.6 ( $J$  = 7.5 Hz), 115.7 ( $J$  = 22.1 Hz), 127.5, 128.7, 139.2, 144.5 ( $J$  = 1.5 Hz), 155.9 ( $J$  = 235.3 Hz); HRESIMS calcd for C<sub>13</sub>H<sub>13</sub>FN [M+H]<sup>+</sup> 202.1032, found 202.1018.

**N-Benzyl-4-iodoaniline (3g):** White crystalline solid (281 mg, 91% yield), mp. 49 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  4.32 (s, 2H), 6.43 (d, 2H,  $J$  = 8.70 Hz), 7.31–7.34 (m, 1H), 7.37–7.40 (m, 4H), 7.44 (d, 2H,  $J$  = 8.70 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  48.1, 78.2, 115.1, 127.4, 128.7, 137.8, 138.9, 147.7; HRESIMS calcd for C<sub>13</sub>H<sub>13</sub>IN [M+H]<sup>+</sup> 310.0093, found 310.0078.

**N-Benzyl-4-methylaniline (3h):** Yellow oil (161.54 mg, 82% yield), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  2.27 (s, 3H), 4.33 (s, 2H), 6.60 (d, 2H,  $J$  = 8.1 Hz), 7.02 (d, 2H,  $J$  = 7.9 Hz), 7.29 (t, 1H,  $J$  = 7.1 Hz), 7.35–7.40 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  20.4, 48.7, 113.0, 126.8, 127.1, 127.5, 128.6, 129.7, 139.6, 145.9; HRESIMS calcd for C<sub>14</sub>H<sub>16</sub>N [M+H]<sup>+</sup> 198.1283, found 198.1265.

**N–Benzyl–4–methoxyaniline (3i):** Dark brown solid (187 mg, 88% yield), mp. 51 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  3.77 (s, 3H), 4.31 (s, 2H), 6.64 (d, 2H,  $J$  = 8.76 Hz), 6.82 (d, 2H,  $J$  = 8.8 Hz), 7.31 (t, 1H,  $J$  = 7.1 Hz), 7.37-7.42 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  49.2, 55.8, 114.1, 114.9, 127.2, 127.6, 128.6, 139.7, 142.5, 152.2; HRESIMS calcd for C<sub>14</sub>H<sub>19</sub>NO [M+H]<sup>+</sup> 214.1232, found 214.1211.

**1-(4-Benzylaminophenyl)ethanone (3j):** Yellow solid (146 mg, 65% yield), 95-96 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  2.49 (s, 3H), 4.41 (s, 3H), 6.62 (d, 2H,  $J$  = 8.3 Hz), 7.36 (s, 5H), 7.83 (d, 2H,  $J$  = 8.3 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  26.4, 47.9, 112.1, 127.3, 127.7, 127.9, 129.2, 131.2, 138.6, 152.4, 196.8; HRESIMS calcd for C<sub>15</sub>H<sub>16</sub>NO [M+H]<sup>+</sup> 226.1232, found 226.1252.

**N–Benzyl–3–cyanoaniline (3k):** Brownish white solid (176 mg, 85% yield), mp. 70 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  4.35 (d, 2H,  $J$  = 4.08 Hz), 4.48 (brs, 1H), 6.84 (d, 2H,  $J$  = 7.14 Hz), 6.97 (d, 1H,  $J$  = 7.26 Hz), 7.23 (t, 1H,  $J$  = 7.74 Hz), 7.39 (brs, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  48.1, 113.2, 115.4, 117.7, 120.0, 121.2, 127.7, 128.0, 129.2, 130.3, 138.7, 148.7; HRESIMS calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub> [M+H]<sup>+</sup> 209.1079, found 209.1057.

**Ethyl–4–(N–benzylamino)benzoate (3l):** White solid (204 mg, 80% yield), mp. 89-90 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  1.25 (t, 3H,  $J$  = 7.11 Hz), 4.20 (q, 2H,  $J$  = 7.1 Hz), 4.27 (d, 2H,  $J$  = 5.2 Hz), 4.44 (brs, 1H), 6.48 (d, 2H,  $J$  = 8.5 Hz), 7.19-7.25 (m, 5H), 7.77 (d, 2H,  $J$  = 8.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  14.4, 47.6, 60.2, 111.6, 119.0, 127.4, 127.5, 128.7, 131.5, 138.4, 151.7, 166.8; HRESIMS calcd for C<sub>16</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 256.1338, found 256.1329.

**N–(Benzo[1,3]dioxol–5–ylmethyl)aniline (3m):** White solid (186 mg, 82% yield), mp. 82-83 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  4.07 (brs, 1H), 4.28 (s, 2H), 5.98 (s, 2H), 6.69-

7.29 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz);  $\delta$  48.5, 101.4, 108.5, 108.7, 113.3, 118.0, 121.0, 129.7, 133.8, 147.2, 148.3, 148.5; HRESIMS calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2$   $[\text{M}+\text{H}]^+$  228.1025, found 228.1018.

**N-(2',4',5'-Trimethoxybenzyl)aniline (3n):** Yellow solid (225mg, 82% yield), mp. 51 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  3.80 (s, 3H), 3.84 (s, 3H), 3.90 (s, 3H), 4.27 (s, 2H), 6.56 (s, 1H), 6.67 (d, 2H,  $J = 7.6$  Hz), 6.72 (t, 1H,  $J = 7.32$  Hz), 6.91 (s, 1H), 7.18 (q, 2H,  $J = 5.30$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz);  $\delta$  43.2, 56.2, 56.3, 56.6, 97.6, 113.1, 113.6, 117.4, 118.8, 129.1, 143.0, 148.5, 148.8, 151.6; HRESIMS calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_3$   $[\text{M}+\text{H}]^+$  274.1443, found 274.1429.

**N-(5'-Allyl-2'-hydroxy-3'-methoxybenzyl)aniline (3o):** Yellow solid (212 mg, 79% yield), mp. 69-70 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  3.31 (d, 2H,  $J = 6.4$  Hz), 3.88 (s, 3H), 4.35 (s, 2H), 5.05–5.09 (m, 2H), 5.91–5.98 (m, 1H), 6.65 (s, 1H), 6.72–6.77 (m, 4H), 7.18–7.21 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz): 39.9, 44.4, 56.0, 110.4, 113.8, 115.6, 118.2, 121.1, 124.3, 129.2, 131.3, 137.7, 142.4, 146.7, 148.1; HRESIMS calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_2$   $[\text{M}+\text{H}]^+$  270.1494, found 270.1481.

**N-(6'-methoxynaphthalen-2-ylmethyl)aniline (3p):** Yellow solid (206 mg, 78% yield), mp. 97 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  3.94 (s, 3H), 4.46 (s, 2H), 6.69 (d, 2H,  $J = 7.7$  Hz), 6.74 (t, 1H,  $J = 7.3$  Hz), 7.71–7.22 (m, 4H), 7.48 (dd, 1H, 3.3 Hz, 1.2 Hz), 7.71–7.76 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  48.4, 55.3, 105.7, 112.9, 117.6, 119.0, 125.9, 126.4, 127.2, 128.9, 129.2, 129.3, 133.9, 134.6, 148.2, 157.6; HRESIMS calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  264.1388, found 264.1365.

**N-(9'-Anthracenylmethyl)aniline (3q):** Yellow solid (242 mg, 85% yield), mp. 155–156,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  5.15 (s, 2H), 6.81–6.85 (m, 3H), 7.31 (t, 2H,  $J = 7.9$

Hz), 7.48–7.54 (m, 4H), 8.04 (d, 2H,  $J$  = 7.9 Hz), 8.28 (d, 2H,  $J$  = 8.5 Hz), 8.48 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  40.8, 112.6, 117.7, 124.2, 125.2, 126.5, 127.9, 129.1, 129.4, 130.4, 131.5, 148.4; HRESIMS calcd for  $\text{C}_{21}\text{H}_{18}\text{N}$  [M+H] $^+$  284.1439, found 284.1417.

**N-Cinnamylaniline (3r):** Yellow viscous oil (169 mg, 81% yield),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  3.95 (d, 2H,  $J$  = 5.6 Hz), 6.35–6.39 (m, 1H), 6.65 (d, 1H,  $J$  = 15.9 Hz), 6.68 (d, 2H,  $J$  = 6.9 Hz), 6.78 (t, 1H,  $J$  = 7.2 Hz), 7.23–7.27 (m, 3H), 7.35 (t, 2H,  $J$  = 7.4 Hz), 7.38 (d, 2H,  $J$  = 7.6 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  46.2, 113.1, 117.6, 126.4, 127.1, 127.5, 128.6, 129.3, 131.5, 136.9, 148.1; HRESIMS calcd for  $\text{C}_{15}\text{H}_{16}\text{N}$  [M+H] $^+$  210.1283, found 210.1269.

**N-(4'-Methoxycinnamyl)aniline (3s):** Yellow brown solid (203 mg, 85% yield), mp. 75 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  3.86 (s, 3H), 3.94 (d, 2H,  $J$  = 11.5 Hz), 6.20–6.29 (m, 1H), 6.60 (d, 1H,  $J$  = 15.9 Hz), 6.74 (d, 2H,  $J$  = 8.28 Hz), 6.80 (t, 1H,  $J$  = 6.9 Hz), 6.93 (d, 2H,  $J$  = 4.32 Hz), 7.24–7.29 (m, 2H), 7.38 (d, 2H,  $J$  = 8.6 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  46.7, 55.7, 113.5, 114.4, 117.9, 125.2, 127.9, 129.7, 130.1, 131.5, 148.6, 159.6; HRESIMS calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}$  [M+H] $^+$  240.1388, found 240.1378.

**1-(1,3-Benzodioxol-5-yl)-N-phenylbutan-3-amine (3t):** (217 mg, 81% yield),  $^1\text{H}$  NMR(600 MHz,  $\text{CDCl}_3$ ): 7.17 (t,  $J$  = 7.47 Hz, 2H), 6.74 (d,  $J$  = 7.74 Hz, 1H), 6.69 (s, 2H), 6.64 (d,  $J$  = 7.56 Hz, 1H), 6.56 (d,  $J$  = 7.68 Hz, 2H), 5.91(s, 2H), 3.50-3.49 (m, 1H), 2.66-2.68 (m, 2H), 1.85-1.83 (m, 1H), 1.75-1.73 (m, 1H), 1.22 (d,  $J$  = 6.12, 3H);  $^{13}\text{C}$  NMR(150MHz,  $\text{CDCl}_3$ ): 147.6, 147.5, 145.6, 135.8, 129.3, 121.1, 117.0, 113.2, 108.9, 108.1, 100.7, 47.8, 39.1, 32.2, 20.8; ESIMS calcd for  $\text{C}_{17}\text{H}_{19}\text{NO}_2$  [M+H] $^+$  270.1494, found 270.3494.

**N-Phenylcyclohexylamine (3u):** Greenish oil (161 mg, 92% yield), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 1.13–1.19 (m, 2H), 1.22–1.28 (m, 2H), 1.35–1.42 (m, 2H), 1.65–1.68 (m, 1H), 1.76–1.79 (m, 2H), 2.06–2.08 (m, 2H), 3.24–3.29 (m, 1H), 6.60 (d, 2H, *J* = 8.1 Hz), 6.67 (t, 1H, *J* = 7.2 Hz), 7.17 (t, 2H, *J* = 7.7 Hz), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 25.0, 25.9, 33.5, 51.7, 113.1, 116.8, 129.2, 147.4; HRESIMS calcd for C<sub>12</sub>H<sub>18</sub>N[M+H]<sup>+</sup> 176.1439, found 176.1453.

**N-(4-methylcyclohexyl)aniline (3v) (cis + trans):** Brownish oil (162 mg, 86% yield), <sup>1</sup>H NMR(600 MHz, CDCl<sub>3</sub>): 7.33 (q, *J* = 7.08 Hz, 2H), 6.84 (t, *J* = 7.02 Hz, 1H), 6.75 (q, *J* = 7.50 Hz, 2H), 3.71 (brs, 1H), 2.29–2.27 (m, 1H), 1.93–1.91 (m, 2H), 1.82–1.78 (m, 1H), 1.73–1.71 (m, 2H), 1.55–1.42 (m, 2H), 1.30–1.20 (m, 2H), 1.14–1.11 (m, 3H); <sup>13</sup>C NMR(150 MHz, CDCl<sub>3</sub>): 147.7, 147.6, 129.44, 129.42, 117.0, 116.9, 113.37, 113.31, 52.2, 48.3, 34.3, 33.7, 32.5, 31.0, 30.0, 29.5, 22.5, 21.5; HRESIMS calcd for C<sub>13</sub>H<sub>20</sub>N[M+H]<sup>+</sup> 190.1596, found 190.1580.

**N-(3-methylcyclohexyl)aniline (3w) (cis + trans):** Brownish oil (155 mg, 82% yield), <sup>1</sup>H NMR(600 MHz, CDCl<sub>3</sub>): 7.18 (d, *J* = 7.20 Hz, 2H), 6.67 (t, *J* = 7.05 Hz, 1H), 6.61–6.60 (m, 2H), 3.69 (brs, 1H), 2.12–2.06 (m, 1H), 1.76–1.52 (m, 6H), 1.28–1.21 (m, 2H), 0.94 (d, *J* = 6.36 Hz, 3H); <sup>13</sup>C NMR(150 MHz, CDCl<sub>3</sub>): 147.4, 129.28, 129.27, 116.8, 116.7, 113.2, 113.0, 52.1, 47.5, 42.5, 38.9, 34.7, 33.9, 33.4, 32.0, 30.5, 27.1, 25.0, 22.5, 21.7, 20.5; HRESIMS calcd for C<sub>13</sub>H<sub>20</sub>N[M+H]<sup>+</sup> 190.1596, found 190.1581.

**N-Phenylcyclopentylamine(3x):** Dark brown oil (143mg, 89% yield), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 1.51–1.53 (m, 2H), 1.64–1.69 (m, 2H), 1.74–1.79 (m, 2H), 2.03–2.09 (m, 2H), 3.81–3.85 (m, 1H), 6.65 (d, 2H, *J* = 7.9 Hz), 6.72 (t, 1H, *J* = 7.2 Hz), 7.21 (2H, t, *J*

$\delta$  = 7.7 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  24.1, 33.6, 54.7, 113.2, 116.9, 129.2, 148.11; HRESIMS calcd for  $\text{C}_{11}\text{H}_{16}\text{N} [\text{M}+\text{H}]^+$  162.1283, found 162.1269.

**N-Furfurylaniline (6a):** Yellow oil (136 mg, 79% yield),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  4.32 (s, 2H), 6.24 (d, 1H,  $J$  = 2.82 Hz), 6.33 (s, 1H), 6.68 (d, 2H,  $J$  = 8.0 Hz), 6.75 (t, 1H,  $J$  = 7.3 Hz), 7.19 (t, 2H,  $J$  = 7.8 Hz), 7.35 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  41.5, 106.9, 110.3, 113.2, 118.0, 129.2, 141.9, 147.6, 152.8; HRESIMS calcd for  $\text{C}_{11}\text{H}_{12}\text{NO} [\text{M}+\text{H}]^+$  174.0919, found 174.0927.

**N-(5-Acetoxymethyl-2-furfuryl)aniline (6b):** Brown red oil (183 mg, 75% yield),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  2.09 (s, 3H), 4.32 (s, 2H), 5.04 (s, 2H), 6.21 (d, 1H,  $J$  = 3.1 Hz), 6.35 (d, 1H,  $J$  = 3.1 Hz), 6.68 (d, 2H,  $J$  = 7.6 Hz), 6.75 (t, 1H,  $J$  = 7.3 Hz), 7.19-7.22 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  20.9, 41.4, 58.1, 108.0, 111.6, 113.2, 118.0, 129.2, 147.5, 148.8, 153.8, 170.6; HRESIMS calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}_3 [\text{M}+\text{H}]^+$  246.1130, found 246.1140.

**N-Benzofuran-2-ylmethylaniline (6C):** Yellow solid (136 mg, 61% yield), mp. 49-50 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  4.49 (s, 2H), 6.61 (s, 1H), 6.71 (d, 2H,  $J$  = 8.0 Hz), 6.75 (t, 1H,  $J$  = 7.2 Hz), 7.19 (t, 3H,  $J$  = 7.7 Hz), 7.24 (t, 1H,  $J$  = 7.5 Hz), 7.45 (d, 1H,  $J$  = 8.1 Hz), 7.50 (d, 1H,  $J$  = 7.5 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  41.9, 103.7, 111.0, 113.2, 118.2, 120.8, 122.7, 123.9, 128.4, 129.3, 147.4, 154.9, 155.6; HRESIMS calcd for  $\text{C}_{15}\text{H}_{14}\text{NO} [\text{M}+\text{H}]^+$  224.1075, found 224.1065.

**N-Benzyl-(6-bromopyridin-3-yl)amine (6d):** Brown solid (188 mg, 72% yield) mp. 106 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.31 (s, 2H), 4.39 (brs, 1H), 6.78 (dd, 1H,  $J$  = 3.0 Hz, 2.9 Hz), 7.20 (d, 1H,  $J$  = 8.5 Hz), 7.36 (m, 5H), 7.79 (d, 1H,  $J$  = 2.9 Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  48.2, 122.5, 127.7, 128.1, 128.6, 129.2, 135.8, 137.1, 138.3, 144.0; HRESIMS calcd for  $\text{C}_{12}\text{H}_{12}\text{BrN}_2 [\text{M}+\text{H}]^+$  263.0184, found 263.0170.

**N-Benzyl-(5-bromopyridin-3-yl)amine (6e):** Brown solid (117 mg, 45% yield), mp. 69-70 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 4.30 (s, 2H), 7.02 (t, 1H, J = 2.0 Hz), 7.30-7.38 (m, 5H), 7.95 (d, 1H, J = 2.4 Hz), 7.98 (d, 1H, J = 1.6 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 47.7, 120.7, 121.1, 127.4, 127.7, 128.9, 134.3, 137.7, 139.2, 144.9; HRESIMS calcd for C<sub>12</sub>H<sub>12</sub>BrN<sub>2</sub> [M+H]<sup>+</sup> 263.0184, found 263.0165.

**N-Cinnamoyl-(6-bromopyridin-3-yl)amine (6f):** Brown solid (207 mg, 72% yield), mp. 88-89 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 3.77 (d, 2H, J = 5.3 Hz), 6.09-6.13 (m, 1H), 6.47 (d, 1H, J = 15.9 Hz), 6.69 (q, 1H, J = 3.8 Hz), 7.08 (d, 1H, J = 8.64 Hz), 7.12 (t, 1H, J = 7.2 Hz), 7.18-7.23 (m, 4H), 7.68 (d, 1H, J = 2.82 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 45.7, 122.3, 125.4, 126.4, 127.7, 127.8, 128.3, 128.6, 132.2, 135.5, 136.4, 143.5; HRESIMS calcd for C<sub>14</sub>H<sub>14</sub>BrN<sub>2</sub> [M+H]<sup>+</sup> 289.0340, found 289.0328.

**N-Benzyl-(6-chloropyridin-3-yl)amine (6g):** Colourless solid (207 mg, 95% yield), mp, 94 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 4.29 (s, 2H), 4.67 (brs, 1H), 6.85 (dd, 1H, J = 2.4 Hz, 2.4 Hz), 7.04 (d, 1H, J = 8.4 Hz), 7.33 (m, 5H), 7.75 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 48.1, 122.6, 124.4, 127.7, 127.9, 129.2, 134.9, 138.6, 139.0, 143.8; HRESIMS calcd for C<sub>12</sub>H<sub>12</sub>ClN<sub>2</sub> [M+H]<sup>+</sup> 219.0689, found 219.0676.

**N-Cinnamoyl-(6-chloropyridin-3-yl)amine (6h):** Brown solid (190 mg, 78% yield), mp. 98-99 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.90 (d, 2H, J = 5.3 Hz), 3.91 (brs, 1H), 6.22-6.26 (m, 1H), 6.58 (d, 1H, J = 15.8 Hz), 6.89 (q, 1H, J = 3.7 Hz), 7.07 (d, 1H, J = 8.5 Hz), 7.18 (t, 1H, J = 7.62 Hz), 7.18-7.23 (m, 4H), 7.68 (d, 1H, J = 2.4 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 45.8, 122.3, 124.0, 125.5, 126.4, 127.8, 128.6, 132.2, 134.7, 136.4, 139.0, 143.1; HRESIMS calcd for C<sub>14</sub>H<sub>14</sub>ClN<sub>2</sub> [M+H]<sup>+</sup> 245.0845, found 245.0824.

**6-(*N*-Benzylamino)benzothiazole (**6i**):** Brown solid (206 mg, 86% yield), mp. 98 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 4.37 (s, 2H), 6.83 (dd, 1H, *J* = 2.16 Hz, 1.80 Hz), 7.03 (d, 1H, *J* = 1.92 Hz), 7.30 (d, 1H, *J* = 7.02 Hz), 7.38 (m, 4H), 7.90 (d, 1H, *J* = 8.82 Hz), 8.66 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 48.4, 102.1, 114.8, 123.7, 127.4, 128.7, 138.8, 146.6, 149.3; HRESIMS calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>S[M+H]<sup>+</sup> 241.0799, found 241.0774.

