

## Supporting Information

### **PtO<sub>2</sub>/PTSA system Catalyzed Regioselective Hydration of internal Arylalkynes Bearing Electron Withdrawing Groups**

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## General experimental details

Solvent peaks were used as reference values, with  $\text{CDCl}_3$  at 7.26 ppm for  $^1\text{H}$  NMR and 77.16 ppm for  $^{13}\text{C}$  NMR, with  $\text{CD}_3\text{COCD}_3$  at 2.05 ppm for  $^1\text{H}$  NMR and 29.84 ppm for  $^{13}\text{C}$  NMR. Chemical shifts  $\delta$  are given in ppm, and the following abbreviations are used: singlet (s), doublet (d), doublet of doublet (dd), triplet (t), multiplet (m) and broad singlet (bs). Reaction courses and product mixtures were routinely monitored by TLC on silica gel, and compounds were visualized with phosphomolybdic acid/ $\Delta$ , anisaldehyde/ $\Delta$ , or vanillin/ $\Delta$ . Flash chromatography was performed using silica gel 60 (40–63 mm, 230–400 mesh) at medium pressure (200 mbar). Diethylether ( $\text{Et}_2\text{O}$ ), piperidine, trimethylamine, and tetrahydrofuran (THF) were dried using the procedures described in D. Perrin Purification of Laboratory Chemicals.<sup>1</sup>  $\text{PdCl}_2(\text{PPh}_3)_2$  was prepared following literature procedure<sup>2</sup> Organic extracts were, in general, dried over  $\text{MgSO}_4$  or  $\text{Na}_2\text{SO}_4$ . High-resolution mass spectra were recorded on a MicrOTOF-Q II. All products reported showed  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in agreement with the assigned structures.

**General Procedure for the Pd0/Cu1 Catalyzed Cross Coupling Reaction of aryl iodides and 1-alkynes.** To a flame-dried flask under a nitrogen atmosphere was added a solution of  $\text{PdCl}_2(\text{PPh}_3)_2$  (120 mg, 0.17 mmol),  $\text{CuI}$  (76 mg, 0.4 mmol), aryl halide (4.0 mmol), piperidine (1.2 mL, 12.0 mmol) in THF (12 mL). To this mixture, 1-alkyne (6.0 mmol) was added dropwise. After stirring at room temperature for 12 h, the mixture was diluted in  $\text{Et}_2\text{O}$  (25 mL), then washed with aqueous saturated  $\text{NH}_4\text{Cl}$ . The aqueous solution was extracted with  $\text{Et}_2\text{O}$  (25 mL) twice, and the organic extract was dried over  $\text{MgSO}_4$ . After concentration under reduced pressure, the residue was purified by column chromatography over silica gel, to yield the pure alkyne.

**Method A. Typical Procedure of 5 mol% PtO<sub>2</sub>/PTSA Catalyzed Hydration of alkynes.**

Into a Pyrex-glass vial equipped with screw-cap (volume: 10 mL) were successively added alkyne **1** (1 mmol), PtO<sub>2</sub> (1 mol%), MeOH (2.2 mL), PTSA monohydrate (0.1 mmol), and H<sub>2</sub>O (60 μL). The mixture was stirred at 90 °C for 5 h. After the reaction was completed, the crude reaction mixture was allowed to cool to room temperature. EtOAc was added to the mixture, which was filtered through celite. The solvents were evaporated under reduced pressure and the crude residue was purified by flash chromatography on silica gel.

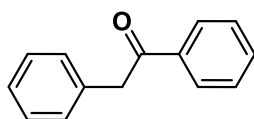
**Method B.** The same as method A, but heating was performed at 130 °C.

**Method C.** The same as method A, but without the addition of PtO<sub>2</sub>.

**Method D. Typical procedure of 1.0 mol% PtO<sub>2</sub>/PTSA Catalyzed Hydration of alkynes.**

Into a Pyrex-glass screw-cap vial (volume: 10 mL) were successively added alkyne (1 mmol), and PTSA monohydrate (0.1 mmol). A stock solution of PtO<sub>2</sub> (0.01 M in MeOH/H<sub>2</sub>O, 1 mL, 0.01 mmol) was introduced to the mixture. The mixture was stirred at 90 °C overnight. After the reaction was completed, the catalyst was removed by filtration through celite. After evaporation, the crude filtrate was directly subjected to column chromatography on silica gel.

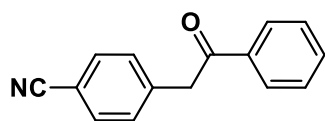
**Characterization data for the products**



*1,2-Diphenylethan-1-one (2a)*.<sup>3</sup> Was prepared according to method A.

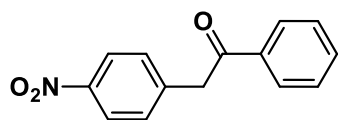
Flash chromatography on silica gel afforded 192 mg of **2a** (0.98 mmol, yield 98%). White solid; m.p.: 50–52 °C; TLC: R<sub>f</sub> = 0.27 (Et<sub>2</sub>O/Cyclohexane, 2/8, SiO<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.4 Hz, 2H), 8.03 (d, *J* = 7.4 Hz, 2H), 7.69–7.01 (m, 6H), 4.30 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm) 197.8 (CO), 136.7 (C), 134.6 (C), 133.9 (CH),

133.3 (CH), 130.3 (CH), 129.6 (CH), 128.7 (3CH), 128.6 (2CH), 127.0 (CH), 45.6 (CH<sub>2</sub>); HRMS (ESI) (M + H)<sup>+</sup> *m/z* calcd for C<sub>14</sub>H<sub>13</sub>O 197.0966 found 197.0967.



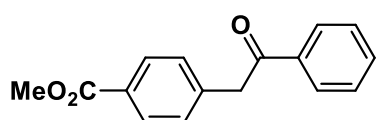
*4-(2-Oxo-2-phenylethyl)benzonitrile (2bβ)*.<sup>4</sup> Was prepared according

to method A. Flash chromatography on silica gel afforded 140 mg of **2bβ** (0.63 mmol, yield 63%). Yellow solid; m.p.: 112-114 °C. TLC: R<sub>f</sub> = 0.27 (Et<sub>2</sub>O/Cyclohexane, 2/8, SiO<sub>2</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ ppm 8.00 (d, *J* = 7.3 Hz, 2H), 7.63-7.59 (m, 3H), 7.51-7.48 (m, 2H), 7.38-7.36 (m, 2H), 4.36 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR(75 MHz, CDCl<sub>3</sub>) δ ppm 196.1 (CO), 140.0 (C), 136.2 (C), 133.7 (CH), 132.3 (2CH), 130.5 (2CH), 128.8 (2CH), 128.4 (2CH), 118.8 (C), 111.0 (C), 45.2 (CH<sub>2</sub>); HRMS (ESI) (M + H)<sup>+</sup> *m/z* calcd for C<sub>15</sub>H<sub>12</sub>NO 222.0919 found 222.0919.



*2-(4-Nitrophenyl)-1-phenylethanone (2cβ)*.<sup>5</sup> Was prepared

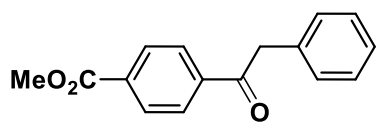
according to method B. Flash chromatography on silica gel afforded 150 mg of **2cβ** (0.62 mmol, yield 62%). Yellow solid; m.p.: 109-111 °C. TLC: R<sub>f</sub> = 0.2 (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 196.1 (CO), 147.2 (C), 142.2 (C), 136.3 (C), 133.9 (CH), 130.8 (2CH), 129.0 (2CH), 128.6 (2CH), 123.9 (2CH), 45.1 (CH<sub>2</sub>); HRMS (ESI) (M-H)<sup>-</sup> *m/z* calcd for C<sub>14</sub>H<sub>10</sub>NO<sub>3</sub> 240.0661 found 240.0663.



*Methyl 4-(2-oxo-2-phenylethyl)benzoate (2dβ)*.<sup>6</sup> Was prepared

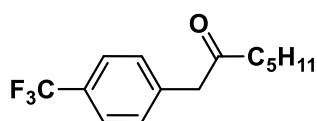
according to method A. Flash chromatography on silica gel afforded 153 mg of **2dβ** (0.60 mmol, yield 60%). White solid; m.p.: 94-95 °C. TLC: R<sub>f</sub> = 0.25 (EtOAc/Cyclohexane, 1/9,

SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.01-7.95 (m, 4H), 7.60 - 7.55 (m, 1H), 7.49 - 7.44 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.34 (s, 2H), 3.90 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 196.9 (CO), 167.0 (C), 139.9 (C), 136.5 (C), 133.5 (CH), 130.0 (2CH), 129.7 (2CH), 129.0 (C), 128.9 (2CH), 128.7 (2CH), 52.2 (CH<sub>3</sub>), 45.5 (CH<sub>2</sub>); HRMS (ESI) (M + H)<sup>+</sup> *m/z* calcd for C<sub>16</sub>H<sub>15</sub>O<sub>3</sub> 255.1021 found 255.1018.



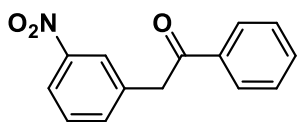
*Methyl 4-(2-phenylacetyl)benzoate (2dα)*.<sup>6</sup> Was prepared

according to method A. Flash chromatography on silica gel afforded 38 mg of **2dα** (0.15 mmol, yield 15%). White solid; m.p.: 107-109 °C. TLC: *R<sub>f</sub>* = 0.33 EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.36 - 7.25 (m, 5H), 4.31 (s, 2H), 3.94 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 197.3 (CO), 166.3 (C), 140.0 (C), 134.1 (C), 134.1 (C), 130.0 (2CH), 129.6 (2CH), 128.9 (2CH), 128.6 (2CH), 127.2 (CH), 52.6 (CH<sub>3</sub>), 46.0 (CH<sub>2</sub>); HRMS (ESI) (M + H)<sup>+</sup> *m/z* calcd for C<sub>16</sub>H<sub>15</sub>O<sub>3</sub> 255.1021 found 255.1016.



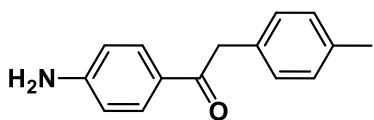
*1-(4-(Trifluoromethyl)phenyl)heptan-2-one (2eβ)*. Was prepared

according to method A. Flash chromatography on silica gel afforded 235 mg of **2eβ** (0.91 mmol, yield 91%). Colorless oil; TLC: *R<sub>f</sub>* = 0.43 (EtOAc/Cyclohexane, 5/95, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.75 (s, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.58 (p, *J* = 7.3 Hz, 2H), 1.32 - 1.21 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 207.5 (C), 138.4 (C), 130.0 (2CH), 125.7 (CH), 125.7 (CH), 49.6 (CH<sub>2</sub>), 42.6 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 23.5 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.56; HRMS (ESI) (M + Na)<sup>+</sup> *m/z* calcd for C<sub>14</sub>H<sub>17</sub>F<sub>3</sub>NaO 281.1129 found 281.1134.



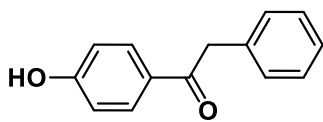
*2-(3-nitrophenyl)-1-phenylethanone (2fβ)*.<sup>5</sup> Was prepared according to

method B. Flash chromatography on silica gel afforded 155 mg of **2fβ** (0.64 mmol, yield 64%). Yellow oil; TLC:  $R_f = 0.28$  (EtOAc/Cyclohexane, 1/90, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 – 8.13 (m, 2H), 8.04 – 8.01 (m, 2H), 7.64 – 7.59 (m, 2H), 7.54 – 7.48 (m, 2H), 4.42 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  196.2 (CO), 148.5 (C), 136.5 (C), 136.3 (C), 136.2 (CH), 133.8 (CH), 129.5 (CH), 129.0 (2CH), 128.5 (2CH), 124.9 (CH), 122.2 (CH), 44.7 (CH<sub>2</sub>); HRMS (ESI) (M+Na)<sup>+</sup>  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>NO<sub>3</sub>Na 264.0637, found 264.0635.



*1-(4-Aminophenyl)-2-(p-tolyl)ethan-1-one (2gα)*.<sup>7</sup> Was prepared

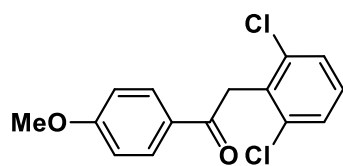
according to method D. Flash chromatography on silica gel afforded 192 mg of **2gα** (0.85 mmol, yield 85%). White solid; m.p: 149-151 °C; TLC:  $R_f = 0.26$  (EtOAc/Cyclohexane, 3/7, SiO<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.86 (d, 2H,  $J = 8.0$  Hz), 7.16 (d, 2H,  $J = 8.0$  Hz), 7.11 (d, 2H,  $J = 8.0$  Hz), 6.62 (d, 2H,  $J = 8.0$  Hz), 4.14 (s, 2H, brs, 2H), 2.31 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  ppm 196.2 (CO), 151.2 (C), 136.3 (C), 132.5 (C), 131.3 (2 CH), 129.4 (2 CH), 129.3 (2 CH), 127.3 (C), 113.7 (2 CH), 44.7 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>); HRMS (ESI) (M+H)<sup>+</sup>  $m/z$  calcd for C<sub>15</sub>H<sub>16</sub>NO 226.1232, found: 226.1230.



*1-(4-Hydroxyphenyl)-2-phenylethanone (2hα)*.<sup>8</sup> Was prepared

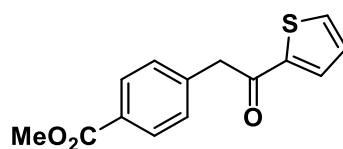
according to method D. Flash chromatography on silica gel afforded 191 mg of **2hα** (0.90 mmol, yield 90%). Yellow solid; m.p: 151-152 °C; TLC:  $R_f = 0.3$  (EtOAc/Cyclohexane, 2/8, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d,  $J = 8.7$  Hz, 2H), 7.36 – 7.27 (m, 5H), 6.87 (d,  $J = 8.7$  Hz, 2H), 6.03 (brs, 1H), 4.25 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  196.8 (CO),

160.4 (C), 134.9 (C), 131.5 (2CH), 129.7 (C), 129.5 (2CH), 128.8 (2CH), 127.0 (CH), 115.6 (2CH), 45.4 (CH<sub>2</sub>); HRMS (ESI) (M+H)<sup>+</sup> *m/z* calcd for C<sub>14</sub>H<sub>13</sub>O<sub>2</sub> 213.0916, found 213.0910.



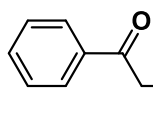
2-(2,6-Dichlorophenyl)-1-(4-methoxyphenyl)ethanone (**2iα**). Was

prepared according to method D. Flash chromatography on silica gel afforded 162 mg of **2iα** (0.55 mmol, yield 55%). Yellow oil; TLC: *R<sub>f</sub>* = 0.4 (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.15 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.65 (s, 2H), 3.90 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 193.2 (CO), 163.9 (C), 136.3 (2C), 132.6 (C), 130.6 (2CH), 129.7 (C), 128.8 (CH), 128.1 (2CH), 114.0 (2CH), 55.7 (CH<sub>3</sub>), 41.1 (CH<sub>2</sub>); HRMS (ESI) (M+H)<sup>+</sup> *m/z* calcd for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>Cl<sub>2</sub> 295.0293 found 295.0294.

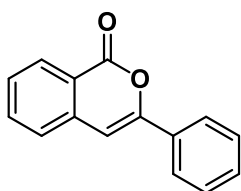


Methyl 4-(2-oxo-2-(thiophen-2-yl)ethyl)benzoate (**2jβ**). Was

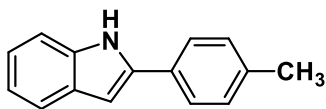
prepared according to method D. Flash chromatography on silica gel afforded 131 mg of **2jβ** (0.50 mmol, yield 50%). Brown solid; m.p: 109-111 °C; TLC: *R<sub>f</sub>* = 0.23 (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 3.8 Hz, 1H), 7.66 (d, *J* = 4.4 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 4.4 Hz, 1H), 4.25 (s, 2H), 3.89 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 189.7 (CO), 167.0 (CO), 139.6 (2C), 134.5 (CH), 132.8 (CH), 130.1 (2CH), 129.6 (2CH), 129.1 (C), 128.4 (CH), 52.2 (CH<sub>3</sub>), 46.3 (CH<sub>2</sub>); HRMS (ESI) (M+H)<sup>+</sup> *m/z* calcd for C<sub>14</sub>H<sub>13</sub>O<sub>3</sub>S 261.0585 found 261.0581.



**3-Methoxy-1-phenylpropan-1-one (2ka)**.<sup>9</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 135 mg of **2ka** (0.82 mmol, yield 82%). Yellow oil; TLC:  $R_f = 0.4$  (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d,  $J = 7.4$  Hz, 2H), 7.57 - 7.52 (m, 1H), 7.46 - 7.41 (m, 2H), 3.81 (t,  $J = 6.4$  Hz, 2H), 3.36 (s, 3H), 3.22 (t,  $J = 6.5$  Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  198.3 (CO), 137.1 (C), 133.2 (CH), 128.7 (2CH), 128.2 (2CH), 67.9 (CH<sub>2</sub>), 59.0 (CH<sub>3</sub>), 38.7 (CH<sub>2</sub>); HRMS (ESI) (M+H)<sup>+</sup>  $m/z$  calcd for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub> 165.0916 found 165.0912.



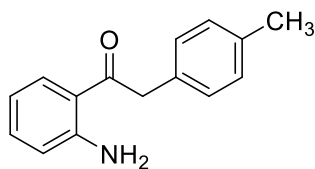
**3-Phenyl-1H-isochromen-1-one (2l)**.<sup>10</sup> Was prepared according to method B. Flash chromatography on silica gel afforded 178 mg of **2l** (0.80 mmol, yield 80%). Yellow solid; m.p: 111–112 °C; TLC:  $R_f = 0.43$  (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.32 (d,  $J = 8.0$  Hz, 1H), 7.89 (dd,  $J = 8.0, 1.7$  Hz, 2H), 7.75 – 7.70 (m, 1H), 7.53 – 7.45 (m, 5H), 6.96 (s, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  162.5 (C), 137.7 (C), 135.0 (CH), 132.1 (C), 130.1 (CH), 129.8 (CH), 129.0 (2CH), 128.3 (CH), 126.1 (CH), 125.4 (2CH), 120.7 (C), 102.0 (CH); HRMS (ESI) (M + H)<sup>+</sup>  $m/z$  calcd for C<sub>15</sub>H<sub>11</sub>O<sub>2</sub> 223.0759 found 223.0758.



**2-(p-Tolyl)-1H-indole (2m)**.<sup>11</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 170 mg of **2m** (0.82 mmol, yield 82%). Red oil; TLC:  $R_f = 0.4$  (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (brs, 1H), 7.63 (d,  $J = 7.6$  Hz, 1H), 7.57 (d,  $J = 8.0$  Hz, 2H), 7.40 (d,  $J = 7.9$  Hz, 1H), 7.27 – 7.25 (m, 2H), 7.22 – 7.10 (m, 2H), 6.80 (s, 1H), 2.40 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  138.2

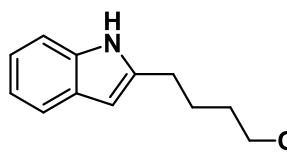


(C), 137.8 (2C), 136.8 (C), 129.8 (2CH), 129.5 (C), 125.2 (2CH), 122.2 (CH), 120.6 (CH), 120.3 (CH), 110.9 (CH), 99.5 (CH), 21.4 (CH<sub>3</sub>); HRMS (ESI) (M+H)<sup>+</sup> *m/z* calcd for C<sub>15</sub>H<sub>14</sub>N 208.1126 found 208.1127.

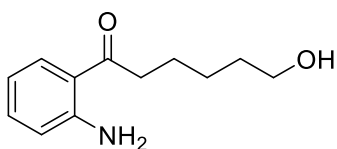


*1-(2-aminophenyl)-2-(p-tolyl)ethanone (2mα)*. Was prepared

according to method C. Flash chromatography on silica gel afforded 113 mg of **2mα** (0.50 mmol, yield 50%); Brown solid; m.p 138–140 °C; TLC: *R<sub>f</sub>* = 0.45 (EtOAc/Cyclohexane, 3/7, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.13 (q, *J* = 8.1 Hz, 4H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.14 (s, 2H), 2.31 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.2 (C), 151.3 (C), 136.3 (C), 132.5 (C), 131.3 (2CH), 129.4 (2CH), 129.3 (2CH), 127.2 (C), 113.9 (2CH), 44.7 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>); HRMS (ESI) (M + H)<sup>+</sup> *m/z* calcd for C<sub>15</sub>H<sub>16</sub>NO 226.1232, found 226.1230.

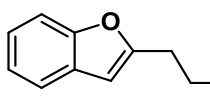


*4-(1H-Indol-2-yl)butan-1-ol (2n)*.<sup>12</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 155 mg of **2n** (0.82 mmol, yield 82%); Purple solid; m.p. 51–52 °C; TLC: *R<sub>f</sub>* = 0.37 (EtOAc/Cyclohexane, 4/6, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.08 (br s, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.15 – 7.06 (m, 2H), 6.25 (s, 1H), 3.68 (t, *J* = 6.3 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 1.84 – 1.75 (m, 3H), 1.69 – 1.60 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 139.7 (C), 136.0 (C), 128.9 (C), 121.1 (CH), 119.9 (CH), 119.7 (CH), 110.5 (CH), 99.7 (CH), 62.7 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>); HRMS (ESI) (M+H)<sup>+</sup> *m/z* calcd for C<sub>12</sub>H<sub>16</sub>NO 190.1232 found 190.1230.



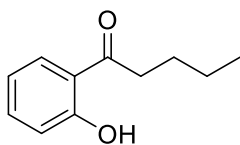
*1-(2-Aminophenyl)-6-hydroxyhexan-1-one (2nα)*. Was prepared

according to method C. Flash chromatography on silica gel afforded 63 mg of **2nα** (0.30 mmol, yield 30%); dark green oil; TLC:  $R_f = 0.25$  (EtOAc/Cyclohexane, 3/7, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d,  $J = 8.4$  Hz, 1H), 7.25 (t,  $J = 7.7$  Hz, 1H), 6.66 – 6.62 (m, 2H), 3.67 (t,  $J = 6.1$  Hz, 2H), 2.95 (t,  $J = 7.1$  Hz, 2H), 1.81 – 1.71 (m, 2H), 1.68 – 1.58 (m, 2H), 1.51 – 1.41 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  203.0 (CO), 150.5(C), 134.3 (CH), 131.3 (CH), 118.1 (C), 117.5 (CH), 115.9 (CH), 62.8 (CH<sub>2</sub>), 39.2 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 24.6 (CH<sub>2</sub>); HRMS (ESI) (M + H)<sup>+</sup>  $m/z$  calcd for C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub> 208.1338 found 208.1331.



*2-Propylbenzofuran (2o)*.<sup>13</sup> Was prepared according to method D. Flash

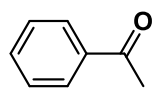
chromatography on silica gel afforded 151 mg of **2o** (0.94 mmol, yield 94%); dark green oil; TLC:  $R_f = 0.83$  (EtOAc/Cyclohexane, 1/9, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.38- 7.35 (m, 1H), 7.32 – 7.29 (m, 1H), 7.12 – 7.04 (m, 2H), 6.26 (s, 1H), 2.63 (t,  $J = 7.4$  Hz, 2H), 1.73 – 1.61 (m, 2H), 0.90 (t,  $J = 7.4$  Hz, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  159.7 (C), 154.8 (C), 129.2 (C), 123.2 (CH), 122.5 (CH), 120.3 (CH), 110.8 (CH), 102.0 (CH), 30.6 (CH<sub>2</sub>), 21.2 (CH<sub>2</sub>), 13.9 (CH<sub>3</sub>). HRMS (ESI) (M + H)<sup>+</sup>  $m/z$  calcd for C<sub>11</sub>H<sub>13</sub>O 161.0966 found 161.0955.



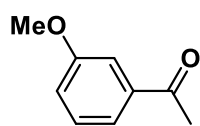
*1-(2-hydroxyphenyl)pentan-1-one (2oα)*. Was prepared according to

method C. Flash chromatography on silica gel afforded 72 mg of **2oα** (0.4 mmol, yield 40%); yellow oil;  $R_f = 0.6$  (EtOAc/Cyclohexane, 5/95, SiO<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  12.41

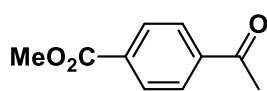
(s, 1H), 7.76 (d,  $J = 8.0$  Hz, 1H), 7.45 (t,  $J = 7.8$  Hz, 1H), 6.98 (d,  $J = 8.4$  Hz, 1H), 6.89 (t,  $J = 7.6$  Hz, 1H), 2.98 (t,  $J = 7.4$  Hz, 2H), 1.78 – 1.68 (m, 2H), 1.49 – 1.36 (m, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  207.1 (CO), 162.6 (C), 136.3 (CH), 130.1 (CH), 119.5 (C), 118.9 (CH), 118.6 (CH), 38.2 ( $\text{CH}_2$ ), 26.7 ( $\text{CH}_2$ ), 22.6 ( $\text{CH}_2$ ), 14.0 ( $\text{CH}_3$ ); HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_{15}\text{O}_2$  [(M+ H) $^+$ ] 179.1072, found 179.1075.



*Acetophenone* (**2p**).<sup>14</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 90 mg of **2p** (0.75 mmol, yield 75%); colorless oil; TLC:  $R_f = 0.27$  ( $\text{Et}_2\text{O}/\text{Cyclohexane}$ , 2/8,  $\text{SiO}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 7.3$  Hz, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.43 (m, 2H), 2.60 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.2 (CO), 137.3 (C), 133.2 (CH), 128.7 (2CH), 128.4 (2CH), 26.7 ( $\text{CH}_3$ ); HRMS (ESI) (M + H) $^+$   $m/z$  calcd for  $\text{C}_8\text{H}_9\text{O}$  121.0653 found 121.0654.

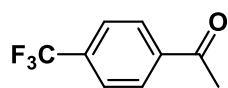


*1-(3-Methoxyphenyl)ethanone* (**2q**).<sup>15</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 113 mg of **2q** (0.75 mmol, yield 75%); colorless oil; TLC:  $R_f = 0.20$  ( $\text{Et}_2\text{O}/\text{Cyclohexane}$ , 2/8,  $\text{SiO}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.45 (m, 2H), 7.34 (t,  $J = 7.9$  Hz, 1H), 7.08 (dd,  $J = 8.2, 2.3$  Hz, 1H), 3.82 (s, 3H), 2.56 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.9 (CO), 159.9 (C), 138.6 (C), 129.6 (CH), 121.1 (CH), 119.6 (CH), 112.4 (CH), 55.5 ( $\text{CH}_3$ ), 26.7 ( $\text{CH}_3$ ); HRMS (ESI) (M+H) $^+$   $m/z$  calcd for  $\text{C}_9\text{H}_{11}\text{O}_2$  151.0759 found 151.0757.

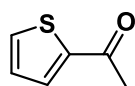


*Methyl 4-acetylbenzoate* (**2r**).<sup>16</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 121 mg of **2r** (0.68 mmol, yield 68%); yellow solid; m.p 94–95 °C; TLC:  $R_f = 0.10$  ( $\text{Et}_2\text{O}/\text{Cyclohexane}$ , 3/8,  $\text{SiO}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J = 8.3$  Hz, 2H), 8.00 (d,  $J = 8.3$  Hz, 2H), 3.95 (s, 3H), 2.64 (s, 3H);

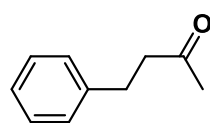
$^{13}\text{C}\{1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.7 (CO), 166.4 (C), 140.4 (C), 134.1 (C), 130.0 (2CH), 128.4 (2CH), 52.6 ( $\text{CH}_3$ ), 27.0 ( $\text{CH}_3$ ); HRMS (ESI) ( $\text{M} + \text{H}$ ) $^+$   $m/z$  calcd for  $\text{C}_{10}\text{H}_{11}\text{O}_3$  179.0708 found 179.0717.



*1-(4-(Trifluoromethyl)phenyl)ethanone (2s)*.<sup>17</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 126 mg of **2s** (0.67 mmol, yield 67%); brown oil; TLC:  $R_f = 0.40$  (EtOAc/Cyclohexane, 5/95,  $\text{SiO}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.2$  Hz, 2H), 7.73 (d,  $J = 8.2$  Hz, 2H), 2.65 (s, 3H);  $^{13}\text{C}\{1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2 (CO), 139.8 (C), 134.3 (C), 128.8 (2CH), 125.8 (CH), 125.8 (CH), 121.9 (C), 26.9 ( $\text{CH}_3$ );  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.31.

