

Supporting Information

Cyclopentadienone Iron Tricarbonyl Complexes-Catalyzed Hydrogen Transfer in Water.

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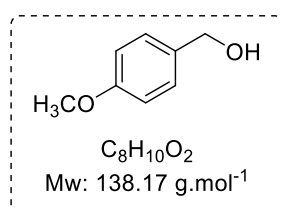
- Part 1:** Scope of the reaction for chemoselective aldehyde reduction and reductive amination by hydride transfer reaction with sodium formate.
- Part 2:** Synthesis of the water-soluble iron complexes
- Part 3:** Copies of NMR spectra.

General Considerations: All reactions were carried out using Schlenk or autoclave under an atmosphere of dry Argon. Water was degassed prior to use by bubbling argon gas directly in the solvent. Other solvents were purchased from Carlo Erba and degassed prior to use by freeze-pump thaw procedure (3 times). NMR spectra were recorded on a 400 MHz and 500 MHz Brücker spectrometer. Proton (^1H) NMR information is given in the following format: multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; sept, septet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), number of protons. The prefix app is occasionally applied when the true signal multiplicity was unresolved and br indicates the signal in question broadened. Carbon NMR spectra are reported in ppm (δ) relative to CDCl_3 (δ 77.16) unless noted otherwise. HRMS analyses were performed by using the LCMT analytical facilities. Neutral activated aluminium oxide was purchased from Alfa Aesar (Brockmann Grade I, 58 Angstroms, -60 Mesh Powder, S.A. 150 m^2/g) and from Merck (Grade I, 90 Angstroms, 70-230 Mesh ASTM). Basic aluminium oxide was purchased from Alfa Aesar (Brockmann Gradel, 58 Angstroms, -60 Mesh Powder, S.A. 150 m^2/g). NMR solvents were filtered through a pad of basic alumina for NMR analysis of iron complexes.

Part 1: Scope of the reaction for reduction of aldehydes and reductive amination by hydride transfer reaction with formate.

- **General procedure A for reduction of aldehydes by hydrogen transfer reaction.**

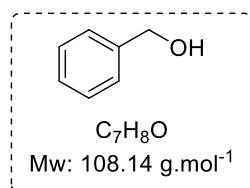
In a dried flamed Schlenk tube under argon, the corresponding aldehyde (1 equiv.) and sodium formate (170 mg, 5 equiv.) were mixed in water (0.5 M). The iron complex **Fe4** (5 mg, 2 mol %) and Me₃NO (1 mg, 2.5 mol %) were then added. The mixture was stirred and heated at 80 °C for 24 h. After cooling-down to room temperature, the resulting solution was quenched with a saturated aqueous solution of sodium bicarbonate and extracted three times with ethyl acetate. The organic phase was dried over MgSO₄, filtrated and concentrated under vacuum to afford the crude product. A purification by flash chromatography on silica gel furnished the alcohol.



(4-methoxyphenyl)methanol (4a)

Following the general procedure A, starting from 4'-methoxybenzaldehyde (61 μL, 0.5 mmol), alcohol **4a** was obtained as a colorless oil (68 mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.30 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 4.62 (s, 2H), 3.81 (s, 3H) ppm (OH signal not observed). ¹³C-NMR (CDCl₃, 126 MHz) δ 159.2, 133.1, 128.7, 114.0, 65.1, 55.3 ppm. Data are in accordance with the literature.¹

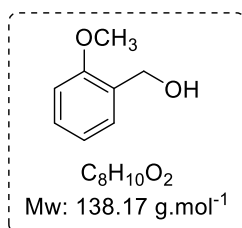


Benzyl alcohol (4b)

Following the general procedure A, starting from benzaldehyde (51 μL, 0.5 mmol), alcohol **4b** was obtained as a colorless oil (52 mg, 96 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.37 (d, *J* = 4.4 Hz, 4H), 7.33-7.29 (m, 1H), 4.70 (s, 2H), 1.70 (s, 1H) ppm. ¹³C-NMR (CDCl₃, 126 MHz) δ 140.9, 128.6, 127.7, 127.0, 65.4 ppm. Data are in accordance with the literature.¹

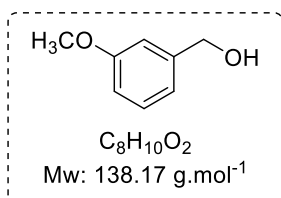
¹ Yang, Z.; Zhu, Z.; Luo, R.; Qiu, X.; Liu, J.-T.; Yang, J.-K.; Tang, W. *Green Chem.* **2017**, *19*, 3296.



(2-methoxyphenyl)methanol (4c)

Following the general procedure A, starting from 2-methoxybenzaldehyde (68 mg, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4c** was obtained as a colorless oil (63 mg, 91 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [9:1] then [7:3]).

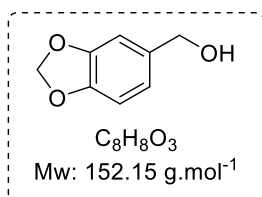
¹H-NMR (CDCl₃, 500 MHz) δ 7.30-7.26 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.69 (d, *J* = 5.0 Hz, 2H), 3.88 (s, 3H), 2.30 (s, 1H) ppm. ¹³C-NMR (CDCl₃, 126 MHz) δ 157.5, 129.0, 128.8, 120.7, 110.2, 62.3, 55.3 ppm. Data are in accordance with the literature.²



(3-methoxyphenyl)methanol (4d)

Following the general procedure A, starting from 3-methoxybenzaldehyde (61 μL, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4d** was obtained as a colorless liquid (67 mg, 97 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [9:1]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.29 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 4.68 (s, 2H), 3.82 (s, 3H), 1.66 (s, 1H) ppm. ¹³C-NMR (CDCl₃, 126 MHz) δ 159.9, 142.5, 129.6, 119.1, 113.3, 112.3, 65.3, 55.3 ppm. Data are in accordance with the literature.²



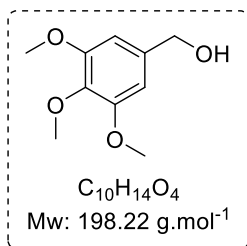
Piperonyl alcohol (4e)

Following the general procedure A, starting from piperonal (75 mg, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4e** was obtained as a white solid (72 mg, 95 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]).

¹H-NMR (CDCl₃, 500 MHz) δ 6.88 (s, 1H), 6.80 (q, *J* = 7.9 Hz, 2H), 5.96 (s, 2H), 4.59 (s, 2H) ppm (OH signal not observed). ¹³C-NMR (CDCl₃, 126 MHz) δ 147.9, 147.1, 134.9, 120.5, 108.2, 107.9, 101.0, 65.3 ppm. Data are in accordance with the literature.³

² Wu, X.; Corcoran, C.; Yang, S.; Xiao, J. *ChemSusChem* **2008**, *1*, 71.

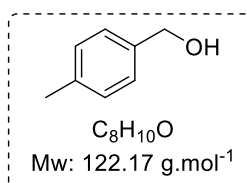
³ Ovia, J. M.; Kelly, C. B.; Pistrutto, V. A.; Leadbeater, N. E. *Org. Lett.*, **2017**, *19*, 1286-1289.



(3,4,5-trimethoxyphenyl)methanol (4f)

Following the general procedure A, starting from (3,4,5-trimethoxy)benzaldehyde (98 mg, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4f** was obtained as a thick colorless oil (98 mg, 99 %) purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]).

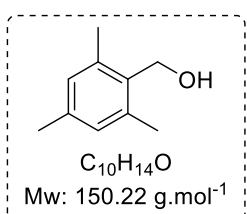
¹H-NMR (CDCl₃, 500 MHz) δ 6.60 (s, 2H), 4.64 (s, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 1.72 (s, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 153.4, 137.3, 136.6, 103.8, 65.6, 60.9, 56.1 ppm. Data are in accordance with the literature.⁴



p-tolylmethanol (4g)

Following the general procedure A, starting from 4-methylbenzaldehyde (59 μL, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4g** was obtained as a white solid (59 mg, 96 %) purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.19 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 4.58 (s, 2H), 2.28 (s, 3H) ppm (OH signal not observed). **¹³C-NMR (CDCl₃, 126 MHz)** δ 137.9, 137.4, 129.3, 127.1, 65.3, 21.2 ppm. Data are in accordance with the literature.²



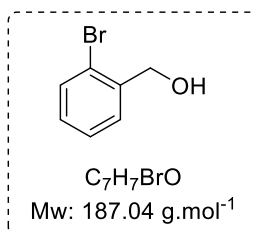
(2,4,6-trimethylphenyl)methanol (4h)

Following the general procedure A, starting from (2,4,6-trimethyl)benzaldehyde (74 μL, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4h** was obtained as a white solid (74 mg, 99 %) purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]).

¹H-NMR (CDCl₃, 500 MHz) δ 6.87 (s, 2H), 4.71 (s, 2H), 2.40 (s, 6H), 2.27 (s, 3H), 1.18 (s, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 137.8, 137.3, 133.7, 129.2, 59.2, 21.0, 19.4 ppm. Data are in accordance with the literature.⁵

⁴ Elangovan, S.; Garbe, M.; Jiao, H.; Spanneberg, A.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 15364-15368.

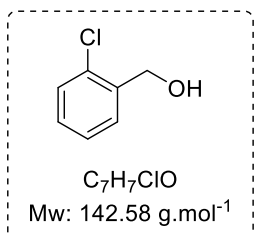
⁵ Plank, T. N.; Drake, J. L.; Kim, D. K.; Funk, T. W. *Adv. Synth. Catal.* **2012**, *354*, 597.



(2-bromophenyl)methanol (4i)

Following the general procedure A, starting from 2-bromobenzaldehyde (58 μ L, 0.5 mmol), alcohol **4i** was obtained as a white powder (70 mg, 75 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]).

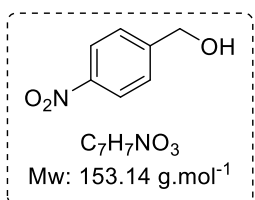
¹H-NMR (CDCl₃, 500 MHz) δ 7.55 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 4.76 (d, J = 5.8 Hz, 2H), 1.97 (t, J = 5.8 Hz, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 139.7, 132.6, 129.2, 128.9, 127.7, 122.6, 65.1 ppm. Data are in accordance with the literature.⁶



(2-chlorophenyl)methanol (4j)

Following the general procedure A, starting from 2-chlorobenzaldehyde (56 μ L, 0.5 mmol), alcohol **4j** was obtained as a white powder (66 mg, 92 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.48 (d, J = 7.4 Hz, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 4.79 (d, J = 6.2 Hz, 2H), 1.93 (t, J = 6.2 Hz, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 138.2, 132.8, 129.4, 128.9, 128.8, 127.1, 62.9 ppm. Data are in accordance with the literature.⁶

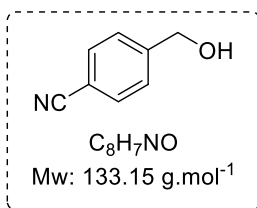


(4-nitrophenyl)methanol (4k)

Following the general procedure A, starting from 4-nitrobenzaldehyde (75 mg, 0.5 mmol), alcohol **4k** was obtained as a yellow powder (74 mg, 96 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]).

¹H-NMR (CDCl₃, 500 MHz) δ 8.22 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 4.84 (d, J = 5.6 Hz, 2H), 1.91 (t, J = 5.6 Hz, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 148.1, 147.3, 127.0, 123.8, 64.1 ppm. Data are in accordance with the literature.⁶

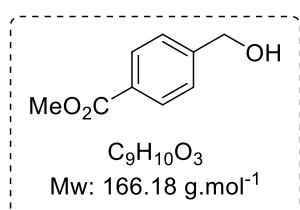
⁶ Widegren, M. B.; Harkness, G. J.; Slawin, A. M. Z.; Cordes, D. B.; Clarke, M. L. *Angew. Chem. Int. Ed.* **2017**, *56*, 5825.



(4-cyanophenyl)methanol (**4l**)

Following the general procedure A, starting from 4-cyanobenzaldehyde (65 mg, 0.5 mmol), alcohol **4l** was obtained as a white powder (65 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]).

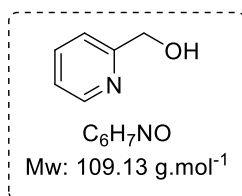
¹H-NMR (CDCl₃, 500 MHz) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 4.79 (d, *J* = 3.3 Hz, 2H), 1.94 (s, 1H) ppm. ¹³C-NMR (CDCl₃, 126 MHz) δ 146.1, 132.4, 127.0, 118.9, 111.2, 64.3 ppm. Data are in accordance with the literature.⁵



methyl 4-(hydroxymethyl)benzoate (**4m**)

Following the general procedure A, starting from methyl 4-formylbenzoate (82 mg, 0.5 mmol), alcohol **4m** was obtained as a colorless oil (80 mg, 96 %) after purification by flash column chromatography on silica (eluent: pentane/Et₂O [1:1]).

¹H-NMR (CDCl₃, 500 MHz) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H), 4.77 (d, *J* = 4.7 Hz, 2H), 3.93 (s, 3H) ppm (OH signal not observed). ¹³C-NMR (CDCl₃, 126 MHz) δ 166.9, 145.9, 129.9, 129.4, 126.5, 64.7, 52.1 ppm. Data are in accordance with the literature.⁷

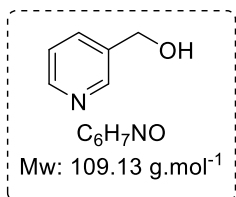


Pyridin-2-ylmethanol (**4n**)

Following the general procedure A, starting from 2-pyridinecarboxaldehyde (48 μL, 0.5 mmol), alcohol **4n** was obtained as a colorless oil (45 mg, 82 %) after purification by flash column chromatography on silica (eluent: AcOEt to AcOEt/MeOH [95:5]).

¹H-NMR (CDCl₃, 500 MHz) δ 8.55 (d, *J* = 4.7 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 4.7 Hz, 1H), 4.76 (s, 2H), 3.95 (s, 1H) ppm. ¹³C-NMR (CDCl₃, 126 MHz) δ 159.0, 148.5, 136.7, 122.4, 120.5, 64.1 ppm. Data are in accordance with the literature.⁷

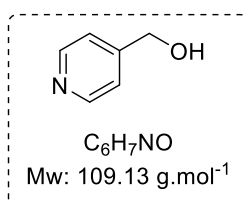
⁷ Zhao, M.; Xie, W.; Cui, C. *Chem. Eur. J.* **2014**, *20*, 9259.



Pyridin-3-ylmethanol (4o)

Following the general procedure A, starting from 3-pyridinecarboxaldehyde (47 μ L, 0.5 mmol), alcohol **4o** was obtained as a colorless oil (41 mg, 75 %) after purification by flash column chromatography on silica (eluent: AcOEt to AcOEt/MeOH [95:5]).

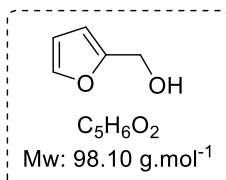
¹H-NMR (CDCl₃, 500 MHz) δ 8.55 (s, 1H), 8.50 (d, J = 3.8 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.29 (dd, J = 7.5, 5.0 Hz, 1H), 4.73 (s, 2H) (OH signal not observed) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 148.8, 148.4, 136.4, 134.9, 123.6, 62.6 ppm. Data are in accordance with the literature.⁶



Pyridin-4-ylmethanol (4p)

Following the general procedure A, starting from 4-pyridinecarboxaldehyde (47 μ L, 0.5 mmol), alcohol **1p** was obtained as a white powder (50 mg, 91 %) after purification by flash column chromatography on silica (eluent: AcOEt to AcOEt/MeOH [9:1]).

¹H-NMR (CDCl₃, 500 MHz) δ 8.49 (d, J = 4.8 Hz, 2H), 7.29 (d, J = 4.8 Hz, 2H), 4.74 (s, 2H) ppm (OH signal not observed). **¹³C-NMR (CDCl₃, 126 MHz)** δ 150.8, 149.5, 121.2, 63.1 ppm. Data are in accordance with the literature.⁸

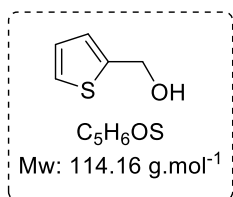


Furan-2-ylmethanol (4q)

Following the general procedure A, starting from furfural (41 μ L, 0.5 mmol), alcohol **4q** was obtained as a yellow oil (48 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.40 (dd, J = 1.9, 0.8 Hz, 1H), 6.34 (dd, J = 3.2, 1.9 Hz, 1H), 6.30 (d, J = 3.2 Hz, 1H), 4.61 (s, 2H), 1.76 (s, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 153.9, 142.6, 110.4, 107.8, 57.5 ppm. Data are in accordance with the literature.¹

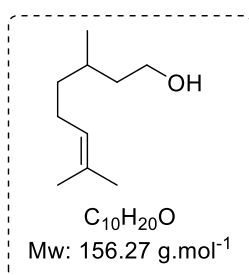
⁸ Shi, L.; Liu, Y.; Liu, Q.; Wei, B.; Zhang, G. *Green Chem.* **2012**, *14*, 1372.



Thiophen-2-ylmethanol (4r)

Following the general procedure A, starting from 2-thiophenecarboxaldehyde (47 μ L, 0.5 mmol), alcohol **4r** was obtained as a colorless oil (52 mg, 91 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]).

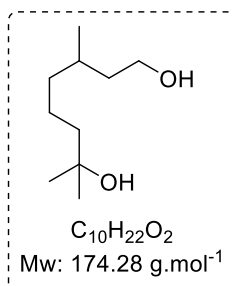
¹H-NMR (CDCl₃, 500 MHz) δ 7.29 (d, J = 5.0 Hz, 1H), 7.02 (s, 1H), 6.98 (t, J = 4.0 Hz, 1H), 4.84 (s, 2H), 1.83 (s, 1H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 144.0, 126.9, 125.7, 125.5, 60.1 ppm. Data are in accordance with the literature.¹



Citronellol (4s)

Following the general procedure A, starting from citronellal (90 μ L, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **4s** was obtained as a colorless oil (77 mg, 99 %) without purification.

¹H-NMR (CDCl₃, 500 MHz) δ 5.09 (*app* t, J = 7.2 Hz, 1H), 3.67-3.55 (m, 2H), 2.00-1.82 (m, 2H), 1.62 (s, 3H), 1.60-1.45 (m, 5H), 1.38-1.22 (m, 2H), 1.19-1.06 (m, 2H), 0.90 (d, J = 7.2 Hz, 3H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 131.3, 124.7, 61.2, 39.9, 37.2, 29.2, 25.7, 25.5, 19.5, 17.7 ppm. Data are in accordance with the literature.⁹



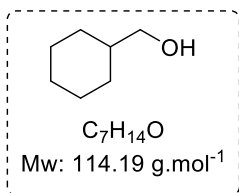
3,7-dimethyloctane-1,7-diol (4t)

Following the general procedure A, starting from 7-hydroxycitronellal (93 μ L, 0.5 mmol), in an equimolar mixture H₂O/EtOH, diol **4t** was obtained as a thick colorless oil (85 mg, 98 %) without purification.

¹H-NMR (CDCl₃, 500 MHz) δ 3.73-3.64 (m, 2H), 1.64-1.57 (m, 2H), 1.44-1.31 (m, 8H), 1.21 (s, 6H), 1.17-1.13 (m, 1H), 0.90 (d, J = 6.6 Hz, 3H) ppm. **¹³C-NMR (CDCl₃, 126 MHz)** δ 71.1, 61.2, 44.1, 39.9, 37.6, 29.5, 29.4, 29.2, 21.7, 19.6 ppm. Data are in accordance with the literature.¹⁰

⁹ Mérel, D. S.; Elie, M.; Lohier, J.-F.; Gaillard, S.; Renaud, J.-L. *ChemCatChem*. **2013**, *5*, 2939.

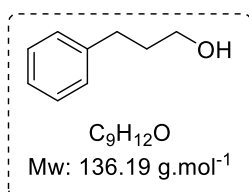
¹⁰ Wang, D.; Shuler, W. G.; Pierce, C. J.; Hilinski, M. K. *Org. Lett.*, **2016**, *18*, 3826.



Cyclohexylmethanol (4u)

Following the general procedure A, starting from cyclohexane carboxaldehyde (60 μ L, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **1u** was obtained as a clear yellow oil (56 mg, 98 %) without purification.

¹H-NMR (CDCl₃, 500 MHz) δ 3.44 (d, *J* = 6.4 Hz, 2H), 1.76-1.72 (m, 4H), 1.69-1.66 (m, 1H), 1.51-1.43 (m, 1H), 1.27-1.14 (m, 3H), 0.97-0.88 (m, 2H) ppm (OH signal not observed). ¹³C-NMR (CDCl₃, 126 MHz) δ 68.8, 40.5, 29.6, 26.6, 25.8 ppm. Data are in accordance with the literature.²



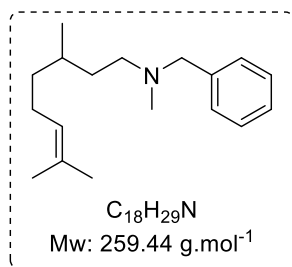
3-phenylpropan-1-ol (4v)

Following the general procedure A, starting from hydrocinnamaldehyde (66 μ L, 0.5 mmol) in an equimolar mixture H₂O/EtOH, alcohol **1v** was obtained as a colorless oil (63 mg, 92 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [9:1] to [7:3]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 3.69 (*app t*, *J* = 6.1 Hz, 2H), 2.72 (*app t*, *J* = 6.1 Hz, 2H), 1.93-1.88 (m, 2H), 1.25 (s, 1H) ppm. ¹³C-NMR (CDCl₃, 126 MHz) δ 141.8, 128.5, 128.4, 125.9, 62.3, 34.2, 32.1 ppm. Data are in accordance with the literature.⁴

- **General procedure B for reductive amination by hydrogen transfer reaction.**

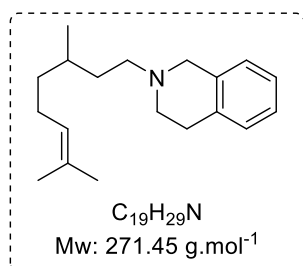
In a dried flamed Schlenk tube under argon, the aldehyde (1 equiv.), the amine (2 equiv.) and ammonium formate (205 mg, 6.5 equiv.) were mixed in water (0.5 M). The iron complex **Fe5** (5 mg, 2 mol %) and Me₃NO (1 mg, 2.5 mol %) were then added. The mixture was stirred and heated at 90 °C for 24-48 h. After cooling-down to room temperature, the resulting solution was quenched with a saturated aqueous solution of sodium bicarbonate and extracted three times with ethyl acetate. The organic phase was dried over MgSO₄, filtrated and concentrated under vacuum to afford the crude product. A purification by flash chromatography on silica gel furnished the amine.



***N*-benzyl-*N*,3,7-trimethyloct-6-en-1-amine (5a)**

Following the general procedure B, starting from citronellal (91 μ L, 0.5 mmol) and *N*-methylbenzylamine (150 μ L, 1 mmol) for 24 h, the corresponding amine **5a** was obtained as a yellow oil (91 mg, 70 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [99:1]).

¹H-NMR (CDCl₃, 400 MHz) δ 7.31 (d, J = 4.4 Hz, 4H), 7.26-7.22 (m, 1H), 5.09 (t, J = 7.1 Hz, 1H), 3.48 (q, J = 13.0 Hz, 2H), 2.39 (t, J = 7.5 Hz, 2H), 2.18 (s, 3H), 2.04-1.90 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58-1.55 (m, 1H), 1.50-1.46 (m, 1H), 1.34-1.29 (m, 2H), 1.19-1.11 (m, 1H), 0.87 (d, J = 6.6 Hz, 3H) ppm. **¹³C-NMR (CDCl₃, 125 MHz)** δ 139.3, 131.1, 129.1, 128.2, 126.9, 124.9, 62.4, 55.6, 42.3, 37.3, 34.4, 30.9, 25.8, 25.5, 19.7, 17.7 ppm. Data are in accordance with the literature.¹¹

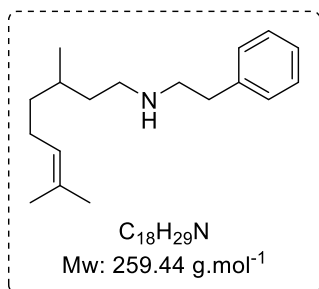


2-(3,7-dimethyloct-6-en-1-yl)-1,2,3,4-tetrahydroisoquinoline (5b)

Following the general procedure B, starting from citronellal (91 μ L, 0.5 mmol) and 1,2,3,4-tetrahydroisoquinoline (125 μ L, 1 mmol) for 24 h, the corresponding amine **5b** was obtained as a yellow oil (83 mg, 61 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]).

¹H-NMR (CDCl₃, 500 MHz) δ 7.12-7.08 (m, 3H), 7.03-7.01 (m, 1H), 5.11 (t, J = 7.1 Hz, 1H), 3.62 (s, 2H), 2.91 (t, J = 5.9 Hz, 2H), 2.73 (td, J = 6.0, 3.0 Hz, 2H), 2.52 (dt, J = 9.5, 5.6 Hz, 2H), 2.06-1.93 (m, 2H), 1.69 (s, 3H), 1.67-1.63 (m, 1H), 1.61 (s, 3H), 1.55-1.48 (m, 1H), 1.45-1.33 (m, 2H), 1.29-1.17 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H). **¹³C-NMR (CDCl₃, 125 MHz)** δ 135.0, 134.4, 131.2, 128.7, 126.6, 126.1, 125.6, 124.9, 56.6, 56.4, 51.1, 37.3, 34.3, 31.2, 29.2, 25.7, 25.5, 19.8, 17.7 ppm. Data are in accordance with the literature.¹²

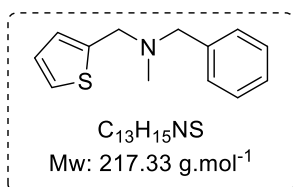
¹¹ Moulin, S.; Dentel, H.; Pagnoux-Ozherelyeva, A.; Gaillard, S.; Poater, A.; Cavallo, L.; Lohier, J.-F.; Renaud, J.-L. *Chem. Eur. J.* **2013**, *19*, 17881-17890.



3,7-dimethyl-*N*-phenethyloct-6-en-1-amine¹² (**5c**)

Following the general procedure B, starting from citronellal (91 μ L, 0.5 mmol) and phenethylamine (126 μ L, 1 mmol) for 24 h, the corresponding amine **5c** was obtained as a yellow oil (27 mg, 21 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [98:2]).

¹H-NMR (CDCl₃, 400 MHz) δ 7.33-7.22 (m, 3H), 7.24-7.17 (m, 2H), 5.14-5.03 (m, 1H), 2.94- 2.86 (m, 2H), 2.85-2.77 (m, 2H), 2.70-2.56 (m, 2H), 2.04-1.88 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.54-1.42 (m, 2H), 1.40-1.21 (m, 3H), 1.20-1.09 (m, 1H), 0.87 (d, J = 6.5 Hz, 3H) ppm. **¹³C-NMR (CDCl₃, 125 MHz)** δ 140.0, 131.2, 128.7, 128.4, 126.1, 124.7, 51.2, 47.8, 37.1, 36.3, 30.6, 25.7, 25.4, 19.6, 17.6 ppm. Data are in accordance with the literature.¹¹

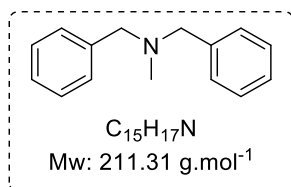


N-benzyl-*N*-methyl-1-(thiophen-2-yl)methanamine (**5d**)

Following the general procedure B, starting from 2-thiophenecarboxaldehyde (47 μ L, 0.5 mmol) and *N*-methylbenzylamine (150 μ L, 1 mmol) for 48 h, the corresponding amine **5d** was obtained as a yellow oil (69 mg, 64 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]).

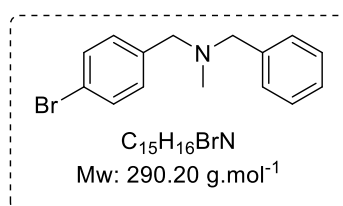
¹H-NMR (CDCl₃, 500 MHz) δ 7.27 (d, J = 7.5 Hz, 2H), 7.22 (t, J = 7.4 Hz, 2H), 7.16-7.13 (m, 2H), 6.85-6.84 (m, 1H), 6.83 (s, 1H), 3.66 (s, 2H), 3.44 (s, 2H), 2.15 (s, 3H) ppm. **¹³C-NMR (CDCl₃, 125 MHz)** δ 142.9, 139.0, 128.9, 128.3, 127.0, 126.4, 125.7, 124.9, 61.1, 56.1, 42.2 ppm. **IR (neat)** ν 3027, 2924, 2837, 2785, 1495, 1452, 1418, 1366, 1340, 1277, 1253, 1222, 1168, 1130, 1075, 1023, 973, 908, 863, 820, 736, 694, 606, 502, 479 cm⁻¹. **HRMS (m/z):** [M+H]⁺ calculated for C₁₃H₁₆NS: 218.1003; found: 218.1009.

¹² Pagnoux-Ozherelyeva, A.; Pannetier, N.; Mbaye, M. D.; Gaillard, S.; Renaud, J.-L. *Angew. Chem. Int. Ed.* **2012**, *51*, 4976–4980.



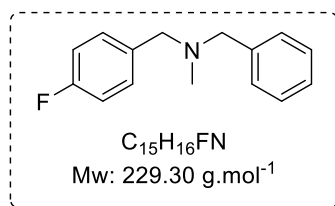
***N*-benzyl-*N*-methyl-1-phenylmethanamine (5e)**

Following the general procedure B, starting from benzaldehyde (51 μL , 0.5 mmol) and *N*-methylbenzylamine (150 μL , 1 mmol) for 48 h, the corresponding amine **5d** was obtained as a yellow oil (56 mg, 53 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [97:3]). **$^1\text{H-NMR}$ (CDCl_3 , 500 MHz)** δ 7.37 (d, $J = 7.4$ Hz, 4H), 7.32 (t, $J = 7.4$ Hz, 4H), 7.25 (t, $J = 7.4$ Hz, 2H), 3.53 (s, 4H), 2.19 (s, 3H) ppm. **$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz)** δ 139.4, 128.9, 128.2, 126.9, 61.9, 42.3 ppm. Data are in accordance with the literature.¹³



***N*-benzyl-1-(4-bromophenyl)-*N*-methylmethanamine¹⁴ (5f)**

Following the general procedure B, starting from 4-bromobenzaldehyde (93 mg, 0.5 mmol) and *N*-methylbenzylamine (150 μL , 1 mmol) for 24 h, the corresponding amine **5f** was obtained as a yellow oil (75 mg, 52 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [98:2] to [95:5]). **$^1\text{H-NMR}$ (CDCl_3 , 500 MHz)** δ 7.37 (d, $J = 8.05$ Hz, 2H), 7.27 (m, 2H), 7.18 (m, 5H), 3.44 (s, 2H), 3.39 (s, 2H), 2.09 (s, 3H) ppm. **$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz)** δ 131.3, 130.6, 128.9, 128.3, 127.0, 61.9, 61.1, 42.2 ppm. Data are in accordance with the literature.¹³



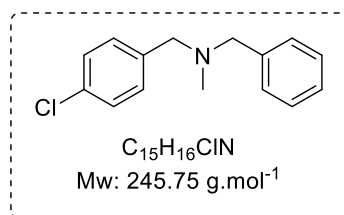
***N*-benzyl-1-(4-fluorophenyl)-*N*-methylmethanamine¹¹ (5g)**

Following the general procedure B, starting from 4-fluorobenzaldehyde (54 μL , 0.5 mmol) and *N*-methylbenzylamine (150 μL , 1 mmol) for 24 h, the corresponding amine **5f** was obtained as a yellow oil (58 mg, 51 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). **$^1\text{H-NMR}$ (CDCl_3 , 500 MHz)** δ 7.28-7.23 (m, 6H), 7.18-7.16 (m, 1H), 6.92 (t, $J = 8.3$ Hz, 2H), 3.43 (s, 2H), 3.40 (s, 2H), 2.09 (s, 3H) ppm. **$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz)** δ 162.9, 161.0, 139.2, 135.1,

¹³ Kirinde Arachchige, P. T.; Lee, H.; Yi, C. S. *J. Org. Chem.* **2018**, *83*, 4932-4947.

¹⁴ Milne, K.; Sun, J.; Zaal, E. A.; Mowat, J.; Celie, P. H. N. Fish, A.; Berkers, C. R.; Forlanif, G.; Loayza-Puch, F.; Jamieson, C.; Agami, R. *Bioorg. Med. Chem. Letters* **2019**, *29*, 2626-2631.

130.4, 130.3, 128.9, 128.3, 127.0, 115.1, 114.9, 61.9, 61.1, 42.2 ppm. $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ -116.16 ppm. Data are in accordance with the literature.¹⁵

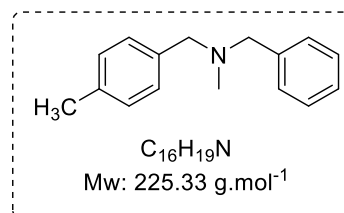


***N*-benzyl-1-(4-chlorophenyl)-*N*-methylmethanamine (5h)**

Following the general procedure B, starting from 4-chlorobenzaldehyde (70 mg, 0.5 mmol) and *N*-methylbenzylamine (150 μL , 1 mmol) for 24 h, the corresponding amine **5h** was obtained as a yellow oil (65 mg, 53 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]).

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 7.32-7.21 (m, 10H), 3.48 (s, 2H), 3.45 (s, 2H), 2.14 (s, 3H) ppm.

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 139.1, 137.9, 132.6, 130.2, 128.9, 128.4, 128.3, 127.1, 61.9, 61.1, 42.2 ppm. IR (neat) ν 3028, 2924, 2840, 2786, 1598, 1490, 1452, 1406, 1364, 1284, 1263, 1240, 1192, 1132, 1088, 1025, 1015, 979, 939, 908, 867, 838, 799, 737, 697, 671, 634, 611, 536, 488, 456 cm^{-1} . HRMS (m/z): [M+H]⁺ calculated for $\text{C}_{15}\text{H}_{17}\text{ClN}$: 246.1050; found: 246.1052.

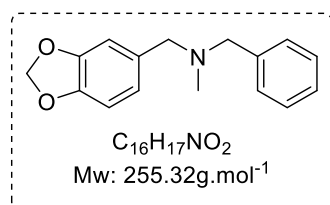


***N*-benzyl-*N*-methyl-1-(*p*-tolyl)methanamine¹³ (5i)**

Following the general procedure B, starting from *p*-tolualdehyde (59 μL , 0.5 mmol) and *N*-methylbenzylamine (150 μL , 1 mmol) for 24 h, the corresponding amine **5i** was obtained as a yellow oil (50 mg, 53 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]).

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 7.27-7.24 (m, 3H), 7.18 (d, $J = 7.9$ Hz, 4H), 7.06 (d, $J = 7.6$ Hz, 2H), 3.43 (d, 4H), 2.26 (s, 3H), 2.09 (s, 3H) ppm.

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ 139.4, 136.5, 136.2, 128.9, 128.2, 126.9, 61.8, 61.6, 42.2, 21.1 ppm. Data are in accordance with the literature.¹³



1-(benzo[*d*][1,3]dioxol-5-yl)-*N*-benzyl-*N*-methylmethanamine¹⁶ (5j)

¹⁵ Kazuya, Y.; Jinling, H.; Takamishi, O.; Noritaka, M. *Chem. Eur. J.*, **2010**, *16*, 7199-7204

¹⁶ Jung, Y. J.; Bae, J. W.; Park, E. S.; Chang, Y. M.; Yoon, C. M. *Tetrahedron* **2003**, *59*, 10331-10338.

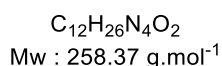
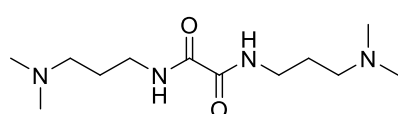
Following the general procedure B, starting from piperonal (75 mg, 0.5 mmol) and *N*-methylbenzylamine (150 μ L, 1 mmol) for 24 h, the corresponding amine **5j** was obtained as a yellow oil (17 mg, 13 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]).

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ 7.36-7.31 (m, 4H), 7.26-7.23 (m, 1H), 6.91 (s, 1H), 6.77 (q, $J = 7.9$ Hz, 2H), 5.9 (s, 2H), 3.51 (s, 2H), 3.43 (s, 2H), 2.17 (s, 2H) ppm. **$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ** 147.7, 146.5, 139.4, 133.4, 128.9, 128.3, 126.9, 121.9, 109.3, 107.9, 100.9, 61.8, 61.6, 42.1 ppm. Data are in accordance with the literature.

Part 2: Preparation of water-soluble complexes

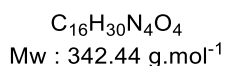
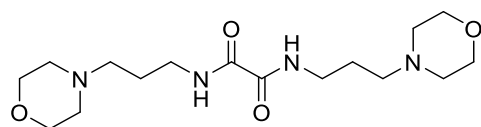
- Preparation of *N*¹,*N*²-bisalkylethane-1,2-diamine derivatives.

General procedure C:¹⁷ To a stirring mixture of diethyl oxalate (1 equiv.) in absolute ethanol (C = 0.3 M) was added the corresponding amine (2 equiv.). The mixture was stirred and heated under reflux for 2 hours. The resulting mixture was cooled-down to 0°C and the precipitated solid was isolated by filtration. The solid was then washed with cold diethylether and dried under vacuum to afford the pure product.



***N*¹,*N*²-bis(3-(dimethylamino)propyl)oxalamide (5).** Following the general procedure C, starting from diethyl oxalate (1.9 mL, 13.4 mmol) and *N,N*-dimethyl-1,3-propanediamine (3.4 mL, 27.4 mmol), **5** was obtained as a white powder (3.54 g, 100 %).

¹H-NMR (CDCl₃, 400 MHz) δ 8.41 (s, 2H), 3.37 (q, *J* = 6.4 Hz, 4H), 2.36 (t, *J* = 6.4 Hz, 4H), 2.22 (s, 12H), 1.69 (p, *J* = 6.4 Hz, 4H) ppm. **¹³C-NMR (CDCl₃, 100 MHz)** δ 160.0, 58.1, 45.4, 39.0, 26.3 ppm. **IR (neat)** ν 3291, 2812, 2765, 1650, 1523, 1465, 1434, 1377, 1303, 1276, 1240, 1214, 1147, 1129, 1111, 1071, 1040, 1017, 985, 919, 888, 863, 798, 784, 761 cm⁻¹. **HRMS (m/z):** [M+H]⁺ calculated for C₁₂H₂₇N₄O₂: 259.2134; found: 259.2135.

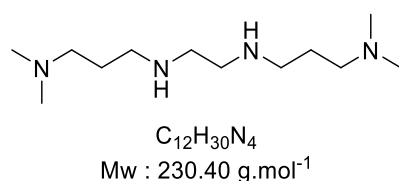


***N*¹,*N*²-bis(3-morpholinopropyl)oxalamide (6).** Following the general procedure C, starting from diethyl oxalate (1.9 mL, 13.4 mmol) and 3-morpholinopropylamine (4.0 mL, 27.4 mmol), **1d** was obtained as a white needles (4.7 g, 100 %).

¹⁷ Rice, L. M.; Grogan, C. H.; Reid, E. E. *J. Am. Chem. Soc.*, **1953**, *75*, 242–243.

