Supplementary Material (ESI) for Chemical Communications

One-component catalysts for cyclic carbonate synthesis

Supporting Information

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Contents

Chemicals and Equipment

Commercially available chemicals (Alfa, Aldrich, Fluka) were used as received. Chromatographic separations were performed using silica gel 60 (230-400 mesh, Davisil). ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C. All spectra were recorded in $CDCl_3$ at room temperature unless stated otherwise. Infra red spectra of liquids or of solids dissolved in a solvent were recorded between NaCl plates on a PE Spectrum 1 spectrometer. Infra red spectra of pure solids were recorded on a Nicolet380 FTIR spectrometer fitted with a 'Smart orbit' attachment. Optical rotations were measured on a Perkin-Elmer 343 polarimeter at the sodium D-line using 0.25 and 0.5 dm thermostated cuvettes and a suitable solvent that is reported along with the concentration (g/100 mL). Low and high resolution mass spectra were recorded on a Waters LCT Premier LCMS spectrometer. ICPMS was performed on a Unicam 701 Series Emission Spectrometer.

Gas chromatography was performed on a Varian CP-800 instrument with a TCD detector using a FactorFour (VF-1 ms) capillary column (15 m × 0.25 mm) with hydrogen as the carrier gas. The conditions used were: initial temperature 60 ^oC, hold at initial temperature for 2 minutes then ramp rate 15 ^oC/min to 270 ^oC; hold at final temperature for 5 minutes. GCMS (EI and CI) were recorded on a Varian CP-800-SATURN 2200 GC/MS ion-trap mass spectrometer using a FactorFour (VF-5 ms) capillary column (30 m × 0.25 mm) with hydrogen as the carrier gas. The conditions used were: initial temperature 60 ^oC, hold at initial temperature for 3 minutes then ramp rate 15 ^oC/min to 270 ^oC; hold at final temperature for 5 minutes. For the first 3.50 minutes, the eluent was routed away from the mass detector. Subsequently, the detector was operated in full EI or CI scan mode.

Analytical chiral HPLC was performed on a Varian ProStar HPLC system fitted with a diode array detector. Separation of styrene oxide enantiomers was achieved on a Chiralpack ADH column using a solvent system of hexane / propan-2-ol (99:1) and a flow rate of 0.3 mL/min: T_R 18.6 and 20.4 minutes. Separation of styrene carbonate enantiomers was achieved on a Chiracel OD column using a solvent system of hexane / propan-2-ol (85:15) and a flow rate of 0.8 mL/min: T_R 23.9 and 27.8 minutes.

Synthesis of catalysts

*3-Tert-butyl-5-diethylaminomethylsalicylaldehyde hydrochloride **3a***

To a solution of 3-*tert*-butyl-5-chloromethylsalicylaldehyde (226.5 mg, 1 mmol) in acetonitrile (60 mL), diethylamine (73 mg, 1 mmol) was added dropwise to give a greenish solution. The reaction was stirred at 30 ºC overnight. Evaporation of volatiles *in vacuo* gave compound **3a** (231 mg, 77%) as a green oil which was used without purification. ν_{max} 3300, 2899, and 1720 cm^{-1}. δ_H 1.35 (9H, s, $C(CH_3)_3$), 1.45 (6H, t *J* 7.2 Hz, $2\times CH_2C\mathit{H}_3$), 3.43 (4H, q *J* 7.2 Hz, $2\times C\mathit{H}_2CH_3$), 4.90 (2H, s, CCH_2N), 7.57 (1H, d *J* 2.1 Hz, H_{Ar}), 8.03 (1H, d, *J* 2.1 Hz, H_{Ar}), 9.98 (1H, s, CHO), 12.00 (1H, br s, OH). δ_C 11.9, 29.4, 34.9, 46.9, 57.1, 120.6, 130.9, 131.4, 134.8, 138.1, 160.2, 197.1. m/z(ES^+) 264 (MH^+, 100), 265 (20), 266 (10). HRMS (ESI): Calculated for MH^+ ($C_{16}H_{26}NO_2^+$) 264.1964, found 264.1953.

