SUPPORTING INFORMATION

Cobalt-catalysed selective synthesis of aldehydes and alcohols from esters

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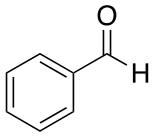
General experimental: All catalytic reaction were performed under nitrogen atmosphere.All stochiometric reactions were performed under nitrogen atmosphere MBRAUN glove box. Chemicals were purchased from sigma-Aldrich, across, Alfa-aesar, Himedia chemicals were used without further purification. Catalyst **1** was prepared following our previous report.[1] ^{1}H and ^{13}C spectra were recorded on Bruker AV-400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100.6 MHz) machine. ^{1}H and ^{13}C NMR chemical shifts were reported in ppm down field from tetramethylsilane. Multiplicity abbreviated as: s , singlet; d, doublet; t, triplet; q, quartet; sept, septate; m, multiplet; Assignment of ^{13}C NMR signals was done based on one dimensional(dept-135) NMR technique.

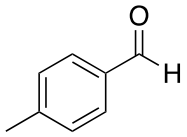
General procedure for synthesis of aldehydes: Oven dryed scintilation vial containing a stir bar was charged with catalyst **1** (1 mol%), KO^{t}Bu (4 mol%), ester (1 mmol), diethylsilane (1.5 mmol) and toluene (1 mL) under nitrogen atmosphere. The closed vial was then placed in a preheated oil bath at 50 °C for 12 h with stirring. After cooling to room temperature, the reaction was quenched with a mixture of THF/HCl(1 N) (2 mL each) and stirred at room temperature for 2 h. Then organic phase was extracted with diethylether and both aqueous phase, organic phase dried under vacuum and further purified by silica gel column chromatography to give the desired product.

Spectral data of aldehydes:

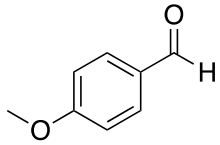
Benzaldehyde (2a): Colourless liquid. Yield 95, 86, 77 mg (89, 81, 72 %). IR (DCM): ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.89-7.87 (m, 2H, ArC*H*), 7.64-7.61 (t, 2H, *J* = 8 Hz, ArC*H*), 7.54-7.50 (t, 2H, *J* = 8 Hz, ArC*H*). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 192.38 (s), 136.41 (Ar*C*H), 134.45 (Ar*C*H), 129.72 (Ar*C*H), 128.99 (Ar*C*H).



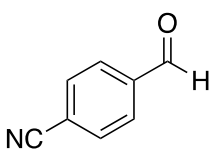
4-Methyl benzaldehyde (2b): Colourless liquid. Yield 94 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ δ 9.94 (s, 1H), 7.77-7.75 (m, 2H, ArC*H*), 7.31-7.30 (m, 2H, ArC*H*), 2.41 (s, 3H, CH_3). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 192.01 (s), 145.55 (Ar*C*H), 134.19 (Ar*C*H), 129.83 (Ar*C*H), 129.71 (Ar*C*H), 21.82 (*C*H_3).



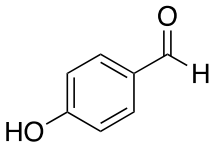
4-Methoxy benzaldehyde (2c): Colourless liquid. Yield 124 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.83-7.81 (t, 2H, *J* = 8 Hz, ArC*H*), 7.00-6.98 (t, 2H, *J* = 8 Hz, ArC*H*), 3.87 (s, 3H, OCH_3). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 190.70 (s), 164.64 (Ar*C*H), 131.92 (Ar*C*H), 130.02 (Ar*C*H), 114.32 (Ar*C*H), 55.53 (O*C*H_3).



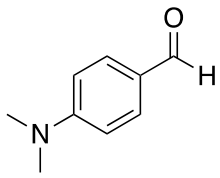
4-Cyano benzonitrile (2d): White solid. Yield 102 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.85-7.83 (d, 2H, *J* = 8 Hz, ArC*H*), 7.01-6.99 (d, 2H, *J* = 8 Hz, ArC*H*). $^{13}C\{1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 191.28 (s), 161.65 (Ar*C*H), 132.54 (Ar*C*H), 129.85 (Ar*C*H), 116.03 (*C*N).



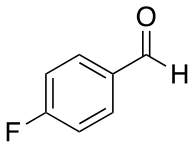
4-Hydroxy benzaldehyde (2e): White solid. Yield 102 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.02-8.00 (d, 2H, J = 8 Hz, ArC*H*), 7.87-7.85 (d, 2H, J = 8 Hz, ArC*H*). ^{13}C {1H} NMR (100.6 MHz, $CDCl_3$): δ 182.14 (s), 137.12 (Ar*C*H), 134.81 (Ar*C*H), 122.74 (Ar*C*H), 122.72 (Ar*C*H).



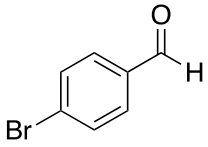
4-Dimethylamino benzaldehyde (2f): White solid. Yield 58 mg (39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75–9.74 (m, 1H), 7.75-7.72 (m, 2H, ArC*H*), 6.72-6.70 (m, 2H, ArC*H*), 3.09 (s, 6H, N(CH_3)$_2$). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ 190.24 (s), 154.32 (Ar*C*H), 131.97 (Ar*C*H), 125.56 (Ar*C*H), 111.06 (Ar*C*H), 40.10 (N(*C*H$_3$)$_2$).



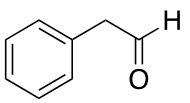
4-Fluoro benzaldehyde (2g): Colourless liquid. Yield 91 mg (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.90-7.86 (m, 2H, ArC*H*), 7.20-7.10 (m, 2H, ArC*H*). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ 190.53 (s), 167.76 (Ar*C*H), 165.21 (Ar*C*H), 132.93 (Ar*C*H), 132.25-132.16 (Ar*C*H), 116.42-116.20 (Ar*C*H).



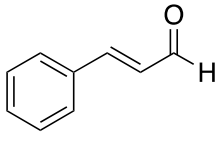
4-Bromo benzaldehyde (2h): White solid. Yield 94 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.78-7.77 (d, 2H, J = 4 Hz, ArC*H*), 7.72-7.71 (d, 2H, J = 4 Hz, ArC*H*). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ191.11 (s), 135.09 (Ar*C*H), 132.47 (Ar*C*H), 131.00 (Ar*C*H), 129.81 (Ar*C*H).



2-Phenylacetaldehyde (2i): Colourless liquid. Yield 97 mg (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.44-7.25 (m, 5H, ArC*H*), 3.72-3.71 (d, 2H, J = 4 Hz, CH_2). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ195.51 (s), 131.95 (Ar*C*H), 129.69 (Ar*C*H), 129.05 (Ar*C*H), 127.45 (Ar*C*H), 50.58 (*C*H$_2$).



Cinnamaldehyde (2j): Yellow liquid. Yield 101 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71–9.69 (d, 1H), 7.57-7.55 (m, 2H, ArC*H*), 7.49-7.43 (m, 4H, ArC*H*), 6.74-6.68 (m, 1H, Oleifinic C*H*). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ 193.68 (s), 152.78 (Oleifinic *C*H), 134.03 (Ar*C*H), 131.29 (Ar*C*H), 191.12 (Ar*C*H), 128.58 (Ar*C*H), 128.52 (Oleifinic *C*H).

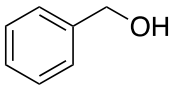


General procedure for synthesis of alcohols: Oven dryed scintilation vial containing a stir bar was charged with catalyst **1** (2 mol %), KO^{t}Bu (10 mol %), ester (1 mmol), diethylsilane (3 mmol) and toluene (1 mL) under nitrogen atmosphere. The closed vial was then placed in a preheated oil bath at 50 °C for 20 min with stirring. After cooling to room temperature, the

reaction was quenched with a mixture of THF/HCl(1 N) (2 mL each) and stirred at room temperature for 2 h. Then organic phase was extracted with diethylether and both aqueous phase, organic phase dried under vacuum and further purified by silica gel column chromatography using ethylacetate/hexane eluent to give the desired product.

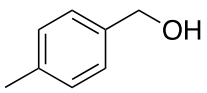
Spectral data of alcohols:

Phenylmethanol (3a): Colourless liquid. Yield 104, 100, 94 mg (96, 92, 87 %). ^{1}H NMR



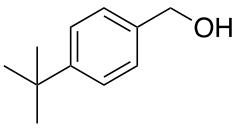
(400 MHz, $CDCl_3$):δ7.41-7.31 (m, 5H, ArC*H*), 4.67-4.66 (d, 2H, *J* = 4 Hz, CH_2), 2.65-2.57 (d, 1H, O*H*). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ140.95 (Ar*C*H), 128.59 (Ar*C*H), 127.64 (Ar*C*H), 127.07 (Ar*C*H), 65.18 (*C*H_2).

P-Tolylmethanol (3b): White solid. Yield 116 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$):



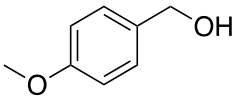
δ7.28-7.26 (d, 2H, *J* = 8 Hz, , ArC*H*), 7.22-7.20 (d, 2H, *J* = 8 Hz, , ArC*H*), 4.60 (s, 2H, CH_2), 3.03 (s, 1H, O*H*), 2.41 (s, 3H, CH_3) . ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ138.05 (Ar*C*H), 137.20 (Ar*C*H), 129.20 (Ar*C*H), 127.17 (Ar*C*H), 64.90 (*C*H_2), 21.19 (*C*H_3).

4-(Tert-butyl)phenylmethanol (3c): Colourless liquid. Yield 100 mg (91%). ^{1}H NMR (400 MHz, $CDCl_3$):δ 7.44-7.42 (d, 2H, *J* = 8 Hz, , ArC*H*), 7.34-7.32 (d, 2H, *J* = 8 Hz, , ArC*H*),



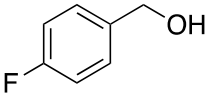
4.66 (s, 2H, CH_2), 2.65-2.57 (d, 1H, O*H*). 1.37 (s, 9H, Tertbutyl CH_3). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$):δ 150.68 (Ar*C*H), 137.97 (Ar*C*H), 126.96 (Ar*C*H), 125.51 (Ar*C*H), 65.05 (*C*H_2), 34.59 (quat *C*), 31.41 (Tertbutyl *C*H_3).

4-(Methoxy)phenylmethanol (3d): Colourless liquid. Yield 136 mg (98%). IR (DCM): ^{1}H



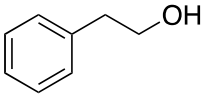
NMR (400 MHz, $CDCl_3$):δ 7.28-7.26 (d, 2H, *J* = 8 Hz, , ArC*H*), 6.90-6.98 (d, 2H, *J* = 8 Hz, , ArC*H*), 4.57 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3). 2.47 (s, 1H, O*H*).^{13}C{1H} NMR (100.6 MHz, $CDCl_3$):δ 159.12 (Ar*C*H), 133.22 (Ar*C*H), 128.64 (Ar*C*H), 113.92 (Ar*C*H), 64.79 (*C*H_2). 55.29 (O*C*H_3).

4-(Fluoro)phenylmethanol (3e): Colourless liquid. Yield 111 mg (88%). ^{1}H NMR (400



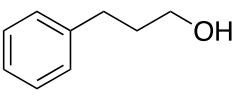
MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H, ArC*H*), 7.03-6.99 (m, 2H, ArC*H*), 4.54-4.52 (m, 2H, CH_2), 3.69-3.52 (m, 1H, O*H*). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ163.46 (Ar*C*H), 161.02 (Ar*C*H), 136.61-136.59 (Ar*C*H), 128.77-128.69 (Ar*C*H), 115.36-115.15 (Ar*C*H), 64.10 (*C*H_2).

2-Phenylethan-1-ol (3f): Colourless liquid. Yield 114 mg (93%). ^{1}H NMR (400 MHz,



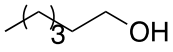
$CDCl_3$): δ 7.38-7.35 (m, 2H, ArC*H*), 7.30-7.27 (t, 3H, *J* = 8 Hz, ArC*H*), 3.87-3.84 (t, 2H, *J* = 8 Hz, CH_2), 2.91-2.88 (t, 2H, *J* = 8 Hz, CH_2). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ 138.63 (Ar*C*H), 129.05 (Ar*C*H), 128.53 (Ar*C*H), 126.41 (Ar*C*H), 63.55 (*C*H_2). 29.15 (*C*H_2).

3-Phenylpropan-1-ol (3g): Colourless liquid. Yield 122 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.27 (m, 5H, ArC*H*), 3.73-3.69 (m, 2H, CH_2), 2.79-2.75 (m, 2H, CH_2), 1.99-

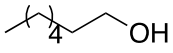


1.94 (m, 2H, CH_2). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): δ 141.09 (Ar*C*H), 128.52 (Ar*C*H), 148.47 (Ar*C*H), 125.92 (Ar*C*H), 62.05 (*C*H_2). 34.25 (*C*H_2), 32.16 (*C*H_2).

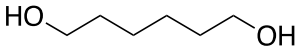
Hexan-1-ol (3h): Colourless liquid. Yield 88 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.67-3.60 (m, 2H, CH_2), 2.05-1.92 (m, 2H, CH_2), 1.31 (s, 6H, CH_2), 0.94-0.89 (m, 3H, CH_3). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): 62.94 (*C*H_2). 32.72 (*C*H_2), 31.63 (*C*H_2), 25.42 (*C*H_2). 22.61 (*C*H_2), 13.99 (*C*H_3).



Heptan-1-ol (3i): Colourless liquid. Yield 98 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.62-3.59 (m, 2H, CH_2), 2.31(s, 1H, O*H*), 1.57-1.53(t, 3H,*J* = 8 Hz, CH_2), 1.30_1.28 (m, 8H, CH_2), 0.89-0.86 (m, 3H, CH_3). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): 62.84 (*C*H_2). 32.73 (*C*H_2), 31.82 (*C*H_2), 29.10 (*C*H_2),25.71 (*C*H_2), 22.57 (*C*H_2), 14.02 (*C*H_3).

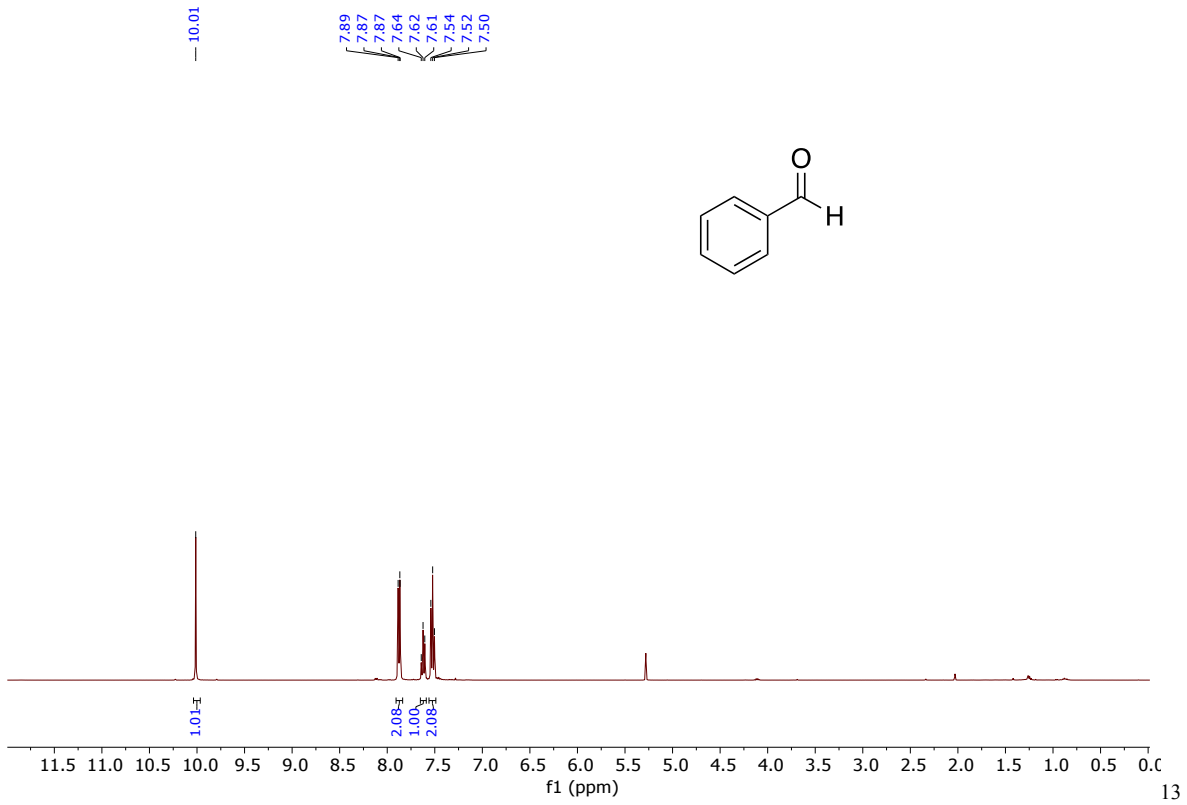


Hexane-1,6-diol (3j): White solid. Yield 102 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$): 3.65-3.62 (m, 4H, *J* = 4 Hz, CH_2), 2.12 (s, 2H, O*H*), 1.60-1.57 (t, 4H, *J* = 4 Hz, CH_2), 1.42-1.38 (m, 4H, CH_2). ^{13}C{1H} NMR (100.6 MHz, $CDCl_3$): 62.74 (*C*H_2). 32.62 (*C*H_2), 25.49 (*C*H_2).