**6-(*N*-cinnamylamino)benzothiazol (**6j**):** Yellow solid (212 mg, 80% yield), mp. 107 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.98 (d, 2H, *J* = 5.6 Hz), 6.30-6.39 (m, 1H), 6.64 (d, 1H, *J* = 15.9 Hz), 6.85 (dd, 1H, *J* = 3.7 Hz), 7.10 (d, 1H, *J* = 2.2 Hz), 7.27-7.42 (m, 6H), 7.92 (d, 1H, *J* = 8.7 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 46.7, 102.7, 115.3, 124.2, 126.7, 128.1, 129.0, 132.2, 136.3, 137.1, 146.4, 146.9, 149.6; HRESIMS calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>S [M+H]<sup>+</sup> 267.0956, found 267.0934.

**N-Furfuryl (6-chloropyridin-3-yl)amine (**6k**):** Brown solid (156 mg, 75% yield), mp. 61 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 4.29 (s, 3H, NH & -CH<sub>2</sub>- merged), 6.21 (d, 1H, *J* = 3.06 Hz), 6.30 (t, 1H, *J* = 2.2 Hz), 6.90-6.92 (dd, 1H, *J* = 3.0 Hz), 7.06 (d, 1H, *J* = 8.6 Hz), 7.34 (s, 1H), 7.79 (d, 1H, *J* = 3.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 41.0, 107.5, 110.4, 122.5, 124.0, 134.8, 139.4, 142.2, 142.7, 151.4; HRESIMS calcd for C<sub>10</sub>H<sub>10</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> 209.0482, found 209.0478.

**6-(*N*-furfurylamino)benzothiazol (**6l**):** Dark brown viscous oil (165 mg, 72% yield), IR  $\tilde{\nu}$  (KBr) (cm<sup>-1</sup>): 729, 815, 1143, 1261, 1481, 1562, 1602; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 4.37 (s, 3H, NH & -CH<sub>2</sub>- merged), 6.26 (d, 1H, *J* = 5.9 Hz), 6.33-6.35 (m, 1H), 6.85 (dd, 1H, *J* = 3.6 Hz, 4.8 Hz), 7.11 (d, 1H, *J* = 2.1 Hz), 7.39 (d, 1H, *J* = 1.0 Hz), 7.89 (d, 1H, *J* = 8.8 Hz), 8.6 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): 42.0, 102.9, 107.6, 110.8, 115.3,

124.2, 142.5, 146.4, 146.7, 149.8, 152.5; HRESIMS calcd for C<sub>12</sub>H<sub>11</sub>N<sub>2</sub>OS [M+H]<sup>+</sup> 231.0592, found 231.0584.

**N-(1-Adamantile)-4-chlorobenzamide (7a):** White solid (231 mg, 80%), <sup>1</sup>H NMR(600 MHz, CDCl<sub>3</sub>): 7.71 (d, *J* = 8.22 Hz, 2H), 7.41 (d, *J* = 8.22 Hz, 2H), 6.36 (brs, 1H), 4.24 (d, *J* = 7.02 Hz, 1H), 2.04 (s, 2H), 1.90 (brs, 6H), 1.84 (d, *J* = 13.08 Hz, 2H), 1.78 (s, 2H), 1.71 (d, *J* = 12.84 Hz, 2H); <sup>13</sup>C NMR(150 MHz, CDCl<sub>3</sub>): 165.5, 137.4, 133.7, 128.8, 128.2, 53.8, 37.4, 37.1, 32.1, 31.9, 27.2, 27.1. HRESIMS calcd for C<sub>17</sub>H<sub>21</sub>ClNO [M+H]<sup>+</sup> 290.1312, found 290.1301.

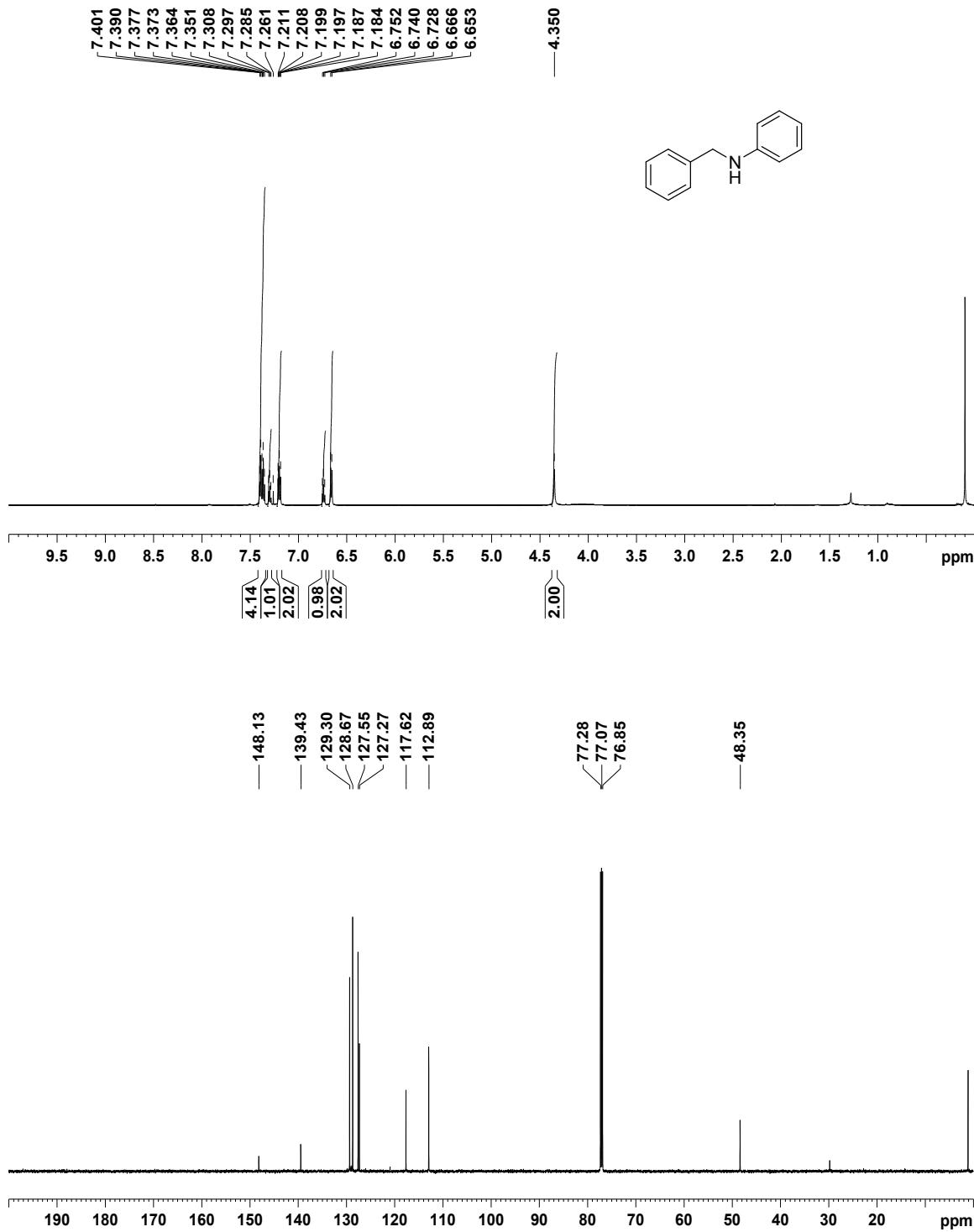
**1-(2-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (7b):** White solid (76 mg, 90%), <sup>1</sup>H NMR(600 MHz, CDCl<sub>3</sub>): 8.15 (d, *J* = 8.10 Hz, 1H), 7.93 (s, 1H), 7.83 (d, *J* = 7.32 Hz, 2H), 7.60 (t, *J* = 7.26 Hz, 1H), 7.52 (t, *J* = 7.50 Hz, 1H), 7.42 (t, *J* = 7.68 Hz, 2H), 7.33 (t, *J* = 7.41 Hz, 1H), 7.14 (d, *J* = 7.74 Hz, 1H), 5.98 (s, 2H); <sup>13</sup>C NMR(150 MHz, CDCl<sub>3</sub>): 148.3, 147.4, 134.4, 130.7, 130.3, 130.2, 129.6, 128.9, 128.3, 125.7, 125.3, 120.6, 50.8. HRESIMS calcd for C<sub>15</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub> [M+H]<sup>+</sup> 281.1039, found 281.1017.

## 5. References

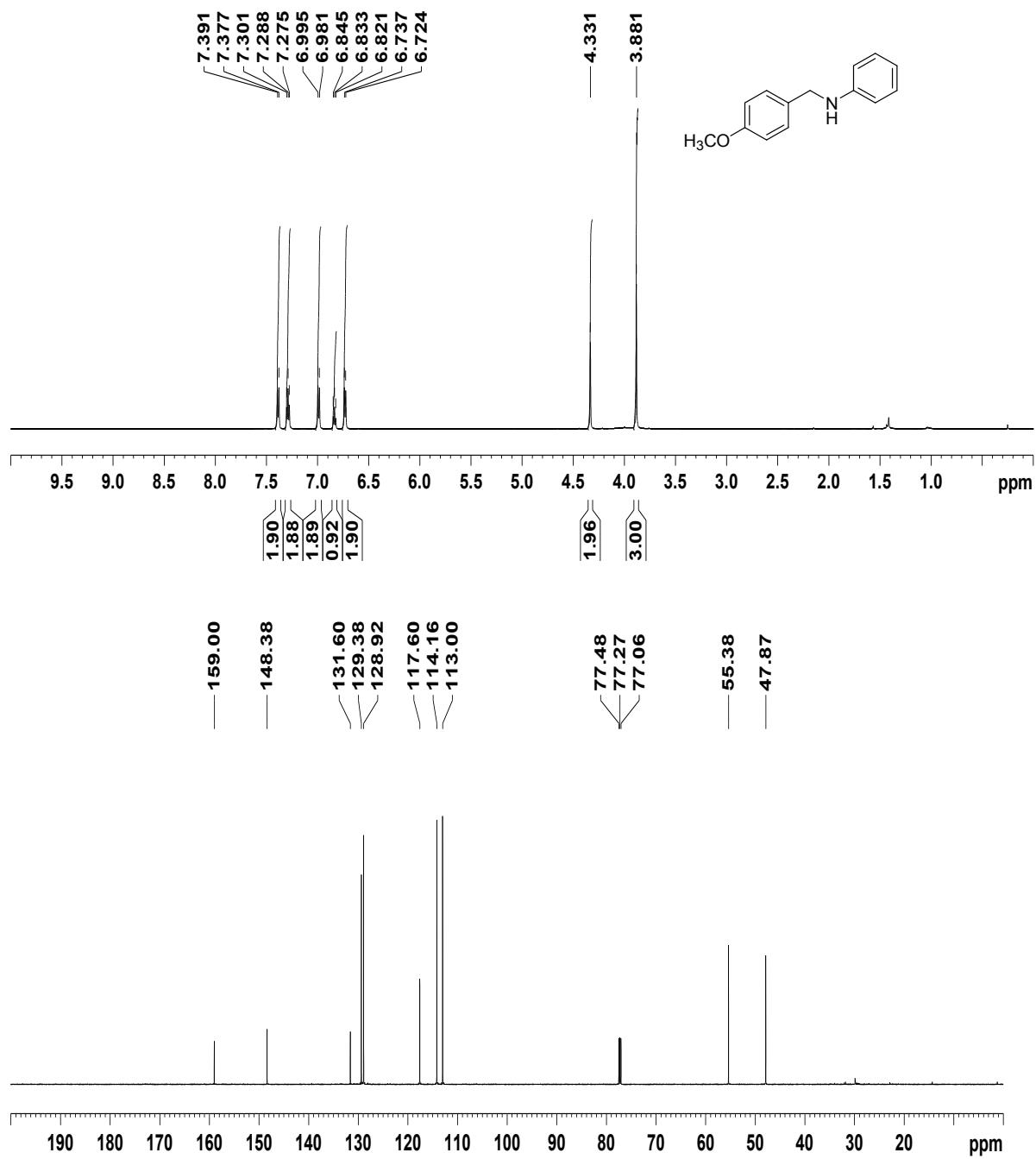
1. C. Schneider, M. Sablier, B. Desmazieres, *Rapid Commun. Mass Spectrom.*, **2008**, *22*, 3353-3361 (for polysiloxane generation).
2. a) Kumar, V.; Sharma, U.; Verma, P. K.; Kumar, N.; Singh, B. *Adv. Synth. Catal.* **2012**, *354*, 870–878; b) Kumar, V.; Sharma, S.; Sharma, U.; Kumar, N.; Singh, B. *Green Chem.* **2012**, *14*, 3410–3414 (for NMR values).

## 6. NMR spectra

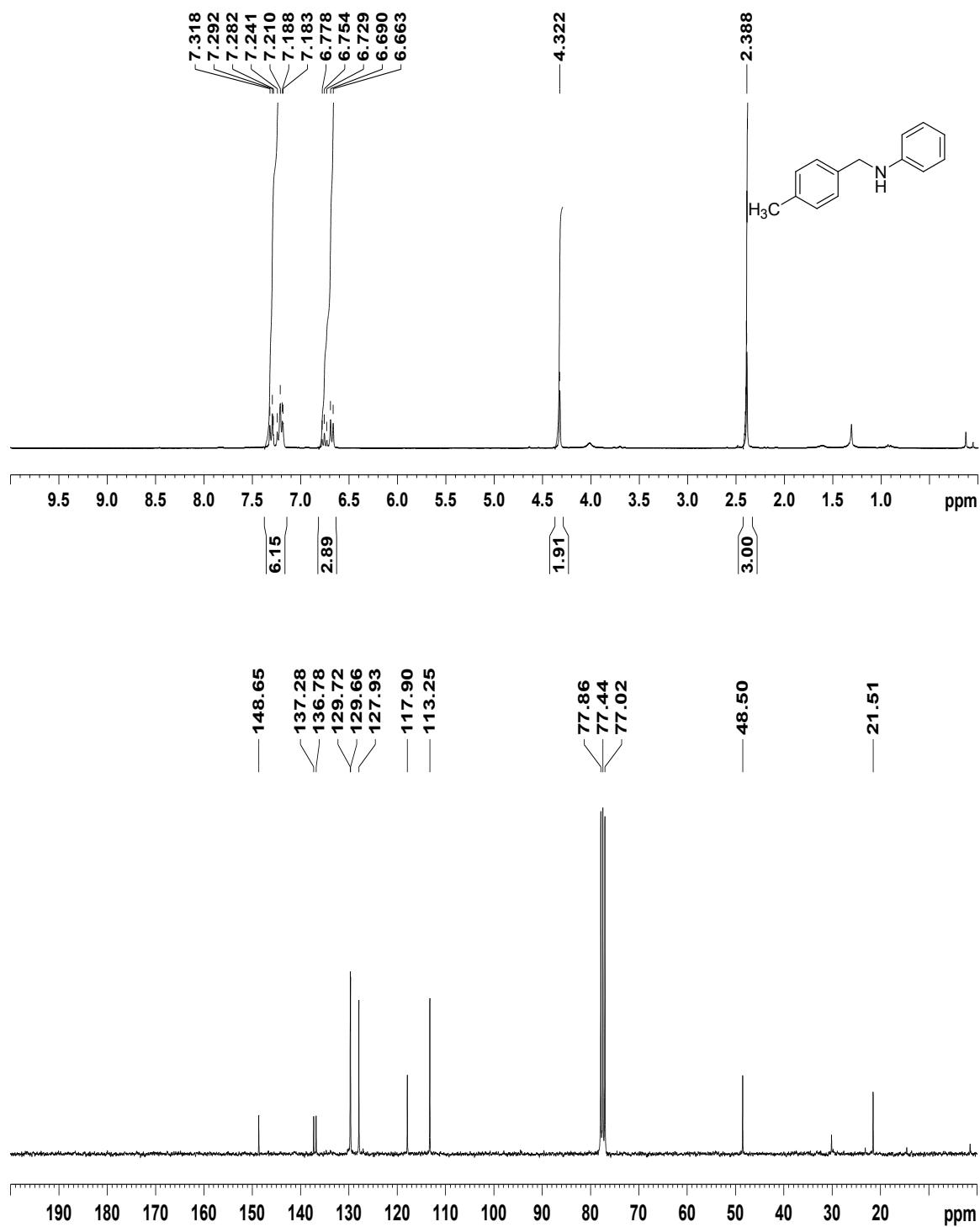
*N*-benzylaniline (3a):



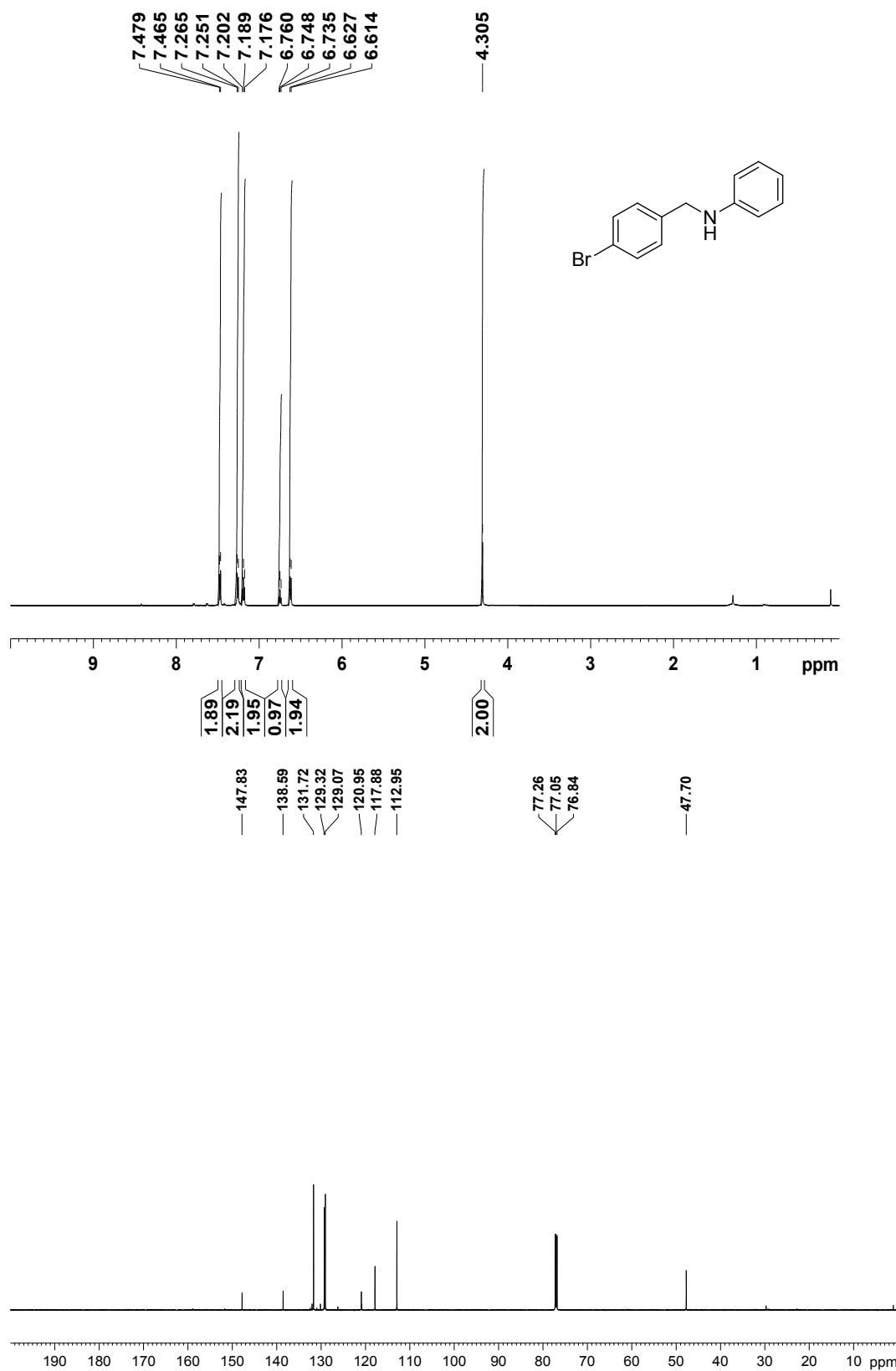
**N-(4'-Methoxybenzyl)aniline (3b):**



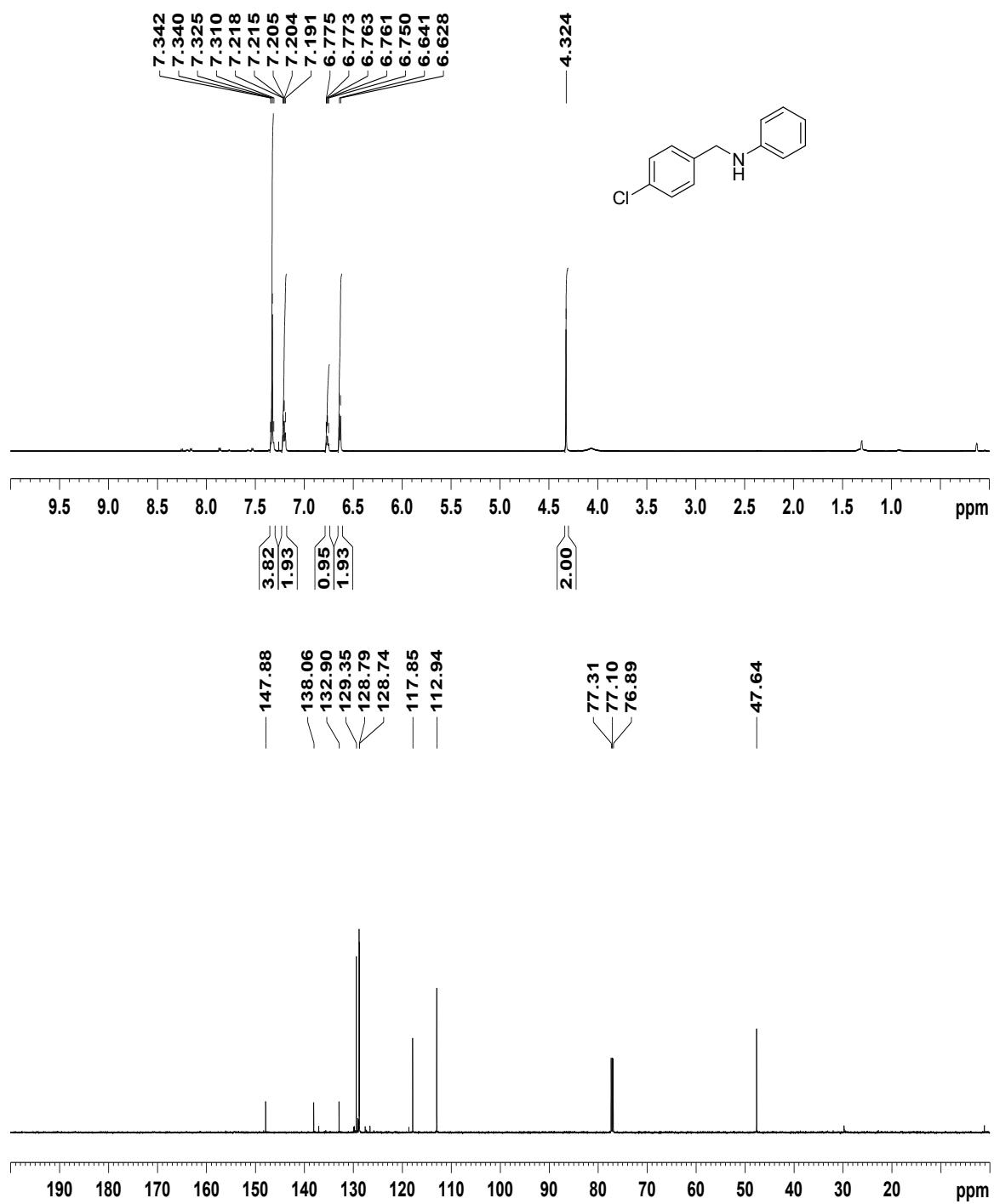
*N*-(4'-Methylbenzyl)aniline (3c):



