

# Mild and efficient rhodium-catalyzed deoxygenation of ketones to alkanes

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## Supporting information:

- I      General procedure for deoxygenation of ketones and hydrogenolysis of alcohols**
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- III     $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all isolated compounds**
- IV     $^1\text{H}$  NMR spectra of unpurified compounds**
- V     Hydrosilylation of compounds 1v and 1w**

All NMR spectra were recorded on a Bruker Avance 300 instrument in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relatively to TMS or  $\text{CDCl}_3$  as internal standard.

## I General procedure for deoxygenation of ketones and hydrogenolysis of alcohols

In a round-bottom flask under argon, the substrate (1 mmol) and the catalyst (3.9 mg, 0.01 mmol) were dissolved in DCM (3 mL). After addition of the silane (2 mmol) at 0 °C, the reaction mixture was slowly warmed to RT and stirred for 24 h. The volatile material was evaporated and the residue was purified by silica gel column chromatography.

## II Results and analytical data

**4-Ethyl-1,1'-biphenyl (3a).** Pentane. White solid (from **1a**: 152 mg, 84% yield; from **2a**: 161 mg, 88% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.59-7.50 (m, 4H), 7.44-7.39 (m, 2H), 7.33-7.25 (m, 3H), 2.68 (q,  $J$  = 9.0 Hz, 2H), 1.27 (t,  $J$  = 9.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 143.5, 141.3, 138.7, 128.8, 128.4, 127.2, 127.1, 127.0, 28.6, 15.7.

**2-Ethynaphthalene (3b).** Pentane. Colorless oil (129 mg, 83% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.80-7.74 (m, 3H), 7.61 (s, 1H), 7.43-7.32 (m, 3H), 2.80 (q,  $J$  = 9.0 Hz, 2H), 1.31 (t,  $J$  = 9.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 141.8, 133.8, 132.0, 127.9, 127.7, 127.5, 127.2, 125.9, 125.6, 125.1, 29.1, 15.6.

**1-Ethyl-4-methylbenzene (3e).** Pentane. Colorless oil (75 mg, 63% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.08 (s, 4H), 2.60 (q,  $J$  = 9.0 Hz, 2H), 2.31 (s, 3H), 1.21 (t,  $J$  = 9.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 141.3, 135.1, 129.1, 127.8, 28.5, 21.1, 15.9.

**1-Ethyl-2-methylbenzene (3f).** Pentane. Colorless oil (80 mg, 67% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.16-7.11 (m, 4H), 2.63 (q,  $J$  = 9.0 Hz, 2H), 2.30 (s, 3H), 1.21 (t,  $J$  = 9.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 142.4, 135.8, 130.1, 128.0, 126.1, 125.8, 26.3, 19.3, 14.5.

**1,2,3,4-Tetrahydronaphthalene (3g).** Pentane. Colorless oil (82 mg, 62% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.07 (d,  $J$  = 3.5 Hz, 2H), 7.06 (d,  $J$  = 3.5 Hz, 2H), 2.79-2.75 (m, 4H), 1.82-1.77 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 137.2, 129.2, 125.5, 29.5, 23.3.

**Ethylferrocene (3j).** Pentane. Yellow solid (188 mg, 88% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 4.10 (s, 5H), 4.06 (d,  $J$  = 4.0 Hz, 2H), 4.03 (d,  $J$  = 4.0 Hz, 2H), 2.34 (q,  $J$  = 6.0 Hz, 2H), 1.17 (t,  $J$  = 6.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 91.2, 68.5, 67.5, 67.0, 22.3, 14.7.

**Benzylferrocene (3k).** Cyclohexane/ $\text{Et}_2\text{O}$  (49/1). Orange solid (260 mg, 94% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.24-7.15 (m, 5H), 4.10 (s, 5H), 4.07 (s, 4H), 3.68 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 141.7, 128.4, 128.3, 126.0, 88.0, 68.7, 68.7, 67.6, 36.1.

**1-Ethyl-4-methoxybenzene (3l).** Cyclohexane/ $\text{Et}_2\text{O}$  (49/1). Colorless oil (from **1l**: 80 mg, 59% yield; from **2l**: 100 mg, 74% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.10 (d,  $J$  = 8.8 Hz, 2H), 6.82 (d,  $J$  = 8.8 Hz, 2H), 3.77 (s, 3H), 2.58 (q,  $J$  = 6.0 Hz, 2H), 1.21 (t,  $J$  = 6.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 157.7, 136.5, 128.8, 113.8, 55.3, 28.1, 16.0.

**6-Methoxy-1,2,3,4-tetrahydronaphthalene (3m).** Pentane/ $\text{Et}_2\text{O}$  (99/1). Colorless oil (112 mg, 69% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 6.96 (d,  $J$  = 9.0 Hz, 1H), 6.68-6.60 (m, 2H), 3.76 (s, 3H), 2.74-2.69 (m, 4H), 1.79-1.74 (m, 4H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 157.4, 138.2, 130.0, 129.3, 113.7, 111.8, 55.3, 29.8, 28.6, 23.5, 23.3.

**Diphenylmethane (3r).** Pentane. White solid (from **1r**: 130 mg, 77% yield; from **2r**: 117 mg, 70% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.30-7.16 (m, 10H), 3.97 (s, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 141.2, 129.0, 128.5, 126.1, 42.0.

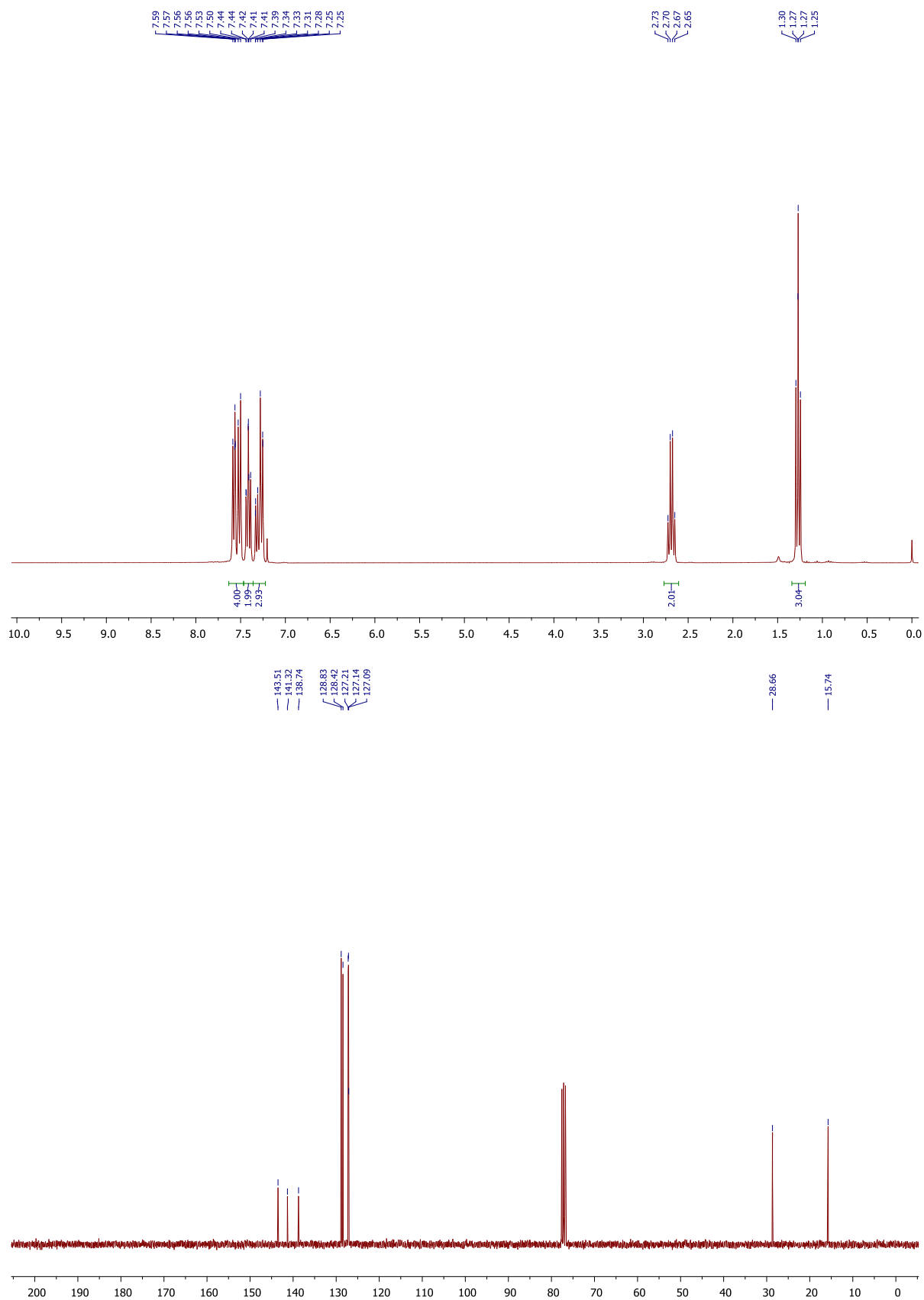
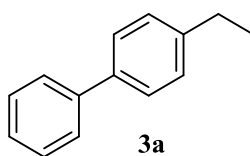
**4-Ethylphenol (3s).** PE/ $\text{Et}_2\text{O}$  (9/1). Colorless oil (55 mg, 45% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.06 (d,  $J$  = 9.0 Hz, 2H), 6.75 (d,  $J$  = 9.0 Hz, 2H), 4.63 (s, 1H), 2.57 (q,  $J$  = 9.0 Hz, 2H), 1.20 (t,  $J$  = 9.0 Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 153.5, 136.7, 129.0, 115.2, 28.1, 16.0.

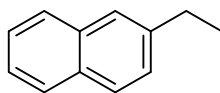
**4-(Triethylsilyloxy)acetophenone (4).** PE/ $\text{Et}_2\text{O}$  (9/1). Colorless oil (75 mg, 30% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.87 (d,  $J$  = 8.5 Hz, 2H), 6.88 (d,  $J$  = 8.5 Hz, 2H), 2.55 (s, 3H), 1.00 (t,  $J$  = 6.0 Hz, 9H), 0.77 (q,  $J$  = 6.0 Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 196.9, 160.3, 130.9, 130.6, 119.8, 26.4, 6.6, 5.1.

**1,3-Diphenylpropan-1-one (6).** PE/Et<sub>2</sub>O (9/1). Colorless oil (160 mg, 76% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.93 (d,  $J$  = 9.0 Hz, 2H), 7.53-7.40 (m, 3H), 7.29-7.19 (m, 5H), 3.28 (t,  $J$  = 6.0 Hz, 2H), 3.06 (t,  $J$  = 6.0 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 199.2, 141.3, 136.9, 133.1, 128.6, 128.6, 128.5, 128.1, 126.2, 40.5, 30.2.

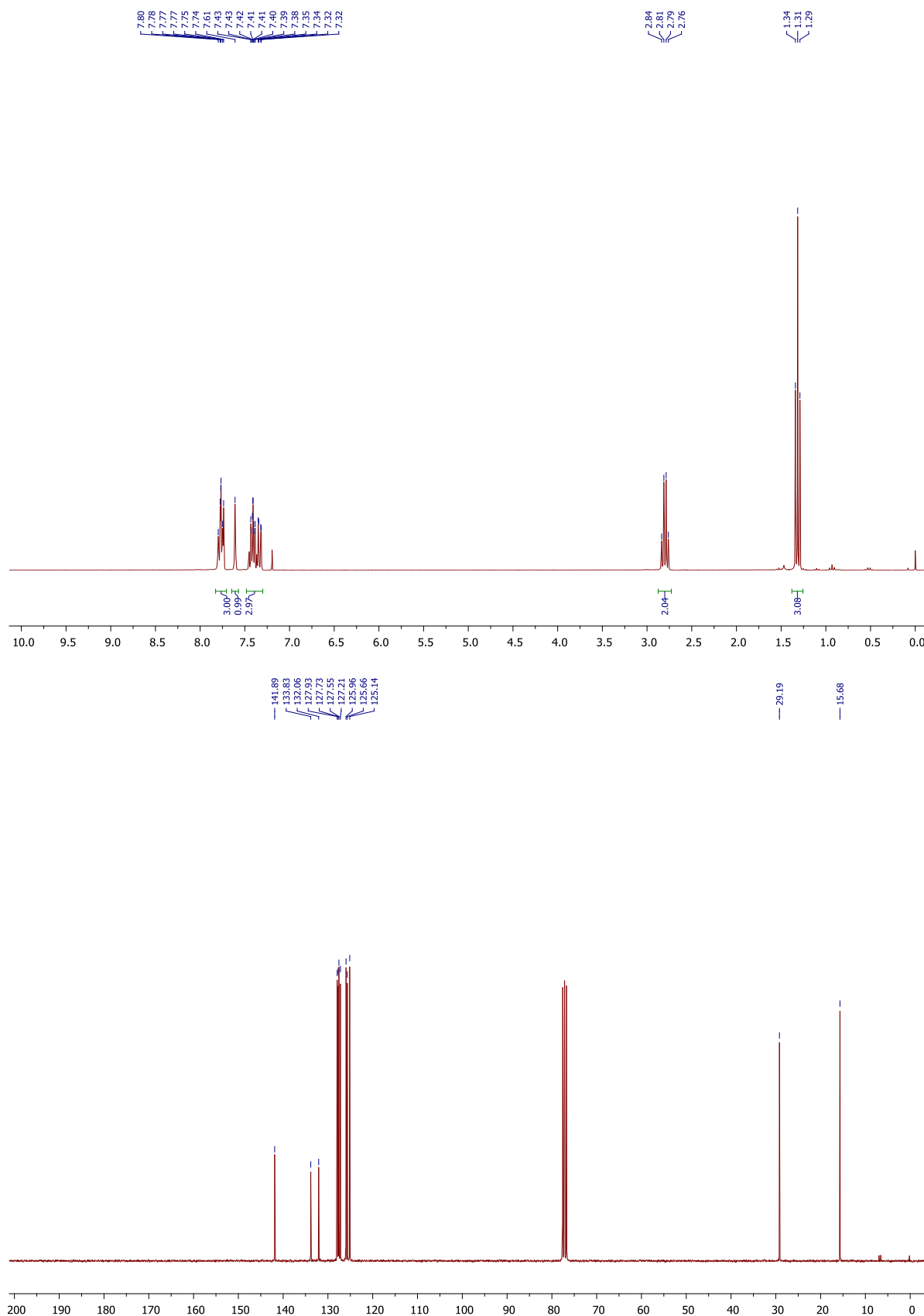
**2-Phenylchroman-4-one (7).** Cyclohexane/Et<sub>2</sub>O (19/1). Off white solid (119 mg, 53% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.94 (dd,  $J$  = 8.1 and 2.4 Hz, 1H), 7.54-7.38 (m, 6H), 7.08-7.03 (m, 2H), 5.48 (dd,  $J$  = 13.2 and 3.0 Hz, 1H), 3.10 (dd,  $J$  = 17.0 and 13.2 Hz, 1H), 2.88 (dd,  $J$  = 17.0 and 3.0 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 192.1, 161.6, 138.8, 136.3, 129.0, 128.9, 127.1, 126.2, 121.7, 121.0, 118.2, 79.7, 44.8.

