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SUPPORTING INFORMATION

Title: A Simple and Efficient Synthetic Route to Enantiopure Scorpionate Ligands
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*Experimental procedures and characterization data for compounds **1-6**.*

The compounds *tert*-butyl isocyanate, (*S*)-(–)-α-methyl isocyanate, *tert*-butyl isothiocyanate and (*S*)-(–)-1-phenylpropyl isothiocyanate were purchased from Aldrich or Lancaster. The compound bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane] was prepared as reported previously.

Synthesis of [Li(tbpam)]$_2$ (1). Bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane] (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) in a 250 cm^3 Schlenk tube and the solution was cooled to –70 ºC. A 1.6 M solution of Bu^{n}Li (3.06 cm^3, 4.89 mmol) in hexane was added and the solution was stirred for 1 h. The reaction mixture was warmed to 0 ºC and the resulting yellow solution was treated with *tert*-butyl isocyanate (0.56 cm^3, 4.89 mmol), after which the solution was colourless. The solvent was removed and hexane (70 cm^3) was added. A white solid was obtained and this was crystallised from a mixture of THF-hexane. Yield 86%. (Found: C, 62.01; H, 7.45; N, 22.23. $C_{32}H_{48}Li_2N_{10}O_2$ requires C, 62.12; H, 7.81; N, 22.64). ^{1}H NMR (DMSO, 297 K), δ 6.30 (s, 1 H, CH), 5.81 (s, 2 H, H^4), 2.07 (s, 6 H, Me^3), 2.27 (s, 6 H, Me^5), 1.10 [s, 9 H, $C(CH_3)_3$]. ^{13}C-{^{1}H}-NMR (DMSO, 297 K), δ 72.3 (CH), 146.9, 140.0 ($C^{3 \text{ or } 5}$), 106.3 (C^4), 13.6 (Me^3), 10.9 (Me^5), 30.9 [$\underline{C}(CH_3)_3$], 28.8 [$C(\underline{CH_3})_3$], 162.3 (N=C–O). Mass spectrum: (*m*/*z* assignment, % intensity): 316 [M – tbpam], 100.

Synthesis of [Li(S-mbbpam)]$_2$ (2). Bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane] (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) in a 250 cm^3 Schlenk tube and the solution was cooled to –70 ºC. A 1.6 M solution of Bu^{n}Li (3.06 cm^3, 4.89 mmol) in hexane was added and the solution was stirred for 1 h. The reaction mixture was warmed to 0 ºC and the resulting yellow solution was treated with (*S*)-(–)-α-methylbenzyl isocyanate (0.70 cm^3, 4.89 mmol), after which the solution was yellow in colour. The solvent was removed and hexane (70 cm^3) was added to give a pale yellow solid. The solid was crystallised from a mixture of THF-hexane. Yield 85%. $[\alpha]_D^{25}$ -39.6 (*c* 1.00, MeOH). (Found: C, 67.92; H, 6.93; N, 19.51. $C_{40}H_{48}Li_2N_{10}O_2$ requires C, 67.87; H, 6.83; N, 19.78). ^{1}H NMR (DMSO, 297 K), δ 6.49 (s, 1 H, CH), 5.83 (s, 1 H, $H^{4'}$), 5.80 (s, 1 H, H^4), 2.00 (s, 3 H, $Me^{3'}$), 1.98 (s, 3 H, Me^3), 2.31 (s, 3 H, $Me^{5'}$), 2.28 (s, 3 H, Me^5), 7.31–7.04 (m, 5 H, *Ph*CHMeN), 4.82 (q, 1 H, $^3J_{HH}$ = 7.2 Hz, Ph*CH*MeN), 1.13 (d, 3 H, $^3J_{HH}$ = 7.2 Hz, PhCH*Me*N). ^{13}C-{^{1}H}-NMR (DMSO, 297 K), δ 72.1 (CH), 147.2, 147.1, 140.3, 140.2, ($C^{3,3' \text{ or } 5,5'}$), 106.0 ($C^{4'}$), 105.8 ($C^4$), 13.9 ($Me^{3,3'}$), 11.6, 11.5 ($Me^{5,5'}$), 163.0 (N=C–O), 128.0–125.1 (*Ph*CHMeN), 52.2 (Ph*CH*MeN), 26.0 (PhCH*Me*N). Mass spectrum: (*m*/*z* assignment, % intensity): 358 [M – mbbpam], 100.