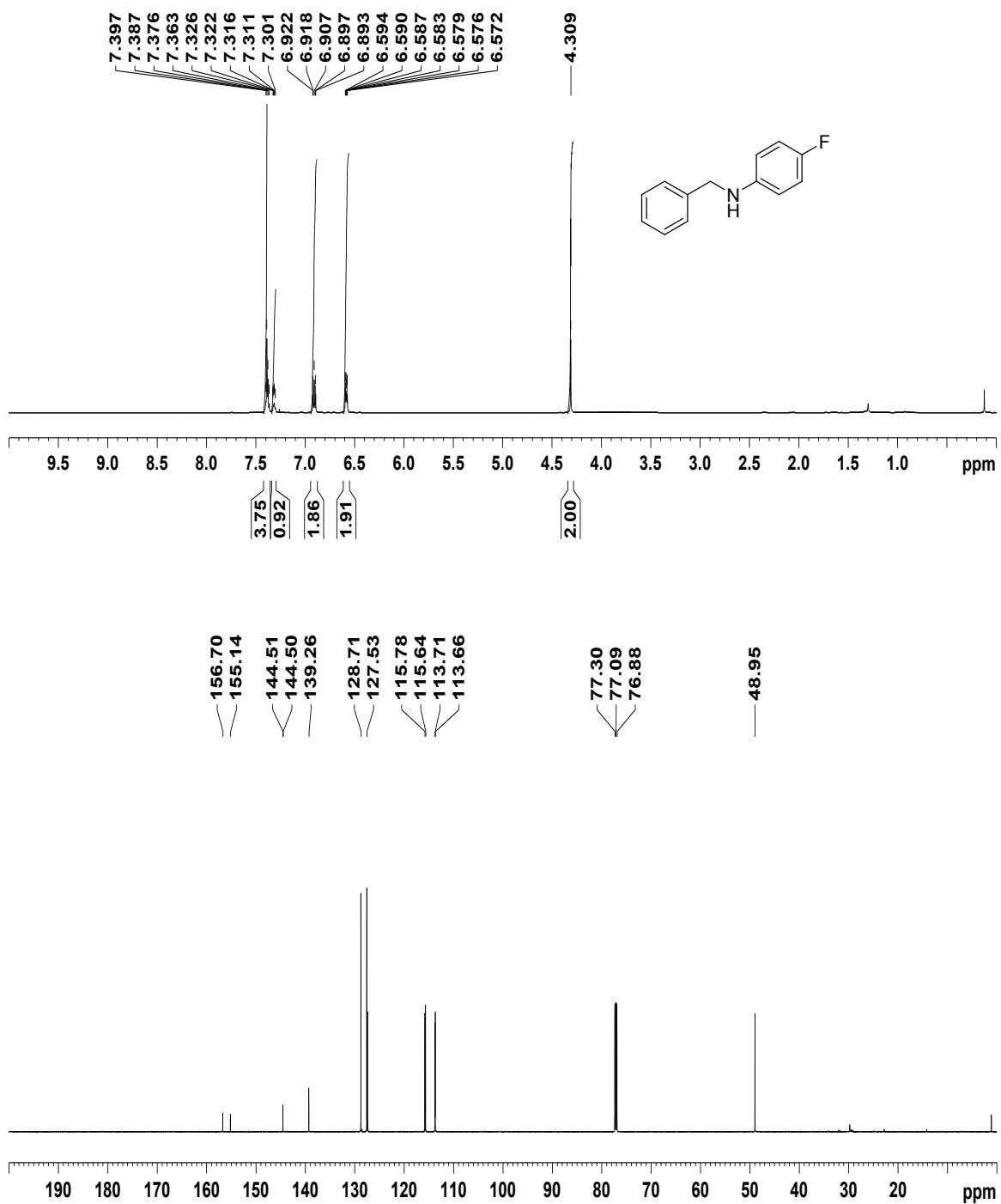
***N*-(4'-bromobenzyl)aniline (3d):**



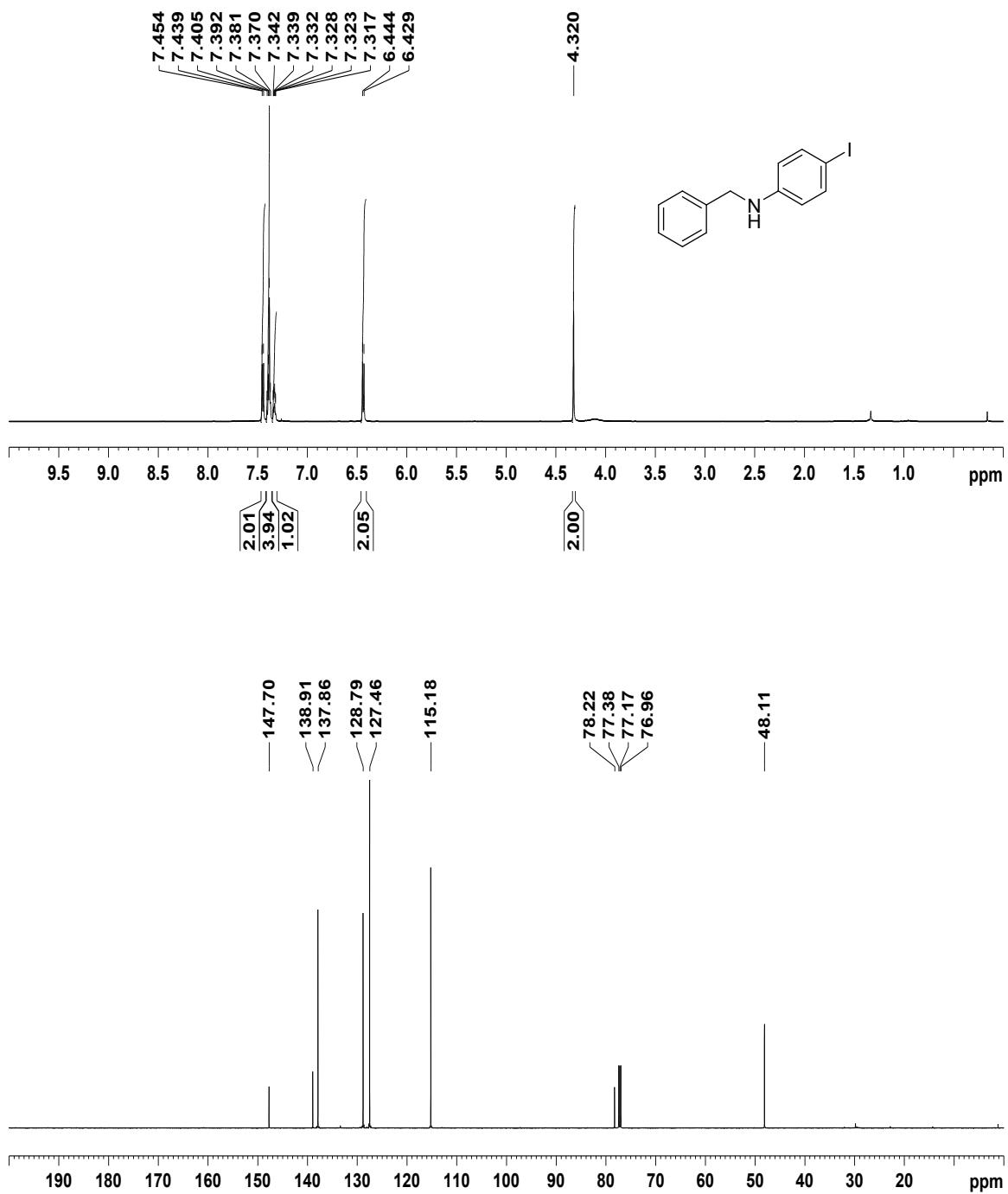
*N*-(4'-chlorobenzyl)aniline (**3e**):



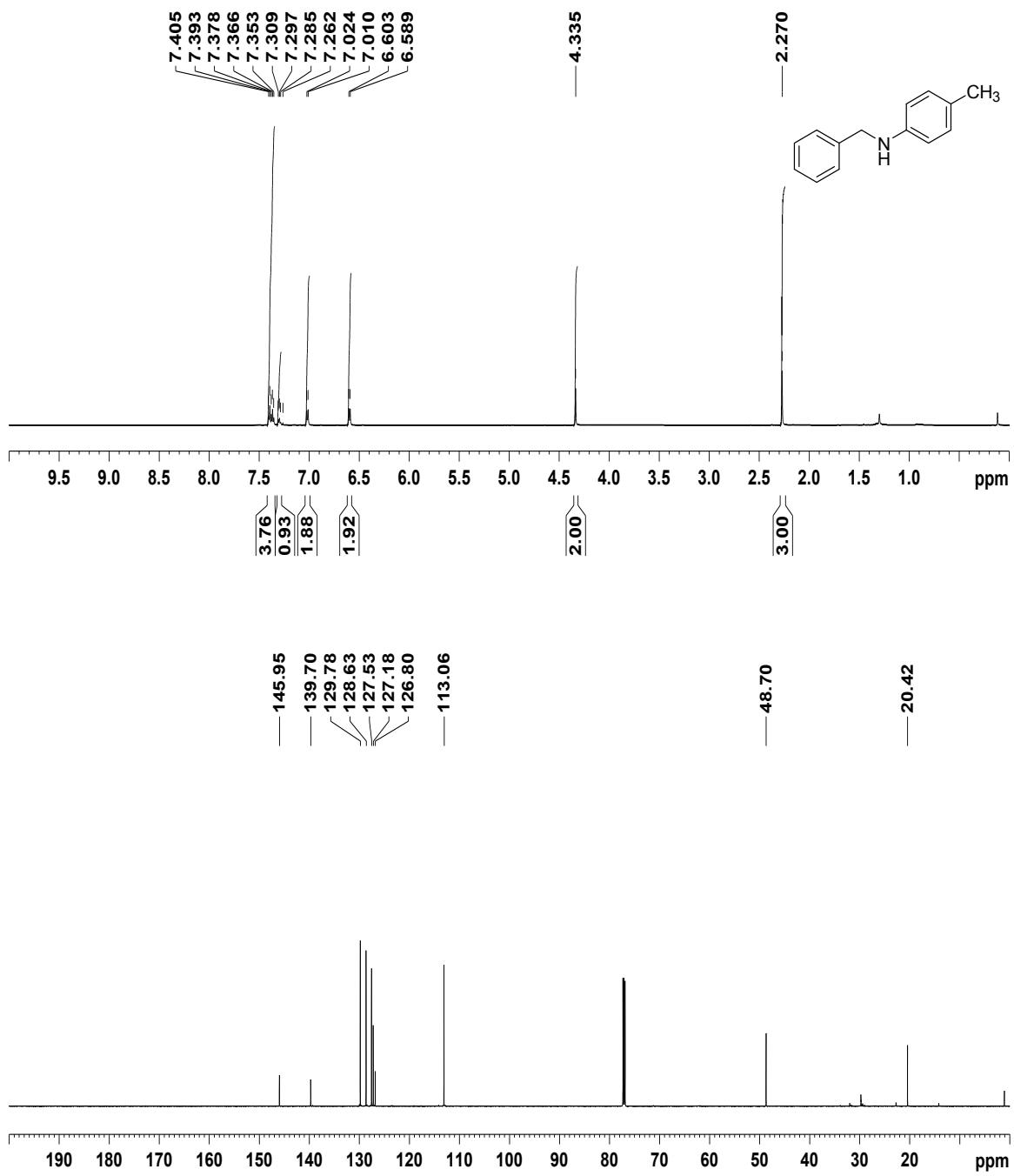
*N*-Benzyl-4-fluoroaniline (3f):



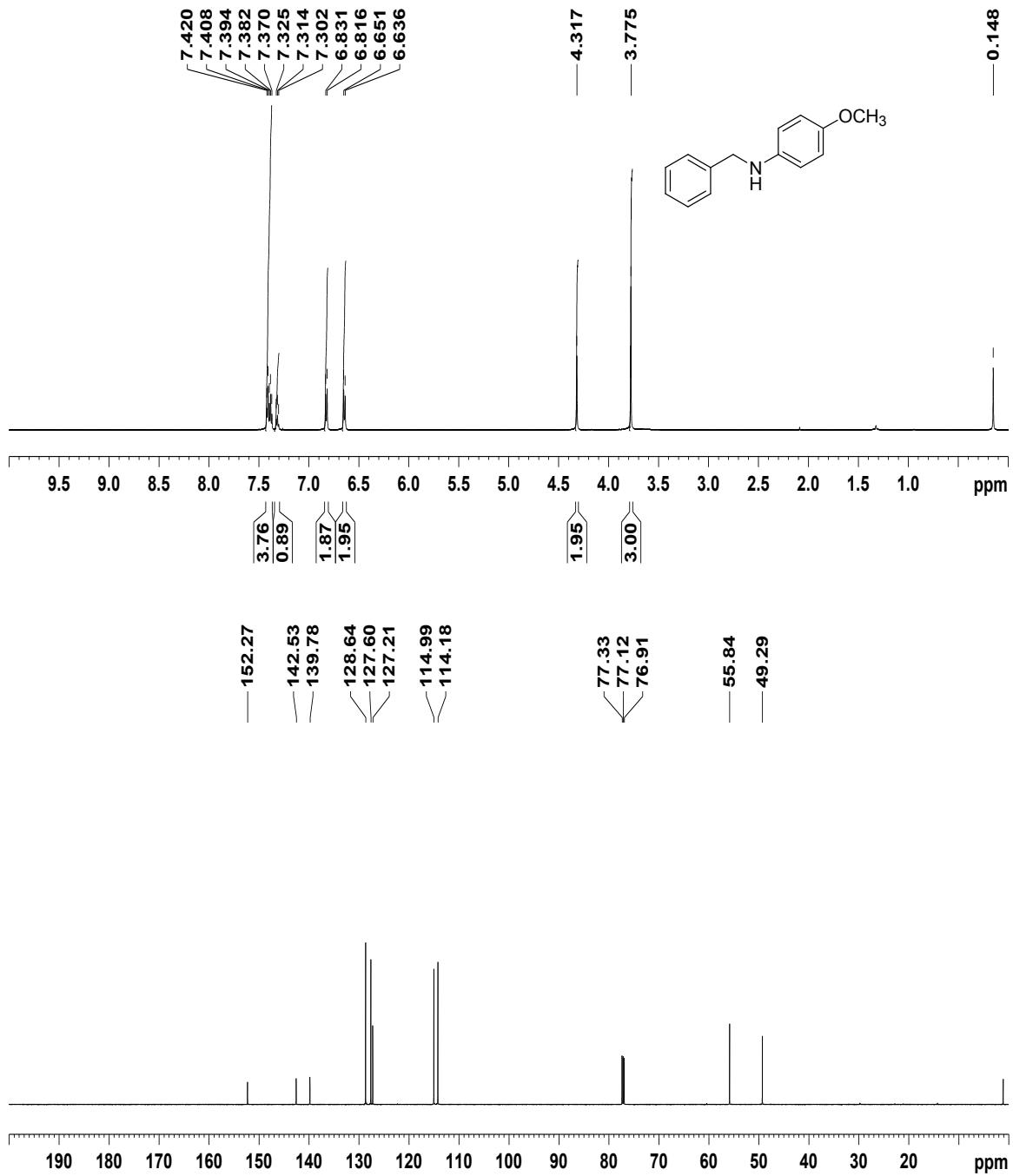
*N*-Benzyl-4-iodoaniline (3g):