*5-Diethylaminomethylsalicylaldehyde hydrochloride **3b***

To a solution of 4-(chloromethyl)salicylaldehyde (341 mg, 2 mmol) in acetonitrile (70 mL), diethylamine (0.21 mL, 2mmol) was added and the mixture refluxed overnight. Then, the solvent was evaporated to give compound **3b** (482 mg, 99%) as a yellow oil. ν_{max} 3383, 2648 and 1653 cm^{-1}. δ_H 1.37 (6H, t *J* 7.2 Hz, $2\times CH_2C\mathit{H}_3$), 3.43 (4H, q *J* 7.2 Hz, $2\times C\mathit{H}_2CH_3$), 4.09 (2H, s, CCH_2N), 7.05 (1H, d *J* 8.6 Hz, H_{Ar}), 8.03 (1H, d *J* 8.6 Hz, H_{Ar}), 8.14 (1H, s, H_{Ar}), 9.98 (1H, s, CHO), 12.32 (1H, br s, OH). δ_C 11.4, 46.4, 56.0, 118.8, 121.3, 136.7, 139.0, 162.7, 196.5. m/z(ES^+) 208 (MH^+, 100), 293 (30), 317 (10). HRMS (ESI): Calculated for M^+ ($C_{12}H_{18}NO_2^+$) 208.1338, found 208.1355.

*Synthesis of salen ligands **5a-d***

The appropriate 1,2-diamine dihydrochloride (0.5 mmol) and NaOMe (55 mg, 1 mmol) were stirred in MeOH (10 mL) for 30 minutes. Then, a solution of salicylaldehyde derivative **3a** or **3b** (1 mmol) in MeOH (5 mL) was added and the solution was stirred overnight at 30 ºC. MeOH was evaporated *in vacuo* and a saturated aqueous solution of Na_2CO_3 (20 mL) was added to the residue. The product was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried over $MgSO_4$ and volatiles were removed *in vacuo* to give compounds **5a-d** which were used without further purification.

Data for **5a:** greenish oil obtained in 71% yield. $[\alpha]^{20}_D$ -184.5 (*c* 1.0, $CHCl_3$). ν_{max} 3410, 2899, 1610, 1550 and 830 cm^{-1}. δ_H 0.99 (12H, t *J* 7.2 Hz, 4×CH_2CH_3), 1.40 (18H, s, 2×$C(CH_3)_3$), 1.50–2.05 (8H, m, $(CH_2)_4$), 2.44 (8H, q *J* 7.2 Hz, 4×CH_2CH_3), 3.1–3.2 (2H, m, 2×CHN), 3.4–3.5 (4H, m, 2×CCH_2N), 6.95 (2H, d *J* 1.8 Hz, 2×H_{Ar}), 7.17 (2H, d, *J* 1.8 Hz, 2×H_{Ar}), 8.28 (2H, s, 2×HC=N), 13.77 (2H, br s, 2×OH). δ_C 11.9, 24.4, 29.6, 33.2, 34.8, 46.8, 57.3, 72.5, 118.4, 128.8, 129.8, 130.1, 136.9, 159.3, 165.7. m/z(ESI) 605 (MH^+, 20), 564 (100). HRMS (ESI): Calculated for MH^+ ($C_{38}H_{61}N_4O_2^+$) 605.4795, found 605.4783.

Data for **5b:** yellow oil obtained in 56% yield. ν_{max} 2965, 2524 and 1629 cm^{-1}. δ_H 1.44 (12H, t *J* 7.5 Hz, 4×CH_2CH_3), 1.51 (18H, s, 2×$C(CH_3)_3$), 2.78 (8H, q *J* 7.2 Hz, 4×CH_2CH_3), 3.6–3.8 (4H, m, 2×CH_2N), 3.9-4.1 (4H, m, CCH_2N), 7.0–7.4 (4H, m, 4×H_{Ar}), 8.25 (2H, s, 2×HC=N), 13.99 (2H, br s, 2×OH). δ_C 10.4, 28.0, 33.3, 45.2, 55.7, 58.1, 116.8, 128.2, 128.8, 135.6, 157.7, 165.3, 165.8. m/z(ESI) 551 (MH^+, 100), 524 (30). HRMS (ESI): Calculated for MH^+ ($C_{34}H_{55}N_4O_2^+$) 551.4325, found 551.4294.

