

Electronic Supplementary Information

Topologically diverse shape-persistent bis-(Zn-salphen) catalysts: efficient cyclic carbonate formation under mild conditions

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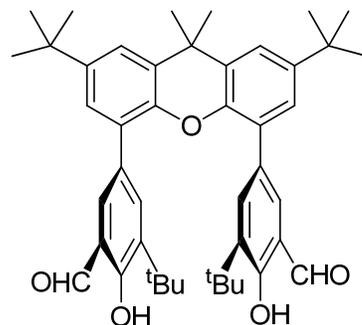
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Experimental Section

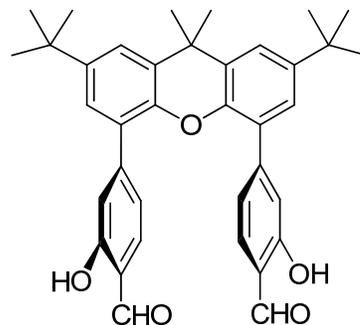
General Considerations and Instrumentation: Propylene oxide, epoxybutane and 1,2-epoxyhexane (Sigma-Aldrich) were distilled from CaH_2 , and 2-butanone (MEK, methyl ethyl ketone) was distilled from K_2CO_3 , and all were stored over 4 Å molecular sieves. Carbon dioxide (research grade, 99.999%) was purchased from HK Scientific Gas Engineering Co., Ltd. and used as received. Mesitylene was dried over 4 Å molecular sieves. Tetrabutylammonium iodide (Acros) was recrystallized using dry acetone and diethyl ether (1/10), and dried in a vacuum oven at 90 °C for 48 h. All reactions that describe the use of dry solvents were performed under a nitrogen atmosphere, and the solvents were appropriately dried and distilled prior to use; for the remaining reactions, solvents (analytical grade) were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 298 K on Bruker Avance III 300, 400 and 600 MHz NMR spectrometers (ppm; referenced to residual solvent peaks). ESI mass spectra were measured on a Perkin-Elmer SCIEX API 365 mass spectrometer. Elemental analyses were performed on a Vario EL elemental analyzer (Elementar Analysensysteme GmbH). The synthesis of **L1**,^{1,2} **L2**,^{2,3} **L5**,^{4,5} **L8**,² **L9**,² and complex **1**,² were described previously.

General Procedure for CO_2 Reactions: CO_2 reactions were performed using a Teflon liner in a 100-mL Parr stainless steel high-pressure reactor equipped with a paddle-like stirrer. The epoxide (in MEK [5 mL] or neat [epoxypropane and -hexane: 3 mL; epoxybutane: 5 mL]), catalyst, $n\text{Bu}_4\text{NI}$ cocatalyst and mesitylene (internal standard) were introduced into the reactor, which was then subjected to three cycles of pressurization and depressurization with CO_2 (at half of reacting pressure), before final stabilization at the chosen reacting pressure. The reactor was sealed, heated to the required temperature, and stirred at 500 rpm for the prescribed time. The reactor was then cooled to 10 °C using ice water, and the remaining pressure was slowly vented. An aliquot (60 μL) of the reaction mixture, combined with CDCl_3 (440 μL), was taken for ^1H NMR analysis (90° flip angle; 30 seconds relaxation delay). The % conversion, which was reproducible within $\pm 2\%$ in at least 3 independent runs for selected experiments, was calculated from the ^1H NMR integration of the cyclic carbonate product against the mesitylene internal standard.

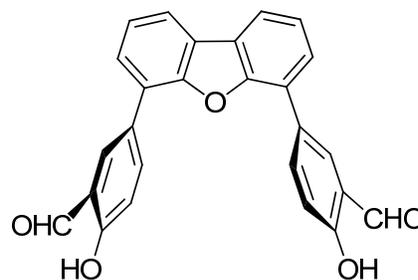
Compound L3: **L1** (0.82 g, 2.0 mmol), 2-hydroxy-3-*tert*-butyl-5-bromobenzaldehyde (1.22 g, 4.76 mmol) and Pd(PPh₃)₄ (0.05 g, 0.04 mmol) were suspended in a deoxygenated solution of K₂CO₃ (1.22 g, 8.80 mmol) in DME/DI water (3/1, 40 mL). The reaction mixture, which became a clear orange solution upon heating, was then stirred under reflux for 3 h, during which the color of the solution became dark brown. The mixture was cooled to 0 °C, after which 1 M aqueous HCl (20 mL) was added and the mixture was stirred at room temperature for 1 h. Water (100 mL) and chloroform (200 mL) were added to the resulting orange suspension. After stirring at room temperature for 1 h, the organic layer was separated and washed with water. The resultant orange solution was dried over MgSO₄, filtered and concentrated to dryness. The crude product was further purified by column chromatography (SiO₂, hexane/CH₂Cl₂, 1/1) to give the desired product as a yellow solid. Yield: 0.92 g, 68%. ¹H NMR (300 MHz, DMSO-d₆) δ 11.71 (s, 2H, OH), 9.47 (s, 2H, CHO), 7.60–7.43 (m, 6H), 7.19 (d, *J* = 2.2 Hz, 2H), 1.73 (s, 6H, CH₃), 1.34 (s, 18H, ^tBu), 1.20 (s, 18H, ^tBu).



