Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Zirconium-Catalysed Hydrosilylation of Esters and Depolymerisation of Polyester Plastic Waste

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1. General Considerations

Unless otherwise stated, all reactions and manipulations were performed in a recirculating *mBraunLabMasterDP* inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 80 ºC. NMR spectra were obtained using a *Bruker AVANCE Neo 400 MHz* spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR were referenced to solvent impurities.[1] Proton multiplicity is recorded as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br).

The 4 Å molecular sieves (Aldrich) were activated by drying under dynamic vacuum at 250 °C for 48 h prior to use. Mesitylene (Aldrich) was stored over activated 4 Å molecular sieves and used directly without further purification. d_6-benzene (C_6D_6), *d*-chloroform ($CDCl_3$), d_2-dichloromethane (CD_2Cl_2) and d_8-tetrahydrofuran (THF-d_8) were purchased from Eurisotop and used without further purification.

All monomeric esters, hydrosilanes (Et_3SiH, Ph_3SiH, $(EtO)_3SiH$, polyméthylhydrosiloxane (PMHS), $Me(OMe)_2SiH$ (DMMS)) and hydroboranes (pinacholborane (HBpin), catecholborane (HBCat)) were purchased from commercial suppliers, stored in the glovebox and used as received. $Cp_2Zr(H)Cl$ was purchased from Aldrich and stored inside the freezer (−40 °C) of an Ar-filled glovebox. Polycaprolactone (**PCL**) was purchased from Aldrich, stored in the glovebox and used without further purification. White and blue poly(lactic acid) (**PLA**) were obtained from 3D printer wires. Polyethylene terephthalate (**PET**) chunks were obtained from a commercial Evian® water bottle and used without additional treatment.

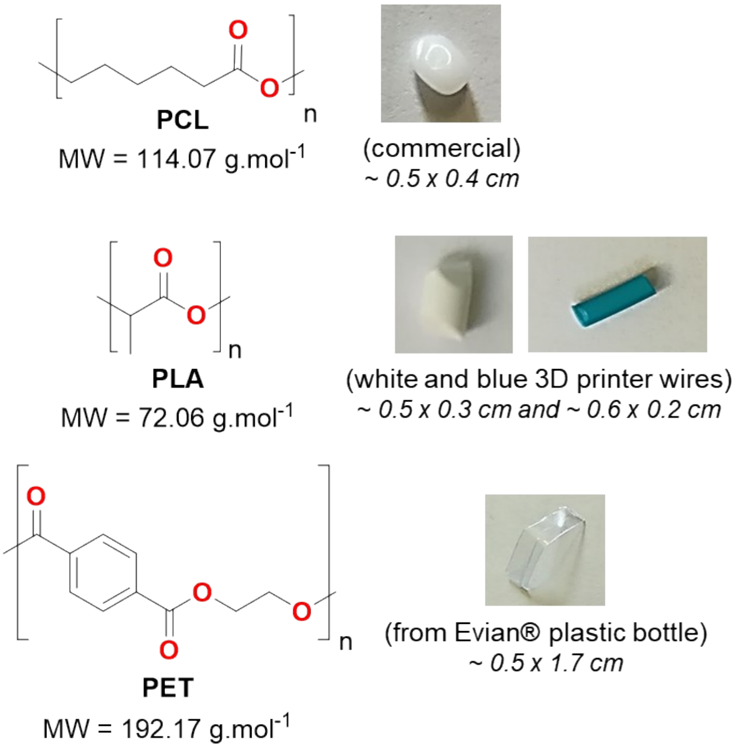
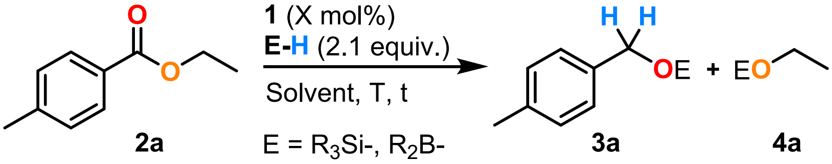


Figure S1. Molecular weights of the monomers related to the different polymers.

2. Reaction Optimisation

Procedure for the optimisation of the reaction conditions for the reduction of monomeric esters using ester **2a** as a model substrate:

The appropriate reductant (0.63 mmol, 2.1 equiv.) was added to a mixture of ethyl 4-methylbenzoate **2a** (48 μL, 0.30 mmol, 1 equiv.), $Cp_2Zr(H)Cl$ **1** (0.8/3.9/8 mg, 0.003/0.015/0.03 mmol, 1/5/10 mol%) and mesitylene as an internal standard (20 μL, 0.14 mmol) in the appropriate solvent (0.5 mL) in a J. Young NMR tube. The tube was then sealed and rotated at room temperature (25 °C) or warmed in a silicon oil bath maintained at 80 or 60 °C for the required time. The yields of the reduced products **3a** and **4a** were determined by ^1H NMR spectroscopy by integration against mesitylene (δ_H = 6.73 and 2.28 ppm in THF-d_8; δ_H = 6.58 and 2.08 ppm in C_6D_6).



Entry	X (cat. mol%)	Solvent	Reductant	T (°C)	Time (h)	Conversion[a] (%)	Yield[a] (%) in 3a
1	10	THF-d_8	DMMS	80	1	>95	>95
2	5	THF-d_8	DMMS	80	1	86	86
					2	>95	>95
3	1	THF-d_8	DMMS	80	1	48	48
					2	61	61
					18	80	81
4	5	THF-d_8	PMHS	80	7	<5	<5
5	5	THF-d_8	Et_3SiH	80	7	n.d.	n.d.
6	5	THF-d_8	Ph_3SiH	80	7	n.d.	n.d.
7	5	THF-d_8	$(EtO)_3SiH$	80	1	31	31
					2	65	65
					5	>95	>95
8	5	C_6D_6	DMMS	80	1	>95	>95
9	5	CD_2Cl_2	DMMS	80	1	72	72
					2	>95	>95
10	5	Anisole	DMMS	80	1	85	85
					2	>95	>95

11	5	C_6D_6	DMMS	25	1	34	30
					7	86	81
					12	>95	>95
12	5	C_6D_6	DMMS	60	1	72	70
					2	>95	>95
13	0	C_6D_6	DMMS	80	12	n.d.	n.d.
14	5	C_6D_6	None	80	12	<5	<5
15	5	C_6D_6	HBpin	80	2	>95	>95
16	5	C_6D_6	HBCat	80	2	8	6
					20	42	42

Table S1. Optimisation of the reaction conditions for the reduction of ester **2a**. ^{a} Conversion and yields measured by ^{1}H NMR spectroscopy against mesitylene as an internal standard. n.d. = not detected.

According to the ^{1}H NMR spectra, we observe a mixture of silylated alcohol products when DMMS or $(EtO)_3SiH$ was used as the reductant, which is due to a mixture of substitution patterns on the silicon atom. As described in the literature,[2] the rearrangement of the alkoxy substituents on silanes can be catalysed by Group IV metallocene complexes.

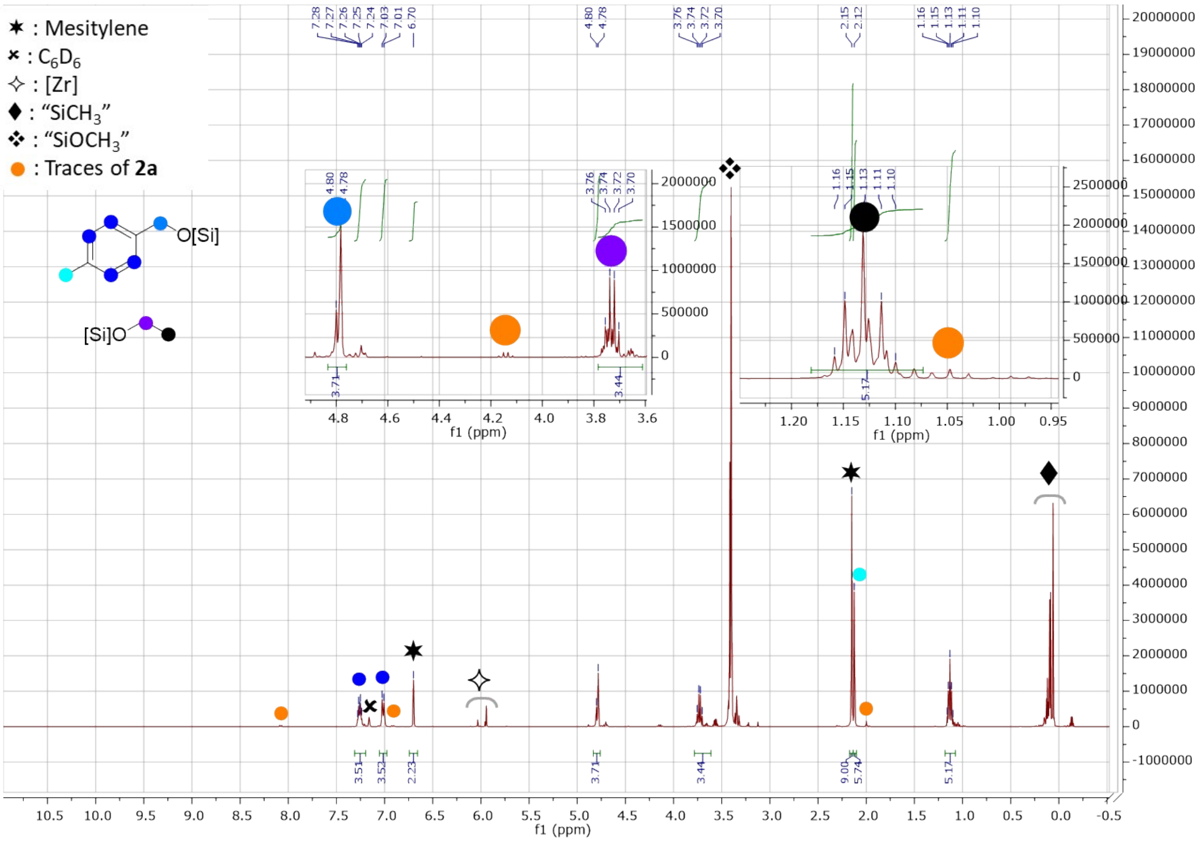
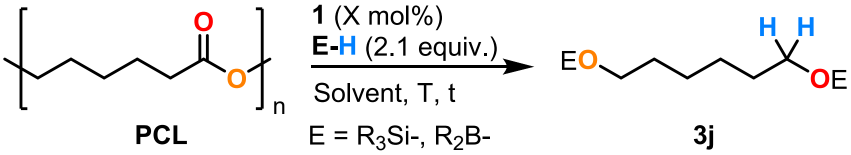


Figure S2. ^{1}H NMR spectra of the reduction of **2a** of Entry 8 in Table S1 (5 mol% of **1**, 2.1 equiv. of DMMS in C_6D_6 at 80 °C for 1 h). Identification of the characteristic peaks of the silylated monomers **3a** and **4a**.

Procedure for the optimisation of the reaction conditions for polyester reduction using **PCL** as a model substrate:

Pellets of **PCL** (34 mg, 0.30 mmol, 1 equiv.) and $Cp_2Zr(H)Cl$ **1** (0.8/3.9/8 mg, 0.003/0.015/0.03 mmol, 1/5/10 mol%) were added to a J. Young NMR tube followed by the appropriate solvent (0.5 mL) and mesitylene as an internal standard (20 µL, 0.14 mmol). To the resulting mixture was added the hydride donor (0.63 mmol, 2.1 equiv.). The tube was then sealed and rotated at room temperature (25 °C) or warmed in a silicon oil bath maintained at 80 °C for the required time. The yields of the reduced monomeric products **3j** were determined by ^1H NMR spectroscopy by integration against mesitylene (δ_H = 6.73 and 2.28 ppm in THF-d_8; δ_H = 6.58 and 2.08 ppm in C_6D_6).



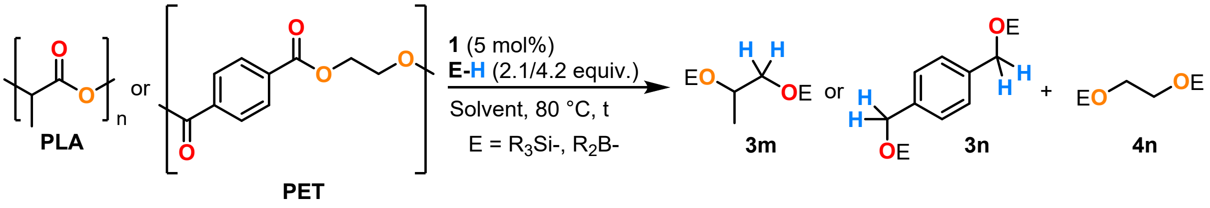
Entry	X (cat. mol%)	Solvent	Reductant	T (°C)	Time (h)	Yield[a] (%) in 3j
1	10	THF-d_8	DMMS	80	1	90
					3	95
2	5	THF-d_8	DMMS	80	1	82
					4	94
3	1	THF-d_8	DMMS	80	1	45
					3	80
					7	>95
4	10	THF-d_8	PMHS	80	19	n.d.
5	10	THF-d_8	TMDS	80	19	n.d.
6	10	THF-d_8	Cl_3SiH	80	19	n.d.
7	10	THF-d_8	$(MeO)_3SiH$	80	1	88
					3	94
8	5	C_6D_6	DMMS	80	4	49
					8	91
9	5	Anisole	DMMS	80	4	65
					21	>95
10	10	THF-d_8	DMMS	25	1	46
					3	74

11	5	THF-d_8	HBpin	80	1	65
					3	>95
12	5	THF-d_8	HBCat	80	4	39
					36	61

Table S2. Optimisation of the reaction conditions for the reduction of **PCL**. [a] Conversion and yields measured by ^{1}H NMR spectroscopy against mesitylene as an internal standard. n.d. = not detected.

Optimisation of the depolymerisation of **PLA** (blue and white) and **PET**:

Pellets or chunks of the appropriate plastic polymer (0.30 mmol, 1 equiv.) and $Cp_2Zr(H)Cl$ **1** (3.9 mg, 0.015 mmol, 5 mol%) were added to a J. Young NMR tube followed by the appropriate solvent (0.5 mL) and mesitylene as an internal standard (20 µL, 0.14 mmol). To the resulting mixture was added the hydride donor (0.63/1.26 mmol, 2.1/4.2 equiv.). The tube was then sealed and warmed in a silicon oil bath maintained at 80 °C for the required time. The yields of the reduced monomeric products **3m**, **3n** and **4n** were determined by ^{1}H NMR spectroscopy by integration against mesitylene (δ_H = 6.73 and 2.28 ppm in THF-d_8; δ_H = 6.58 and 2.08 ppm in C_6D_6).



Entry	Polymer	Solvent	Reductant	T (°C)	Time (h)	Yield[a] (%) in 3m or 3n
1	PLA blue	THF-d_8	DMMS	80	4	>95
2	PLA blue	THF-d_8	HBpin	80	4	66
					38	89
3	PLA blue	THF-d_8	HBCat	80	4	47
					38	58
4	PLA blue	Anisole	DMMS	80	4	55
					38	92
5	PLA white	THF-d_8	DMMS	80	4	75
6	PLA white	THF-d_8	HBpin	80	4	62
					38	74

7	PLA white	THF-d_8	HBCat	80	4	28
					38	57
8	PLA white	Anisole	DMMS	80	4	58
					38	81
9	PET	THF-d_8	DMMS	80	22	>95
10	PET	THF-d_8	HBpin	80	22	92
					54	93
11	PET	THF-d_8	HBCat	80	22	21
					54	41
12	PET	Anisole	DMMS	80	22	55
					54	84

Table S3. Optimisation of the reductive depolymerisation of **PLA (**blue and white) and **PET**. [a] Conversion and yields measured by ^{1}H NMR spectroscopy against mesitylene as an internal standard.

