

***Supporting information for***

**Cobalt-Copper Dual Light-Driven  
Catalytic Reduction of Aldehydes and  
Aromatic Ketones in Aqueous Media**

Arnau Call,<sup>[a]</sup> Carla Casadevall,<sup>[a]</sup> Ferran Acuña-Parés,<sup>[a]</sup> Alicia Casitas,<sup>[a]</sup> and  
Julio Lloret-Fillo<sup>[a, b]\*</sup>

[a] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain.

[b] Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluïa Companys, 23, 08010, Barcelona (Spain).

Corresponding author: [jlloret@iciq.es](mailto:jlloret@iciq.es)

***SI.2. NMR spectra and GC chromatograms of the substrates and products***

## **Table of Contents**

1. $^1\text{H}$ - NMR spectra of the cobalt complexes .....	3
2. Experimental NMR data of the synthesised substrates .....	6
3. $^1\text{H}$ - NMR spectra of isolated alcohols .....	8
4. NMR of the deuterated products .....	41
5. Intramolecular reduction .....	49
6. NMR of the radical clock ring-opening products .....	58
7. GC chromatograms from the catalysis .....	61
8. Selected chromatograms of the selectivity studies .....	72

## 1. <sup>1</sup>H-NMR spectra of the cobalt complexes

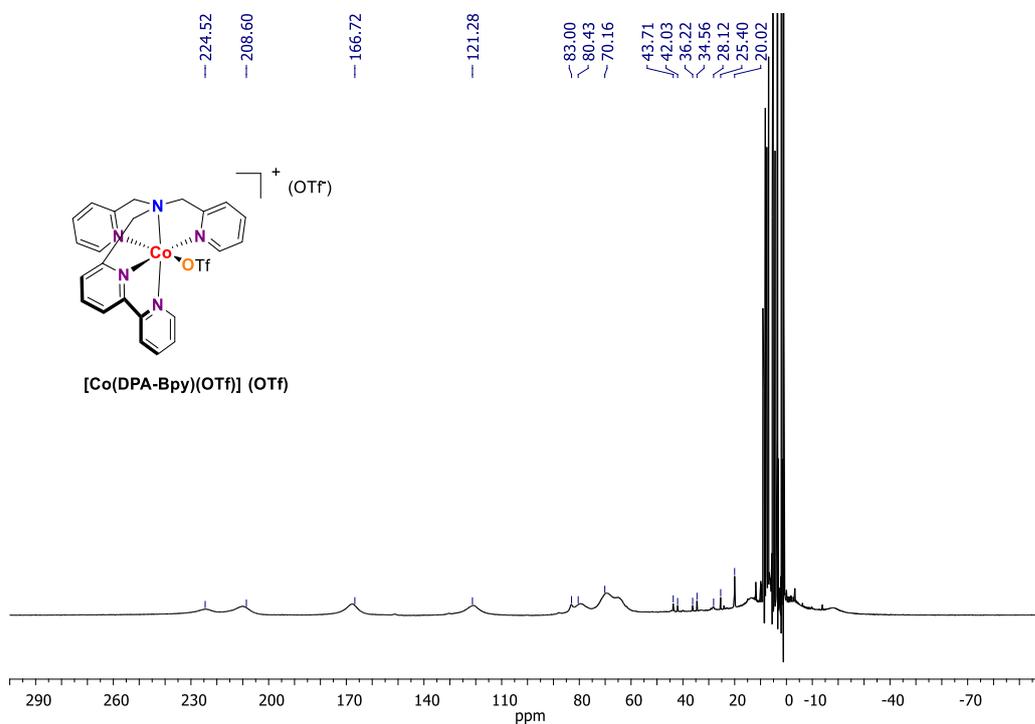


Figure SI.2.1. <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 400 MHz, 260 K) spectrum of [Co(OTf)(DPA-Bpy)](OTf).

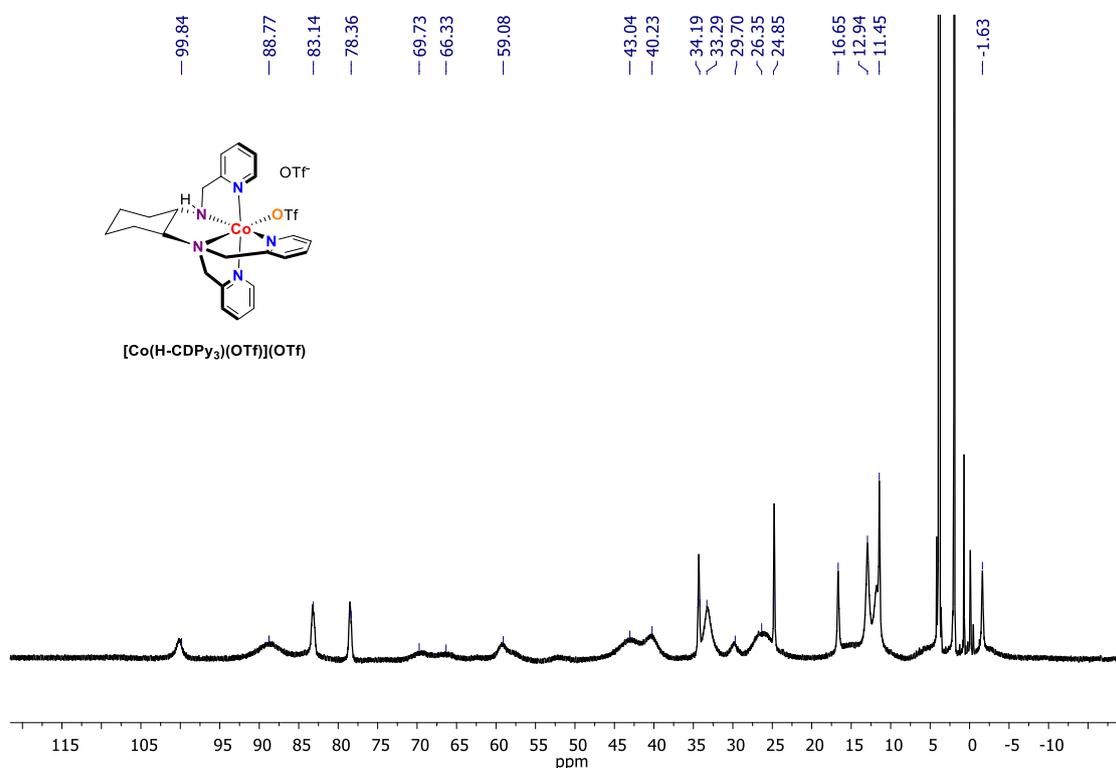


Figure SI.2.2. <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 500 MHz, 260 K) spectrum of [Co(OTf)(H-CDPy<sub>3</sub>)](OTf).

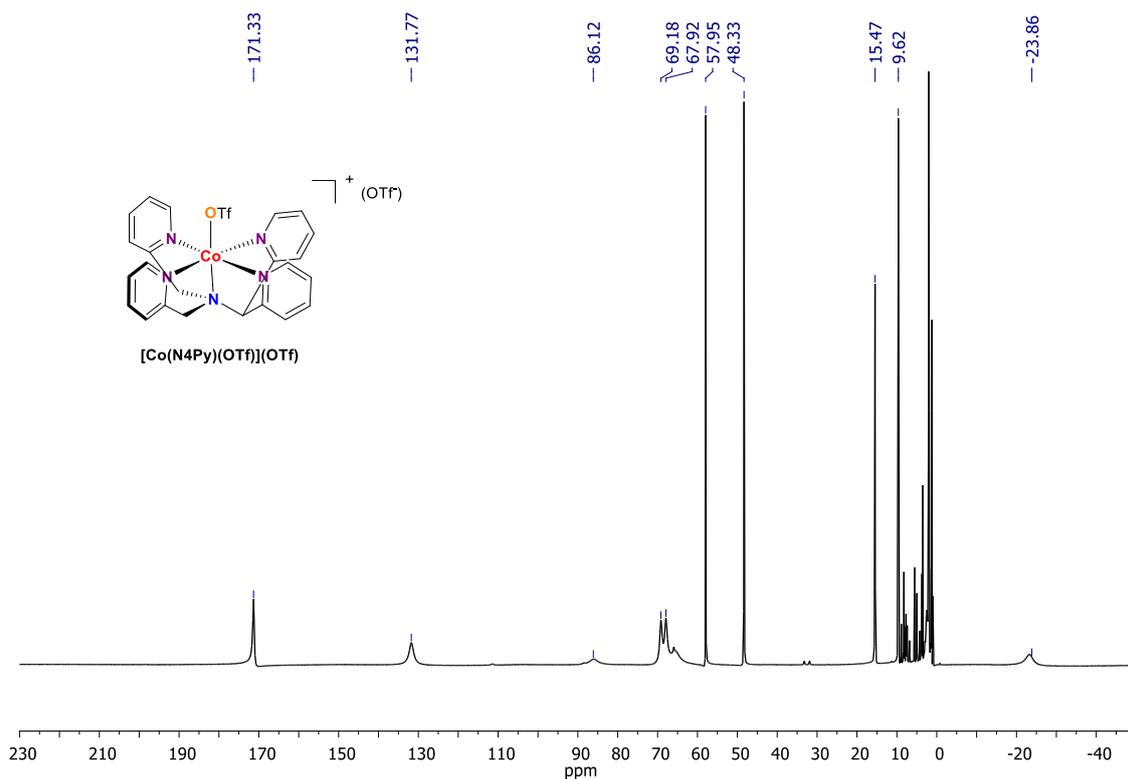


Figure SI.2.3.  $^1\text{H-NMR}$  (CD<sub>3</sub>CN, 400 MHz, 260 K) spectrum of **[Co(OTf)(N4Py)](OTf)**.

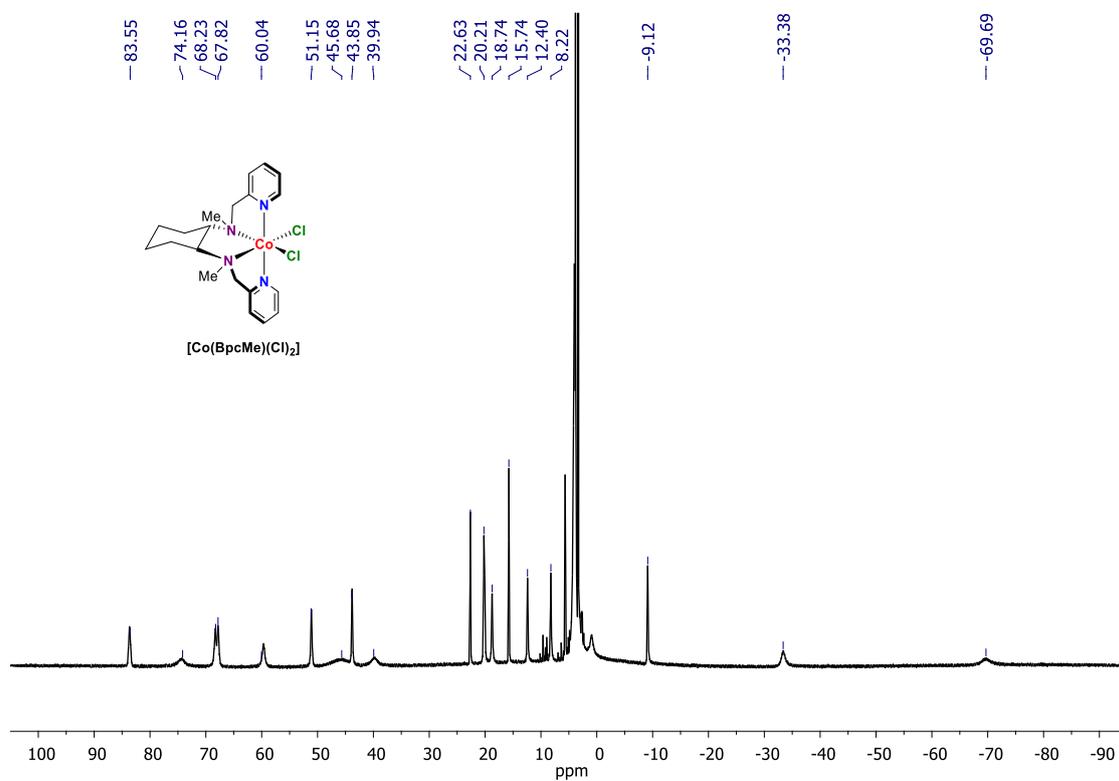


Figure SI.2.4.  $^1\text{H-NMR}$  (CD<sub>3</sub>CN, 500 MHz, 260 K) spectrum of **[Co(BpcMe)Cl<sub>2</sub>]**.

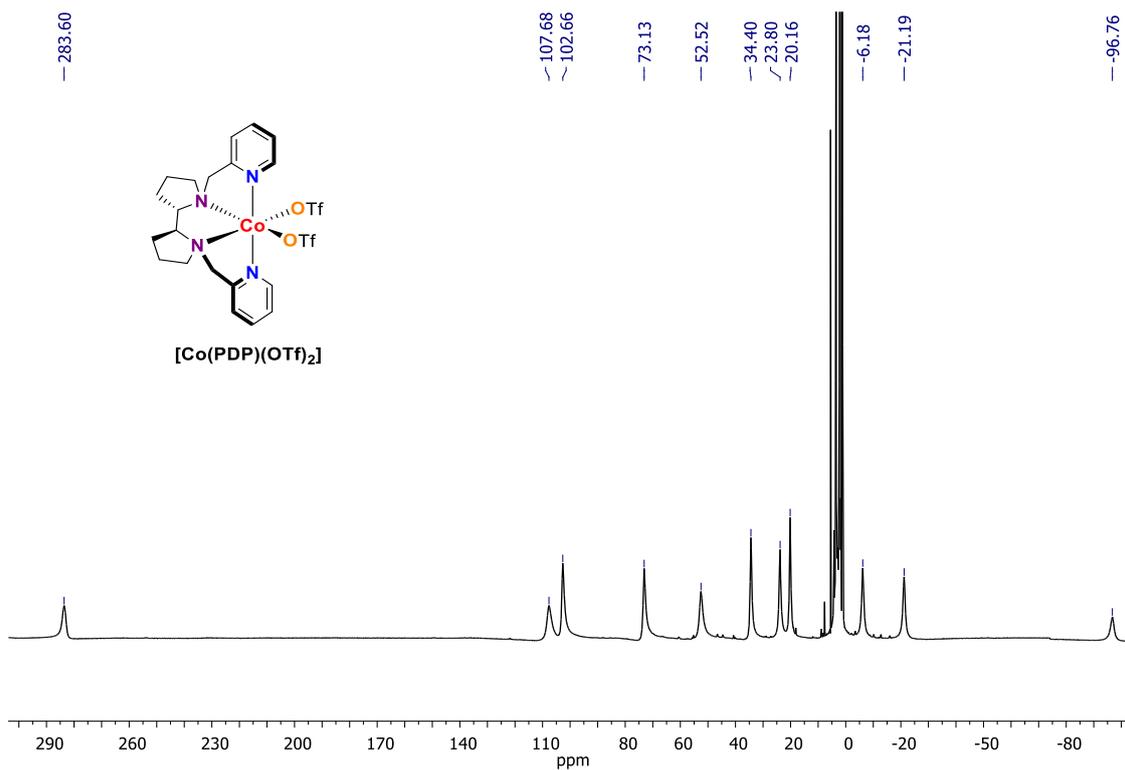


Figure SI.2.5.  $^1\text{H-NMR}$  ( $\text{CD}_3\text{CN}$ , 400 MHz, 260 K) spectrum of  $[\text{Co}((\text{S,S})\text{-PDP})(\text{OTf})_2]$ .

## 2. Experimental NMR data of the synthesised substrates

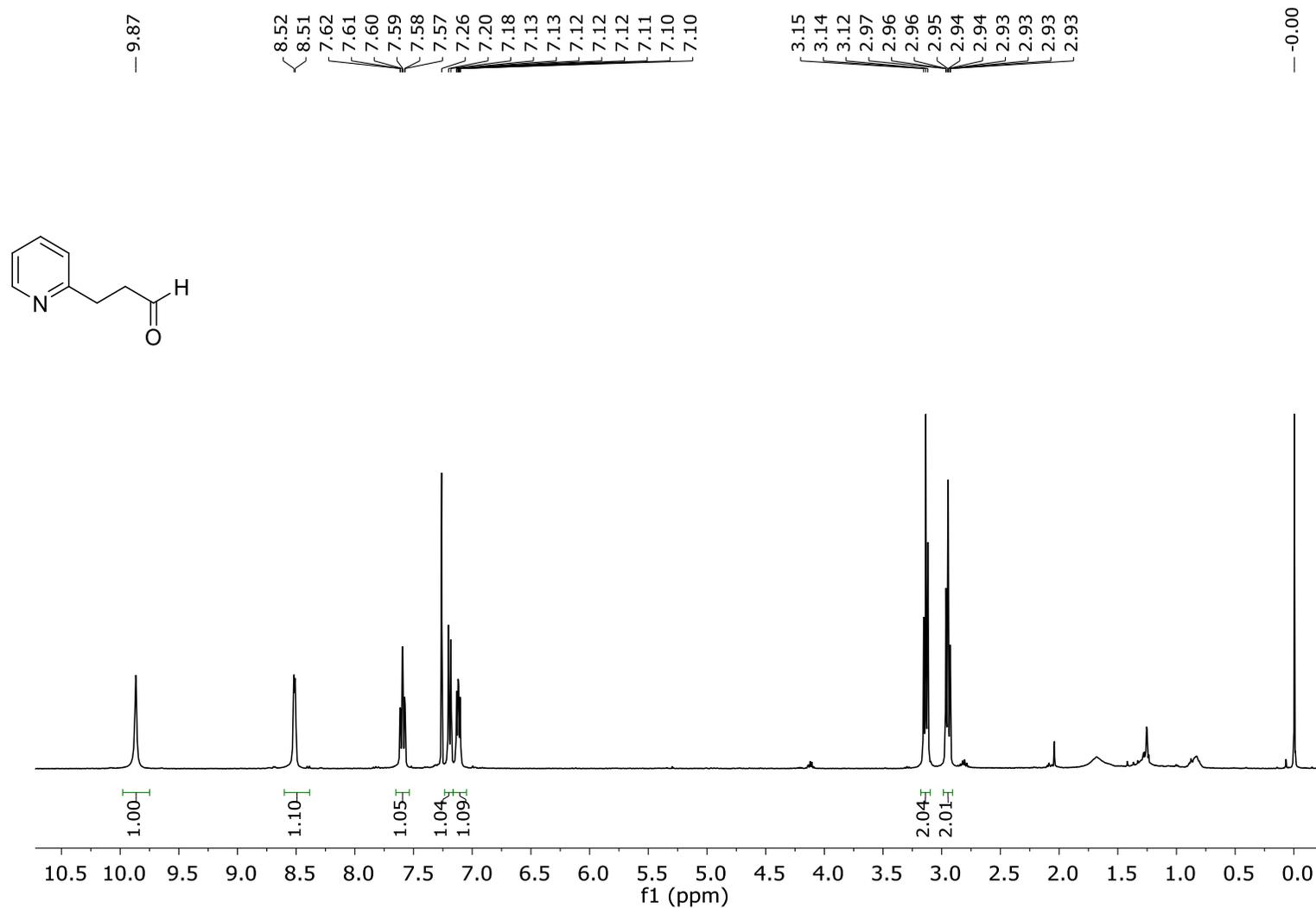


Figure SI.2.6.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, 300 K) spectrum of substrate 11f.

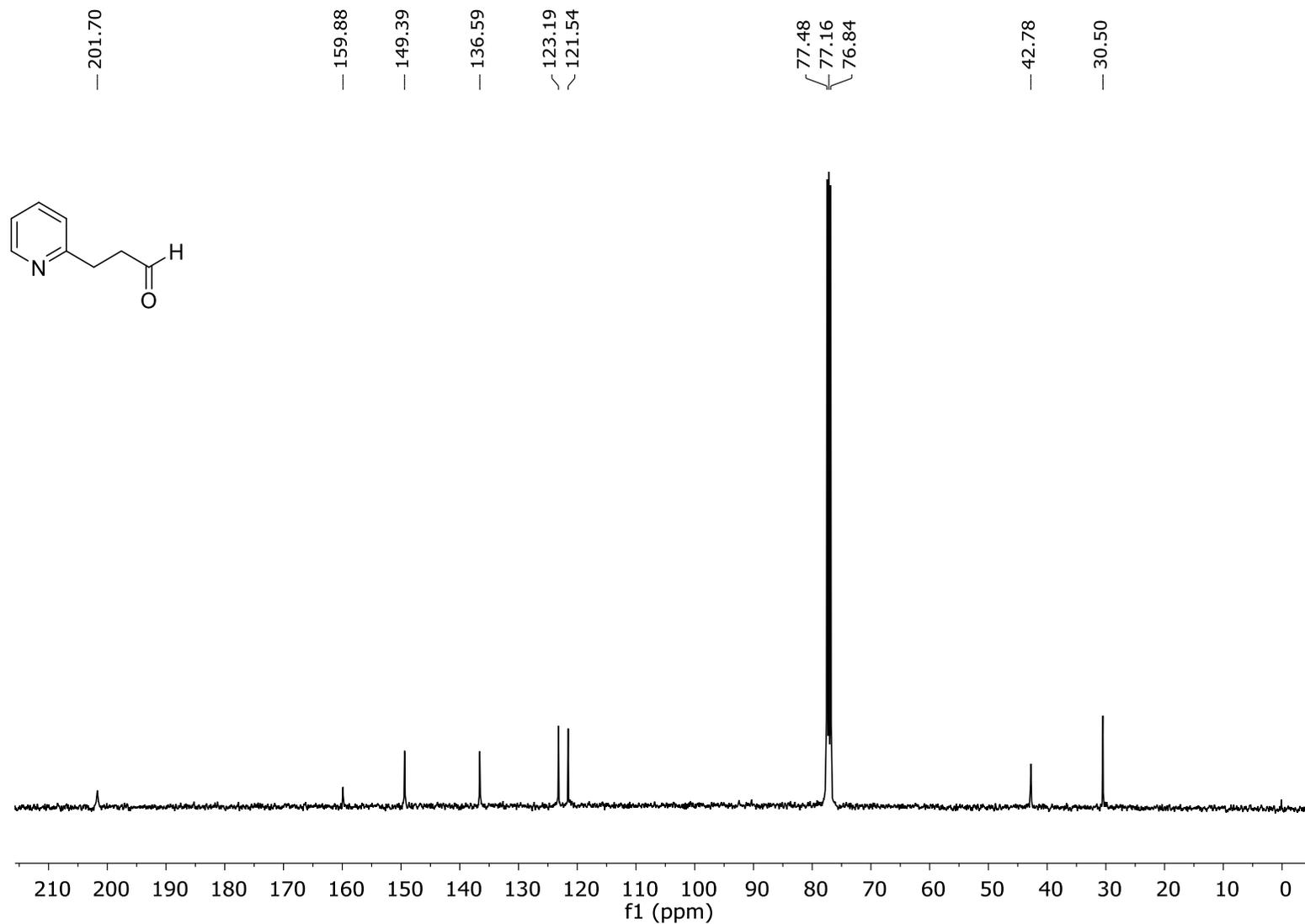


Figure S1.2.7.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 100.6 MHz, 300 K) spectrum of substrate 11f.

### 3. $^1\text{H}$ -NMR spectra of isolated alcohols

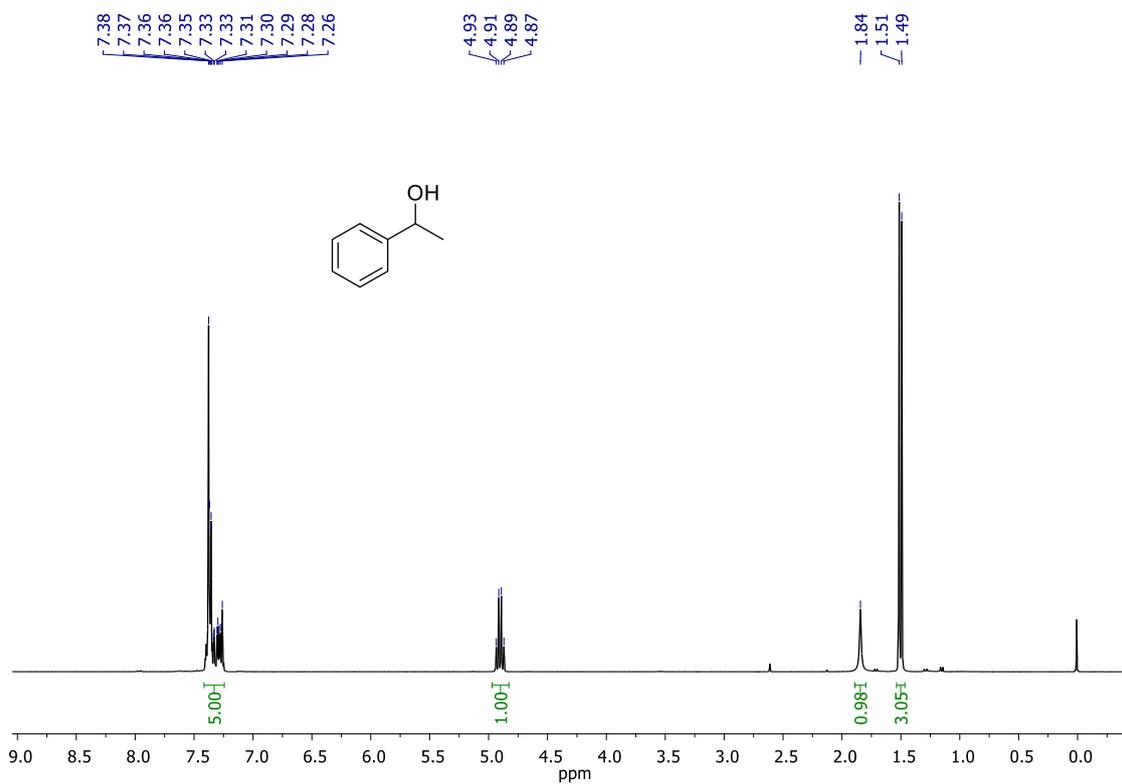


Figure SI.2.8.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product 10a.

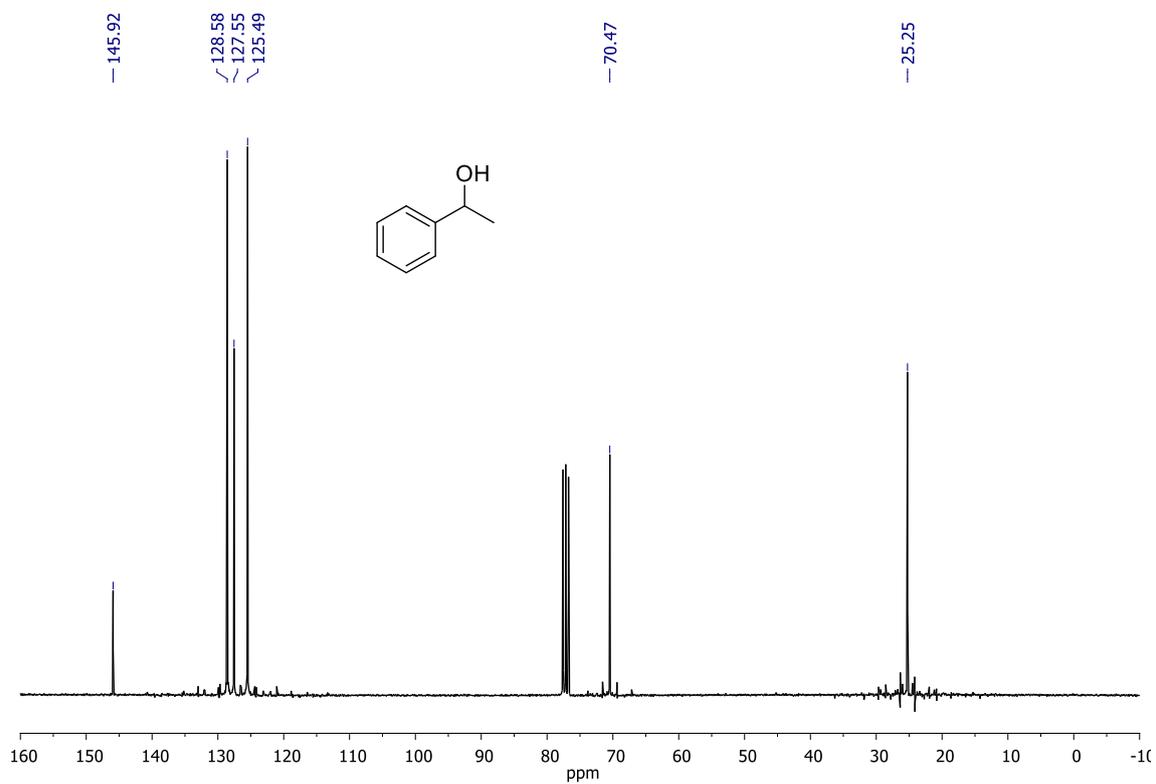


Figure SI.2.9.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product 10a.

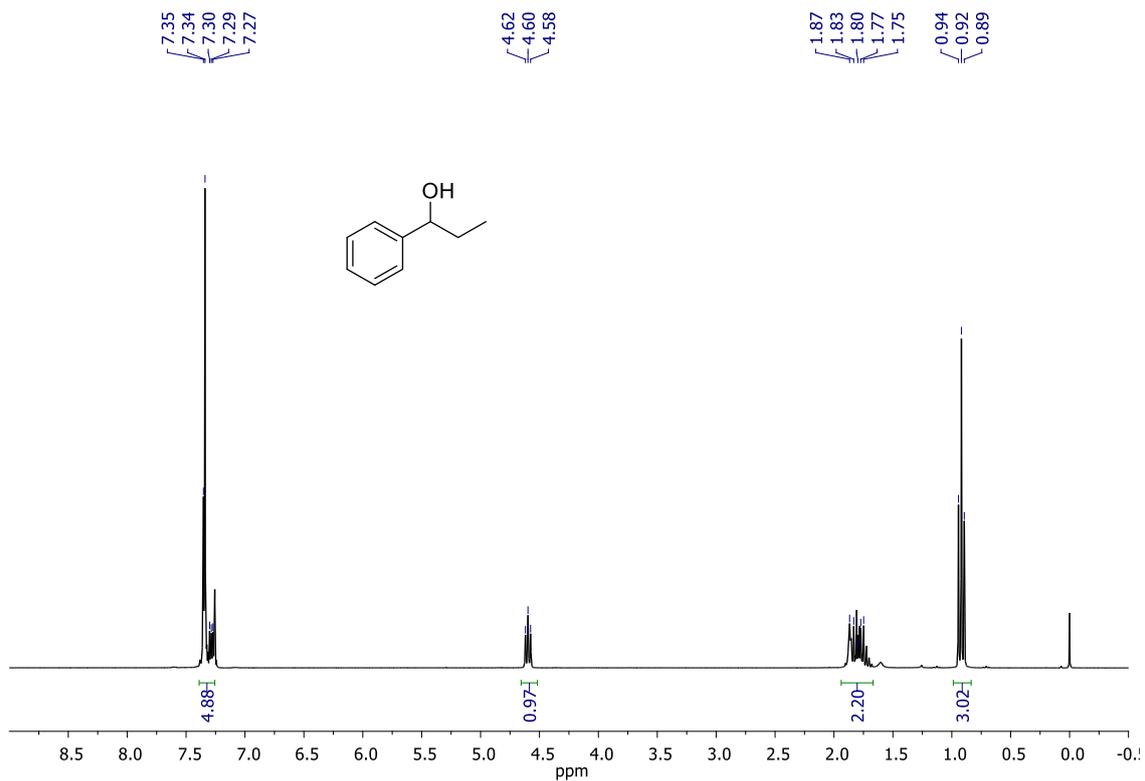


Figure SI.2.10.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10b**.

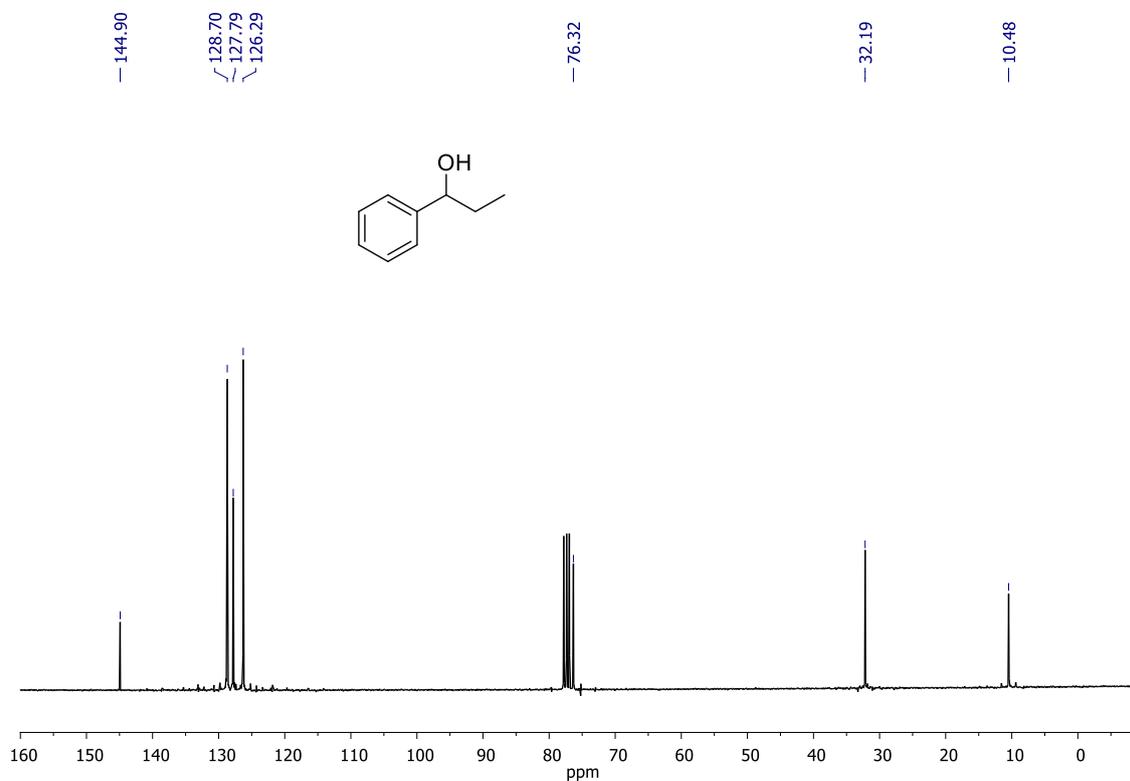


Figure SI.2.11.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **10b**.

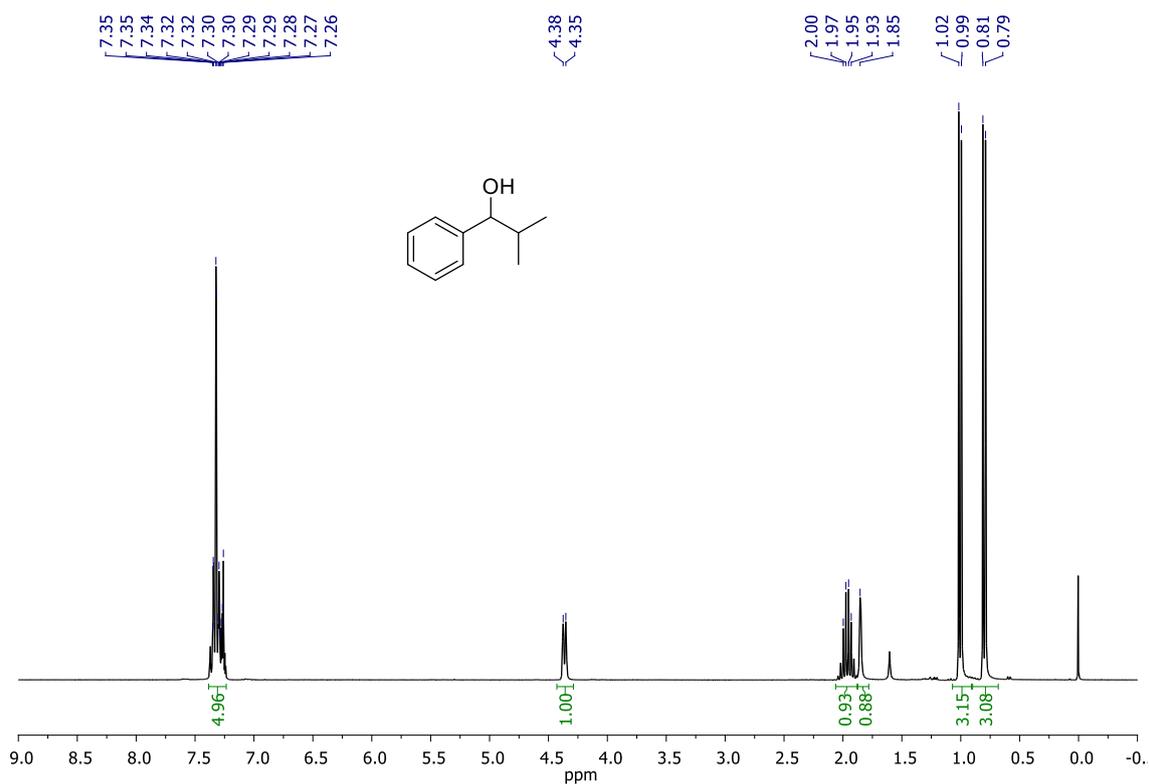


Figure SI.2.12.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10c**.

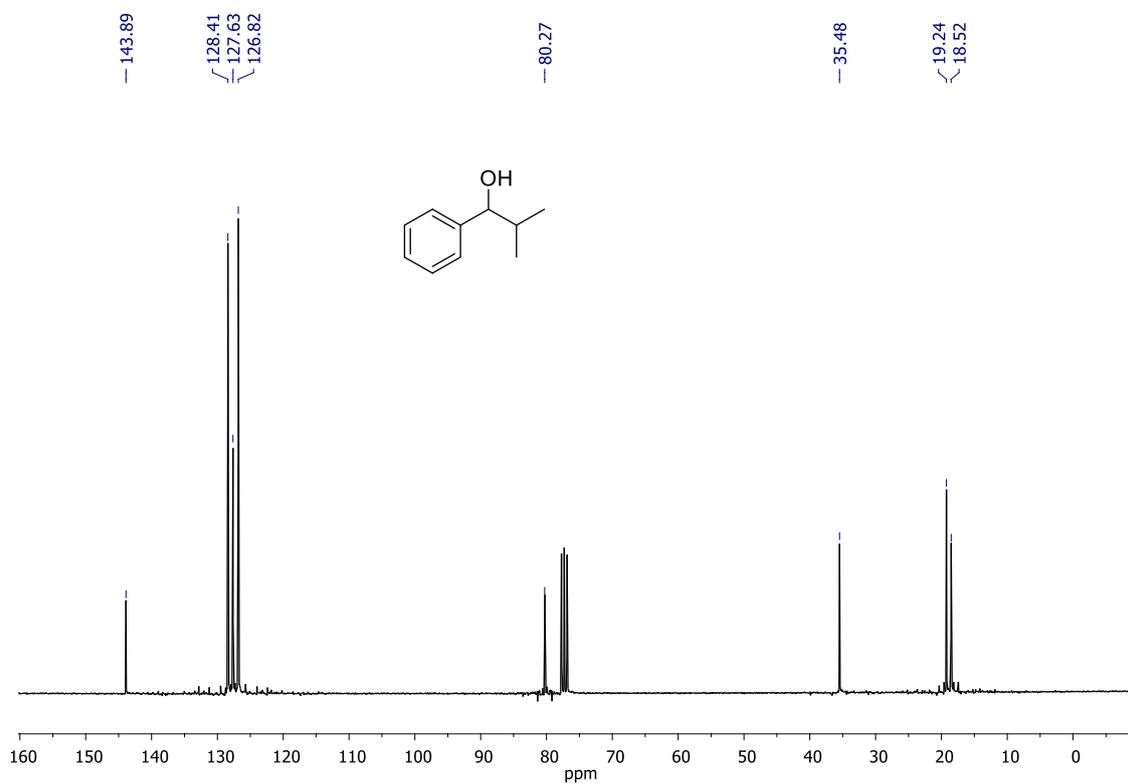


Figure SI.2.13.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **10c**.

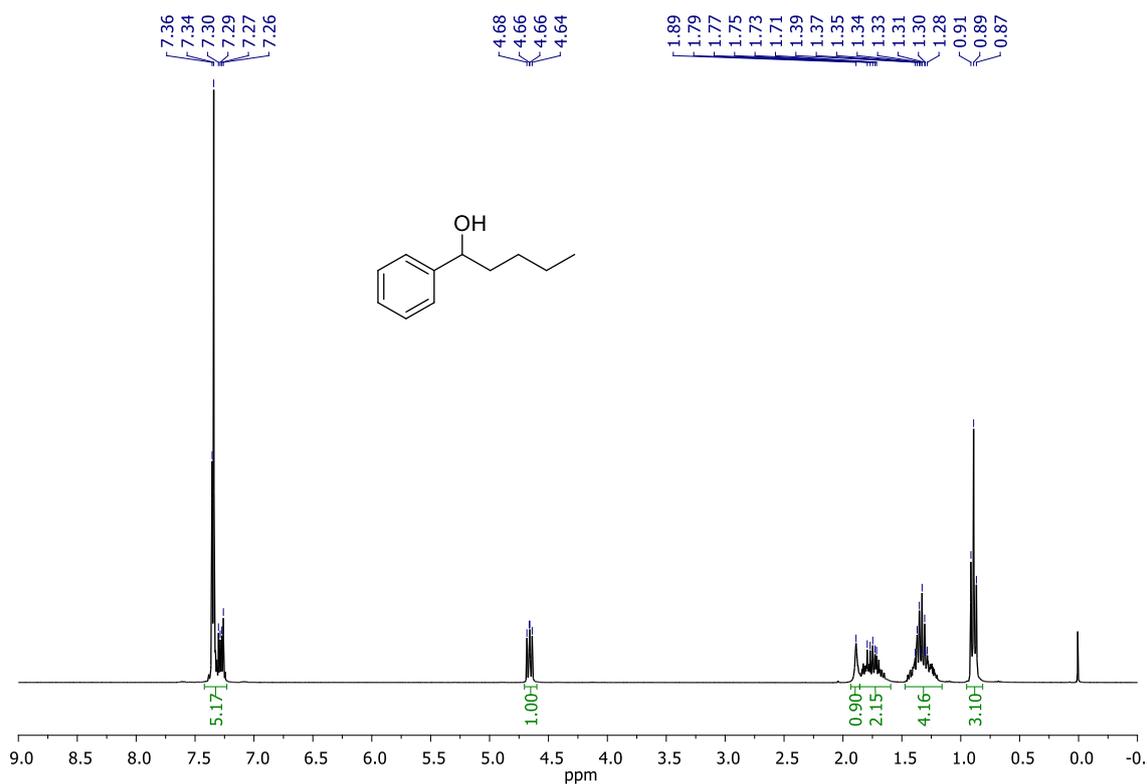


Figure SI.2.14.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10d**.