The synthetic procedure of a racemic mixture of **2** was the same as that for anantiopure complex $[Li(S\text{-}mbbpam)]_2$ **(2)**, using bdmpzm (1.50 g, 7.33 mmol), Bu^{n}Li 1.6 M solution (4.58 cm^3, 7.33 mmol) and an equimolar mixture of (*R*)/(*S*)-(±)-α-methylbenzyl isocyanate (1.05 cm^3, 7.33 mmol). Yield 85%. $[\alpha]_D^{25}$ 0.0 (*c* 1.00, MeOH). ^{1}H NMR (DMSO, 297K), δ 6.49 (s, 1 H, CH), 5.83 (s, 1 H, $H^{4'}$), 5.80 (s, 1 H, H^4), 2.00 (s, 3 H, $Me^{3'}$), 1.98 (s, 3 H, Me^3), 2.31 (s, 3 H, $Me^{5'}$), 2.28 (s, 3 H, Me^5), 7.31-7.04 (m, 5 H, *Ph*CHMeN), 4.82 (q, 1 H, $^3J_{HH}$=6.9 Hz, Ph*CH*MeN), 1.13 (d, 3 H, $^3J_{HH}$=6.9 Hz, PhCH*Me*N).

Synthesis of $[Li(tbptam)]_2$ (3). Bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane] (1.00 g, 4.89 mmol) was dissolved in dry THF (70 cm^3) in a 250 cm^3 Schlenk tube and the solution was cooled to –70 ºC. A 1.6 M solution of Bu^{n}Li (3.06 cm^3, 4.89 mmol) in hexane was added and the solution was stirred for 1 h. The reaction mixture was warmed to 0 ºC and the resulting yellow solution was treated with *tert*-butyl isothiocyanate (0.62 cm^3, 4.89 mmol), after which the solution was pale yellow. The solvent was removed and hexane (70 cm^3) was added to give a yellow solid. This solid was crystallised from a mixture of THF-hexane. Yield 89%. (Found: C, 59.10; H, 7.32; N, 21.10. $C_{32}H_{48}Li_2N_{10}S_2$ requires C, 59.05; H, 7.43; N, 21.52). ^{1}H NMR (DMSO, 297 K), δ 6.64 (s, 1 H, CH), 5.70 (s, 2 H, H^4), 2.03 (s, 6 H, Me^3), 2.25 (s, 6 H, Me^5), 1.24 [s, 9 H, $C(CH_3)_3$]. ^{13}C-{^{1}H}-NMR

(DMSO, 297 K), δ 82.1 (CH), 144.8, 140.15 ($C^{3\text{ or }5}$), 104.8 (C^4), 13.4 (Me^3), 11.7 (Me^5), 31.8 [$\underline{C}(CH_3)_3$], 28.3$C(\underline{CH_3})_3$], 172.0 (N=C–S). Mass spectrum: (*m*/*z* assignment, % intensity): 332 [M – tbptam], 100.

Synthesis of [Li(S-ppbptam)]$_2$ (4). Bdmpzm [bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane] (1.15 g, 5.64 mmol) was dissolved in dry THF (70 cm^3) in a 250 cm^3 Schlenk tube and the solution was cooled to –70 ºC. A 1.6 M solution of Bu^nLi (3.53 cm^3, 5.64 mmol) in hexane was added and the solution was stirred for 1 h. The reaction mixture was warmed to 0 ºC and the resulting yellow solution was treated with (*S*)-(–)-1-phenylpropyl isothiocyanate (1.00 g, 5.64 mmol), after which the solution was yellow in colour. The solvent was removed and hexane (70 cm^3) was added to give a pale yellow solid. This solid was crystallised from a mixture of THF-hexane. Yield 90%. $[\alpha]_D^{25}$ -22.8 (*c* 1.00, MeOH) (Found: C, 64.85; H, 7.60; N, 17.50. $C_{42}H_{56}Li_2N_{10}S_2$ requires C, 64.75; H, 7.24; N, 17.98). ^1H NMR (DMSO, 297 K), δ 6.82 (s, 1 H, CH), 5.76 (s, 1 H, H^4), 5.73 (s, 1 H, $H^{4'}$), 2.08 (s, 6 H, $Me^{3,3'}$), 2.50 (s, 3 H, Me^5), 2.39 (s, 3 H, $Me^{5'}$), 7.18–7.04 [m, 5 H, $\underline{Ph}CH(CH_2CH_3)N$], 5.11 [t, 1 H, $^3J_{HH}$ = 6.3 Hz, $Ph\underline{CH}(CH_2CH_3)N$], 1.58 [m, 2 H, $PhCH(\underline{CH_2}CH_3)N$], 0.63 [t, 3 H, $^3J_{HH}$ = 7.3 Hz $PhCH(CH_2\underline{CH_3})N$]. $^{13}C\text{-}\{^1H\}$-NMR (DMSO, 297 K), δ 82.1 (CH), 147.7, 147.6, 145.7, 145.5, ($C^{3,3'\text{ or }5,5'}$), 105.6, 105.5 ($C^{4,4'}$), 14.1, 14.0 ($Me^{3,3'}$), 12.3 ($Me^{5,5'}$), 178.2 (N=C–S), 130.0–125.1 [$\underline{Ph}CH(CH_2CH_3)N$], 65.7 [$Ph\underline{CH}(CH_2CH_3)N$], 30.8 [$PhCH(\underline{CH_2}CH_3)N$], 11.0 [$PhCH(CH_2\underline{CH_3})N$]. Mass spectrum: (*m*/*z* assignment, % intensity): 366 [M – ppbptam], 100.

