

## Arylation of $\alpha$ -Pivalate Ketones via Ni-Catalyzed sp<sup>3</sup> C–O Activation with Arylboroxine

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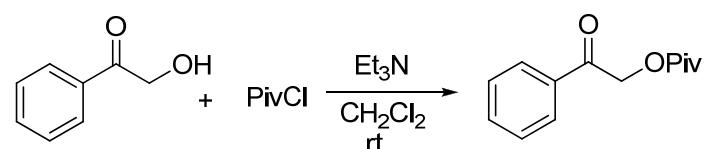
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**General:**

All the reactions were carried out under nitrogen atmosphere using standard Schlenk technique.  $\text{NiCl}_2(\text{PCy}_3)_2$  was synthesized according to literature method<sup>1</sup>.  $\text{Ni}(\text{COD})_2$ , boronic acids and  $\text{NaOtBu}$  were purchased from Alfa Aesar Company. Toluene was freshly distilled over sodium with the use of diphenyl ketone as an indicator under nitrogen. *N,N*-dimethyl formate (DMF) was dried using standard method. Pivalates were prepared by treating the corresponding alcohols with trimethyl amine followed by PivCl in  $\text{CH}_2\text{Cl}_2$ .  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR (50 MHz) were registered on Varian 300 M or 200 M spectrometers with  $\text{CDCl}_3$  as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the  $^1\text{H}$  spectrum as 0.00 ppm and  $\text{CDCl}_3$  resonance in the  $^{13}\text{C}$  spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. IR, GC, MS, and HRMS were performed by the State-authorized Analytical Center in Peking University.

**Typical procedure:**

**Synthesis of 2-oxo-2-phenylethyl pivalate (1a):**



2-hydroxyacetophenone (680 mg, 5 mmol) was placed in a dry 100 ml flask, and DCM (30 mL) was added into the flask. Then  $\text{Et}_3\text{N}$  (1.01 g, 10 mmol) and PivCl (720 mg, 6 mmol) were added at room temperature. The resulting mixture was stirred overnight. 40 mL distilled water was added into the mixture and the aqueous phase was extracted with DCM (30 mL). The combined organic layers were washed with brine before being dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of solvent, the product was obtained in 88% yield by silicon gel column chromatography.

The substrates of **1j-1y** were prepared in a similar way.

**The reaction of  $\alpha$ -pivalate ketones with boronic acids:**

An oven-dried Schlenk tube was charged with  $\alpha$ -pivalate ketones **1** (0.25 mmol), boronic acid **2** (1.0 mmol) or boroxines (0.33 mmol),  $\text{Ni}(\text{PCy}_3)_2\text{Cl}_2$  (17.3 mg, 0.025 mmol), and  $\text{NaOtBu}$  (48 mg, 0.5 mmol).

The tube was evacuated and refilled with N<sub>2</sub> and this process was repeated three times. Then freshly distilled toluene (1.0 mL) and DMF (0.5 mL) were injected and the resulting mixture was stirred at 100 °C for 40 minutes. The mixture was cooled to room temperature under N<sub>2</sub>, quenched via the addition of saturated aqueous ammonium chloride (4 mL) and water (8 mL). The aqueous phase was extracted with ethyl acetate (10 x 3 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The product was obtained by silicon gel short column chromatography.

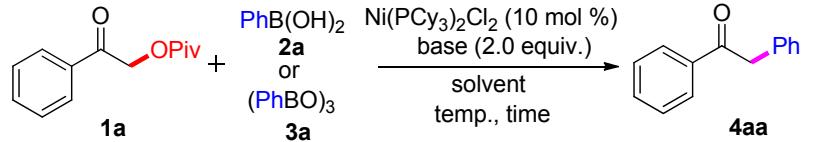
The products of **4aa-4af** and **4ja-4ya** were prepared in the same way

#### **The reaction of α-pivalate ketones with boroxines:**

An oven-dried Schlenk tube was charged with α-pivalate ketones **1** (0.25 mmol), boroxines **3** (0.33 mmol), Ni(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (17.3 mg, 0.025 mmol), and NaOtBu (48 mg, 0.5 mmol). The tube was evacuated and refilled with N<sub>2</sub> and this process was repeated three times. Then freshly distilled toluene (1.0 mL) and DMF (0.5 mL) were injected and the resulting mixture was stirred at 100 °C for 60 minutes. The mixture was cooled to room temperature under N<sub>2</sub>, quenched via the addition of saturated aqueous ammonium chloride (4 mL) and water (8 mL). The aqueous phase was extracted with ethyl acetate (10 x 3 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The product was obtained by silicon gel short column chromatography.

The products of **4ag-4an** were prepared in the same way.

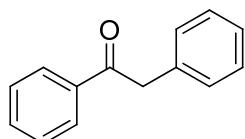
**Table S1.** Investigation of the Suzuki-Miyaura Reaction under Various Conditions.<sup>a</sup>



entry	<b>2</b> (equiv)	base	temp. (°C)	time	solvent	<b>4aa</b> (%) <sup>b</sup>
1	<b>2a</b> (2.0)	NaOtBu	90	10 (h)	PhMe	24
2	<b>2a</b> (2.0)	KOtBu	90	10 (h)	PhMe	14
3	<b>2a</b> (2.0)	LiOtBu	90	10 (h)	PhMe	< 5
4	<b>2a</b> (2.0)	NaH	90	10 (h)	PhMe	8
5	<b>2a</b> (2.0)	K <sub>3</sub> PO <sub>4</sub>	90	10 (h)	PhMe	-
6	<b>2a</b> (2.0)	K <sub>2</sub> CO <sub>3</sub>	90	10 (h)	PhMe	-
7	<b>2a</b> (2.0)	Cs <sub>2</sub> CO <sub>3</sub>	90	10 (h)	PhMe	-
8	<b>2a</b> (2.0)	LiNEt <sub>2</sub>	90	10 (h)	PhMe	-
9	<b>3a</b> (1.3)	NaOtBu	90	10 (h)	PhMe	32
10	<b>3a</b> (1.3)	NaOtBu	80	10 (h)	PhMe	33
11	<b>3a</b> (1.3)	NaOtBu	100	10 (h)	PhMe	41
12	<b>2a</b> (4.0)	NaOtBu	80	3 (h)	PhMe	43
13	<b>2a</b> (4.0)	NaOtBu	80	3 (h)	dioxane	15
14	<b>2a</b> (4.0)	NaOtBu	80	3 (h)	DMF	30
15	<b>2a</b> (4.0)	NaOtBu	80	3 (h)	DCE	21
16	<b>2a</b> (4.0)	NaOtBu	90	5.5 (h)	PhMe/DCE (2 : 1)	34
17	<b>2a</b> (4.0)	NaOtBu	100	40 (min)	PhMe/DMF (1 : 1)	65 <sup>c</sup>
18	<b>2a</b> (4.0)	NaOtBu	100	40 (min)	PhMe/DMF (3 : 1)	83 (75 <sup>c</sup> )
19	<b>2a</b> (4.0)	NaOtBu	100	40 (min)	PhMe/DMF (2 : 1)	81 <sup>c</sup>
20	<b>2a</b> (4.0)	NaOtBu	90	2 (h)	PhMe/DMF (2 : 1)	71 <sup>c</sup>
21	<b>2a</b> (4.0)	NaOtBu	80	3 (h)	PhMe/DMF (2 : 1)	76 <sup>c</sup>
22	<b>3a</b> (1.3)	NaOtBu	100	40 (min)	PhMe/DMF (2 : 1)	71 <sup>c</sup>

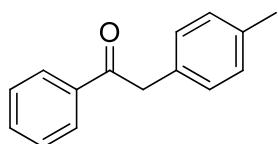
<sup>a</sup> All the reactions were carried out on the scale of 0.25 mmol of **1a** and 1.0 mmol of **2a** or 0.33 mmol of **3a** under N<sub>2</sub>. <sup>b</sup> GC yield with the use of n-dodecane as an internal standard. <sup>c</sup> Isolated yield.

**Analytical and spectral data of compounds 4aa-4an and 4ja-4ya**



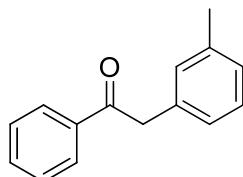
**1,2-diphenylethanone (4aa)<sup>2</sup>**

The product was obtained (39.7 mg, 81%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.08-8.09 (m, 2H), 7.28-7.64 (m, 8H), 4.35 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.5, 136.4, 134.6, 133.0, 129.3, 128.5, 128.3, 126.7, 45.3; MS (EI) m/z: 196 (M<sup>+</sup>).



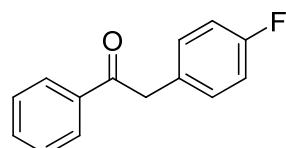
**1-phenyl-2-p-tolylethanone (4ab)<sup>3</sup>**

The product was obtained (39.4 mg, 75%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.99-8.02 (m, 2H), 7.52-7.54 (m, 1H), 7.42-7.47 (m, 2H), 7.14-7.24 (m, 4H), 4.24 (s, 2H), 2.31 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.9, 136.4, 133.0, 131.5, 129.4, 129.3, 128.6, 128.54, 128.53, 45.1, 21.0; MS (EI) m/z: 210 (M<sup>+</sup>).



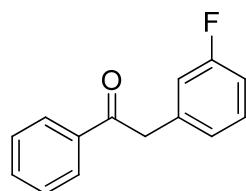
**1-phenyl-2-m-tolylethanone (4ac)<sup>4</sup>**

The product was obtained (35.1 mg, 67%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.06-8.09 (m, 2H), 7.51-7.61 (m, 3H), 7.27-7.32 (m, 2H), 7.11-7.14 (m, 2H), 4.30 (s, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 198.1, 138.3, 133.1, 130.1, 128.62, 128.6, 128.5, 127.6, 126.5, 45.5, 21.4; MS (EI) m/z: 210 (M<sup>+</sup>).



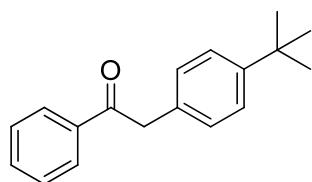
**2-(4-fluorophenyl)-1-phenylethanone (4ad)<sup>5</sup>**

The product was obtained (40.7 mg, 76%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.00-8.03 (m, 2H), 7.56-7.59 (m, 1H), 7.46-7.51 (m, 2H), 7.21-7.27 (m, 2H), 7.00-7.06 (m, 2H), 4.28 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.6, 164.4, 159.5, 136.5, 133.3, 131.1, 130.9, 130.2, 128.7, 128.5, 115.7, 115.3, 44.5; MS (EI) m/z: 214 (M<sup>+</sup>).



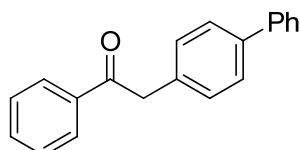
**2-(3-fluorophenyl)-1-phenylethanone (4ae)<sup>4</sup>**

The product was obtained (36.4 mg, 68%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.92-8.19 (m, 2H), 7.55-7.60 (m, 1H), 7.40-7.52 (m, 2H), 7.25-7.32 (m, 1H), 6.92-7.05 (m, 3H), 4.26 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.0, 165.7, 136.4, 133.3, 130.1, 130.0, 128.7, 128.5, 125.2, 116.7, 116.3, 114.1, 113.6, 45.0; MS (EI) m/z: 214 (M<sup>+</sup>).



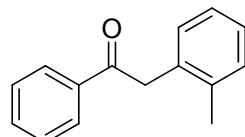
**2-(4-tert-butylphenyl)-1-phenylethanone (4af)<sup>6</sup>**

The product was obtained (44.7 mg, 71%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.01-8.04 (m, 2H), 7.46-7.56 (m, 3H), 7.33-7.36 (m, 2H), 7.19-7.25 (m, 2H), 4.26 (s, 2H), 1.29 (s, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.9, 149.5, 136.9, 133.0, 131.4, 129.1, 128.6, 128.5, 125.6, 44.9, 34.4, 31.3; MS (EI) m/z: 252 (M<sup>+</sup>).



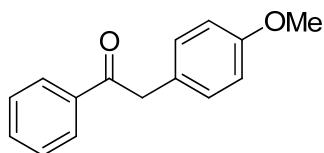
**2-(biphenyl-4-yl)-1-phenylethanone (4ag)<sup>7</sup>**

The product was obtained (45.5 mg, 67%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.03-8.06 (m, 2H), 7.25-7.59 (m, 12H), 4.33 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.7, 140.7, 139.9, 136.7, 133.2, 129.9, 128.7, 128.6, 128.5, 127.4, 127.2, 127.0, 45.1; MS (EI) m/z: 272 (M<sup>+</sup>).



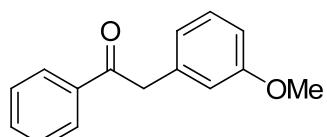
**1-phenyl-2-o-tolylethanone (4ah)<sup>3</sup>**

The product was obtained (28.9 mg, 55%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.02-8.05 (m, 2H), 7.46-7.59 (m, 3H), 7.23-7.15 (m, 4H), 4.32 (s, 2H), 2.28 s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.5, 136.8, 133.4, 133.1, 130.3, 130.2, 128.6, 128.3, 127.2, 126.1, 43.4, 19.7; MS (EI) m/z: 210 (M<sup>+</sup>).



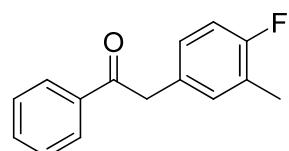
**2-(4-methoxyphenyl)-1-phenylethanone (4ai)<sup>3</sup>**

The product was obtained (34.5 mg, 61%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.97-8.00 (m, 2H), 7.43-7.56 (m, 3H), 7.15-7.18 (m, 2H), 6.83-6.87 (m, 2H), 4.21 (s, 2H), 3.76 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.9, 158.6, 133.0, 130.4, 128.6, 128.54, 128.52, 126.5, 114.1, 55.2, 44.6; MS (EI) m/z: 226 (M<sup>+</sup>).



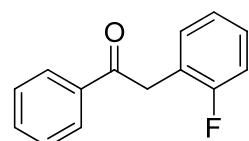
**2-(3-methoxyphenyl)-1-phenylethanone (4aj)<sup>8</sup>**

The product was obtained (36.1 mg, 64%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.98-8.02 (m, 2H), 7.44-7.54 (m, 3H), 7.19-7.29 (m, 1H), 6.80-6.86 (m, 3H), 4.24 (s, 2H), 3.76 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.2, 159.6, 136.4, 135.8, 132.8, 129.3, 128.4, 128.3, 128.2, 121.5, 114.8, 112.1, 54.8, 45.2; MS (EI) m/z: 226 (M<sup>+</sup>).



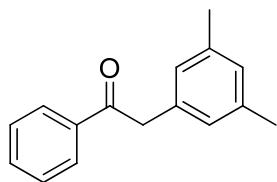
**2-(4-fluoro-3-methylphenyl)-1-phenylethanone (4ak)**

The product was obtained (38.8 mg, 68%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.99-8.02 (m, 2H), 7.44-7.57 (m, 3H), 6.95-7.08 (m, 3H), 4.22 (s, 2H), 2.25 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.6, 162.0, 158.9, 136.5, 133.2, 132.5, 128.7, 128.6, 128.4, 128.2, 128.1, 115.2, 114.9, 44.5, 14.5; MS (EI) m/z: 228 (M<sup>+</sup>); HRMS (ESI): Calcd. (M+H<sup>+</sup>) 229.10232, Found: 229.10196. IR (cm<sup>-1</sup>): ν 2989, 2911, 2900, 1788, 1393, 1077, 1066, 740.



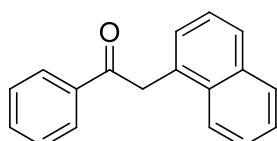
**2-(2-fluorophenyl)-1-phenylethanone (4al)<sup>9</sup>**

The product was obtained (32.6 mg, 61%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.02-8.07 (m, 2H), 7.45-7.58 (m, 3H), 7.22-7.28 (m, 2H), 7.05-7.13 (m, 2H), 4.33 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 196.3, 136.2, 133.3, 131.6, 131.5, 128.9, 128.8, 128.7, 128.4, 124.2, 124.1, 115.6, 115.1, 38.6; MS (EI) m/z: 214 (M<sup>+</sup>). HRMS (ESI): Calcd. (M+H<sup>+</sup>), Found:; IR (cm<sup>-1</sup>): ν 2989, 2911, 2900, 1788, 1393, 1077, 1066, 740.



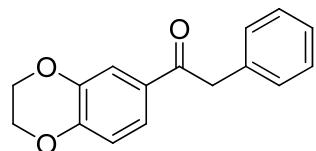
**2-(3,5-dimethylphenyl)-1-phenylethanone (4am)<sup>10</sup>**

The product was obtained (41.4 mg, 74%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.02-8.05 (m, 2H), 7.46-7.59 (m, 3H), 6.81-6.92 (m, 3H), 4.20 (s, 2H),  
2.29 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 198.0, 138.1, 136.6, 134.3, 133.1, 128.6, 128.5, 127.1, 45.3,  
21.2; MS (EI) m/z: 224 (M<sup>+</sup>).



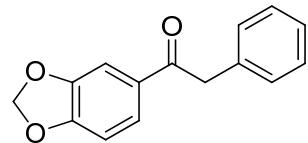
**2-(naphthalen-1-yl)-1-phenylethanone (4an)<sup>6</sup>**

The product was obtained (40.6 mg, 66%) starting from 0.25 mmol of **1a** and 0.33 mmol of boroxines;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.07-8.10 (m, 2H), 7.79-7.89 (m, 3H), 7.57-7.59 (m, 1H), 7.25-7.51 (m,  
6H), 4.74 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.6, 136.6, 133.8, 133.2, 132.2, 131.3, 128.7, 128.6,  
128.4, 128.0, 126.2, 125., 123.8, 43.0; MS (EI) m/z: 246 (M<sup>+</sup>).



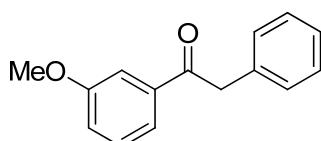
**1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-phenylethanone (4ja)<sup>11</sup>**

The product was obtained (48.9 mg, 77%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.54-7.57 (m, 2H), 7.23-7.34 (m, 5H), 6.88-6.91 (m, 1H), 4.22-4.31 (m,  
4H), 4.19 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 196.1, 148.1, 143.4, 134.9, 130.5, 129.4, 129.3, 128.6,  
126.8, 126.7, 122.79, 122.78, 118.1, 117.3, 117.2, 64.7, 64.1, 45.2; MS (EI) m/z: 254 (M<sup>+</sup>).



