Supporting Information
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General procedure for the synthesis of binaphthalene-derived azepines from (S)-2,2′bis(bromomethyl)-[1,1′]binaphthalene and primary amines.

The primary amine (1.1 eq) was added to a nitrogen purged, stirred solution of (S)-2,2′-bis(bromomethyl)-[1,1′]binaphthalene (1.0 eq) and potassium carbonate (3.0 eq) in acetonitrile (10 mL per gram of dibromide) at room temperature. The reaction mixture was heated to reflux and stirred overnight or until the disappearance of starting material was seen by TLC. The mixture was cooled to room temperature and diluted with dichloromethane (40 mL per gram of dibromide) then washed with water (2 x 30 mL per gram of dibromide) and brine (2 x 30 mL per gram of dibromide). The organic phase was separated, dried (MgSO₄) and the solvent was removed in vacuo to give the desired crude products which were then purified as necessary.

(S)-N-Methyl-2,7-dihydrodinaphtho[2,1-c;1′,2′-e]azepine 1

Prepared according to the general procedure from methylamine (2M solution in THF, 856 μL, 1.5 mmol). The crude product was purified by column chromatography (4:1 petrol:EtOAc) and gave the title compound 1 as a colourless solid (300 mg, 85%), mp 168-170 °C; [α]$_{D}^{20}$ +561.6° (c. 1.00, CHCl₃); ν$_{max}$ (DCM) /cm$^{-1}$ 3046, 2936, 2784, 1462, 1366, 1248, 1099, 1018, 819, 752; δ$_{H}$ (400 MHz, CDCl₃) δ 2.42 (3H, s), 3.24 (d, 2H, J = 12 Hz), 3.62 (d, 2H, J = 12 Hz), 7.25-7.29 (m, 2H), 7.44-7.48 (m, 4H), 7.57 (d, 2H, J = 8 Hz), 7.94-7.97 (m, 4H); δ$_{C}$ (100 MHz, CDCl₃) 43.1, 57.2, 125.4, 125.7, 127.4, 127.7, 128.30, 128.33, 131.4, 133.1, 133.2, 134.8; HRMS (Cl+): calc. for C$_{23}$H$_{19}$N (MH$^+$) 309.15175, found: 309.15125.
\((S)-N-2-(1\text{-Hydroxyethyl})-(S)-2,7\text{-dihydrodinaphtho}[2,1-c;1',2'-e]azepine\ 3\)

Prepared according to the general procedure from 2-aminoethanol (62 μL, 1.03 mmol). The title compound 3 was isolated as a colourless foam (215 mg, 0.88 mmol, 94%), \([\alpha]^{20}\text{D} +328.4^\circ\) (c. 1.00, CHCl₃); \(v_{\text{max}}\) (DCM) /\(\text{cm}^{-1}\) 3385, 3049, 2936, 1507, 1461, 1048, 818, 751; \(\delta_H\) (400 MHz, CDCl₃) 2.52-2.58 (m, 1H), 2.85-2.90 (m, 1H), 3.26 (d, 2H, \(J = 12\) Hz), 3.68 (2H, d, \(J = 12\) Hz), 3.71-3.79 (m, 2H), 7.26-7.30 (m, 2H), 7.42-7.49 (m, 4H), 7.53 (m, 4H), 7.95-7.97 (m, 4H), \(\delta_H\) (100 MHz, CDCl₃) \(\delta\) 55.2, 58.5, 125.5, 125.8, 127.4, 127.6, 128.3, 128.5, 131.4, 133.2, 135.0; HRMS (Cl⁺): calc. for \(C_{24}H_{22}NO\) (MH⁺) 340.1701, found: 340.1704

\((S,S)-1,2\text{-Di}[3H\text{-naphtho}[7,6,1,2-cde]azepin-4\text{-yl}]\text{ethane}\ 4\)

