Supplementary Information

Efficient catalytic upcycling of polyester and polycarbonate plastics using NNN-based iron catalyst

Chu et al.

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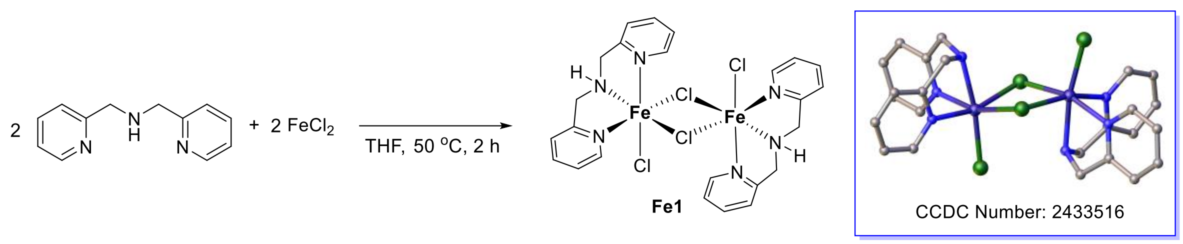
1. General information

All manipulations were done under a N_2 atmosphere using standard Schlenk line techniques or in a glovebox, unless otherwise stated. The reaction gas hydrogen (5.0) was supplied by Feiyuan and used without further purification. All reagents were purchased from Sigma-Aldrich, TCI or Acros and used without further purification. Methanol, toluene, and THF, were purified using a Glass Contour solvent purification system consisting of a neutral alumina, copper catalyst, and activated molecular sieves, then passed through an in-line, 2 μm filter immediately before being dispensed. $CDCl_3$ were dried over CaH_2 and purified by vacuum transfer. NMR spectra were recorded on Bruker Avance 500 spectrometer in NMR tubes at room temperature. ^{1}H and ^{13}C NMR chemical shifts are referenced to the proton signal of the deuterated solvent. MS (HRMS) measured with ThermoFisher Q-Exactive Mass Spectrometer.

2. Synthesis of the catalyst



Bis(pyridin-2-ylmethyl)amine (199 mg, 1 mmol) and $FeCl_2$ (125 mg, 1 mmol) were added to a Schlenk bottle with 20 mL THF. The mixture was heated to 50 ^{o}C and stirred for 2 hours. Then, the suspension was recrystallized at -30 ^{o}C and yellow microcrystals were obtained (267 mg, 82% yield).

3. General procedure for transfer hydrogenation of esters

In a glovebox under an N_2 atmosphere, a scintillation vial (with a magnetic stir bar) was charged with esters (1.0 mmol), and $H_3N{\cdot}BH_3$ (1.0 mmol, 31 mg). The catalyst **Fe1** (0.02 mmol, 7 mg), KO*t*Bu (0.05 mmol, 6 mg), and THF (2 mL) were added. The mixture was stirred at 60 ^{o}C. After the indicated time, the reaction mixture was isolated by chromatography on silica gel to give the product.

4. General procedure for catalytic methanolysis/hydrogenative depolymerization of polyester and polycarbonate plastics

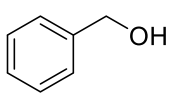
For all polymers, the used molar amount was calculated based on the respective repetition unit. In a glovebox under an N_2 atmosphere, a scintillation vial (with a magnetic stir bar) was charged with **Fe1** (0.02 mmol, 7 mg), KO*t*Bu (0.05 mmol, 6 mg), $H_3N \cdot BH_3$ (0.02 mmol, 1 mg) and MeOH (2 mL). Then, the polymer (1.0 mmol) was added. The mixture was stirred at 80 ^oC. After the indicated time, the reaction mixture was isolated by chromatography on silica gel to give the esters product. After that, the obtained esters were processed according to Section S3 to get diols.

5. General procedure for autoclave reactions

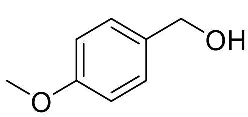
Experiments with compressed gases must be carried out only with appropriate equipment and under rigorous safety precautions.

Processed polymer was filled under air into a glass insert of an autoclave, a stir bar was added, and the insert was placed in a 250 mL steel autoclave. Subsequently, the autoclave was evacuated and backfilled with N_2 three times. **Fe1** and KO*t*Bu were weighed in a 10 mL Schlenk tube and dissolved in 5 mL THF. The solution was transferred via syringe, equipped with a cannular, into the autoclave in an N_2 counter stream. The autoclave was pressurized with 20 bar of H_2. The reaction was stirred at 120 °C for 24 hours. After completion of the reaction time, the autoclave was cooled down to room temperature in an ice bath and carefully vented to atmosphere. The reaction mixture was isolated by chromatography on silica gel to give the product.

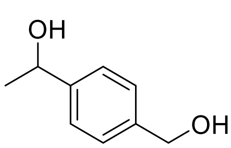
6. Characterization data for hydrogenation products



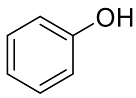
phenylmethanol (1-4): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.25 (m, 4H), 7.25-7.15 (m, 1H), 4.58 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.89 (s), 128.58 (s), 127.67 (s), 127.02 (s), 77.33 (s), 77.08 (s), 76.82 (s), 65.33 (s).



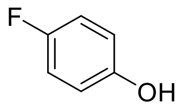
(4-methoxyphenyl)methanol (5): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 4.46 (s, 2H), 3.69 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.12 (s), 133.20 (s), 128.65 (s), 113.92 (s), 77.39 (s), 77.13 (s), 76.88 (s), 64.82 (s), 55.30 (s).



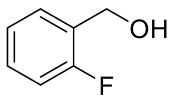
1-(4-(hydroxymethyl)phenyl)ethan-1-one (6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 17.15 (q, J = 8.1 Hz, 4H), 4.70 (q, J = 6.4 Hz, 1H), 4.45 (s, 2H), 1.33 (d, J = 6.5 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 145.10 (s), 139.99 (s), 127.09 (s), 125.54 (s), 77.37 (s), 77.11 (s), 76.86 (s), 69.97 (s), 64.62 (s), 25.13 (s).



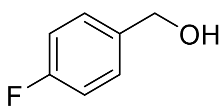
phenol (7): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.30 (m, 2H), 7.19 (dd, J = 13.3, 5.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.11 (s), 151.02 (s), 129.60 (s), 126.33 (s), 120.94 (s), 77.30 (s), 77.05 (s), 76.79 (s).



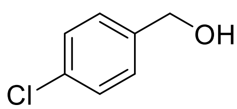
4-fluorophenol (8): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91-6.77 (m, 2H), 6.75-6.62 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.27 (s), 155.38 (s), 150.29 (d, J = 2.2 Hz), 115.47-115.02 (m), 114.92 (s), 76.27 (s), 76.01 (s), 75.76 (s).



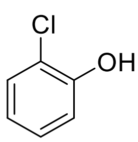
(2-fluorophenyl)methanol (9): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.23 (m, 1H), 7.15 (ddd, J = 7.4, 6.5, 1.6 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.96-6.87 (m, 1H), 4.58 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.55 (s), 159.60 (s), 129.42-129.18 (m), 127.82 (d, J = 14.7 Hz), 124.21 (d, J = 3.3 Hz), 115.29 (s), 115.12 (s), 77.38 (s), 77.12 (s), 76.87 (s), 59.04 (d, J = 4.5 Hz).



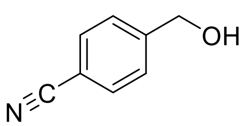
(4-fluorophenyl)methanol (10): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, J = 8.6, 5.5 Hz, 2H), 6.95 (t, J = 8.7 Hz, 2H), 4.54 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.28 (s), 161.33 (s), 136.58 (d, J = 3.1 Hz), 128.76 (d, J = 8.2 Hz), 115.46 (s), 115.29 (s), 77.31 (s), 77.06 (s), 76.81 (s), 64.56 (s).



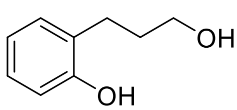
(4-chlorophenyl)methanol (11): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dt, J = 17.4, 5.3 Hz, 4H), 4.60 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.26 (s), 133.38 (s), 128.70 (s), 128.29 (s), 77.28 (s), 77.03 (s), 76.77 (s), 64.59 (s).



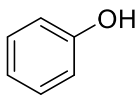
2-chlorophenol (12): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (dd, J = 8.0, 1.3 Hz, 1H), 7.03 (td, J = 8.2, 1.4 Hz, 1H), 6.90 (dd, J = 8.2, 1.3 Hz, 1H), 6.72 (td, J = 8.0, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.26 (s), 127.98 (s), 127.34 (s), 120.35 (s), 118.86 (s), 115.27 (s), 76.29 (s), 76.03 (s), 75.78 (s).



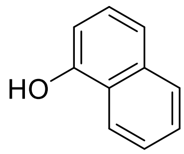
4-(hydroxymethyl)benzonitrile (13): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J = 8.1 Hz, 3H), 7.23 (d, J = 8.0 Hz, 1H), 4.60 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.90 (s), 128.04 (s), 127.06 (s), 126.59 (s), 116.90 (s), 76.31 (s), 76.05 (s), 75.80 (s), 63.55 (s), 22.30 (s).



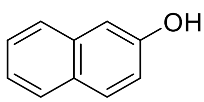
2-(3-hydroxypropyl)phenol (14): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (ddd, J = 6.8, 5.5, 1.6 Hz, 2H), 6.78 (td, J = 8.3, 2.4 Hz, 2H), 3.56 (t, J = 5.8 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 1.84-1.75 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.45 (s), 129.62 (s), 126.53 (s), 126.26 (s), 119.79 (s), 115.00 (s), 76.26 (s), 76.01 (s), 75.75 (s), 59.78 (s), 31.22 (s), 24.17 (s).



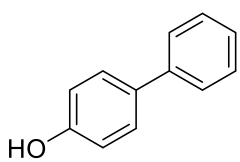
phenol (15-17): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 7.8 Hz, 2H), 6.86 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.37 (s), 128.66 (s), 119.82 (s), 114.27 (s), 76.25 (s), 76.00 (s), 75.74 (s).



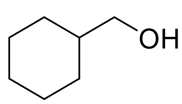
naphthalen-1-ol (18): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24-8.09 (m, 1H), 7.89-7.74 (m, 1H), 7.60-7.39 (m, 3H), 7.30 (t, J = 7.8 Hz, 1H), 6.80 (d, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.37 (s), 134.78 (s), 127.71 (s), 126.47 (s), 125.86 (s), 125.30 (s), 124.36 (s), 121.55 (s), 120.73 (s), 108.63 (s), 77.31 (s), 77.06 (s), 76.80 (s).



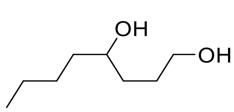
naphthalen-2-ol (19): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (t, J = 8.0 Hz, 2H), 7.61 (d, J = 8.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 7.03 (dd, J = 8.8, 2.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.28 (s), 133.56 (s), 128.84 (s), 127.94 (s), 126.74 (s), 125.52 (s), 125.33 (s), 122.61 (s), 116.69 (s), 108.46 (s), 76.24 (s), 75.99 (s), 75.74 (s).



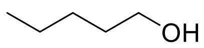
[1,1'-biphenyl]-4-ol (20): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.49-7.46 (m, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 4.6 Hz, 1H), 6.92-6.87 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.10 (s), 140.76 (s), 134.00 (s), 128.67 (d, J = 13.6 Hz), 128.39 (s), 127.06 (s), 126.71 (d, J = 2.4 Hz), 115.64 (s), 77.25 (d, J = 6.0 Hz), 77.02 (s), 76.76 (s).



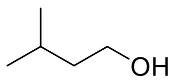
cyclohexylmethanol (21): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (d, J = 6.4 Hz, 2H), 1.77-1.56 (m, 5H), 1.46-1.33 (m, 1H), 1.24-1.06 (m, 3H), 0.94-0.80 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 76.33 (s), 76.07 (s), 75.82 (s), 67.64 (s), 39.44 (s), 28.51 (d, J = 17.0 Hz), 25.59 (s), 24.84 (s).



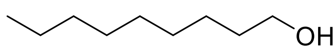
octane-1,4-diol (22): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.53-4.33 (m, 1H), 2.46 (dd, J = 9.6, 7.0 Hz, 2H), 2.26 (td, J = 13.4, 6.7 Hz, 1H), 1.79 (dtd, J = 12.7, 9.5, 8.2 Hz, 1H), 1.67 (dddd, J = 13.4, 9.9, 8.3, 4.8 Hz, 1H), 1.58-1.47 (m, 1H), 1.42-1.22 (m, 4H), 0.85 (dd, J = 9.4, 4.7 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 176.36 (s), 80.09 (s), 76.47 (s), 76.22 (s), 75.96 (s), 34.25 (s), 27.86 (s), 27.00 (s), 26.34 (s), 21.42 (s), 12.91 (s).



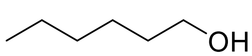
pentan-1-ol (23): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (t, J = 6.7 Hz, 2H), 1.58-1.42 (m, 2H), 1.32-1.16 (m, 4H), 0.83 (dd, J = 9.6, 4.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 76.36 (s), 76.22 (d, J = 32.0 Hz), 75.83 (s), 61.84 (s), 31.42 (s), 26.93 (s), 21.50 (s), 13.03 (s).



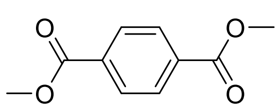
3-methylbutan-1-ol (24): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.52 (t, J = 7.1 Hz, 2H), 1.62 (dt, J = 13.4, 6.7 Hz, 1H), 1.36 (dd, J = 14.1, 7.0 Hz, 2H), 0.83 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 76.35 (s), 76.09 (s), 75.84 (s), 60.07 (s), 40.63 (s), 23.69 (s), 21.60 (s).



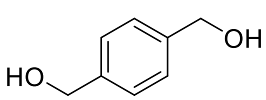
nonan-1-ol (25): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.56 (t, J = 6.7 Hz, 2H), 1.68 (s, 1H), 1.57-1.41 (m, 2H), 1.34-1.10 (m, 11H), 0.81 (t, J = 6.9 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 76.29 (s), 76.03 (s), 75.78 (s), 62.01 (s), 31.78 (s), 30.81 (s), 28.70 (s), 28.34 (d, J = 15.5 Hz), 24.75 (s), 21.65 (s), 13.07 (s).



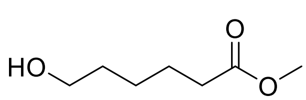
hexan-1-ol (26): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.57 (s, 2H), 1.49 (d, J = 6.0 Hz, 2H), 1.24 (s, 6H), 0.83 (s, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 76.14 (d, J = 32.0 Hz), 76.00-75.96 (m), 75.76 (s), 31.75 (s), 30.62 (s), 24.40 (s), 21.62 (s), 13.02 (s).



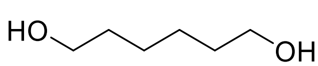
dimethyl terephthalate (P1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 4H), 3.88 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.32 (s), 133.92 (s), 129.58 (s), 77.28 (s), 77.03 (s), 76.77 (s), 52.47 (s).



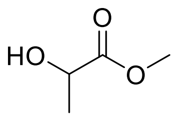
1,4-phenylenedimethanol (P1'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 4H), 4.63 (s, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 139.30 (s), 126.23 (s), 76.25 (s), 75.99 (s), 75.74 (s), 64.12 (s).



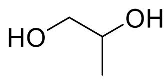
methyl 6-hydroxyhexanoate (P2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.54 (s, 3H), 3.48 (t, J = 6.6 Hz, 2H), 2.95 (d, J = 4.0 Hz, 1H), 2.20 (t, J = 7.5 Hz, 2H), 1.53 (dt, J = 15.3, 7.5 Hz, 2H), 1.48-1.39 (m, 2H), 1.35-1.17 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.37 (s), 76.55 (s), 76.29 (s), 76.04 (s), 61.22 (s), 50.51 (s), 32.99 (s), 31.24 (s), 24.33 (s), 23.68 (s).



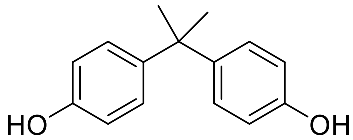
hexane-1,6-diol (P2'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (t, J = 6.0 Hz, 4H), 1.52 (s, 4H), 1.34 (d, J = 6.8 Hz, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 76.28 (s), 76.03 (s), 75.77 (s), 61.76 (s), 31.61 (s), 24.49 (s).



methyl 2-hydroxypropanoate (P3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 (q, J = 6.9 Hz, 1H), 3.70 (d, J = 9.6 Hz, 3H), 1.35 (d, J = 6.9 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 175.12 (s), 76.47 (s), 76.22 (s), 75.96 (s), 65.80 (s), 51.43 (s), 19.30 (d, J = 3.5 Hz).



propane-1,2-diol (P3'): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95-3.61 (m, 1H), 3.48 (dd, J = 11.4, 3.0 Hz, 1H), 3.29 (dd, J = 11.4, 7.8 Hz, 1H), 1.05 (d, J = 6.5 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 76.44 (s), 76.19 (s), 75.93 (s), 67.29 (s), 66.78 (s), 17.69 (s).



4,4'-(propane-2,2-diyl)diphenol (P4): ^{1}H NMR (500 MHz, MeOD) δ 7.02 (d, J = 8.6 Hz, 4H), 6.66 (d, J = 8.7 Hz, 4H), 1.57 (s, 6H).^{13}C NMR (126 MHz, MeOD) δ 154.53 (s), 142.09 (s), 127.35 (s), 114.15 (s), 48.14 (s), 47.97 (s), 47.80 (s), 47.63 (s), 47.46 (s), 47.29 (s), 47.12 (s), 41.10 (s), 30.30 (s).

