

## **Efficient Synthesis of Alkyl Aryl Ketones & ketals via Palladium-catalyzed Regioselective Arylation of Vinyl Ethers**

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## 1. General Information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Model Avance DMX 300 Spectrometer ( $^1\text{H}$  300 MHz and  $^{13}\text{C}$  75 MHz respectively) and a Bruker Model Avance DMX 400 Spectrometer ( $^1\text{H}$  400 MHz and  $^{13}\text{C}$  106.6 MHz, respectively). Chemical shifts ( $\delta$ ) are given in ppm and are referenced to residual solvent peaks. All organic solvents were used as received. 1-Ethoxy-2-methylpropene was prepared according to the literature report.<sup>1</sup> All other chemicals were used as received from Aldrich or Acros without further purification.

## 2. General procedure for the Heck arylation of vinyl ethers

A stock solution of 0.1 mol% (1 mmol, 2.2 mg) palladium acetate together with 0.2 mol% dppp (2 mmol, 8.2 mg) was prepared in 10 mL degassed ethylene glycol, which was used as the mother solution to which subsequent dilutions were made. To ensure the mixture was homogeneous, the solution was left stirring under nitrogen at 60 °C for 12 h. The solution turned deep orange, with no sign of residue indicating that the Pd/dppp was dissolved homogeneously. To make a  $1 \times 10^{-2}$  mol% stock solution, 1 mL was taken from this mother solution and added (under nitrogen) to 9 mL of degassed ethylene glycol. This procedure was followed to make more dilution solutions when necessary.

An oven-dried, two necked round-bottom flask containing a stirrer bar was charged with an aryl halide (1.0 mmol), Pd-dppp stock solution (2.0 mL) under nitrogen atmosphere at room temperature. After degassing three times,  $\text{NEt}_3$  (2.0 mmol) was injected. The vinyl ether (2.0 mmol) was added after 2-4 minutes of pre-mixing at 145 °C in an oil bath. After an appropriate reaction time, the flask was removed from the oil bath and cooled to room temperature. For products requiring acid hydrolysis, aqueous HCl (5%, 5 mL) was added and following stirring for 0.5-3 h,  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was added. After separation of the  $\text{CH}_2\text{Cl}_2$  phase, the aqueous layer was

extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL), and the combined organic layer was washed with water until neutrality, dried ( $\text{Na}_2\text{SO}_4$ ), filtered and concentrated in vacuo. The product was purified via flash chromatography on silica gel using a mixture of ethyl acetate and hexane.

**2-Acetonaphthonone (3a).**<sup>2</sup>  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (s, 1H), 8.03 (dd,  $J = 8.58, 1.75$  Hz, 1H), 7.95 (d,  $J = 8.58$  Hz, 1H), 7.88 (dd,  $J = 6.20, 5.56$  Hz, 2H), 7.60-7.55 (m, 2H), 2.71(s, 3H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.5, 136.0, 134.9, 132.9, 130.6, 129.9, 128.9, 128.8, 128.2, 127.2, 124.3, 27.1; IR (neat,  $\text{cm}^{-1}$ ): 1676; CI-MS  $m/z$  188  $[(\text{M} + \text{NH}_4)^+, 100]$ , 171 (90); HRMS calcd for  $\text{C}_{12}\text{H}_{10}\text{O}$ : 170.0732; Found 170.0731.

**1-Acetyl-3,4,5-trimethoxybenzene (3b).**<sup>3</sup>  $^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.54 (s, 3H), 3.87-3.88 (m, 9H), 7.17 (s, 2H);  $^{13}\text{C}$  NMR(100 MHz,  $\text{CDCl}_3$ ): 26.4, 56.2, 60.9, 105.7, 132.4, 142.5, 153.0, 196.8; IR (neat,  $\text{cm}^{-1}$ ): 1680; EI-MS  $m/z$  210 ( $\text{M}^+, 90$ ), 195 (100); HRMS calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_4$ : 210.0892; Found 210.0889.

**1,4-Diacetylbenzene (3c).**<sup>4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (s, 4H), 2.65 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 140.6, 128.9, 27.2; IR (neat,  $\text{cm}^{-1}$ ): 1676; CI-MS  $m/z$  180  $[(\text{M} + \text{NH}_4)^+, 100]$ ; HRMS calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_2$ : 162.0681; Found: 162.0684.

**Acetophenone (3d).**<sup>2,4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97-7.94 (m, 2H), 7.58-7.54 (m, 1 H), 7.48-7.44 (m, 2H), 2.60 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.5, 137.6, 133.5, 129.0, 128.7, 26.9; IR (neat,  $\text{cm}^{-1}$ ): 1684; CI-MS  $m/z$  121  $[(\text{M} + \text{H})^+, 100]$ , 105 (86); HRMS calcd for  $\text{C}_8\text{H}_8\text{O}$ : 120.0575; Found: 120.0576.

**1-Acetonaphthonone (3e).**<sup>2,4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.78 (d,  $J = 8.75$  Hz, 1H), 7.92 (dt,  $J = 7.84$ , 1.60 Hz, 3H), 7.61 (dt,  $J = 7.84$ , 1.43 Hz, 1H), 7.53 (m, 2H), 2.73 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  202.2, 135.8, 134.4, 133.4, 130.5, 129.1, 128.8, 128.5, 126.8, 126.4, 124.7, 30.4; IR (neat,  $\text{cm}^{-1}$ ): 1674; CI-MS  $m/z$  188 [(M + NH<sub>4</sub>)<sup>+</sup>, 88], 171 (100). HRMS calcd for C<sub>12</sub>H<sub>10</sub>O: 170.0732; Found 170.0728.

**4-Fluoroacetophenone (3f).**<sup>2,4a-c</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.96 (m, 2H), 7.15-7.11 (m, 2H), 2.58 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.8, 166.2 (d,  $J_{\text{CF}} = 254$  Hz), 133.9 (d,  $J_{\text{CF}} = 2$  Hz), 131.3 (d,  $J_{\text{CF}} = 9$  Hz), 116.0 (d,  $J_{\text{CF}} = 22$  Hz), 26.8; IR (neat,  $\text{cm}^{-1}$ ): 1681; CI-MS  $m/z$  156 [(M + NH<sub>4</sub>)<sup>+</sup>, 100]; HRMS calcd for C<sub>8</sub>H<sub>7</sub>FO: 138.0481; Found: 138.0480.

**Methyl-4-acetylbenzoate (3g).**<sup>2a,4a</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J = 6.8$  Hz, 2H), 8.01 (d,  $J = 6.8$  Hz, 2H), 3.96 (s, 3H), 2.65 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.9, 166.6, 140.6, 134.2, 130.2, 128.6, 52.8, 27.3; IR (neat,  $\text{cm}^{-1}$ ): 1678, 1722; CI-MS  $m/z$  178 (M<sup>+</sup>, 100); HRMS calcd for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>: 178.0630; Found 178.0626.

**2-Acetyl-6-methoxynaphthalene (3h).**<sup>5</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.41 (s, 1H), 8.02 (dd,  $J = 6.8$ , 2.0 Hz, 1H), 7.86 (d,  $J = 8.8$  Hz, 1H), 7.78 (d,  $J = 8.8$  Hz, 1H), 7.17-7.24 (m, 2H), 3.97 (s, 3H), 2.72 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.8, 159.8, 137.3, 132.6, 131.1, 130.1, 127.8, 127.1, 124.7, 119.7, 55.4, 26.6; IR (neat,  $\text{cm}^{-1}$ ): 1674; Cl-MS  $m/z$  201 [(M + H)<sup>+</sup> 100]; HRMS calcd for C<sub>13</sub>H<sub>12</sub>O<sub>2</sub>: 200.0837; Found: 224.0841.

**4-Methylacetophenone (3i).**<sup>2,4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (d,  $J = 8$  Hz, 2H),

7.25 (d,  $J = 8$  Hz, 2H), 2.57 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.2, 144.2, 135.2, 129.6, 128.8, 26.9, 22.0; IR (neat,  $\text{cm}^{-1}$ ): 1680; CI-MS  $m/z$  135 [ $(\text{M}+\text{H})^+$ , 100], 119 (21); HRMS calcd for  $\text{C}_9\text{H}_{10}\text{O}$ : 134.0732; Found: 134.0735.

**4-Methoxyacetophenone (3j).**<sup>2,4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.93 (d,  $J = 8.8$  Hz, 2H), 6.92 (d,  $J = 8.8$  Hz, 2H), 3.86 (s, 3H), 2.54 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.1, 163.9, 131.0, 130.8, 114.1, 55.8, 26.7; IR (neat,  $\text{cm}^{-1}$ ): 1666; CI-MS  $m/z$  151 [ $(\text{M}+\text{H})^+$ , 100], 135 (20); HRMS calcd for  $\text{C}_9\text{H}_{11}\text{O}_2$  ( $\text{M} + \text{H}$ ) $^+$ : 151.0759; Found: 151.0759.

**3-Acetylbenzophenone (3k).**<sup>6</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.38 (s, 1H), 8.20 (d,  $J = 7.8$  Hz, 1H), 8.00 (d,  $J = 7.6$  Hz, 1H), 7.81 (d,  $J = 7.2$  Hz, 2H), 7.64 (dd,  $J = 16.9, 8.4$  Hz, 2H), 7.50-7.54 (m, 2H), 2.67 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.1, 195.6, 138.0, 137.2, 137.0, 134.1, 132.8, 131.7, 129.9, 129.5, 128.7, 128.5, 26.6; IR (neat,  $\text{cm}^{-1}$ ): 1686; EI-MS  $m/z$  224 ( $\text{M}^+$ , 60), 209 (80), 105 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_2$ : 224.0837; Found: 224.0839.

**3-Methylacetophenone (3l).**<sup>2,4a-b</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78-7.75 (m, 2H), 7.38-7.31 (m, 2H), 2.59 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.7, 138.8, 137.7, 134.2, 129.2, 128.8, 126.0, 27.0, 21.7; IR (neat,  $\text{cm}^{-1}$ ): 1684; CI-MS  $m/z$  135 [ $(\text{M}+\text{H})^+$ , 100], 119 (26); HRMS calcd for  $\text{C}_9\text{H}_{10}\text{O}$ : 134.0732; Found: 134.0734.

**3-Methoxyacetophenone (3m).**<sup>2a-b,4a-c</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51–7.44 (m, 2H), 7.36–7.30 (m, 1H), 7.09–7.06 (m, 1H), 3.81 (s, 3H), 2.56 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.2, 160.3, 139.4, 129.9, 121.5, 120.0, 112.8, 55.8, 27.0; IR (neat,

$\text{cm}^{-1}$ ): 1688; CI-MS  $m/z$  150 ( $\text{M}^+$ , 100), 135 (48); HRMS calcd for  $\text{C}_9\text{H}_{10}\text{O}_2$ : 150.0681; Found: 150.0682.

**2-Methoxyacetophenone (3n).**<sup>2a-b,4a-c</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74-7.72 (m, 1H), 7.48-7.43 (m, 1 H), 7.01-6.95 (m, 2H), 3.89 (s, 3H), 2.61 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.2, 159.3, 134.0, 130.7, 128.8, 121.0, 112.0, 55.9, 32.2; IR (neat,  $\text{cm}^{-1}$ ): 1670; CI-MS  $m/z$  168 [ $(\text{M} + \text{NH}_4)^+$ , 100]; HRMS calcd for  $\text{C}_9\text{H}_{10}\text{O}_2$ : 150.0681; Found: 150.0684.

**2-Fluoroacetophenone (3o).**<sup>2a-b,4a-c</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88-7.84 (m, 1H), 7.54-7.48 (m, 1H), 7.23-7.19 (m, 1 H), 7.16-7.10 (m, 1H), 2.63 (d,  $J = 5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 162.7 (d,  $J_{\text{CF}} = 253$  Hz), 135.0 (d,  $J_{\text{CF}} = 9$  Hz), 131.0 (d,  $J_{\text{CF}} = 3$  Hz), 126.1 (d,  $J_{\text{CF}} = 13$  Hz), 124.8 (d,  $J_{\text{CF}} = 4$  Hz), 117.1 (d,  $J_{\text{CF}} = 24$  Hz), 31.8 (d,  $J_{\text{CF}} = 8$  Hz); IR (neat,  $\text{cm}^{-1}$ ): 1686; CI-MS  $m/z$  156 [ $(\text{M} + \text{NH}_4)^+$ , 100]; HRMS calcd for  $\text{C}_8\text{H}_7\text{FO}$ : 138.0481; Found: 138.0483.

**1,3-Diacetylbenzene (3p).**<sup>4a</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.50-8.49 (m, 1H), 8.15-8.13 (m, 2H), 7.60-7.57 (m, 1H), 2.66 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 137.7, 132.9, 129.4, 128.3, 27.1; IR (neat,  $\text{cm}^{-1}$ ): 1688; CI-MS  $m/z$  180 [ $(\text{M} + \text{NH}_4)^+$ , 100]; HRMS calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}$  ( $\text{M} + \text{NH}_4$ ) $^+$ : 180.1045. Found: 180.1023.

**2-Methyl-2-(naphthalen-1-yl)-1,3-dioxolane (3eb).**<sup>2b,7</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.51 (d,  $J = 9.0$  Hz, 1H), 7.72-7.64 (m, 3H), 7.40-7.27 (m, 3H), 3.98-3.94 (m, 2H), 3.69-3.65 (m, 2 H), 1.78 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  137.4, 133.5, 129.3, 128.0, 127.6, 125.3, 124.7, 124.3, 123.8, 122.6, 108.6, 61.2, 26.5; IR (neat,  $\text{cm}^{-1}$ ): 1196; CI-MS  $m/z$  215 [ $(\text{M} + \text{H})^+$ , 100]; HRMS calcd for  $\text{C}_{14}\text{H}_{15}\text{O}_2$  [ $\text{M}+\text{H}]^+$ : 215.1072;

found: 213.1078.

**1-(4-(2-Methyl-1,3-dioxolan-2-yl)phenyl)ethanone (3cb).**<sup>2b,7</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.83 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 3.96–3.91 (m, 2 H), 3.67–3.63 (m, 2H), 2.48 (s, 3 H), 1.54 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.9, 148.9, 137.1, 128.7, 125.9, 108.8, 64.9, 27.7, 26.9; IR (neat, cm<sup>-1</sup>): 1682, 1198; CI-MS *m/z* 207 [(M + H)<sup>+</sup>, 100]; HRMS calcd for C<sub>12</sub>H<sub>15</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 207.1021; found: 207.1023.

**1-(Naphthalen-2-yl)propan-1-one (3ac).**<sup>2b,8</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.38 (s, 1H), 7.76–7.96 (m, 4H), 7.42–7.52 (m, 2H), 3.04 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.7, 134.6, 133.4, 131.6, 128.5, 128.4, 127.4, 127.3, 126.8, 125.7, 122.9, 30.8, 7.4; IR (neat, cm<sup>-1</sup>): 1683; CI-MS *m/z* 185 [(M + H)<sup>+</sup>, 100]; HRMS calcd for C<sub>13</sub>H<sub>12</sub>O: 184.0888; found: 184.0893.

**1-(3,4,5-Trimethoxyphenyl)propan-1-one (3bc).**<sup>9</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.22 (s, 2H), 3.91 (m, 9H), 2.97 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 199.2, 153.0, 142.5, 132.1, 105.6, 60.6, 56.1, 31.3, 8.2; IR (neat, cm<sup>-1</sup>): 1688; EI-MS *m/z* 224 (M<sup>+</sup>, 85), 195 (100); HRMS calcd for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>: 224.1049; found: 224.1051.

**Methyl 4-propionylbenzoate (3gc).**<sup>10</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.12 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 7.8 Hz, 2H), 3.96 (s, 3H), 3.03 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 200.2, 166.2, 140.1, 133.7, 129.8, 127.8, 52.4, 32.2, 8.0; IR (neat, cm<sup>-1</sup>): 1679, 1722; EI-MS *m/z* 192 (M<sup>+</sup>, 10), 163 (100);

HRMS calcd for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: 192.0786; found: 192.0786.

**1-p-Tolylpropan-1-one (3ic).**<sup>8b,11</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.80 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 6.8 Hz, 2H), 2.91 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 199.5, 142.5, 133.5, 128.2, 127.1, 30.6, 20.6, 7.3; IR (neat, cm<sup>-1</sup>): 1680; EI-MS *m/z* 149 [(M+H)<sup>+</sup>, 45], 119 (100); HRMS calcd for C<sub>10</sub>H<sub>12</sub>O: 148.0888; found: 148.0891.

**1-(4-Methoxyphenyl)propan-1-one (3jc).**<sup>4c,8b,11b</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.95 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H), 2.95 (q, J = 7.2 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 199.5, 163.3, 130.2, 130.1, 113.7, 55.4, 31.4, 8.4; IR (neat, cm<sup>-1</sup>): 1676; EI-MS *m/z* 165 [(M+1)<sup>+</sup>, 40], 135 (100); HRMS calcd for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>: 164.0837; Found: 164.0834.

**1-(3-Benzoylphenyl)propan-1-one (3kc).**<sup>12</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.18-8.19 (m, 1H), 7.99 (d, J = 1.2 Hz, 1H), 7.98 (d, J = 5.2 Hz, 1H), 7.97 (d, J = 1.2 Hz, 2H), 7.58-7.64 (m, 2H), 7.49-7.53 (m, 2H), 3.04 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 200.0, 195.9, 138.0, 137.1, 137.0, 134.0, 132.9, 131.5, 130.0, 129.4, 128.7, 128.5, 32.0, 8.1; IR (neat, cm<sup>-1</sup>): 1692; EI-MS *m/z* 238 (M<sup>+</sup>, 21), 209 (100); HRMS calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: 238.0994; Found: 238.0993.

**1-(3,4,5-Trimethoxyphenyl)butan-1-one (3bd).** <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.23 (s, 2H), 3.91-3.92 (m, 9H), 2.92 (t, J = 7.2 Hz, 2H), 1.74-1.81 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 199.1, 153.1, 142.6, 132.5, 105.7, 60.9, 56.3, 40.2, 17.9, 13.9; IR (neat, cm<sup>-1</sup>): 1688; EI-MS *m/z* 238 (M<sup>+</sup>, 45), 195 (100); HRMS

calcd for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: 238.1205; Found: 238.1209; Anal. Calcd for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: C, 65.53; H, 7.61; Found: C, 65.44; H, 7.69.

**1-Phenylbutan-1-one (3dd).**<sup>4c, 13</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98-7.95 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.44 (m, 2H), 2.95 (t, J = 7Hz, 2H), 1.80-1.75 (m, 2H), 1.01 (t, J = 7Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.9, 137.5, 133.3, 129.0, 128.5, 40.9, 18.2, 14.3; IR (neat, cm<sup>-1</sup>): 1685; CI-MS *m/z* 166 [(M + NH<sub>4</sub>)<sup>+</sup>, 100]; HRMS calcd for C<sub>10</sub>H<sub>12</sub>O: 148.0888; Found: 148.0886.

