Supporting Information for

Mechanically Accelerated Catalytic Hydrogenation: Correlating Physical State, Reaction Rate, And Interface Area

Federico Cuccu, Francesco Basoccu, Claudia Fattuoni, Andrea Porcheddu

Number of pages: 80

Number of figures: 4

Number of schemes: 3

Number of tables: 1

Contents

1. General information

Commercially available reagents were purchased from Acros, Aldrich, Strem Chemicals, Alfa-Aesar, TCI Europe and used as received. All reactions were monitored by thin-layer chromatography (TLC) performed on glass-backed silica gel 60 F254, 0.2 mm plates (Merck), and compounds were visualized under UV light (254 nm) or using cerium ammonium molybdate solution with subsequent heating. The eluents were technical grade. Mechanochemical reactions were carried out using a MM 500 Vario ball mill apparatus. The reagents were milled using a Stainless Steel (SUS 304) and Zirconia screw capped grinding jar (10 mL and 5 mL) equipped with balls (ϕ = 8 mm) of the same material, or with Ertalyte® SmartSnap jars equipped with ZrO_2 balls (ϕ = 8 mm). Precisely, the zirconium oxide of the vessels and balls used for all reactions accomplished in the mixer mill is yttrium oxide stabilized (ZrO_2-Y). These parameters were applied if not stated otherwise. ^{1}H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III HD 600 MHz NMR spectrometer at 298 K and were calibrated using trimethylsylane (TMS). Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referred to the residual hydrogen in the solvent ($CHCl_3$, 7.27 ppm or DMSO 2.54 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br s = broad singlet, and combination of thereof), coupling constant (*J*) in Hertz (Hz) and integration. Carbon chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$, δ 77.0 ppm or δ DMSO-d_6 δ 39.5 ppm). Deuterated NMR solvents were obtained from Aldrich and TCI. Samples were analysed using an Agilent 5977B MS interfaced to the GC 7890B equipped with a DB-5ms column (J & W), injector temperature at 230 °C, detector temperature at 280 °C, helium carrier gas flow rate of 1 ml/min. The GC oven temperature program was 60°C initial temperature with 4 min hold time and ramping at 15°C/min to a final temperature of 270°C with 7 min hold time. 1 µL of each sample was injected in split (1:20) mode. After a solvent delay of 3 minutes mass spectra were acquired in full scan mode using 2.28 scans/s with a mass range of 50–500 Amu. Retention times of different compounds were determined by injecting pure compound under identical conditions. All the experiments were carried out in duplicate to ensure reproducibility of the experimental data. Yields refer to pure isolated materials, if not otherwise stated.

2. List of reagents

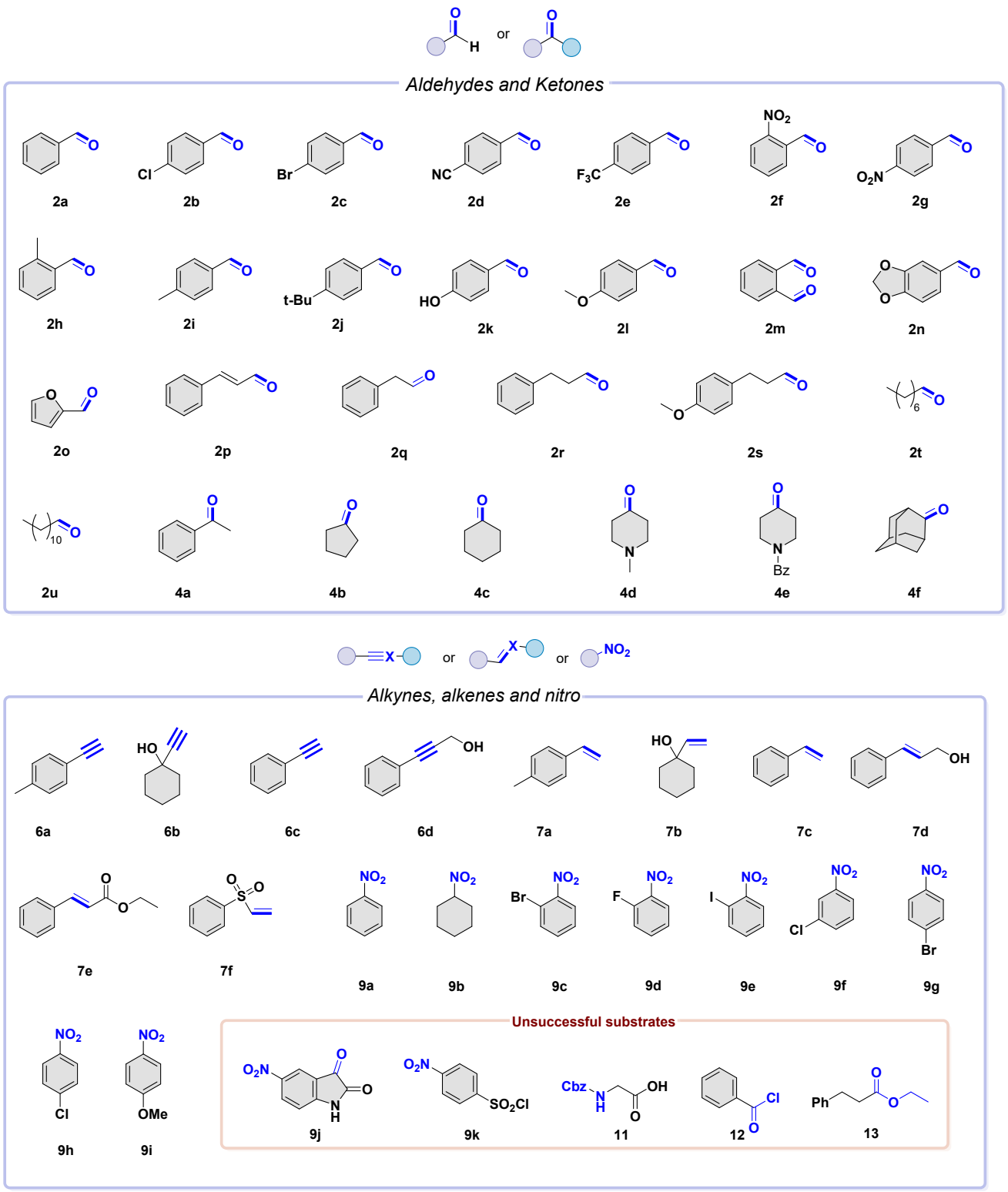


Figure S1. The list of all the substrates used for generating the scope and limitations of this work.

3. Pressure calculation

We considered the following equation for calculating an approximate value of hydrogen pressure inside our vessels under different conditions:

$$P = \frac{(n \cdot R \cdot T)}{V}$$

Where P is the pressure (atm) of the system, *n* is the number of moles of H_2, R is the gas constant [(l · atm) / (mol · K)], T is the temperature (K) and V is the volume (L).

Calculation of the H_2 pressure (1 mmol scale, scope)

Considering the volume of the jar (10 mL = 0.01 L), and subtract the volume occupied by an 8 mm ball (267,95 mm^3 = 0,00026795 L). We neglected the volume of the reagent.

We then have a total volume of **0,00973205 L**.

The number of moles of H_2 is stoichiometric with the number of moles of diboron compound **1** and water (2 mmol = **0.002 mol**).

The overall temperature has been approximated to ambient temperature (25 °C = **298 K**).

The gas constant is **0,0821 · [(l · atm) / (mol · K)]**

$$P = \frac{(0.002\,mol \cdot 0{,}0821\ \cdot\ [(l\ \cdot\ atm)\ /\ (mol\ \cdot\ K)] \cdot 298\,K)}{0{,}00973205\,L} = \mathbf{5.02\ atm}$$

Calculation of the H_2 pressure (0.3 mmol scale, kinetics)

Considering the volume of the jar (5 mL = 0.005 L), and subtract the volume occupied by an 8 mm ball (267,95 mm^3 = 0,00026795 L). We neglected the volume of the reagent.

We then have a total volume of **0,00473205 L**.

The number of moles of H_2 is stoichiometric with the number of moles of diboron compound **1** and water (0.6 mmol = **0.0006 mol**).

The overall temperature has been approximated to ambient temperature (25 °C = **298 K**).

The gas constant is **0,0821 · [(l · atm) / (mol · K)]**

$$P = \frac{(0.0006\,mol \cdot 0{,}0821\ \cdot\ [(l\ \cdot\ atm)\ /\ (mol\ \cdot\ K)] \cdot 298\,K)}{0{,}00473205\ \ L} = \mathbf{3{,}10\ atm}$$

Calculation of the H_2 pressure (20 mmol scale, scale-up)

Considering the volume of the jar (50 mL = 0.05 L), and subtract the volume occupied by a 10 mm ball (523,60 mm^3 = 0,00052360 L). We neglected the volume of the reagent.

We then have a total volume of **0,0494764 L**.

The number of moles of H_2 is stoichiometric with the number of moles of diboron compound **1** and water (20 mmol = **0.02 mol**).

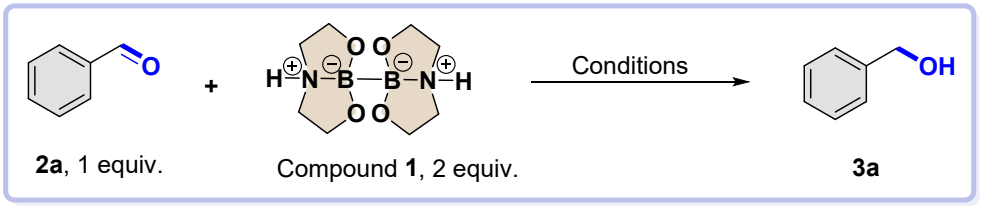
The overall temperature has been approximated to ambient temperature (25 °C = **298 K**).

The gas constant is **0,0821 · [(l · atm) / (mol · K)]**

$$P = \frac{(0.02\,mol \cdot 0{,}0821\ \cdot\ [(l\ \cdot\ atm)\ /\ (mol\ \cdot\ K)] \cdot 298\,K)}{0{,}0494764\ \ L} = \mathbf{9{,}89\ atm}$$

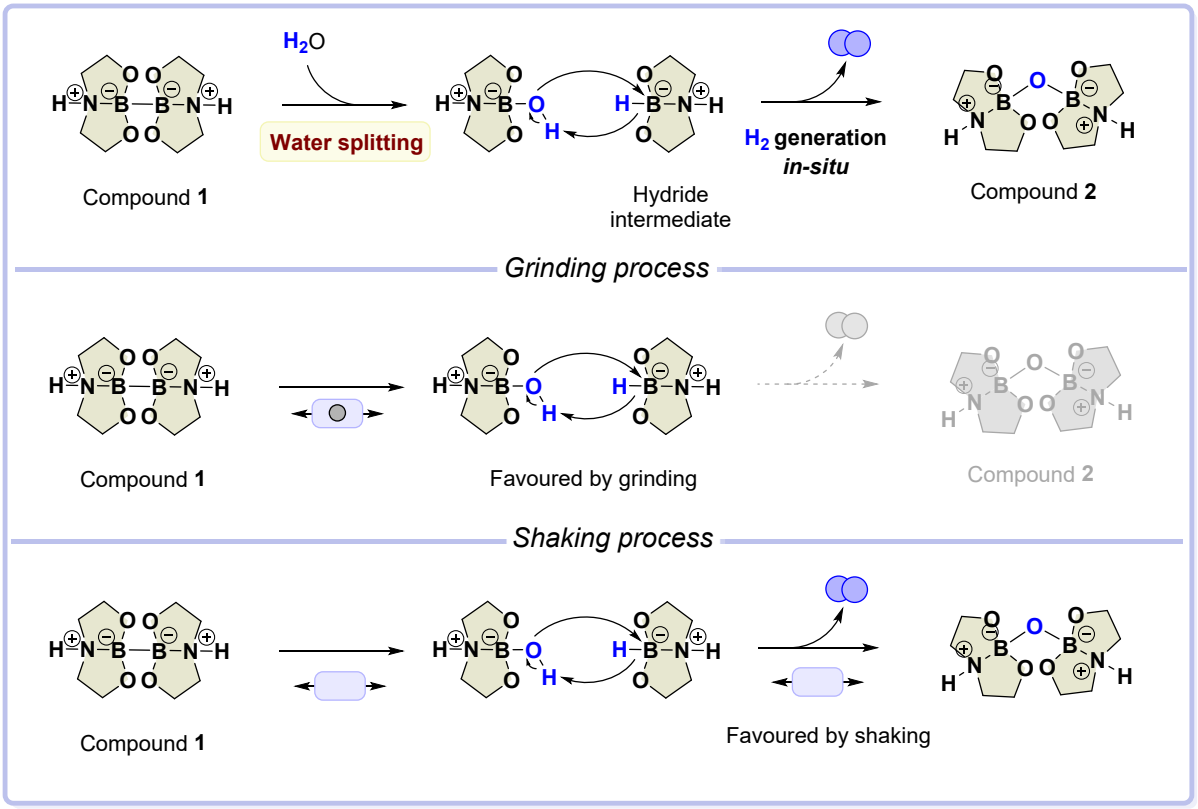
4. Optimization for the carbonyl reduction and reaction mechanism

Table S1. Table for the optimization of the carbonyl reduction



Entry	Time	Frequency	Material	Balls	Yield[c]
1	**90 min**	**30 Hz**	**SS**	**1 (8 mm)**	**98%**
2	90 min	25 Hz	SS	1 (8 mm)	76%
3	90 min	30 Hz	ZrO_2	1 (8 mm)	96%
4	90 min	30 Hz	Ertalyte®	1 (8 mm)[a]	97%
5	90 min	30 Hz	SS	1 (2 mm)	23%
6	90 min	30 Hz	SS	-	8%
7[b]	90 min	30 Hz	SS	1 (8 mm)	95%

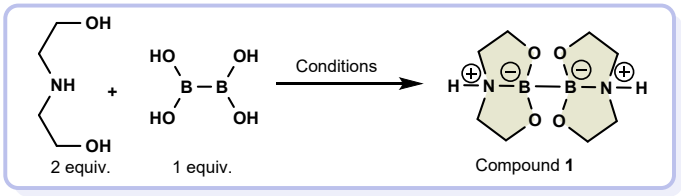
Reaction conditions: benzaldehyde **2a** (1 mmol), diboron compound **1** (2 mmol) and H_2O (2 mmol) were placed inside the vessel (10 mL volume) and the milling process was started. [a] ZrO_2 ball. [b] D_2O in place of H_2O. [c] Yields refers to GC-MS analysis.



Scheme S1. Proposed reaction mechanism for the water splitting process mediated by the diboron compound **1**. The mechanism is supported by the hydrogen generation (detected by GC-MS) and by the crystallographic data showing the generated compound **2**.

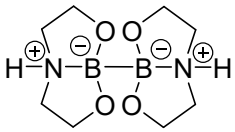
5. Synthetic procedures

5.1. Synthesis of 2,2'-Bi(1,3,6,2-dioxazaborocane) (Compound 1)



A 10 mL SS jar equipped with one SS milling ball (8 mm φ, $mass_{tot}$ 2.09 g) was filled with tetrahydroxydiboron (1 mmol) and diethanolamine (2 mmol). The vessel was then closed, and the reaction was conducted for 20 min at a frequency of 30 Hz. At the end of the reaction, the mixture was rinsed in EtOAc (10 mL), and the solvent was removed with a Pasteur pipette. Lastly, the pure compound **1** was concentrated under reduced pressure (in the case of one pot synthesis, the solid was let to evaporate under the fume hood for around 20 min)

Compound 1 (2,2'-Bi(1,3,6,2-dioxazaborocane))



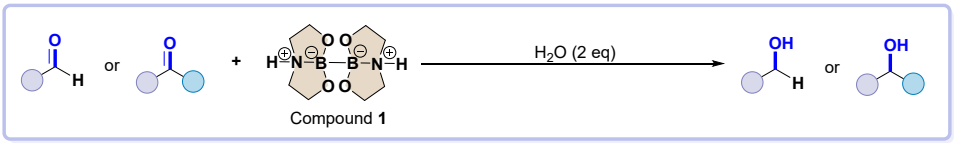
The title compound was synthesized according to the general procedure stated above. Tetrahydroxydiboron (89.7 mg, 1 mmol) and diethanolamine (192 µL, 2 mmol) were used, to afford **1** as a white solid (193.7 mg, 0.85 mmol, 85%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.85-3.83 (t, J = 6 Hz, 8H), 3.02-3.00 (t, J = 6 Hz, 8H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 58.9, 49.5.

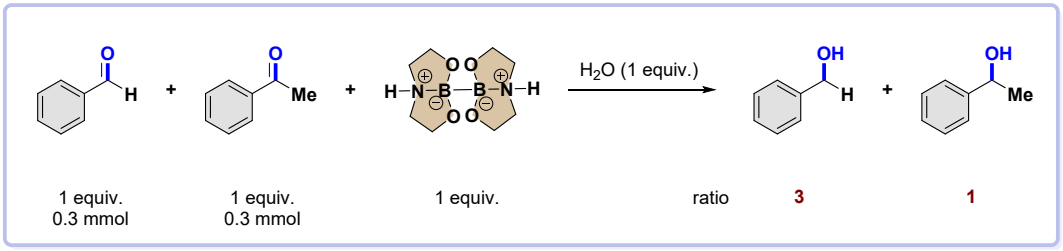
The spectroscopic data closely match the ones previously reported in the literature.[1]

5.2. General procedure for the synthesis of primary and secondary alcohols



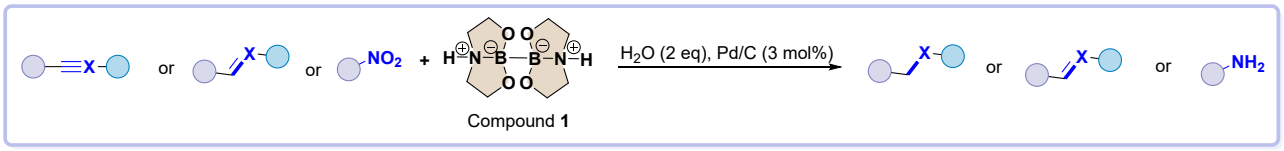
A 10 mL SS jar equipped with one SS milling ball (8 mm φ, $mass_{tot}$ 2.09 g) was filled with aldehyde **2a-u** or ketone **4a-f** (1 mmol), diboron compound **1** (2 mmol) and H_2O (2 mmol). The addition of 1 mmol of LiCl was required in the case of substrates **2q-u** and ketones **4a-f**. The vessel was then closed, and the reaction was conducted under ball milling conditions for 90 min at a frequency of 30 Hz. At the end of the reaction, the crude was recovered with EtOAc (10 mL) and filtered on paper. In few cases for ketones and aliphatic aldehydes, a short silica pad (1.0 g) was required for a further purification. Lastly, the solvent was removed under reduced pressure to afford the pure alcohols **3a-u** and **5a-f**.

Carbonyl competition experiments



A 5 mL SS jar equipped with one SS milling ball (8 mm φ, $mass_{tot}$ 2.09 g) was filled with aldehyde **2a** (1 mmol) and ketone **4a** (1 mmol), diboron compound **1** (1 mmol) and H_2O (1 mmol). The vessel was then closed, and the reaction was conducted under ball milling conditions for 90 min at a frequency of 30 Hz. At the end of the reaction, the crude was recovered with EtOAc (10 mL) and filtered on paper. The crude was analysed *via* GC-MS.

5.3. General procedure for the synthesis of alkenes, alkanes and amines



➢ A 10 mL SS jar equipped with one SS milling ball (8 mm φ, $mass_{tot}$ 2.09 g) was filled with alkyne **6a-c** and **6g** (1 mmol), **1** (2 mmol), Pd/C (3 mol %) and H_2O (2 mmol). The vessel was then closed, and the reaction was conducted for 90 min at a frequency of 30 Hz. At the end of the reaction, the crude was recovered with EtOAc (10 mL). In some cases, a short silica pad (1 g) was required for further purification. Lastly, the solvent was removed under reduced pressure to afford the pure alkane **8a-c** and **8g**.

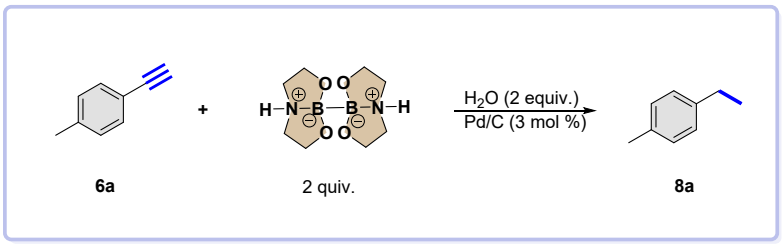
➢ A 10 mL SS jar was filled with alkyne **7a-b, 7d-f**, **8g**, and **11a** (1 mmol), **1** (2 mmol), Pd/C (3 mol %), and H_2O (2 mmol). The vessel was then closed, and the reaction was conducted for 90 min at a frequency of 30 Hz *without any grinding ball*. At the end of the reaction, the crude was recovered with EtOAc (10 mL). Lastly, the solvent was removed under reduced pressure to afford the pure alkane **8a-b**, **8d-f**, **8h** and **11b**.

➢ A 10 mL SS jar equipped with one SS milling ball (8 mm φ, $mass_{tot}$ 2.09 g) was filled with nitro compounds **9a-i** (1 mmol), **1** (3 mmol), Pd/C (3 mol %) and H_2O (3 mmol). The vessel was then closed, and the reaction was conducted for 90 min at a frequency of 30 Hz. At the end of the reaction, the crude was recovered with EtOAc (10 mL). Lastly, the solvent was removed under reduced pressure to afford the pure alkane **10a-i**.

Scale up experiments

A 50 mL SS jar equipped with one SS milling ball (10 mm φ, $mass_{tot}$ 3.89 g) was filled with alkyne **6a** (10 mmol), **1** (20 mmol), Pd/C (3 mol %) and H_2O (20 mmol). The vessel was then closed, and the reaction was conducted for 90 min at a frequency of 30 Hz. At the end of the reaction, the crude was recovered with EtOAc (10 mL). Lastly, the solvent was removed under reduced pressure to afford the pure alkane **8a** in 90% yield.

Catalyst reuse experiments



A 10 mL Erthalyte® jar equipped with one ZrO_2 milling ball (8 mm diameter) was filled with alkyne **6a** (1 mmol), **1** (2 mmol), Pd/C (3 mol %) and H_2O (2 mmol). The vessel was then closed and the mechanochemical reaction was conducted for 90 min at a frequency of 30 Hz. At the end of the reaction, the crude was recovered in EtOAc (10 mL) and analysed by GC-MS. Subsequently, once the jar was cleaned with ethyl acetate and the solvent was removed, the jar walls appeared covered by the catalyst (black coloured). The reaction was performed again adding new reagents except for the Pd catalyst. In the following plot are shown the results.

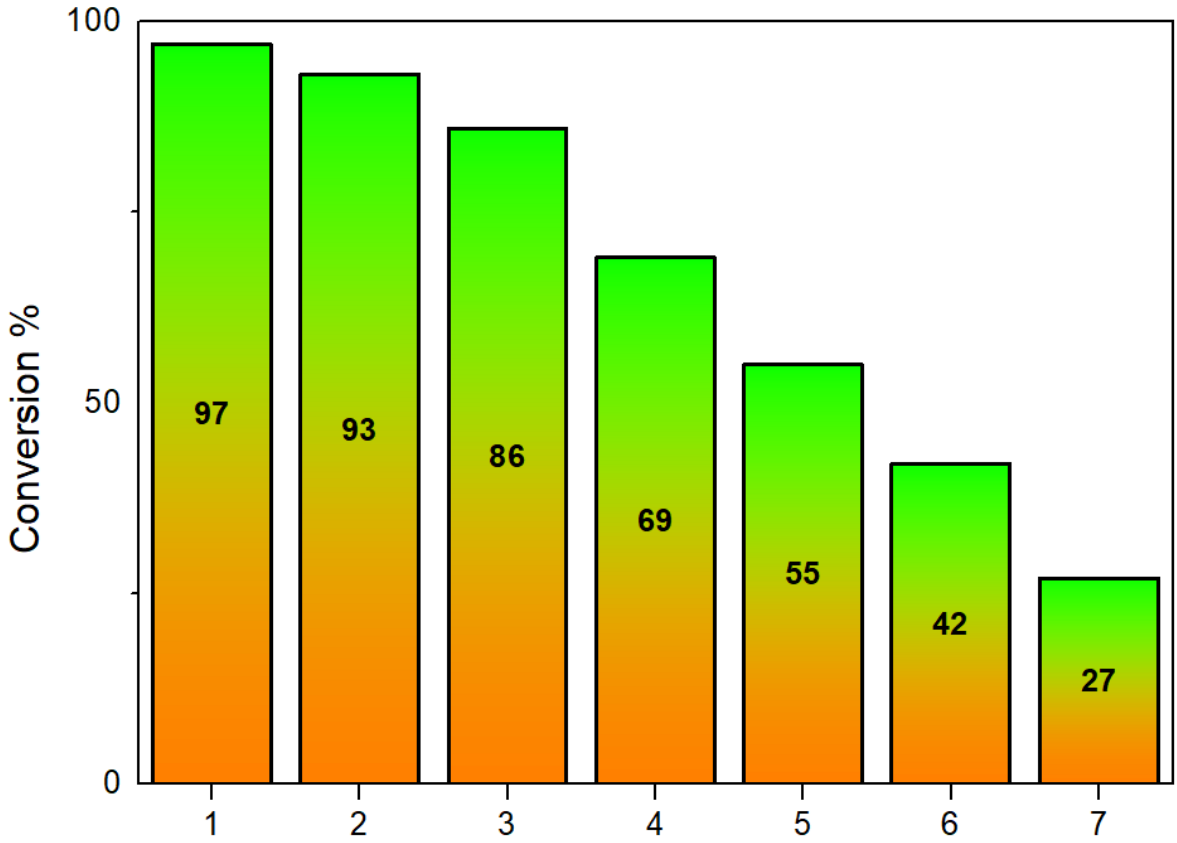


Figure S2. The reuse plot for the Pd/C incorporated in the Erthalyte® jar.

6. SEM images and general considerations

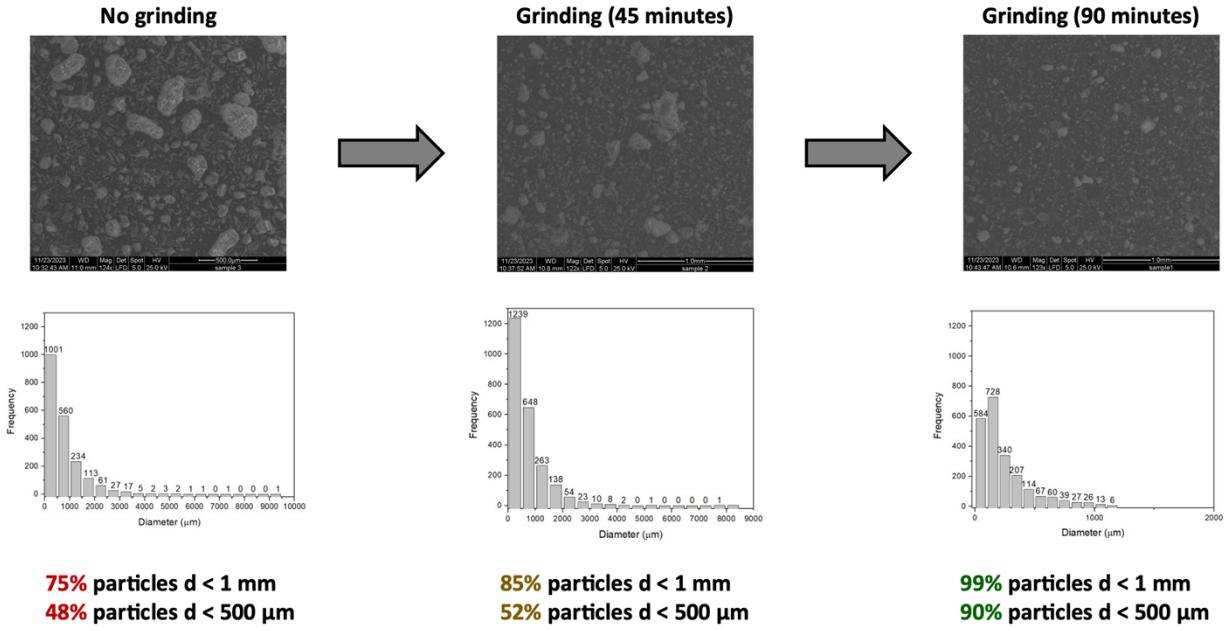
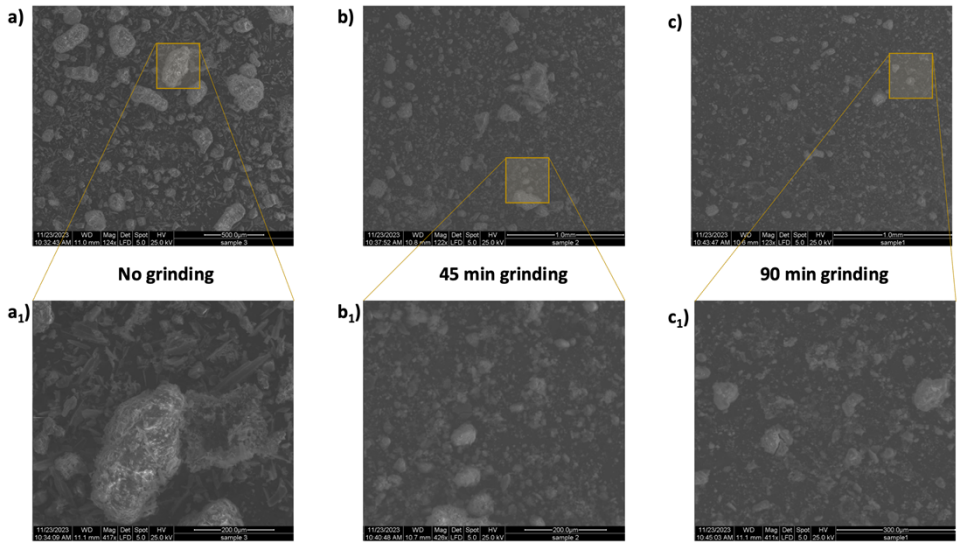
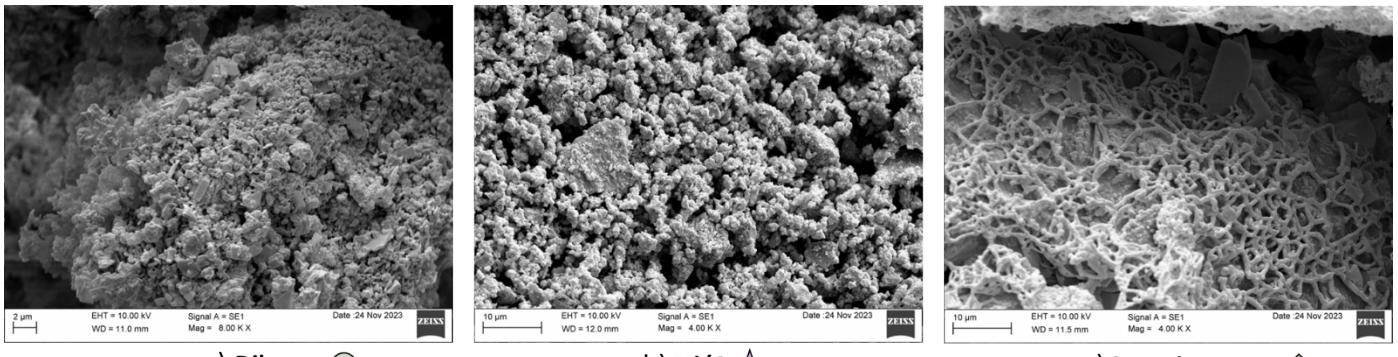


Figure S3. SEM images and size/particle distribution.

General considerations

The images demonstrate a clear and systematic reduction in particle size achieved through grinding. Over a period of 90 minutes, the observable reduction in particle size progresses from a non-grinding state to complete diminution. The initial assessment reveals a consistent evolution in size distribution, particularly distinguished by particles with diameters below 500 µm. The discernible changes in the observed patterns highlight the evident average percentage of particles within this specified diameter range, reaching the maximum of 90% after 90 minutes of grinding. The image below shows the "*erosion-like*" effect, which is clearly evident in snapshots **b**/**b1** and eventually leads to a total reduction in the size of the particles (going from **a**/**a**$_1$ to **c**/**c**$_1$).





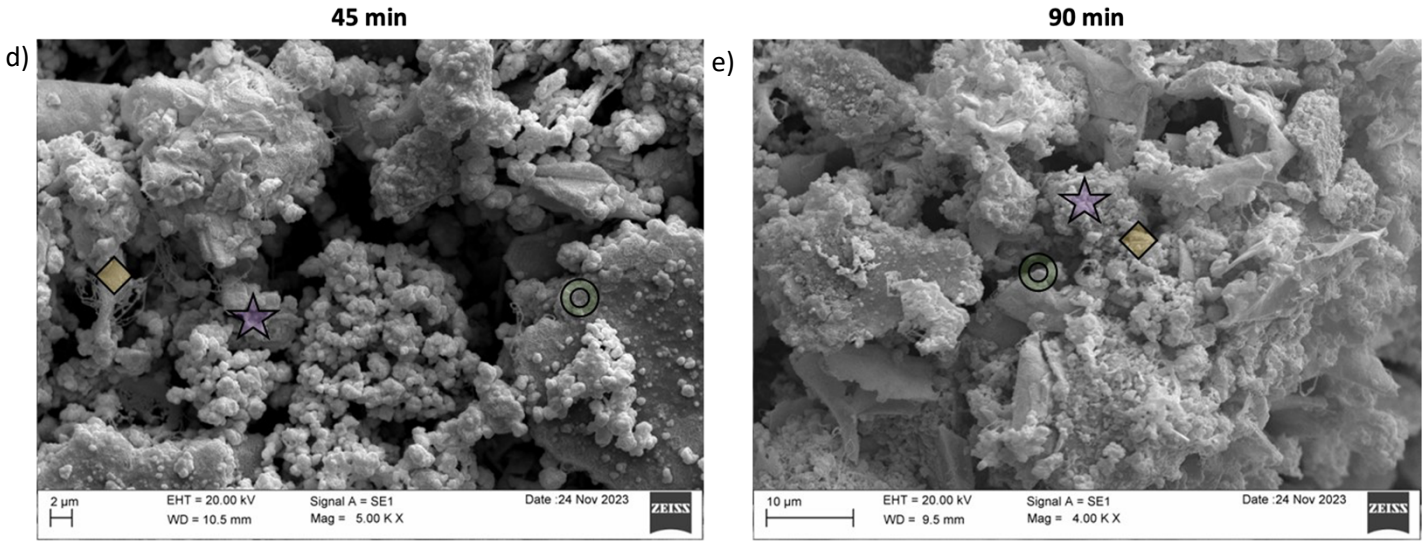
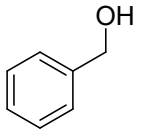


Figure S4. SEM images of the reagents; a) diboron compound **1**; b) Pd/C; c) Phenyl vinyl sulfone; d) reaction mixture after 45 minutes grinding; e) reaction mixture after 90 minutes grinding.

7. Characterization data of products

Benzyl alcohol 3a



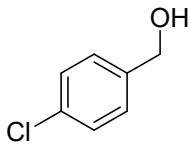
The title compound was synthesized according to the general procedure stated above. **2a** (102 µl, 1 mmol), (456 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3a** as a colourless liquid (106.3 mg, 0.98 mmol, 98%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.25 (m, 5H), 4.60 – 4.58 (m, 2H), 2.66 – 2.48 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 140.9, 128.6, 127.6, 127.1, 65.2.

The spectroscopic data closely match the ones previously reported in the literature.[1]

4-Chloro benzyl alcohol 3b



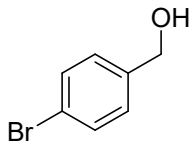
The title compound was synthesized according to the general procedure A. **2b** (140.6, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3b** as a white solid (134.9 mg, 0.95 mmol, 95%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.32 (d, J = 8.8 Hz, 2H), 7.30-7.29 (d, J = 8.8 Hz, 2H), 4.67 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.4, 133.5, 128.8, 128.4, 64.7.

The spectroscopic data closely match the ones previously reported in the literature.[2]

4-Bromo benzyl alcohol 3c



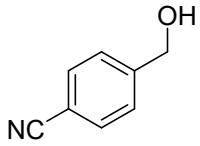
The title compound was synthesized according to the general procedure A. **2c** (185.0, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3c** as a pale-yellow solid (179.6 mg, 0.96 mmol, 96%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.49-7.48 (m, 2H), 7.25-7.24 (m, 2H), 4.66 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.9, 131.8, 128.7, 121.6, 64.8.

The spectroscopic data closely match the ones previously reported in the literature.[1]

4-Cyano benzyl alcohol 3d



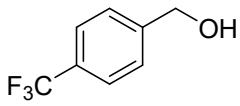
The title compound was synthesized according to the general procedure A. **2d** (131.1, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3d** as a colourless solid (123.8 mg, 0.93 mmol, 93%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63-7.62 (d, J = 7.8 Hz, 2H), 7.47-7.46 (d, J = 7.8 Hz, 2H), 4.76 (s, 2H), 2.34-2.39 (bs, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.4, 132.4, 127.2, 119.0, 111.3, 64.3.

The spectroscopic data closely match the ones previously reported in the literature.[3]

4-Trifluoromethyl benzyl alcohol 3e



The title compound was synthesized according to the general procedure A. **2e** (174.1 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3e** as a yellowish liquid (174.4 mg, 0.99 mmol, 99%).

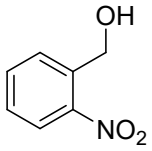
^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.61-7.60 (d, J = 8.4 Hz, 2H), 7.47-7.45 (d, J = 8.4 Hz, 2H), 4.75-4.74 (s, 2H), 2.12 (bs, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.8, 129.1 (q, $J_{C\text{-}F}$ = 135.9 Hz), 125.7, 125.6, 123.9 (q, $J_{C\text{-}F}$ = 271.8 Hz), 64.6.

^{19}F NMR (565 MHz, $CDCl_3$): δ= -62.55.

The spectroscopic data closely match the ones previously reported in the literature.[4]

2-Nitro benzyl alcohol 3f

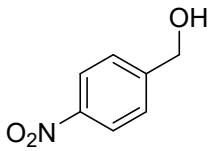


The title compound was synthesized according to the general procedure A. **2f** (151.1 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3f** as a yellowish liquid (79.6 mg, 0.52 mmol, 52%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.11-8.10 (m, 1H), 7.75-7.73 (m, 1H), 7.69-7.66 (m, 1H), 7.49-7.47 (m, 1H), 4.98-4.97 (s, 2H), 2.53-2.51 (bs, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.0, 136.9, 134.3, 130.2, 128.7, 125.2, 62.7.

The spectroscopic data closely match the ones previously reported in the literature.[5]



4-Nitro benzyl alcohol 3g

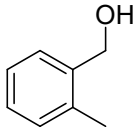
The title compound was synthesized according to the general procedure A. **2g** (151.1 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3g** as a yellowish liquid (145.5 mg, 0.95 mmol, 95%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.22 – 8.21 (m, 2H), 7.54-7.53 (m, 2H), 4.84 (s, 2H), 1.98 (bs, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 148.3, 147.5, 127.2, 123.9, 64.2.

The spectroscopic data closely match the ones previously reported in the literature.[1]

2-Methyl benzyl alcohol 3h



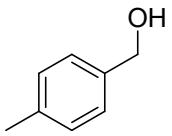
The title compound was synthesized according to the general procedure A. **2h** (120.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3h** as a colourless liquid (114.8 mg, 0.94 mmol, 94%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36-7.35 (m, 1H), 7.22-7.18 (m, 3H), 4.71 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.8, 136.3, 130.5, 128.0, 127.9, 126.2, 63.7, 18.8.

The spectroscopic data closely match the ones previously reported in the literature.[5]

4-Methyl benzyl alcohol 3i



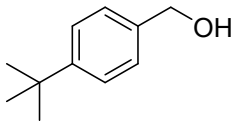
The title compound was synthesized according to the general procedure A. **2i** (120.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), and H_2O (36 µl, 2 mmol) were used to afford **3i** as a white solid (118.5 mg, 0.97 mmol, 97%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26-7.25 (dd, J = 7.9 Hz, 2H), 7.18-7.17 (dd, J = 7.9 Hz, 2H), 4.65-4.64 (d, J = 5.8 Hz, 2H), 2.36 (s, 3H), 1.67-1.65 (t, J = 5.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.1, 137.5, 129.4, 127.3, 65.4, 21.3.

The spectroscopic data closely match the ones previously reported in the literature.[2]

4-*tert*-Buthyl benzyl alcohol 3j

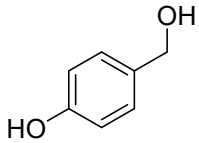


The title compound was synthesized according to the general procedure A. **2j** (162.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3j** as a colourless liquid (161.0 mg, 0.98 mmol, 98%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41-7.40 (dd, J = 8.8 Hz, 2H), 7.32-7.31 (dd, J = 8.8 Hz, 2H), 4.66 (s, 2H), 1.34 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.9, 138.1, 127.0, 125.6, 65.4, 34.7, 31.5.

The spectroscopic data closely match the ones previously reported in the literature.[6]



4-hydroxy benzyl alcohol 3k

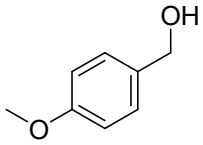
The title compound was synthesized according to the general procedure A. **2k** (122.1 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3k** as a colourless liquid (111.7 mg, 0.90 mmol, 90%).

^{1}H NMR (600 MHz, DMSO): δ = 9.21 (s, 1H), 7.11-7.09 (dd, J = 7.6 Hz, 2H), 6.71-6.69 (dd, J = 7.6 Hz, 2H), 4.93 (s, 1H), 4.36 (s, 2H).

^{13}C NMR (151 MHz, DMSO): δ = 156.2, 132.8, 128.0, 114.8, 62.8.

The spectroscopic data closely match the ones previously reported in the literature.[5]

4-Methoxy benzyl alcohol 3l

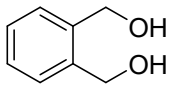


The title compound was synthesized according to the general procedure A. **2l** (136.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3l** as a colourless liquid (136.8 mg, 0.99 mmol, 99%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 – 7.27 (dd, J = 8.3 Hz, 2H), 6.90 – 6.88 (dd, J = 8.3 Hz, 2H), 4.59 (s, 2H), 3.80 (s, 3H), 1.99 – 1.83 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 159.3, 133.3, 128.7, 114.1, 65.1, 55.4.

The spectroscopic data closely match the ones previously reported in the literature.[1]



1,2-Benzenedimethanol 3m

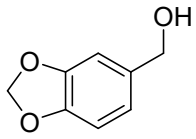
The title compound was synthesized according to the general procedure A. **2m** (134.1 mg, 1 mmol), **1** (683.7 mg, 3 mmol) and H_2O (48 µl, 3 mmol) were used, to afford **3m** as a white solid (123.0 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30 (m, 4H), 4.62 (s, 4H), 3.76 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 139.5, 129.8, 128.6, 64.1.

The spectroscopic data closely match the ones previously reported in the literature.[7]

Piperonyl alcohol 3n



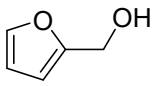
The title compound was synthesized according to the general procedure A. **2n** (150.1 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3n** as a white solid (138.1 mg, 0.91 mmol, 91%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.85 – 6.76 (m, 3H), 5.94 (s, 2H), 4.55 (s, 2H), 1.95 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.9, 147.2, 135.0, 120.6, 108.3, 108.0, 101.1, 65.3.

The spectroscopic data closely match the ones previously reported in the literature.[6]

Furfuryl alcohol 3o



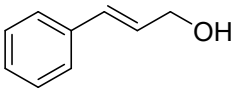
The title compound was synthesized according to the general procedure A. **2o** (96.1 mg, 1 mmol), **1** (455.8 mg, 2 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3o** as a yellowish liquid (94.2 mg, 0.96 mmol, 96%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35 (m, 1H), 6.30 – 6.29 (m, 1H), 6.23 – 6.22 (m, 1H), 4.49 (s, 2H), 3.43 (bs, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.1, 142.4, 110.3, 107.6, 57.0.

The spectroscopic data closely match the ones previously reported in the literature.[8]

Cinnamyl alcohol 3p

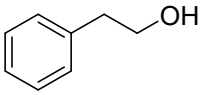


The title compound was synthesized according to the general procedure A. **2p** (132.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), and H_2O (36 µl, 2 mmol) were used to afford **3p** as a colourless liquid (126.1 mg, 0.94 mmol, 94%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34 – 7.19 (m, 5H), 6.58 – 6.54 (m, 1H), 6.32-6.28 (m,1H), 4.26-4.25 (m, 2H), 2.58 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 136.8, 131.0, 128.7, 128.6, 127.7, 126.5, 63.5.

The spectroscopic data closely match the ones previously reported in the literature.[1]



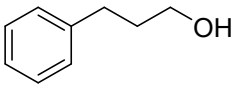
2-Phenyl-1-ethanol 3q

The title compound was synthesized according to the general procedure B. **2q** (120.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3q** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 95:5% to acetate 100% v/v) as a colourless liquid (45.2 mg, 0.37 mmol, 37%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30 – 7.20 (m, 5H), 3.81-3.79 (t, J = 5.8 Hz, 2H), 2.84-2.82 (t, J = 5.8 Hz, 2H), 1.99 (bs, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 138.6, 129.1, 128.6, 126.5, 63.7, 39.2.

The spectroscopic data closely match the ones previously reported in the literature.[9]



3-Phenyl-1-propanol 3r

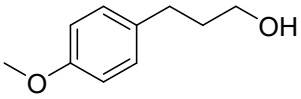
The title compound was synthesized according to the general procedure B. **2r** (134.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), LiCl (42,4 mg, 1 mmol), and H_2O (36 µl, 2 mmol) were used, to afford **3r** after a short silica pad (SiO_2/n-heptane:ethyl acetate 95:5% to acetate 100% v/v) as a colourless liquid (54.5 mg, 0.40 mmol, 40%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31-7.28 (m, 2H), 7.21 – 7.18 (m, 3H), 3.69-3.67 (t, 2H), 2.73 – 2.71 (m, 2H), 1.93 – 1.88 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 142.0, 128.6, 128.5, 126.0, 62.4, 34.4, 32.2.

The spectroscopic data closely match the ones previously reported in the literature.[10]

3-(4-Hydroxyphenyl)-1-propanol 3s



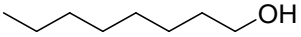
The title compound was synthesized according to the general procedure B. **2s** (164.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3s** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 95:5% to acetate 100% v/v) as a yellowish liquid (69.8 mg, 0.42 mmol, 42%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.13-7.11 (d, J = 8.3, Hz, 2H), 6.84-6.83 (dd, J = 8.3 Hz, 2H), 3.79 (s, 3H), 3.67 – 3.65 (m, 2H), 2.67 – 2.64 (m, 2H), 1.89 – 1.84 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.9, 134.0, 129.4, 114.0, 62.4, 55.4, 34.6, 31.3.

The spectroscopic data closely match the ones previously reported in the literature.[10]

Octanol 3t



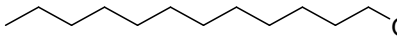
The title compound was synthesized according to the general procedure B. **2t** (128.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3t** after a short silica pad (SiO_2/*n*-heptane: ethyl acetate 95:5% to acetate 100% v/v) as a colourless liquid (45.6 mg, 0.35 mmol, 35%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.57-3.54 (m, 2H), 2.64 – 2.51 (bs, 1H), 1.53-1.49 (m, 2H), 1.31-1.22 (m, 10H), 0.85-0.83 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 62.9, 32.8, 31.9, 29.5, 29.4, 25.9, 22.7, 14.1.

The spectroscopic data closely match the ones previously reported in the literature.[5]

Dodecanol 3u



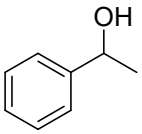
The title compound was synthesized according to the general procedure B. **2u** (184.3 mg, 1 mmol), **1** (455.8 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **3u** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 95:5% to acetate 100% v/v) as a colourless solid (59.6 mg, 0.32 mmol, 32%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.64-3.62 (m, 2H), 1.58-1.54 (m, 2H), 1.36-1.26 (m, 19H), 0.89-0.86 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 63.2, 33.0, 32.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 25.9, 22.8, 14.3.

The spectroscopic data closely match the ones previously reported in the literature.[11]

1-Phenyl-1-ethanol 5a

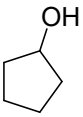


The title compound was synthesized according to the general procedure B. **4a** (120.2, 1 mmol),**1** (456 mg, 2 mmol), LiCl (42,4 mg, 1 mmol), and H_2O (36 µl, 2 mmol) were used, to afford **5a** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 95:5% to acetate 100% v/v) as a colourless liquid (52.5 mg, 0.43 mmol, 43%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32-7.22 (m, 5H), 4.82-4.78 (m, 1H), 2.54-2.41 (m, 1H), 1.44-1.42 (d, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 145.9, 128.5, 127.4, 125.5, 70.3, 25.2.

The spectroscopic data closely match the ones previously reported in the literature.[2]



Cyclopentanol 5b

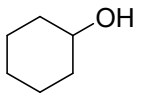
The title compound was synthesized according to the general procedure B. **4b** (84.12 mg, 1 mmol),**1** (456 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **5b** as a colourless liquid (85.3 mg, 0.99 mmol, 99%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.33-4.32 (m, 1H), 1.80-1.72 (m, 4H), 1.59-1.53 (m, 4H), 1.38-1.36 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$): δ = 74.2, 35.7, 23.4.

