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Enantioselective allylation of aldehydes with allyltrichlorosilane promoted by new chiral dipyridylmethane N-oxides

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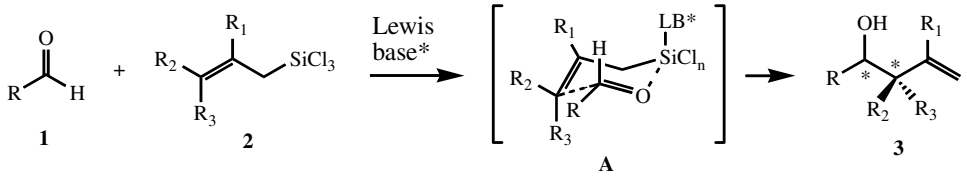
Abstract—New chiral dipyridine N-monoxides and N,N′-dioxides, which possess an isopropylidene backbone between two pyridine rings, have been prepared from naturally occurring monoterpenes. Their utility as organocatalysts has been demonstrated in the enantioselective addition of allyltrichlorosilane to aldehydes. Enantioselectivities up to 85% ee have been obtained.

1. Introduction

Chiral Lewis base-catalyzed stereoselective allylation of aldehydes with allyltrichorosilanes has been recognised to be one of the most efficient methods of obtaining homoallylic alcohols with high enantioselectivity (Scheme 1).[1,2] The generally good selectivity obtained with several types of bases indicates that the reaction likely proceeds via closed cyclic chair-like transition states involving hypervalent silicates (TSs **A**, Scheme 1).

Among chiral bases used to promote this process, heteroaromatic amine N-oxides have recently become a popular choice of oxygen donors for developing new chiral oxygen-containing ligands.[3] Although good results have been initially obtained with C_2-symmetric biquinoline and bipyridine N,N′-dioxides, recent studies have shown that neither the presence of a stereogenic axis nor C_2-symmetry is an absolute prerequisite for getting a high enantioselectivity in the allylation.[4] Thus, for instance, Malkov and Kocovsky showed that in the allylation of the benzaldehyde with allyltrichlorosilane, the terpene-derived bipyridine N-monoxide PINDOX **4a** (Fig. 1) afforded high enantioselectivity (up to 92% ee) and was more selective than the related C_2-symmetric bipyridine N,N′-dioxide **4b** that produced the opposite enantiomer in only 41% ee.[5] Moreover, **4a** was found to be only a little less enantioselective than the related axially chiral bipyridine N-monoxide **4c** (98% ee) that was in turn much more successful than the corresponding C_2-symmetric axially chiral N,N′-dioxide **4d** (up to 14% ee).[5]

To explain the high selectivity obtained in the PINDOX-promoted allylation, Malkov and Kocovsky have proposed the transition structure **B** (Fig. 1), in which the ligand functions as an *N*,*O*-bidentate ligand at hexacoordinated silicon. In a similar fashion, the related



Scheme 1.

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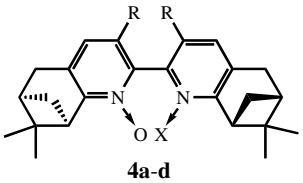
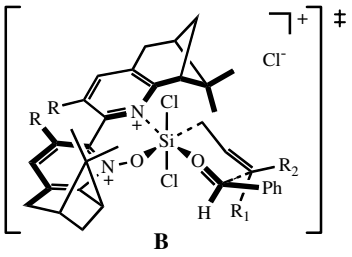


4a-d

a: X= no atom, R= H; **b**: X= O, R= H;
c: X= no atom, R= Me; **d**: X= O, R= Me



B

Figure 1.

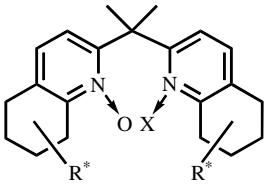


Figure 2. New organocatalysts of type **5** (X = O or no atom).

