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New chiral imino- and amino-sulfoxides as activators of allyl trichlorosilane in the asymmetric allylation of aldehydes

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Dedicated to Professor Henri Kagan on the occasion of his 80th birthday

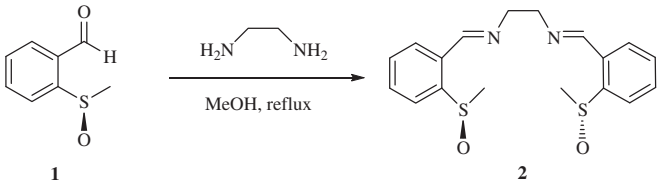
ABSTRACT

Chiral 2-methylsulfinyl benzaldehyde proved to be a valuable starting material for a convenient approach towards a variety of imino- and amino-sulfoxides. The catalytic properties of these new ligands, as potential activators of allyl trichlorosilane, have been exploited in new catalytic procedures for the synthesis of enantioenriched homoallylic alcohols.

1. Introduction

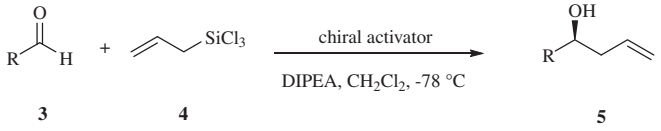
In the past two decades, enantiopure sulfoxides have widely proven to be among the most efficient and versatile chiral controllers in asymmetric synthesis as both chiral inductors and ligands.[1] In particular, chiral sulfoxides have been used as ligands in many preparative processes, such as Diels–Alder reactions,[2] allylic alkylations,[3] cyanohydrin syntheses,[4] 1,2-additions to carbonyl compounds[5] and hydrogenations.[6]

A further important application of sulfoxides concerns their recent employment, as activators of allyl trichlorosilane,[7] in procedures for the asymmetric allylation of aldehydes[8] and benzoylhydrazones.[9] Nevertheless, the attainment of good yields and/or enantiomeric excesses (ees) usually required stoichiometric or over-stoichiometric amounts of activators (up to 3 equiv). This disadvantage could not be circumvented by using a chiral sulfoxide covalently bonded to mesoporous silica (SBA-15),[10] as confirmed by the rather modest yields and ees observed. Conversely, a C_2 symmetric tetradentate bis-imino-sulfoxide **2**, easily accessible from chiral 2-methylsulfinyl benzaldehyde **1**, (Scheme 1) proved to be a more convenient activator of allyl trichlorosilane[11] since, under very reduced catalyst loading (0.3 equiv) the formation of the corresponding homoallylic alcohols **5** (Scheme 2) was found to occur albeit in moderate yields (up to 69%) and enantioselectivity (up to 70%).



1 **2**

Scheme 1.



3 **4** **5**

Scheme 2.

2. Results and discussion

The easy access to chiral 2-methylsulfinyl benzaldehyde **1** with satisfactory efficiency (65–70% yield) and high enantioselectivity (96–99% ee) after one crystallization suggested its exploitation, as a starting material, for the synthesis of a set of new chiral bidentate imino- and amino-sulfoxides and, furthermore, the evaluation of their catalytic properties as potential activators of allyl trichlorosilane **4** in asymmetric allylation reactions. Taking advantage of our preliminary report,[11] a very simple synthetic sequence allowed the conversion of **1**, used in 99% ee, into imino-sulfoxide **6**, as well as amino-sulfoxides **7** and **8**, in high yields and ees (Scheme 3).

Successively, the catalytic properties of the chiral ligands **6**, **7** and **8** were evaluated in the allylation reaction of aldehydes, choosing **3a** and **3b** as representative substrates, under reduced catalyst loading conditions (0.3 equiv) as reported in Table 1.

With respect to the monodentate (*R*)-methyl *p*-tolyl sulfoxide (entry 1) catalyst **6** seemed to have a better efficiency but, conversely, a very poor enantioselectivity (entries 2 and 3), while no reaction was found to take place in both entries 4 and 5 because of a rapid decomposition of the allylating agent promoted by the

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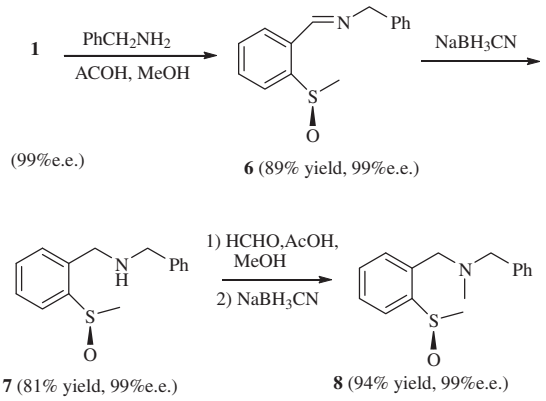
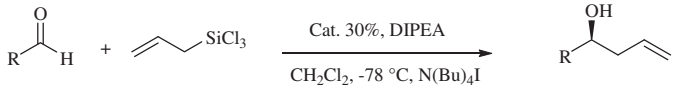


Scheme 3.

