Electronic Supporting Information

Polymer-supported Manganese-Catalysed Transformation of Esters and Aldehydes to Alcohols: Catalyst Priming leads to a more active and viable recyclable catalyst system

V. Kishore Kumar Pampana,[a] Si Lok Ko,[a] Eimear Courtney,[a] Benjamin R. O'Donoghue,[a] David J. Jones,[a] Simon K. Beaumont,[b] Davinder Singh,[c] Charlotte Willans,[d] Ian J. S. Fairlamb,*[d] Jason M. Lynam,*[d] Gerard P McGlacken*[a]

[a]School of Chemistry, Analytical and Biological Chemistry Research Facility (ABCRF), University College Cork, T12 YN60, Ireland. E-mail: g.mcglacken@ucc.ie.

[b]Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK.

[c]Tyndall National Institute, Cork T12 R5CP, Ireland

[d]Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. E-mail: ian.fairlamb@york.ac.uk, jason.lynam@york.ac.uk.

Table of Contents

1. General Methods

1.1 General Information

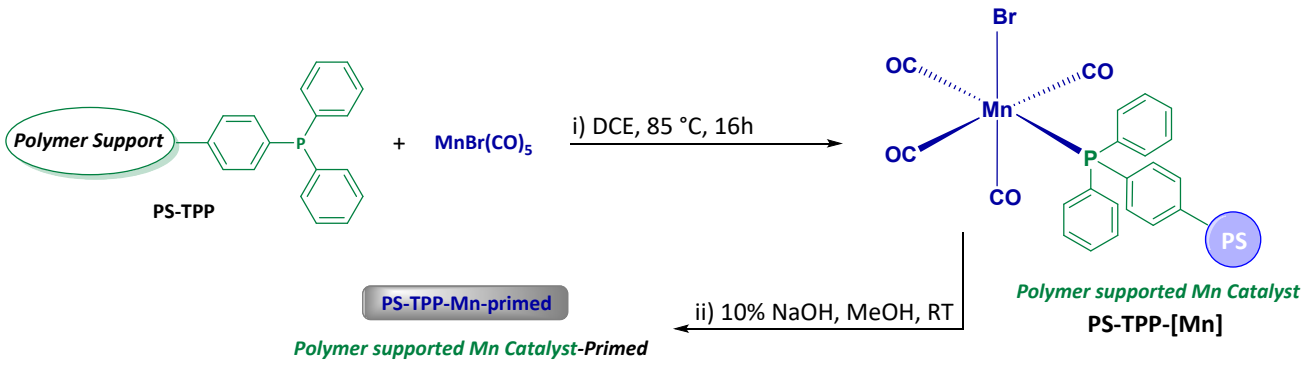
All chemicals, reagents, and solvents for the synthesis of the compounds were an analytical grade, purchased from commercial sources (Sigma Aldrich, FluoroChem, Alfa Aesar, Tokyo Chemical Industry) and used without further purification unless otherwise specified. Wet flash column chromatography was carried out using Kieselgel silica gel 60, 0.040–0.063 μm (Merck). Thin-layer chromatography (TLC) was carried out on pre-coated silica gel plates (Merck 60 PF254). Visualisation of the developed plates was achieved under UV light. Infrared (IR) analysis was performed on solid samples using a PerkinElmer Spectrum Two ATR-FTIR spectrometer. All the solution phase Nuclear magnetic resonance (NMR) spectra were run in DMSO-d6 and $CDCl_3$ using tetramethylsilane (TMS) as the internal standard at 20 °C unless otherwise stated. ^{1}H NMR (500 MHz), and ^{1}H NMR (300 MHz) spectra were recorded on a Bruker Advance 500, and Bruker Advance 300 NMR spectrometers respectively. ^{13}C NMR (126 MHz), and ^{13}C NMR (75 MHz) spectra were recorded on Bruker Advance 500, and Bruker Avance 300 NMR spectrometers respectively in proton decoupled mode. All ^{1}H, ^{13}C and ^{19}F spectra were recorded at University College Cork. Chemical shifts δH and δC are expressed as parts per million (ppm), positive shift being downfield from TMS (δH = 0 ppm); coupling constants (J) are expressed in hertz (Hz). Splitting patterns in ^{1}H NMR spectra are designated as singlet (s), broad singlet (bs), broad doublet (bd), broad triplet (bt) doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt), doublet of triplets (dt), doublet of quartets (dq), triplet (t), triplet of doublets (td), quartet (q) and multiplet (m). Solid state ^{31}P NMR analysis was recorded at Trinity College Dublin. ICP-OES Analysis was completed at the University of York with an Agilent ICP-OES 5800 VDV spectrometer. Samples were aliquoted into acid-leached teflon digestion tubes and accurately weighed (0.30 - 22.9 mg). HCl (1.35 mL, 37%, certified AR grade, supplied by Fisher Chemical™) and HNO_3 (3.85 mL, 70%, certified AR grade, supplied by Fisher Chemical™) were added. Samples were digested in an Anton-Paar Multiwave Go Plus with microwave irradiation, ramp rate 18 °C min^{-1}, ultimate temperature 180 °C, dwell time 15 minutes. Samples allowed to cool and diluted to 50 mL total volume with ultrapure water (Milli-Q type 1 ultrapure water system supplied by Merck). Samples were allowed to stand for 72 hours and carefully decanted to remove undissolved solid. Working standard solutions were prepared from commercial reference standard CCS-6 supplied by inorganic ventures, traceable to NIST certified reference materials. All working standards were matrix matched to the digestion media. Mn analysis was completed at 259.372 nm, with internal standard Y 371.029 nm. Measurements were made in axial configuration, plasma flow 12.0 L min^{-1}, auxiliary flow 1.00 L min^{-1}, RF power 1.20 kW. For imaging analysis Tescan Solaris FESEM was used. Low beam current was used to minimize charging effect. Elemental analysis and mapping of sphere samples was done using attached Oxford ULTIM Max EDX detector.

Ex situ X-ray absorption fine structure (XAFS) spectroscopy measurements were performed in transmission mode at the Durham University XAFS facility using a EasyXAFS300+ using the (4,4,0) reflection of a Si (1,1,0) spherically bent crystal analyser (SBCA), a 1200 W proto-X-ray tube with an Mo anode. The power of the X-ray source was set to maintain a collection deadtime on the silicon drift detector of <30 %. Samples were prepared for Mn K-edge XAFS measurements by adding 15 - 40 mg of each catalyst and 50-70 mg of polyethylene glycol binder and grinding in an agate mortar and pestle until homogenous (masses targeting optimal transmission edge jumps versus total absorption, or determined by material available for recycle experiments). Pellets were produced from the resulting mixture by transfer to a 1.0 cm diameter die and applying up to 2 tonnes of pressure for 60 s using a Specac hydraulic press. Spectra were obtained around the step edge from 6524 to 6589 eV with 0.25 eV steps and 5.6 s dwell time, and at lower resolution above and below the edge for normalisation. Four spectra were acquired for each sample, checked for consistency and normalised. Energy calibration was carried out by scanning a Mn foil using the same acquisition parameters and correcting to the maximum of the first derivative at 6539 eV. Transmission spectra were obtained using a separately recorded background (I_0) scan. Data collected from the instrument was background corrected using the python based EasyXAFS software (easyXAFS, WA). Processing of XAFS data produced was performed using IFEFFIT with the demeter package using Athena for normalisation,[1] plotting and edge position determination. Edge position of samples was taken to be 50% of the normalised step edge height to avoid possible interference of pre-edge features in determination by other methods.

1.2 General procedure for the synthesis of Triphenyl Phosphine bound polymer supported Manganese catalyst PS-TPP-[Mn]

In an oven dried pressure tube, add 10 mL of anhydrous DCE to Triphenylphosphine, polymer-bound (100-200 mesh, extent of labeling: ~1.6 mmol g^{-1} loading) **PS-TPP** (419 mg, 0.67 mmol of PPh_3 approximately based on supplier's loading) and homogeneous manganese bromo pentacarbonyl **$MnBr(CO)_5$** (548mg, 2.0 mmol) and stirred at 85 ^oC in an oil bath for 16h. Filter the solid in Hirsh funnel using a filter paper and wash the solid with DCM and MeOH (remove the excess unreacted homogeneous Mn catalyst) and later dried under vacuum, results in an Yellowish orange solid PS-TPP-**[Mn]** (575 mg).

PS-TPP-**[Mn]** can be primed by treating with 10% NaOH and MeOH solution overnight at room temperature to enhance the activity, exclusively for selective reduction of esters and aldehydes, which resulted in producing enhanced yields of the desired reduction products.



Scheme S1. General procedure for the synthesis of Heterogeneous Mn catalyst

1.3 Determination of catalyst loading by ICP-OES

The mol% catalyst loading was determined for the reactions using the processed ICP result that the polymer-supported catalyst contained 7 wt.% Mn as follows:

$$Mol\%\ loading\ in\ reaction = \frac{moles\ Mn}{moles\ substrate} \times 100\%$$

$$Mol\%\ loading\ in\ reaction = \left(\frac{Mn\ wt.\%\ in\ catalyst\ \times mass\ of\ catalyst\ in\ reaction \div Mr\ (Mn)}{moles\ of\ substrate\ in\ reaction}\right) \times 100\%$$

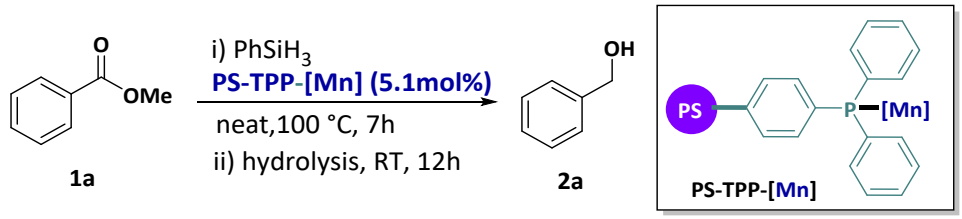
$$Mol\%\ loading\ in\ reaction = \left(\frac{\left(\frac{7.0}{100}\right) \times 20\ mg\ \div 54.938\ mg\ mmol^{-1}}{0.5\ mmol}\right) \times 100\% = 5.1\ \%$$

S.No	**Catalyst**	**Mn in mol%**
1	Fresh PS-TPP-[Mn]	5.1%
2	PS-TPP-[Mn]-used once	4.2 %
3	PS-TPP-[Mn]-used twice	3.9%
4	Fresh PS-TPP-[Mn]-Primed	5.1%
5	PS-TPP-[Mn]-Primed used once	4.7%

1.4 General procedure for the transformation of Esters and Aldehydes using Supported Manganese catalyst

Esters or aldehydes (0.5 mmol), Phenyl silane (2.0-3.0 equiv.), and Triphenyl Phosphine Polymer-supported Mn catalyst PS-TPP-**[Mn]** (20 mg, 5.1 mol%) were transferred into a dry test tube fitted with a screw cap and a magnetic stir bar. The reaction mixture was then heated at 100 ˚C in an oil bath for 7 to 8h. Thereafter, the reaction mixture was cooled down to r.t. and MeOH (3 mL) and 10 % aq. NaOH solution (2 mL) was added

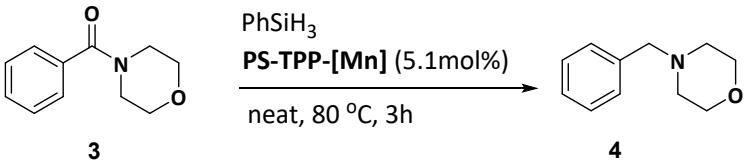
slowly. The resulting mixture was stirred overnight for complete hydrolysis. Organic compounds were extracted from the mixture with CH_2Cl_2 (3 x 12 mL). The organic fraction was dried over Na_2SO_4 and all volatiles were removed using rotary evaporator. Crude product was purified by column chromatography using silica as stationary phase and a mixture of hexanes and ethyl acetates as eluents to afford respective alcohols as products in good to excellent yields.



Scheme S2. General procedure for selective reduction of esters and aldehydes to alcohols

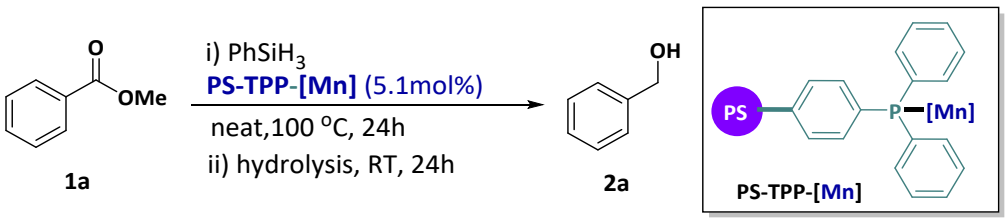
1.5 General procedure for the reduction of amides using Supported Manganese catalyst

A dry test tube fitted with a screw cap containing a stir bar was charged with the morpholino(phenyl)methanone **3** (0.5 mmol) and PS-TPP-**[Mn]** (20 mg, 5.1 mol%) and Phenyl silane (2.0 equiv.) were added sequentially. The mixture was stirred under air at 80 °C for 3 h. The cooled reaction mixture was then filtered and separated from heterogeneous Mn catalyst using MeOH. Separated reaction mixture was then concentrated under reduced pressure and then purified by filtering through silica gel column chromatography affording reduced amine **4** in excellent yield.



1.6 Recyclability of the Heterogeneous Mn catalyst

1a (2.0 mmol), Phenyl silane (4.0 mmol, 2.0 equiv.), PS-TPP-**[Mn]** (80mg, 5.1 mol%) stirred in an oven dried Schlenk tube under neat conditions at 100 °C in an oil bath. After 24h, reaction was cooled down to RT and added 10% NaOH (6 mL) and MeOH (10 mL) and stirred at RT for complete hydrolysis. After 24h, add MeOH (5-10 mL) allows the Heterogeneous Mn catalyst to settle down at the bottom of the reaction tube. Decant the reaction mixture in to a separating funnel and extract the organic layer with DCM as mentioned in general procedure **1.3** and isolate the desired product **2a** using column chromatography. Recycle the heterogeneous catalyst by using a Hirsch funnel. Wash it with methanol and DCM to remove any remaining organic material, then dry it for use in the next run. Repeat the same procedure (2^{nd} to 4^{th} run) using recycled catalyst at the end of each run.

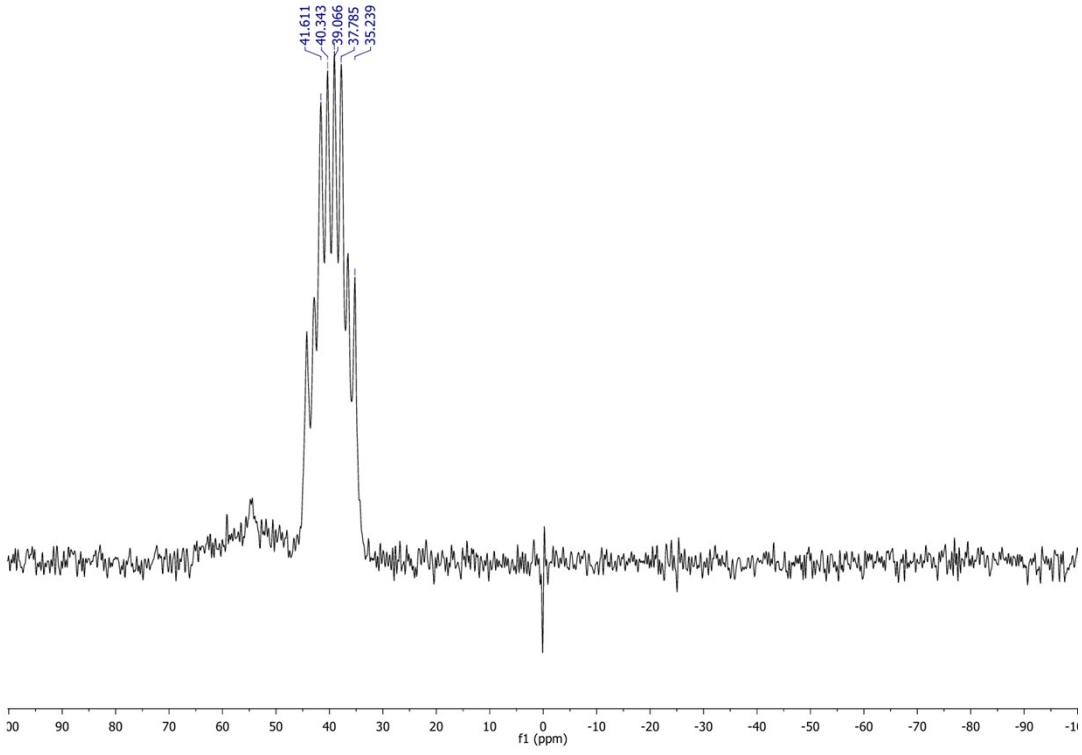


1.7 Hot filtration test

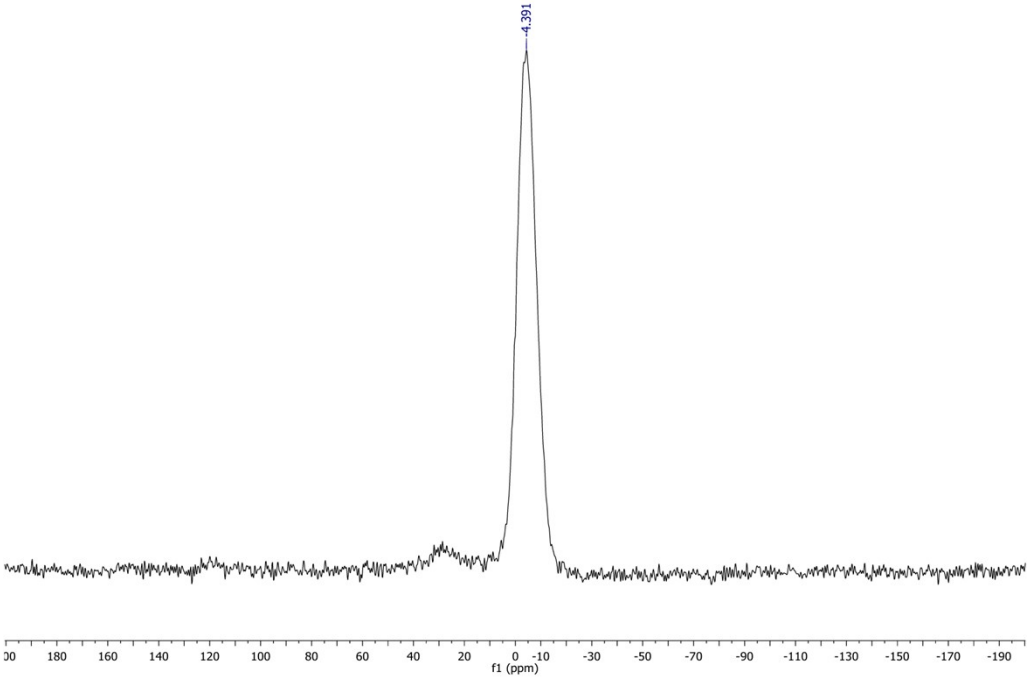
GP 1.4 was followed using methyl benzoate 1a (0.5 mmol), Phenyl silane (2.0 equiv.), and PS-TPP-**[Mn]** (20 mg, 5.1 mol%) were transferred in to a dry test tube fitted with a screw cap and a magnetic stir bar. The reaction mixture was then heated at 100 °C in an oil bath. After 2 hours, PS-TPP-**[Mn]** was carefully filtered over celite and the filtrate was directly transferred in to another dry test tube fitted with a screwcap. This was directly transferred to pre-heated oil-bath and the reaction continued for 6 h. Thereafter, the reaction mixture was cooled down to r.t. and MeOH (3 mL) and 10 % aq. NaOH solution (2 mL) was added slowly. The resulting mixture was stirred overnight at for complete hydrolysis. Organic compounds were extracted from the mixture with CH_2Cl_2 (3 x 12 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo which afforded the alcohol **2a** in 6% confirming the heterogeneity of the synthesised Mn heterogeneous catalyst.

1.8 Solid state ^{31}P NMR analysis

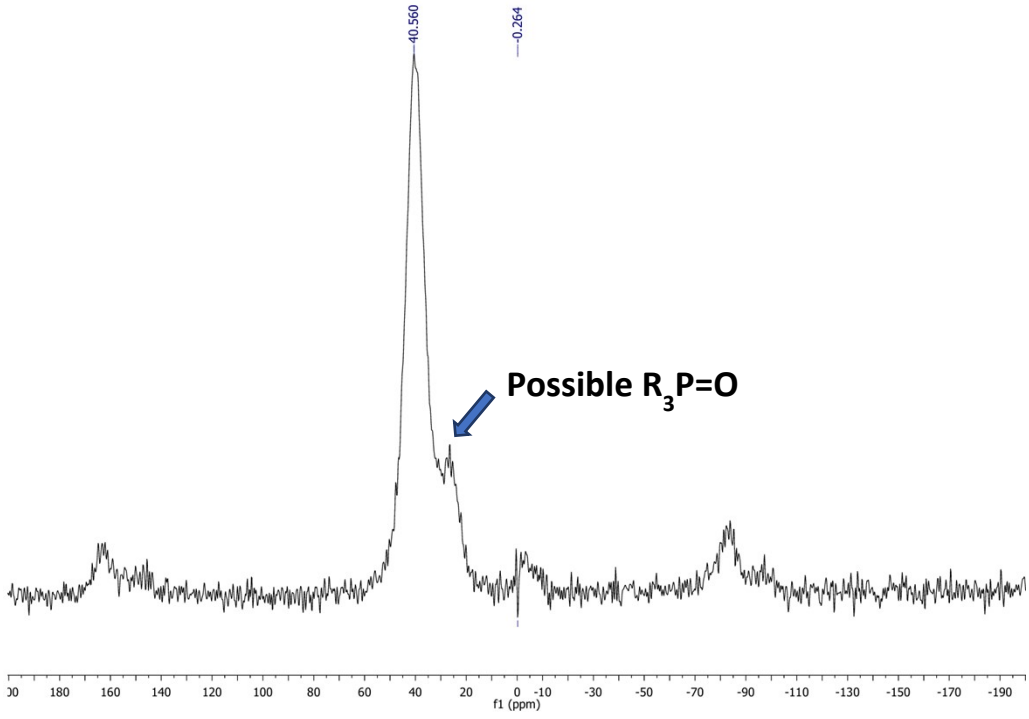
SS ^{31}P NMR of $MnBrCO_4(PPh_3)$ homogeneous complex



SS ^{31}P NMR of Free polymer supported phosphine ligand (PS-TPP)