7. NMR spectra of the products

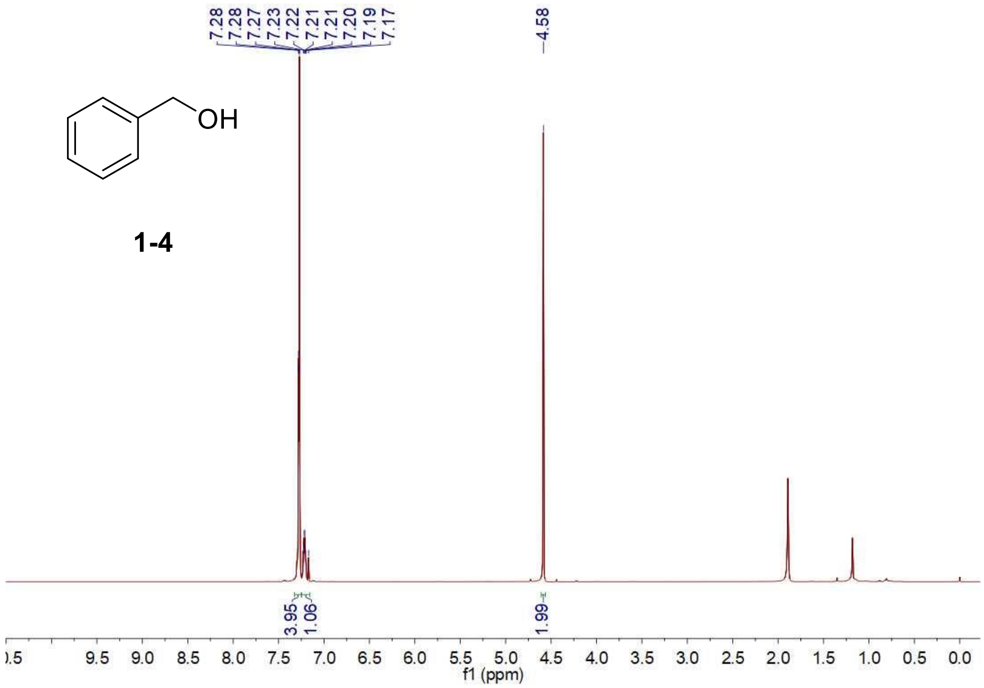


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1**.

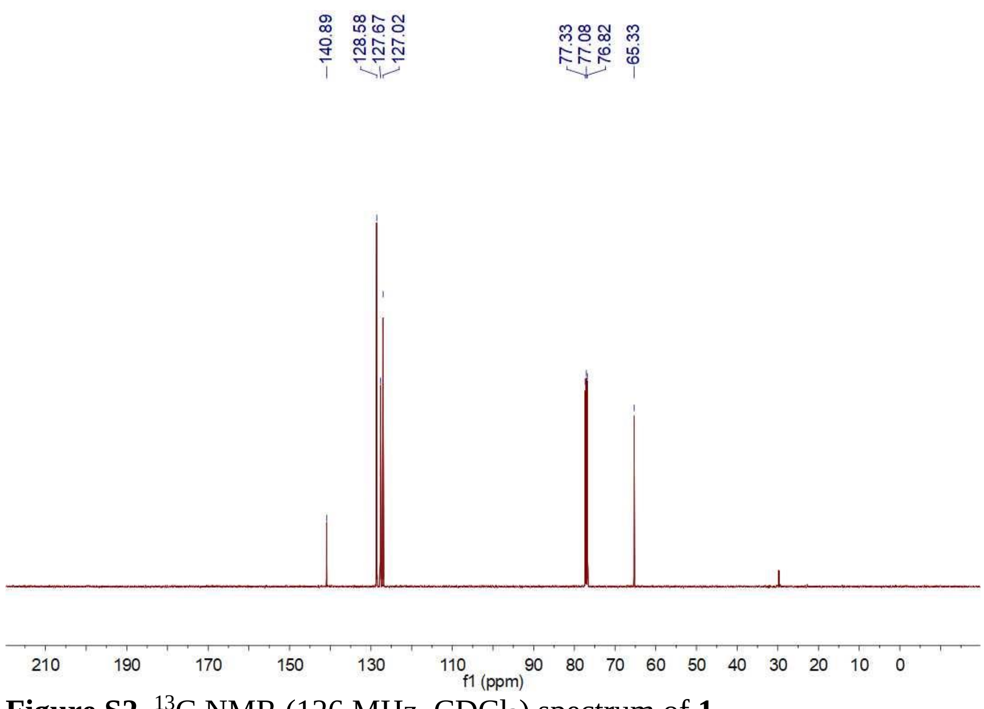


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **1**.

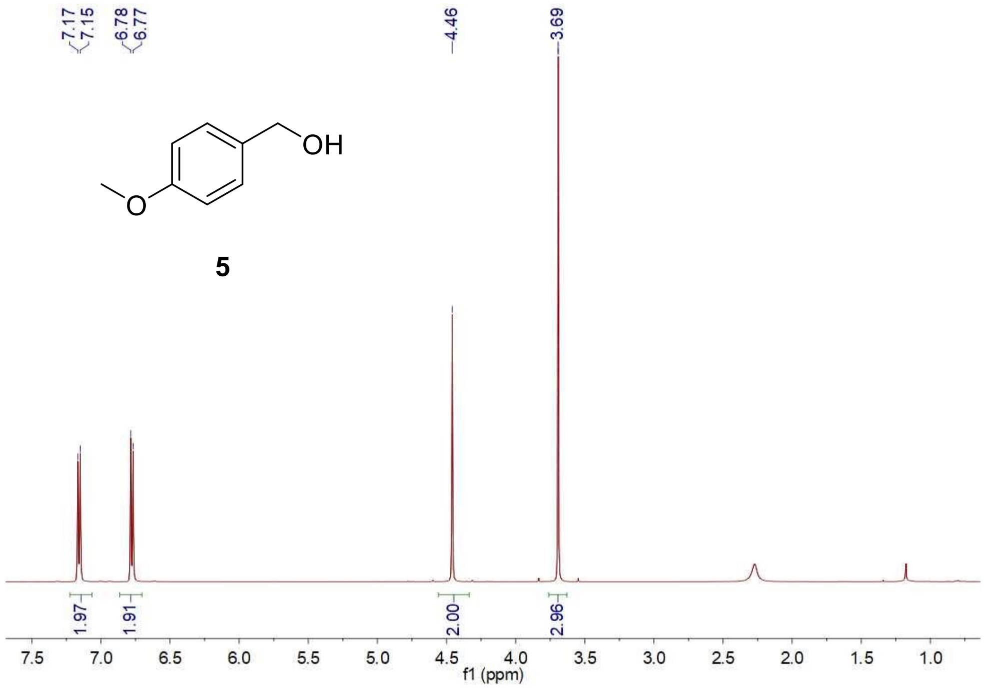


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Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5**.

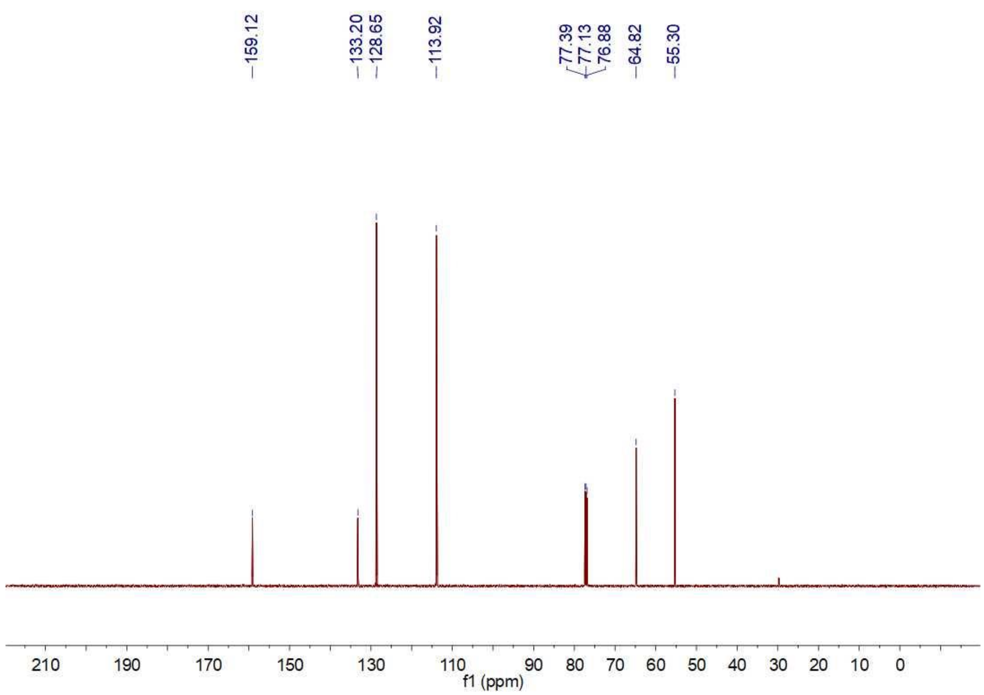

Figure S4. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **5**.

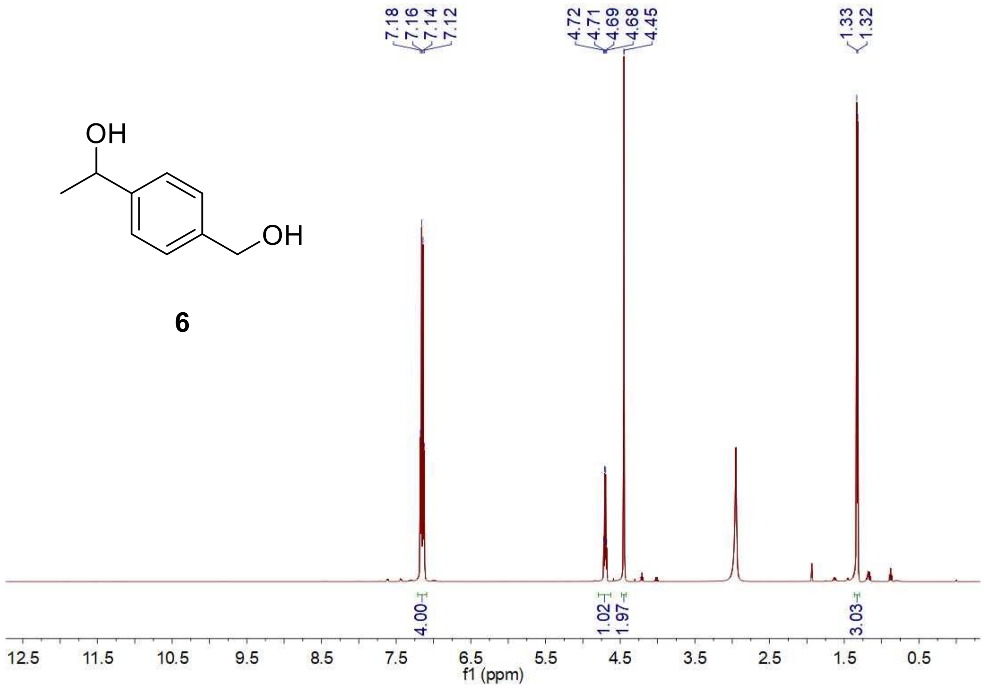

Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6**.

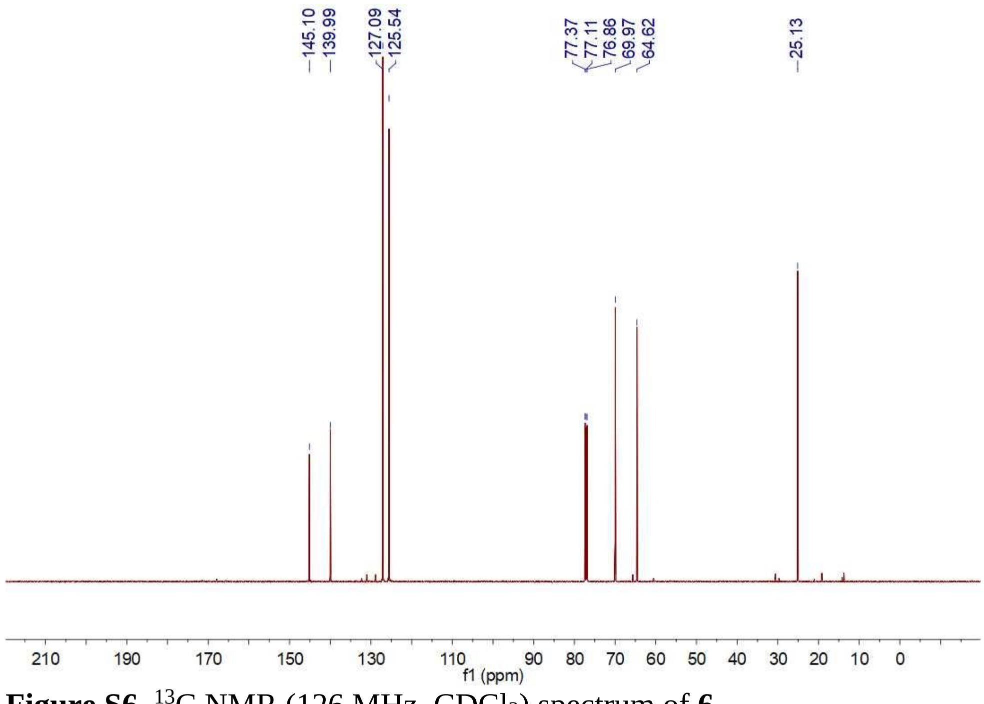

Figure S6. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **6**.

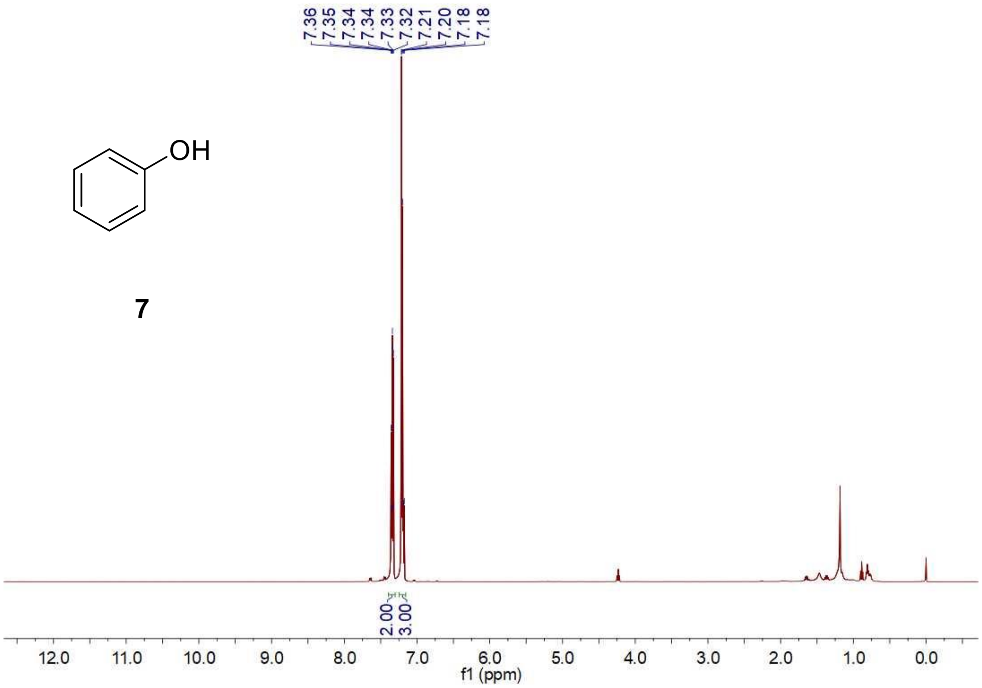

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Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7**.

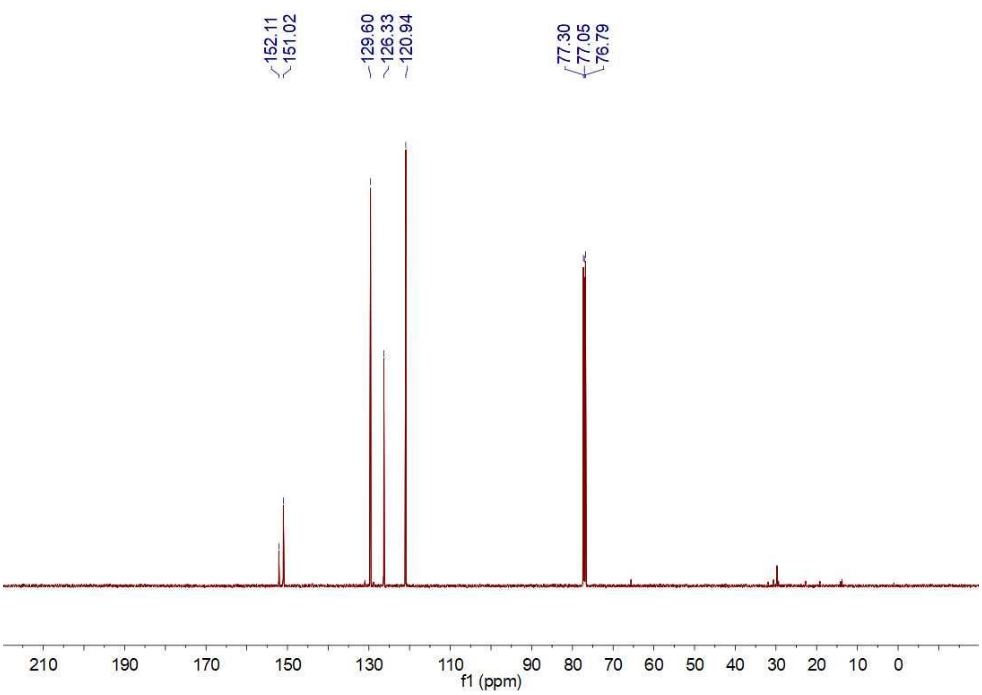

Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **7**.

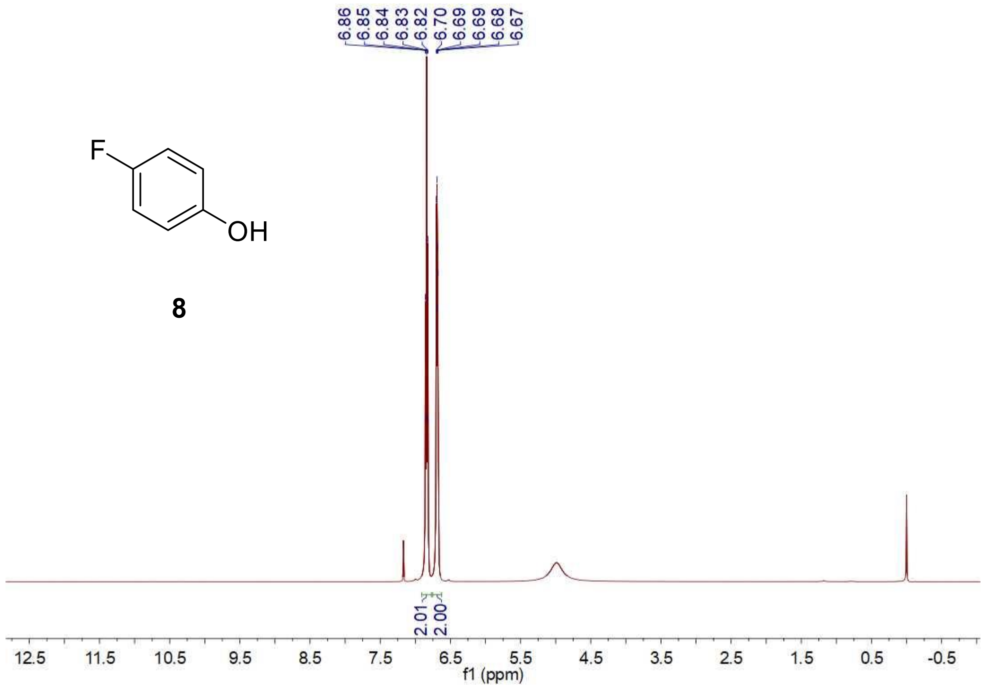

Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8**.