Table 1
Asymmetric allylation of representative RCHO **3** with allyl trichlorosilane activated with catalysts **6–8**



3 **4** **5**

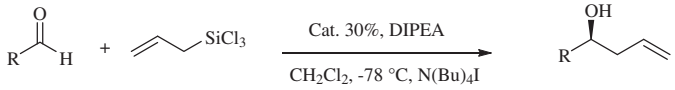
Entry	Cat.	R	Time (h)	Yield[a] (%)	ee[b] (%)
1	—[c]	Ph **3a**	18	35	44
2	**6**	Ph **3a**	18	58	23
3	**6**	5-NO_2-2-furyl **3b**	19	63	40
4	**7**	Ph **3a**	18	/	/
5	**7**	5-NO_2-2-furyl **3b**	18	/	/
6	**8**	Ph **3a**	18	56	46
7	**8**	5-NO_2-2-furyl **3b**	16	47	87

[a] All the yields refer to isolated chromatographically pure compounds, whose structures were confirmed by analytical and spectroscopic data.
[b] ees were determined by chiral HPLC. (*S*)-Configuration was assigned by comparing the sign of the specific rotations with the ones reported in the literature.
[c] In this entry (*R*)-methyl *p*-tolyl sulfoxide (0.3 equiv) was used as an activator.

catalyst **7**. More satisfactory results were obtained by using the ligand **8** (entries 6 and 7), especially as regards aldehyde **3b** whose conversion into the corresponding homoallylic alcohol occurred in modest yield (47%) but rather good enantiomeric excess (87% ee).

The scope of the procedure was checked on a set of aldehydes and, as reported in Table 2, moderate efficiency was generally observed in all entries, while the best levels of enantioselectivity were obtained in the case of aromatic and hetero-aromatic aldehydes bearing a strong electron-withdrawing group as in entries 2–4 and 10. Notably, more prolonged reaction times allowed an increase of efficiency (compare entries 2 and 3). The level of enantioselectivity was shown to strongly depend on the electronic properties of the substituents on the aromatic ring: in fact, the presence of an electron-donor group, as in entry 7, caused a dramatic drop in ee.

Table 2
Asymmetric allylation of RCHO **3** with allyl trichlorosilane activated with catalyst **8**



3 **4** **5**

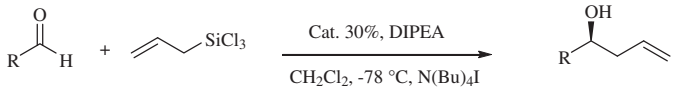
Entry	R	Time (h)	Yield (%)	ee (%)
1	Ph **3a**	18	56	46
2	5-NO_2-2-furyl **3b**	16	47	87
3	5-NO_2-2-furyl **3b**	48	56	89
4	5-NO_2-2-thienyl **3c**	23	48	89
5	$PhCH_2CH_2$ **3d**	24	43	64
6	*p*-CNC_6H_4 **3e**	24	44	65
7	*p*-$MeOC_6H_4$ **3f**	24	40	38
8	*o*-$NO_2C_6H_4$ **3g**	24	46	65
9	*p*-$MeSC_6H_4$ **3h**	24	43	54
10	*p*-$NO_2C_6H_4$ **3i**	24	50	81

[a] All the yields refer to isolated chromatographically pure compounds, whose structures were confirmed by analytical and spectroscopic data.
[b] ees were determined by chiral HPLC. Absolute configurations were assigned by comparison of the sign of the specific rotations with the ones reported in the literature.

Furthermore, an appreciable enantioselectivity (64% ee) was obtained in the case of aliphatic aldehydes (entry 5), since the currently available procedures leading to the corresponding homoallylic alcohols often afford rather disappointing results.

In an attempt to improve the procedure, catalyst **2** was further elaborated by the exploitation of the synthetic approach depicted in Scheme 3. In this manner, the new chiral monodentate ligand **9** and bidentate **10** were obtained in high yields and ees (Scheme 4) and their catalytic properties were examined under the typical conditions of the allylation reaction (Table 3).

