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# Supporting Information

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# Regiospecific conversion of a linear, low-density polyethylene to a material with boryl, hydroxyl, amino and formyl groups at the termini of side chains

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**General comments.** Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. **1** was obtained from Dow Chemical Company and used as supplied. Bis(pinacolato)diboron ($B_2pin_2$) was obtained from Frontier Scientific Co. and was used without further purification. $(Cp^*RhCl_2)_2$,[1] $Cp^*Rh(C_2H_4)_2$,[2] and $Cp^*Rh(\eta^4\text{-}C_6Me_6)$[3] were synthesized according to literature methods. The borylation reactions were assembled in an inert atmosphere glove box. $^1$H NMR spectra were acquired at 400 or 500 MHz; proton-decoupled $^{13}$C NMR spectra were obtained at 100 or 125 MHz, and $^{11}$B NMR spectra were obtained at 80 MHz. $^1$H and $^{13}$C chemical shifts are referenced to TMS, and $^{11}$B chemical shifts are reported relative to an external standard, $BF_3$-$Et_2O$; resonances downfield of the standard are reported as positive. Cyclooctane and toluene were distilled from sodium/benzophenone under nitrogen.

Size exclusion chromatography (SEC) analyses were obtained using a Hewlett Packard Series 1100 liquid chromatography equipped with three Jordi polydivinylbenzene columns of $10^4$, $10^2$, and 500 Å and a HP 1047A refractive index detector at 40 $^{o}$C. Tetrahydrofuran was the mobile phase and the flow rate was set at 1.0 mL/min. $M_n$ and PDI of **1**-Bpin and **1**-OH were recorded from THF solutions (10 mg/mL) of their isolated polymers. Because **1** was significantly less soluble in THF than the functionalized polymers, a toluene solution of **1** (4 mg/mL) was injected into SEC with THF as the eluent to obtain the $M_n$ and PDI of **1.** For measurement of molecular weight parameters of **1**-CHO, **1**-NHBn, and **1**-NHPMB, crude toluene solutions of the functionalized polymers were used for SEC analysis after dilution with toluene to make 4 mg/mL.

**1:** $^1$H NMR (500 MHz, 1,2,4-trichlorobezene/$C_6D_6$ at 110 $^{o}$C) $\delta$ = 0.85 (s, $CH_3$), 1.10–1.50 (s, $CH_2$ and CH); $^{13}$C{$^1$H} NMR (125 MHz, 1,2,4-trichlorobezene/$C_6D_6$ at 110 $^{o}$C) $\delta$ = 14.0 ($CH_3$), 22.9 ($CH_2$), 27.1–27.4 ($CH_2$), 30.0–30.5 ($CH_2$), 32.2 ($CH_2$), 34.6–35.2 ($CH_2$), 36.0 (CH), 38.3 (CH), 40.4 ($CH_2$).

**General procedure for gram scale borylation of 1 using $B_2pin_2$: Synthesis of 1-Bpin (entry 5 of Table 2).** In an inert atmosphere glove box, a mixture of **1** (5.05 g, 16.8 mmol of hexyl side chain), $B_2pin_2$ (1.28 g, 5.04 mmol), Cp*Rh($\eta^4$-$C_6Me_6$) (100 mg, 0.252 mmol), cyclooctane (5.64 g, 50.0 mmol), and a magnetic stirring bar were placed in a 300 mL flask equipped with a reflux condenser and an $N_2$ inlet. The flask was removed from the box and placed in an oil bath at 150 $^{o}$C for 36 h under $N_2$. After cooling to room temperature, the mixture was dissolved in hot toluene (150 mL), and the toluene solution was added to cold methanol (250 mL) to precipitate the polymer. Repeated dissolution and precipitation gave the borylated polymer as a white solid. The polymer was filtered and dried in vacuo at 70 $^{o}$C overnight (5.14

g): $^{1}H$ NMR (500 MHz, $CDCl_3$) δ = 0.75 (t, J = 7.8 Hz, $C\underline{H}_2Bpin$), 0.87 (t, J = 6.7 Hz, $CH_3$), 0.95–1.40 (s, $CH_2$ and CH); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 50 °C) δ = 14.0 ($CH_3$), 22.7 ($CH_2$), 24.0 ($CH_2\underline{C}H_2CH_2Bpin$), 24.9 ($BOC\underline{C}H_3$), 26.6–26.8 ($CH_2$), 29.5–30.2 ($CH_2$), 32.0 ($CH_2$), 32.5 ($\underline{C}H_2CH_2CH_2Bpin$), 33.9–34.3 ($CH_2$), 35.0 (CH), 37.5 (CH), 39.3 ($CH_2$), 82.8 ($BO\underline{C}CH_3$), $\underline{C}H_2Bpin$ not detected; $^{11}B$ NMR (80 MHz, $CDCl_3$) δ = 33.7 (br).

**General procedure for borylation of 1 using HBpin: Synthesis of 1-Bpin (entry 4 of Table 1).** In an inert atmosphere glove box, a mixture of **1** (204 mg, 0.689 mmol of hexyl side chain), HBpin (44.2 mg, 0.345 mmol), Cp*Rh(η$^4$-$C_6Me_6$) (6.9 mg, 0.17 mmol) were placed in a tube, sealed under vacuum, and placed in an oil bath at 150 °C for 36 h. After cooling to room temperature, the tube was open and the mixture was dissolved in hot toluene (10 mL). The toluene solution was added to cold methanol (10 mL) giving a precipitate. Repeated dissolution and precipitation gave the borylated polymer as a white solid. The polymer was filtered and dried in vacuo at room temperature overnight.

**General procedure for gram scale oxidation of 1-Bpin: Synthesis of 1-OH (entry 5 of Table 2).** **1**-Bpin (1.94 g) was dissolved in THF (350 mL) in a 1 L flask. A mixture of 1 N NaOH (30 mL) and 30 % $H_2O_2$ (15 mL) was added slowly to the polymer solution at room temperature. The resulting suspension was stirred at room temperature for 12 h. The solution was then concentrated by rotary evaporation and neutralized with 1 N HCl. Addition of methanol (100 mL) and $H_2O$ (100 mL) produced a white precipitation that was stirred for 1 h, filtered, and washed with methanol (2 x 50 mL). The polymer was air-dried, dissolved in hot toluene (150 mL), and filtered. The filtrate was added to cold methanol (350 mL) to precipitate the material. The polymer was filtered and dried in vacuo at 70 °C overnight. The hydroxylated polymer was isolated as a white solid (1.84 g, 97 % yield based on polymer weight from **1**): $^{1}H$ NMR (500

MHz, $CDCl_3$) δ = 0.88 (t, J = 6.9 Hz, $CH_3$), 0.95–1.40 (s, $CH_2$ and CH), 1.57 (pentet, J = 6.7 Hz, $C\underline{H}_2CH_2OH$), 3.64 (t, J = 6.7 Hz, $C\underline{H}_2OH$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 50 °C) δ = 14.0 ($CH_3$), 22.7 ($CH_2$), 25.9 ($\underline{C}H_2CH_2CH_2OH$), 26.6–26.8 ($CH_2$), 29.5–30.2 ($CH_2$), 32.0 ($CH_2$), 33.1 ($CH_2\underline{C}H_2CH_2OH$), 34.1–34.5 ($CH_2$), 35.3 (CH), 37.8 (CH), 39.3 ($CH_2$), 63.2 ($\underline{C}H_2OH$).