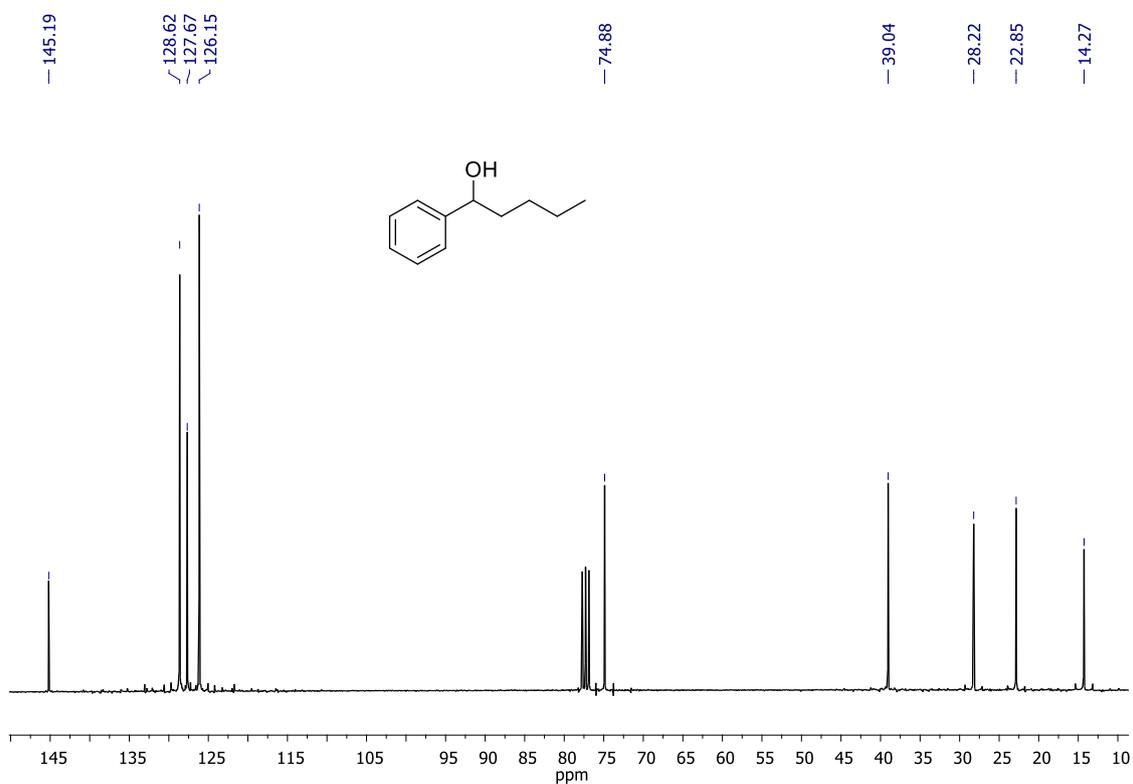
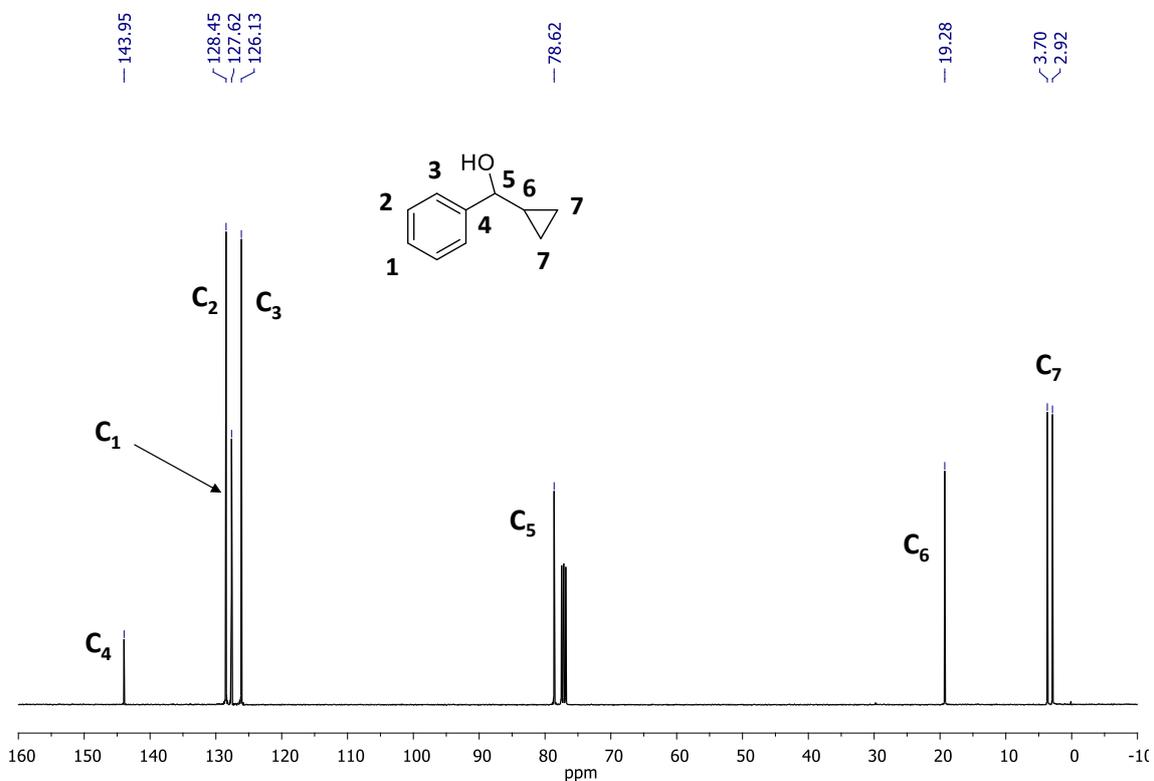
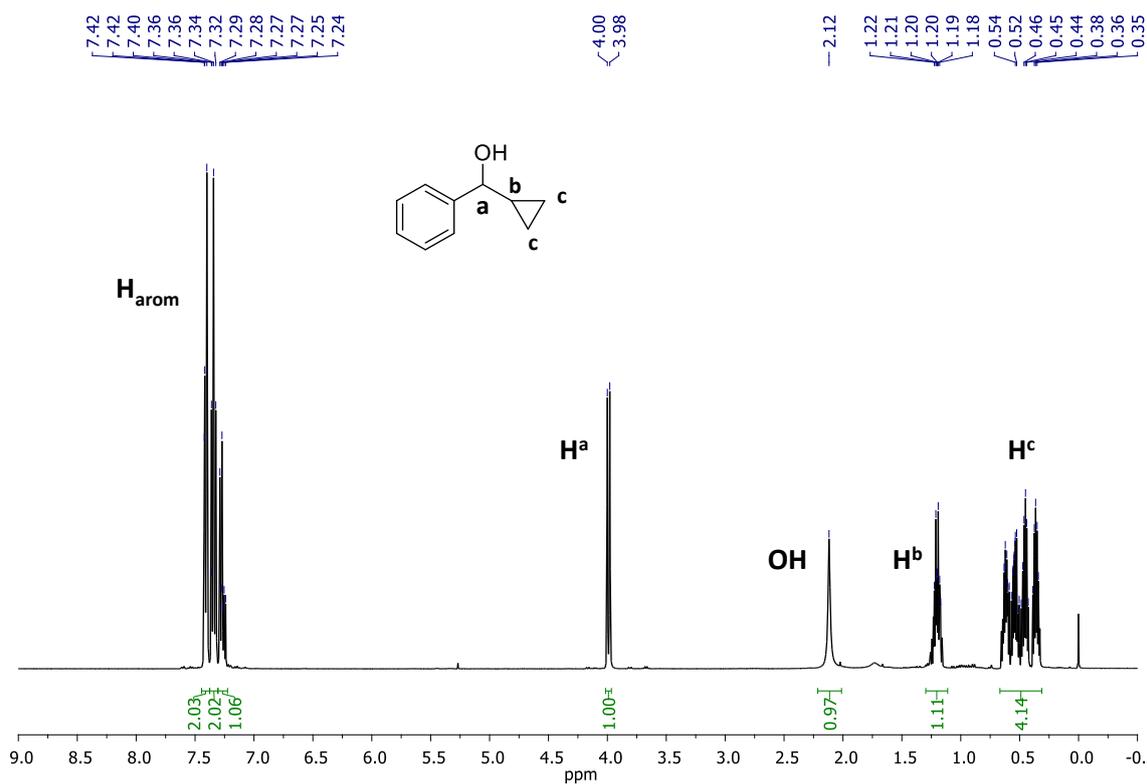
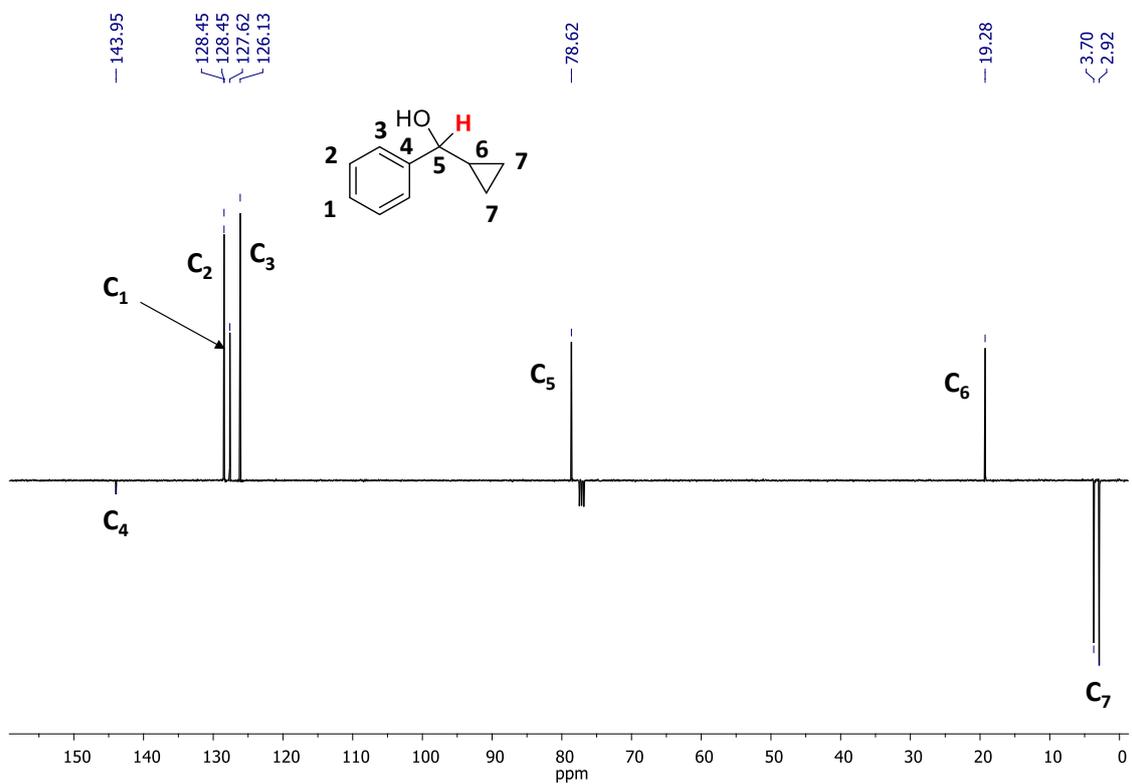
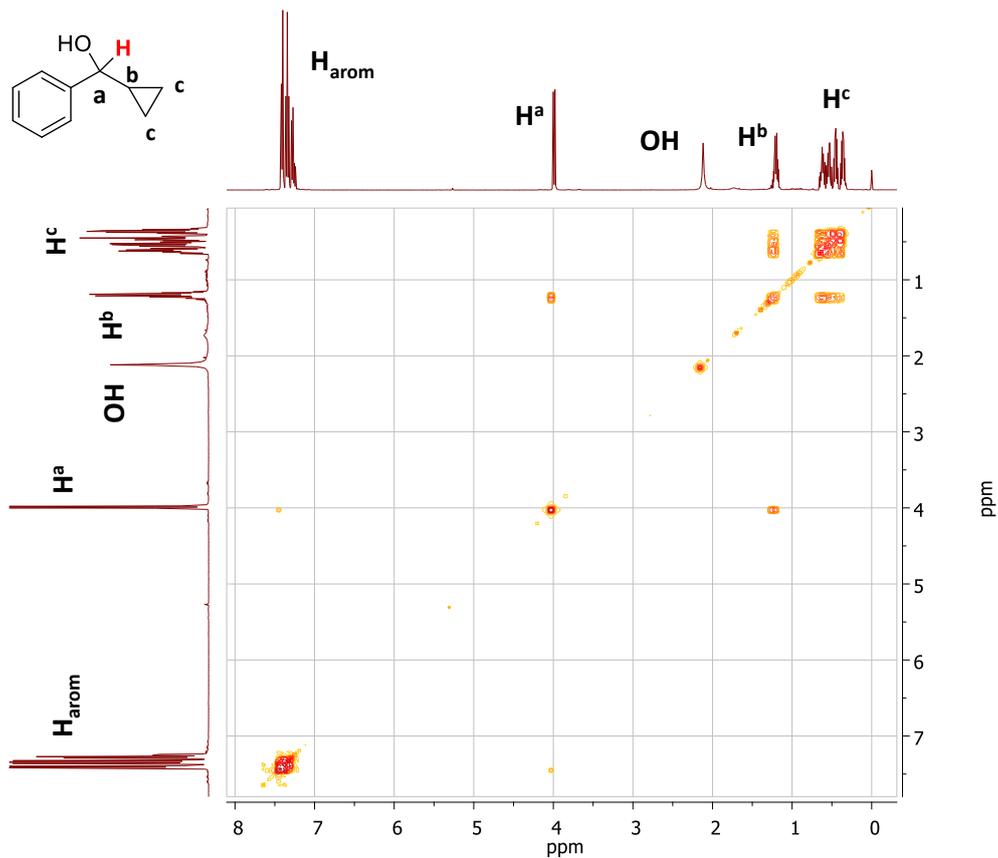


Figure SI.2.15.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **10d**.





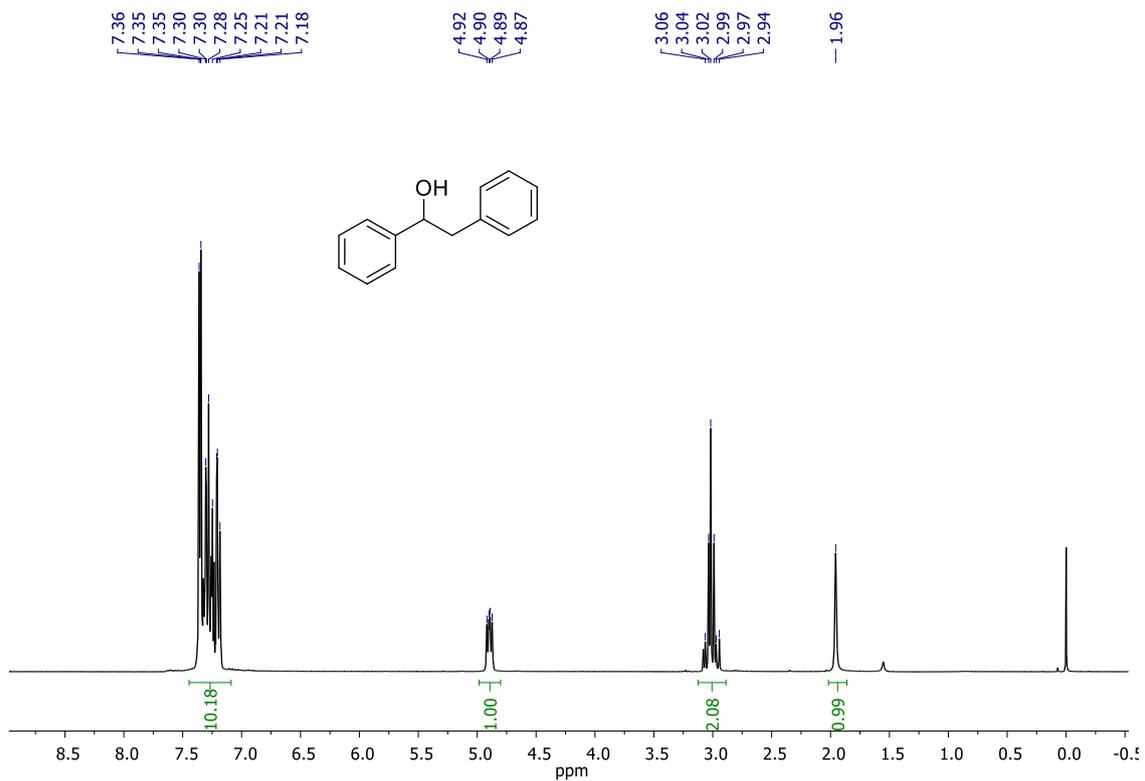


Figure SI.2.20.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10f**.

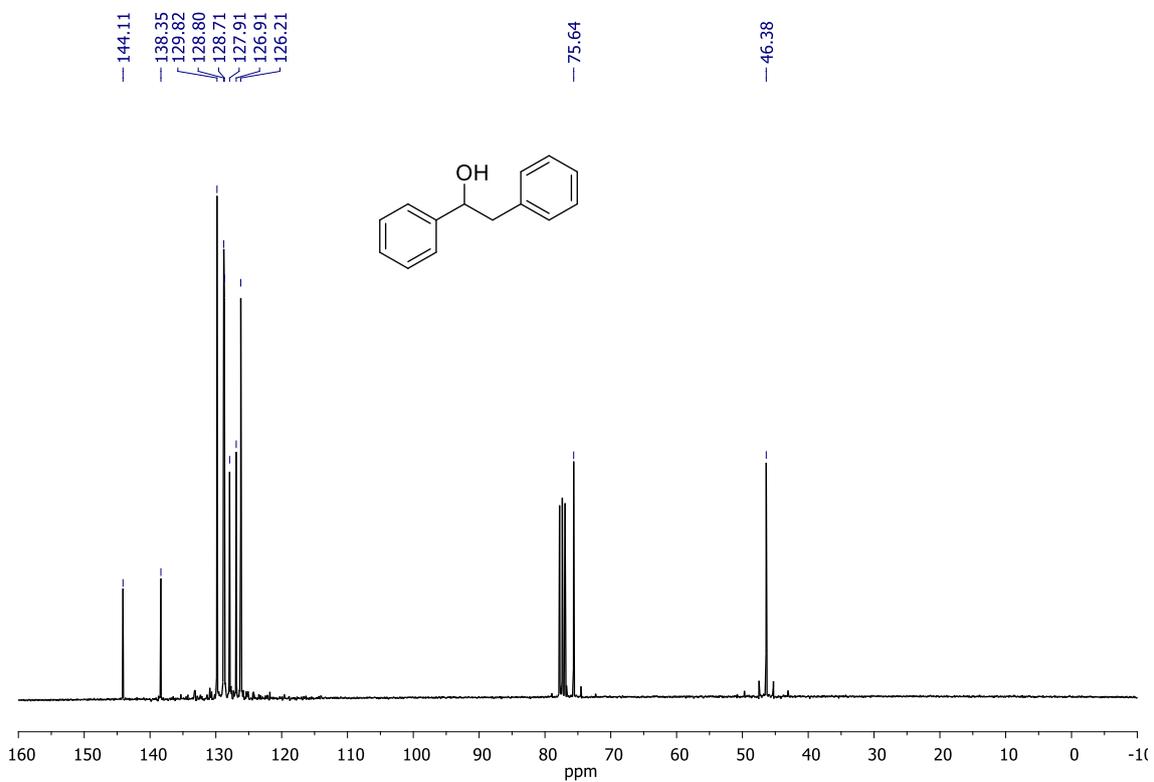


Figure SI.2.21.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **10f**.

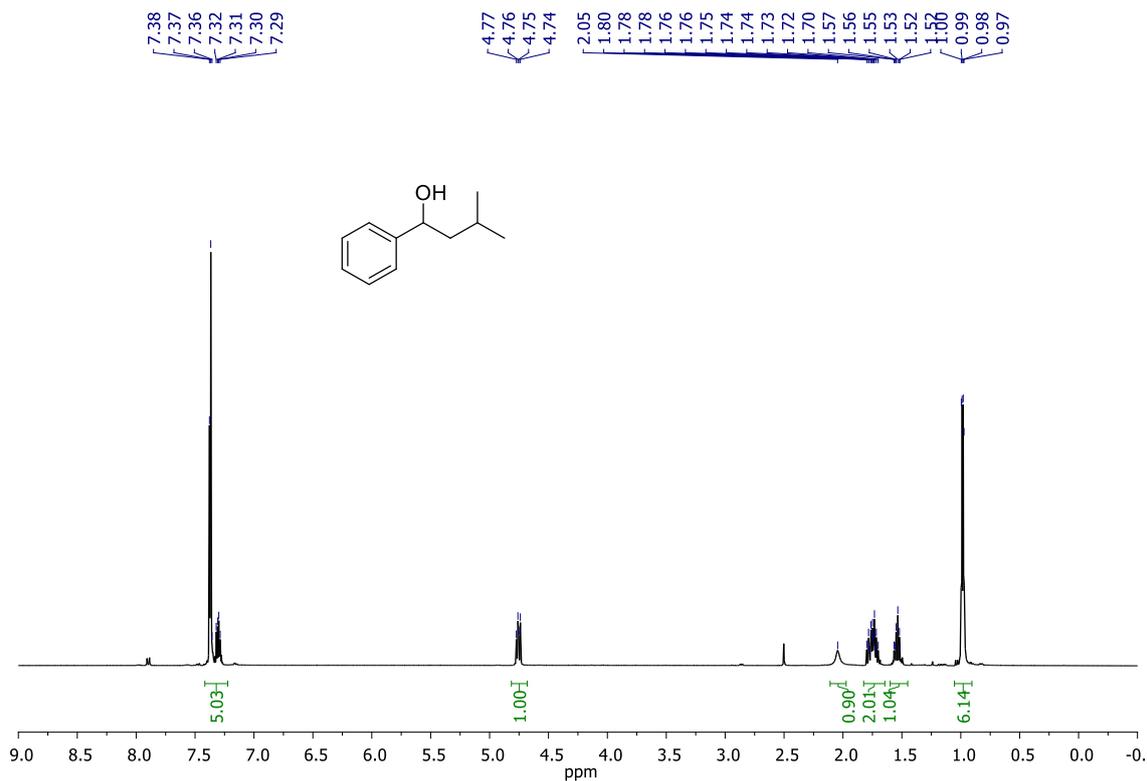


Figure SI.2.22. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **10g**.

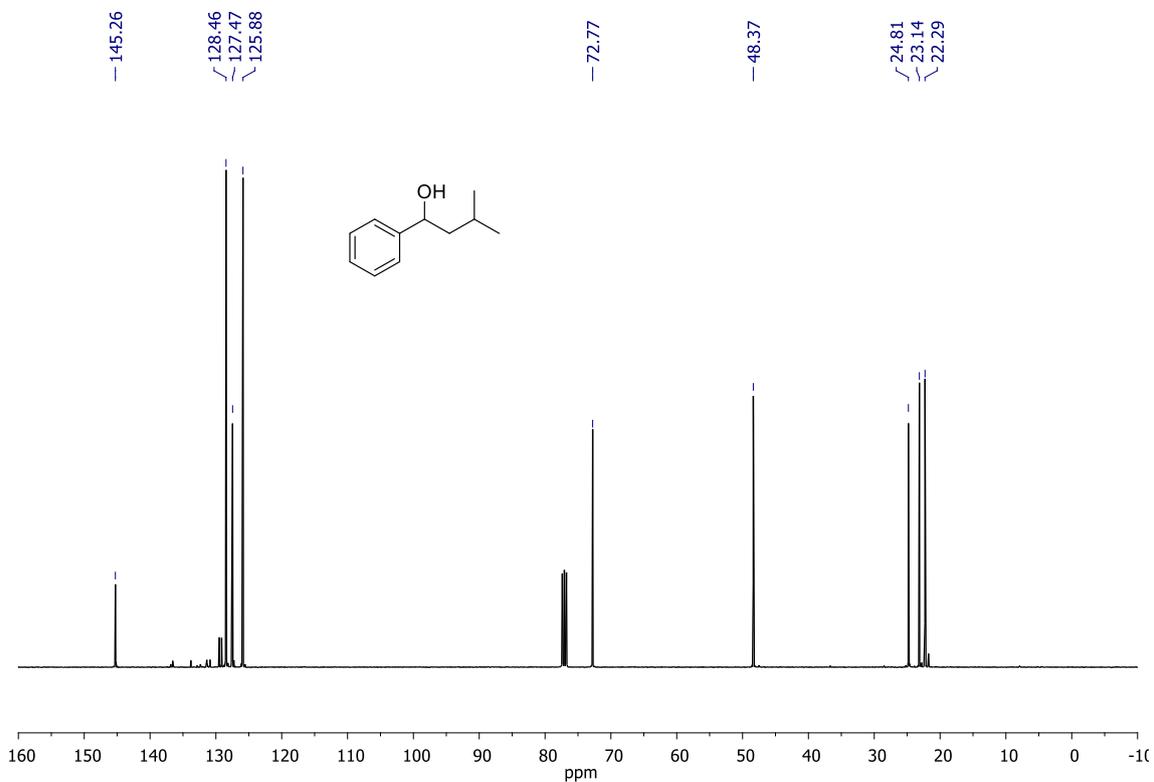


Figure SI.2.23. <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10g**.

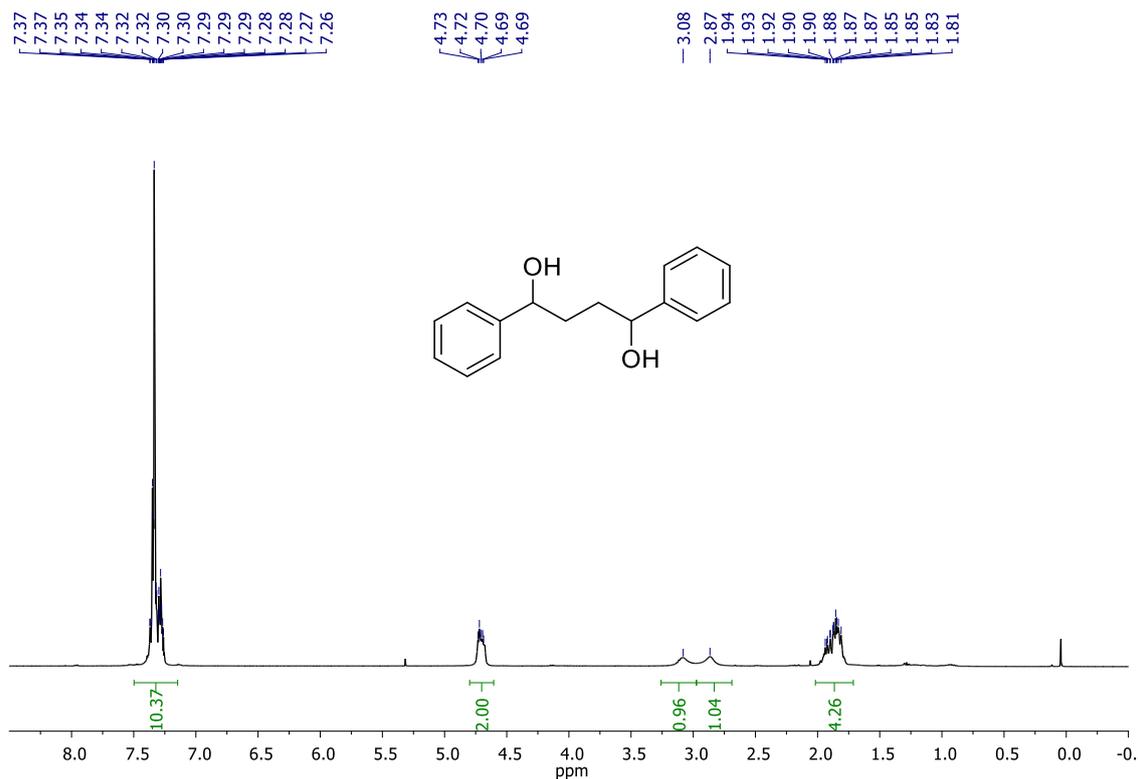


Figure SI.2.24. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **10i**.

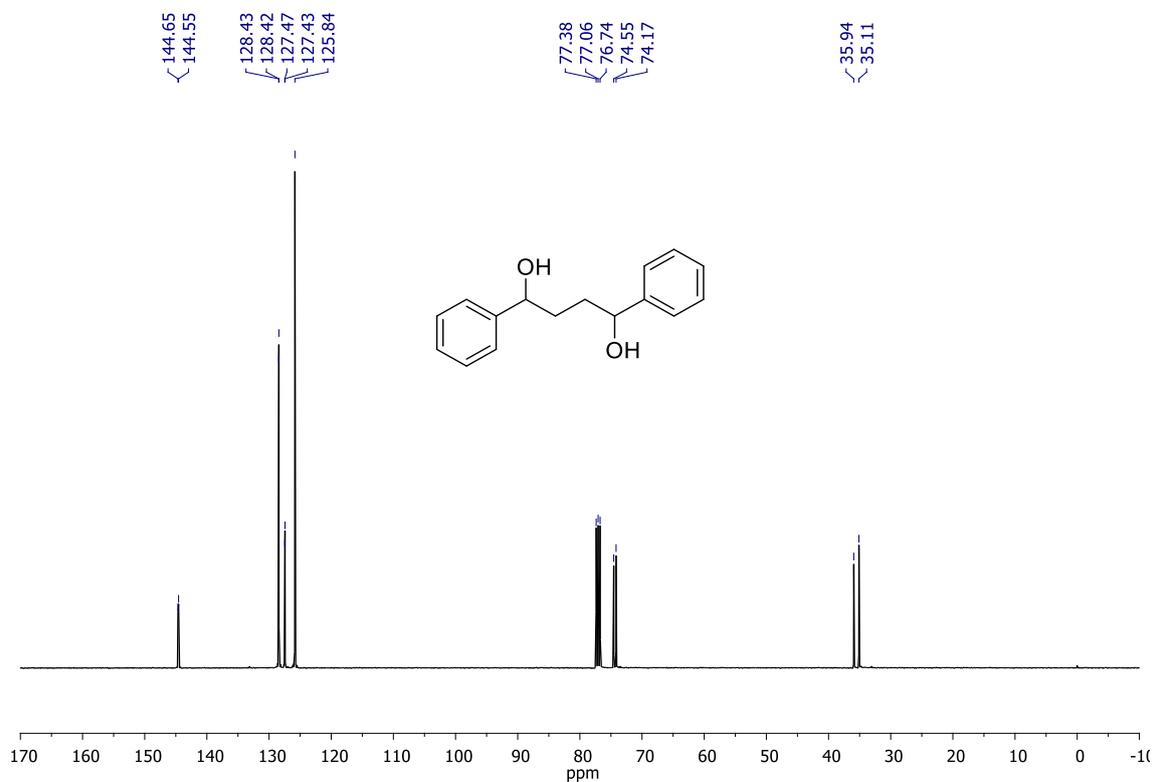


Figure SI.2.25. <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10i**.

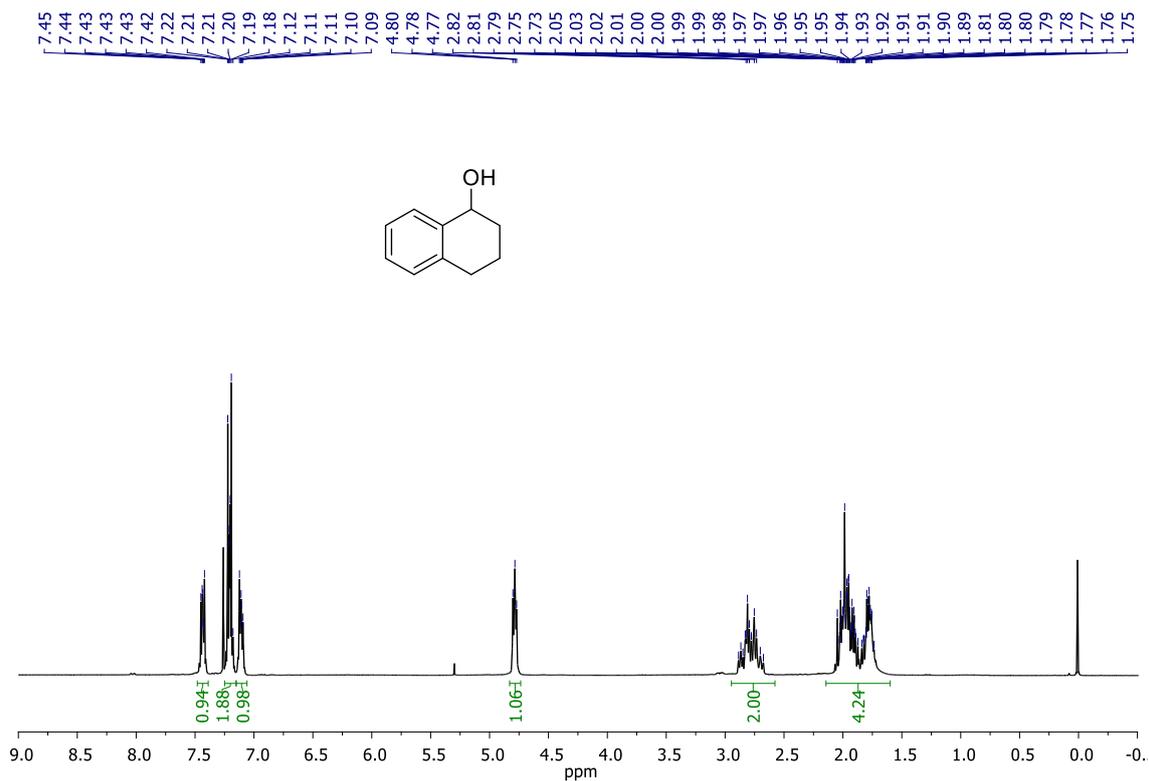


Figure SI.2.26.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product 10j.

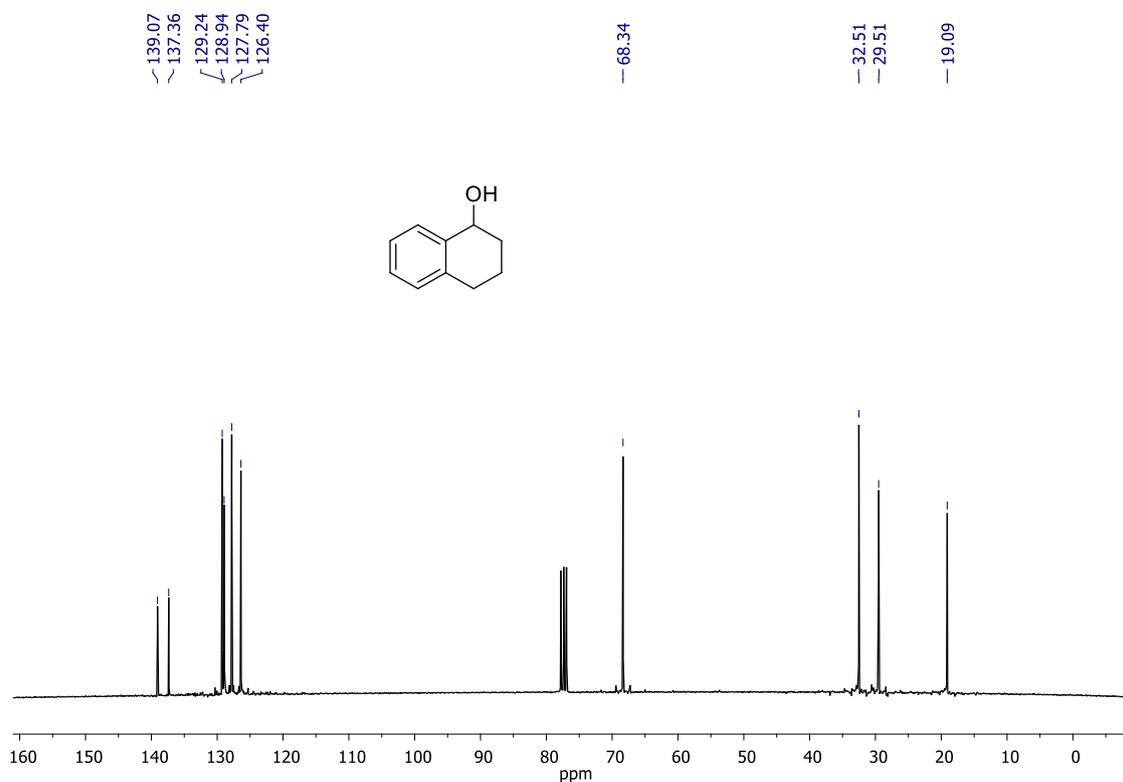


Figure SI.2.27.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product 10j.

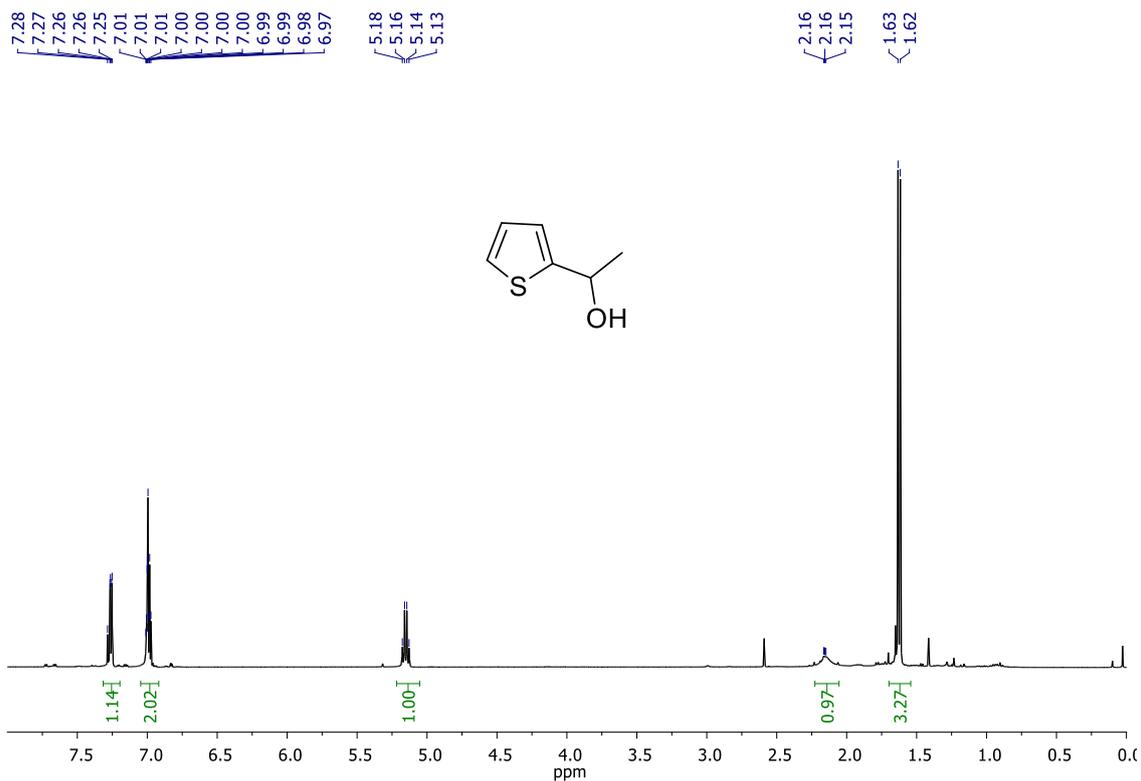


Figure SI.2.28. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **10k**.

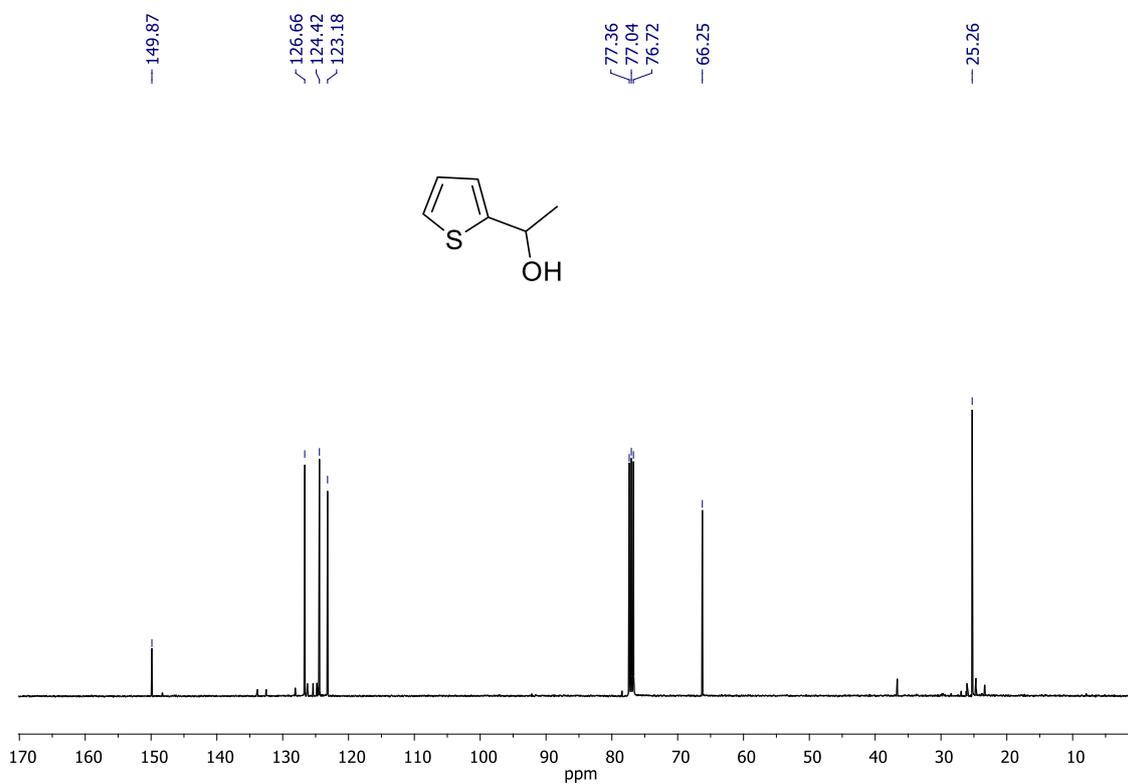


Figure SI.2.29. <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10k**.

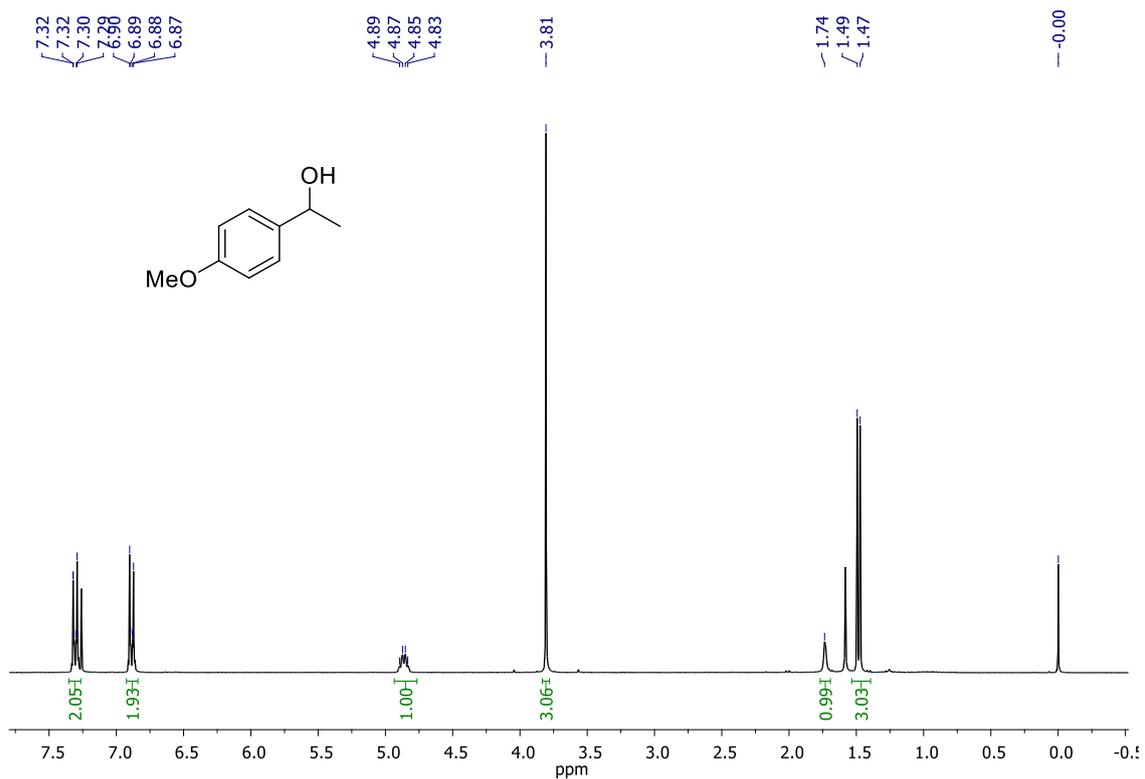


Figure SI.2.30.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10I**.

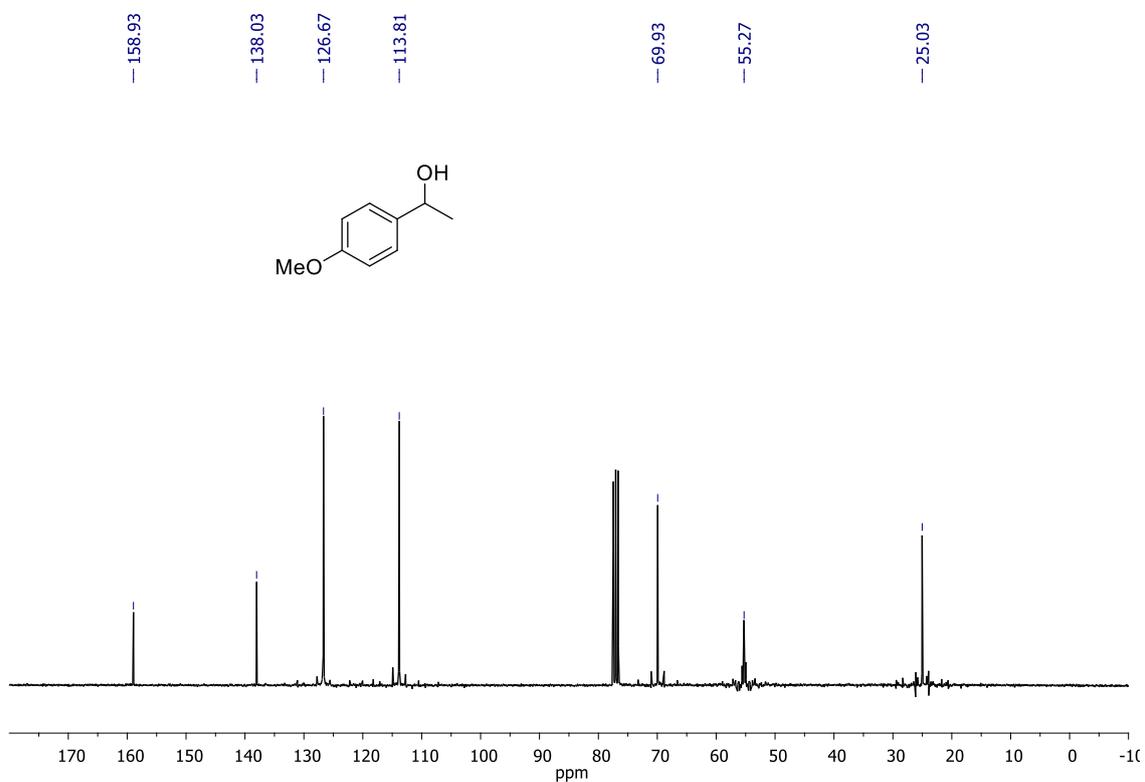


Figure SI.2.31.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **10I**.

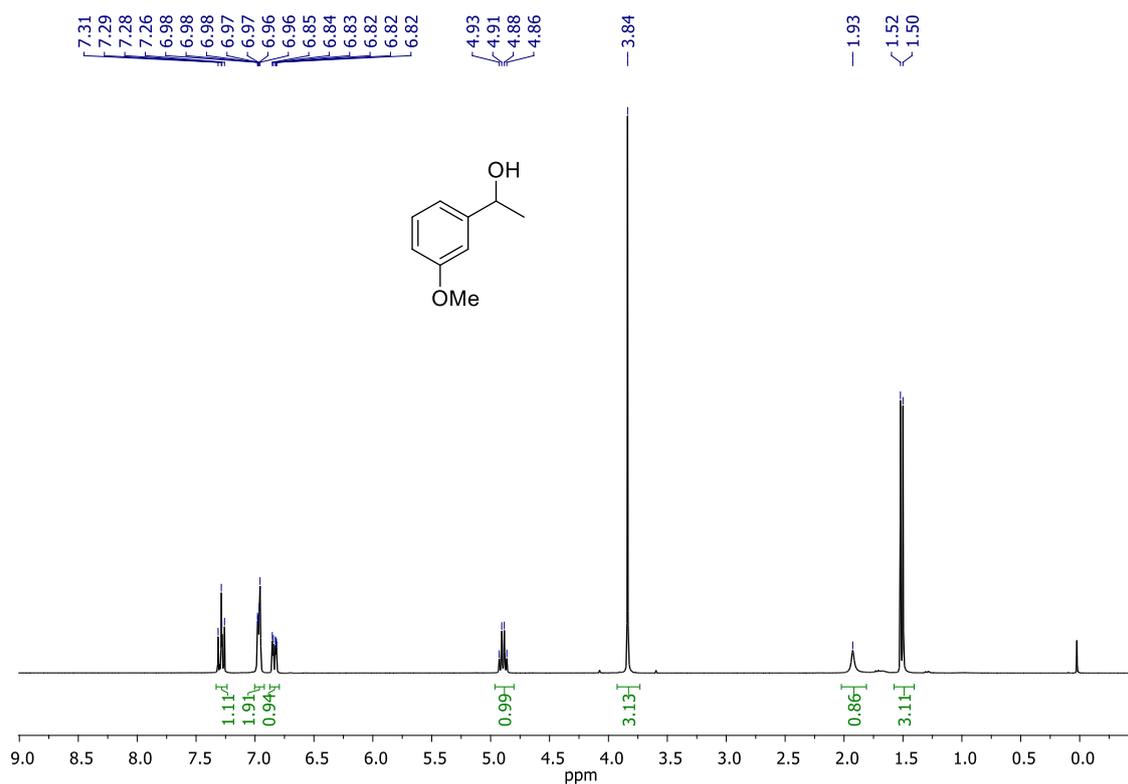


Figure SI.2.32. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 300 K) spectrum of product **10m**.

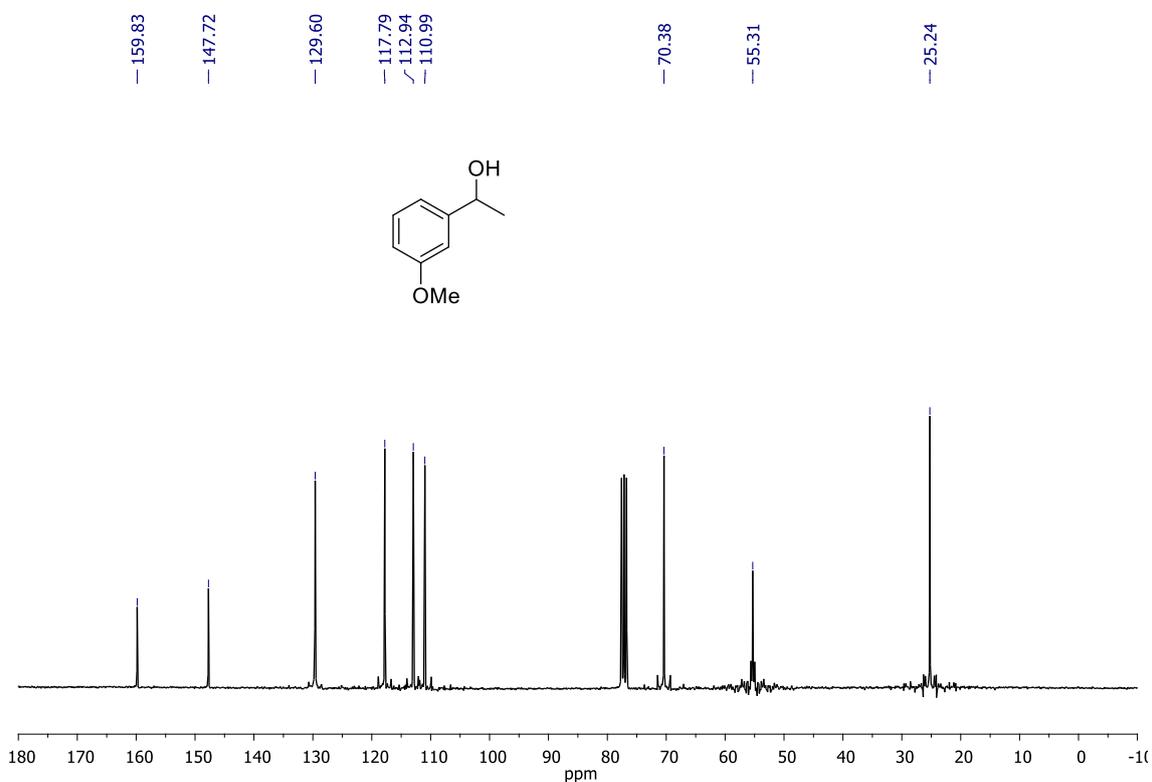


Figure SI.2.33. <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 75.4 MHz, 300 K) spectrum of product **10m**.

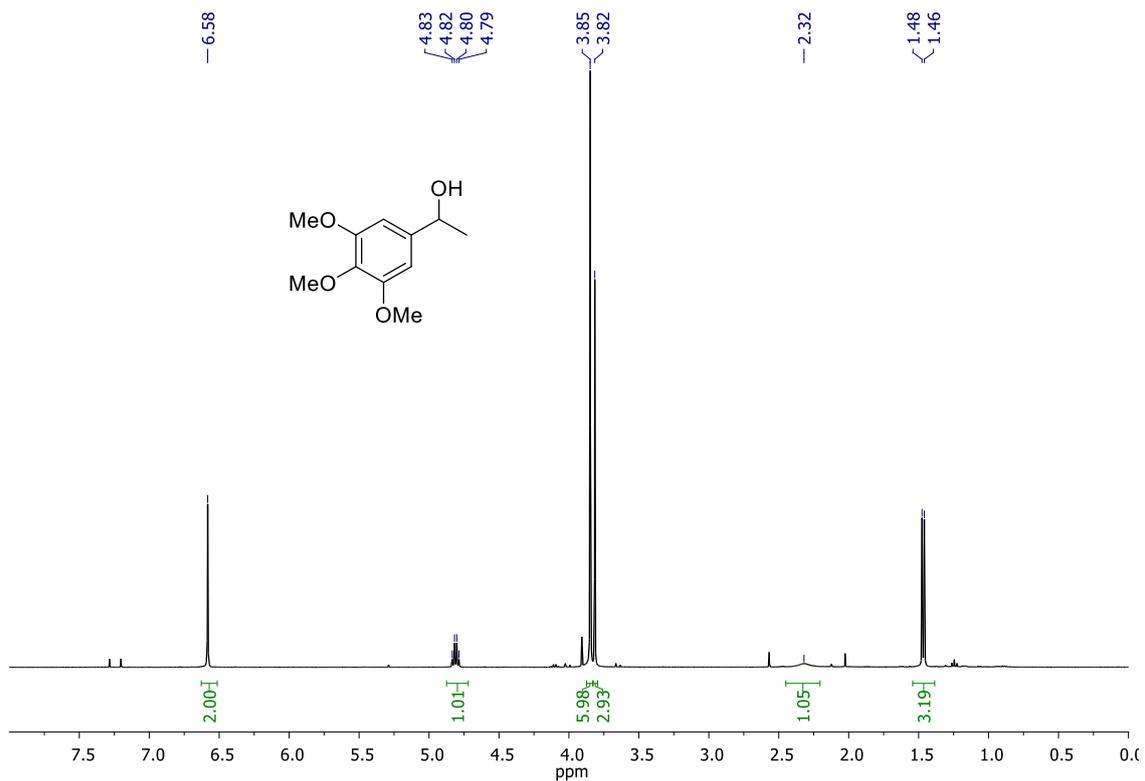


Figure SI.2.34.  $^1\text{H-NMR}$  (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **10n**.

