Supplementary Material (ESI) for Chemical Communications

Dicationic and zwitterionic catalysts for the amine-initiated, immortal ring-opening polymerisation of *rac*-lactide: facile synthesis of amine-terminated, highly heterotactic PLA

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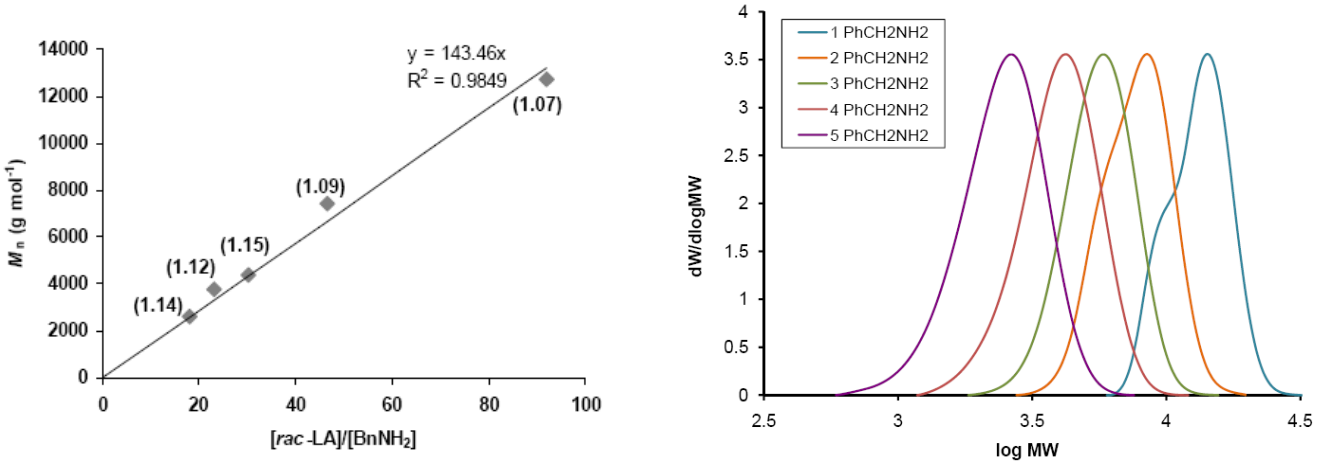
Supporting information

Figure S1. **(a)** M_n *vs* $[rac\text{-LA}]_0:[BnNH_2]_0$ for the ROP of *rac*-LA (100 equivs) using **3**. The line is that predicted based on %conversion and the numbers in parentheses are the PDIs. **(b)** The corresponding GPC traces.



(a) **(b)**

Figure S2. MALDI-ToF-MS spectrum of the BnNH-[poly(*rac*-LA)]-H prepared using **3** with a $[rac\text{-LA}]_0:[BnNH_2]_0$ ratio of 100:4. The cationization agent used was potassium trifluoroacetate (Fluka, >99%).

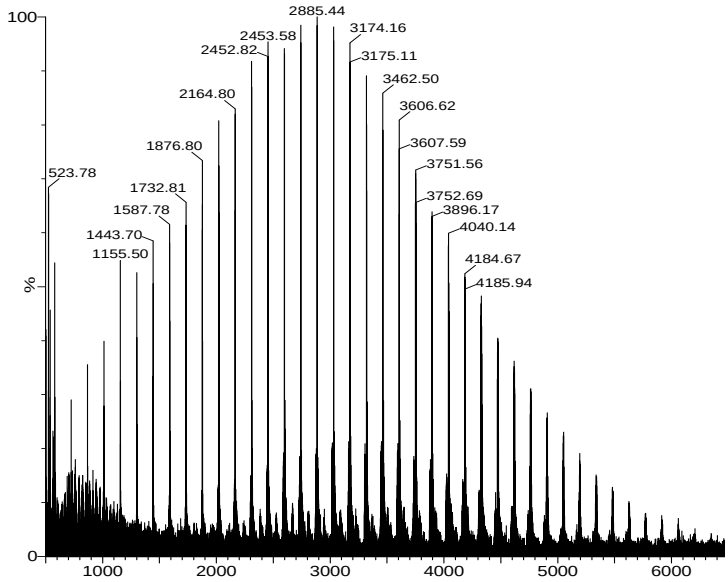


Figure S3. ^{1}H NMR spectrum (300.1 MHz, 293 K, $CDCl_3$) of BnNH-[poly(*rac*-LA)]-H precipitated twice from MeOH and then once from hexanes. M_n (GPC) = 2690 g mol^{-1}; M_n (NMR) = 2660 g mol^{-1} (DP ~ 18).