**1-(Naphthalen-2-yl)-2-phenylethanone (3ae).**<sup>14</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.46 (s, 1H), 7.97 (dd, J = 8.5, 1.8 Hz, 1H), 7.80-7.86 (m, 1H), 7.76-7.78 (m, 2H), 7.44-7.53 (m, 2H), 7.22-7.26 (m, 4H), 7.16-7.18 (m, 1H), 4.33 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.6, 135.6, 134.7, 134.0, 132.5, 130.4, 129.6, 129.5, 128.7, 128.6, 128.5, 127.8, 126.9, 126.8, 124.3, 45.6; IR (neat, cm<sup>-1</sup>): 1680; EI-MS *m/z* 246 (M<sup>+</sup>, 20), 155 (100); HRMS calcd for C<sub>18</sub>H<sub>14</sub>O: 246.1045; Found: 246.1047.

**2-Phenyl-1-(3,4,5-trimethoxyphenyl)ethanone (3be).**<sup>15</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.23-7.32 (m, 7H), 4.24 (s, 2H), 3.86-3.90 (m, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 196.4, 153.0, 142.6, 134.9, 131.7, 129.3, 128.8, 126.9, 106.2, 60.9, 56.2, 45.6; IR (neat, cm<sup>-1</sup>): 1687; EI-MS *m/z* 286 (M<sup>+</sup>, 40), 195 (100); HRMS calcd for C<sub>17</sub>H<sub>18</sub>O<sub>4</sub>: 286.1205; Found: 286.1209.

**1-(4-Acetylphenyl)-2-phenylethanone (3ce).**<sup>16</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.02-8.10 (m, 4H), 7.27-7.35 (m, 5H), 4.32 (s, 2H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.4, 197.1, 140.2, 139.7, 134.0, 129.4, 128.8, 128.5, 128.1, 127.1, 45.9,

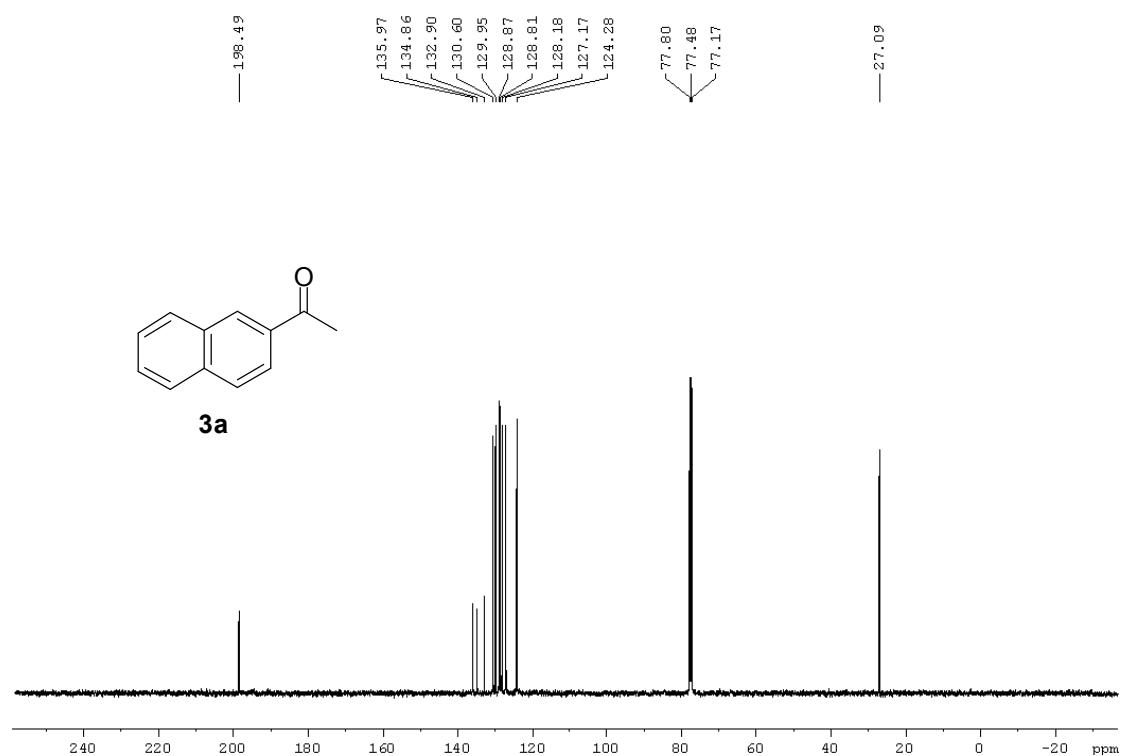
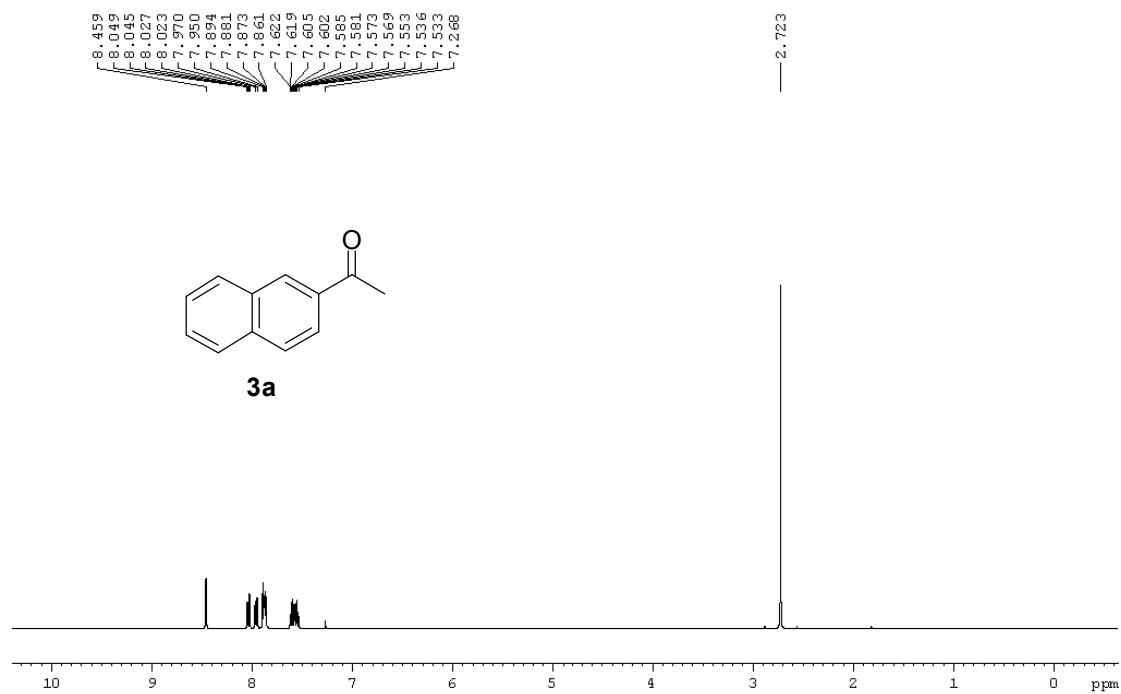
26.9; IR (neat,  $\text{cm}^{-1}$ ): 1682; EI-MS  $m/z$  238 ( $\text{M}^+$ , 15), 147 (100); HRMS calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_2$ : 238.0994; Found: 238.0999.

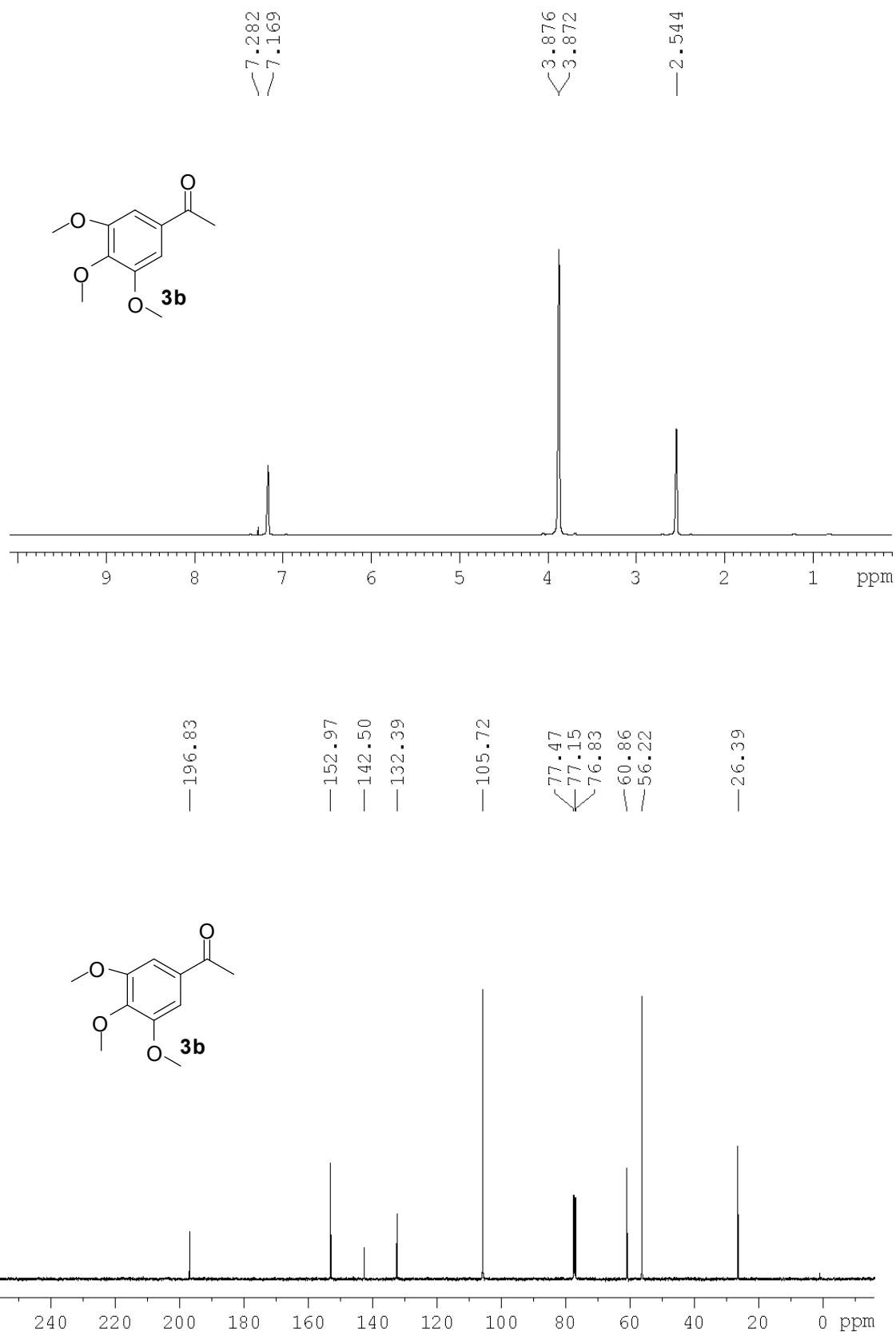
**1-(4-Methoxyphenyl)-2-phenylethanone (3je).**<sup>14,17</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.90 (dd,  $J = 8.5, 2.0$  Hz, 2H), 7.14-7.24 (m, 5H), 6.82 (dd,  $J = 8.5, 2.0$  Hz, 2H), 4.13 (s, 2H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ ):  $\delta$  195.2, 162.5, 134.0, 129.9, 128.6, 128.4, 127.6, 125.7, 112.8, 54.4, 44.2; IR (neat,  $\text{cm}^{-1}$ ): 1672; EI-MS  $m/z$  226 ( $\text{M}^+$ , 10), 135 (100); HRMS calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2$ : 226.0994; Found: 226.0995.

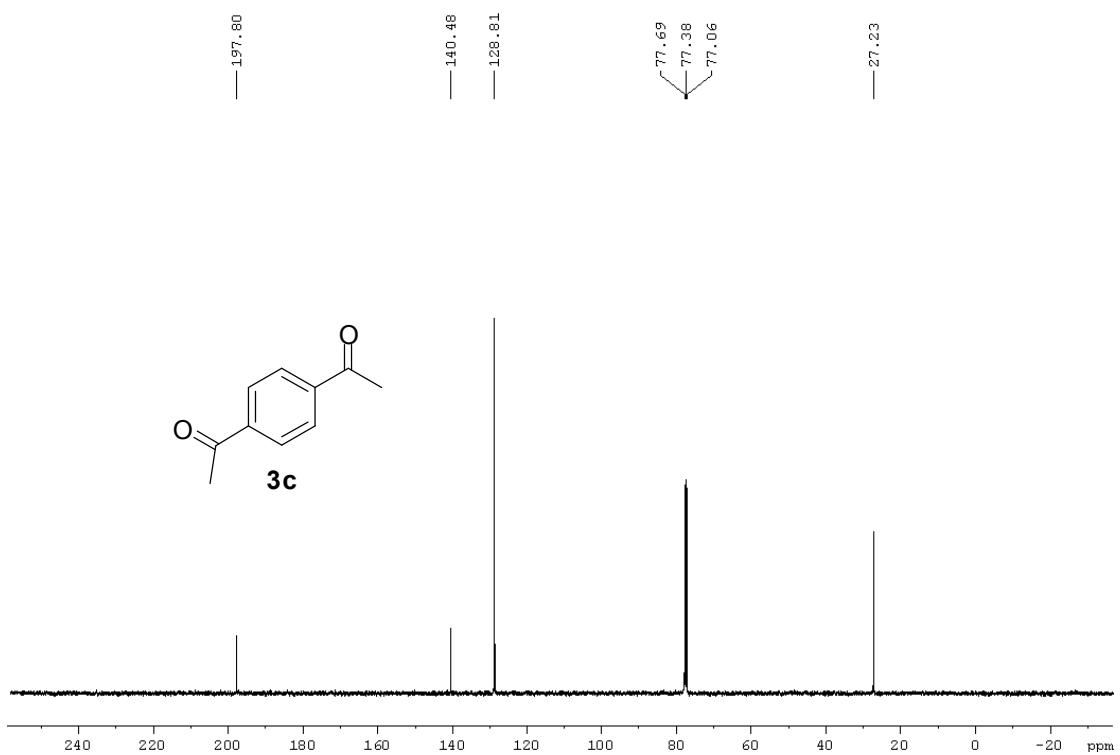
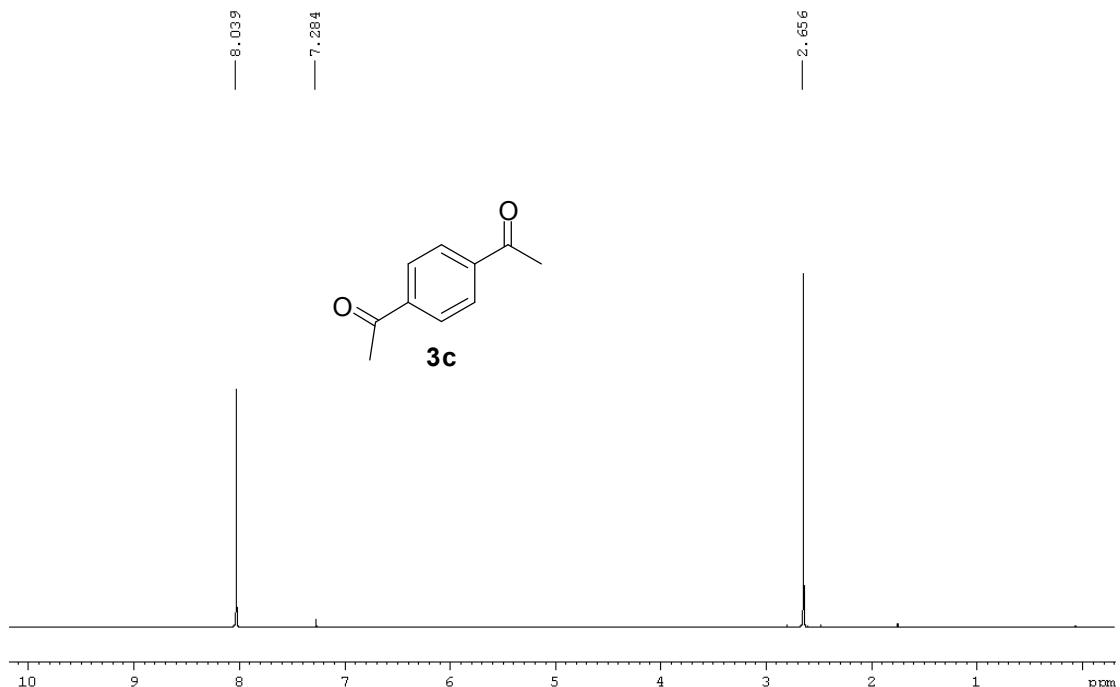
**2-Methyl-1-(3,4,5-trimethoxyphenyl)propan-1-one (3bf).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22 (s, 2H), 3.90-3.91 (m, 9H), 3.49-3.56 (m, 1H), 1.21 (d,  $J = 7.2$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.3, 153.1, 142.3, 131.4, 105.8, 60.9, 56.3, 35.1, 19.4; IR (neat,  $\text{cm}^{-1}$ ): 1690; EI-MS  $m/z$  238 ( $\text{M}^+$ , 36), 195 (100); HRMS calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_4$ : 238.1205; Found: 238.1203; Anal. Calcd for  $\text{C}_{13}\text{H}_{18}\text{O}_4$ : C, 65.53; H, 7.61; Found: C, 65.50; H, 7.65.