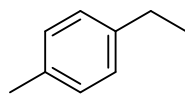
### III $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of all isolated compounds



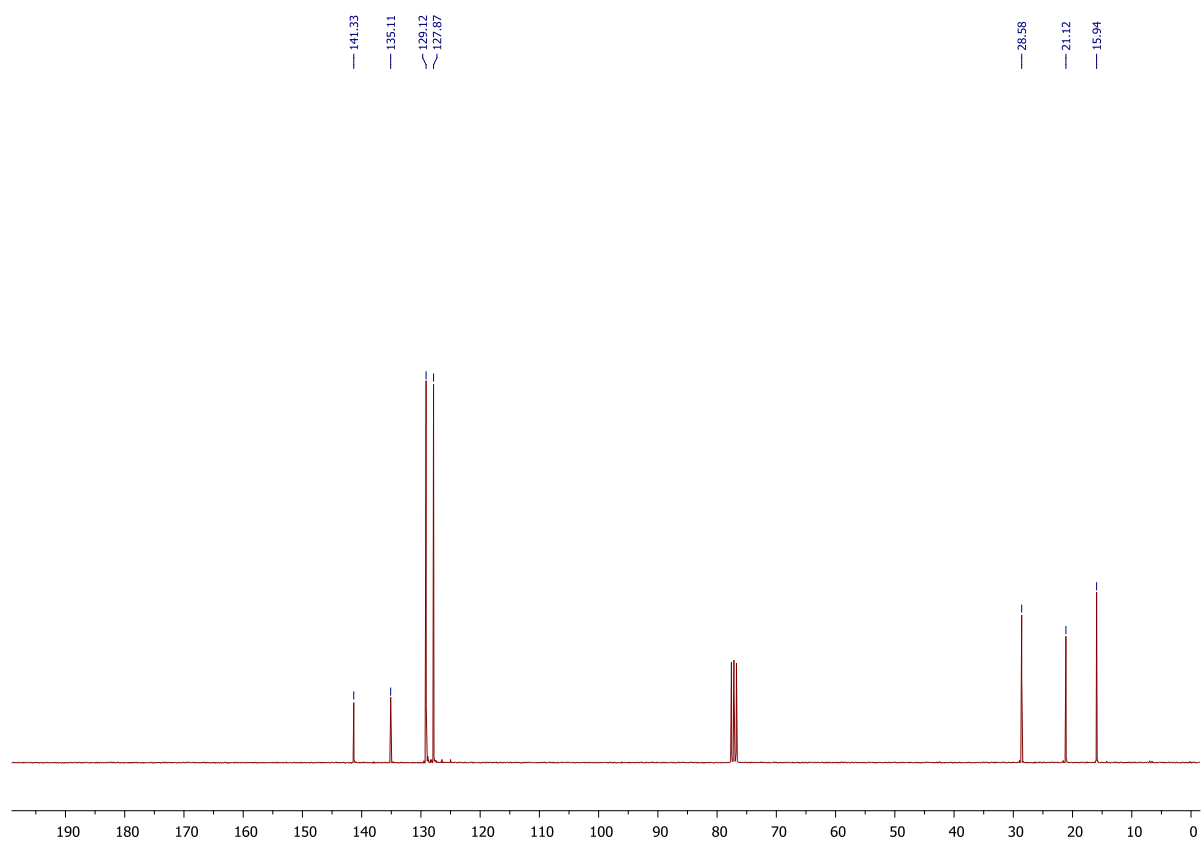
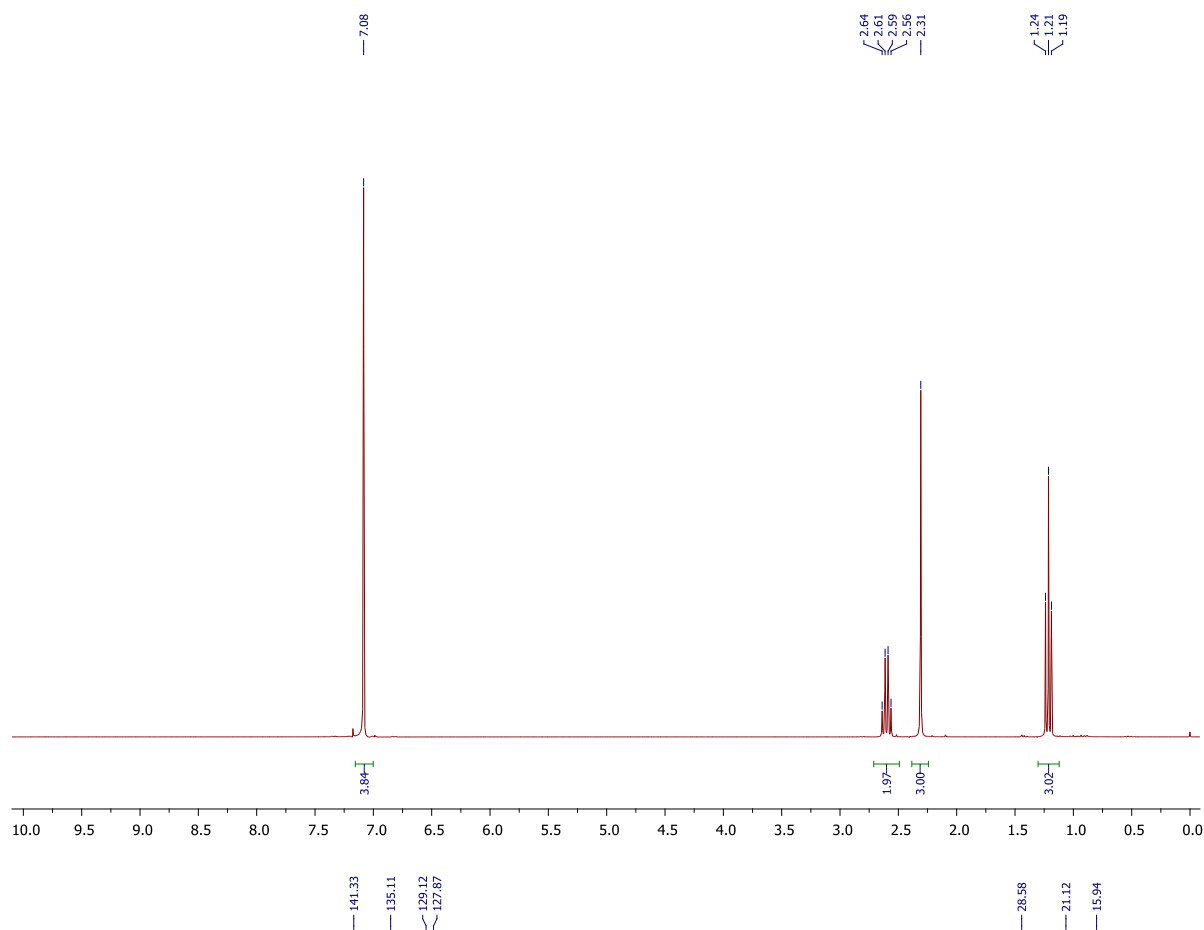


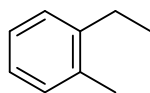
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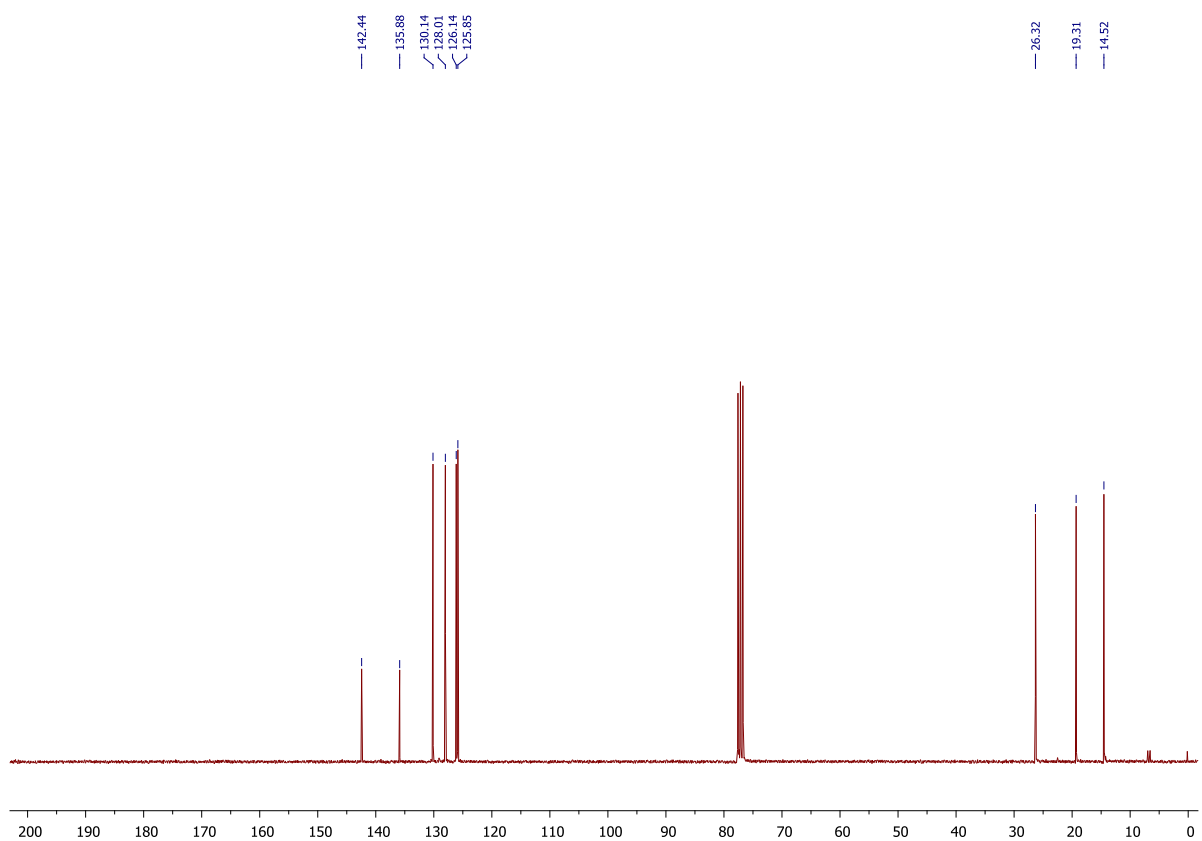
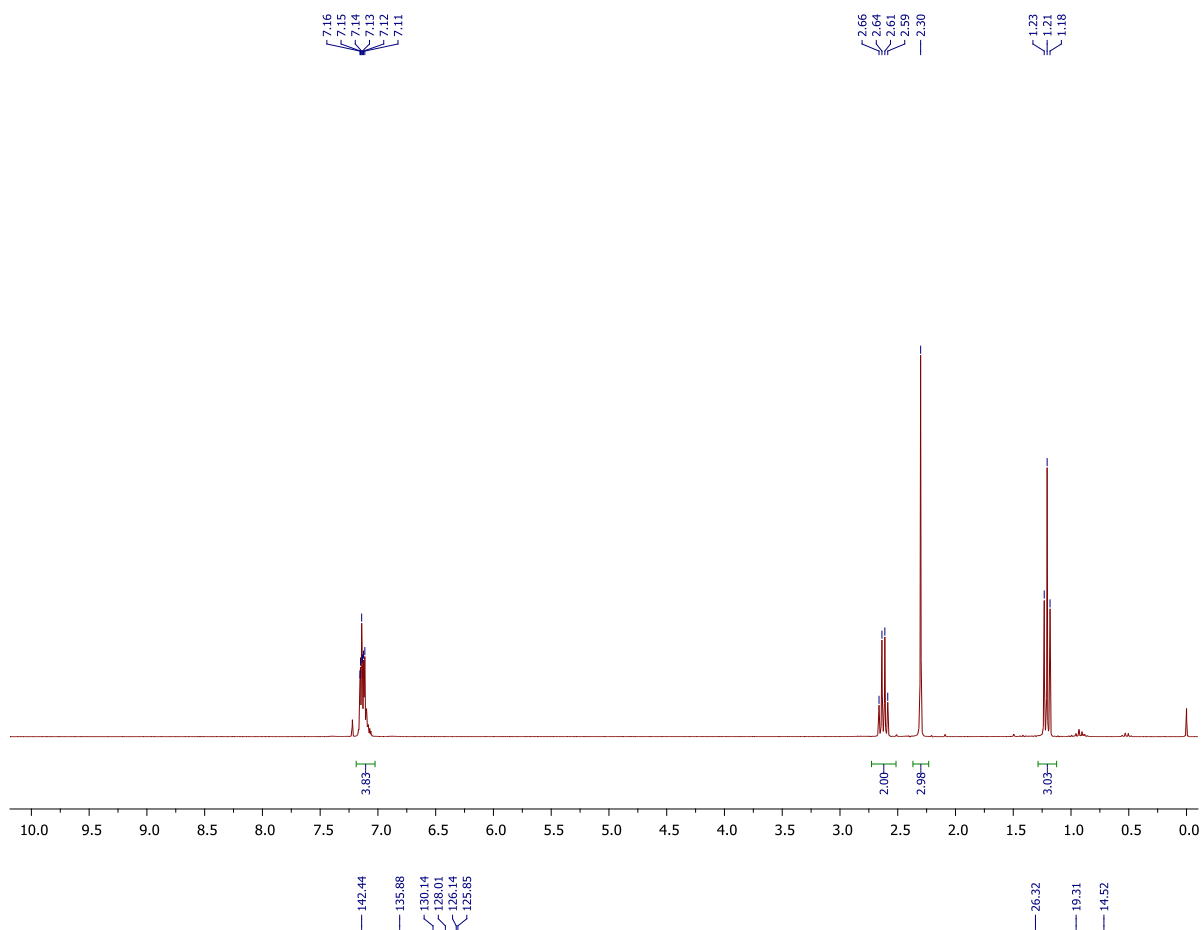