¹H-NMR (CDCl₃, 400 MHz) δ 8.58 (s, 2H), 3.77 (t, *J* = 6.1 Hz, 8H), 3.41 (q, *J* = 6.1 Hz, 4H), 2.48-2.45 (m, 12H), 1.72 (q, *J* = 6.1 Hz, 6H) ppm. **¹³C-NMR (CDCl₃, 100 MHz)** δ 160.0, 66.9, 57.7, 53.8, 39.4, 24.8 ppm. **IR (neat)** ν 3289, 2973, 2937, 2873, 2811, 2766, 1647, 1522, 1465, 1434, 1377, 1303, 1275, 1254, 1240, 1214, 1147, 1129, 1112, 1070, 1039, 1017, 985, 919, 888, 863, 979, 783, 762, 734 cm⁻¹. **HRMS (m/z):** [M+H]⁺ calculated for C₁₆H₃₁N₄O₄: 343.2345; found: 343.2346.

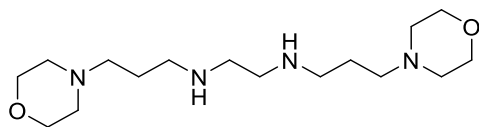
General procedure D:¹⁸ To a stirred solution of the corresponding amide (1 equiv.) in THF (0.3 M) at 0 °C, was added by portions LiAlH₄ (5-8 equiv.) under an argon atmosphere at such a rate that the temperature was maintained at 0 °C. The resulting suspension was stirred and heated at reflux for 2h. After cooling to 0 °C, dichloromethane (0.3 mL/mmol) was added followed by a dropwise addition of an aqueous saturated solution of Na₂SO₄ until gas evolution ceased and apparition of white salts. The solids were removed by filtration through Celite® and the filter cake was washed with a (9:1) mixture of CH₂Cl₂-MeOH. The filtrate was dried with MgSO₄, filtrated and evaporated under reduced pressure to give the pure product.



N¹,N^{1'}-(ethane-1,2-diyl)bis(N³,N^{3'}-dimethylpropane-1,3-diamine) (3). Following the general procedure D, starting from oxalamide **5** (2.0 g, 7.7 mmol) and lithium aluminium hydride (1.47 g, 38.7 mmol), **3** was obtained as a colorless liquid (1.65 g, 93 %).

¹H-NMR (CDCl₃, 400 MHz) δ 2.72 (s, 4H), 2.64 (t, *J* = 7.1 Hz, 4H), 2.30 (t, *J* = 7.1 Hz, 4H), 2.21 (s, 12H), 1.65 (p, *J* = 7.1 Hz, 4H) ppm (NH signal not observed). **¹³C-NMR (CDCl₃, 100 MHz)** δ 58.0, 49.5, 48.4, 45.6, 28.2 ppm. **IR (neat)** ν 2816, 2770, 1632, 1606, 1486, 1461, 1374, 1318, 1300, 1167, 1126, 1099, 1014, 908, 844, 731 cm⁻¹. **HRMS (m/z):** [M+H]⁺ calculated for C₁₂H₃₁N₄: 231.2549; found: 231.2553.

¹⁸ Bilke, J. L.; O'Brien, P. J. *Org. Chem.*, **2008**, *73*, 6452-6454.



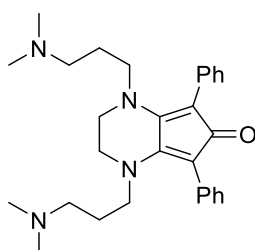
$C_{16}H_{34}N_4O_2$
Mw : 314.47 g.mol⁻¹

***N*¹,*N*²-bis(3-morpholinopropyl)ethane-1,2-diamine (4).** Following the general procedure D, starting from oxalamide **6** (2.0 g, 5.8 mmol) and lithium aluminium hydride (1.11 g, 29.2 mmol), **4** was obtained as a colorless oil (1.75 g, 95 %).

¹H-NMR (CDCl₃, 400 MHz) δ 3.72-3.69 (m, 8H), 2.71 (s, 4H), 2.65 (t, *J* = 7.0 Hz, 4H), 2.42-2.37 (m, 14H), 1.68 (q, *J* = 7.0 Hz, 4H) ppm. ¹³C-NMR (CDCl₃, 100 MHz) δ 67.0, 57.3, 53.8, 49.6, 48.5, 27.0 ppm. IR (neat) ν 2814, 1658, 1632, 1606, 1488, 1449, 1424, 1372, 1318, 1167, 1117, 1011, 906, 729 cm⁻¹. HRMS (*m/z*): [M+H]⁺ calculated for C₁₆H₃₅N₄O₂: 315.2760; found: 315.2762.

- **Preparation of water-soluble complexes.**

General procedure E:¹⁹ In a Schlenk tube, diphenylcyclopentanetrione (1 equiv.) and *N,N'*-dimethylethylenediamine (1 equiv.) were introduced in methanol (C = 0.5 M). The reaction mixture was heated under reflux overnight. After complete consumption of the starting materials, the solvent was removed under vacuum. Purification by flash chromatography on alumina with dichloromethane, and precipitation in a mixture of Et₂O/pentane (1:1) furnish the pure product as a purple powder.



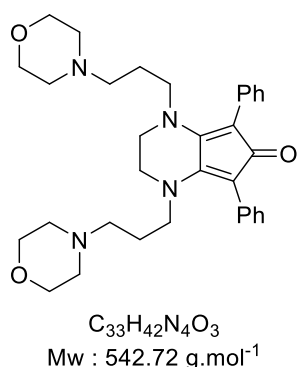
$C_{29}H_{38}N_4O$
Mw : 458.65 g.mol⁻¹

1,4-bis(3-(dimethylamino)propyl)-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[*b*]pyrazin-6-one (1). Following the general procedure E, starting from

¹⁹ Haak, E. *Eur. J. Org. Chem.* **2007**, 17, 2815-2824.

diphenylcyclopentanetrione (1.83 g, 6.9 mmol) and **3** (1.60 g, 6.9 mmol), ligand **1** was obtained as a dark purple powder (2.50 g, 79 %).

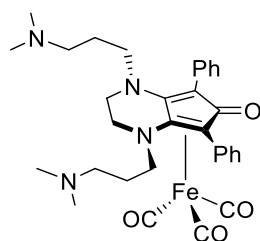
¹H-NMR (CDCl₃, 400 MHz) δ 7.31-7.23 (m, 8H), 7.19-7.15 (m, 2H), 3.38 (s, 4H), 3.24-3.20 (m, 4H), 2.04 (s, 12H), 1.73-1.69 (m, 4H), 1.54-1.47 (m, 4H) ppm. **¹³C-NMR (CDCl₃, 100 MHz)** δ 195.4, 149.5, 134.0, 131.4, 127.4, 125.8, 98.7, 56.4, 50.9, 48.3, 45.3, 24.3 ppm. **IR (neat)** ν 3289, 2938, 2812, 2783, 1651, 1582, 1523, 1492, 1464, 1456, 1429, 1371, 1349, 1302, 1275, 1215, 1197, 1156, 1140, 1110, 1040, 1017, 985, 944, 919, 889, 863, 836, 824, 806, 766, 757, 727, 968 cm⁻¹. **HRMS (m/z):** [M+H]⁺ calculated for C₂₉H₃₉N₄O: 459.3124; found: 459.3124.



1,4-bis(3-morpholinopropyl)-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one (2). Following the general procedure F, starting from diphenylcyclopentanetrione (1.47 g, 5.6 mmol) and **4** (1.75 g, 5.6 mmol), ligand **2** was obtained as a purple powder (2.66 g, 88 %). **¹H-NMR (CDCl₃, 400 MHz)** δ 7.31-7.22 (m, 8H), 7.18-7.14 (m, 2H), 3.59 (t, *J* = 4.4 Hz, 8H), 3.39 (s, 4H), 3.26 (t, *J* = 7.8 Hz, 4H), 2.17 (s, 8H), 1.81 (t, *J* = 7.2 Hz, 4H), 1.58-1.49 (m, 4H) ppm. **¹³C-NMR (CDCl₃, 100 MHz)** δ 195.3, 149.5, 133.9, 131.3, 127.4, 125.8, 98.7, 66.9, 55.7, 53.5, 51.1, 48.3, 23.2 ppm. **IR (neat)** ν 3291, 2938, 2874, 2811, 2766, 2325, 2111, 1794, 1651, 1603, 1523, 1466, 1434, 1377, 1361, 1303, 1276, 1240, 1214, 1169, 1147, 1129, 1112, 1071, 1039, 1017, 985, 919, 888, 863, 798, 784, 762 cm⁻¹. **HRMS (m/z):** [M+H]⁺ calculated for C₃₃H₄₃N₄O₃: 543.3335; found: 543.3333.

General procedure F: In a dried Schlenk tube under argon, the cyclopentadienone derivative (1 equiv.) and Fe₂(CO)₉ (2 equiv.) were introduced in dry and degassed toluene (C = 0.3 M). The reaction mixture was stirred overnight at 110°C. The resulting mixture was cooling down to room temperature and purified on neutral alumina oxide column chromatography

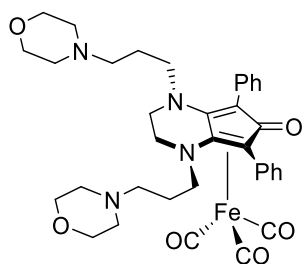
surrounded by a pad of Celite® (eluent: CH₂Cl₂ to CH₂Cl₂/MeOH [98:2]). Precipitation on diethylether/pentane (1:1) and filtration under vacuum furnish the pure product.



C₃₂H₃₈FeN₄O₄
Mw : 598.53 g.mol⁻¹

Iron complex (Fe6). Following the general procedure F, starting from cyclopentadienone ligand **1** (1.0 g, 2.2 mmol) and Fe₂(CO)₉ (1.59 g, 4.4 mmol), iron complex **Fe6** was obtained as a yellow powder (625 mg, 48 %).

¹H-NMR (CDCl₃, 400 MHz) δ 7.53 (d, *J* = 7.1 Hz, 4H), 7.41-7.28 (m, 6H), 3.56-3.50 (m, 2H), 2.96-2.84 (m, 4H), 2.40-2.31 (m, 2H), 2.09 (s, 12H), 1.81-1.69 (m, 4H), 1.55-1.52 (m, 2H), 1.41-1.36 (m, 2H) ppm. ¹³C-NMR (CDCl₃, 100 MHz) δ 210.2, 166.0, 132.2, 132.1, 128.4, 127.9, 114.4, 71.0, 56.5, 50.8, 47.2, 45.4, 25.5 ppm. IR (neat) ν 2815, 2775, 2724, 2032, 1961, 1919, 1628, 1608, 1578, 1526, 1493, 1455, 1439, 1357, 1317, 1287, 1168, 1154, 1097, 1071, 1040, 950, 890, 853, 821, 749, 731, 698 cm⁻¹. HRMS (*m/z*): [M+H]⁺ calculated for C₃₂H₃₉N₄O₄Fe: 599.2321; found: 599.2322. Anal. Calcd. for C₃₂H₃₉N₄O₄Fe: C, 64.22; N, 9.24; H, 6.40. Found: C, 63.87; N, 9.24; H, 6.54.



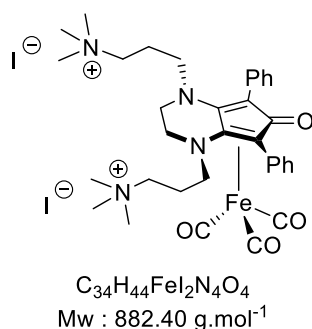
C₃₆H₄₂FeN₄O₆
Mw : 682.60 g.mol⁻¹

Iron complex (Fe7). Following the general procedure F, starting from cyclopentadienone ligand **2** (300 mg, 0.55 mmol) and Fe₂(CO)₉ (402 mg, 1.1 mmol), iron complex **Fe7** was obtained as a yellow powder (285 mg, 76 %).

¹H-NMR (CDCl₃, 400 MHz) δ 7.53 (d, *J* = 7.1 Hz, 4H), 7.40-7.31 (m, 6H), 3.60 (t, *J* = 4.2 Hz, 8H), 3.53-3.48 (m, 2H), 2.96-2.87 (m, 4H), 2.41-2.30 (m, 2H), 2.30-2.14 (m, 8H), 1.92-1.76 (m, 4H),

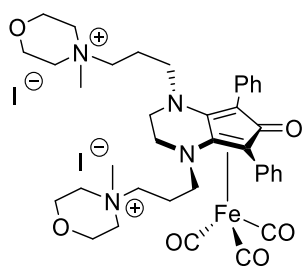
1.60-1.48 (m, 2H), 1.48-1.35 (m, 2H) ppm. $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ 210.1, 165.9, 132.1, 132.1, 128.4, 127.9, 114.4, 70.9, 66.9, 55.7, 53.6, 51.2, 47.2, 24.3 ppm. **IR (neat)** ν 2951, 2888, 2805, 2326, 2025, 1967, 1946, 1619, 1560, 1493, 1469, 1445, 1363, 1316, 1304, 1282, 1180, 1146, 1114, 1070, 1024, 1004, 969, 948, 917, 879, 856, 801, 758, 728, 703 cm^{-1} . **HRMS (m/z):** $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{43}\text{N}_4\text{O}_6\text{Fe}$: 683.2532; found: 683.2529. Analysis of **Fe3d** CIF file (see below) showed that 1 molecule of water crystallized with 4 molecules of complex. Anal. Calcd. for $\text{C}_{36}\text{H}_{43}\text{N}_4\text{O}_6\text{Fe} \cdot (\text{H}_2\text{O})_{0.25}$: C, 62.93; N, 8.15; H, 6.23. Found: C, 63.10; N, 8.35; H, 6.41.

General procedure G: In a two necked round bottom flask under argon atmosphere, the corresponding iron complex (**Fe6** or **Fe7**, 1 equiv.) was introduced in dry dichloromethane ($\text{C} = 0.3 \text{ mL}$). Methyl iodide (2-3 equiv.) was added dropwise and the resulting mixture was stirred overnight at room temperature. The solvent was partially removed and a mixture of pentane/ Et_2O (50:50) was added resulting in precipitation. Filtration afforded the pure cationic complex.



Water-soluble iron complex (Fe4). Following the general procedure G, starting from iron complex **Fe6** (100 mg, 0.17 mmol) and iodomethane (33 μL , 51 mmol), **Fe4** was obtained as a yellow powder (144 mg, 98 %).

$^1\text{H-NMR}$ (D_2O , 600 MHz) δ 7.64 (d, $J = 6.4 \text{ Hz}$, 4H), 7.56-7.52 (m, 6H), 3.56-3.54 (m, 2H), 3.05-3.03 (m, 2H), 2.94 (s, 18H), 2.90-2.85 (m, 2H), 2.74-2.69 (m, 2H), 2.65 (ddd, $J = 13.9, 9.3, 4.9 \text{ Hz}$, 2H), 2.53 (td, $J = 12.5, 4.4 \text{ Hz}$, 2H), 1.90-1.81 (m, 2H), 1.71-1.57 (s br, 2H) ppm. $^{13}\text{C-NMR}$ (D_2O , 151 MHz) δ 161.3, 132.6, 130.5, 129.1, 129.0, 114.2, 72.0, 63.5, 52.9, 48.8, 46.7, 20.8 ppm (CO ligands signal missing). **IR (neat)** ν 3010, 2804, 2038, 1955, 1615, 1538, 1490, 1474, 1456, 1439, 1365, 1304, 1287, 1264, 1206, 1175, 1142, 1106, 1075, 1053, 1002, 965, 917, 870, 813, 797, 779, 757, 729, 703, 657 cm^{-1} . **HRMS (m/z):** $[\text{M}]^{2+}$ calculated for $\text{C}_{34}\text{H}_{44}\text{FeN}_4\text{O}_4$: 314.1356; found: 314.1350.



$C_{38}H_{48}FeI_2N_4O_6$
 Mw : 966.48 g.mol⁻¹

Water-soluble iron complex (Fe5). Following the general procedure H, starting from iron complex **Fe7** (100 mg, 0.15 mmol) and iodomethane (27 μ L, 0.45 mmol), **Fe5** was obtained as a yellow powder (145 mg, 100 %).

¹H-NMR (D₂O, 600 MHz) δ 7.67 (d, J = 6.4 Hz, 4H), 7.56-7.53 (m, 6H), 3.97-3.95 (m, 4H), 3.91-3.89 (m, 2H), 3.56 (d, J = 6.0 Hz, 2H), 3.31-3.24 (m, 8H), 3.05-3.00 (m, 2H), 3.00 (s, 6H), 2.95-2.90 (m, 2H), 2.86 (td, J = 12.6, 4.4 Hz, 2H), 2.73-2.67 (m, 4H), 1.92-1.81 (m, 2H), 1.73-1.61 (s *br*, 1H) ppm. **¹³C-NMR (D₂O, 151 MHz)** δ 161.4, 132.7, 130.6, 129.1, 129.1, 114.2, 71.9, 60.2, 60.2, 59.6, 59.6, 48.8, 46.7, 19.4 ppm (CO ligands signal missing). **IR (neat)** ν 2873, 2034, 1957, 1621, 1533, 1495, 1452, 1441, 1362, 1260, 1203, 1119, 1074, 1018, 964, 922, 904, 876, 849, 759, 731, 705, 625, 615, 586, 554, 528 cm⁻¹. **HRMS (m/z):** [M]²⁺ calculated for C₃₈H₄₈N₄O₆Fe: 356.1462; found: 356.1468.

Part 3: Copies of NMR spectra.

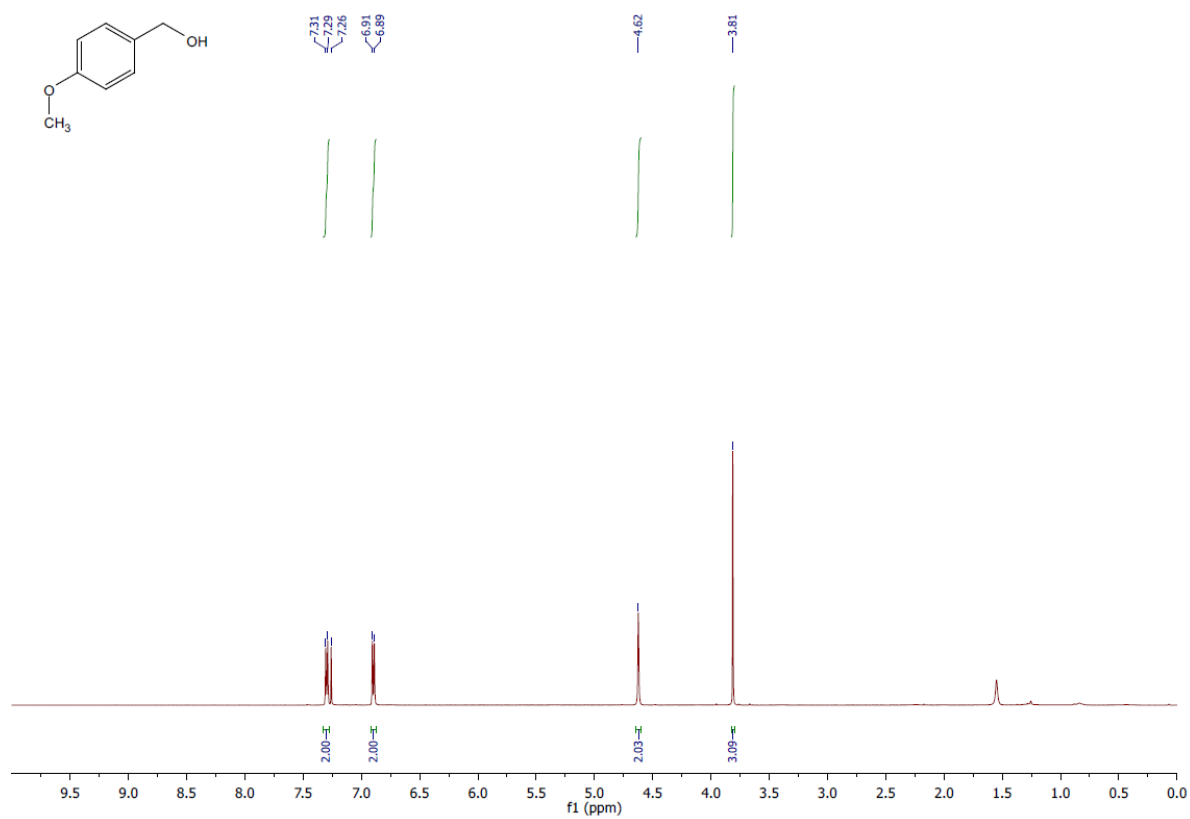


Figure S1. ¹H-NMR spectrum of alcohol 4a.

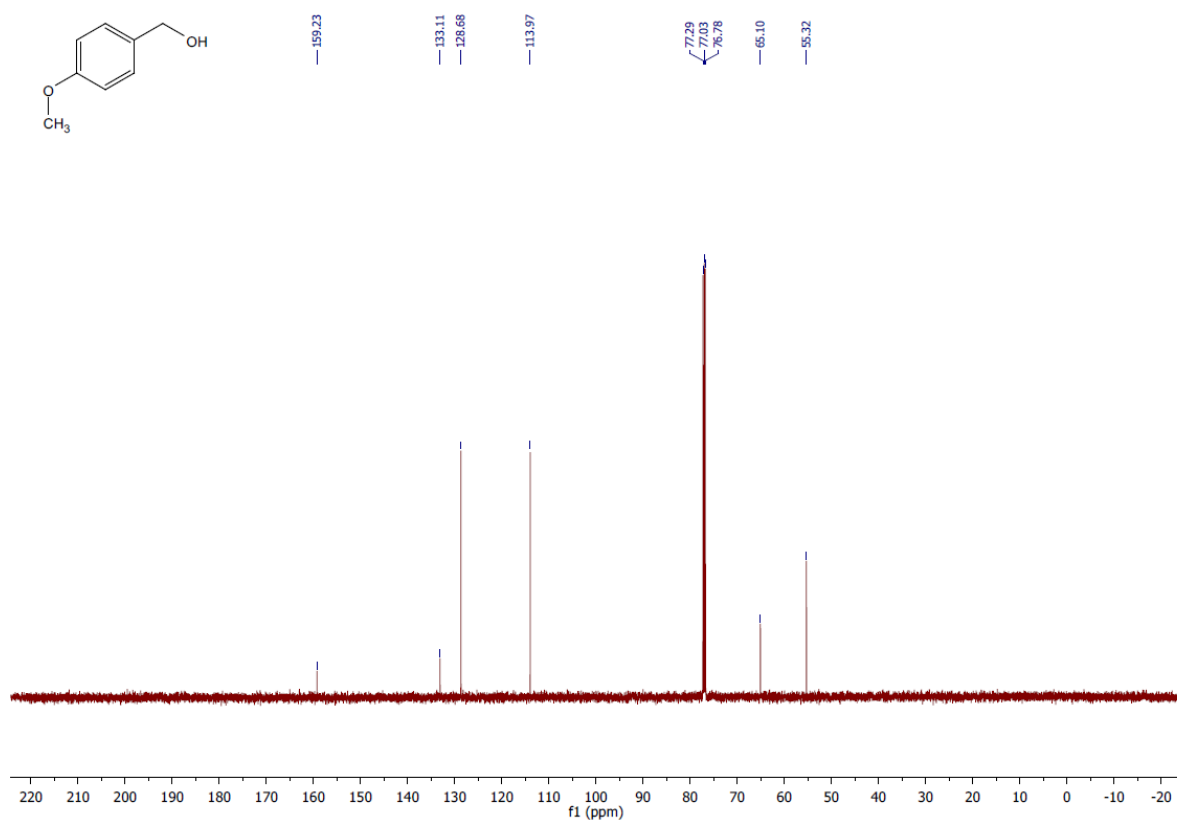


Figure S2. ¹³C-NMR spectrum of alcohol 4a.

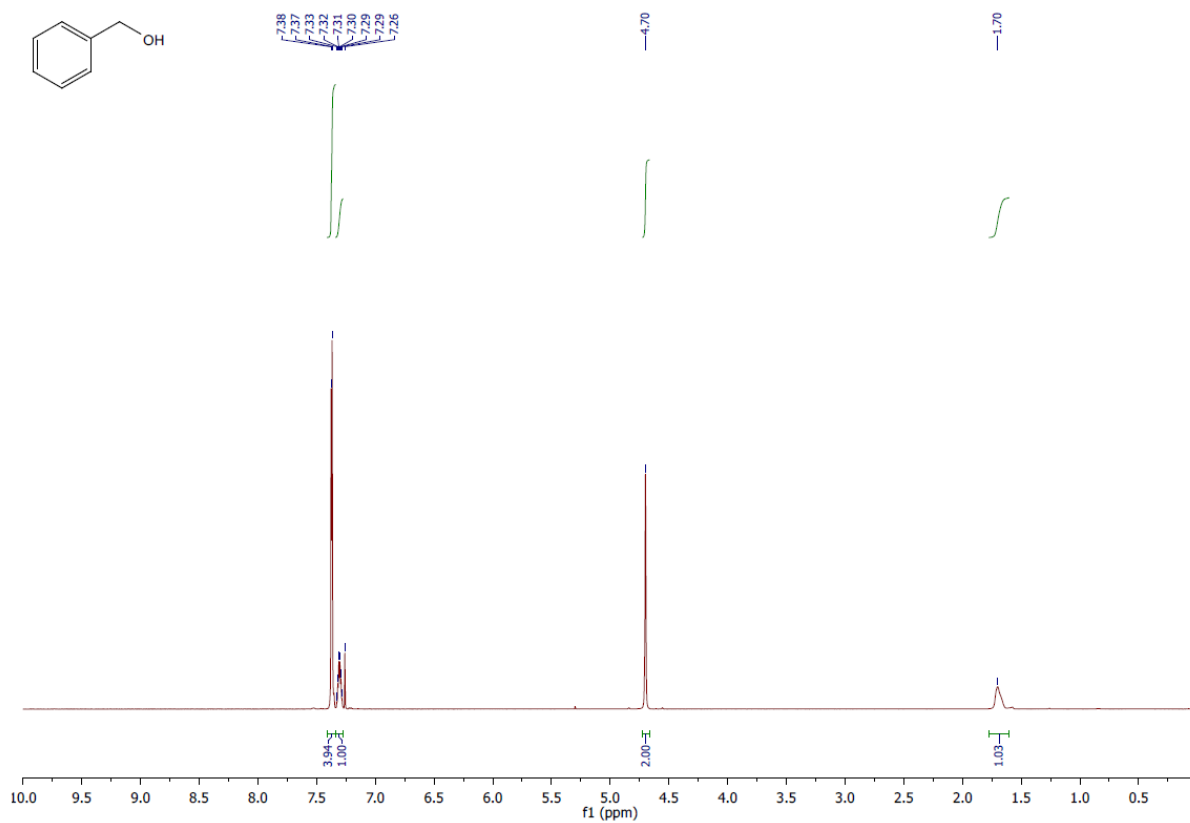


Figure S3. $^1\text{H-NMR}$ spectrum of alcohol **4b**.

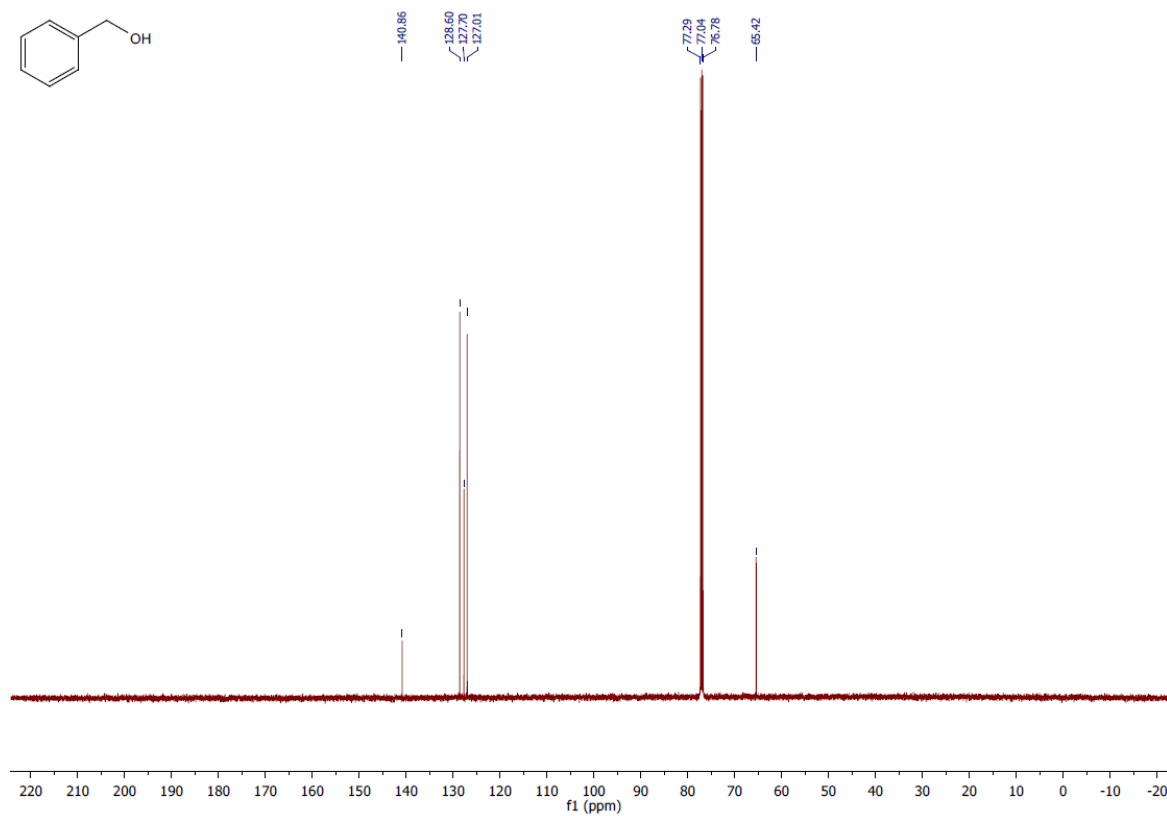


Figure S4. $^{13}\text{C-NMR}$ spectrum of alcohol **4b**.

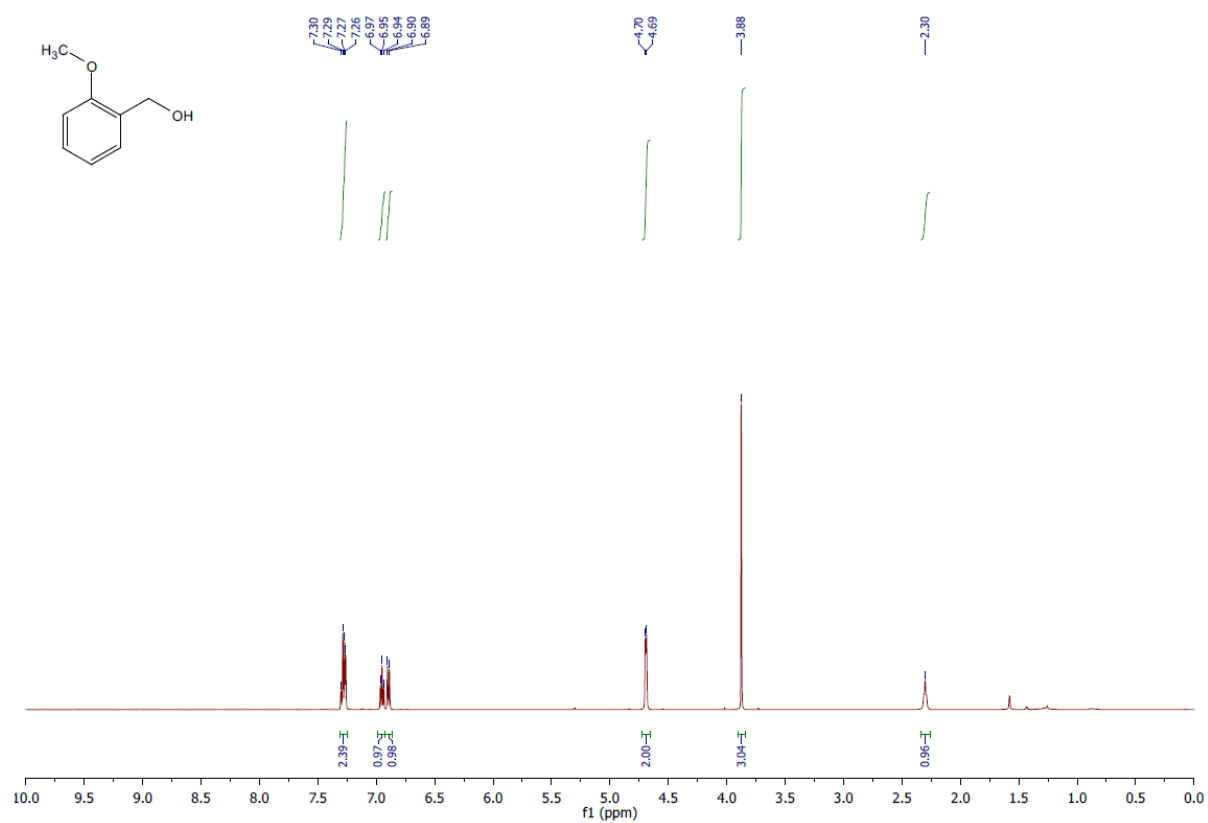


Figure S5. ¹H-NMR spectrum of alcohol **4c**.

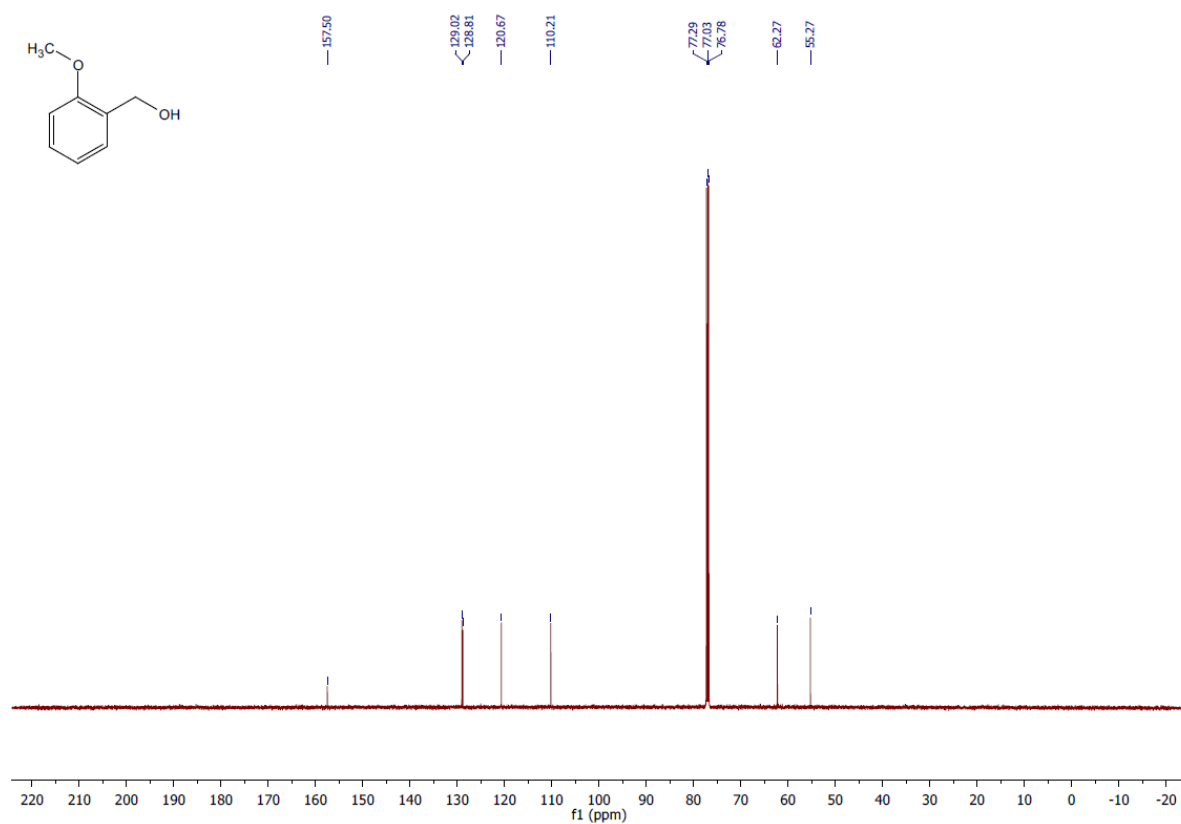


Figure S6. ¹³C-NMR spectrum of alcohol **4c**.

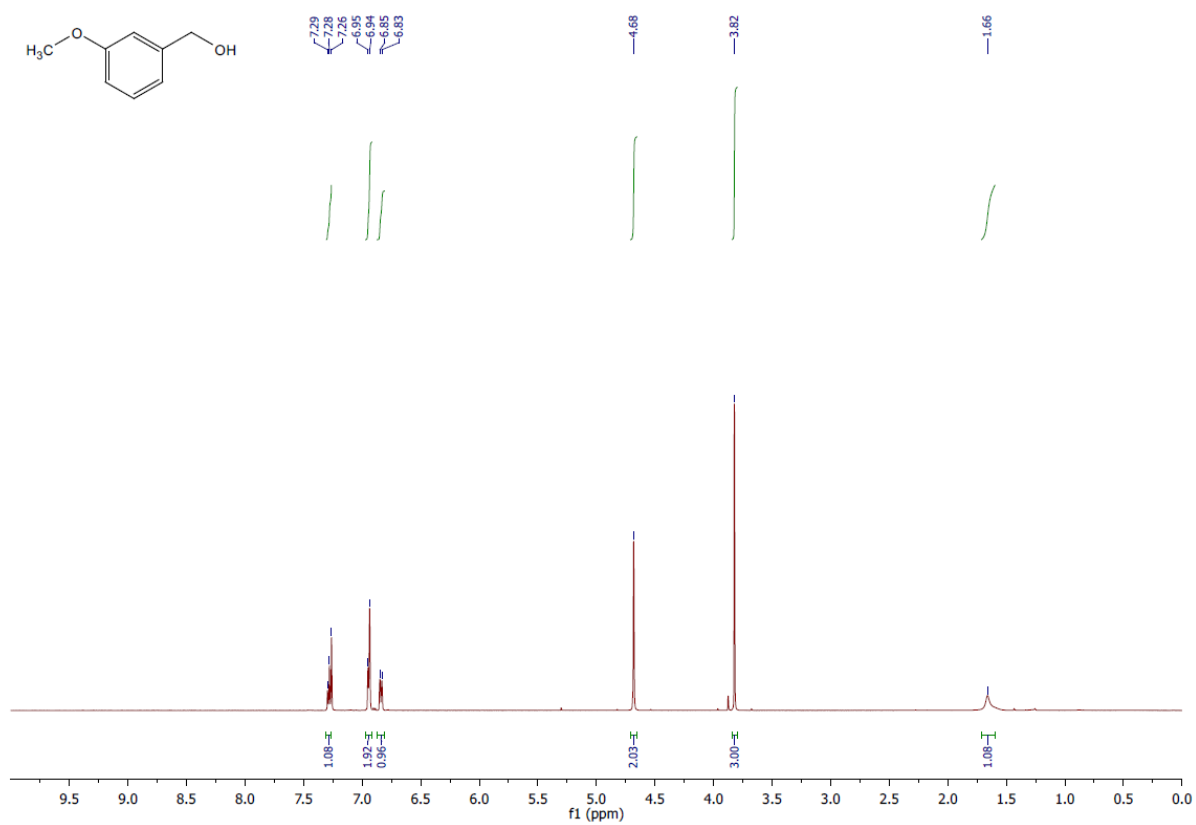


Figure S7. ¹H-NMR spectrum of alcohol 4d.