Prepared according to the general procedure from ethane-1,2-diamine (38 μL, 0.57 mmol, 0.51 eq.). The crude product was purified by column chromatography (4:1 petrol:EtOAc) and gave the title compound 4 as a colourless solid (338 mg, 0.55 mmol, 96%), \([\alpha]^{20}\text{D} +251.9^\circ\) (c. 1.08, CHCl₃); \(v_{\text{max}}\) (DCM) /\(\text{cm}^{-1}\) 3049, 2947, 2811, 1507, 1462, 1365, 1096, 1027, 818, 751; \(\delta_H\) (400 MHz, CDCl₃) 2.63-2.68 (m, 2H), 2.94-2.99 (m, 2H), 3.25 (d, 4H, \(J = 12\) Hz), 3.75 (d, 4H, \(J = 12\) Hz), 7.25-7.29 (m, 4H), 7.43-7.49 (m, 8H), 7.61 (d, 4H, \(J = 8\) Hz), 7.95-7.99 (m, 8H); \(\delta_C\) (100 MHz, CDCl₃) 54.0, 55.9, 125.4, 125.8, 127.5, 127.8, 128.3, 128.35, 133.2, 133.4, 135.0.
(S)-N-Isopropyl-2,7-dihydro-dinaphtho[2,1-c;1',2'-e]azepine 5

Prepared according to the general procedure using isopropylamine (0.15 g, 2.27 mmol, 1.1 eq.). Trituration of the crude product in acetone (5 mL) gave the analytically pure title compound 5 as colourless powder (0.65 g, 1.92 mmol, 85%), m.p. 159-160 °C, [α]D20 +336.4 (c 1.00, acetone), \( \nu_{\text{max}}(\text{solid})/\text{cm}^{-1} \) 3044, 2965, 2802, 1590, 1505, 1459, 1372, 1348, 1238, 1158, \( \delta_\text{H} \) (400 MHz; CDCl3) 1.15 (3H, d, J = 6 Hz), 1.29 (3H, d, J = 6 Hz), 2.76 (1H, septet, J = 6 Hz), 3.26 (2H, d, J = 12 Hz), 3.93 (2H, d, J = 12 Hz), 7.24-7.28 (2H, m), 7.44-7.48 (4H, m), 7.59 (2H, d, J = 8 Hz), 7.94 (4H, d, J = 8 Hz), \( \delta_\text{C} \) (75 MHz; CDCl3) 19.4, 20.0, 50.4, 51.0, 123.5, 124.0, 125.7, 126.2, 126.4, 126.5, 129.6, 131.3, 132.6, 133.2, HRMS (Cl+): calc. for C25H23N (MH+) 337.1831, found 337.1826.

(S)-3-Phenyl-2,2'-dimethyl-1,1'-binaphthalene 12

(S)-2,2'-bis[(Trifluoromethanesulfonyl)oxy]-3'-phenyl-1,1'-binaphthalene (390 mg, 0.62 mmol) and 1,3-bis(diphenylphosphino)propane nickel (II) chloride (25 mg, 0.05 mmol) were dissolved in diethyl ether (10 mL) and the solution was cooled to -30 °C. A solution of methylmagnesium bromide (3 M in Et2O, 0.83 mL, 1.36 mmol) was then added dropwise. The reaction was allowed to reach room temperature and stirred overnight. The dark/green mixture was diluted with diethyl ether (10 mL) and filtered through pad of celite. The filtrate was washed with 35% aq. hydrochloric acid (1 x 2 mL), water (5 mL) and brine (5 mL), and dried (Na2SO4). The solvent was removed under reduced pressure to afford a colourless oil. The product was purified by column chromatography on silica gel (light petroleum) to afford the title compound 12 (120 mg, 54%) as
a colourless solid, [α]_{D}^{26} = -77.2° (c. 0.98, CHCl₃); ν_{max} (DCM) / cm⁻¹ 2922, 1493, 1422, 1216, 748; δ_H (400 MHz, CDCl₃) 1.90 (s, 3H), 2.08 (s, 3H), 7.01 (d, 1H, J = 9 Hz), 7.13-7.25 (m, 3H), 7.34-7.49 (m, 7H), 7.52 (d, 1H, J = 8 Hz), 7.84 (1H, s), 7.88 (d, 2H, J = 8 Hz), 7.90 (d, 1H, J = 8 Hz); δ_C (100 MHz, CDCl₃) 18.3, 20.3, 125.1, 125.5, 125.9, 126.2, 126.3, 127.1, 127.2, 127.6, 128.1, 128.2, 128.3, 128.4, 129.4, 129.7, 131.7, 132.2, 132.8, 132.9, 134.5, 134.8, 135.6, 135.8, 136.2, 136.7; MS (EI+) m/z 358 ([M]+), 343, 265, 215, 163, 77; HRMS (Cl+): calc. for C_{28}H_{32} (MH⁺) 358.1716, found: 358.1719.