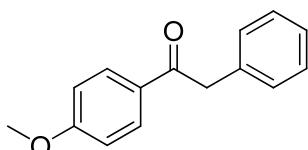
**1-(benzo[d][1,3]dioxol-5-yl)-2-phenylethanone (4ka)<sup>12</sup>**

The product was obtained (43.2 mg, 72%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.61-7.65 (m, 1H), 7.47-7.48 (m, 1H), 7.24-7.35 (m, 5H), 6.82-6.85 (m,  
1H), 6.04 (t, J = 6 Hz, 2H), 4.21 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 195.7, 151.8, 148.2, 131.5, 129.3,  
128.6, 126.8, 125.0, 108.3, 107.9, 101.8, 45.3; MS (EI) m/z: 240 (M<sup>+</sup>).



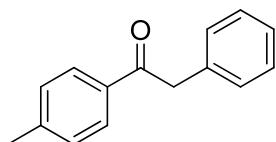
**1-(3-methoxyphenyl)-2-phenylethanone (4la)<sup>3</sup>**

The product was obtained (40.1 mg, 71%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.51-7.60 (m, 3H), 7.07-7.37 (m, 6H), 4.25 (s, 2H), 3.82 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.3, 134.5, 129.6, 129.4, 128.6, 126.9, 121.3, 119.6, 112.9, 55.4, 45.6; MS (EI) m/z: 226 (M<sup>+</sup>).



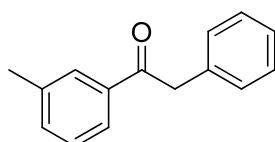
**1-(4-methoxyphenyl)-2-phenylethanone (4ma)<sup>2</sup>**

The product was obtained (36.7 mg, 65%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.99-8.02 (m, 2H), 7.26-7.33 (m, 5H), 6.91-6.94 (m, 2H), 4.24 (s, 2H), 3.86 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 196.2, 163.5, 1350, 130.9, 129.6, 129.4, 129.3, 128.6, 128.5, 126.7, 113.8, 113.7, 55.4, 45.2; MS (EI) m/z: 226 (M<sup>+</sup>).



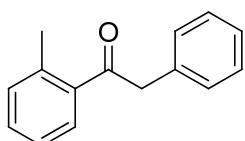
**2-phenyl-1-p-tolylethanone (4na)<sup>2</sup>**

The product was obtained (37.8 mg, 72%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.89-7.92 (m, 2H), 7.23-7.29 (m, 7H), 4.25 (s, 2H), 2.39 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.1, 143.9, 134.7, 134.3, 129.4, 129.2, 128.7, 128.6, 126.8, 45.4, 21.6; MS (EI) m/z: 210 (M<sup>+</sup>).



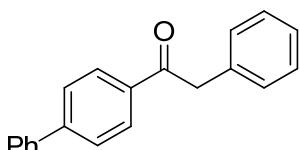
**2-phenyl-1-m-tolylethanone (4oa)<sup>3</sup>**

The product was obtained (36.2 mg, 69%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.79-7.82 (m, 2H), 7.24-7.36 (m, 7H), 4.27 (s, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.9, 156.7, 138.4, 136.7, 134.7, 133.9, 129.4, 129.1, 128.6, 128.4, 126.8, 125.8, 45.5, 21.3; MS (EI) m/z: 210 (M<sup>+</sup>).



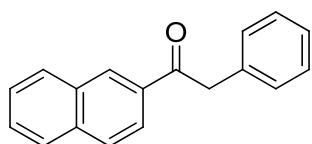
**2-phenyl-1-*o*-tolylethanone (4pa)<sup>6</sup>**

The product was obtained (35.1 mg, 67%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.69-7.72 (m, 1H), 7.20-7.36 (m, 8H), 4.20 (s, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 201.6, 138.4, 134.5, 131.9, 131.3, 129.5, 128.6, 128.5, 126.8, 125.6, 48.6, 21.2; MS (EI) m/z: 210 (M<sup>+</sup>).



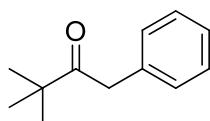
**1-(biphenyl-4-yl)-2-phenylethanone (4qa)<sup>13</sup>**

The product was obtained (49.6 mg, 73%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.06-8.09 (m, 2H), 7.60-7.69 (m, 4H), 7.25-7.46 (m, 8H), 4.31 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.2, 145.8, 139.8, 134.6, 129.4, 129.2, 128.9, 128.6, 127.2, 126.8, 45.5; MS (EI) m/z: 272 (M<sup>+</sup>).



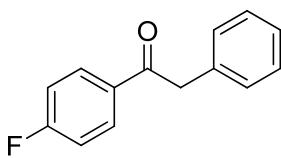
**1-(naphthalen-2-yl)-2-phenylethanone (4ra)<sup>14</sup>**

The product was obtained (41.8 mg, 68%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.55-8.56 (m, 1H), 8.05-8.09 (m, 1H), 7.86-7.98 (m, 3H), 7.55-7.61 (m, 2H), 7.33-7.35 (m, 5H), 4.43 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.6, 135.7, 134.7, 132.5, 130.4, 129.6, 129.5, 128.7, 128.5, 127.7, 126.9, 126.8, 124.2, 45.5; MS (EI) m/z: 246 (M<sup>+</sup>).



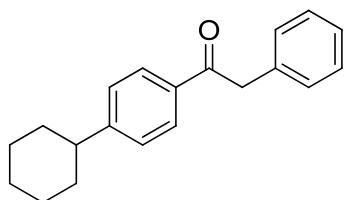
**3,3-dimethyl-1-phenylbutan-2-one (4sa)<sup>15</sup>**

The product was obtained (41.8 mg, 68%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.55-8.56 (m, 1H), 8.05-8.09 (m, 1H), 7.86-7.98 (m, 3H), 7.55-7.61 (m, 2H), 7.33-7.35 (m, 5H), 4.43 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.6, 135.7, 134.7, 132.5, 130.4, 129.6, 129.5, 128.7, 128.5, 127.7, 126.9, 126.8, 124.2, 45.5; MS (EI) m/z: 246 (M<sup>+</sup>).



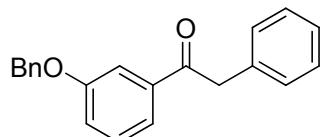
**1-(4-fluorophenyl)-2-phenylethanone (4ta)<sup>3</sup>**

The product was obtained (43.8 mg, 82%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.80-8.06 (m, 2H), 7.24-7.35 (m, 5H), 7.08-7.15 (m, 2H), 4.25 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 196.1, 168.3, 163.3, 134.0, 131.3, 131.1, 129.3, 128.7, 126.9, 115.9, 115.5, 45.5; MS (EI) m/z: 214 (M<sup>+</sup>).



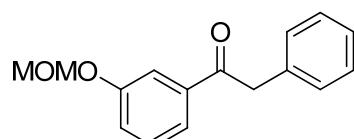
**1-(4-cyclohexylphenyl)-2-phenylethanone (4ua)<sup>16</sup>**

The product was obtained (39.6 mg, 57%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.91-7.98 (m, 2H), 7.11-7.39 (m, 7H), 4.23 (s, 2H), 2.51-2.55 (m, 1H), 1.74-1.92 (m, 6H), 1.36-1.46 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.2, 153.8, 134.9, 134.5, 129.4, 128.8, 128.6, 128.5, 127.1, 127.0, 126.7, 45.4, 44.6, 34.0, 26.7, 26.0; MS (EI) m/z: 278 (M<sup>+</sup>).



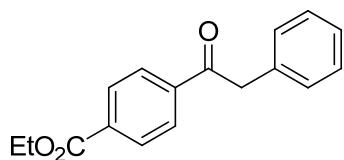
**1-(3-(benzyloxy)phenyl)-2-phenylethanone (4va)<sup>17</sup>**

The product was obtained (64.9 mg, 86%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.59-7.61 (m, 2H), 7.14-7.45 (m, 7H), 5.11 (s, 2H), 4.25 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.2, 158.8, 137.7, 136.2, 134.2, 129.3, 129.1, 128.4, 128.3, 127.8, 127.2, 126.5, 121.2, 120.1, 113.7, 69.9, 45.3; MS (EI) m/z: 302 (M<sup>+</sup>).



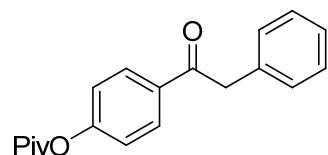
**1-(3-(methoxymethoxy)phenyl)-2-phenylethanone (4wa)**

The product was obtained (45.4 mg, 71%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.65-7.68 (m, 2H), 7.24-7.39 (m, 7H), 5.20 (s, 2H), 4.26 (s, 2H), 3.48 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.2, 157.5, 137.9, 134.4, 129.6, 129.4, 128.6, 126.8, 122.2, 121.2, 116.0, 94.4, 56.1, 45.6; MS (EI) m/z: 256 (M<sup>+</sup>). HRMS (ESI): Calcd. 257.11722, (M+H<sup>+</sup>), Found: 257.11708; IR (cm<sup>-1</sup>): ν 2917, 2849, 1761, 1554, 1393, 1231, 1027, 852, 727.



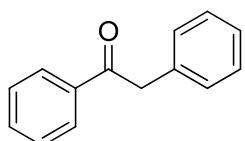
**ethyl 4-(2-phenylacetyl)benzoate (4xa)<sup>11</sup>**

The product was obtained (32.0 mg, 48%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.03-8.13 (m, 4H), 7.24-7.33 (m, 5H), 4.36 (q, J = 7.2, 2H), 4.31 (s, 2H),  
1.41 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 197.2, 165.8, 139.6, 134.2, 1339, 129.8, 129.4,  
128.7, 128.5, 127.0, 61.4, 45.8, 14.3; MS (EI) m/z: 268 (M<sup>+</sup>).

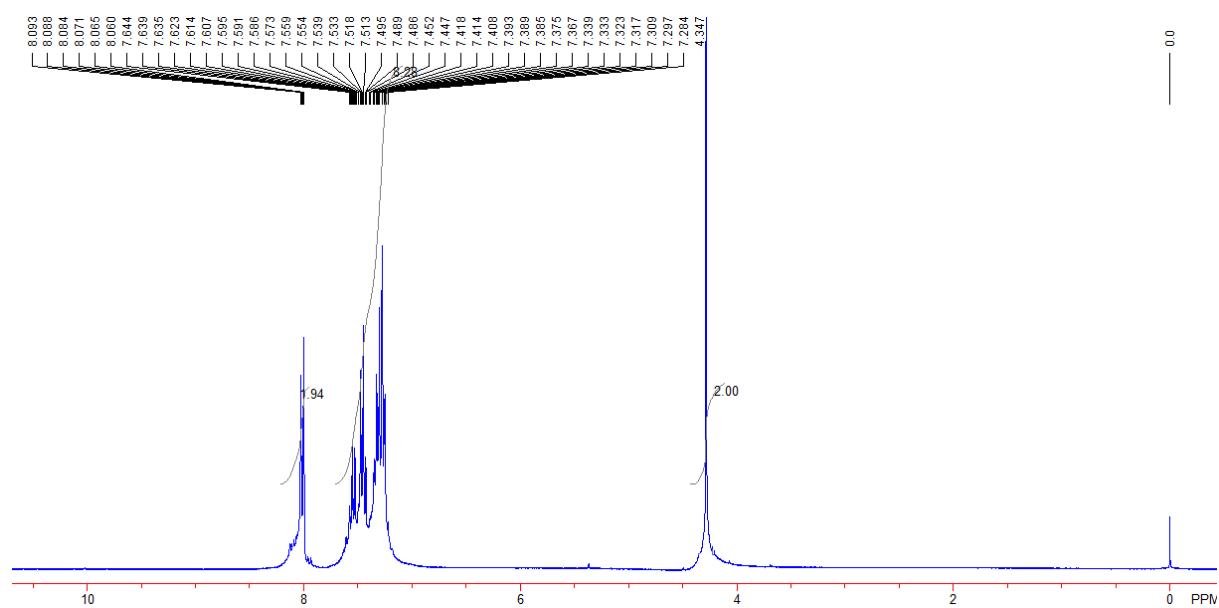


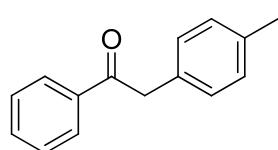
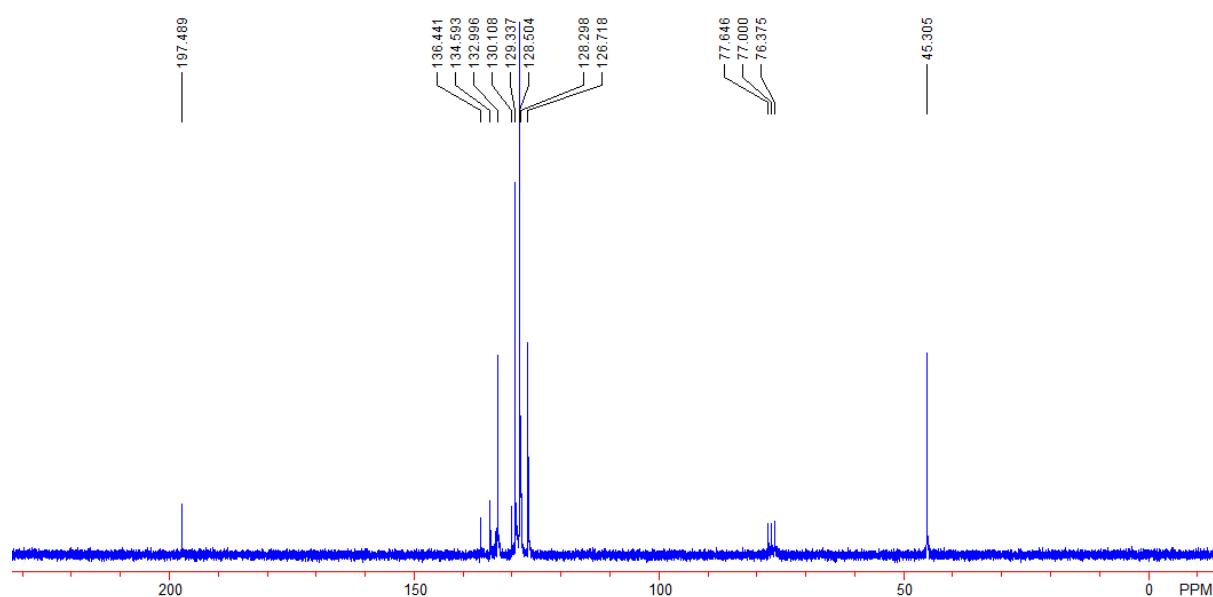
**4-(2-phenylacetyl)phenyl pivalate (4ya)<sup>18</sup>**

The product was obtained (41.4 mg, 56%) starting from 0.25 mmol of **1a** and 1 mmol of boronic acid;  
<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 8.08-8.11 (m, 2H), 7.30-7.38 (m, 5H), 7.19-7.22 (m, 2H), 4.32 (s, 2H),  
1.41 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 196.7, 176.1, 154.6, 134.2, 133.6, 129.9, 128.4, 126.6,  
121.4, 45.2, 38.8, 26.7; MS (EI) m/z: 296 (M<sup>+</sup>).

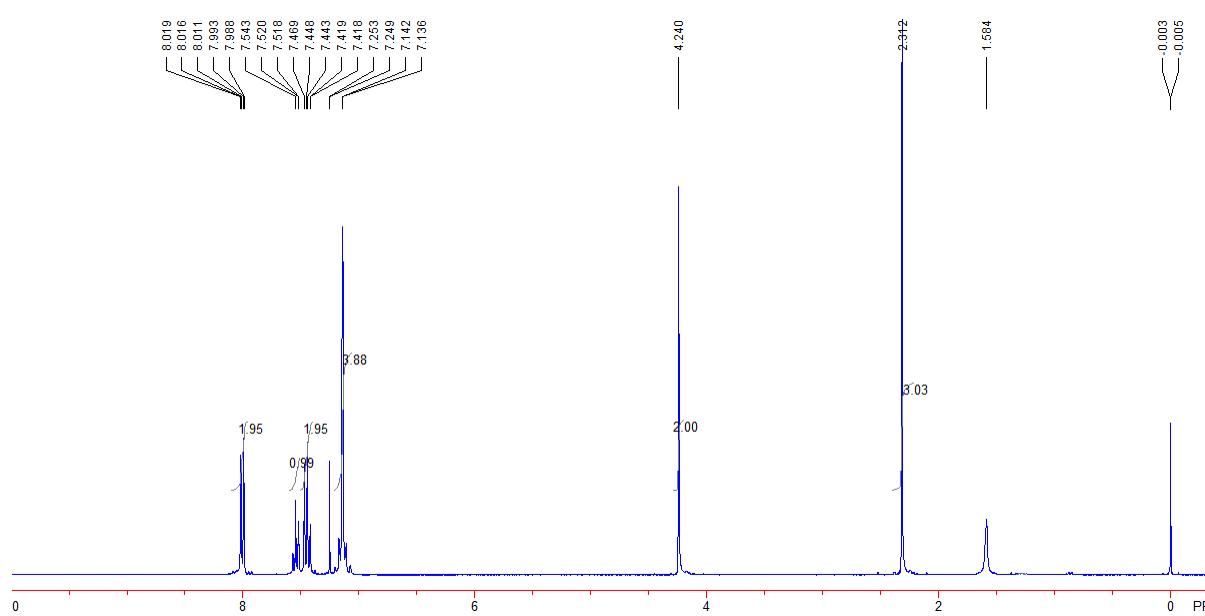


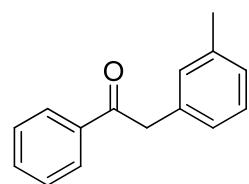
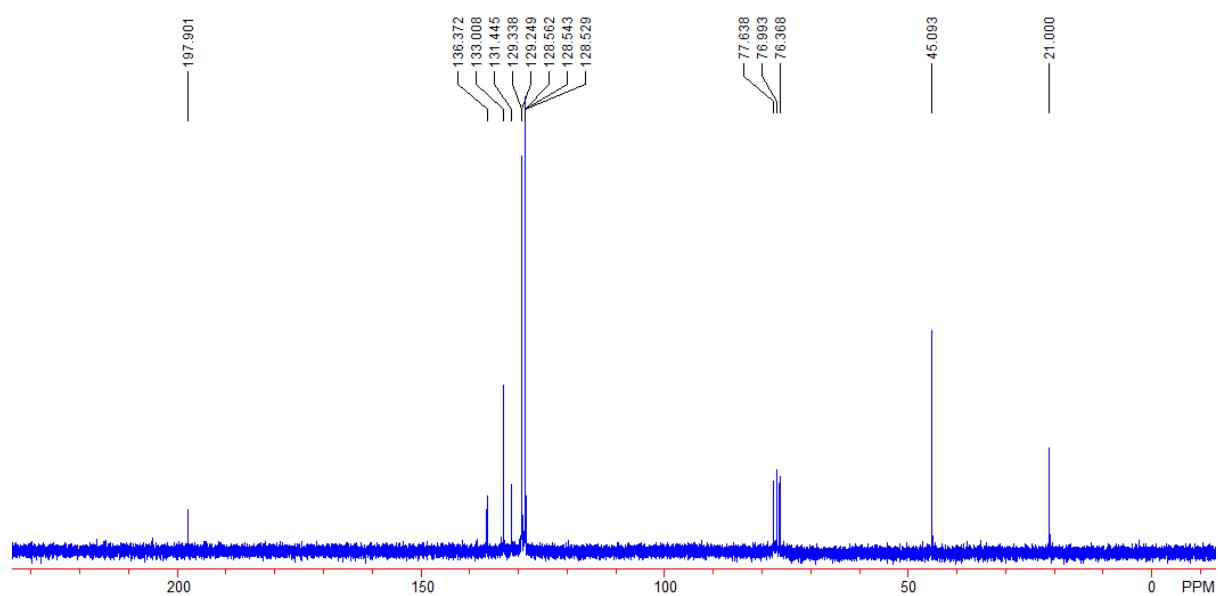
**1,2-diphenylethanone (4aa)**



