Supporting Information for

Copper-Catalyzed *anti*-Stereocontrolled Ring-Opening of Azabicyclic Alkenes with Grignard Reagents

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General methods.

Melting points are taken in open-end capillary tubes on a Gallenkamp melting point apparatus. NMR spectra were recorded on a Bruker AC-200 [200 MHz (^1H), 50 MHz (^{13}C)] or AC-300 [300 MHz (^1H), 75 MHz (^{13}C)] at room temperature in CDCl_3 calibrated at 7.26 ppm (^1H) or 77.0 ppm (^{13}C). For fluoro containing compounds the observed list of peaks is given as the ^{13}C NMR data, except for those cases where the $J_{\text{F-C}}$ has been unequivocally determined. Mass spectra (MS) were determined at an ionizing voltage of 70 eV. All the reactions were carried out in anhydrous solvents and under argon atmosphere. 1,2-Dichloroethane (DCE), CH_2Cl_2 and toluene were dried and stored over microwave-activated 4Å molecular sieves. Flash column chromatography was performed using silica gel Merk-60 (230-400 mesh). All Grignard and organozinc reagents and copper salts were purchased from commercially available sources and used as received. CuTC was prepared according to the literature procedure.¹ The known azabicyclic substrates **2** and **5** were prepared according to literature procedures.²

***N*-(2'-Thiophenesulfonyl)pyrrole:** To a solution of NaH (0.7 g, 17.5 mmol) in DMF (7 mL) was added a solution of pyrrole (1.0 mL, 14.3 mmol) in DMF (5 mL) at 0 °C. The resulting suspension was stirred for 15 min at 0 °C and it was treated with a solution of 2-thiophenesulfonyl chloride (3.1 g, 17.2 mmol) in DMF (4 mL). The reaction mixture was allowed to warm to rt and stirred for further 2 h, then brine (10 mL) was added. The aqueous layer was extracted twice with diethyl ether and the combined organic layer was washed several times with water, dried (MgSO_4) and concentrated. The residue was purified by flash chromatography (*n*-hexane-EtOAc 10:1), to afford the product (2.6 g, 85% yield) as a white solid; mp= 101-102 °C. ^1H NMR (300 MHz): δ 7.66 (dd, J = 3.8,

¹ Alfred, G. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 2748-2749.

² (a) Lautens, M.; Fagnou, K.; Zunic, V. *Org. Lett.* **2002**, *4*, 3465-3468. (b) Carpino, L. A.; Barr, D. E. *J. Org. Chem.* **1966**, *31*, 764

1.2 Hz, 1H), 7.63 (dd, J = 5.0, 1.4 Hz, 1H), 7.19-7.17 (m, 2H), 7.06 (dd, J = 5.0, 3.8 Hz, 1H), 6.32-6.31 (m, 2H). ^{13}C NMR (75 MHz): δ 133.8, 133.4, 127.5, 120.7, 113.9. MS (EI+) m/z 213 (M^+ , 60), 147 (100), 99 (31), 57 (34).

***N*-(2'-Pyridylsulfonyl)pyrrole:** To a suspension of NaH (0.7 g, 17.5 mmol) in DMF (7 mL) was added a solution of pyrrole (1.0 mL, 14.3 mmol) in DMF (5 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and it was treated with a solution of 2-pyridylsulfonyl chloride³ (3.0 g, 17.2 mmol) in DMF (4 mL). The reaction mixture was allowed to warm to rt and it was stirred for further 2 h, then brine (10 mL) was added. The aqueous layer was extracted twice with ether and the combined organic layer was washed several times with water, dried (MgSO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography (*n*-hexane- CH_2Cl_2 1:1) to afford a white solid (2.5 g, 84% yield); mp= 106-107 °C. ^1H NMR (300 MHz): δ 8.66 (d, J = 4.6 Hz, 1H), 8.03 (dd, J = 7.9, 0.8 Hz, 1H), 7.91 (td, J = 7.9, 1.8 Hz, 1H), 7.50 (ddd, J = 7.7, 4.8, 1.2 Hz, 1H), 7.23 (t, J = 2.2 Hz, 2H), 6.31 (t, J = 2.4 Hz, 2H). ^{13}C NMR (75 MHz): δ 156.0, 150.4, 138.2, 127.5, 121.9, 121.5, 113.6. MS (EI+) m/z 208 (M^+ , 25), 144 (13), 117 (83), 78 (100).