NMR spectra of aldehydes and alcohols

^{1}H NMR spectrum of benzaldehyde (400 MHZ, $CDCl_3$)



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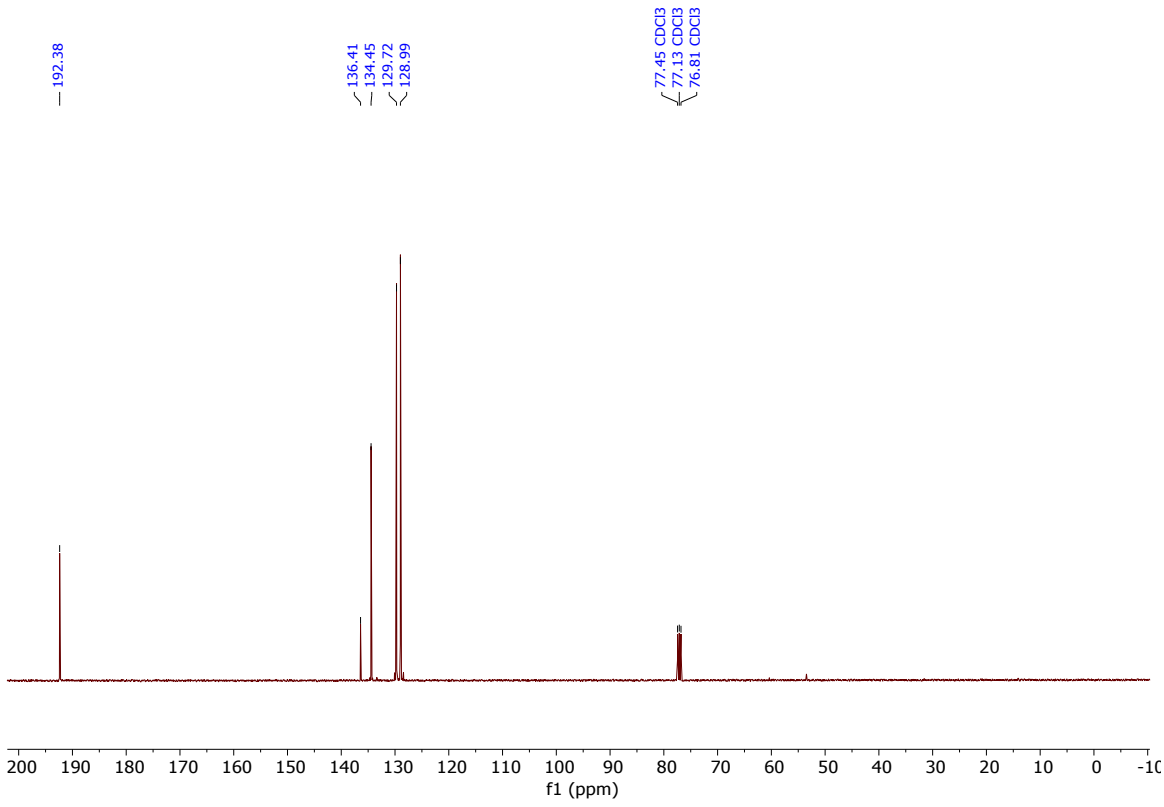
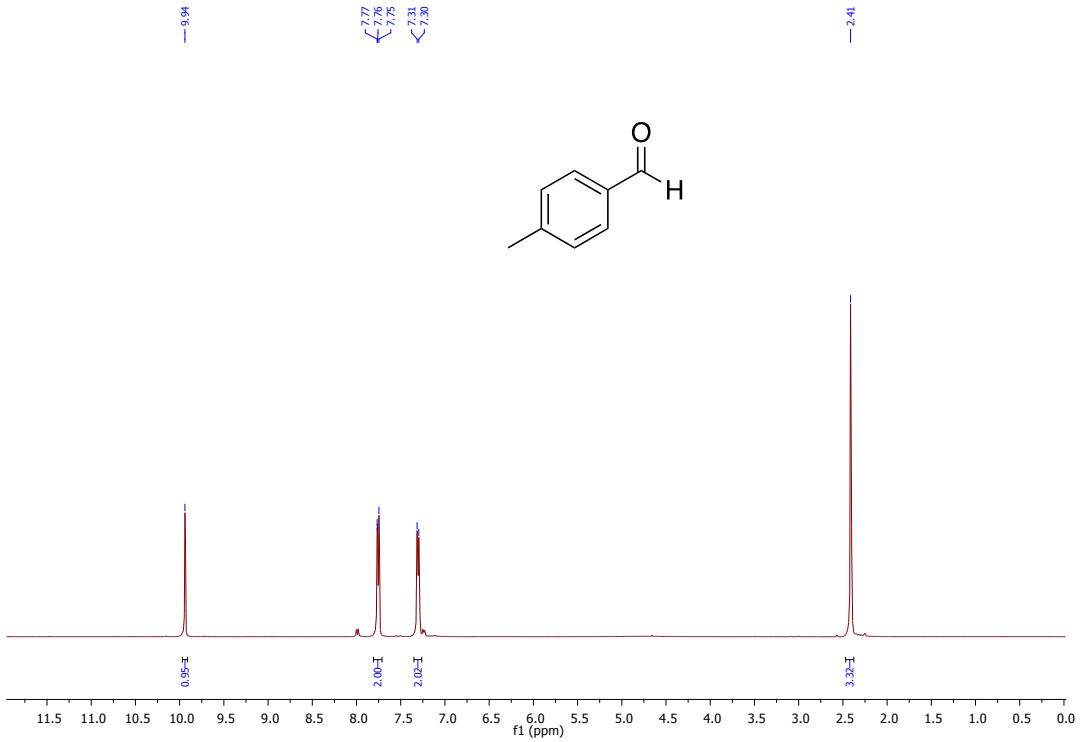
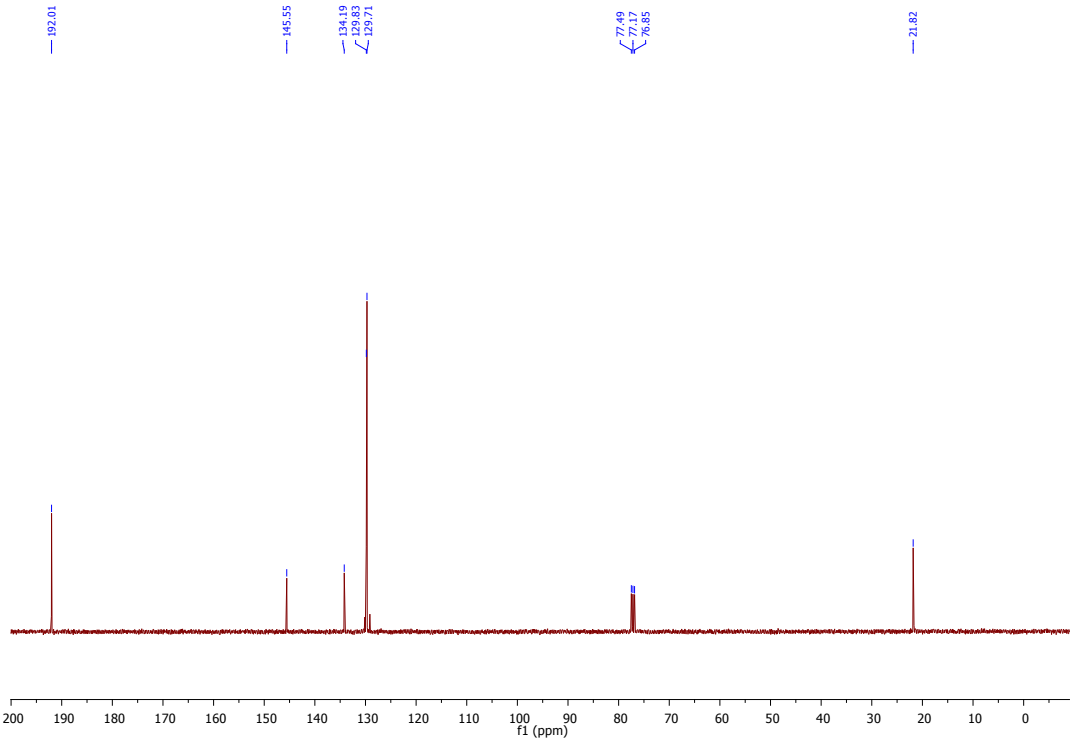
C NMR spectrum of benzaldehyde (400 MHZ, $CDCl_3$)



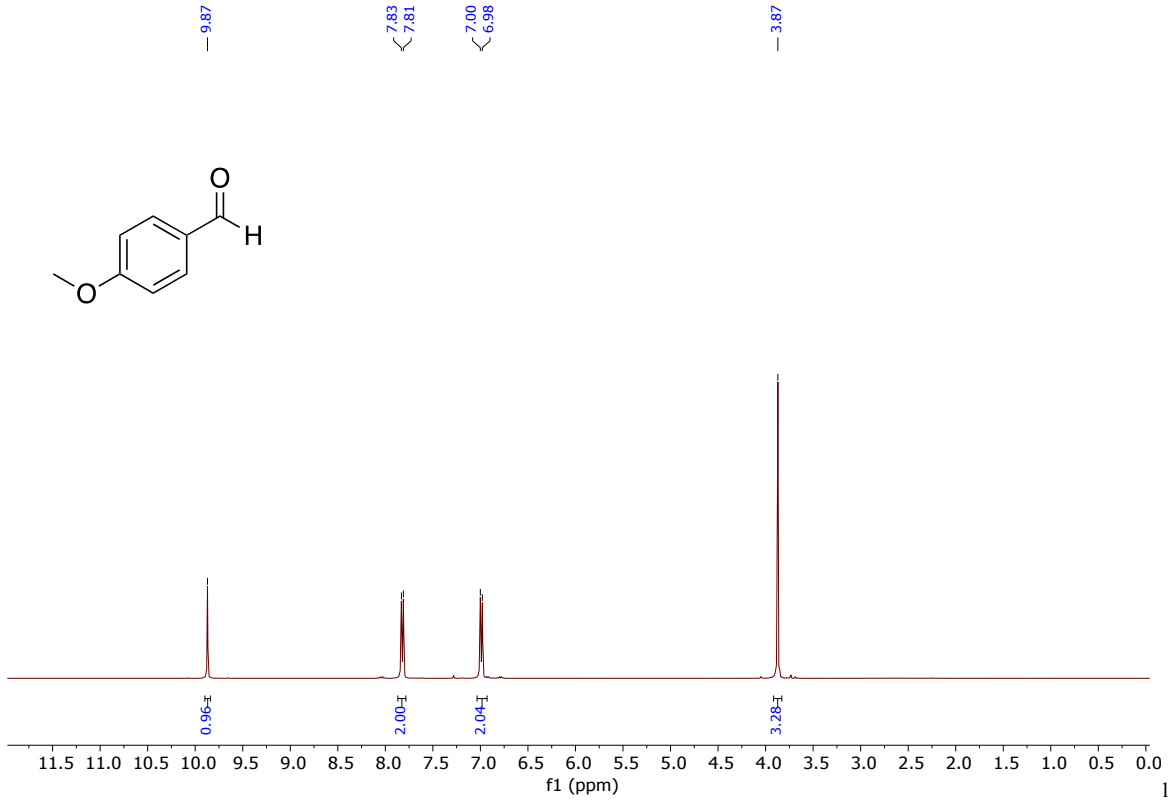
^{1}H NMR spectrum of 4-methyl benzaldehyde (400 MHZ, $CDCl_3$)



^{13}C NMR spectrum of 4-methyl benzaldehyde (400 MHZ, $CDCl_3$)



^{1}H NMR spectrum of 4-methoxybenzaldehyde (400 MHZ, $CDCl_3$)



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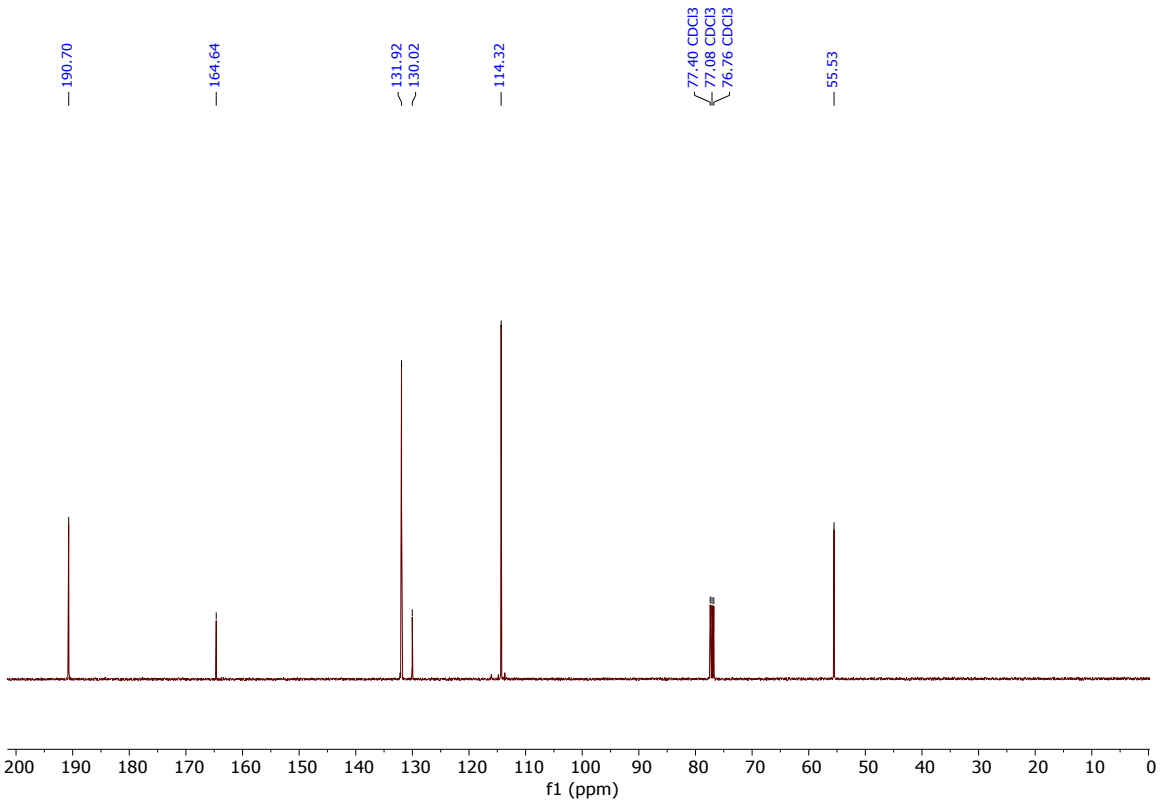
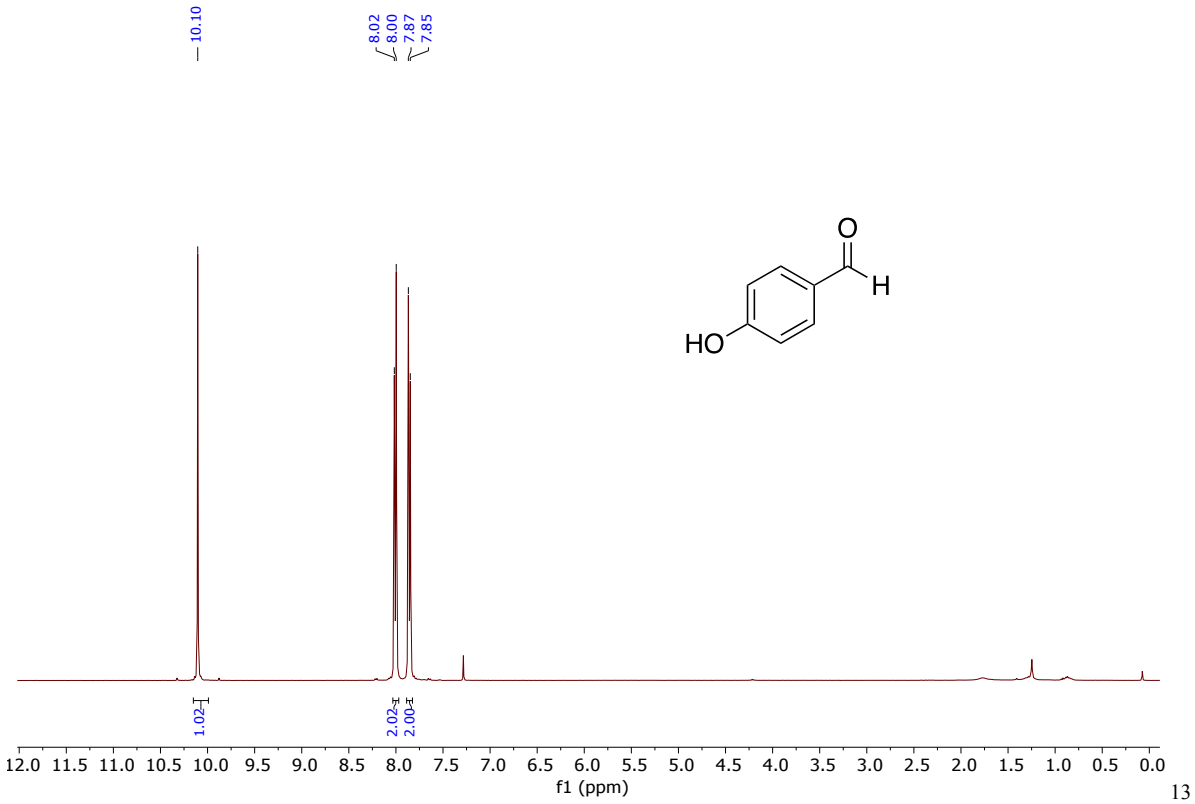
C NMR spectrum of 4-methoxybenzaldehyde (400 MHZ, $CDCl_3$)



^{1}H NMR spectrum of 4-hydroxybenzaldehyde (400 MHZ, $CDCl_3$)



