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Supporting Information

for

Highly Diastereoselective [3+2] Cycloadditions between Non-racemic *p*-Tolylsulfinimines and Iminoesters: an Efficient Entry to Enantiopure Imidazolidines and Vicinal Diaminoalcohols.

By

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Starting Materials: Most starting materials were known compounds (**1a-n,**[1] **1m**,[2] **2**[3]) and their synthesis was carried out following procedures previously reported except for hydrocinnamaldehyde derived sulfinimine **1i**:

(*S*)-(+)-*N*-(3-Phenylpropylidene)-*p*-toluenesulfinamide, **1i**. A 50 mL round-bottomed flask fitted with a stirring bar and a condenser was charged with anhydrous CH_2Cl_2 (12 mL/mmol), (*S*)-(+)-*p*-toluenesulfinamide (186 mg, 1.20 mmol), 1 equiv of hydrocinnamaldehyde (161 mg, 0.16 mL, 1.20 mmol) and 5 equiv of $Ti(OEt)_4$ (1370 mg, 1.25 mL, 6.00 mmol). The mixture was refluxed until starting material disappearance monitored by TLC (4 h 30 min). The reaction was quenched at 0 ºC with H_2O (12 mL/mmol), filtered through celite and the layers were separated. The aqueous layer was washed with CH_2Cl_2 (2 x 8 mL/mmol) and the organic extracts were washed with a saturated solution of NaCl (5 mL/mmol), dried over Na_2SO_4, filtered and concentrated under reduced pressure to give a crude product that was purified by column chromatography on silica gel (5-20% EtOAc-hexane) affording 275 mg (85%) of pure sulfinimine **1i** as a colorless oil. Compound **1i**: R_f = 0.15 (15% EtOAc-hexane); $[\alpha]^{20}_D$ = +196.4 (*c* = 1.37); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.26 (t, 1 H, *J* = 4.2 Hz, H-1), 7.48 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.11-7.28 (m, 7 H, Ar-H), 2.89-2.97 (m, 2 H, CH_2), 2.74-2.84 (m, 2 H, CH_2), 2.38 (s, 3 H, Me-Tol); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.2, 141.6, 140.2, 137.0, 129.7 (2 C), 128.8 (2 C), 128.3 (2 C), 126.2, 125.6 (2 C), 37.3, 31.5, 21.4; IR (film): ν

= 3027, 2923, 1724, 1621, 1495, 1453, 1261, 11778, 1098, 1074, 1017, 810, 749, 700 cm^{-1}; MS(ES): m/z (%): 272 $[M+1]^+$ (100%).

General Procedure for the 1,3-Dipolar Cycloaddition of Sulfinimines with Azomethine Ylides: A 100 mL round-bottomed flask fitted with a stirring bar and a rubber septum, under an atmosphere of Argon, was charged with anhydrous THF (5 mL/mmol) and 2.1 equiv of *i*Pr_2NH. The mixture was cooled to 0 ºC and 2.1 equiv of *n*BuLi was added dropwise. The reaction mixture was stirred at 0 ºC for 10 min and then cooled to –78 ºC and stirred for 10 additional min. A solution of 2.0 equiv of the *N*-(benzylidene)aminoester, in THF (5 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at –78 ºC for 25 min and then a solution of 1 equiv of the corresponding sulfinimine in THF (5 mL/mmol), previously dried over 4 Å sieves, was added dropwise. The reaction vessel was sealed under argon and placed in a refrigerator (ca. 4 ºC). After 20 h, the reaction was quenched with a saturated solution of NH_4Cl (4 mL/mmol), diluted with EtOAc (8 mL/mmol) and the layers were separated. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica gel, using the appropriate mixture of solvents.

(–)-Methyl [(2*S*,4*R*,5*R*,S_S)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 3a, and methyl [(2*R*,4*S*,5*S*,S_S)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 4a. From a solution of LDA, [*i*Pr_2NH (27 µL, 21 mg, 0.21 mmol) and *n*BuLi (1.31 M, 0.16 mL, 0.21 mmol)] with a solution of methyl 2-benzyl-2-(benzylideneamino)acetate (**2a**, 53 mg, 0.20 mmol) and a solution of (*S*)-(+)-*N*-benzylidene-*p*-toluenesulfinamide (**1a**, 24 mg, 0.10 mmol), according to the general procedure (20 h) a 95:5 mixture of cycloadducts **3a** and **4a** (55%) and 15% of starting material **1a** was obtained after purification by chromatography (5-30% EtOAc-hexane). From this mixture of **3a** and **4a**, pure **3a** (25 mg, 50%) was obtained by recrystallization (20% Et_2O-hexane) as a white solid. Compound **3a**: R_f = 0.43 (30% EtOAc-hexane); m.p. 155-159 °C; $[\alpha]^{20}_D$ = –71.8 (*c* = 1.10); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (dm, *J* = 6.7 Hz, 2 H, Ar-H), 7.44-7.54 (m, 3 H, Ar-H), 7.16-7.26 (m, 7 H, Ar-H), 7.16-7.26 (m, 7 H, Ar-H), 6.88-6.97 (m, 3 H, Ar-H), 6.82 (d, *J* = 7.9 Hz, 4 H, Ar-H), 5.92 (d, *J* = 11.5 Hz, 1 H, H-2), 4.75 (s, 1 H, H-5), 3.40 (s, 2 H, CH_2Ph), 3.37 (d, *J* = 11.2 Hz, 1 H, NH-3), 2.97 (s, 3 H, CO_2Me), 2.16 (s, 3 H, Me-Tol); DNOE between H-2/(CH_2)Bn: 4.3%, H-2/H-5: 1.3%, H-2/Ar-H (7.80): 4.3%, H-5/(CH_2)Bn: 4.0%, H-5/H-2: 0.8%, H-5/Ar-H (6.82): 3.0%; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.5, 141.0, 140.2, 138.5, 138.2, 136.3, 130.2, 129.2, 129.0 (2 C), 128.7 (2 C), 128.0 (2 C), 127.7 (2 C), 127.6 (2 C), 127.1 (2 C), 126.7, 126.6 (2 C), 125.2 (2 C), 77.2, 76.0, 65.7, 51.5, 40.6, 21.1; IR (KBr): ν = 3450, 3020, 2940, 1740 (C=O), 1600, 1490, 1450,

1430, 1260, 1210, 1090, 1070, 860, 810, 750, 700 cm^{-1}; MS(EI): m/z (%): 511 $[M+1]^+$ (11), 371 (7), 311 (10), 279 (17), 268 (58), 247 (25), 208 (38), 176 (100), 139 (81), 116 (60), 91 (83), 77 (55); elemental analysis calcd (%) $C_{31}H_{30}N_2O_3S$ (510.63): C 72.91, H 5.92, N 5.49, S 6.28; found: C 72.62, H 5.69, N 5.21, S 5.91. Compound **4a** (partial data): R_f = 0.39 (30% EtOAc-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (d, *J* = 11.6 Hz, 1 H, H-2), 5.03 (s, 1 H, H-5), 3.43 (s, 2 H, CH_2Ph), 3.25 (d, *J* = 11.6 Hz, 1 H, NH-3), 3.10 (s, 3 H, CO_2Me), 2.16 (s, 3 H, Me-Tol). Compound **3a'** (partial data): R_f = 0.46 (30% EtOAc-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80-7.84 (m, 2 H, Ar-H), 7.46-7.58 (m, 3 H, Ar-H), 7.21-7.31 (m, 7 H, Ar-H), 6.82-7.00 (m, 7 H, Ar-H), 5.94 (d, *J* = 11.5 Hz, 1 H, H-2), 5.03 (s, 1 H, H-5), 3.40 (m, 2 H, CH_2Ph), 3.09 (d, *J* = 10.9 Hz, 1 H, NH-3), 2.19 (s, 3 H, Me-Tol), 1.05-1.15 (m, 4 H, CH_2-*n*-Bu), 0.70-0.80 (m, 3 H, Me-*n*-Bu); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.2, 140.9, 140.3, 138.5, 138.3, 136.4, 130.2 (2 C), 129.2, 128.9 (2 C), 128.6 (2 C), 127.9 (2 C), 127.7 (4 C), 127.2 (2 C), 126.7, 126.6, 125.3 (2 C), 77.2, 75.7, 75.7, 65.7, 64.9, 40.7, 29.9, 21.1, 18.9, 13.5.

(–)-Methyl [(2*S*,4*R*,5*R*,S_S)-4-methyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 3b, and methyl [(2*R*,4*S*,5*S*,S_S)-4-methyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 4b. From a solution of LDA, [*i*Pr_2NH (27 μL, 21 mg, 0.21 mmol) and *n*BuLi (1.61 M, 0.13 mL, 0.21 mmol)] with a solution of methyl 2-(benzylideneamino)propanoate (**2b**, 38 mg, 0.20 mmol) and a solution of (*S*)-(+)-*N*-benzylidene-*p*-

toluenesulfinamide (**1a**, 24 mg, 0.10 mmol), according to the general procedure (20 h) a 95:5 mixture of cycloadducts **3b** and **4b** (53%) and 25% of starting material **1a** was obtained after purification by chromatography (5-30% EtOAc-hexane). From this mixture of **3b** and **4b**, pure **3b** (20 mg, 47%) was obtained by recrystallization (20% Et_2O-hexane) as a white solid. Compound **3b**: R_f = 0.16 (30% EtOAc-hexane); m.p. 190-191 °C; $[\alpha]^{20}_D$ = –99.2 (*c* = 0.68); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78-7.81 (m, 2 H, Ar-H), 7.45-7.50 (m, 3 H, Ar-H), 7.20 (d, 2 H, *J* = 8.2 Hz, Ar-H), 6.88-6.99 (m, 3 H, ArH), 6.77-6.82 (m, 4 H, Ar-H), 5.72 (d, 1 H, *J* = 12.5 Hz, H-2), 4.62 (s, 1 H, H-5), 3.57 (d, 1 H, *J* = 12.4 Hz, NH-3), 3.02 (s, 3 H, CO_2Me), 2.14 (s, 3 H, Me-Tol), 1.68 (s, 3 H, Me-C-4); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.7, 140.9, 140.2, 138.7, 138.2, 129.1, 129.0 (2 C), 128.6 (2 C), 127.6 (2 C), 127.3 (2 C), 127.1 (2 C), 126.6, 125.2 (2 C), 77.9, 71.4, 65.6, 51.7, 23.2, 21.0; IR ($CDCl_3$): ν = 3350, 3025, 1735, 1590, 1215, 760 cm^{-1}; MS(EI): m/z (%): 343 (2), 244 (2), 235 (9), 194 (21), 191 (100), 139 (50), 131 (65), 91 (64), 77 (59), 65 (44), 51 (33); elemental analysis calcd (%) $C_{25}H_{26}N_2O_3S$ (434.54): C 69.10, H 6.03, N 6.45, S 7.38; found: C 68.76, H 6.06, N 6.25, S 7.06. Compound **4b** (partial data): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, *J* = 12.6 Hz, H-2), 4.90 (s, 1 H, H-5), 3.15 (s, 3 H, CO_2Me), 2.15 (s, 3 H, Me-Tol).

(–)-Methyl [(2*S*,4*R*,5*R*,S_S)-4-(2-methyl)propyl-5-*p*-nitrophenyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 3d, and methyl [(2*R*,4*S*,5*S*,S_S)-4-(2-methyl)propyl-5-*p*-nitrophenyl-2-

phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 4d. From a solution of LDA, [*i*Pr_2NH (51 µL, 40 mg, 0.39 mmol) and *n*BuLi (1.60 M, 0.20 mL, 0.32 mmol)] with a solution of methyl 2-(2-methylpropyl)-2-(benzylideneamino)acetate (**2c**, 70 mg, 0.30 mmol) and a solution of (*S*)-(+)-*N*-*p*-nitrobenzylidene-*p*-toluenesulfinamide (**1b**, 43 mg, 0.15 mmol), according to the general procedure (20 h) a 98:2 mixture of cycloadducts **3d** and **4d** (70%) and traces of sulfinimine **1b** was obtained after purification by chromatography (5-30% EtOAc-hexane). From this mixture of **3d** and **4d**, pure **3d** (47 mg, 60%) was obtained by recrystallization (hexane) as a pale yellow solid. Compound **3d:** R_f = 0.20 (15% EtOAc-hexane); m.p. 72-76 °C; $[\alpha]^{20}_D$ = –144.3 (*c* = 0.46); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.74 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.48-7.57 (m, 3 H, Ar-H), 7.17 (d, 2 H, *J* = 8.2 Hz, Ar-H), 6.96 (dm, 2 H, *J* = 8.0 Hz, Ar-H), 6.81 (d, 2 H, *J* = 8.2 Hz, Ar-H), 5.66 (d, 1 H, *J* = 12.3 Hz, H-2), 4.64 (s, 1 H, H-5), 3.48 (d, 1 H, *J* = 12.4 Hz, NH-3), 3.04 (s, 3 H, CO_2Me), 2.13 (s, 3 H, Me-Tol), 2.08 (m, 2 H, H-1'), 1.84 (m, 1 H, H-2'), 1.06 (d, 3 H, *J* = 6.6 Hz, H-3'), 0.78 (d, 3 H, *J* = 6.7 Hz, H-3'); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.6, 147.8, 146.4, 141.7, 138.8, 137.7, 129.4, 129.1 (2 C), 128.8 (2 C), 128.4 (4 C), 127.4, 125.0 (2 C), 122.2 (2 C), 78.3, 74.9, 65.4, 51.7, 43.6, 24.8, 24.1, 22.2, 21.0; IR ($CDCl_3$): ν = 3320, 2960, 2880, 1745 (C=O), 1600, 1525, 1495, 1455, 1350, 1260, 1235, 1155, 1095, 1070, 1030, 950, 860, 700 cm^{-1}; MS(EI): m/z (%): 445 (4), 444 (16), 322 (100), 276 (43), 246 (9), 238 (11), 190 (19), 155 (16), 130 (18), 103 (25), 91 (42), 89 (21), 77 (18);

elemental analysis calcd (%) $C_{28}H_{31}N_3O_5S$ (521.63): C 64.47, H 5.99, N 8.06, S 6.15, found: C 64.29, H 6.06, N 7.90, S 6.31. Compound **4d** (partial data): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, *J* = 12.3 Hz, H-2), 4.87 (s, 1 H, H-5), 3.17 (s, 3 H, CO_2Me).

(–)-Methyl [(2*S*,4*R*,5*S*,*S*$_S$)-4-benzyl-5-(2-furyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 3f, and methyl [(2*R*,4*S*,5*R*,*S*$_S$)-4-benzyl-2-phenyl-5-(2-furyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 4f. From a solution of LDA, [*i*Pr_2NH (94 µL, 73 mg, 0.72 mmol) and *n*BuLi (1.6 M, 0.40 mL, 0.60 mmol)] with a solution of methyl 2-benzyl-2-(benzylideneamino) acetate (**2a**, 160 mg, 0.60 mmol) and a solution of (*S*)-(+)-*N*-(2-furylmethylidene)-*p*-toluenesulfinamide (**1d**, 70 mg, 0.30 mmol), according to the general procedure (17 h), a 98:2 mixture of cycloadducts **3f** and **4f** at 50% conversion was obtained. Purification by chromatography (5-50% EtOAc-hexane) gave pure cycloadduct **3f** (54 mg, 37%) and starting material **1d** (24 mg, 33%). Compound **3f**: R_f = 0.25 (20% EtOAc-hexane); m.p. 138-139 °C (50% Et_2O-hexane); $[\alpha]^{20}_D$ = –70.8 (*c* = 0.90); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (dm, *J* = 8.1 Hz, 2 H, Ar-H), 7.38-7.50 (m, 3 H, Ar-H), 7.16-7.30 (m, 7 H, Ar-H), 7.14 (dd, *J* = 1.8, 0.8 Hz, 1 H, Ar-H), 7.02 (dm, *J* = 7.9 Hz, 2 H, Ar-H), 5.93 (dd, *J* = 3.3, 1.8 Hz, 1 H, Ar-H), 5.83 (d, *J* = 11.8 Hz, 1 H, H-2), 5.38 (dd, *J* = 3.3, 0.8 Hz, 1 H, Ar-H), 4.86 (s, 1 H, H-5), 3.43 (dd, *J* = 11.7, 1.3 Hz, 1 H, NH-3), 3.37 (d, *J* = 14.4 Hz, 1 H, CH_2Ph), 3.29 (dd, *J* = 14.4, 1.3 Hz, 1 H, CH_2Ph), 3.27 (s, 3 H, CO_2Me), 2.28 (s, 3 H, Me-Tol); ^{13}C

NMR (50 MHz, $CDCl_3$): δ = 170.2, 152.7, 141.5, 140.9, 139.8, 138.9, 136.1, 130.1 (2 C), 129.2, 128.9 (2 C), 128.8 (2 C), 128.8 (2 C), 128.0, 126.7, 125.0 (2 C), 109.8, 107.3, 78.6, 75.0, 58.7, 51.9, 39.9, 21.2; IR ($CDCl_3$): ν = 3320, 3030, 2960, 2920, 1745 (C=O), 1605, 1595, 1495, 1460, 1430, 1340, 1260, 1210, 1150, 1120, 1090, 1070, 1040, 1010, 960, 850, 700 cm^{-1}; elemental analysis calcd (%) $C_{29}H_{28}N_2O_4S$ (500.61): C 69.58, H 5.64, N 5.59, S 6.41; found: C 69.72, H 5.64, N 5.50, S 6.23.