Compound L4: The procedure for the synthesis of **L3** was adopted, using **L1** (0.70 g, 1.7 mmol) and 2-hydroxy-4-iodobenzaldehyde (1.0 g, 4.0 mmol). The crude product was purified by column chromatography (SiO₂, hexane/CH₂Cl₂, 1/2) to give the desired product as a pale yellow solid. Yield: 0.51 g, 53%. ¹H NMR (300 MHz, DMSO-d₆) δ 10.14 (s, 2H, CHO), 7.56 (d, *J* = 2.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 2.3 Hz, 2H), 6.84 (d, *J* = 1.2 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 1.70 (s, 6H, CH₃), 1.32 (s, 18H, ^tBu).

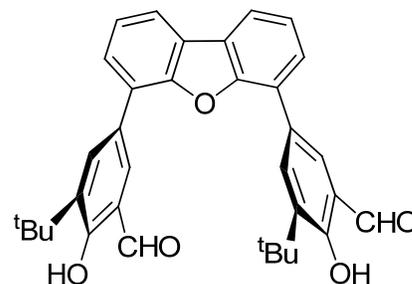


Compound L6: The procedure for the synthesis of **L3** was adopted, using **L5** (2.00 g, 7.82 mmol) and 2-hydroxy-5-bromobenzaldehyde (3.46 g, 17.2 mmol). The crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to give the desired product as a pale yellow solid. Yield: 2.4 g, 75%. ¹H NMR (300 MHz, DMSO-d₆) δ 11.02 (s, 2H, OH),

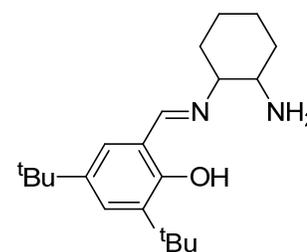


10.36 (s, 2H, CHO), 8.30 (s, 2H), 8.24–8.07 (m, 4H), 7.73 (d, $J = 7.6$ Hz, 2H), 7.49 (dd, $J = 7.8$ and 7.5 Hz, 2H), 7.20 (d, $J = 8.6$ Hz, 2H).

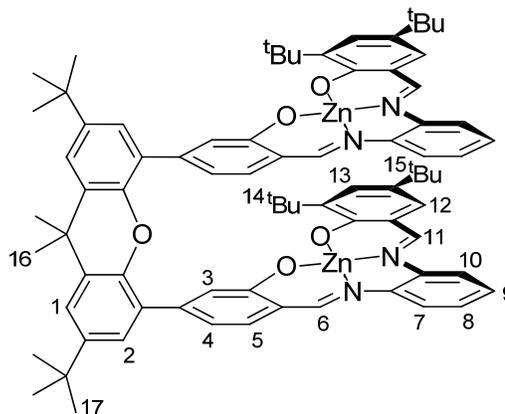
Compound L7: The procedure for the synthesis of **L3** was adopted, using **L5** (0.80 g, 3.1 mmol). The crude product was purified by flash chromatography (SiO₂, CH₂Cl₂/hexane, 1/1) to give the desired product as a yellow powder. Yield: 1.2 g, 74%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.89 (s, 2H, OH), 10.05 (s, 2H, CHO), 8.23–8.19 (m, 4H), 7.93 (d, $J = 2.2$ Hz, 2H), 7.73 (dd, $J = 7.6$ and 1.2 Hz, 2H), 7.55 (t, $J = 7.6$ Hz, 2H), 1.33 (s, 18H, ^tBu).



Compound L10: To a vigorously stirred solution of 1,2-cyclohexanediamine (0.80 g, 7.0 mmol) in dry CH₂Cl₂ (15 mL) at 0 °C, was added dropwise a solution of 3,5-di-*tert*-butylbenzaldehyde (1.09 g, 4.67 mmol) in dry CH₂Cl₂ (10 mL) at 0 °C over 30 min. The mixture was then stirred at 0 °C for 3 h. The resulting yellow solution was evaporated under reduced pressure at 5 °C to give a pale yellow oil, which was purified by column chromatography (SiO₂, ethyl acetate) to give the desired product as a pale yellow solid. Yield: 0.52 g, 34%. ¹H NMR (400 MHz, CDCl₃): δ 13.71 (s, 1H, OH), 8.43 (s, 1H), 7.39 (d, $J = 2.4$ Hz, 1H), 7.10 (d, $J = 2.4$ Hz, 1H), 4.12 (q, $J = 7.1$ Hz, 2H), 2.93–2.74 (m, 2H), 1.99–1.89 (m, 2H), 1.83–1.71 (m, 4H), 1.70–1.57 (m, 2H), 1.45 (s, 9H, ^tBu), 1.30 (s, 9H, ^tBu).

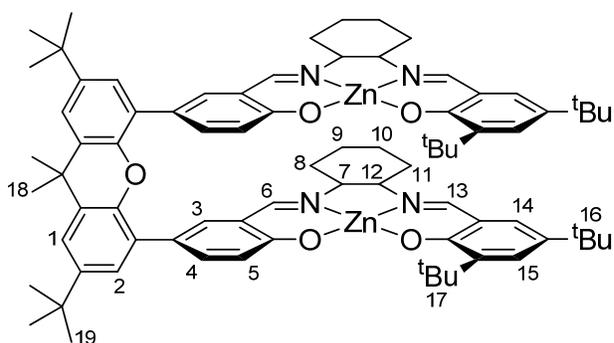


Complex 2: Compound **L4** (33 mg, 0.059 mmol in powder form) and triethylamine (1 mL) were added to a stirred solution of **L9** (42 mg, 0.13 mmol) and Zn(OAc)₂·2H₂O (28 mg, 0.13 mmol) in MeOH (20 mL) at room temperature. The reaction mixture was stirred at room temperature for 20 h to give a yellow precipitate, which was collected and washed copiously with MeOH to afford **2** as a bright yellow solid. Yield: 64 mg, 78%. Anal. Calcd for C₇₉H₈₆N₄O₅Zn₂·(H₂O)₅ (1392.45): C, 68.14; H, 6.95; N, 4.02. Found: C, 68.51; H, 6.70; N, 4.04.



