Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Entry to new *N,O*-ligands from oxygen-depleted calixarenes

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General Information

All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled Innovative Technology glovebox. All solvents were degassed and stored under high-purity nitrogen over activated 4Å molecular sieves. All deuterated solvents were stored under high-purity nitrogen over 3Å molecular sieves. Commercially available reagents were purchased from Aldrich and used as received. The NMR spectra were recorded on Bruker AC 200MHz and Bruker AMX 400MHz spectrometers. ^{1}H and ^{13}C NMR signals are reported in ppm downfield from TMS. ^{1}H signals are referenced to the residual proton of a deuterated solvent (7.26 ppm for $CDCl_3$, 7.15 ppm for C_6D_6). For ^{13}C NMR spectra, the following signals were used as a reference: 77.36 ppm for $CDCl_3$, 128.62 ppm for C_6D_6. t-Butylcalix[4]arene 1,3-di-*O*-triflate was prepared according to ref. 1. Abbreviations: DBU= 1,8-Diazabicyclo[5.4.0]undec-7-ene, dba= Dibenzylideneacetone, DMF= *N*,*N*-Dimethylformamide.

Synthesis of **1**.

The reaction was carried out under an inert atmosphere of pure nitrogen. To a solution of $P(t\text{-}Bu)_3H^+$ BF_4^- (16mg, 0.055mmol) and Pd_2dba_3 (12.5 mg, 0.014 mmol) in 10 ml of dry DMF, CuI (250 mg, 1.31 mmol), DBU (334 mg, 2.20 mmol), trimethylsilylacetylene (540 mg, 5.5 mmol) and t-butylcalix[4]arene 1,3-di-*O*-triflate (500 mg, 0.55 mmol) were added and the mixture was heated at 100°C for 4 hours. The solvent was evaporated and the resulting crude product was dissolved in CH_2Cl_2 (40ml), washed with saturated aqueous NH_4Cl (20ml) and H_2O (20ml). Drying the CH_2Cl_2 extract over $MgSO_4$ followed by solvent removal under vacuum gave the crude product. The product was dissolved in 3ml of CH_2Cl_2 and precipitated with 15ml of MeOH giving 350 mg of **1** (79% yield). ^{1}H NMR ($CDCl_3$): 0.32 (18H, s, TMS), 0.82 (18H, s, t-Bu), 1.35 (18H, s, t-Bu), 3.57 (4H, d, $^{2}J_{HH}$= 13.6 Hz, CH_2), 4.60 (4H, d, $^{2}J_{HH}$= 13.6 Hz, CH_2), 5.25 (2H, s, OH), 6.59 (4H, s, Ar-H), 7.12 (4H, s, Ar-H). ^{13}C NMR: 0.66 (TMS), 30.95, 32.09 (CMe_3), 34.26, 34.44 (CMe_3), 36.74 (CH_2), 103.03, 103.28 (C≡C), all aromatic (s): 119.41, 124.08, 125.69, 129.00, 141.78, 142.31, 150.97, 151.48. IR (film) 2144 cm^{-1} (C≡C). M. p. 263.2-265.7 ºC.

Synthesis of **2**.

To a solution of **1** (70mg, 0.087mmol) in 2ml THF and 10ml methanol, K_2CO_3 (94mg, 0.68mmol) was added. The whole mixture was stirred under nitrogen for 4 hours and quenched with water. The product was extracted with CH_2Cl_2 and the organic layer dried over $MgSO_4$. Solvent evaporation afforded pure **2** (60mg, 86% yield).

^{1}H NMR: 0.92 (18H, s, tBu), 1.35 (18H, S, tBu), 3.59 (6H, d, $^{2}J_{HH}$= 13.7 Hz, CH_2, overlapped with 2H of HC≡C), 4.49 (4H, d, $^{2}J_{HH}$= 13.7 Hz, CH_2), 5.00 (2H, s, OH), 6.77 (4H, s, Ar-H), 7.15 (4H, s, Ar-H). ^{13}C NMR: 31.11, 32.15 (CMe_3), 34.33, 34.62 (CMe_3), 37.32 (*C*H_2), 81.87, 85.91 (C≡C), all aromatic (s):118.20, 124.69, 126.41, 128.63, 142.49, 142.63, 151.29, 151.48. MS-ESI: Measured (Calc.) 664.4270 (664.4280), $C_{48}H_{56}O_2$. IR (film) 2097 cm^{-1} (C≡C).

Synthesis of **3**.

To a solution of **2** (50mg, 0.075mmol) and benzyl azide (30mg, 0.165mmol) in 5ml of dry DMF, $CuSO_4{\cdot}5H_2O$ (19mg, 0.075mmol) and sodium ascorbate (15mg, 0.075mmol) were added. The mixture was stirred under nitrogen for 18 hours, the solution was filtered through celite. CH_2Cl_2 and brine were added and the organic product was extracted and dried over $MgSO_4$. CH_2Cl_2 was evaporated and the product was re-dissolved in 1ml of DCM. Precipitation with 10ml of MeOH gave a white powder of **3** (50mg, 72% yield).