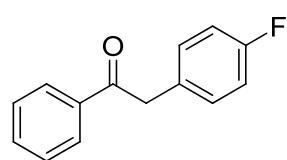
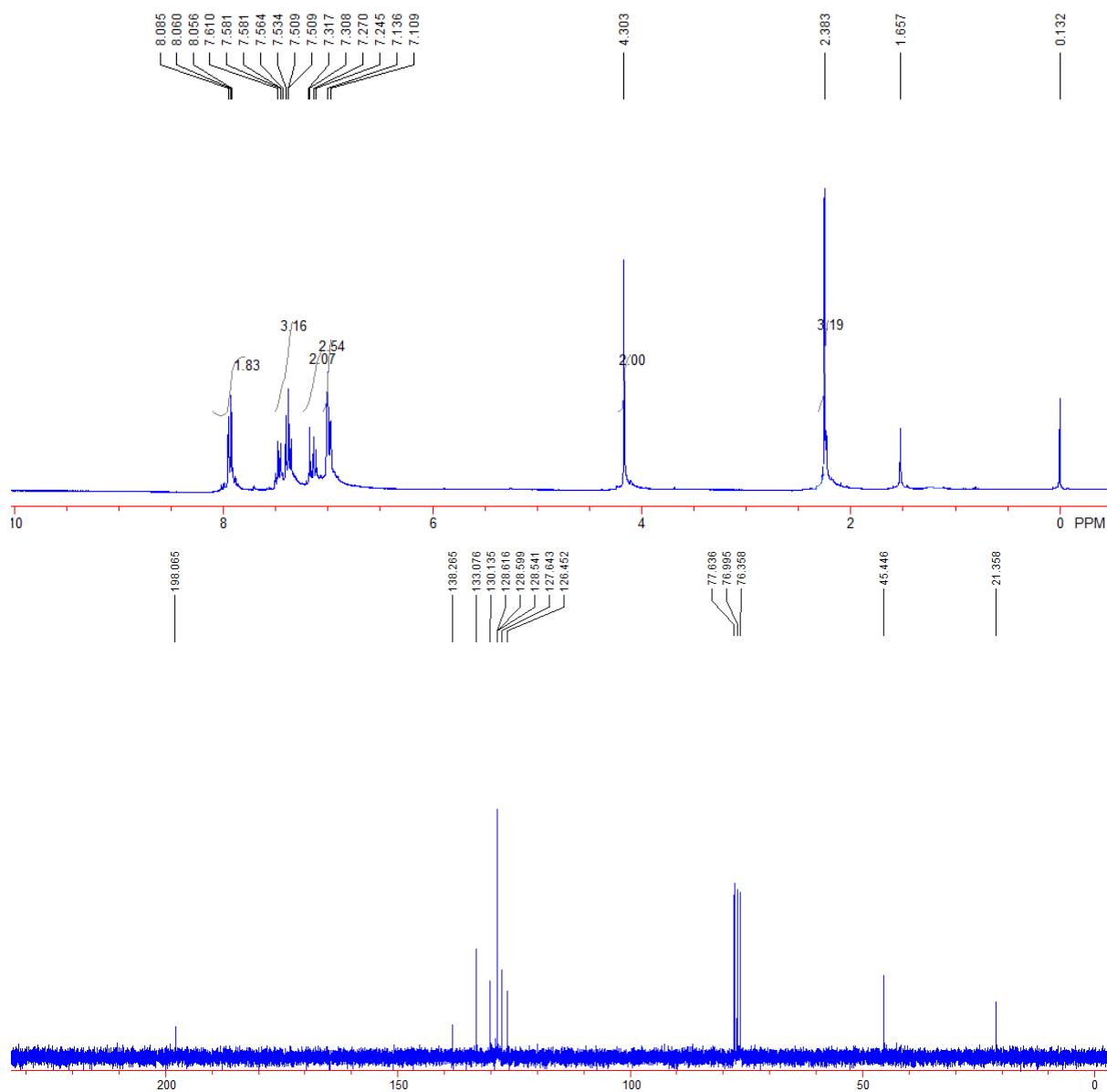


**1-phenyl-2-p-tolylethanone (4ab)**

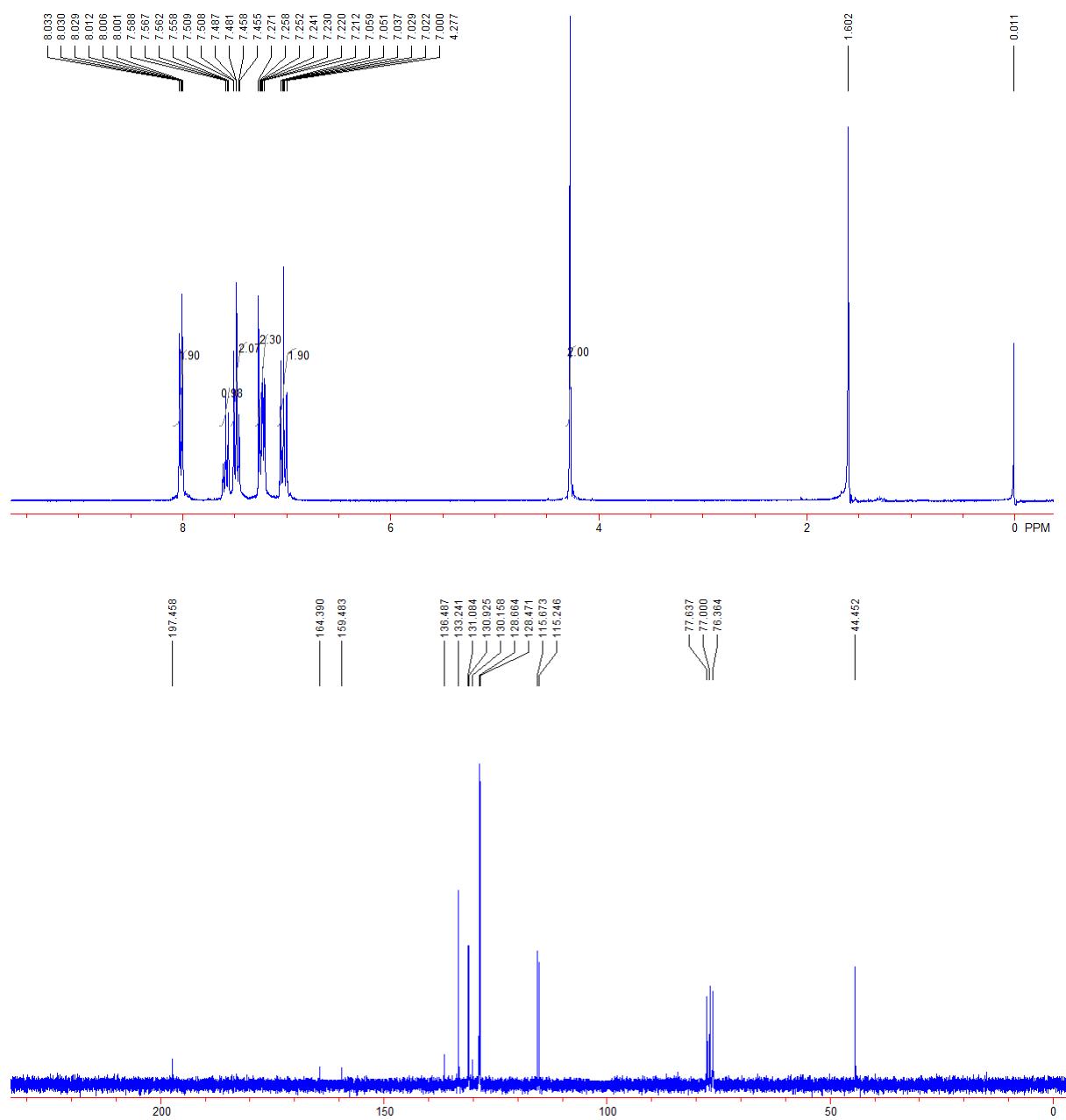


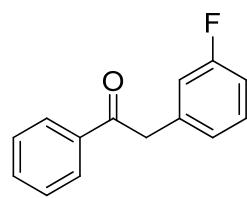


**1-phenyl-2-*m*-tolylethanone (4ac)**

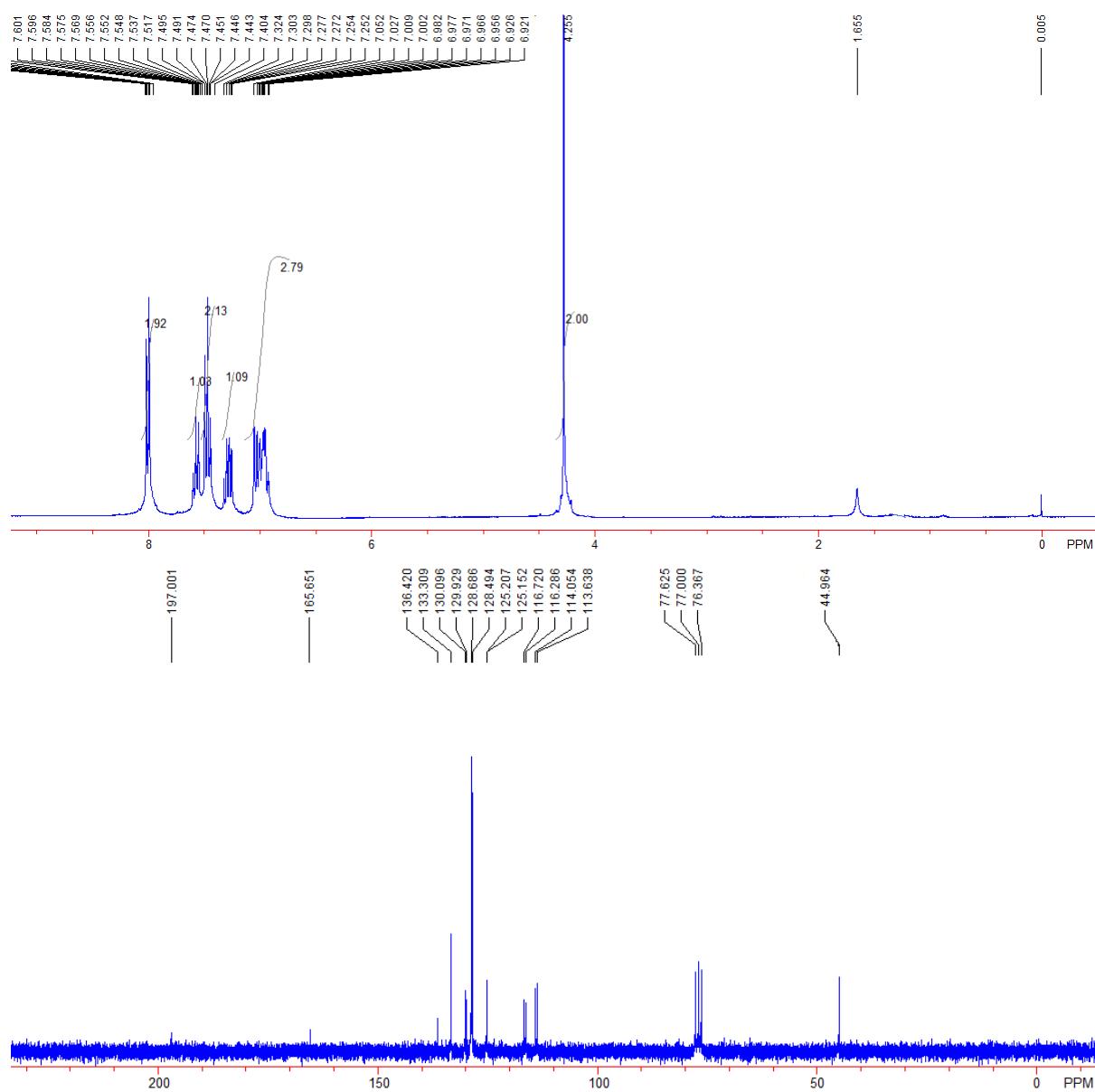


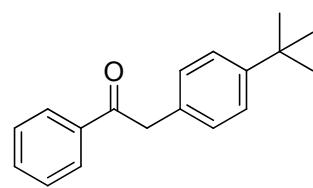
**2-(4-fluorophenyl)-1-phenylethanone (4ad)**



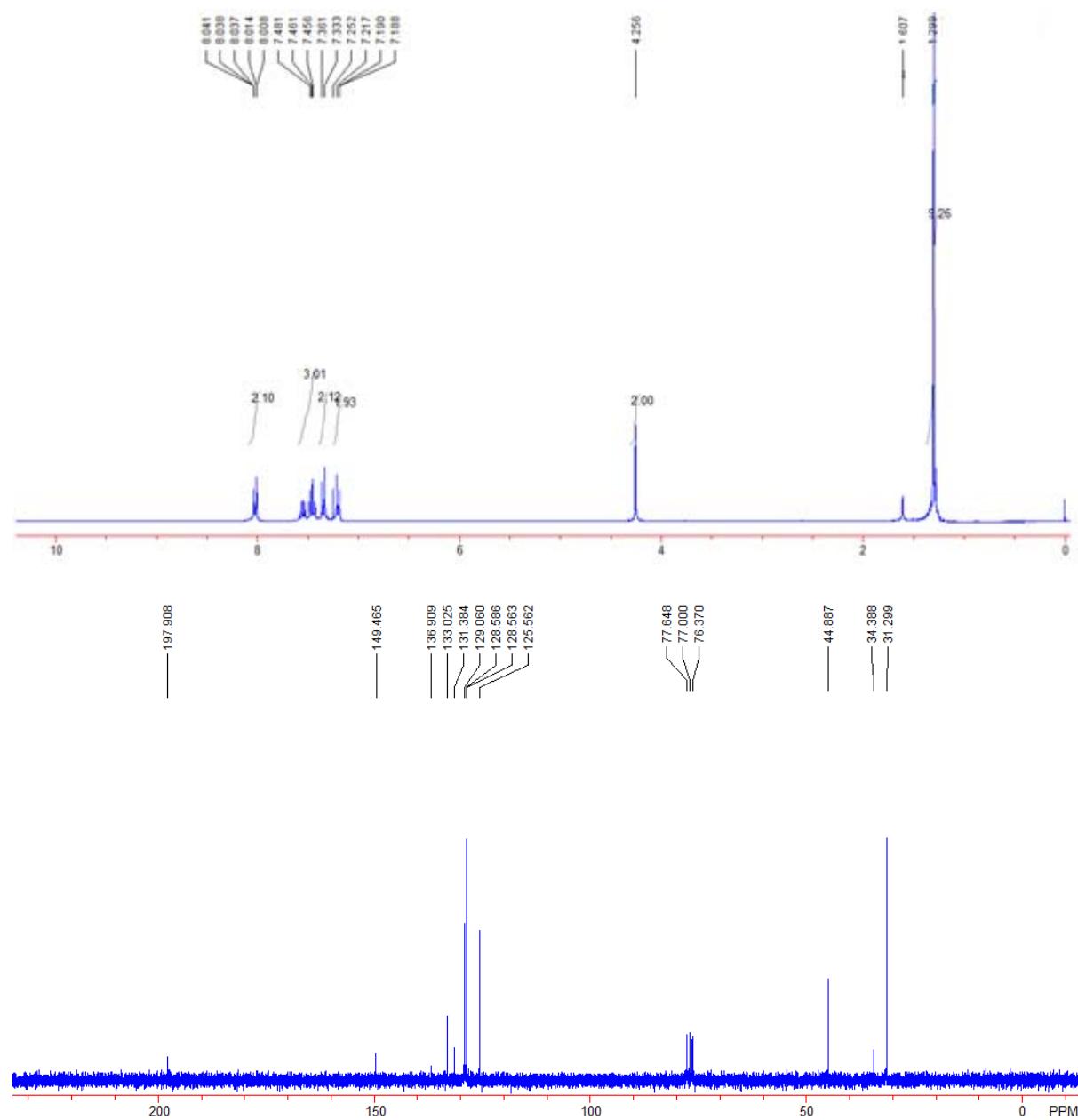


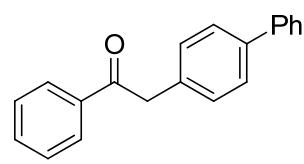
**2-(3-fluorophenyl)-1-phenylethanone (4ae)**