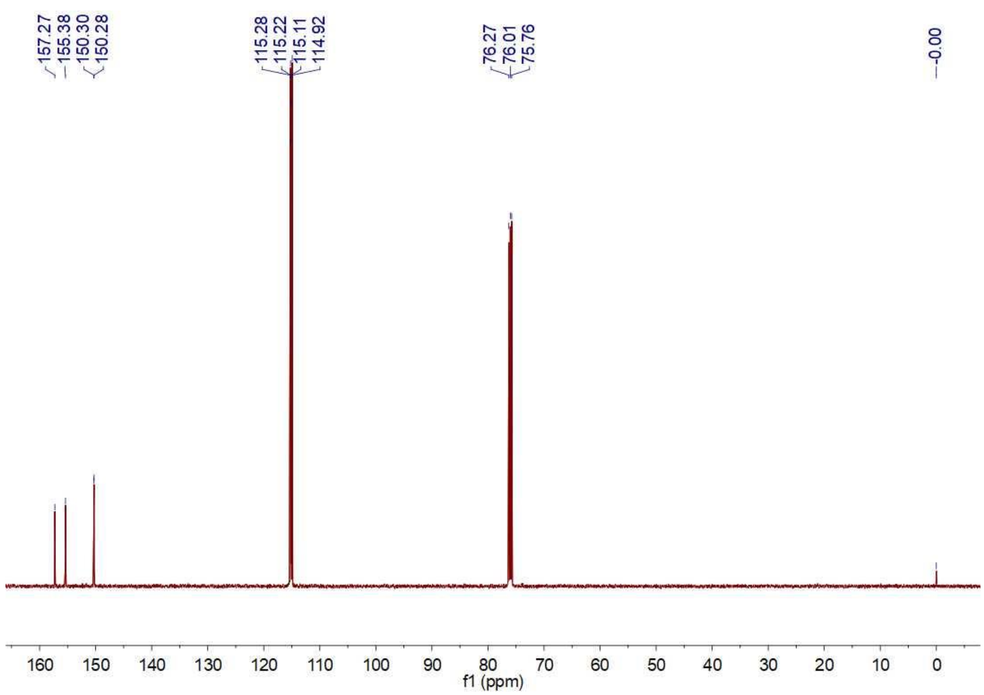

Figure S10. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **8**.

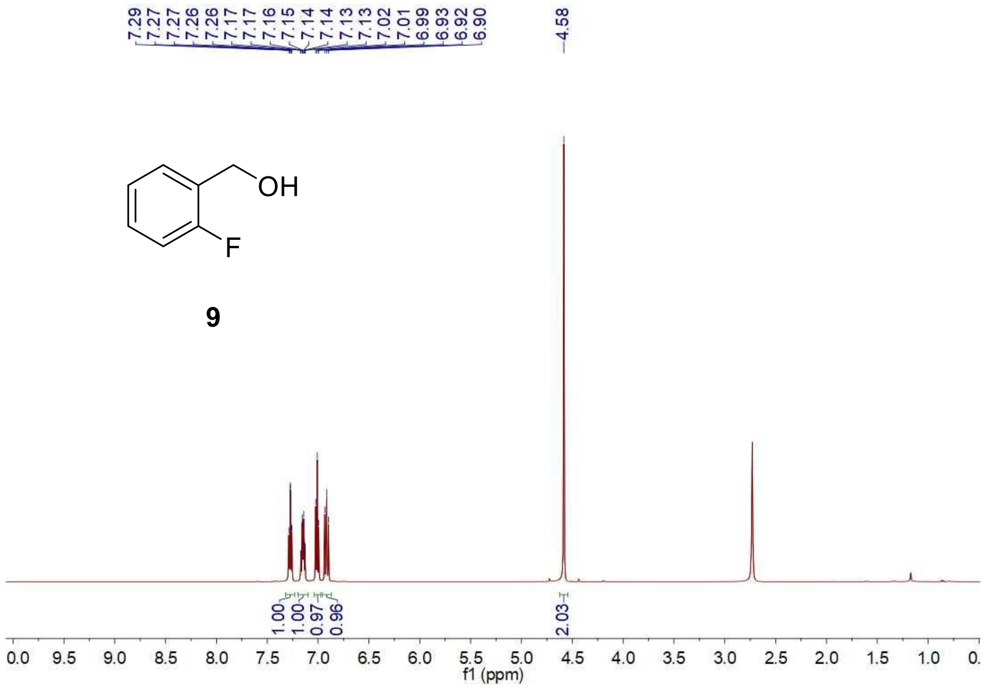

Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **9**.

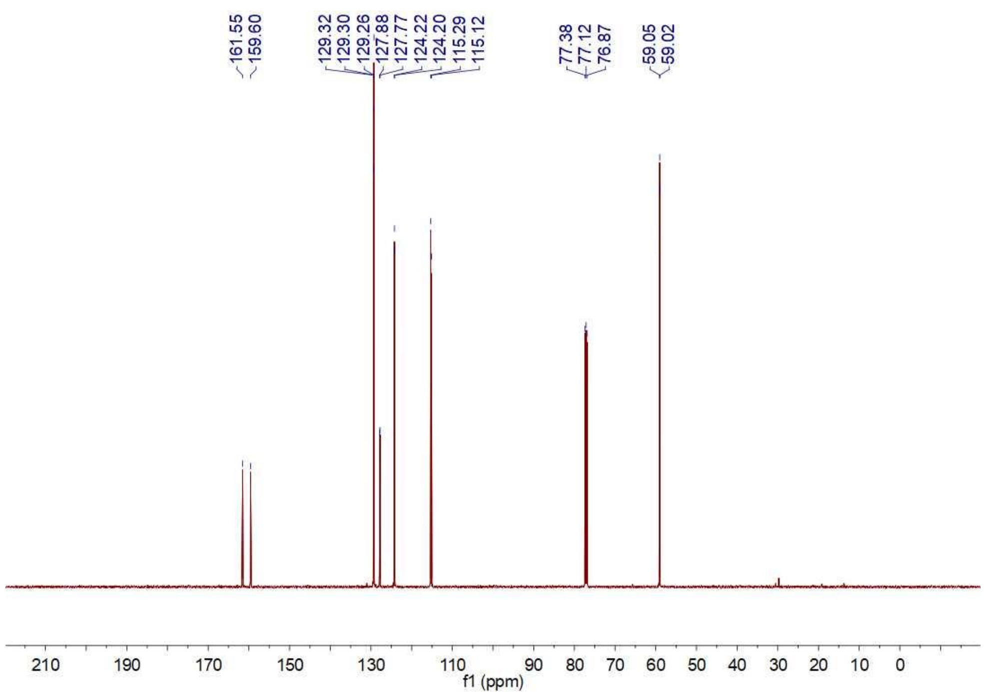

Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **9**.

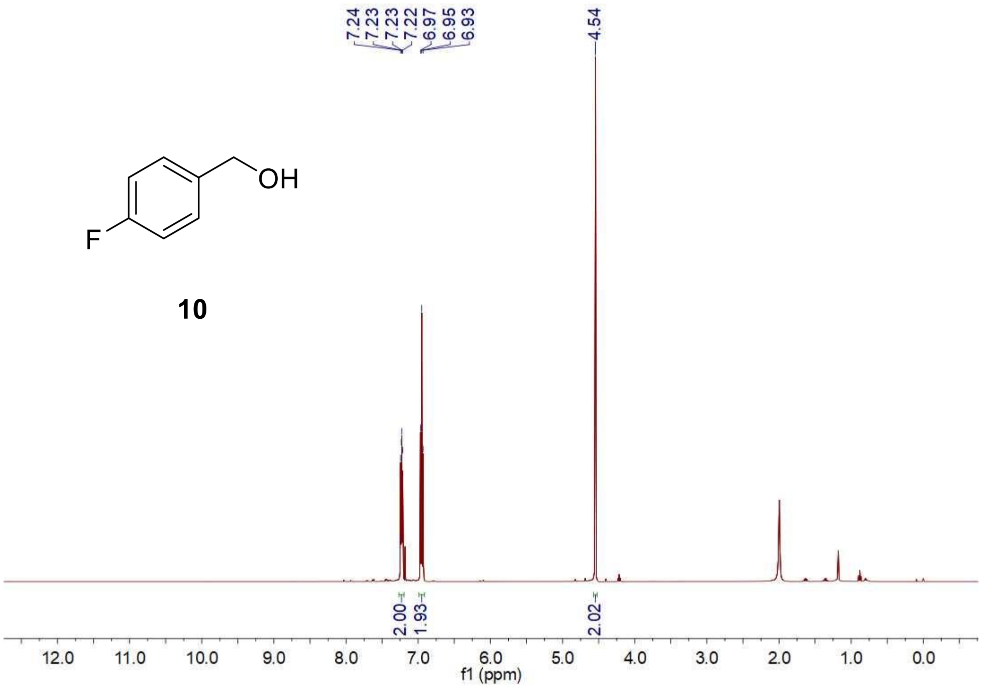

Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10**.

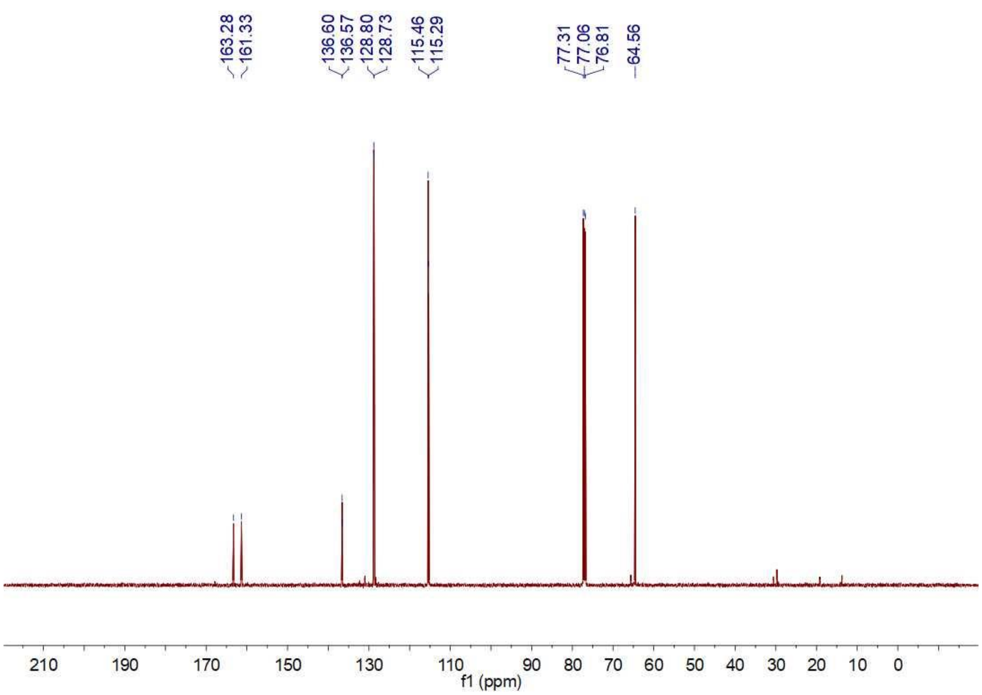

Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **10**.

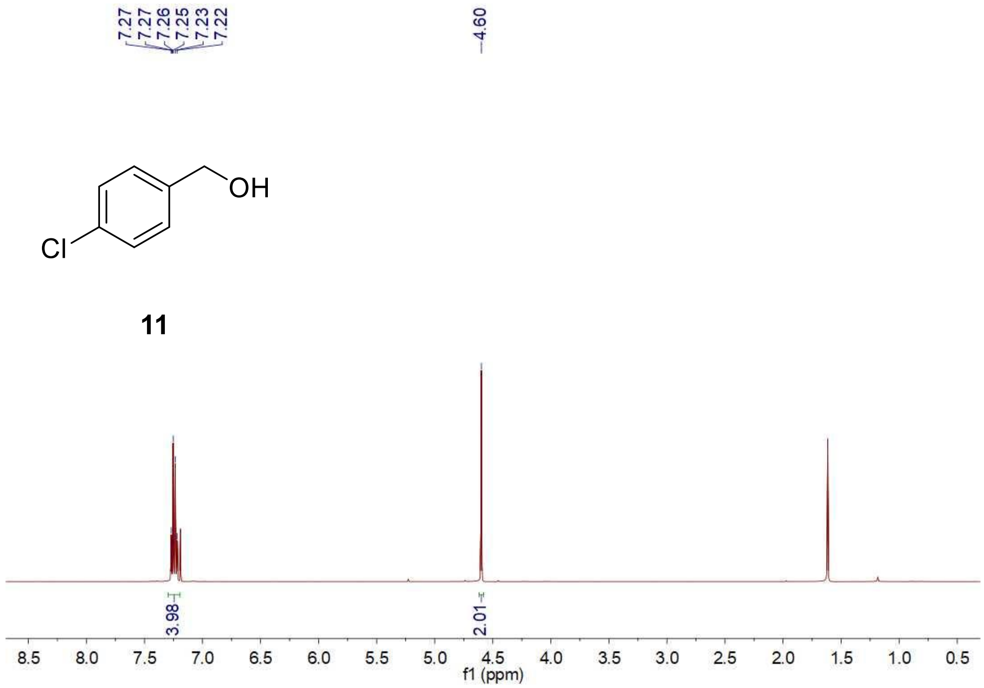

Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **11**.

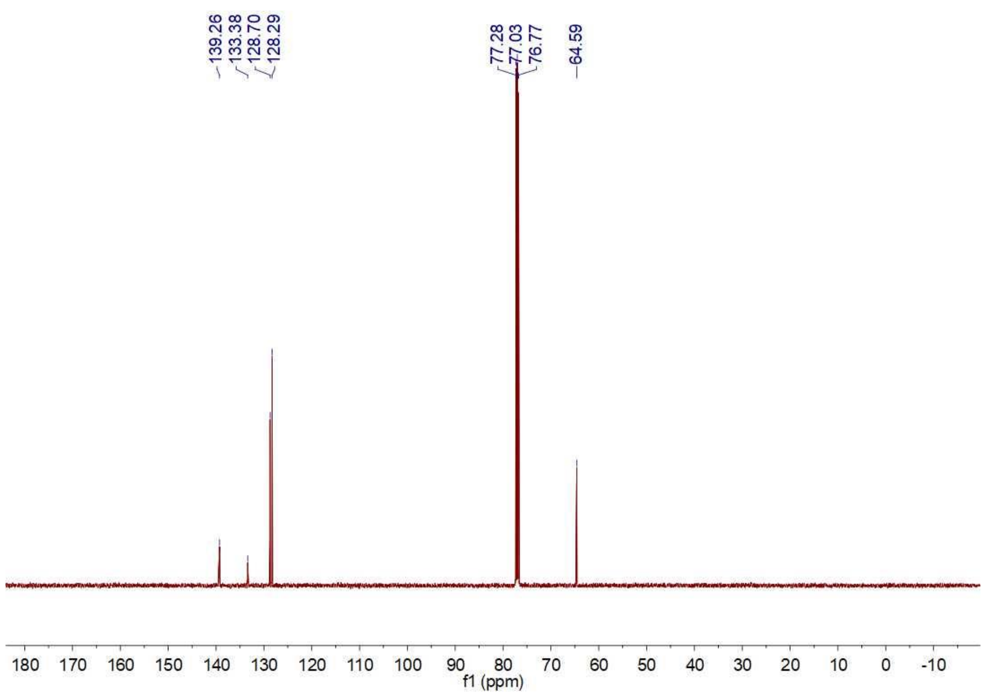

Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **11**.

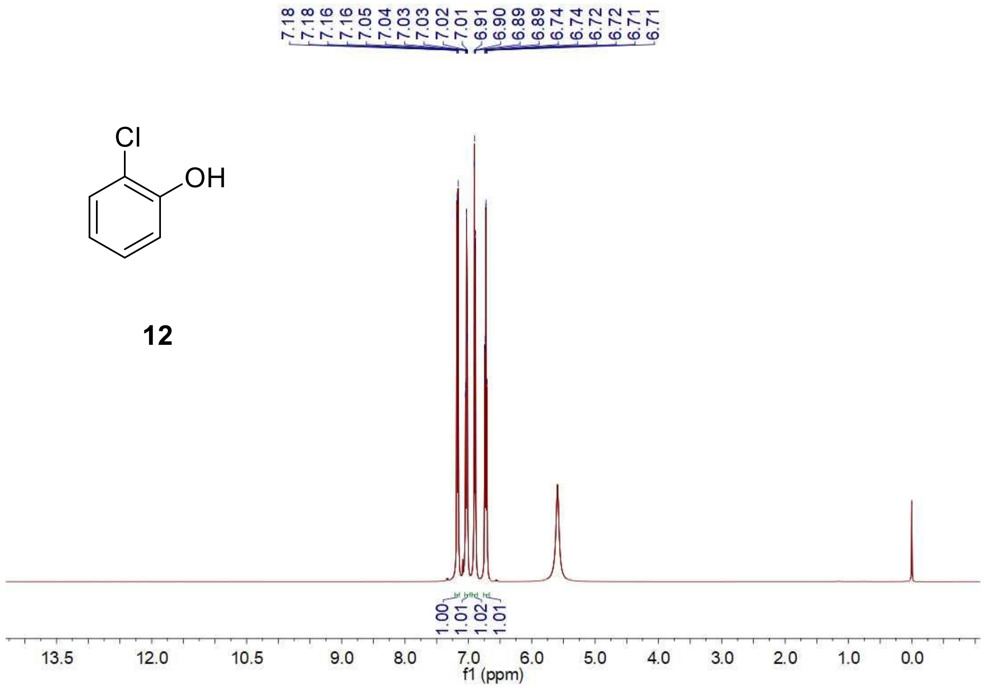

Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **12**.