The spectroscopic data closely match the ones previously reported in the literature.[12]

Cyclohexanol 5c



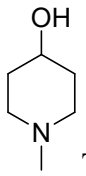
The title compound was synthesized according to the general procedure B. **4c** (98.2 mg, 1 mmol),**1** (456 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **5c** as a colourless liquid (98.2 mg, 0.98 mmol, 98%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.55-3-51 (m, 1H), 2.54-2.39 (m, 1H), 1.84-1.81 (m, 2H), 1.69-1.65 (m, 2H), 1.50-1.47 (m, 1H), 1.25-1.09 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 70.3, 35.5, 25.5, 24.2.

The spectroscopic data closely match the ones previously reported in the literature.[13]

4-Hydroxy-1-methylpiperidine 5d

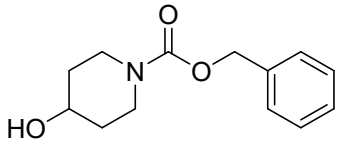


The title compound was synthesized according to the general procedure B. **4d** (113.16 mg, 1 mmol), **1** (456 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **5d** as a colourless liquid (112.69 mg, 0.98 mmol, 98%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.55 (m, 1H), 2.66 – 2.63 (m, 2H), 2.18 (s, 3H), 2.04 (m, 2H), 1.81 – 1.78 (m, 2H), 1.54 – 1.50 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 66.9, 53.4, 46.1, 34.4.

The spectroscopic data closely match the ones previously reported in the literature.[14]



1-(4-Hydroxy-1-piperidinyl)-2-phenylethanone 5e

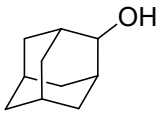
The title compound was synthesized according to the general procedure above. **4e** (233.3 mg, 1 mmol),**1** (456 mg, 2 mmol), (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **5e** as a yellowish oil (223.5 mg, 0.95 mmol, 95%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.37-7.29 (m, 5H), 5.12 (s, 2H), 3.91-3.81 (m, 3H), 3.15-3.11 (m, 2H), 2.22-2.08 (bs, 1H), 1.86 -1.83 (m, 2H), 1.48-1.47 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 155.4, 136.8, 128.6, 128.1, 127.9, 67.4, 67.2, 41.5, 34.1.

The spectroscopic data closely match the ones previously reported in the literature.[15]

2-Adamantanol 5f

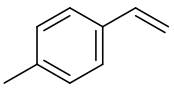


The title compound was synthesized according to the general procedure above. **4f** (150.2 mg, 1 mmol),**1** (456 mg, 2 mmol), LiCl (42,4 mg, 1 mmol) and H_2O (36 µl, 2 mmol) were used, to afford **5f** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 95:5% to acetate 100% v/v) as a white solid (63.8 mg, 0.42 mmol, 42%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.87 (s, 1H), 2.08-2.05 (m, 2H), 1.89-1.79 (m, 6H), 1.72-1.69 (m, 4H), 1.57-1.52 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 74.7, 37.7, 36.7, 34.7, 31.2, 27.7, 27.2.

The spectroscopic data closely match the ones previously reported in the literature.[16]



4-Methyl styrene7a

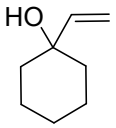
The title compound was synthesized according to the general procedure above. **6a** (116.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **5a** as a colourless liquid (115.8 mg, 0.98 mmol, 98%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.29-7.27 (d, J = 8.8 Hz, 2H), 7.11-7.09 (d, J = 8.8 Hz 2H), 6.69-6.64 (m, 1H), 5.69-5.65 (m, 1H), 5.17-5.15 (m, 1H), 2.31 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 137.7, 136.9, 135.0, 129.3, 126.3, 112.8, 21.3.

The spectroscopic data closely match the ones previously reported in the literature.[17]

1-Ethenylcyclohexanol 7b



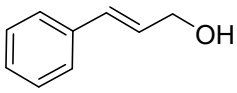
The title compound was synthesized according to the general procedure above. **6b** (124.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford an inseparable mixture of **7b** and unreacted **6b** (116.1 mg, 0.92 mmol, 92%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.98 (dd, J = 17.4, 10.8, 1H), 5.24 (dd, J = 17.4, 1.4, 1H), 5.04 (dd, J = 10.8, 1.4, 1H), 1.69–1.62 (m, 2H), 1.59–1.49 (m, 7H), 1.35–1.27 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.2, 111.6, 71.9, 37.7, 25.7, 22.2.

The spectroscopic data closely match the ones previously reported in the literature.[18]

Cinnamyl alcohol 7c



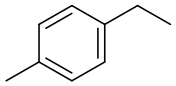
The title compound was synthesized according to the general procedure above. **6c** (132.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **7c** as a yellowish liquid (124.8 mg, 0.93 mmol, 93%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.35-7.33 (d, J = 7.8 Hz, 2H), 7.27-7.25 (m, 1H), 7.21-7.20 (d, J = 7.8 Hz, 2H), 6.58-6.56 (m, 1H), 5.89-5.85 (m, 1H), 4.44-4.43 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 136.7, 131.3, 131.2, 128.9, 128.4, 127.4, 59.8.

The spectroscopic data closely match the ones previously reported in the literature.[1]

4-methyl ethylbenzene 8a



The title compound was synthesized according to the general procedure above. **6a** (116.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **8a** as a colourless liquid (113.0 mg, 0.94 mmol, 94%).

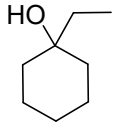
The title compound was synthesized according to the general procedure above. **7a** (118.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **8a** as a colourless liquid (116.6 mg, 0.97 mmol, 97%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.10 (m, 4H), 2.64-2.60 (q, J = 5.9 Hz, 2H), 2.32 (s, 3H), 1.24 – 1.21 (t, J = 5.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 141.4, 135.1, 129.1, 127.9, 28.6, 21.1, 15.9.

The spectroscopic data closely match the ones previously reported in the literature.[19]

1-Ethylcyclohexanol 8b



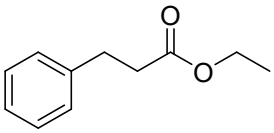
The title compound was synthesized according to the general procedure above. **6b** (124.2 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **8b** as a brownish oil (113.0 mg, 0.94 mmol, 94%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.61-1.24 (m, 13H), 0.90-0.88 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 71.6, 37.1, 35.0, 26.0, 22.4, 7.3.

The spectroscopic data closely match the ones previously reported in the literature.[20]

Ethyl 3-phenylpropanoate 8f



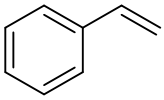
The title compound was synthesized according to the general procedure above. **7f** (176.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **8f** as a yellow liquid (172.9 mg, 0.97 mmol, 97%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30-7.28 (m, 2H), 7.22-7.19 (m, 3H), 4.15-4.11 (q, J = 7.0 Hz, 2H), 2.97-2.94 (t, J = 7.0 Hz, 2H), 2.64-2.61 (t, J = 6.5 Hz, 2H), 1.25-1.23 (t, J = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 173.1, 140.7, 128.6, 128.4, 126.4, 60.5, 36.1, 31.1, 14.3.

The spectroscopic data closely match the ones previously reported in the literature.[20]

Styrene 8g



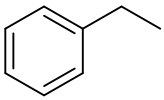
The title compound was synthesized according to the general procedure above. **6g** (102.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **8g** as a yellow liquid (103.2 mg, 0.99 mmol, 99%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, J = 7.6 Hz, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.7, 137.0, 128.7, 127.9, 126.4, 113.9.

The spectroscopic data closely match the ones previously reported in the literature.[20]

Ethylbenzene 8h



The title compound was synthesized according to the general procedure above. **6g** (102.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **8h** as a yellow liquid (101,9 mg, 0.96 mmol, 96%).

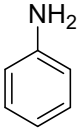
The title compound was synthesized according to the general procedure above. **6g** (104.2 mg, 1 mmol), **1** (227.9 mg, 1 mmol), Pd/C (3 mol %) and H_2O (18 µl, 1 mmol) were used, to afford **8h** as a yellow liquid (101,9 mg, 0.96 mmol, 96%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 2H), 7.25 – 7.15 (m, 3H), 2.68 (dtd, J = 10.1, 7.7, 2.3 Hz, 2H), 1.27 (tdd, J = 7.7, 3.5, 1.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 144.4, 128.5, 128.0, 125.7, 29.0, 15.8.

The spectroscopic data closely match the ones previously reported in the literature.[20]

Aniline 10a



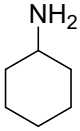
The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.21-7.19 (t, *J* = 7.8 Hz 2H), 6.82-6.80 (t, *J* = 7.8 Hz 1H), 6.72-6.71 (d, *J* = 7.7 Hz 2H), 3.65 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 146.5, 129.3, 118.6, 115.2.

The spectroscopic data closely match the ones previously reported in the literature.[21]

Cyclohexylamine 10b

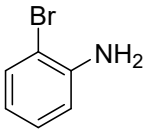


The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %), and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane: ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.61 (tt, *J* = 10.5, 3.9 Hz, 1H), 1.80 (dt, *J* = 12.5, 3.9 Hz, 2H), 1.70 (dp, *J* = 11.6, 3.9 Hz, 2H), 1.63 – 1.54 (m, 1H), 1.37 (s, 2H), 1.25 (qt, *J* = 12.7, 3.6 Hz, 2H), 1.12 (tt, *J* = 12.5, 3.7 Hz, 1H), 1.03 (qd, *J* = 12.5, 3.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 50.6, 37.1, 25.8, 25.3.
The spectroscopic data closely match the ones previously reported in the literature.[21]

2-Bromo aniline 10c



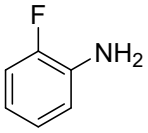
The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.13 – 7.08 (m, 1H), 6.76 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.65 – 6.60 (m, 1H), 4.07 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.2, 132.7, 128.5, 119.5, 115.9, 109.5.
The spectroscopic data closely match the ones previously reported in the literature.[21]

2-Fluoro aniline 10d

The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after

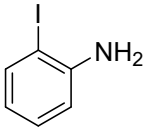


a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (m, 1H), 6.93 (m, 1H), 6.81 – 6.75 (m, 1H), 6.72 – 6.66 (m, 1H), 3.71 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 134.7 (d, J_{C-F} = 255.2 Hz), 124.6 (d, J_{C-F} = 15.1 Hz), 118.8, 117.1, 115.4 (d, J_{C-F} = 30.2 Hz).
The spectroscopic data closely match the ones previously reported in the literature.[21]

2-Iodo aniline 10e

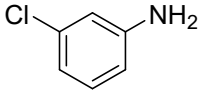


The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.8, 1.4 Hz, 1H), 7.14 (td, J = 7.6, 1.4 Hz, 1H), 6.75 (dd, J = 8.0, 1.5 Hz, 1H), 6.47 (td, J = 7.6, 1.5 Hz, 1H), 4.18 – 3.98 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 139.0, 129.3, 120.0, 114.7, 84.2.
The spectroscopic data closely match the ones previously reported in the literature.[21]

3-Chloro aniline 10f

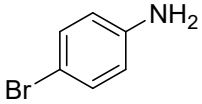


The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (m, 1H), 6.75 – 6.70 (m, 1H), 6.69 – 6.64 (m, 1H), 6.54 (m, Hz, 1H), 3.71 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 135.0, 130.4, 118.6, 115.1, 113.3.
The spectroscopic data closely match the ones previously reported in the literature.[21]

4-Bromo aniline 10g

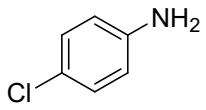


The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, J = 8.8 Hz, 2H), 6.59 – 6.54 (d, J = 8.8 Hz, 2H), 3.65 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.6, 132.1, 116.8, 110.3.
The spectroscopic data closely match the ones previously reported in the literature.[21]

4-Chloro aniline 10h

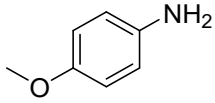


The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 2H), 6.65 – 6.58 (m, 2H), 3.64 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.1, 129.3, 123.3, 116.4.
The spectroscopic data closely match the ones previously reported in the literature.[21]

4-Methoxy aniline 10i



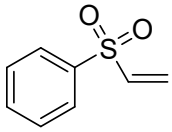
The title compound was synthesized according to the general procedure above. **9** (123.11 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **10** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 85:15%) as a colourless liquid (82.9 mg, 0.89 mmol, 89%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.77 – 6.73 (m, 2H), 6.68 – 6.63 (m, 2H), 3.75 (d, *J* = 0.7 Hz, 3H), 3.36 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.00, 140.1, 116.6, 115.0, 55.9.

The spectroscopic data closely match the ones previously reported in the literature.[21]

Phenyl ethyl sulfone 8f



The title compound was synthesized according to the general procedure above. **7f** (168.23 mg, 1 mmol), **1** (455.8 mg, 2 mmol), Pd/C (3 mol %) and H_2O (36 µl, 2 mmol) were used, to afford **8f** after a short silica pad (SiO_2/*n*-heptane:ethyl acetate 90:10%) as a white solid (102.14 mg, 0.60mmol, 60%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.66 (td, J = 7.5, 1.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 3.11 (qd, *J* = 7.4, 1.2 Hz, 2H), 1.27 (td, *J* = 7.4, 1.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.7, 133.8, 129.4, 128.3, 50.7, 7.6.

The spectroscopic data closely match the ones previously reported in the literature.[22]

8. References

1. Flinker, M.; Yin, H.; Juhl, R. W.; Eikeland, E. Z.; Overgaard, J.; Nielsen, D. U.; Skrydstrup, T.; *Angew. Chem. Int. Ed.* **2017**, 56, 15910.

2. García-Muñoz, A.; Ortega-Arizmendi, A. I.; García-Carrillo M. A.; Díaz, E.; Gonzalez-Rivas, N.; Cuevas-Yañez, E.; *Synth.* **2012**, 44, 14, 2237-2242

3. Tanwar, L.; Börgel, J.; Ritter, T.; *J. Am. Chem. Soc.* **2019**, 141, 45, 17983-17988

4. https://www.sigmaaldrich.com/IT/it/product/aldrich/232025.

5. Wang, R.; Tang, Y.; Xu, M.; Meng, C.; Li F.; *J. Org. Chem.* **2018,** 83, 4, 2274-2281.

6. Shaikh, N. S.; Junge, K.; Beller, M.; *Org. Lett.* **2007,** 9, 26, 5429-5432.

7. Chojnacka, K.; Santoro S., Awartani, R.; Richards, N. G. J.; Himo, F.; Aponick, A.; *Org. Biomol. Chem.* **2011**, 9, 15, 5350-5353.

8. Shi, J.; Ray A. S.; Mathew, J. S.; Anderson, K. S.; Chu, C. K.; Schinazi, R. F.; *Bioorg. Med. Chem. Lett.* **2004,** 14, 9, 2159-2162.

9. Shahnaz, P.; Arfa, Y.; Muhammad, K. A.; Ahsana, D.; Rehana, J.; Amir, A.; *Lett. Drug Des. Discov.*, **2010,** 7, 1.

10. S. N., Khan; M. K., Zaman; R., Li; Z., Sun; *J. Org. Chem.* **2020,** 85, 7, 5019-5026.

11. N., Sakai; K., Kawana; R., Ikeda; Y., Nakaike; T., Konakahara; *Eur. J. Org. Chem.* **2011**, 17, 3178-3183.

12. Molander, G. A.; L. N., Cavalcanti; *J. Org. Chem.* **2011,** 76, 2, 623-630.

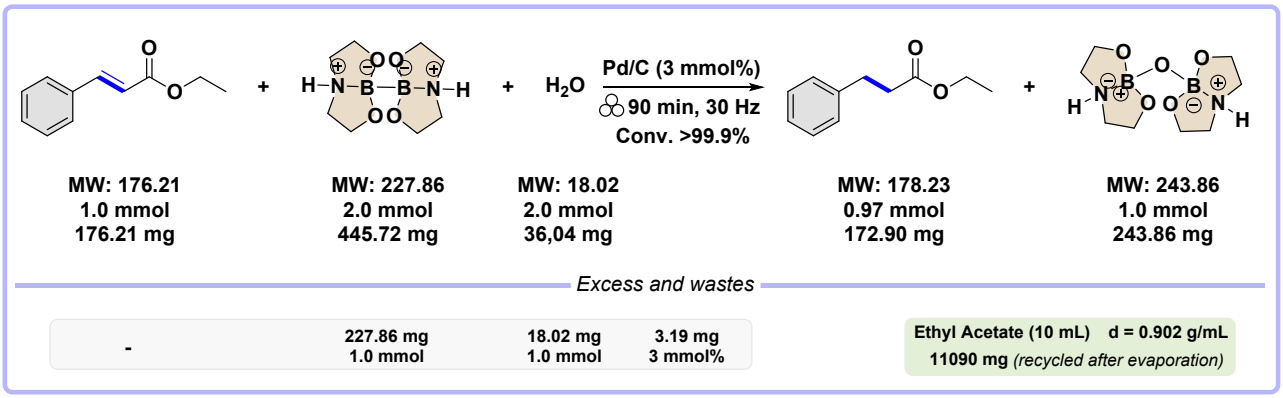
13. Song, H.-T.; Ding, W.; Zhou, Q.-Q.; Liu, J.; Lu, L.-Q.; Xiao, W.-J.; *J. Org. Chem.* **2016** 81, 16, 7250-7255.

14. V. K., Yu; A. Z., Kabdraissova; K. D., Praliyev; S. N., Shin; K. D., Berlin; *J. Saudi Chem. Soc.* **2009,** 13, 2, 209-217.

15. P., Wessig; K., Möllnitz; C., Eiserbeck; *Chem. Eur. J.* **2007**, 13, 17, 4859-4872.
16. K., Kamata; K., Yonehara; Y., Nakagawa; K., Uehara; N., Mizuno; *Nat. Chem.* **2010**, 2, 6, 478-483.
17. C.-P., Zhang; Z.-L., Wang; Q.-Y., Chen; C.-T., Zhang; Y.-C., Gu; J.-C., Xiao; *Chem. Comm.* **2011**, 47, 23, 6632-6634.
18. https://scifinder-n.cas.org/searchDetail/substance/627a52f41ed5577845091638/substanceDetails
19. T., Krüger; K., Vorndran; T., Linker; *Chem. Eur. J.* **2009**, 15, 44, 12082-12091.
20. K., Kamata; K., Yonehara; Y., Nakagawa; K., Uehara; N., Mizuno; *Nat. Chem.* **2010**, 2, 6, 478-483.
21. G.-Q., Kong; S., Ou; C., Zou; C.-D., Wu; *J. Am. Chem. Soc.* **2012**, 134, 48, 19851-19857.
22. S., Ahammed; A., Saha; B. C., Ranu; *J. Org. Chem.* **2011**, 76, 17, 7235-7239.

9. Green metrics calculations

*9.1. Calculation of the Green Chemistry Metrics for the Mechanochemical Preparation of **8f***



Scheme S2. Mechanochemical preparation of **8f**.

$$\textbf{A}\text{tom }\textbf{E}\text{conomy} = \frac{\text{Mass of desired useful product}}{\text{Total Mass of all reactants}} \times 100 = \frac{178.23}{425.28} \times 100 = 41.91\%$$

$$\textbf{E}\text{nvironmental }\textbf{F}\text{actor} = \frac{\text{Mass of total waste}}{\text{Mass of desired product}} = \frac{227.86 + 18.02 + 3.19 + 11090}{172.90} = 65.58$$

$$\textbf{Environmental Factor} = \frac{\text{Mass of total waste}}{\text{Mass of desired product}} = \frac{227.86 + 18.02 + 3.19}{172.90} = 1.44$$

$$\textbf{Reaction Mass Efficiency} = \frac{\text{actual mass of desired product}}{\text{mass of reactants}} \times 100 = \frac{172.90}{176.21 + 445.72 + 36.04 + 3.19} \times 100 = 26.15\%$$

9.2. The Eco-scale Score for the Mechanochemical Preparation of ***8f***

Reagents

Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1		Ethyl trans-cinnamate	C11H12O2	176.21	1,05	100%	NaN	0.17621	1	1
2		(2,2'-Bi(1,3,6,2-dioxazaborocane))	C8H18B2N2O4	227.86		100%	0	0.45572	2	2
3		H2O	H2O	18.02	1	100%	0.03604	0.03604	2	2
4		Palladium on activated carbon	Pd	106.42		100%	0	0.003193	0.03	0.03

Products

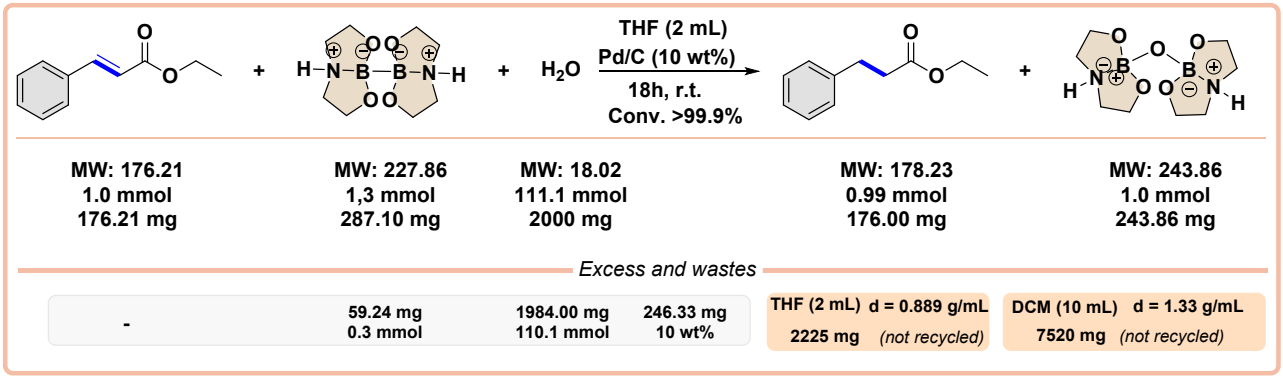
identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	Ethyl 3-phenylpropionate	C11H14O2	178.23096	0.1729	0.970089596	0.178231	97.0089

Conditions

Reagents	Name	mmoles	eq.	Bp	Hazard	Price	
	Ethyl trans-cinnamate	5.78	1	247			
	(2,2'-Bi(1,3,6,2-dioxazaborocane))	11.56	2				
	H2O	11.56	2				
	Palladium on activated carbon	0.17	0.03				
Yield	97						-1
Price / availability							-15
Safety							-15
Technical setup	Possible items: Common set-up, Instruments for controlled addition of chemicals, Unconventional activation technique					Selected items: Common set-up	0
Temperature / time	Possible items: Room temperature, < 1h, Room temperature, < 24h, Heating, < 1h					Selected items: Room temperature, < 24h	-1
Workup and purification	Possible items: Sublimation, Liquid - liquid extraction or washing, Classical chromatography					Selected items: Adding solvent	0
EcoScale							68

[a]Values calculated using the eco scale calculator software available at the link: http://ecoscale.cheminfo.org/calculator

*9.3. Calculation of the Green Chemistry Metrics for the In-solution Preparation of **8f***



Scheme S3. In-solution* preparation of **8f**.

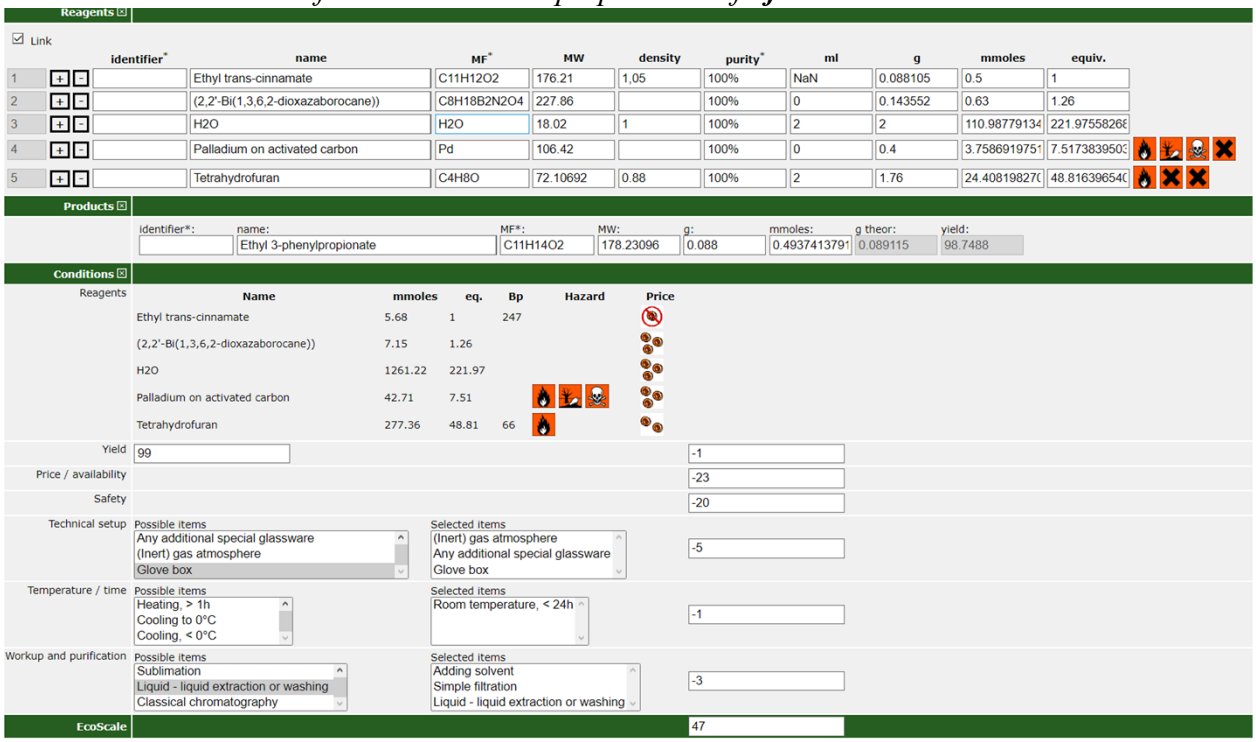
*Flinker, M.; Yin, H.; Juhl, R. W.; Eikeland, E. Z.; Overgaard, J.; Nielsen, D. U.; Skrydstrup, T.; *Angew. Chem. Int. Ed.* **2017**, 56, 15910.

$$\textbf{A}\text{tom }\textbf{E}\text{conomy} = \frac{\text{Mass of desired useful product}}{\text{Total Mass of all reactants}} \times 100 = \frac{178.23}{425.28} \times 100 = 41.91\%$$

$$\textbf{E}\text{nvironmental }\textbf{F}\text{actor} = \frac{\text{Mass of total waste}}{\text{Mass of desired product}} = \frac{59.24 + 1984.00 + 246.33 + 2225.00 + 7520.00}{176.00} = 69.60$$

$$\text{Reaction Mass Efficiency} = \frac{\text{actual mass of desired product}}{\text{mass of reactants}} \times 100 = \frac{172.90}{176.21 + 287.10 + 2000.00 + 246.3} \times 100 = 6.38\%$$

9.4. The Eco-scale Score for the in-solution preparation of ***8f***



Reagents

Link

	identifier*	name	MF*	MW	density	purity*	ml	g	mmoles	equiv.
1		Ethyl trans-cinnamate	C11H12O2	176.21	1,05	100%	NaN	0.088105	0.5	1
2		(2,2'-Bi(1,3,6,2-dioxazaborocane))	C8H18B2N2O4	227.86		100%	0	0.143552	0.63	1.26
3		H2O	H2O	18.02	1	100%	2	2	110.98779134	221.97558268
4		Palladium on activated carbon	Pd	106.42		100%	0	0.4	3.758691975	7.517383950
5		Tetrahydrofuran	C4H8O	72.10692	0.88	100%	2	1.76	24.40819827	48.81639654

Products

identifier*:	name:	MF*:	MW:	g:	mmoles:	g theor:	yield:
	Ethyl 3-phenylpropionate	C11H14O2	178.23096	0.088	0.493741379	0.089115	98.7488

Conditions

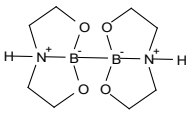
Reagents

Name	mmoles	eq.	Bp	Hazard	Price
Ethyl trans-cinnamate	5.68	1	247		
(2,2'-Bi(1,3,6,2-dioxazaborocane))	7.15	1.26			
H2O	1261.22	221.97			
Palladium on activated carbon	42.71	7.51			
Tetrahydrofuran	277.36	48.81	66		

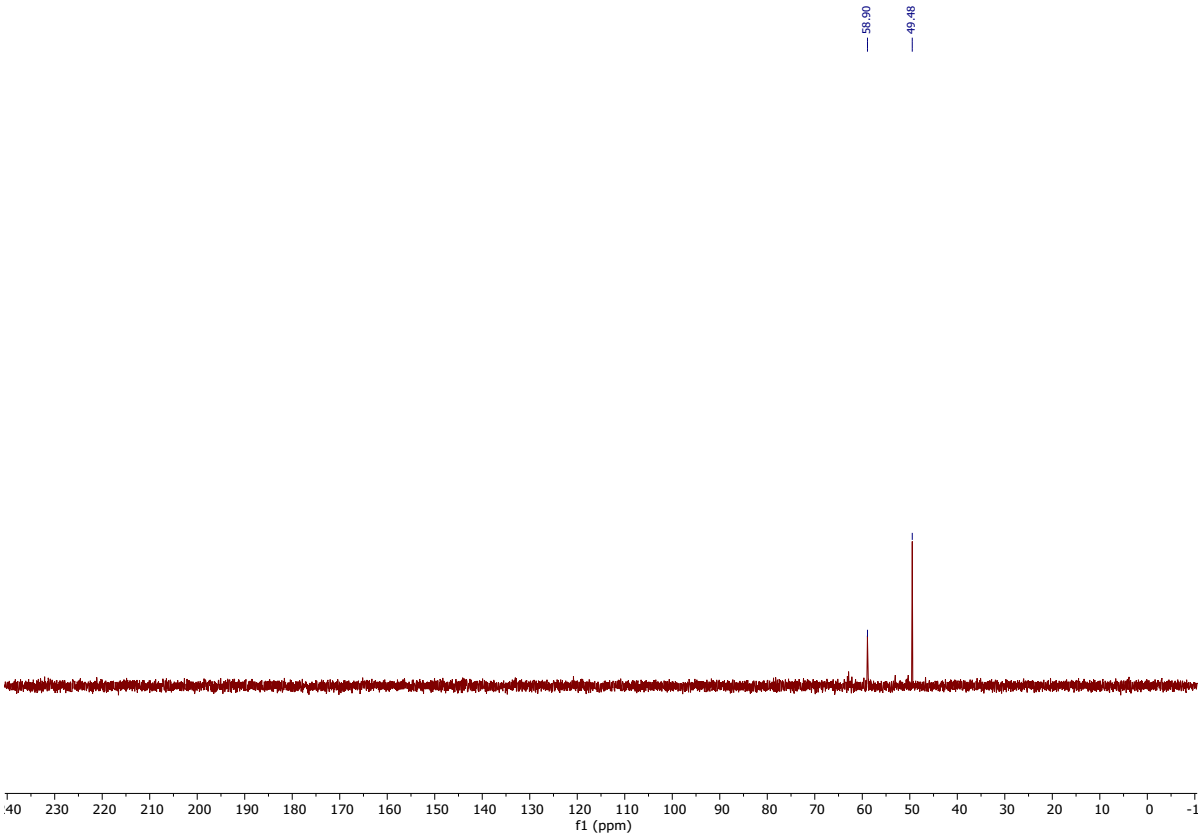
Yield	99		-1
Price / availability			-23
Safety			-20
Technical setup	Possible items: Any additional special glassware; (Inert) gas atmosphere; Glove box	Selected items: (Inert) gas atmosphere; Any additional special glassware; Glove box	-5
Temperature / time	Possible items: Heating, > 1h; Cooling to 0°C; Cooling, < 0°C	Selected items: Room temperature, < 24h	-1
Workup and purification	Possible items: Sublimation; Liquid - liquid extraction or washing; Classical chromatography	Selected items: Adding solvent; Simple filtration; Liquid - liquid extraction or washing	-3
EcoScale			47

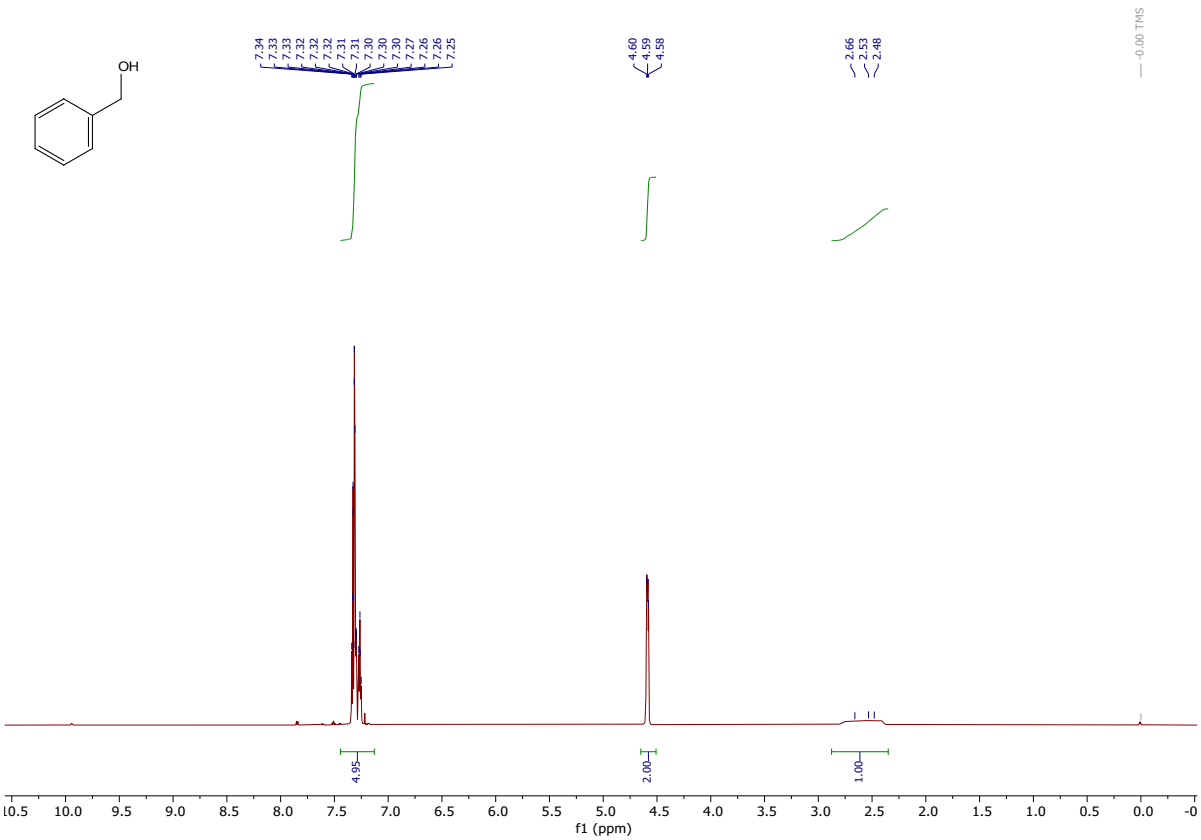
Values calculated using the eco scale calculator software available at the link:
http://ecoscale.cheminfo.org/calculator

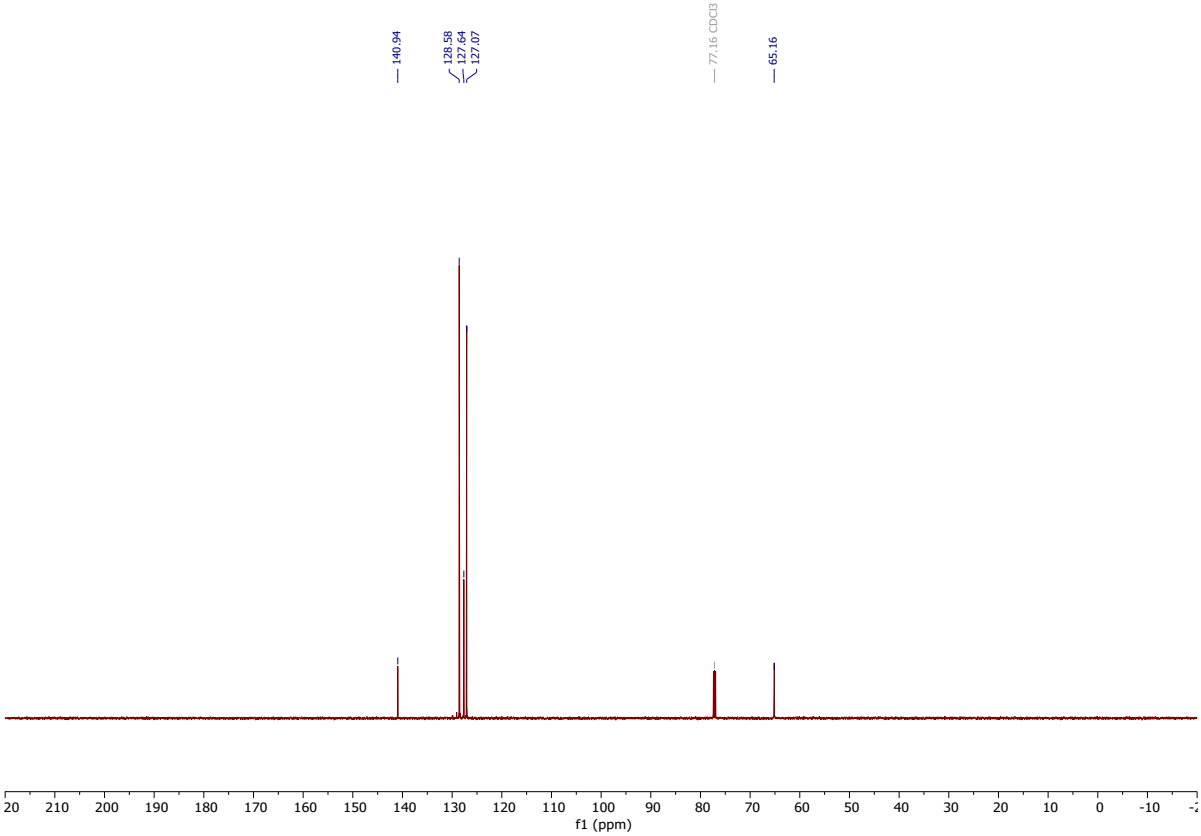
10. Spectra

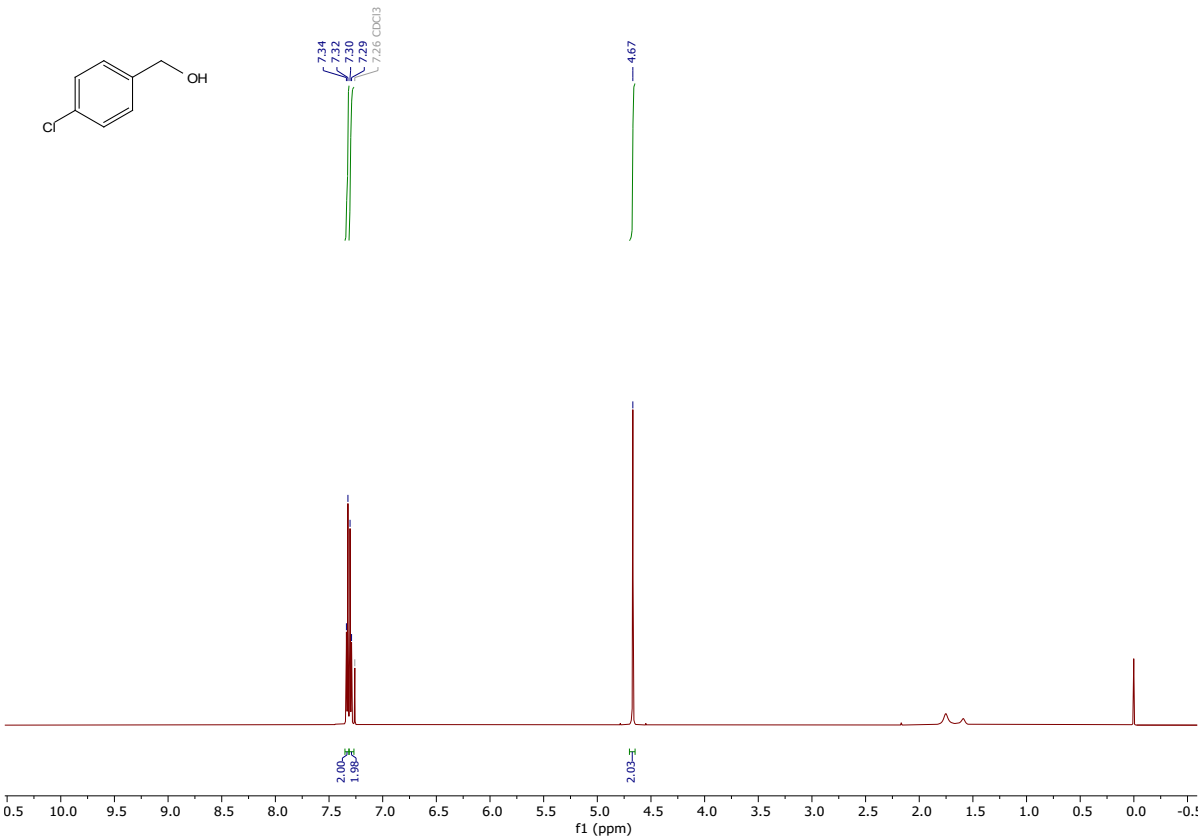


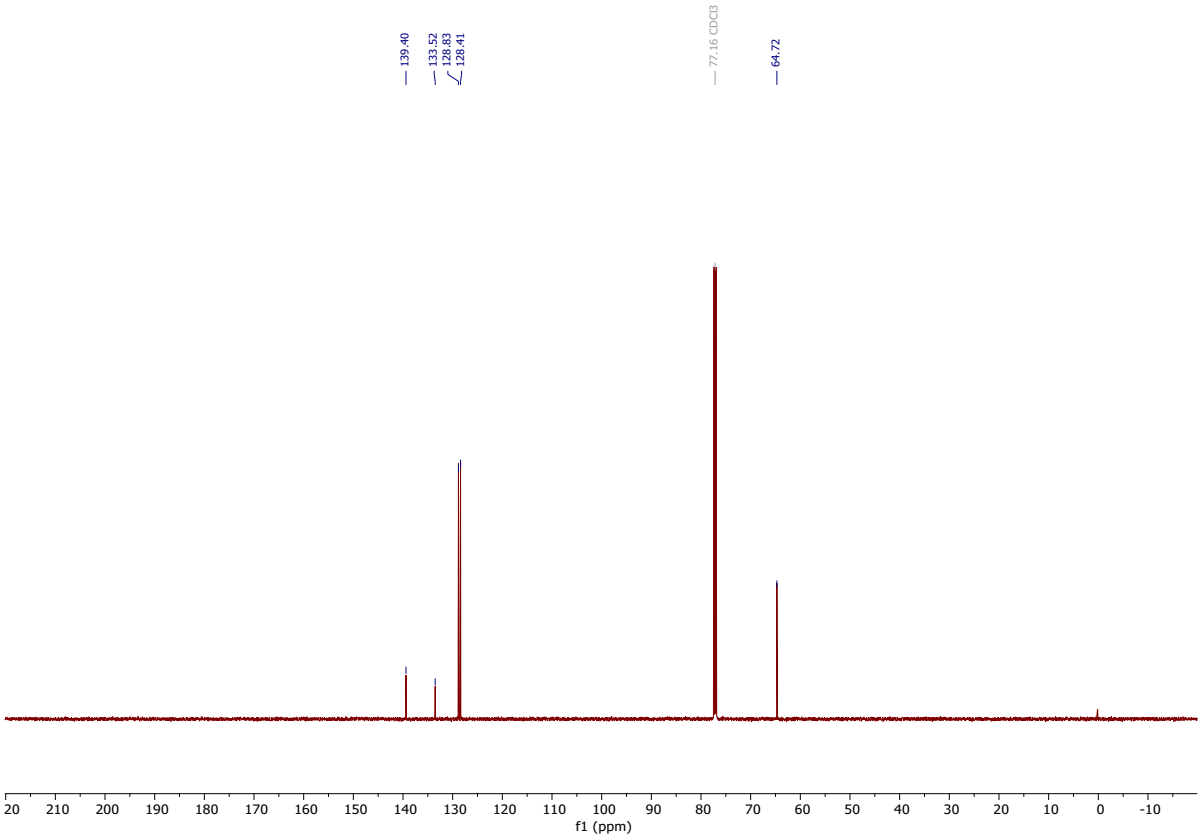
3.85
3.84
3.83
3.02
3.01
3.00
8.00
8.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

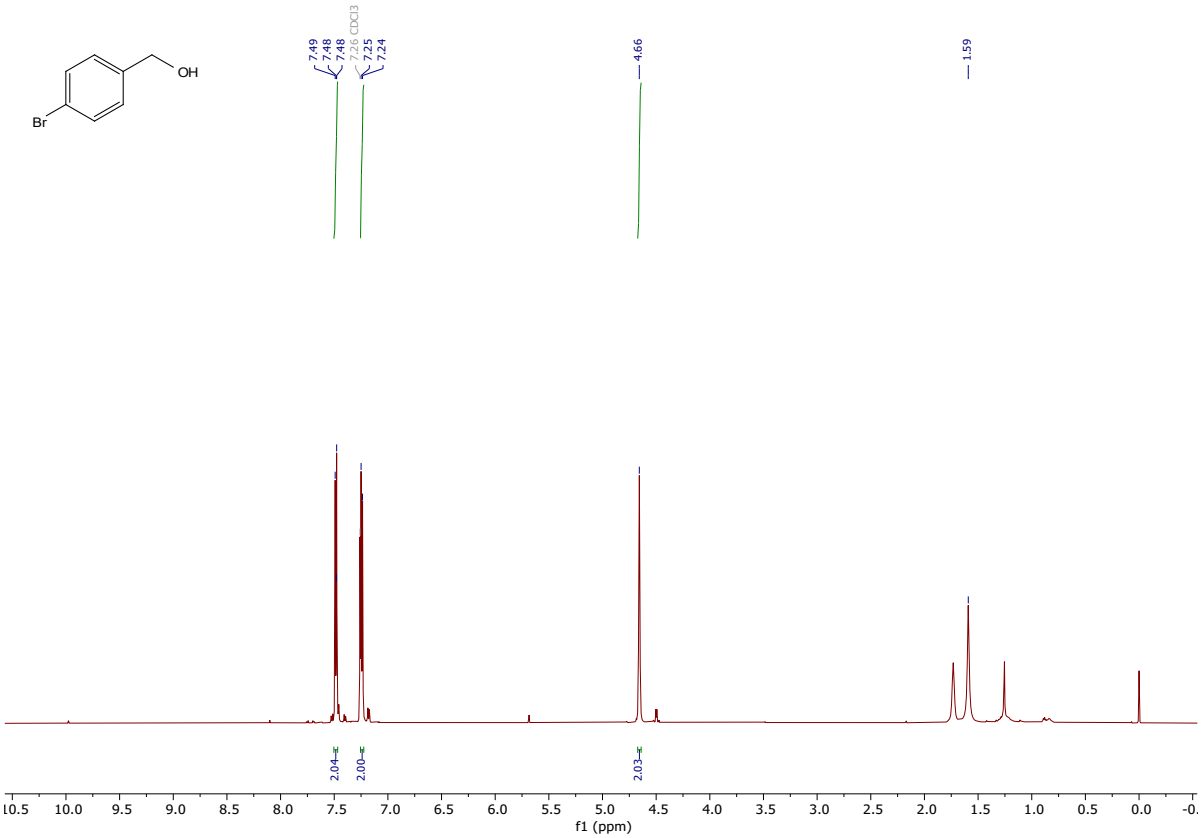

58.90
49.48
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

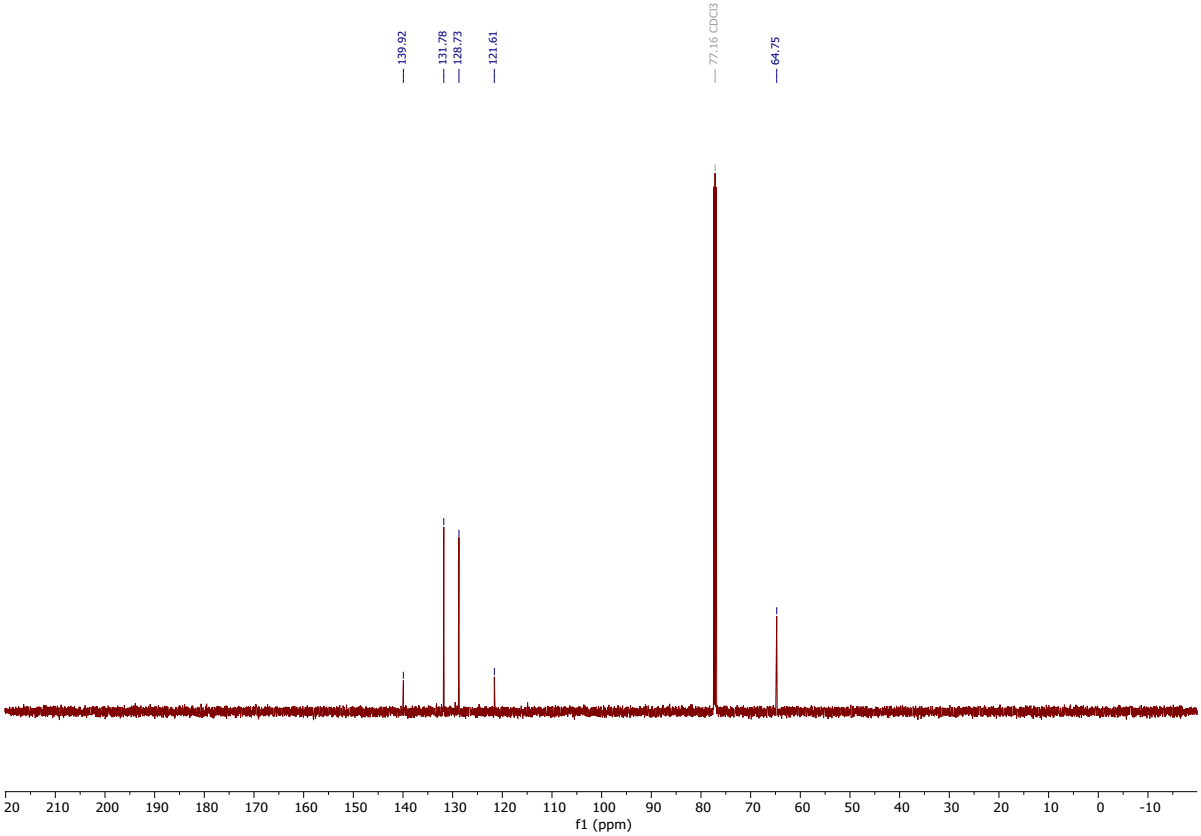

OH
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.27
7.26
7.26
7.25
4.60
4.59
4.58
2.66
2.53
2.48
0.00 TMS
4.95
2.00
1.00
f1 (ppm)