Data for **5c:** yellow oil obtained in 65% yield. $[\alpha]^{20}_D$ -302 (*c* 0.1, $CHCl_3$). ν_{max} 2939, 1631, 1089 cm^{-1}. δ_H 1.25 (12H, t *J* 7.2 Hz, 4×CH_2CH_3), 1.5–2.0 (8H, m, $(CH_2)_4$) 2.89 (8H, q *J* 7.6 Hz, 4×CH_2CH_3), 2.9–3.0 (4H, m, 2×CCH_2N), 3.9–4.0 (2H, m, 2×CHN), 6.83 (2H, d *J* 8.3 Hz, 2×H_{Ar}), 7.36 (2H, d *J* 8.4 Hz, 2×H_{Ar}), 7.43 (2H, s, 2×H_{Ar}) 8.25 (2H, s, 2×HC=N), 13.40 (2H, br s, 2×OH). δ_C 9.5, 24.4, 33.0, 46.9, 56.0, 72.6, 117.7, 118.9, 120.8, 134.3, 134.8, 161.4, 165.3. m/z(ES^+) 493 (MH^+, 100), 420 (20). HRMS (ESI): Calculated for MH^+ ($C_{30}H_{45}N_4O_2^+$) 493.3542, found 493.3544.

Data for **5d:** yellow oil obtained in 53% yield. ν_{max} 2801, 1632, 1083 cm^{-1}. δ_H 1.21 (12H, t *J* 7.5 Hz, 4×CH_2CH_3), 2.96 (8H, q *J* 7.2 Hz, 4×CH_2CH_3), 3.4–3.5 (4H, m, CCH_2N), 3.8–4.0 (4H, m, 2×CH_2), 6.83 (2H, d *J* 8.6 Hz, 2×H_{Ar}), 7.26 (2H, d *J* 8.6 Hz, 2×H_{Ar}), 7.42 (2H, s, 2×H_{Ar}), 8.34 (2H, s, 2×HC=N), 13.21 (2H, br s, 2×OH). δ_C 11.9, 43.5, 47.8, 57.2, 117.0, 129.6, 126.5, 130.4, 132.0, 133.4, 166.9. m/z(ES^+) 439 (MH^+, 100), 420 (20). HRMS (ESI): Calculated for MH^+ ($C_{34}H_{55}N_4O_2^+$) 439.3073, found 439.3090.

*Synthesis of bis-ammonium salts **6a-d***

To a solution of compound **5a-d** (1 mmol) in acetonitrile (60 mL), benzyl bromide (342 mg, 2 mmol) was added dropwise to give a yellow solution. The reaction was stirred at 30 ºC overnight. After evaporation of volatiles *in vacuo*, a yellow oil was obtained which was recrystallized from *n*-hexane to give compounds **6a-d**.

Data for **6a:** yellow solid obtained in 71% yield. $[\alpha]^{20}_D$ -38.6 (*c* 1.0, $CHCl_3$). ν_{max} 3392, 2960, 1608, 1545 and 1470 cm^{-1}. δ_H 1.0–1.4 (20H, m, 4×CH_3CH_2 + $(CH_2)_4$), 1.90 (18H, s, 2×$C(CH_3)_3$), 3.4–3.5 (2H, m, 2×CHN), 3.56 (8H, q *J* 7.5 Hz, 4×CH_2CH_3), 4.20 (4H, s, 2×CCH_2N), 4.99 (4H, s, 2×CCH_2N), 6.44 (2H, d *J* 2.4 Hz, 2×H_{Ar}), 7.1–7.3 (10H, m, 10×H_{Ar}), 7.65 (2H, d *J* 2.4 Hz, 2×H_{Ar}), 8.38 (2H, s, 2×HC=N), 14.30 (2H, br s, 2×OH). δ_C 11.3, 23.4, 29.3, 31.2, 35.1, 51.1, 60.3, 60.4, 72.7, 120.2, 128.6, 128.8, 129.2, 129.9, 130.6, 134.9, 157.2, 163.9.

Data for **6b:** ν_{max} 3383, 2648, and 1647 cm^{-1}. δ_H 1.3–1.4 (30H, m, 4×CH_3CH$_2$ + 2×C(CH$_3$)$_3$), 2.9–3.0 (8H, m, 4×CH_2CH$_3$), 3.4–3.5 (4H, m, 2×CH$_2$N), 4.20 (4H, s, 2×CCH$_2$N), 4.61 (4H, s, 2×CCH$_2$N), 7.0–7.8 (14H, m, 14×H$_{Ar}$), 8.84 (2H, s, 2×HC=N), 14.17 (2H, br s, 2×OH). δ_C 10.9, 29.6, 35.1, 46.5, 56.6, 59.7, 65.7, 118.8, 121.1, 127.5, 128.8, 129.0, 129.5, 135.5, 137.3, 139.6, 141.0, 162.6.