N,N′-dioxide **4b** would act as a *O*,*O*-bidentate ligand at silicon.[2] Therefore, the most relevant difference between these ligands is the chelate ring size of silicon. In fact, PINDOX **4a** would generate a six-membered ring, whereas chelation with N,N′-dioxide **4b** would lead to a seven-membered ring. Since to obtain an effective transfer of the chiral information from the catalyst to the product a careful evaluation of the ligand bite angle would be contemplated in the ligand design,[6] we have considered the possibility to extend the chelate ring size of these systems.[7] Therefore we decided to prepare new chiral organocatalysts containing two pyridine rings connected by a proper, tunable spacer.

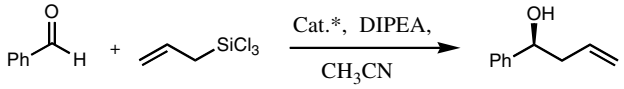
Herein, we report the preparation of new enantiomerically pure dipyridine N-monoxides and N,N′-dioxides of type **5** (Fig. 2), from naturally occurring monoterpenes, which possess an isopropylidene backbone between two pyridine rings. Their efficiency as organocatalysts[2c] has also been investigated in the enantioselective addition of allyltrichlorosilane to aromatic, heteroaromatic and nonaromatic aldehydes.

2. Results and discussion

Starting our investigation, N-monoxide **7**[8] and N,N′-dioxide **8**[8] were prepared by MCPBA oxidation[9] in CH_2Cl_2 of the known parent dipyridylmethane ligand **6**[6e] (Scheme 2). These ligands were then assessed in the asymmetric addition of allyltrichlorosilane to benzaldehyde, that is, used as the testing ground for new chiral nucleophilic catalysts.

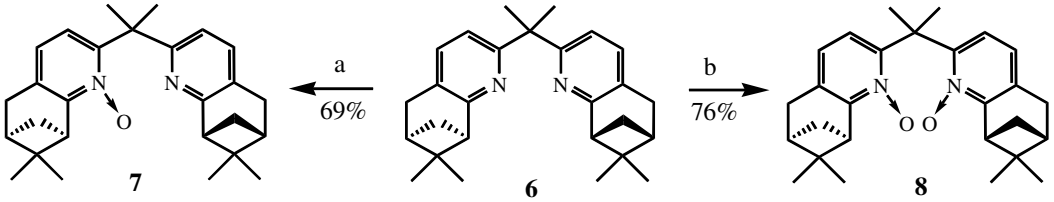
A typical experiment involved the use of 0.1 mol equiv of the catalyst, 1.2 mol equiv of allyl(trichloro)silane and 3 mol equiv of diisopropylethylamine (DIPEA) in acetonitrile at different temperatures.[10] Isolated yields and ees, as determined by HPLC, are collected in Table 1; the (*S*) absolute configuration was assigned to the predominant isomer by comparison of optical rotation.[11] While mono N-oxide **7** showed to be a poor catalyst, dipyridylmethane N,N′-dioxide **8** catalysed the allylation affording (*S*)-**3** (Scheme 1, R = Ph, $R^1 = R^2 =$

Table 1. Allylation of benzaldehyde with allyltrichlorosilane[a]