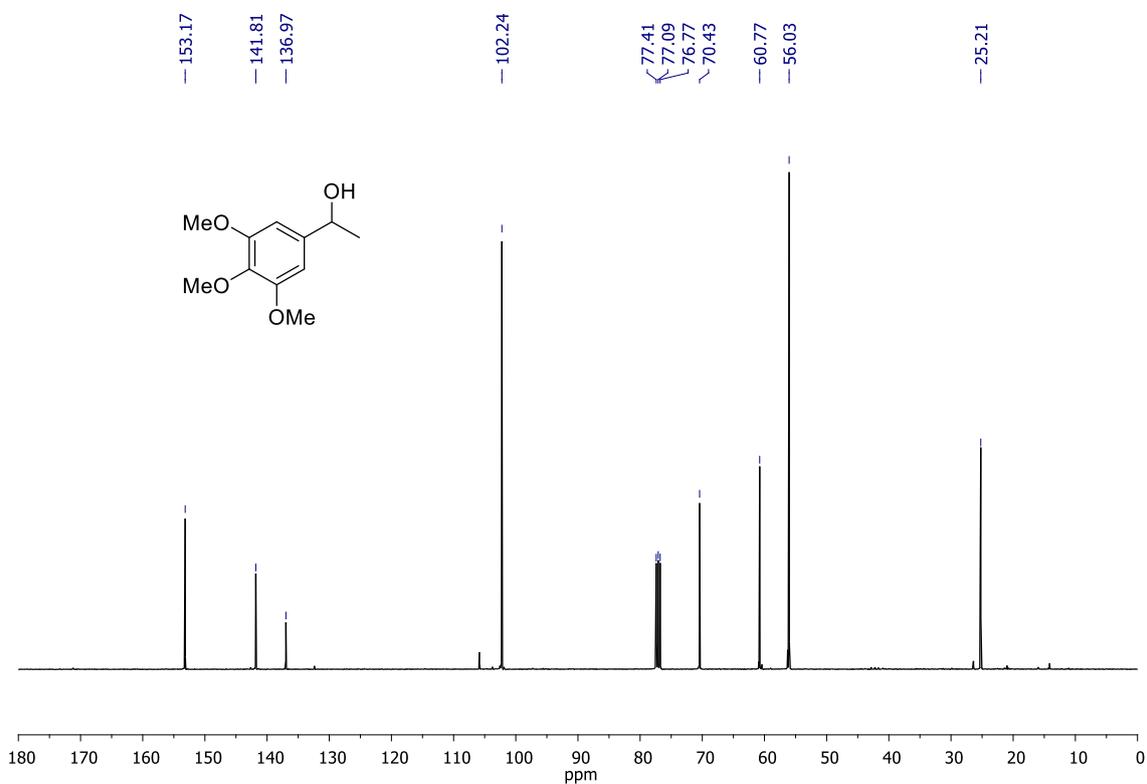


Figure SI.2.35.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10n**.

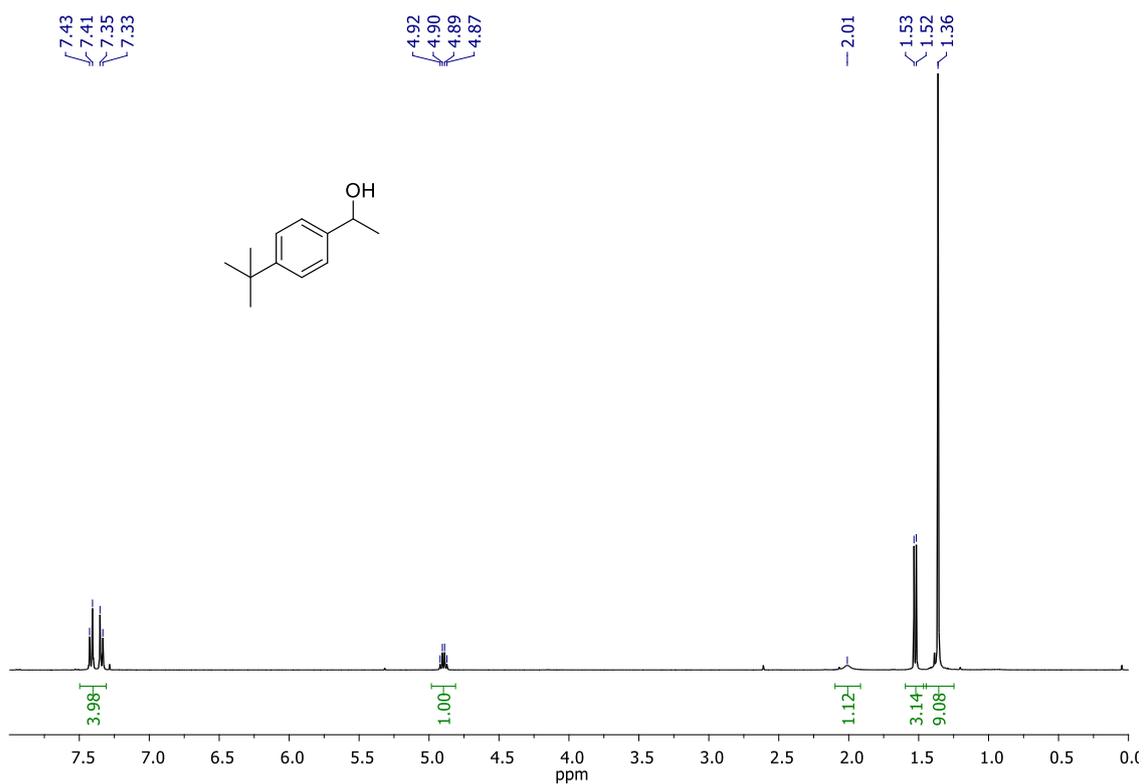


Figure SI.2.36.  $^1\text{H-NMR}$  (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **10o**.

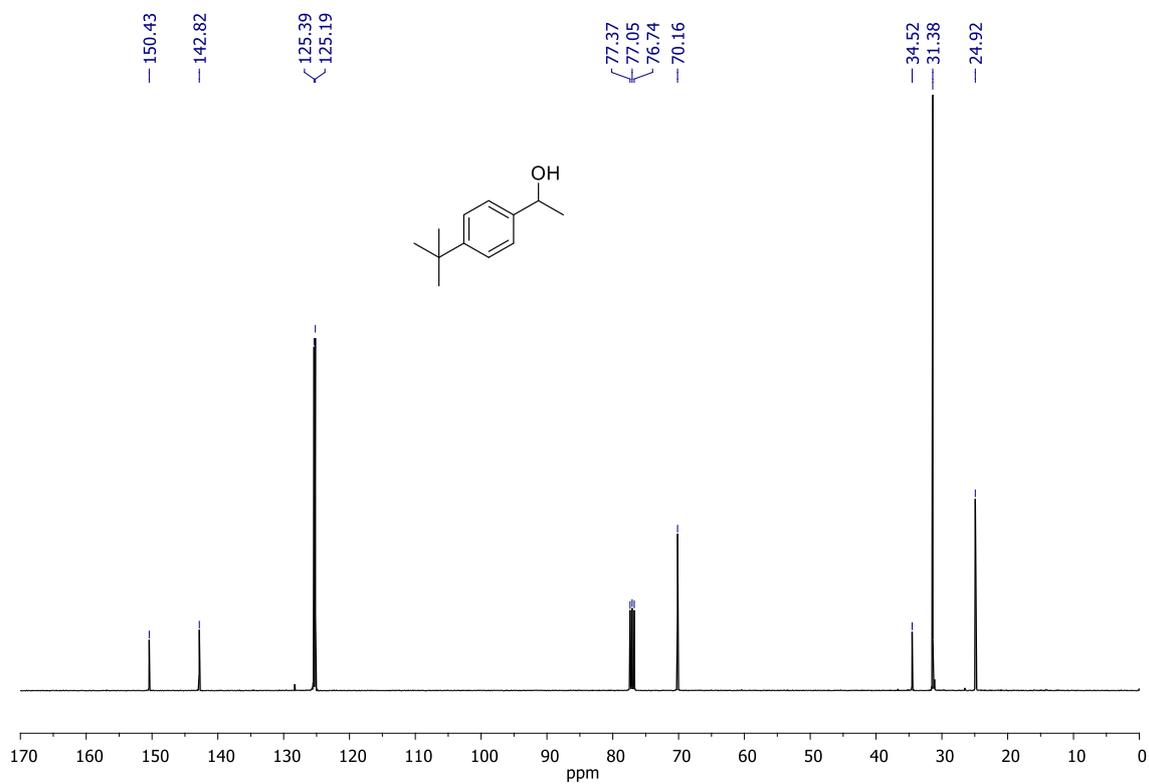


Figure SI.2.37.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10o**.

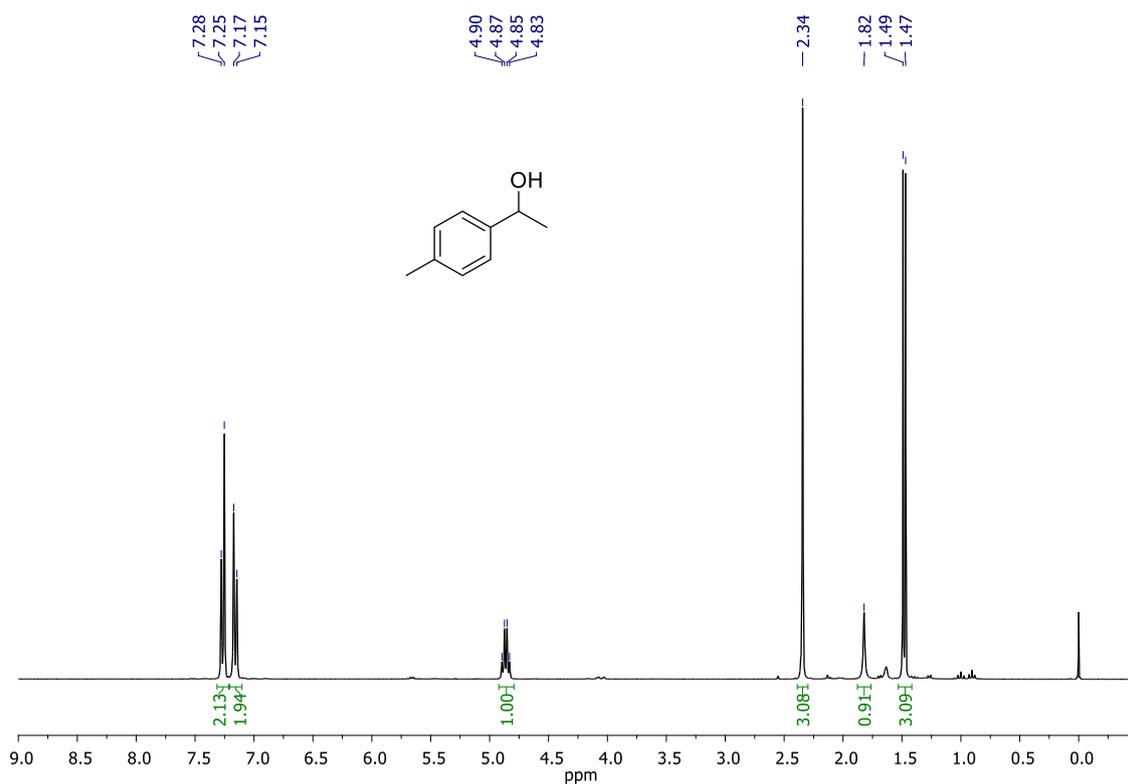


Figure SI.2.38.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10p**.

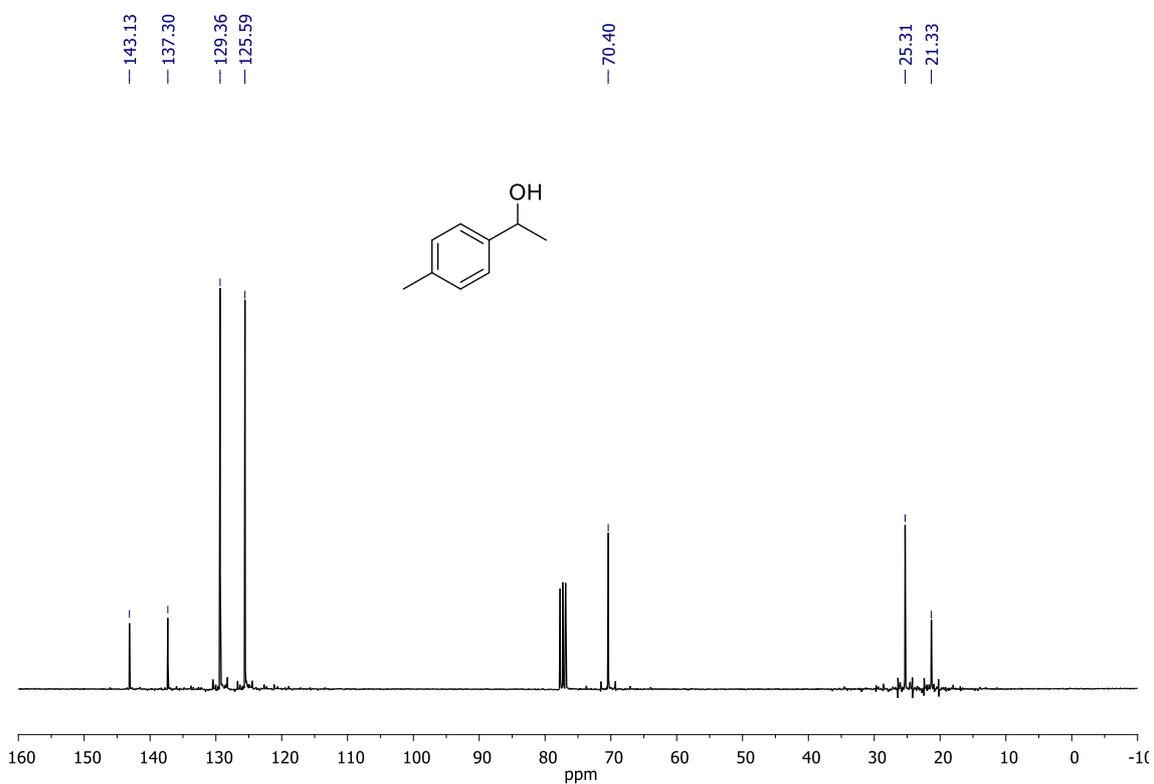


Figure SI.2.39.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **10p**.

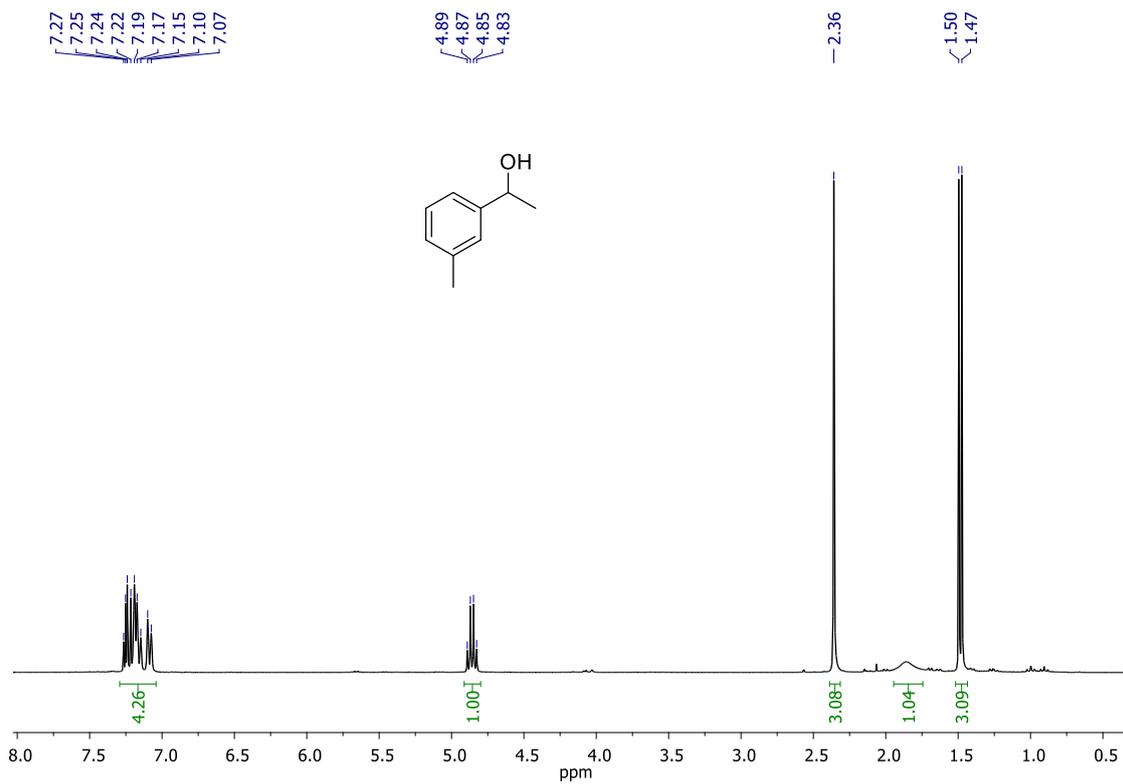


Figure SI.2.40.  $^1\text{H-NMR}$  (CDCl<sub>3</sub>, 300 MHz, 300 K) spectrum of product **10q**.

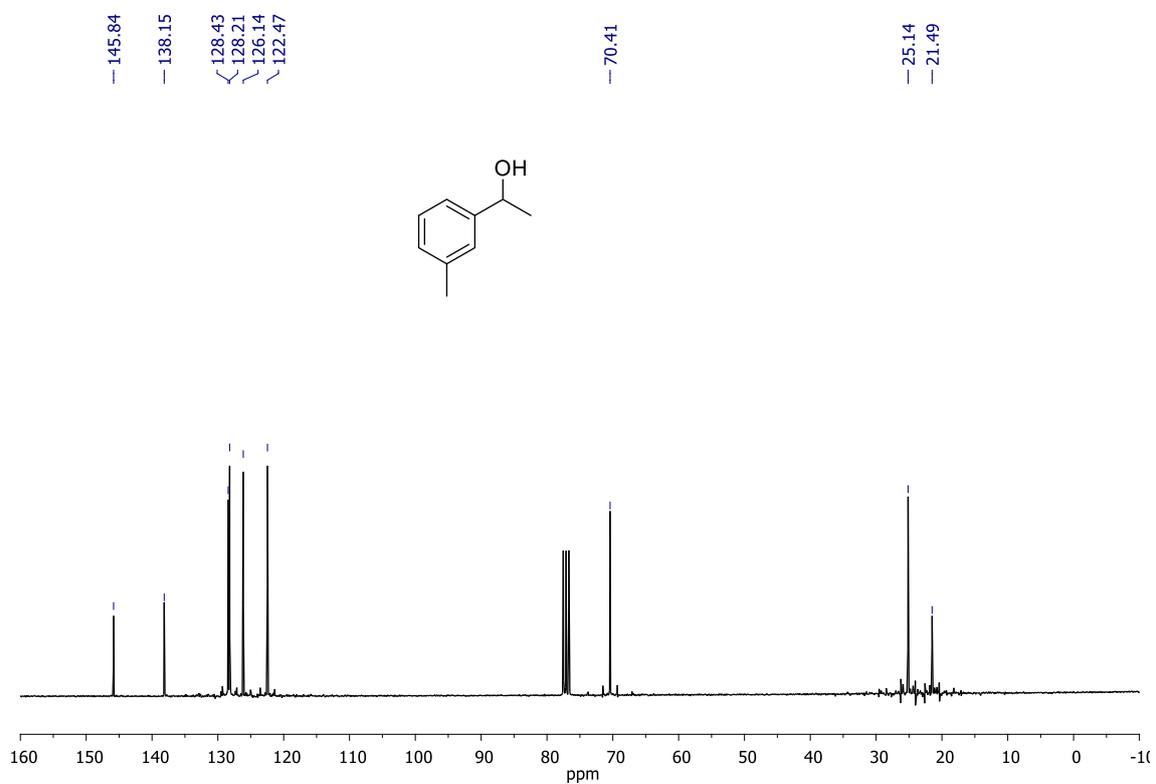


Figure SI.2.41.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 75.4 MHz, 300 K) spectrum of product **10q**.

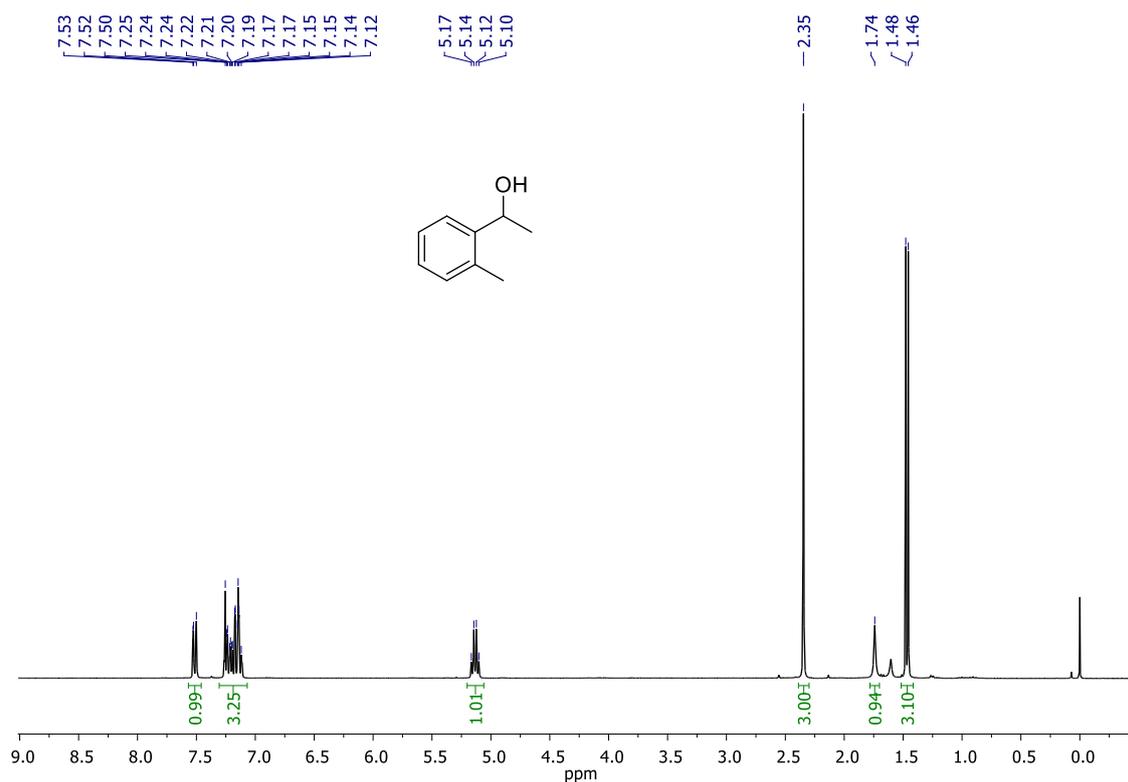


Figure SI.2.42.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **10r**.

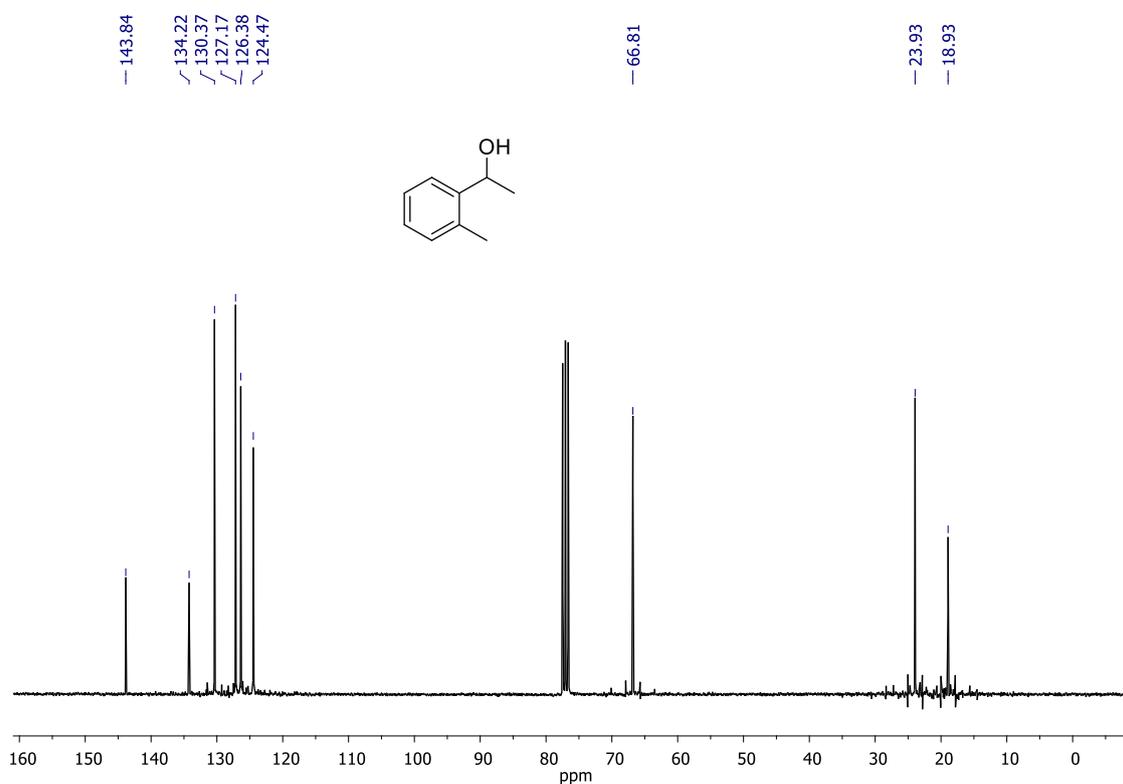
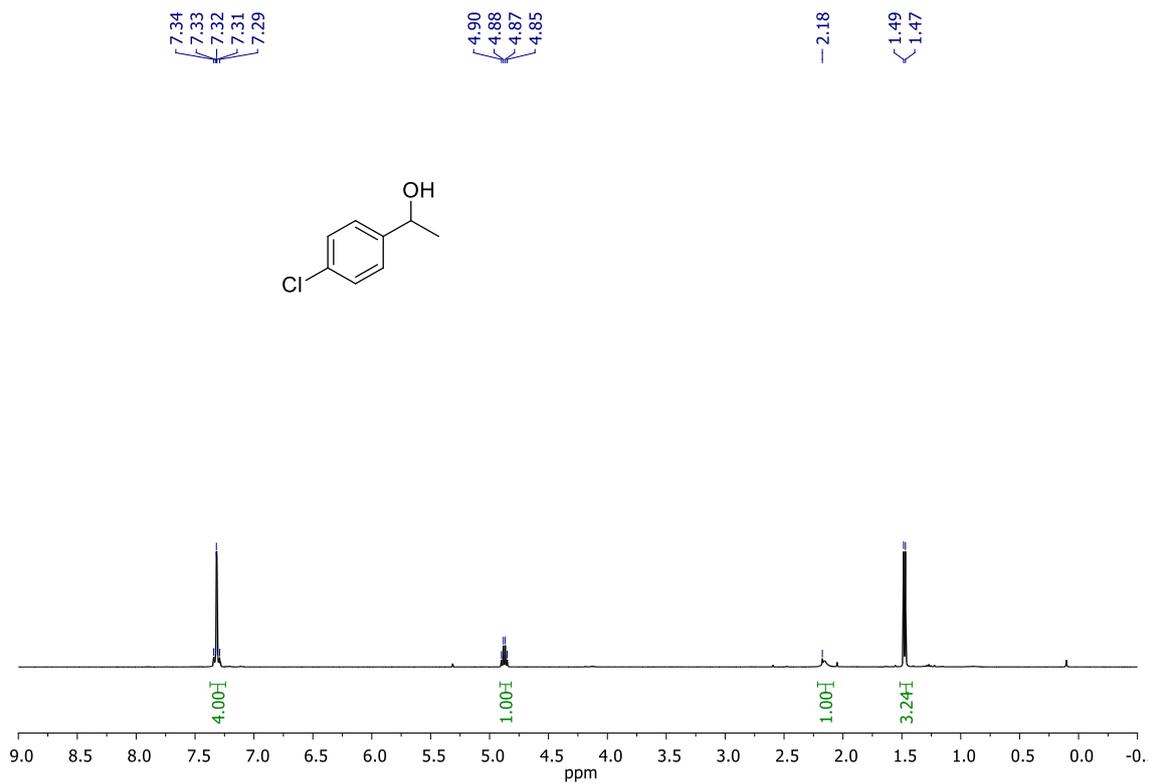
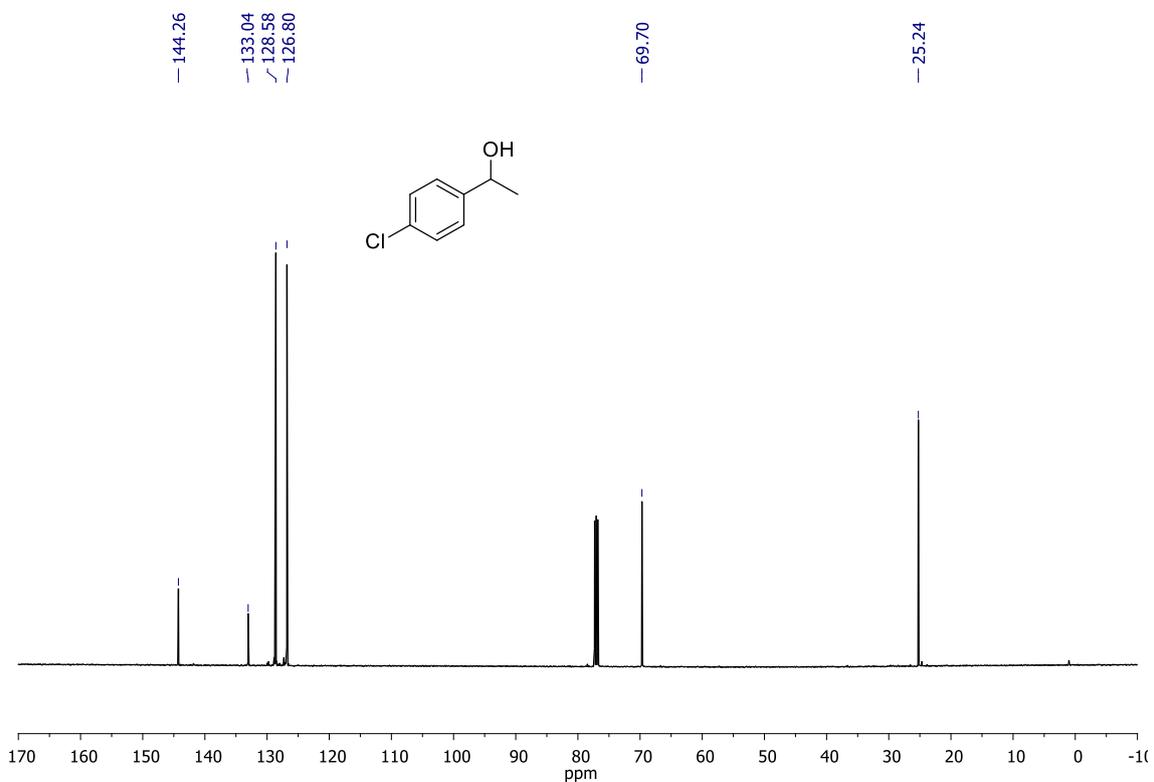


Figure SI.2.43.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75 MHz, 300 K) spectrum of product **10r**.



**Figure SI.2.44.** <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **10s**.



**Figure SI.2.45.** <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10s**.

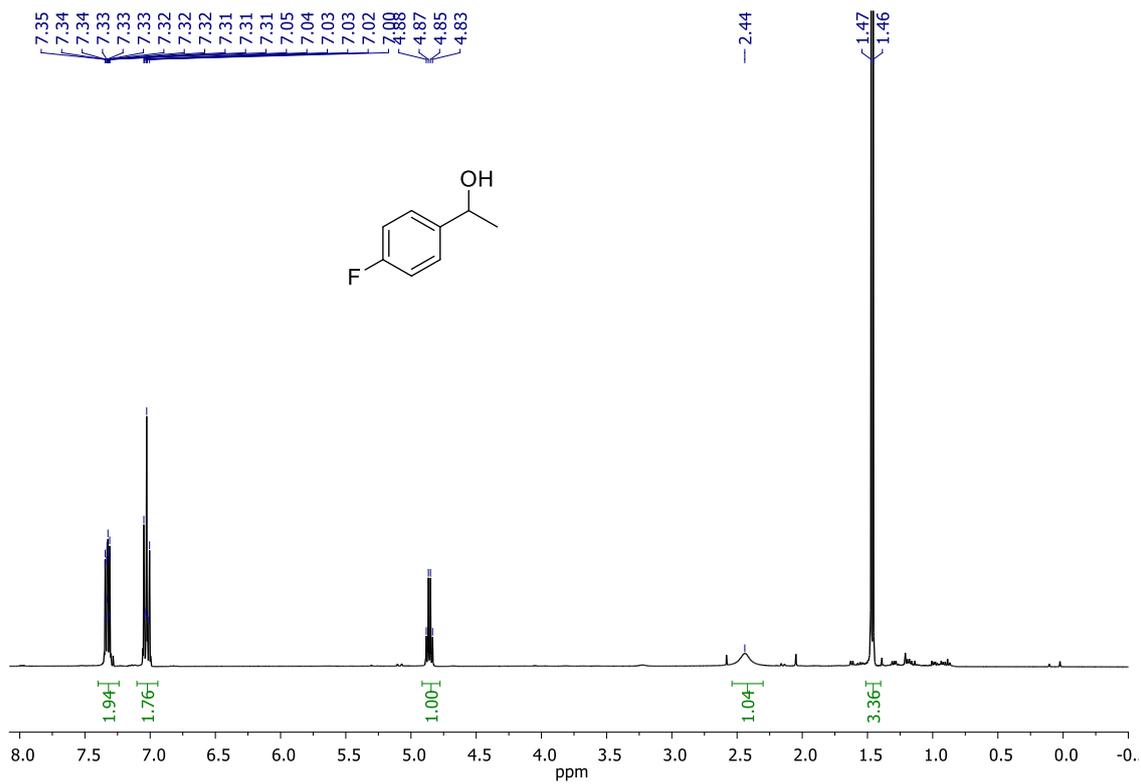


Figure SI.2.46.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz, 300 K) spectrum of product **10t**.

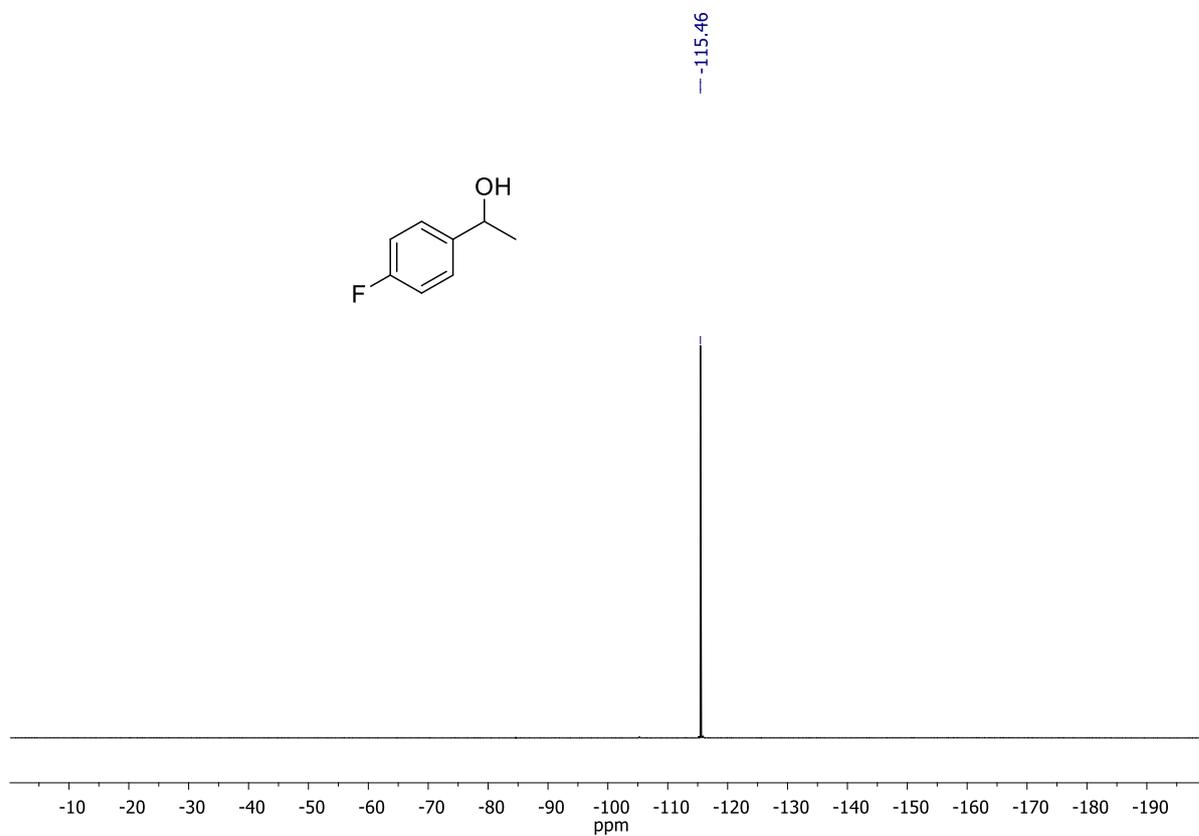


Figure SI.2.47.  $^{19}\text{F}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 376 MHz, 300 K) spectrum of product **10t**.

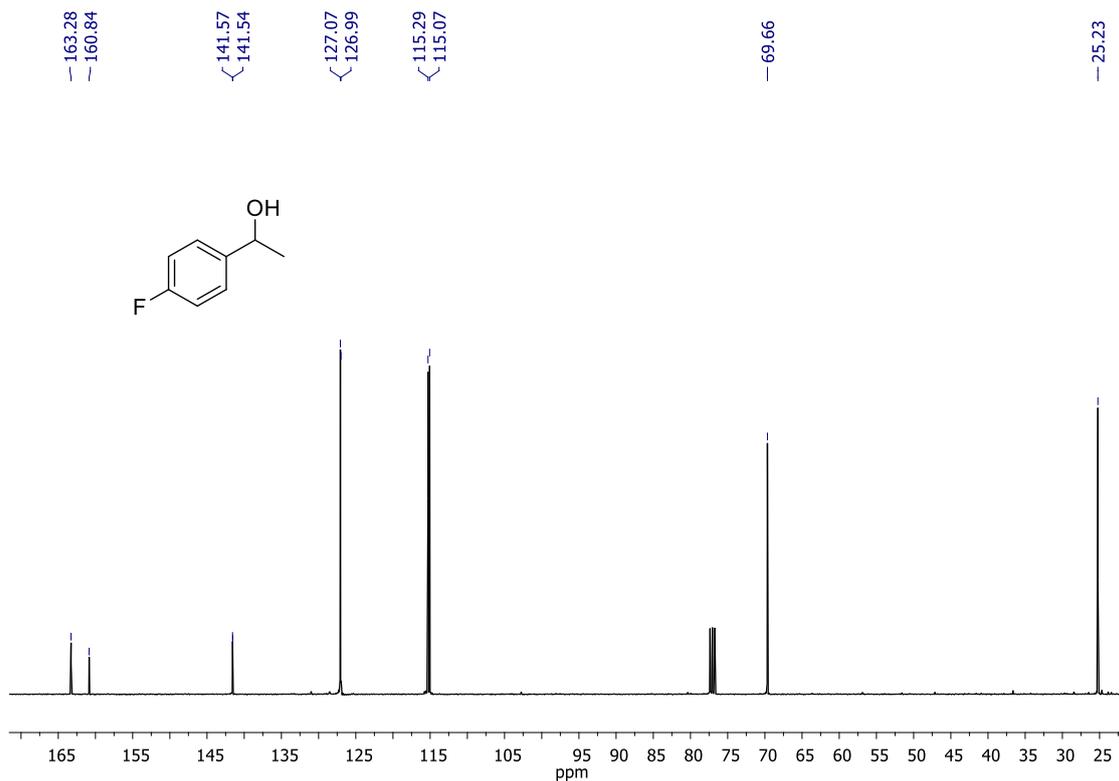


Figure SI.2.48.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 100.6 MHz, 300 K) spectrum of product **10t**.

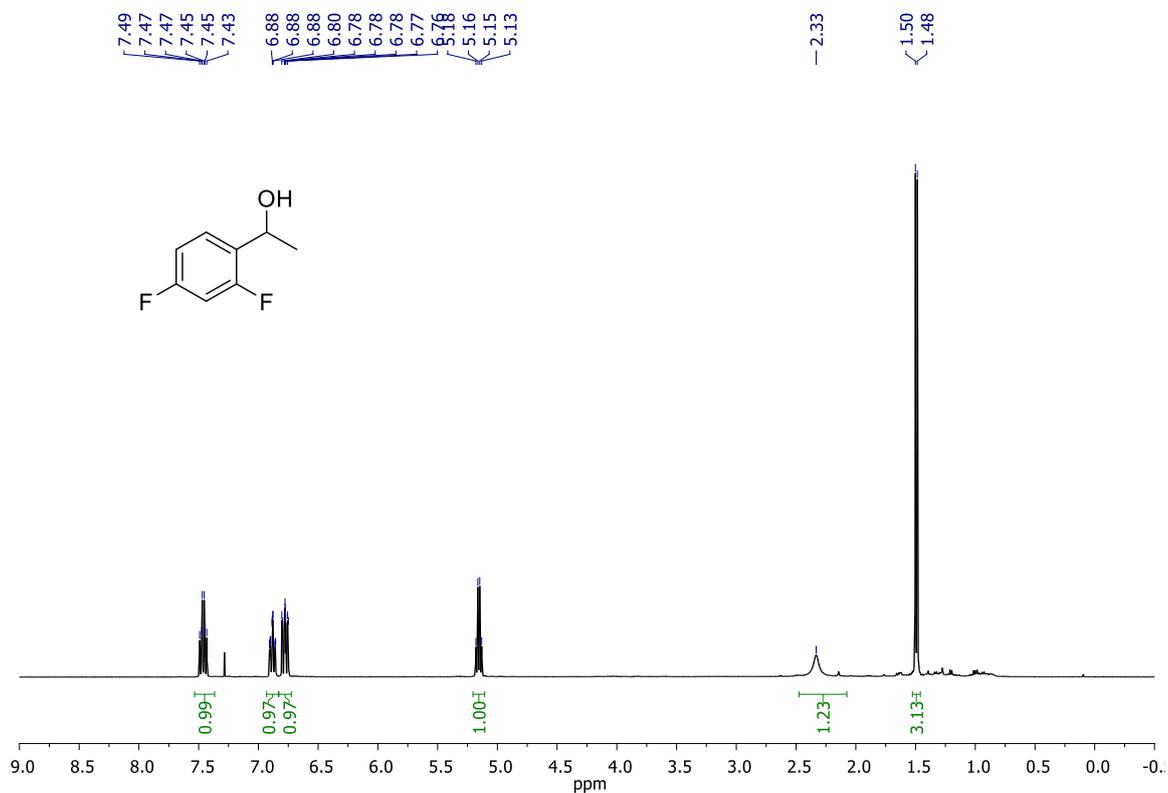
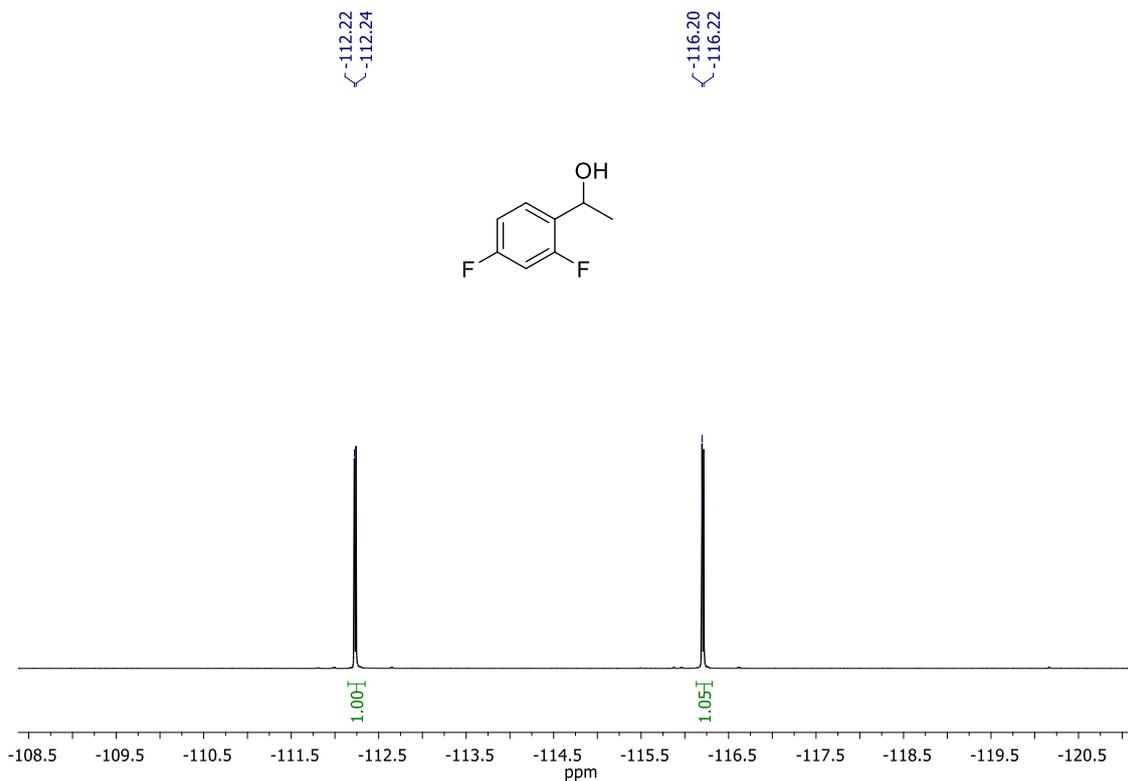
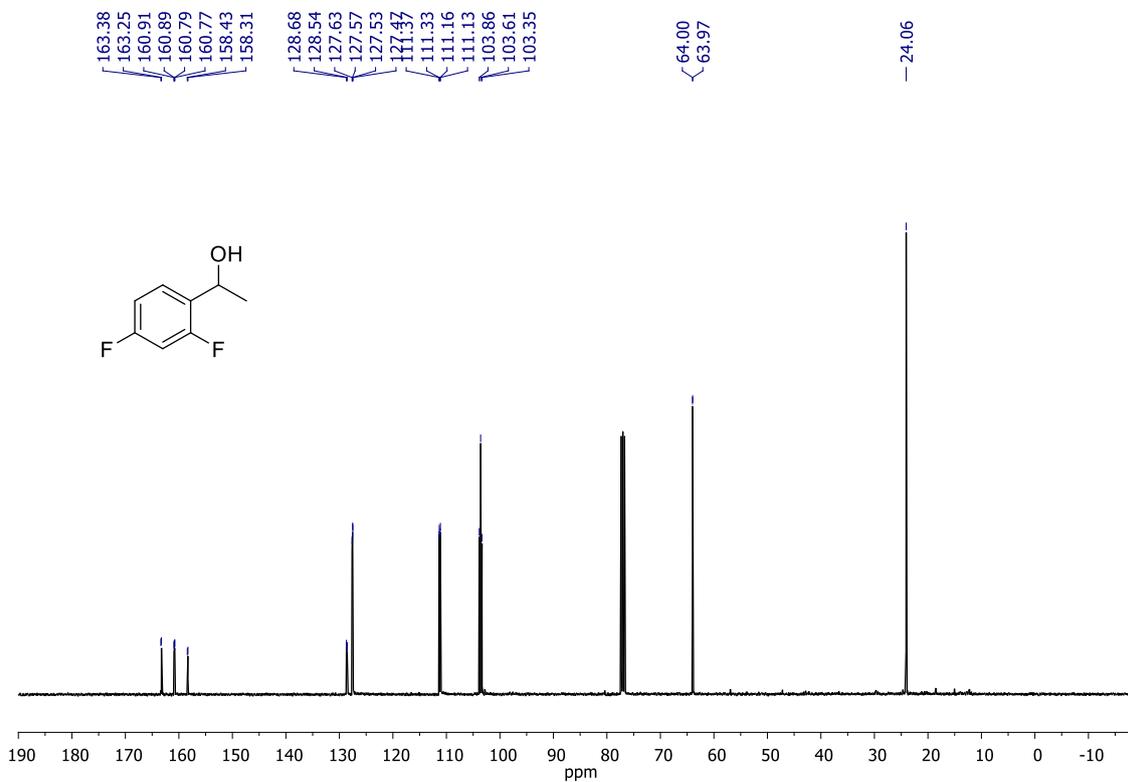


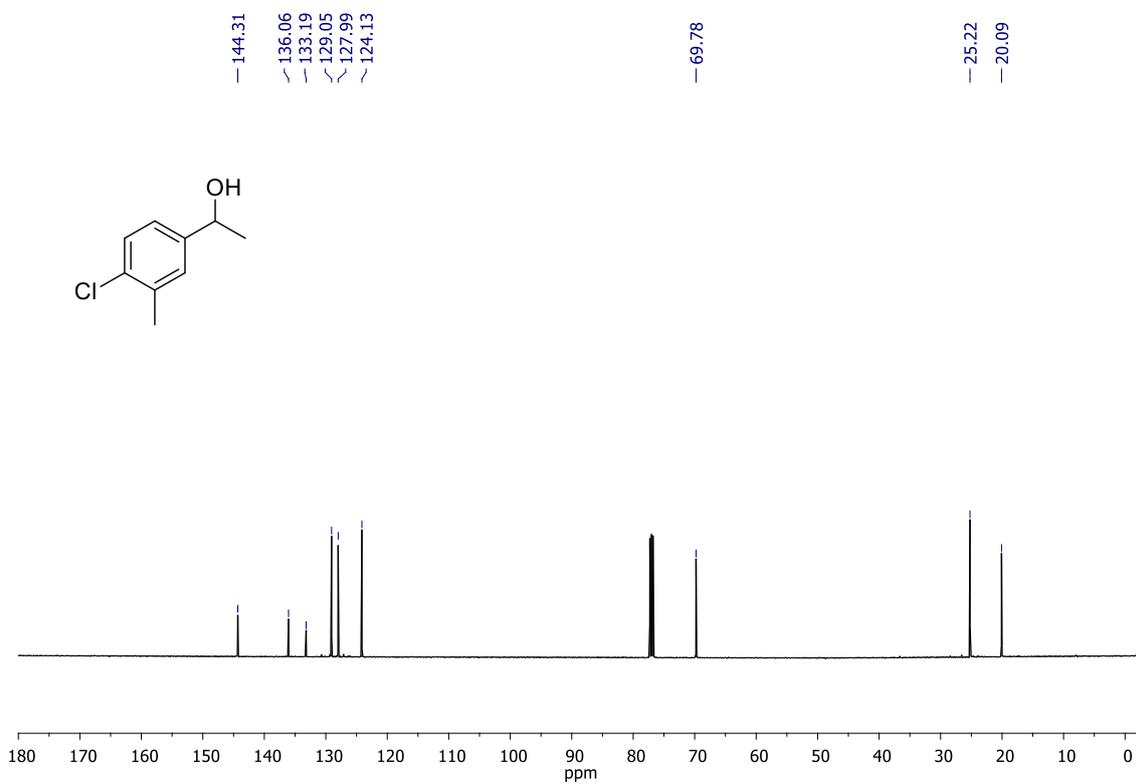
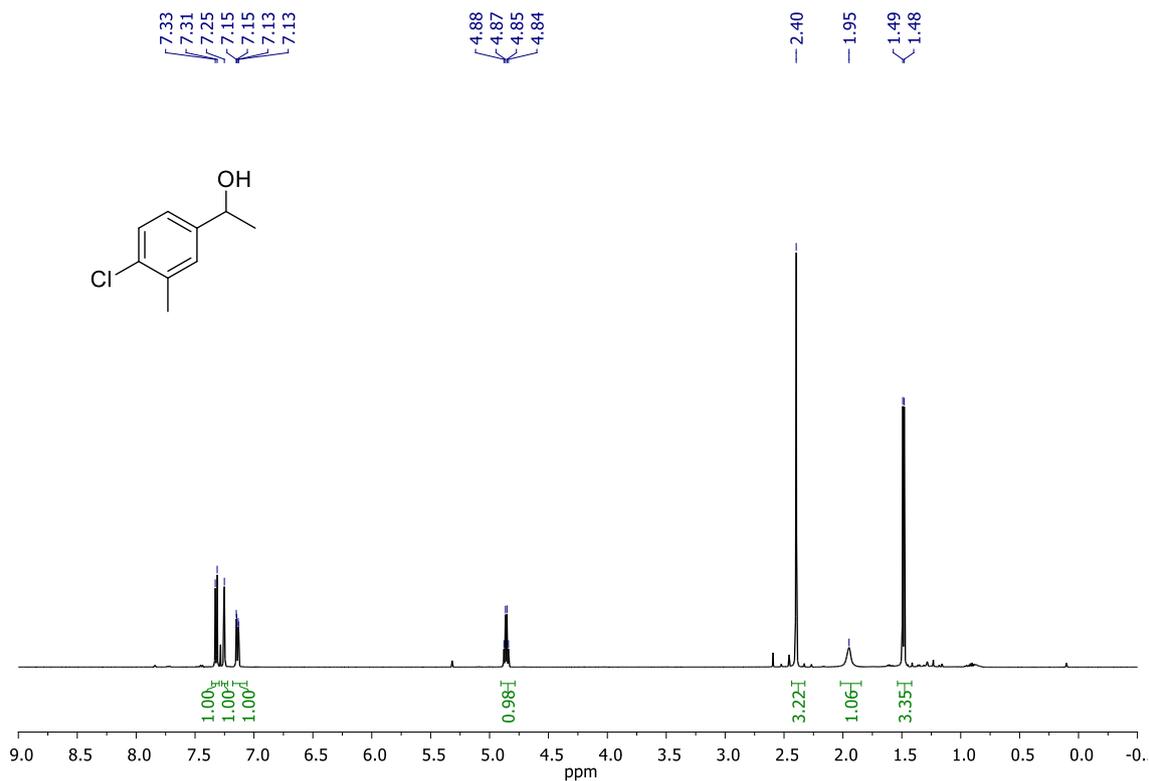
Figure SI.2.49.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz, 300 K) spectrum of product **10v**.