3. Mechanistic Study

Stepwise addition of reaction components:

Ethyl 4-methylbenzoate **2a** (48 µL, 0.30 mmol, 1 equiv.) and $Cp_2Zr(H)Cl$ **1** (77.4 mg, 0.30 mmol, 1 equiv.) were added to a J. Young NMR tube followed by C_6D_6 (0.5 mL) and mesitylene as an internal standard (20 µL, 0.14 mmol). The tube was then sealed and warmed in a silicon oil bath maintained at 80 °C for 16 h. The reaction was followed by ^1H NMR spectroscopy and the conversion and yields of the alkoxy zirconocene products **3a**$^{\mathbf{Zr}}$ and **4a**$^{\mathbf{Zr}}$ were determined by ^1H NMR spectroscopy by integration against mesitylene (δ_H = 6.58 and 2.08 ppm in C_6D_6). To the resulting solution was added DMMS (39 µL, 0.33 mmol, 1.1 equiv.). The tube was then sealed and warmed in a silicon oil bath maintained at 80 °C for 25 h. Again, the reaction was followed by ^1H NMR spectroscopy to determine the conversion and yields of alkoxy zirconocene products **3a**$^{\mathbf{Zr}}$ and **4a**$^{\mathbf{Zr}}$ and silyl ether products **3a**$^{\mathbf{Si}}$ and **4a**$^{\mathbf{Si}}$ by ^1H NMR spectroscopy by integration against mesitylene (δ_H = 6.58 and 2.08 ppm in C_6D_6).

2a **3a**$^{\mathbf{Zr}}$ **4a**$^{\mathbf{Zr}}$ **3a**$^{\mathbf{Si}}$ **4a**$^{\mathbf{Si}}$

Time (h)	Conversion[a] (%) of 2a	Yield[a] (%) in 3a^{Zr}	Yield[a] (%) in 4a^{Zr}	Yield[a] (%) in 3a^{Si}	Yield[a] (%) in 4a^{Si}
1	40	42	43	-	-
2	47	49	50	-	-
16	47	48	51	-	-
Add of DMMS					
17	100	42	24	61	78
18	100	39	23	64	79
41	100	38	23	64	78

Table S4. Time-step analysis by ^1H NMR of the stepwise stoichiometric reduction of **2a** by complex **1** and DMMS. [a] Conversion and yields measured by ^1H NMR against mesitylene as an internal standard.

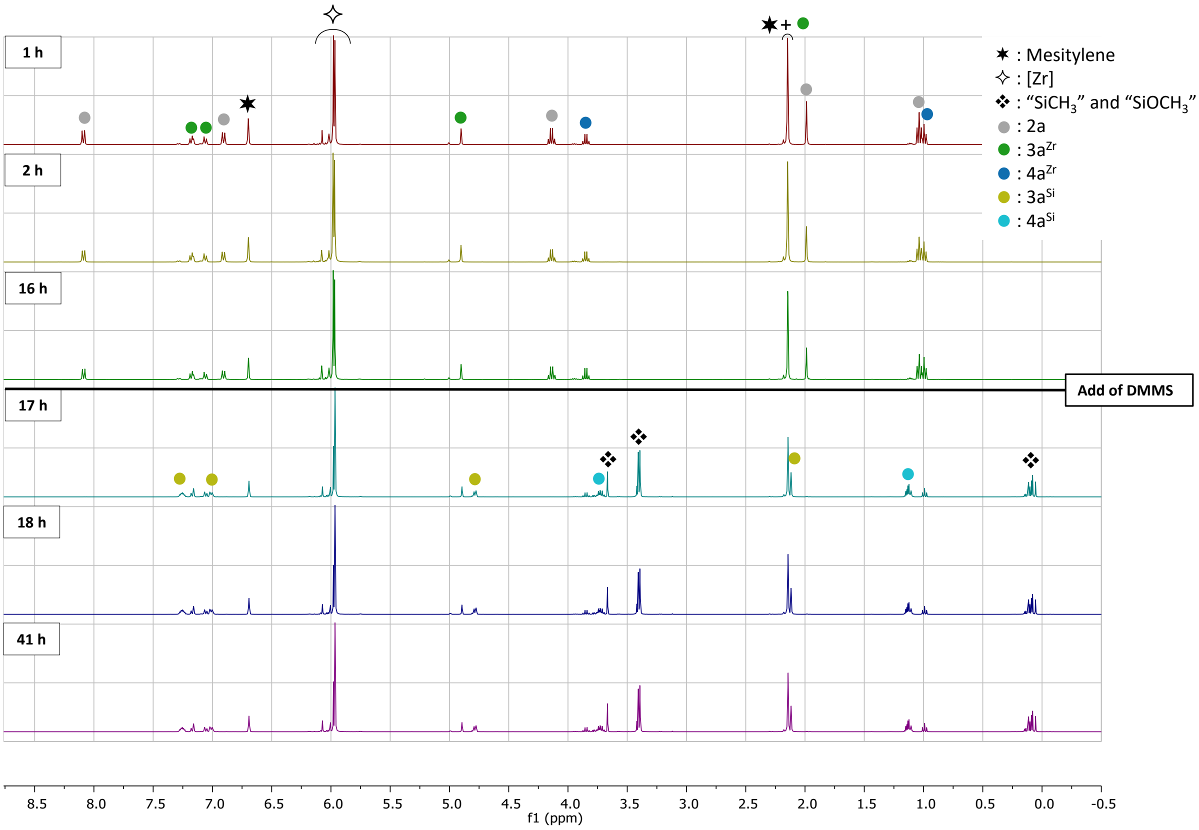
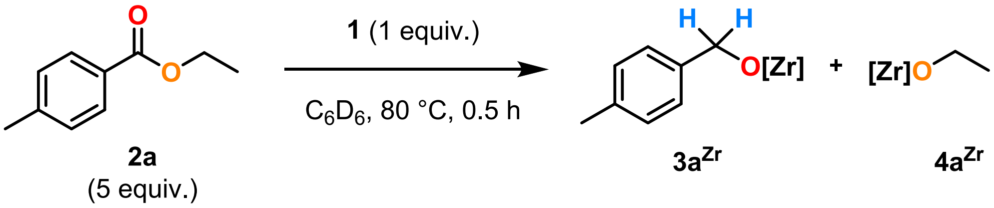


Figure S3. ^{1}H NMR spectra of the stepwise stoichiometric reduction of **2a** by complex **1** and DMMS. Identification of the characteristic peaks of the alkoxy zirconocene products **3a**^{Zr} and **4a**^{Zr} and silyl ether products **3a**^{Si} and **4a**^{Si}.

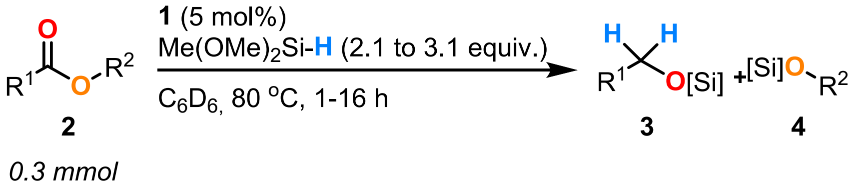
Slow addition of **1** to an excess of **2a**:



Cp$_2$Zr(H)Cl **1** (77.4 mg, 0.30 mmol) was added in portions to a solution of Ethyl 4-methylbenzoate **2a** (240 μL, 1.50 mmol, 5 equiv.) in C$_6$D$_6$ (0.5 mL) and mesitylene as an internal standard (20 μL, 0.14 mmol). The resulting mixture was transferred to a J. Young NMR tube. The tube was sealed and shaken vigorously and warmed in a silicon oil bath maintained at 80 °C for 0.5 h. The reaction mixture was analysed by ^{1}H NMR spectroscopy to determine the conversion and yields of alkoxy zirconocene products **3a**^{Zr} (34%) and **4a**^{Zr} (39%) by integration against mesitylene (δ_H = 6.58 and 2.08 ppm in C$_6$D$_6$). No hemiacetal or aldehyde intermediates were observed by NMR spectroscopy.

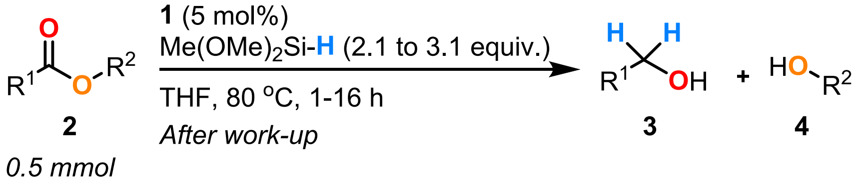
4. Monomeric Ester Reduction Scope and Characterisation

General NMR-scale procedure for the reduction of monomeric esters:



DMMS (77/114 μL, 0.63/0.93 mmol, 2.1/3.1 equiv.) was added to a mixture of the appropriate ester **2** (0.30 mmol, 1 equiv.), $Cp_2Zr(H)Cl$ (3.9 mg, 0.015 mmol, 5 mol%) and mesitylene (20 μL, 0.14 mmol) as an internal standard in C_6D_6 (0.5 mL) in a J. Young NMR tube. The tube was then sealed and warmed in a silicon oil bath maintained at 80 or 40 °C for 1–16 h. Yields of the silylated alcohol products **3** and **4** were determined by ^1H NMR spectroscopy by integration against mesitylene (δ_H = 6.58 and 2.08 ppm in C_6D_6).

General scale-up and characterisation procedure for the reduction of monomeric esters:

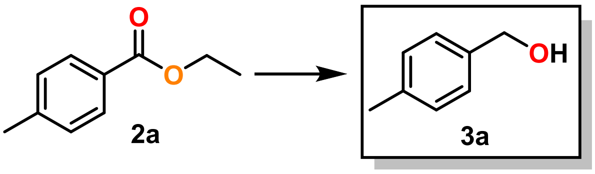


DMMS (128/189 μL, 1.05/1.55 mmol, 2.1/3.1 equiv.) was added to a mixture of the appropriate ester **2** (0.50 mmol, 1 equiv.) and $Cp_2Zr(H)Cl$ (6.5 mg, 0.025 mmol, 5 mol%) in THF (1.3 mL) in a sealed round-bottom flask. The reaction was removed from the glovebox and heated in a silicon oil bath at 80 or 40 °C with stirring for 1–16 h. The reaction mixture was allowed to cool to room temperature and was quenched with 10 wt% NaOH in MeOH/H_2O (1:1) solution (1 mL). The reaction mixture was stirred for 2 h at room temperature. The alcohol product **3** or **4** was isolated according to workup procedure A or B.

Workup A:
The reaction mixture was diluted with EtOAc (5 mL) and separated. The aqueous layer was extracted with EtOAc (4x5 mL) and the combined organics were dried over $MgSO_4$ and filtered. The crude solution was then either poured over a silica plug (eluting with 50 mL of EtOAc) to give the analytically pure alcohol product **3** or **4**.

Workup B:
The organic solvents were removed under vacuum (45 °C, ~300 mbar) and the mixture was diluted with H_2O (5 mL). The crude aqueous mixture was extracted with Et_2O (4x5 mL) and the combined organics were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give the analytically pure alcohol product **3** or **4**.

4-Methylbenzyl alcohol **3a** from ethyl 4-methylbenzoate **2a**

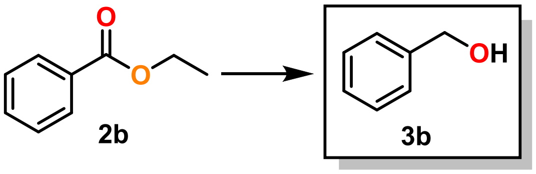


According to the general scale-up procedure with workup A, **3a** was formed in a yield of 66% from **2a**. NMR data is in accordance with those previously reported in the literature.[3]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.26 (d, J = 8.0 Hz, 2H, H^{Ar}), 7.18 (d, J = 7.9 Hz, 2H, H^{Ar}), 4.65 (s, 2H, CH_2), 2.35 (s, 3H, CH_3). Hydroxyl proton not visible on the spectra most likely due to it being very broad

^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) = 138.1 ($C_{\mathrm{q}}^{\mathrm{Ar}}$), 137.6 ($C_{\mathrm{q}}^{\mathrm{Ar}}$), 129.4 ($C^{\mathrm{Ar}}$), 127.3 ($C^{\mathrm{Ar}}$), 65.5 ($CH_2$), 21.3 ($CH_3$).

Benzyl alcohol **3b** from ethyl benzoate **2b**

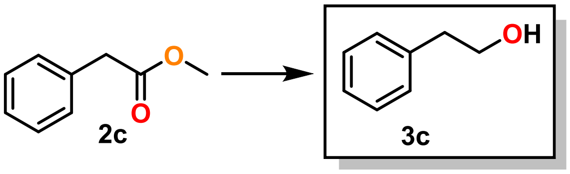


According to the general scale-up procedure with workup A, **3b** was formed in a yield of 57% from **2b**. NMR data is in accordance with those previously reported in the literature.[4]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.40 – 7.27 (m, 5H, H^{Ar}), 4.69 (s, 2H, CH_2), 1.94 (s, br, 1H, OH).

^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) = 140.9 ($C_{\mathrm{q}}^{\mathrm{Ar}}$), 128.6 ($C^{\mathrm{Ar}}$), 127.7 ($C^{\mathrm{Ar}}$), 127.0 ($C^{\mathrm{Ar}}$), 65.4 ($CH_2$).

2-Phenylethanol **3c** from methyl phenylacetate **2c**

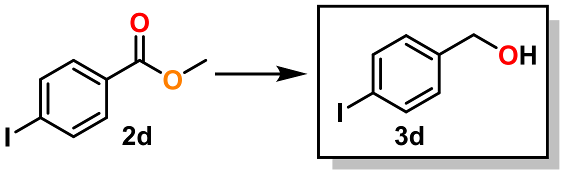


According to the general scale-up procedure with workup A, **3c** was formed in a yield of 83% from **2c**. NMR data is in accordance with those previously reported in the literature.[5]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.36 – 7.30 (m, 2H, H^{Ar}), 7.28 – 7.22 (m, 3H, H^{Ar}), 3.87 (t, J = 6.6 Hz, 2H, CH_2OH), 2.88 (t, J = 6.6 Hz, 2H, ArCH_2), 1.66 (s, br, 1H, OH).

^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) = 138.6 ($C_{\mathrm{q}}^{\mathrm{Ar}}$), 129.2 ($C^{\mathrm{Ar}}$), 128.7 ($C^{\mathrm{Ar}}$), 126.6 ($C^{\mathrm{Ar}}$), 63.8 ($CH_2$), 39.3 ($CH_2$).

4-Iodobenzyl alcohol **3d** from methyl 4-iodobenzoate **2d**

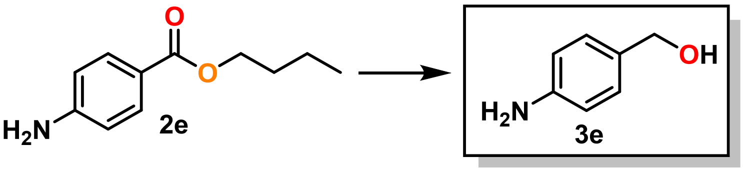


According to the general scale-up procedure with workup A, **3d** was formed in a yield of 72% from **2d**. NMR data is in accordance with those previously reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.69 (d, J = 8.3 Hz, 2H, H^{Ar}), 7.12 (d, J = 8.4 Hz, 2H, H^{Ar}), 4.65 (s, 2H, CH_2), 1.97 (s, br, 1H, OH).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 140.6 (C_q^{Ar}), 137.8 (C^{Ar}), 129.0 (C^{Ar}), 93.1 (C_q^{Ar}), 64.8 (CH_2).