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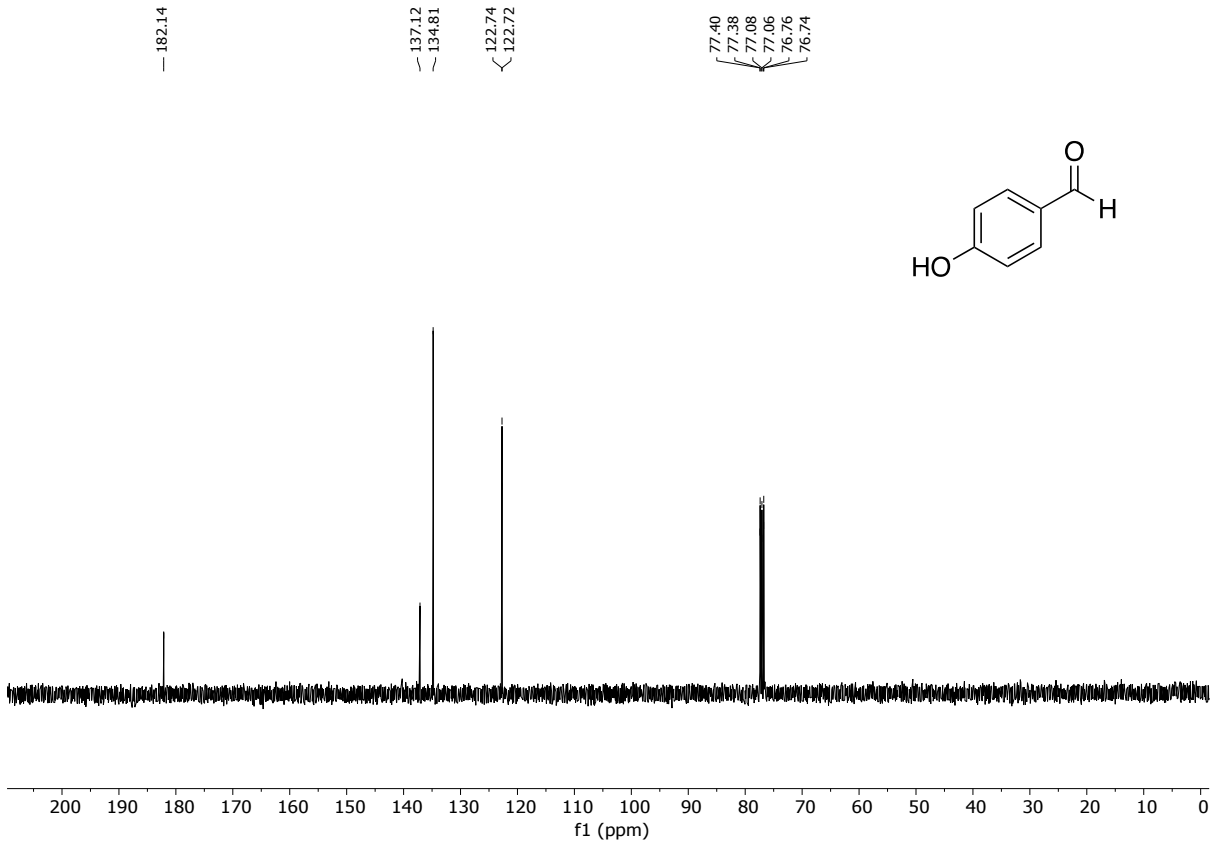
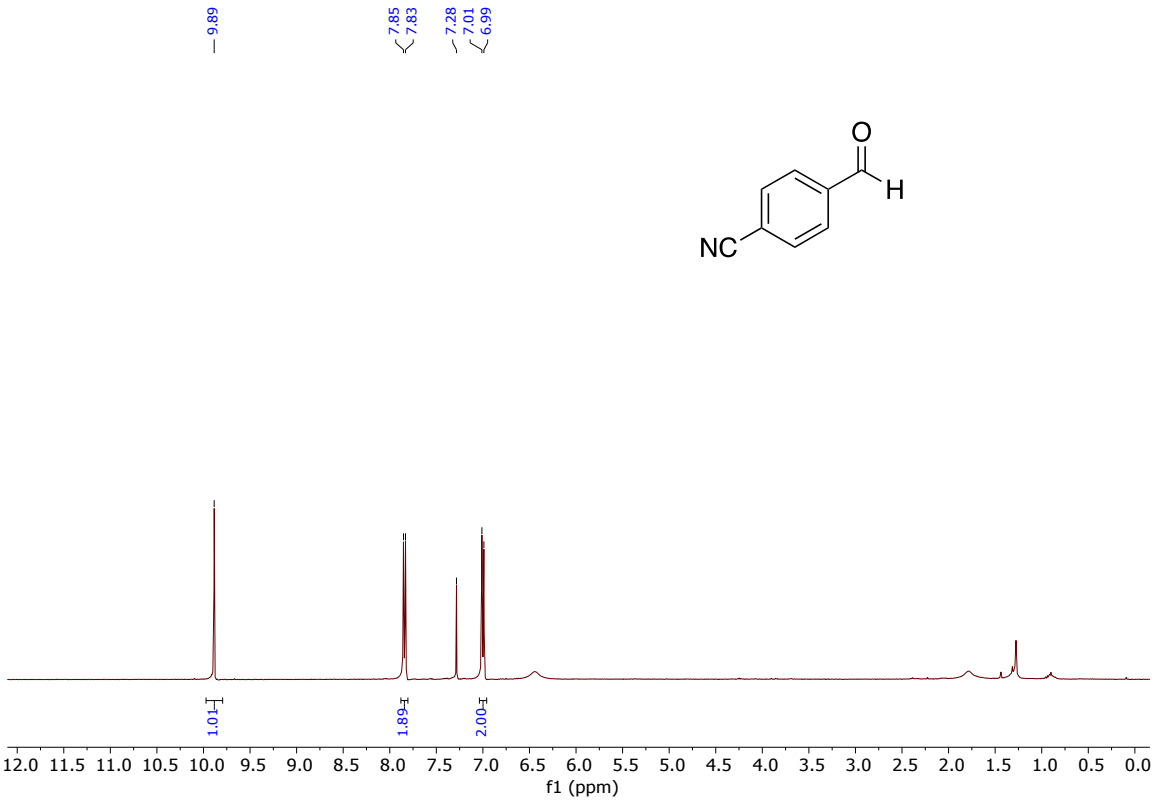
C NMR spectrum of 4-hydroxybenzaldehyde (400 MHZ, $CDCl_3$)



^{1}H NMR spectrum of 4-formyl benzonitrile (400 MHZ, $CDCl_3$)



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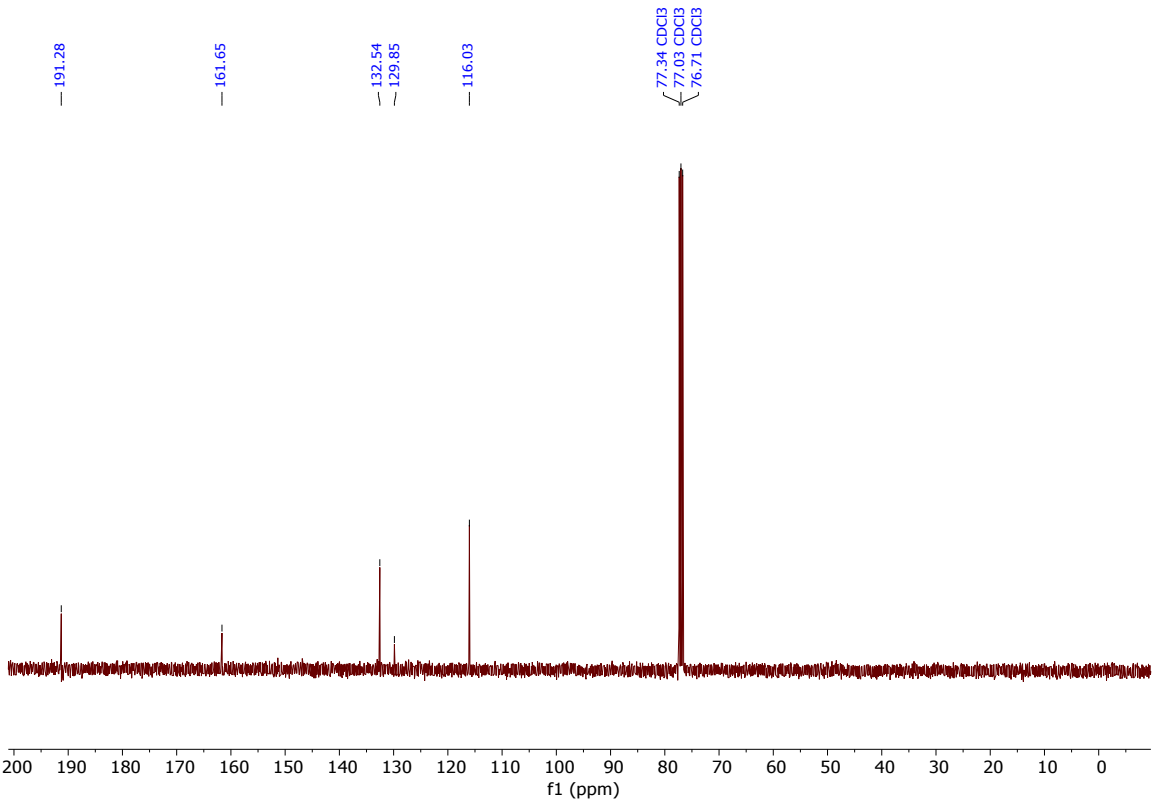
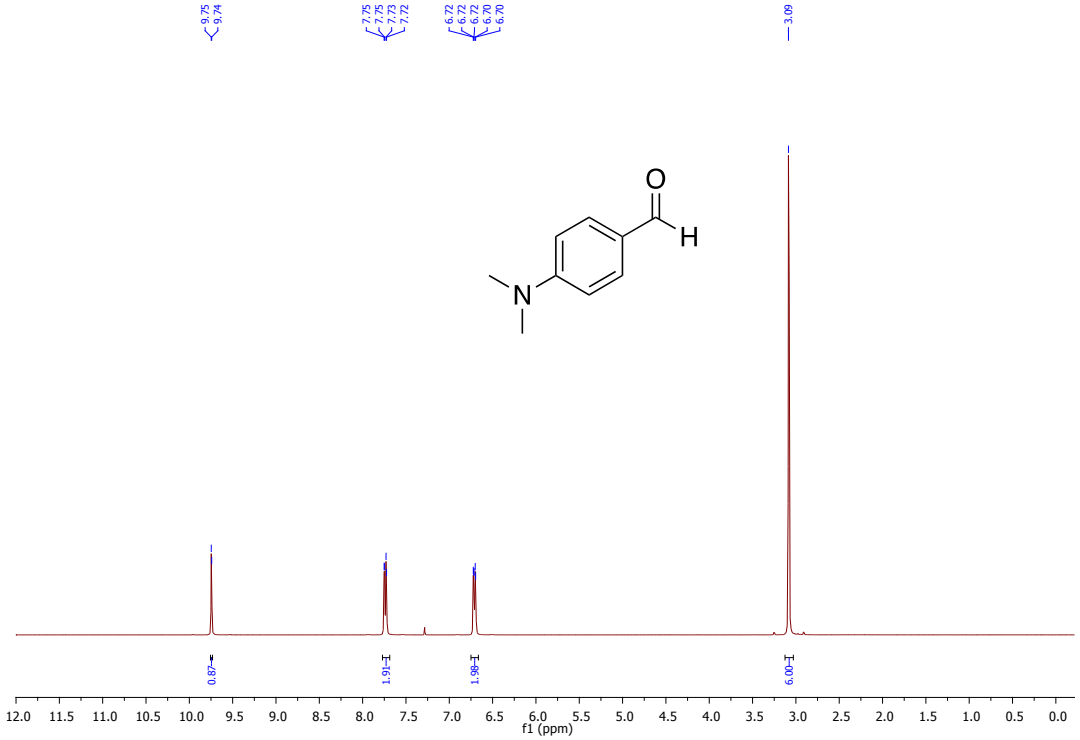
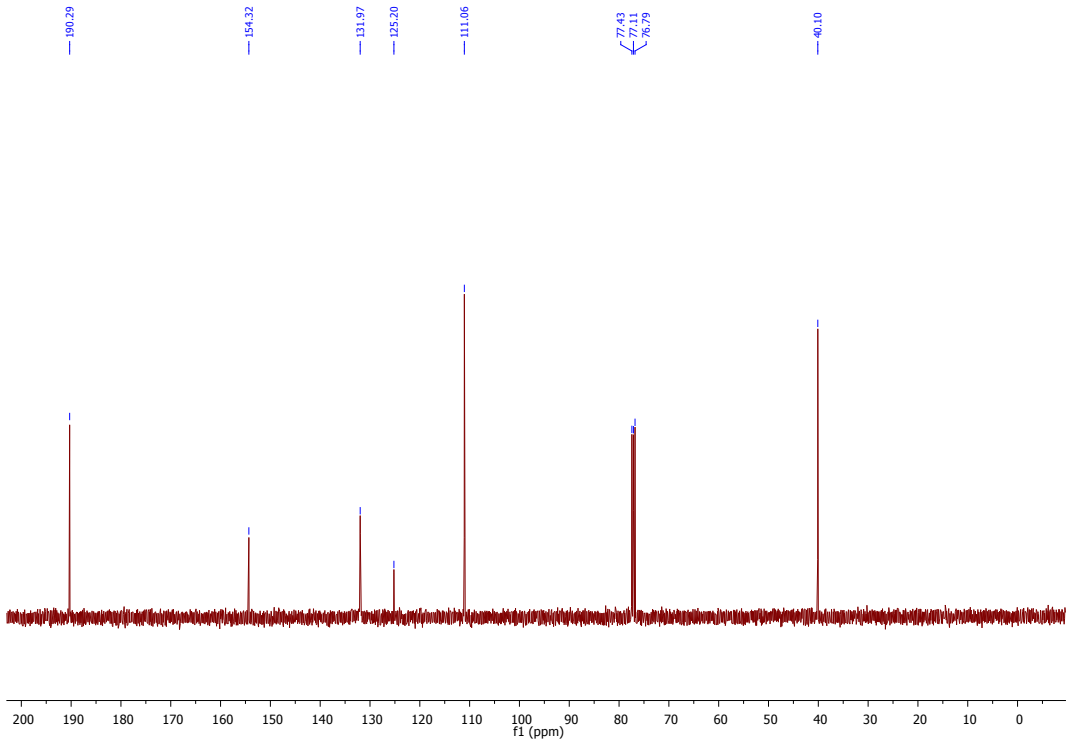
C NMR spectrum of 4-formyl benzonitrile (400 MHZ, $CDCl_3$)



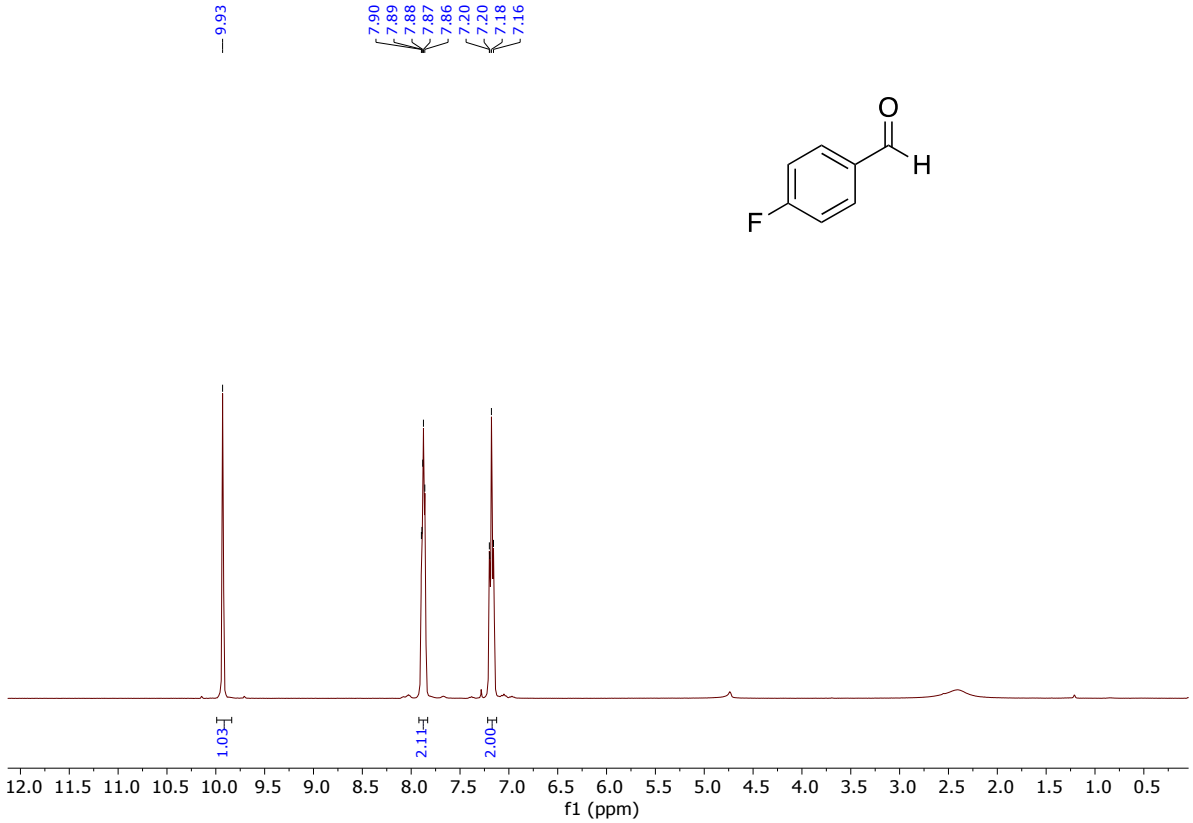
^{1}H NMR spectrum of 4-dimethylamino benzaldehyde (400 MHZ, $CDCl_3$)