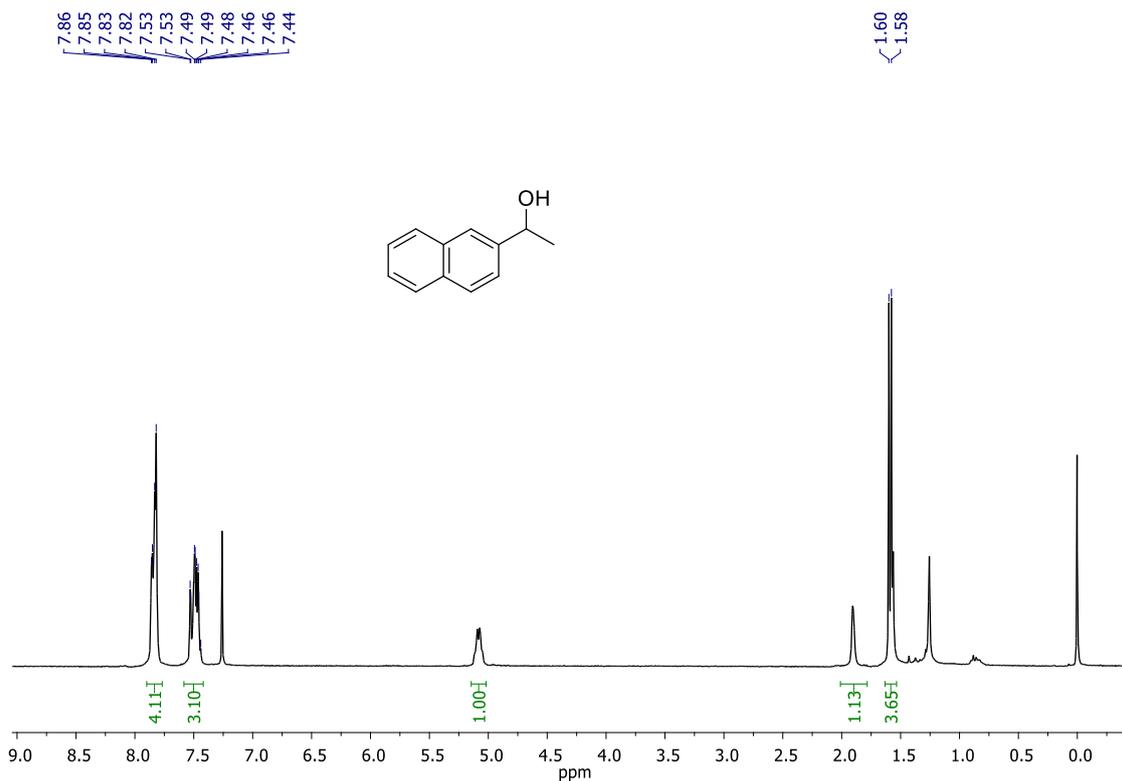


**Figure SI.2.50.**  $^{19}\text{F}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 376 MHz, 300 K) spectrum of product **10v**.

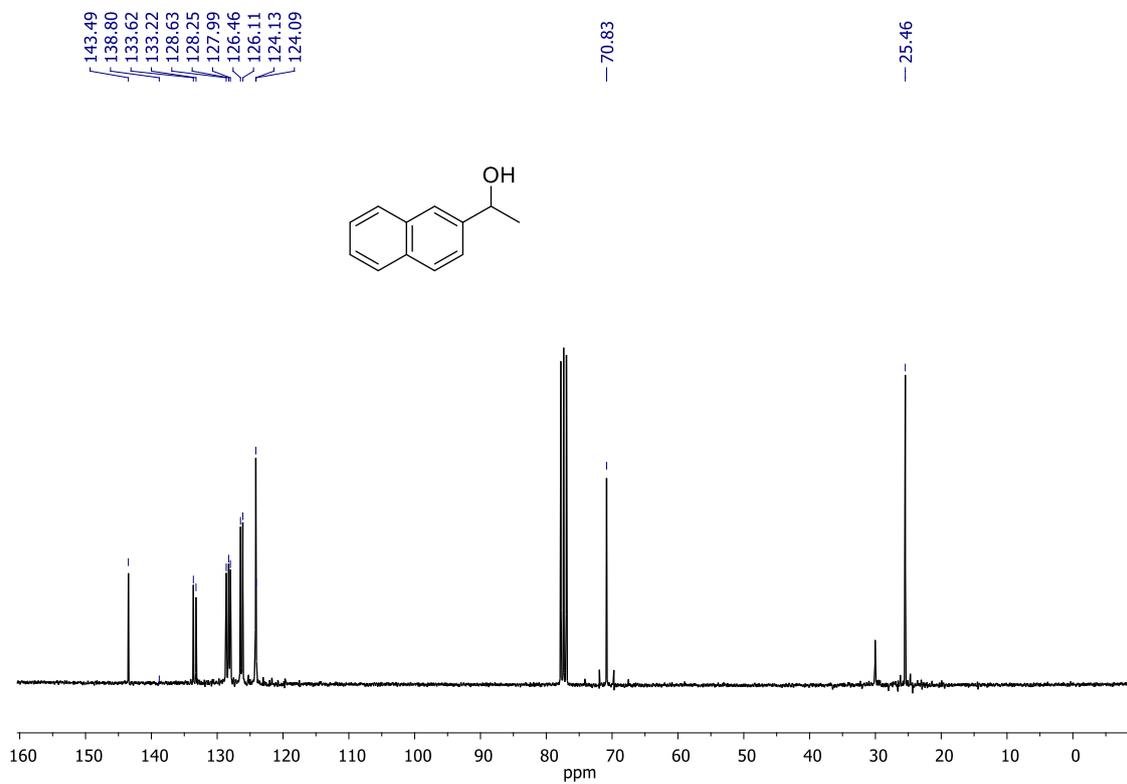


**Figure SI.2.51.**  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **10v**.





**Figure SI.2.54.** <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 300 K) spectrum of product **10x**.



**Figure SI.2.55.** <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 75.4 MHz, 300 K) spectrum of product **10x**.

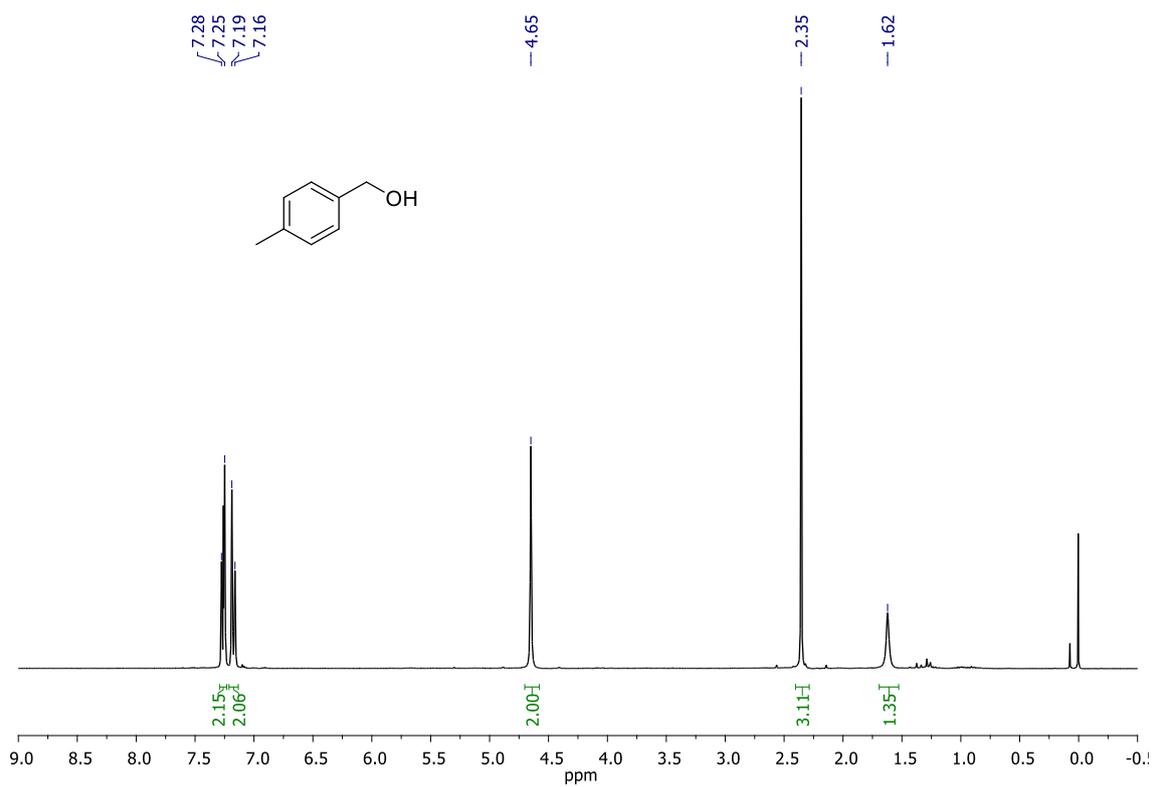


Figure SI.2.56.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, 300 K) spectrum of product **12a**.

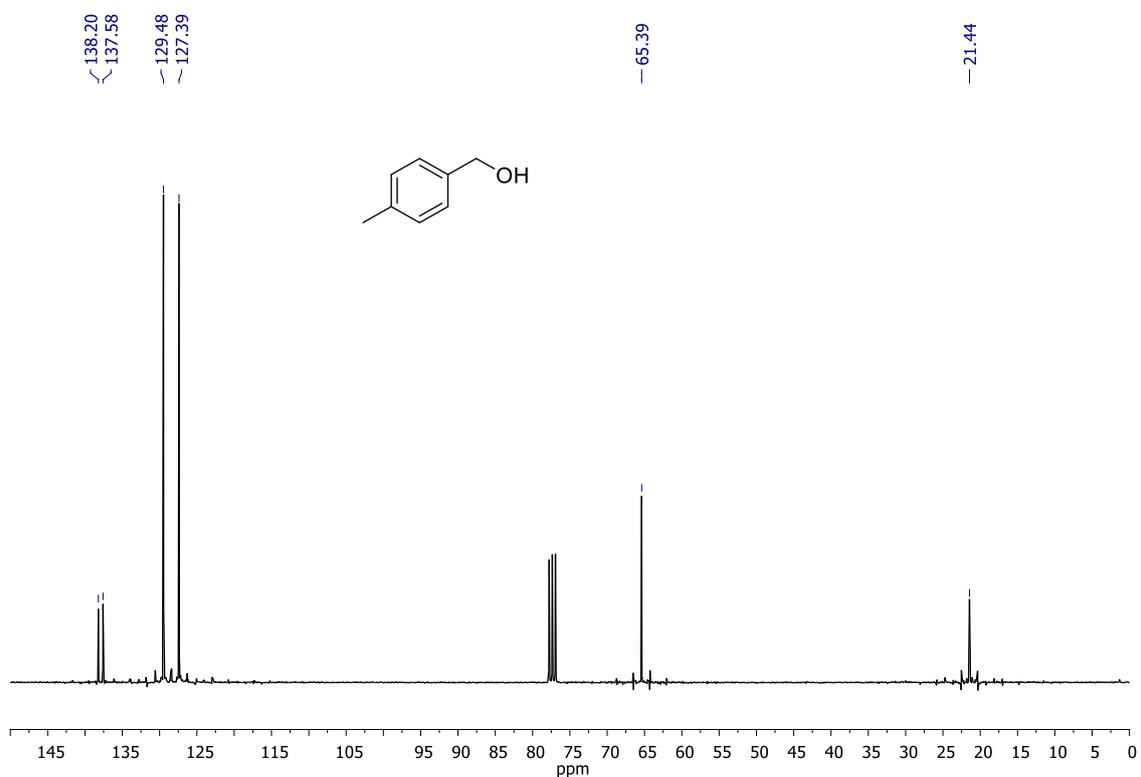


Figure SI.2.57.  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 75.4 MHz, 300 K) spectrum of product **12a**.

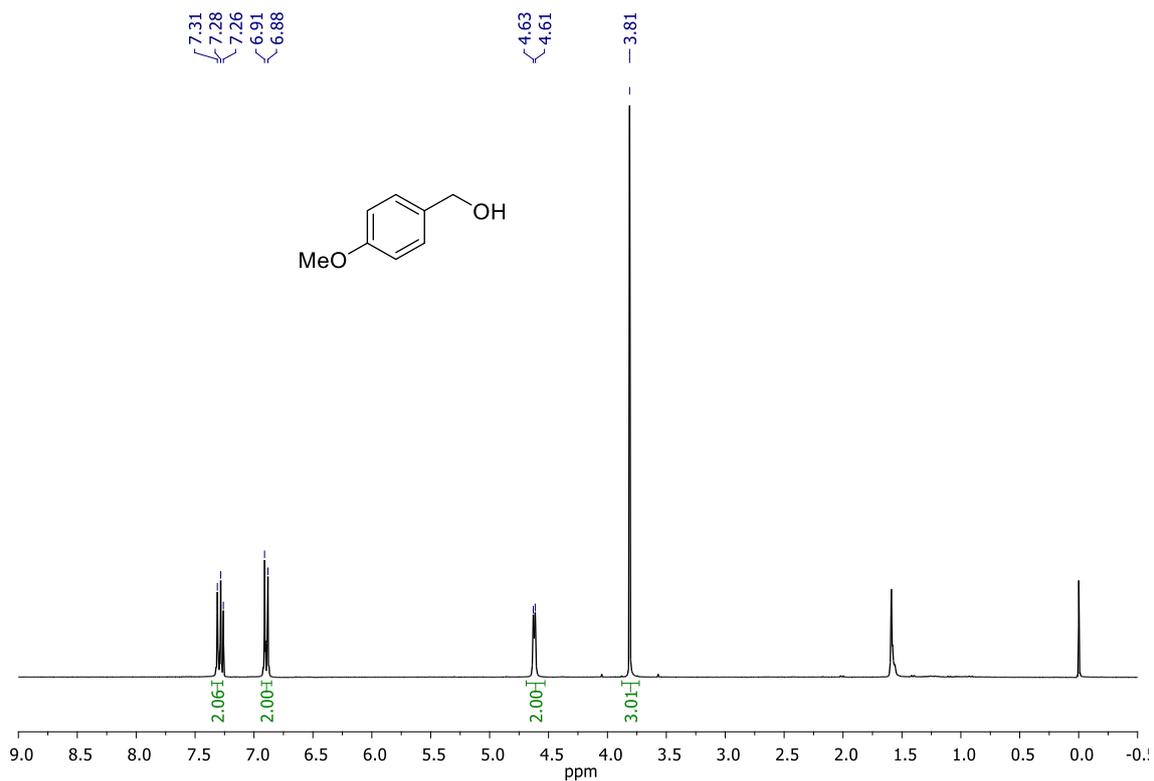


Figure SI.2.58. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, 300 K) spectrum of product **12b**.

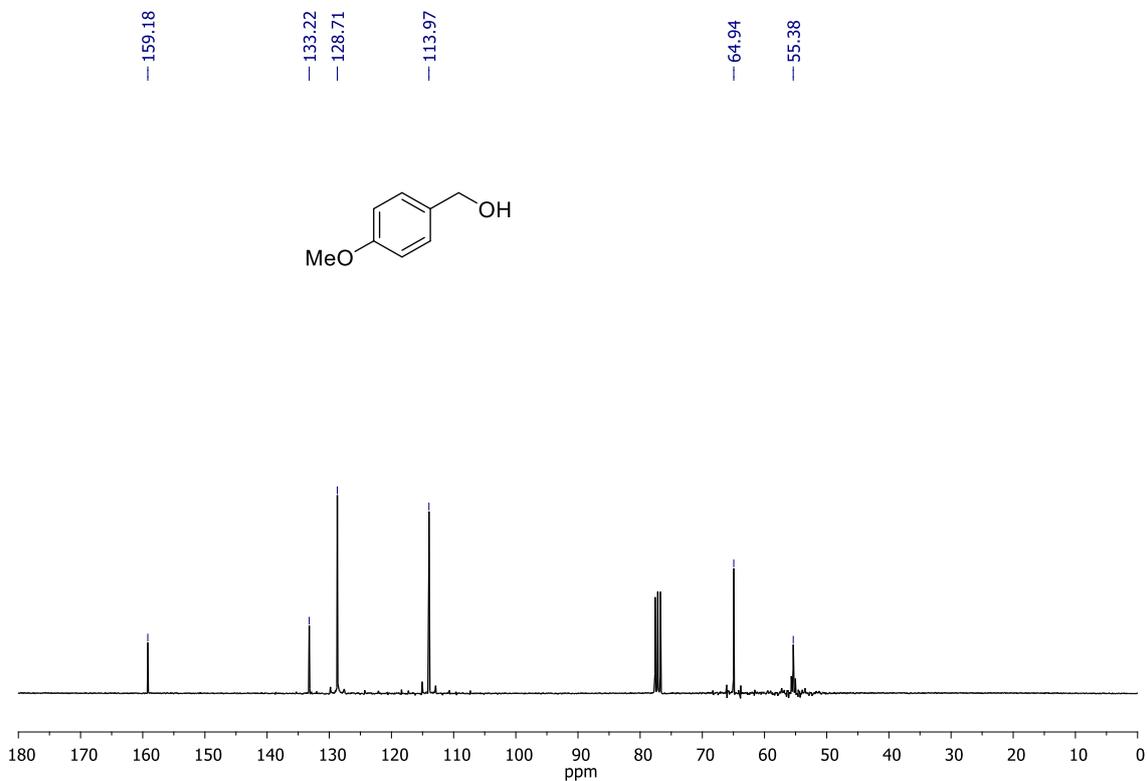


Figure SI.2.59. <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 75.4 MHz, 300 K) spectrum of product **12b**.

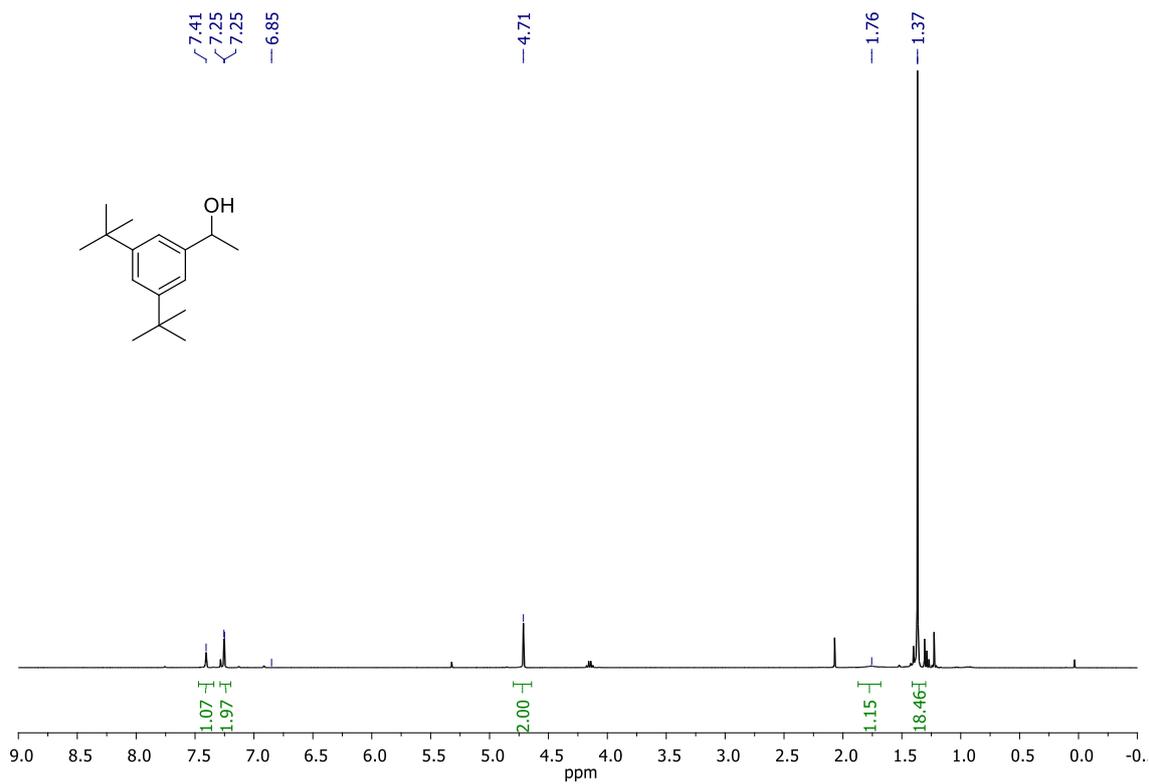


Figure SI.2.60.  $^1\text{H-NMR}$  (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product **12c**.

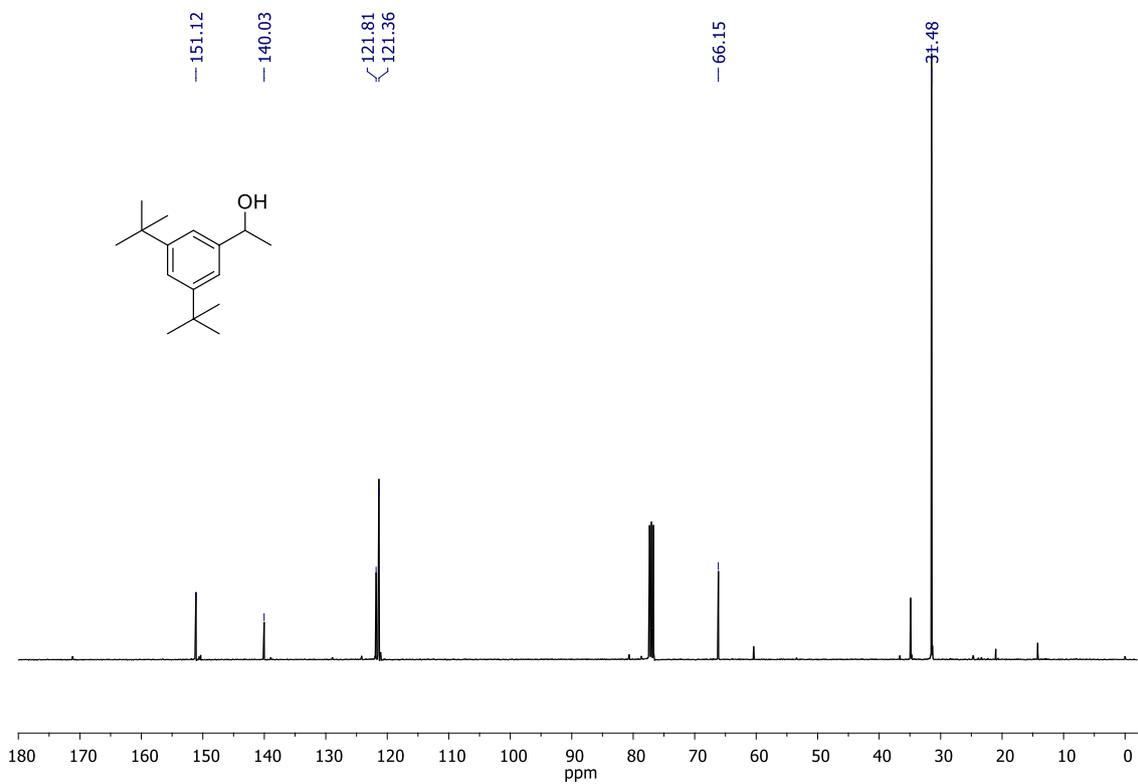


Figure SI.2.61.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product **12c**.

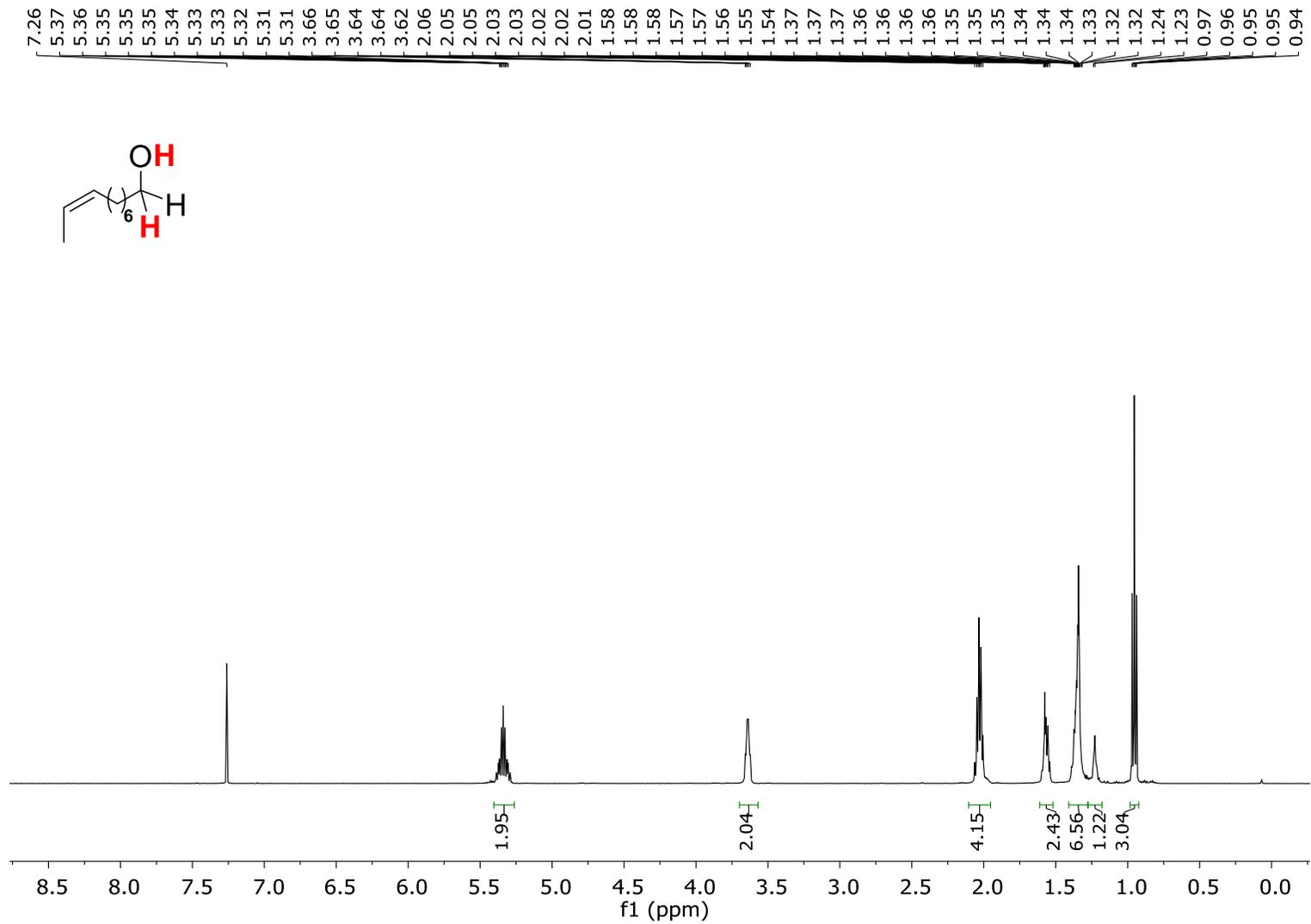


Figure SI.2.62.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 500 MHz, 300 K) spectrum of product **12d**.

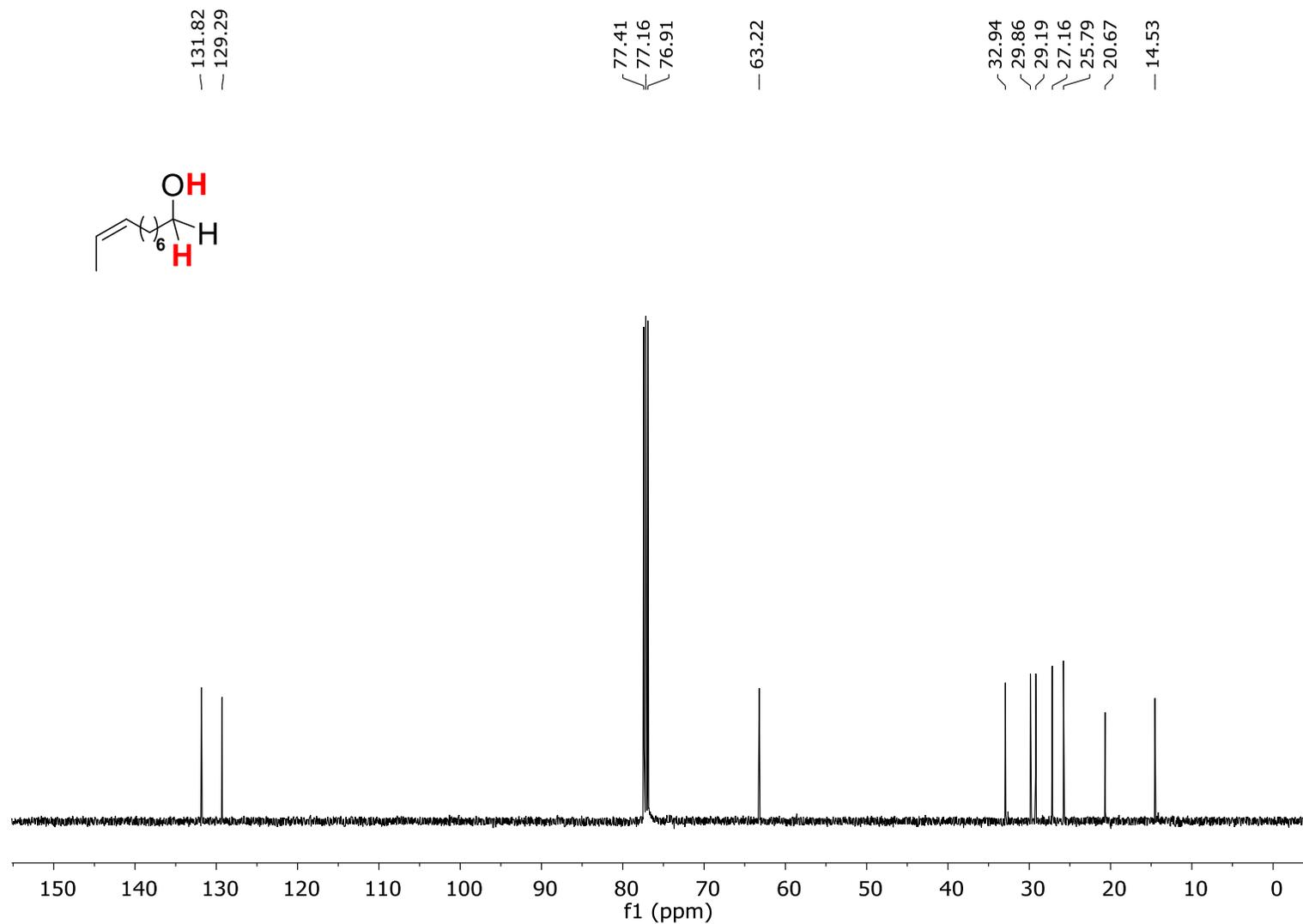


Figure SI.2.63.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 125.8 MHz, 300 K) spectrum of product 12d.

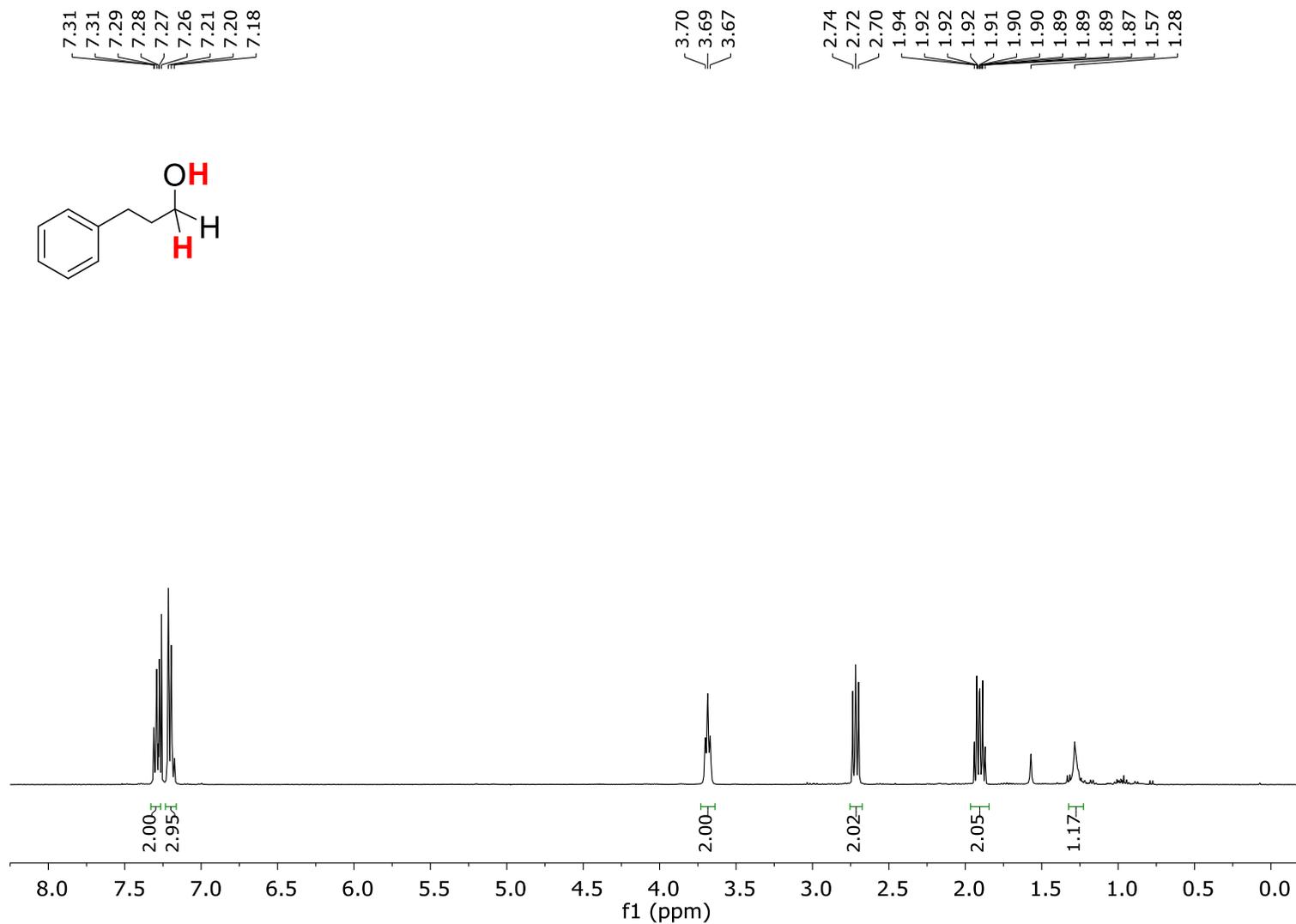


Figure SI.2.64. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product 12e.

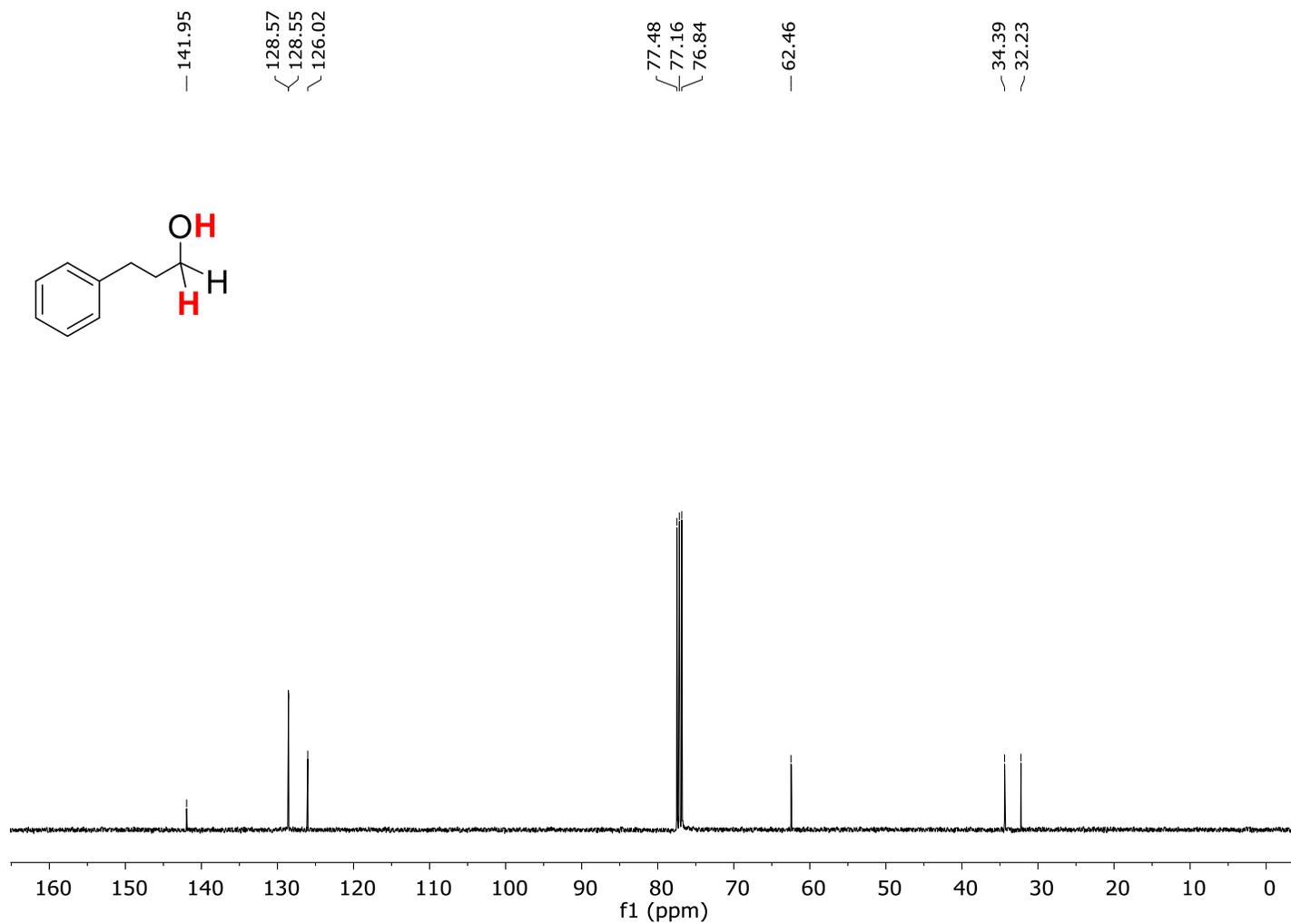


Figure S1.2.65.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product 12e.

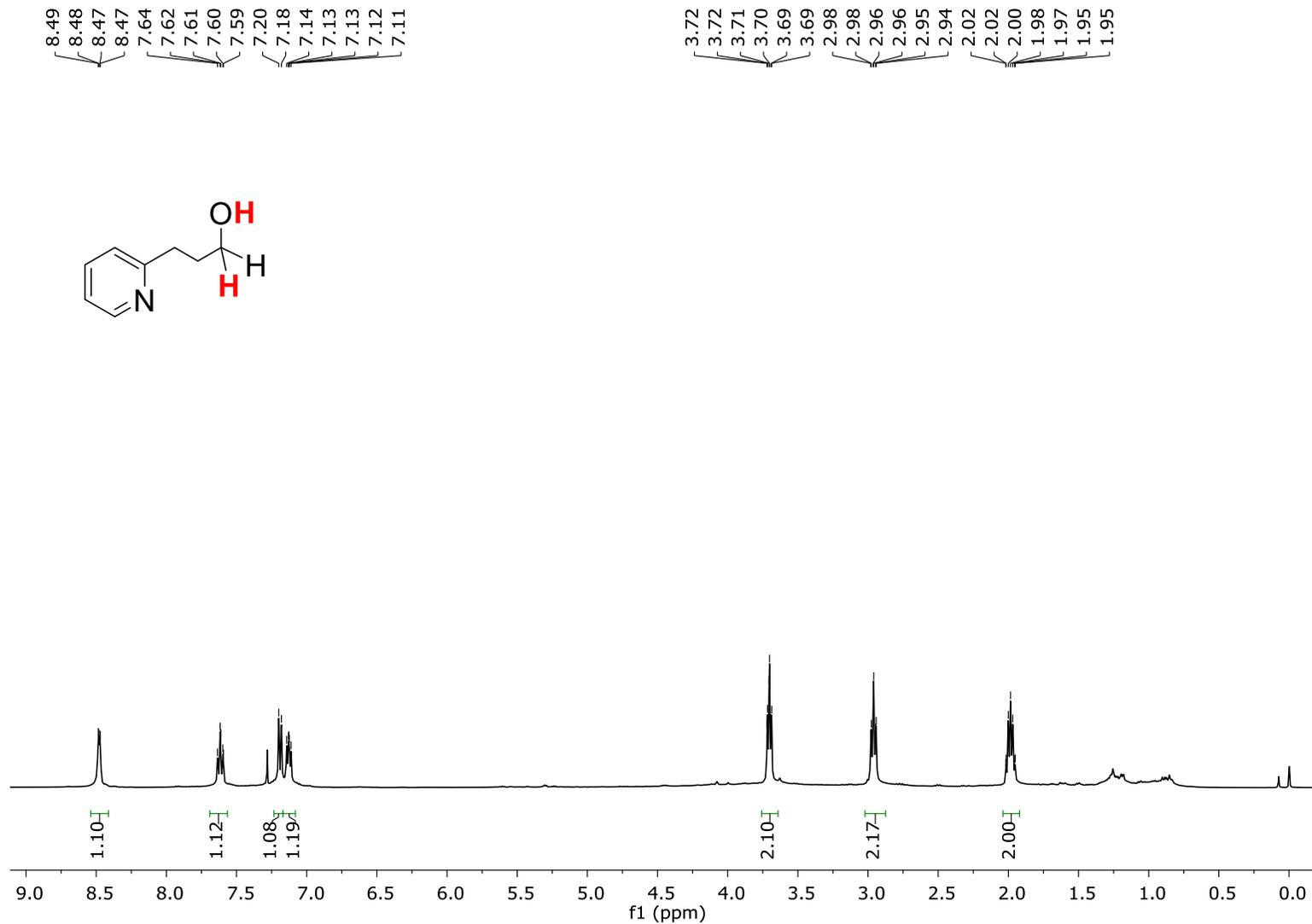


Figure SI.2.66. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of product 12f.

