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SUPPORTING INFORMATION

Hydrosilylation of carbonyl and carboxyl groups catalysed by Mn(I) complexes bearing triazole ligands

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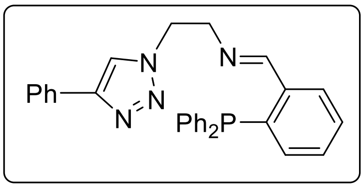
General considerations

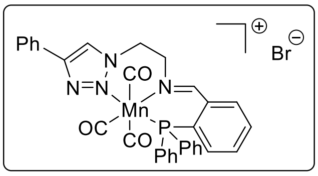
All air and moisture-sensitive experiments were conducted under dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. Solvents for air- and moisture-sensitive experiments were purified using a two-column solid state purification system (MBraun-SPS-7) and transferred to the glovebox without exposure to air. Deuterated solvents were obtained packaged under argon and stored over activated molecular sieves prior to use. Phenylacetylene was purchased from fluorochem, and all other chemicals were purchased from Sigma-Aldrich and used as received. 1-Azidoethylamine[1] and 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)ethanamine[2] were synthesized according to the literature procedures. NMR spectra were recorded on Bruker AV-400 and Bruker AV-500 spectrometers at the indicated temperatures with the chemical shifts (δ) given in ppm relative to TMS and the coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (DMSO-d$_6$: δ_H = 2.50 ppm, δ_C = 39.5 ppm; acetone-d$_6$: δ_H = 2.05 ppm, δ_C = 206.3, 29.8; THF-d$_8$: δ_H = 3.58, 1.72 ppm, δ_C = 67.2, 25.3 ppm). CHN elemental microanalyses were measured at “Mikroanalytisches Labor Kolbe” (c/o Fraunhofer Institut UMSICHT). HR-MS spectra were recorded on a Bruker ESQ3000 spectrometer. Infrared spectra were recorded on a Termo Scientific Nicolet™ iS5 Spectrometer with an ID7 ATR accessory.

Experimental procedures

Synthesis of ligand 2 and complex 3



(2(diphenylphosphaneyl)phenyl)-N-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)methanimine (2): A mixture of **1**, (188.2 mg, 1 mmol), 2-(Diphenylphosphino)benzaldehyde, (299.3 µL, 1 mmol) and $MgSO_4$ (1.2 g, 10 mmol) in 5 mL of toluene was stirred at 105 ºC for 16 hours. The reaction mixture was then cooled to room temperature and filtered through a cannula. Finally, removal of the solvent under reduced pressure provided (2-(diphenylphosphaneyl)phenyl)-N-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)methanimine (**2**, 290.2 mg, 9.93 mmol, 99 %) as a reddish solid. **^{1}H NMR** (400 MHz, $CDCl_3$, 298K) δ: 8.61 – 8.55 (m, 1H), 7.74 (ddd, *J* = 7.9, 3.9, 1.4 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.52 (s, 1H), 7.32 (ddd, *J* = 7.9, 6.3, 1.4 Hz, 3H), 7.26 – 7.20 (m, 8H), 7.19 – 7.13 (m, 4H), 6.83 (ddd, *J* = 7.8, 4.5, 1.3 Hz, 1H), 4.46 (dd, *J* = 6.6, 4.8 Hz, 2H), 3.88 (td, *J* = 5.7, 1.4 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298K) δ: 162.8, 162.7, 147.4, 138.7, 138.5, 138.0, 137.1, 137.0, 134.0, 133.9, 133.8, 130.9, 130.6, 129.1, 128.8, 128.7, 128.6, 128.0, 125.7, 120.80, 60.3, 50.9. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 298K) δ: 12.2. **HR-MS (ESI+)** calcd. for $[C_{29}H_{25}N_4P]^+$: 460.18910; found: 460.18896. **Anal. calcd. (%)** for $[C_{29}H_{25}N_4P]$ (460.18) : C 75.64, H 5.47, N 12.17, found: C 75.37, H 5.43, N 12.17.



Complex 3. A mixture of Bromopentacarbonylmanganese(I) (179.1 mg, 0.65 mmol) and **2** (300 mg, 0.65 mmol) in dry toluene (15 mL) was vigorously stirred at r.t. for 60 h. At that time, the formation of a yellow precipitate was observed. The precitate was filtered and washed with pentane (2 × 10 mL) and **3** was isolated as a yellow powder (130 mg, 0.3 mmol, 46%). **^{1}H NMR** (400 MHz, CD_2Cl_2, 298K) δ: 8.15 (s, 1H), 7.97 – 7.87 (m, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.29 (m, 12H), 7.19 – 7.18

(m, 1H), 7.12 – 7.08 (m, 1H), 6.89 (dd, *J* = 9.5, 7.6 Hz, 1H), 6.79 (s, 1H), 5.11 (d, *J* = 11.8 Hz, 1H), 4.95 (d, *J* = 13.7 Hz, 1H), 4.57 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.2 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_2Cl_2, 298K) δ: 136.1, 136.0, 135.2, 135.1, 133.7, 133.4, 133.4, 133.0, 132.9, 131.8, 131.8, 130.9, 130.8, 129.2, 129.1, 129.00, 128.5, 126.1, 73.1, 49.0. **$^{31}P\{^1H\}$ NMR** (166 MHz, CD_2Cl_2, 298 K) δ: 44.0. **HR-MS (ESI+)** calcd. for $[C_{32}H_{25}MnN_4O_3P]^+$: 599.10427; found: 599.10393. **Anal. calcd. (%)** for $[C_{32}H_{25}BrMnN_4O_3P](C_7H_8)_1$ (770.08) : C 56.57, H 3.71, N 8.25, found: C 56.57, H 3.71, N 8.25.

General procedure for the catalytic hydrosilylation of carbonyl substrates

Selected ketone (0.5 mmol), phenylsilane (0.5 mmol), and mesitylene or tetradecane (0.5 mmol) were added to a stock solution (0.51 mg in 0.2 mL THF) of the Mn(I) catalyst **8** (0.25 mol%) in THF. The reaction mixture was stirred at 80 °C for the required time (1 h). After this time, the reaction was cooled to room temperature and the corresponding hydrolysis was performed (see below). After hydrolysis, the sample was diluted with $CDCl_3$ (0.6 mL), and subjected to ^{1}H-NMR spectroscopy to determine the yield of the product.

General procedure for the catalytic hydrosilylation of ester substrates

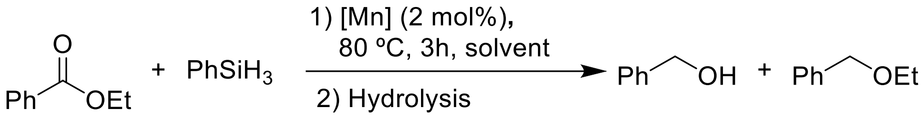
Selected ester (0.5 mmol), phenylsilane (1 mmol), and mesitylene or tetradecane (0.5 mmol) were added to a stock solution (6.79 mg in 0.2 mL THF) of the Mn(I) catalyst **3** (2 mol%) in THF. The reaction mixture was stirred at 80 °C for the required time (3 h). After this time, the reaction was cooled to room temperature and the corresponding hydrolysis was performed (see below). After hydrolysis, the sample was diluted with $CDCl_3$ (0.6 mL), and subjected to ^{1}H-NMR spectroscopy to determine the yield of the product.

General procedure for the catalytic hydrosilylation of acid substrates

Selected acid (0.5 mmol), phenylsilane (1 mmol), and mesitylene (0.5 mmol) were added to a stock solution (6.79 mg in 0.2 mL THF) of the Mn(I) catalyst **3** (2 mol%) in THF. The reaction mixture was stirred at 80 °C for the required time (2 h). After this time, the reaction was cooled to room temperature and the corresponding hydrolysis was performed (see below). After hydrolysis, the sample was diluted with $CDCl_3$ (0.6 mL), and subjected to ^{1}H-NMR spectroscopy to determine the yield of the product.

Solvent screening for the hydrosilylation of ethyl benzoate

Several solvents were tested for the hydrosilylation of ethyl benzoate with catalyst **3**. The results are summarized in Figure S1.



9 **10** **11**

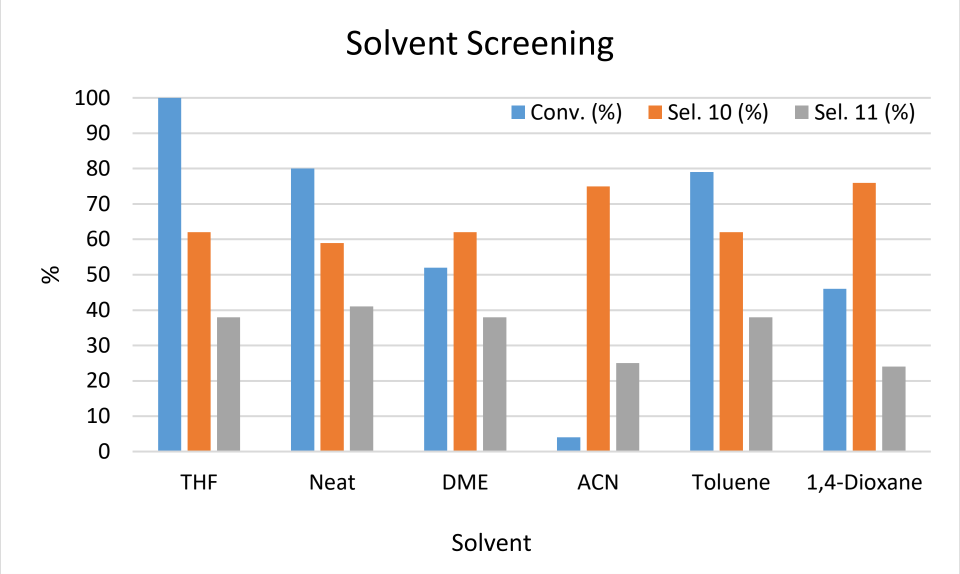


Figure S1. 0.5 mmol ethyl benzoate, 2 mol% of **3**, 0.2 mL solvent, 3h at 80 ºC. Quantified by ^{1}H NMR using tetradecane as standard.

Silanes screening and additives effect in the hydrosilylation of esters

Diphenylsilane and triphenylsilane were also verified in the catalytic hydrosilylation of ethyl benzoate by catalysts **3** or **8**. These results are summarized in Table S1.

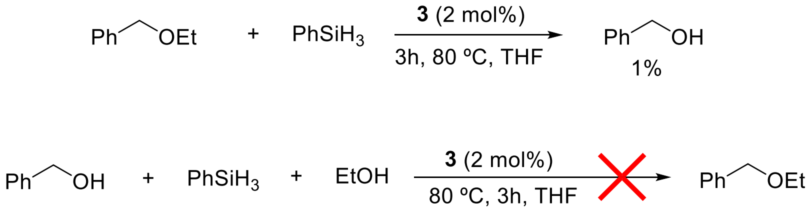
Table S1: Effect of the silanes and additives on the hydrosilylation of esters

Entry	Silane	Additive (mmol)	cat (mol%)	Conv.[a] (%)	Sel. 10[a] (%)	Sel. 11[a] (%)
1	Ph_2SiH_2	-	**3** (2)	25	72	28
2	Ph_3SiH	-	**3** (2)	0	0	0
3	$PhSiH_3$	$AgBF_4$ (0.01)	**8** (2)	58	34	66
4	$PhSiH_3$	$AgBF_4$ (0.01)	-	0	0	0

0.5 mmol ethyl benzoate, 1 mmol silane, 0.2 mL of THF, 3h at 80 ºC. [a]Quantified by ^{1}H NMR using tetradecane as an internal standard.

Study of the possible interconversion of the products

To verify the possible interconversion between alcohol and ether in the catalytic hydrosilylation of esters, following reactions were performed.



Scheme S1. 0.5 mmol substrates, 2 mol% of **3**, 0.2 mL THF, 3h. Quantified by ^{1}H NMR using tetradecane as standard.

Work up procedures used for the hydrosilylation of ketones, esters and acids

Ketones

After completion of the reaction, MeOH (1.5 mL) was added to the crude reaction mixture. Next, a solution of NaOH (10%, 2 mL) was slowly added, which leads to gas evolution. The reaction mixture was then stirred overnight to ensure complete hydrolysis. Subsequently, an extraction with DCM (3x2 mL) was performed. The combined organic layers were filtered through celite, dried over MgSO4 and evaporated to dryness. The product was quantified by ^{1}H NMR analysis.

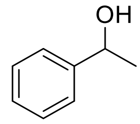
Esters and acids

After completion of the reaction, DCM (1 mL) was added to the crude reaction mixture. Next, a solution of NaOH (20%, 3 mL) was slowly added, which leads to gas evolution. The reaction mixture was then stirred overnight to ensure complete hydrolysis. Subsequently, an extraction with DCM (3x2 mL) was performed. The combined organic layers were filtered through celite, dried over MgSO4 and evaporated to dryness. The product was quantified by ^{1}H NMR analysis.

Modified work up procedure for the selective etherification (Table 2, entry 14)

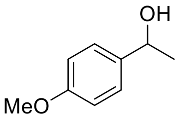
Upon completion of the reaction, the aliquot was diluted with 2 mL of THF, followed by addition of $Me_4NF.4H_2O$ (0.5 mmol) and stirred overnight. After that time, NaH (10 equivalents) were added which led to gas evolution while stirring. After 15 minutes, ethylbromide (5 quivalents) was added. The reaction mixture was stirred at room temperature for 1h. Thereafter, the solvent was evaporated, and 2 mL of water were added. The product was extracted with DCM (3x2 mL) and dried over $MgSO_4$. The combined organic layers were filtered through celite, evaporated to dryness and quantified by ^{1}H NMR analysis.

NMR data of alcohols 5



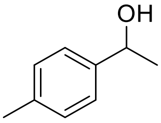
α-Methyl-benzyl alcohol (5a)[3]

^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 7.28-7.22 (m, 5H, ArC*H*), 4.77 (q, J = 6.5 Hz, 1H, ArC*H*OHCH$_3$), 2.60 (br. s, O*H*, 1H), 1.39 (d, J = 6.4 Hz, 3H, ArCHOHC*H*$_3$).



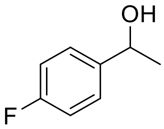
4-Methoxy-α-methyl-benzenemethanol (5b)[4]

^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 7.31 (d, J = 8.7 Hz, 1H, ArC*H*), 6.89 (d, J = 8.7 Hz, 1H, ArC*H*), 4.83 (q, J = 6.4 Hz, 1H, ArC*H*OHCH$_3$), 3.81 (s, 2H, ArOC*H*$_3$), 2.90 (br. s, O*H*, 1H), 1.48 (d, J = 6.5 Hz, 2H, ArCHOHC*H*$_3$).



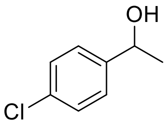
4-Methyl-α-methyl-benzenemethanol (5c)[5]

^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 7.31 (d, J = 8.1 Hz, 1H, ArC*H*), 7.21 (d, J = 7.9 Hz, 1H, ArC*H*), 4.88 (q, J = 6.4 Hz, 1H, ArC*H*OHCH$_3$), 2.81 (br. s, O*H*, 1H), 2.40 (s, ArC*H*$_3$, 3H), 1.52 (d, J = 6.4 Hz, 2H, ArCHOHC*H*$_3$).



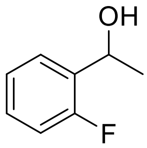
4-Fluoro-α-methyl-benzenemethanol (5d)[6]

^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 7.34 (dd, J = 8.6, 5.5 Hz, 1H, ArC*H*), 7.01 (t, J = 8.7 Hz, 1H, ArC*H*), 4.84 (q, J = 6.5 Hz, 1H, ArC*H*OHCH$_3$), 3.50 (br. s, O*H*, 1H), 1.45 (d, J = 6.5 Hz, 2H, ArCHOHC*H*$_3$).



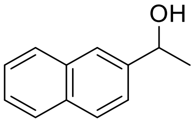
4-Chloro-α-methyl-benzenemethanol (5e)[3]

^{1}H NMR (400 MHz, CDCl$_3$, 298K) δ: 7.29 (s, 4H, ArC*H*), 4.82 (q, J = 6.5 Hz, 1H, ArC*H*OHCH$_3$), 3.24 (br. s, O*H*, 1H), 1.44 (d, J = 6.5 Hz, 3H, ArCHOHC*H*$_3$).



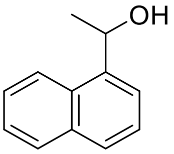
2-Fluoro-α-methyl-benzenemethanol (5g)[7]

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ: 7.96 (dd, *J* = 8.9, 5.4 Hz, 2H, ArC*H*), 7.31 (dd, *J* = 8.6, 5.5 Hz, 2H, ArC*H*), 4.82 (q, *J* = 6.4 Hz, 1H, ArC*H*OHCH_3), 3.16 (s, 1H, br. s, O*H*, 1H), 1.43 (d, *J* = 6.4 Hz, 3H, ArCHOHCH_3).



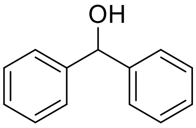
α-Methyl-2-naphthalenemethanol (5j)[8]

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ: 7.88 – 7.64 (m, 4H, ArC*H*), 7.58 – 7.35 (m, 3H, ArC*H*), 4.97 (q, *J* = 6.5 Hz, 1H, ArC*H*OHCH_3), 3.31 (s, 1H, br. S, O*H*, 1H), 1.52 (d, *J* = 6.5 Hz, 3H, ArCHOHCH_3).



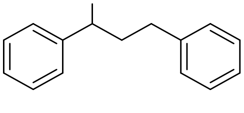
α-Methyl-1-naphthalenemethanol (5k)[9]

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ: 8.21 – 8.11 (m, 1H, ArC*H*),7.96 – 7.89 (m, 1H, ArC*H*), 7.82 (d, *J* = 8.2, 1H, ArC*H*), 7.74 (d, *J* = 7.2, 1H, ArC*H*), 7.64 – 7.45 (m, 3H, ArC*H*), 5.67 (q, *J* = 6.4 Hz, 1H ArC*H*OHCH_3), 3.04 (s, 1H, s, 1H, br. s, O*H*, 1H), 1.70 (d, *J* = 6.5 Hz, 3H, ArCHOHCH_3).



α-Phenyl-benzenemethanol (5l)[10]

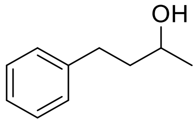
^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ: 7.39 – 7.17 (m, 10H, ArC*H*), 5.74 (s, 1H, ArC*H*OHAr), 2.87 (br. s, O*H*, 1H).



1,3-Diphenyl-1-propanol (5m)[11]

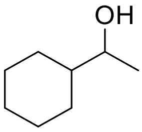
^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ: 7.29 (d, *J* = 4.4 Hz, 4H, ArC*H*), 7.25 – 7.17 (m, 4H, ArC*H*), 7.12 (d, *J* = 7.5 Hz, 2H), 4.63 (m, 1H, ArC*H*OHCH_3), 2.64 (m, 2H, CH_2), 2.07 (m, 2H, CH_2), 1.76 (d, *J* = 3.4 Hz, 1H. O*H*).

4-Phenyl-2-butanol (5n)[12]



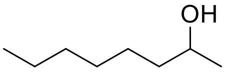
^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298K) δ: 7.26 – 7.18 (m, 2H, Ar$\mathrm{C}H$), 7.13 (m, 2H, Ar$\mathrm{C}H$), 3.76 (q, J = 6.2 Hz, 1H, $\mathrm{CH_2C}H\mathrm{OHCH_3}$), 2.90 – 2.38 (m, 2H, $\mathrm{C}H_2$), 1.70 (m, 2H, $\mathrm{C}H_2$), 1.27 (br. s, O*H*, 1H), 1.16 (d, J = 6.1 Hz, 3H, $\mathrm{C}H_3$).