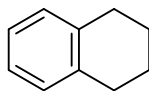
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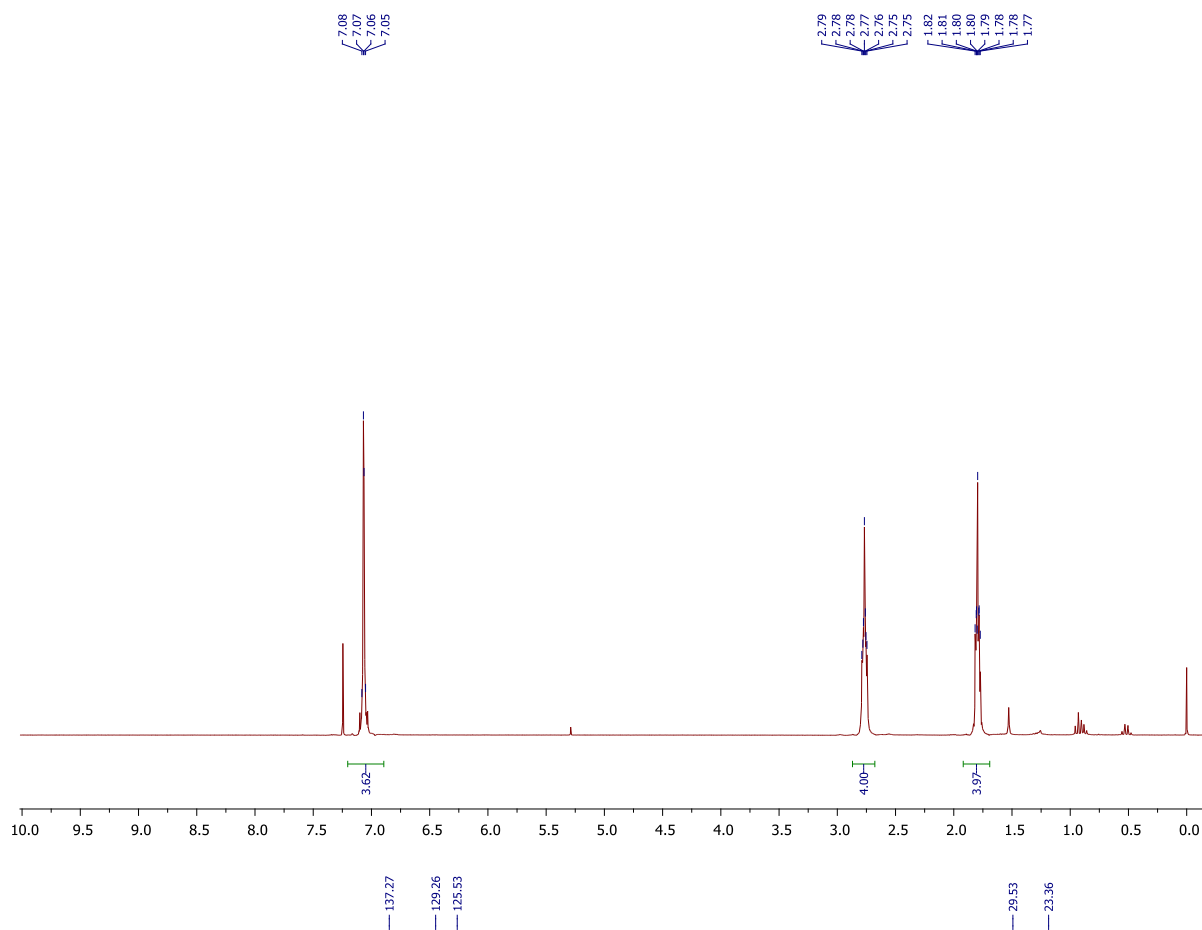


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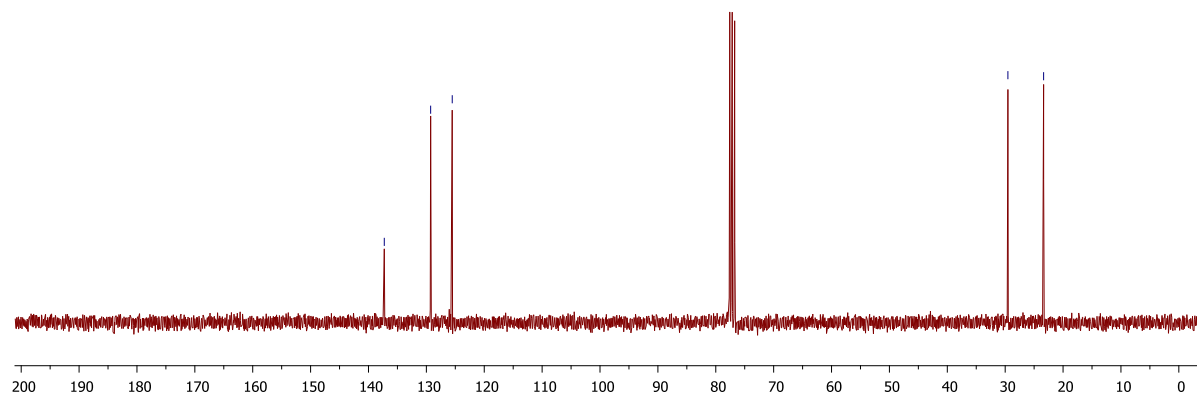


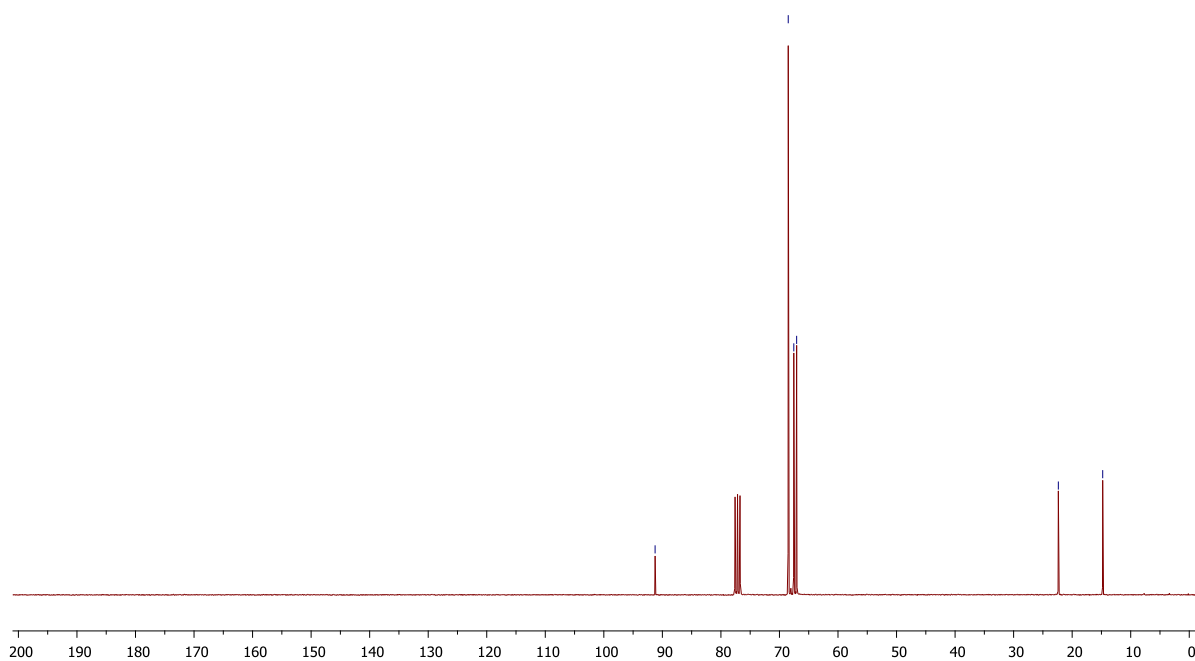
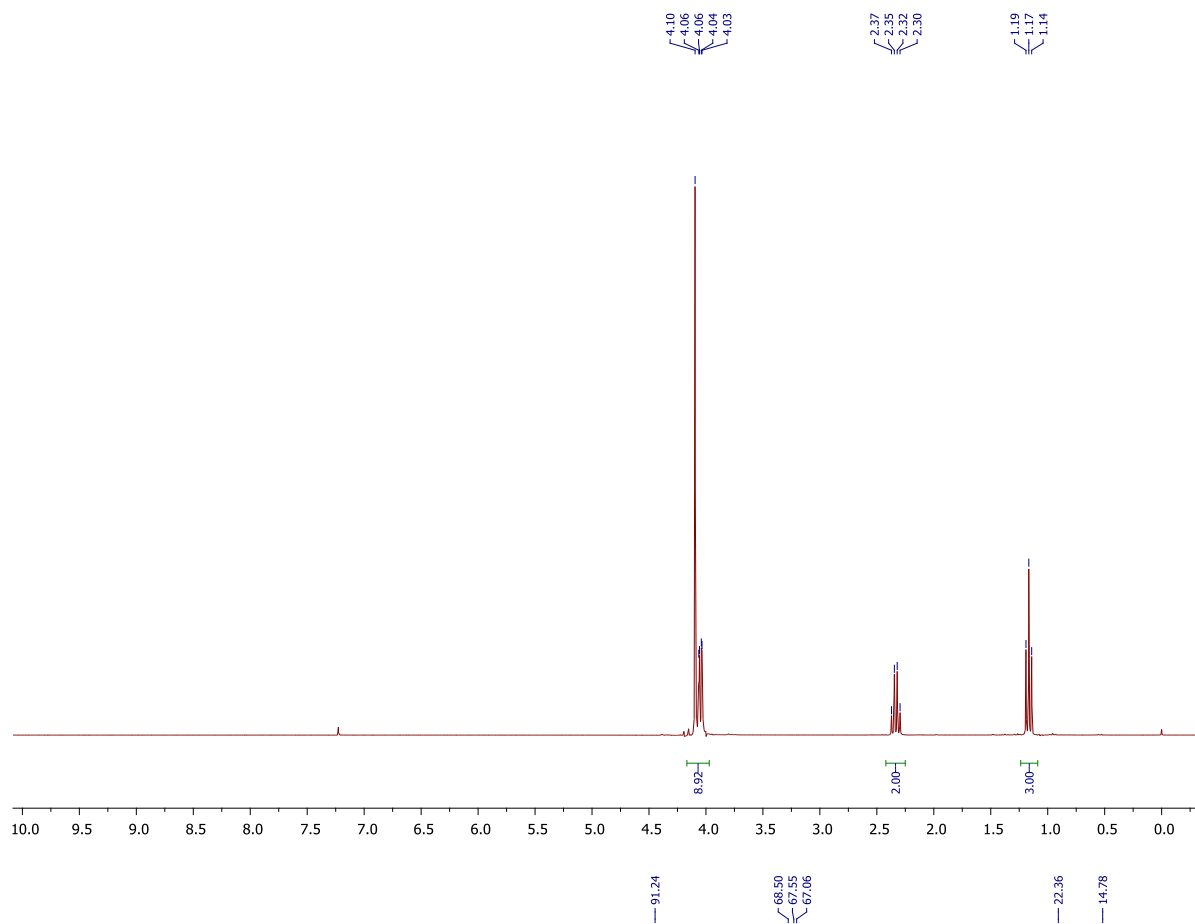
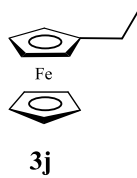
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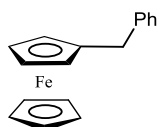