Typical procedure for the Diels-Alder cycloaddition between benzyne and *N*-protected pyrrole: ***N*-(*tert*-Butoxycarbonyl)-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (1):**² To a solution of *N*-(*tert*-butoxycarbonyl) pyrrole (2.8 g, 17.8 mmol) in DME (7 mL) at 50 °C in a three-neck flask fitted with a reflux condenser and 2 addition funnels, was simultaneously and dropwise added a solution of anthranilic acid (2.4 g, 17.8 mmol) in DME (18 mL) and a solution of isoamyl nitrite (2.9 mL, 21.4 mmol) in DME (11 mL) separately. After the slow addition the reaction was stirred at 50 °C for 2 h. The mixture was concentrated and the residue was dissolved in diethyl ether and washed with saturated K_2CO_3 . The aqueous layer was extracted twice with diethyl ether and the combined organic layers were washed with brine. The combined organic layer was dried (MgSO_4) and concentrated. The residue was purified by column chromatography (*n*-hexane-EtOAc 20:1) affording **1** as a white solid (3.4 g, 79% yield); mp= 74-75 °C [mp(lit)^{2b}=72-73 °C]. ^1H NMR (200 MHz): δ 7.28-7.24 (m, 2H), 7.00-6.93 (m, 4H), 5.49 (bs, 2H), 1.38 (s, 9H).

³ Diltz, S.; Aguirre, G.; Ortega, F.; Walsh, P. *Tetrahedron: Asymmetry* **1997**, 21, 3559.

***N*-(2'-Thiophenesulfonyl)-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (3):**

Following the general procedure, the Diels-Alder cycloaddition between benzyne and *N*-(2'-thiophenesulfonyl)pyrrole gave **3** as a white solid. Yield: 60%; mp= 179-180 °C. ¹H NMR (300 MHz): δ 7.45 (dd, *J*= 5.0, 1.2 Hz, 1H), 7.23 (dd, *J*= 3.8, 1.4 Hz, 1H), 7.09 (dd, *J*= 5.3, 3.0 Hz, 2H), 6.89 (dd, *J*= 5.0, 3.6 Hz, 1H), 6.84 (dd, *J*= 5.0, 3.0 Hz, 2H), 6.76 (t, *J*= 1.6 Hz, 2H), 5.48 (t, *J*= 1.4 Hz, 2H). ¹³C NMR (75 MHz): δ 146.9, 141.4, 138.5, 133.3, 132.8, 127.7, 125.2, 121.2, 67.9.

***N*-(2'-Pyridylsulfonyl)-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (4):** Following the general procedure, the Diels-Alder cycloaddition of benzyne and *N*-(2'-pyridylsulfonyl)pyrrole gave **4** as a white solid. Yield: 51%; mp= 178-179 °C (decomp). ¹H NMR (300 MHz): δ 8.58 (dt, *J*= 4.8, 1.4 Hz, 1H), 7.75-7.69 (m, 2H), 7.39-7.29 (m, 1H), 7.09 (dd, *J*= 5.3, 3.0 Hz, 2H), 6.83 (t, *J*= 1.4 Hz, 2H), 6.80 (dd, *J*= 5.3, 3.0 Hz, 2H), 5.65 (t, *J*= 1.6 Hz, 2H). ¹³C NMR (75 MHz): δ 155.8, 149.9, 147.2, 142.5, 137.5, 126.1, 125.0, 123.4, 121.1, 67.9. MS (EI+) *m/z* 286 [M⁺-(2H), 1], 219 (100), 142 (46), 115 (75), 78 (58).

General procedure for the copper-catalyzed ring-opening of azabicyclic alkenes with Grignard reagents: To a solution of CuCN (1.8 mg, 0.02 mmol) and the corresponding azabenzobicyclic alkene (0.2 mmol) in anhydrous CH₂Cl₂ (2 mL), was slowly added at room temperature the Grignard reagent (1.5 equiv). The mixture was stirred at room temperature and it was monitored by TLC, then saturated aqueous NH₄Cl solution (2 mL) was added. The aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL) and the combined organic layer was dried (MgSO₄) and concentrated to dryness. The residue was purified by flash chromatography.