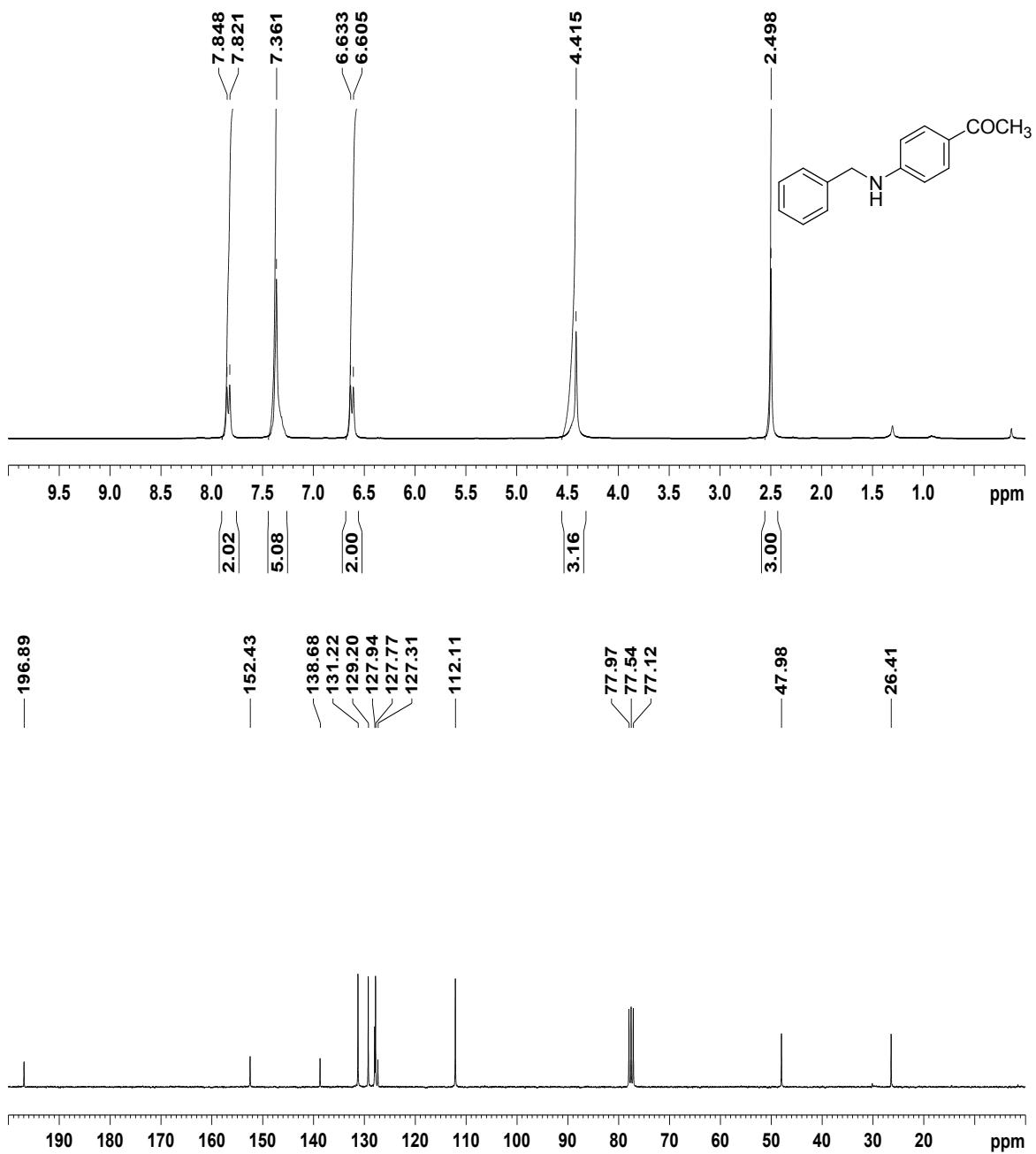
**N-Benzyl-4-methylaniline (3h):**



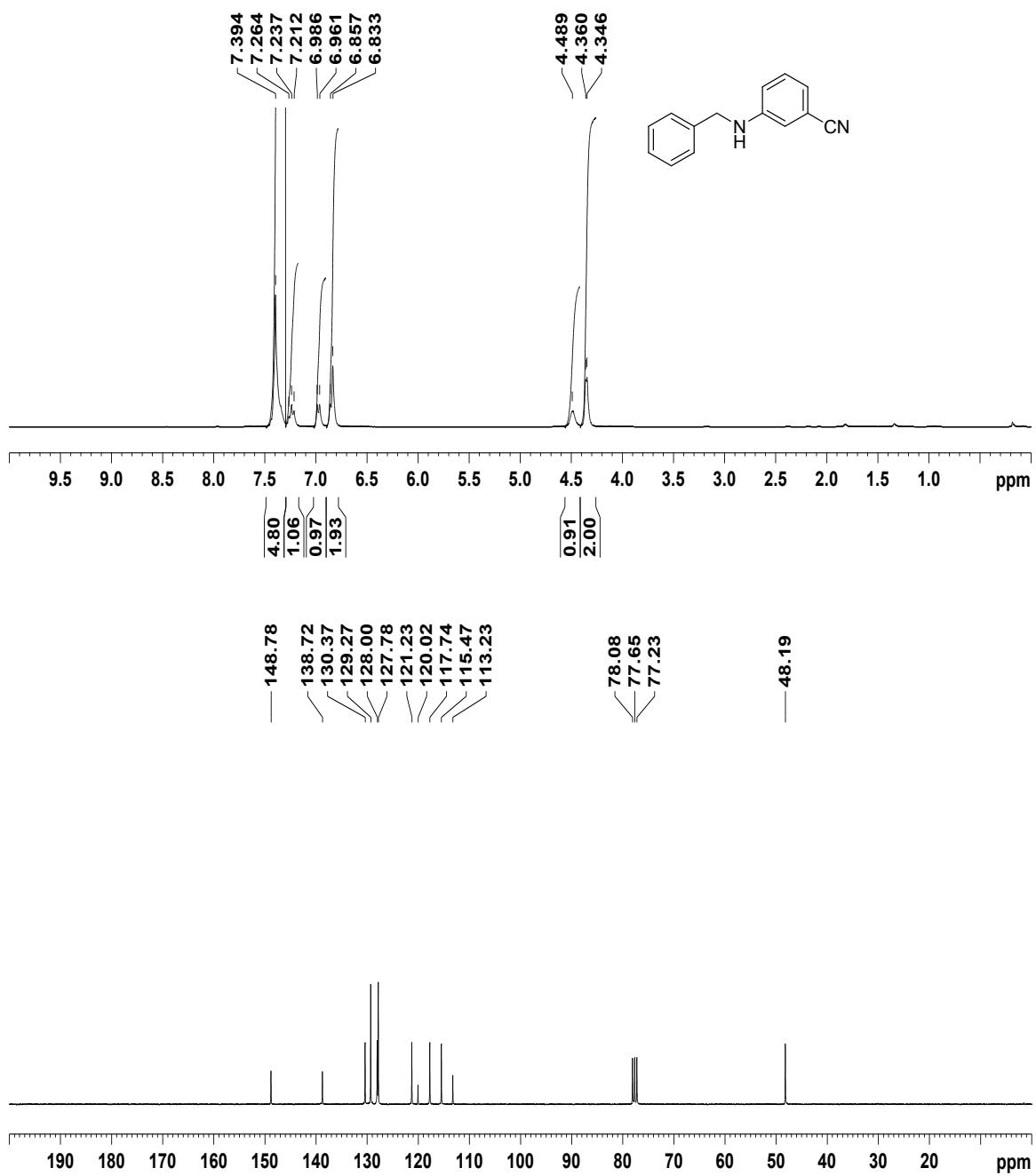
*N*-Benzyl-4-methoxyaniline (**3i**):



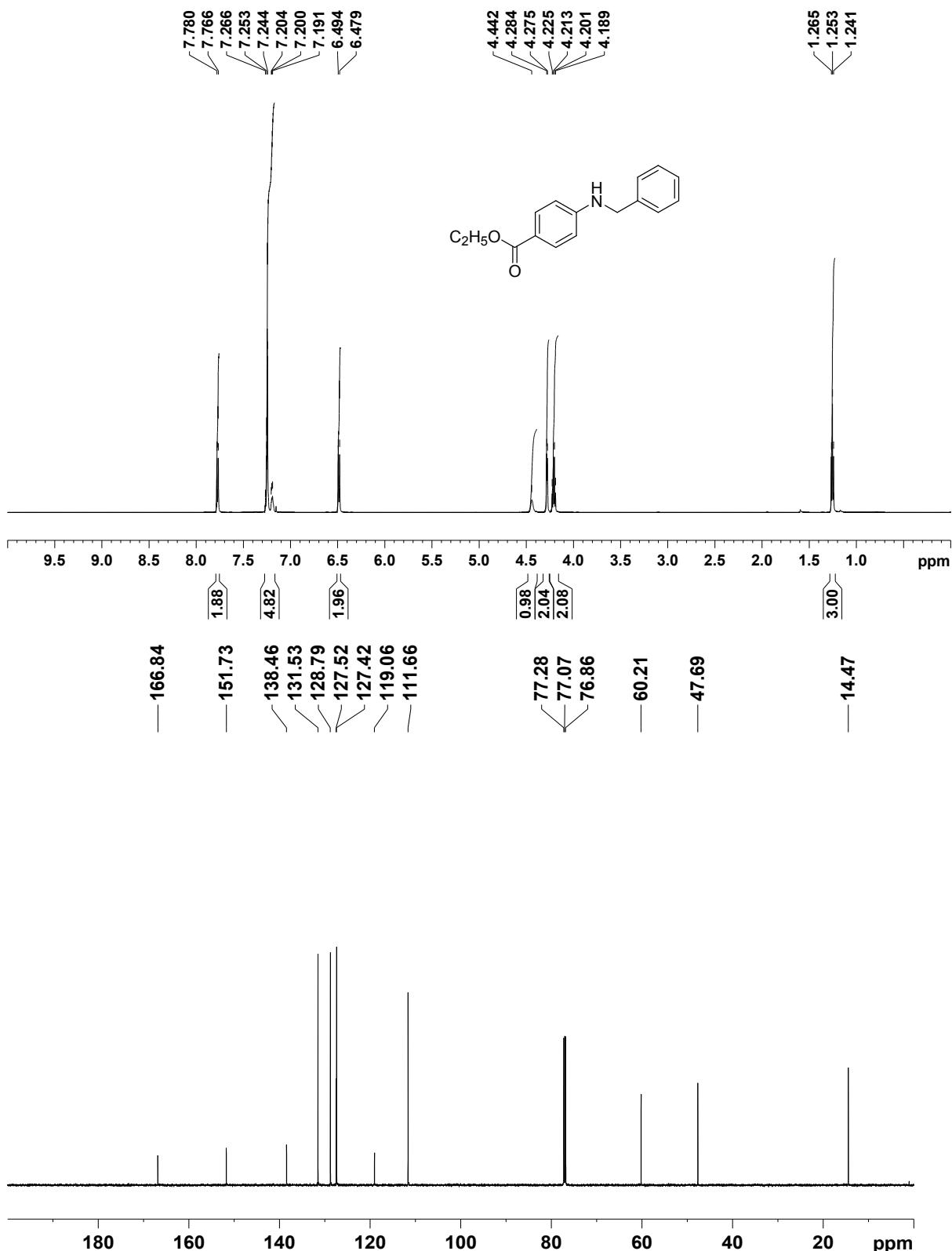
**1-(4-benzylaminophenyl)ethanone (3j):**



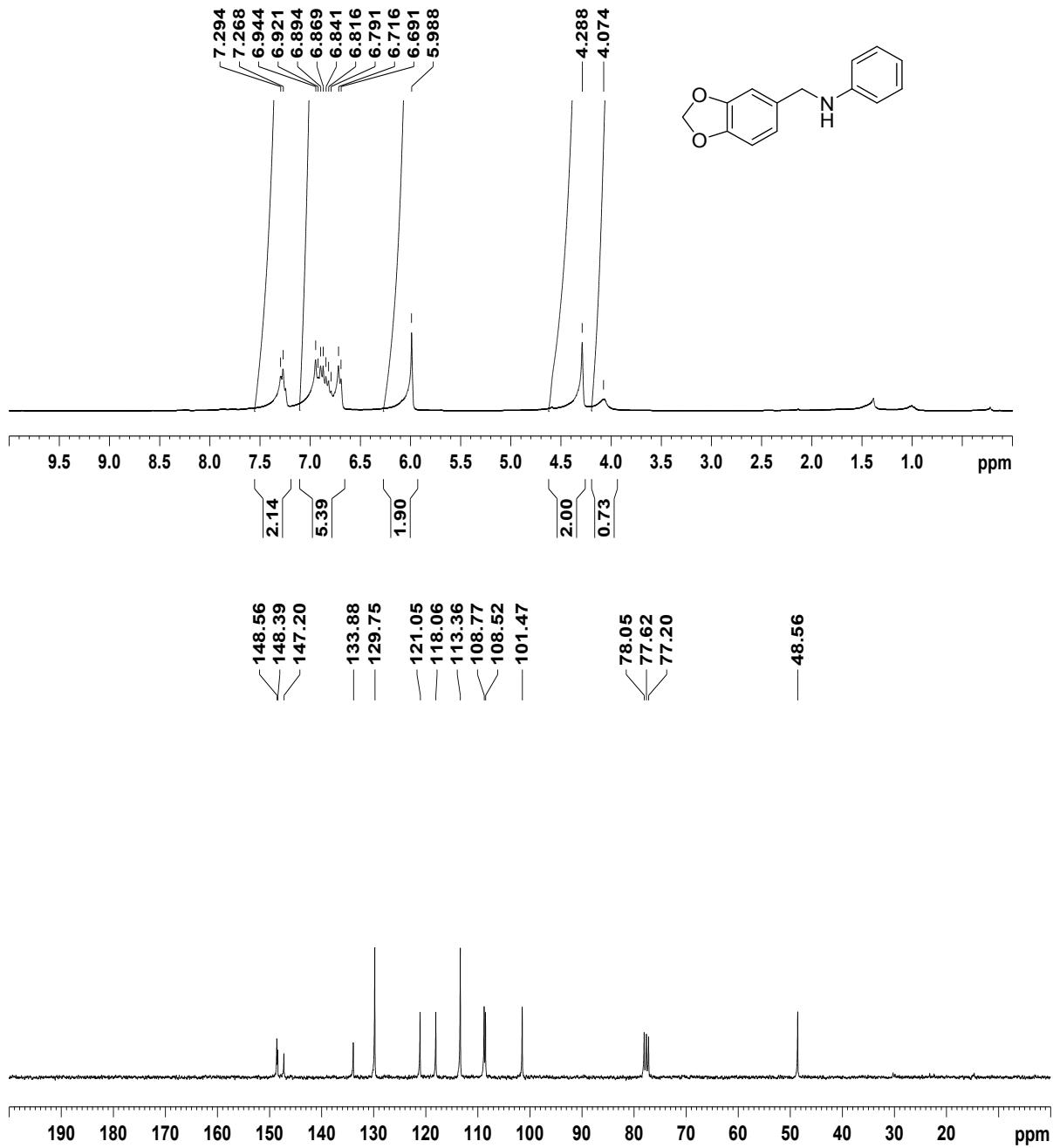
**N–Benzyl–3–cyanoaniline (3k):**



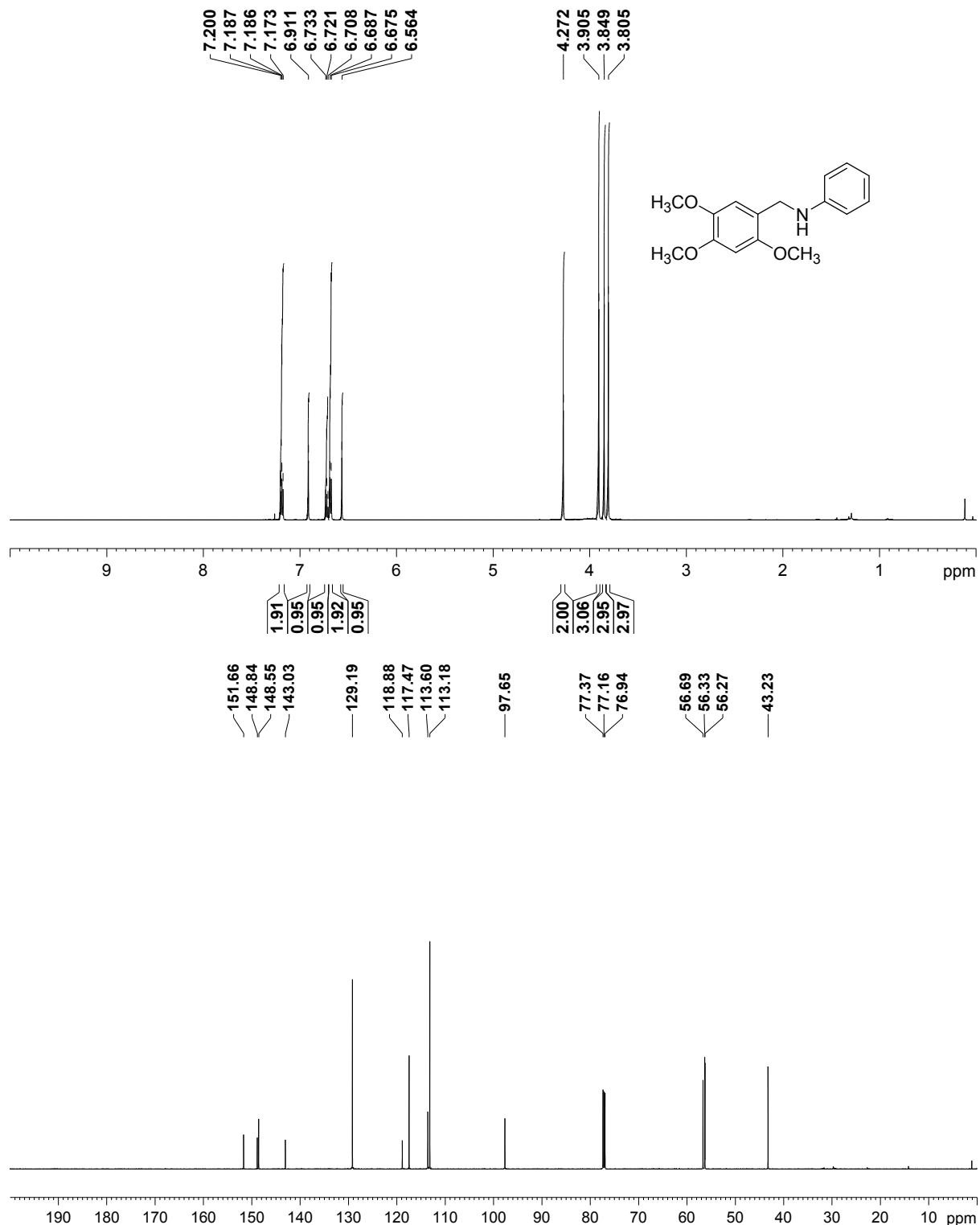
**Ethyl-4-(*N*-benzylamino)benzoate (3l):**



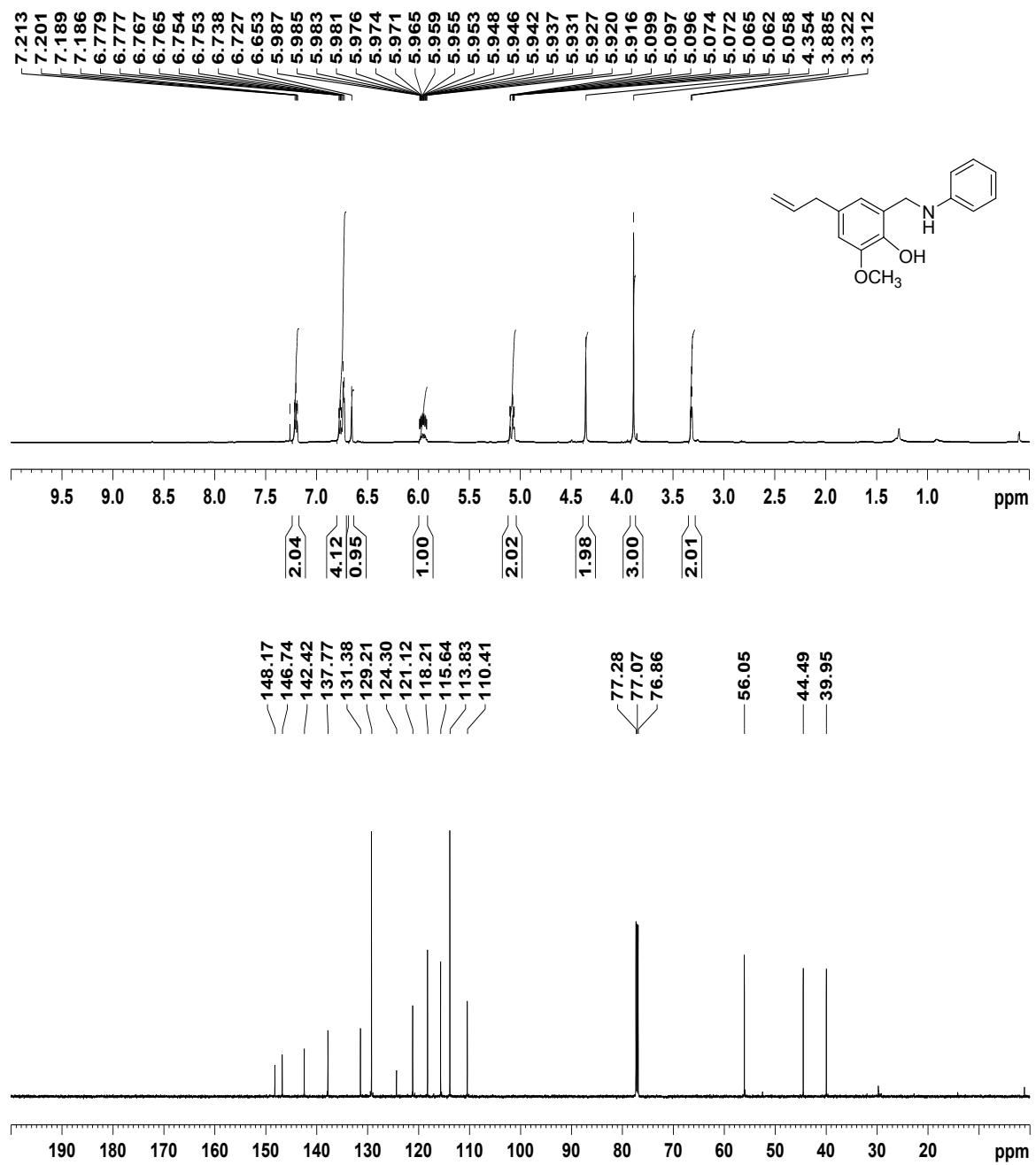
*N*-(Benzo[1,3]dioxol-5-ylmethyl)aniline (3m):



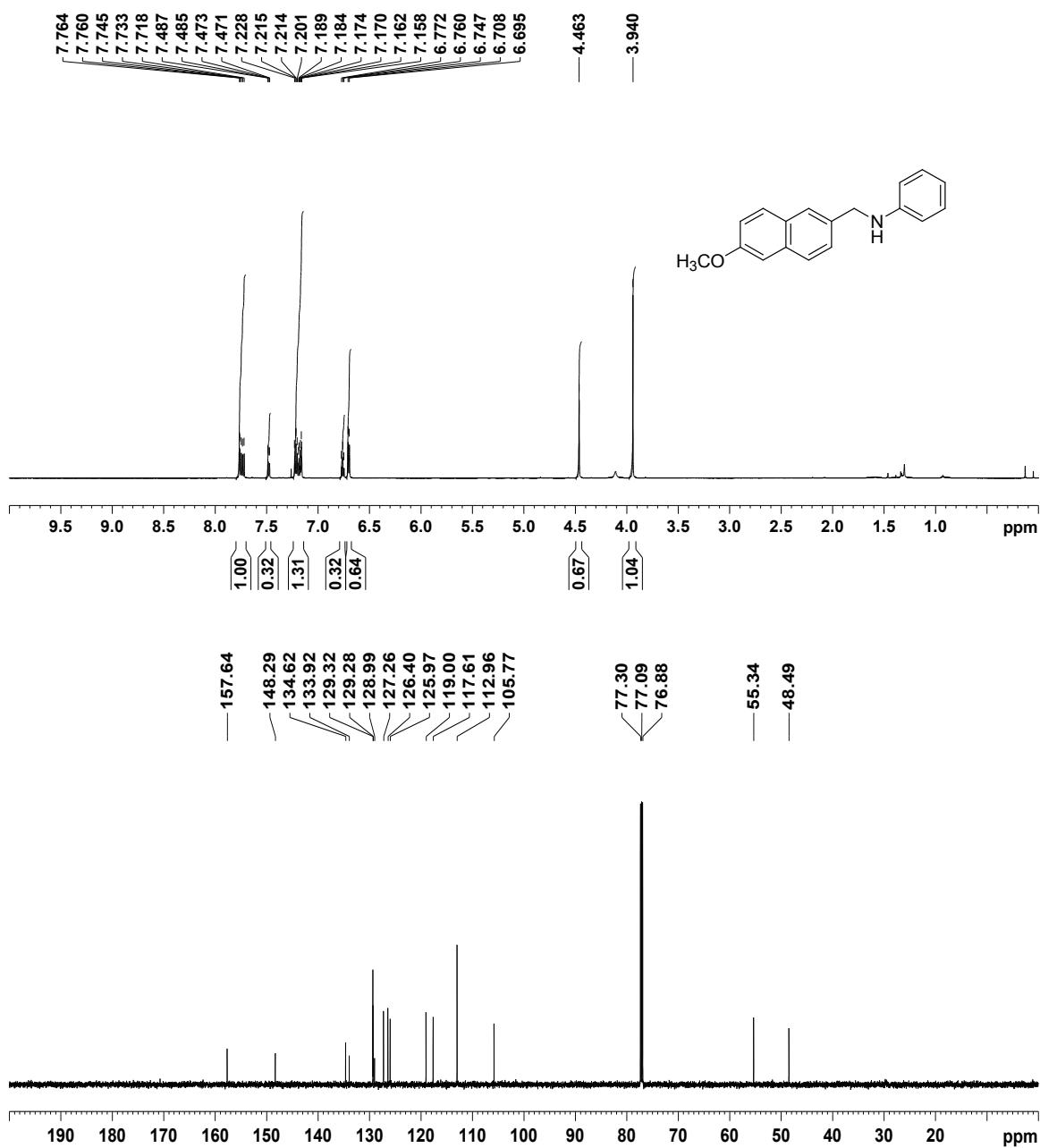
*N*-(2',4',5'-trimethoxybenzyl)aniline (**3n**):