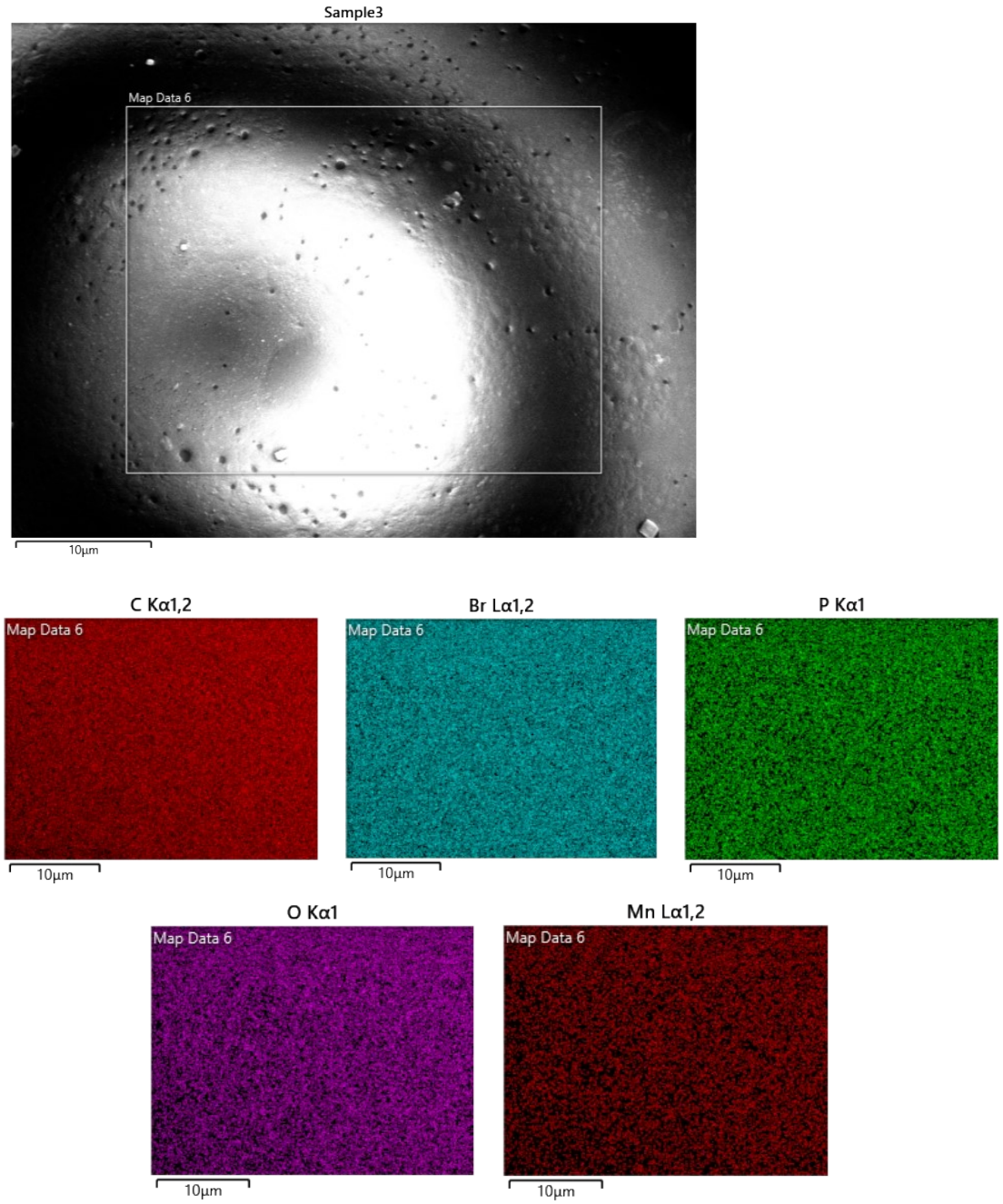


SS ^{31}P NMR of polymer supported Mn catalyst PS-TPP-[**Mn]**

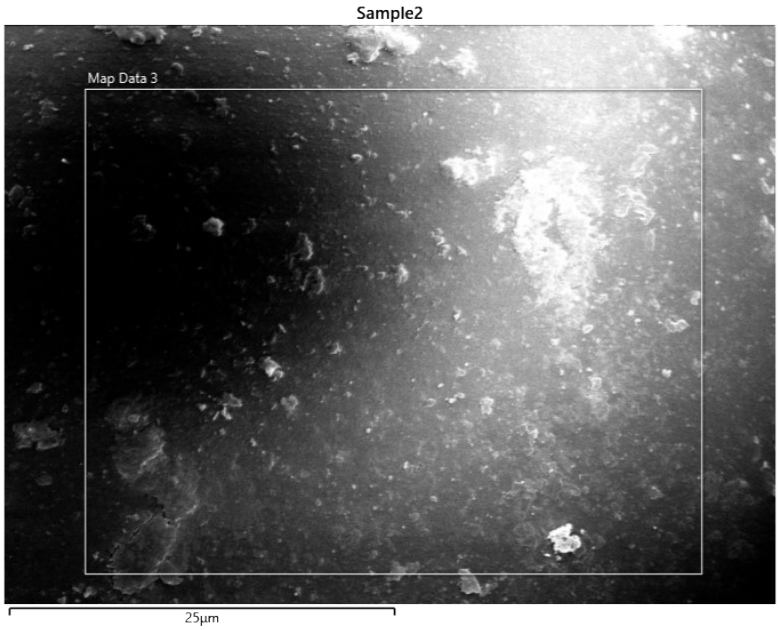


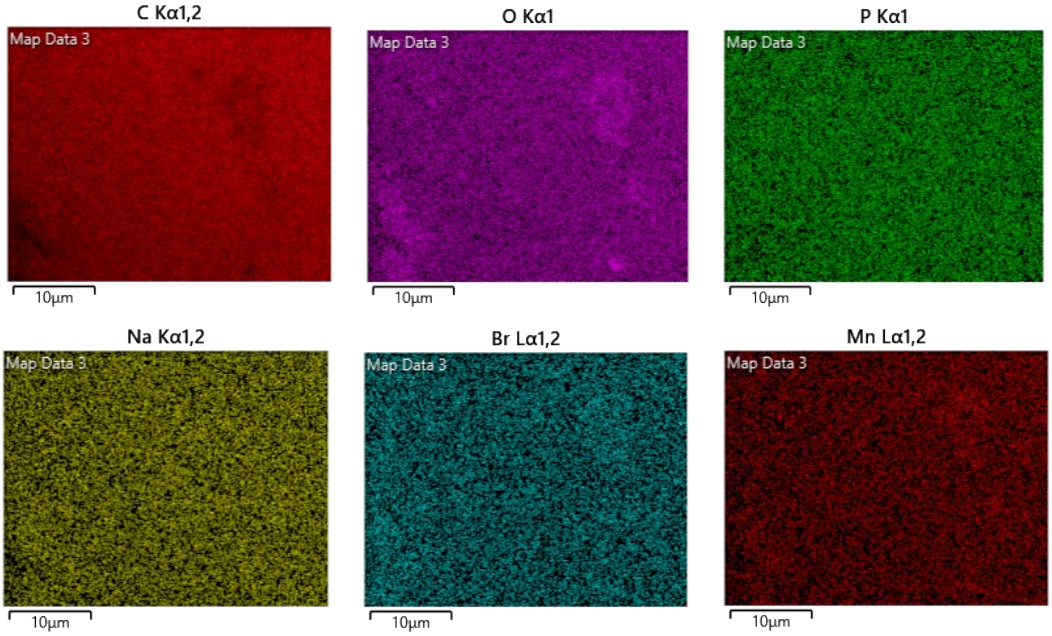
1.9 SEM-EDX mapping analysis

a) EDX mapping analysis of **unused** PS-TPP-**[Mn]**

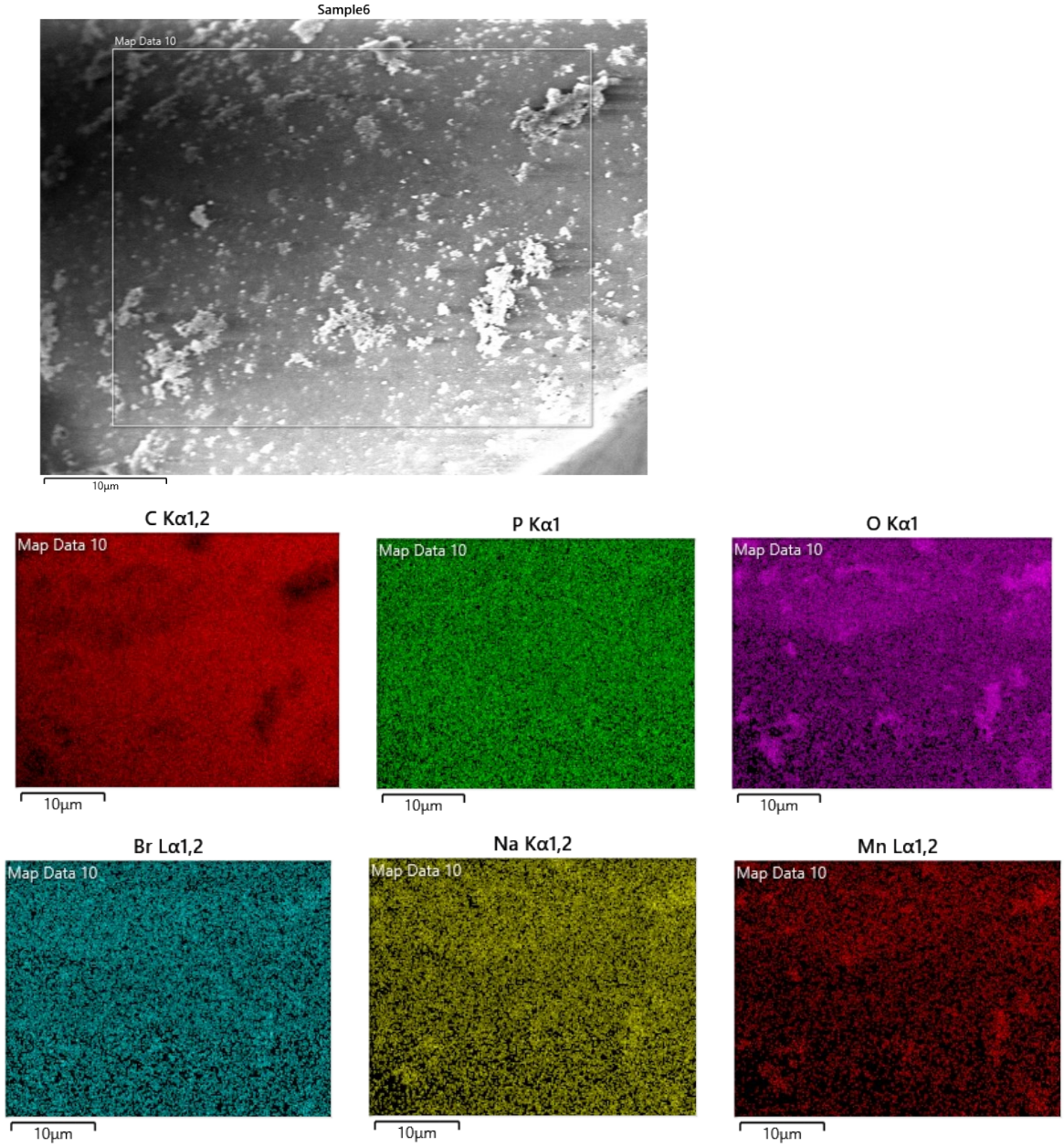


b) EDX mapping analysis of PS-TPP-**[Mn]-Primed**



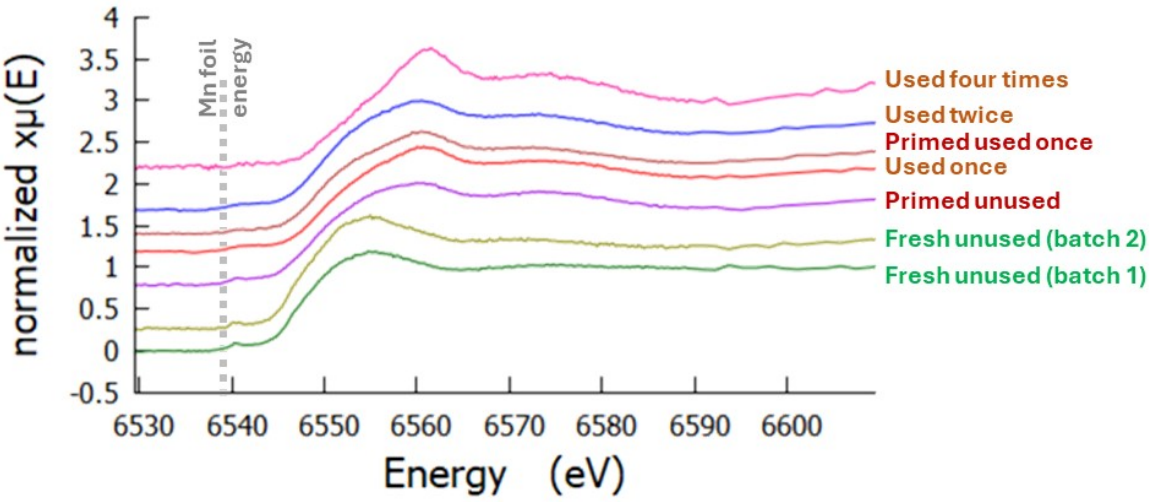


c) EDX mapping analysis of PS-TPP-[**Mn**]-**recycled**

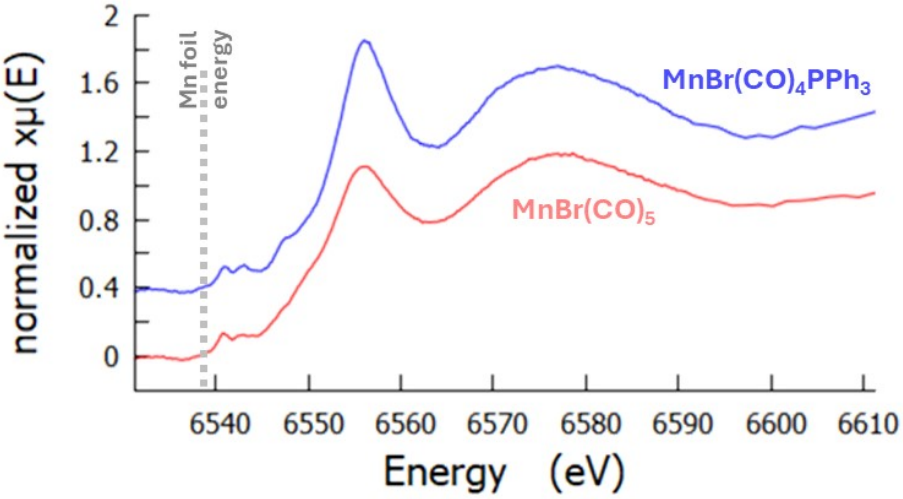


1.10 **XAFS spectra**

a) Normalised Mn K-edge XANES spectra for series of PS-TPP-**[Mn]** samples. Spectra are energy corrected based on the energy of a separately acquired Mn foil spectrum and offset vertically for clarity. The energy position of Mn foil is marked for comparison. There is a noticeable change in shape, pre-edge feature and white line position, in addition to the changes in edge position documented in the main text – this occurs in the groupings “Fresh catalysts,” “Primed and/or reused 1-2 times ” and “reused 4 times,” which contain similar spectral shapes in each case, again pointing to changes in catalyst structure.

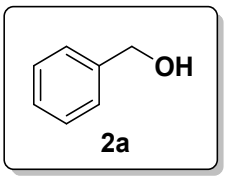


b) Normalised Mn K-edge XANES spectra for reference compounds $MnBr(CO)_4PPh_3$ and $MnBr(CO)_5$. Spectra are energy corrected based on the energy of a separately acquired Mn foil spectrum and offset vertically for clarity. The energy position of Mn foil is marked for comparison.



2. Analytical Data

Phenylmethanol, 2a[2a]



Compound **2a** was prepared according to the general procedure **1.4.** using **methyl benzoate (1a)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2a** as a colourless liquid (41 mg, 76%). The NMR data is in accordance with the literature.[2a]

Compound **2a** was also prepared according to the general procedure **1.4.** using **Ethyl benzoate (1b)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2a** as a colourless liquid (10 mg, 18%).

Compound **2a** was prepared according to the general procedure **1.4.** using **benzaldehyde (1n)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2a** as a colourless liquid (43 mg, 80%).

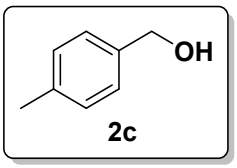
Compound **2a** was prepared according to the general procedure **1.4.** using **benzaldehyde (1n)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2a** as a colourless liquid (45 mg, 85%).

Compound **2a** was prepared according to the general procedure **1.4.** using **methyl benzoate (1a)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2a** as a colourless liquid (44 mg, 80%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 4.71 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 128.5, 127.6, 127.0, 65.2.

***p*-tolylmethanol, 2c**[2a]



Compound **2c** was prepared according to the general procedure **1.4.** using **methyl 4-methylbenzoate (1c)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2c** as a colourless liquid (42 mg, 69%). The NMR data is in accordance with the literature.[2]

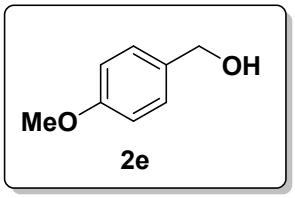
Compound **2c** was also prepared according to the general procedure **1.4.** using **methyl 4-Ethylbenzoate (1d)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2c** as a colourless liquid (24 mg, 40%).

Compound **2c** was also prepared according to the general procedure **1.4.** using **4-methyl benzaldehyde (1s)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2c** as a colourless liquid (57 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 7.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 4.64 (s, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 137.4, 129.2, 127.1, 65.3, 21.1.

(4-methoxyphenyl)methanol, 2e[2b]



Compound **2e** was prepared according to the general procedure **1.4.** using **4-methoxybenzaldehyde (1t)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2e** as a colourless liquid (66 mg, 96%), whereas the same substrate using unprimed catalyst afforded **2e** as a colourless liquid (55 mg, 83%). The NMR data is in accordance with the literature.[2b]

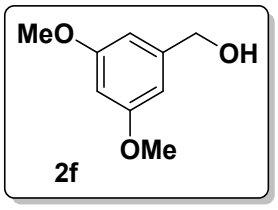
Compound **2e** was prepared according to the general procedure **1.4.** using **4-methoxybenzyl acetate (1e)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2e** as a colourless liquid (37 mg, 53%).

Compound **2e** was prepared according to the general procedure **1.4.** using **methyl 4-methoxybenzoate (1x)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2e** as a colourless liquid (55 mg, 82%), whereas the same substrate using unprimed catalyst afforded **2e** as a colourless liquid (53 mg, 77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.6 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 4.47 (s, 2H), 3.73 (s, 3H), 2.93 (bs, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 133.1, 128.6, 113.9, 64.9, 55.3.

(3,5-dimethoxyphenyl)methanol, 2f[2c]



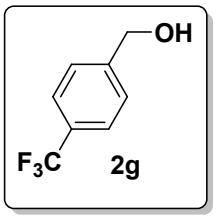
Compound **2f** was prepared according to the general procedure **1.4.** using **methyl 3,5-dimethoxybenzoate (1f)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2f** as a colourless liquid (74 mg, 89%). The NMR data is in accordance with the literature.[2c]

Compound **2f** was prepared according to the general procedure **1.4.** using **methyl 3,5-dimethoxybenzaldehyde (1u)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2f** as a colourless liquid (83 mg, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (d, J = 2.3 Hz, 2H), 6.39 (t, J = 2.3 Hz, 1H), 4.64 (s, 2H), 3.80 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 143.3, 104.5, 99.7, 65.3, 55.3.

(4-(trifluoromethyl)phenyl)methanol, 2g[2a]



Compound **2g** was prepared according to the general procedure **1.4.** using **4-(trifluoromethyl)benzaldehyde (1h)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2g** as a colourless liquid (26 mg, 30%). The NMR data is in accordance with the literature.[2a]

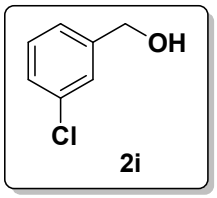
Compound **2g** was also prepared according to the general procedure **1.4.** using **methyl 4-(trifluoromethyl)benzoate (1g)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2g** as a colourless liquid (66 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.1 Hz, 2H), 7.50 – 7.45 (m, 2H), 4.77 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7(s), 129.8 (q, J = 32.6 Hz) , 126.8 (s), 125.4 (q, J = 3.7 Hz), 124.2 (q, J = 271.5 Hz), 64.4(s).

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.5.

(3-chlorophenyl) methanol, 2i[3]

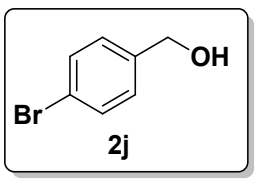


Compound **2h** was prepared according to the general procedure **1.4.** using **methyl 4-chlorobenzoate (1i)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2i** as a colourless liquid (45 mg, 63%). The NMR data is in accordance with the literature.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.24 – 7.20 (m, 3H), 4.63 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 134.4, 129.8, 127.6, 126.9, 124.8, 64.4.

(4-bromophenyl) methanol, 2j[2a]

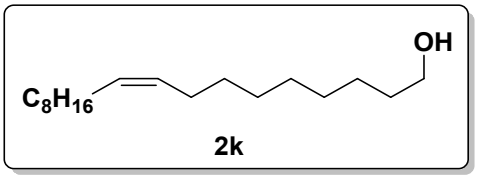


Compound **2j** was prepared according to the general procedure **1.4.** using **methyl 4-bromobenzoate (1j)**. The crude compound was purified by silica gel column chromatography (1:1, hexane:EA) to give the title compound **2i** as a colourless liquid (63 mg, 67%). The NMR data is in accordance with the literature.[2a]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 4.65 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 131.6, 128.5, 121.4, 64.6.

(Z)-octadec-9-en-1-ol, 2k[3]

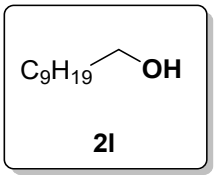


Compound **2k** was prepared according to the general procedure **1.4.** using **methyl oleate (1k)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2k** as a colourless liquid (69 mg, 52%). The NMR data is in accordance with the literature.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35 (t, J = 5.5 Hz, 2H), 3.64 (t, J = 6.6 Hz, 2H), 2.11 – 1.95 (m, 4H), 1.55 (dd, J = 13.7, 6.8 Hz, 2H), 1.39 – 1.21 (m, 22H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 129.9, 63.0, 32.8, 31.9, 29.7, 29.5, 29.4, 29.3, 29.2, 27.2, 27.1, 25.7, 22.6, 14.0 (several CH_2 carbons along the chain overlap due to pseudo symmetry; only distinct peaks are listed).[3]

Decan-1-ol, 2l[2a]



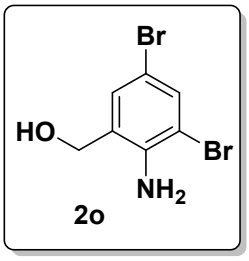
Compound **2l** was prepared according to the general procedure **1.4.** using **methyl decanoate (1l)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2l** as colourless liquid (54 mg, 68%). The NMR data is in accordance with the literature.[2a]

Compound **2l** was prepared according to the general procedure **1.4.** using **1-Decanal (1m)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2l** as colourless liquid (67 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.64 (t, J = 6.6 Hz, 2H), 1.58 (dd, J = 13.3, 5.5 Hz, 2H), 1.39 – 1.15 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 63.1, 32.8, 31.8, 29.6, 29.5, 29.4, 29.3, 25.7, 22.6, 14.0.

(2-amino-3,5-dibromophenyl)methanol, 2o



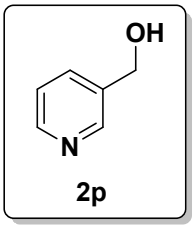
Compound **2o** was prepared according to the general procedure **1.4.** using **2-amino-3,5-dibromobenzaldehyde (1o)**. The crude compound was purified by silica gel column chromatography (1:1, hexane:EA) to give the title compound **2o** as a pale yellow liquid (99 mg, 71%).

^{1}H NMR (300 MHz, DMSO-d6) δ 7.47 (d, J = 2.2 Hz, 1H), 7.28 (d, J = 2.1 Hz, 1H), 5.33 (t, J = 5.5 Hz, 1H), 5.20 (s, 2H), 4.40 (d, J = 5.5 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d6) δ 142.6, 132.3, 129.8, 129.3, 108.8, 106.9, 60.8.

HRMS (ESI-TOF) m/z: $[M\text{-}OH]^+$ calcd. for $\mathbf{C_7H_6Br_2N^+}$: 261.88615, found 261.88627.

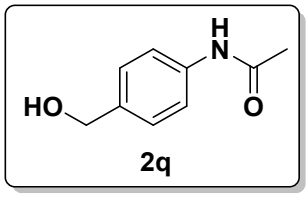
Pyridin-3-ylmethanol, 2p[4a]



Compound **2p** was prepared according to the general procedure **1.4.** using **nicotinaldehyde (1p)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2p** as a colourless liquid (54 mg, 80%). The NMR data is in accordance with the literature (Note: δ 8.46 (s, 1H) likely an unresolved doublet, literature 400 MHz spectrum shows a doublet, unresolved at 300 MHz).[4a]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.46 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.28-7.24 (m, 1H), 4.69 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 148.2, 136.6, 135.0, 123.5, 62.4.

N-(4-(hydroxymethyl)phenyl)acetamide, 2q[2b]

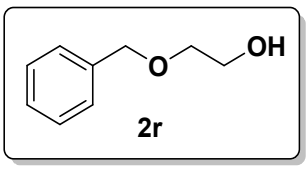


Compound **2q** was prepared according to the general procedure **1.4.** using **N-(4-formylphenyl)acetamide (1q)**. The crude compound was purified by silica gel column chromatography (1:1, hexane:EA) to give the title compound **2q** as a pale yellow liquid (22 mg, 26%). The NMR data is in accordance with the literature.[2b]

^{1}H NMR (300 MHz, DMSO-d6) δ 9.87 (s, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.5 Hz, 2H), 5.08 (t, J = 5.7 Hz, 1H), 4.44 (d, J = 5.7 Hz, 2H), 2.04 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d6) δ 168.5, 138.4, 137.5, 127.3, 119.2, 63.1, 24.4.

2-(benzyloxy)ethan-1-ol, 2r[4b]

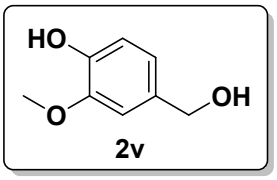


Compound **2r** was prepared according to the general procedure **1.4.** using **2-(benzyloxy)acetaldehyde (1r)**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2r** as a colourless liquid (38 mg, 50%). The NMR data is in accordance with the literature.[4b]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 4.56 (s, 2H), 3.76 – 3.73 (m, 2H), 3.60 – 3.51 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 128.4, 127.8, 73.3, 71.4, 61.8.

4-(hydroxymethyl)-2-methoxyphenol, 2v[4c]



2v

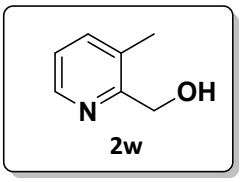
Compound **2v** was prepared according to the general procedure **1.4.** using **4-hydroxy-3-methoxybenzaldehyde (1v)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (1:1, hexane:EA) to give the title compound **2v** as a pale yellow liquid (38 mg, 50%). The NMR data is in accordance with the literature.[4c]

Compound **2v** was prepared according to the general procedure **1.4.** using **4-hydroxy-3-methoxybenzaldehyde (1v)** using un-primed **PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (1:1, hexane:EA) to give the title compound **2v** as a pale yellow liquid (23 mg, 30%).

^{1}H NMR (300 MHz, DMSO-d6) δ 8.73 (s, 1H), 6.87 (s, 1H), 6.70 (s, 2H), 4.96 (s, 1H), 4.37 (d, J = 3.2 Hz, 2H), 3.74 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d6) δ 147.8, 145.7, 133.9, 119.5, 115.4, 111.5, 63.4, 55.9.

(3-methylpyridin-2-yl)methanol 2w[5]



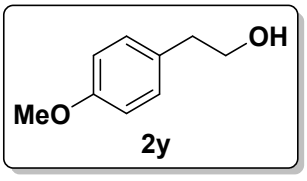
2w

Compound **2w** was prepared according to the general procedure **1.4.** using **methyl 3-methylpicolinate (1w)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (10:1, hexane:EA) to give the title compound **2w** as a yellow liquid (39 mg, 50%). The NMR data is in accordance with the literature.[5]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.13 (dd, J = 7.3, 4.6 Hz, 1H), 4.67 (s, 2H), 2.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 145.1, 137.5, 129.5, 122.0, 61.4, 16.4.

2-(4-methoxyphenyl)ethan-1-ol, 2y[3]



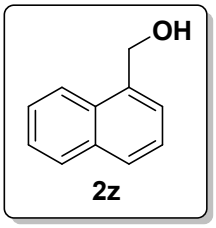
2y

Compound **2y** was prepared according to the general procedure **1.4.** using **methyl 2-(4-methoxyphenyl) acetate (1y)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2y** as a colourless liquid (69 mg, 92%). The NMR data is in accordance with the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 – 7.12 (m, 2H), 6.87 – 6.85 (m, 2H), 3.85 – 3.80 (m, 2H), 3.79 (s, 3H), 2.81 (t, J = 6.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 130.4, 129.9, 114.0, 63.8, 55.2, 38.2.

Naphthalen-1-ylmethanol, 2z[2a]

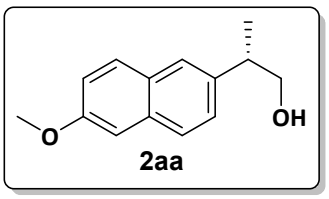


Compound **2z** was prepared according to the general procedure **1.4.** using **methyl 1-naphthoate (1z)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (1:1, hexane:EA) to give the title compound **2z** as off white solid (67mg, 85%). The NMR data is in accordance with the literature.[2a]

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.0, 1.1 Hz, 1H), 7.95 – 7.76 (m, 2H), 7.62 – 7.40 (m, 4H), 5.17 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 133.8, 131.2, 128.6, 128.6, 126.3, 125.8, 125.4, 125.3, 123.6, 63.7.

(S)-2-(6-methoxynaphthalen-2-yl) propan-1-ol, 3a (naproxen), 2aa[6a]

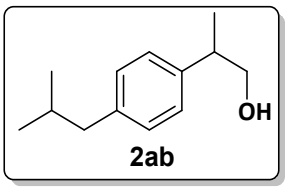


Compound **2aa** was prepared according to the general procedure **1.4.** using **methyl (S)-2-(6-methoxynaphthalen-2-yl) propanoate (1aa)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2aa** as a pale yellow oil (89 mg, 83%). The NMR data is in accordance with the literature.[6a]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.5, 4.9 Hz, 2H), 7.61 (d, J = 1.1 Hz, 1H), 7.35 (dd, J = 8.5, 1.8 Hz, 1H), 7.18 – 7.10 (m, 2H), 3.92 (s, 3H), 3.78 (d, J = 6.8 Hz, 2H), 3.09 (sext, J = 6.9 Hz, 1H), 1.36 (d, J = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 138.6, 133.5, 129.1, 129.0, 127.2, 126.2, 125.9, 118.9, 105.6, 68.6, 55.3, 42.4, 17.6.