— 137.27  
— 129.26  
— 125.53

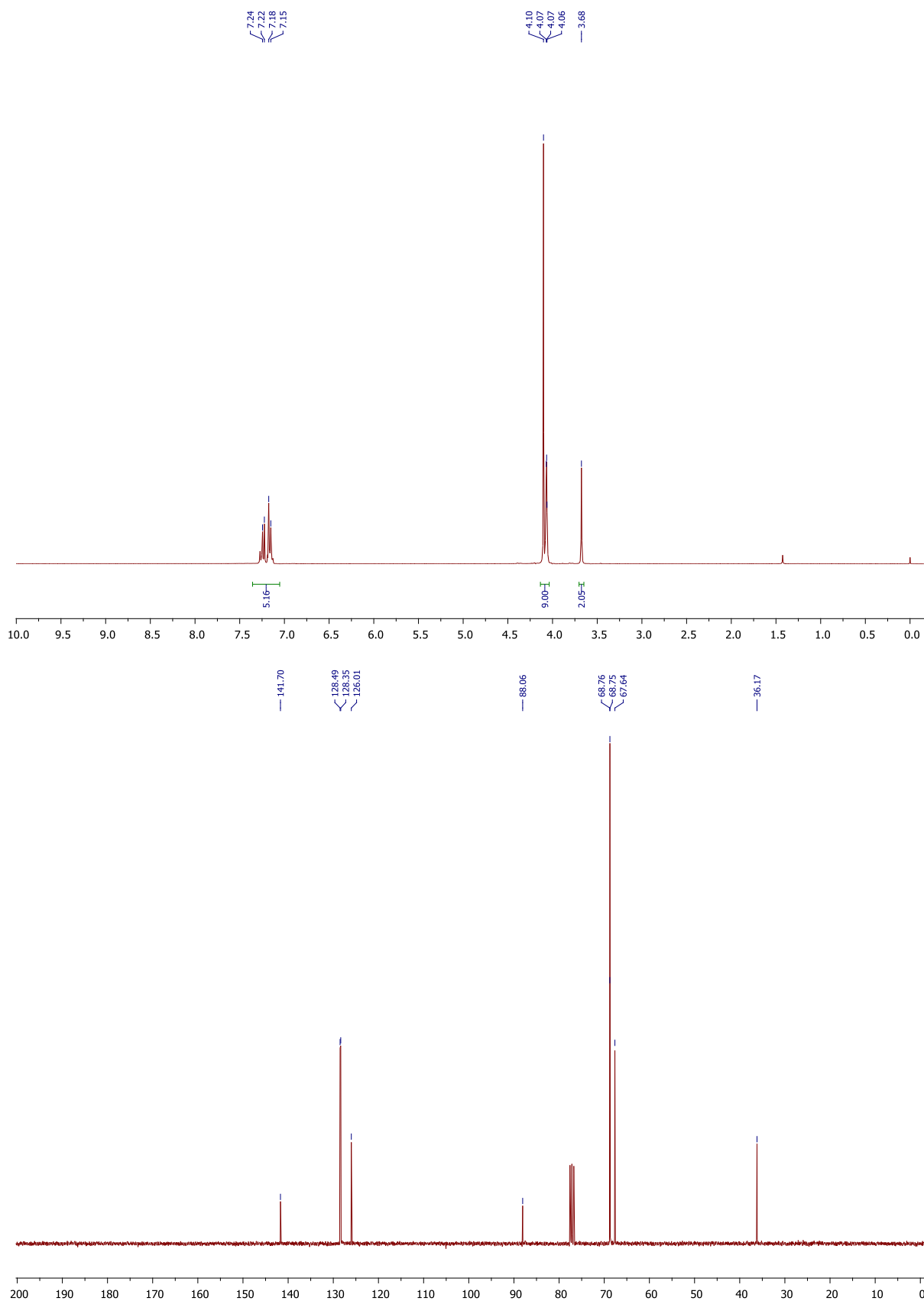
— 29.53  
— 23.36

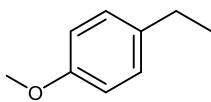




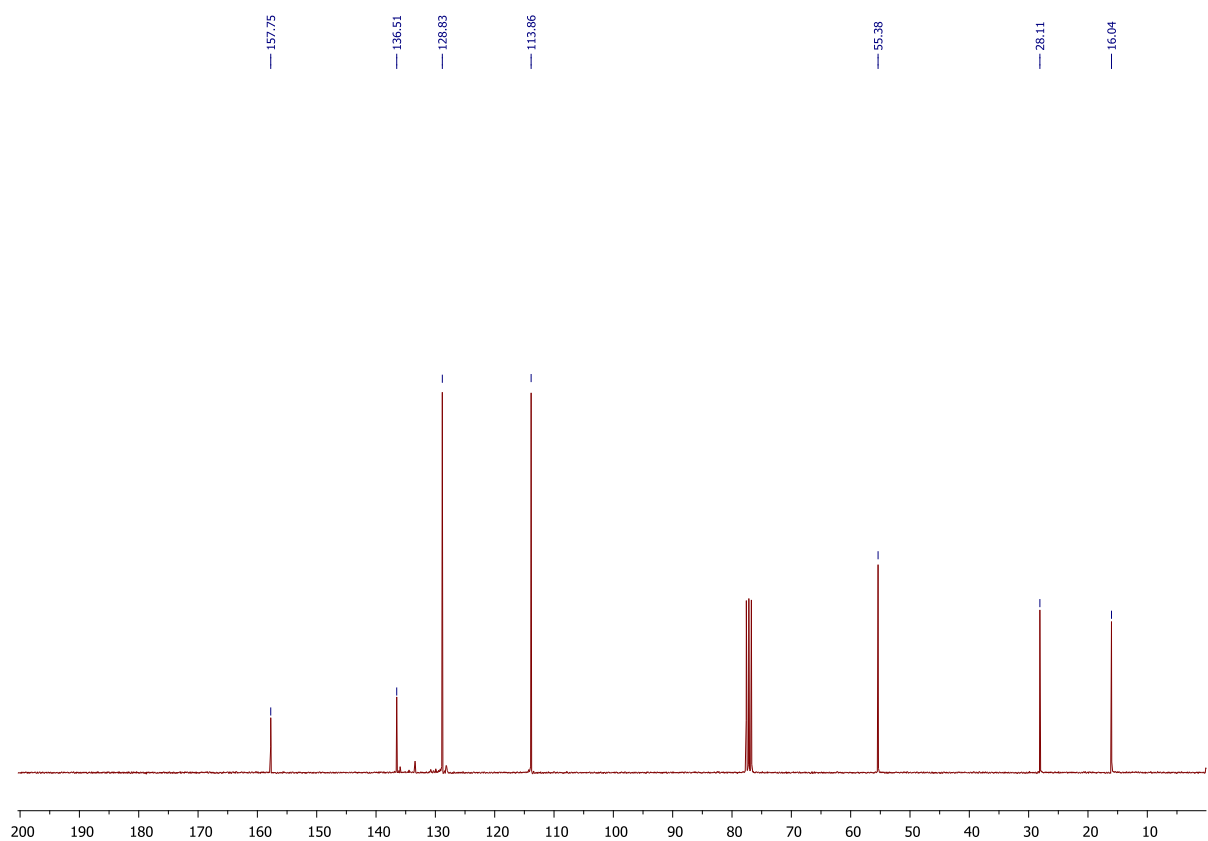
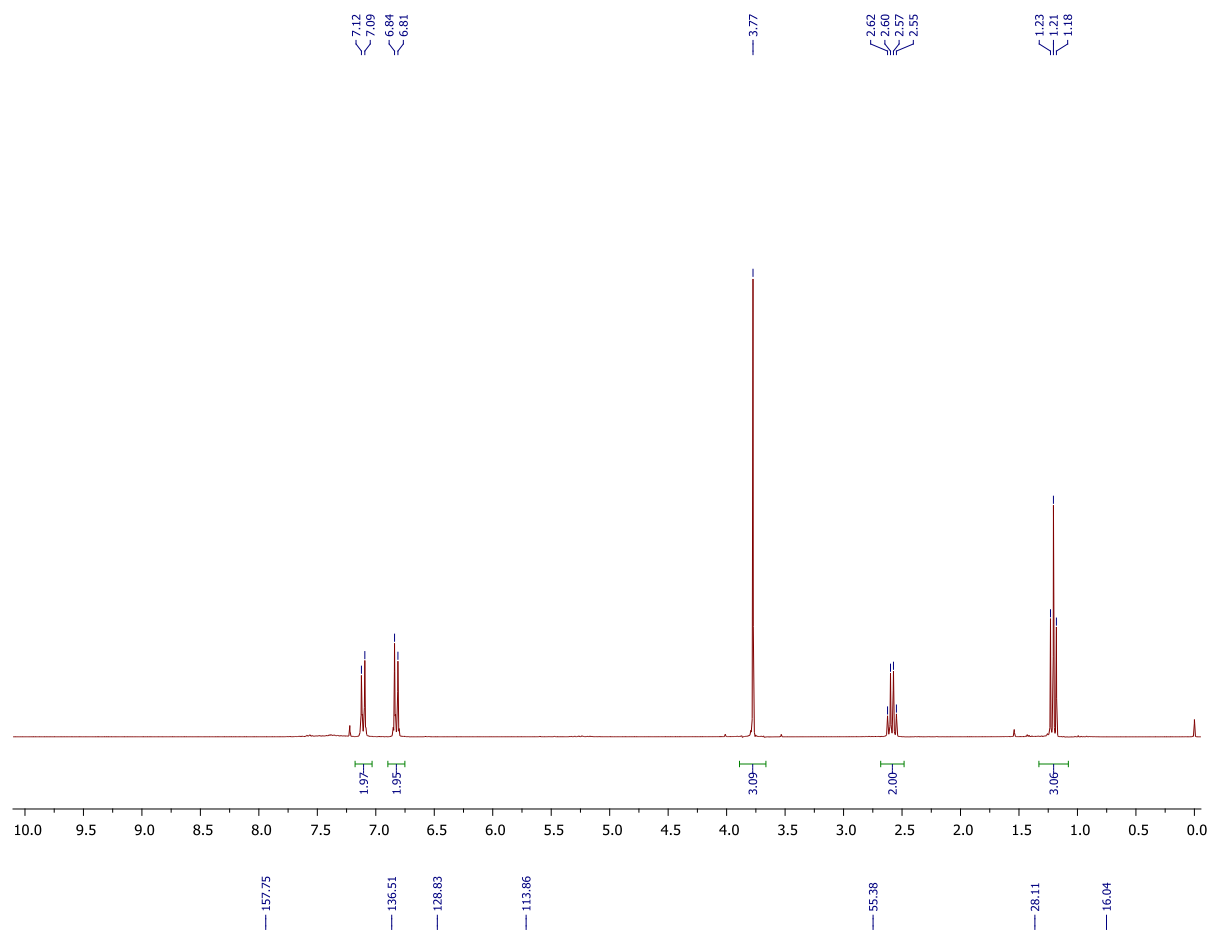


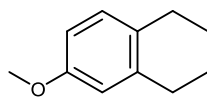
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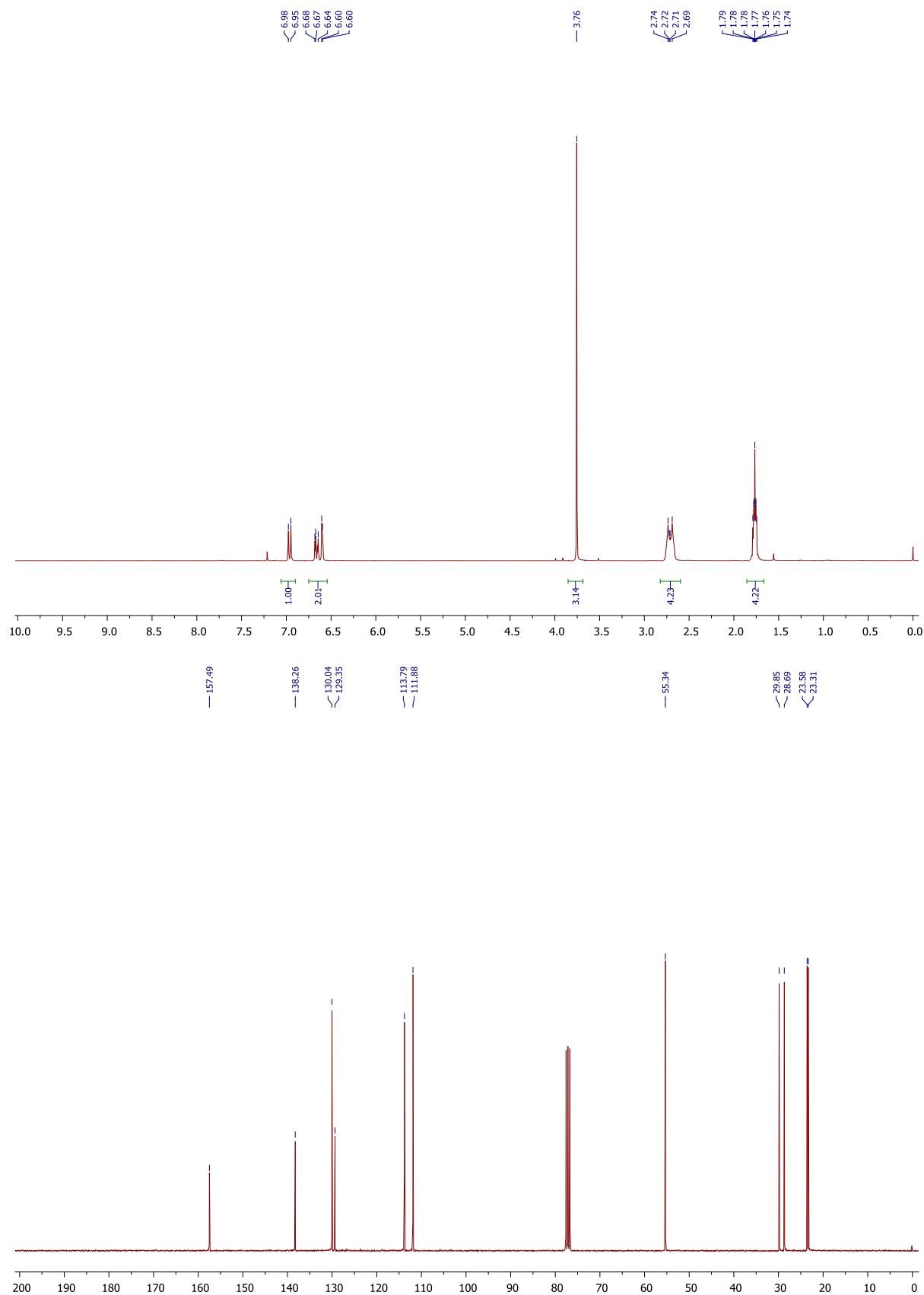