Synthesis of one-component catalysts ***7a,b***

These reactions were performed under an inert atmosphere in dry conditions. Ligand **6a,b** (1 mmol) and Al(OEt)$_3$ (324 mg, 2 mmol) were dissolved in a mixture of toluene (5 mL) and ethanol (5 mL) and heated to reflux for 5 hours. Any alumina which formed was removed by filtering through a sinter funnel. The filtrate was then evaporated *in vacuo* and water (30 mL) and CH$_2$Cl$_2$ (30 mL) were added. The complex was extracted using CH$_2$Cl$_2$ (3×20 mL) and the combined organic layers were dried over MgSO$_4$. Volatiles were removed *in vacuo* to give a solid residue which was recrystallized from Et$_2$O to give catalysts **7a,b**.

Data for **7a:** pale yellow solid obtained in 33% yield. $[\alpha]^{20}_D$ -281 (*c* 1.0, CHCl$_3$). ν_{max} 2946, 1624, 1551, 1470, 1208 and 1030 cm^{-1}. δ_H 1.05 (24H, t *J* 7.3 Hz, 8×CH$_2$CH_3), 1.45 (36H, s, 4×C(CH$_3$)$_3$), 1.5–2.2 (16H, m, 2×(CH$_2$)$_4$), 2.4–2.5 (16H, m, 8×CH_2CH$_3$), 3.1–3.2 (2H, m, 2×CHN), 3.4–3.5 (16H, m, 8×CCH$_2$N), 3.8–3.9 (2H, m, 2×CHN), 7.1–7.5 (28H, m, 28×H$_{Ar}$), 8.20 (2H, s, 2×HC=N), 8.35 (2H, s, 2×HC=N). δ_C 10.3, 24.5, 30.0, 30.2, 34.6, 48.3, 57.6, 60.2, 73.8, 119.1, 119.6, 124.6, 127.4, 127.9, 128.9, 135.2, 141.6, 156.5, 166.1.

Data for **7b:** pale yellow solid obtained in 42% yield. ν_{max} 2950, 1634, 1029 cm^{-1}. δ_H 1.05 (24H, t *J* 7.3 Hz, 8×CH$_2$CH_3), 1.45 (36H, s, 4×C(CH$_3$)$_3$), 2.9–3.2 (16H, m, 8×CH_2CH$_3$), 3.2–3.8 (8H, m, 4×CH$_2$N), 4.0–4.5 (16H, m, 8×CCH$_2$N), 7.1–7.5 (28H, m, 28×H$_{Ar}$), 8.00 (2H, s, 2×HC=N), 8.13 (2H, s, 2×HC=N). δ_C 11.5, 30.0, 35.7, 46.91, 55.4, 57.3, 65.7, 119.2, 119.6, 126.3, 131.1, 132.5, 132.6, 134.4, 141.9, 164.9, 170.1.

Synthesis of bimetallic aluminium complexes ***8a-d***

These reactions were performed under an inert atmosphere in dry conditions. Ligand **5a-d** (1 mmol) and Al(OEt)$_3$ (324.1 mg, 2 mmol) were dissolved in toluene (10 mL) and heated to reflux for 5 hours. Any alumina which formed was removed by filtering through a sinter funnel. The filtrate was then evaporated *in vacuo* and water (30 mL) and CH$_2$Cl$_2$ (30 mL) were added. The complex was extracted using CH$_2$Cl$_2$ (3×20 mL) and the combined organic layers were dried over MgSO$_4$. Volatiles were removed *in vacuo* to give a solid residue which was recrystallized from MeCN to give complexes **8a-d**.

Data for **8a:** pale green solid obtained in 40% yield. $[\alpha]^{20}_D$ -522 (*c* 1.0, CHCl$_3$). ν_{max} 2865, 1626, 1548, 1440, 1027, 836 and 577 cm^{-1}. δ_H 1.02 (24H, t *J* 7.2 Hz, 8×CH$_2$CH_3), 1.46 (36H, s, 4×C(CH$_3$)$_3$), 1.5–2.2 (16H, m, 2×(CH$_2$)$_4$), 2.5–2.6 (16H, m, 8×CH_2CH$_3$), 3.1–3.2 (2H, m, 2×CHN), 3.50 (8H, m, 4×CCH$_2$N), 3.8–3.9 (2H, m, 2×CHN), 7.09 (4H, d *J* 5.7 Hz, 4×H$_{Ar}$), 7.35 (4H, d *J* 5.7 Hz, 4×H$_{Ar}$), 8.19 (2H, s, 2×HC=N), 8.37 (2H, s, 2×HC=N). δ_C 10.2, 24.7, 29.9, 30.1, 35.0, 47.1, 57.6, 73.2, 118.9, 119.2, 128.9, 135.3, 141.7, 157.2, 165.1. m/z(ESI) 1280 (4), 1279 (16), 1278 (32), 1277 (72), 1276 (MH$^+$, 80), 662 (100). HRMS (ESI): Calculated for MH$^+$ ($C_{76}H_{117}N_8O_5Al_2^+$) 1275.8778, found 1275.8796.

