Supporting Information

Vanadium-catalyzed enantioselective Friedel–Crafts-type reactions of imines

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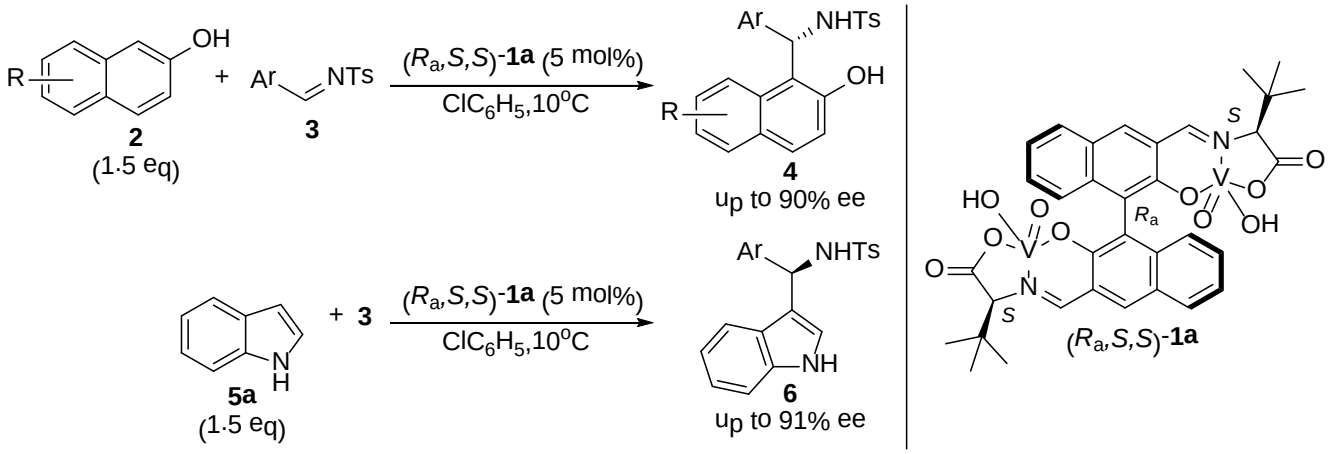
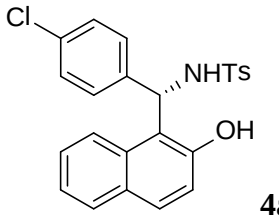
General information

^{1}H- and ^{13}C-NMR spectra were recorded with JEOL JMN LA-400 FT NMR (^{1}H-NMR 400 MHz, ^{13}C-NMR 100 MHz). ^{1}H-NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CHCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, q = quartet, t = triplet, m = multiplet), and coupling constants (Hz). ^{13}C-NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. FAB-Mass spectra were obtained with JEOL JMS-700. Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH or EtOH as eluents. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). Column chromatography on SiO_2 was performed with Kanto Silica Gel 60 (40-100 μm). Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled from sodium/benzophenone or CaH_2.

General procedure for enantioselective Friedel–Crafts (FC)-type reactions

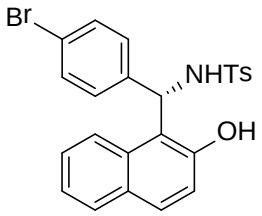
Under N_2 atmosphere, a test tube was charged with 2-naphthols **2** or indole (**5a**) (0.15 mmol), imine **3** (0.10 mmol) and the catalyst (R_a,*S*,*S*)-**1** (3.7 mg, 0.005 mmol, 5 mol%) in ClC_6H_5 (0.4 mL). The reaction mixture was stirred at 10°C. After the purification via SiO_2 column chromatography the desired product **4** or **6** was obtained. The products **4a-c**, **4e-h** and **6a-d** were identical in all respects with reported in the literature.[1,2]





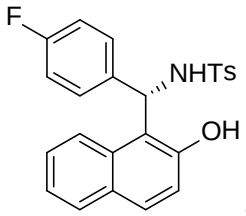
4a[1]

Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.70 (1H, d, *J* = 9.2 Hz), 7.66 (1H, d, *J* = 8.7 Hz), 7.55 (1H, d, *J* = 8.7 Hz), 7.41 (1H, t, *J* = 7.8 Hz), 7.31 (2H, d, *J* = 8.2 Hz), 7.23 (2H, d, *J* = 8.7 Hz), 7.18 (2H, d, *J* = 8.2 Hz), 6.83 (1H, d, *J* = 8.7 Hz), 6.64 (2H, d, *J* = 7.8 Hz), 6.60 (1H, bs), 6.35 (1H, d, *J* = 10.1 Hz), 6.29 (1H, bs), 2.10 (3H, s); Enantiomeric excess: 85%, determined by HPLC (Chiralpak IC, *n*-hexane/*i*-PrOH = 95/5, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 14.8 min, minor isomer: t_R = 12.9 min.



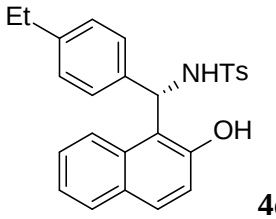
4b[1]

Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.70 (1H, d, *J* = 8.2 Hz), 7.67 (1H, d, *J* = 7.3 Hz), 7.56 (1H, d, *J* = 9.2 Hz), 7.42 (1H, t, *J* = 7.3 Hz), 7.29-7.36 (5H, m), 7.18 (2H, d, *J* = 8.2 Hz), 6.80 (1H, d, *J* = 9.2 Hz), 6.66 (2H, d, *J* = 8.2 Hz), 6.49 (1H, s), 6.34 (1H, d, *J* = 9.2 Hz), 5.98 (1H, s), 2.11 (3H, s); Enantiomeric excess: 85%, determined by HPLC (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 4/1, flow rate: 1.0 mL/min, 234 nm): major isomer: t_R = 29.0 min, minor isomer: t_R = 14.5 min.



4c[1]

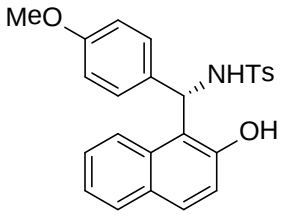
Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.72 (1H, d, *J* = 8.7 Hz), 7.68 (1H, d, *J* = 8.2 Hz), 7.56 (1H, d, *J* = 8.7 Hz), 7.44-7.40 (1H, m), 7.35-7.25 (5H, m), 6.95-6.90 (2H, m), 6.79 (1H, d, *J* = 8.7 Hz), 6.67 (2H, d, *J* = 8.2 Hz), 6.45-6.35 (2H, m), 5.79 (1H, s), 2.12 (3H, s); Enantiomeric excess: 76%, determined by HPLC (Chiralpak AS-H, *n*-hexane/*i*-PrOH = 4/1, flow rate: 1.0 mL/min, 234 nm): major isomer: t_R = 22.7 min, minor isomer: t_R = 15.8 min.



4d

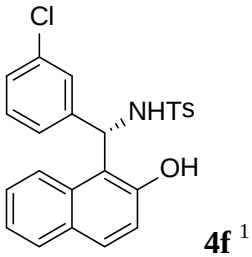
Yield 67%; ^{1}H-NMR ($CDCl_3$) δ: 7.74 (1H, d, *J* = 8.7 Hz), 7.66 (1H, d, *J* = 6.9 Hz), 7.55 (1H, d, *J* = 8.7 Hz), 7.31-7.40 (4H, m), 7.21 (2H, d, *J* = 8.2 Hz), 7.07 (2H, d, *J* = 8.2 Hz), 6.80 (1H, d, *J* = 8.7 Hz), 6.70 (2H, d, *J* = 7.8 Hz), 6.39 (1H, d, *J* = 8.7 Hz), 6.31 (1H, d, *J* = 8.7 Hz), 6.07 (1H, s), 2.58 (2H, q, *J* = 7.6 Hz), 2.13 (3H, s), 1.17 (3H, t, *J* = 7.6 Hz); ^{13}C-NMR ($CDCl_3$) δ: 151.2, 143.3, 142.7, 137.2, 136.2, 132.3, 129.7, 129.5, 128.6, 128.3, 127.8, 127.0, 126.8, 126.6, 126.4, 123.2, 121.9, 118.2, 54.4, 28.3, 21.1, 15.4; IR (neat) 3357, 2349, 1514, 1437, 1328, 1272, 1155, 1094, 902 cm^{-1}; HRMS(FAB) calcd for $C_{26}H_{26}NO_3S$ $(M+H)^+$ 432.1633, found 432.1637; Enantiomeric excess: 81%, determined by HPLC

