

## Dismantling the salen framework: design of new asymmetric silylcyanation catalysts.

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**General Methods:** All reagents and solvents were commercial grade and purified prior to use when necessary.  $^1\text{H}$  and  $^{13}\text{C}$  NMR were acquired on a Bruker 300 MHz instrument. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to  $\delta = 7.26$  ppm and  $\delta = 77.1$  ppm ( $\text{CDCl}_3$ ) for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Enantiomeric excesses were determined with a Shimadzu instrument (Chirasil-DEX CB, 25m\*0.25 mm column). Absolute configurations were determined by comparison the known order of elution of the two enantiomers or the sign of optical rotation with literature data.<sup>1</sup> Infrared spectra were recorded on a Nicolet 6700 FTIR. Elemental analyses were conducted with a VarioMIRO Superuser automatic analyzer in the UCCS, Villeneuve d'Ascq, or from Steven Boyer, in London Metropolitan University, for air-sensitive compounds. For the crystal structure determination of **2a**, diffraction data were collected at 100 K using a Bruker X8 APEX2 apparatus. Crystal data and details of data collection and structure refinement for the different compounds are given in Table S5. All substrates, TMSCN, substituted salicylaldehydes and (1*R*,2*R*)-diamines were purchased from Acros, Aldrich, and Fluka, and were used without further purification. Solvents and substrates were purified by conventional methods.

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<sup>1</sup> a) K. Yoshinaga and T. Nagata, *Adv. Synth. Catal.*, 2009, **351**, 1495; b) N. Kurono, K. Arai, M. Uemura and T. Ohkuma, *Angew. Chem. Int. Ed.*, 2008, **47**, 6643; c) W. B. Yang and J. M. Fang, *J. Org. Chem.*, 1998, **63**, 1356.

### Preparation of ligands 1a-j:

To a solution of the selected aminosulfonamide (1 mmol) in dichloromethane (5 ml), a mixture of the selected salicylaldehyde derivative (1 mmol) in dichloromethane (3ml) was added at room temperature. The mixture was stirred overnight.  $\text{MgSO}_4$  was then added, the mixture was filtered and evaporated to dryness. After crystallization in ethanol, yellow crystals were obtained.

**Ligand 1a:** Yield = 95%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 13.00 (s, 1H, OH), 8.18 (s, 1H, CH=N), 7.40 (d,  $^3J = 8.1$  Hz, 2H,  $H_{p\text{-Tolyl}}$ ), 7.25–7.02 (m, 2H,  $H_{\text{PhOH}}$ ), 6.95 (d,  $^3J = 8.1$  Hz, 2H,  $H_{p\text{-Tolyl}}$ ), 4.90 (d,  $^2J = 6.3$  Hz, 1H, NH), 3.27–3.20 (m, 1H, CH-N), 3.04–2.96 (m, 1H, CH-NH), 2.24 (s, 3H,  $\text{CH}_3$ ), 2.40–2.30 (m, 1H,  $\text{CH}_2$ ), 1.49 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.62–1.21 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 168.8 (CH=N), 158.0 (C-OH), 142.1, 140.6, 137.9, 136.9, 129.1, 127.9, 126.9, 126.4, 117.6 ( $C_{\text{Ar}}$ ), 71.9 (CH-N), 57.5 (CH-NH), 35.5, 34.5, 33.2, 32.4, 31.8, 29.9, 24.2, 23.7, 21.9. IR(KBr):  $\nu = 3300\text{--}2853$  (large,  $\nu\text{O-H}$ ), 3277 ( $\nu\text{N-H}$ ), 2948 ( $\nu\text{C}_{\text{sp}2\text{-H}_{\text{Ar}}}$ ), 1629 ( $\nu\text{C=N}$ ), 1322, 1257, 1169, 1066  $\text{cm}^{-1}$ .

**Ligand 1b:** Yield = 94%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 13.30 (s, 1H, OH), 8.18 (s, 1H, CH=N), 7.63 (d,  $^3J = 8.1$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 7.34 (d,  $^3J = 7.6$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.01 (d,  $^3J = 8.1$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 6.96 (d,  $^3J = 7.6$  Hz, 1H,  $H_{\text{PhOH}}$ ), 6.77 (t,  $J = 7.6$  Hz, 1H,  $H_{\text{PhOH}}$ ), 4.9 (d,  $J = 6.2$  Hz, 1H, NH), 3.27–3.20 (m, 1H, CH-N), 3.04–2.96 (m, 1H, CH-NH), 2.24 (s, 3H,  $\text{CH}_3$ ), 2.41–2.31 (m, 1H,  $\text{CH}_2$ ), 1.46 (s, 9H, *t*-Bu), 1.60–1.21 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 166.2 (CH=N), 160.1 (C-OH), 143.1, 137.3, 137.0, 129.9, 129.5, 126.7, 126.6, 118.3, 117.8 ( $C_{\text{Ar}}$ ), 71.7 (CH-N), 57.5 (CH-NH), 34.9, 33.6, 32.9, 29.4, 24.3, 23.7, 21.4. IR(KBr):  $\nu = 3300\text{--}2800$  (large,  $\nu\text{O-H}$ ), 3293 ( $\nu\text{N-H}$ ), 2939 ( $\nu\text{C}_{\text{sp}2\text{-H}_{\text{AR}}}$ ), 1628 ( $\nu\text{C=N}$ ), 1320,

