

SUPPORTING INFORMATION

Title: Synthesis of Cyclic Carbonates from Atmospheric Pressure Carbon Dioxide Using Exceptionally Active Aluminium(salen) Complexes as Catalysts

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Experimental details

General procedure for the synthesis of catalysts 1a–h

Al(OEt)₃ (0.28 g, 1.72 mmol) was added to toluene (60 mL) and stirred under reflux for 1 hour. The appropriate salen ligand (1.68 mmol) dissolved in toluene (40 mL) was then added and the reaction mixture was stirred under reflux for a further 3 hours before being allowed to cool to room temperature. The solution was dried (Na₂SO₄) and solvents were evaporated *in vacuo* to give a solid which was purified as specified below.

Data for complex **1a**:^[S1] Yellow solid purified by washing with cold hexane. Yield 63%; [α]_D²⁰ -548 (c= 0.11); $\nu_{\max}(\text{CH}_2\text{Cl}_2)$ 2953 m, 1626 m, and 1474 cm⁻¹ m; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.35 (2H, s, CH=N), 8.15 (2H, s, CH=N), 7.52 (4H, d *J* 2.3 Hz, 4 x ArH), 7.07 (4H, d *J* 2.3 Hz, 4 x ArH), 3.9–3.7 (2H, br m, CHN), 3.2–3.0 (2H, br m, CHN), 2.7–1.8 (16H, m, 2 x (CH₂)₄), 1.50 (36H, s, 4 x (CH₃)₃), 1.29 (36H, s, 4 x (CH₃)₃); m/z (ESI) 1159.7 (MH⁺), 649.4, 623.4, 603.4, 569.3; Found (ESI) 1159.7684, C₇₂H₁₀₅N₄O₅Al₂ (MH⁺) requires 1159.7716.

Data for complex **1b**: Orange solid purified by washing with Et₂O. Yield 63%; [α]_D²⁰ -575 (c= 0.1, toluene); $\nu_{\max}(\text{ATR})$ 2925 w, 1638 m, 1599 m, and 1573 cm⁻¹ m; $\delta_{\text{H}}(\text{CDCl}_3)$ 8.64 (4H, s, 4 x CH=N), 8.36 (4H, s, 4 x ArH), 8.02 (4H, s, 4 x ArH), 3.7–3.8 (4H, br, CHN), 3.7–2.0 (16H, m, 2 x (CH₂)₄), 1.55 (36H,

s, 4 x (CH₃)₃); m/z (ESI) 1115.4 (MH⁺); Found (ESI) 1115.4536 C₅₆H₆₉N₈O₁₃Al₂ (MH⁺) requires 1115.4615.

Data for complex **1c**:^[S1,S2] Yellow solid purified by washing with cold Et₂O. Yield 50%; ν_{\max} (ATR) 2950 m, 2866 w, 1628 m, and 1538 cm⁻¹ m; δ_{H} (CDCl₃) 8.38 (4H, s, 4 x CH=N), 7.52 (4H, d *J* 2.5 Hz, 4 x ArH), 7.04 (4H, d *J* 2.6 Hz, 4 x ArH), 4.2–4.1 (4H, br, (CH₂)₂), 3.8–3.7 (4H, br, (CH₂)₂), 1.30 (36H, s, 4 x (CH₃)₃), 1.55 (36H, s, 4 x (CH₃)₃); m/z (ESI) 1051.7 (MH⁺), 664.5, 638.5, 549.4, 517.3; Found (ESI) 1051.6721 C₆₄H₉₃N₄O₅Al₂ (MH⁺) requires 1051.6777.

Data for complex **1d**:^[S3] The reaction was heated at reflux overnight and gave an orange powder. Yield 60%; ν_{\max} (CH₂Cl₂) 2952 m, 2868 m, 1614 s, 1583 s, and 1531 cm⁻¹ s; δ_{H} (CDCl₃) 8.66 (4H, s, 4 x CH=N), 7.43 (4H, d *J* 2.3 Hz, 4 x ArH), 7.3–7.2 (4H, m, 4 x ArH), 7.2–7.0 (8H, m, 8 x ArH), 1.43 (36H, s, 4 x (CH₃)₃), 1.32 (36H, s, 4 x (CH₃)₃); m/z (Maldi) 1147.7 (MH⁺), 582.3, 540.4; Found (ESI) 1147.6801 C₇₂H₉₃N₄O₅Al₂ (MH⁺) requires 1147.6777.