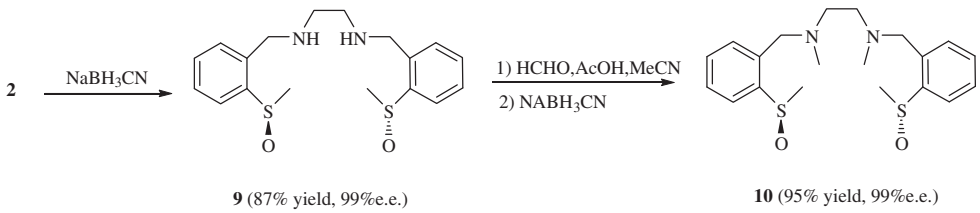
Table 3
Asymmetric allylation of RCHO **3** with allyl trichlorosilane activated with catalysts **9** and **10**



3 **4** **5**

Entry	Cat.	R	Time (h)	Yield[a] (%)	ee[b] (%)
1	**9**	Ph **3a**	18	/	/
2	**9**	5-NO_2-2-furyl **3b**	18	/	/
3	**10**	Ph **3a**	20	60	56
4	**10**	5-NO_2-2-furyl **3b**	24	64	90
5	**10**	5-NO_2-2-thienyl **3c**	24	66	89
6	**10**	*p*-$NO_2C_6H_4$ **3i**	24	62	82
7	**10**	$PhCH_2CH_2$ **3d**	24	60	72

[a] All the yields refer to isolated chromatographically pure compounds, whose structures were confirmed by analytical and spectroscopic data.
[b] ees were determined by chiral HPLC. Absolute configurations were assigned by comparison of the sign of the specific rotations with the ones reported in the literature.



Scheme 4.

As already found for catalyst **7** (Table 1, entries 4 and 5), the presence of a secondary amine functionality seemed to be responsible for the failure of the procedure by using ligand **9** as an activator, since the rapid decomposition of allyl trichlorosilane was again detected (Table 3, entries 1 and 2). Conversely, the employment of **10** proved to be successful for the occurrence of the process, resulting, more importantly, in a notable enhancement of the yields in all the reported entries. As regards the level of enantioselectivity, the best results were again given by electron-poor aromatic and hetero-aromatic aldehydes (up to 90% ee, entries 4–6), as well as aliphatic aldehydes (72% ee, entry 7).

3. Conclusion

In conclusion, easily available chiral 2-methylsulfinyl benzaldehyde proved to be a valuable starting material for the synthesis of a variety of new mono- and polydentate imino- and amino-sulfoxides through appropriate elaboration of the aldehyde functionality. Furthermore, an accurate evaluation of their catalytic properties, as activators, allowed the achievement of new catalytic procedures for the asymmetric allylation of aldehydes with allyl trichlorosilane proceeding in moderate yields and moderate to high ees.

4. Experimental

4.1. General

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an atmosphere of dry nitrogen. All the solvents for the reactions were of reagent grade and were dried and distilled immediately before use (dichloromethane from calcium hydride, diethyl ether from lithium aluminium hydride). Column chromatographic purification of products was carried out using Silica Gel 60 (70–230 mesh, Merck). The reagents (Aldrich and Fluka) were used without further purification. The NMR spectra were recorded on a Bruker DRX 400 (400 MHz, ^{1}H; 100 MHz, ^{13}C). Spectra were referenced to residual chloroform (7.26 ppm, ^{1}H, 77.23 ppm, ^{13}C). Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintept), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hz. Yields are given for isolated products showing one spot on a TLC plate and no impurities detectable in the NMR spectrum. Mass spectrometry analysis was carried out using an electrospray spectrometer Waters 4 micro quadrupole. HPLC analyses were performed with Waters Associates equipment (Waters 2487 Dual l absorbance Detector) and using a CHIRALPAK AD, CHIRALCEL OD, CHIRALCEL OB, CHIRALCEL AS, CHIRALCEL OD-H, CHIRALCEL AS-H, CHIRALCEL AD-H column with hexane/isopropyl alcohol mixtures and flow rates as indicated. Chiral GC (Supelco β-DEX 120) analyses were performed with FOCUS GC/FID Thermo Scientific. The HPLC and GC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured with a JASCO DIP-1000 polarimeter. Elemental analyses were performed with FLASHEA 1112 series-Thermo Scientific for CHNS-O.

