Masked Oxo Sulfinimines (*N*-Sulfinyl Imines) in the Asymmetric Synthesis of Proline and Pipecolic Acid Derivatives

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Supporting Information

General Procedure. Column chromatography was performed on silica gel, Merck grade 60 (230-400 mesh). Analytical and preparative thin layer chromatography was performed on pre-coated silica gel plates (250 and 1000 microns) purchased from Analtech Inc. TLC plates were visualized with UV in an iodine chamber or with phosphomolybdic acid unless noted otherwise. THF was freshly distilled under nitrogen from a purple solution of sodium and benzophenone.

Unless stated otherwise, all reagents were purchased from commercial sources and used without additional purification. Methyl 4,4-dimethoxybutanoate (**3a**),[1] ethyl levulineate ethylene acetal (**3b**),[2] ethyl 5,5-(ethylenedioxy)hexanoate (**3c**),[3] ethyl 6-phenyl 5,5-(ethylenedioxy) hexanoate (**3d**),[4] and ethyl 3,3-(ethylenedioxy)-3-phenylpropanoate (**3e**)[5] were prepared according to literature procedures.

General procedure for preparation of Mosher amides. In an oven-dried 5-mL single-necked round-bottom flask fitted with a magnetic stir bar and a rubber septum under an argon balloon was placed approximately 0.005 g of the pyrroline or pipecolic acid derivative, 0.005 g of Mosher's chloride, and 0.028 mL of distilled Et_3N. The suspension was stirred at rt for 30 h, washed with 1 N HCl (2 x 1 mL), brine (1 mL), dried ($MgSO_4$), and concentrated. Preparative TLC (EtOAc:hexane, 50:50) afforded the Mosher amides. The racemic Mosher amides where prepared in a similar manner. Evaluation of the ^{19}F and ^1H NMR spectra were used to determine the enantiomeric purity of the acids.

Typical procedure for the reduction of esters to aldehydes. 3,3-(Ethylenedioxy)-3-phenylpropanal (4e): In a 250-mL single necked round-bottom flask equipped with a magnetic stir bar, a thermometer, and an argon inlet was placed 2.44 g (10.3 mmol) of **3e** in dry CH_2Cl_2 (80 mL) at -78^{o}C. Diisobutylaluminum hydride, 13 mL (13 mmol, 1 M solution in CH_2Cl_2, Aldrich) was added slowly via syringe to prevent the inner temperature from rising above -65 ^{o}C. The reaction mixture was stirred at -78 ^{o}C and monitored by TLC. When all of the starting material had disappeared (3 h), the reaction mixture was quenched at -78 ^{o}C with MeOH (1 mL) and saturated Na_2SO_4 solution (4 mL). After stirring at rt for 18 h, white precipitates were formed and 5 g of solid anhydrous Na_2SO_4 was added. The reaction mixture was stirred for another 1 h, then the salts were filtered and washed with CH_2Cl_2 (2 x 20 mL). The combined organic phases were concentrated to give 1.88 g (95%) of **4e** as an oil whose spectral properties were consistent with literature values.[6]

4,4-Dimethoxybutanal (4a): oil; yield 74%. Spectral properties were consistent with literature values.[7]

4,4-(Ethylenedioxy)pentanal (4b): oil; yield 92%; ^1H NMR ($CDCl_3$) δ 9.71 (t, 1H, J = 1.8 Hz), 3.86-3.95 (m, 4H), 2.46 (dt, 2H, J = 1.8 and 7.0 Hz), 2.06 (t, 2H, J = 7.0 Hz), 1.32 (s, 3H).[8]

5,5-(Ethylenedioxy)hexanal (4c): oil; yield 90%. Spectral properties were consistent with literature values.[9]

5,5-(Ethylenedioxy)-5-phenylpentanal (4d): oil; yield 65%. Spectral properties were consistent with literature values.[10]