4-Aminobenzyl alcohol **3e** from butyl 4-aminobenzoate **2e**

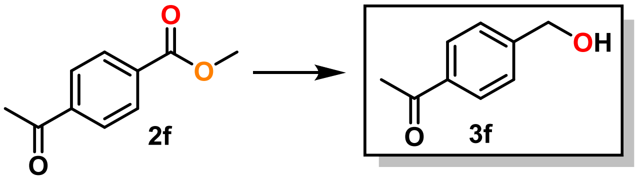


According to the general scale-up procedure with workup A, **3e** was formed in a yield of 91% from **2e**. NMR data is in accordance with those previously reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.16 (d, J = 8.4 Hz, 2H, H^{Ar}), 6.68 (d, J = 8.4 Hz, 2H, H^{Ar}), 4.56 (s, 2H, CH_2), 3.69 (s, br, 2H, NH_2), 1.58 (s, br, 1H, OH).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 146.3 (C_q^{Ar}), 131.2 (C_q^{Ar}), 128.9 (C^{Ar}), 115.3 (C^{Ar}), 65.5 (CH_2).

4-(1-Hydroxyethyl)benzyl alcohol **3f** from methyl 4-acetylbenzoate **2f**

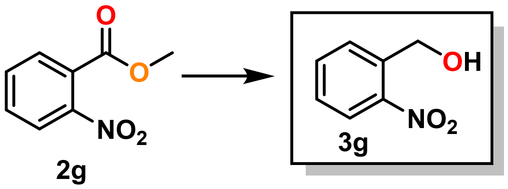


According to the general scale-up procedure with workup A, **3f** was formed in a yield of 77% from **2f**. NMR data is in accordance with those previously reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.39 – 7.30 (m, 4H, H^{Ar}), 4.89 (q, J = 6.5 Hz, 1H, CH), 4.66 (s, 2H, CH_2), 1.97 (s, br, 2H, OH), 1.48 (d, J = 6.5 Hz, 3H, CH_3).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 145.4 (C_q^{Ar}), 140.2 (C_q^{Ar}), 127.3 (C^{Ar}), 125.7 (C^{Ar}), 70.3 (CH_3), 65.2 (CH_2), 25.3 (CH).

2-Nitrobenzyl alcohol **3g** from methyl 2-nitrobenzoate **2g**

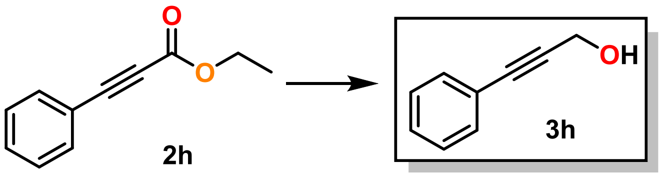


According to the general scale-up procedure with workup A, **3g** was formed in a yield of 64% from **2g**. NMR data is in accordance with those previously reported in the literature.[9]

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.11 (dd, J = 8.2, 1.1 Hz, 1H, H^{Ar}), 7.75 (d, J = 7.7 Hz, 1H, H^{Ar}), 7.68 (td, J = 7.5, 1.2 Hz, 1H, H^{Ar}), 7.52 – 7.45 (m, 1H, H^{Ar}), 4.98 (s, 2H, CH_2), 2.51 (s, br, 1H, OH).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 136.8 (C_q^{Ar}), 134.2 (C^{Ar}), 130.1 (C^{Ar}), 128.6 (C^{Ar}), 125.06 (C^{Ar}), 62.6 (CH_2).

3-Phenyl-2-propyn-1-ol **3h** from ethyl phenylpropiolate **2h**

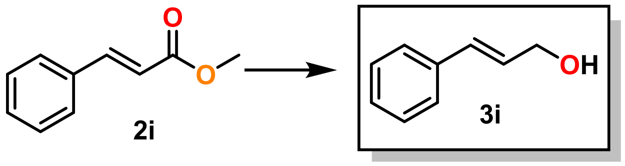


According to the general scale-up procedure with workup A, **3h** was formed in a yield of 66% from **2h**. NMR data is in accordance with those previously reported in the literature.[10]

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50 – 7.44 (m, 2H, H^{Ar}) 7.35 (m, 3H, H^{Ar}), 4.53 (s, 2H, CH_2), 1.82 (s, br, 1H, OH).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 131.7 (C^{Ar}), 128.4 (C^{Ar}), 122.6 (C_q^{Ar}), 87.2 (Ph-C≡*C*-CH_2-OH), 85.8 (Ph-*C*≡C-CH_2-OH), 51.7 (CH_2).

(E)-Cinnamyl alcohol **3i** from methyl cinnamate **2i**

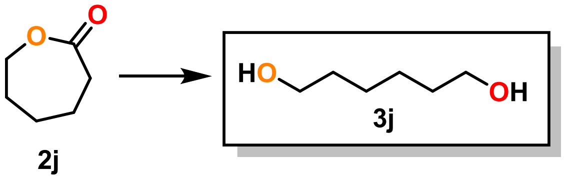


According to the general scale-up procedure with workup B, **3i** was formed in a yield of 82% from **2i**. NMR data is in accordance with those previously reported in the literature.[11]

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.42 – 7.37 (m, 2H, H^{Ar}), 7.36 – 7.30 (m, 2H, H^{Ar}), 7.28 – 7.23 (m, 1H, H^{Ar}), 6.62 (d, J = 15.9 Hz, 1H, ArC*H*=CH), 6.37 (dt, J = 15.9, 5.7 Hz, 1H, ArCH=C*H*), 4.33 (dd, J = 5.7, 1.6 Hz, 2H, CH_2), 1.64 (s, br, 1H, OH).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 136.7 (C_q^{Ar}), 131.2 (Ph-*C*=C-CH_2-OH), 128.6 (Ph-C=*C*-CH_2-OH), 128.5 (C^{Ar}), 127.7 (C^{Ar}), 126.5 (C^{Ar}), 63.8 (CH_2).

1,6-Hexanediol **3j** from Ɛ-caprolactone **2j**

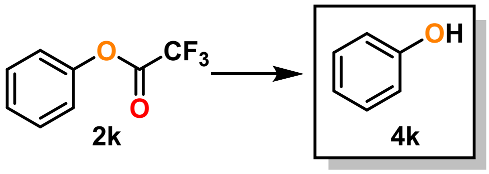


According to the general scale-up procedure with workup B, **3j** was formed in a yield of 66% from **2j**. NMR data is in accordance with those previously reported in the literature.[12]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 3.63 (t, *J* = 6.5 Hz, 4H, C*H*$_2$OH), 1.82 (s, br, 2H, O*H*), 1.63 – 1.50 (m, 4H, C*H*$_2$CH$_2$OH), 1.46 – 1.31 (m, 4H, C*H*$_2$CH$_2$CH$_2$OH).

^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) = 62.9 (*C*H$_2$OH), 32.8 (*C*H$_2$CH$_2$OH), 25.6 (*C*H$_2$CH$_2$CH$_2$OH).

Phenol **4k** from phenyl trifluoroacetate **2k**

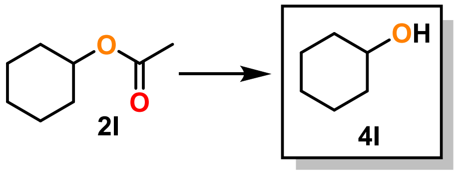


According to the general scale-up procedure, **4k** was formed in a yield of 27% from **2k**. NMR data is in accordance with those previously reported in the literature.[13]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.35 – 7.22 (m, 2H, *H*^{Ar}), 6.97 (t, *J* = 7.4 Hz, 1H, *H*^{Ar}), 6.87 (d, *J* = 7.7 Hz, 2H, *H*^{Ar}), 4.90 (s, br, 1H, O*H*).

^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) = 155.5 (*C*$_q^{Ar}$), 129.7 (*C*^{Ar}), 120.8 (*C*^{Ar}), 115.3 (*C*^{Ar}).

Cyclohexanol **4l**



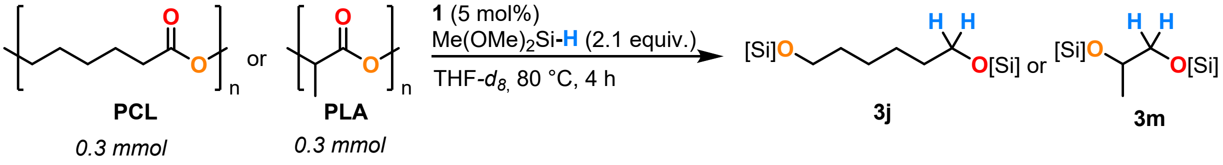
According to the general scale-up procedure with workup B, **4l** was formed in a yield of 62% from **2l**. NMR data is in accordance with those previously reported in the literature.[14]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 3.71 – 3.52 (m, 1H, C*H*), 1.94 – 1.82 (m, 2H, C*H*$_2$), 1.75 – 1.67 (m, 3H, C*H*$_2$), 1.58 – 1.49 (m, 1H, C*H*$_2$), 1.33 – 1.08 (m, 5H, C*H*$_2$).

^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm) = 70.3 (*C*H(OH)), 35.5 (*C*H$_2$), 25.4 (*C*H$_2$), 24.2 (*C*H$_2$).

5. Polyester Reductive Depolymerisation Scope and Characterisation

NMR-scale procedure for the depolymerisation of **PCL** and **PLA**:

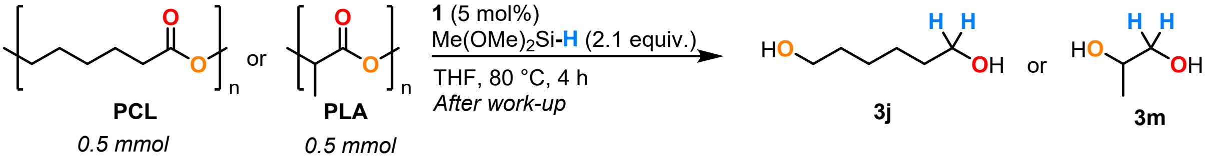


In a glovebox under a purified argon atmosphere, DMMS (77 µL, 0.63 mmol, 2.1 equiv.) was added to a mixture of pellets and chunks of a plastic polymer (0.30 mmol, 1 equiv.), $Cp_2Zr(H)Cl$ (3.9 mg, 0.015 mmol, 5 mol%) and mesitylene (20 µL, 0.14 mmol) as an internal standard in THF-d_8 (0.5 mL) in a J. Young NMR tube. The tube was then sealed and warmed in a silicon oil bath maintained at 80 °C for 4 h at which point the plastic has disappeared. Yields of the silylated alcohol products **3j** or **3m** were determined by ^{1}H NMR spectroscopy by integration against mesitylene (δ_H = 6.73 and 2.28 ppm in THF-d_8).

At the end of the reaction, the pellets/chunks of the polymer have completely disappeared. In blue or white **PLA** reaction mixtures, the solution were colourless and contained blue or white suspension and deposits of the additives (Figure S2).

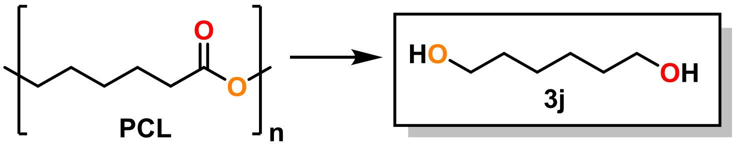
Figure S4. NMR tubes after depolymerisation of blue and white **PLA**, with the deposits of the additives in the crude mixture.

Scale-up procedure for the depolymerisation of **PCL** and **PLA**:



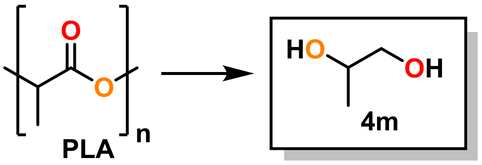
DMMS (128 µL, 1.05 mmol, 2.1 equiv.) was added to a mixture of pellets and chunks of the plastic polymer (0.50 mmol, 1 equiv.) and $Cp_2Zr(H)Cl$ (6.5 mg, 0.025 mmol, 5 mol%) in THF (1.3 mL) in a sealed round-bottom flask. The flask was removed from the glovebox and heated at 80 °C with stirring for 4 h. The reaction mixture was allowed to cool to room temperature and was quenched with 10 wt% NaOH in MeOH/H_2O (1:1) solution (1 mL). The reaction mixture was stirred for 2 h at room temperature. The organic solvents were removed under vacuum (45 °C, ~300 mbar) and the mixture was diluted with H_2O (5 mL).. The aqueous layer was extracted with Et_2O (4x5 mL) and the combined organics were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give the analytically pure alcohol product **3j** or **3m**.

1,6-Hexanediol **3j** from **PCL**



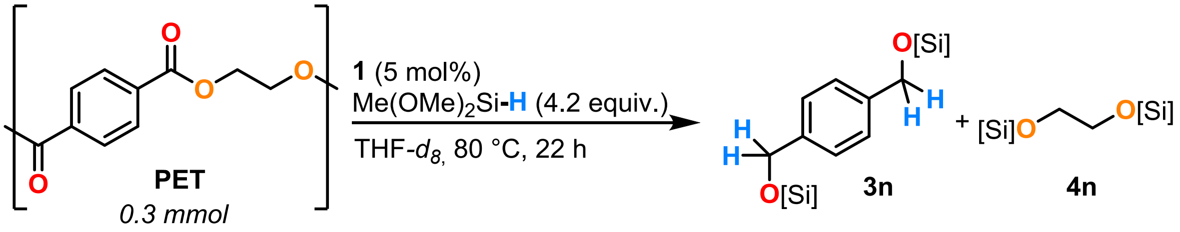
According to the general scale-up procedure, **3j** was formed in a yield of 42% from **PCL**. NMR data is in accordance with those previously reported in the literature.[12]
^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.63 (t, *J* = 6.5 Hz, 4H, C*H*$_2$OH), 1.82 (s, br, 2H, O*H*), 1.63 – 1.50 (m, 4H, C*H*$_2$CH$_2$OH), 1.46 – 1.31 (m, 4H, C*H*$_2$CH$_2$CH$_2$OH).
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 62.9 (*C*H$_2$OH), 32.8 (*C*H$_2$CH$_2$OH), 25.6 (*C*H$_2$CH$_2$CH$_2$OH).

1,2-Propanediol **3m** from **PLA**



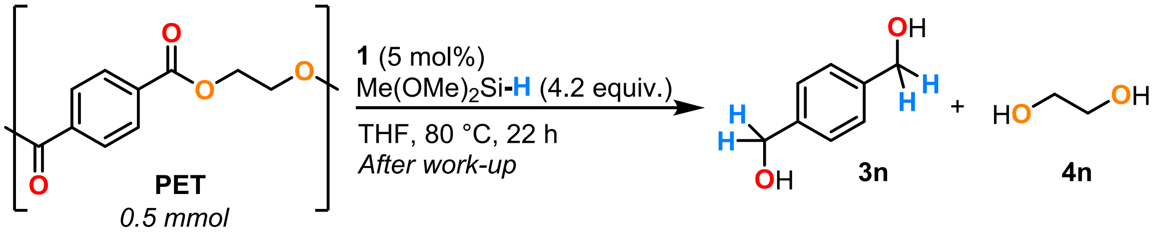
According to the general scale-up procedure, **3m** was formed in a yield of 32% from **PLA**. NMR data is in accordance with those previously reported in the literature.[12]
^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.00 – 3.82 (m, 1H, C*H*), 3.64 – 3.61 (m, 1H, C*H$_2$*), 3.42 – 3.38 (m, 1H, C*H$_2$*), 2.31 (s, br, 1H, O*H*), 2.19 (s, br, 1H, O*H*), 1.17 (d, *J* = 6.4 Hz, 3H, C*H$_3$*).
^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) = 68.5 (*C*H), 68.2 (*C*H$_2$), 19.0 (*C*H$_3$).