(1-Hydroxyethyl)cyclohexane (5p)[13]



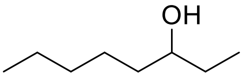
^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298K) δ: 3.44 (p, J = 6.3 Hz, 1H, $\mathrm{CHC}H\mathrm{OHCH_3}$), 1.74 – 1.49 (m, 4H, $\mathrm{C}H_2$), 1.36 – 1.08 (m, 4H, $\mathrm{C}H_2$), 1.06 (d, J = 6.3 Hz, 3H, $\mathrm{C}H_3$), 1.01 – 0.79 (m, 2H, $\mathrm{C}H_2$).

2-Octanol (5q)[14]



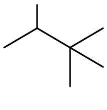
^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298K) δ: $\mathrm{CH_2C}H\mathrm{OH}$ peak overlapped with solvent, 1.46 – 1.16 (m, 10H, $\mathrm{C}H_2$), 1.09 (m, 3H, $\mathrm{CH_3}$), 0.95 – 0.72 (m, 3H, $\mathrm{CH_3}$).

3-Octanol (5r)[8]



^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298K) δ: 3.53 (m, 1H, $\mathrm{CH_2C}H\mathrm{OH}$), 1.67 – 1.23 (m, 11H, $10\mathrm{C}H_2$ and one O*H*), 0.94 (m, *6*H, 2 $\mathrm{C}H_3$).

3,3-Dimethyl-2-butanol (5s)[15]



^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298K) δ: $\mathrm{CH_2C}H\mathrm{OH}$ peak overlapped with solvent, 1.01 (d, J = 4 Hz, $\mathrm{C}H_3$, 3H), 0.80 (s, 9H, ^{t}Bu-$\mathrm{C}H_3$).

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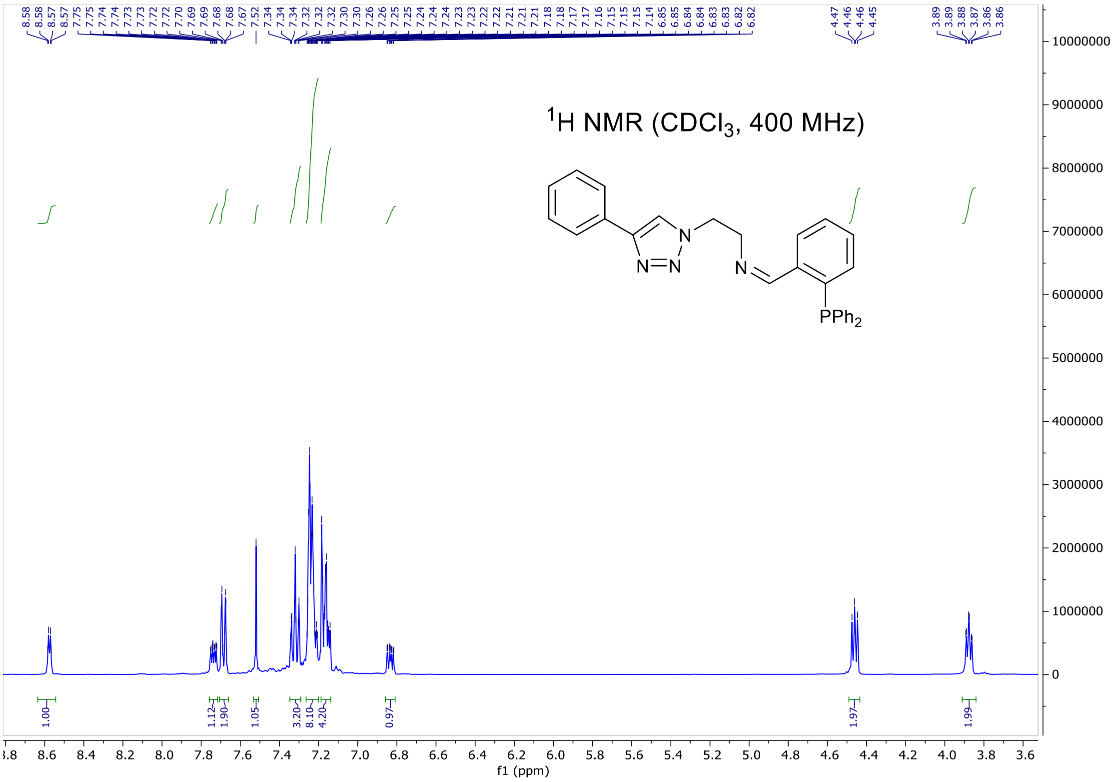
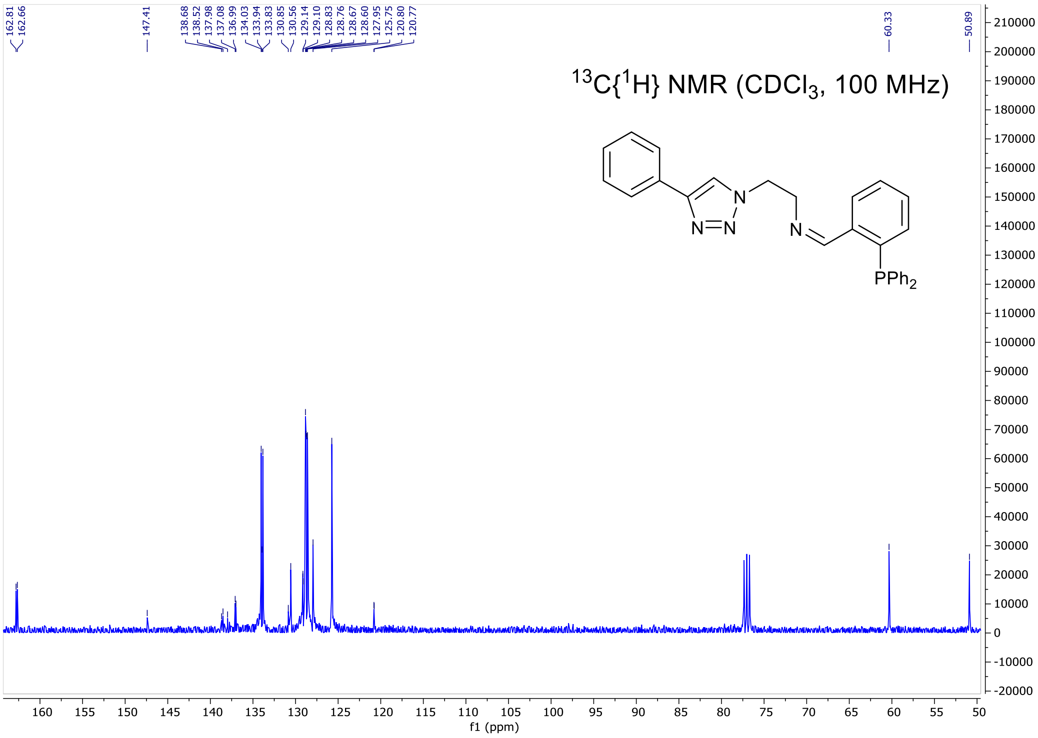
NMR Spectra of ligand 2 and complex 3