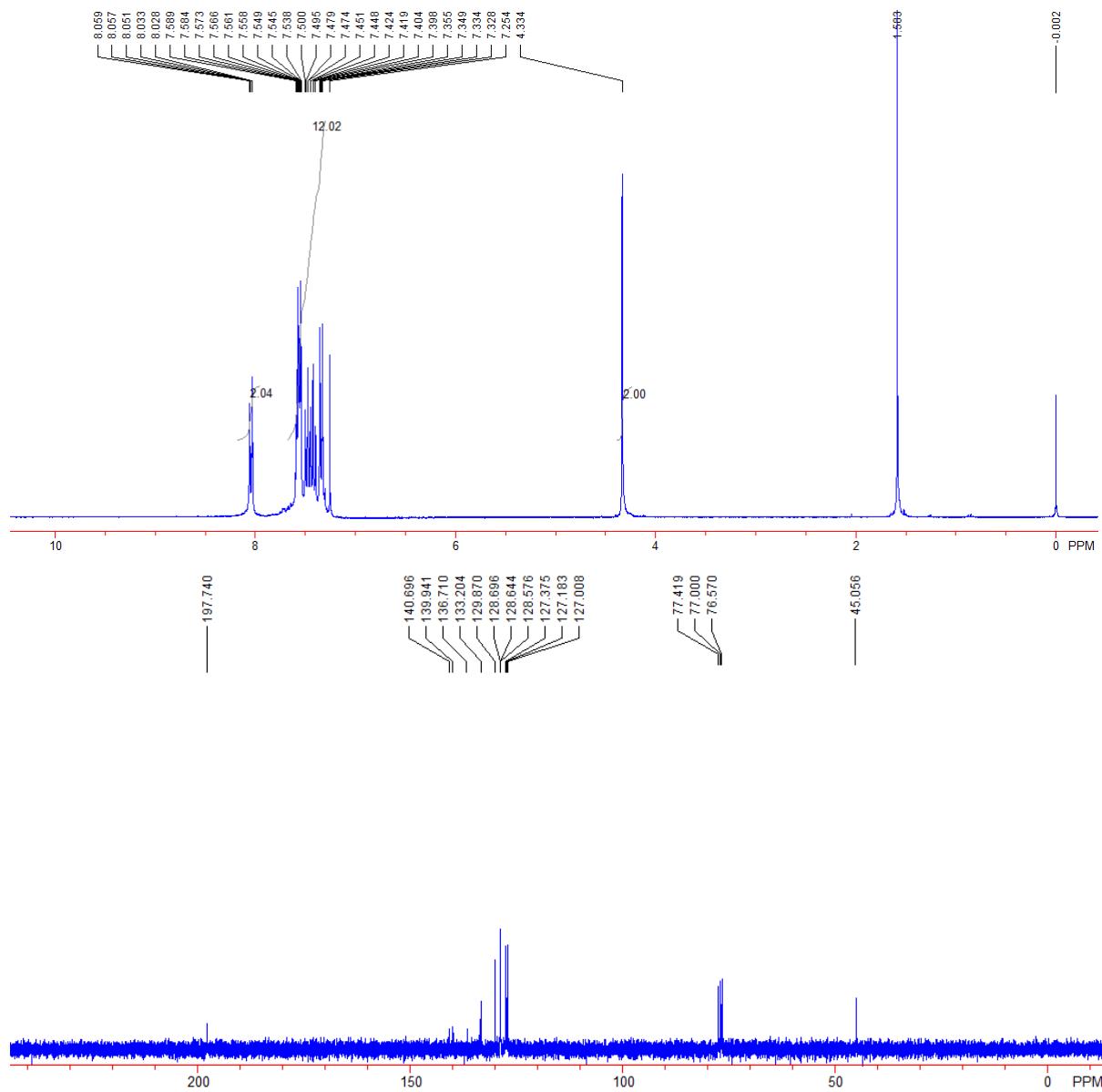


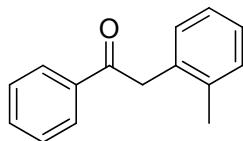
**2-(4-*tert*-butylphenyl)-1-phenylethanone (4af)**



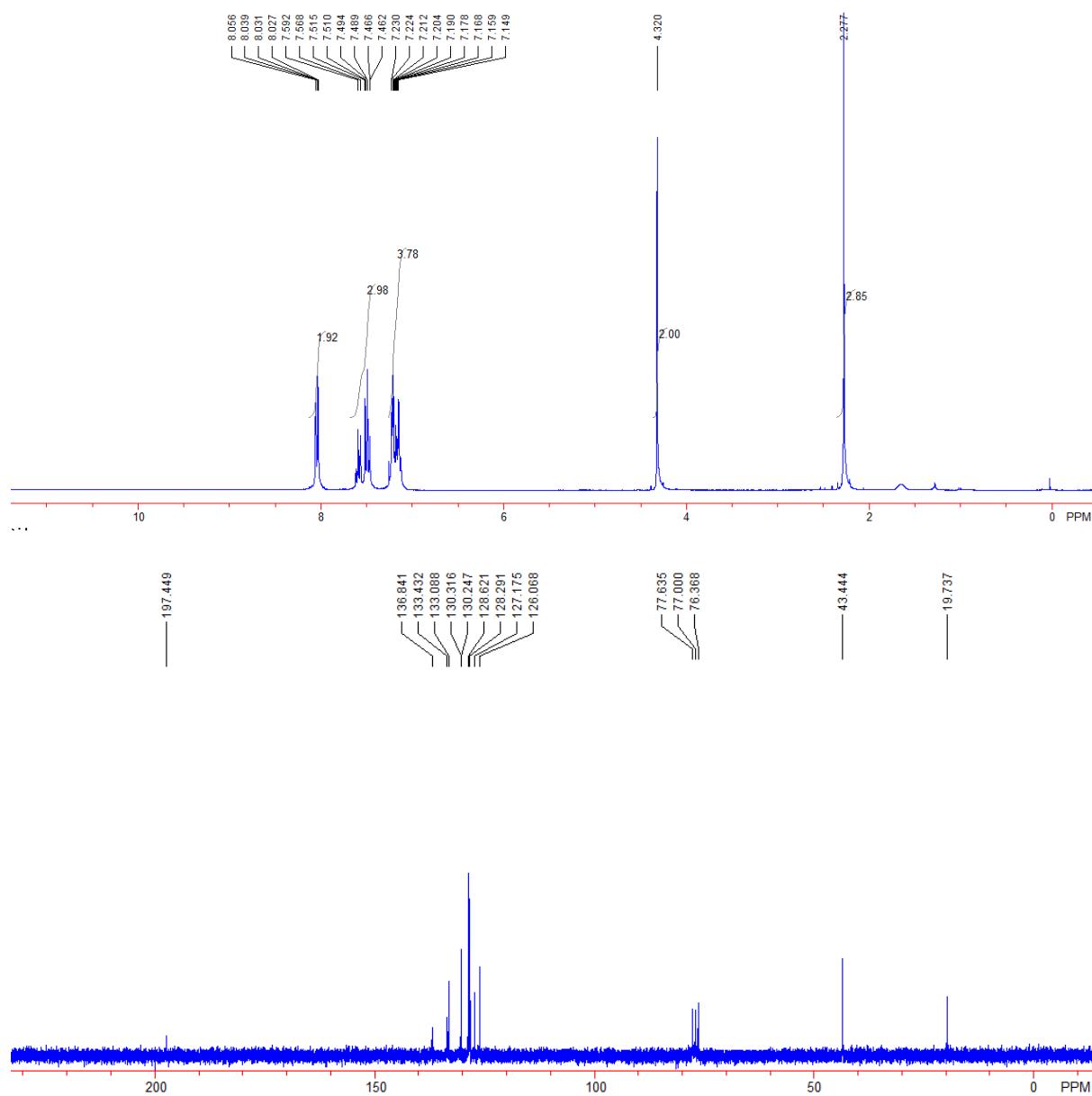


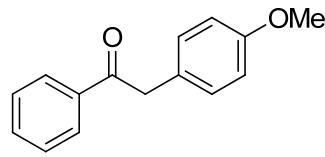
**2-(biphenyl-4-yl)-1-phenylethanone (4ag)**



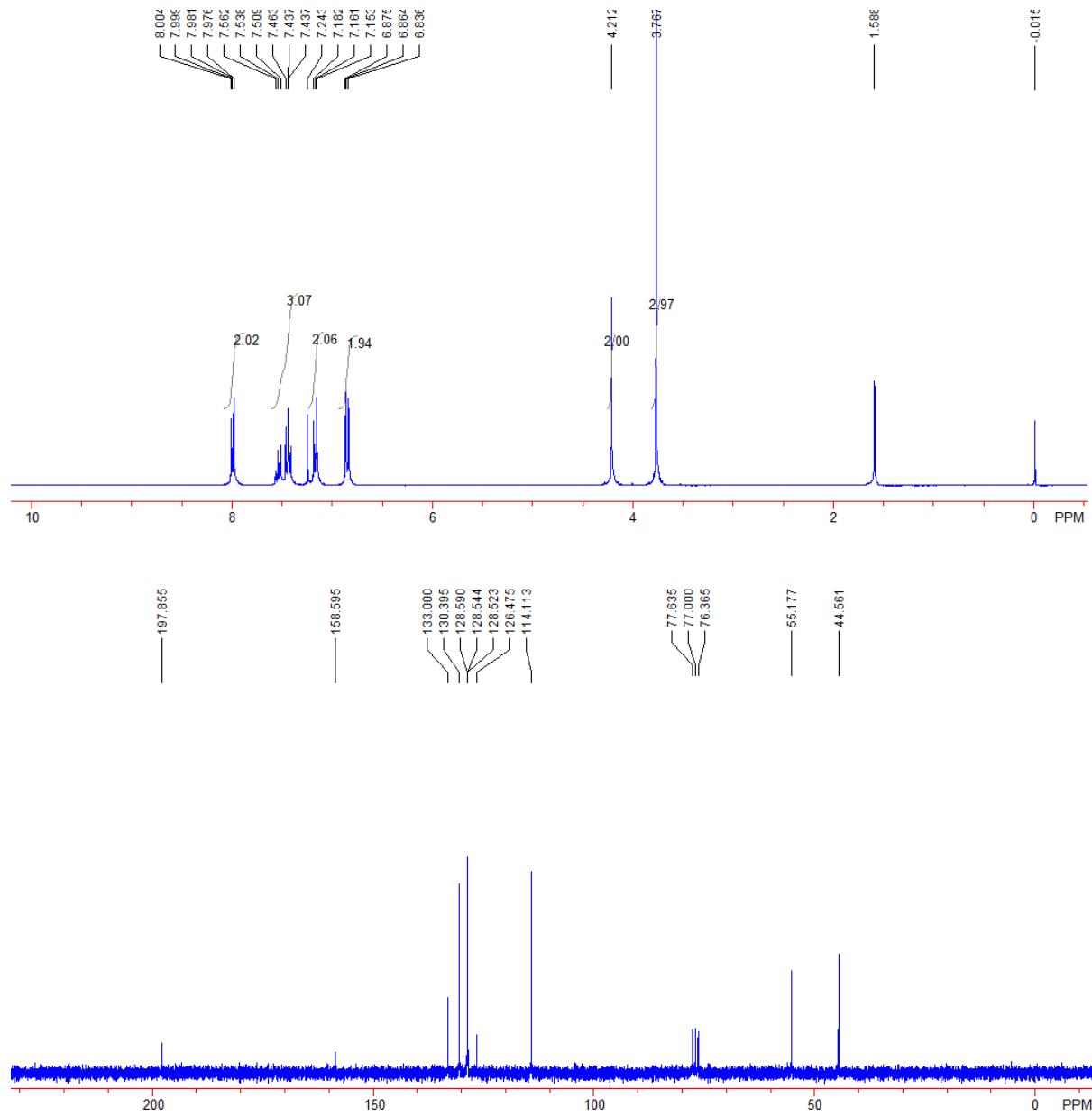


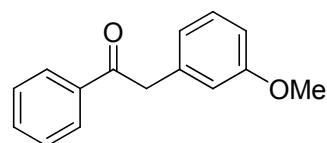
**1-phenyl-2-o-tolylethanone (4ah)**



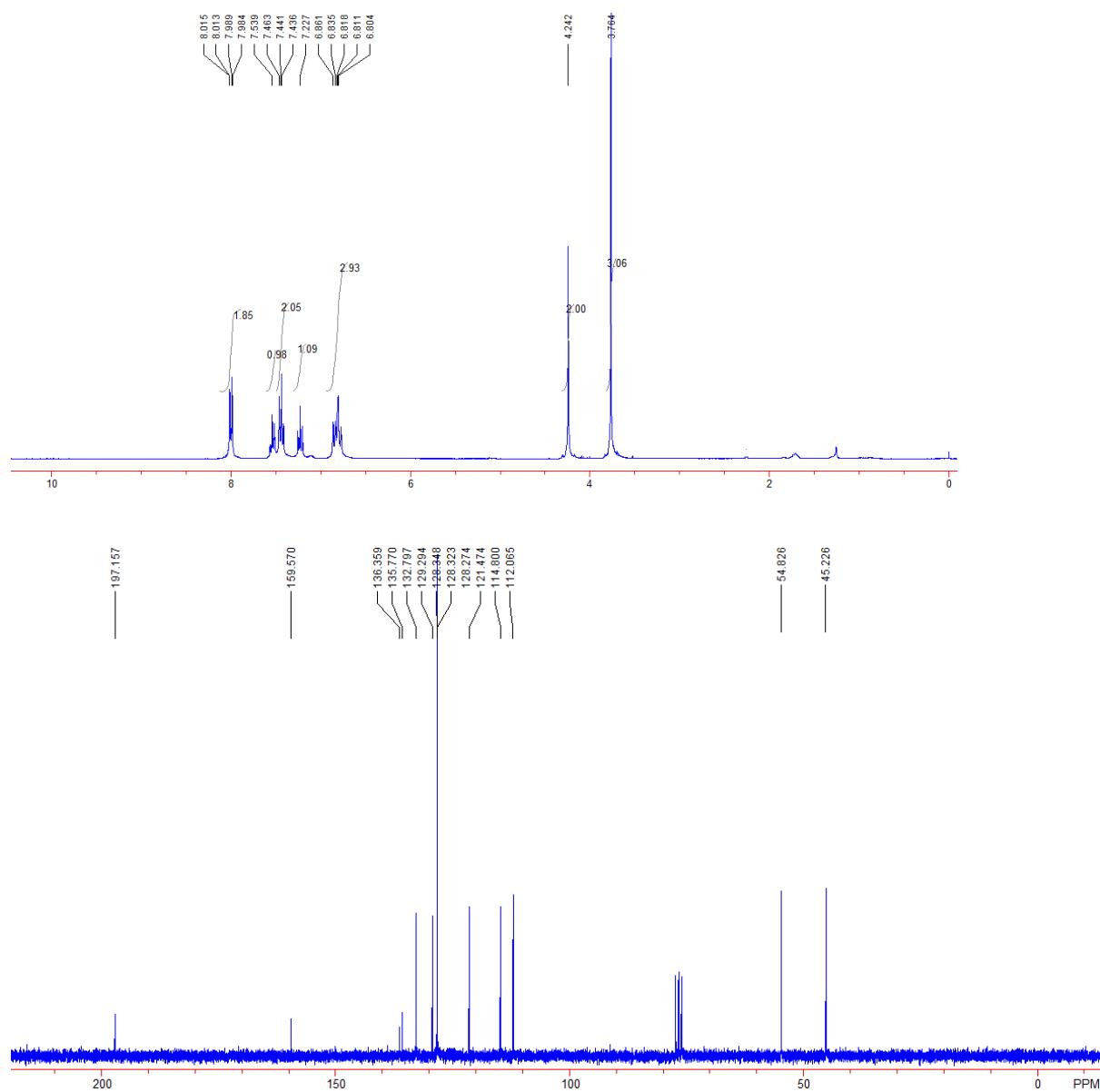


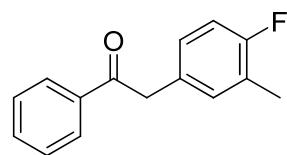
**2-(4-methoxyphenyl)-1-phenylethanone (4ai)**



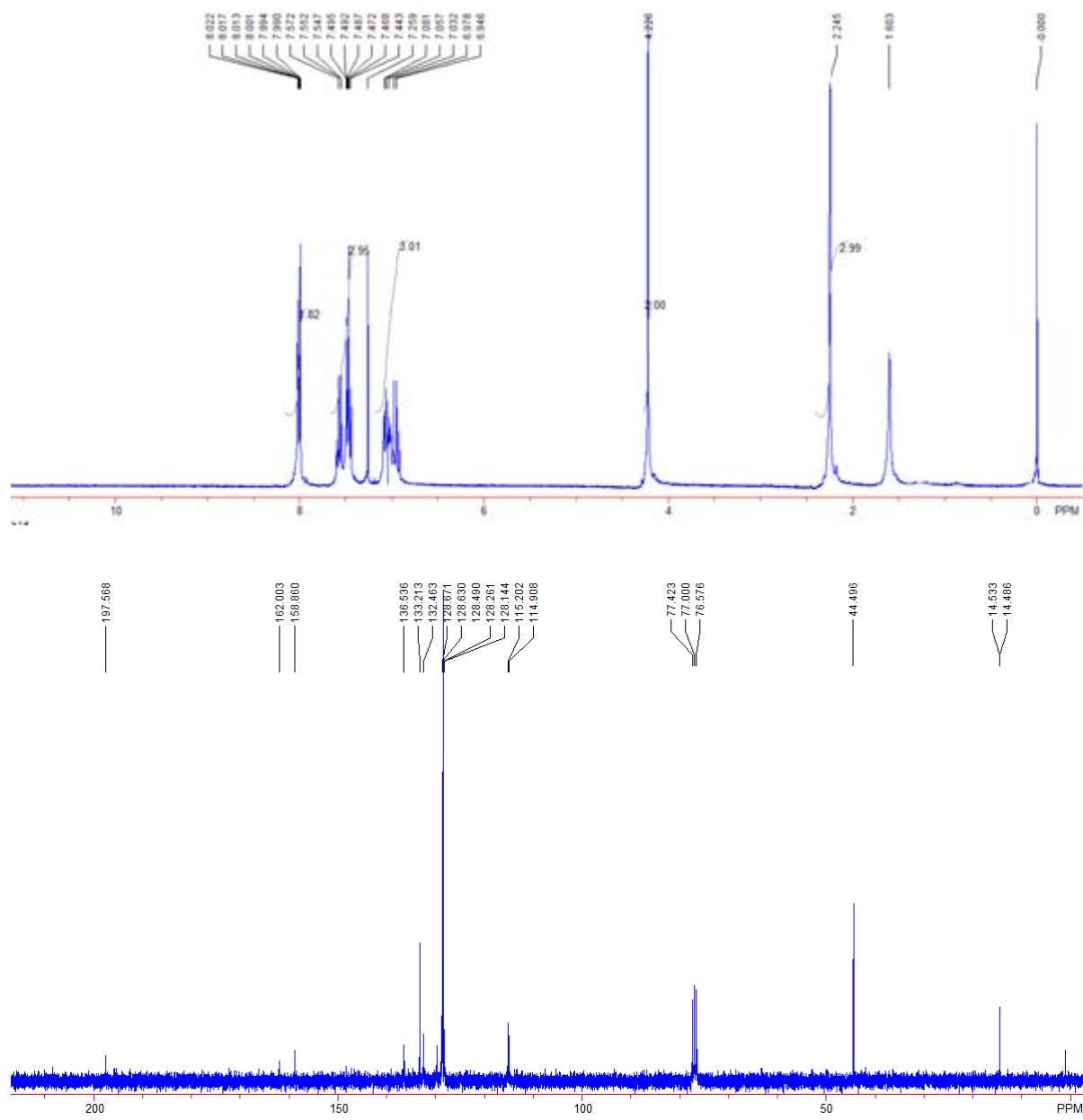


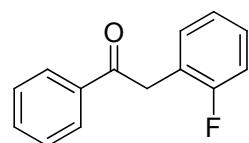
**2-(3-methoxyphenyl)-1-phenylethanone (4aj)**