2-(4-isobutylphenyl) propan-1-ol, 2ab[6b]

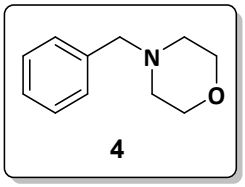


Compound **2ab** was prepared according to the general procedure **1.4.** using **methyl 2-(4-isobutylphenyl) propanoate (1ab)** using **primed PS-TPP-[Mn] catalyst**. The crude compound was purified by silica gel column chromatography (3:2, hexane:EA) to give the title compound **2ab** as a white solid (81 mg, 85%). The NMR data is in accordance with the literature.[6b]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 4H), 3.69 (d, J = 6.8 Hz, 2H), 2.93 (dd, J = 13.9, 6.9 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 1.84 (td, J = 13.6, 6.8 Hz, 1H), 1.27 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 140.0, 129.3, 127.1, 68.7, 45.0, 42.0, 30.2, 22.4, 17.6.

4-benzylmorpholine, 4[7]



4

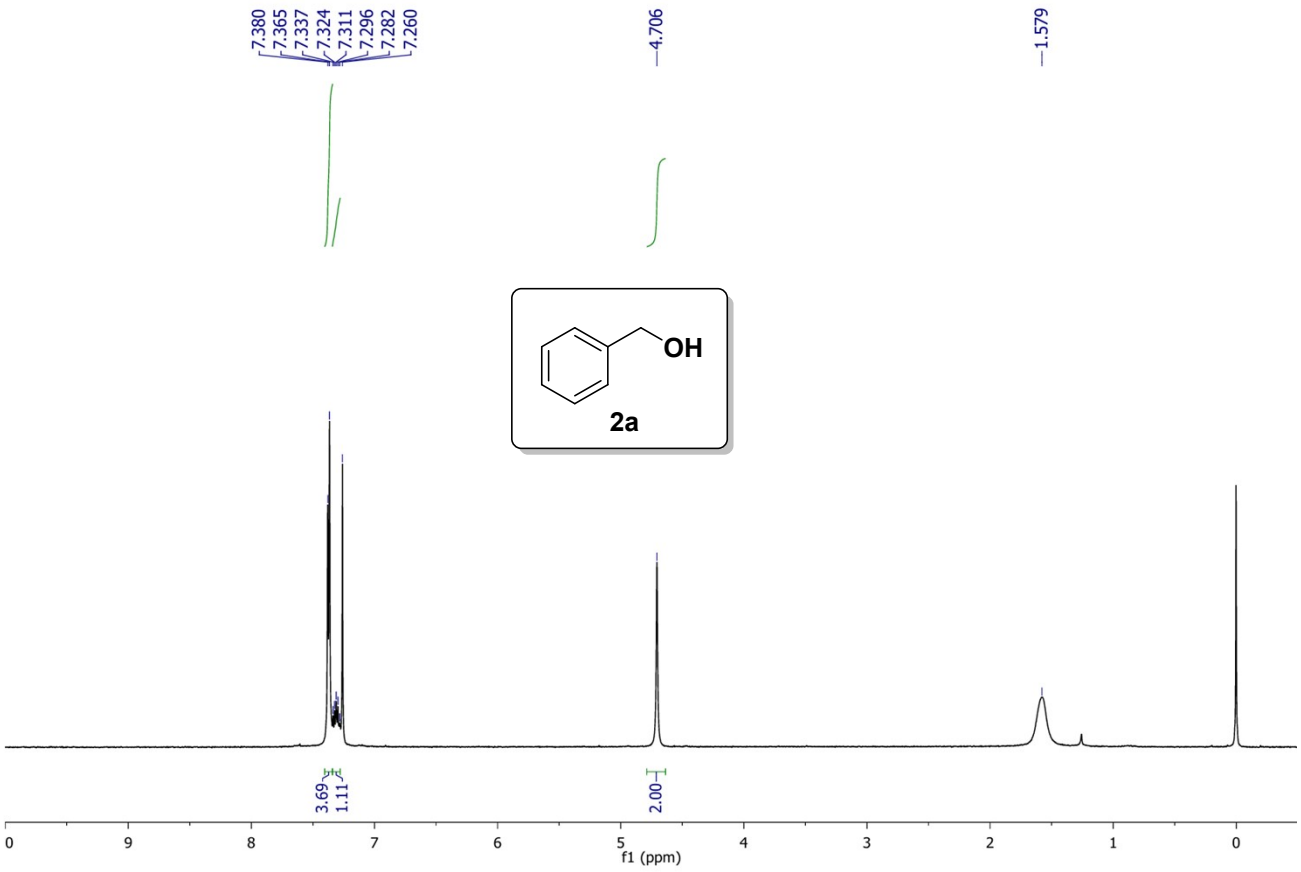
Compound **4** was prepared using similar procedure as **1.4**. **Morpholino(phenyl)methanone (3)** (0.5mmol), Phenyl silane (2.0 equiv.) and Triphenyl Phosphine Polymer-supported Mn catalyst PS-TPP-[Mn] (20 mg, 4.2 mol%) were charged in to a dry test tube fitted with a screw cap and magnetic stir bar. The reaction was then heated at 100 °C in an oil bath for 3h. The crude compound was purified by silica gel column chromatography (9:1 hexane:EA) to give the title compound **4** as a colourless liquid (87 mg, 98%). The NMR data is in accordance with the literature.[7]

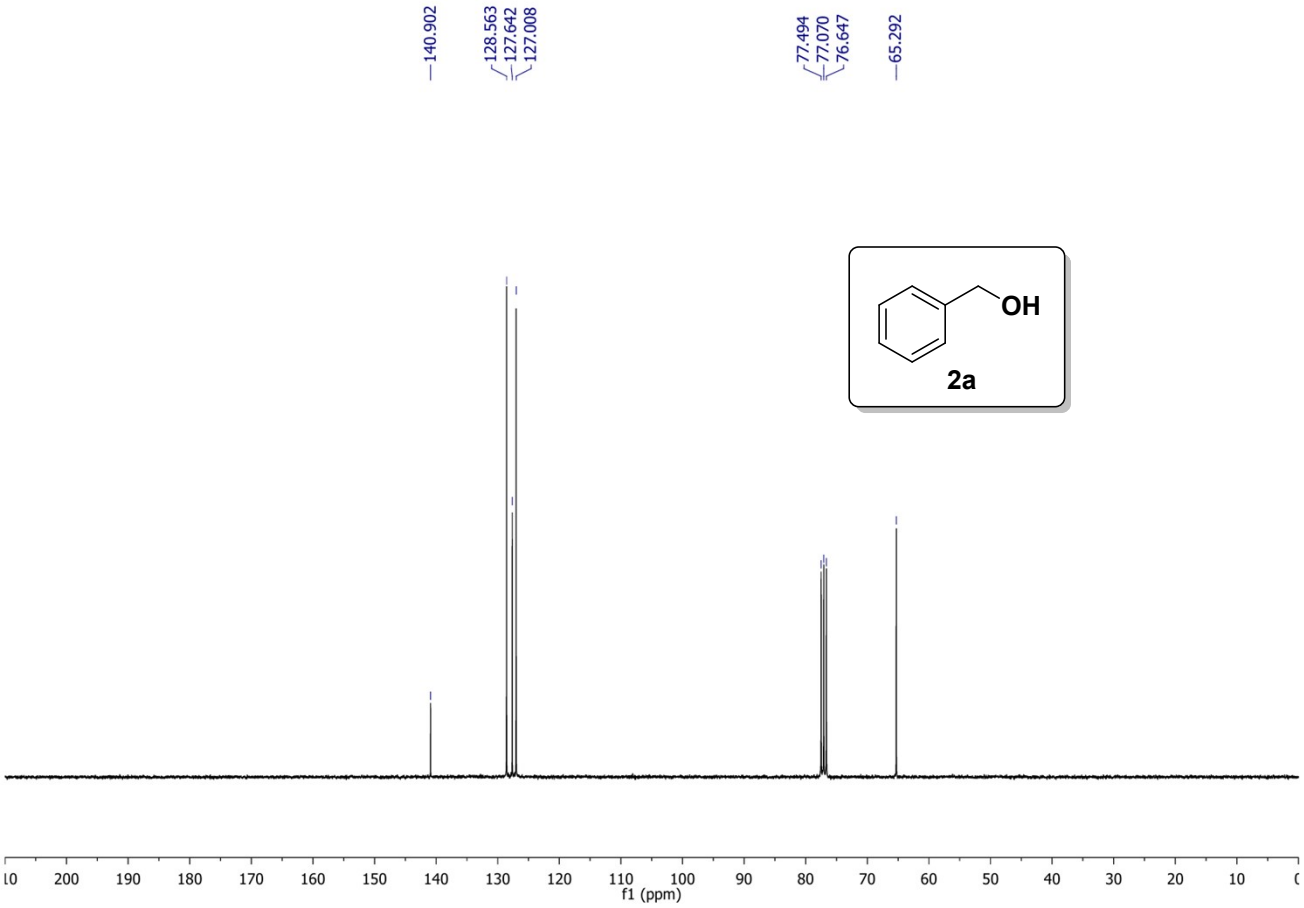
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 5H), 3.75 – 3.64 (m, 4H), 3.49 (s, 2H), 2.46 – 2.39 (t, 4H).

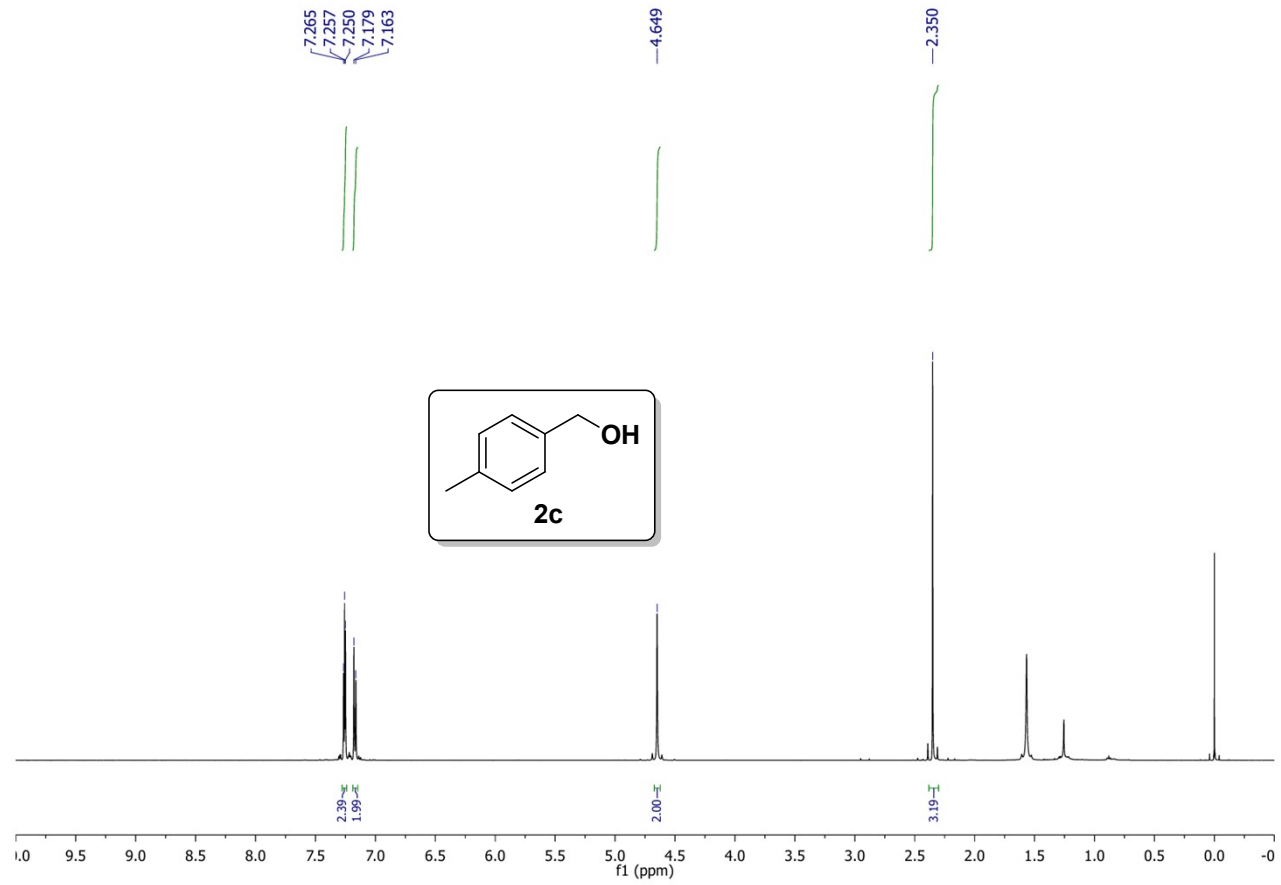
^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 129.2, 128.2, 127.1, 67.0, 63.4, 53.6.

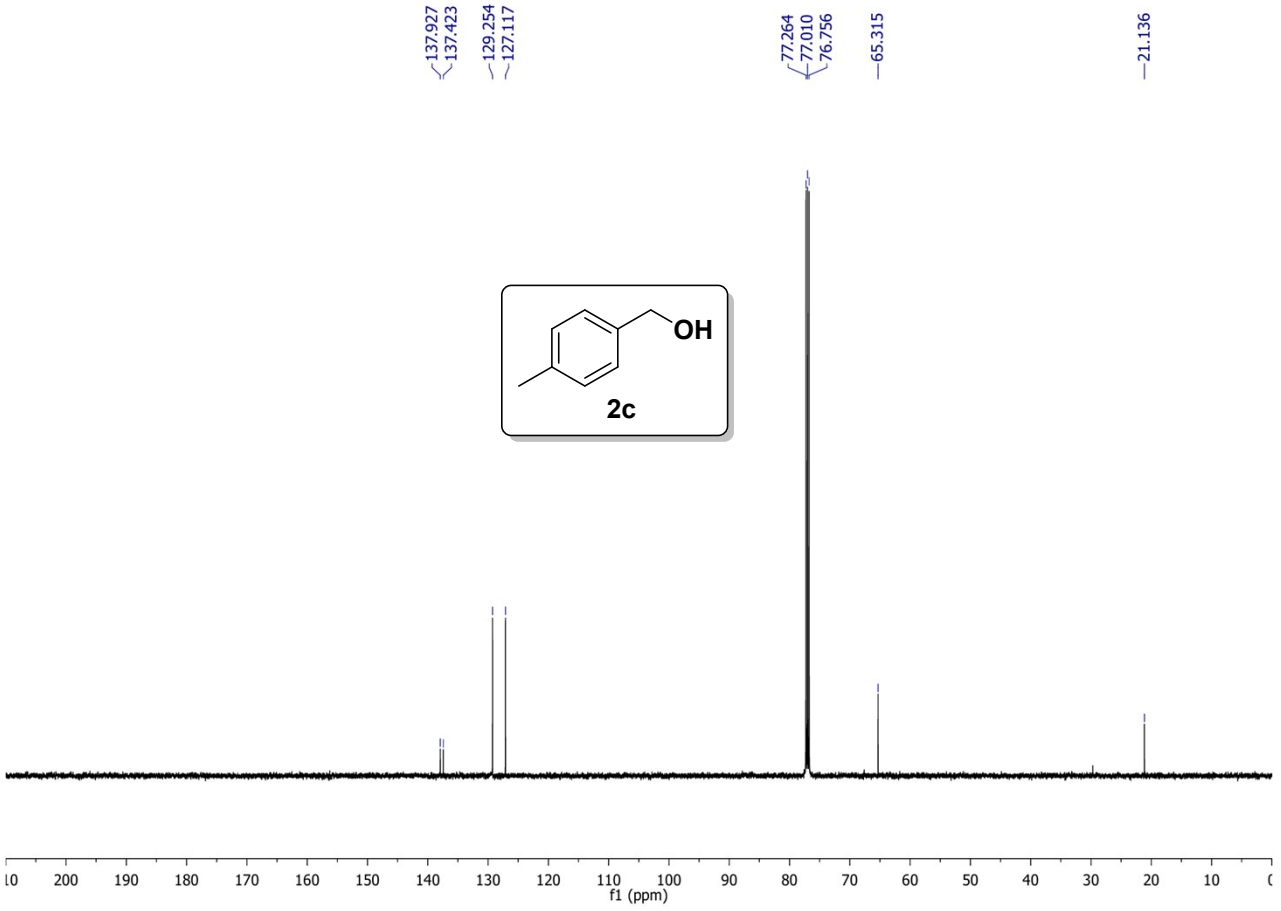
References:

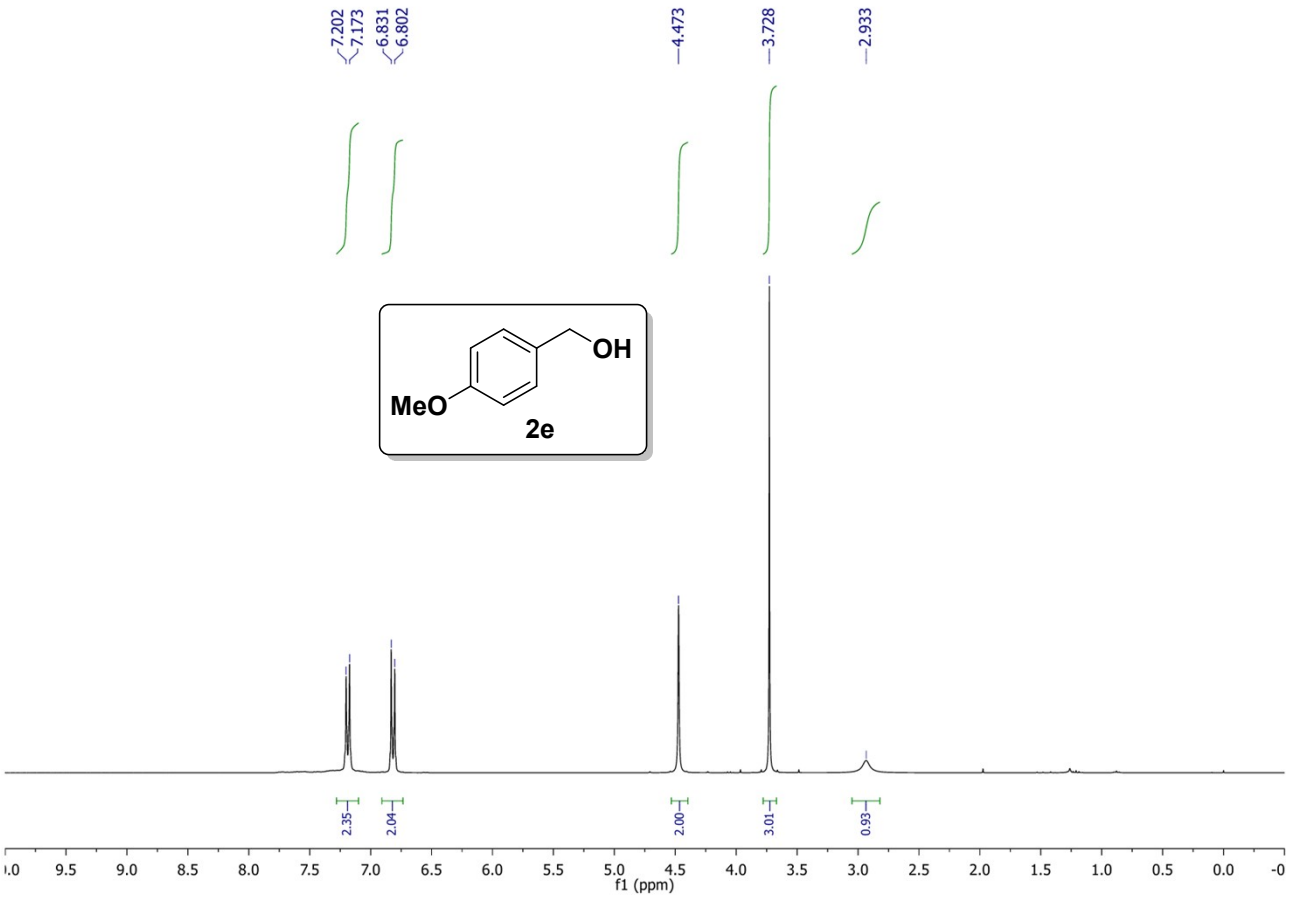
1. B. Ravel and M. Newville, *J Synchrotron Radiat*, **2005**, *12*, 537-541.
2. a) G. Hamasaka, H. Tsuji, Y. Uozumi, *Synlett,* **2015**; 26(*14*) 2037-2041; b) C. Kuloor, Akash, V. Goyal, R. Zbořil, M. Beller, R. V. Jagadeesh, *Angew. Chem. Int. Ed.* **2025**, *64*, e202414689; c) M. Prakashni, S. Dasgupta, *Org. Biomol. Chem.,* **2024**, *22*, 1871–1884.
3. R. R. Behera, R. Ghosh, S. Panda, S. Khamari, and B. Bagh, *Org. Lett*., **2020**, *22*, 3642−3648.
4. a) S. Yadav and M. R. Kuram, *Eur. J. Org. Chem.* **2023**, *26*, e202201344; b) L. Saudan, J. Quintaine*, ChemCatChem,* **2023**, *15*, e202300508; c) M. Abid, R. Nouch, T. D. Bradshaw, W. Lewis, S. Woodward, *Eur. J. Inorg. Chem.* **2019**, 2774–2780.
5. A. Gambino, J. C. Burnett, K. Koide, *ACS Medicinal Chemistry Letters* **2020**, *11*, 1893.
6. a) P. Galletti, E. Emer, G. Gucciardo, A. Quintavalla, M. Pori, D. Giacomini *Org. Biomol. Chem.*, **2010**, *8*, 4117–4123; b) E. A. Wappes, K. M. Nakafuku, D. A. Nagib*, J. Am. Chem. Soc.* **2017**, *139*, 10204−10207.
7. C. M. Kelly, R. McDonald, O. L. Sydora, M. Stradiotto, L. Turculet, *Angew. Chem. Int. Ed.* **2017**, *56*, 15901 – 15904.

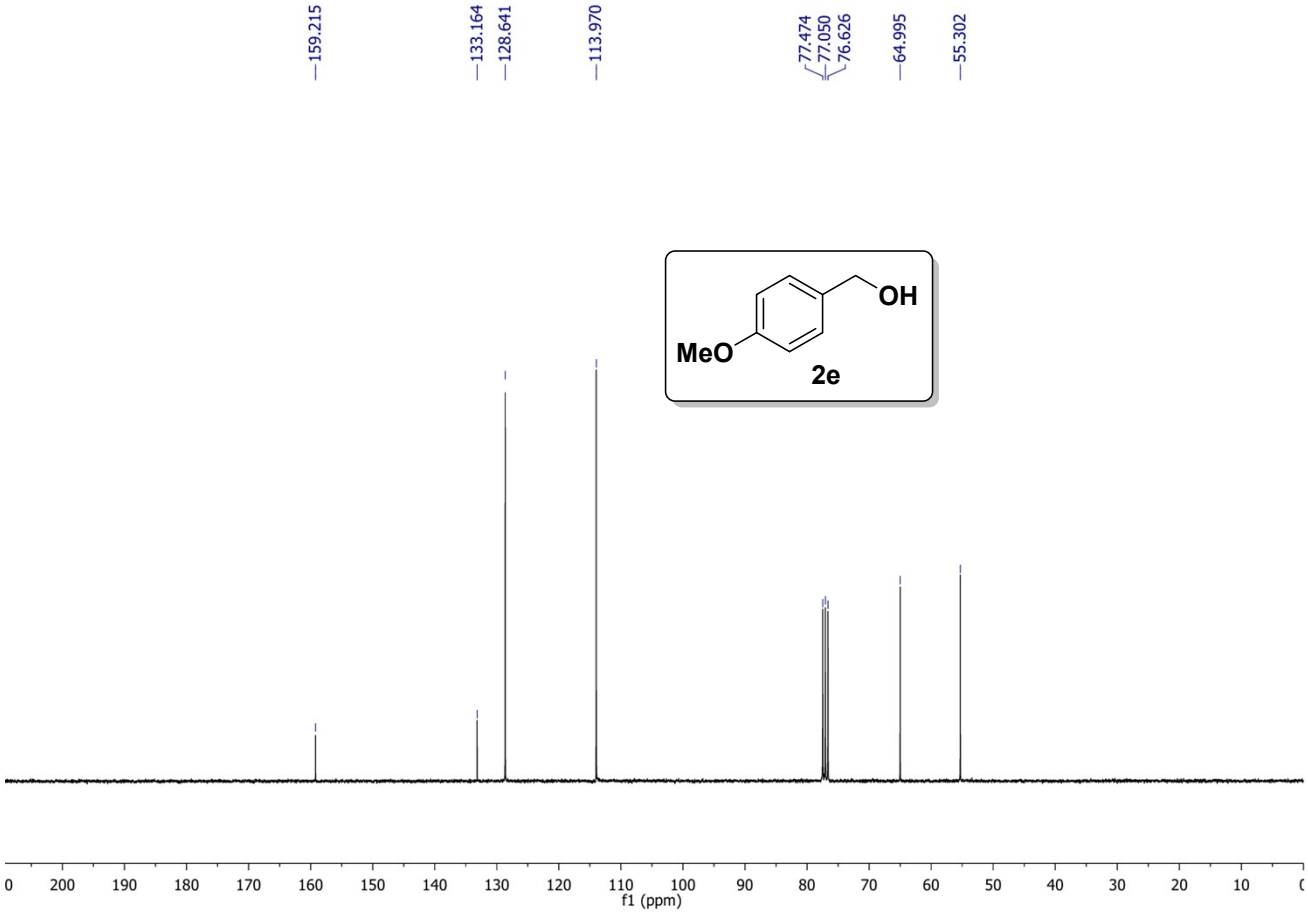

7.380
7.365
7.337
7.324
7.311
7.296
7.282
7.260
4.706
1.579
OH
2a
3.69
1.11
2.00
f1 (ppm)