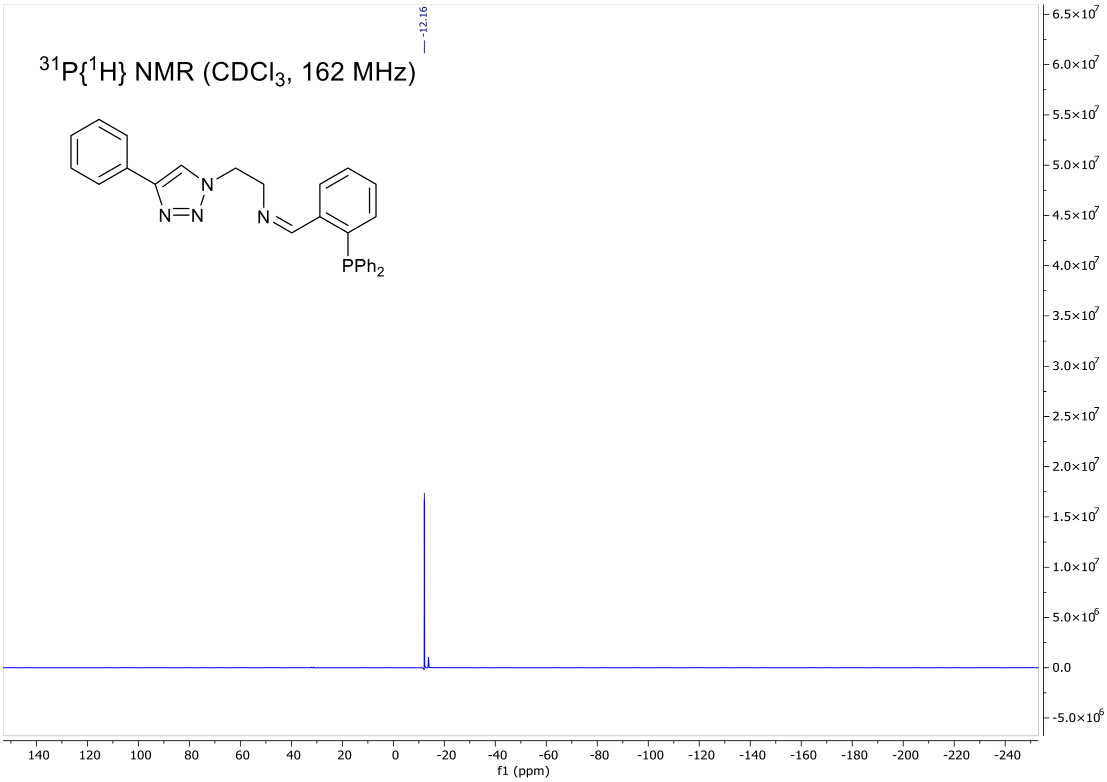
^{1}H NMR spectrum of 2



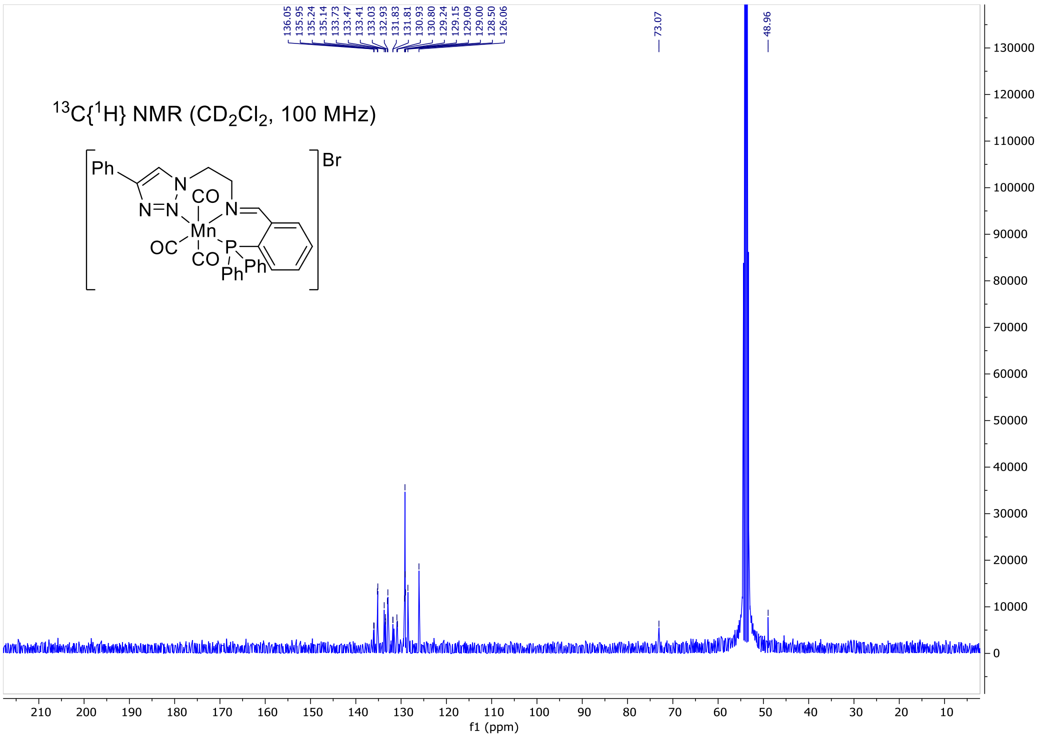
^{13}C{^{1}H} NMR spectrum of 2



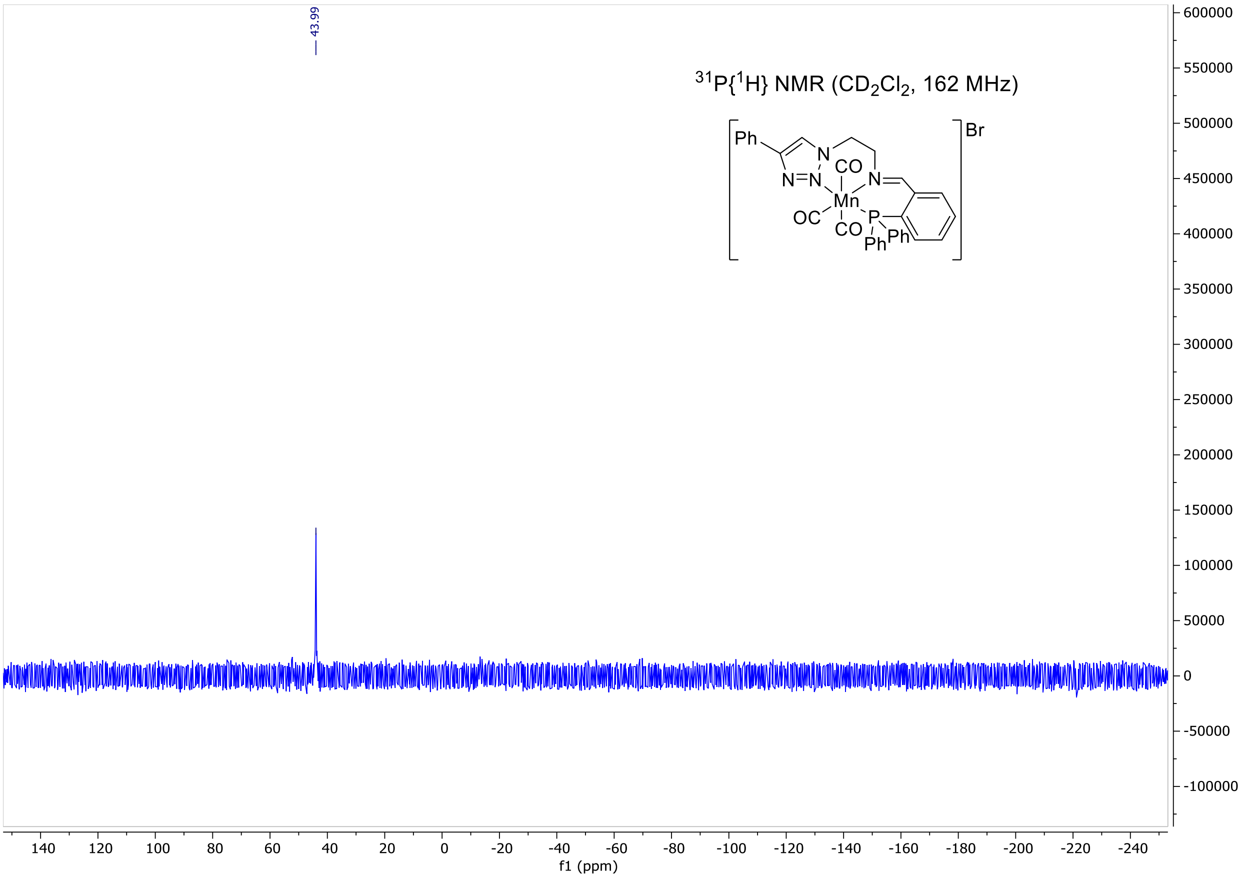
^{31}P{^{1}H} NMR spectrum of **2**



^{13}C{^{1}H} NMR spectrum of **3**

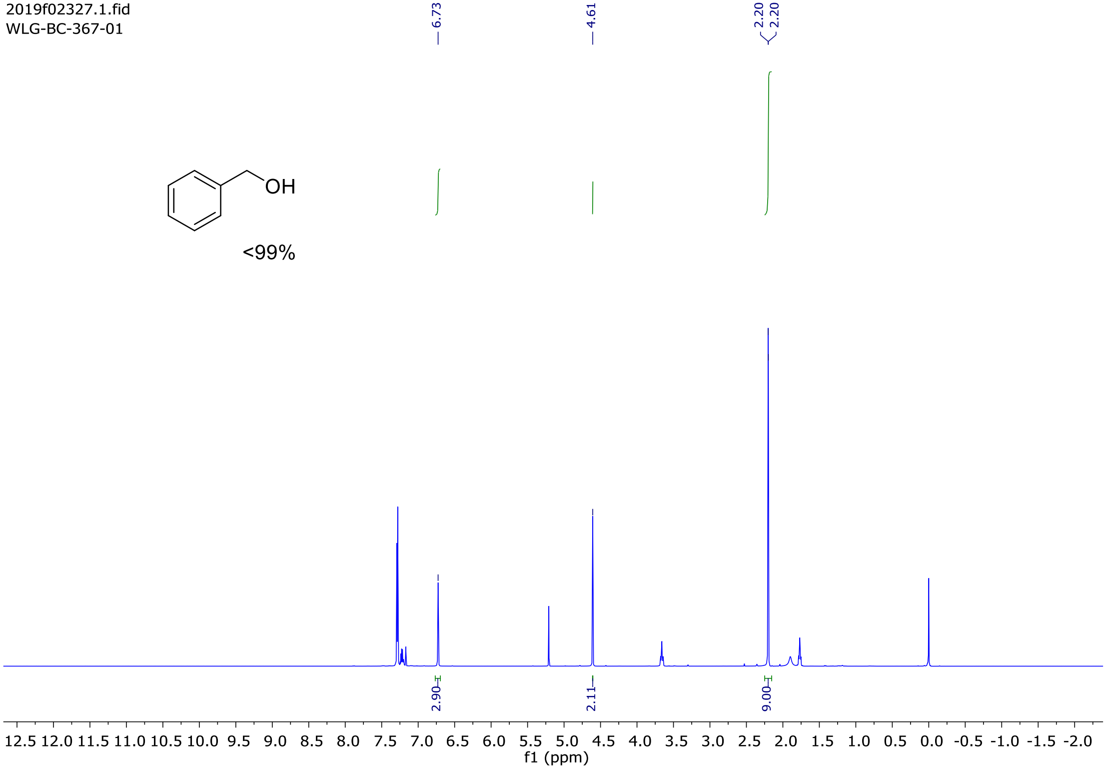


^{31}P{^{1}H} NMR spectrum of 3

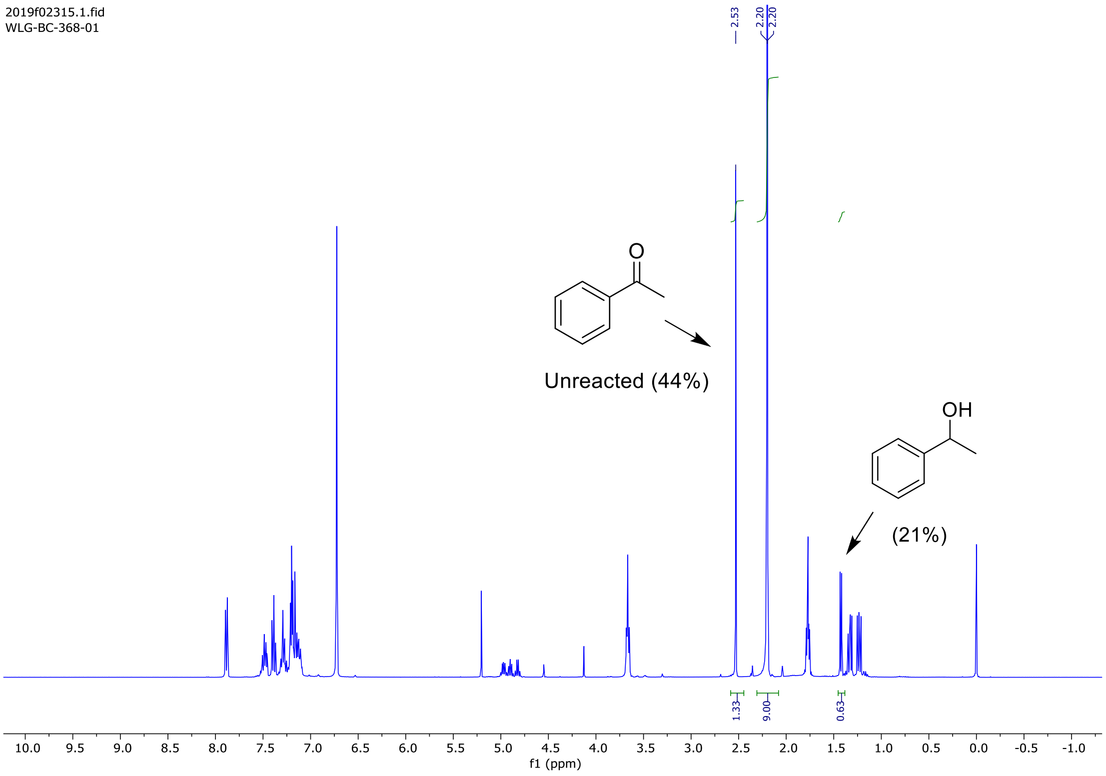


NMR spectra of the Mn(I) catalyzed hydrosilylation

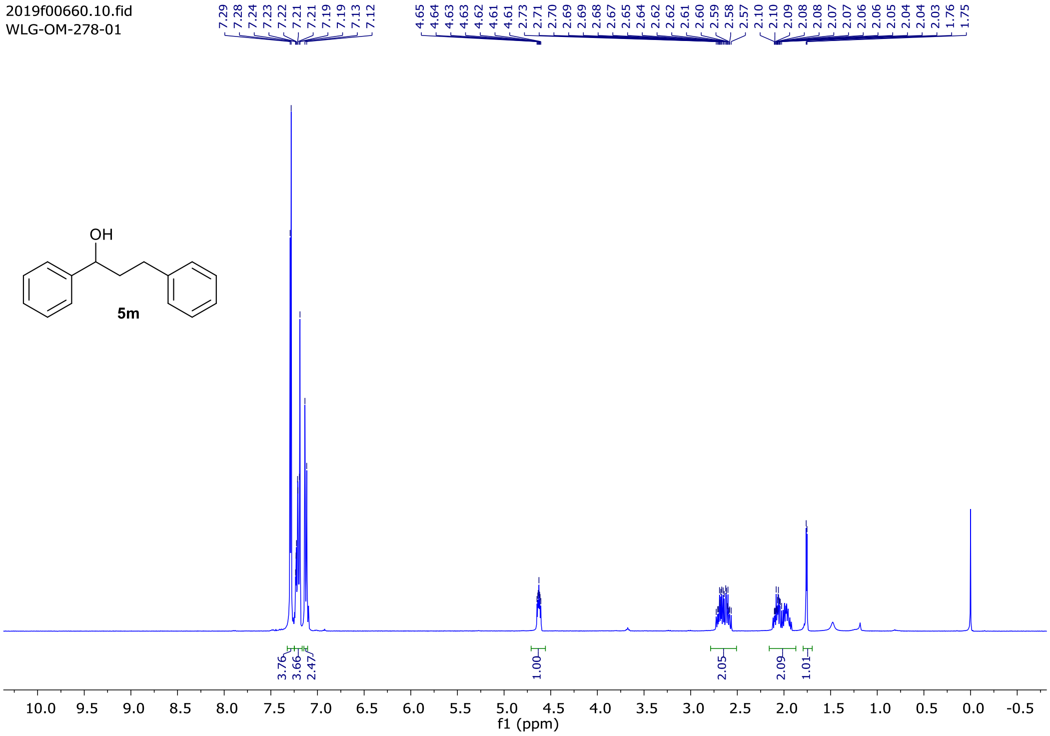
^{1}H NMR spectrum of benzyl alcohol obtained from hydrosilylation of benzaldehyde (Mesitylene is used as internal standard)



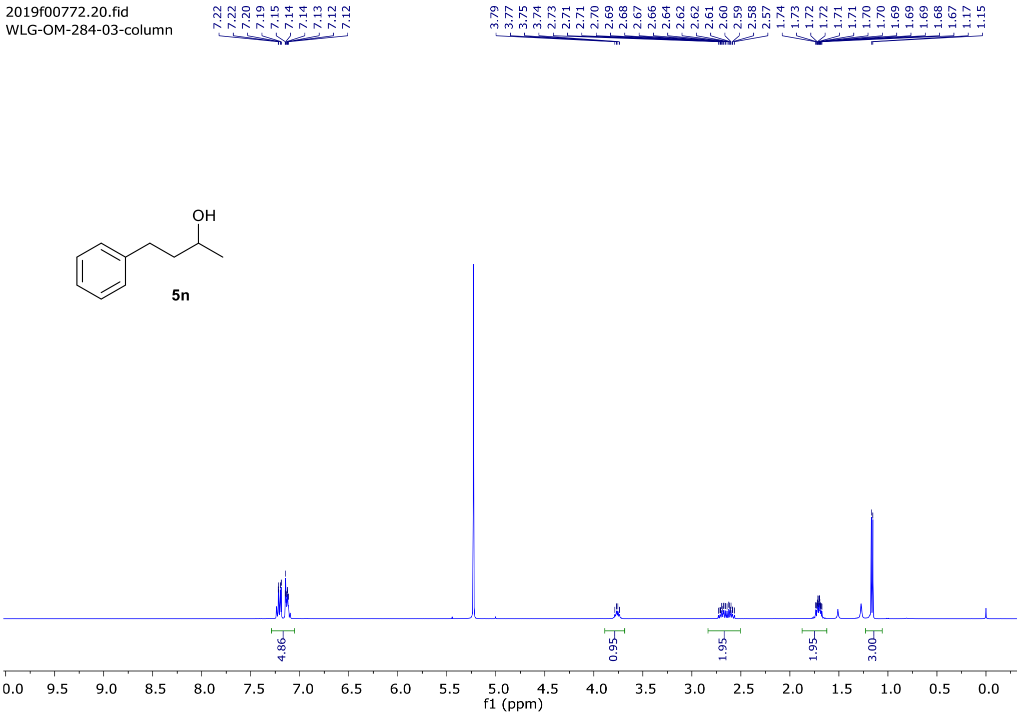
^{1}H NMR spectrum of the reaction mixture for the hydrosilylation of acetophenone catalyzed by $MnBr(CO)_5$: (Mesitylene is used as standard)



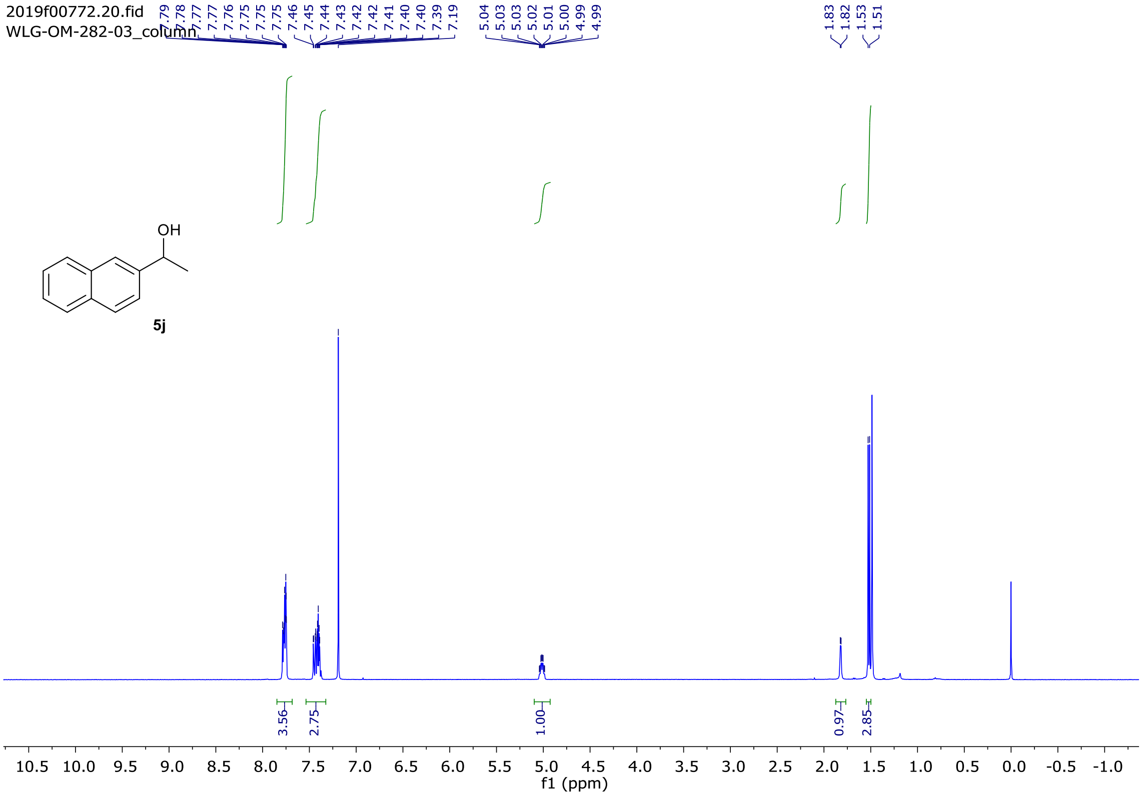
^{1}**H NMR** spectrum of isolated **5m**



^{1}**H NMR** spectrum of isolated **5n**

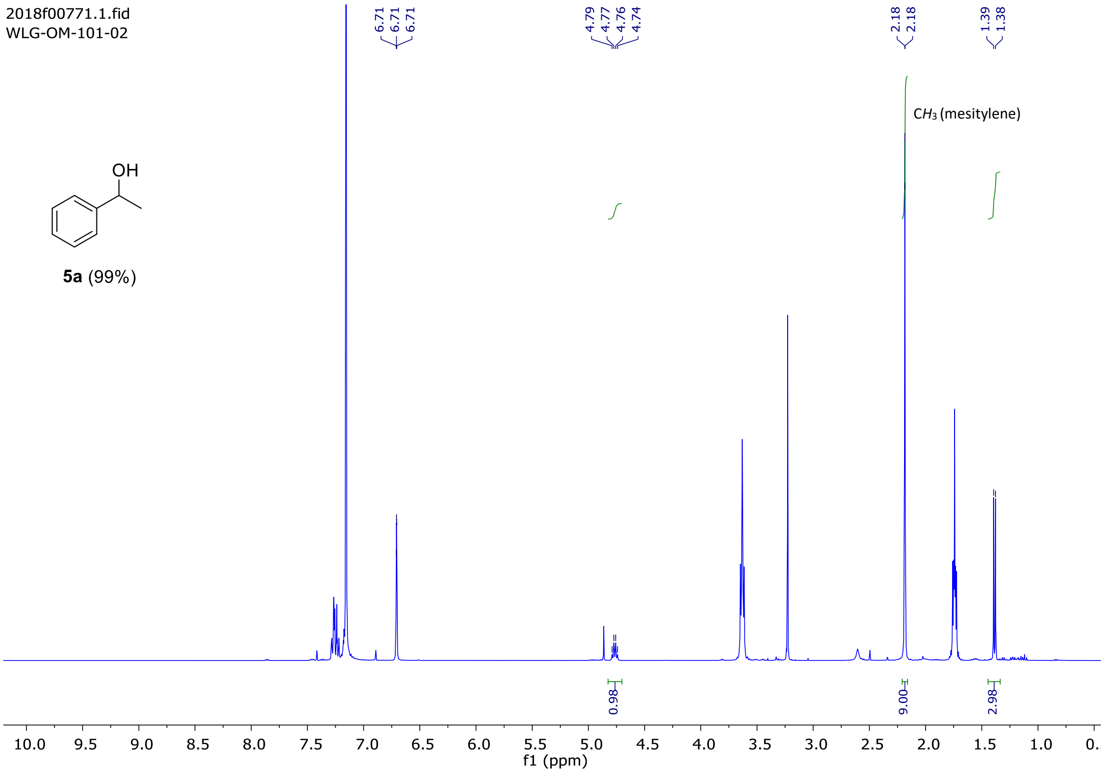


^{1}H NMR spectrum of isolated **5j**



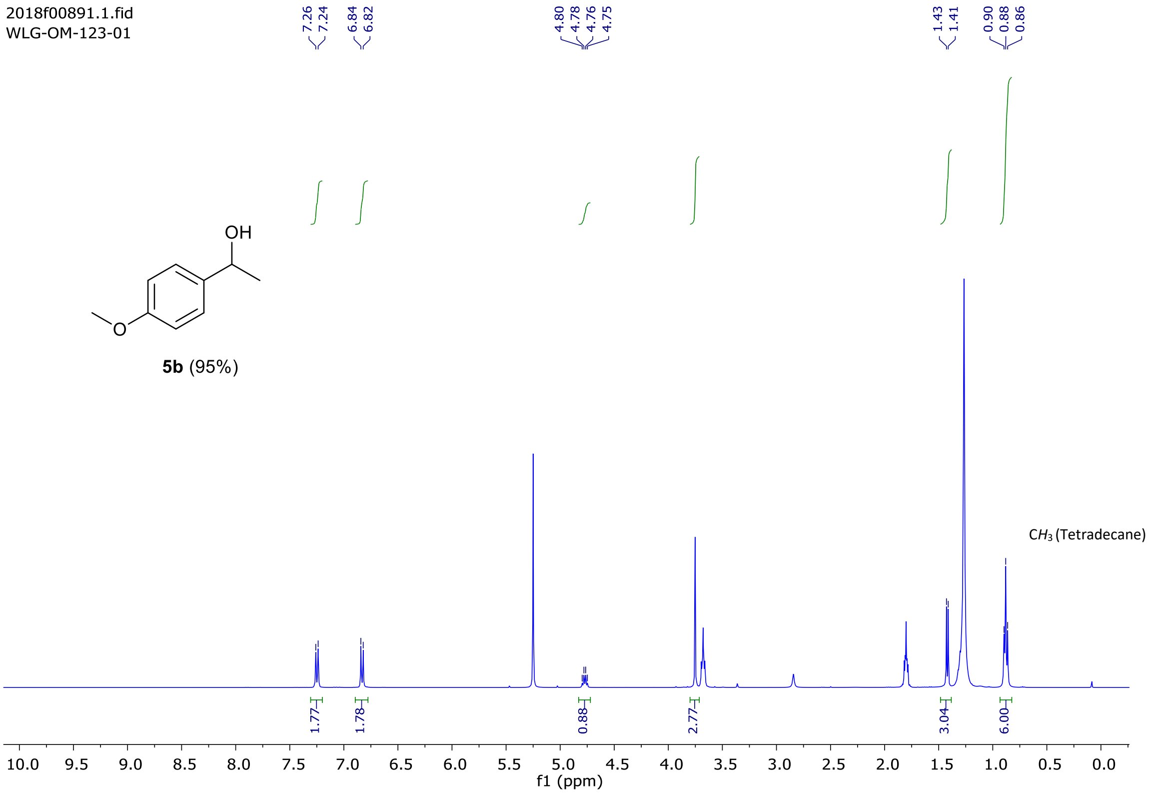
^{1}H NMR spectrum of the reaction mixture in the case of **5a**

(Table 1, entry 4, mesitylene was used as an internal standard)



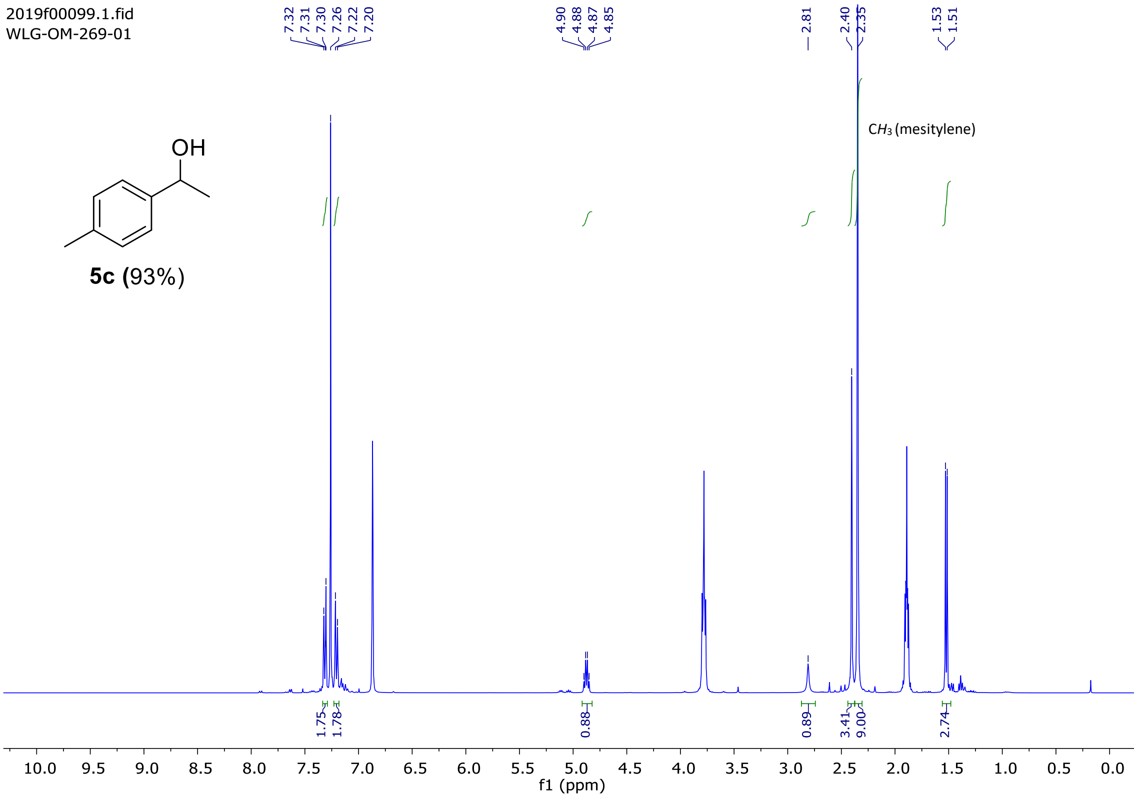
^{1}**H NMR** spectrum of the reaction mixture in the case of **5b**

(Tetradecane was used as an internal standard).



