Sulfonamide Ligands from Chiral Aziridines − Application to the Titanium-Mediated Addition of Diethylzinc to Benzaldehyde

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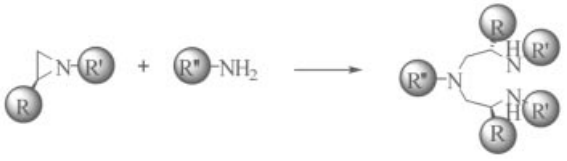
A modular approach was developed for the preparation of chiral, enantiopure sulfonamide ligands with C_1, C_2, and C_3 symmetry by ring opening of chiral *N*-sulfonylaziridines with ammonia, primary amines, and diamines. The new ligands were assessed in the titanium-mediated addition of diethylzinc to benzaldehyde, giving the product with selectivities up to 76% *ee*.

Introduction

Chiral sulfonamides are known to serve as versatile ligands for a variety of catalytic applications. Thus, high enantioselectivity has been achieved in titanium-mediated additions of diethylzinc to aldehydes catalysed by bis(sulfonamides),[1−11] copper-catalysed Michael additions of diethylzinc,[12−14] cyclopropanations[15] by zinc bis(sulfonamide) complexes,[16−25] aluminium bis(sulfonamide) catalysed ketene aldehyde[26−28] and Diels−Alder cycloadditions,[29−31] and in transfer hydrogenations of ketones catalysed by ruthenium sulfonamide complexes.[32] Furthermore, magnesium sulfonamide compounds have been successfully employed for the merged enolisation and enantioselective amination of *N*-acyloxazolidinones,[33] lanthanide sulfonamide complexes for the Mukaiyama aldol reaction,[34] and boron sulfonamides for the enantioselective allylation of aldehydes[35] and Ireland−Claisen rearrangement of esters.[36]

The sulfonamides are usually prepared in high yields by treatment of chiral amines with the appropriate sulfonyl chloride or other suitable sulfonic acid derivatives.[37−40] In order to allow for efficient screening of catalysts for the optimization of catalytic processes, it is desirable to have easy access to synthetic methods permitting facile structural variation of the ligands.[41,42] Of special interest are methods built on a modular approach, allowing the preparation of ligands in few high-yielding steps employing methods that allow simple variation of ligand structures.

We have recently applied nucleophilic ring opening of chiral activated aziridines for the preparation of ligands carrying sulfonamido functionalities.[43,44] The required aziridines are conveniently accessible from amino alcohols,[45,46] in turn obtained from synthetic or naturally occurring amino acids. We realized that this synthetic method should permit extensive facile structural variations as suitable building blocks can be combined in various ways. Thus, amines with various structures can be used for the ring opening of aziridines with different substituents in 2-position and different *N*-activating groups (Scheme 1). With this synthetic methodology efficient screening of the ligands as catalysts should be possible.



Scheme 1

To test the usefulness of this idea, the methodology previously developed has now been extended to include new types of primary amines, primary amines carrying additional functional groups, primary diamines, and ammonia. We present here the synthesis of a range of ligands, most of which on the experimental timescale have C_2 symmetry, with the chirality due to the presence of stereogenic centres, axes or planes together with an improved procedure for previously described C_3-symmetric ligands.[44] The new ligands were assessed as catalysts in the titanium-mediated addition of diethylzinc to benzaldehyde.

Results and Discussion

Preparation of Ligands

Aziridines with electron-withdrawing groups on the nitrogen atom readily undergo ring opening when treated with nucleophiles.[45,46] The nucleophilic attack generally

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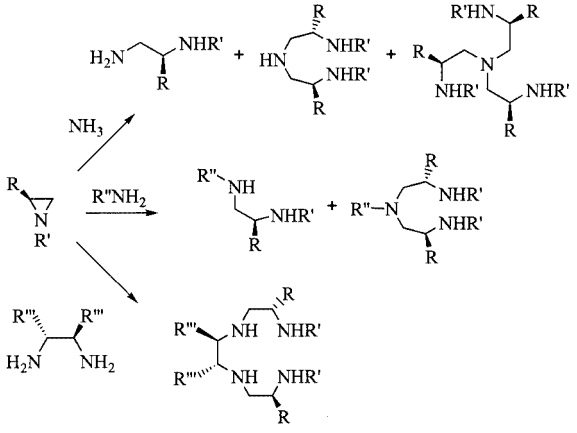
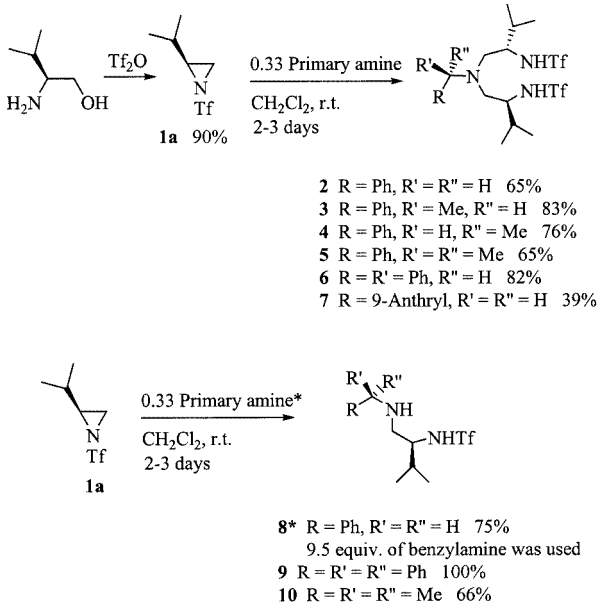
occurs at the sterically least hindered carbon atom. Secondary amines yield monosulfonamides by reaction with 1 equiv. of the corresponding aziridine,[47,48] while monosulfonamides,[47−51] as well as bis(sulfonamides) may be isolated from reactions with primary amines.[43,52−54] Reaction of 3 equiv. of the aziridine with ammonia yields C_3-symmetric tris(sulfonamides),[44] but the reactions can be stopped after the introduction of merely 1[55] or 2 equiv. of the aziridine, and thus afford mono- as well as bis(sulfonamides) (Scheme 2). Furthermore, from diamines tetradentate amines are accessible by reaction with 2 equiv. of the aziridine; reaction with additional aziridine was not observed. Occasionally, a Lewis acid is employed in order to accelerate the process. Thus, for example ytterbium(III) triflate has been used for the ring opening of *N*-tosylaziridines with primary and secondary amines.[56]

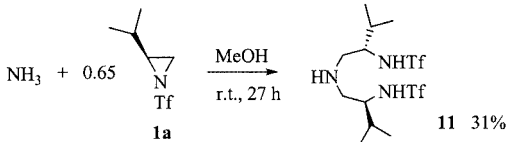


Scheme 2

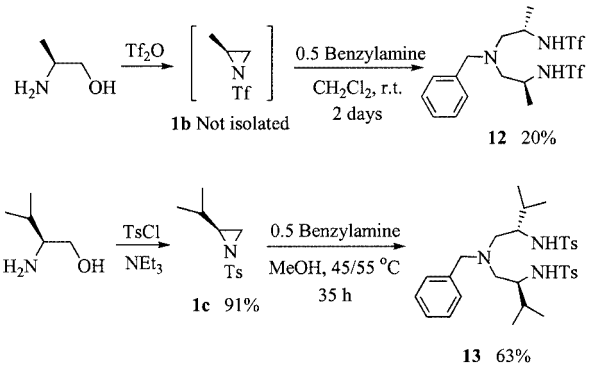
The reaction of benzylamine with 2 equiv. of (*S*)-2-isopropyl-*N*-(trifluoromethylsulfonyl)aziridine (**1a**) has previously been shown to yield bis(sulfonamide) **2**,[43] which serves as a versatile ligand in the titanium-mediated addition of diethylzinc to benzaldehyde,[43,57] as well as in the aluminium-catalysed ketene aldehyde cycloadditions.[26,27] The synthetic approach used for the preparation of **2** allows for wide structural variations of the product, as both aziridines with different substituents and a variety of primary amines can be used in the process. Thus, ligand **3**, containing an additional stereocentre, was prepared in the same manner as **2** by exchanging benzylamine for (*R*)-1-phenylethylamine (Scheme 3). Highest yield (83%) was obtained when dichloromethane was used as solvent, acetonitrile, methanol, and *tert*-butyl alcohol/2-propanol (70:30) providing the same compound in yields of 63, 58, and 64%, respectively. However, the reaction was considerably slower in dichloromethane, requiring a reaction time of about 40 h for completion, compared to around 16 h for the other three solvent systems. In the alcoholic solvents, small amounts of a by-product resulting from ring opening of the aziridine by the solvent were formed. Use of (*S*)-1-phenylthylamine as the nucleophile gave the diastereomer **4** in 76% yield. Ligands **5**−**7**, with more bulky substituents at the benzylic position, were obtained from the reaction of **1a** with 1-methyl-1-phenylethylamine, 1,1-diphenylmethylamine, and (9-anthrylmethyl)amine in 65, 82, and 39% yield, respectively. It was interesting to note that the ring-opening reaction could be stopped after the addition of 1 equiv. of the aziridine, provided that a large excess of amine was used.[55] Thus, the reaction using an excess of benzylamine (9.5 equiv.) resulted in the mono- and bis(adducts) **8** and **2** in a ratio of 10:1. In contrast, when bulky amines such as tritylamine or *tert*-butylamine were employed, no bis(adducts) were formed and the reaction stopped after the first step, allowing the isolation of the monoadducts **9** and **10** in 100 and 66% yield, respectively. Starting from ammonia, conditions favouring mono- or tris(adduct) formation can be found, using an excess of either ammonia or the aziridine, but a problem arises when the bis(adduct) is the desired product. However, the bis(adduct) **11** was obtained as the major product in 31% yield by using 0.65 equiv. of aziridine **1a**, together with 21% of the C_1-symmetric mono- and 8% of the C_3-symmetric tris(adduct) (Scheme 4). Compound **12** was obtained in a one-pot reaction starting from (*S*)-alaninol by the ring opening of aziridine **1b** in 20% yield [based on (*S*)-alaninol]; aziridine **1b** is susceptible to polymerization and has to be treated in situ directly after preparation. (*S*)-2-Isopropyl-*N*-tosylaziridine (**1c**) is less reactive than the corresponding *N*-trifluoromethylsulfonyl analogue **1a** and heating at 55 °C in methanol was required for its reaction with benzylamine to form bis(adduct) **13** (Scheme 5).