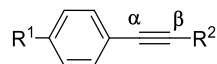


*1-(Thiophen-2-yl)ethanone (2t)*.<sup>18</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 78 mg of **2t** (0.62 mmol, yield 62%); brown oil; TLC:  $R_f = 0.30$  (EtOAc/Cyclohexane, 5/95,  $\text{SiO}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 3.7$  Hz, 1H), 7.63 (d,  $J = 4.9$  Hz, 1H), 7.12 (t,  $J = 4.9$  Hz, 1H), 2.56 (s, 3H);  $^{13}\text{C}\{1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  190.9 (CO), 144.7 (C), 133.9 (CH), 132.6 (CH), 128.2 (CH), 27.1 ( $\text{CH}_3$ ); HRMS (APCI) ( $\text{M} + \text{H}$ ) $^+$   $m/z$  calcd for  $\text{C}_6\text{H}_7\text{OS}$  127.0212 found 127.0207.



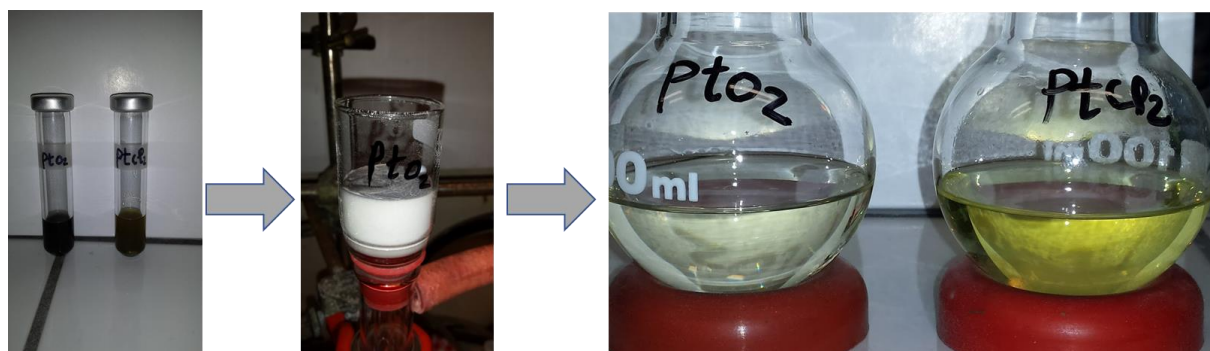
*4-Phenylbutan-2-one (2u)*.<sup>19</sup> Was prepared according to method D. Flash chromatography on silica gel afforded 98 mg of **2u** (0.66 mmol, yield 66%); yellow oil; TLC:  $R_f = 0.6$  (EtOAc/Cyclohexane, 2/8,  $\text{SiO}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 2.93 – 2.88 (m, 2H), 2.78 – 2.73 (m, 2H), 2.14 (s, 3H);  $^{13}\text{C}\{1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  208.0 (CO), 141.1 (C), 128.6 (2CH), 128.4 (2CH), 126.2 (CH), 45.3 ( $\text{CH}_2$ ), 30.2 ( $\text{CH}_3$ ), 29.8 ( $\text{CH}_2$ ); HRMS (ESI) ( $\text{M} + \text{Na}$ ) $^+$   $m/z$  calcd for  $\text{C}_{10}\text{H}_{12}\text{ONa}$  171.0786 found 171.0779.

**Table 1. Experimental  $^{13}\text{C}$  NMR Chemical Shifts of Actetylenic Carbons of *Para*-alkynes 1.**



Entry	R <sup>1</sup>	R <sup>2</sup>	$^{13}\text{C}$ shifts (ppm)		$\Delta\text{C}\beta-\text{C}\alpha$	Ratio $2\alpha:2\beta$
			$\delta\text{C}\alpha$	$\delta\text{C}\beta$		
1	H	H	89.3	89.3	0	-
2	<i>p</i> -CN	Ph	87.6	93.7	6.1	0:100
3	<i>p</i> -O <sub>2</sub> N	Ph	87.5	94.7	7.2	0:100
	<i>m</i> -O <sub>2</sub> N	Ph	87.0	92.1	5.1	5:95
4	<i>p</i> -MeCO <sub>2</sub>	Ph	88.6	92.4	3.8	20:80
5	<i>p</i> -CF <sub>3</sub>	C <sub>5</sub> H <sub>11</sub>	79.5	93.4	13.9	0:100
6	<i>p</i> -NH <sub>2</sub>	<i>p</i> -MePh	89.4	87.5	-1.9	100:0
7	<i>p</i> -OH	Ph	89.2	88.1	-1.1	100:0
8	<i>p</i> -MeOPh	<i>o,o'</i> -Cl	100.3	82.6	-17.7	100:0
9	H	CH <sub>2</sub> OH	87.4	85.7	-1.7	100:0

### Separation of PtO<sub>2</sub> by simple filtration

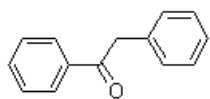


1. W. L. F. Armarego and C. Chai, in *Purification of Laboratory Chemicals (Seventh Edition)*, Butterworth-Heinemann, Boston, 2013, pp. 103.
2. L. Brandsma, H. D. Verkruisje and S. F. Vasilevsky, in *Application of Transition Metal Catalysts in Organic Synthesis*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1999, pp. 1.
3. Z.-W. Chen, D.-N. Ye, Y.-P. Qian, M. Ye and L.-X. Liu, *Tetrahedron*, 2013, **69**, 6116.
4. X.-F. Wu, H. Neumann and M. Beller, *Adv. Synth. Catal.*, 2011, **353**, 788.
5. P. Wan and S. Muralidharan, *J. Am. Chem. Soc.*, 1988, **110**, 4336.
6. A. Rühling, H.-J. Galla and F. Glorius, *Chem. Eur. J.*, 2015, **21**, 12291.
7. G. Le Bras, O. Provot, J. F. Peyrat, M. Alami and J. D. Brion, *Tetrahedron Lett.*, 2006, **47**, 5497.
8. G. K. S. Prakash, C. Panja, T. Mathew and G. A. Olah, *Catal. Lett.*, 2007, **114**, 24.
9. C. W. Downey, M. W. Johnson and K. J. Tracy, *J. Org. Chem.*, 2008, **73**, 3299.
10. Y. Liang, Y.-X. Xie and J.-H. Li, *Synthesis*, 2007, **2007**, 400.

11. S.-D. Yang, C.-L. Sun, Z. Fang, B.-J. Li, Y.-Z. Li and Z.-J. Shi, *Angew. Chem. Int. Ed.*, 2008, **47**, 1473.
12. Y. Miyazaki and S. Kobayashi, *J. Comb. Chem.*, 2008, **10**, 355.
13. A. Fürstner and P. W. Davies, *J. Am. Chem. Soc.*, 2005, **127**, 15024.
14. J. Ruan, X. Li, O. Saidi and J. Xiao, *J. Am. Chem. Soc.*, 2008, **130**, 2424.
15. J. Mo, L. Xu and J. Xiao, *J. Am. Chem. Soc.*, 2005, **127**, 751.
16. S. Liu, N. Berry, N. Thomson, A. Pettman, Z. Hyder, J. Mo and J. Xiao, *J. Org. Chem.*, 2006, **71**, 7467.
17. L. Chu and F.-L. Qing, *Org. Lett.*, 2010, **12**, 5060.
18. W. Pei, J. Mo and J. Xiao, *J. Organomet. Chem.*, 2005, **690**, 3546.
19. D. J. Fox, D. S. Pedersen and S. Warren, *Org. Biomol. Chem.*, 2006, **4**, 3102.

**$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra**

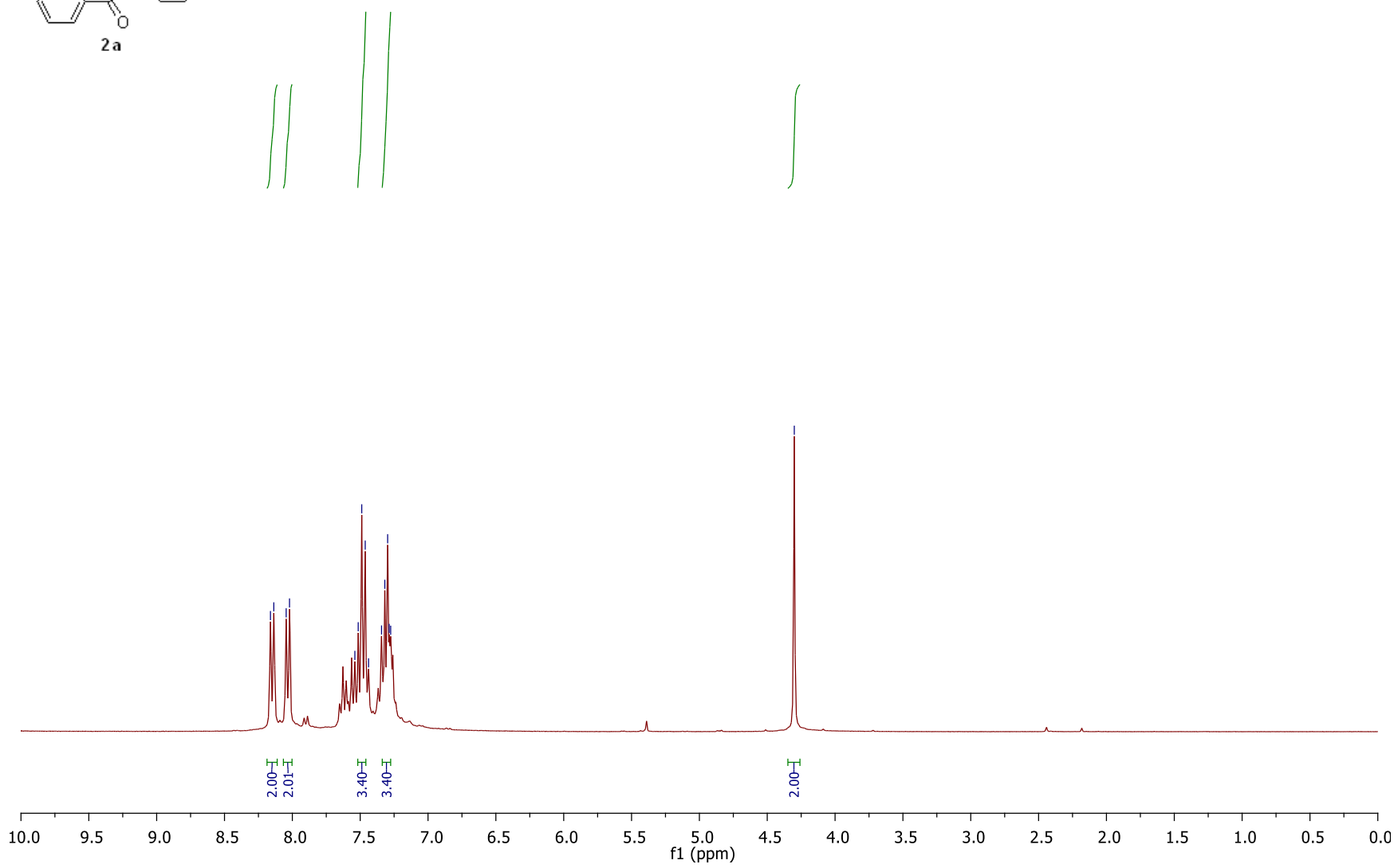
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**2a**

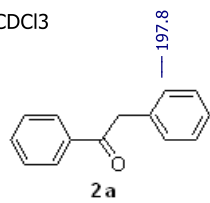
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4.30



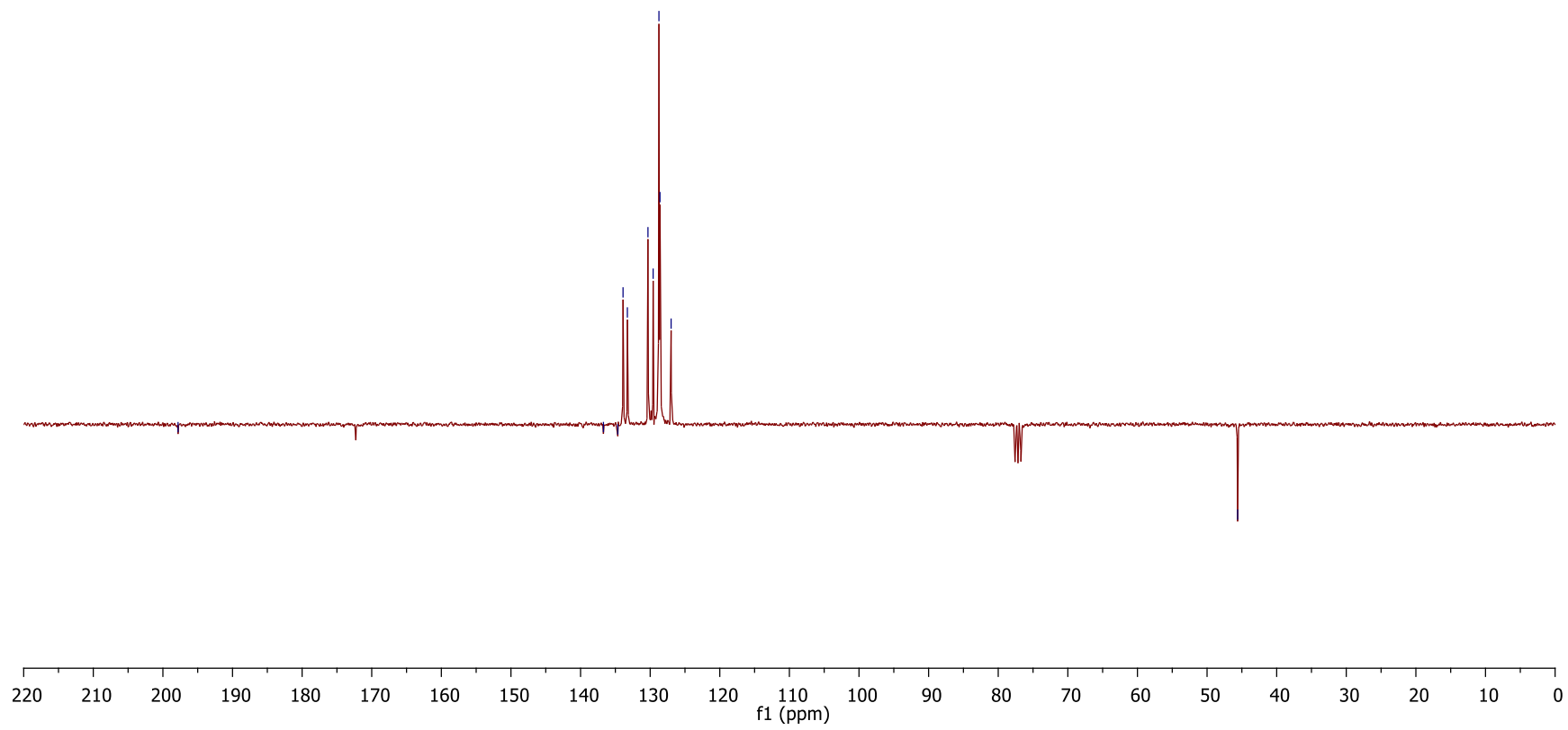


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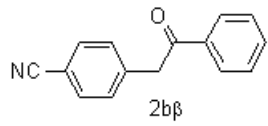
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45.6



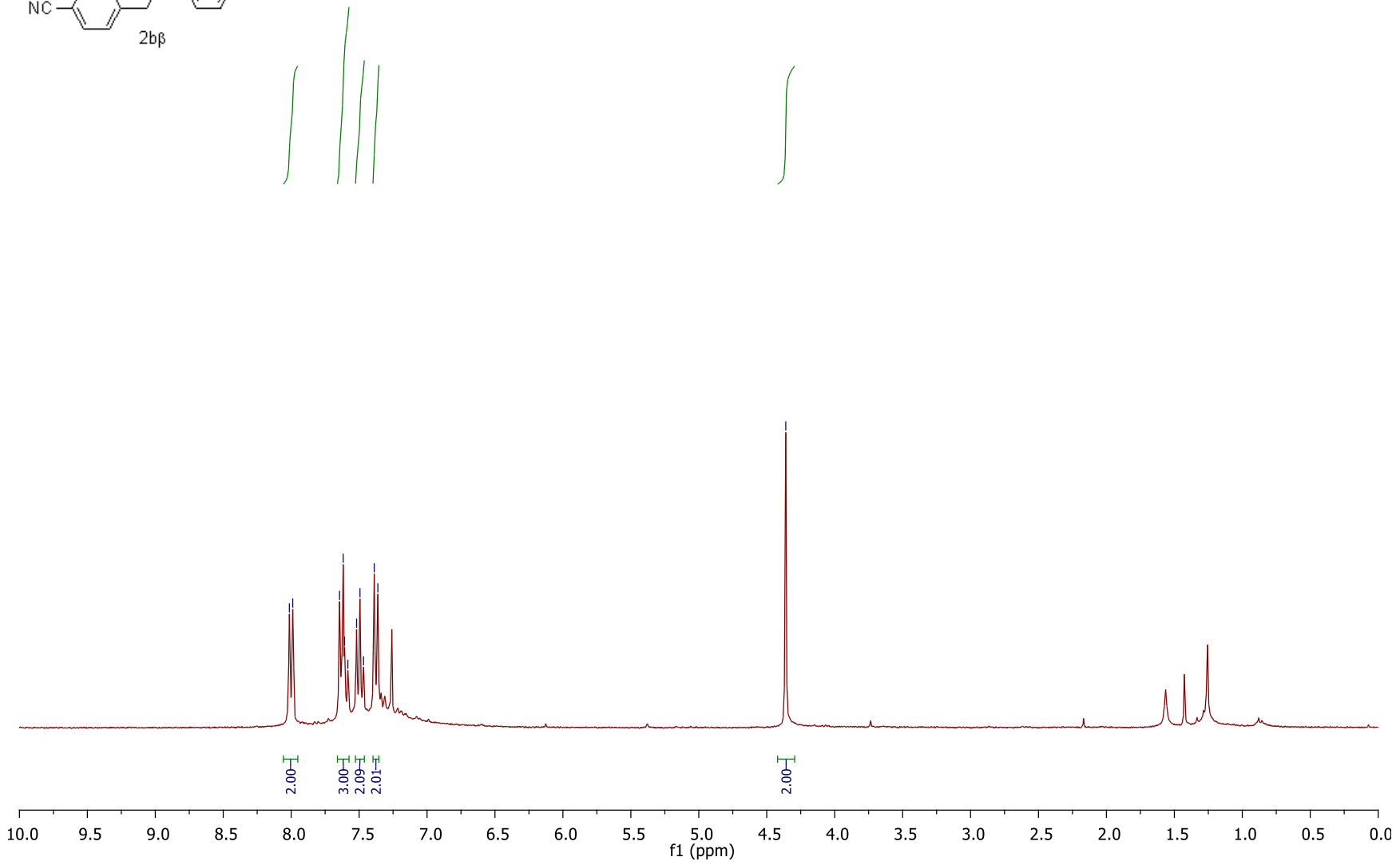
S17

CDCl3

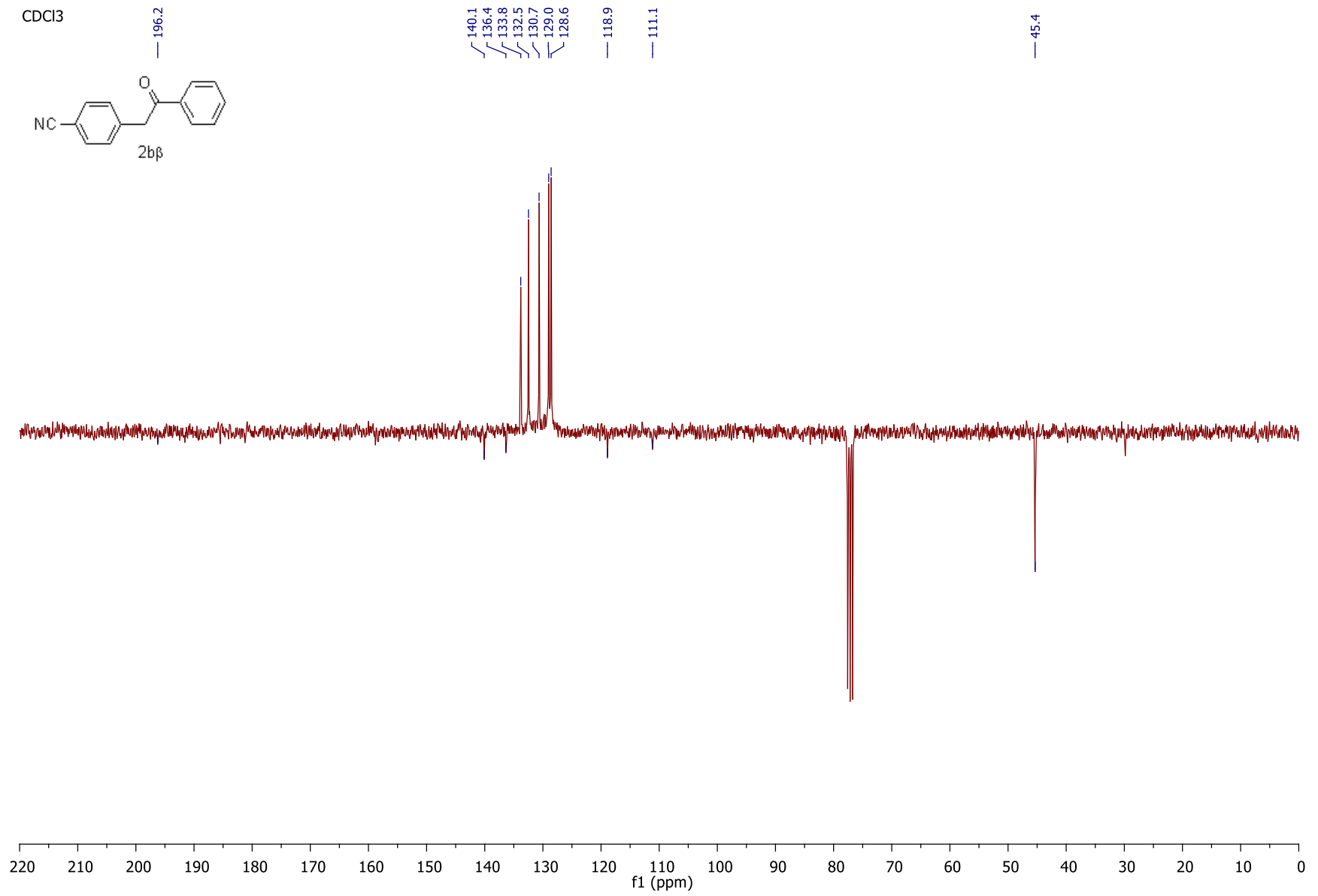
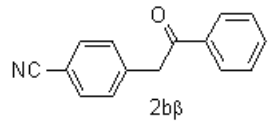


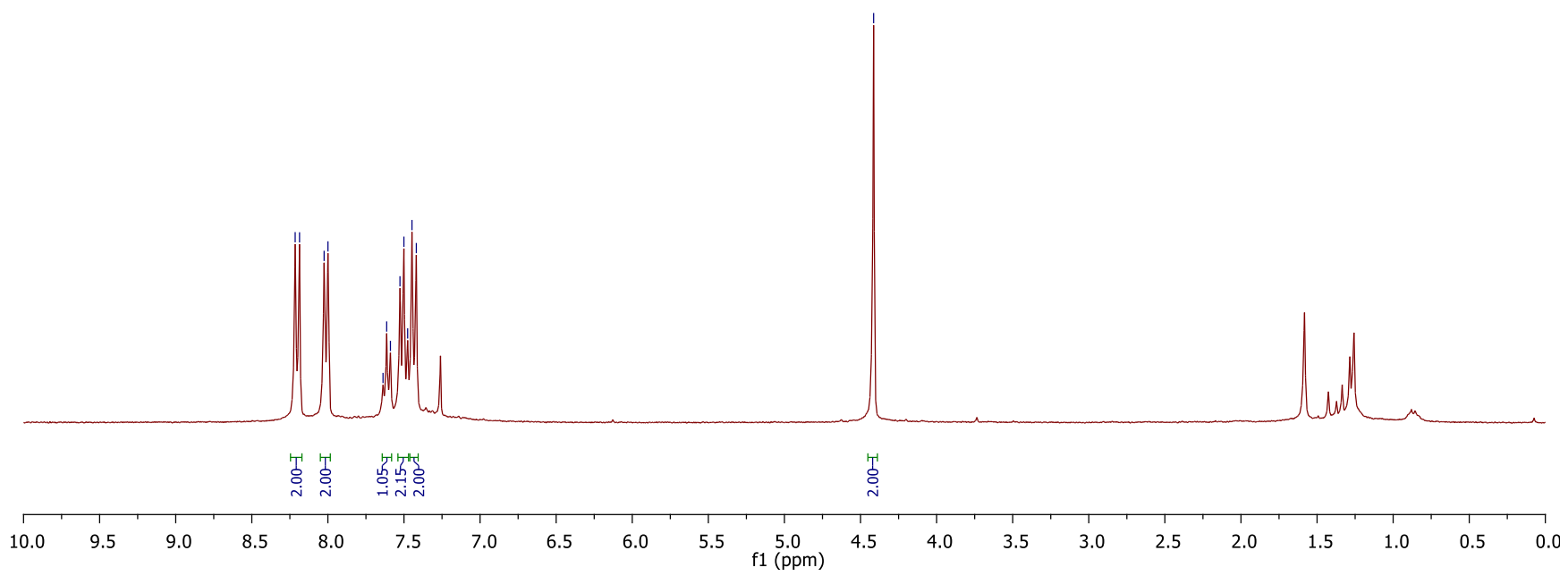
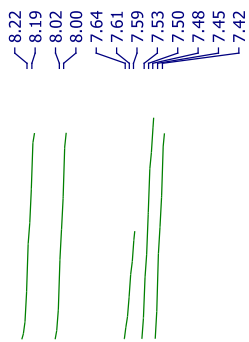
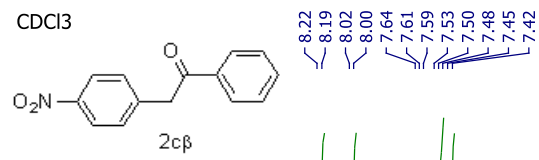
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4.36



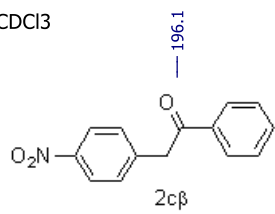
CDCl<sub>3</sub>





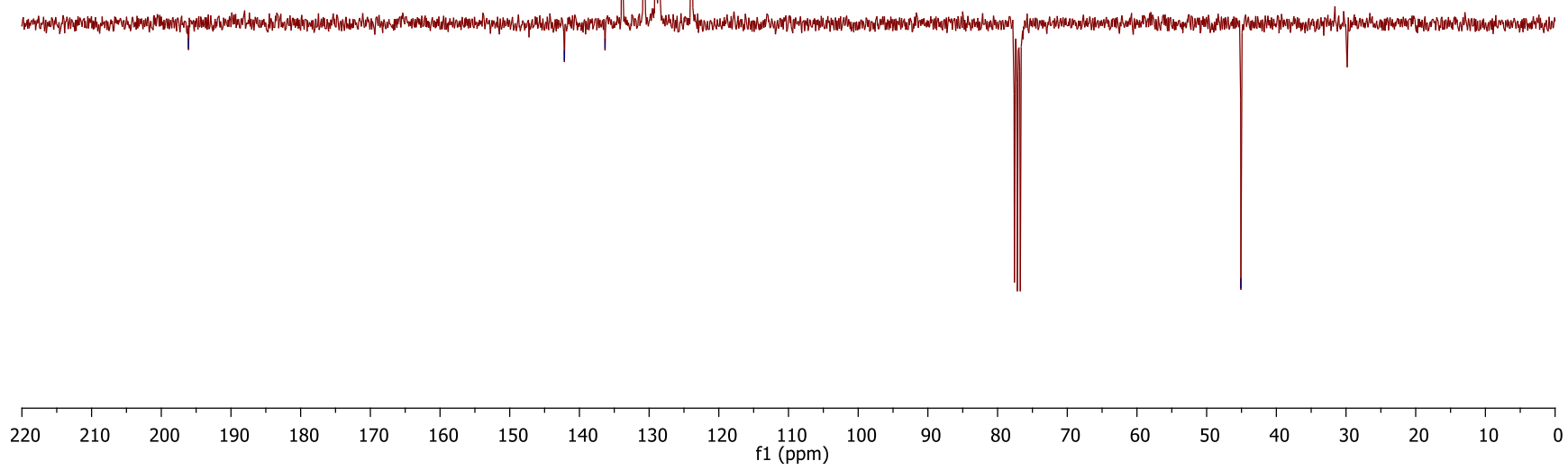
S20

CDCl<sub>3</sub>



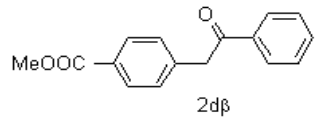
142.2  
136.3  
133.9  
130.8  
129.0  
128.6  
123.9

