

**Support Information belonging to the paper:**

**Synthesis of Arylzinc Thiolates Containing Perfluoroalkyl Chains.  
Model Catalyst Precursors for the Enantioselective Zinc-Mediated  
1,2-Addition of Dialkylzincs to Aldehydes in Fluorous Biphasic  
Systems.**

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### General Procedure for Ligands 3a-5a:

To a stirred solution of 5 mmol of (+) *N,N*-dimethyl-4-bromo- $\alpha$ -methylbenzylamine or (+)-*N*-[4-bromo- $\alpha$ -methyl-benzyl]-pyrrolidine in 20 mL of diethyl ether was added 5 mmol of a 1.7 M solution of *t*-BuLi in pentane at  $-70$  °C. After stirring at this temperature for 30 min. 5 mmol of the appropriate perfluorochlorosilane was added. The cooling bath was removed and the mixture was stirred for 1-3 h. Subsequently, the mixture was poured into a saturated aqueous ammonium chloride solution. After separation of the organic layer, the water layer was extracted once with 40 mL of pentane. The combined organic layers were dried over sodium sulfate. The product was isolated as a colorless liquid by removal of the solvents in vacuo and purified by fractional distillation in vacuo.

**3a:** Yield 56%. bp 125-135 °C/0.6 mmHg.  $[\alpha]_D^{20} = +22.12$ ,  $c = 7.66$  (n-hexane).  $^1\text{H}$  NMR  $\text{CDCl}_3(\delta)$ : 7.45 d 2H ( $J = 8.0$  Hz) aromatic $H$ ; 7.32 d 2H ( $J = 8.0$  Hz) aromatic $H$ ; 3.25 (q, 1H,  $J = 7.7$  Hz, CHN); 2.21 (s, 6H,  $[\text{N}(\text{CH}_3)_2]$ ); 2.20-1.90 (m, 2H FC- $\text{CH}_2$ ); 1.38 (d, 3H,  $J = 7.7$  Hz, NCH $\text{CH}_3$ ); 1.02-0.96 (m, 2H, Si $\text{CH}_2$ ); 0.33 (s, 6H, Si( $\text{CH}_3$ ) $_2$ ).

$^{13}\text{C}$  NMR  $\text{CDCl}_3$  ( $\delta$ ): 145.5, 135.5, 133.4 and 127.2 (aromatic C); 65.9 (CHN); 43.2 ( $\text{N}(\text{CH}_3)_2$ ); 25.9 (t, JF-C = 24 Hz, FC- $\text{CH}_2$ ); 20.0 (NCH $\text{CH}_3$ ); 5.2 (Si $\text{CH}_2$ ); -3.5 (Si $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{20}\text{F}_{13}\text{H}_{24}\text{NSi}$ : C 43.40, H 4.37, N 2.53. Found: C 42.41, H 4.10, N 2.74.

**4a:** Yield 82%. mp 52 °C.  $[\alpha]_D^{20} = +16.96$ ,  $c = 1.14$  (n-hexane).  $^1\text{H}$  NMR  $\text{C}_6\text{D}_6(\delta)$ : 7.37 (d, 2H,  $J = 8.2$  Hz, aromatic $H$ ); 7.33 (d, 2H,  $J = 8.2$  Hz, aromatic $H$ ); 3.08 (q, 1H,  $J = 6.6$  Hz, CHN); 2.09 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ); 2.09-1.87 (m, 2H, FC- $\text{CH}_2$ ); 1.23 (d, 3H,  $J = 6.6$  Hz, NCH $\text{CH}_3$ ); 0.91-0.85 (m, 2H, Si $\text{CH}_2$ ); 0.08 (s, 6H, Si( $\text{CH}_3$ ) $_2$ ).