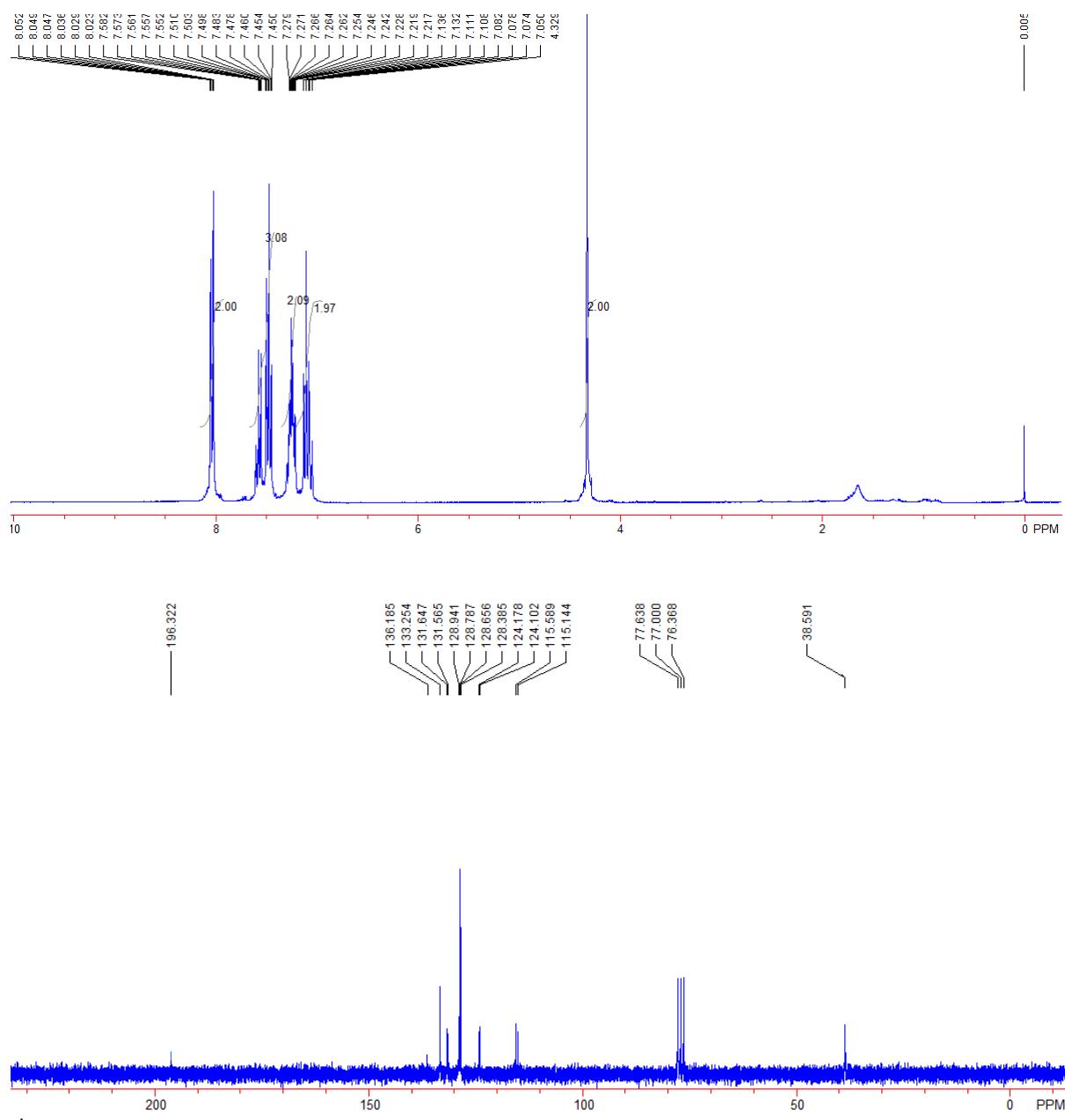


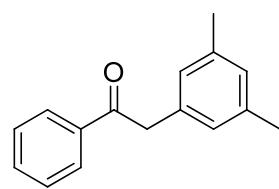
**2-(4-fluoro-3-methylphenyl)-1-phenylethanone (4ak)**



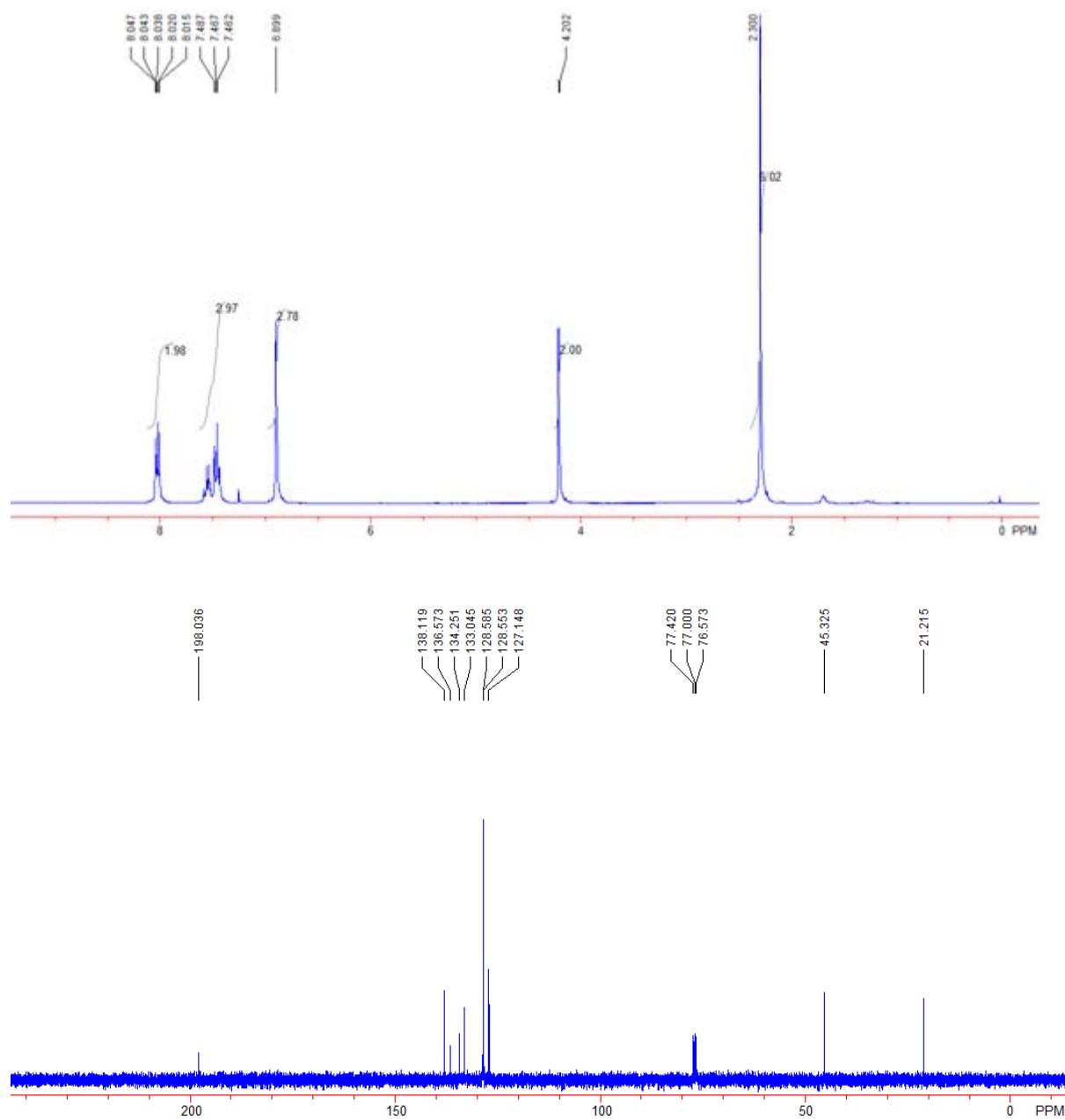


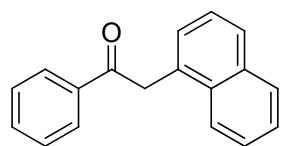
**2-(2-fluorophenyl)-1-phenylethanone (4al)**



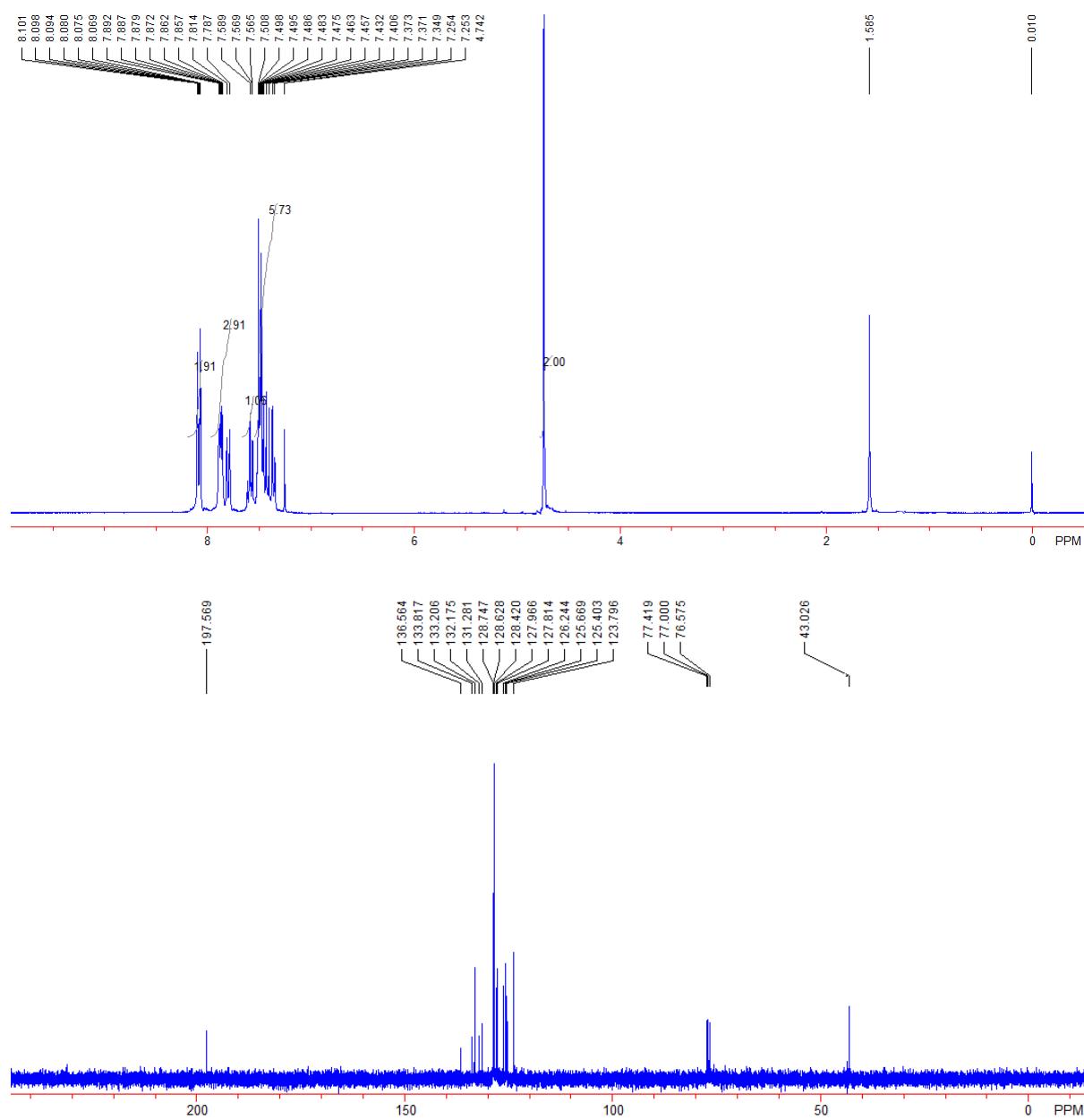


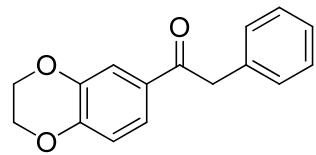
**2-(3,5-dimethylphenyl)-1-phenylethanone (4am)**



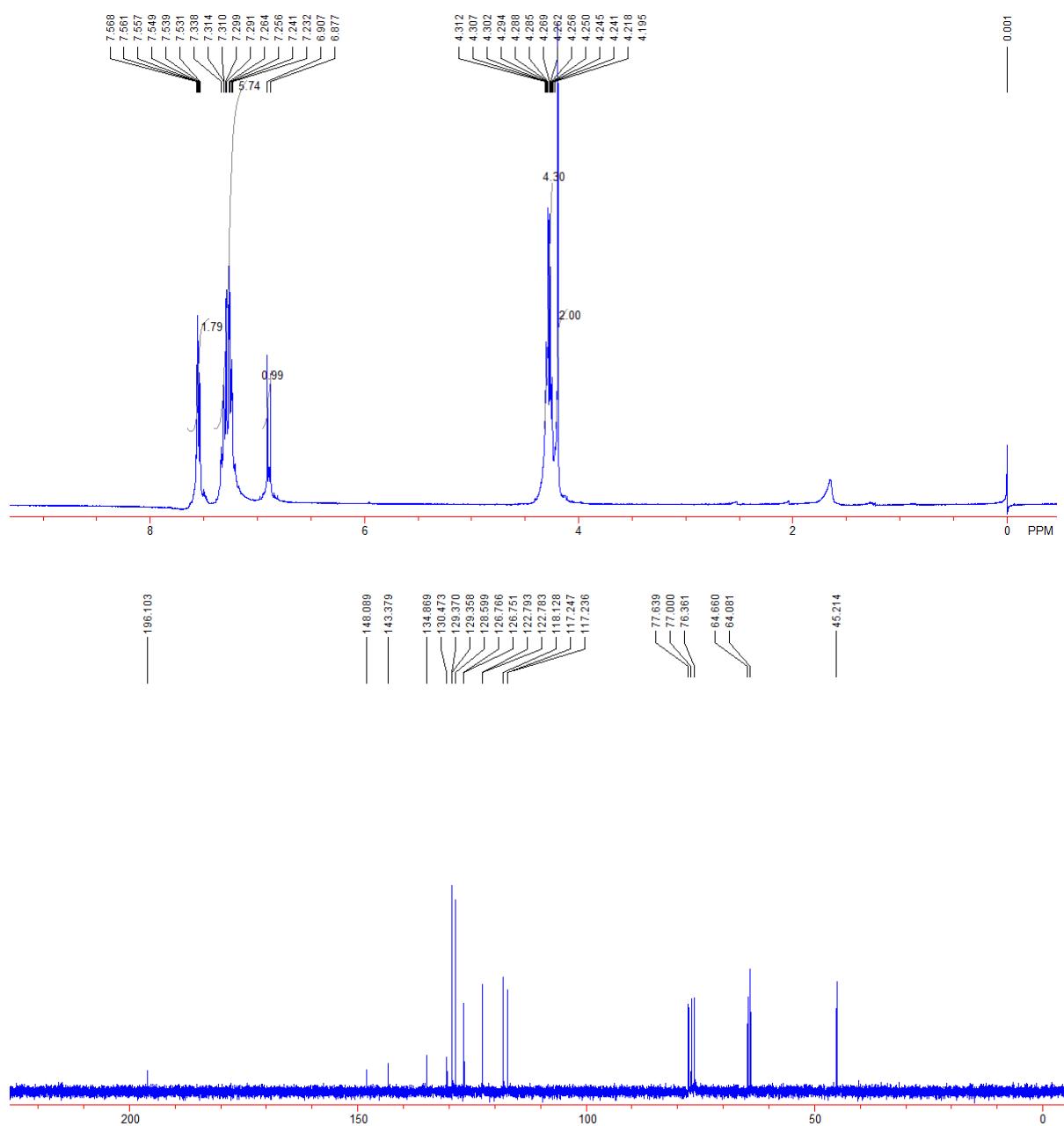


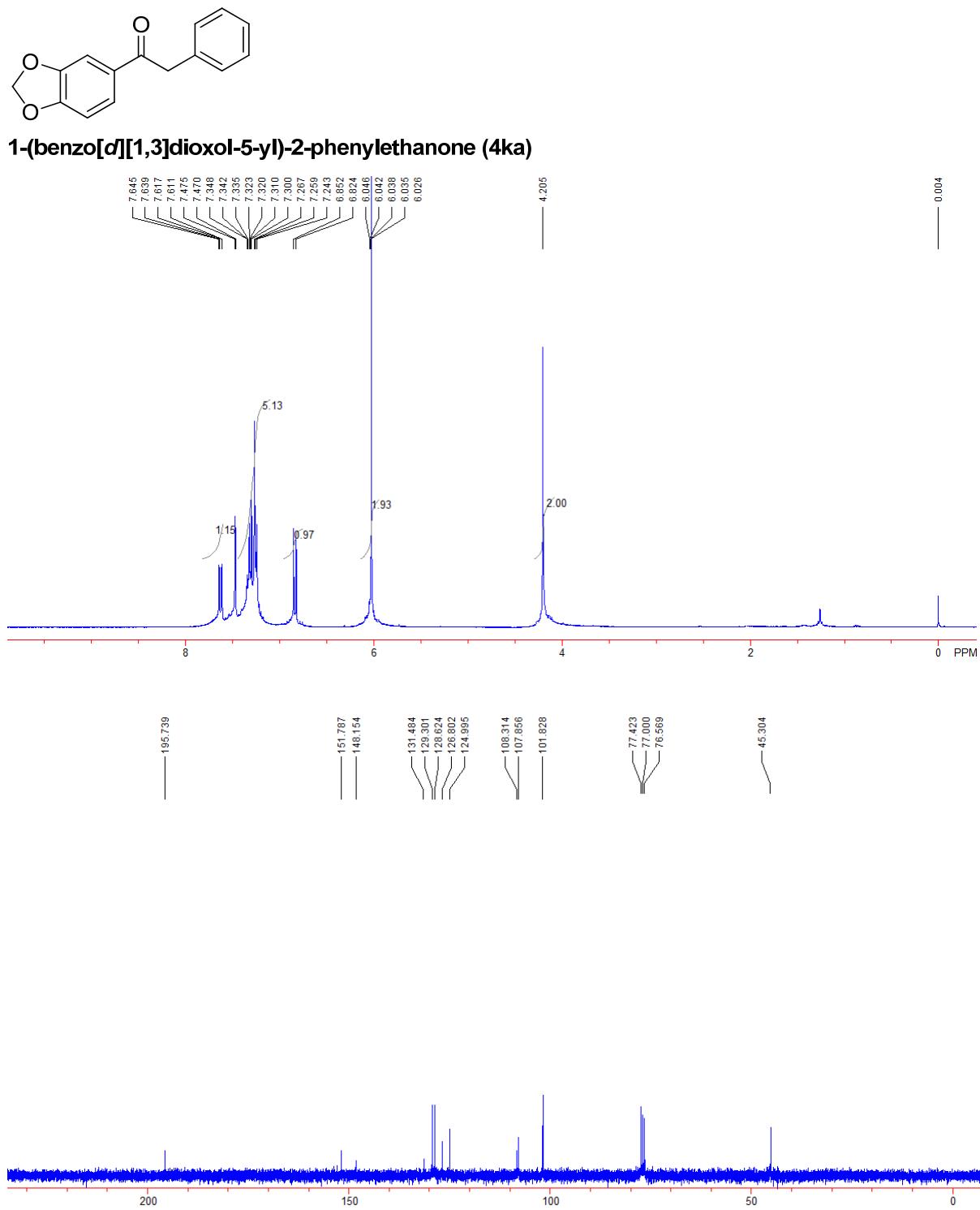
**2-(naphthalen-1-yl)-1-phenylethanone (4an)**