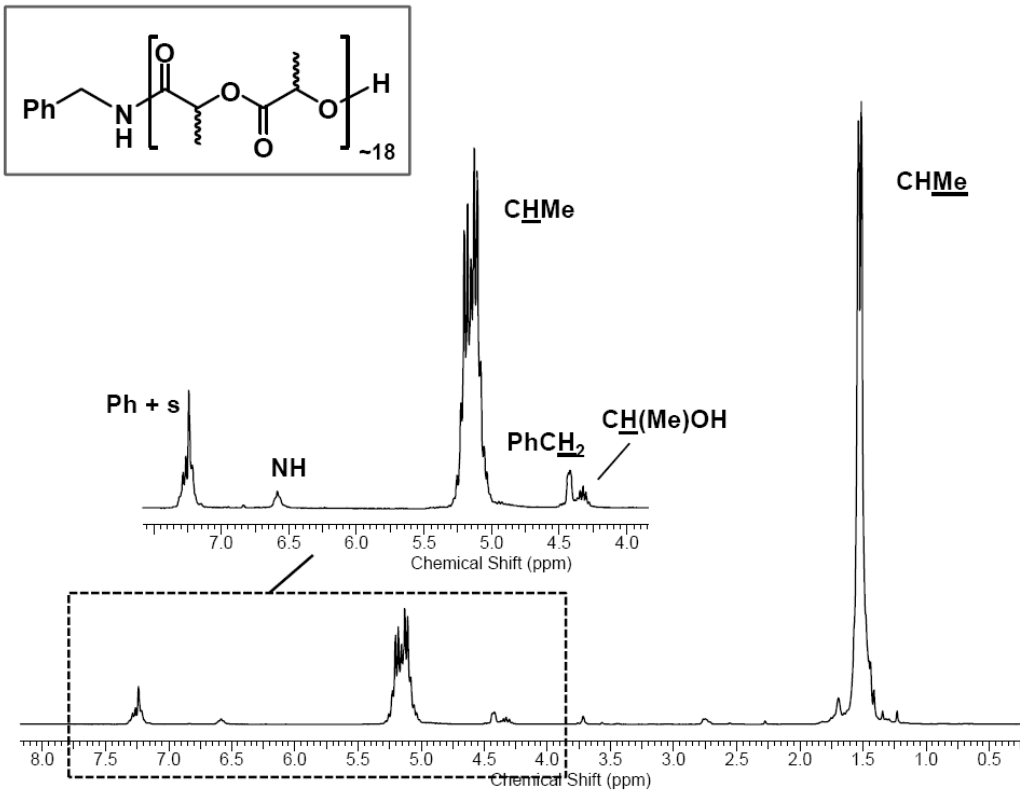
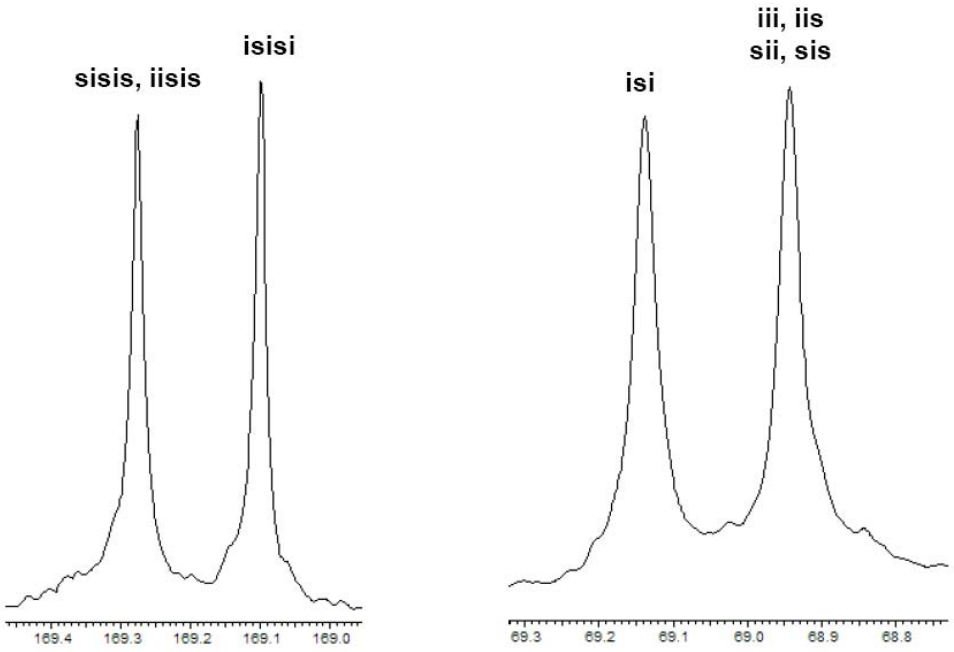