^{1}H NMR: 0.95 (18H, s, tBu), 1.31 (18H, S, tBu), 3.37 (4H, d, $^{2}J_{HH}$= 13.7 Hz, CH_2), 3.96 (4H, d, $^{2}J_{HH}$= 13.7 Hz, CH_2), 5.66 (4H, s, CH_2-Ph), 6.82 (4H, s, Ar-H), 6.95 (4H, s, Ar-H), 7.36 (m, 10H, Ar-H) 7.66 (2H, s, HC═C), 8.69 (2H, s-broad, OH). ^{13}C NMR: 31.01, 31.96 (CMe_3), 33.93, 34.15 (CMe_3), 36.35 (*C*H_2), 54.47 (CH_2-Ph), 124.66, 124.96 (C═C), all aromatic (s): 125.42, 125.52, 128.18, 128.73, 129.03, 129.27, 135.08, 139.13, 140.86, 145.68, 150.11, 151.90. MS-ESI: Measured (Calc.) 930.5556 (930.5560), $C_{62}H_{70}N_6O_2$.

Synthesis of **4**.

Ligand **3** (10mg, 0.011mmol) was dissolved in about 3ml of dry toluene and 12µL of a $TiCl_4$ solution in toluene (1.0M, 0.012mmol,) was added. The resulting red mixture was heated at 100 °C for 18 hrs and the solvent was evaporated giving the crude product. After precipitation from toluene/pentane (0.5ml of toluene – 3ml of pentane), 8mg of pure red product was obtained (71% yield).

^{1}H NMR: 0.93 (18H, s, t-Bu), 1.28 (18H, s, t-Bu), 3.21 (4H, d, $^{2}J_{HH}$= 13.8 Hz, CH_2), 3.63 (4H, d, $^{2}J_{HH}$= 13.8 Hz, CH_2), 5.77 (4H, s, CH_2-Ph), 6.57 (4H, s, Ar-H), 6.90 (4H, s, Ar-H), 7.24 (2H, s, HC═C), 7.36-7.46 (m, 10H, Ar-H). ^{13}C NMR: 31.09, 31.64 (CMe_3), 34.03, 34.38 (CMe_3), 37.96 (*C*H_2), 56.08 (CH_2-Ph), 122.97, 123.23 (C═C), all aromatic (s):125.26, 126.59, 128.38, 129.10, 129.42, 129.60, 132.97, 133.11, 140.81, 143.08, 146.11, 152.29. FAB-MS: Measured (Calc.) 976(976); $C_{62}H_{68}Cl_2N_6O_2Ti$.

Synthesis of **5**.

To a solution of **4** (5mg, 0.005mmol) in 3 ml of dry CH_2Cl_2 catechol (0.5 mg, 0.005 mmol) or (S)-BINOL (1.4mg, 0.005mmol) was added and the mixture stirred at room temperature overnight. The solvent was evaporated to give the crude product. After precipitation from CH_2Cl_2/pentane (0.5ml of CH_2Cl_2 – 5ml of pentane), pure **5** (**a** or **b)** was obtained as red solid in 70-75% yield.

5a: ^{1}H NMR ($CDCl_3$): 0.99 (18H, s, t-Bu), 1.26 (18H, S, t-Bu), 3.37 (4H, d, $^2J_{HH}$= 15.0 Hz, CH_2), 3.69 (4H, d, $^2J_{HH}$= 15.0 Hz, CH_2), 5.67 (4H, s, CH_2-Ph), 6.15 (4H, s, Ar-H), 6.58-6.86 (8H, m, Ar-H), 7.40 (m, 10H, Ar-H), 7.78 (2H, s). ^{13}C NMR δ, 31.70, 32.25 (CMe_3), 34.18, 35.32 (CMe_3), 39.94 (*C*H_2), 57.06 (CH_2-Ph), 124.45, 125.43 (C═C), all aromatic (s):116.26 121.91, 126.61, 127.38, 128.28, 128.87, 129.55, 130.29, 130.39, 133.25, 136.08, 143.5, 144.31, 152.04, 154.55.

5b: ^{1}H NMR ($CDCl_3$): 0.93 (18H, s, t-Bu), 1.28 (18H, S, t-Bu), 3.21 (4H, d, $^2J_{HH}$= 13.8 Hz, CH_2), 3.62 (4H, d, $^2J_{HH}$= 13.8 Hz, CH_2), 5.22 (2H, s, Ar-BINOL), 5.69 (4H, s, CH_2-Ph), 6.56 (4H, s, Ar-H), 6.89 (4H, s, Ar-H), 7.12-7.44 (m, 16H, Ar-H), 7.87-7.98 (6H, m, Ar-H, overlapped with 2H of the triazole ring). ^{13}C NMR δ, 31.62, 32.17 (CMe_3), 34.57, 34.91 (CMe_3), 38.47 (*C*H_2), 56.53 (CH_2-Ph), 123.50, 123.79 (C═C), all aromatic (s):118.55, 123.61, 124.63, 124.97, 125.76, 127.13, 128.07, 129.07, 129.60, 129.72, 129.93, 130.10, 131.97, 133.51, 133.60, 134.00, 134.13, 141.32, 143.65, 146.61, 152.83, 153.48; FAB-MS: Measured (Calc.) 1262 (1262); $C_{82}H_{80}N_6O_4Ti$.

Trimethylsilyl addition of benzaldehyde.[2]

General procedure: In a vial, catalyst **4** (12.2mg, 0.0125mmol, 1 mol%) dissolved in 2 ml of dry CH_2Cl_2 under nitrogen and benzaldehyde (133 mg, 1.25 mmol) and trimethylsylilcyanide (137mg, 1.38 mmol) were added with syringe via rubber septum. The solution was stirred for 8 hours and the solvent evaporated. To the crude product, about 2ml of methanol were added to remove the catalyst. The combined solvent was evaporated giving 240mg (92% yield) of the product.

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