



Efficient recycling of fluororous versions of highly enantioselective *S,N*-chelated zinc aminoarene thiolate catalysts for the 1,2-addition of diethylzinc to benzaldehydes

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ABSTRACT

New enantiomerically pure *S,N*-chelated (*R*)-Zn(Et)SR complexes, **3a–3c** ($R = 2\text{-}[\text{CHMeN}(\text{CH}_2)_4]\text{-5-}[\text{SiMe}_{3-n}(\text{CH}_2\text{CH}_2\text{C}_x\text{F}_{2x+1})_n]\text{C}_6\text{H}_5$; $n = 1, x = 10$; $n = 2, 3$ and $x = 8$), have been synthesized from the reaction of EtZnCl and the corresponding trimethylsilyl(aminoaryl) thioethers, or lithium aminoarene thiolate **2c**.

Complexes **3a–3c** were successfully used as highly enantioselective catalysts for the 1,2-addition (*e.e.* up to 92%) of diethylzinc to benzaldehyde in perfluoromethylcyclohexane/*n*-octane. At 2.5 mol%, catalyst **3c**, thanks to its three $\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$ tails, could be reused at least 10 times with retention of its initial high enantioselectivity, thereby significantly increasing the turnover number per unit amount of catalyst in comparison with earlier studies.

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1. Introduction

Previously we have shown that in addition to the large number of reported zinc catalysts also enantiopure zinc *ortho*-aminoarene thiolate compounds are excellent catalysts for the enantioselective addition of dialkylzincs to aldehydes (Scheme 1) [1,2].

Following the invention of using fluororous biphasic systems (FBS) by Horváth and Rábai [3] for the recycling of homogeneous catalysts, we developed a strategy for the application of the FBS approach in the 1,2-addition of dialkylzinc to benzaldehyde [4]. We reported on the synthesis of monoperfluoroalkyl-functionalized arene thiolate ligands, their conversion into ethylzinc thiolate catalysts [4b] and their modest retention values in FBS recycling experiments. To this end we developed zinc *ortho*-aminoarene thiolate catalysts with a fluororous silicon substituent at the 5-position (see Scheme 2). Other groups reported the application of fluororous zinc catalysts based on fluororous BINOL ligands [5] and fluororous β -aminoalcohols [6]. In earlier work concerning the

use of perfluoroalkylsilyl-substituted arylphosphine complexes in homogeneous catalysis [4] we noticed that functionalization of a silicon atom with more than one perfluoroalkyl chain gave a much higher fluorophilicity under FBS conditions [4e]. In this paper, we have applied the latter insights to the preparation of bis-, and tris(perfluoroalkyl)silyl-functionalized versions of highly enantioselective zinc aminoarene thiolate complexes that demonstrate significantly improved recycling efficiencies compared to those already known in the literature.

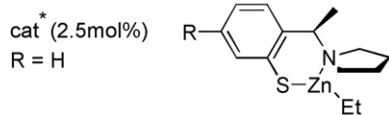
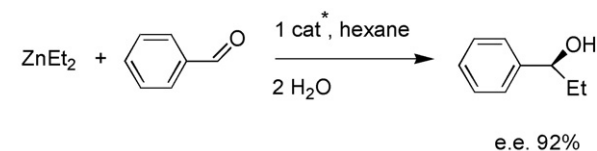
2. Results and discussion

The synthesis of **1a** starts with the conversion of enantiomerically pure (*e.e.* = 98.9%) (*R*)-(+)-*N*-(1-(4-bromophenyl)ethyl)amine into the corresponding pyrrolidine derivative **4**. Introduction of the perfluoroalkyl-group was carried out by reacting **4** with 2 equiv. of *tert*-butyllithium at -70°C in diethyl ether. The resulting lithium compound was reacted with $\text{C}_{10}\text{F}_{21}(\text{CH}_2)_2\text{SiMe}_2\text{Cl}$ to give **1a** in high yield (see Scheme 2).

For the syntheses of compounds **3b** and **3c** with two and three perfluoroalkyl chains, respectively, suitable bis- and tris(perfluoroalkyl)silyl building blocks have been developed in our laboratory as part of other FBS-type applications [4e]. For

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Scheme 1.

synthetic reasons the fluoros tails were shortened from $-C_{10}F_{21}$ (**1a**) to $-C_8F_{17}$ for the higher molecular weight derivatives (**1b** and **1c**). The new building blocks were coupled with the *in situ* generated aryllithium derivatives in almost quantitative yields, using the same methods as described earlier for the mono(perfluoroalkyl)silyl-functionalized aminoarene thiolate ligands [4b].