**General procedure for amination of 1-OH: Synthesis of 1-NHBn.** Amination of **1**-OH was performed using a modified procedure of literature method.[4] In an inert atmosphere glove box, a mixture of **1**-OH (104 mg, 0.0345 mmol of hydroxyl group based on 10 mol % hydroxylated hexyl side chain), $K_2CO_3$ (5 mg), $(Cp^*IrCl_2)_2$ (2.0 mg, 0.0025 mmol), toluene (1 mL), and a magnetic stirring bar were placed in a 4 mL vial equipped with a Teflon-lined screw-cap. The vial was removed from the box and placed in an oil bath at 80 °C for 10 min to dissolve the polymer. The vial was brought to the glove box and benzylamine (200 mg, 1.87 mmol) was added. The reaction mixture was stirred at 140 °C for 48 h. After cooling to room temperature, the mixture was dissolved in toluene (10 mL), filtered through short plug of Celite. Cold methanol (10 mL) was added the filtrate to precipitate the polymer. Repeated dissolution and precipitation gave the benzylamine functionalized polymer as a white solid. The polymer was filtered and dried in vacuo at room temperature overnight (97.2 mg): $^1H$ NMR (500 MHz, $CDCl_3$) δ = 0.88 (t, J = 6.8 Hz, $CH_3$), 0.95–1.40 (s, $CH_2$ and CH), 1.52 (pentet, J = 7.3 Hz, $PhCH_2NHCH_2C\underline{H}_2$), 2.62 (t, J = 7.3 Hz, $PhCH_2NHC\underline{H}_2CH_2$), 3.79 (s, $PhC\underline{H}_2NHCH_2CH_2$). 7.22–7.28, 7.30–7.32 ($H_{arom}$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 50 °C) δ = 14.0 ($CH_3$), 22.7 ($CH_2$), 26.6–26.8 ($CH_2$), 27.5 ($PhCH_2NHCH_2CH_2\underline{C}H_2$), 29.5–30.2 ($CH_2$), 30.7 ($PhCH_2NHCH_2\underline{C}H_2CH_2$), 32.0 ($CH_2$), 33.9–34.4 ($CH_2$), 35.1 (CH), 37.7 (CH), 39.4 ($CH_2$), 49.6 ($PhCH_2NH\underline{C}H_2CH_2CH_2$), 54.1 ($Ph\underline{C}H_2NHCH_2CH_2CH_2$), 126.9, 128.2, 128.4 ($C_{arom}$), $C_{ipso}$ not detected due to low concentration.

**Synthesis of 1-NHPMB.** 4-Methoxybenzylamine functionalized polymer was prepared according to the similar procedure described for synthesis of **1**-NHBn using 4-methoxybenzylamine (200 mg, 1.46 mmol), **1**-OH (105 mg, 0.0350 mmol of hydroxyl group based on 10 mol % functionalized hexyl side chain), $K_2CO_3$ (5 mg), $(Cp^*IrCl_2)_2$ (0.7 mg, 0.0009 mmol), and toluene (1 mL): $^1$H NMR (400 MHz, $CDCl_3$) $\delta = 0.86$ (t, J = 6.7 Hz, $CH_3$), 0.95–1.40 (s, $CH_2$ and CH), 2.59 (t, J = 7.1 Hz, 4-$CH_3O$-$C_6H_4$-$CH_2NHC\underline{H}_2$), 3.70 (s, 4-$CH_3O$-$C_6H_4$-$C\underline{H}_2NHCH_2$), 3.77 (s, 4-$C\underline{H}_3O$-$C_6H_4$-$CH_2NHCH_2$), 6.83 (d, J = 8.8 Hz, $H_{arom}$), 7.21 (d, J = 8.1 Hz, $H_{arom}$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 50 $^oC$) $\delta = 14.0$ ($CH_3$), 22.7 ($CH_2$), 26.6–26.8 ($CH_2$), 29.5–30.2 ($CH_2$), 30.7 (4-$CH_3O$-$C_6H_4$-$CH_2NHCH_2\underline{C}H_2$), 32.0 ($CH_2$), 33.9–34.4 ($CH_2$), 35.1 (CH), 37.7 (CH), 39.4 ($CH_2$), 49.2 (4-$CH_3O$-$C_6H_4$-$CH_2NH\underline{C}H_2CH_2$), 53.2 (4-$CH_3O$-$C_6H_4$-$\underline{C}H_2NHCH_2CH_2$), 55.4 ($OCH_3$), 114.1, 129.6 ($C_{arom}$), 159.1 ($C_{ipso}$).

**General procedure for oxidation of 1-OH: Synthesis of 1-CHO.** Oxidation of **1**-OH using molecular oxygen was performed according to literature methods.[5] To a mixture of $Pd(OAc)_2$ (1.0 mg, 0.0045 mmol), toluene (3 mL), and MS3A (250 mg) in a 25 mL flask was added pyridine (5.0 mg, 0.063 mmol). The yellow solution turned to a yellow-white solution when pyridine was added. Oxygen gas was introduced to the flask by purging the flask with $O_2$-filled balloon three times, and the reaction mixture was stirred at 85 $^oC$ for 10 min. **1**-OH (100.0 mg, 0.0332 mmol of hydroxyl group based on 10 mol % functionalized hexyl side chain) was dissolved in toluene (10 mL). **1**-OH in toluene solution was added slowly to flask at 85 $^oC$ over 20 min and the reaction mixture was stirred at 85 $^oC$ for 12 h under $O_2$ pressure using $O_2$-filled balloon. After cooling to room temperature the solution was filtered through short plug of Celite. Addition of cold methanol (10 mL) produced a white precipitation that was filtered and washed with methanol (2 x 5 mL). The filtered polymer was dried in vacuo at room temperature overnight. The aldehyde-containing polymer was isolated as a white solid (95.3 mg): $^1$H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, J = 6.2 Hz, $CH_3$), 0.95–1.40 (s, $CH_2$ and CH), 1.64 (pentet, J = 6.7 Hz, $C\underline{H}_2CH_2CHO$), 2.42 (t, J = 7.1 Hz, $C\underline{H}_2CHO$), 9.77 (s, CHO); $^{13}C\{^1H\}$ NMR (125 MHz, $CD_2Cl_4$, 85 °C) δ = 14.0 ($CH_3$), 22.4 ($\underline{C}H_2CH_2CHO$), 22.7 ($CH_2$), 26.6–26.8 ($CH_2$), 29.5–30.2 ($CH_2$), 32.0 ($CH_2$), 34.1–34.5 ($CH_2$), 35.3 (CH), 37.8 (CH), 39.7 ($CH_2$), 44.0 ($CH_2\underline{C}H_2CHO$), 202.4 (CHO); FT-IR (film) ν = 1711 $cm^{-1}$(C=O).

## Supporting Figures

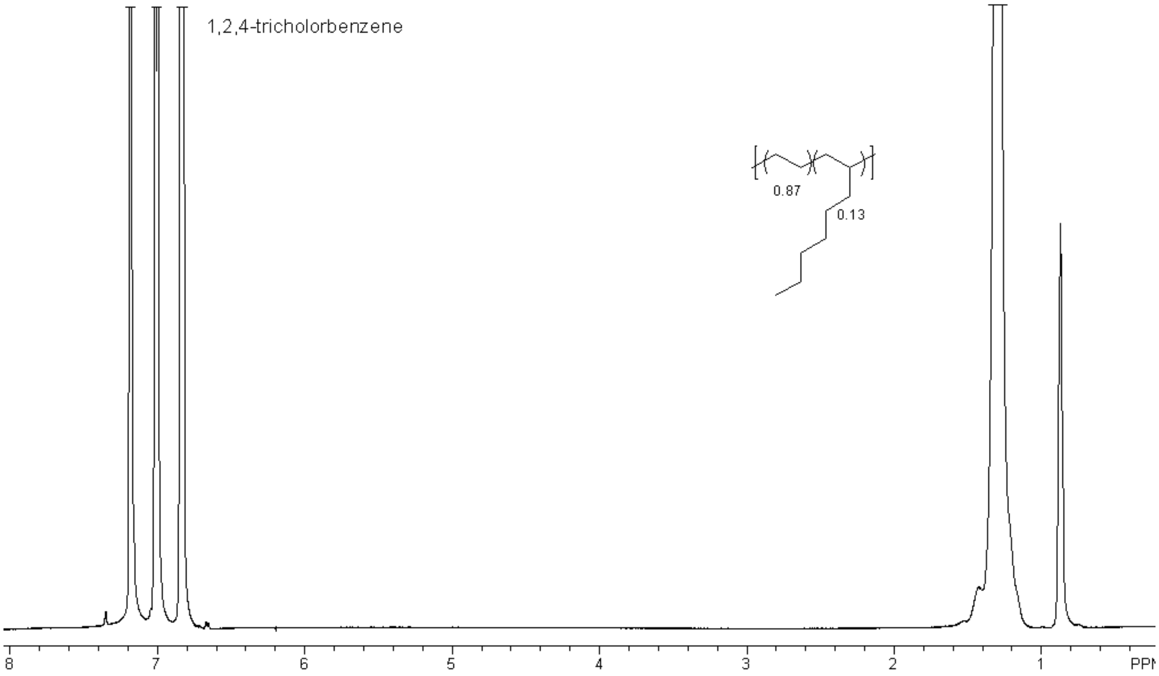

**Figure S1:** $^1$H NMR spectrum [delay time = 1 s, number of transients = 16] of **1** [100 mg/mL in 60/40 1,2,4-trichlorobenzene/$C_6D_6$ at 110 $^o$C].