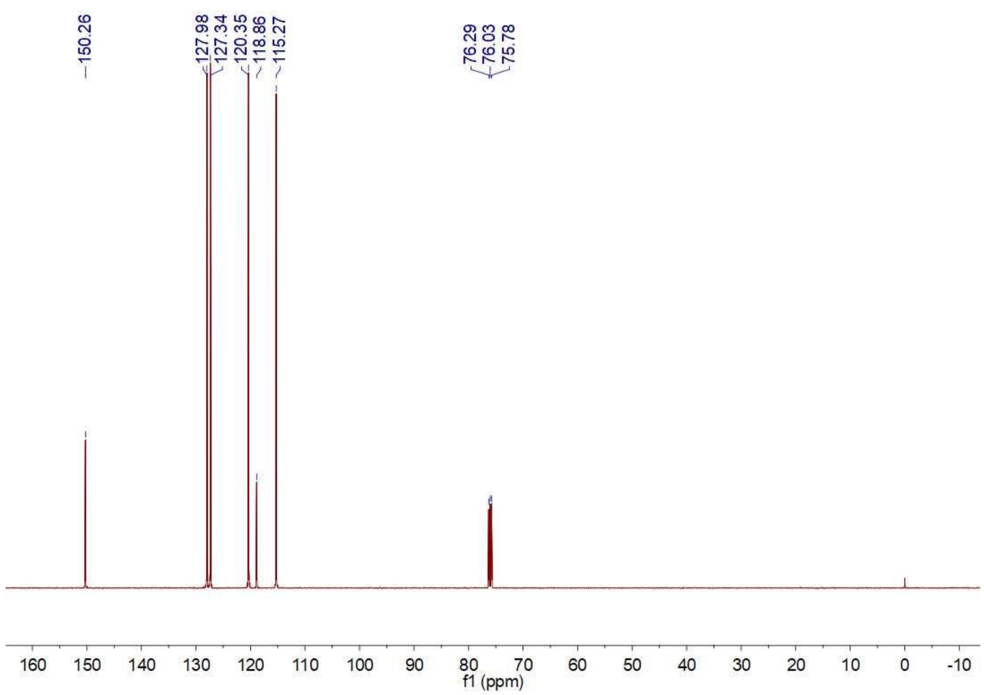

Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of 1**2**.

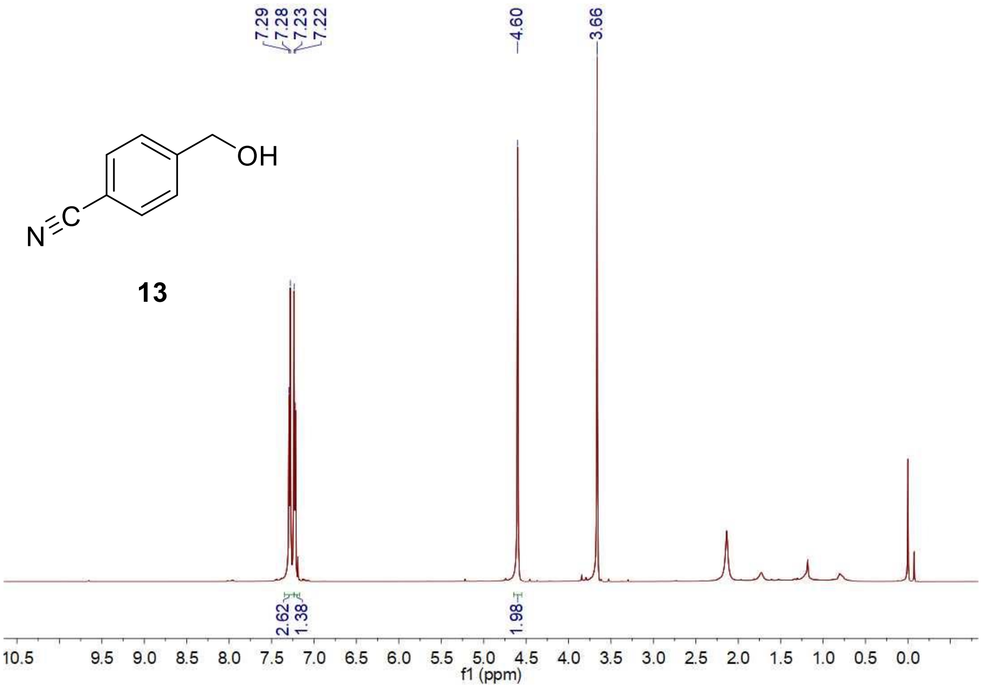

Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **13**.

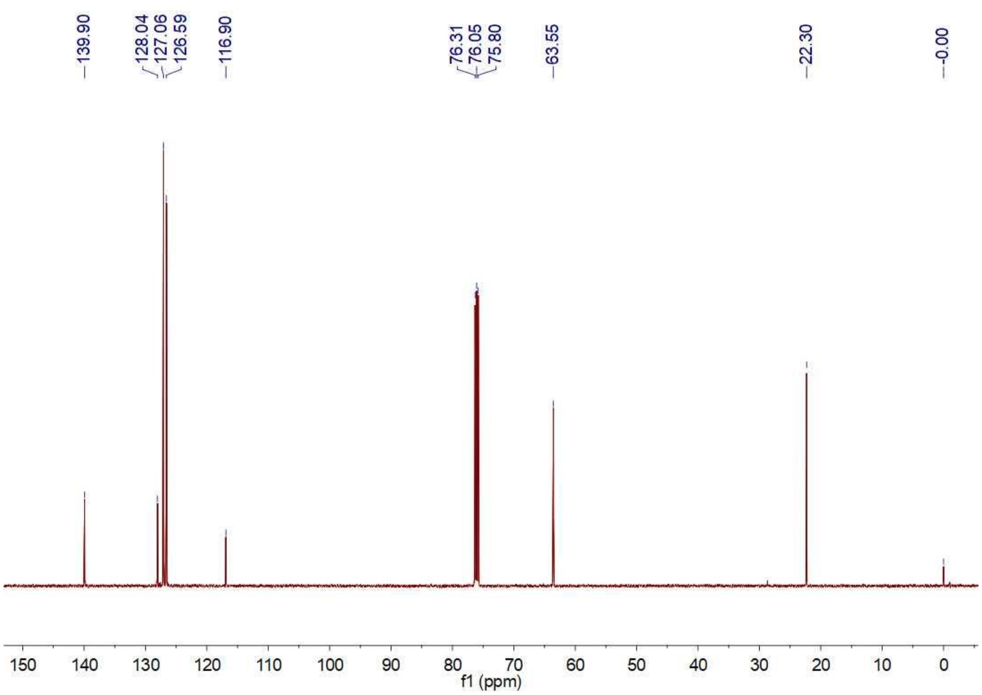

Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **13**.

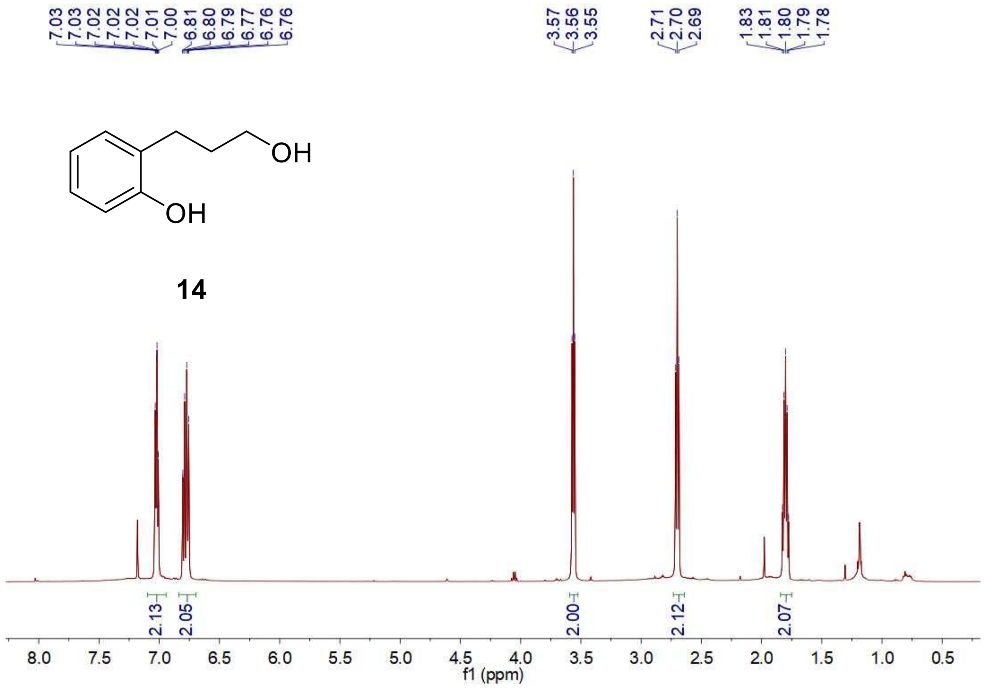

Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **14**.

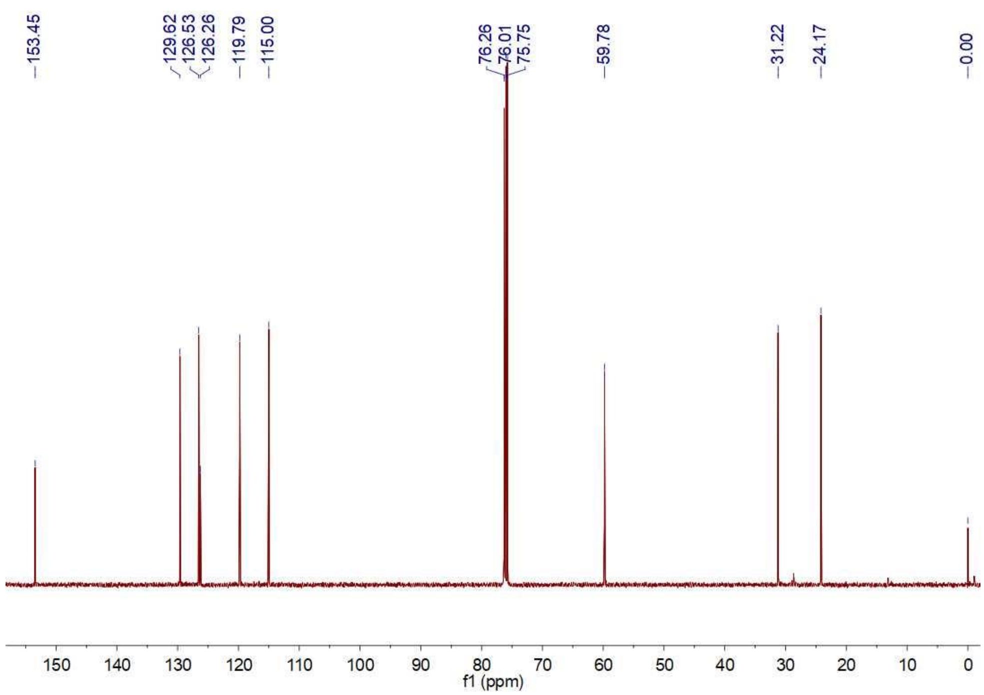

Figure S22. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **14**.

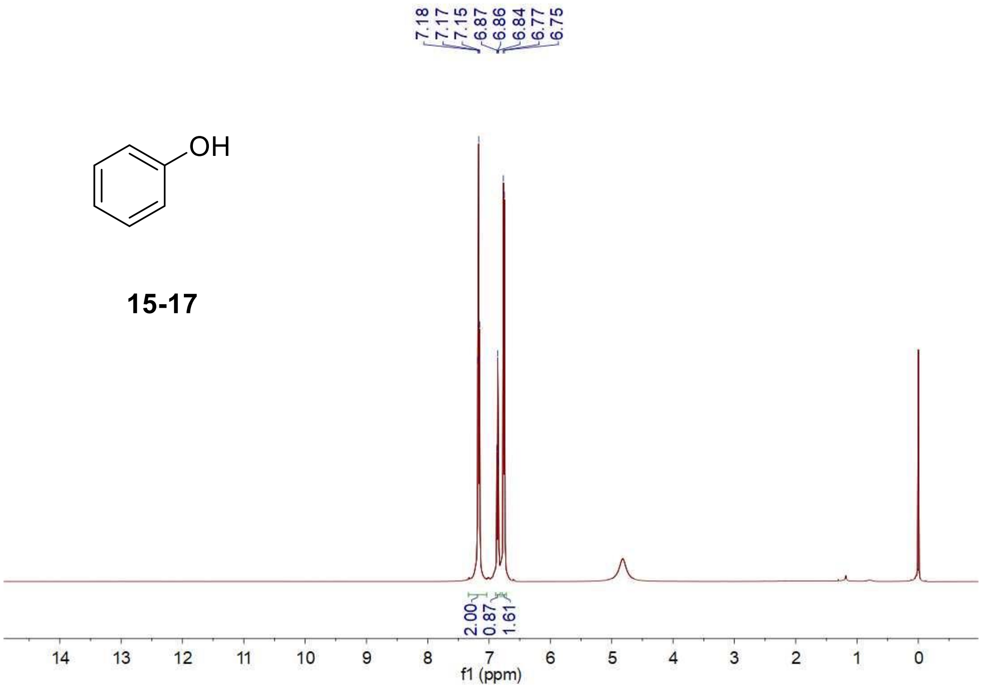

Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **15-17**.

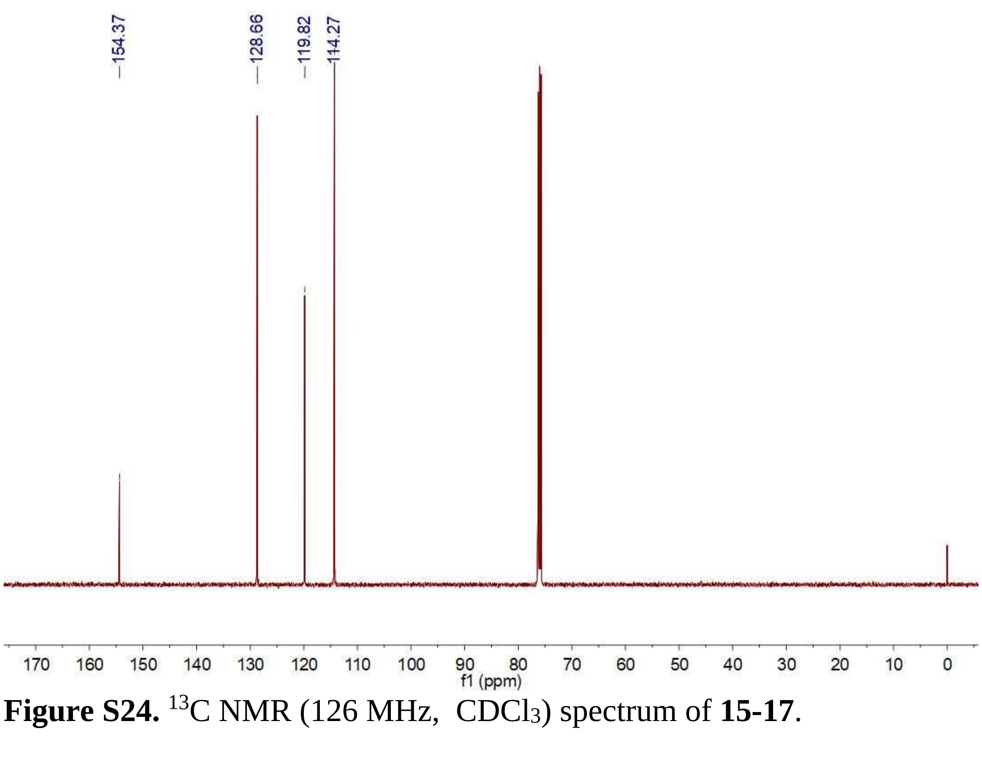

Figure S24. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **15-17**.

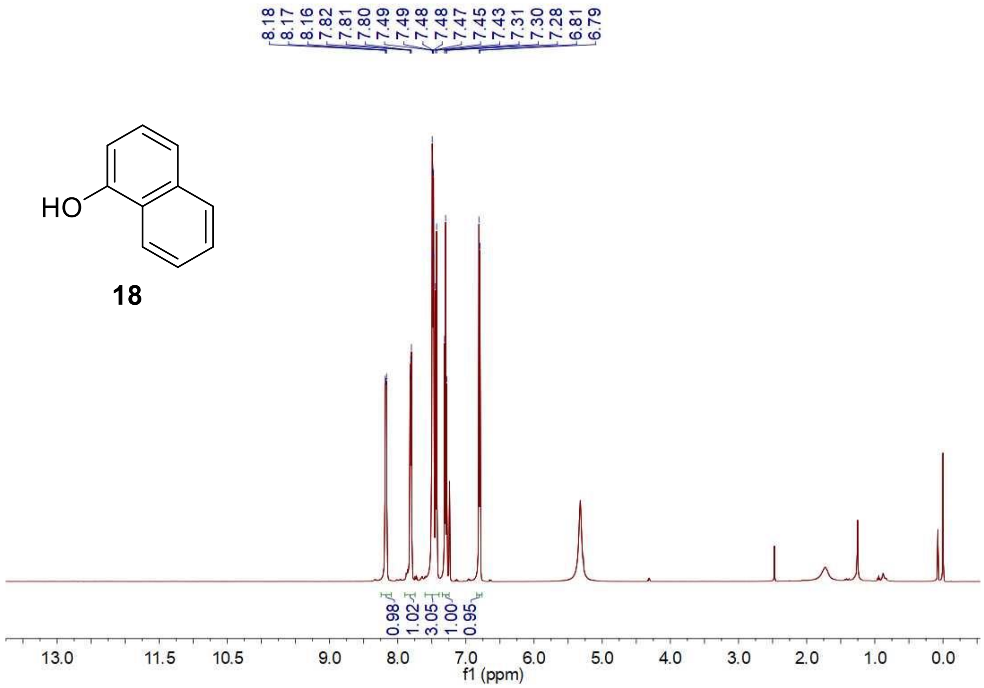

Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **18**.