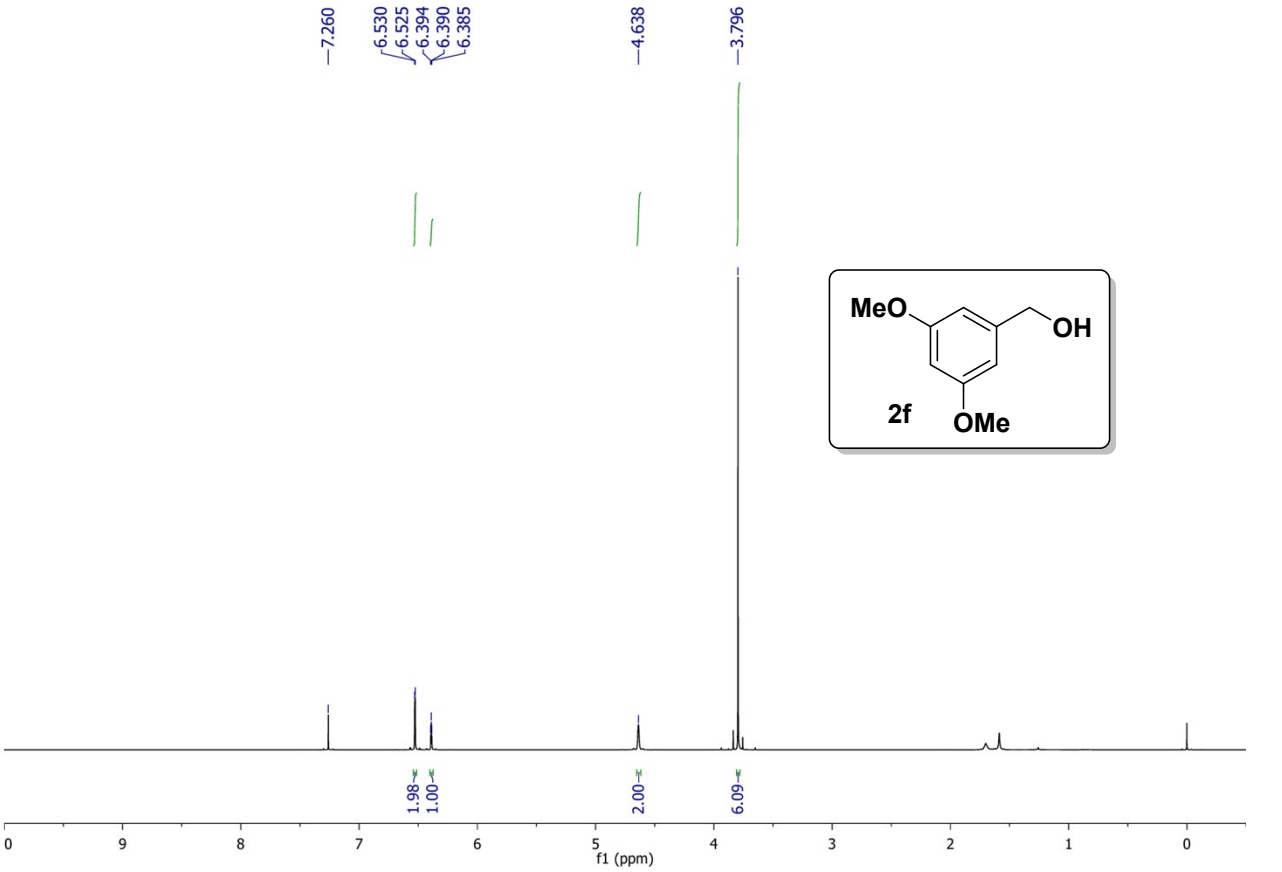

140.902
128.563
127.642
127.008
77.494
77.070
76.647
65.292
OH
2a
f1 (ppm)

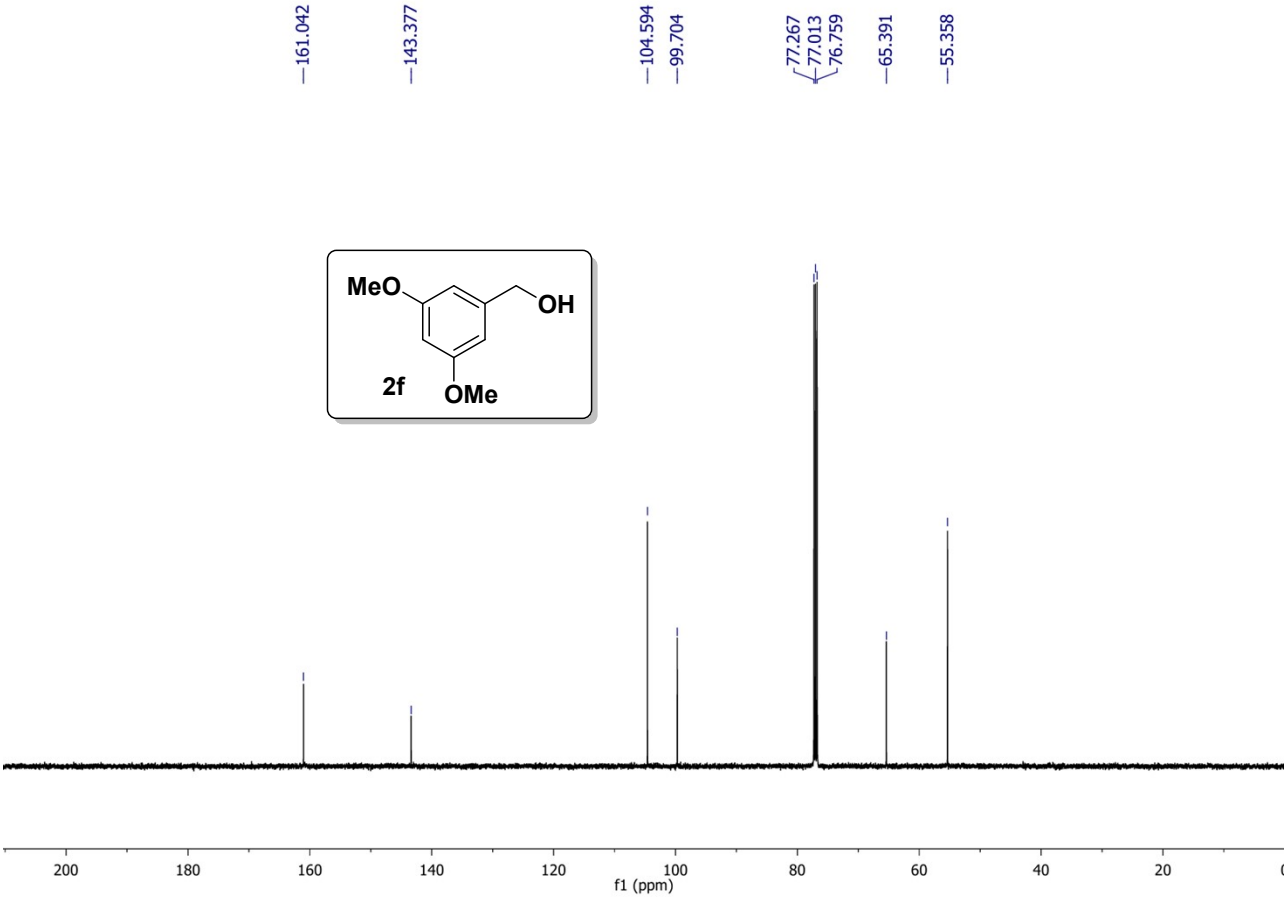

7.265
7.257
7.250
7.179
7.163
4.649
2.350
OH
2c
2.39
1.99
2.00
3.19
f1 (ppm)

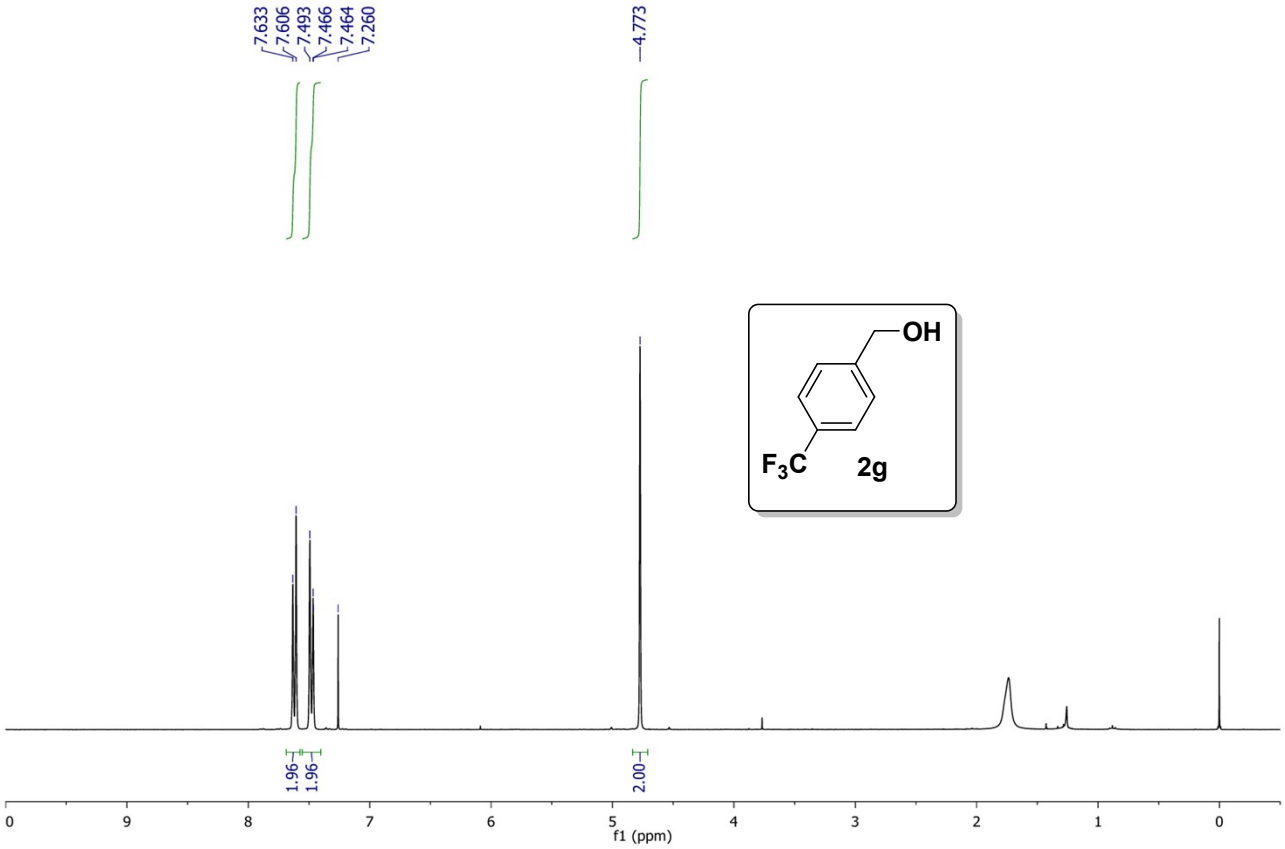

137.927
137.423
129.254
127.117
77.264
77.010
76.756
65.315
21.136
OH
2c
f1 (ppm)

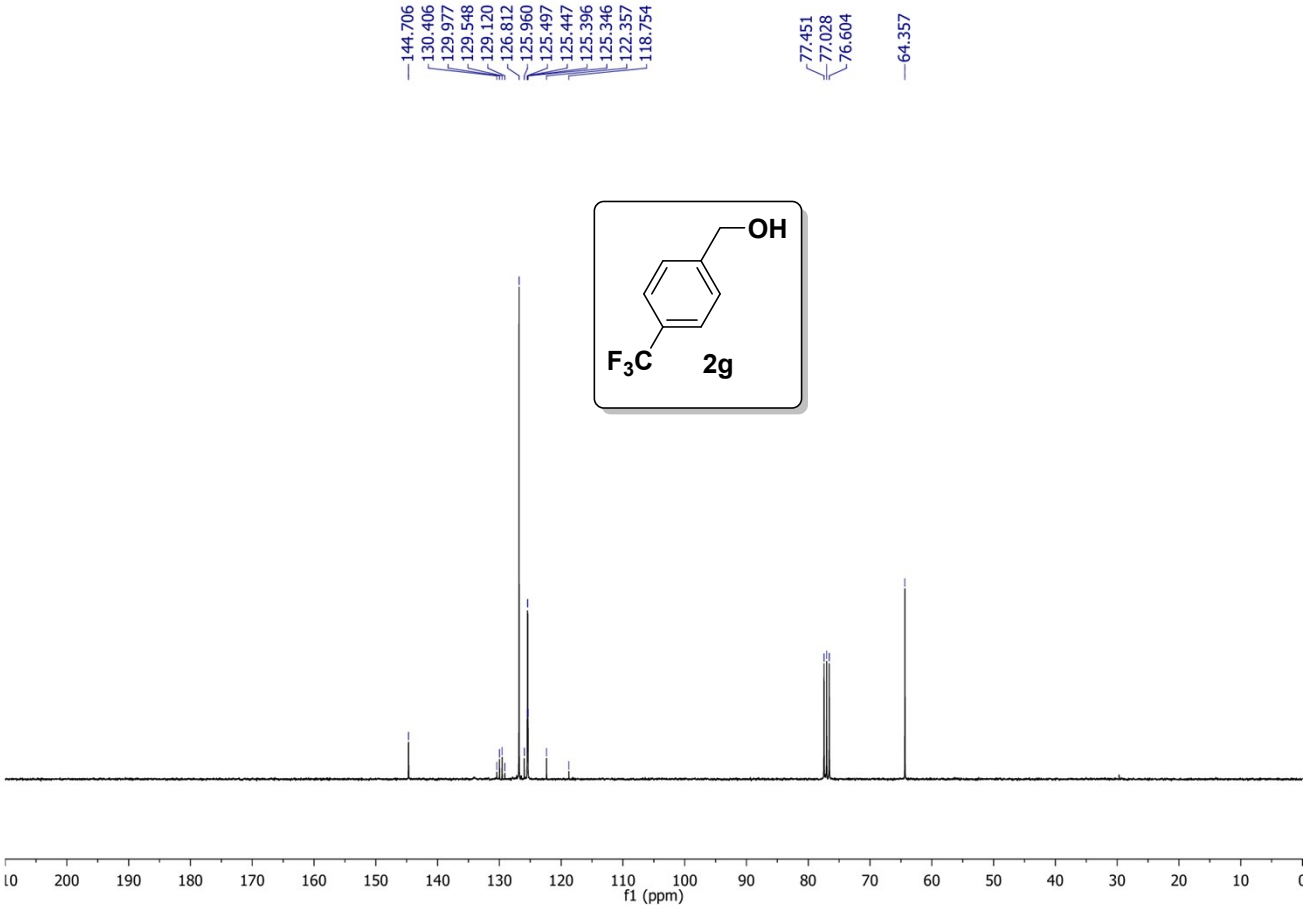

7.202
7.173
6.831
6.802
4.473
3.728
2.933
OH
MeO
2e
2.35
2.04
2.00
3.01
0.93
f1 (ppm)

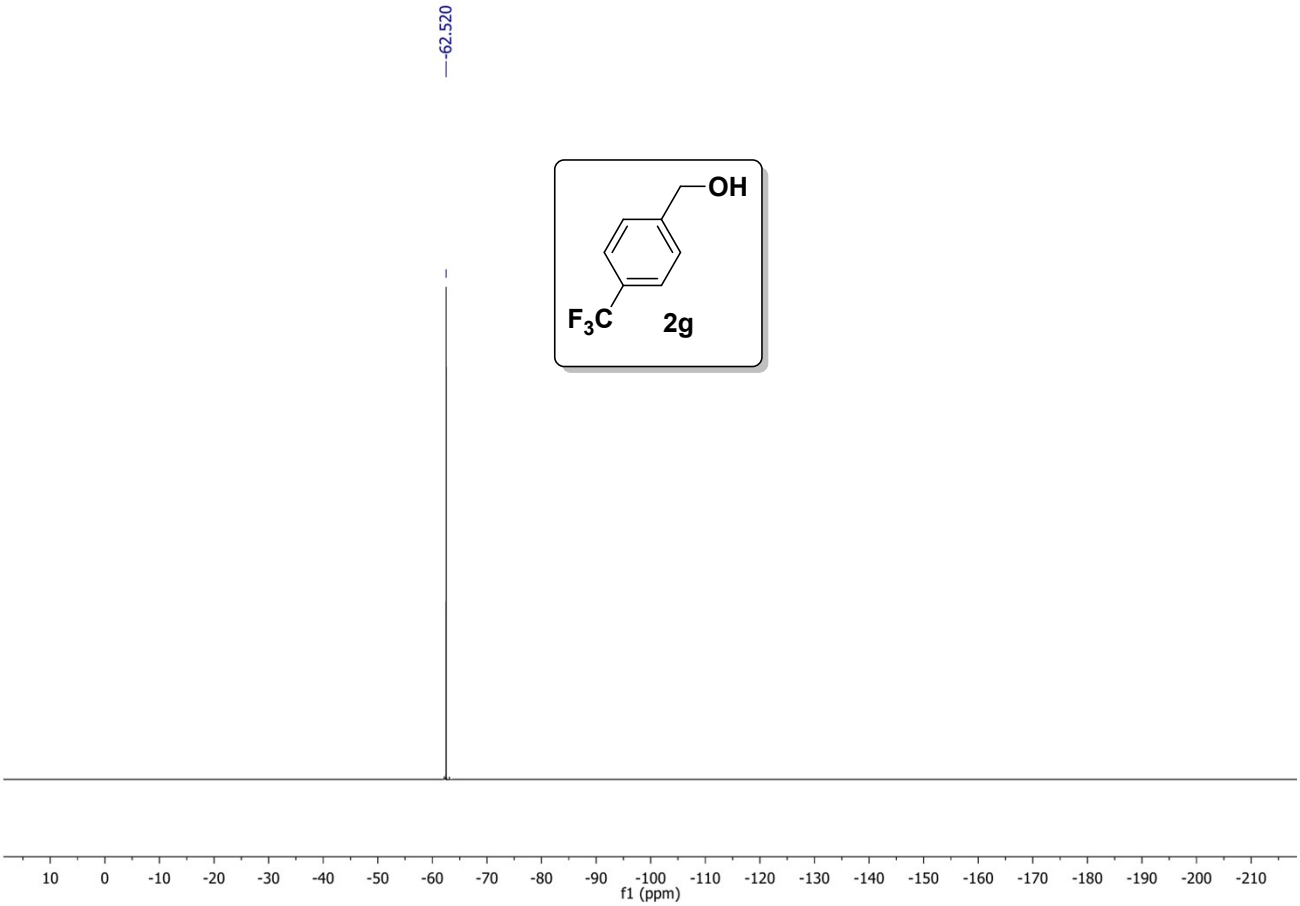

159.215
133.164
128.641
113.970
77.474
77.050
76.626
64.995
55.302
OH
MeO
2e
f1 (ppm)

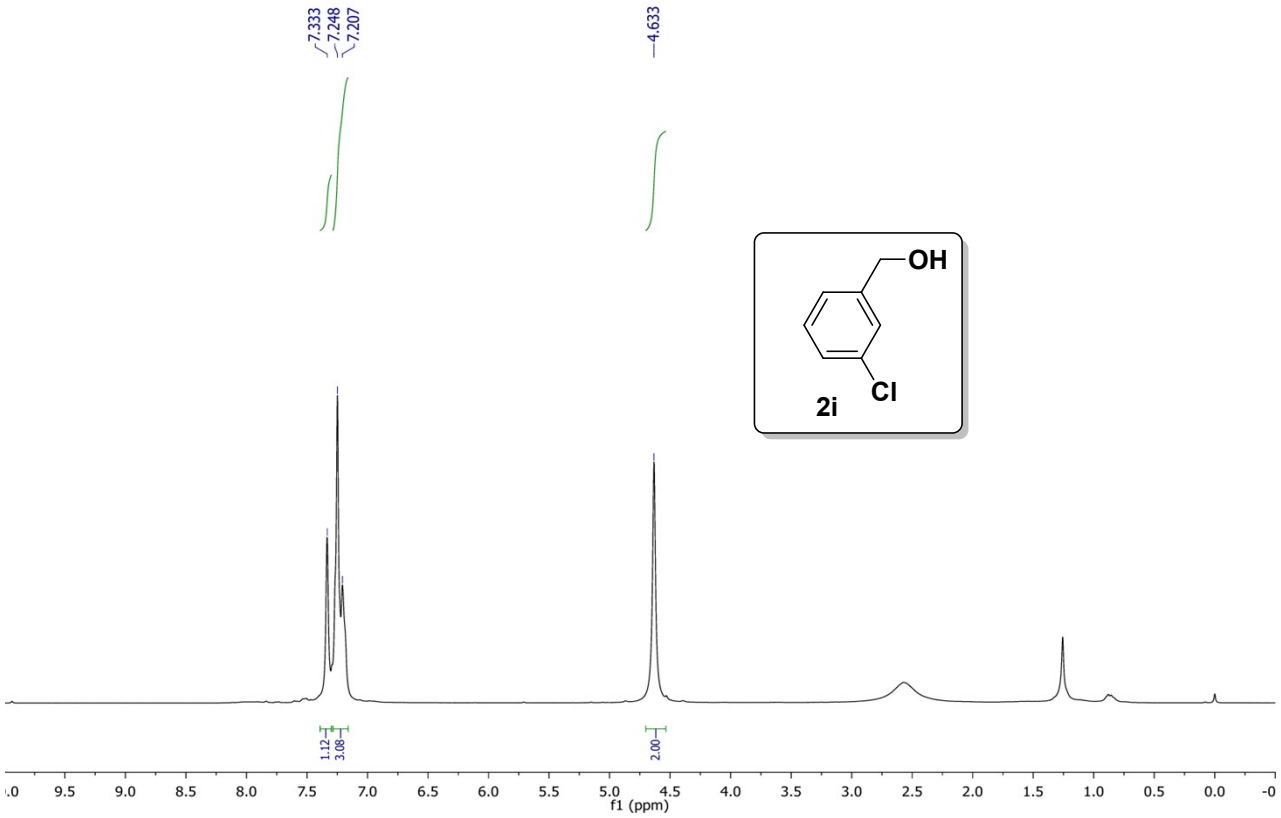

7.260
6.530
6.525
6.394
6.390
6.385
4.638
3.796
MeO
OH
2f
OMe
1.98
1.00
2.00
6.09
f1 (ppm)

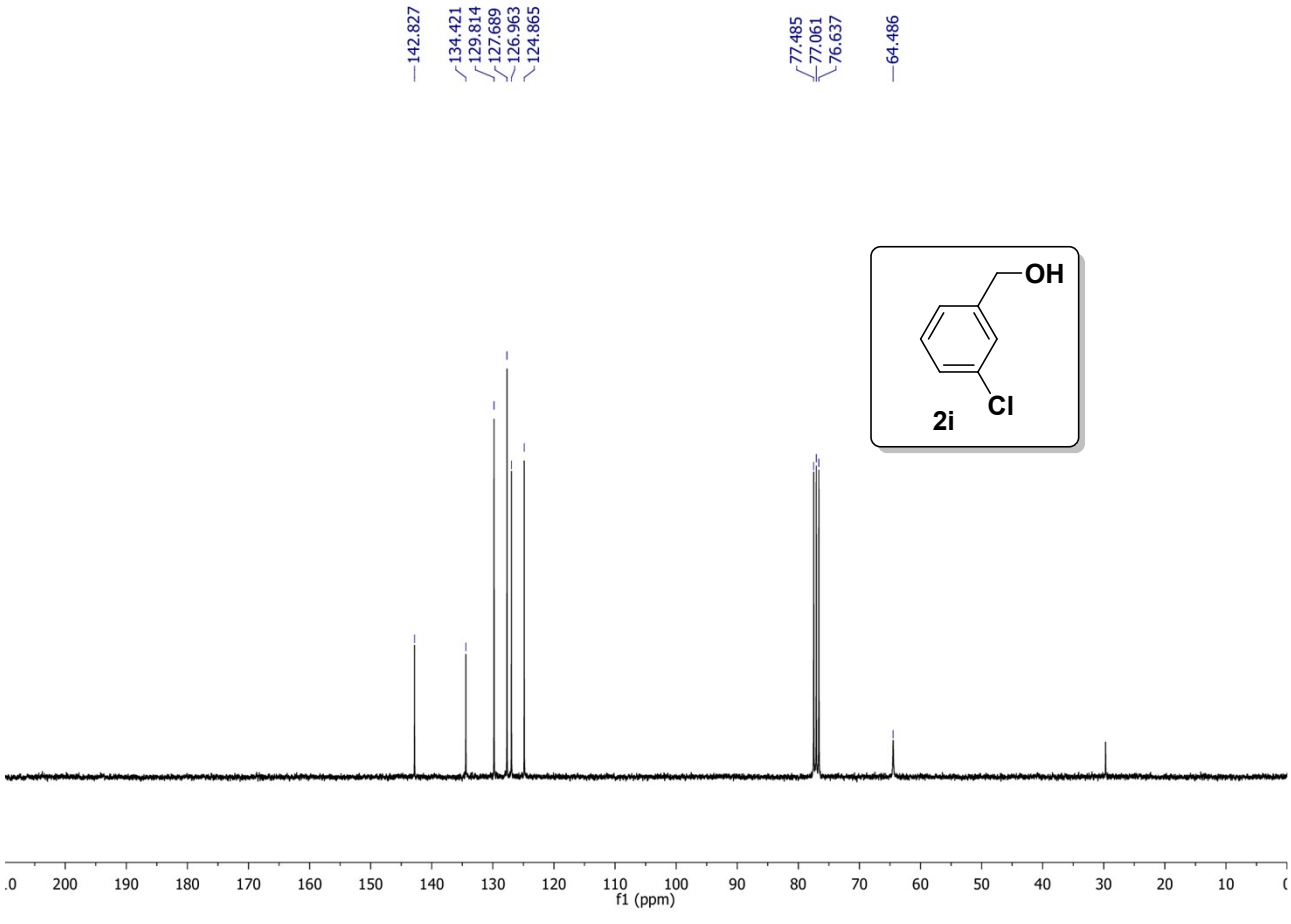

161.042
143.377
104.594
99.704
77.267
77.013
76.759
65.391
55.358
MeO
OH
2f
OMe
f1 (ppm)