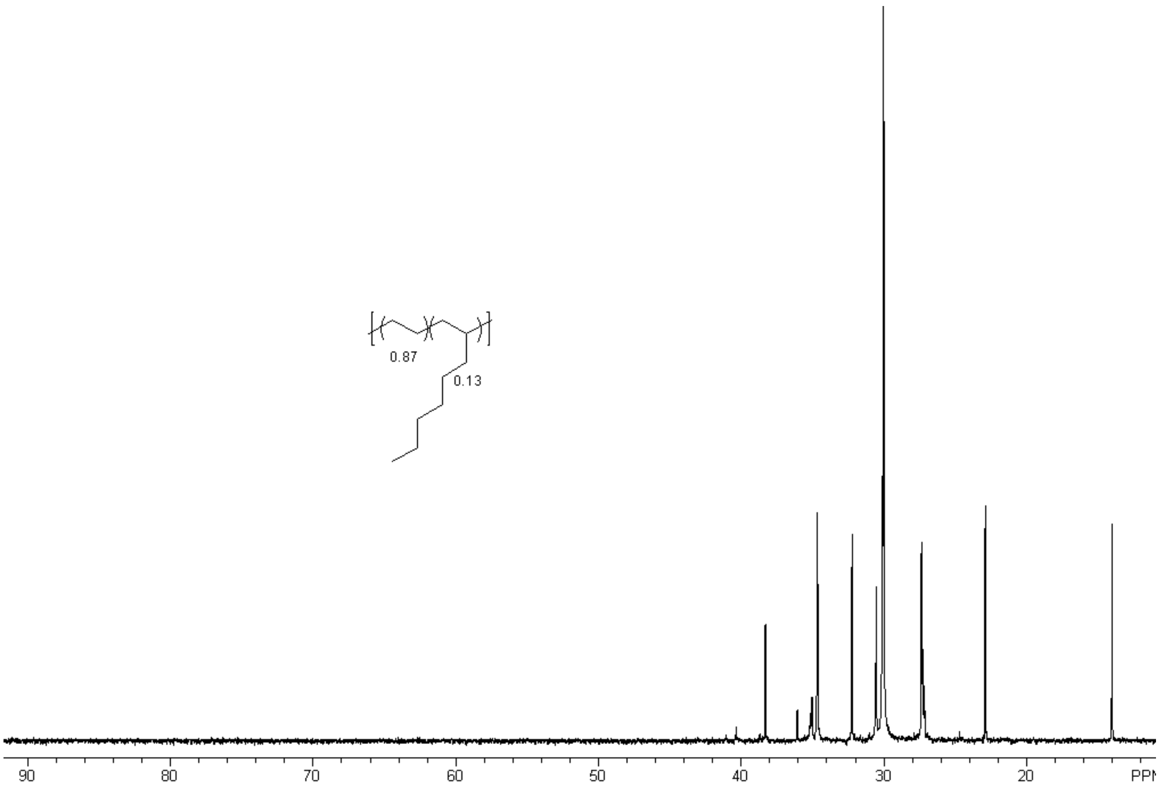

**Figure S2:** $^{13}$C NMR spectrum [delay time = 4 s, number of transients = 595] of **1** [100 mg/mL in 60/40 1,2,4-trichlorobenzene/$C_6D_6$ at 110 $^{o}$C].

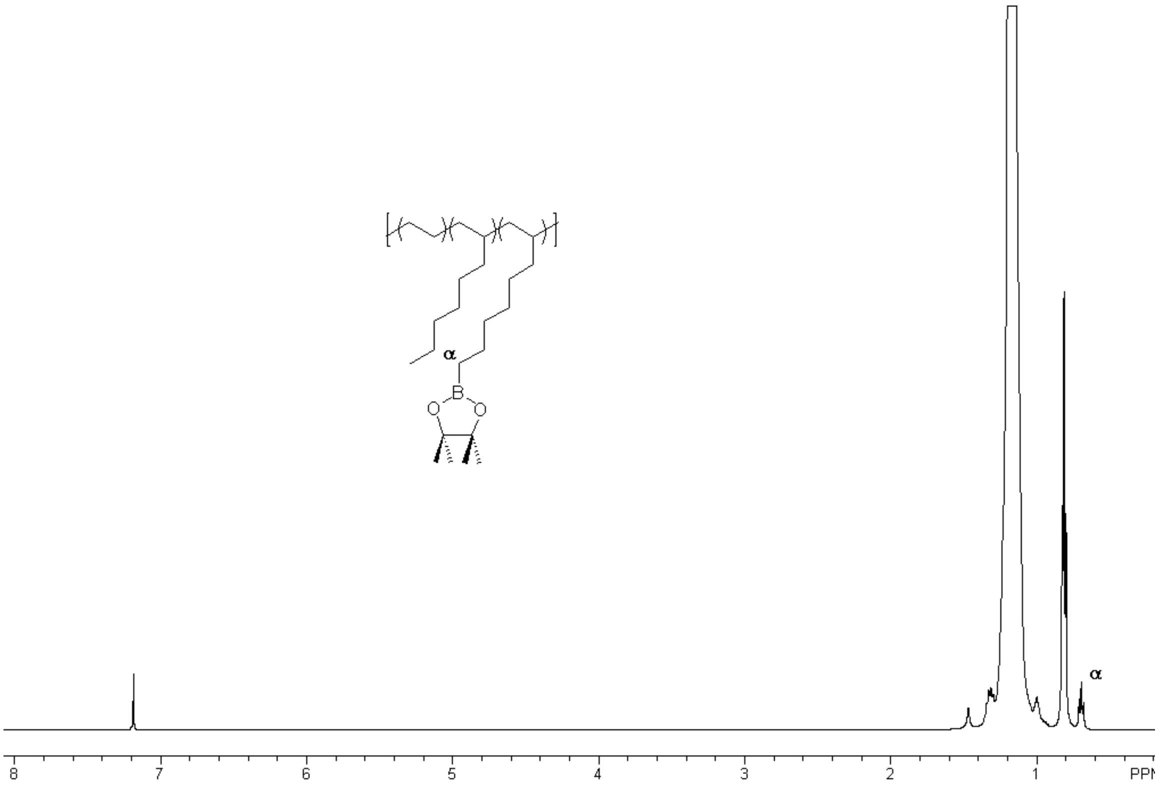

**Figure S3:** $^{1}$H NMR spectrum [delay time = 1 s, number of transients = 16] of **1**-Bpin [50 mg/mL $CDCl_3$ at 40 $^{o}$C] (entry 7 of Table 2).