1267, 1166, 1062  $\text{cm}^{-1}$ . Elemental Anal. Calculated for  $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_3\text{S}$  (428.21  $\text{g}\cdot\text{mol}^{-1}$ ): C 67.26; H 7.53; N 6.54; S 7.48; found 67.68; H 7.77; N 6.48; S 7.15.

**Ligand 1c:** Yield = 93%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 12.30 (s, 1H, OH), 8.20 (s, 1H, CH=N), 7.63 (d,  $^3J = 8.1$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 7.34 (d,  $^3J = 7.6$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.10 (s, 1H,  $H_{\text{PhOH}}$ ), 6.99 (d,  $^3J = 8.1$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 6.82 (d,  $^3J = 7.6$  Hz, 1H,  $H_{\text{PhOH}}$ ), 4.83 (d,  $^3J = 6.2$  Hz, 1H, NH), 3.27-3.20 (m, 1H, CH-N), 3.02-2.98 (m, 1H, CH-NH), 2.27 (s, 3H,  $\text{CH}_3$ ), 2.41-2.32 (m, 1H,  $\text{CH}_2$ ), 1.30 (s, 9H, *t*-Bu), 1.61-1.21 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 165.5 (CH=N), 158.5 (C-OH), 143.1, 141.2, 137.3, 129.6, 129.5, 127.8, 126.6, 117.7, 116.3 ( $\text{C}_{\text{Ar}}$ ), 72.3 (CH-N), 57.3 (CH-NH), 33.9, 33.6, 33.3, 31.4, 24.4, 23.6, 21.6. IR(KBr):  $\nu = 3300\text{-}2800$  (large,  $\nu\text{O-H}$ ), 3301 ( $\nu\text{N-H}$ ), 2938 ( $\nu\text{C}_{\text{sp}2\text{-H}_{\text{AR}}}$ ), 1635 ( $\nu\text{C=N}$ ), 1315, 1269, 1167, 1066  $\text{cm}^{-1}$ . Elemental Anal. Calculated for  $\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_3\text{S}$  (428.21  $\text{g}\cdot\text{mol}^{-1}$ ): C 67.26; H 7.53; N 6.54; S 7.48; found 67.57; H 7.77; N 6.43; S 7.10.

**Ligand 1d:** Yield = 90%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 8.12 (s, 1H, OH), 8.07 (s, 1H, CH=N), 8.05 (dd,  $^3J = 9.2$  Hz,  $^4J = 2.6$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.94 (d,  $^4J = 2.4$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.50 (d,  $^3J = 8.0$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 6.95 (d,  $^3J = 8.0$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 6.83 (d,  $^3J = 9.3$  Hz, 1H,  $H_{\text{PhOH}}$ ), 4.89 (d,  $^3J = 8.2$  Hz, 1H, NH), 3.36-3.28 (m, 1H, CH-N), 3.04-2.96 (m, 1H, CH-NH), 2.24 (s, 3H,  $\text{CH}_3$ ), 2.3-2.4 (m, 1H,  $\text{CH}_2$ ), 1.80-1.20 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 168.3(CH=N), 163.9 (C-OH), 145.2, 143.1, 138.8, 137.8, 129.5, 128.1, 127.8, 126.5, 118.4, 116.8 ( $\text{C}_{\text{Ar}}$ ), 71.3 (CH-N), 57.1 (CH-NH), 33.5, 33.2, 24.6, 23.6, 21.4. IR(KBr):  $\nu = 3300\text{-}2800$  (large,  $\nu\text{O-H}$ ), 3278 ( $\nu\text{N-H}$ ), 2933 ( $\nu\text{C}_{\text{sp}2\text{-H}_{\text{AR}}}$ ), 1632 ( $\nu\text{C=N}$ ), 1322, 1267, 1160, 1064  $\text{cm}^{-1}$ . Elemental Anal. Calculated for  $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_5\text{S}$  (417.48  $\text{g}\cdot\text{mol}^{-1}$ ): C 57.54; H 5.55; N 10.07; S 7.68; found C 57.05; H 5.46; N 10.67; S 7.35.