(±)-Methyl [(2*S*,4*R*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl]carboxylate, (±)-5a, and (±)-methyl (2*S*,4*S*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl]carboxylate, (±)-12a. From a solution of LDA, *i*Pr_2NH (170 µL, 131 mg, 1.30 mmol) and *n*BuLi (0.70 M, 1.70 mL, 1.20 mmol) with a solution of methyl 2-benzyl-2-(benzylideneamino)acetate (267 mg, 1.00 mmol) and a solution of *N*-benzylidene-*p*-toluenesulfonamide (**1m**, 130 mg, 0.50 mmol), according to the general procedure (–78 °C to –50 °C, 1 h 30 min), an 89:11 mixture of cycloadducts **(±)-5a** and **(±)-12a** and about 10% of minor products tentatively assigned as sulfonyl diaminoesters was obtained. Purification by chromatography (5-20% EtOAc-hexane) gave pure cycloadduct **(±)-5a** (117 mg, 46%) and **(±)-12a** (10 mg, 4%) as white solids with spectral data identical to that found for optically pure products.

General Procedure for the Lewis Acid Catalyzed Condensation between Iminoester Enolates and *p*-Tolylsulfinimines. A 100 mL round-bottomed flask fitted with a stirring bar and a rubber septum, under an atmosphere of Argon, was charged with anhydrous THF (5 mL/mmol of sulfinimine) and 2.6 equiv of *i*Pr_2NH. The mixture was cooled to 0 °C and 2.1 equiv of *n*BuLi was added dropwise. The reaction mixture was stirred at 0 °C for 10 min and then cooled to –78 °C and stirred for 10 additional min. A solution of 2.0 equiv of the *N*-(benzylidene)aminoester, in THF (5 mL/mmol of sulfinimine), previously dried over 4 Å sieves, was added dropwise. The reaction mixture was stirred at –78 °C for 25-30 min and then a solution of 1 equiv of the corresponding sulfinimine in THF (5 mL/mmol), previously dried over 4 Å sieves, was added dropwise followed by 3.25 equiv of freshly distilled $BF_3 \cdot OEt_2$. Upon addition of the Lewis acid, the orange reaction mixture turned pale yellow and the mixture was allowed to warm up slowly to ca. –20 °C until disappearance of starting material (15 min-3 h). The reaction was then quenched with a 5% solution of $NaHCO_3$ (6 mL/mmol). When the mixture had reached about 0 °C the layers were separated and the organic phase was washed with a saturated solution of NaCl (4 mL/mmol). The aqueous layer was extracted twice with CH_2Cl_2 and the combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a crude product as a yellow oil. This crude mixture was dissolved in $CHCl_3$ (0.1 M) and the ensuing cyclization was monitored by ^1H NMR. After 2-4 days, the mixture was purified by

column chromatography on silica gel, using the appropriate mixture of solvents as eluent. In an alternative procedure, 0.5 equiv of PhCHO and $MgSO_4$ (1.3 g/mmol) was added to the $CHCl_3$ solution to accelerate the cyclization. In all experiments, variable amounts of a related imidazolidine formed by dimerization of the iminoester was also obtained.

(—)-Methyl [(2*S*,4*S*,5*R*,*S*$_S$)-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7a, and methyl [(2*R*,4*R*,5*S*,*S*$_S$)-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8a. From a solution of LDA, [*i*Pr_2NH (1.052 g, 1.46 mL, 10.40 mmol) and *n*BuLi (1.60 M, 7.80 mL, 9.00 mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 1.418 g, 8.00 mmol) and a solution of (*S*)-(+)-*N*-benzylidene-*p*-toluenesulfinamide (**1a**, 973 mg, 4.00 mmol) adding $BF_3{\cdot}OEt_2$ (1.845 g, 1.65 mL, 13.00 mmol) according to the general procedure, (1 h) an 83:17 mixture of cycloadducts **7a** and **8a** was obtained, along with about 5% of sulfinyldiaminoesters after standing in $CHCl_3$ (3 days). Purification by chromatography (30-100% Et_2O-hexane) gave a pure mixture of **7a** and **8a** (1.425 g, 85%). From this mixture, a pure sample of **7a** (20 mg) and a sample enriched in **8a** was obtained by a second careful chromatography ($CHCl_3$-Et_3N-EtOH, 20:0.04:0.1) as colorless oils. Compound **7a**: R_f = 0.19 ($CHCl_3$-Et_3N-EtOH, 20:0.04:0.1); R_f = 0.13 (60% Et_2O-hexane); $[\alpha]^{20}_D$ = —42.3 (*c* = 0.88); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.2 Hz, 2 H, Ar-H), 7.25-7.51 (m, 6 H, Ar-H), 6.90-6.95 (m, 1 H, Ar-H), 6.84-6.90

(m, 3 H, Ar-H), 6.64 (d, *J* = 7.8 Hz, 2 H, Ar-H), 6.03 (s, 1 H, H-2), 4.88 (d, *J* = 5.9 Hz, 1 H, H-5), 3.84 (d, *J* = 5.7 Hz, 1 H, H-4), 3.75 (s, 3 H, CO_2Me), 3.20 (br s, 1 H, NH-3), 2.18 (s, 3 H, Me-Tol); DNOE between H-2/NH-3: 4.6%, H-2/H-4: 1.9%, H-2/H-5: 1.9%, H-2/Ar-H (6.64): -1.6%, H-2/Ar-H (7.74): 3.7%, H-4/NH: -19.6%, H-4/H-5: 2.3%, H-4/H-2: 2.3%, H-4/Ar-H (6.64): 3.4%, H-4/Ar-H (7.74): 1.4%, H-5/H-4: 3.7%, H-5/Ar-H (6.64): 5.7%, H-5/Ar-H (7.24): 2.6%, Ar-H (6.64)/H-4: 5.5%, Ar-H (6.64)/H-5: 11.9%, Ar-H (6.64)/Ar-H (7.25): 2.3%, Ar-H (6.64)/Ar-H (7.74): 2.7%; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.3, 141.2, 141.1, 140.2, 139.1, 128.8 (2 C), 128.7 (2 C), 128.6 (2 C), 127.7 (2 C), 127.4, 127.0 (2 C), 126.5, 125.6 (2 C), 80.5, 68.8, 60.4, 52.5, 21.1; IR ($CHCl_3$): ν = 3130, 2920, 2890, 2810, 2790, 1680, 1530, 1425, 1380, 1150, 1055, 1020, 1000, 860, 840, 680, 630, 600 cm^{-1}. MS(ES): m/z (%): 443 $[M+Na]^+$ (100); elemental analysis calcd (%) $C_{24}H_{24}N_2O_3S$ (420.52): C 68.55, H 5.75, N 6.66, S 7.63, found: C 68.27, H 5.99, N 6.92, S 7.30. Compound **8a** (partial data from a 14:86 mixture): R_f = 0.17 ($CHCl_3$-Et_3N-EtOH, 20:0.04:0.1); R_f = 0.13 (60% Et_2O-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.93 (s, 1 H, H-2), 5.07 (d, *J* = 7.2 Hz, 1 H, H-5), 4.01 (d, *J* = 7.2 Hz, 1 H, H-4), 3.76 (s, 3 H, CO_2Me),2.28 (s, 3 H, Me-Tol). Partial data of **methyl 2-amino-3-phenyl-3-(*p*-tolylsulfinylamino)propanoate** (from the mixture of *N*-sulfinyldiaminoesters): R_f = 0.24 (25:1 CH_2Cl_2-MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d,*J* = 8.3, 2 H, Ar-H), 7.07-7.24 (m, 7 H, Ar-H), 5.48 (d, *J* = 7.6 Hz, 1 H, S-NH), 4.71 (dd, *J* = 7.6, 4.0 Hz,

1 H, H-3), 3.81 (d, *J* = 4.0 Hz, 1 H, H-2), 3.73 (s, 3 H, CO_2Me), 2.29 (s, 3 H, Me-Tol), 1.54 (br s, 2 H, NH_2).

Methyl [(2*S*,4*S*,5*R*,S_S)-2-(*p*-methoxyphenyl)-5-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7b, and methyl [(2*R*,4*R*,5*S*,S_S)-2-(*p*-methoxyphenyl)-5-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8b. From a solution of LDA, [*i*Pr_2NH (110 µL, 71 mg, 0.78 mmol) and *n*BuLi (1.60 M, 0.40 mL, 0.63 mmol)], with a solution of methyl 2-(*p*-methoxybenzylideneamino)acetate (**2e**, 124 mg, 0.60 mmol) and a solution of (*S*)-(+)-*N*-benzylidene-*p*-toluenesulfinamide (**1a**, 73 mg, 0.30 mmol), adding $BF_3{\cdot}OEt_2$ (123 mg, 0.12 mL, 0.98 mmol) according to the general procedure (2 h 30 min), an 87:13 mixture of cycloadducts **7b** and **8b** (71 mg, 53%) contaminated with a small amount of *p*-methoxybenzaldehyde was obtained after purification by chromatography (0-20% Et_2O-CH_2Cl_2). Therefore it appears that cycloadducts **7b** and **8b** are moderately unstable under these conditions. Compound **7b,** from the mixture: R_f = 0.23 (10% Et_2O-CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.23 (d, *J* = 7.6 Hz, 2 H, Ar-H), 6.83-7.01 (m, 7 H, Ar-H), 6.67 (d, *J* = 6.8 Hz, 2 H, Ar-H), 5.95 (s, 1 H, H-2), 4.87 (d, *J* = 5.5 Hz, 1 H, H-5), 3.85 (s, 3 H, O-Me), 3.75 (s, 3 H, CO_2Me), 3.69-3.87 (m, 1 H, H-4), 2.17 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.4, 159.9, 141.5, 141.0, 139.0, 132.1, 128.7 (4 C), 127.7 (2 C), 127.3, 127.0 (2 C), 126.5, 125.6 (2 C), 114.0 (2 C), 80.1, 68.7, 60.1, 55.3, 52.5, 21.1; IR (CCl_4): ν = 3300, 3010, 2990,

2940, 2910, 2820, 1740, 1600, 1500, 1440, 1290, 1240, 1200, 1160, 1080, 1060, 1020, 900, 690 cm^{-1}. Compound **8b** (partial data from the mixture): R_f = 0.23 (10% Et_2O-CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$): δ = 6.56 (d, *J* = 8.8 Hz, 2 H, Ar-H), 5.88 (s, 1 H, H-2), 2.29 (s, 3 H, Me-Tol).

(–)-Methyl [(2*S*,4*S*,5*R*,S_S)-5-(*p*-methoxyphenyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7c, and methyl [(2*R*,4*R*,5*S*,S_S)-4-(*p*-methoxyphenyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8c. From a solution of LDA, [*i*Pr_2NH (110 µL, 71 mg, 0.78 mmol) and *n*BuLi (1.25 M, 0.50 mL, 0.63 mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 107 mg, 0.60 mmol) and a solution of (*S*)-(+)-*N*-(*p*-methoxybenzylidene)-*p*-toluenesulfinamide (**1e**, 82 mg, 0.30 mmol), adding $BF_3{\cdot}OEt_2$ (123 mg, 0.12 ml, 0.98 mmol) according to the general procedure (3 h) a 76:24 mixture of cycloadducts **7c** and **8c** (90 mg, 67%) was obtained after purification by chromatography (40-100% Et_2O-hexane). From this mixture, pure **7c** (67 mg, 50%) and pure **8c** (3 mg) were obtained as colorless oils by a second careful chromatography ($CHCl_3$). Compound **7c**: R_f = 0.27 ($CHCl_3$); $[\alpha]^{20}_D$ = – 42.1 (*c* = 0.69); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, 2 H, *J* = 7.4 Hz, Ar-H), 7.36-7.45 (m, 3 H, Ar-H), 7.24 (m, 2 H, Ar-H), 6.88 (d, 2 H, *J* = 8.8 Hz, Ar-H), 6.50 (d, 2 H, *J* = 8.8 Hz, Ar-H), 6.39 (d, 2 H, *J* = 8.6 Hz, Ar-H), 5.99 (d, 1 H, *J* = 6.7 Hz, H-2), 4.80 (d, 1 H, *J* = 6.0 Hz, H-5), 3.72 (s, 3 H, O-Me), 3.69-3.81 (m, 1 H, H-4), 3.63 (s, 3 H, O-Me), 3.17 (t, 1 H, *J* = 8.2 Hz, NH-3), 2.19 (s, 3

H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.4, 158.4, 141.0, 140.4, 139.2, 133.4, 128.8 (2 C), 128.7 (2 C), 128.5, 128.3 (2 C), 127.4 (2 C), 125.7 (2 C), 113.1 (2 C), 80.5, 68.7, 60.1, 55.2, 52.5, 21.2; IR (CCl_4): ν = 3300, 2920, 2900, 1730, 1590, 1500, 1480, 1430, 1230, 1160, 1070, 1050, 1030, 910, 890, 680 cm^{-1}; MS(EI): m/z (%): 274 (38), 251 (6), 224 (16), 176 (13), 139 (100), 117 (35), 104 (7), 91 (35), 77 (15), 65 (18); MS(APCI): m/z (%): 451 $[M+1]^+$ (100%). Compound **8c** (partial data): R_f = 0.23 ($CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.26 (d, 2 H, *J* = 6.6 Hz, Ar-H), 6.94-7.09 (m, 7 H, Ar-H), 6.86 (d, 2 H, *J* = 8.5 Hz, Ar-H), 5.90 (s, 1 H, H-2), 4.99 (d, 1 H, *J* = 7.6 Hz, H-5), 3.95 (d, 1 H, *J* = 7.6 Hz, H-4), 3.80 (s, 3 H, O-Me), 3.75 (s, 3 H, O-Me), 2.27 (s, 3 H, Me-Tol).

(–)-Methyl [(2*S*,4*S*,5*R*,S_S)-5-(*p*-chlorophenyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7d, and methyl [(2*R*,4*R*,5*S*,S_S)-5-(*p*-chlorophenyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8d. From a solution of LDA, [*i*Pr_2NH (110 μL, 71 mg, 0.78 mmol) and *n*BuLi (1.42 M, 0.44 mL, 0.63 mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 107 mg, 0.60 mmol) and a solution of (*S*)-(+)-*N*-(*p*-chlorobenzylidene)-*p*-toluenesulfinamide (**1f**, 83 mg, 0.30 mmol), adding $BF_3{\cdot}OEt_2$ (123 mg, 0.12 mL, 0.98 mmol) according to the general procedure (5 h), a 90:10 mixture of cycloadducts **7d** and **8d** (83 mg, 61%) was obtained after purification by chromatography (50-100% CH_2Cl_2-hexane, then 2-20% Et_2O-CH_2Cl_2). From this mixture,

pure **7d** (68 mg, 50%) was obtained as a colorless oil by a second careful chromatography and preparative TLC (3% Et_2O-hexane). Compound **7d**: R_f = 0.30 (10% Et_2O-CH_2Cl_2); $[\alpha]^{20}_D$ = –59.8 (*c* = 0.51); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, 2 H, *J* = 7.3 Hz, Ar-H), 7.37-7.47 (m, 3 H, Ar-H), 7.24 (d, 4 H, *J* = 8.0 Hz, Ar-H), 6.91 (d, 2 H, *J* = 8.3 Hz, Ar-H), 6.55 (d, 2 H, *J* = 8.3 Hz, Ar-H), 6.02 (d, 1 H, *J* = 7.0 Hz, H-2), 4.83 (d, 1 H, *J* = 6.0 Hz, H-5), 3.75-3.81 (m, 1 H, H-4), 3.75 (s, 3 H, CO_2Me), 3.21 (t, 1 H, *J* = 7.8 Hz, NH-3), 2.23 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 141.5, 140.1, 139.8, 139.0, 132.5, 128.9 (2 C), 128.8 (2 C), 128.7, 128.5 (2 C), 127.8 (2 C), 127.3 (2 C), 125.6 (2 C), 80.5, 68.6, 59.7, 52.6, 21.1; IR (CCl_4): ν = 3250, 3000, 2910, 2890, 2800, 1720, 1465, 1420, 1235, 1190, 1150, 1070, 1045, 990, 910, 890, 680 cm^{-1}; MS(EI): m/z (%): 363 (9), 177 (56), 139 (100), 117 (49), 91 (36), 77 (10); elemental analysis calcd (%)$C_{24}H_{23}ClN_2O_3S$ (454.97): C 63.36, H 5.10, Cl 7.79, N 6.16, S 7.05, found: C 63.57, H 5.23, Cl 7.57, N 6.03, S 7.28. Compound **8d** (partial data): R_f = 0.26 (10% Et_2O-CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94 (s, 1 H, H-2), 5.01 (d, 1 H, *J* = 7.2 Hz, H-5), 3.77 (s, 3 H, CO_2Me), 2.30 (s, 3 H, Me-Tol).