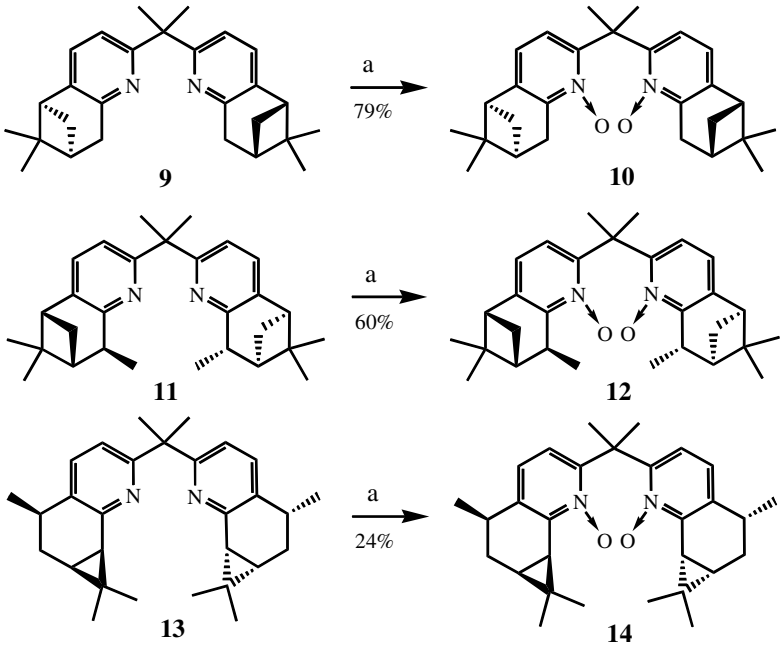


Entry	Catalyst	Temperature (°C)	Time (h)	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	**7**	−40	48	—	—	—
2	**7**	0	48	17	6	—
3	**8**	−40	67	37	85	*S*
4	**8**	0	67	58	83	*S*
5	**8**	25	67	97	77	*S*
6[e]	**8**	0	67	98	64	*S*
7	**10**	0	72	30	4	*S*
8	**12**	0	72	24	30	*S*
9	**14**	0	72	22	35	*S*

[a] The reaction was carried out at a 0.3 mmol scale in CH_3CN (2 ml) with allyl(trichloro)silane (1.2 equiv), catalyst (10 mol %), DIPEA (3 equiv) for 60 h.
[b] Isolated yields after flash chromatography.
[c] Determined by HPLC on a Chiracel OD column (hexane:isopropanol 95:5; flow rate 0.8 ml/min; λ 220 nm): $t_R = 10.4$ min, $t_S = 11.3$ min.
[d] Assigned by comparison of optical rotation.
[e] Reaction run in CH_2Cl_2.



Scheme 2. Reagents and conditions: (a) MCPBA, CH_2Cl_2, excess of **6**, rt 24 h; (b) MCPBA (excess), CH_2Cl_2, rt 24 h.

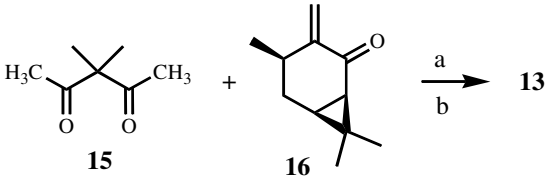


Scheme 3. Reagents and conditions: (a) MCPBA (excess), CH_2Cl_2, rt, 24 h.

$R^3 = H$) in 37% yield and 85% ee at −40 °C (Table 1, entry 3). Raising the temperature at 0 °C and 25 °C brought about a higher yield (58 and 98%, respectively) with only a slight decrease in the enantioselectivity (83% and 77% ee, respectively; entries 4,5 vs 3). Changing the solvent from MeCN to CH_2Cl_2 led to a quantitative yield, but had a negative effect on the enantioselectivity (entry 6 vs 4).[10] It is worth mentioning that **8** showed a selectivity similar to that of bipyridine N-monoxide **1a**, but clearly higher than that of bipyridine N,N′-dioxide **1b**.

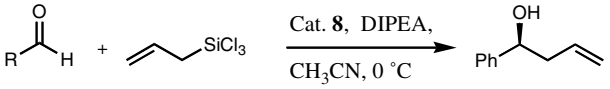
The interesting results obtained with **8** prompted us to prepare its other congeners. Thus, N,N′-dioxides **10**, **12** and **14**[8] were prepared by MCPBA oxidation[9] in CH_2Cl_2 of the parent dipyridylmethane ligands **9**, **11** and **13** (Scheme 3). Whereas **9** and **11** were known compounds,[6e] dipyridylmethane **13**[8] was prepared in a two-step sequence from α,β-unsaturated ketone **16**, available from (+)-2-carene in several steps.[12] Thus, the conjugate addition of the lithium enolate of 3,3-dimethylpentane-2,4-dione **15**[13] (generated by treatment with lithium diisopropylamine (LDA) at −78 °C for 2 h) with **17** (from −78 °C to room temperature) was performed, followed by the aza-annulation of the unisolated 1,5-dicarbonyl intermediate with the ammonium acetate/acetic acid system (AcOH, $AcONH_4$, reflux, 5 h)[6e] (Scheme 4). However, in the allylation reaction, carried out under the usual conditions (0 °C, 60 h), all new catalysts exhibited both lower yields and enantioselectivities than its congener **8** (Table 1, entries 7–9).