45.1



S21

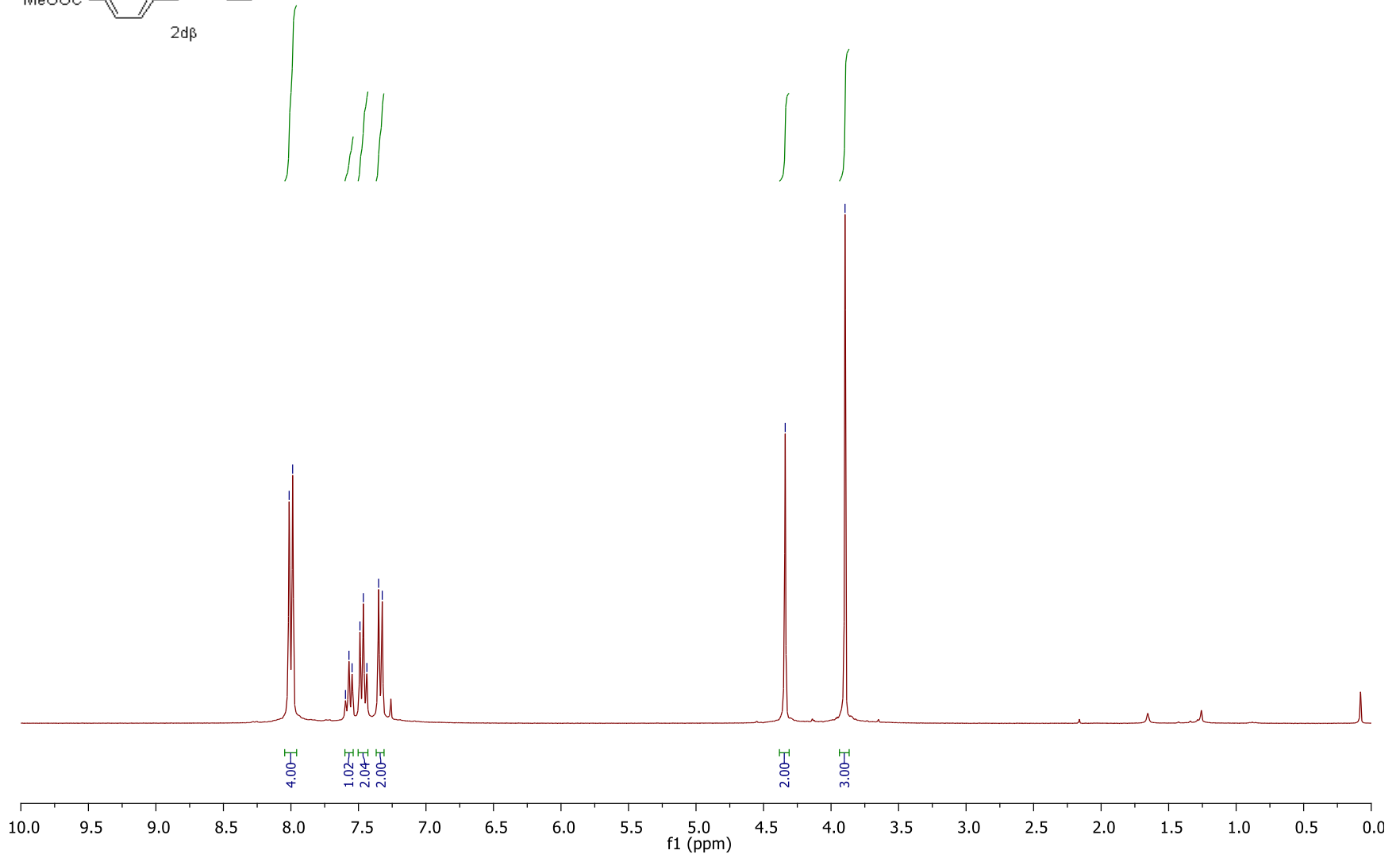
CDCl3



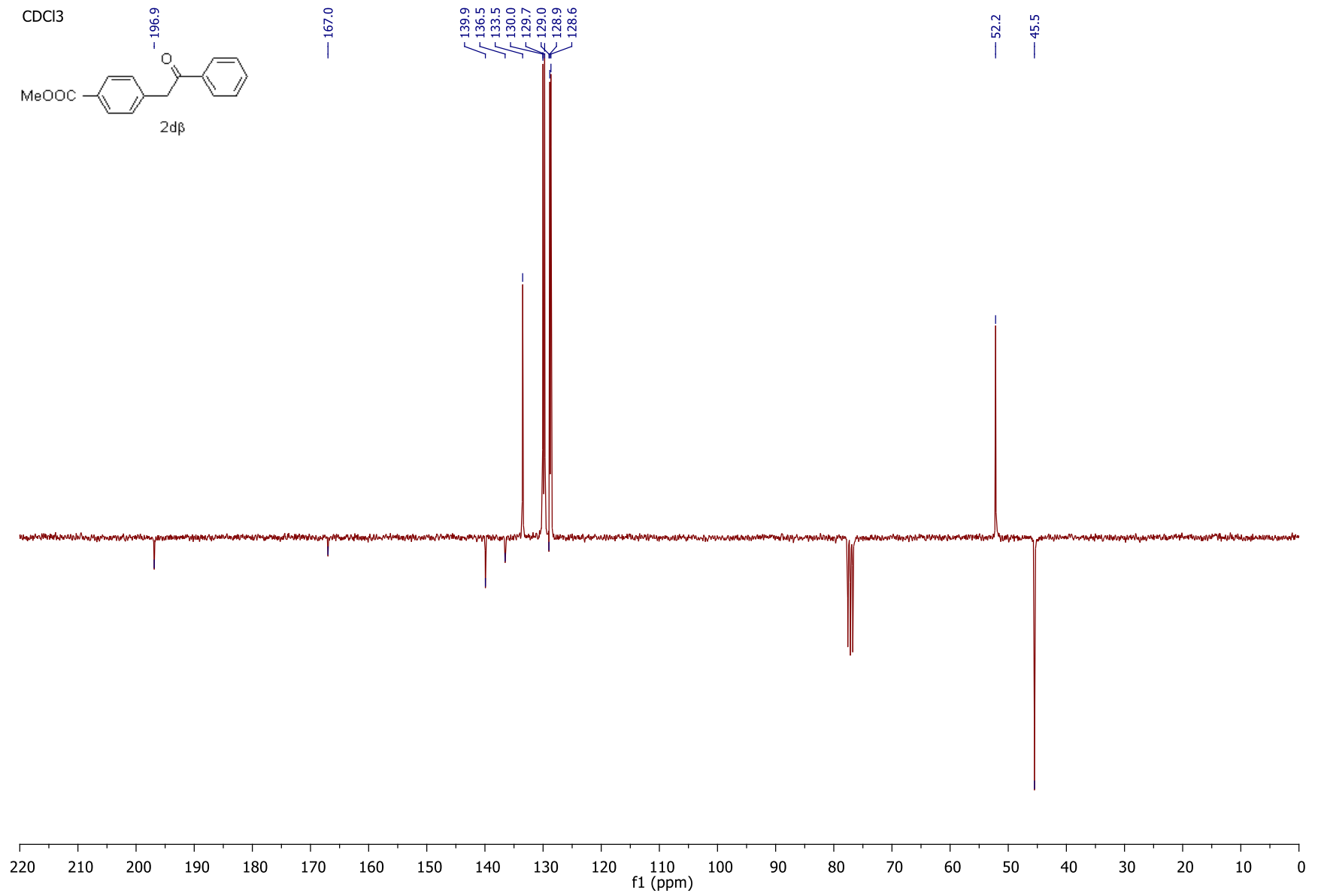
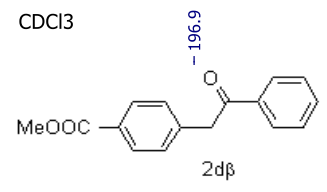
8.01  
7.99  
7.60  
7.57  
7.55  
7.49  
7.46  
7.44  
7.35  
7.32

4.34

3.90

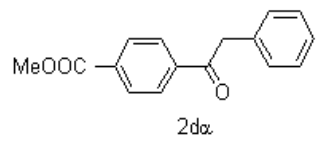


S22

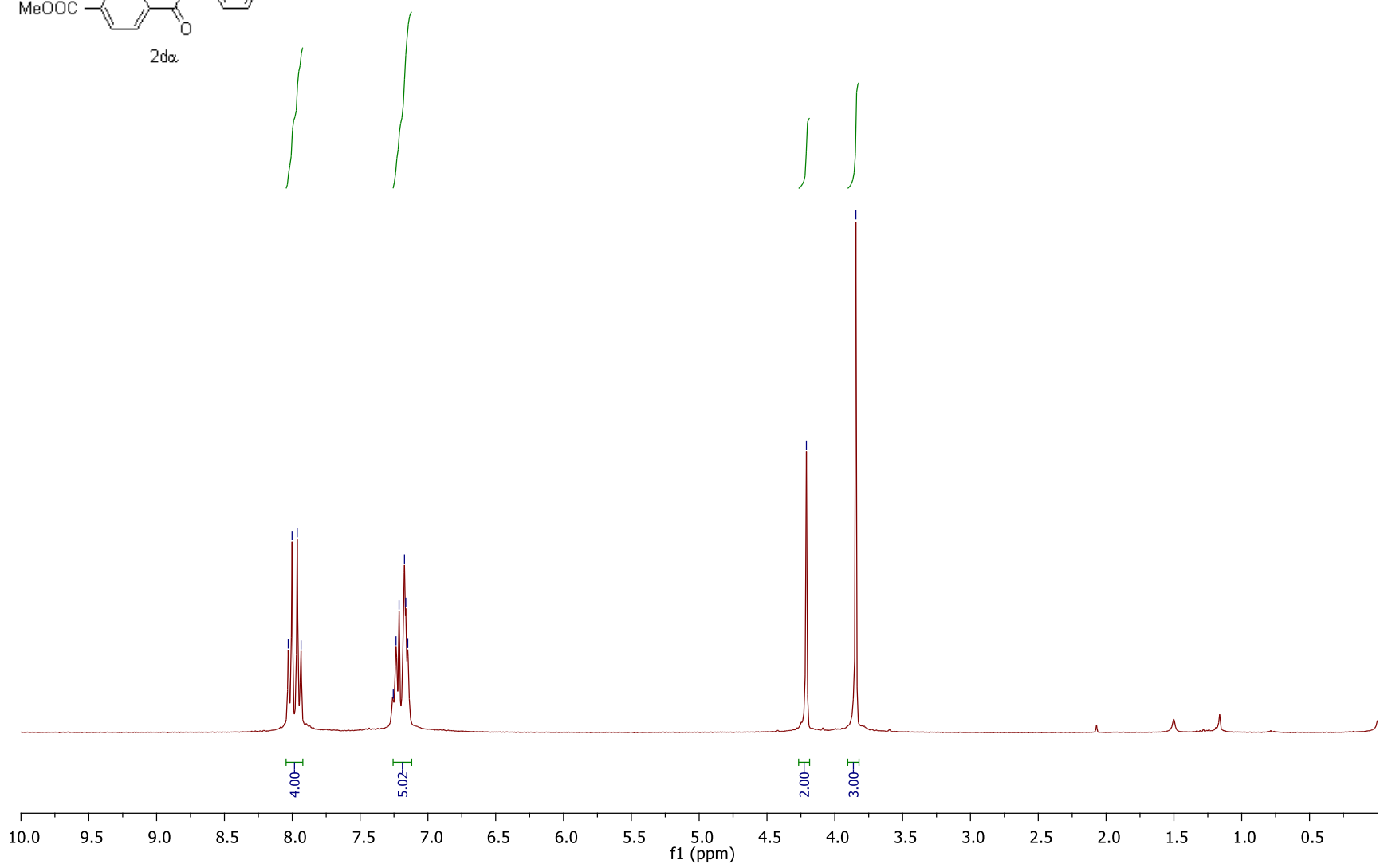


S23

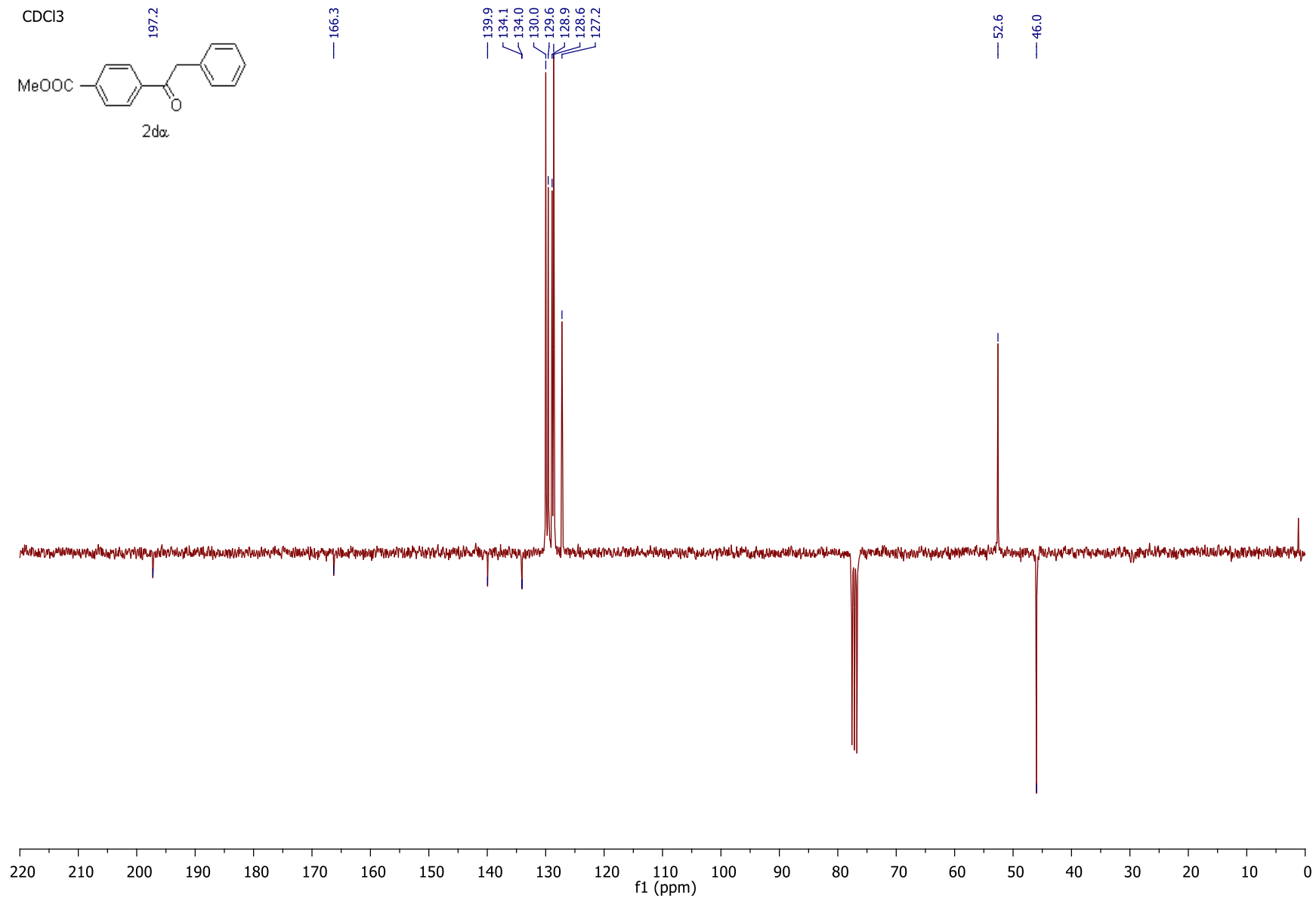
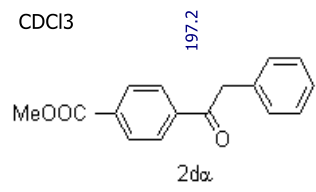
CDCl3



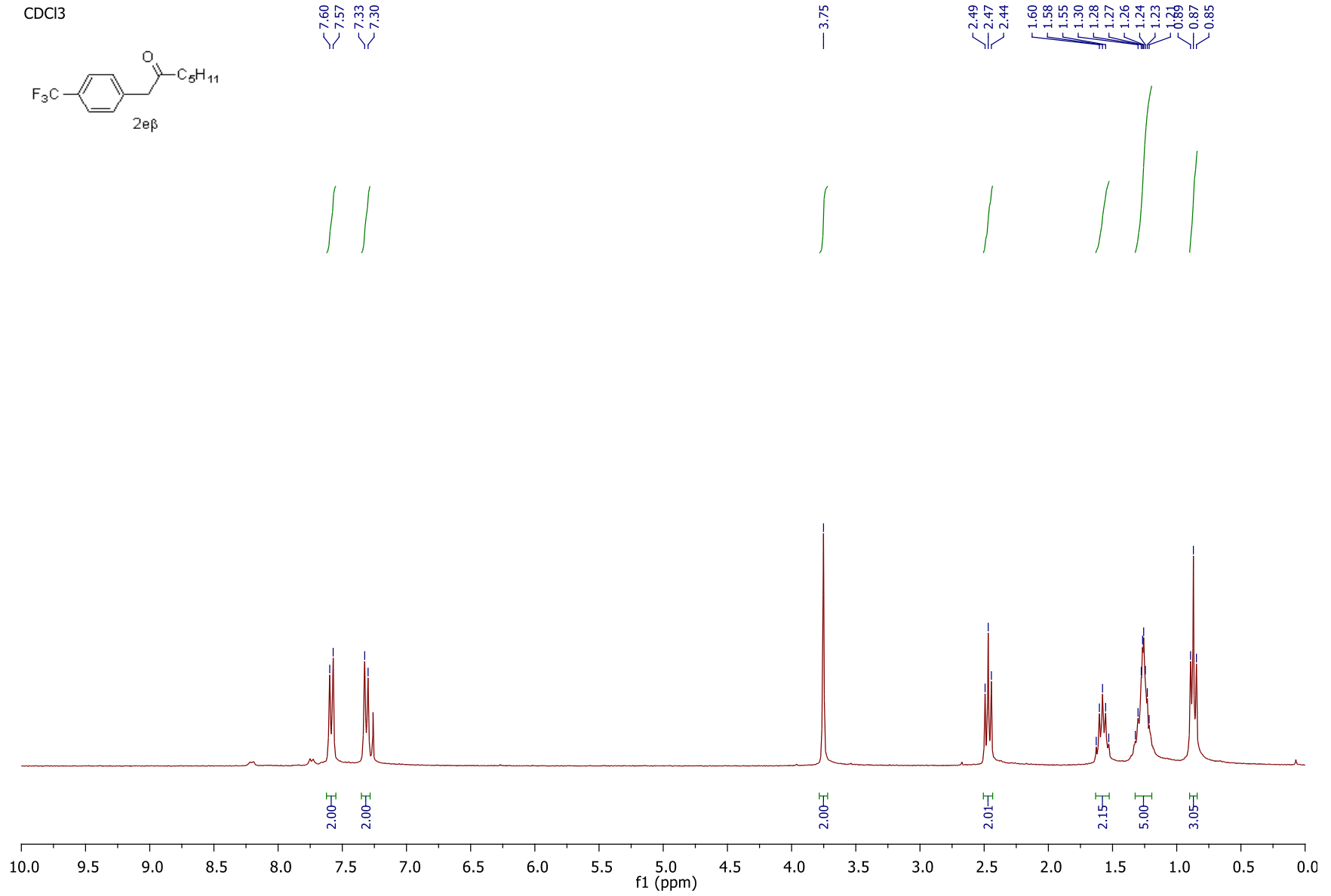
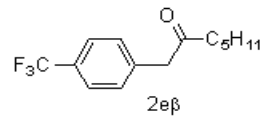
8.03  
8.00  
7.96  
7.94  
7.26  
7.24  
7.21  
7.17  
7.16  
7.15  
4.21  
3.84



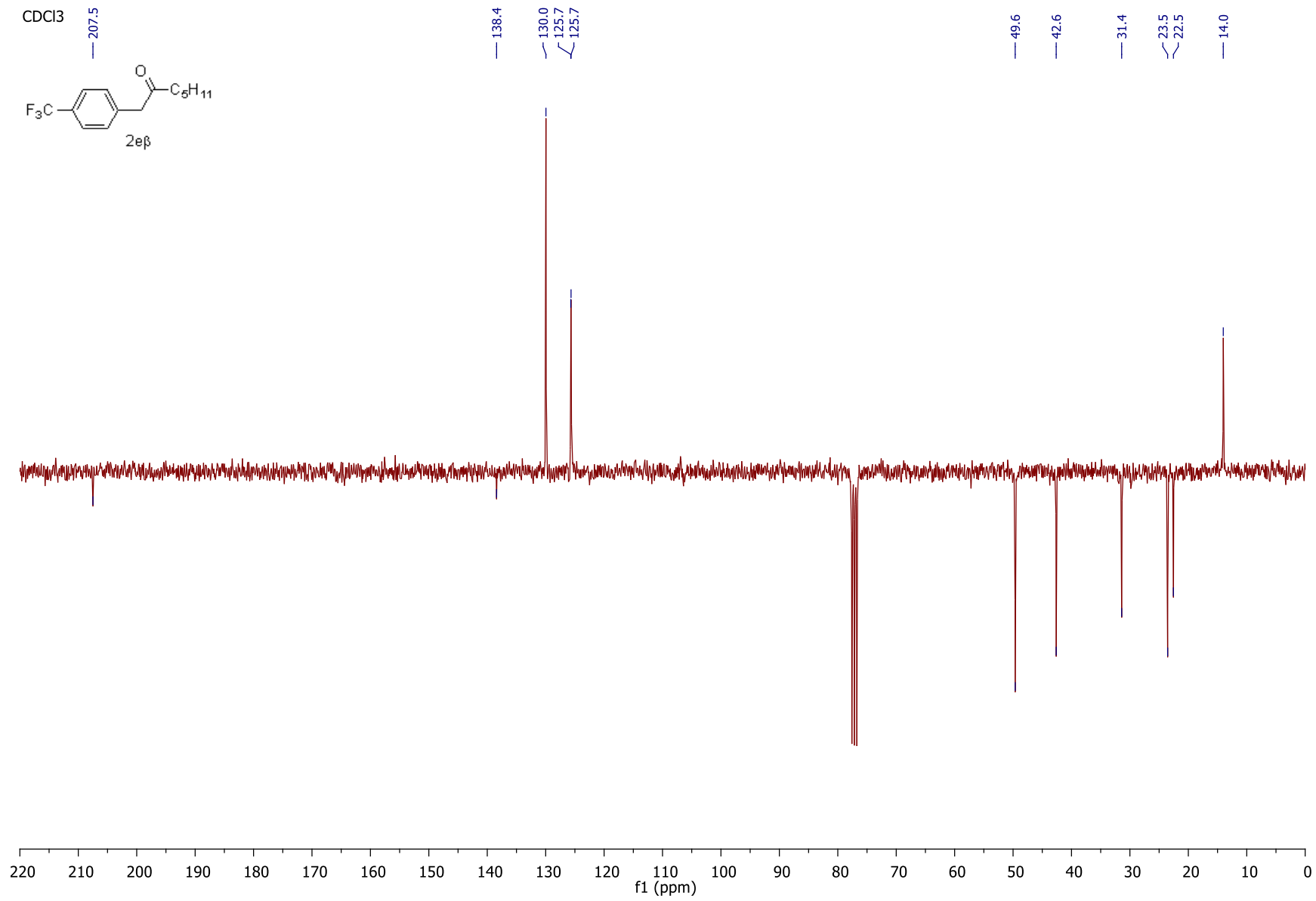
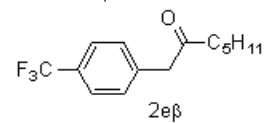




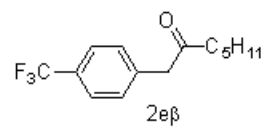
CDCl3



CDCl<sub>3</sub>



CDCl3 F19



-62.56

CDCl3 F19

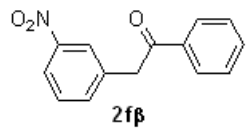
-62.56

-62.40 -62.45 -62.50 -62.55 -62.60 -62.65  
f1 (ppm)

-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100  
f1 (ppm)

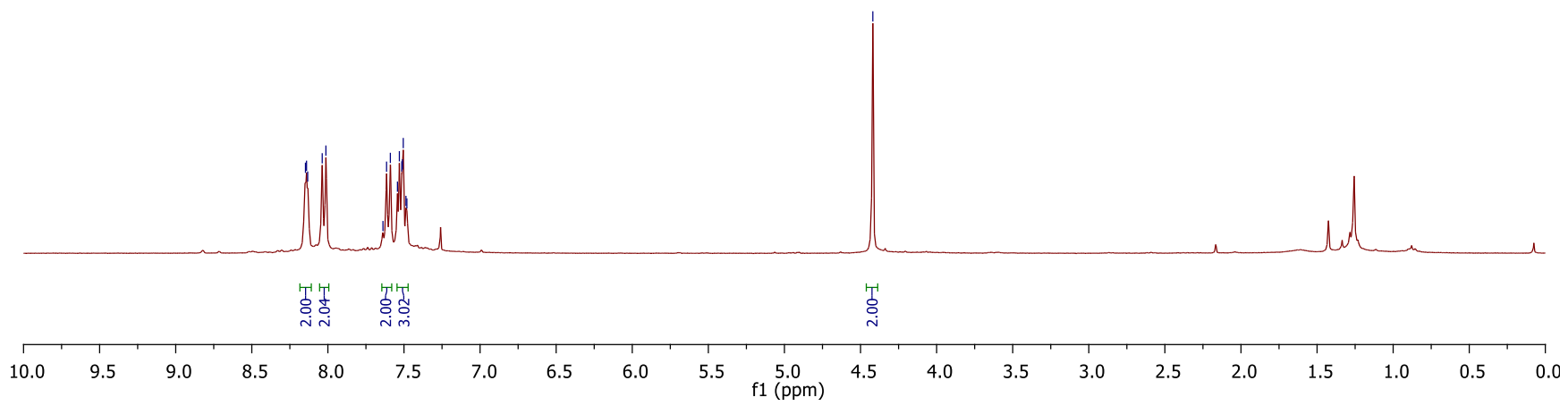
S28

CDCl3

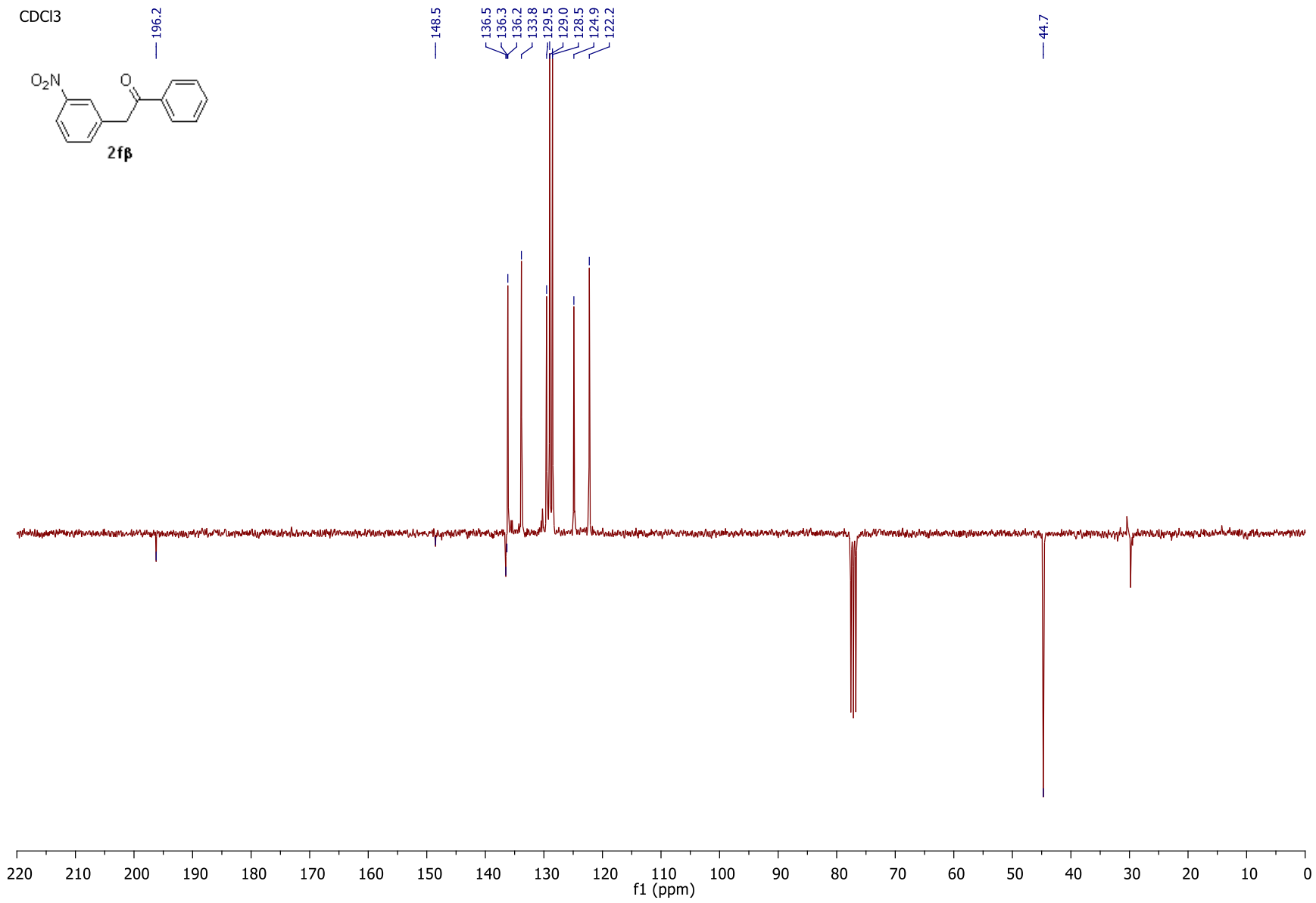
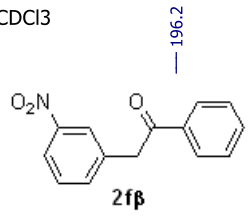