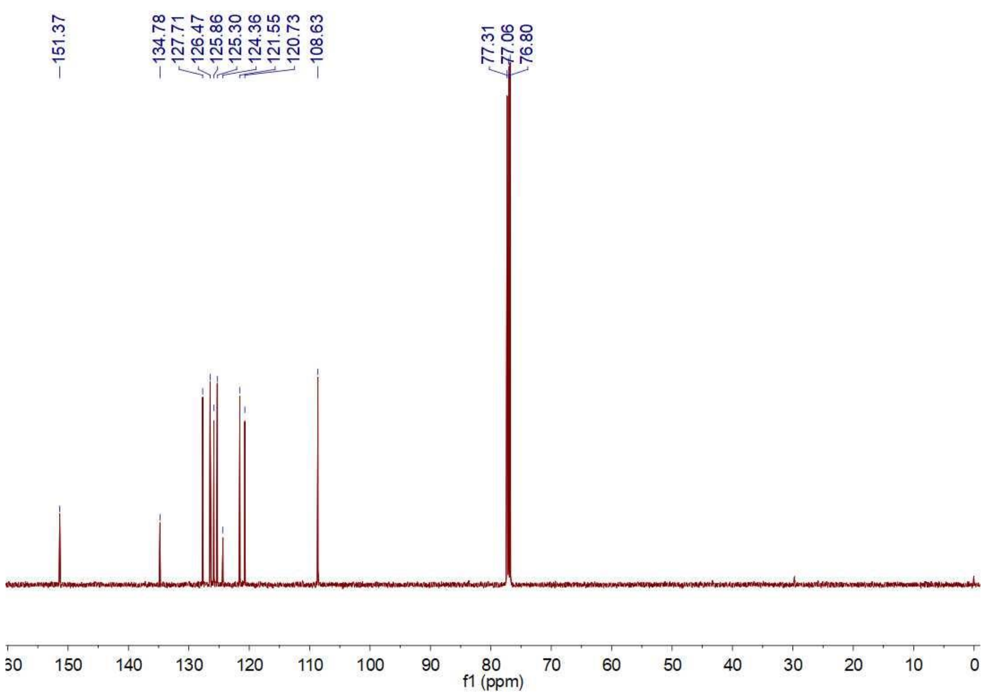

Figure S26. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **18**.

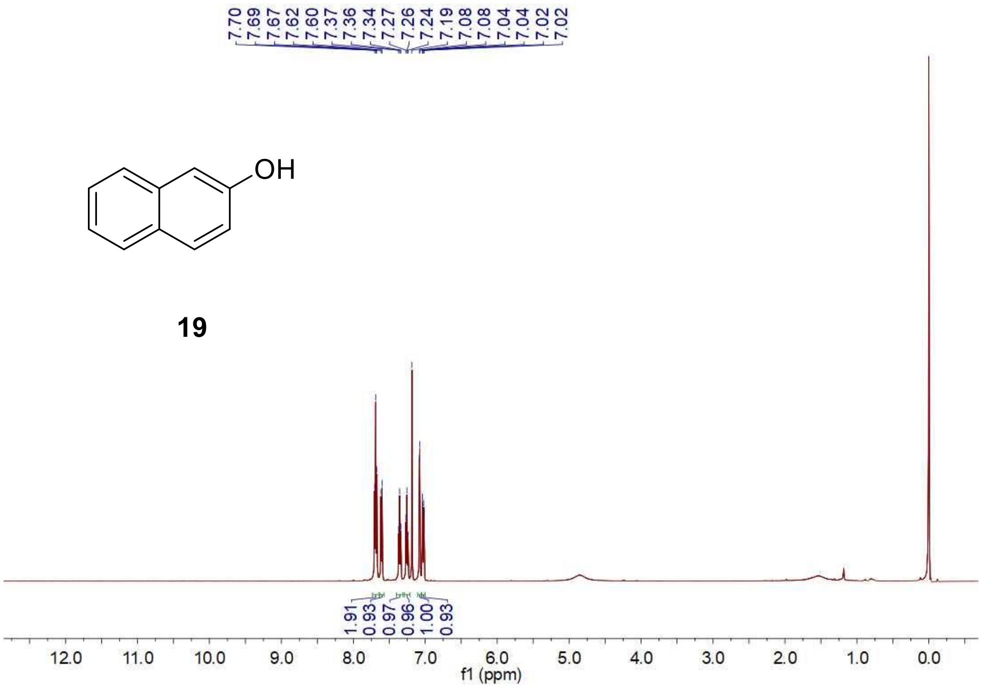

Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **19**.

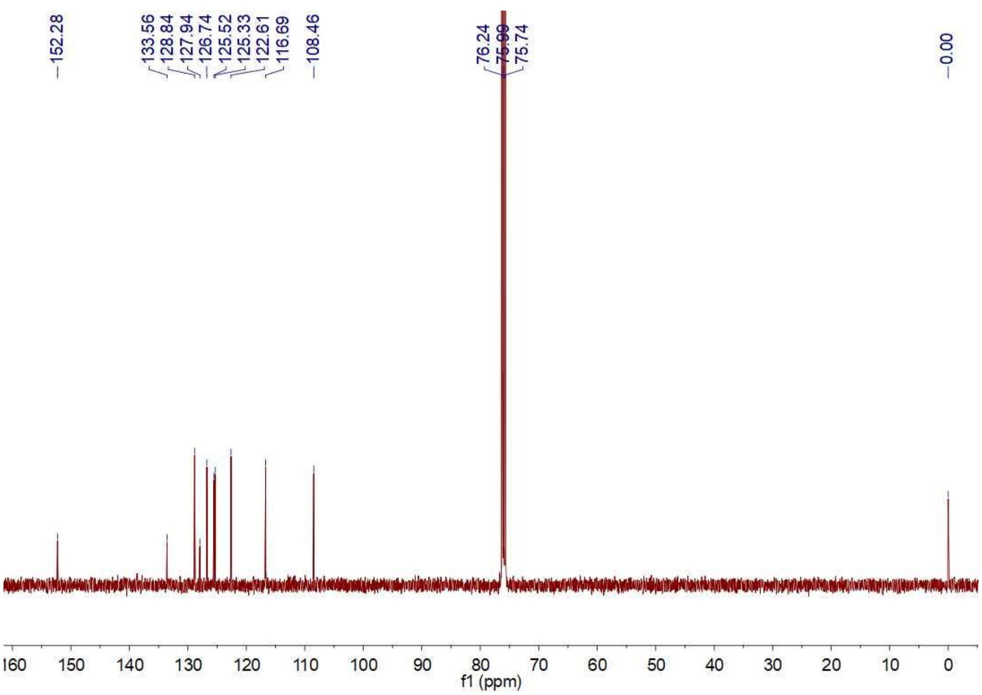

Figure S28. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **19**.

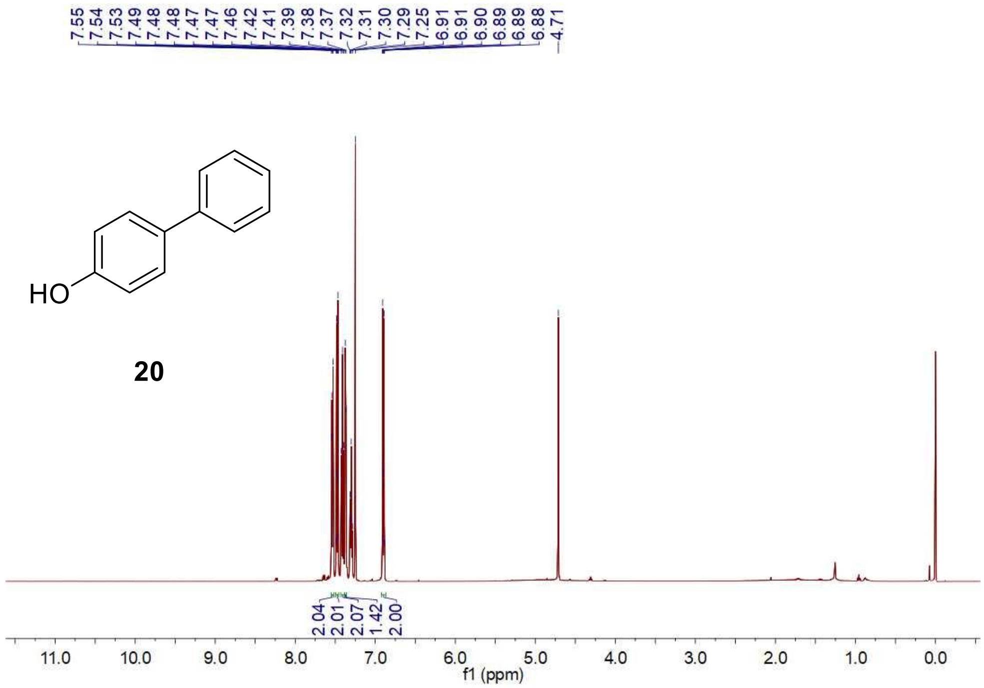

Figure S29. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **20**.

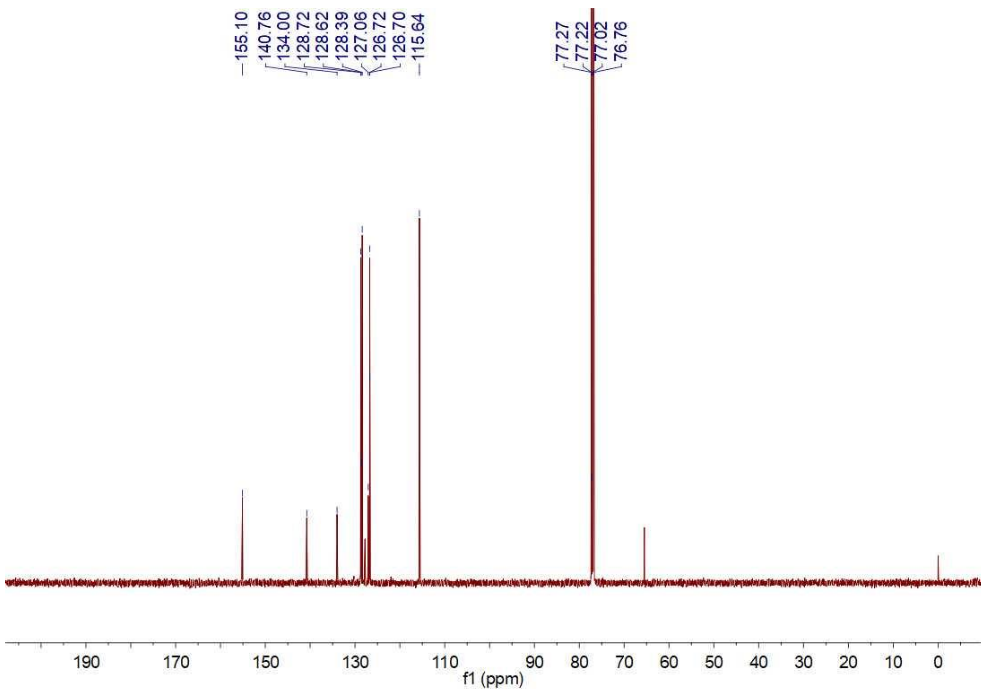

Figure S30. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **20**.

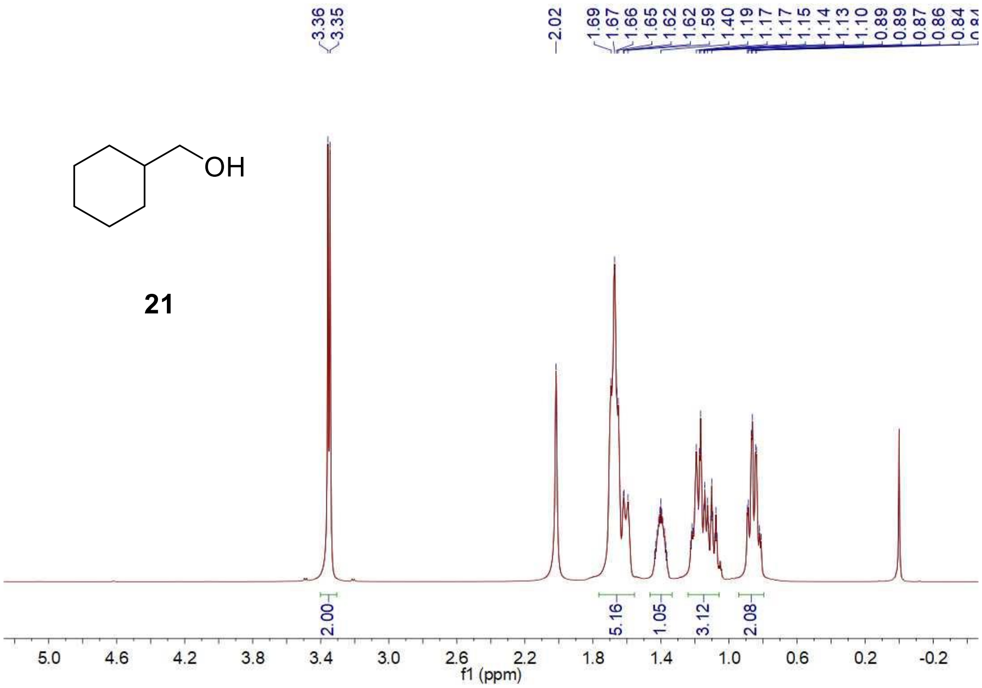

Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **21**.

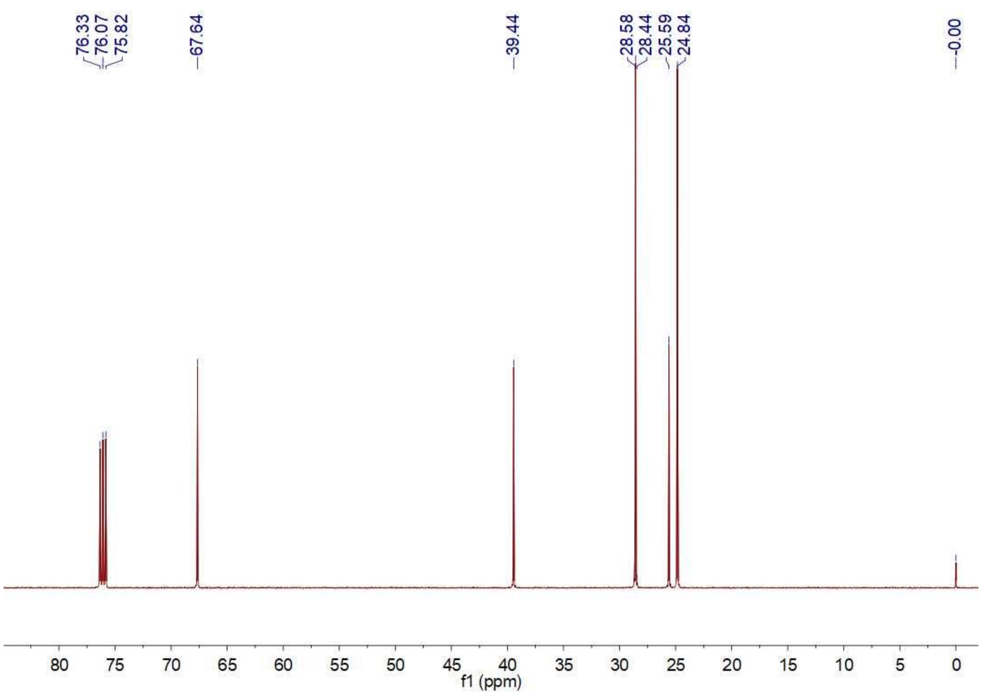

Figure S32. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **21**.

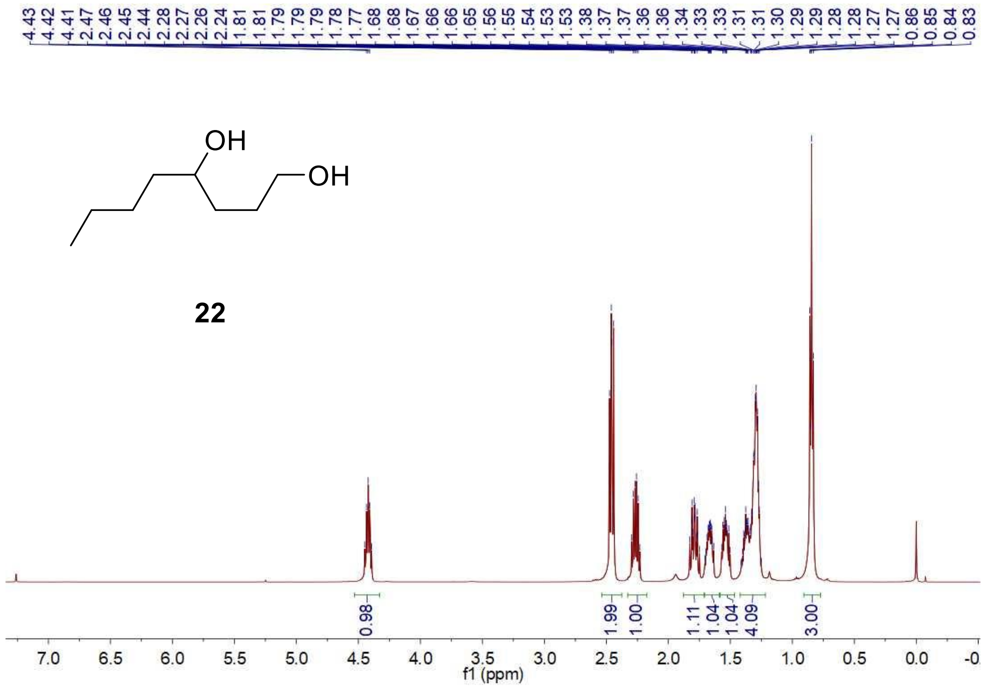

Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **22**.

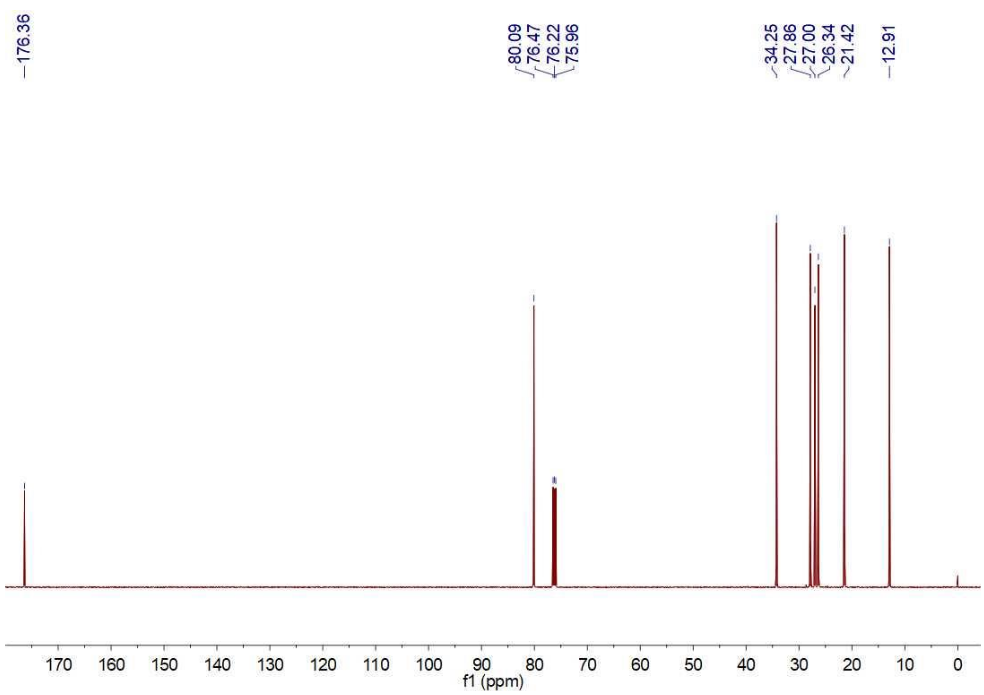

Figure S34. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **22**.