4.2. Synthesis of (*R*)-(+)-*N*-(2-(methylsulfinyl)benzylidene)-(phenyl)methanamine 6

To a solution of (*R*)-(+)-2-(methylsulfinyl)benzaldehyde **1** (53.0 mg, 0.32 mmol, 99% ee) in MeOH (3.0 mL), benzylamine (84.0 μL, 0.77 mmol) and acetic acid (27.5 μL, 0.48 mmol) were added at room temperature and the mixture was stirred for 1 h. At the end of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (3.0 mL), and the mixture was extracted with 10 × 3 mL of CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude oil was purified by silica gel flash chromatography by elution with chloroform (99% yield). ^{1}H NMR δ 2.73 (s, 3H), 4.82 (s, 2H), 7.25–7.35 (m, 5H), 7.50–7.67 (m, 3H), 8.28 (d, 1H, *J* = 7.8 Hz), 8.42 (s, 1H). ^{13}C NMR δ 43.0, 64.0, 123.1, 126.2, 126.8, 127.6, 129.1, 130.2, 130.5, 131.8, 137.5, 146.6, 159.0. ESI-MS *m/z* 258 $[MH]^+$. $[\alpha]_D$ = +190.3 (*c* 1.0, $CHCl_3$). Ee 99%. Anal. Calcd for $C_{15}H_{15}NOS$: C, 70.01; H, 5.87; N, 5.44; S, 12.46. Found: C, 70.23; H, 5.62; N, 5.67; S, 12.71.

4.3. One-pot synthesis of (*R*)-(+)-*N*-(2-(methylsulfinyl)benzyl)-(phenyl)methanamine 7

To a solution of (*R*)-(+)-2-(methylsulfinyl)benzaldehyde **1** (54.0 mg, 0.32 mmol, 99% ee) in MeOH (3.5 mL), benzylamine (77.0 μL, 0.70 mmol) and acetic acid (27.5 μL, 0.48 mmol) wereadded at room temperature. The mixture was stirred for 1 h and then $NaBH_3CN$ (60.3 mg, 0.96 mmol) was added. At the end of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (3.0 mL), and the mixture was extracted with 10 × 3 mL of CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude oil was purified by silica gel flash chromatography by elution with chloroform (97% yield). ^{1}H NMR δ 1.70 (br s, 1H), 2.82 (s, 3H), 3.75 (d, 1H, *J* = 12.7 Hz), 3.76 (s, 2H), 3.96 (d, 1H, *J* = 12.7 Hz), 7.25–7.35 (m, 6H), 7.43 (dt, 1H, *J* = 7.5 Hz, *J* = 1.1 Hz), 7.51 (t, 1H, *J* = 7.5 Hz), 8.07 (d, 1H, *J* = 7.7 Hz). ^{13}C NMR δ 43.2, 49.4, 52.3, 122.7, 126.2, 127.1, 127.5, 127.9, 128.2, 129.6, 130.1, 138.5, 144.9. ESI-MS *m/z* 260 $[MH]^+$. $[\alpha]_D$ = +29.6 (*c* 0.2, $CHCl_3$). Ee 99%. Anal. Calcd for $C_{15}H_{17}NOS$: C, 69.46; H, 6.61; N, 5.40; S, 12.36. Found: C, 69.73; H, 6.42; N, 5.65; S, 12.10.

4.4. Synthesis of (*R*)-(+)-*N*-(2-(methylsulfinyl)benzyl)-*N*-methyl-(phenyl)methanamine 8

To a solution of (*R*)-(+)-*N*-(2-(methylsulfinyl)benzyl)(phenyl)-methanamine **7** (55.0 mg, 0.21 mmol, 99% ee) in CH_3CN (4.5 mL), formaldehyde (156.4 μL, 2.10 mmol) and acetic acid (27.0 μL, 0.32 mmol) were added at room temperature. The mixture was stirred for 1 h and then $NaBH_3CN$ (52.8 mg, 0.84 mmol) was added. At the end of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (3.0 mL), and the mixture was extracted with 10 × 3 mL of CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude oil was purified by silica gel flash chromatography by elution with chloroform (99% yield). ^{1}H NMR δ 1.92 (s, 3H), 2.76 (s, 3H), 3.20 (d, 1H, *J* = 12.8 Hz), 3.47 (d, 1H, *J* = 12.6 Hz), 3.65 (d, 1H, *J* = 12.6 Hz), 4.03 (d, 1H, *J* = 12.8 Hz), 7.23–7.55 (m, 8H), 8.06 (dd, 1H, *J* = 7.8 Hz, *J* = 1.2 Hz). ^{13}C NMR δ 39.0, 42.8, 58.9, 61.4, 71.2, 122.9, 126.4, 127.2, 127.3, 128.1, 128.4, 128.5, 128.6, 128.7, 129.6, 136.4, 144.8. ESI-MS *m/z* 274 $[MH]^+$. $[\alpha]_D$ = +55.5 (*c* 1.0, $CHCl_3$). Ee 99%. Anal. Calcd for $C_{16}H_{19}NOS$: C, 70.29; H, 7.00; N, 5.12; S, 11.73. Found: C, 70.58; H, 7.21; N, 5.01; S, 11.87.