Data for **8b:** pale yellow solid obtained in 55% yield. ν_{max} 2522 and 2159 cm^{-1}. δ_H 1.1–1.2 (24H, m, 8×CH$_2$CH_3), 1.43 (36H, s, 4×C(CH$_3$)$_3$), 2.9–3.3 (16H, m, 8×CH_2CH$_3$), 3.5–3.6 (8H, m, 4×CCH$_2$N), 3.7–4.0 (8H, m, 4×CH$_2$N), 7.19 (4H, s, 4×H$_{Ar}$), 7.30 (4H, s, 4×H$_{Ar}$), 8.33 (4H, s, 4×HC=N). δ_C 11.2, 24.2, 33.6, 46.5, 55.3, 55.9, 120.9, 135.5, 137.5, 137.8, 139.6, 140.9, 162.0. m/z(ESI) 1170 (10), 1169 (35), 1168 (90), 1167 (MH$^+$, 100). HRMS (ESI): Calculated for MH$^+$ ($C_{68}H_{104}N_8O_5Al_2^+$) 1167.7839, found 1167.7799.

Data for **8c:** pale yellow solid obtained in 67% yield. $[\alpha]^{20}_{D}$ -170 (*c* 0.01, DMSO). ν_{max} 2859, 1631 and 1084 cm^{-1}. δ_H(DMSO-d_6): 1.0–1.5 (24H, m, 8×CH_2CH_3), 1.5–2.2 (16H, m, 2×$(CH_2)_4$), 2.5–2.6 (16H, m, 8×CH_2CH_3), 3.1–4.5 (12H, m, 4×CHN + 4×CCH_2N), 6.91 (4H, d *J* 7.6 Hz, 4×H_{Ar}), 7.40 (4H, d *J* 7.6 Hz, 4×H_{Ar}), 7.55 (4H, s, 4×H_{Ar}), 8.43 (4H, s, 4×HC=N). m/z(ESI) 1048 (100), 1049 (70), 1050 (25), 1051 (8). HRMS (ESI): Calculated for MH^+ ($C_{60}H_{82}N_8O_5Al_2^+$) 1048.6039, found 1048.6069.

Data for **8d:** pale yellow solid obtained in 65% yield. ν_{max} 2971, 2225 and 1634 cm^{-1}. δ_H (DMSO-d_6): 1.05 (24H, m, 8×CH_2CH_3), 2.1–3.5 (24H, m, 8×CH_2CH_3 + 4×CCH_2N), 3.9–4.0 (8H, m, CH_2N), 6.81 (4H, d *J* 5.7 Hz, 4×H_{Ar}), 7.32 (8H, m, 8×H_{Ar}), 8.50 (4H, s, HC=N). m/z(ESI) 943 (100), 944 (65), 945 (20), 946 (6). HRMS (ESI): Calculated for MH^+ ($C_{52}H_{72}N_8O_5Al_2^+$) 943.5334, found 943.5408.

Synthesis of one-component catalysts ***7c,d***
Benzyl bromide (0.07 mL, 0.6 mmol) was added to a solution of bimetallic complex **8c**,**d** (0.1 mmol) in propylene carbonate or acetonitrile (10 mL) and the reaction stirred at 80-85 °C for 16 hours. The solvent was evaporated *in vacuo* to give compounds **7c,d** as pale orange powders.

Data for **7c:** pale orange solid obtained in 52% yield. $[\alpha]^{20}_{D}$ -240 (*c* 0.01, DMSO). ν_{max} 2923, 1625, 1088 cm^{-1}. δ_H (DMSO-d_6): 1.0–2.0 (24H, m, 8×CH_2CH_3), 1.5–2.2 (16H, m, 2×$(CH_2)_4$), 2.5–2.6 (16H, m, 8×CH_2CH_3), 3.1–3.9 (12H, m, 4×CHN + 4×CCH_2N), 4.50 (8H, s, 4×CCH_2N), 6.74 (4H, d *J* 7.3 Hz, 4×H_{Ar}), 6.82 (4H, d *J* 7.3 Hz, 4×H_{Ar}), 7.1–7.5 (24H, m, 24×H_{Ar}), 8.43 (4H, s, 4×HC=N).