Methyl [(2*S*,4*S*,5*R*,S_S)-5-(*p*-fluorophenyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7e, and methyl [(2*R*,4*R*,5*S*,S_S)-5-(*p*-fluorophenyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8e. From a solution of LDA, [*i*Pr_2NH (0.17 mL, 121 mg, 1.20 mmol) and *n*BuLi (2.0 M, 0.60 mL, 1.20

mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 177 mg, 1.00 mmol) and a solution of (*S*)-(+)-*N*-(*p*-fluorobenzylidene)-*p*-toluenesulfinamide (**1g**, 131 mg, 0.50 mmol), adding $BF_3 \cdot OEt_2$ (231 mg, 0.20 mL, 1.625 mmol) according to the general procedure (10 min), an 83:17 mixture of cycloadducts **7e** and **8e** (145 mg, 66%) was obtained after purification by chromatography (80-100% CH_2Cl_2-hexane, then 0-30% Et_2O-CH_2Cl_2) as a colorless oil. Highly enriched imidazolidine **7e** (87 mg, 40%) was obtained by a second careful chromatography (Et_2O-hexane-Et_3N, 75:25:0.1). Compound **7e**: R_f = 0.22 (75:25:0.1 Et_2O-hexane-Et_3N), 0.42 (20% Et_2O-CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (m, 2 H, Ar-H), 7.38-7.48 (m, 3 H, Ar-H), 7.26 (d, 2 H, *J* = 7.8 Hz, Ar-H), 6.91 (d, 2 H, *J* = 7.8 Hz, Ar-H), 6.54-6.59 (m, 4 H, Ar-H), 6.02 (s, 1 H, H-2), 4.85 (d, 1 H, *J* = 6.1 Hz, H-5), 3.80 (m, 1 H, H-4), 3.75 (s, 3 H, CO_2Me), 3.22 (s, 1 H, NH-3), 2.21 (s, 3 H, Me-Tol); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 161.6 (d, 1 C, J_{ipso} C-F = 245.2 Hz), 141.3, 140.1, 139.0, 137.0 (2 C), 128.8 (4 C), 128.7 (2 C), 128.6 (2 C), 127.3, 125.6 (2 C), 114.4 (d, 2 C, J_o C-F= 21.4 Hz), 80.5, 68.7, 59.7, 52.6, 21.1; IR ($CHCl_3$): ν = 3309, 3029, 2953, 1742, 1604, 1509, 1492, 1448, 1222, 1091, 1069, 931, 911, 839, 809, 757, 699 cm^{-1}. MS (ES): m/z (%):899 $[2M+Na]^+$.(44), 439 $[M+1]^+$ (100). Compound **8e** (partial data from the mixture): R_f = 0.17 (Et_2O-hexane-Et_3N, 75:25:0.1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.96 (s, 1 H, H-2), 5.02 (d, 1 H, *J* = 7.3 Hz, H-5), 3.76 (s, 3 H, CO_2Me), 2.29 (s, 3 H, Me-Tol).

Methyl [(2*S*,4*S*,5*R*,S_S)-5-(1-naphtyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl)]carboxylate, 7g, and methyl [(2*R*,4*R*,5*S*,S_S)-5-(1-naphtyl)-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl)]carboxylate, 8g. From a solution of LDA, [*i*Pr_2NH (52 μL, 37 mg, 0.369 mmol) and *n*BuLi (1.6 M, 0.20 mL, 0.312 mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 50 mg, 0.284 mmol) and a solution of (*S*)-(+)-*N*-1-naphthylmethylidene-*p*-toluenesulfinamide (**1h**, 40 mg, 0.142 mmol), adding $BF_3{\cdot}OEt_2$ (65 mg, 58 μL, 0.461 mmol) according to the general procedure (10 min) and adding 0.5 equiv of PhCHO (7 μL, 7 mg, 0.071 mmol) and 1.3 g/mmol of sulfinimine of $MgSO_4$ (185 mg), an 83:17 mixture of cycloadducts **7g** and **8g** (47 mg, 72%) was obtained after purification by chromatography (30-60% Et_2O-hexane) as a yellowish oil. A second chromatography (0-30% Et_2O-$CHCl_3$) afforded imidazolidine **7g** (33 mg, 50%), along with a very small amount of iminoester dimer (3%) that could not be separated by chromatographic methods. Compound **7g**: R_f = 0.24 (80% Et_2O-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.3 Hz, 1 H, Ar-H), 7.83 (d, *J* = 7.3 Hz, 2 H, Ar-H),7.67 (m, 1 H, Ar-H), 7.58-7.36 (m, 6 H, Ar-H), 7.23 (m, 2 H, Ar-H), 7.12 (m, 2 H, Ar-H), 6.50 (d, *J* = 8.1 Hz, 2 H, Ar-H), 6.03 (br s, 1 H, H-2), 5.89 (d, *J* = 4.6 Hz, 1 H, H-5), 3.98 (br s, 1 H, H-4), 3.79 (s, 3 H, CO_2Me), 1.88 (s, 3 H, Me-Tol); DNOE between H-2/ Ar-H (7.83): 1.2%, H-4/Ar-H (8.07): 1.99%, H-4/Ar-H (7.83): 0.5%, H-4/Ar-H (7.23): 0.7%, H-4/H-5: 1.9%, H-5/Ar-H (8.07): 7.0%, H-5/Ar-H (7.23): 2.5%, H-5/H-4: 6.9%, Ar-H (6.50)/ArH (7.12): 1.5%, Ar-H (6.50)/Me-Tol: 0.7%; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.8, 140.6,

139.7, 138.6, 137.0, 133.2, 128.9, 128.8 (2 C), 128.4, 128.3 (2 C), 127.5 (2 C), 127.4, 125.7, 125.4, 125.3, 125.0 (2 C), 124.8, 123.1, 79.7, 68.1, 56.3, 52.8, 20.8; IR (KBr): ν = 3436, 3055, 2923, 1739, 1597, 1492, 1448, 1262, 1206, 1091, 1068, 799, 777, 700 cm^{-1}; MS(ES): m/z (%): 471 $[M+1]^+$ (100); Compound **8g** (partial data from the mixture): R_f = 0.20 (80% Et_2O-hexane); ^1H NMR (200 MHz, $CDCl_3$): δ = 6.65 (d, *J* = 8.2 Hz, 2 H, Ar-H), 6.07 (s, 1 H, H-2), 5.94 (br s, 1 H, H-5), 2.26 (s, 3 H, Me-Tol).

(+)-Methyl [(2*S*,4*S*,5*R*,S_S)-2-phenyl-5-(2-phenylethyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7h, and methyl [(2*R*,4*R*,5*S*,S_S)-2-phenyl-5-(2-phenylethyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8h. From a solution of LDA, [*i*Pr_2NH (1.46 mL, 1.052 g, 10.40 mmol) and *n*BuLi (1.6 M, 5.5 mL, 8.80 mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 1.418 g, 8.00 mmol) and a solution of (*S*)-(+)-*N*-(3-phenylpropylidene)-*p*-toluenesulfinamide (**1i**, 966 mg, 4.00 mmol), adding $BF_3 \cdot OEt_2$ (1.845 g, 1.65 mL, 13.00 mmol) according to the general procedure (10 min), a 98:2 mixture of cycloadducts **7h** and **8h** (1.490 g, 83%) was obtained after purification by chromatography (25-60% Et_2O-hexane) as a white foam. Pure imidazolidine **7h** (1.075 g, 60%) was obtained by recrystallization from Et_2O-hexane. Compound **7h**: R_f = 0.25 (50% Et_2O-hexane); m.p. 116-119 ºC [**(±)-7h**]; m.p. 125-127 ºC [**(+)-7h**]; $[\alpha]^{20}_D$ = +19.6 (*c* = 0.23); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.3 Hz, 2 H, Ar-H), 7.51 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.32-7.41 (m, 3 H, Ar-H),

7.26 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.12 (m, 3 H, Ar-H), 6.69 (dm, *J* = 8.3 Hz, 2 H, Ar-H), 5.94 (s, 1 H, H-2), 4.01 (ddd, *J* = 8.9, 5.0, 3.8 Hz, 1 H, H-5), 3.83 (s, 3 H, CO_2Me), 3.69 (d, *J* = 3.8 Hz, 1 H, H-4), 3.08 (br s, 1 H, NH-3), 2.40 (s, 3 H, Me-Tol), 2.12 (t, *J* = 8.7 Hz, 2 H, CH_2Ph), 1.36-1.46 (m, 1 H, H-1b'), 1.04-1.18 (m, 1 H, H-1a'); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.7, 141.3, 140.8, 140.6, 140.4 , 129.3 (2 C), 128.2 (2 C), 128.1, 127.9 (2 C), 127.8 (2 C), 126.8 (2 C), 125.5, 125.1(2 C), 80.7, 65.1, 56.9, 52.3, 37.7, 32.0, 21.1; IR ($CHCl_3$): ν = 3312, 3027, 2952, 1741, 1601, 1493, 1454, 1206, 1091, 1069, 910, 812, 736, 690 cm^{-1}; MS (ES): m/z (%): 471 $[M+Na]^+$ (100); elemental analysis calcd (%) $C_{26}H_{28}N_2O_3S$ (448.61): C 69.60, H 6.30, N 6.24, S 7.15; found: C 69.85, H 6.57, N 6.51, S 7.34. Compound **8h** (partial data from the mixture): R_f = 0.25 (50% Et_2O-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.89 (s, 1 H, H-2), 3.81 (s, 3 H, CO_2Me), 3.52 (d, *J* = 3.2 Hz, 1 H, H-4), 2.35 (s, 3 H, Me-Tol).

(+)-Methyl [(2*S*,4*S*,5*R*,S_S)-5-ethyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7i, and methyl [(2*R*,4*R*,5*S*,S_S)-5-ethyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8i. From a solution of LDA, [*i*Pr_2NH (0.44 mL, 316 mg, 3.12 mmol) and *n*BuLi (1.16 M, 2.28 mL, 2.64 mmol)], with a solution of methyl 2-(benzylideneamino)acetate (**2d**, 425 mg, 2.40 mmol) and a solution of (*S*)-(+)-*N*-(propylidene)-*p*-toluenesulfinamide (**1j**, 234 mg, 1.20 mmol), adding $BF_3{\cdot}OEt_2$ (554 mg, 0.49 mL, 3.90 mmol) according to the general procedure (10

min), a 95:5 mixture of cycloadducts **7i** and **8i** was obtained which gave pure **7i** (100 mg, 22%) and a mixture of imidazolidines **7i** and **8i** (188 mg, 42%) (64% global yield), after purification by chromatography (30-100% Et_2O-hexane) as colorless oils. Compound **7i**: R_f = 0.36 (Et_2O); $[\alpha]^{20}_D$ = +10.5 (*c* = 1.15); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, 2 H, *J* = 8.4 Hz, Ar-H), 7.53 (d, 2 H, *J* = 8.2, Ar-H), 7.24-7.41 (m, 5 H, Ar-H), 5.91 (s, 1 H, H-2), 3.86 (m, 1 H, H-5), 3.80 (s, 3 H, CO_2Me), 3.61 (d, 1 H, *J* = 4.0 Hz, H-4), 3.00 (br s, 1 H, NH-3), 2.38 (s, 3 H, Me-Tol), 1.04-1.11 (m, 1 H, CH_2 Et), 0.80-0.88 (m, 1 H, CH_2 Et), 0.42 (t, 3 H, *J* = 7.4 Hz, CH_3 Et); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.1, 141.5, 141.0, 129.5 (3 C), 128.4 (2 C), 128.2, 127.1 (2 C), 125.5 (2 C), 81.1, 66.1, 59.0, 52.5, 28.9, 21.4, 10.2; IR (CCl_4): ν = 3260, 2980, 2900, 2880, 2820, 1710, 1620, 1570, 1460, 1420, 1180, 1100, 1070, 1040, 910, 880 cm^{-1}; MS (ES): m/z (%): 767 $[2M+Na]^+$ (14), 395 $[M+Na]^+$ (100); elemental analysis calcd (%) $C_{20}H_{24}N_2O_3S$ (372.48): C 69.49, H 6.49, N 7.52, S 8.61; found: C 69.72, H 6.68, N 7.24, S 8.33. Compound **8i** (partial data from the mixture): R_f = 0.36 (Et_2O); ^1H NMR (400 MHz, $CDCl_3$): δ = 5.75 (s, 1 H, H-2).

(+)-Methyl [(2*S*,4*S*,5*R*,S_S)-2-phenyl-5-(*i*-propyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 7j, and methyl [(2*R*,4*R*,5*S*,S_S)-2-phenyl-5-(*i*-propyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 8j. From a solution of LDA, [$i Pr_2NH$ (3.6 equiv, 0.10 mL, 73 mg, 0.72 mmol) and *n*BuLi (3.1 equiv, 1.35 M, 0.46 mL, 0.62 mmol)], with a solution of methyl 2-

(benzylideneamino)acetate (**2d**, 3.0 equiv, 106 mg, 0.60 mmol) and a solution of (*S*)-(+)-*N*-(*i*-butylidene)-*p*-toluenesulfinamide (**1k**, 42 mg, 0.20 mmol), adding $BF_3 \cdot OEt_2$ (4.25 equiv, 121 mg, 0.11 mL, 0.85 mmol) according to the general procedure (10 min), a 95:5 mixture of cycloadducts **7j** and **8j** (72 mg, 93%) was obtained after purification by chromatography (30-100% Et_2O-hexane) as a white foam that crystallized from hexane and was recrystallized from Et_2O to yield pure imidazolidine **7j** (46 mg, 60%). Compound **7j**: R_f = 0.31 (80% Et_2O-hexane); m.p. 139-140 °C; $[\alpha]^{20}_D$ = +52.5 (*c* = 1.09); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, 2 H, *J* = 8.0 Hz, Ar-H), 7.50 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.22-7.38 (m, 5 H, Ar-H), 5.84 (s, 1 H, H-2), 3.82 (s, 3 H, CO_2Me), 3.75-3.81 (m, 2 H, H-4, H-5), 2.89 (br s, 1 H, NH-3), 2.38 (s, 3 H, Me-Tol), 0.82-0.93 (m, 1 H, CH *i*Pr), 0.69 (d, 3 H, *J* = 6.6 Hz, Me *i*Pr), 0.35 (d, 3 H, *J* = 6.7 Hz, Me *i*Pr; ^1H NMR (400 MHz, C_6D_6): δ = 7.59 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.48 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.03-7.16 (m, 3 H, Ar-H), 6.75 (d, 2 H, *J* = 7.8 Hz, Ar-H), 5.83 (s, 1 H, H-2), 3.95 (dd, 1 H, *J* = 7.7, 3.2 Hz, H-5), 3.55 (d, 2 H, *J* = 2.7 Hz, H-4), 3.44 (s, 3 H, CO_2Me), 2.95 (br s, 1 H, NH-3), 1.82 (s, 3 H, Me-Tol), 0.82-0.93 (m, 1 H, CH *i*Pr), 0.60 (d, 3 H, *J* = 6.7 Hz, Me *i*Pr), 0.28 (d, 3 H, *J* = 6.9 Hz, Me *i*Pr); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.4, 142.3, 141.4, 141.2, 130.1 (2 C), 129.1 (2 C), 129.0, 127.8 (2 C), 125.9, 81.6, 63.7, 63.4, 53.7, 32.7, 22.1, 20.4, 18.8; IR ($CHCl_3$-CCl_4): ν = 3620, 3420, 3300, 3000, 2920, 2820, 2700, 2410, 1940, 1845, 1790, 1720, 1575, 1470, 1430, 1350, 1180, 1070, 790, 730, 680, 640 cm^{-1}; MS (ES): m/z (%): 387 $[M+1]^+$ (100); elemental analysis calcd

(%) $C_{21}H_{26}N_2O_3S$ (386.51): C 65.26, H 6.78, N 7.25, S 8.30; found: C 65.07, H 6.43, N 7.56, S 8.53. Compound **8j** (partial data from the mixture): R_f = 0.30 (80% Et_2O-hexane); ^1H NMR (300 MHz, $CDCl_3$): δ = 5.75 (s, 1 H, H-2), 3.82 (s, 3 H, CO_2Me), 2.31 (s, 3 H, Me-Tol), 1.48 (m, 1 H, CH *i*Pr), 1.07 (d, 3 H, *J* = 6.7 Hz, Me *i*Pr), 0.97 (d, 1 H, *J* = 6.7 Hz, Me *i*Pr).