**Ligand 1e:** Yield = 90%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 14.85 (s, 1H, OH), 8.20 (s, 1H, CH=N), 8.10 (d,  $^4J = 2.5$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.80 (d,  $^4J = 2.5$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.58 (d,  $^3J = 8.0$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 7.01 (d,  $^3J = 8.0$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 5.45 (d,  $^3J = 7.5$  Hz, 1H, NH), 3.27-3.20 (m, 1H, CH-N), 3.04-2.96 (m, 1H, CH-NH), 2.18 (s, 3H,  $\text{CH}_3$ ), 2.40-2.30 (m, 1H,  $\text{CH}_2$ ), 1.45 (s, 9H, *t*-Bu), 1.60-1.20 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 168.3 (CH=N), 165.0 (C-OH), 143.1, 139.6, 137.9, 137.8, 129.4, 126.7, 126.4, 124.7, 116.4 ( $C_{\text{Ar}}$ ), 70.5 (CH-N), 57.3 (CH-NH), 35.5, 33.4, 33.2, 29.1, 24.5, 23.6, 21.3. IR(KBr):  $\nu = 3300\text{-}2800$  (large,  $\nu\text{O-H}$ ), 3298 ( $\nu\text{N-H}$ ), 2958 ( $\nu\text{C}_{\text{sp}2\text{-H}_{\text{AR}}}$ ), 1638 ( $\nu\text{C=N}$ ), 1327, 1263, 1169, 1088  $\text{cm}^{-1}$ . Elemental Anal. Calculated for  $\text{C}_{24}\text{H}_{31}\text{N}_3\text{O}_5\text{S}$  (473.20  $\text{g}\cdot\text{mol}^{-1}$ ): C 60.87; H 6.60; N 8.87; S 6.77; found C 60.54; H 6.54; N 9.46; S 6.68.

**Ligand 1f:** Yield = 85%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 12.52 (s, 1H, OH), 8.19 (s, 1H, CH=N), 7.65 (d,  $^4J = 2.4$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.43 (d,  $^3J = 8.0$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 7.31 (d,  $^4J = 2.4$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.29-7.10 (m, 15H,  $H_{\text{Trityl}}$ ), 6.98 (d,  $^3J = 8.0$  Hz, 2H,  $H_{p\text{-Tol}}$ ), 4.49 (b, 1H, NH), 3.04-2.96 (m, 1H, CH-N), 2.75-2.70 (m, 1H, CH-NH), 2.24 (s, 3H,  $\text{CH}_3$ ), 1.29 (s, 9H, *t*-Bu), 1.60-1.15 (m, 8H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 167.1 (CH=N), 156.8 (C-OH), 144.9 ( $3\text{C}_{\text{Trityl}}$ ), 141.5, 136.2, 135.0, 130.8 ( $6\text{C}_{\text{Trityl}}$ ), 128.9, 127.8 ( $6\text{C}_{\text{Trityl}}$ ), 126.9, 126.8, 125.8 ( $3\text{C}_{\text{Trityl}}$ ), 120.2 ( $C_{\text{Ar}}$ ), 71.5 (CH-N), 63.1 (C-CPh<sub>3</sub>), 57.5 (CH-NH), 34.2 (C-(Me)<sub>3</sub>), 31.3 (3  $\text{CH}_3$ ), 28.8, 28.3, 24.6, 24.4. IR(KBr):  $\nu = 3300\text{-}2800$  (large,  $\nu\text{O-H}$ ), 3286 ( $\nu\text{N-H}$ ), 2958 ( $\nu\text{C}_{\text{sp}2\text{-H}_{\text{AR}}}$ ), 1629 ( $\nu\text{C=N}$ ), 1362, 1270, 1158, 1066  $\text{cm}^{-1}$ . Elemental Anal. Calculated for  $\text{C}_{43}\text{H}_{46}\text{N}_2\text{O}_3\text{S}$  (670.90  $\text{g}\cdot\text{mol}^{-1}$ ): C 76.98; H 6.91; N 4.18; S 4.78; found C 77.29; H 6.98; N 3.52; S 3.50.

**Ligand 1g:** Yield = 88%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 12.86 (s, 1H, OH), 8.16 (s, 1H, CH=N), 8.01 (d,  $^3J = 7.8$  Hz, 1H,  $H_{\text{O-Nosyl}}$ ), 7.43 (t,  $^3J = 7.5$  Hz, 1H,  $H_{\text{O-Nosyl}}$ ), 7.35-7.20