(1*S,2*R**)-2-Methyl-*N*-tosyl-1,2-dihydronaphthalen-1-amine (anti-7a).**

Chromatography: *n*-hexane-EtOAc 4:1. Yield: 10%. White solid; mp= 129-130 °C. ¹H NMR (300 MHz): δ 7.70 (d, *J*= 8.5 Hz, 2H), 7.28 (d, *J*= 9.1 Hz, 2H), 7.19 (td, *J*= 7.5, 1.2 Hz, 1H), 7.04-6.99 (m, 2H), 6.77 (d, *J*= 7.9 Hz, 1H), 6.43 (d, *J*= 9.8 Hz, 1H), 5.92 (dd, *J*= 9.7, 6.3 Hz, 1H), 4.68 (d, *J*= 8.1 Hz, 1H), 4.20 (dd, *J*= 8.1, 3.6 Hz, 1H), 2.69-2.62 (m, 1H), 2.44 (s, 3H), 0.89 (d, *J*= 7.3 Hz, 3H). MS (EI+) *m/z* 158 [M⁺-(SO₂Tol), 25], 142 (100), 91 (17).

(1*S,2*R**)-2-Methyl-*N*-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9a).** Chromatography: *n*-hexane-EtOAc 2:1. Yield: 89%. White solid; mp= 167-168 °C.

^1H NMR (300 MHz): δ 8.53 (d, J = 4.6 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.85 (td, J = 7.9, 1.6 Hz, 1H), 7.41 (ddd, J = 7.5, 4.6, 1.2 Hz, 1H), 7.13 (td, J = 7.5, 1.4 Hz, 1H), 6.99 (d, J = 6.7 Hz, 1H), 6.91 (td, J = 7.5, 1.2 Hz, 1H), 6.84 (d, J = 6.9 Hz, 1H), 6.44 (d, J = 9.5 Hz, 1H), 5.95 (dd, J = 9.5, 5.5 Hz, 1H), 5.31-5.28 (m, 1H), 4.41-4.37 (m, 1H), 2.78-2.67 (m, 1H), 0.91 (d, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz): δ 158.3, 149.9, 137.7, 132.1, 131.6, 131.4, 128.6, 128.5, 127.4, 126.4, 126.2, 126.1, 121.6, 57.7, 36.2, 16.7. MS (EI+) m/z 158 [M^+ -(SO_2Py), 21], 142 (100), 115 (10), 78 (12).

(1S*,2R*)-N-[(2'-Pyridyl)sulfonyl]-2-[(1'-trimethylsilyl)methyl]-1,2-dihydronaphthalen-1-amine (anti-**9b**). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 73%. White solid; mp= 126-127 °C. ^1H NMR (300 MHz): δ 8.51-8.49 (m, 1H), 7.93 (dt, J = 7.9, 1.0 Hz, 1H), 7.83 (td, J = 7.7, 1.6 Hz, 1H), 7.39 (ddd, J = 7.7, 4.6, 1.2 Hz, 1H), 7.13 (td, J = 7.3, 1.4 Hz, 1H), 6.99 (d, J = 6.5 Hz, 1H), 6.91 (td, J = 7.5, 1.4 Hz, 1H), 6.82 (d, J = 7.3 Hz, 1H), 6.41 (d, J = 7.7 Hz, 1H), 5.98 (ddd, J = 9.7, 5.9, 1.0 Hz, 1H), 5.36 (d, J = 8.5 Hz, 1H), 4.38 (d, J = 8.5 Hz, 1H), 2.74-2.66 (m, 1H), 0.54 (dd, J = 14.3, 5.9 Hz, 1H), 0.43 (dd, J = 14.3, 9.7 Hz, 1H), -0.02 (s, 9H). ^{13}C NMR (75 MHz): δ 158.4, 149.8, 137.6, 132.1, 132.0, 131.4, 129.0, 128.5, 127.3, 126.4, 126.1, 125.6, 121.6, 58.8, 37.6, 19.6, -0.8.