Typical One-Pot Procedure for the Synthesis of Sulfinimines. (*S*)-(+)-*N*-[3,3-(Ethylenedioxyl)-3-phenylpropylidene]-*p*-toluenesulfinamide (7e).[11] In a 100-mL two-necked round-bottomed flask equipped with a magnetic stir bar, a rubber septum, and an argon inlet was placed 0.488 g (1.66 mmol) of (1*R*,2*S*,5*R*)-(-)-menthyl (*S*)-*p*-toluenesulfinate (**5**)[12] (Aldrich) in THF (20 mL) and the mixture was cooled to -78 ^{o}C. A solution of 2.0 mL (1.0 M in THF, Aldrich) of LiHMDS was added via syringe, warmed to rt after 15 min, and stirred for 1.5 h, while being monitored by TLC (20% ethyl acetate/pentane) for the absence of **5**. At this time the solution was cooled to -78 ^{o}C and 0.35 g (1.82 mmol) of aldehyde **4e** was added via syringe. The reaction mixture was kept at this temperature 4 h, quenched with sat. NH_4Cl solution (0.6 mL), diluted with H_2O (30 mL) and EtOAc (30 mL). The phases were separated and the aqueous phase was washed with EtOAc (3 x 30 mL). The combined organic phases were washed with brine (30 mL), dried ($MgSO_4$), and concentrated to give a solid that was purified by flash chromatography (20% EtOAc/pentane) to give 0.37 g (68%) of **7e**; mp 54-55 ^{o}C; $[\alpha]^{20}_{D}$ +220.2 (*c* 1.0, $CHCl_3$); IR (KBr) 1627 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.29 (dd, 1 H, *J* = 5.1, 5.5 Hz), 7.47 (m, 4 H), 7.32 (m, 5 H), 4.04 (m, 2 H), 3.80 (m, 2 H), 3.06 (dd, 1H, *J* = 5.1and 9.9 Hz), 3.09 (dd, 1 H, *J* =5.5, and 9.9), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 164.0, 142.4, 142.2, 142.0, 130.5, 129.1, 126.1, 125.3, 109.3, 65.48, 65.45, 47.0, 22.1. Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.88; H, 6.00; N, 4.49.

(*R*)-(-)-*N*-(4,4-Dimethoxybutanylidene)-*p*-toluenesulfinimide (7a): (1*S*,2*R*,5*S*)-(+)-menthyl-(*R*)-*p*-toluenesulfinate (**5**)[12,13] was used to prepared (-)-**7a**; yield 58%; oil; $[\alpha]^{20}_{D}$ -320.0 (*c* 1.1, $CHCl_3$); IR (neat): 1622, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.24 (t, 1 H, *J* = 4.4 Hz), 7.56 (d, 2 H, *J* = 8.1 Hz), 7.30 (d, 2 H, *J* = 8.1 Hz), 4.36 (t, 1 H, *J* = 5.9 Hz), 3.29 (s, 3 H), 3.28 (s, 3 H), 2.56 (m, 2 H), 2.40 (s, 3 H), 1.99 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 167.0, 142.5, 142.3, 130.4, 125.2, 104.3, 53.9, 53.8, 31.7, 28.8, 22.0. Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.97; H, 7.11; N, 5.20. Found: C, 57.83; H, 7.32; N, 5.42.

(*S*)-(+)-*N*-[4-(1,3-Dioxolan-2-yl)pentanylidene]-*p*-toluenesulfinamide (7b): yield 54%; mp 48-50^{o}C; $[\alpha]^{20}_{D}$ +254.8 (*c* 1.0, $CHCl_3$); IR (KBr) 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.25 (t, 1 H, *J* = 4.4 Hz), 7.56 (m, 2 H), 7.30 (m, 2H), 3.85 (m, 4 H), 2.58 (m, 2 H), 2.40 (s, 3 H), 1.99 (m, 2 H), 1.31 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.8, 142.5, 142.3, 130.4, 125.2, 109.8, 65.4, 65.3, 35.1, 31.3, 24.8, 22.1. Anal. Calcd for $C_{14}H_{19}NO_3S$: C, 59.76; H, 6.81; N, 4.98. Found: C, 60.06; H, 6.87; N, 4.78.