(S)-3-[(Naphthalen-1-yl)-2,2'-dimethyl-1,1'-binaphthalene 13

(S)-2,2'-bis[(Trifluoromethanesulfonyl)oxy]-3-[(naphthalene-1-yl)-1,1'-binaphthalene (1.5 g, 2.4 mmol) and 1,3-bis(diphenylphosphino)propane nickel (II) chloride (645 mg, 0.12 mmol) were dissolved in diethyl ether (50 mL) and the solution was cooled to −30 °C. A solution of methylmagnesium bromide (3 M in Et₂O, 2.4 mL, 7.2 mmol) was then added dropwise. The reaction was allowed to reach room temperature and stirred overnight. The dark/green mixture was diluted with diethyl ether (50 mL) and filtered through pad of celite. The filtrate was washed with 35% aq. hydrochloric acid (1 x 5 mL), water (20 mL) and brine (20 mL), and dried (Na₂SO₄). The solvent was removed under reduced pressure to afford an orange foam. The product was purified by column chromatography on silica gel (light petroleum/DCM 95:05) to afford the title compound 13 (430 mg, 44%) as a colourless solid, [α]_{D}^{26} = -79.6° (c. 1.02, CHCl₃); ν_{max} (DCM) / cm⁻¹ 3051, 2918, 1593, 1415, 1209, 1139, 905, 810, 778, 741; 2 conformations A and B were observed (the major conformation is represented by A); δ_H (400 MHz, CDCl₃) 1.67 (s, 3Hₐ + 3H₉), 2.12 (s, 3Hₐ), 2.20 (s, 3H₉), 7.10–7.13 (m, 1Hₐ + 1H₉), 7.18–7.36 (m, 3Hₐ + 3H₉), 7.37–7.64 (m, 8Hₐ + 8H₉), 7.88–7.95 (m, 6Hₐ + 6H₉), δ_C (100 MHz, CDCl₃) 17.8, 20.4, 124.8, 125.0, 125.1, 125.6, 125.62, 125.65, 125.7, 125.9, 125.95, 125.98, 126.0, 126.03, 126.2, 126.3,
126.35, 126.36, 126.4, 127.1, 127.66, 127.7, 127.82, 127.85, 128.11, 128.14, 128.2, 128.3, 128.4, 128.5, 128.9, 129.1; HRMS (Cl+): calc. for C_{32}H_{28} (MH+) 408.1873. Found: 408.1869.

(S)-3-Phenyl-2,2′-bis-bromomethyl-[1,1’]binaphthylene 14

(S)-3-Phenyl-2,2′-dimethyl-1,1′-binaphthylene (285 mg, 0.75 mmol) was dissolved in cyclohexane (15 mL). N-bromosuccinimide (297 mg, 1.6 mmol) and azobisisobutyronitrile (12 mg, 0.075 mmol) were then added. The mixture was stirred at room temperature for 3 hours. After cooling, water was added and the mixture was extracted with ethyl acetate (2 x 20 mL). The organic extracts were washed with brine and dried (Na2SO4). The solvent was removed under reduced pressure to afford a yellow foam. The product was purified by column chromatography on silica gel (light petroleum) to afford the title compound 14 (330 mg, 85%) as a colourless foam, [α]^{25}_D −158.8° (c. 1.02, CHCl₃); ν_max (DCM) /cm⁻¹ 3055, 1588, 1494, 1435, 1216, 1026, 751; δ_H (400 MHz, CDCl₃) 4.16 (d, 1H, J = 10 Hz), 4.25 (d, 1H, J = 10 Hz), 4.28 (d, 1H, J = 10 Hz), 4.39 (d, 1H, J = 10 Hz), 7.12 (d, 1H, J = 9 Hz), 7.13 (d, 1H, J = 8 Hz), 7.26-7.32 (m, 2H), 7.42-7.53 (m, 5H), 7.61-7.63 (m, 2H), 7.77 (d, 1H, J = 9 Hz), 7.90-7.94 (m, 3H), 8.03 (d, 1H, J = 9 Hz), δ_C (100 MHz, CDCl₃) 31.6, 33.5, 126.9, 126.95, 127.0, 127.1, 127.2, 127.5, 127.8, 128.05, 128.07, 128.1, 128.4, 129.6, 129.8, 130.5, 132.2, 132.6, 132.7, 133.3, 133.5, 134.3, 134.6, 136.2, 140.6, 141.0; HRMS (Cl+): calc. for C_{28}H_{29}^{79}Br₂ (MH+) 513.9930, found: 513.9926.
(S)-3-(Naphthalen-1-yl)-2,2'-bis-bromomethyl-[1,1']binaphthalene 15