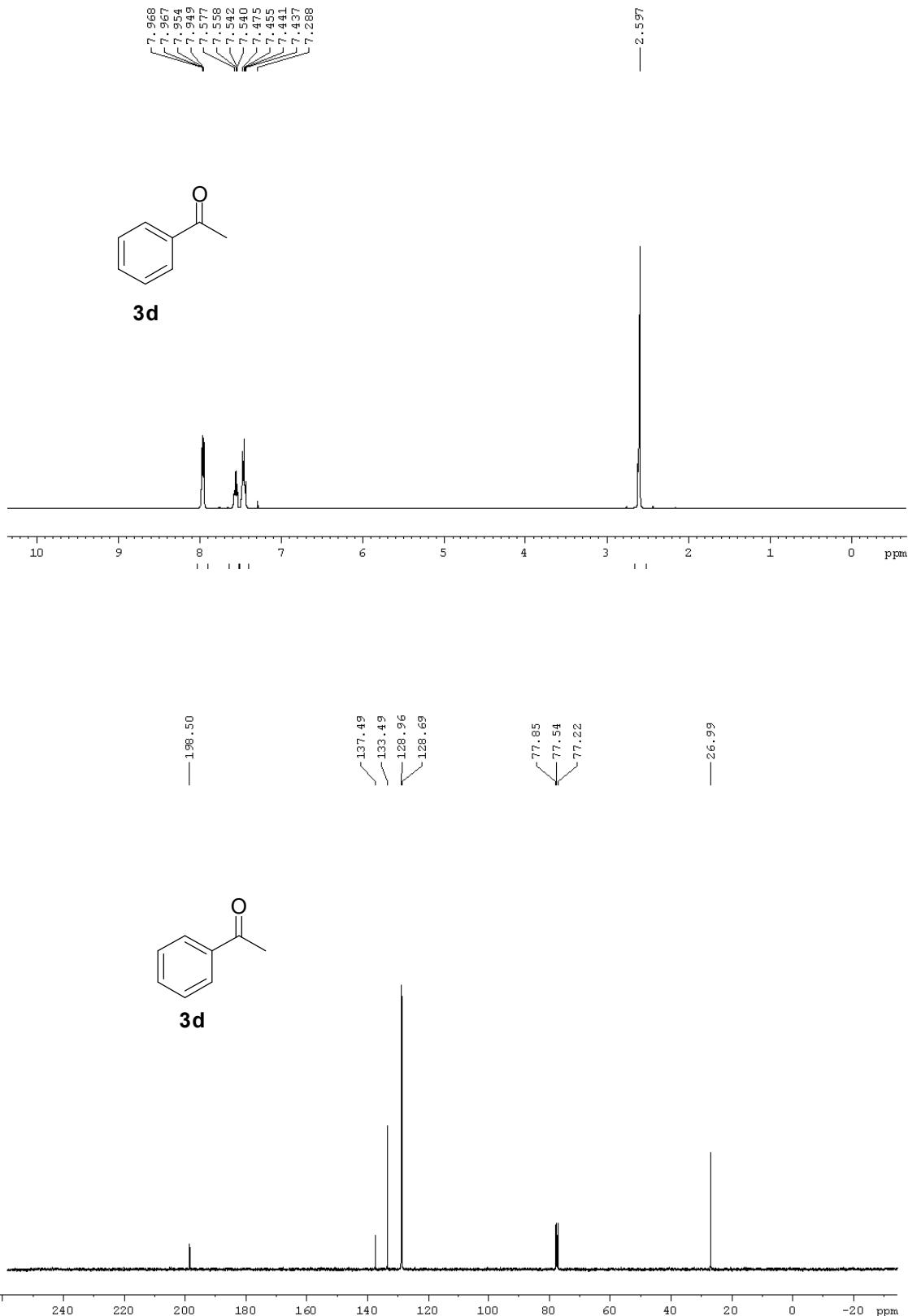
**1-(4-Acetylphenyl)-2-methylpropan-1-one (3cf).**<sup>18</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (s, 4H), 3.52-3.61 (m, 1H), 2.67 (s, 3H), 1.23 (d,  $J = 6.9$  Hz, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.9, 197.5, 140.0, 139.6, 128.5, 128.4, 35.9, 26.8, 18.9; IR (neat,  $\text{cm}^{-1}$ ): 1682; CI-MS  $m/z$  191 [ $(\text{M}+1)^+$ , 10], 147 (100); HRMS calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2$ : 190.0994; Found: 190.0996.

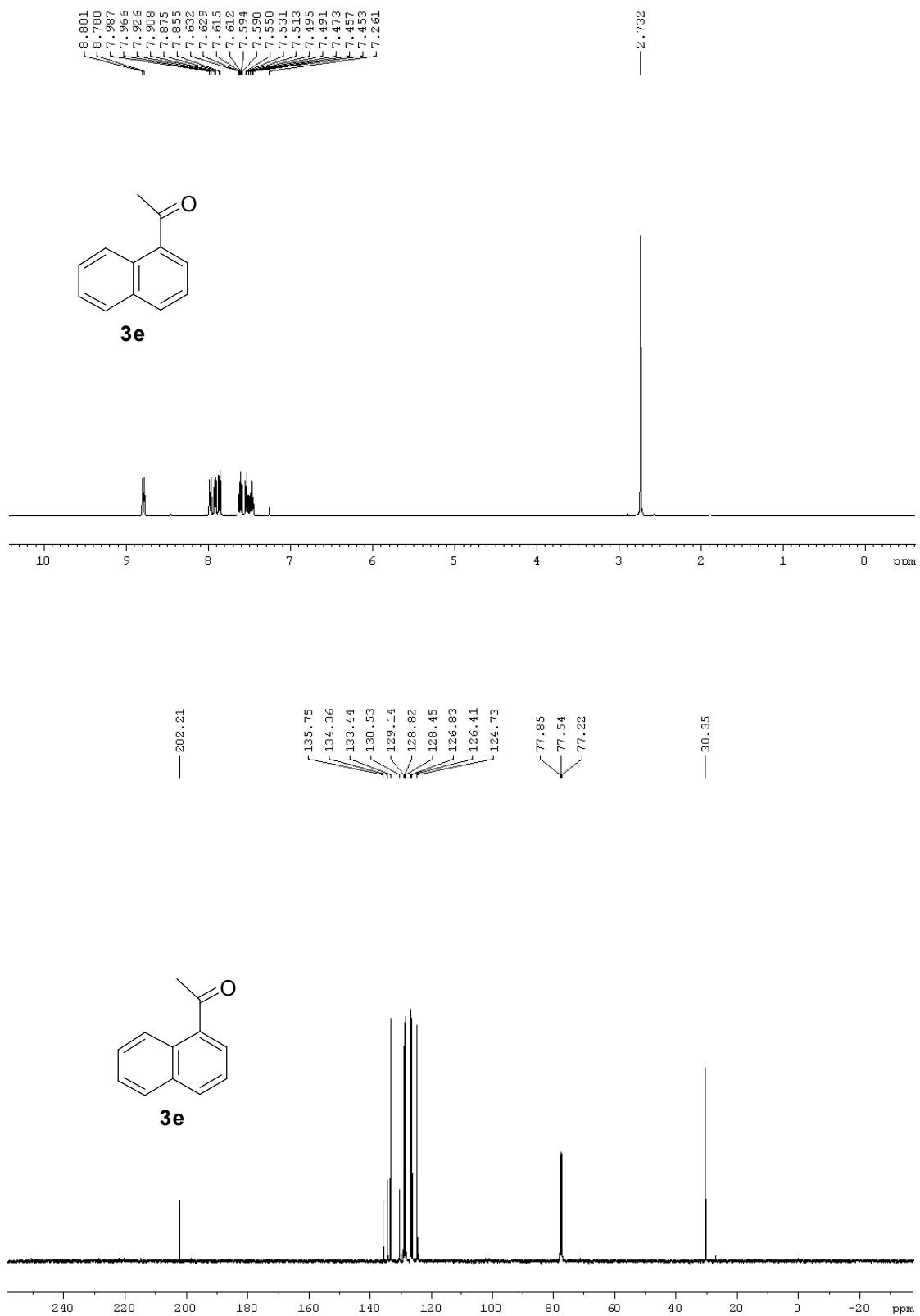
### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of aryl alkyl ketones