(–)-Methyl [(2*S*,4*S*,5*R*,*S*$_S$)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 9a, and 3a, 4a, 11a and 10a. From a solution of LDA, [*i*Pr_2NH (2.2 equiv, 89 mg, 116 µL, 0.88 mmol) and *n*BuLi (2.2 equiv, 1.6 M, 0.55 mL, 0.88 mmol)], with a solution of methyl 2-benzyl-2-(benzylideneamino)acetate (**2a**, 214 mg, 0.80 mmol) and a solution of (*S*)-(+)-*N*-benzylidene-*p*-toluenesulfinamide (**1a**, 96 mg, 0.4 mmol), adding $BF_3{\cdot}OEt_2$ (3.25 equiv, 93 mg, 0.084 mL, 0.65 mmol) according to the general procedure (–78 ºC, 1 h, to rt over 12 h), a 12:12:64:12 mixture of cycloadducts **3a**:**4a**:**9a**:**11a** was obtained. Purification by chromatography (5-30% EtOAc-hexane) gave **3a**+**4a**, (41 mg, 20%) as a white solid, **9a** as a colorless oil (47 mg, 25%), a mixture of **11a**, **9a** and minor amounts of its epimer at the aminal (84 mg, 42%) as a colorless oil and starting material (5%), (87% combined yield). Pure **9a** was also obtained by preparative TLC (30% EtOAc-hexane) from the mixture of **11a**, **9a** and its epimer at the aminal and recrystallization from 20% EtOAc-hexane. A similar procedure was followed using Cp_2TiCl_2 (1.5 equiv) instead of $BF_3{\cdot}Et_2O$ yielding **4a**:**9a**:**11a** in a 30:60:10 ratio (combined yield 88%). We were able

to isolate pure **4a** (25%) by chromatography of this mixture. When $TiCl_4$ was employed as Lewis acid a mixture of **4a**:**9a**:**10a**:**11a** (4:30:62:4; combined yield 54%). Sulfenamide **10a** was isolated pure from this mixture (36%) and was fully characterized. Compound **9a**: R_f = 0.22 (30% EtOAc-hexane); m.p. 62-65 ºC; $[\alpha]^{20}_D$ = –16.1 (*c* = 1.8); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (d, 2 H, *J* = 7.9 Hz, Ar-H), 7.43-7.53 (m, 3 H, Ar-H), 7.07-7.17 (m, 5 H, Ar-H), 7.04 (br s, 5 H, Ar-H), 6.96 (dm, 2 H, Ar-H), 6.80 (d, 2 H, *J* = 8.0 Hz, Ar-H), 5.71 (d, 1 H, *J* = 4.5 Hz, H-2), 5.22 (s, 1 H, H-5), 3.81 (s, 3 H, CO_2Me), 2.90 (d, 1 H, *J* = 4.8 Hz, NH-3), 2.55 (d, 1 H, *J* = 13.3 Hz, CH_2-Ph), 2.15 (s, 3 H, Me-Tol), 2.15 (d, 1 H, *J* = 13.3 Hz, CH_2-Ph); DNOE between H-2/NH: 7.7%, H-2/H-5: 3.4%, H-2/ArH (6.80): –1.3%, H-2/Ar-H (7.04): -3.4%, H-2/ArH (7.83): 5.2%, H-5/H-2: 1.0%, H-5/CH_2Ph (2.55): 2.0%, H-5/Ar-H (7.07-7.17): 2.1%, OMe/H-2: 3.9%, OMe/H-5: 2.6%, NH/H-5: 1.3%, NH/H-2: 18.6%, NH/Ar-H (6.96): 3.4%, Ar-H (6.80)/H-5: 3.4%, Ar-H (6.80)/Me-Tol: 1.2%, Ar-H (6.80)/Ar-H (6.96-7.04): -7.2, Ar-H (7.83)/H-5: 0.8%, Ar-H (7.83)/H-2: 2.3%, Ar-H (7.83)/Ar-H (7.04): -1.6%, Ar-H (7.83)/Ar-H (7.43-7.53): 2.0%; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 174.2, 140.7, 140.3, 139.5, 138.8, 136.0, 129.3 (2 C), 128.9, 128.7 (2 C), 128.6 (2 C), 128.5 (2 C), 128.3 (2 C), 128.1 (2 C), 127.4 (2 C), 126.9, 126.7, 125.6 (2 C), 76.0, 73.3, 61.9, 52.7, 42.6, 21.1; IR (KBr): ν = 3460, 3340, 3060, 3030, 2960, 2930, 2860, 1740, 1605, 1495, 1455, 1435, 1400, 1260, 1210, 1180, 1085, 1070, 1030, 1020, 810, 700 cm^{-1}; MS (EI): m/z (%): 511 $[M+1]^+$ (0.1), 419 (0.34), 311 (14), 267 (46), 207 (25), 139 (30), 91 (100), 77 (18); elemental analysis calcd

(%) $C_{31}H_{30}N_2O_3S$ (510.63): C 72.91, H 5.92, N 5.49, S 6.28; found: C 72.62, H 5.69, N 5.30, S 6.04. Partial data of **methyl [(2*R*,4*R*,5*R*,*S*$_S$)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate** (epimer at the aminal of **9a**, from the mixture): R_f = 0.19 (30% EtOAc-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05-7.40 (m, 19 H, Ar-H), 5.95 (d, 1 H, *J* = 6.0 Hz, H-2), 4.64 (s, 1 H, H-5), 3.24 (d, 1 H, *J* = 13.0 Hz, CH_2Ph), 3.13 (s, 3 H, CO_2Me), 3.05 (d, 1 H, *J* = 13.0 Hz, CH_2Ph), 2.37 (s, 3 H, Me-Tol). Partial data of **methyl [(2*R*,4*R*,5*S*,*S*$_S$)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate**, **11a** (from the mixture): R_f = 0.22 (30% EtOAc-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.77 7.75 (m, 19 H, Ar-H), 5.64 (s, 1 H, H-2), 5.48 (s, 1 H, H-5), 3.77 (s, 3 H, CO_2Me), 2.85 (br s, 1 H, NH-3), 2.70 (d, 1 H, *J* = 13.3 Hz, CH_2Ph), 2.30 (d, 1 H, *J* = 13.2 Hz, CH_2Ph), 2.18 (s, 3 H, Me-Tol). Compound **4a**: R_f = 0.39 (30% EtOAc-hexane); $[\alpha]^{20}_D$ = +17.0 (*c* = 1.5); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, 2 H, *J* = 7.8 Hz, Ar-H), 7.33-7.44 (m, 3 H, Ar-H), 7.10-7.30 (m, 9 H, Ar-H), 6.95-7.07 (m, 3 H, Ar-H), 6.80 (d, 2 H, *J* = 8.0 Hz, Ar-H), 5.77 (d, 1 H, *J* = 11.6 Hz, H-2), 5.03 (s, 1 H, H-5), 3.43 (br s, 2 H, CH_2Ph), 3.25 (d, 1 H, *J* = 11.6 Hz, NH-3), 3.10 (s, 3 H, CO_2Me), 2.17 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.2, 140.9, 139.9, 138.3, 138.2, 136.4, 130.5 (2 C), 128.7 (2 C), 128.3 (2 C), 128.2, 128.1 (2 C), 127.9 (6 C), 127.6, 126.7, 125.4 (2 C), 75.2, 75.1, 72.1, 51.7, 41.8, 21.1; IR (KBr): ν = 3430, 3060, 3025, 2945, 1740, 1600, 1495, 1455, 1430, 1260, 1210, 1125, 1095, 1070, 1030, 815, 755, 700 cm^{-1}; MS (EI): m/z (%): 493 (10), 451 (25), 267

(25), 195 (22), 176 (60), 139 (82), 116 (38), 91 (100), 77 (55); elemental analysis calcd (%) $C_{31}H_{30}N_2O_3S$ (510.63): C 72.91, H 5.92, N 5.49, S 6.28; found: C 73.20, H 5.68, N 5.43, S 5.98. Compound **10a**: R_f = 0.75 (CH_2Cl_2); m.p. 148-149 °C; $[\alpha]^{20}_D$ = –34.6 (*c* = 0.76); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (dm, 2 H, *J* = 6.4 Hz, Ar-H), 7.58 (d, 2 H, *J* = 7.1 Hz, Ar-H), 7.36-7.50 (m, 6 H, Ar-H), 7.07-7.13 (m, 7 H, Ar-H), 6.91-6.94 (m, 2 H, Ar-H), 4.91 (s, 1 H, H-2), 4.51 (s, 1 H, H-5), 3.55 (s, 3 H, CO_2Me), 2.66 (br s, 1 H, NH-3), 2.54 (d, 1 H, *J* = 13.2 Hz, CH_2Ph), 2.42 (d, 1 H, *J* = 13.2 Hz, CH_2Ph), 2.32 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.2, 140.1, 139.2, 137.7, 136.1, 134.3, 129.6 (2 C), 129.5 (2 C), 129.4 (2 C), 128.8, 128.4 (2 C), 128.1 (4 C), 128.0, 126.7, 79.4, 73.0, 70.8, 52.1, 43.5, 21.2; IR (KBr): ν = 3450, 3375, 3070, 3035, 2950, 1730, 1600, 1495, 1455, 1435, 1400, 1245, 1215, 1090, 835, 810, 700 cm^{-1}; MS (EI): m/z (%): 267 (100), 207 (68), 194 (13), 123 (16), 91 (83), 77 (12).

(–)-Methyl [(2*S*,4*S*,5*R*,*S*$_S$)-5-(*p*-chlorophenyl)-4-methyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 9b, methyl [(2*S*,4*R*,5*R*,*S*$_S$)-5-(*p*-chlorophenyl)-2-phenyl-4-methyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 3g, and methyl [(2*R*,4*R*,5*S*,*S*$_S$)-5-(*p*-chlorophenyl)-4-methyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 4g. From a solution of LDA, [*i*Pr_2NH (40 mg, 51 µL, 0.39 mmol) and *n*BuLi (1.6 M, 0.20 mL, 0.32 mmol)], with a solution of methyl 2-(benzylideneamino)propanoate (**2b**, 57 mg, 0.30 mmol) and a solution

of (*S*)-(+)-*N*-(*p*-chlorobenzylidene)-*p*-toluenesulfinamide (**1f**, 42 mg, 0.15 mmol), adding $BF_3 \cdot OEt_2$ (70 mg, 60 µL, 0.49 mmol) according to the general procedure (30 min), a 63:22:15 mixture of cycloadducts **9b**, **3g** and **11b** was obtained. Purification by chromatography (5-100% EtOAc-hexane) gave starting material (6 mg, 14%) and mixture of cycloadducts (55 mg, 80%). A second chromatography (30-65% Et_2O-hexane) gave pure **9b** (25 mg, 35%) as a white solid that was recrystallized from 25% Et_2O-hexane. Compound **9b**: R_f = 0.33 (75% Et_2O-hexane); m.p. 88-89 °C; $[\alpha]^{20}_D$ = –10.7 (*c* = 0.40); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.76 (dd, 2 H, *J* = 8.0, 2.0 Hz, Ar-H), 7.42-7.53 (m, 3 H, Ar-H), 7.13 (d, 2 H, *J* = 8.2 Hz, Ar-H), 6.88-6.99 (m, 4 H, Ar-H), 6.84 (d, 2 H, *J* = 8.0 Hz, Ar-H), 5.68 (s, 1 H, H-2), 5.16 (s, 1 H, H-5), 3.90 (s, 3 H, CO_2Me), 3.09 (s, 1 H, NH-3), 2.19 (s, 3 H, Me-Tol), 0.86 (s, 3 H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 175.5, 141.2, 139.4, 138.9, 138.4, 132.6, 129.6 (2 C), 129.1, 128.8 (2 C), 128.7 (2 C), 127.9 (2 C), 127.5 (2 C), 123.4 (2 C), 76.5, 69.2, 60.7, 53.2, 22.3, 21.1; IR (CCl_4): ν = 3340, 3040, 2960, 1740, 1600, 1495, 1460, 1440, 1245, 1110, 1090, 1070, 1020, 840, 700 cm^{-1}. Compound **11b** (partial data): R_f = 0.26 (75% Et_2O-hexane); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.60 (s, 1 H, H-2), 4.83 (s, 1 H, H-5), 3.85 (s, 3 H, CO_2Me), 2.39 (s, 3 H, Me-Tol), 0.94 (s, 3 H, Me). Compound **3g** (partial data): R_f = 0.26 (75% Et_2O-hexane). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.64 (s, 1 H, H-2), 5.36 (s, 1 H, H-5), 3.21 (s, 3 H, CO_2Me), 2.16 (s, 3 H, Me-Tol), 1.69 (s, 3 H, Me).

Methyl [(2*S*,4*S*,5*R*,S_S)-4-methyl-2-phenyl-5-(*i*-propyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl] carboxylate, 9c, and (–)-methyl [(2*S*,4*R*,5*R*,S_S)-4-methyl-2-phenyl-5-(*i*-propyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl] carboxylate, 3h. From a solution of LDA, [3.6 equiv. *i*Pr_2NH (76 mg , 0.13 mL, 0.90 mmol) and *n*BuLi (3.2 equiv 2.0 M, 0.40 mL, 0.80 mmol)], with a solution of methyl 2-(benzylideneamino)propanoate (**2b**, 133 mg, 0.75 mmol) and a solution of (*S*)-(+)-*N*-(*i*-butylidene)-*p*-toluenesulfinamide (**1k**, 52 mg, 0.25 mmol), adding $BF_3{\cdot}OEt_2$ (4 equiv, 142 mg, 0.13 mL, 1.00 mmol) according to the general procedure (3 h), a 16:84 mixture of imidazolidines *syn*(**3h**):*anti*(**9c**+epimer at C-2) was obtained. Purification by chromatography (30-100% Et_2O-hexane) gave a mixture of the above cycloadducts (80 mg, 80%). Recrystallization of this mixture (5% CH_2Cl_2-hexane), gave pure **3h** (10 mg, 10%) and an inseparable mixture of **9c** and its epimer at C-2. We have noticed that epimerization at the aminal is especially slow for **9c** and may be promoted by silica gel. These mixtures have been used for reduction with $LiAlH_4$ to give **17e**, thus securing the structural assignments. Compound **3h**: R_f = 0.42 (Et_2O); m.p. 144-145 ^oC; $[\alpha]^{20}_D$ = –17.6 (*c* = 0.50); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, 2 H, *J* = 8.3 Hz, Ar-H), 6.76-7.02 (m, 7 H, Ar-H), 5.40 (d, 1 H, *J* = 9.3 Hz, H-2), 3.74 (s, 3 H, CO_2Me), 3.61 (d, 1 H, *J* = 7.8 Hz, H-5), 2.97 (d, 1H, *J* = 10.8 Hz, NH-3), 2.13 (s, 3 H, Me-Tol), 2.01 (m, 1 H, CH *i*Pr), 1.64 (s, 3 H, Me), 1.20 (d, 3 H, *J* = 6.6 Hz, Me *i*Pr), 0.98 (d, 3 H, *J* = 6.6 Hz, Me *i*Pr); DNOE between Me/H-5:

2.0%, Me/H-2: 1.9%, H-5/Me (0.98): 1.2%, H-5/Me (1.20): 0.5%, H-5/Me: 1.5%, H-5/CH (*i*-Pr): 2.6%, H-5/H-2: 0.7%, H-2/Me: 2.4%, H-2/NH: 2.2%, H-2/H-5: 1.2%, H-2/ArH (6.82): 2.6%, H-2/Ar-H (7.27): 1.2%; Ar-H (7.27)/Me (0.98): 0.1%, Ar-H (7.27)/Me (1.20): 0.3%, Ar-H (7.27)/H-2: 0.4%, Ar-H (7.27)/Ar-H (6.80): 1.1%; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.8, 141.1, 139.8, 138.5, 128.6 (2 C), 127.7 (2 C), 127.2, 127.0 (2 C), 125.5 (2 C), 71.3, 68.0, 52.4, 30.9, 23.0, 21.2, 20.2; IR (CCl_4): ν = 3438, 2987, 1721, 1435, 1287, 1260, 1152, 1087, 1066, 1044, 941, 816, 784, 761, 742, 702, 592 cm^{-1}; MS (APCI): m/z (%): 401 $[M+1]^+$ (80), 261 $[M+1-(SO-p\text{-}Tol+1)]^+$ (100), 192 (30), 132 (28); elemental analysis calcd (%) $C_{22}H_{28}N_2O_3S$ (400.59): C 65.96, H 7.06, N 6.99, S 8.00; found: C 66.04, H 7.18, N 7.20, S 8.13. Compound **9c** (partial data from the mixture): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.72 (s, 1 H, H-2), 3.98 (d, 1 H, *J* = 6.4 Hz, H-5), 3.86 (s, 3 H, CO_2Me), 2.35 (s, 3 H, Me-Tol), 1.44 (s, 3 H, Me), 0.53 (d, 3 H, *J* = 6.8 Hz, Me *i*Pr), 0.30 (d, 3 H, *J* = 6.7 Hz, Me *i*Pr). Partial data of the epimer at C^2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.40 (s, 1 H, H-2), 1.53 (s, 3 H, Me), 1.33 (d, 3 H, *J* = 6.1 Hz, Me *i*Pr), 0.94 (d, 3 H, *J* = 6.5 Hz, Me *i*Pr).