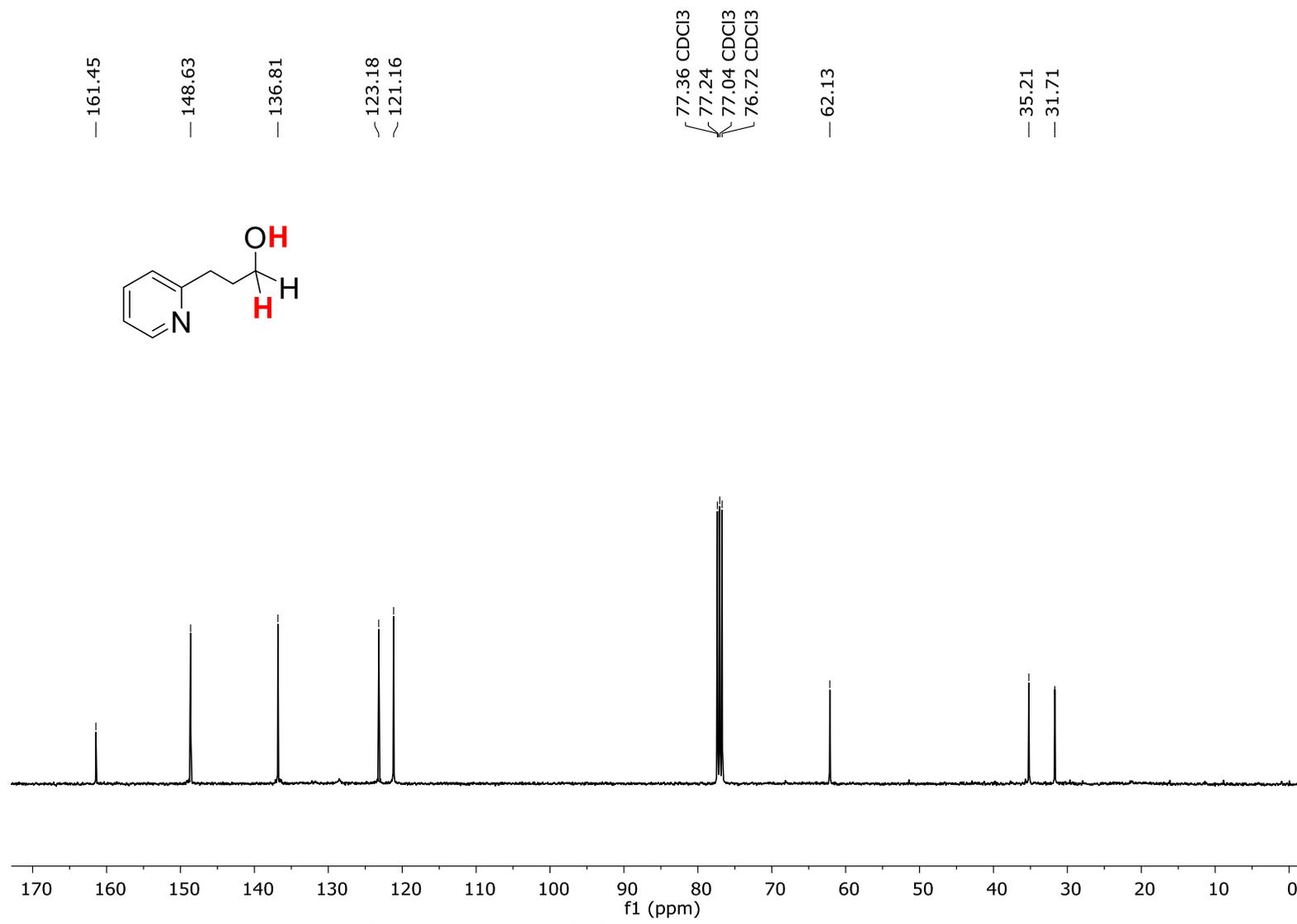
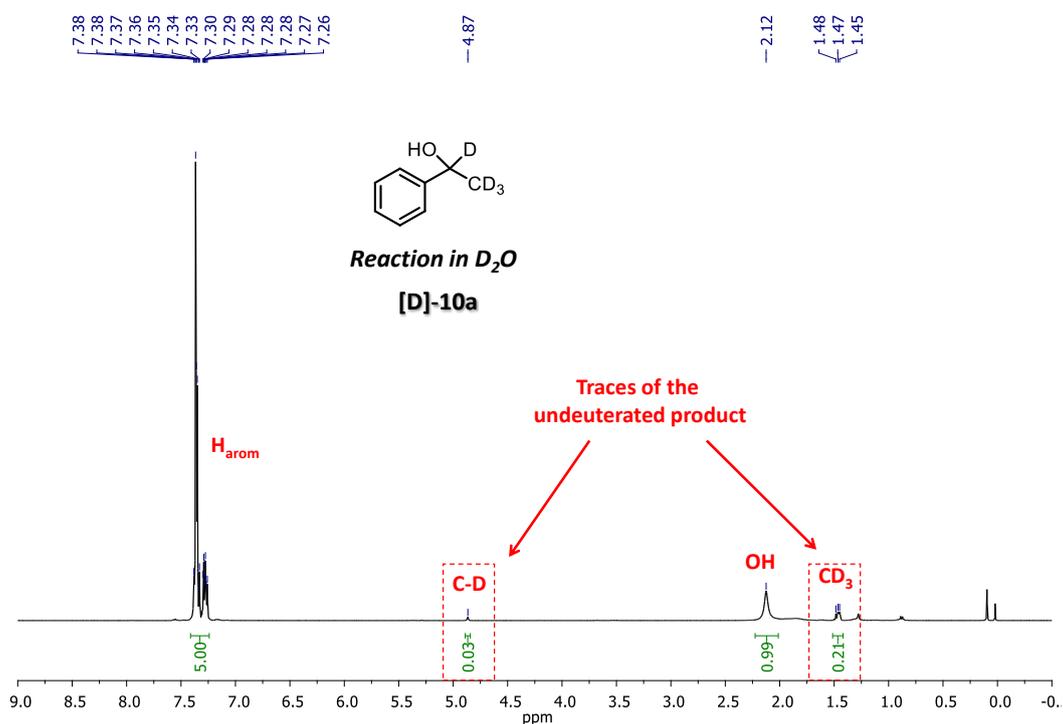
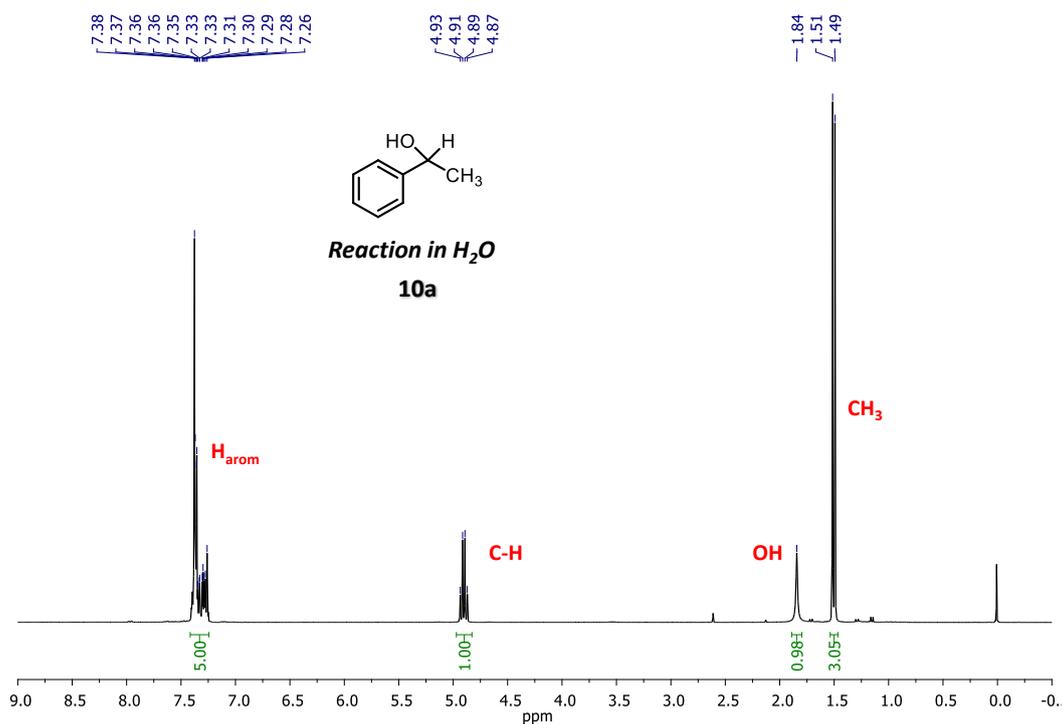
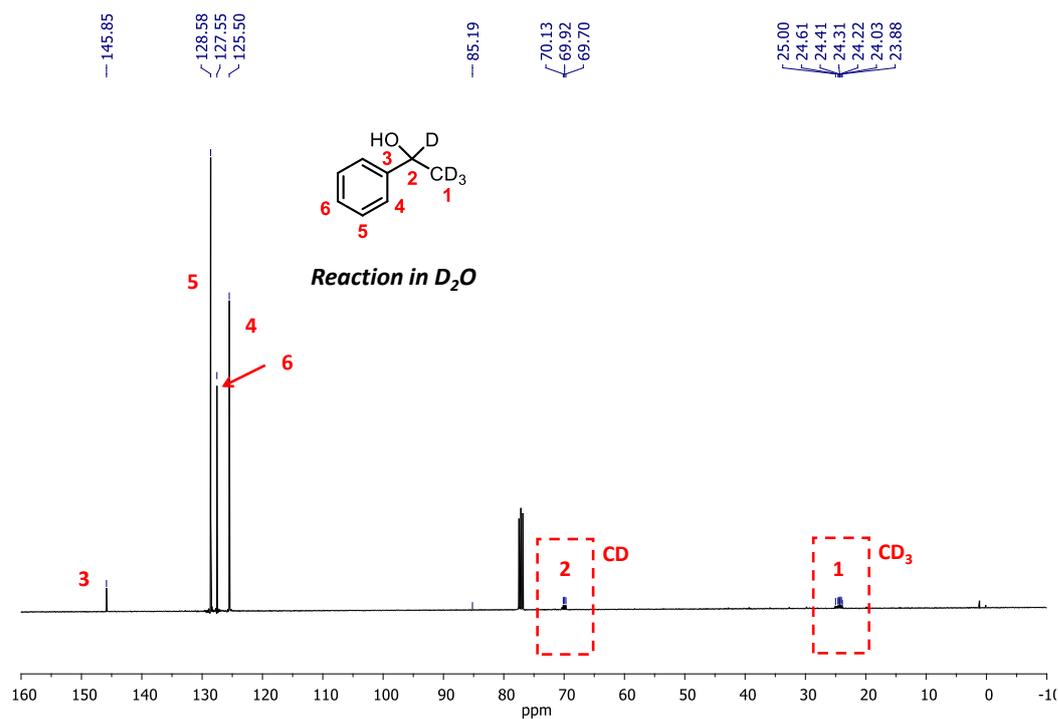
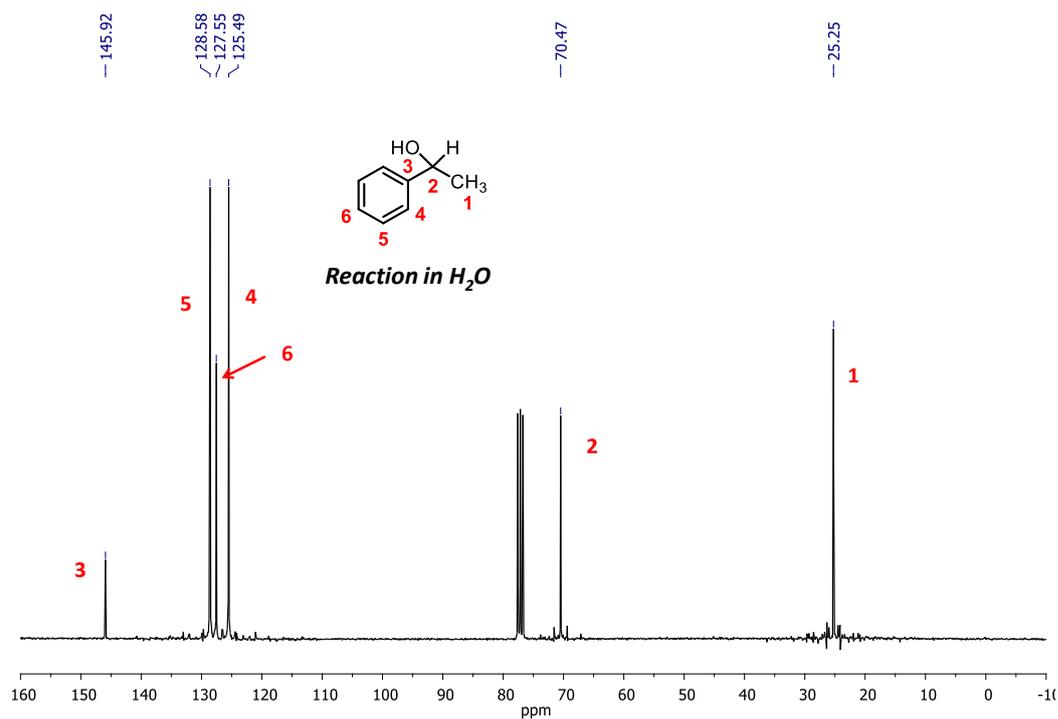


Figure SI.2.67.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of product 12f.

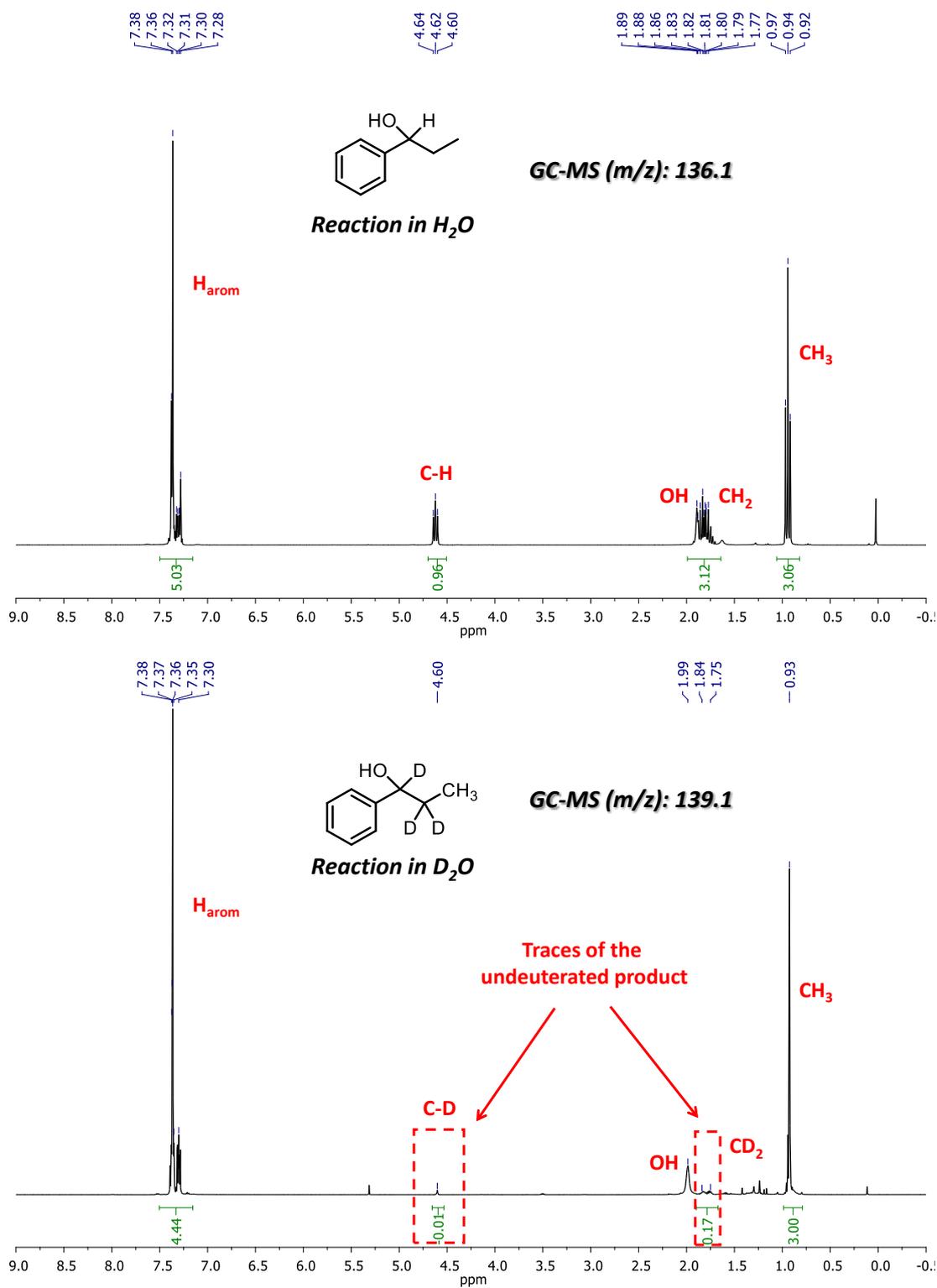
#### 4. NMR of the deuterated products



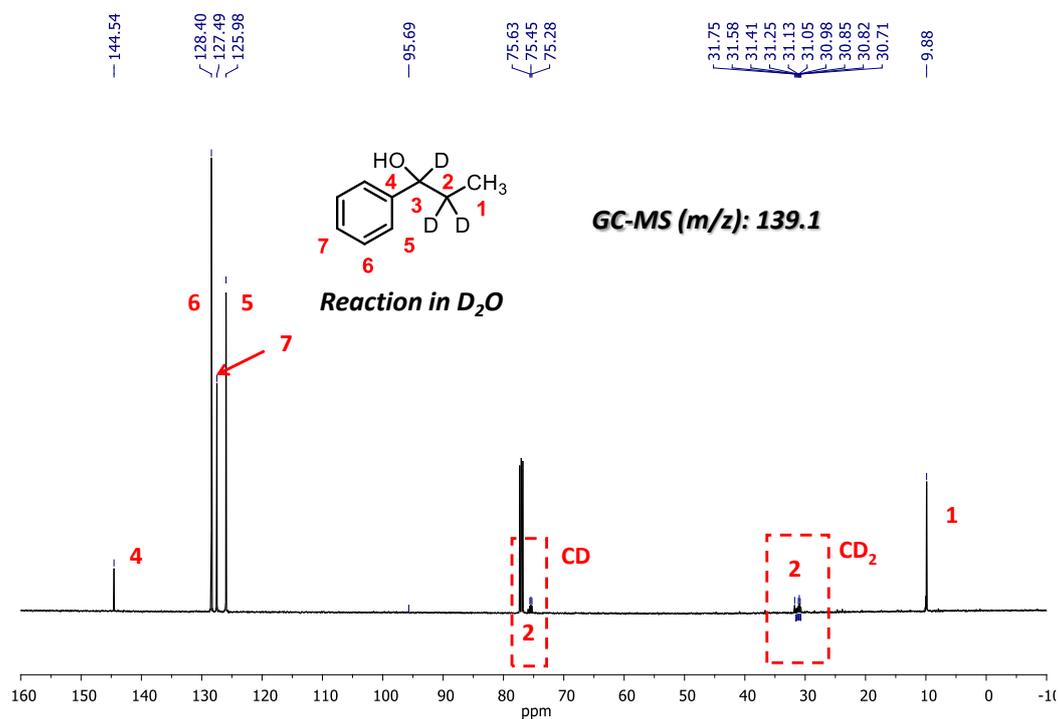
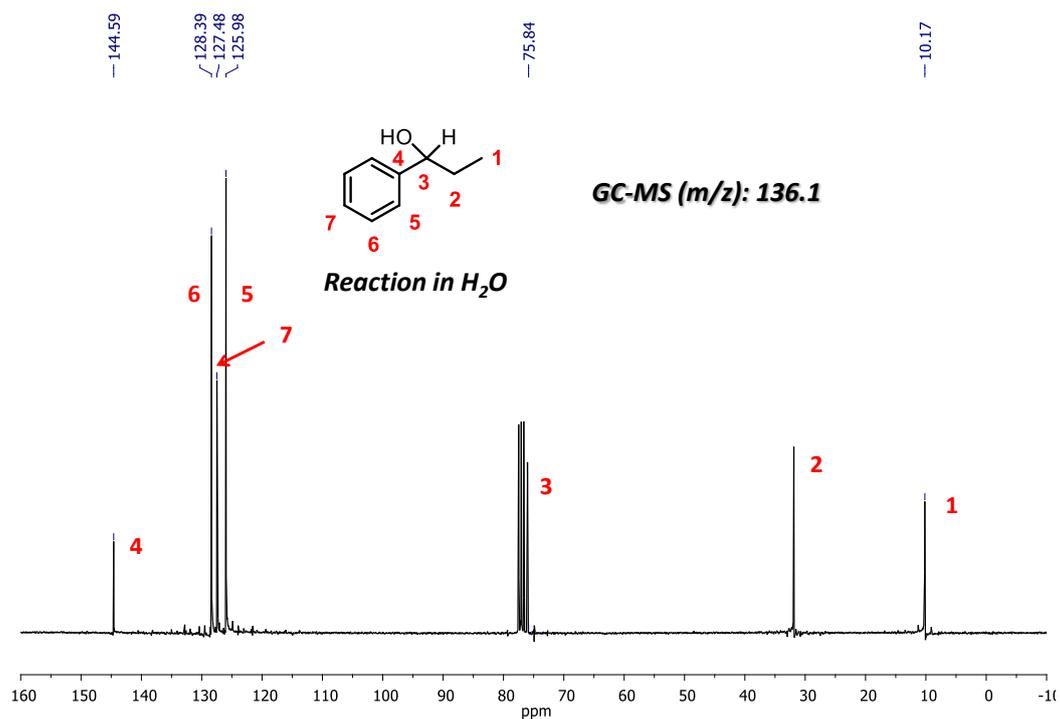
**Figure SI.2.68.** <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 300 K) of the isolated product **10a** and **[D]-10a** using H<sub>2</sub>O (Top) or D<sub>2</sub>O (99.9% in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (3.8 μmol, 3 mol%), **PSi<sub>r</sub>** (2.5 μmol, 2 mol%), substrate (0.126 mmols, 12.4 mM) in H<sub>2</sub>O (or D<sub>2</sub>O):CH<sub>3</sub>CN:Et<sub>3</sub>N (7:3:0.2 mL) irradiated at λ= 447 nm and 30 °C, under N<sub>2</sub>.



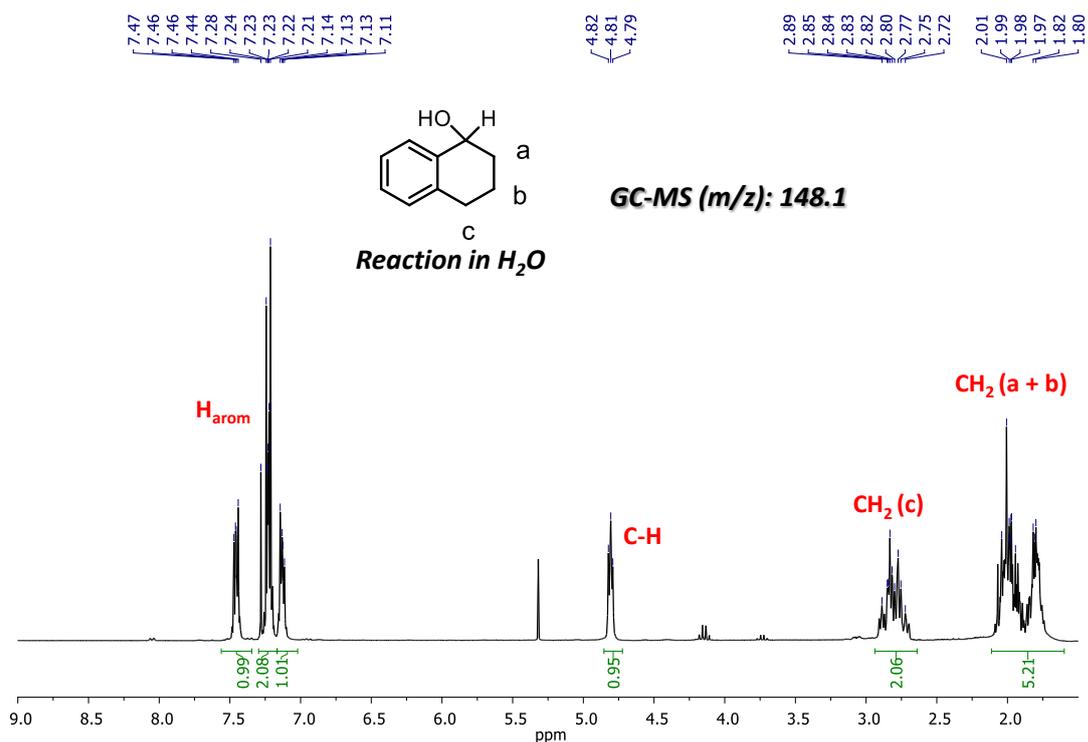
**Figure SI.2.69.**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum ( $\text{CDCl}_3$ , 100.6 MHz, 300 K) of the isolated product **10a** and **[D]-10a** using  $\text{H}_2\text{O}$  (Top) or  $\text{D}_2\text{O}$  (99.9% in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (3.8  $\mu\text{mol}$ , 3 mol%), **PS<sub>Ir</sub>** (2.5  $\mu\text{mol}$ , 2 mol%), substrate (0.126 mmols, 12.4 mM) in  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ): $\text{CH}_3\text{CN}$ : $\text{Et}_3\text{N}$  (7:3:0.2 mL) irradiated at  $\lambda = 447$  nm and 30  $^\circ\text{C}$ , under  $\text{N}_2$ .



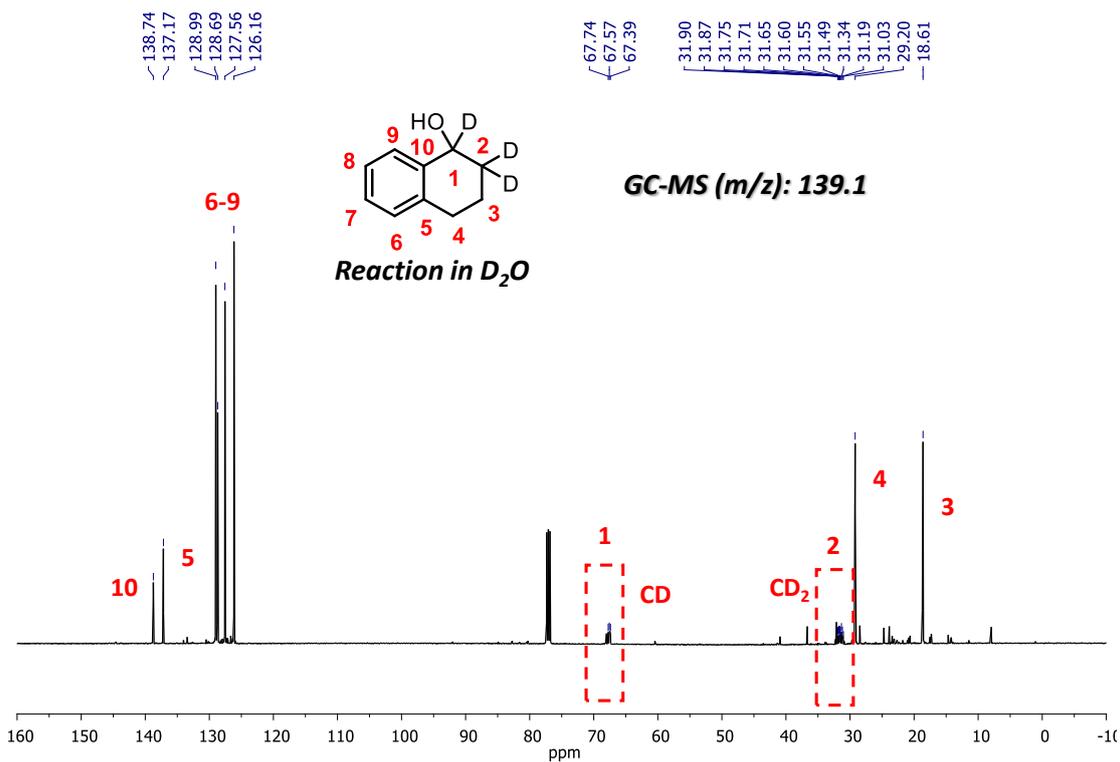
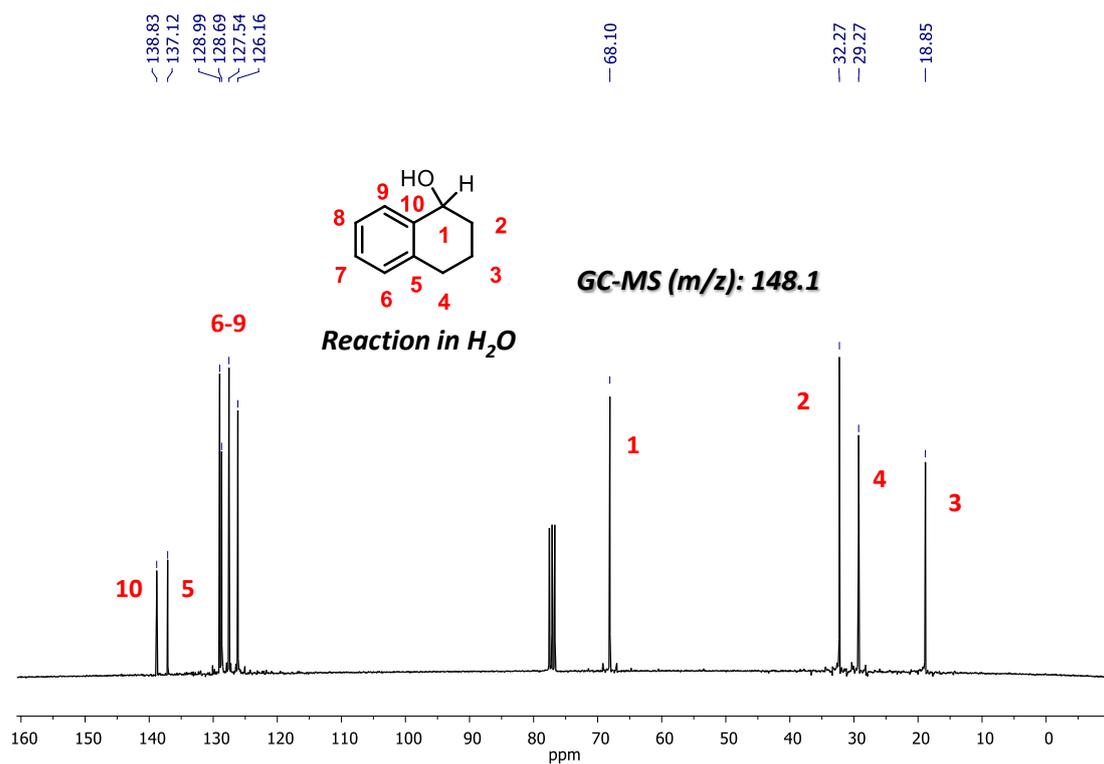
**Figure SI.2.70.** <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 300 K) of the isolated product **10b** and **[D]-10b** using H<sub>2</sub>O (Top) or D<sub>2</sub>O (99.9 % in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (3.8 μmol, 3 mol%), **PS<sub>Ir</sub>** (2.5 μmol, 2 mol%), substrate (0.126 mmol, 12.4 mM) in H<sub>2</sub>O (or D<sub>2</sub>O):CH<sub>3</sub>CN:Et<sub>3</sub>N (7:3:0.2 mL) irradiated at λ= 447 nm and 30 °C, under N<sub>2</sub>.



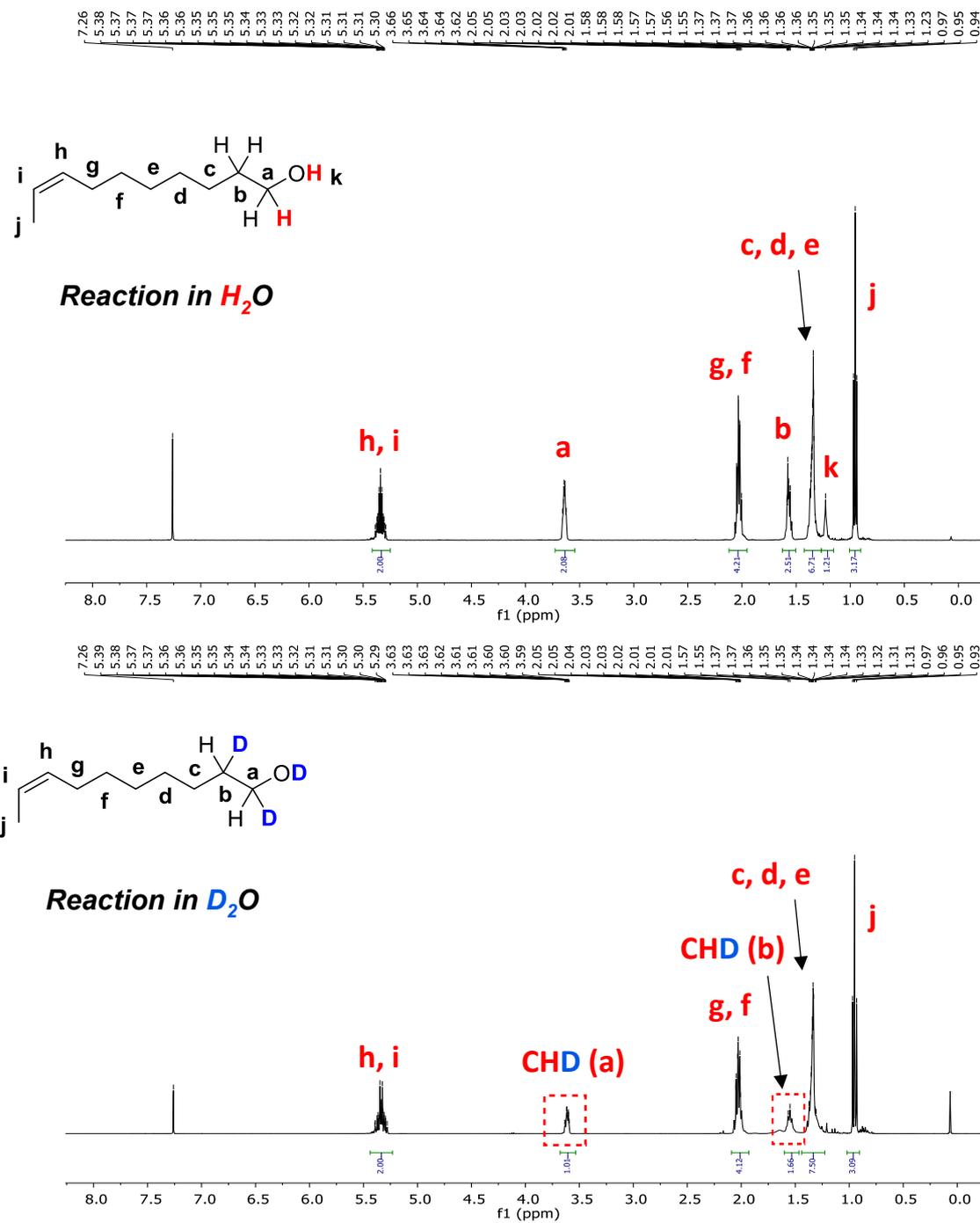
**Figure SI.2.71.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (CDCl<sub>3</sub>, 100.6 MHz, 300 K) of the isolated product **10b** and **[D]-10b** using H<sub>2</sub>O (Top) or D<sub>2</sub>O (99.9 % in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (3.8 μmol, 3 mol%), **PS<sub>r</sub>** (2.5 μmol, 2 mol%), substrate (0.126 mmol, 12.4 mM) in H<sub>2</sub>O (or D<sub>2</sub>O):CH<sub>3</sub>CN:Et<sub>3</sub>N (7:3:0.2 mL) irradiated at λ= 447 nm and 30 °C, under N<sub>2</sub>.



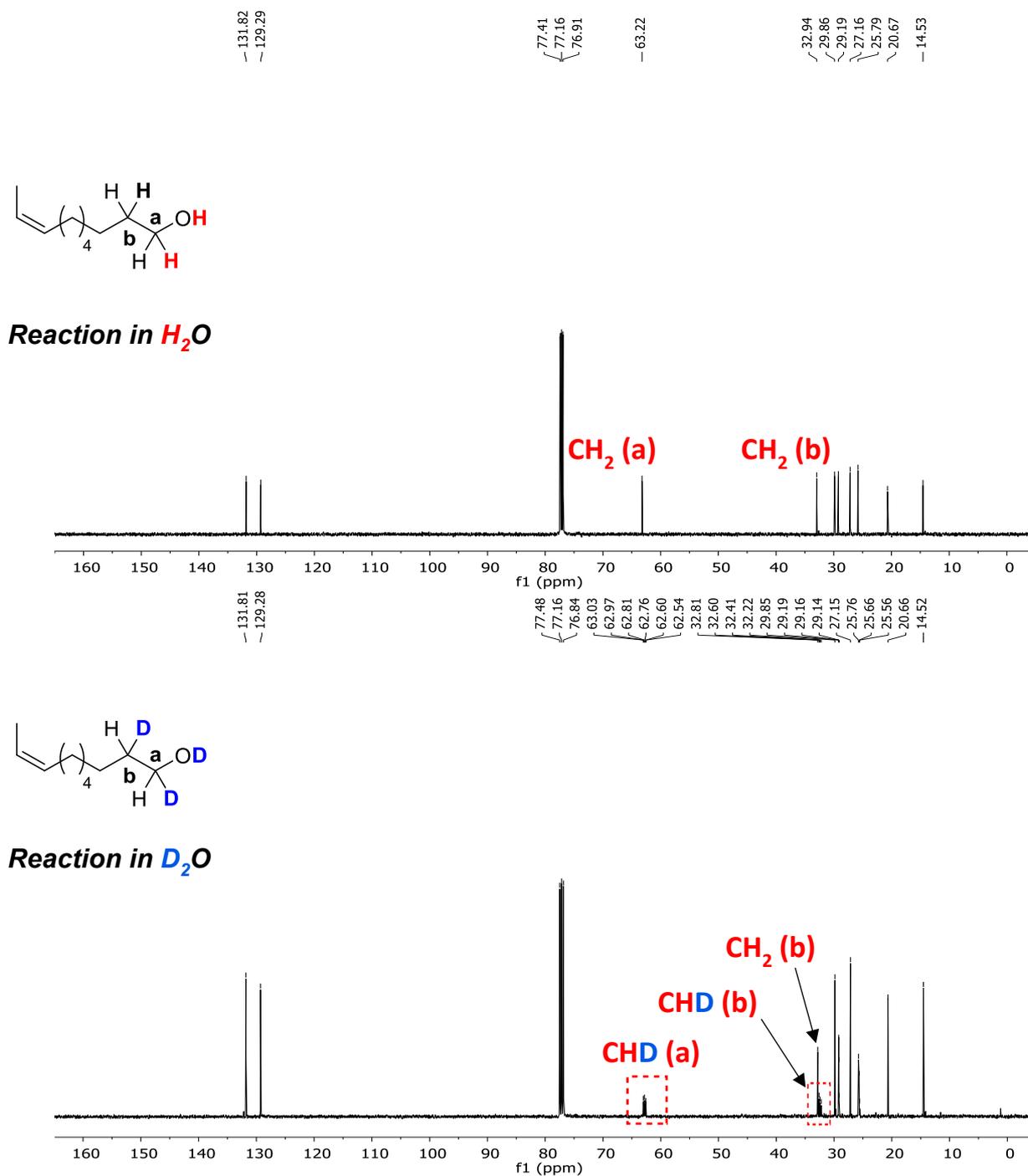
**Figure SI.272.** <sup>1</sup>H-NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 300 K) of the isolated product **10j** and **[D]-10j** using H<sub>2</sub>O (Top) or D<sub>2</sub>O (99.9 % in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (3.8 μmol, 3 mol%), **PS<sub>Ir</sub>** (2.5 μmol, 2 mol%), substrate (0.126 mmol, 12.4 mM) in H<sub>2</sub>O (or D<sub>2</sub>O):CH<sub>3</sub>CN:Et<sub>3</sub>N (7:3:0.2 mL) irradiated at λ= 447 nm and 30 °C, under N<sub>2</sub>.



**Figure SI.2.73.**  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum ( $\text{CDCl}_3$ , 100.6 MHz, 300 K) of the isolated product **10j** and **[D]-10j** using  $\text{H}_2\text{O}$  (Top) or  $\text{D}_2\text{O}$  (99.9 % in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (3.8  $\mu\text{mol}$ , 3 mol%), **PS<sub>ir</sub>** (2.5  $\mu\text{mol}$ , 2 mol%), substrate (0.126 mmol, 12.4 mM) in  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ): $\text{CH}_3\text{CN}$ : $\text{Et}_3\text{N}$  (7:3:0.2 mL) irradiated at  $\lambda = 447$  nm and 30  $^\circ\text{C}$ , under  $\text{N}_2$ .



**Figure SI.2.74.**  $^1H$ -NMR spectrum ( $CDCl_3$ , 400 MHz, 300 K) of the isolated products **16h** and **[D]-16h** using  $H_2O$  (Top) or  $D_2O$  (99.9% in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (6 mol%), **PS<sub>Cu</sub>** (6 mol%), substrate (0.044 mmol, 4.4 mM) in  $H_2O$  (or  $D_2O$ ): $CH_3CN$ : $Pr_2EtN$  (6:4:0.2 mL) irradiated at  $\lambda = 447$  nm and 15 °C for 5h, under  $N_2$ .



**Figure SI.2.75.**  $^{13}C\{^1H\}$ -NMR spectrum (CDCl<sub>3</sub>, 100.6 MHz, 300 K) of the isolated products **16h** and **[D]-16h** using  $H_2O$  (Top) or  $D_2O$  (99.9 % in deuterium) (Bottom) in the solvent mixture, respectively. Conditions: **1** (6 mol%), **PS**<sub>Cu</sub> (6 mol%), substrate (0.044 mmol, 4.4 mM) in  $H_2O$  (or  $D_2O$ ):CH<sub>3</sub>CN:Pr<sub>2</sub>EtN (6:4:0.2 mL) irradiated at  $\lambda = 447$  nm and 15 °C for 5h, under N<sub>2</sub>.

## 5. Intramolecular reduction

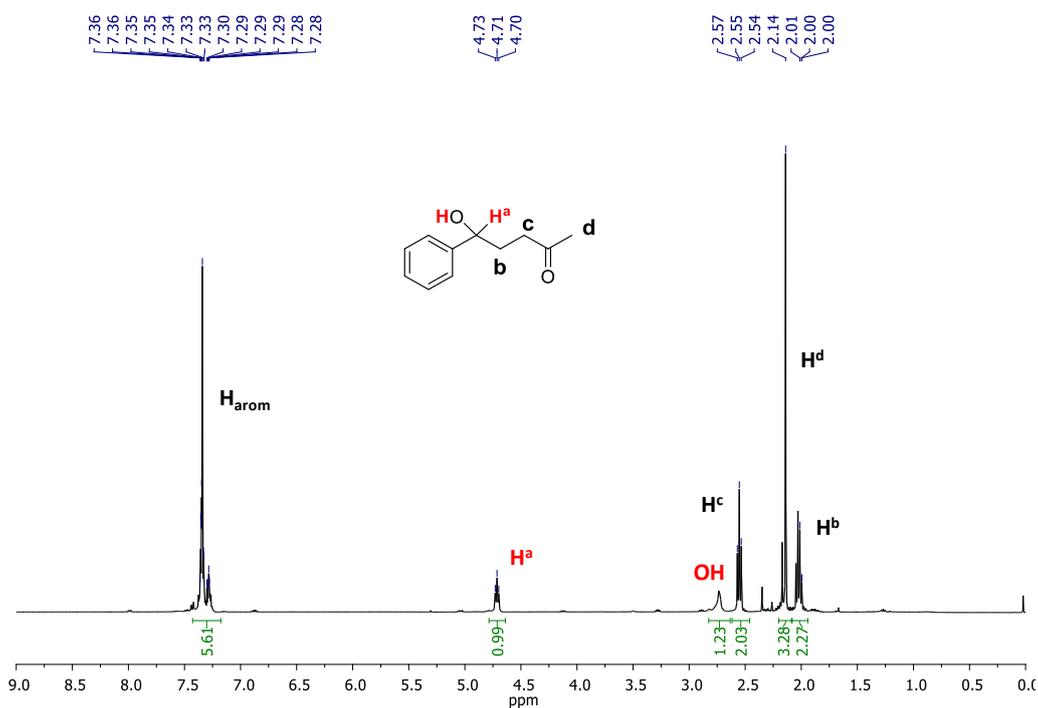


Figure SI.2.76. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of the isolated product **5-Hydroxy-5-phenylpentan-2-one (9af)**.

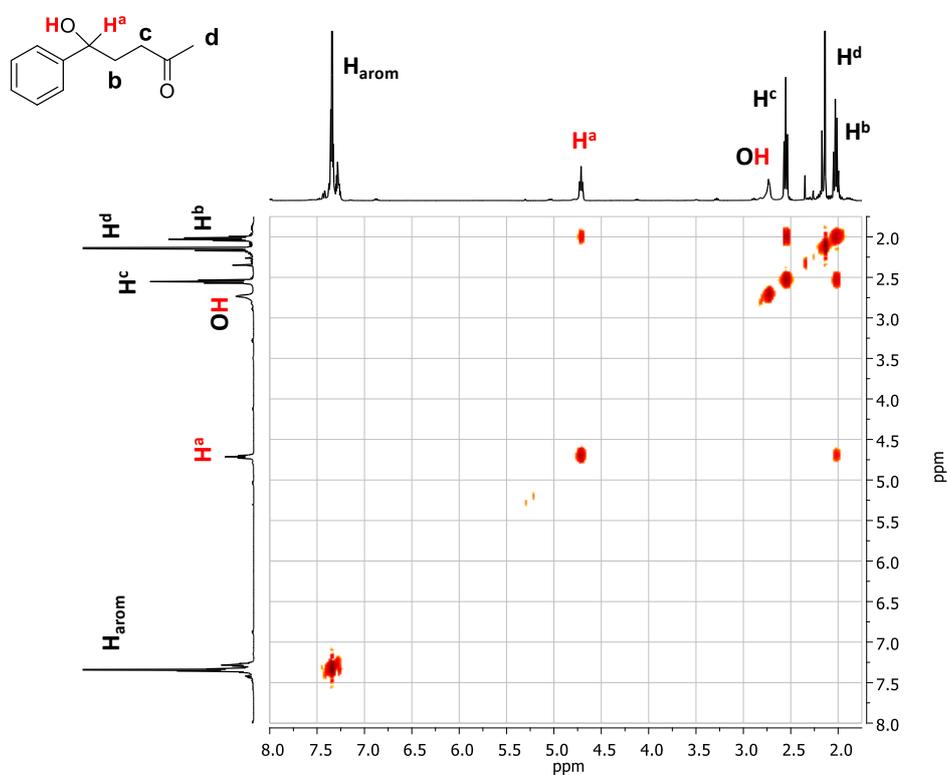


Figure SI.2.77. <sup>1</sup>H-<sup>1</sup>H COSY (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of the isolated product **5-Hydroxy-5-phenylpentan-2-one (9af)**.



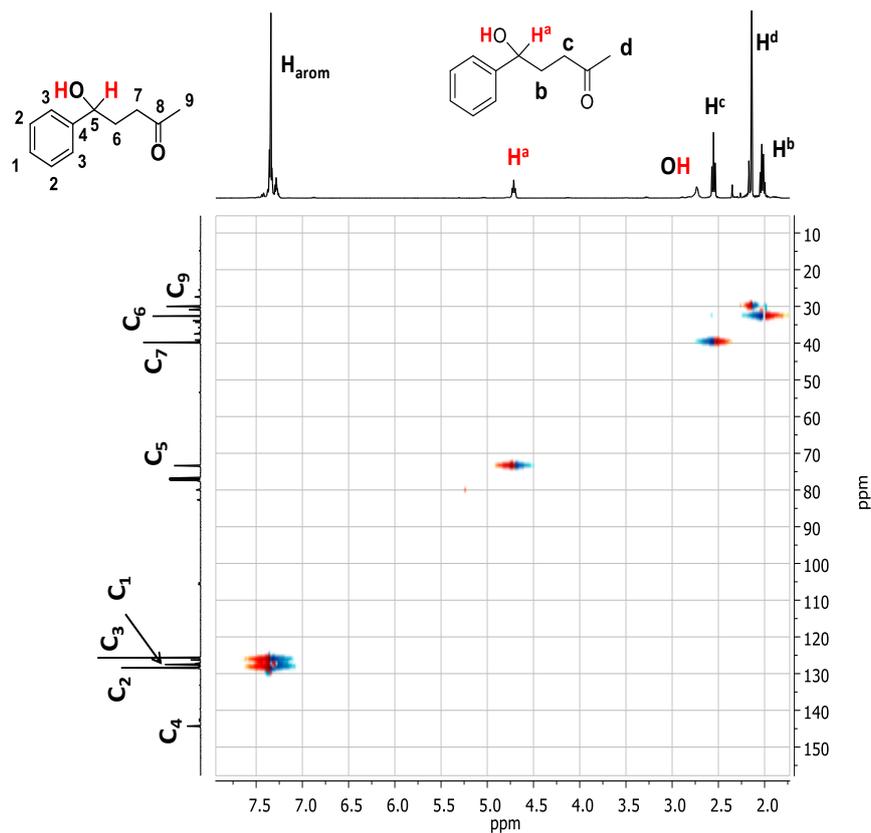


Figure SI.2.80.  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 5-Hydroxy-5-phenylpentan-2-one (9af).