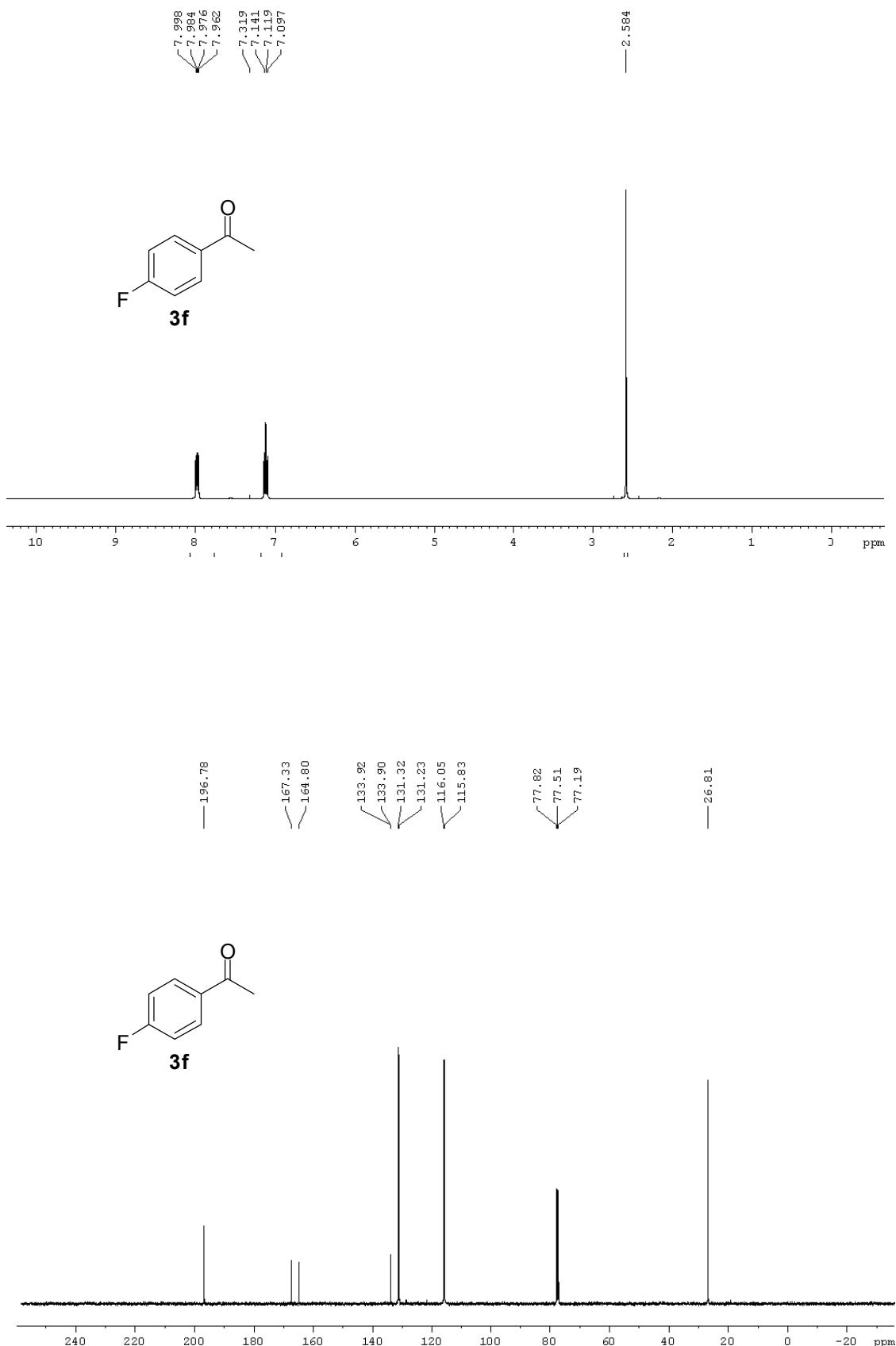


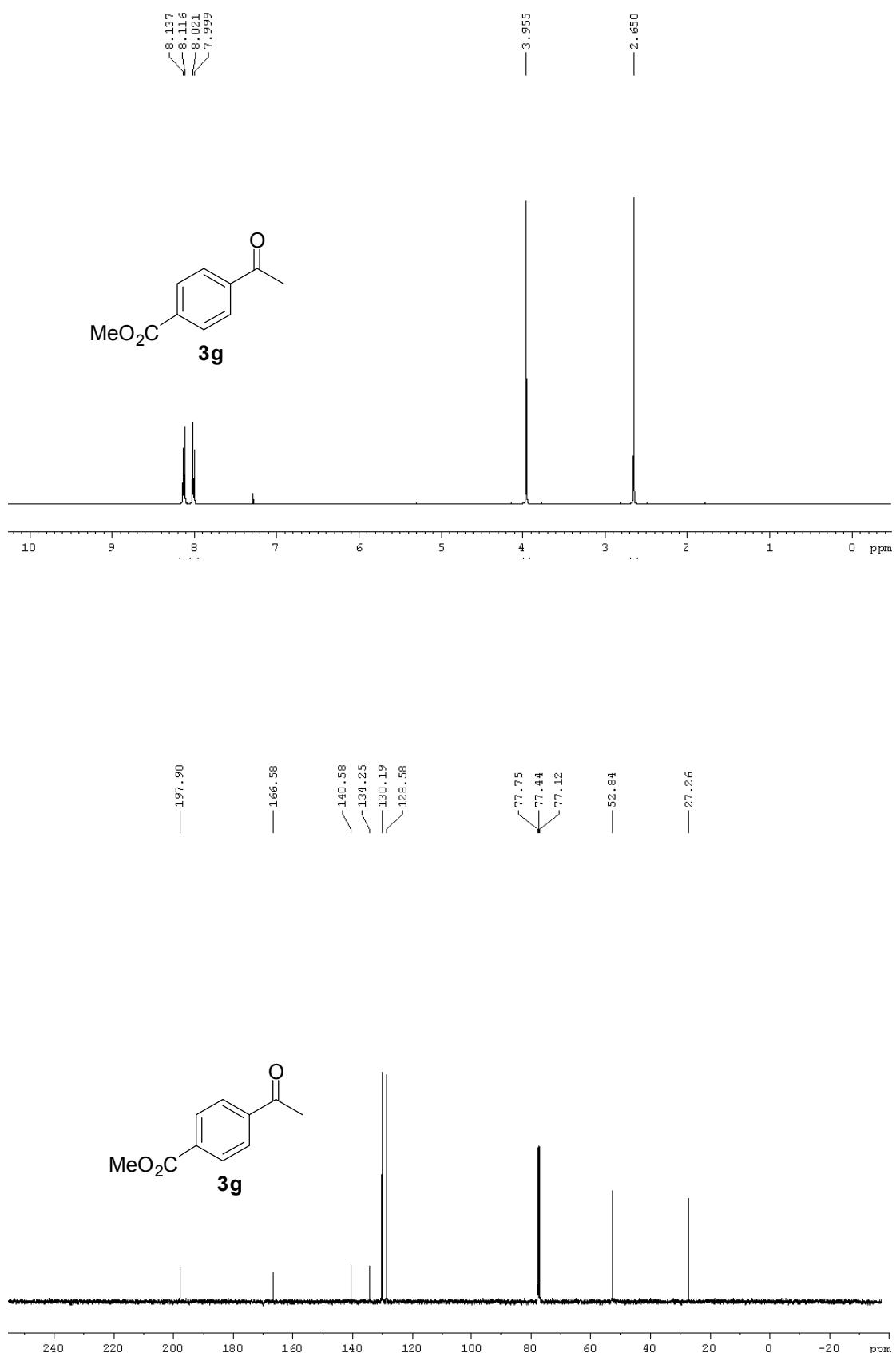


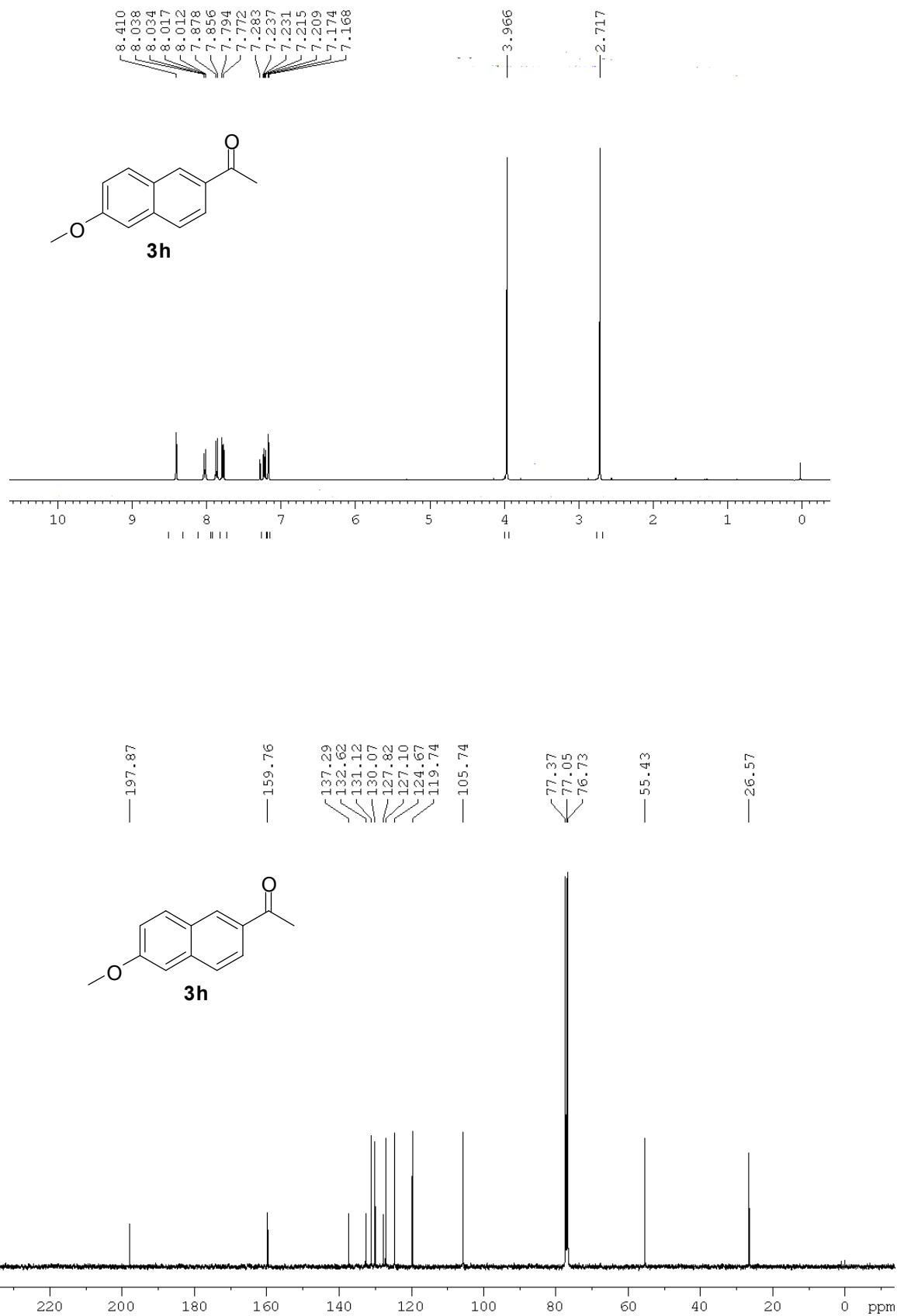


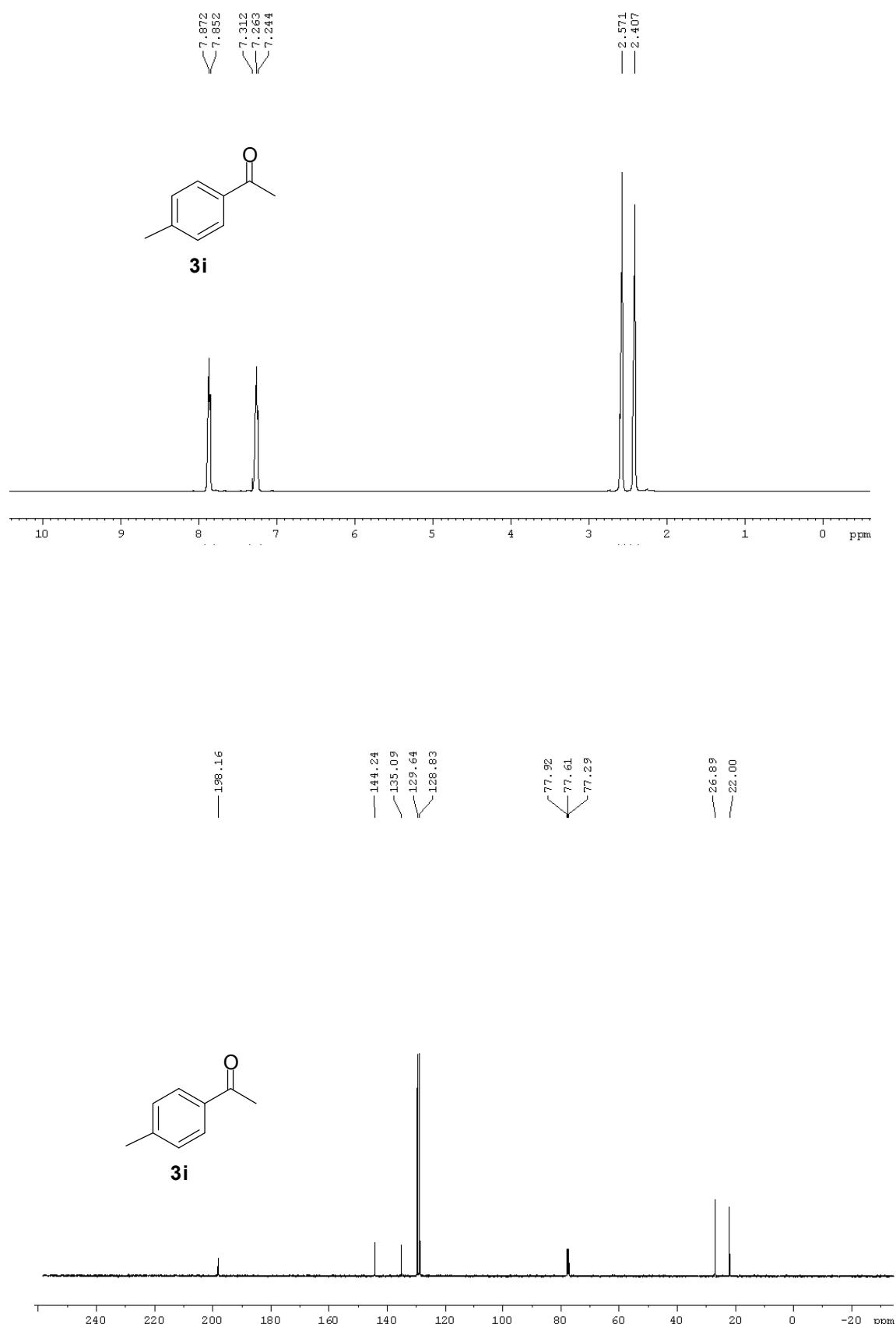


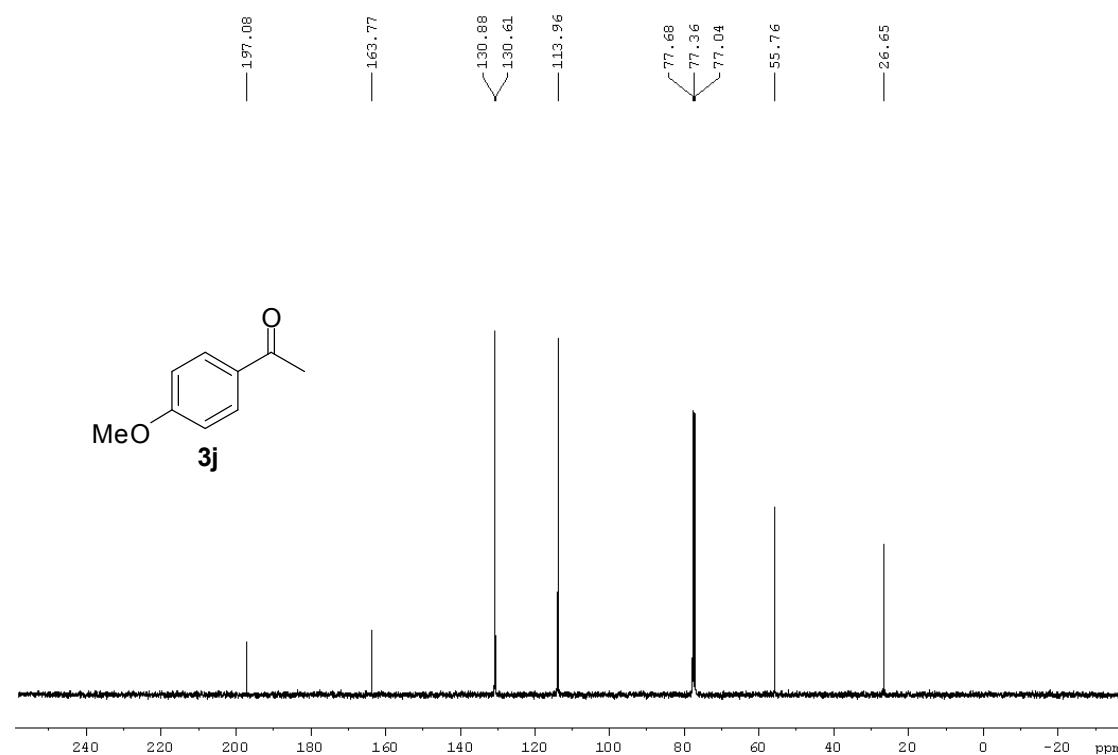
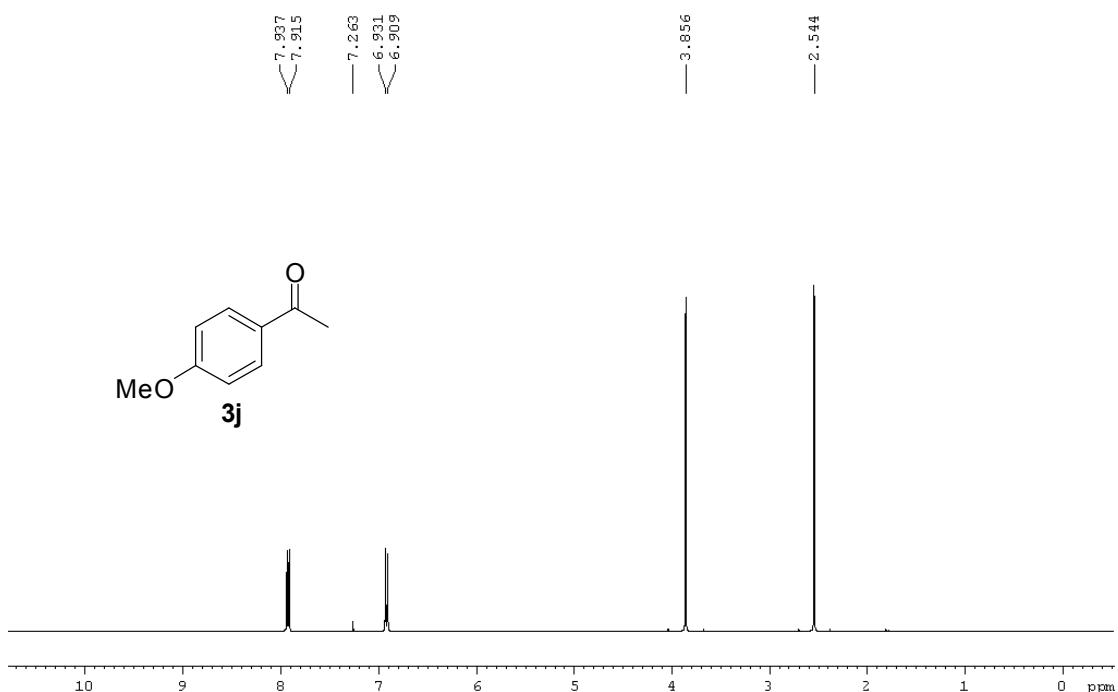