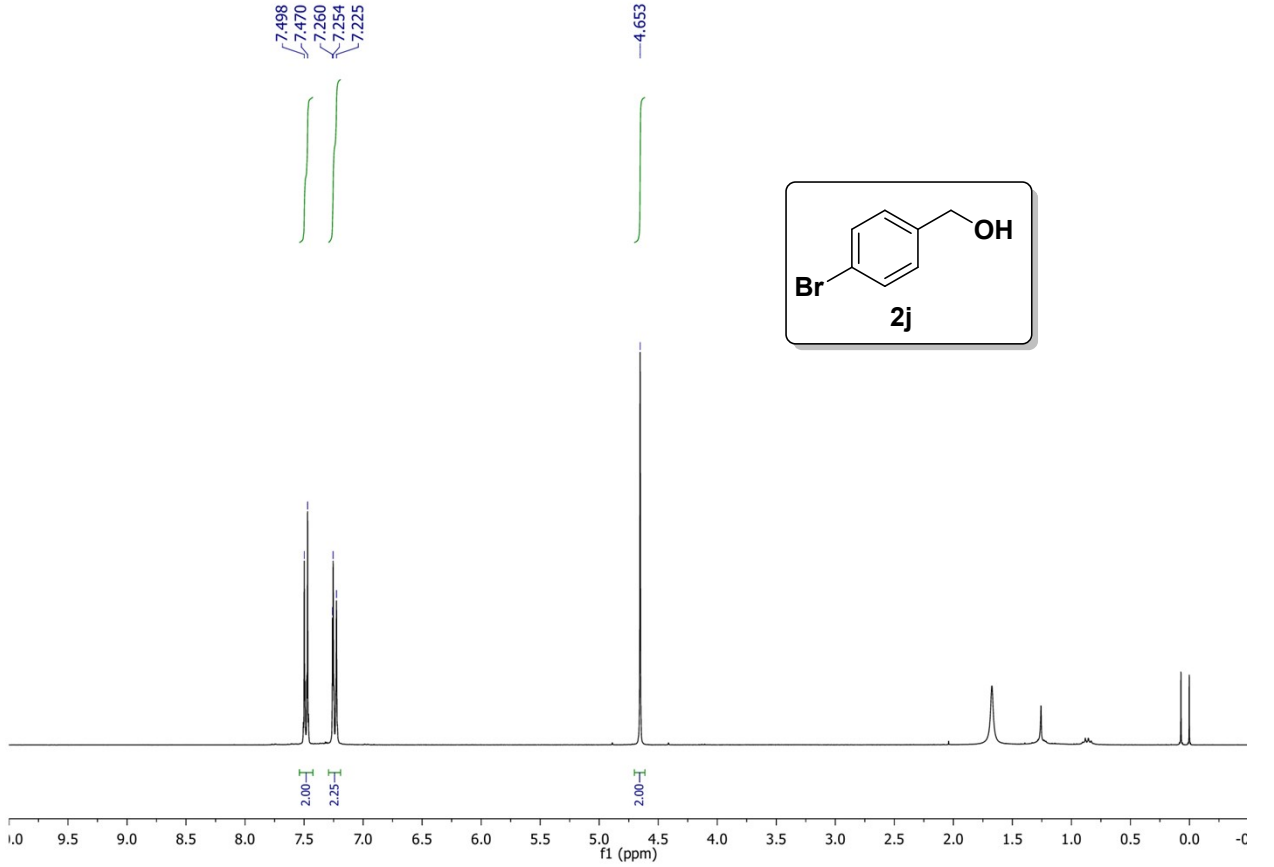

7.633
7.606
7.493
7.466
7.464
7.260
4.773
OH
F3C
2g
1.96
1.96
2.00
f1 (ppm)

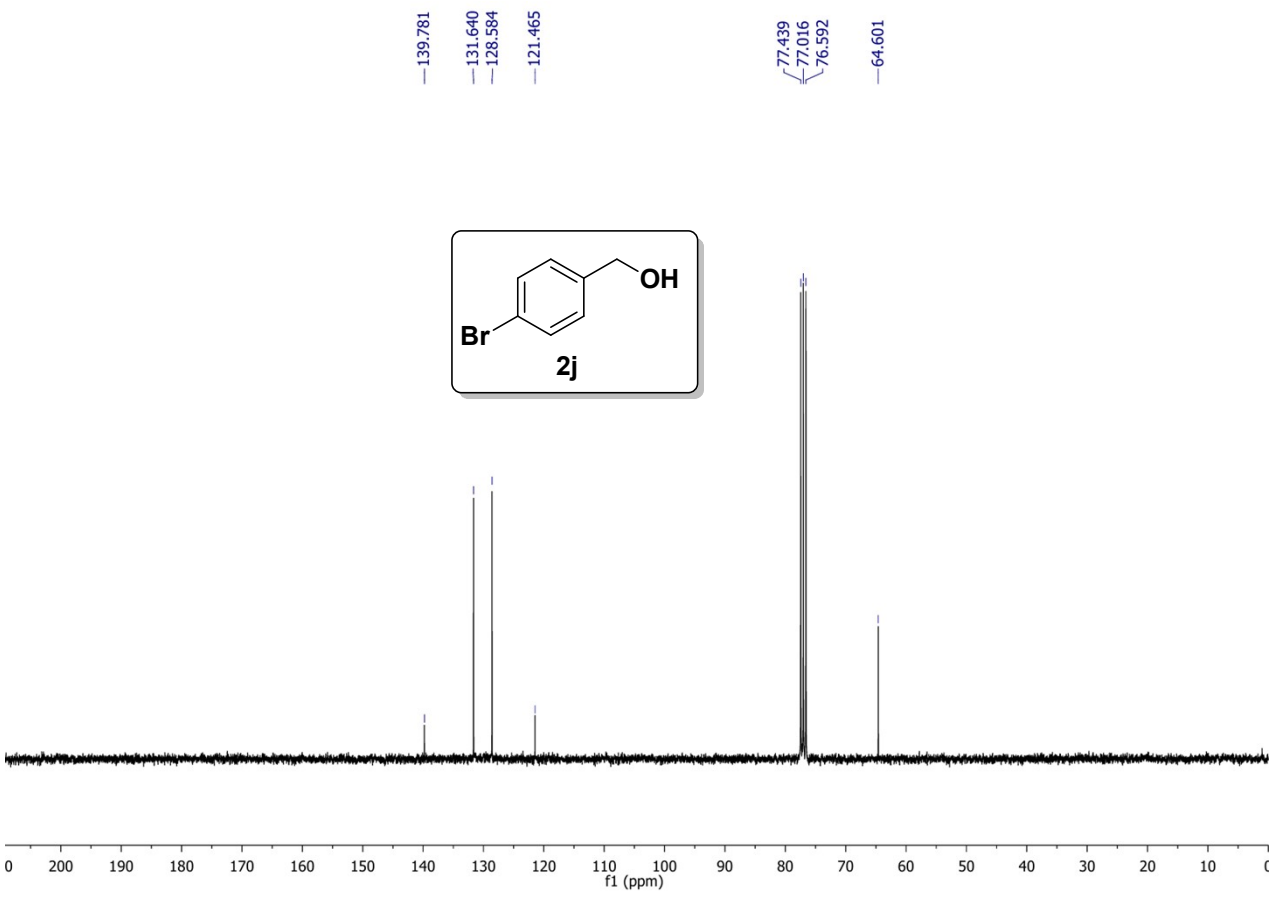

144.706
130.406
129.977
129.548
129.120
126.812
125.960
125.497
125.447
125.396
125.346
122.357
118.754
77.451
77.028
76.604
64.357
OH
F3C
2g
f1 (ppm)

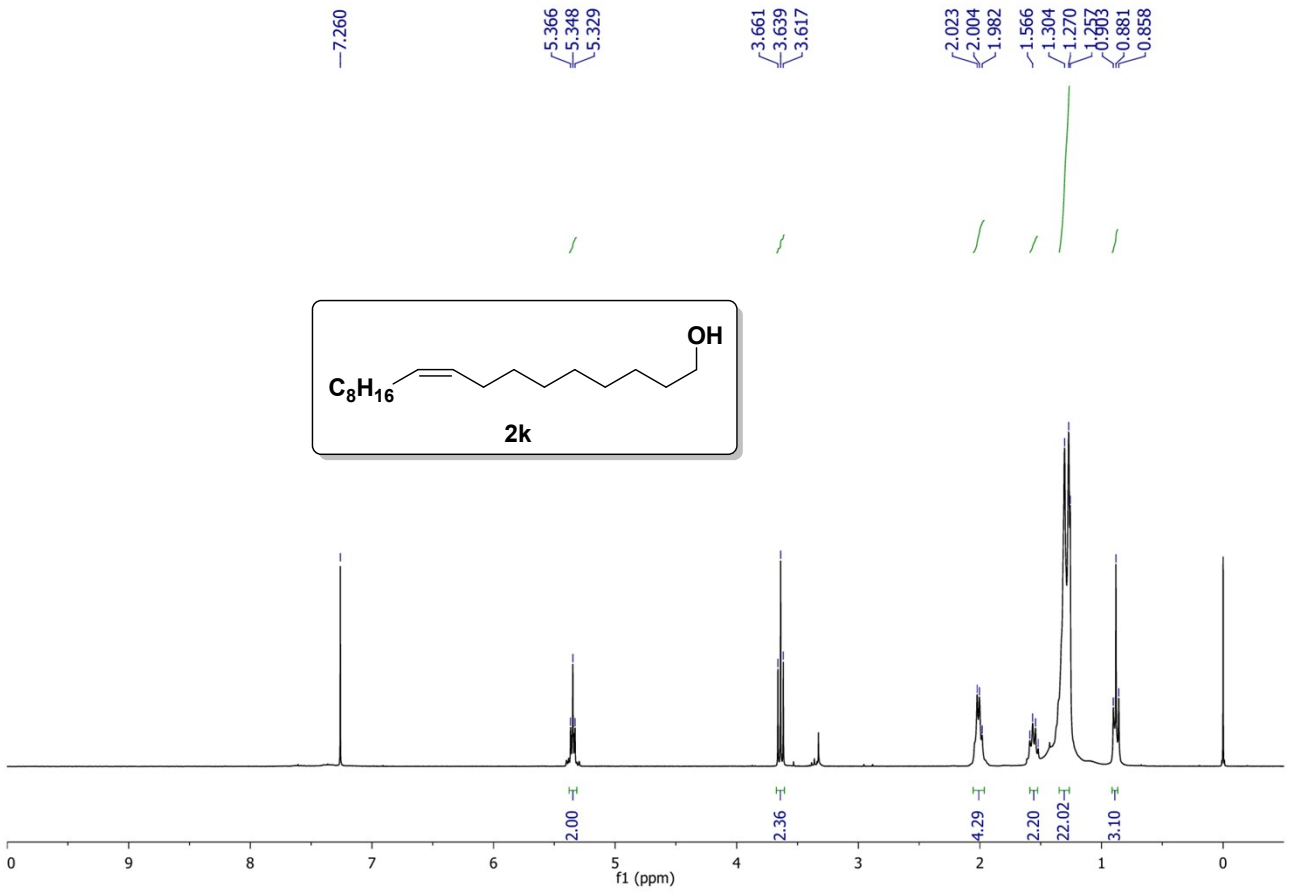

-62.520
OH
F3C
2g
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

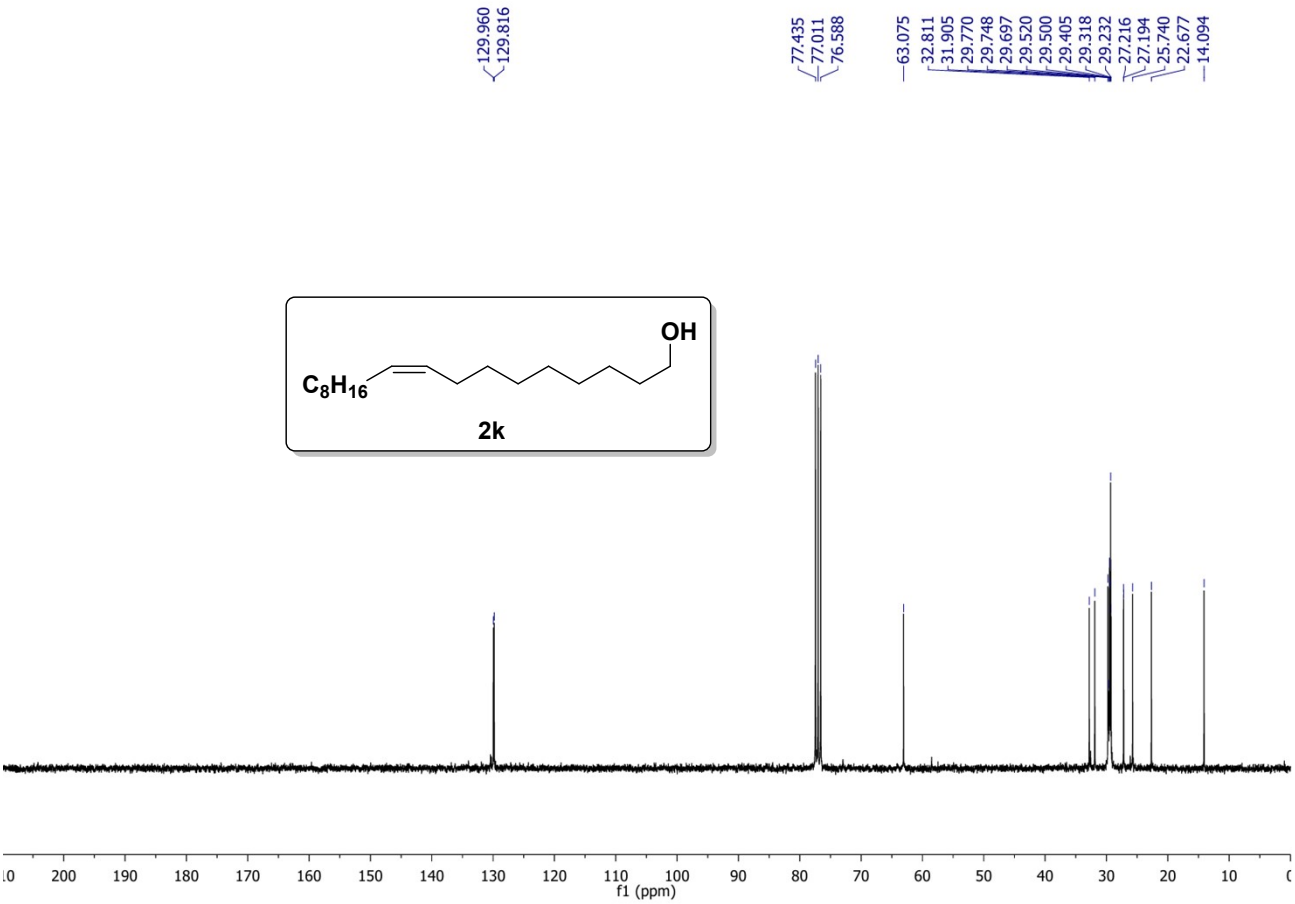

7.333
7.248
7.207
4.633
OH
Cl
2i
1.12
3.08
2.00
f1 (ppm)

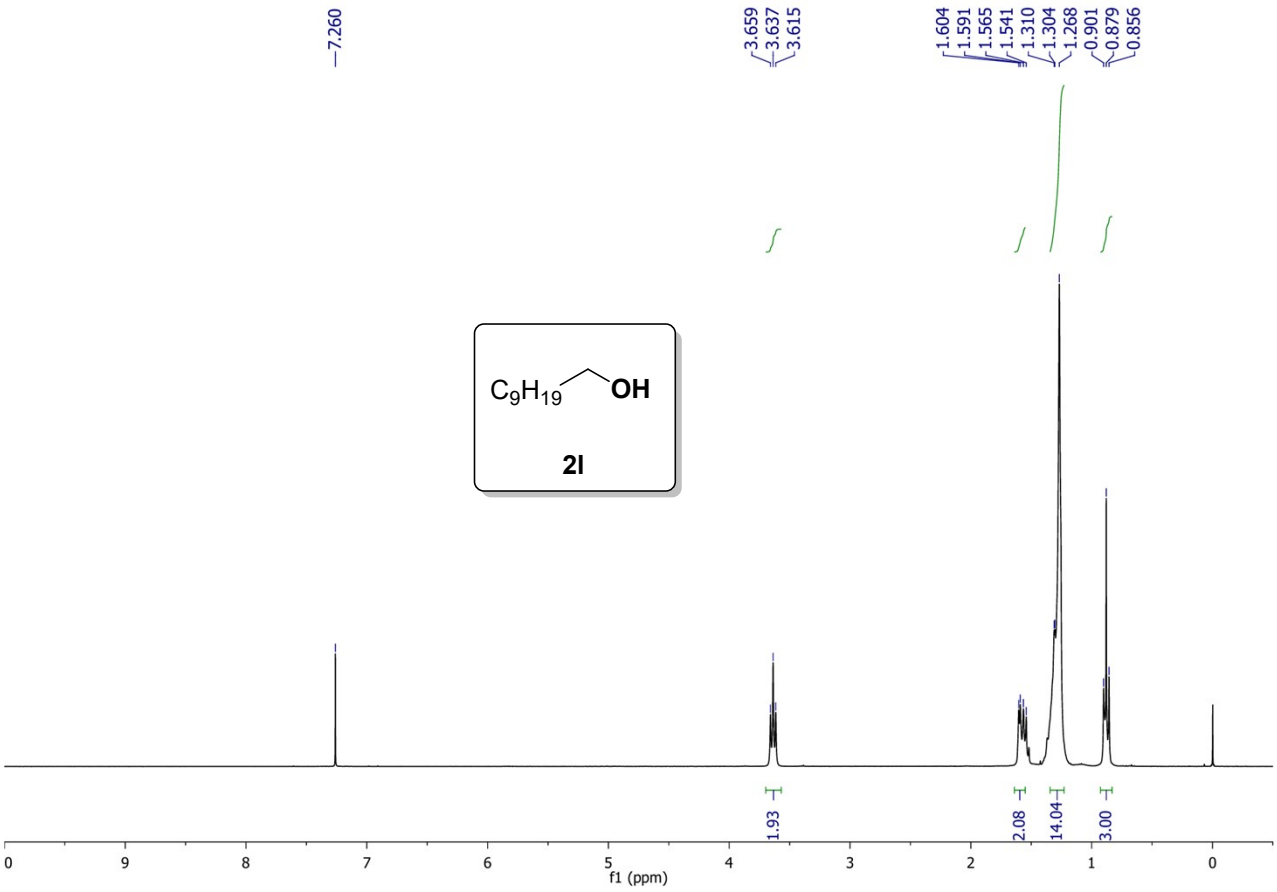

142.827
134.421
129.814
127.689
126.963
124.865
77.485
77.061
76.637
64.486
OH
Cl
2i
f1 (ppm)

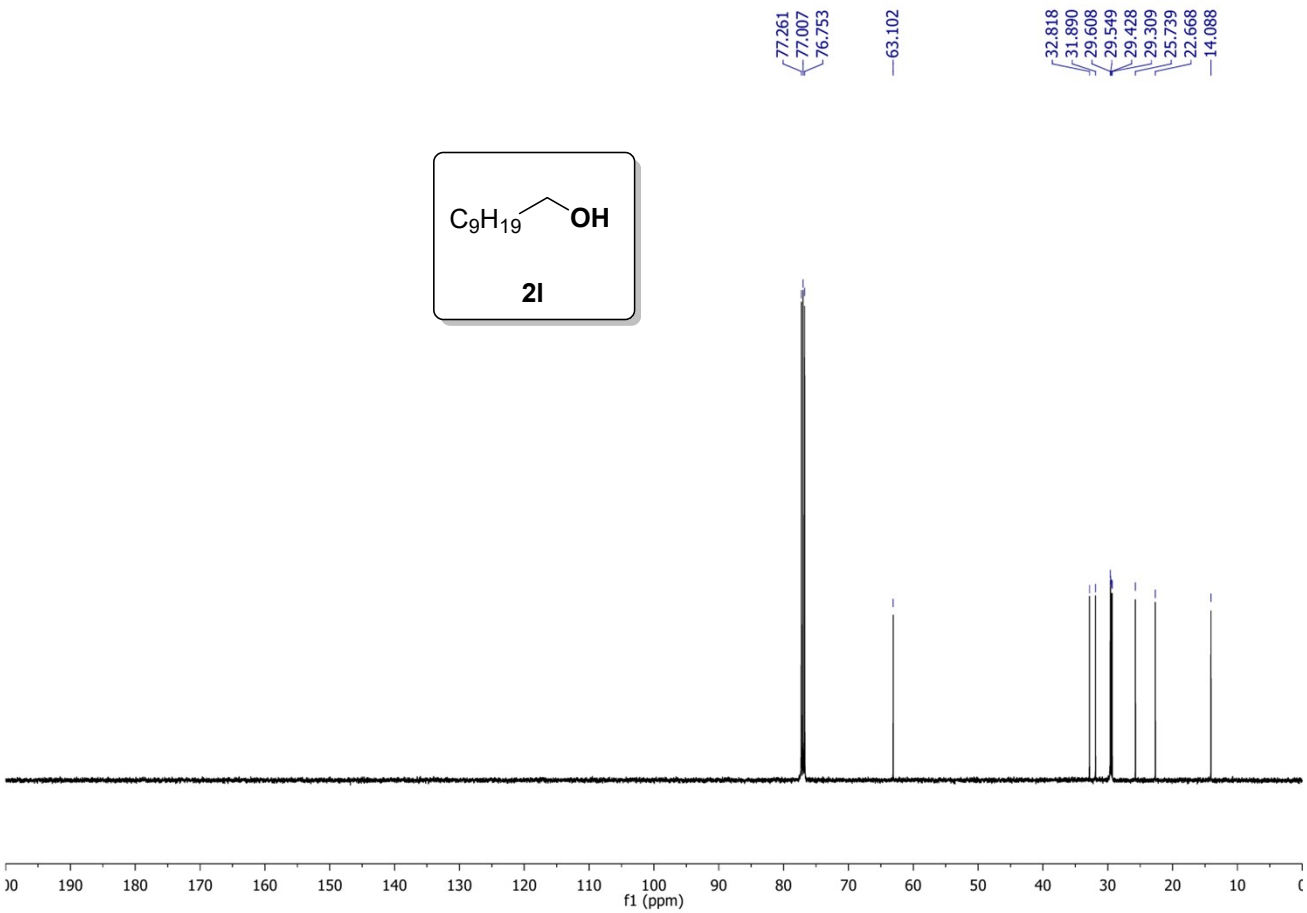

7.498
7.470
7.260
7.254
7.225
4.653
OH
Br
2j
2.00
2.25
2.00
f1 (ppm)

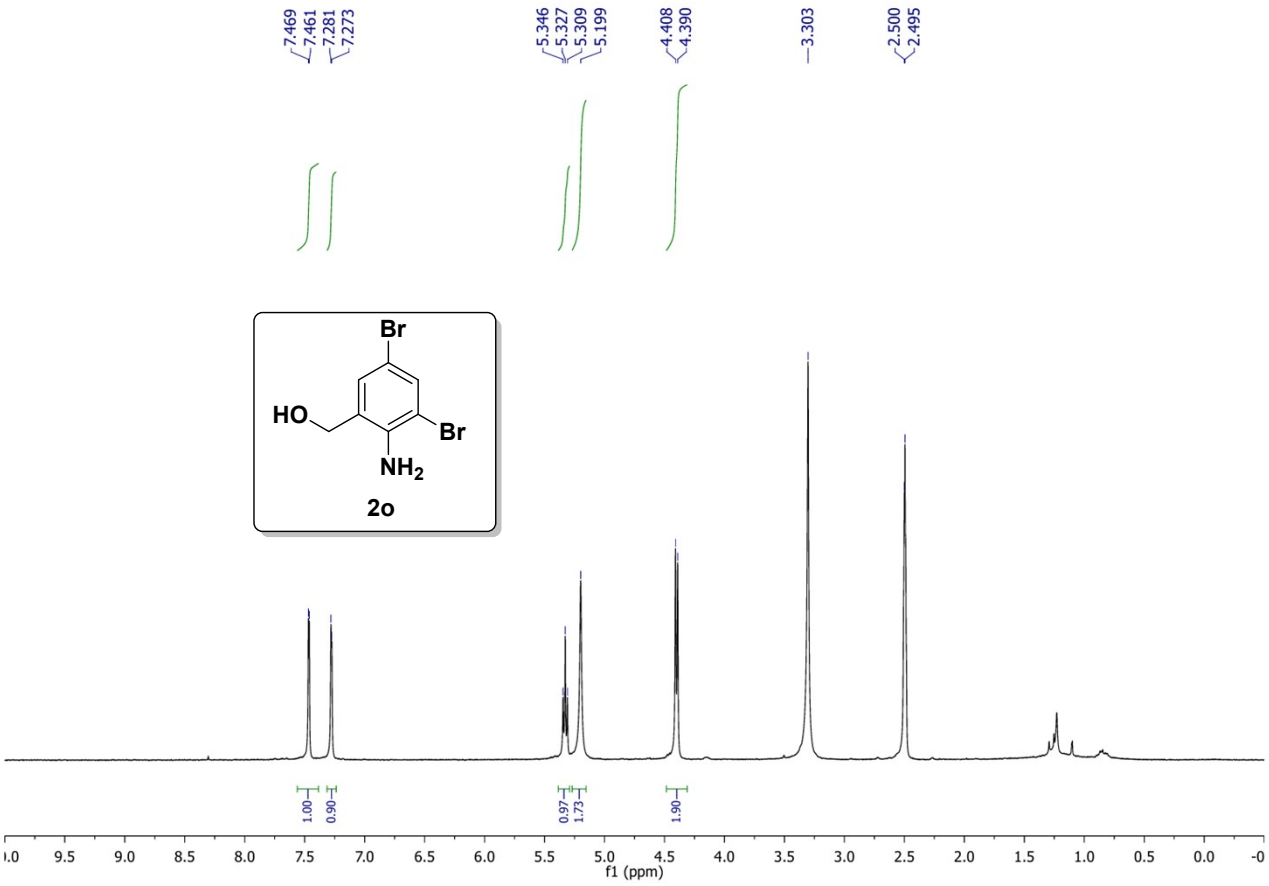

139.781
131.640
128.584
121.465
77.439
77.016
76.592
64.601
OH
Br
2j
f1 (ppm)