(1S*, 2R*)-2-Ethyl-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-**9c**). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 65%. White solid; mp= 117-118 °C. ^1H NMR (300 MHz): δ 8.52 (dq, J = 4.6, 1.0 Hz, 1H), 7.93 (dt, J = 7.9, 1.2 Hz, 1H), 7.84 (td, J = 7.7, 1.8 Hz, 1H), 7.40 (ddd, J = 7.5, 4.6, 1.2 Hz, 1H), 7.12 (td, J = 7.5, 1.6 Hz, 1H), 6.98 (dd, J = 7.5, 1.2 Hz, 1H), 6.90 (td, J = 7.5, 1.4 Hz, 1H), 6.84 (dd, J = 7.5, 1.0 Hz, 1H), 6.47 (d, J = 9.7 Hz, 1H), 6.00 (ddd, J = 9.7, 5.9, 1.2 Hz, 1H), 5.33 (d, J = 9.1 Hz, 1H), 4.47 (dd, J = 9.3, 3.0 Hz, 1H), 2.56-2.48 (m, 1H), 1.25 (pent, J = 7.3 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz): δ 158.4, 149.8, 137.6, 132.2, 131.6, 130.3, 128.7, 128.5, 127.4, 126.7, 126.4, 126.1, 121.6, 55.8, 42.9, 24.5, 11.6.

(1S*, 2R*)-2-Benzyl-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-**9d**). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 53%. White solid; mp= 112-113 °C. ^1H NMR (300 MHz): δ 8.51 (dq, J = 4.6, 0.8 Hz, 1H), 7.80-7.71 (m, 2H), 7.39 (ddd, J = 6.5, 4.6, 1.8 Hz, 1H), 7.29-7.16 (m, 4H), 7.06-6.97 (m, 4H), 6.86 (dd, J = 7.5, 0.6 Hz, 1H), 6.53 (d, J = 9.7 Hz, 1H), 5.90 (ddd, J = 9.7, 5.9, 1.2 Hz, 1H), 5.36 (d, J = 8.3 Hz, 1H), 4.34 (d, J = 8.3 Hz, 1H), 2.93-2.85 (m, 1H), 2.53 (dd, J = 13.3, 7.5 Hz, 1H), 2.38

(dd, J = 13.5, 8.5 Hz, 1H). ^{13}C NMR (75 MHz): δ 157.9, 149.8, 138.8, 137.6, 132.0, 131.1, 129.8, 129.0, 128.9, 128.7, 128.4, 127.7, 127.0, 126.6, 126.3, 126.1, 121.9, 55.0, 42.5, 37.3.

(1S*, 2R*)-2-Decyl-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9e). Chromatography: *n*-hexane-EtOAc 4:1. Yield: 74%. Colorless oil. ^1H NMR (300 MHz): δ 8.51 (dq, J = 4.6, 0.8 Hz, 1H), 7.93 (dt, J = 7.9, 1.0 Hz, 1H), 7.83 (td, J = 7.7, 1.8 Hz, 1H), 7.39 (ddd, J = 7.5, 4.6, 1.2 Hz, 1H), 7.12 (td, J = 7.3, 1.4 Hz, 1H), 6.97 (d, J = 7.5 Hz, 1H), 6.90 (td, J = 7.5, 1.4 Hz, 1H), 6.84 (dd, J = 7.5, 1.4 Hz, 1H), 6.46 (d, J = 9.7 Hz, 1H), 5.99 (ddd, J = 9.7, 5.9, 1.0 Hz, 1H), 5.35 (d, J = 8.7 Hz, 1H), 4.44 (d, J = 10.1 Hz, 1H), 2.61-2.55 (m, 1H), 1.32-1.12 (m, 18H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz): δ 158.4, 149.8, 137.6, 132.1, 131.6, 130.6, 128.8, 128.5, 127.4, 126.5, 126.4, 126.1, 121.6, 56.1, 41.2, 31.9, 31.5, 29.6, 29.4, 29.3, 27.2, 22.7, 14.1. MS (EI+) m/z 284 [M^+ -(SO₂Py), 35], 268 (100), 141 (71), 79 (25).

(1S*, 2S*)-2-Phenyl-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9f). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 93%. White solid; mp = 136-137 °C. ^1H NMR (300 MHz): δ 8.58-8.56 (m, 1H), 7.96-7.93 (m, 1H), 7.85 (td, J = 7.7, 1.6 Hz, 1H), 7.43 (ddd, J = 7.7, 4.8, 1.2 Hz, 1H), 7.19-7.04 (m, 7H), 6.95 (td, J = 7.5, 1.4 Hz, 1H), 6.78-6.73 (m, 2H), 6.04 (ddd, J = 9.5, 5.5, 0.8 Hz, 1H), 5.41 (d, J = 7.9 Hz, 1H), 4.69 (dd, J = 8.3, 2.6 Hz, 1H), 4.01 (dd, J = 5.7, 2.8 Hz, 1H). ^{13}C NMR (75 MHz): δ 158.2, 149.9, 138.6, 137.8, 132.6, 131.2, 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 127.1, 126.5, 126.3, 121.7, 58.4, 47.7. MS (EI+) m/z 220 [M^+ -(SO₂Py), 50], 204 (100), 115 (12), 91 (13), 78 (13).