The heteroatom-assisted *ortho*-lithiation (Li–H exchange) of chiral α -substituted benzylamine derivatives in apolar solvents has been well established and usually produces the corresponding lithiated compounds within a few hours in quantitative yield [7]. However, quantitative lithiation of fluoros ligand **1a** with *tert*-butyllithium in pentane required more than 5 days. The lithiated compound was converted *in situ* into the thiol derivatives by reaction with a stoichiometric amount of elemental sulfur at -70°C in the presence of added THF ((pentane/THF)=(40/60)). Subsequent treatment of the resulting lithium thiolate with an excess of trimethylsilyl chloride afforded trimethylsilyl thioether **2a**, which was used without further purification.

Complete *ortho*-lithiation of **1b** and **1c** could not be achieved with 1 equiv. of *tert*-butyllithium. Under these conditions a maximum of 33% conversion of **1b** into the lithio-compound was obtained after 7 days stirring at room temperature. Most likely formation of mixed aggregates of aryllithium and *tert*-butyllithium [8] stabilized by the presence of the fluoros tails might be a reason for this low conversion. The lithiation of **1b** (in C_6D_6 as solvent) was studied in more detail by ^1H NMR spectroscopy. It appeared that 4 equiv. of *tert*-butyllithium were required to reach full lithiation. Under these conditions the aromatic as well as the α -H pattern of the lithio-compound of **1b** was already observed after 2 h of reac-

tion time. After 16 h the lithiation was complete, showing only one pattern for the aromatic and α protons.

The amount of elemental sulfur added was stoichiometric to the amount of *tert*-butyllithium used (4 equiv.). Quenching of the reaction mixture with trimethylsilyl chloride gave **2b** in high yield. The side product trimethylsilyl *tert*-butylthioether was easily removed because of its volatility.

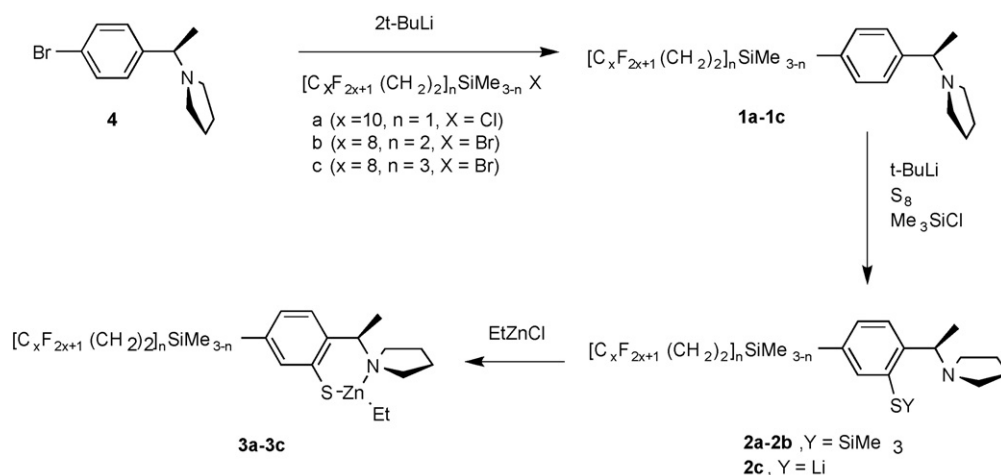
The synthesis of **2c** was complicated by the very low solubility of **1c** in pentane. To realize homogeneous reaction conditions it was necessary to add 25–50 wt.% of perfluoro solvent FC-72 to the solution. With 4 equiv. of *tert*-butyllithium a reaction time of 2 days was required for complete conversion. Sulfur insertion occurred as expected. However, according to ^1H NMR spectroscopy measurements, the quench with trimethylsilyl chloride failed to give the corresponding trimethylsilyl thioether. MALDI TOF analysis confirmed the formation and isolation of the expected thiol ($M+H$)⁺ (m/z 1578). This indicates that the insertion of elemental sulfur into the lithium thiolate intermediate was successful. For **2b** the same problem occurred when FC-72 was present, whereas complete silylation was observed in the absence of FC-72. Apparently the fluoros lithium aminoarene thiolate intermediates are solvated in such a way by FC-72 that the subsequent reaction with trimethylsilyl chloride is extremely slow or even hampered.