Scheme 3

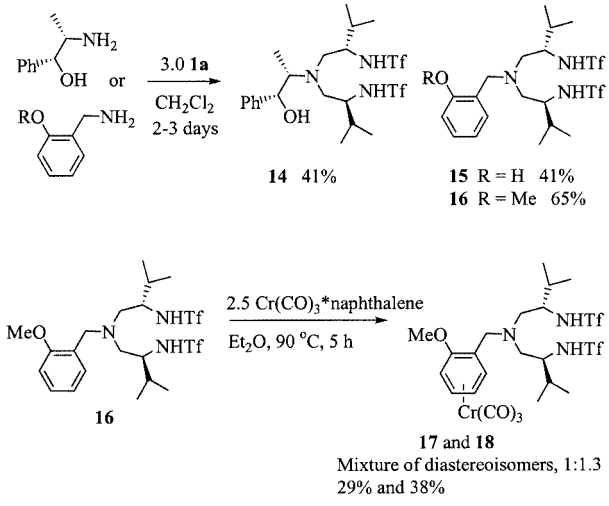


Scheme 4



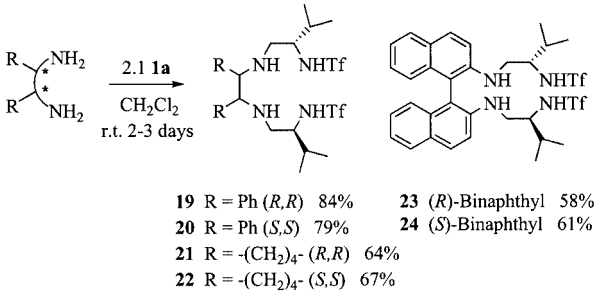
Scheme 5

Next, ligands containing additional functional groups were prepared. Compound **14** was obtained by treatment of **1a** with (−)-norephedrine, whereas **15** and **16** were prepared analogously using 2-hydroxy- and 2-methoxybenzylamine, respectively, as nucleophile (Scheme 6). As the latter ligands contain a prostereogenic aryl group, the preparation of ligands possessing planar chirality is possible. Upon reaction with tricarbonyl(naphthalene)chromium,[58] **16** afforded two diastereomeric chromium compounds with planar chirality, **17** and **18**. The diastereomers, which were obtained as best in a ratio of 1:1.33, could be separated by column chromatography to yield the pure stereoisomers. The complexes were unstable and gave rise to broad signals in their NMR spectra, which unfortunately hampered their characterization.



Scheme 6

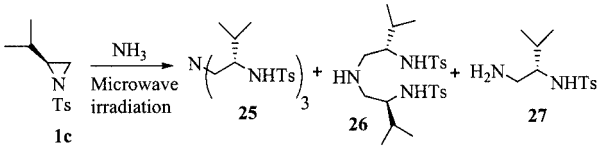
The present methodology could also be employed for the preparation of tetradentate ligands by exchanging the primary amines for C_2-symmetric primary diamines. Thus, from (*R*,*R*)- and (*S*,*S*)-1,2-diamino-1,2-diphenylethane diastereomeric ligands **19** and **20** were obtained in 84 and 79% yield, respectively, whereas the two enantiomers of 1,2-diaminocyclohexane afforded **21** and **22** in 64 and 67% yield, respectively (Scheme 7). Finally, tetradentate ligands with axial chirality, **23** and **24**, were obtained from (*R*)- and (*S*)-binaphthylamine in 58 and 61% yield, respectively, showing



Scheme 7

that these aromatic amines are sufficiently reactive to open **1a**. No further reaction of the secondary amine moieties in compounds **19**−**24** was observed, probably due to steric hindrance.

Exchanging the primary amines for ammonia gives access to C_3-symmetric tripodal tris(sulfonamides) (Scheme 8).[44] These ligands were previously obtained by reaction of the aziridine with ammonia in methanol in a rather sluggish process, tosyl derivative **25** requiring 4 d at 50 °C for completion (70% yield). We have now developed an improved procedure, resulting in higher yield within shorter time, employing microwave irradiation.[59] It was found that after 30 min at 160 °C, a 3.1:1 ratio of aziridine **1c** and ammonia afforded **25** in 60% yield along with 16 and 20% of the bis- and the mono(tosyl)amines **26** and **27** (Table 1, Entry 1). Extending the reaction time to 75 min did not significantly improve the yield of **25** (61%, Entry 2). Use of larger amounts of the aziridine relative to ammonia resulted in higher yields of the product, however. Thus, reactions at 160 °C between **1c** and ammonia in ratios of 3.5:1 and 4:1 gave **25** in 68 and 77% yield after 45 min along with decreasing amounts of bis- and mono(tosyl)amines. Using a ratio of 4:1 and extending the reaction time to 75 min improved the yield of **25** to 85% (Entry 5), while an increase



Scheme 8

Table 1. Microwave-assisted ring opening of aziridine **1c** with ammonia at 160 °C (Scheme 8)

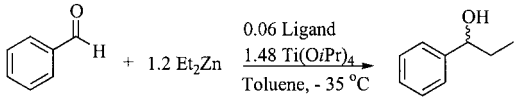
Entry	Time [min]	**1c**/NH_3	**25** [%][a]	**26** [%][a]	**27** [%][a]
1	30	3.1:1	60	16	20
2	75	3.1:1	61	14	23
3	45	3.5:1	68	7	15
4	45	4:1	77[b]	–	9
5	75	4:1	85	6	7
6	45	4.5:1	88[c]	–	–

[a] Isolated yields. [b] 13% of **1c** was recovered. [c] 12% of **1c** was recovered.

of the ratio to 4.5:1 afforded the best yield, 88%, after 45 min at 160 °C.

Titanium-Mediated Addition of Diethylzinc to Benzaldehyde

In order to assess the importance of the structure of the sulfonamide ligands for the outcome in a catalytic application, the addition of diethylzinc to benzaldehyde in the presence of $Ti(OiPr)_4$ was investigated (Scheme 9). We have previously demonstrated that the enantioselectivity as well as the reactivity vary considerably with the reaction conditions.[57] The amount of $Ti(OiPr)_4$ employed in the process was found to be particularly crucial. In the present study, the conditions found to result in highest enantioselectivity of the product for ligand **2** were employed, although optimal conditions probably have to be determined for each particular ligand. Thus, best conditions for ligand **2** were previously found to be a ligand/$Ti(OiPr)_4$/Et_2Zn ratio of 0.06:1.48:1.20, affording a 90% yield of the (*S*) product with 72% *ee* within 45 min at −35 °C (Entry 1, Table 2). The introduction of a methyl group, and thus an additional ste-



Scheme 9

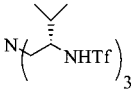
Table 2. Titanium-mediated addition of diethylzinc to benzaldehyde (Scheme 9)