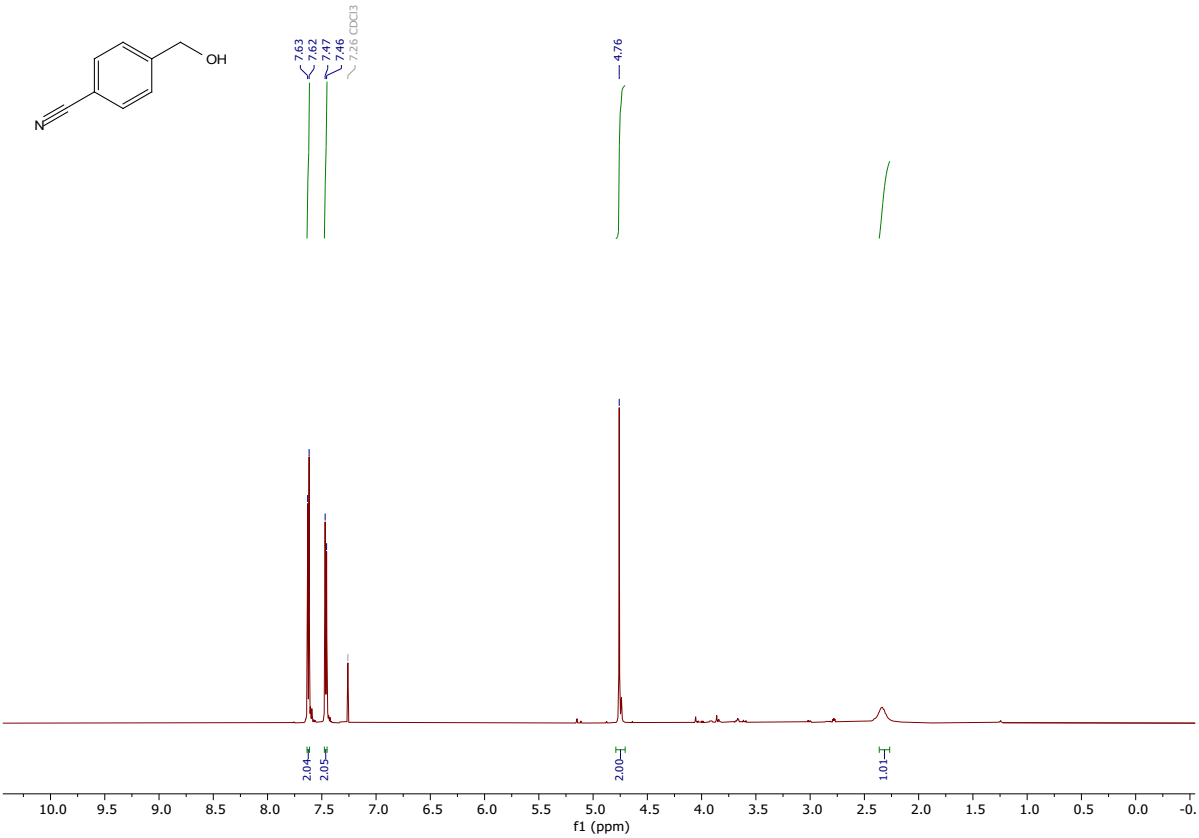

140.94
128.58
127.64
127.07
77.16 CDCl3
65.16
f1 (ppm)

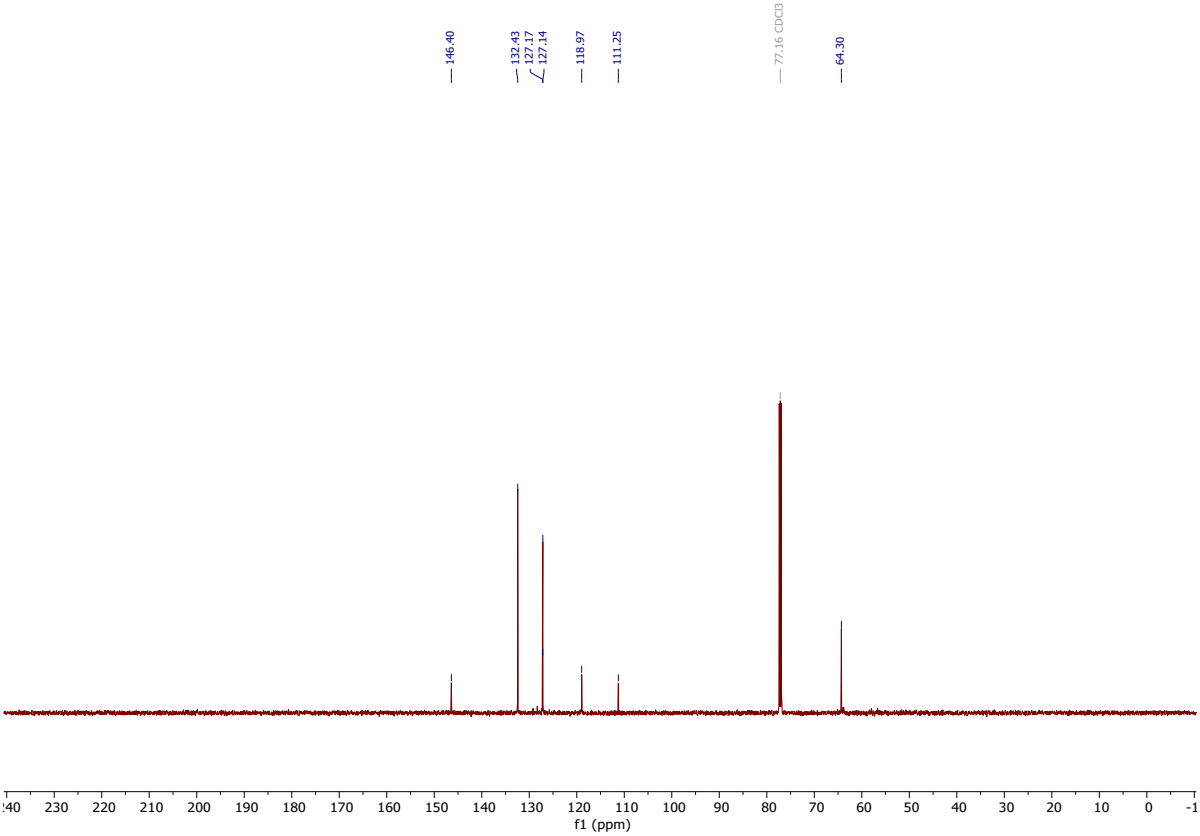

OH
Cl
7.34
7.32
7.30
7.29
7.26 CDCl3
4.67
2.00
1.98
2.03
f1 (ppm)

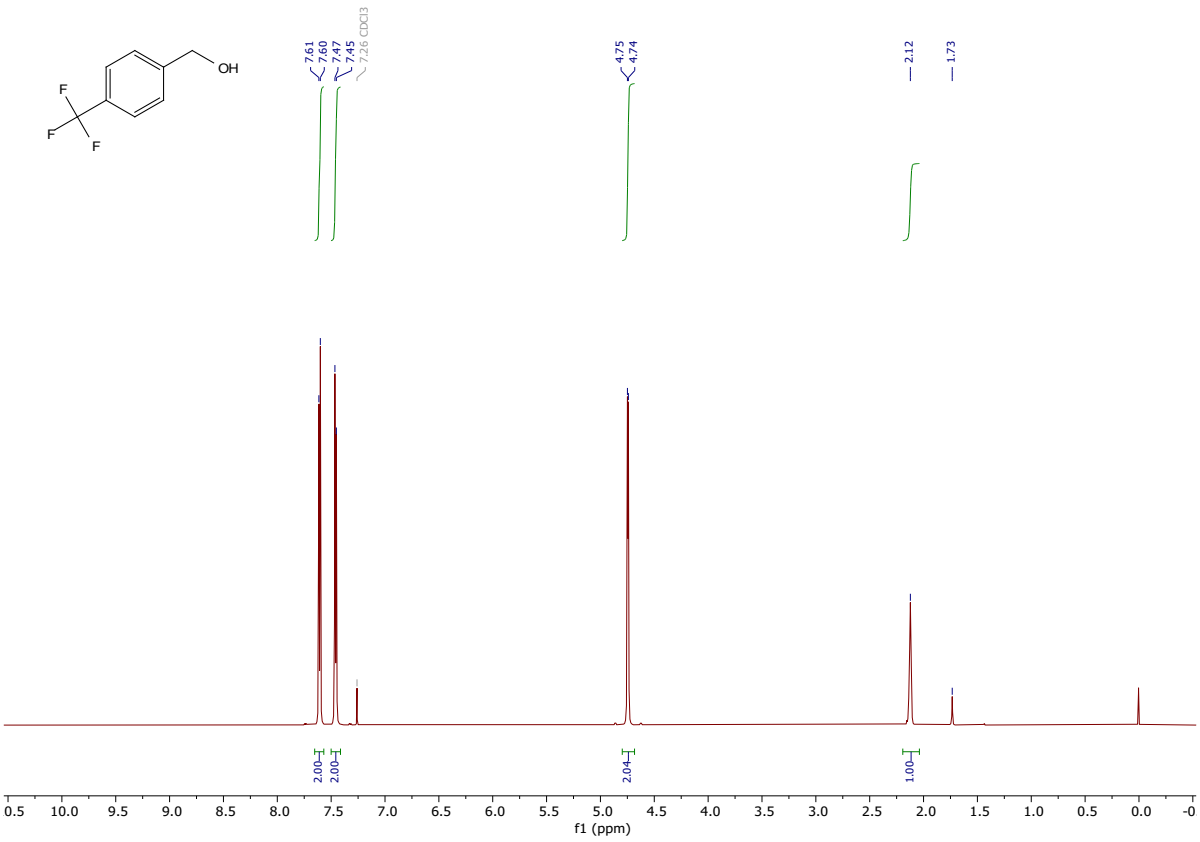

139.40
133.52
128.83
128.41
77.16 CDCl3
64.72
f1 (ppm)

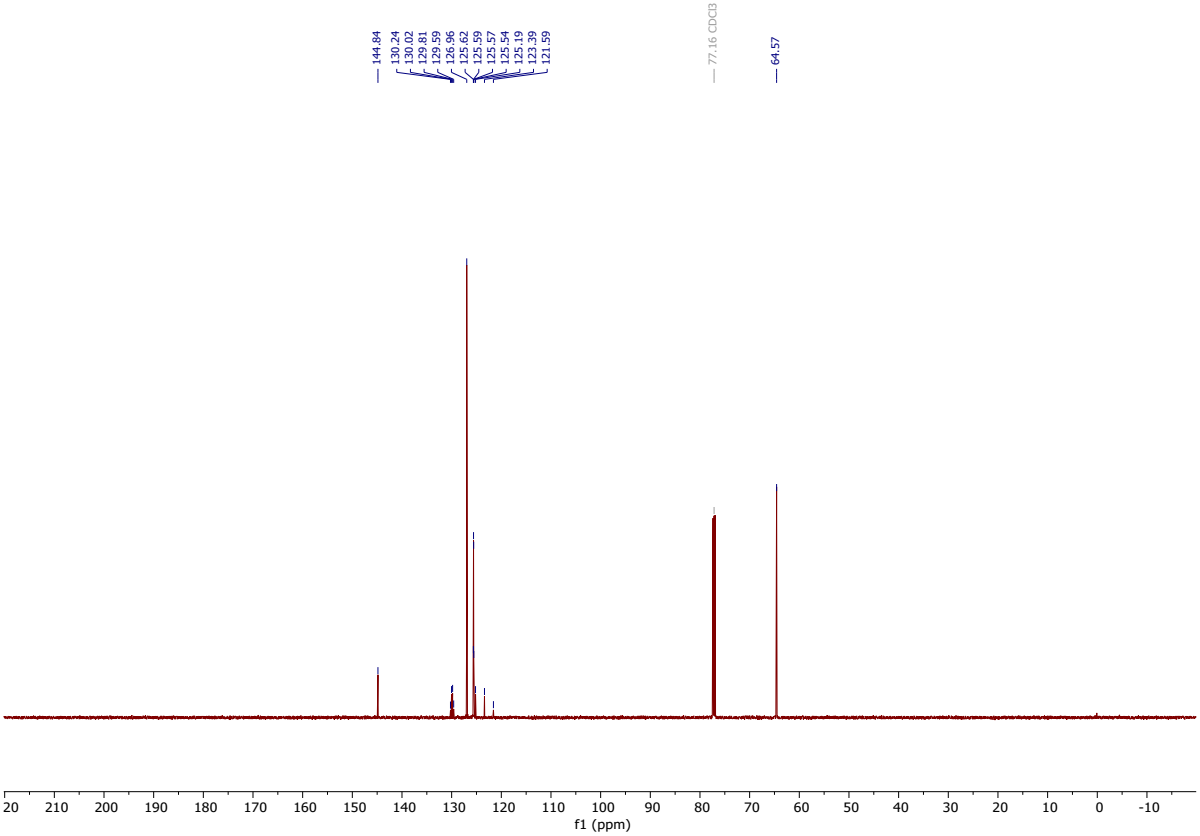

OH
Br
7.49
7.48
7.48
7.26 CDCl3
7.25
7.24
4.66
1.59
2.04
2.00
2.03
f1 (ppm)

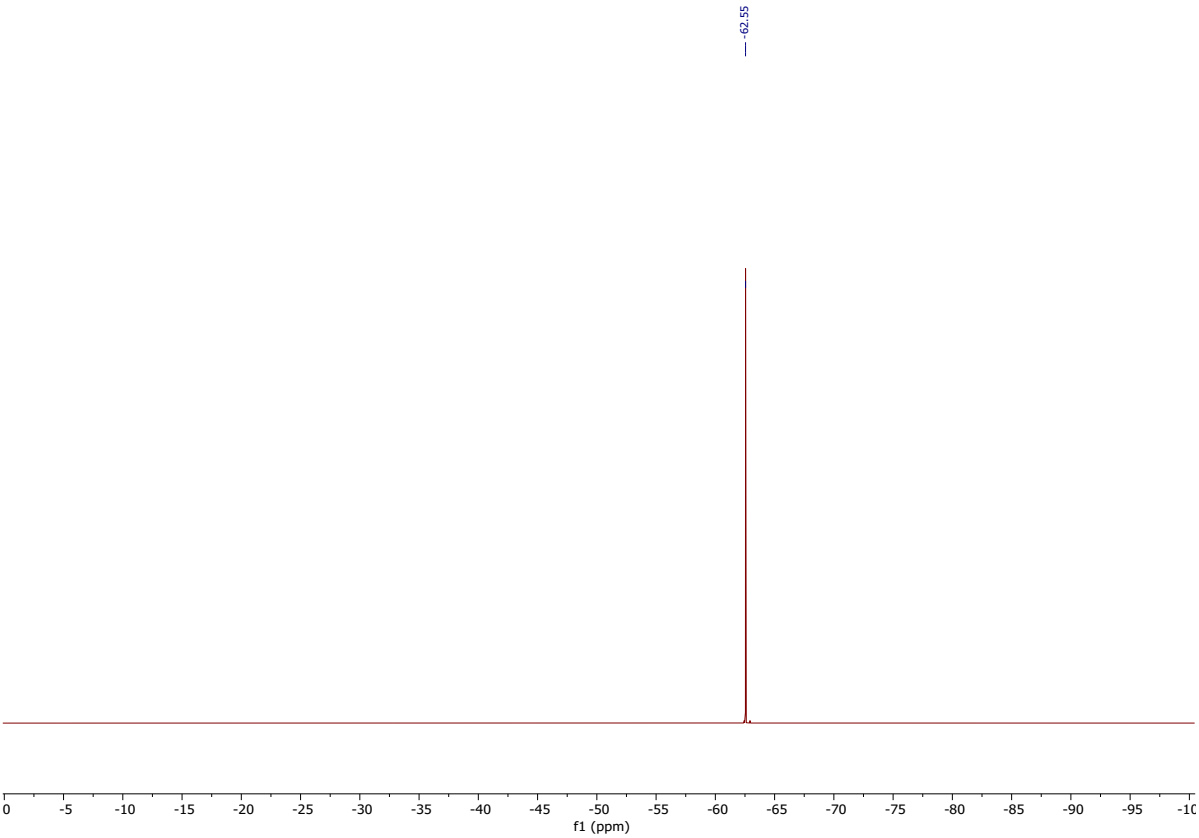

139.92
131.78
128.73
121.61
77.16 CDCl3
64.75
f1 (ppm)

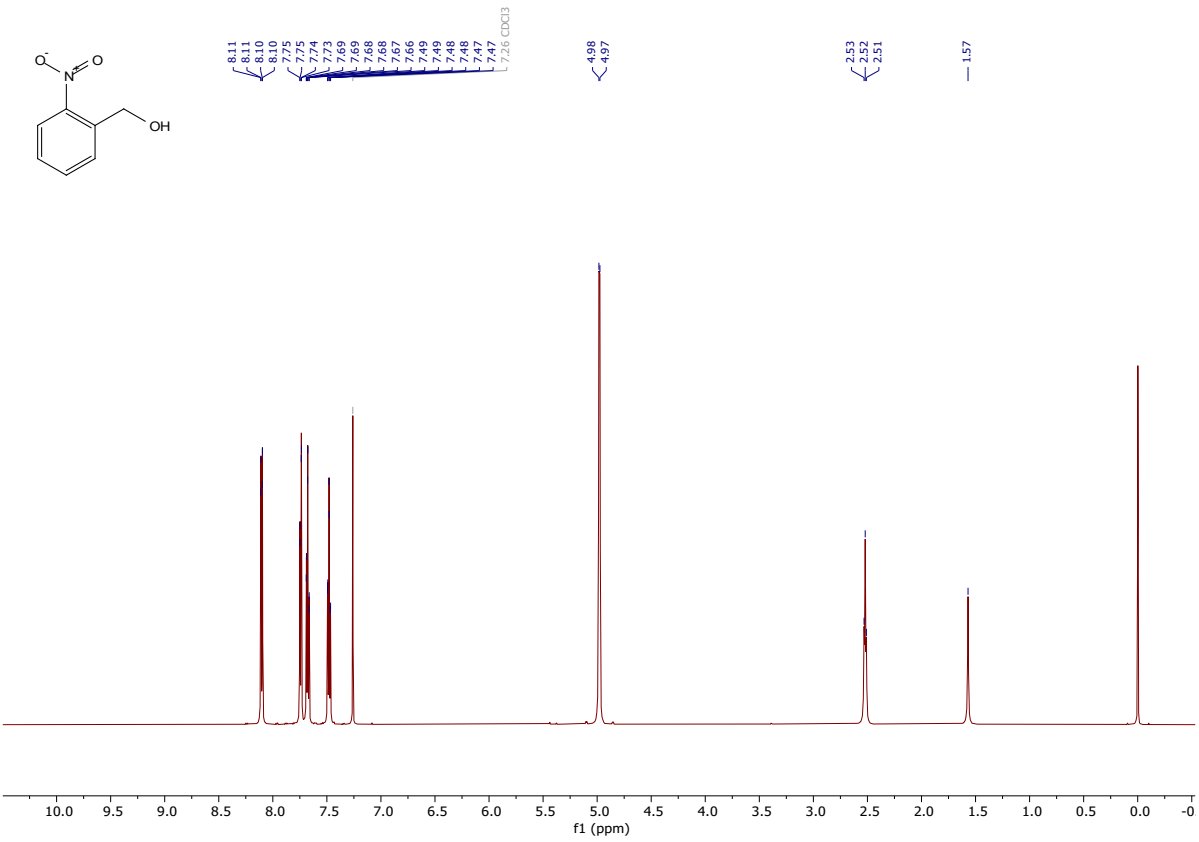

OH
N
7.63
7.62
7.47
7.46
7.26 CDCl3
4.76
2.04
2.05
2.00
1.01
f1 (ppm)

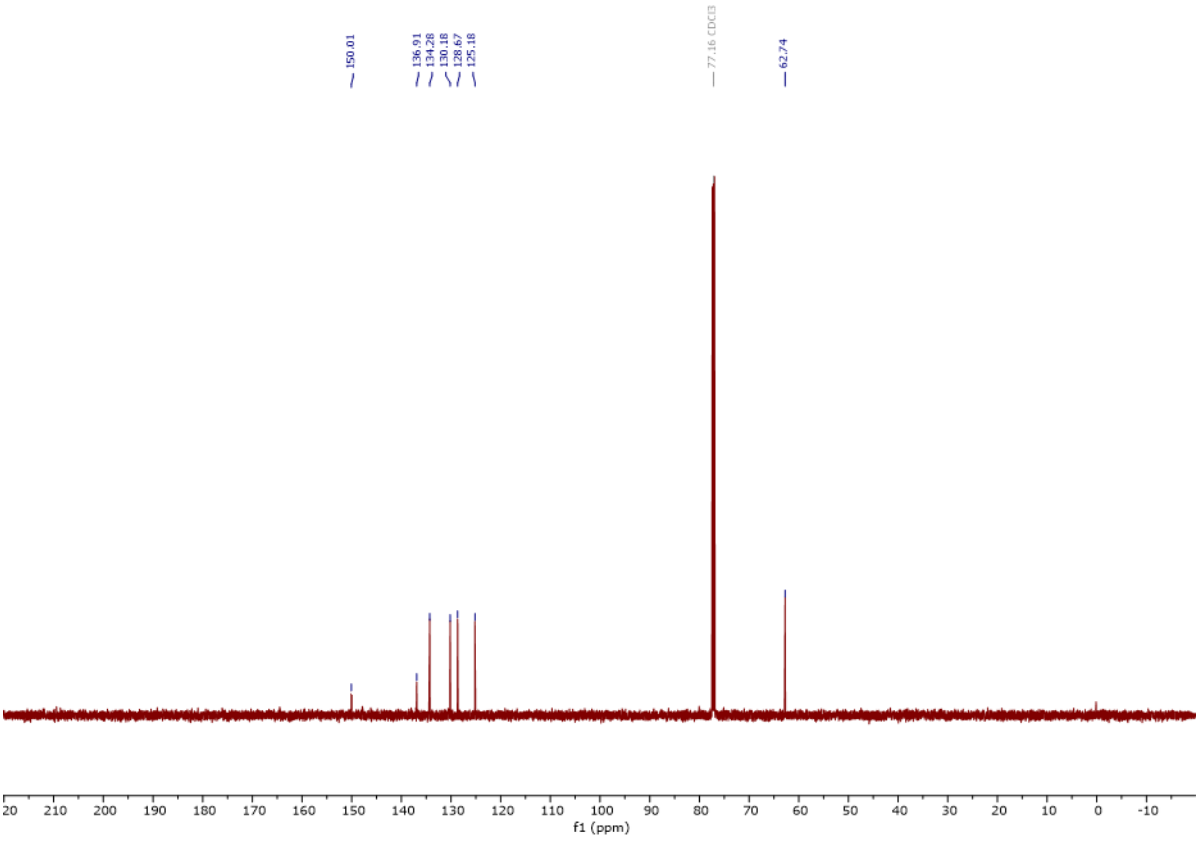

146.40
132.43
127.17
127.14
118.97
111.25
77.16 CDCl3
64.30
f1 (ppm)

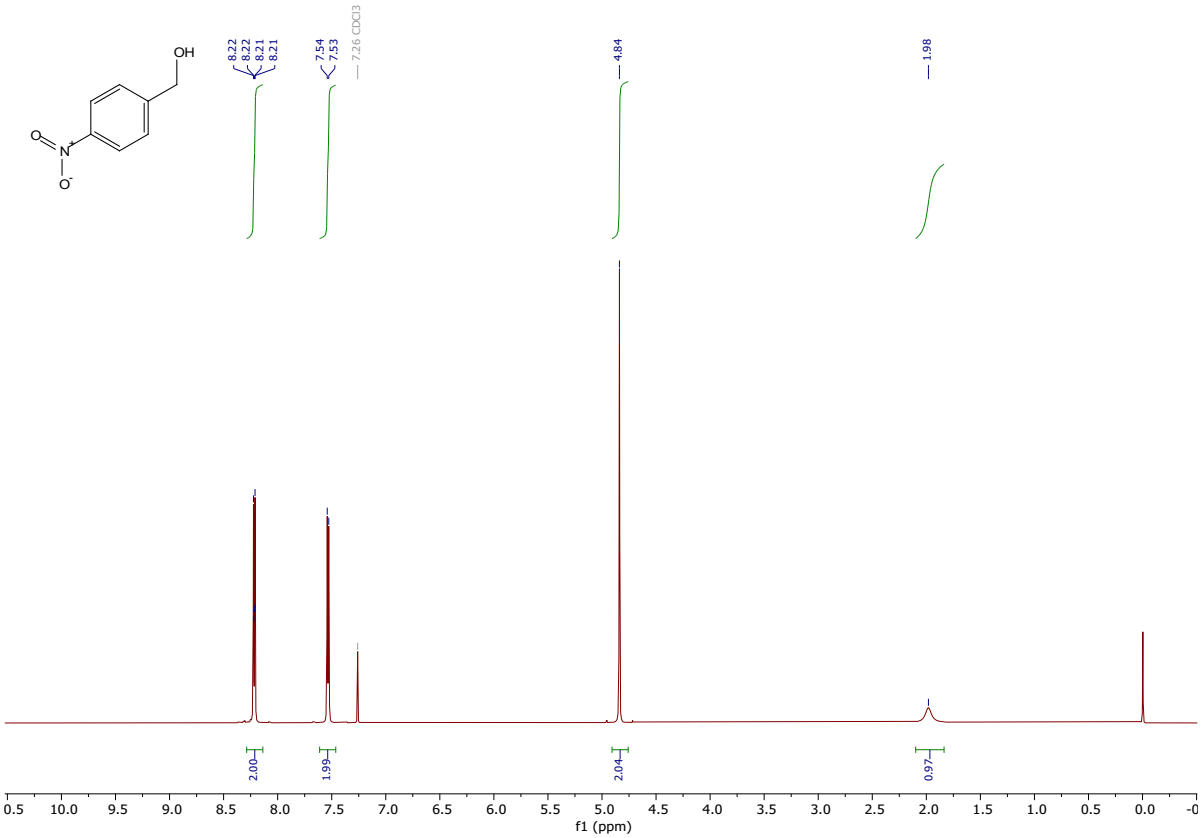

F
F
F
OH
7.61
7.60
7.47
7.45
7.26 CDCl3
4.75
4.74
2.12
1.73
2.00
2.00
2.04
1.00
f1 (ppm)

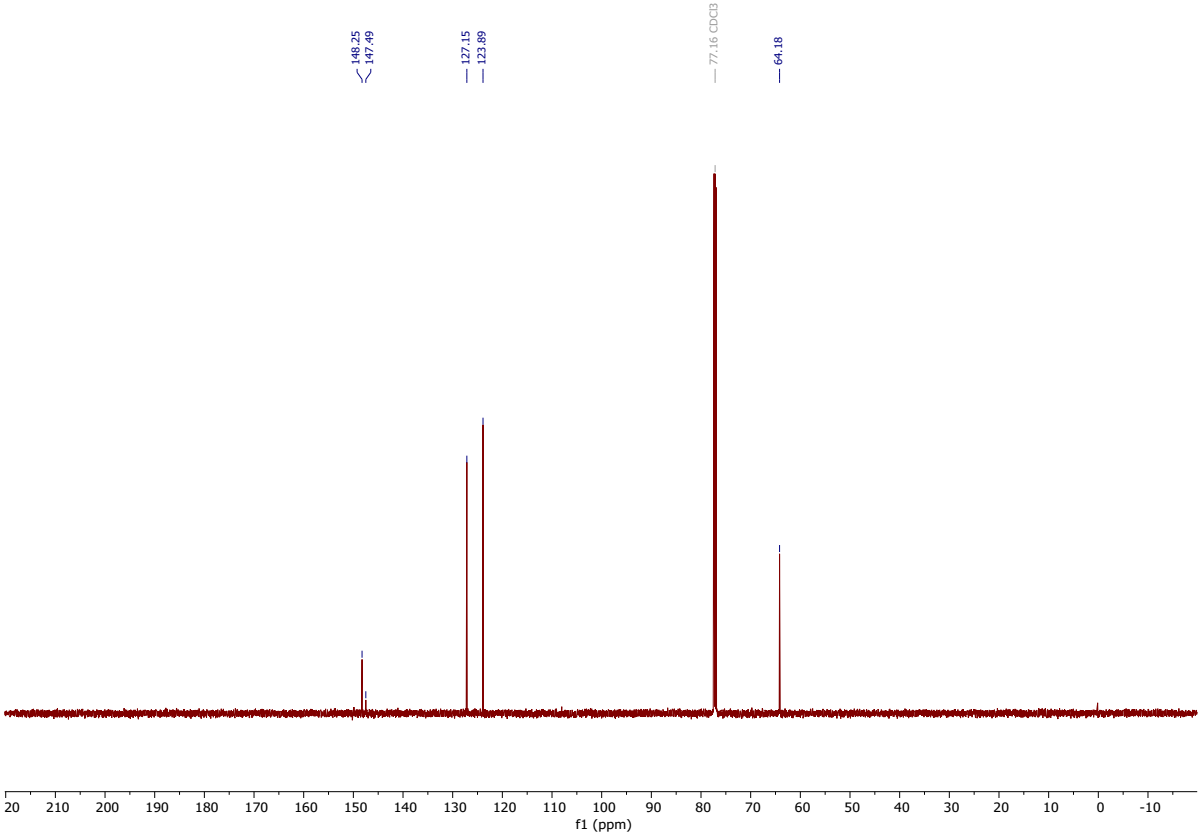

144.84
130.24
130.02
129.81
129.59
126.96
125.62
125.59
125.57
125.54
125.19
123.39
121.59
77.16 CDCl3
64.57
f1 (ppm)

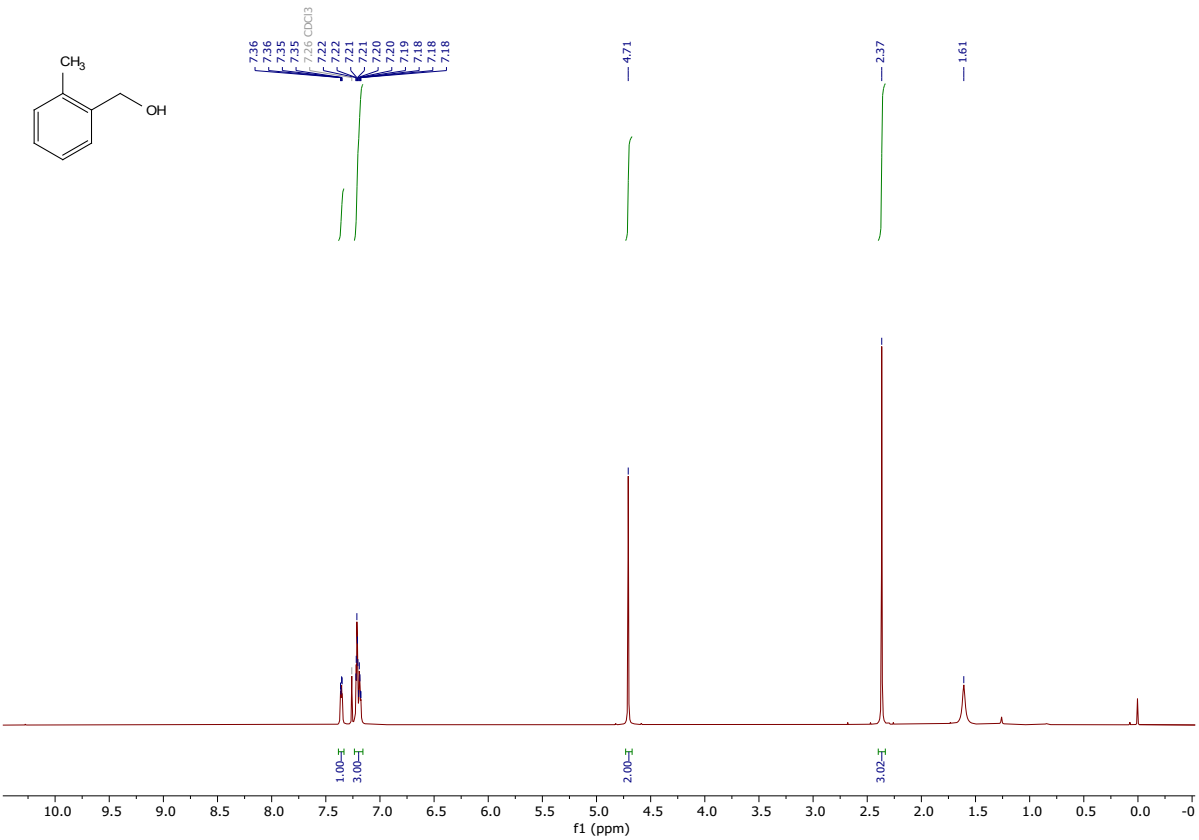

-62.55
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-10
f1 (ppm)

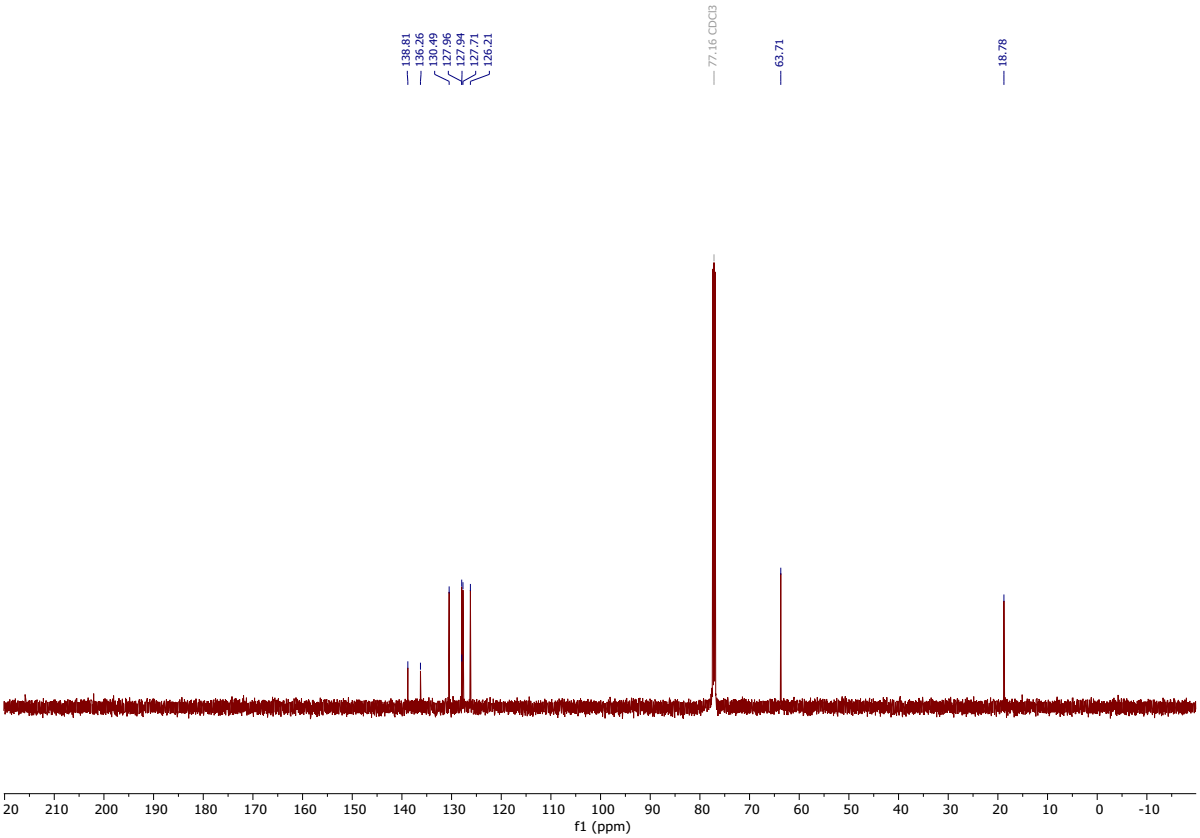

8.11
8.11
8.10
8.10
7.75
7.75
7.74
7.73
7.69
7.69
7.68
7.68
7.67
7.66
7.49
7.49
7.48
7.48
7.47
7.47
7.26 CDCl3
4.98
4.97
2.53
2.52
2.51
1.57
OH
f1 (ppm)

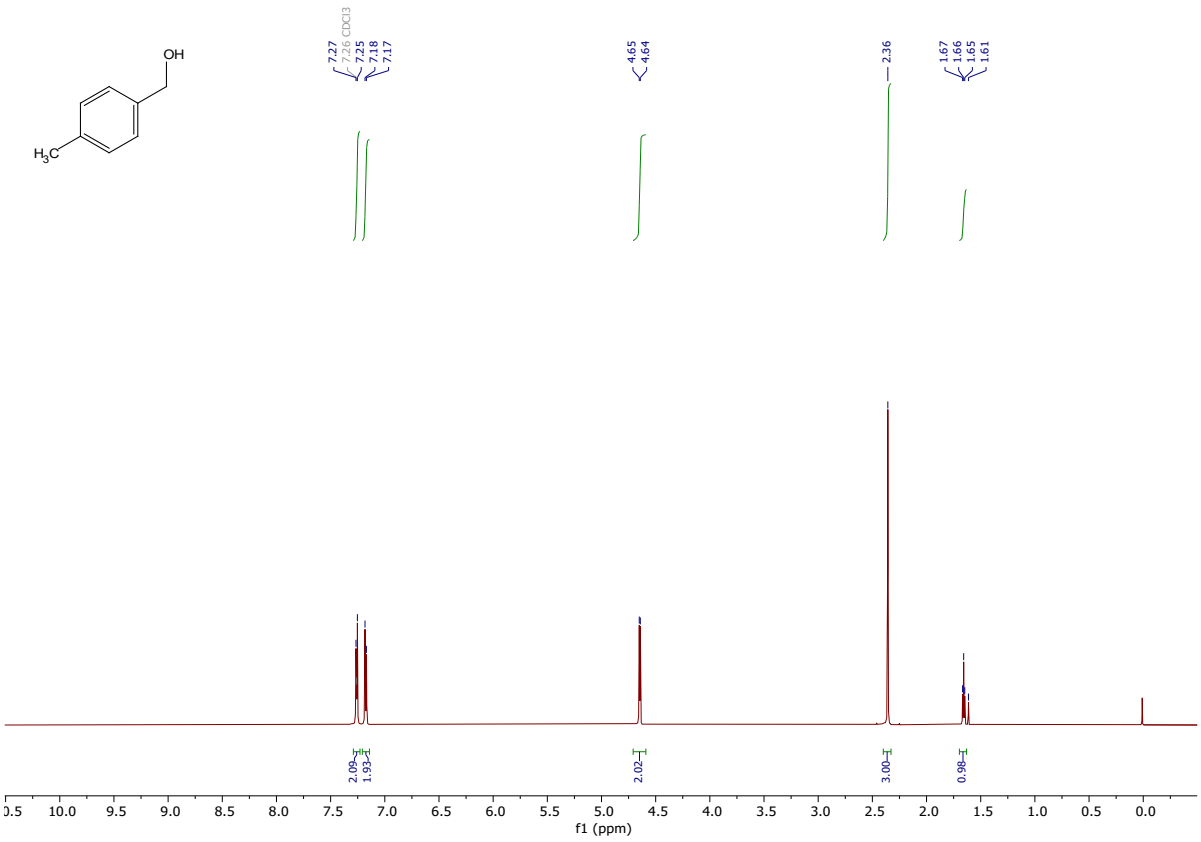

150.01
136.91
134.28
130.18
128.67
125.18
77.16 CDCl3
62.74
f1 (ppm)

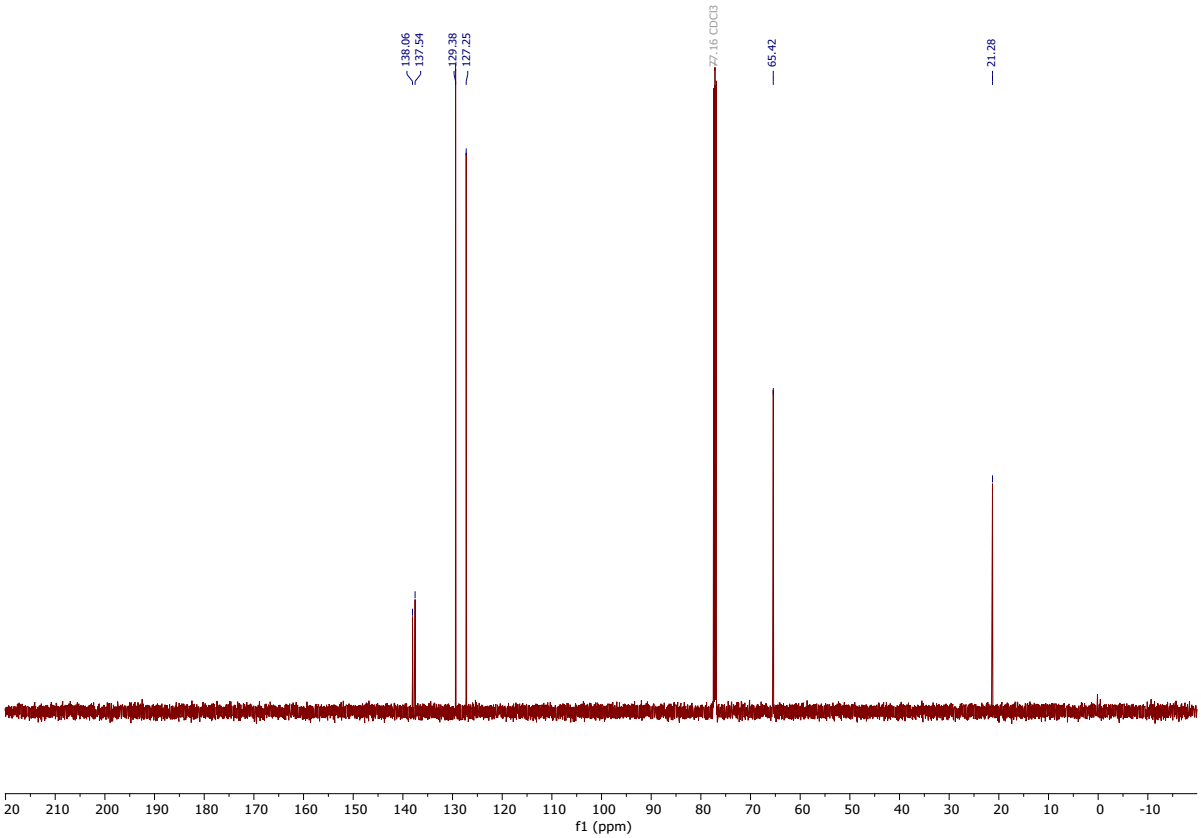

OH
O
N+
O-
8.22
8.22
8.21
8.21
7.54
7.53
7.26 CDCl3
4.84
1.98
2.00
1.99
2.04
0.97
f1 (ppm)

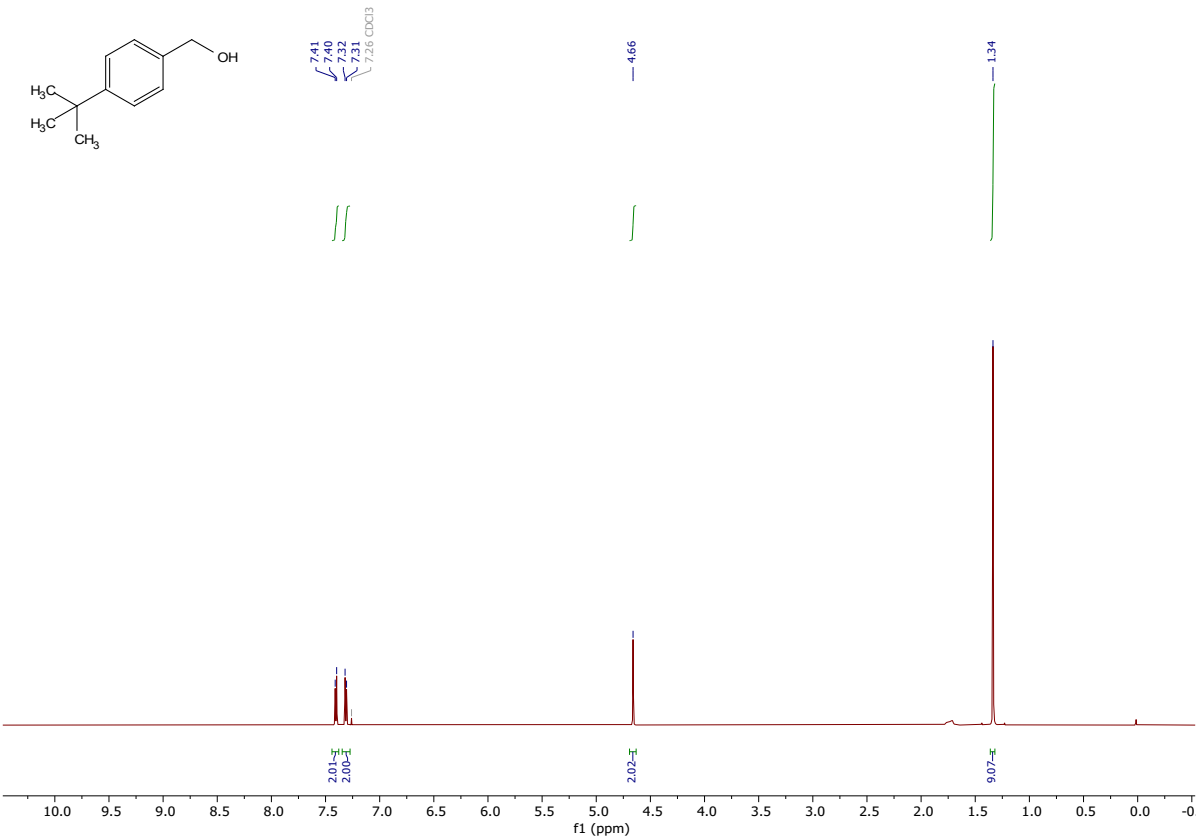

148.25
147.49
127.15
123.89
77.16 CDCl3
64.18
f1 (ppm)

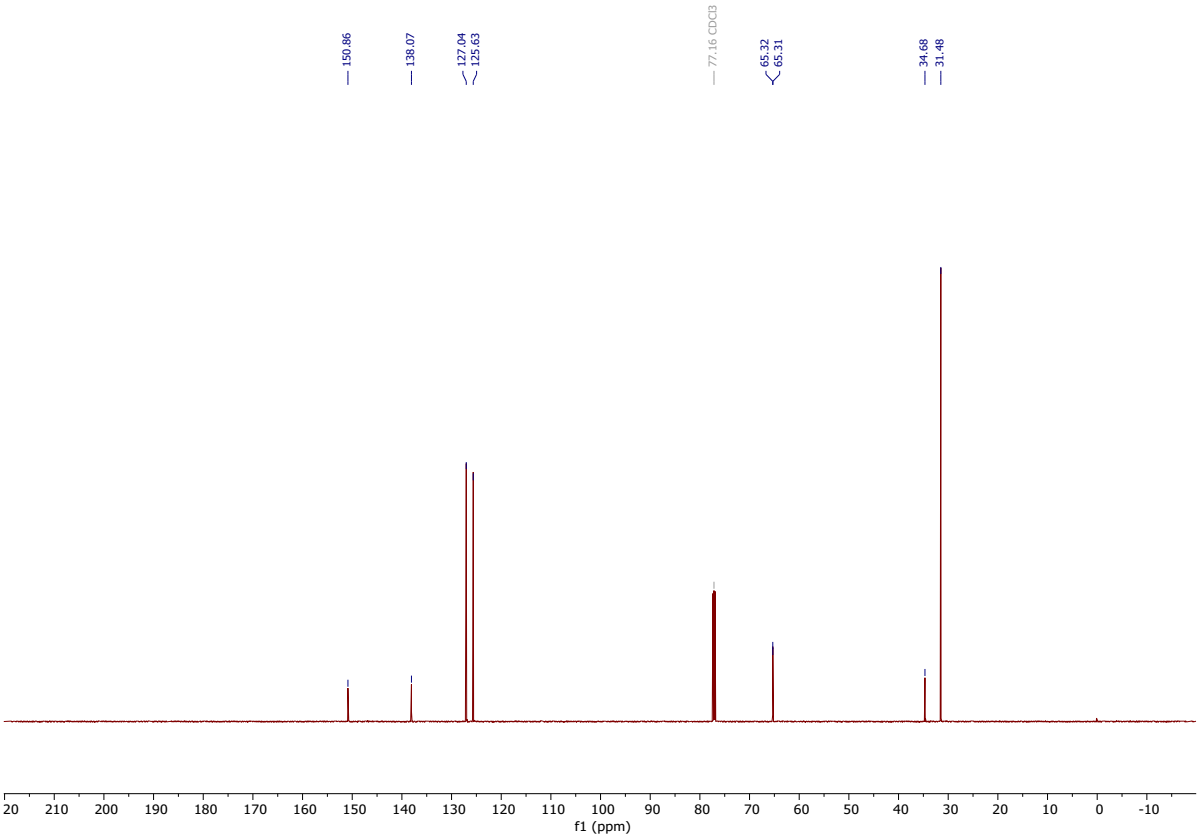

CH3
OH
7.36
7.36
7.35
7.35
7.26 CDCl3
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.18
4.71
2.37
1.61
1.00
3.00
2.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