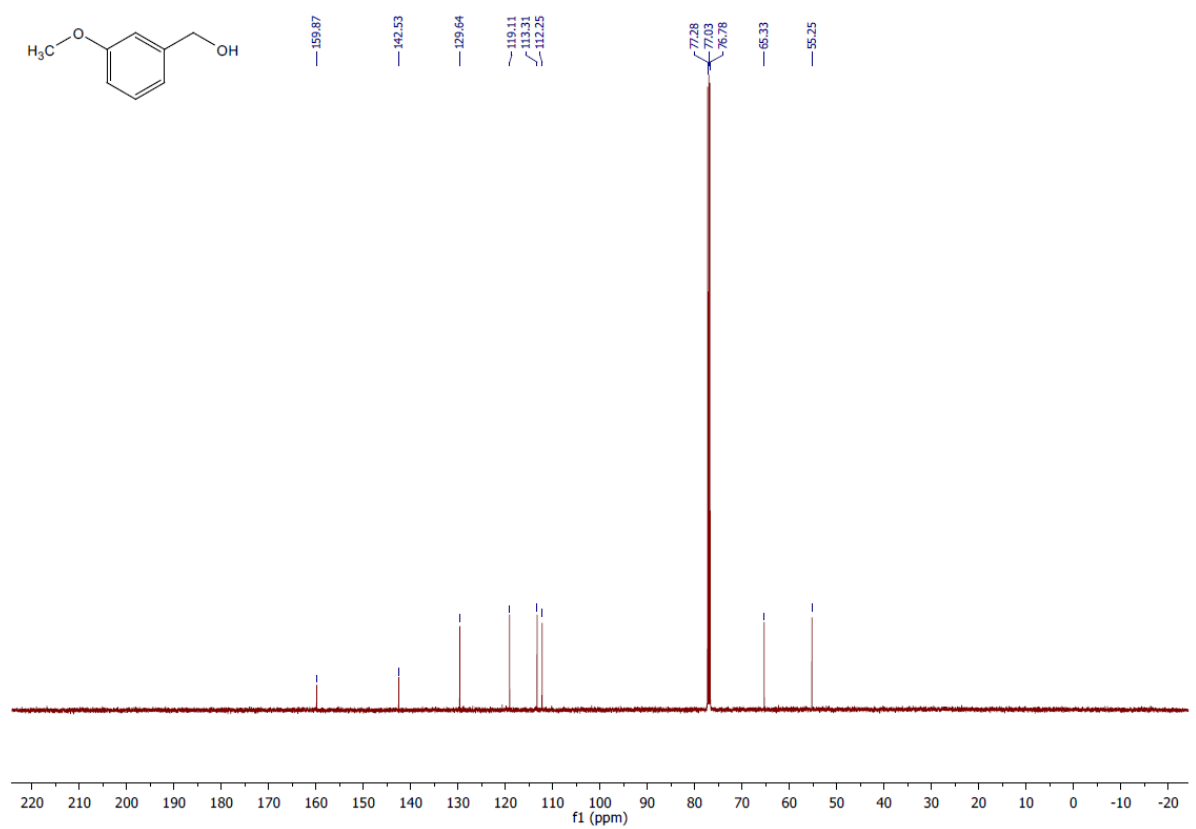


Figure S8. ¹³C-NMR spectrum of alcohol 4d.

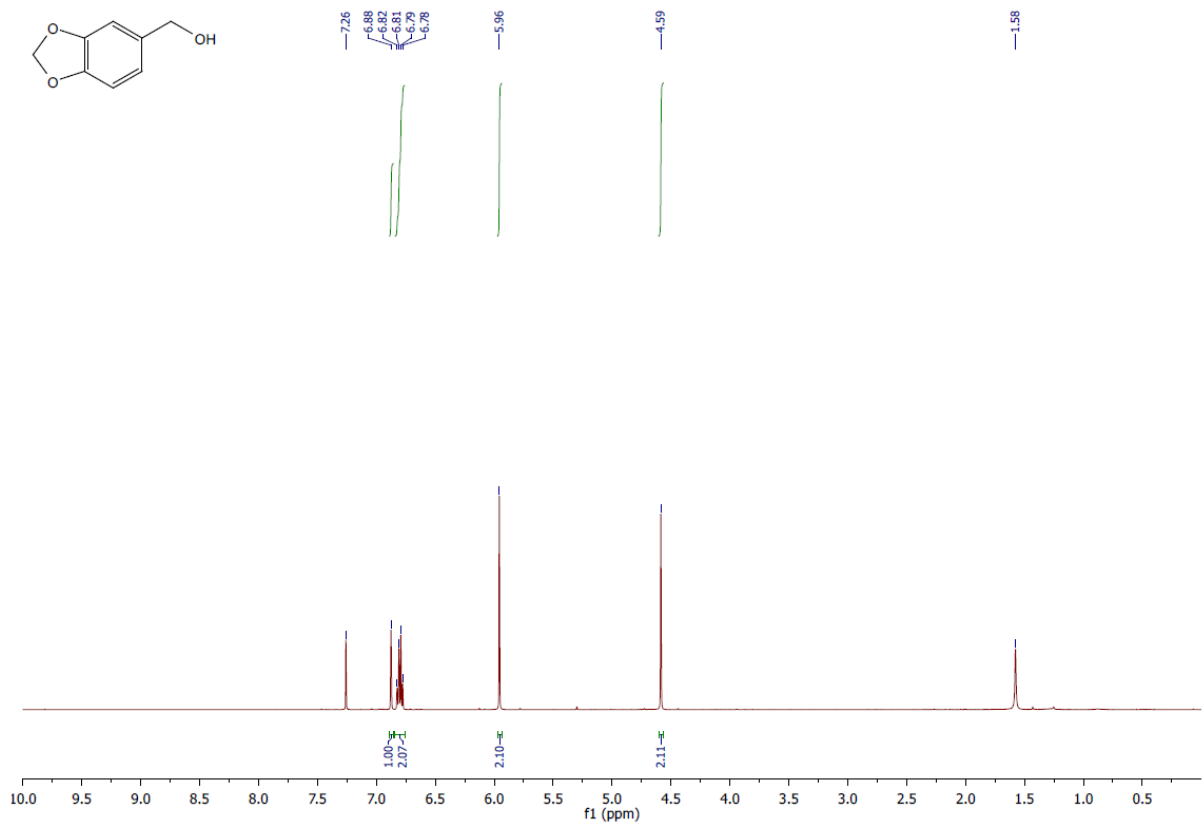


Figure S9. ¹H-NMR spectrum of alcohol 4e.

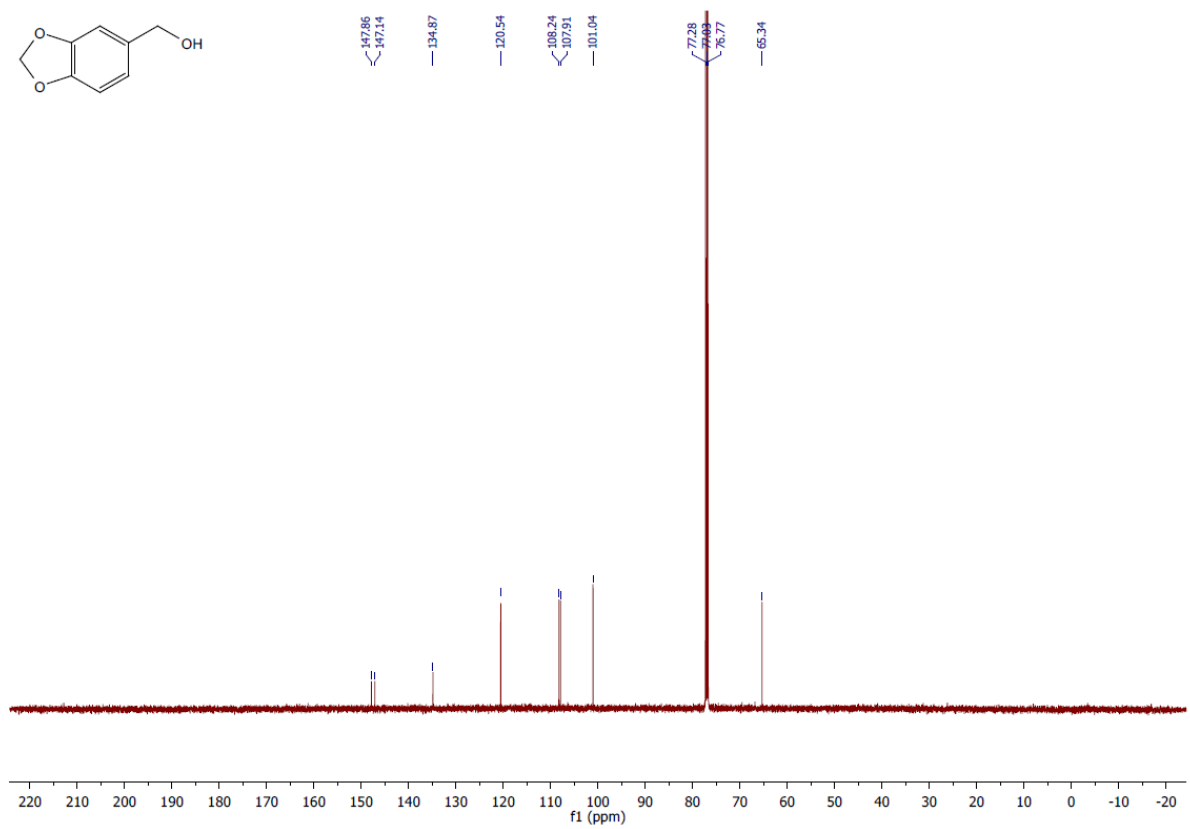


Figure S10. ¹³C-NMR spectrum of alcohol 4e.

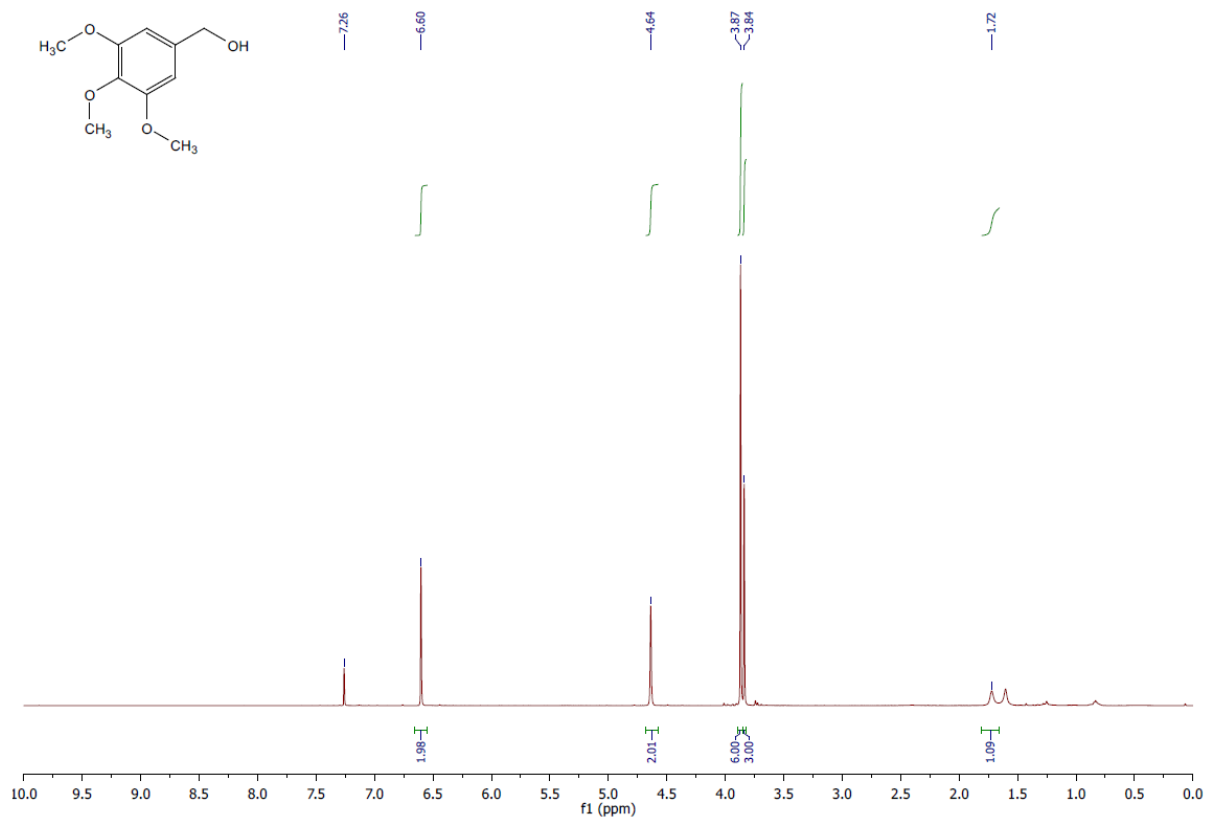


Figure S11. ¹H-NMR spectrum of alcohol 4f.

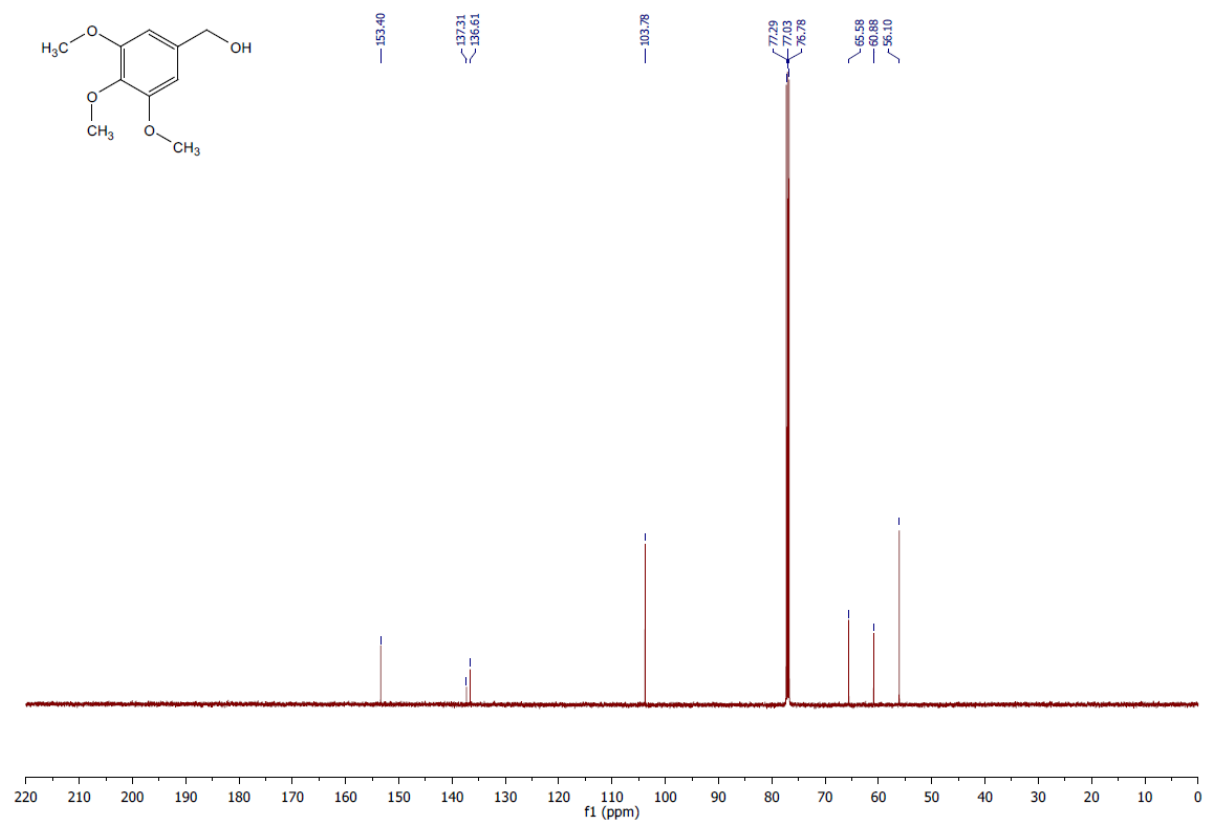


Figure S12. ¹³C-NMR spectrum of alcohol 4f.

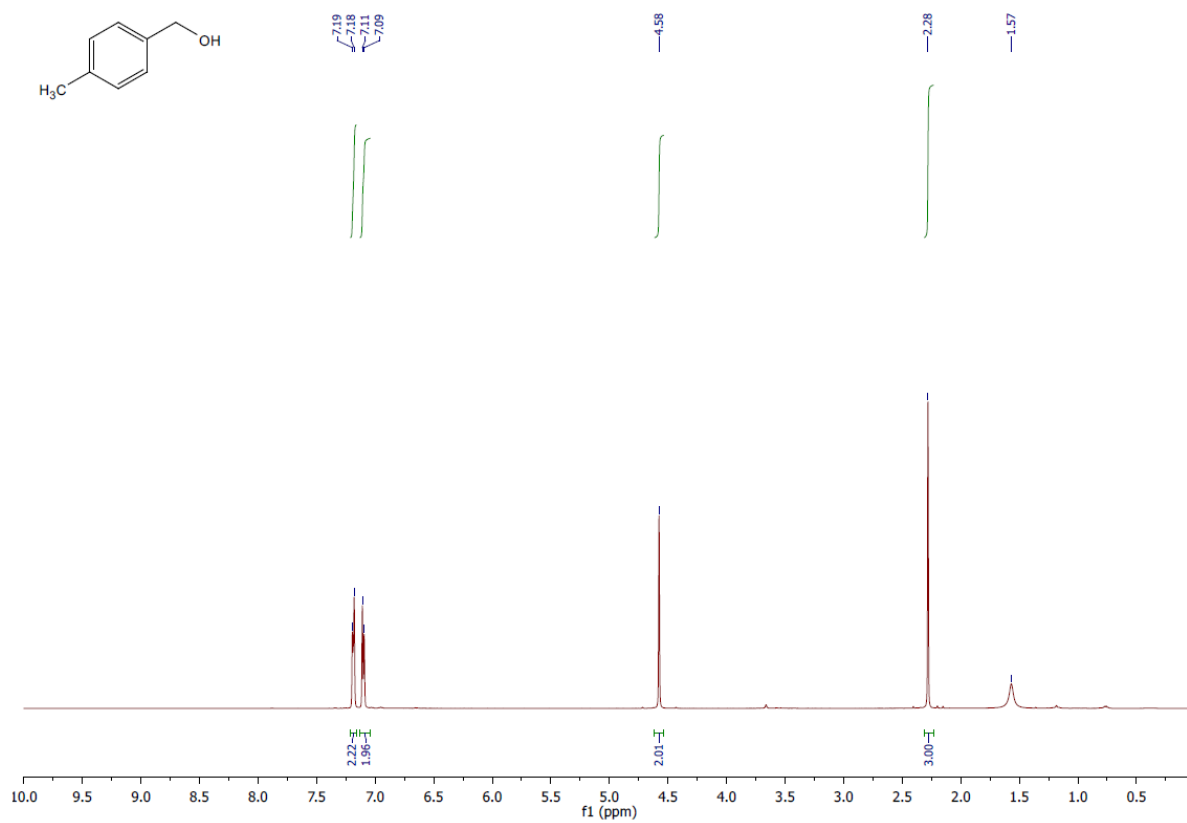


Figure S13. ¹H-NMR spectrum of alcohol **4g**.

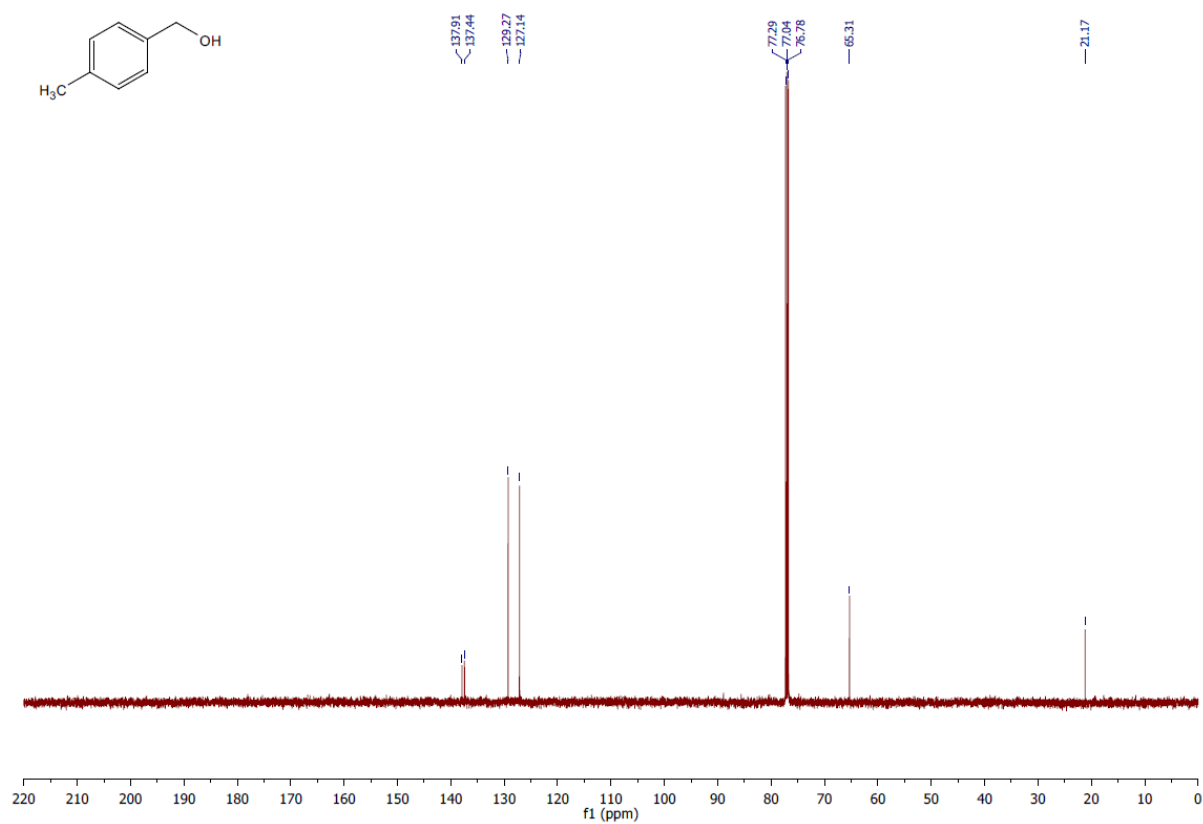


Figure S14. ¹³C-NMR spectrum of alcohol **4g**.

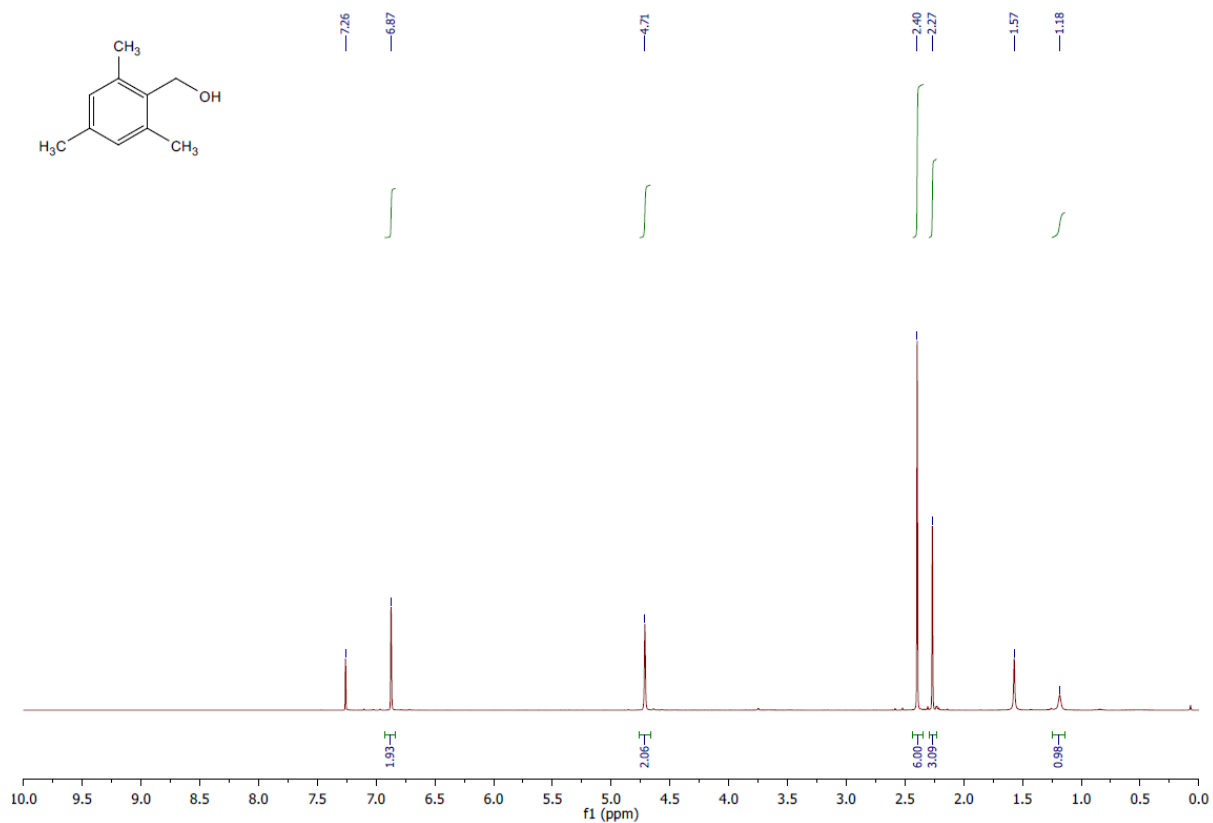


Figure S15. ¹H-NMR spectrum of alcohol 4h.

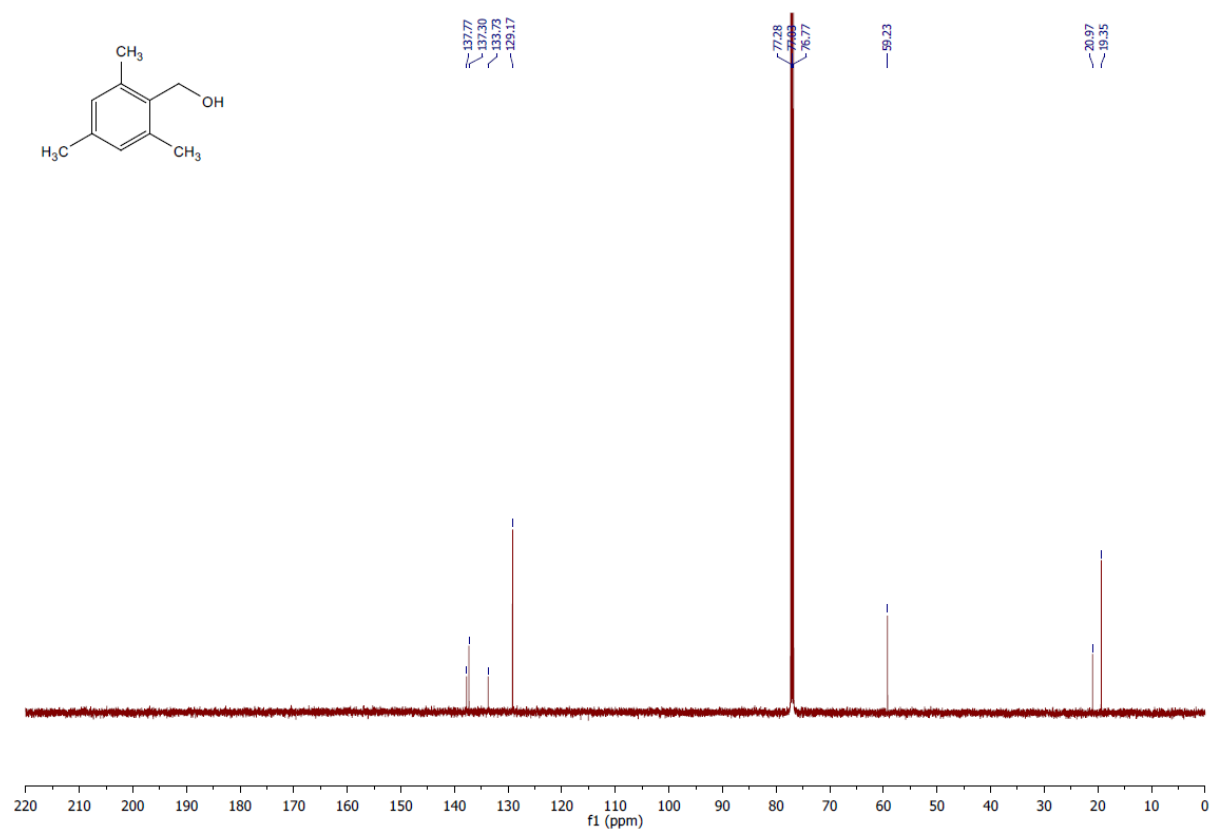


Figure S16. ¹³C-NMR spectrum of alcohol 4h.

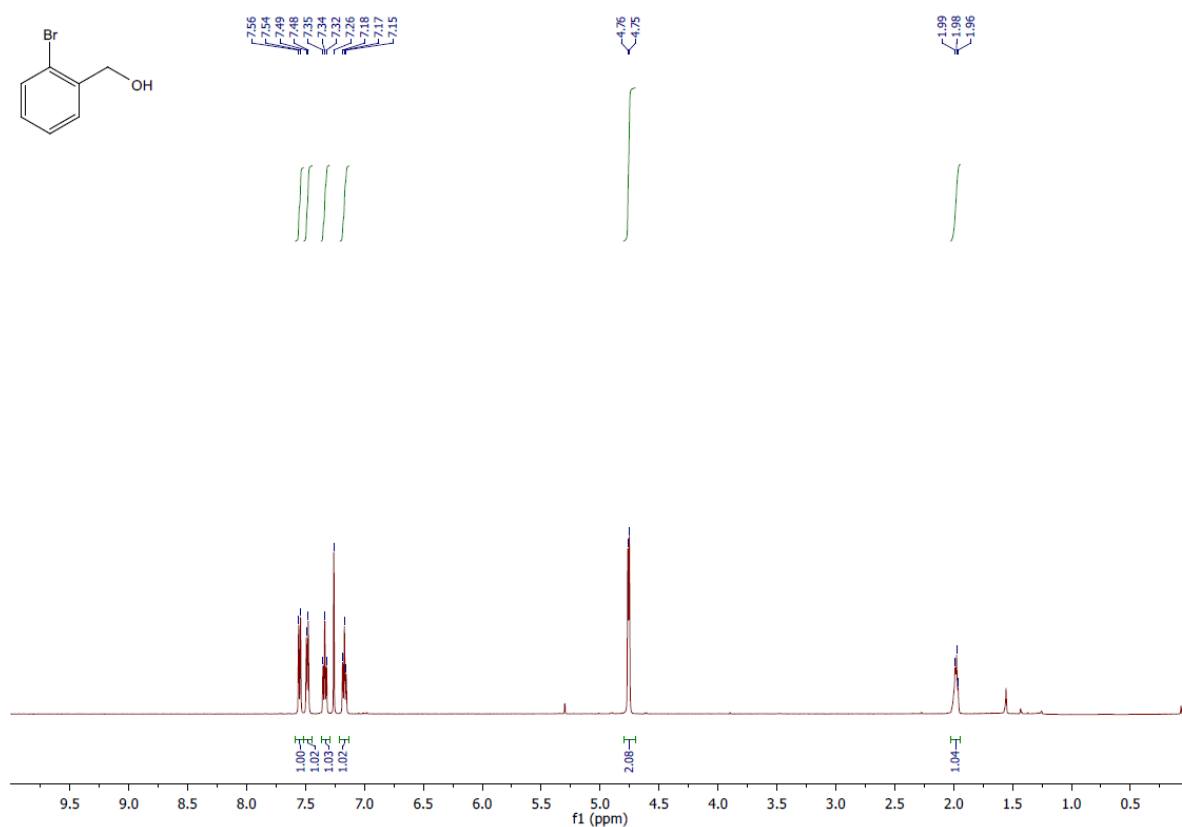


Figure S17. ¹H-NMR spectrum of alcohol **4i**.

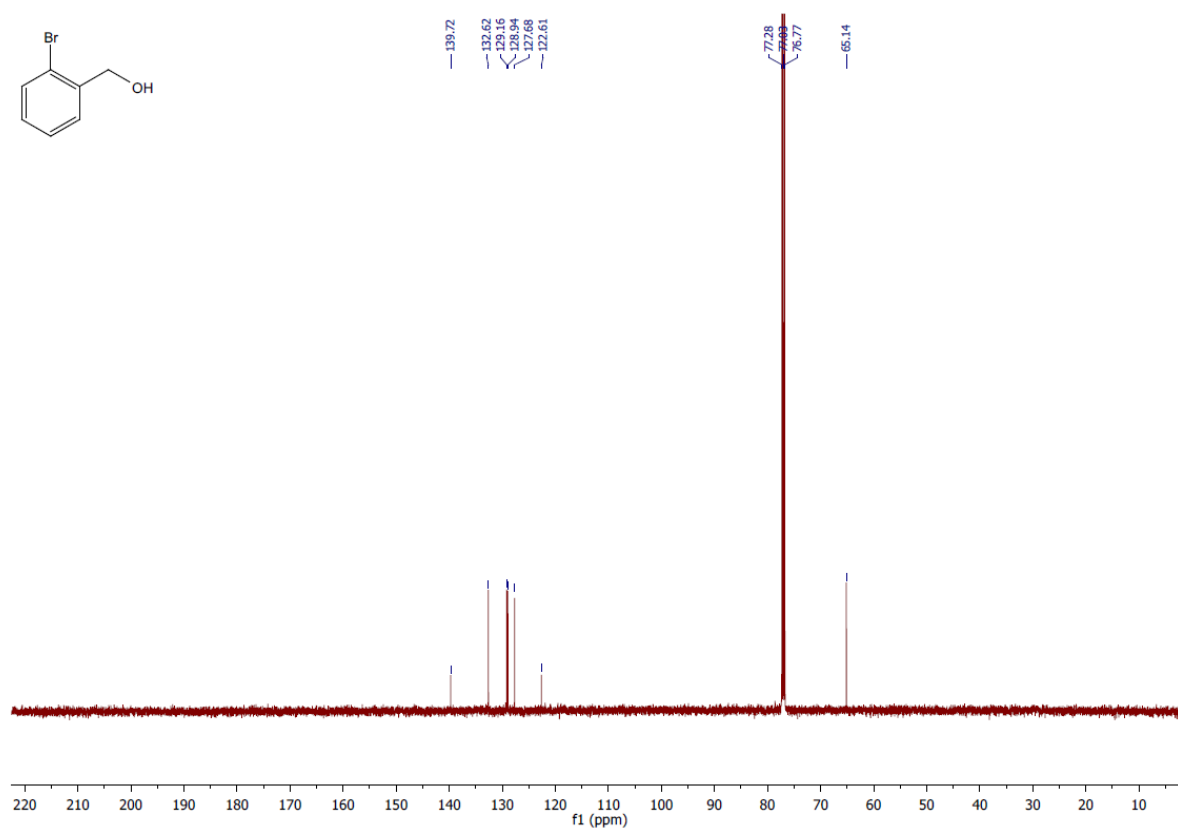


Figure S18. ¹³C-NMR spectrum of alcohol **4i**.

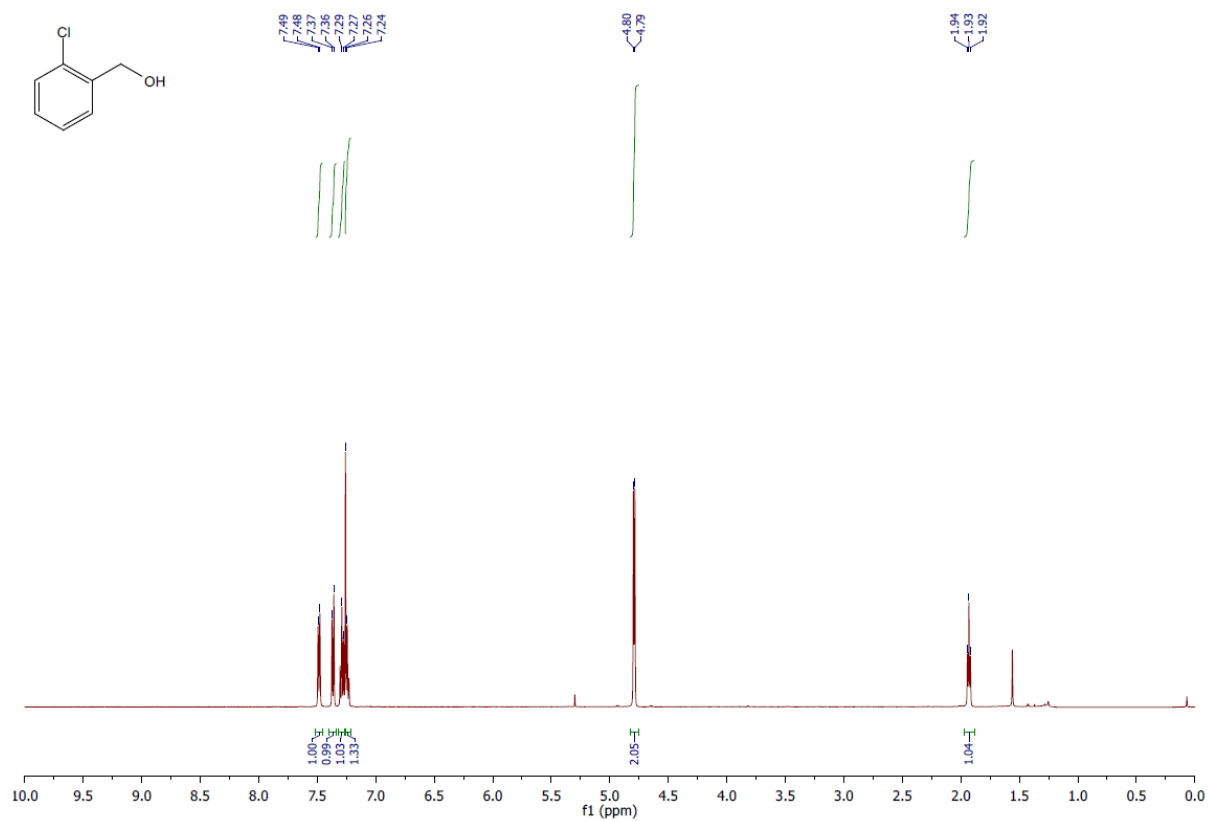


Figure S19. ¹H-NMR spectrum of alcohol **4j**.