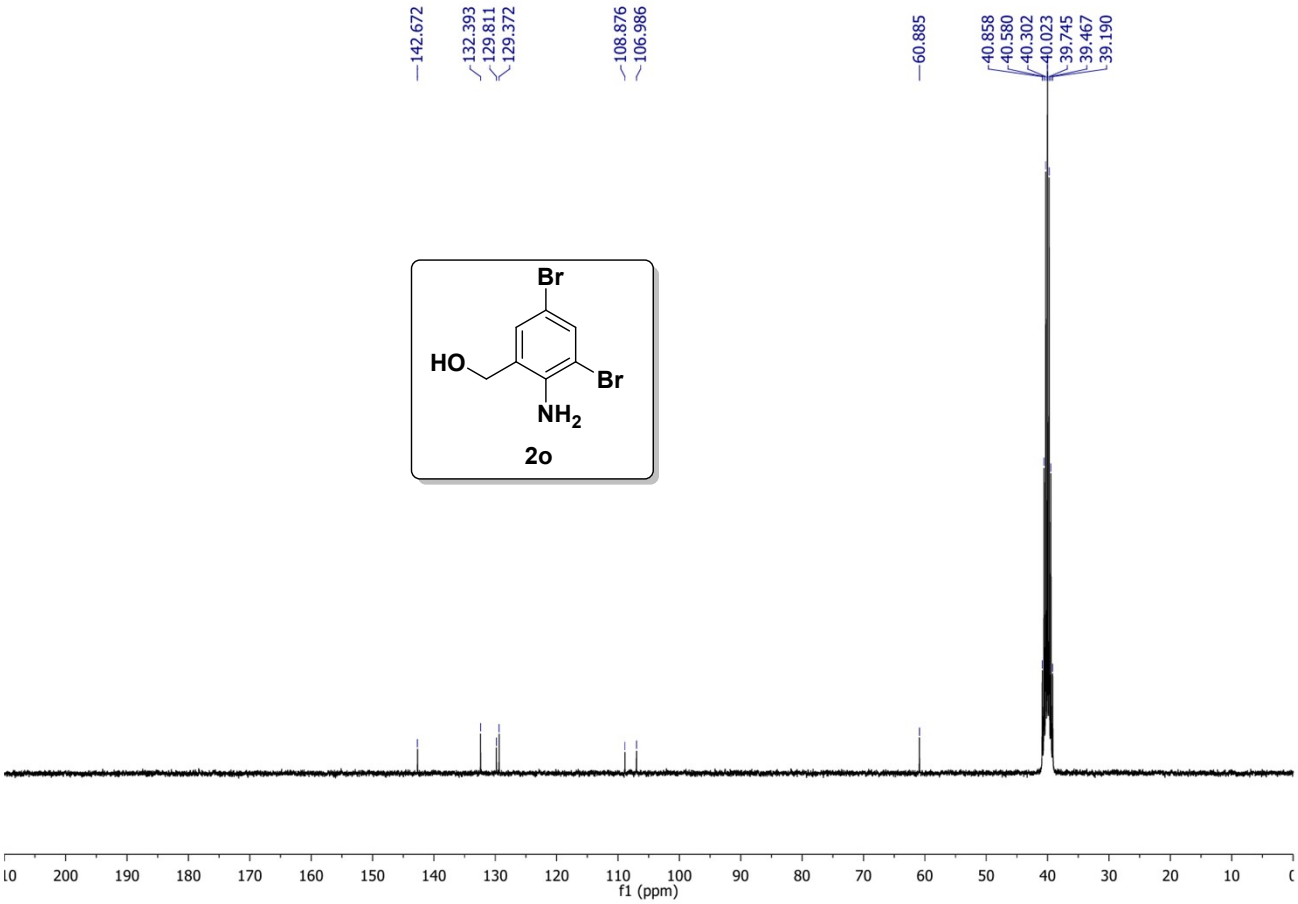

7.260
5.366
5.348
5.329
3.661
3.639
3.617
2.023
2.004
1.982
1.566
1.304
1.270
0.881
0.858
OH
C8H16
2k
2.00
2.36
4.29
2.20
22.02
3.10
f1 (ppm)

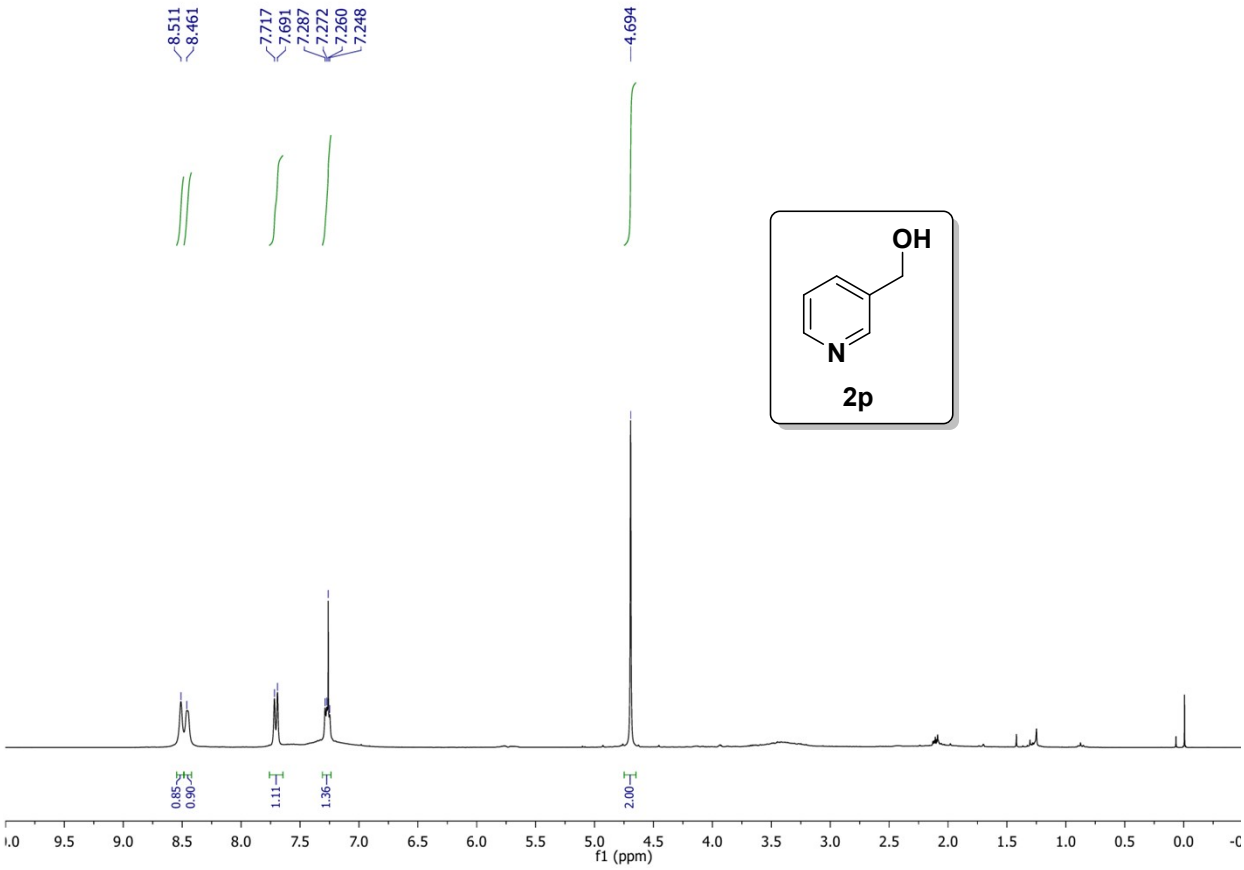

129.960
129.816
77.435
77.011
76.588
63.075
32.811
31.905
29.770
29.748
29.697
29.520
29.500
29.405
29.318
29.232
27.216
27.194
25.740
22.677
14.094
OH
C8H16
2k
f1 (ppm)

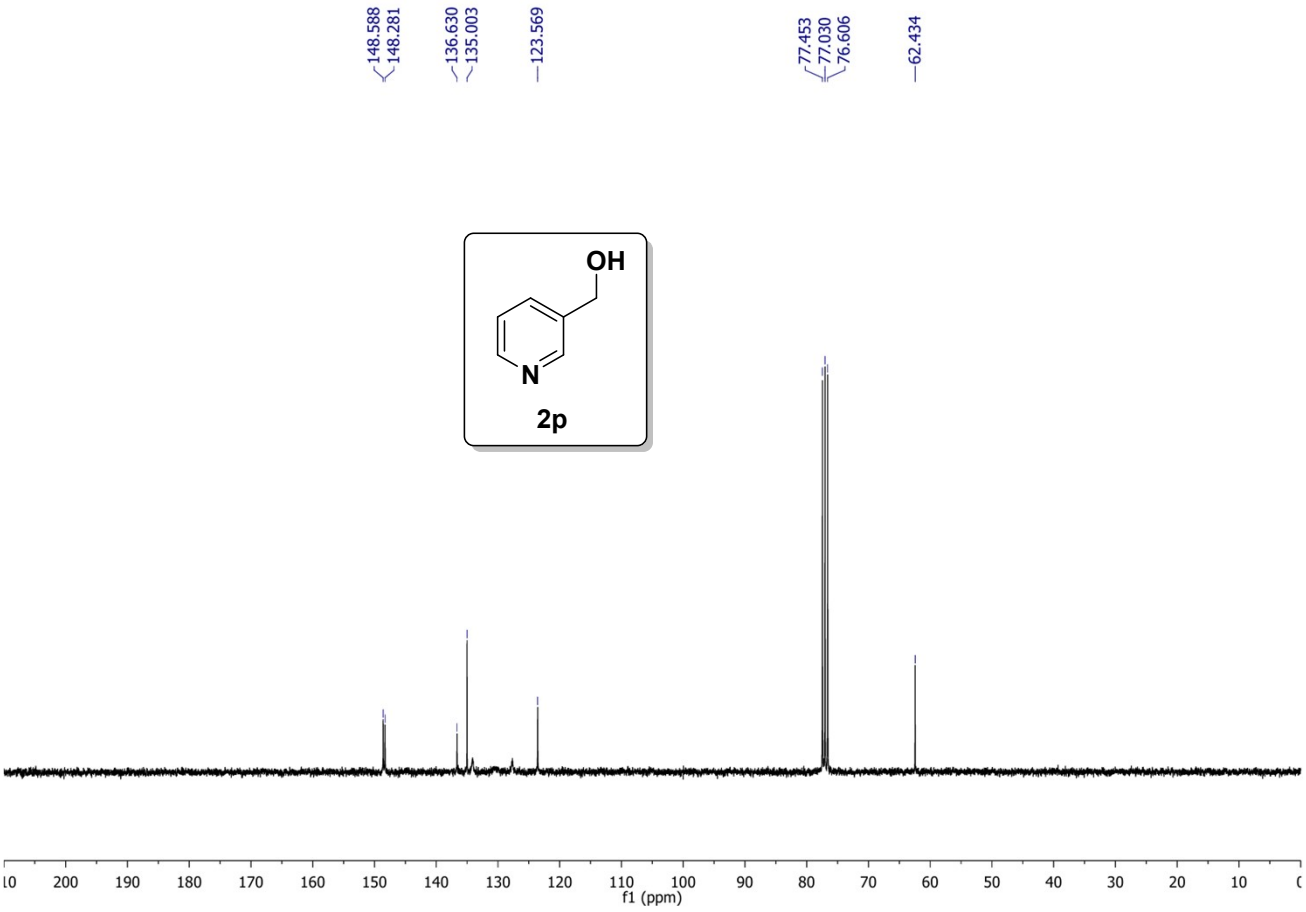

7.260
3.659
3.637
3.615
1.604
1.591
1.565
1.541
1.310
1.304
1.268
0.901
0.879
0.856
C9H19
OH
2l
1.93
2.08
14.04
3.00
f1 (ppm)

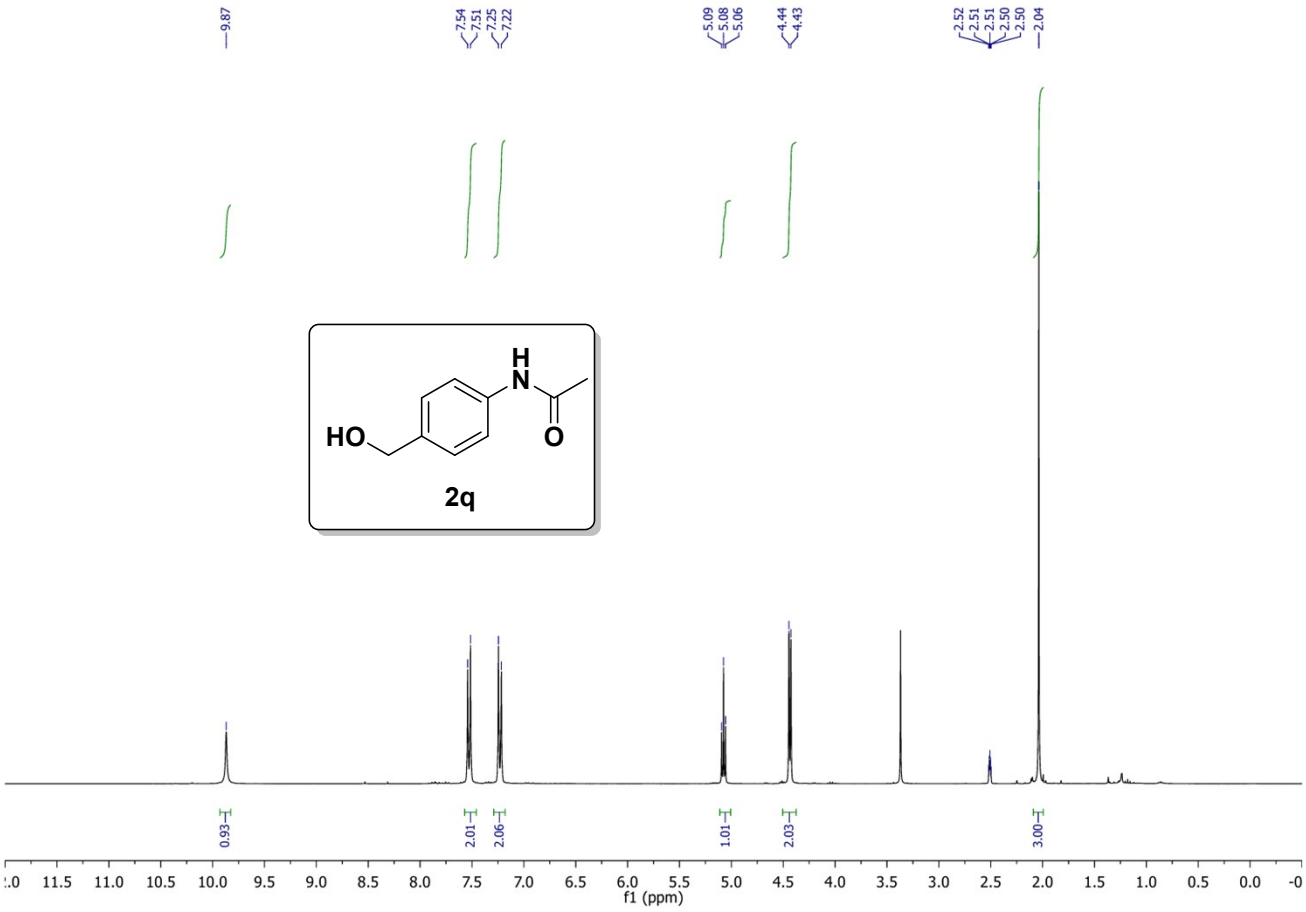

77.261
77.007
76.753
63.102
32.818
31.890
29.608
29.549
29.428
29.309
25.739
22.668
14.088
C9H19
OH
2l
f1 (ppm)

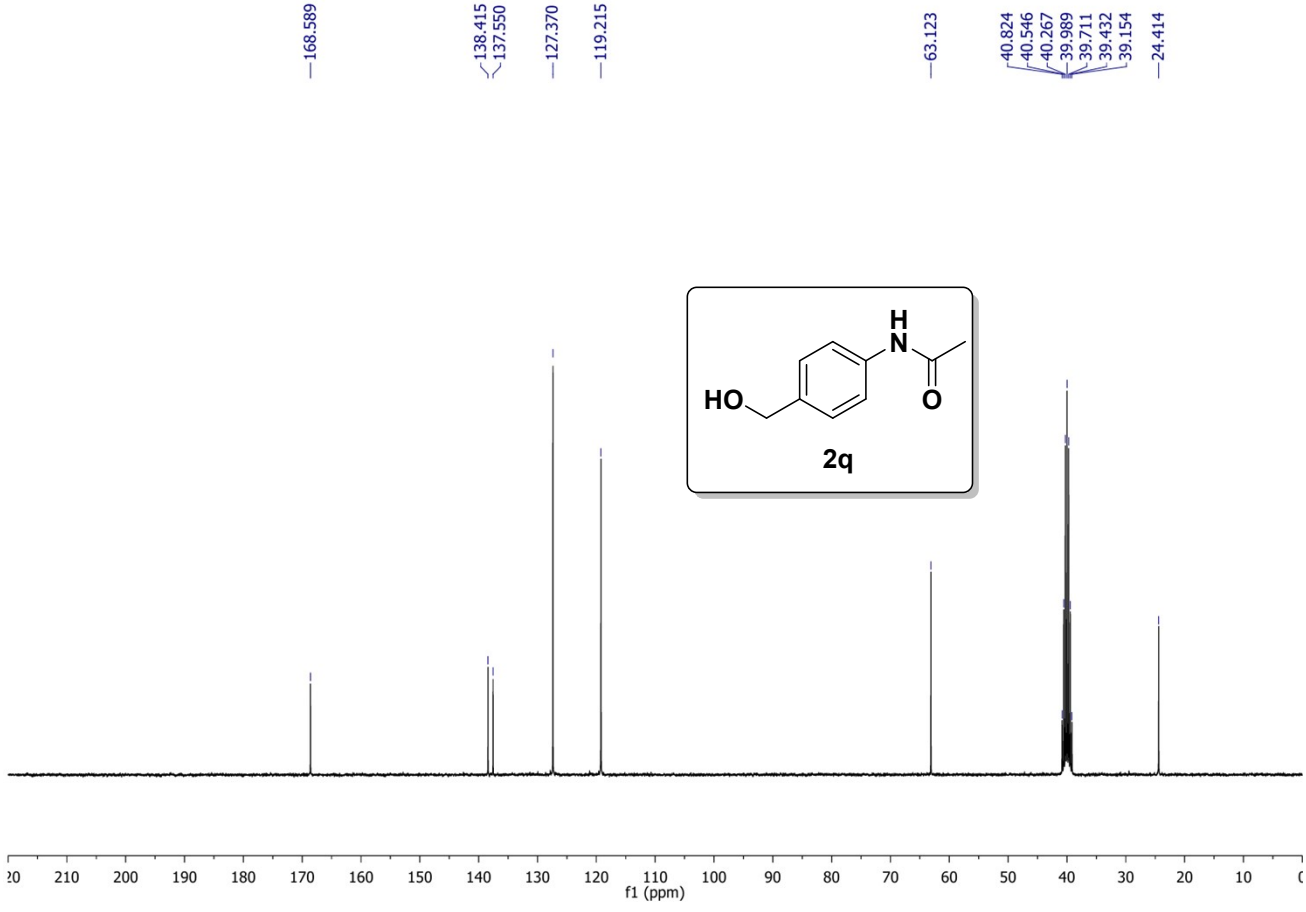

7.469
7.461
7.281
7.273
5.346
5.327
5.309
5.199
4.408
4.390
3.303
2.500
2.495
Br
HO
Br
NH2
2o
1.00
0.90
0.97
1.73
1.90
f1 (ppm)

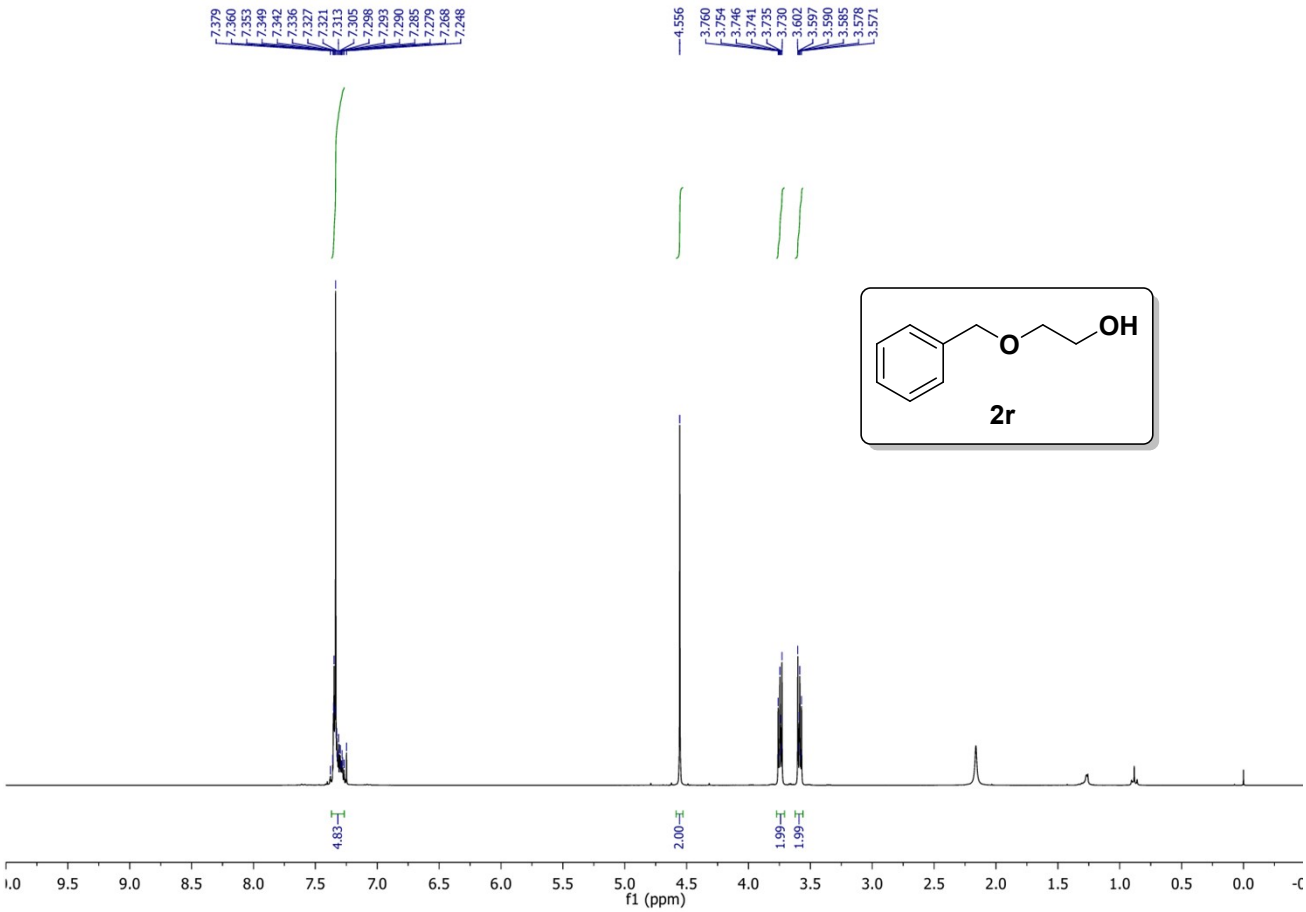

142.672
132.393
129.811
129.372
108.876
106.986
60.885
40.858
40.580
40.302
40.023
39.745
39.467
39.190
Br
HO
Br
NH2
2o
f1 (ppm)

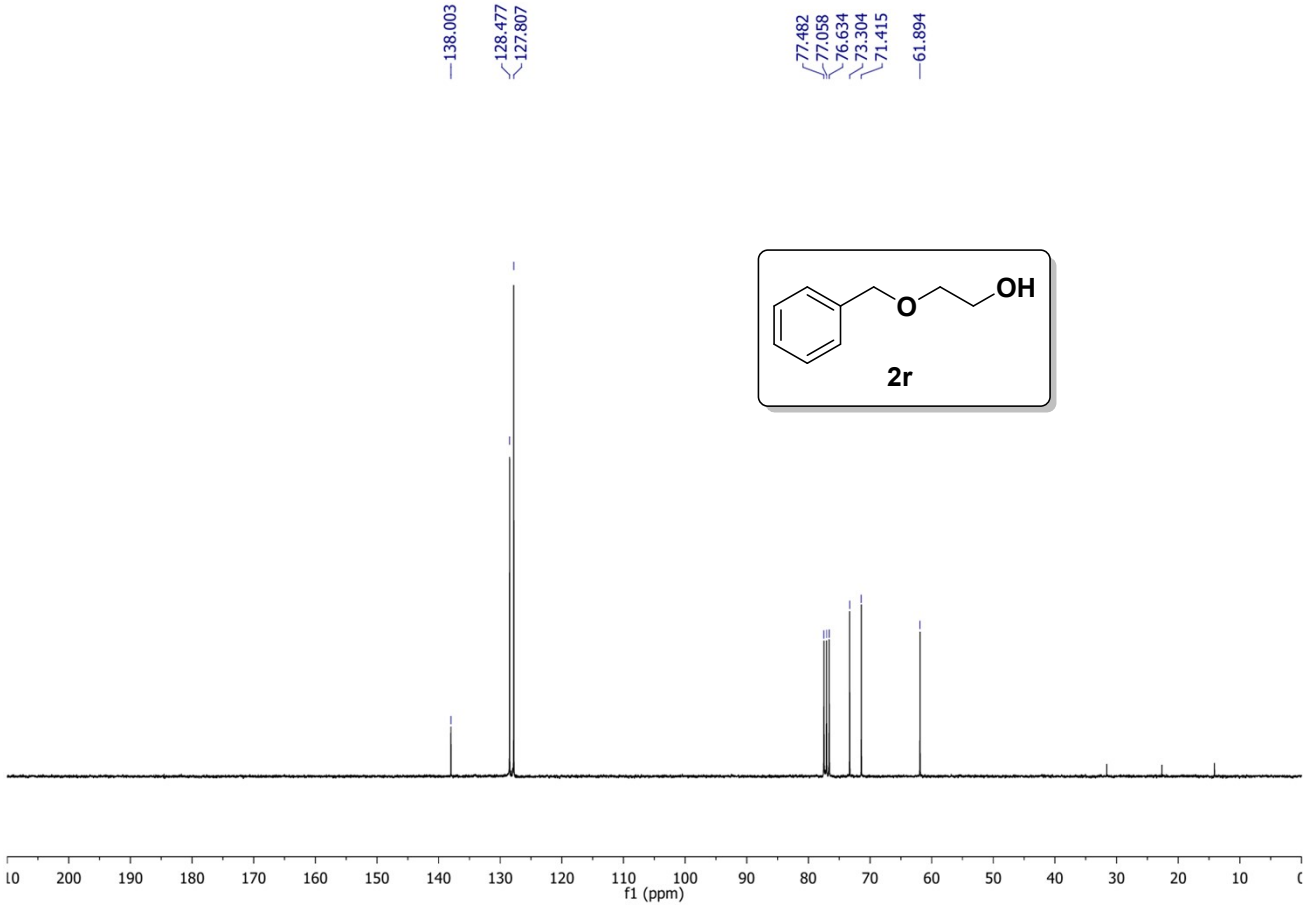

8.511
8.461
7.717
7.691
7.287
7.272
7.260
7.248
4.694
OH
N
2p
0.85
0.90
1.11
1.36
2.00
f1 (ppm)