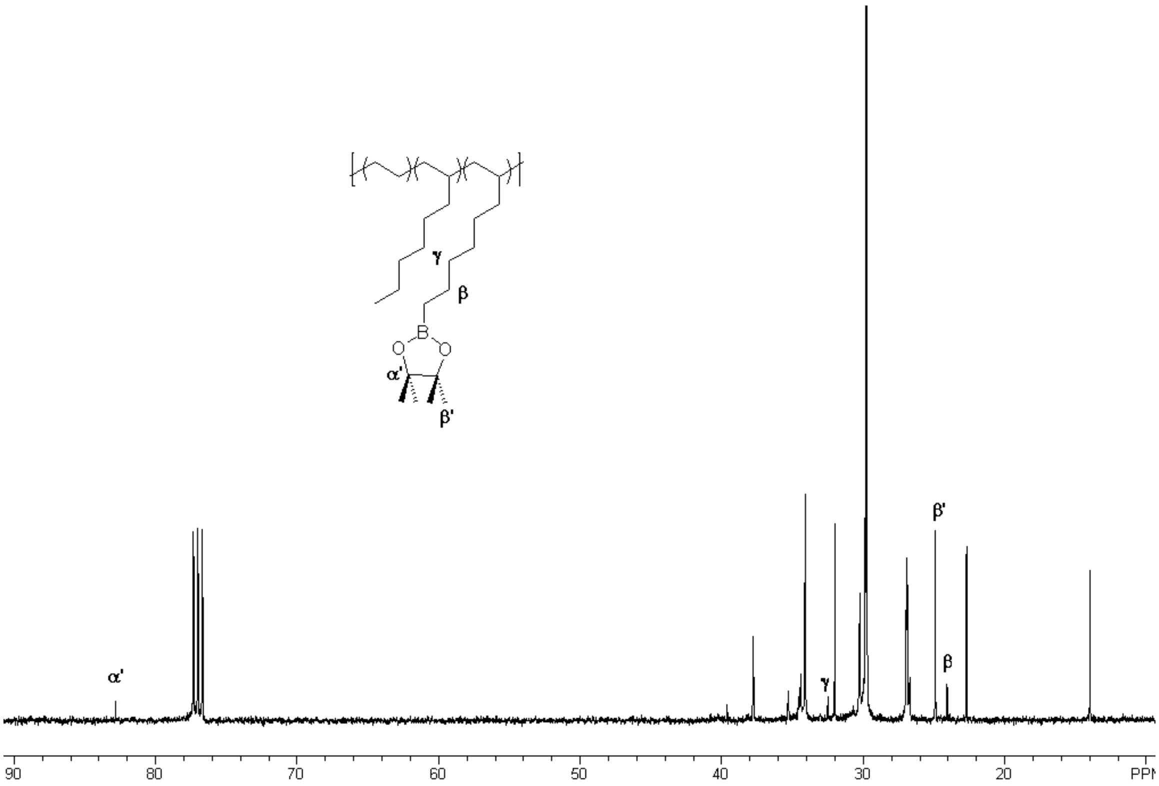

**Figure S4:** $^{13}$C NMR spectrum [delay time = 4 s, number of transients = 1024] of **1**-Bpin [50 mg/mL $CDCl_3$ at 40 $^{o}$C] (entry 7 of Table 2).

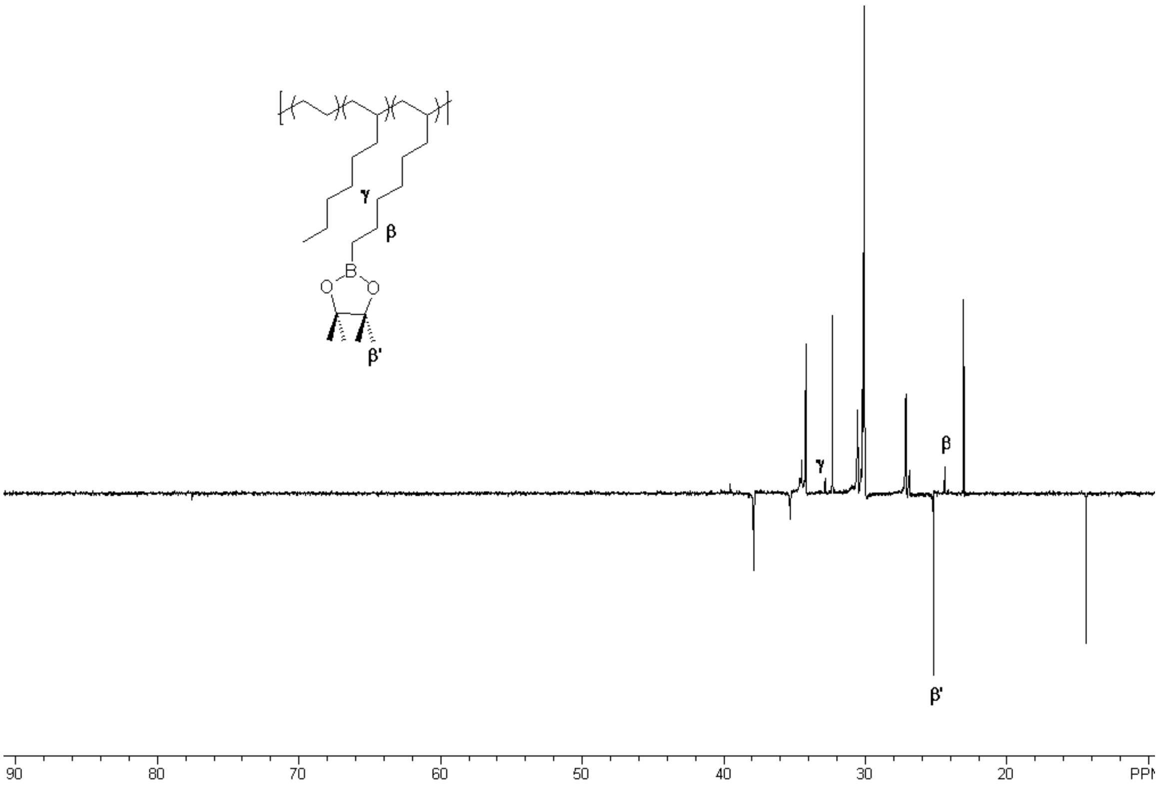

**Figure S5:** DEPT $^{13}$C NMR spectrum [delay time = 4 s, number of transients = 1024] of **1**-Bpin [50 mg/mL $CDCl_3$ at 40 $^{o}$C] (entry 7 of Table 2).

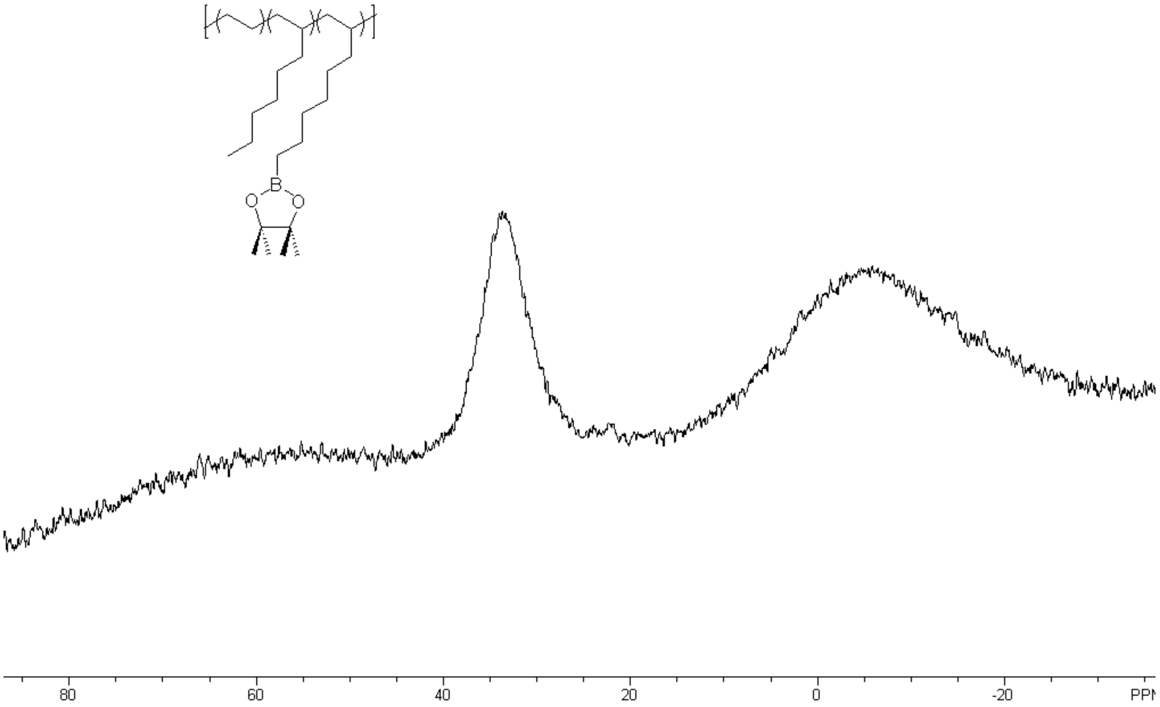

**Figure S6:** $^{11}$B NMR spectrum [delay time = 1 s, number of transients = 2500] of **1**-Bpin [50 mg/mL $CDCl_3$ at 40 $^{o}$C] (entry 7 of Table 2).