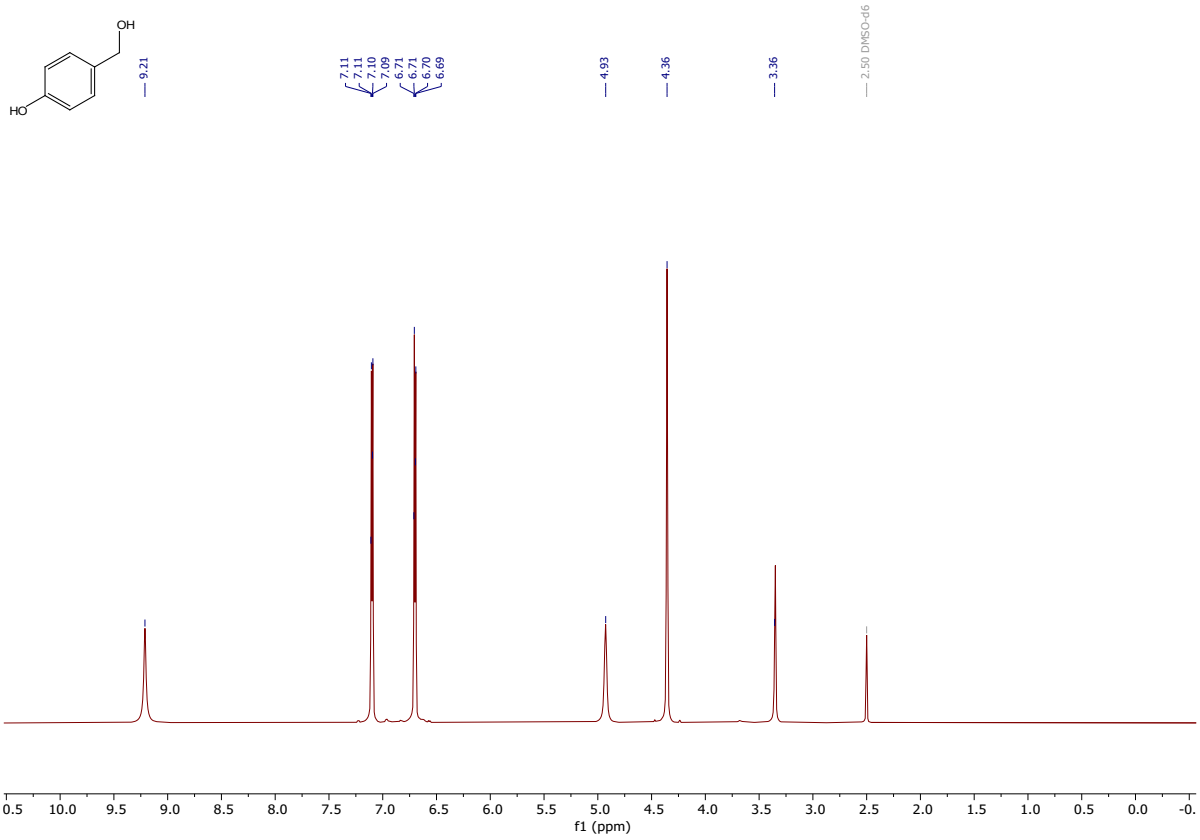

138.81
136.26
130.49
127.96
127.94
127.71
126.21
77.16 CDCl3
63.71
18.78
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

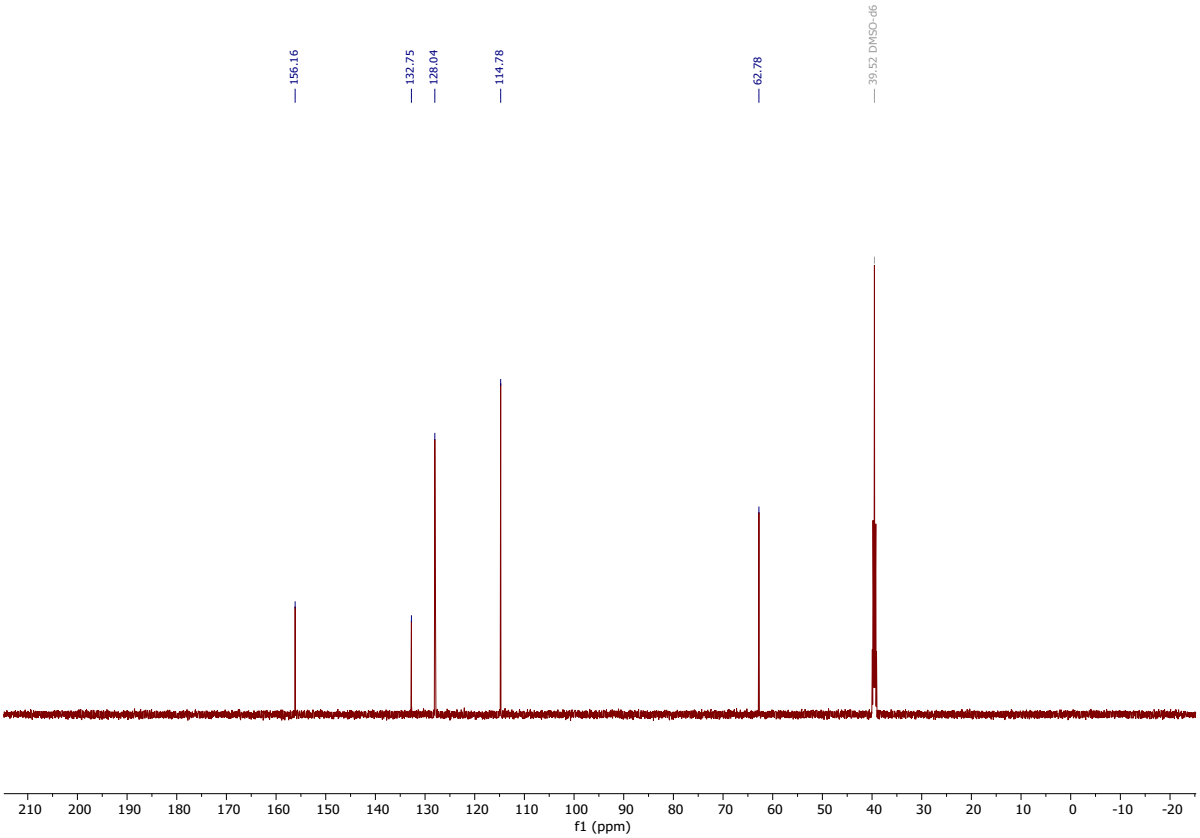

OH
H3C
7.27
7.26 CDCl3
7.25
7.18
7.17
4.65
4.64
2.36
1.67
1.66
1.65
1.61
2.09
1.93
2.02
3.00
0.98
f1 (ppm)

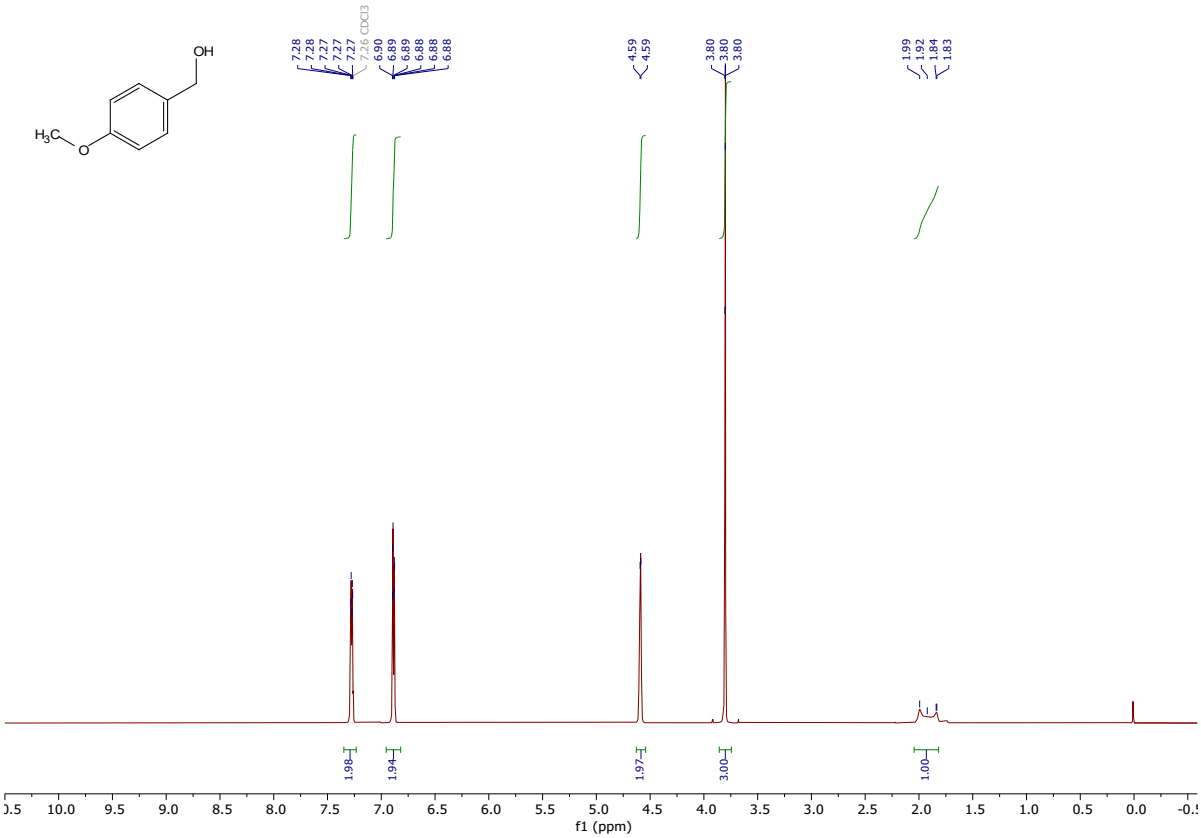

138.06
137.54
129.38
127.25
77.16 CDCl3
65.42
21.28
f1 (ppm)

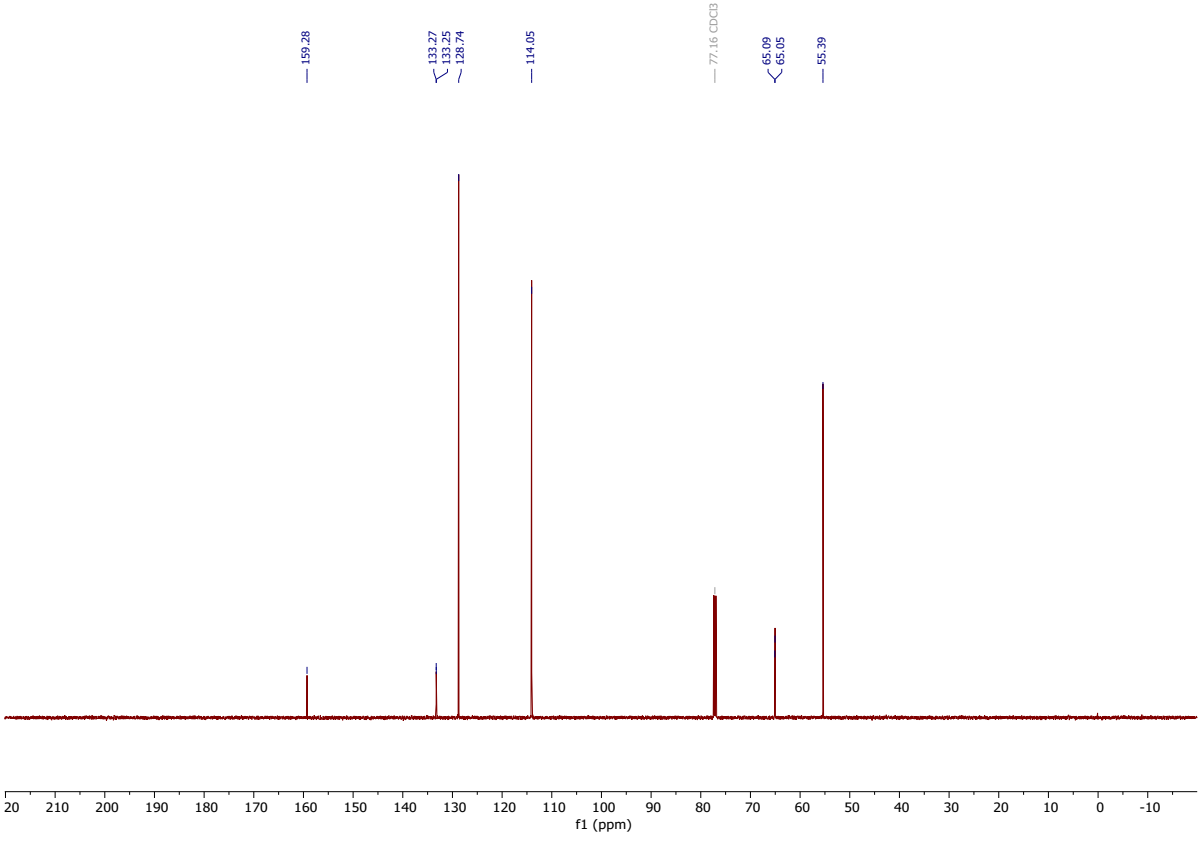

OH
H3C
H3C
CH3
7.41
7.40
7.32
7.31
7.26 CDCl3
4.66
1.34
2.01
2.00
2.02
9.07
f1 (ppm)

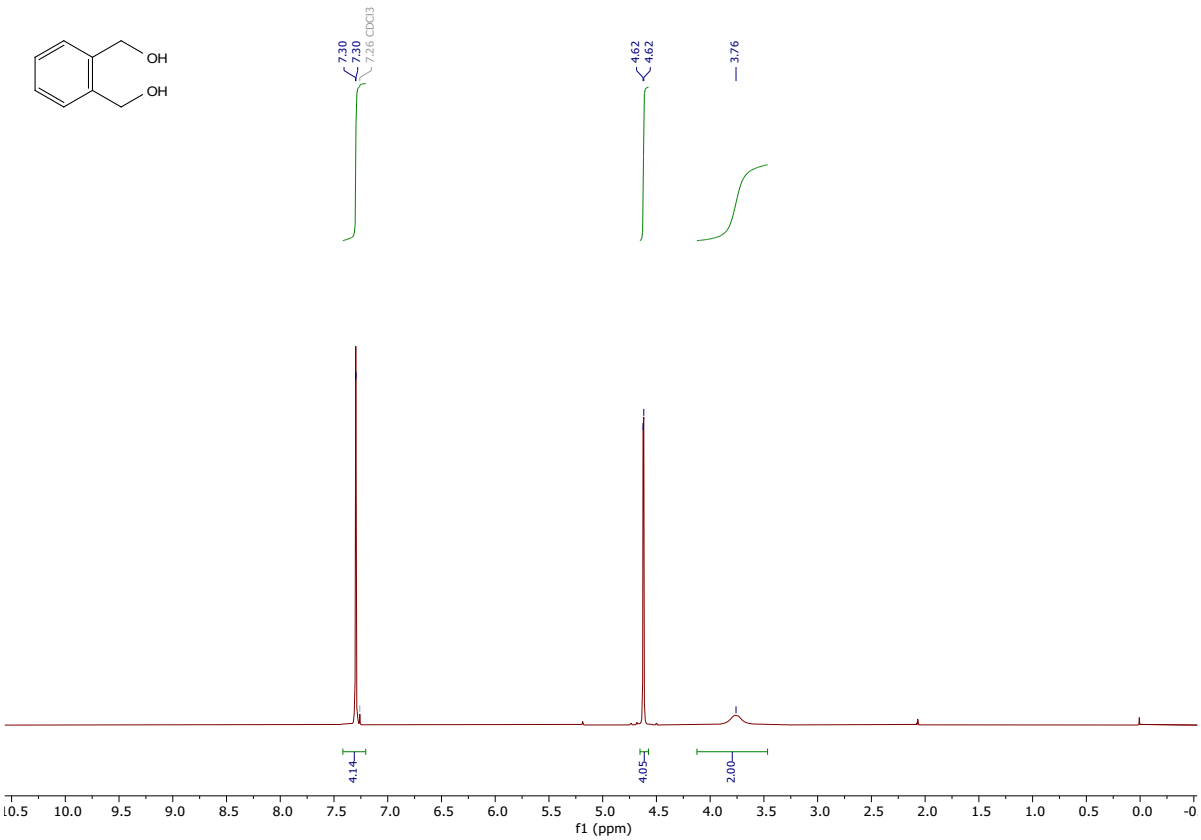

150.86
138.07
127.04
125.63
77.16 CDCl3
65.32
65.31
34.68
31.48
f1 (ppm)

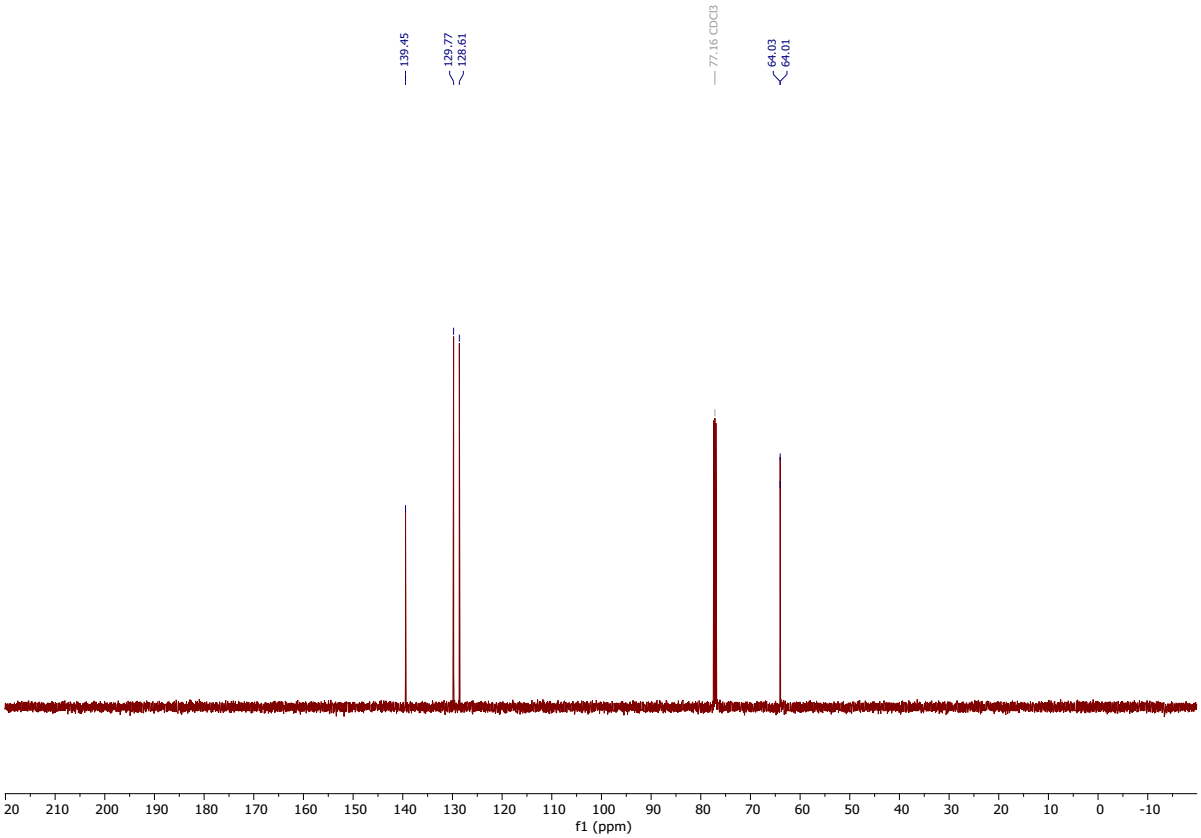

OH
HO
9.21
7.11
7.11
7.10
7.09
6.71
6.71
6.70
6.69
4.93
4.36
3.36
2.50 DMSO-d6
f1 (ppm)

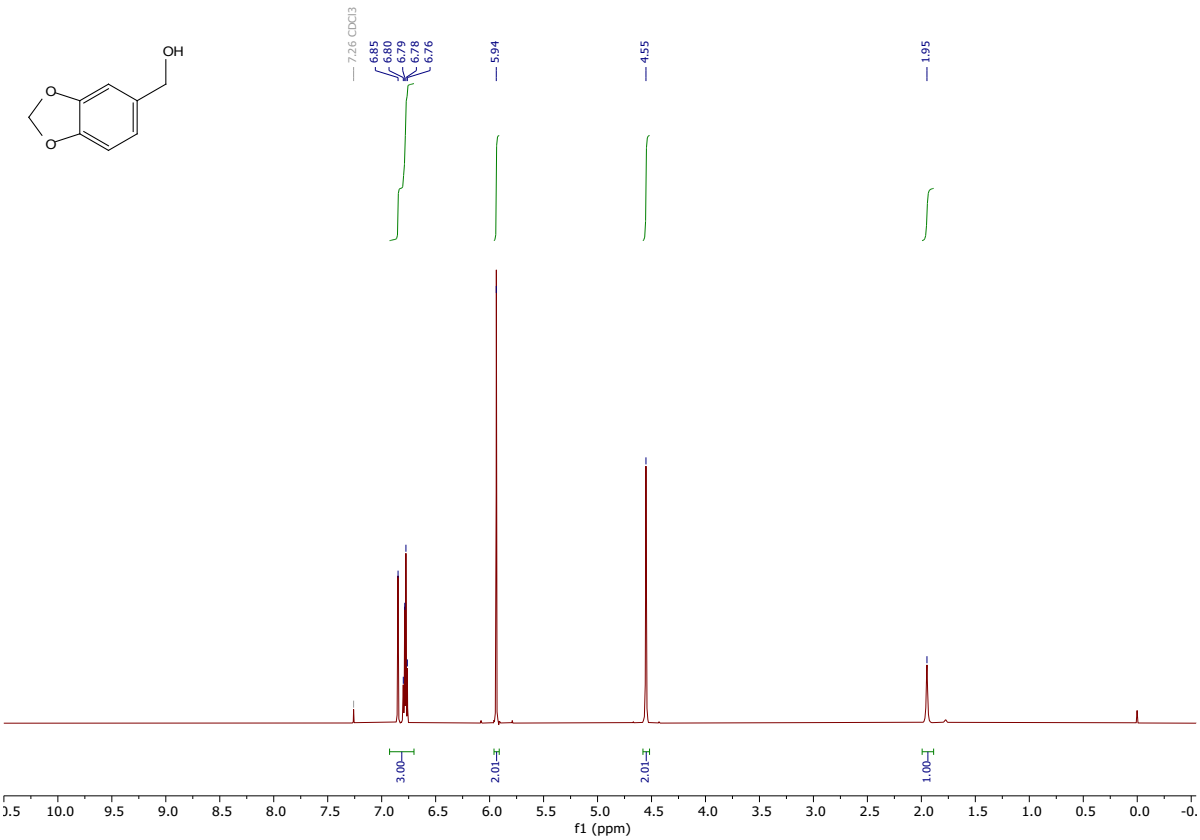

156.16
132.75
128.04
114.78
62.78
39.52 DMSO-d6
f1 (ppm)

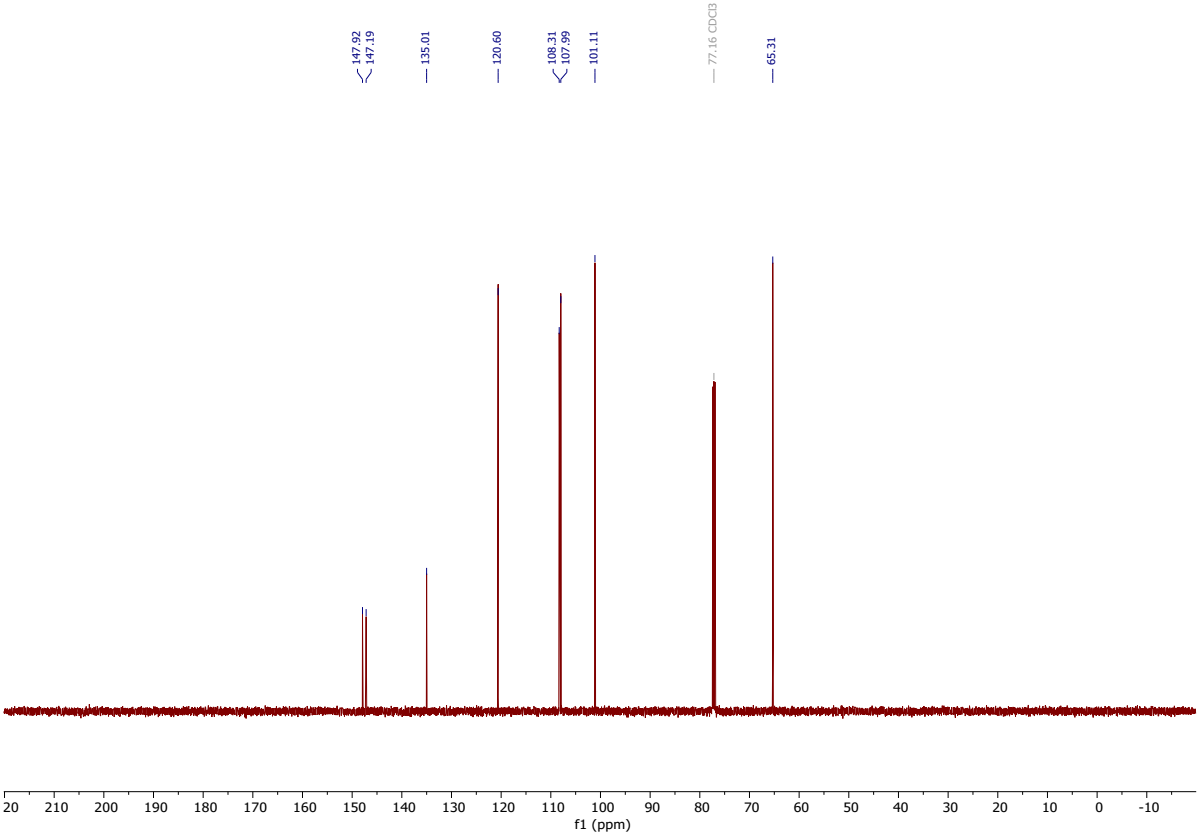

OH
H3C
O
7.28
7.28
7.27
7.27
7.27
7.26 CDCl3
6.90
6.89
6.89
6.88
6.88
6.88
6.88
4.59
4.59
3.80
3.80
3.80
1.99
1.92
1.84
1.83
1.98
1.94
1.97
3.00
1.00
f1 (ppm)

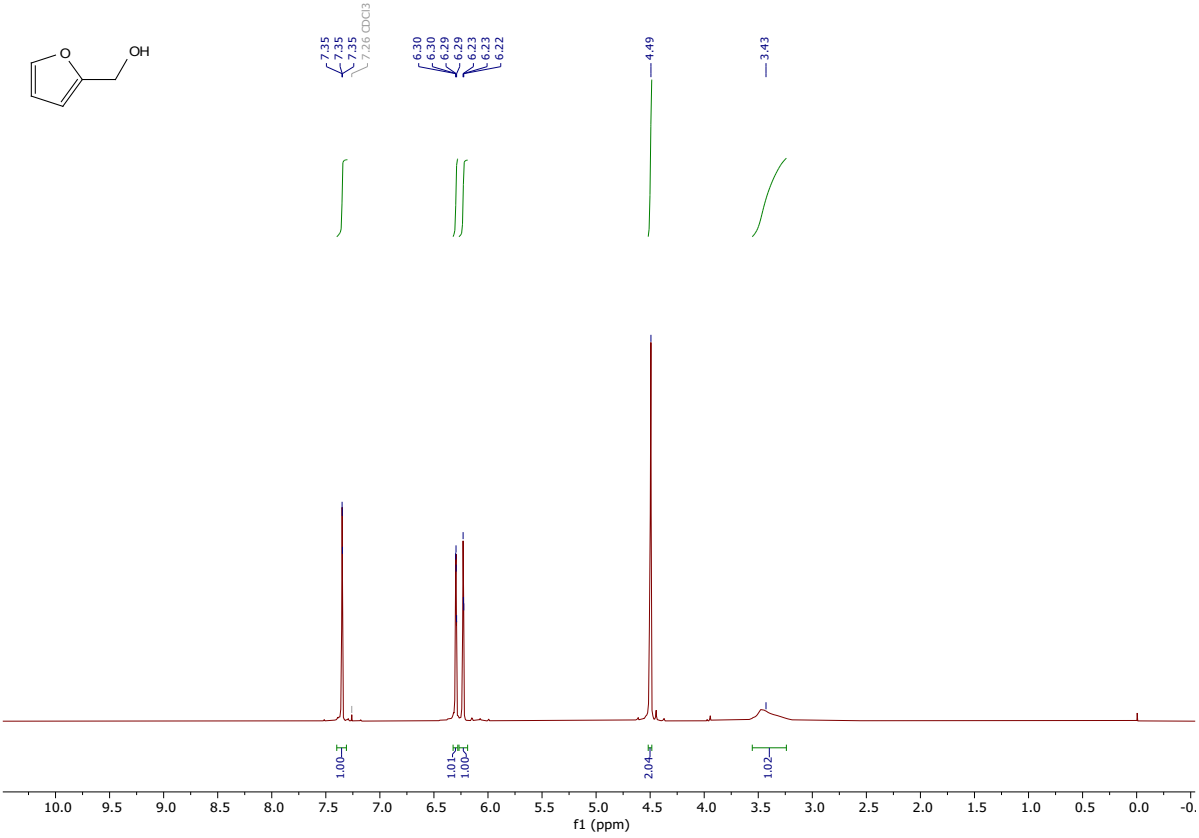

159.28
133.27
133.25
128.74
114.05
77.16 CDCl3
65.09
65.05
55.39
f1 (ppm)

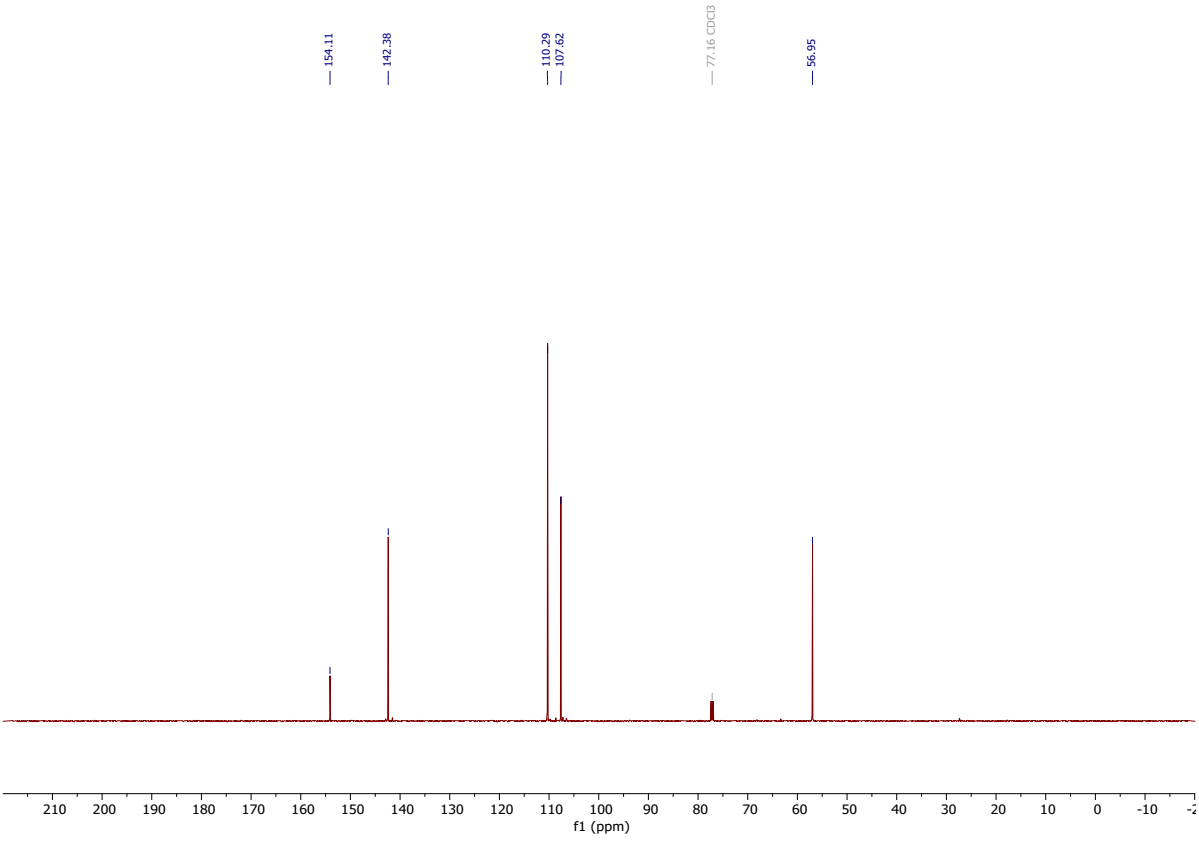

OH
OH
7.30
7.30
7.26 CDCl3
4.62
4.62
3.76
4.14
4.05
2.00
f1 (ppm)

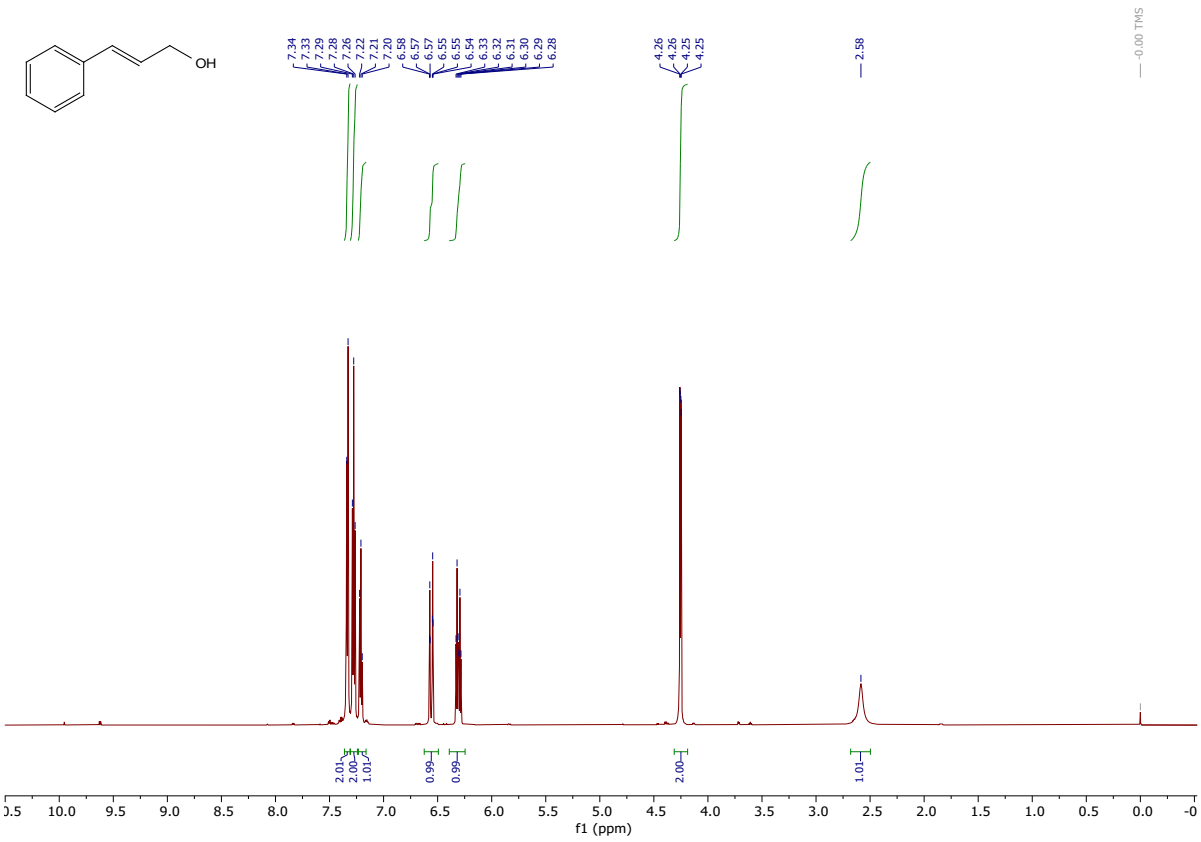

139.45
129.77
128.61
77.16 CDCl3
64.03
64.01
f1 (ppm)

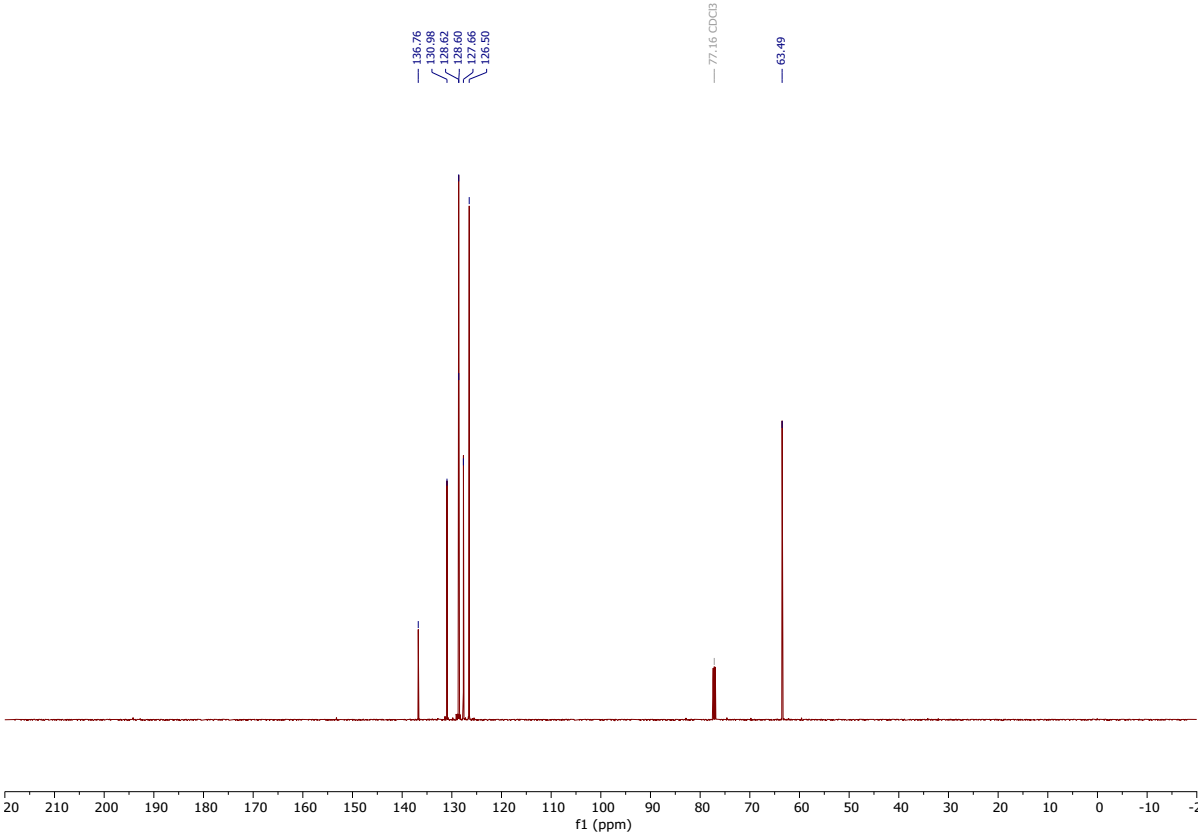

OH
O
O
7.26 CDCl3
6.85
6.80
6.79
6.78
6.76
5.94
4.55
1.95
3.00
2.01
2.01
1.00
f1 (ppm)

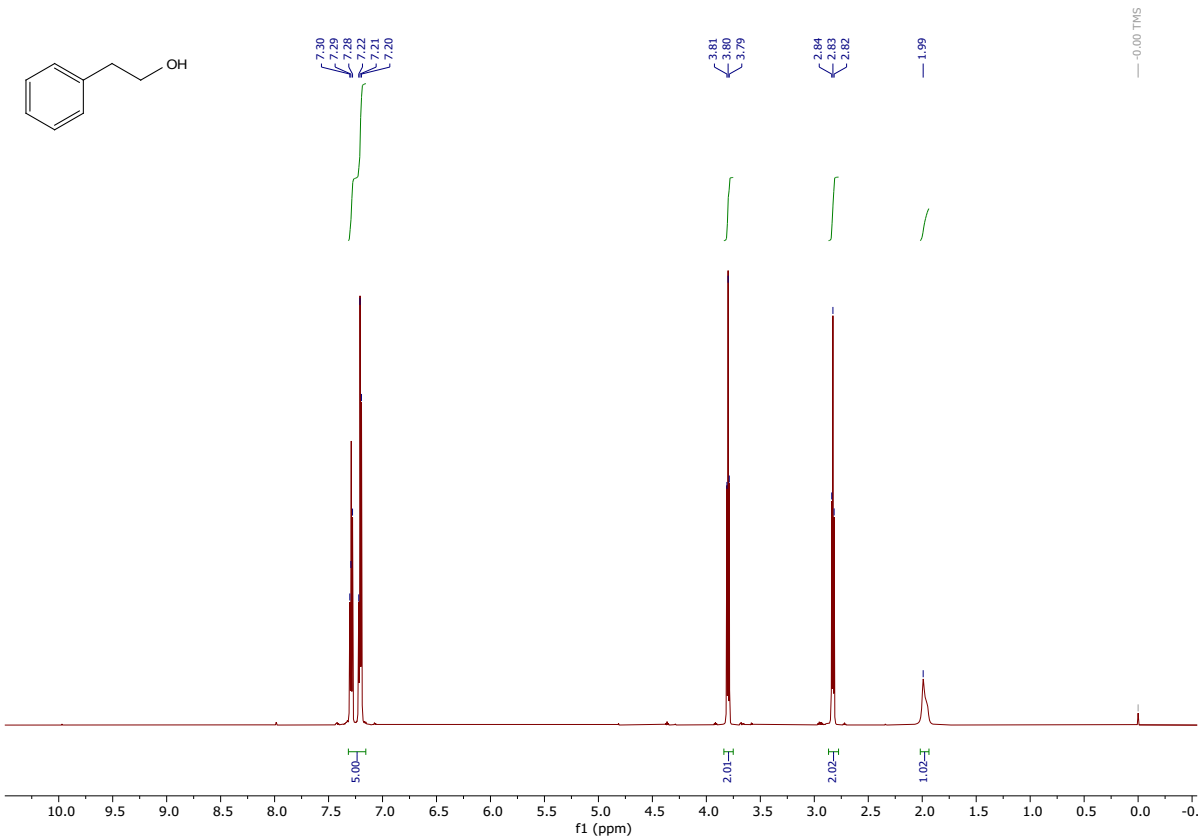

147.92
147.19
135.01
120.60
108.31
107.99
101.11
77.16 CDCl3
65.31
f1 (ppm)

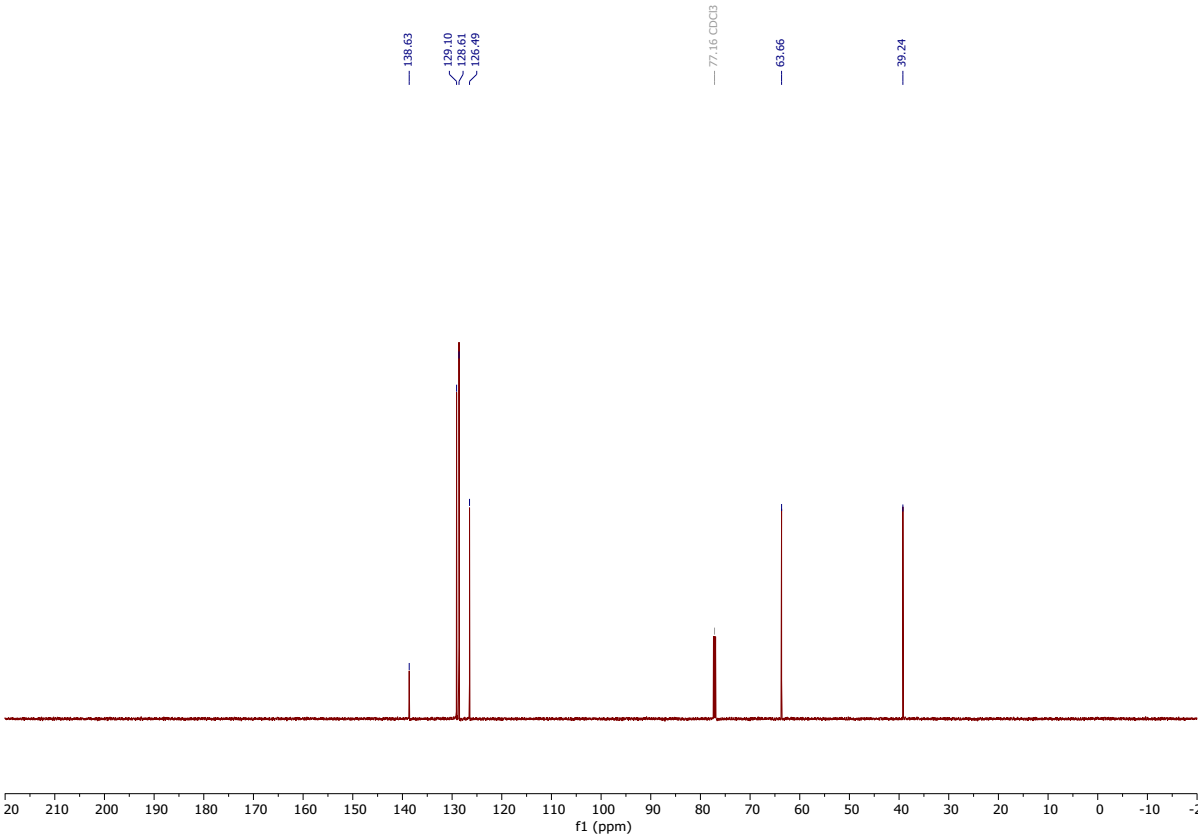

O
OH
7.35
7.35
7.35
7.26 CDCl3
6.30
6.30
6.29
6.29
6.23
6.23
6.22
4.49
3.43
1.00
1.01
1.00
2.04
1.02
f1 (ppm)

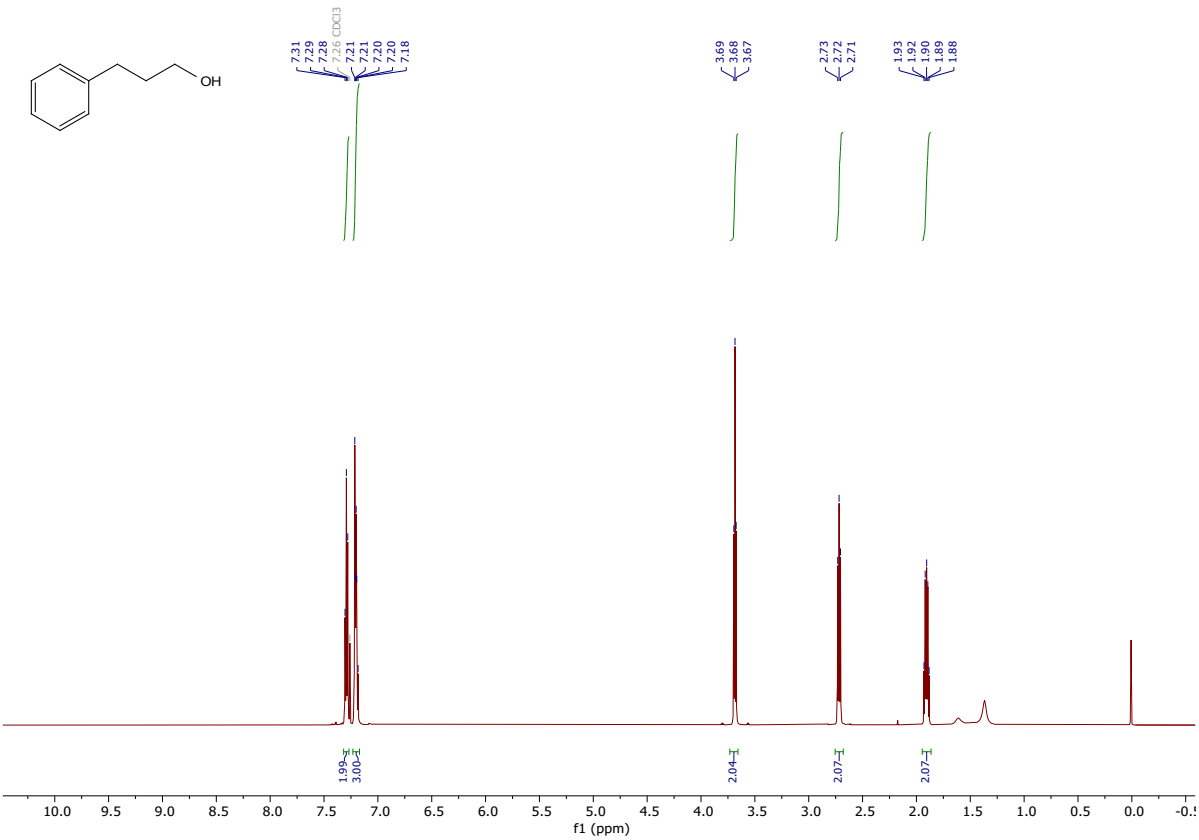

154.11
142.38
110.29
107.62
77.16 CDCl3
56.95
f1 (ppm)