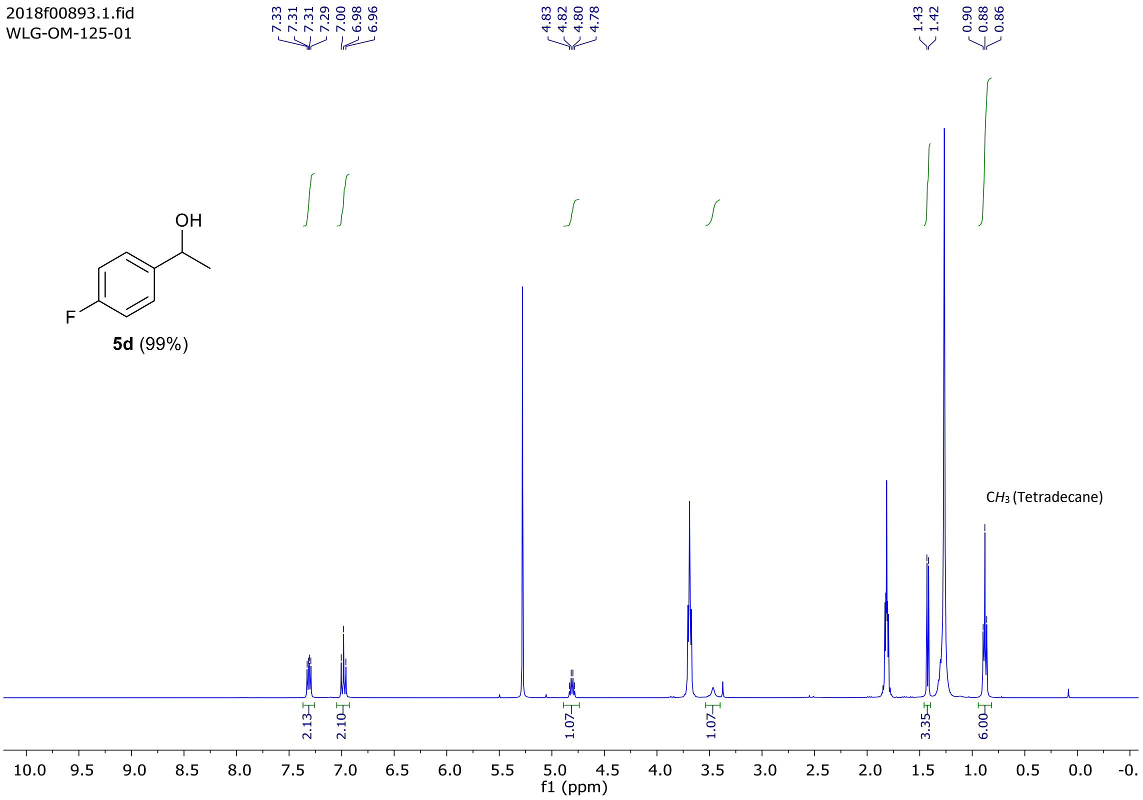
^{1}**H NMR** spectrum of the reaction mixture in the case of **5c**

(Mesitylene was used as an internal standard)



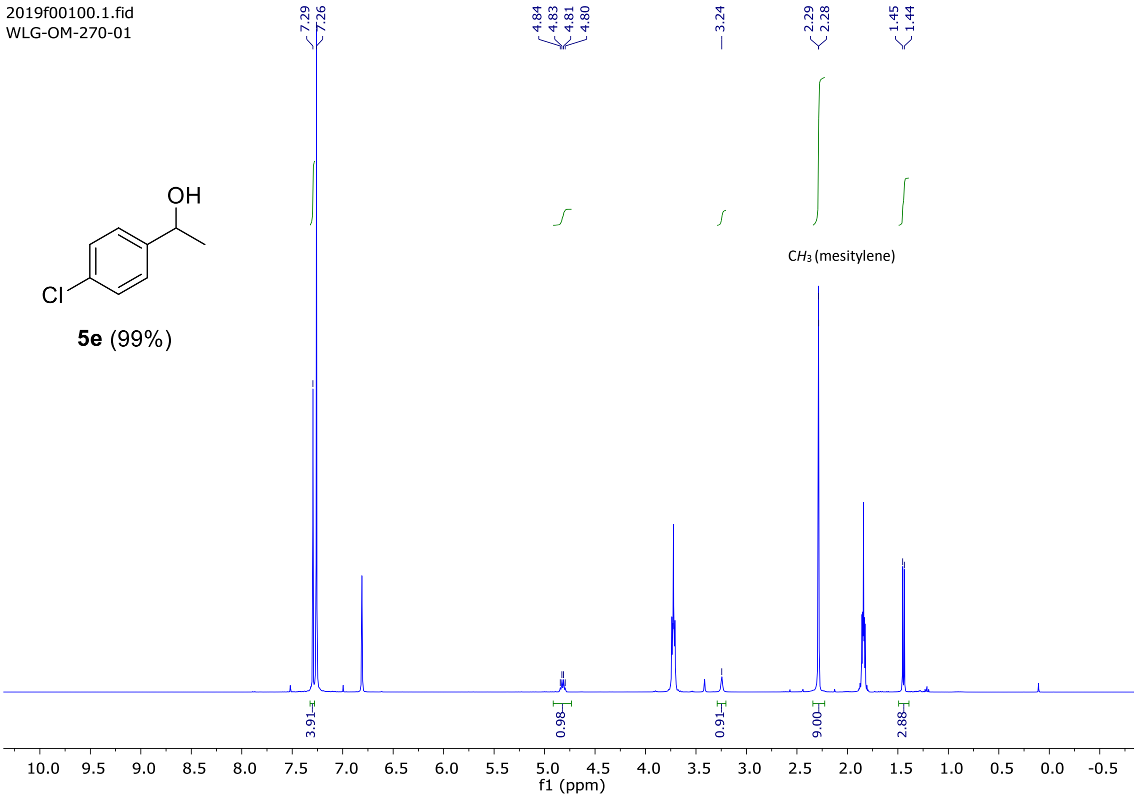
^{1}**H NMR** spectrum of the reaction mixture in the case of **5d**

(Tetradecane was used as an internal standard)



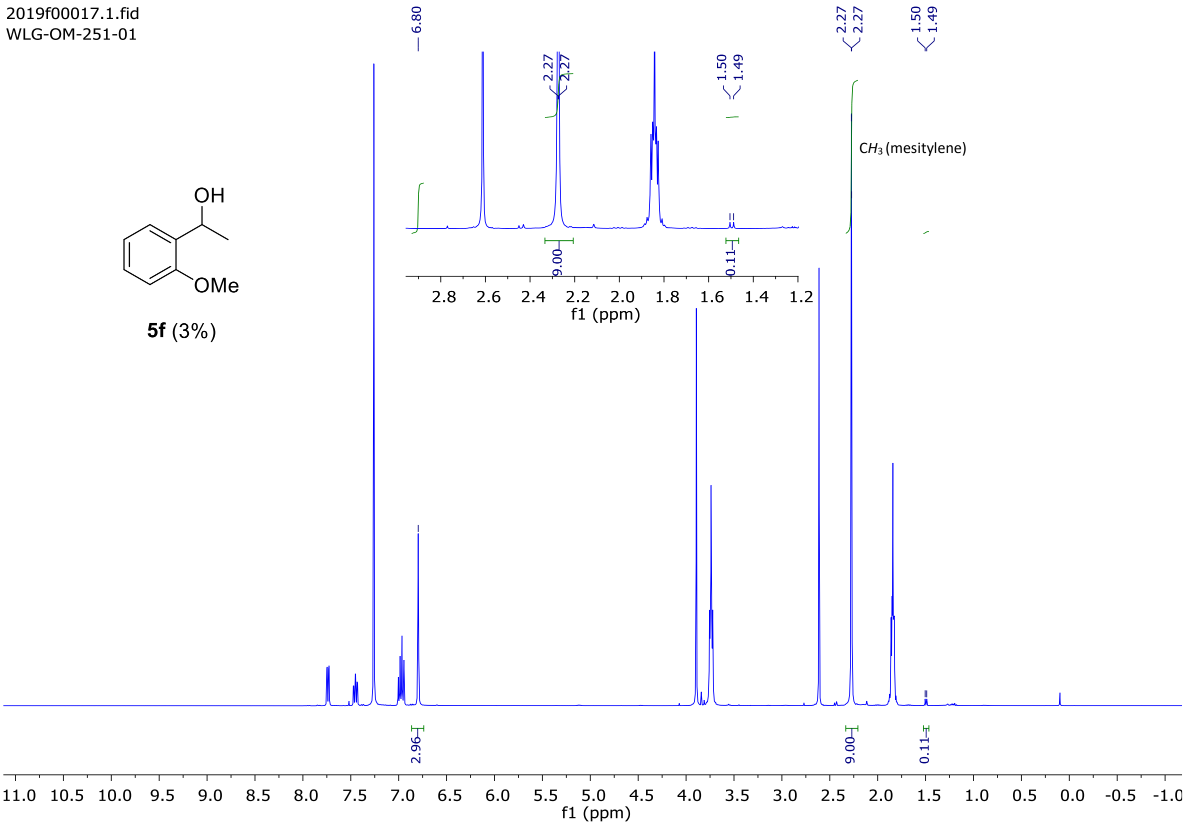
^{1}**H NMR** spectrum of the reaction mixture in the case of **5e**

(Mesitylene was used as an internal standard)



^{1}H NMR spectrum of the reaction mixture in the case of 5f

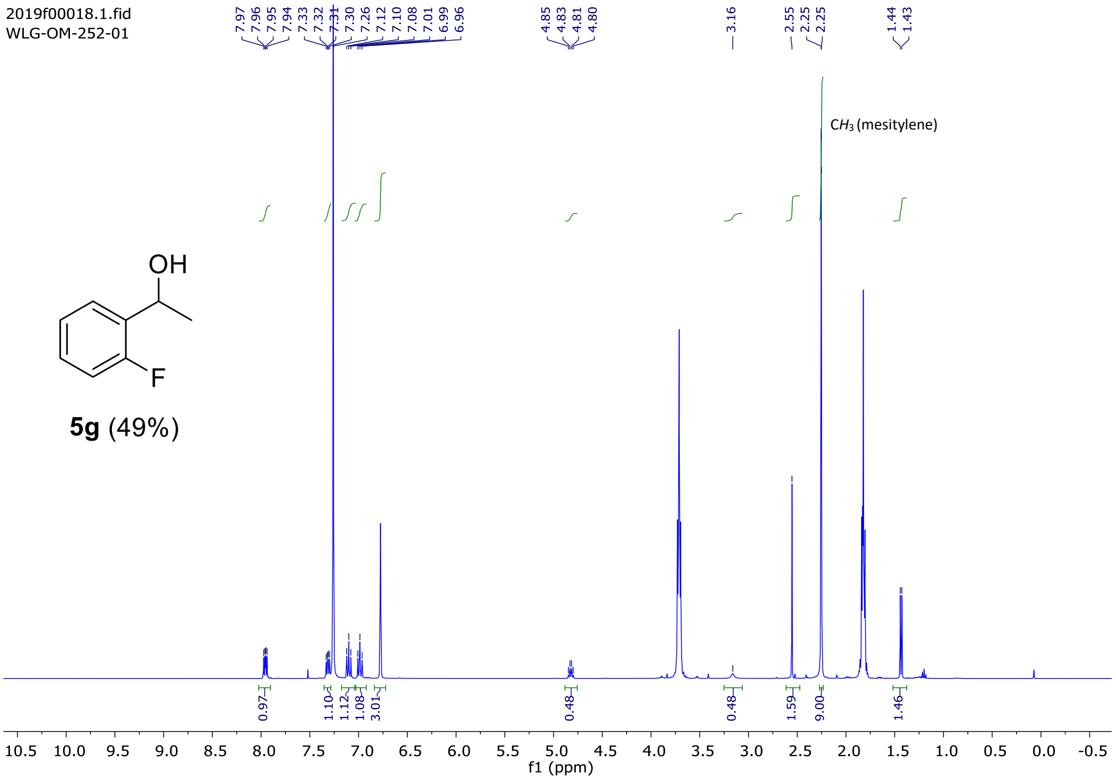
(Mesitylene was used as an internal standard)



5f (3%)

^{1}H NMR spectrum of the reaction mixture in the case of 5g

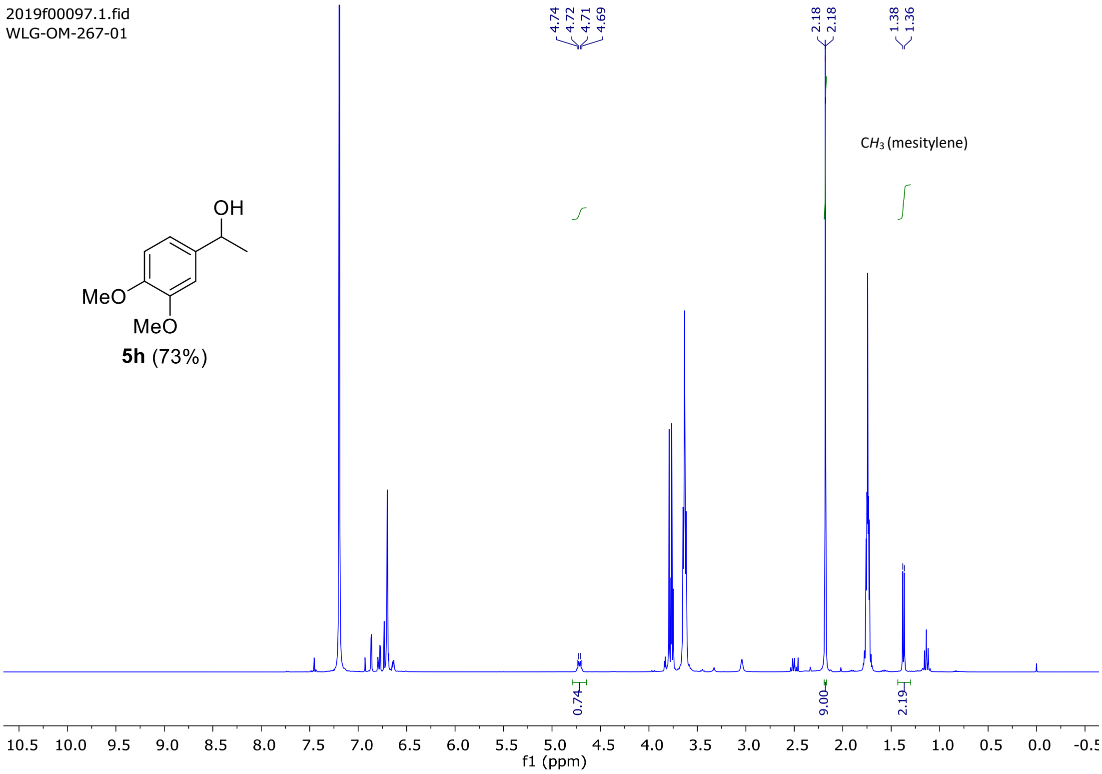
(Mesitylene was used as an internal standard)



5g (49%)

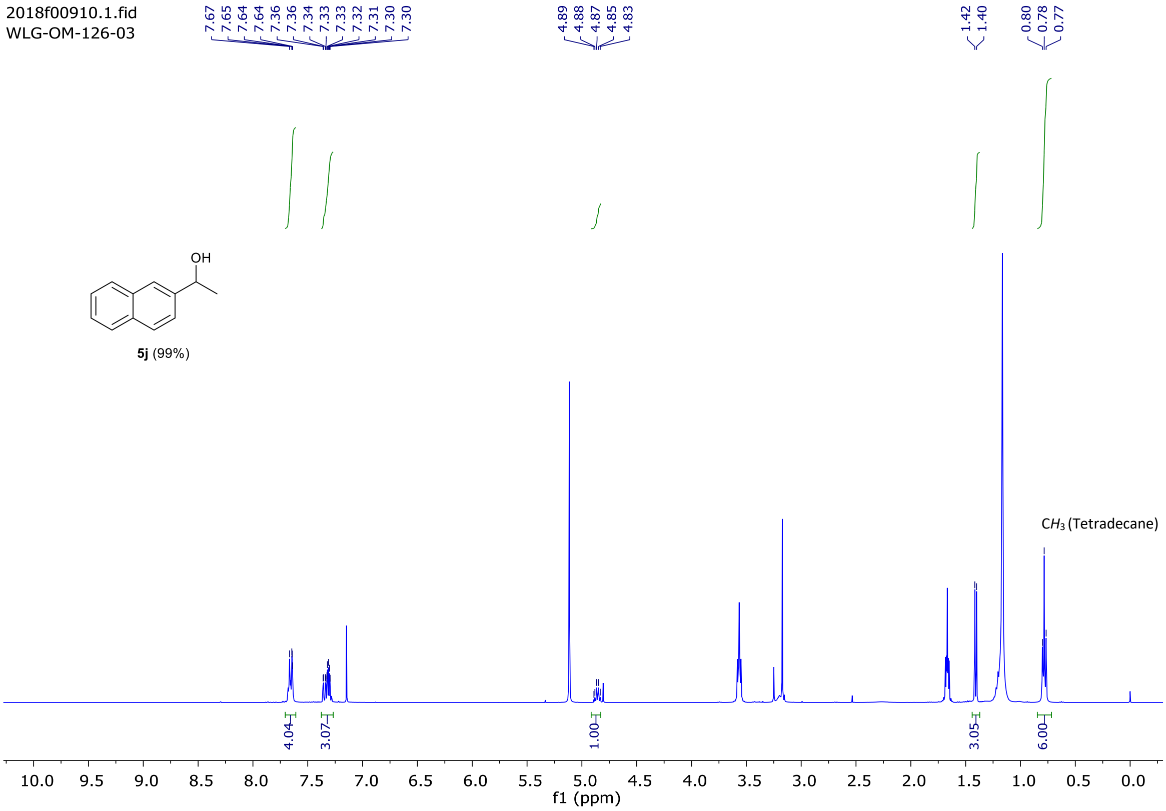
^{1}H NMR spectrum of the reaction mixture in the case of **5h**

(Mesitylene was used as an internal standard)



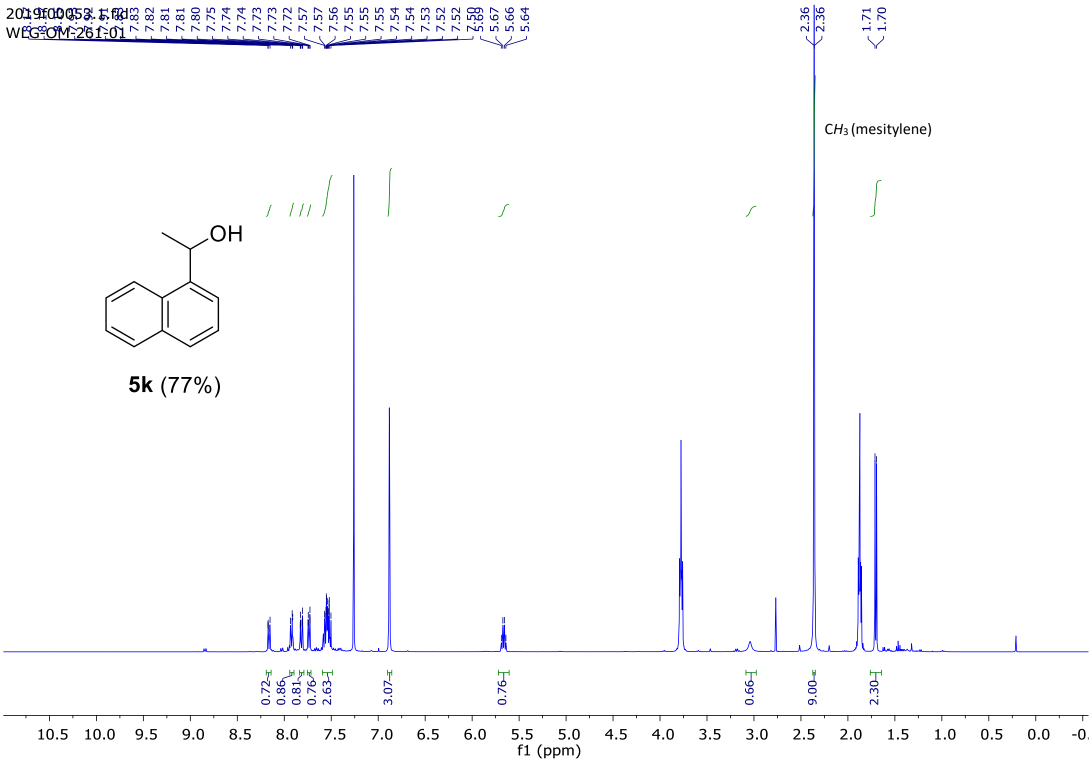
^{1}H NMR spectrum of the reaction mixture in the case of **5j**

(Tetradecane was used as an internal standard)