(±)-Methyl [(2*S*,4*R*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl]carboxylate, (±)-5a, and (±)-methyl [(2*S*,4*S*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl]carboxylate, (±)-12a. From a solution of LDA, [*i*Pr$_2$NH (421 mg, 0.54 mL, 4.16 mmol) and *n*BuLi (1.6 M, 2.10 mL, 3.36 mmol)], with a solution of methyl 2-benzyl-2-

(benzylideneamino)acetate (**2a**, 855 mg, 3.20 mmol) and a solution of *N*-(benzylidene)-*p*-toluenesulfonamide (**1m**, 519 mg, 2.00 mmol), adding $BF_3 \cdot OEt_2$ (922 mg, 0.80 mL, 6.50 mmol) according to the general procedure (2 h 30 min), a 67:33 mixture of imidazolidines **(±)-5a** and **(±)-12a** was obtained. Purification by chromatography (5-100% EtOAc-hexane) gave pure **(±)-5a** (134 mg, 13%) and a 39:61 mixture of cycloadducts **(±)-12a** and **(±)-5a** (780 mg, 75%). Recrystallization from 20% CH_2Cl_2-hexane gave pure **(±)-5a** (357 mg, 34%) as a white solid. Concentration of the mother liquours gave **(±)-12a** (230 mg, 22%). The data found for **(±)-5a** and **(±)-12a** was identical to that obtained before for optically pure compounds.

(±)-Methyl (2*R*,3*R*)-2-amino-3-phenyl-3-tosylaminopropanoate, (±)-13 *anti* and (±)-methyl (2*S*,3*R*)-2-amino-3-phenyl-3-tosylaminopropanoate, (±)-13 *syn*. From a solution of LDA, [$i Pr_2NH$ (100 mg, 0.14 mL, 0.993 mmol) and *n*BuLi (1.6 M, 0.50 mL, 0.800 mmol)], with a solution of methyl 2-benzyl-2-(benzylideneamino)acetate (**2a**, 135 mg, 0.764 mmol) and a solution of *N*-(benzylidene)-*p*-toluenesulfonamide (**1m**, 99 mg, 0.382 mmol), adding $BF_3 \cdot OEt_2$ (176 mg, 0.16 mL, 1.241 mmol) according to the general procedure (45 min), a 70:30 mixture of tosyldiaminoesters **(±)-13 *anti*** and **(±)-13 *syn*** was obtained. Purification by chromatography (5-30% Et_2O-CH_2Cl_2, then 5% MeOH-Et_2O) gave **(±)-13 *anti*** and **(±)-13 *syn*** (109 mg, 75%); a second chromatography (0-2% MeOH-CH_2Cl_2) and recrystallization from 20% EtOAc-hexane gave mixtures enriched in **(±)-13 *anti*** or **(±)-13 *syn***. The structural

assignment is tentative. Compound **(±)-13** ***anti*** (from a 90:10 mixture): R_f = 0.23 (2% MeOH-CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, 2 H, *J* = 8.3 Hz, Ar-H), 6.94-7.20 (m, 7 H, Ar-H), 6.15 (br s, 1 H, S-NH), 4.85 (d, 1 H, *J* = 4.2 Hz, H-3), 3.72 (d, 1 H, *J* = 4.4 Hz, H-2), 3.59 (s, 3 H, CO_2Me), 2.29 (s, 3 H, Me-Tol), 1.75 (br s, 2 H, NH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.8, 143.0, 137.9, 136.0, 129.3 (2 C), 128.3 (2 C), 127.9, 127.0 (2 C), 126.9 (2 C), 58.8, 58.5, 52.2, 21.3; IR (KBr): ν = 3431, 1736, 1629, 1455, 1324, 1213, 1160, 1091, 810, 703, 655, 562 cm^{-1}; MS (ES): m/z (%): 697 $[2M+1]^+$ (34), 349 $[M+1]^+$ (100). Compound **(±)-13** ***syn*** (from a 90:10 mixture): R_f = 0.19 (2% MeOH-CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.00-7.20 (m, 7 H, Ar-H), 6.00 (br s, 1 H, S-NH), 4.72 (d, 1 H, *J* = 4.2 Hz, H-3), 3.69 (d, 1 H, *J* = 4.2 Hz, H-2), 3.51 (s, 3 H, CO_2Me), 1.75 (br s, 2 H, NH_2).

General Procedure for Oxidation of Sulfinamides to Sulfonamides with *m*CPBA. To a solution of the sulfinamide in CH_2Cl_2 (10 mL/mmol) was added 1.5-3.0 equiv of 70% *m*CPBA, at 0 ºC and under an argon atmosphere. The reaction mixture was allowed to warm up slowly to rt and monitored by TLC. The reaction was quenched with 1 M aqueous $Na_2S_2O_4$ (5 mL/mmol), a saturated solution of $NaHCO_3$ (3 mL/mmol) and H_2O (4 mL/mmol), diluted with EtOAc (8 mL/mmol), the layers were separated and the aqueous layer was extracted with EtOAc (3 times, 5 mL/mmol). The organic layer was washed with a saturated solution of NaCl (4 mL/mmol), dried over $MgSO_4$, filtered

and concentrated under reduced pressure to give a crude product that was purified by column chromatography.

(–)-Methyl [(2*S*,4*S*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl]carboxylate, 12a. From sulfinamide **9a** (37 mg, 0.072 mmol) and *m*CPBA (37 mg, 0.217 mmol), according to the general procedure (12 h), sulfonamide **12a** (24.2 mg, 67%) was obtained after chromatography (50% CH_2Cl_2-hexane-20% EtOAc-CH_2Cl_2) as a viscous oil, that was recrystallized from Et_2O to give a white solid. Compound **12a**: R_f = 0.28 (30% EtOAc-hexane); m.p. 56-58 ºC; $[\alpha]^{20}_D$ = –9.7 (*c* = 1.2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69-7.70 (m, 2 H, Ar-H), 7.58 (d, 2 H, *J* = 6.4 Hz, Ar-H), 7.26-7.40 (m, 8 H, Ar-H), 7.05-7.13 (m, 5 H, Ar-H), 6.86-6.89 (m, 2 H, Ar-H), 5.52 (d, 1 H, *J* = 5.4 Hz, H-2), 5.37 (s, 1 H, H-5), 3.44 (s, 3 H, CO_2Me), 2.76 (d, 1 H, *J* = 5.5 Hz, NH-3), 2.61 (d, 1 H, *J* = 13.5 Hz, CH_2Ph), 2.33 (s, 3 H, Me-Tol), 2.16 (d, 1 H, *J* = 13.4 Hz, CH_2Ph); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.5, 143.2, 139.1, 138.3, 135.5, 129.5, 129.3 (2 C), 129.1 (2 C), 128.9, 128.6 (2 C), 128.3 (4 C), 128.2 (2 C), 128.1 (2 C), 127.9 (2 C), 127.1, 75.8, 72.3, 52.4, 42.6, 21.5; IR ($CHCl_3$): ν = 3350, 3040, 2950, 2880, 1740, 1600, 1500, 1460, 1405, 1360, 1220, 1170, 1095, 1025, 760, 705, 670 cm^{-1}; MS (EI): m/z (%): 523 (0.2), 465 (2), 433 (2), 369 (3), 259 (3), 208 (6), 176 (18), 155 (30), 116 (14), 91 (100), 65 (42).

General Procedure for the Reaction between Sulfinylimidazolidines and $LiAlH_4$. A round-bottomed flask was charged with anhydrous Et_2O

or THF (6 mL/mmol of imidazolidine) and 3-9 equiv of $LiAlH_4$ was added. After 10 min, the resulting suspension was cooled to 0 ºC and a solution of the corresponding imidazolidine in anhydrous Et_2O or THF (4 mL/mmol), was added dropwise and the reaction mixture was stirred at room temperature and monitored by TLC. When the reaction had reached completion (2-18 h), the mixture was quenched with a saturated $NaHCO_3$ solution (4 mL/mmol), H_2O (4 mL/mmol) and diluted with CH_2Cl_2 (8 mL/mmol). The resulting suspension was filtered through celite and the residue was thoroughly washed with CH_2Cl_2 and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 times, 8 mL/mmol). The combined organic extracts were washed with a saturated NaCl solution (4 mL/mmol), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a crude product, which was purified by chromatography on silica gel.

(+)-[(2*R*,3*R*,S_S)-2-Benzyl-2-(benzylamino)-3-phenyl-3-(*p*-tolylsulfinylamino)propan-1-ol, 17a and (–)-[(2*S*,4*R*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfenyl)-1,3-imidazolidin-4-yl]methanol, 14a. From a suspension of $LiAlH_4$ (6 equiv, 18 mg, 0.46 mmol) in Et_2O and sulfinamide **3a** (40 mg, 0.08 mmol), with addition of 3 equiv of $LiAlH_4$ after 1 h at rt, according to the general procedure (18 h), after chromatography (25-100% Et_2O-hexane), sulfenamide **14a** (24 mg, 65%) was obtained as a colorless oil. Additionally we have observed the formation of variable amounts of **17a** depending on the experimental conditions and the batch of $LiAlH_4$ employed. For

example, from a suspension of $LiAlH_4$ (4 equiv, 15 mg, 0.404 mmol) in THF and sulfinamide **3a** (52 mg, 0.101 mmol), with addition of 3 equiv of $LiAlH_4$ after 1 h at –20 °C, according to the general procedure (–20 °C to 5 °C, 23 h), after chromatography (0-5% *i*PrOH-CH_2Cl_2), sulfenamide **14a** (4 mg, 9%) and sulfinamide **17a** (20 mg, 42%) were obtained as colorless oil and a white solid respectively. Compound **14a**: R_f = 0.26 (30% EtOAc-hexane); R_f = 0.47 (75% Et_2O-hexane); $[\alpha]^{20}_D$ = –36.3 (*c* = 0.90); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59-7.62 (m, 2 H, Ar-H), 7.05-7.49 (m, 17, Ar-H), 4.66 (s, 1 H, H-2), 4.13 (s, 1 H, H-5), 3.21 (d, *J* = 11.7 Hz, 1 H, CH_2OH), 3.11 (d, *J* = 11.7 Hz, 1 H, CH_2OH), 2.73 (s, 2 H, CH_2Ph), 2.40 (s, 3 H, Me-Tol), 1.50-2.00 (br s, 2 H, NH, OH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.0, 139.7, 137.5, 136.5, 136.2, 130.9 (4 C), 129.5 (2 C), 128.7 (2 C), 128.1 (2 C), 127.9 (4 C), 126.8 (2 C), 126.5 (2 C), 79.1, 71.1, 66.4, 65.6, 42.4, 21.4,; IR (CCl_4): ν = 3400, 2920, 2850, 1490, 1455, 1060, 1030, 790, 750, 700, 610 cm^{-1}; elemental analysis calcd (%) $C_{30}H_{30}N_2OS$ (466.64): C 77.22, H 6.48, N 6.00, S 6.87; found: C 77.01, H 6.35, N 5.83, S 6.59. Compound **17a**: R_f = 0.33 (5% *i*PrOH-CH_2Cl_2); m.p. 167-170 °C; $[\alpha]^{20}_D$ = +25.8 (*c* = 0.41); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21-7.38 (m, 12 H, Ar-H), 6.99-7.18 (m, 5 H, Ar-H), 6.90 (d, *J* = 8.1 Hz, 2 H Ar-H), 6.06 (d, *J* = 6.1 Hz, 1 H, S-NH), 4.64 (d, *J* = 6.3 Hz, 1 H, H-3), 4.03 (d, *J* = 12.0 Hz, 1 H, N-CH_2Ph), 3.94 (d, *J* = 12.0 Hz, 1 H, N-CH_2Ph), 3.60 (d, *J* = 11.7 Hz, 1 H, CH_2OH), 3.39 (d, *J* = 11.7 Hz, 1 H, CH_2OH), 2.77 (d, *J* = 14.2 Hz, 1 H, CH_2Ph), 2.64 (d, *J* = 14.2 Hz, 1 H, CH_2Ph), 2.23 (s, 3 H, Me-Tol), 1.98 (br s, 1 H, NH or OH), 1.40 (br

s, 1 H, NH or OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.8, 140.4, 140.1, 139.6, 136.7, 130.4 (2 C), 128.8 (4 C), 128.5 (2 C), 128.4 (2 C), 128.1 (2 C), 127.7 (2 C), 127.0, 126.9, 126.6, 125.6 (2 C), 64.8, 61.3, 58.6, 45.6, 37.7, 21.2; IR (KBr): ν = 3430, 2922, 1631, 1493, 1453, 1261, 1086, 1042, 806, 740, 703 cm^{-1}; MS(ES): m/z (%): 485 $[M+1]^+$ (100).

Reaction of (–)-methyl[(2*S*,4*R*,5*R*,S_S)-4-benzyl-2-phenyl-5-(3-pyridyl)-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]carboxylate, 3e with $LiAlH_4$. From a suspension of $LiAlH_4$ (4 equiv, 18 mg, 0.476 mmol) in Et_2O-THF 9:1 and cycloadduct **3e** (61 mg, 0.119 mmol), according to the general procedure (20 h), a 30:50:20 mixture of alcohols **14b:14c:17b** was obtained. Purification by chromatography (0-20% MeOH-Et_2O), gave pure alcohol **17b** (7 mg, 12%) and a mixture of **14b** and **14c** (32 mg, 57%). Compound **14b** (partial data from a 90:10 mixture): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.75-8.52 (m, 18 H, Ar-H), 4.69 (s, 1 H, H-2), 4.12 (s, 1 H, H-5), 3.18 (d, 1 H, *J* = 11.0 Hz, CH_2OH), 3.05 (d, 1 H, *J* = 11.2 Hz, CH_2OH), 2.86 (d, 1 H, *J* = 13.7 Hz, CH_2Ph), 2.69 (d, 1 H, *J* = 13.7 Hz, CH_2Ph), 2.39 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ= 151.2, 149.0, 140.3, 139.4, 79.1, 68.9, 66.1, 65.5, 42.1, 21.4; IR (film): ν = 3292, 3028, 2923, 1595, 1493 1454, 1428, 1066, 1028, 812, 756, 700 cm^{-1}; MS (ES): m/z (%): 468 $[M+1]^+$ (100). Compound **14c** (partial data from a 1:1 mixture): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.97 (s, 1 H, H-2), 4.92 (s, 1 H, H-5), 3.17 (br s, 2 H, CH_2Ph), 3.05 (d, 1 H, *J* = 10.7 Hz, CH_2Ph), 2.97 (d, 1 H, *J* = 11.3 Hz, CH_2Ph), 2.12 (s, 3 H, Me-Tol);

^{13}C NMR (50 MHz, $CDCl_3$): δ = 68.6, 63.1, 60.1, 53.4, 39.4, 21.1; MS (ES): m/z (%): 484 $[M+1]^+$ (100). Compound **17b**: R_f = 0.29 (5% MeOH-CH_2Cl_2); m.p. 154-157 °C; $[\alpha]^{20}_D$ = +5.9 (*c* = 0.76); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (dd, 1 H, *J* = 4.6, 1.5 Hz, Ar-H), 8.16 (br s, 1 H, Ar-H), 7.10-7.50 (m, 13 H, Ar-H), 7.01 (dd, 1 H, *J* = 8.1, 4.6 Hz, Ar-H), 6.92 (d, 2 H, *J* = 7.8 Hz, Ar-H), 6.40 (d, 1 H, *J* = 6.4 Hz, S-NH), 4.69 (d, 1 H, *J* = 6.4 Hz, H-3), 4.11 (d, 1 H, *J* = 12.2 Hz, N-CH_2Ph), 4.02 (d, 1 H, *J* = 12.2 Hz, N-CH_2Ph), 3.63 (d, 1 H, *J* = 12.0 Hz, CH_2OH), 3.50 (d, 1 H, *J* = 12.0 Hz, CH_2OH), 2.80 (d, 1 H, *J* = 14.7 Hz, CH_2Ph), 2.60 (d, 1 H, *J* = 14.7 Hz, CH_2Ph), 2.23 (s, 3 H, Me-Tol), 2.15 (br s, 2 H, NH, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 147.9, 141.1, 140.2, 139.3, 136.5, 136.1, 135.6, 130.2 (2 C), 129.0 (2 C), 128.6 (2 C), 128.1 (2 C), 127.2, 126.9, 125.6 (2 C), 122.4, 64.5, 61.1, 55.6, 45.4, 37.4, 21.2; IR (KBr): ν = 3326, 3025, 2923, 1600, 1576, 1494, 1477, 1452, 1423, 1316, 1243, 1086, 1045, 890, 812, 742, 702 cm^{-1}; MS(ES): m/z (%): 993 $[2M+Na]^+$ (13), 508 $[M+Na]^+$ (41), 486 $[M+1]^+$ (100).