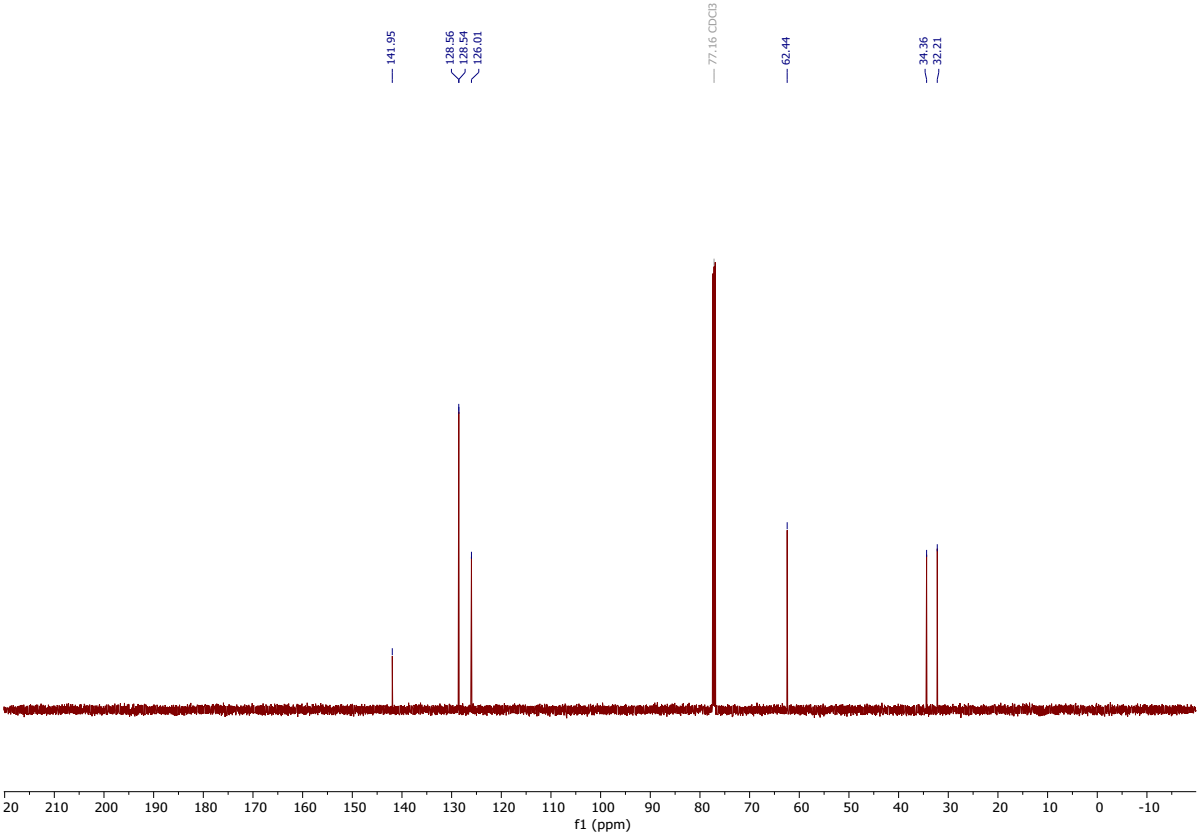

OH
7.34
7.33
7.29
7.28
7.26
7.22
7.21
7.20
6.58
6.57
6.57
6.55
6.55
6.54
6.33
6.32
6.31
6.30
6.29
6.28
4.26
4.26
4.25
4.25
2.58
0.00 TMS
2.01
2.00
1.01
0.99
0.99
2.00
1.01
f1 (ppm)

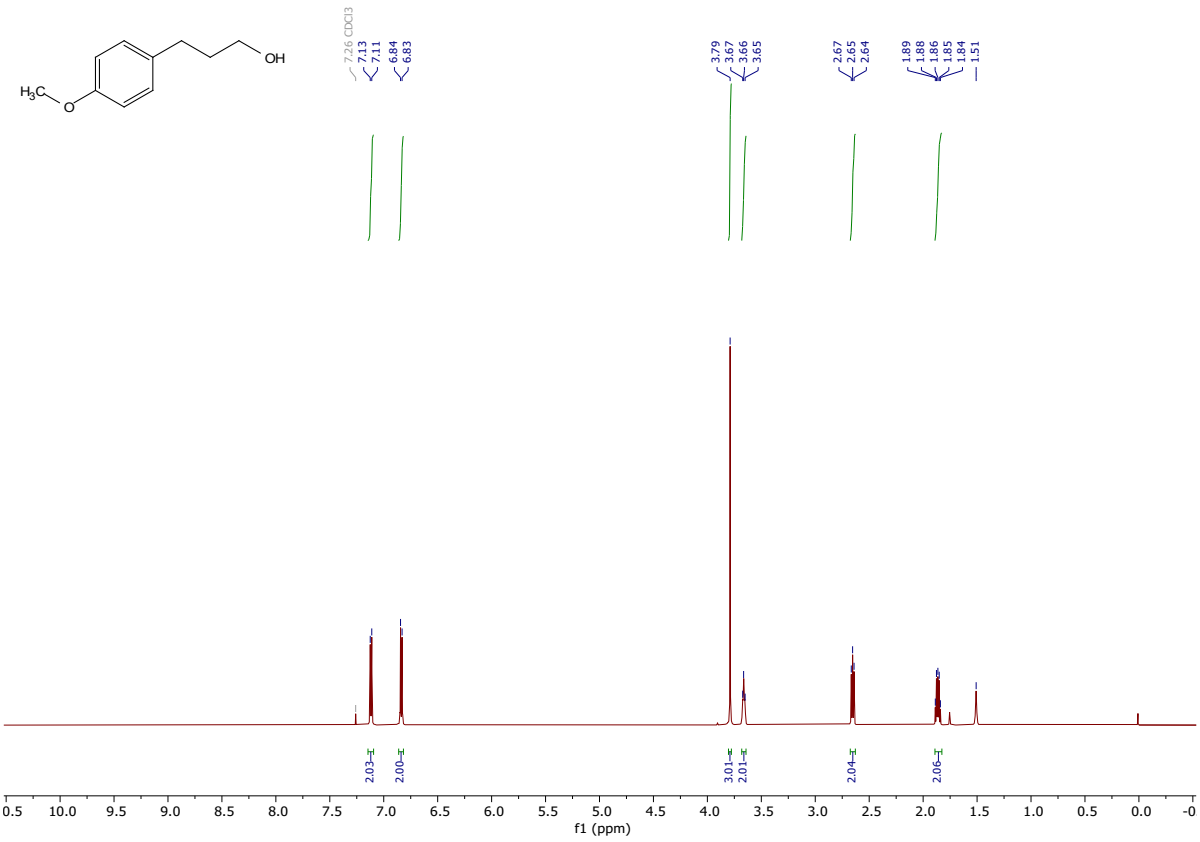

136.76
130.98
128.62
128.60
127.66
126.50
77.16 CDCl3
63.49
f1 (ppm)

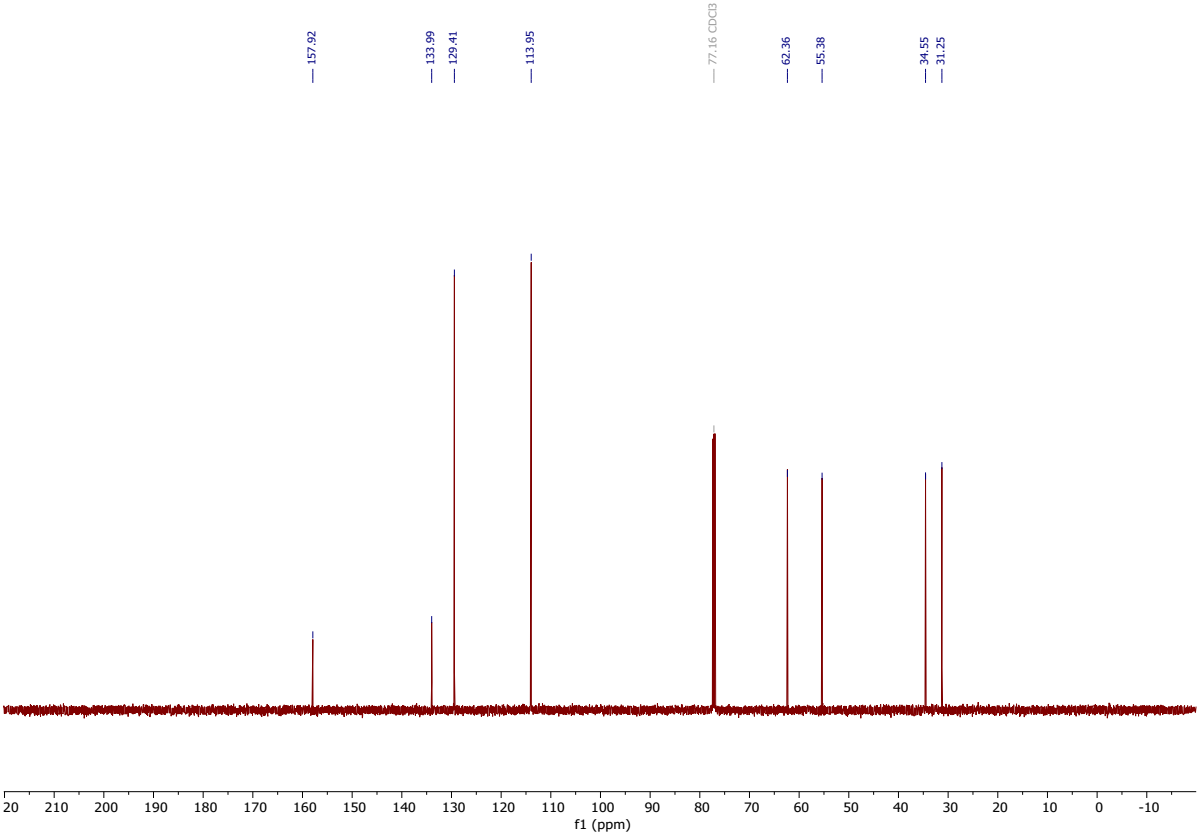

OH
7.30
7.29
7.28
7.22
7.21
7.20
3.81
3.80
3.79
2.84
2.83
2.82
1.99
0.00 TMS
5.00
2.01
2.02
1.02
f1 (ppm)

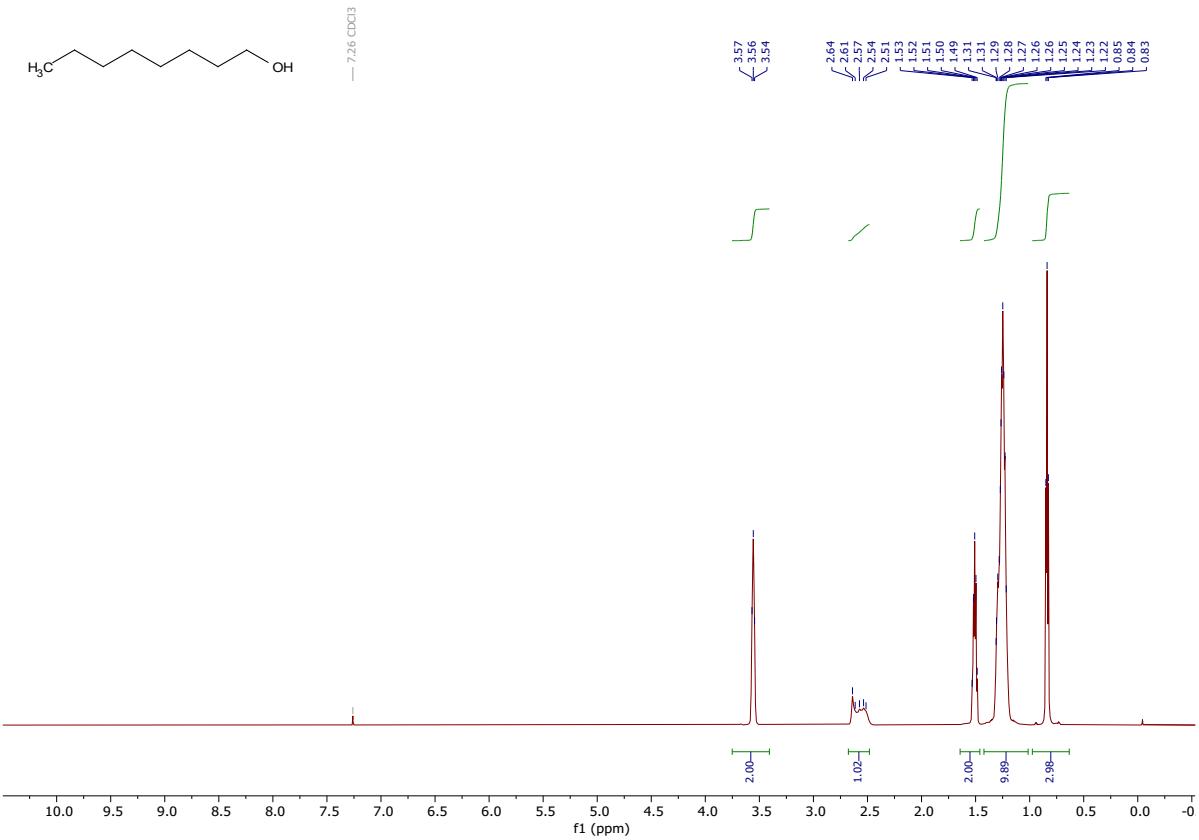

138.63
129.10
128.61
126.49
77.16 CDCl3
63.66
39.24
f1 (ppm)

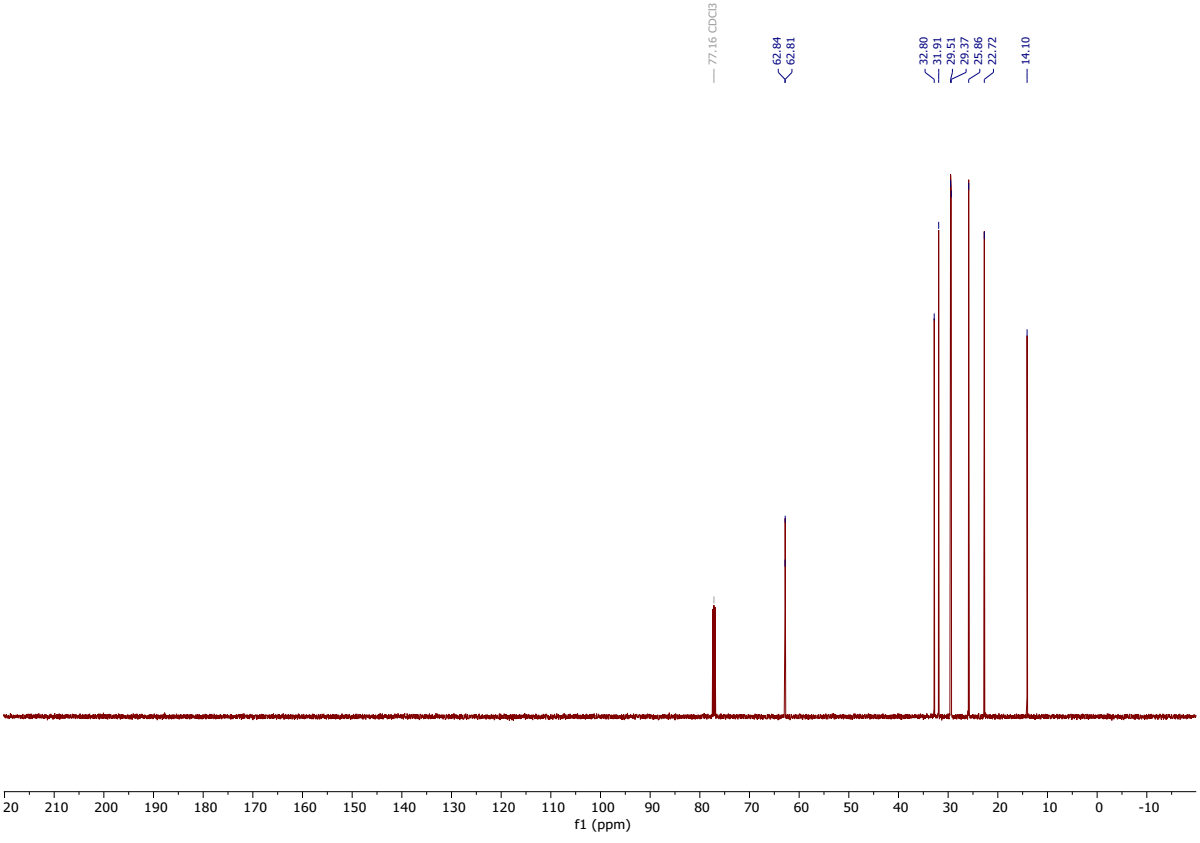

OH
7.31
7.29
7.28
7.26
CDCl3
7.21
7.21
7.20
7.20
7.18
3.69
3.68
3.67
2.73
2.72
2.71
1.93
1.92
1.90
1.89
1.88
1.99
3.00
2.04
2.07
2.07
f1 (ppm)

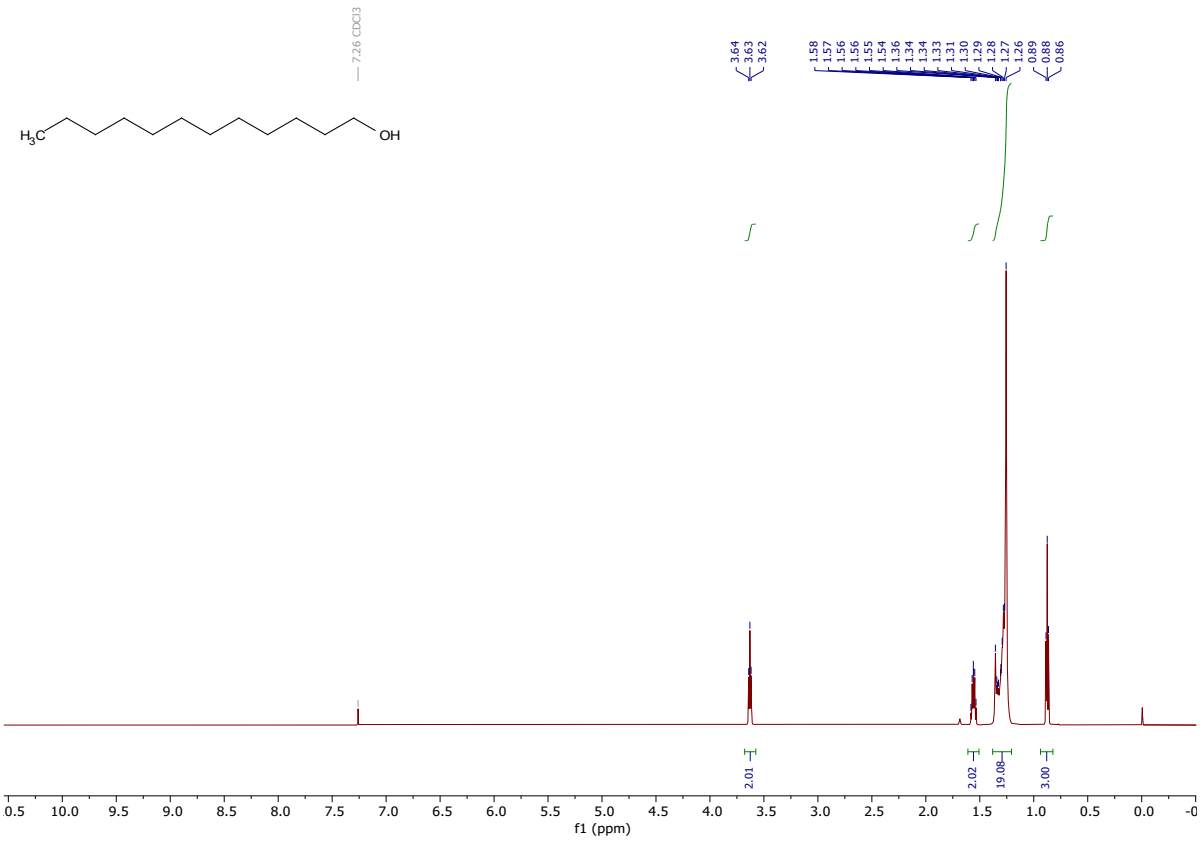

141.95
128.56
128.54
126.01
77.16 CDCl3
62.44
34.36
32.21
f1 (ppm)

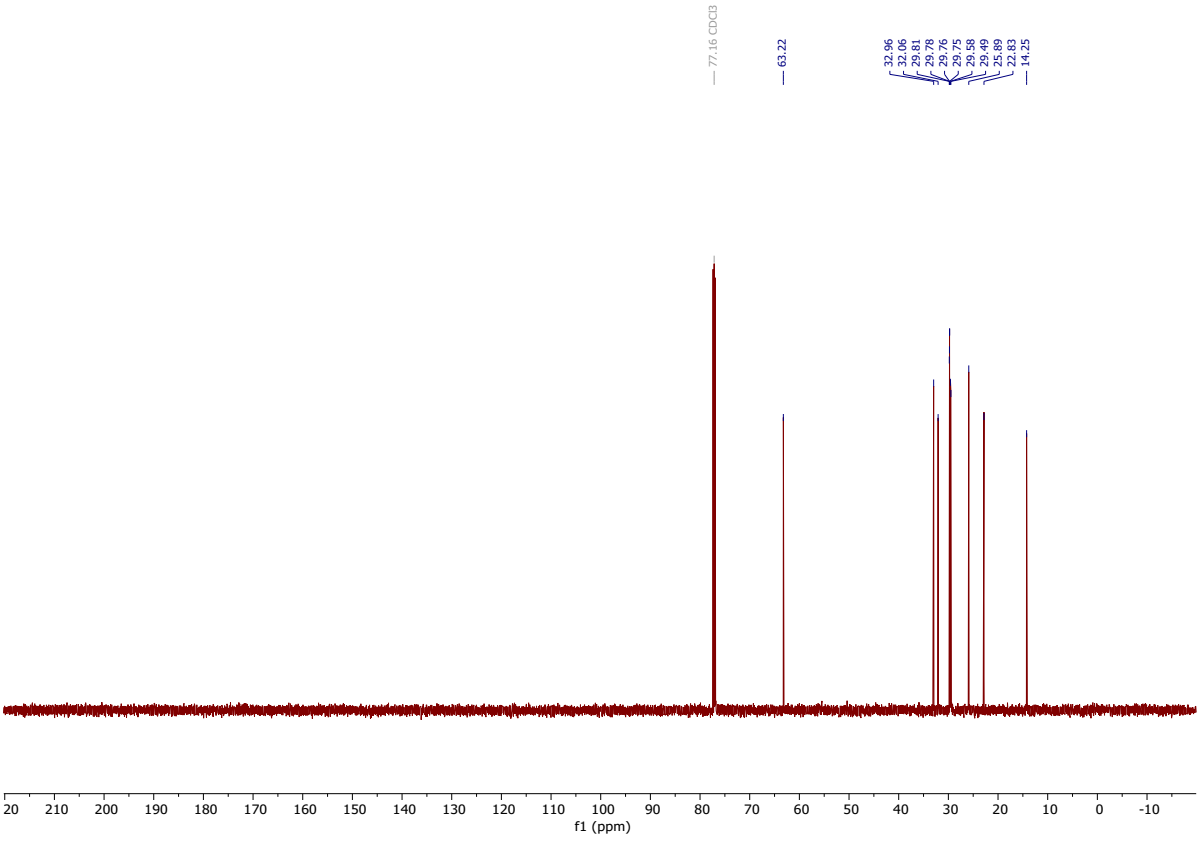

OH
H3C
O
7.26 CDCl3
7.13
7.11
6.84
6.83
3.79
3.67
3.66
3.65
2.67
2.65
2.64
1.89
1.88
1.86
1.85
1.84
1.51
2.03
2.00
3.01
2.01
2.04
2.06
f1 (ppm)

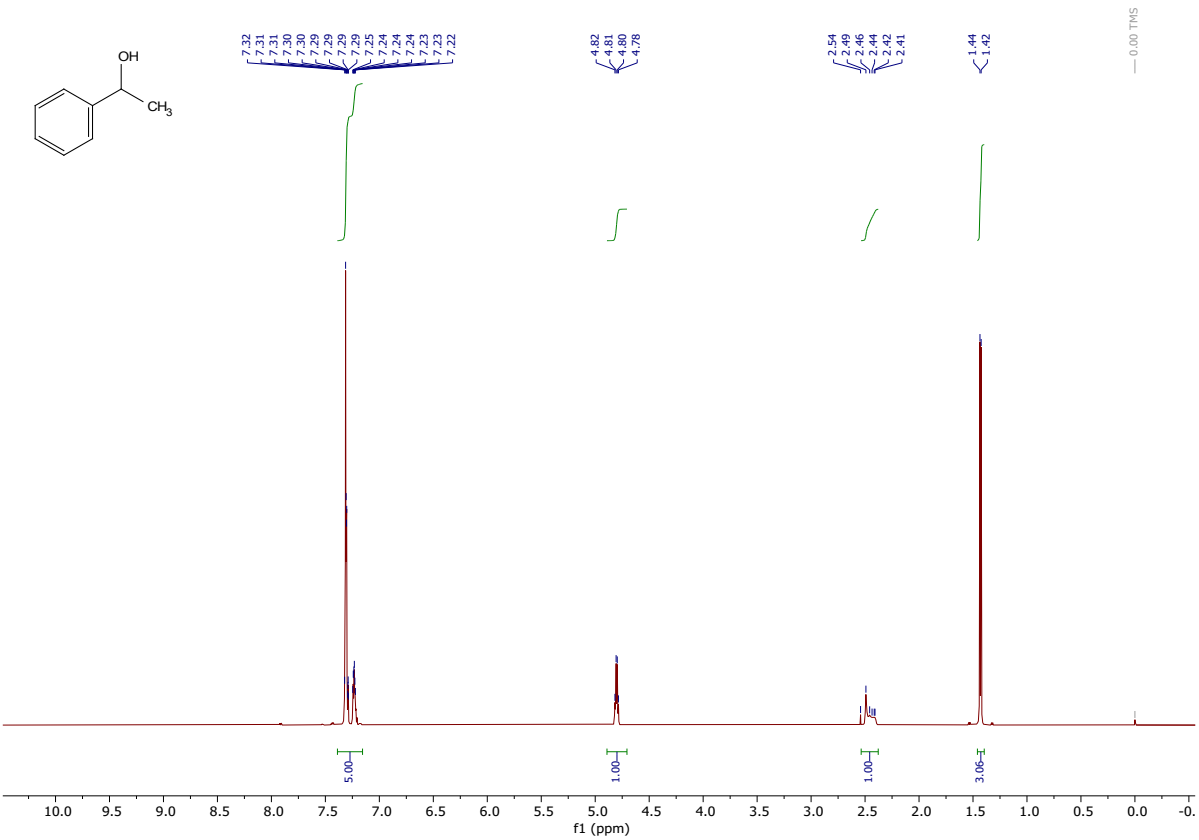

157.92
133.99
129.41
113.95
77.16 CDCl3
62.36
55.38
34.55
31.25
f1 (ppm)

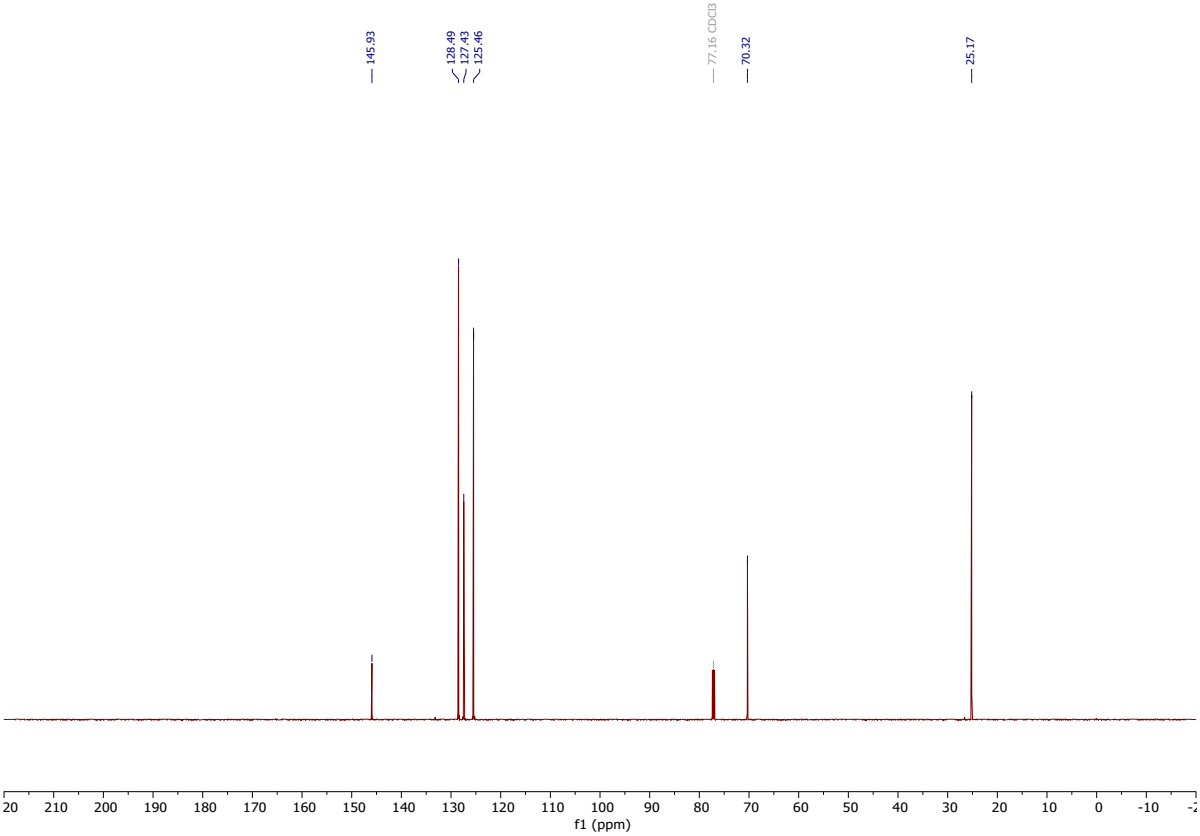

H3C
OH
7.26 CDCl3
3.57
3.56
3.54
2.64
2.61
2.57
2.54
2.51
1.53
1.52
1.51
1.50
1.49
1.31
1.31
1.29
1.28
1.27
1.26
1.26
1.25
1.24
1.23
1.22
0.85
0.84
0.83
2.00
1.02
2.00
9.89
2.98
f1 (ppm)

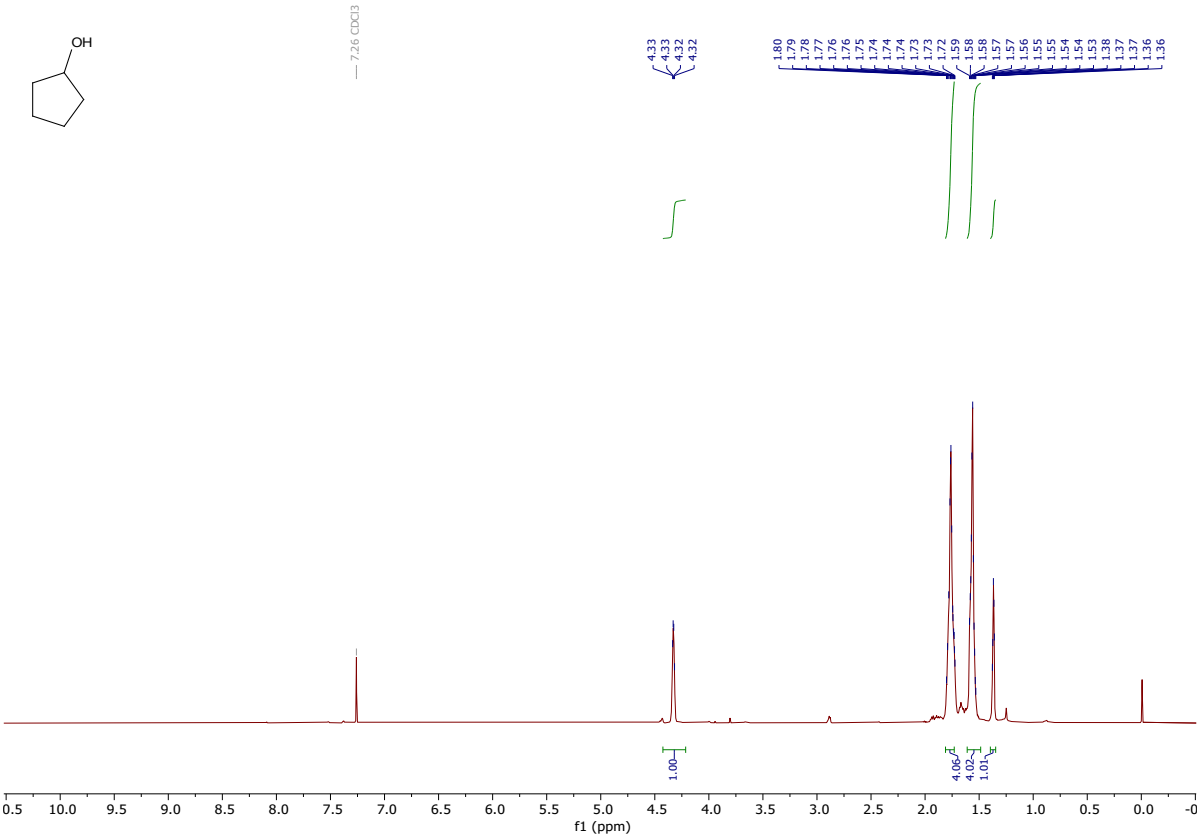

77.16 CDCl3
62.84
62.81
32.80
31.91
29.51
29.37
25.86
22.72
14.10
f1 (ppm)

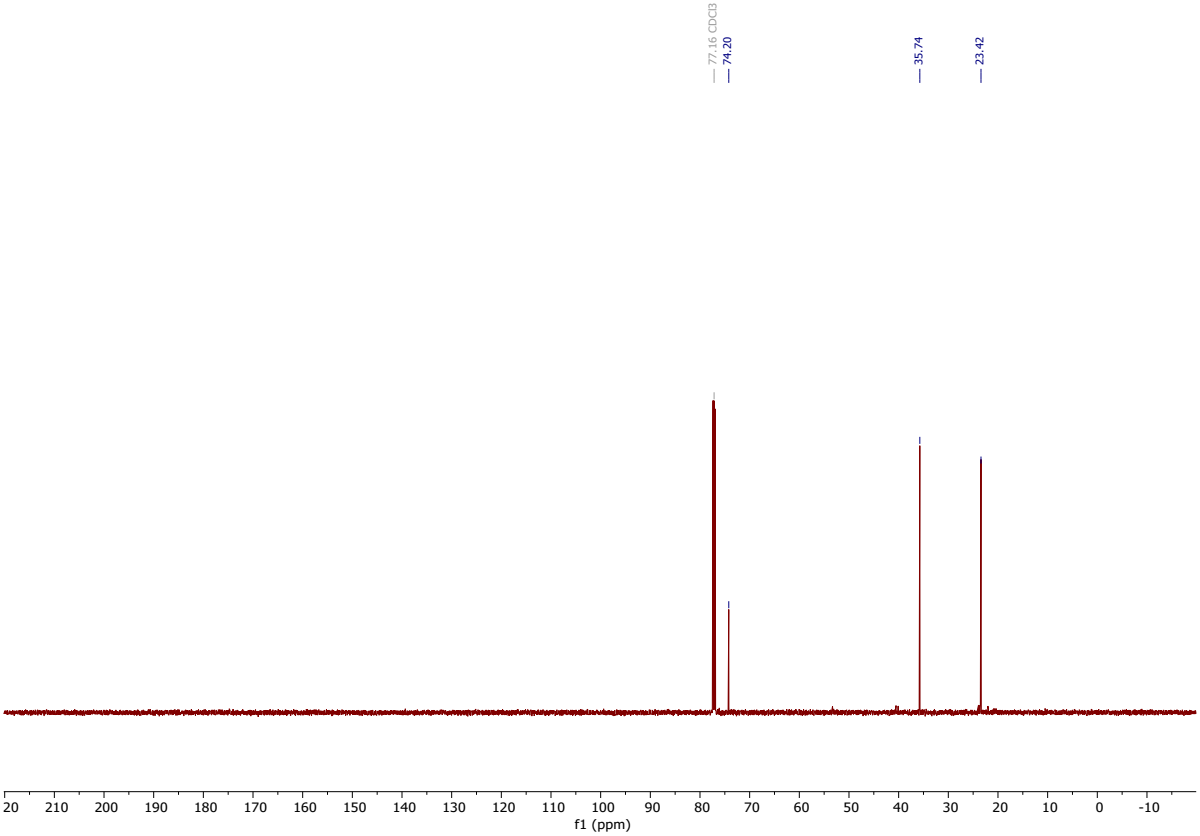

7.26 CDCl3
H3C
OH
3.64
3.63
3.62
1.58
1.57
1.56
1.56
1.55
1.54
1.36
1.34
1.34
1.33
1.31
1.30
1.29
1.28
1.27
1.26
0.89
0.88
0.86
2.01
2.02
19.08
3.00
f1 (ppm)

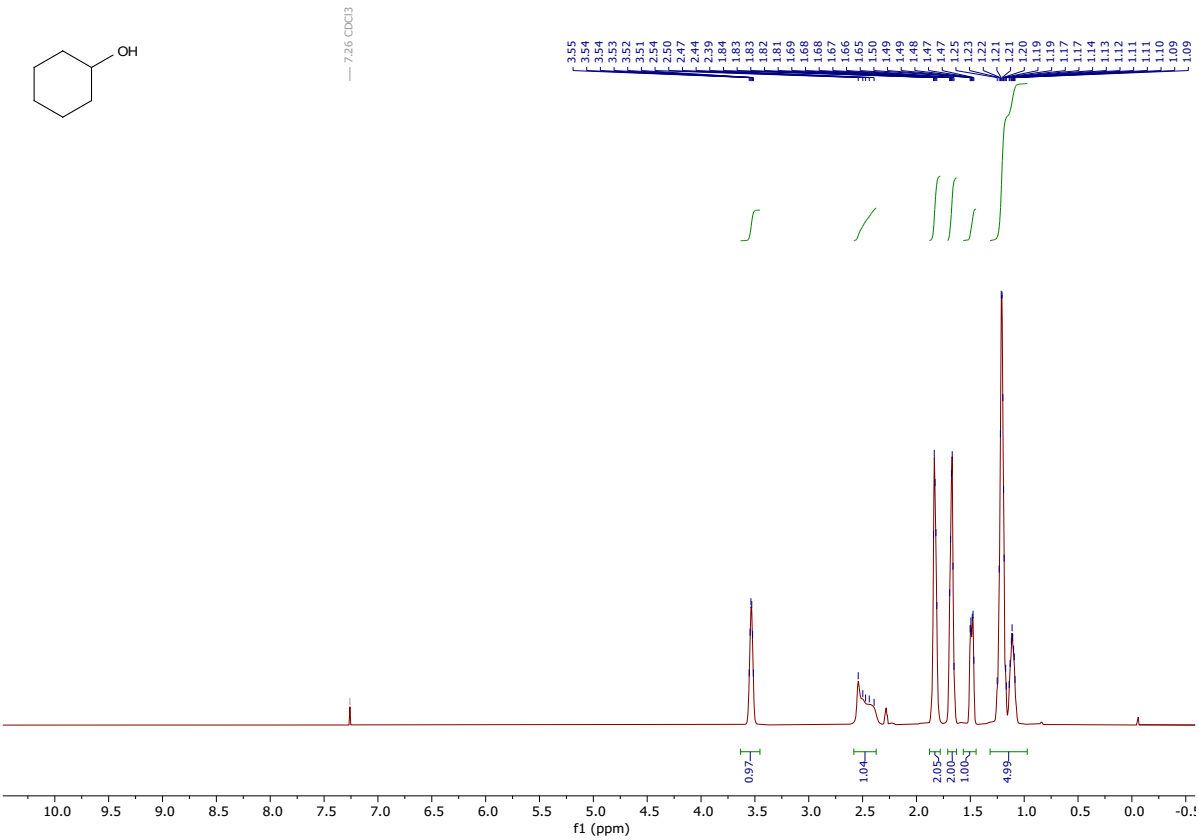

77.16 CDCl3
63.22
32.96
32.06
29.81
29.78
29.76
29.75
29.58
29.49
25.89
22.83
14.25
f1 (ppm)

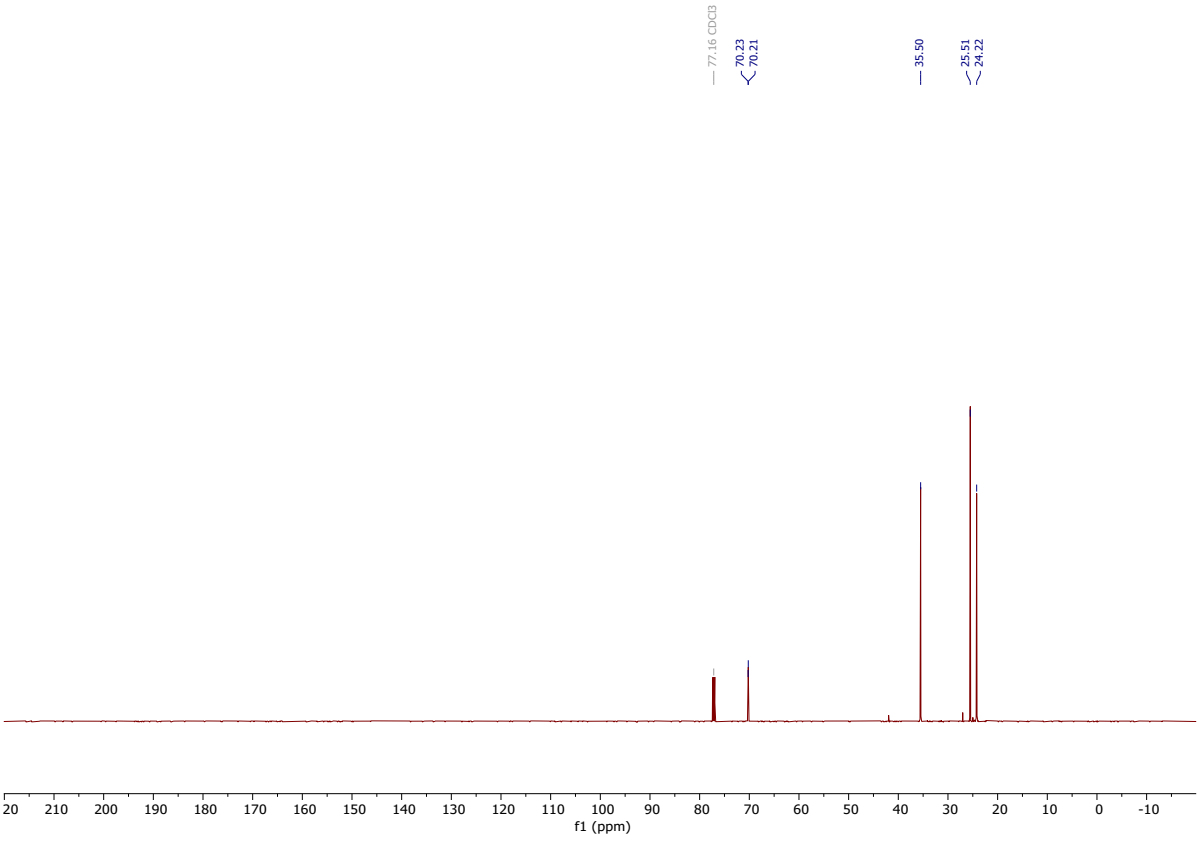

OH
CH3
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.29
7.25
7.24
7.24
7.24
7.23
7.23
7.22
4.82
4.81
4.80
4.78
2.54
2.49
2.46
2.44
2.42
2.41
1.44
1.42
0.00 TMS
5.00
1.00
1.00
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

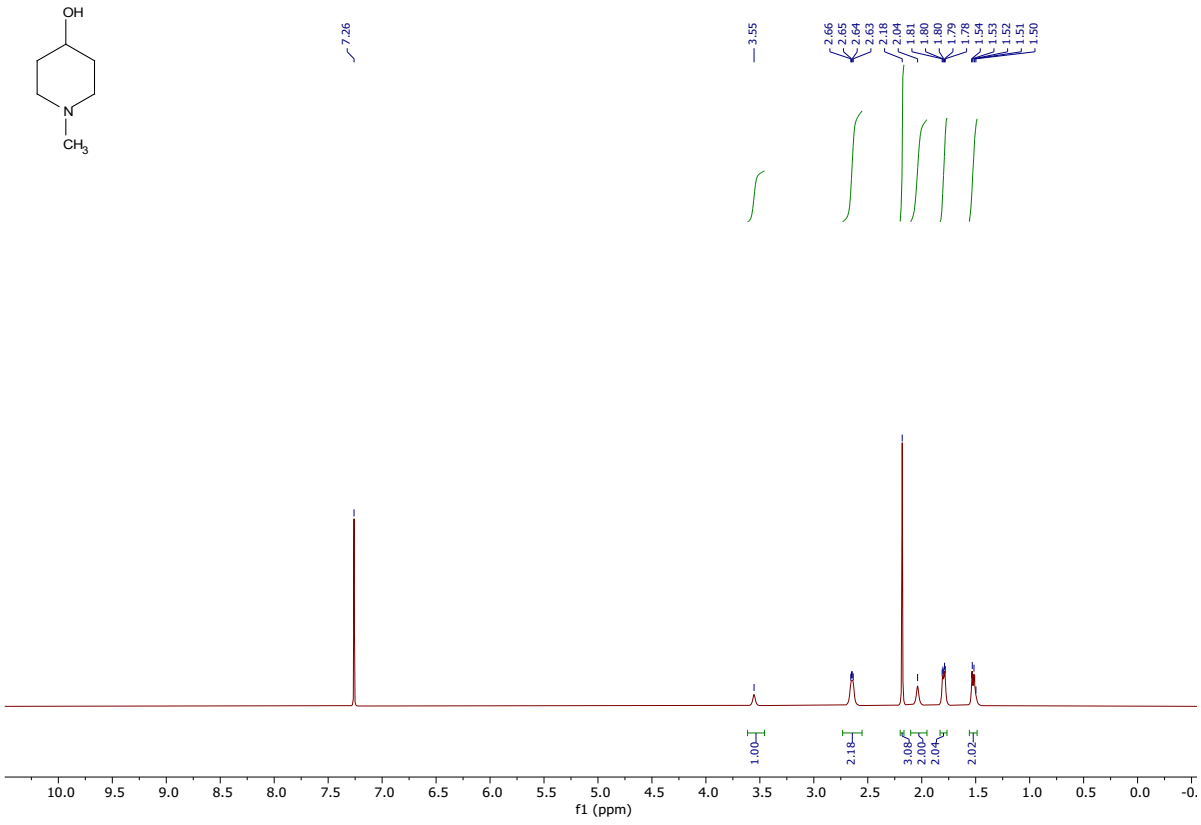

145.93
128.49
127.43
125.46
77.16 CDCl3
70.32
25.17
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

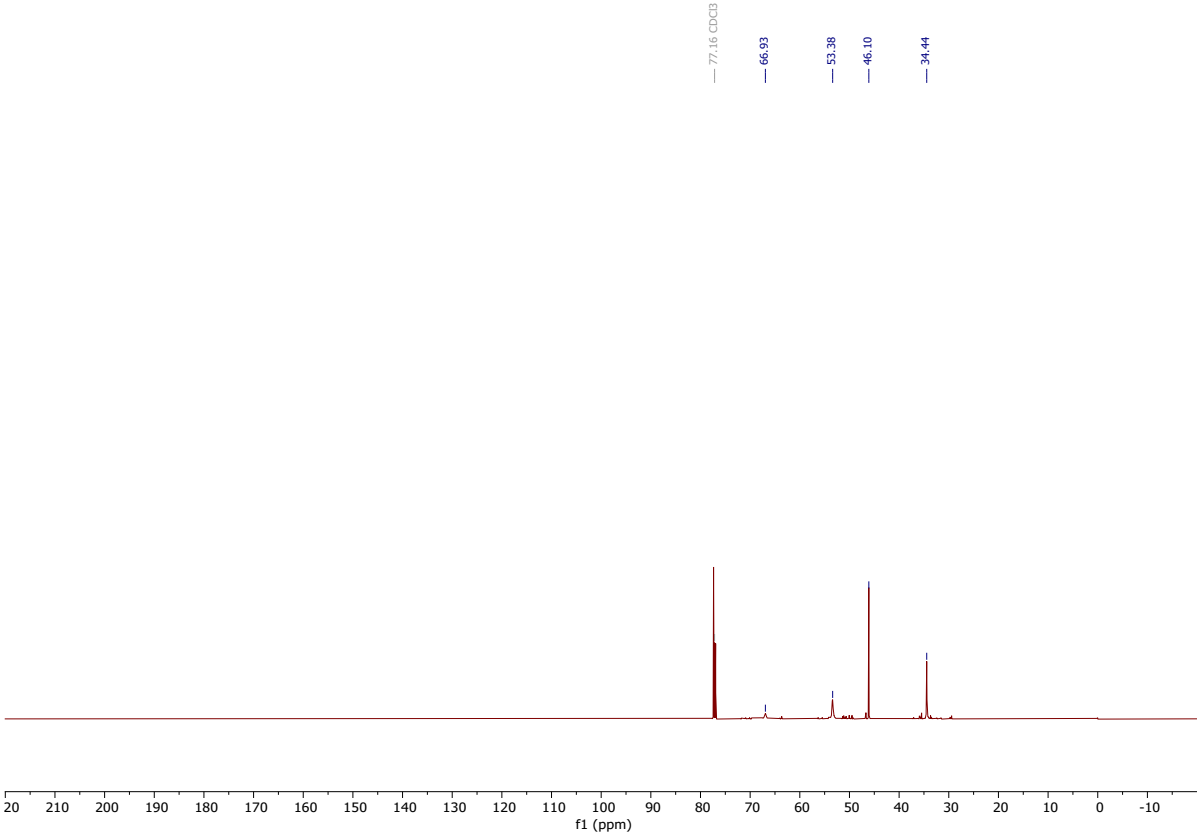

OH
7.26 CDCl3
4.33
4.33
4.32
4.32
1.80
1.79
1.78
1.77
1.76
1.76
1.75
1.74
1.74
1.74
1.73
1.73
1.72
1.59
1.59
1.58
1.58
1.57
1.57
1.56
1.55
1.55
1.54
1.54
1.53
1.38
1.37
1.37
1.36
1.36
1.00
4.06
4.02
1.01
f1 (ppm)