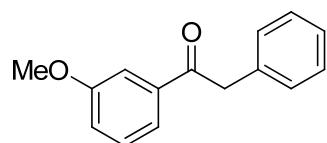




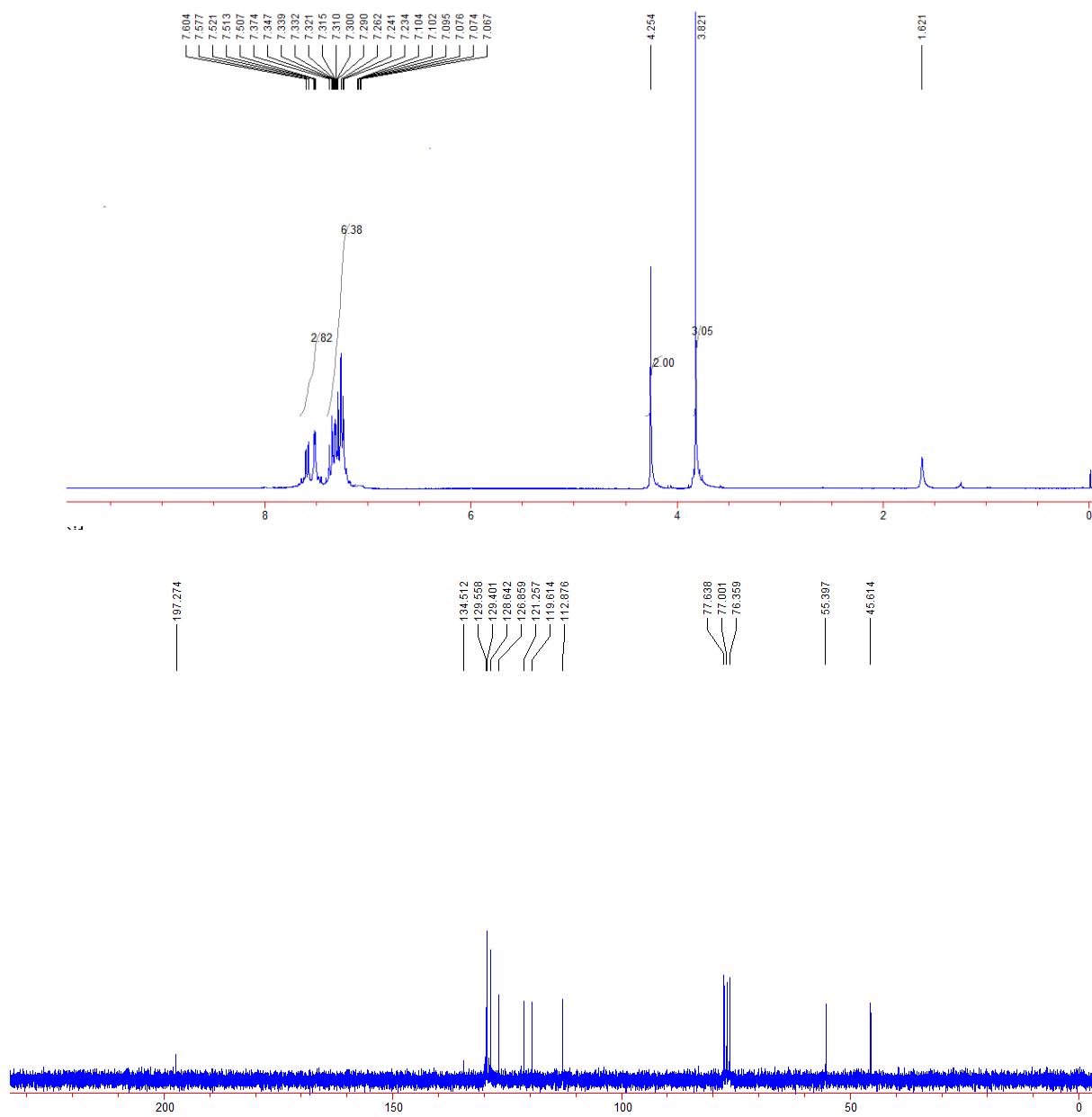
**1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-phenylethanone (4ja)**

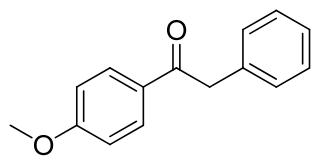




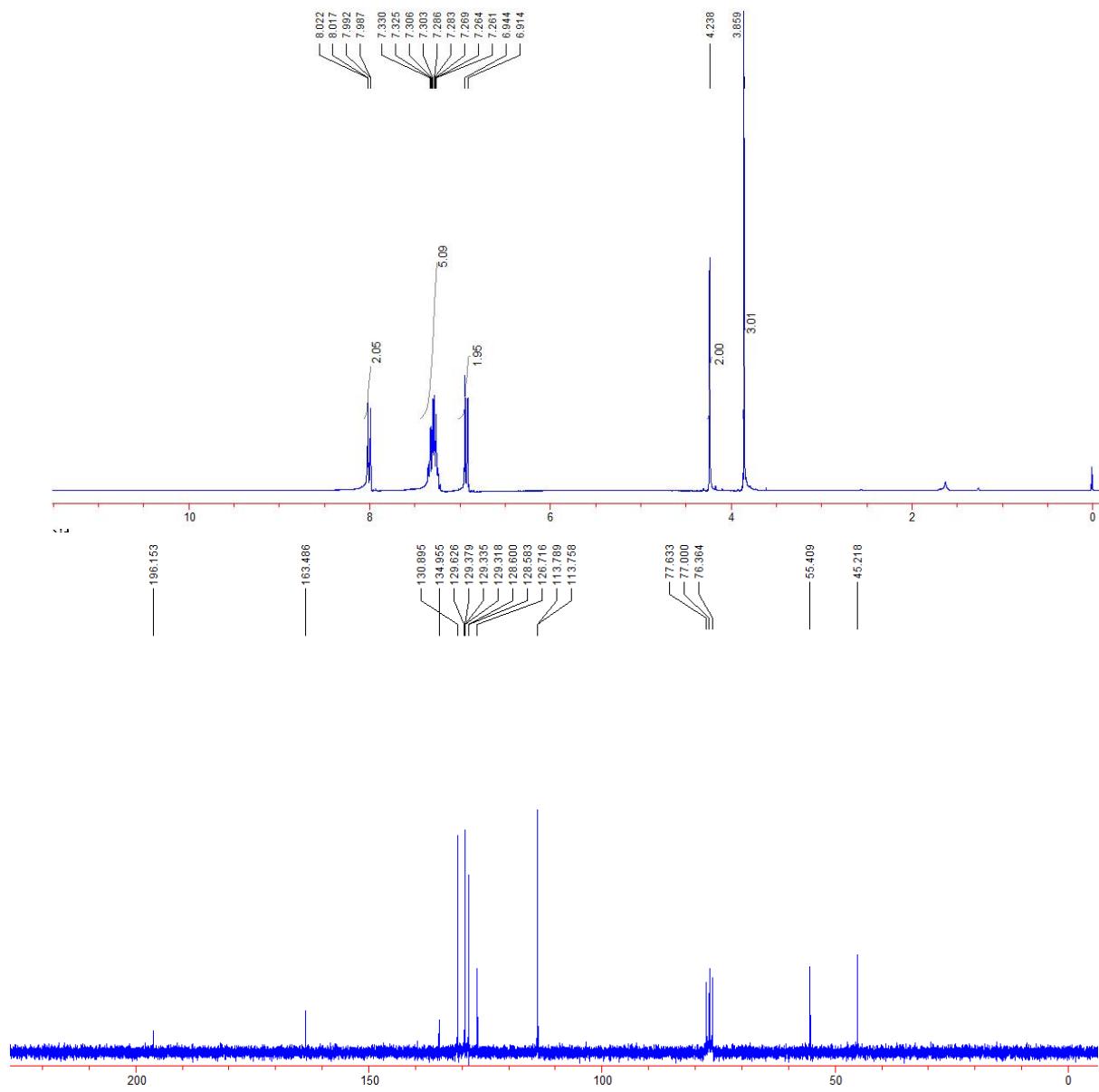


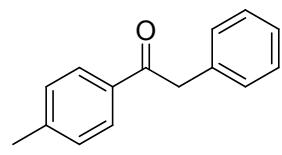
**1-(3-methoxyphenyl)-2-phenylethanone (4la)**



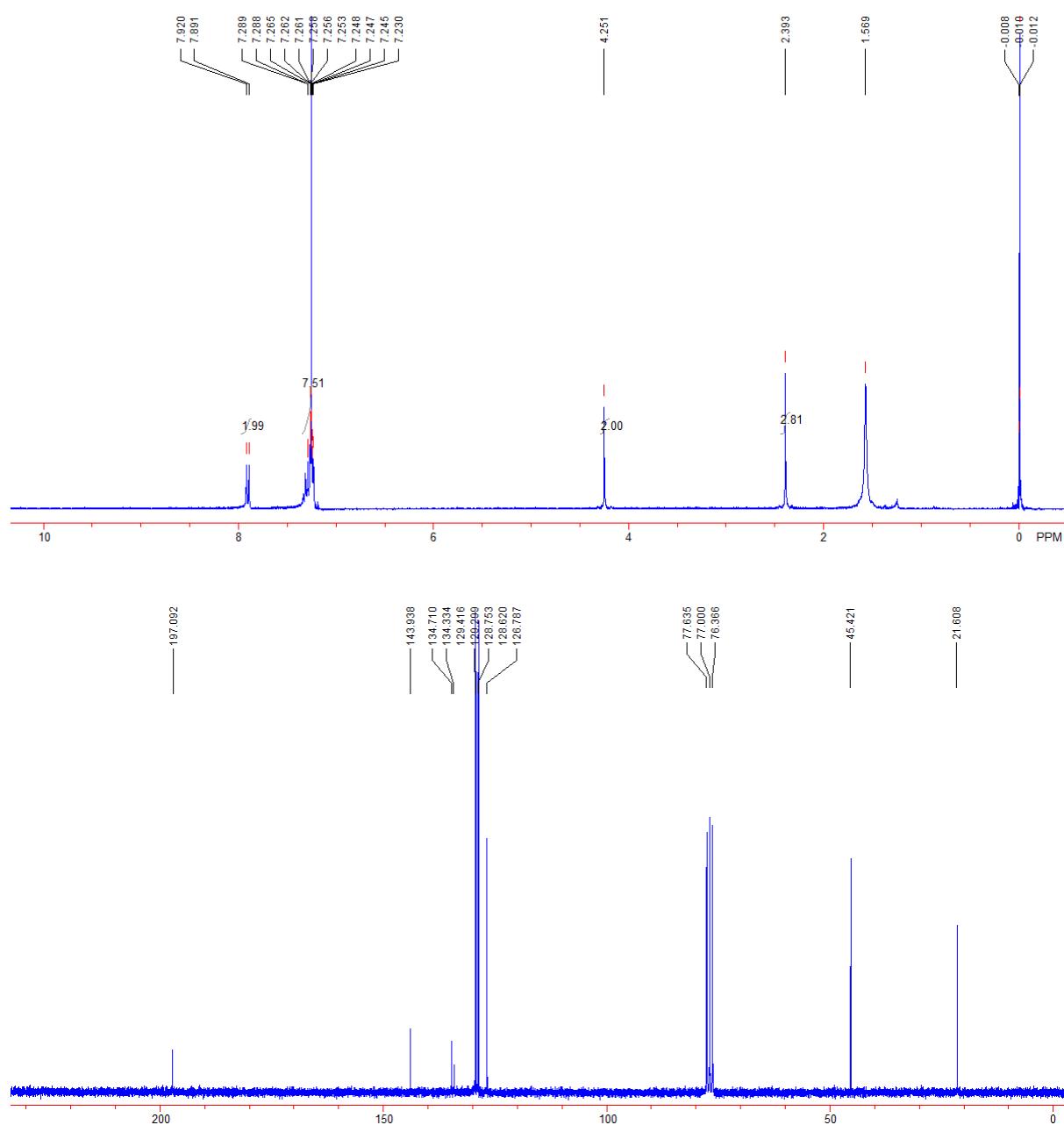


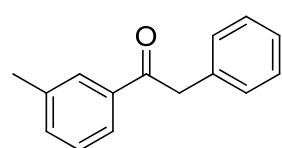
**1-(4-methoxyphenyl)-2-phenylethanone (4ma)**