Reaction of (±)-methyl [(2*S*,4*R*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl]carboxylate, (±)-5a with $LiAlH_4$. From a suspension of $LiAlH_4$ (3.25 equiv, 14 mg, 0.384 mmol) in THF and sulfonamide **(±)-5a** (62 mg, 0.118 mmol), according to the general procedure (–20 °C to 0 °C, 45 min), after chromatography (20-75% EtOAc-hexane), sulfonamide **(±)-14d** (10 mg, 17%) was obtained as a white solid, further recrystallized from 25% CH_2Cl_2-hexane, along with starting material (2.5 mg, 4%) and *N*-

sulfonyldiaminoalcohol **17c** (24 mg, 41%). Compound **(±)-14d**: R_f = 0.20 (30% EtOAc-hexane); m.p. 97-99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, 2 H, *J* = 7.2 Hz, Ar-H), 7.16-7.44 (m, 15 H, Ar-H), 7.07 (d, 2 H, *J* = 8.0 Hz, Ar-H), 5.78 (d, 1 H, *J* = 10.1 Hz, H-2), 4.77 (s, 1 H, H-5), 3.07 (dd, 1 H, *J* = 11.8, 3.8 Hz, CH_2OH), 2.95 (d, 1 H, *J* = 13.9 Hz, CH_2Ph), 2.76 (dd, 1 H, *J* = 11.8, 9.9 Hz, CH_2OH), 2.73 (d, 1 H, *J* = 13.9 Hz, CH_2Ph), 2.62 (d, 1 H, *J* = 9.9 Hz, NH-3), 2.35 (s, 3 H, Me-Tol), 1.01 (dd, 1 H, *J* = 9.9, 3.8 Hz, OH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.6, 140.2, 137.9, 135.5, 134.6, 130.8 (2 C), 129.5 (2 C), 128.6 (2 C), 128.5 (2 C), 127.9 (2 C), 127.8 (2 C), 127.4 (2 C), 127.0 (2 C), 126.9, 77.0, 69.0, 63.0, 53.4, 39.7, 21.5; IR (KBr): ν = 3480, 3320, 3060, 3030, 2920, 1600, 1490, 1450, 1345, 1305, 1265, 1200, 1165, 1095, 1055, 1040, 1030, 1020, 995, 930, 860, 830, 805, 775, 760, 745, 735, 730, 700, 680, 665 cm^{-1}; elemental analysis calcd (%) $C_{30}H_{30}N_2O_3S$ (498.65): C 72.26, H 6.06, N 5.62, S 6.43; found: C 71.90, H 5.71, N 5.30, S 5.00. Compound **(±)-17c**: R_f = 0.10 (30% EtOAc-hexane); m.p. 178-180 °C (25% Et_2O-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.43 (dm, 2 H, *J* = 7.9 Hz, Ar-H), 7.19-7.37 (m, 7 H, Ar-H), 7.03-7.13 (m, 8 H, Ar-H), 6.88 (dm, 2 H, *J* = 7.9 Hz, Ar-H), 6.50 (br s, 1 H, NH-3), 4.72 (s, 1 H, H-3), 4.04 (d, 1 H, *J* = 11.3 Hz, N-CH_2-Ph), 3.98 (d, 1 H, *J* = 11.5 Hz, N-CH_2-Ph), 3.51 (d, 1 H, *J* = 12.0 Hz, CH_2-OH), 3.25 (d, 1 H, *J* = 11.5 Hz, CH_2-OH), 2.97 (d, 1 H, *J* = 14.0 Hz, CH_2-Ph), 2.50 (d, 1 H, *J* = 14.0 Hz, CH_2-Ph), 2.25 (s, 3 H, Me-Tol), 1.64 (br s, 2 H, NH-2, OH); ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 142.3, 140.0, 138.0, 137.1, 137.0, 136.2, 130.4, 128.9 (2 C), 128.8 (2 C), 128.6, 128.3

(2 C), 128.0 (2 C), 127.3, 127.2, 126.8 (2 C), 65.4, 62.5, 61.0, 45.4, 37.3, 21.3; IR (KBr): ν = 3460, 3310, 3280, 3060, 3030, 2950, 2860, 1600, 1495, 1470, 1455, 1425, 1360, 1330, 1210, 1180, 1160, 1090, 1055, 1030, 925, 910, 880, 835, 810, 760, 755, 735, 705, 670 cm^{-1}; elemental analysis calcd (%) $C_{30}H_{32}N_2O_3S$ (500.36): C 71.96, H 6.45, N 5.60, S 6.40; found: C 71.58, H 6.07, N 5.25, S 6.02.

(±)-(2*S*,4*S*,5*R*)-4-Benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-1,3-imidazolidin-4-yl-methanol, (±)-15b, and (±)-*N*-{(*R*)-[(2*R*,4*S*)-4-benzyl-2-phenyloxazolidin-4-yl]phenylmethyl}-*p*-toluenesulfonamide, (±)-16. From a suspension of $LiAlH_4$ (3 equiv, 13 mg, 0.354 mmol) in THF and cycloadduct **(±)-12a** (62 mg, 0.117 mmol), according to the general procedure (–20 °C, then 0 °C, 10 min), an 80:20 mixture of alcohol **(±)-15b** and **(±)-16**, along with a small amount of **(±)-17d**, was obtained. Purification by chromatography (5-50% EtOAc-hexane), gave pure alcohol **(±)-17d** (10 mg, 17%) and **(±)-15b** (48 mg, 82%) contaminated with traces of **(±)-16**. Upon recrystallization (25% CH_2Cl_2-hexane), complete formation of **(±)-16** was observed (^{1}H NMR) and, upon standing in CH_2Cl_2 solution, formation of **(±)-15b** was observed. Compound **(±)-15b**: R_f = 0.21 (5% EtOAc-CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.68-7.77 (m, 19 H, Ar-H), 5.59 (s, 1 H, H-2), 4.93 (s, 1 H, H-5), 3.22 (br s, 2 H, CH_2OH), 2.47 (d, 1 H, J = 13.9 Hz, CH_2Ph), 2.34 (s, 3 H, Me-Tol), 2.17 (d, 1 H, J = 14.1 Hz, CH_2Ph); ^{13}C NMR (50 MHz, $CDCl_3$, partial data from the mixture): δ = 78.0, 62.0, 39.6, 21.5. Compound **(±)-16**: R_f = 0.21 (5% EtOAc-

CH_2Cl_2); ^1H NMR (200 MHz, $CDCl_3$): δ = 7.55 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.10-7.38 (m, 13 H, Ar-H), 6.97 (m, 2 H, Ar-H), 6.66 (dm, 2 H, *J* = 8.1 Hz, Ar-H), 5.94 (d, 1 H, *J* = 3.9 Hz, H-2), 4.83 (d, 2 H, *J* = 11.0 Hz, CH-N, NH), 4.14 (d, 1 H, *J* = 4.0 Hz, NH-1), 4.05 (d, 1 H, *J* = 8.8 Hz, CH_2OH), 3.78 (d, 1 H, *J* = 8.9 Hz, CH_2OH), 2.79 (d, 1 H, *J* = 14.1 Hz, CH_2Ph), 2.53 (d, 1 H, *J* = 13.8 Hz, CH_2Ph), 2.37 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$, partial data from the mixture): δ = 92.3, 70.1, 61.6, 38.1, 21.5; IR (film): ν = 3307, 3063, 3030, 2926, 1599, 1495, 1454, 1332, 1216, 1160, 1091, 1055, 1029, 918, 813, 754, 700, 665 cm^{-1}; MS (ES): m/z (%): 533 $[M+NH_4OH]^+$ (58), 499 $[M+1]^+$ (73), 497 $[M-1]^+$ (100).

(–)-(2*S*,3*R*,S_S)-2-(Benzylamino)-3-phenyl-3-(*p*-tolylsulfinylamino)propan-1-ol, 17f, and (2*R*,3*S*,S_S)-2-(benzylamino)-3-phenyl-3-(*p*-tolylsulfinylamino)propan-1-ol, 17f'

From a suspension of $LiAlH_4$ (287 mg, 7.56 mmol) in Et_2O and an 84:16 mixture of **7a** and **8a** (795 mg, 1.89 mmol), according to the general procedure (2 h), diaminoalcohols **17f** and **17f'** were obtained. Purification by chromatography (CH_2Cl_2 to 1:20 EtOH-CH_2Cl_2) afforded 257 mg (0.65 mmol) of diaminoalcohol **17f** as a white solid and 380 mg (0.96 mmol) of a mixture of diaminoalcohols **17f** and **17f'** (85% combined yield), which after recrystallization from Et_2O-CH_2Cl_2, afforded 300 mg of pure diaminoalcohol **17f** (40%). This reaction has also been carried out using pure **7a** as starting material with parallel results (83%); however, sometimes we have found convenient to carry out the reduction of the mixture of

diastereomers **7**/**8** due to their tedious separation. Compound **17f**: R_f = 0.18 (Et_2O); m.p. 134-135 ºC; $[\alpha]^{20}_D$ = –126.7 (*c* = 0.80); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.38 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.13-7.25 (m, 6 H, Ar-H), 6.99-7.08 (m, 6 H, Ar-H), 5.64 (d, 1 H, *J* = 7.5 Hz, S-NH), 4.45 (dd, 1 H, *J* = 7.5, 3.5 Hz, H-3), 3.56 (m, 2 H, CH_2OH), 3.51 (d, 1 H, *J* = 13.3 Hz, CH_2Ph), 3.36 (d, 1 H, *J* = 13.3 Hz, CH_2Ph), 2.88 (ddd, 1 H, *J* = 8.8, 5.3, 3.5 Hz, H-2), 2.25 (s, 3 H, Me-Tol), 1.60 (br s, 1 H, Bn-NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.5, 141.1, 139.8, 139.1, 129.1 (2 C), 128.4 (2 C), 128.1 (2 C), 127.9 (2 C), 127.1, 126.8, 126.6 (2 C), 126.2 (2 C), 62.8, 60.9, 53.0, 51.9, 21.1; IR (KBr): ν = 3390, 3180, 2940, 2860, 1630, 1490, 1460, 1450, 1425, 1340, 1260, 1200, 1175, 1080, 1055, 1030, 950, 920, 890, 850, 830, 810, 750, 700 cm^{-1}; MS (EI): m/z (%): 303 (1), 285 (3), 278 (1), 223 (6), 150 (97), 106 (31), 92 (20), 91 (100), 77 (13), 65 (16), 51 (4); elemental analysis calcd (%) $C_{23}H_{26}N_2O_2S$ (394.53): C 70.02, H 6.64, N 7.10, S 6.13; found: C 69.93, H 6.56, N 7.16, S 6.01. Compound **17f'** (partial data): R_f = 0.12 (Et_2O); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.40 (d, 1 H, *J* = 7.5 Hz, S-NH), 4.70 (dd, 1 H, *J* = 7.5, 3.5 Hz, H-3), 2.44 (s, 3 H, Me-Tol).

(–)-(2*S*,3*R*,S_S)-2-(benzylamino)-3-*p*-fluorophenyl-3-(*p*-tolylsulfinylamino)propan-1-ol, 17g, and (+)-(2*R*,3*S*,S_S)-2-(benzylamino)-3-*p*-fluorophenyl-3-(*p*-tolylsulfinylamino)propan-1-ol, 17g'. From a suspension of $LiAlH_4$ (33 mg, 0.88 mmol) in Et_2O and an 83:17 mixture of **7e** and **8e** (95 mg, 0.22 mmol), according to the general procedure (2 h), diaminoalcohols **17g** and **17g'** were

obtained. Purification by chromatography (0-3% EtOH-CH_2Cl_2) afforded diaminoalcohol **17g** (40 mg, 0.10 mmol, 45%) as a white solid, further recrystallized from Et_2O, and a mixture of diaminoalcohols **17g** and **17g'** (23 mg, 0.06 mmol, 27%; 72% combined yield). Chromatography of this mixture (1:40 EtOH-CH_2Cl_2) gave pure diaminoalcohol **17g'**(7 mg) as a colorless oil. This reaction has been carried out on a mixture of **7e** and **8e** to avoid their tedious separation; this has led to the characterization of **17g'**. Compound **17g**: R_f = 0.32 (1:40 EtOH-CH_2Cl_2); m.p. 122-124 °C; $[\alpha]^{20}_D$ = –155.0 (*c* = 1.49); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.18-7.28 (m, 3 H, Ar-H), 6.94-7.06 (m, 6 H, Ar-H), 6.84 (ap t, 2 H, *J* = 8.7 Hz, Ar-H), 5.63 (d, 1 H, *J* = 7.5 Hz, S-NH), 4.42 (dd, 1 H, *J* = 7.3, 3.5 Hz, H-3), 4.30 (br s, 1 H, OH), 3.57 (dd, 1 H, *J* = 11.7, 4.6 Hz, H-1), 3.50 (m, 1 H, H-1), 3.48 (d, 1 H, *J* = 13.4 Hz, CH_2Ph), 3.33 (d, 1 H, *J* = 13.4 Hz, CH_2Ph), 2.81 (ddd, 1 H, *J* = 8.2 Hz, 4.6 Hz, 3.5 Hz, H-2), 2.24 (s, 3 H, Me-Tol), 1.56 (br s, 1 H, Bn-NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.7 (1 C, d, J_{ipso} C-F = 245.3 Hz), 141.3, 139.9, 139.4, 137.5, 129.1 (2 C), 128.5 (2 C), 128.2 (2 C, d, J_m C-F = 8.0 Hz), 127.9 (2 C), 127.2, 126.1 (2 C), 114.9 (2 C, d, J_o C-F = 21.5 Hz), 63.1, 61.1, 52.4, 52.2, 21.1; IR (KBr): ν = 3401, 1690, 1508, 1221, 1037 cm^{-1}; MS (ES): m/z (%): 413 $[M+1]^+$ (100); elemental analysis calcd (%) $C_{23}H_{25}FN_2O_2S$ (412.57): C 66.95, H 6.12, N 6.79, S 7.77; found: C 66.72, H 6.11, N 6.73, S 8.02. Compound **17g'**: R_f = 0.30 (1:40 EtOH-CH_2Cl_2); $[\alpha]^{20}_D$ = +63.6 (*c* = 1.38); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.16-7.38 (m, 7 H, Ar-H), 7.02-7.10

(m, 4 H, Ar-H), 5.41 (d, 1 H, *J* = 4.4 Hz, S-NH), 4.65 (dd, 1 H, *J* = 6.3, 4.5 Hz, H-3), 3.60-3.71 (m, 1 H, H-1), 3.65 (d, 1 H, *J* = 13.4 Hz, CH_2Ph), 3.50 (m, 1 H, H-1), 3.48 (d, 1 H, *J* = 13.4 Hz, CH_2Ph), 2.77 (m, 1 H, H-2), 2.42 (s, 3 H, Me-Tol), 1.65 (br s, 1 H, Bn-NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 162.3 (d, 1 C, J_{ipso} C-F = 246.4 Hz), 142.1, 141.5, 139.9, 136.1 (d, 1 C, J_p C-F = 3.0 Hz), 129.6 (2 C), 129.5 (d, 2 C, J_m C-F = 9.9 Hz), 128.3 (2 C), 128.1 (2 C), 127.0, 125.2 (2 C), 115.5 (d, 2 C, J_o C-F = 21.3 Hz), 62.8, 59.2, 58.0, 51.2, 21.4; IR (KBr): ν = 3435, 2920, 1631, 1508, 1223, 1045 cm^{-1}; MS (ES): m/z (%): 413 $[M+1]^+$ (100).

(–)-(2*S*,3*R*,*S*$_S$)-2-benzylamino-3-(3-pyridyl)-3-(*p*-tolylsulfinylamino)propan-1-ol, 17h. $LiAlH_4$ (8 mg, 0.20 mmol) was added to a suspension of **7f** (21 mg, 0.05 mmol) in anhydrous Et_2O (15 mL/mmol). Standard work-up according to the general procedure (7 h) gave *N*-benzyldiaminoalcohol **17h** (14 mg, 71%) as a colorless oil after chromatography (2.5-15% EtOH-Et_2O). Compound **17h**: R_f = 0.23 (10% EtOH-Et_2O); $[\alpha]^{20}_D$ = –110.7 (*c* = 0.84); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.37 (dm, *J* = 4.6 Hz, 1 H, Ar-H), 8.29 (d, *J* = 2.0 Hz, 1 H, Ar-H), 7.34 (m, 3 H, Ar-H), 7.21-7.23 (m, 3 H, Ar-H), 7.03-7.08 (m, 3 H, Ar-H), 7.01 (d, *J* = 7.9 Hz, 2 H, Ar-H), 5.68 (d, *J* = 7.3 Hz, 1 H, S-NH), 4.48 (dd, *J* = 7.1, 3.0 Hz, 1 H, H-3), 3.48-3.63 (m, 2 H, CH_2OH), 3.45 (d, *J* = 13.2 Hz, 1 H, CH_2Ph), 3.31 (d, *J* = 13.2 Hz, 1 H, CH_2Ph), 2.82-2.88 (m, 1 H, H-2), 2.23 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.5, 148.1, 141.5, 139.5, 139.0, 137.4, 134.3, 129.2 (2 C), 128.5 (2 C), 127.9 (2 C), 127.3,

126.0 (2 C), 122.8, 62.9, 61.1, 52.4, 50.8, 21.2; IR (CCl_4): ν = 3300, 3000, 2900, 2820, 1560, 1480, 1430, 1410, 1120, 1080 cm^{-1}; MS (EI): m/z (%): 150 (51), 139 (19), 108 (15), 91 (100), 65 (10); elemental analysis calcd (%) $C_{22}H_{25}N_3O_2S$ (395.52): C 66.81, H 6.37, N 10.62, S 8.11; found: C 66.93, H 6.05, N 10.51, S 8.35.