Data for complex **1e**: The reaction was heated at reflux overnight and gave a yellow powder which was purified by washing with cold Et₂O. Yield 35%; $[\alpha]_{\text{D}}^{20}$ -753 (c= 0.1, CHCl₃); ν_{\max} (ATR) 2937 m, 2838 m, 1606 s, and 1537 cm⁻¹ s; δ_{H} (CDCl₃) 9.87 (4H, s, 4 x CH=N), 7.18 (4H, dd *J* 8.9, 3.0 Hz, 4 x ArH), 7.03 (4H, d *J* 3.1 Hz, 4 x ArH), 6.97 (4H, d *J* 9.0 Hz, 4 x ArH), 3.82 (12H, s, 4 x OCH₃), 3.8–3.5 (4H, m, 4 x CHN), 1.5–1.2 (16H, m 2 x (CH₂)₄); m/z (Maldi) 831.3 (MH⁺), 789.3, 662.4, 407.1; Found (ESI) 831.3139 C₄₄H₄₉N₄O₉Al₂ (MH⁺) requires 831.3130.

Data for complex **1f**: The reaction was heated at reflux overnight and gave a yellow powder which was purified by washing with cold Et₂O. Yield 33%; $[\alpha]_{\text{D}}^{20}$ -381 (c= 0.1, CHCl₃); ν_{\max} (ATR) 2863 w, 1628 s, 1601 m, and 1537 cm⁻¹ m; δ_{H} (CDCl₃) 8.27 (4H, s, CH=N), 7.5–7.4 (4H, m, ArH), 7.2–7.1 (4H, m, ArH), 7.0–6.9 (4H, m, ArH), 6.9–6.8 (4H, m, ArH), 3.4–3.3 (4H, m, CHN), 2.0–1.5 (16H, m, 2 x (CH₂)₄); m/z

(Maldi) 711.3 (MH⁺), 669.3, 364.1, 347.1; Found (ESI) 711.2708 C₄₀H₄₁N₄O₅Al₂ (MH⁺) requires 711.2708.

Data for complex **1g**: The reaction was heated at reflux overnight and gave a yellow powder which was purified by washing with cold Et₂O followed by chromatography on Sephadex LH50 using toluene / ethanol (1:1) as eluent. Yield 45%; [α]_D²⁰ -372 (c= 0.1, CHCl₃); ν_{\max} (ATR) 2951 m, 1633 s, and 1538 cm⁻¹ m; δ_{H} (CDCl₃) 8.28 (4H, s, 4 x CH=N), 7.29 (4H, dd *J* 8.1, 2.1 Hz, 4 x ArH), 7.14 (4H, d *J* 2.7 Hz, 4 x ArH), 6.84 (4H, d *J* 8.7 Hz, 4 x ArH), 3.4–3.2 (4H, m, 4 x CHN), 2.0–1.4 (16H, m 2 x (CH₂)₄), 1.45 (36H, s, 4 x C(CH₃)₃); m/z (Maldi) 935.5 (MH⁺), 893.6, 847.5, 775.4, 573.4, 459.3; Found (ESI) 935.5223 C₅₆H₇₃N₄O₅Al₂ (MH⁺) requires 935.5212.

Data for complex **1h**: The reaction was heated at reflux overnight and gave a yellow powder which was purified by washing with cold Et₂O followed by chromatography on Sephadex LH50 using toluene / ethanol (1:1) as eluent. Yield 30%; [α]_D²⁰ -612 (c= 0.1, CHCl₃); ν_{\max} (ATR) 2949 m, 1627 s, and 1552 cm⁻¹ m; δ_{H} (CDCl₃) 8.26 (4H, s, 4 x CH=N), 6.91 (4H, d *J* 3.0 Hz, 4 x ArH), 6.49 (4H, d *J* 3.0 Hz, 4 x ArH), 3.70 (12H, s, 4 x OCH₃), 3.4–3.2 (4H, m, 4 x CHN), 2.0–1.4 (16H, m 2 x (CH₂)₄), 1.41 (36H, s, 4 x C(CH₃)₃); m/z (Maldi) 1055.6 (MH⁺), 876.6, 848.5, 519.3, 494.3; Found (ESI) 1055.5641 C₆₀H₈₁N₄O₉Al₂ (MH⁺) requires 1055.5634.

General procedure for the synthesis of cyclic carbonates 3a–e

A mixture of an epoxide **2a–e** (2 mmol), tetrabutylammonium bromide (0–2.5 mol-%) and the appropriate catalyst **1a–h** (0–2.5 mol-%) was vigorously stirred until complete dissolution occurred, then CO₂ was passed through the flask at atmospheric pressure. After being stirred at 25 °C for the time specified in Table 1 or Table 2, a sample of the reaction was analysed by ¹H NMR spectroscopy to determine the conversion, and the reaction mixture was purified by flash chromatography to give cyclic carbonate **3a–e**.