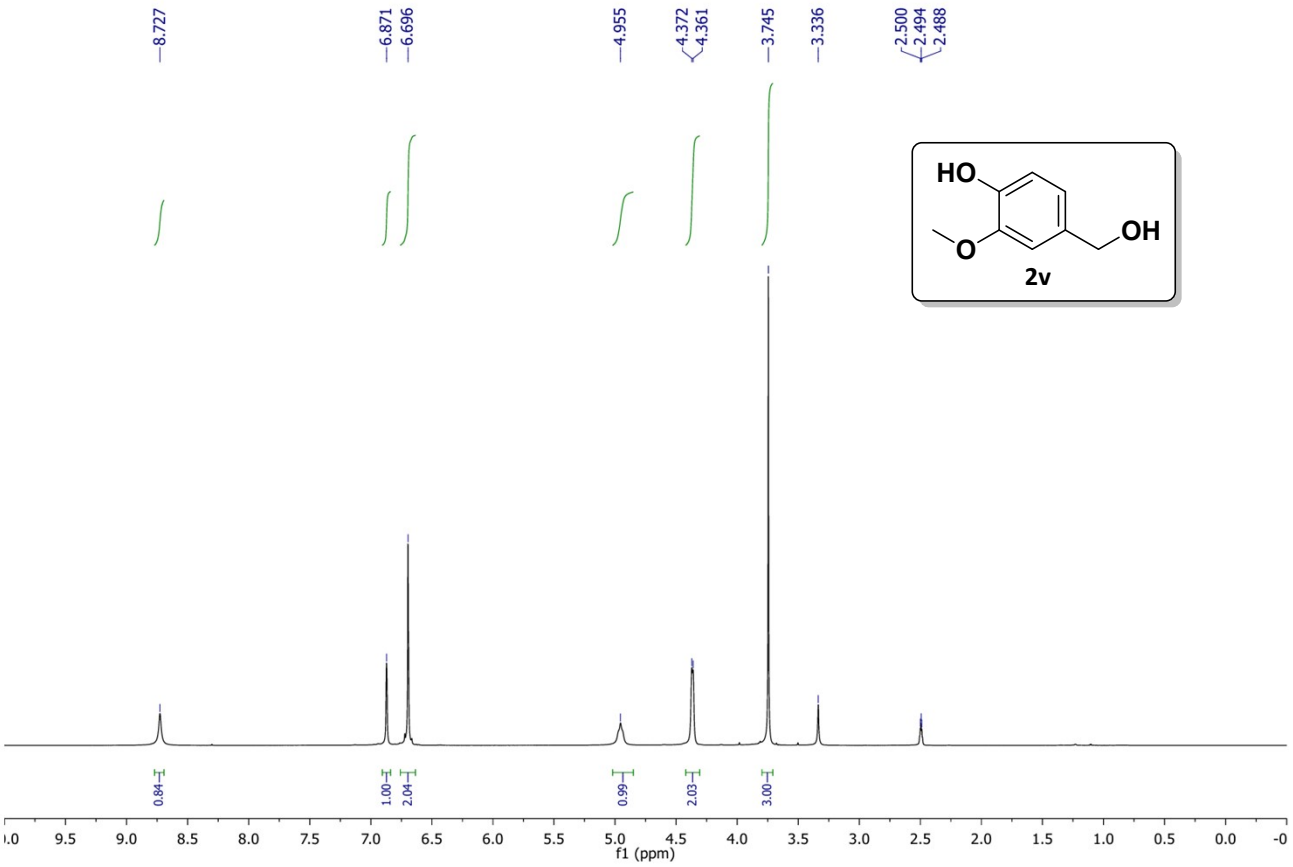

148.588
148.281
136.630
135.003
123.569
77.453
77.030
76.606
62.434
OH
N
2p
f1 (ppm)

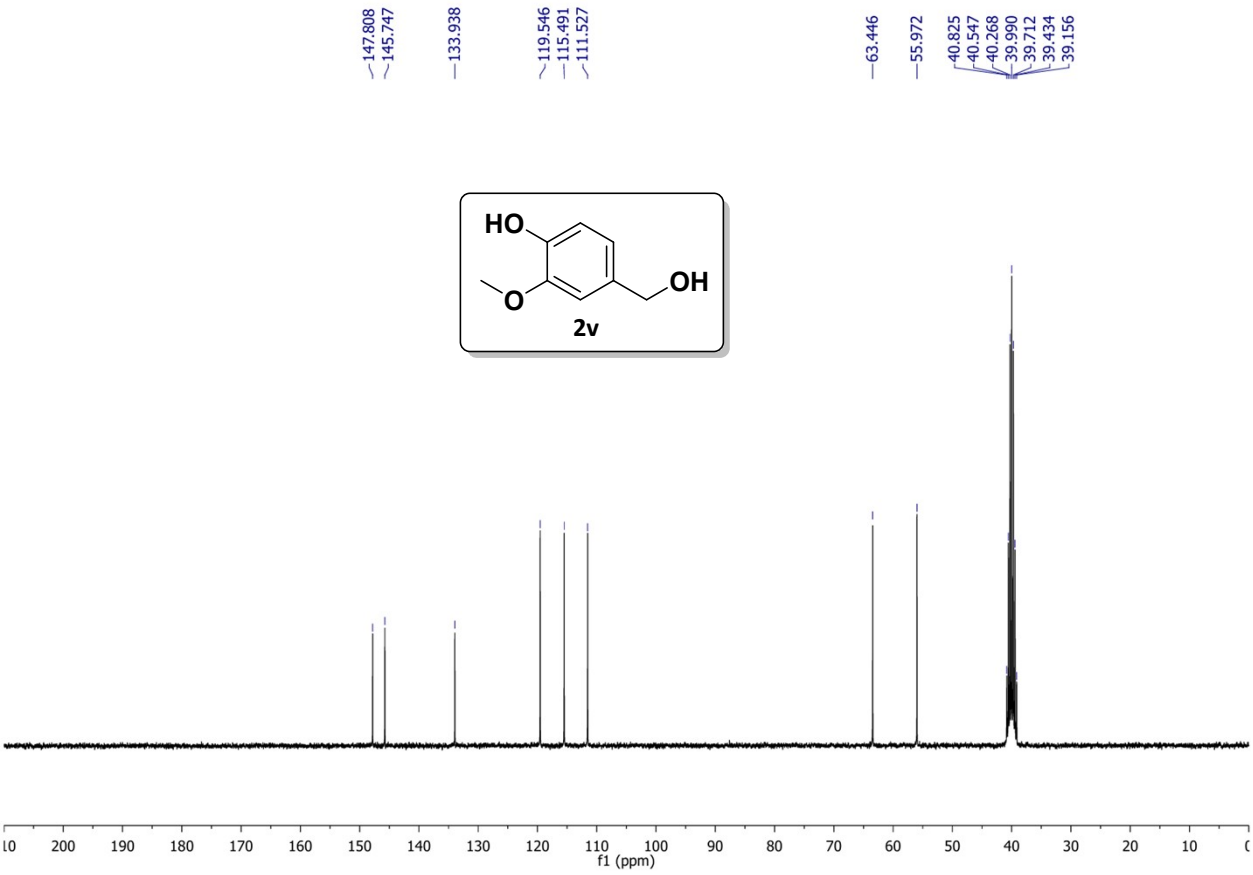

9.87
7.54
7.51
7.25
7.22
5.09
5.08
5.06
4.44
4.43
2.52
2.51
2.51
2.50
2.50
2.04
HO
H
N
O
2q
0.93
2.01
2.06
1.01
2.03
3.00
f1 (ppm)

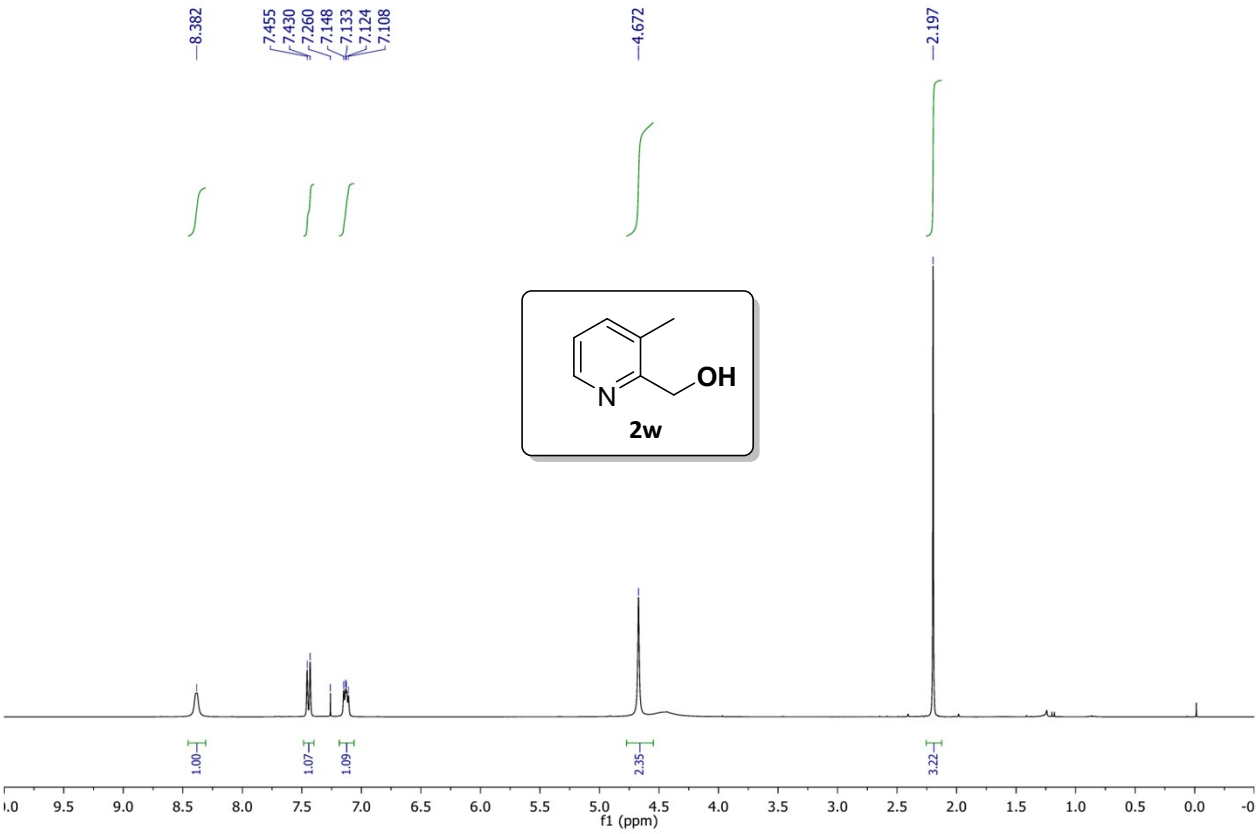

168.589
138.415
137.550
127.370
119.215
63.123
40.824
40.546
40.267
39.989
39.711
39.432
39.154
24.414
HO
H
N
O
2q
f1 (ppm)

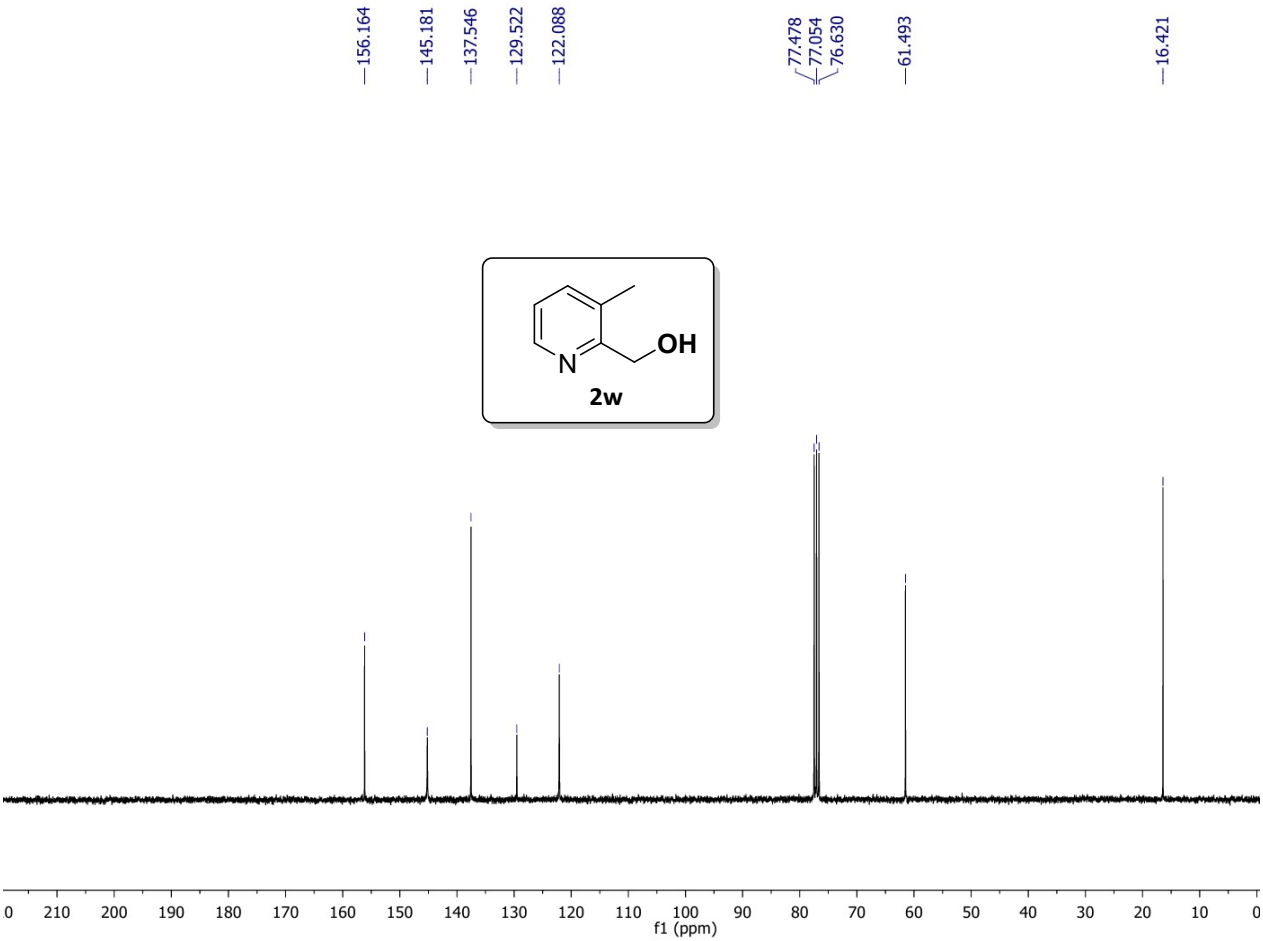

7.379
7.360
7.353
7.349
7.342
7.336
7.327
7.321
7.313
7.305
7.298
7.293
7.290
7.285
7.279
7.268
7.248
4.556
3.760
3.754
3.746
3.741
3.735
3.730
3.602
3.597
3.590
3.585
3.578
3.571
OH
O
2r
4.83
2.00
1.99
1.99
f1 (ppm)

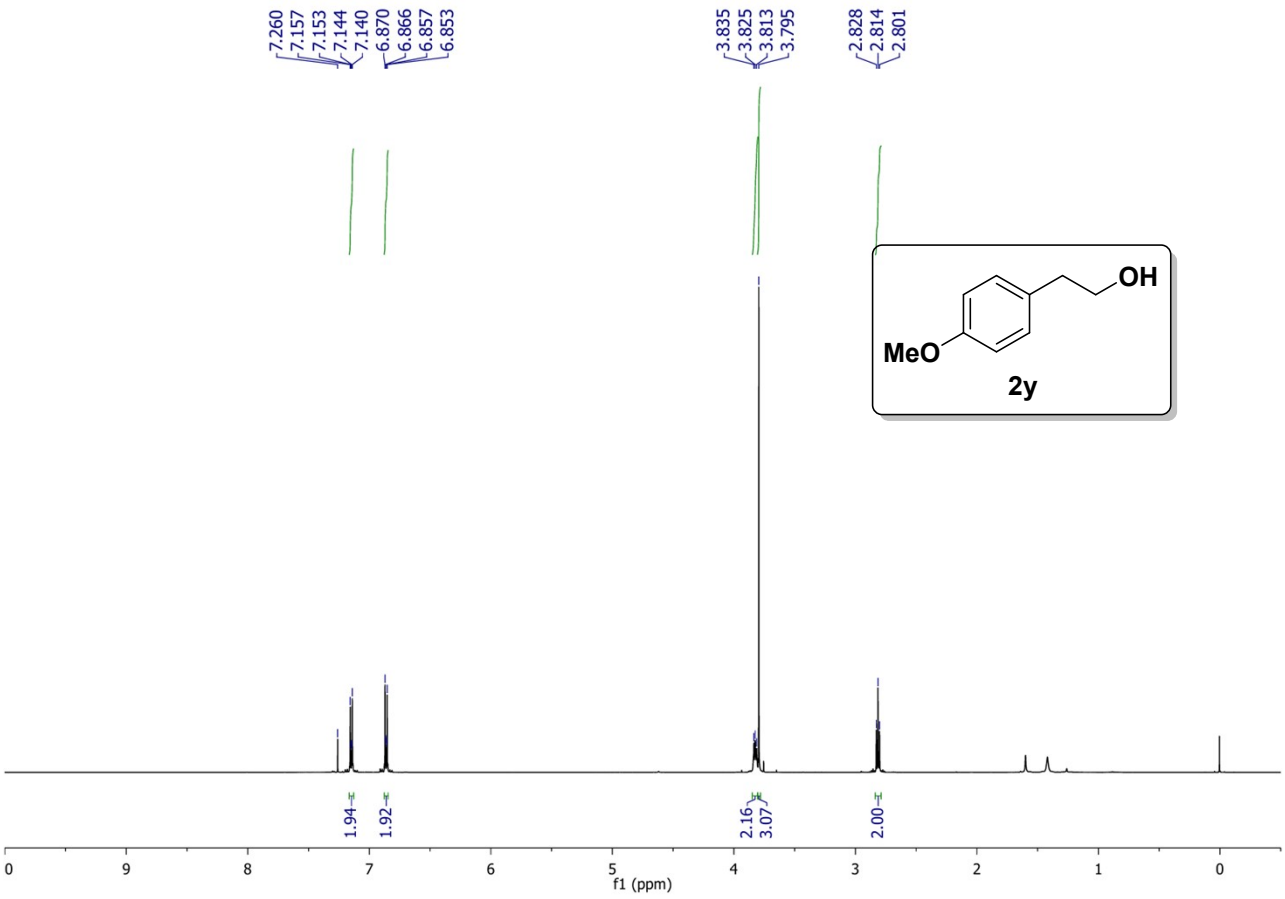

138.003
128.477
127.807
77.482
77.058
76.634
73.304
71.415
61.894
OH
O
2r
f1 (ppm)

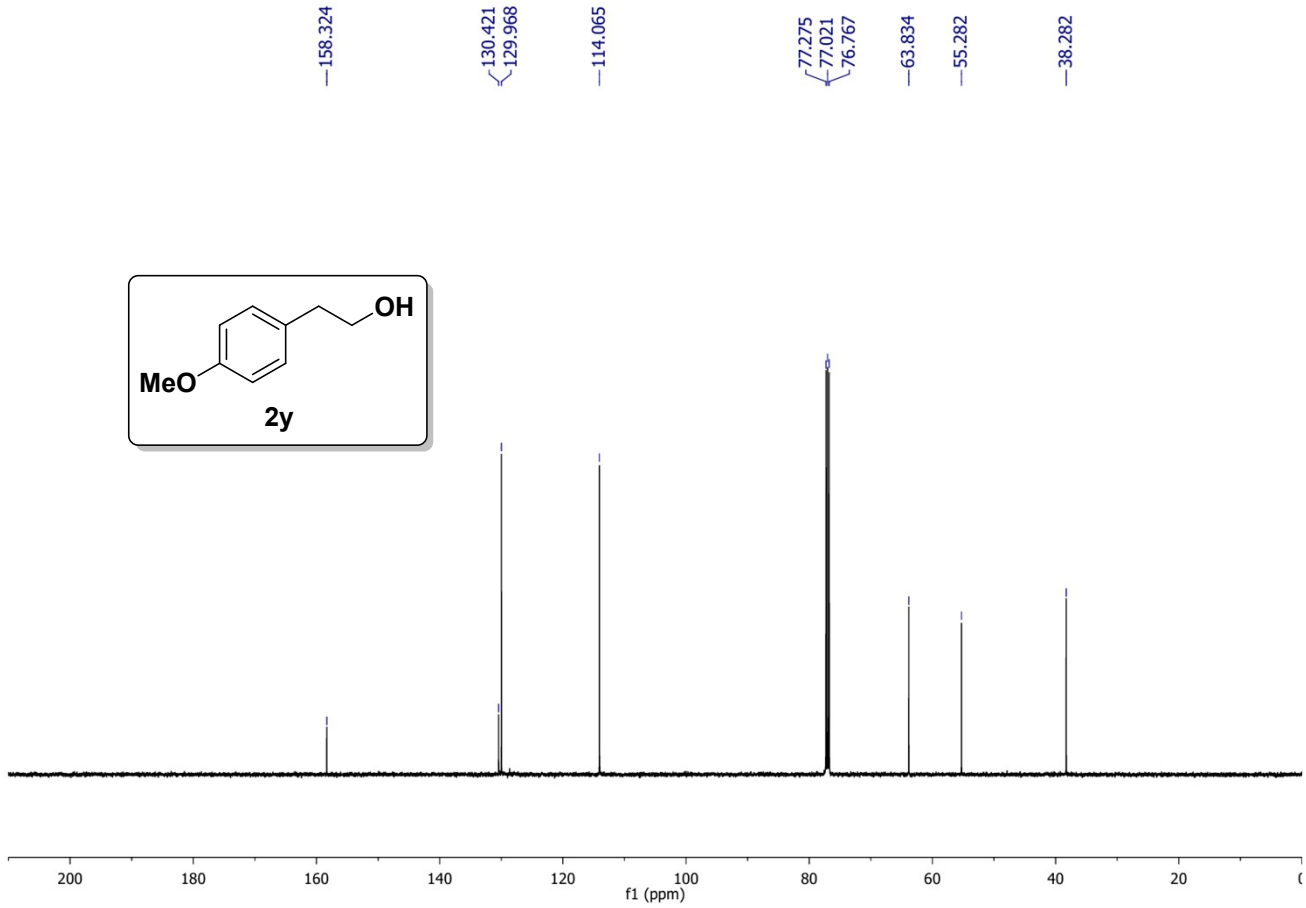

8.727
6.871
6.696
4.955
4.372
4.361
3.745
3.336
2.500
2.494
2.488
HO
O
OH
2v
0.84
1.00
2.04
0.99
2.03
3.00
f1 (ppm)

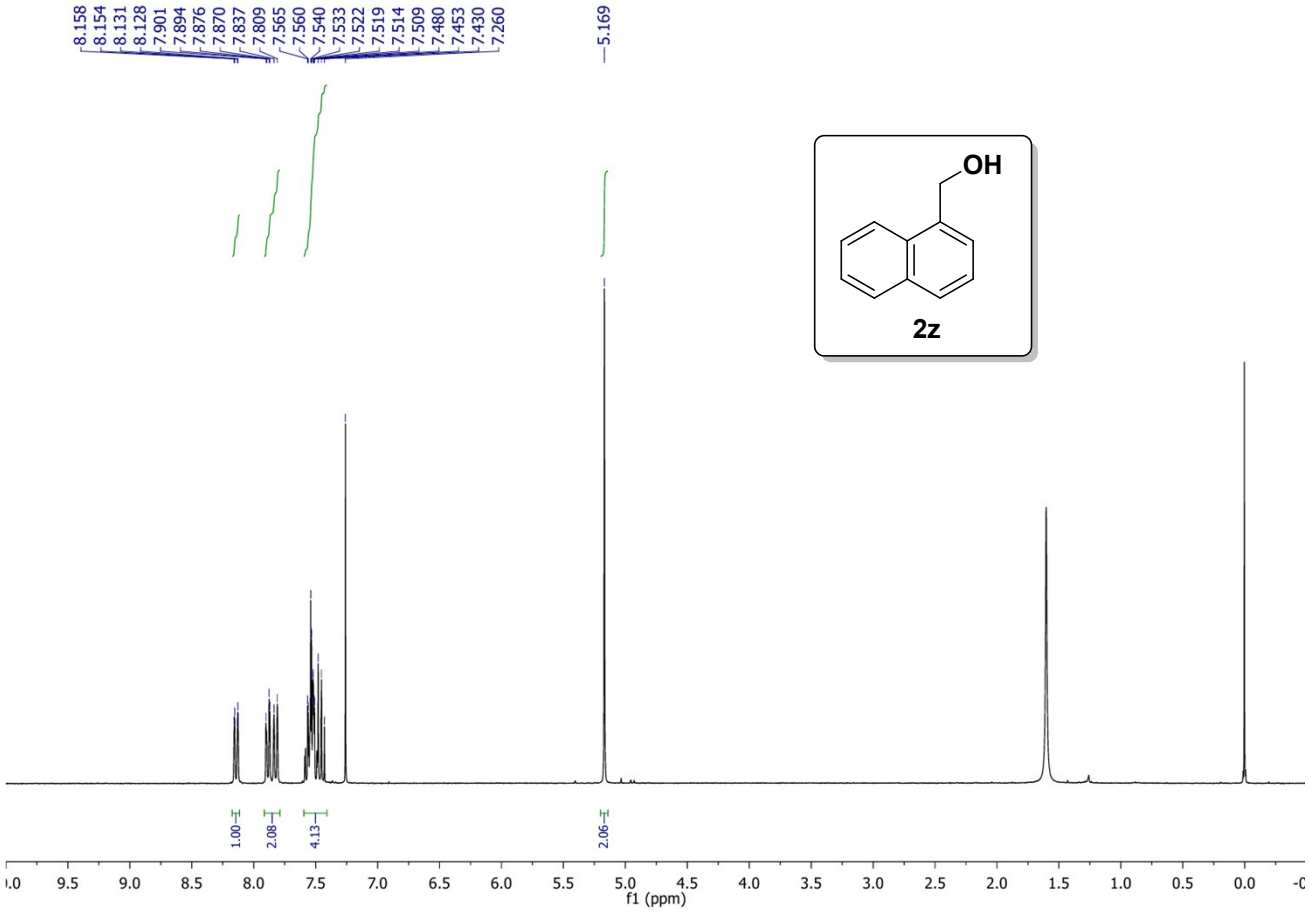

147.808
145.747
133.938
119.546
115.491
111.527
63.446
55.972
40.825
40.547
40.268
39.990
39.712
39.434
39.156
HO
O
OH
2v
f1 (ppm)