$^{13}\text{C}$  NMR  $\text{C}_6\text{D}_6$  ( $\delta$ ): 147.2, 135.3, 133.8 and 127.5 (aromatic C); 66.2 (CHN); 43.3 ( $\text{N}(\text{CH}_3)_2$ ); 26.3 (t, JF-C = 24 Hz, FC- $\text{CH}_2$ ); 20.6 (NCH $\text{CH}_3$ ); 5.4 (Si $\text{CH}_2$ ); -3.6 (Si $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{24}\text{F}_{21}\text{H}_{24}\text{NSi}$ : C 38.26, H 3.21, N 1.86. Found: C 38.33, H 3.25, N 1.89.

**5a:** Yield 98%. bp 160 °C/0.5mmHg. mp 45 °C.  $[\alpha]_D^{20} = +19.36$ ,  $c = 2.9$  (n-hexane).  $^1\text{H}$  NMR  $\text{C}_6\text{D}_6(\delta)$ : 7.40 (d, 2H,  $J = 7.4$  Hz, aromatic  $H$ ); 7.36 (d, 2H,  $J = 7.4$  Hz, aromatic  $H$ ); 3.07 (q, 1H,  $J = 6.4$  Hz, CH $\text{CH}_3$ ); 2.43-2.41 (m, 2H, NCH $_2$ ); 2.39-2.29 (m, 2H, NCH $_2$ ); 2.04-1.87 (m, 2H,  $\text{F}_{21}\text{C}_{10}\text{CH}_2$ ); 1.63-1.54 (m, 4H, NCH $_2\text{CH}_2$ ); 1.32 (d, 3H,  $J = 6.4$  Hz, CH $\text{CH}_3$ ); 0.96-0.86 (m, 2H,  $\text{F}_{21}\text{C}_{10}\text{CH}_2\text{CH}_2$ ); 0.08 (s, 6H, Si $\text{CH}_3$ ).  $^{13}\text{C}$  NMR  $\text{C}_6\text{D}_6(\delta)$ : 148.3, 135.2, 133.7 and 127.1 (aromatic C); 65.9 (CH $\text{CH}_3$ ); 52.8 (NCH $_2$ ); 26.1 (t, JF-C = 24 Hz, FC $\text{CH}_2$ ); 23.7 (NCH $_2\text{CH}_2$ ); 23.6 (CH $_3$ ); 5.3 (Si $\text{CH}_2$ ); -3.8 (Si $\text{CH}_3$ ). Anal. Calc. for  $\text{C}_{26}\text{H}_{26}\text{F}_{21}\text{NSi}$ : C 40.06, H 3.36, N 1.80. Found: C 40.16, H 3.46, N 1.85.

### General Procedure for Trimethylsilylthio-compounds **3b-5b**:

To a stirred solution of 10 mmol of ligand in 30 mL of pentane was added 6.8 mL of *t*-Buli (1.5 M solution in pentane) at  $-70\text{ }^{\circ}\text{C}$ . After removing the cooling bath, the reaction mixture was stirred for 5 days at room temperature. The clear brown solution was cooled down to  $-70\text{ }^{\circ}\text{C}$ , 50 mL of cold THF was added, followed by the addition of 10 mmol of sulfur. The reaction mixture was allowed to rise to room temperature and stirred for 2 h to complete the sulfur insertion. The thiolate anion was quenched with 2 mL of trimethylchlorosilane. After 1 h, the lithium chloride which precipitated was separated from the reaction mixture by centrifugation and subsequent decantation of the organic layer. The product was isolated by evaporation of the solvent and was used as crude products. The extremely moisture sensitive thioethers were characterised by GCMS and NMR and were used without further purification.