Figure S4. The C=O (left) and CHMe regions of $^{13}C\{^{1}H\}$ NMR spectra (75.4 MHz, 293 K, $CDCl_3$) of BnNH-[poly(*rac*-LA)]-H prepared using **3**. The assigments are made according to J. E. Kasperczyk, *Macromolecules*, 1995, **28**, 3937 referenced to $\delta(CDCl_3)$ = 77.0 ppm.

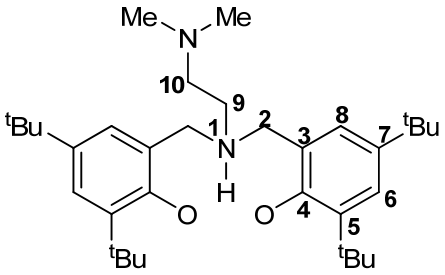


Data for $[Y\{HC(Me_2pz)_3\}(O^iPr)(THF)_3][BPh_4]_2$ (1-$[BPh_4]_2$).

^{1}H NMR (CD_2Cl_2, 299.9 MHz, 293 K): 7.76 (1 H, s, $\underline{H}C(Me_2pz)_3$), 7.33 (16 H, m, *m*-$B(C_6\underline{H}_5)_4$), 6.97 (16 H, d, ^3J = 7.5 Hz, *o*- $B(C_6\underline{H}_5)_4$), 6.81 (8 H, t, ^3J = 7.5 Hz, *p*- $B(C_6\underline{H}_5)_4$), 6.02 (3 H, s, $HC(Me_2\underline{pz})_3$), 4.07 (1 H, sept., ^3J = 6.5 Hz, $OC\underline{H}Me_2$), 3.73 (12 H, m, $OC\underline{H}_2CH_2$), 2.29 (9 H, s, 3-$HC(\underline{Me}_2pz)_3$), 2.24 (9 H, s, 5-$HC(\underline{Me}_2pz)_3$), 1.89 (12 H, m, $OCH_2C\underline{H}_2$), 1.16 (6 H, d, ^3J = 6.5 Hz, $OCH\underline{Me}_2$) ppm. ^{13}C-{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 293 K): 164.6 (3-$HC(Me_2\underline{pz})_3$), 139.5 (5-$HC(Me_2\underline{pz})_3$), 136.8 (*m*-$B(\underline{C}_6H_5)_4$), 129.2 (4-$HC(Me_2\underline{pz})_3$), 126.5 (*o*-$B(\underline{C}_6H_5)_4$), 122.7 (*p*-$B(\underline{C}_6H_5)_4$), 70.3 ($O\underline{C}HMe_2$), 69.1 ($H\underline{C}(Me_2pz)_3$), 67.8 ($O\underline{C}H_2CH_2$), 27.3 ($OCH\underline{Me}_2$), 26.4 ($OCH_2\underline{C}H_2$), 14.4 (5-$HC(\underline{Me}_2pz)_3$), 12.0 (3-$HC(\underline{Me}_2pz)_3$); *ipso*-C_6H_5 not observed. IR (NaCl plates, Nujol Mull): 2726 (m), 1460 (m), 1377 (m), 1304 (m), 1261 (s), 1093 (m), 1018 (m), 799 (s), 722 (s) cm^{-1}. Anal. found (calcd. for $C_{79}H_{93}B_2N_6O_4Y_1$): C, 72.75 (72.88); H, 7.38 (7.21); N, 6.27 (6.46) %. Diffraction-quality crystals were grown from a pentane layered THF solution at room temperature.

Data for $Y(O_2NN')(HO_2NN')$ (3).

The numbering scheme for compound **3** is depicted in the structure below. In addition, **a**, **b**, **c** and **d** denote the resonances corresponding to each phenolate side arm, as observed by ^{1}H, ^{13}C and two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. **′** denotes the resonances assigned to the tetradentate coordinated bisphenolate ligand.