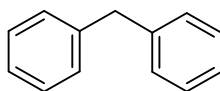
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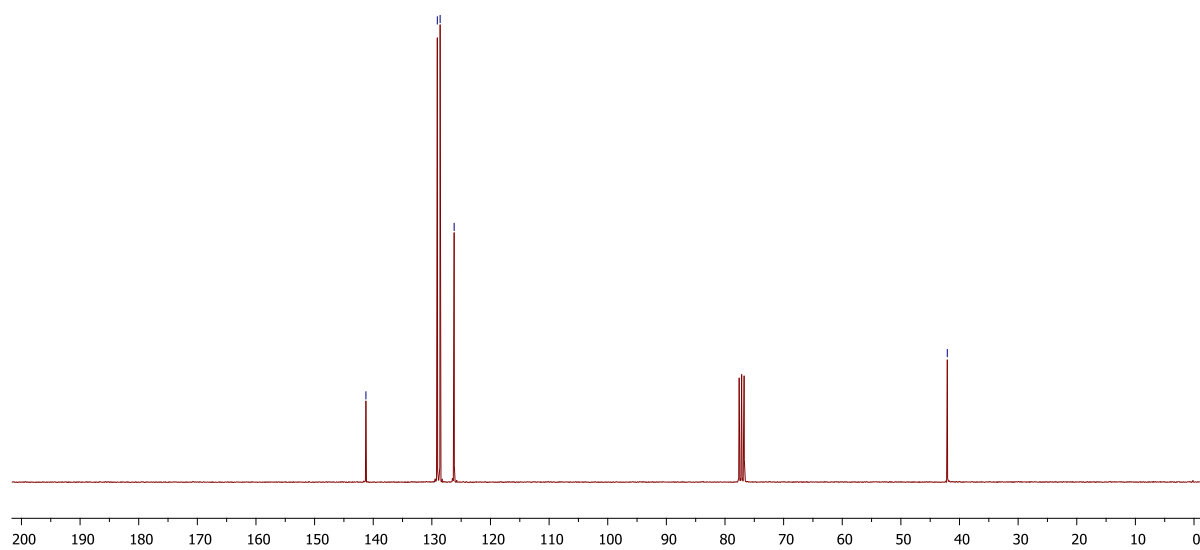
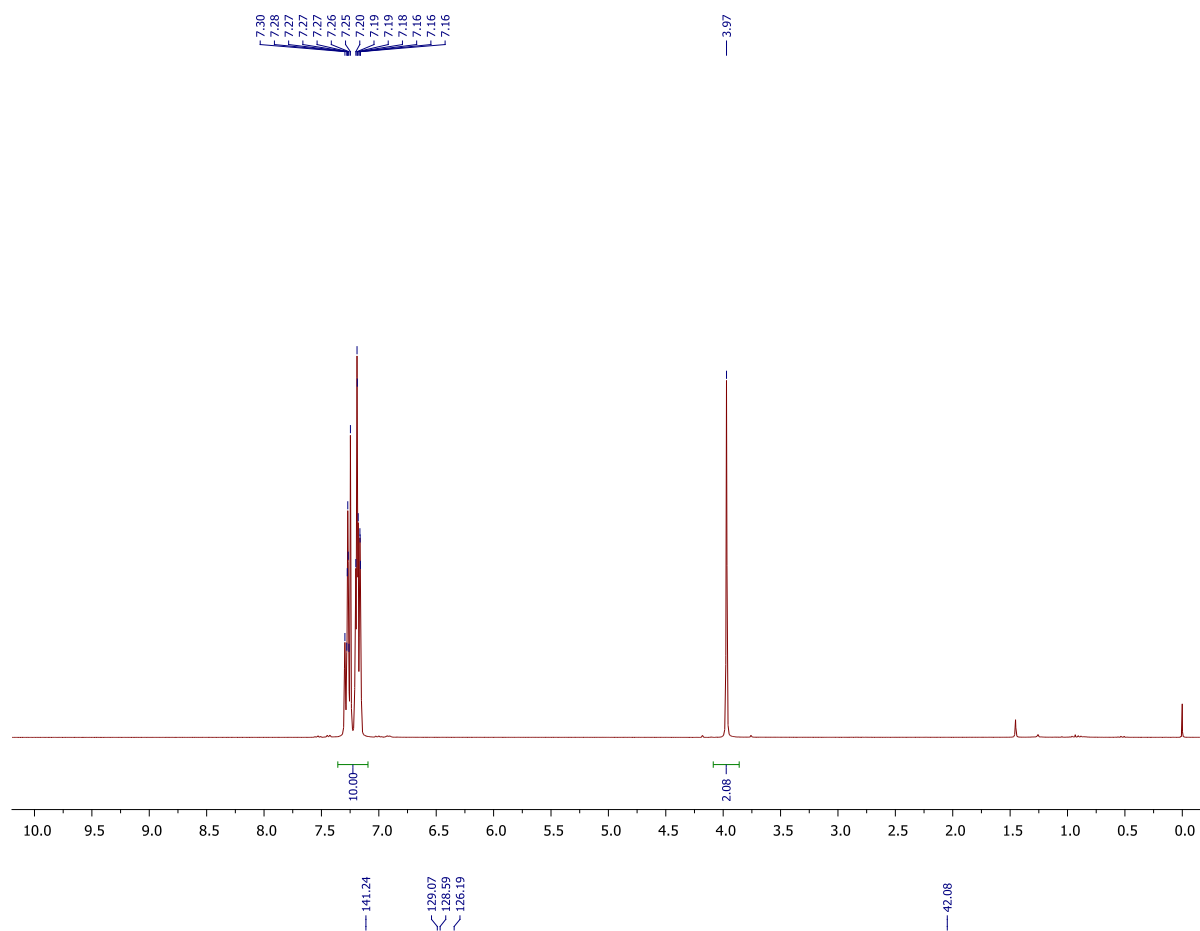


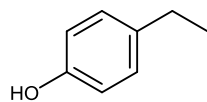
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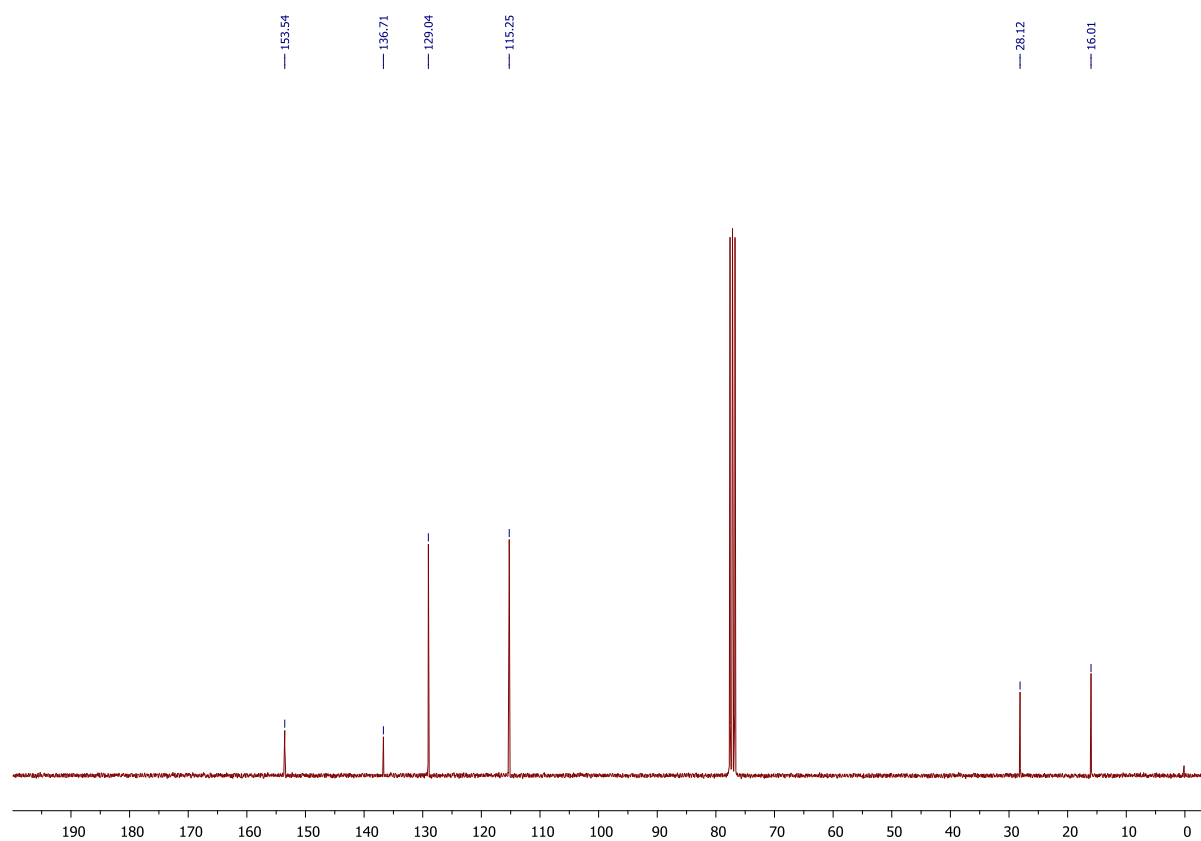
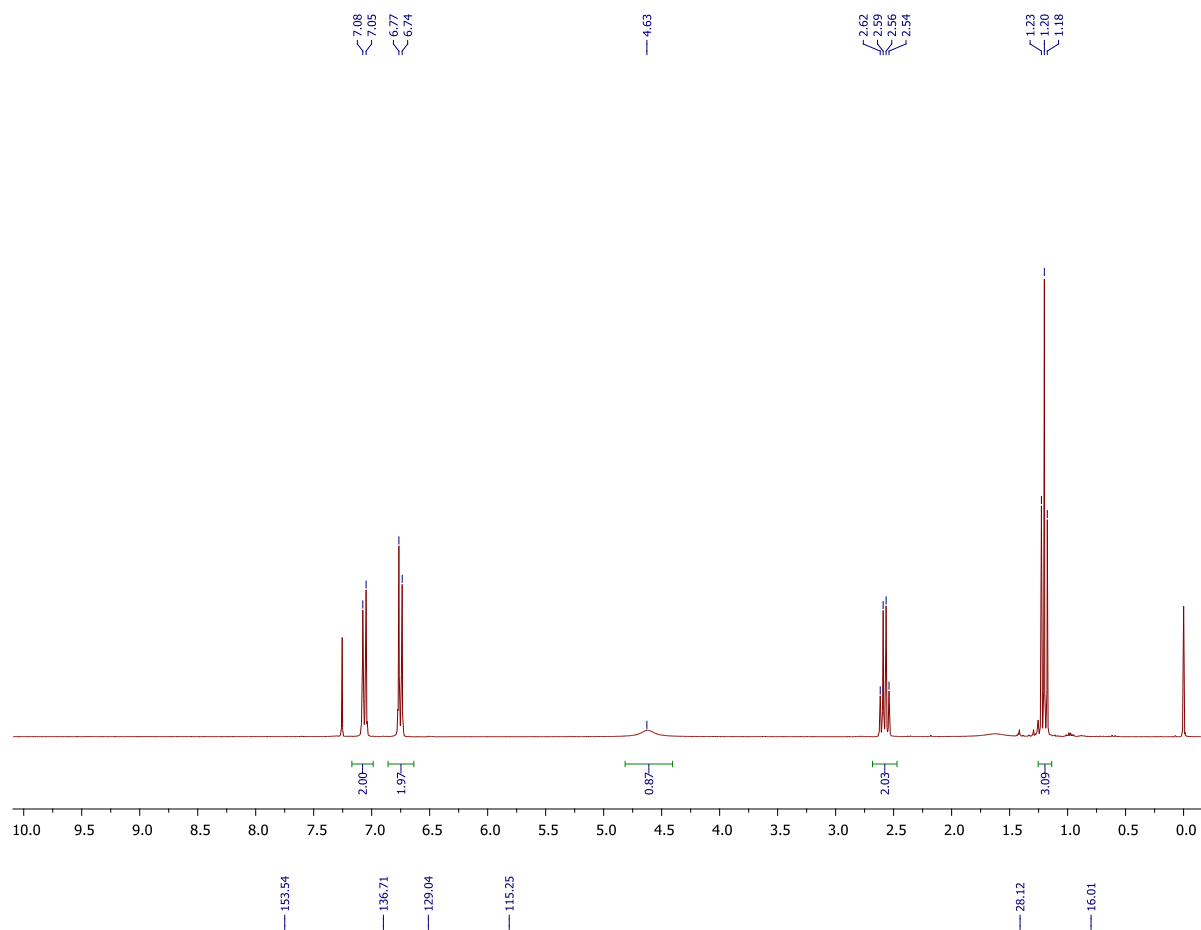