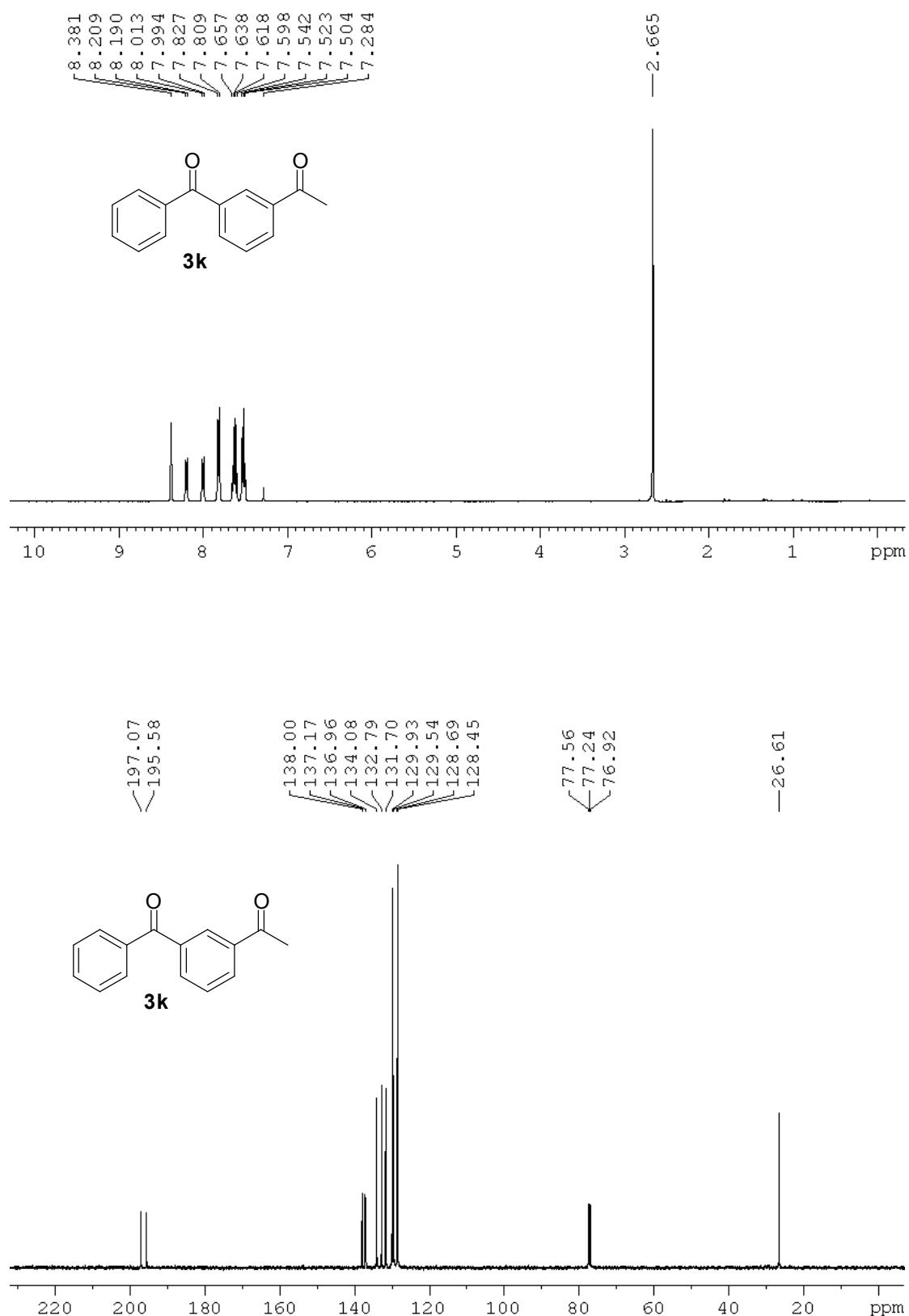


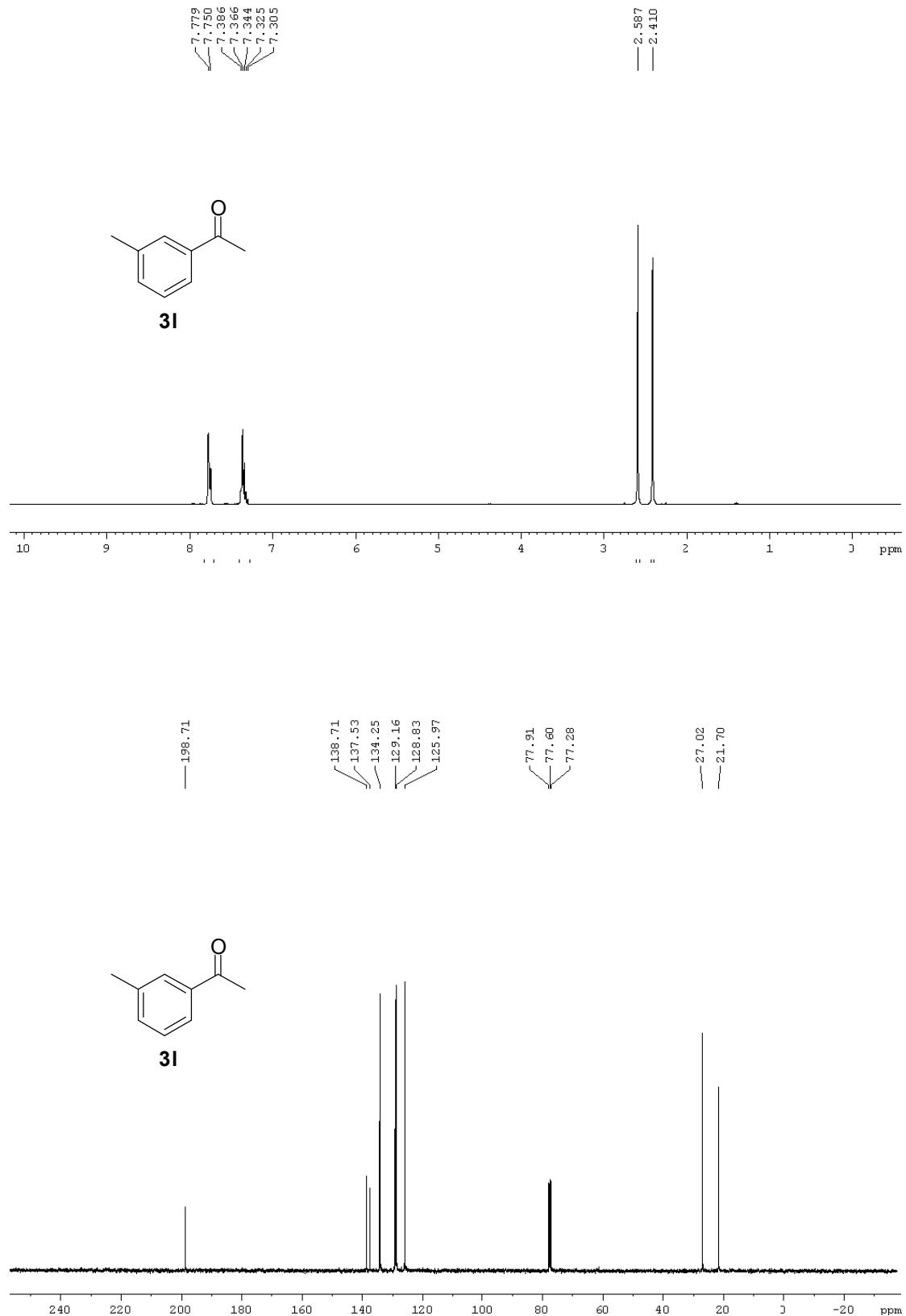


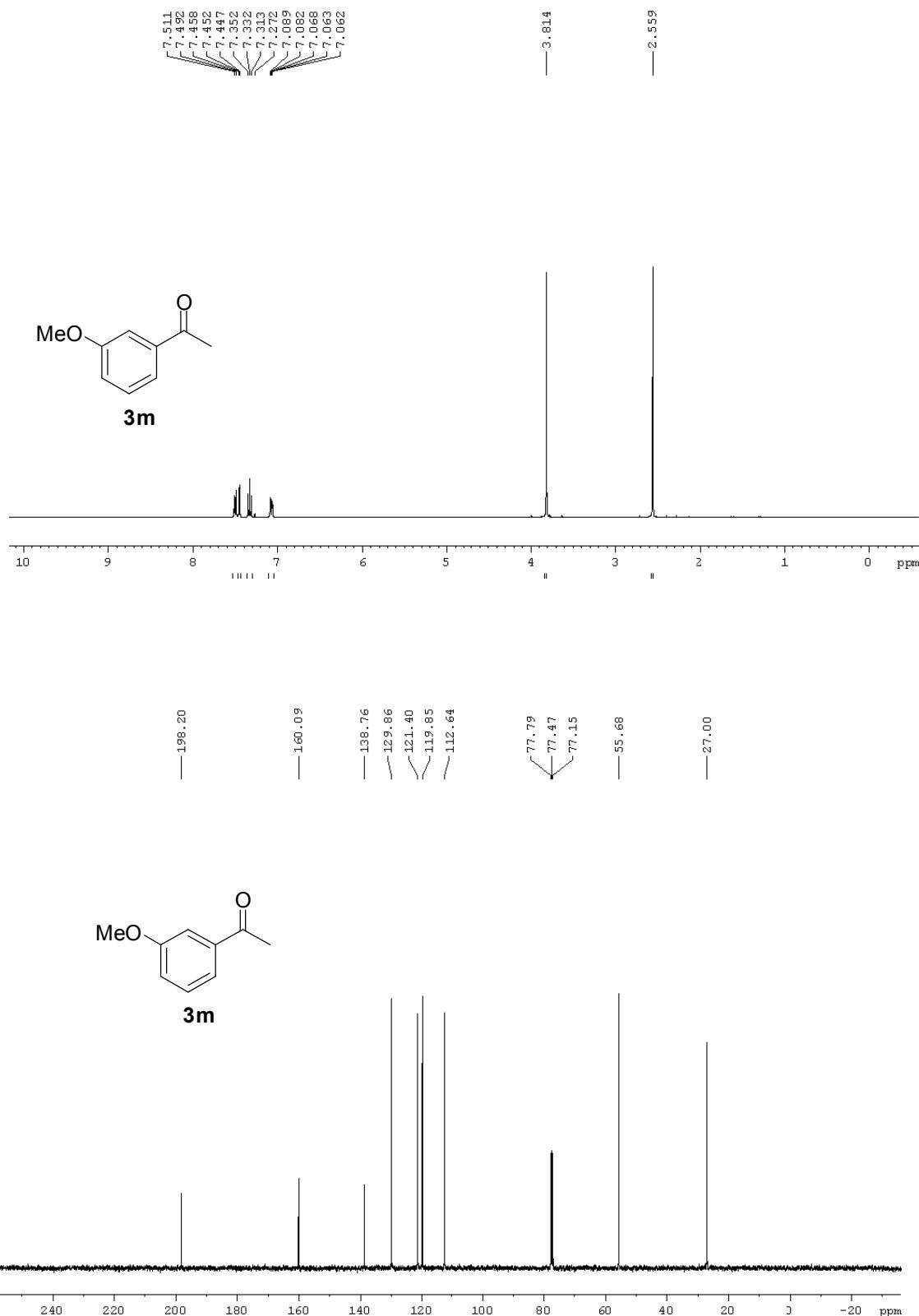


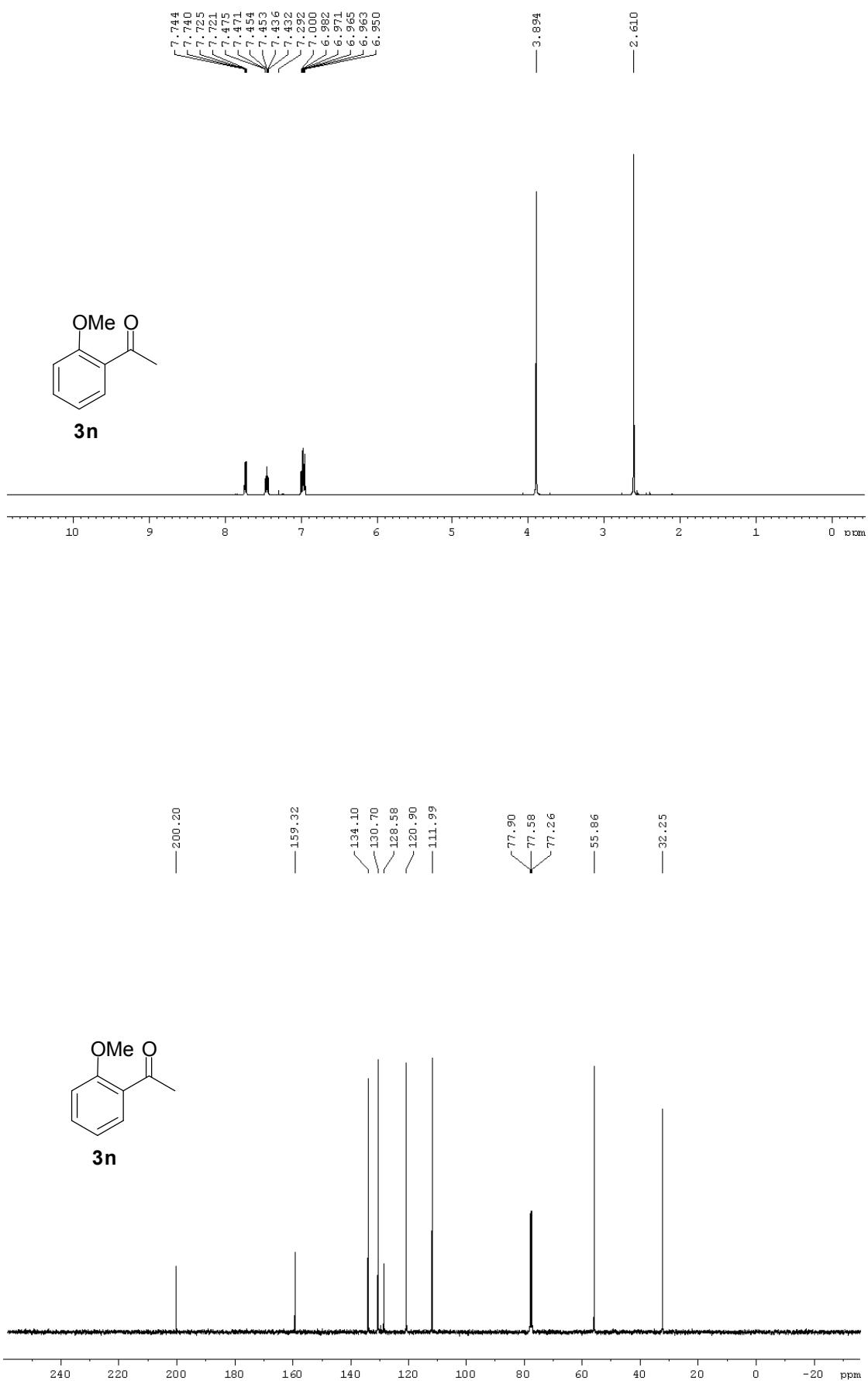


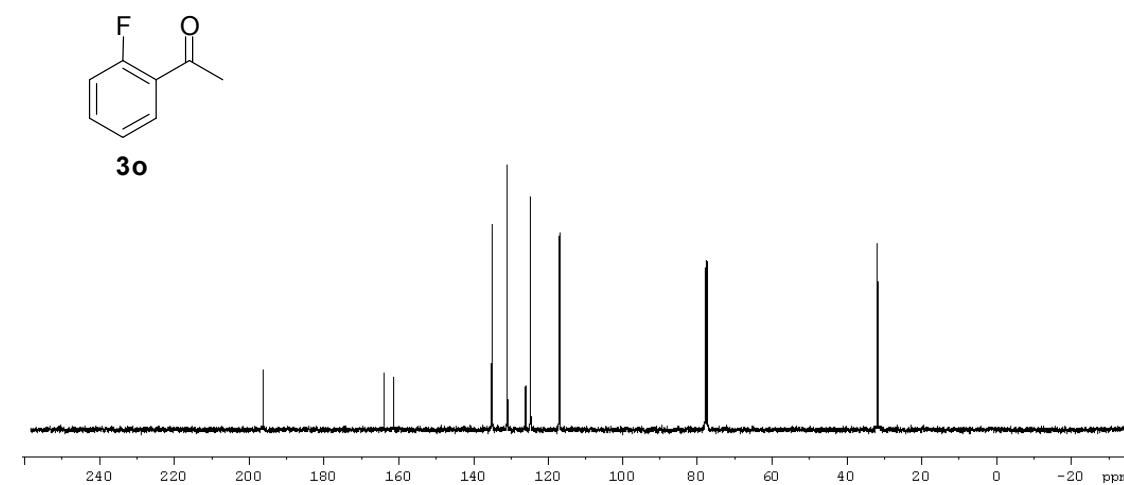
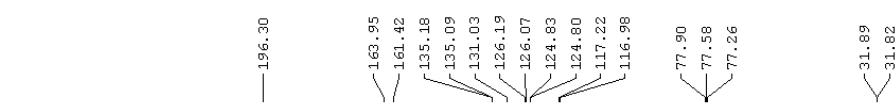
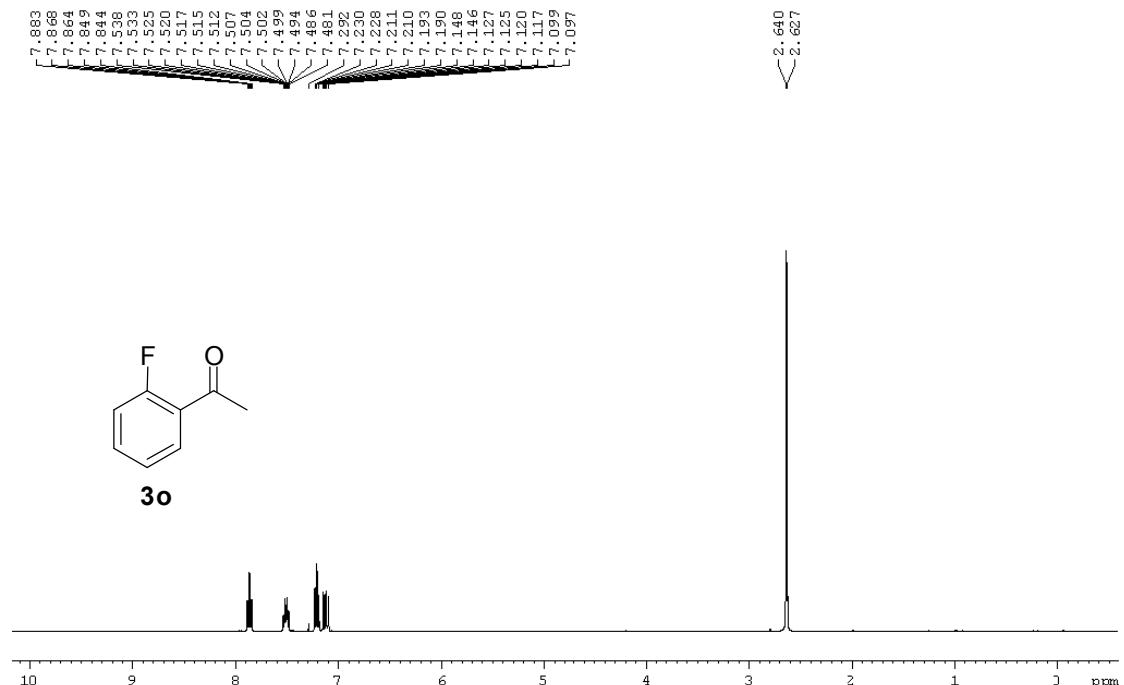