(Chiralpak IC, *n*-hexane/*i*-PrOH = 4/1, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 6.9 min, minor isomer: t_R = 5.1 min; $[\alpha]_D^{27}$ +25.0° (*c* 0.2, $CHCl_3$).



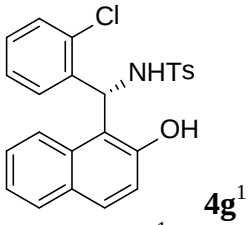
4e[1]

Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.71 (1H, d, *J* = 8.2 Hz), 7.65 (1H, d, *J* = 7.8 Hz), 7.53 (1H, d, *J* = 9.2 Hz), 7.31-7.38 (6H,m), 7.21 (2H, d, *J* = 8.2 Hz), 6.82 (1H, d, *J* = 8.7 Hz), 6.75 (2H, d, *J* = 8.7 Hz), 6.66 (2H, d, *J* = 7.8 Hz), 6.34 (1H, d, *J* = 9.2 Hz), 3.73 (3H, s), 2.11 (3H, s); Enantiomeric excess: 71%, determined by HPLC (Chiralpak AD-H, *n*-hexane/*i*-PrOH = 4/1, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 23.3 min, minor isomer: t_R = 13.0 min.



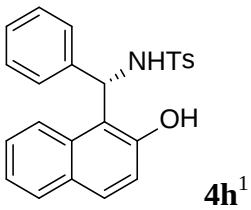
4f [1]

Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.68 (3H, dd, *J* = 13.5, 8.0 Hz), 7.54 (1H, d, *J* = 8.7 Hz), 7.40 (1H, d, *J* = 7.3 Hz), 7.33-7.29 (2H, m), 7.24 (2H, d, *J* = 8.2 Hz), 7.18 (2H, t, *J* = 4.4 Hz), 6.83 (1H, d, *J* = 8.7 Hz), 6.64 (2H, d, *J* = 8.2 Hz), 6.34 (2H, d, *J* = 10.1 Hz), 4.81 (1H, s), 2.09 (3H, s); Enantiomeric excess: 89%, determined by HPLC (Chiralpak IC, *n*-hexane/*i*-PrOH = 95/5, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 15.8 min, minor isomer: t_R = 13.5 min.



4g[1]

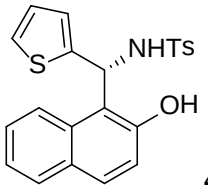
Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.67 (3H, d, *J* = 7.6 Hz), 7.46 (2H, d, *J* = 8.2 Hz), 7.41-7.28 (4H, m), 7.19 (1H, td, *J* = 7.6, 1.8 Hz), 7.11-7.07 (1H, m), 6.97 (2H, d, *J* = 8.2 Hz), 6.91 (1H, d, *J* = 8.2 Hz), 6.70 (1H, d, *J* = 5.0 Hz), 5.66 (1H, d, *J* = 5.0 Hz), 4.75 (1H, s), 2.31 (3H, s); Enantiomeric excess: 90%, determined by HPLC (Chiralpak IC, *n*-hexane/*i*-PrOH = 95/5, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 12.6 min, minor isomer: t_R = 14.5 min.