Entry	Ligand	Time[a] [h]	*ee* [%][b] (abs. conf.)	Yield[b] [%]	Conversion[b] [%]	Conversion[c] 15 min [%]
1	**2**	0.75	72 (*S*)	90	97	90
2	**3**	0.25	75 (*S*)	97	97	97
3	**4**	0.25	76 (*S*)	93	99	99
4	**5**	0.25	48 (*S*)		42	
5	**5**	1	55 (*S*)		89	
6	**5**[d]	2.5	56 (*S*)	91	95	42
7	**6**	0.25	69 (*S*)	93	96	96
8	**7**	0.25	56 (*S*)		73	
9	**7**	1.25	63 (*S*)		96	
10	**7**	2.33	63 (*S*)	98	98	73
11	**11**	0.25	0		44	
12	**11**	1.33	8 (*S*)		94	
13	**11**	2.7	10 (*S*)	100	100	44
14	**8**	19	3 (*S*)	88	95	6
15	**12**	0.25	7 (*S*)		11	
16	**12**	1.5	17 (*S*)		67	
17	**12**	3.5	23 (*S*)		89	
18	**12**	19.3	19 (*S*)	97	100	11
19	**13**	0.25	31 (*R*)		18	
20	**13**	1	49 (*R*)		65	
21	**13**	4.5	50 (*R*)	99	99	18
22	**14**	0.25	41 (*S*)		30	
23	**14**	18	29 (*S*)	92	96	30
24	**15**[e]	4.5	20 (*S*)	90	93	22
25	**16**	1.67	61 (*S*)	90	98	86
26	**17**	1.67	65 (*S*)	78	95	74
27	**18**	1.67	65 (*S*)	78	94	76
28	**19**	0.25	80 (*R*)		29	
29	**19**	1.67	65 (*R*)		73	
30	**19**[e]	5	59 (*R*)	79	87	29
31	**20**[e]	5.25	12 (*R*)	87	87	27
32	**21**[f]	18.25	0	89	94	5
33	**22**	18	0	95	95	4
34	**23**	3.67	9 (*R*)	83	92	25
35	**24**	3.33	5 (*R*)	84	93	35
36	**25**	0.25	25 (*R*)		20	
37	**25**	18	31 (*R*)	91	96	20
38	**28**	0.25	17 (*R*)		29	
39	**28**	1.75	9 (*S*)		91	
40	**28**	2.67	10 (*S*)		95	
41	**28**[g]	3.3	11 (*S*)	89	97	29

[a] Reaction time at −35 °C. [b] Determined by chiral GLC. [c] Determined by chiral GLC after 15 min at −35 °C. [d] 12% *ee* of the (*S*) product was obtained at 14% conversion after 15 min when the reaction was performed in THF (THF was used to solubilize the ligand). [e] 5% of the ligand was used. [f] Similar results were obtained when THF was used as the solvent (in which the ligand is completely soluble). [g] THF (0.30 mL) was added to dissolve the ligand.

reogenic centre, at the benzylic position had only a minor effect on the enantioselectivity, the absolute configuration at that centre also being of minor importance (**3** and **4**, Entries 2 and 3, Table 2). The reactions catalysed by ligands **3** and **4** turned out to be slightly faster than the reaction catalysed by **2** and full conversion was achieved after only 15 min at −35 °C. A lower selectivity, 48% *ee*, was observed when the sterically more demanding ligand **5**, containing one additional methyl group at the benzylic position, was employed as a catalyst, although the selectivity increased slightly over time (to 56% *ee*, Entries 4−6). Due to the poor solubility of the ligand in toluene, the reaction was also run in THF. In this solvent a lower *ee* (12%) was observed, however. The reason for the increase in enantioselectivity over time is unclear, but it has been previously observed that the addition of for example chiral alcohols affects the stereoselectivity of the reaction.[57] That steric bulk in the side chain did not improve the stereoselectivity was further demonstrated by use of ligand **6** (69% *ee*, Entry 7), which bears two phenyl groups at the benzylic position, and ligand **7** (63% *ee*, Entry 10), which contains an anthracene group at the same position. The reaction catalysed by ligand **6** proved to be as fast as those catalysed by **3** and **4**, and full conversion was achieved after 15 min. For ligand **7** a small change in the enantioselectivity over time was observed (from 56 to 63% *ee*, Entries 8−10). The absence of a side chain had a detrimental effect on the selectivity, as shown by ligand **11** (10% *ee*, Entries 11−13). Likewise, the absence of one coordinating arm resulted in a ligand exhibiting poor enantioselectivity and low reaction rate (**8**, 3% *ee*, Entry 14). Ligand **12**, derived from aziridine **1b**, induced considerably lower enantioselectivity (19% *ee*) in the catalytic reaction than the isopropyl analogue **2** (72% *ee*), although the selectivity increased over time, and the reaction was slower (Entries 15−18). A slow catalytic process was also observed for the bis(tosylated) ligand **13** (Entries 19−21), which, surprisingly, afforded a product with a configuration opposite to that obtained using the *N*-trifluoromethylsulfonyl ligands. Also when ligand **13** was employed in the catalytic reaction the enantioselectivity increased over time (from 31 to 50% *ee*). The presence of a hydroxy group seemed to be unfavourable for the stereoselectivity, as use of ligands **14** and **15** resulted in formation of products with moderate enantioselectivity (29 and 20% *ee*, Entries 23 and 24, respectively). Higher selectivity was achieved when *O*-methyl-substituted derivative **16** was used (61% *ee*, Entry 25). One reason might be that the hydroxy functions take part in coordination to the metal ion, thereby changing the structure of the catalytic intermediates in an unfavourable manner. The diastereomeric chromium complexes **17** and **18** afforded results very similar to those of **16** (65% *ee*, Entries 26 and 27). This might be due to instability of the complexes or that the planar chirality is situated too remote from the catalytic centre.

Major differences in the selectivity were observed between diastereomers of the tetradentate ligands. Use of ligand **19**, synthesised from (*R*,*R*)-1,2-diamino-1,2-diphenylethane, resulted in quite high enantioselectivity in the initial part of the reaction (80% *ee* at 29% conversion, Entry 28), but the enantiomeric excess decreased as the reaction proceeded (59% *ee* at 87% conversion, Entry 30). The diastereomer **20** gave a product with the same absolute configuration, although the enantioselectivity was lower (12% *ee*, Entry 31). 1,2-Diaminocyclohexane derivatives **21** and **22** afforded racemic products, and binaphthyl ligands **23** and **24** exhibited low selectivity, (9 and 5% *ee*, respectively, Entries 34 and 35). It is interesting to note that ligands derived from diamines, e.g. **19**, **20**, **23**, and **24**, gave the (*R*) enantiomer of the product, and that the absolute configuration thus is determined by the configuration of the part in the ligand originating from aziridine **1a**. Finally, the C_3-symmetric ligands **25** and **28** exhibited low selectivity in the catalytic reaction. In analogy to what was observed for ligands **2** and **13**, the tosyl derivative gave a product where the (*R*) enantiomer dominated (31% *ee*) whereas the trifluoromethylsulfonyl-substituted ligand gave a product where the (*S*) enantiomer dominated (11% *ee*), although the (*R*) product dominated at low conversion (Entries 38−41).



28 53%

Conclusion

A large variety of sulfonamide ligands were prepared by ring opening of aziridines with amines. The methodology developed gives access to libraries useful for optimization of catalytic processes. Use of the ligands in the titanium-mediated addition of diethylzinc to benzaldehyde demonstrated that the substitution pattern had a profound effect on the enantioselectivity and the rate of the catalytic reaction. Bis(sulfonamides) prepared from primary amines had properties superior to bis(sulfonamides) prepared from ammonia and also to a ligand prepared from a primary amine and 1 equiv. of the aziridine. Furthermore, ligands derived from aziridines bearing an isopropyl group induced higher selectivity than those derived from aziridines bearing a methyl substituent. Tetradentate ligands obtained from diamines were inferior to bis(sulfonamides) obtained from monoamines. Ligands containing a hydroxy group did not lead to improved results in the catalytic reaction. Finally, use of a tosylamide resulted in a product with different absolute configuration than that obtained using and the analogous trifluoromethylsulfonamide. With these ligands in hand, other catalytic processes are to be tested.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DMX 500 instrument or with a Bruker Avance 400 instrument at 25 °C in $CDCl_3$, using the residual signals from $CHCl_3$ (^{1}H: δ = 7.26 ppm; ^{13}C: δ = 77.2 ppm) as internal standard. Optical rotations were recorded with a Perkin−Elmer 343 polarimeter at the