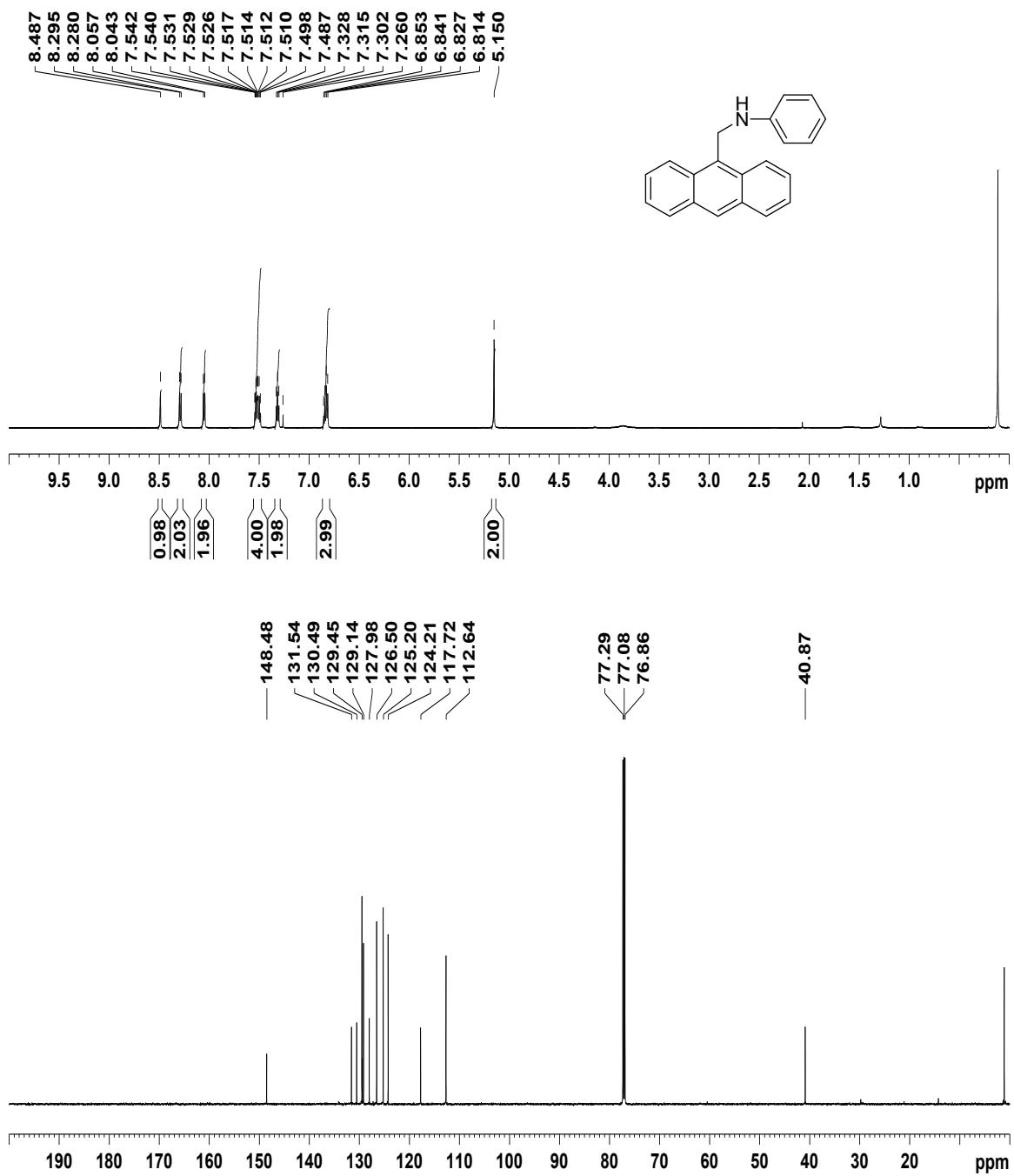
**N-(5'-Allyl-2'-hydroxy-3'-methoxybenzyl)aniline (3o):**



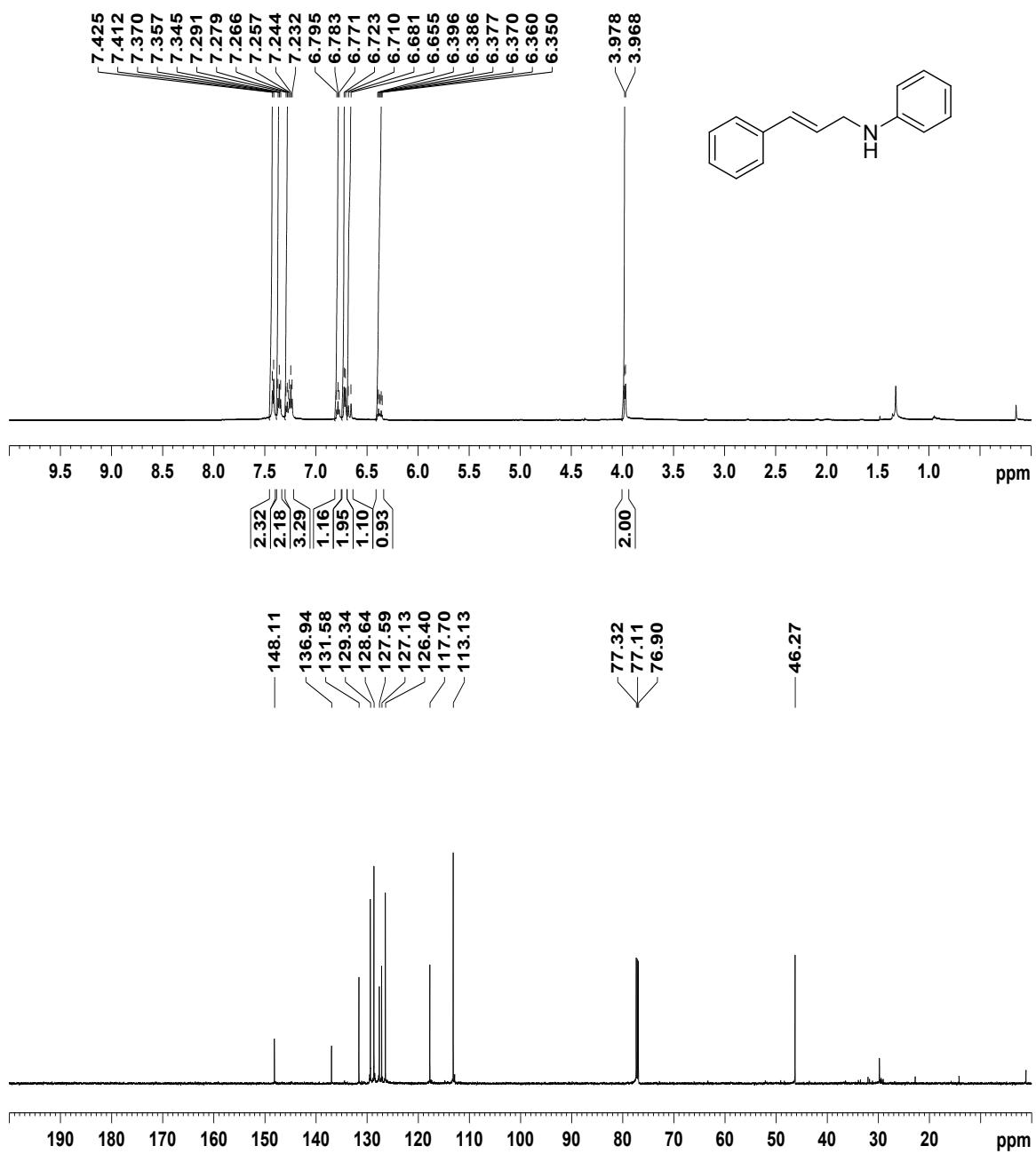
*N*-(6'-methoxynaphthalen-2-ylmethyl)aniline (3p):



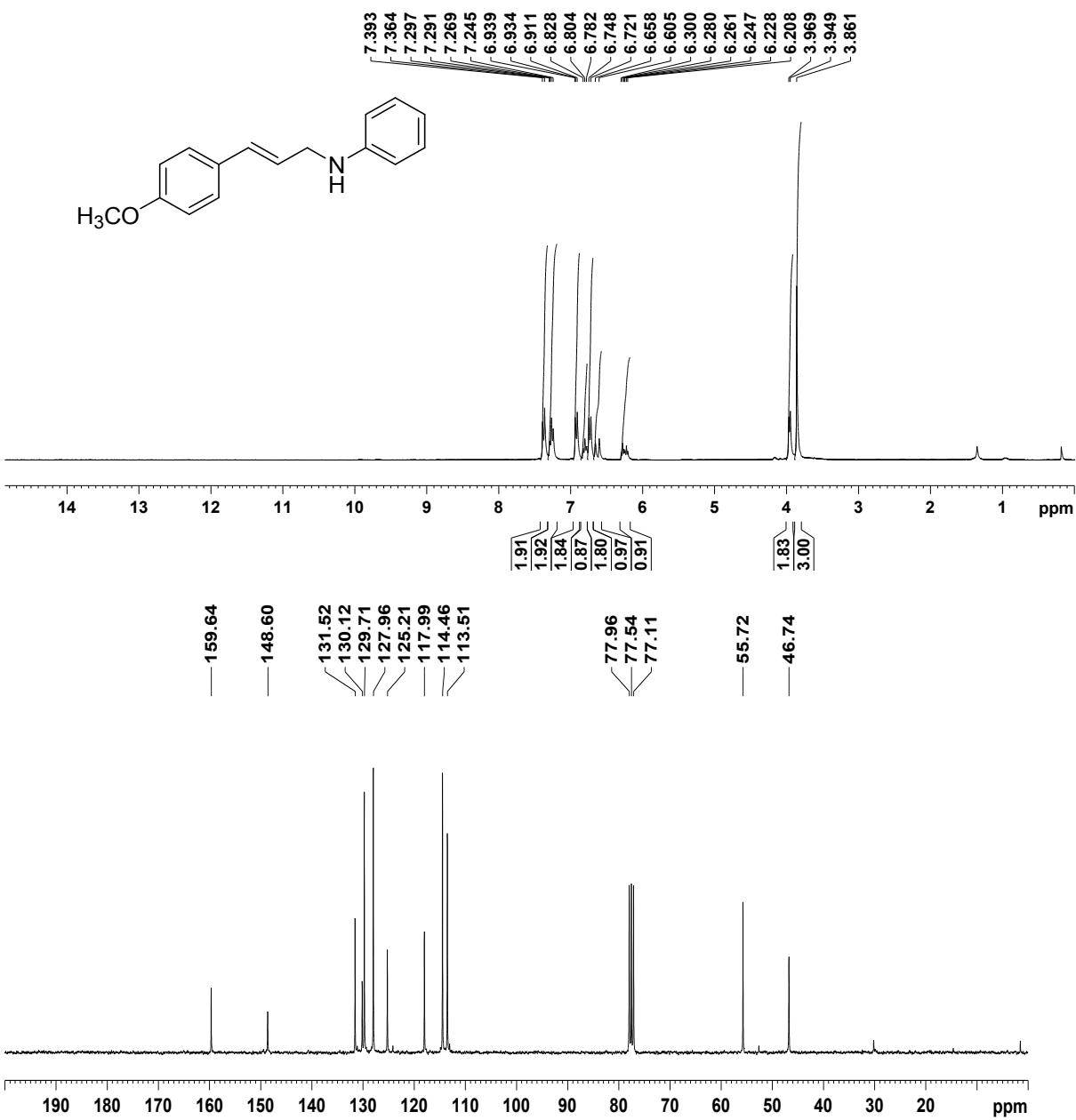
***N*-(9'-Anthracenebenzyl)aniline (3q):**



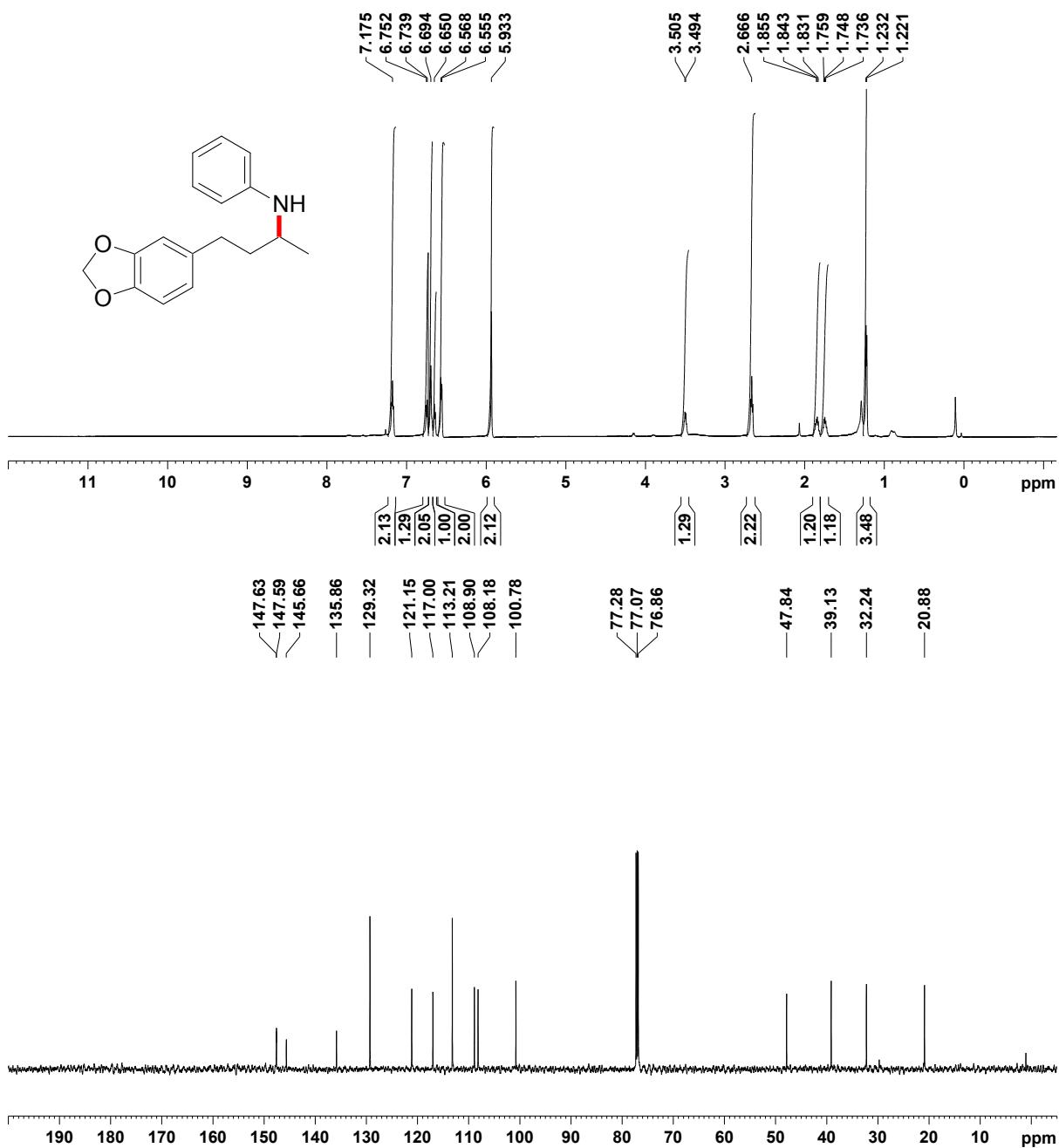
**N-Cinnamylaniline (3r):**



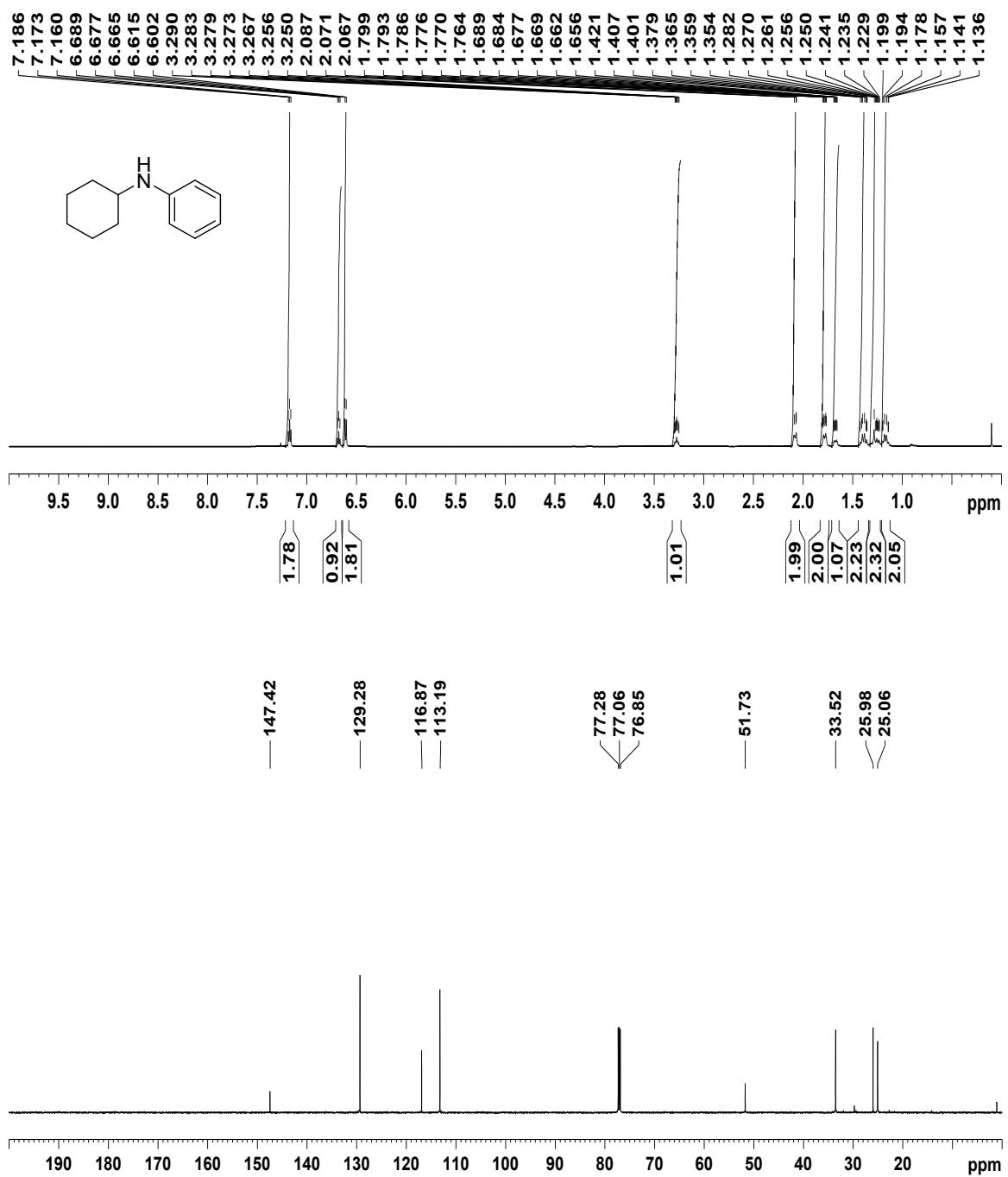
*N*-(4'-methoxyCinnamyl)aniline (**3s**):