Having thus identified catalyst **8** as the more efficient one, its use was extended to the addition of allyltrichlorosilane to other aromatic aldehydes (Table 2). The reported data show that ee's equal to or greater than 70% and yields constantly higher than 58% could be obtained (entries 1–5).



Scheme 4. Reagents and conditions: (a) **15**, LDA, THF, −78 °C, 2 h, then **16** from −78 °C to slowly rt; (b) AcOH, $AcONH_4$, THF, reflux, 5 h.

Table 2. Allylation of aldehydes with allyltrichlorosilane with **8** as the catalyst (Scheme 1, $R^1 = R^2 = R^3 = H$)[a]



Entry	R	Yield[b] (%)	ee[c] (%)	Configuration[d]
1	Ph	58	83	*S*
2	*p*-$O_2NC_6H_4$	68	70	*S*
3	*p*-$MeOC_6H_4$	65	80	*S*
4	2-Thiophenyl	60	75	*S*
5	3-Thiophenyl	61	73	*S*
6	Ph–CH=CH	41	18	*S*
7	Ph–CH_2CH_2	46	4	*S*

[a] The reaction was carried out at a 0.3 mmol scale in CH_3CN (2 ml) with allyl(trichloro)silane (1.2 equiv), catalyst (10 mol %), DIPEA (3 equiv) at 0 °C for 60 h.
[b] Isolated yields after flash chromatography.
[c] Determined by HPLC on a chiral column.
[d] Assigned by comparison of optical rotation.

From these preliminary results it seems that an electron-withdrawing group at the *para*-position of benzaldehyde exhibits a negative impact on the enantioselectivity (entry 2), whereas the substrate bearing an electron-donat-

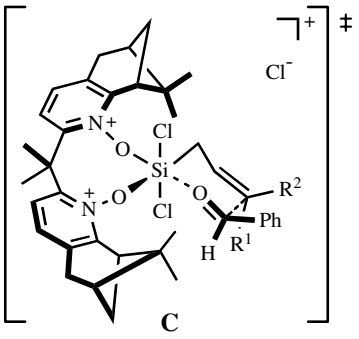


Figure 3.

ing group at the *para*-position does not seem to affect the stereoselectivity (entry 3). A marginal difference in selectivity and yield was observed for the two isomeric thiophene–carboxaldehydes (entries 4 and 5) showing the compatibility of the new catalyst in the reaction with heteroaromatic systems. Finally, both α,β-unsaturated and saturated aldehydes such as cinnamaldehyde and dihydrocinnamaldehyde, respectively, afforded the corresponding homoallylic alcohols with low enantiomeric excesses (entries 6 and 7).[14]

The comparison between a homogeneous series of N-monoxides and N,N′-dioxides derived from bipyridine and dipyridylmethane ligands suggests that both catalytic activity and stereoselectivity of the allylation reaction appear to depend on the chelate ring size of silicon in the hypothesized transition state. Bipyridine N-monoxide **4a** (87% ee at −40 °C) is more stereoselective than bipyridine N,N′-dioxide **4b** (41% ee at −90 °C), which is in turn a better catalyst than dipyridylmethane N-monoxide **7** (no activity at −40 °C), but less selective than dipyridylmethane N,N′-dioxide **8** (85% ee at −40 °C), which shows similar selectivity of **4a**. In other words, it seems that in the dipyridine series, ligands forming an even-membered chelate ring (**4a** and **8**) are more stereoselective than those generating an odd-membered ring (**4b** and **7**). On the basis of these observations and previous studies from other groups on *O*-based bidentate ligands,[1,2] a possible transition state model **C** compatible with the stereoselection observed for the new organocatalysts such as **8** is proposed in Figure 3, as a working hypothesis for future studies.

In conclusion, the first examples of N-monoxides and N,N′-dioxides based on the framework of dipyridylmethane ligands have been prepared and their potentiality as organocatalysts has been demonstrated in the addition of allyltrichorosilanes to aldehydes. Moreover, the information gained by these *O*-ligands gives some new insights into the relationship between catalytic activity and/or stereoselectivity and ligand bite angle for the examined stereoselective allylation process.