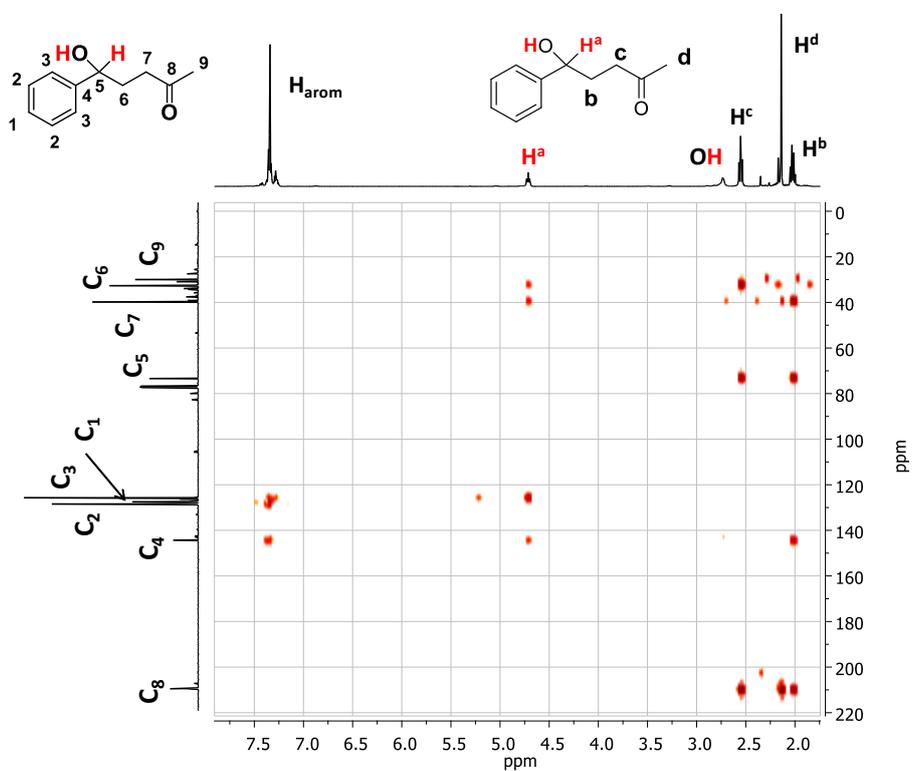
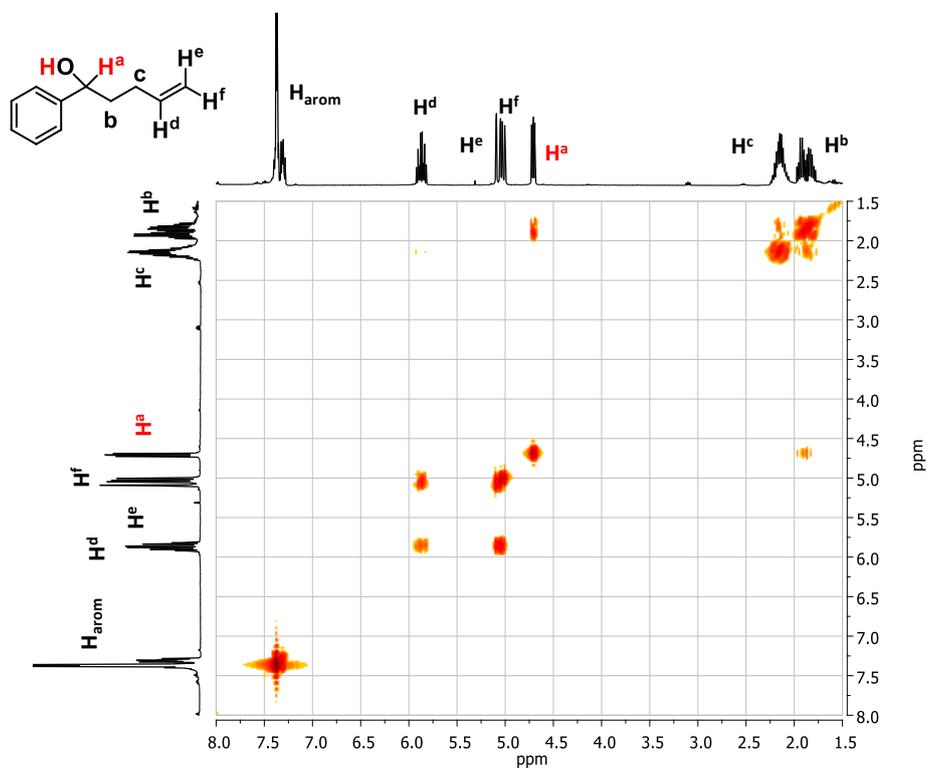
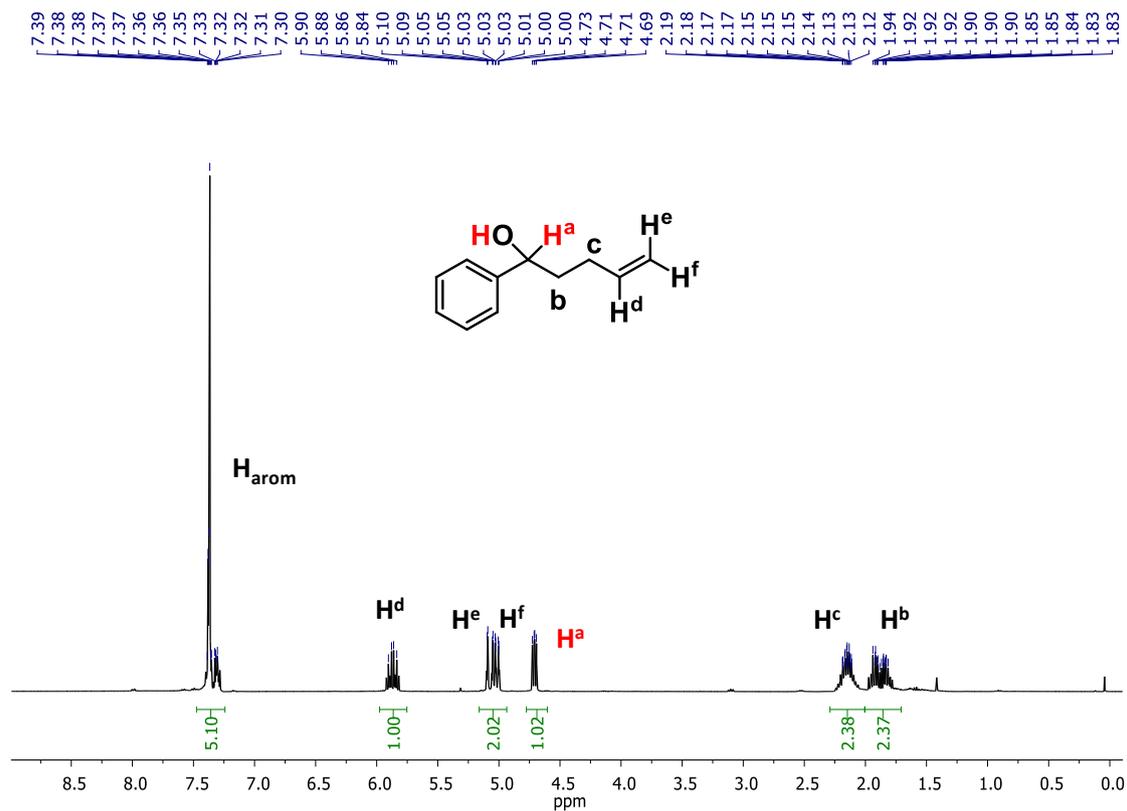
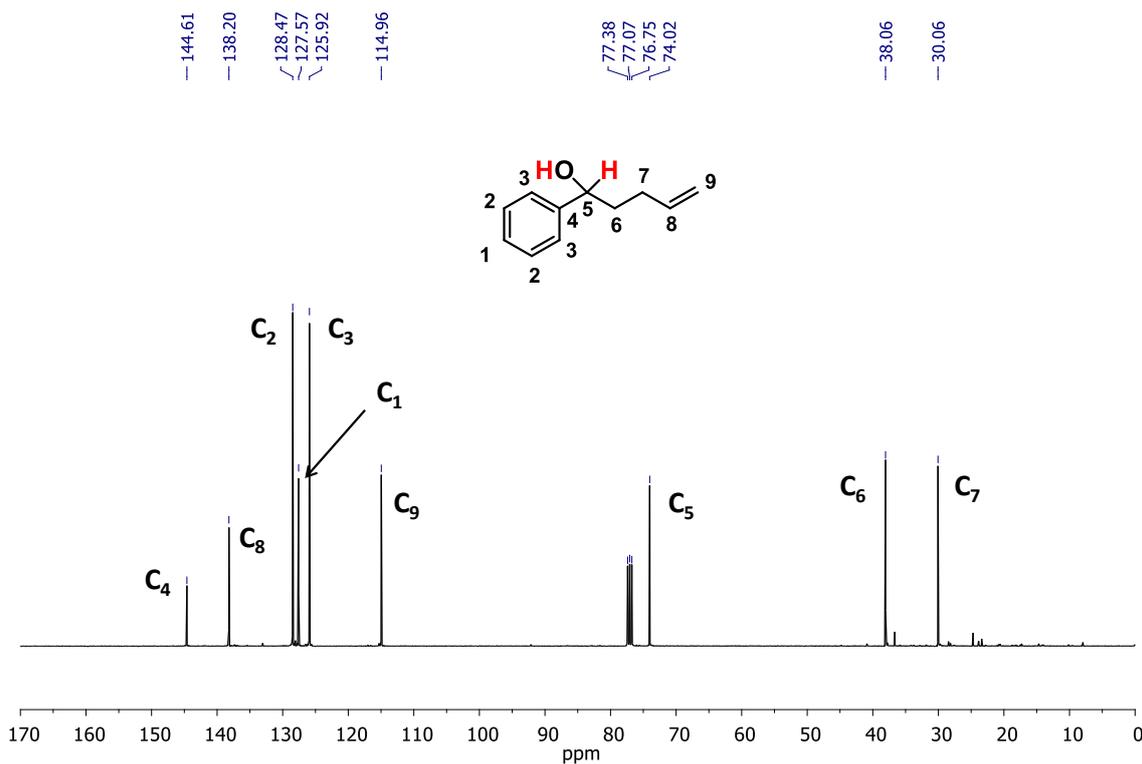
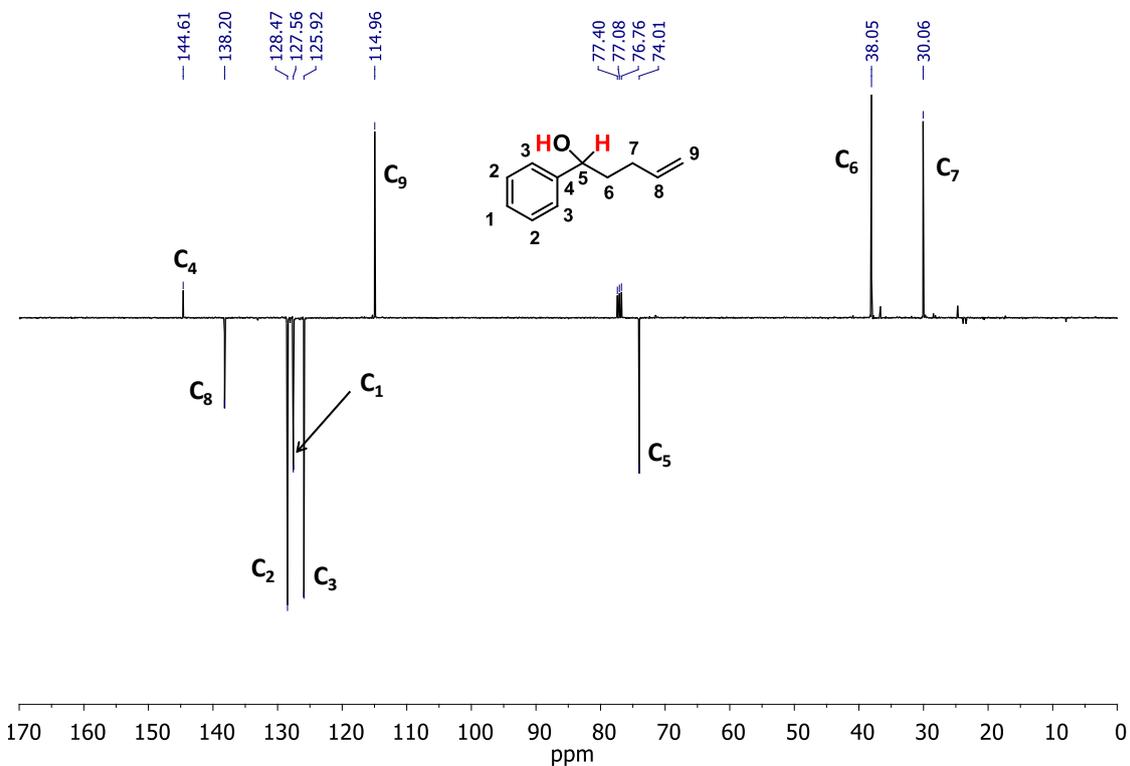


Figure SI.2.81.  $^1\text{H}$ - $^{13}\text{C}$  HMBC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 5-Hydroxy-5-phenylpentan-2-one (9af).

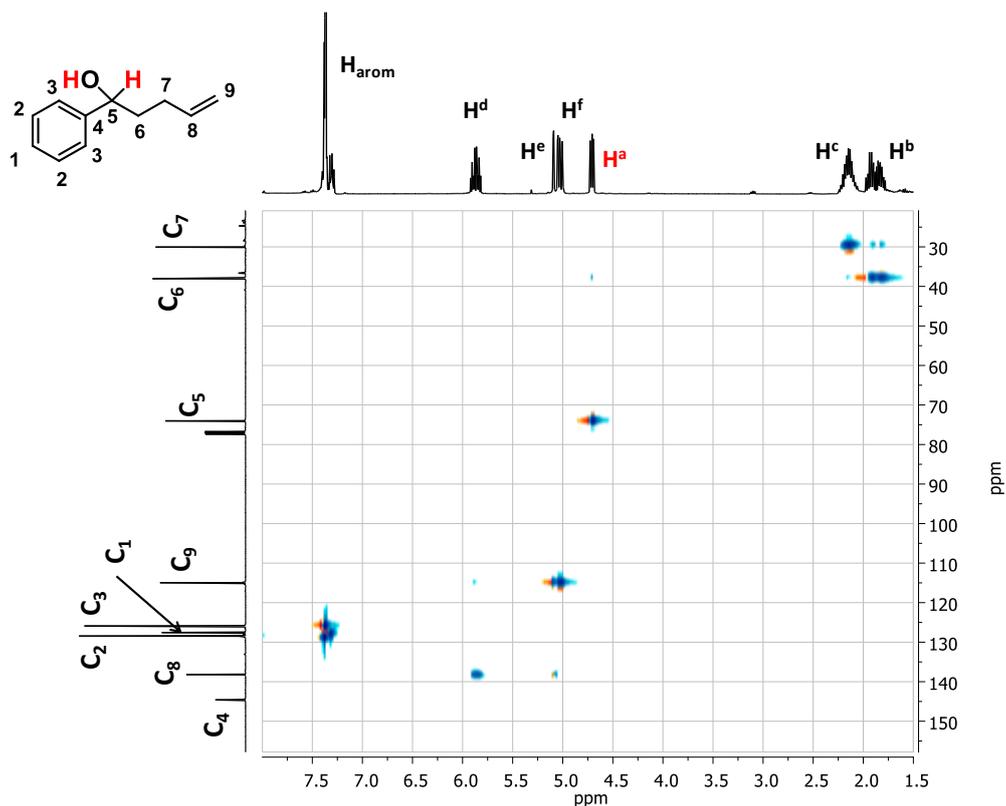




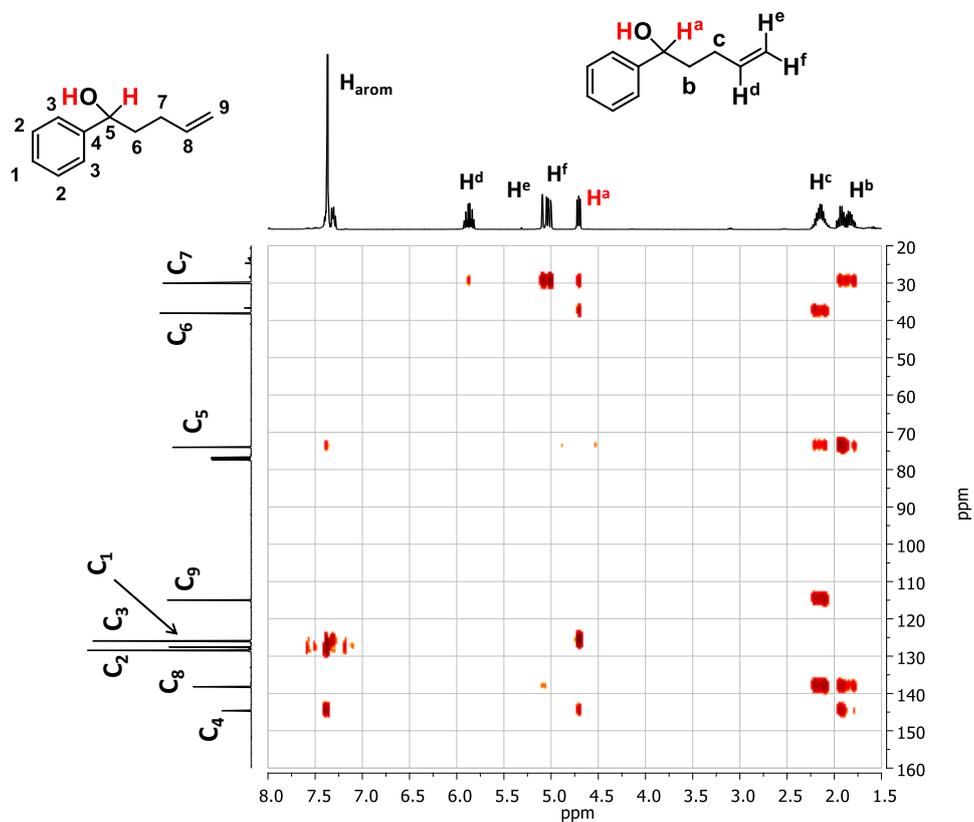
**Figure SI.2.84.**  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ , 100.6 MHz, 300 K) spectrum of the isolated product **1-Phenyl-4-penten-1-ol (9ag)**.



**Figure SI.2.85.**  $^{13}\text{C}\{^1\text{H}\}$ -DEPTQ-135-NMR ( $\text{CDCl}_3$ , 100.6 MHz, 300 K) spectrum of the isolated product **1-Phenyl-4-penten-1-ol (9ag)**.



**Figure SI.2.86.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 1-Phenyl-4-penten-1-ol (**9ag**).



**Figure SI.2.87.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 1-Phenyl-4-penten-1-ol (**9ag**).

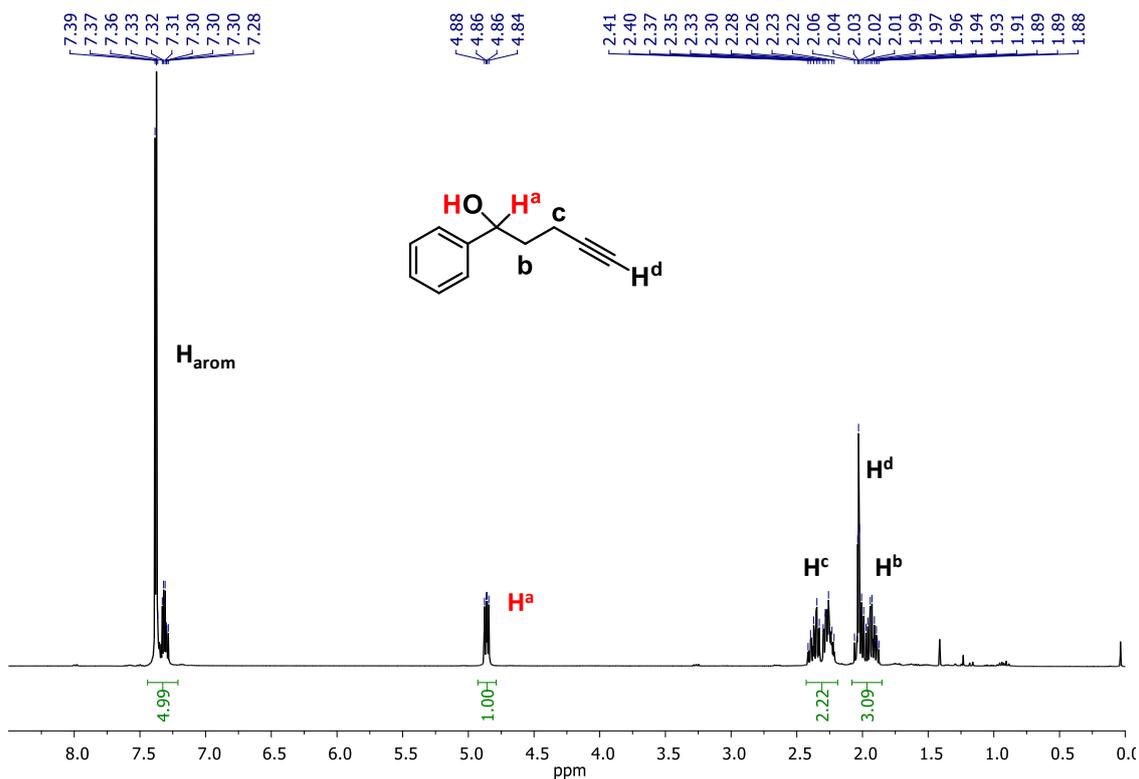


Figure SI.2.88.  $^1\text{H-NMR}$  (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of the isolated product **1-Phenyl-4-pentyn-1-ol (9ah)**.

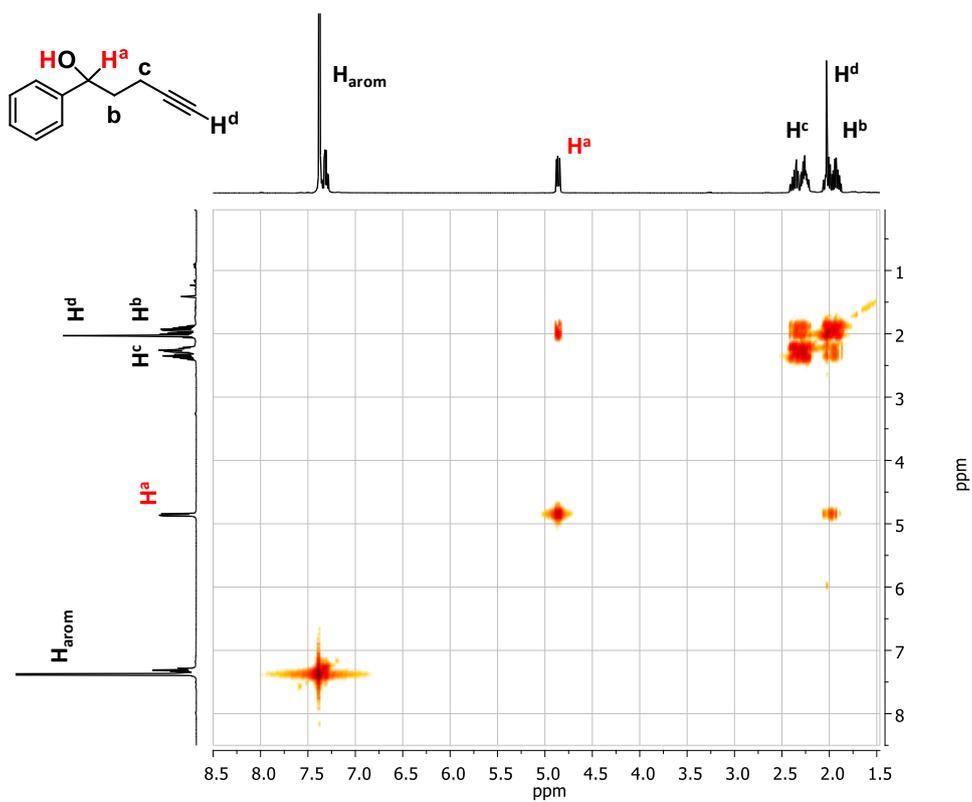


Figure SI.2.89.  $^1\text{H-}^1\text{H COSY}$  (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of the isolated product **1-Phenyl-4-pentyn-1-ol (9ah)**.

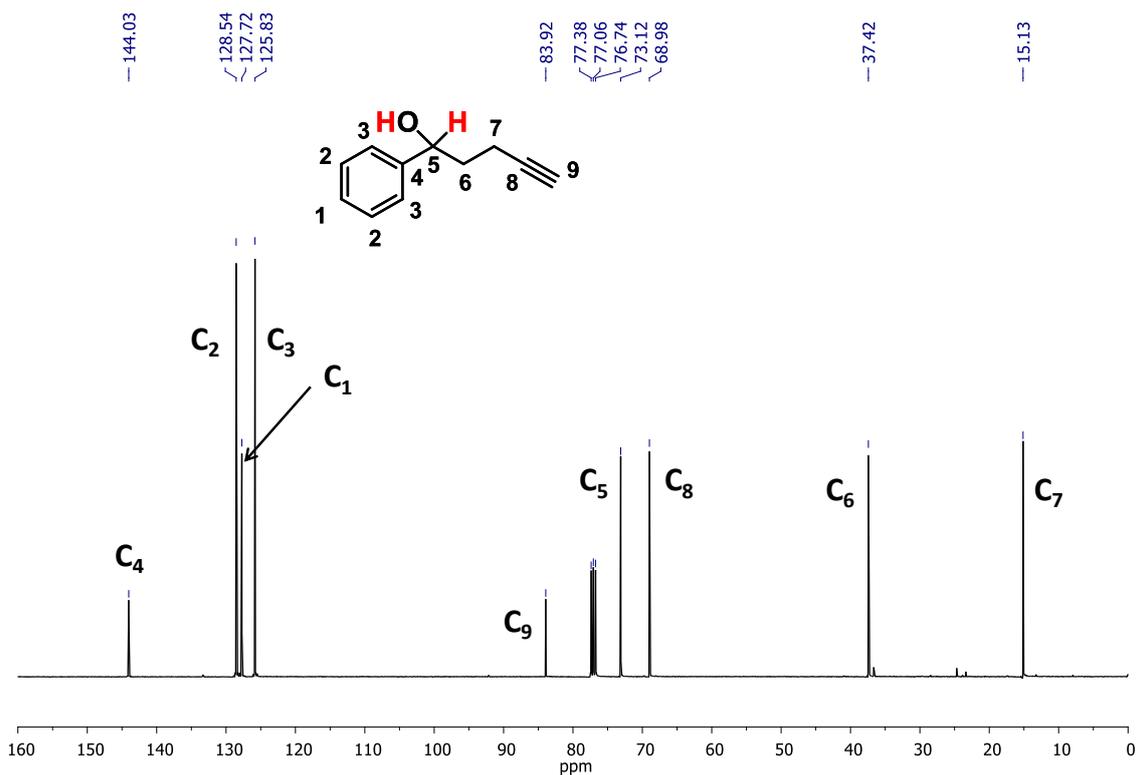


Figure SI.2.90.  $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of the isolated product **1-Phenyl-4-pentyn-1-ol (9ah)**.

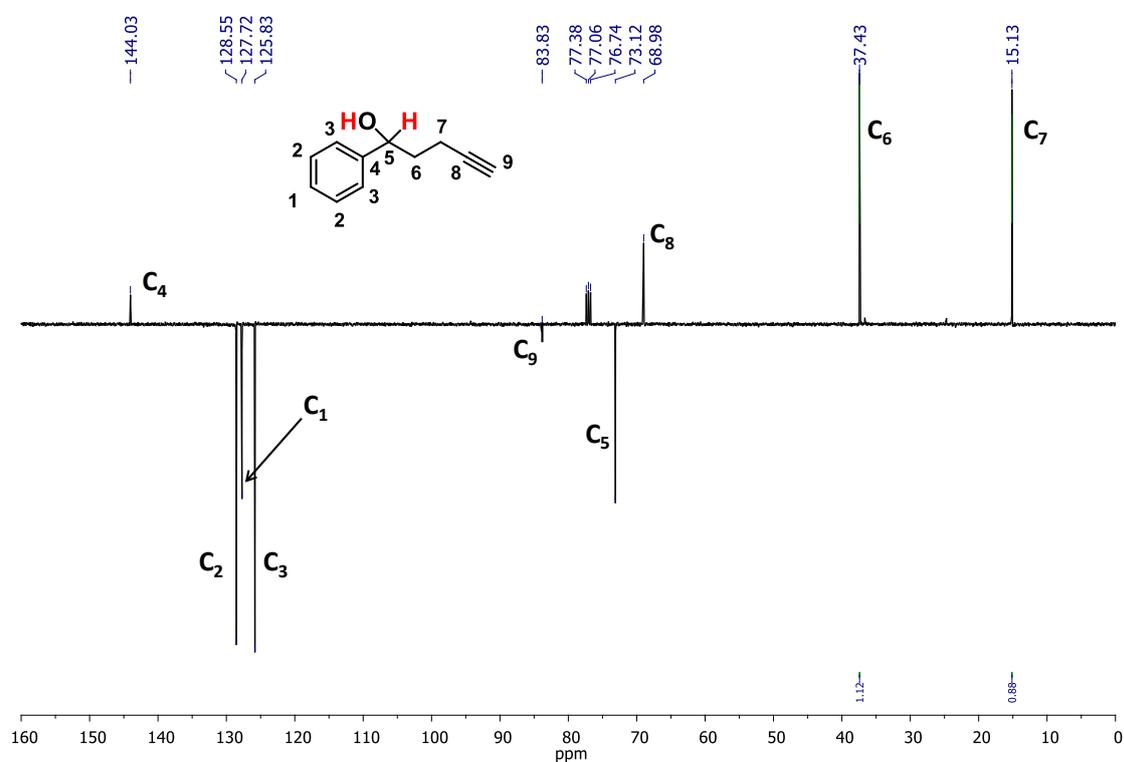


Figure SI.2.91.  $^{13}\text{C}\{^1\text{H}\}$ -DEPTQ-135-NMR (CDCl<sub>3</sub>, 100.6 MHz, 300 K) spectrum of the isolated product **1-Phenyl-4-pentyn-1-ol (9ah)**.

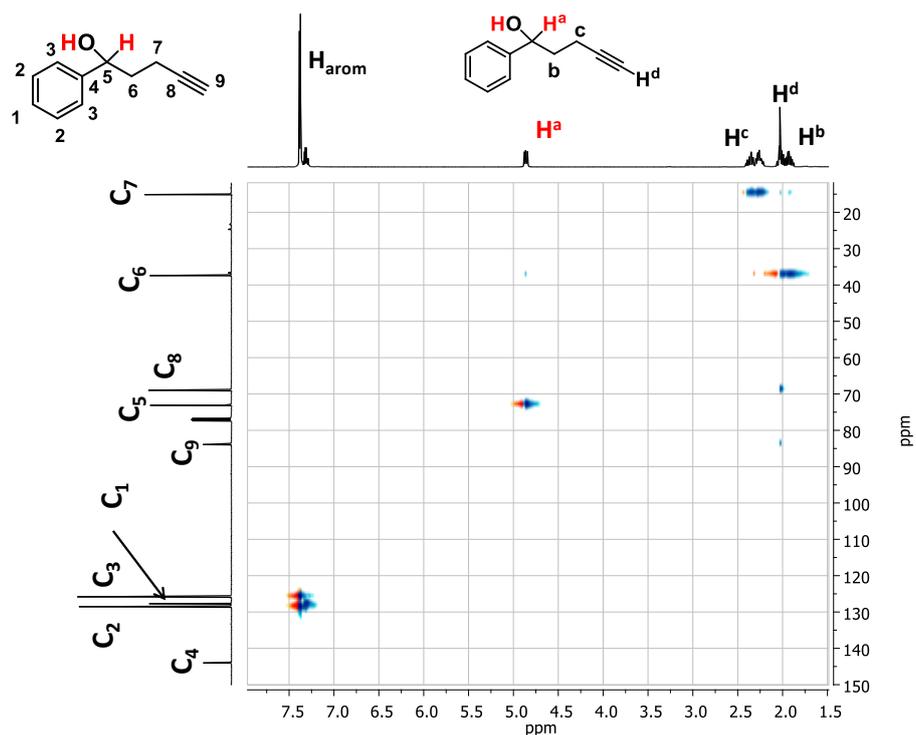


Figure SI.2.92.  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 1-Phenyl-4-pentyn-1-ol (9ah).

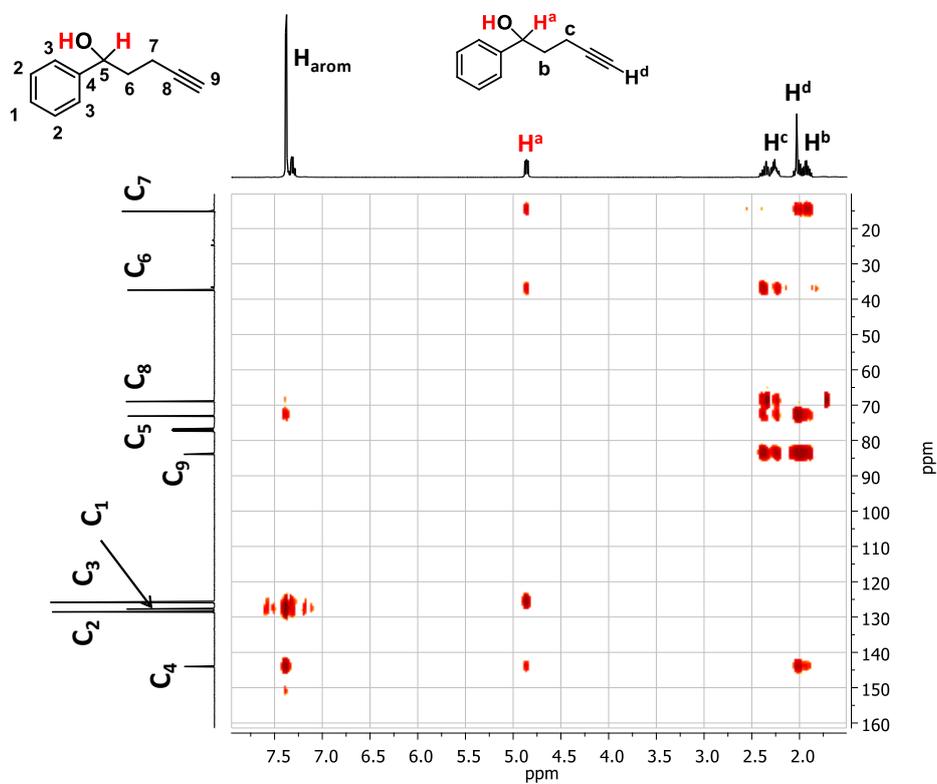


Figure SI.2.93.  $^1\text{H}$ - $^{13}\text{C}$  HMBC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 1-Phenyl-4-pentyn-1-ol (9ah).

## 6. NMR of the radical clock ring-opening products

### Phenyl(2-phenylcyclopropyl)methanone

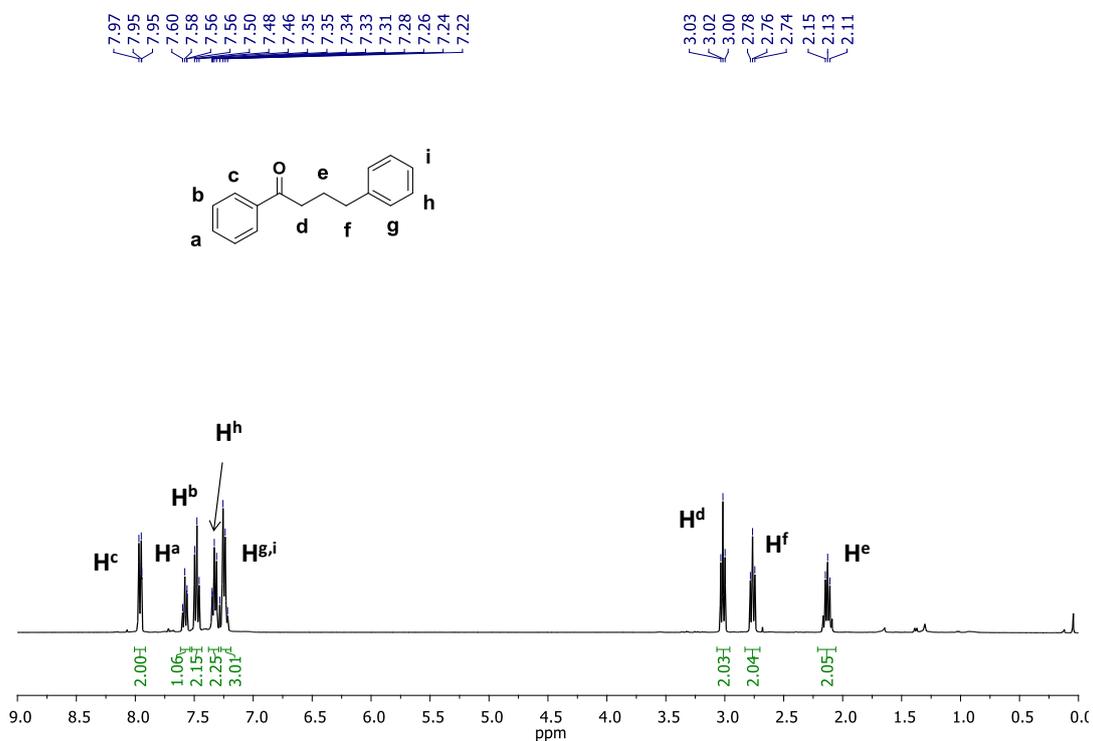


Figure SI.2.94. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of the isolated product 1,4-diphenylbutan-1-one.

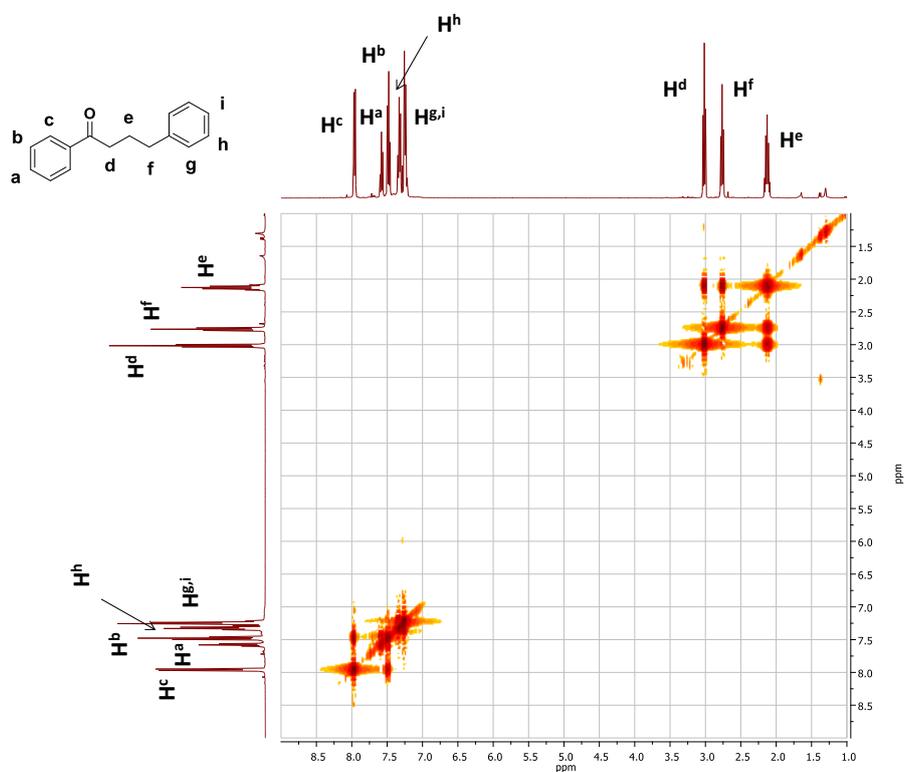
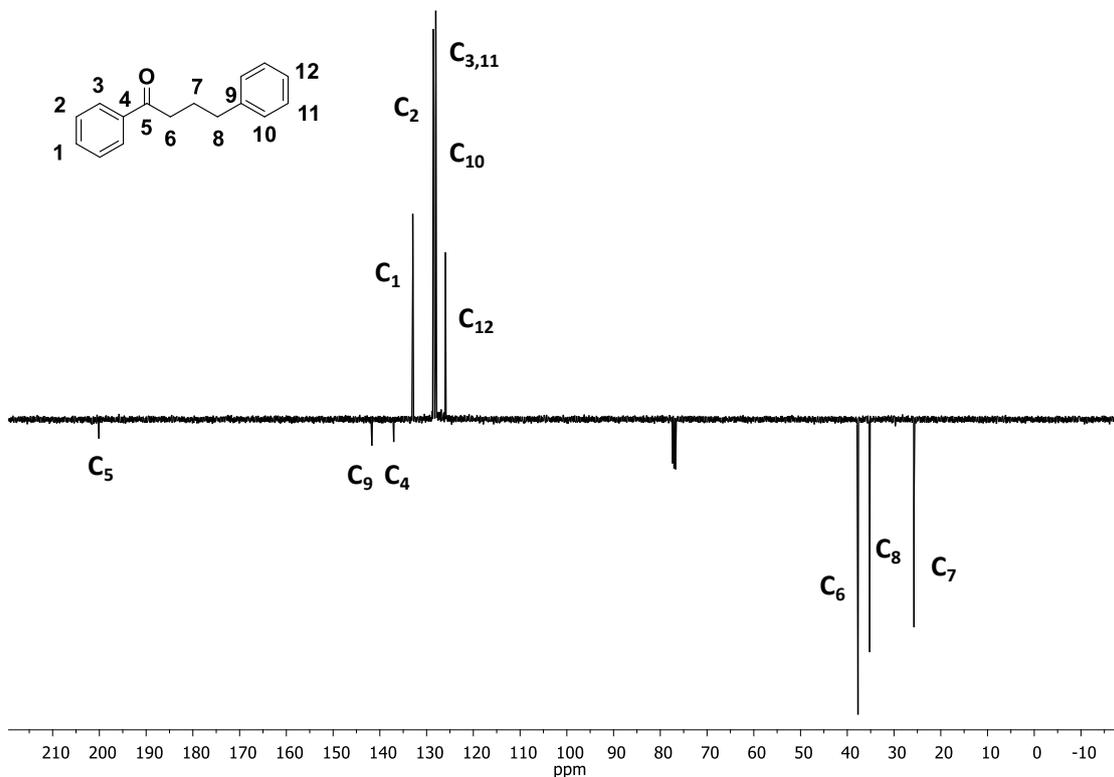
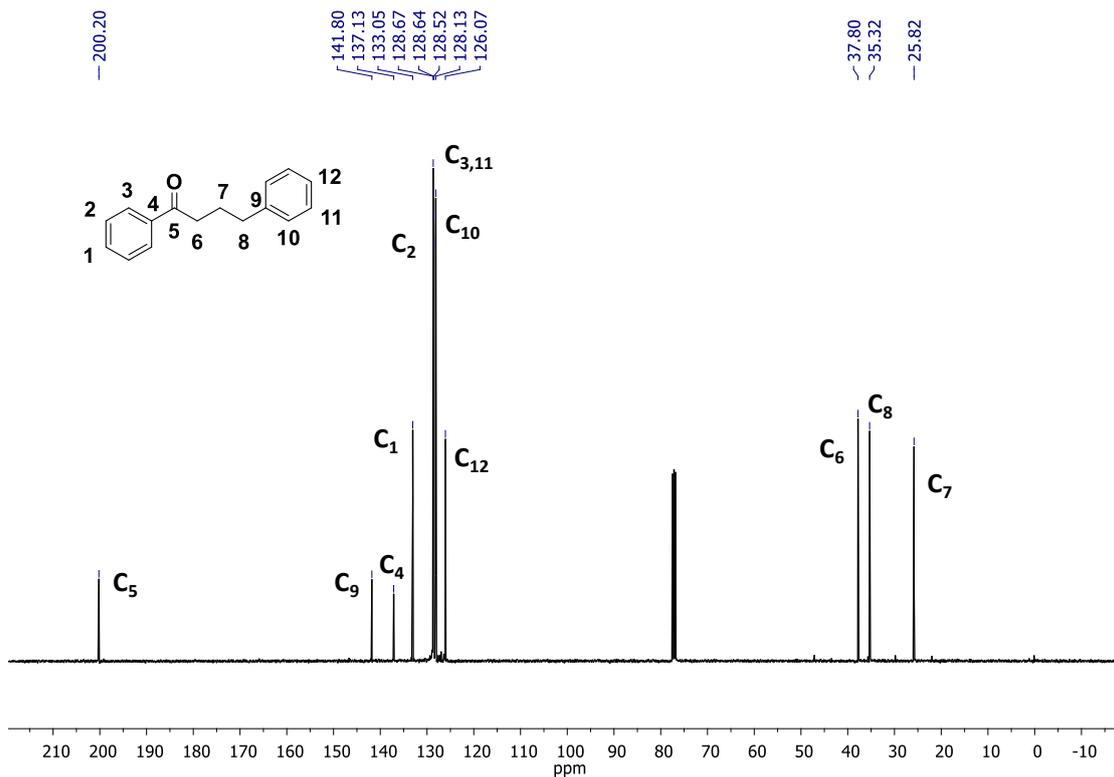
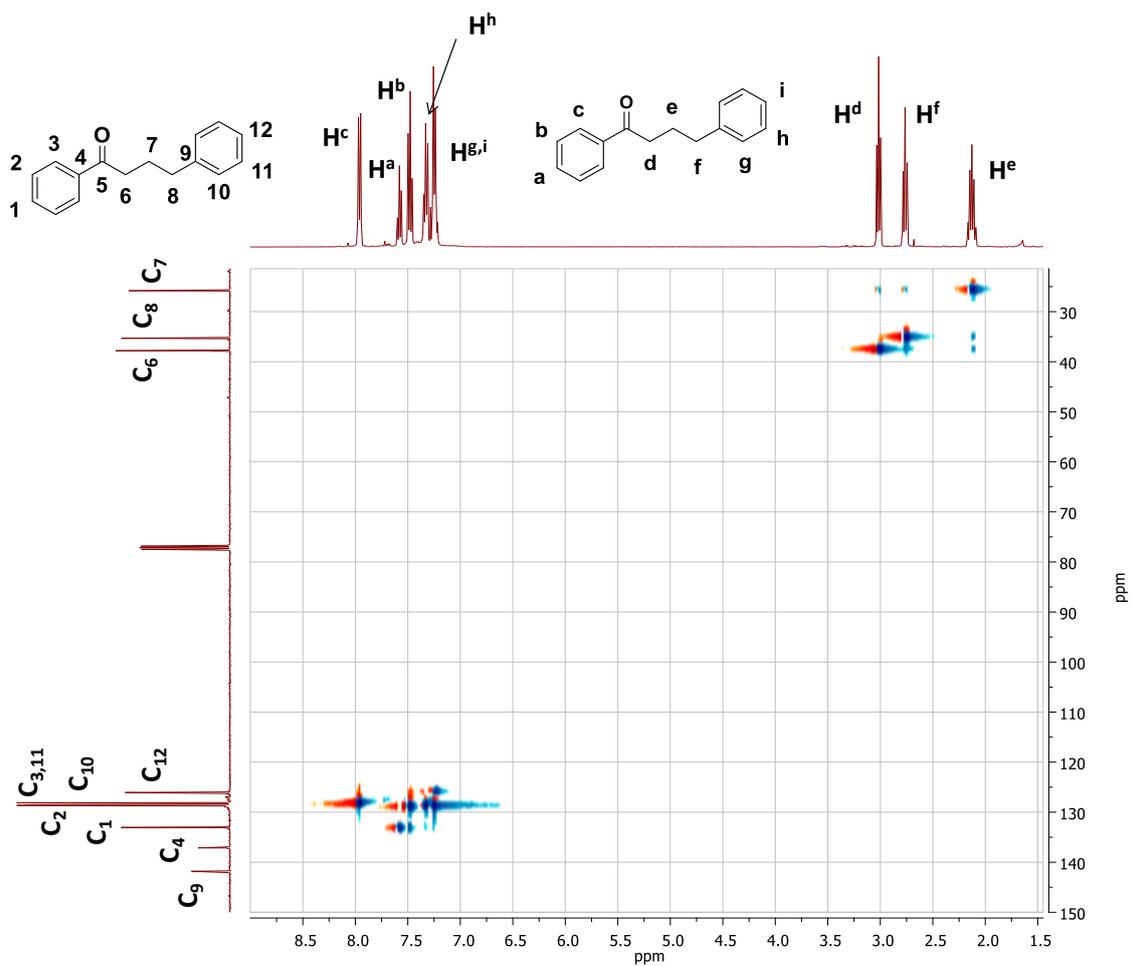


Figure SI.2.95. <sup>1</sup>H-<sup>1</sup>H COSY (CDCl<sub>3</sub>, 400 MHz, 300 K) spectrum of the isolated product 1,4-diphenylbutan-1-one.





**Figure SI.2.98.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 1,4-diphenylbutan-1-one.

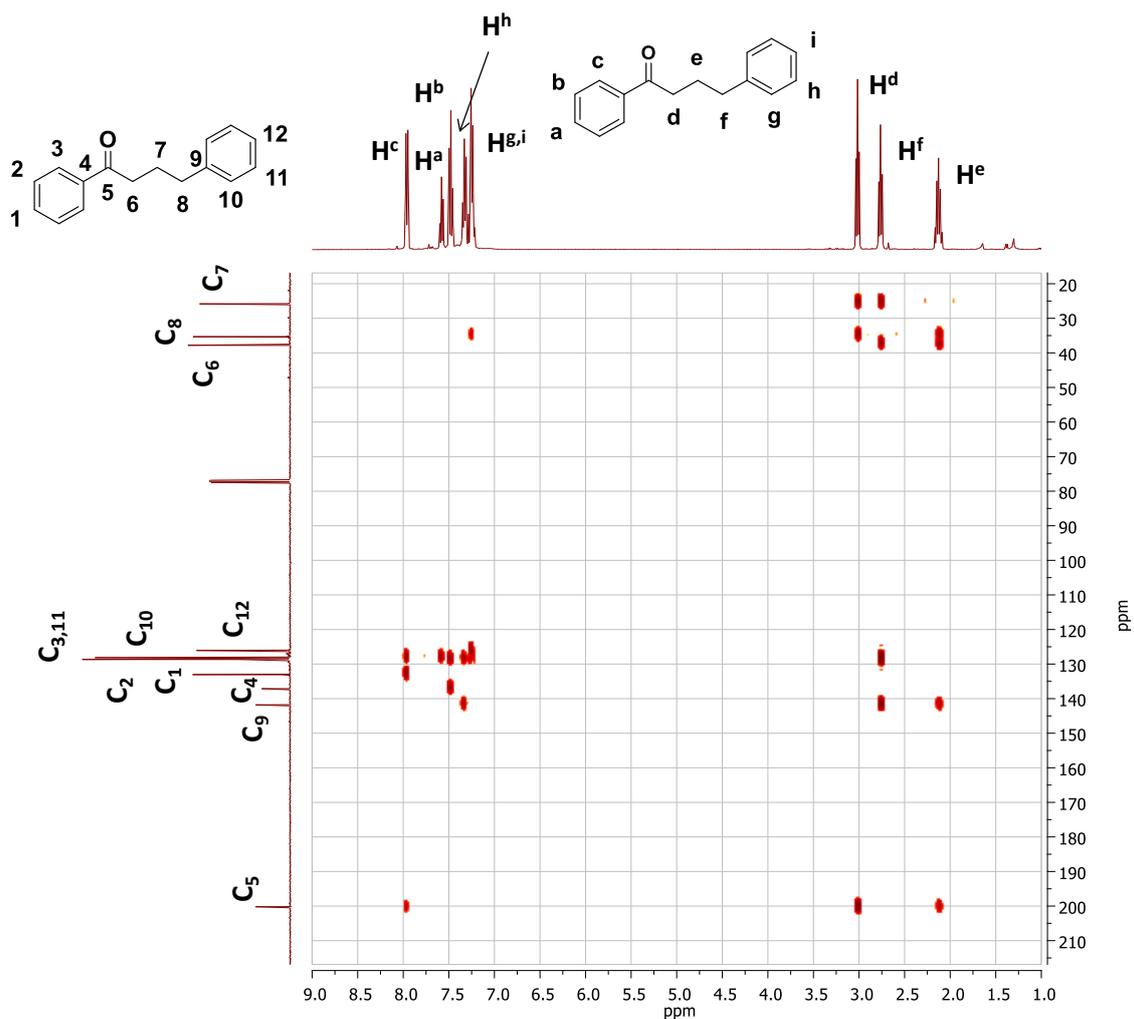


Figure SI.2.99.  $^1\text{H}$ - $^{13}\text{C}$  HMBC ( $\text{CDCl}_3$ , 400 MHz, 300 K) phase sensitive spectrum of the isolated product 1,4-diphenylbutan-1-one.