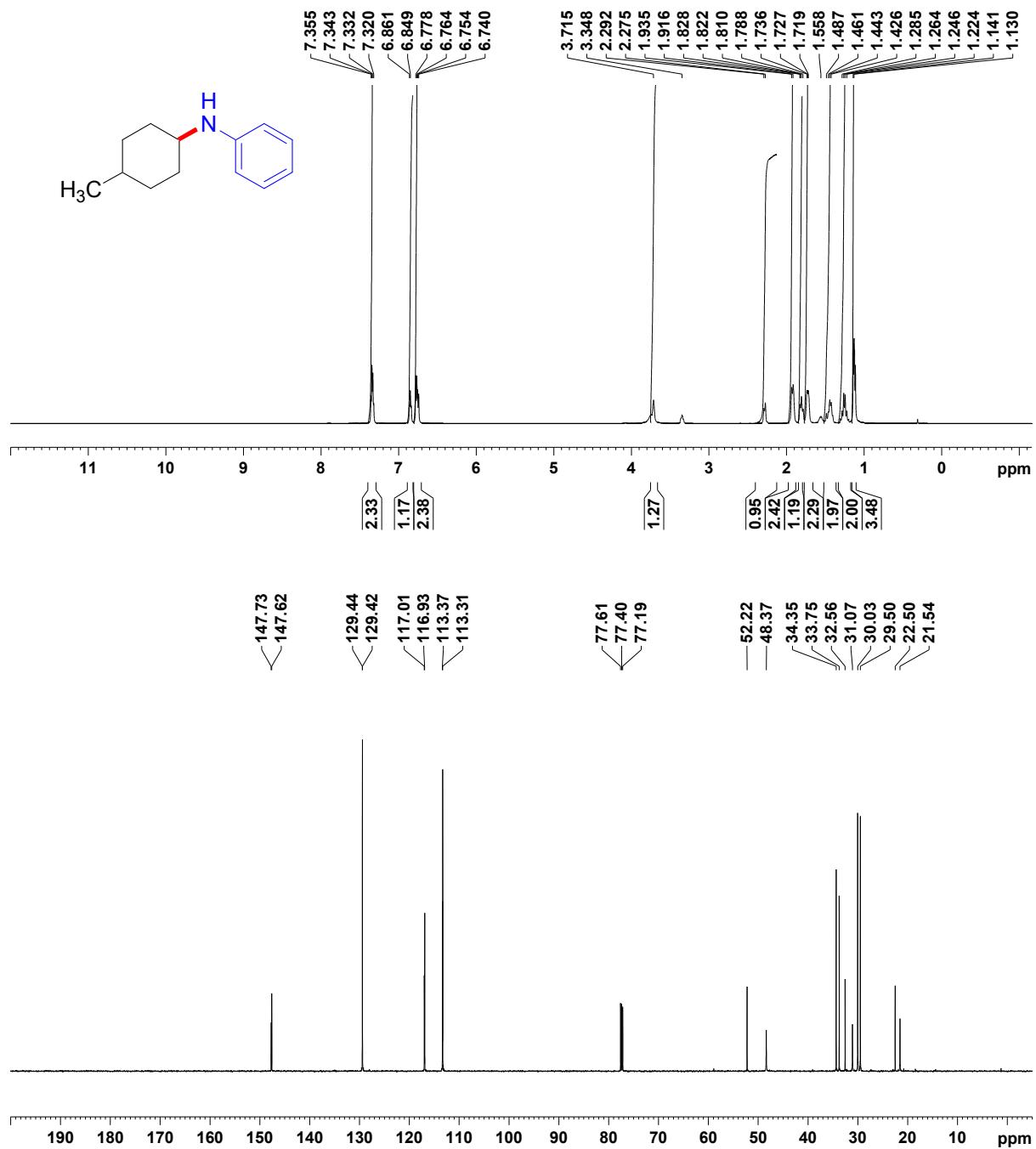
**1-(1,3-Benzodioxol-5-yl)-N-phenylbutan-3-amine (3t):**



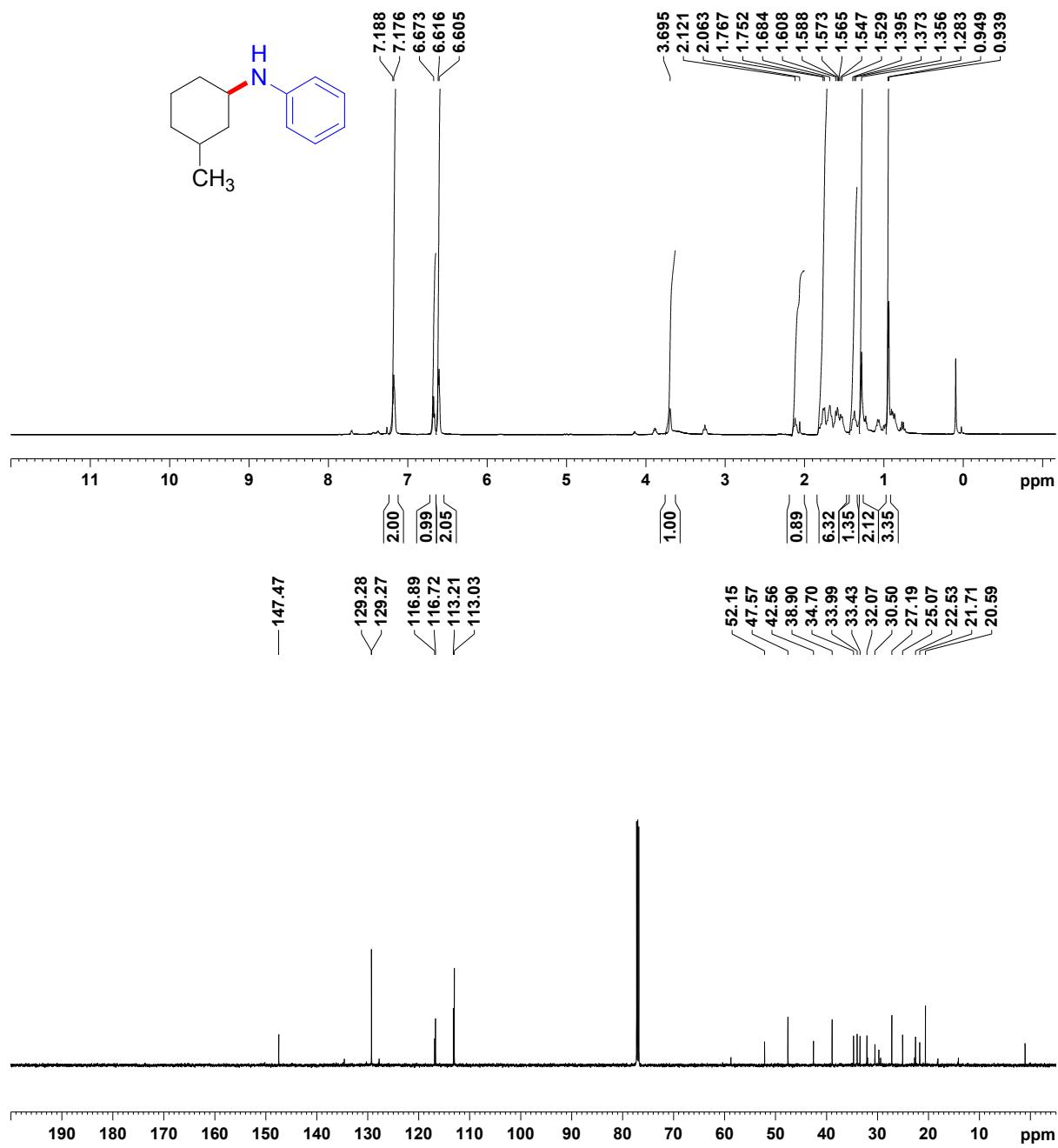
**N-Phenylcyclohexylamine (3u):**



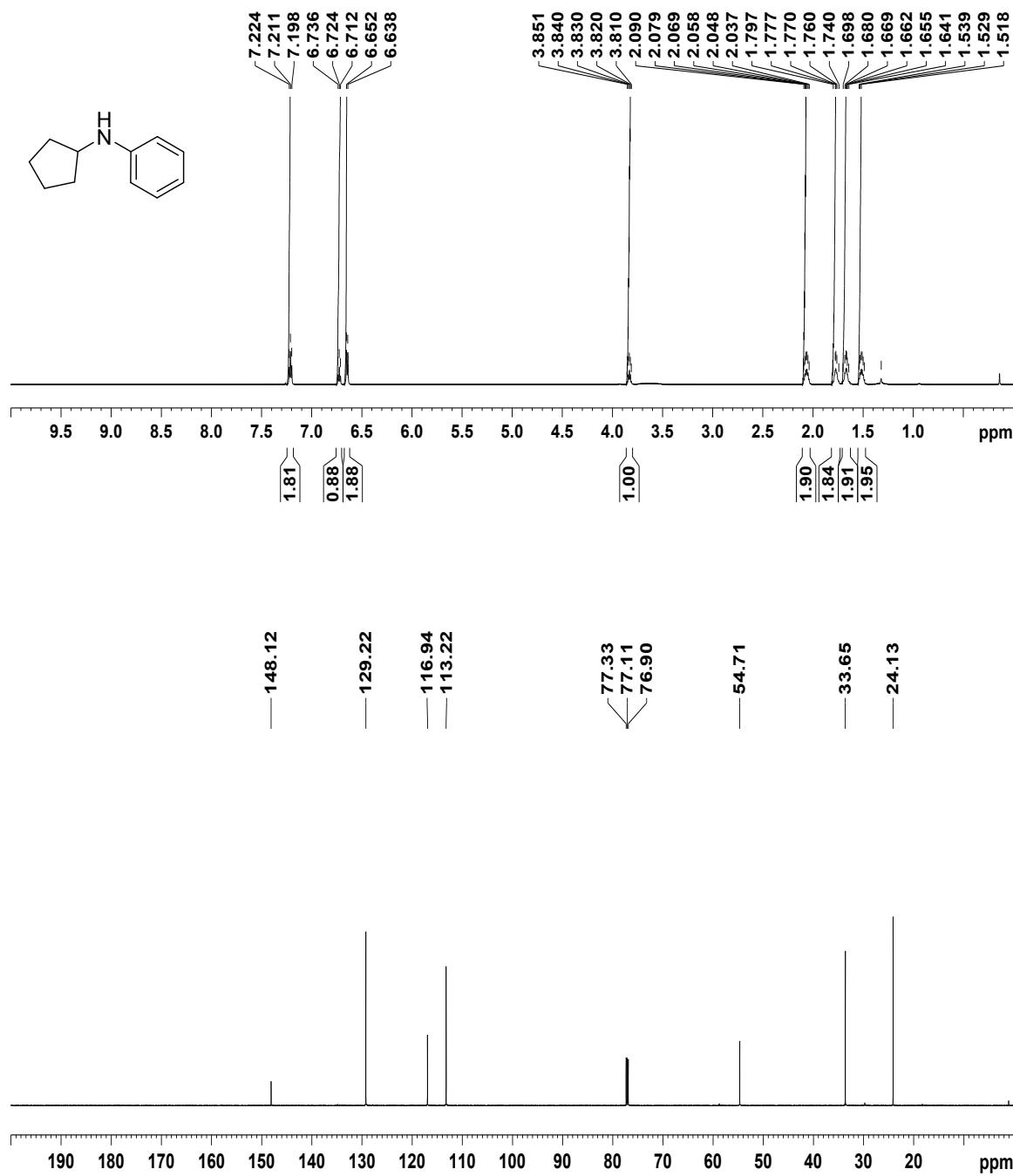
*N*-(4-Methylcyclohexyl)aniline (**3v**):



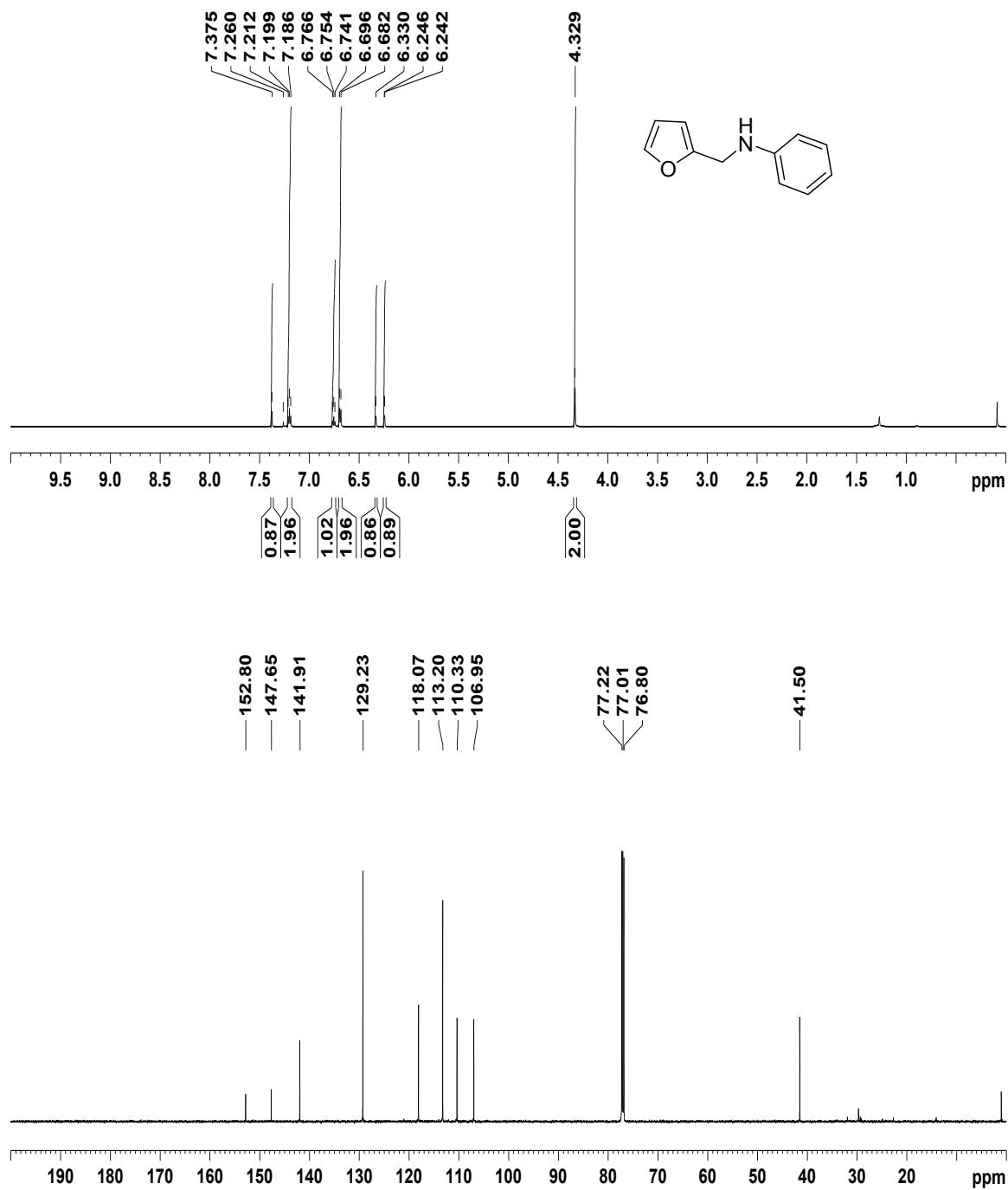
***N*-(3-Methylcyclohexyl)aniline (**3w**):**



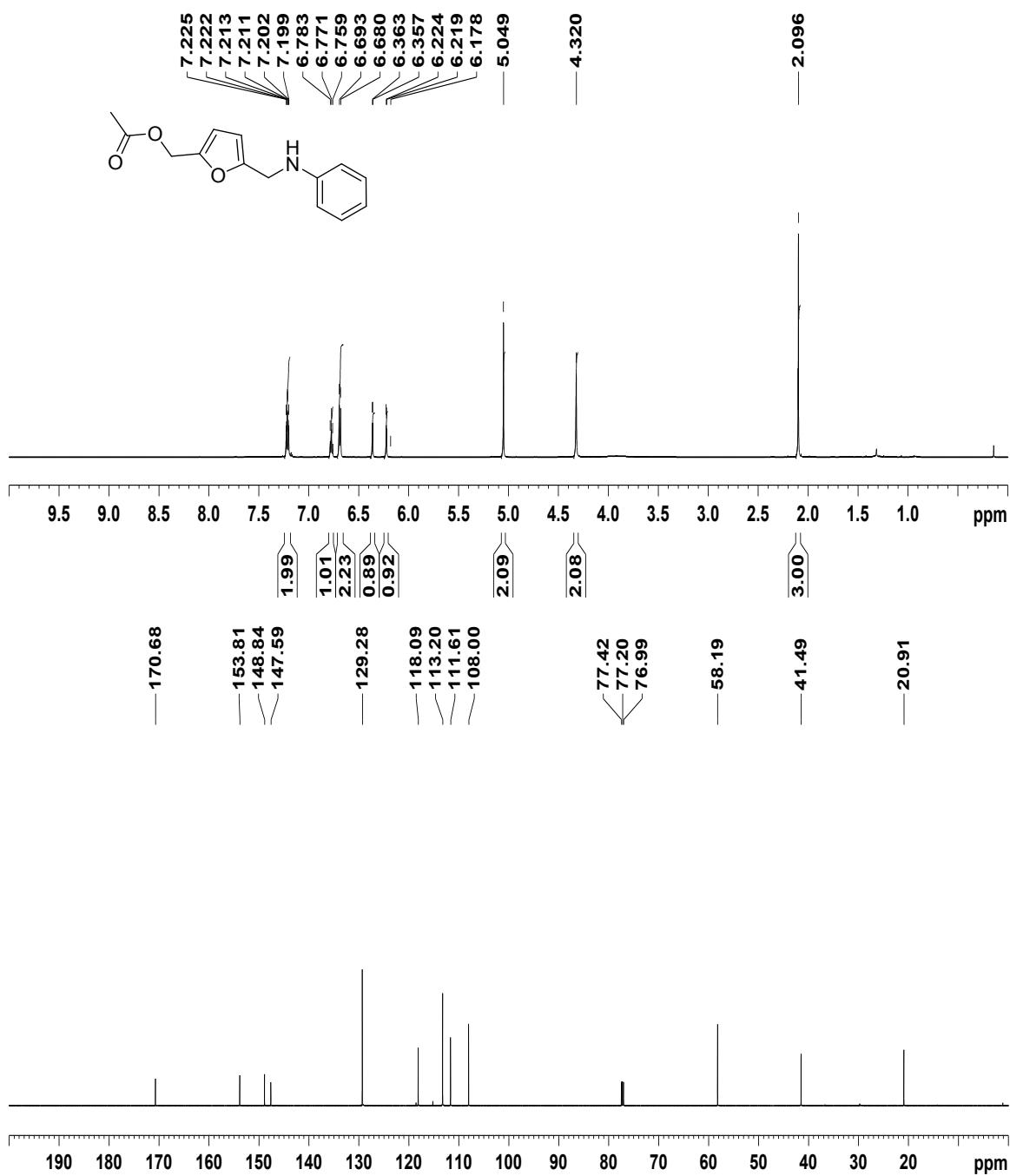
**N-Phenylcyclopentylamine (3x):**



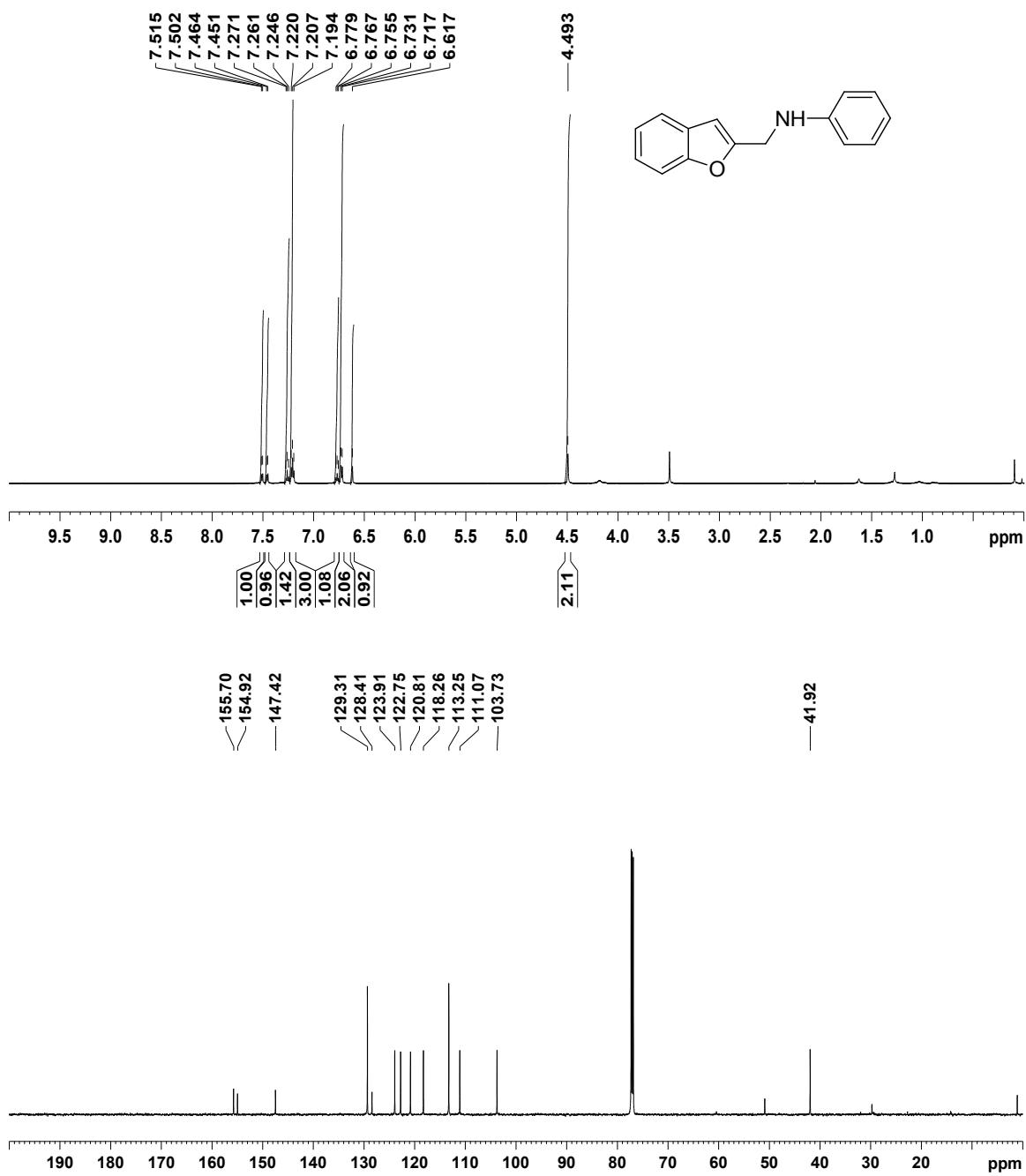
*N*-Furfurylaniline (6a):