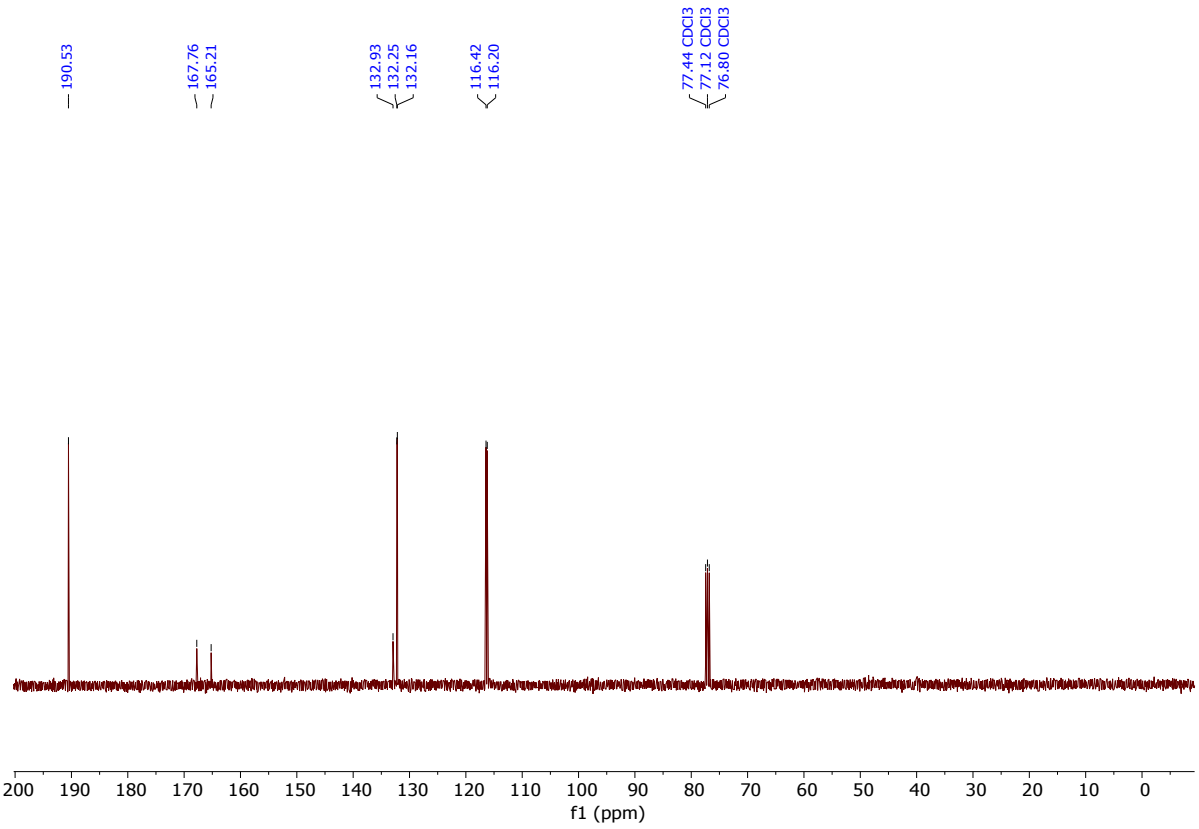
^{13}C NMR spectrum of 4-dimethylamino benzaldehyde (400 MHZ, $CDCl_3$)



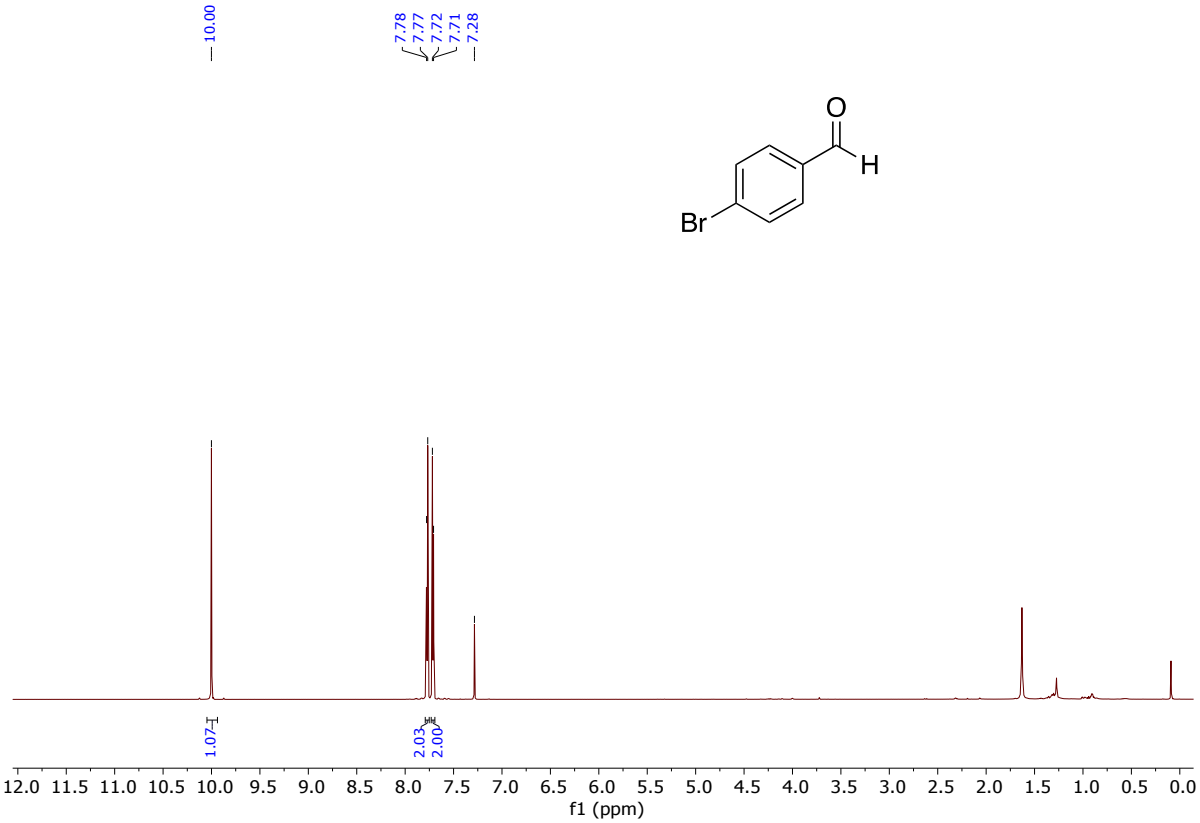
^{1}H NMR spectrum of 4-fluorobenzaldehyde (400 MHZ, $CDCl_3$)



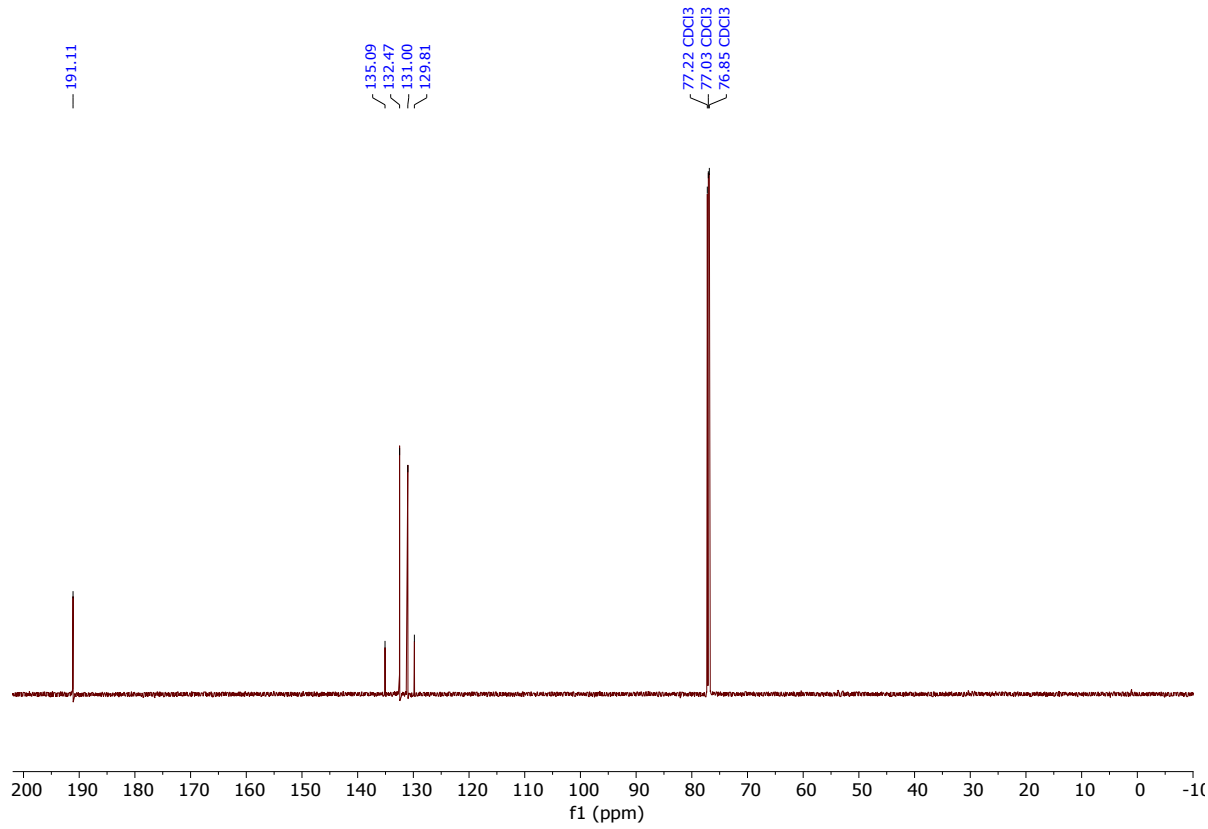
^{13}C NMR spectrum of 4-fluorobenzaldehyde (400 MHZ, $CDCl_3$)



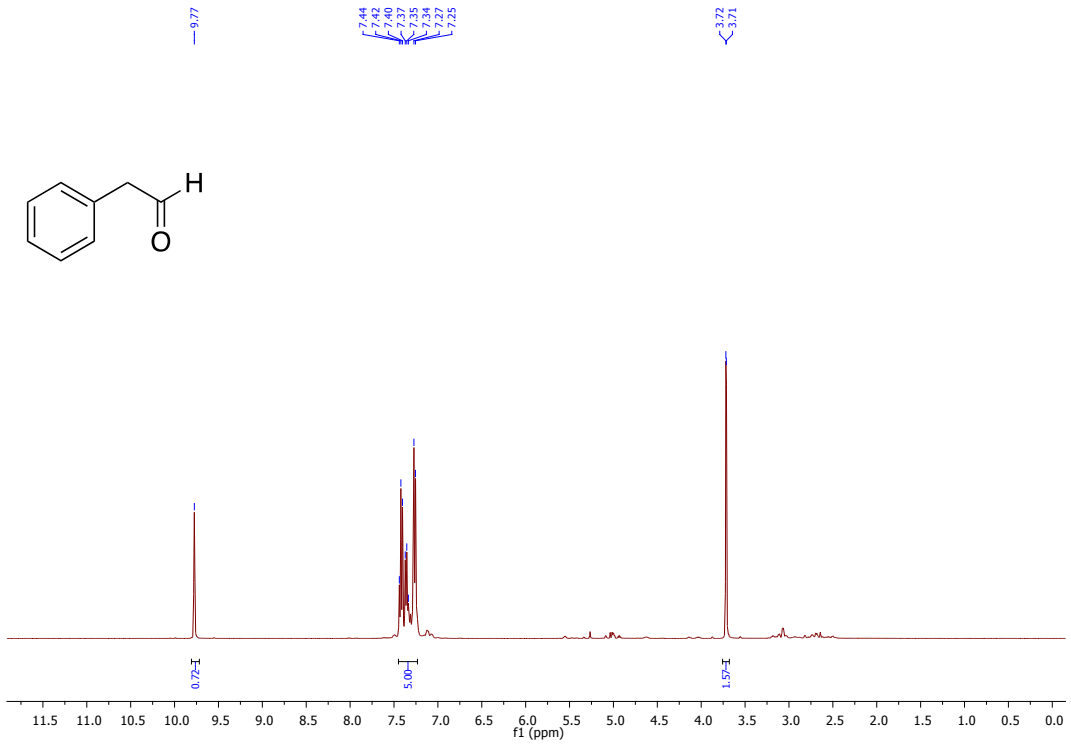
^{1}H NMR spectrum of 4-bromo benzaldehyde (400 MHZ, $CDCl_3$)



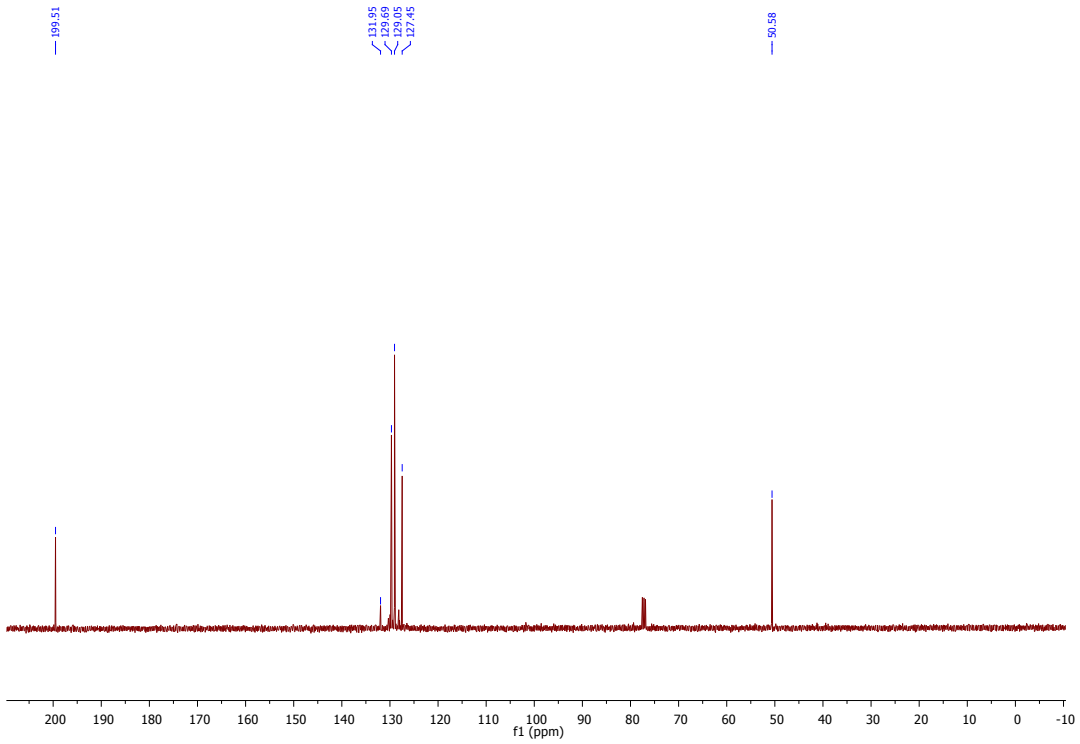
^{13}C NMR spectrum of 4-bromo benzaldehyde (400 MHZ, $CDCl_3$)



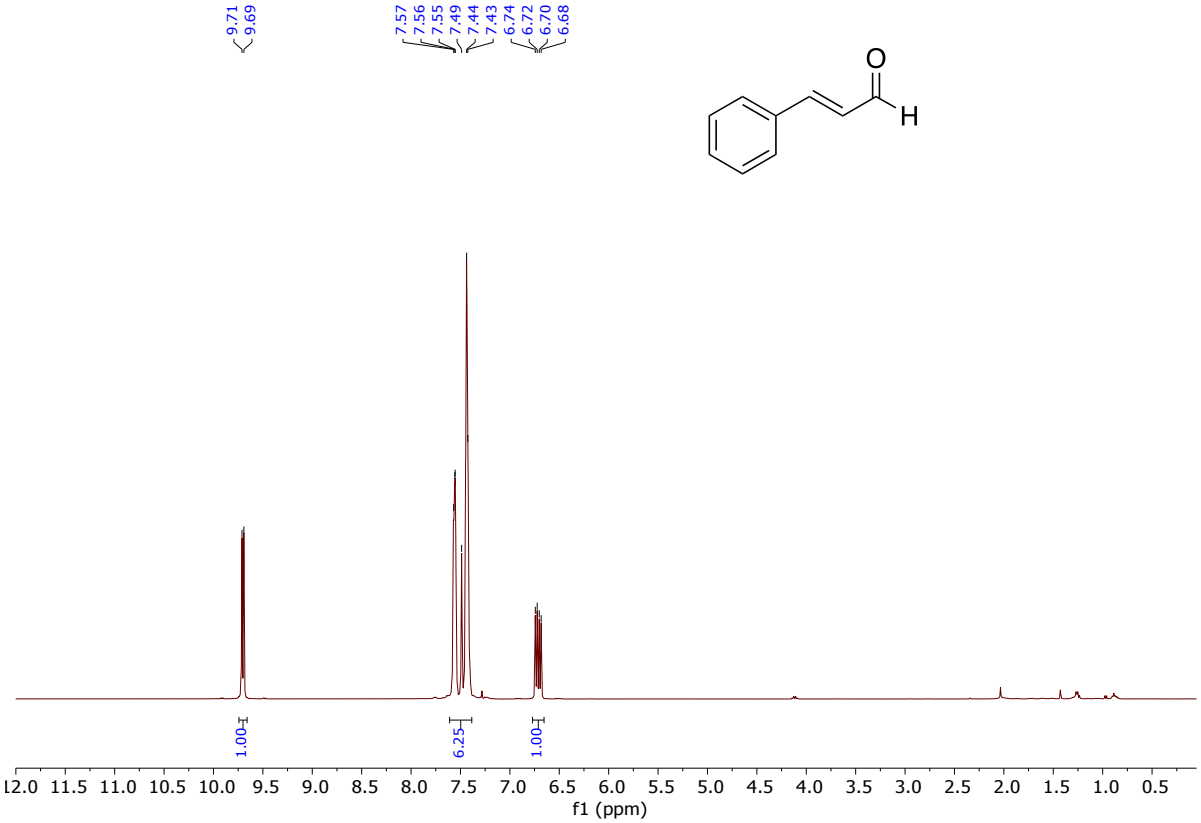
^{1}H NMR spectrum of 2-phenylacetaldehyde (400 MHZ, $CDCl_3$)