## 7. GC chromatograms from the catalysis

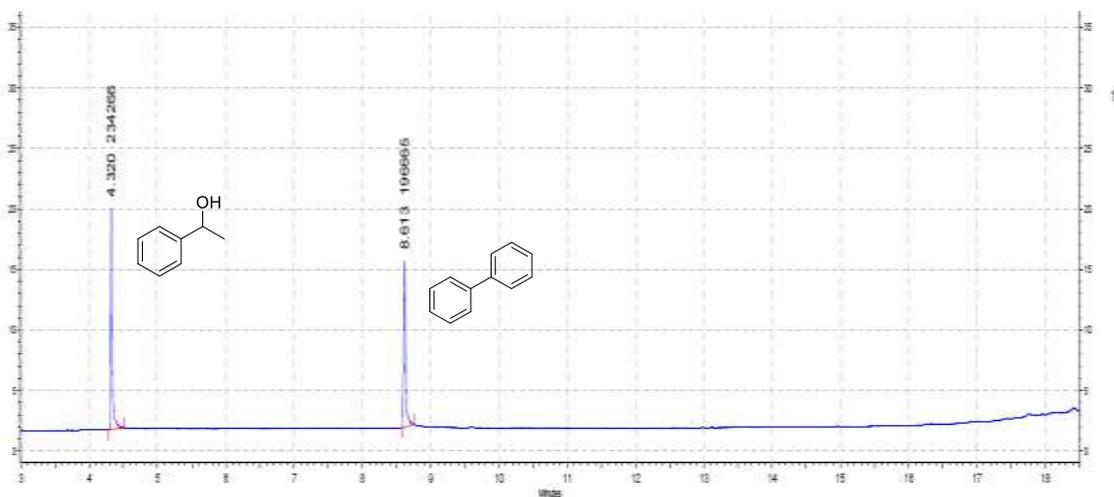


Figure SI.2.100. GC-FID chromatogram of the reduced product **10a** from the catalysis.



Figure SI.2.101. GC-FID chromatogram of the reduced product **10b** from the catalysis.

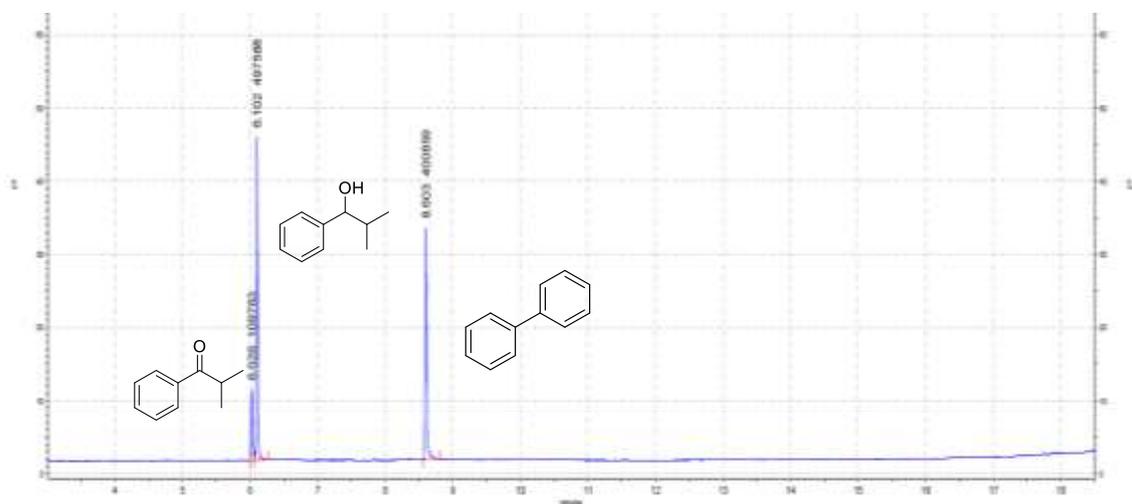


Figure SI.2.102. GC-FID chromatogram of the reduced product **10c** from the catalysis.

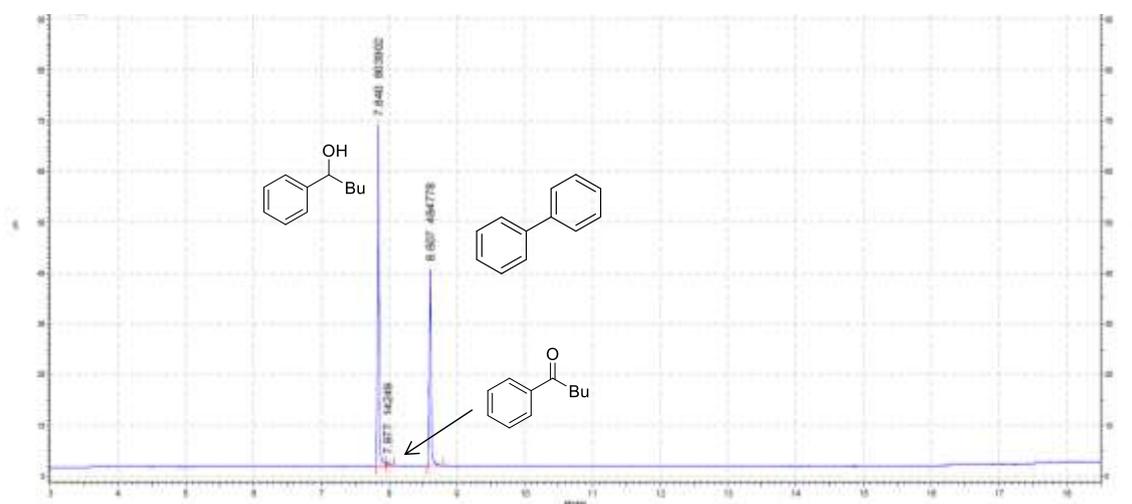


Figure SI.2.103. GC-FID chromatogram of the reduced product **10d** from the catalysis.

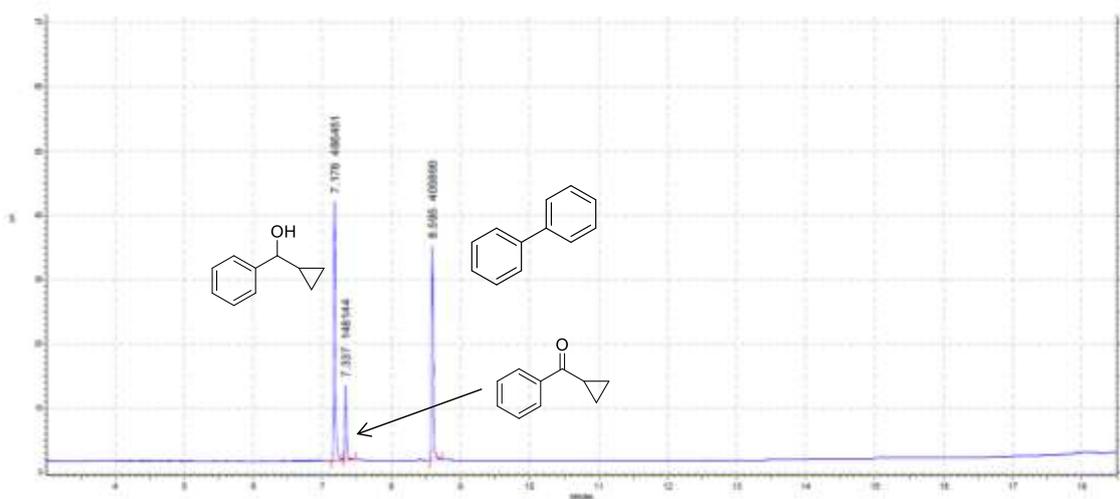


Figure SI.2.104. GC-FID chromatogram of the reduced product **10e** from the catalysis.

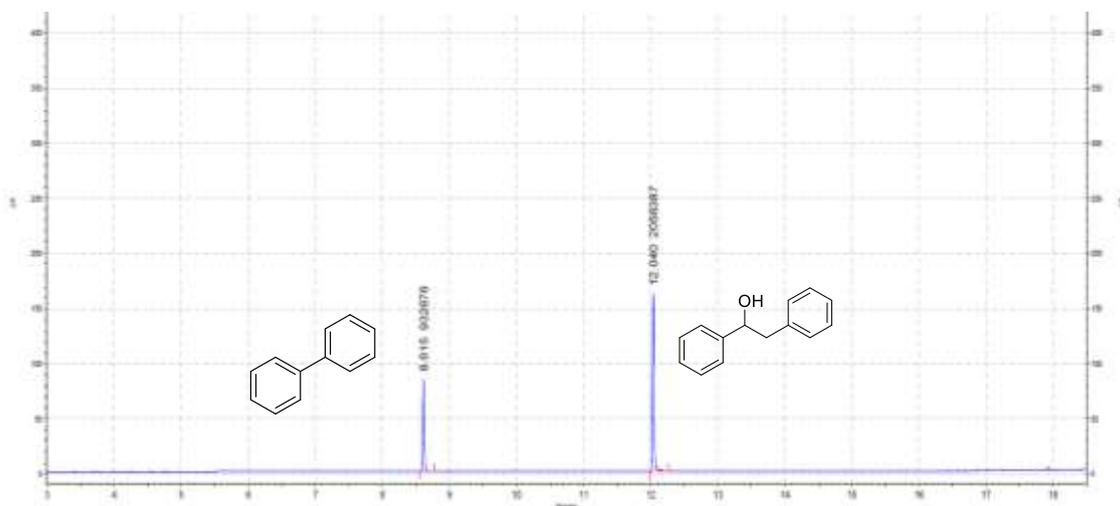


Figure SI.2.105. GC-FID chromatogram of the reduced product **10f** from the catalysis.

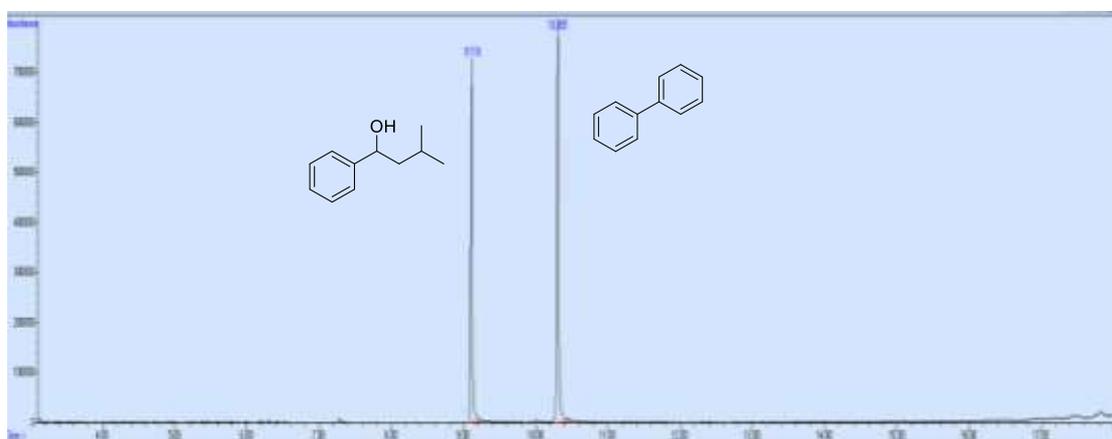


Figure SI.2.106. GC-FID chromatogram of the reduced product **10g** from the catalysis.

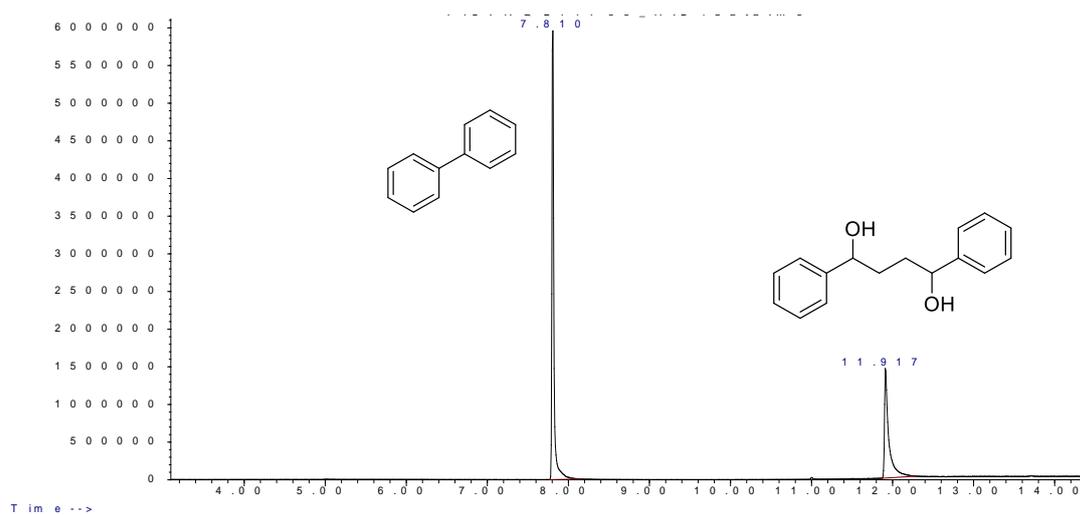


Figure SI.2.107. GC-FID chromatogram of the reduced product **10i** from the catalysis.

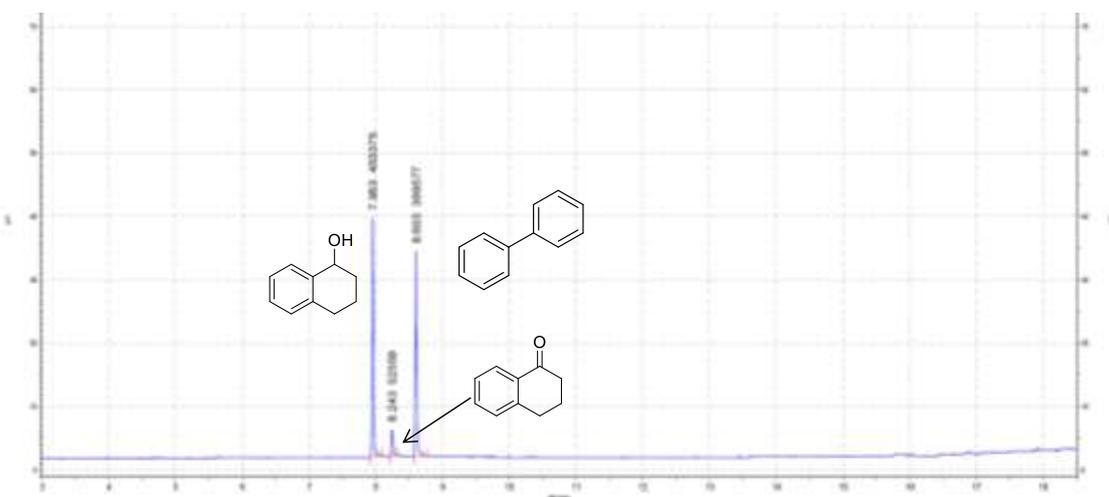


Figure SI.2.108. GC-FID chromatogram of the reduced product **10j** from the catalysis.

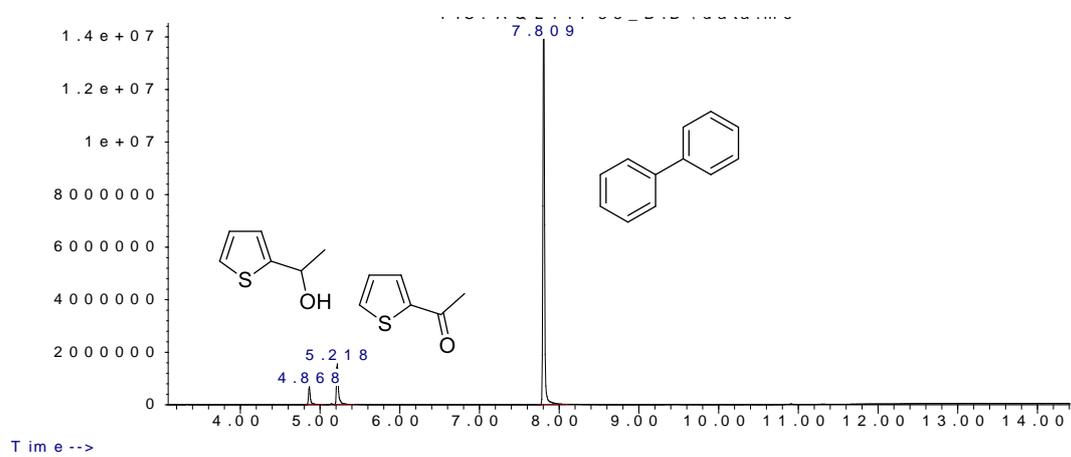


Figure SI.2.109. GC-FID chromatogram of the reduced product **10k** from the catalysis.

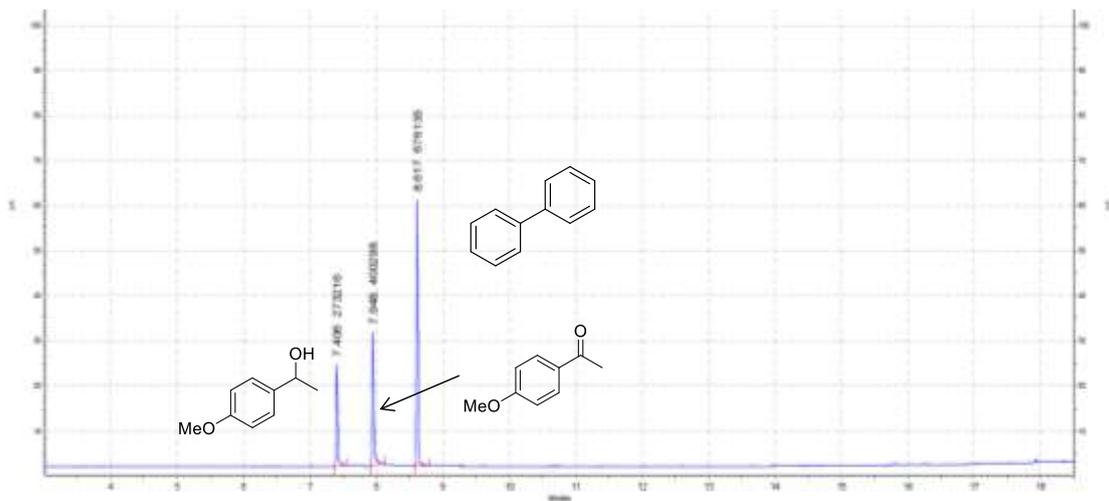


Figure SI.2.110. GC-FID chromatogram of the reduced product **10l** from the catalysis.

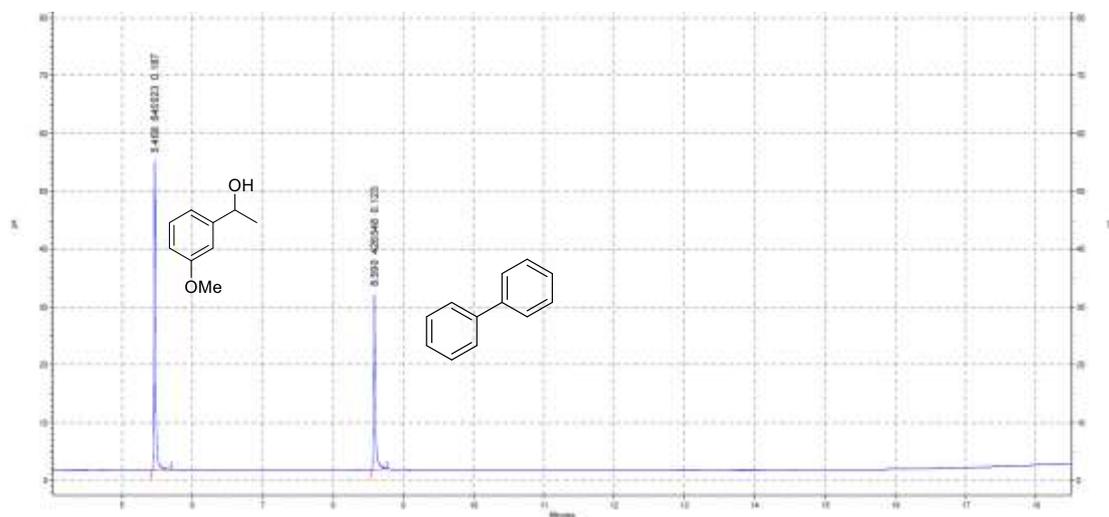


Figure SI.2.111. GC-FID chromatogram of the reduced product **10m** from the catalysis.

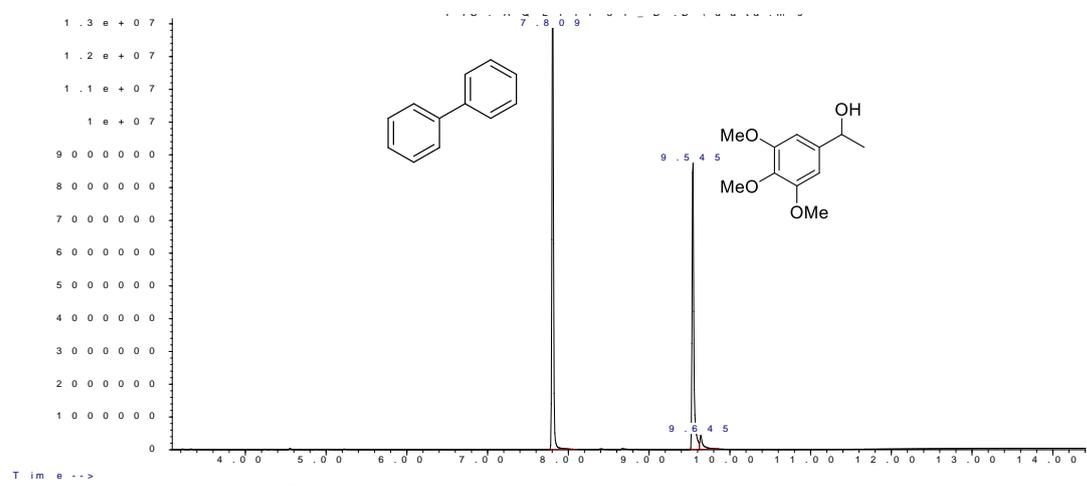


Figure SI.2.112. GC-FID chromatogram of the reduced product **10n** from the catalysis.

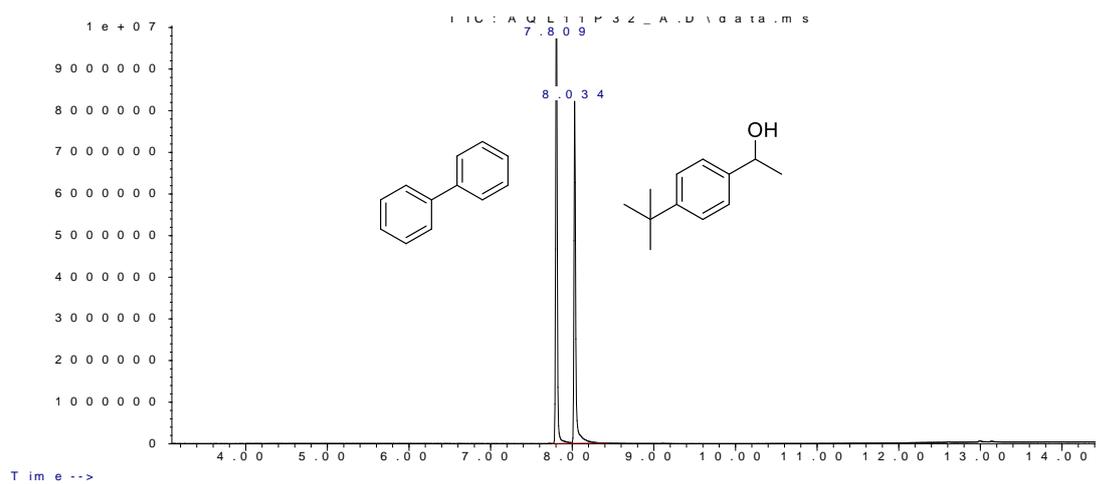


Figure SI.2.113. GC-FID chromatogram of the reduced product **10o** from the catalysis.

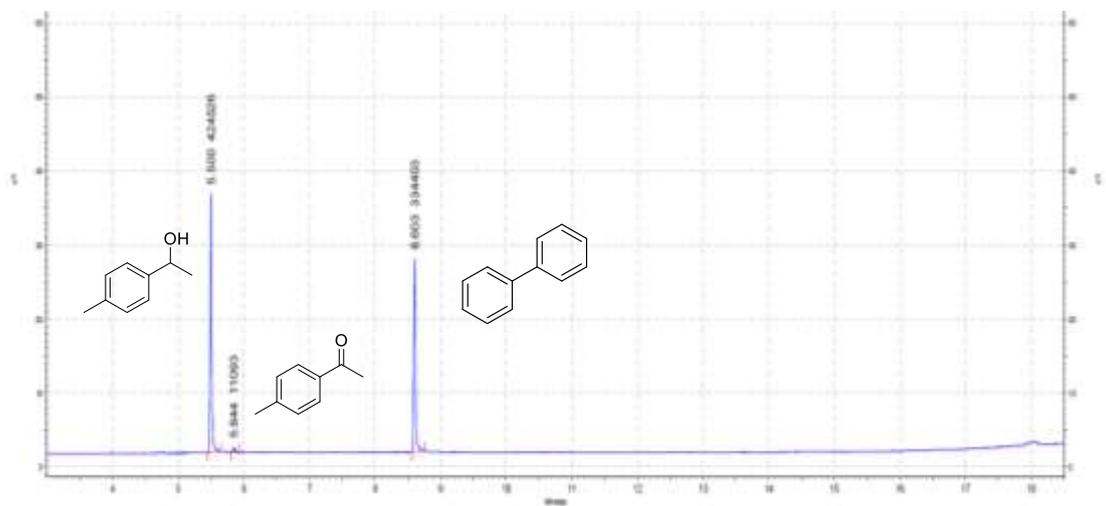


Figure SI.2.114. GC-FID chromatogram of the reduced product **10p** from the catalysis.

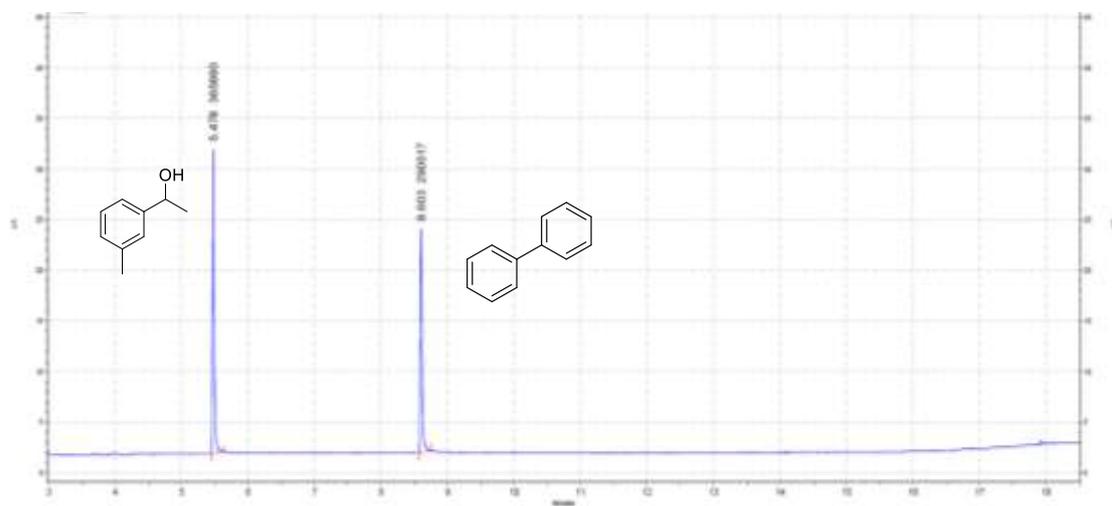


Figure SI.2.115. GC-FID chromatogram of the reduced product **10q** from the catalysis.

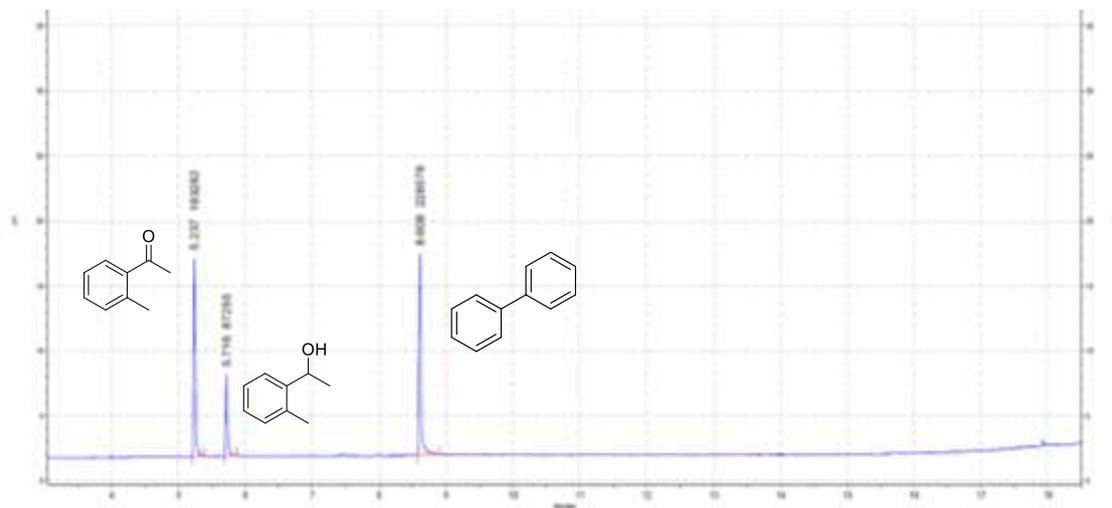


Figure SI.2.116. GC-FID chromatogram of the reduced product **10r** from the catalysis.

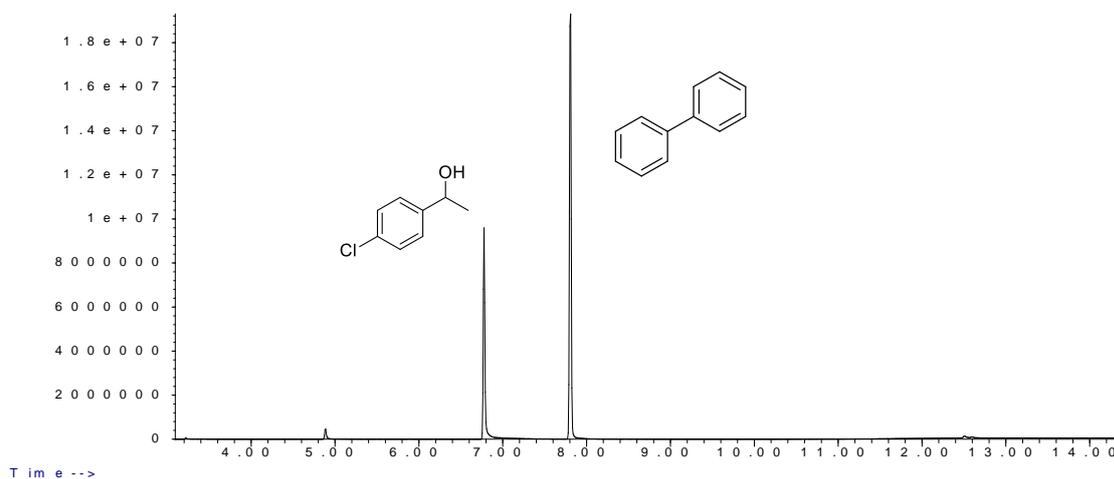


Figure SI.2.117. GC-FID chromatogram of the reduced product **10s** from the catalysis.

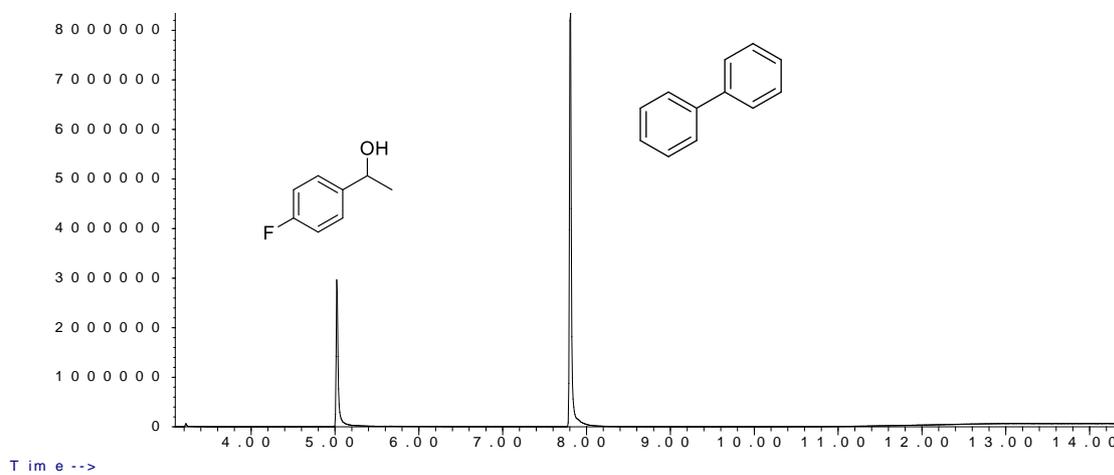
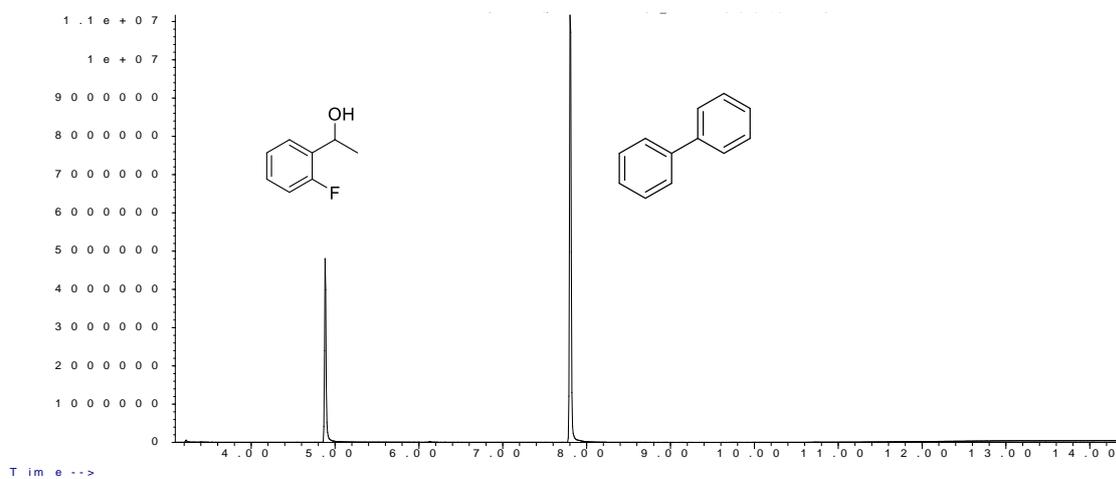
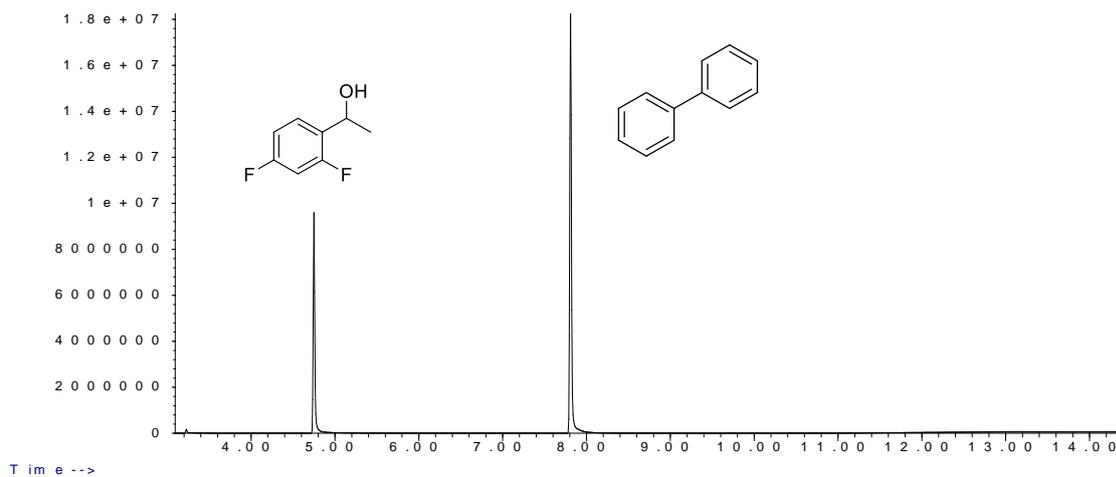


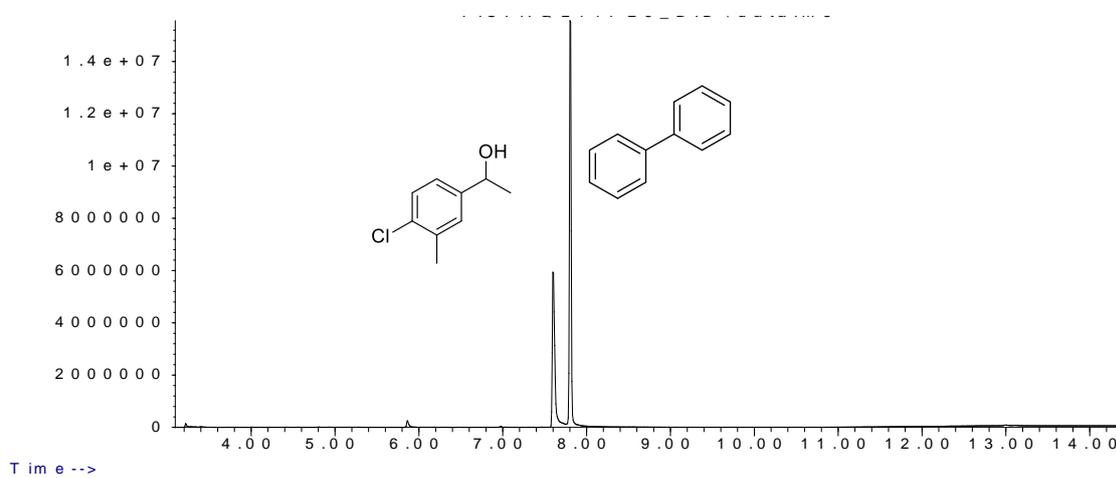
Figure SI.2.118. GC-FID chromatogram of the reduced product **10t** from the catalysis.



**Figure SI.2.119.** GC-FID chromatogram of the reduced product **10u** from the catalysis.



**Figure SI.2.120.** GC-FID chromatogram of the reduced product **10v** from the catalysis.



**Figure SI.2.121.** GC-FID chromatogram of the reduced product **10w** from the catalysis.

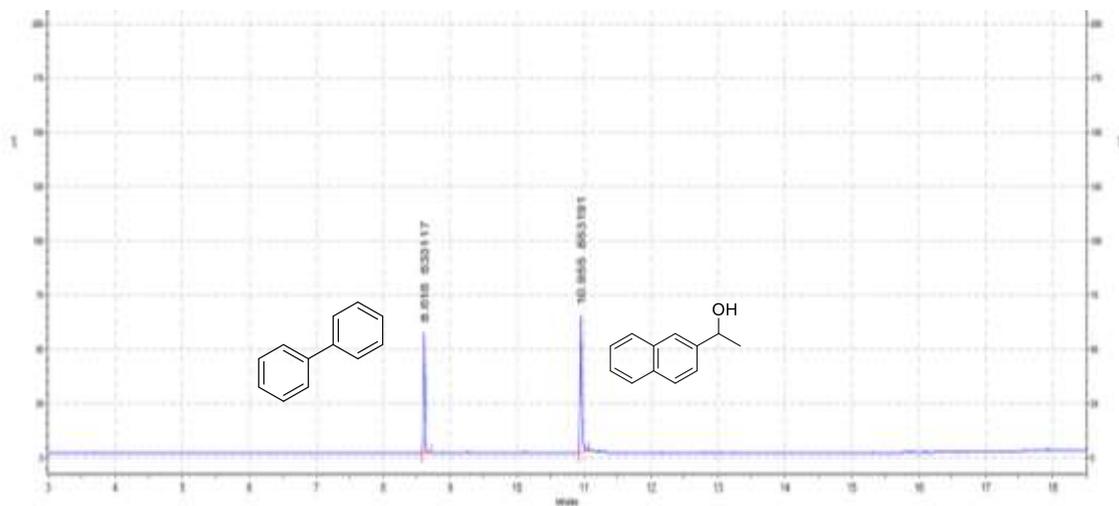


Figure SI.2.122. GC-FID chromatogram of the reduced product **10x** from the catalysis.

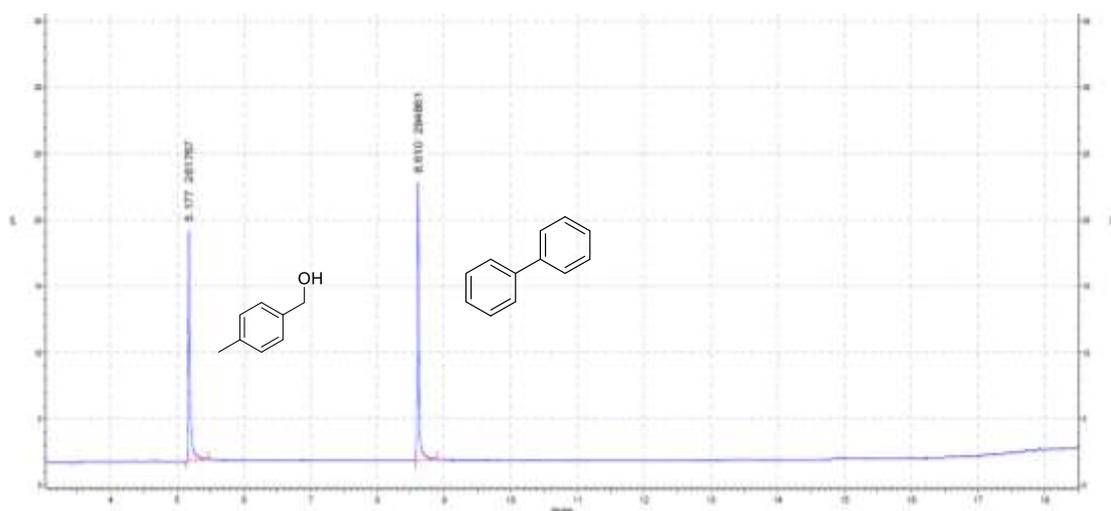


Figure SI.2.123. GC-FID chromatogram of the reduced product **12a** from the catalysis.

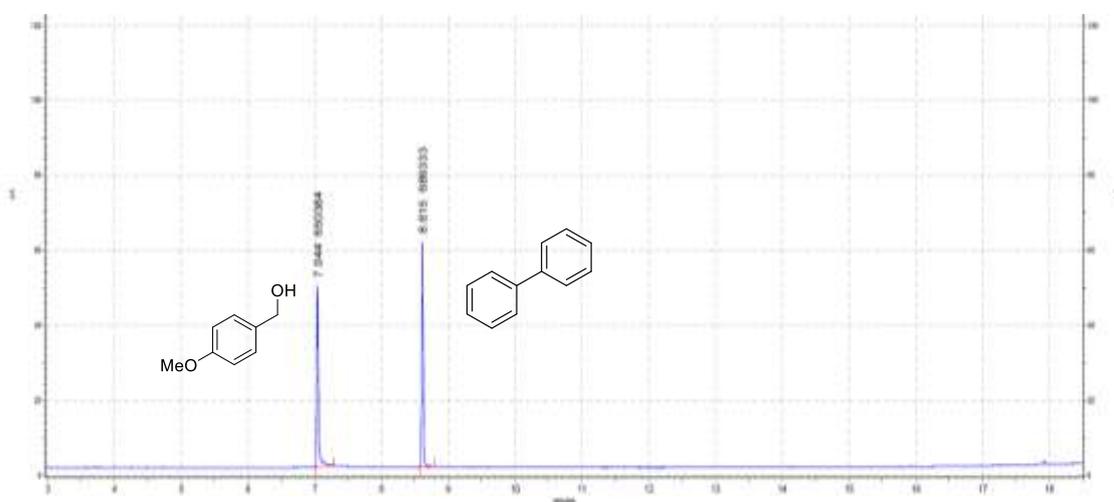


Figure SI.2.124. GC-FID chromatogram of the reduced product **12b** from the catalysis.

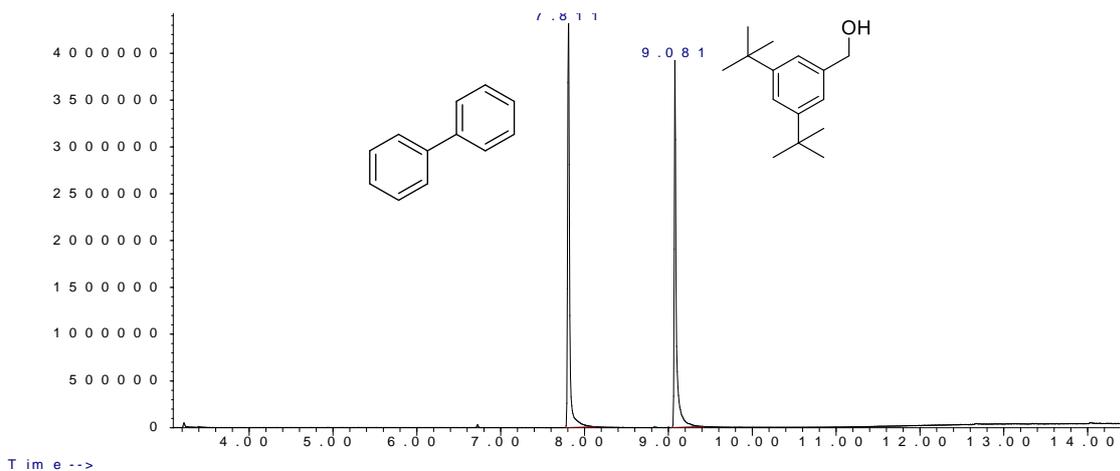


Figure SI.2.125. GC-FID chromatogram of the reduced product **12c** from the catalysis.

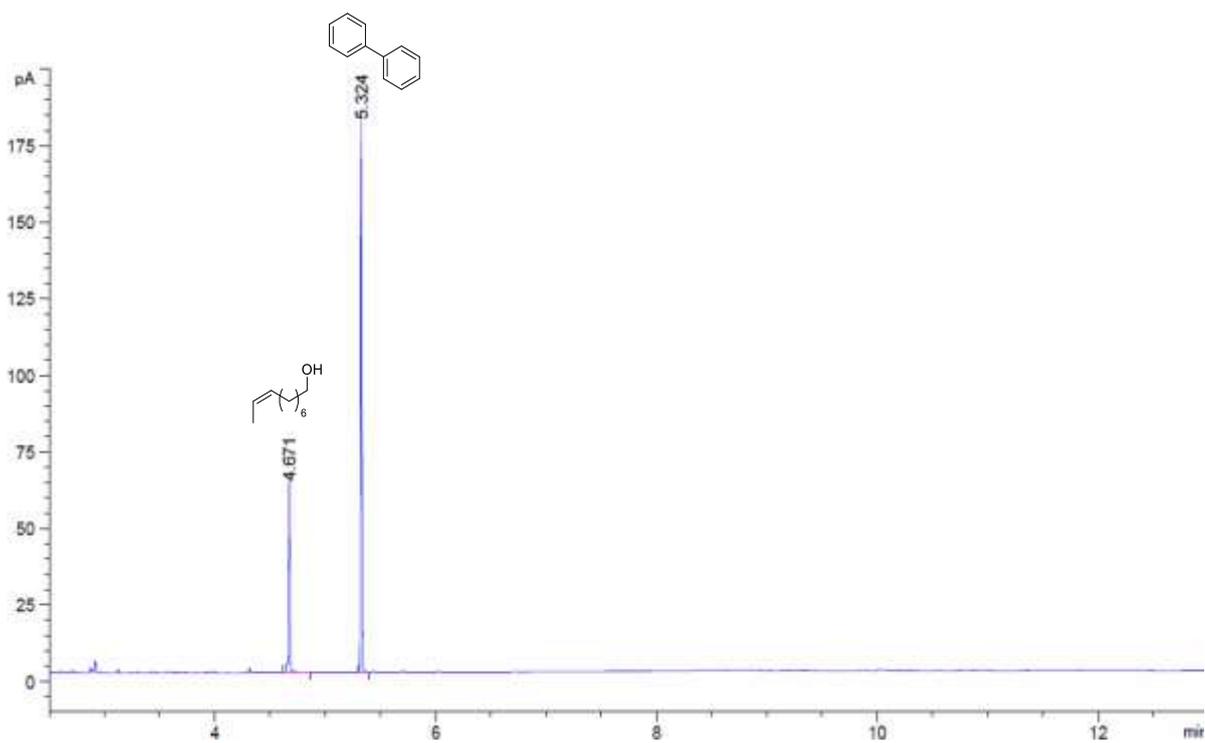


Figure SI.2.126. GC-FID chromatogram of the reduced product **12d** from the catalysis.