Synthesis of [TiCl$_3$(S-mbbpamH)]Cl (5). To a cold THF (50 mL) solution of $TiCl_4{\cdot}2THF$ (0.28 g, 0.84 mmol) was added an equimolar quantity of [Li(S-mbbpam)]$_2$ **(2)** (0.30 g, 0.42 mmol). The mixture of reaction was stirred for 12 h at –70 ºC. The solvent was removed under vacuum, and the solid was extracted with CH_2Cl_2. A red solid was obtained after removal of the CH_2Cl_2, which was crystallised from a mixture of THF/hexane. Yield 60 %. $[\alpha]_D^{25}$ –80.0 (*c* 0.5, THF) (Found: C, 44.62; H, 4.91; N, 12.61. $C_{20}H_{25}Cl_4N_5OTi$ requires C, 44.39; H, 4.65; N, 12.94). ^1H NMR ($CDCl_3$, 297K), δ 6.64

(s, 1 H, CH), 6.10 (s, 1 H, $H^{4'}$), 6.01 (s, 1 H, H^4), 2.85 (s, 3 H, $Me^{3'}$), 1.63 (s, 3 H, Me^3), 2.76 (s, 3 H, $Me^{5'}$), 2.71 (s, 3 H, Me^5), 7.53-7.04 (m, 5 H, *Ph*CHMeN), 5.15 (q, 1 H, $^3J_{HH}$=7.3 Hz, Ph*CH*MeN), 1.75 (d, 3 H, $^3J_{HH}$=7.3 Hz, PhCH*Me*N), 9.33 (br s, 1 H, N-H). ^{13}C-{^{1}H}-NMR ($CDCl_3$, 297K), δ 72.1 (CH), 147.2, 147.1, 140.3, 140.2, ($C^{3,3' \text{ or } 5,5'}$), 106.0 ($C^{4'}$), 105.8 ($C^4$), 13.9 ($Me^{3,3'}$), 11.6, 11.5 ($Me^{5,5'}$), 163.0 (N=C-O), 128.0-125.1 (*Ph*CHMeN), 52.2 (Ph*CH*MeN), 26.0 (PhCH*Me*N).

Synthesis of [TiCl$_3$(tbptamH)]Cl (6). The siynthetic procedure was the same as that for complex **5**, using $TiCl_4$·2THF (0.49 g, 1.49 mmol) and [Li(tbptam)]$_2$ **(3)** (0.49 g, 0.74 mmol) to give **6** as a red solid. Yield 59%. (Found: C, 37.90; H, 4.98; N, 13.46. $C_{16}H_{25}Cl_4N_5STi$ requires C, 37.74; H, 4.94; N, 13.75). ^{1}H NMR ($CDCl_3$, 297K), δ 9.14 (s, 1 H, CH), 6.13 (s, 2 H, H^4), 2.79 (s, 6 H, Me^3), 2.97 (s, 6 H, Me^5), 1.22 [s, 9 H, C(CH_3)$_3$], 14.20 (br s, 1 H, N-H). ^{13}C-{^{1}H}-NMR (CDCl3, 297K), δ 66.8 (CH), 157.8, 145.9 ($C^{3 \text{ or } 5}$), 109.8 (C^4), 17.6 (Me^3), 13.8 (Me^5), 61.0 [*C*(CH_3)$_3$], 27.5 [C(*CH_3*)$_3$], 181.9 (N=C-S).