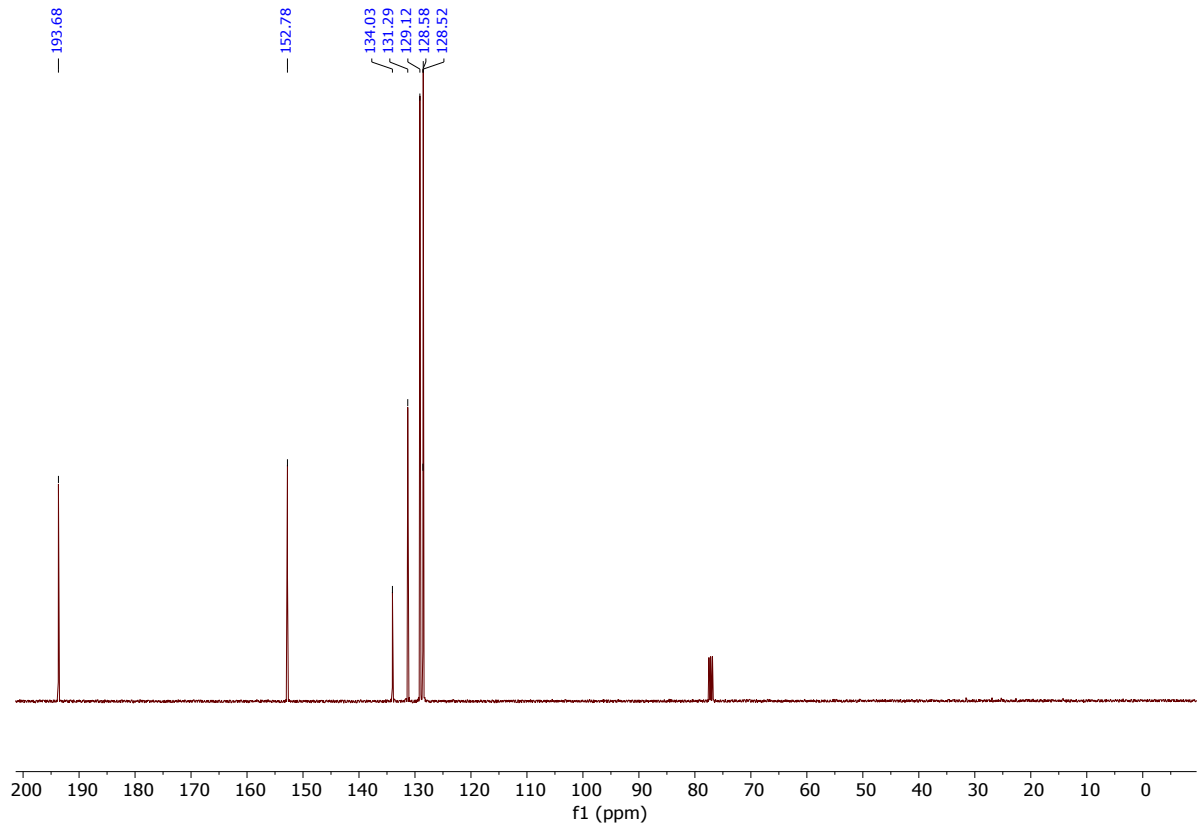
^{13}C NMR spectrum of 2-phenylacetaldehyde (400 MHZ, $CDCl_3$)



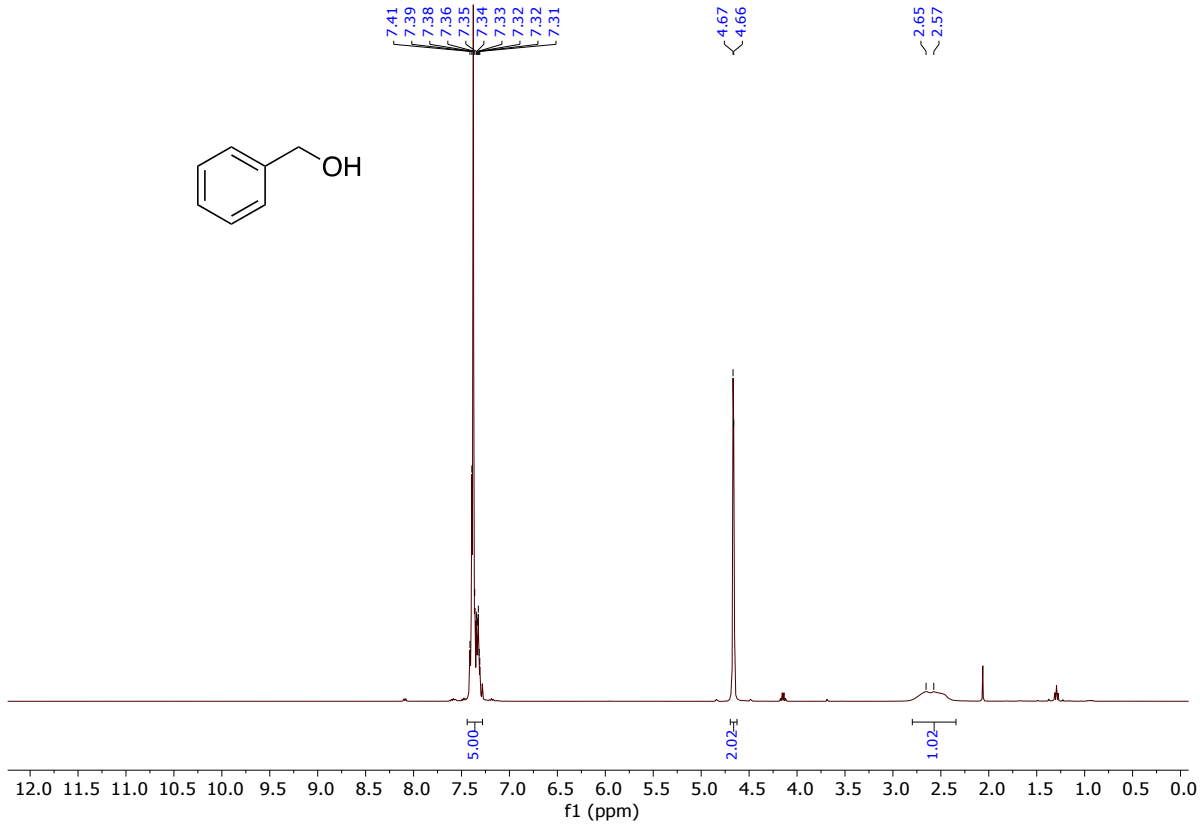
^{1}H NMR spectrum of cinnamaldehyde (400 MHZ, $CDCl_3$)



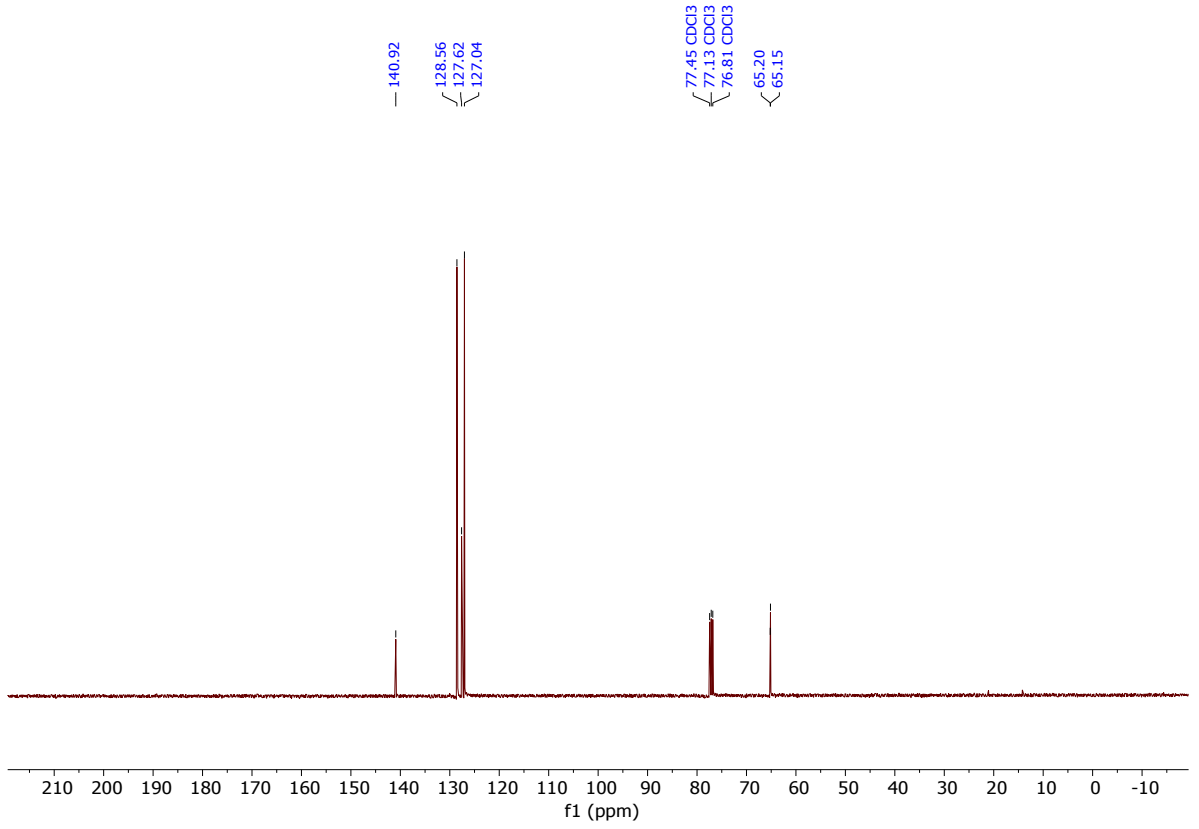
^{13}C NMR spectrum of cinnamaldehyde (400 MHZ, $CDCl_3$)



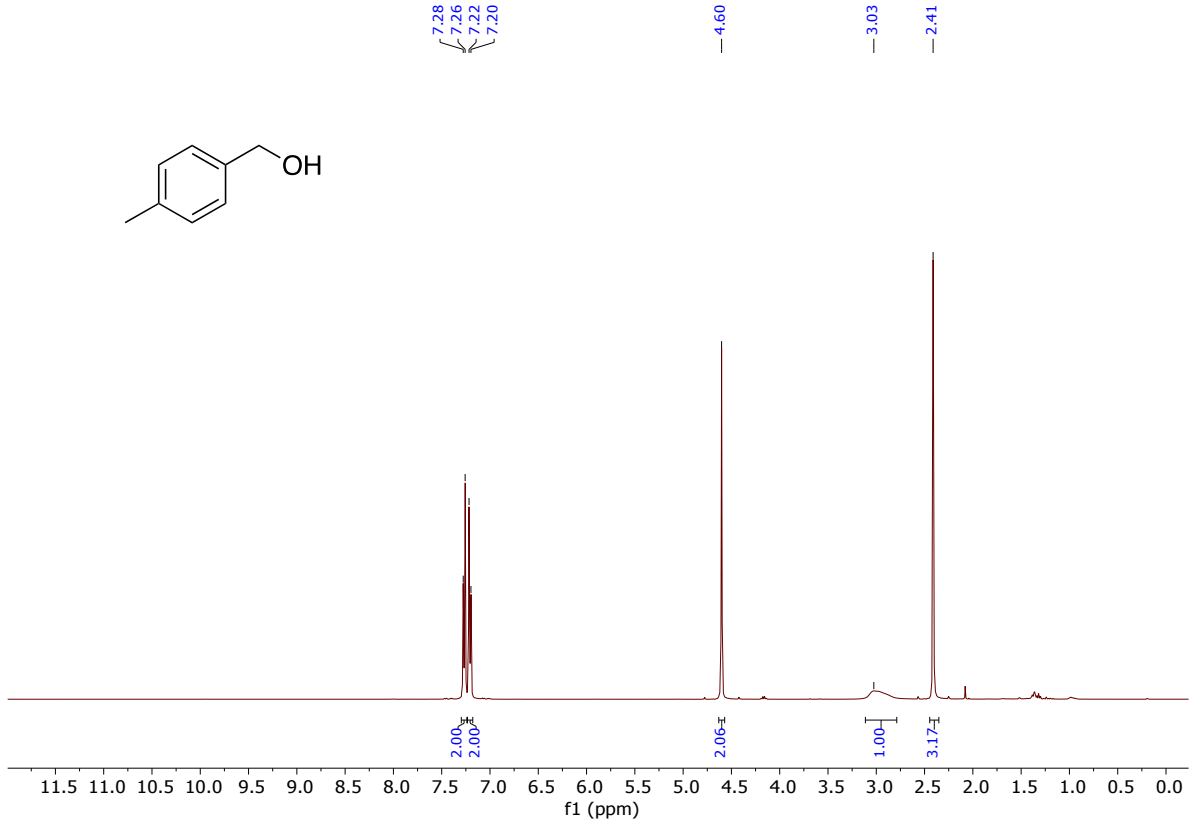
^{1}H NMR spectrum of benzyl alcohol (400 MHZ, $CDCl_3$)



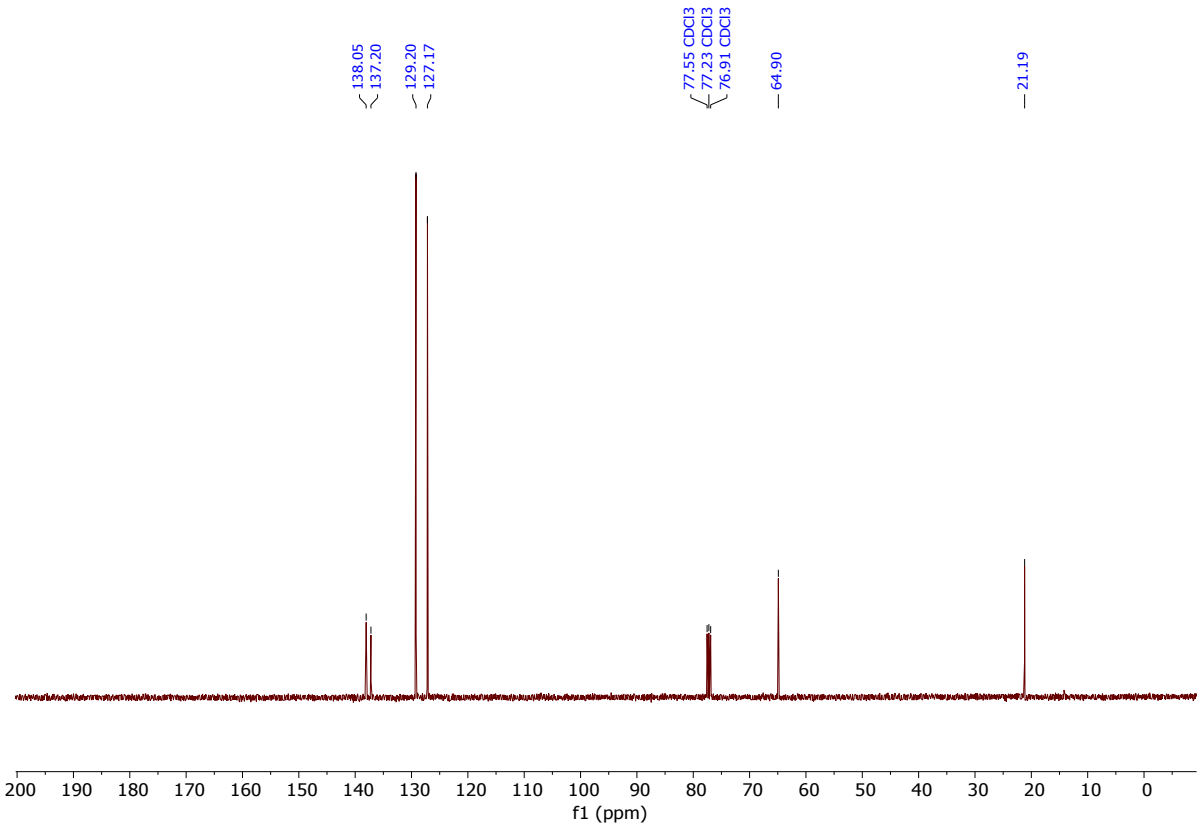
^{13}C NMR spectrum of benzyl alcohol (400 MHZ, $CDCl_3$)



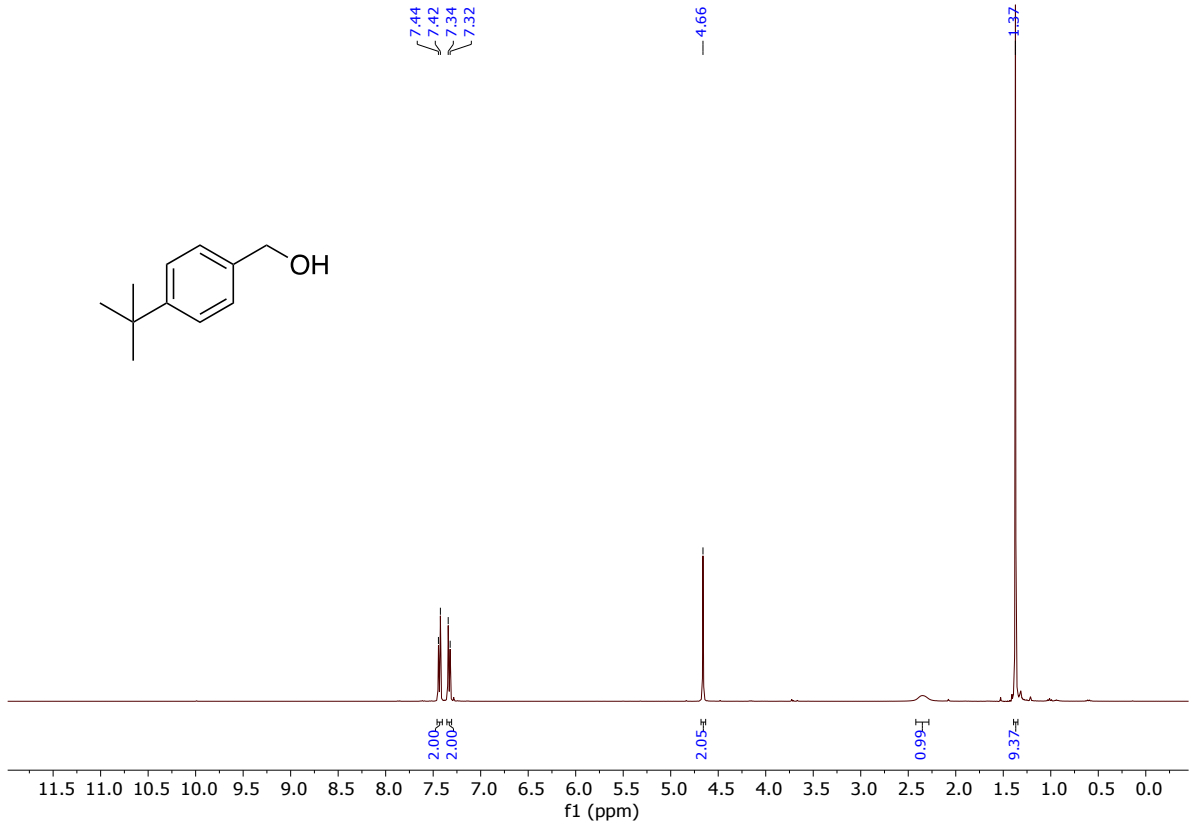
^{1}H NMR spectrum of p-tolylmethanol (400 MHZ, $CDCl_3$)