(S)-3-(Naphthalen-1-yl)-2,2'-dimethyl-1,1'-binaphthalene (420 mg, 1.03 mmol) was dissolved in cyclohexane (30 mL). N-bromosuccinimide (384 mg, 1.1 mmol) and azobisisobutyronitrile (17 mg, 0.1 mmol) were then added. The mixture was stirred at room temperature for 3 hours. After cooling, water was added and the mixture was extracted with ethyl acetate. The organic extracts were washed with brine and dried (Na₂SO₄). The solvent was removed under reduced pressure to afford a yellow foam. The product was purified by column chromatography on silica gel (light petroleum/DCM 9:1) to afford the title compound (335 mg, 58%) as a colourless foam, [α]²⁵D −195.7° (c. 1.03, CHCl₃); νmax (DCM) /cm⁻¹ 3054, 2923, 1589, 1435, 1264, 820, 777, 751; δH (400 MHz, CDCl₃) 3.98 (d, 1H, J = 10 Hz), 4.14 (d, 1H, J = 10 Hz), 4.27 (d, 1H, J = 10 Hz), 4.43 (d, 1H, J = 10 Hz), 7.09 (d, 1H, J = 8 Hz), 7.22-7.26 (m, 3H), 7.39-7.41 (m, 1H), 7.47-7.53 (m, 3H), 7.58-7.62 (m, 2H), 7.70-7.74 (m, 2H), 7.90-8.00 (m, 6H); δC (100 MHz, CDCl₃) 31.3, 32.9, 125.4, 126.1, 126.4, 126.6, 126.7, 127.0, 127.1, 127.2, 127.4, 127.9, 128.1, 128.2, 128.25, 128.49, 128.52, 128.6, 129.7, 131.4, 132.5, 132.6, 133.4, 133.6, 133.66, 133.7, 134.1, 135.1, 138.5, 137.5, 139.3, 167.2; HRMS (Cl⁺): calc. for C₃₂H₂₂Br₂(MH⁺) 564.0083, found: 564.0085.
(S)-3-Phenyl-N-methyl-2,7-dihydronaphtho[2,1-c;1’,2’-e]azepine 6

(S)-3-Phenyl-2,2’-bis-bromomethyl-[1,1’]binaphthalene (150 mg, 0.29 mmol) was dissolved in acetonitrile (10 mL). Potassium carbonate (125 mg, 0.9 mmol) and methylamine (2M solution in THF, 1.5 mL, 2.9 mmol) were added and the mixture heated at reflux overnight. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM. The organic layers were washed with water (3 x 10 mL) and brine (2 x 10 mL). The combined organic extracts were dried (MgSO₄) and the solvent removed under reduced pressure to give a colourless foam. The product was purified by column chromatography on silica gel (light petroleum/ethyl acetate 98:02) to afford the title compound 6 (105 mg, 94%) as a colourless foam, [α]D25 +174.2° (c. 1.04, CHCl₃); νmax (DCM) /cm⁻¹ 3053, 2932, 1721, 1495, 1216, 1101, 1027, 752; δH (400 MHz, CDCl₃) 2.16 (s, 3H), 2.82 (d, 1H, J = 12 Hz), 3.49 (d, 1H, J = 12 Hz), 3.59 (d, 1H, J = 12 Hz), 3.78 (d, 1H, J = 12 Hz), 7.21-7.30 (m, 2H), 7.38-7.54 (m, 8H), 7.63 (d, 2H, J = 7 Hz), 7.93-7.97 (m, 4H); δc (100 MHz, CDCl₃) 43.3, 57.3, 57.4, 125.5, 125.8, 125.9, 126.0, 127.3, 127.72, 127.74, 127.9, 128.3, 128.4, 128.45, 128.5, 129.4, 130.2, 130.9, 131.7, 132.5, 132.8, 133.0, 133.3, 135.1, 136.1, 140.7, 141.6, 167.2; HRMS (Cl+): calc. for C₂₉H₂₃N (MH⁺) 384.1747, found: 384.1742.
(S)-3-Phenyl-N-isopropyl-2,7-dihydrodinaphtho[2,1-c;1',2'-e]azepine 7