8.15  
8.14  
8.13  
8.04  
7.64  
7.61  
7.59  
7.54  
7.53  
7.51  
7.50  
7.49  
7.48

4.42

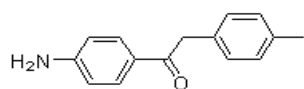


CDCl3

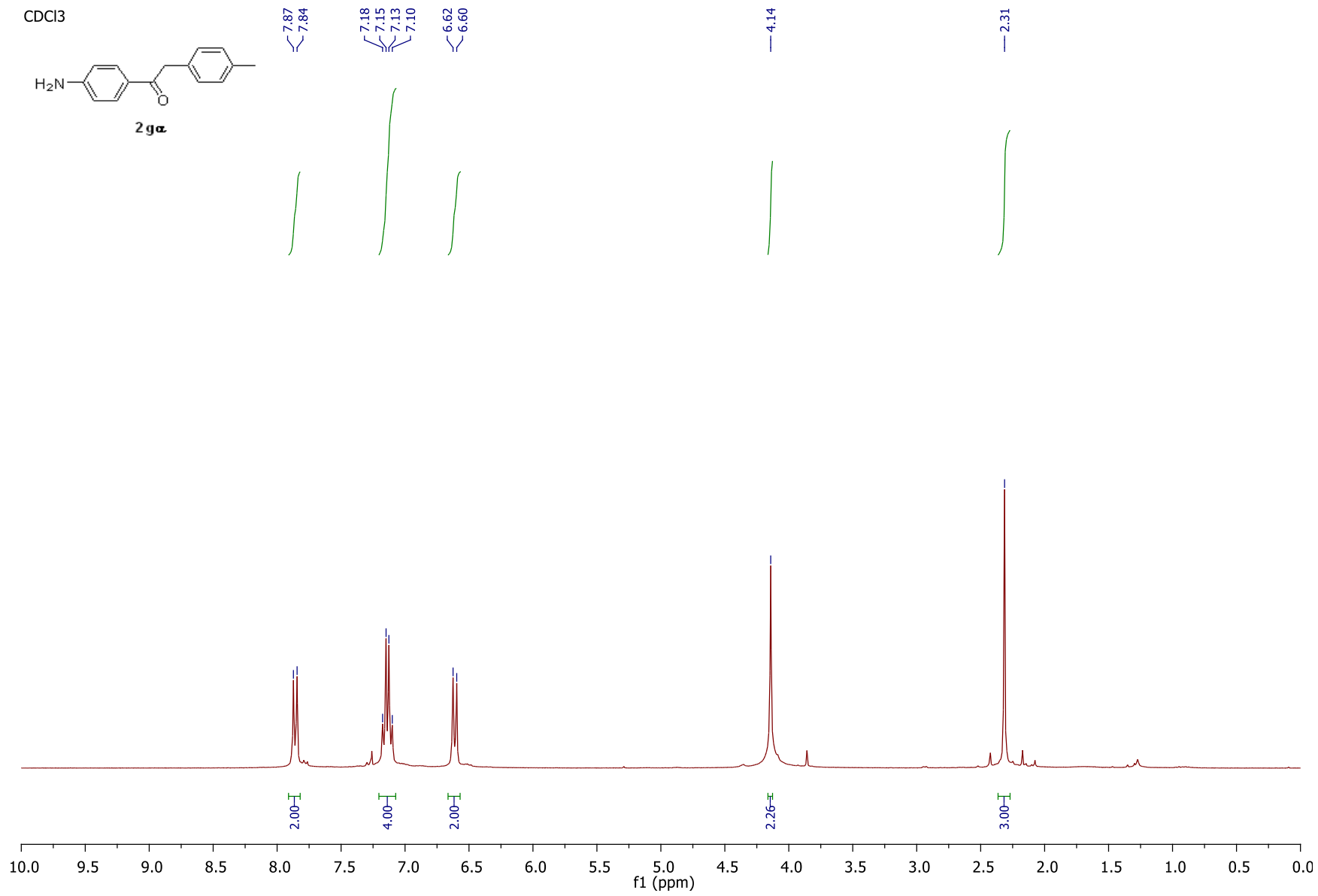


S30

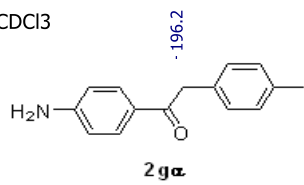
CDCl<sub>3</sub>



**2ga**



CDCl<sub>3</sub>



151.3

136.3

132.5

131.3

129.4

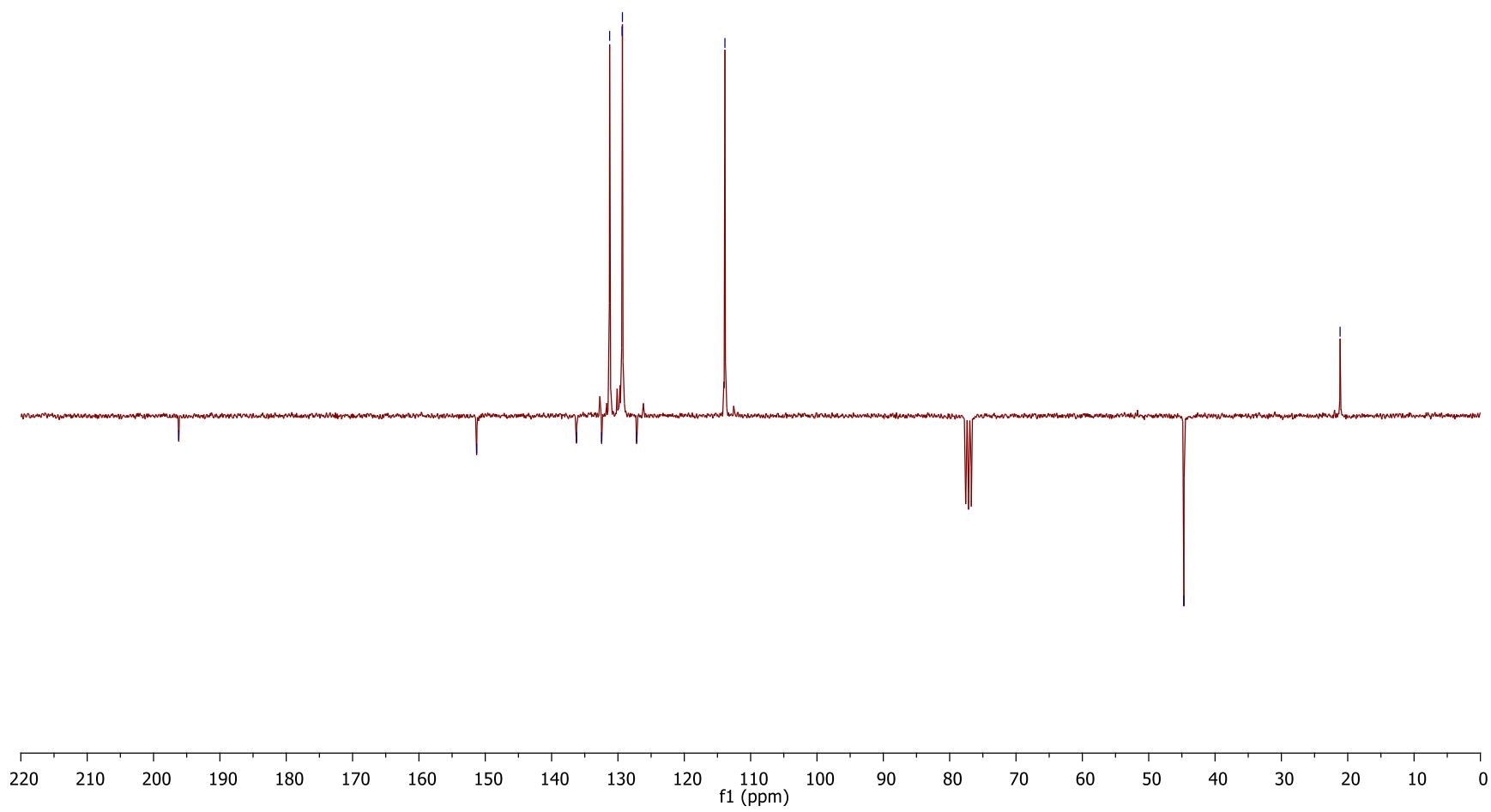
129.3

127.2

113.9

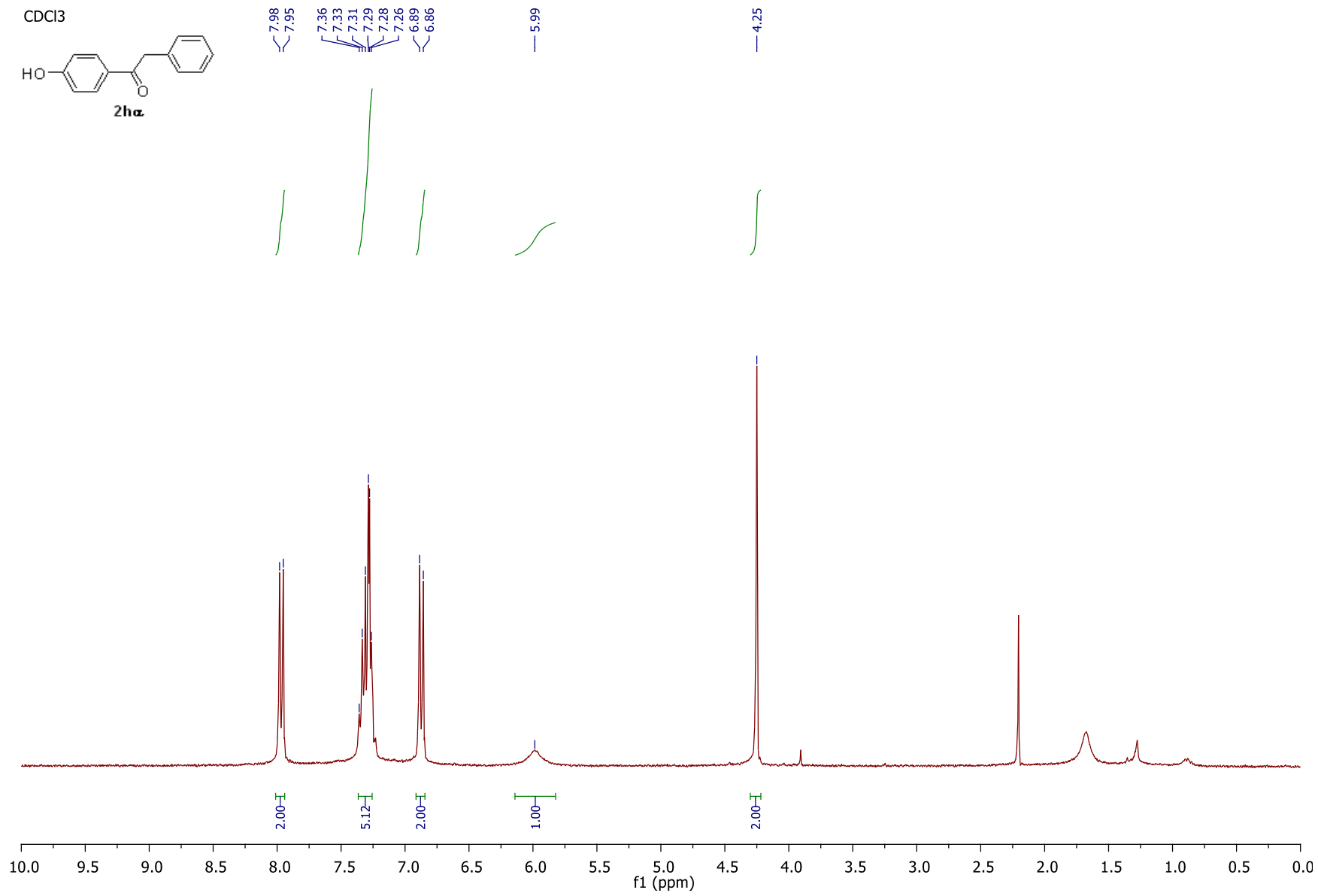
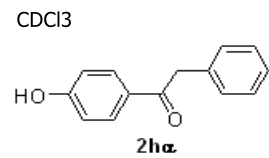
44.7

21.2

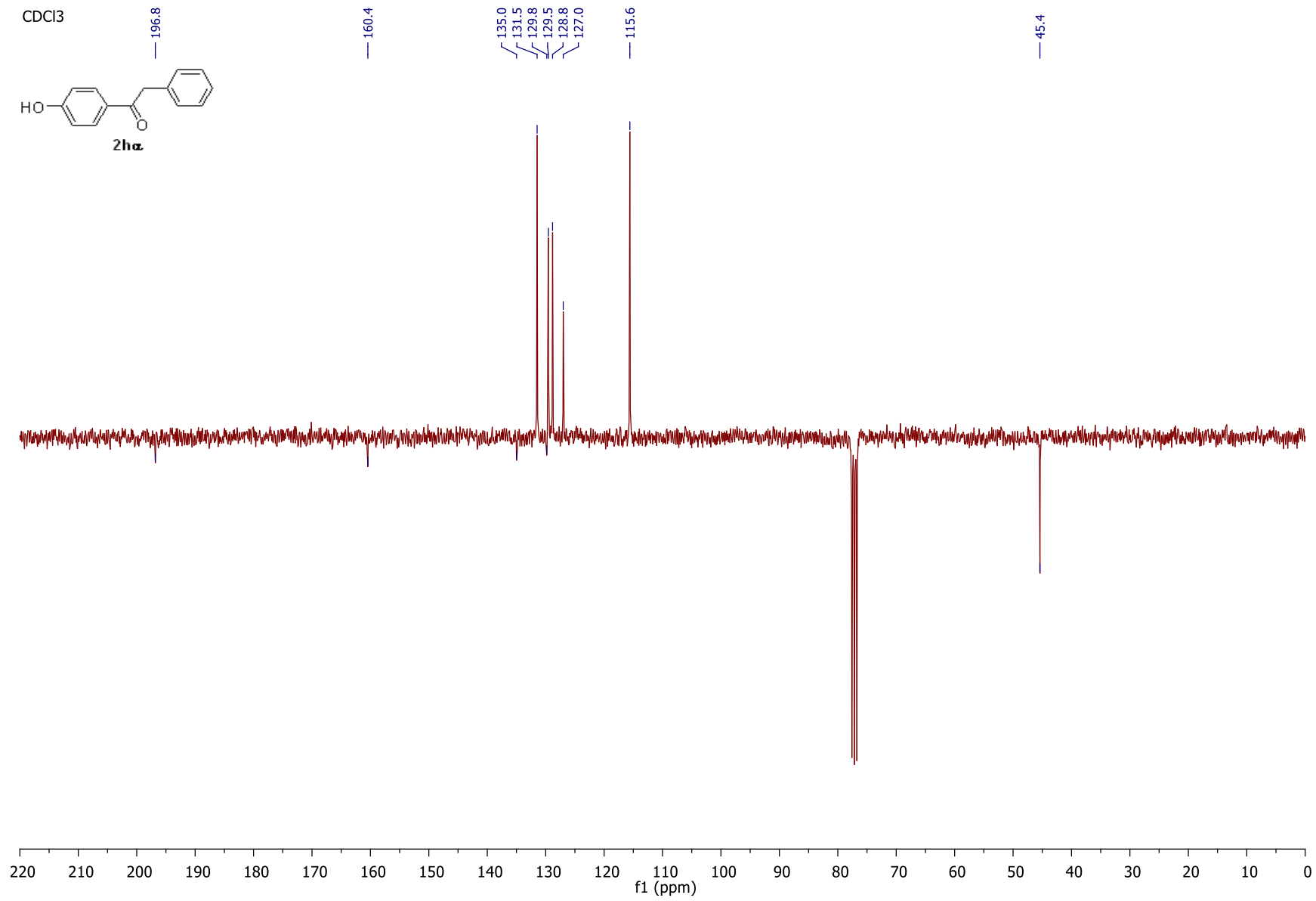
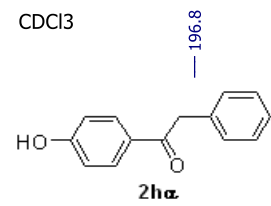


S32

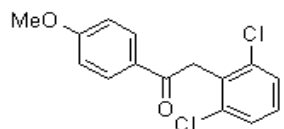




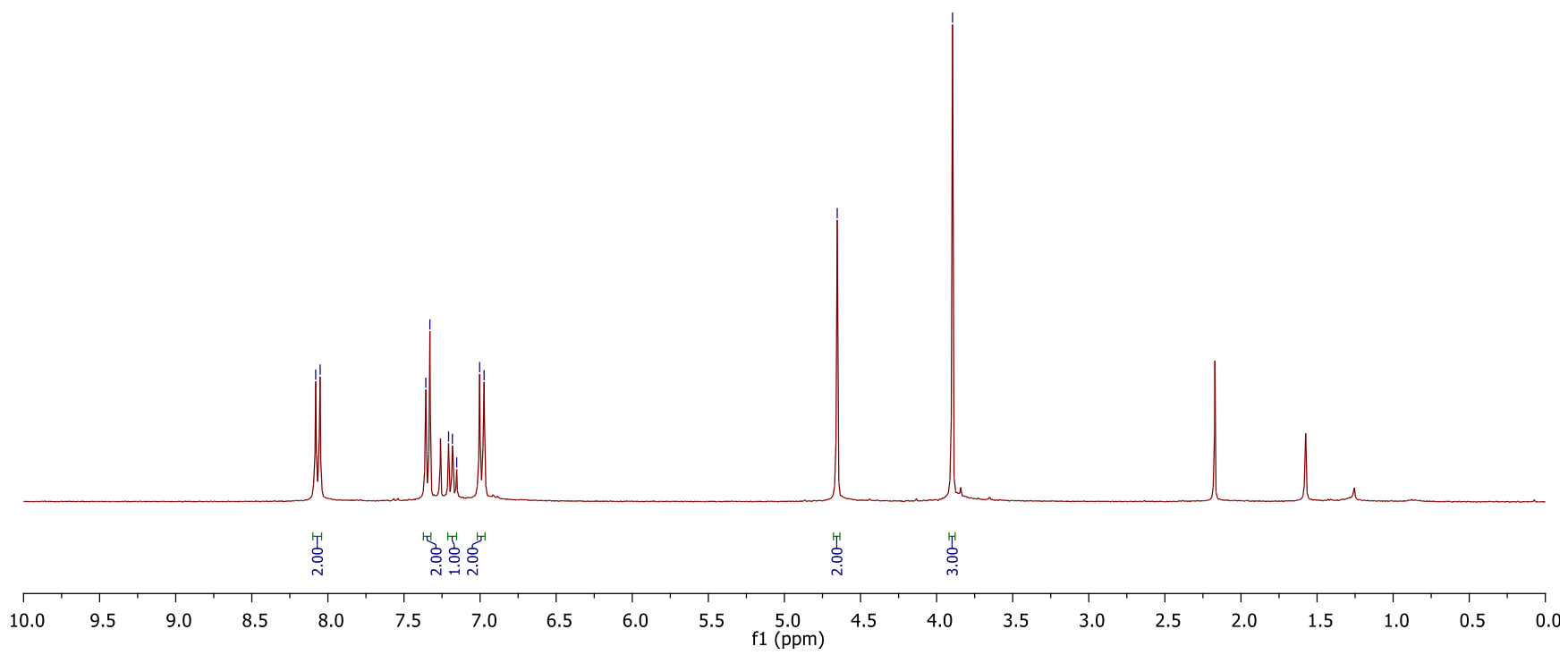
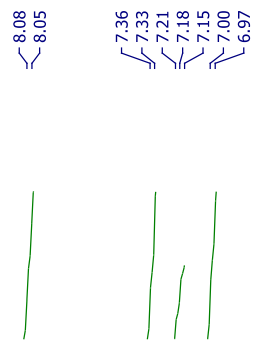
S33



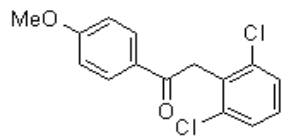
CDCl<sub>3</sub>



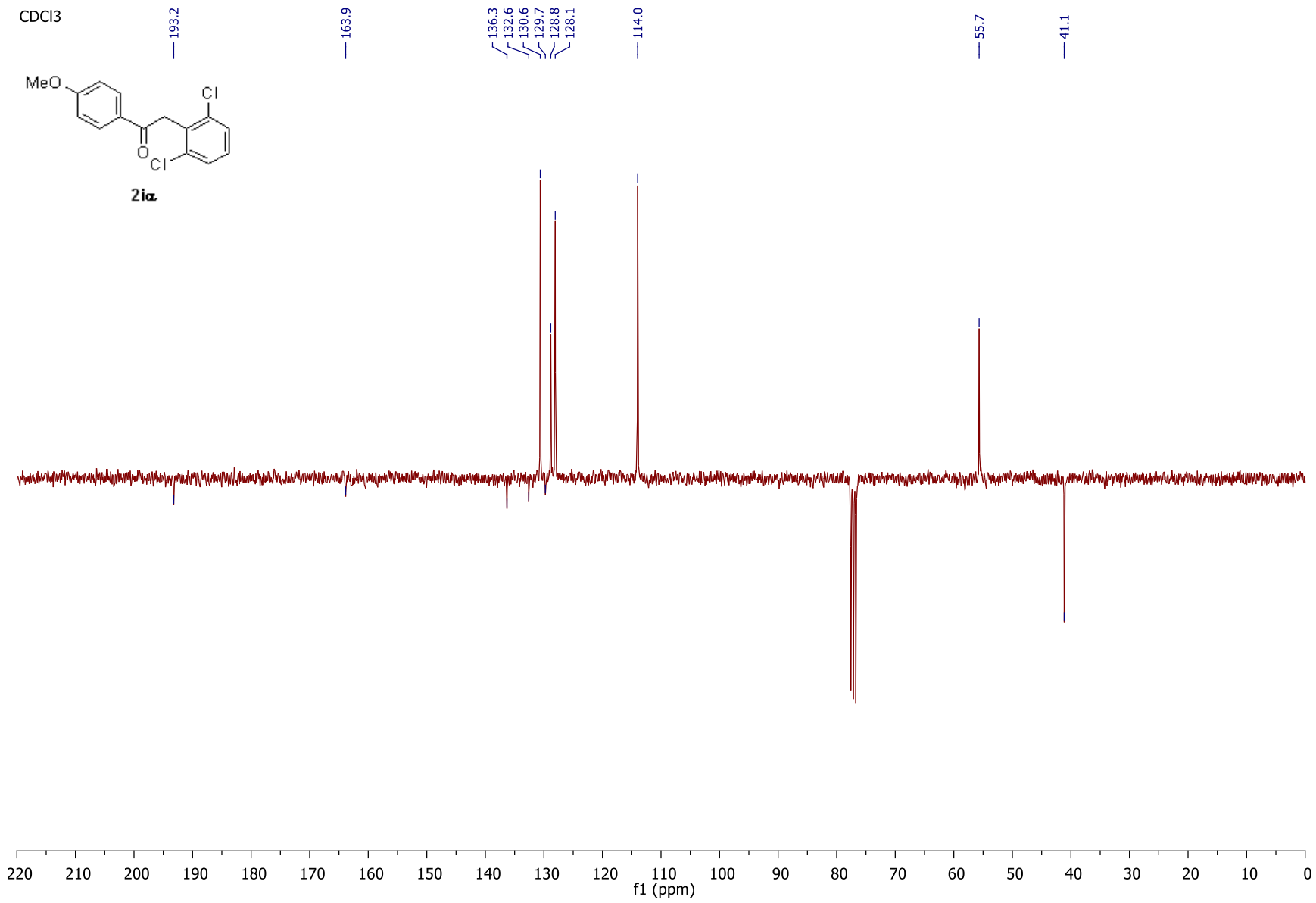
**2ia**

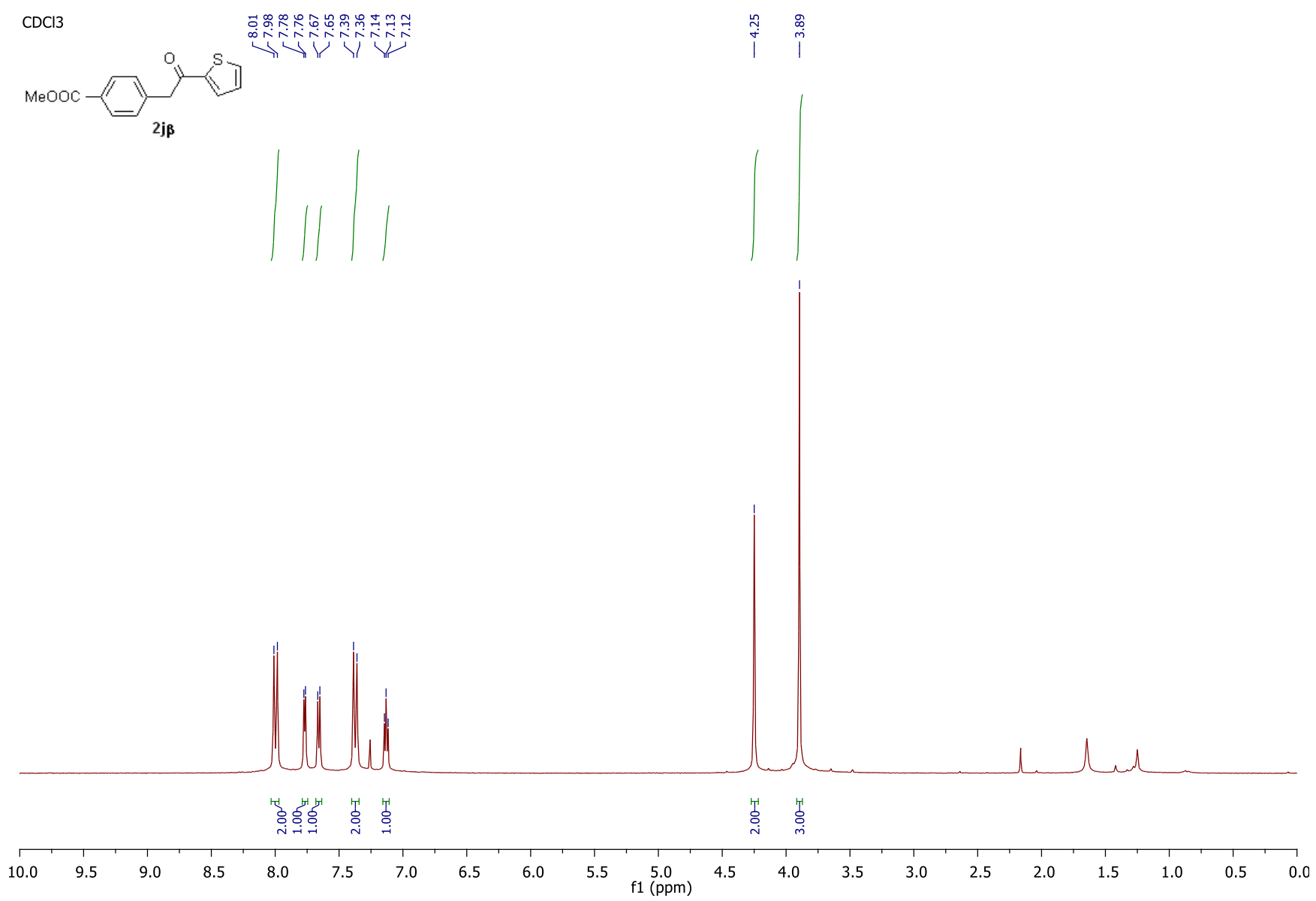


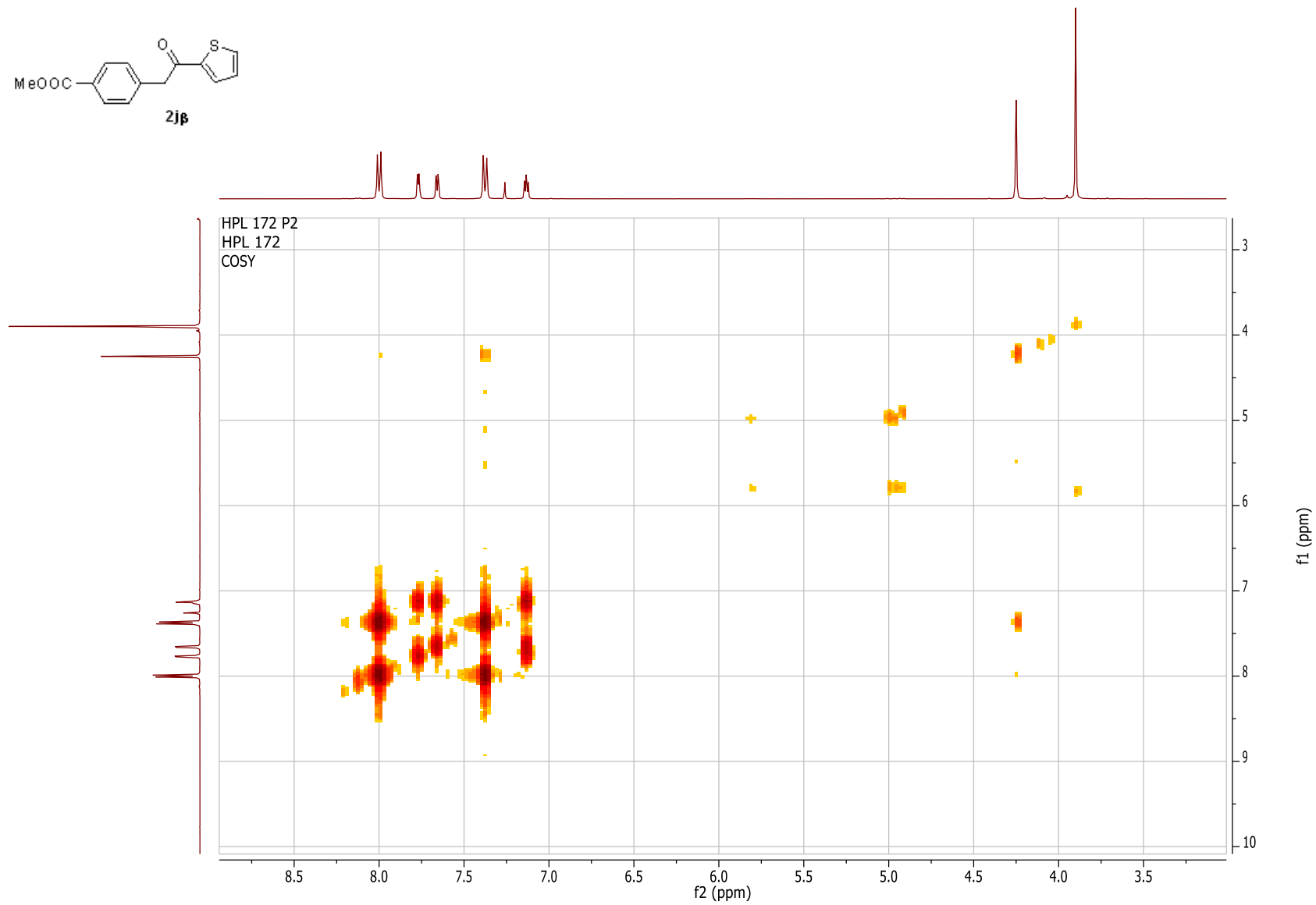
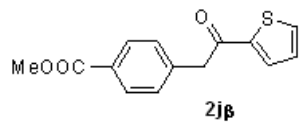
CDCl<sub>3</sub>