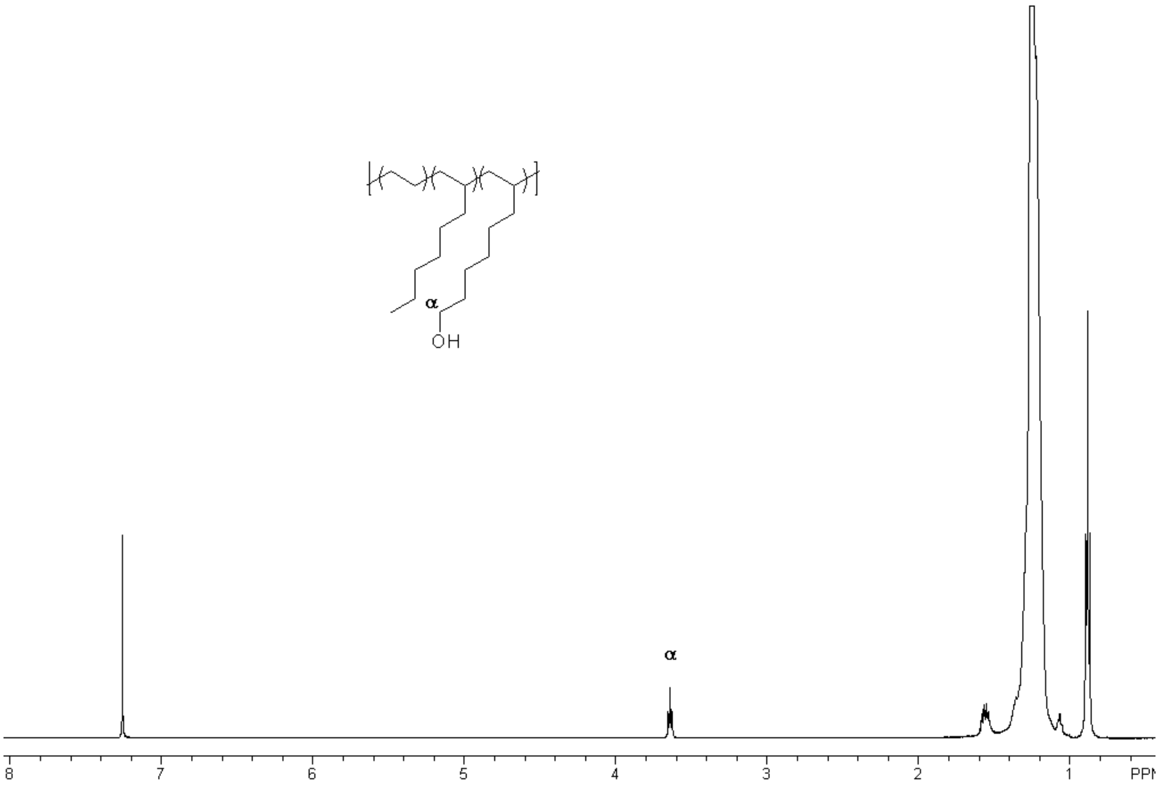

**Figure S7:** $^{1}$H NMR spectrum [delay time = 1 s, number of transients = 16] of **1**-OH [15 mg/mL $CDCl_3$ at room temperature] (entry 7 of Table 2).

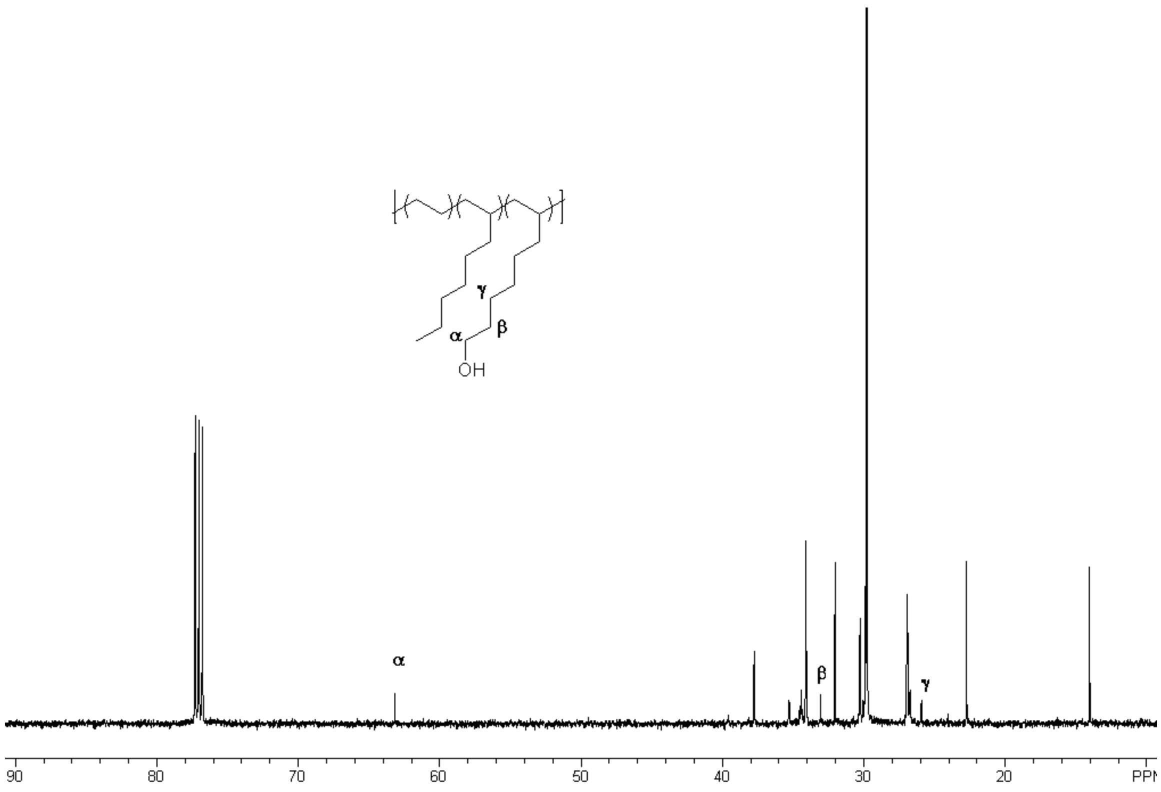

**Figure S8:** $^{13}$C NMR spectrum [delay time = 4 s, number of transients = 315] of **1**-OH [50 mg/mL CDCl$_3$ at 40 $^{o}$C] (entry 7 of Table 2).