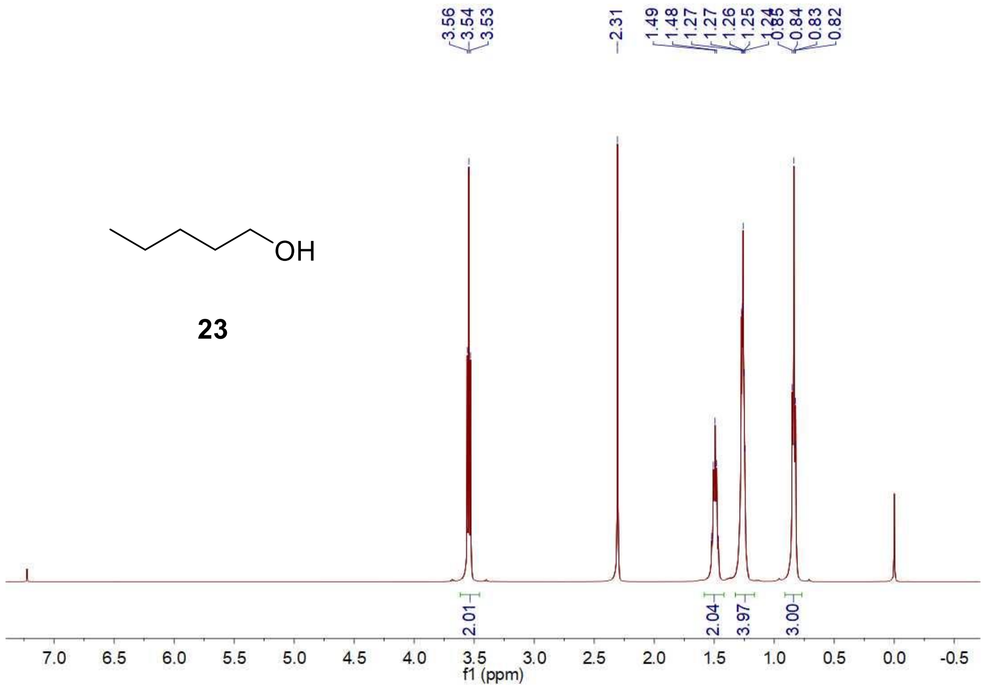

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Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **23**.

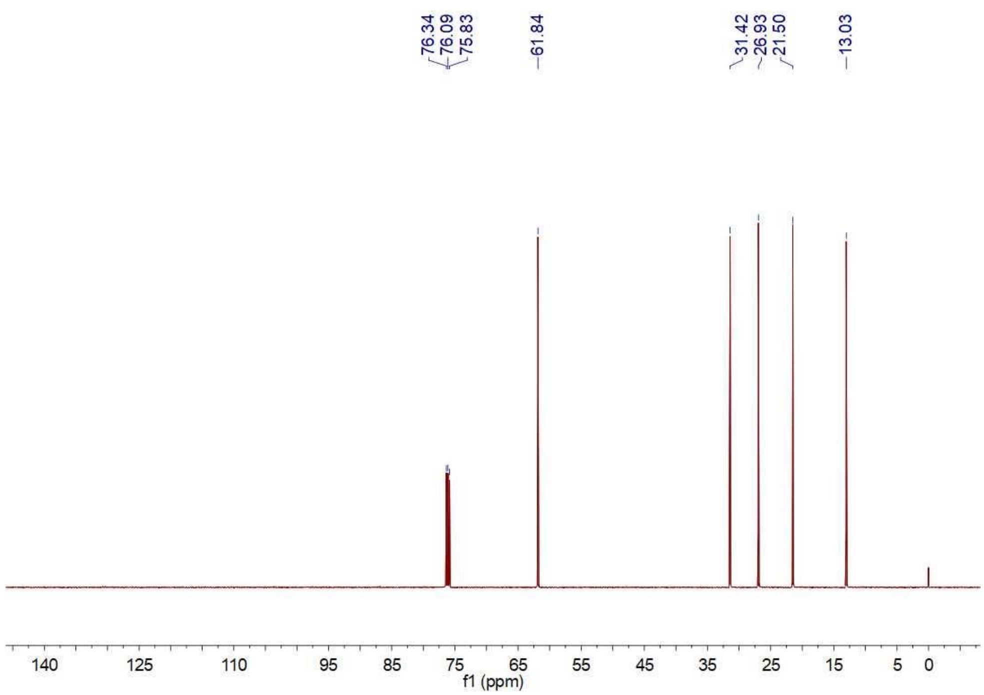

Figure S36. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **23**.

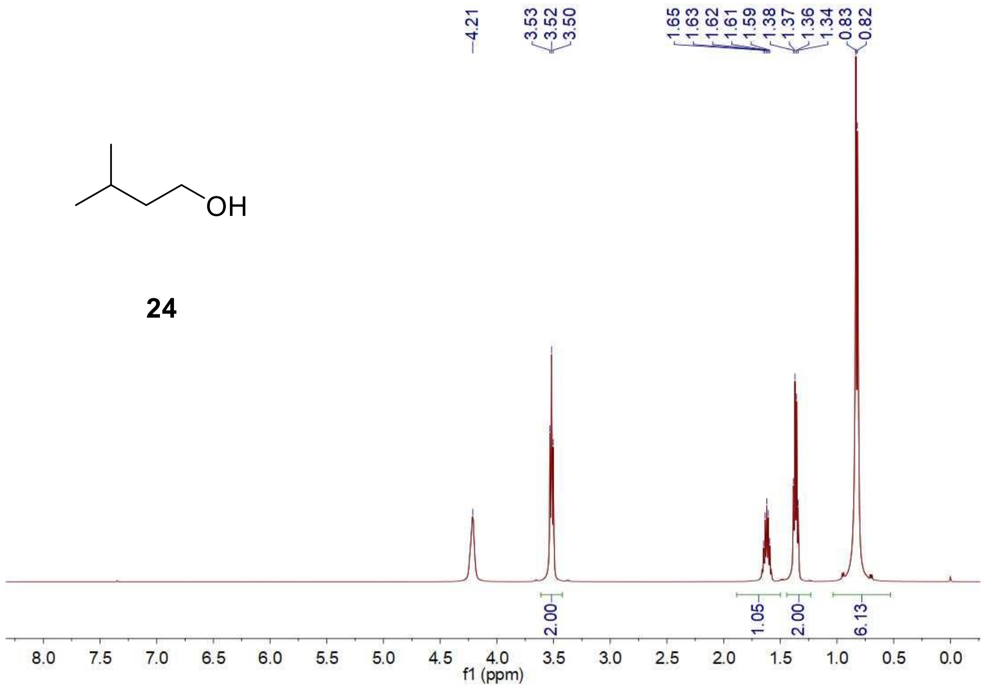

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Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **24**.

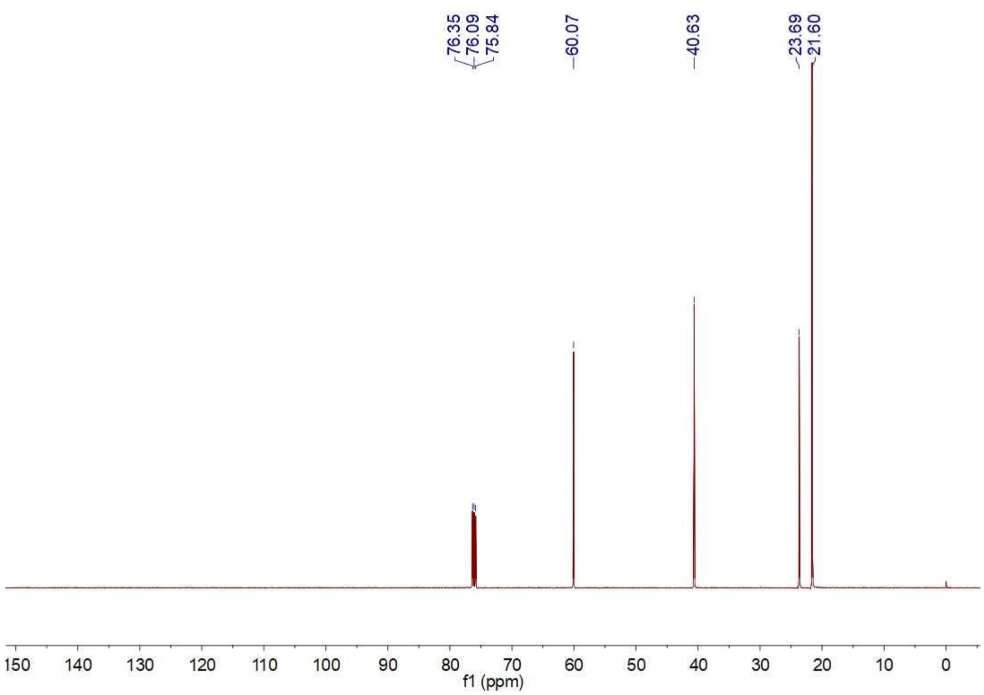

Figure S38. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **24**.

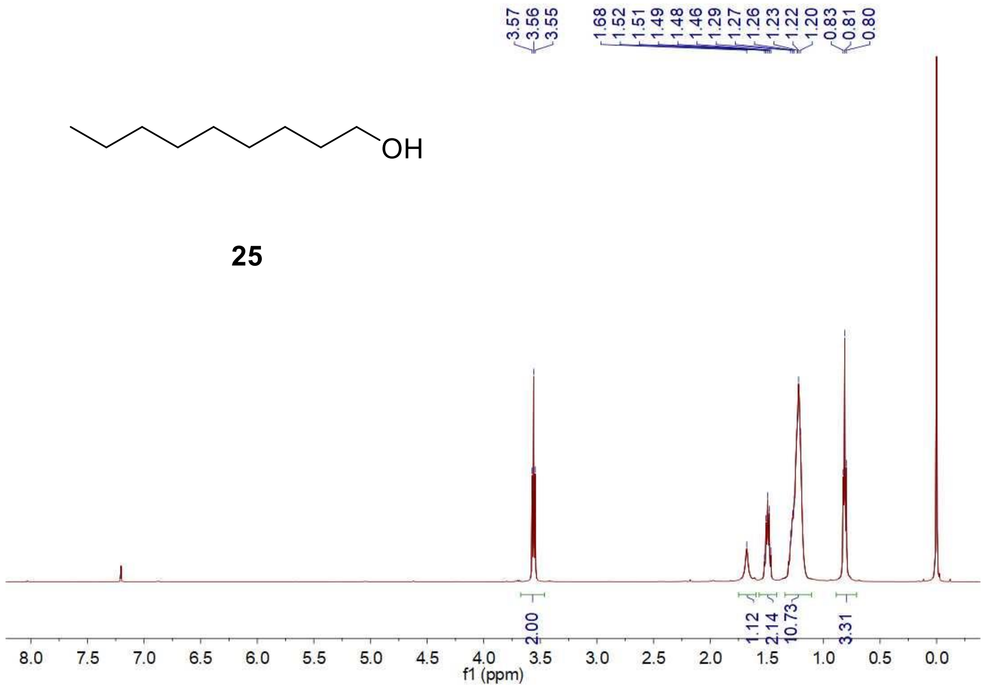

Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **25**.

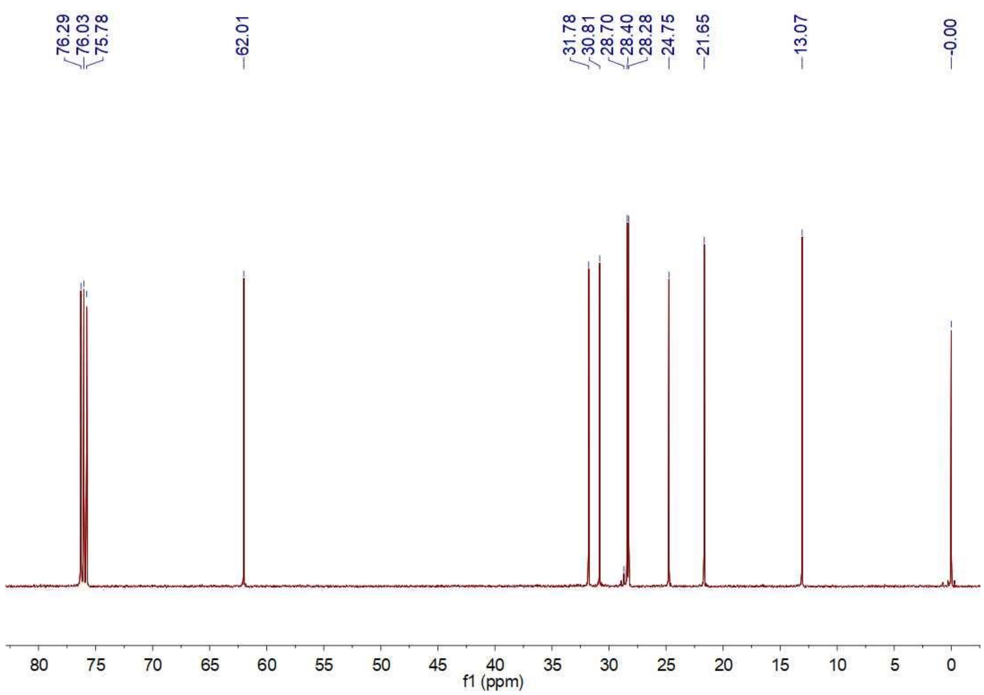

Figure S40. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **25**.

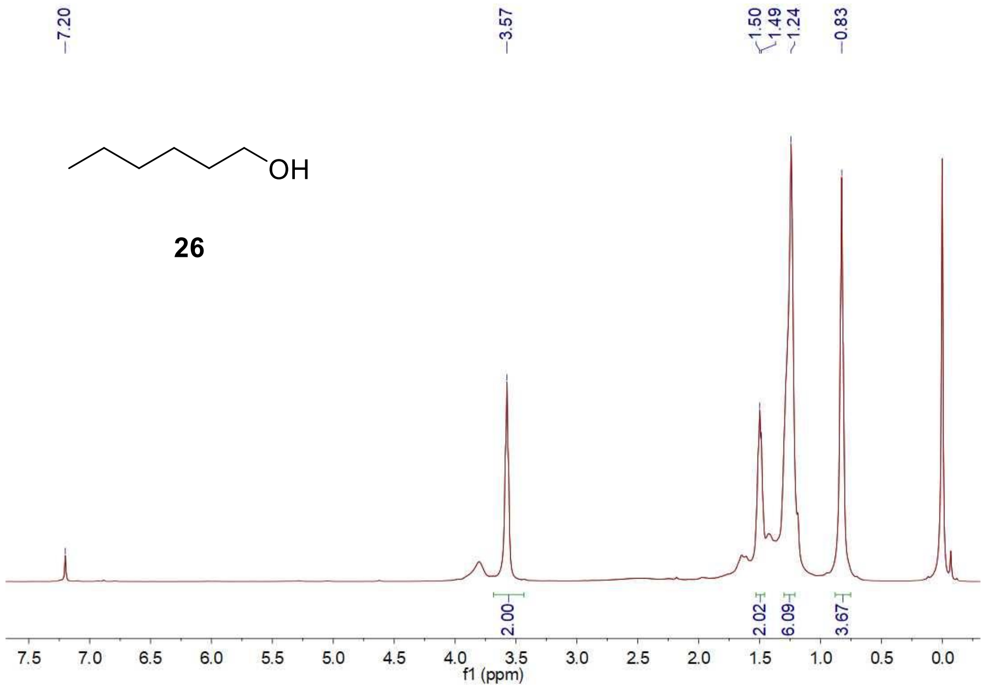

Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **26**.

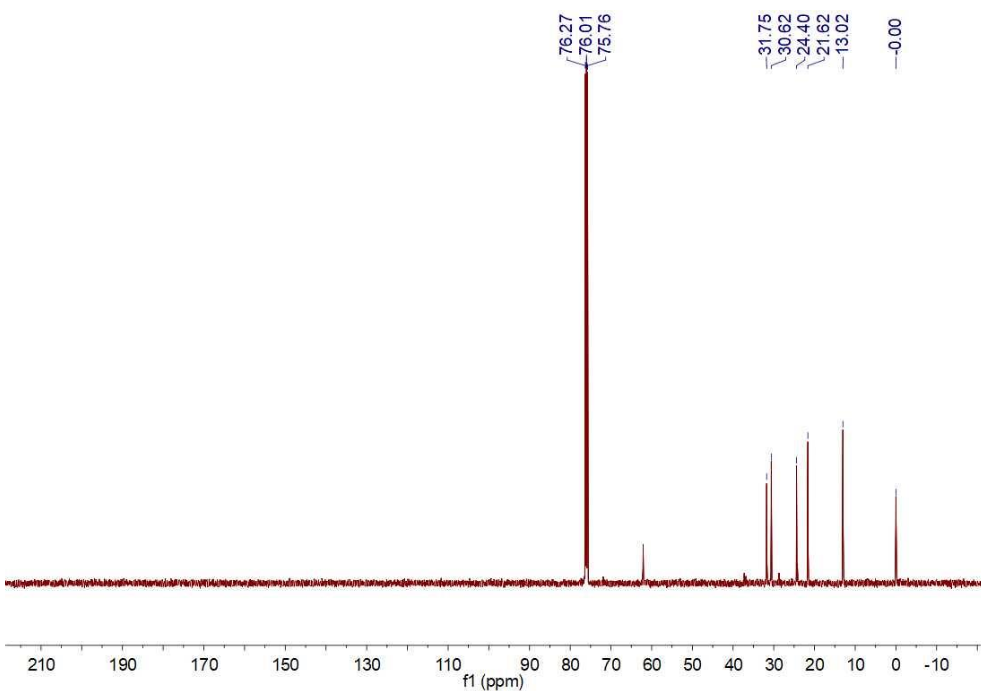

Figure S42. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **26**.