NMR-scale procedure for the depolymerisation of **PET**:



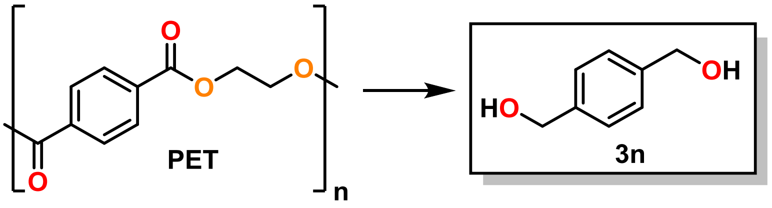
In a glovebox under a purified argon atmosphere, DMMS (154 µL, 1.26 mmol, 4.2 equiv.) was added to a mixture of chunks of a plastic Evian bottle (58 mg, 0.30 mmol, 1 equiv.), $Cp_2Zr(H)Cl$ (3.9 mg, 0.015 mmol, 5 mol%) and mesitylene (20 µL, 0.14 mmol) as an internal standard in THF-d_8 (0.5 mL) in a J. Young NMR tube. The tube was then sealed and warmed in a silicon oil bath maintained at 80 °C for 22 h at which point the plastic has disappeared. Yields of the silylated alcohol products **3n** and **4n** were determined by ^1H NMR spectroscopy by integration against mesitylene (δ_H = 6.73 and 2.28 ppm in THF-d_8).

Scale-up procedure for the depolymerisation of **PET**:



DMMS (256 µL, 2.1 mmol, 4.2 equiv.) was added to a mixture of chunks of a plastic Evian bottle (96 mg, 0.50 mmol, 1 equiv.) and $Cp_2Zr(H)Cl$ (6.5 mg, 0.025 mmol, 5 mol%) in THF (1.3 mL) in a sealed round-bottom flask. The flask was removed from the glovebox and heated at 80 °C with stirring for 22 h. The reaction mixture was allowed to cool to room temperature and was quenched with 10 wt% NaOH in $MeOH/H_2O$ (1:1) solution (1 mL). The reaction mixture was stirred for 2 h at room temperature. The organic solvents were removed under vacuum (45 °C, ~300 mbar) and the mixture was diluted with H_2O (5 mL). The aqueous layer was extracted with Et_2O (4x5 mL) and the combined organics were dried over $MgSO_4$ and filtered. The solvent was removed under vacuum to give the analytically pure alcohol product **3n**.

1,4-Benzenedimethanol **3n** from **PET**



According to the general scale-up procedure, **3n** was formed in a yield of 54% from **PET**. NMR data is in accordance with those previously reported in the literature.[12]

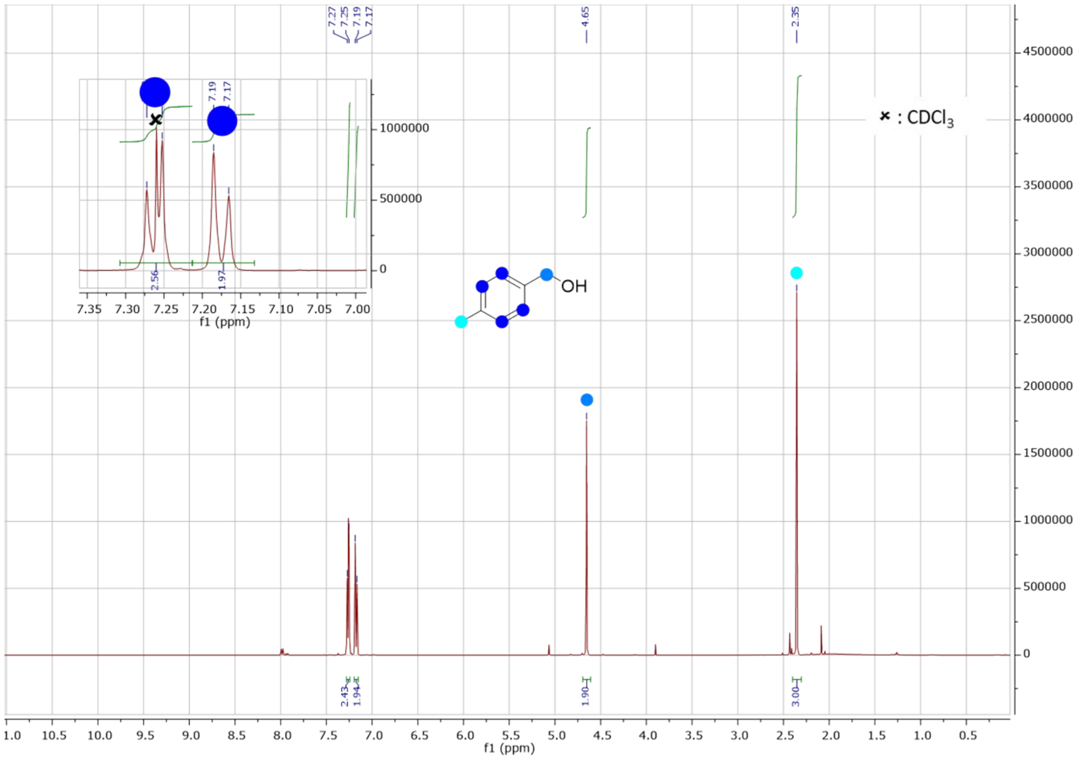
^1H NMR (400 MHz, THF-d_8) δ (ppm) = 7.26 (s, 4H, H^{Ar}), 4.53 (d, J = 5.8 Hz, 4H, CH_2), 4.04 (t, J = 5.8 Hz, 2H, OH).

^{13}C NMR (400 MHz, THF-d_8) δ (ppm) = 142.1 (C_q^{Ar}), 126.8 (C^{Ar}), 64.5 (CH_2).

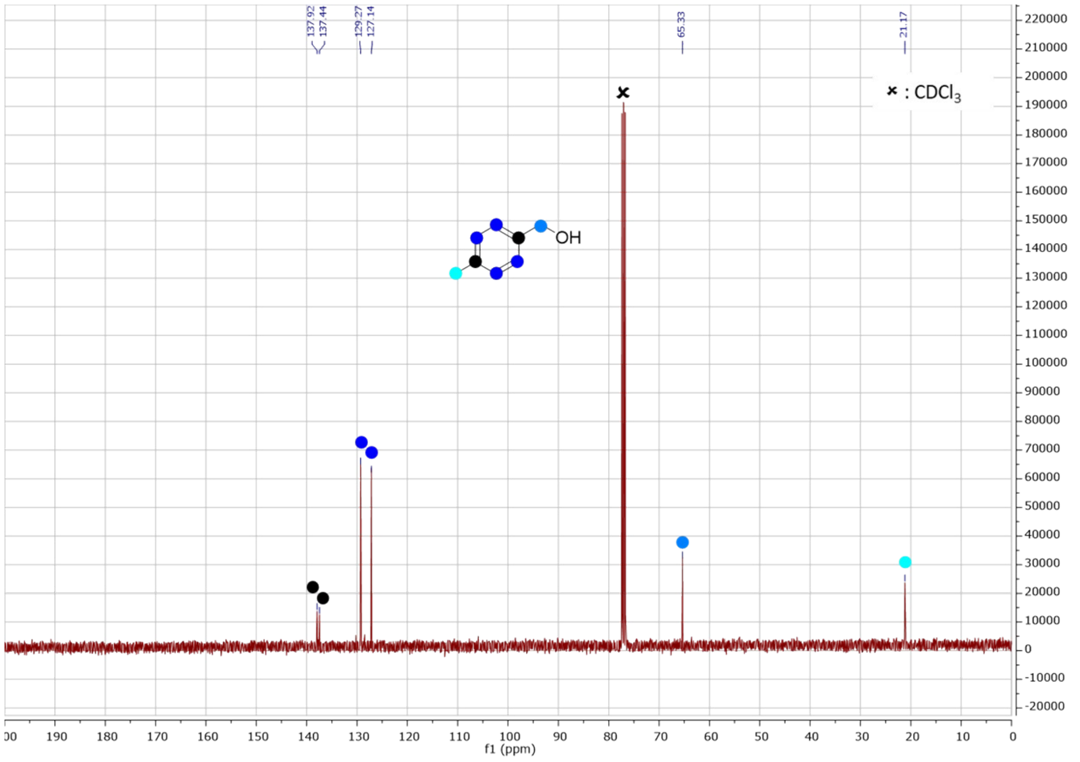
6. ^{1}H and ^{13}C NMR Spectra

4-Methylbenzyl alcohol **3a**

^{1}H NMR (400 MHz, $CDCl_3$)

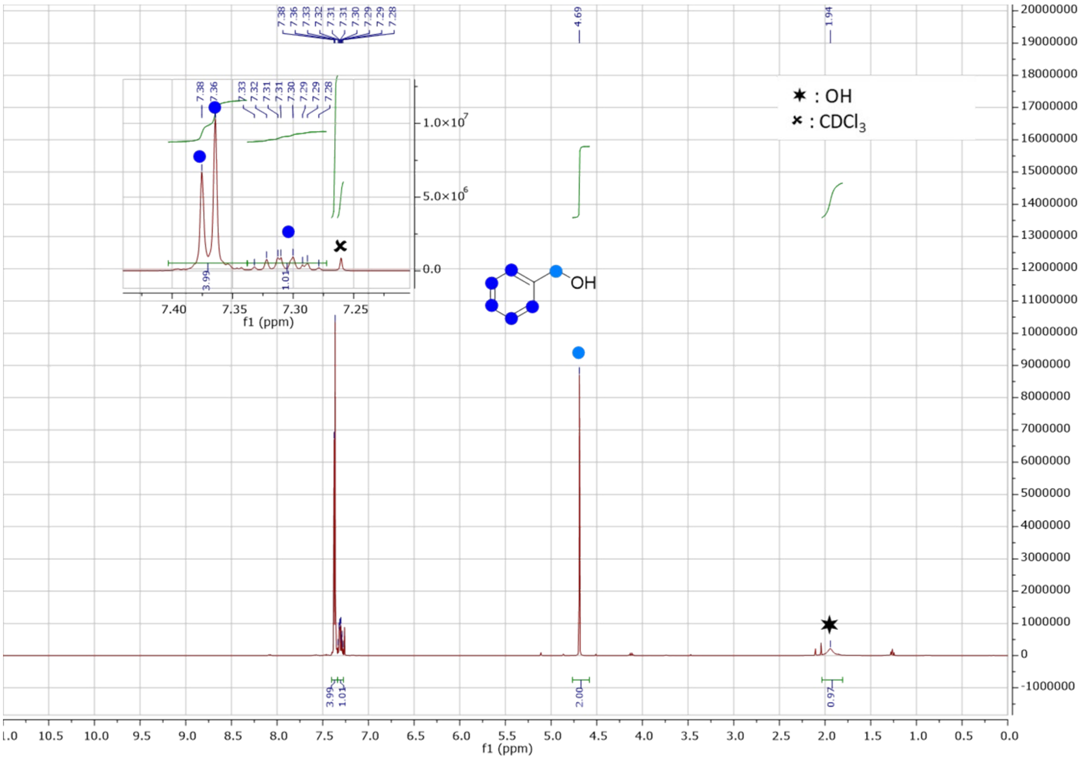


^{13}C NMR (400 MHz, $CDCl_3$)

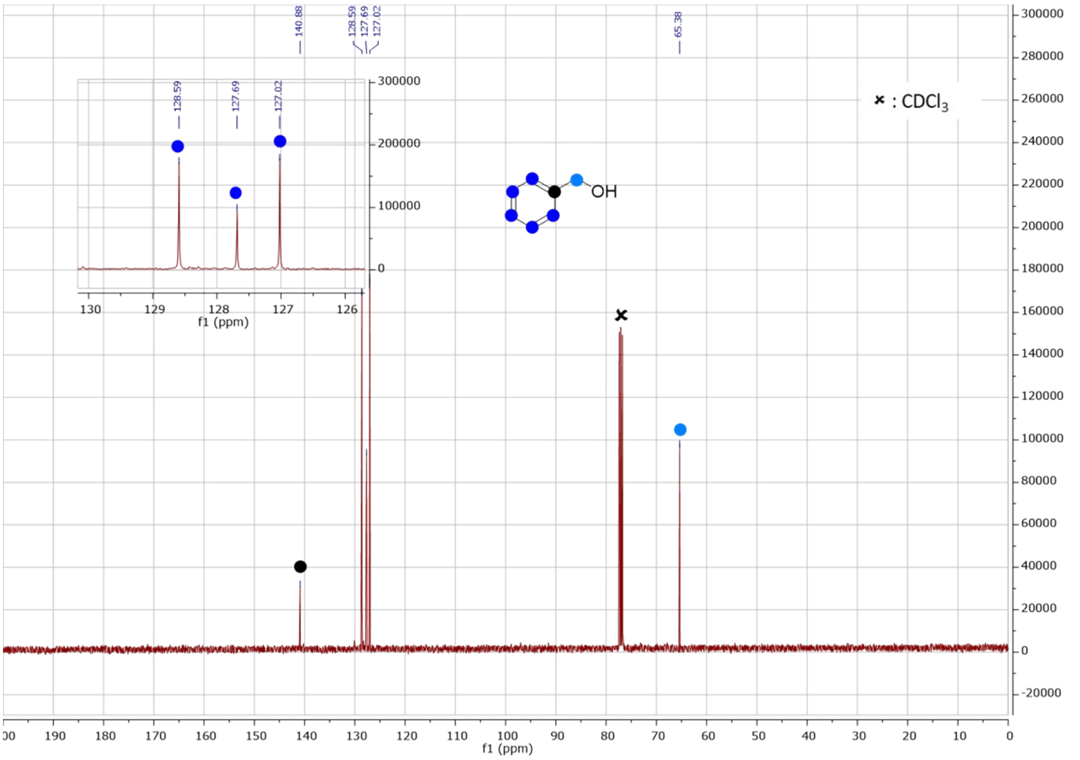


Benzyl alcohol **3b**

^{1}H NMR (400 MHz, CDCl$_3$)

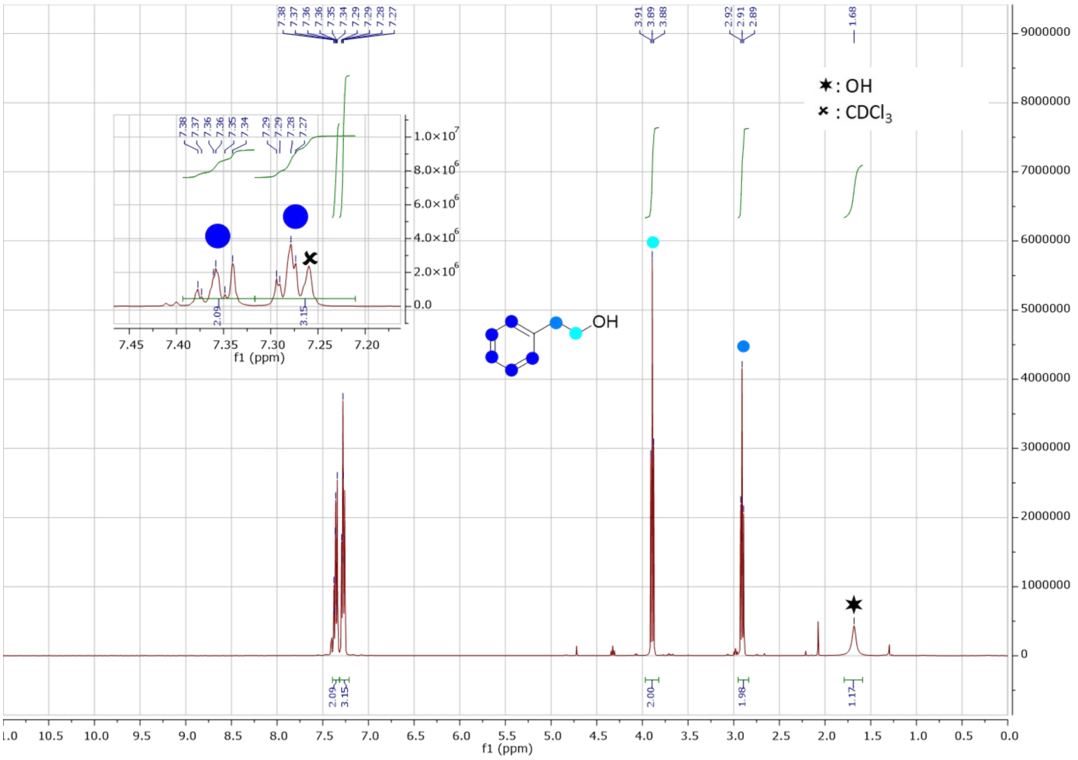


^{13}C NMR (400 MHz, CDCl$_3$)