4h[1]

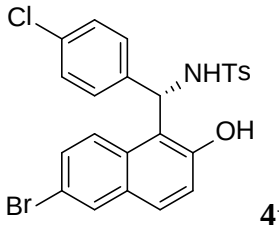
Yield 70%; ^{1}H-NMR ($CDCl_3$) δ: 7.74 (1H, d, *J* = 8.7 Hz), 7.67 (1H, d, *J* = 7.8 Hz), 7.55 (1H, d, *J* = 8.2 Hz), 7.32-7.39 (9H, m), 6.81 (1H, d, *J* = 8.7 Hz), 6.69 (2H, d, *J* = 7.8 Hz), 6.42 (2H, s), 6.07 (1H, s), 2.12 (3H, s); Enantiomeric excess: 71%, determined by HPLC (Chiralpak AS-H, *n*-hexane/*i*-PrOH =

4/1, flow rate: 1.0 mL/min, 234 nm): major isomer: t_R = 25.8 min, minor isomer: t_R = 20.1 min.



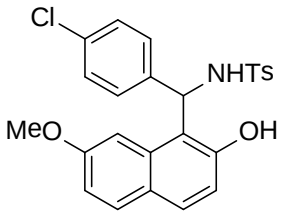
4i

Yield 80%; ^{1}H-NMR ($CDCl_3$) δ: 7.68 (1H, d, *J* = 8.2 Hz), 7.56 (1H, d, *J* = 8.7 Hz), 7.17-7.44 (7H, m), 6.83 (1H, dd, *J* = 5.0, 3.7 Hz), 6.80 (1H, d, *J* = 8.7 Hz), 6.72 (3H, m), 6.58 (2H, s), 2.14 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 151.3, 144.9, 143.6, 142.8, 136.2, 131.9, 129.8, 129.7, 128.7, 128.4, 127.2, 126.8, 126.6, 126.4, 125.1, 125.0, 123.4, 118.1, 51.6, 21.5; IR (neat) 3391, 2979, 2918, 2368, 2347, 1631, 1512, 1434, 1334, 1265, 1235, 1159, 1096, 902 cm^{-1}; HRMS(FAB) calcd for $C_{22}H_{20}NO_3S_2$ $(M+H)^+$ 410.0885, found 410.0885; Enantiomeric excess: 60%, (Chiralpak IC, *n*-hexane/*i*-PrOH = 4/1, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 7.0 min, minor isomer: t_R = 5.4 min; $[\alpha]_D^{26}$ +23.9° (*c* 0.36, $CHCl_3$).



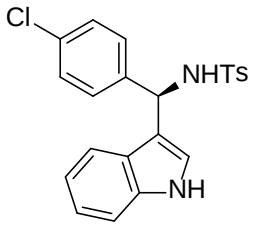
4j

Yield 77%; ^{1}H-NMR ($CDCl_3$) δ: 7.83 (1H, d, *J* = 2.3 Hz), 7.57 (1H, d, *J* = 9.0 Hz), 7.47 (2H, dt, *J* = 9.0, 2.3 Hz), 7.32 (2H, d, *J* = 8.2 Hz), 7.20 (4H, m), 6.85 (1H, d, *J* = 9.0 Hz), 6.72 (2H, d, *J* = 8.2 Hz), 6.41 (1H, s), 6.15-6.31 (2H, m), 2.16 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 151.4, 143.1, 138.4, 136.1, 133.2, 130.8, 130.4, 130.2, 129.7, 128.9, 128.8, 128.4, 128.1, 126.6, 126.4, 123.5, 119.2, 117.1, 53.7, 21.2; IR (neat) 3368, 2947, 2834, 2343, 1650, 1451, 1194, 1023 cm^{-1}; HRMS(FAB) calcd for $C_{24}H_{20}BrClNO_3S$ $(M+H)^+$ 516.0036, found 516.0035; Enantiomeric excess: 88%, determined by HPLC (Chiralpak AS-H, *n*-hexane/EtOH = 9/1, flow rate: 1.0 mL/min, 238 nm): major isomer: t_R = 20.2 min, minor isomer: t_R = 12.9 min; $[\alpha]_D^{26}$ +50.4° (*c* 0.25, $CHCl_3$).