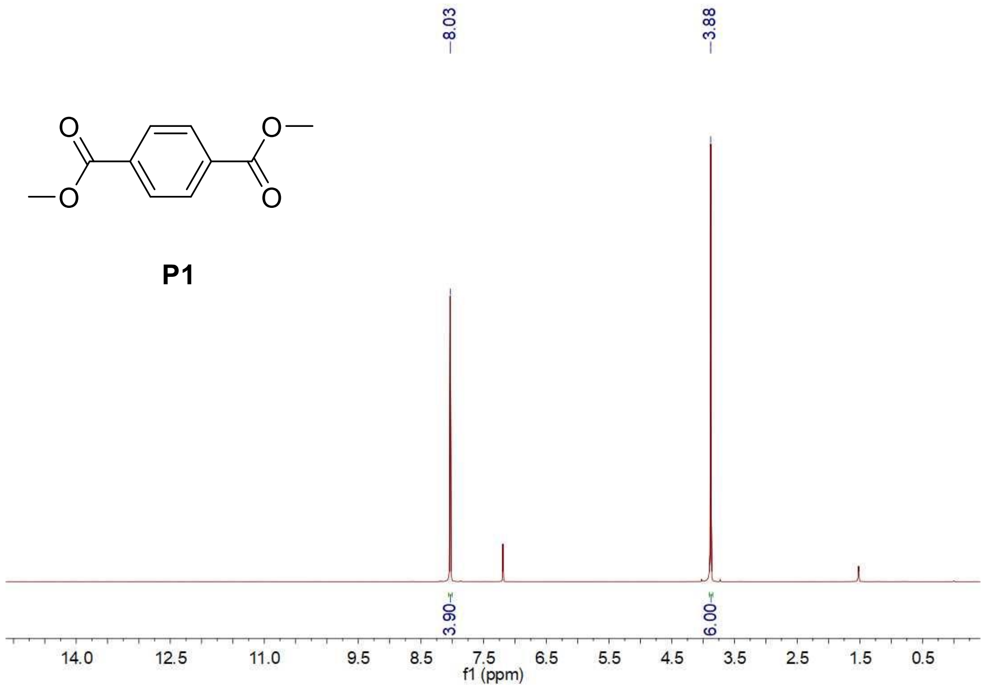

Figure S43. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P1**.

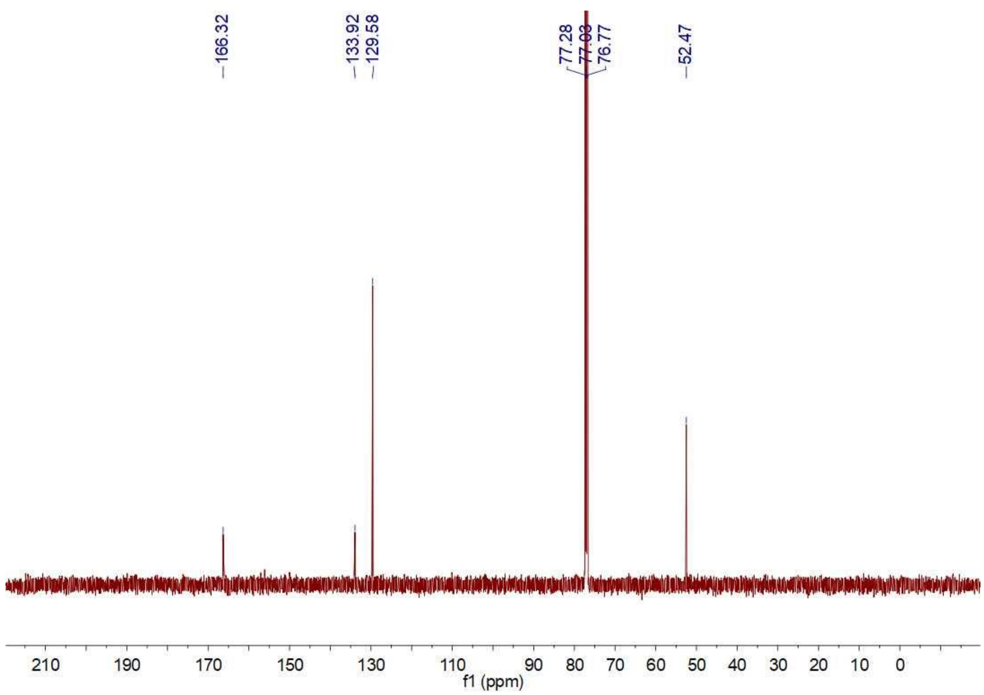

Figure S44. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **P1**.

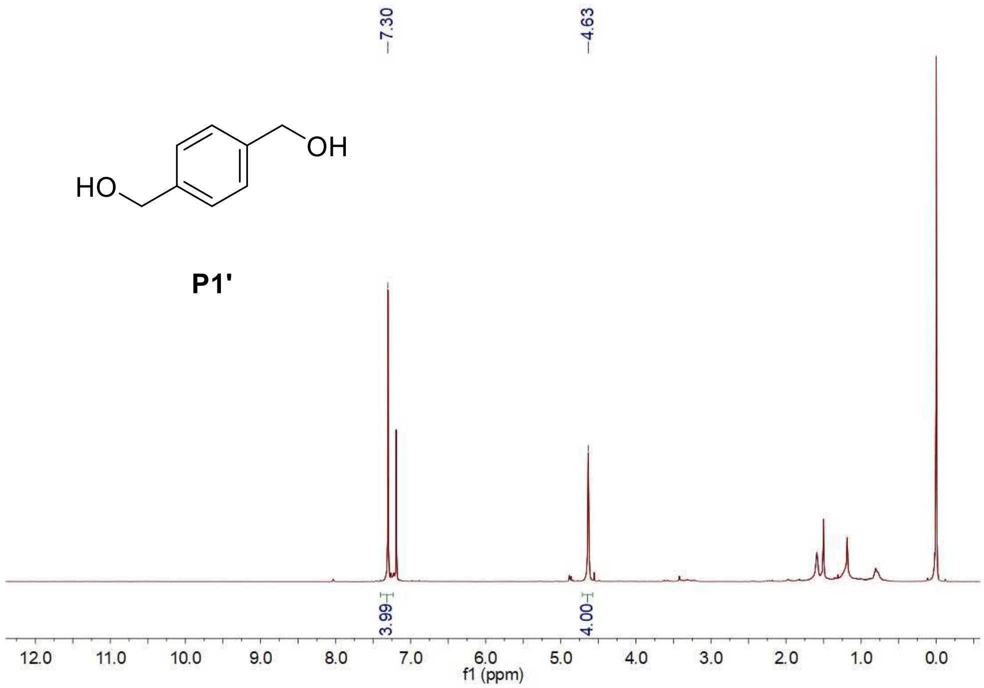

Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P1’**.

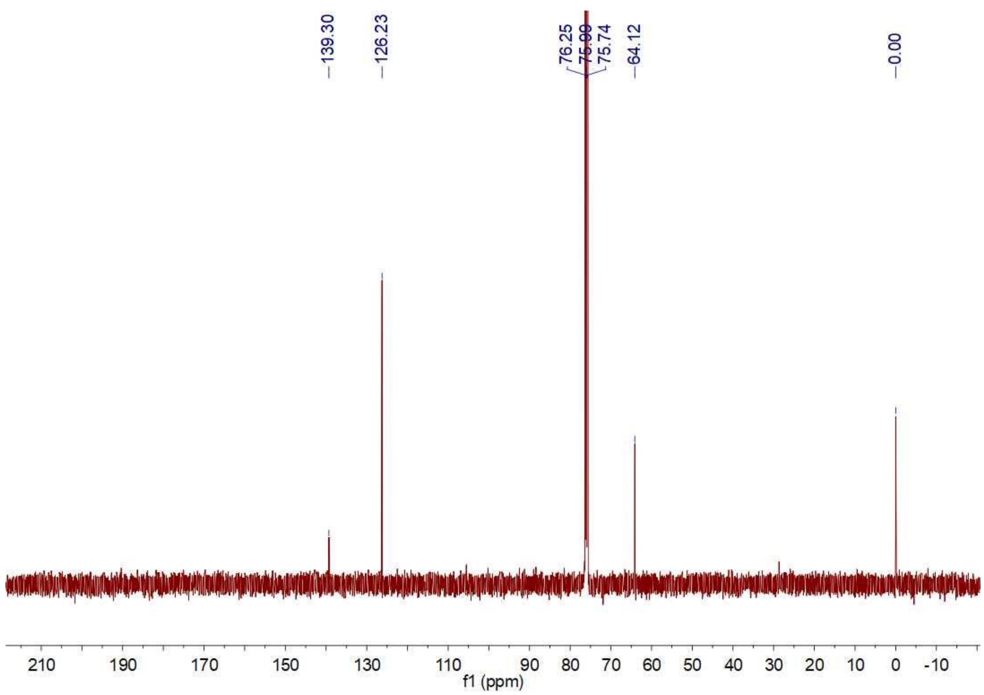

Figure S46. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **P1’**.

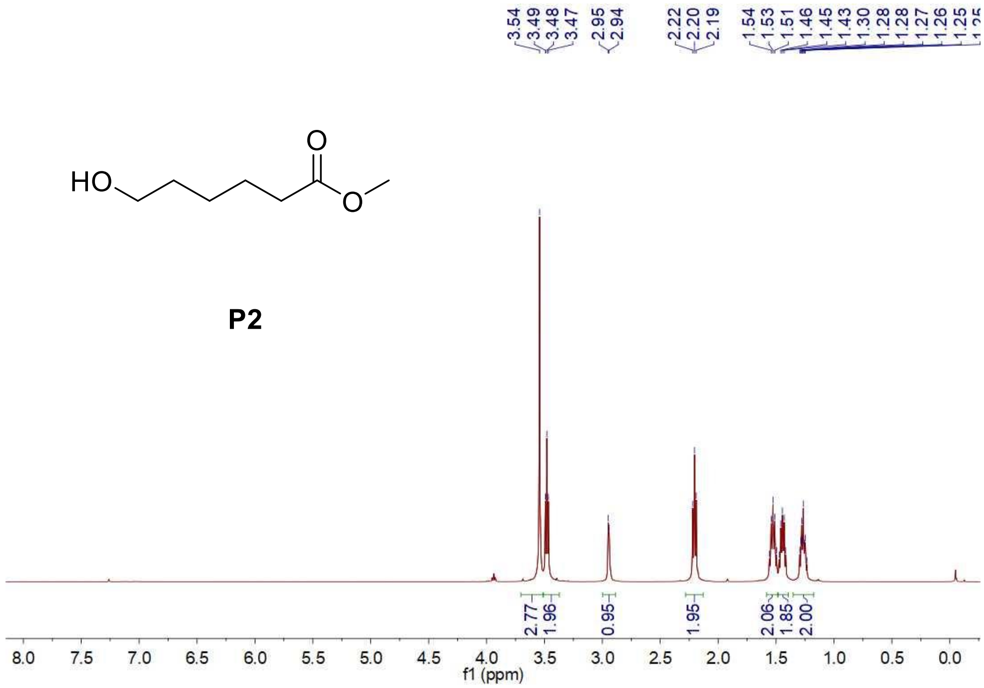

Figure S47. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P2**.

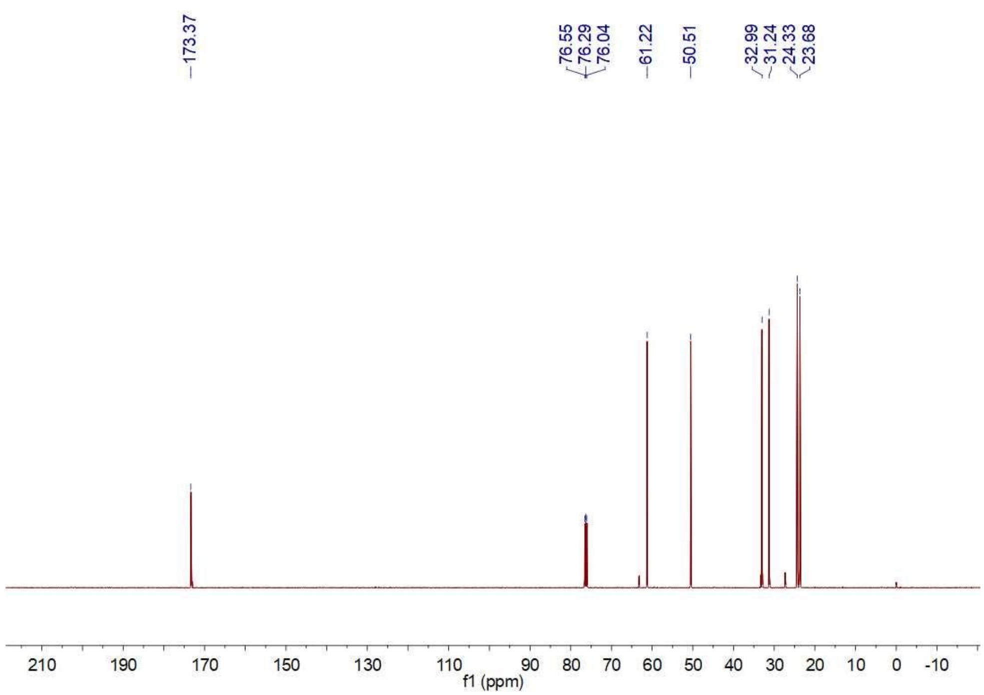

Figure S48. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **P2**.

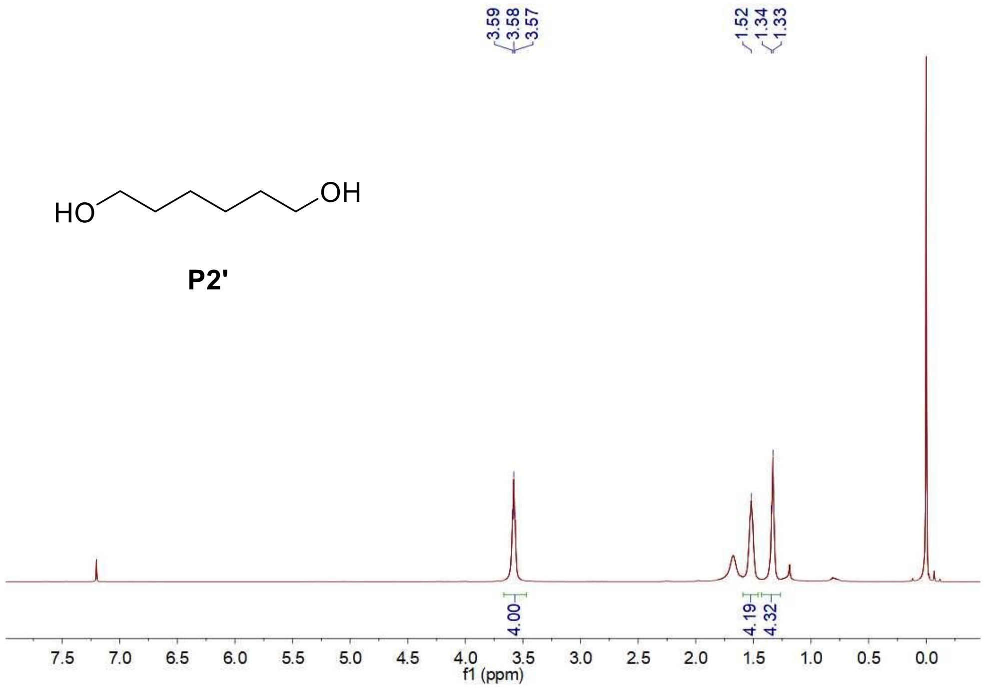

Figure S49. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P2'**.

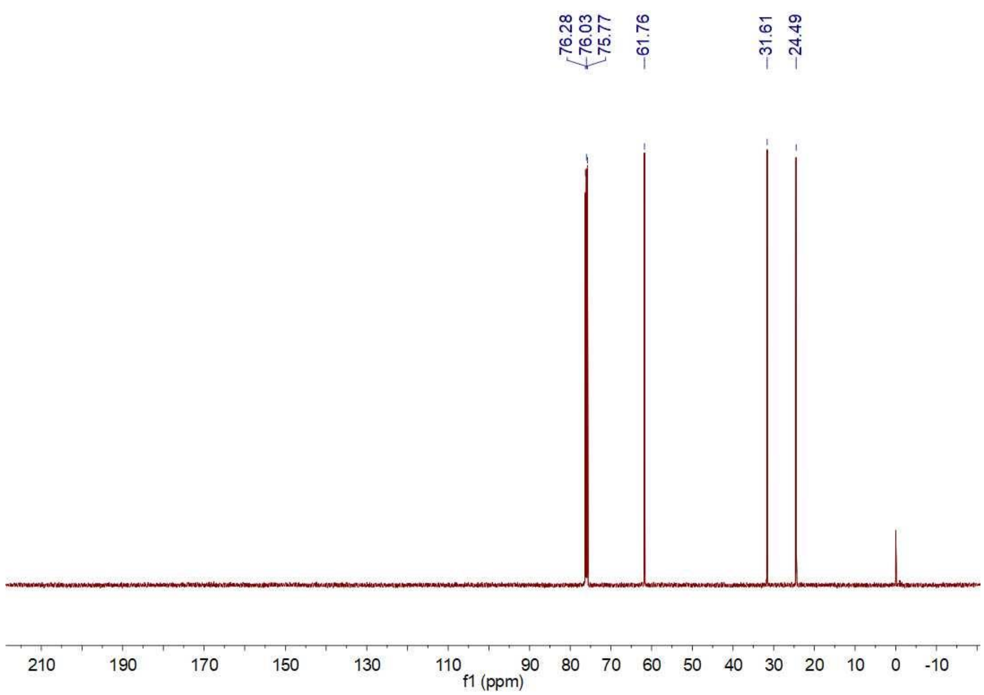

Figure S50. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **P2'**.