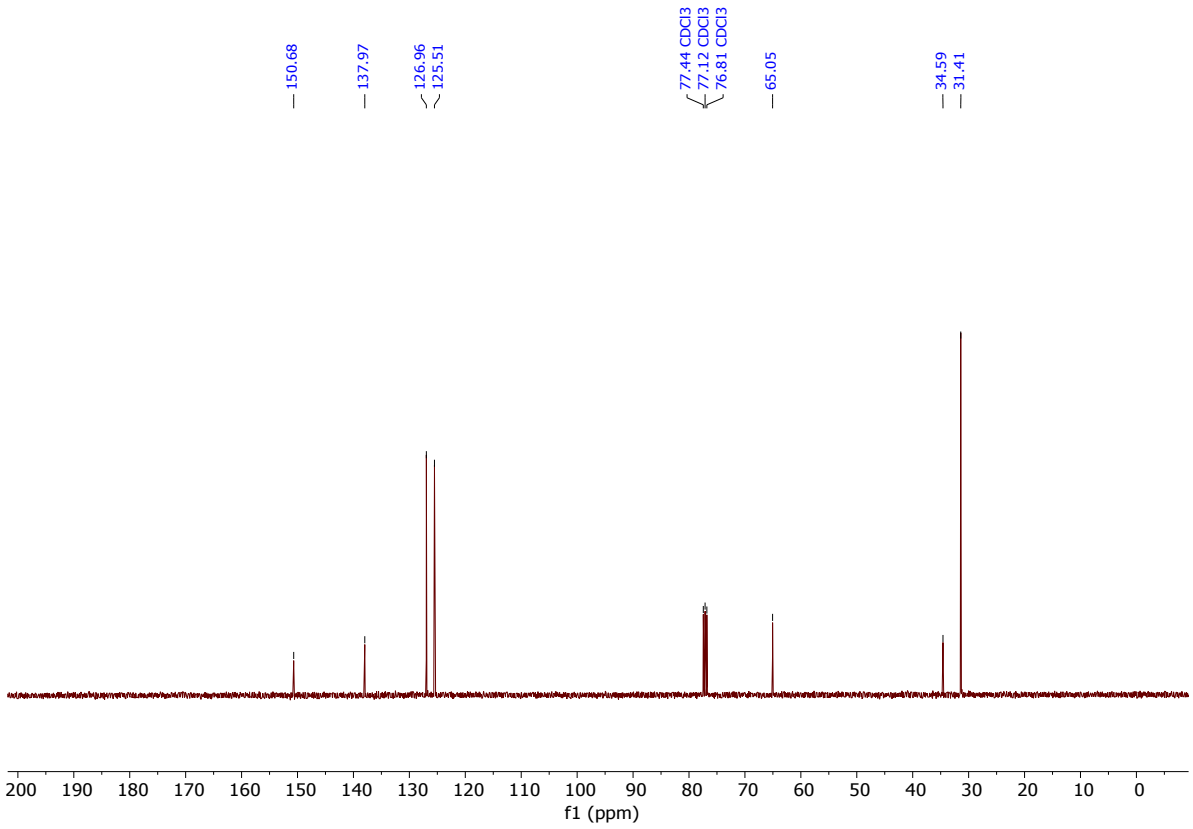
^{13}C NMR spectrum of p-tolylmethanol (400 MHZ, $CDCl_3$)



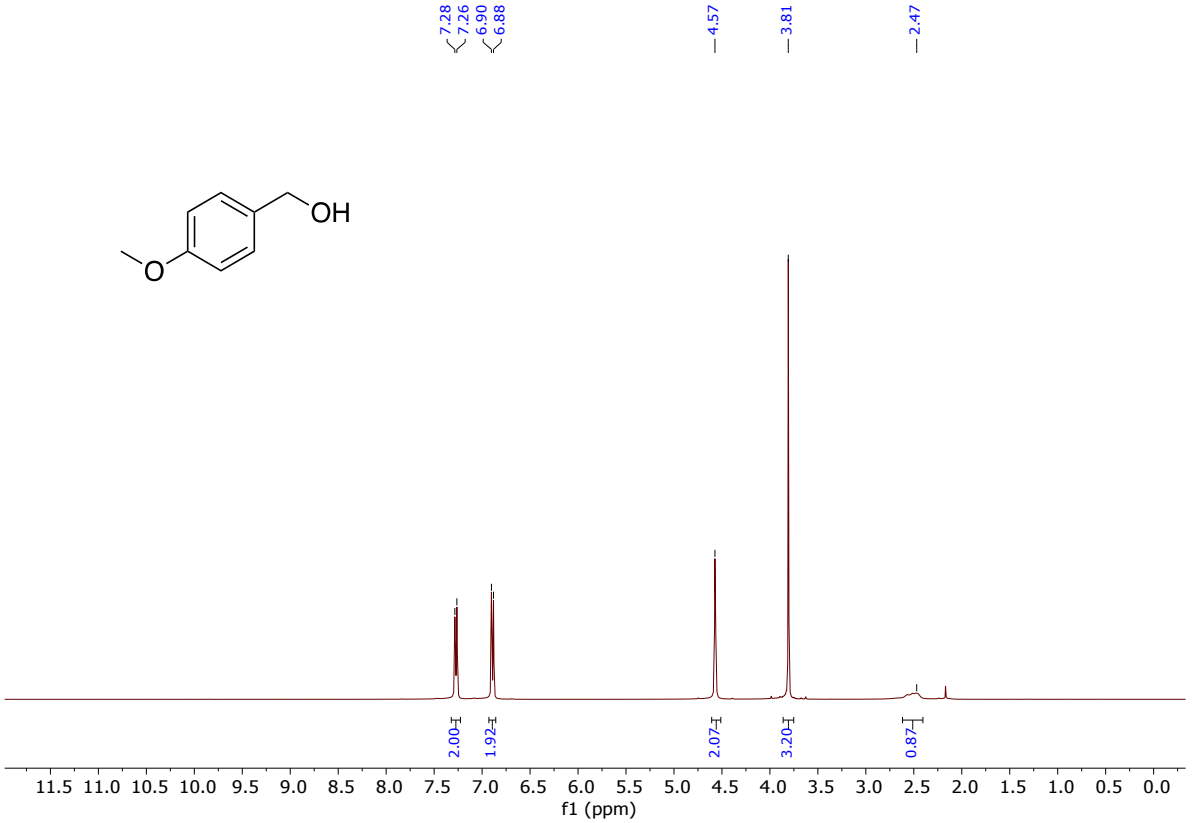
^{1}H NMR spectrum of 4-(tert-butyl)phenylmethanol (400 MHZ, $CDCl_3$)



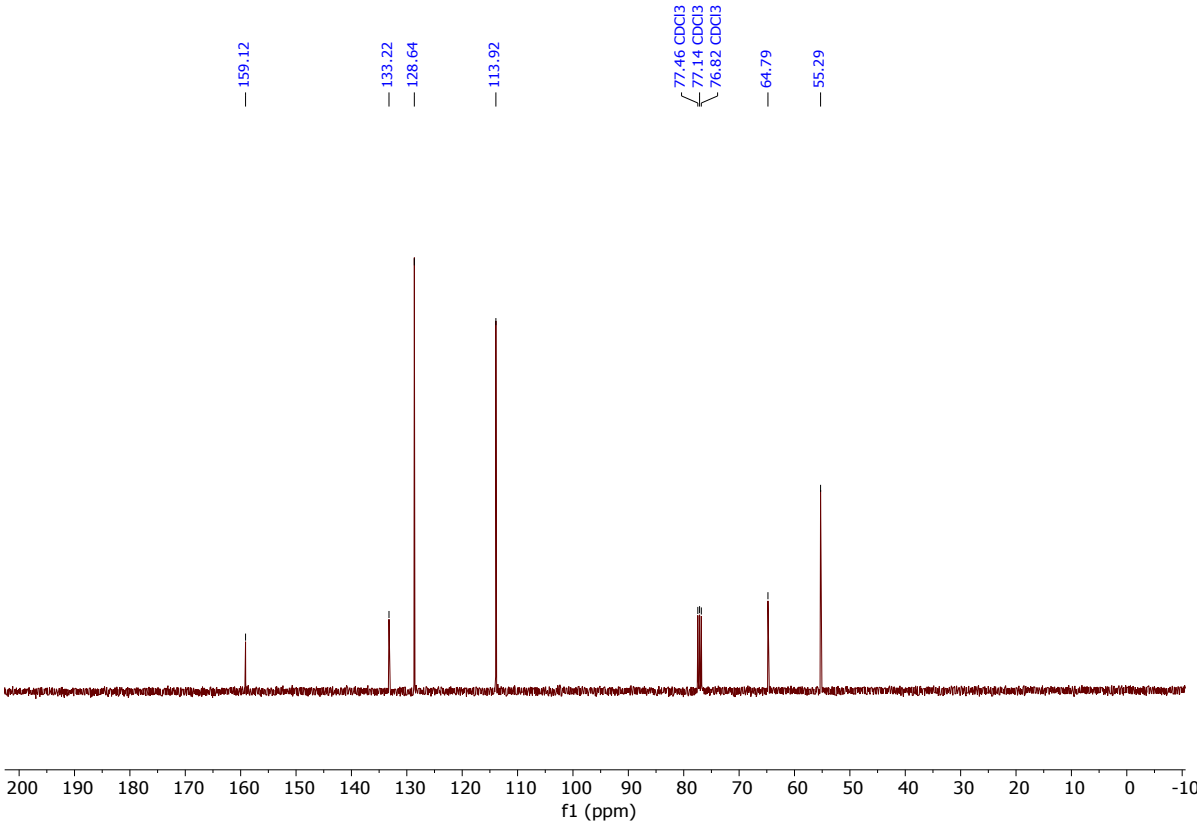
^{13}C NMR spectrum of 4-(tert-butyl)phenylmethanol (400 MHZ, $CDCl_3$)



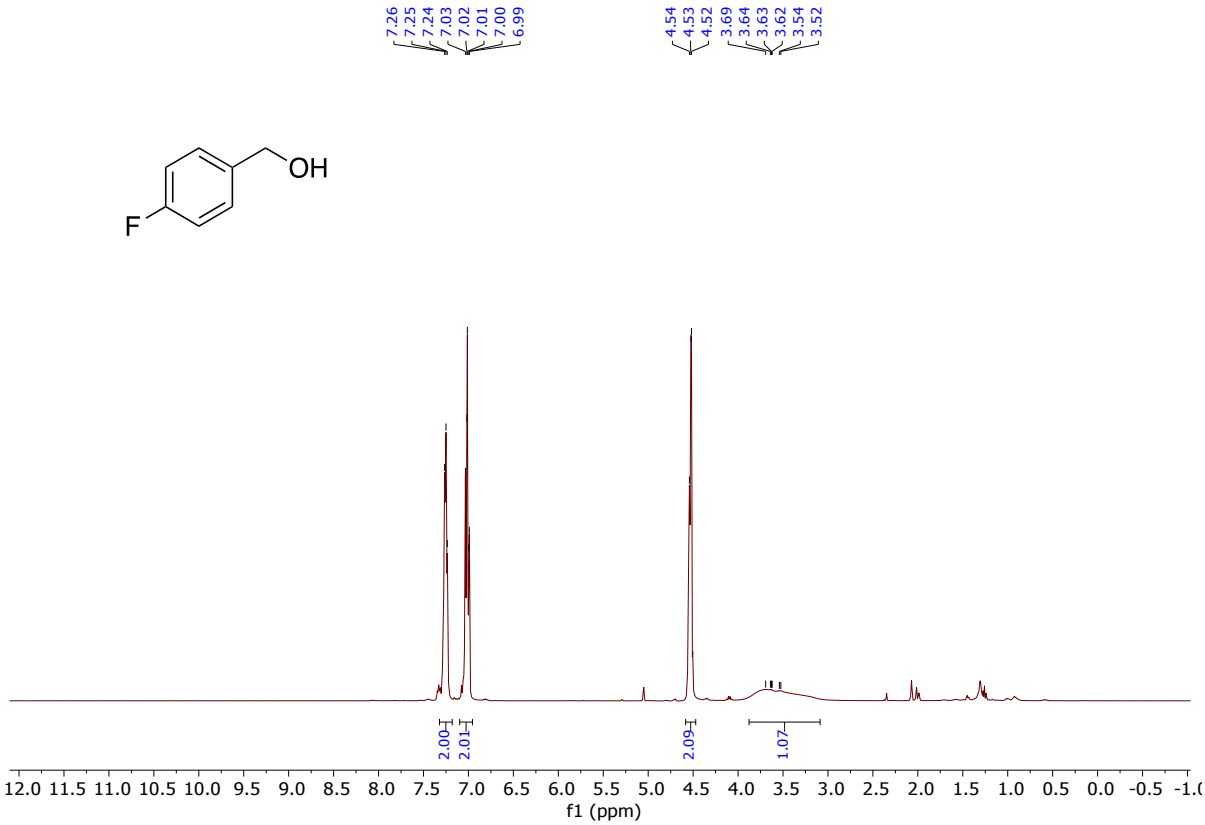
^{1}H NMR spectrum of 4-(methoxy)phenylmethanol (400 MHZ, $CDCl_3$)



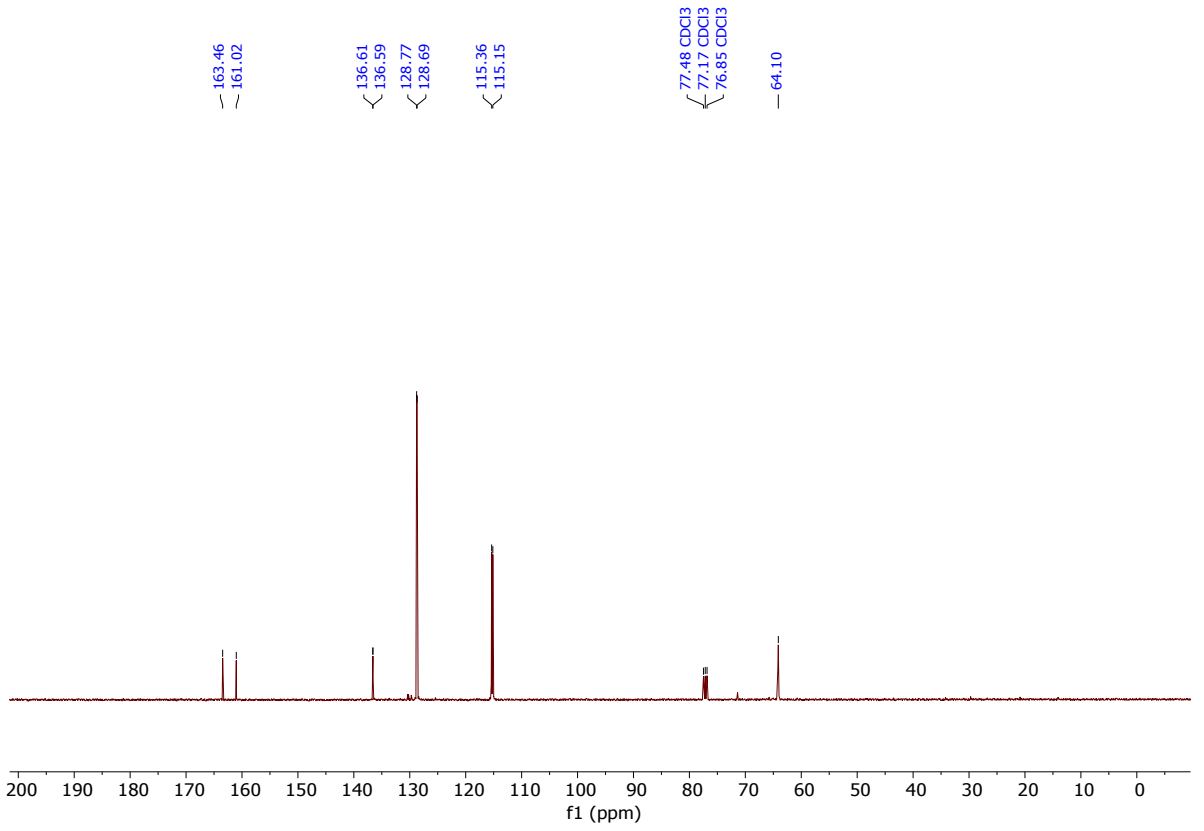
^{13}C NMR spectrum of 4-(methoxy)phenylmethanol (400 MHZ, $CDCl_3$)