(m, 3H,  $H_{\text{O-Nosyl et PhOH}}$ ), 6.78 (s, 1H,  $H_{\text{PhOH}}$ ), 5.21 (b, 1H, NH), 3.50-3.40 (m, 1H, CH-N), 3.02-2.90 (m, 1H, CH-N), 2.48-2.40 (m, 1H,  $\text{CH}_2$ ), 1.39 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 1.65-1.05 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 166.3 (CH=N), 157.5 (C-OH), 147.7, 140.2, 136.1, 134.8, 133.0, 132.3, 129.7, 125.8, 124.5, 117.0 ( $C_{\text{Ar}}$ ), 72.9 (CH-N), 58.8 (CH-NH), 35.0, 34.6, 34.0, 33.8, 31.5, 29.5, 24.8, 23.7. IR(KBr):  $\nu = 3300\text{-}2850$  (large,  $\nu\text{O-H}$ ), 3303 ( $\nu\text{N-H}$ ), 2957 ( $\nu\text{C}_{\text{sp}^2}\text{-H}_{\text{AR}}$ ), 1626 ( $\nu\text{C=N}$ ), 1535, 1339, 1268, 1160, 1069  $\text{cm}^{-1}$ . Elemental Anal. Calculated for  $\text{C}_{27}\text{H}_{37}\text{N}_3\text{O}_5\text{S}$  (515.25  $\text{g}\cdot\text{mol}^{-1}$ ): C 62.89; H 7.23; N 8.15; S 6.22; found C 62.20; H 7.16; N 8.69; S 5.90.

**Ligand 1h:** Yield = 80%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 12.75 (s, 1H, OH), 8.60 (t,  $^4J = 1.9$  Hz, 1H,  $H_{\text{m-Nosyl}}$ ), 8.51 (s, 1H,  $H_{\text{m-Nosyl}}$ ), 8.20 (s, 1H, CH=N), 8.14-8.05 (m, 1H,  $H_{\text{Nosyl}}$ ), 7.40 (d,  $^4J = 2.4$  Hz, 1H,  $H_{\text{PhOH}}$ ), 7.33 (t,  $^3J = 8.0$  Hz, 1H,  $H_{\text{m-Nosyl}}$ ), 6.95 (d,  $^4J = 2.4$  Hz, 1H,  $H_{\text{PhOH}}$ ), 5.01 (b, 1H, NH), 3.50-3.40 (m, 1H, CH-N), 3.02-2.92 (m, 1H, CH-N), 2.48-2.40 (m, 1H,  $\text{CH}_2$ ), 1.39 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 1.60-1.03 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 166.3 (CH=N), 157.5 (C-OH), 147.6, 142.7, 140.4, 136.3, 131.9, 130.3, 127.8, 126.3, 121.7, 117.2 ( $C_{\text{Ar}}$ ), 72.4(CH-N), 58.5 (CH-NH), 35.0, 34.0, 31.3, 30.1, 29.9, 29.4, 24.7, 23.8. IR(KBr):  $\nu = 3300\text{-}2800$  (large,  $\nu\text{O-H}$ ), 3286 ( $\nu\text{N-H}$ ), 2949 ( $\nu\text{C}_{\text{sp}^2}\text{-H}_{\text{AR}}$ ), 1627 ( $\nu\text{C=N}$ ), 1533, 1321, 1267, 1169, 1067  $\text{cm}^{-1}$ . Elemental Anal. Calculated  $\text{C}_{27}\text{H}_{37}\text{N}_3\text{O}_5\text{S}$  (515.25  $\text{g}\cdot\text{mol}^{-1}$ ): C 62.89; H 7.23; N 8.15; S 6.22; found C 62.70; H 7.18; N 8.49; S 6.03.

**Ligand 1i:** Yield = 93%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 12.9 (s, 1H, OH), 8.11 (s, 1H, CH=N), 8.03 (d,  $^3J = 8.9$  Hz, 1H,  $H_{\text{p-Nosyl}}$ ), 7.87 (d,  $^3J = 8.9$  Hz, 1H,  $H_{\text{p-Nosyl}}$ ), 7.38 (d,  $^4J = 2.3$  Hz, 1H,  $H_{\text{PhOH}}$ ), 6.85 (d,  $^4J = 2.3$  Hz, 1H,  $H_{\text{PhOH}}$ ), 4.92 (b, 1H, NH), 3.50-3.40 (m, 1H, CH-N), 2.92-2.70 (m, 1H, CH-NH), 2.48-2.40 (m, 1H,  $\text{CH}_2$ ), 1.39 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 1.63-1.03 (m, 7H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz,  $\delta$  ppm): 166.4 (CH=N), 157.4 (C-OH),

146.5, 140.5, 136.4, 127.8, 127.5, 125.9, 124.2, 117.2 ( $C_{Ar}$ ), 72.4 (CH-N), 58.5 (CH-NH), 35.0, 34.2, 34.1, 34.0, 31.4, 30.9, 29.3, 24.7. IR(KBr):  $\nu = 3300-2800$  (large,  $\nu O-H$ ), 3292 ( $\nu N-H$ ), 2958 ( $\nu C_{sp^2}-H_{AR}$ ), 1623 ( $\nu C=N$ ), 1532, 1314, 1274, 1164, 1052  $cm^{-1}$ .