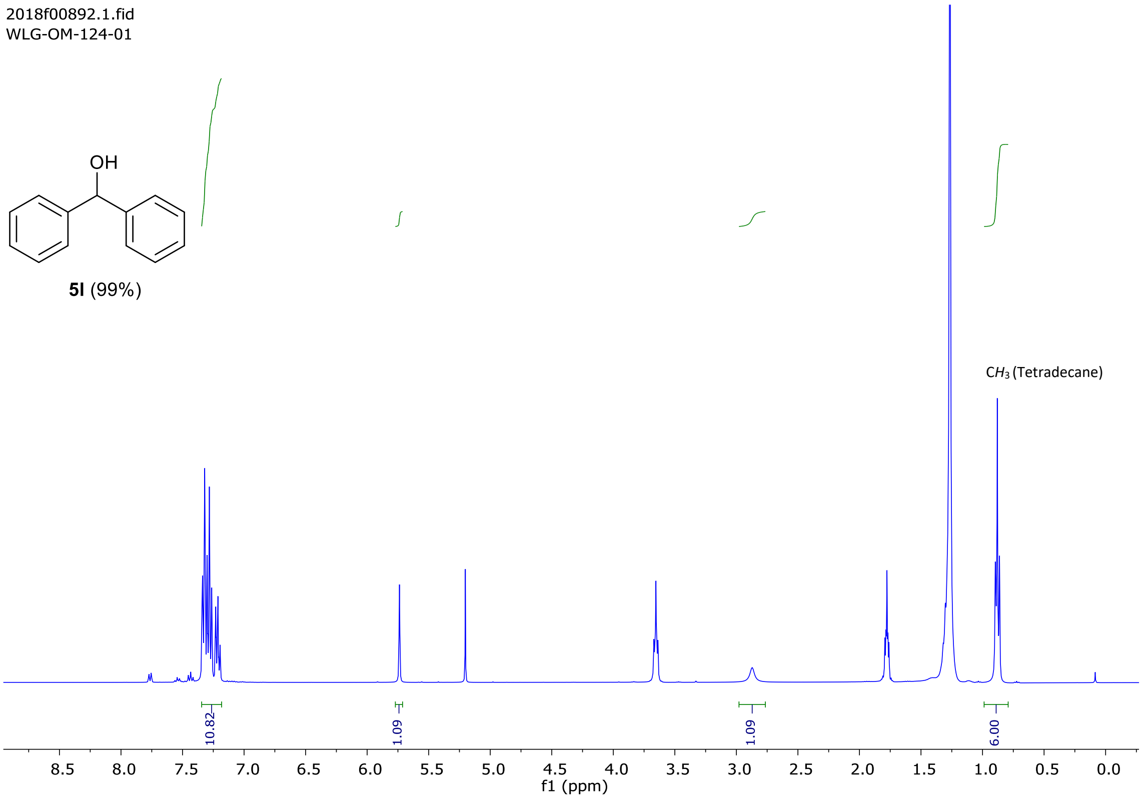
^{1}H NMR spectrum of the reaction mixture in the case of **5k**

(Mesitylene used as an internal standard)



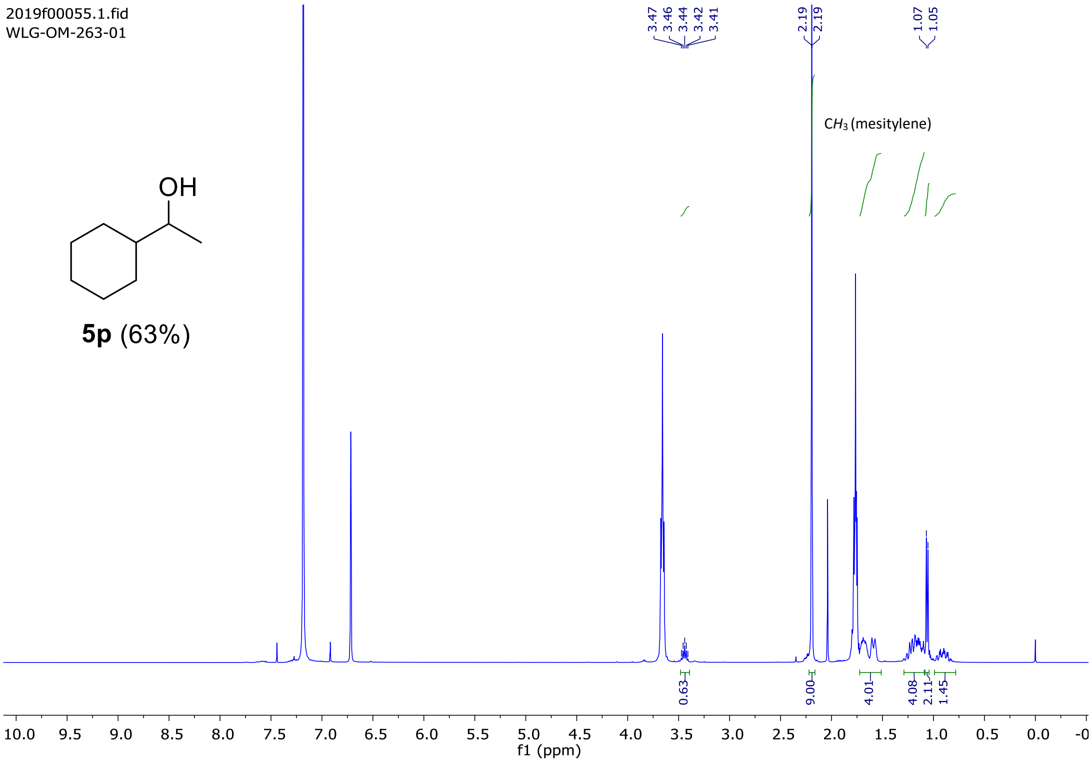
^{1}H NMR spectrum of the reaction mixture in the case of **5l**

(Tetradecane was used as an internal standard)



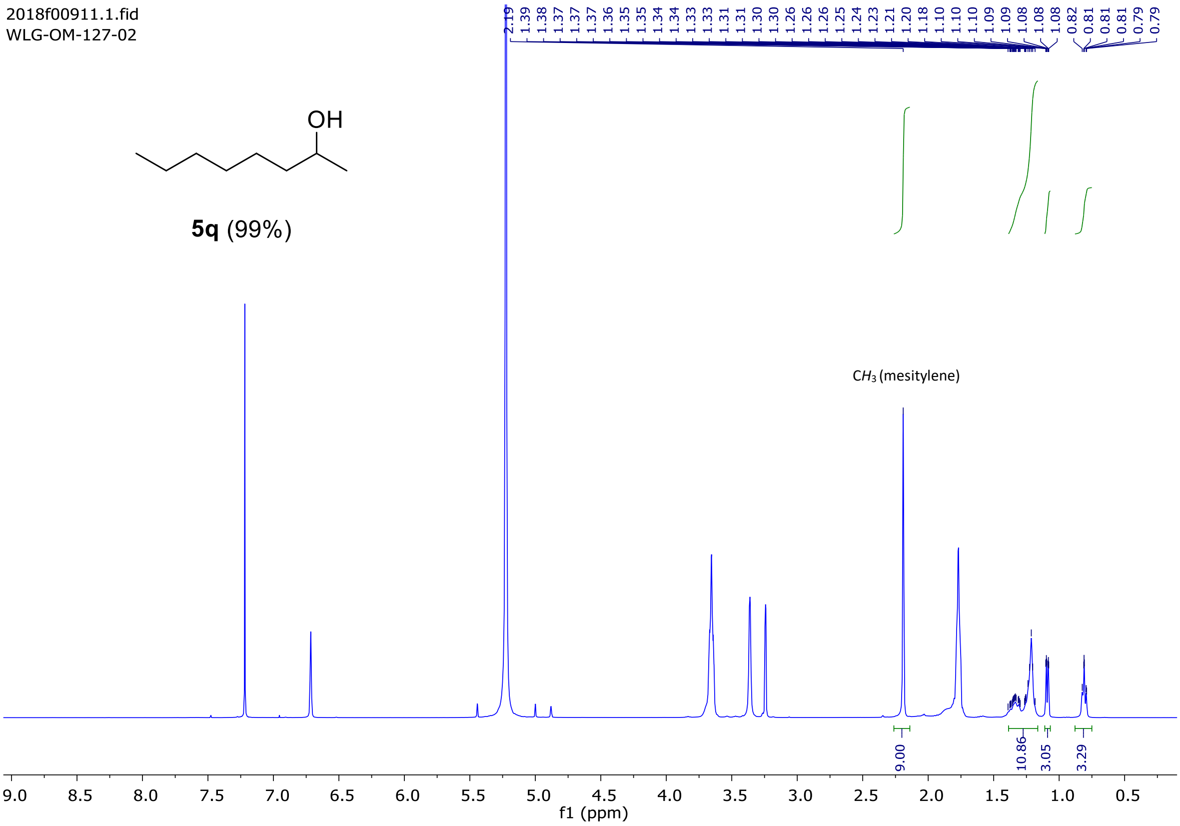
^{1}H NMR spectrum of the reaction mixture in the case of **5p**

(Mesitylene was used as an internal standard)



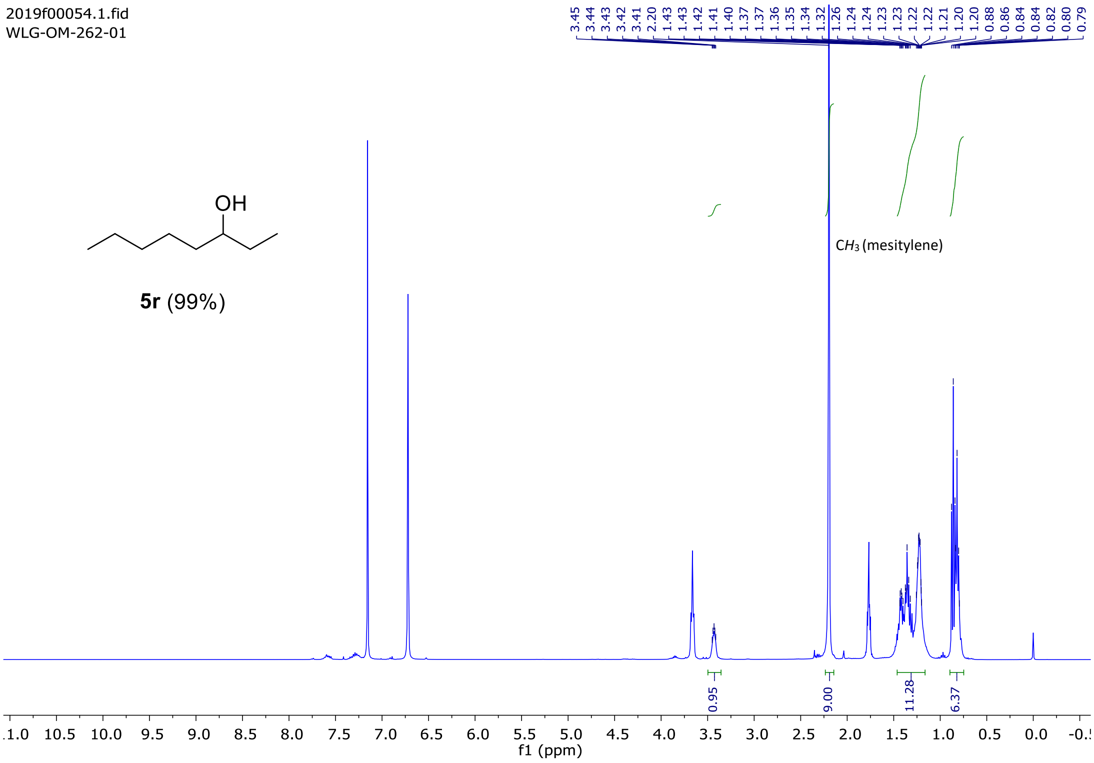
^{1}H NMR spectrum of the reaction mixture in the case of **5q**

(Mesitylene was used as an internal standard)



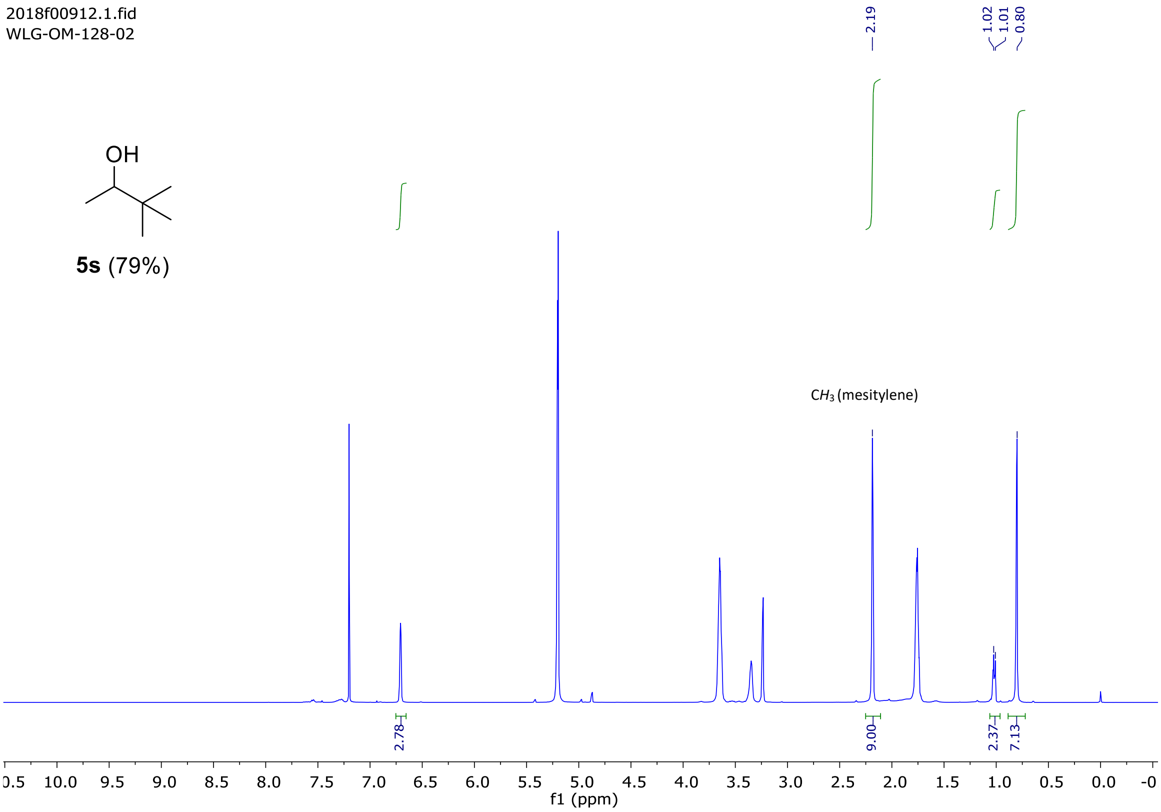
^{1}**H NMR** spectrum of the reaction mixture in the case of **5r**

(Mesitylene was used as an internal standard)



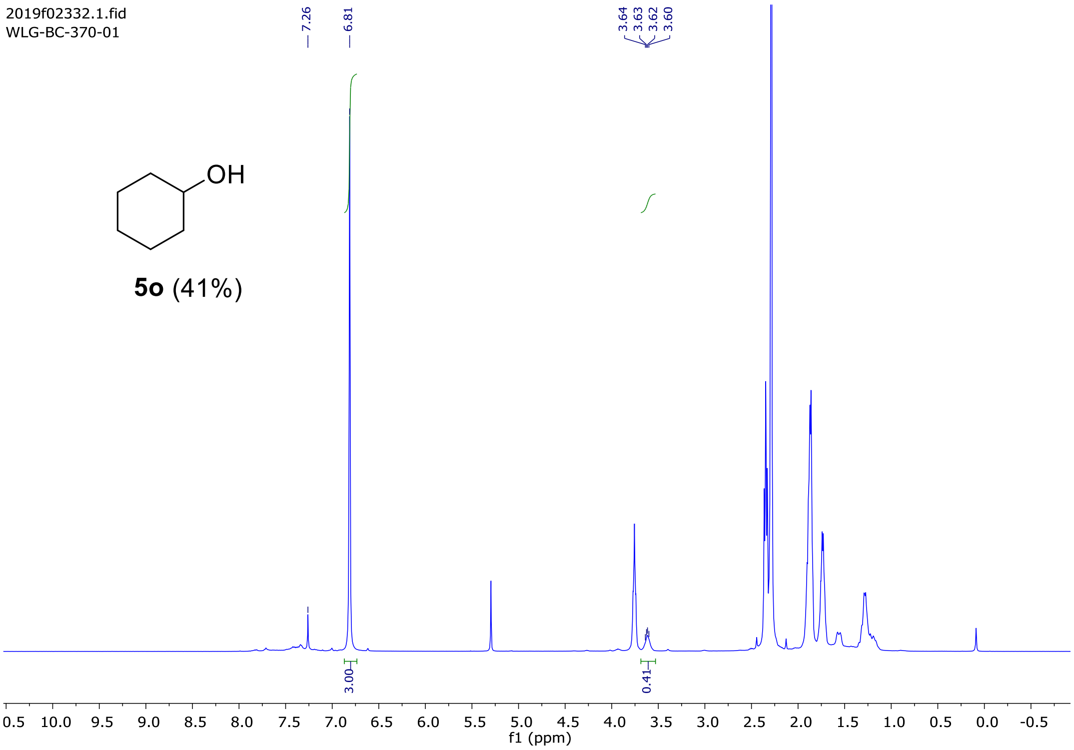
^{1}**H NMR** spectrum of the reaction mixture in the case of **5s**

(Mesitylene was used as an internal standard)



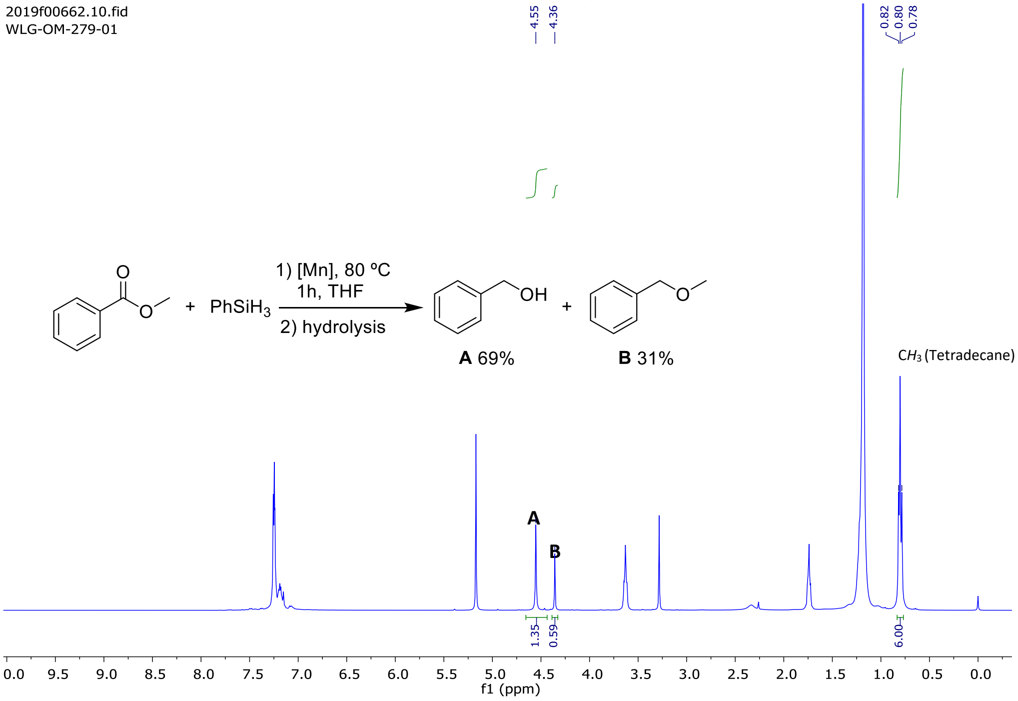
^{1}**H NMR** spectrum of the reaction mixture in the case of **5o**

(Mesitylene was used as an internal standard)