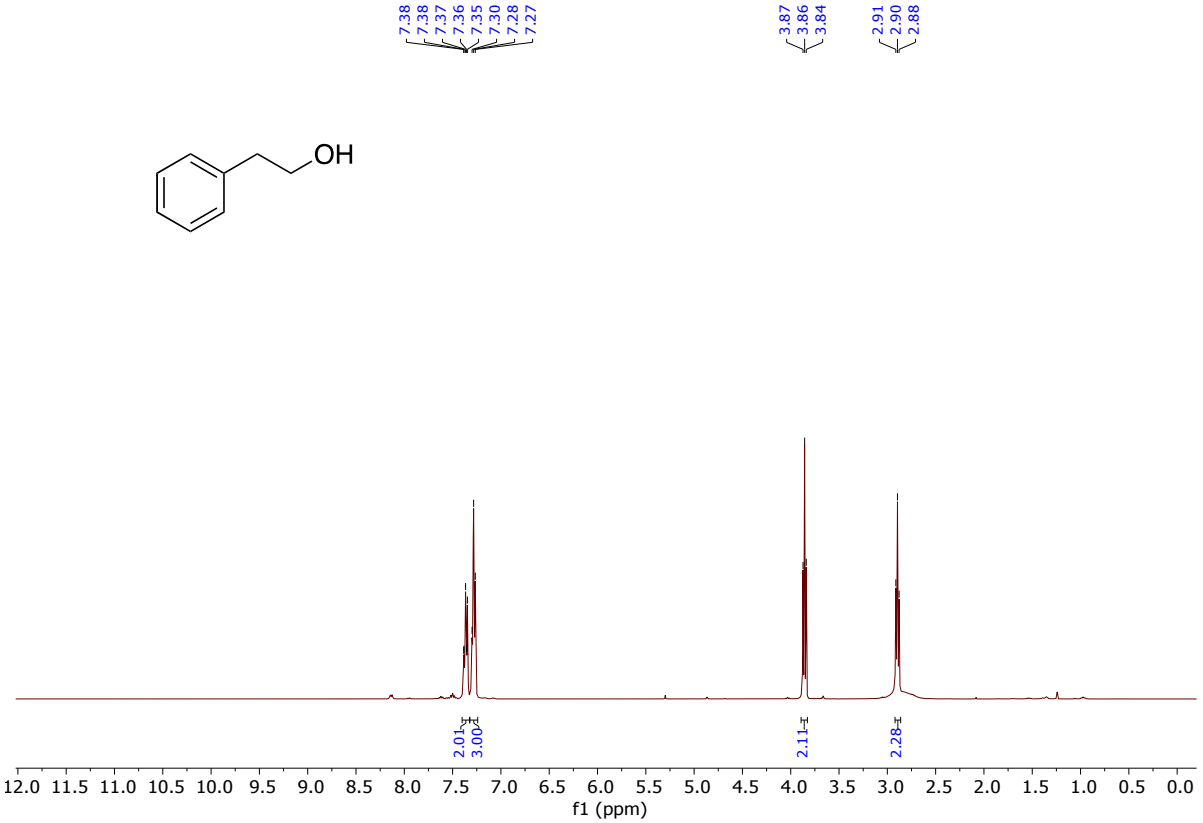
^{1}H NMR spectrum of 4-(fluoro)phenylmethanol (400 MHZ, $CDCl_3$)



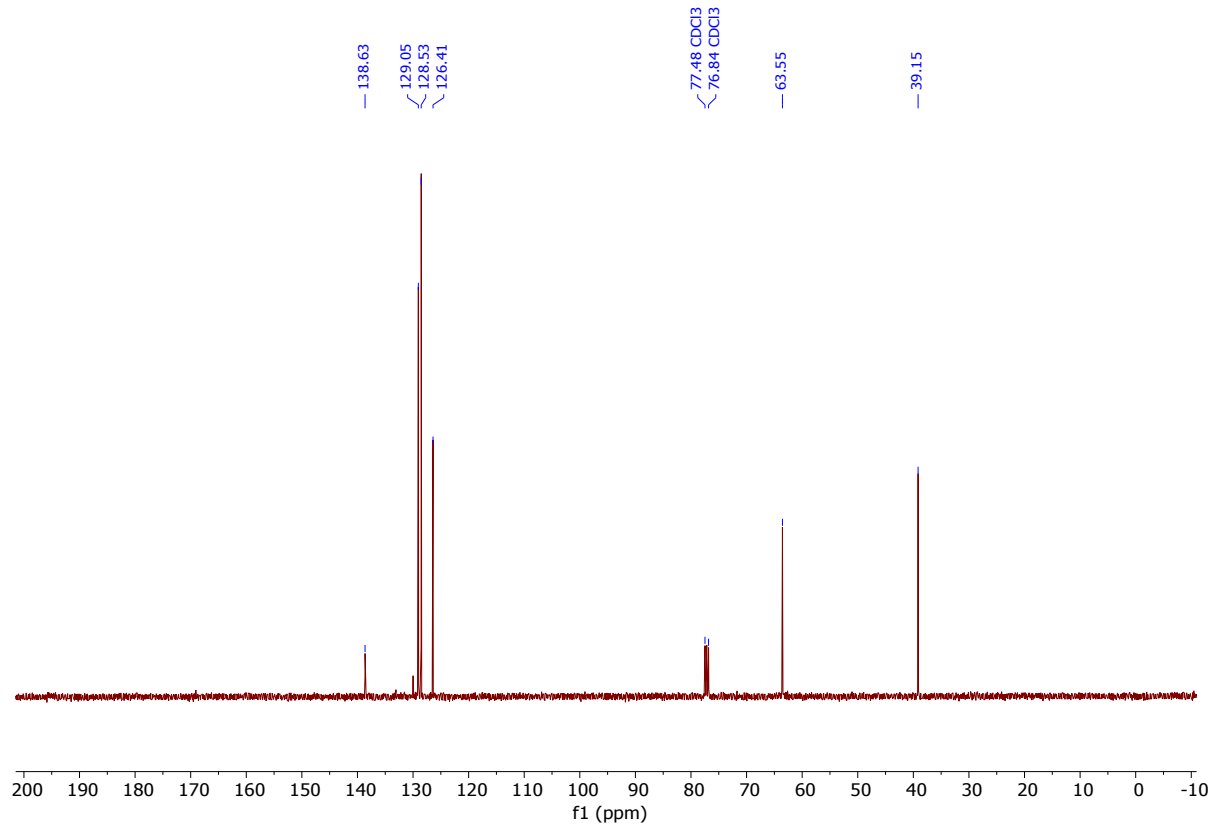
^{13}C NMR spectrum of 4-(fluoro)phenylmethanol (400 MHZ, $CDCl_3$)



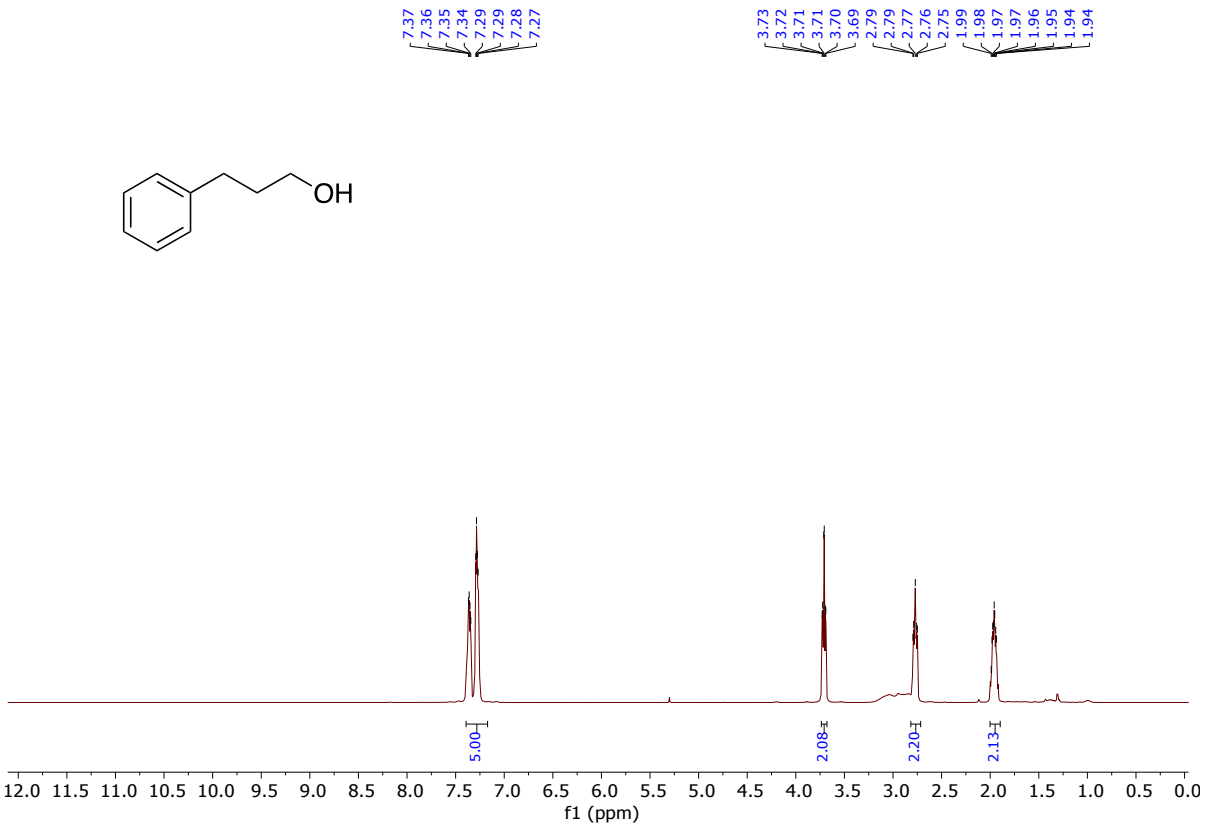
^{1}H NMR spectrum of 2-phenylethan-1-ol (400 MHZ, $CDCl_3$)



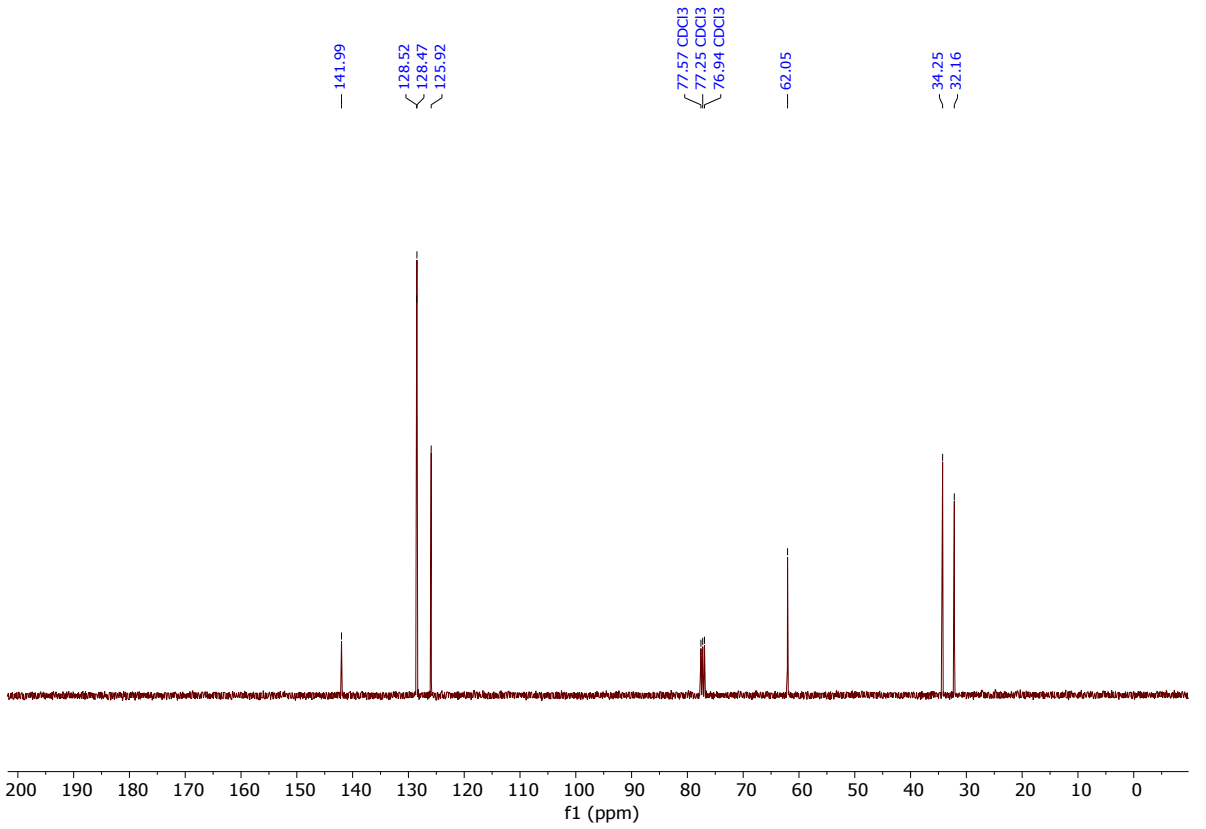
^{13}C NMR spectrum of 2-phenylethan-1-ol (400 MHZ, $CDCl_3$)



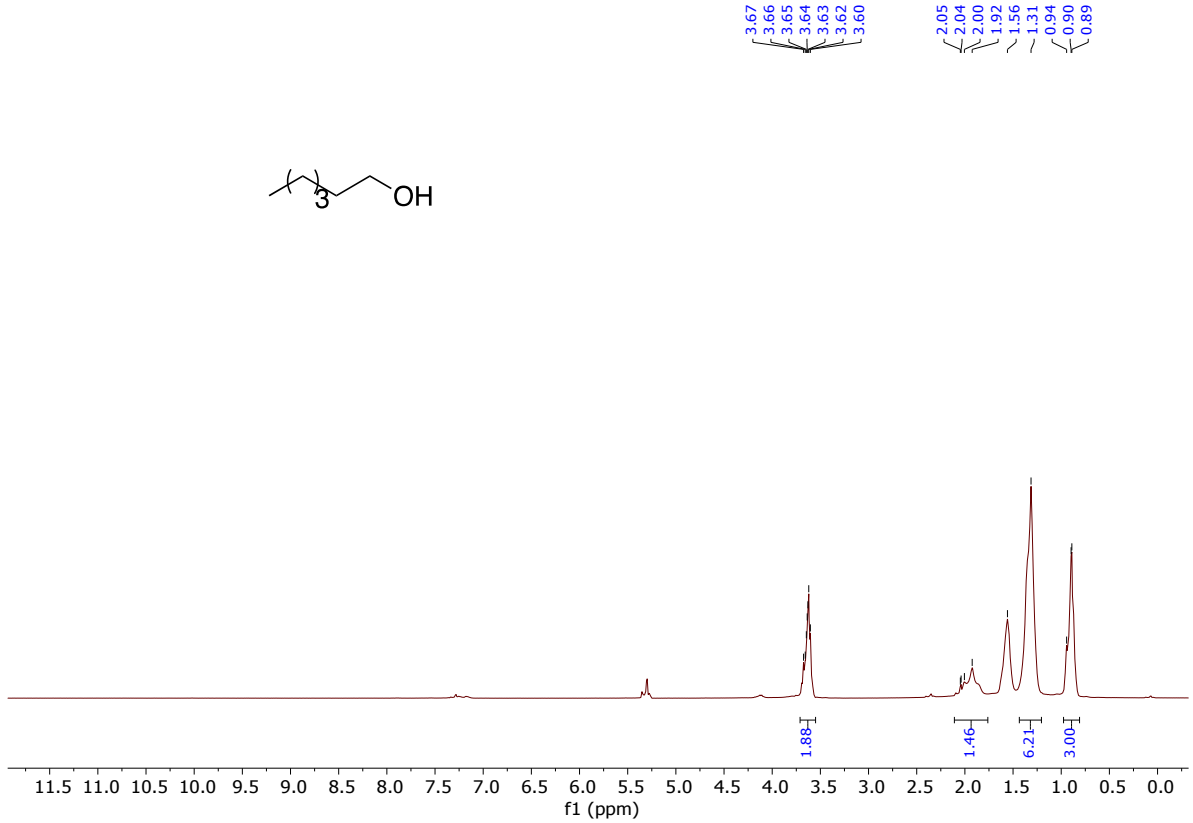
^{1}H NMR spectrum of 3-phenylpropan-1-ol (400 MHZ, $CDCl_3$)