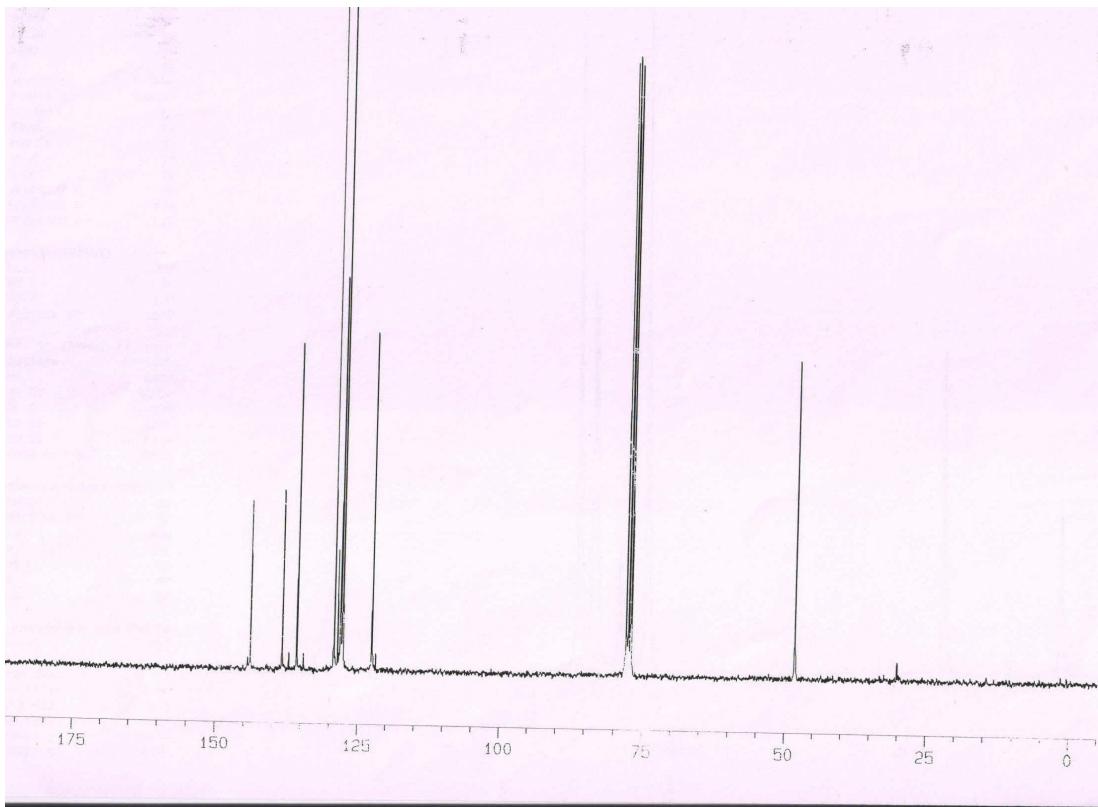
***N*-(5-acetoxymethyl-2-furyl)aniline (6b):**



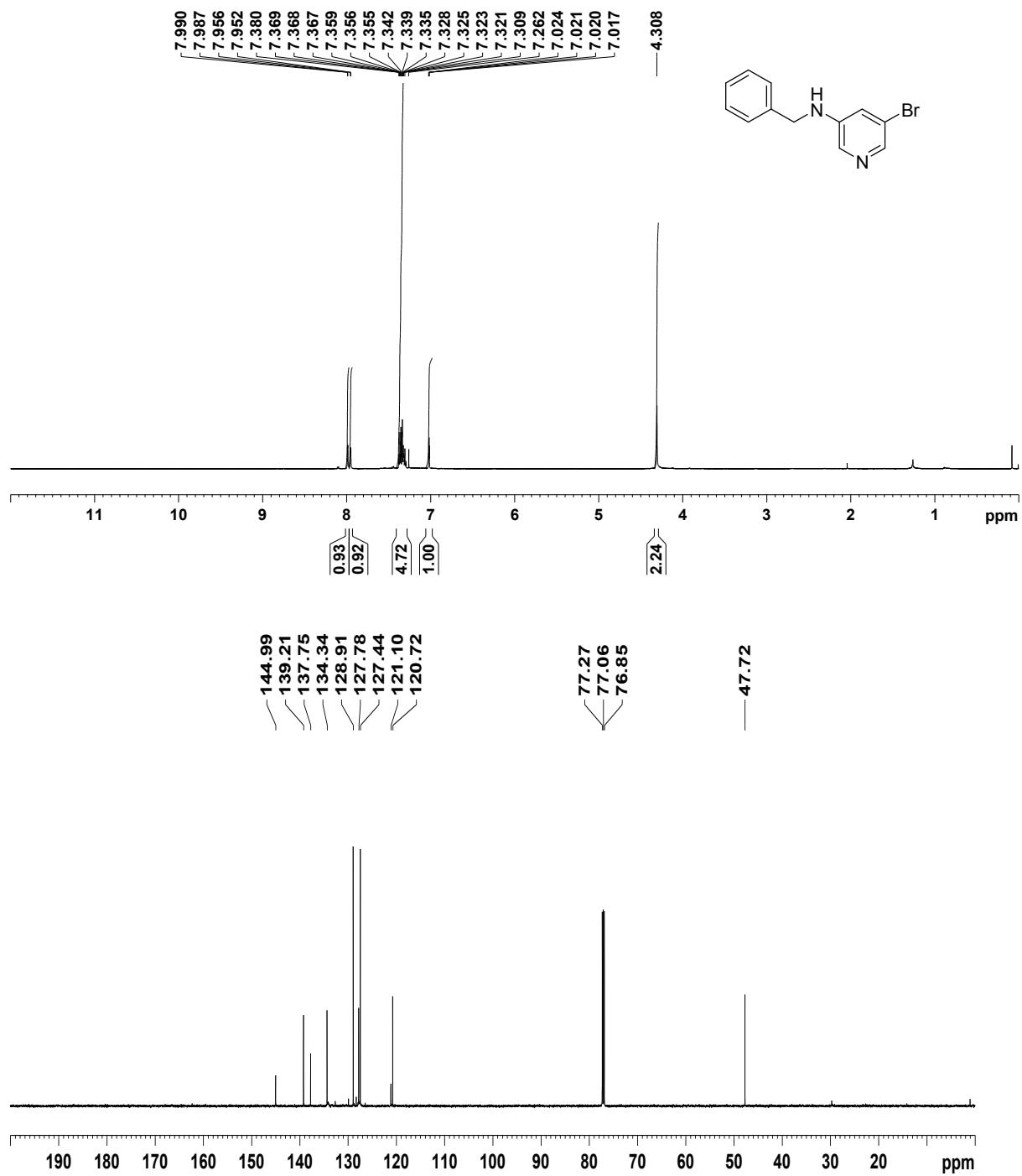
*N*-(benzofuranyl-2-methyl)phenylaniline (**6c**):



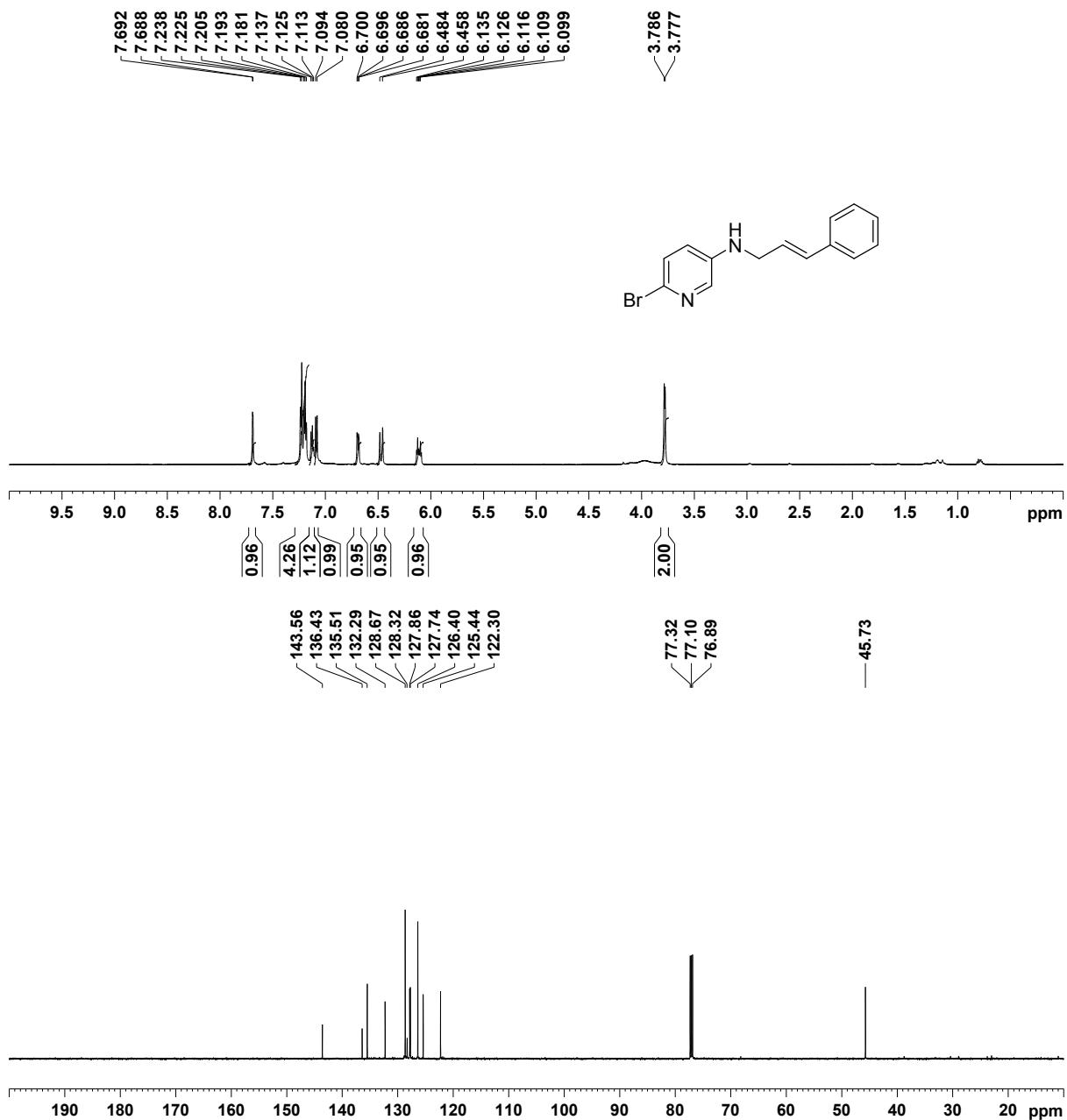
**N-Benzyl-(6-bromopyridin-3-yl)amine (6d):**



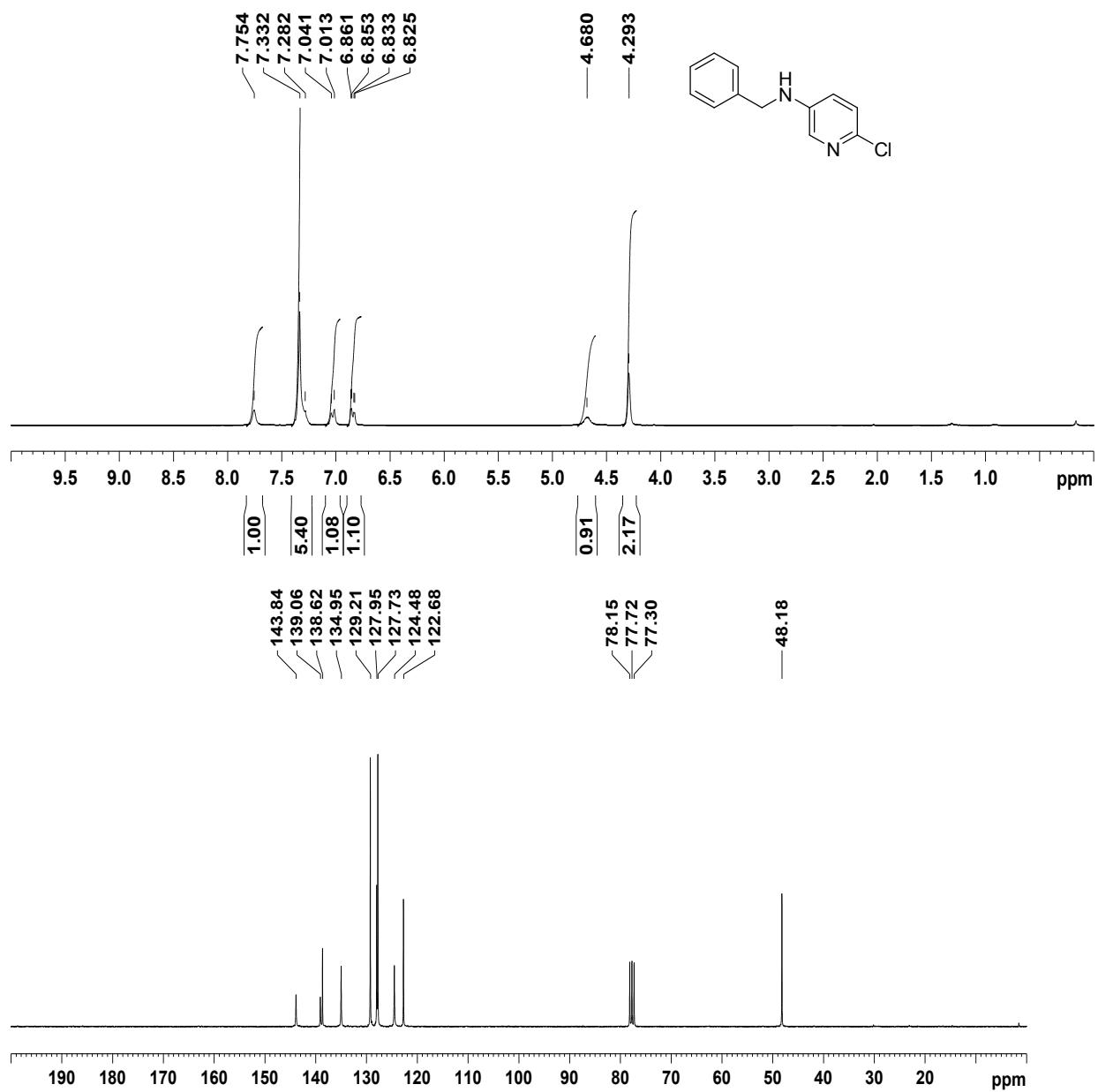
**N–benzyl–(5– bromopyridin-3-yl)amine (6e):**



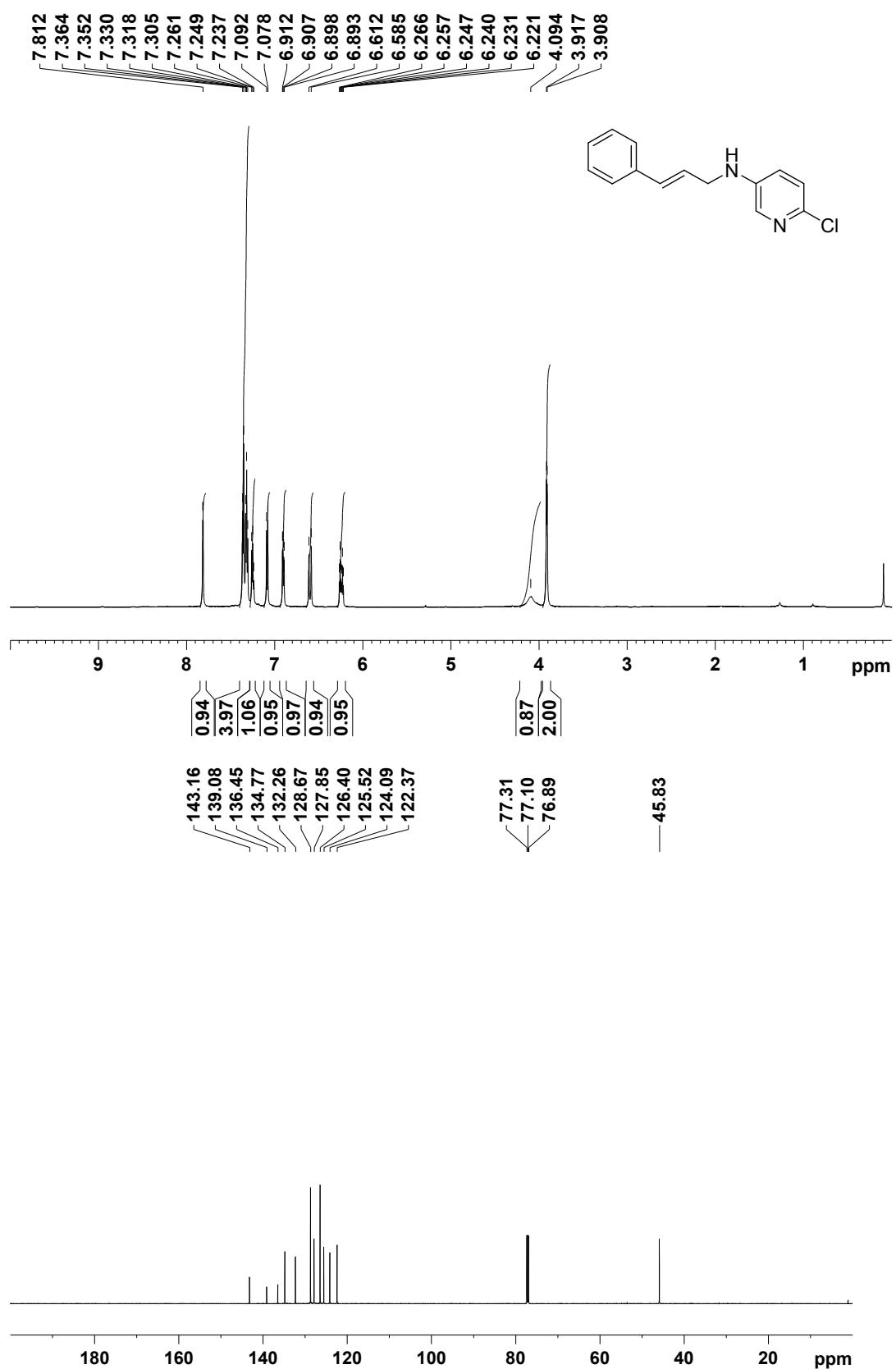
*N*-Cinnamyl-(6-brobopyridin-3-yl)amine (**6f**):