The formation of the ethylzinc aminoarene thiolates **3a–3c** involved the reaction of the respective thioether (**2a** and **2b**) or lithium thiolate (**2c**) with EtZnCl . The products **3a–3c** were obtained in quantitative yield (see Scheme 2) [9]. Crystallization from hexane gave novel **3a** as a colorless solid that was characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy.

Crude ethylzinc aminoarene thiolates **3b** and **3c** were obtained as brown waxes. They could only be characterized by elemental analyses. Not surprisingly due to their high molecular weight, the ^1H NMR spectra of both compounds showed very broad lines even at higher temperatures (up to 95°C).

3. Determination of partition coefficients

The values for the partition coefficients of the three compounds **1** and zinc compounds **3** are presented in Table 1. It can be seen that there is a clear correlation with the number of fluoroalkyl tails that have been attached to the silicon tethering point. Compounds with one fluoroalkyl tail (**1a** and **3a**) dissolve to a significant extent in the octane layer, whereas the compounds with three fluoroalkyl tails



Scheme 2.

Table 1

Partition coefficients of the fluoros aminoarenes and the corresponding ethylzinc aminoarene thiolate complexes determined at 0 °C^a

Compound	<i>P</i>
1a	0.3
1b	5.0
1c	14.6
3a	2.8
3b	10.3
3c	21.1

The two layers were warmed to 50 °C until a clear, mono-phase solution was obtained. Then the solution was equilibrated at 0 °C for 30 min. When two separated layers were obtained, each layer was taken apart and the solvent evaporated. The weight of each residue was determined. The partition coefficients were calculated by dividing the amount found in the fluoros phase by the amount of material found in the organic phase (=P).

^a A known amount of the compound (between 1 and 25 μmol) was added to a mixture of PFMCH (7.0 mL) and *n*-octane (7.0 mL).

(**1c** and **3c**) dissolve preferentially in the PFMCH layer. Compounds with two fluoroalkyl tails (**1b** and **3b**) still have modest affinity for the octane phase. From these results we can also conclude that for efficient fluoros biphasic separation strategies three fluoros alkyl tails are needed.

3.1. Catalytic reactions in hexane

Experiments in hexane confirmed that these enantiopure, fluoros ethylzinc *ortho*-aminoarene thiolates are active catalysts in the 1,2-addition of diethylzinc to benzaldehyde (Fig. 1). The activity and enantioselectivity of these catalysts were comparable with the parent zinc *ortho*-aminoarene thiolate catalysts we published earlier [1a].

When the activities of pre-catalysts **3a**, **3b** and **3c** are compared it is rather surprising that **3b** reacts slower than **3c** while the opposite would be expected on the basis of steric requirements. So far we do not have an explanation for this behavior.

3.2. Catalytic reactions in a fluoros biphasic solvent system (FBS)

Fig. 2 shows the results of the catalytic experiments in octane/PFMCH 1/1 (v/v). After 3 h reaction time stirring was stopped, the reaction mixture was cooled to 0 °C, and the octane layer with the product was removed as much as possible, hydrolyzed and then analyzed. In each cycle ca. 10% of the organic layer was left behind to limit the effect of phase separation errors on catalyst retention. After phase separation new portions of benzaldehyde and Et₂Zn in octane (1.0 M) were added to the fluoros layer and stirring was continued. Due to the large

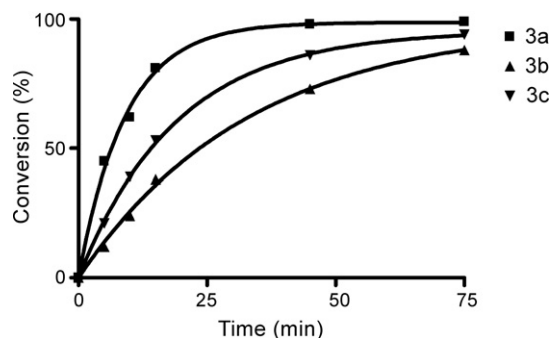


Fig. 1. 1,2-Addition of Et₂Zn to PhC(O)H in hexane with 2.5 mol% of fluoros catalyst. Reaction conditions: 5.0 mmol of PhC(O)H, 6.0 mmol of Et₂Zn, 1 M solution in hexane, 4 mL of hexane, 2.5 mol% of **3a–3c**, room temperature. The experiments were performed in duplicate.