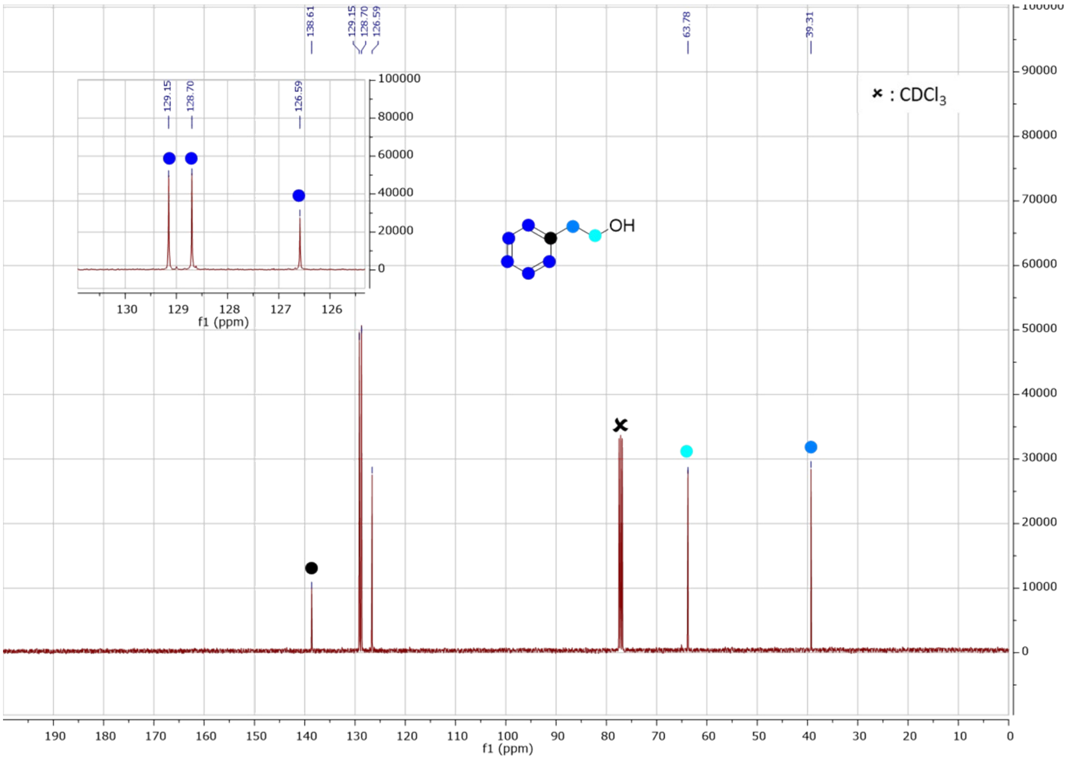


2-Phenylethanol **3c**

^1H NMR (400 MHz, $CDCl_3$)

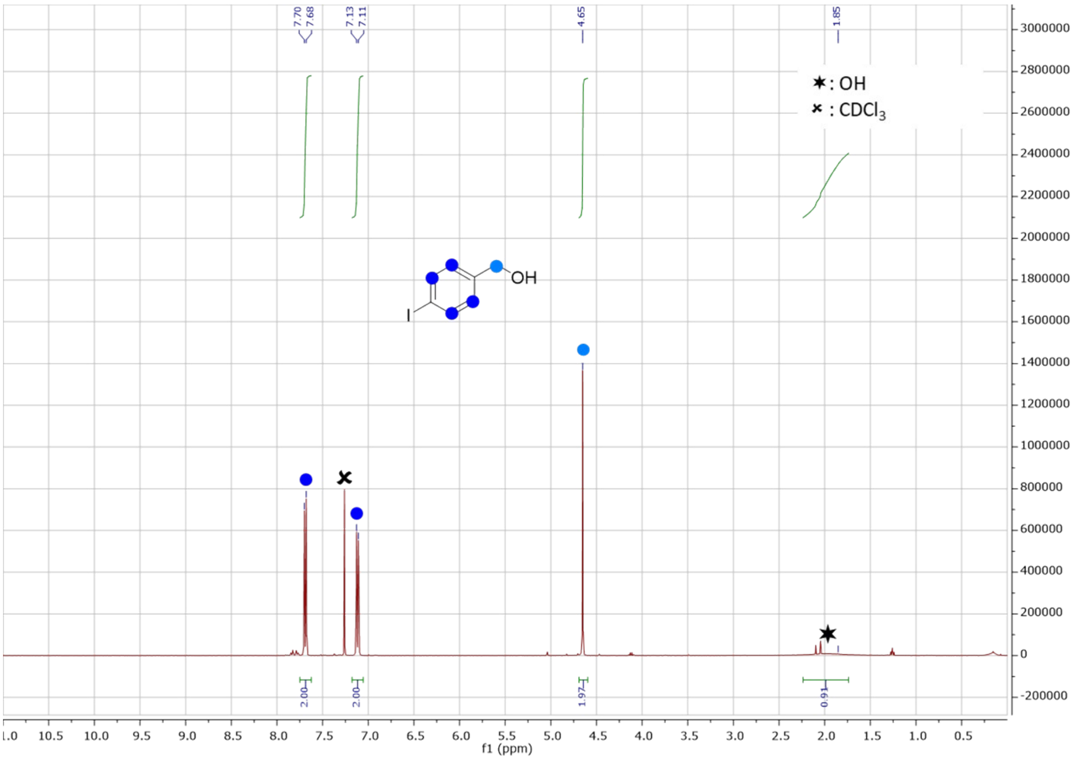


^{13}C NMR (400 MHz, $CDCl_3$)

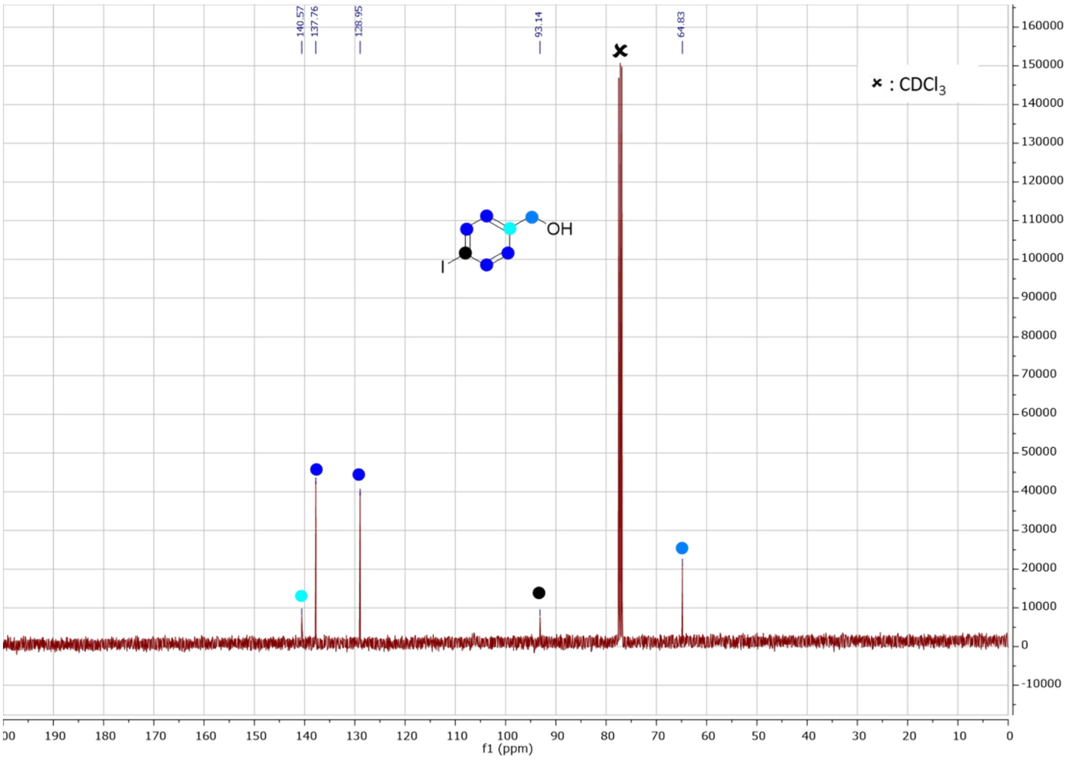


4-Iodobenzyl alcohol **3d**

^{1}H NMR (400 MHz, CDCl$_3$)

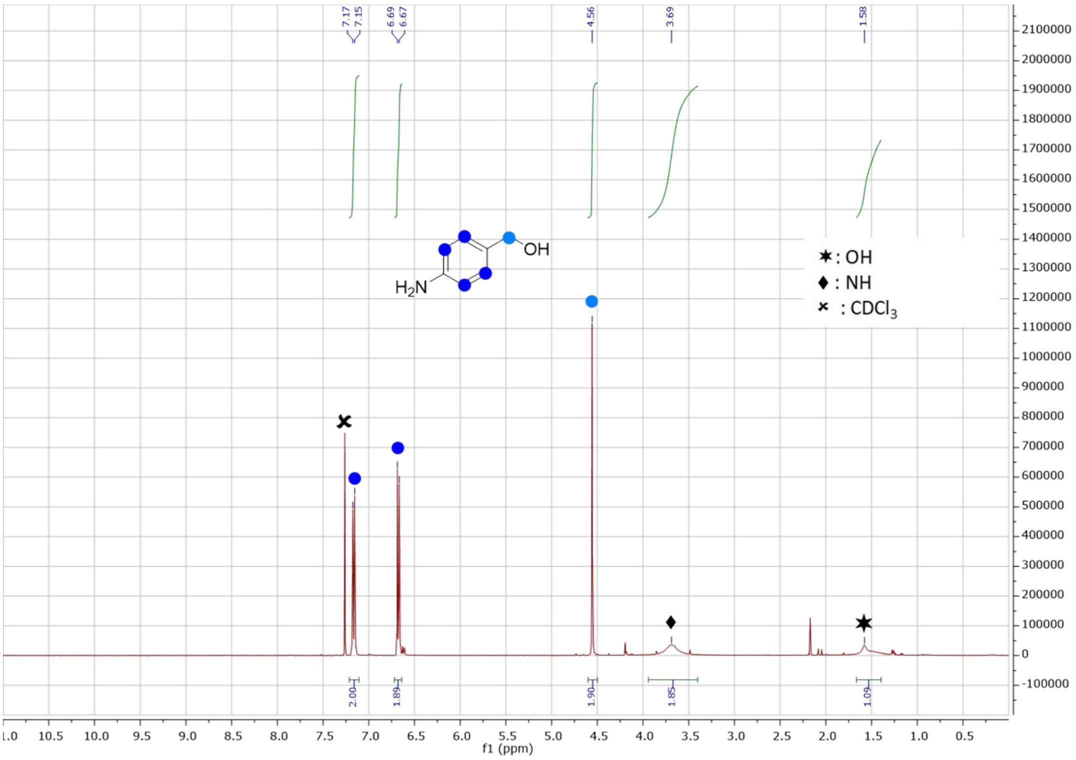


^{13}C NMR (400 MHz, CDCl$_3$)

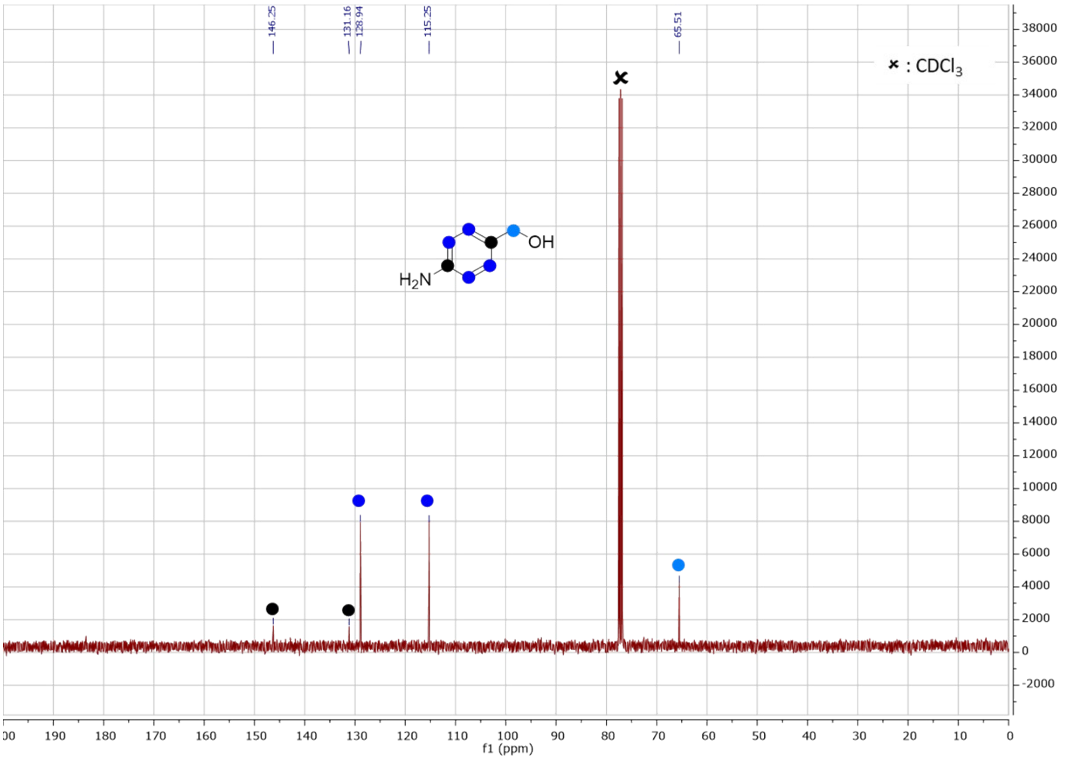


4-Aminobenzyl alcohol **3e**

^{1}H NMR (400 MHz, CDCl$_3$)

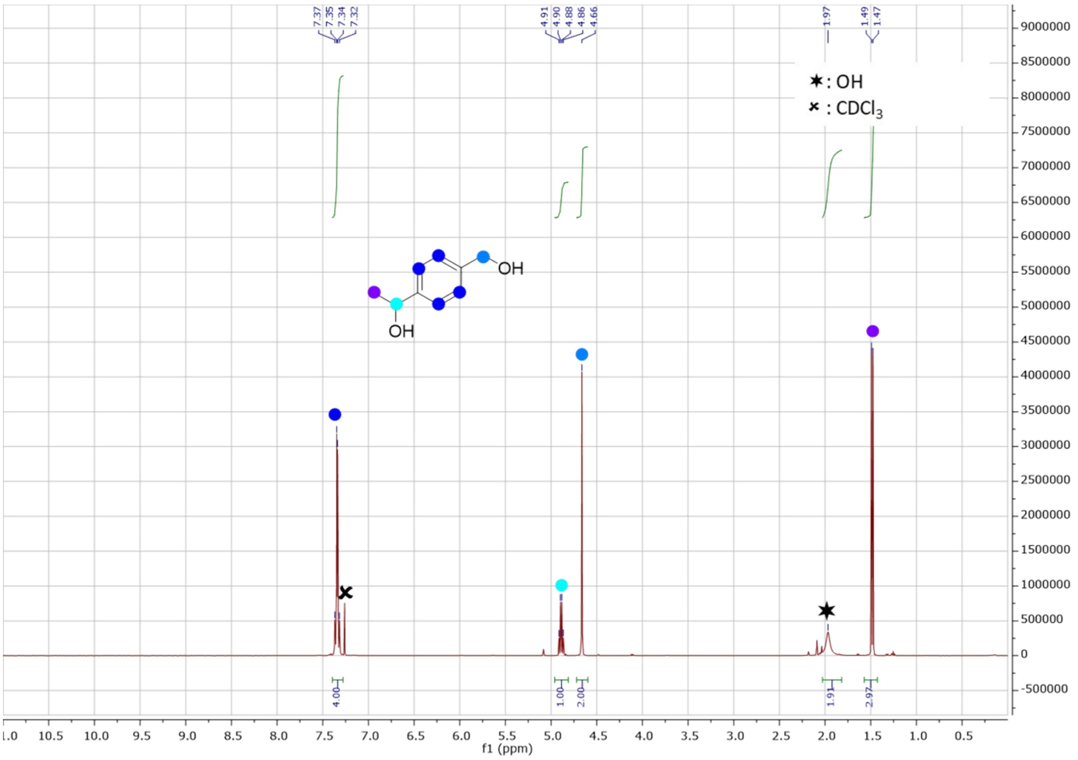


^{13}C NMR (400 MHz, CDCl$_3$)