(1S*, 2S*)-2-(*p*-Tolyl)-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9g). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 91%. White solid; mp = 183-184 °C. ^1H NMR (300 MHz): δ 8.57 (dq, J = 4.8, 1.0 Hz, 1H), 7.94 (dt, J = 7.9, 1.0 Hz, 1H), 7.84 (td, J = 7.7, 1.6 Hz, 1H), 7.43 (ddd, J = 7.5, 4.6, 1.2 Hz, 1H), 7.18 (td, J = 7.5, 1.4 Hz, 1H), 7.10 (dd, J = 7.5, 1.4 Hz, 1H), 6.97-6.91 (m, 5H), 6.77-6.71 (m, 2H), 6.03 (ddd, J = 9.5, 5.5, 1.0 Hz, 1H), 5.30 (d, J = 8.1 Hz, 1H), 4.65 (dd, J = 8.1, 3.0 Hz, 1H), 3.96 (ddd, J = 5.5, 2.8, 1.0 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (75 MHz): δ 158.2, 149.9, 137.7, 136.7, 135.4, 132.6, 131.3, 129.2, 128.8, 128.6, 127.9, 127.8, 126.5, 126.3, 121.8, 58.5, 47.3, 20.9. MS (EI+) m/z 234 [M^+ -(SO₂Py), 38], 218 (100), 202 (11), 78 (13).

(1S*, 2S*)-2-(*p*-Methoxyphenyl)-*N*-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9h). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 98%. White solid; mp= 160-161 °C. ¹H NMR (300 MHz): δ 8.56 (dq, *J*= 4.6, 1.0 Hz, 1H), 7.93 (dt, *J*= 7.9, 1.0 Hz, 1H), 7.84 (td, *J*= 7.7, 1.6 Hz, 1H), 7.43 (ddd, *J*= 7.5, 4.6, 1.2 Hz, 1H), 7.18 (td, *J*= 7.5, 1.2 Hz, 1H), 7.10 (dd, *J*= 7.5, 1.4 Hz, 1H), 6.98-6.92 (m, 3H), 6.77 (dd, *J*= 7.5, 0.6 Hz, 1H), 6.72 (d, *J*= 9.5 Hz, 1H), 6.68-6.64 (m, 2H), 6.03 (ddd, *J*= 9.5, 5.4, 1.0 Hz, 1H), 5.36 (d, *J*= 8.5 Hz, 1H), 4.64 (dd, *J*= 8.1, 2.8 Hz, 1H), 3.96-3.93 (m, 1H), 3.70 (s, 3H). ¹³C NMR (75 MHz): δ 158.6, 158.2, 149.9, 137.7, 132.6, 131.3, 130.5, 129.0, 128.8, 128.7, 127.9, 127.8, 126.5, 126.3, 121.7, 114.0, 113.9, 58.6, 55.1, 46.9. MS (EI+) *m/z* 250 [*M*⁺-(SO₂Py), 33], 234 (100), 219 (13), 78 (11).

(1S*, 2S*)-2-(*p*-Fluorophenyl)-*N*-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9i). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 92%. White solid; mp= 183-184 °C. ¹H NMR (300 MHz): δ 8.54-8.52 (m, 1H), 7.89 (dt, *J*= 7.9, 1.0 Hz, 1H), 7.82 (td, *J*= 7.7, 1.8 Hz, 1H), 7.41 (ddd, *J*= 7.5, 4.6, 1.2 Hz, 1H), 7.17 (td, *J*= 7.5, 1.4 Hz, 1H), 7.08 (dd, *J*= 7.3, 1.2 Hz, 1H), 7.02-6.97 (m, 2H), 6.93 (dd, *J*= 7.5, 1.4 Hz, 1H), 6.80-6.73 (m, 3H), 6.70 (d, *J*= 9.7 Hz, 1H), 5.99 (ddd, *J*= 9.5, 4.8, 1.2 Hz, 1H), 5.34 (d, *J*= 8.3 Hz, 1H), 4.62 (dd, *J*= 8.3, 3.2 Hz, 1H), 3.99-3.96 (m, 1H). ¹³C NMR (75 MHz): δ 161.9 (d, *J*_{C-F}= 244.0 Hz), 158.2, 149.9, 137.7, 134.3 (d, *J*_{C-F}= 3.0 Hz), 132.5, 131.1, 129.6 (d, *J*_{C-F}= 8.4 Hz), 128.9, 128.7, 128.3, 128.2, 128.1, 126.6, 126.4, 121.7, 115.3 (d, *J*_{C-F}= 20.9 Hz), 58.6, 46.9. MS (EI+) *m/z* 238 [*M*⁺-(SO₂Py), 52], 222 (100), 109 (13), 78 (15).