Further studies are in progress to explore this trend and to assess these new ligands in other enantioselective organocatalyzed reactions.

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8. *2-Bis[(6R,8R)-6,8-methano-7,7-dimethyl-5,6,7,8-tetrahydroquinolin-2-yl]propane N-oxide* (**7**): mp 85–90 °C; $[\alpha]_D^{25}$ +35.7 (*c* 0.83, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, 1H, $J = 3.9$ Hz), 7.28 (d, 1H, $J = 3.3$ Hz), 7.05 (d, 1H, $J = 8.1$ Hz), 6.98 (d, 1H, $J = 7.8$ Hz), 3.90 (t, 1H, $J = 5.4$), 2.94 (s, 2H), 2.85 (s, 2H), 2.73 (t, 1H, $J = 11.1$ Hz), 2.61–2.52 (m, 2H), 2.28–2.21 (m, 2H), 1.84 (s, 3H), 1.72 (s, 3H), 1.37 (s, 3H), 1.33 (s, 3H), 1.18–1.31 (m, 2H), 0.63 (s, 3H), 0.58 (s, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 164.36, 161.84, 156.15, 154.37, 135.14, 130.99, 125.94, 124.48, 120.68, 116.12, 50.04, 45.25, 40.16, 39.99, 39.65, 38.99, 38.93, 31.18, 30.85, 30.61, 30.19, 28.06, 26.04, 25.65, 25.28, 21.02, 20.96. Anal. Calcd for $C_{27}H_{34}N_2O$: C, 80.55; H, 8.51; N, 6.96. Found: C, 80.50; H, 8.52; N, 6.98. *2-Bis[(6R,8R)-6,8-methano-7,7-dimethyl-5,6,7,8-tetrahydroquinolin-2-yl]propane N,N′-dioxide* (**8**): mp 82–84 °C; $[\alpha]_D^{25}$ −35.9 (*c* 0.22, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.33 (d, 2H, $J = 8.1$ Hz), 7.06 (d, 2H, $J = 8.1$ Hz), 3.83 (t, 2H, $J = 2.7$ Hz), 2.90 (dq, 4H, $J = 17.1$ Hz, $J = 2.7$ Hz), 2.66–2.54 (m, 2H), 2.27–2.18 (m, 2H), 1.88 (s, 6H), 1.36 (s, 6H), 1.80 (s, 2H), 0.63 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 158.11, 154.87, 153.52, 130.01, 125.70, 119.99, 42.45, 40.14, 39.86, 39.04, 31.17, 29.91, 25.75, 24.31, 21.01. Anal. Calcd for $C_{27}H_{34}N_2O_2$: C, 77.48; H, 8.19; N, 6.69. Found: C, 77.50; H, 8.15; N, 6.68. *2-Bis[(5S,7S)-5,7-methano-6,6-dimethyl-5,6,7,8-tetrahydroquinolin-2-yl]propane N,N′-dioxide* (**10**): mp 202–205 °C; $[\alpha]_D^{25}$ −7.28 (*c* 0.11, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.31 (d, 2H, $J = 8.1$), 6.89 (d, 2H, $J = 8.1$ Hz), 2.89 (dq, 4H, $J = 18.9$ Hz, $J = 2.7$ Hz), 2.73 (t, 2H, $J = 5.4$ Hz), 2.63–2.53 (m, 2H), 2.36–2.28 (m, 2H), 1.89 (s, 6H), 1.37 (s, 6H), 1.36–1.18 (m, 2H), 0.62 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 153.94, 145.16, 141.56, 123.22, 119.51, 45.64, 41.90, 39.28, 39.26, 31.10, 30.69, 25.74, 24.42, 20.80. Anal. Calcd for $C_{27}H_{34}N_2O_2$: C, 77.48; H, 8.19; N, 6.69. Found: C, 77.51; H, 8.16; N, 6.66. *2-Bis[(5R,7R,8S)-5,7-methano-6,6,8-trimethyl-tetrahydroquinolin-2-yl]propane N,N′-dioxide* (**12**): mp185–188 °C; $[\alpha]_D^{25}$ +91.9 (*c* 0.43, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, 2H, $J = 8.1$ Hz), 6.86 (d, 2H, $J = 8.1$ Hz), 3.23–3.09 (m, 2H), 2.71 (t, 2H, $J = 5.7$), 2.52–2.40 (m, 2H), 2.10–2.01 (m, 2H), 1.84 (s, 6H), 1.41 (m, 2H), 1.37 (s, 6H), 1.22 (d, 6H, $J = 6.6$ Hz), 0.58 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 