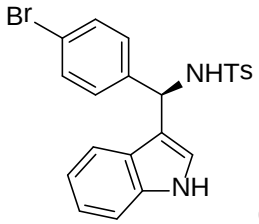
4k

Yield 82%; ^{1}H-NMR ($CDCl_3$) δ: 7.55 (1H, d, *J* = 8.7 Hz), 7.47 (1H, d, *J* = 8.7 Hz), 7.32 (2H, d, *J* = 8.7 Hz), 7.27 (2H, d, *J* = 8.7 Hz), 7.20 (2H, d, *J* = 8.7 Hz), 6.97 (1H, dd, *J* = 9.2, 2.3 Hz), 6.91 (1H, d, *J* = 2.3 Hz), 6.69 (2H, d, *J* = 8.7 Hz), 6.66 (1H, d, *J* = 8.7 Hz), 6.51 (1H, d, *J* = 10.1 Hz), 6.24 (1H, d, *J* = 10.1 Hz), 6.03 (1H, s), 3.84 (3H, s), 2.12 (3H, s). ^{13}C-NMR ($CDCl_3$) δ: 158.8, 151.8, 142.8, 138.9, 136.1, 133.6, 132.9, 129.9, 129.7, 129.5, 128.6, 128.3, 128.1, 126.5, 124.2, 116.5, 115.5, 115.3, 60.6, 55.3, 21.0; IR (neat) 3358, 2946, 2833, 1649, 1453, 1234, 1096, 1025 cm^{-1}; HRMS(FAB) calcd for $C_{25}H_{23}ClNO_4S$ $(M+H)^+$ 468.1036, found 468.1035; Enantiomeric excess: 61%, determined by HPLC (Chiralpak AS-H, *n*-hexane/EtOH = 9/1, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 20.1 min, minor isomer: t_R = 15.7 min; $[\alpha]_D^{18}$ +17.3° (*c* 0.23, $CHCl_3$).



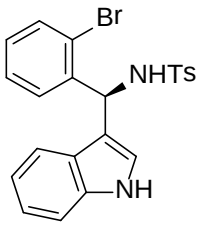
6a[2]

Yield 80%; ^{1}H-NMR ($CDCl_3$) δ: 8.00 (1H, s), 7.57 (2H, d, *J* = 8.7 Hz), 7.32 (1H, d, *J* = 7.8 Hz), 7.22-7.19 (6H, m), 7.15 (2H, d, *J* = 8.2 Hz), 7.02 (1H, t, *J* = 7.6 Hz), 6.65 (1H, d, *J* = 2.3 Hz), 5.82 (1H, d, *J* = 6.4 Hz), 5.00 (1H, d, *J* = 6.4 Hz), 2.40 (3H, s); Enantiomeric excess: 76%, determined by HPLC (Chiralcel OD, *n*-hexane/IPA = 4/1, flow rate: 1.0 mL/min, 254 nm): first peak: t_R = 7.3 min, second peak: t_R = 9.4 min.



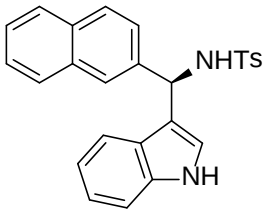
6b[2]

Yield 80%; ^{1}H-NMR ($CDCl_3$) δ: 8.02 (1H, s), 7.57 (2H, d, *J* = 8.2 Hz), 7.33 (2H, d, *J* = 8.2 Hz), 7.22-7.13 (7H, m), 7.02 (1H, t, *J* = 7.6 Hz), 6.65 (1H, d, *J* = 2.7 Hz), 5.81 (1H, d, *J* = 6.9 Hz), 5.00 (1H, d, *J* = 6.9 Hz), 2.41 (3H, s); Enantiomeric excess: 76%, determined by HPLC (Chiralcel OD-H, *n*-hexane/IPA = 4/1, flow rate: 1.0 mL/min, 254 nm): major isomer: t_R = 16.6 min, minor isomer: t_R = 32.2 min.