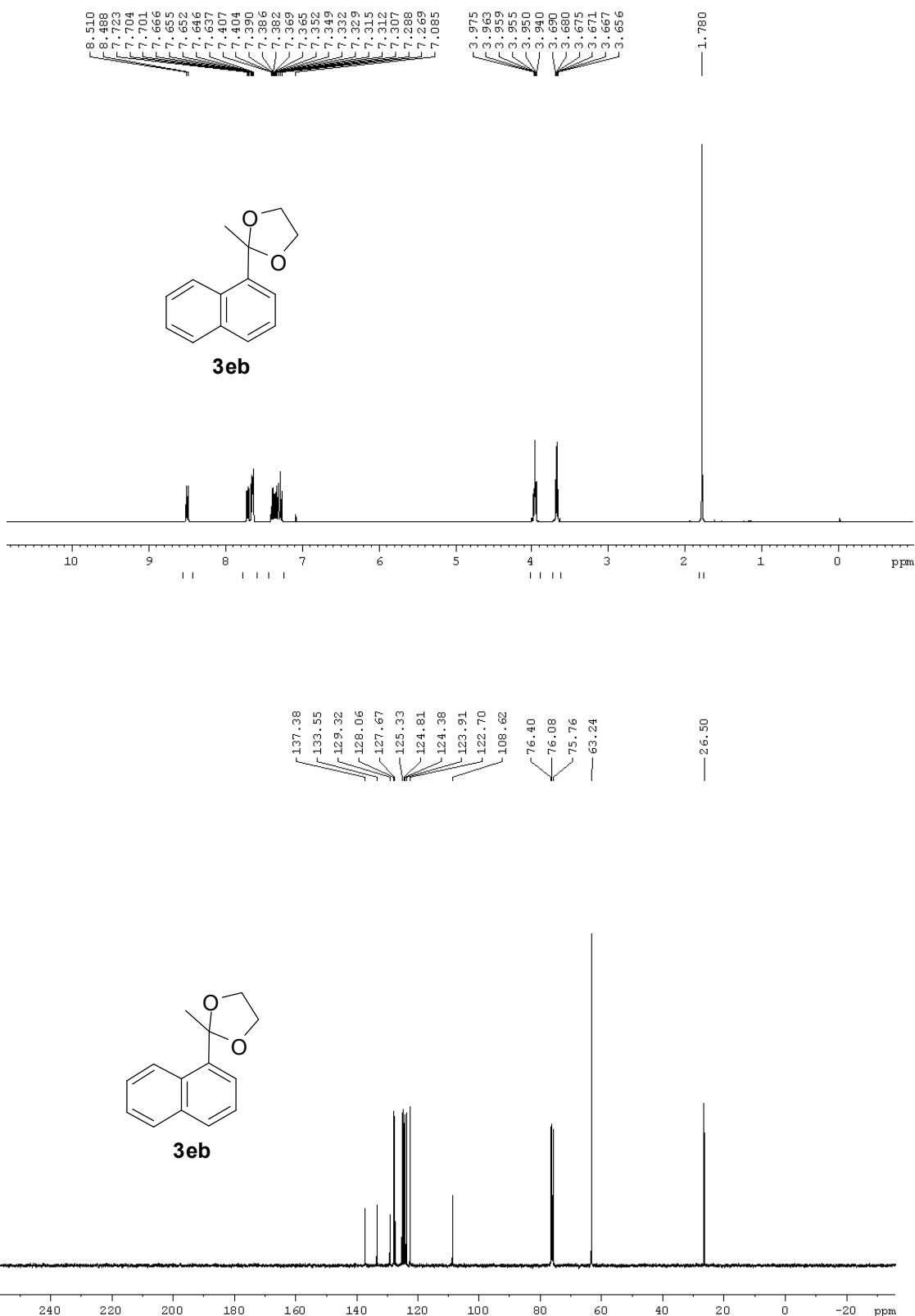


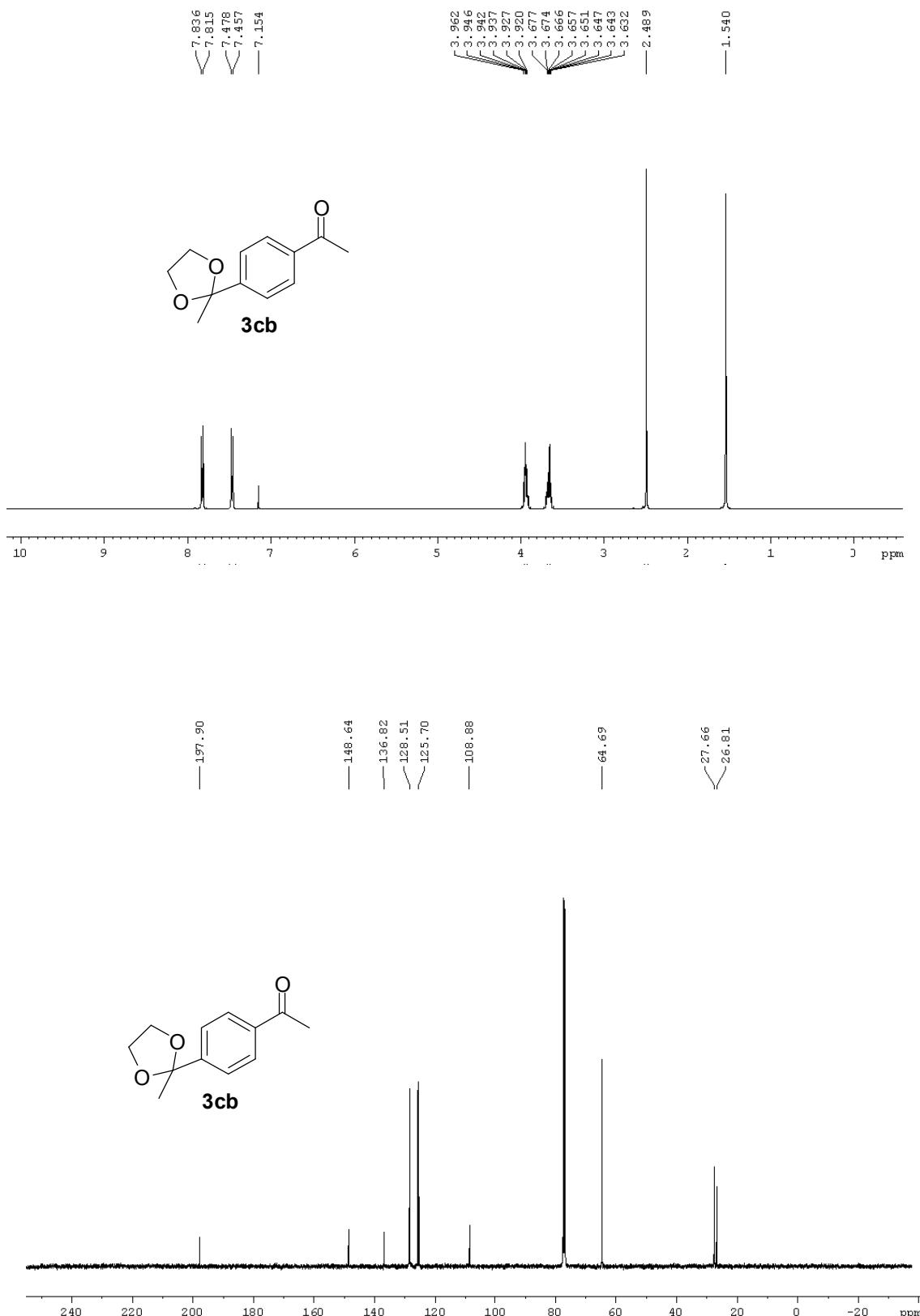


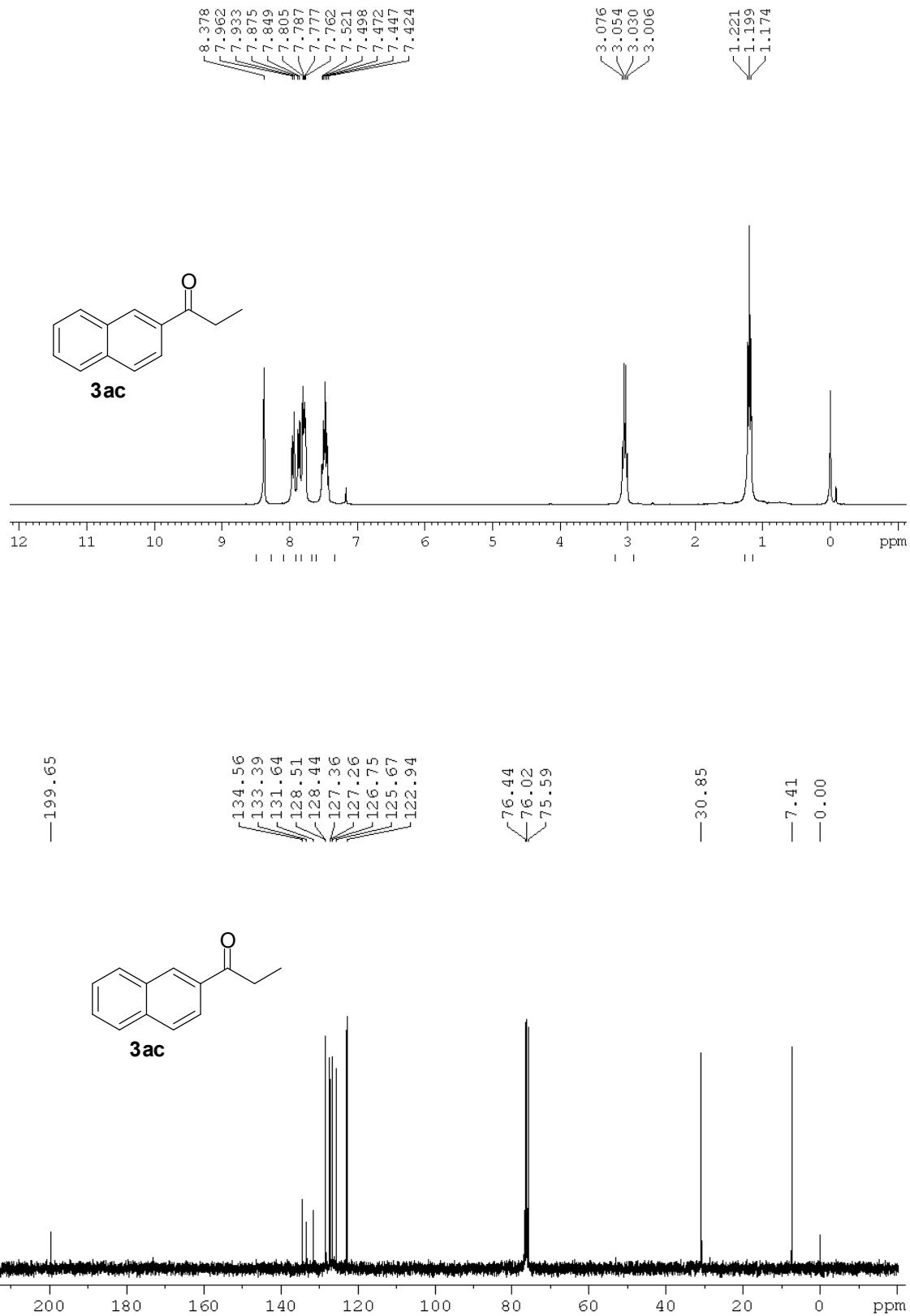


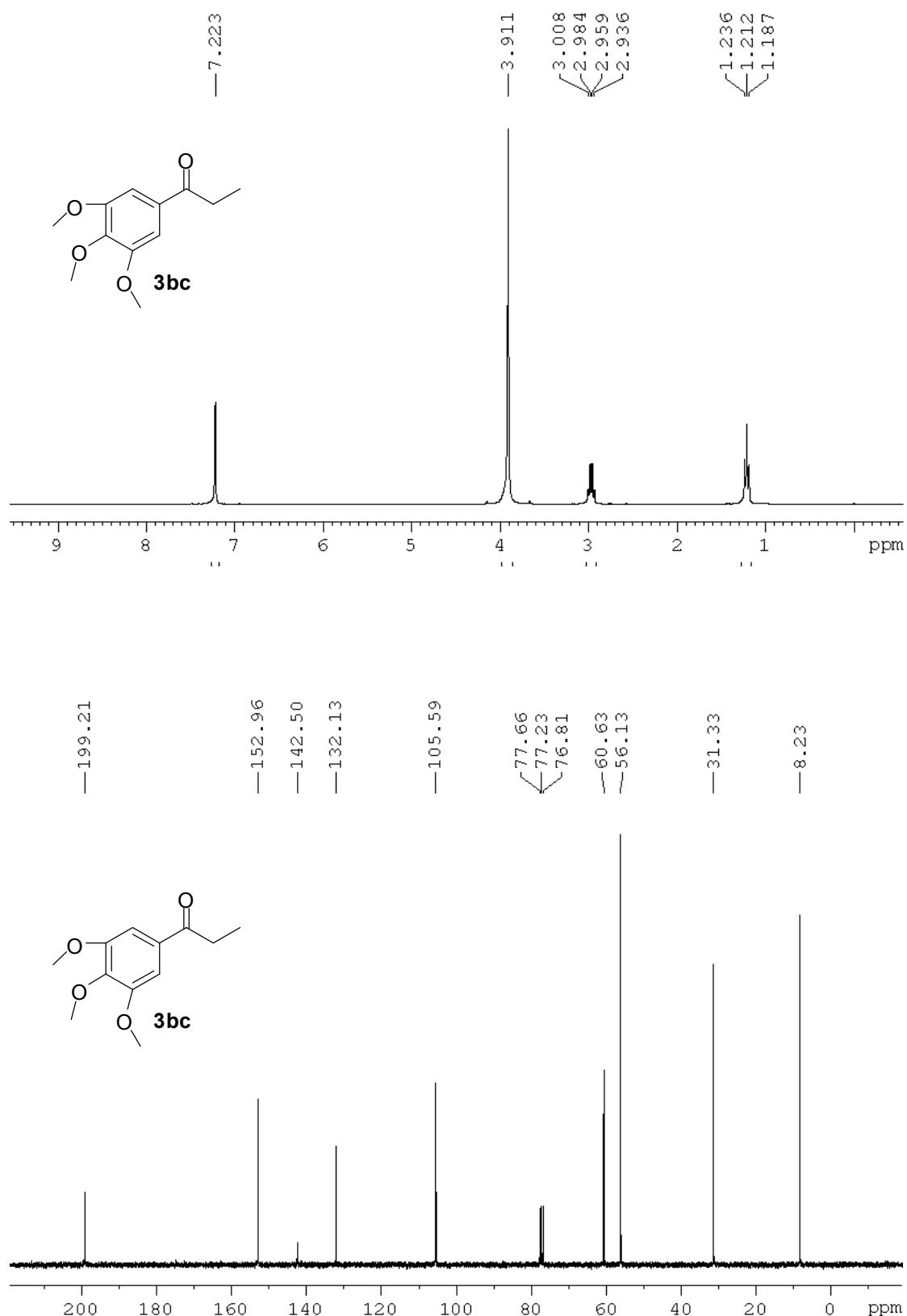


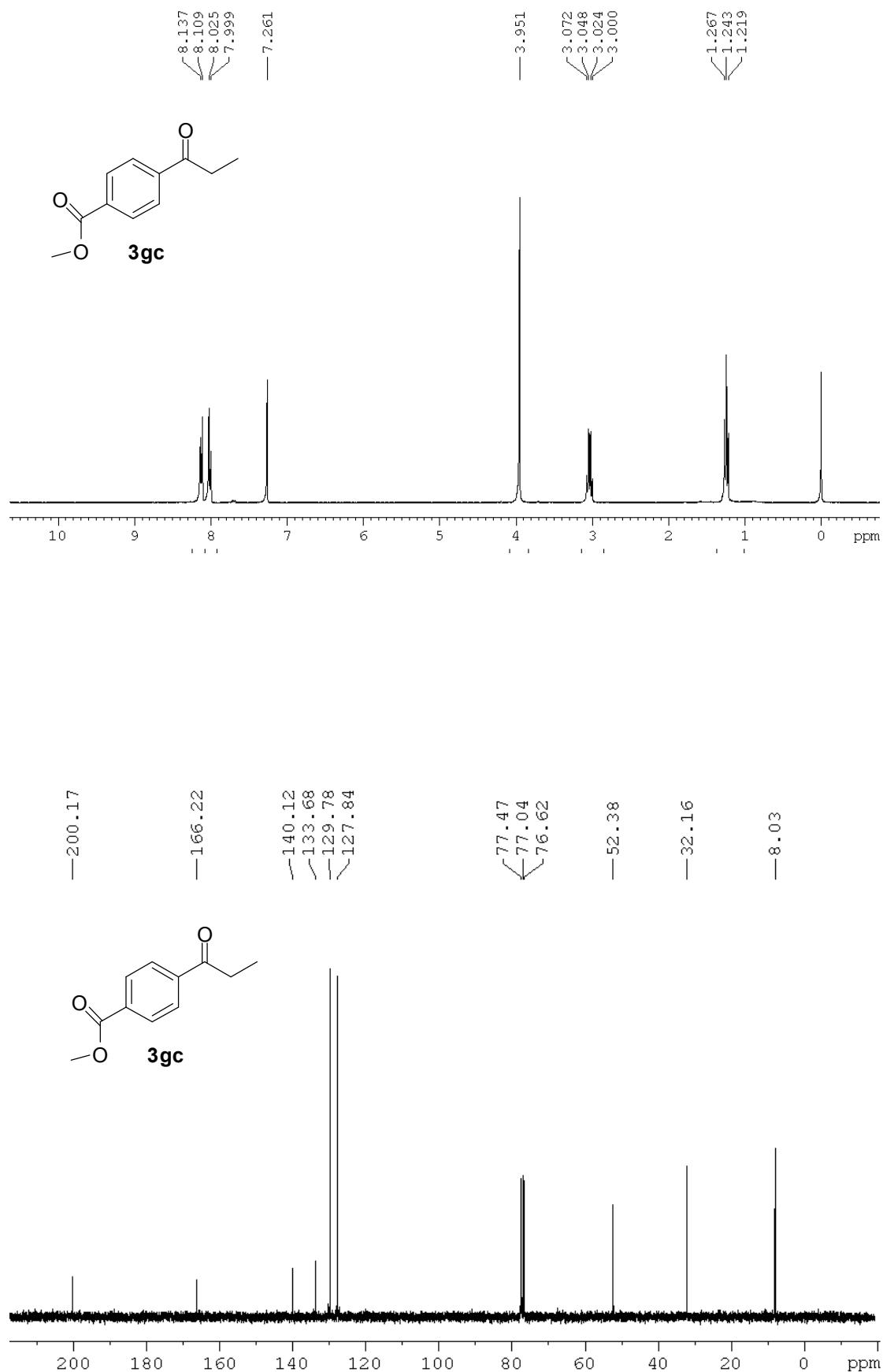


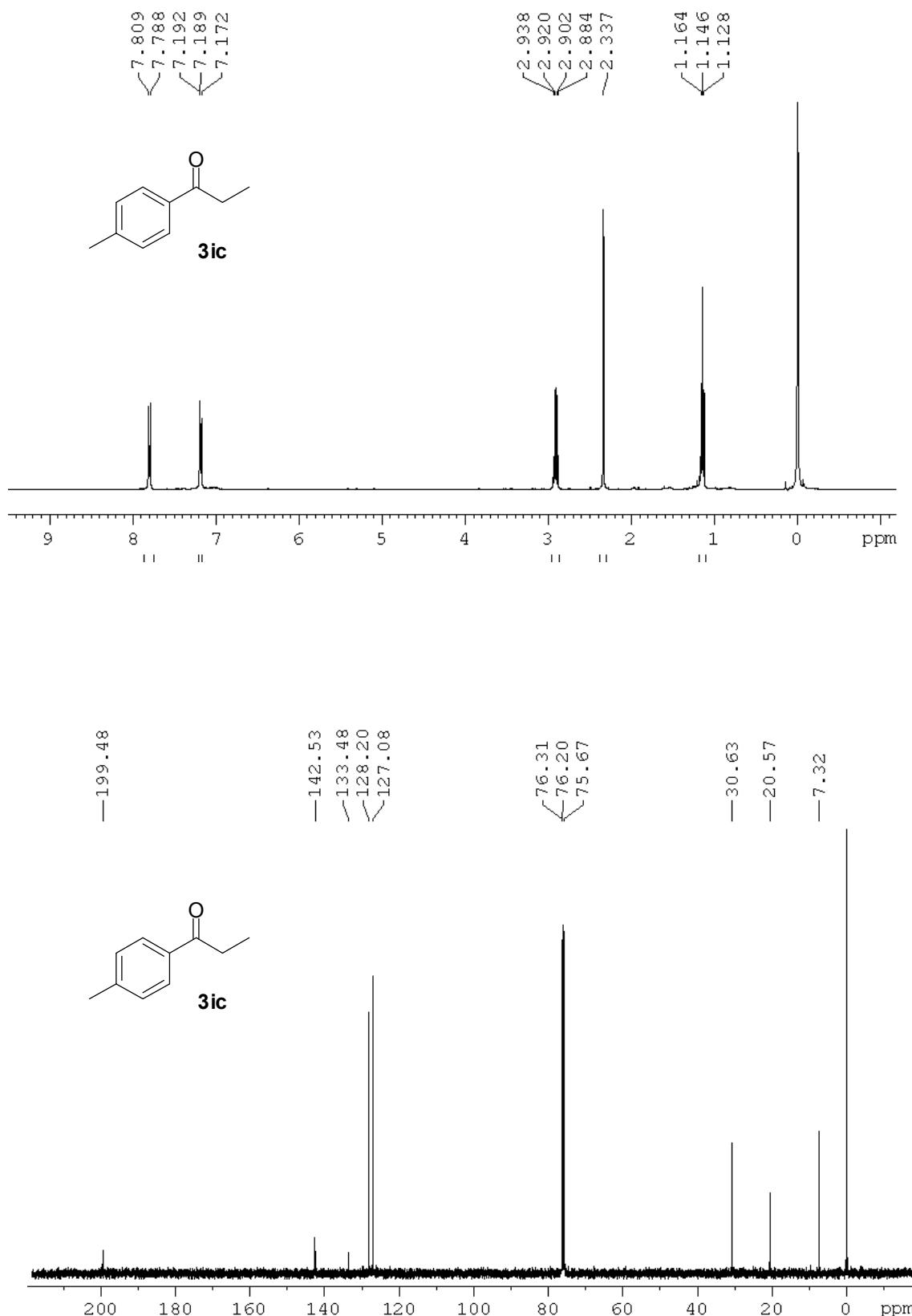


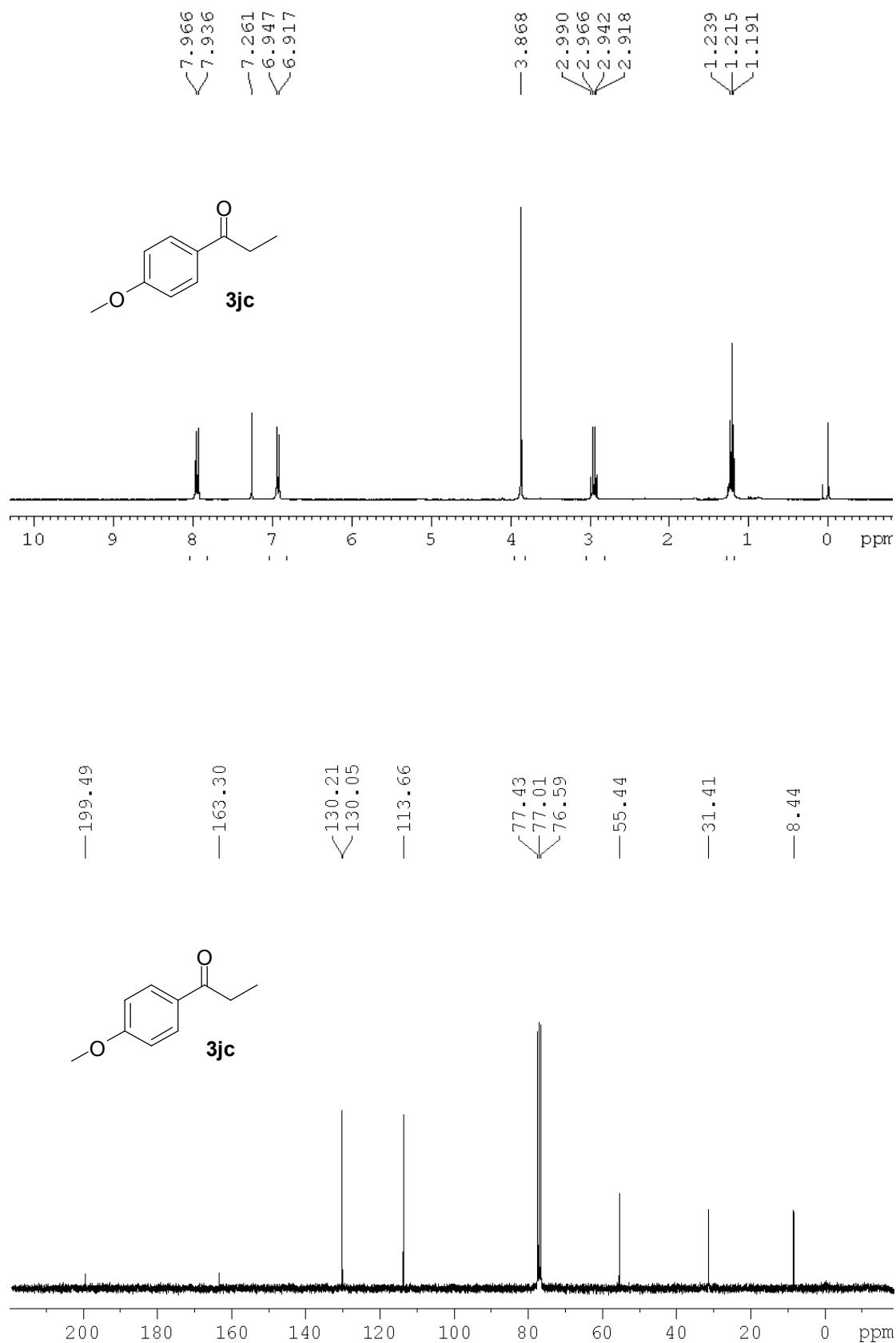


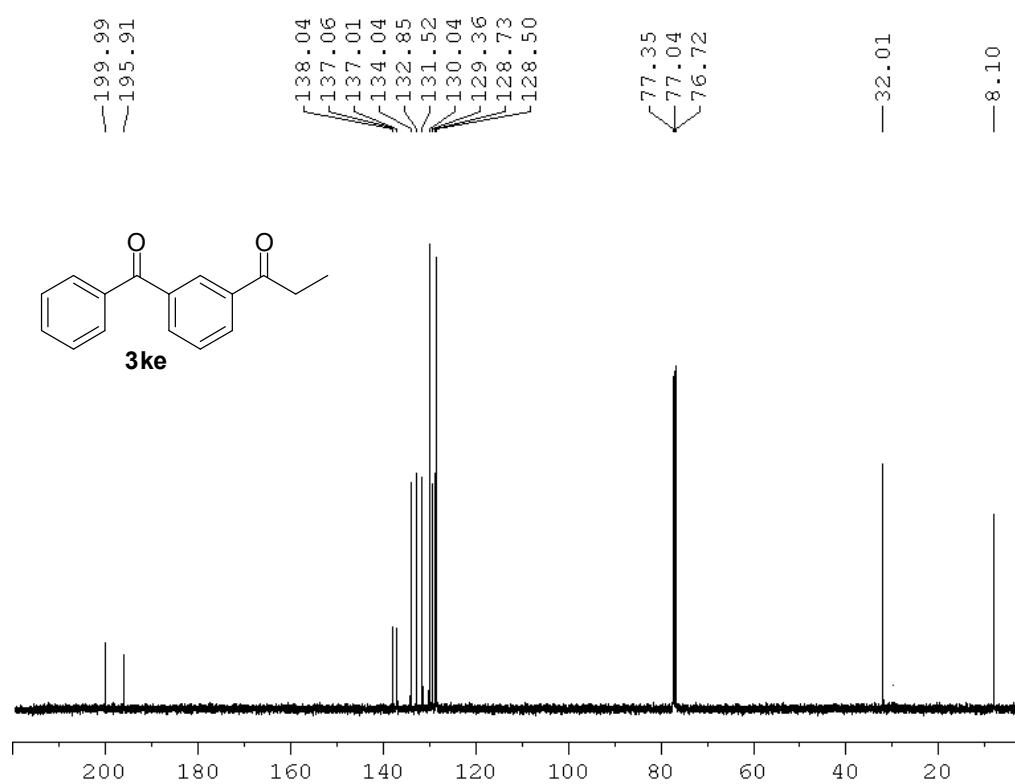
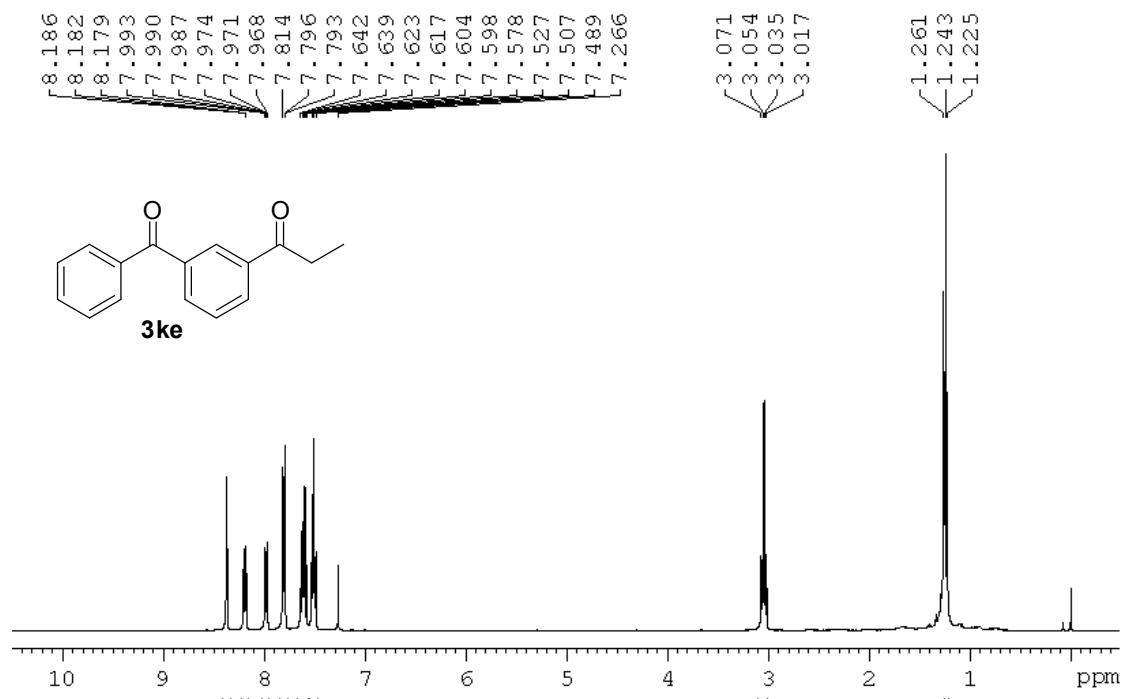