155.06, 148.16, 141.06, 123.13, 118.55, 47.11, 46.43, 41.81, 41.38, 34.27, 28.14, 25.83, 24.98, 20.40, 14.12. Anal. Calcd for $C_{29}H_{38}N_2O_2$: C, 77.99; H, 8.58; N, 6.27. Found: C, 77.98; H, 8.58; N, 6.28. *2-Bis[(5R,7R,8S)-5,7-methano-6,6,8-trimethyl-5,6,7,8-tetrahydroquinolin-2-yl]propane N,N′-dioxide* (**14**): mp 94–97 °C; $[\alpha]_D^{25}$ +151.2 (*c* 0.36, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, 2H, $J = 8.4$ Hz), 7.11 (d, 2H, $J = 8.4$ Hz), 2.89–2.74 (m, 2H), 2.28–2.08 (m, 4H), 1.80 (s, 6H), 1.39–1.26 (m, 4H), 1.25 (d, 6H, $J = 6.6$ Hz), 1.22 (s, 6H), 0.62 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 153.80, 147.47, 138.37, 121.75, 118.87, 88.96, 41.84, 32.24, 29.82, 27.52, 24.75, 24.02, 23.24, 22.40, 17.98, 15.15. Anal. Calcd for $C_{29}H_{38}N_2O_2$: C, 77.99; H, 8.58; N, 6.27. Found: C, 77.82; H, 8.57; N, 6.25. *2-Bis[(5R,7R,8S)-7,8-methano-5,11,11-trimethyl-5,6,7,8-tetraidroquinolin-2-yl]-propane* (**14**): oil; $[\alpha]_D^{20}$ −26.5 (*c* 0.61, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, 2H, $J = 6$ Hz), 6.78 (d, 2H, $J = 6$ Hz), 2.92–2.81 (m, 2H), 2.21–2.13 (m, 2H), 1.80 (d, 2H, $J = 6.3$ Hz), 1.77 (s, 6H), 1.36–1.22 (m, 4H), 1.23 (s, 6H), 1.19 (d, 6H, $J = 5.4$ Hz), 0.62 (s, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 164.71, 155.39, 134.79, 131.27, 118.43, 47.22, 32.27, 30.28, 28.67, 28.14, 26.97, 23.67, 23.01, 18.06, 16.26. Anal. Calcd for $C_{29}H_{38}N_2$: C, 84.01; H, 9.24; N, 6.76. Found: C, 84.00; H, 9.26; N, 6.75.
9. In order to obtain the selective formation of *N*-monoxide **7**, a large excess of dipyridylmethane ligand **6** with respect to MCPBA was used. The unconverted starting material and **7** were recovered by flash chromatography. On the other hand, *N*,*N*′-dioxides were prepared using an excess of MCPBA.
10. The use of other solvents (toluene, DME, THF) led to lower yields and ee.
11. *Typical procedure:* to a stirred solution of the catalyst (0.03 mmol) in acetonitrile (2 ml) kept under nitrogen, an aldehyde (0.3 mmol) and diisopropylethylamine (DIPEA, 0.154 ml, 0.9 mmol) were added in this order. The mixture was then cooled to 0 °C and allyl(trichloro)silane (0.054 ml, 0.36 mmol) was added dropwise by means of a syringe. After 48 h stirring at 0 °C the reaction was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (1 ml). The mixture was allowed to warm up to room temperature and water (2 ml) and EtOAc (5 ml) were added. After usual work up the crude products were purified by flash chromatography with different hexane:EtOAc mixtures as eluents.
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14. Thus, the reactivity trend observed with new type **5** catalyst (aromatic aldehydes > α,β-unsaturated aldehydes and aliphatic aldehydes) does not differ very much from that of most of the other N-oxides described in the literature.