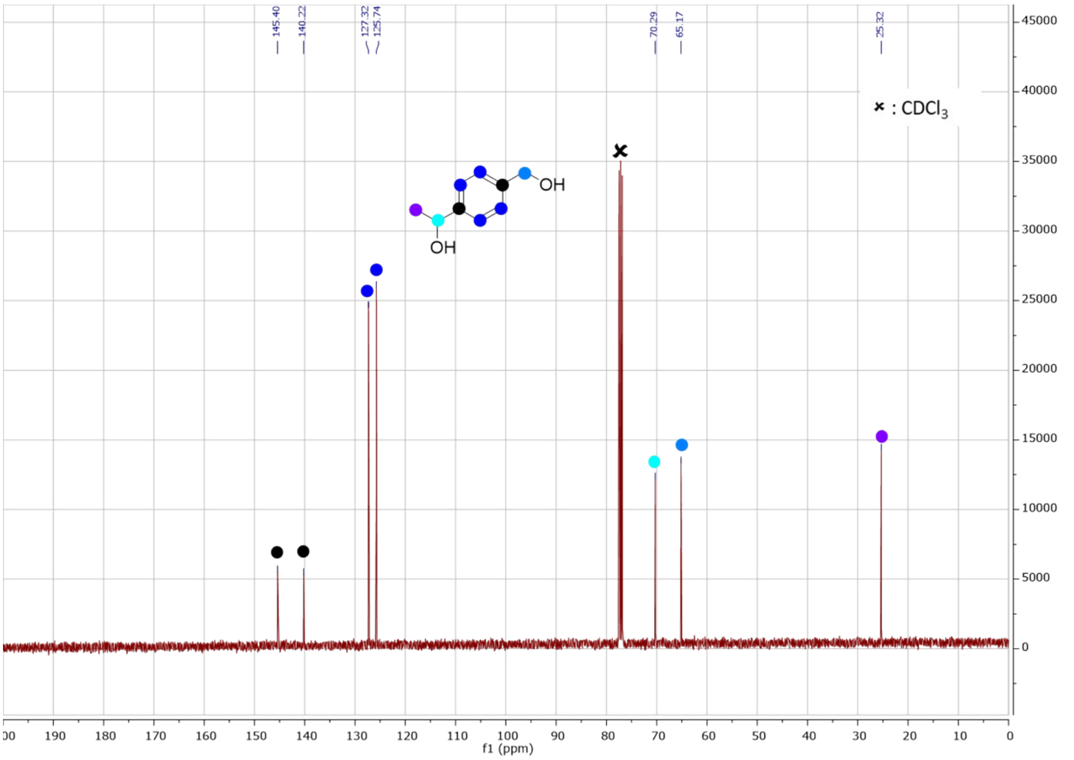


4-(1-Hydroxyethyl)benzyl alcohol **3f**

^{1}H NMR (400 MHz, $CDCl_3$)

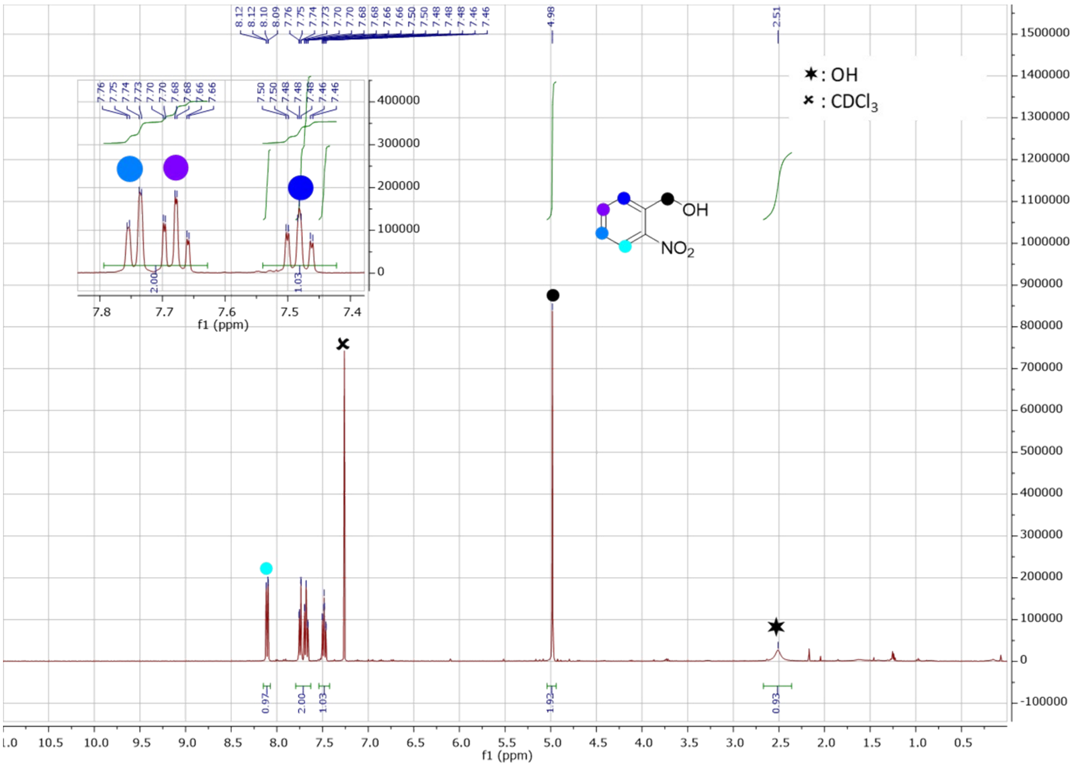


^{13}C NMR (400 MHz, $CDCl_3$)

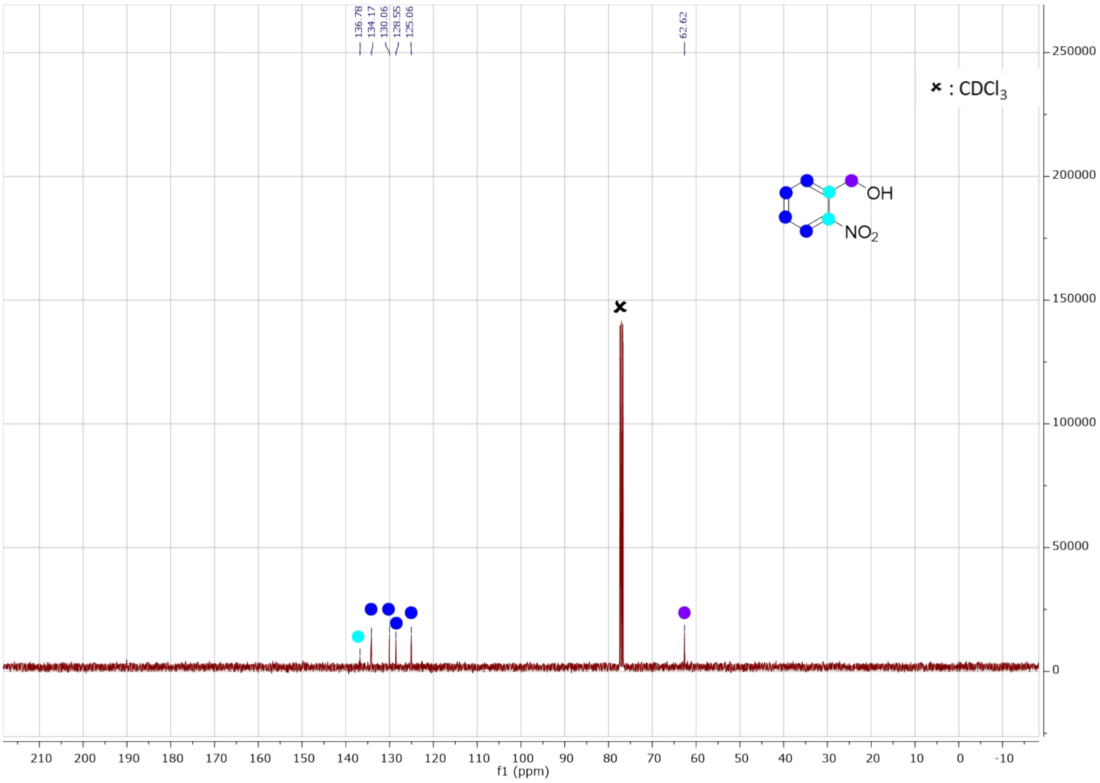


2-Nitrobenzyl alcohol **3g**

^{1}H NMR (400 MHz, $CDCl_3$)

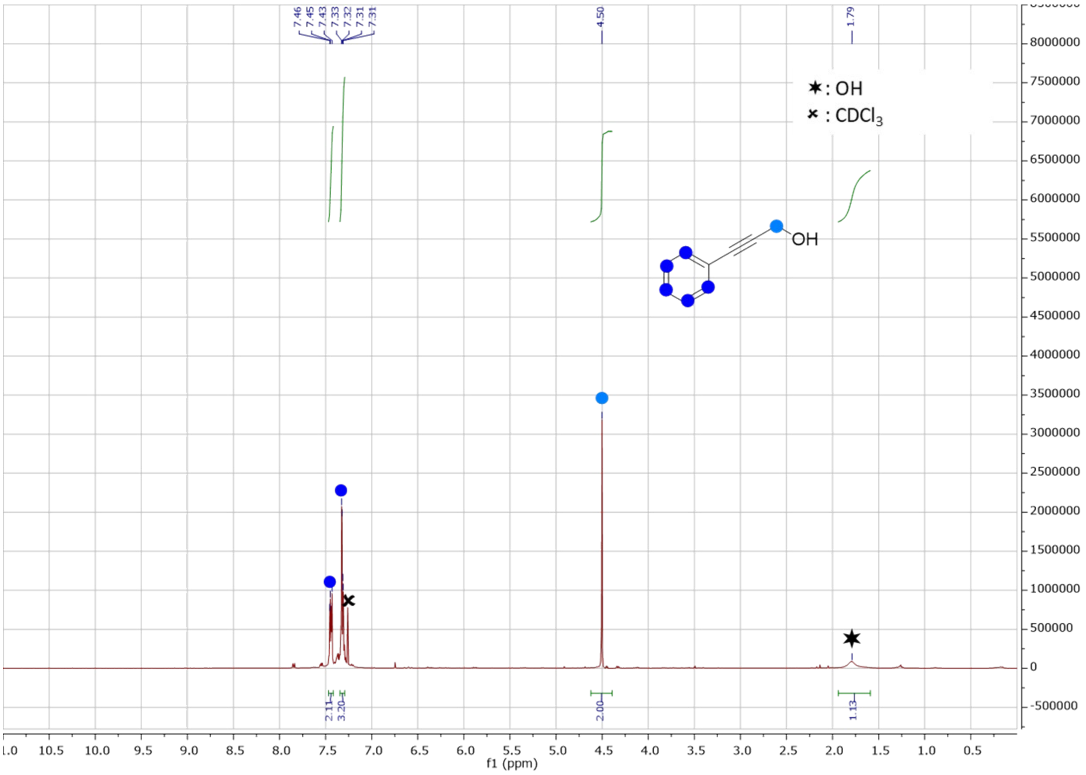


^{13}C NMR (400 MHz, $CDCl_3$)

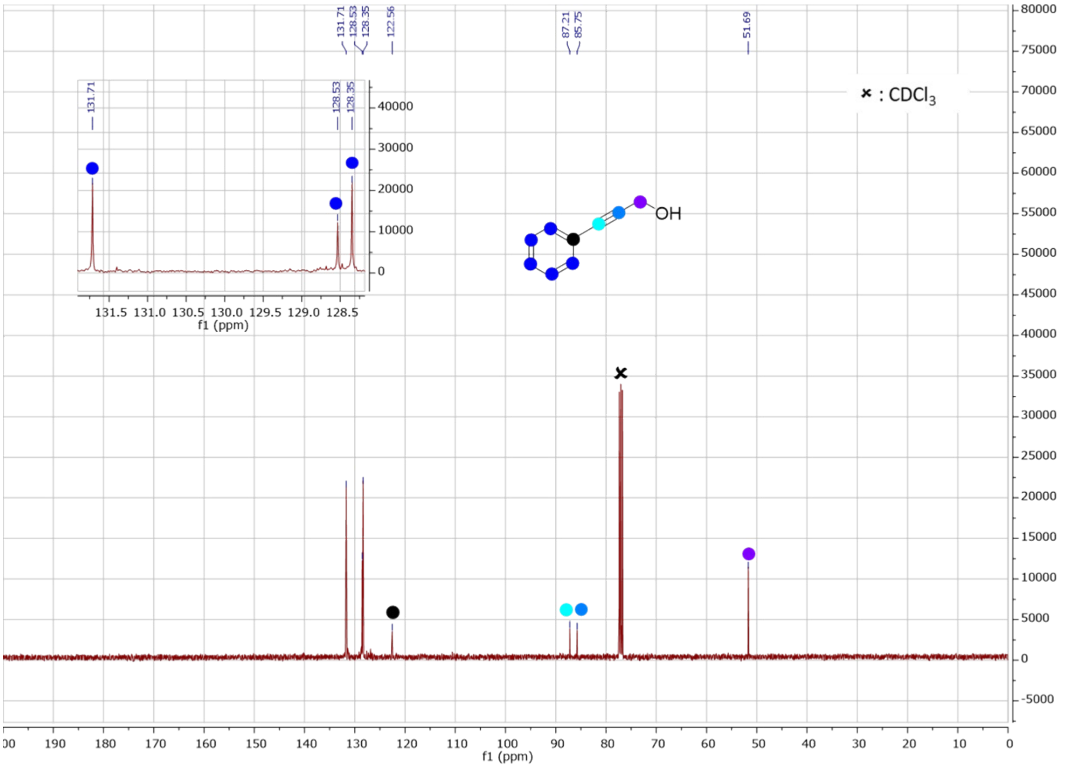


3-Phenyl-2-propyn-1-ol **3h**

^{1}H NMR (400 MHz, $CDCl_3$)