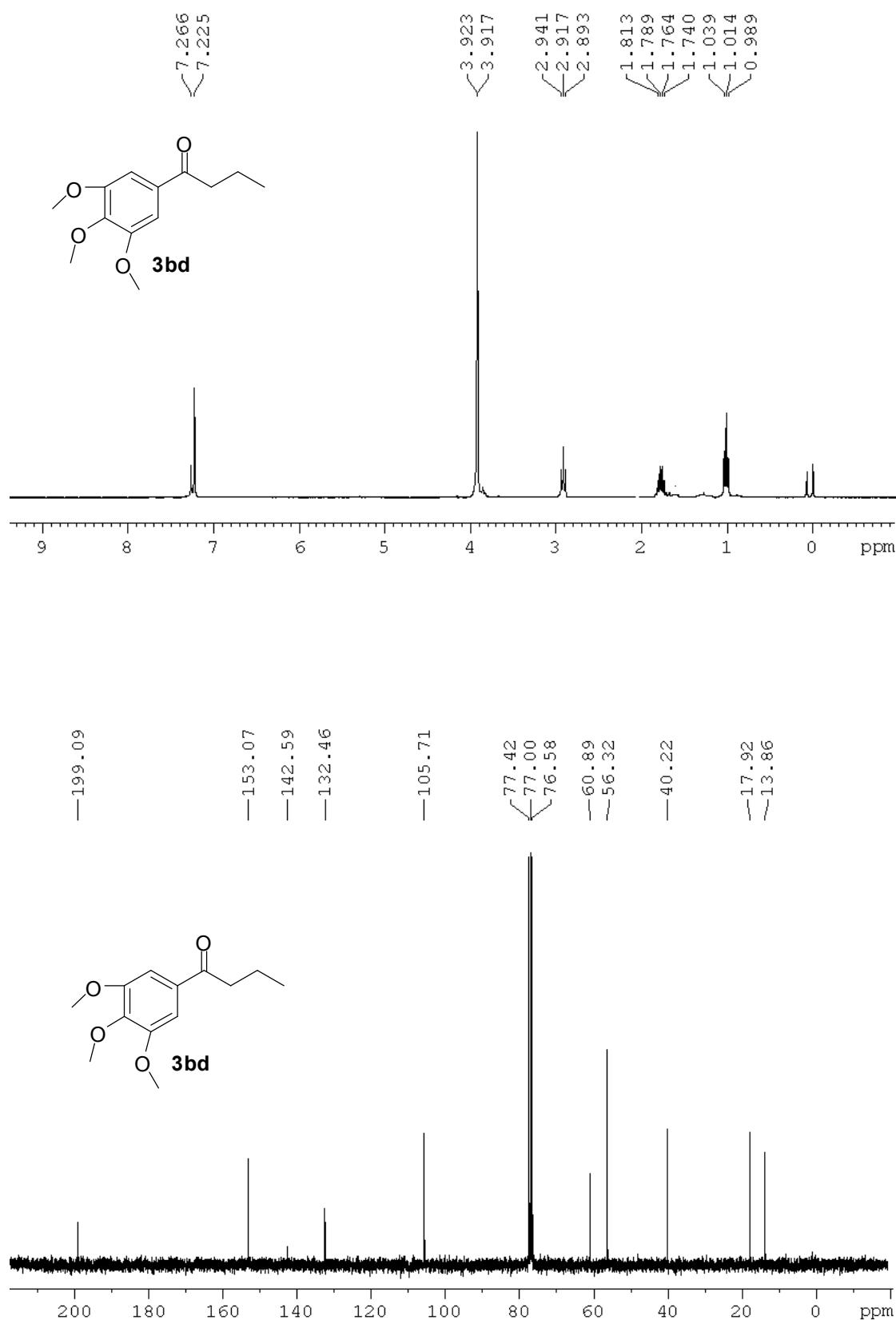


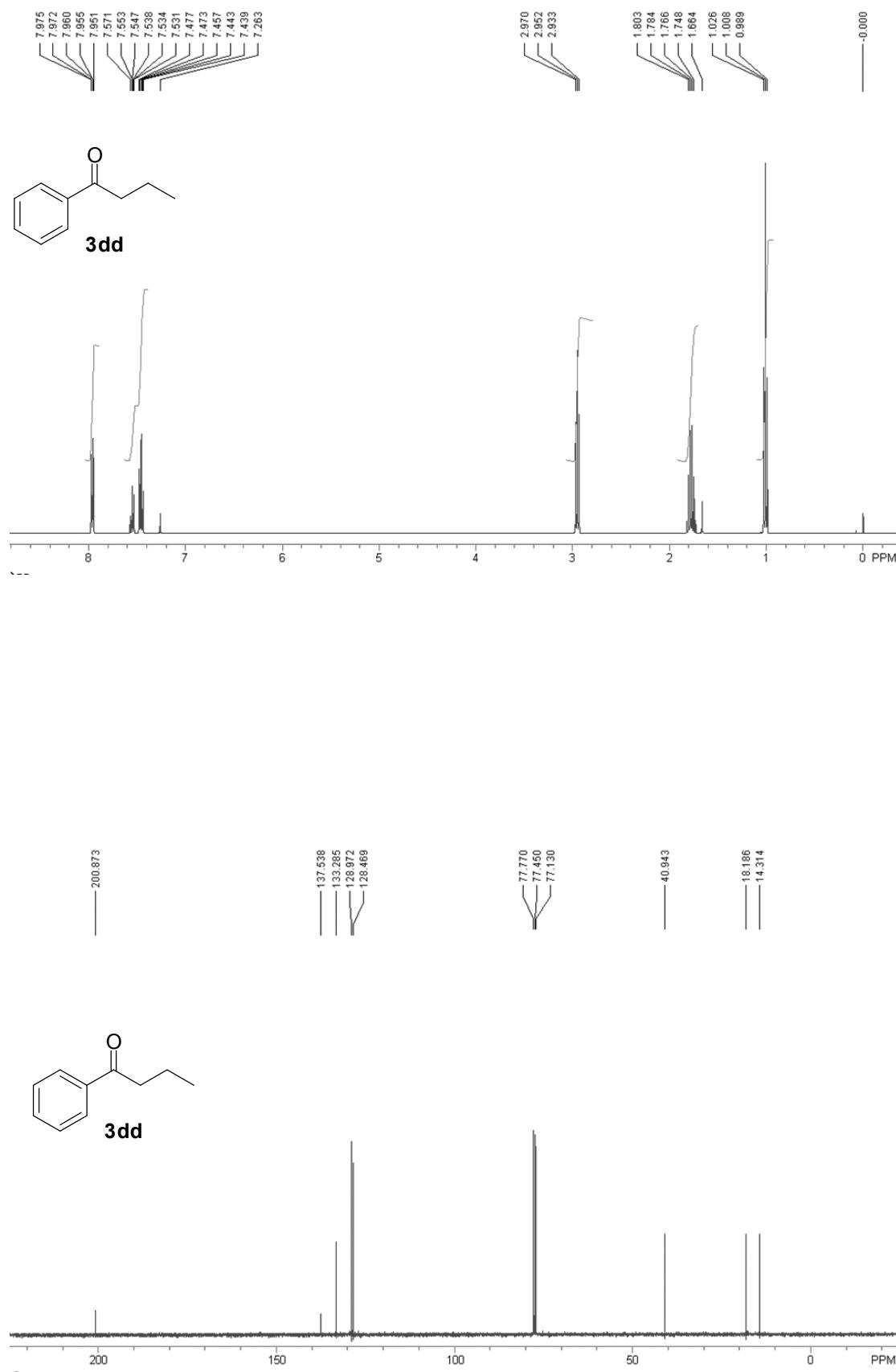


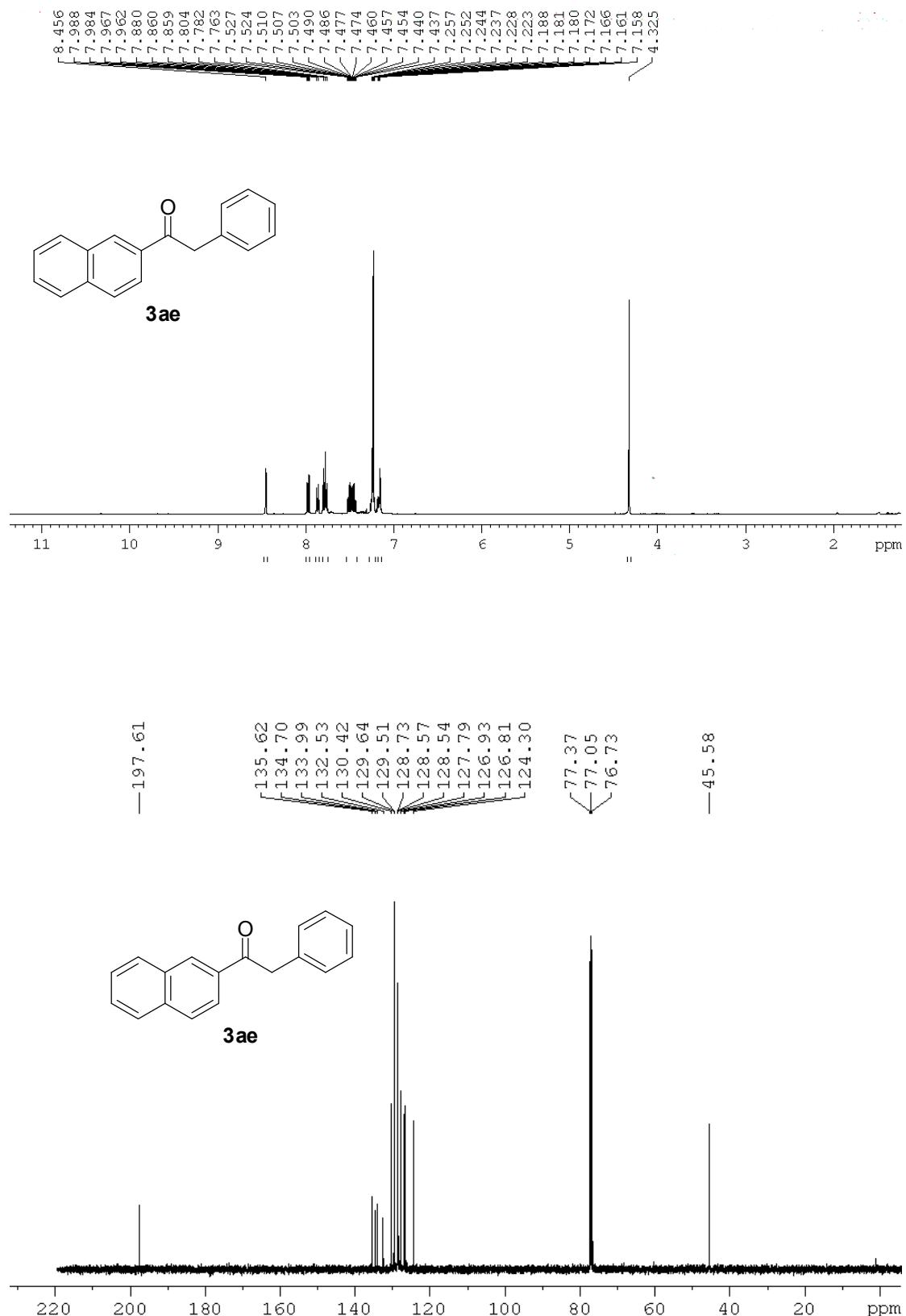


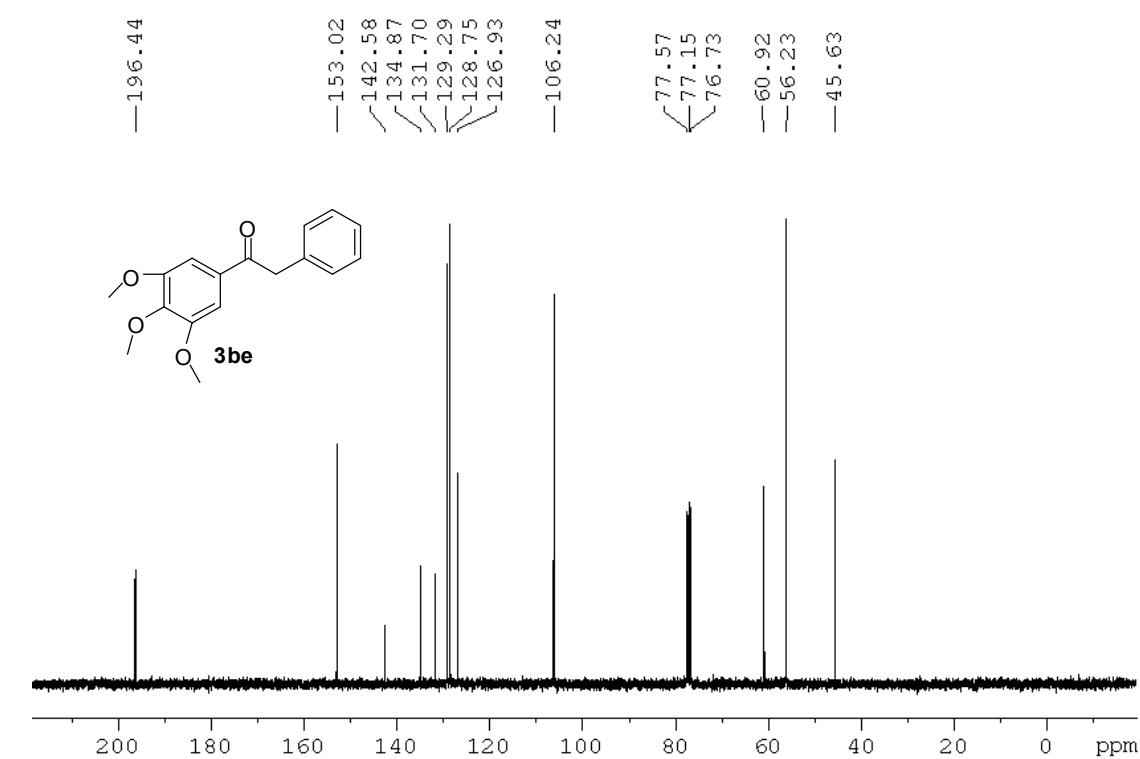
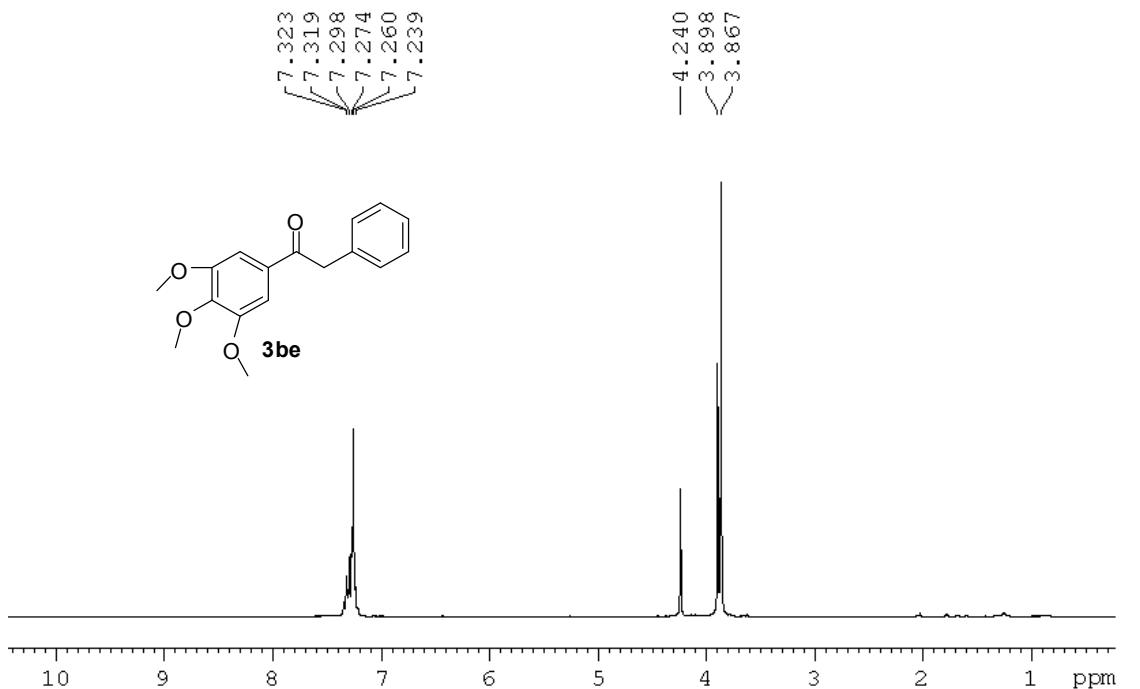