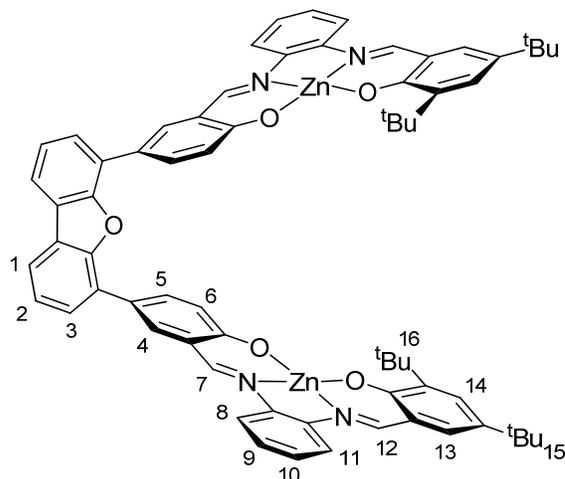
^1H NMR (300 MHz, DMSO- d_6): δ 8.97 (s, 2H, H¹¹), 8.73 (s, 2H, H⁶), 7.84 (d, J = 7.9 Hz, 2H, H¹⁰), 7.53 (d, J = 2.2 Hz, 2H, H¹), 7.36 (d, J = 8.5 Hz, 2H, H⁷), 7.32–7.19 (m, 8H, H⁵, H⁹, H¹², H¹³), 7.18 (d, J = 2.2 Hz, 2H, H²), 6.91 (dd, J = 7.8 and 7.5 Hz, 2H, H⁸), 6.60 (d, J = 1.3 Hz, 2H, H³), 6.47 (dd, J = 12.4 and 2.2 Hz, 2H, H⁴), 1.71 (s, 6H, H¹⁶), 1.45 (s, 18H, H¹⁴), 1.34 (s, 18H, H¹⁷), 1.27 (s, 18H, H¹⁵). ^{13}C NMR (101 MHz, DMSO- d_6): δ 171.7, 170.3, 163.3, 161.5, 145.6, 145.1, 143.9, 140.7, 139.8, 139.2, 135.5, 133.4, 130.4, 129.6, 128.9, 128.4, 126.9, 126.5, 124.8, 123.2, 122.0, 118.3, 118.2, 116.3, 115.8, 115.5, 35.2, 34.8, 34.3, 33.6, 31.5, 31.4, 29.7. ESI-MS (+ve mode): m/z 1304 [M + H]⁺.

Complex 3: Compound **L2** (0.25 g, 0.45 mmol in powder form) was added to a stirred solution of sodium methoxide (0.15 g, 2.7 mmol) and zinc chloride (0.13 g, 0.98 mmol) in degassed EtOH/CH₂Cl₂ (1/2, 20 mL) at 0 °C. The mixture was stirred for 5 min, after which **L10** (0.29 g, 0.89 mmol) in EtOH/CH₂Cl₂ (1/2,

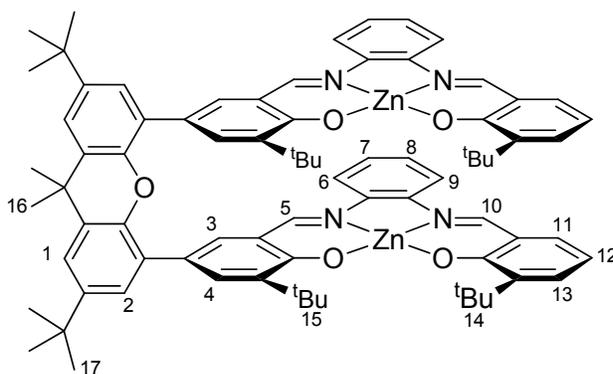


10 mL) was added. The reaction mixture was stirred at room temperature for 12 h to give a pale yellow suspension. The filtrate was collected, and all volatiles were removed under reduced pressure to give a yellow solid, which was purified by column chromatography (Et₃N-saturated SiO₂, hexane/CH₂Cl₂, 1/1) to afford **3** as a pale yellow solid. Yield: 0.13 g, 21%. Anal. Calcd for C₇₉H₉₈N₄O₅Zn₂·C₆H₁₄ (1400.64): C, 72.89; H, 8.06; N, 4.00. Found: C, 72.69; H, 7.82; N, 3.77. ^1H NMR (300 MHz, CD₂Cl₂) δ 7.65 (s, 2H, H¹³), 7.50 (d, J = 2.2 Hz, 2H, H¹⁵), 7.49 (s, 2H, H⁶), 7.45 (dd, J = 8.7 and 2.3 Hz, 2H, H⁴), 7.42 (d, J = 2.3 Hz, 2H, H¹), 7.31 (d, J = 2.3 Hz, 2H, H³), 7.20 (d, J = 2.3 Hz, 2H, H²), 6.94 (d, J = 8.8 Hz, 2H, H⁵), 6.53 (d, J = 2.3 Hz, 2H, H¹⁴), 3.79–3.59 (m, 4H, H⁷, H¹²), 1.87–1.63 (m, 8H, H⁸, H¹¹), 1.73 (s, 6H, H¹⁸), 1.50–1.28 (m, 8H, H¹⁰, H⁹), 1.47 (s, 18H, H¹⁷), 1.37 (s, 18H, H¹⁹), 1.32 (s, 18H, H¹⁶), 1.28–1.24 (m, C₆H₁₄), 0.88 (t, C₆H₁₄). ^{13}C NMR (101 MHz, CD₂Cl₂) δ 173.7, 172.8, 170.2, 168.7, 145.9, 145.5, 141.7, 138.5, 138.2, 135.9, 131.4, 130.0, 129.8, 128.3, 126.7, 124.9, 123.7, 121.9, 117.8, 117.4, 69.8, 68.6, 38.3, 38.3, 35.8, 35.1, 34.8, 34.3, 33.3, 31.7, 31.6, 30.1, 25.6, 25.3. ESI-MS (+ve mode): m/z 1316 [M + H]⁺.