Data for **7d:** pale orange solid obtained in 40% yield. ν_{max} 2960, 1644, 1032 cm^{-1}. δ_H (DMSO-d_6): 0.99 (12H, m, 4×CH_3CH_2), 1.52 (12H, m, 4×CH_3CH_2), 3.21 (16H, q *J* 7.1 Hz, 8×CH_2CH_3), 4.1–4.3 (16H, m, 4×CCH_2N + 4×CH_2N), 4.57 (8H, s, 4×CCH_2N), 6.97 (4H, d, *J* 8.3 Hz, 4×H_{Ar}), 7.1–7.4 (24H, m, 24×H_{Ar}), 7.5–7.6 (4H, m, 4×H_{Ar}), 7.60 (4H, s, 4×HC=N).

Synthesis of immobilized one-component catalysts ***9a,b***
Merrifield resin (1.0 g) was swollen in a minimal amount of DMF/CH_2Cl_2 and tetrabutylammonium bromide (1.692 g, 5.1 mmol) was added and the mixture left to stir for two days. The resulting resin was filtered, washed with DMF (10 mL), DMF/CH_2Cl_2 (1:1) (10 mL) and CH_2Cl_2 (10 mL), then dried *in vacuo*. A sample of the bromomethyl resin (120 mg) was then swollen in a minimal amount of DMF/CH_2Cl_2. Complex **6a,b** (0.4 mmol) was added and the mixture was stirred for 24 hours at 30 ºC. The resin was filtered and washed with DMF (10 mL), DMF/CH_2Cl_2 (1:1) (10 mL), CH_2Cl_2 (10 mL), then dried *in vacuo* to give a yellow-coloured resin.

Data for **9a**: 70% yield. ν_{max} 2920, 2160, 1634, 1450 and 1066 cm^{-1}. ICPMS (5 mg of resin digested with 10 mL of 1M HCl) gave an aluminium concentration of 4.04 ppm, corresponding to a catalyst loading of 0.15 mmol per gram of support.

Data for **9b**: 75% yield. ν_{max} 2963, 2159, 1634, 1451 and 1091 cm^{-1}. ICPMS (10 mg of resin digested with 10 mL of 1M HCl) gave an aluminium concentration of 17.73 ppm, corresponding to a catalyst loading of 0.32 mmol per gram of support.

Synthesis of immobilized one-component catalysts ***10a,b***
A sample of resins **9a,b** (0.04 mmol) was swollen in DMF/CH_2Cl_2 and a large excess of benzyl bromide (40 mg, 0.24 mmol) was added. The mixture was stirred at room temperature for 24 hours, then the reaction was filtered and the resin washed with DMF (10 mL), DMF/CH_2Cl_2 (1:1) (10 mL), CH_2Cl_2 (10 mL), then dried *in vacuo* to give a yellow-coloured resin.

Data for **10a**: 75% yield. ν_{max} 2922, 2158, 1634, 1635, 1450 and 1028 cm^{-1}. ICPMS (5 mg of resin digested with 10 mL of 1M HCl) gave an aluminium concentration of 5.20 ppm, corresponding to a catalyst loading of 0.19 mmol per gram of support.

Data for **10b**: 83% yield. ν_{max} 2961, 2153, 1636, 1544 and 1023 cm^{-1}. ICPMS (10 mg of resin digested with 10 mL of 1M HCl) gave an aluminium concentration of 8.14 ppm, corresponding to a catalyst loading of 0.15 mmol per gram of support.

Cyclic carbonate synthesis

*Using one-component catalyst **7a-d***

An epoxide (1.66 mmol) and catalyst **7a-d** (0.0415 mmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26 ^oC (or an ice/water bath at 0^oC when propylene carbonate was the substrate). Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred for 6-24 hours with samples being removed after 3 and 6 hours for analysis by ^1H NMR spectroscopy to determine the conversion of epoxide to cyclic carbonate. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *in vacuo* to give either the pure cyclic carbonate (when the epoxide was volatile) or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography in the stated solvent system to give the pure cyclic carbonate.