sodium D line at ambient temperature. Analytical TLC was performed on SDS silica gel 60 F_{254} plates. The plates were visualized using a 5% ethanolic solution of phosphomolybdic acid. Flash chromatography and MPLC (medium pressure liquid chromatography) were carried out using SDS silica gel 60 (40−63 μm). Melting points are uncorrected and were determined in open capillary tubes using an Electrothermal instrument. Microwave heating was performed in a SmithCreator™ single-mode microwave cavity from Personal Chemistry AB, Sweden. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. Enantiomeric excesses and yields were determined by GLC using a Chrompack CP-cyclodextrin β-2,3,6-M-19 50-m column [110−140 °C, 2 °C/min, 5 min at 140 °C, 20 psi, benzaldehyde *t*: 8.6 min, naphthalene (external standard) *t*: 14.7 min, (*R*) enantiomer t_R: 18.0 min, (*S*) enantiomer t_S: 18.3 min]. The assignment of the absolute configuration of (*R*)- and (*S*)-1-phenylpropanol was made according to our previous work.[43] All reactions were perfomed in flame-dried glassware under argon. Toluene, THF, and diethyl ether were distilled from Na/benzophenone and CH_2Cl_2 was distilled from CaH_2. Benzaldehyde and $Ti(OiPr)_4$ were freshly distilled prior to use. A 1.1 M solution of Et_2Zn in toluene was used. All amines were obtained from Aldrich, Lancaster or Tokyo Kasei (1-methyl-1-phenylethylamine) and used as received except for (9-anthrylmethyl)amine which was prepared according to a literature procedure,[60] and 2-(aminomethyl)phenol which was prepared from 2-cyanophenol by a procedure similar to that published.[61] The concentration of the ammonia in methanol solution was determined by titration using a 0.0978 N solution of HCl with methyl red as indicator. Aziridine **1a** was prepared according to our published method, except that ice-cold solutions of 0.1 M HCl and Na_2CO_3 (sat.) were used during a fast workup procedure;[44] **1a** is quite unstable and was therefore used directly without further purification. Aziridine **1b** was prepared by the same procedure as that used for **1a** but polymerized upon evaporation of the solvent; it should therefore be used in situ. Aziridine **1c** was prepared in a similar way to that described in the literature.[52] Compounds **2**[43] and **28**[44] were prepared by our previous methods.

General Procedure for the Preparation of Compounds 3−7, 9−10, and 14−16: The amine (1.03 mmol) was added to a 10-mL flask and dissolved in dichloromethane (0.80 mL). The solution was cooled to 0 °C and aziridine **1a** (0.80 g, 3.68 mmol, ca. 85% pure according to ^{1}H NMR) was added dropwise. The cooling bath was removed after 30 min and the mixture was stirred at room temperature for 48−72 h. SiO_2 (5 g) and dichloromethane (10 mL) were added, the solvent was evaporated and the residue was purified by chromatography.

General Procedure for the Preparation of Compounds 19−24: The same procedure as that described above was used, except that 2.5 mmol of **1a** (ca 85% pure) per mmol of diamine was used.

Compound 3: Purification by MPLC (gradient 1−40% EtOAc in hexanes) followed by recrystallization from a mixture of EtOAc/hexanes gave colourless crystals. Yield: 83%. M.p. 136−138 °C. $[\alpha]_D^{20} = -45.7$ (*c* = 0.74, MeOH). $R_f = 0.38$ (20% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.72 (d, ^3J = 7.0 Hz, 6 H, *i*Pr CH_3), 0.98 (d, ^3J = 6.9 Hz, 6 H, *i*Pr CH_3), 1.44 (d, ^3J = 6.9 Hz, 3 H, CHC*H*$_3$), 2.01−2.07 [m, 2 H, C*H*$(CH_3)_2$], 2.36 (dd, ^2J = 13.6, ^3J = 7.0 Hz, 2 H, NCH*H*), 2.62 (dd, ^2J = 13.5, ^3J = 7.8 Hz, 2 H, NC*H*H), 3.59−3.63 (m, 2 H, C*H*NHTf), 4.08 (q, ^3J = 6.9 Hz, 1 H, $C_{benzylic}$H), 5.20 (br. s, 2 H, N*H*Tf), 7.20 (d, ^3J = 7.1 Hz, 2 H, H_{ortho}), 7.28 (t, ^3J = 7.3 Hz, 1 H, H_{para}), 7.35 (app t, ^3J = 7.1 Hz, 2 H, H_{meta}) ppm. ^{13}C NMR (125.8 MHz) 15.4, 16.8, 18.8, 29.6, 51.2, 57.2, 58.6, 119.8 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 128.0, 128.69, 128.71, 140.0 ppm. $C_{20}H_{31}F_6N_3O_4S_2$ (555.60): calcd. C 43.24, H 5.62, N 7.56; found C 43.09, H 5.61, N 7.40.

Compound 4: For purification, see ligand **3**. Colourless crystals. Yield: 76%. M.p. 157−158 °C. $[\alpha]_D^{20} = -47.7$ (*c* = 0.61, MeOH). $R_f = 0.43$ (20% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.85 (d, ^3J = 7.0 Hz, 6 H, *i*Pr CH_3), 0.87 (d, ^3J = 7.1 Hz, 6 H, *i*Pr CH_3), 1.34 (d, ^3J = 7.0 Hz, 3 H, CHC*H*$_3$), 2.02 [d of sept, ^3J = 7.0, ^3J = 3.9 Hz, 2 H, C*H*$(CH_3)_2$], 2.51 (ABX system, ^2J = 13.7, ^3J = 10.8 Hz, 2 H, NCH*H*), 2.53 (ABX system, ^2J = 13.7, ^3J = 7.9 Hz, 2 H, NC*H*H), 3.59−3.64 (m, 2 H, C*H*NHTf), 4.22 (q, ^3J = 6.8 Hz, 1 H, $C_{benzylic}$H), 4.99 (br. s, 2 H, NHTf), 7.29 (t, ^3J = 7.3 Hz, 1 H, H_{para}), 7.38 (app t, ^3J = 7.5 Hz, 2 H, H_{meta}), 7.47 (d, ^3J = 7.5 Hz, 2 H, H_{ortho}) ppm. ^{13}C NMR (125.8 MHz) 10.4, 17.4, 18.0, 30.3, 50.2, 56.7, 58.1, 119.7 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 128.1, 128.9, 129.0, 142.0 ppm. $C_{20}H_{31}F_6N_3O_4S_2$ (555.60): calcd. C 43.24, H 5.62, N 7.56; found C 43.43, H 5.77, N 7.56.

Compound 5: For purification, see ligand **3**. White crystals. Yield 65%. M.p. 142.5−143 °C. $[\alpha]_D^{20} = -16.6$ (*c* = 0.37, MeOH). R_f = 0.56 (20% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.66 (d, ^3J = 6.9 Hz, 6 H, *i*Pr CH_3), 0.89 (d, ^3J = 6.9 Hz, 6 H, *i*Pr CH_3), 1.43 (s, 3 H, $C_{benzylic}CH_3$), 1.45 (s, 3 H, $C_{benzylic}CH_3$), 2.18 [d of sept, ^3J = 6.9, ^3J = 2.2 Hz, 2 H, C*H*$(CH_3)_2$], 2.61 (ABX system, ^2J = 14.0, ^3J = 6.3 Hz, 2 H, NCH*H*), 2.65 (ABX system, ^2J = 14.0, ^3J = 8.6 Hz, 2 H, NC*H*H), 3.47−3.50 (m, 2 H, C*H*NHTf), 4.55 (br. s, 2 H, NHTf), 7.25 (t, ^3J = 7.2 Hz, 1 H, H_{para}), 7.35 (app t, ^3J = 7.5 Hz, 2 H, H_{meta}), 7.47 (d, ^3J = 7.6 Hz, 2 H, H_{ortho}) ppm. ^{13}C NMR (125.8 MHz) 15.8, 18.7, 23.9, 25.7, 27.9, 54.8, 60.9, 62.3, 119.5 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 123.3, 126.6, 127.4, 128.8, 148.0 ppm. $C_{21}H_{33}F_6N_3O_4S_2$ (569.63): calcd. C 44.28, H 5.84, N 7.38; found C 44.35, H 5.85, N 7.30.

Compound 6: MPLC (gradient 1−40% EtOAc in hexanes) gave a white powder. Yield. 82%. M.p. 134.5−135.5 °C. $[\alpha]_D^{20} = 5.3$ (*c* = 0.34, MeOH). R_f = 0.40 (20% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.70 (d, ^3J = 7.0 Hz, 6 H, CH_3), 0.82 (d, ^3J = 6.9 Hz, 6 H, CH_3), 1.95−2.00 [m, 2 H, C*H*$(CH_3)_2$], 2.61 (dd, ^2J = 13.6, ^3J = 5.1 Hz, 2 H, NCH*H*), 2.74 (dd, ^2J = 13.6, ^3J = 9.7 Hz, 2 H, NC*H*H), 3.64−3.65 (m, 2 H, C*H*NHTf), 5.12 (br. s, 2 H, NHTf), 5.30 (s, 1 H, $CH_{benzylic}$), 7.27−7.37 (m, 6 H, $H_{aromatic}$), 7.38−7.42 (m, 4 H, $H_{aromatic}$) ppm. ^{13}C NMR (125.8 MHz) 17.4, 17.5, 30.3, 51.4, 58.2, 68.5, 122.0 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 127.8, 128.0, 128.8, 128.9, 129.6, 129.7, 138.3, 140.2 ppm. $C_{25}H_{33}F_6N_3O_4S_2$ (617.67): calcd. C 48.61, H 5.39, N 6.80; found C 48.64, H 5.56, N 6.60.