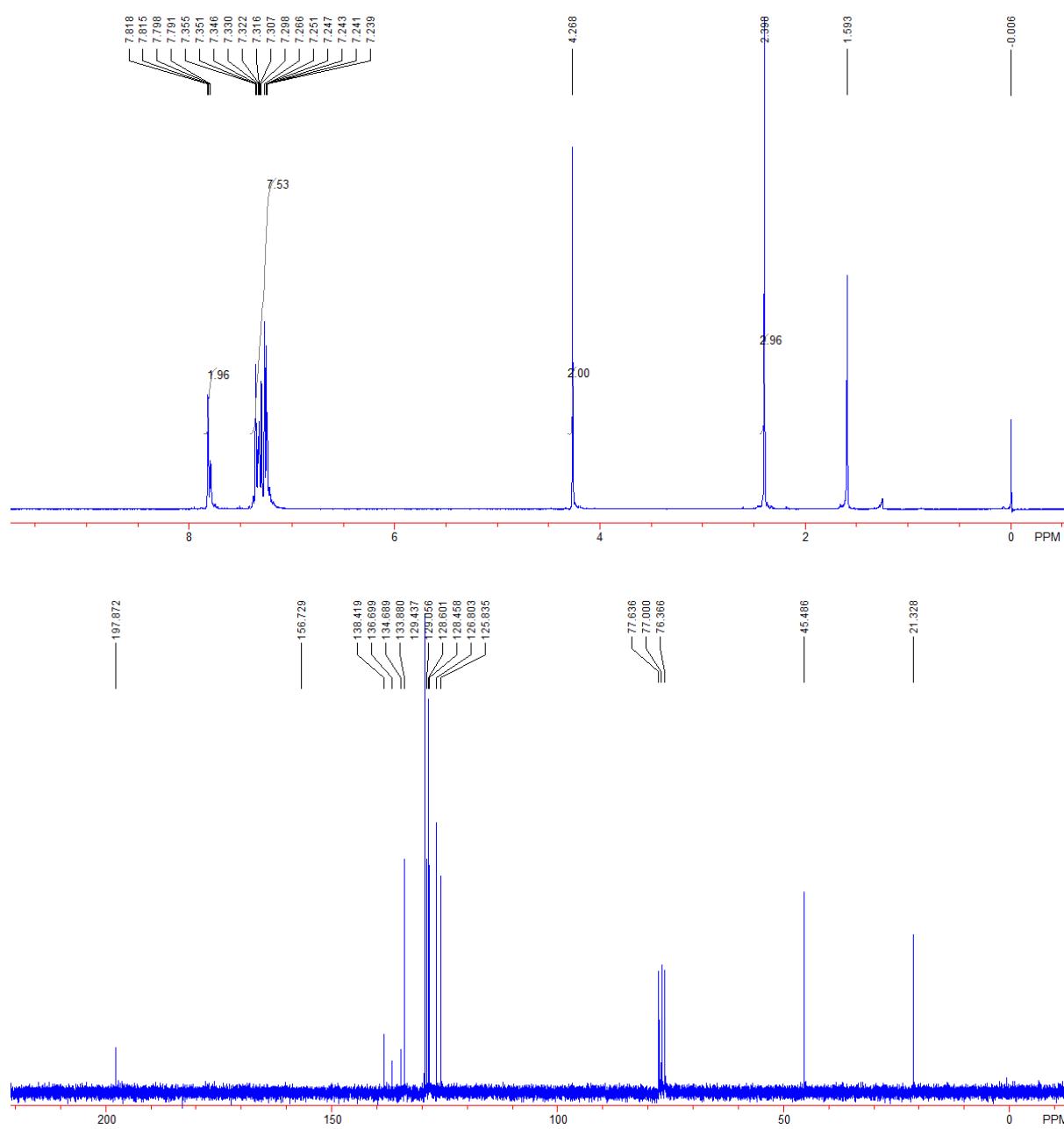


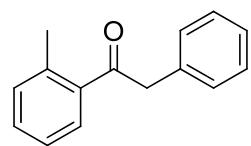
**2-phenyl-1-p-tolylethanone (4na)**



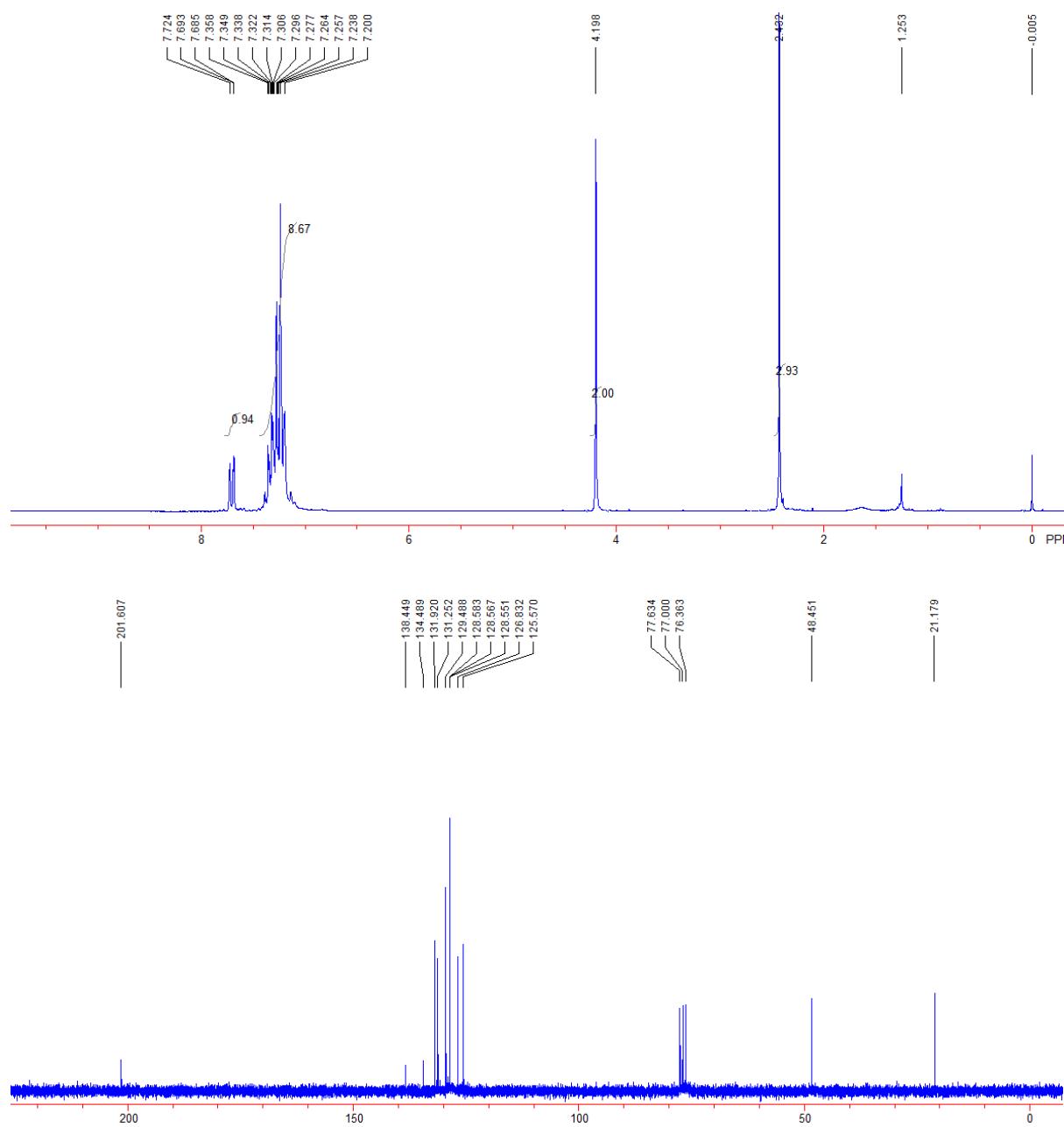


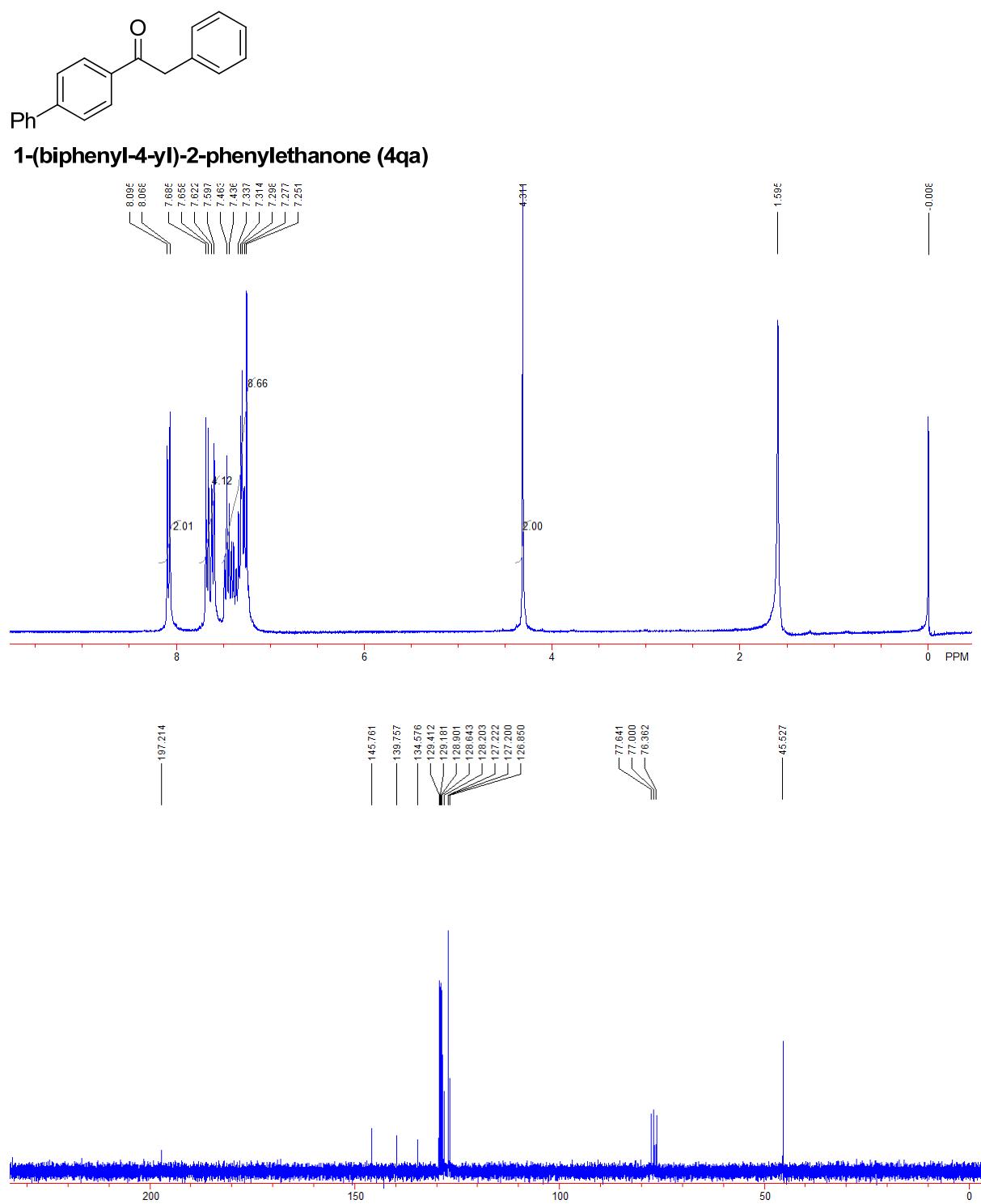
**2-phenyl-1-m-tolylethanone (4oa)**

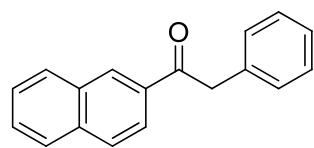




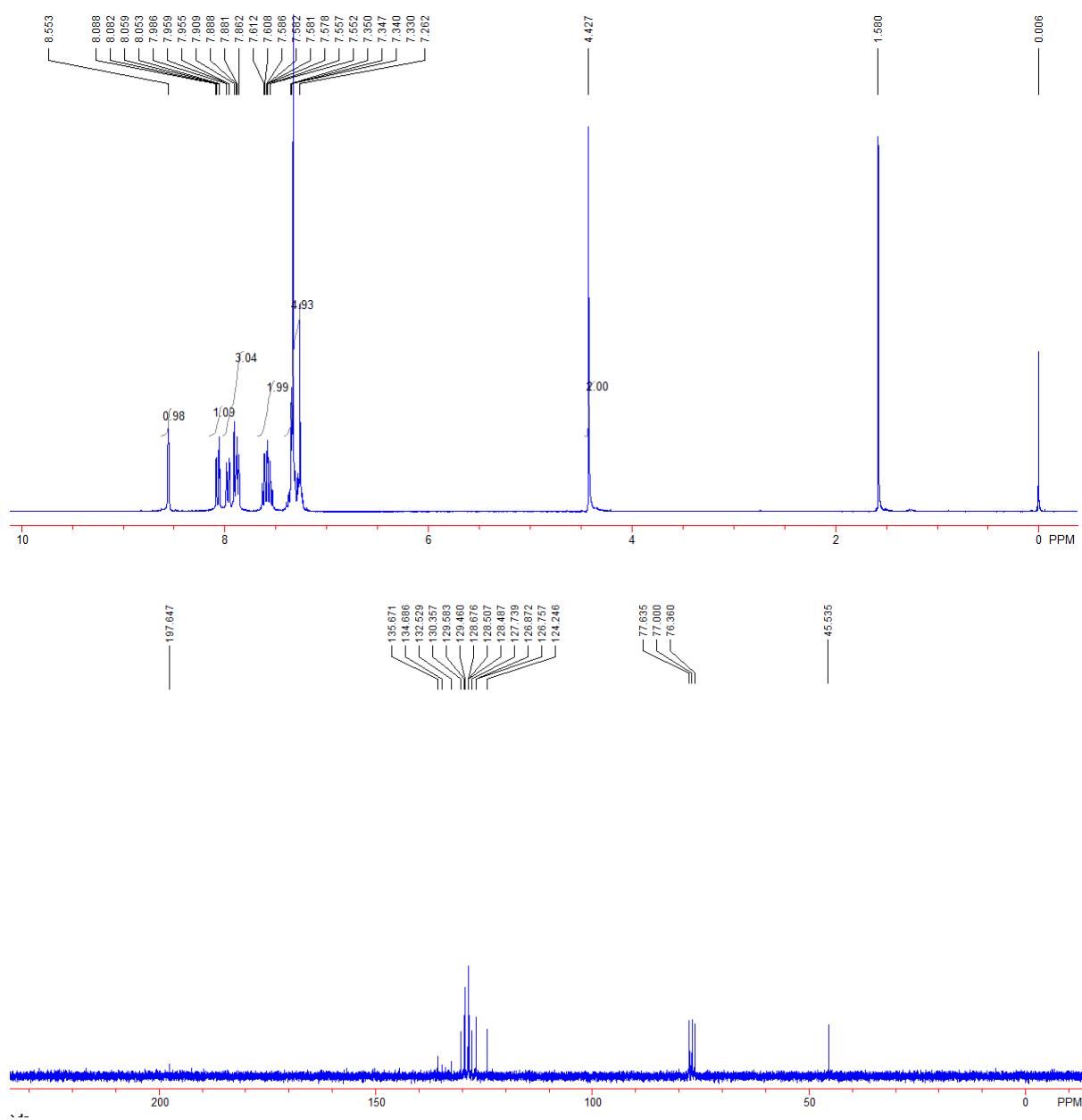
**2-phenyl-1-o-tolylethanone (4pa)**

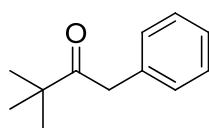




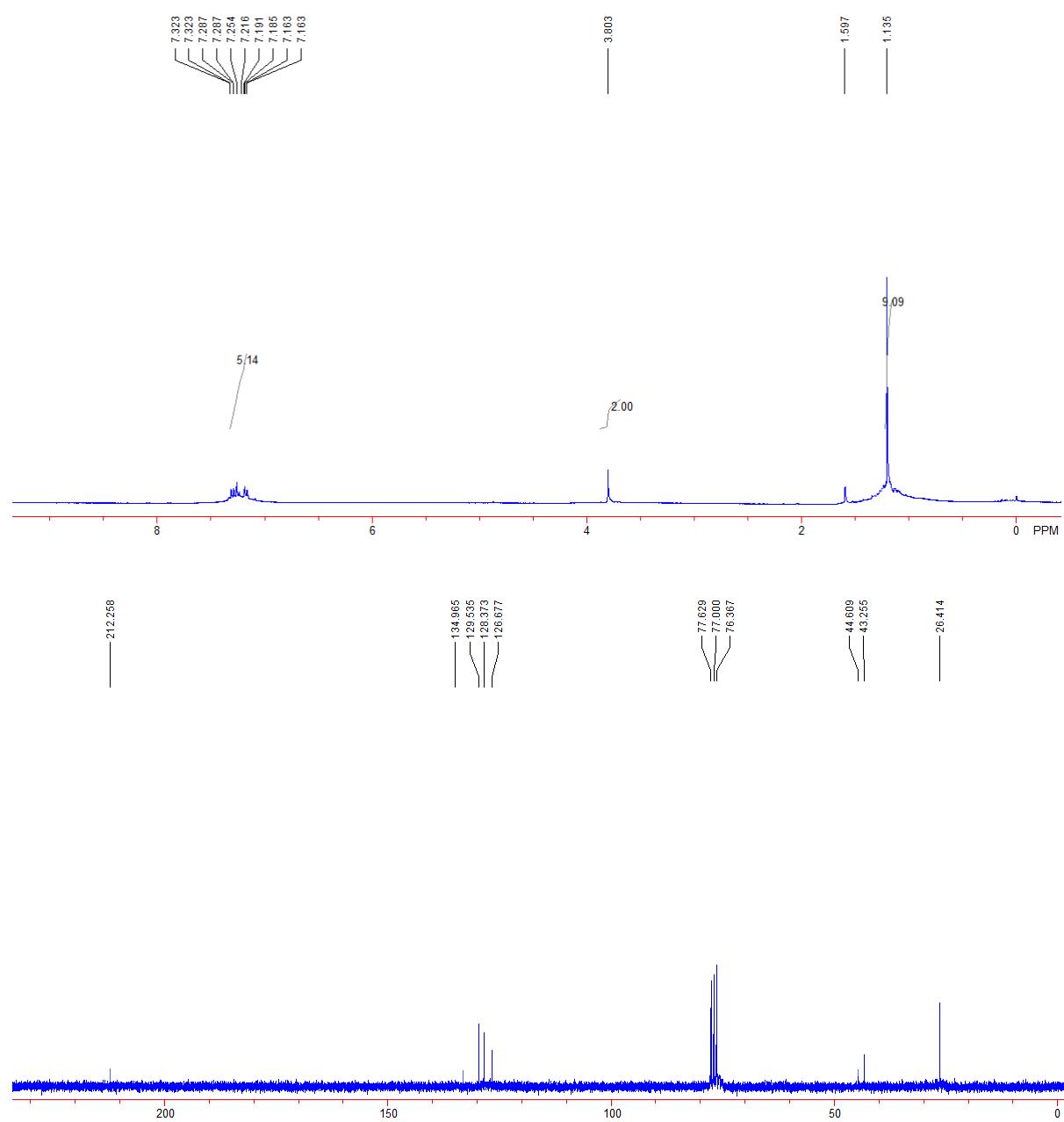


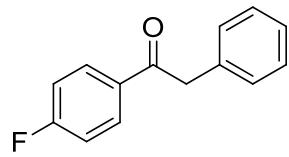
### **1-(naphthalen-2-yl)-2-phenylethanone (4ra)**



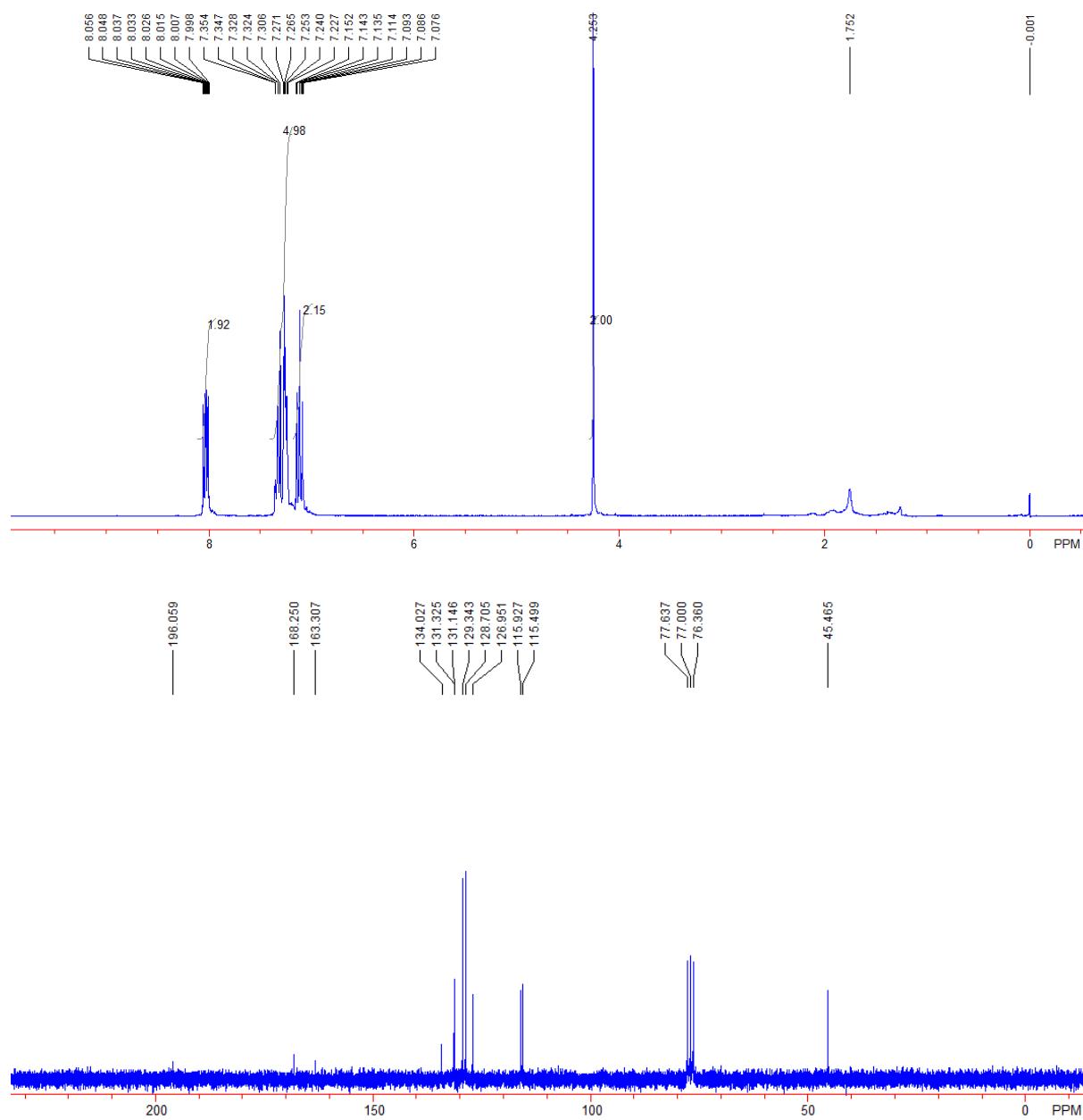


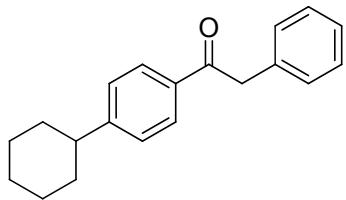
**3,3-dimethyl-1-phenylbutan-2-one (4sa)**