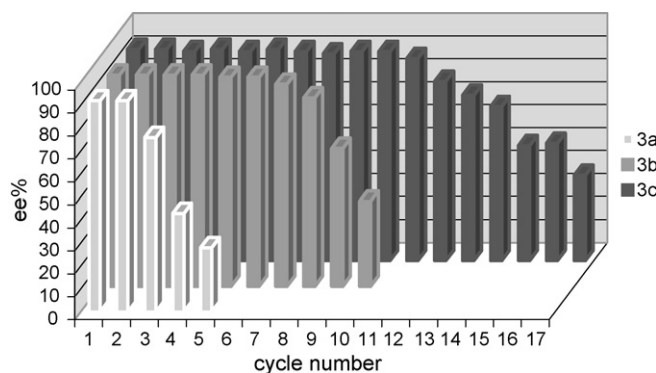


Fig. 2. FBS experiments with 2.5 mol% of fluoros catalyst **3a–3c**, diethylzinc and benzaldehyde. Reaction conditions: 5.0 mmol of PhC(O)H, 6.0 mmol of Et₂Zn, 1.0 M solution in octane, 6.0 mL of PFMCH, 2.5 mol% of **3a–3c**, 3 h at room temperature. *e.e.* % was determined by HPLC analysis; Daicel Chiralcel O.D. column, 25 cm × 4.6 mm; eluents *i*-propanol/hexane 2/98 (v/v).

amount of diethylzinc present in the organic phase, the reaction mixture remained biphasic during the course of each run. Despite the biphasic conditions, conversions in each run were high (>98%). No correction for the leaching of fluoros solvent was needed due to its low solubility in the organic phase.

The enantioselectivities obtained in each cycle are shown in Fig. 2 and can be considered as first approximation of the recycling efficiency of the catalyst. Pre-catalyst **3a** with one fluoros tail failed to give a high *e.e.* already after three cycles. This is as expected from the partitioning experiments which showed that the fluoros catalyst dissolves well enough in the octane layer to be almost completely removed from the fluoros phase after five cycles. Consequently a rapid decrease in the *e.e.* from 92 to 28% is observed when pre-catalyst **3a** is used. However pre-catalyst **3c** can be used for 10 cycles with high *e.e.* and it is only during cycles 10–17 that the value of the *e.e.* starts to diminish slowly. The behavior of **3b** is intermediate between that of **3a** and **3c**.

To find out the minimal amount of pre-catalyst needed for the chiral induction observed, some experiments in hexane were carried out in which different amounts of **3b** were used. With 1.0 and 0.1 mol% of fluoros catalyst, product *e.e.*'s of 92 and 74%, respectively, were obtained. With 0.01 mol% of fluoros catalyst the *e.e.* dropped to 24% while at 0.001 mol% no *e.e.* was observed. This indicates that a significant drop in *e.e.* is observed once the catalyst concentration has dropped below 1.0 mol% relative to substrate. This corresponds to minimum retention values of 40, 83 and 90% per cycle for **3a**, **3b** and **3c**, respectively. It should be realized that in some earlier studies based on different ligand systems much higher catalyst concentrations (in the order of 10–20 mol%) have been used [5,6]. In such cases, even at moderate retention of the ligand, the *e.e.*'s only start to suffer when already significant amounts of the ligand has been lost. In recycling studies, it is therefore essential to use the minimum amount of catalyst needed if one wants to use conversion or selectivity data to estimate recycling efficiency of the catalyst.

The effect of auto-catalysis [10] by the remainder of zinc (*R*)- α -methylbenzylalcoholate that is left in the fluoros phase after phase separation (ca. 10 mol%) was also studied in a separate experiment in hexane by adding 10 mol% of (*R*)- α -methylbenzylalcohol (*e.e.* 99%), and by assuming that the zinc alcoholate would be formed *in situ*. The observation of an *e.e.* of 46% for the latter reaction corresponds very well with the values published [10] and indicates that the high enantiomeric excess obtained in the presence of **3a–3c** is indeed the result of a catalyzed reaction by the ethylzinc arene thiolate rather than by an auto-catalytic effect

caused by the 10 mol% of zinc alcoholate product left in the PFMCH phase from incomplete separation during previous cycles.