(*S*)-(+)-*N*-[5,5-(Ethylenedioxy)hexanylidene]-*p*-toluenesulfinamide (7c): yield 61%; oil; $[\alpha]^{D}_{20}$ +279.6 (*c* 0.5, $CHCl_3$); IR (neat) 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.22 (t, 1 H, *J* = 4.4 Hz), 7.55 (d, 2 H, *J* = 8.1 Hz), 7.29 (d, 2 H, *J* = 8.1 Hz), 3.87-3.93 (m, 4 H), 2.49 (m, 2 H), 2.40 (s, 3 H), 1.72 (m, 2 H), 1.67 (m, 2 H), 1.29 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.5, 142.5, 142.3, 130.4, 125.2, 110.3, 65.3, 40.0, 36.5, 24.4, 22.1, 20.6. Anal. Calcd for $C_{15}H_{21}NO_3S$; C, 60.99; H, 7.17; N, 4.74. Found: C, 60.65; H, 7.20; N, 4.49.

(*S*)-(+)-*N*-[5,5-(Ethylenedioxyl)-5-phenylpentylidene]-*p*-toluenesulfinamide (7d). In an oven-dried 100-mL single-necked round-bottom flask fitted with a magnetic stir bar and a rubber septum under an argon balloon was placed 1.1 g (6.8 mmol) of (*S*)-(+)-*p*-toluenesulfinamide (**6**)[12] (Aldrich) and 0.5 g (2.3 mmol) of **4d** in CH_2Cl_2 (25 mL). Titanium (IV) ethoxide, 4.0 mL (18.0 mmol) was added, the reaction mixture was stirred at rt for 0.5 h, cooled to 0 ^oC, and H_2O (10 mL) was added. The solution was filtered through Celite, the phases were separated and the organic phase was washed with brine (5 mL), dried ($MgSO_4$), and concentrated. Flash chromatography (EtOAc:hexane, 20:80) afforded 0.66 g (80%) of (+)-**7d** as an oil; $[\alpha]^{20}_D$ +208 (*c* 1.0 $CHCl_3$); IR (neat) 2987, 1588, 1098 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (m, 2 H), 1.91 (m, 2 H), 2.39 (s, 3 H), 2.46 (m, 2 H), 3.76 (m, 2 H), 3.98 (m, 2 H), 7.31 (m, 5 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.52 (m, 2 H), 8.17 (t, *J* = 4.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.5, 21.3, 35.6, 39.5, 64.4, 109.8, 124.5, 125.8, 127.8, 128.2, 129.6, 141.4, 141.8, 142.2, 166.8. Anal. Calcd for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92. Found: C, 67.31; H, 6.69; N, 3.69.