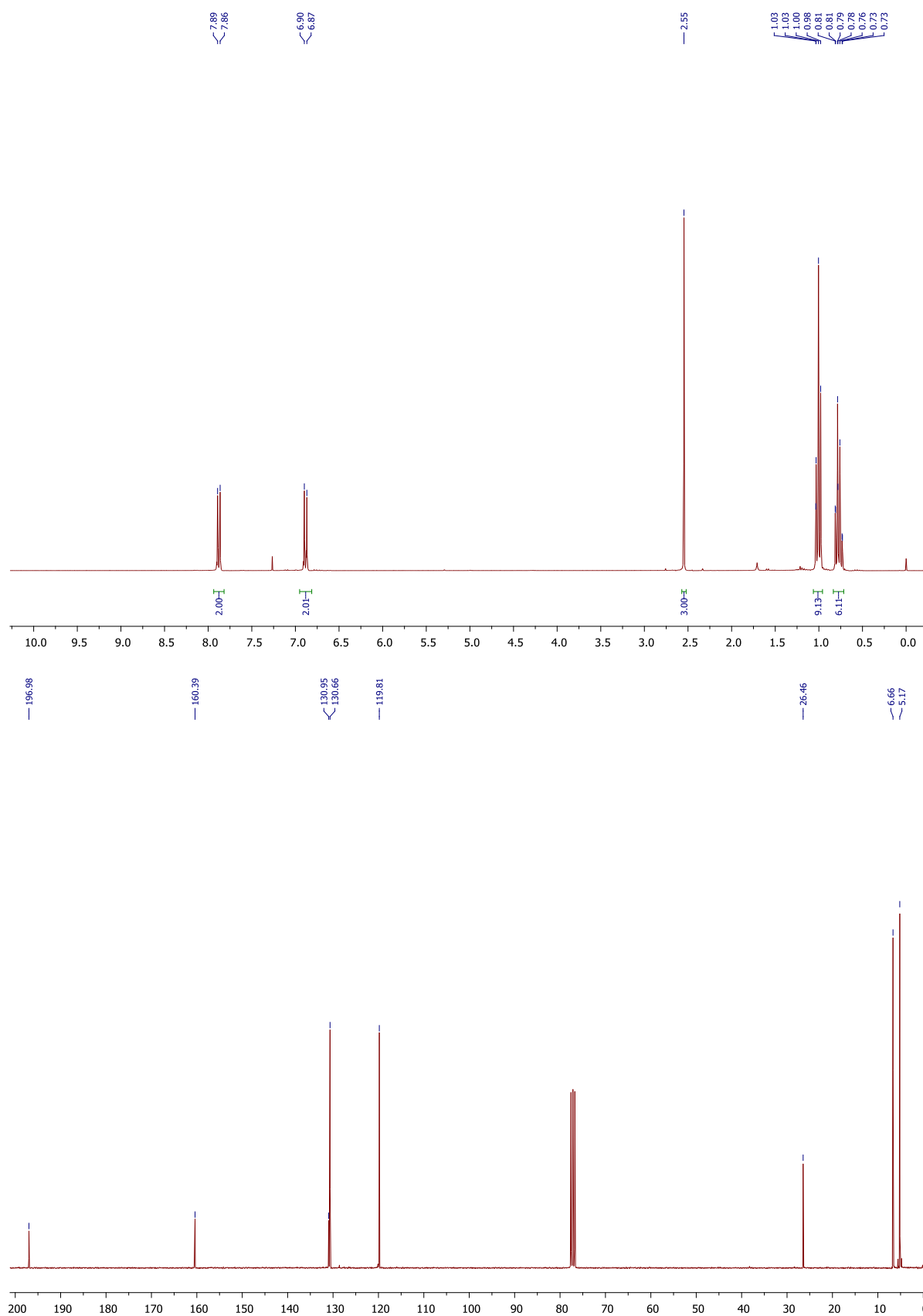
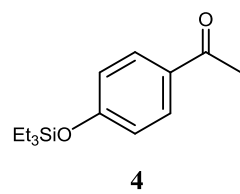
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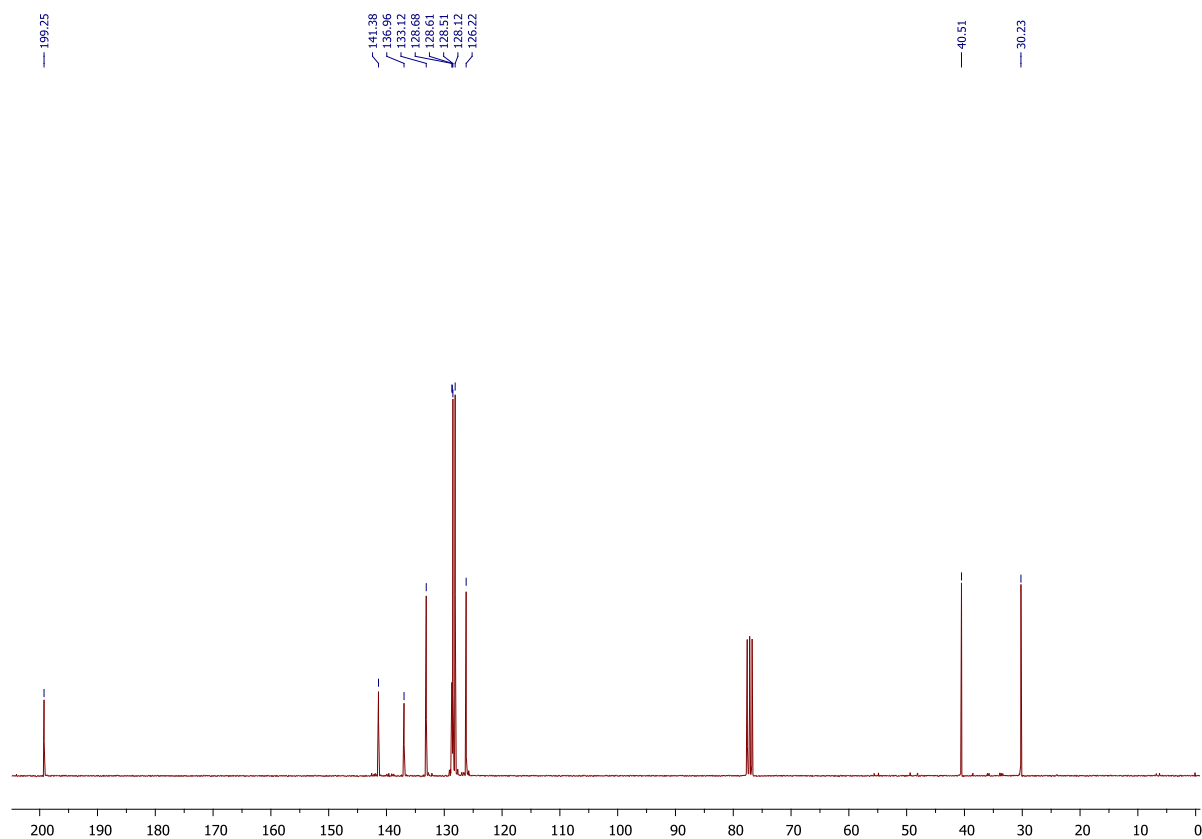
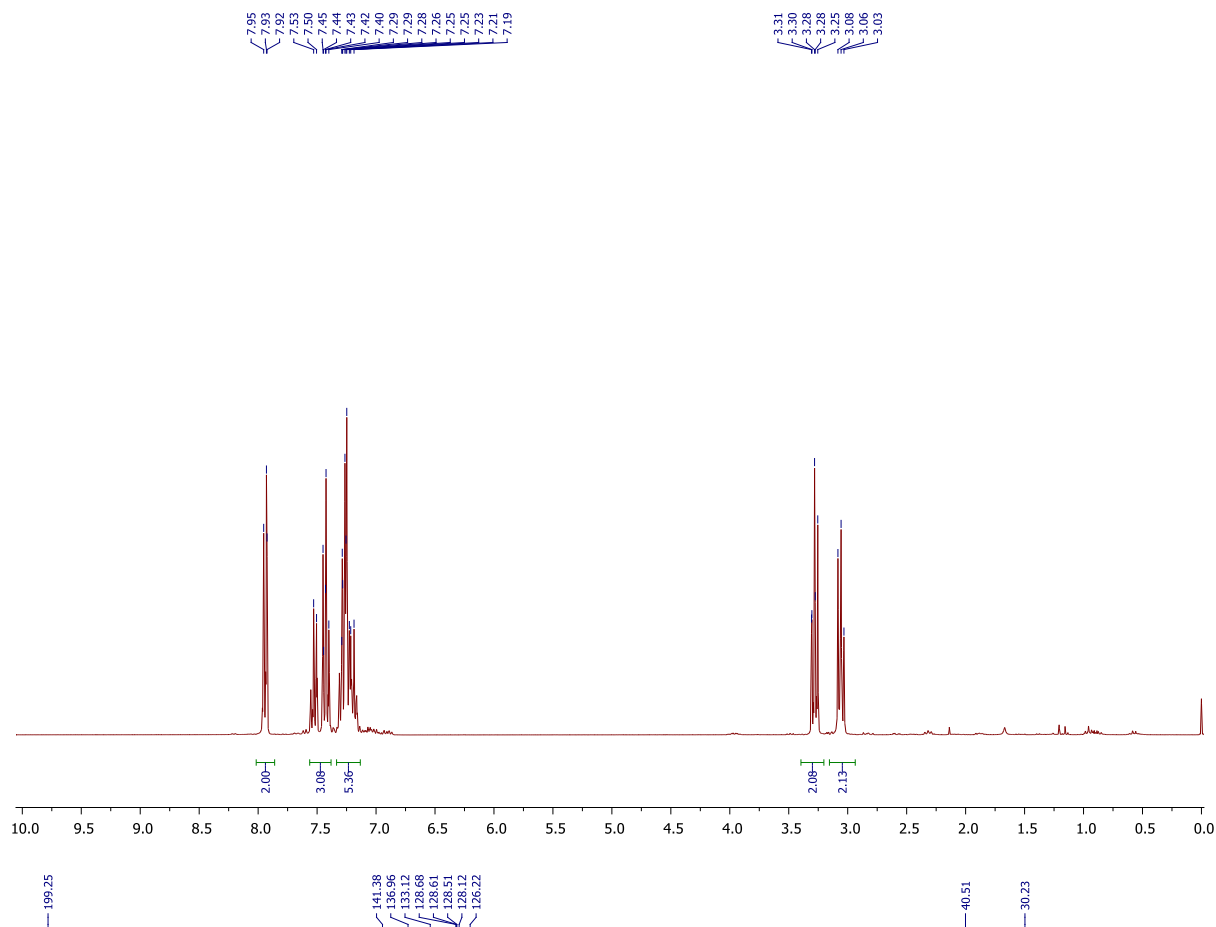
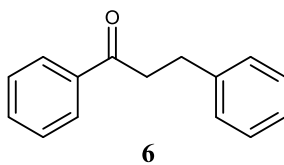


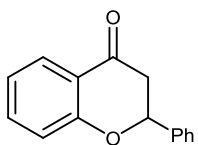


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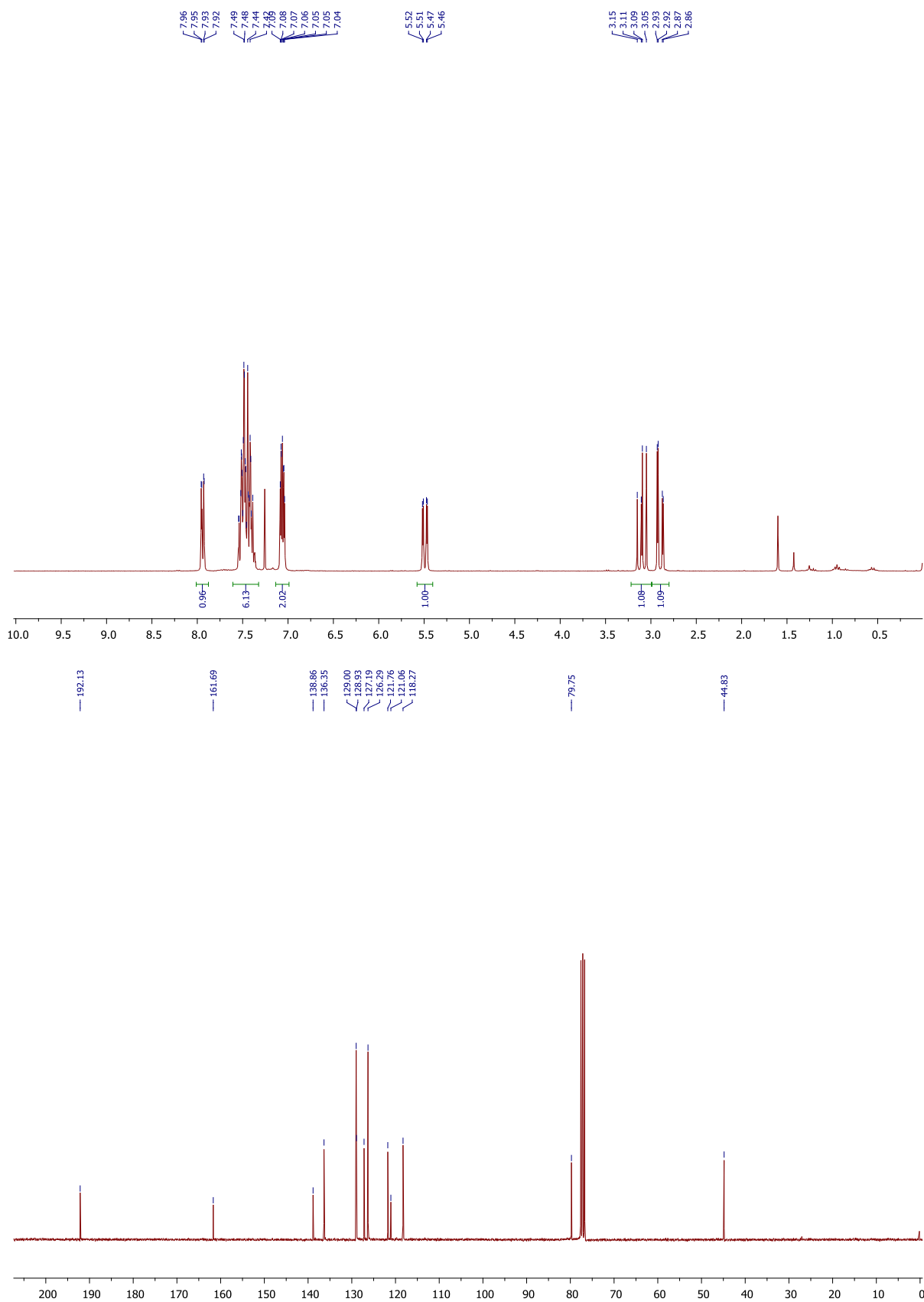




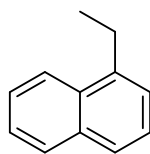




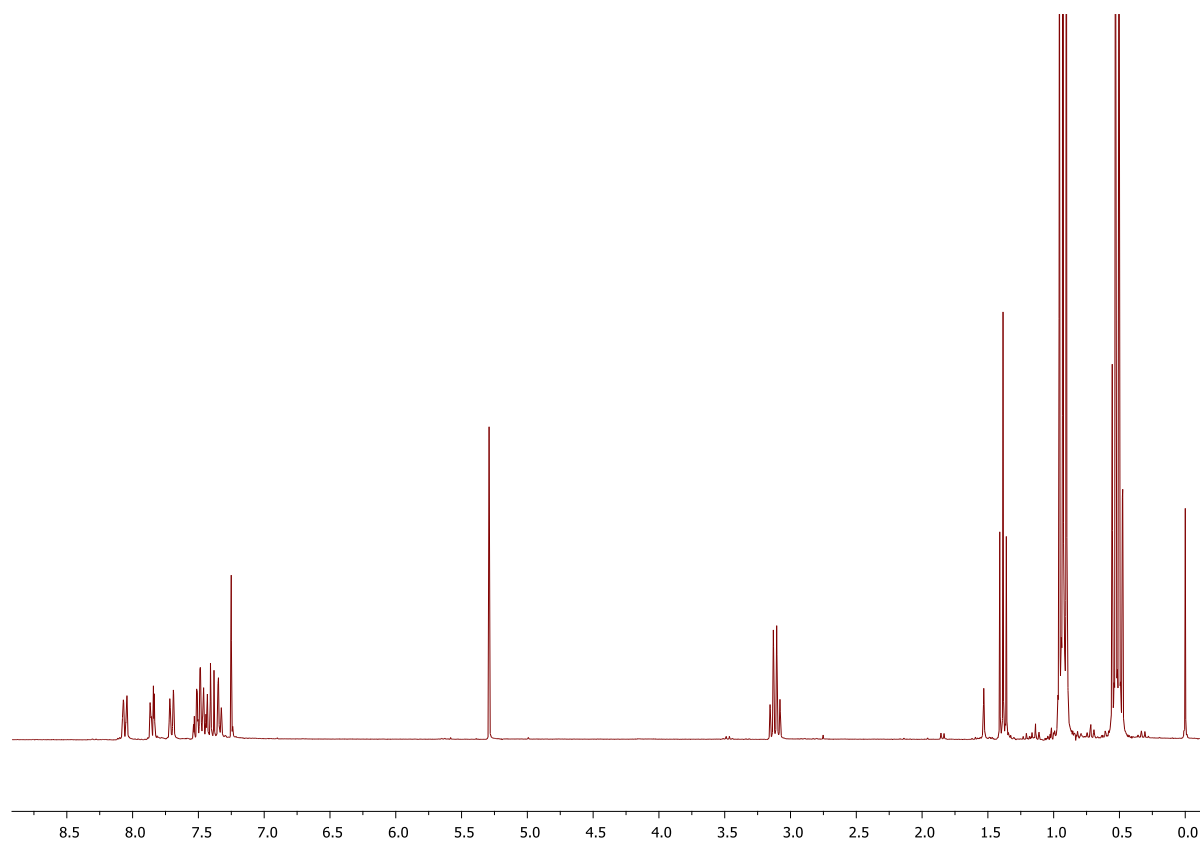
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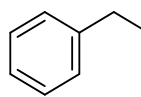