Data for styrene carbonate. Isolated yield 89% after a reaction time of 6 hours with catalyst **7a** and purification using hexane / EtOAc (2:3). Mp 49–52 ^oC. ν_{max} 3047, 3020, 2968, 2899, 1812 and 1592 cm^{-1}. δ_H 4.35 (1H, t *J* 8.4 Hz, OCH_2), 4.81 (1H, t *J* 8.5 Hz, OCH_2), 5.68 (1H, t *J* 8.0 Hz, PhCHO), 7.2–7.5 (5H, m, ArH). δ_C 71.3, 78.1, 126.0, 129.3, 129.8, 135.9, 154.9. m/z(EI) 164 (M^+, 100), 119 (10), 105 (10). When styrene oxide with >99% ee (confirmed by chiral HPLC analysis) was used, chiral HPLC analysis of samples withdrawn after 3 and 6 hours showed that enantiomerically pure styrene carbonate was formed. The reaction had gone to completion after 6 hours.

Data for hex-1-ene carbonate. Isolated yield 63% after a reaction time of 6 hours with catalyst **7a**. ν_{max} 2960, 2934, 2874 and 1797 cm^{-1}. δ_H 0.95 (3H, t *J* 7.1 Hz, CH_3), 1.2–1.6 (4H, m, $2\times CH_2$), 1.6–2.0 (2H, m, CH_2), 4.09 (1H, dd *J* 8.4, 7.2 Hz, OCH_2), 4.46 (1H, t *J* 7.8 Hz, OCH_2), 4.64 (1H, qd *J* 7.5, 5.4 Hz, OCH). δ_C 13.9, 22.4, 26.5, 33.7, 69.5, 77.2, 155.2. m/z(CI, NH_3), 162 ($M+NH_4^+$, 100), 161 (40), 100 (10).

Data for dec-1-ene carbonate. Isolated yield 68% after a reaction time of 6 hours with catalyst **7a** and purification using a solvent system of Et_2O. ν_{max}(neat) 2928 s, 2857 s, 1805 cm^{-1} s; δ_H 0.90 (3H, t *J* 6.6 Hz, CH_3), 1.2–1.6 (12H, m, 6 x CH_2), 1.6–1.9 (2H, m, CH_2), 4.09 (1H, t *J* 7.5 Hz, OCH_2), 4.54 (1H, t *J* 8.1 Hz, OCH_2), 4.72 (1H, qd *J* 7.5, 5.7 Hz, OCH); δ_C 14.2, 22.7, 24.5, 29.1, 29.2, 29.4, 31.9, 34.0, 69.5, 77.1, 155.2; m/z (EI), 162 (M^+, 8), 95 (38), 67 (100).

Data for hydroxymethyl ethylene carbonate. Isolated yield 65% after a reaction time of 6 hours with catalyst **7a** and purification using a solvent system of first hexane, then 3:1 hexane: EtOAc, then EtOAc. ν_{max} 3400, 2933 and 1789 cm^{-1}. δ_H 3.65 (1H, br, OH), 3.72 (1H, dd *J* 3.5, 12.7 Hz, CH_2O), 4.04 (1H, dd *J* 3.2, 12.9 Hz, CH_2O), 4.4–4.5 (2H, m, CH_2O), 4.8–4.9 (1H, m, CHO); δ_C 61.6, 65.8, 75.0, 155.2; m/z(CI, NH_3), 119 (MH^+, 100), 118 (M^+, 10).

Data for chloromethyl ethylene carbonate. Isolated yield 81% after a reaction time of 6 hours with catalyst **7a** and purification using hexane / EtOAc (2:3). ν_{max} 3467, 1960 and 1799 cm^{-1}. δ_H 3.3–3.8 (2H, m, CH_2Cl), 4.40 (1H, dd *J* 9.0, 8.7 Hz, OCH_2), 4.59 (1H, dd *J* 8.7, 8.4 Hz, OCH_2), 4.9–5.0 (1H, m, OCH). δ_C 43.9, 67.4, 74.6, 154.4. m/z(CI, NH_3) 156 ((^{37}Cl)M+NH_4^+, 50) 154 ((^{35}Cl)M+NH_4^+, 100), 120 (25).

Data for propylene carbonate. Isolated yield 62% after a reaction time of 6 hours with catalyst **7a**. ν_{max} 2991, 2921 and 1786 cm^{-1}. δ_H 1.49 (3H, d *J* 6.3 Hz, CH_3), 4.02 (1H, dd *J* 8.4, 7.3 Hz OCH_2), 4.55 (1H, t *J* 8.4 Hz OCH_2), 4.8–4.9 (1H, m, CHO). δ_C 19.7, 70.9, 73.7, 154.5. m/z(EI) 102 (M^+, 100), 100 (5).