Typical procedure for the addition of diethylaluminum cyanide isopropoxide to sulfinimines. (R_S,*R*)-(-)-(*N*-*p*-Toluenesulfinyl)-2-amino-5,5-dimethoxypentanonitrile (8a). In a single-necked 25-mL round-bottomed flask equipped with a magnetic stir bar, a rubber septum,and an argon inlet was placed 34 μL (0.45 mmol) of *i*-PrOH and 0.67 mL (1.0 M solution in toluene) of Et_2AlCN (Aldrich) in THF (6 mL). The solution was stirred at rt for 30 min and cooled to -78 ºC. At this time a -78 ºC solution of 0.129 g (0.45 mmol) of (-)-**7a** in THF (15 mL), in a single-necked 100 mL round-bottomed flask, was added via cannula. The reaction mixture was kept at -78 ^oC for 15 min, warm up to rt, and stirred for 3.5 h until the starting material had disappeared (monitored by TLC, 40% EtOAc/*n*-pentane). To the reaction mixture was added sat. NH_4Cl (0.2 mL), EtOAc (20 mL), H_2O (20 mL), and the solution was filtered through Celite. The aqueous phase was washed with EtOAc (3 x 20 mL), and the combined organic phases were washed with brine (5 mL), dried ($MgSO_4$), and concentrated to give 0.119 g (90%) of the crude amino nitriles in 84% de. The diastereoisomers were separated by flash chromatography (2% MeOH/CH_2Cl_2) to give 0.109 g (83%) of (R_S,*R*)-(-)-**8a** as an oil; $[\alpha]^{20}_D$ -40.4 (*c* 1.5, $CHCl_3$); IR (neat): 3197, 2241, 1436, 1089, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60 (d, 2 H, *J* = 8.1 Hz), 7.35 (d, 2 H, *J* = 8.1 Hz), 5.09 (d, 1 H, *J* = 7.3Hz), 4.39 (t, 1 H, *J* = 5.1 Hz), 4.19 (m, 1 H), 3.34 (s, 6 H), 2.43 (s, 3 H), 1.95 (m, 2 H), 1.83 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 143.0, 140.1, 130.6, 126.7, 119.4, 104.3, 54.4, 54.0, 42.1, 30.6, 29.0, 22.1. Anal. Calcd for $C_{14}H_{20}N_2O_3S$; C, 56.73; H, 6.80; N, 9.45. Found: C, 56.60; H, 6.95; N, 9.09.

(*S*)-(+)-(*N*-(*S*)-*p*-Toluenesulfinyl)-2-amino-5,5-(ethylenedioxy)-hexanonitrile (8b): oil; de 90%; purified by flash chromatography (2% MeOH/CH_2Cl_2) 88% yield; mp 84-85^oC; $[\alpha]^{20}_D$ +37.1 (*c* 0.8, $CHCl_3$); IR (KBr) 3204, 2241, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.61 (d, 2 H, *J* = 8.4 Hz), 7.76 (d, 2 H, *J* = 8.1 Hz), 5.11 (d, 1 H, *J* = 7.0 Hz), 4.21 (m, 1H), 3.98 (s, 4 H), 2.44 (s, 3 H), 1.89-2.00 (m, 4 H), 1.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.9, 140.0, 130.6, 126.7, 119.5, 109.7, 65.4, 41.8, 34.9, 29.9, 24.6, 22.1. Anal. Calcd. for $C_{15}H_{20}N_2O_3S$: C, 58.42; H, 6.54; N, 9.08. Found: C, 58.31; H, 6.62; N, 9.52.

(*S*)-(+)-(*N*-(*S*)-*p*-Toluenesulfinyl)-2-amino-5,5-(ethylenedioxy)-heptanonitrile (8c): oil; yield 95%; de 95%; $[\alpha]^{20}_D$ +62.9 (*c*, 1.7, $CHCl_3$); IR (neat) 3204, 2241, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.61 (dd, 2 H, *J* = 6.23 and 1.47 Hz), 7.36 (m, 2 H), 4.64 (d, 1 H, *J* = 7.7 Hz),

4.12 (m, 1 H), 3.91-3.95 (m, 4 H), 2.44 (s, 3 H), 1.89 (m, 2 H), 1.65 (m, 4 H), 1.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.1, 140.0, 130.7, 126.7, 119.3, 110.2, 65.3, 42.4, 38.6, 36.0, 24.5, 22.1, 20.6. Anal. Calcd for $C_{16}H_{22}N_2O_3S$: C, 59.60; H, 6.88; N, 8.69. Found: C, 59.69; H, 7.22; N, 8.37.