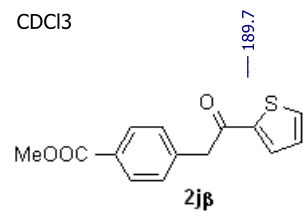
**2ia**







CDCl<sub>3</sub>



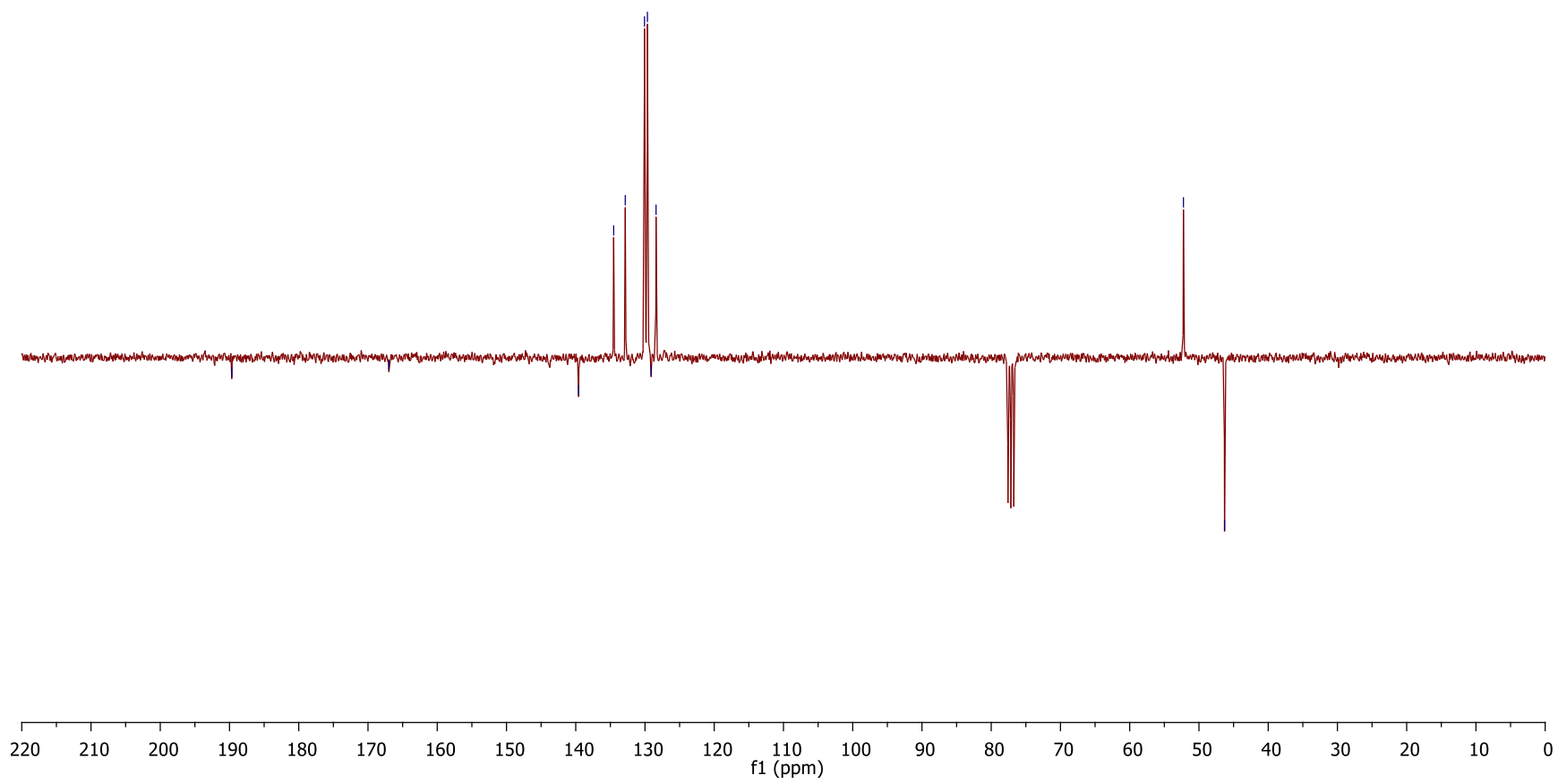
— 189.7

— 167.0

139.6  
134.5  
132.8  
130.1  
129.6  
129.1  
128.4

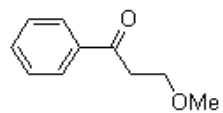
— 52.2

— 46.3



S39

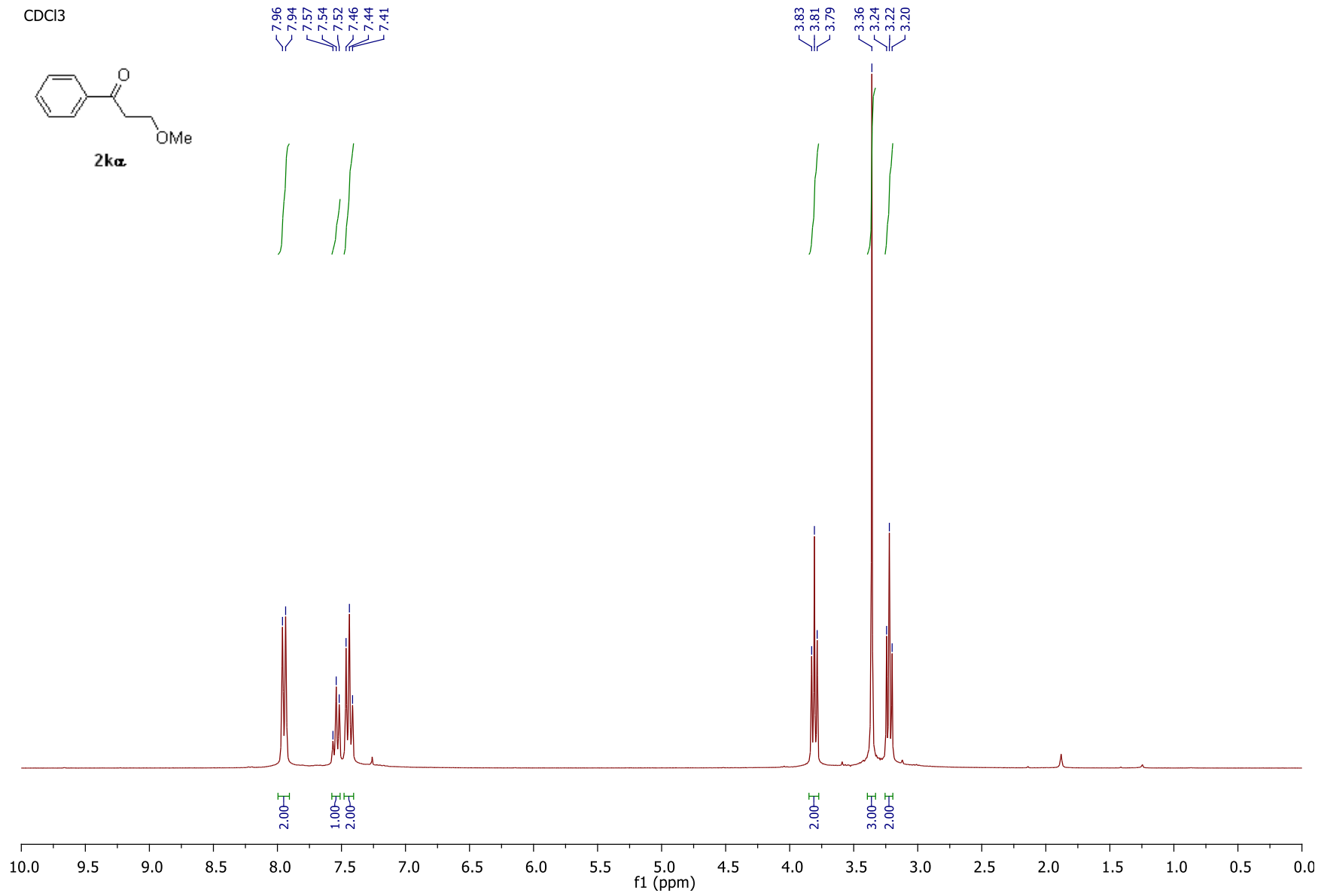
CDCl<sub>3</sub>



**2ka**

7.96  
7.94  
7.57  
7.54  
7.52  
7.46  
7.44  
7.41

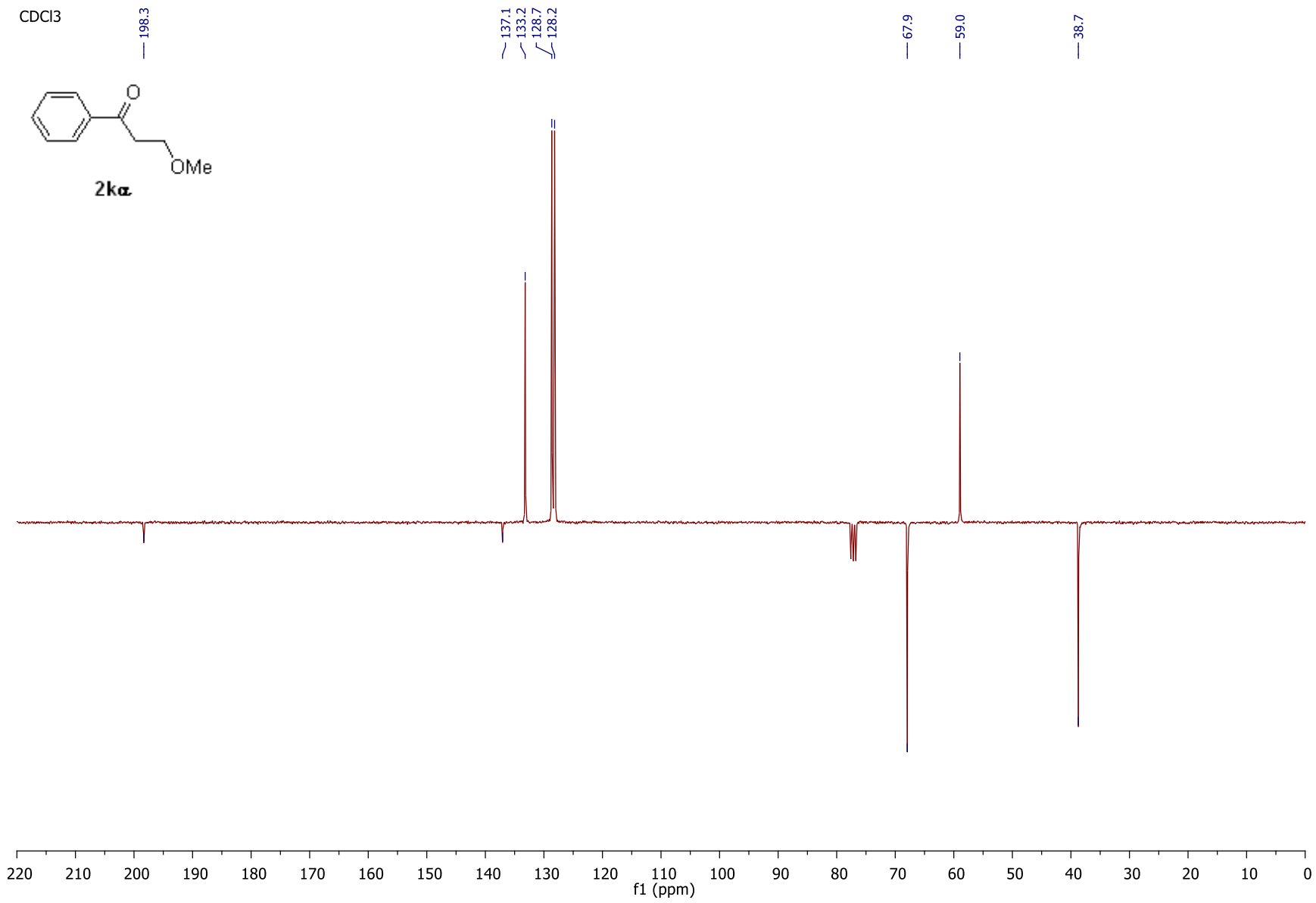
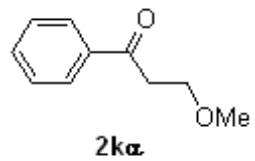
3.83  
3.81  
3.79  
3.36  
3.24  
3.22  
3.20



S40

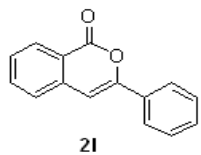


CDCl<sub>3</sub>

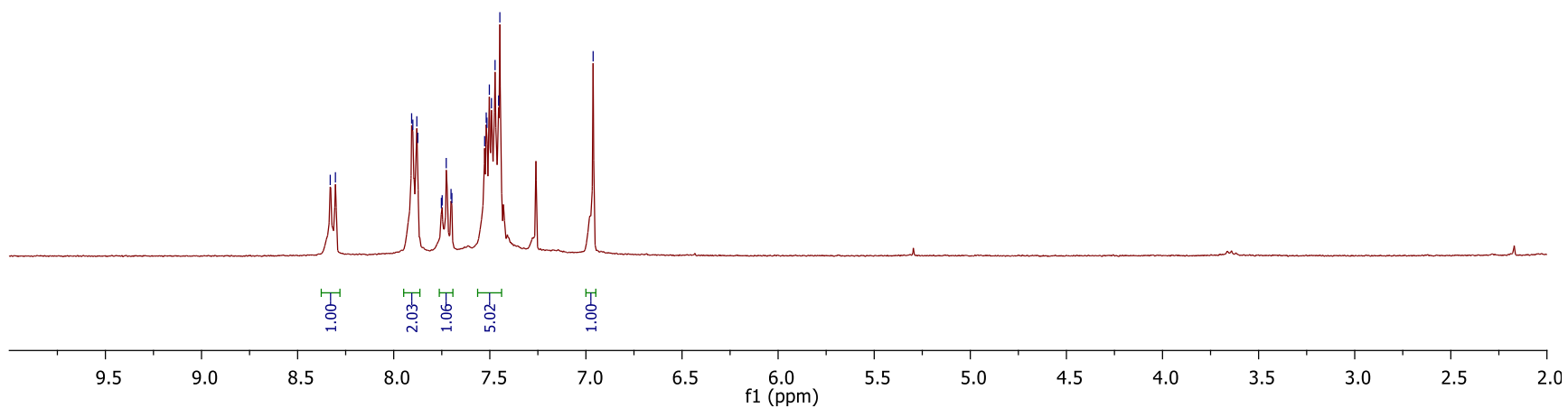
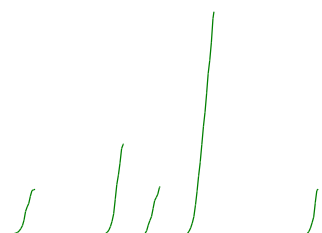


S41

CDCl<sub>3</sub>

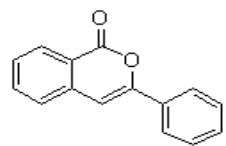


8.33  
8.30  
7.91  
7.90  
7.88  
7.87  
7.53  
7.52  
7.51  
7.50  
7.49  
7.47  
7.45  
6.96



S42

CDCl<sub>3</sub>

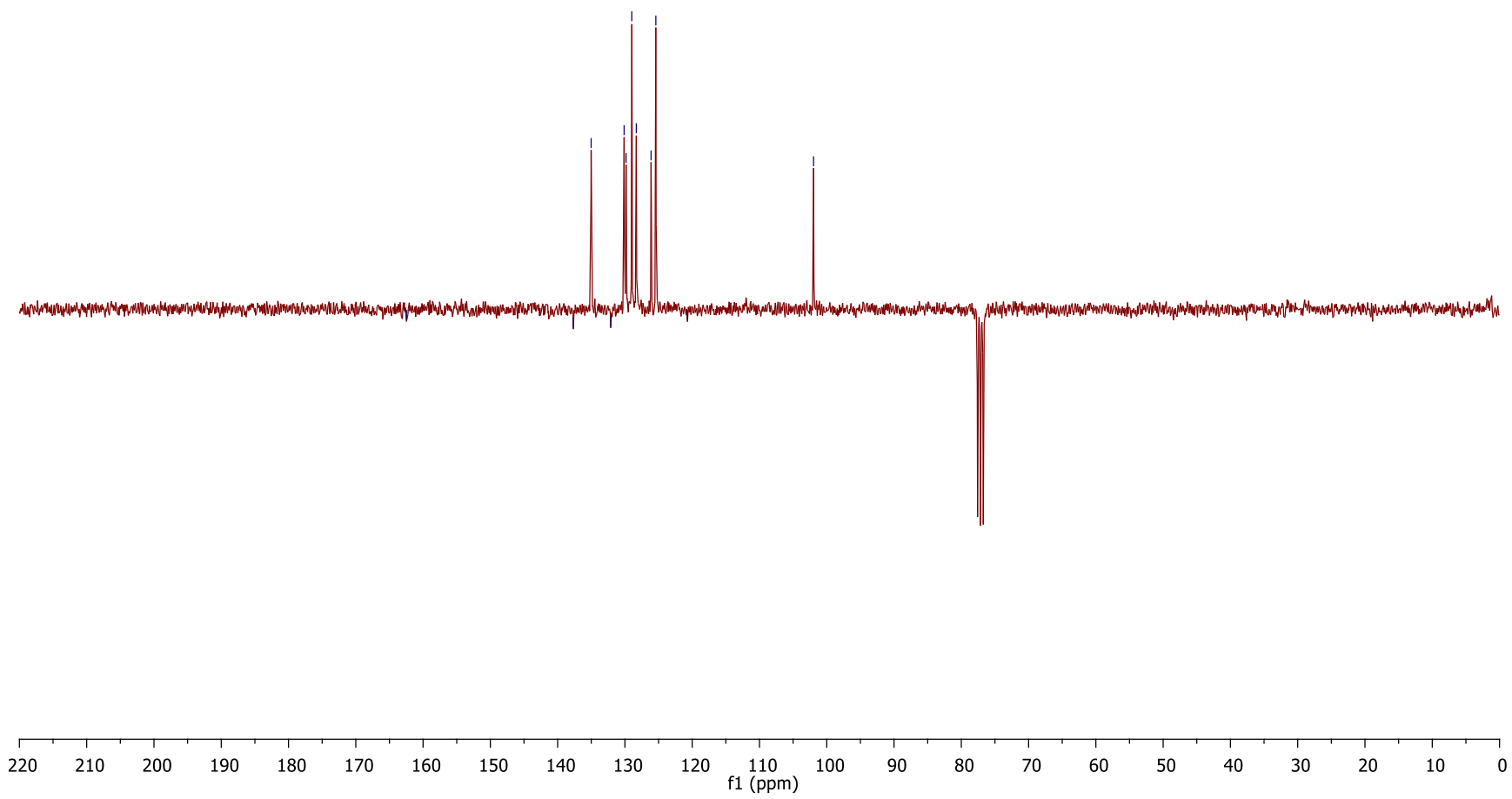


**21**

— 162.5

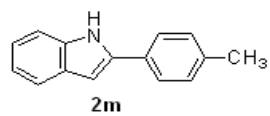
137.7  
135.0  
132.1  
130.1  
129.8  
129.0  
128.3  
126.1  
125.4  
120.7

— 102.0

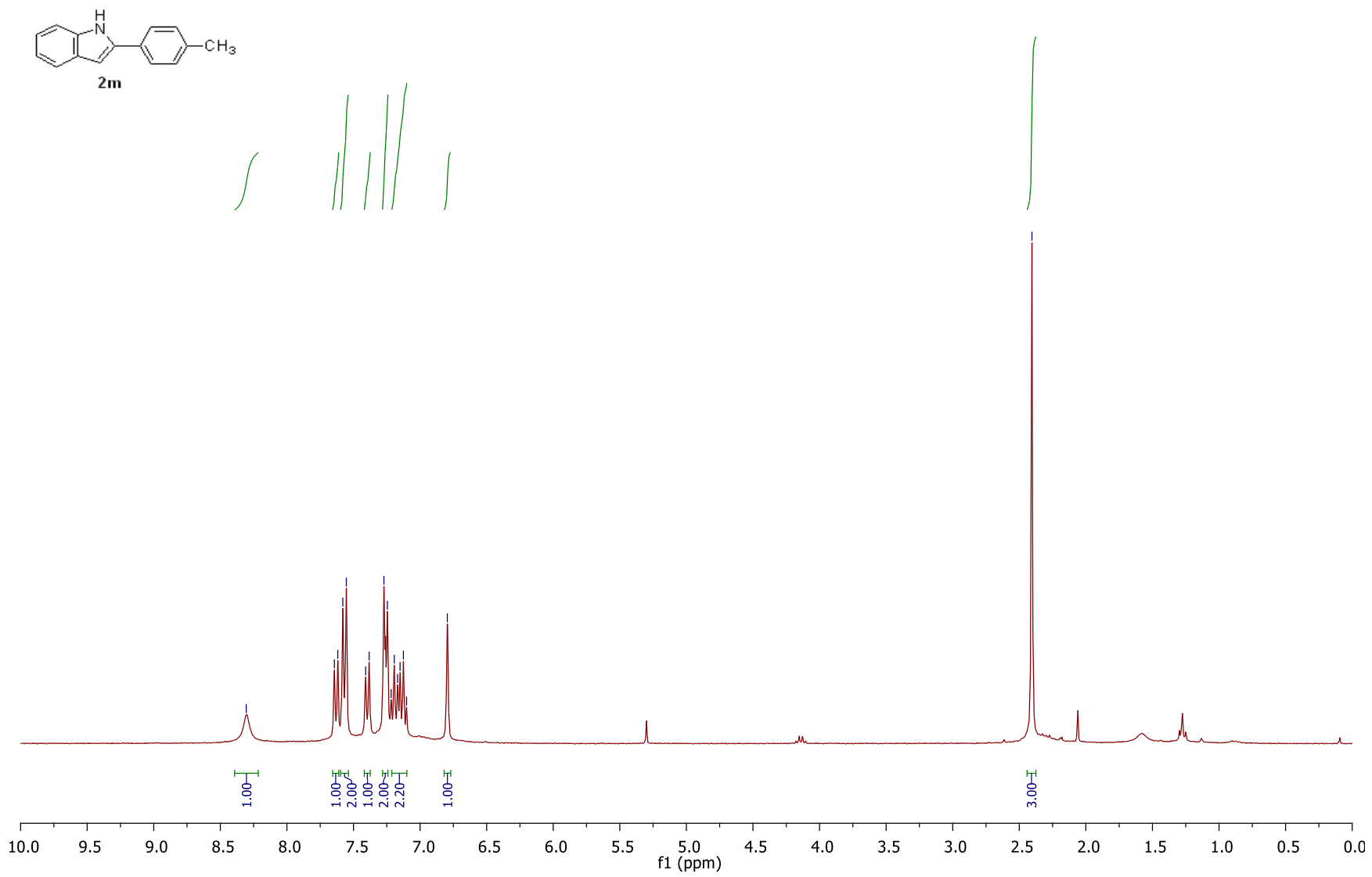


S43

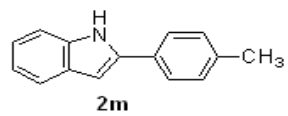
CDCl<sub>3</sub>



8.31  
7.64  
7.62  
7.58  
7.55  
7.41  
7.38  
7.27  
7.25  
7.19  
7.15  
6.88