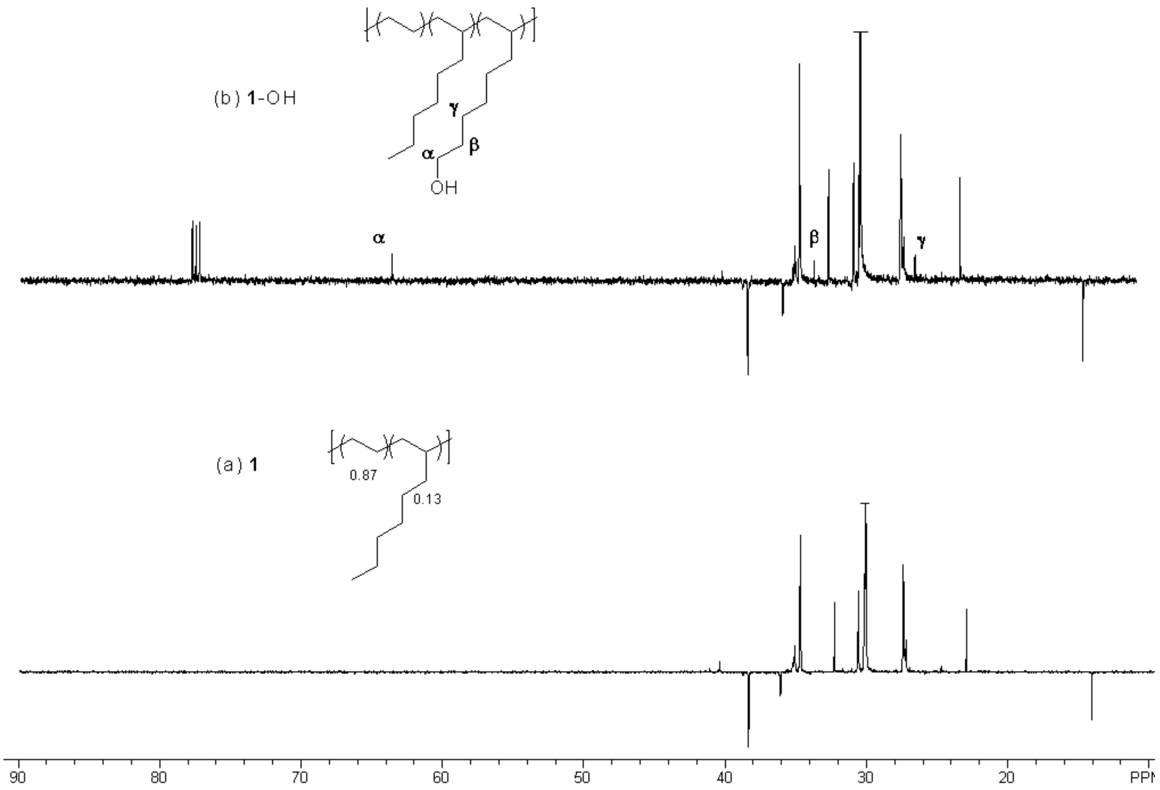

**Figure S9:** APT $^{13}$C NMR spectra of (a) **1** [delay time = 4 s, number of transients = 512, 100 mg/mL in 60/40 1,2,4-trichlorobenzene/$C_6D_6$ at 110 $^{o}$C] and (b) **1**-OH [delay time = 4 s, number of transients = 240, 50 mg/mL $CDCl_3$ at 40 $^{o}$C] (entry 7 of Table 2).

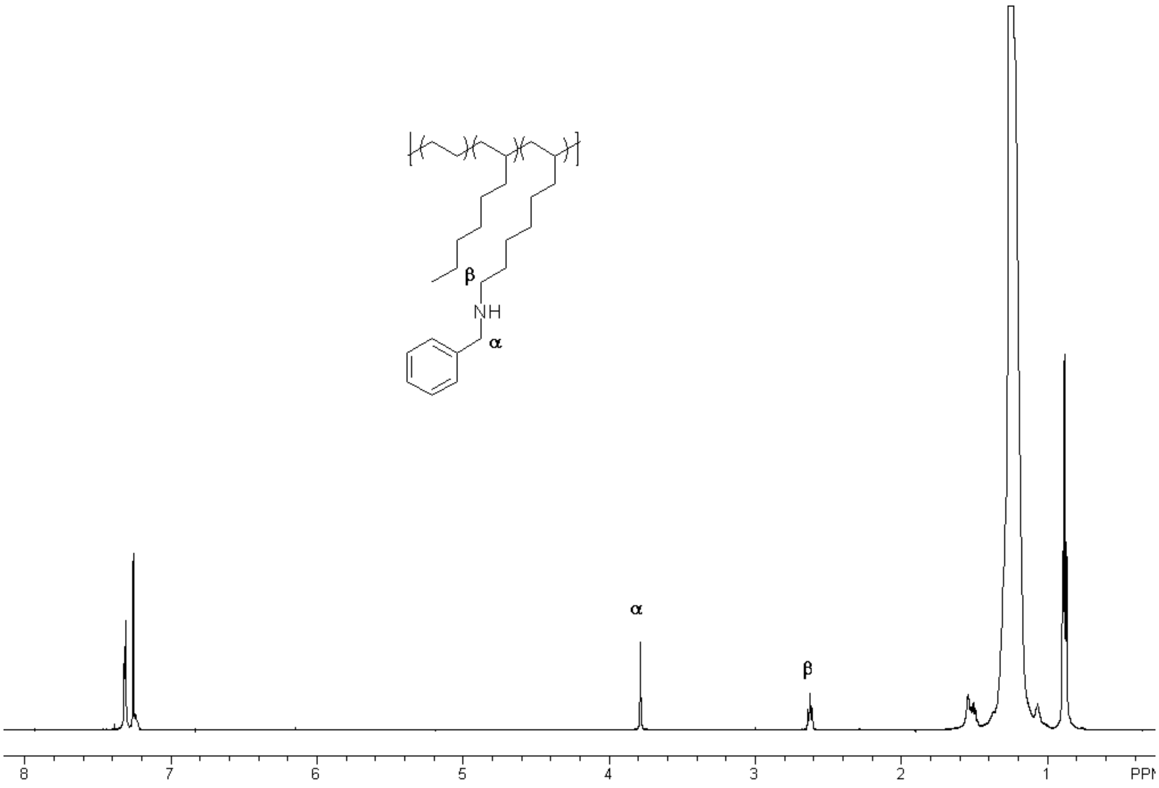

**Figure S10:** $^1$H NMR spectrum [delay time = 1 s, number of transients = 16] of **1**-NHBn [15 mg/mL $CDCl_3$ at room temperature].

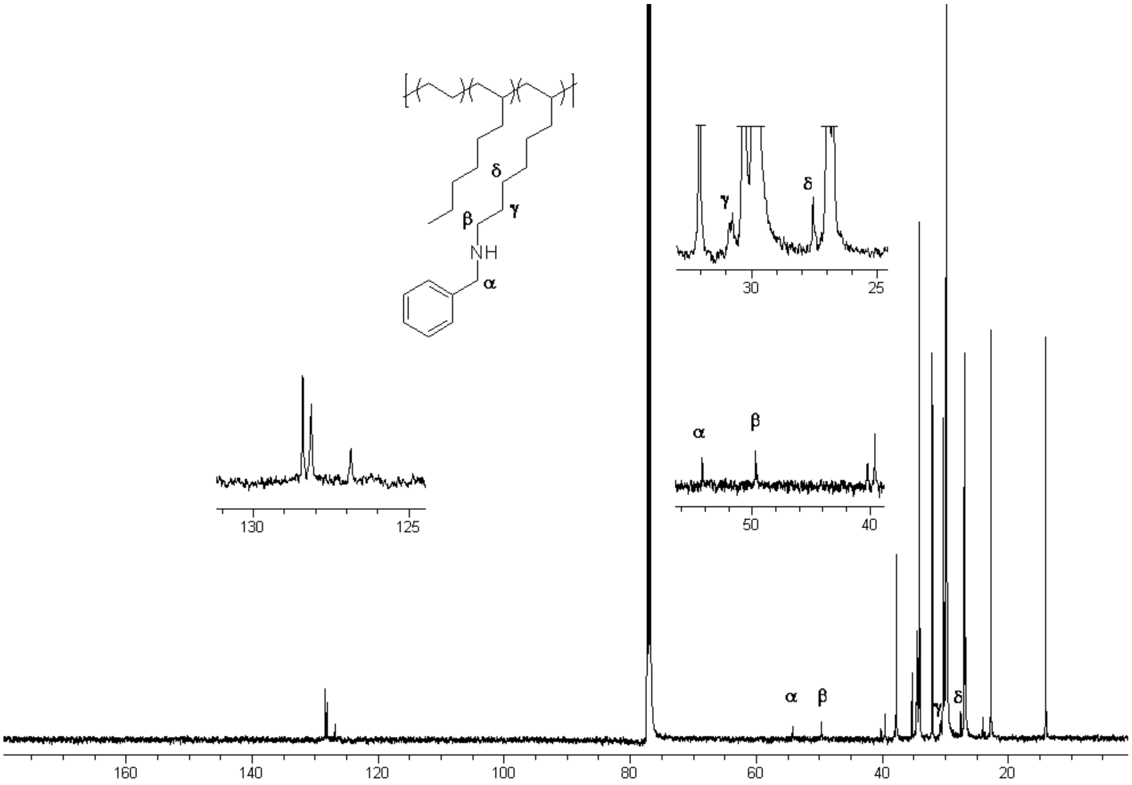

**Figure S11:** $^{13}$C NMR spectrum [delay time = 4 s, number of transients = 6000] of **1**-NHBn [50 mg/mL $CDCl_3$ at 55 $^{o}$C].