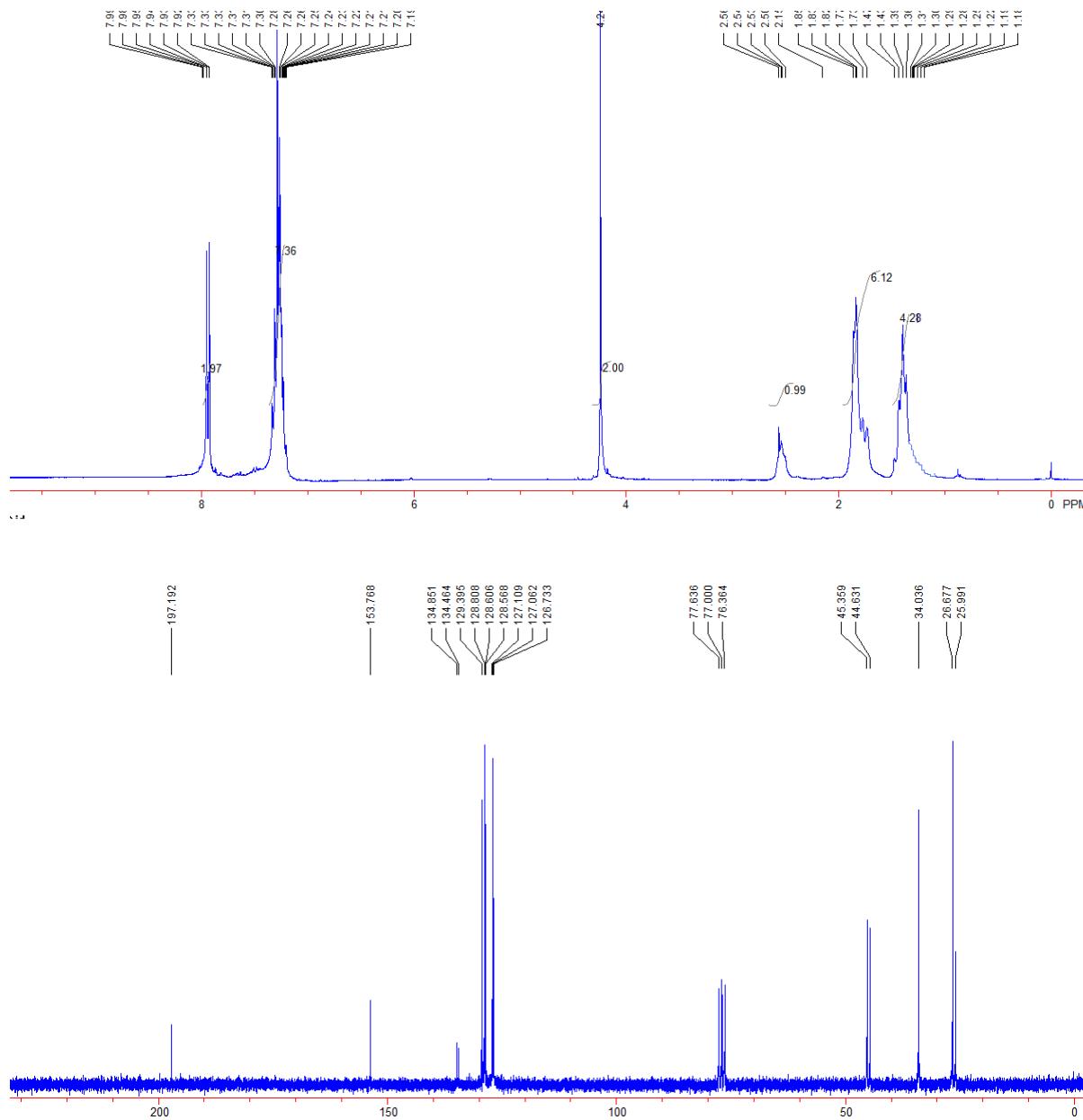


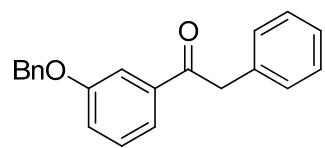
**1-(4-fluorophenyl)-2-phenylethanone (4ta)**



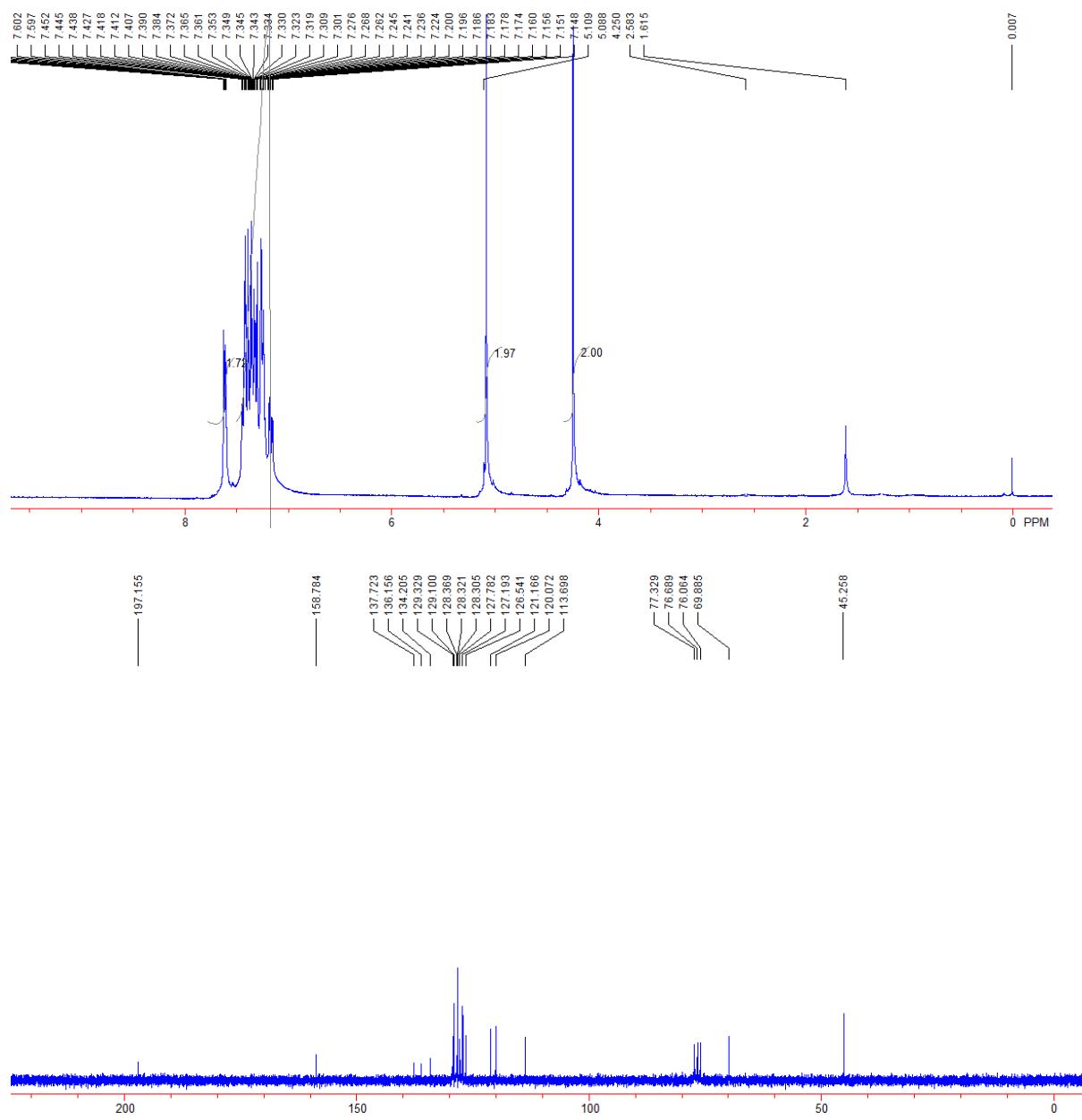


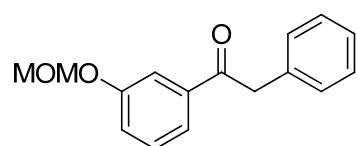
**1-(4-cyclohexylphenyl)-2-phenylethanone (4ua)**



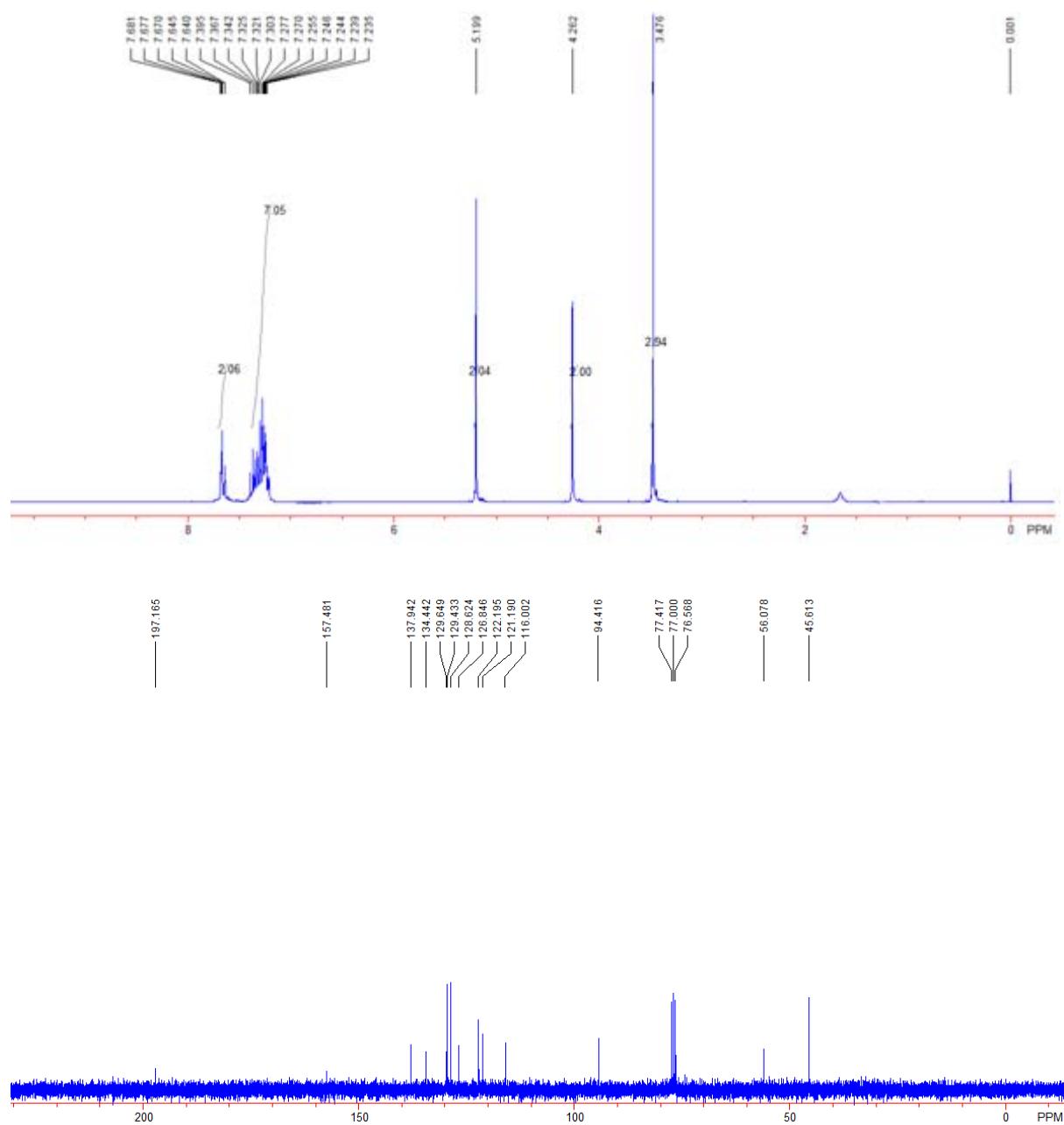


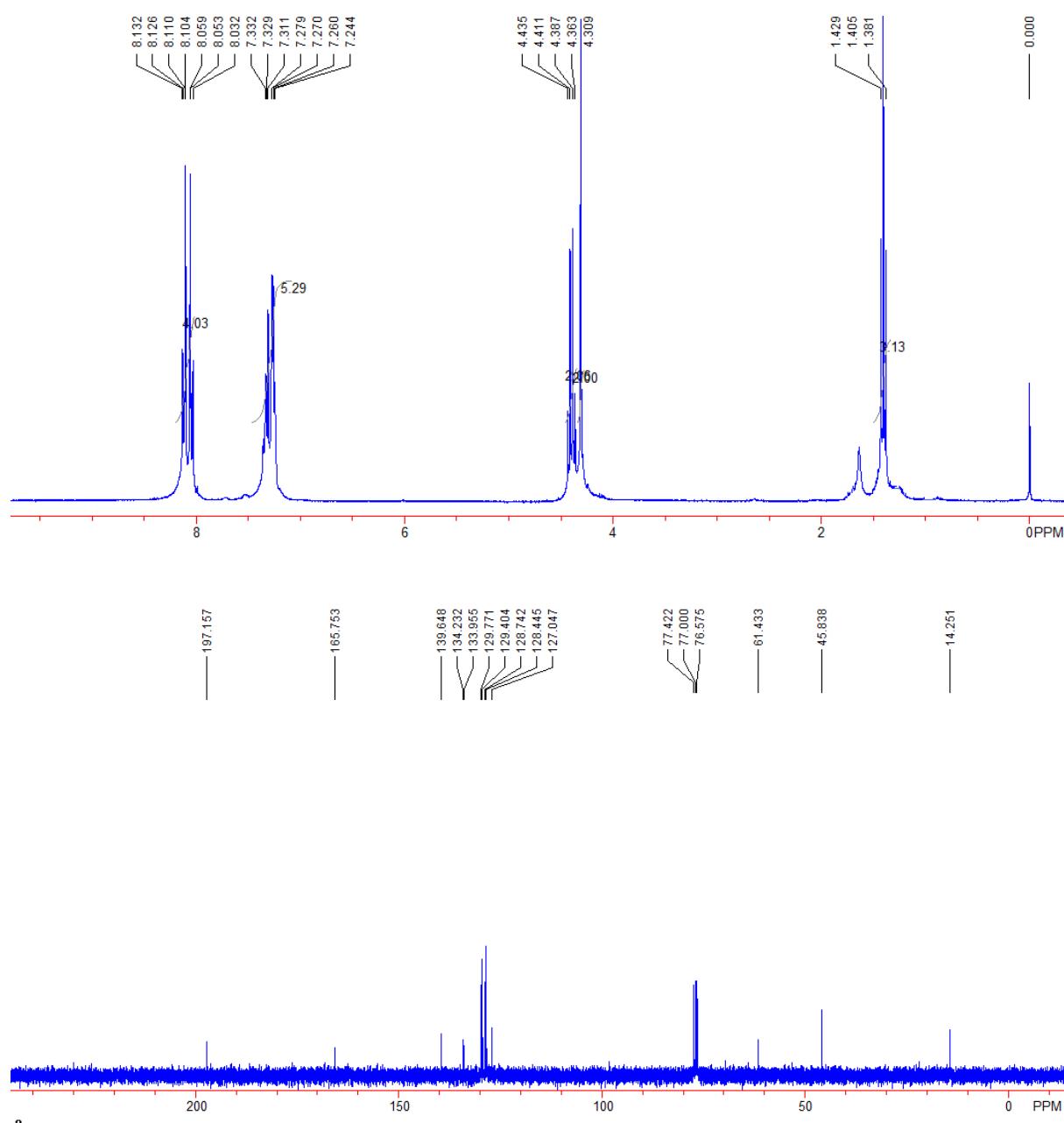
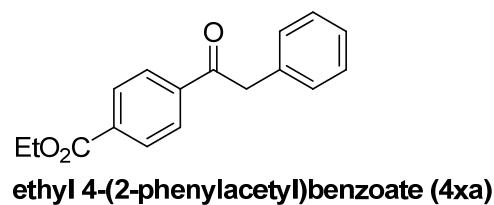
**1-(3-(benzyloxy)phenyl)-2-phenylethanone (4va)**

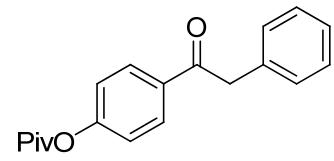




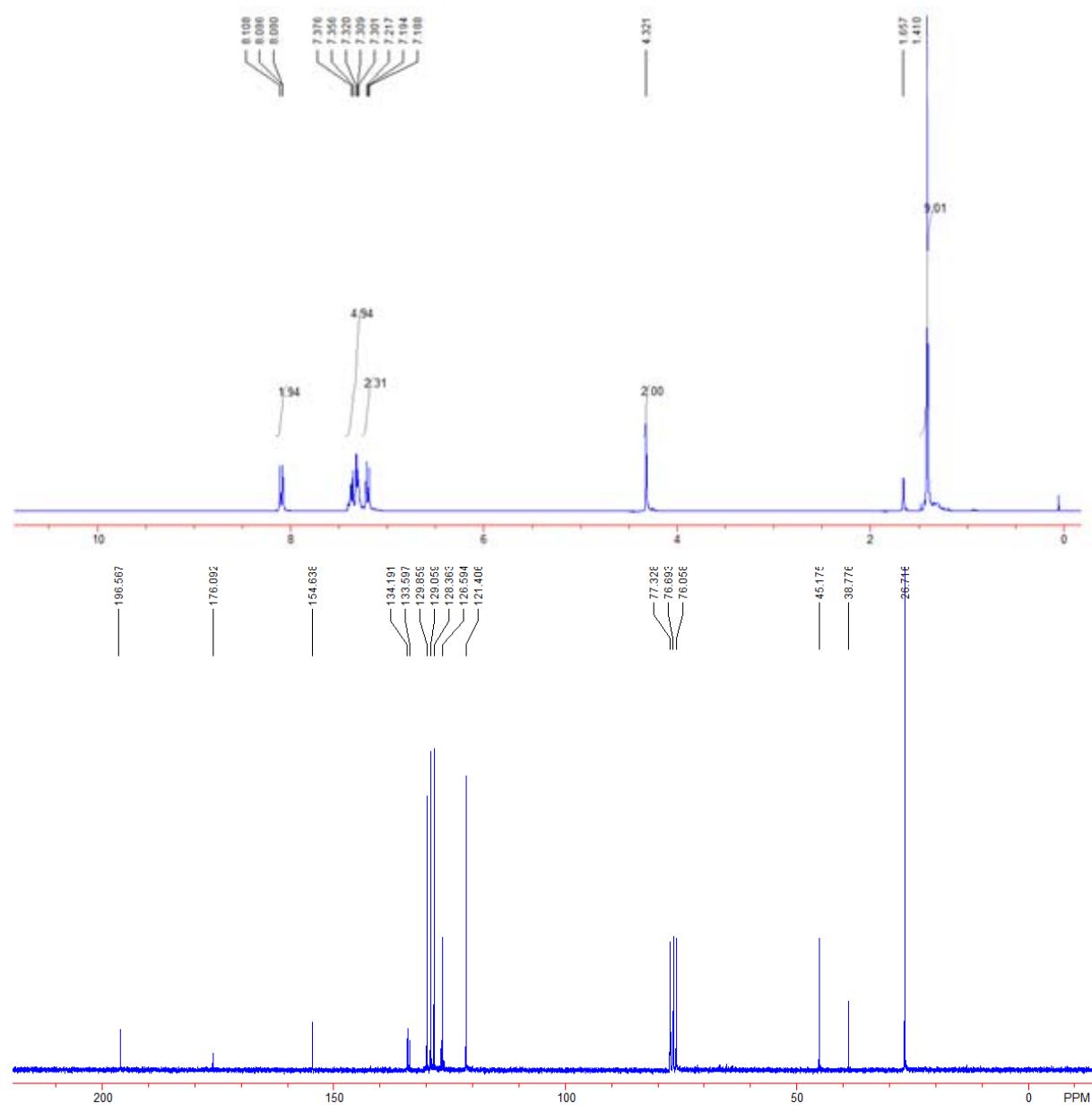
**1-(3-(methoxymethoxy)phenyl)-2-phenylethanone (4wa)**







**4-(2-phenylacetyl)phenyl pivalate (4ya)**



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