**Ligand 1j:** Yield = 90%.  $^1H$  NMR ( $CDCl_3$ , 300 MHz,  $\delta$  ppm): 14.45 (s, 1H, OH), 8.57 (t,  $^4J = 1.9$  Hz, 1H,  $H_{m-Nosyl}$ ), 8.29 (s, 1H, CH=N), 8.16 (d,  $^4J = 2.7$  Hz, 1H,  $H_{PhOH}$ ), 8.02 (m, 2H,  $H_{m-Nosyl}$ ), 7.90 (d,  $^4J = 2.7$  Hz, 1H,  $H_{PhOH}$ ), 7.45 (t,  $^3J = 8.0$  Hz, 1H,  $H_{m-Nosyl}$ ), 5.51 (b, 1H, NH), 3.50-3.40 (m, 1H, CH-N), 3.02-2.90 (m, 1H, CH-NH), 2.48-2.40 (m, 1H,  $CH_2$ ), 1.41 (s, 9H, *t*-Bu), 1.60-1.05 (m, 7H,  $CH_2$ ).  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz,  $\delta$  ppm): 167.5 (CH=N), 165.1 (C-OH), 147.8, 143.0, 139.5, 138.2, 132.0, 130.4, 126.6, 126.4, 125.1, 121.8, 116.5 ( $C_{Ar}$ ), 71.1 (CH-N), 57.7 (CH-NH), 35.2, 33.8, 33.4, 28.9, 24.6, 23.6. IR(KBr):  $\nu = 3300-2800$  (large,  $\nu O-H$ ), 3287 ( $\nu N-H$ ), 2969 ( $\nu C_{sp^2}-H_{AR}$ ), 2856 ( $\nu C_{sp^3}-H_{AR}$ ), 1632 ( $\nu C=N$ ), 1327, 1282, 1159, 1074  $cm^{-1}$ . Elemental Anal. Calculated  $C_{23}H_{28}N_4O_7S$  (504.17  $g \cdot mol^{-1}$ ): C 54.75; H 5.59; N 11.10; S 6.36; found C 54.64; H 5.52; N 11.90; S 6.13.

**Complex 2a:** To a stirring solution of (*R,R*)-**1a** (0.970 g, 2 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of diethylaluminum chloride (1M, 25% in toluene, 0.482 g, 1 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred for another 24 h. After removal of solvent, the yellow crude product was recrystallized from dry pentane (50 mL) to afford complex **2a** as a yellow solid. Yield = 86%.  $^1H$  NMR ( $C_6D_6$ , 300 MHz,  $\delta$  ppm)  $\delta$  8.16 (s, 1H, CH=N), 8.02 (d,  $^3J = 8.2$  Hz, 2H,  $H_{p-Tol}$ ), 7.52 (d,  $^4J = 2.5$  Hz, 1H,  $H_{PhOH}$ ), 6.68 (m, 1H,  $H_{PhOH}$ ), 6.80 (d,  $^3J = 8.2$  Hz, 2H,  $H_{p-Tol}$ ), 4.61-4.52 (m, 1H, CH-NHSO<sub>2</sub>), 3.80-3.62 (m, 1H, CH-N=C), 2.95-2.74 (m, 1H,  $CH_2$ -CH-NHSO<sub>2</sub>), 2.69-2.51 (m, 1H,  $CH_2$ -CH-N=C), 1.83 (s, 3H,  $CH_3$ -tosyl), 1.36 (s, 9H, *t*-Bu), 1.32 (s, 9H, *t*-Bu), 1.02-0.72 (m, 6H,  $CH_2$ -cyclohexyl).  $^{13}C$  NMR ( $C_6D_6$ , 75 MHz,  $\delta$  ppm): 168.7 (CH=N), 159.4 (C-OAl),

141.6, 139.4, 139.2, 138.7, 137.6, 130.1, 129.3, 129.0, 126.4, 125.4, 119.7 ( $C_{Ar}$ ), 63.2 (CH-N=C), 57.3 (CH-NHSO<sub>2</sub>), 36.3, 35.0, 33.8, 31.3, 29.5, 24.9, 21.1, 6.7. IR(KBr):  $\nu = 3312$  ( $\nu_{N-H}$ ), 2980 ( $\nu(sp^3-CH)$ ), 1631 ( $\nu_{C=N}$ )  $cm^{-1}$ .