(S)-3-Phenyl-2,2'-bis-bromomethyl-[1,1']binaphthalene (145 mg, 0.28 mmol) was dissolved in acetonitrile (10 mL). Potassium carbonate (120 mg, 0.84 mmol) and isopropylamine (0.694 mL, 2.8 mmol) were added and the mixture heated at reflux overnight. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM and the organic layers were washed with water (3 x 10 mL) and brine (2 x 10 mL). The combined organic extracts were dried (MgSO4) and the solvent removed under reduced pressure to give a yellow foam. The product was purified by column chromatography on silica gel (light petroleum/ethyl acetate 95:05) to afford the title compound 7 (115 mg, 99%) as a yellow foam, [α]25D +179.0° (c. 1.05, CHCl3); νmax (DCM) /cm⁻¹ 3053, 2967, 1494, 1382, 1324, 1215, 1159, 1036, 751; δH (400 MHz, CDCl3) δ 0.88 (d, 3H, J = 6 Hz), 0.92 (d, 3H, J = 6 Hz), 2.61 (septet, 1H, J = 6 Hz), 2.96 (d, 1H, J = 12 Hz), 3.43 (d, 1H, J = 13 Hz), 3.93 (d, 1H, J = 13 Hz), 4.02 (d, 1H, J = 13 Hz), 7.25-7.29 (m, 1H), 7.38-7.52 (m, 7H), 7.57 (d, 1H, J = 8 Hz), 7.70-7.74 (m, 2H), 7.91-7.95 (m, 4H); δC (100 MHz, CDCl3) 21.4, 21.9, 47.9, 52.8, 53.0, 125.4, 125.7, 125.8, 125.9, 127.3, 127.7, 127.8, 128.0, 128.3, 128.4, 128.5, 129.4, 130.4, 130.8, 131.6, 132.7, 133.1, 135.4, 136.2, 140.8, 141.7, 167.2; HRMS (CI+): calc. for C31H26N ([M-H]⁺) 412.2065, found: 412.2055.
(S)-3-(Naphthalen-1-yl)-N-methyl-2,7-dihydrodinaphtho[2,1-c;1’,2’-e]azepine 8

(S)-3-(Naphthalen-1-yl)-2,2’-bis-bromomethyl-[1,1’]binaphthalene (80 mg, 0.141 mmol) was dissolved in acetonitrile (10 mL). Potassium carbonate (60 mg, 0.42 mmol) and methylamine (2M solution in THF, 0.705 mL, 1.4 mmol) were added. The mixture was heated under reflux and stirred overnight. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM and washed with water (3 x 10 mL) and brine (2 x 10 mL). The combined organic extracts were dried (MgSO4), and the solvent removed under reduced pressure to give a colourless foam. The product was purified by column chromatography on silica gel (light petroleum/ethyl acetate 98:02) to afford the title compound 8 (54 mg, 88%) as a colourless foam, [α]25D +28.8° (c. 1.0, CHCl3); νmax (DCM)/cm⁻¹ 3052, 2929, 1720, 1507, 1465, 1389, 1265, 1019, 780, 752; 2 conformations A and B were observed (the major conformation is represented by A); δH (400 MHz, CDCl₃) 1.81 (s, 3Ha), 2.07 (s, 3Hα), 2.98 (d, 1Hα, J = 13 Hz), 3.25-3.35 (m, 2Ha + 2Hβ), 3.56-3.62 (m, 1Hα + 1Hβ), 3.69-3.73 (d, 1Hβ, J = 13 Hz), 7.28-7.72 (m, 10Hα + 10Hβ), 7.91-8.00 (m, 8Hα + 8Hβ); δC (100 MHz, CDCl₃) 43.3, 43.4, 52.9, 53.1, 53.2, 57.4, 125.5, 125.9, 126.0, 126.1, 126.12, 126.2, 127.6, 126.7, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 130.0, 130.8, 132.6, 132.9, 136.2, 137.1, 138.2, 140.1, 144.3, 145.2, 147.0, 147.9, 149.8, 150.7, 167.23, 167.24; HRMS (Cl⁺): calc. for C₃₃H₂₆N (MH⁺) 436.20908, found: 436.20623.