4. Conclusion

A method for the attachment of perfluoroalkyl chains to chiral aminoarenethiolates is now available and leads the way to a new family of mono-, bis- and tris(perfluoroalkyl)silyl-functionalized arenethiolate ligands. These can be converted into the corresponding ethylzinc thiolate compounds which are active catalyst in the 1,2-addition reaction of Et₂Zn to benzaldehyde. Especially the tris(perfluoroalkyl)silyl-modified ethylzinc aminoarenethiolate **3c** is an excellent catalyst for the use in a FBS medium and can be reused for several cycles with high conversions and enantioselectivity.

5. Experimental procedures

All manipulations were carried out using standard Schlenk techniques under an inert atmosphere of dry, oxygen-free nitrogen. Organic solvents were distilled from sodium prior to use. (*R*)-4-BrC₆H₄CH(Me)NH₂ with an optical purity of 98.9% was obtained commercially. The synthesis of the fluorinated tails has been described in Ref. [3e]. ¹H and ¹³C NMR spectra were recorded on a Varian Inova 300 MHz spectrometer. Chemical shifts (δ) are given in ppm relative to SiMe₄ as internal standard. HPLC was performed on a Daicel Chiracel O.D. column, 25 cm × 4.6 mm. Optical rotations were determined on a PerkinElmer 241 polarimeter. Elemental analyses were obtained from Kolbe Mikroanalytisch Laboratorium, Mülheim a.d. Ruhr, Germany. MALDI-TOF-MS spectrometric measurements were acquired using a Voyager-DE BioSpectrometry Workstation (PerSeptive Biosystems Inc., Framingham, MA, USA) mass spectrometer and 3,5-dihydroxybenzoic acid was used as matrix. IR spectra were measured on a Perkin Elmer Spectrum One FT-IR spectrometer.

5.1. General procedure for the preparation of fluorinated ligands

1a–1c

To a stirred solution of 5 mmol of (+)-*N*-(1-(4-bromophenyl)ethyl)pyrrolidine in Et₂O (20 mL) was added 10 mmol of *tert*-butyllithium (1.7 M) in pentane at –70 °C. This solution was stirred for 1 h followed by the addition of 5 mmol of either ClSi(Me)₂CH₂CH₂C_xF_{2x+1} or BrSiMe_{3–n}C_xF_{2x+1} (*n* = 2, 3 and *x* = 8). The reaction mixture was allowed to rise to room temperature and stirred for another 3 h. Subsequently the resulting mixture was poured into saturated aqueous ammonium chloride (50 mL). After separation of the organic layer, the water layer was extracted once with pentane (40 mL). The combined organic layers were dried on sodium sulfate. The product was isolated as a colorless liquid by removal of the solvents *in vacuo*. Fluorinated ligand **1a** was purified by fractional distillation under reduced pressure. Fluorinated ligands **1b** and **1c** could not be distilled and were used as obtained from the respective reaction.

1a yield: 98%, bp 160 °C/0.5 mmHg, mp 45 °C. $[\alpha]_D^{20} = +19.36^\circ$, *c* = 2.9 (*n*-hexane). ¹H NMR C₆D₆: δ 7.40 (d, *J* = 7.4 Hz, 2H, aromatic *H*), 7.36 (d, *J* = 7.4 Hz, 2H, aromatic *H*), 3.07 (q, *J* = 6.4 Hz, 1H, CHCH₃), 2.43–2.41 (m, 2H, NCH₂), 2.39–2.29 (m, 2H, NCH₂), 2.04–1.87 (m, 2H, F₂₁C₁₀CH₂), 1.63–1.54 (m, 4H, NCH₂CH₂), 1.32 (d, *J* = 6.4 Hz, 3H, CHCH₃), 0.96–0.86 (m, 2H, F₂₁C₁₀CH₂CH₂), 0.08 (s, 6H, SiCH₃). ¹³C NMR in C₆D₆: δ 148.3, 135.2, 133.7 and 127.1 (aromatic C), 65.9 (CHCH₃), 52.8 (NCH₂), 26.1 (*t*, *J*_{F–C} = 24 Hz, FCCH₂), 23.7 (NCH₂CH₂), 23.6 (CHCH₃), 5.3 (SiCH₂), –3.8 (SiCH₃). GCMS, *m/z* 780 [M]⁺. Anal. calc. for C₂₆H₂₆F₂₁NSi: C 40.06, H 3.36, N 1.80, Si 3.60. Found: C

40.16, H 3.46, N 1.85, Si 3.68. IR (ATR neat, cm^{–1}) 2965 (w), 2935 (w), 1600 (w), 1203 (s), 1148 (s), 1111 (m).