Data for styrene carbonate **3a**:^[S4] Conversion 62%, isolated yield 57% (Table 1: entry 9) after purification by flash chromatography (hexane / EtOAc 2:3). Mp 49–52 °C; ν_{\max} (ATR) 3047 m, 3020 m, 2968 m, 2899 m, 1812 s, and 1592 cm^{-1} w; δ_{H} 7.5–7.2 (5H, m, ArH), 5.68 (1H, t J 8.0 Hz, PhCHO), 4.81 (1H, t J 8.5 Hz, OCH₂), 4.35 (1H, t J 8.4 Hz, OCH₂) δ_{C} 154.9, 135.9, 129.8, 129.3, 126.0, 78.1, 71.3; m/z (EI) 164 (M⁺, 100), 119 (10), 105 (10).

Data for propylene carbonate **3b**:^[S5] Reaction carried out at 0 °C, conversion 82%, isolated yield 77% (Table 2: entry 1) after purification by flash chromatography (hexane / EtOAc 4:1). ν_{\max} (neat) 2991 m, 2921 m, 1786 cm^{-1} s; δ_{H} 4.9–4.8 (1H, m, CHO), 4.55 (1H, t J 8.4 Hz OCH₂), 4.02 (1H, dd J 8.4, 7.3 Hz OCH₂), 1.49 (3H, d J 6.3 Hz, CH₃); δ_{C} 154.5, 73.7, 70.9, 19.7; m/z (EI) 102 (M⁺, 100), 100 (5).

Data for allylbenzene carbonate **3c**:^[S6] Conversion 50%, isolated yield 44% (Table 2: entry 4) after purification by flash chromatography (hexane / EtOAc 2:3). ν_{\max} (neat) 3064 w, 3031 w, 2980 w, 2920 w, 1800 cm^{-1} s; δ_{H} 7.2–7.0 (5H, m, ArH), 4.85 (1H, m, OCH), 4.35 (1H, t J 7.8 Hz, OCH₂), 4.08 (1H, dd J 8.4, 6.9 Hz, OCH₂), 3.06 (1H, dd J 14.1, 6.3 Hz, CH₂Ph), 2.90 (1H, dd J 14.1, 6.3 Hz, CH₂Ph); δ_{C} 154.5, 134.1, 129.3, 128.9, 127.5, 76.8, 68.5, 39.6; m/z (EI), 178 (M⁺, 20), 91 (100).

Data for hex-1-ene carbonate **3d**:^[S5] Conversion 90%, isolated yield 87% (Table 2: entry 6) after purification by flash chromatography (hexane / EtOAc 2:3). ν_{\max} (neat) 2960 s, 2934 s, 2874 m, 1797 cm^{-1} s; δ_{H} 4.64 (1H, qd J 7.5, 5.4 Hz, OCH), 4.46 (1H, t J 7.8 Hz, OCH₂), 4.09 (1H, dd J 8.4, 7.2 Hz, OCH₂), 2.0–1.6 (2H, m, CH₂), 1.6–1.2 (4H, m, 2 x CH₂), 0.95 (3H, t J 7.1 Hz, CH₃); δ_{C} 155.2, 77.2, 69.5, 33.7, 26.5, 22.4, 13.9; m/z (CI, NH₃), 162 (M+NH₄⁺, 100), 161 (40), 100 (10).

Data for dec-1-ene carbonate **3e**:^[S7] Conversion 70%, isolated yield 64% (Table 2: entry 7) after purification by flash chromatography (Et₂O). ν_{\max} (neat) 2928 s, 2857 s, 1805 cm^{-1} s; δ_{H} 4.72 (1H, qd J 7.5,

5.7 Hz, OCH), 4.54 (1H, t *J* 8.1 Hz, OCH₂), 4.09 (1H, t *J* 7.5 Hz, OCH₂), 1.9–1.6 (2H, m, CH₂), 1.6–1.2 (12H, m, 6 x CH₂), 0.90 (3H, t *J* 6.6 Hz, CH₃); δ_C 155.2, 77.1, 69.5, 34.0, 31.9, 29.4, 29.2, 29.1, 24.5, 22.7, 14.2; m/z (EI), 162 (M⁺, 8), 95 (38), 67 (100).

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