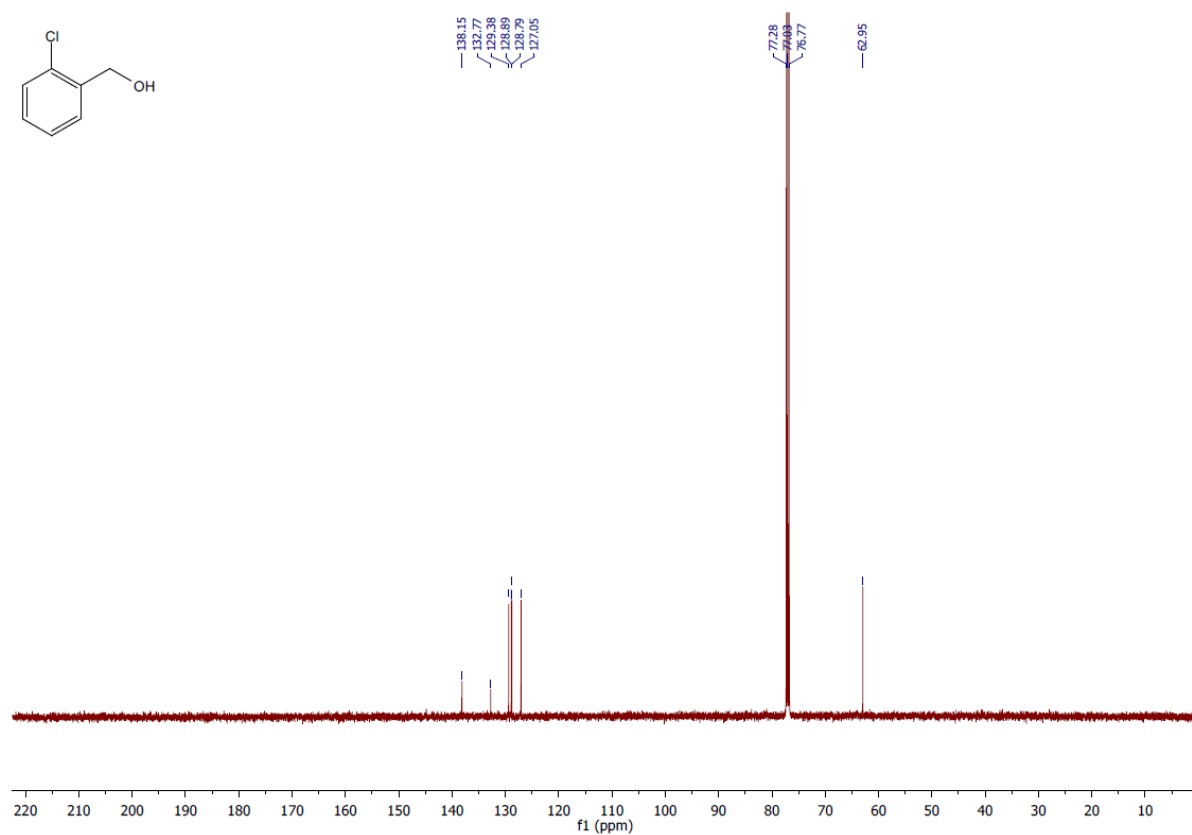


Figure S20. ¹³C-NMR spectrum of alcohol **4j**.

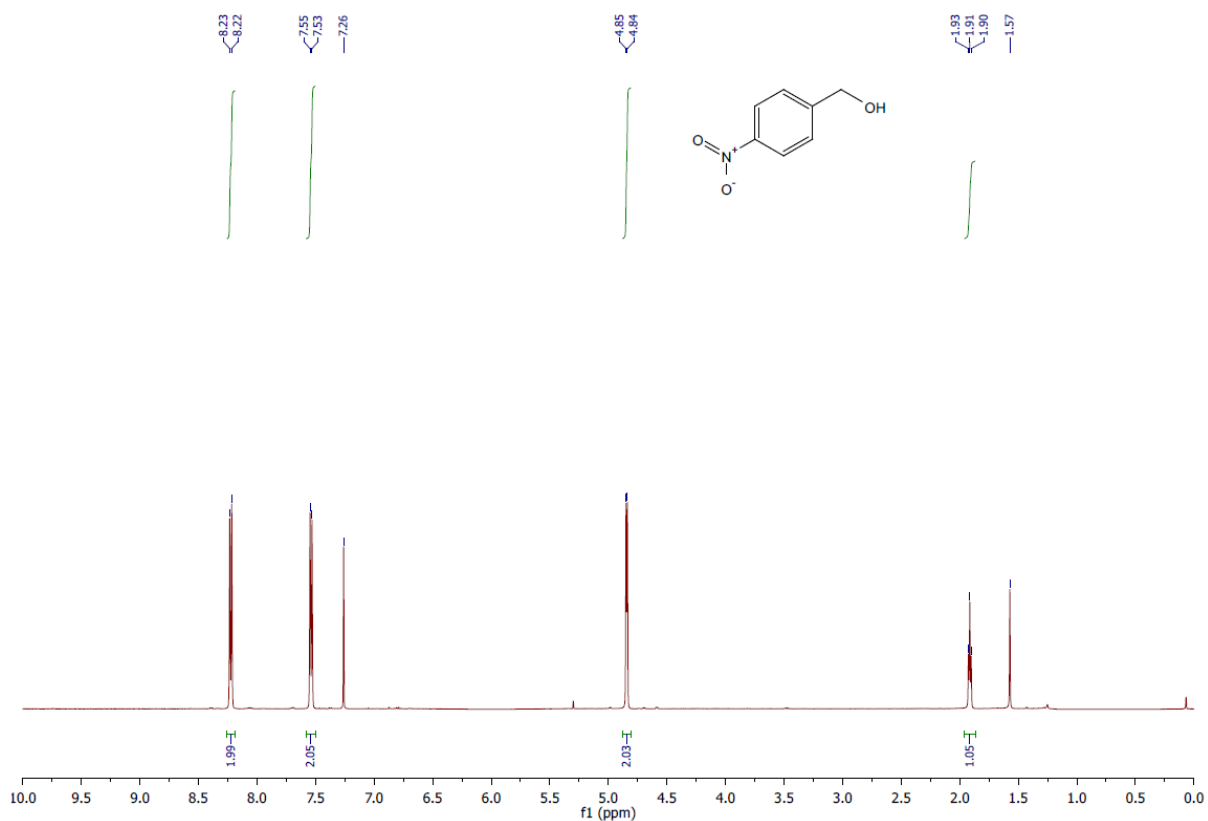


Figure S21. ¹H-NMR spectrum of alcohol 4k.

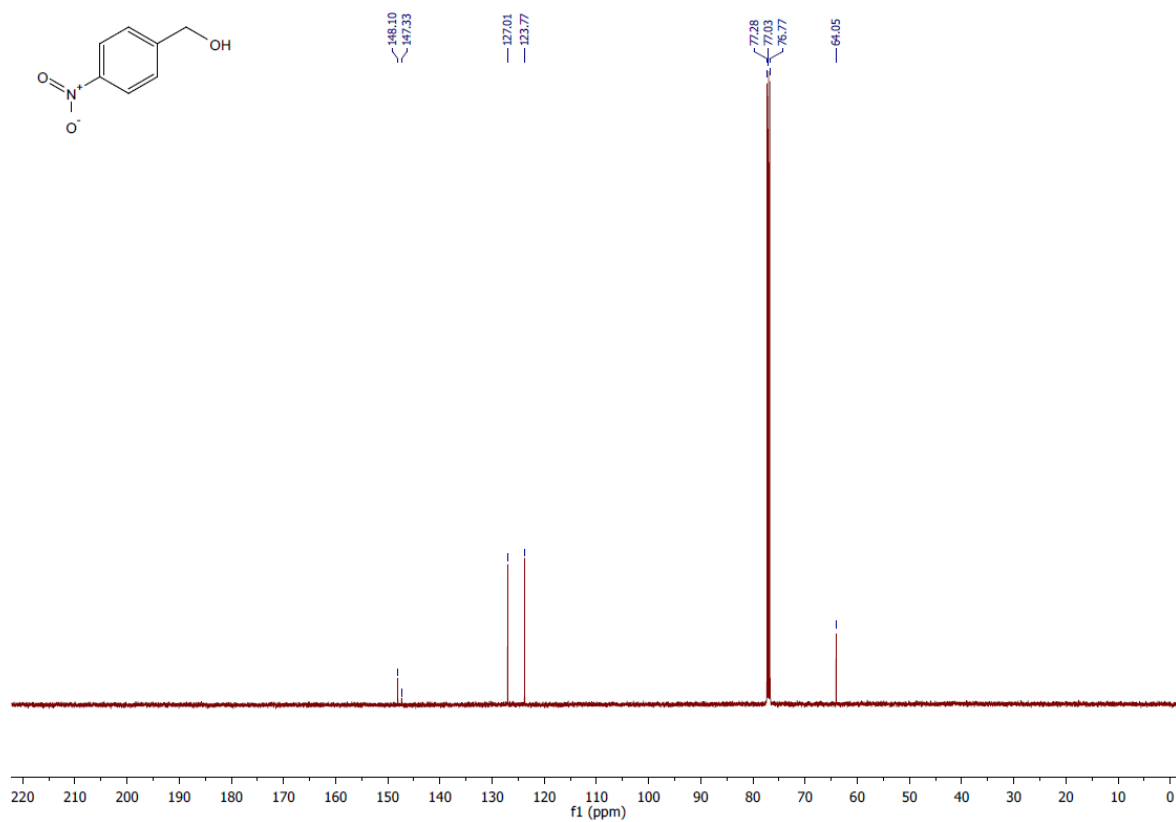


Figure S22. ¹³C-NMR spectrum of alcohol 4k.

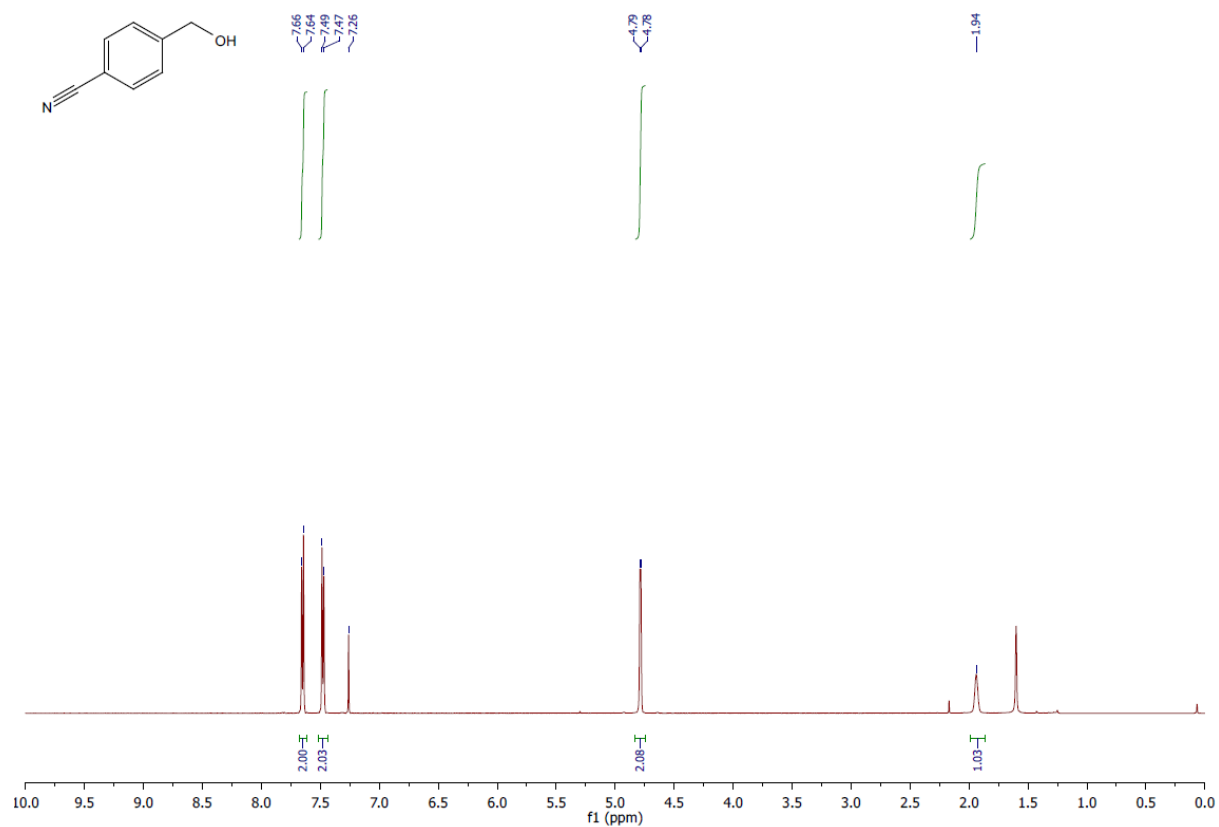


Figure S23. ¹H-NMR spectrum of alcohol 4I.

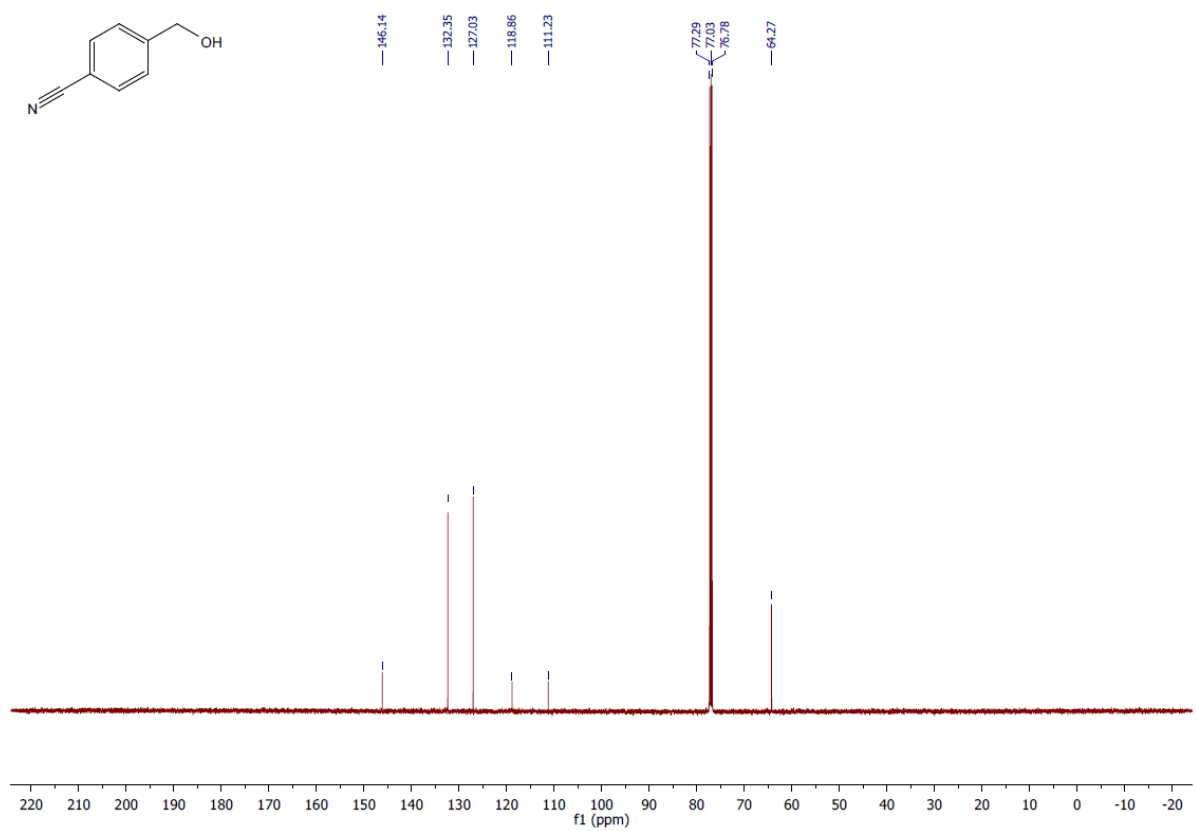


Figure S24. ¹³C-NMR spectrum of alcohol 4I.

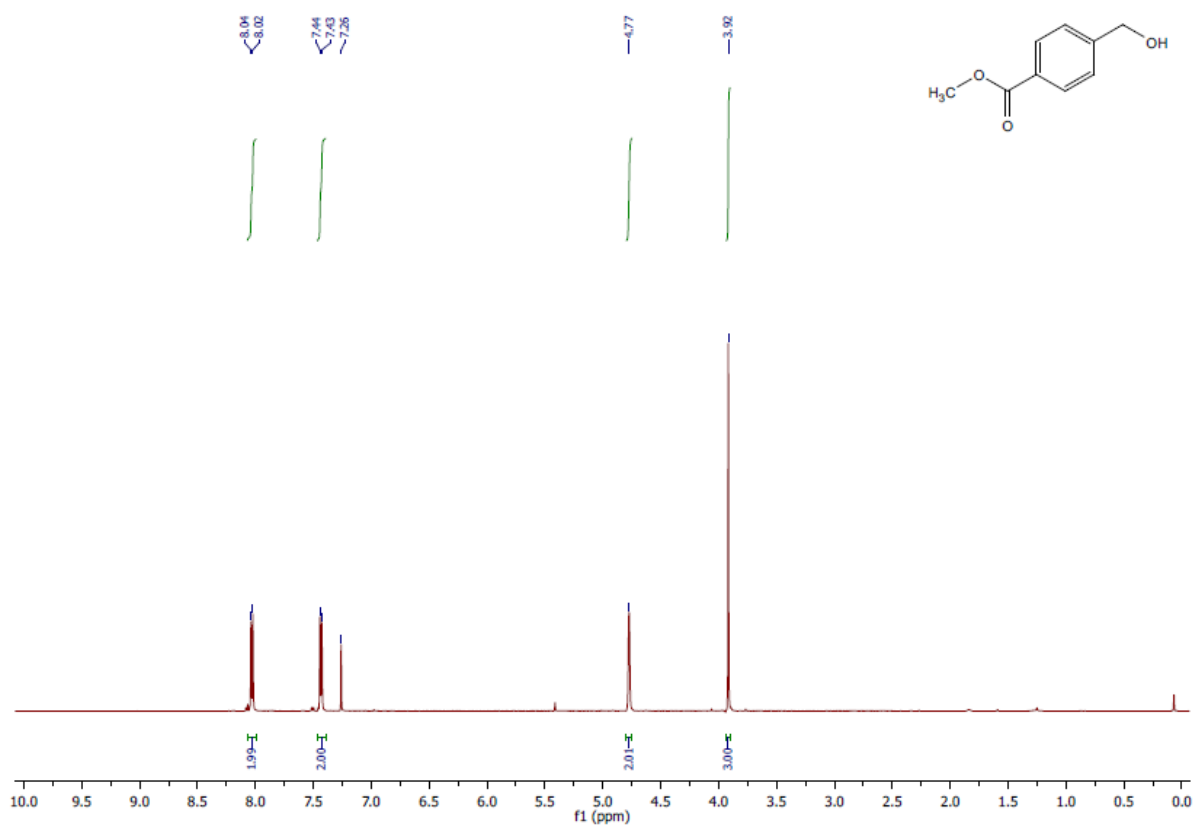


Figure S25. ¹H-NMR spectrum of alcohol 4m.

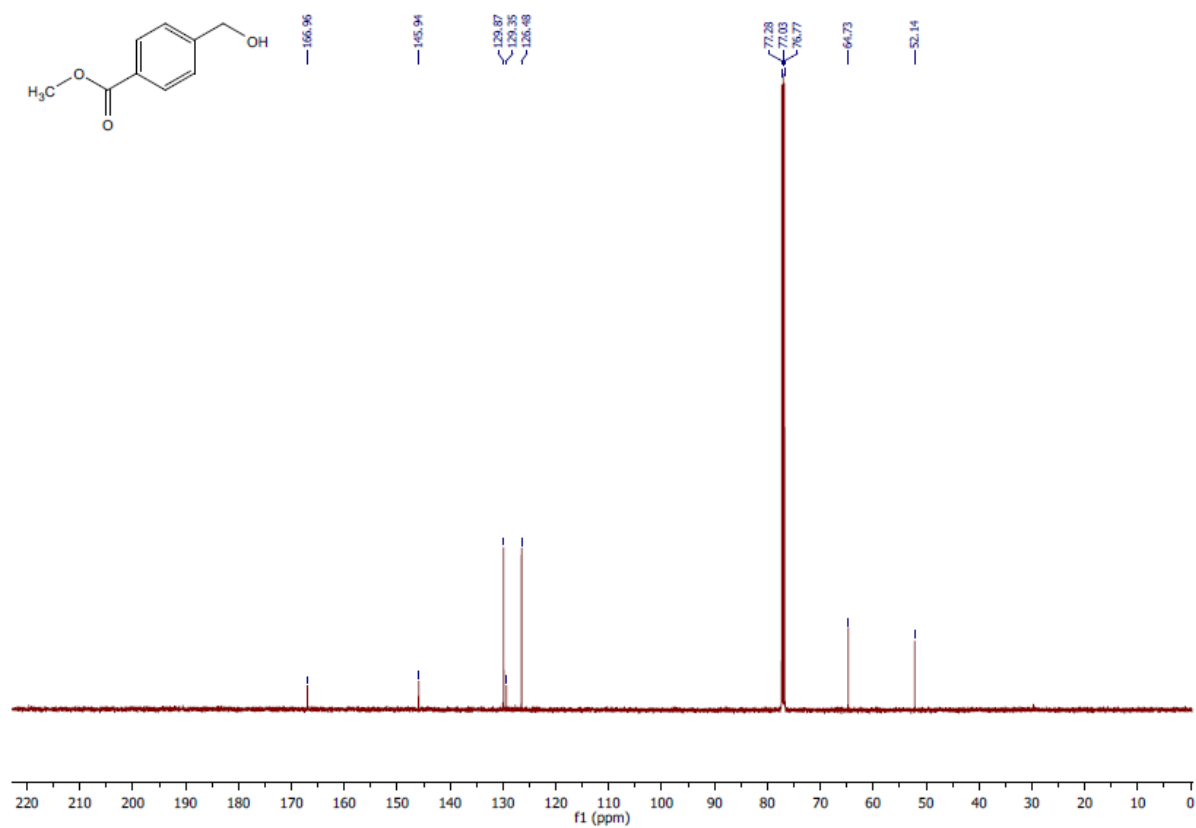


Figure S26. ¹³C-NMR spectrum of alcohol 4m.

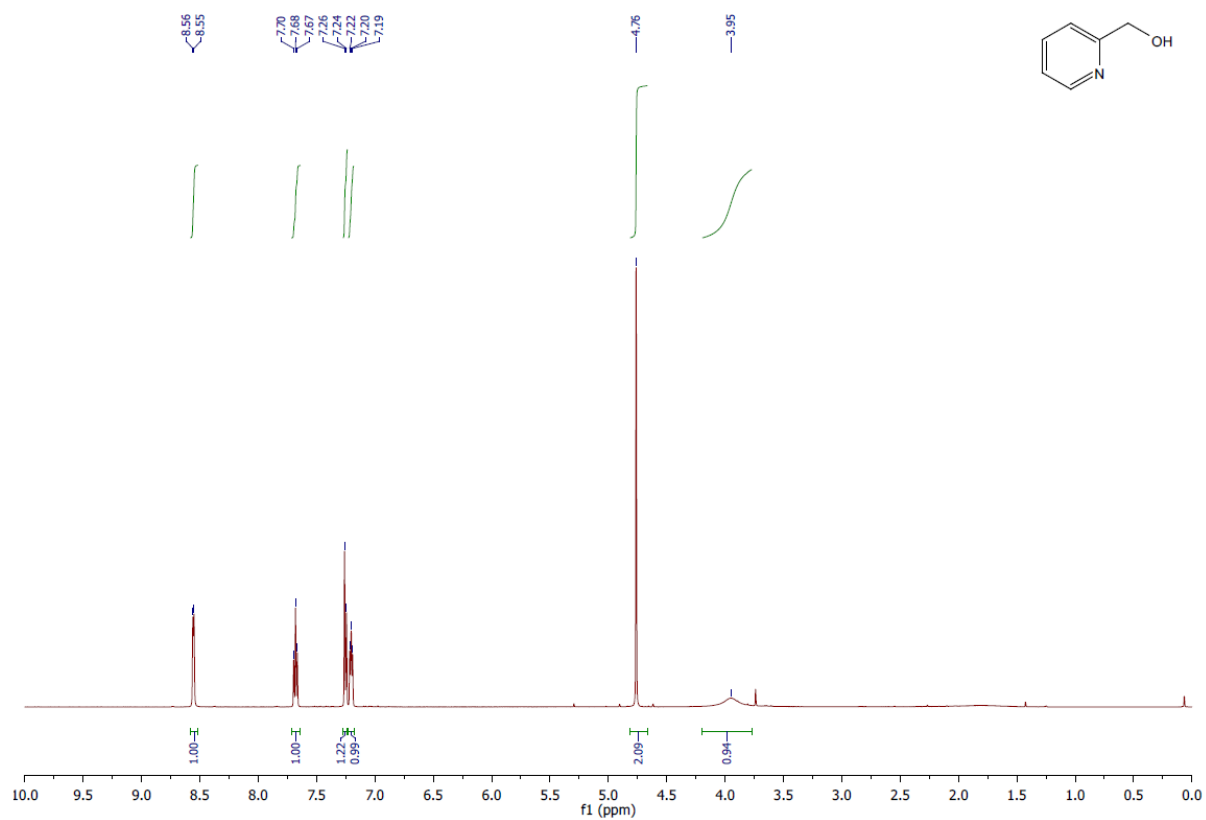


Figure S27. $^1\text{H-NMR}$ spectrum of alcohol **4n**.

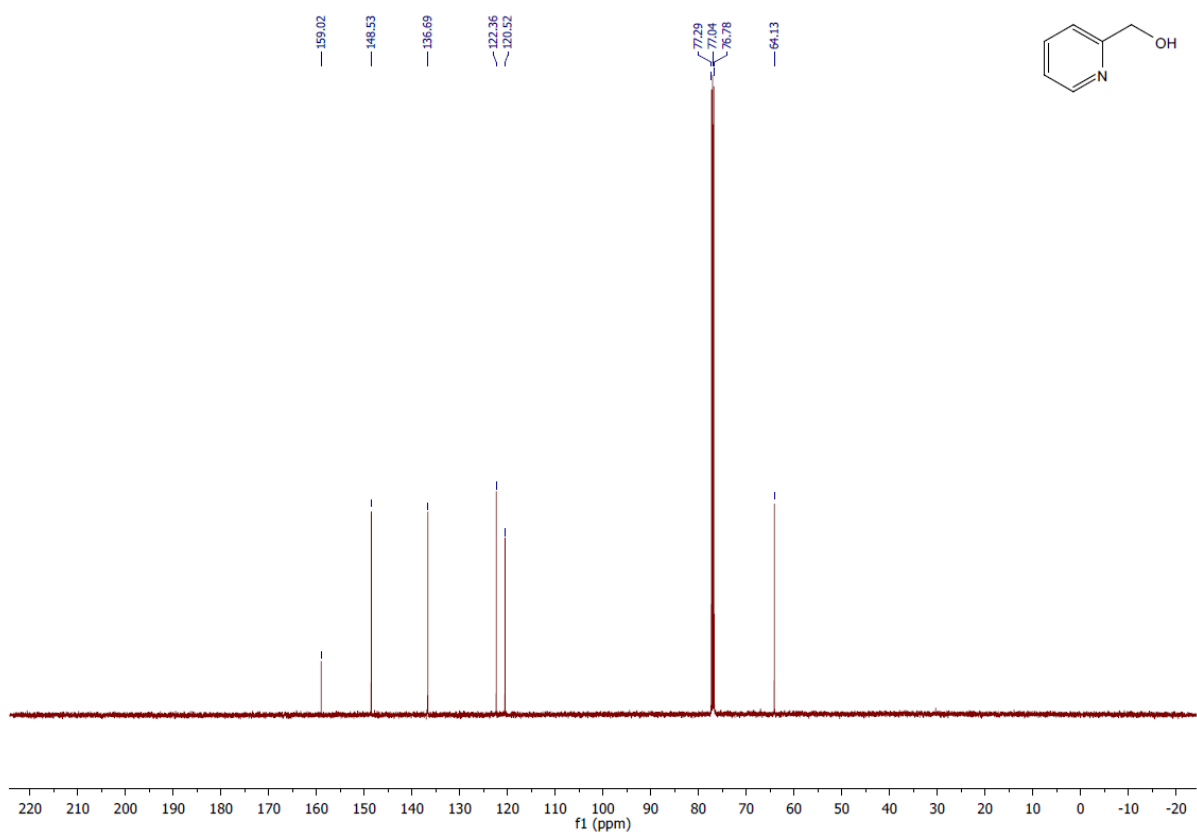


Figure S28. $^{13}\text{C-NMR}$ spectrum of alcohol **4n**.

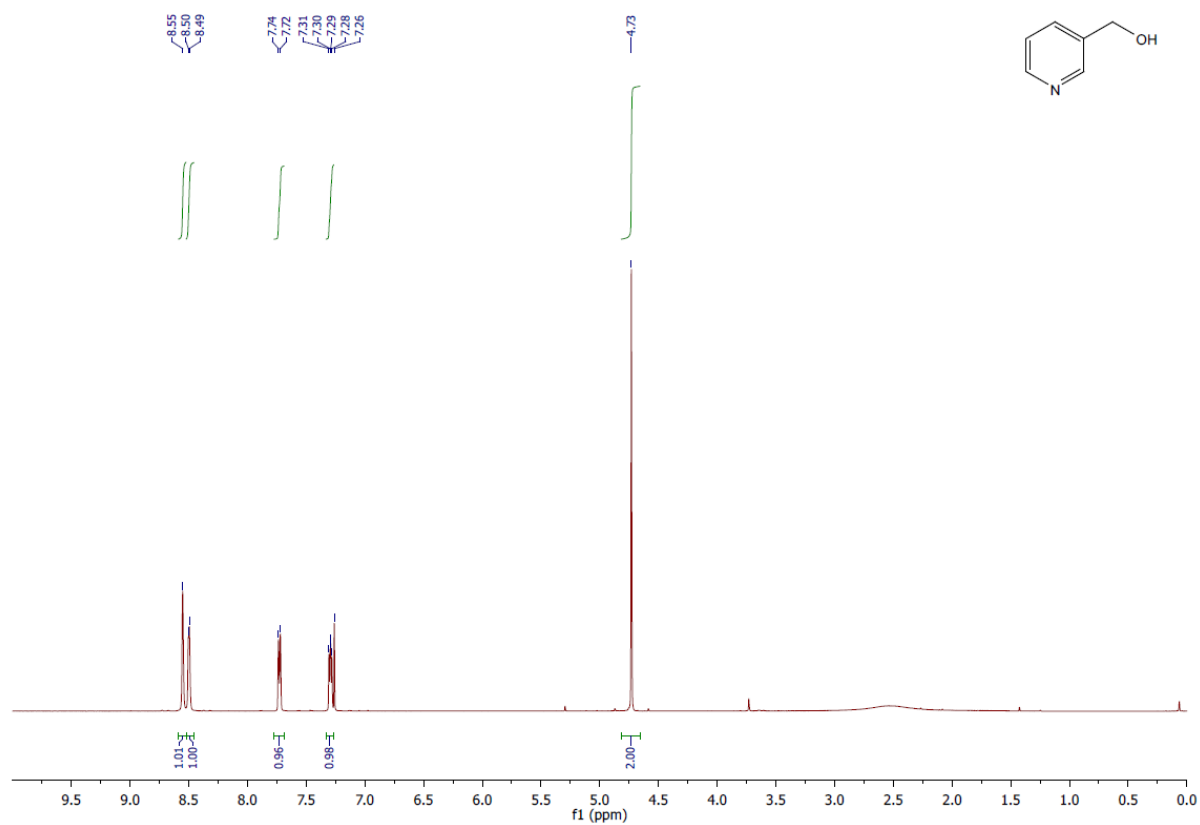


Figure S29. $^1\text{H-NMR}$ spectrum of alcohol **4o**.

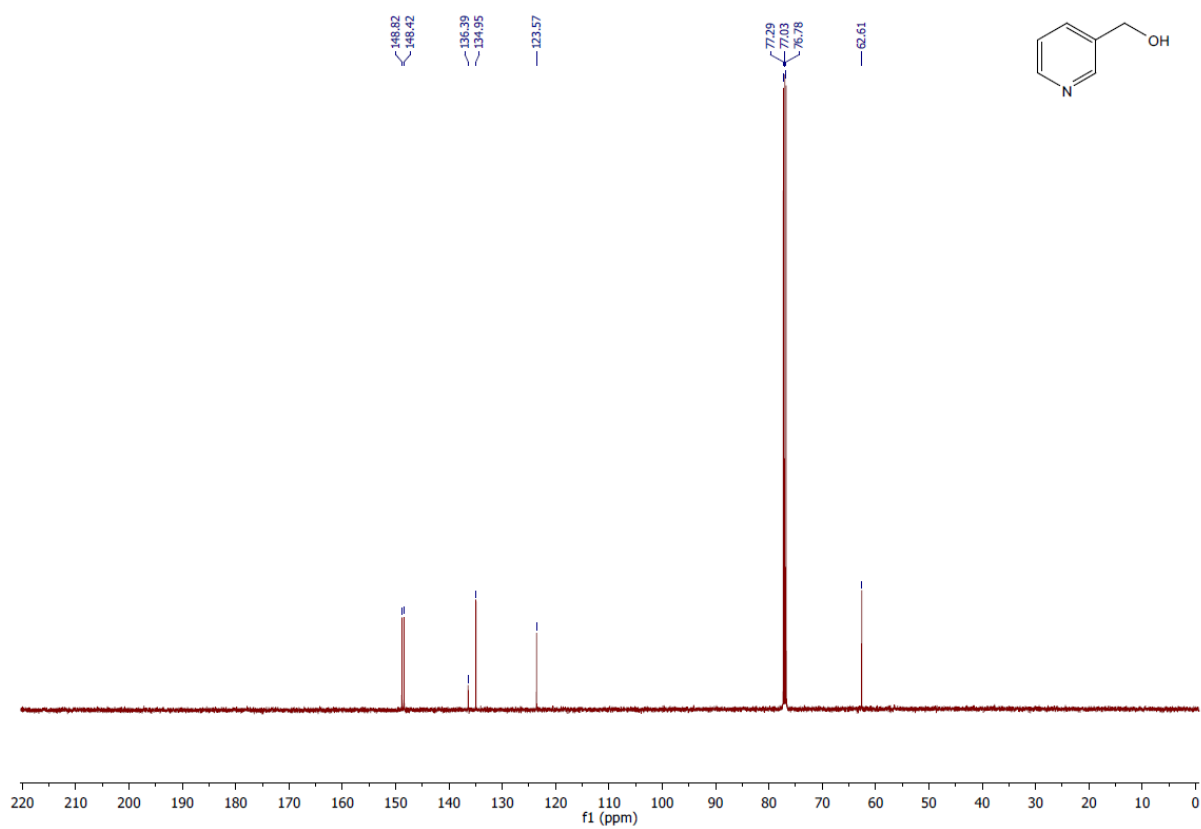


Figure S30. $^{13}\text{C-NMR}$ spectrum of alcohol **4o**.

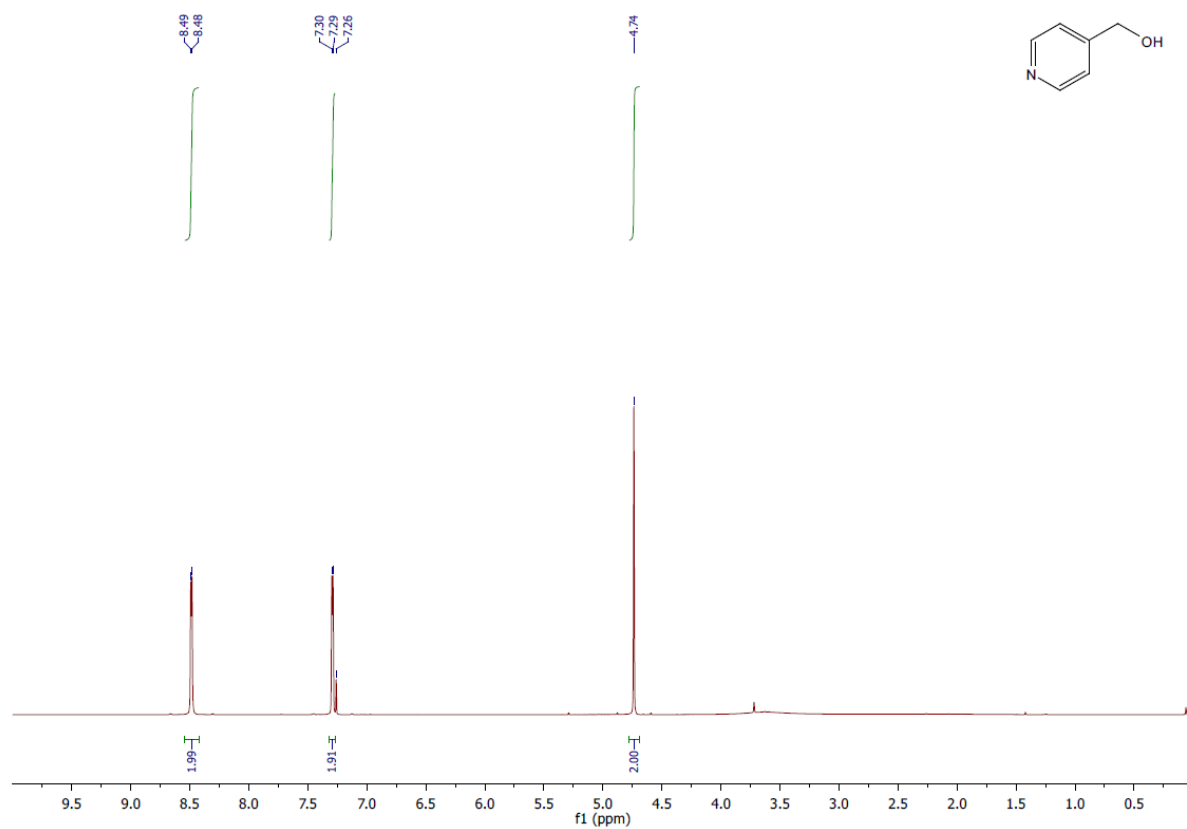


Figure S31. $^1\text{H-NMR}$ spectrum of alcohol **4p**.

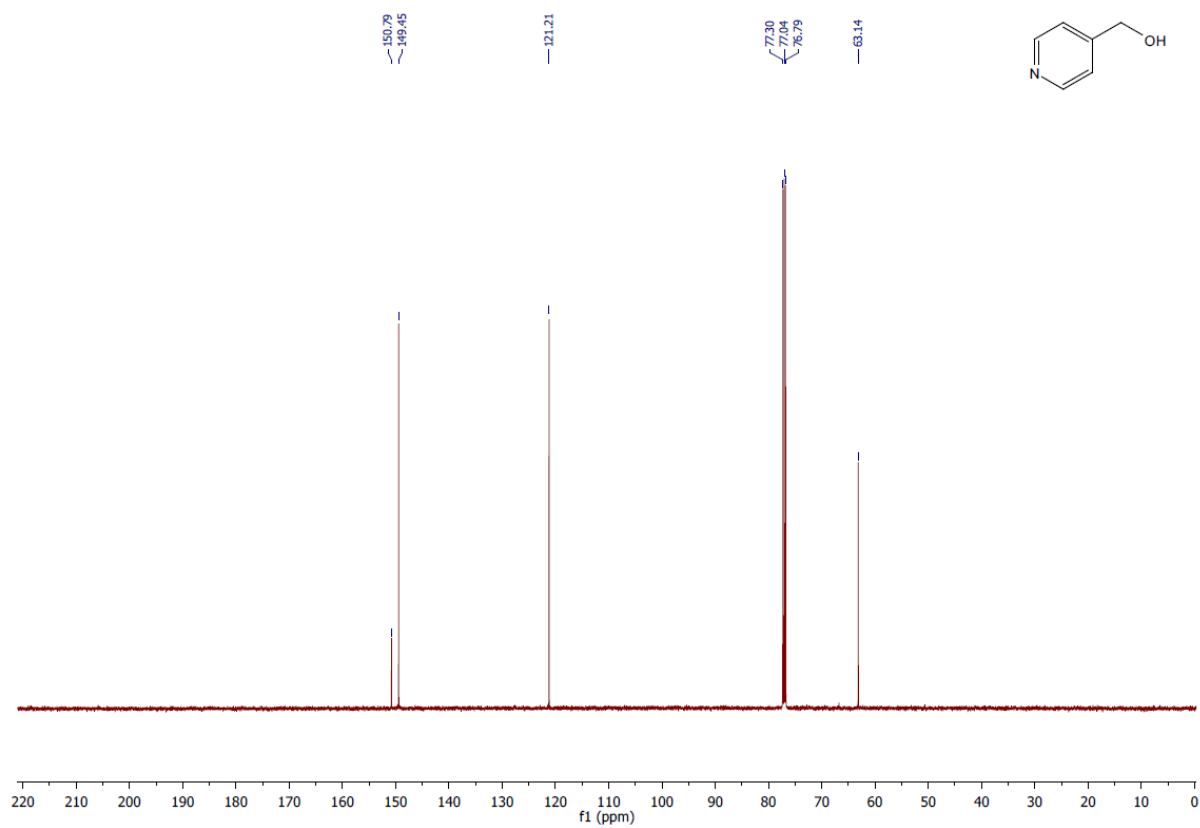


Figure S32. $^{13}\text{C-NMR}$ spectrum of alcohol **4p**.