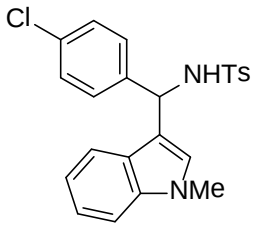
6c[2]

Yield 77%; ^{1}H-NMR ($CDCl_3$) δ: 8.01 (1H, s), 7.70 (2H, d, *J* = 8.2 Hz), 7.55 (2H, dd, *J* = 7.8, 1.5 Hz), 7.45 (1H, dd, *J* = 7.8, 1.5 Hz), 7.23-7.08 (6H, m), 7.01 (1H, t, *J* = 7.6 Hz), 6.55 (1H, d, *J* = 2.3 Hz), 6.19 (1H, d, *J* = 5.5 Hz), 5.07 (1H, d, *J* = 5.5 Hz), 2.41 (3H, s); Enantiomeric excess: 91%, determined by HPLC (Chiralcel OD, *n*-hexane/IPA = 4/1, flow rate: 1.0 mL/min, 222 nm): major isomer: t_R = 8.48 min, minor isomer: t_R = 13.3 min.



6d[2]

Yield 90%; ^{1}H-NMR ($CDCl_3$) δ: 8.02 (1H, s), 7.81 (1H, m), 7.66 (2H, d, *J* = 6.2 Hz), 7.55 (2H, d, *J* = 8.2 Hz), 7.45 (2H, d, *J* = 6.2 Hz), 7.31 (5H, m), 7.18 (1H, m), 7.01 (2H, t, *J* = 8.2 Hz), 6.71 (1H, s), 6.03 (1H, d, *J* = 6.9 Hz), 5.15 (1H, d, *J* = 6.9 Hz), 2.43 (3H, s); Enantiomeric excess: 64%, determined by HPLC (Chiralcel OD-H, *n*-hexane/IPA = 4/1, flow rate: 1.1 mL/min, 226 nm): major isomer: t_R = 24.9 min, minor isomer: t_R = 40.4 min.



6e

Yield 72%; ^{1}H-NMR ($CDCl_3$) δ: 7.57 (2H, d, *J* = 8.2 Hz), 7.28-7.12 (9H, m), 7.02-6.98 (1H, m), 6.44 (1H, s), 5.79 (1H, d, *J* = 6.4 Hz), 4.94 (1H, d, *J* = 6.4 Hz), 3.64 (3H, s), 2.41 (3H, s); ^{13}C-NMR ($CDCl_3$) δ: 143.3, 137.3, 136.9, 135.6, 129.7, 129.3, 128.6, 128.4, 127.3, 126.5 x 2, 122.3, 120.6, 119.7, 114.2, 109.5, 54.3, 32.7, 21.5; IR (neat) 3495, 2355, 1861, 1629, 1552, 1534, 1499, 1235, 1095 cm^{-1}; HRMS(FAB) calcd for $C_{23}H_{22}ClN_2O_2S$ $(M+H)^+$ 425.1091, found 425.1097; Enantiomeric excess: 0%, determined by HPLC (Chiralcel OD-H, *n*-hexane/IPA = 4/1, flow rate: 1.0 mL/min, 279 nm): first peak: t_R = 7.4 min, second peak: t_R = 9.4 min.

References

1. L.-F. Niu, Y.-C. Xin, R.-L. Wang, F. Jiang, P.-F. Xu, X.-P. Hui, *Synlett*, **2010**, 765.
2. B.-L. Wang, N.-K. Li, J.-X. Zhang, G.-G. Liu, T. Liu, Q. Shen, X.-W. Wang, *Org. Biomol. Chem.*, **2011**, *9*, 2614.