Data for 4-methylstyrene carbonate. Isolated yield 89% after a reaction time of 24 hours with catalyst **7a** and purification using a solvent system of first hexane, then 3:1 hexane: EtOAc, then EtOAc. Mp 39-40 ^oC. ν_{max}(neat) 2950 and 1784 cm^{-1}. δ_H 2.36 (3H, s, CH_3), 4.31 (1H, t *J* 8.4 Hz, OCH_2), 4.76 (1H, t *J* 8.4 Hz, OCH_2), 5.63 (1H, t *J* 8.1 Hz, OCH), 7.23 (4H, s, ArH). δ_C 19.9, 69.9, 76.9, 124.8, 128.7, 132.0, 138.6, 153.6. m/z(EI) 178 (M^+, 80), 163 (35), 134 (20), 119 (95), 104 (75), 91 (100).

Data for 4-bromostyrene carbonate. Isolated yield 85% after a reaction time of 24 hours with catalyst **7a** and purification using a solvent system of first hexane, then 3:1 hexane: EtOAc, then EtOAc. Mp 72-75 ^oC. ν_{max}(neat) 2946, 2518, 2159, 2028, 1976, 1818 and 1785 cm^{-1}. δ_H 4.32 (1H, t *J* 8.5 Hz, OCH_2), 4.83 (1H, t *J* 8.4 Hz, OCH_2), 5.66 (1H, t *J* 7.8 Hz, OCH), 7.27 (2H, dd *J* 8.5, 1.8 Hz, ArH), 7.61 (2H, dd *J* 8.2 Hz, 2.1 Hz, ArH). δ_C 70.9, 77.2, 123.9, 127.4, 132.5, 134.8,154.4. m/z(EI) 244 ((^{81}Br)M^+, 45), 242 ((^{79}Br)M^+, 47), 91 (80), 89 (100).

Data for 4-chlorostyrene carbonate. Isolated yield 83% after a reaction time of 24 hours with catalyst **7a** and purification using a solvent system of first hexane, then 3:1 hexane: EtOAc, then EtOAc. Mp 67-69 ^oC. ν_{max} 2956, 2687, 2159, 2028, 1976 and 1786 cm^{-1}. δ_H 4.30 (1H, t *J* 7.8 Hz, OCH_2), 4.80 (1H, t *J* 8.7 Hz, OCH_2), 5.66 (1H, t *J* 8.1 Hz, OCH), 7.30 (2H, dd *J* 6.6 Hz, 1.8 Hz, ArH), 7.45 (2H, dd *J* 6.9, 1.5 Hz, ArH). δ_C($CDCl_3$) 70.9, 77.2, 127.2, 129.5, 134.3, 135.8, 154.4. m/z(EI) 200 ((^{37}Cl)M^+, 15), 198 ((^{35}Cl)M^+, 50), 163 (30), 124 (60), 91 (40), 89 (100).

Data for 4-thiomethylstyrene carbonate. Isolated yield 51% after a reaction time of 24 hours with catalyst **7a** and purification using solvent systems of first hexane, then 3:1 hexane: EtOAc, then MeOH. Mp 66-67 ^oC. ν_{max}(neat) 1787 cm^{-1}. δ_H 2.49 (3H, s, SCH_3), 4.32 (1H, t *J* 9.0 Hz, OCH_2), 4.77 (1H, t *J* 8.7 Hz, OCH_2), 5.63 (1H, t *J* 8.1 Hz, OCH), 7.28 (4H, s, ArH). δ_C($CDCl_3$) 15.5, 71.1, 77.9, 126.6, 126.7, 132.1, 141.2, 154.7. m/z(EI) 210 (M^+, 100), 166 (40), 137 (40), 91 (25). Found 233.0228, $C_{10}H_{10}O_3NaS$ (M+Na^+) requires 233.0248.

*Using immobilized one-component catalysts **9a,b** or **10a,b***

Catalyst **9a,b** or **10a,b** (0.0415 mmol) was dissolved in propylene carbonate (0.85 g) in a sample vial fitted with a magnetic stirrer bar. Styrene oxide (200 mg, 1.66 mmol) was then added and the sample vial was placed in a large conical flask. The conical flask was placed in an oil bath thermostatted at 26 ^oC. Cardice pellets were added to the conical flask which was fitted with a rubber stopper pierced by a deflated balloon. The reaction was stirred for 20 hours, then filtered to remove the supported catalyst which was washed thoroughly with CH_2Cl_2 (20 mL). The filtrate and washings were combined and evaporated *in vacuo* and the residue analysed by ^1H NMR spectroscopy to determine the conversion of styrene oxide to styrene carbonate. The immobilized catalyst could be returned to the sample vial and reused.