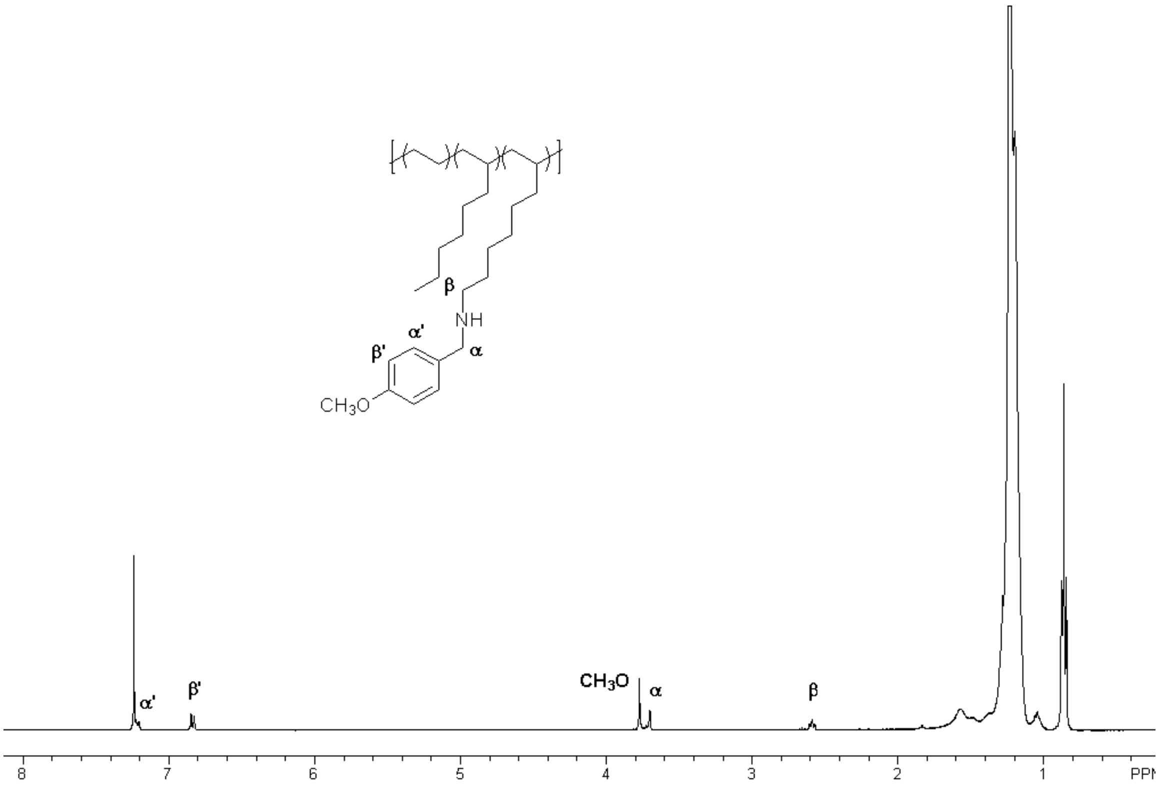

**Figure S12:** $^1$H NMR spectrum [delay time = 1 s, number of transients = 16] of **1**-NHPMB [15 mg/mL $CDCl_3$ at room temperature].

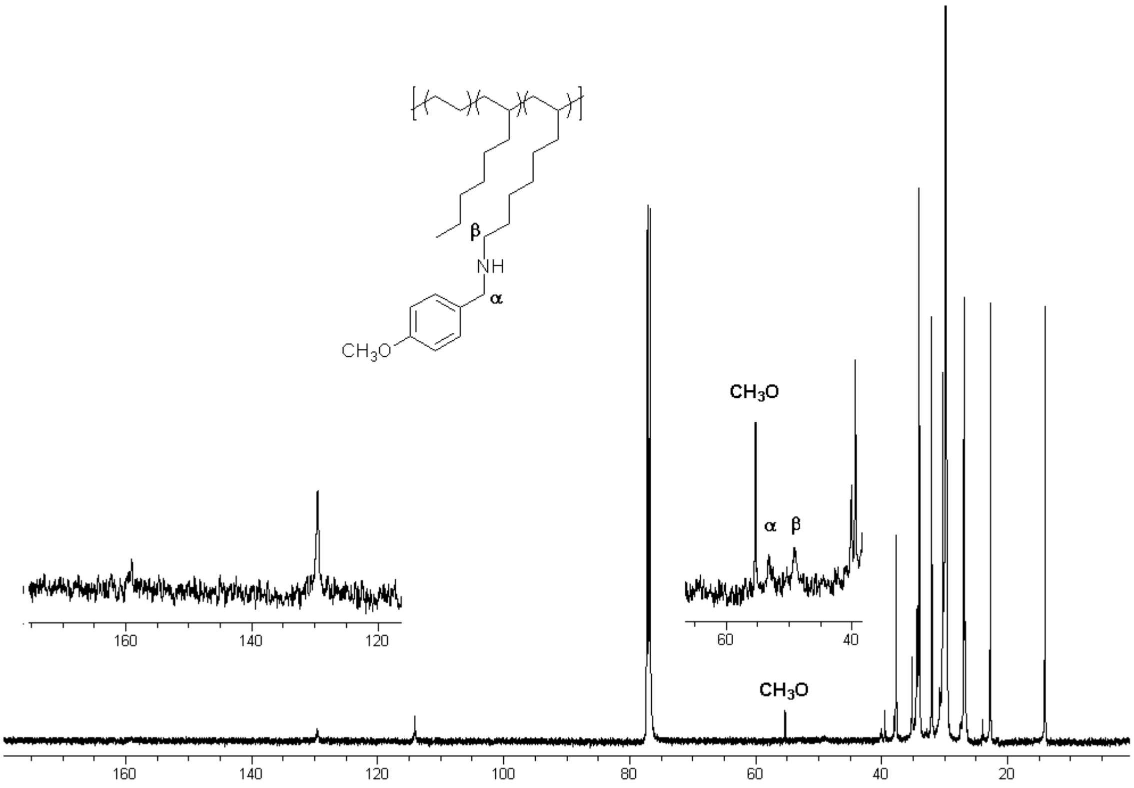

**Figure S13:** $^{13}$C NMR spectrum [delay time = 4 s, number of transients = 7000] of **1**-NHPMB [50 mg/mL $CDCl_3$ at 55 °C].