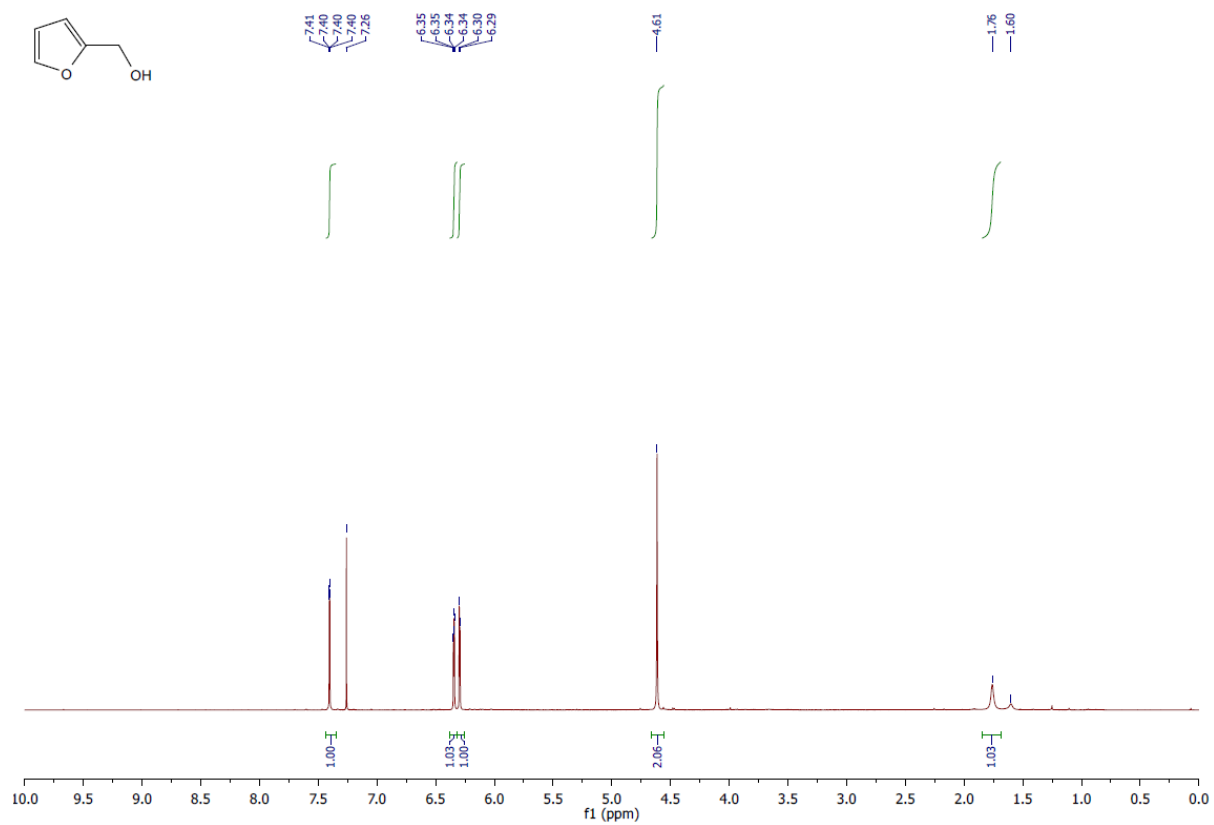


Figure S33. $^1\text{H-NMR}$ spectrum of alcohol **4q**.

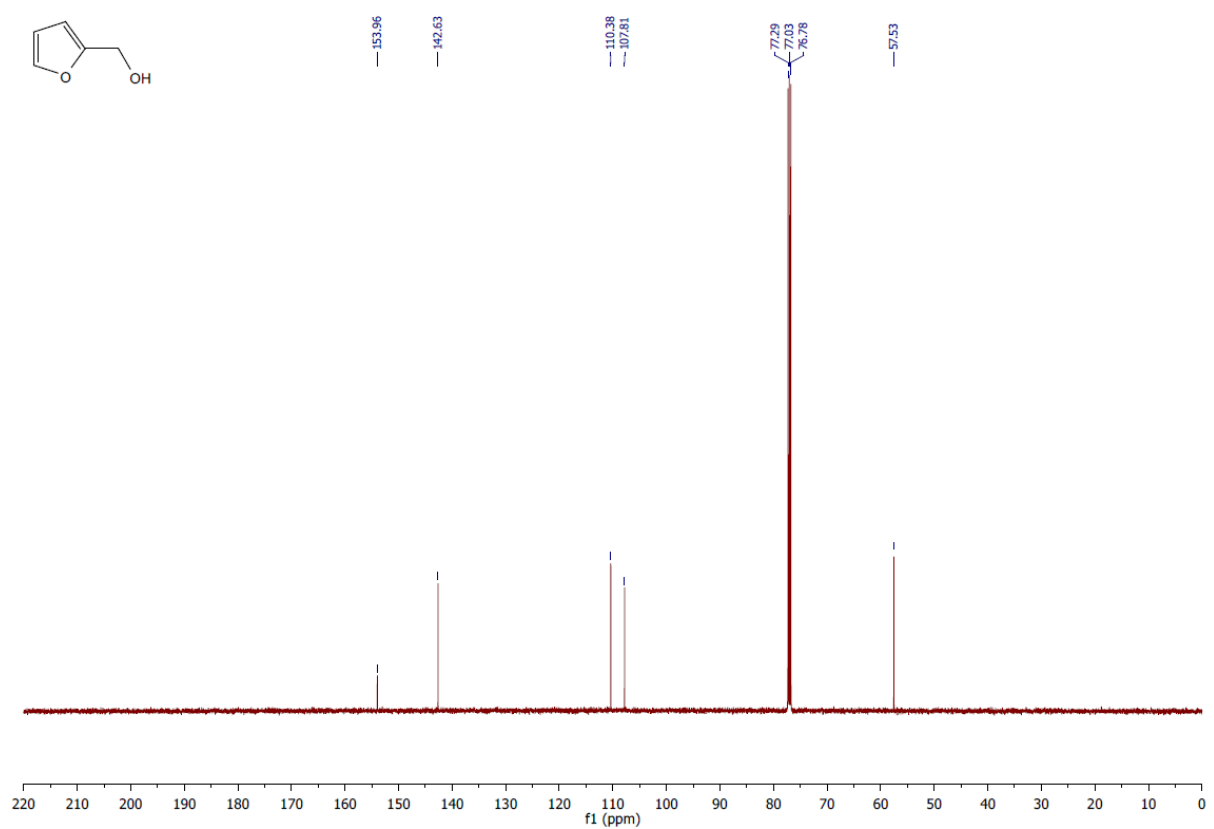


Figure S34. $^{13}\text{C-NMR}$ spectrum of alcohol **4q**.

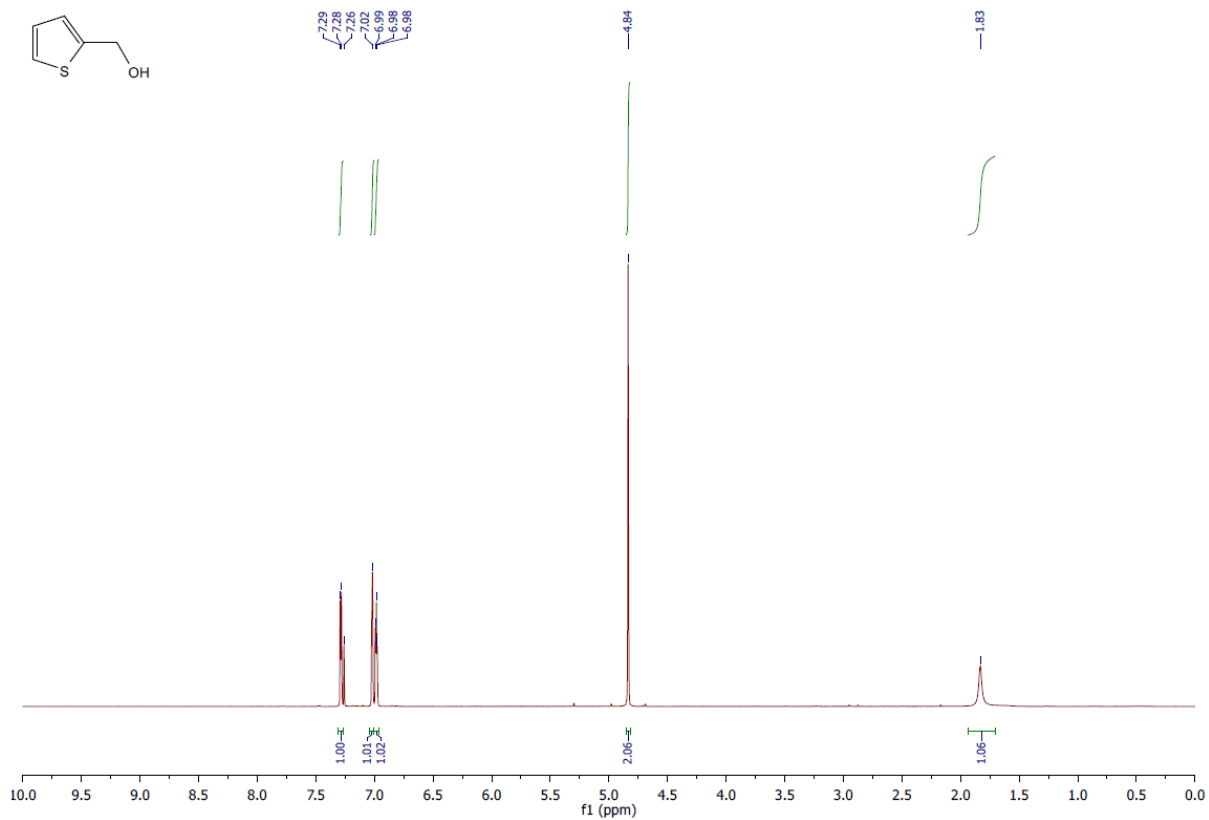


Figure S35. ¹H-NMR spectrum of alcohol **4r**.

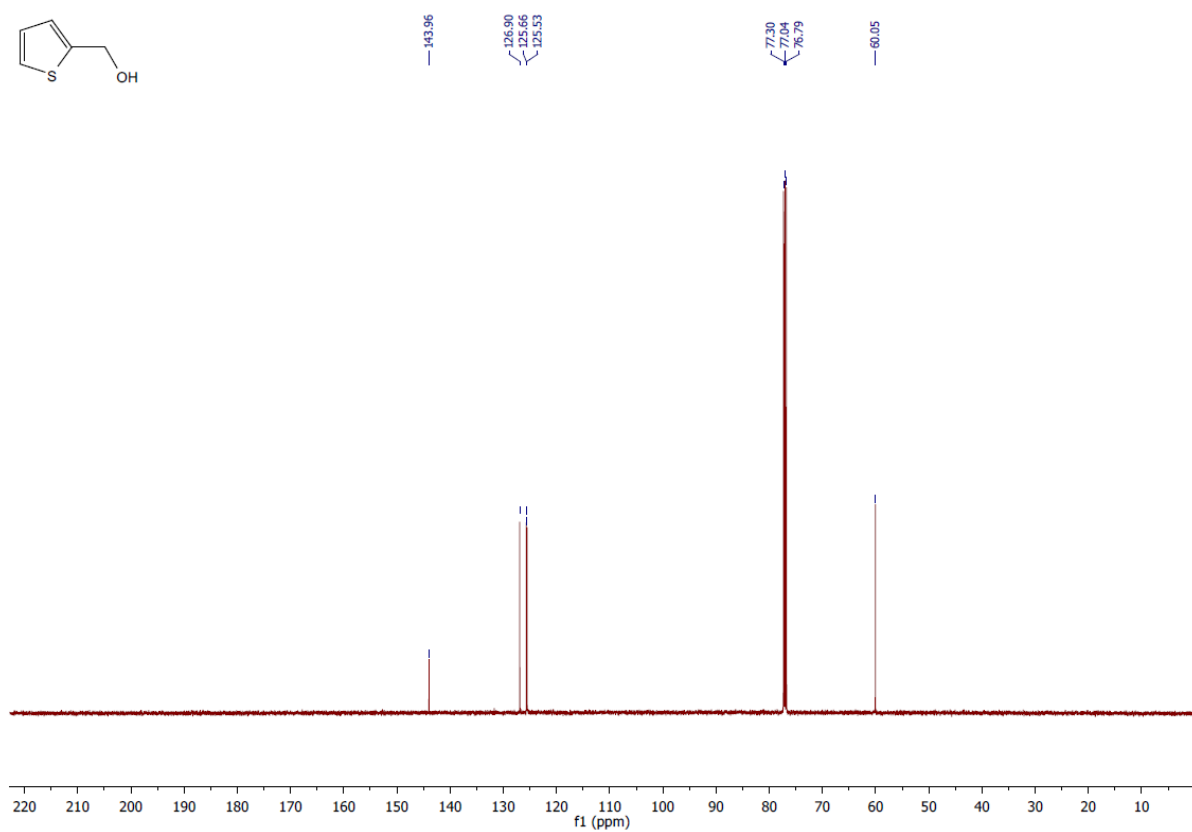


Figure S36. ¹³C-NMR spectrum of alcohol **4r**.

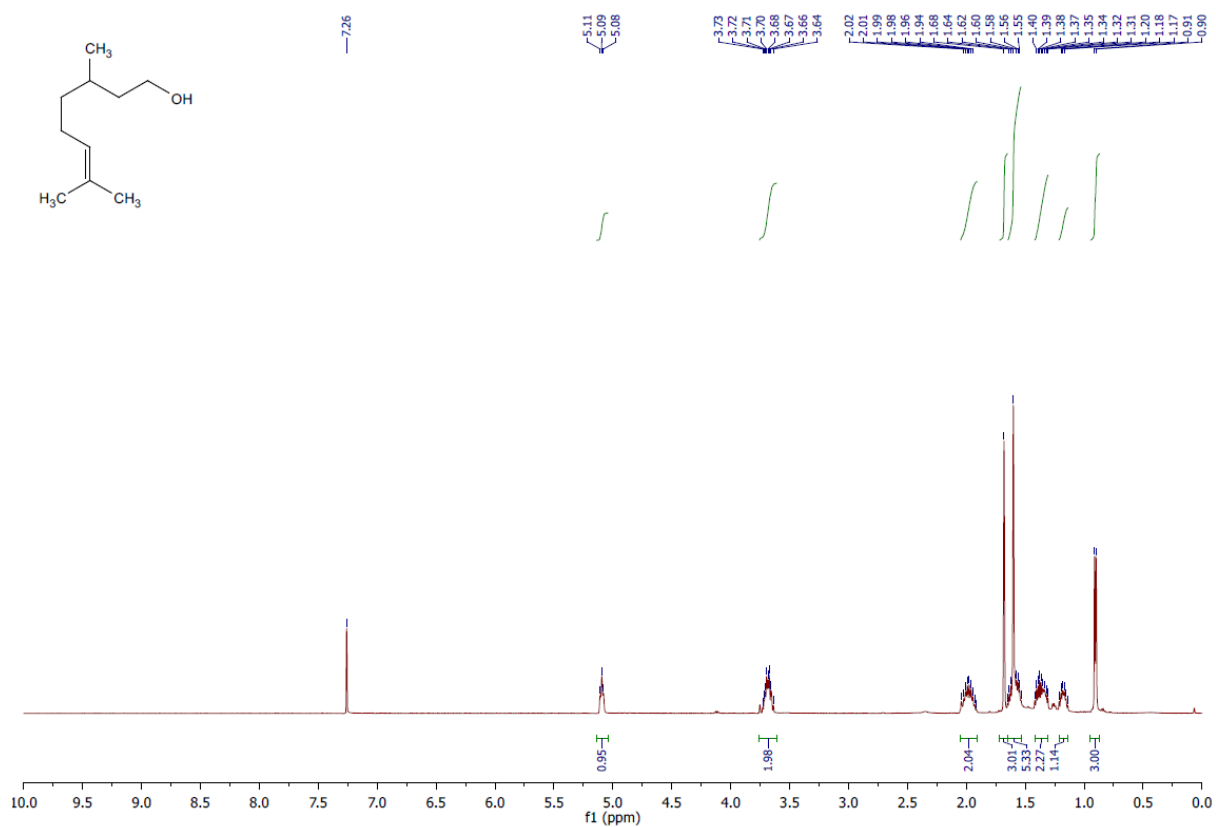


Figure S37. ¹H-NMR spectrum of alcohol 4s.

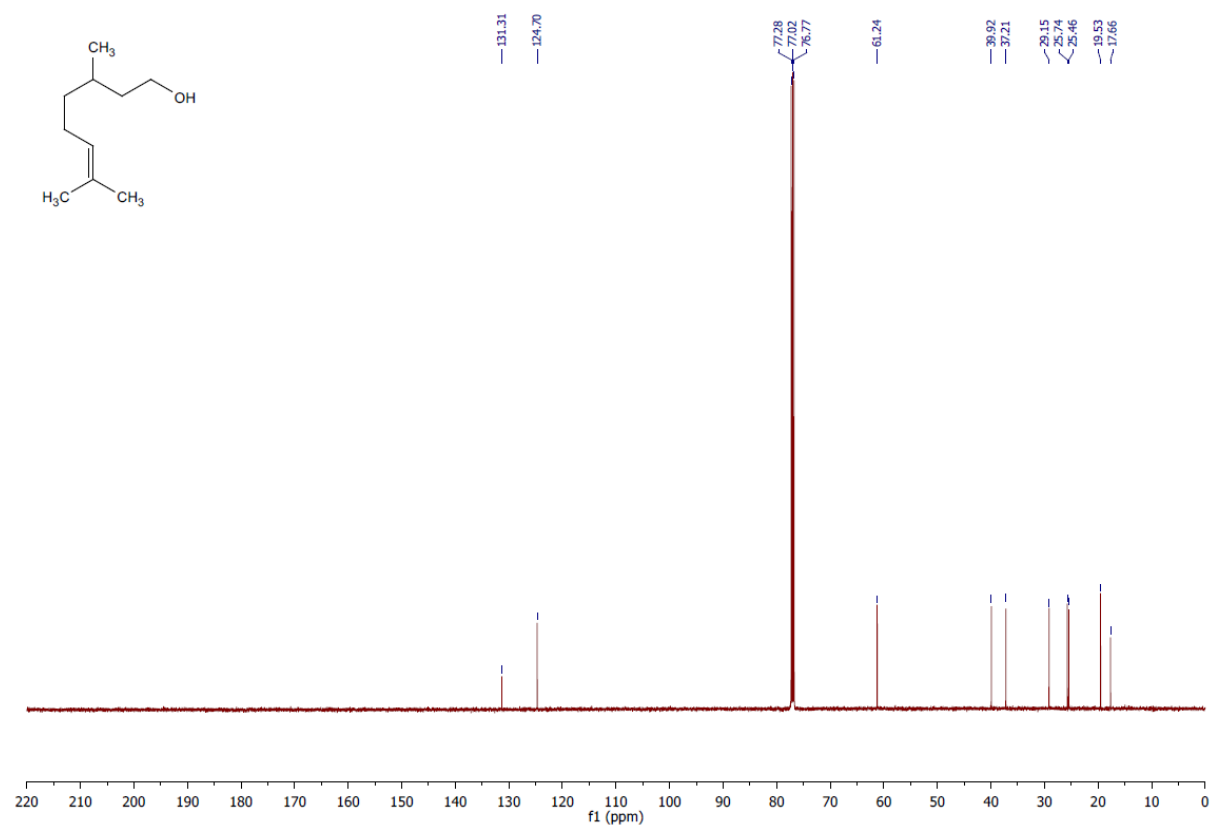


Figure S38. ¹³C-NMR spectrum of alcohol 4s.

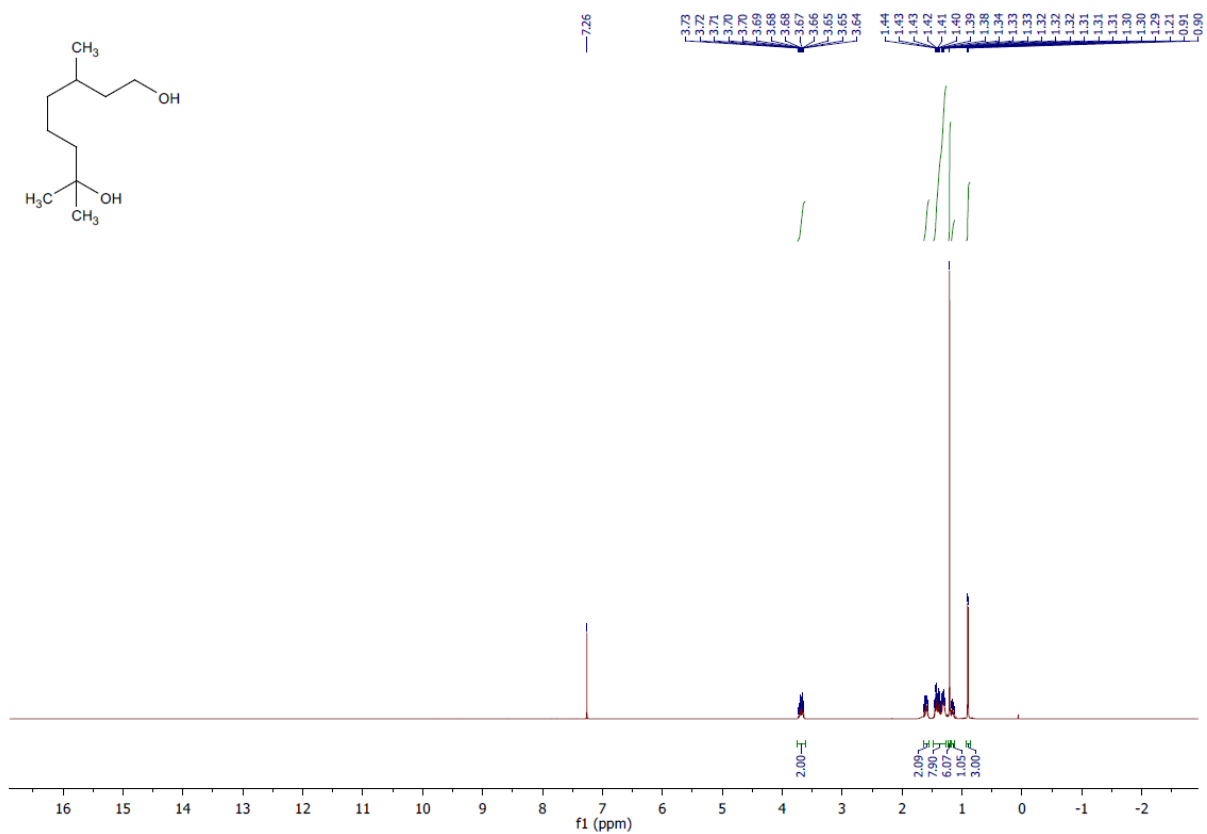


Figure S39. ¹H-NMR spectrum of alcohol 4t.

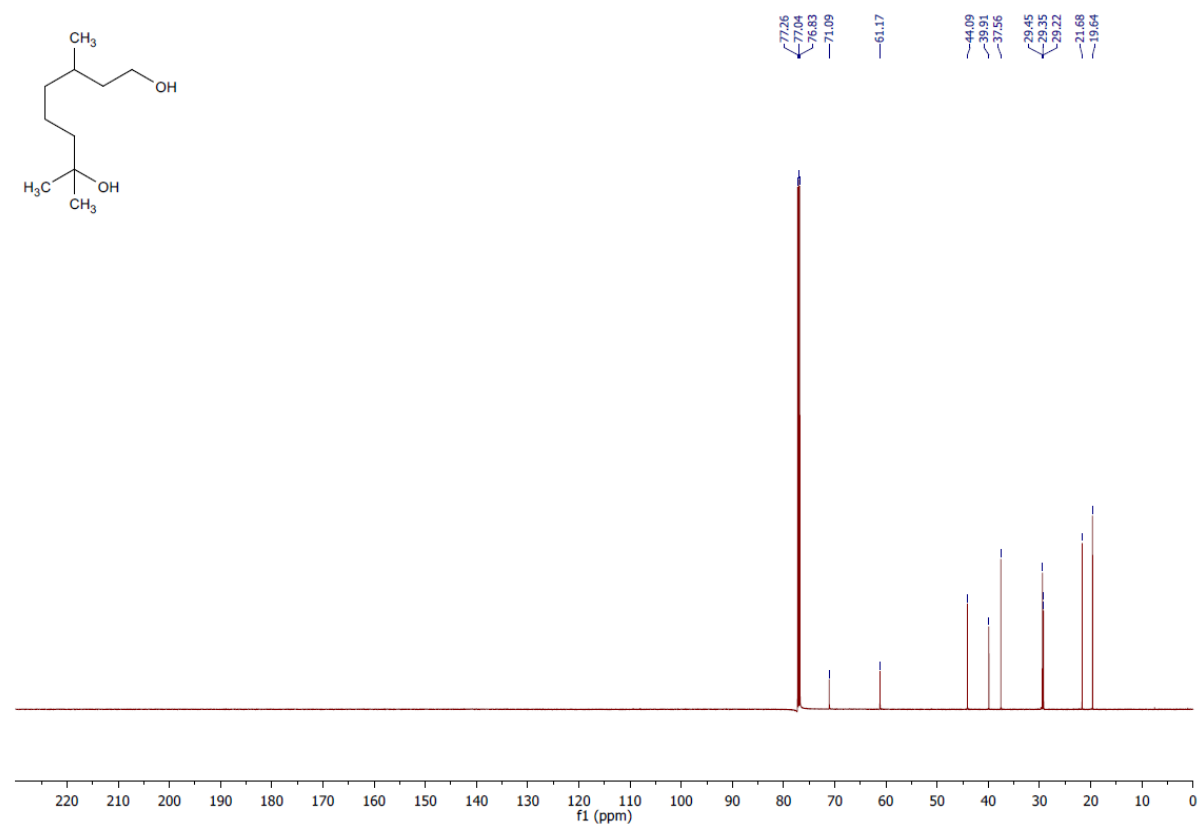


Figure S40. ¹³C-NMR spectrum of alcohol 4t.

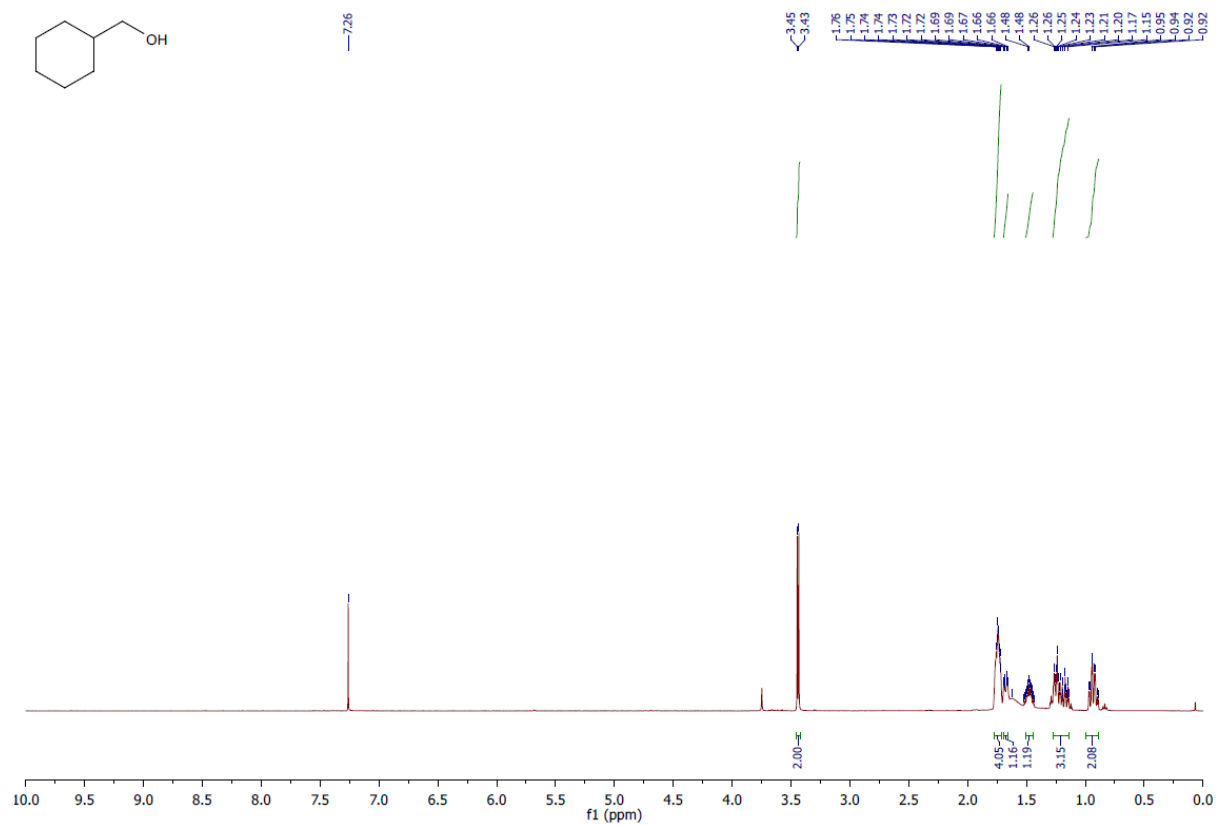


Figure S41. ¹H-NMR spectrum of alcohol **4u**.

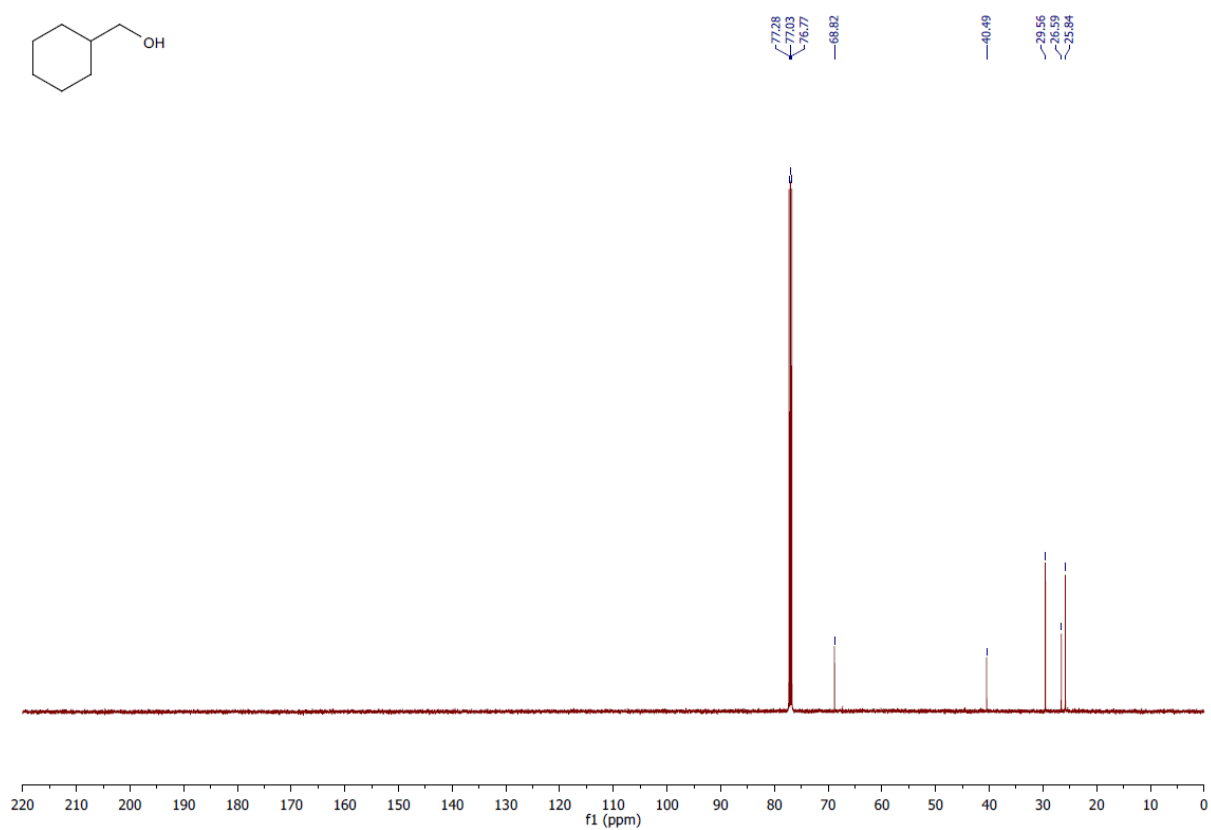


Figure S42. ¹³C-NMR spectrum of alcohol **4u**.

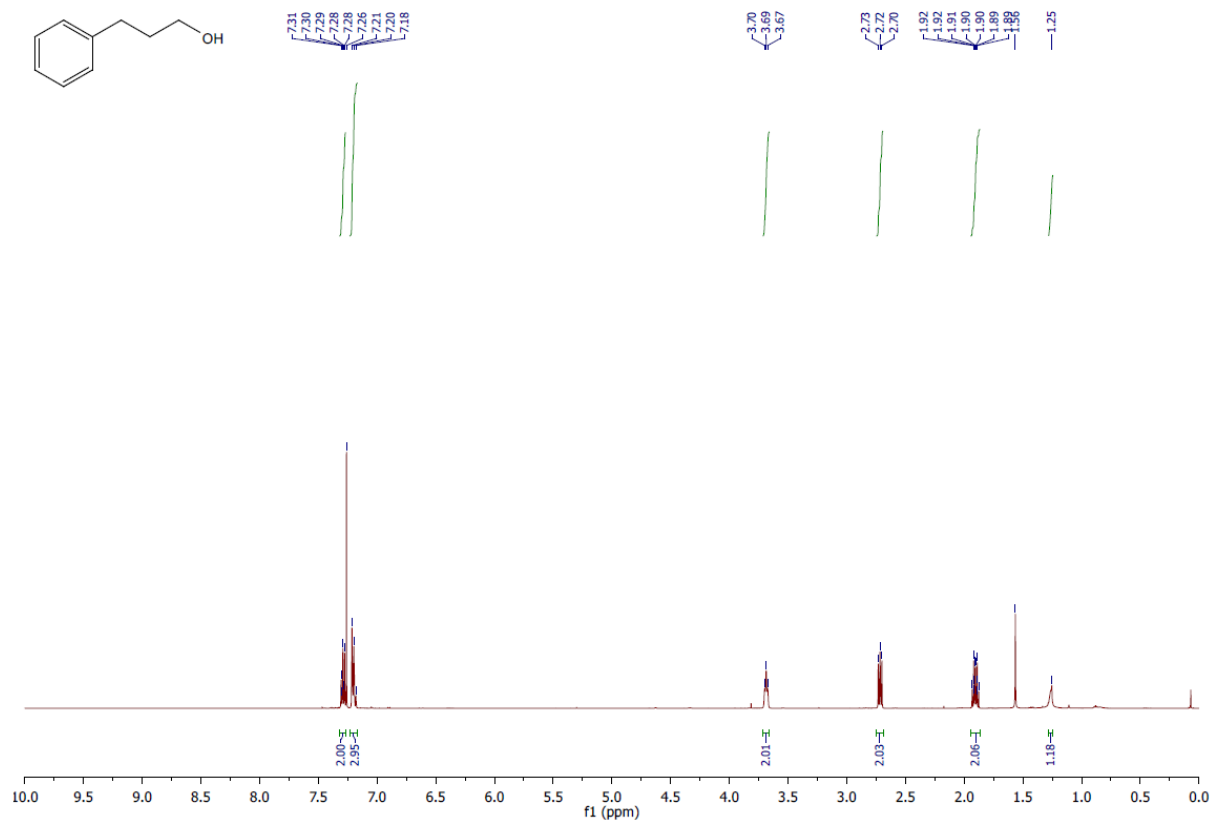


Figure S43. ¹H-NMR spectrum of alcohol **4v**.

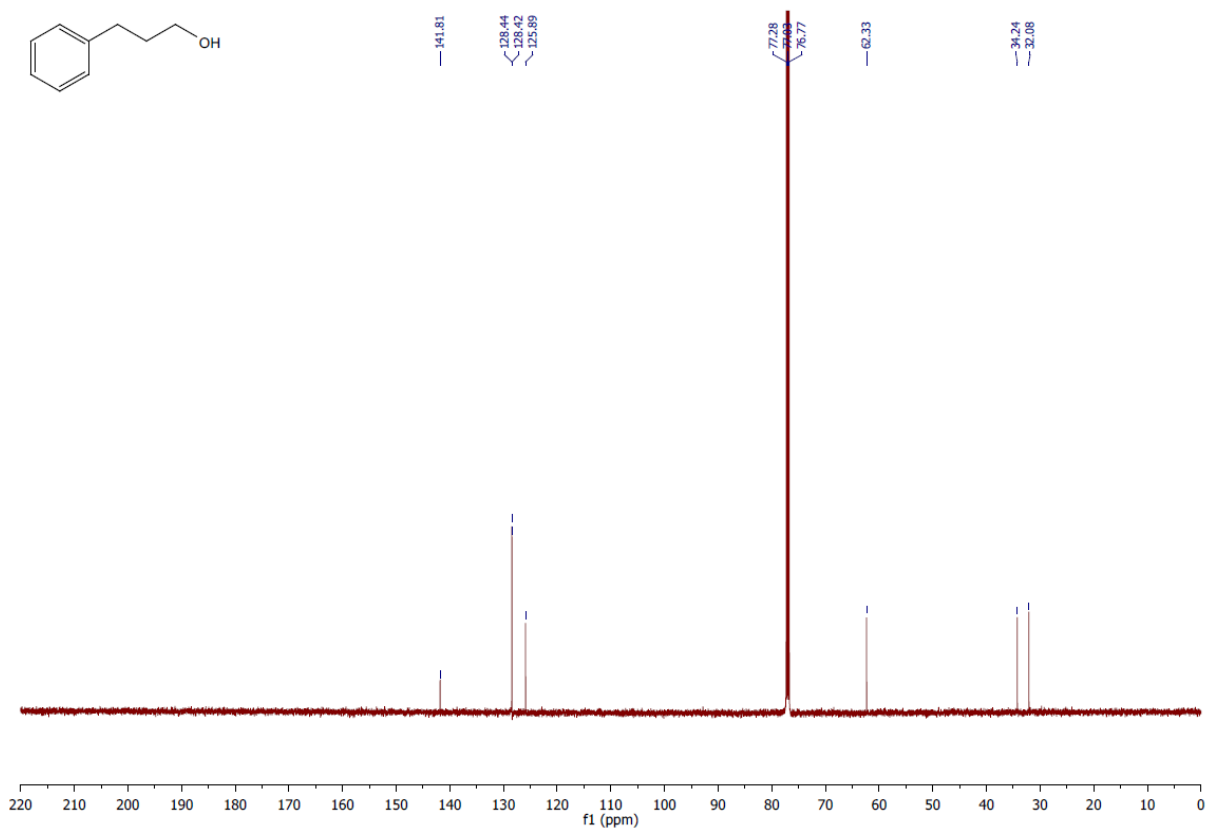


Figure S44. ¹³C-NMR spectrum of alcohol **4v**.