**3b-5b**: Yields 96-98%. Relevant NMR data:  $^1\text{H}$  NMR  $\text{C}_6\text{D}_6(\delta)$ : 7.75 (d, 1H,  $J = 7.6$  Hz, aromatic $H$ ); 7.67 (s, 1H, aromatic $H$ ); 7.22 (d, 1H,  $J = 7.6$  Hz, aromatic $H$ ); 4.18 (q, 1H,  $J = 6.4$  Hz,  $\text{CH}_2\text{N}$ ); 2.16-1.90 (m, 2H,  $\text{CF}_2\text{-CH}_2$ ); 1.26 (d, 3H,  $J = 6.4$  Hz  $\text{NCHCH}_3$ ); 0.90-0.81 (m, 2H,  $\text{Si-CH}_2$ ); 0.22 (s, 9H,  $\text{SSi}(\text{CH}_3)_3$ ); 0.05 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR  $\text{C}_6\text{D}_6(\delta)$ : 150.6, 141.4, 135.2, 133.6, 132.4 and 131.2 (aromatic C); 62.5 ( $\text{CH}_2\text{-N}$ ); 26.1 (t,  $J = 23$  Hz,  $\text{CF}_2\text{-CH}_2$ ); 20.8 ( $\text{NCHCH}_3$ ); 5.2 ( $\text{SiCH}_2$ ); 1.1 ( $\text{SSiCH}_3$ ); -3.9 ( $\text{SiCH}_3$ ).

### General Procedure for Zinc Compounds **3c-5c**:

To a stirred solution of 0.2 g (1.5 mmol) of zinc chloride in 10 mL of diethyl ether was added 4 mL of a 1 M solution of diethylzinc in hexanes. The mixture was stirred until all the zinc chloride was dissolved and converted into ethylzinc chloride. Then 3 mmol of **3b**, **4b** or **5b** in 5 mL of pentane was added. The reaction mixture was stirred for 2 h. The formed trimethylsilyl chloride and solvents were removed by evaporation in vacuo. The products **4c** and **5c** were isolated as white solids after recrystallization from hexane, while **3c** was isolated as an orange oil.

**3c**: Yield 80 %.  $^1\text{H}$  NMR toluene  $d_8$  at  $105\text{ }^{\circ}\text{C}$  ( $\delta$ ): 7.91 (s, 1H, aromatic  $H$ ); 7.16 (d, 1H,  $J = 7.4$  Hz, aromatic $H$ ); 7.87 (d, 1H,  $J = 7.4$  Hz, aromatic  $H$ ); 3.55 (b, 2H,  $\text{CH-N}$ ); 2.20 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ); 2.20-1.90 (m, 2H,  $\text{CF}_2\text{-CH}_2$ ); 1.55 (d, 3H,  $\text{NCHCH}_3$ ); 1.40-1.30 (b, 3H,  $\text{CH}_3\text{-CH}_2\text{-Zn}$ ); 1.20-1.00 (m, 2H,  $\text{CH}_2\text{-Si}$ ); 0.60-0.40 (b, 2H,  $\text{CH}_3\text{-CH}_2\text{-Zn}$ ); 0.34 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR  $\text{C}_6\text{D}_6$  at  $70\text{ }^{\circ}\text{C}$  ( $\delta$ ): 141.3, 138.1, 137.1, 132.4, 131.4 and 129.9 (aromatic C); 61.8 ( $\text{CHCH}_3\text{N}$ ); 43.0 ( $\text{NCH}_3$ ); 26.3 (t,  $J = 23.6$  Hz,  $\text{CF}_2\text{-CH}_2$ ); 19.5 ( $\text{NCHCH}_3$ ); 12.9 ( $\text{CH}_3\text{-CH}_2\text{Zn}$ ); 5.4 ( $\text{SiCH}_2$ ); 2.4 ( $\text{CH}_2\text{Zn}$ ); -3.9 ( $\text{SiCH}_3$ ). Anal. calc. for  $\text{C}_{22}\text{F}_{13}\text{H}_{28}\text{NSSiZn}$ : C 38.92, H 4.16, N 2.06, Si 4.14; found: C 38.65, H 4.21, N 2.08, Si 4.28.