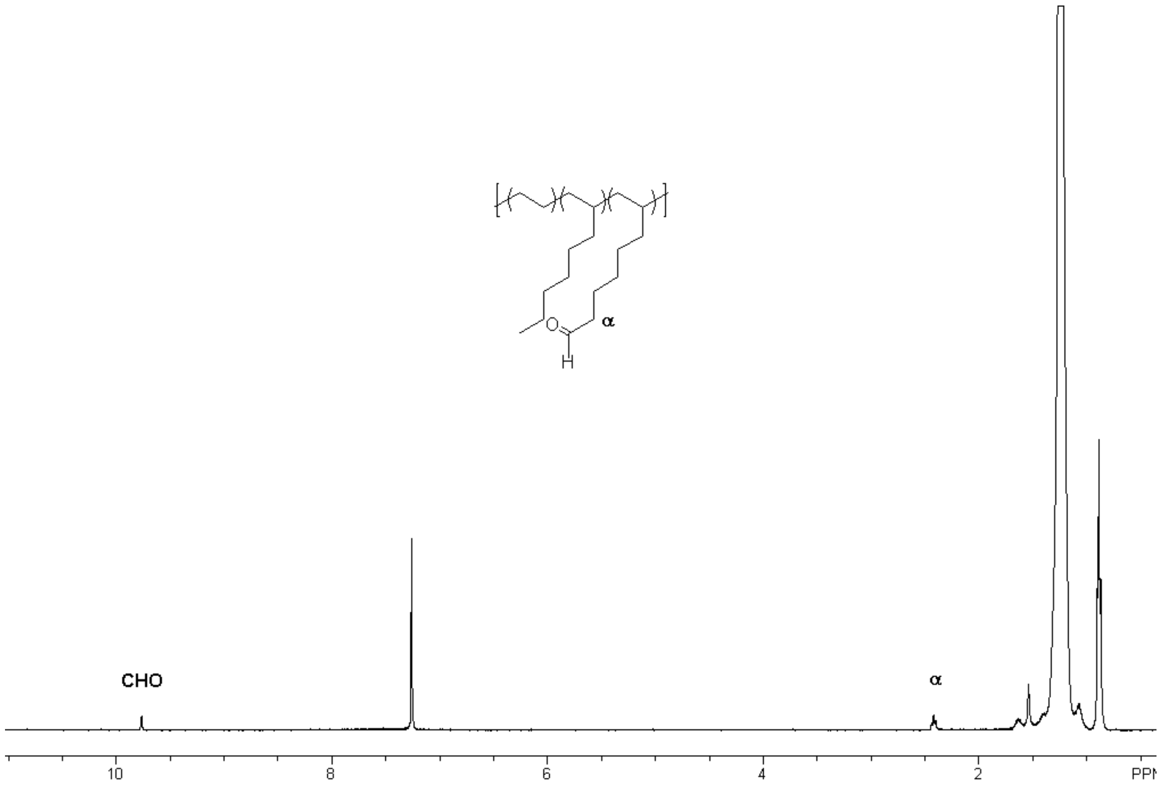

**Figure S14:** $^1$H NMR spectrum of [delay time = 1 s, number of transients = 16] of **1**-CHO [15 mg/mL $CDCl_3$ at room temperature].

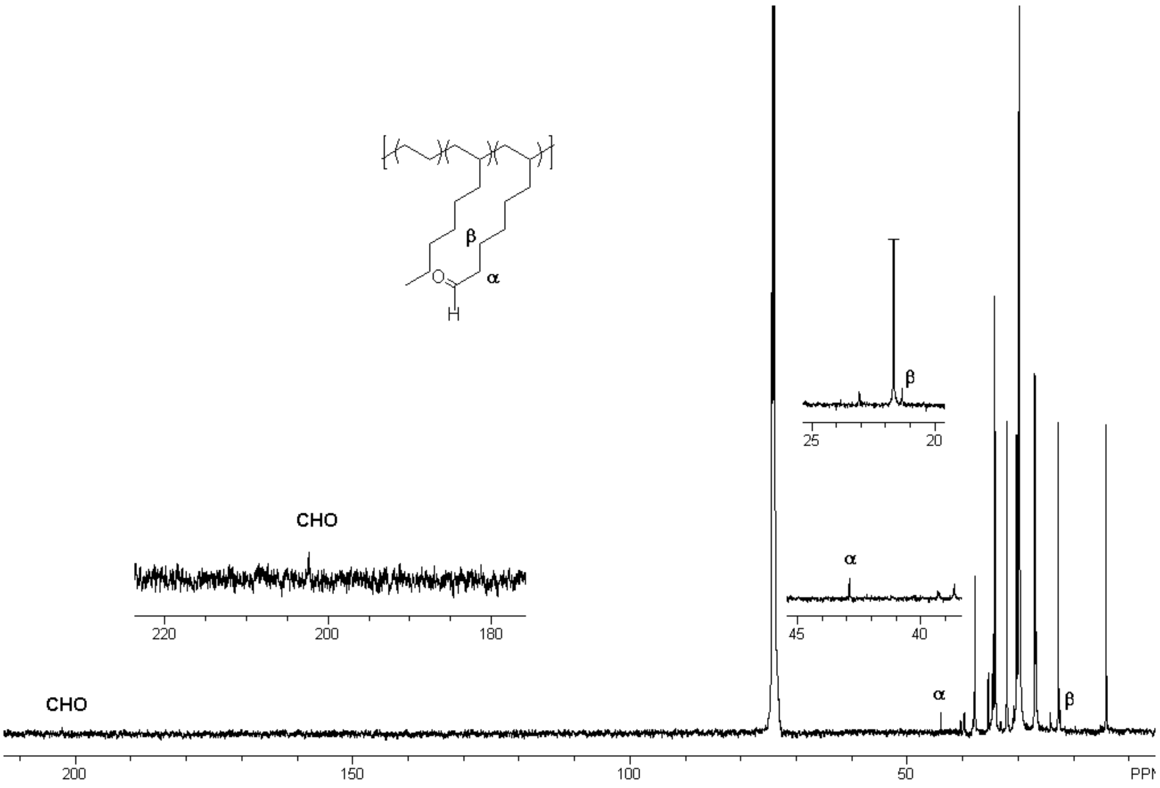

**Figure S15:** $^{13}$C NMR spectrum of [delay time = 4 s, number of transients = 9000] of **1**-CHO [35 mg/mL $C_2D_2Cl_4$ at 85 $^{o}$C].

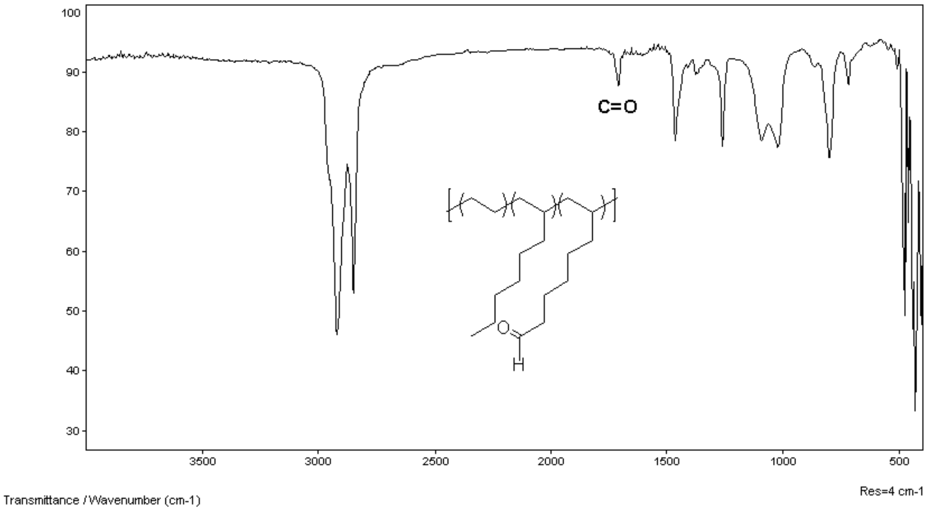

**Figure S16:** FT-IR spectrum of **1**-CHO [film].

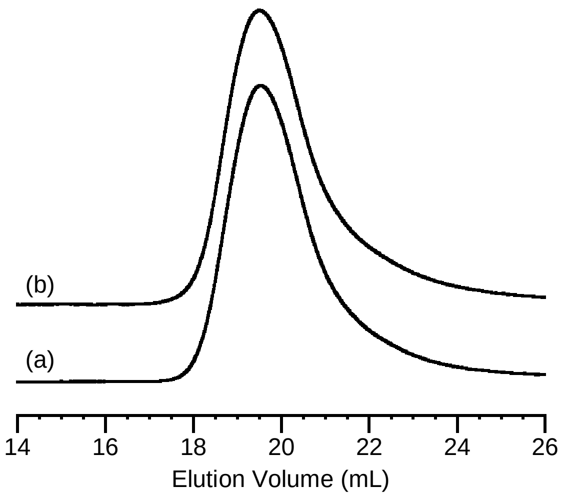

**Figure S17:** Size exclusion chromatogram [10 mg/mL THF] for (a) **1**-Bpin [$M_n$ = 96.5 kg/mol, PDI = 2.0] and (b) **1**-OH [$M_n$ = 94.1 kg/mol, PDI = 2.1] in entry 10 of Table 2. $M_n$ relative to polystyrene standard.

## References to the Supporting Information:

[1] White, C.; Yates, A.; Maitlis, P. M. In *Inorganic Synthesis*; Grimes, R. N., Ed., 1992; Vol. 29, pp 228.
[2] Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. (A)* **1970**, 2875.
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[5] Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750.