(1S*, 2S*)-2-[3',5'-Bis(trifluoromethyl)phenyl]-*N*-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-9j). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 97%. White solid; mp= 218-219 °C. ¹H NMR (300 MHz): δ 8.61 (d, *J*= 4.9 Hz, 1H), 7.98 (d, *J*= 7.7 Hz, 1H), 7.90 (td, *J*= 7.5, 1.6 Hz, 1H), 7.67 (s, 1H), 7.57 (s, 2H), 7.49 (ddd, *J*= 7.5, 4.6, 1.2 Hz, 1H), 7.29 (td, *J*= 7.1, 1.0 Hz, 1H), 7.21 (d, *J*= 6.5 Hz, 1H), 7.09 (dt, *J*= 7.5, 1.4 Hz, 1H), 6.93 (d, *J*= 7.1 Hz, 1H), 6.88 (d, *J*= 9.5 Hz, 1H), 6.04 (dd, *J*= 9.7, 5.3 Hz, 1H), 5.51 (d, *J*= 7.9 Hz, 1H), 4.75 (dd, *J*= 7.9, 3.4 Hz, 1H), 4.22 (t, *J*= 4.4 Hz, 1H). ¹³C NMR (75 MHz): δ 158.1, 150.0, 141.8, 138.0, 132.1, 131.8 (q, *J*_{C-F}= 33.0 Hz), 130.4, 129.7, 129.4, 128.8, 128.7, 128.4 (m), 126.9, 126.6, 126.4, 124.9, 121.7, 121.3 (m), 58.2, 47.1. MS (EI+) *m/z* 356 [*M*⁺-(SO₂Py), 46], 340 (100), 79 (17).

(1S*, 2S*)-2-(1'-Naphthyl)-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-**9k**). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 91%. White solid; mp= 132-133 °C. ¹H NMR (300 MHz): δ 8.46-8.41 (m, 2H), 7.87 (dt, *J*= 7.7, 1.0 Hz, 1H), 7.82 (dd, *J*= 7.8, 1.2 Hz, 1H), 7.75 (td, *J*= 7.7, 1.6 Hz, 1H), 7.64-7.58 (m, 2H), 7.53-7.48 (m, 1H), 7.35 (ddd, *J*= 7.7, 4.6, 1.2 Hz, 1H), 7.20-7.11 (m, 3H), 7.05 (dd, *J*= 7.3, 1.4 Hz, 1H), 6.89-6.83 (m, 2H), 6.57 (d, *J*= 7.3 Hz, 1H), 6.13 (dd, *J*= 9.5, 6.5 Hz, 1H), 5.58 (d, *J*= 8.1 Hz, 1H), 4.86-4.81 (m, 2H). ¹³C NMR (75 MHz): δ 157.9, 149.8, 137.5, 134.2, 132.8, 132.3, 131.9, 131.5, 129.0, 128.9, 128.7, 128.6, 128.5, 127.9, 127.8, 126.7, 126.5, 126.2, 125.6, 125.3, 125.1, 123.6, 121.7, 57.1, 43.3. MS (EI+) *m/z* 270 [M⁺-(SO₂Py), 27], 254 (100), 253 (56), 126 (13), 78 (15).