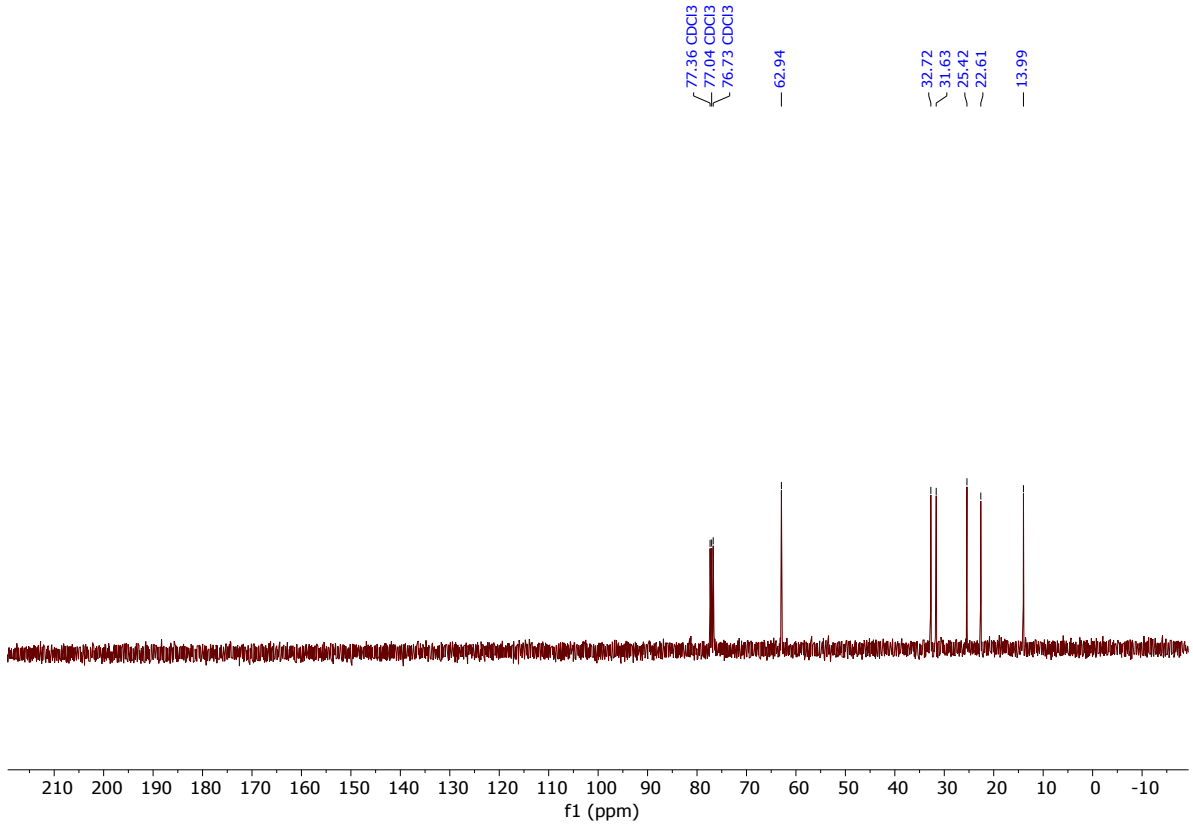
^{13}C NMR spectrum of 3-phenylpropan-1-ol (400 MHZ, $CDCl_3$)



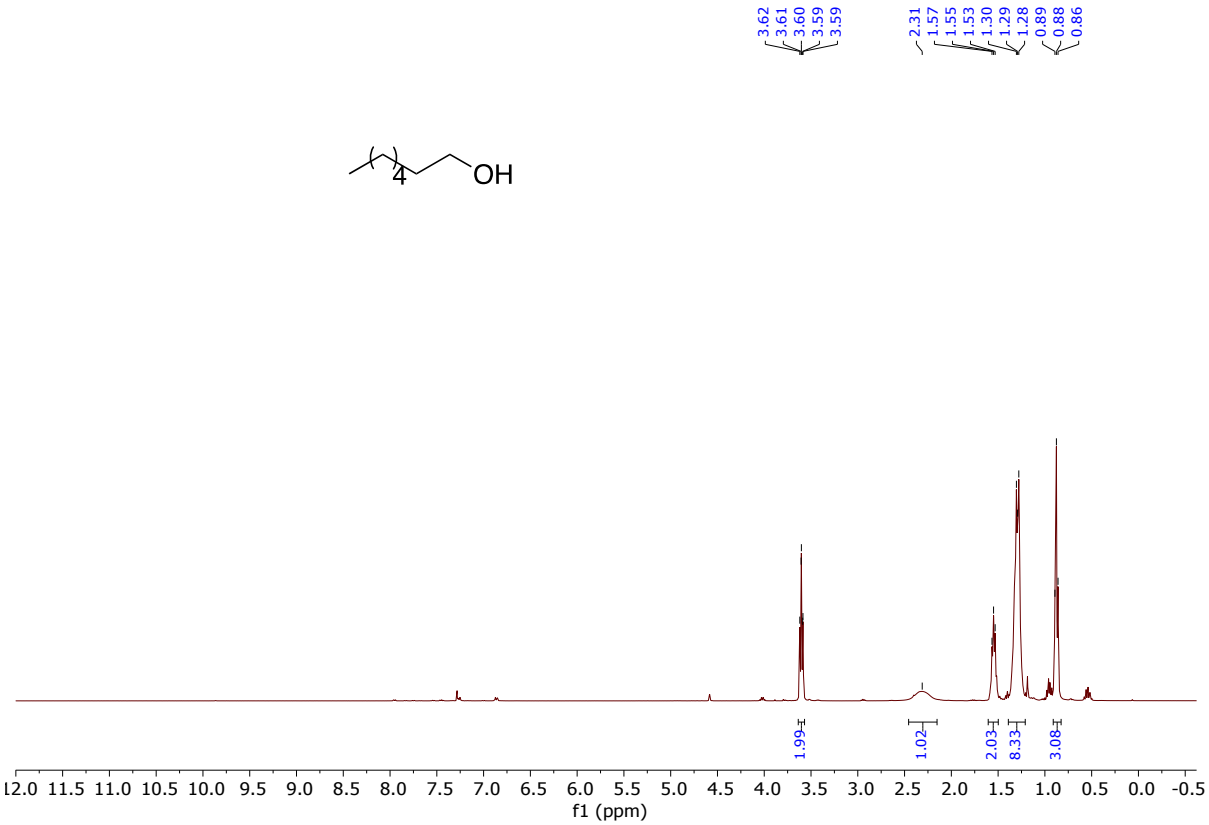
^{1}H NMR spectrum of hexan-1-ol (400 MHZ, $CDCl_3$)



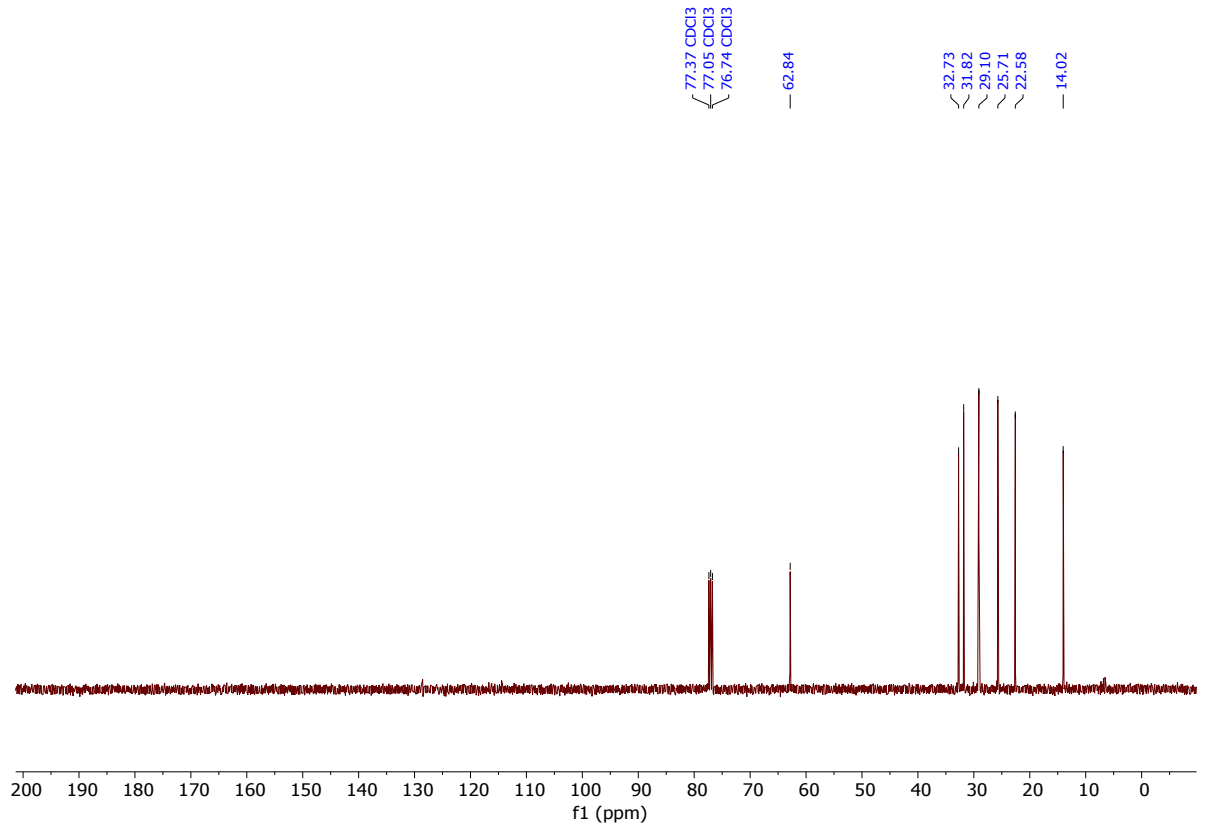
^{13}C NMR spectrum of hexan-1-ol (400 MHZ, $CDCl_3$)



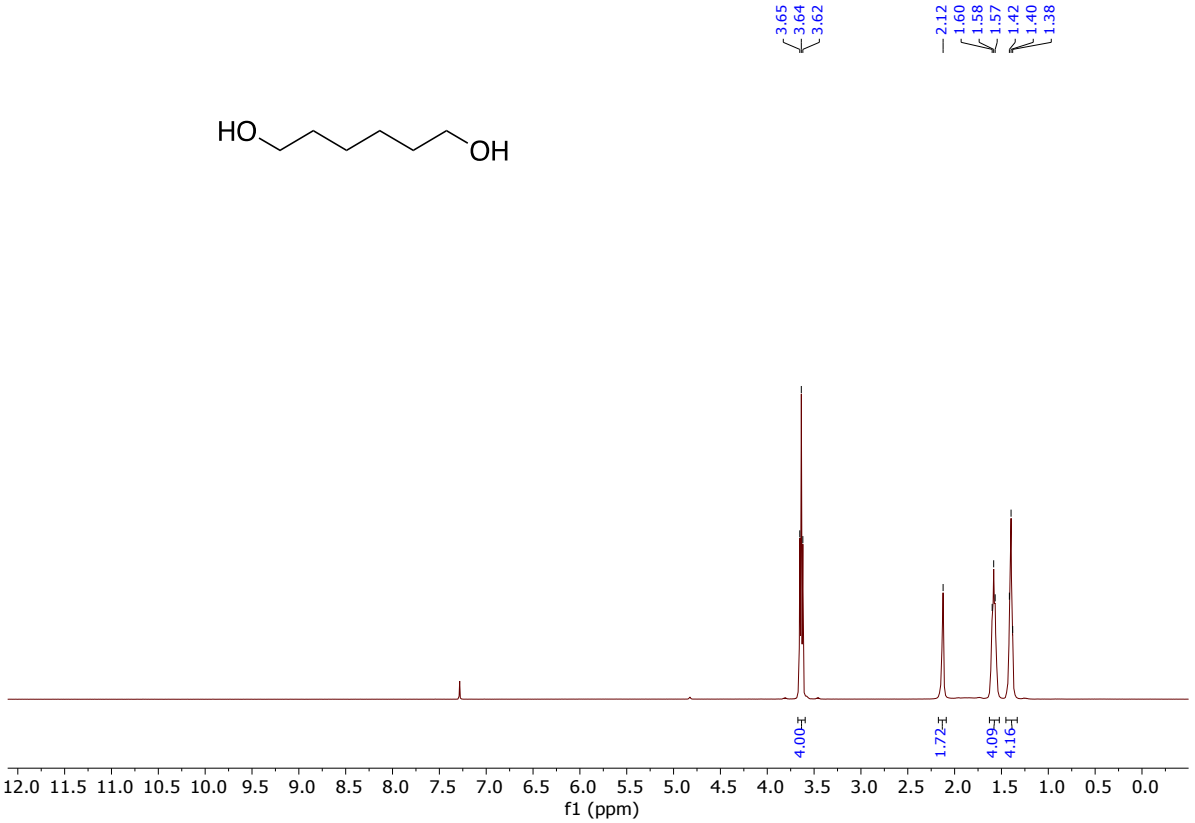
^{1}H NMR spectrum of heptan-1-ol (400 MHZ, $CDCl_3$)



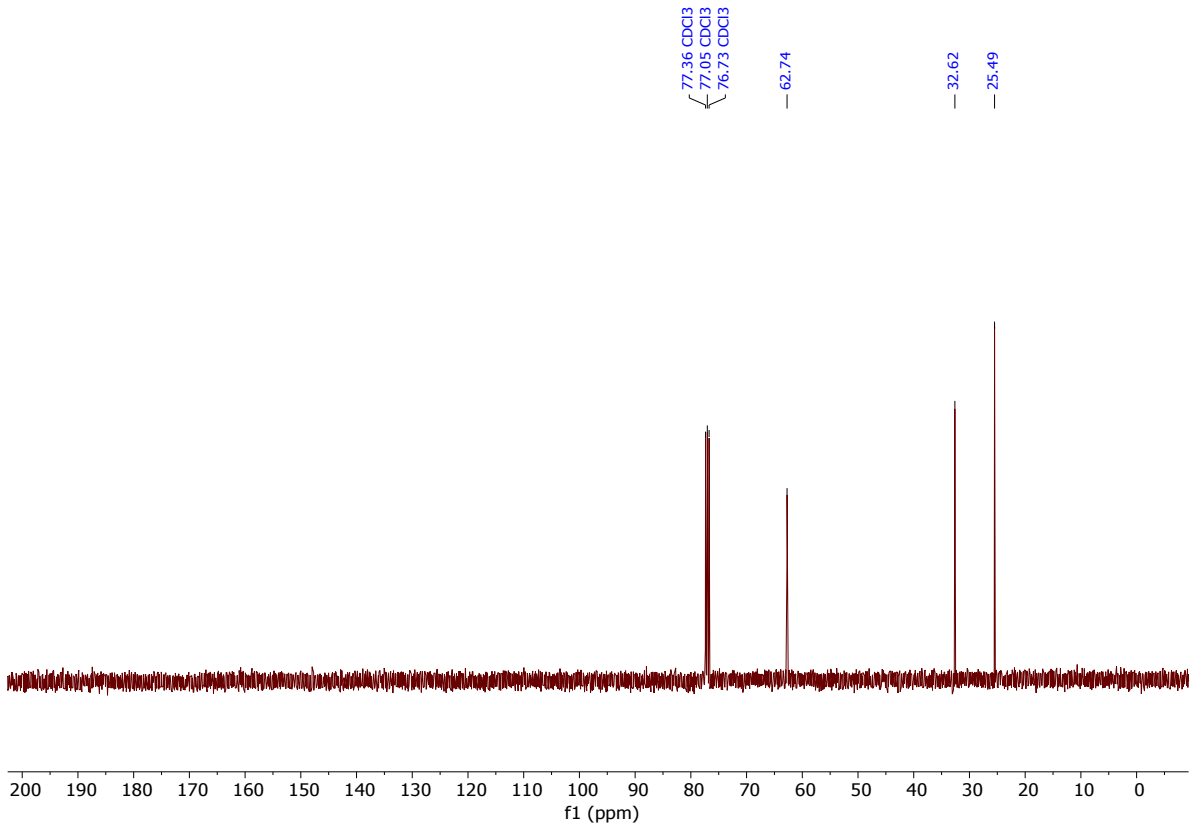
^{13}C NMR spectrum of heptan-1-ol (400 MHZ, $CDCl_3$)



^{1}H NMR spectrum of hexane-1,6-diol (400 MHZ, $CDCl_3$)

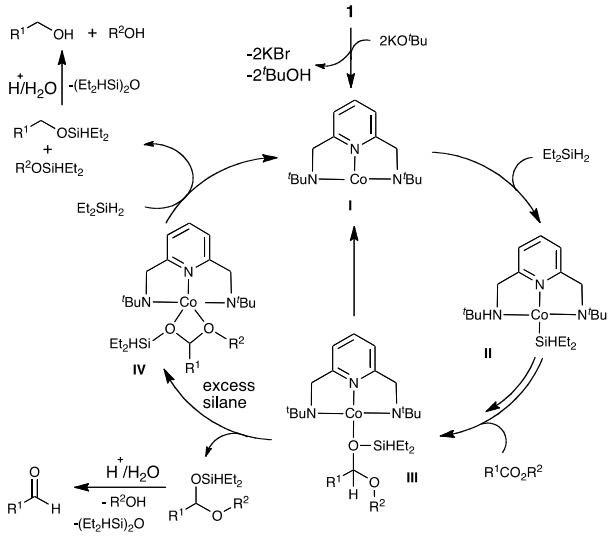


^{13}C NMR spectrum of hexane-1,6-diol (400 MHZ, $CDCl_3$)



Proposed mechanism:

Although more studies are required, a possible mechanism for the selective reduction of esters to aldehydes and alcohols is proposed in Scheme S1. The reaction of catalyst **1** with base provides the coordinatively unsaturated intermediate **I** as established previously.[1] Reaction of intermediate **I** with diethylsilane can generate a complex **II** as a result of Si□H bond activation, facilitated by amine-amide metal-ligand cooperation.[2] Further reaction of **II** with ester may leads to hydrosilylation and formation of coordination complex **III.** The transformation of intermediate II to III may involve the formation of Co-H intermediate and multistep pathway. Dissociation of silylacetal intermediate should then regenerate the active species **I**. In the presence of excess of silane, the intermediate **III** may rearranges to cobalt silylacetal complex **IV**, which upon reaction with diethylsilane provides the silyl ether products and regenerates the intermediate **I**. Acidic work up of the reaction mixture containing either silylacetal or silyl ether intermediates selectively produce aldehydes and alcohols, respectively.



Scheme S1 Proposed mechanism for cobalt catalysed synthesis of aldehydes and alcohols from esters

References:

(1) (a) S. Pattanaik and C. Gunanathan, ***ACS Catal.*** 2019, ***9***, 5552-5561. (b) D. R. Pradhan, S. Pattanaik, J. Kishore and C. Gunanathan, *Org. Lett.* 2020, **22**, 1852-1857.

(2) Reviews on metal-ligand cooperation: (a) J. R. Khusnutdinova, and D. Milstein, *Angew. Chem., Int. Ed.* 2015, **54**, 12236-12273. (b) C. Gunanathan and D. Milstein, *Acc. Chem. Res.* **2011**, *44*, 588–602