**Complex 3a:** To a stirring solution of (*R,R*)-**1a** (0.485 g, 1 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of diethylaluminum chloride (1M, 25% in toluene, 0.482 g, 1 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred for another 2 h. After removal of solvent, the yellow crude product was recrystallized from dry pentane (50 mL) to afford **3a** as a yellow solid (1.43 g, 89.4 %). Yield = 89%. <sup>1</sup>H RMN ( $C_6D_6$ , 300 MHz,  $\delta$  ppm): 8.08 (s, 1H, CH=N), 7.88 (s, 1H, CH=N), 7.83 (d, <sup>3</sup>*J* = 8.0 Hz, 2H,  $H_{p-Tol}$ ), 7.80 (d, <sup>3</sup>*J* = 8.0 Hz, 2H,  $H_{p-Tol}$ ), 7.77-7.72 (m, 2H,  $H_{ArO}$ ), 7.12 (d, <sup>4</sup>*J* = 2.5 Hz, 1H,  $H_{ArO}$ ), 7.05 (d, <sup>4</sup>*J* = 2.5 Hz, 1H,  $H_{ArO}$ ), 6.75 (d, <sup>3</sup>*J* = 8.0 Hz, 2H,  $H_{p-Tol}$ ), 6.73 (d, <sup>3</sup>*J* = 8.0 Hz, 2H,  $H_{p-Tol}$ ), 4.90 (d, <sup>3</sup>*J* = 6.3 Hz, 1H, NH), 4.85 (d, <sup>3</sup>*J* = 6.3 Hz, 1H, NH), 3.80-3.68 (m, 1H, CH-N=C), 3.55-3.39 (m, 1H, CH-N=C), 3.22-3.11 (m, 1H,  $C^H-NHSO_2$ ), 2.89-2.75 (m, 1H, CH-NHSO<sub>2</sub>), 2.26-2.08 (m, 1H, CH<sub>2</sub>), 2.03-1.97 (m, 1H, CH<sub>2</sub>), 1.88 (s, 3H, CH<sub>3</sub>), 1.84 (s, 3H, CH<sub>3</sub>), 1.68 (s, 9H, t-Bu), 1.67 (s, 9H, t-Bu), 1.57 (t, 3H, <sup>3</sup>*J* = 6.3 Hz, CH<sub>2</sub>-CH<sub>3</sub>), 1.28 (s, 9H, t-Bu), 1.26 (s, 9H, t-Bu), 1.02-0.70 (m, 14H, CH<sub>2</sub>), 0.65 (m, 2H, CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR ( $C_6D_6$ , 75 MHz,  $\delta$  ppm) : 174.6 (CH=N), 173.6 (CH=N), 161.0 (C-OAl), 160.9 (C-OAl), 142.6, 142.4, 140.2, 139.9, 139.7, 139.0, 138.4, 137.6, 129.8, 129.5, 129.4, 129.0, 127.4, 126.7, 125.4, 125.2, 118.4, 118.2 ( $C_{Ar}$ ), 70.3 (CH-N=C), 68.7 (CH-N=C), 57.5 (CH-NHSO<sub>2</sub>), 56.2 (CH-NHSO<sub>2</sub>), 35.3, 35.2, 34.9, 34.0, 33.9, 33.8, 32.5, 32.2, 31.3, 31.2, 29.5, 29.4, 24.7, 24.5, 23.8, 23.7, 21.2 (CH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 8.7 (CH<sub>3</sub>-CH<sub>2</sub>-Al), 6.7 (CH<sub>3</sub>-CH<sub>2</sub>-Al). IR(KBr) :  $\nu = 3301$  ( $\nu_{N-H}$ ), 2979 ( $\nu(sp^3-CH)$ ), 1626 ( $\nu_{C=N}$ )  $cm^{-1}$ . Elemental Analysis Calculated for  $C_{30}H_{44}AlClN_2O_3S$  (575.18  $g \cdot mol^{-1}$ ): C 62.64; H 7.71; N 4.87; S 5.57; found C 62.52; H 7.64; N 4.89.