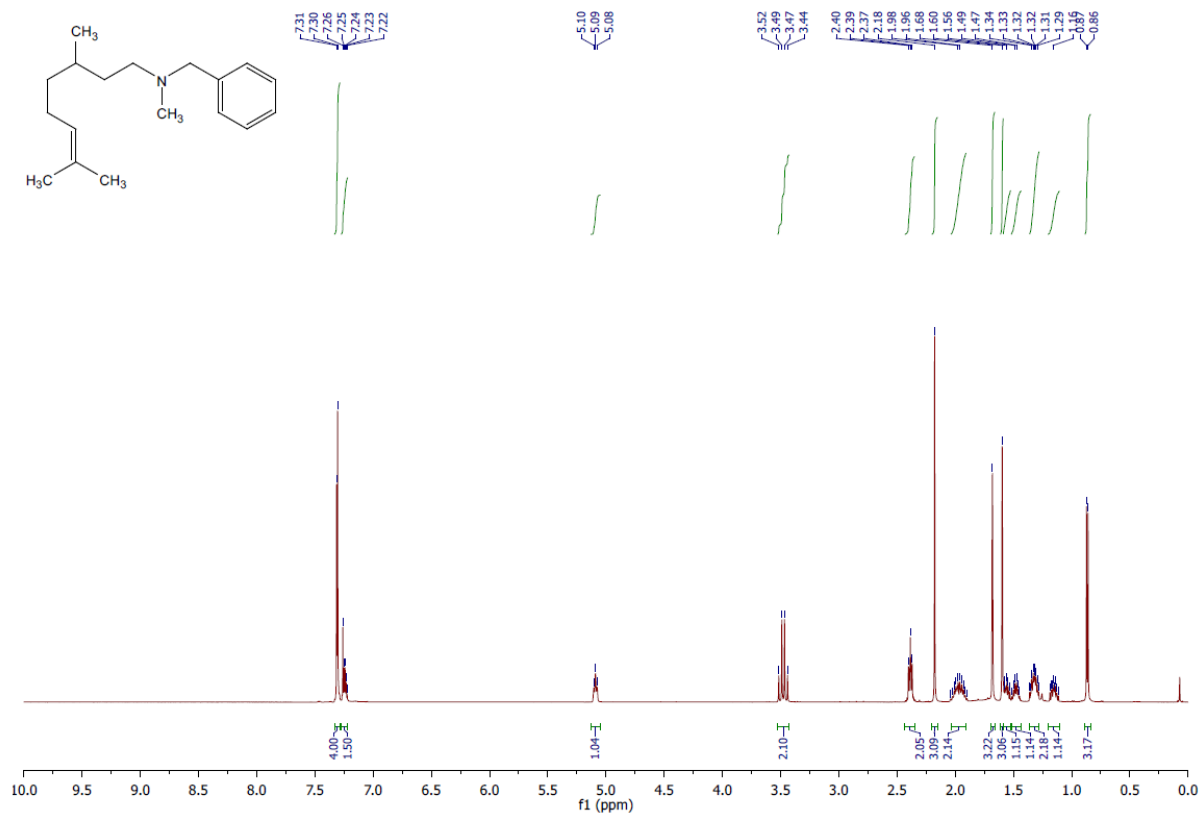


Figure S45. ¹H-NMR spectrum of amine 5a.

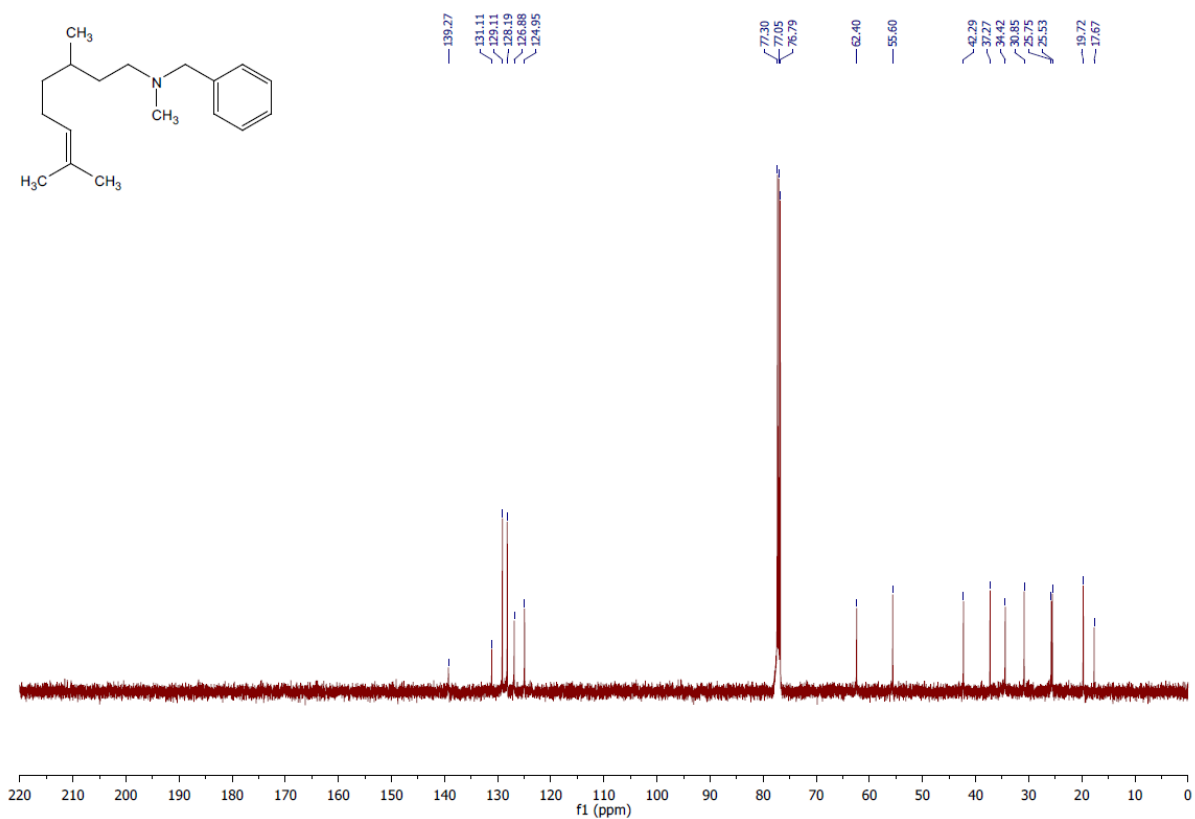


Figure S46. ¹³C-NMR spectrum of amine 5a.

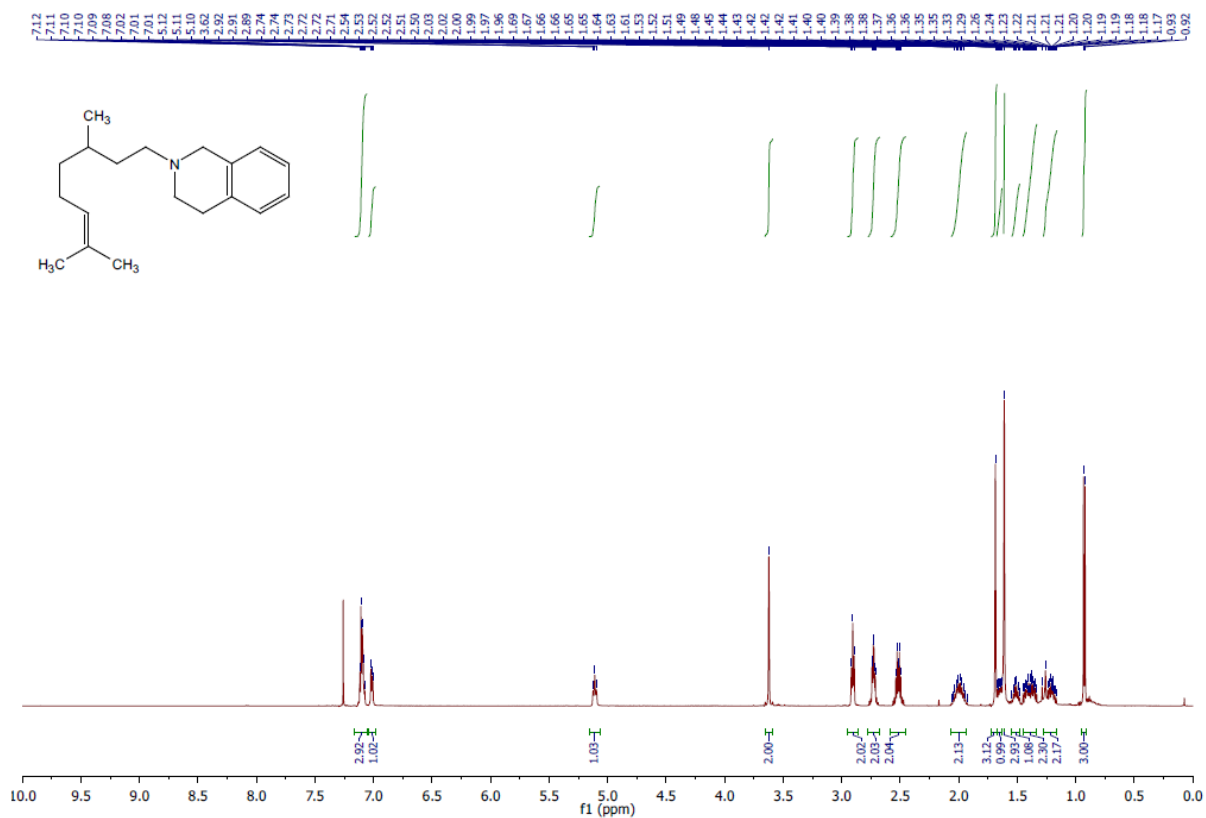


Figure S47. ¹H-NMR spectrum of amine 4b.

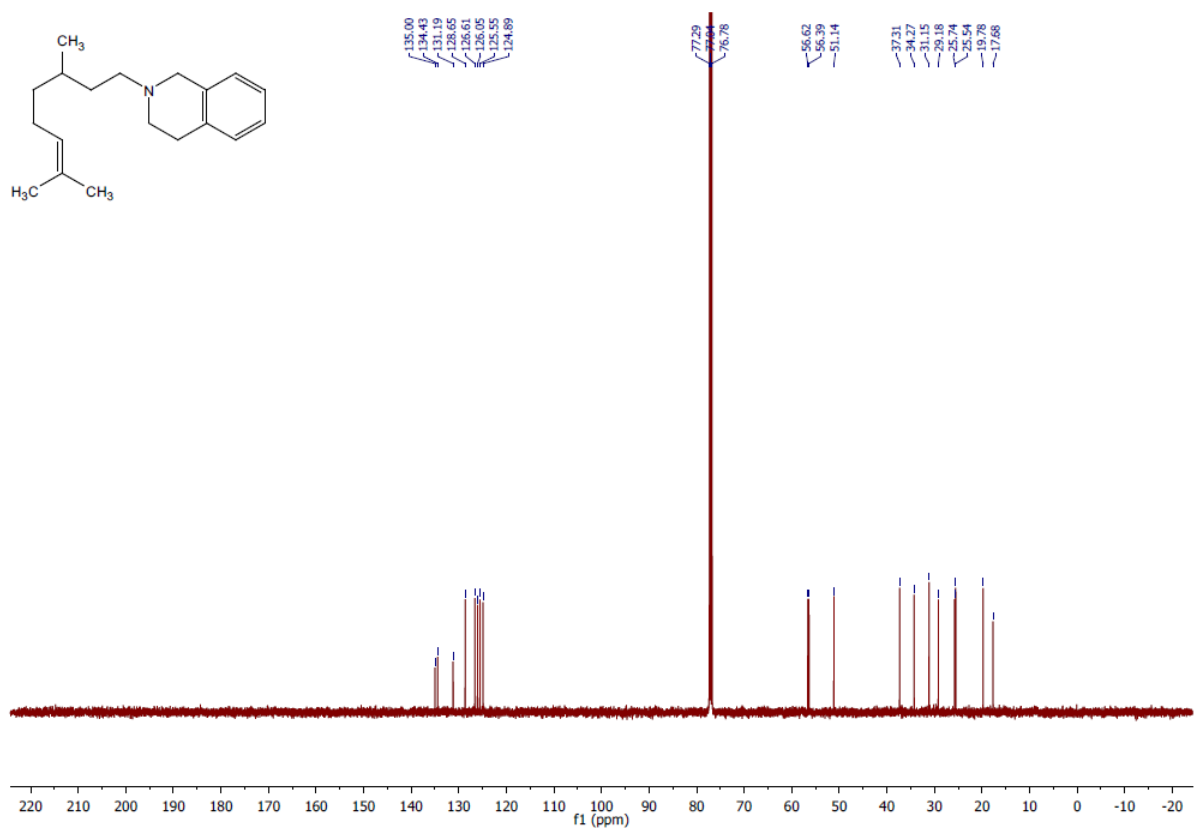


Figure S48. ¹³C-NMR spectrum of amine 5b.

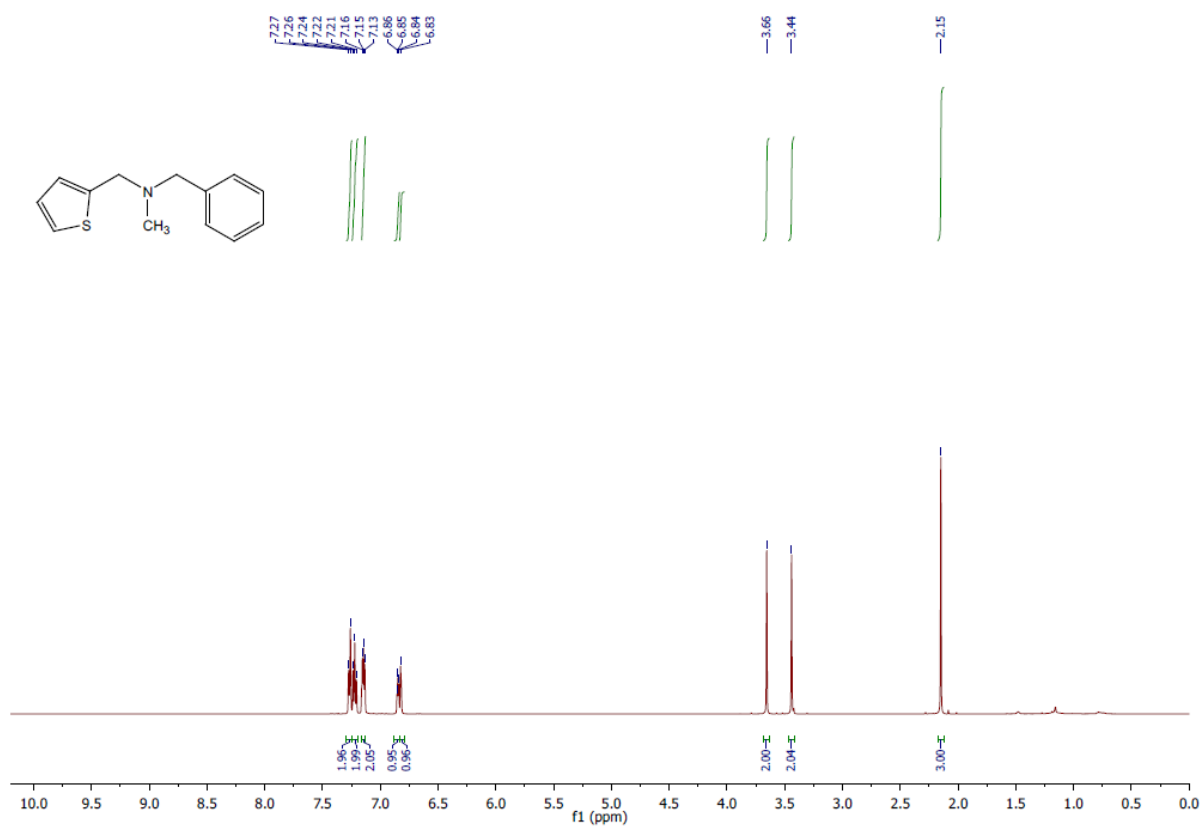


Figure S50. ¹H-NMR spectrum of amine **5d**.

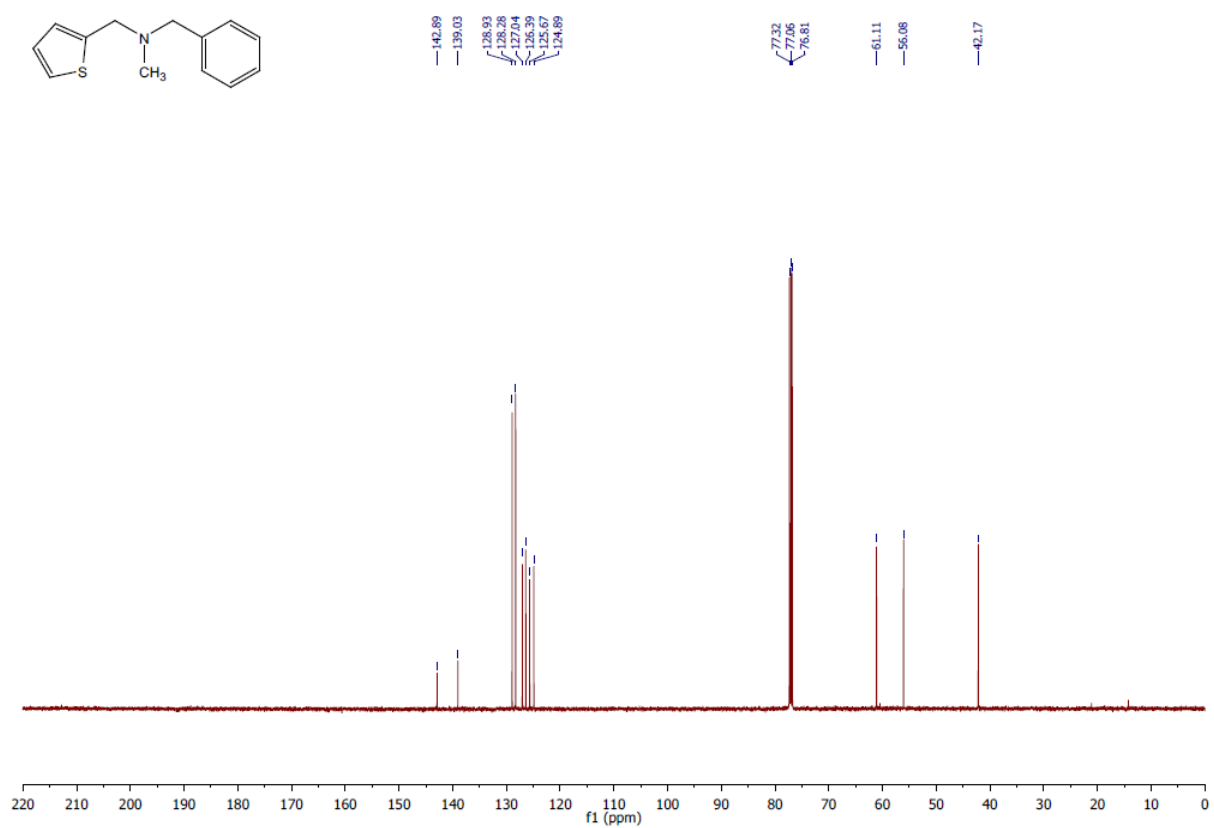


Figure S51. ¹³C-NMR spectrum of amine **5d**.

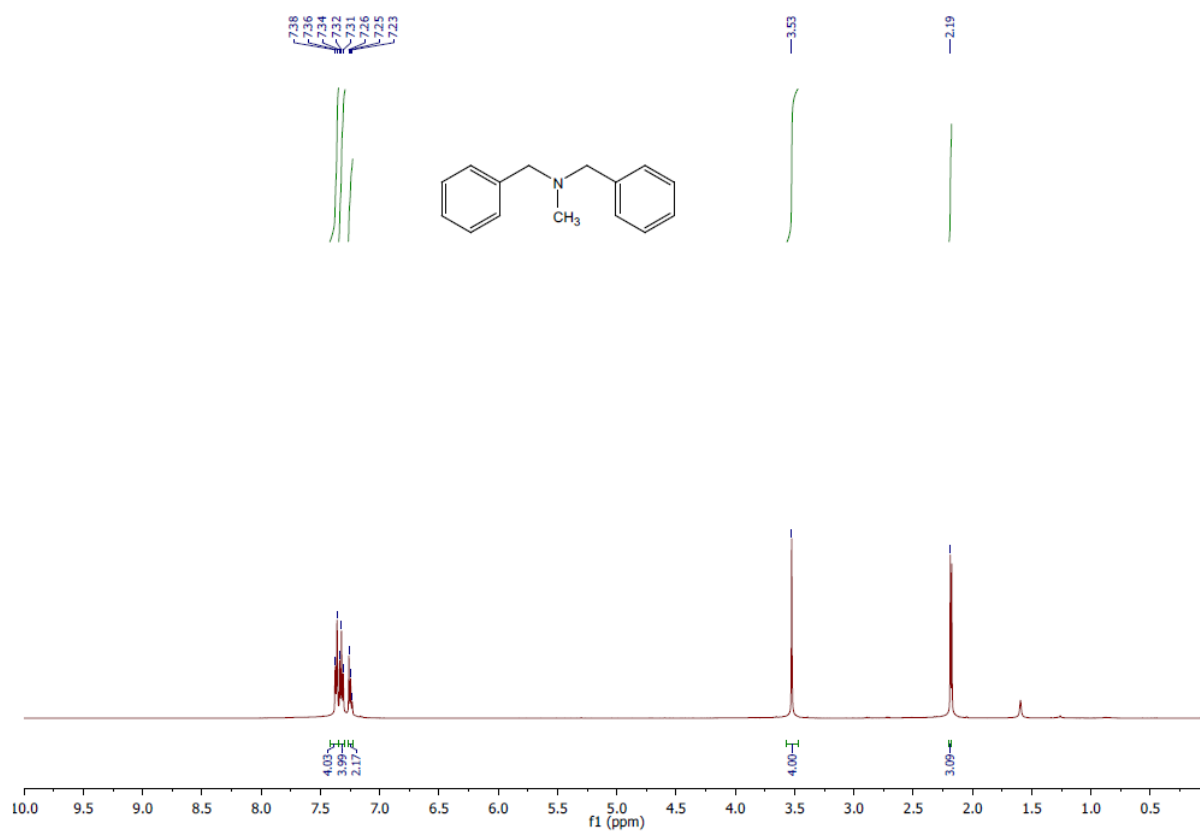


Figure S52. ¹H-NMR spectrum of amine 5e.

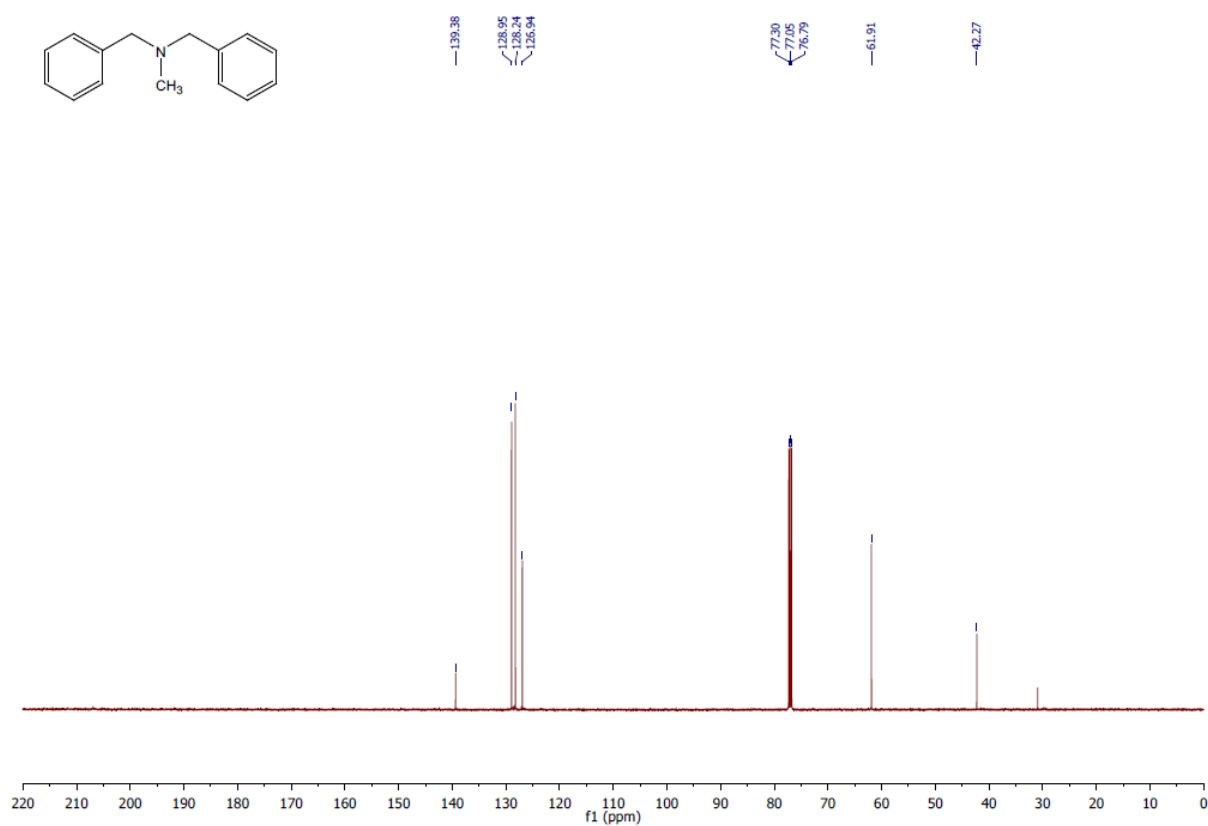


Figure S53. ¹³C-NMR spectrum of amine 5e.

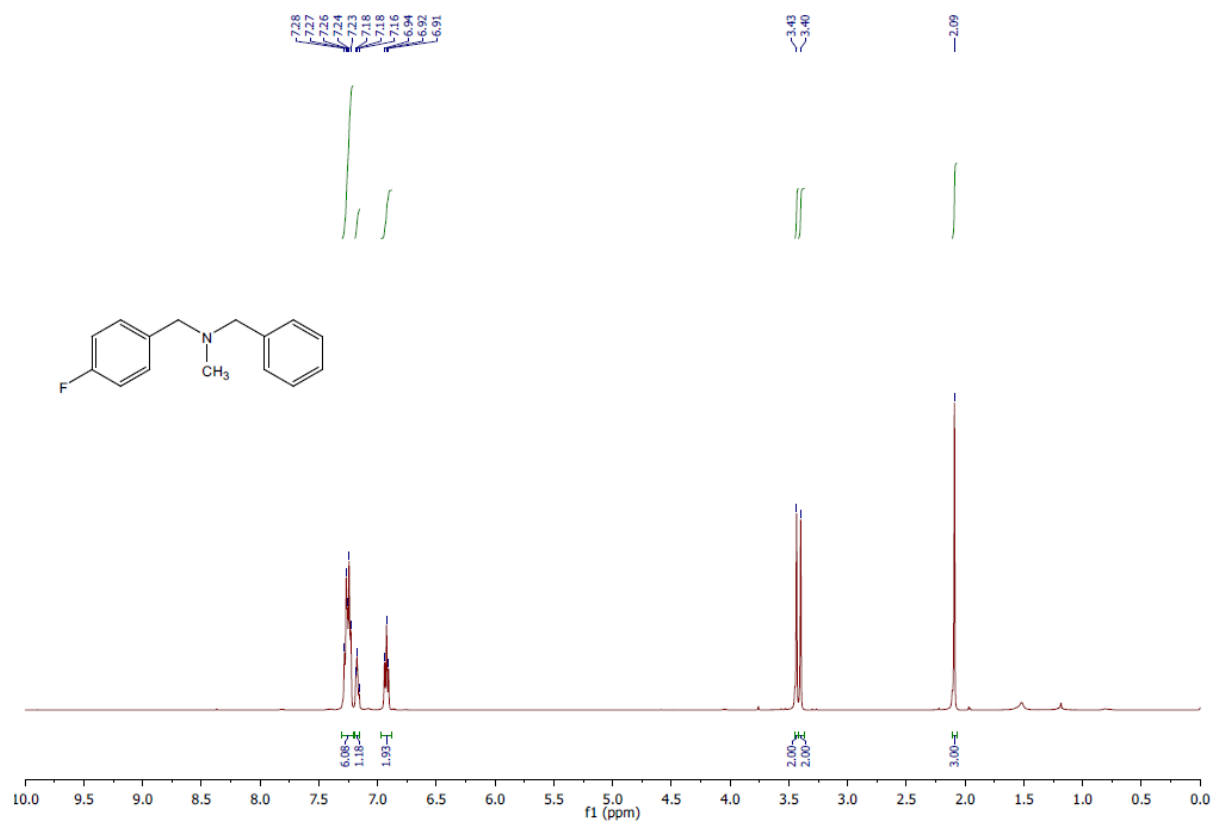


Figure S54. ¹H-NMR spectrum of amine **5f**.

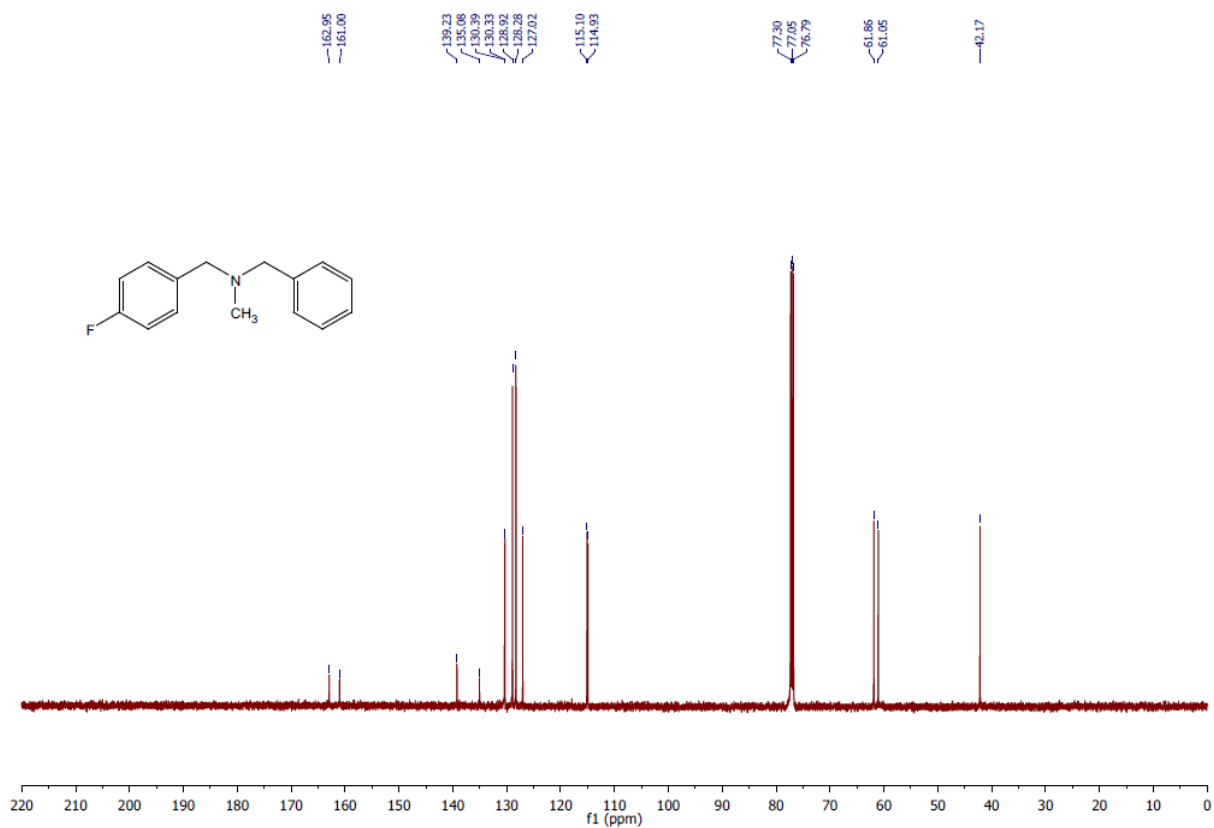


Figure S55. ¹³C-NMR spectrum of amine **5f**.

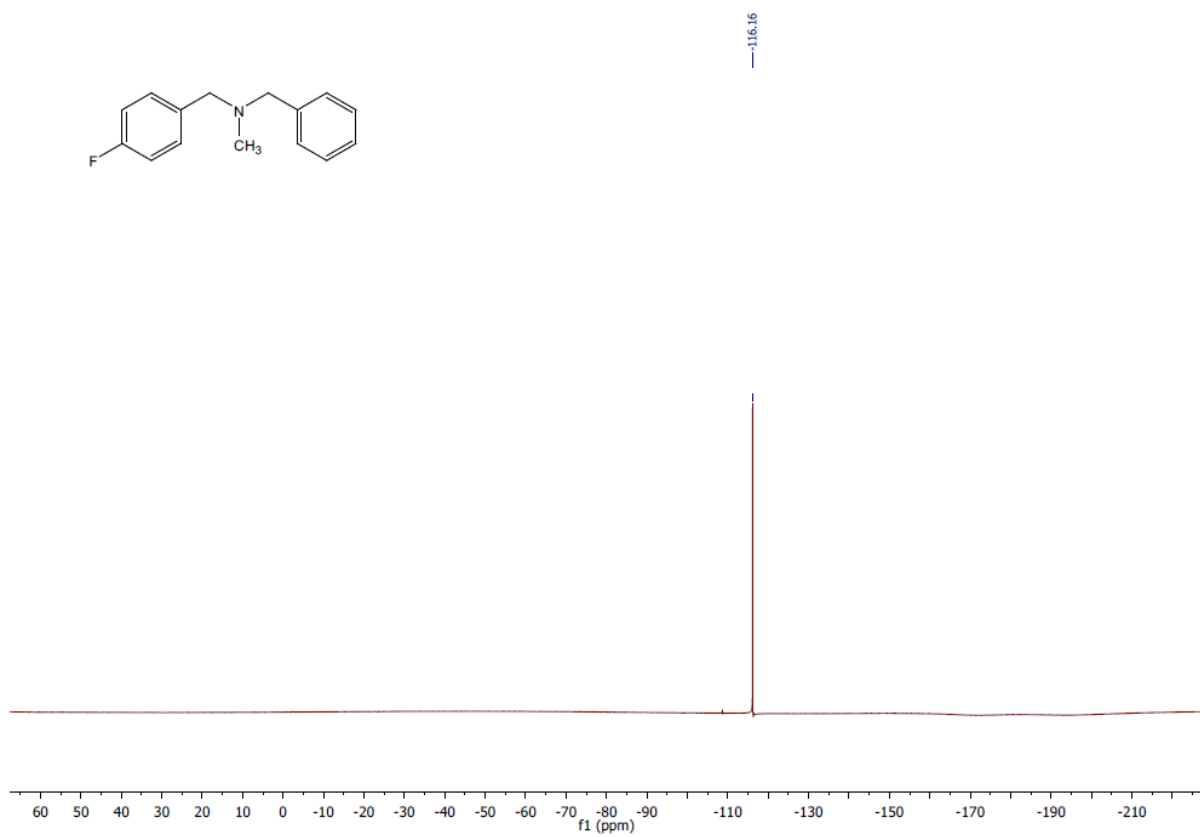


Figure S56. ^{19}F -NMR spectrum of amine 5f.

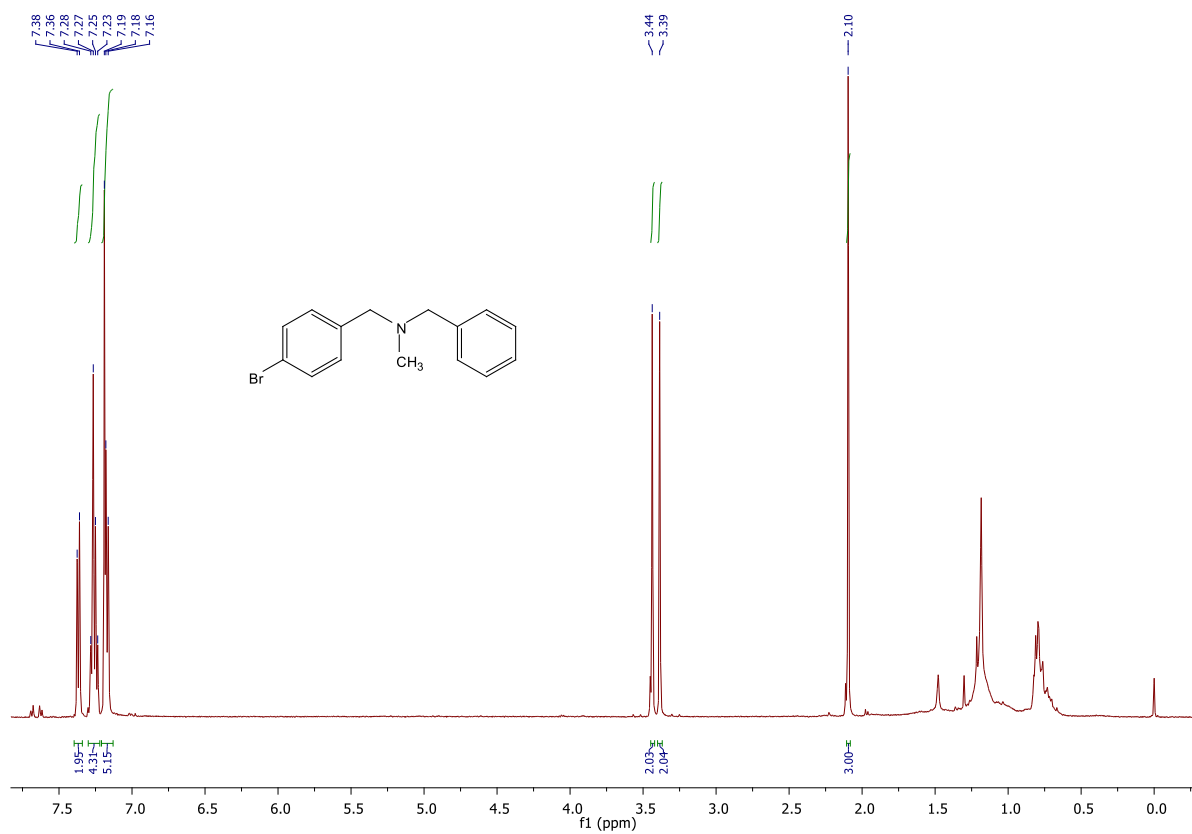


Figure S57. ¹H-NMR spectrum of amine 5g.