#### IV $^1\text{H}$ NMR spectra of unpurified compounds

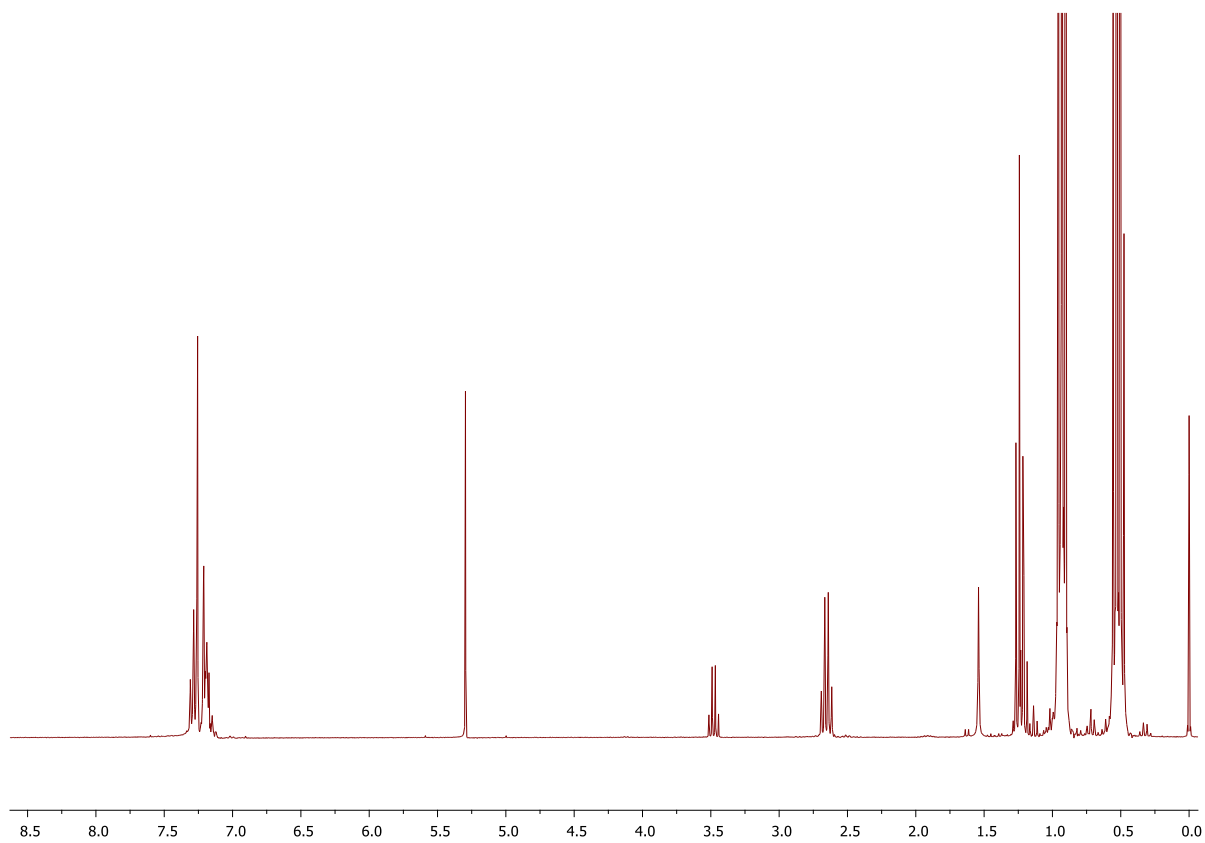


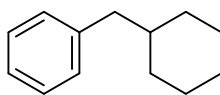
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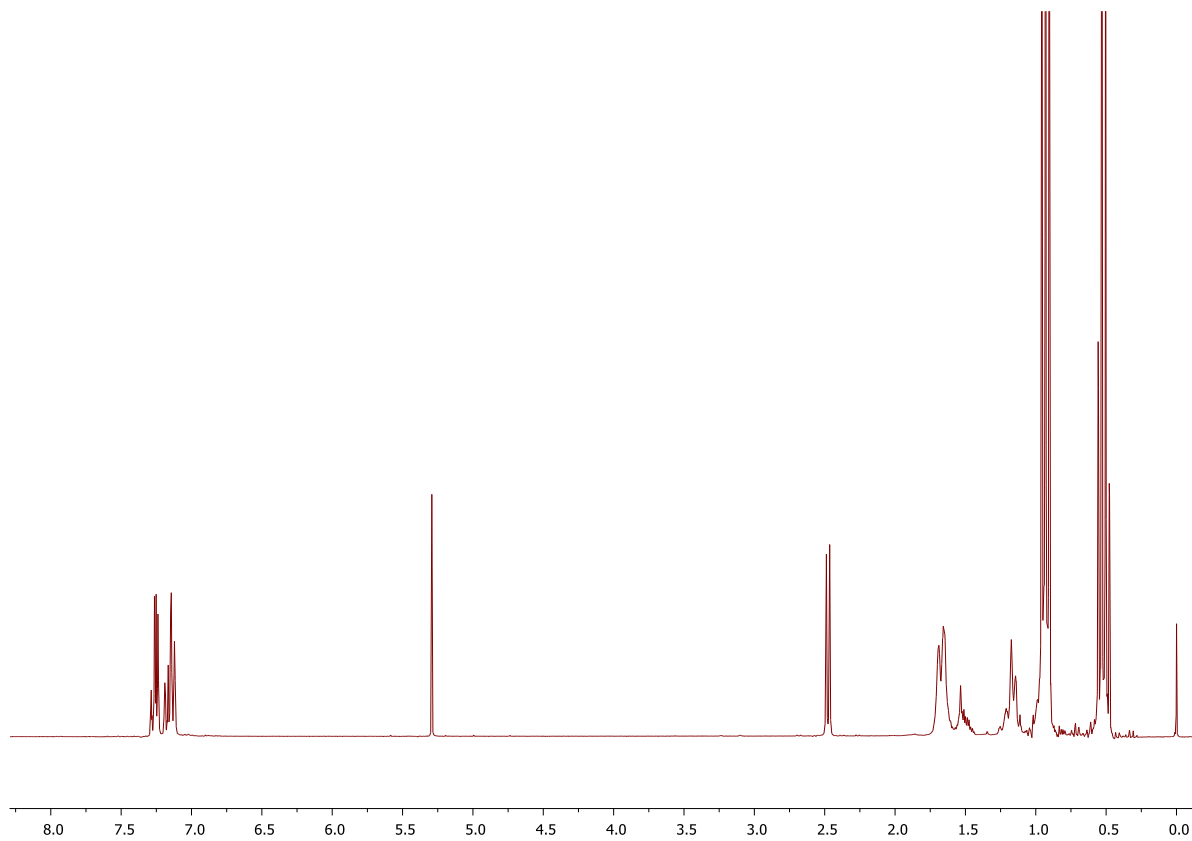


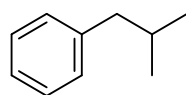
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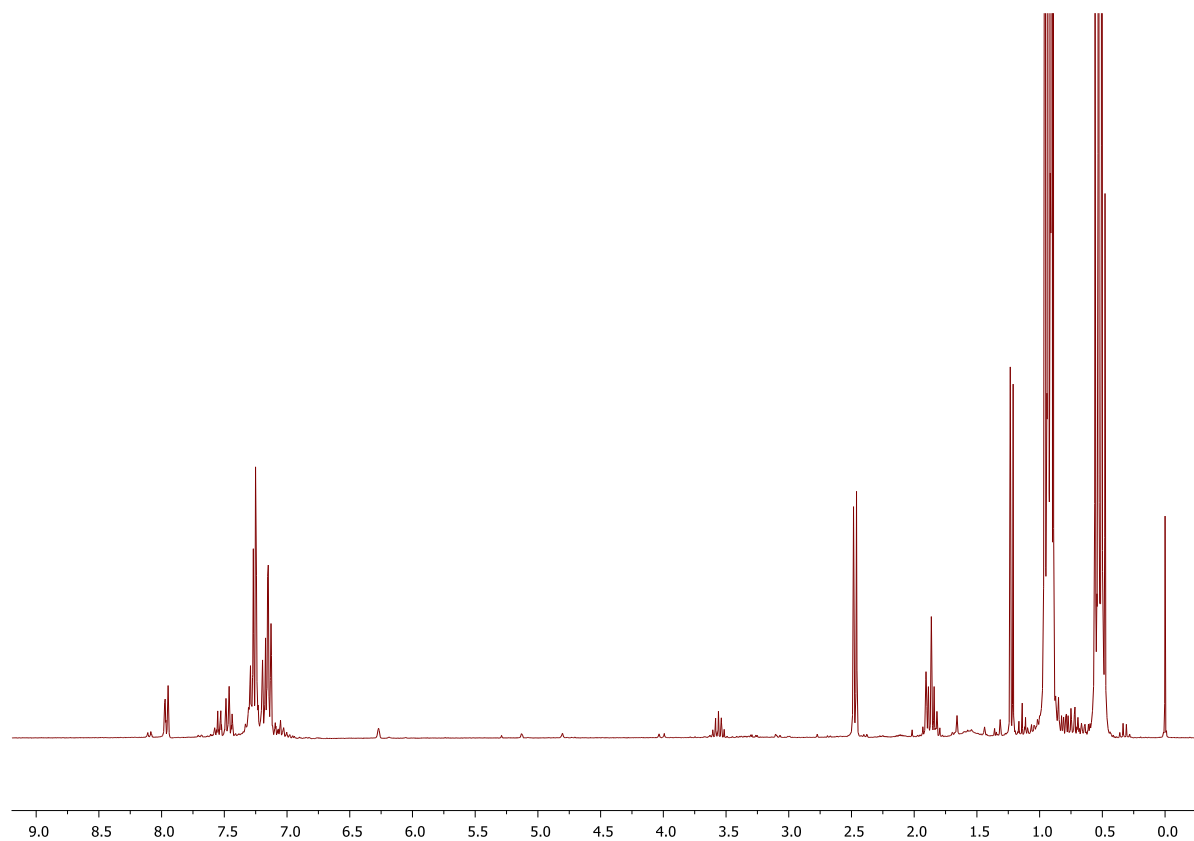


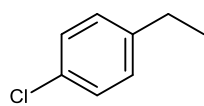
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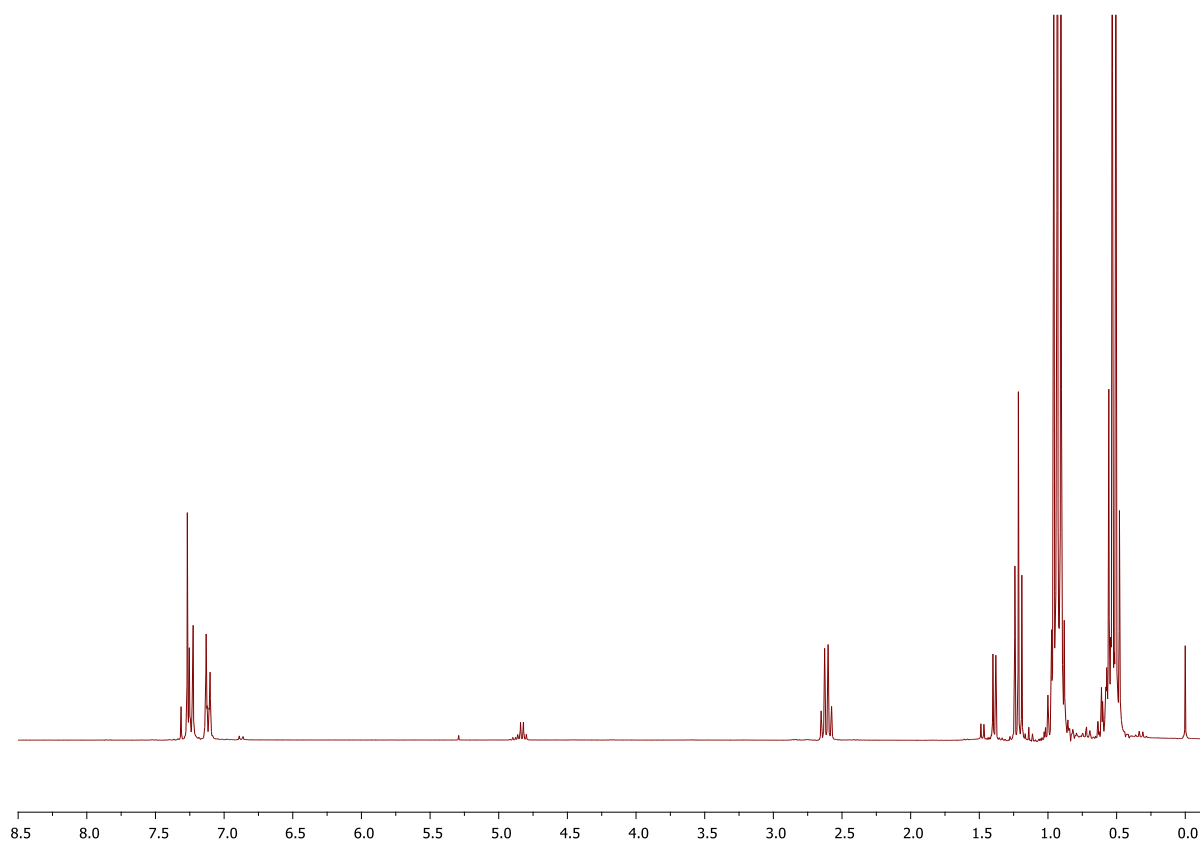