**Complex 3j:** To a stirring solution of (*R,R*)-**1j** (0.504 g, 1 mmol) in dry dichloromethane (20 mL) was added dropwise a solution of diethylaluminum chloride (1M, 25% in toluene, 0.482 g, 1 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred for another 2 h. After removal of solvent, the orange crude product was recrystallized from dry pentane (50 mL) to afford complex **3j** as an orange solid. Yield = 82%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 MHz, δ ppm): 8.47 (t, <sup>4</sup>J = 1.9 Hz, 1H, H<sub>m-Nosyl</sub>), 8.35 (t, <sup>4</sup>J = 1.9 Hz, 0.6 H, H<sub>m-Nosyl</sub>), 8.19 (s, 0.6 H, CH=N), 8.16-7.90 (m, 7.4 H, H<sub>PhO</sub> and <sub>m-Nosyl</sub>), 7.45-7.32 (m, 1.6 H, H<sub>m-Nosyl</sub>), 4.63 (d, <sup>3</sup>J = 7.5 Hz, 1H, NH), 4.38 (d, <sup>3</sup>J = 7.5 Hz, 0.6 H, NH), 3.28-3.08 (m, 0.6 H, CH-N), 3.08-2.87 (m, 2.6 H, CH-N), 2.02-1.92 (m, 1.6 H, CH<sub>2</sub>), 1.31 (s, 9H, *t*-Bu), 1.28 (s, 9H, *t*-Bu), 1.82-1.18 (m, 11.2 H, CH<sub>2</sub>), 0.67 (t, 4.8 H, <sup>3</sup>J = 6.3 Hz, CH<sub>3</sub>-CH<sub>2</sub>), 0.35 (m, 3.2 H, CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz, δ ppm): 174.7 (CH=N), 173.5(CH=N), 161.2 (C-OAl), 160.5 (C-OAl), 147.9, 147.2, 143.1, 143.0, 139.8, 137.4, 137.3, 133.0, 132.9, 129.7, 129.6, 126.4, 126.3, 125.4, 125.2, 121.9, 121.5, 117.4, 117.2 (C<sub>Ar</sub>), 71.5 (CH-N), 70.2 (CH-N), 57.8 (CH-NH), 57.1 (CH-NH), 35.1, 35.0, 34.5, 34.2, 33.9, 33.7, 31.2, 31.0, 29.4, 29.1, 23.7, 23.2, 8.1 (CH<sub>3</sub>-CH<sub>2</sub>-Al), 0.7 (CH<sub>3</sub>-CH<sub>2</sub>-Al).

**General procedure for 1a-j-Al catalyzed asymmetric cyanosilylation of aldehydes:**

A mixture of **1(a-j)** (0.02 mmol) and AlEt<sub>2</sub>Cl (0.02 mmol) in dry dichloromethane (1 ml) was stirred 2 hours at room temperature. Then, benzaldehyde (0.1 ml, 1 mmol) was added and stirred for 0.5 h at room temperature under a nitrogen atmosphere. To the mixture was added *N,N*-dimethylaniline *N*-oxyde (0.015 mmol) and the resulting mixture was stirred for another 0.5 h at the same temperature. Then, the mixture was stirred at -20°C and trimethylsilylcyanide (0.2 ml, 1.5 mmol) was added with a syringe. After stirring for 12–18 h at this temperature, the mixture was concentrated and purified by column chromatography

(200–300 mesh, gradient of petroleum ether/ethyl acetate) to yield the silylated cyanohydrin which was used for further chiral GC analysis.

**General procedure for 3a-catalyzed asymmetric cyanosilylation of aldehydes:**

A mixture of complex **3a** (11 mg, 0.02 mmol), benzaldehyde (0.1 ml, 1 mmol), and dry dichloromethane (1.5 mL) was stirred for 0.5 h at room temperature under a nitrogen atmosphere. To the mixture was added *N*-oxyde (0.015 mmol) and the resulting mixture was stirred for another 0.5 h at the same temperature. Then, the mixture was stirred at -20°C and trimethylsilylcyanide (0.2 ml, 1.5 mmol) was then added with a syringe. After stirring for 12–18 h at this temperature, the mixture was concentrated and purified by column chromatography (200–300 mesh, gradient of petroleum ether/ethyl acetate) to yield the silylated cyanohydrin which was used for further chiral GC analysis.

**Table S1.** Influence of the **1a**-AlEt<sub>2</sub>Cl ratio on the catalytic performances

Entry <sup>[a]</sup>	[1a]:[AlEt <sub>2</sub> Cl] ratio	Conv. [%] <sup>[b]</sup>	ee [%] <sup>[b]</sup>	Config.
<b>1</b>	1:0	5	0	-
<b>2</b>	0:1	96	0	-
<b>3</b>	1:1	45	94	<i>R</i>
<b>4</b>	2:1	35	84	<i>S</i>

<sup>[a]</sup> All reactions were carried out with *N*-oxide (1.5 mol%) at -20 °C for 2 h, TMSCN (1.5 eq), [benzaldehyde] = 0.66M in CH<sub>2</sub>Cl<sub>2</sub>. <sup>[b]</sup> Determined by chiral GC analysis on Chrasil DEX CB.