(*S*)-(+)-(*N*-(*S*)-*p*-Toluenesufinyl)-2-amino-5,5-(ethylenedioxy)-5-phenylhexanonitrile (8d): oil; de 93%; purified by flash chromatography (2% MeOH/CH_2Cl_2) 89% yield; mp 95-96 ^{o}C; $[\alpha]^{20}_D$ +55.8 (*c* 0.5 $CHCl_3$); IR (KBr) 3314, 2231, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56 (m, 2 H), 1.91 (m, 4 H), 2.43 (s, 3 H), 3.75 (m, 2 H), 4.01 (m, 2 H), 4.10 (m, 1 H), 4.58 (d, *J* = 7.7 Hz, 1 H), 7.33 (m, 5 H), 7.42 (m, 2 H), 7.58 (d, *J* = 8.1, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.9, 22.1, 35.8, 39.5, 42.5, 65.0, 110.6, 119.3, 126.4, 126.7, 128.7, 130.5, 130.6, 140.1, 142.8, 143.0. Anal. Calcd for $C_{21}H_{24}N_2O_3S$: C, 65.60; H, 6.29; N, 7.29. Found: C, 65.78; H, 6.68; N, 6.98.

(*S*)-(+)-(*N*-(*S*)-*p*-Toluenesufinyl)-2-amino-3,3-(ethylenedioxy)-3-phenylpropanonitrile (8e): de 74% purified by flash chromatography (2% MeOH/CH_2Cl_2); yield 82%; mp 91-92 ^{o}C; $[\alpha]^{20}_D$ +83.2 (*c* 1.1, $CHCl_3$); IR (KBr): 3203, 2242, 1263, 1063 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.63 (d, 2 H, *J* = 7.7 Hz), 7.45 (m, 2 H), 7.34-7.39 (m, 5 H), 5.72 (d, 1 H, *J* = 5.1 Hz), 4.51 (m, 1 H), 4.20 (m, 2 H), 3.81 (m, 2 H), 2.45 (m, 2 H), 2.43 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 142.9, 141.5, 139.6, 130.5, 129.5, 129.2, 126.8, 126.1, 118.9, 109.6, 65.4, 64.9, 43.5, 36.8, 22.1. Anal. Cacld for $C_{19}H_{20}N_2O_3S$: C, 64.02; H, 5.66; N, 7.86. Found: C, 64.04; H, 5.71; N, 7.73.

Typical procedure for hydrolysis and cyclization. (5*S*,2*S*)-(-)-5-Methylproline (11b). In a 50-mL single-necked round-bottomed flask equipped with a reflux condenser and a magnetic stir bar was placed 0.242 g (0.79 mmol) of **8b** and 6 N HCl (10 mL). A white solid was initially observed, but disappeared on refluxing for 2.5 h. The solution was cooled to rt, extracted with ether (2 x 10 mL), and the aqueous phase was concentrated to dryness. The crude mixture was dissolved in MeOH (10 mL) and was hydrogenated at atmospheric pressure using of 0.1 g of 10 % Pd/C for 3 h. At this time the solution was filtered through Celite and concentrated. The residue was then loaded on a DOWEX-50 ion exchange resin, eluted with ammonium hydroxide solution, and dried. The crude product was recrystallized from *i*-PrOH to give 0.082 g (80%) of **11b**; mp 197 ^{o}C (dec.) [lit.[14] 185-189 ^{o}C]; $[\alpha]^{20}_D$ -64.6 (*c* 0.9, H_2O), [lit.[14] $[\alpha]^{20}_D$ -68]; ^{1}H NMR ($CDCl_3$) δ 4.39 (b, 1 H), 3.72 (b, 1 H), 2.33 (b, 1 H), 2.17 (b, 2 H), 1.63 (b, 1 H), 1.34 (b, 3 H); ^{13}C NMR ($CDCl_3$) δ 172.9, 60.5, 58.1, 31.1, 28.2, 17.1.