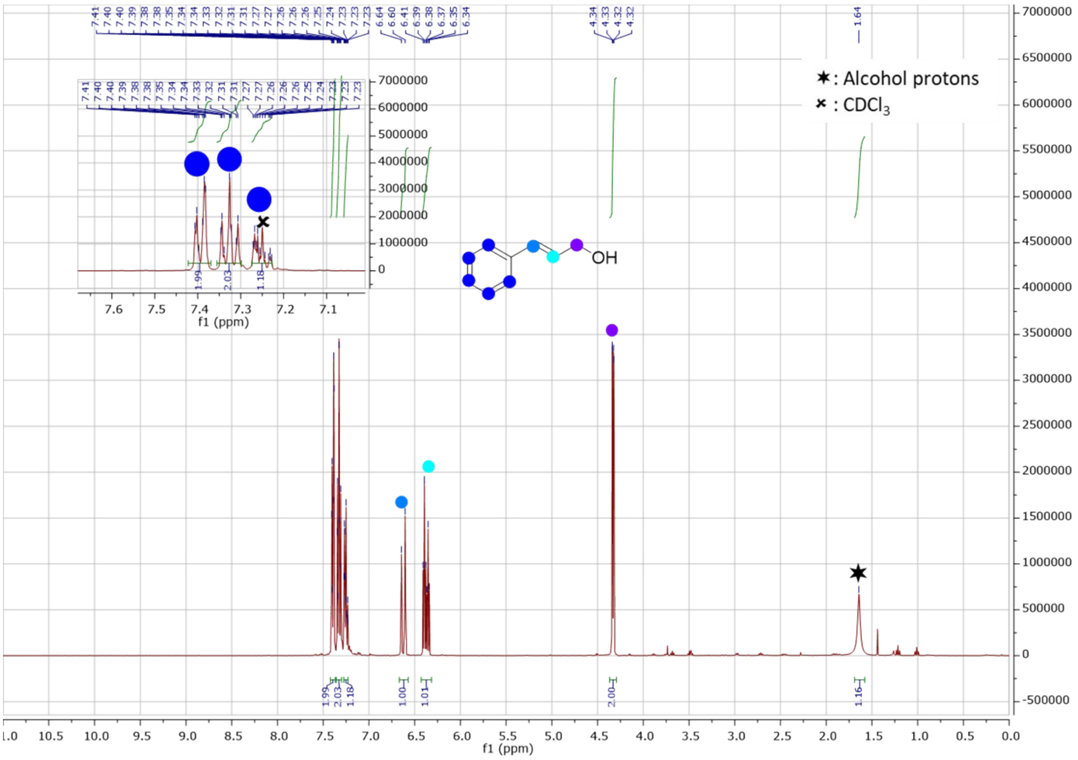


^{13}C NMR (400 MHz, $CDCl_3$)

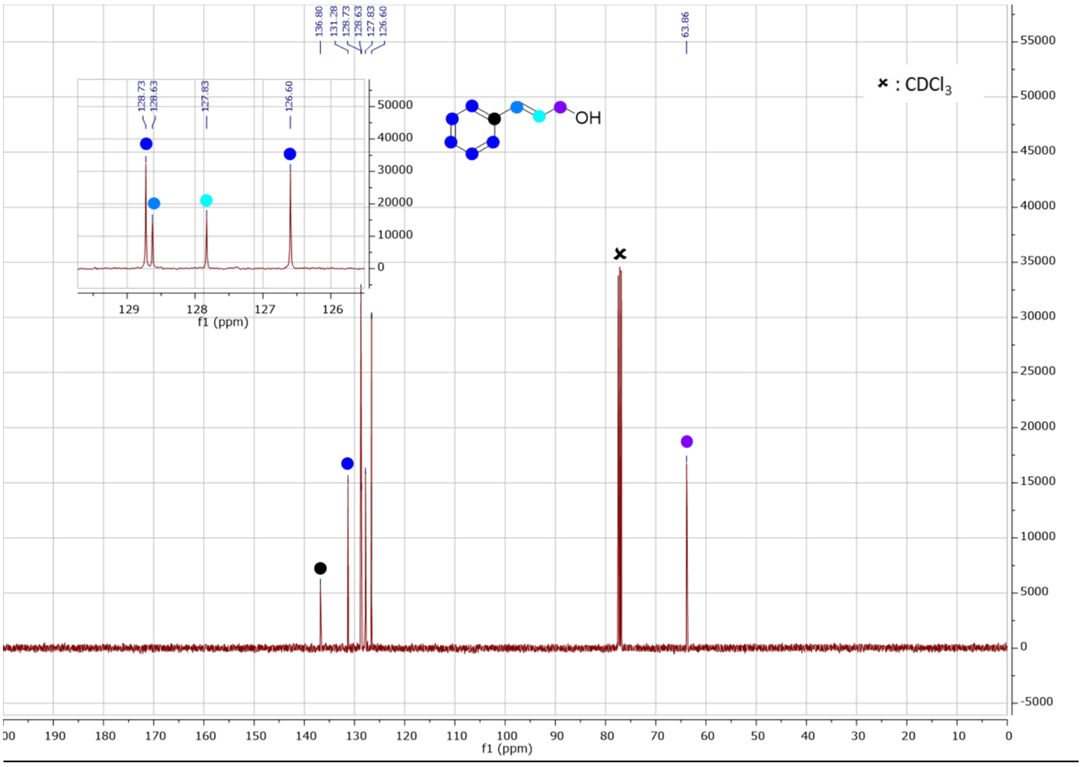


(E)-Cinnamyl alcohol **3i**

^{1}H NMR (400 MHz, $CDCl_3$)

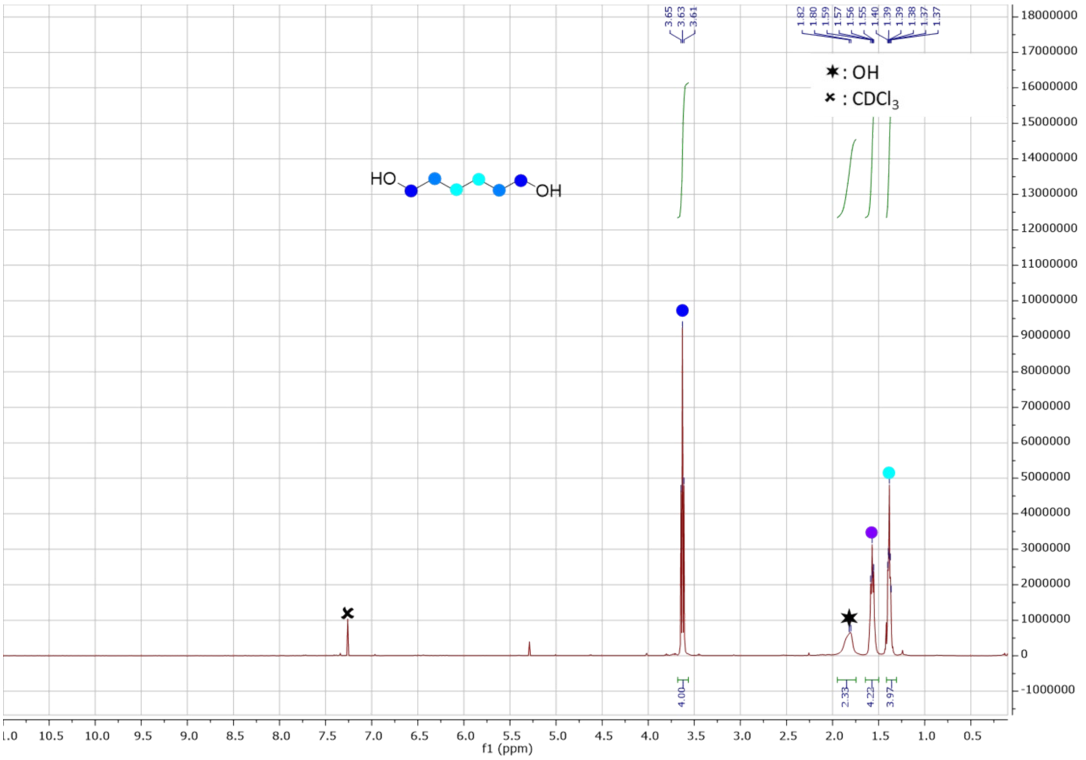


^{13}C NMR (400 MHz, $CDCl_3$)

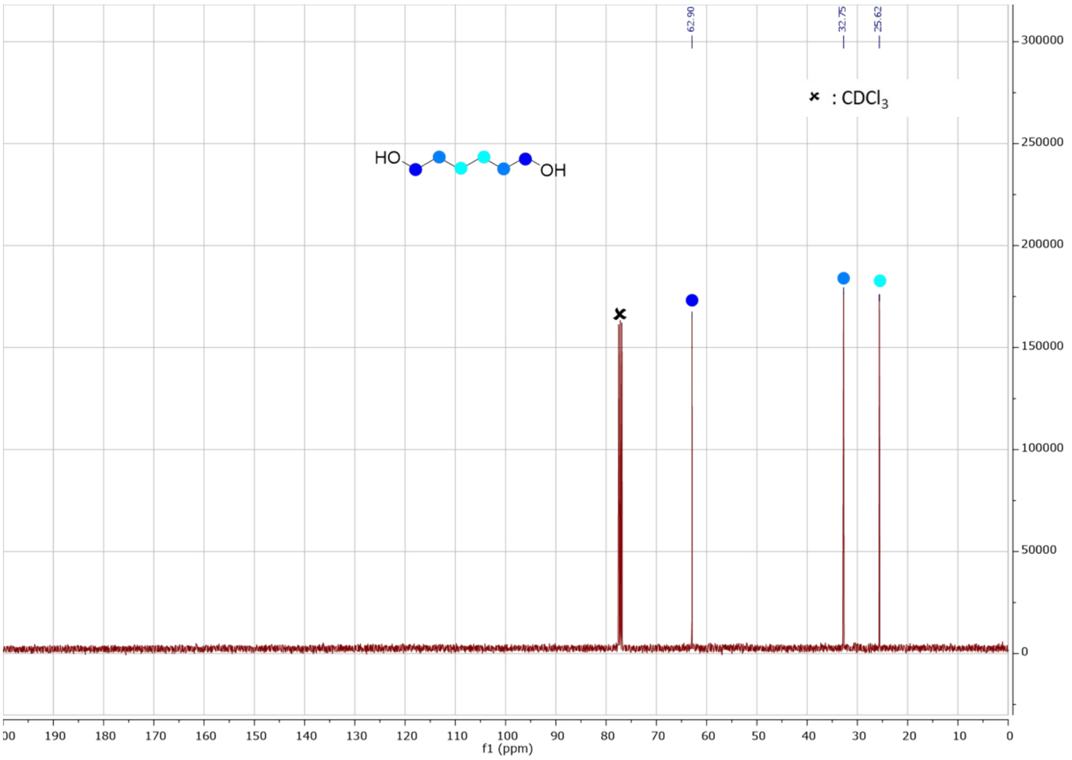


1,6-Hexanediol **3j**

^{1}H NMR (400 MHz, $CDCl_3$)

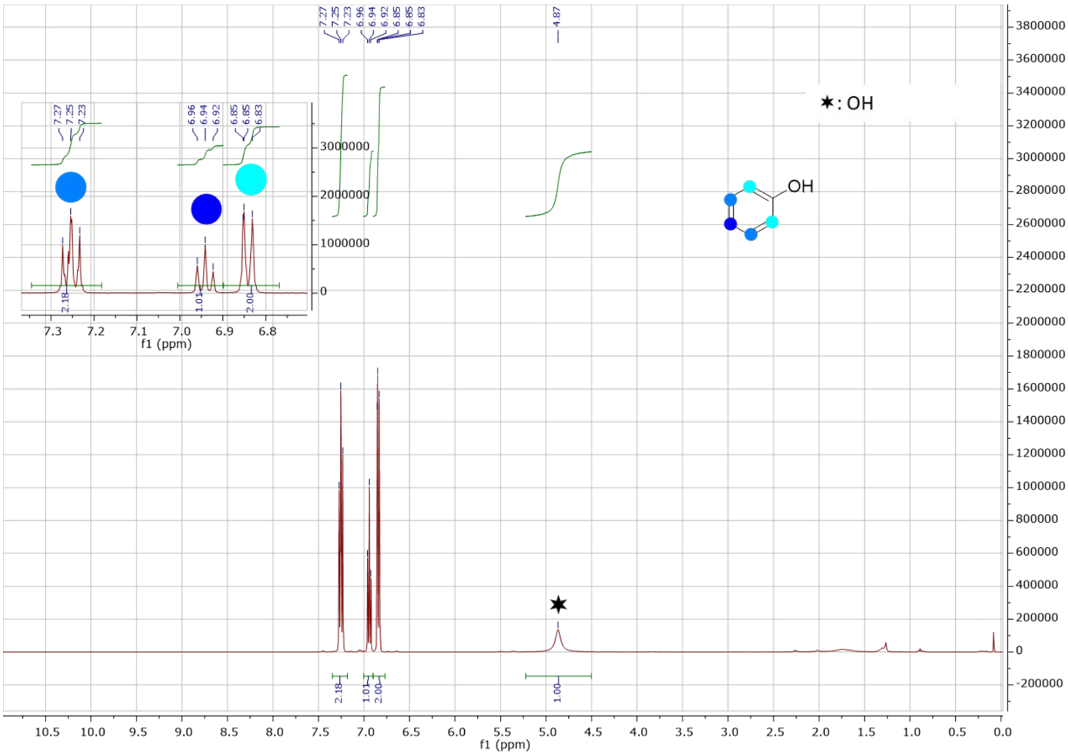


^{13}C NMR (400 MHz, $CDCl_3$)

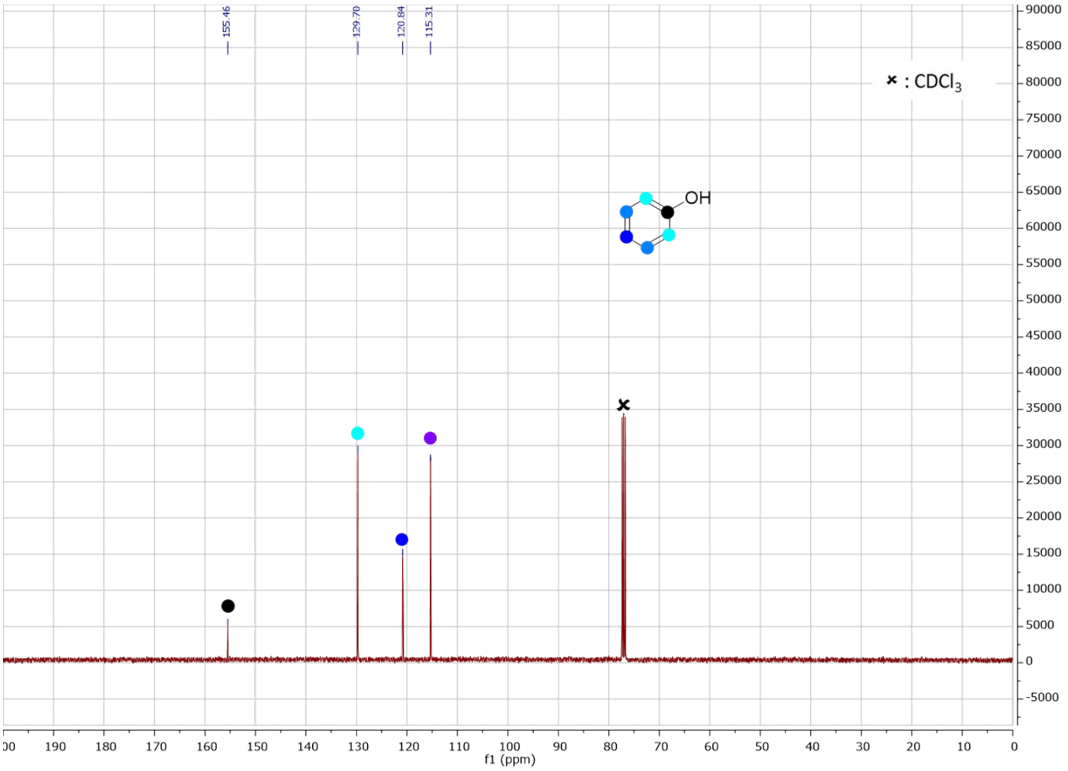


Phenol **4k**

^{1}H NMR (400 MHz, CDCl$_3$)