Compound 7: Flash chromatography (2.5% EtOAc in hexanes) followed by recrystallisation from first toluene/hexanes and then EtOAc/hexanes gave a white powder. Yield: 39% (along with 23% of the monoadduct). M.p. 157−159 °C. $[\alpha]_D^{20} = -44.4$ (*c* = 0.47, MeOH). R_f = 0.43 (10% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 0.38 (d, ^3J = 7.0 Hz, 6 H, C*H*$_3$), 0.75 (d, ^3J = 6.9 Hz, 6 H, CH_3), 1.86 [d of sept, ^3J = 7.0, ^3J = 3.1 Hz, 2 H, C*H*$(CH_3)_2$], 2.66 (ABX system, ^2J = 13.4, ^3J = 5.8 Hz, 2 H, NCH*H*), 2.69 (ABX system, ^2J = 13.4, ^3J = 4.6 Hz, 2 H, NC*H*H), 3.60−3.66 (m, 2 H, C*H*NHTf), 4.58 (d, ^2J = 12.8 Hz, 1 H, $C_{benzylic}$*H*H), 4.73 (d, ^2J = 12.8 Hz, 1 H, $C_{benzylic}$H*H*), 4.76 (br. s, 2 H, NHTf), 7.50 (app dt, ^3J = 7.3, ^4J = 0.8 Hz, 2 H, $H_{anthryl}$), 7.58 (app dt, ^3J = 8.1, ^4J = 1.5 Hz, 2 H, $H_{anthryl}$), 8.02 (br. d, ^3J = 8.4 Hz, 2 H, $H_{anthryl}$), 8.34 (br. d, 2 H, $H_{anthryl}$), 8.47 (s, 1 H, $H_{anthryl}$) ppm. ^{13}C NMR (125.8 MHz) 15.9, 18.8, 28.9, 51.4, 56.6, 58.9, 119.8 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 124.6, 125.5, 126.9, 128.2, 128.8, 129.7, 131.7, 131.7 ppm.

Compound 8: Benzylamine (2.50 mL, 22.9 mmol) was disolved in MeOH (2.5 mL). The solution was cooled to 0 °C and aziridine **1a** (0.62 g, 2.85 mmol, ca 85% pure) was added dropwise during 20 min. After 1 h, the reaction mixture was brought to room temperature and stirred for 20 h. The benzylamine was distilled off and the crude mixture was concentrated onto 3 g of silica and purified by MPLC (gradient 1−100% EtOAc in hexanes) giving (0.59 g, 1.82 mmol) of a white powder. Yield: 75%. M.p. 126 °C. $[\alpha]_D^{20}$ = −5.4 (c = 0.63, MeOH). R_f = 0.59 (80% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 0.93 (d, ^3J = 6.8 Hz, 3 H, CH_3), 0.98 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.85−1.94 [m, 1 H, C*H*$(CH_3)_2$], 2.67 (dd, ^2J = 12.9, ^3J = 4.8 Hz, 1 H, NCH*H*), 2.91 (dd, ^2J = 12.9, ^3J = 4.7 Hz, 1 H, NC*H*H), 3.31−3.36 (m, 1 H, C*H*NHTf), 3.42 (br. s, 2 H, NHTf and NH), 3.78 (AB q, ^2J = 13.3 Hz, 1 H, $C_{benzylic}$*H*H), 3.81 (AB q, ^2J = 13.3 Hz, 1 H, $C_{benzylic}$H*H*), 7.27−7.37 (m, 5 H, $H_{aromatic}$) ppm. ^{13}C NMR (100.6 MHz) 19.0, 19.4, 30.8, 49.3, 54.4, 61.6, 120.1 (q, $^1J_{C,F}$ = 321 Hz, CF_3), 127.8, 128.5, 129.0, 139.8 ppm. $C_{13}H_{19}F_3N_2O_2S$ (324.36): calcd. C 48.14, H 5.90, N 8.64; found C 48.28, H 5.89, N 8.54.

Compound 9: MPLC (gradient 1−80% EtOAc in hexanes) followed by recrystallization from EtOAc/hexanes gave a white powder. Yield: 100%. M.p. 116.5−119.5 °C. $[\alpha]_D^{20}$ = −6.4 (c = 0.57, MeOH). R_f = 0.77 (20% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.75 (d, ^3J = 6.8 Hz, 3 H, CH_3), 0.91 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.87 [app oct, 1 H, C*H*$(CH_3)_2$], 2.20 (dd, ^2J = 12.5, ^3J = 5.3 Hz, 1 H, NCH*H*), 2.45 (br. d, ^2J = 11.8 Hz, 1 H, NC*H*H), 3.37 (br. s, 1 H, C*H*NHTf), 5.15 (br. s, 1 H, NHTf), 7.21 (t, ^3J = 7.3 Hz, 3 H, $H_{aromatic}$), 7.29 (t, ^3J = 8.0 Hz, 6 H, $H_{aromatic}$), 7.45 (d, ^3J = 7.4 Hz, 6 H, $H_{aromatic}$) ppm. ^{13}C NMR (125.8 MHz) 18.7, 18.8, 30.5, 45.1, 62.0, 70.8, 119.8 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 126.8, 128.2, 128.4, 145.4 ppm.

Compound 10: MPLC (gradient 2.5−100% EtOAc in hexanes) gave a white powder. Yield: 66%. M.p. 166−168 °C. $[\alpha]_D^{20}$ = −32.9 (c = 0.49, MeOH). R_f = 0.22 (80% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.94 (d, ^3J = 6.8 Hz, 3 H, *i*Pr CH_3), 1.02 (d, ^3J = 6.8 Hz, 3 H, *i*Pr CH_3), 1.18 (s, 9 H, *t*Bu CH_3), 1.78 [app oct, ^3J = 6.9 Hz, 1 H, C*H*$(CH_3)_2$], 2.74 (dd, ^2J = 12.4, ^3J = 4.3 Hz, 1 H, NCH*H*), 2.95 (dd, ^2J = 12.5, ^3J = 5.7 Hz, 1 H, NC*H*H), 3.22−3.26 (m, 1 H, C*H*NHTf), 3.59 (br. s, 2 H, NH and NHTf) ppm. ^{13}C NMR (125.8 MHz) 20.7, 21.3, 29.1, 33.2, 44.7, 54.8, 60.8, 119.6 (q, $^1J_{C,F}$ = 314 Hz, CF_3) ppm. $C_{10}H_{21}F_3N_2O_2S$ (290.35): calcd. C 41.37, H 7.29, N 9.65; found C 41.36, H 7.36, N 9.64.

Compound 11: Aziridine **1a** (0.52 g, 2.39 mmol, ca 85% pure) was added dropwise to ammonia in methanol (1.6 mL of a 2.0 M solution, 3.2 mmol) in a 10-mL flask at 0 °C. The cooling bath was removed after 1 h and the mixture was stirred at room temperature for 27 h. The crude mixture was concentrated onto 2 g of silica and purified by MPLC (gradient 1−100% EtOAc in hexanes) giving 0.139 g (0.31 mmol) of a white powder. Yield: 31% [along with 21% of the mono- and 8% of the tris(adduct)]. M.p. 107−109 °C. $[\alpha]_D^{20}$ = −7.2 (c = 0.47, MeOH). R_f = 0.67 (80% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 0.98 (d, ^3J = 6.8 Hz, 6 H, CH_3), 0.99 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.85 [oct, ^3J = 6.8 Hz, 2 H, C*H*$(CH_3)_2$], 2.78 (ABX system, ^2J = 13.0, ^3J = 4.2 Hz, 2 H, NCH*H*), 2.82 (ABX system, ^2J = 13.0, ^3J = 6.7 Hz, 2 H, NC*H*H), 3.33−3.38 (m, 2 H, C*H*NHTf) ppm; NHTf and NH signals were not visible. ^{13}C NMR (100.6 MHz) 19.0, 19.4, 30.9, 51.6, 61.9, 119.9 (q, $^1J_{C,F}$ = 320 Hz, CF_3) ppm. $C_{12}H_{23}F_6N_3O_4S_2$ (451.45): calcd. C 31.93, H 5.14, N 9.31; found C 32.07, H 5.01, N 9.18.