CDCl<sub>3</sub>

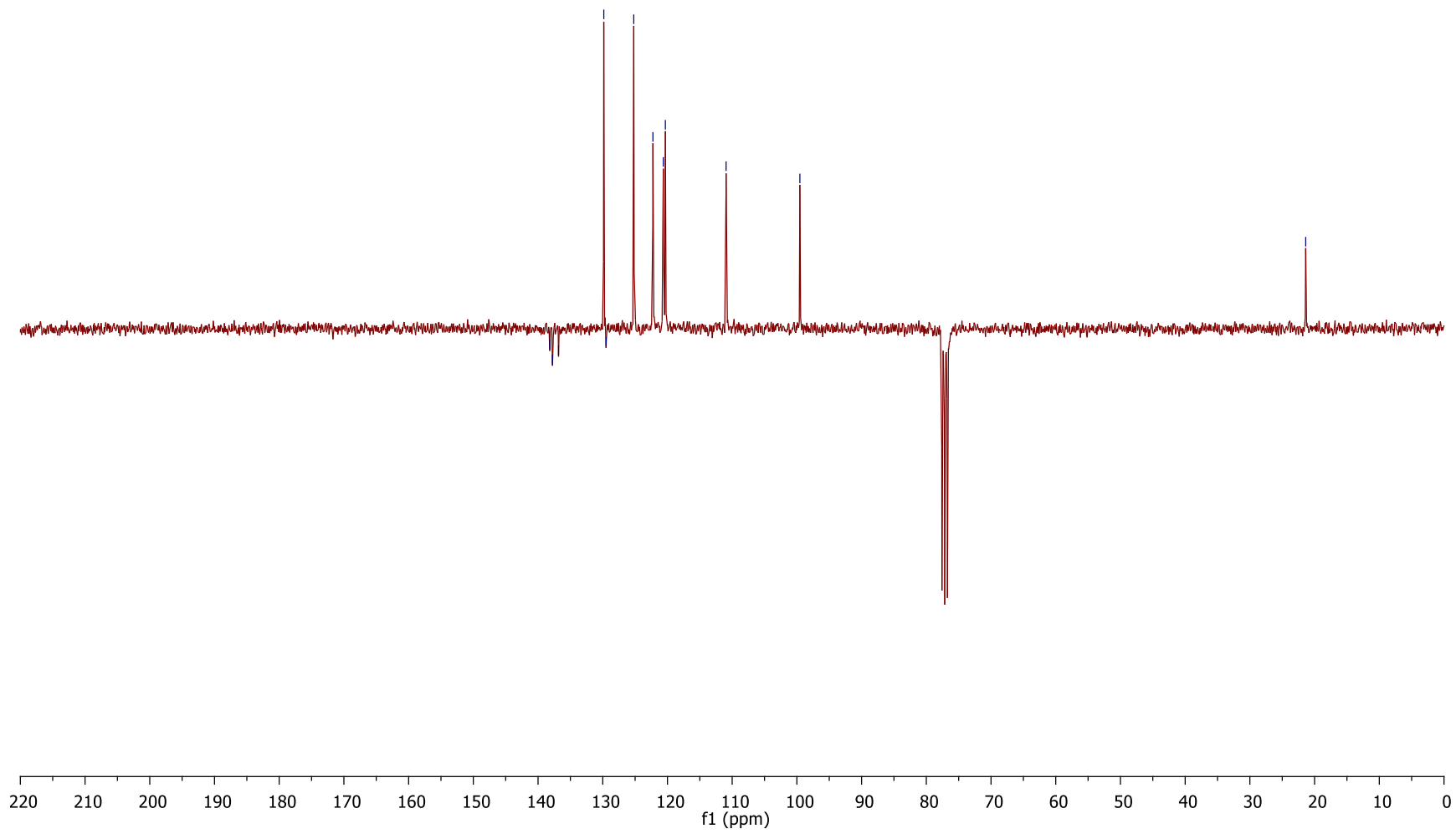


138.2  
137.8  
136.8  
129.8  
129.5  
125.2  
122.2  
120.6  
120.3

110.9

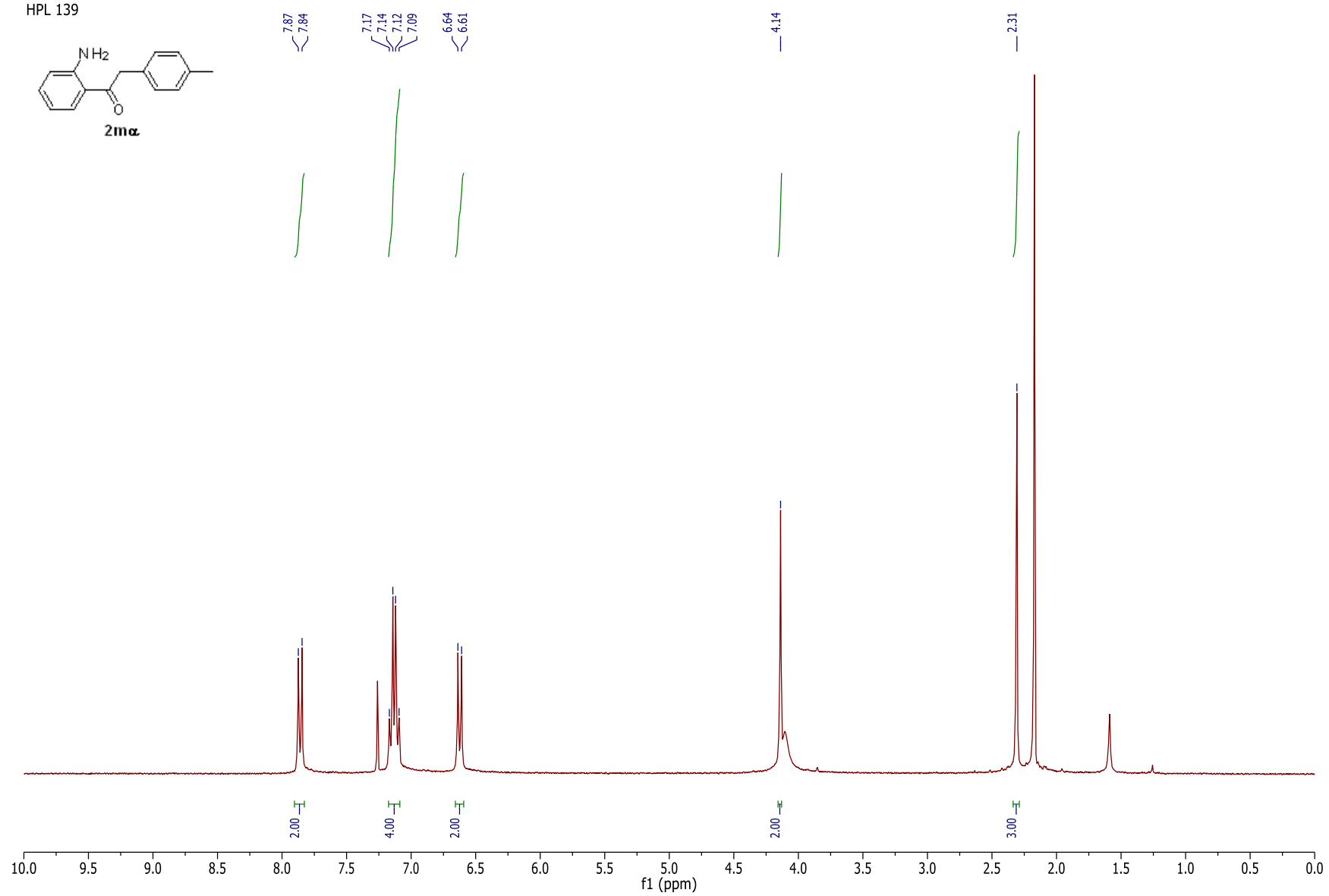
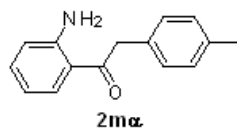
99.5

21.4

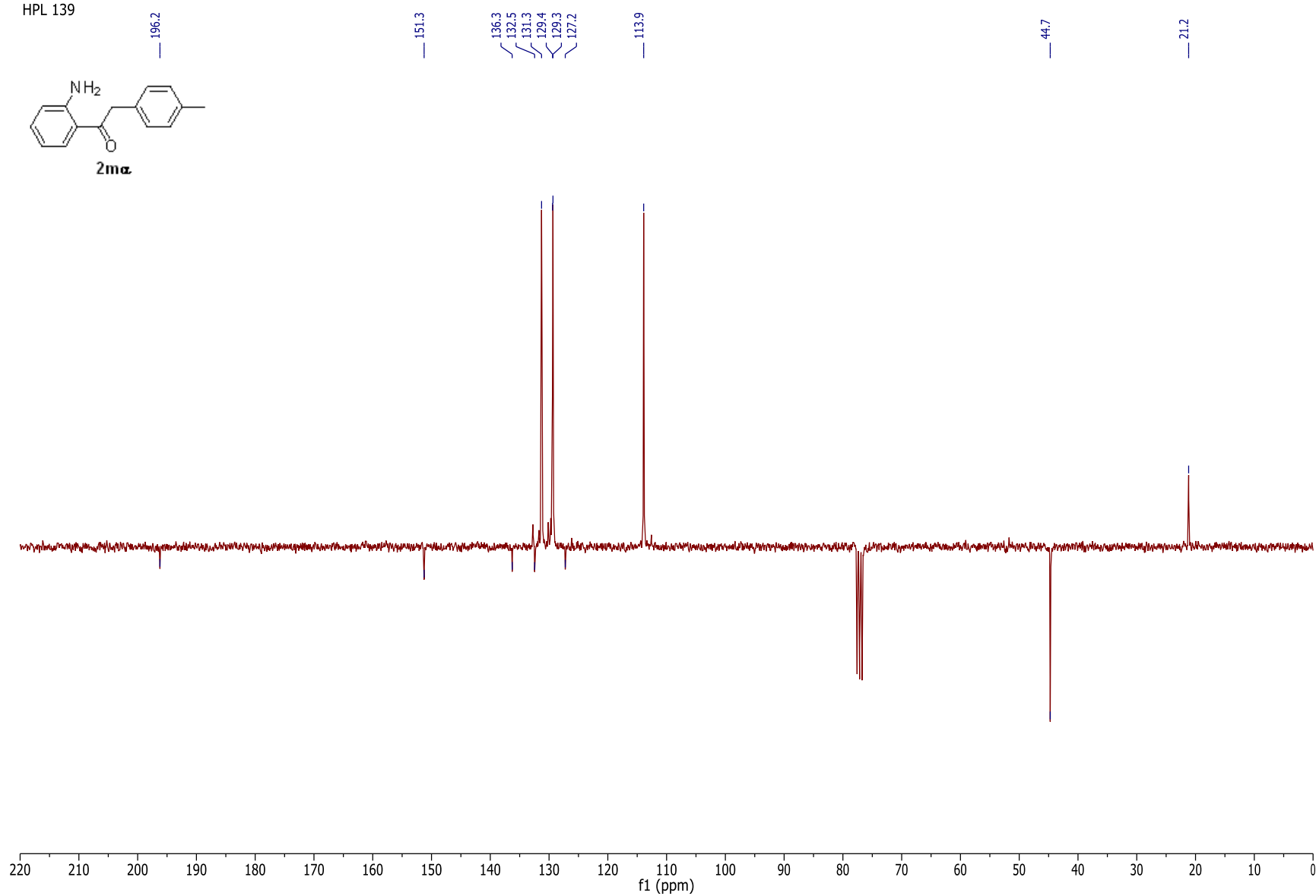
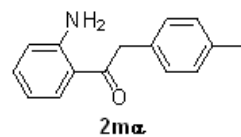


S45

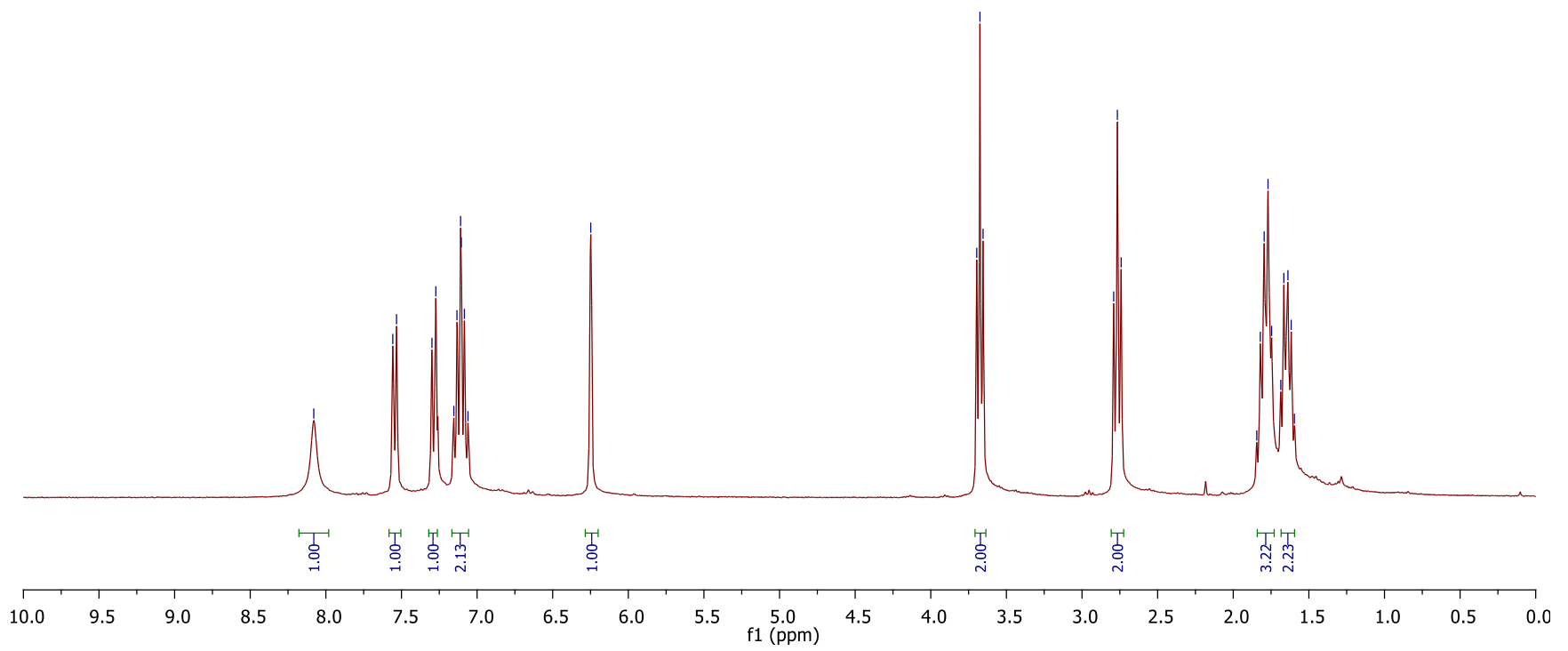
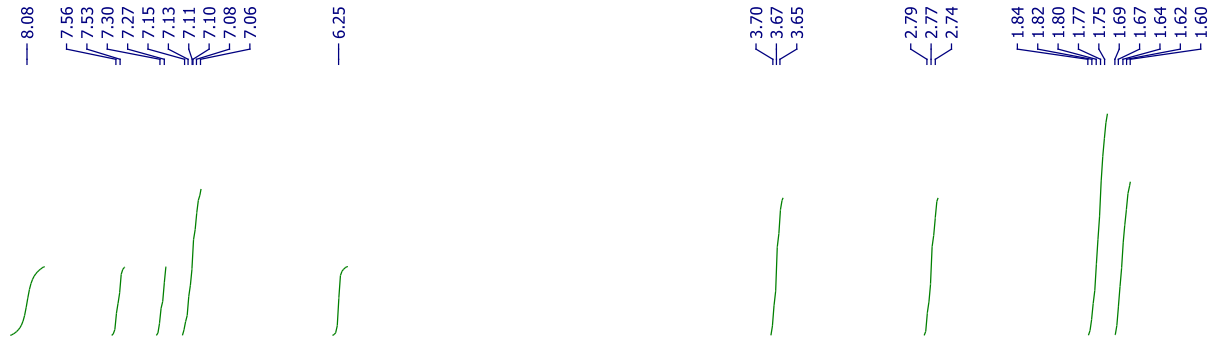
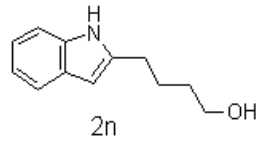
HPL 139



HPL 139

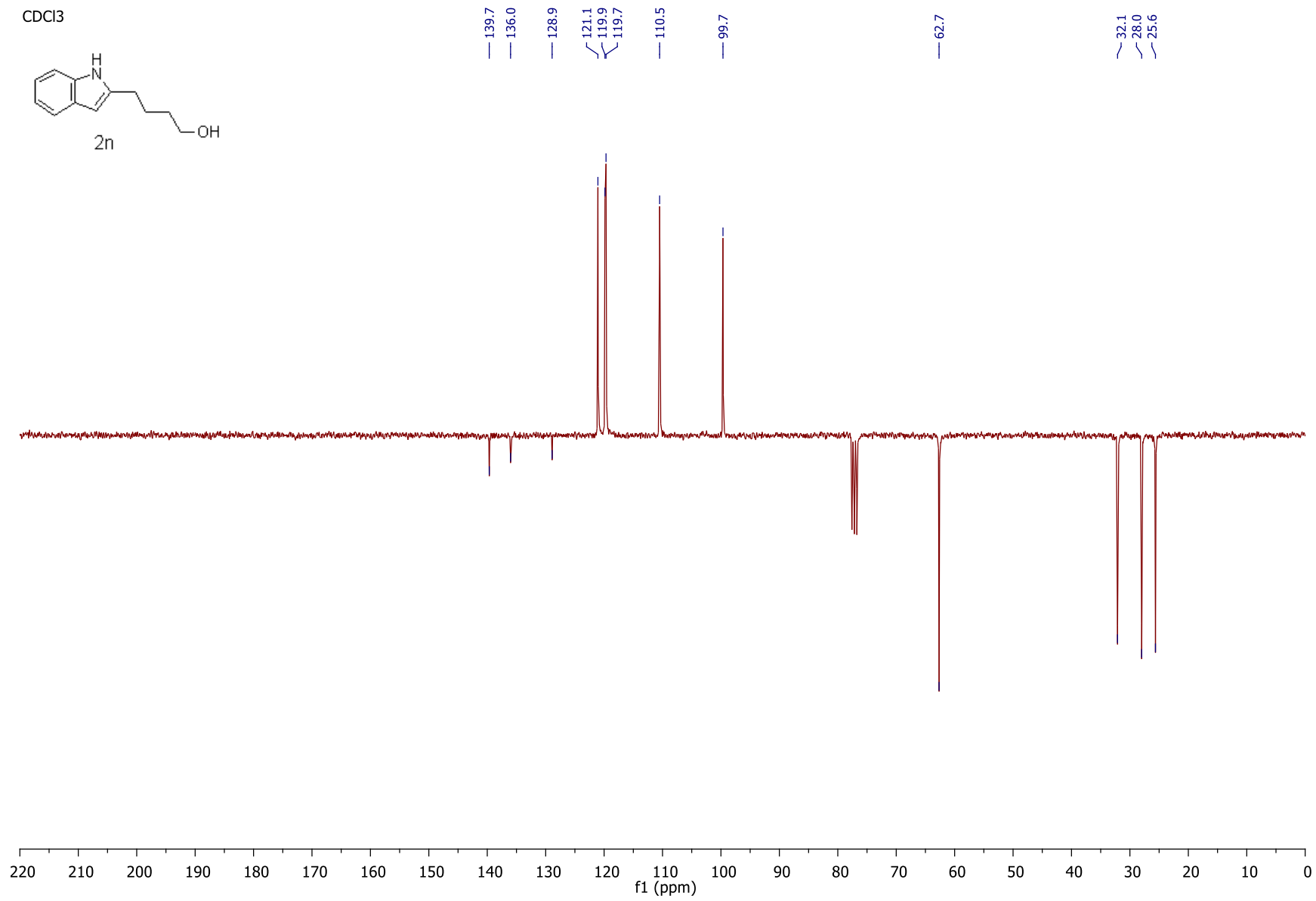
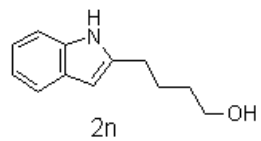


CDCl3



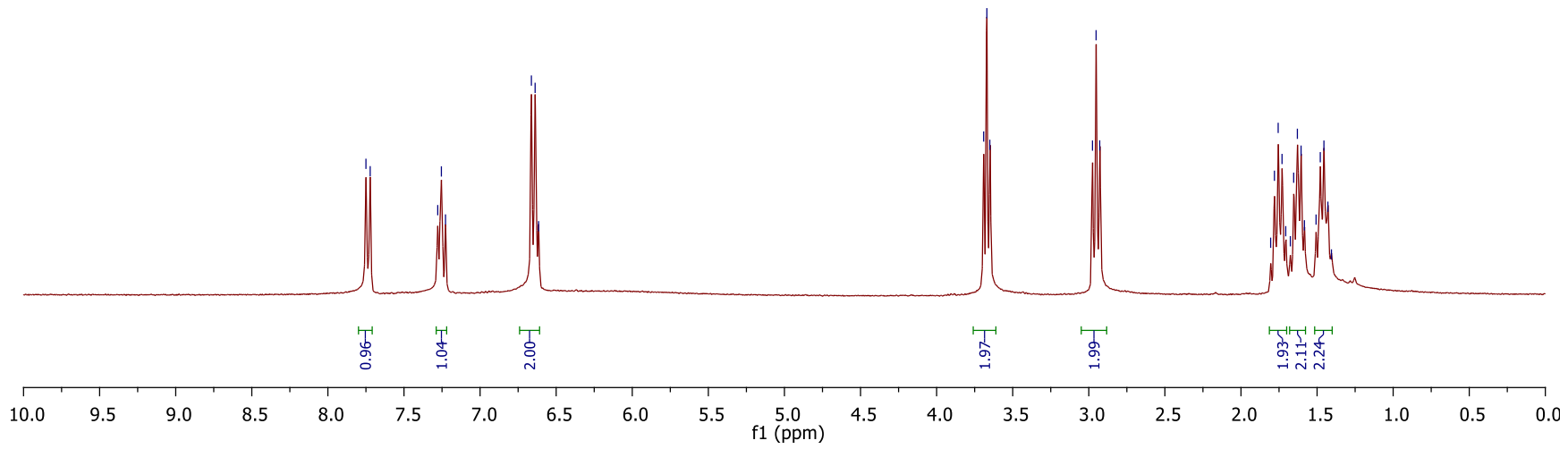
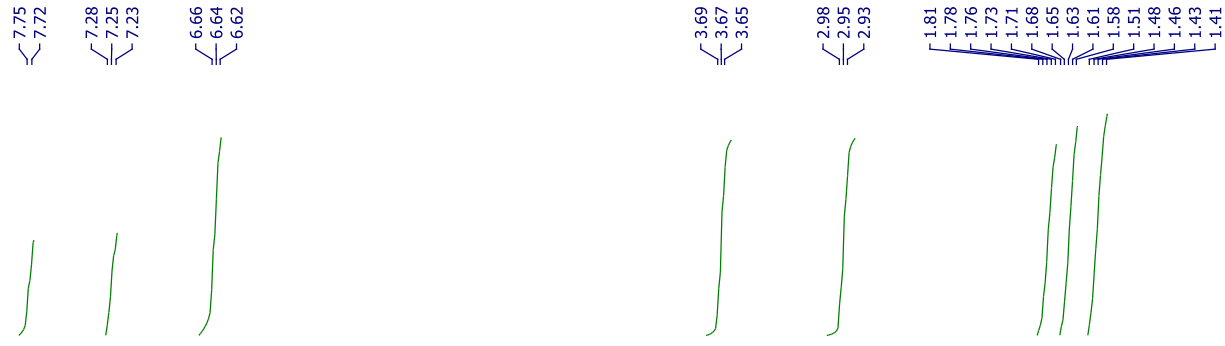
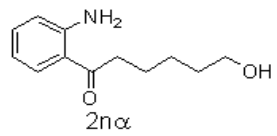


CDCl<sub>3</sub>

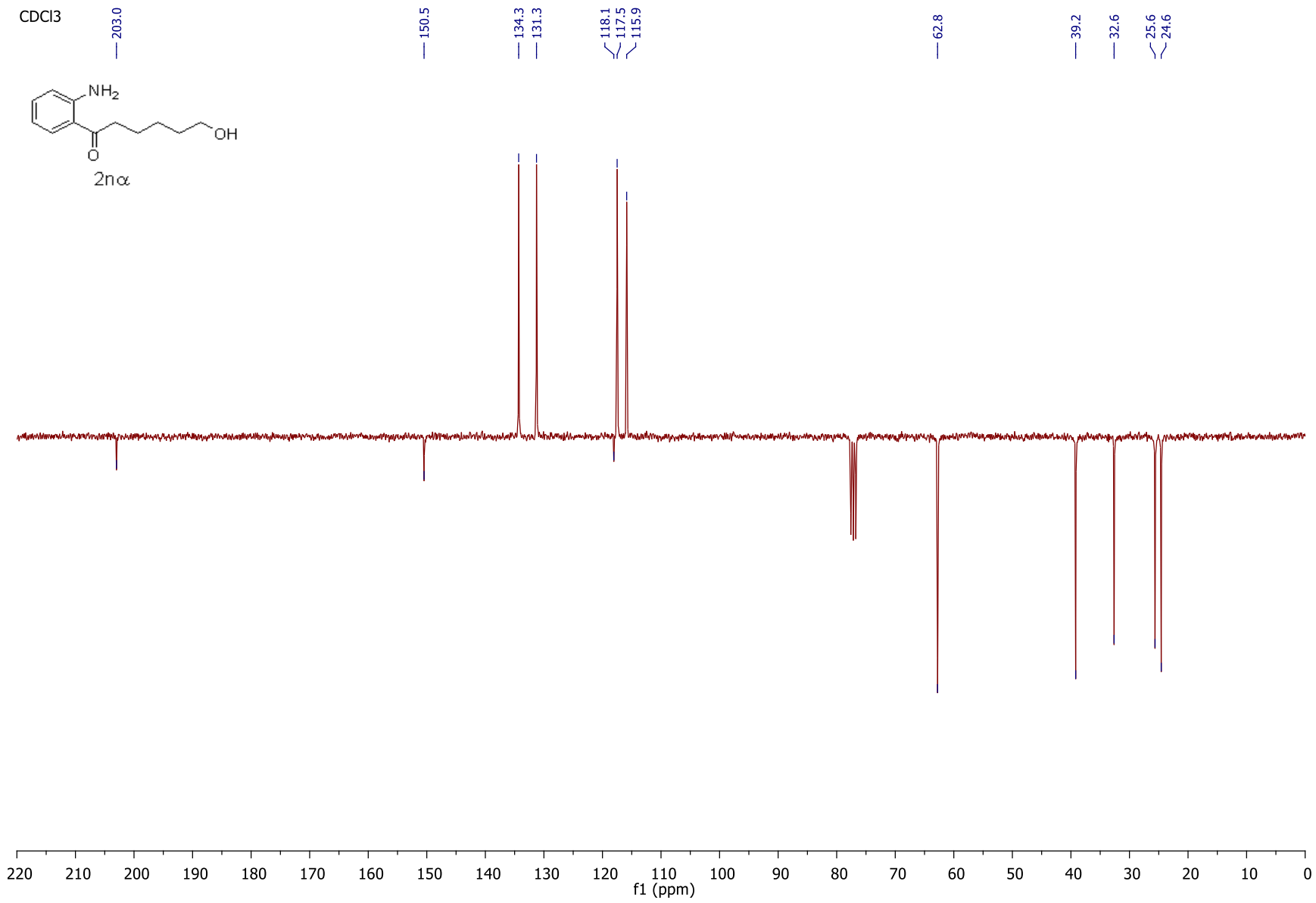
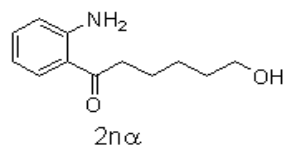


S49

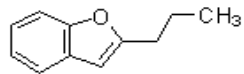
CDCl<sub>3</sub>



CDCl<sub>3</sub>



CDCl<sub>3</sub>



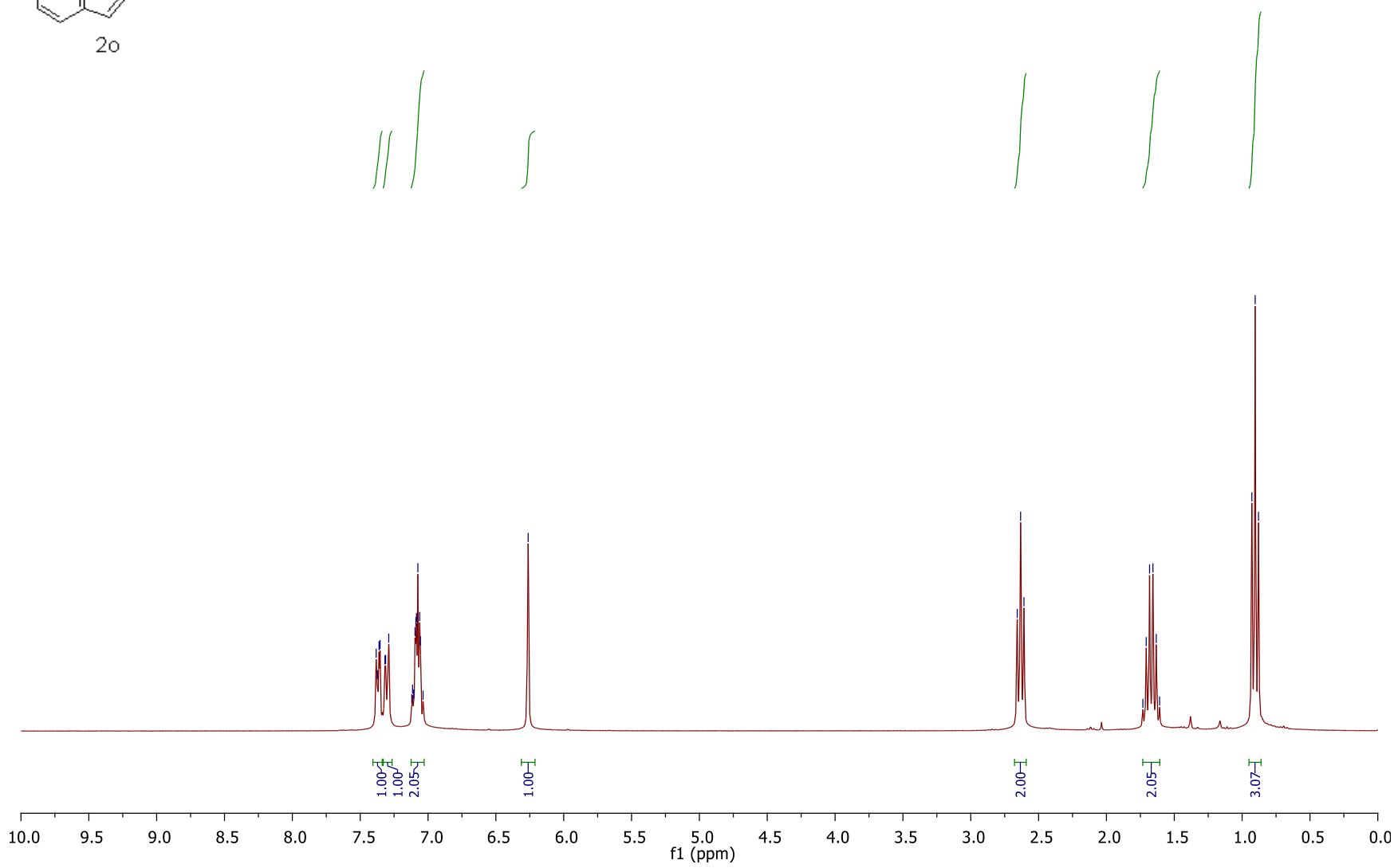
2o

7.38  
7.37  
7.36  
7.35  
7.32  
7.31  
7.29  
7.12  
7.11  
7.11  
7.10  
7.09  
7.08  
7.08  
7.06  
7.06  
7.04  
6.26