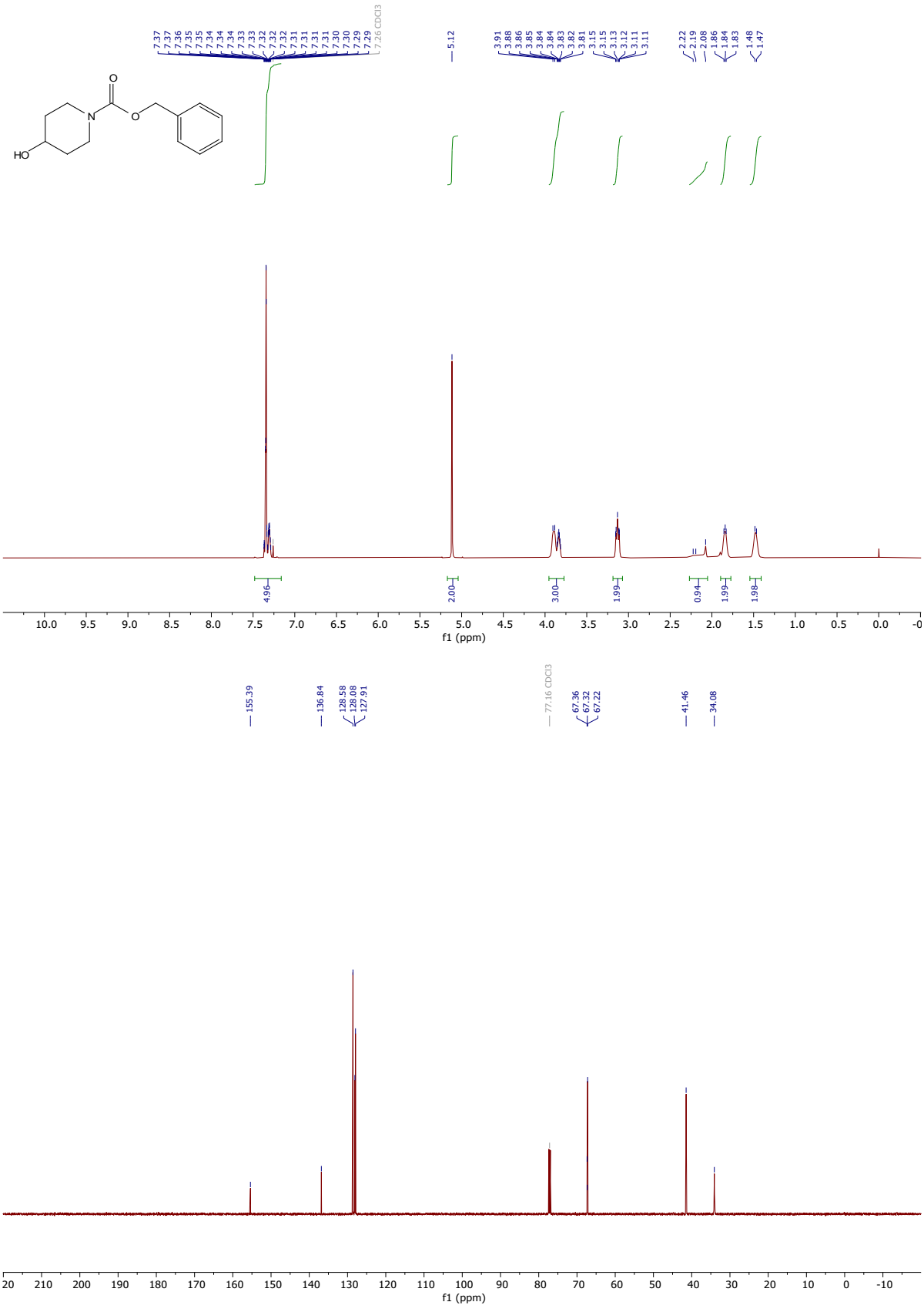

77.16 CDCl3
74.20
35.74
23.42
f1 (ppm)

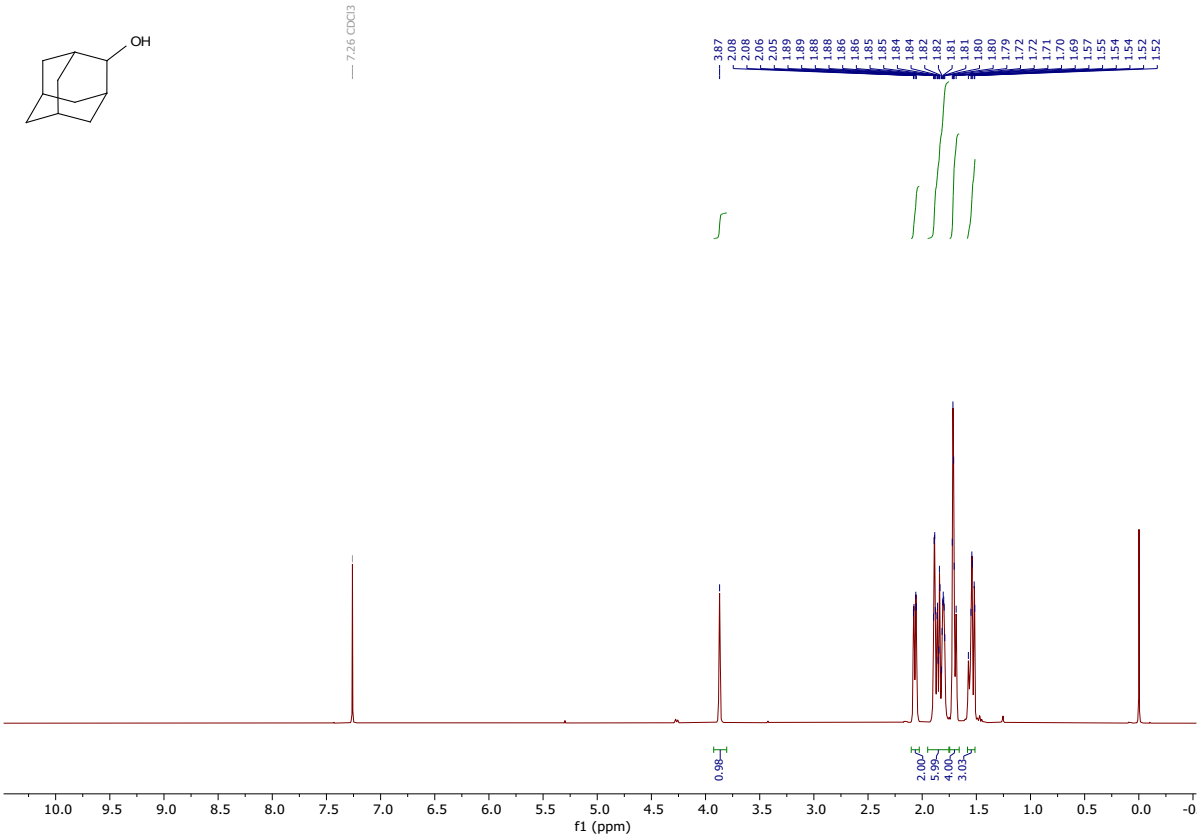

OH
7.26 CDCl3
3.55
3.54
3.54
3.53
3.52
3.51
2.54
2.50
2.47
2.44
2.39
1.84
1.83
1.83
1.82
1.81
1.69
1.68
1.68
1.67
1.66
1.65
1.50
1.49
1.49
1.48
1.47
1.47
1.25
1.23
1.22
1.21
1.21
1.20
1.19
1.19
1.17
1.17
1.14
1.13
1.12
1.11
1.11
1.10
1.09
1.09
0.97
1.04
2.05
2.00
1.00
4.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

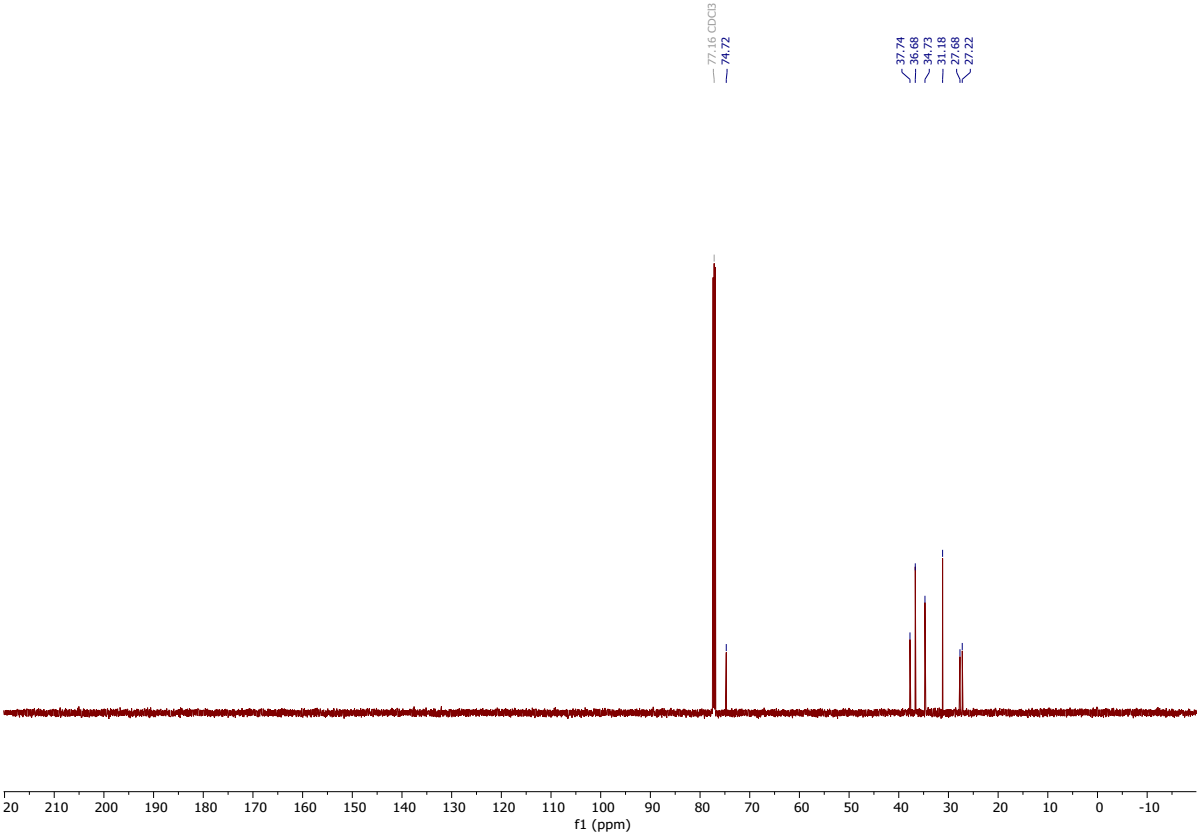

77.16 CDCl3
70.23
70.21
35.50
25.51
24.22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

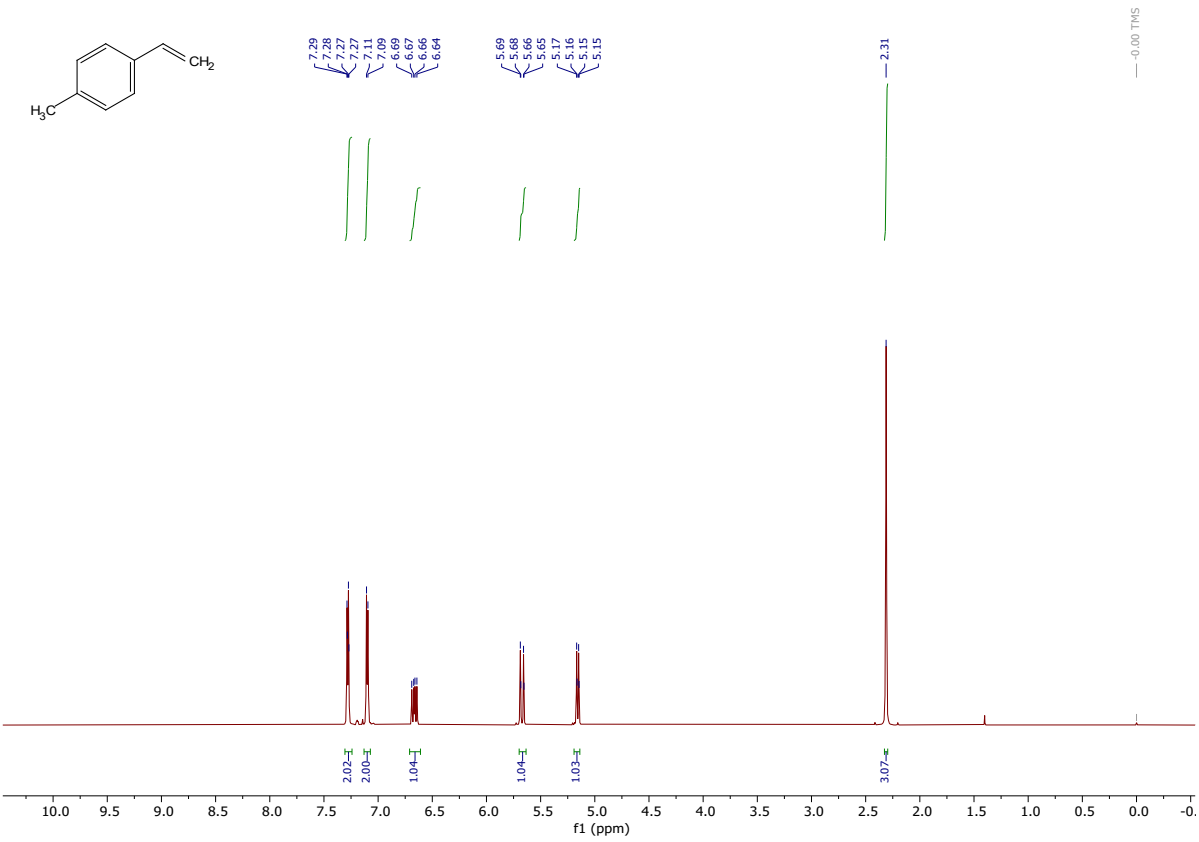

OH
N
CH3
7.26
3.55
2.66
2.65
2.64
2.63
2.18
2.04
1.81
1.80
1.80
1.79
1.78
1.54
1.53
1.52
1.51
1.50
1.00
2.18
3.08
2.00
2.04
2.02
f1 (ppm)

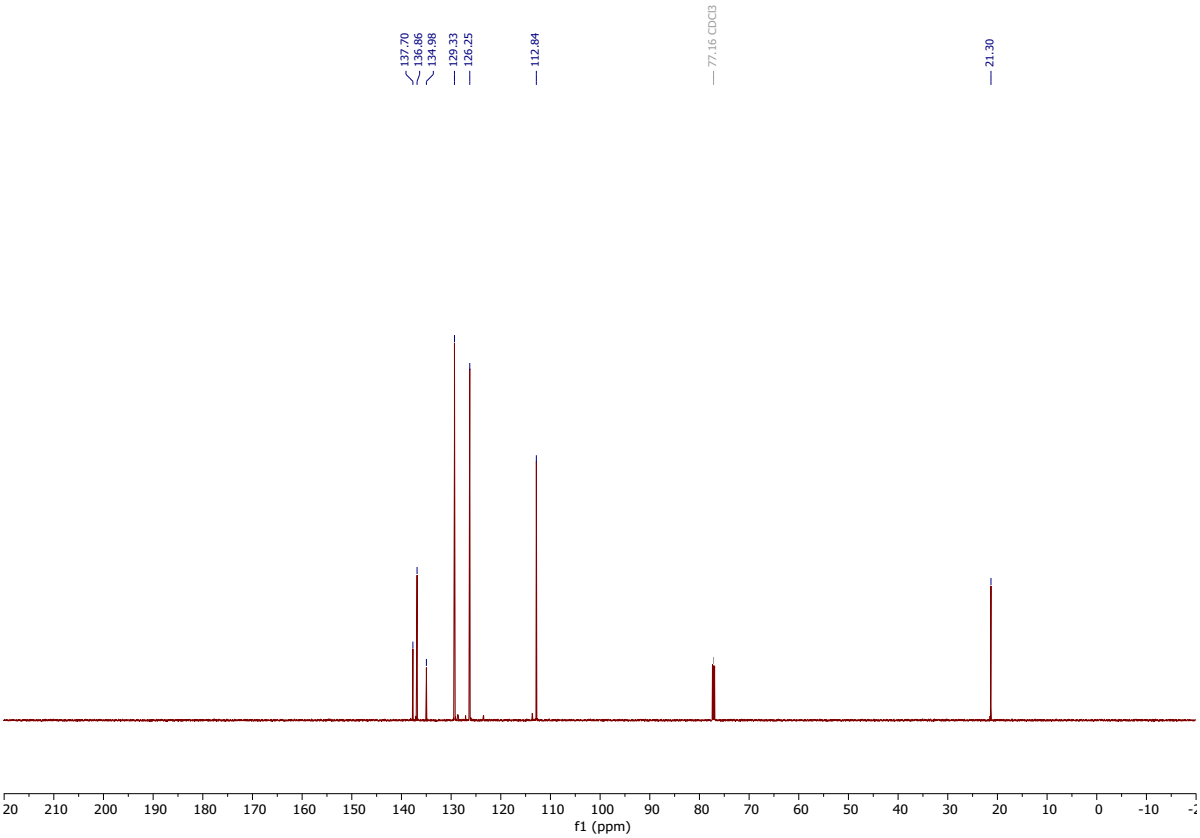

77.16 CDCl3
66.93
53.38
46.10
34.44
f1 (ppm)

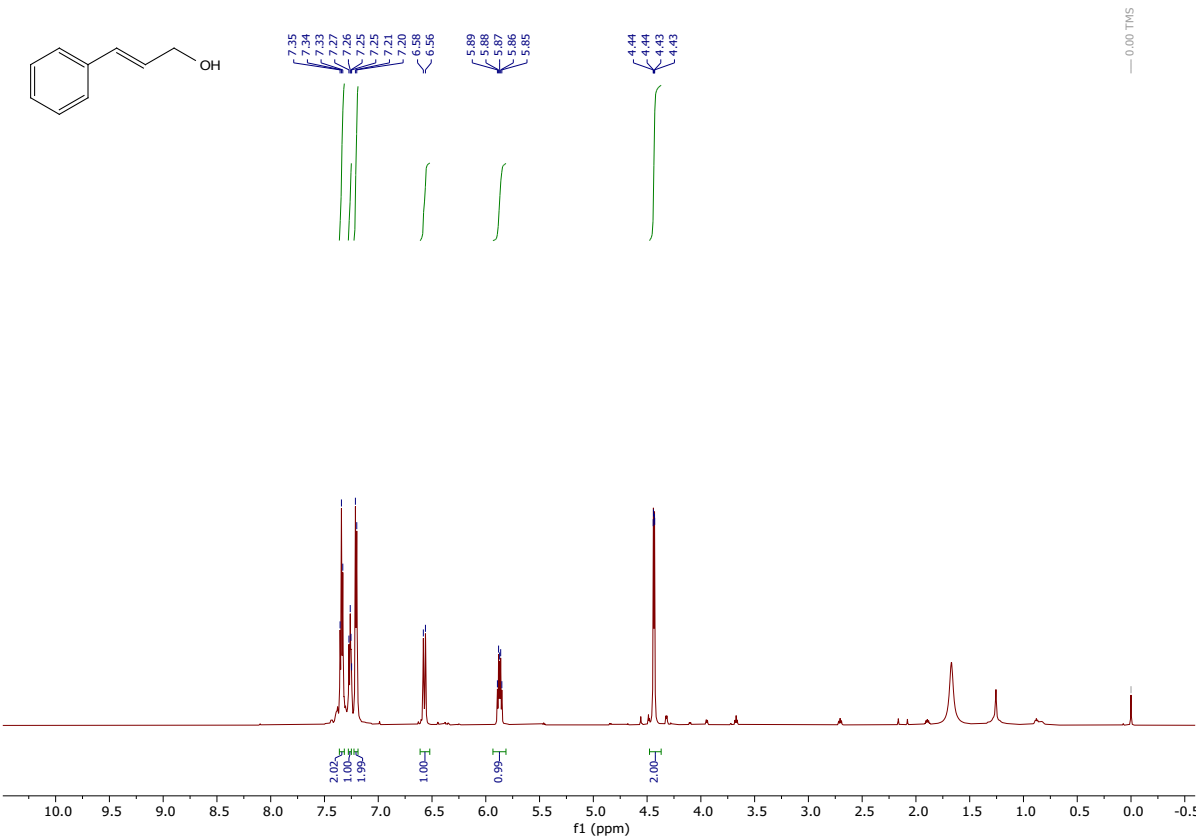

7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.29
7.26 CDCl3
5.12
3.91
3.88
3.86
3.85
3.84
3.84
3.83
3.82
3.81
3.15
3.15
3.13
3.12
3.11
3.11
2.22
2.19
2.08
1.86
1.84
1.83
1.48
1.47
HO
O
N
O
4.96
2.00
3.00
1.99
0.94
1.99
1.98
f1 (ppm)
155.39
136.84
128.58
128.08
127.91
77.16 CDCl3
67.36
67.32
67.22
41.46
34.08
f1 (ppm)

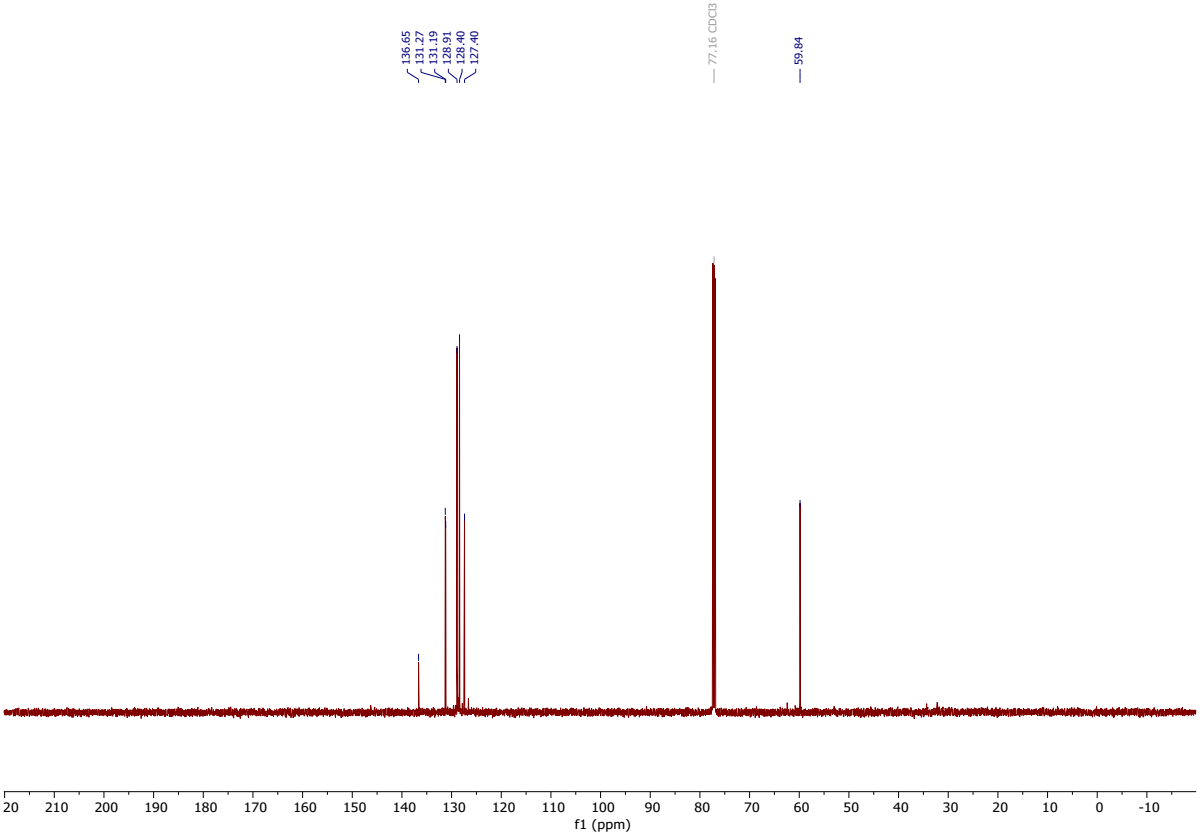

OH
7.26 CDCl3
3.87
2.08
2.08
2.06
2.05
1.89
1.89
1.88
1.88
1.86
1.86
1.85
1.85
1.84
1.84
1.82
1.82
1.81
1.81
1.80
1.80
1.79
1.72
1.72
1.71
1.70
1.69
1.57
1.55
1.54
1.54
1.52
1.52
0.98
2.00
5.99
4.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

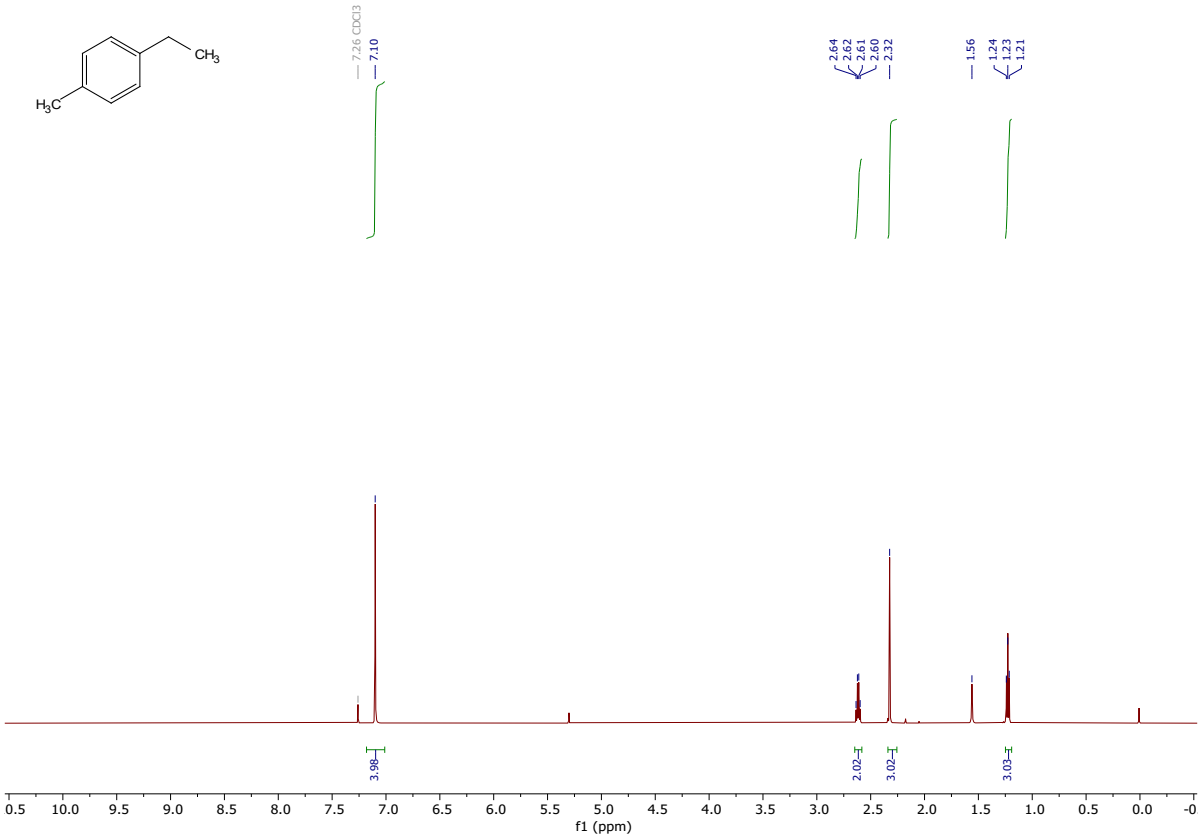

77.16 CDCl3
74.72
37.74
36.68
34.73
31.18
27.68
27.22
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

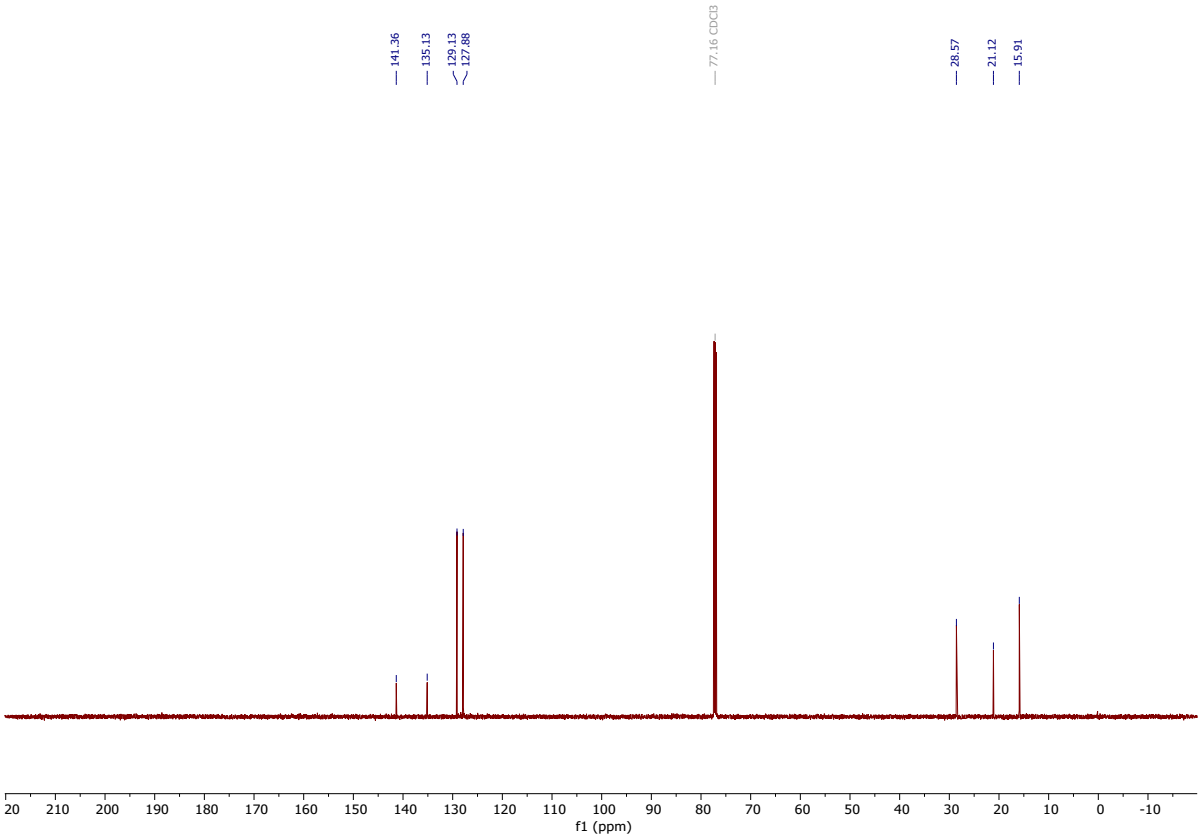

CH2
H3C
7.29
7.28
7.27
7.27
7.11
7.09
6.69
6.67
6.66
6.64
5.69
5.68
5.66
5.65
5.17
5.16
5.15
5.15
2.31
0.00 TMS
2.02
2.00
1.04
1.04
1.03
3.07
f1 (ppm)

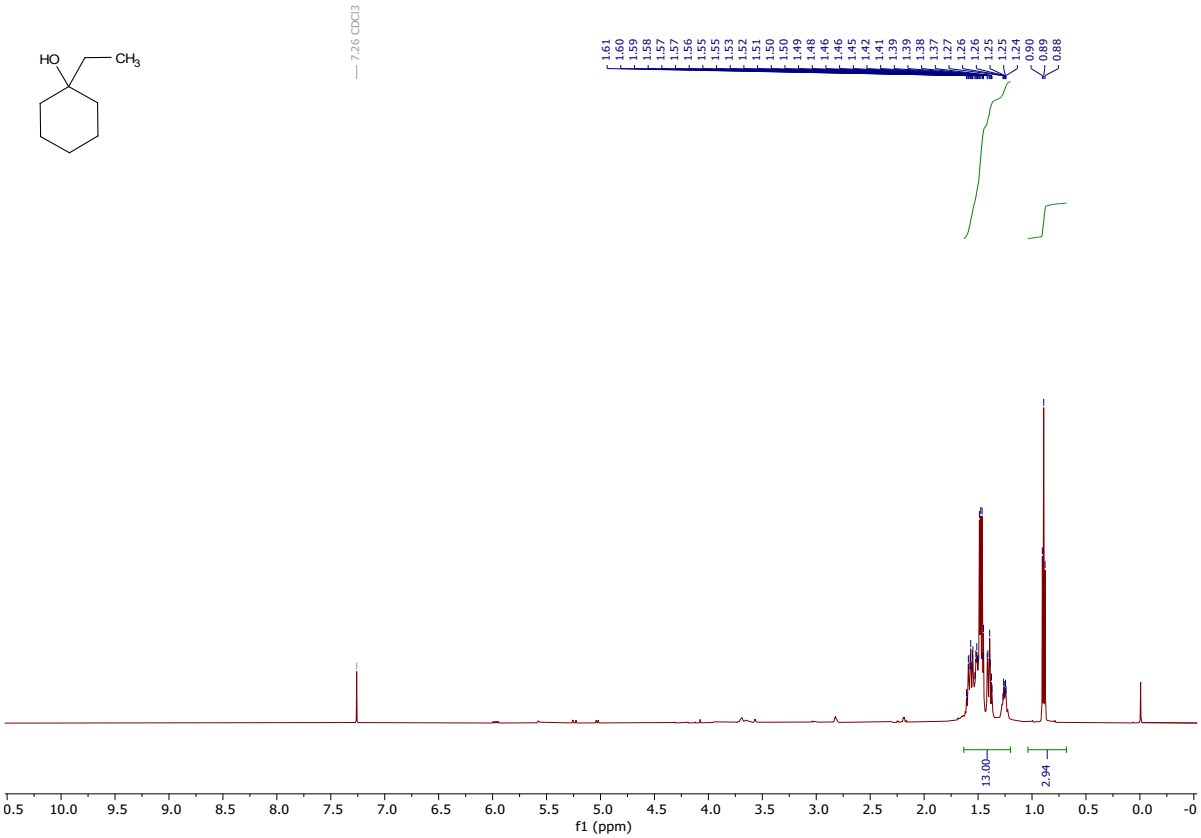

137.70
136.86
134.98
129.33
126.25
112.84
77.16 CDCl3
21.30
f1 (ppm)

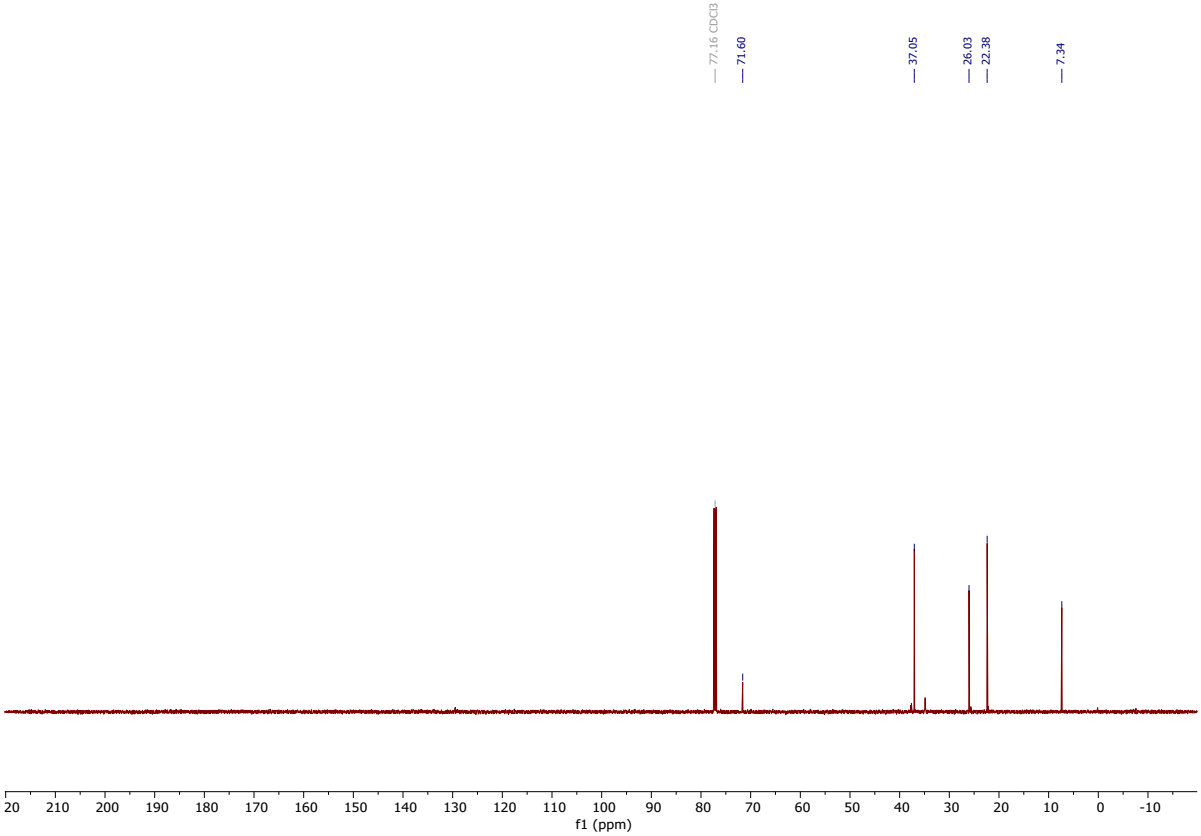

OH
7.35
7.34
7.33
7.27
7.26
7.25
7.25
7.21
7.20
6.58
6.56
5.89
5.88
5.87
5.86
5.85
4.44
4.44
4.43
4.43
0.00 TMS
2.02
1.00
1.99
1.00
0.99
2.00
f1 (ppm)

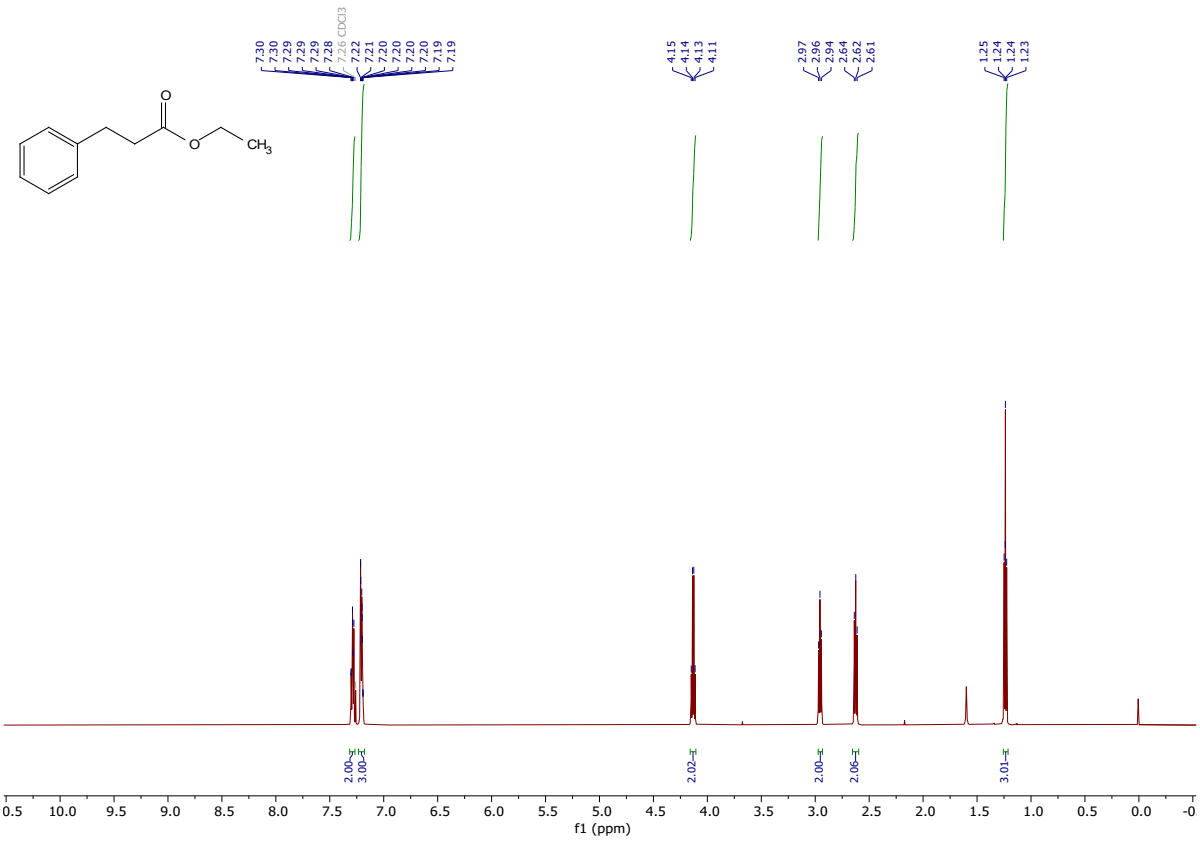

136.65
131.27
131.19
128.91
128.40
127.40
77.16 CDCl3
59.84
f1 (ppm)

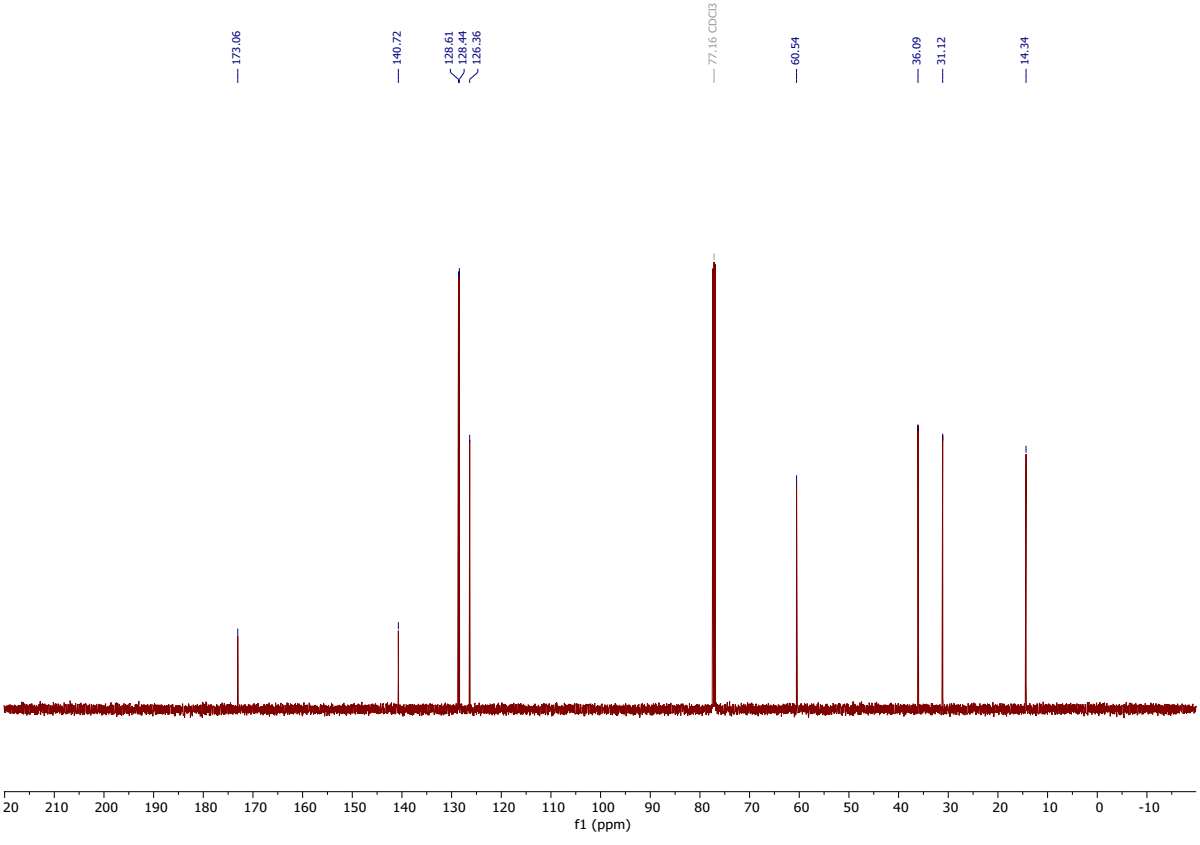

CH3
H3C
7.26 CDCl3
7.10
2.64
2.62
2.61
2.60
2.32
1.56
1.24
1.23
1.21
3.98
2.02
3.02
3.03
f1 (ppm)

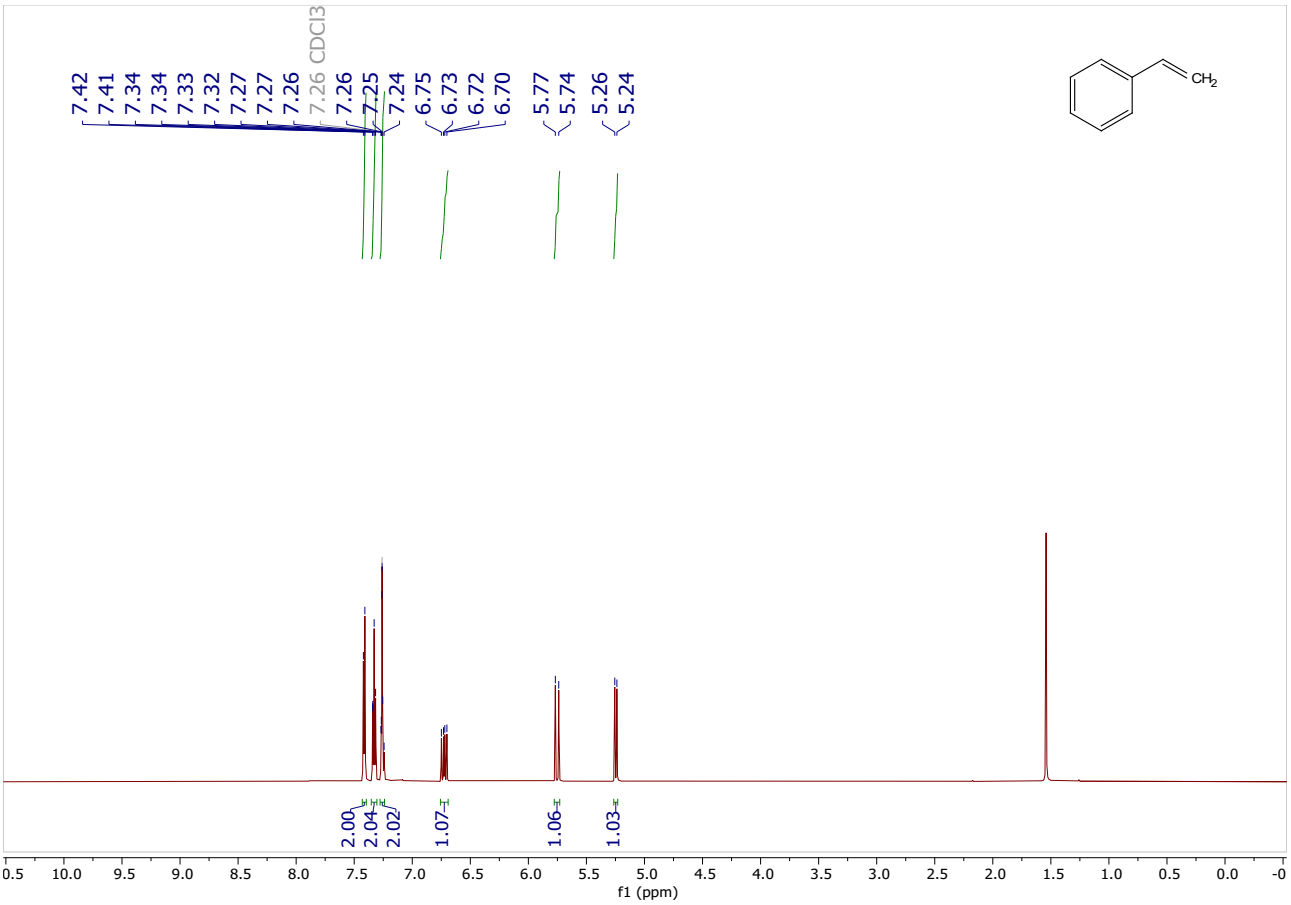

141.36
135.13
129.13
127.88
77.16 CDCl3
28.57
21.12
15.91
f1 (ppm)