1b yield: 91%, brown waxy solid, $[\alpha]_D^{20} = +16.0^\circ$, *c* = 1.134 (*n*-hexane). ¹H NMR C₆D₆ 50 °C: δ 7.35 (d, *J* = 8.1 Hz, 2H, aromatic *H*), 7.21 (d, *J* = 8.1 Hz, 2H, aromatic *H*), 3.06 (q, *J* = 6.4 Hz, 1H, CHCH₃), 2.42–2.32 (m, 2H, NCH₂), 2.32–2.12 (m, 2H, NCH₂), 2.07–1.76 (m, 4H, F₁₇C₈CH₂), 1.56–1.36 (m, 4H, NCH₂CH₂), 1.27 (d, *J* = 6.4 Hz, 3H, CHCH₃), 0.88–0.76 (m, 4H, F₁₇C₈CH₂CH₂), –0.01 (s, 3H, SiCH₃). ¹³C NMR C₆D₆: 50 °C: δ 148.9, 137.0, 132.1 and 127.4 (aromatic C), 65.8 (CHCH₃), 58.7 (NCH₂), 25.9 (*t*, *J*_{F–C} = 24 Hz, FCCH₂), 23.7 (NCH₂CH₂), 23.4 (CHCH₃), 3.5 (SiCH₂), –6.6 (SiCH₃). MALDI-TOF-MS, *m/z* 1112.94 [M+H]⁺ (calc. 1112.61). Anal. calc. for C₃₃H₂₇F₃₄NSi: C 35.66, H 2.45, N 1.26, Si 2.53. Found: C 35.74, H 2.39, N 1.22, Si 2.61. IR (ATR neat, cm^{–1}) 2974 (w), 2791 (w), 1690 (w), 1199 (s), 1144 (s), 1112 (m).

1c yield: 96%, brown waxy solid, $[\alpha]_D^{20} = +9.0^\circ$, *c* = 1.151 (*n*-hexane). ¹H NMR C₆D₆ 70 °C: δ 7.38 (d, *J* = 7.9 Hz, 2H, aromatic *H*), 7.17 (d, *J* = 7.9 Hz, 2H, aromatic *H*), 3.10 (q, *J* = 6.4 Hz, 1H, CHCH₃), 2.42–2.39 (m, 2H, NCH₂), 2.32–2.24 (m, 2H, NCH₂), 2.06–1.82 (m, 6H, F₁₇C₈CH₂), 1.70–1.30 (m, 6H, NCH₂CH₂), 1.27 (d, *J* = 6.4 Hz, 3H, CHCH₃), 0.94–0.80 (m, 6H, F₁₇C₈CH₂CH₂). ¹³C NMR in C₆D₆ 70 °C: δ 149.8, 133.9, 129.3 and 127.6 (aromatic C), 65.4 (CHCH₃), 52.5 (NCH₂), 25.8 (*t*, *J*_{F–C} = 24 Hz, FCCH₂), 23.7 (NCH₂CH₂), 22.9 (CHCH₃), 1.6 (SiCH₂). MALDI-TOF-MS, *m/z* 1545.63 [M+H]⁺ (calc. 1544.68). Anal. calc. for C₄₂H₂₈F₅₁NSi: C 32.68, H 1.83, N 0.91, Si 1.82. Found: C 32.72, H 1.90, N 0.83, Si 1.84. IR (ATR neat, cm^{–1}) 2966 (w), 1684 (w), 1200 (s), 1145 (s), 1113 (m).