4.5. Synthesis of (*R*,*R*)-(+)-*N*1,*N*2-bis-(2-(methylsulfinyl)-benzyl)-ethane-1,2-diamine

To a solution of (*R*,*R*)-(+)-*N*1,*N*2-bis-(2-(methylsulfinyl)-benzylidene)-ethane-1,2-diamine (116.0 mg, 0.32 mmol) in MeOH (3.5 mL), $NaBH_3CN$ (60.3 mg, 0.96 mmol) was added. At the end of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (3.0 mL), and the mixture was extracted with 10 × 3 mL of CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude oil was purified by silica gel flash chromatography with chloroform. Yield: 87%. ^{1}H NMR δ 1.85 (br s, 2H), 2.70 (s, 4H), 2.75 (s, 6H), 3.73 (d, 2H), 3.90 (d, 2H), 7.26 (d, 2H), 7.39 (t, 2H), 7.48 (t, 2H), 8.00 (d, 2H). ^{13}C NMR δ 28.6, 42.9, 47.5, 49.6, 122.7, 127.8, 128.1, 129.7, 136.1, 144.5. ESI-MS *m/z* 365

$[MH]^+$. $[\alpha]_D$ = +69.0 (*c* 0.2, $CHCl_3$). Ee 99%. Anal. Calcd for $C_{18}H_{24}N_2O_2S_2$: C, 59.31; H, 6.64; N, 7.68; S, 17.59. Found: C, 59.53; H, 6.88; N, 7.43; S, 17.84.

4.6. (*R*,*R*)-(+)-*N*1,*N*2-Bis-(2-(methylsulfinyl)-benzyl)-ethane-1,2-dimethandiamine

To a solution of (*R*,*R*)-(+)-*N*1,*N*2-bis-(2-(methylsulfinyl)-benzyl)-ethane-1,2-diamine (77.4 mg, 0.21 mmol) in CH_3CN (4.5 mL), formaldehyde (156.4 μL, 2.10 mmol) and acetic acid (27.0 μL, 0.32 mmol) were added at room temperature. The mixture was stirred for 1 h and then $NaBH_3CN$ (52.8 mg, 0.84 mmol) was added. At the end of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (3.0 mL), and the mixture was extracted with 10 × 3 mL of CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude oil was purified by silica gel flash chromatography with chloroform. Yield: 90%. ^1H NMR δ 2.05 (s, 6H), 2.51–2.60 (m, 4H), 2.72 (s, 6H), 3.18 (d, *J* = 12.9 Hz), 3.93 (d, *J* = 12.9 Hz), 4.27 (s, 2H), 7.24 (d, 2H), 7.38–7.42 (m, 2H), 7.50–7.54 (m, 2H), 8.02 (d, 2H). ^{13}C NMR δ 39.9, 42.7, 53.4, 59.1, 122.8, 128.2, 128.6, 129.6, 135.5, 144.7. ESI-MS *m/z* 393 $[MH]^+$. $[\alpha]_D$ = +103.0 (*c* 0.5, $CHCl_3$). Ee 99%. Anal. Calcd for $C_{20}H_{28}N_2O_2S_2$: C, 61.19; H, 7.19; N, 7.14; S, 16.34. Found: C, 61.33; H, 7.18; N, 7.29; S, 16.59.

4.7. General procedure for the allylation

In a flame-dried, two-necked, round-bottomed flask, allyltrichlorosilane (19 μL, 0.13 mmol) was added to a solution of sulfoxide (0.03 mmol), diisopropylethylamine (20 μL, 0.13 mmol) and $N(Bu)_4I$ (44.3 mg, 0.12 mmol) in dry dichloromethane (0.6 mL) under nitrogen at −78 °C. After 5 min of stirring at that temperature, the aldehyde was added (0.10 mmol). At the end of the reaction, it was quenched with saturated aqueous $NaHCO_3$ (1.0 mL), and the mixture was extracted with 10 × 3 mL of CH_2Cl_2 and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude oil was purified by silica gel flash chromatography.

The analytical and spectroscopic data as well as the absolute configurations of homoallylic alcohols **5a**,[12] **5b**,[11] **5c**,[11] **5d**[13] and **5e**[12] were reported in the literature.

Acknowledgements

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