(S)-3-(Naphthalen-1-yl)-N-methyl-2,7-dihydrodinaphtho[2,1-c;1’,2’-e]azepine 9
(S)-3-(Naphthalen-1-yl)-2,2′-bis-bromomethyl-[1,1′]binaphthalene (115 mg, 0.20 mmol) was dissolved in acetonitrile (10 mL). Potassium carbonate (85 mg, 0.6 mmol) and isopropylamine (0.174 mL, 2.0 mmol) were added. The mixture was heated under reflux and stirred overnight. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM and washed with water (3 x 10 mL) and brine (2 x 10 mL). The combined organic extracts were dried (MgSO₄), and the solvent removed under reduced pressure to give a yellow foam. The product was purified by column chromatography on silica gel (light petroleum/ethyl acetate 95:05) to afford the title compound 9 (85 mg, 90%) as a yellow foam, [α]²⁵ᵇ −25.3° (c. 1.01, CHCl₃); νₘₐₓ (DCM) /cm⁻¹ 3050, 2965, 1507, 1463, 1388, 1324, 1161, 1030, 802, 778, 752; 2 conformations A and B were observed (the major conformation is represented by A); δₜ (400 MHz, CDCl₃) 0.13 (d, 3Hₗ, J = 6 Hz), 0.54 (d, 3Hₕ, J = 6 Hz), 0.66 (d, 3Hₗ, J = 6 Hz), 0.84 (d, 3Hₕ, J = 6 Hz), 2.19 (septet, 1Hₗ, J = 6 Hz), 2.56 (septet, 1Hₕ, J = 6 Hz), 3.02 (d, 1Hₕ, J = 13 Hz), 3.08 (d, 1Hₗ, d, J = 13 Hz), 3.32 (d, 1Hₕ, J = 12 Hz), 3.34 (d, 1Hₗ, J = 12 Hz), 3.54 (d, 1Hₕ, J = 13 Hz), 3.82-3.91 (m, 1Hₗ + 2Hₗ), 7.26-7.66 (m, 10Hₗ + 10Hₕ), 7.75-7.88 (m, 1Hₗ + 1Hₕ), 7.91-7.99 (m, 6Hₗ + 6Hₕ); δₜ (100 MHz, CDCl₃) 20.6, 20.8, 21.9, 43.0, 47.3, 47.5, 52.5, 52.8, 53.2, 53.3, 125.0, 125.1, 125.6, 125.9, 126.0, 126.06, 127.7, 127.8, 128.1, 128.2, 128.4, 128.6, 128.9, 130.3, 131.0, 131.6, 132.5, 133.6, 138.7, 139.7, 142.6, 144.5, 144.7, 145.1, 145.7, 149.2, 149.8, 150.6, 167.23, 167.24; HRMS (Cl⁺): calc. for C₃₅H₃₀N ([M+H]⁺) 464.2373, found: 464.2372.