(*R*)-(+)-Proline (11a): yield 77%; mp 220 ^{o}C (dec.). [lit.[15] mp 220 ^{o}C]; $[\alpha]^{20}_D$ 85.5 (*c* 3, H_2O). [lit.[16] $[\alpha]^{20}_D$ +86.2 (*c* 1.0, H_2O)]. The spectral properties were identical to literature values.[15]

(2*S*,6*S*)-(-)-6-Methyl-2-piperidinecarboxylic acid (11c). In a single-necked 25 mL round-bottomed flask equipped with a magnetic stir bar and a reflux condenser was placed 0.366 g (1.14 mmol) of **8c** and 6 N HCl (8 mL). A white solid was initially formed, but disappeared on heating at reflux for 3 h. The reaction was monitored by TLC and when the starting material had disappeared (2 h) the reaction mixture was cooled to rt and washed with Et_2O (3 x 10 mL). The aqueous phase was concentrated using toluene (4 mL) to promote H_2O removal and under high vacuum gave a wet yellow solid. The solid was dissolved in MeOH (9 mL) and H_2O (1 mL) in a single-necked 25-mL round-bottomed flask and was hydrogenated at atmospheric pressure using

0.01 g of 10% Pd/C catalyst for 8 h. At this time the solution was filtered and concentrated to a wet, white solid containing ethylene glycol. The ethylene glycol was removed by washing with acetone (1-2 mL) to give 0.173 g (85%) of **11c** as a white solid mp >250 ^{o}C (dec) [lit.[17] >250 (dec) ^{o}C], $[\alpha]^{20}_{D}$ -32.4 (*c* 0.84, H_2O), [lit.[17] $[\alpha]^{20}_{D}$ -33.2 (*c* 1.2, H_2O)]; ^{1}H NMR (D_2O) δ 3.84 (bd, 1 H, *J* = 9.6 Hz), 3.22 (m, 1 H), 2.26 (bd, 1 H), 1.90 (m, 2 H), 1.58 (dt, 2 H, *J* = 1.8 and 10.2 Hz), 1.38 (m, 1 H), 1.30 (d, 3 H, *J* = 6.6 Hz); ^{13}C NMR (D_2O) δ 172.7, 58.4, 53.8, 30.1, 26.2, 22.4, 19.1. Its spectral properties were in agreement with literature values.[17,18]

(2*S*,6*R*)-(-)-6-Phenyl-2-piperidinecarboxylic acid hydrochloride (11d): In a single-necked 25-mL round-bottomed flask equipped with a magnetic stir bar and a condenser was placed 0.040 g (0.10 mmol) of (+)-**8d** in 6 N HCl (3 mL). The reaction mixture was refluxed for 5 h, cooled to rt, and extracted with Et_2O (5 x 5 mL). The aqueous phase was concentrated and the resulting solid was dissolved in MeOH (3 mL). The solution was hydrogenated at atmospheric pressure using 0.01 g of Pd/C (10% Pd/C) catalyst for 36 h. The suspension was filtered, concentrated, and dried under vacuum to give a yellow solid which was washed with acetone several times and crystallized (H_2O:MeOH:acetone, 4:1:2) to give 0.012 g (48%) of the hydrochloride of (-)-**1d** as a white solid, mp >235 (dec) ^{o}C, [lit.[19] mp > 230 (dec) ^{o}C]; $[\alpha]^{20}_{D}$ -16.3 (*c* 0.3, 0.1 N HCl), [lit.[19] $[\alpha]^{20}_{D}$ -17.0 (*c* 0.4, 0.1N HCl)]. The spectral properties were consistent with literature values.[19]

(*S*)-(+)-(Benzoyl)alanine (12): yield 95%: mp 157-159^{o}C (dec.) [lit.[20]; mp 155-160 ^{o}C (dec)]; $[\alpha]^{20}_{D}$ +43.4 (*c* 0.4, 6 N HCl), [lit.[21] $[\alpha]^{20}_{D}$ +44.3 (*c* 0.1, 6 N HCl)]. The spectral properties were consistent with literature values.[21]

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