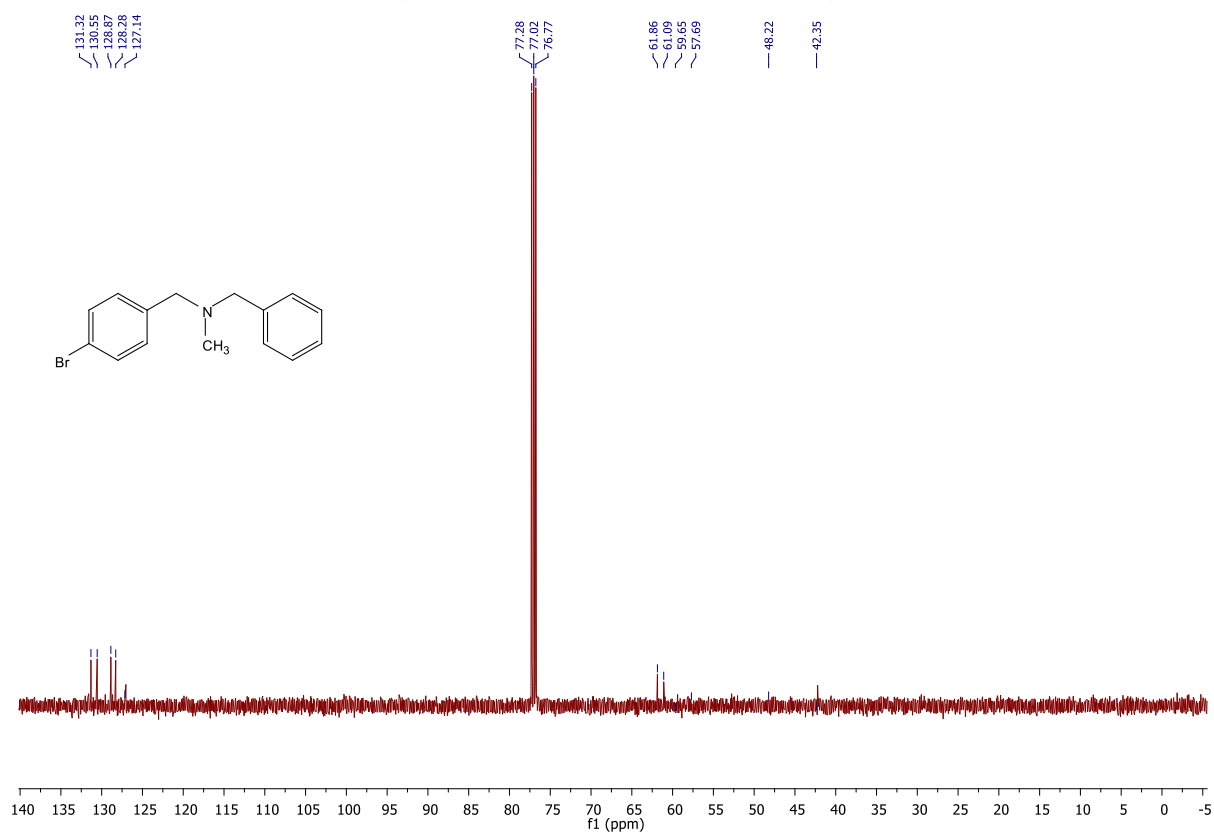


Figure S58. ¹³C-NMR spectrum of amine 5g.

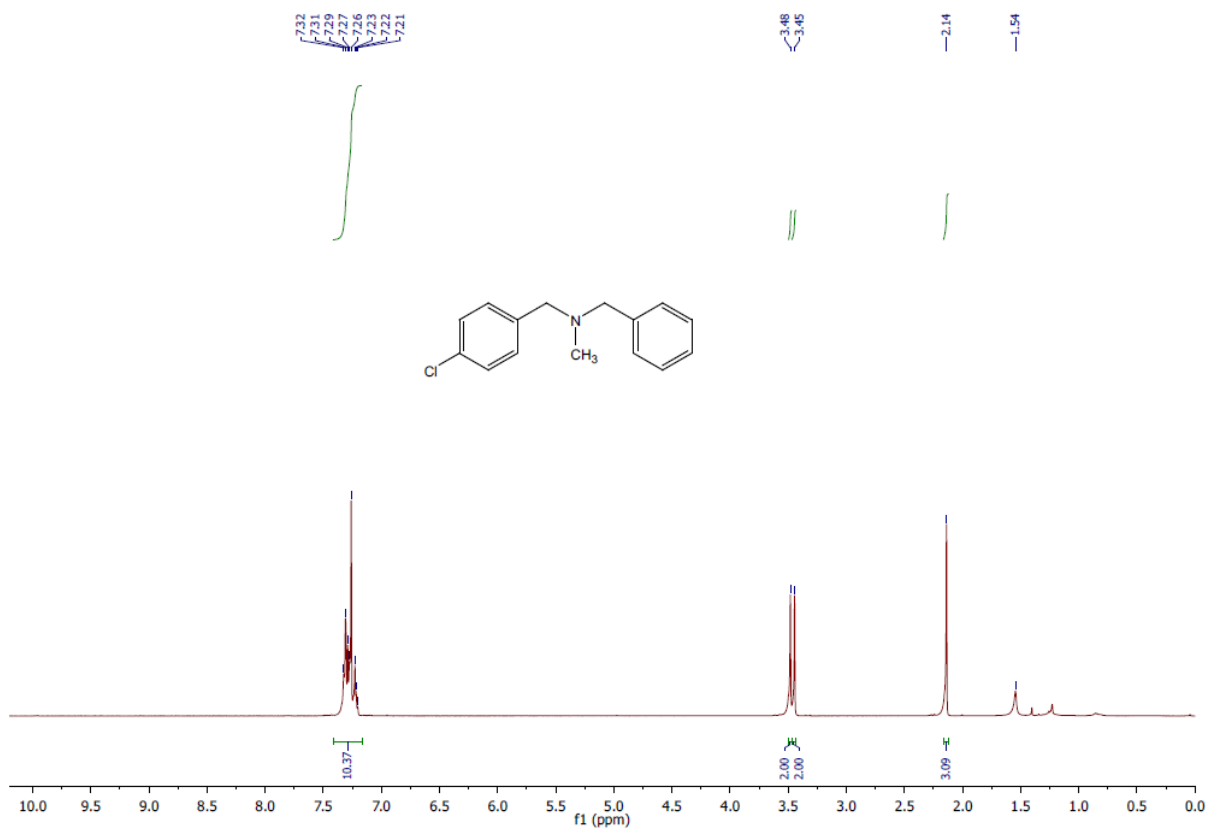


Figure S59. ¹H-NMR spectrum of amine 5h.

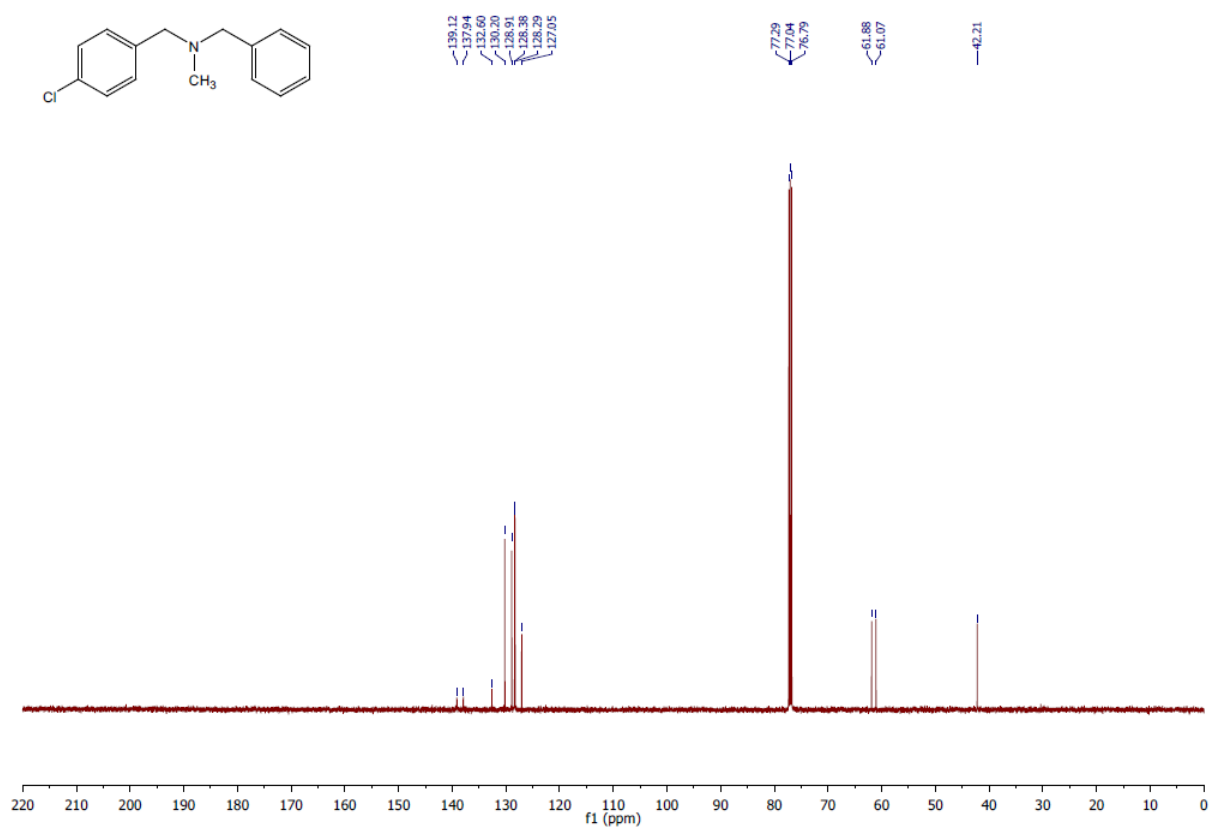


Figure S60. ¹³C-NMR spectrum of amine 5h.

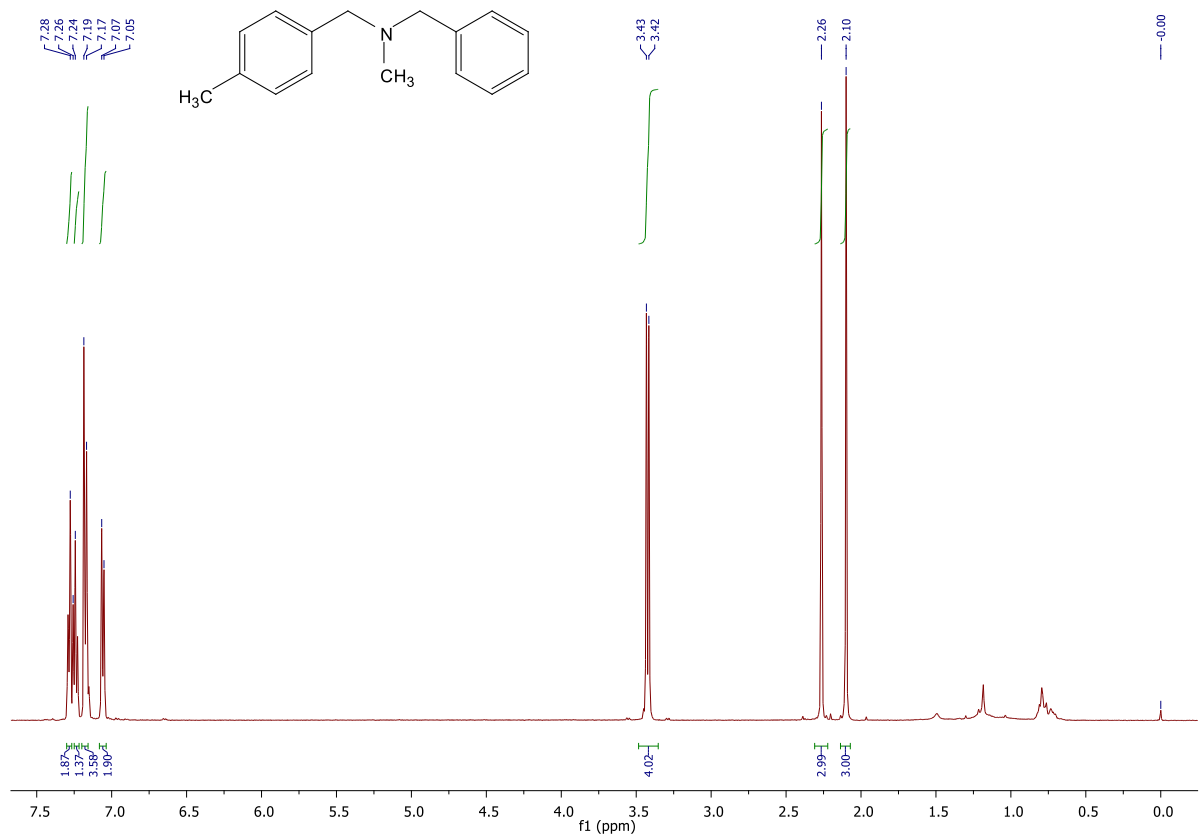


Figure S61. ¹H-NMR spectrum of amine 5i.

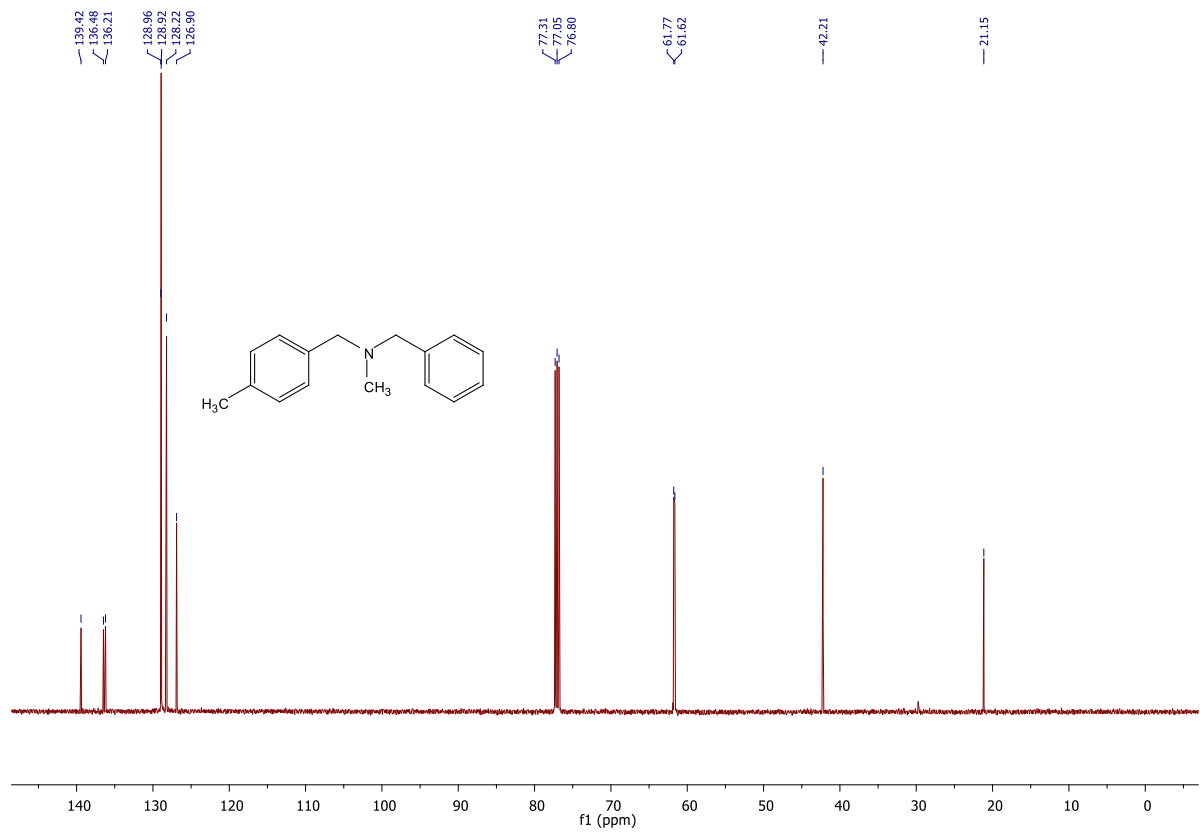


Figure S62. ¹³C-NMR spectrum of amine 5i.

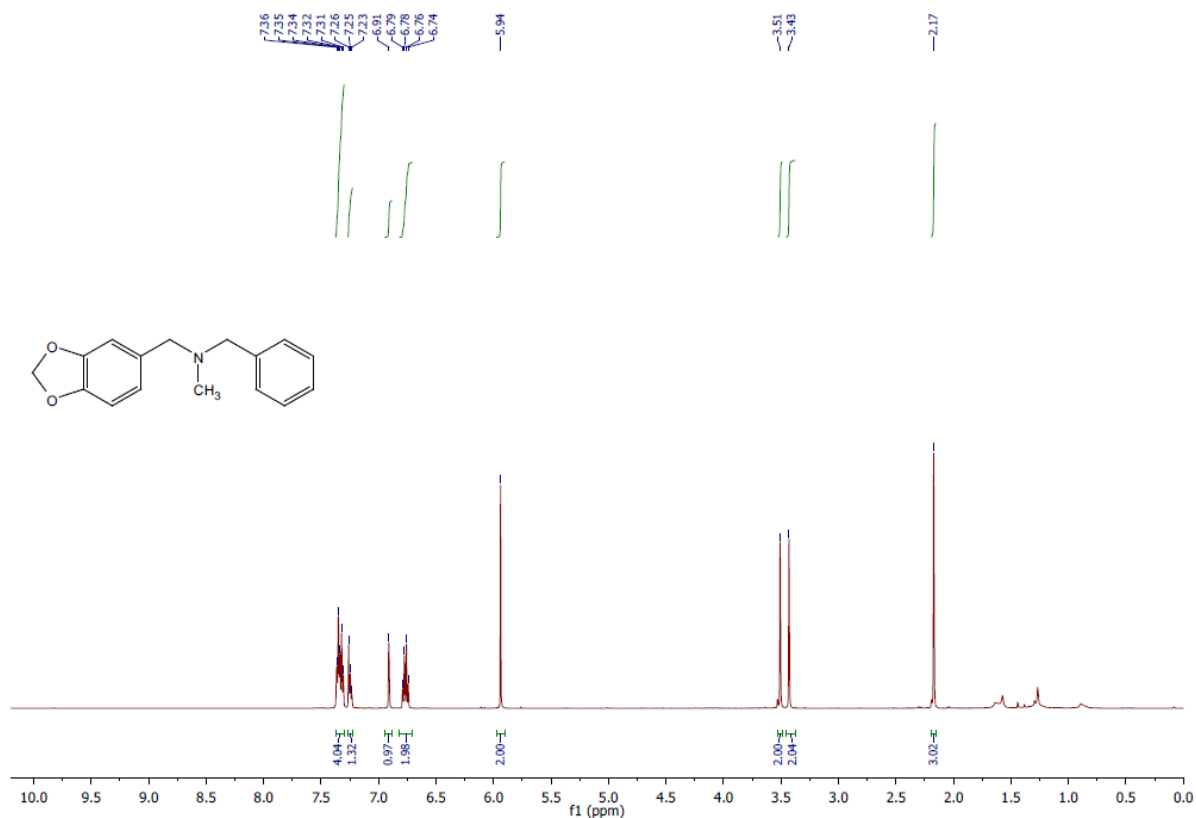


Figure S63. ¹H-NMR spectrum of amine 5j.

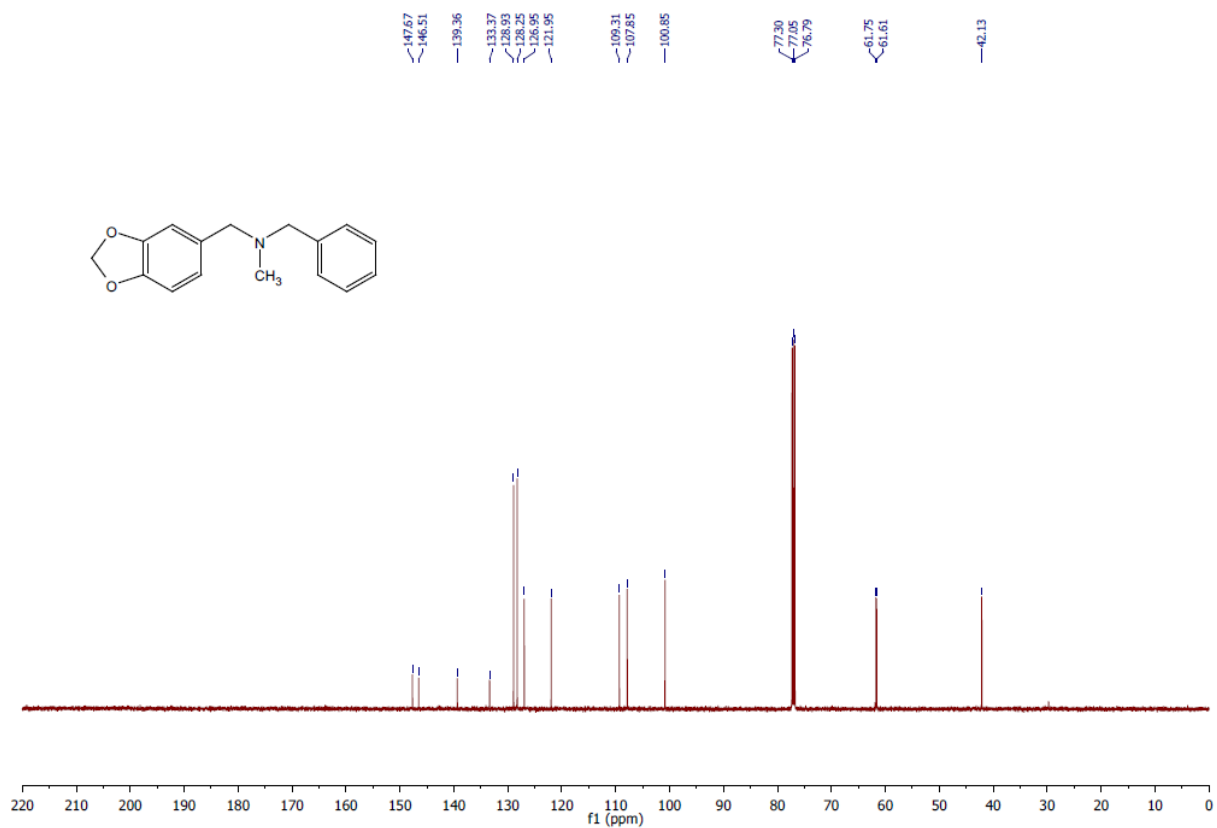


Figure S64. ¹³C-NMR spectrum of amine 5j.

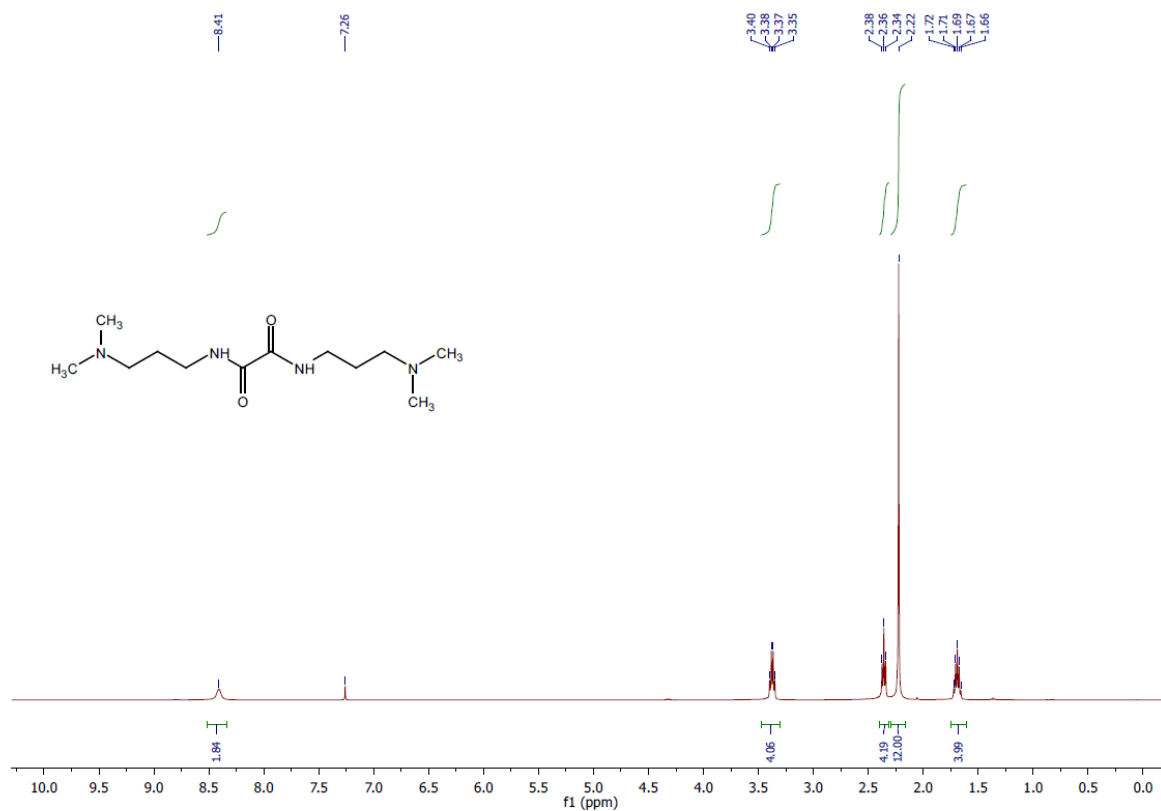


Figure S65: $^1\text{H-NMR}$ spectrum of N^1,N^2 -bis(3-(dimethylamino)propyl)oxalamide (5).

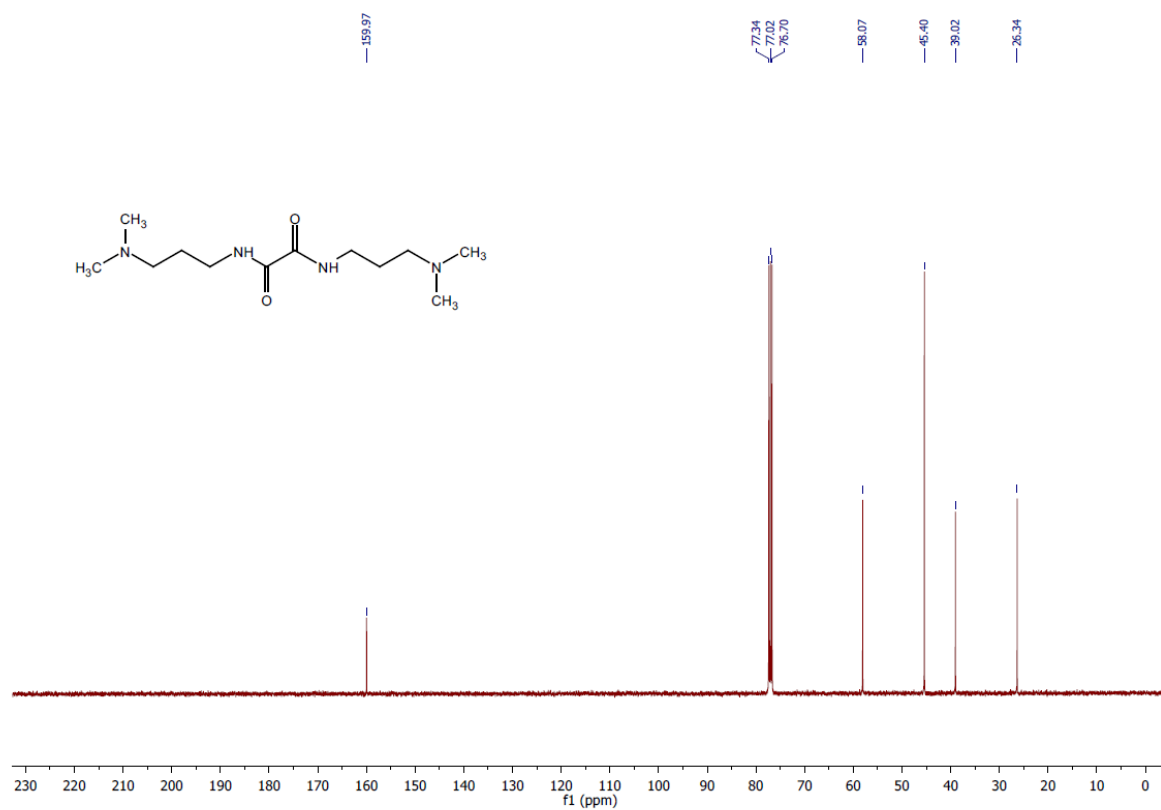


Figure S66: $^{13}\text{C-NMR}$ spectrum of N^1,N^2 -bis(3-(dimethylamino)propyl)oxalamide (5).

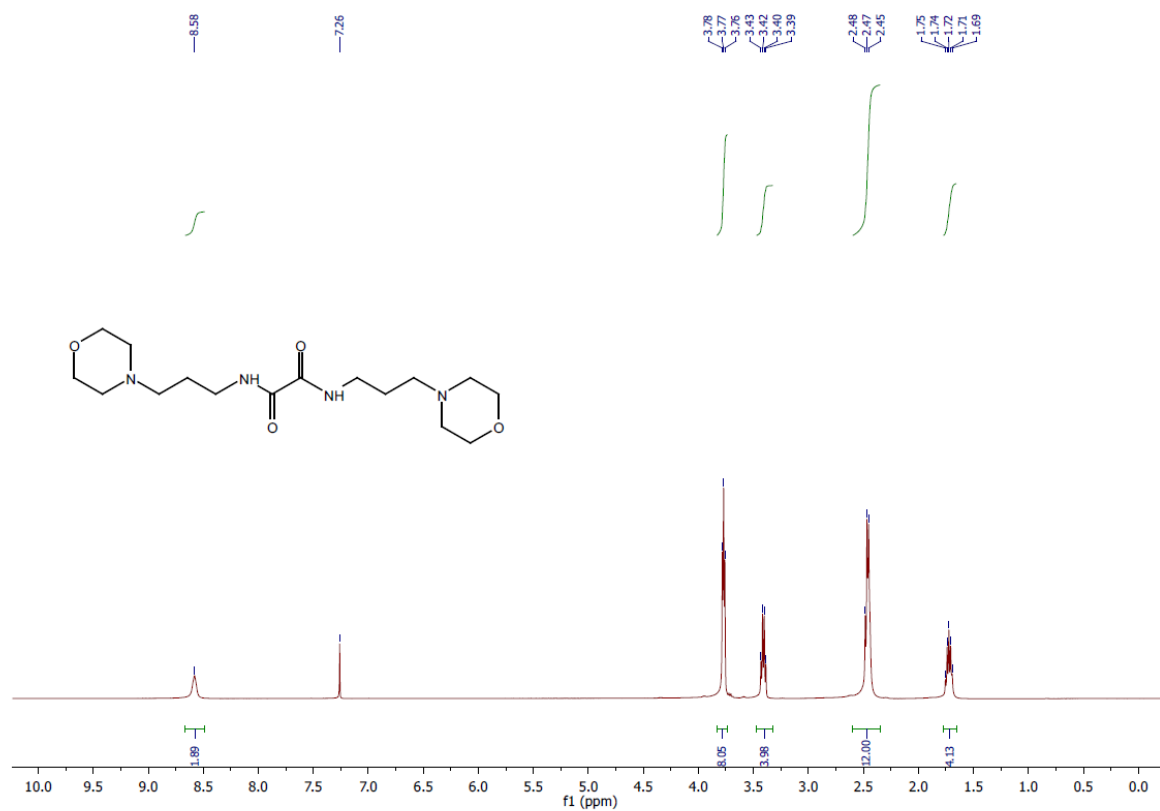


Figure S67: $^1\text{H-NMR}$ spectrum of N^1,N^2 -bis(3-morpholinopropyl)oxalamide (6).

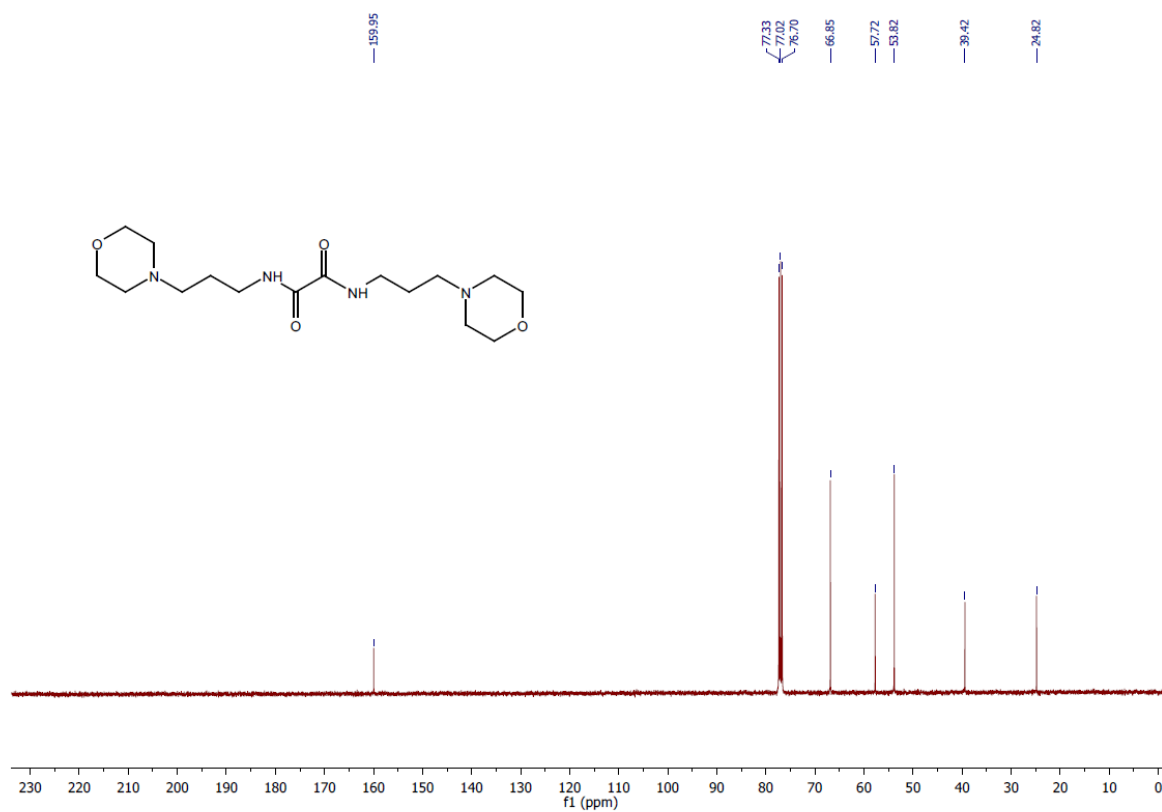


Figure S68: $^{13}\text{C-NMR}$ spectrum of N^1,N^2 -bis(3-morpholinopropyl)oxalamide (6).

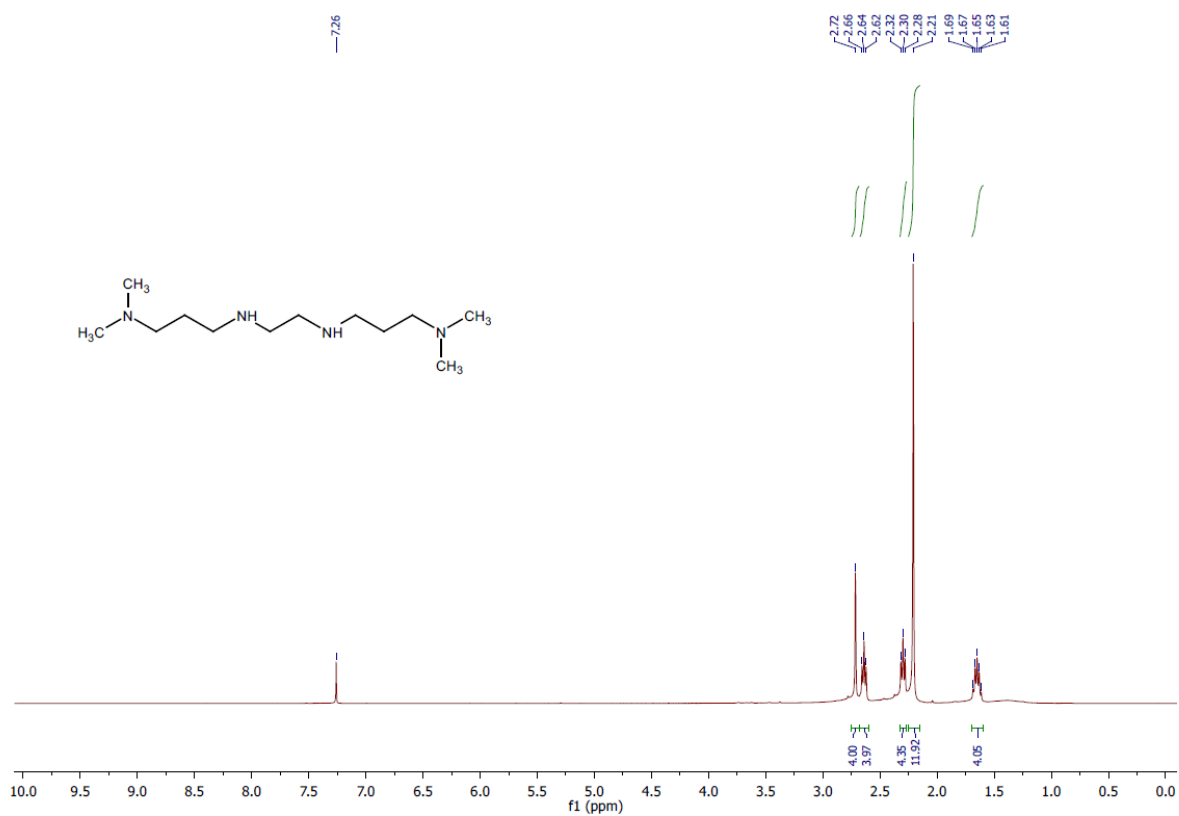


Figure S69: $^1\text{H-NMR}$ spectrum of $N^1,N^{1'}$ -(ethane-1,2-diyl)bis(N^3,N^3' -dimethylpropane-1,3-diamine) (**3**).