Complex 4: The procedure for the synthesis of **2** was adopted, using **L6** (50 mg, 0.12 mmol). A yellow precipitate was formed, which was collected and washed copiously with MeOH and pentane to afford **4** as a yellow solid. Yield: 0.11 g, 78%. Anal. Calcd for $C_{68}H_{64}N_4O_5Zn_2 \cdot (H_2O)_3$ (1202.13): C, 67.94; H, 5.87; N, 4.66. Found: C, 67.87; H, 5.96; N, 4.45. 1H NMR (400 MHz, DMSO- d_6) δ 9.11 (s, 2H, H⁷), 8.93 (s, 2H, H¹²), 8.18 (d, $J = 2.2$ Hz, 2H, H⁴), 8.09 (dd, $J = 2.4$ and 2.6 Hz, 2H, H⁵), 8.05 (d, $J = 6.8$ Hz, 2H, H¹), 7.87 (d, $J = 8.6$ Hz, 2H, H⁸), 7.84 (d, $J = 8.4$ Hz, 2H, H¹¹), 7.75 (d, $J = 7.5$ Hz, 2H, H³), 7.50 (t, $J = 7.6$ Hz, 2H, H²), 7.37 (t, $J = 7.6$ Hz, 2H, H⁹), 7.34 (d, $J = 2.5$ Hz, 2H, H¹⁴), 7.30–7.22 (m, 4H, H¹⁰, H¹³), 6.86 (d, $J = 8.9$ Hz, 2H, H⁶), 1.49 (s, 18H, H¹⁶), 1.28 (s, 18H, H¹⁵). ^{13}C NMR (101 MHz, DMSO- d_6): δ 172.2, 170.7, 163.8, 162.3, 152.4, 141.0, 140.3, 139.1, 136.3, 134.5, 133.7, 129.9, 128.8, 127.8, 127.2, 125.4, 125.2, 124.6, 124.1, 124.0, 120.4, 119.9, 118.9, 118.4, 116.7, 116.3, 35.4, 33.8, 31.6, 29.9. ESI-MS (+ve mode): m/z 1150 [M + H]⁺.



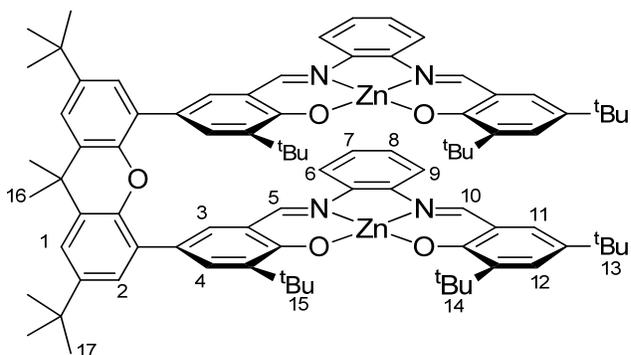
Complex 5: Compound **L3** (88 mg, 0.13 mmol in powder form) and trimethylamine (1 mL) were added to a stirred solution of **L8** (70 mg, 0.26 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (63 mg, 0.29 mmol) in MeOH (20 mL) at room temperature. The reaction mixture was stirred at 75 °C for 20 h to give a yellow precipitate,



which was collected and washed copiously with cold MeOH to afford **5** as a bright yellow solid. Yield: 80 mg, 64%. Anal. Calcd for $C_{79}H_{86}N_4O_5Zn_2 \cdot (CH_3OH)_2$ (1366.46): C, 71.20; H, 6.93; N, 4.10. Found: C, 71.30; H, 6.74; N, 4.13. 1H NMR (400 MHz, DMSO- d_6) δ 8.38 (s, 2H, H¹⁰), 8.18 (s, 2H, H⁵), 7.52–7.35 (m, 8H, H⁴, H³, H⁶, H⁹), 7.39 (s, 2H, H¹), 7.21 (s, 2H, H²), 7.07 (d, $J = 6.7$ Hz, 2H, H¹³), 6.97 (dd, $J = 7.6$ and 7.2 Hz, 2H, H⁷), 6.84 (d, $J = 7.2$ Hz, 2H, H¹¹), 6.76 (dd, $J = 8.0$ and 7.2 Hz, 2H, H⁸), 6.38 (t, $J = 7.6$ Hz, 2H, H¹²), 4.07 (br q, $J = 5.2$ Hz, CH_3OH), 3.18 (d, $J = 5.2$ Hz, CH_3OH), 1.72 (s, 6H, H¹⁶), 1.37 (s, 18H, H¹⁷), 1.25 (s, 18H, H¹⁴), 1.23 (s, 18H, H¹⁵).