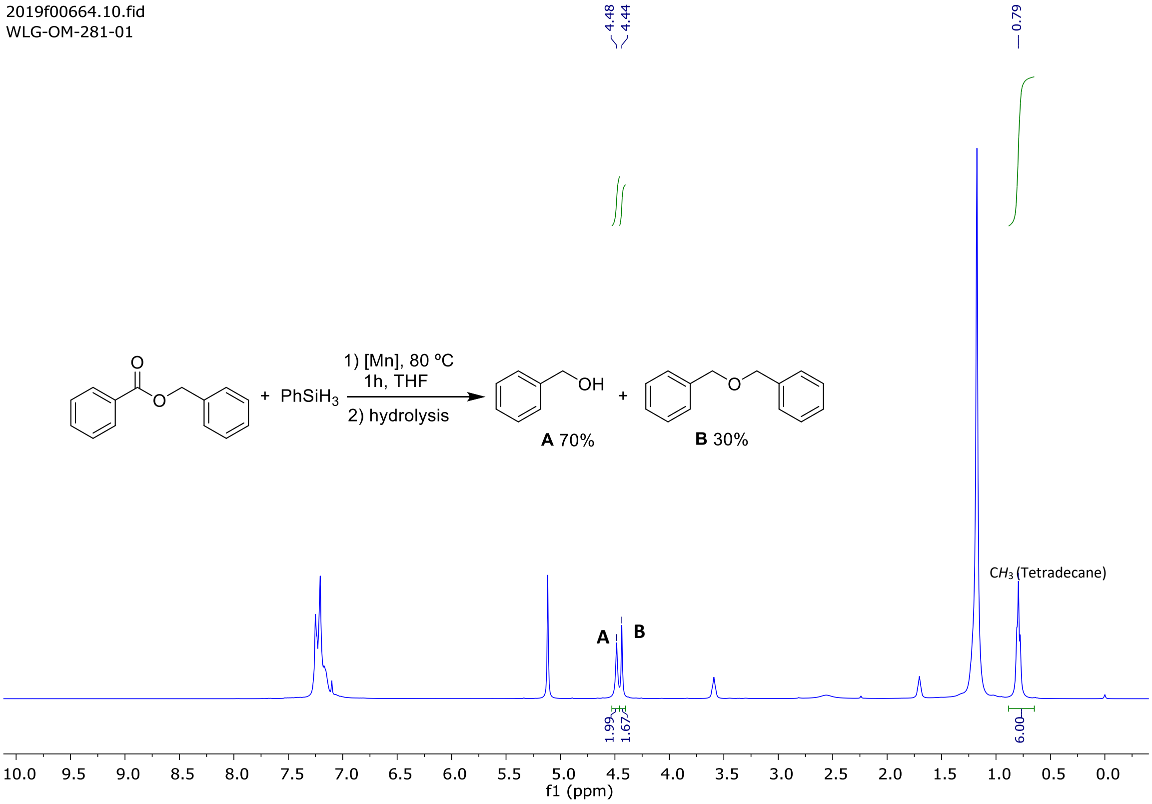


^{1}**H NMR** spectrum of the reaction mixture in the case of Table 3, entry 1

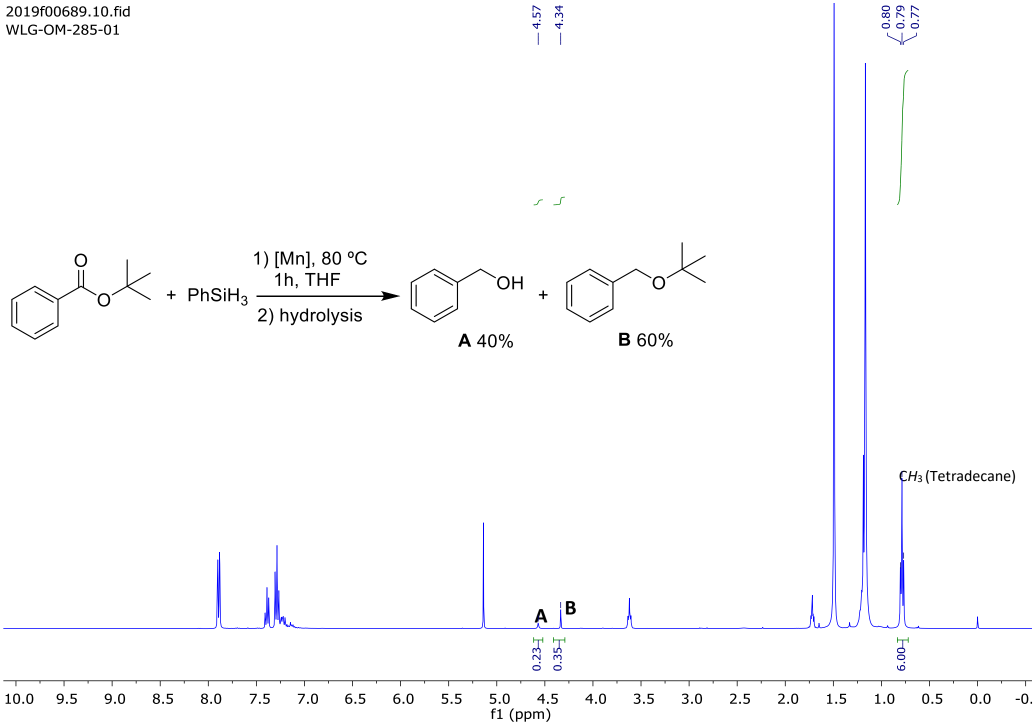
(Tetradecane was used as an internal standard)



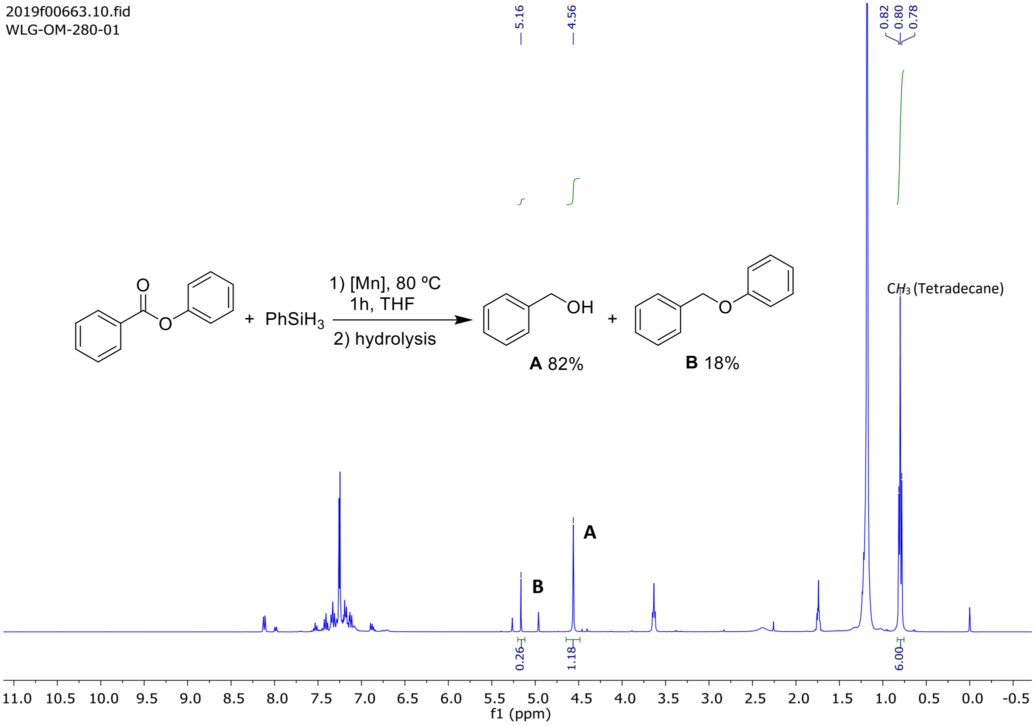
^{1}H NMR spectrum of the reaction mixture in the case of Table 3, entry 3 (Tetradecane was used as an internal standard)



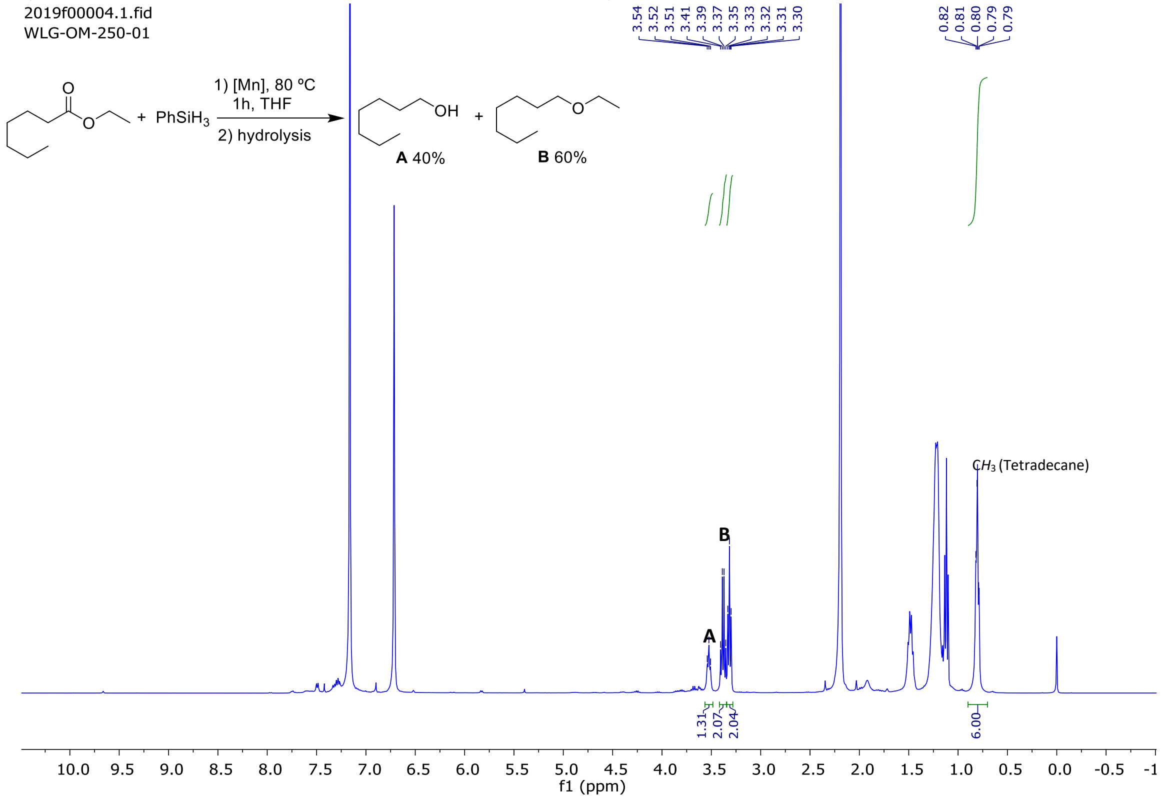
^{1}H NMR spectrum of the reaction mixture in the case of Table 3, entry 4 (Tetradecane was used as an internal standard)



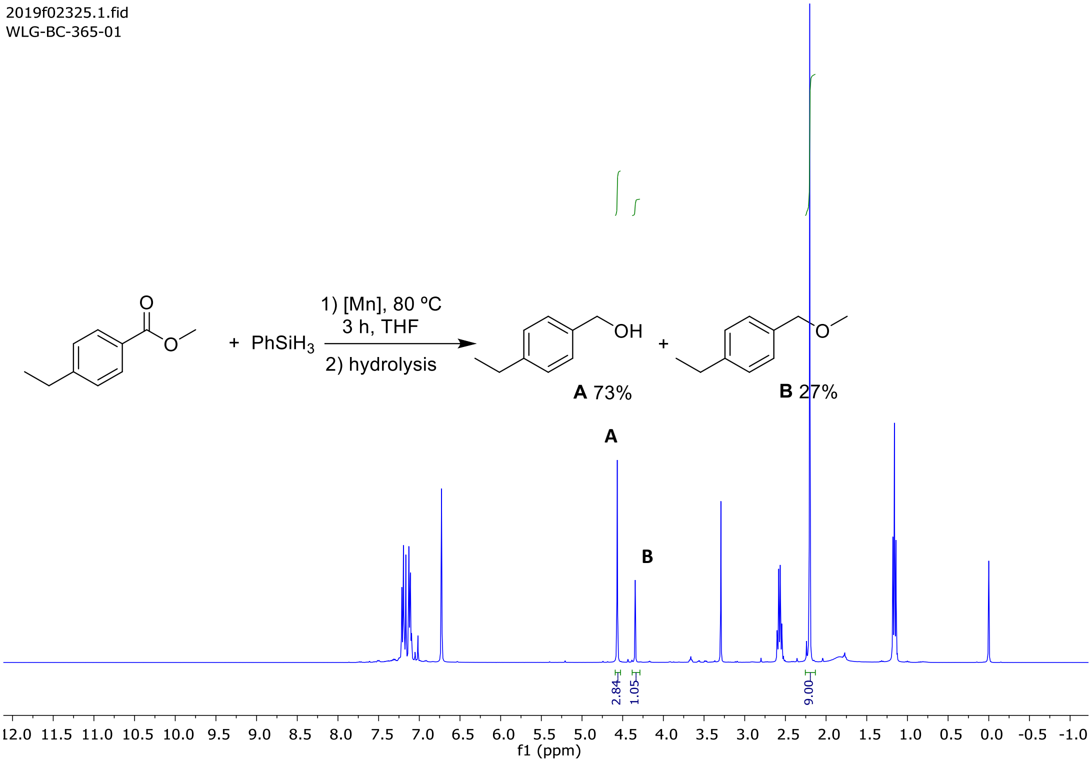
^{1}H NMR spectrum of the reaction mixture in the case of Table 3, entry 5 (Tetradecane was used as an internal standard)



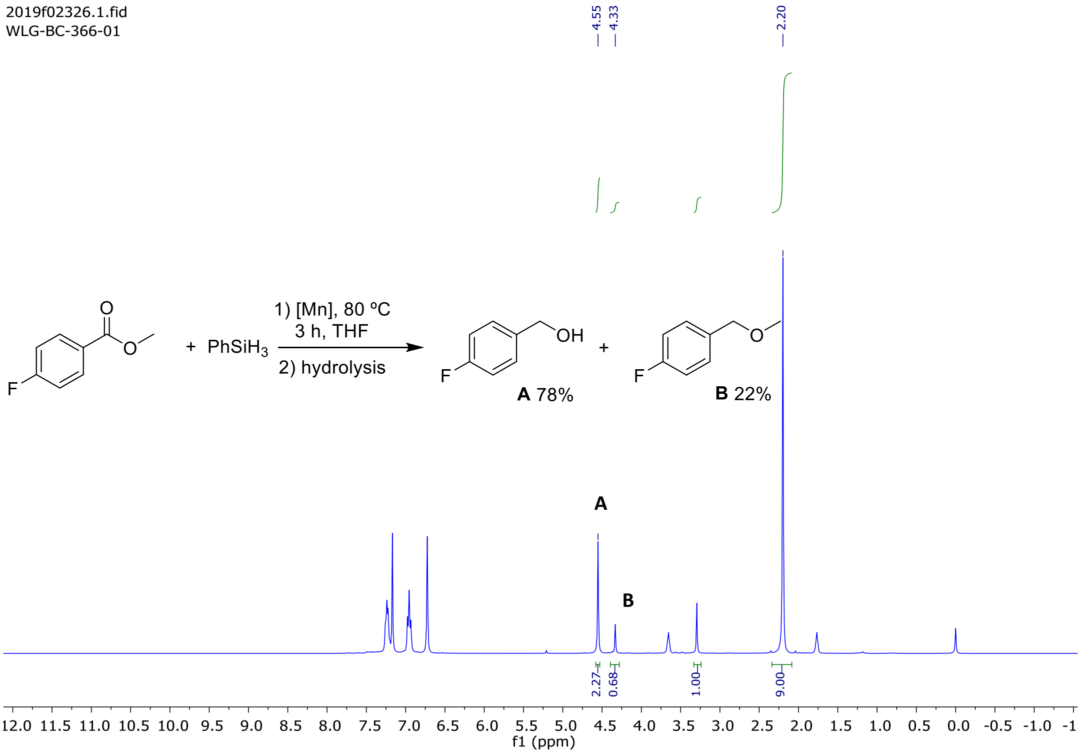
^{1}H NMR spectrum of the reaction mixture in the case of Table 3, entry 6 (Tetradecane was used as an internal standard)



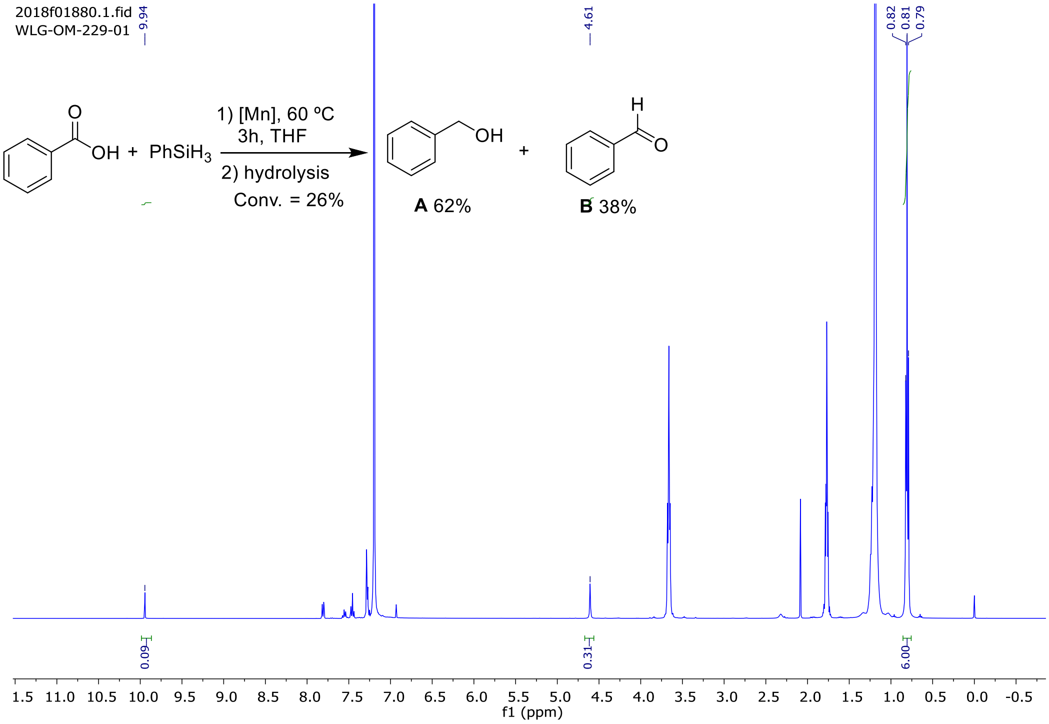
^{1}H NMR spectrum of the reaction mixture in the case of Table 3, entry 7 (Tetradecane was used as an internal standard)



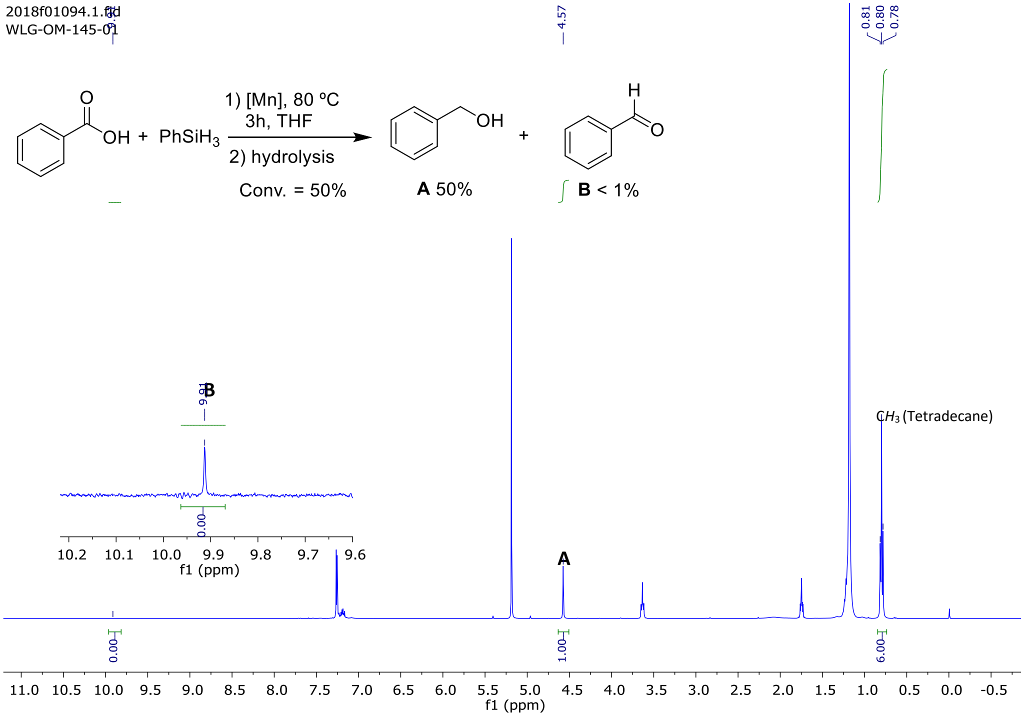
^{1}H NMR spectrum of the reaction mixture in the case of Table 3, entry 8 (Tetradecane was used as an internal standard)