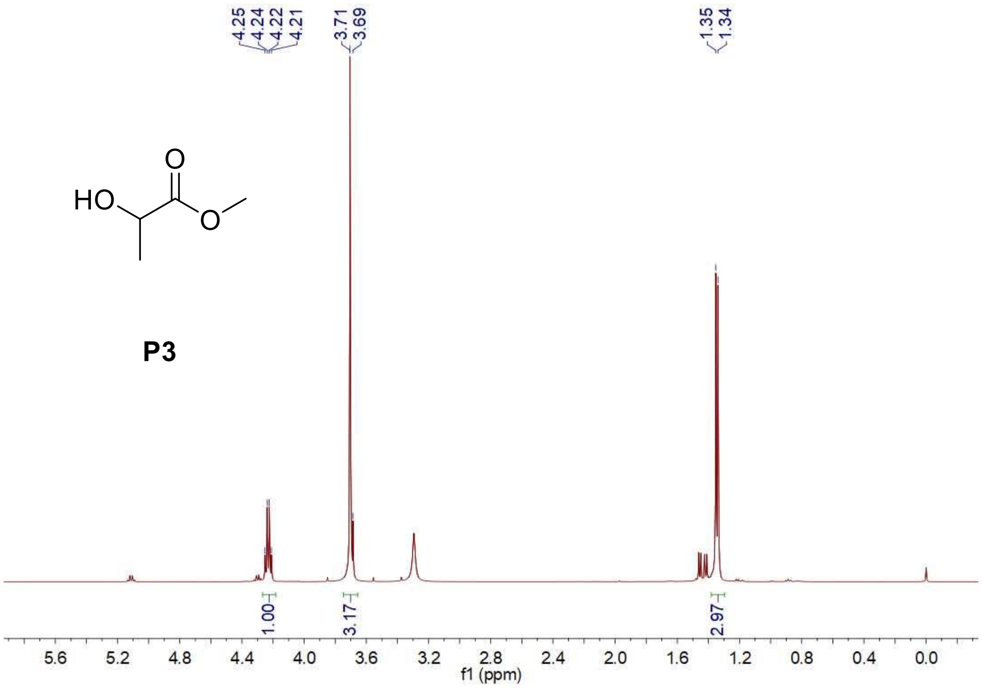

Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P3**.

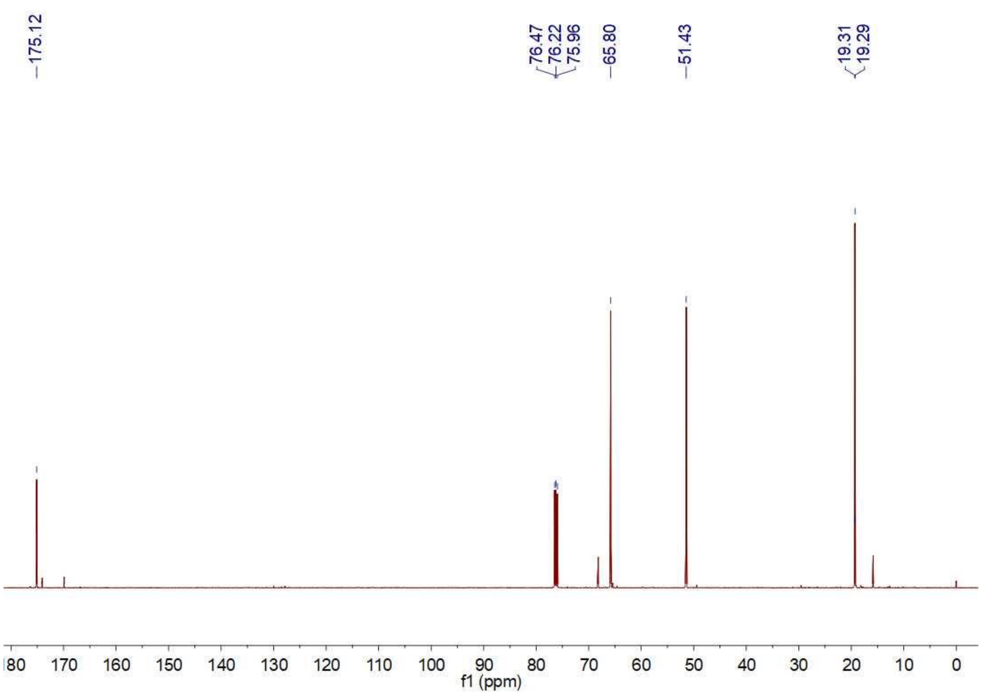

Figure S52. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **P3**.

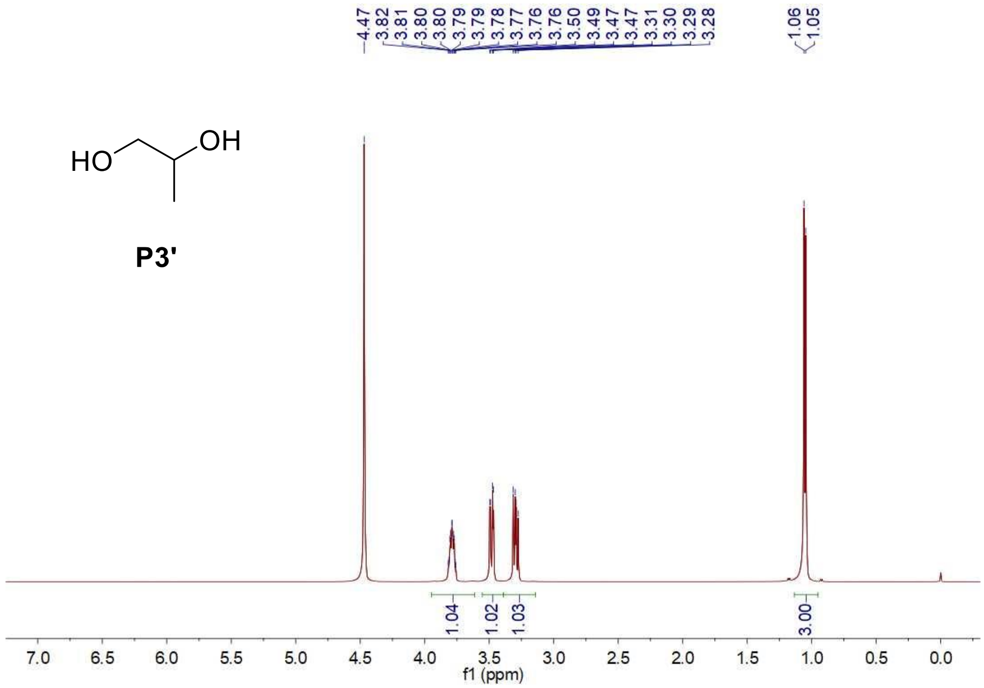

Figure S53. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **P3’**.

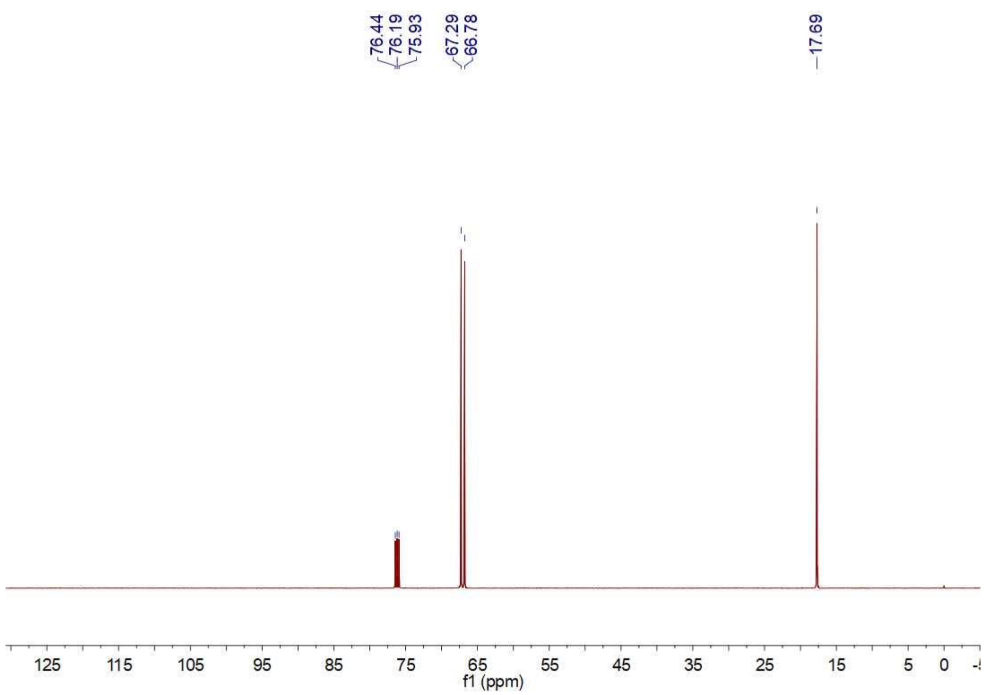

Figure S54. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **P3’**.

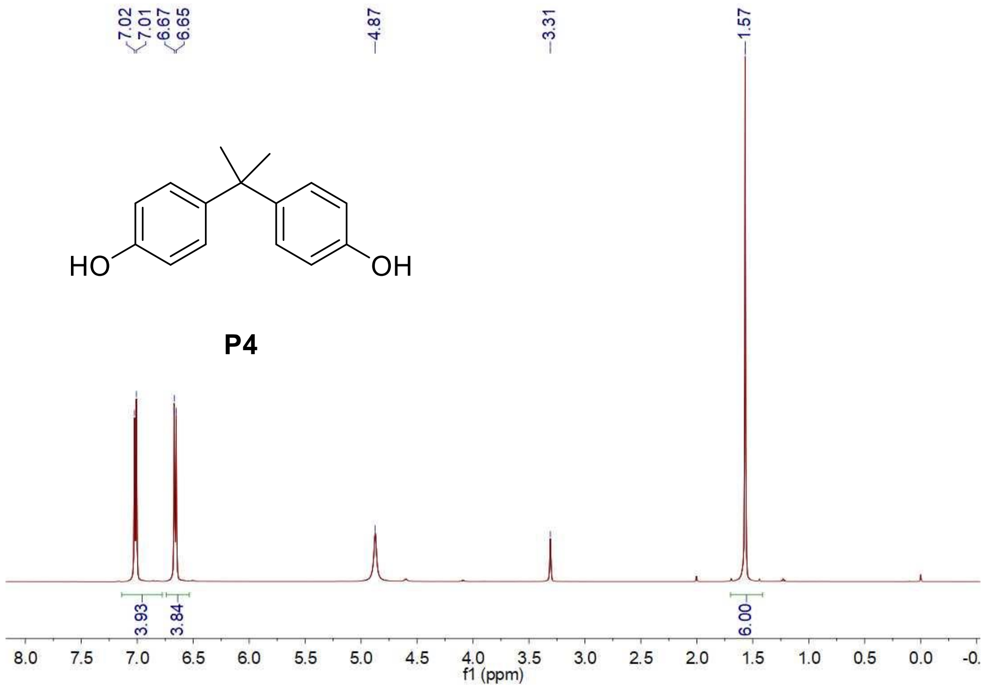

Figure S55. ^{1}H NMR (500 MHz, MeOD) spectrum of **P4**.

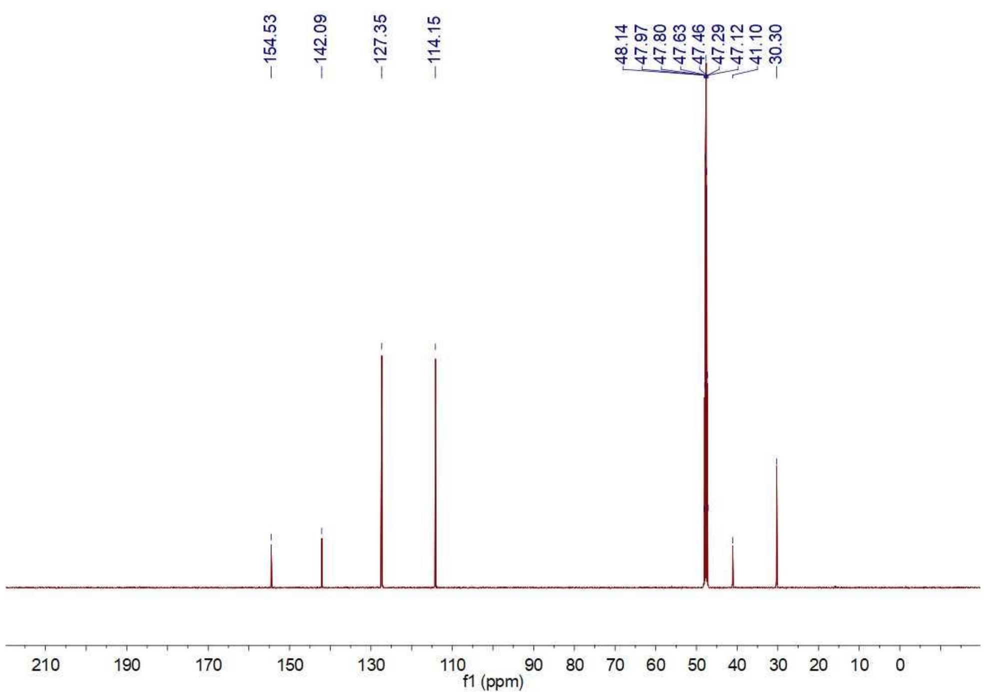

Figure S56. ^{13}C NMR (126 MHz, MeOD) spectrum of **P4**.

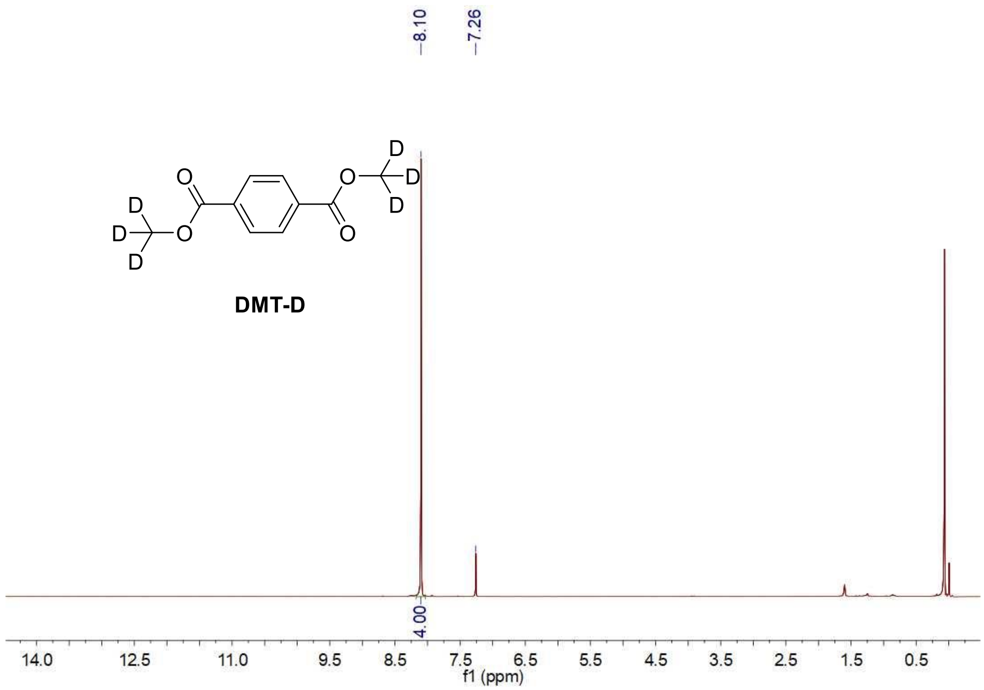

Figure S57. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **DMT-D**.

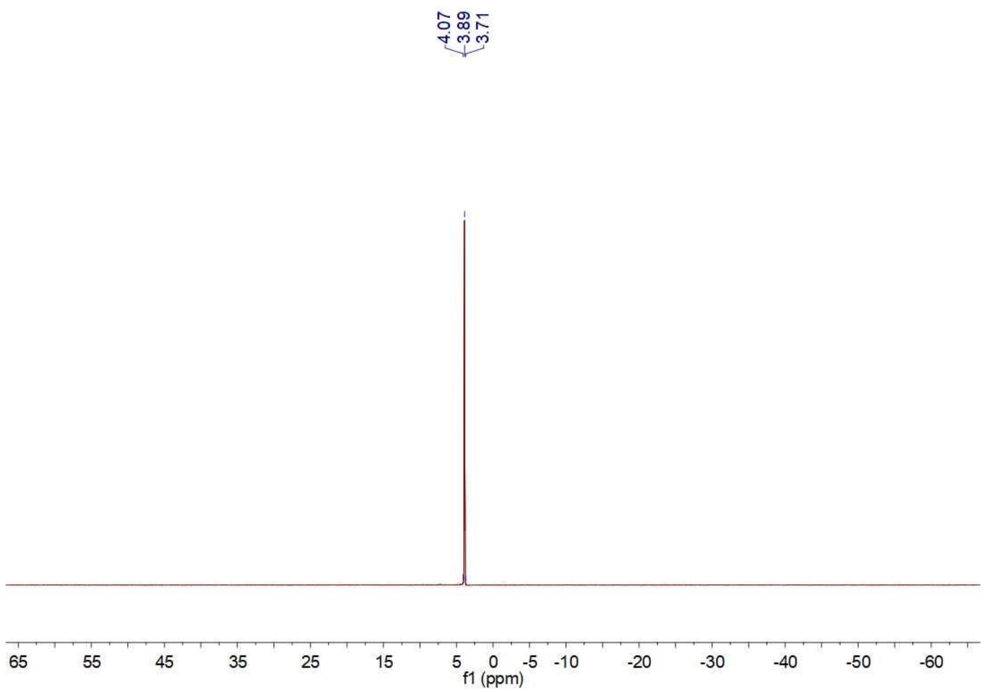

Figure S58. ^{2}H NMR (61 MHz, $CDCl_3$) spectrum of **DMT-D**.

Table S1. Crystal data and structure refinement.

Empirical formula	$C_{39}H_{44}Cl_{11}Fe_3N_9$
Formula weight	1190.32
Temperature/K	298.15
Crystal system	monoclinic
Space group	C2/c
a/Å	41.6176(10)
b/Å	10.7884(2)
c/Å	22.8010(6)
α/°	90
β/°	99.547(2)
γ/°	90
Volume/Å^3	10095.6(4)
Z	8
ρ_{calc}g/cm^3	1.566
μ/mm^{-1}	12.496
F(000)	4824.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.864 to 153.09
Index ranges	$-48 \leq h \leq 52$, $-10 \leq k \leq 13$, $-28 \leq l \leq 28$
Reflections collected	34334
Independent reflections	10116 [R_{int} = 0.0488, R_{sigma} = 0.0457]
Data/restraints/parameters	10116/350/636
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0696, wR_2 = 0.1993
Final R indexes [all data]	R_1 = 0.1061, wR_2 = 0.2304
Largest diff. peak/hole / e Å^{-3}	0.82/-0.81