5.1.1. Preparation of the trimethylsilyl thioether **2a**

To a stirred solution of 10 mmol of **1a** in pentane (30 mL) was added 10 mmol of *tert*-butyllithium (1.5 M solution in pentane) at –70 °C. The resulting reaction mixture was stirred for 5 days at room temperature. The clear brown solution was cooled down to –70 °C, cold THF (50 mL) was added, which was followed by the addition of 10 mmol of elemental sulfur. The reaction mixture was allowed to warm to room temperature and then was stirred for a further 2 h to allow the sulfur insertion to go to completion. The thioether intermediate was quenched with trimethylchlorosilane (2 mL). After 1 h, the lithium chloride precipitate was separated from the reaction mixture by centrifugation. Subsequently the organic layer was decanted from the lithium chloride. Evaporation of the solvent, afforded the crude product **2a** that was used without further purification (*vide infra*). The thioether has been characterized only by NMR.

2a yield: 98%. ¹H NMR C₆D₆: δ 7.88 d (*J* = 7.6 Hz, 1H, aromatic *H*), 7.71 (s, 1H, aromatic *H*), 7.25 (d, *J* = 7.6 Hz, 1H, aromatic *H*), 4.29 (q, *J* = 6.4 Hz, 1H, CHCH₃), 2.55–2.51 (m, 2H, NCH₂), 2.44–2.41 (m, 2H, NCH₂), 2.02–1.84 (m, 2H (F₂₁C₁₀CH₂), 1.60–1.57 (m, 4H, NCH₂CH₂), 1.12 (d, *J* = 6.4 Hz, 3H, CHCH₃), 0.99–0.83 (m, 2H, F₂₁C₁₀CH₂CH₂), 0.24 (s, 9H, SiSiCH₃), 0.06 (s, 6H, SiCH₃). ¹³C NMR C₆D₆: δ 151.1, 141.3, 135.1, 132.6 and 130.5 (aromatic C), 61.8 (CHCH₃), 52.6 (NCH₂), 23.7 (NCH₂CH₂), 22.8 (CHCH₃), 1.2 (SiSiCH₃), –3.9 (SiCH₃).

5.1.2. Preparation of the trimethylsilyl thioether **2b**

The same procedure as described for **2a** was used, except that 4 equiv. of *tert*-butyllithium and **1b** were used. The reaction mixture was stirred for 24 h and then reacted with 4 equiv. of sulfur.

2b yield: 96%, brown waxy solid. ¹H NMR C₆D₆ 60 °C: δ 7.83 (d, *J* = 7.8 Hz, 2H, aromatic *H*), 7.62 (s, 1H, aromatic *H*), 7.15 (d, *J* = 7.8 Hz, 2H, aromatic *H*), 4.26 (q, *J* = 6.4 Hz, 1H, CHCH₃), 2.62–2.48 (m, 2H (NCH₂), 2.48–2.30 (m, 2H, NCH₂), 2.07–1.76 (m, 4H, F₁₇C₈CH₂), 1.62–1.46 (m, 4H, NCH₂CH₂), 1.33 (d, *J* = 6.4 Hz, 3H, CHCH₃), 0.98–0.76 (m, 4H, F₁₇C₈CH₂CH₂), 0.24 (s, 9H, SiSi(CH₃)₃), –0.01 (s, 3H, SiCH₃). ¹³C NMR C₆D₆ 60 °C: δ 151.9, 141.2, 132.4,

131.3 and 128.5 (aromatic C), 61.5 (CHCH₃), 52.4 (NCH₂), 26.0 (t, (*J*_{F–C} = 24 Hz, FCCH₂), 23.7 (NCH₂CH₂), 22.4 (CHCH₃), 3.6 (SiCH₂), 1.1 (SSiCCH₃), –6.6 (SiCH₃).

5.1.3. Preparation of the lithium thiolate **2c**

The same procedure as described for **2b** was used, except that FC-72 (4 mL) was added before the addition of *tert*-butyllithium. The reaction mixture was stirred for 48 h followed by the addition of elemental sulfur. After evaporation of the solvents a sticky brown wax was obtained in nearly quantitative yield.

2c MALDI-TOF-MS, *m/z* 1578 [M+H]⁺ (calc. 1577). Some significant ¹H NMR data C₆D₆ 70 °C: δ 8.3 (d, 1H, aromatic H), 7.9 (s, 1H, aromatic H), 7.4 (d, 1H, aromatic H), 3.8 (q, 1H, CHCH₃).