(1S*, 2S*)-2-(2',4',6'-Trimethylphenyl)-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (anti-**9l**). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 87%. White solid; mp= 152-153 °C. ¹H NMR (300 MHz): δ 8.44 (d, *J*= 4.2 Hz, 1H), 7.67 (d, *J*= 6.1 Hz, 1H), 7.57 (td, *J*= 7.9, 1.6 Hz, 1H), 7.38 (d, *J*= 7.7 Hz, 1H), 7.32-7.25 (m, 3H), 7.11-7.08 (m, 1H), 6.48-6.44 (m, 3H), 5.76 (dd, *J*= 9.7, 2.4 Hz, 1H), 5.47 (dd, *J*= 13.7, 9.5 Hz, 1H), 5.00 (d, *J*= 9.7 Hz, 1H), 4.23 (dt, *J*= 13.9, 2.6 Hz, 1H), 2.22 (s, 6H), 2.13 (s, 3H). ¹³C NMR (75 MHz): δ 157.7, 149.6, 137.3, 137.2, 137.0, 135.7, 134.1, 133.6, 131.9, 130.0, 128.2, 128.1, 126.8, 126.5, 125.9, 125.4, 120.1, 57.4, 43.2, 21.8, 20.7. MS (EI+) *m/z* 262 [M⁺-(SO₂Py), 61], 246 (100), 231 (33), 78 (21).

(1S*, 2R*)-N-[(2'-Pyridyl)sulfonyl]-2-(2'-thienyl)-1,2-dihydronaphthalen-1-amine (anti-**9m**). Chromatography: *n*-hexane-EtOAc 2:1. Yield: 88%. White solid; mp= 153-154 °C. ¹H NMR (300 MHz): δ 8.59-8.56 (m, 1H), 7.98 (d, *J*= 6.9 Hz, 1H), 7.89 (td, *J*= 7.7, 1.8 Hz, 1H), 7.44 (ddd, *J*= 7.7, 4.8, 1.2 Hz, 1H), 7.20 (td, *J*= 7.5, 1.2 Hz, 1H), 7.10 (d, *J*= 6.3 Hz, 1H), 7.01-6.95 (m, 2H), 6.83-6.73 (m, 3H), 6.67 (d, *J*= 9.7 Hz, 1H), 6.11 (ddd, *J*= 9.5, 5.9, 1.0 Hz, 1H), 5.46 (d, *J*= 8.3 Hz, 1H), 4.75 (dd, *J*= 8.1, 2.2 Hz, 1H), 4.26 (dd, *J*= 5.6, 2.4 Hz, 1H). ¹³C NMR (75 MHz): δ 158.1, 149.9, 141.8, 137.8, 132.0, 131.1, 129.0, 128.9, 128.1, 128.0, 127.8, 126.7, 126.6, 126.4, 125.2, 124.2, 121.8, 58.3, 42.4. MS (EI+) *m/z* 226 [M⁺-(SO₂Py), 37], 210 (100), 142 (11), 78 (12).

(1S*, 2S*)-2-Ethyl-N-[(2'-pyridyl)sulfonyl]-1,2-dihydronaphthalen-1-amine (syn-**9c**). To a solution of **4** (58 mg, 0.2 mmol) and Cu(OTf)₂ (7.2 mg, 0.02 mmol) in DCE (3 mL), heated at reflux, was added a 1.0M solution of Et₂Zn in hexanes (400 μL, 0.4 mmol). The reaction mixture was stirred at reflux for 48 h, then H₂O (0.5 mL) was

added and the mixture was stirred at rt for further 45 min. EtOAc (5 mL) was added, the aqueous layer was extracted with EtOAc (2 x 5 mL) and the combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (*n*-hexane-EtOAc 2:1), to afford syn-**9c** (7.7 mg, 12%) as a colorless oil. ^1H NMR (300 MHz): δ 8.36 (dq, J = 4.6, 1.0 Hz, 1H), 7.90 (dt, J = 7.9, 1.2 Hz, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.33 (ddd, J = 7.7, 4.6, 1.2 Hz, 1H), 7.06 (td, J = 6.7, 2.0 Hz, 1H), 6.97 (d, J = 7.3 Hz, 1H), 6.77 (dd, J = 7.5, 1.4 Hz, 1H), 6.73-6.70 (m, 1H), 6.51 (dd, J = 9.7, 2.8 Hz, 1H), 5.81 (dd, J = 9.7, 2.8 Hz, 1H), 5.37 (d, J = 9.7 Hz, 1H), 4.51 (dd, J = 10.1, 4.8 Hz, 1H), 2.46-2.38 (m, 1H), 1.82 (sept, J = 7.5 Hz, 1H), 1.61 (sept, J = 7.5 Hz, 1H), 1.03 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz): δ 158.2, 149.7, 137.4, 133.7, 132.6, 130.9, 128.1, 127.8, 126.9, 126.7, 126.4, 125.9, 121.5, 54.9, 41.1, 22.5, 11.4.