^{1}H NMR (C_6D_6, 299.9 MHz, 298 K): δ 8.74 (1 H, br **NH**), 7.67 (1 H, d, ^4J = 2.7 Hz, **6′d**), 7.66 (1 H, d, ^4J = 2.6 Hz, **6′c**), 7.53 (1 H, d, ^4J = 2.6 Hz, **6b**), 7.46 (1 H, d, ^4J = 2.6 Hz, **6a**), 7.10 (1H, d, ^4J = 2.7 Hz, **8′c**), 7.10 (1H, om, **2b**), 7.05 (1 H, d, ^4J = 2.6 Hz, **8′d**) 6.98 (1 H, d, ^4J = 2.6 Hz, **8b**), 6.72 (1 H, d, ^4J = 2.6 Hz, **8a**), 6.64 (1H, d, ^2J = 11.1 Hz, **2a**), 4.63 (1 H, d, ^2J = 13.3 Hz, **2′c**), 4.32 (1 H, d, ^2J = 12.6 Hz, **2′d**), 3.28 (2 x 1 H, om **10′** and **2b**), 3.02 (1 H, d, ^2J = 13.3 Hz, **2′c**), 2.95 (1 H, m, **2a**), 2.85 (1 H, d, ^2J = 12.6 Hz, **2′d**), 2.77 (1 H, om **9′**), 2.29 (6 H, br, NMe_2′), 2.01 (6 H, br, NMe_2), 1.89 (9 H, s, **5′c**), 1.77 (9 H, s, **5b**), 1.68 (9 H, s, **5′d**), 1.53 (9 H, s, **5a**), 1.47 (9 H, s, **7′d**), 1.45 (9 H, s, **7′c**), 1.36 (9 H, s, **7b**), 1.31 (9 H, s, **7a**) ppm. The remaining resonances could not be observed under these conditions. ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 298 K): δ 163.3 ($^2J_{(C-Y)}$ = 1.3 Hz, **4′c**), 162.8 ($^2J_{(C-Y)}$ = 4.6 Hz, **4b**), 162.6 ($^2J_{(C-Y)}$ = 2.7 Hz, **4′d**), 162.5 ($^2J_{(C-Y)}$ = 4.3 Hz, **4a**), 140.5 (**5a**), 139.4

(**5b**), 138.8 (**7a**), 137.0 (**7b**), 136.6 (**5′c**), 136.5 (**7′d**), 136.2 (**7′c**), 135.9 (**5′d**), 127.2 (**8′d**), 126.2 (**6a**), 125.6 (**6b**), 125.3 (**8′c**), 125.2 (**3′d**), 125.0 (**8b**), 124.9 (**3′c**), 124.8 (**6′d**), 124.4 (**8a**), 123.6 (**6′c**), 122.3 (**3a**), 120.7 (**3b**), 66.0 (**10′**), 64.7 (**10**), 63.2 (**2′c**), 62.7 (**2′d**), 60.8 (**2b**), 60.59 (NMe′), 60.35 (**2a**), 56.7 (NMe’), 55.68 (NMe), 55.45 (NMe), 51.4 (**9**), 48.00 (**9′**), 36.2 (**5′c**, $\underline{C}(CH_3)_3$), 35.9 (**5b**, $\underline{C}(CH_3)_3$), 35.8 (**5a**, $\underline{C}(CH_3)_3$), 35.4 (**5′d**, $\underline{C}(CH_3)_3$), 34.3 (**7′d**, $\underline{C}(CH_3)_3$), 34.1 (**7′c**, **7a** 2 x $\underline{C}(CH_3)_3$), 34.0 (**7b**, $\underline{C}(CH_3)_3$), 32.3 (**7′c**, **7′d** 2 x $C(\underline{C}H_3)_3$), 32.2 (**7b**, $C(\underline{C}H_3)_3$), 31.9 (**7a**, $C(\underline{C}H_3)_3$), 31,7 (**5′d**, $C(\underline{C}H_3)_3$), 31.2 (**5′c**, $C(\underline{C}H_3)_3$), 31.0 (**5b**, $C(\underline{C}H_3)_3$), 30.0 (**5a**, $C(\underline{C}H_3)_3$) ppm. IR (NaCl plates, Nujol mull): 2752(w), 1606(w), 1413(s), 1362(s), 1327(w), 1299(s), 1239(m), 1206(w), 1173(w), 1136(w), 1116(w), 1043(w), 1026(w), 876(w), 834(m), 776(w), 665(m) cm^{-1}. Anal. found (calcd. for $C_{68}H_{109}N_4O_4Y$): C, 72.00 (71.93); N, 4.89 (4.93); H, 9.70 (9.67) %. Diffraction-quality crystals were grown from a saturated pentane solution at -30 °C.