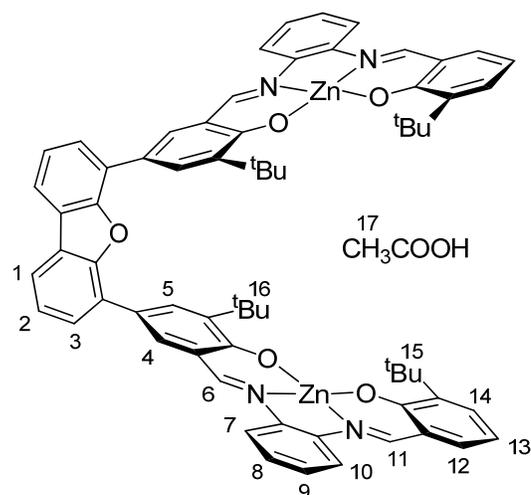
^{13}C NMR (101 MHz, $\text{C}_6\text{D}_6/\text{DMSO-d}_6$, 9/1) δ 172.9, 172.2, 161.4, 161.2, 145.8, 144.8, 142.3, 142.0, 139.8, 139.6, 134.6, 132.9, 130.9, 130.0, 129.9, 126.1, 125.8, 125.7, 122.1, 119.9, 119.4, 119.2, 115.4, 115.1, 112.0, 35.4, 35.3, 34.8, 34.2, 31.4, 29.7, 29.6. ESI-MS (+ve mode): m/z 1304 $[\text{M} + \text{H}]^+$.

Complex 6: The procedure for the synthesis of **5** was adopted, using **L3** (50 mg, 0.074 mmol) and **L9** (48 mg, 0.15 mmol). A orange precipitate was formed, which was collected, washed copiously with cold MeOH, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1/9)



to afford **6** as a bright yellow solid. Yield: 46 mg, 41%. Anal. Calcd for $\text{C}_{87}\text{H}_{102}\text{N}_4\text{O}_5\text{Zn}_2 \cdot (\text{H}_2\text{O})_5$ (1504.66): C, 69.45; H, 7.50; N, 3.72. Found: C, 69.77; H, 7.36; N, 3.89. ^1H NMR (400 MHz, DMSO-d_6) δ 8.80 (s, 2H, H^{10}), 8.52 (s, 2H, H^5), 7.68 (d, $J = 8.0$ Hz, 2H, H^9), 7.63 (d, $J = 8.3$ Hz, 2H, H^6), 7.50 (d, $J = 2.3$ Hz, 2H, H^3), 7.45–7.39 (m, 4H, H^1 , H^4), 7.20 (d, $J = 2.5$ Hz, 2H, H^{12}), 7.17 (d, $J = 2.3$ Hz, 2H, H^2), 7.19–7.12 (m, 2H, H^7), 7.05 (d, $J = 2.6$ Hz, 2H, H^{11}), 7.07–6.99 (m, 2H, H^8), 1.73 (s, 6H, H^{16}), 1.36 (s, 18H, H^{17}), 1.31 (s, 18H, H^{14}), 1.24 (s, 18H, H^{13}), 1.21 (s, 18H, H^{15}). ^{13}C NMR (101 MHz, DMSO-d_6): δ 172.1, 170.8, 162.6, 162.5, 145.2, 144.8, 141.2, 141.1, 139.9, 134.6, 133.2, 132.3, 129.8, 129.2, 128.5, 126.8, 126.7, 126.0, 126.0, 125.0, 121.8, 121.3, 119.6, 118.6, 116.5, 115.9, 35.6, 35.3, 34.8, 34.6, 33.9, 33.6, 31.9, 31.9, 30.0, 29.8. ESI-MS (+ve mode): m/z 1416 $[\text{M} + \text{H}]^+$.

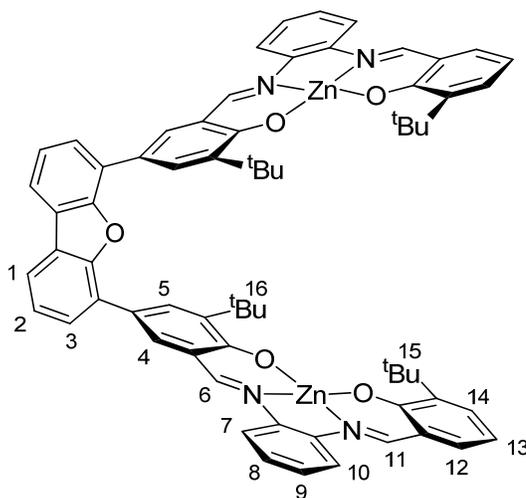
Complex 7 and 7·AcOH: Compound **L7** (60 mg, 0.12 mmol in powder form) and Et_3N (3 mL) were added to a stirred solution of **L8** (62 mg, 0.23 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (56 mg, 0.25 mmol) in MeOH (20 mL) at room temperature. The reaction mixture was stirred at room temperature for 20 h to give a grey solution. All volatiles were removed under reduced pressure, and recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$



(1/9) afforded a yellow crystalline solid, which was characterized as **7·AcOH**. Yield: 98 mg, 68%. Anal. Calcd for $\text{C}_{68}\text{H}_{64}\text{N}_4\text{O}_5\text{Zn}_2 \cdot \text{CH}_3\text{CO}_2\text{H}$, (1208.13): C, 69.59; H, 4.64; N, 5.67. Found:

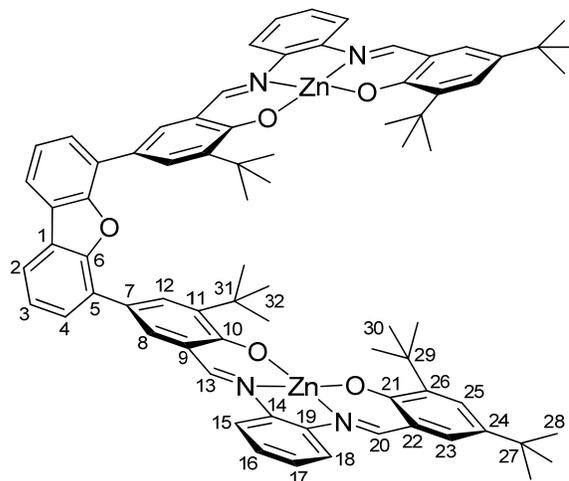
C, 69.99; H, 4.64 ; N, 5.99. ^1H NMR (400 MHz, DMSO- d_6) δ 8.71 (s, 2H, H¹¹), 8.70 (s, 2H, H⁶), 8.32 (d, J = 2.2 Hz, 2H, H⁴), 8.04 (dd, J = 7.6 and 1.1 Hz, 2H, H¹), 7.81–7.72 (m, 4H, H³, H⁵), 7.50 (t, J = 7.6 Hz, 2H, H²), 7.43 (d, J = 7.6 Hz, 2H, H¹⁰), 7.37 (d, J = 8.1 Hz, 2H, H¹²), 7.32 (d, J = 7.9 Hz, 2H, H⁷), 7.27 (d, J = 7.5 Hz, 2H, H¹⁴), 7.01 (t, J = 7.7 Hz, 2H, H⁸), 6.62 (dd, J = 7.9 and 7.5 Hz, 2H, H⁹), 6.50 (t, J = 7.5 Hz, 2H, H¹³), 1.85 (s, 3H, H¹⁷), 1.61 (s, 18H, H¹⁶), 1.56 (s, 18H, H¹⁵). ^{13}C NMR (151 MHz, DMSO- d_6) δ 172.0, 171.9, 171.7, 161.6, 160.5, 152.2, 142.4, 141.4, 139.0, 137.7, 135.0, 134.5, 130.0, 129.9, 126.7, 126.4, 125.6, 124.4, 124.3, 123.6, 119.4, 118.8, 118.4, 118.1, 114.9, 114.6, 111.9, 35.3, 35.0, 29.5, 29.4, 21.0.

The yellow crystalline solid (**7**·AcOH) was dissolved in CH_2Cl_2 (15 mL) and washed with DI water (20 mL \times 3). The organic layer was collected, all volatiles were removed under reduced pressure, and recrystallization from acetone/pentane (1/5) afforded **7** as an orange solid. Yield: 62 mg, 47% (based on **L7**). Anal. Calcd for $\text{C}_{68}\text{H}_{64}\text{N}_4\text{O}_5\text{Zn}_2$ (1148.08): C, 71.14; H, 5.62; N, 4.88. Found: C, 71.16;



H, 5.79; N, 4.73. ^1H NMR (400 MHz, DMSO- d_6) δ 8.70 (s, 2H, H¹¹), 8.69 (s, 2H, H⁶), 8.32 (s, 2H, H⁴), 8.04 (dd, J = 7.7 and 1.0 Hz, 2H, H¹), 7.81–7.72 (m, 4H, H³, H⁵), 7.50 (t, J = 7.6 Hz, 2H, H²), 7.43 (d, J = 8.1 Hz, 2H, H¹⁰), 7.37 (d, J = 6.8 Hz, 2H, H¹²), 7.32 (d, J = 8.0 Hz, 2H, H⁷), 7.27 (d, J = 7.3 Hz, 2H, H¹⁴), 7.01 (dd, J = 7.7 and 7.4 Hz, 2H, H⁸), 6.62 (t, J = 7.5 Hz, 2H, H⁹), 6.50 (t, J = 7.5 Hz, 2H, H¹³), 1.61 (s, 18H, H¹⁶), 1.55 (s, 18H, H¹⁵). ^{13}C NMR (101 MHz, DMSO- d_6) δ 172.0, 171.7, 161.8, 160.6, 152.2, 142.5, 141.4, 139.0, 137.6, 135.2, 134.7, 130.1, 130.0, 126.8, 126.5, 125.6, 124.5, 124.3, 123.8, 119.5, 118.8, 118.5, 118.3, 115.0, 114.6, 112.0, 35.4, 35.2, 29.6, 29.5. ESI-MS (+ve mode): m/z 1150 [M + H]⁺.