General procedure for the *N*-deprotection of the (2-pyridyl)sulfonyl group: A solution of the corresponding compound **9** (0.5 mmol) in a 1:2 mixture of THF/anhydrous methanol (4 mL) was added to Mg power (122.0 mg, 5 mmol) at 0 °C. The reaction mixture was stirred for 2 h, equal volumes of diethyl ether and saturated aq NH_4Cl were added and it was stirred for 2 h. The aqueous layer was extracted with diethyl ether (2 x 10 mL) and the combined organic layers were dried (MgSO_4) and concentrated to dryness to give the pure amine.

(1*S, 2*S**)-(2-Phenyl-1,2-dihydronaphthalen-1-yl) carbamic acid *tert*-butyl ester (anti-**6f**).** Following the above general procedure, compound anti-**9f** (70 mg, 0.19 mmol) was transformed into the corresponding free amine which, without further purification was subsequently dissolved in CH_2Cl_2 (2 mL) and treated with di-*tert*-butylcarbonate (0.6 mmol). The mixture was stirred at rt overnight and concentrated in vacuo. The residue was purified by flash chromatography (*n*-hexane-EtOAc 5:1) to afford anti-**6f** (52 mg, 83%) as a white solid; mp= 121-122 °C. ^1H NMR (300 MHz): δ 7.21-7.14 (m, 9H), 6.71 (d, J = 9.5 Hz, 1H), 6.06 (dd, J = 9.1, 4.2 Hz, 1H), 4.91-4.85 (m, 2H), 3.86 (bs, 1H), 1.41 (s, 9H). ^{13}C NMR (75 MHz): δ 155.0, 132.9, 129.5, 128.4, 128.2, 128.1, 127.9, 126.8, 126.4, 79.4, 55.0, 47.5, 28.4.

(1*S, 2*S**)-2-(*p*-Methoxyphenyl)-1,2-dihydronaphthalen-1-amine (**11**).** Following the general procedure, anti-**9h** (140 mg, 0.36 mmol) was deprotected to afford **11** (68 mg, 86%) as a colorless oil after chromatographic purification (EtOAc-MeOH 9:1). ^1H NMR (300 MHz): δ 7.41-7.38 (m, 1H), 7.32-7.25 (m, 2H), 7.22-7.17 (m, 3H), 6.90-

6.85 (m, 2H), 6.67 (dd, J = 9.5, 1.8 Hz, 1H), 6.05 (dd, J = 9.7, 4.0 Hz, 1H), 4.06 (d, J = 7.7 Hz, 1H), 3.83 (s, 3H), 3.60-3.55 (m, 1H), 1.71 (bs, 2H). ^{13}C NMR (75 MHz): δ 158.5, 138.0, 134.0, 132.5, 130.7, 129.1, 127.9, 127.4, 127.3, 126.3, 126.0, 114.0, 56.4, 55.2, 49.9.

(1*S, 2*S**)-2-(*p*-Methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-amine (anti-**12**).⁴**

A suspension of **11** (50 mg, 0.20 mmol) and Pd(C) (0.02 mmol) in dry methanol (2 mL) was stirred at room temperature under hydrogen (1 atm) overnight. The mixture was filtered through Celite[®] and the filtrate was concentrated to dryness. The residue was purified by flash chromatography (EtOAc-MeOH 9:1) to afford **12** (45.5 mg, 90%) as a yellow solid; mp= 62-63 °C. ^1H NMR (300 MHz): δ 7.68 (d, J = 7.1 Hz, 1H), 7.28-7.14 (m, 5H), 6.93 (d, J = 8.7 Hz, 2H), 4.06 (d, J = 9.7 Hz, 1H), 3.84 (s, 3H), 3.08-2.97 (m, 1H), 2.90 (dt, J = 16.8, 4.0 Hz, 1H), 2.68-2.60 (m, 1H), 2.10-2.03 (m, 2H), 1.47 (bs, 2H).

⁴ Vaccaro, W.; Amore, C.; Berger, J.; Burrier, R.; Clader, J.; Davis, H.; Domalski, M.; Fevig, T.; Salisbury, B.; Sher, R. *J. Med. Chem.* **1996**, 39, 1704-1719.