Compound 12: Aziridine **1b** was prepared in analogy with **1a** starting from (*S*)-alaninol (0.46 g, 6.18 mmol). The cold crude mixture was washed with cold 0.1 M HCl (2 × 60 mL) and with cold sat. Na_2CO_3 (2 × 60 mL). The organic phase was dried with $MgSO_4$ and filtered into a 50-mL flask which was cooled to −40 °C. Benzylamine (0.25 mL, 2.32 mmol, the yield of **1b** was assumed to be 75%) was added dropwise to the mixture and the flask was left in the warming bath. The crude mixture was concentrated onto 2.4 g of silica and purified by flash chromatography (12.5% EtOAc in hexanes) followed by a second flash chromatography (gradient 5−25% of diethyl ether in hexanes) giving 0.30 g of a sticky oil which eventually solidified to a white powder. Yield: 20% [calculated on (*S*)-alaninol]. M.p. 86−87 °C. $[\alpha]_D^{20}$ = −68.6 (c = 0.47, MeOH). R_f = 0.36 (20% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 1.21 (d, ^3J = 6.5 Hz, 6 H, CH_3), 2.39 (dd, ^2J = 13.5, ^3J = 4.1 Hz, 2 H, NCH*H*CH), 2.55 (dd, ^2J = 13.5, ^3J = 10.2 Hz, 2 H, NC*H*HCH), 3.22 (d, ^2J = 13.0 Hz, 1 H, $C_{benzylic}$*H*H), 3.80−3.88 (m, 2 H, C*H*NHTf), 4.02 (d, ^2J = 13.0 Hz, 1 H, $C_{benzylic}$H*H*), 5.26 (br. s, 2 H, NHTf), 7.28−7.39 (m, 5 H, $H_{aromatic}$) ppm. ^{13}C NMR (125.8 MHz) 20.3, 49.5, 58.6, 60.2, 119.8 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 128.3, 129.2, 129.9, 137.5 ppm. $C_{15}H_{21}F_6N_3O_4S_2$ (485.47): calcd. C 37.11, H 4.36, N 8.66; found C 37.27, H 4.20, N 8.55.

Compound 13: Benzylamine (75 μL, 0.68 mmol) was added to aziridine **1c** (0.33 g, 1.37 mmol) in methanol (0.9 mL) in a 10-mL flask at 0 °C. The flask was kept at 0 °C for 10 min and at room temperature for 10 min. The flask was then heated at 45 °C for 21 h and 55 °C for 14 h. The flask was placed at −30 °C until a white powder formed. The powder was collected and washed with hexane giving (0.52 g, 0.43 mmol). Yield: 63%. Melts partly at 69−70 °C. $[\alpha]_D^{20}$ = −79.6 (c = 0.50, MeOH). R_f = 0.20 (20% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 0.63 (d, ^3J = 6.9 Hz, 6 H, *i*Pr CH_3), 0.66 (d, ^3J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.86 [d of sept, ^3J = 6.9, ^3J = 4.0 Hz, 2 H, C*H*$(CH_3)_2$], 2.31 (dd, ^2J = 13.2, ^3J = 5.6 Hz, 2 H, NCH*H*), 2.40 (s, 6 H, $CH_{3\,para}$), 2.47 (dd, ^2J = 13.2, ^3J = 9.0 Hz, 2 H, NC*H*H), 3.27 (d, ^3J = 13.3 Hz, 1 H, $C_{benzylic}$H), 3.44−3.50 (m, 2 H, C*H*NHTs), 3.73 (d, ^3J = 13.2 Hz, 1 H, $C_{benzylic}$H), 5.21 (d, ^3J = 6.5 Hz, 2 H, NHTs), 7.23 (d, ^3J = 8.1 Hz, 6 H, H_{meta}), 7.79 (d, ^3J = 8.3 Hz, 4 H, H_{ortho}) ppm. ^{13}C NMR (100.6 MHz) 17.6, 18.0, 21.7, 29.9, 54.2, 56.1, 56.5, 127.1, 127.4, 128.5, 129.6, 129.7, 137.9, 138.9, 143.1 ppm. $C_{31}H_{43}N_3O_4S_2$ (585.83): calcd. C 63.56, H 7.40, N 7.17; found C 63.56, H 7.38, N 7.15.

Compound 14: MPLC (gradient 1−60% EtOAc in hexanes) and recrystallization from EtOAc/hexanes gave colourless crystals. Yield: 41%. M.p. 147−148 °C. $[\alpha]_D^{20}$ = −31.8 (c = 0.49, MeOH). R_f = 0.29 (20% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.88 (d, ^3J = 6.8 Hz, 3 H, CH_3), 0.94 (d, ^3J = 7.0 Hz, 6 H, *i*Pr CH_3), 0.98 (d, ^3J = 6.9 Hz, 6 H, *i*Pr CH_3), 2.04 (br. s, 1 H, OH), 2.07 [d of sept, ^3J = 7.0, ^3J = 3.8 Hz, 2 H, C*H*$(CH_3)_2$], 2.53 (dd, ^2J = 13.8, ^3J = 4.5 Hz, 2 H, NCH*H*), 2.87 (app t, ^2J = 11.1 Hz, 2 H, NC*H*H), 2.91 (dq, ^3J = 6.8, ^3J = 2.7 Hz, 1 H, C*H*NCH_3), 3.59−3.61 (m, 2 H, C*H*NHTf), 5.32 (d, ^3J = 2.4 Hz, 1 H, $C_{benzylic}$H), 5.99 (br. s, 2 H, NHTf), 7.28−7.29 (m, 1 H, $H_{aromatic}$), 7.35−7.39 (m, 4 H, $H_{aromatic}$) ppm. ^{13}C NMR (125.8 MHz) 15.1, 17.0, 18.1, 30.4, 51.7, 58.4, 58.7, 79.5, 119.5 (q, $^1J_{C,F}$ = 327 Hz, CF_3), 126.0, 128.0, 128.7, 142.4 ppm. $C_{21}H_{33}F_6N_3O_5S_2$ (585.63): calcd. C 43.07, H 5.68, N 7.18; found C 43.16, H 5.65, N 7.03.

Compound 15: Purification by first MPLC (gradient 1−100% EtOAc in hexanes) and then flash chromatography through a short column (gradient 0−100% CH_2Cl_2 in hexanes) gave a white powder. Yield: 41%. M.p. 102−103 °C. $[\alpha]_D^{20}$ = −55.0 (c = 0.75, MeOH). R_f = 0.63 (20% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 0.82 (d, ^3J = 6.7 Hz, 6 H, CH_3), 0.94 (d, ^3J = 6.7 Hz, 6 H, CH_3), 1.56 (br. s, 1 H, OH), 1.99−2.07 [m, 2 H, C*H*$(CH_3)_2$], 2.65 (ABX system, ^2J = 13.8, ^3J = 7.0 Hz, 2 H, NCH*H*), 2.72 (ABX

system, ^2J = 13.7, ^3J = 6.7 Hz, 2 H, NC*H*H), 3.64−3.68 (m, 2 H, C*H*NHTf), 3.69 (d, ^2J = 13.4 Hz, 1 H, $C_{benzylic}H$), 3.89 (d, ^2J = 13.4 Hz, 1 H, $C_{benzylic}H$), 6.83−6.87 (m, 2 H, $C_{3'}H$ and $C_{5'}H$), 7.04 (d, ^3J = 7.3 Hz, 1 H, $C_{6'}H$), 7.21 (d app t, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, $C_{4'}H$) ppm; NHTf signal not visible. ^{13}C NMR (125.7 MHz) 16.4, 18.6, 29.7, 56.5, 58.5, 58.6, 116.4, 119.5 (q, $^1J_{C,F}$ = 321 Hz, CF_3), 120.4, 121.5, 129.8, 130.0, 156.1 ppm. $C_{19}H_{29}F_6N_3O_5S_2$ (557.57): calcd. C 40.93, H 5.24, N 7.54, S 11.50; found C 40.66, H 5.19, N 7.40, S 11.65.

Compound 16: For purification, see ligand **3**. White crystals. Yield: 65%. M.p. 85−86 °C. $[\alpha]_D^{20}$ = −58.9 (*c* = 0.54, MeOH). R_f = 0.55 (20% EtOAc in hexanes). ^1H NMR (400 MHz): δ = 0.82 (d, ^3J = 6.9 Hz, 6 H, CH_3), 0.89 (d, ^3J = 6.8 Hz, 6 H, CH_3), 2.01−2.05 [m, 2 H, C*H*$(CH_3)_2$], 2.61 (ABX system, ^2J = 13.8, ^3J = 6.5 Hz, 2 H, NC*H*H), 2.67 (ABX system, ^2J = 13.8, ^3J = 7.0 Hz, 2 H, HCH*H*), 3.52−3.57 (m, 2 H, C*H*NHTf), 3.73 (AB q, ^2J = 13.3 Hz, 1 H, $C_{benzylic}H$), 3.77 (AB q, ^2J = 13.3 Hz, 1 H, $C_{benzylic}H$), 3.86 (s, 3 H, OCH_3), 5.50 (br. s, 2 H, NHTf), 6.93 (d, ^3J = 8.0 Hz, 1 H, $C_{3'}H$), 6.96 (app t, ^3J = 7.4 Hz, 1 H, $C_{5'}H$), 7.21 (dd, ^3J = 7.4, ^4J = 1.5 Hz, 1 H, $C_{6'}H$), 7.31 (d app t, ^3J = 7.8, ^4J = 1.7 Hz, 1 H, $C_{4'}H$) ppm. ^{13}C NMR (125.8 MHz) 17.6, 18.1, 29.5, 54.3, 55.3, 55.6, 59.2, 111.1, 119.6 (q, $^1J_{C,F}$ = 314 Hz, CF_3), 121.0, 125.1, 129.6, 132.1, 158.1 ppm. $C_{20}H_{31}F_6N_3O_5S_2$ (571.60): calcd. C 42.02, H 5.47, N 7.35; found C 41.87, H 5.32, N 7.28.