Complex 8: The procedure for the synthesis of **4** was adopted, using **L7** (78 mg, 0.15 mmol). A brown precipitate was formed, which was collected and washed copiously with MeOH and pentane to afford **8** as a brownish yellow solid. Yield: 85 mg, 43%. Anal. Calcd for $C_{76}H_{80}N_4O_5Zn_2 \cdot (H_2O)_4$ (1332.35): C, 68.51; H, 6.66; N, 4.21. Found: C, 68.40; H, 6.88; N, 4.29. 1H NMR (400 MHz, DMSO- d_6) δ 8.83 (s, 2H, H¹³), 8.82 (s, 2H, H²⁰), 8.13 (d, $J = 2.2$ Hz, 2H, H⁸), 8.05 (d, $J = 7.6$ Hz, 2H, H²), 7.76 (d, $J = 2.3$ Hz, 2H, H¹²), 7.71 (d, $J = 7.0$ Hz, 2H, H⁴), 7.63 (d, $J = 7.8$ Hz, 2H, H¹⁸), 7.54–7.45 (m, 4H, H^{3,15}), 7.34 (d, $J = 2.5$ Hz, 2H, H²⁵), 7.24 (d, $J = 2.6$ Hz, 2H, H²³), 7.11 (dd, $J = 7.6$ and 7.8 Hz, 2H, H¹⁶), 6.89 (dd, $J = 7.8$ and 8.0 Hz, 2H, H¹⁷), 1.52 (s, 18H, H³²), 1.51 (s, 18H, H³⁰), 1.32 (s, 18H, H²⁸). ^{13}C NMR (151 MHz, DMSO- d_6 ; peak assignments based on combination of DEPT-135, and 2-D 1H - ^{13}C (HSQC and HMBC) and NOE correlation NMR experiments): δ 171.9 (C¹⁰), 170.2 (C²¹), 162.1 (C²⁰), 161.2 (C¹³), 152.3 (C⁶), 142.2 (C¹¹), 140.7 (C²⁶), 139.2 (C¹⁹), 138.2 (C¹⁴), 134.6 (C⁸), 133.1 (C²⁴), 130.1 (C¹²), 129.4 (C²³), 128.1 (C²⁵), 126.6 (C¹⁷), 126.5 (C¹⁶), 125.8 (C⁵), 125.0 (C⁴), 124.3 (C¹), 123.6 (C³), 119.0 (C⁹), 118.8 (C⁷), 118.1 (C²), 118.0 (C²²), 115.2 (C¹⁸), 115.1 (C¹⁵), 35.2 (C^{29,31}), 33.5 (C²⁷), 31.3 (C²⁸), 29.6 (C³⁰), 29.4 (C³²). ESI-MS (+ve mode): m/z 1264 [M + H]⁺.



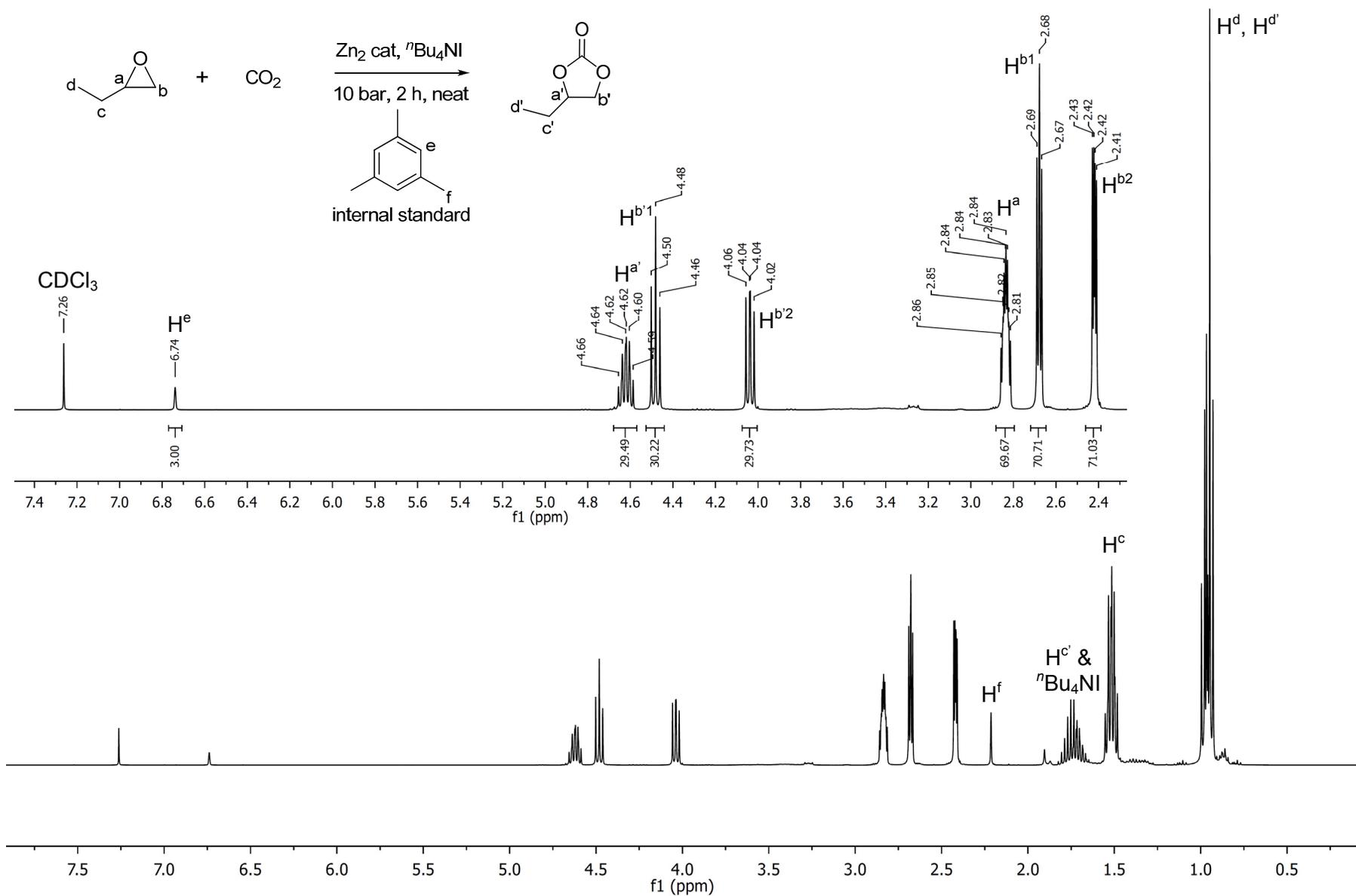


Figure S1. ¹H NMR (400 MHz, CDCl₃, 298 K; inset: expanded) spectrum of reaction mixture corresponding to Run 10 in Table 3 [reaction conditions: 1,2-epoxybutane (57.5 mmol, 5 mL), catalyst **8** (0.0025 mol%), ⁿBu₄NI co-cat. (0.125 mol%), mesitylene (internal standard, 1 mol%), 10 bar CO₂ initial pressure, 95 °C, 2 h].