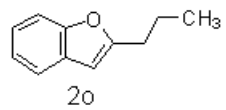
2.66  
2.63  
2.61

1.73  
1.71  
1.68  
1.66  
1.63  
1.61

0.93  
0.90  
0.88



CDCl<sub>3</sub>



— 159.7

— 154.8

— 129.2

— 123.2

— 122.5

— 120.3

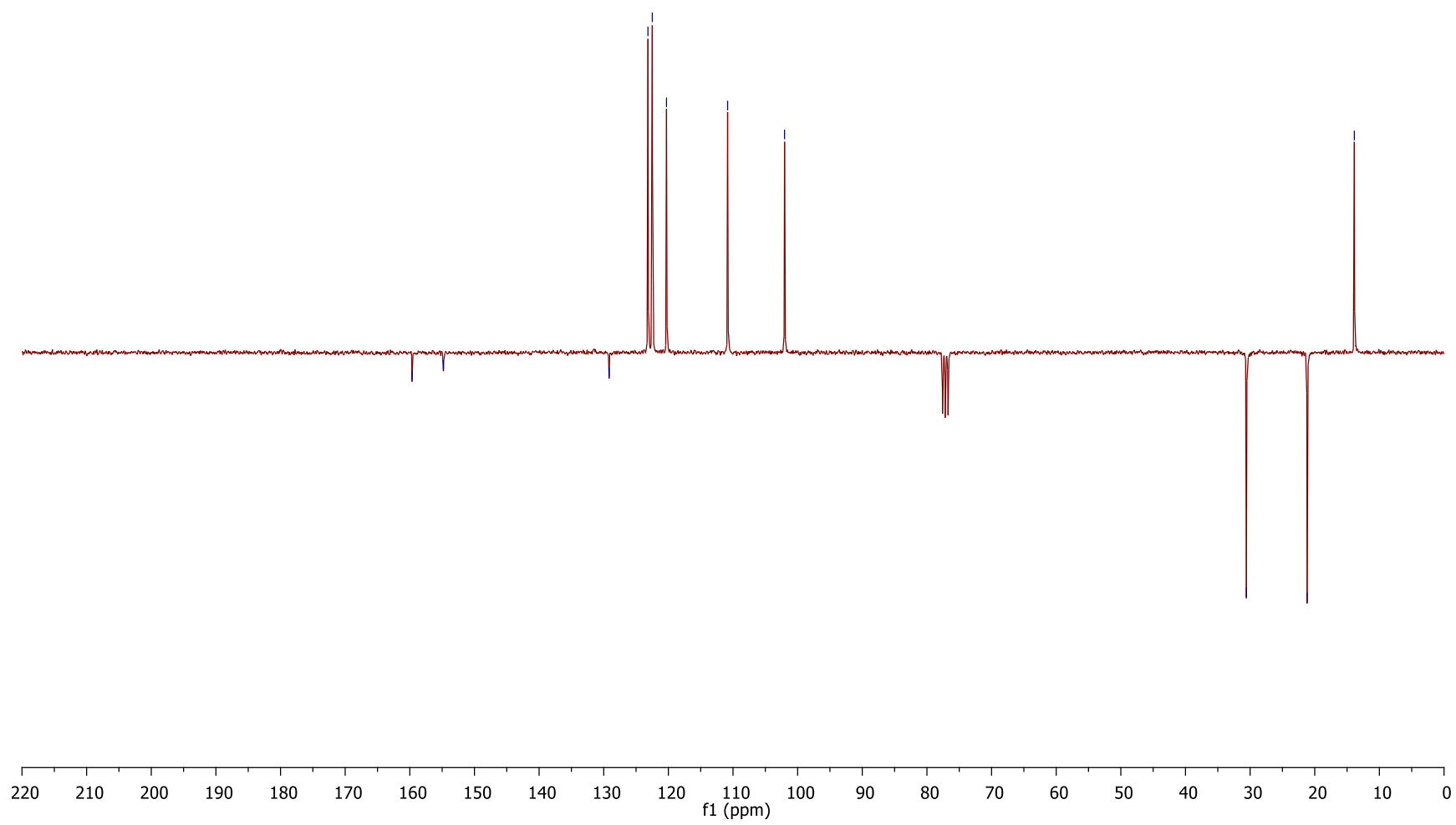
— 110.8

— 102.0

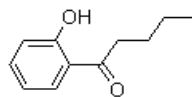
— 30.6

— 21.2

— 13.9



CDCl<sub>3</sub>

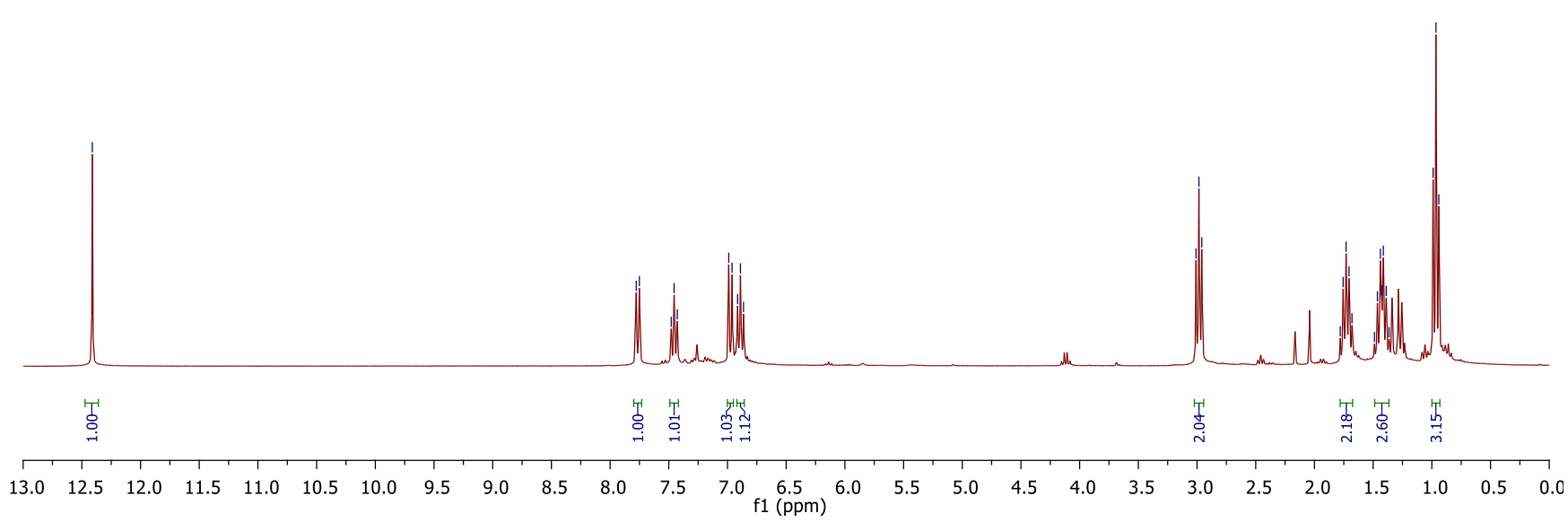


20α

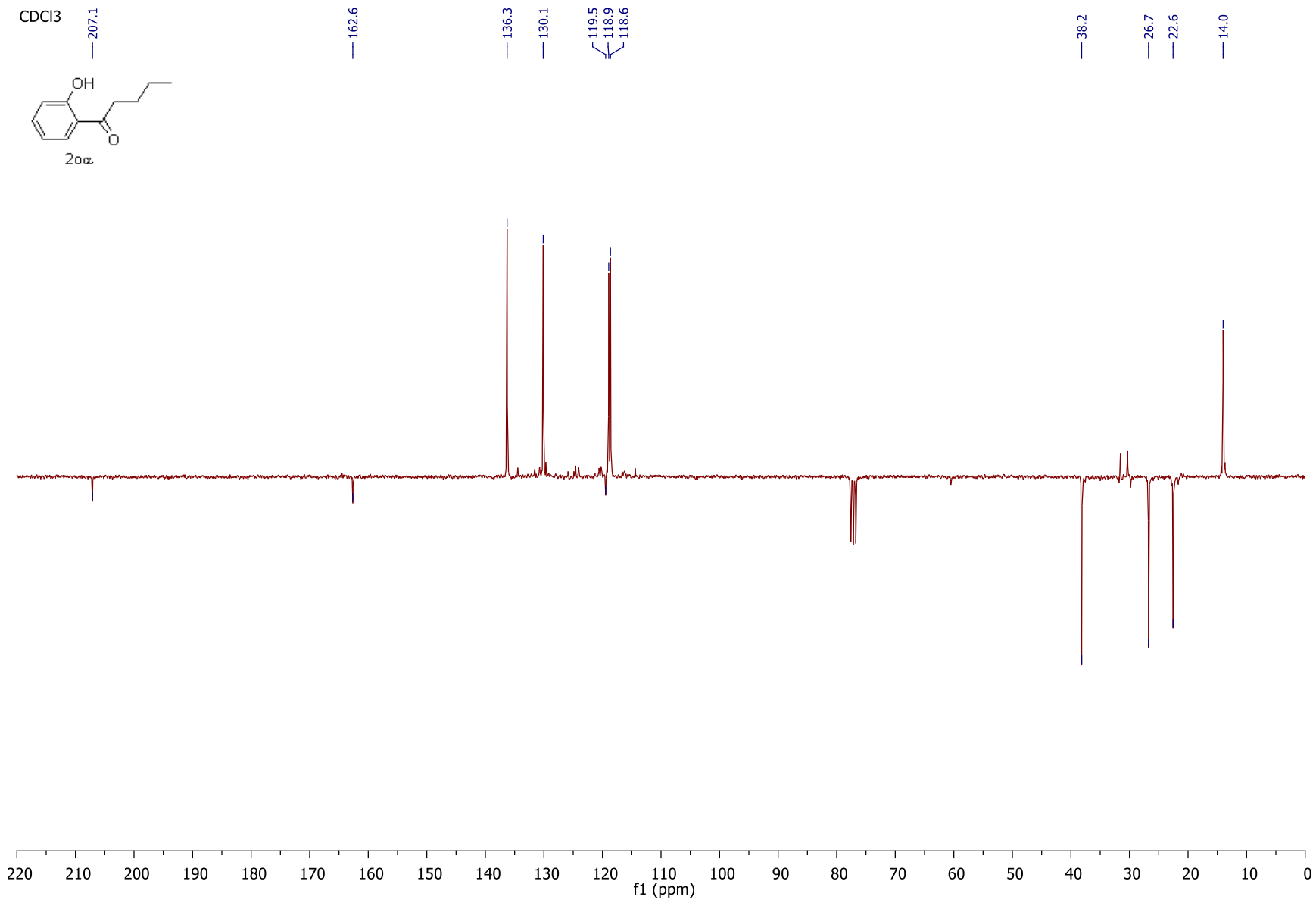
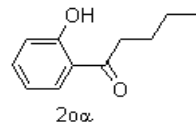
12.41

7.78  
7.75  
7.48  
7.45  
7.43  
6.99  
6.96  
6.91  
6.89  
6.86

3.01  
2.98  
2.96  
1.78  
1.76  
1.73  
1.71  
1.68  
1.46  
1.44  
1.43  
1.41  
0.98  
0.96  
0.94

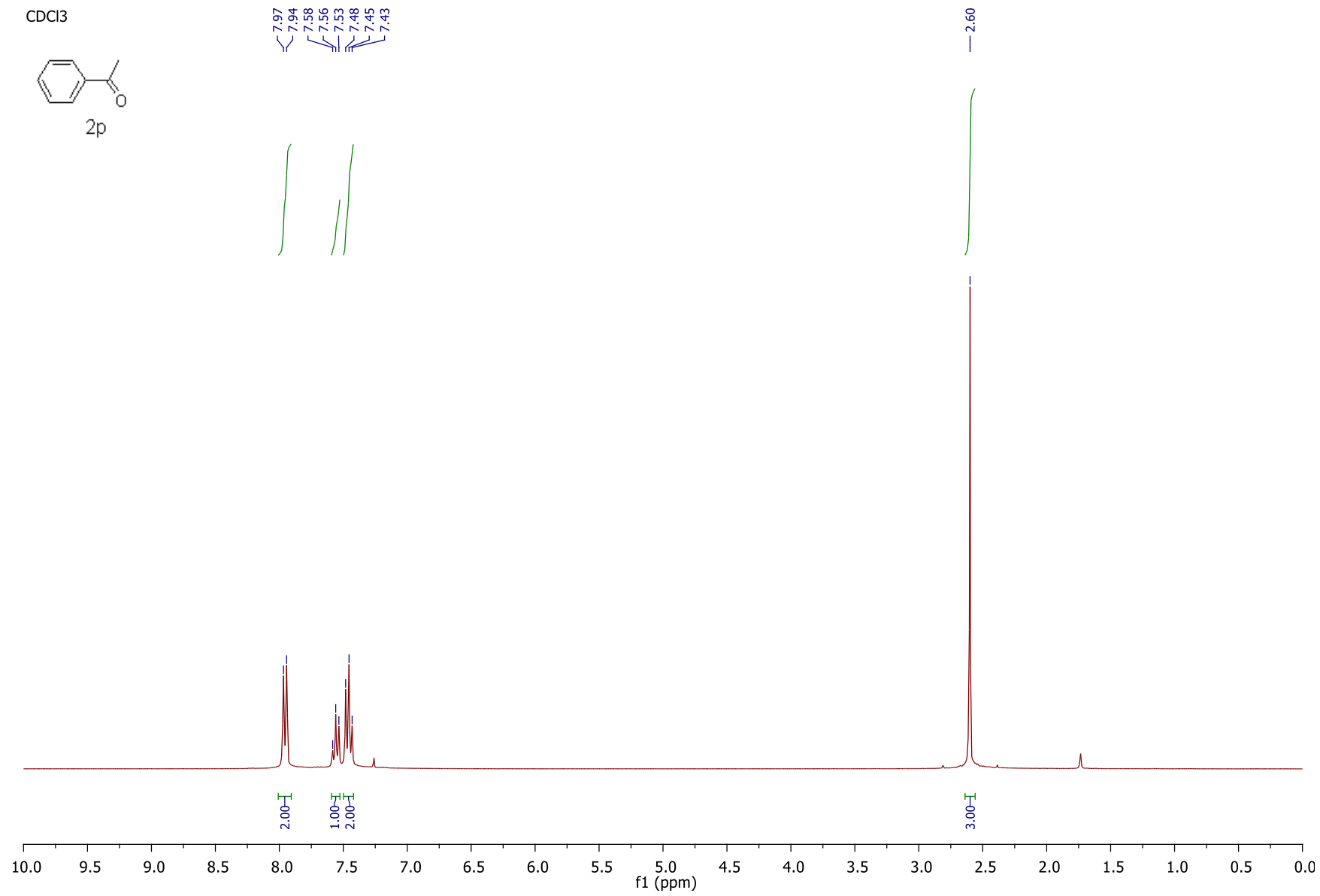
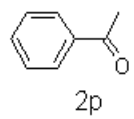


CDCl<sub>3</sub>



S55

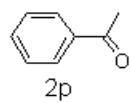
CDCl<sub>3</sub>



S56



CDCl<sub>3</sub>



— 198.2

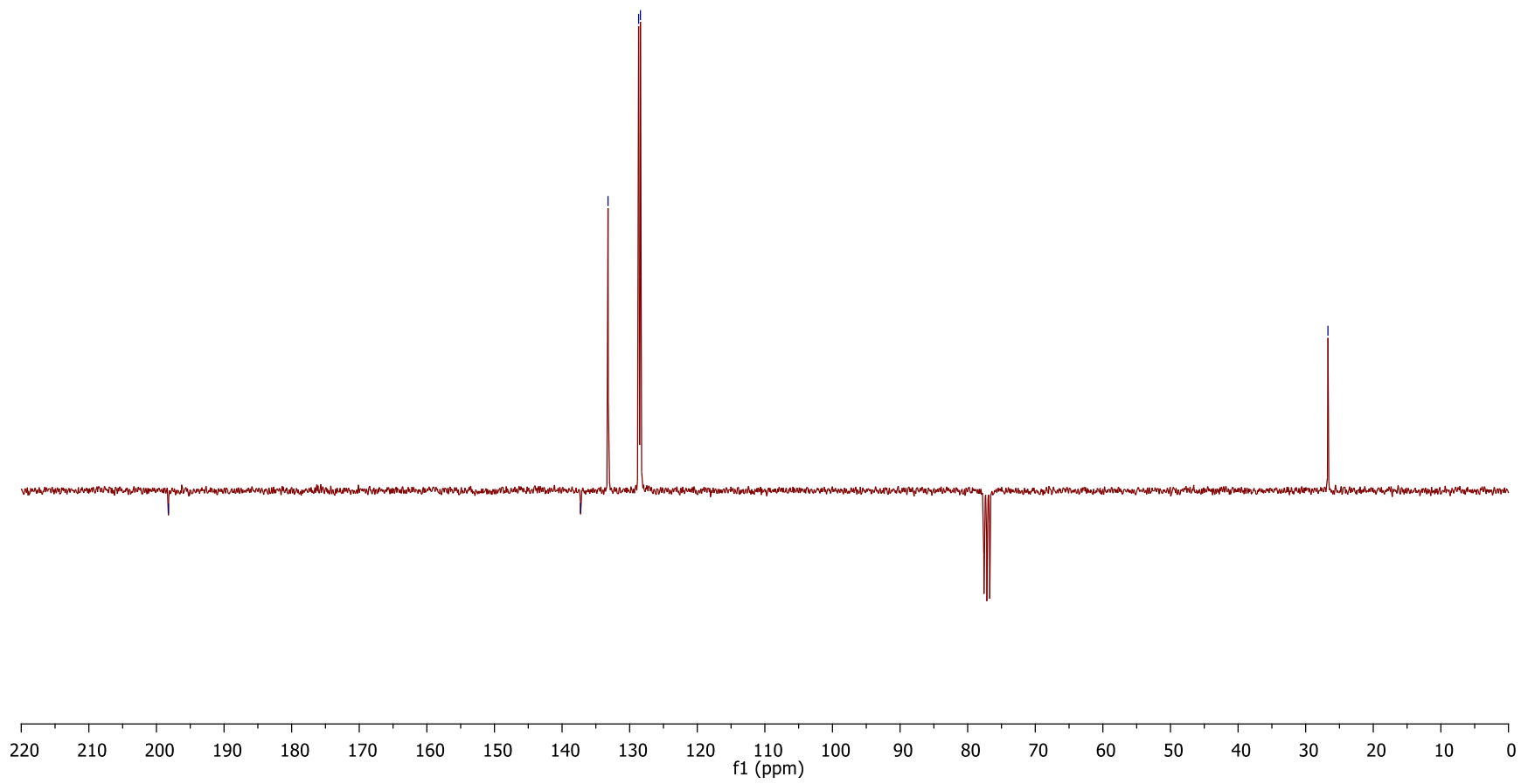
— 137.3

— 133.2

— 128.7

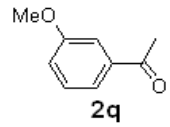
— 128.4

— 26.7



S57

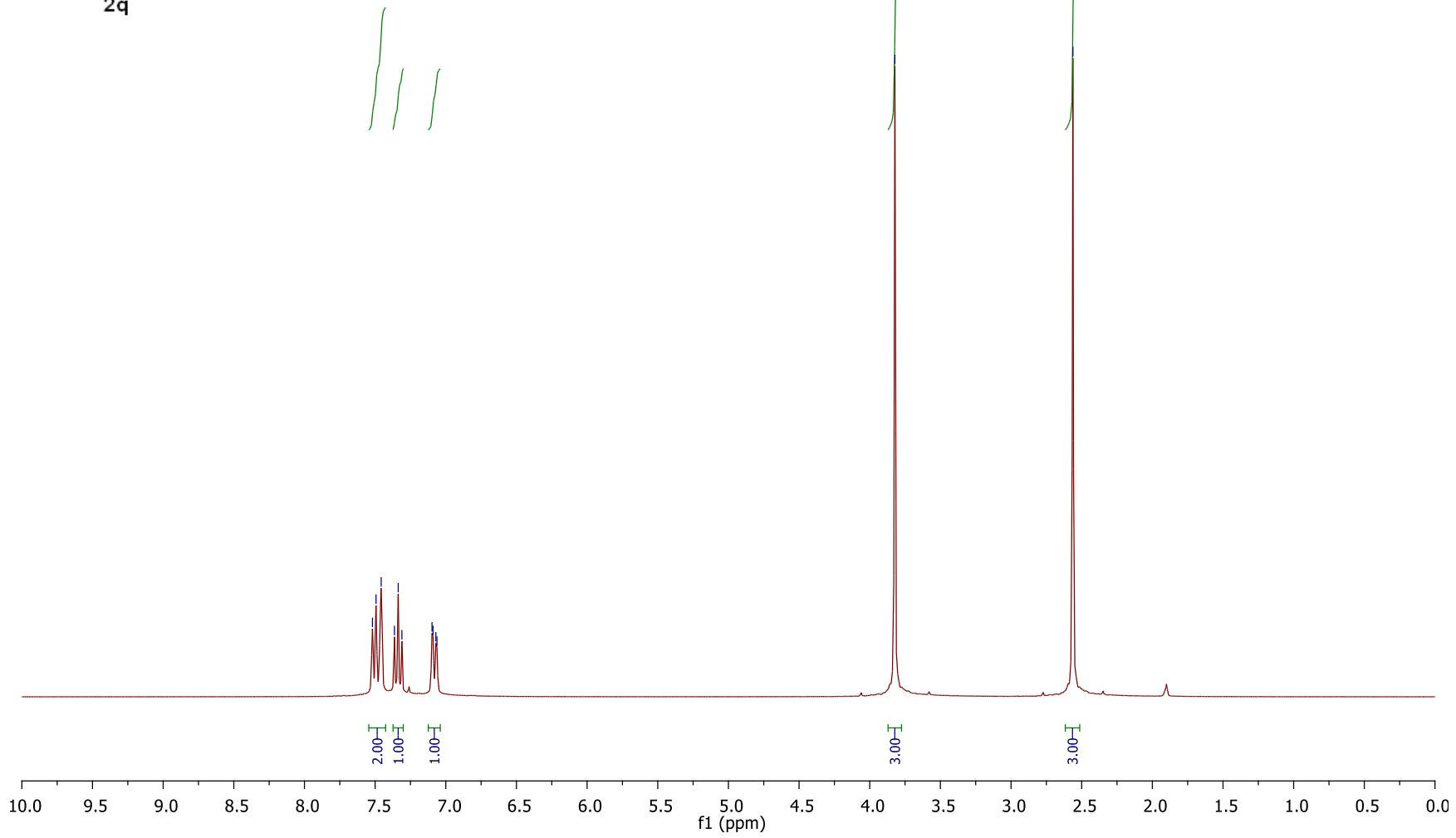
CDCl3



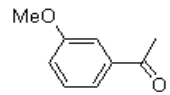
7.52  
7.49  
7.46  
7.36  
7.34  
7.31  
7.10  
7.09  
7.07  
7.06