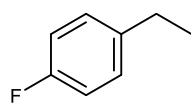
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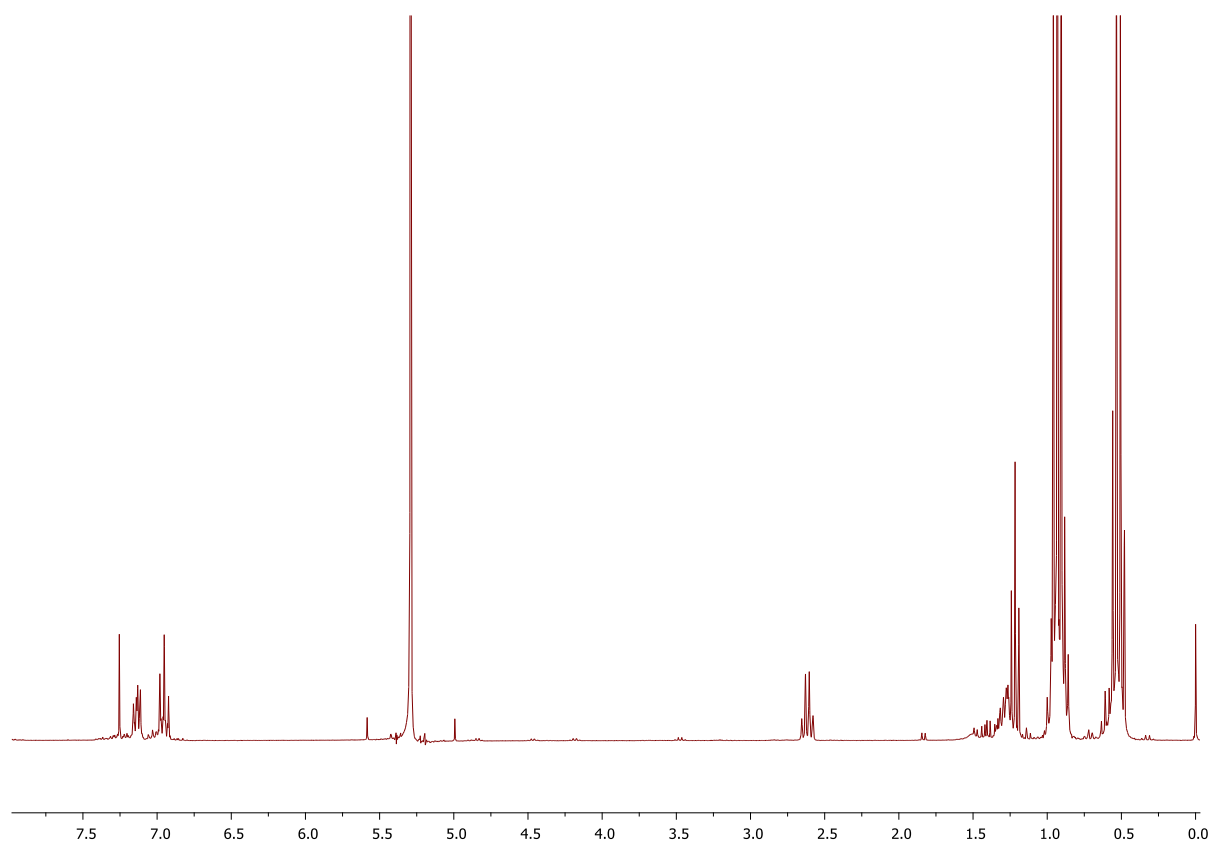


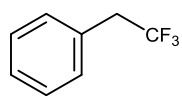
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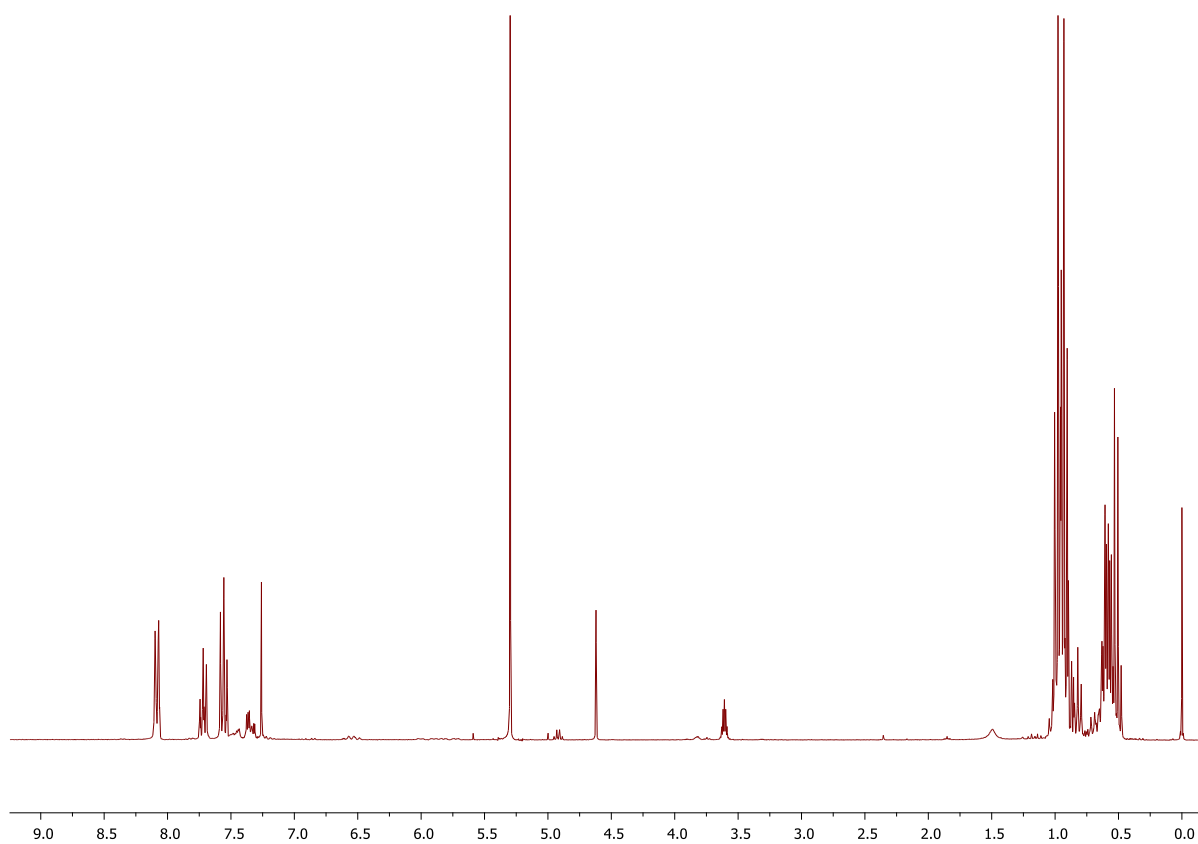


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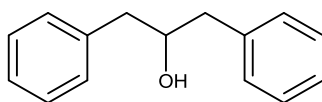


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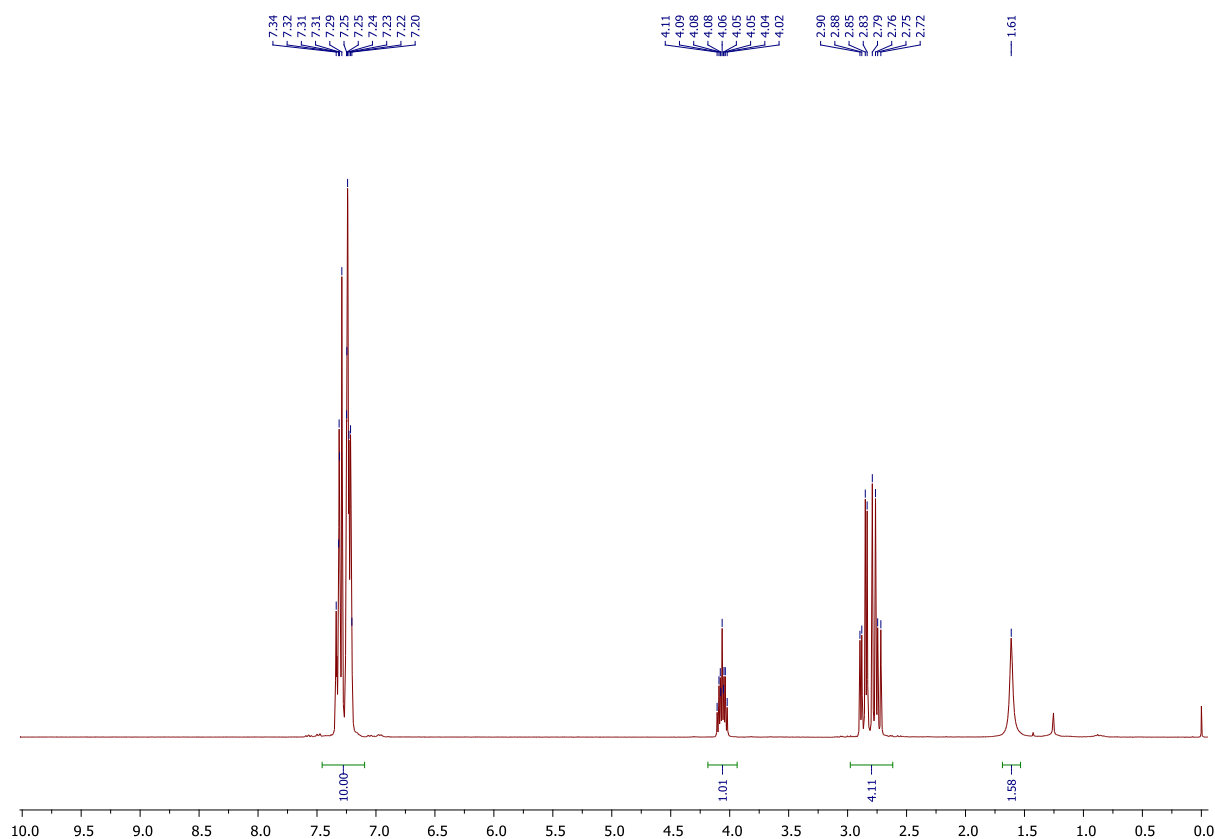


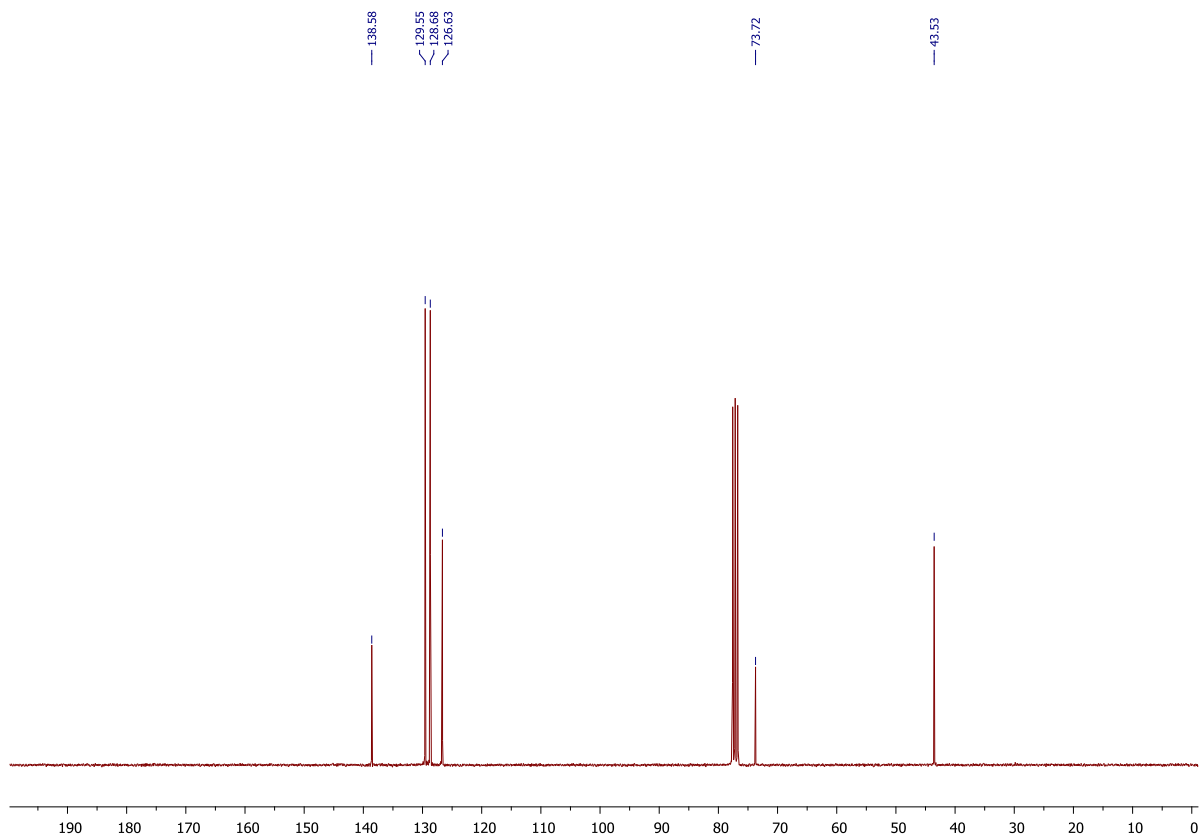
## V Hydrosilylation of compounds 1v and 1w

**1,3-Diphenylpropan-2-ol (2v).** In a round-bottom flask under argon, ketone **1v** (210 mg, 1 mmol) and the catalyst (3.9 mg, 0.01 mmol) were dissolved in DCM (3 mL). After addition of  $\text{HSiEt}_3$  (0.32 mL, 2 mmol) at 0 °C, the reaction mixture was slowly warmed to RT and stirred for 24 h. Aqueous NaOH (1 M, 5 mL) was added and the reaction was stirred for 2 h. The reaction medium was quenched with aqueous HCl (2 M, 5 mL) and extracted with DCM. The combined organic layers were washed with water and dried over anhydrous  $\text{MgSO}_4$ . After filtration, the volatile material was evaporated and the residue was purified by silica gel column chromatography eluting with Cyclohexane/ $\text{Et}_2\text{O}$  (3/1) to afford **2v** as a colorless oil (176 mg, 83% yield).

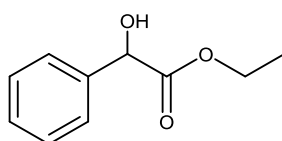


**2v**





**Ethyl mandelate (2w).** In a round-bottom flask under argon, ketone **1w** (160  $\mu$ L, 1 mmol) and the catalyst (3.9 mg, 0.01 mmol) were dissolved in DCM (3 mL). After addition of  $\text{HSiEt}_3$  (0.32 mL, 2 mmol) at 0  $^{\circ}\text{C}$ , the reaction mixture was slowly warmed to RT and stirred for 24 h. Aqueous NaOH (1 M, 5 mL) was added and the reaction was stirred for 2 h. The reaction medium was quenched with aqueous HCl (2 M, 5 mL) and extracted with DCM. The combined organic layers were washed with water and dried over anhydrous  $\text{MgSO}_4$ . After filtration, the volatile material was evaporated. Despite repeated attempts to purify **2w** by silica gel column chromatography, unseparable silylated by-products remained present in the sample.



**2w**