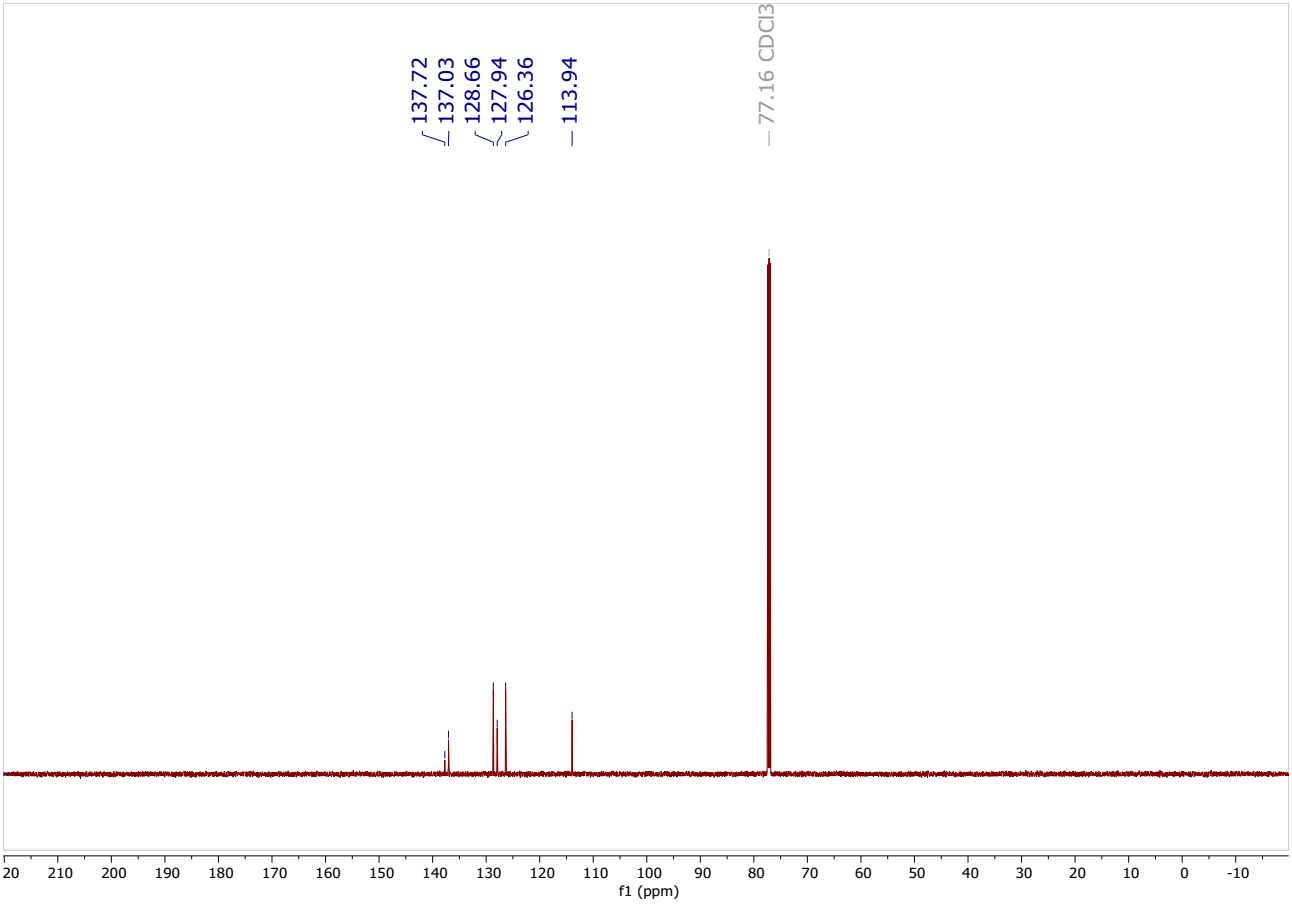

HO
CH3
7.26 CDCl3
1.61
1.60
1.59
1.58
1.57
1.56
1.55
1.53
1.52
1.51
1.50
1.49
1.48
1.46
1.45
1.42
1.41
1.39
1.38
1.37
1.27
1.26
1.25
1.24
0.90
0.89
0.88
13.00
2.94
f1 (ppm)

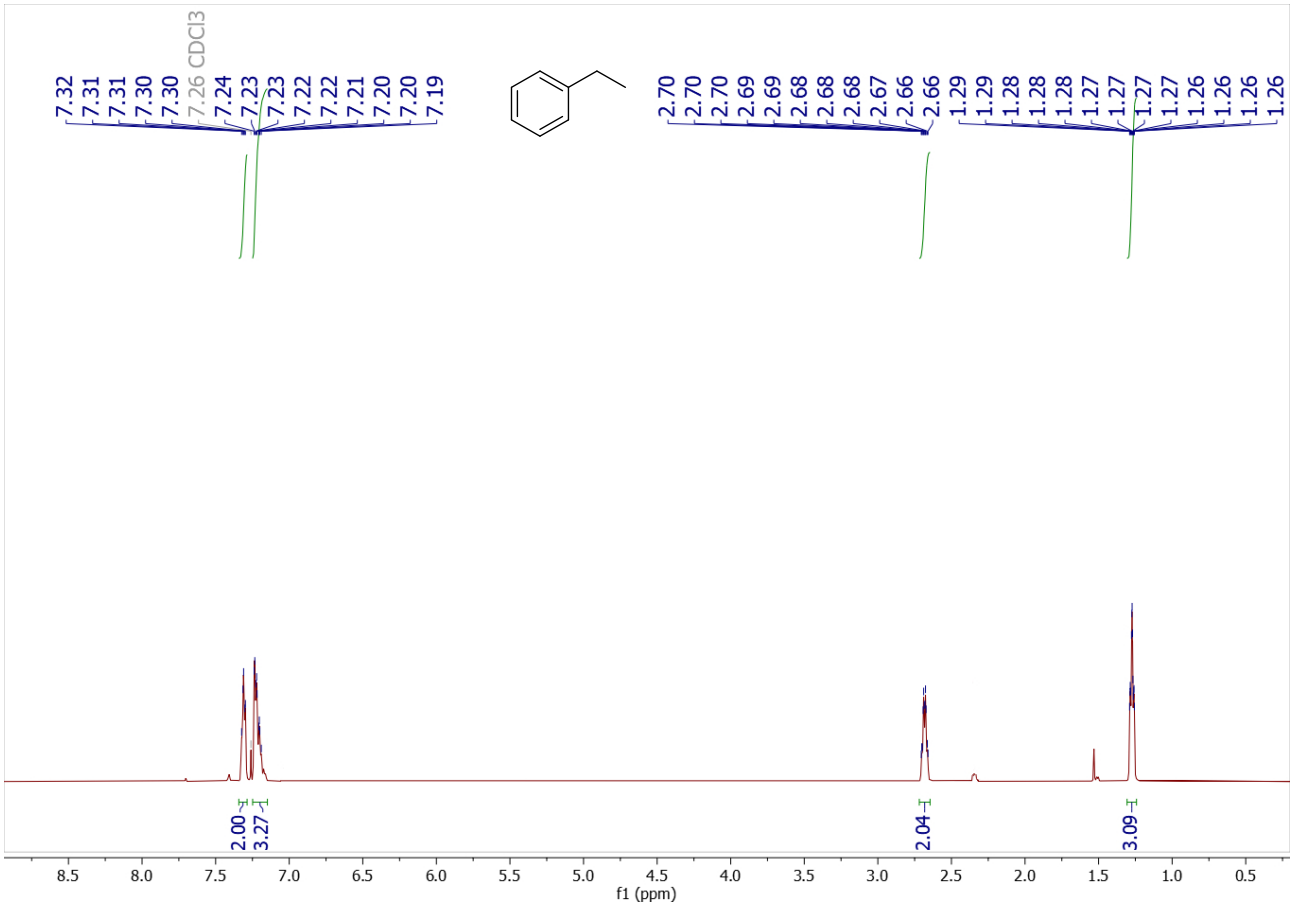

77.16 CDCl3
71.60
37.05
26.03
22.38
7.34
f1 (ppm)

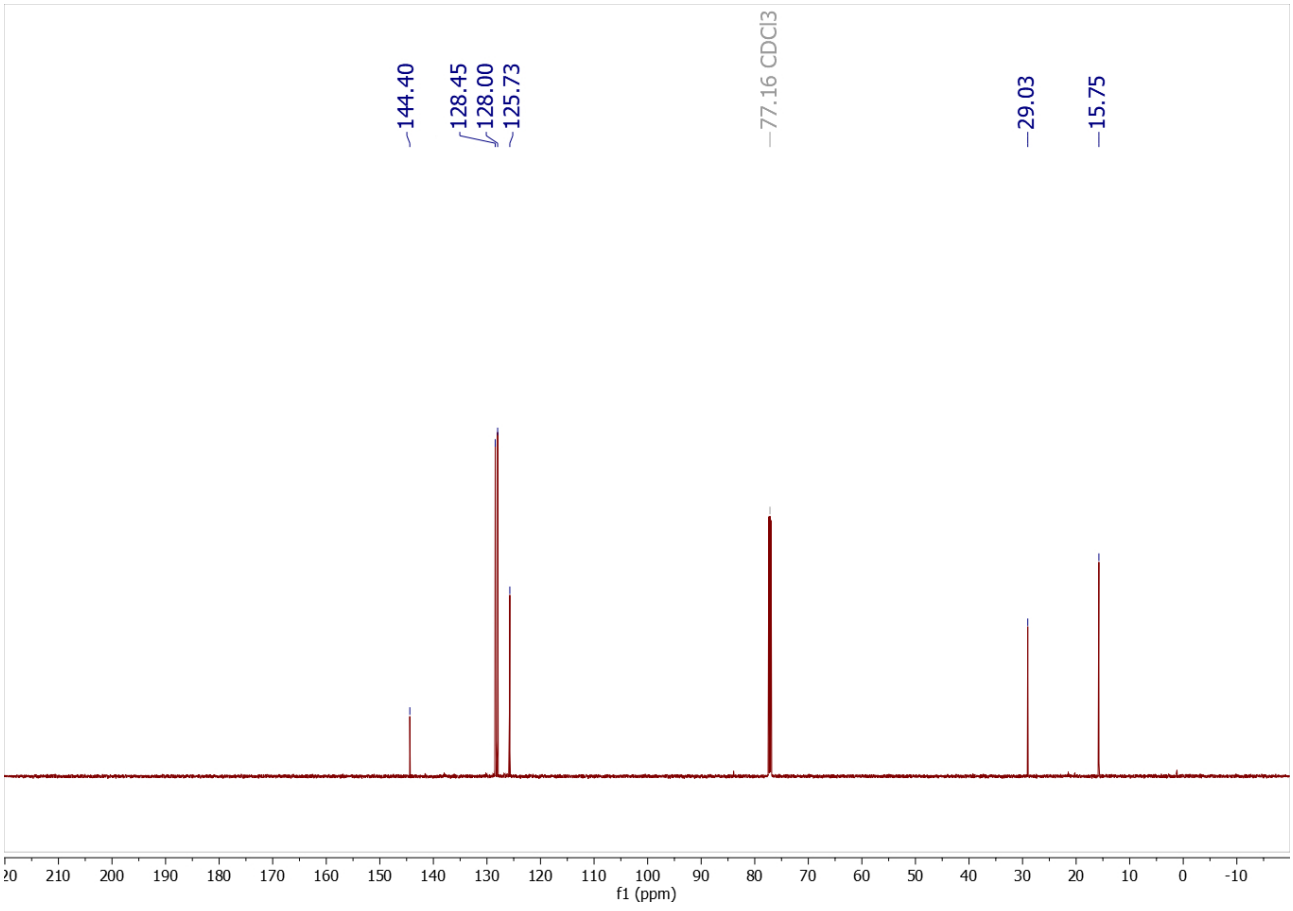

7.30
7.30
7.29
7.29
7.29
7.28
7.26 CDCl3
7.22
7.21
7.20
7.20
7.20
7.20
7.19
7.19
4.15
4.14
4.13
4.11
2.97
2.96
2.94
2.64
2.62
2.61
1.25
1.24
1.24
1.23
O
O
CH3
2.00
3.00
2.02
2.00
2.06
3.01
f1 (ppm)

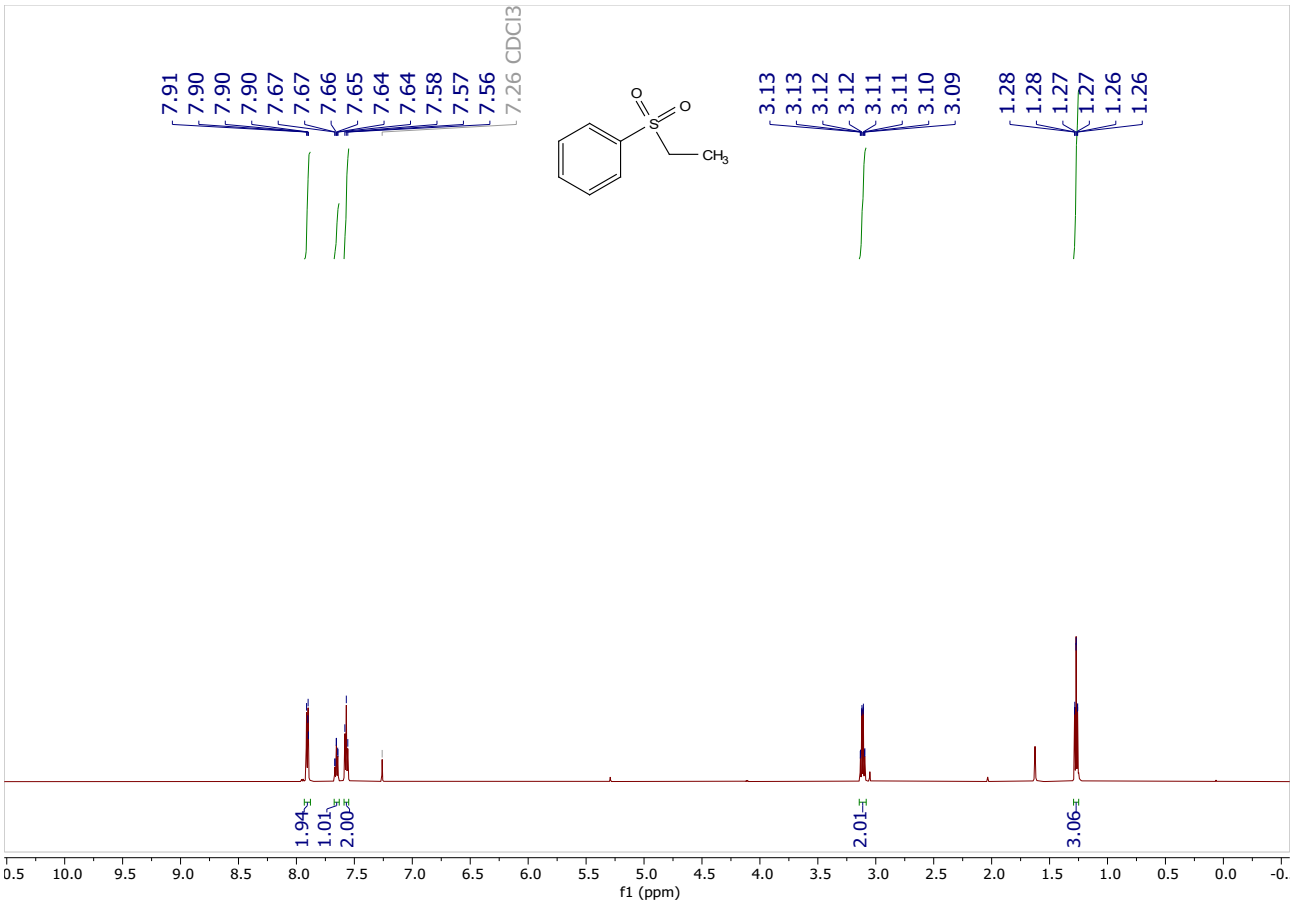

173.06
140.72
128.61
128.44
126.36
77.16 CDCl3
60.54
36.09
31.12
14.34
f1 (ppm)

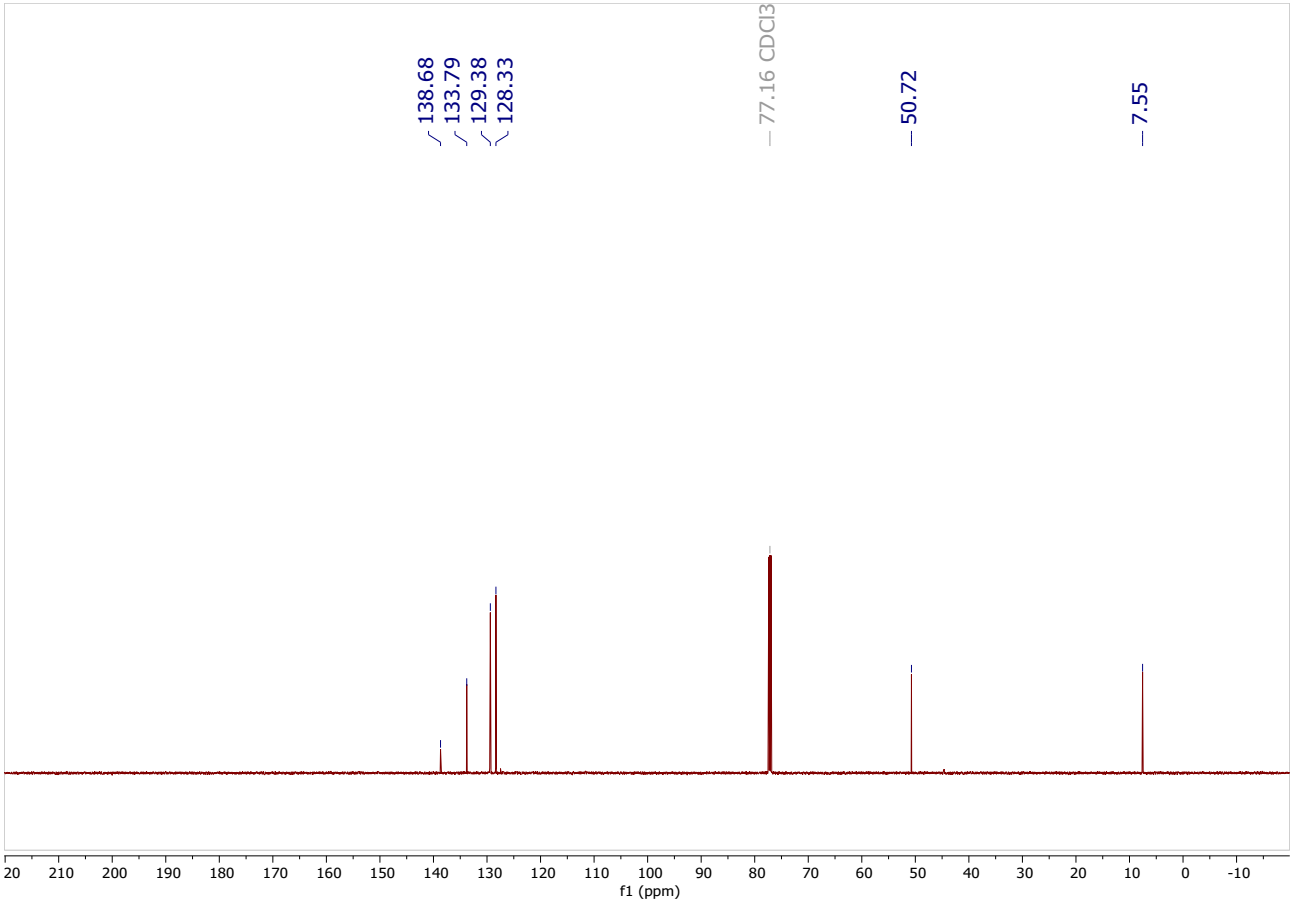

7.42
7.41
7.34
7.34
7.33
7.32
7.27
7.27
7.26
7.26 CDCl3
7.26
7.25
7.24
6.75
6.73
6.72
6.70
5.77
5.74
5.26
5.24
CH2
2.00
2.04
2.02
1.07
1.06
1.03
f1 (ppm)

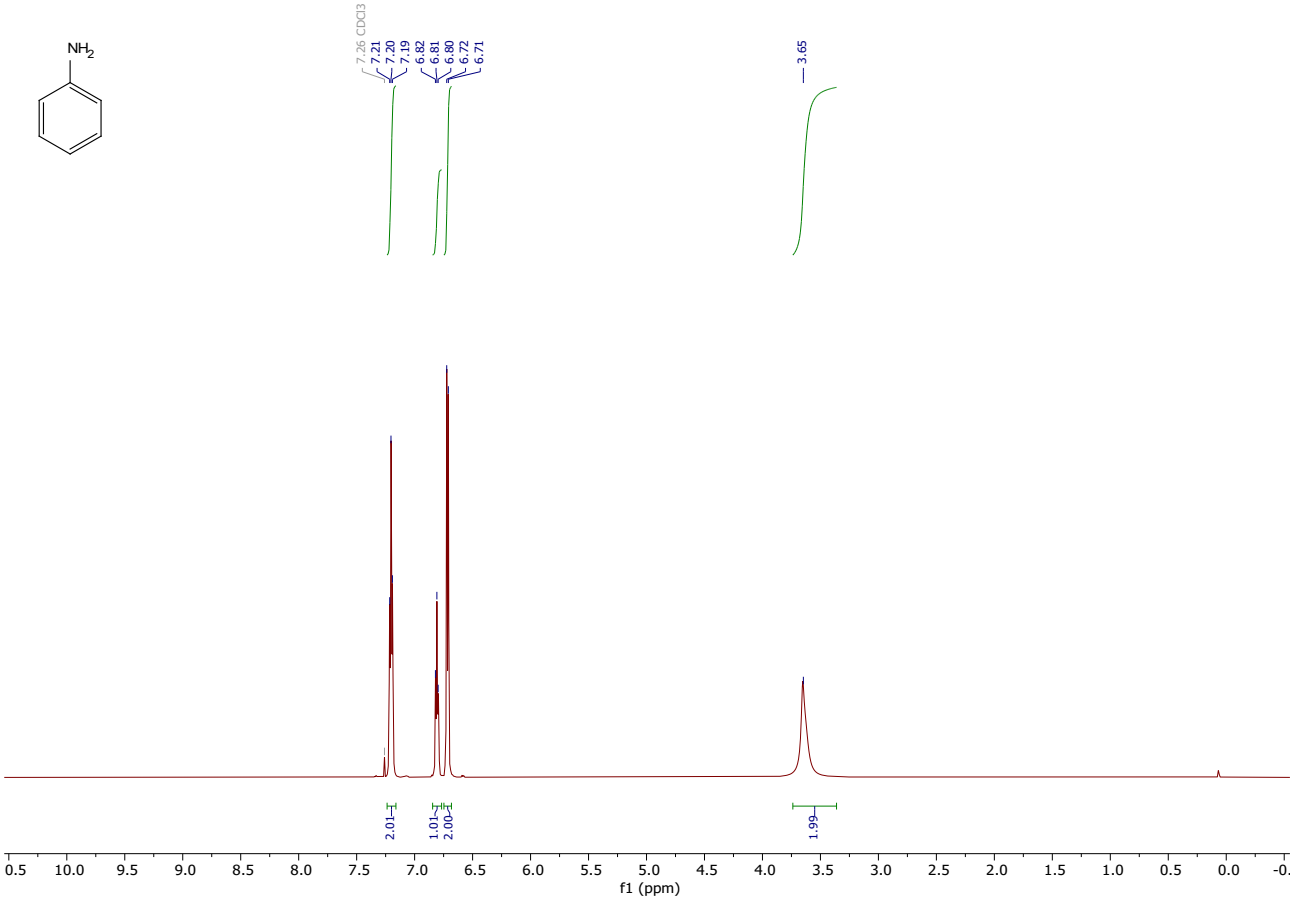

137.72
137.03
128.66
127.94
126.36
113.94
77.16 CDCl3
f1 (ppm)

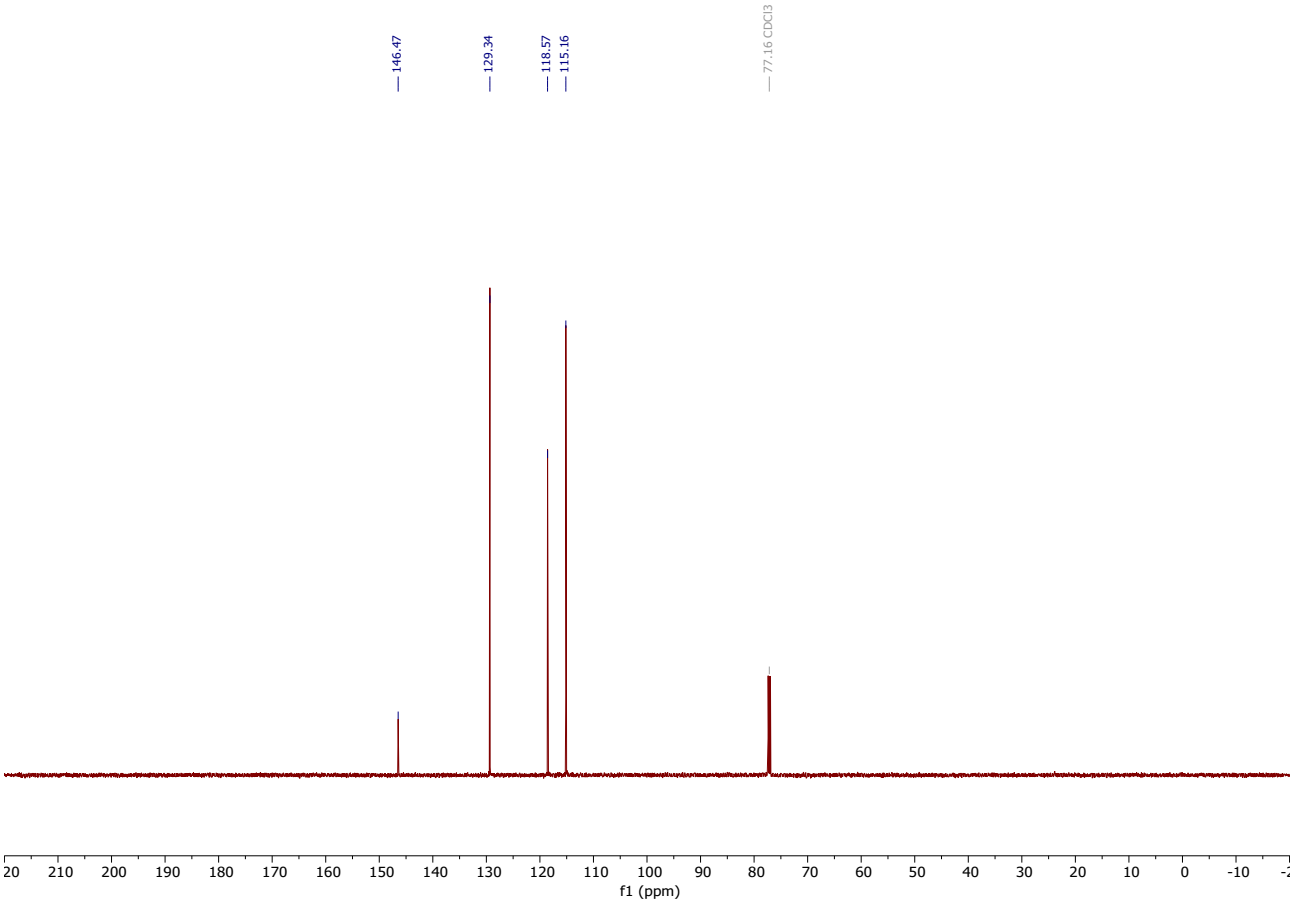

7.32
7.31
7.31
7.30
7.30
7.26 CDCl3
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
2.70
2.70
2.70
2.69
2.69
2.68
2.68
2.68
2.67
2.66
2.66
1.29
1.29
1.28
1.28
1.28
1.27
1.27
1.27
1.27
1.26
1.26
1.26
1.26
2.00
3.27
2.04
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

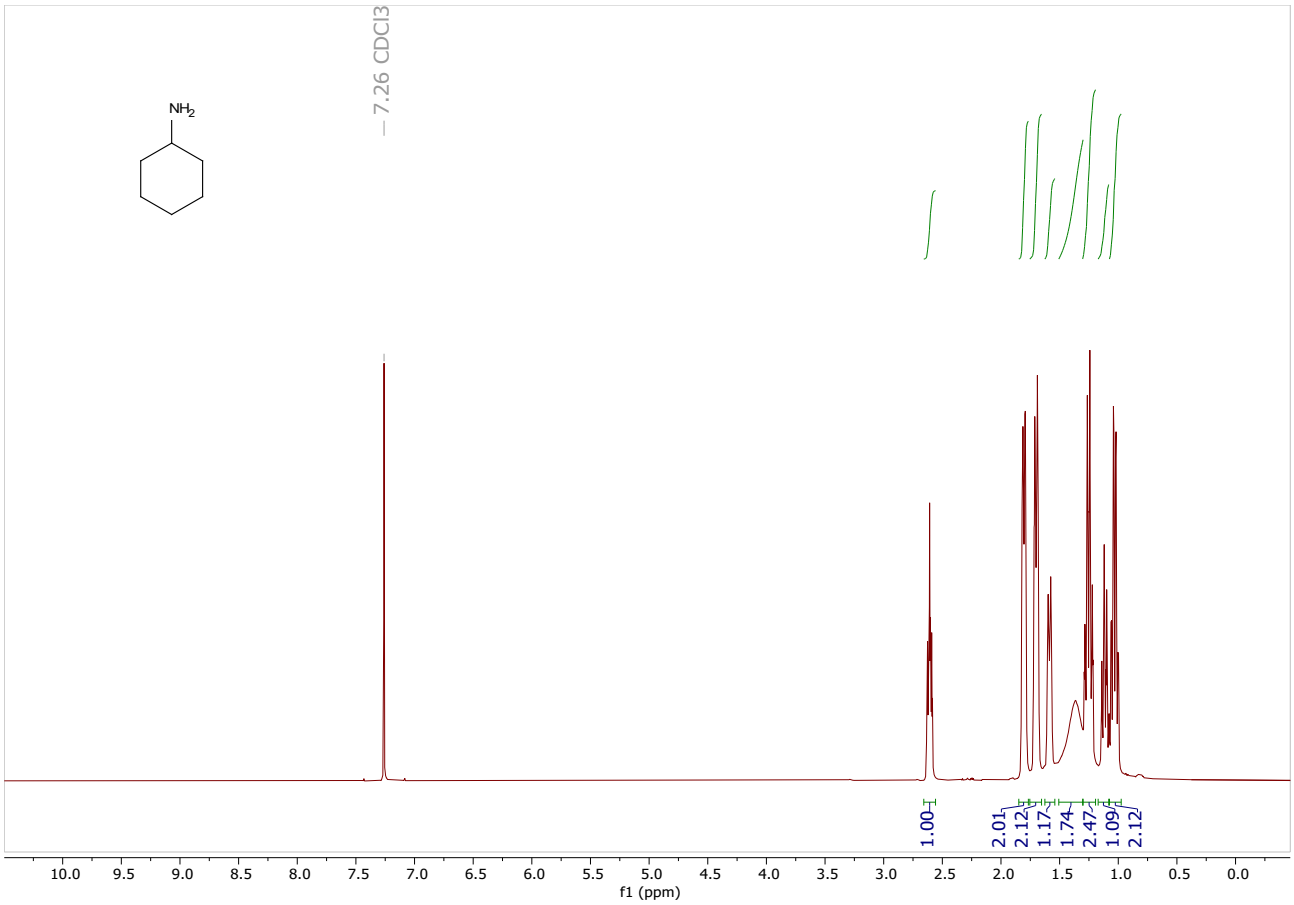

144.40
128.45
128.00
125.73
77.16 CDCl3
29.03
15.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

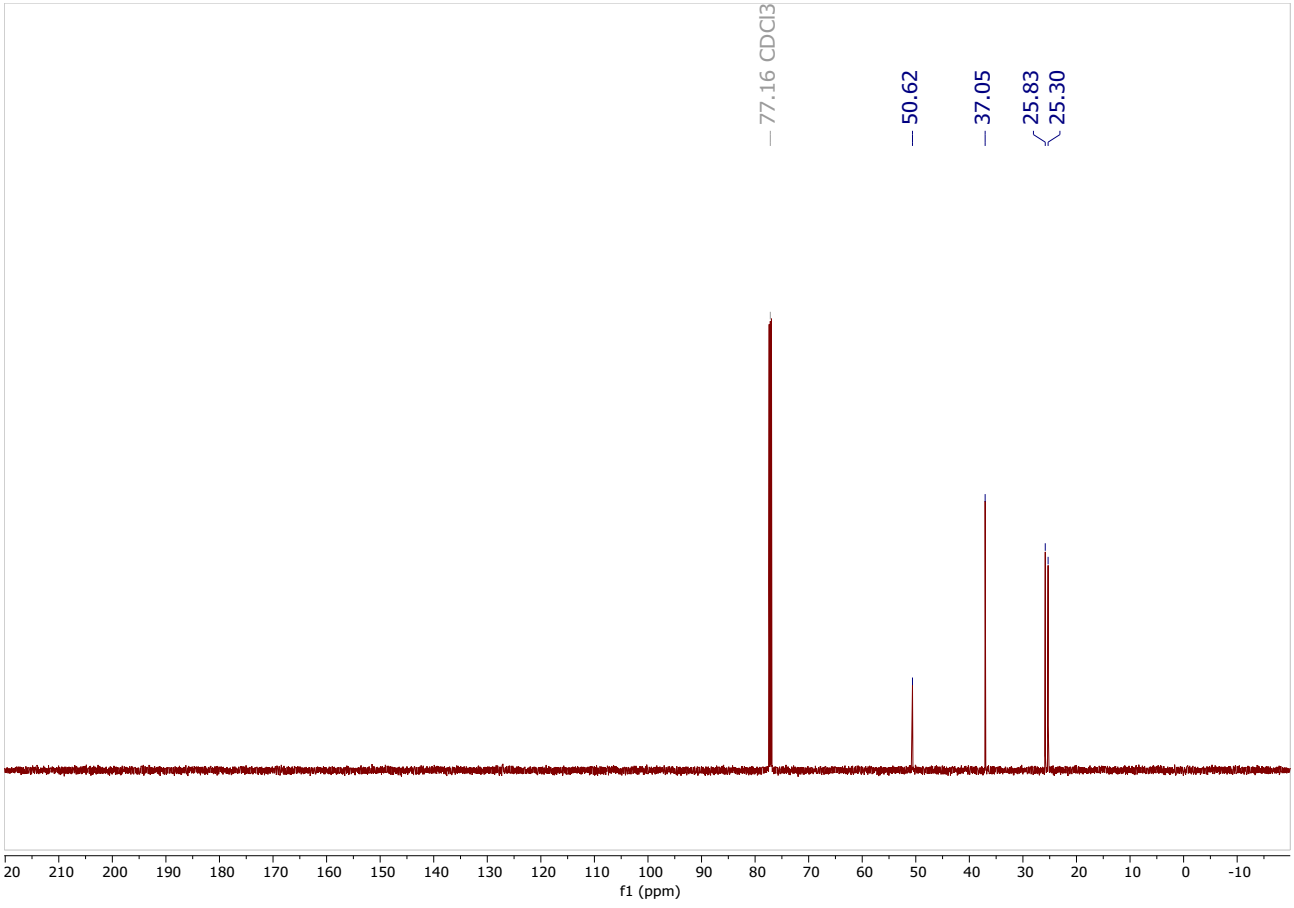

7.91
7.90
7.90
7.90
7.67
7.67
7.66
7.65
7.64
7.64
7.58
7.57
7.56
7.26 CDCl3
O
S
O
CH3
3.13
3.13
3.12
3.12
3.11
3.11
3.10
3.09
1.28
1.28
1.27
1.27
1.26
1.26
1.94
1.01
2.00
2.01
3.06
f1 (ppm)

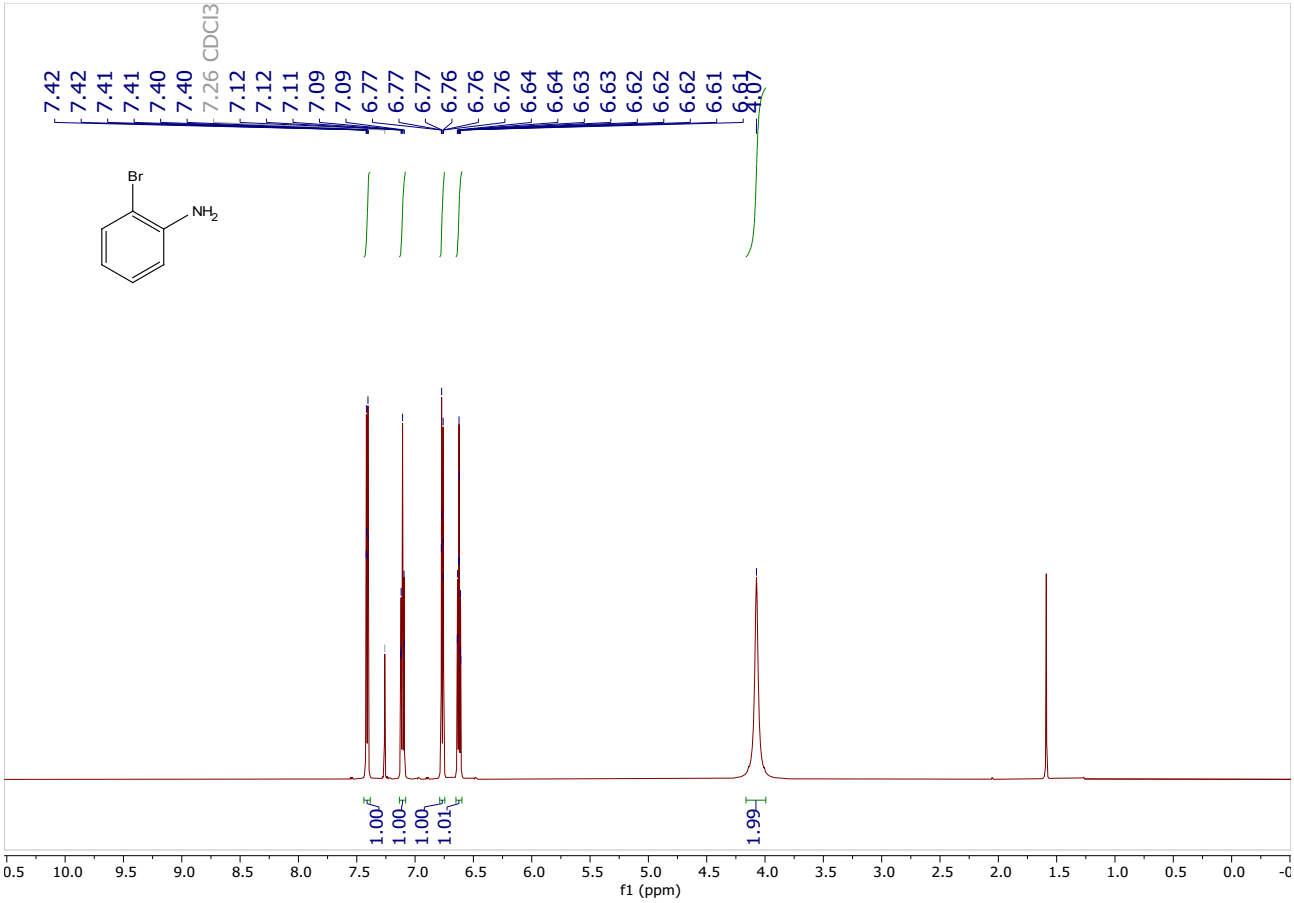

138.68
133.79
129.38
128.33
77.16 CDCl3
50.72
7.55
f1 (ppm)

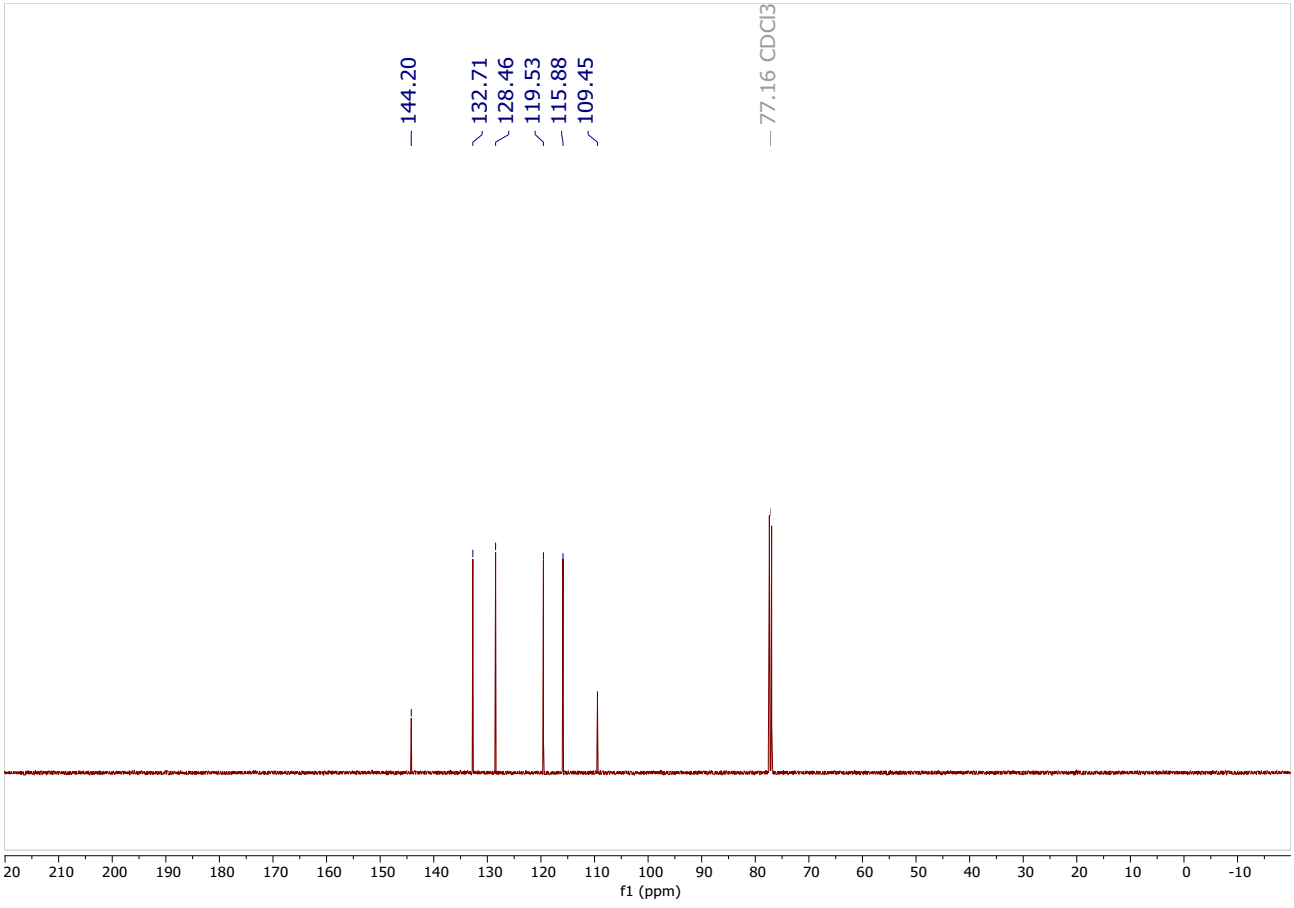

NH2
7.26 CDCl3
7.21
7.20
7.19
6.82
6.81
6.80
6.72
6.71
3.65
2.01
1.01
2.00
1.99
f1 (ppm)

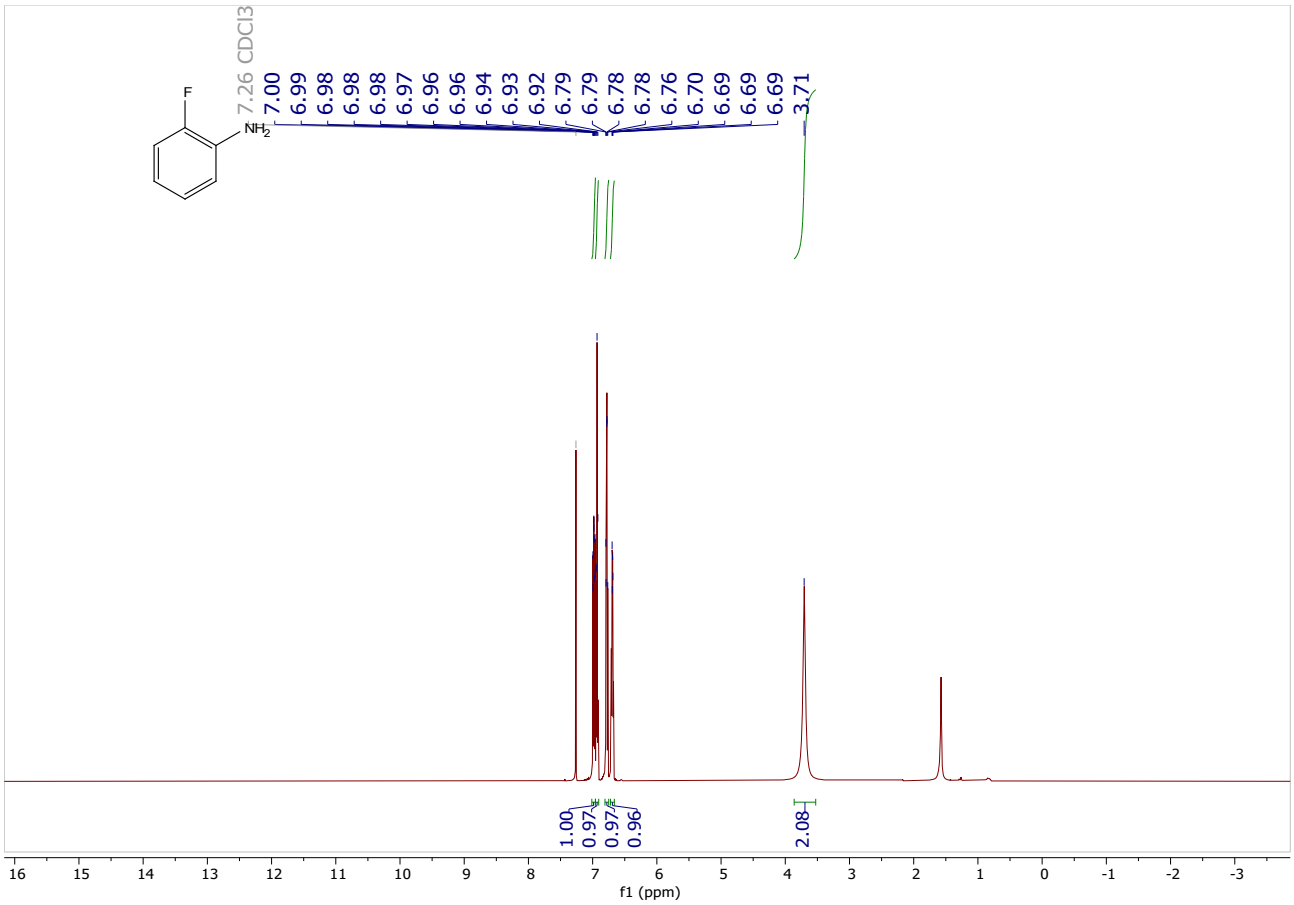

146.47
129.34
118.57
115.16
77.16 CDCl3
f1 (ppm)

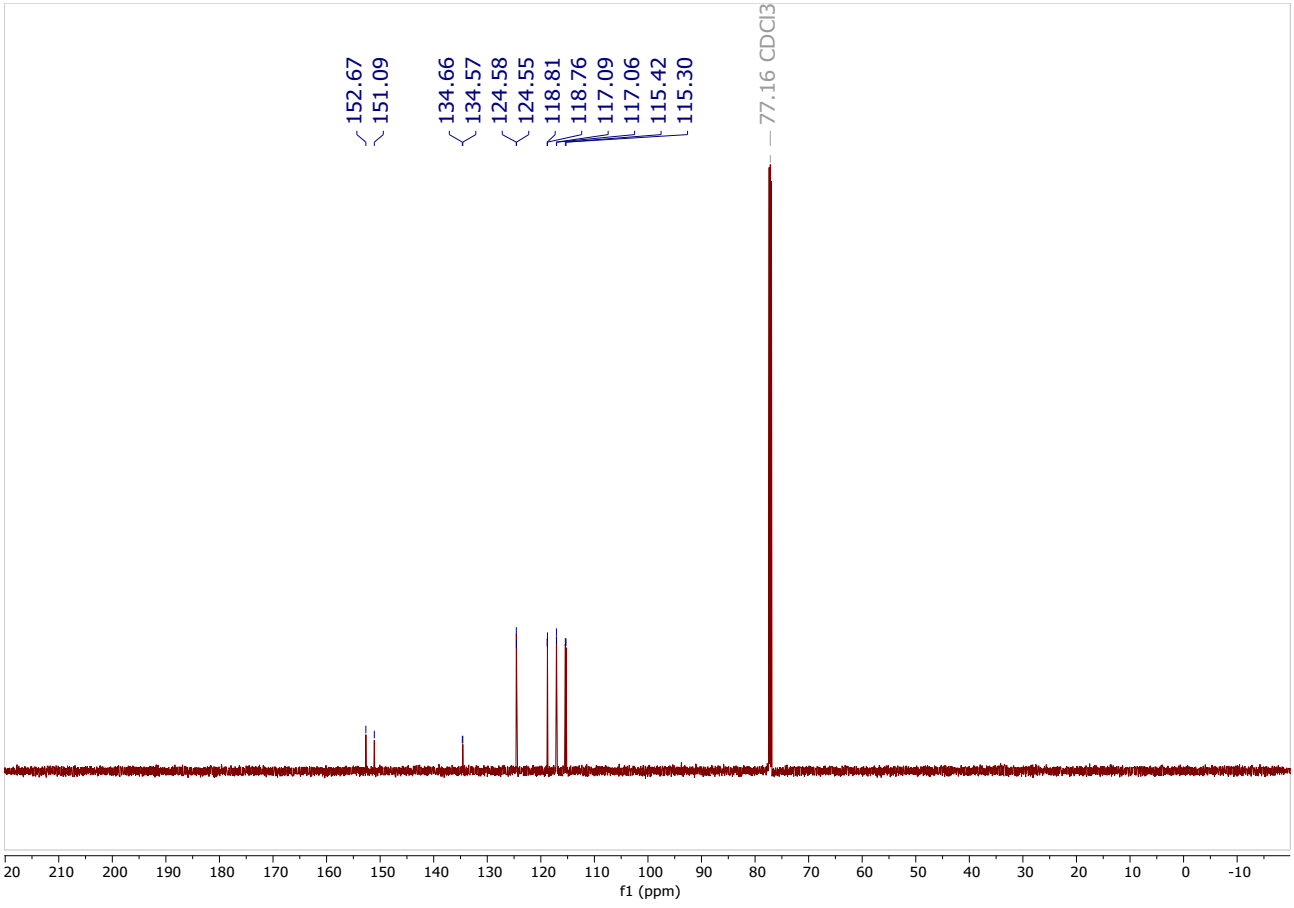

NH2
7.26 CDCl3
1.00
2.01
2.12
1.17
1.74
2.47
1.09
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