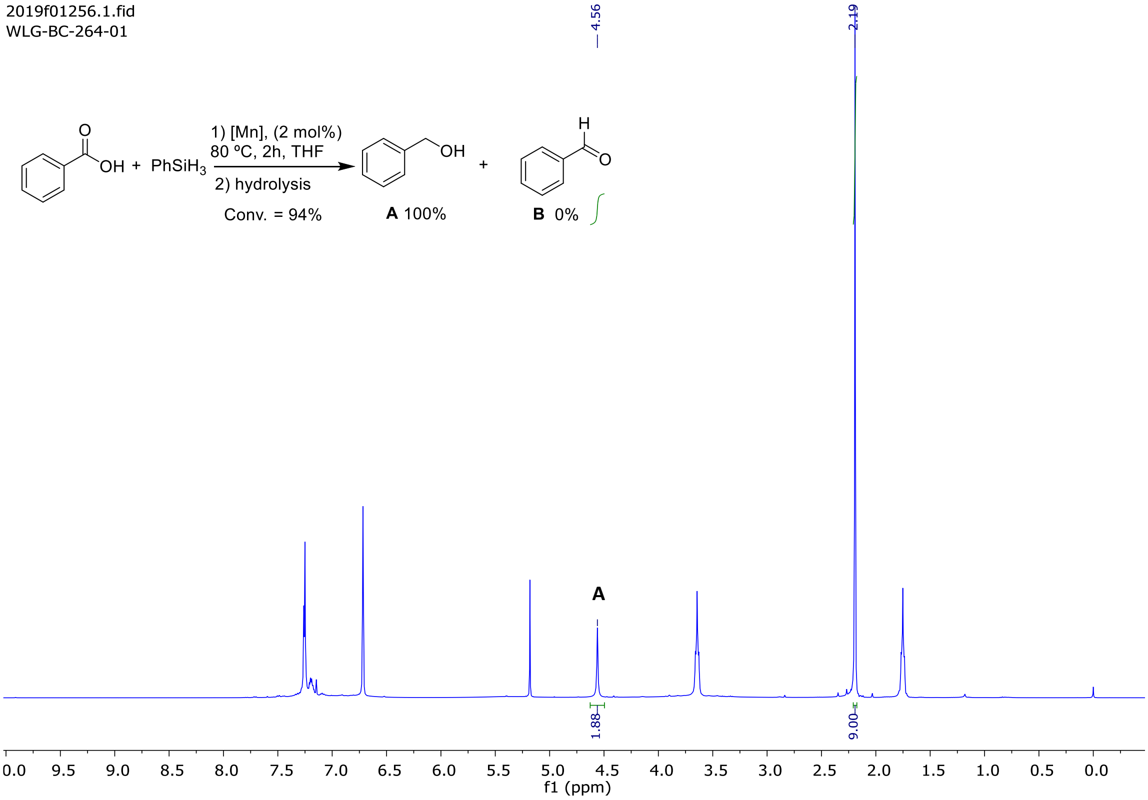
^{1}**H NMR** spectrum of the reaction mixture in the case of Table 4, entry 1 (Tetradecane was used as an internal standard)



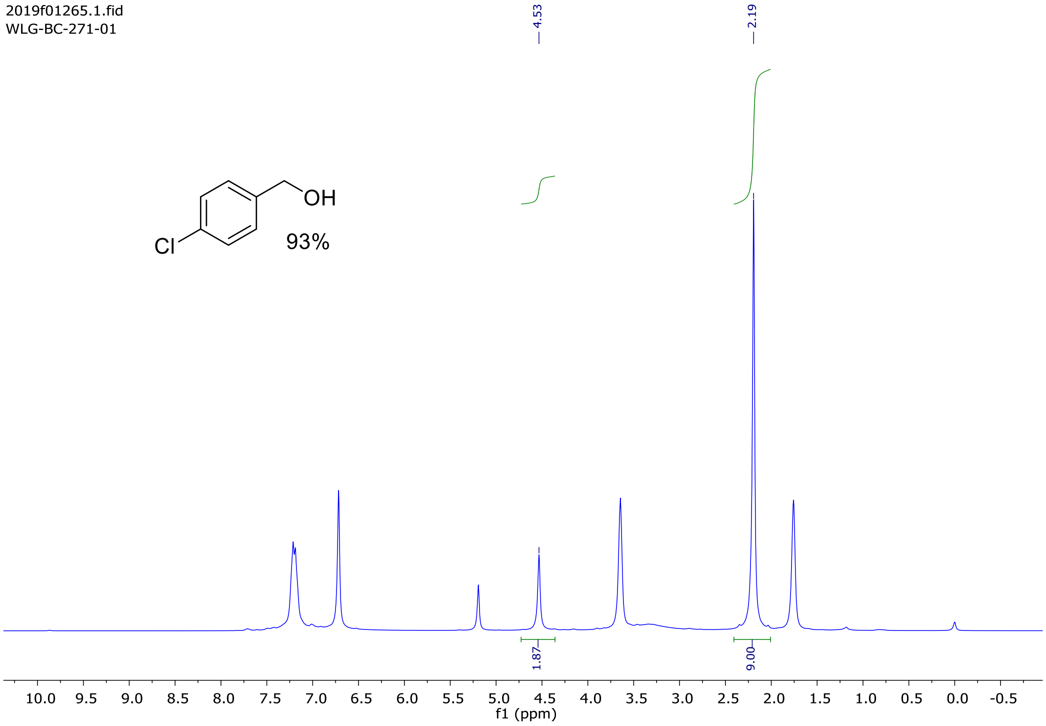
^{1}**H NMR** spectrum of the reaction mixture in the case of Table 4, entry 2 (Tetradecane was used as an internal standard)



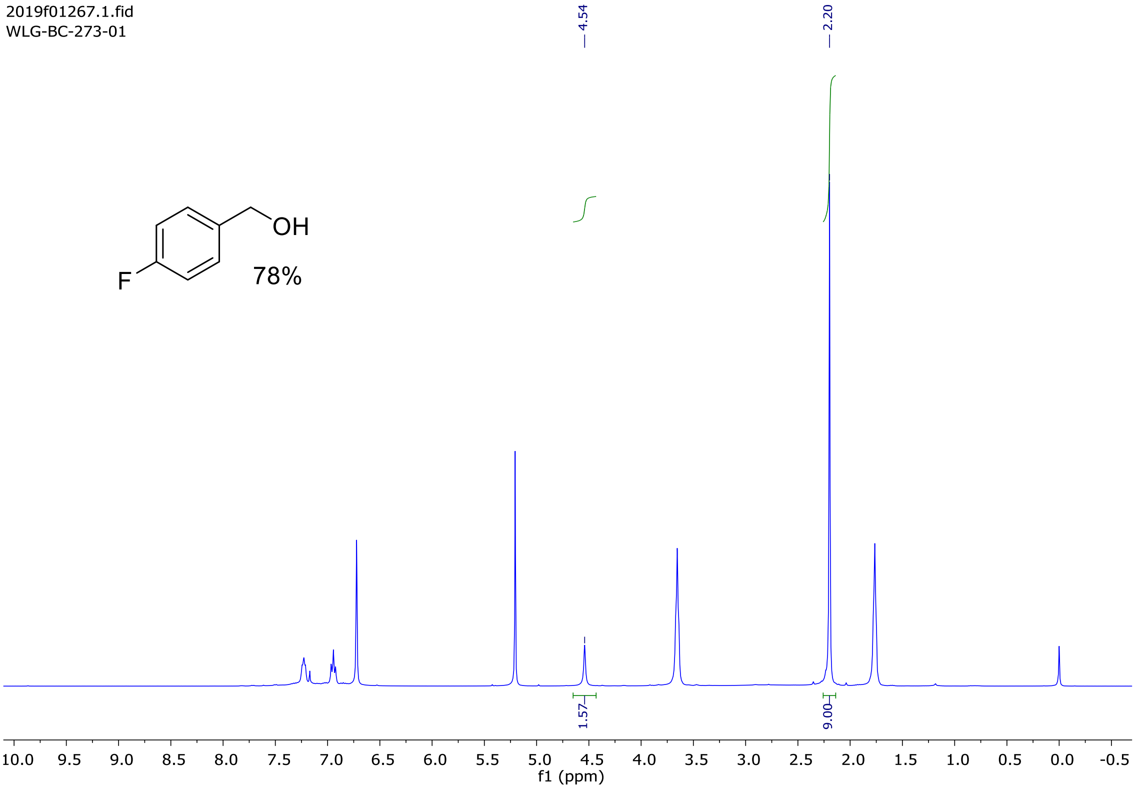
^{1}**H NMR** spectrum of the reaction mixture in the case of Table 4, entry 7 (Mesitylene was used as an internal standard)



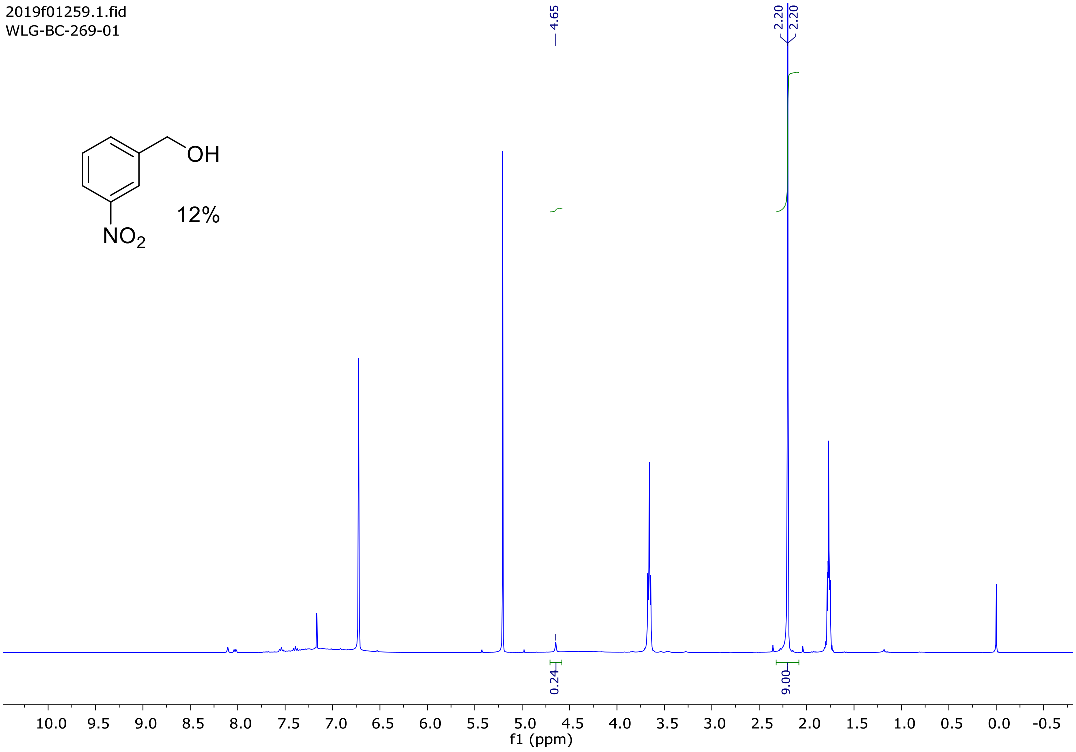
^{1}**H NMR** spectrum of the reaction mixture showing the formation of **15b** (Mesitylene was used as an internal standard)



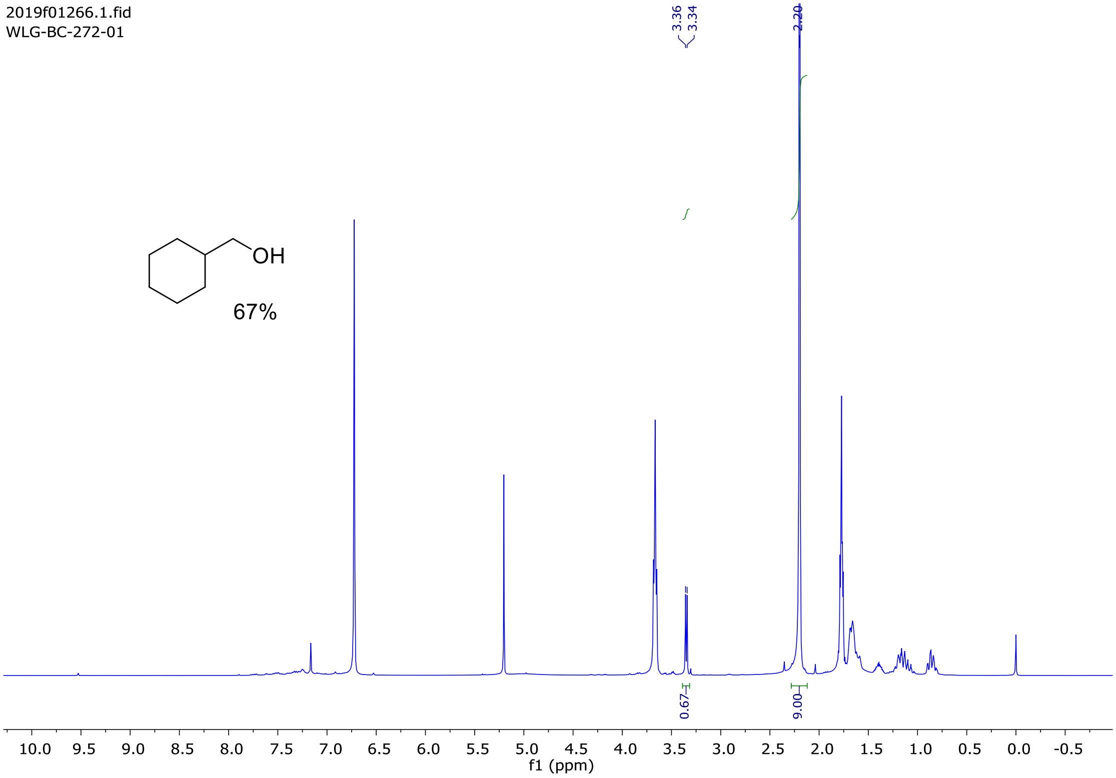
^{1}H NMR spectrum of the reaction mixture showing the formation of **15c**
(Mesitylene was used as an internal standard)



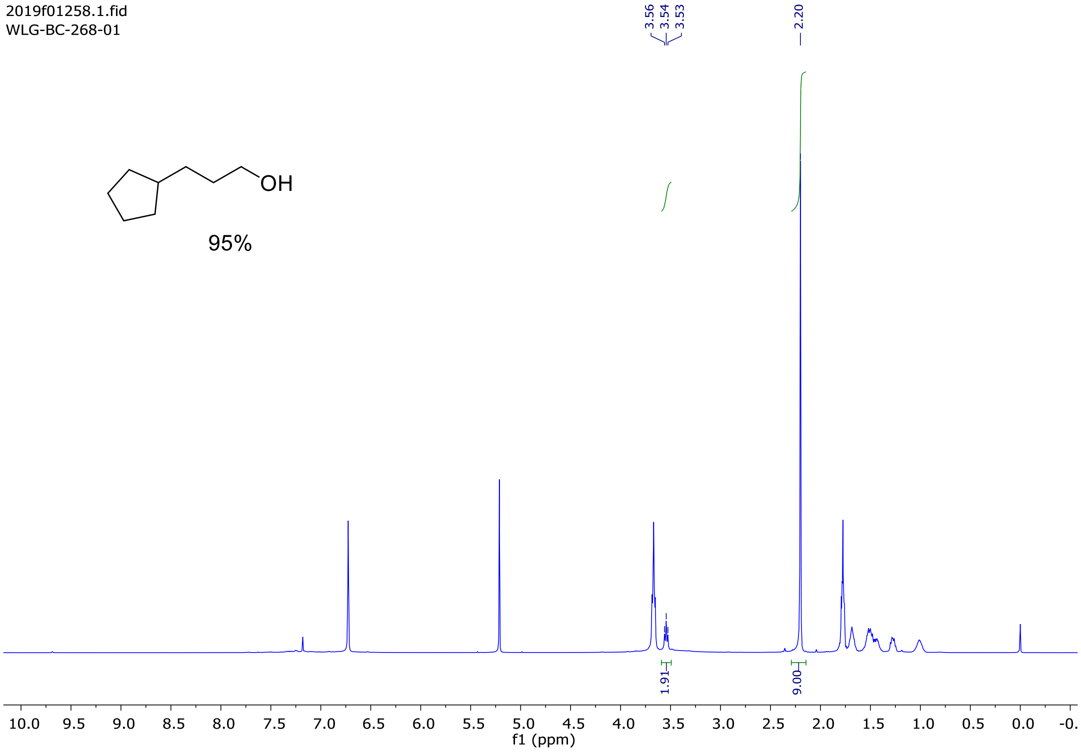
^{1}H NMR spectrum of the reaction mixture showing the formation of **15d**
(Mesitylene was used as an internal standard)



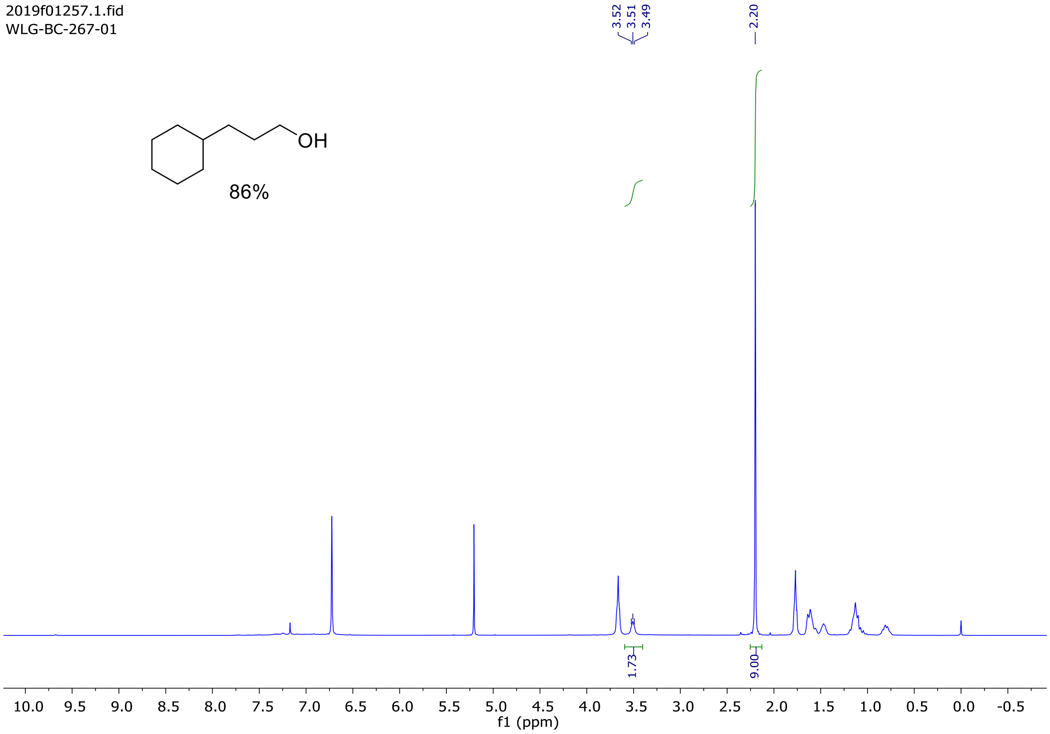
^{1}**H NMR** spectrum of the reaction mixture showing the formation of **15e** (Mesitylene was used as an internal standard)