**Table S2.** Influence of the cocatalyst on the catalytic performances

Entry <sup>[a]</sup>	Catalyst (mol%)	Cocatalyst	Cocat. (mol%)	Conv. [%] <sup>[b]</sup>	ee [%] <sup>[b]</sup>	Config.
<b>1</b>	2	-	-	25	0	-
<b>2</b>	2	MeS(O)Ph	1	5	10	<i>R</i>
<b>3</b>	2	MeS(O)Ph	2	7	13	<i>R</i>
<b>4</b>	2	MeS(O)Ph	5	10	23	<i>R</i>
<b>5</b>	2	Ph <sub>2</sub> S(O)	1	10	15	<i>R</i>
<b>6</b>	2	Ph <sub>2</sub> S(O)	5	7	35	<i>R</i>
<b>7</b>	2	Ph <sub>2</sub> P(O)	10	75	25	<i>R</i>
<b>8</b>	2	Ph <sub>2</sub> P(O)	10	60	17	<i>R</i>
<b>9</b>	2	Ph <sub>3</sub> P(O)	10	55	30	<i>R</i>
<b>10</b>	2	Ph <sub>3</sub> P(O)	10	50	20	<i>R</i>
<b>11</b>	2	Ph <sub>3</sub> P(O)	10	40	7	<i>R</i>
<b>12</b>	2	Ph <sub>3</sub> P(O)	5	30	15	<i>R</i>
<b>13</b>	2	Ph <sub>3</sub> P(O)	20	60	19	<i>R</i>
<b>14</b>	2	Dimethylaniline <i>N</i> -oxide	1	65	63	<i>R</i>
<b>15</b>	2	Dimethylaniline <i>N</i> -oxide	5	70	26	<i>R</i>
<b>16</b>	2	Methylmorpholine <i>N</i> -oxide	1	50	25	<i>R</i>
<b>17</b>	2	Methylmorpholine <i>N</i> -oxide	5	75	11	<i>R</i>

<sup>[a]</sup> All reactions were carried out with *N*-oxide (1.5 mol%) at -20 °C for 2 h, TMSCN (1.5 eq), [benzaldehyde] = 0.66M in CH<sub>2</sub>Cl<sub>2</sub>. <sup>[b]</sup> Determined by chiral GC analysis on Chrasil DEX CB after 2 hours.

**Table S3.** Influence of the substrate concentration on the catalytic performances.

Entry <sup>[a]</sup>	[S] (mol %)	Conv. [%] <sup>[b]</sup>	ee [%] <sup>[b]</sup>	Config.
1	0.33	30	90	<i>R</i>
2	0.66	45	94	<i>R</i>
3	1	50	94	<i>R</i>

<sup>[a]</sup> All reactions were carried out with **3** (2 mol%) and *N*-oxide (1.5 mol%) at -20 °C for 2 h, TMSCN (1,5 eq) in CH<sub>2</sub>Cl<sub>2</sub>. <sup>[b]</sup> Determined by chiral GC analysis on Chirasil DEX CB.

**Table S4.** Influence of the amount of TMSCN on the catalytic performances.

Entry <sup>[a]</sup>	TMSCN (eq)	Conv. [%] <sup>[b]</sup>	e.e. [%] <sup>[b]</sup>	Config.
1	1,2	42	82	<i>R</i>
2	1,5	45	94	<i>R</i>
3	1,8	50	93	<i>R</i>
4	2	52	87	<i>R</i>
5	2,5	55	85	<i>R</i>

<sup>[a]</sup> All reactions were carried out with **3** (2 mol%) and *N*-oxide (1.5 mol %) at -20 °C for 2 h, [benzaldehyde] = 0,66 M in CH<sub>2</sub>Cl<sub>2</sub>. <sup>[b]</sup> Determined by chiral GC analysis on Chirasil DEX CB.

**Table S5.** Crystal data and structure refinement for complex **2**

empirical formula	$C_{56}H_{78}AlClN_4O_6S_2 \cdot 4(C_6H_6)$
fw/g · mol <sup>-1</sup>	1342.28
temperature/K	100(2)
wavelength/Å	0.71073
crystal system	tetragonal
space group	$P4_12_12$
<i>a</i> [Å]	13.6143 (3)
<i>b</i> [Å]	13.6143 (3)
<i>c</i> [Å]	38.6616 (8)
$\alpha$ /deg	90
$\beta$ /deg	90
$\gamma$ /deg	90
volume/ Å <sup>3</sup>	7165.9 (3)
<i>Z</i>	4
density (calcd) Mg·m <sup>-3</sup>	1.244
absorp coeff/mm <sup>-1</sup>	0.18
<i>F</i> (000)	2880
crystal size/mm <sup>3</sup>	0.2 × 0.14 × 0.12
$\theta$ range for data collection/deg	1.6 to 28.3
index ranges	$-18 \leq h \leq 13$ $-18 \leq k \leq 17$ $-51 \leq l \leq 51$
reflns collected	76565
indep reflns	5918 [R(int) = 0.075]
refinement method	Full-matrix least-squares on <i>F</i>
data /restraints/params	4383 / 22 / 431
goodness-of-fit on <i>F</i> <sup>2</sup>	1.09
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	$R_1 = 0.0713$ $wR_2 = 0.083$
<i>R</i> indices (all data)	$R_1 = 0.0751$ $wR_2 = 0.085$
largest diff. peak and hole/ e·Å <sup>-3</sup>	0.92 and -0.82