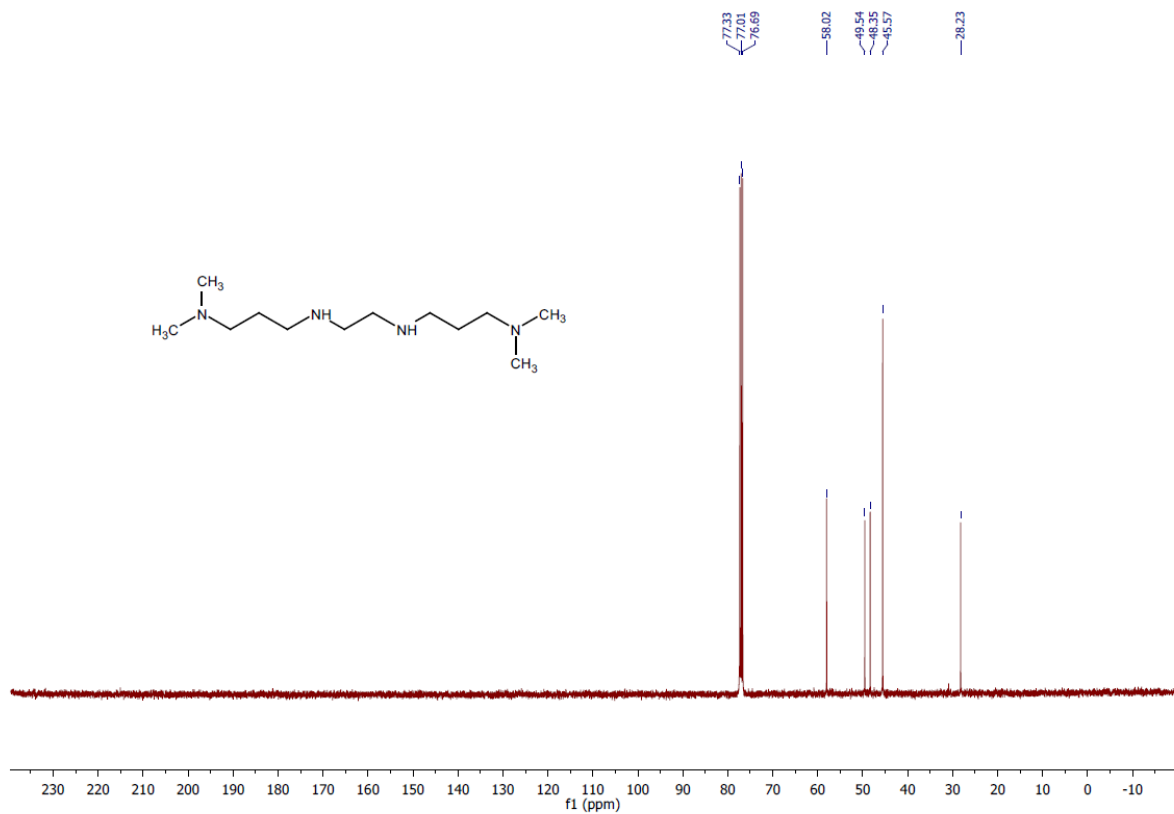
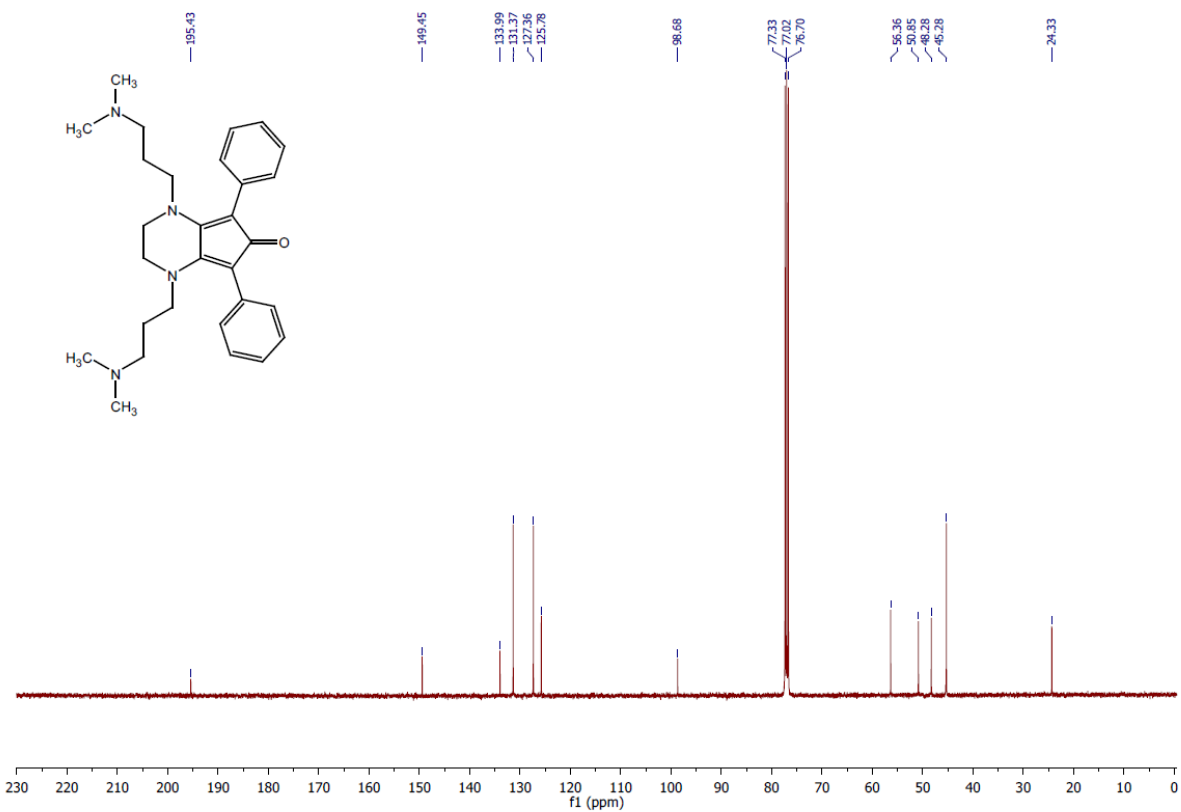
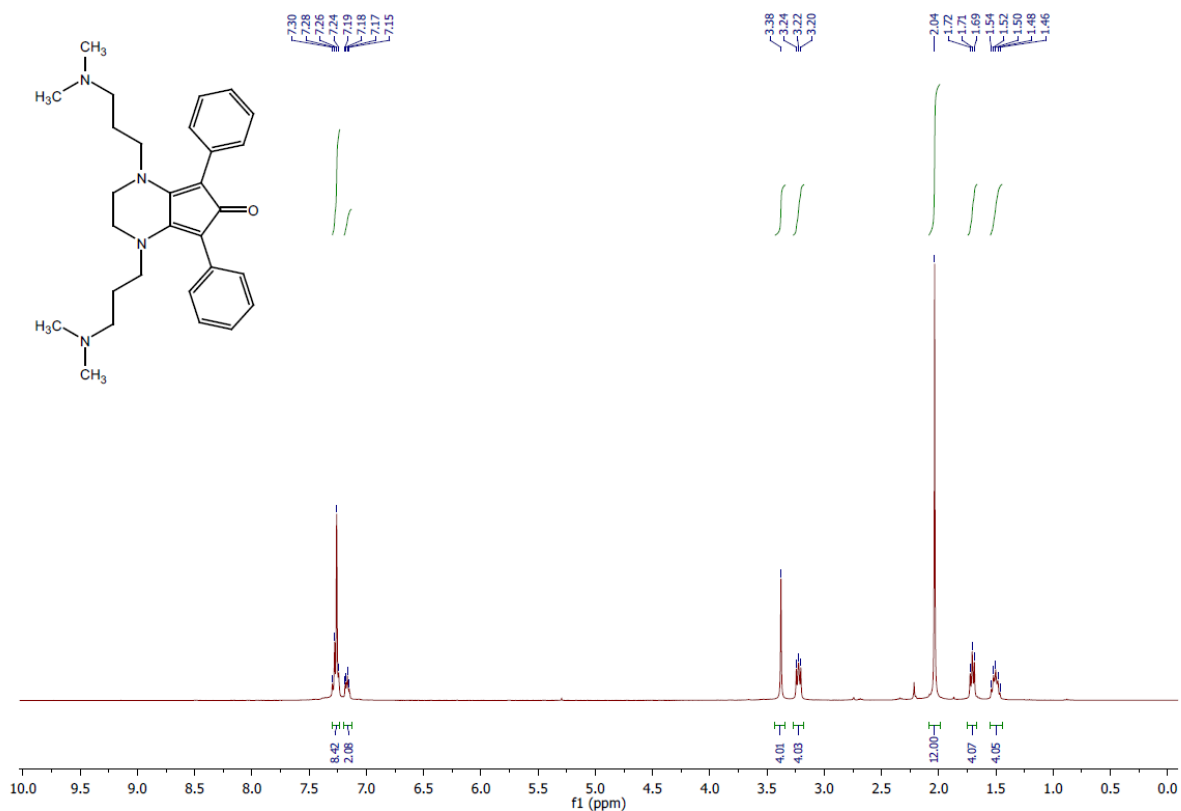


Figure S70: $^{13}\text{C-NMR}$ spectrum of $N^1,N^{1'}$ -(ethane-1,2-diyl)bis(N^3,N^3' -dimethylpropane-1,3-diamine) (**3**).



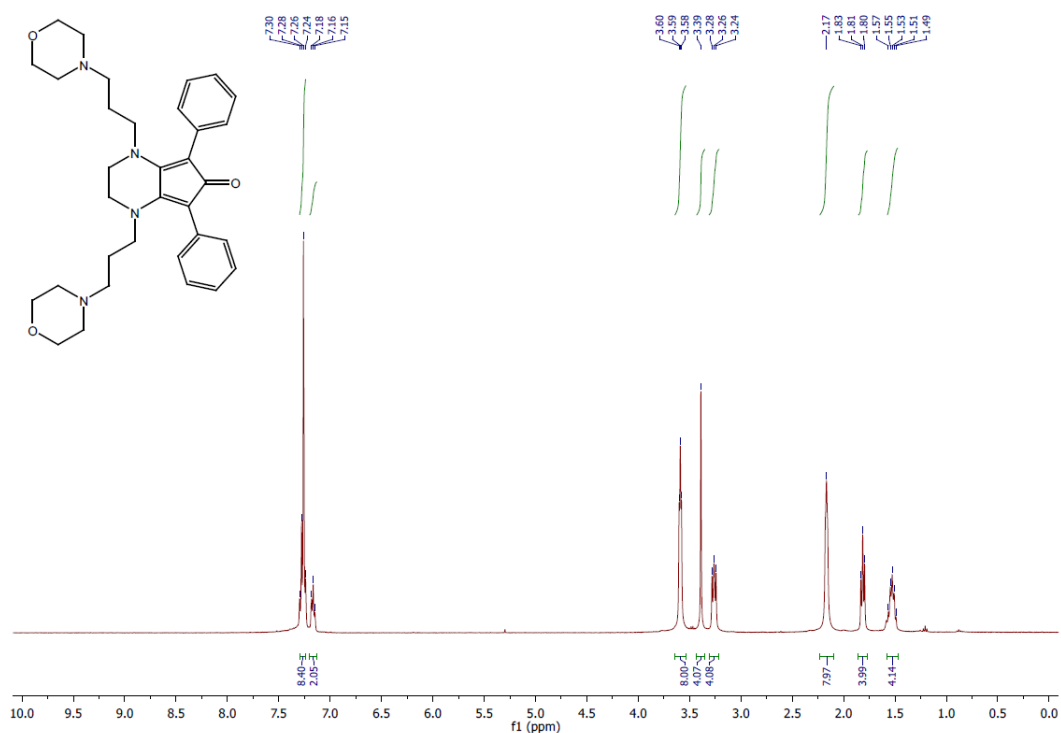


Figure S75: ¹H-NMR spectrum of 1,4-bis(3-morpholinopropyl)-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one (**2**).

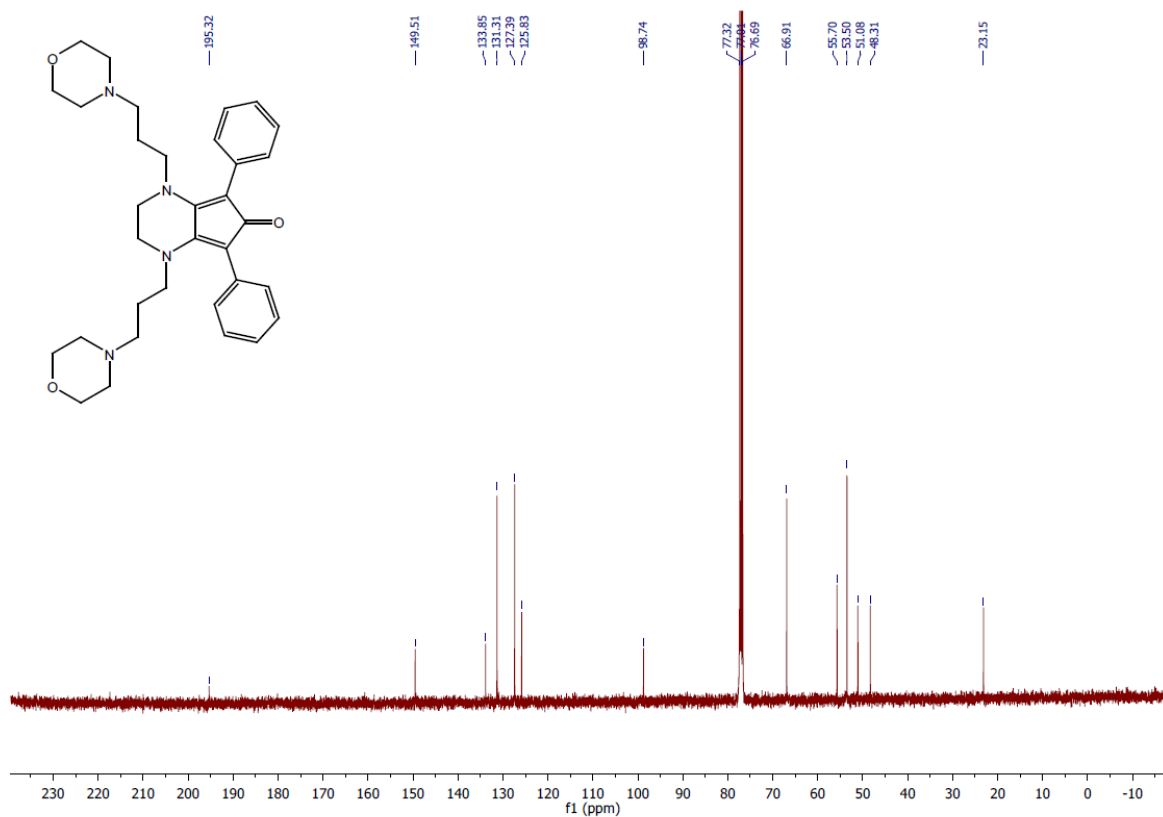


Figure S76: ¹³C-NMR spectrum of 1,4-bis(3-morpholinopropyl)-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one (**2**).

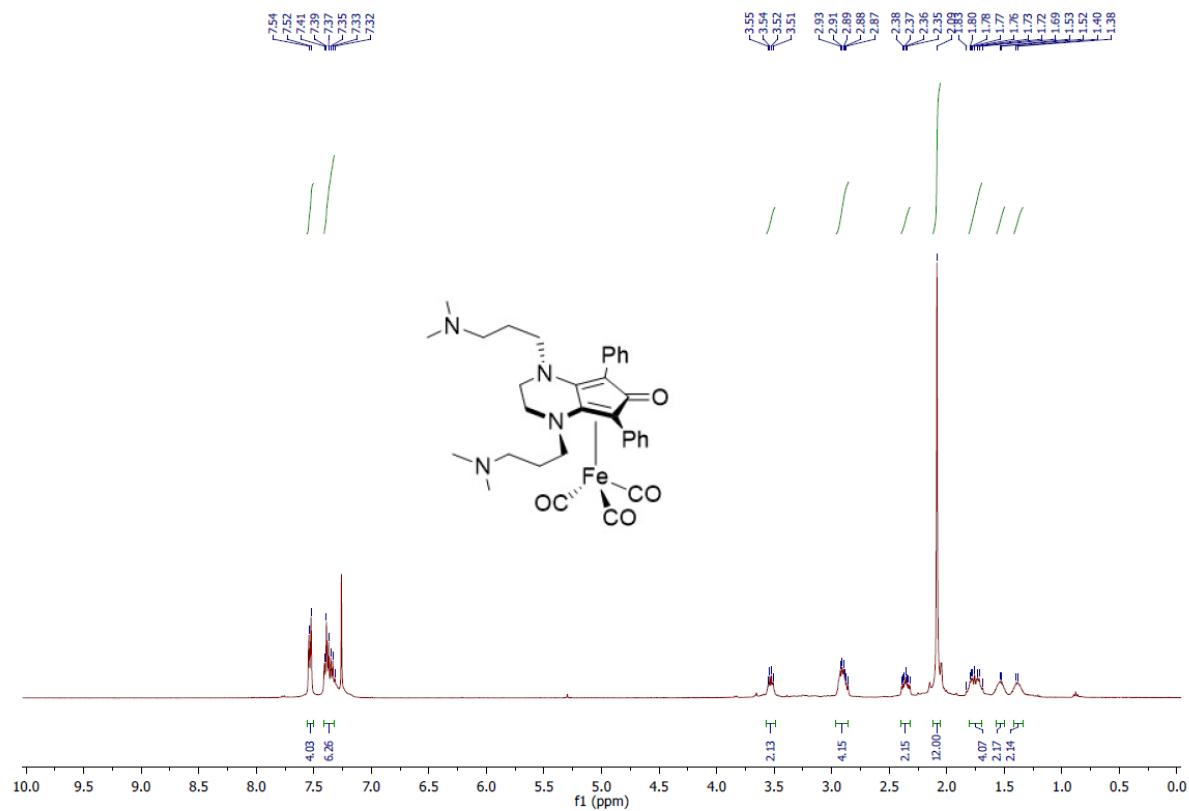


Figure S77: ¹H-NMR spectrum of iron complex Fe6.

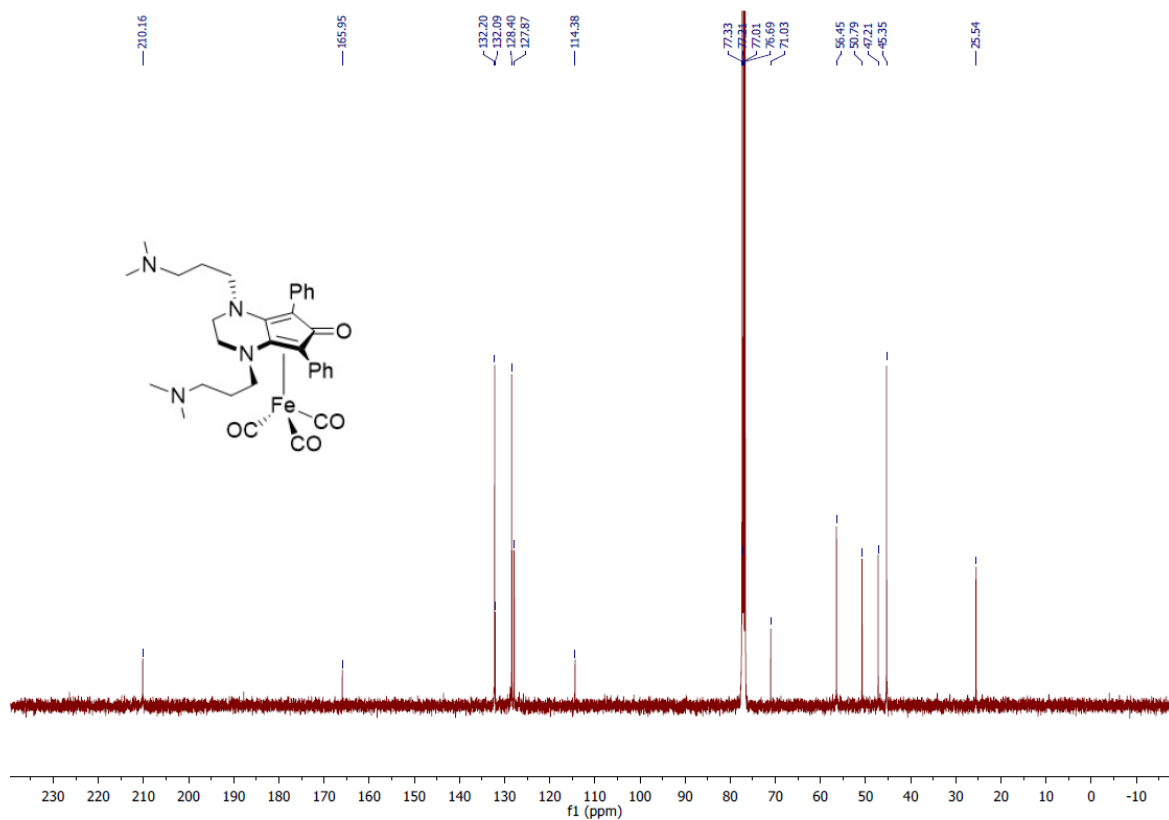


Figure S78: ¹³C-NMR spectrum of iron complex Fe6.

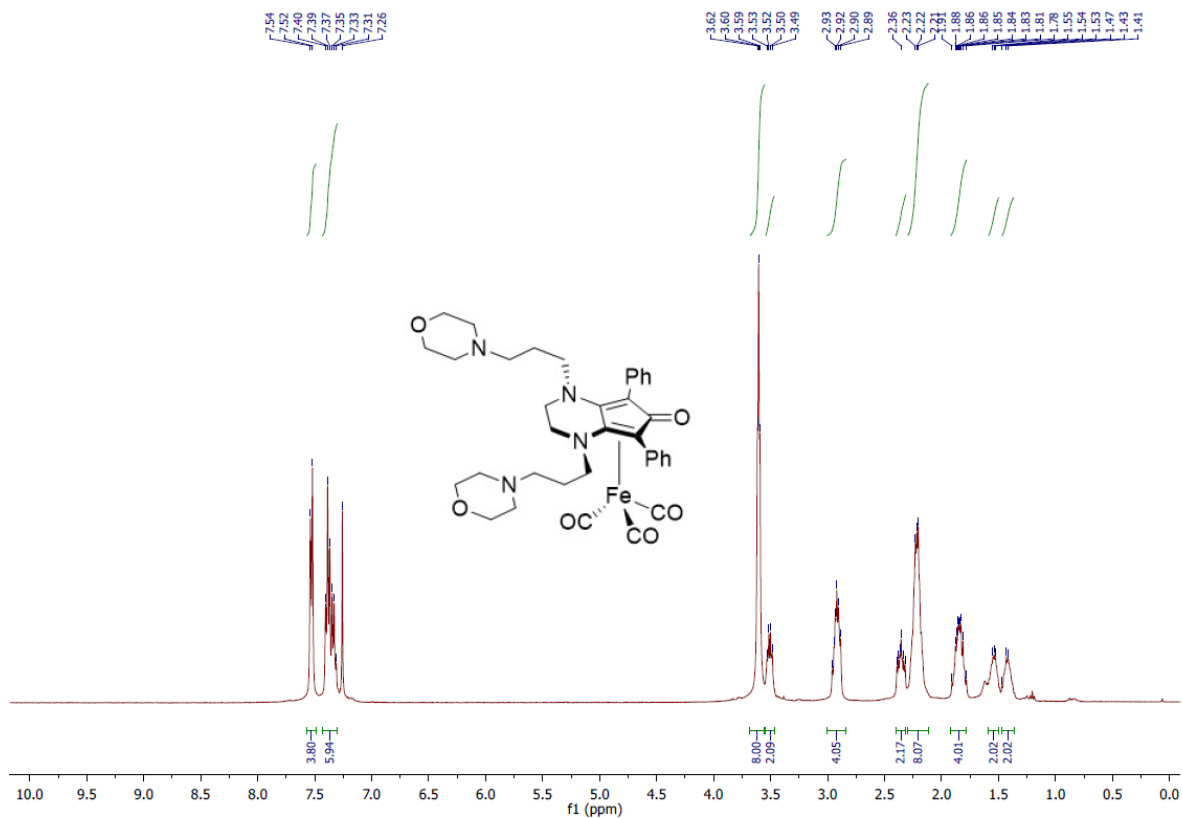


Figure S79: $^1\text{H-NMR}$ spectrum of iron complex Fe7.

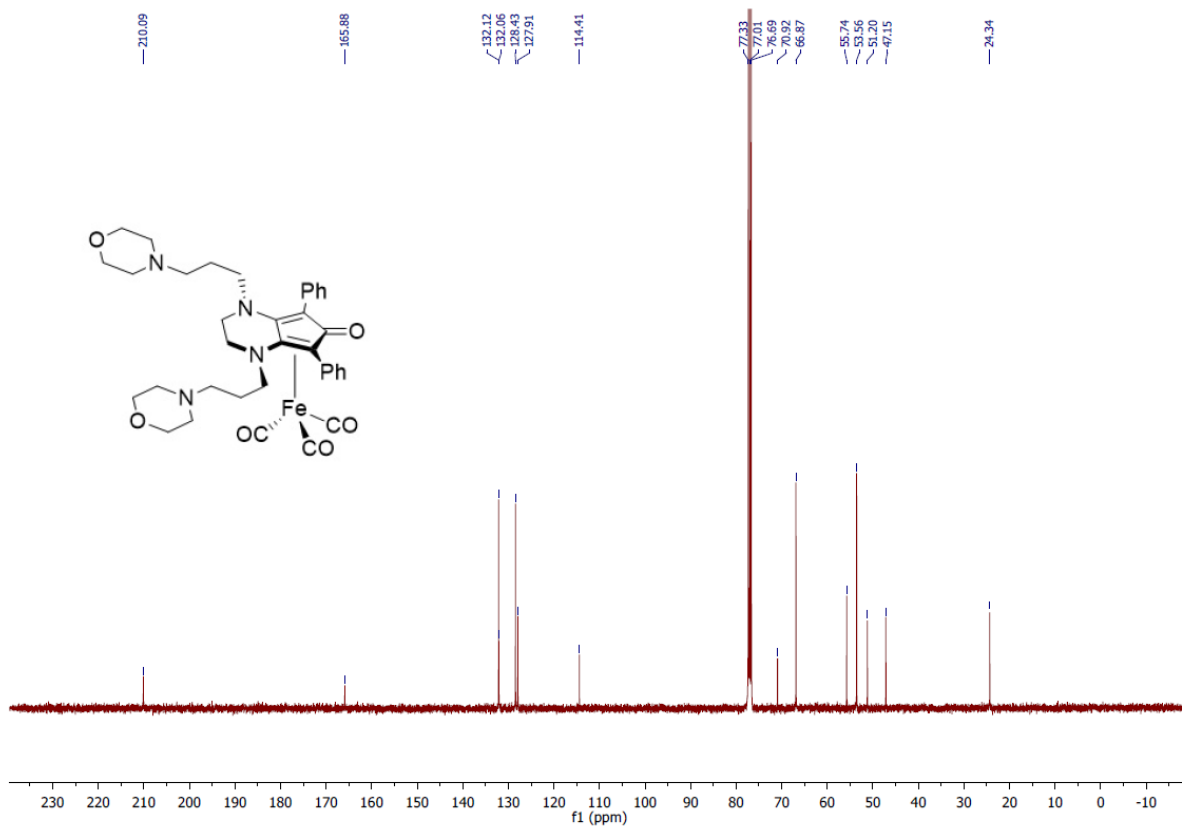


Figure S80: $^{13}\text{C-NMR}$ spectrum of iron complex Fe7.

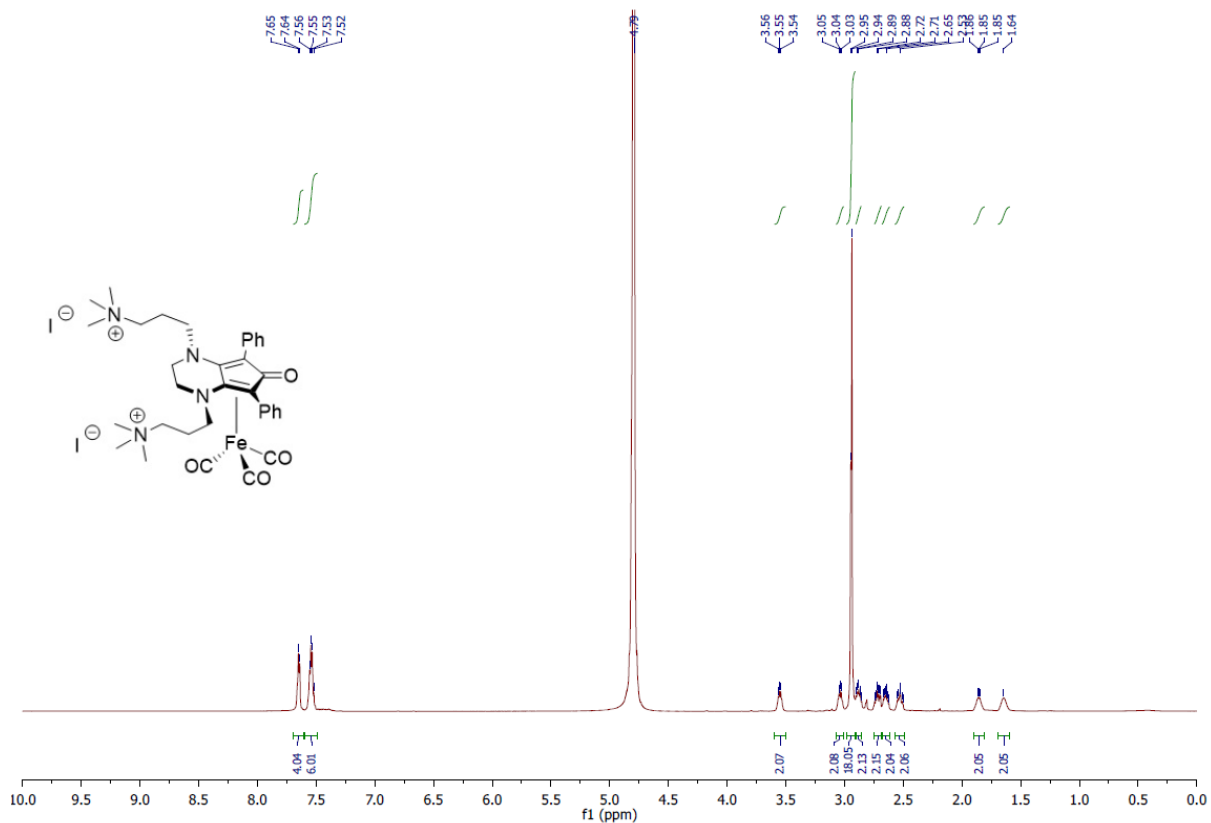


Figure S81: ^1H -NMR spectrum of water-soluble iron complex Fe4.

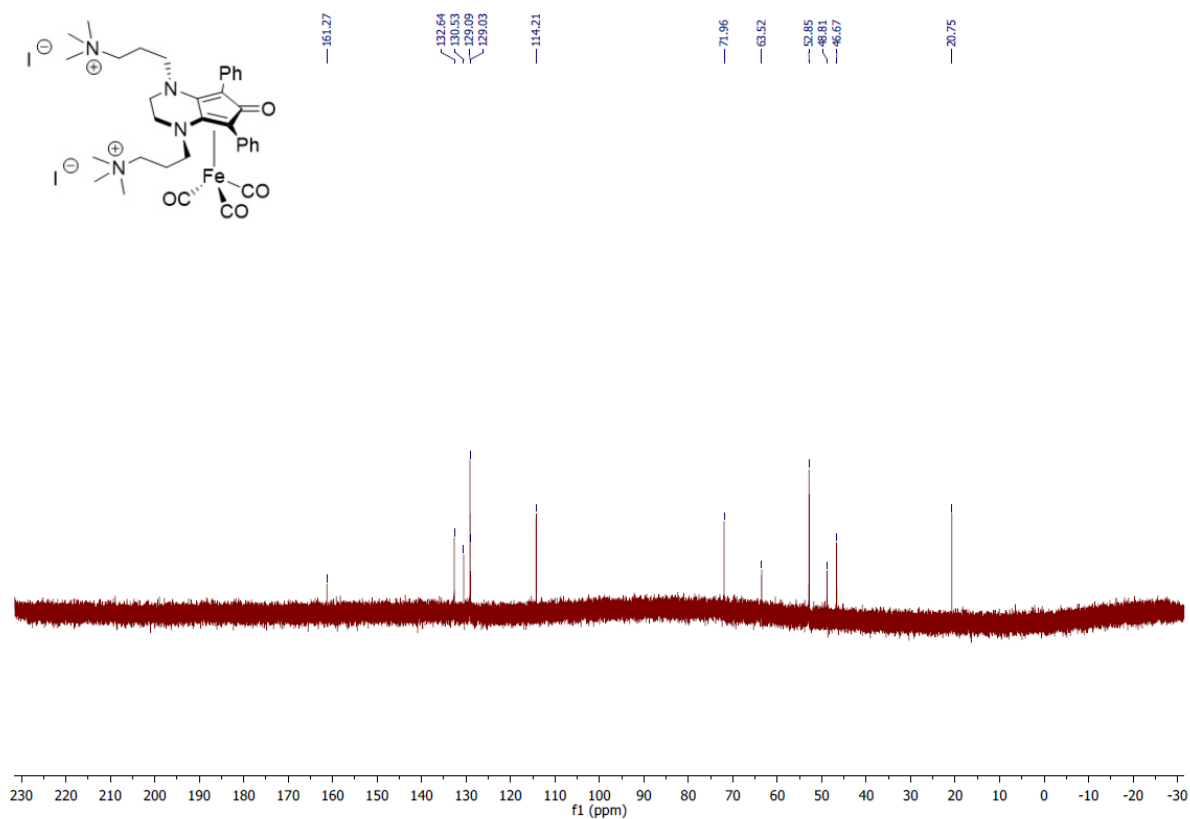


Figure S82: ^{13}C -NMR spectrum of water-soluble iron complex Fe4.

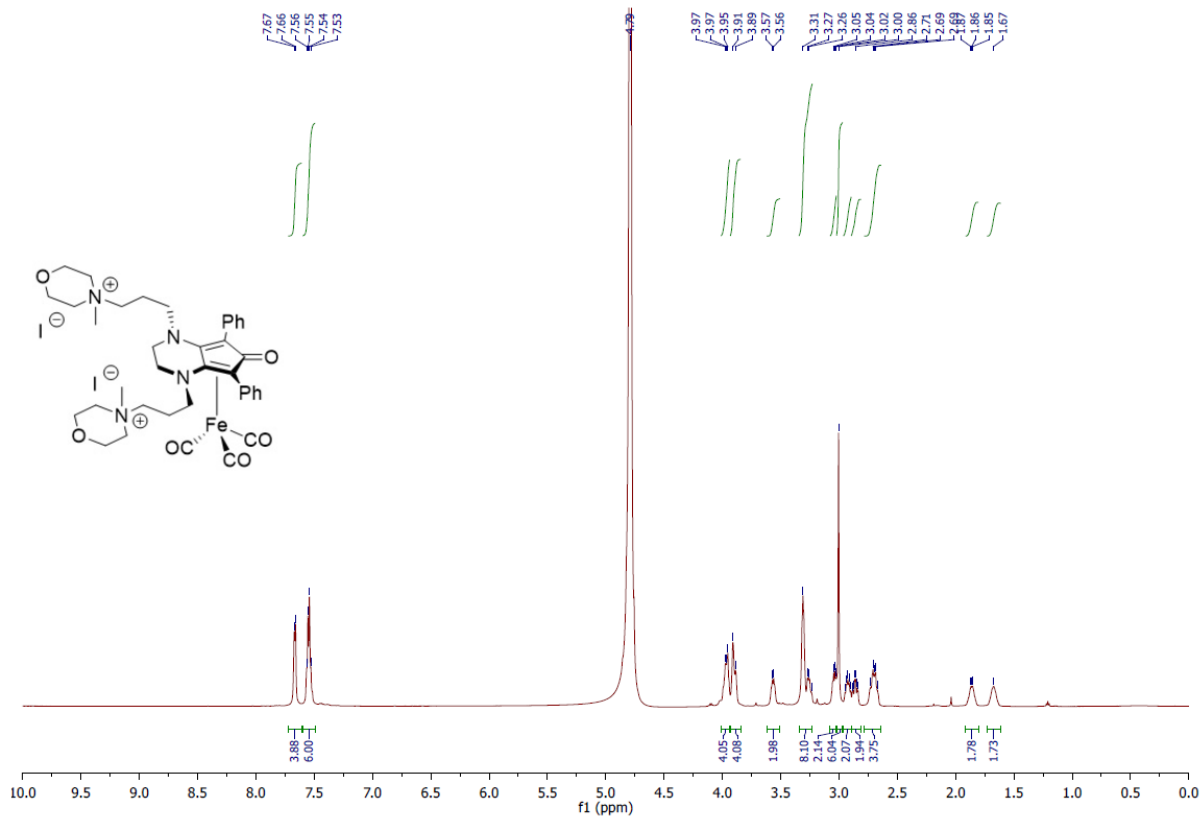


Figure S83: ¹H-NMR spectrum of water-soluble iron complex **Fe5**.

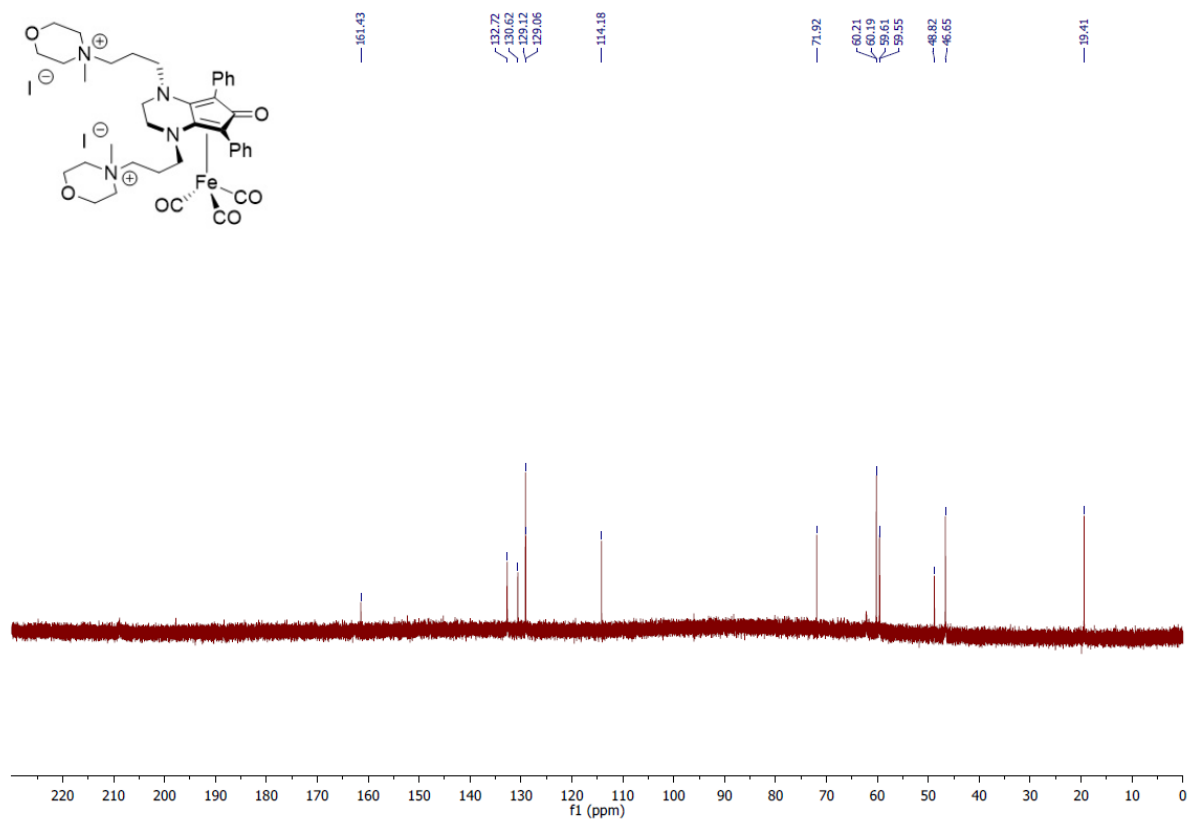


Figure S84: ¹³C-NMR spectrum of water-soluble iron complex **Fe5**.