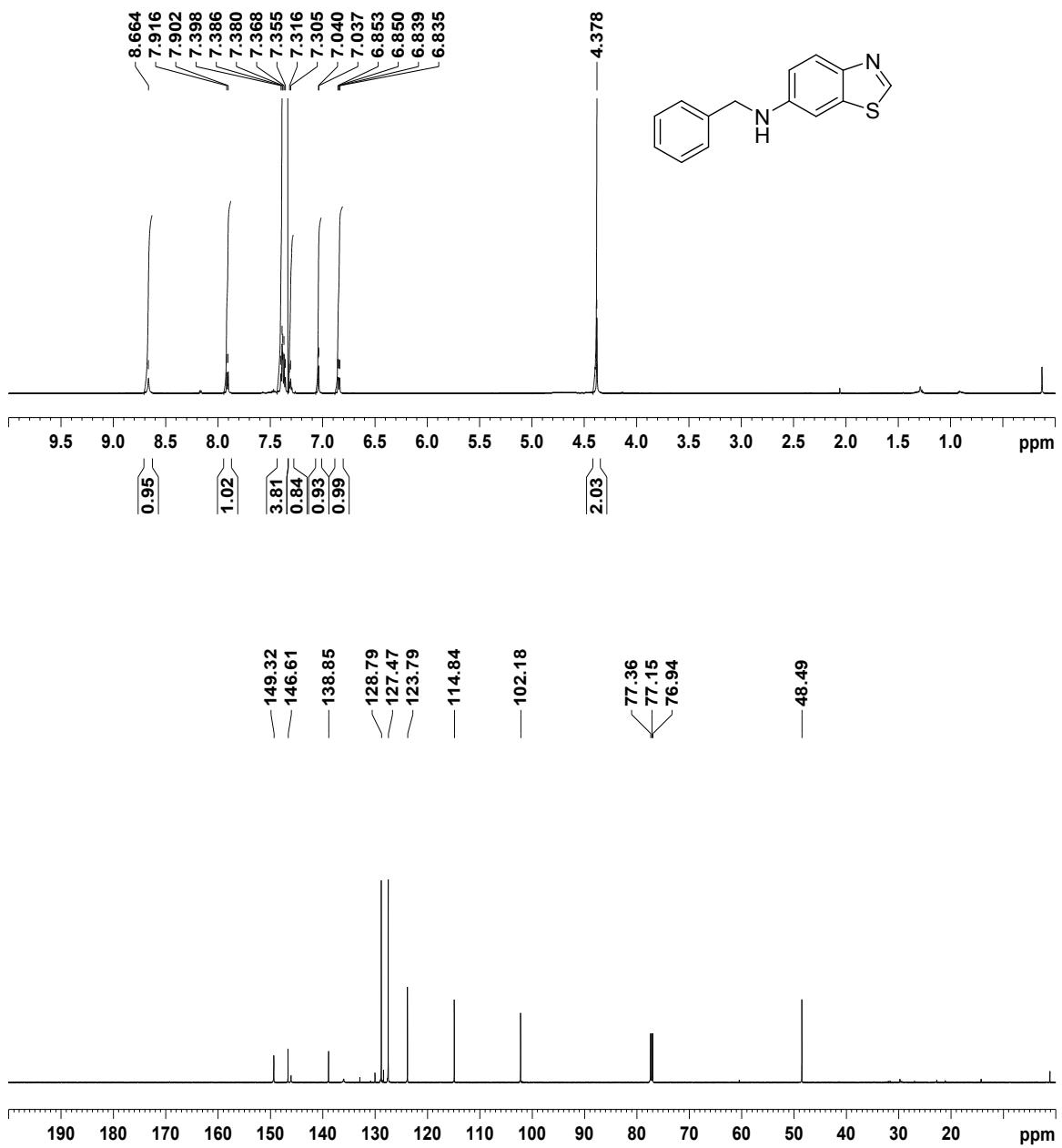
*N*-benzyl-(6-chloropyridin-3-yl)amine (6g):



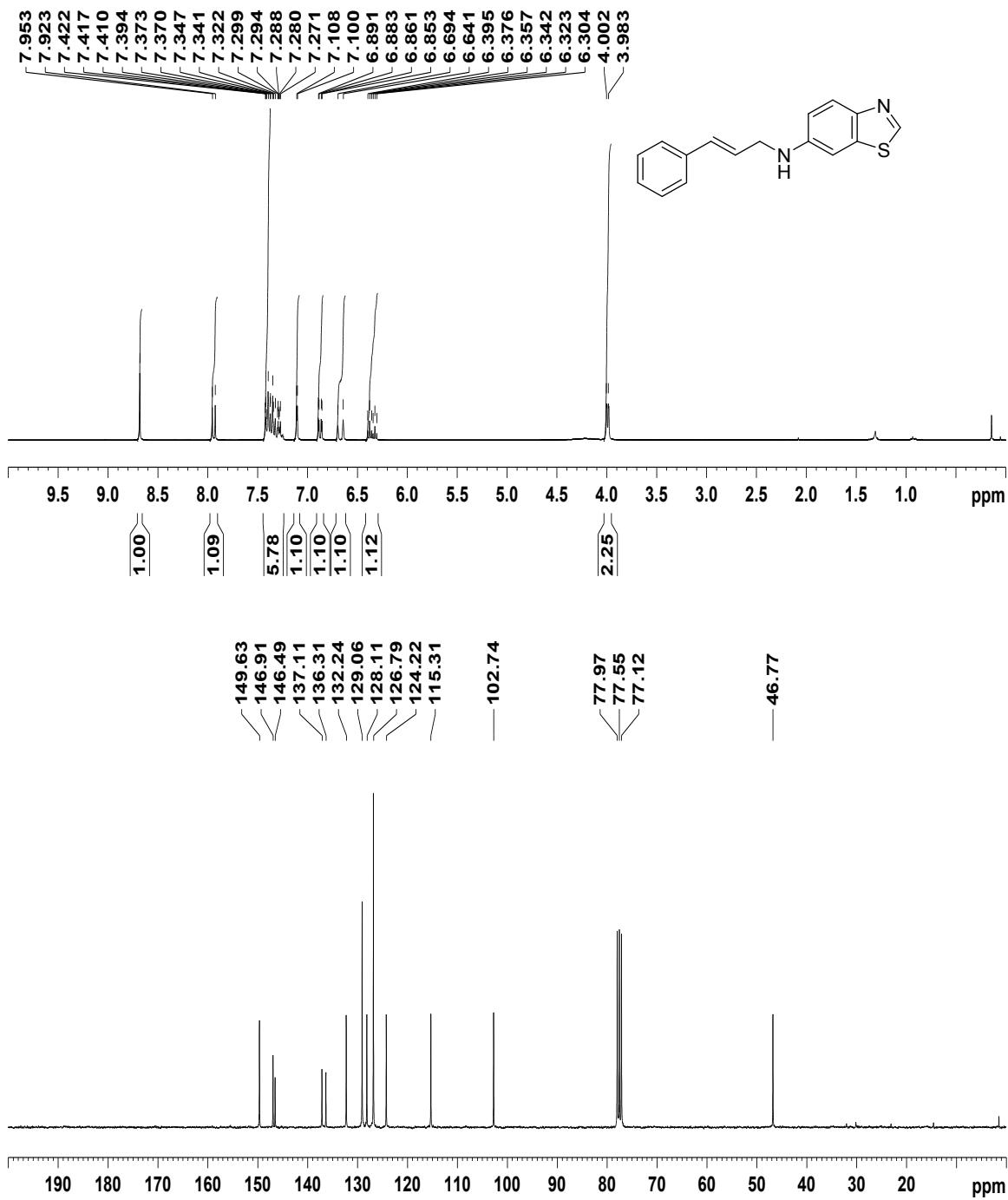
**N-Cinnamyl-(6-chloropyridin-3-yl)amine (6h):**



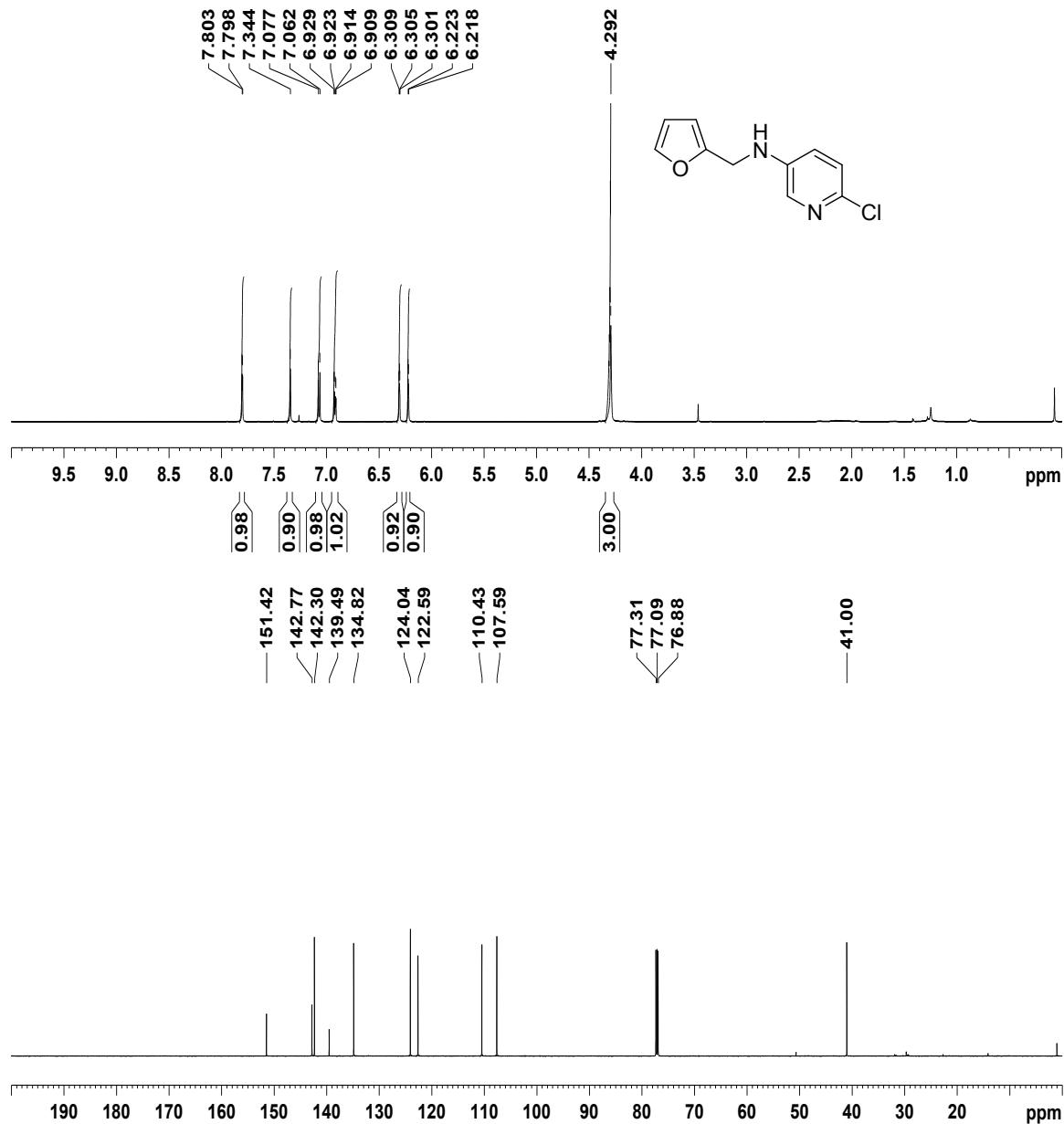
**6-(*N*-Benzylamino)benzothiazole (6i)**



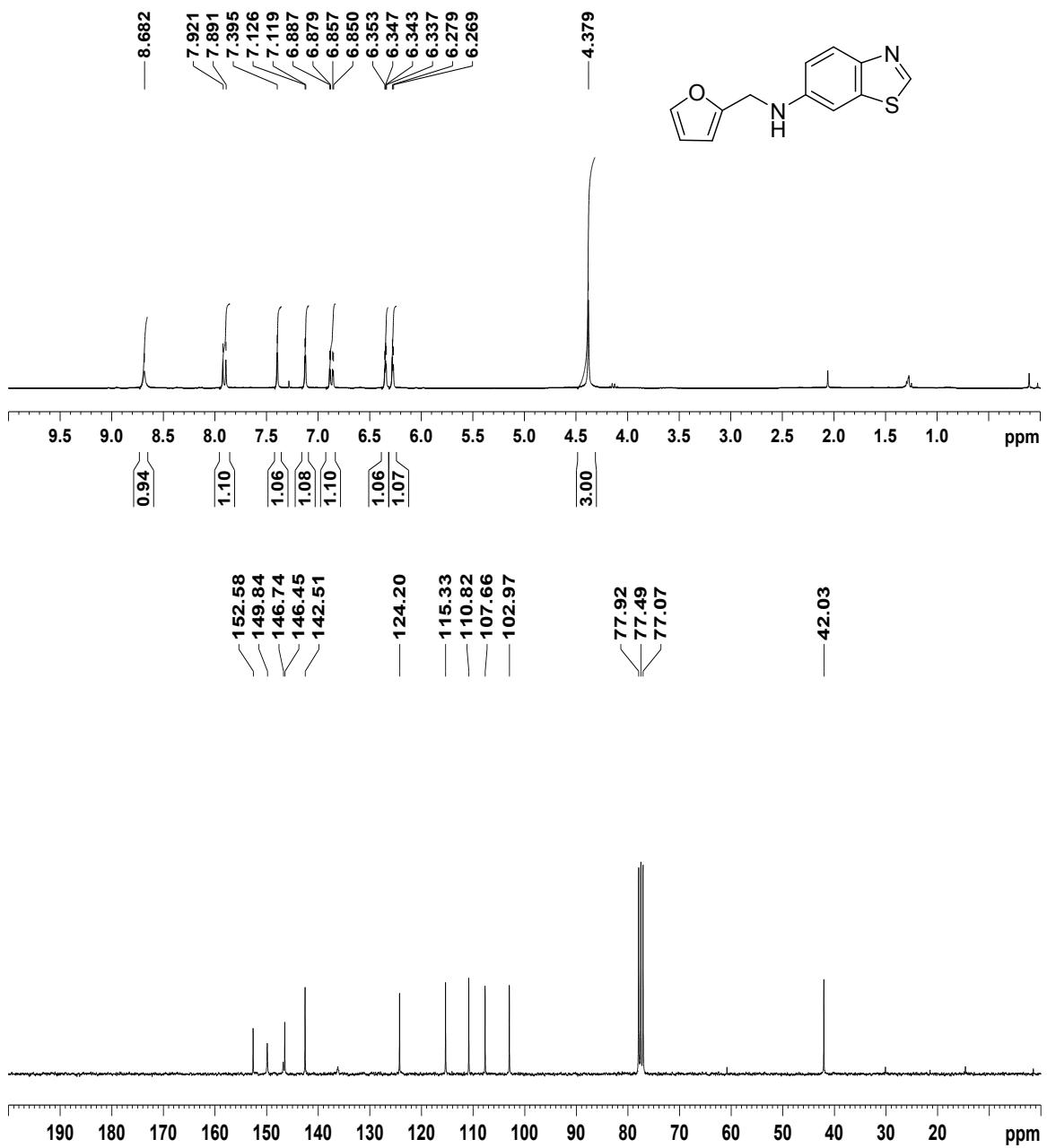
**6-(*N*-cinnamylamino)benzothiazole (6j):**



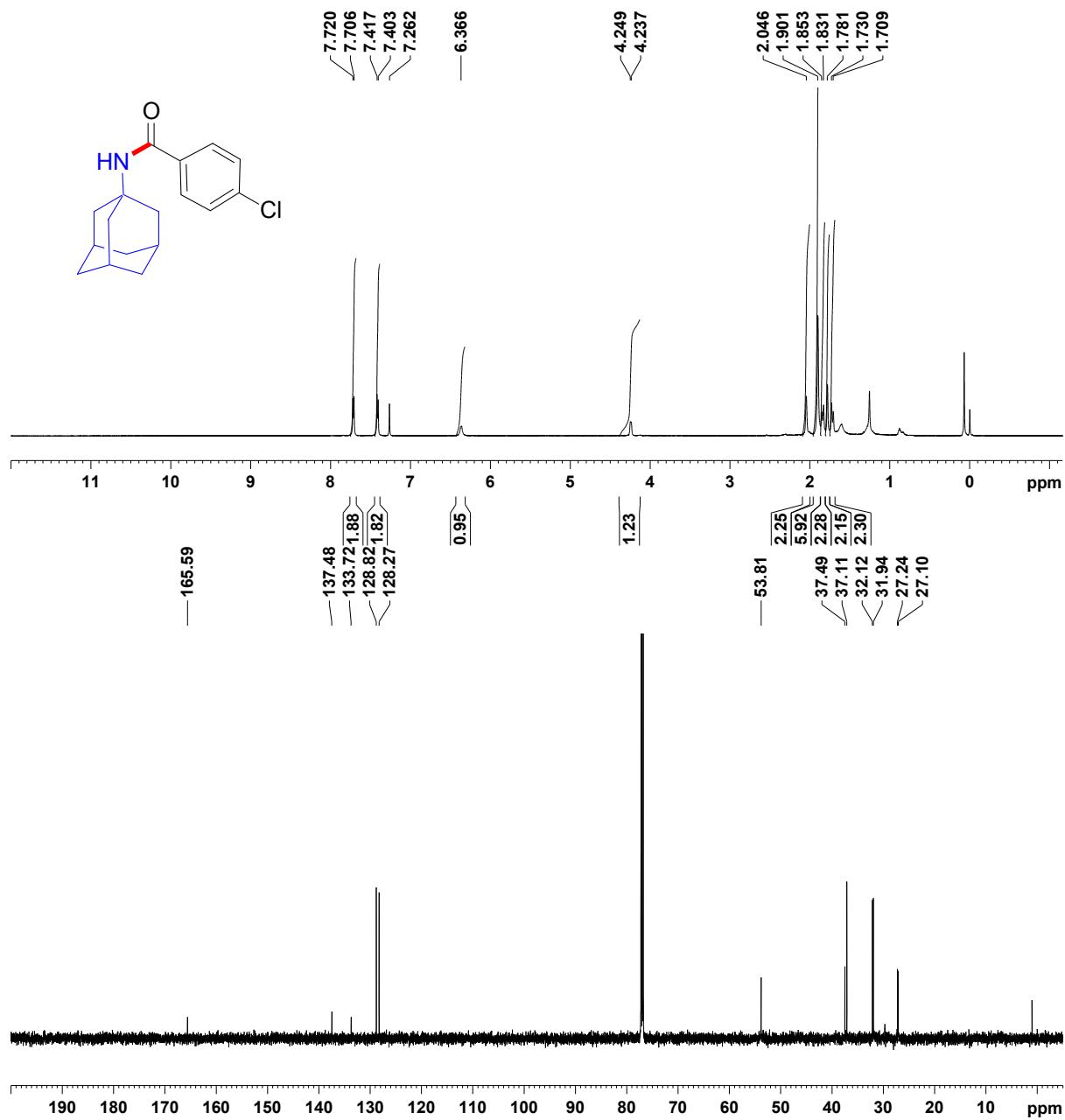
*N*-(Furfuryl-5-amino-2-chloro)pyridine (6k):



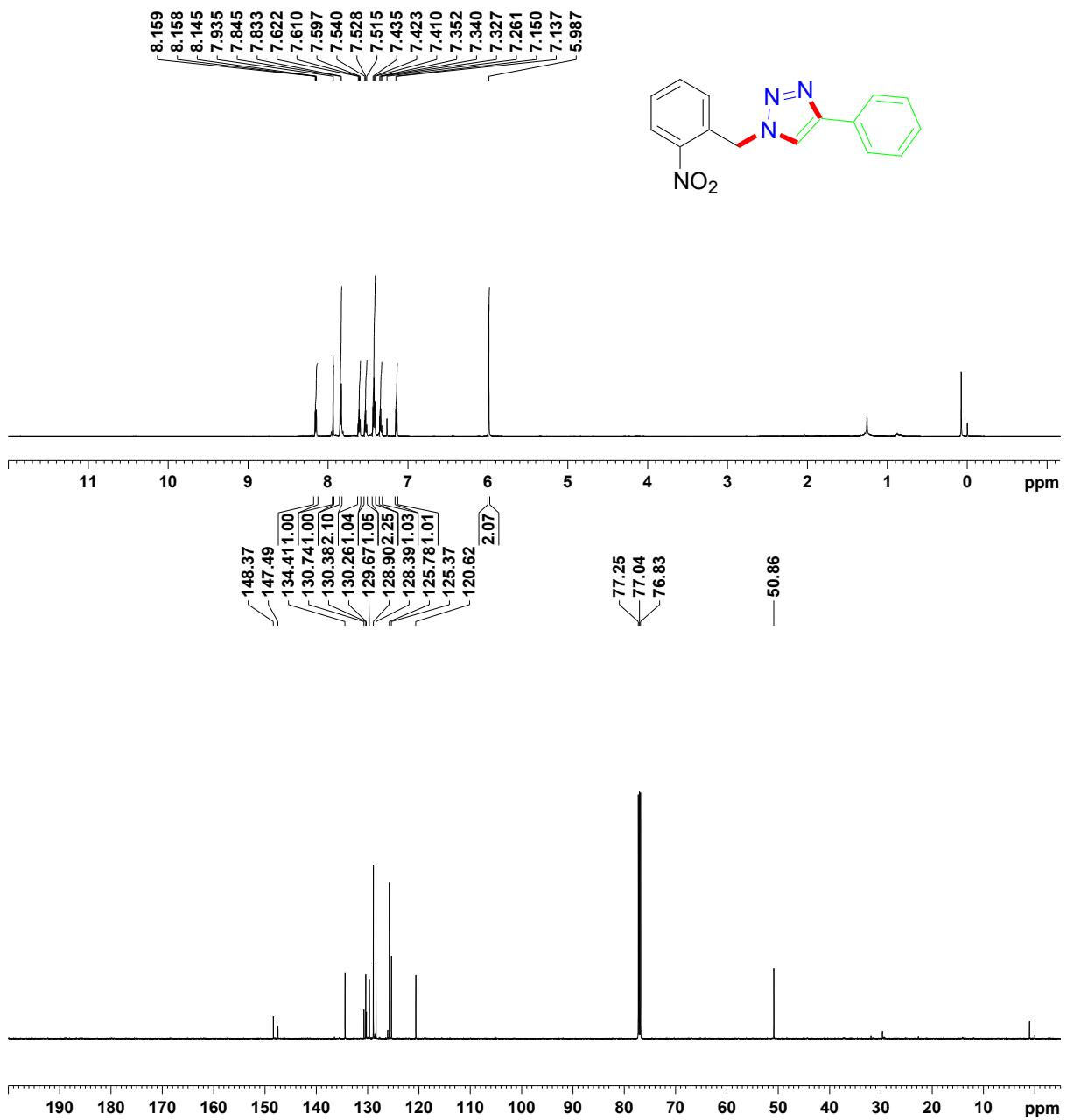
**6-(*N*-Furfurylamino)benzothiazole (**6l**):**



*N*-(1-adamantile)-4-chlorobenzamide (7a)



**1-(2-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (7b)**



## 8. FTIR Spectra of Unknown compound

6-(*N*-furfurylamino)benzothiazol (4m):