Compounds 17 and 18: Compound **16** (101 mg, 0.177 mmol) and tricarbonyl(naphthalene)chromium (114 mg, 0.432 mmol) were added to a vial. The vial was sealed and THF (0.05 mL) and ether (1.35 mL) were added. The vial was heated at 90 °C in an oil bath for 5.25 h. ***CAUTION:*** High pressure! The crude mixture was purified by MPLC (gradient 0−80% EtOAc in hexanes) giving a 1:1.3 mixture of the diastereoisomers according to ^1H NMR. The two diastereoisomers were separated by flash chromatography (gradient 30−70% CH_2Cl_2 in pentane) giving 36.0 mg (0.051 mmol, 29%) of the early isomer as a yellow oil, R_f = 0.21 (50% CH_2Cl_2 in pentane), and 47.0 mg (0.066 mmol, 38%) of the late isomer as a yellow oil, R_f = 0.05 (50% CH_2Cl_2 in pentane). ^1H NMR (400 MHz) from the crude mixture (some signals could not be assigned definitely). Early: δ = 0.90 (d, ^3J = 6.8 Hz, 6 H, *i*Pr CH_3), 0.92 (d, ^3J = 6.8 Hz, 6 H, *i*Pr CH_3), 1.84−1.95 [m, 2 H, C*H*$(CH_3)_2$], 3.04 (d, ^2J = 11.3 Hz, 1 H, $C_{benzylic}H$), 3.07 (d, ^2J = 11.6 Hz, 1 H, $C_{benzylic}H$), 3.45−3.57 (m, 4 H, NCH_2), 3.63−3.66 (m, 2 H, C*H*NHTf), 3.77 (s, 3 H, OCH_3), 4.97 (t, ^3J = 5.9 Hz, 1 H, $H_{aromatic}$), 5.83 (d, ^3J = 5.9 Hz, 1 H, $H_{aromatic}$), 5.07 (app t, ^3J = 6.8 Hz, 2 H, $H_{aromatic}$). Late: δ = 0.98 (d, ^3J = 7.0 Hz, 6 H, *i*Pr CH_3), 1.00 (d, ^3J = 6.9 Hz, 6 H, *i*Pr CH_3), 1.97−2.03 [m, 2 H, C*H*$(CH_3)_2$], 2.67−2.80 (m, 4 H, NCH_2), 3.31 (d, ^2J = 13.9 Hz, 1 H, $C_{benzylic}H$), 3.35 (d, ^2J = 14.9 Hz, 1 H, $C_{benzylic}H$), 3.72 (s, 3 H, OCH_3), 3.75−3.77 (m, 2 H, C*H*NHTf), 5.12 (d, ^3J = 6.7 Hz, 1 H, $H_{aromatic}$), 5.56 (t, ^3J = 6.2 Hz, 1 H, $H_{aromatic}$), 6.40 (d, ^3J = 6.3 Hz, 1 H, $H_{aromatic}$) ppm; the signal of one aromatic proton is probably hidden under the signals of naphthalene.

Compound 19: Purification by MPLC (gradient 1−60% EtOAc in hexanes) followed by recrystallization from EtOAc/toluene/hexanes gave a white powder. Yield: 84%. M.p. 162−163 °C. $[\alpha]_D^{20}$ = −25.2 (*c* = 0.59, MeOH). R_f = 0.43 (20% EtOAc in hexanes). ^1H NMR (500 MHz): δ = 0.89 (d, ^3J = 5.1 Hz, 6 H, CH_3), 0.90 (d, ^3J = 5.2 Hz, 6 H, CH_3), 1.78 [app oct, ^3J = 5.3 Hz, 2 H, C*H*$(CH_3)_2$], 2.57 (ABX system, ^2J = 12.0, ^3J = 9.5 Hz, 2 H, NCH*H*), 2.61 (ABX system, ^2J = 12.0, ^3J = 4.2 Hz, 2 H, NC*H*H), 3.39−3.43 (m, 2 H, C*H*NHTf), 3.55 (s, 2 H, $C_{benzylic}H$), 3.88 (br. s, 2 H, NH), 7.01 (d, ^3J = 6.1 Hz, 4 H, H_{ortho}), 7.09−7.15 (m, 6 H, H_{para} and H_{meta}) ppm. ^{13}C NMR (125.8 MHz) 18.4, 19.1, 31.0, 48.6, 62.6, 69.6, 119.7 (q, $^1J_{C,F}$ = 314 Hz, CF_3), 127.3, 127.9, 128.3, 141.2 ppm. $C_{26}H_{36}F_6N_4O_4S_2$ (646.71): calcd. C 48.29, H 5.61, N 8.66; found C 48.45, H 5.74, N 8.57.

Compound 20: MPLC (gradient 1−60% EtOAc in hexanes) gave a white powder. Yield: 79%. M.p. 124−125 °C. $[\alpha]_D^{20}$ = −6.0 (*c* = 0.53, MeOH). R_f = 0.36 (20% EtOAc in hexanes). ^1H NMR (400 MHz): δ = 0.80 (d, ^3J = 6.8 Hz, 6 H, CH_3), 0.94 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.85−1.95 [m, 2 H, C*H*$(CH_3)_2$], 2.63 (dd, ^2J = 13.3, ^3J = 4.0 Hz, 2 H, NCH*H*), 2.75 (dd, ^2J = 13.1, ^3J = 5.0 Hz, 2 H, NC*H*H), 3.28−3.34 (m, 2 H, C*H*NHTf), 3.73 (s, 2 H, $C_{benzylic}H$), 3.95 (br. s, 4 H, NHTf and NH), 7.04 (d, ^3J = 7.3 Hz, 4 H, H_{ortho}), 7.12−7.18 (m, 6 H, H_{para} and H_{meta}) ppm. ^{13}C NMR (100.6 MHz) 18.8, 19.5, 30.1, 48.4, 61.7, 68.6, 119.8 (q, $^1J_{C,F}$ = 321 Hz, CF_3), 127.6, 127.8, 128.4, 140.0 ppm. $C_{26}H_{36}F_6N_4O_4S_2$ (646.71): calcd. C 48.29, H 5.61, N 8.66; found C 48.12, H 5.44, N 8.50.

Compound 21: MPLC (gradient 2.5−100% EtOAc in hexanes) gave a white powder. Yield: 64%. M.p. 185−186 °C. $[\alpha]_D^{20}$ = −60.9 (*c* = 0.40, MeOH). R_f = 0.18 (60% EtOAc in hexanes). ^1H NMR (400 MHz): δ = 0.93 (d, ^3J = 6.8 Hz, 6 H, CH_3), 0.98 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.24−1.29 (m, 2 H, C4′*H*H and C5′*H*H), 1.33−1.38 (m, 2 H, C3′*H*H and C6′*H*H), 1.80−1.82 (m, 2 H, C4′*H*H and C5′*H*H), 1.90−1.95 [m, 2 H, C*H*$(CH_3)_2$], 2.14 (br. d, ^2J = 12.6 Hz, 2 H, C3′*H*H and C6′*H*H), 2.50−2.52 (m, 2 H, C*H*N), 2.82 (dd, ^2J = 12.2, ^3J = 8.5 Hz, 2 H, NCH*H*), 3.02 (dd, ^2J = 12.2, ^3J = 4.4 Hz, 2 H, NC*H*H), 3.27 (app dt, ^3J = 8.0, ^3J = 2.7 Hz, 2 H, C*H*NHTf), 4.20 (br. s, 4 H, NHTf and NH) ppm. ^{13}C NMR (100.6 MHz) 18.7, 19.7, 24.7, 30.4, 30.6, 48.0, 60.4, 61.7, 120.6 (q, $^1J_{C,F}$ = 323 Hz, CF_3) ppm. $C_{18}H_{34}F_6N_4O_4S_2$ (548.60): calcd. C 39.41, H 6.25, N 10.21; found C 39.20, H 6.08, N 10.05.