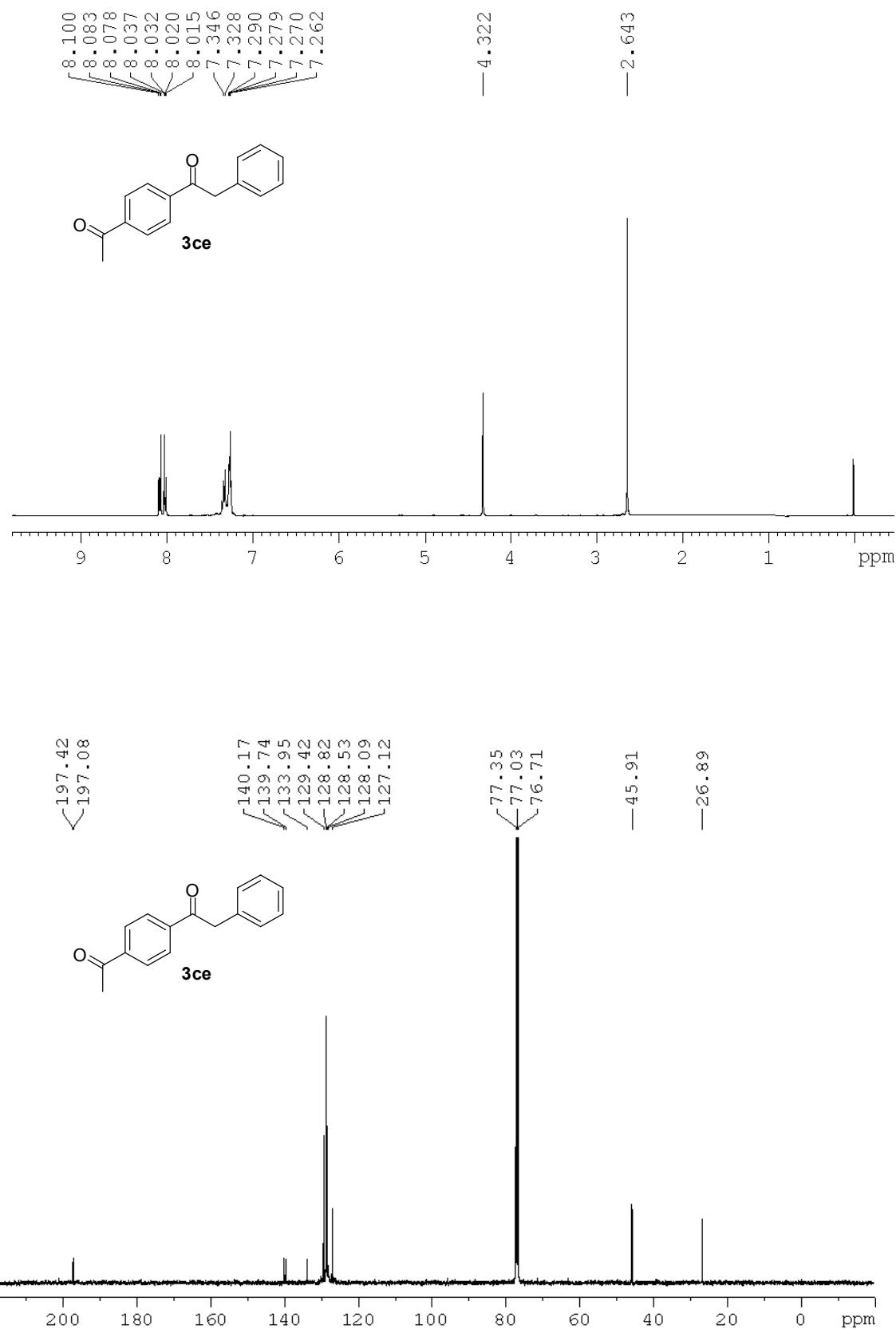


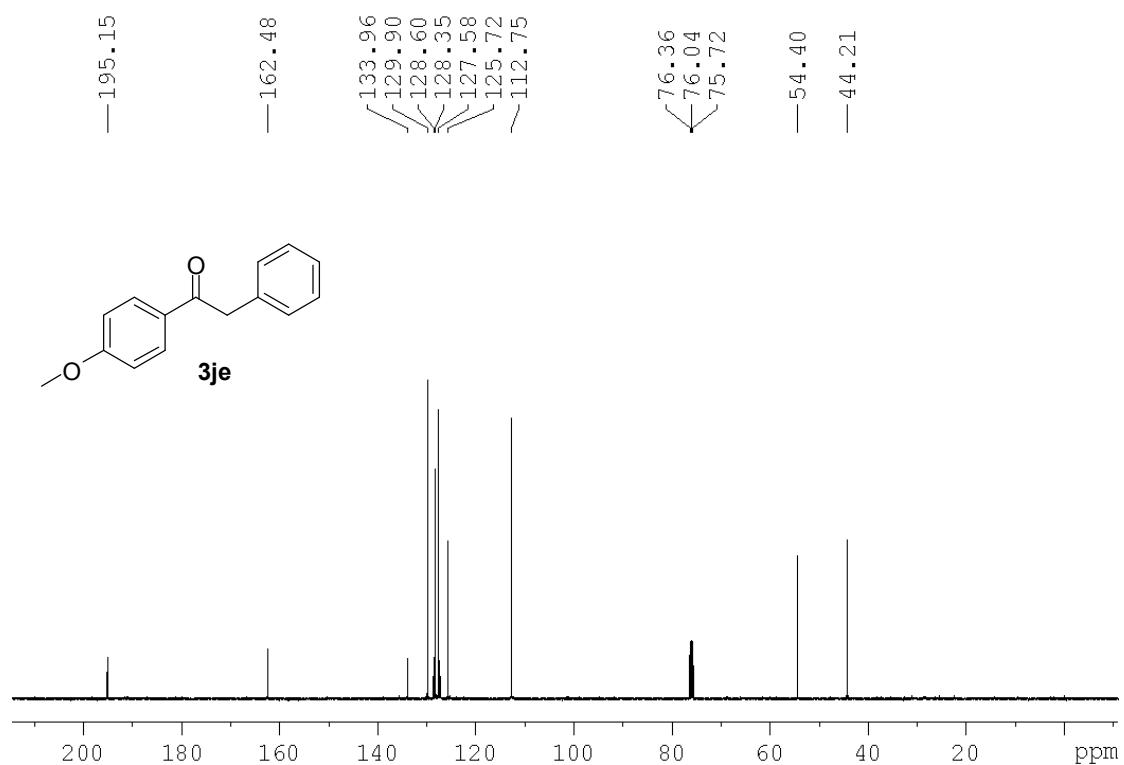
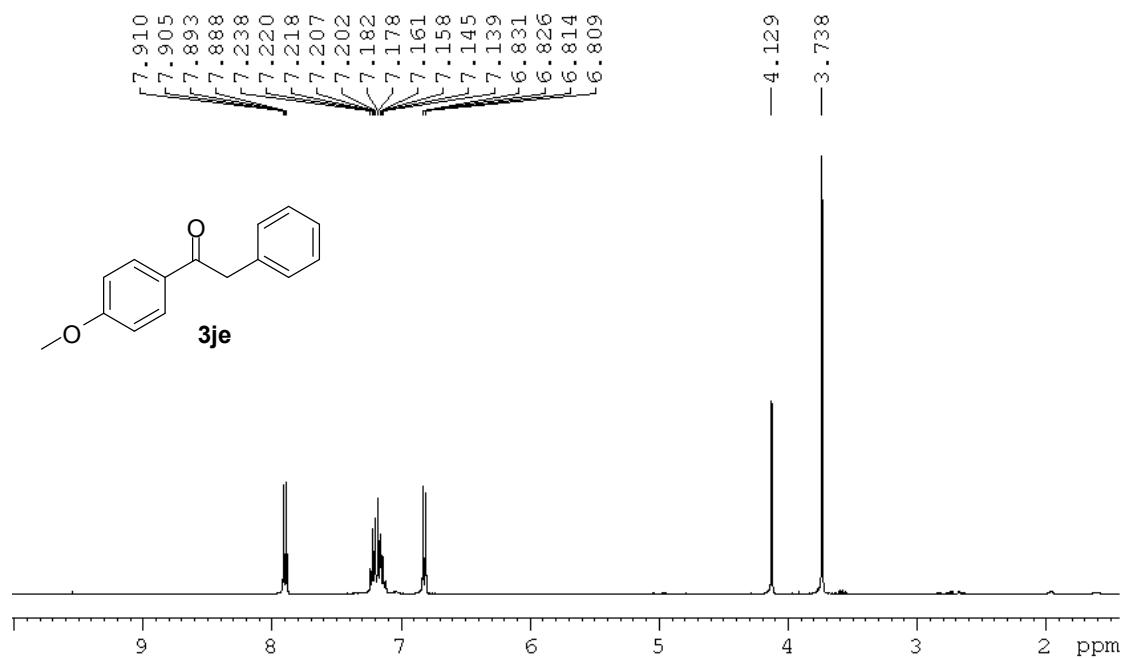


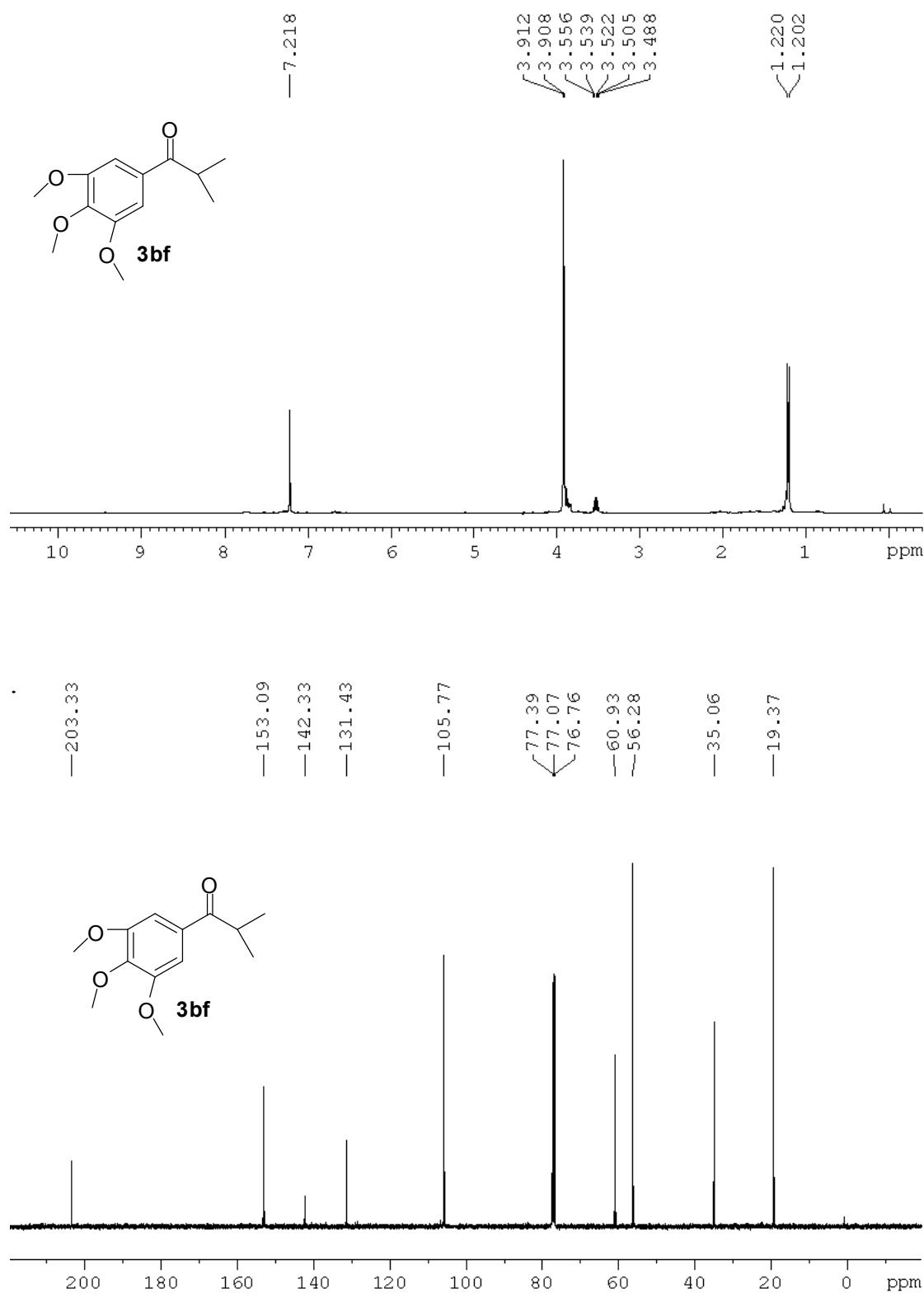


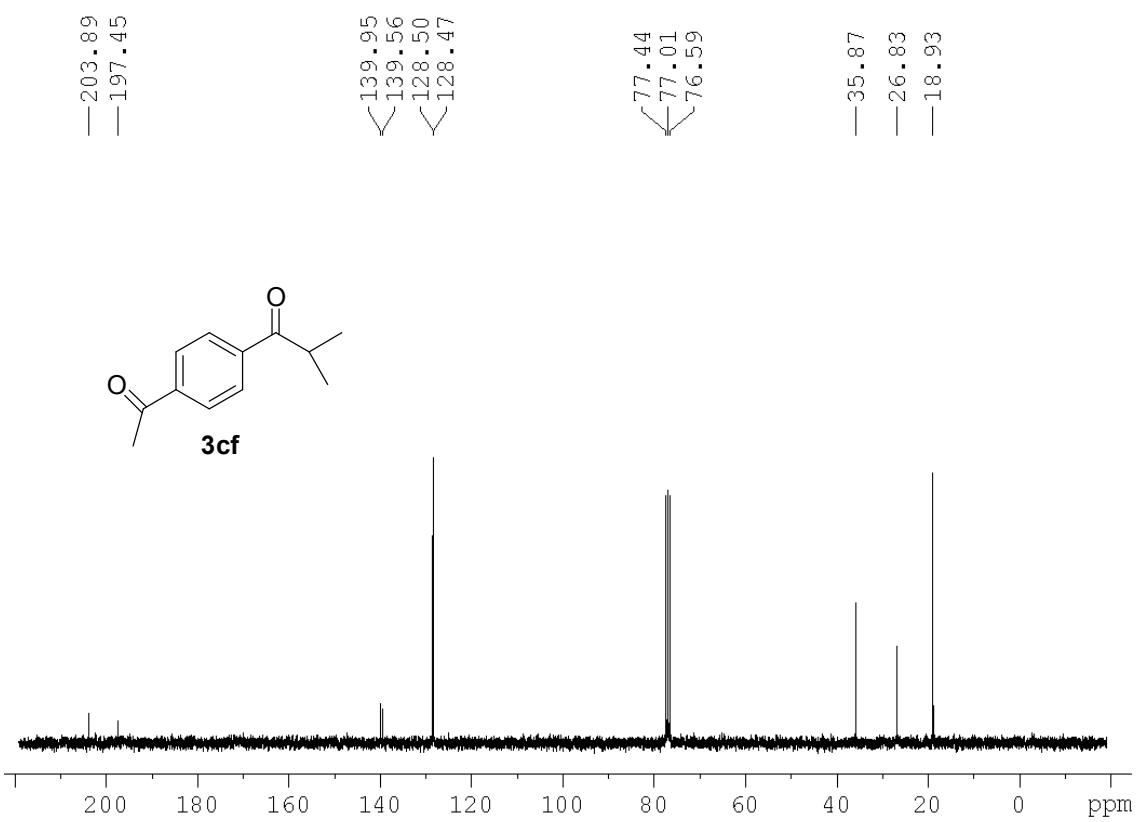
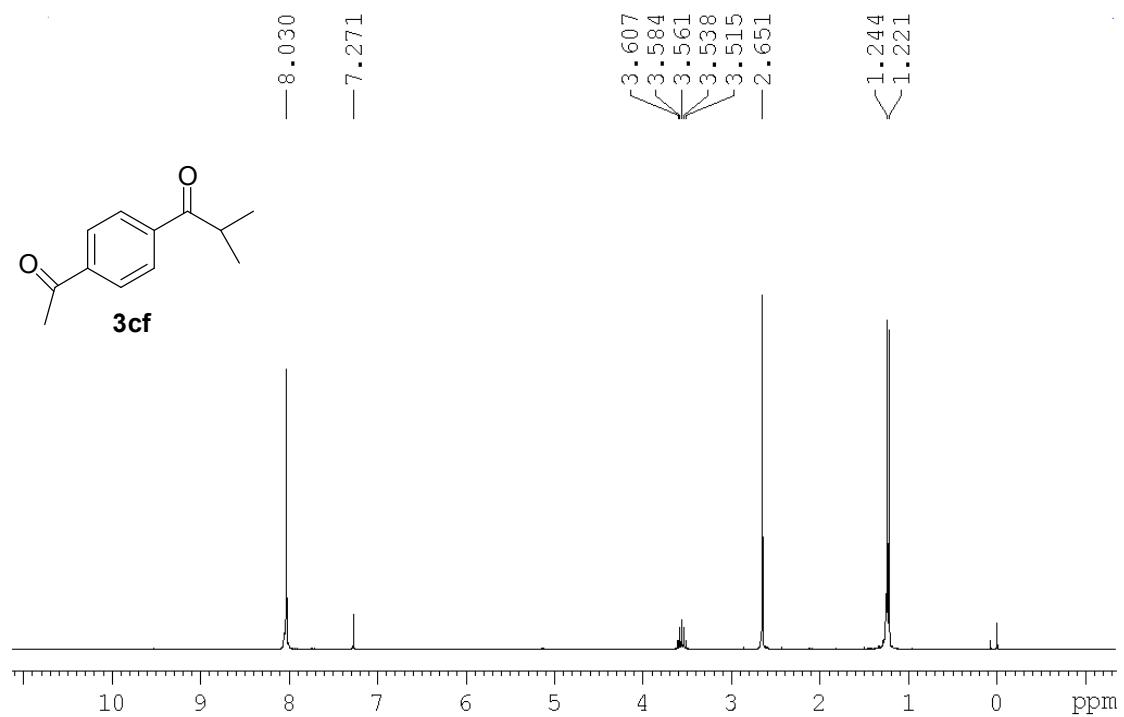












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