(+)-(2*S*,3*R*,S_S)-2-(Benzylamino)-3-(*p*-tolylsulfinylamino)pentan-1-ol, 17j, and (2*S*,3*S*,S_S)-2-(benzylamino)-3-(*p*-tolylsulfinylamino)pentan-1-ol, 17j'. From a suspension of $LiAlH_4$ (480 mg, 12.64 mmol) in Et_2O and **7i** (1179 mg, 3.16 mmol), according to the general procedure (4 h 30 min), diaminoalcohol **17j** was obtained. Purification by chromatography (0-5% MeOH-CH_2Cl_2) afforded diaminoalcohol **17j** (866 mg, 2.50 mmol, 79%). This reaction has also been carried out with a 90:10 mixture of **7i** and **8i** which has allowed to isolate and characterize after chromatography (15% MeOH-toluene) diaminoalcohol **17j'** (10 mg). Compound **17j**: R_f = 0.37 (5% MeOH-CH_2Cl_2); $[\alpha]^{20}_D$ = +21.5 (*c* = 1.11); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.26 (m, 7 H, Ar-H), 4.94 (d, 1 H, *J* = 8.4 Hz, S-NH), 3.87 (d, 1 H, *J* = 13.0 Hz, CH_2Ph), 3.73 (d, 1 H, *J* = 13.0 Hz, CH_2Ph), 3.60 (m, 2 H, 2 H-1), 3.17 (m, 1H, H-3), 2.67 (ddd, 1 H, *J* = 5.1, 3.4, 2.1 Hz, H-2), 2.39 (s, 3 H, Me-Tol), 1.27-1.42 (m, 1 H, H-4), 1.13-1.25 (m, 1 H, H-4), 0.50 (t, 3 H, *J* = 7.4 Hz, CH_3 Et); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4, 140.3, 140.1, 129.4 (2 C), 128.5 (2 C), 128.2 (2 C), 127.2, 125.9 (2 C), 61.4, 58.6, 53.1, 52.9, 27.0, 21.4, 10.2; IR (film): ν = 3307, 3027, 2929, 2874, 1597, 1493, 1453, 1261, 1086, 1045, 812,

737, 699 cm^{-1}; MS (ES): m/z (%): 347 $[M+1]^+$ (100); elemental analysis calcd (%) $C_{19}H_{26}N_2O_2S$ (346.54): C 65.89, H 7.57, N 8.09, S 9.20; found: C 65.74, H 7.80, N 8.11, S 9.43. Compound **17j'**: R_f = 0.37 (30% MeOH-toluene); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.21-7.32 (m, 7 H, Ar-H), 4.54 (d, 1 H, *J* = 8.9 Hz, S-NH), 3.79 (d, 1 H, *J* = 13.3 Hz, CH_2Ph), 3.68 (d, 1 H, *J* = 13.3 Hz, CH_2Ph), 3.61 (dd, 1 H, *J* = 11.1, 4.3 Hz, H-1), 3.53 (dd, 1 H, *J* = 11.1, 5.5 Hz, H-1), 3.42 (m, 1 H, H-3), 2.60 (m, 1 H, H-2), 2.37 (s, 3 H, Me-Tol), 1.59 (quint, 1 H, *J* = 7.2 Hz, H-4), 0.99 (t, 3 H, *J* = 7.4 Hz, CH_3 Et); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 141.5, 140.1, 129.6 (2 C), 128.4 (2 C), 128.2 (2 C), 127.0, 125.4 (2 C), 60.1, 59.6, 59.1, 51.2, 27.1, 21.3, 11.1; IR (KBr): ν = 3427, 3289, 3210, 2963, 2920, 2869, 1627, 1595, 1490, 1452, 1414, 1378, 1085, 1033, 816, 734, 695 cm^{-1}; MS (ES): m/z (%): 347 $[M+1]^+$ (100%).

(+)-(2*S*,3*R*,*S*$_S$)-2-(benzylamino)-4-methyl-3-(*p*-tolylsulfinylamino)pentan-1-ol, 17k. From a suspension of $LiAlH_4$ (140 mg, 3.68 mmol) in Et_2O and **7j** (357 mg, 0.92 mmol), according to the general procedure (5 h), diaminoalcohol **17k** was obtained. Purification by chromatography (0-5% MeOH-CH_2Cl_2) afforded diaminoalcohol **17k** (250 mg, 0.69 mmol, 75%) as a white foam. Compound **17k**: R_f = 0.27 (5% MeOH-CH_2Cl_2); $[\alpha]^{20}_D$ = +58.8 (*c* = 0.98); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, 2 H, 2 H, *J* = 8.2 Hz, Ar-H), 7.25-7.32 (m, 7 H, Ar-H), 5.00 (d, 1 H, *J* = 8.7 Hz, S-NH), 3.89 (d, 1 H, *J* = 12.9 Hz, CH_2Ph), 3.71 (d, 1 H, *J* = 12.8 Hz, CH_2Ph),

3.67 (dd, 1 H, *J* = 11.6, 6.0 Hz, H-1), 3.59 (dd, 1 H, *J* = 11.6, 3.6 Hz, H-1), 3.02 (m, 1 H, H-3), 2.64 (m, 1 H, H-2), 2.60 (br s, 2 H, Bn-NH, OH), 2.39 (s, 3 H, Me-Tol), 1.48 (m, 1 H, CH *i*Pr), 0.59 (d, 3 H, *J* = 6.7 Hz, Me *i*Pr), 0.51 (d, 3 H, *J* = 6.8 Hz, Me *i*Pr); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.6, 140.4, 140.1, 129.4 (2 C), 128.5 (2 C), 128.3 (2 C), 127.2, 125.9 (2 C), 62.5, 57.7, 56.5, 52.5, 31.4, 21.4, 19.3, 18.4; IR (film): ν = 3307, 2925, 1592, 1493, 1453, 1086, 1050, 811, 752, 699 cm^{-1}; MS (ES): m/z (%): 361 $[M+1]^+$ (100).

(+)-(2*S*,3*R*,S_S)-2-(Benzylamino)-2,4-dimethyl-3-(*p*-tolylsulfinylamino)pentan-1-ol, 17e. From a suspension of $LiAlH_4$ (311 mg, 8.20 mmol) in Et_2O and (821 mg, 2.05 mmol) of an 80:20 mixture of **9c** and its epimer at C^2, according to the general procedure (15 h), diaminoalcohol **17e** was obtained. Purification by chromatography (0-5% MeOH-CH_2Cl_2) afforded diaminoalcohol **17e** (483 mg, 1.29 mmol, 63%) as a white solid further recrystallized from Et_2O. This experiment is an additional proof of our structural assignment of **9c** and its epimer at C^2. Compound **17e**: R_f = 0.25 (5% EtOH-CH_2Cl_2); m.p. 128-131 ºC; $[\alpha]^{20}_D$ = +15.0 (*c* = 1.35); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.33 (m, 5 H, Ar-H), 7.25 (d, 2 H, *J* = 8.2 Hz, Ar-H), 4.67 (d, 1 H, *J* = 9.5 Hz, S-NH), 3.67 (s, 2 H, H-1), 3.59 (d, 1 H, *J* = 11.2 Hz, CH_2Ph), 3.45 (d, 1 H, *J* = 11.2 Hz, CH_2Ph), 3.25 (dd, 1H, *J* = 9.5, 1.9 Hz, H-3), 2.38 (s, 3 H, Me-Tol), 1.88 (dquint, 1 H, *J* = 6.8, 1.9 Hz, H-4), 1.16 (s, 3 H, Me), 0.77 (d, 3 H, *J* = 6.9 Hz, Me *i*Pr), 0.57

(d, 3 H, *J* = 6.9 Hz, Me *i*Pr); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.1, 141.6, 140.6, 129.5, 128.5 (2 C), 128.1 (2 C), 127.1, 125.6 (2 C), 64.8, 60.9, 60.6, 45.9, 26.8, 22.9, 21.4, 18.7, 18.6; IR (KBr): ν = 3430, 2945, 1464, 1091, 1069, 1040, 814, 747, 702 cm^{-1}; MS (ES): m/z (%):397 $[M+Na]^+$(52), 375 $[M+1]^+$ (100); elemental analysis calcd (%) $C_{21}H_{30}N_2O_2S$ (374.54): C 67.34, H 8.07, N 7.48, S 8.56; found: C 67.09, H 8.13, N 7.58, S 8.25.

(±)-(*2S*,*3R*)-2-Benzyl-2-benzylamino-3-phenyl-3-(*p*-tolylsulfonylamino)propan-1-ol, (±)-17d. From a suspension of 3 equiv of $LiAlH_4$ (11 mg, 0.300 mmol) in Et_2O and 10% THF and **12a** (53 mg, 0.100 mmol), according to the general procedure (2 h), diaminoalcohol **17d** was obtained. Purification by chromatography (15-75% Et_2O-hexane) afforded diaminoalcohol **17d** (38 mg, 0.076 mmol, 75%) as a white solid further recrystallized from Et_2O. Compound **17d**: R_f = 0.15 (50% Et_2O-hexane); m.p. 130-131 ºC; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.11-7.28 (m, 15 H, Ar-H), 6.95 (d, 2 H, *J* = 8.2 Hz, Ar-H), 6.30 (br s, 1 H, S-NH), 4.57 (s, 1 H, H-3), 3.78 (dd, 1 H, *J* = 9.9, 3.0 Hz, N-CH_2Ph), 3.61 (dd, 1 H, *J* = 9.9, 6.5 Hz, N-CH_2Ph), 3.49 (d, 1 H, *J* = 12.3 Hz, CH_2OH), 3.39 (d, 1 H, *J* = 12.3 Hz, CH_2OH), 3.02 (d, 1 H, *J* = 13.8 Hz, CH_2Ph), 2.46 (d, 1 H, *J* = 13.8 Hz, CH_2Ph), 2.26 (s, 3 H, Me-Tol), 2.09 (s, 1 H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.9, 140.2, 137.0, 130.5 (2 C), 129.1 (2 C), 128.6 (2 C), 128.5 (2 C), 128.4 (2 C), 128.2, 128.0 (2 C), 127.7 (2 C), 127.5, 127.1 (2 C), 126.8, 125.3, 62.9, 61.8, 60.7, 45.9, 39.5, 21.3; IR (KBr): ν =

3520, 3300, 3060, 3030, 2940, 1600, 1495, 1420, 1350, 1330, 1305, 1290, 1165, 1090, 1060, 1025, 930, 805, 760, 750, 740, 705, 680, 660 cm^{-1}. MS (ES): m/z (%): 501 $[M+1]^+$ (100); elemental analysis calcd (%) $C_{30}H_{32}N_2O_3S$ (500.66): C 71.96, H 6.45, N 5.60, S 6.40; found: C 72.21, H 6.70, N 5.89, S 6.21.

General Procedure for the Reaction between Sulfinylimidazolidines and $NaBH_4$/LiI. A round-bottomed flask was charged with anhydrous THF (2 mL/mmol of imidazolidine) and 2-3 equiv of LiI was added, followed by 2-3 equiv of $NaBH_4$. The resulting suspension was cooled to 0 °C and a solution of the corresponding imidazolidine in anhydrous THF (6 mL/mmol), was added dropwise and the reaction mixture was stirred at 0 °C (30 min) and at room temperature and monitored by TLC. When the reaction had reached completion, (2-3 h), the mixture was quenched with a 5% $NaHCO_3$ solution (2 mL/mmol) and diluted with CH_2Cl_2 (8 mL/mmol) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 times, 8 mL/mmol). The combined organic extracts were washed with a saturated NaCl solution (4 mL/mmol), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to give a crude product, which was purified by column chromatography on silica gel.

(–)-[(2*S*,4*S*,5*R*,S_S)-2,5-Diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]methanol, 15c, and [(2*R*,4*R*,5*S*,S_S)-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]methanol, 15c'. From LiI (128 mg, 0.96 mmol) in THF, with $NaBH_4$ (38 mg, 0.96 mmol) and a

77:23 mixture of **7a** and **8a** (200 mg, 0.48 mmol), according to the general procedure (2 h), a 77:23 mixture of alcohols **15c** and **15c'** (144 mg, 78%) was obtained after chromatography (80-100% Et_2O-CH_2Cl_2 then 2% EtOH-Et_2O) as a colorless oil. A pure sample of **15c** (55%) and enriched samples of **15c'** (10:90) were obtained by a second careful chromatography. When this reaction was carried out in refluxing THF, a 50:12:30:8 mixture of **15c**, **15c'** and *N*-benzyldiaminoalcohols **17f** and **17f'** was obtained. When **15c** was treated with $LiAlH_4$ in Et_2O at 0 °C complete conversion to **17f** was observed. Compound **15c**: R_f = 0.24 (75% EtOAc-hexane); R_f = 0.66 (3% EtOH-Et_2O); $[\alpha]^{20}_D$ = –63.9 (*c* = 0.23); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dm, 2 H, *J* = 7.4 Hz, Ar-H), 7.24-7.48 (m, 6 H, Ar-H), 6.84-7.00 (m, 4 H, Ar-H), 6.66 (dm, 2 H, *J* = 7.4 Hz, Ar-H), 5.94 (s, 1 H, H-2), 4.65 (d, 1 H, *J* = 5.5 Hz, H-5), 3.71-3.76 (m, 2 H, CH_2OH), 3.27 (q, 1 H, *J* = 5.6 Hz, H-4), 2.70 (br s, 2 H, NH, OH), 2.17 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.0, 141.1, 140.2, 138.9, 128.8 (4 C), 127.7 (2 C), 127.3 (2 C), 127.0, 126.8 (2 C), 126.2, 125.5 (2 C), 80.1, 69.1, 61.2, 58.6, 21.1; IR (CCl_4): ν = 3400, 3070, 3030, 2960, 1650, 1600, 1495, 1455, 1260, 1200, 1090, 1065, 1040, 1020, 950, 910, 870, 700 cm^{-1}; MS (ES): m/z (%): 807 $[2M+Na]^+$ (19), 393 $[M+1]^+$ (100). Compound **15c'** (partial data): R_f = 0.24 (75% EtOAc-hexane); R_f = 0.59 (3% EtOH-Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (s, 1 H, H-2), 4.92 (d, 1 H, *J* = 7.3 Hz, H-5), 2.23 (s, 3 H, Me-Tol).

(±)-[(2*S*,4*S*,5*R*,S_S)-5-*p*-Fluorophenyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]methanol, 15d and (±)-[(2*R*,4*R*,5*S*,S_S)-5-*p*-fluorophenyl-2-phenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]methanol, 15d'. From LiI (128 mg, 0.96 mmol) in THF, with $NaBH_4$ (38 mg, 0.96 mmol) and an 83:17 mixture of **7e** and **8e** (210 mg, 0.48 mmol), according to the general procedure (45 min), an 83:17 mixture of alcohols **15d** and **15d'** (139 mg, 71%) was obtained after chromatography (40:1 CH_2Cl_2-EtOH) as a white foam. Pure alcohol **15d** (78 mg, 40%) was obtained by recrystallization from 30% Et_2O-hexane. This reaction has been carried out using a mixture of **7e** and **8e** to avoid their tedious separation; this has lead to the partial characterization of **15d'**. Compound **15d**: R_f = 0.22 (30:1 CH_2Cl_2-EtOH); m.p. 120-121 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.37-7.51 (m, 3 H, Ar-H), 7.30 (m, 2 H, Ar-H), 6.90 (d, *J* = 7.8 Hz, 2 H, Ar-H), 6.54-6.64 (m, 4 H, Ar-H), 5.97 (s, 1 H, H-2), 4.69 (d, *J* = 6.2 Hz, 1 H, H-5), 3.79 (dd, *J* = 11.6, 1 H, 4.2 Hz, CH_2OH), 3.68 (dd, *J* = 11.6, 5.5 Hz, 1 H, CH_2OH), 3.20 (ap q, *J* = 5.7 Hz, 3 H, H-4, NH-3, OH), 2.21 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 161.4 (1 C, d, J_{ipso} = 244.9 Hz), 141.3, 140.4, 138.7, 137.6, 128.8 (4 C), 128.5 (2 C, d, J_m C-F = 8.0 Hz), 128.4, 127.1 (2 C), 125.5 (2 C), 114.4 (2 C, d, J_o C-F = 21.4 Hz), 80.2, 69.1, 60.6, 57.9, 21.1; IR (KBr): ν = 3309, 2924, 1603, 1509, 1450, 1221, 1086, 1040, 947, 826, 745, 528 cm^{-1}; MS(ES): m/z (%): 843 $[2M+Na]^+$ (9), 411 $[M+1]^+$ (100), 323 (27); elemental analysis calcd (%) $C_{23}H_{23}N_2O_2FS$ (410.55): C 67.28, H 5.66, N 6.82, S 7.81; found: C 66.90, H 5.60, N 6.76, S 7.77. Compound

21b' (partial data from an 83:17 mixture): R_f = 0.17 (30:1 CH_2Cl_2-EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79 (s, 1 H, H-2), 4.94 (d, *J* = 7.6 Hz, 1 H, H-5), 3.36 (m, 1 H, CH_2OH), 2.25 (s, 3 H, Me-Tol).