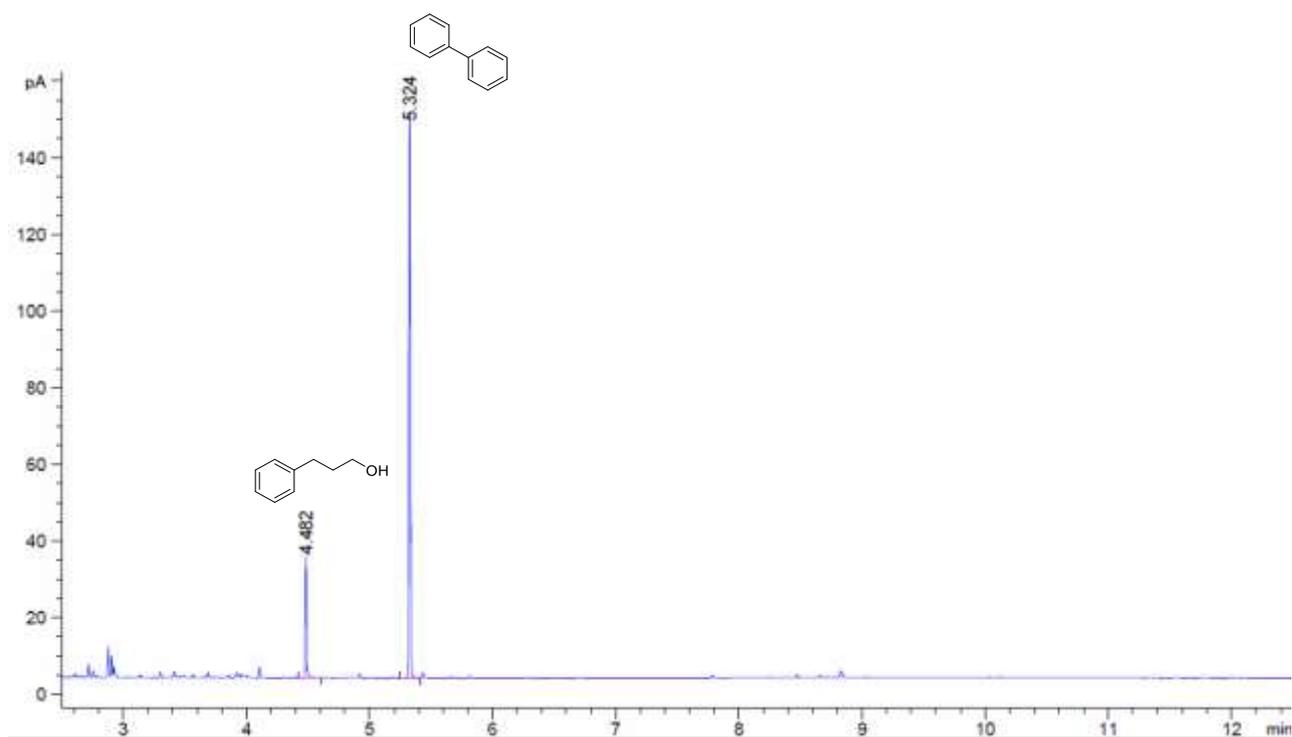


Figure SI.2.127. GC-FID chromatogram of the reduced product **12e** from the catalysis.

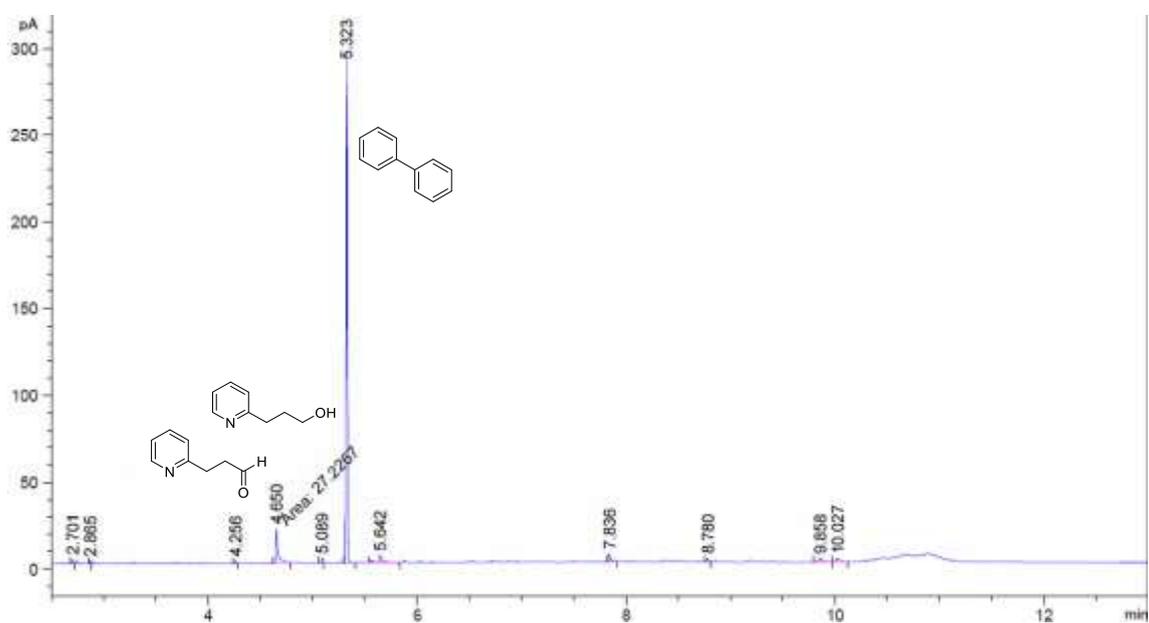
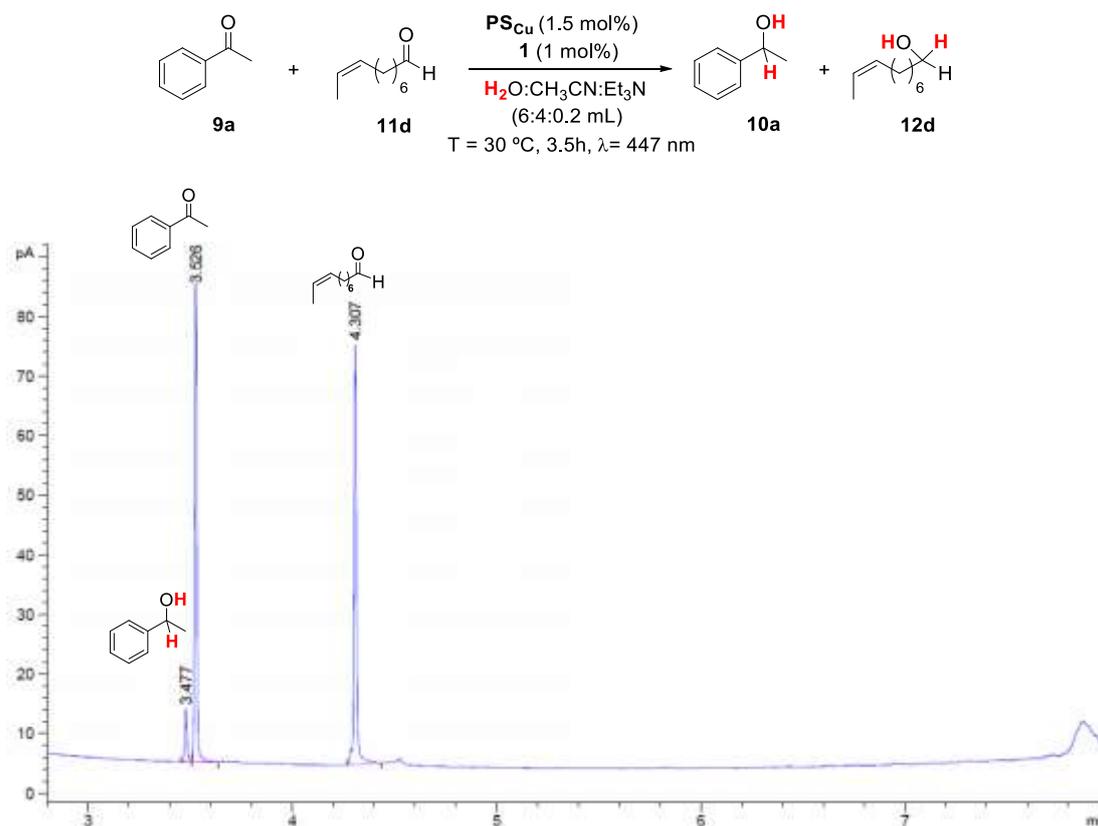


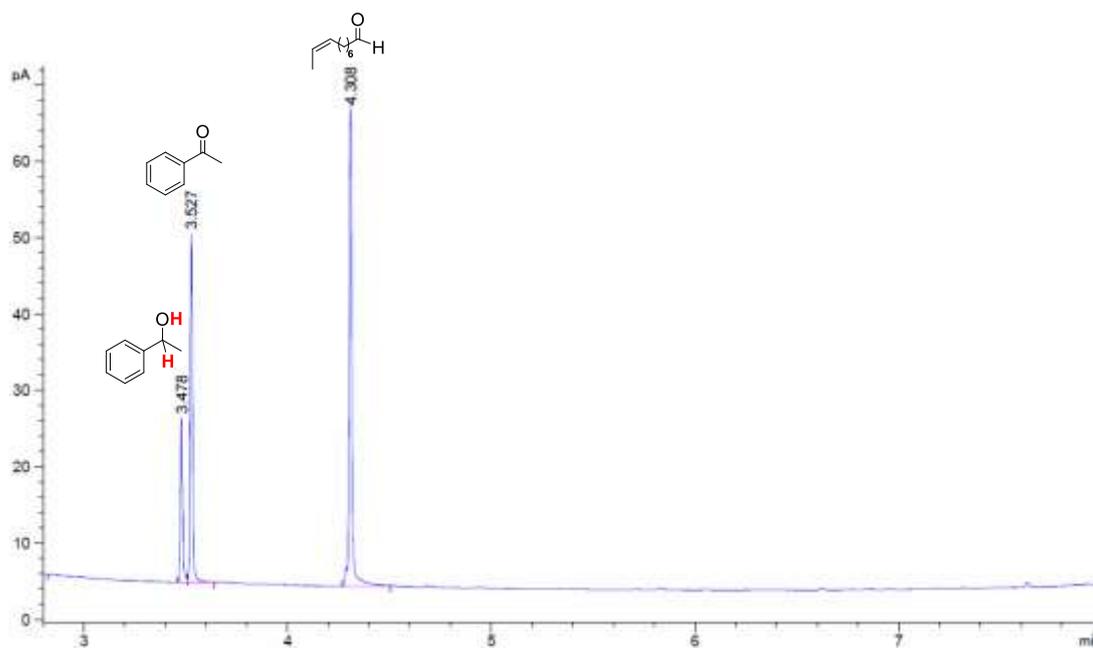
Figure SI.2.128. GC-FID chromatogram of the reduced product **12f** from the catalysis.

## 8. Selected chromatograms of the selectivity studies

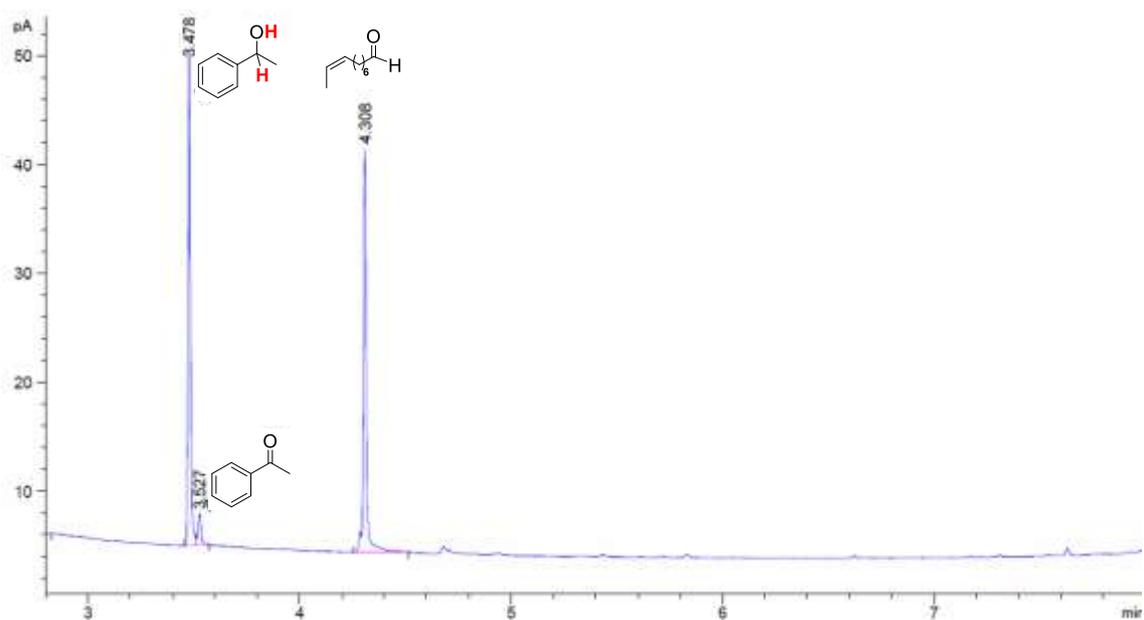
### Competition experiments



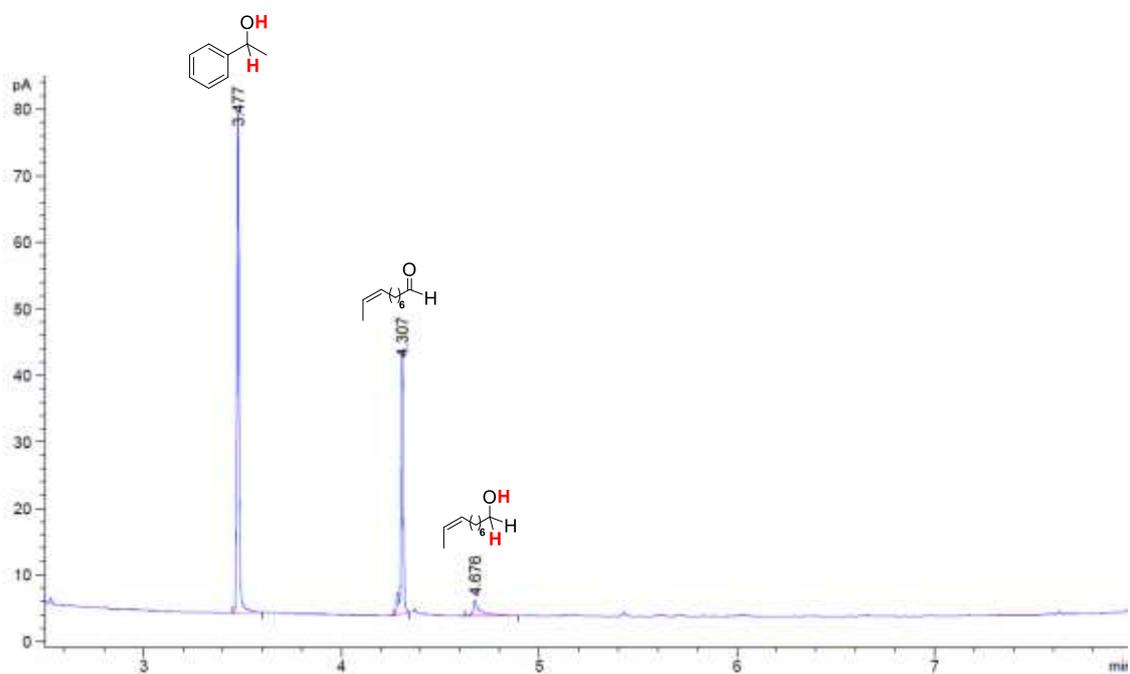
**Figure SI.2.129.** GC-FID chromatogram of the monitoring of the photoreduction of acetophenone (**9a**) in the presence of (Z)-dec-8-enal (**11d**) after 4 minutes of irradiation.



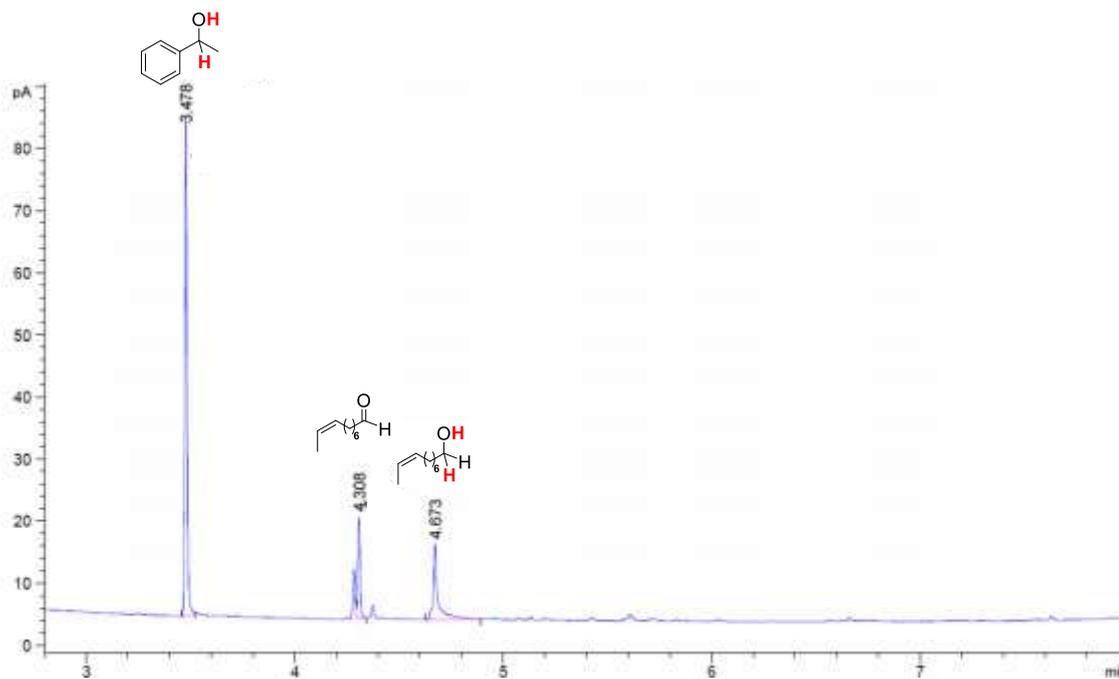
**Figure SI.2.130.** GC-FID chromatogram of the monitoring of the photoreduction of acetophenone (**9a**) in the presence of (Z)-dec-8-enal (**11d**) after 10 minutes of irradiation.



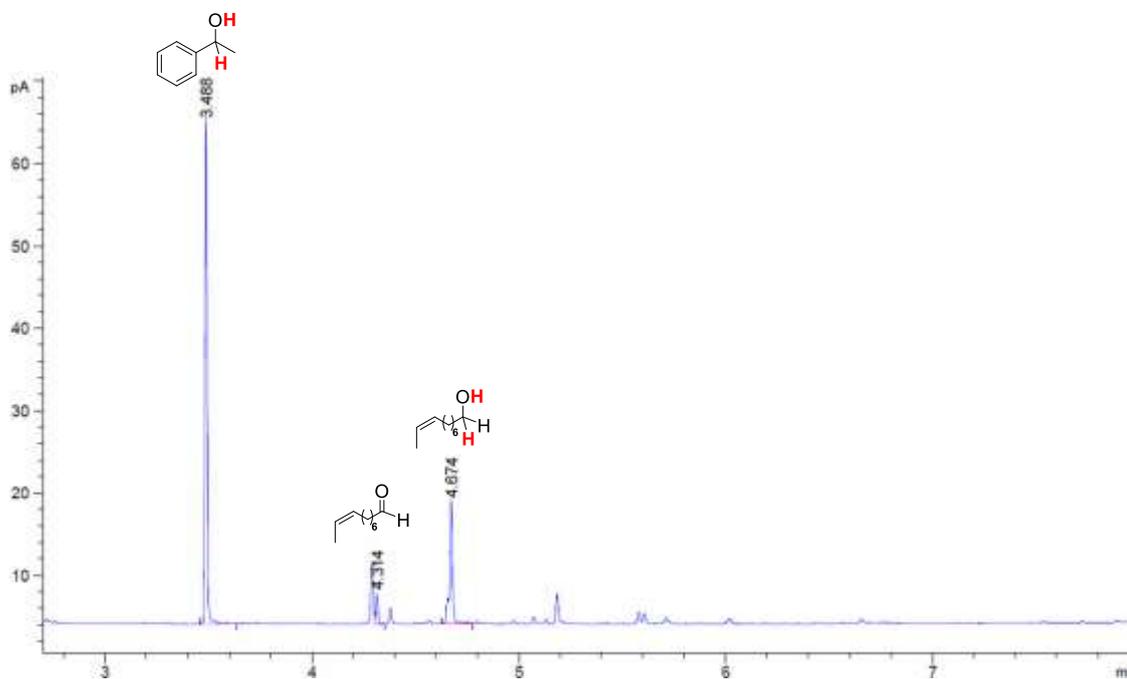
**Figure SI.2.131.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of (Z)-dec-8-enal (**11d**) after 30 minutes of irradiation.



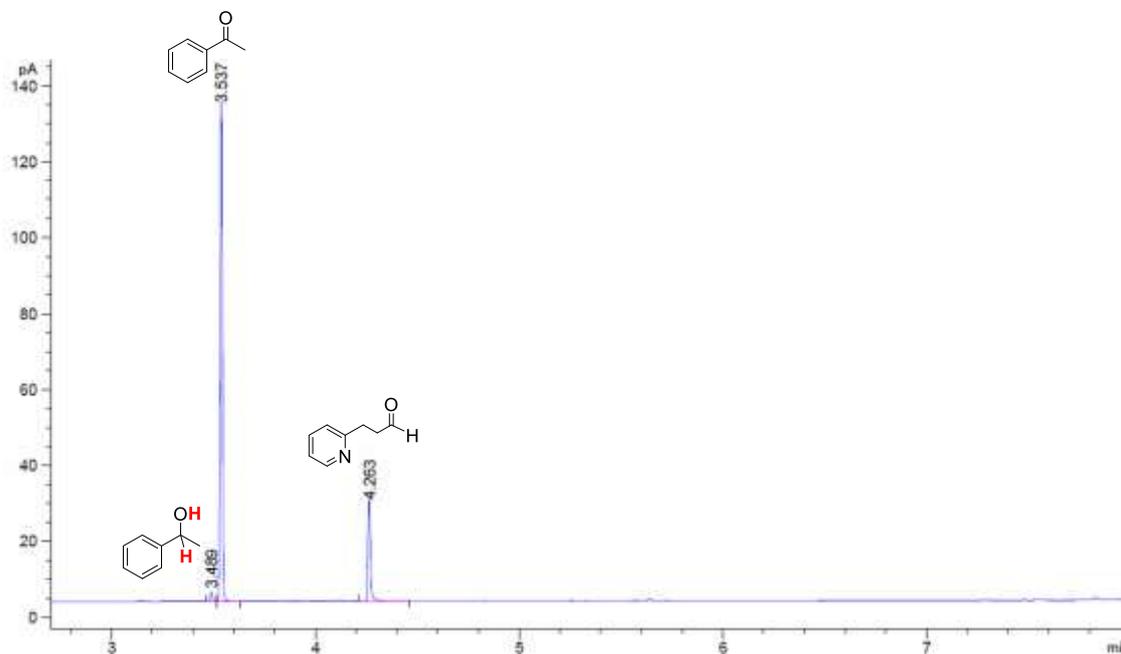
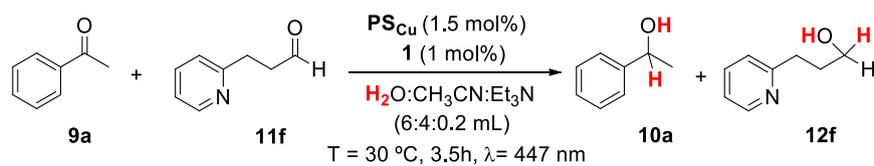
**Figure SI.2.132.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of (Z)-dec-8-enal (**11d**) after 50 minutes of irradiation.



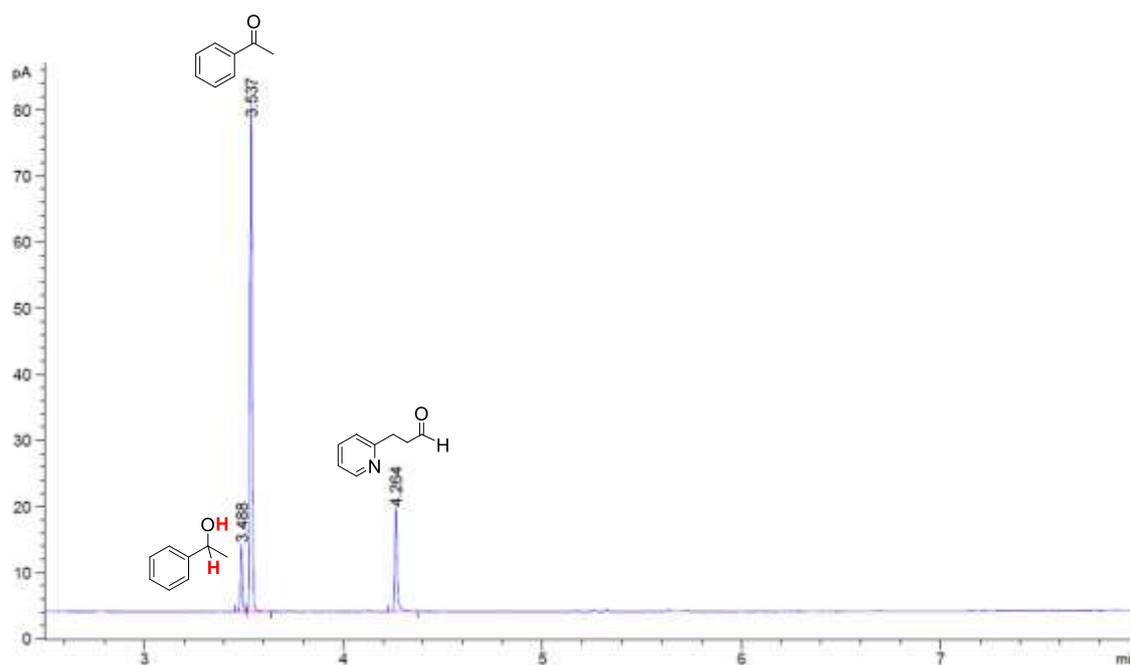
**Figure SI.2.133.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of (Z)-dec-8-enal (**11d**) after 120 minutes of irradiation.



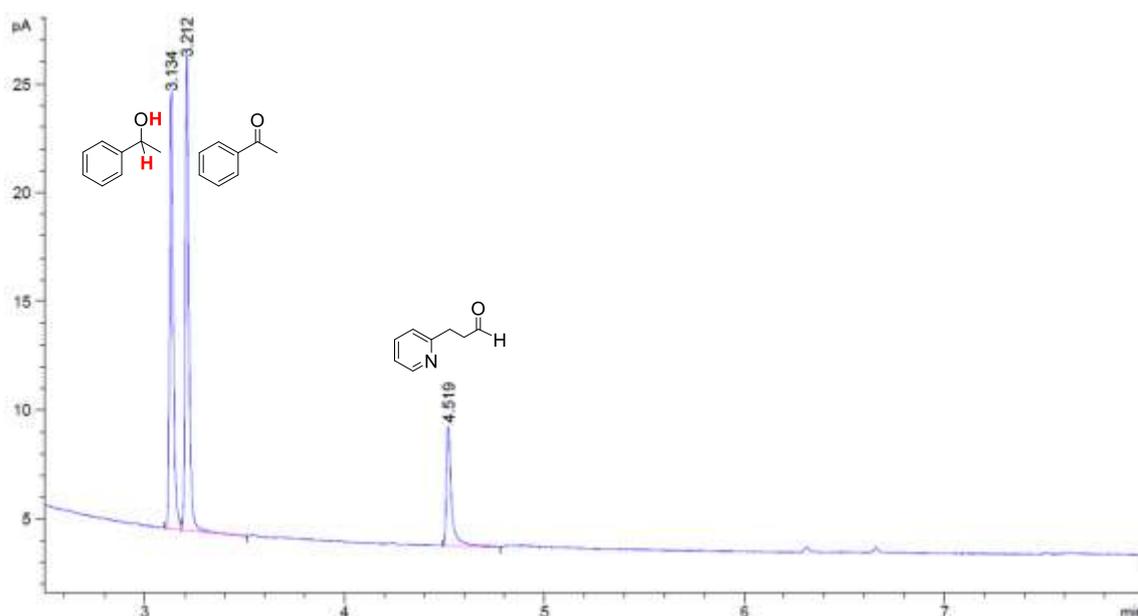
**Figure SI.2.134.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of (Z)-dec-8-enal (**11d**) after 210 minutes of irradiation.



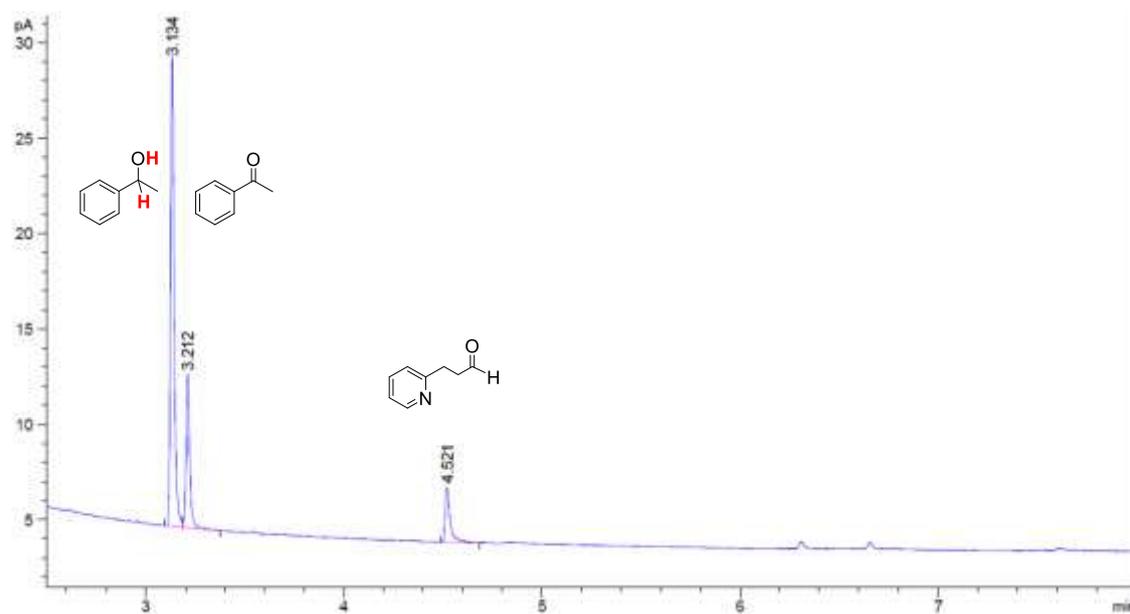
**Figure SI.2.135.** GC-FID chromatogram of the monitorization of the photoreduction of acetophenone (**9a**) in the presence of 3(pyridin-2-yl)propanal (**11f**) after 4 minutes of irradiation.



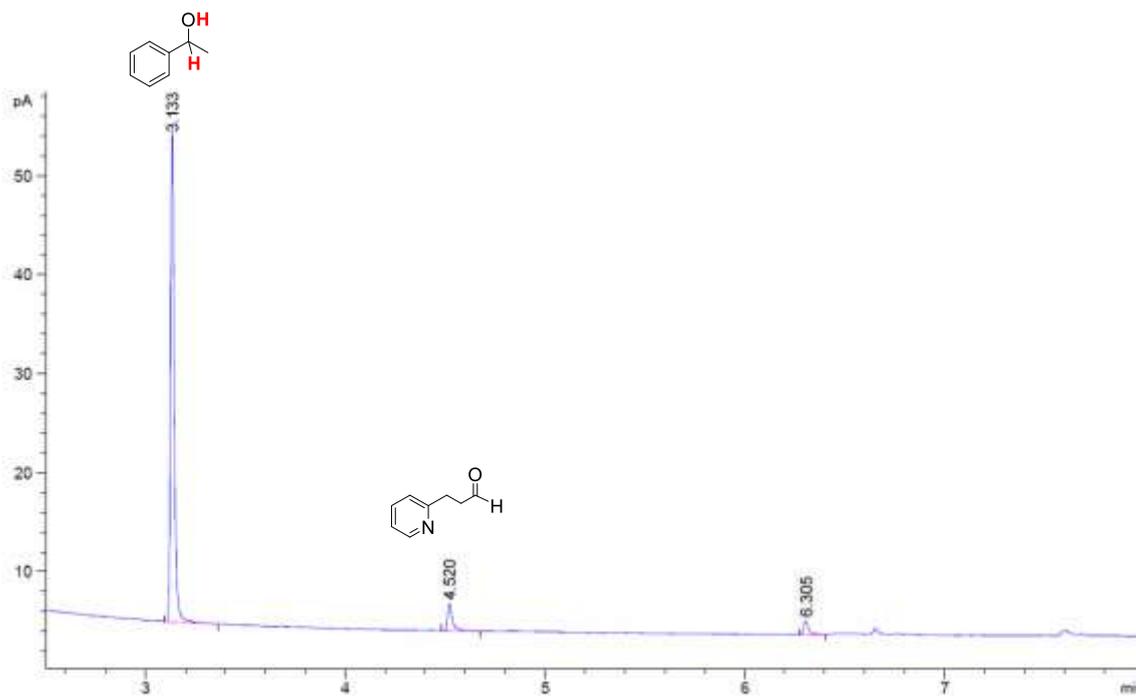
**Figure SI.2.136.** GC-FID chromatogram of the monitorization of the photoreduction of acetophenone (**9a**) in the presence of 3(pyridin-2-yl)propanal (**11f**) after 10 minutes of irradiation.



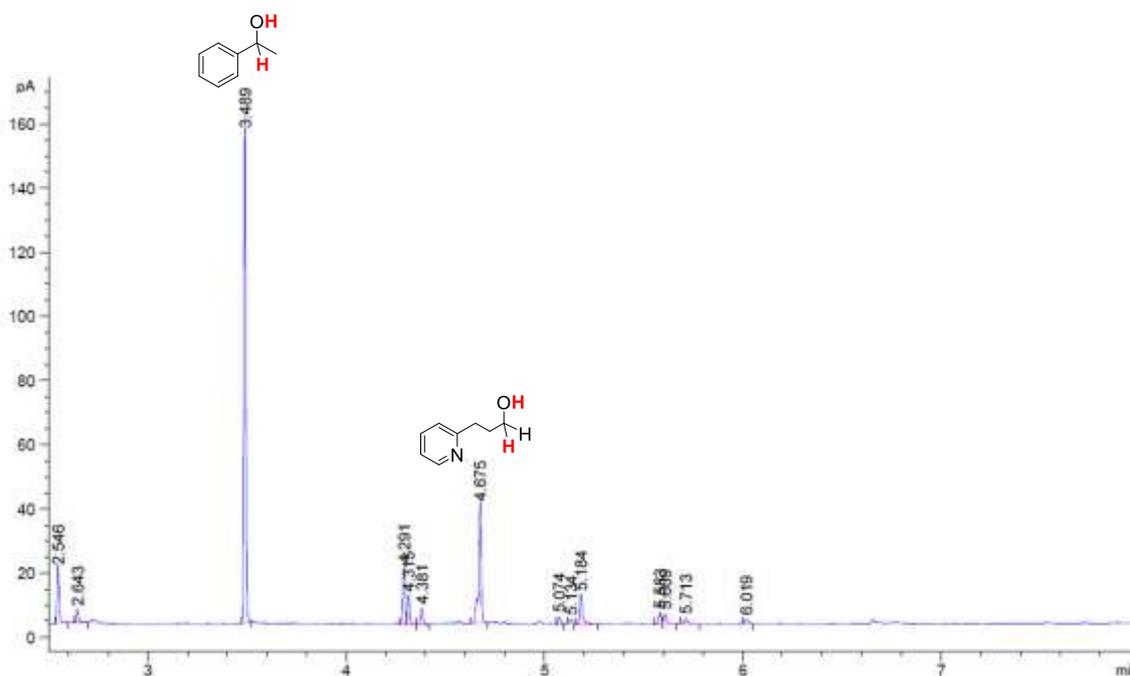
**Figure SI.2.137.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3(pyridin-2-yl)propanal (**11f**) after 20 minutes of irradiation.



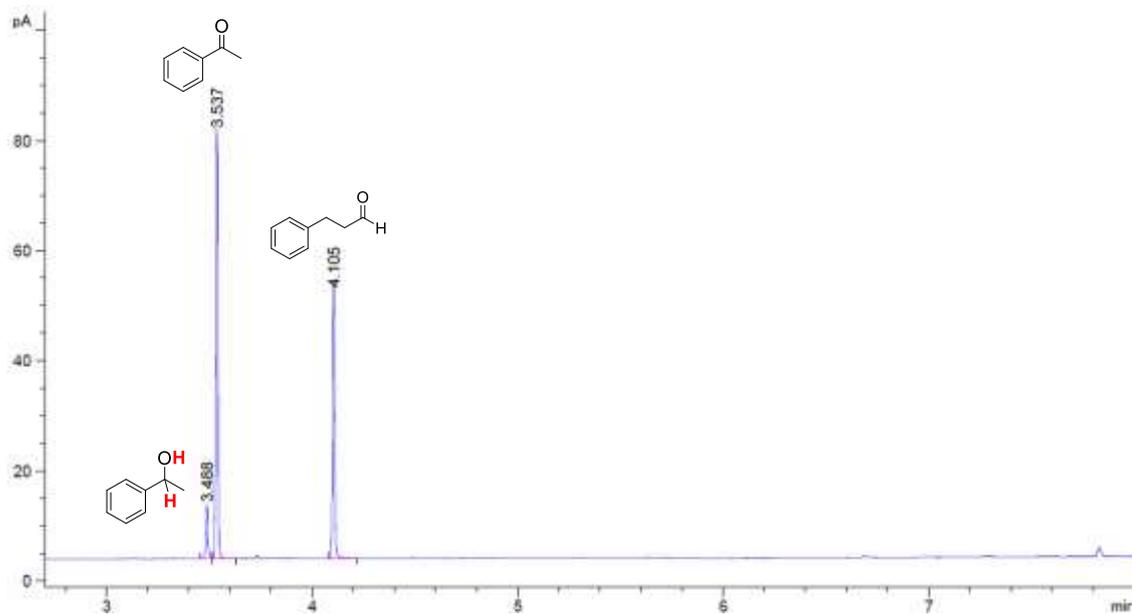
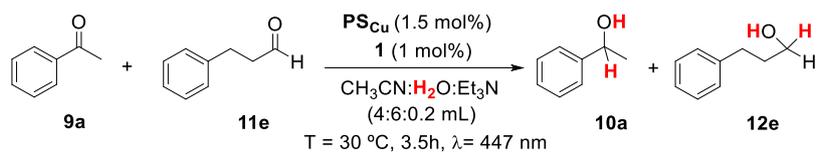
**Figure SI.2.138.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3(pyridin-2-yl)propanal (**11f**) after 30 minutes of irradiation.



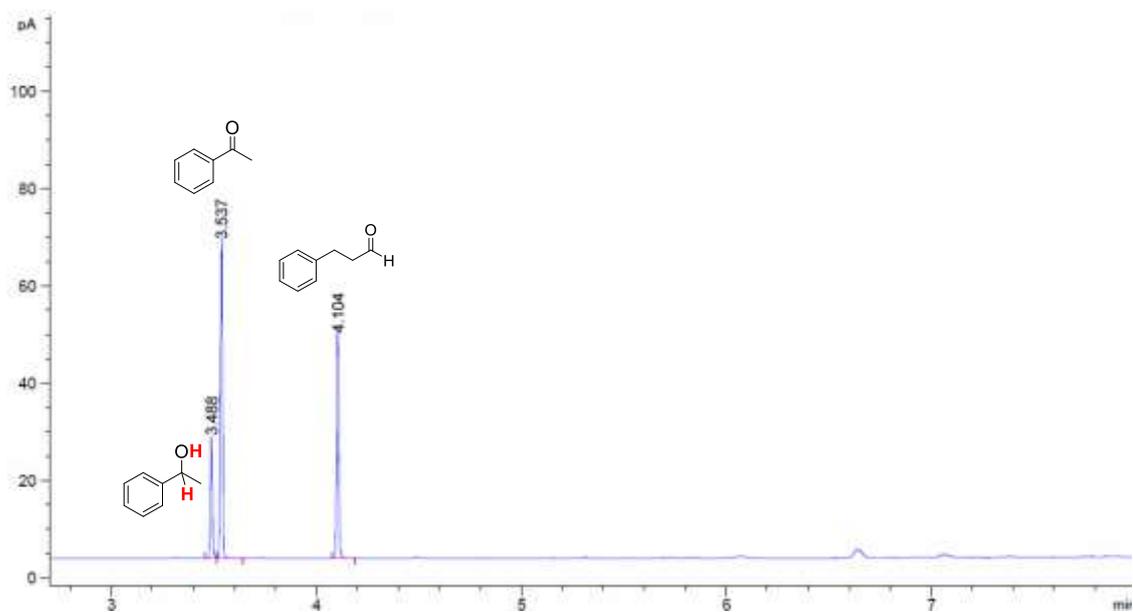
**Figure SI.2.139.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3(pyridin-2-yl)propanal (**11f**) after 50 minutes of irradiation.



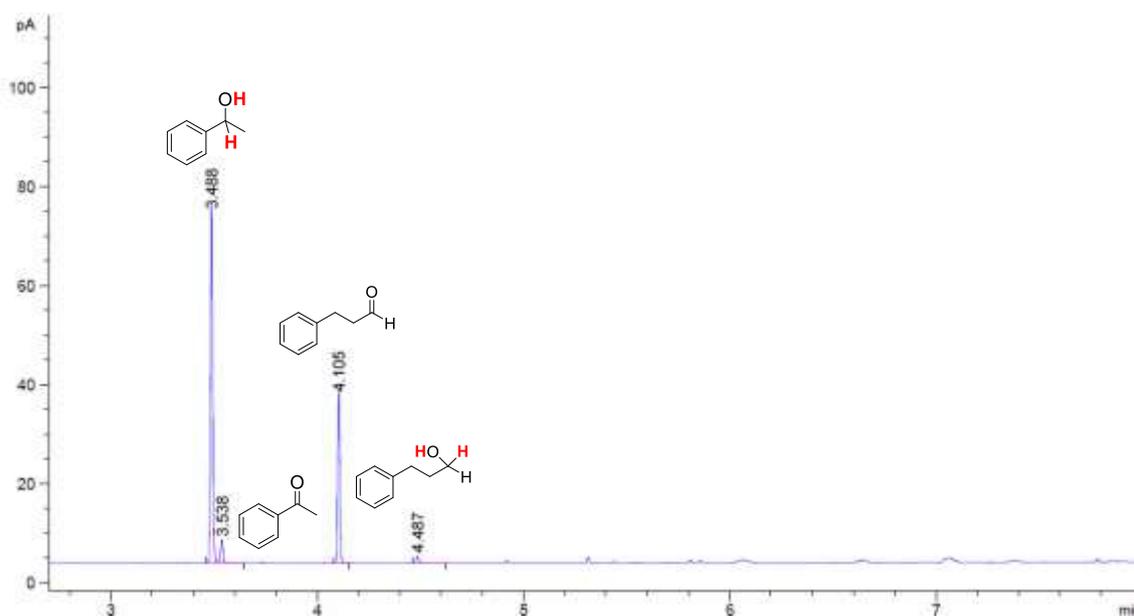
**Figure SI.2.140.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3(pyridin-2-yl)propanal (**11f**) after 210 minutes of irradiation.



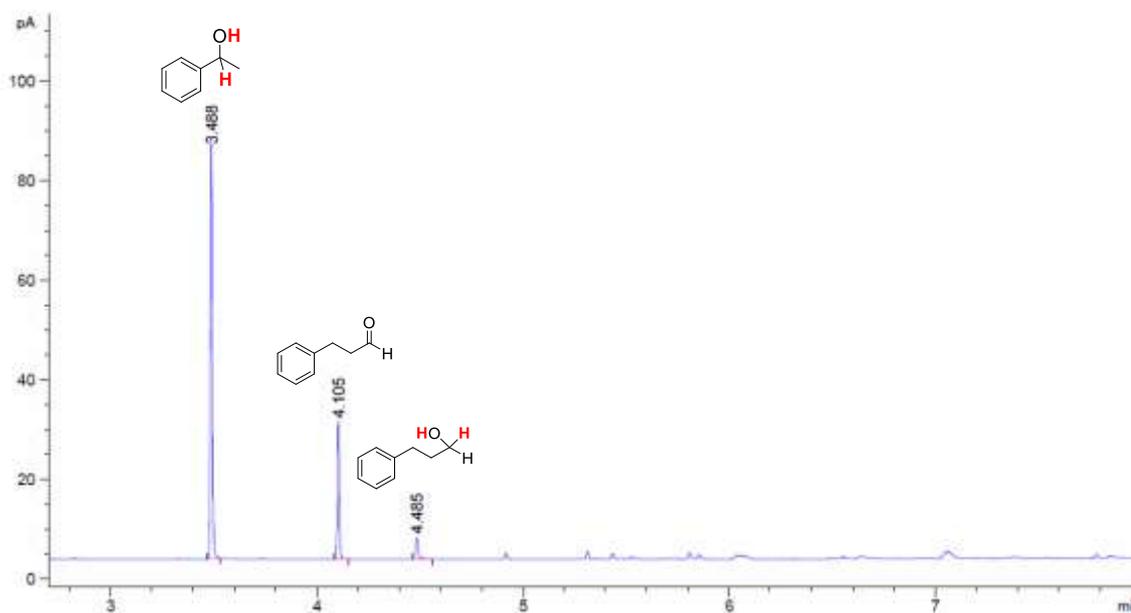
**Figure SI.2.141.** GC-FID chromatogram of the monitoring of the photoreduction of acetophenone (**9a**) in the presence of 3-phenylpropanal (**11e**) after 4 minutes of irradiation.



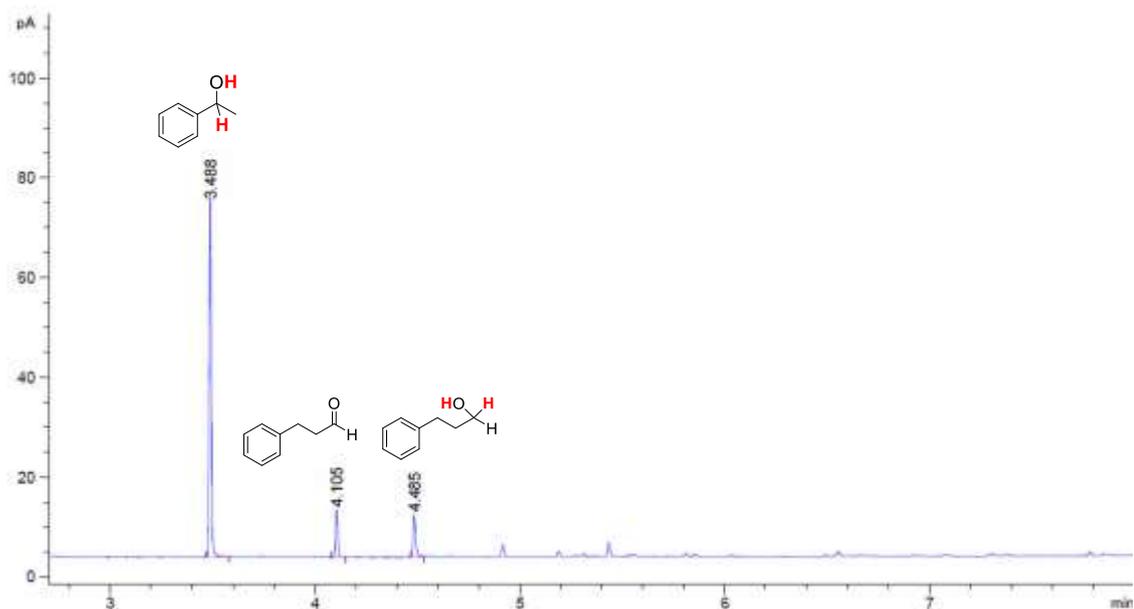
**Figure SI.2.142.** GC-FID chromatogram of the monitoring of the photoreduction of acetophenone (**9a**) in the presence of 3-phenylpropanal (**11e**) after 10 minutes of irradiation.



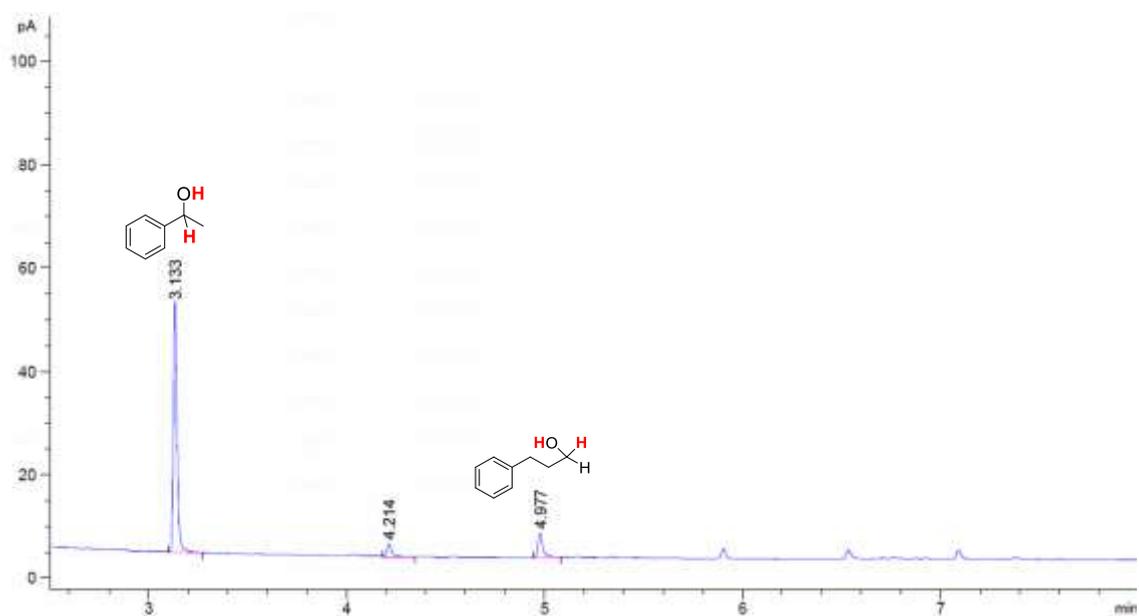
**Figure SI.2.143.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3-phenylpropanal (**11e**) after 30 minutes of irradiation.



**Figure SI.2.144.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3-phenylpropanal (**11e**) after 50 minutes of irradiation.



**Figure SI.2.145.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3-phenylpropanal (**11e**) after 120 minutes of irradiation.



**Figure SI.2.146.** GC-FID chromatogram of the monitorization of the photoreduccion of acetophenone (**9a**) in the presence of 3-phenylpropanal (**11e**) after 200 minutes of irradiation.