3.82

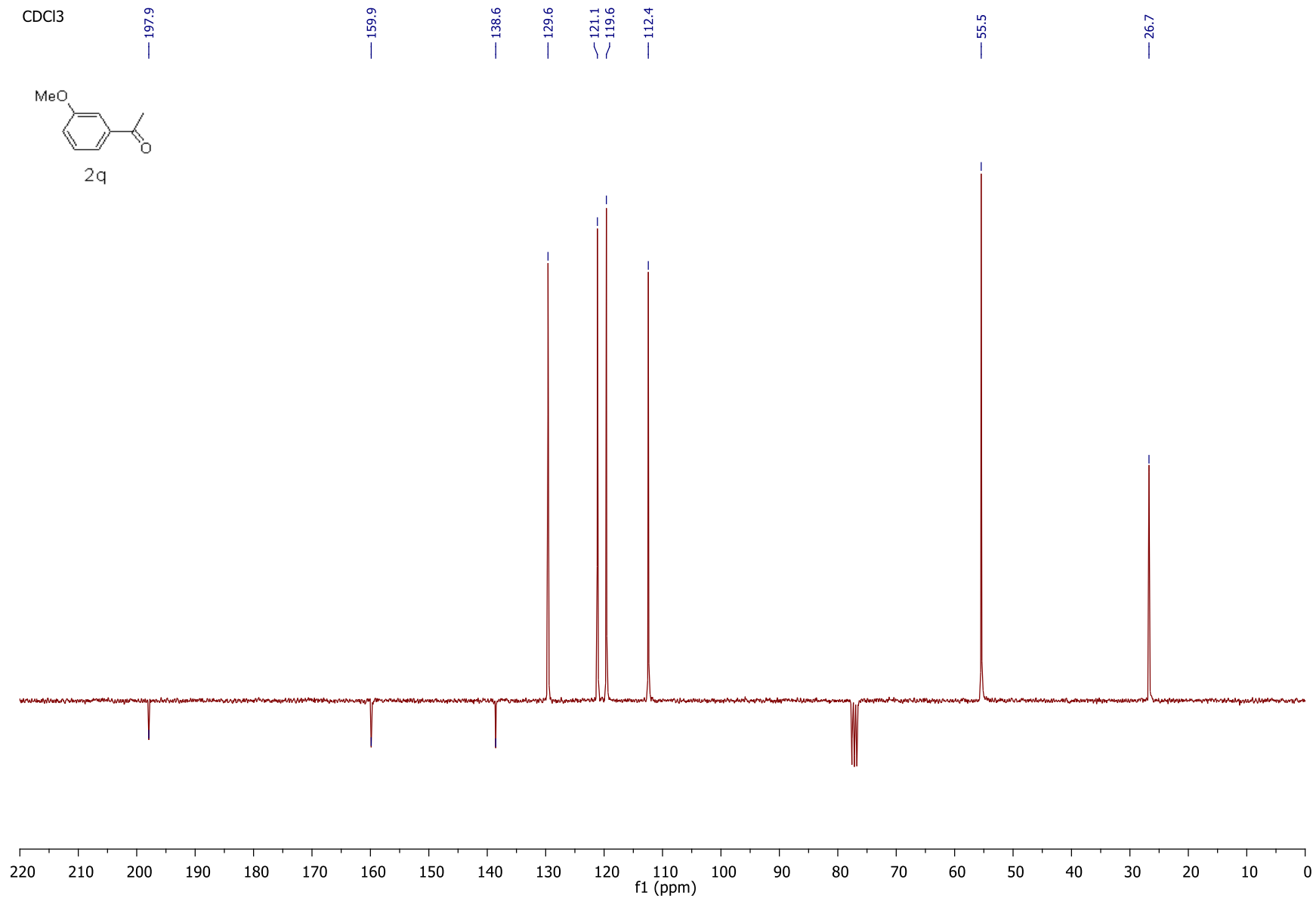
2.56



CDCl3

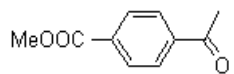


2q



S59

CDCl<sub>3</sub>



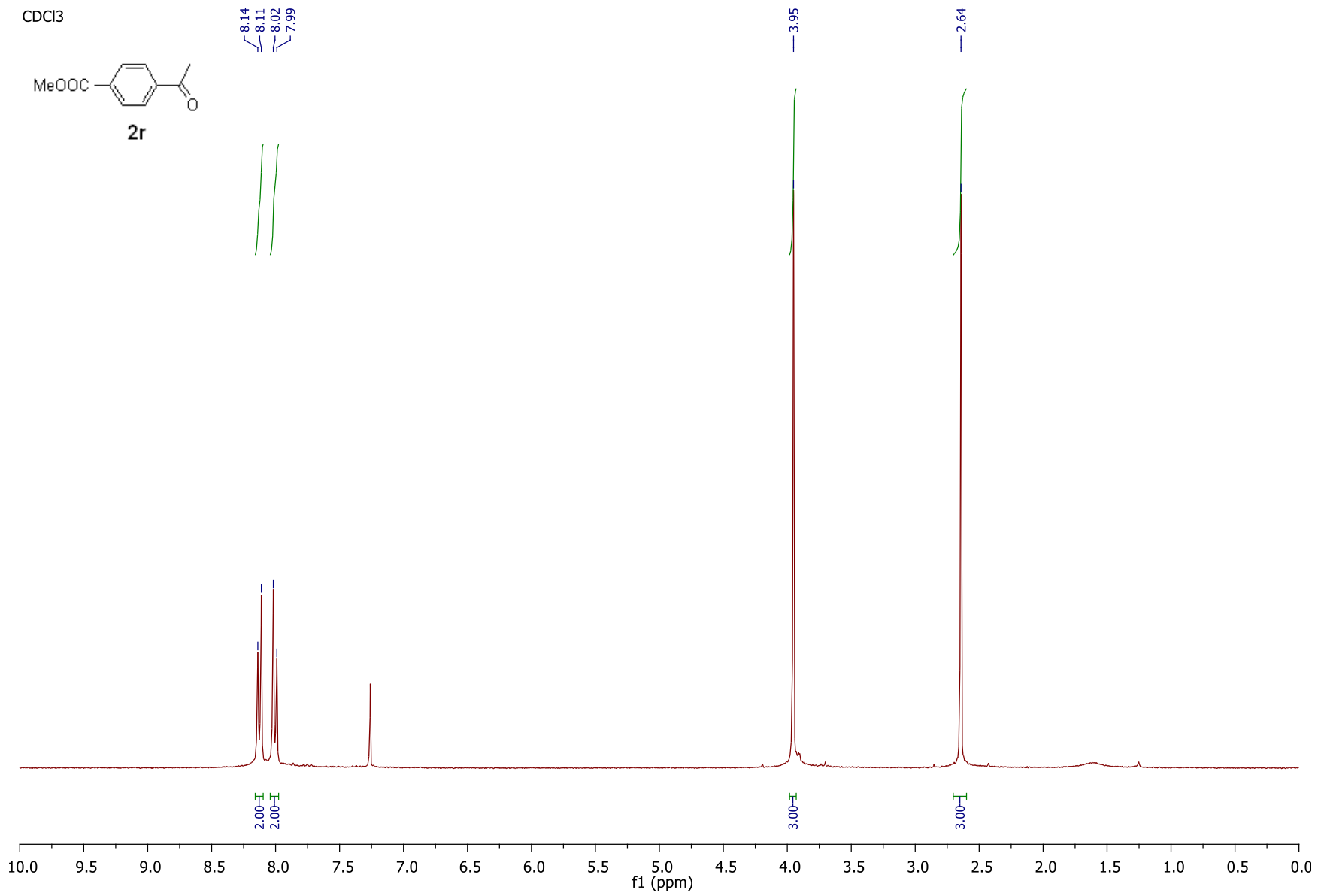
2r

8.14  
8.11  
8.02  
7.99



3.95

2.64



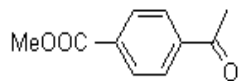
2.00  
2.00

3.00

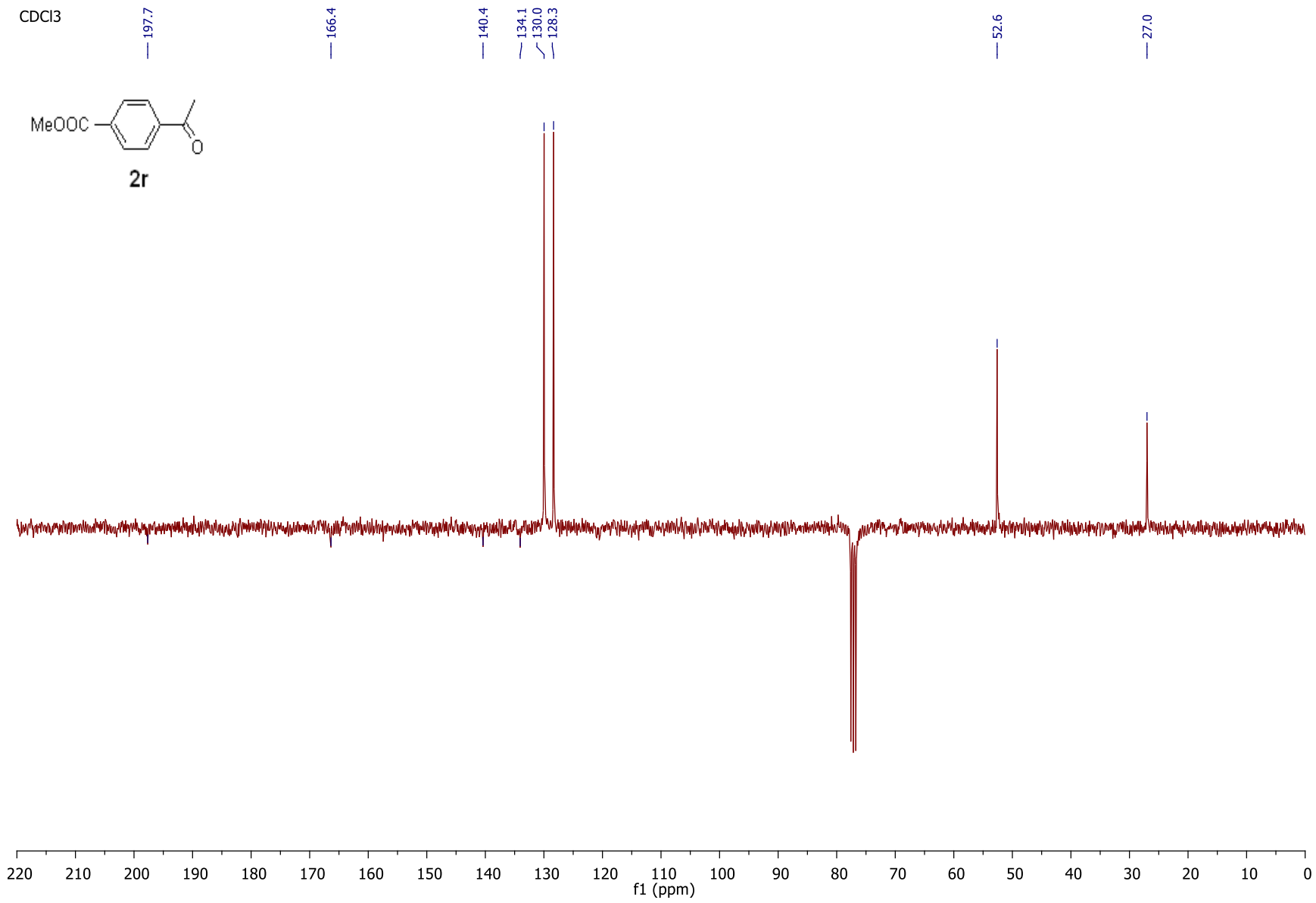
3.00

S60

CDCl3

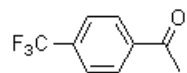


2r



S61

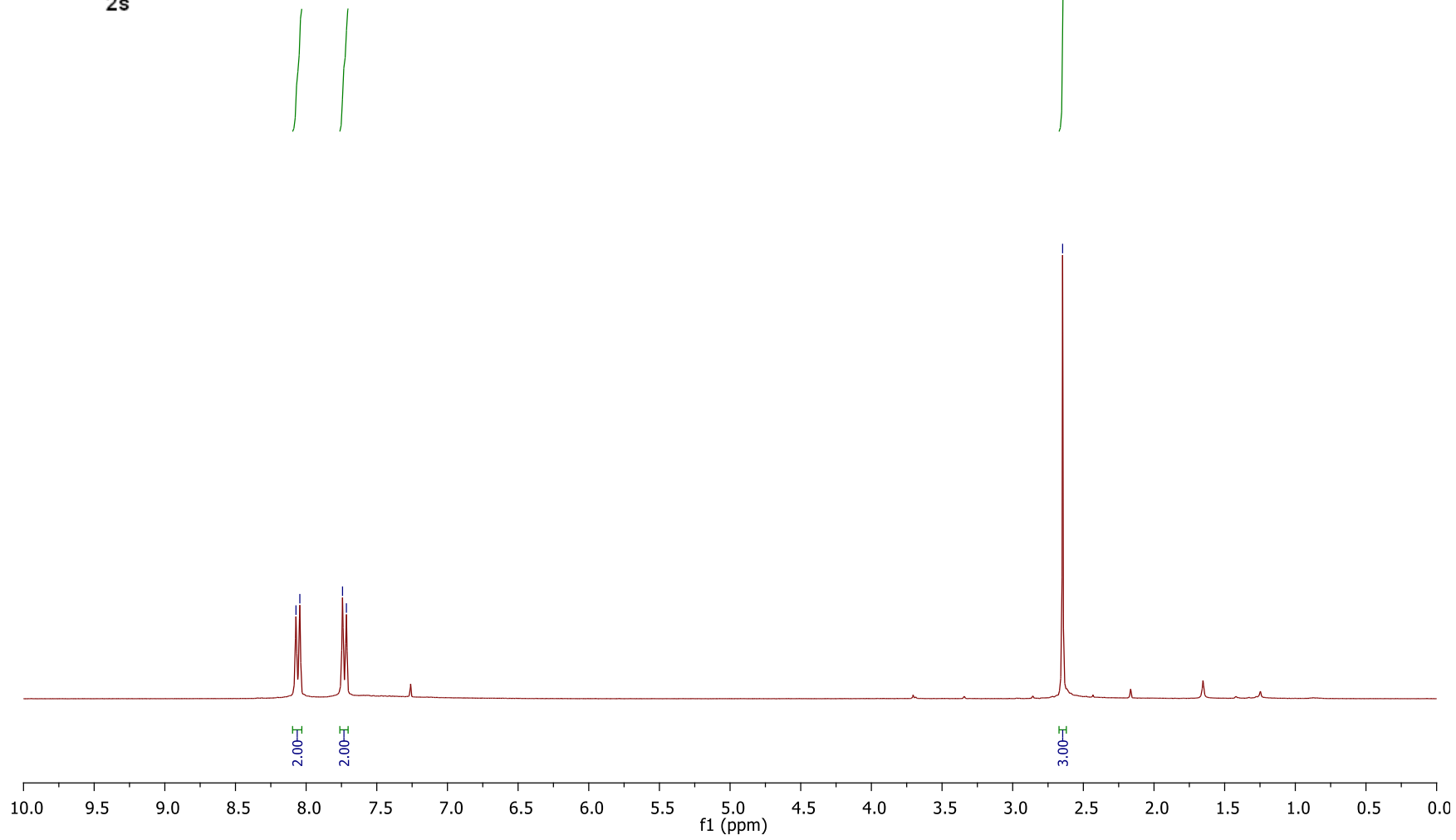
CDCl<sub>3</sub>



**2s**

8.07  
8.04  
7.74  
7.72

2.65



S62

CDCl<sub>3</sub>

— 197.2

— 139.8

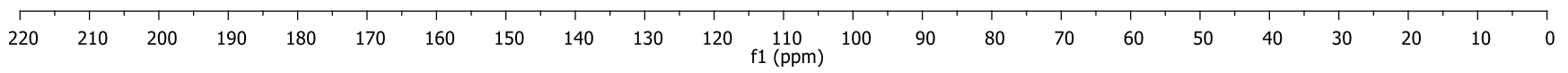
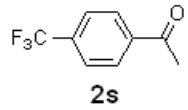
— 134.3

— 128.8

— 125.8

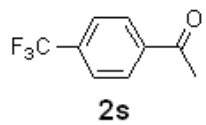
— 121.9

— 26.9



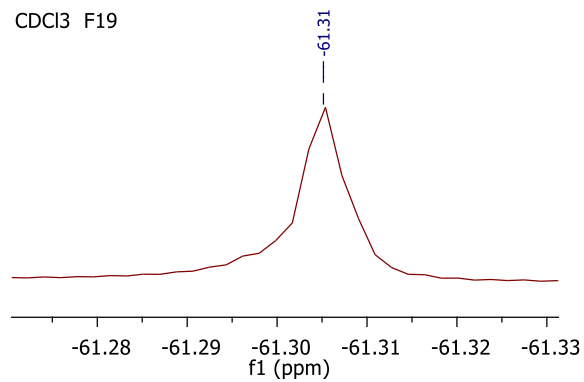
S63

CDCl3 F19

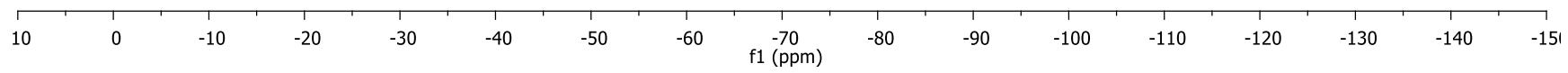


-61.31

CDCl3 F19

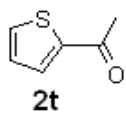


-61.31



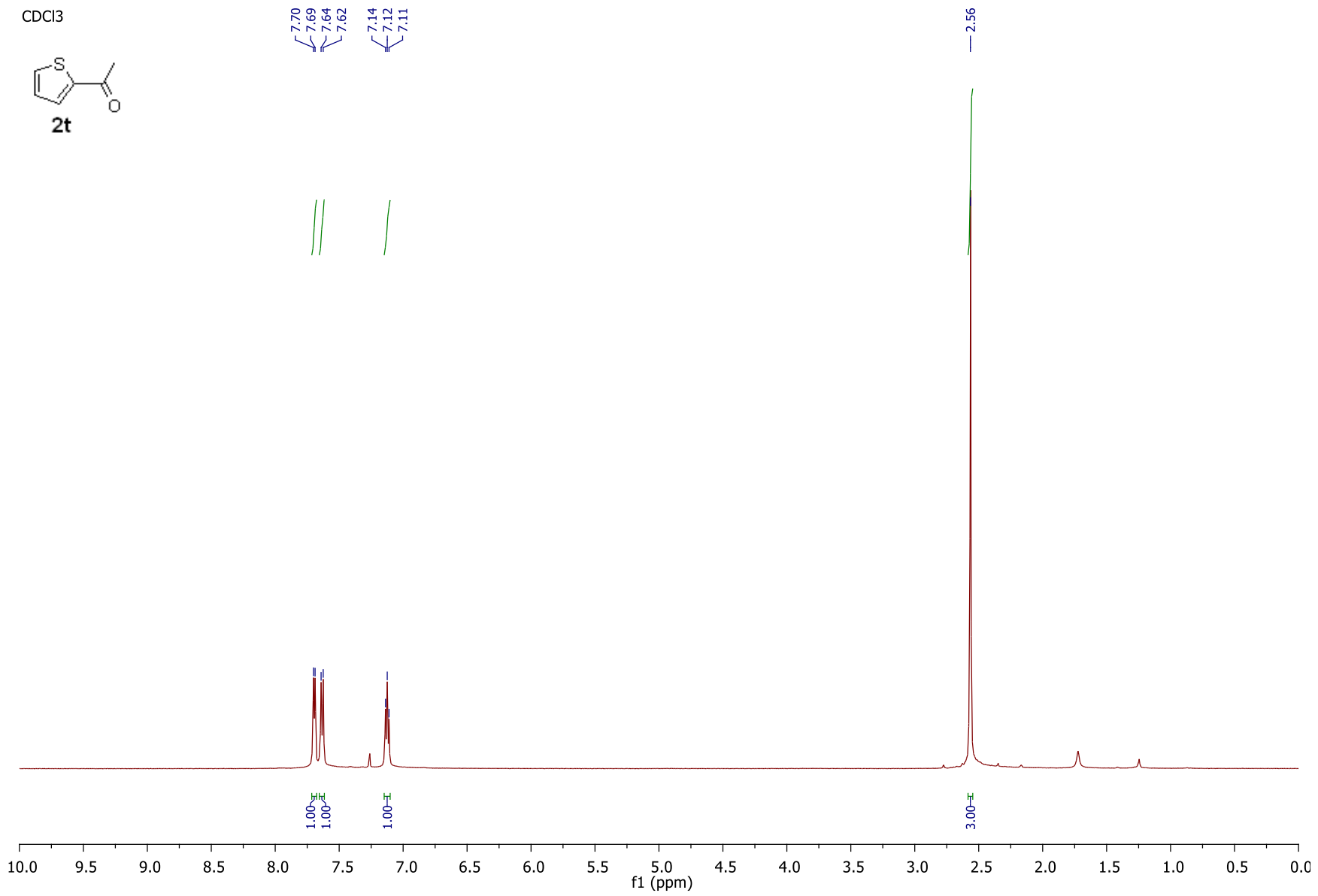


CDCl3



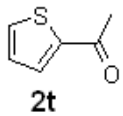
7.70  
7.69  
7.64  
7.62  
7.14  
7.12  
7.11

2.56



S65

CDCl<sub>3</sub>



— 190.9

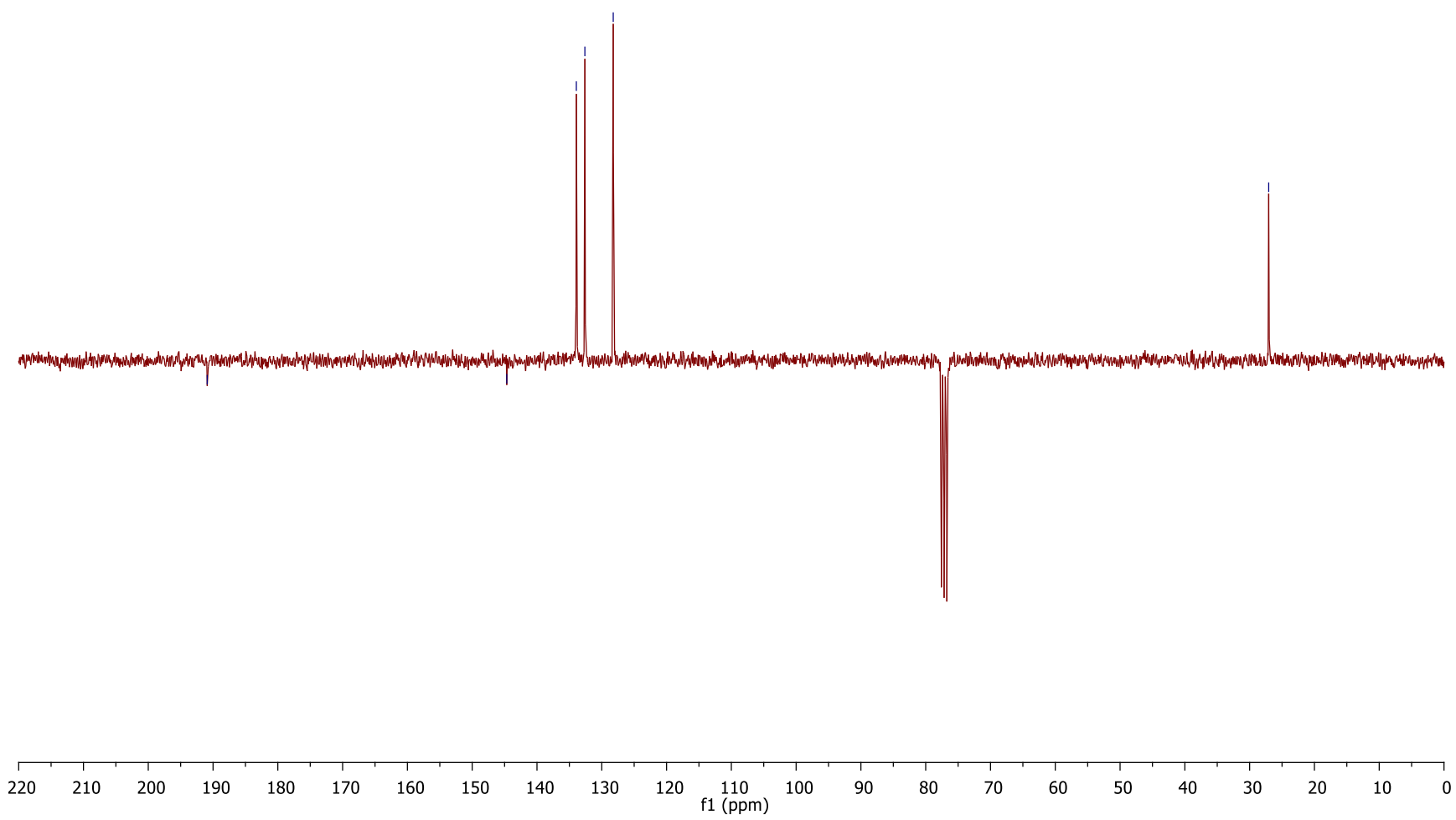
— 144.7

— 133.9

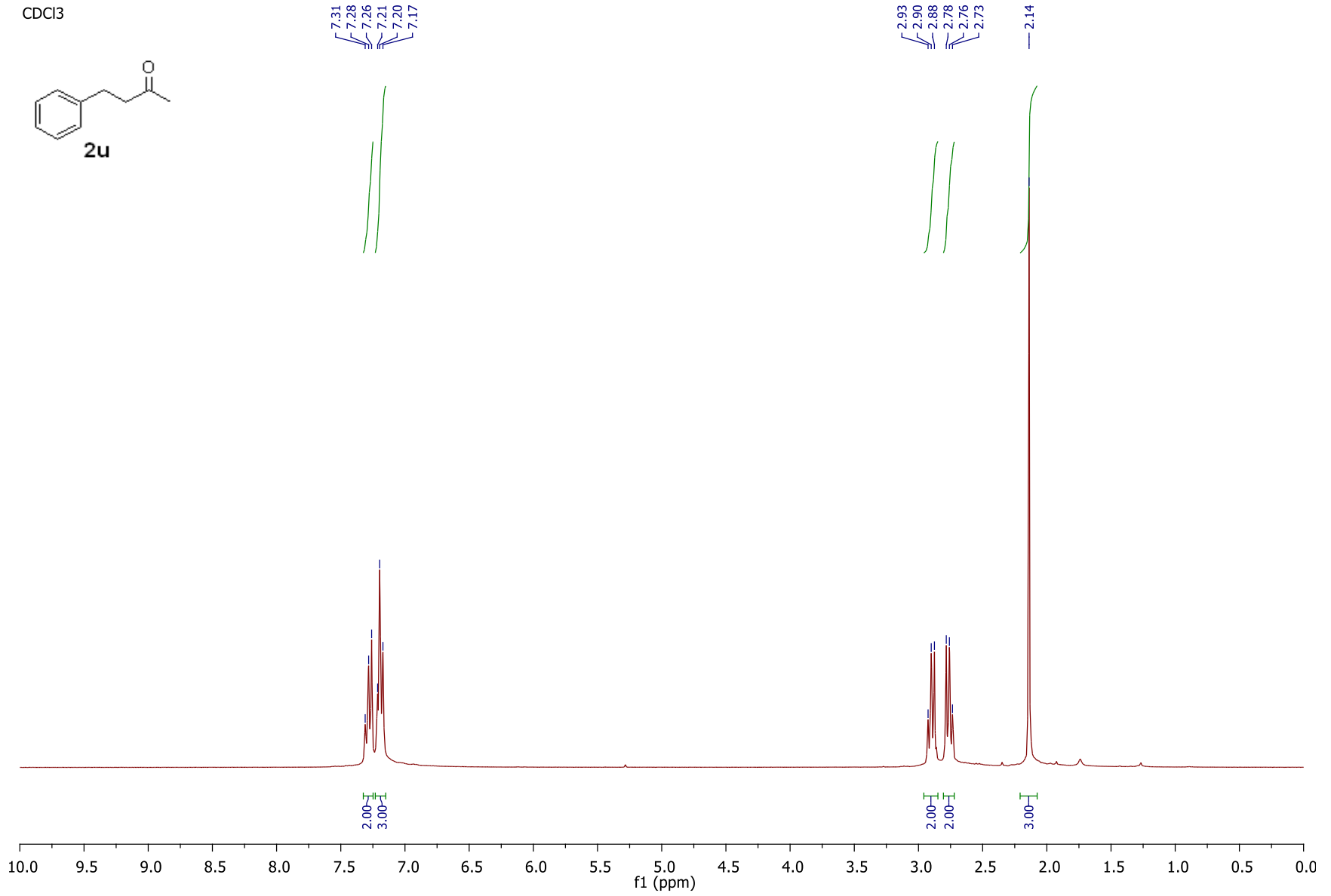
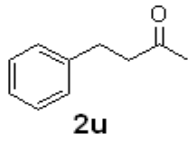
— 132.6

— 128.2

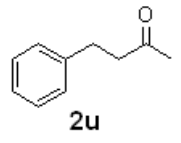
— 27.1



CDCl3



CDCl<sub>3</sub>  
— 208.0

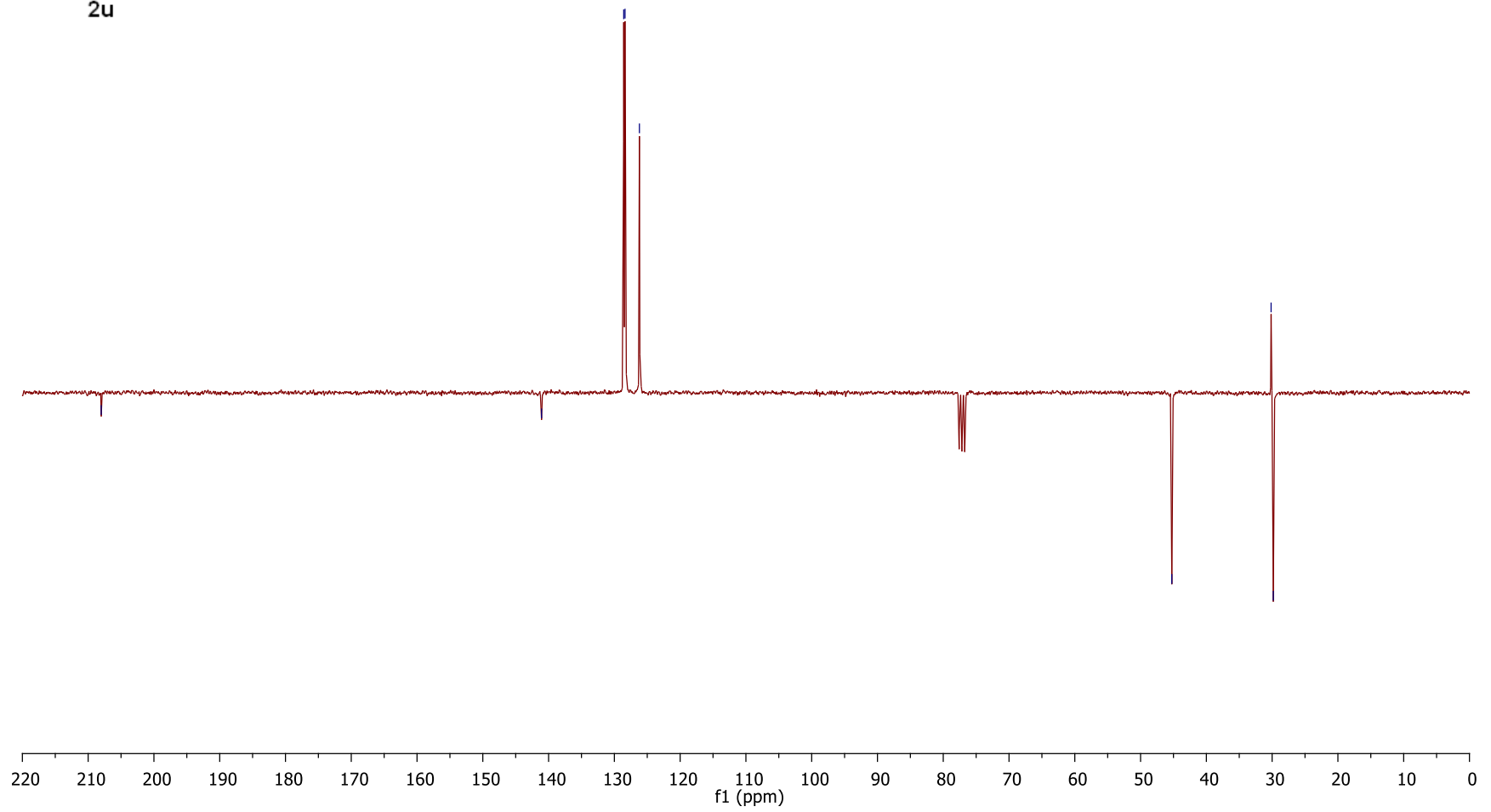


— 141.1

128.6  
128.4  
126.2

— 45.3

30.2  
29.8



S68