General Procedure for *p*-Nitrobenzoylation of Sulfinyl Imidazolidinyl Alcohols. To a cold (0 ºC) solution of 1 equiv of alcohol in CH_2Cl_2 (10-40 mL/mmol) was added Et_3N (4.4 equiv) followed by *p*-nitrobenzoyl chloride (2 equiv) and a catalytic amount of DMAP (2-3 crystals) and the reaction mixture was stirred at 0 ºC and monitored by TLC until starting material disappearance. Then, the reaction was quenched with a saturated solution of NaCl (4 mL/mmol), diluted with of CH_2Cl_2 (4 mL/mmol) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over Na_2SO_4 and concentrated under reduced pressure to give a crude product that was chromatographed to give the corresponding *p*-nitrobenzoate.

(+)-*p*-Nitrobenzoate of (+)-[(2*S*,4*S*,5*R*,S_S)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfinyl)-1,3-imidazolidin-4-yl]methanol, 15a'. From sulfinylimidazolidine **15a** (20 mg, 0.04 mmol), Et_3N (2.2 equiv, 9.4 mg, 13 µL, 0.09 mmol), DMAP (two crystals) and *p*-nitrobenzoyl chloride (2 equiv, 16 mg, 0.08 mmol) in 0.5 mL of CH_2Cl_2, following the general procedure (30 min), after chromatography (5-50% EtOAc-hexane), *p*-nitrobenzoate **15a'** (24 mg, 92%) was obtained as a white solid that was recrystallized from Et_2O to give pure **15a'** (20 mg,

76%). A second recrystallization from *i*PrOH gave suitable crystals for X-ray diffraction analysis. Compound **15a'**: R_f = 0.34 (30% EtOAc-hexane); m.p. 163-165 °C (Et_2O); $[\alpha]^{20}_D$ = +41.9 (*c* = 0.87); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.30 (d, 2 H, *J* = 8.9 Hz, Ar-H), 8.09 (d, 2 H, *J* = 8.9 Hz, Ar-H), 7.80-7.83 (m, 2 H, Ar-H), 7.44-7.56 (m, 3 H, Ar-H), 7.01-7.16 (m, 10 H, Ar-H), 6.90-6.94 (m, 1 H, Ar-H), 6.80 (d, 2 H, *J* = 8.2 Hz, Ar-H), 5.80 (s, 1 H, H-2), 4.88 (s, 1 H, H-5), 4.50 (d, 1 H, *J* = 11.2 Hz, CH_2OH), 4.36 (d, 1 H, *J* = 11.1 Hz, CH_2OH), 2.57 (br s, 1 H, NH-3), 2.40 (d, 1 H, *J* = 14.2 Hz, CH_2Ph), 2.20 (d, 1 H, *J* = 14.3 Hz, CH_2Ph), 2.16 (s, 3 H, Me-Tol); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.9, 150.6, 140.9, 140.2, 139.5, 138.7, 136.5, 135.5, 130.9, 130.7 (2 C), 129.9, 129.8 (2 C), 129.2 (2 C), 128.9, 128.8 (2 C), 128.6 (2 C), 128.3 (2 C), 128.2 (2 C), 127.9 (2 C), 127.7 (2 C), 126.8, 126.7, 125.3, 123.7 (2 C), 123.6, 66.4, 65.6, 62.5, 41.9, 21.1; IR (CCl_4): ν = 3350, 3120, 2935, 1735, 1600, 1530, 1450, 1350, 1270, 1120, 1090, 1070, 700, 610 cm^{-1}; elemental analysis calcd (%) $C_{37}H_{33}N_3O_5S$ (631.74): C 70.34, H 5.27, N 6.65, S 5.08; found: C 70.46, H 5.26, N 6.69, S 5.04.

(±)-*p*-Nitrobenzoate of (±)-[(2*S*,4*S*,5*R*)-4-benzyl-2,5-diphenyl-1-(*p*-tolylsulfonyl)-imidazolidin-4-yl]methanol, (±)-15f. From sulfonylimidazolidine **(±)-15b** (18 mg, 0.037 mmol), Et_3N (3.0 equiv, 22 mg, 30 μL, 0.22 mmol), DMAP (two crystals) and *p*-nitrobenzoyl chloride (2.7 equiv, 19 mg, 0.10 mmol) in 2 mL of CH_2Cl_2, following the general procedure (30 min), after chromatography (15-75% EtOAc-hexane), *p*-nitrobenzoate **(±)-15f** (16 mg, 68%) was obtained

as a white solid further recrystallized from 25% Et_2O-hexane. Compound **(±)-15f**: R_f = 0.29 (20% EtOAc-hexane); m.p. 127-128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, 2 H, *J* = 8.5 Hz, Ar-H), 8.18 (d, 2 H, *J* = 8.6 Hz, Ar-H), 7.68 (m, 2 H, Ar-H), 7.35-7.44 (m, 10 H, Ar-H), 6.95-7.09 (m, 5 H, Ar-H), 6.81 (m, 2 H, Ar-H), 5.66 (d, 1 H, *J* = 9.6 Hz, H-2), 5.05 (s, 1 H, H-5), 3.93 (d, 1 H, *J* = 11.4 Hz, CH_2OH), 3.55 (d, 1 H, *J* = 11.5 Hz, CH_2OH), 2.49 (d, 1 H, *J* = 14.2 Hz, CH_2Ph), 2.39 (d, 1 H, *J* = 9.6 Hz, NH-3), 2.27 (s, 3 H, Me-Tol), 2.09 (d, 1 H, *J* = 14.5 Hz, CH_2Ph); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.9, 139.0, 138.8, 135.5, 135.0, 134.8, 130.6 (2 C), 129.8(2 C), 129.3 (2 C), 129.0, 128.7 (2 C), 128.6 (2 C), 128.4 (2 C), 128.3 (2 C), 127.7 (2 C), 127.6 (2 C), 126.9, 123.9 (2 C), 123.5, 78.5, 69.3, 66.6, 65.8, 41.5, 21.5 quaternary carbons not detected due to lack of material; IR (CCl_4): ν = 3330, 3100, 3060, 3040, 2960, 2930, 2860, 1745, 1700, 1575, 1495, 1430, 1265, 1210, 1090, 1070, 1020, 960, 940, 700 cm^{-1}.

General Procedure for Desulfinylation and Solvolysis with TFA. To a solution of 1 equiv of substrate in MeOH (10-20 mL/mmol, in some cases of scarce solubility in MeOH, 10-20% of CH_2Cl_2 was employed) was added 5-10 equiv trifluoroacetic acid (TFA) and the reaction mixture was stirred at rt and monitored by TLC (this often required spotting from aliquots worked-up with saturated aqueous K_2CO_3). Upon completion (5-24 h), the solvent was removed in vacuo, the residue was diluted with CH_2Cl_2 (10 mL/mmol) and extracted with 15% aqueous HCl (2 x 10 mL/mmol), the combined aqueous layer was

cooled to 5 °C, and CH_2Cl_2 (10 mL/mmol) was added. The resulting biphasic solution was carefully neutralized with solid $NaHCO_3$, to pH 7.5-9, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL/mmol). The combined organic extracts were washed with water (4 mL/mmol) and brine (6 mL/mmol), dried (Na_2SO_4), concentrated and purified by column chromatography on silica gel. Alternatively, upon completion of the reaction, solid NaOH (ca. 7.5 mmol/mmol of starting material) was added and the mixture was stirred at rt (ca. 10 h), the solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2 and then 10-20% EtOH-CH_2Cl_2 and filtered through a short plug of silica gel.

(–)-(2*S*,3*R*)-2-Benzyl-2,3-diamino-3-phenyl-propan-1-ol, 18b. From sulfinamide **15a** (10 mg, 0.0207 mmol), with 5 equiv of TFA (8 µL, 11.8 mg, 0.103 mmol) in MeOH according to the general procedure (15 h), diaminoalcohol **18b** (5.3 mg, 95%) was obtained as a colorless oil after chromatography (0-65% MeOH-Et_2O). In the early experiments, isolation was carried out with EtOAc instead of CH_2Cl_2 and this resulted in the isolation of a monoacetylated diaminoalcohol, tentatively assigned as acetylated at N^2. Compound **18b**: R_f = 0.18 (30% MeOH-Et_2O); $[\alpha]^{20}_D$ = –6.9 (*c* = 0.43); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.25-7.38 (m, 8 H, Ar-H), 4.11 (s, 1 H, H-3), 3.43 (d, 1 H, *J* = 11.2 Hz, CH_2OH), 3.28 (d, 1 H, *J* = 11.1 Hz, CH_2OH), 3.10 (d, 1 H, *J* = 13.1, CH_2Ph), 2.57 (d, 1 H, *J* = 13.1 Hz, CH_2Ph), 2.10-2.30 (br s, 5 H, 2

NH_2, OH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.9, 136.5, 130.8 (2 C), 128.3 (2 C), 128.2 (2 C), 128.1 (2 C), 127.9, 126.7, 67.6, 63.7, 56.2, 41.4; IR (CCl_4): ν = 3350, 2930, 2850, 1590, 1490, 1450, 700 cm^{-1}; MS (EI): m/z (%): 256 (0.4), 209 (4), 195 (8), 165 (9), 151 (11), 150 (40), 133 (25), 106 (43), 91 (100), 77 (31), 69 (23), 57 (34), 55 (27). Partial data of monoacetylated diaminoalcohol: R_f = 0.30 (30% MeOH-EtOAc); ^1H NMR (200 MHz, $CDCl_3$): δ = 7.00-7.40 (m, 10 H, Ar-H), 4.40 (q, 1 H, *J* = 5.6 Hz, NH-COMe), 3.93 (s, 1 H, CH-NH), 3.73 (d, 1 H, *J* = 11.5 Hz, CH_2OH), 3.46 (d, 1 H, *J* = 11.5 Hz, CH_2OH), 2.57 (d, 1 H, *J* = 13.6 Hz, CH_2Ph), 2.33 (d, 1 H, *J* = 13.5 Hz, CH_2Ph), 1.85-2.30 (br s, 3 H, NH_2, OH), 1.36 (d, 3 H, *J* = 5.6 Hz, MeCO-NH).

(±)-(2*S*,3*R*)-2-Amino-2-benzyl-3-phenyl-3-(*p*-tolylsulfonylamino)propan-1-ol, (±)-18c. From sulfonyl imidazolidine **(±)-15b** (20 mg, 0.04 mmol), with 10 equiv of TFA (46 mg, 31 μL, 0.40 mmol) in MeOH according to the general procedure (24 h), diaminoalcohol **(±)-18c** (10 mg, 75%) was obtained after chromatography (0-10% EtOH-CH_2Cl_2) as a white solid that was recrystallized from 5% Et_2O-CH_2Cl_2. Compound **(±)-18c**: R_f = 0.26 (5% EtOH-CH_2Cl_2); m.p. 140-142 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 (dm, 2 H, *J* = 8.3 Hz, Ar-H), 7.18-7.27 (m, 3 H, Ar-H), 7.11-7.16 (m, 3 H, Ar-H), 7.05-7.09 (m, 4 H, Ar-H), 6.99 (dm, 2 H, *J* = 8.5 Hz, Ar-H), 5.88 (br d, 1 H, *J* = 8.4 Hz, NH), 4.42 (d, *J* = 8.4 Hz, 1 H, H-3), 3.57 (br d, 1 H, *J* = 11.1 Hz, CH_2OH), 3.09 (dd, 1 H, *J* = 11.1, 7.0 Hz, CH_2OH), 2.91 (d, 1 H, *J* = 13.3 Hz, CH_2Ph), 2.61 (br

t, 1 H, OH), 2.28 (s, 3 H, Me-Tol), 2.03 (d, 1 H, *J* = 13.4 Hz, CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0, 136.7, 136.4, 135.5, 130.8 (2 C), 129.1 (2 C), 128.4 (2 C), 128.3 (2 C), 128.1 (2 C), 127.5, 127.0 (2 C), 126.8, 62.8, 60.8, 49.5 (2 C), 40.0, 21.4; IR (KBr): ν = 3525, 3060, 2925, 2874, 1754, 1599, 1495, 1455, 1321, 1151, 1090, 1064, 921, 812, 761, 705 cm^{-1}; MS(ES): m/z (%): 411 $[M+1]^+$ (100%).

(±)-*p*-Nitrobenzoate of (2*S*,3*R*)-2-amino-2-benzyl-3-phenyl-3-(*p*-tolylsulfonylamino)propan-1-ol, (±)-18d. From sulfonyl imidazolidine **(±)-15f** (7 mg, 0.01 mmol), with 8 equiv of TFA (9 mg, 6 μL, 0.08 mmol) in MeOH according to the general procedure (48 h), diaminoalcohol **(±)-18d** (5.0 mg, 89%) was obtained after chromatography (50% CH_2Cl_2-hexane then Et_2O) as a white solid that was recrystallized from 10% Et_2O-hexane. Compound **(±)-18d**: R_f = 0.20 (CH_2Cl_2); m.p. 180-182 ºC; ^1H NMR (300 MHz, $CDCl_3$): δ = 8.32 (dm, *J* = 8.9 Hz, 2 H, Ar-H), 8.12 (dm, *J* = 9.0 Hz, 2 H, Ar-H), 7.40 (dm, *J* = 8.3 Hz, 2 H, Ar-H), 7.12-7.24 (m, 8 H, Ar-H), 6.93-7.00 (m, 4 H, Ar-H), 5.94 (d, *J* = 9.5 Hz, 1 H, NH), 4.54 (d, *J* = 6.7 Hz, 1 H, H-3), 4.22 (d, *J* = 11.2 Hz, 1 H, CH_2OH), 3.90 (d, *J* = 11.2 Hz, 1 H, CH_2OH), 2.78 (d, *J* = 13.6 Hz, 1 H, CH_2Ph), 2.38 (d, *J* = 13.7 Hz, 1 H, CH_2Ph), 2.25 (s, 3 H, Me-Tol), 1.06 (br s, 2 H, NH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.3, 150.0, 142.9, 140.2, 136.4, 135.1, 130.7 (2 C), 130.3 (2 C), 129.8, 129.1 (2 C), 128.6 (2 C), 128.5 (2 C), 128.3 (2 C), 128.0, 127.2, 127.0 (2 C), 123.7 (2 C), 66.5, 61.7, 57.2, 43.1, 21.4; IR (KBr): ν = 3370, 3270,

2930, 2860, 1750, 1600, 1530, 1495, 1455, 1390, 1310, 1210, 1160, 1095, 1015, 900, 820, 705, 660 cm^{-1}; elemental analysis calcd (%) $C_{30}H_{29}N_3O_6S$ (559.65): C 64.39, H 5.22, N 7.51, S 5.73; found: C 64.09, H 4.98, N 7.20, S 5.44.

(–)-(2*S*,3*R*)-3-Amino-2-(benzylamino)-2,4-dimethylpentan-1-ol, 18e. From sulfinyl diaminoalcohol **17e** (94 mg, 0.251 mmol), with 5 equiv of TFA (97 μL, 1.255 mmol) in MeOH according to the general procedure (rt, 17 h; reflux, 7 h adding other 3 equiv of TFA), diaminoalcohol **18e** (46 mg, 0.20 mmol, 80%) was obtained after chromatography (0-30% MeOH-CH_2Cl_2) as a colorless oil. Compound **18e**: R_f = 0.20 (20% MeOH-CH_2Cl_2); $[\alpha]^{20}_D$ = –3.9 (*c* = 0.90); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21-7.36 (m, 5 H, Ar-H), 3.73 (d, 1 H, *J* = 12.2 Hz, CH_2Ph), 3.68 (d, 1 H, *J* = 11.0 Hz, H-1), 3.65 (d, 1 H, *J* = 12.2 Hz, CH_2Ph), 3.48 (d, 1 H, *J* = 11.0 Hz, H-1), 2.63 (d, 1 H, *J* = 2.2 Hz, H-3), 2.47 (br s, 4 H, -NH_2, Bn-NH, OH), 2.03 (dsept, 1 H, *J* = 6.8, 2.2 Hz, CH *i*Pr), 1.01 (s, 3 H, Me), 0.95 (d, 3 H, *J* = 6.8 Hz, Me *i*Pr), 0.90 (d, 3 H, *J* = 6.8 Hz, Me *i*Pr); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.3, 128.3 (2 C), 128.2 (2 C), 126.7, 68.5, 63.3, 58.2, 46.1, 28.3, 22.6, 18.8, 16.2; IR (film): ν = 3338, 2932, 2859, 1450, 1060, 968, 733 cm^{-1}; MS (ES): m/z (%): 237 $[M+1]^+$ (100%); elemental analysis calcd (%) $C_{14}H_{24}N_2O$ (236.35): C 71.14, H 10.23, N 11.85; found: C 71.27, H 10.28, N 11.74.

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