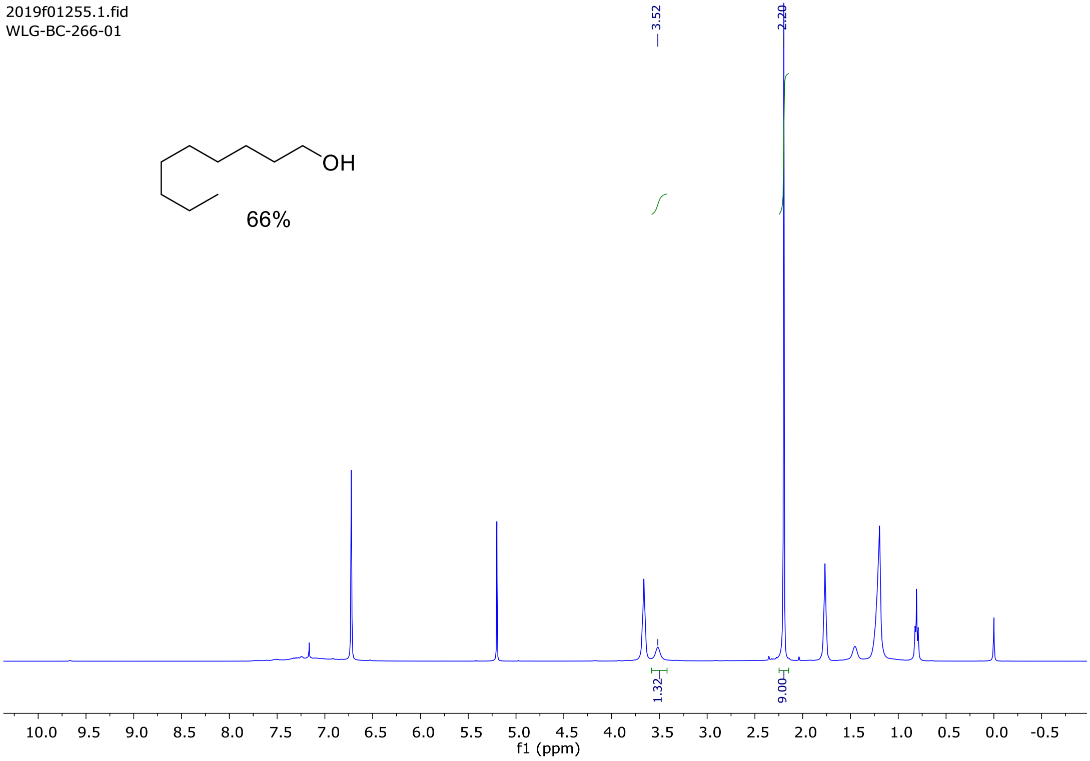
^{1}**H NMR** spectrum of the reaction mixture showing the formation of **15f** (Mesitylene was used as an internal standard)



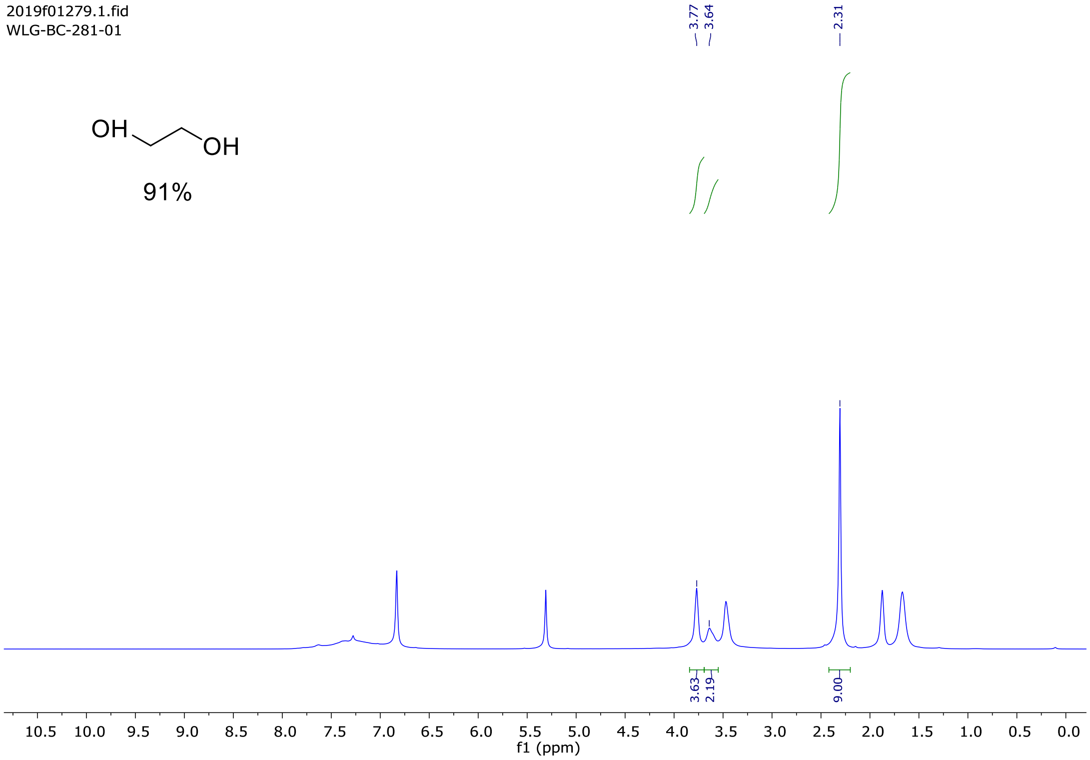
^{1}**H NMR** spectrum of the reaction mixture showing the formation of **15g** (Mesitylene was used as an internal standard)



^{1}**H NMR** spectrum of the reaction mixture showing the formation of **15h** (Mesitylene was used as an internal standard)

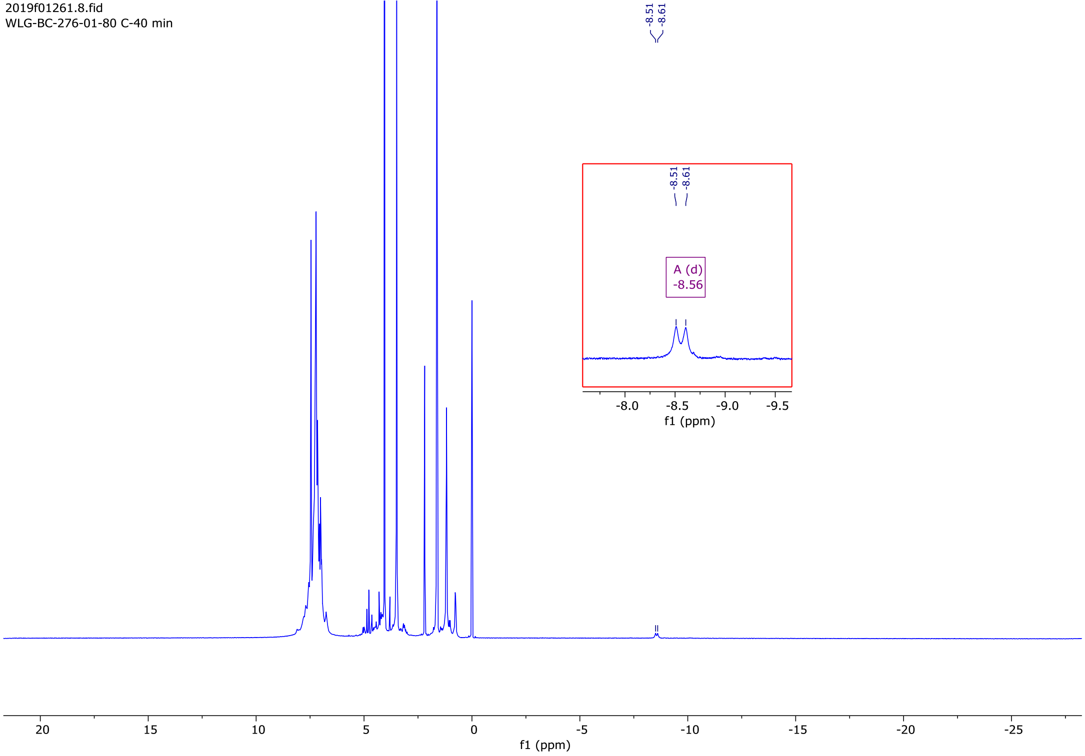


^{1}H NMR spectrum of the reaction mixture showing the formation of **15i** (Mesitylene was used as an internal standard)

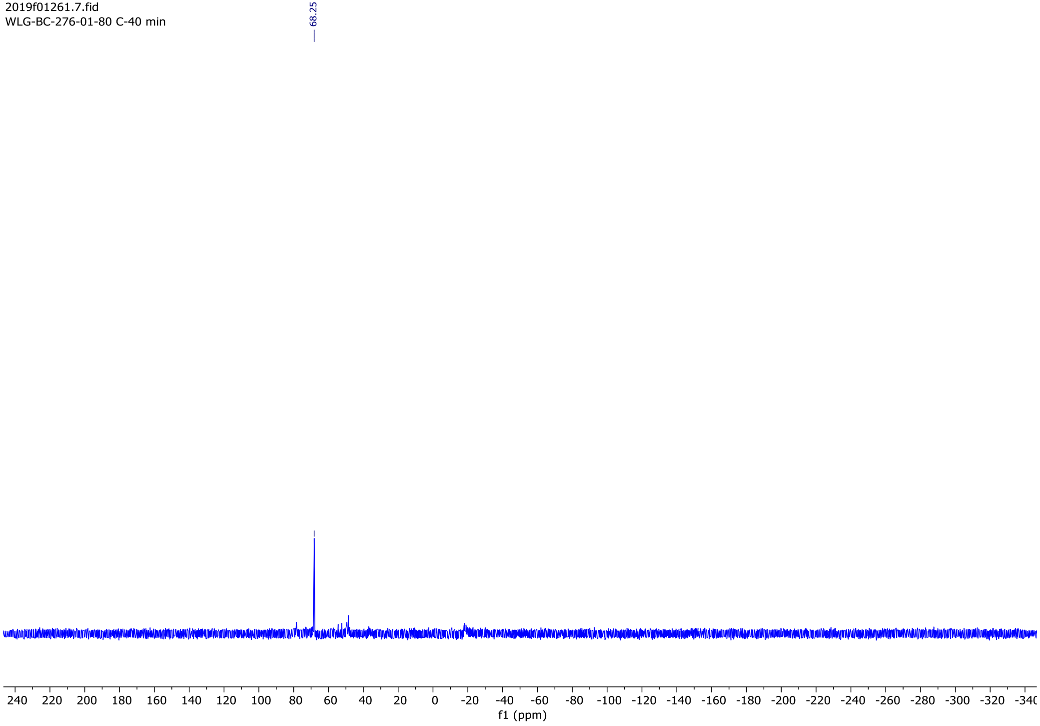


Observation of complex 16 by ^{1}H-NMR, HR-MS and IR

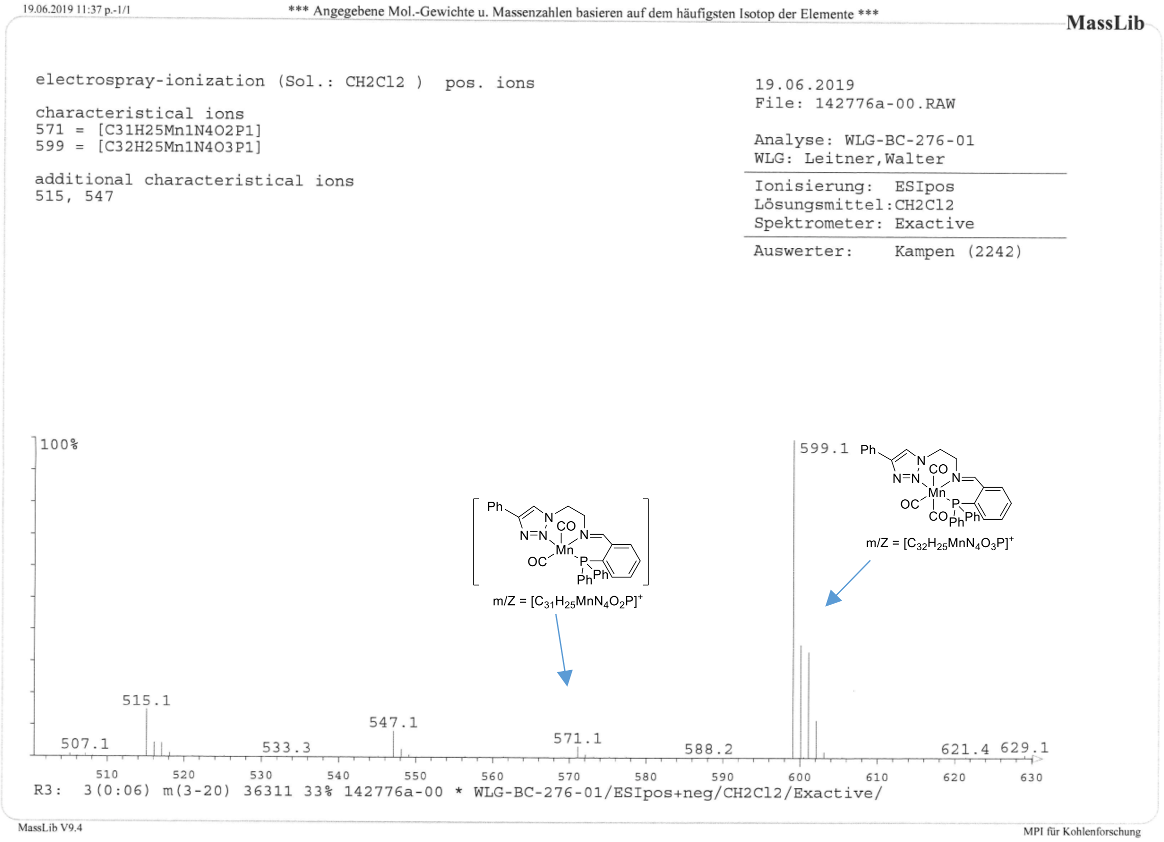
^{1}H NMR spectrum of the reaction mixture, showing the formation of a manganese hydride (In accord with intermediate **I**)



^{31}P{^{1}H} NMR spectrum of the reaction mixture containing the manganese hydride (complex **16**)



Analysis of the reaction mixture containing **16** by high-resolution mass spectrometry.



19.06.2019 11:37 p.-1/1 *** Angegebene Mol.-Gewichte u. Massenzahlen basieren auf dem häufigsten Isotop der Elemente ***

MassLib

```
electrospray-ionization (Sol.: CH2Cl2 )  pos. ions

characteristical ions
571 = [C31H25Mn1N4O2P1]
599 = [C32H25Mn1N4O3P1]

additional characteristical ions
515, 547
```

```
19.06.2019
File: 142776a-00.RAW

Analyse: WLG-BC-276-01
WLG: Leitner,Walter
Ionisierung:   ESIpos
Lösungsmittel:CH2Cl2
Spektrometer: Exactive
Auswerter:     Kampen (2242)
```

m/Z = $[C_{31}H_{25}MnN_4O_2P]^+$

m/Z = $[C_{32}H_{25}MnN_4O_3P]^+$

```
R3:  3(0:06) m(3-20) 36311 33% 142776a-00 * WLG-BC-276-01/ESIpos+neg/CH2Cl2/Exactive/
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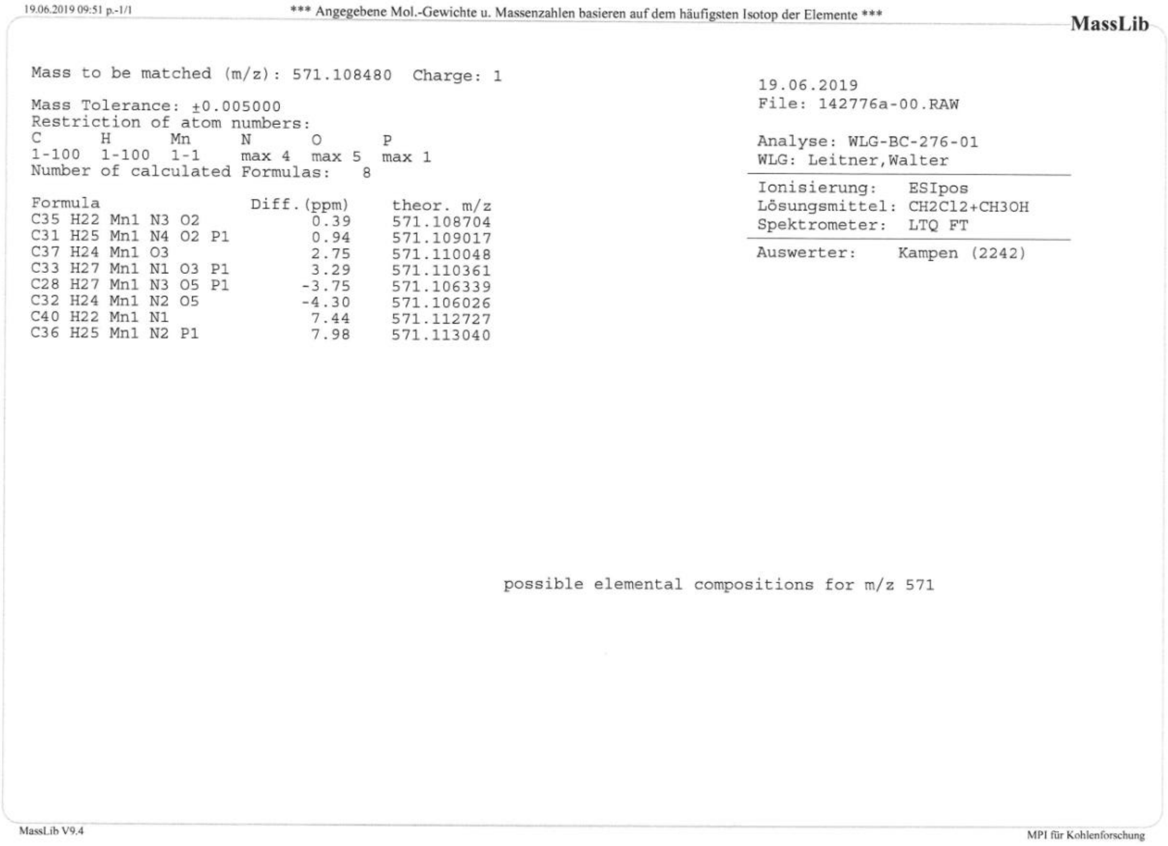
MassLib V9.4

MPI für Kohlenforschung



19.06.2019 09:51 p.-1/1 *** Angegebene Mol.-Gewichte u. Massenzahlen basieren auf dem häufigsten Isotop der Elemente ***

MassLib

```
Mass to be matched (m/z): 571.108480  Charge: 1

Mass Tolerance: ±0.005000
Restriction of atom numbers:
C       H       Mn     N       O       P
1-100   1-100   1-1    max 4   max 5   max 1
Number of calculated Formulas:   8

Formula                    Diff.(ppm)     theor. m/z
C35 H22 Mn1 N3 O2              0.39      571.108704
C31 H25 Mn1 N4 O2 P1           0.94      571.109017
C37 H24 Mn1 O3                 2.75      571.110048
C33 H27 Mn1 N1 O3 P1           3.29      571.110361
C28 H27 Mn1 N3 O5 P1          -3.75      571.106339
C32 H24 Mn1 N2 O5             -4.30      571.106026
C40 H22 Mn1 N1                 7.44      571.112727
C36 H25 Mn1 N2 P1              7.98      571.113040
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19.06.2019
File: 142776a-00.RAW

Analyse: WLG-BC-276-01
WLG: Leitner,Walter
Ionisierung:    ESIpos
Lösungsmittel: CH2Cl2+CH3OH
Spektrometer:  LTQ FT
Auswerter:     Kampen (2242)
```

```
possible elemental compositions for m/z 571
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MassLib V9.4

MPI für Kohlenforschung

Analysis of the reaction mixture containing **16** by IR-spectroscopy.