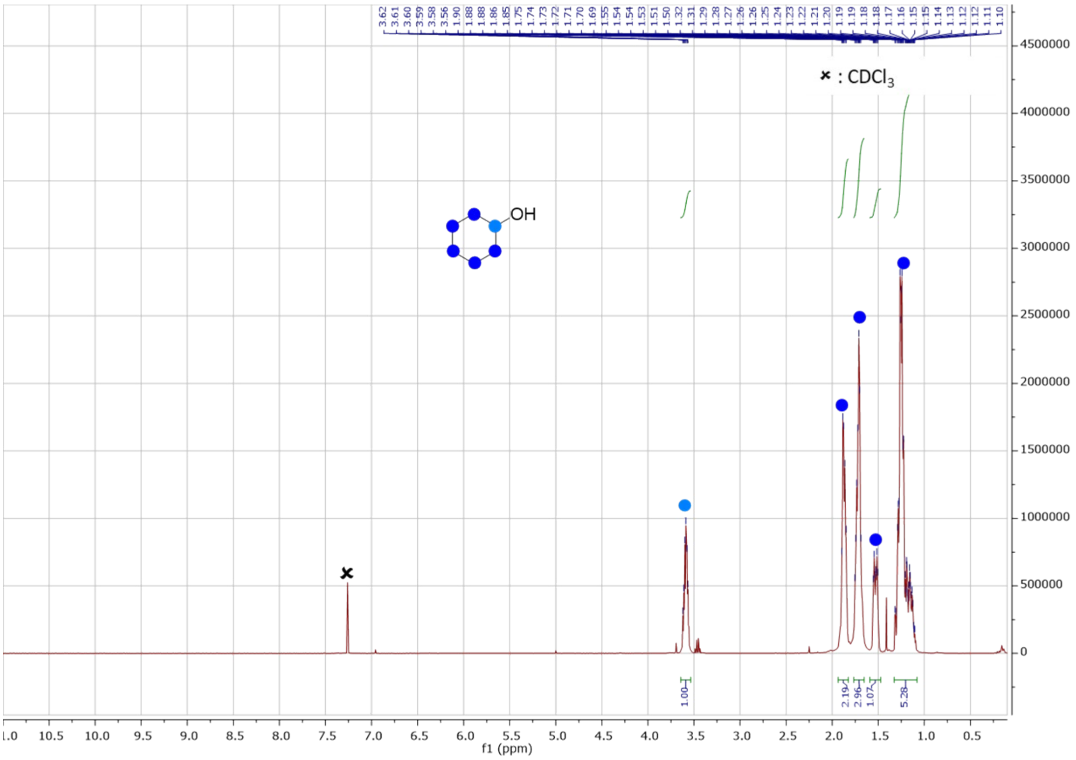


^{13}C NMR (400 MHz, CDCl$_3$)

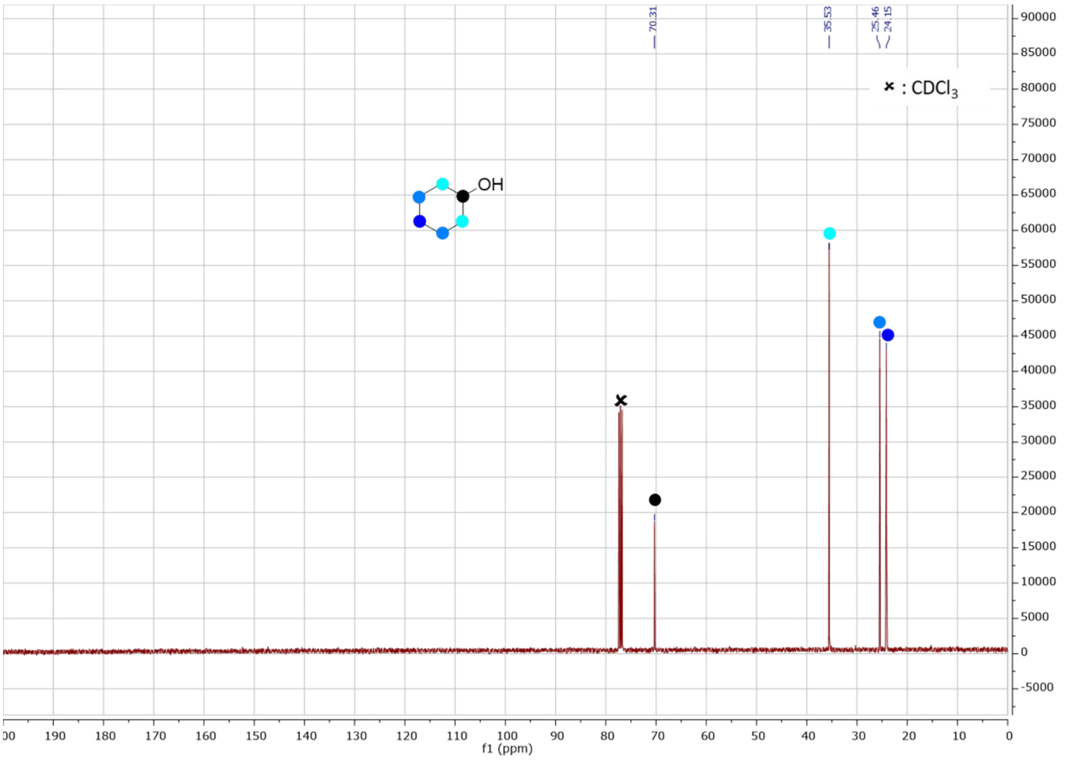


Cyclohexanol **4l**

^{1}H NMR (400 MHz, CDCl$_3$)

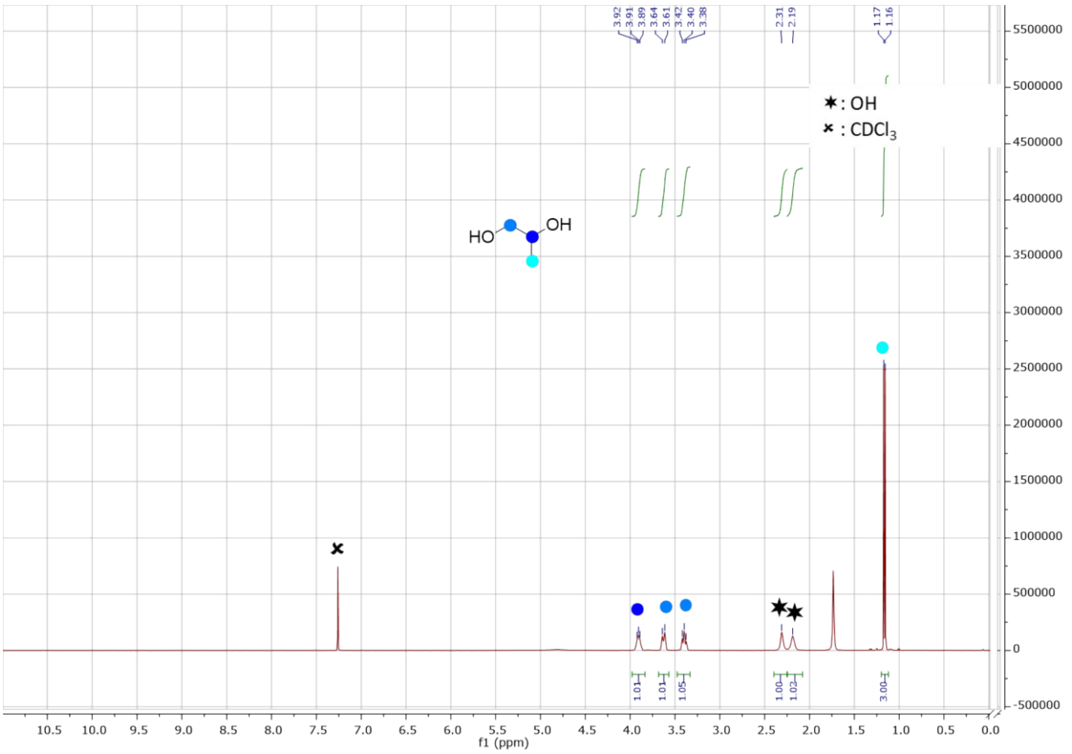


^{13}C NMR (400 MHz, CDCl$_3$)

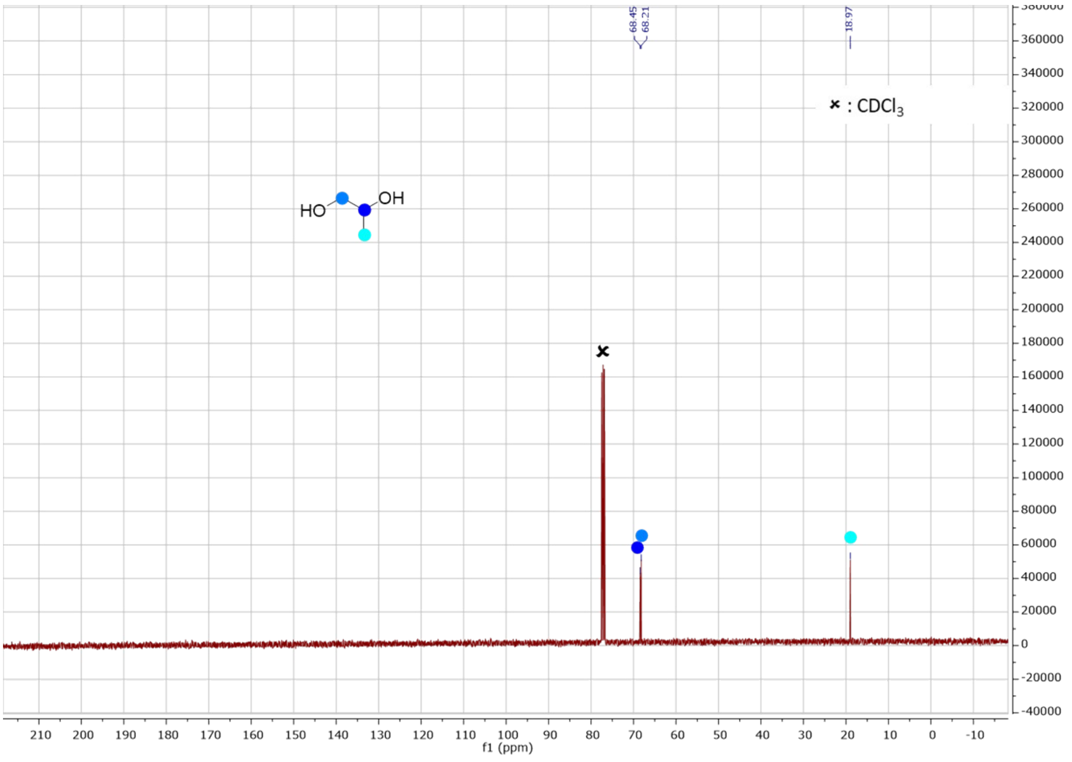


<u>1,2-Propanediol **3m**</u>

^{1}H NMR (400 MHz, CDCl$_3$)

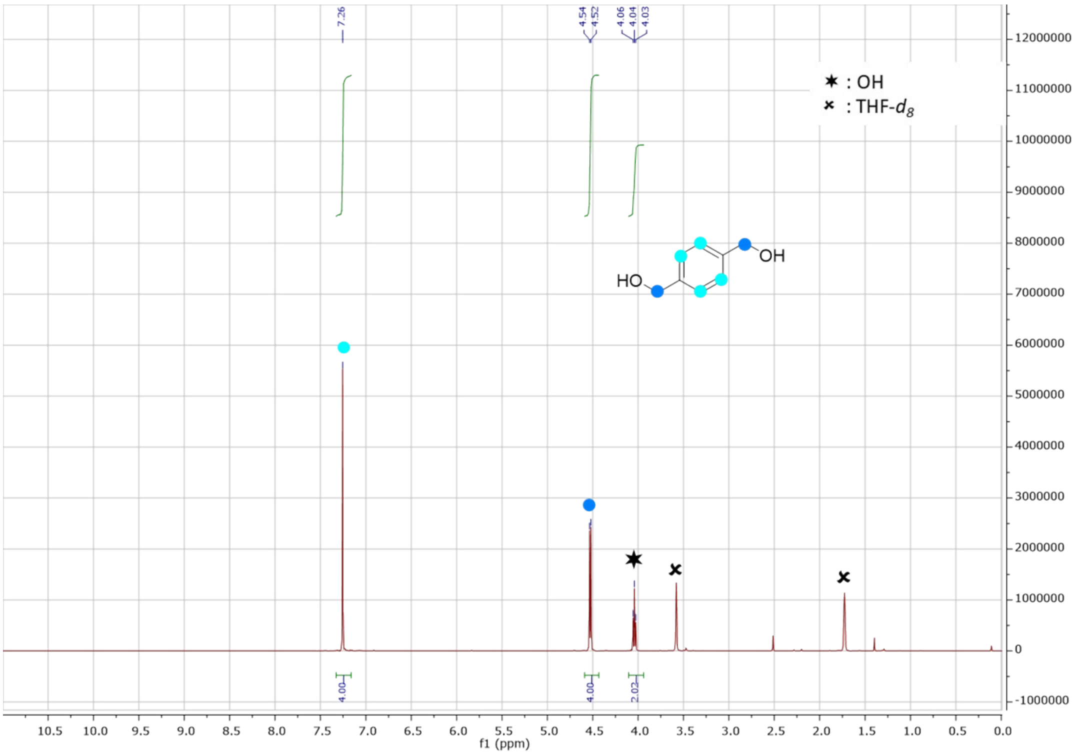


^{13}C NMR (400 MHz, CDCl$_3$)

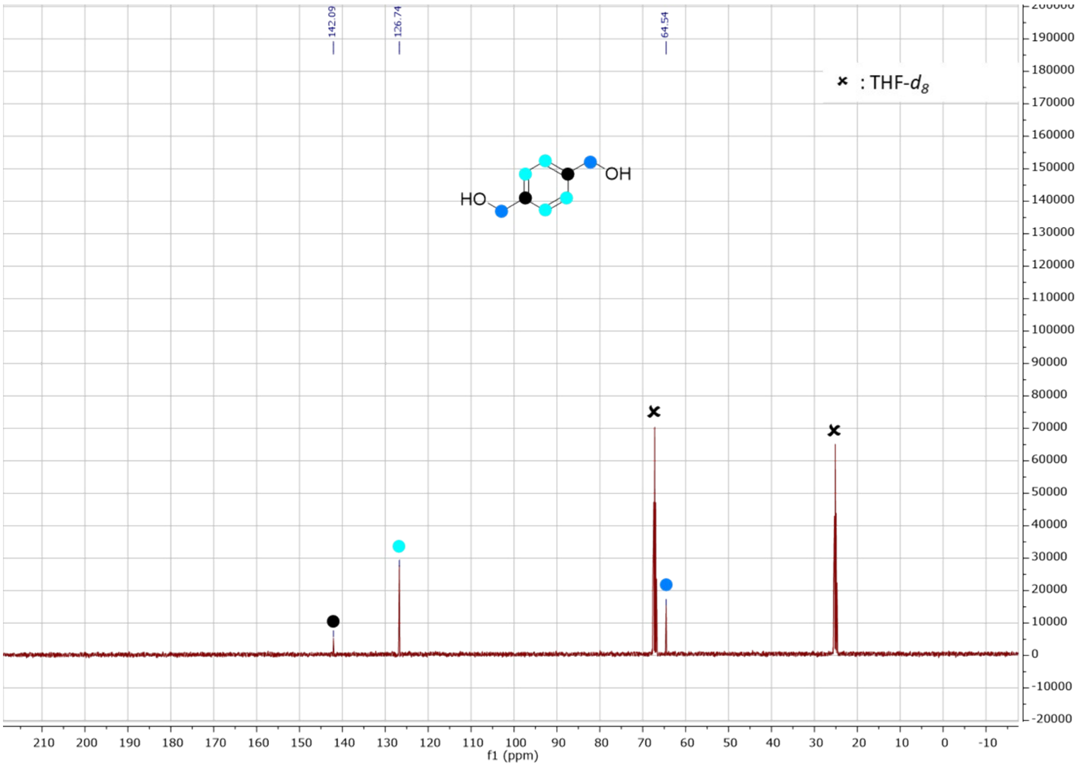


1,4-Benzenedimethanol **3n**

^{1}H NMR (400 MHz, THF-d_8)



^{13}C NMR (400 MHz, THF-d_8)



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