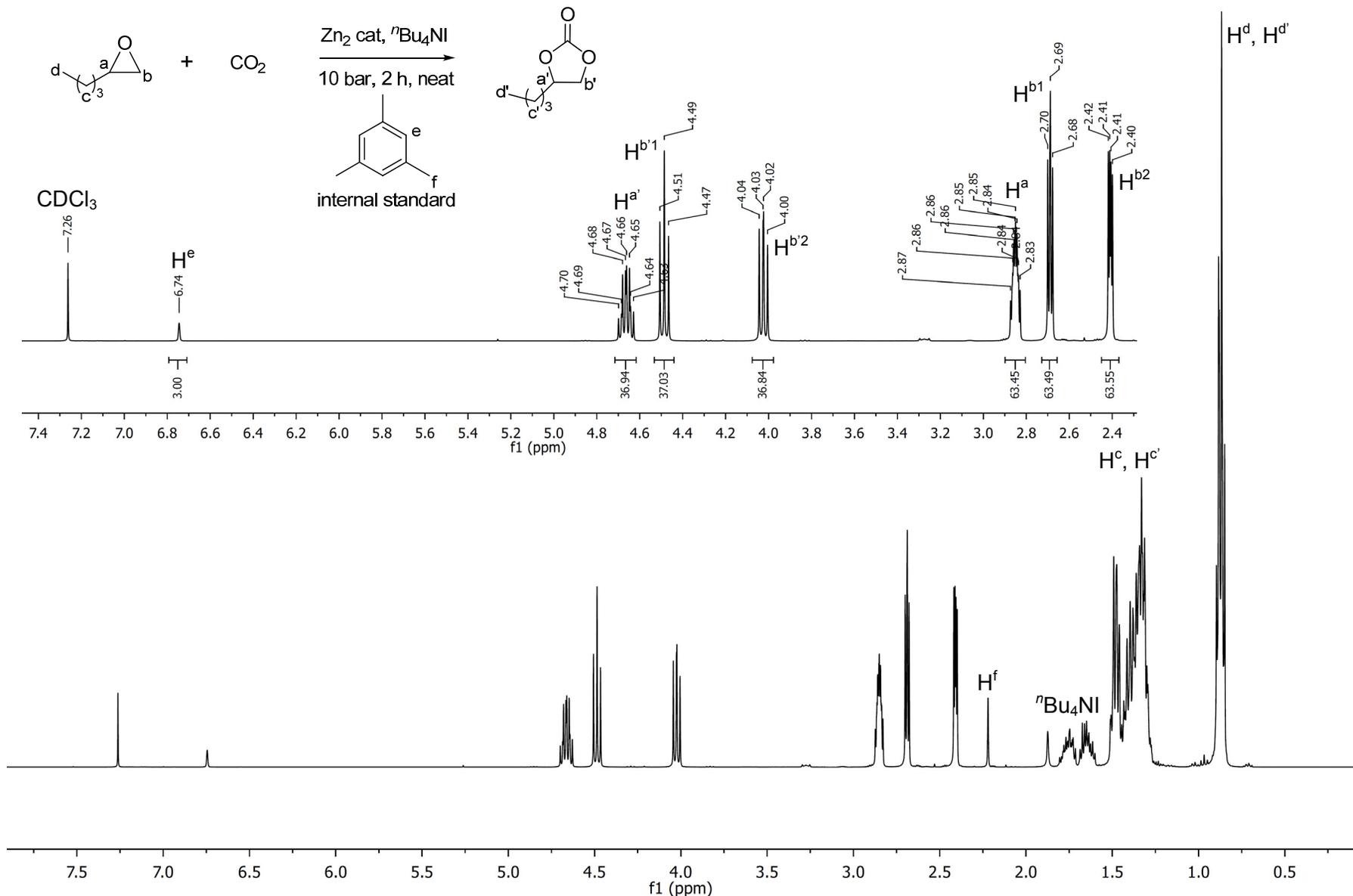


Figure S2. ¹H NMR (400 MHz, CDCl₃, 298 K; inset: expanded) spectrum of reaction mixture corresponding to Run 12 in Table 3 [reaction conditions: 1,2-epoxyhexane (24.9 mmol, 3 mL), catalyst **8** (0.0025 mol%), ⁿBu₄NI co-cat. (0.125 mol%), mesitylene (internal standard, 1 mol%), 10 bar CO₂ initial pressure, 95 °C, 2 h].

ESI References

- 1 R. Okamura, T. Wada, K. Aikawa, T. Nagata and K. Tanaka, *Inorg. Chem.*, 2004, **43**, 7210.
- 2 W.-L. Tong, S.-M. Yiu and M. C. W. Chan, *Inorg. Chem.*, 2013, **52**, 7114.
- 3 M. Hirotsu, N. Ohno, T. Nakajima, C. Kushibe, K. Ueno and I. Kinoshita, *Dalton Trans.*, 2010, **39**, 139.
- 4 E. B. Schwartz, C. B. Knobler and D. J. Cram, *J. Am. Chem. Soc.*, 1992, **114**, 10775.
- 5 Z. Guo, S.-M. Yiu and M. C. W. Chan, *Chem. Eur. J.*, 2013, **19**, 8937.