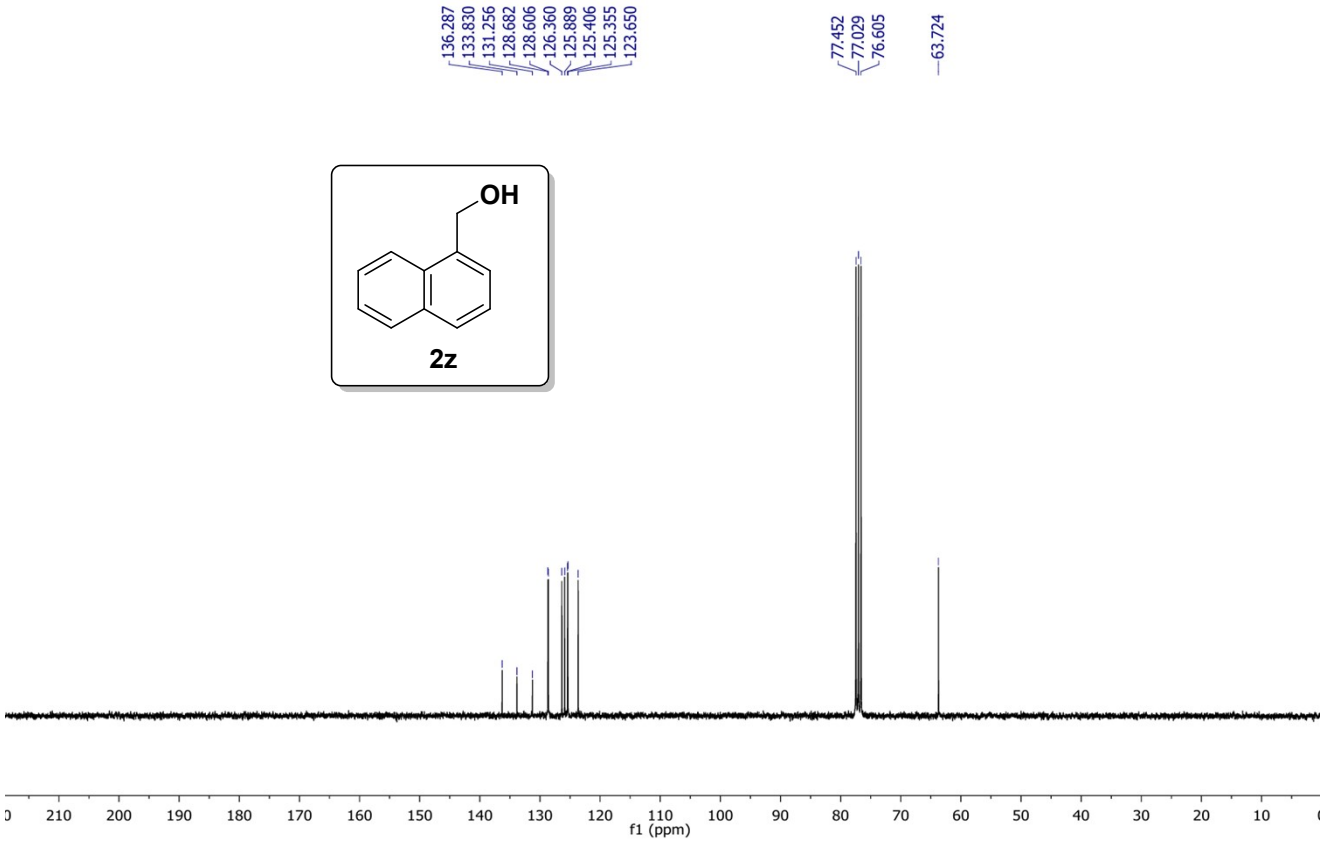

8.382
7.455
7.430
7.260
7.148
7.133
7.124
7.108
4.672
2.197
OH
N
2w
1.00
1.07
1.09
2.35
3.22
f1 (ppm)

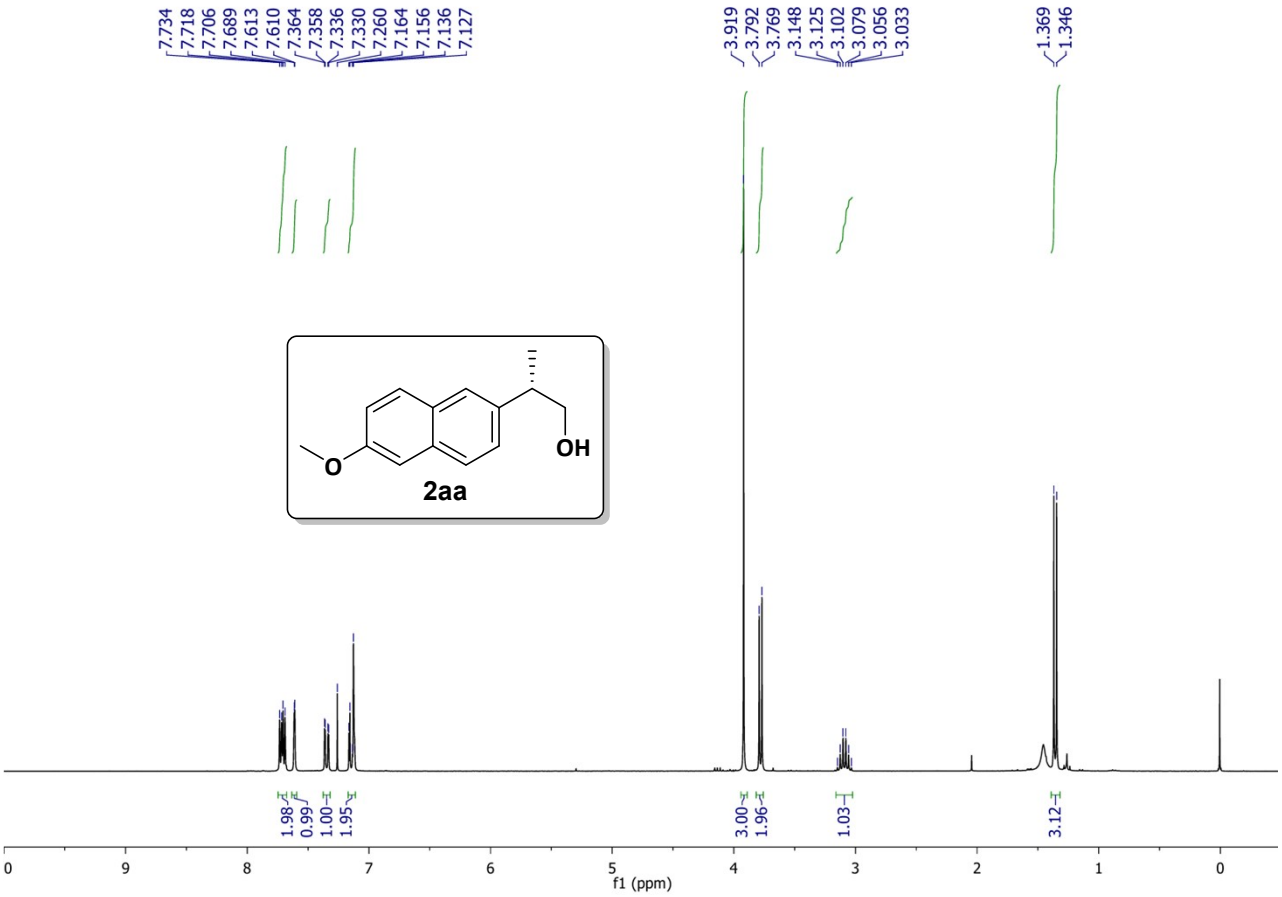

156.164
145.181
137.546
129.522
122.088
77.478
77.054
76.630
61.493
16.421
OH
N
2w
f1 (ppm)

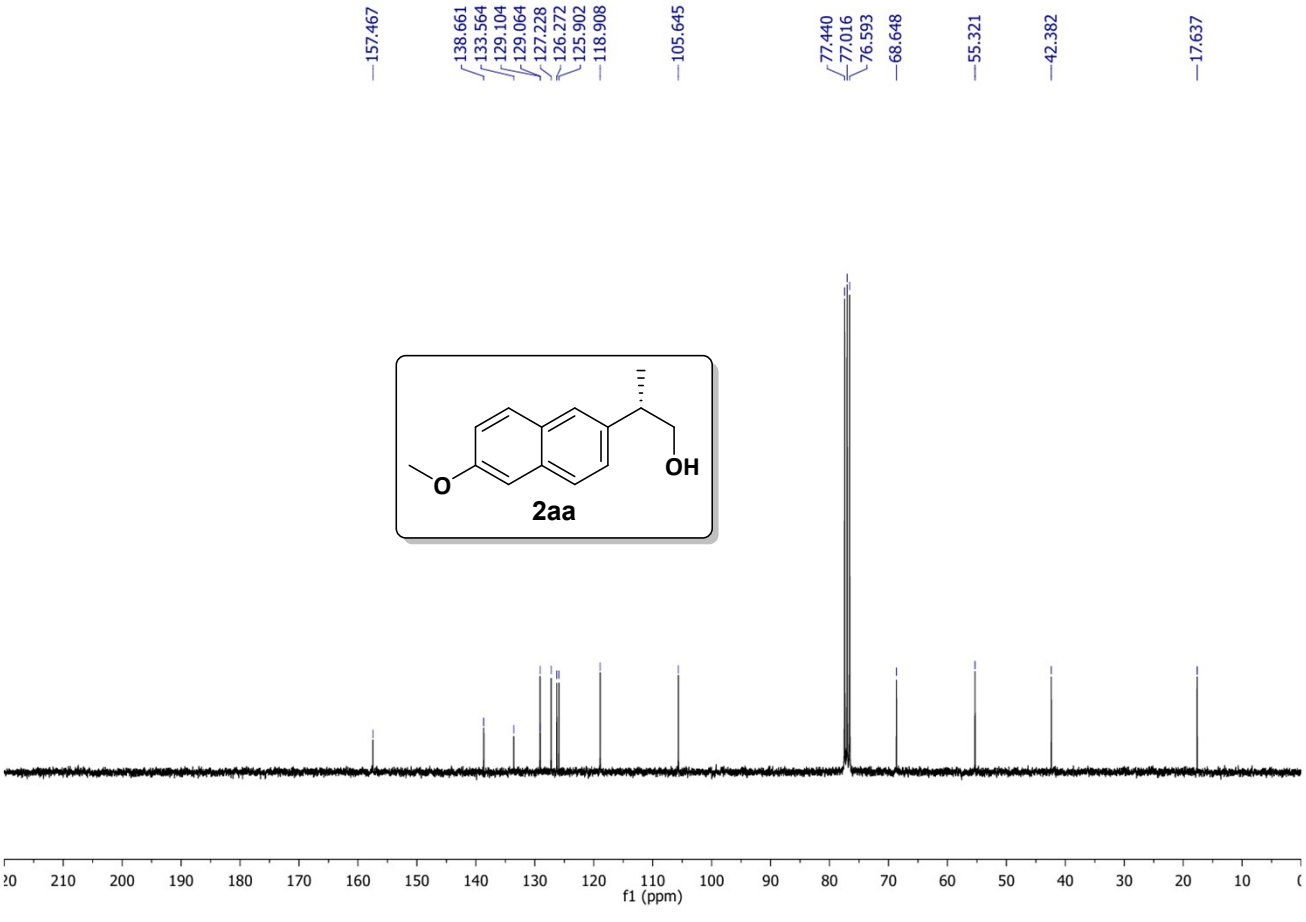

7.260
7.157
7.153
7.144
7.140
6.870
6.866
6.857
6.853
3.835
3.825
3.813
3.795
2.828
2.814
2.801
OH
MeO
2y
1.94
1.92
2.16
3.07
2.00
f1 (ppm)

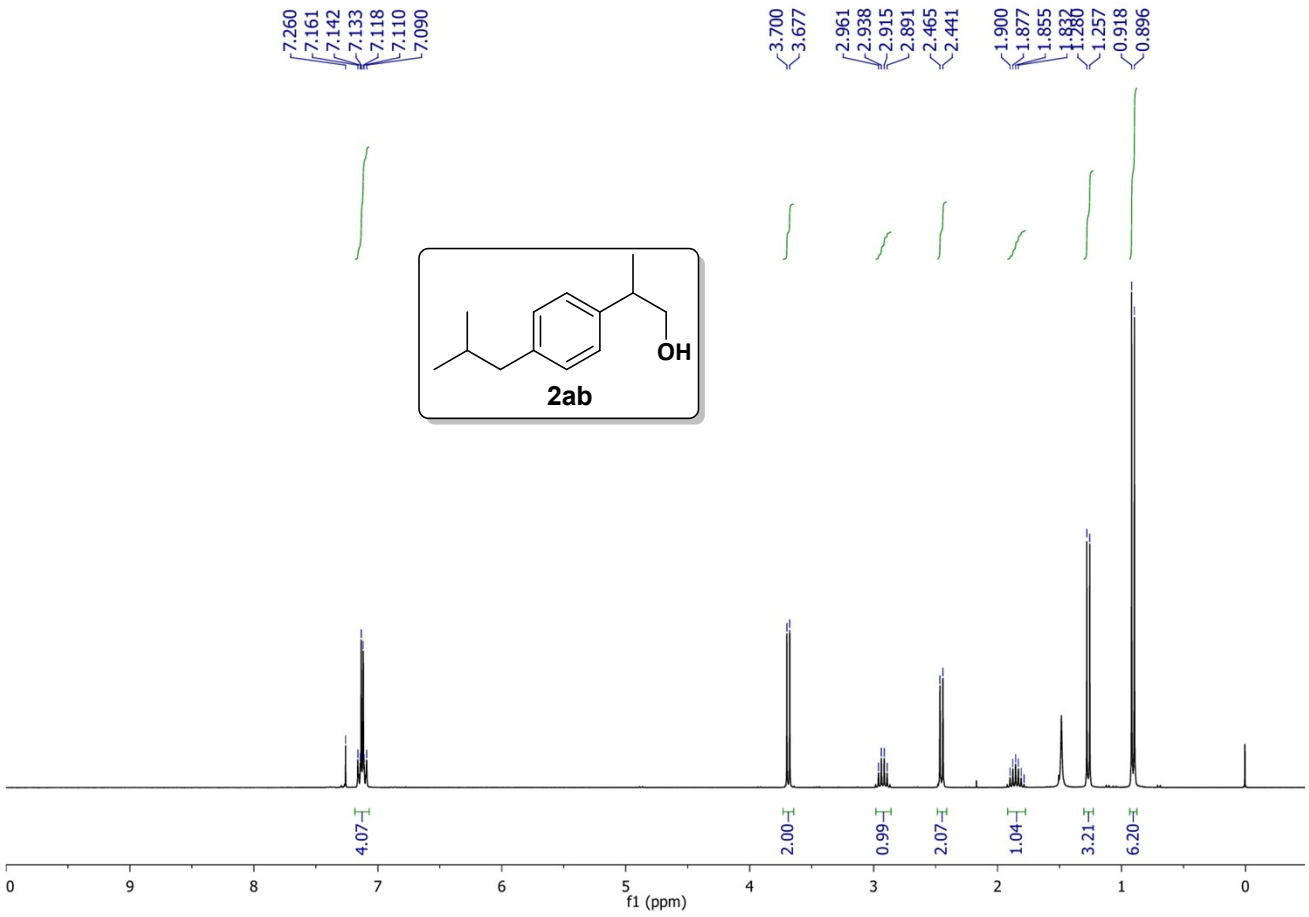

158.324
130.421
129.968
114.065
77.275
77.021
76.767
63.834
55.282
38.282
OH
MeO
2y
f1 (ppm)

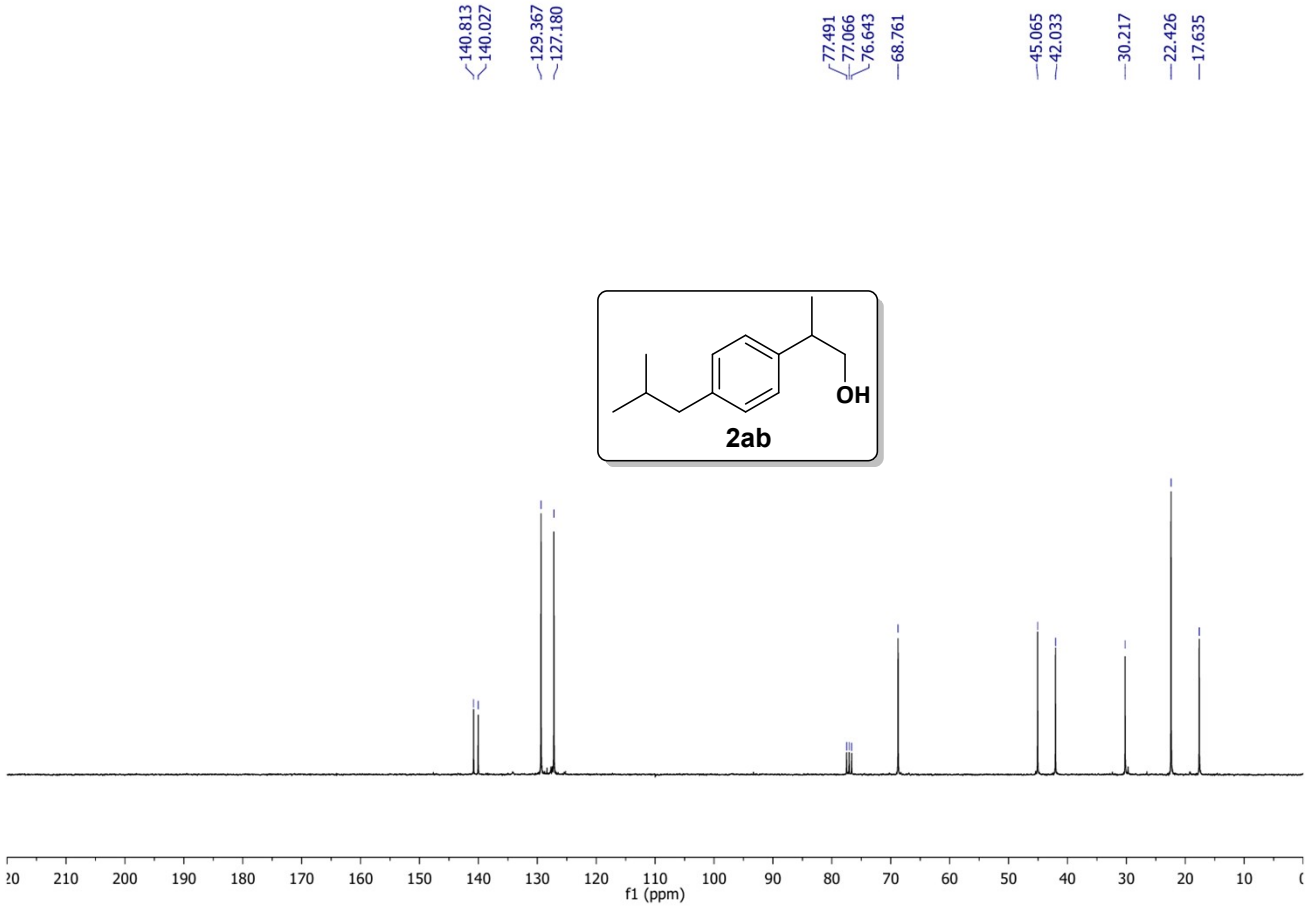

8.158
8.154
8.131
8.128
7.901
7.894
7.876
7.870
7.837
7.809
7.565
7.560
7.540
7.533
7.522
7.519
7.514
7.509
7.480
7.453
7.430
7.260
5.169
OH
2z
1.00
2.08
4.13
2.06
f1 (ppm)

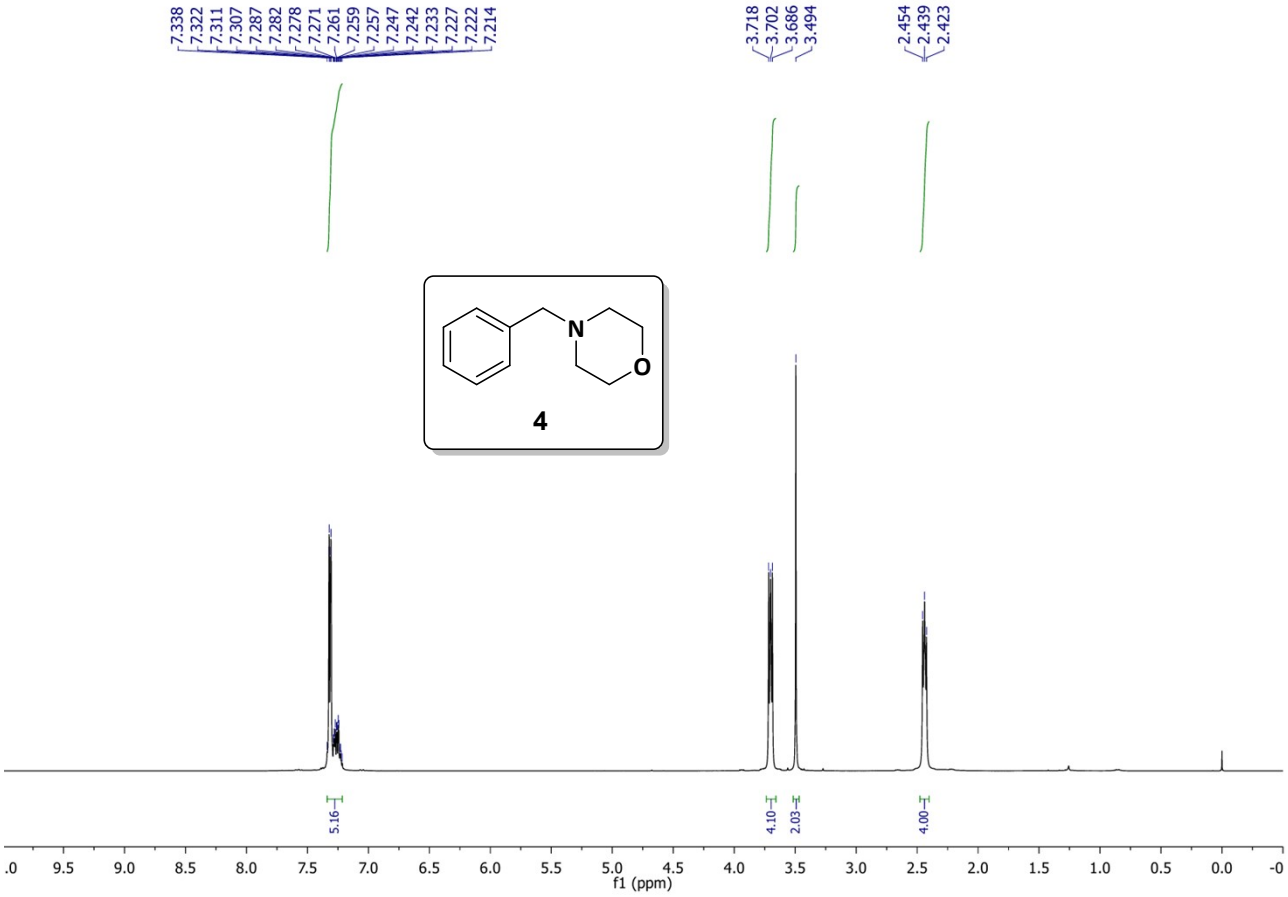

136.287
133.830
131.256
128.682
128.606
126.360
125.889
125.406
125.355
123.650
77.452
77.029
76.605
63.724
OH
2z
f1 (ppm)

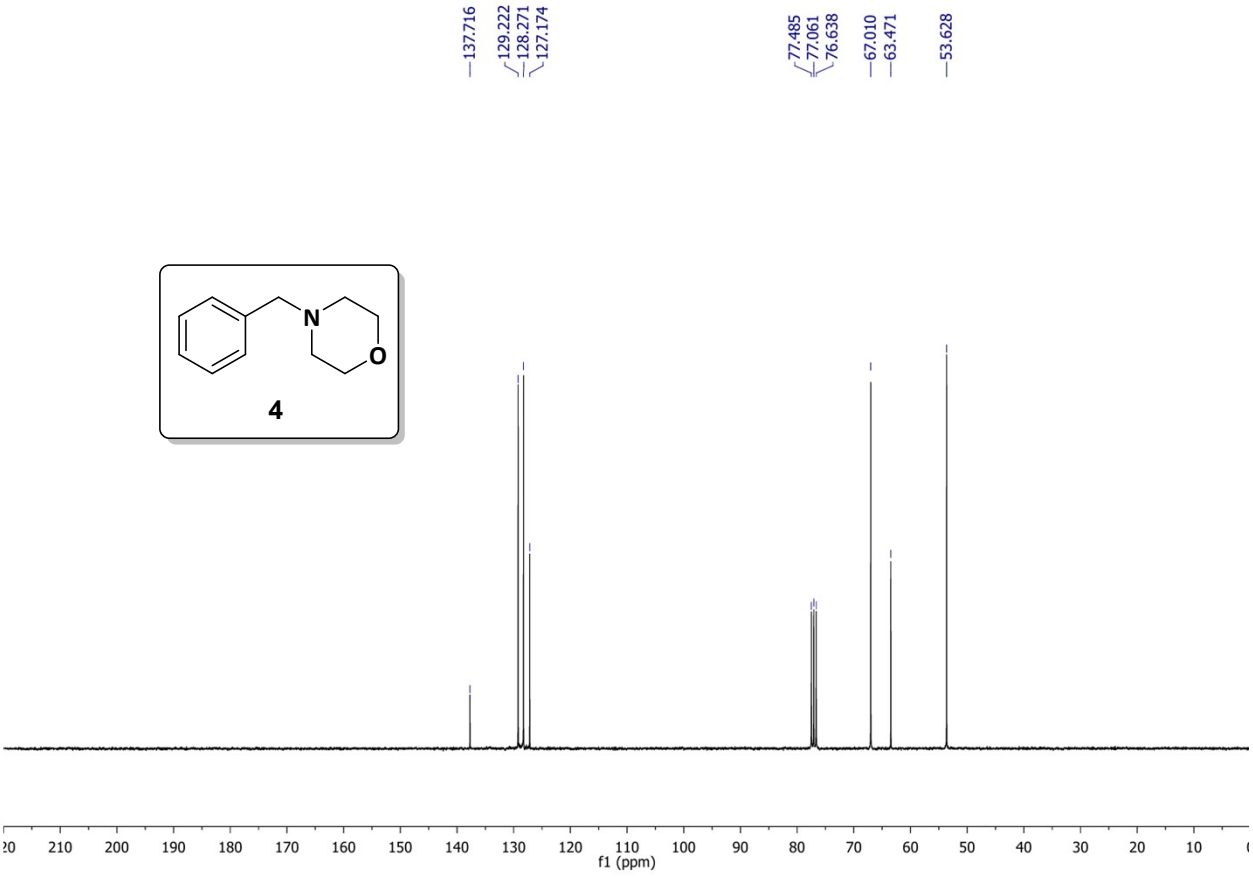

7.734
7.718
7.706
7.689
7.613
7.610
7.364
7.358
7.336
7.330
7.260
7.164
7.156
7.136
7.127
3.919
3.792
3.769
3.148
3.125
3.102
3.079
3.056
3.033
1.369
1.346
OH
O
2aa
1.98
0.99
1.00
1.95
3.00
1.96
1.03
3.12
f1 (ppm)


157.467
138.661
133.564
129.104
129.064
127.228
126.272
125.902
118.908
105.645
77.440
77.016
76.593
68.648
55.321
42.382
17.637
OH
O
2aa
f1 (ppm)


7.260
7.161
7.142
7.133
7.118
7.110
7.090
3.700
3.677
2.961
2.938
2.915
2.891
2.465
2.441
1.900
1.877
1.855
1.257
0.918
0.896
OH
2ab
4.07
2.00
0.99
2.07
1.04
3.21
6.20
f1 (ppm)


140.813
140.027
129.367
127.180
77.491
77.066
76.643
68.761
45.065
42.033
30.217
22.426
17.635
OH
2ab
f1 (ppm)


7.338
7.322
7.311
7.307
7.287
7.282
7.278
7.271
7.261
7.259
7.257
7.247
7.242
7.233
7.227
7.222
7.214
3.718
3.702
3.686
3.494
2.454
2.439
2.423
N
O
4
5.16
4.10
2.03
4.00
f1 (ppm)


137.716
129.222
128.271
127.174
77.485
77.061
76.638
67.010
63.471
53.628
N
O
4
f1 (ppm)