**4c**: Yield: 90 %. mp  $105\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR toluene  $d_8$   $104\text{ }^{\circ}\text{C}$  ( $\delta$ ): 7.92 (s, 1H, aromatic  $H$ ); 7.09 (d, 1H,  $J = 7.6$  Hz, aromatic $H$ ); 6.75 (d, 1H,  $J = 7.3$  Hz, aromatic  $H$ ); 3.42 (b, 1H,  $\text{CHCH}_3$ ); 2.19 (s, 6H,  $\text{NCH}_3$ ); 2.18-1.99 (m, 2H,  $\text{F}_{21}\text{C}_{10}\text{CH}_2$ ); 1.46 (d, 3H,  $J = 6.7$  Hz,  $\text{CHCH}_3$ ); 1.35 (t, 3H,  $J = 8.2$  Hz,  $\text{ZnCH}_2\text{CH}_3$ ); 1.05-0.99 (m,  $\text{F}_{21}\text{C}_{10}\text{CH}_2\text{CH}_3$ ); 0.47 (q, 2H,  $J = 8.2$  Hz,  $\text{ZnCH}_2$ ); 0.26 (s, 6H,  $\text{SiCH}_3$ ).  $^{13}\text{C}$  NMR toluene  $d_8$  at  $100\text{ }^{\circ}\text{C}$  ( $\delta$ ): no aromatic peaks could be distinguished due to the solvent peaks; 62.0 ( $\text{CH-N}$ ); 43.1 ( $\text{NCH}_3$ ); 26.8 (t,  $J = 23$  Hz,  $\text{CF}_2\text{CH}_2$ ); 20.9 ( $\text{CHCH}_3$ ); 12.7 ( $\text{CH}_3\text{CH}_2\text{Zn}$ ); 5.8 ( $\text{CH}_2\text{Si}$ ); -0.4 ( $\text{CH}_3\text{CH}_2\text{Zn}$ ); -3.7 ( $\text{SiCH}_3$ ). Anal. calc. for  $\text{C}_{26}\text{H}_{28}\text{F}_{21}\text{NSSiZn}$ : C 35.53, H 3.21, N 1.59, Si 3.20. Found: C 35.39, H 3.18, N 1.54, Si 3.29.

**5c:** Yield: 88% . mp 128 °C. <sup>1</sup>H NMR THF *d*<sub>8</sub> at 59 °C (δ): 7.54 (s, 1H), 7.06 (d, 1H, J = 7.3 Hz); 6.92 (d, 1H, J = 7.3 Hz, aromatic *H*); 3.40 (q, 1H, *CHCH*<sub>3</sub>); 3.0 - 1.8 (br m, 8H, *NCH*<sub>2</sub>*CH*<sub>2</sub>); 1.74 (br, 2H, *CF*<sub>2</sub>*CH*<sub>2</sub>); 1.64 (d, 3H, J = 6 Hz, *CHCH*<sub>3</sub>); 0.97 (m, 2H, *CH*<sub>2</sub>*Si*); 0.82 (t, J = 7.9 Hz, *CH*<sub>3</sub>*CH*<sub>2</sub>*Zn*); 0.26 (s, 6H, *SiCH*<sub>3</sub>); 0.06 (q, 2H, J = 7.9 Hz, *CH*<sub>2</sub>*Zn*). <sup>13</sup>C NMR THF *d*<sub>8</sub> at 59 °C (δ): 141.7, 140.2, 135.1, 129.1 and 127.6 (aromatic *C*); 71.2 (*CHCH*<sub>3</sub>); 55.5 (*CH*<sub>2</sub>*N*); 24.6 (t, J = 23.8 Hz, *CF*<sub>2</sub>*CH*<sub>2</sub>); 22.4 (*CH*<sub>2</sub>*CH*<sub>2</sub>*N*); 16.8 (*CHCH*<sub>3</sub>); 10.6 (*ZnCH*<sub>2</sub>*CH*<sub>3</sub>); 3.6 (*CH*<sub>2</sub>*Si*); -1.0 (*ZnCH*<sub>2</sub>*CH*<sub>3</sub>); -5.8 (*SiCH*<sub>3</sub>). Anal. calc. for C<sub>28</sub>H<sub>30</sub>F<sub>21</sub>NSSiZn: C 37.16, H 3.34, N 1.55, Si 3.10, Zn 7.22. Found: C 37.28, H 3.31, N 1.65, Si 3.08, Zn 7.34.