5.2. General procedure for the preparation of zinc compounds **3a** and **3b**

To a stirred solution of zinc chloride (1.5 mmol) in diethyl ether (10 mL) was added 1.5 mL of a 1 M solution of diethylzinc in hexane. The mixture was stirred until all zinc chloride was dissolved and converted into ethylzinc chloride. Then 3 mmol of the appropriate thiolate ester in pentane (5 mL) was introduced. The reaction mixture was stirred for 2 h. The formed trimethylsilyl chloride and solvents were evaporated. The product **3a** was isolated as a white solid after recrystallization from hexane.

3a yield: 88%, mp 128 °C. ¹H NMR THF *d*₈ 59 °C: δ 7.54 (br s, 1H), 7.06 (d, *J* = 7.3 Hz, 1H and 6.92 (d, *J* = 7.3 Hz, 1H, aromatic H), 3.40 (br q, 1H, CHCH₃), 3.0–1.8 (br m, 8H, NCH₂CH₂), 1.74 (br s, 2H, CF₂CH₂), 1.64 (d, *J* = 6 Hz, 3H, CHCH₃), 0.97 (m, 2H, CH₂Si), 0.82 (t, *J* = 7.9 Hz, 3H, CH₃CH₂Zn), 0.26 (s, 6H, SiCH₃), 0.06 (q, *J* = 7.9 Hz, 2H, CH₂Zn). ¹³C NMR THF-*d*₈ 59 °C: δ 141.7, 140.2, 135.1, 129.1 and 127.6 (aromatic C), 71.2 (CHCH₃), 55.5 (CH₂N), 24.6 (t, *J*_{F–C} = 23 Hz, CF₂CH₂), 22.4 (CH₂CH₂N), 16.8 (CHCH₃), 10.6 (ZnCH₂CH₃), 3.6 (CH₂Si), –1.0 (ZnCH₂CH₃), –5.8 (SiCH₃). Anal. calc. for C₂₈H₃₀F₂₁NSSiZn: 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. IR (ATR neat, cm^{–1}) 2966 (w), 2863 (w), 1632 (w), 1203 (s), 1150 (s), 1104 (m).

3b yield: 80%, light brown wax. Anal. calc. for C₃₅H₃₁F₃₄NSSiZn: C 33.98, H 2.53, N 1.13, Si 2.27, Zn 5.28. Found: C 33.86, H 2.65, N 1.07, Si 2.30, Zn 5.17. IR (ATR neat, cm^{–1}) 2965 (w), 2792 (w), 1602 (w), 1200 (s), 1145 (s), 1113 (m).

5.3. General procedure for the preparation of zinc compound **3c**

A slightly modified procedure was used for the preparation of **3c**.

To a stirred solution of zinc chloride (1 mmol) in Et₂O (20 mL) was added 1 mL of a 1 M solution of diethylzinc in hexane. The mixture was stirred until all zinc chloride was dissolved and converted into ethylzinc chloride. Then 2 mmol of the aminoarenethiolate-lithium intermediate was introduced. The reaction mixture was stirred for 48 h. Stirring was stopped and the vessel was stored at –40 °C. The solvents were decanted from the brown wax that covered the bottom of the vessel. The wax was washed with Et₂O (10 mL) and decanted. The product **3c** was isolated as a brown wax after evaporation of the small amount of remaining solvents. Yield 50%, anal. calc. for C₄₄H₃₂F₅₁NSSiZn: C 31.66, H 1.93, N 0.84, Si 1.68, Zn 3.92. Found: C 31.72, H 2.06, N 0.78, Si 1.73, Zn 3.86. IR (ATR neat, cm^{–1}) 2969 (w), 1583 (w), 1199 (s), 1144 (s), 1113 (m).

5.4. General procedure for the FBS experiments

To a solution of 2.5 mol% of catalyst in PFMCH (6 mL) was added a 1 M solution of Et₂Zn in octane (6 mL) and freshly distilled benzaldehyde (0.5 mL). The mixture was stirred for 3 h at room temperature. Stirring was stopped and two phases were allowed to separate. The organic layer was removed as much as possible with a syringe and then poured into a saturated solution of NH₄Cl/H₂O (2 mL). To this mixture pentane (10 mL) was added. The organic layer was separated, dried, concentrated in vacuum and subsequently analyzed with ¹H NMR, GC and HPLC. This procedure presented one cycle. To the remaining perfluoro layer new portions of Et₂Zn in octane (1 M) and benzaldehyde were added. The whole procedure was repeated 5–17 times.

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