Compound 22: MPLC (gradient 2.5−100% EtOAc in hexanes) followed by recrystallization from EtOAc/hexanes gave white crystals. Yield: 67%. M.p. 146−147 °C. $[\alpha]_D^{20}$ = −5.4 (*c* = 0.63, MeOH). R_f = 0.38 (80% EtOAc in hexanes). ^1H NMR (400 MHz): δ = 0.92 (d, ^3J = 6.6 Hz, 6 H, CH_3), 1.01 (d, ^3J = 6.6 Hz, 6 H, CH_3), 1.11−1.13 (m, 2 H, C3′*H*H and C6′*H*H), 1.22−1.27 (m, 2 H, C4′*H*H and C5′*H*H), 1.79−1.81 (m, 2 H, C4′*H*H and C5′*H*H), 1.85−1.92 [m, 2 H, C*H*$(CH_3)_2$], 2.18 (br. d, ^2J = 12.2 Hz, 2 H, C3′*H*H and C6′*H*H), 2.45−2.47 (m, 2 H, CHN), 2.68 (br. d, ^2J = 12.2 Hz, 2 H, NCH*H*), 3.11 (dd, ^2J = 12.6, ^3J = 4.4 Hz, 2 H, NC*H*H), 3.23−3.25 (m, 2 H, C*H*NHTf), 4.85 (br. s, 4 H, NHTf and NH) ppm. ^{13}C NMR (100.6 MHz) 19.2, 20.0, 24.5, 29.9, 30.6, 47.7, 60.9, 60.9, 120.9 (q, $^1J_{C,F}$ = 324 Hz, CF_3) ppm. $C_{18}H_{34}F_6N_4O_4S_2$ (548.60): calcd. C 39.41, H 6.25, N 10.21; found C 39.61, H 6.26, N 10.27.

Compound 23: MPLC (gradient 1−100% EtOAc in hexanes) gave a white solid which was treated with pentane. The solution was placed at −30 °C until a white solid formed. The solid was collected and washed with a small amount of cold pentane. Yield: 58%. Melts partly at 73−77 °C. $[\alpha]_D^{20}$ = 69.5 (*c* = 0.54, MeOH). R_f = 0.29 (20% EtOAc in hexanes). ^1H NMR (500 MHz): δ = 0.93 (app t, ^3J = 6.6 Hz, 12 H, CH_3), 1.83−1.86 [m, 2 H, C*H*$(CH_3)_2$], 3.20 (d, ^2J = 11.3 Hz, 2 H, NCH*H*), 3.26−3.30 (m, 2 H, NC*H*H), 3.35−3.38 (ABX system, 2 H, C*H*NHTf), 3.88 (br. s, 2 H, NH), 5.74 (d, ^3J = 8.7 Hz, 2 H, NHTf), 6.95 (br. d, ^3J = 8.4 Hz, 2 H, $H_{binaphthyl}$), 7.16 (app dt, ^3J = 6.7, ^4J = 1.2 Hz, 2 H, $H_{binaphthyl}$), 7.19 (d, ^3J = 9.0 Hz, 2 H, $H_{binaphthyl}$), 7.21 (app dt, ^3J = 7.3, ^4J = 1.0 Hz, 2 H, $H_{binaphthyl}$), 7.82 (d, ^3J = 7.8 Hz, 2 H, $H_{binaphthyl}$), 7.93 (d, ^3J = 9.0 Hz, 2 H, $H_{binaphthyl}$) ppm. ^{13}C NMR (125.8 MHz) 17.7, 18.7, 31.7, 44.5, 60.8, 112.2, 113.7, 119.3 (q, $^1J_{C,F}$ = 319 Hz, CF_3), 122.0, 124.1, 126.7, 128.1, 128.4, 129.9, 134.0, 144.2 ppm.

$C_{32}H_{36}F_6N_4O_4S_2$ (718.21): calcd. C 53.47, H 5.05, N 7.79; found C 53.44, H 5.03, N 7.79.

Compound 24: For purification, see ligand **23**. Yield: 61%. Melts partly at 74−77 °C. $[\alpha]_D^{20}$ = 16.4 (*c* = 0.54, MeOH). R_f = 0.65 (40% EtOAc in hexanes). ^{1}H NMR (500 MHz): δ = 0.67 (app t, ^3J = 6.6 Hz, 12 H, CH_3), 1.28−1.33 [m, 2 H, C*H*(CH_3)$_2$], 3.37−3.45 (m, 6 H, NC*HH* and C*H*NHTf), 3.64 (br. s, 2 H, NH), 5.59 (d, ^3J = 8.7 Hz, 2 H, NHTf), 7.02 (d, ^3J = 8.3 Hz, 2 H, $H_{binaphthyl}$), 7.22 (m, 2 H, $H_{binaphthyl}$), 7.28 (app dt, ^3J = 7.5, ^4J = 1.1 Hz, 2 H, $H_{binaphthyl}$), 7.33 (d, ^3J = 9.0 Hz, 2 H, $H_{binaphthyl}$), 7.84 (d, ^3J = 8.0 Hz, 2 H, $H_{binaphthyl}$), 7.97 (d, ^3J = 9.0 Hz, 2 H, $H_{binaphthyl}$) ppm. ^{13}C NMR (125.8 MHz) 17.4, 19.1, 28.8, 45.9, 60.4, 113.8, 114.8, 119.6 (q, $^1J_{C,F}$ = 321 Hz, CF_3), 123.2, 123.9, 127.3, 128.61, 128.64, 130.6, 133.7, 143.5 ppm. $C_{32}H_{36}F_6N_4O_4S_2$ (718.21): calcd. C 53.26, H 5.15, N 7.64; found C 53.44, H 5.03, N 7.79.

Compound 25: Aziridine **1c** (0.50 g, 2.09 mmol) was added to a SmithProcessVial™, the vial was sealed and charged with a solution of ammonia (0.27 mL, 2.1 M in methanol, 0.57 mmol) and methanol (0.20 mL). The vial was placed in the microwave cavity for 75 min at 160 °C. ***CAUTION:*** High pressure! The mixture was cooled in an ice bath and the white crystals were collected and washed with cold methanol, giving 0.35 g (0.48 mmol, 85%) of **25**. M.p. 187−188 °C. $[\alpha]_D^{20}$ = 108 (*c* = 0.80, $CHCl_3$). R_f = 0.43 (40% EtOAc in hexanes). ^{1}H NMR (400 MHz): δ = 0.77 (d, ^3J = 6.8 Hz, 9 H, *i*Pr CH_3), 0.80 (d, ^3J = 6.9 Hz, 9 H, *i*Pr CH_3), 1.66−1.73 [m, 3 H, C*H*(CH_3)$_2$], 2.15 (dd, ^2J = 12.6, ^3J = 4.6 Hz, 3 H, NCH*H*), 2.38 (s, 9 H, CH_{3para}), 2.96 (app t, ^2J = 12.2, ^3J = 12.2 Hz, 3 H, NC*H*H), 3.79−3.86 (m, 3 H, C*H*NHTs), 6.20 (d, ^3J = 7.0 Hz, 3 H, CHN*H*Ts), 7.23 (d, ^3J = 8.1 Hz, 6 H, H_{meta}), 7.83 (d, ^3J = 8.3 Hz,6 Hz, H_{ortho}) ppm. ^{13}C NMR (100.6 MHz) 18.3, 18.5, 21.6, 31.6, 52.1, 55.3, 58.1, 126.7, 129.4, 139.8, 142.6 ppm. $C_{36}H_{54}N_4O_6S_3$ (735.03): calcd. C 58.83, H 7.40, N 7.62; found C 58.64, H 7.33, N 7.48.

General Procedure for the Addition of Diethylzinc to Benzaldehyde: Ligand (0.06 mmol) was added to a 10-mL flask. The flask was evacuated during 2 min and filled with argon, and the cycle was repeated twice. The ligand was dissolved in toluene (1.0 mL) and Ti(O*i*Pr)$_4$ (1.48 mmol, 0.44 mL) was added. The mixture was cooled to −78 °C and Et_2Zn (1.20 mmol, 1.09 mL) was added dropwise after 20 min. The temperature of the cooling bath was allowed to reach −20 °C during 1 h, whereafter the flask was kept at 0 °C for 15 min followed by 140 min at room temperature and then cooled to −78 °C. Benzaldehyde (1 mmol, 101.6 μL) was added after 15 min at this temperature. The flask was placed at −35 °C after 20 min. The mixture was maintained at this temperature and aliqouts were removed with a syringe and quenched with 0.3 M HCl, extracted with ether, filtered through a short pad of silica (around 0.5 cm), eluted with ether, and injected on a chiral GLC column. The reaction was quenched with 0.3 M HCl when all aldehyde was consumed. The aqueous phase was extracted four times with ether and the combined organic phases were dried with Na_2SO_4 and filtered, and the solvent was evaporated. The yield and entiomeric excess were determined by GLC using naphthalene as external standard.

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