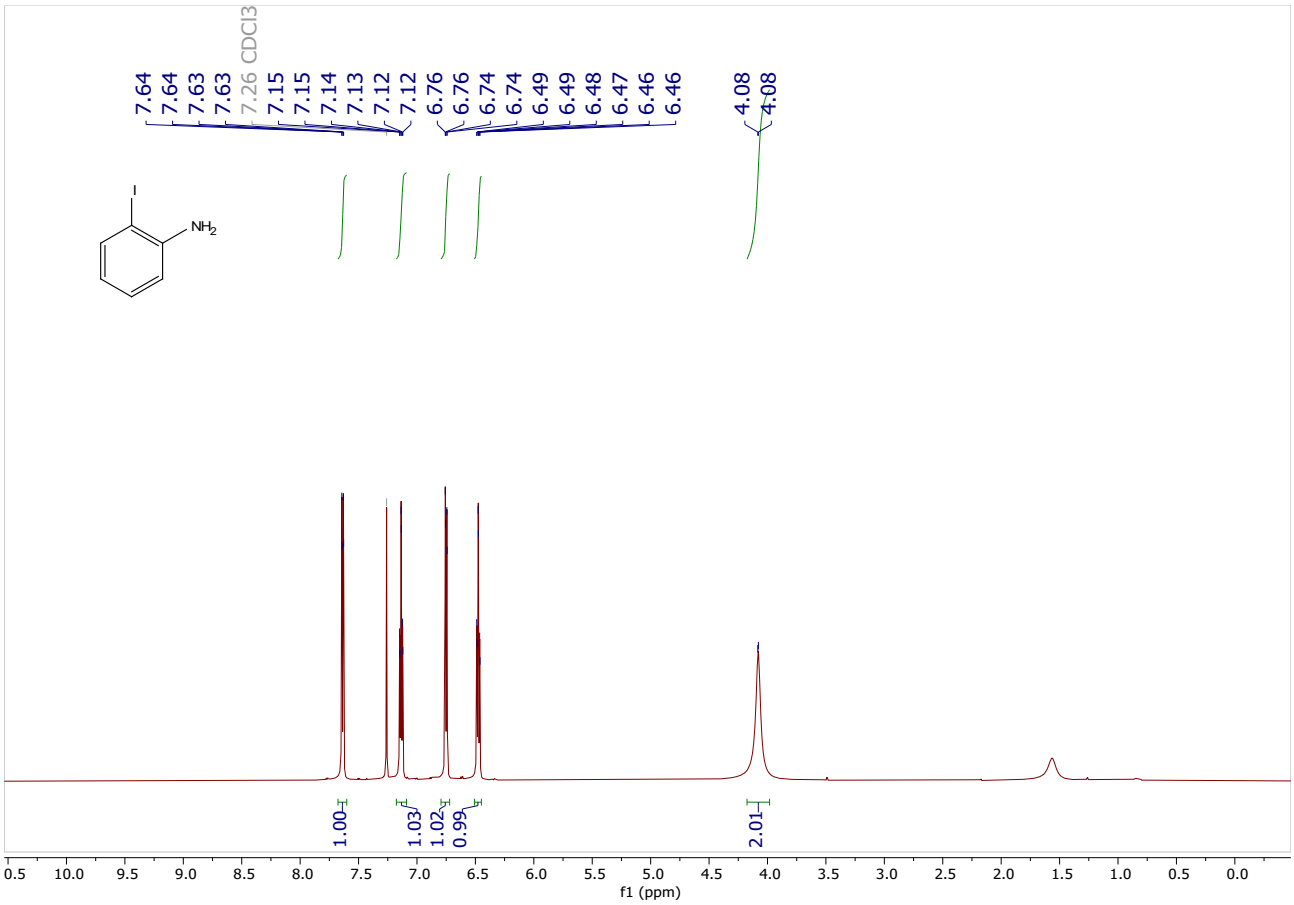

77.16 CDCl3
50.62
37.05
25.83
25.30
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

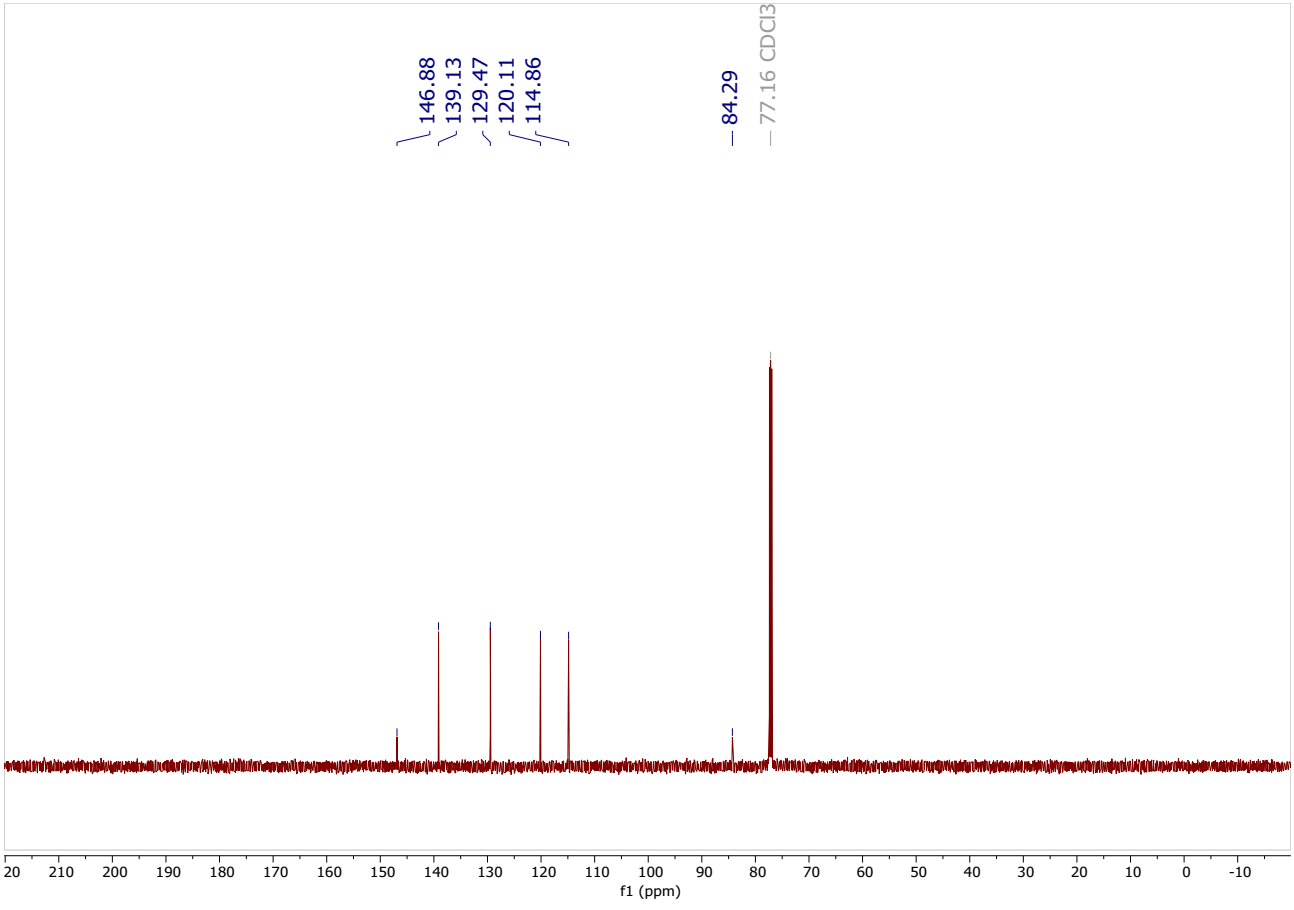

7.42
7.42
7.41
7.41
7.40
7.40
7.26 CDCl3
7.12
7.12
7.11
7.09
7.09
6.77
6.77
6.77
6.76
6.76
6.76
6.64
6.64
6.63
6.63
6.62
6.62
6.62
6.61
6.61
4.07
Br
NH2
1.00
1.00
1.00
1.01
1.99
f1 (ppm)

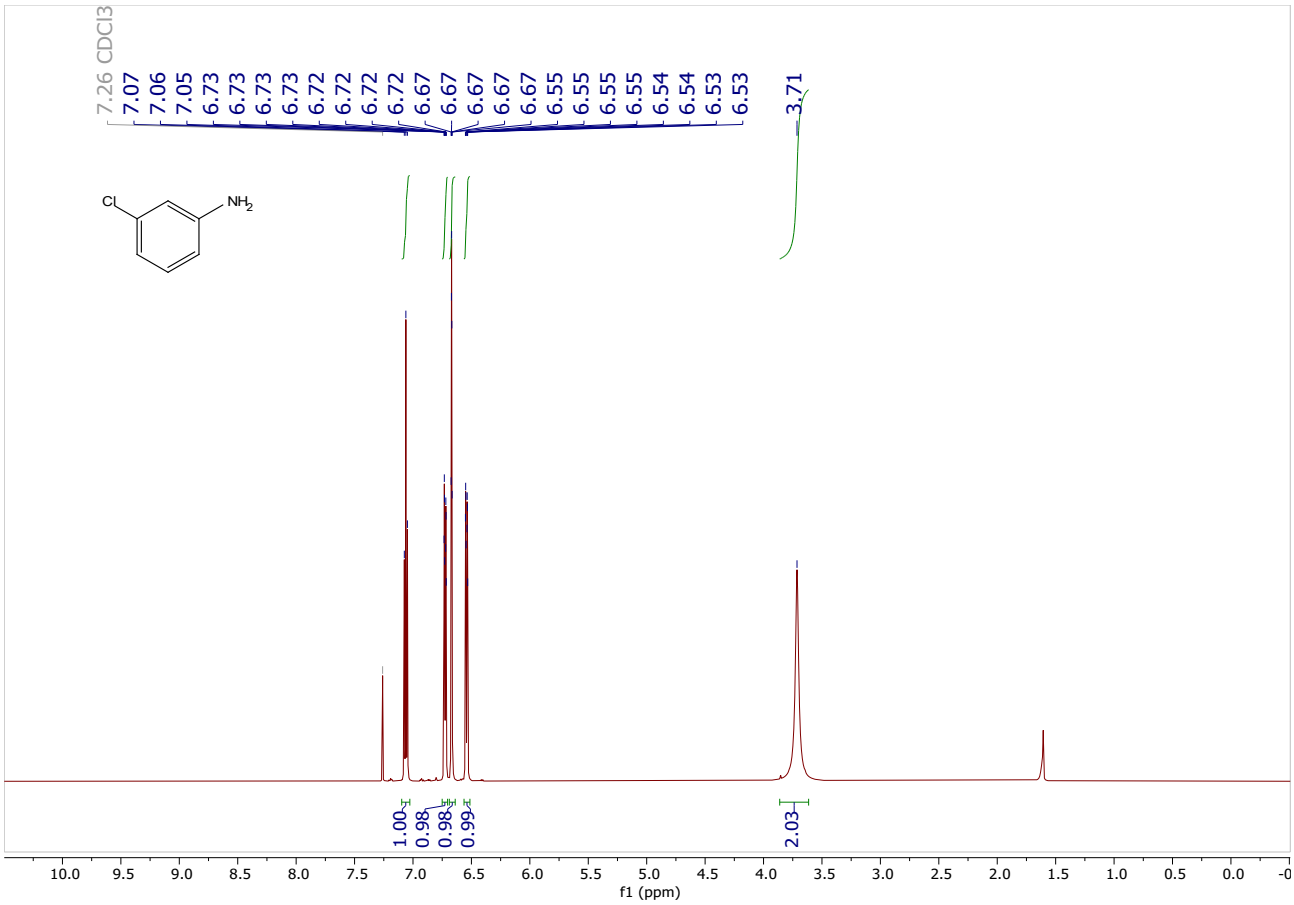

144.20
132.71
128.46
119.53
115.88
109.45
77.16 CDCl3
f1 (ppm)

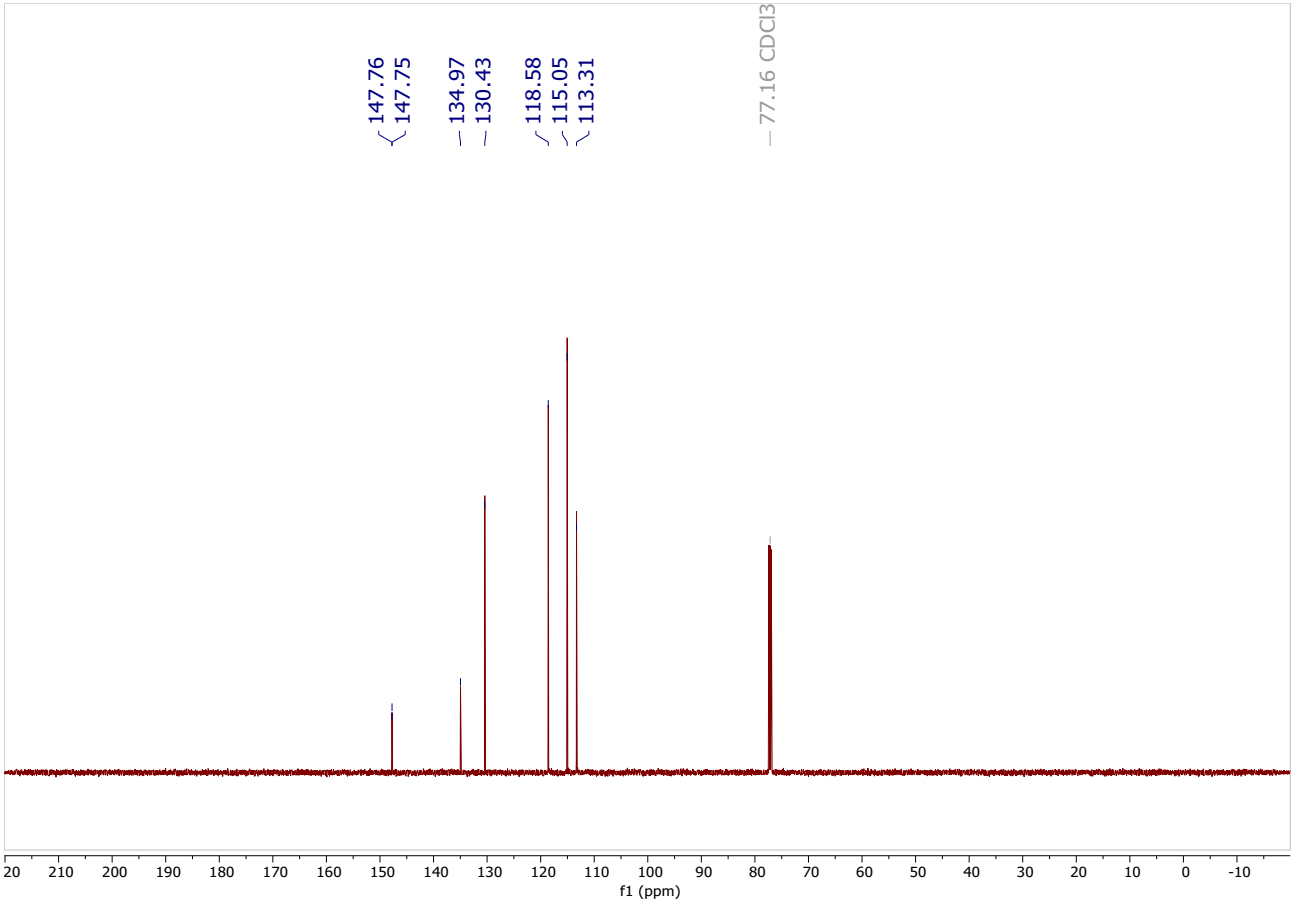

F
NH2
7.26 CDCl3
7.00
6.99
6.98
6.98
6.98
6.97
6.96
6.96
6.94
6.93
6.92
6.79
6.79
6.78
6.78
6.76
6.70
6.69
6.69
6.69
3.71
1.00
0.97
0.97
0.96
2.08
f1 (ppm)

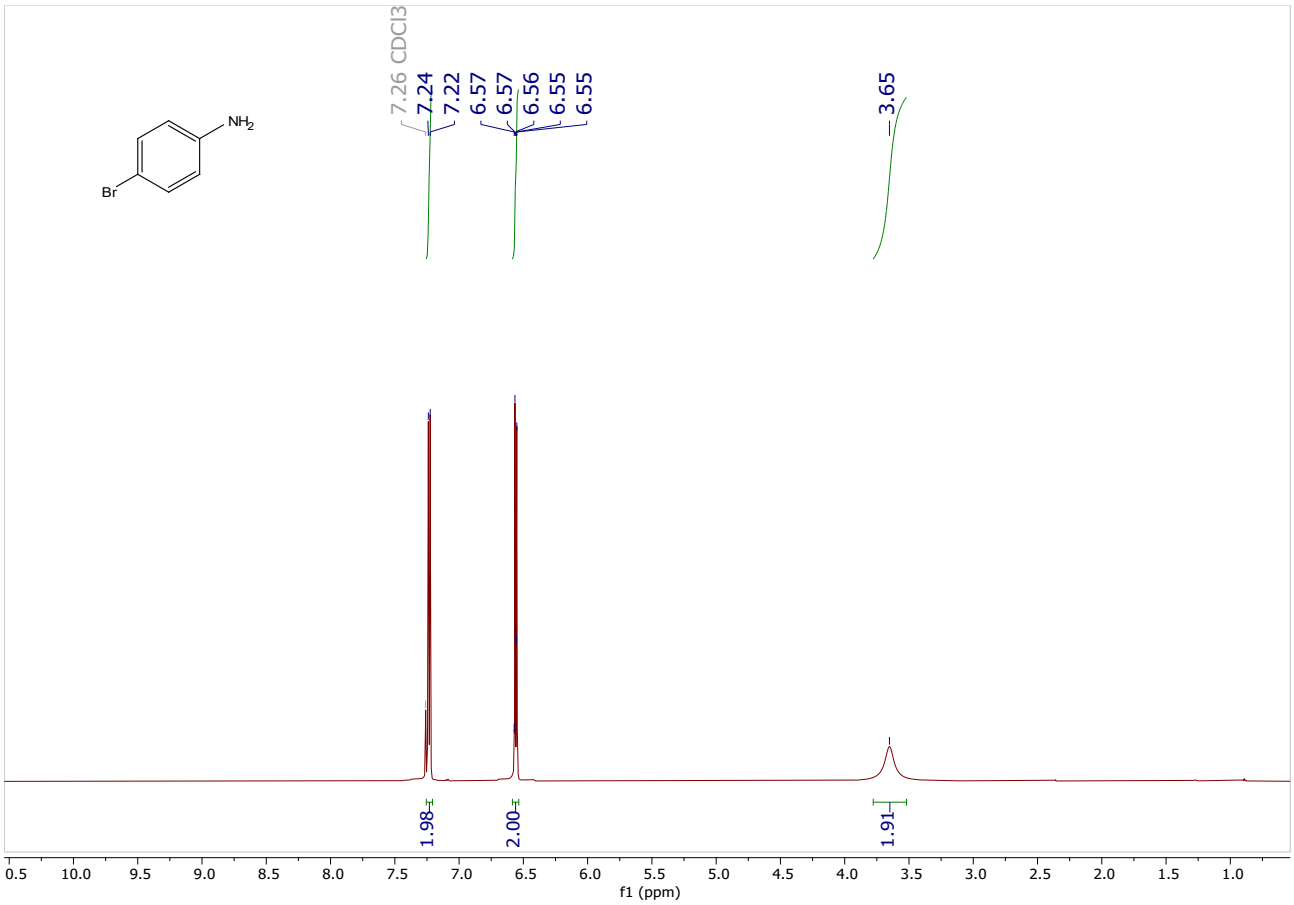

152.67
151.09
134.66
134.57
124.58
124.55
118.81
118.76
117.09
117.06
115.42
115.30
77.16 CDCl3
f1 (ppm)

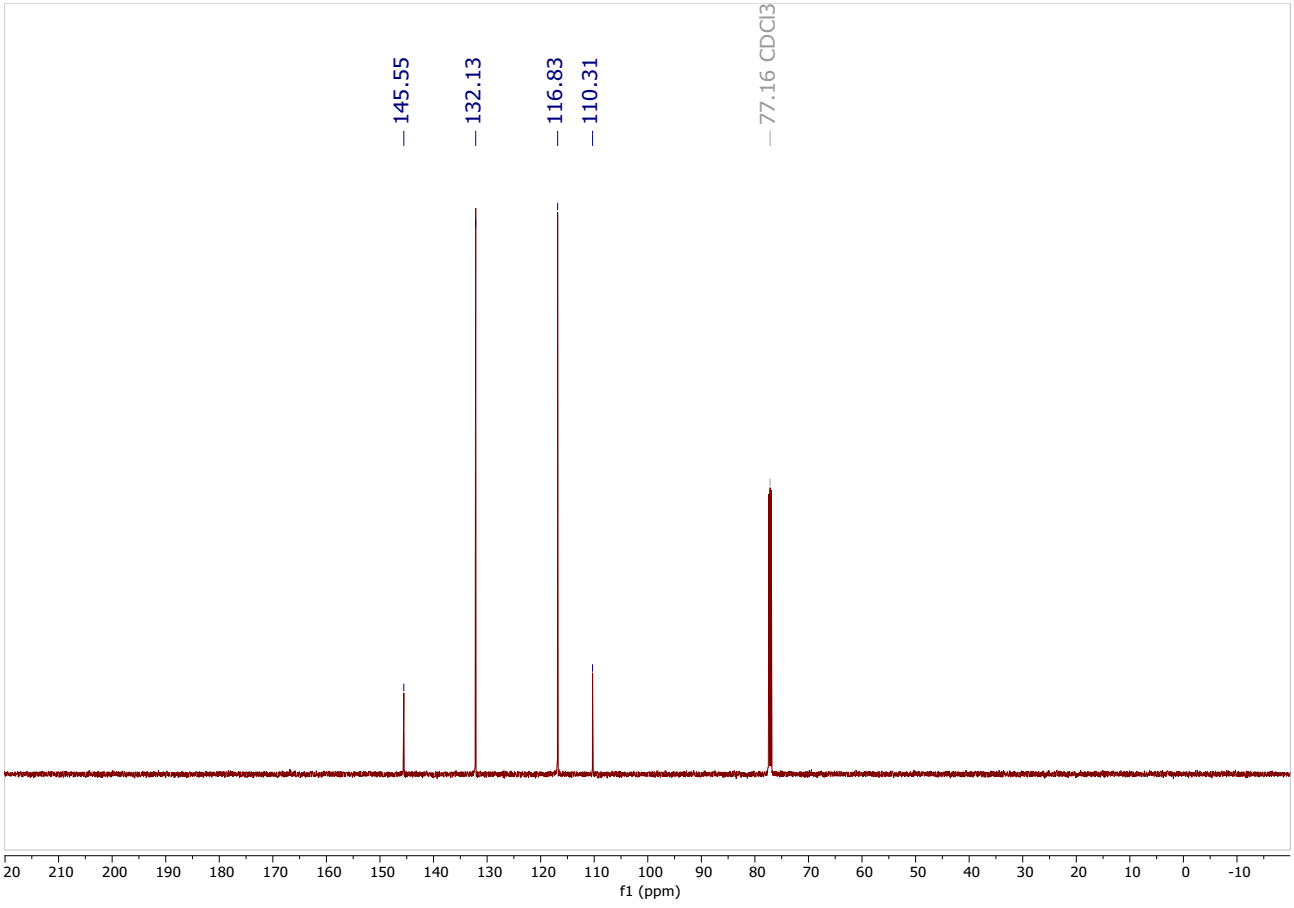

7.64
7.64
7.63
7.63
7.26 CDCl3
7.15
7.15
7.14
7.13
7.12
7.12
6.76
6.76
6.74
6.74
6.49
6.49
6.48
6.47
6.46
6.46
4.08
4.08
I
NH2
1.00
1.03
1.02
0.99
2.01
f1 (ppm)

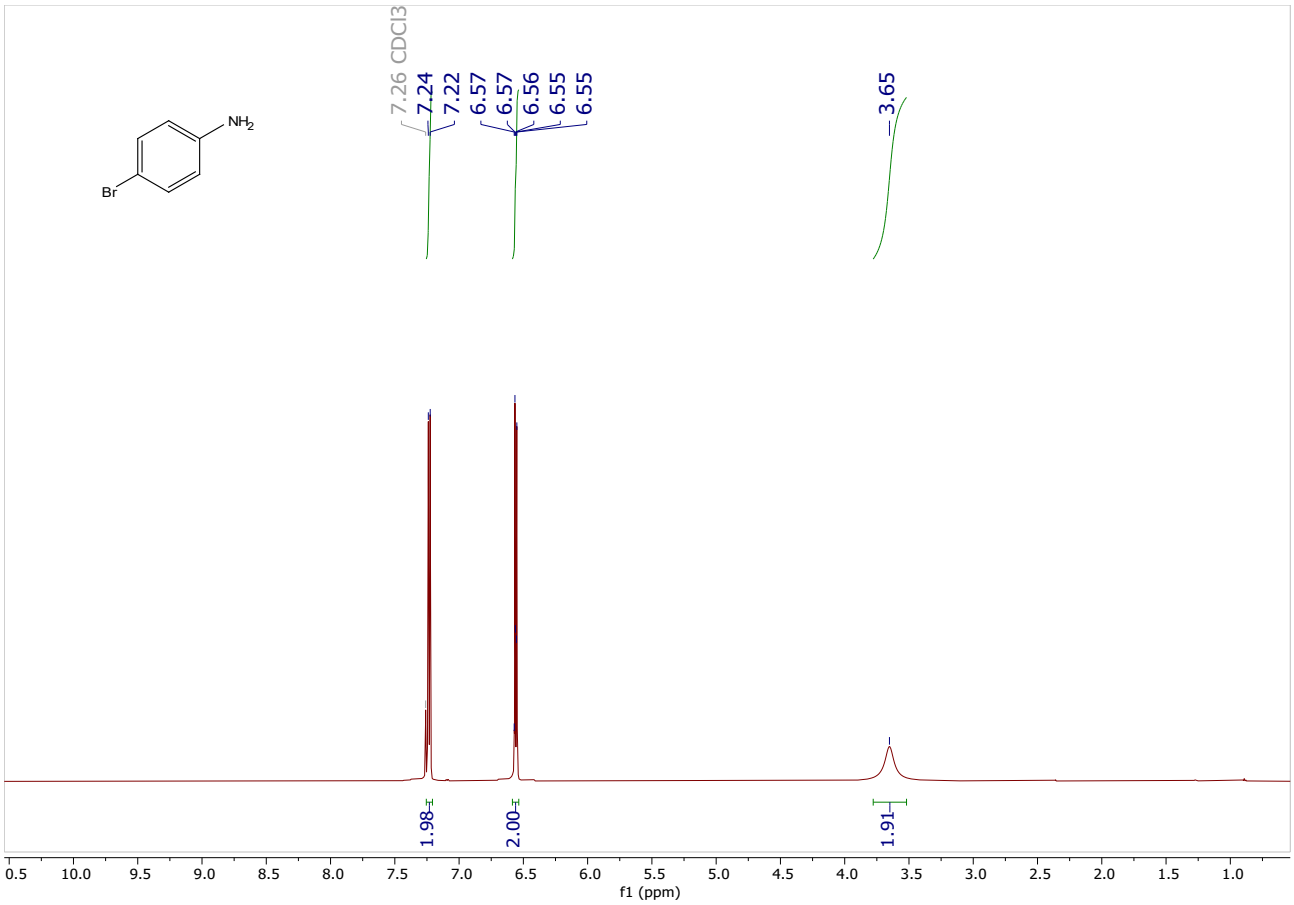

146.88
139.13
129.47
120.11
114.86
84.29
77.16 CDCl3
f1 (ppm)

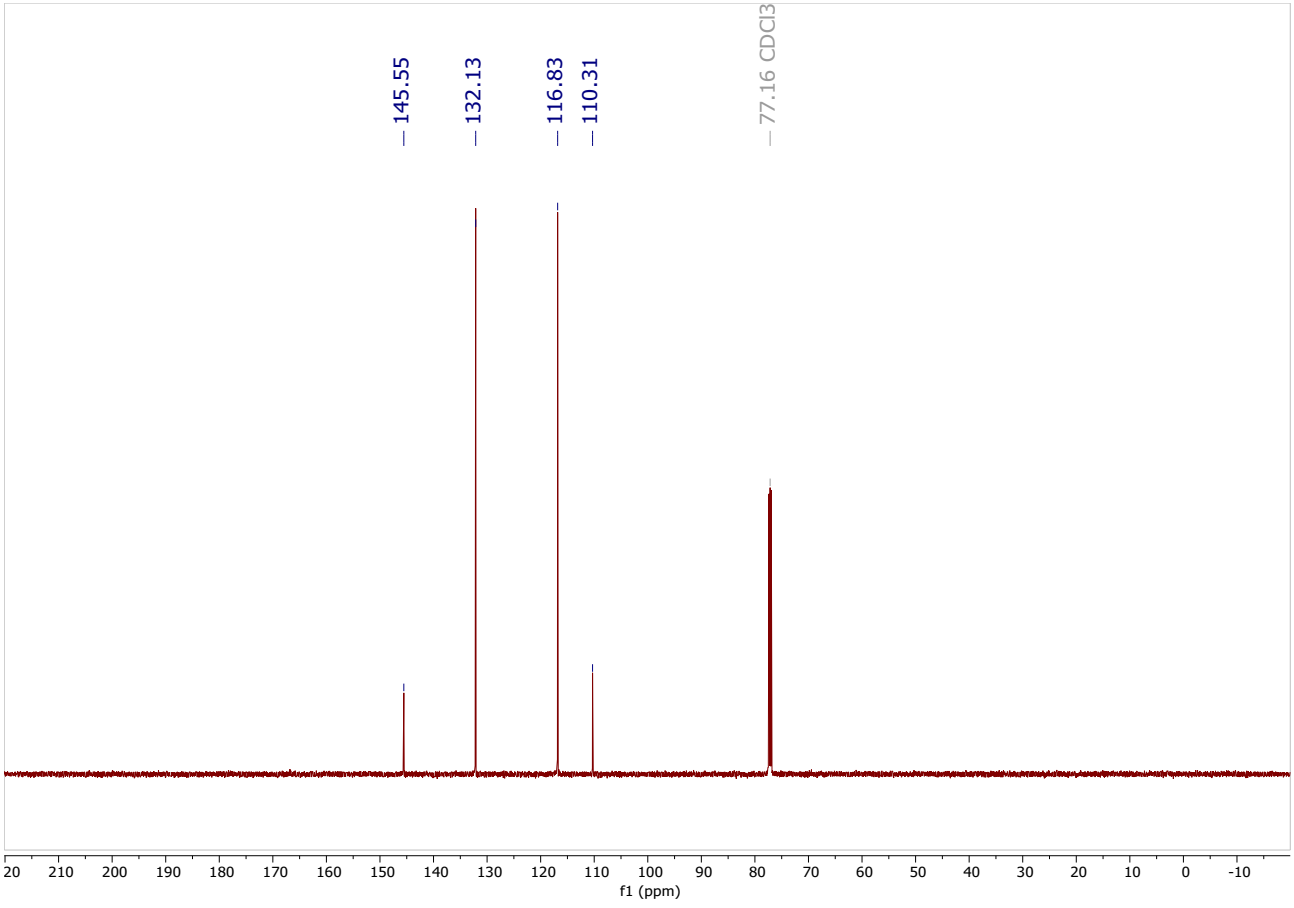

7.26 CDCl3
7.07
7.06
7.05
6.73
6.73
6.73
6.73
6.72
6.72
6.72
6.72
6.67
6.67
6.67
6.67
6.67
6.55
6.55
6.55
6.55
6.54
6.54
6.53
6.53
3.71
Cl
NH2
1.00
0.98
0.98
0.99
2.03
f1 (ppm)

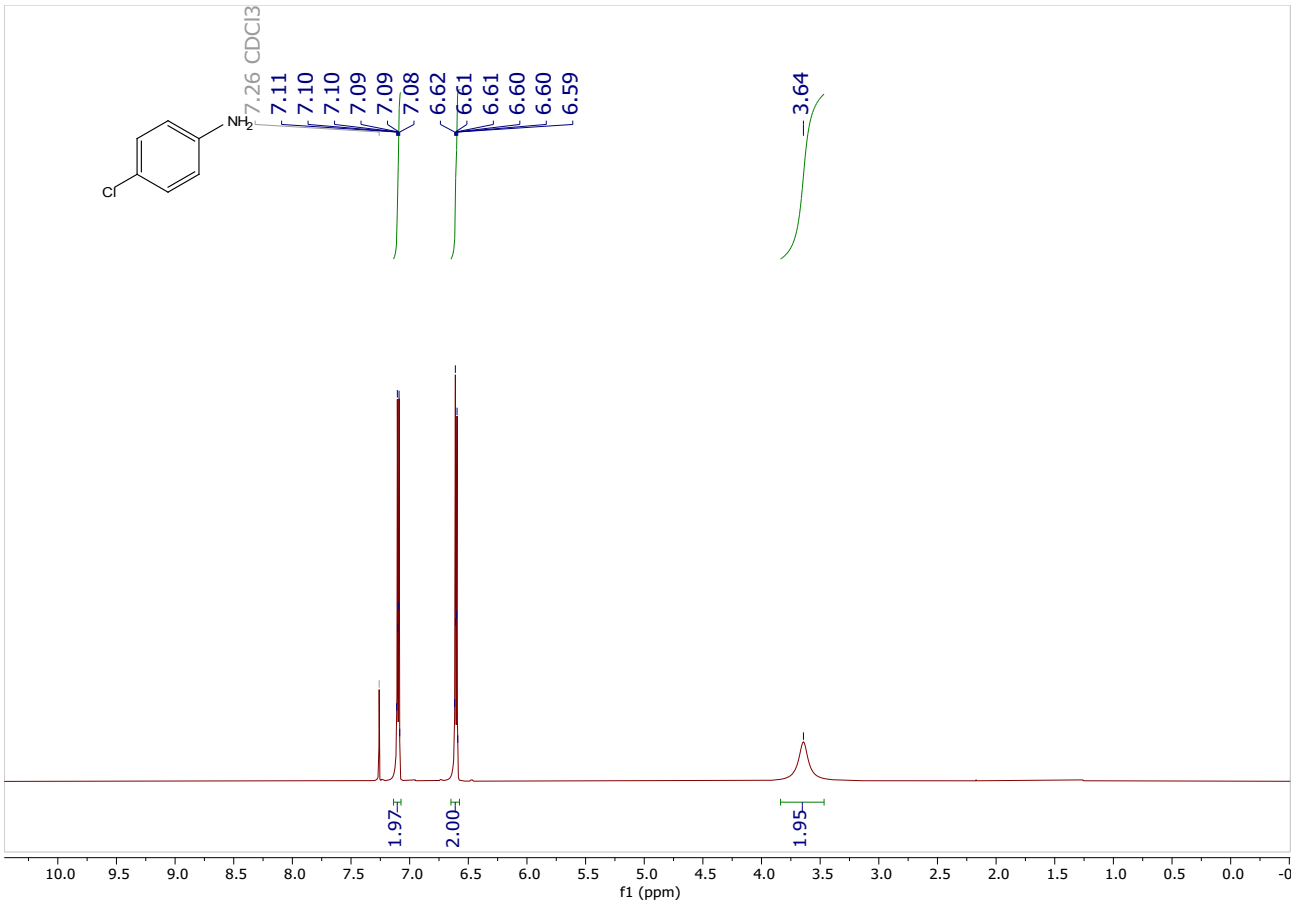

147.76
147.75
134.97
130.43
118.58
115.05
113.31
77.16 CDCl3
f1 (ppm)

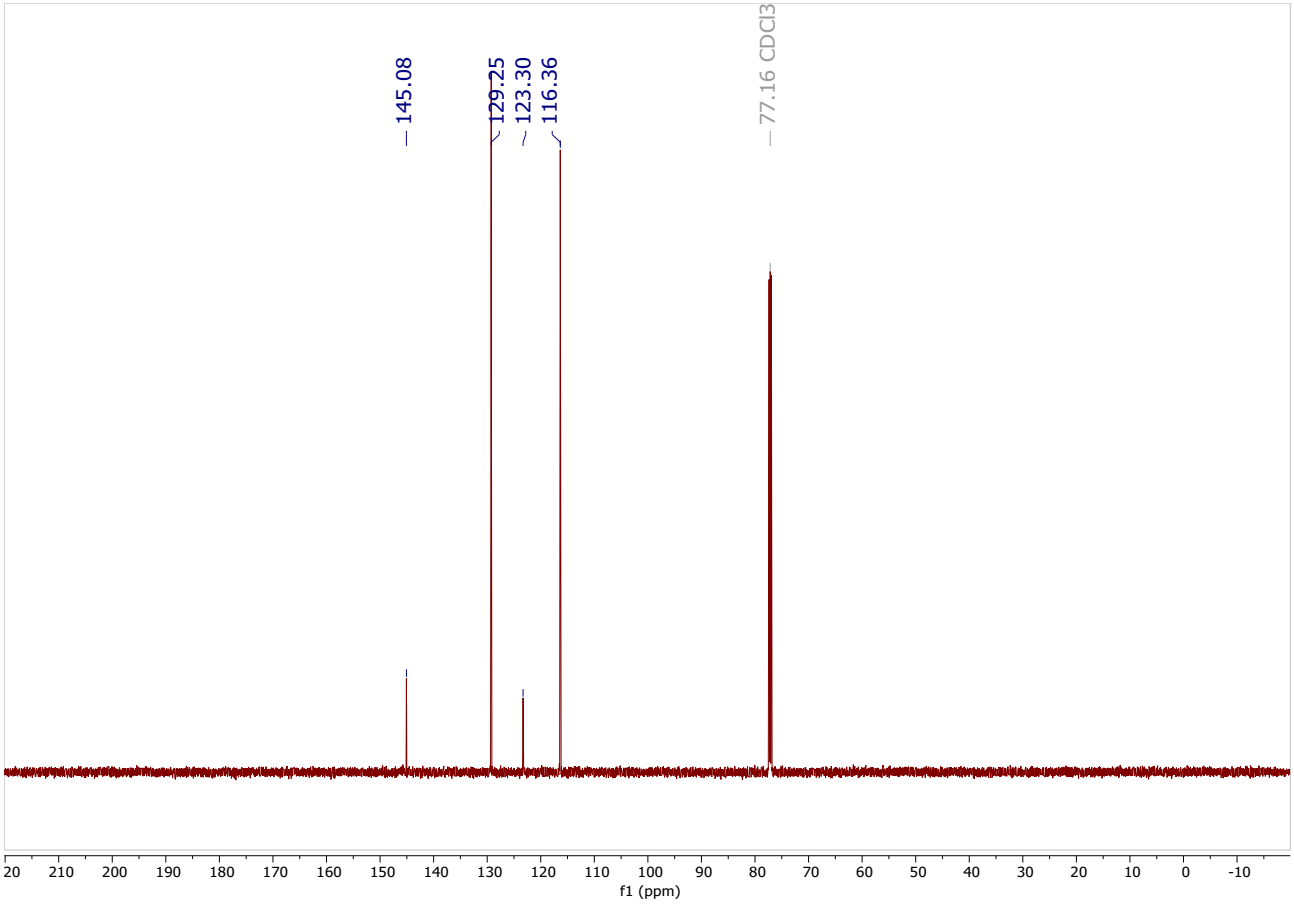

NH2
Br
7.26 CDCl3
7.24
7.22
6.57
6.57
6.56
6.55
6.55
3.65
1.98
2.00
1.91
f1 (ppm)

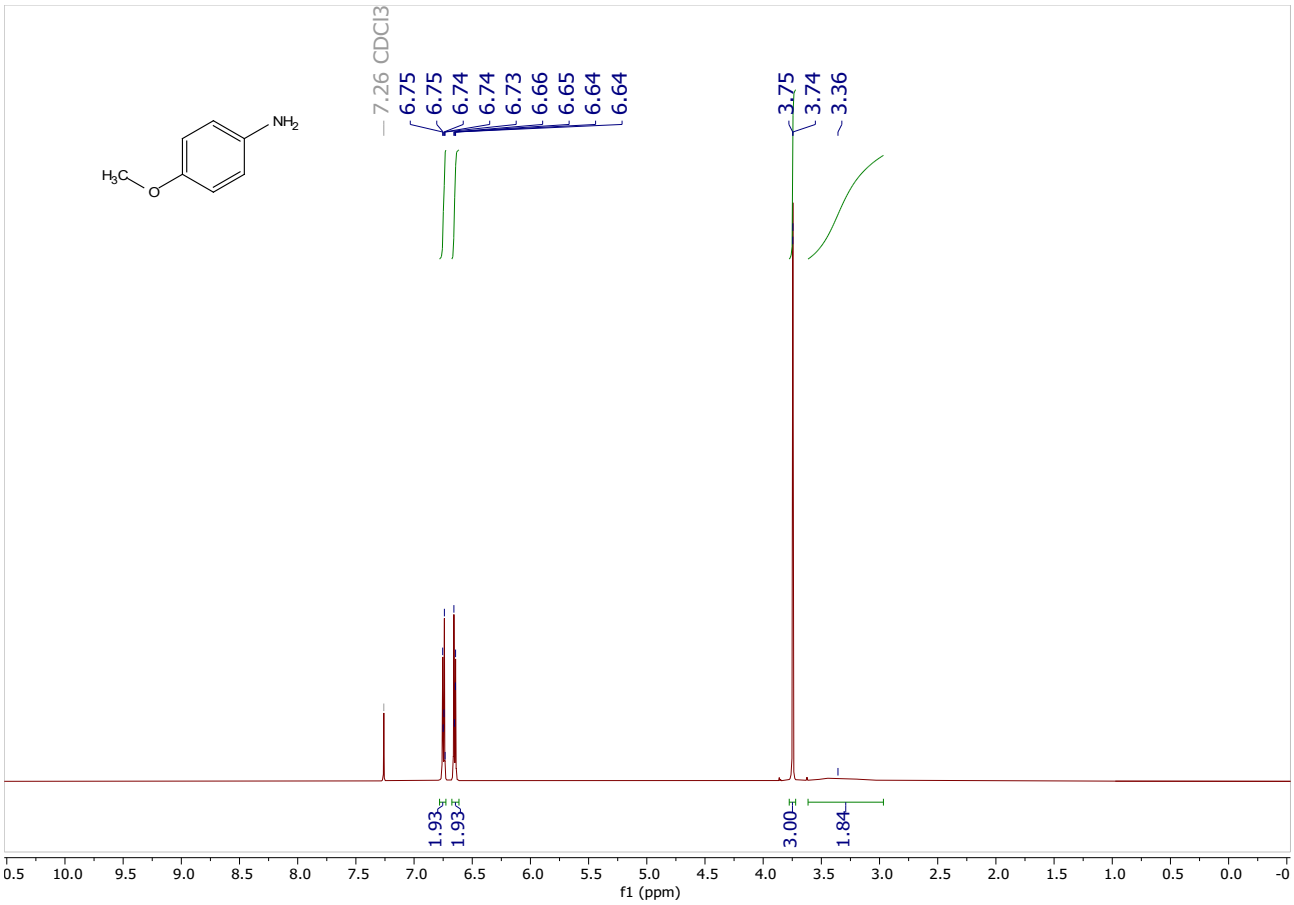

145.55
132.13
116.83
110.31
77.16 CDCl3
f1 (ppm)

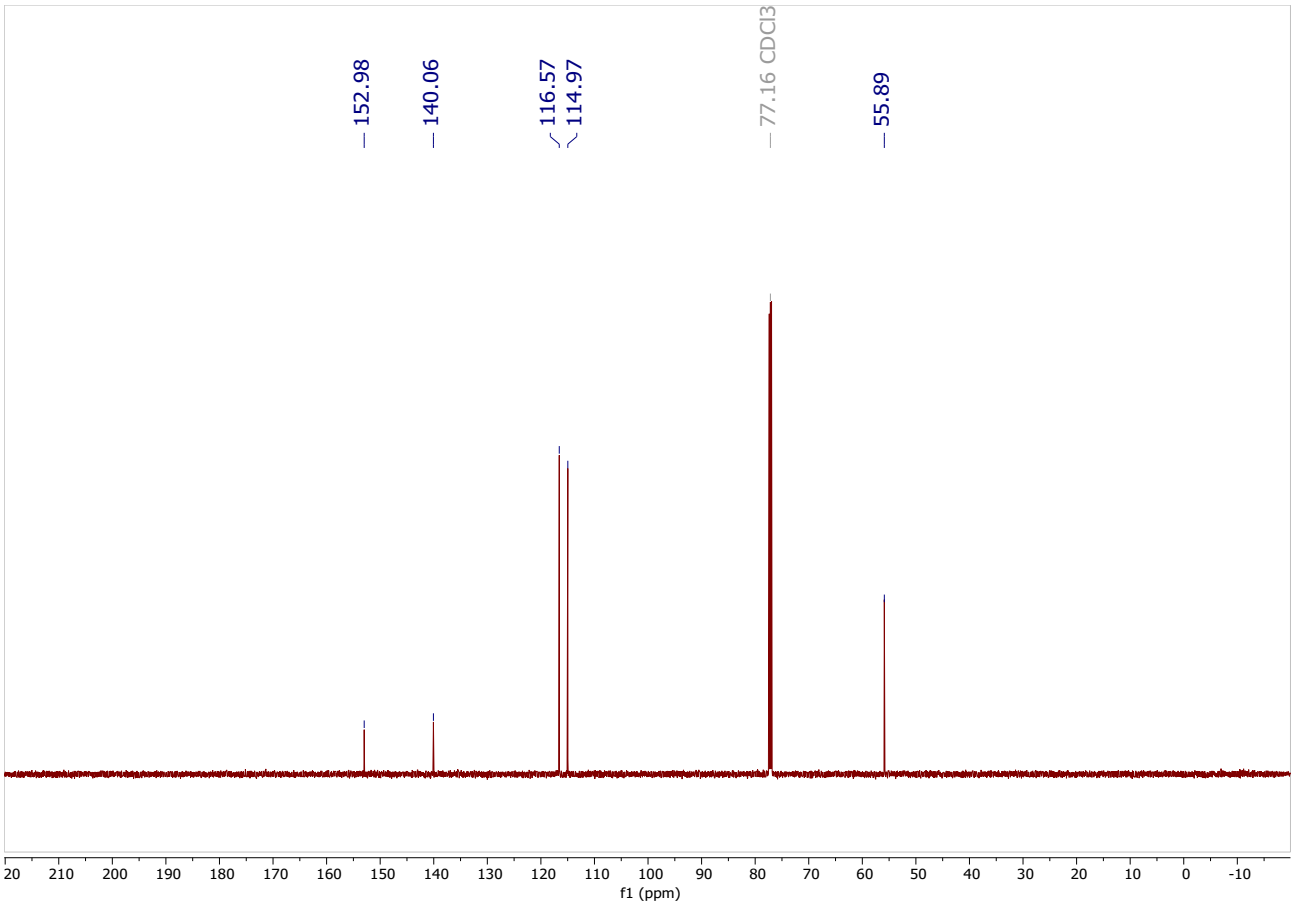

NH2
Br
7.26 CDCl3
7.24
7.22
6.57
6.57
6.56
6.55
6.55
3.65
1.98
2.00
1.91
f1 (ppm)


145.55
132.13
116.83
110.31
77.16 CDCl3
f1 (ppm)


7.26 CDCl3
7.11
7.10
7.10
7.09
7.09
7.08
6.62
6.61
6.61
6.60
6.60
6.59
3.64
NH2
Cl
1.97
2.00
1.95
f1 (ppm)


145.08
129.25
123.30
116.36
77.16 CDCl3
f1 (ppm)


7.26 CDCl3
6.75
6.75
6.74
6.74
6.73
6.66
6.65
6.64
6.64
3.75
3.74
3.36
NH2
H3C
O
1.93
1.93
3.00
1.84
f1 (ppm)


152.98
140.06
116.57
114.97
77.16 CDCl3
55.89
f1 (ppm)