(S)-3,3′-bis(3,5-bis-(Trifluoromethyl)phenyl)-N-methyl-2,7-dihydronaphtho[2,1-c;1′,2′-e]azepine 16
(S)-3,3’-bis(3,5-Trifluoromethyl)-phenyl)-2,2’-bis(bromomethyl)-1,1’-binaphthalene (300 mg, 0.35 mmol) was dissolved in acetonitrile (10 mL). Potassium carbonate (150 mg, 1.0 mmol) and methylamine (2M solution in THF, 500 μL, 1.0 mmol) were added and the mixture heated at reflux overnight. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM. The organic layers were washed with water (3 x 10 mL) and brine (2 x 10 mL). The combined organic extracts were dried (MgSO₄) and the solvent removed under reduced pressure to give a colourless foam. The product was purified by column chromatography on silica gel (light petroleum/ ethyl acetate 95:05) to afford the title compound 16 (130 mg, 51%) as a colourless foam; [α]20D −104.8° (c. 1.00, CHCl₃); v_max (DCM) /cm⁻¹ 3054, 2971, 2955, 2841 1372, 1277, 1179, 1132, 682; δH (400 MHz, CDCl₃) 1.93 (s, 3H), 3.58 (d, 2H, J = 13 Hz), 4.12 (d, 2H, J = 13 Hz), 7.34-7.37 (m, 2H), 7.47 (d, 2H, J = 8 Hz), 7.51-7.57 (m, 2H), 7.90-8.02 (m, 6H), 8.14 (br s, 4H); δC (100 MHz, CDCl₃) 42.5, 52.7, 121.0, 123.3 (q, J_C,F = 270 Hz), 126.5, 126.7, 127.4, 128.5, 129.6, 130.2, 130.8, 131.2, 131.4, 131.7, 132.4, 136.3, 137.2, 143.3; δF (376 MHz, CDCl₃) 99.5; HRMS (Cl+): calc. for C₃₉H₂₃F₁₂N (MH⁺) 733.1640, found: 733.1652.

(S)-3,3’-bis(3,5-bis(Trifluoromethyl)phenyl)-N-isopropyl-2,7-dihydrodinaphtho[2,1-c;1’,2’-e]azepine 17
(S)-3,3’-bis(3,5-Trifluoromethyl)-phenyl)-2,2’-bis(bromomethyl)-1,1’-binaphthalene (300 mg, 0.35 mmol) was dissolved in acetonitrile (10 mL). Potassium carbonate (150 mg, 1.0 mmol) and isopropylamine (177 μL, 2.1 mmol) were added and the mixture heated at reflux overnight. The mixture was allowed to cool to room temperature, and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM. The organic layers were washed with water (3 x 10 mL) and brine (2 x 10 mL). The combined organic extracts were dried (MgSO₄) and the solvent removed under reduced pressure to give a yellow foam. The product was purified by column chromatography on silica gel (light petroleum/ ethyl acetate 98:02) to afford the title compound 17 (220 mg, 83%) as a colourless foam, [α]²₀° –64.4° (c. 1.00, CHCl₃); νmax (DCM)/cm⁻¹ 3054, 2974, 2811, 1372, 1277, 1176, 1134; δH (400 MHz, CDCl₃) 0.40 (d, 3H, J = 6 Hz), 0.67 (d, 3H, J = 6 Hz), 2.23 (septet, 1H, J = 6 Hz), 3.12 (d, 2H, J = 13 Hz), 3.90 (d, 2H, J = 13 Hz), 7.33–7.37 (m, 2H), 7.46–7.48 (m, 2H), 7.51–7.56 (m, 2H), 7.92–8.01 (m, 6H), 8.17 (br s, 4H); δC (100 MHz, CDCl₃) 20.6, 21.2, 47.9, 51.4, 121.0, 123.3 (q, JCF = 270 Hz), 126.4, 126.7, 127.5, 128.5, 129.8, 130.3, 131.1, 131.4, 131.6, 131.7, 132.4, 136.6, 137.3, 143.5, δF (376 MHz, CDCl₃) 99.55; HRMS (Cl⁺): calc. for C₄₁H₂₇F₁₂N (MH⁺) 761.2028, found: 761.2028.

(S)-N-Cyclohexyl-2,7-dihydro-dinaphtho[2,1-c;1’,2’-e]azepine 19
Prepared according to the general procedure from cyclohexylamine (0.29 mL, 2.50 mmol, 1.1 eq). The title compound 19 was isolated as a colourless foam which solidified upon drying (0.81 g, 2.15 mmol, 95%), m.p. 81-82 °C, [α]$_D^{20}$ +252 (c 1.00, CHCl$_3$), $\nu_{\max}$(solid) /cm$^{-1}$, 3046, 2922, 2850, 1593, 1506, 1447, 1361, 1343, 1236, 1113, 1092, $\delta_H$ (400 MHz; CDCl$_3$) 1.18-1.40 (5H, m), 1.64 (1H, m), 1.76-1.97 (1H, m), 2.22 (1H, d, J = 12.2 Hz), 2.40-2.42 (1H, m), 3.29 (2H, d, J = 13 Hz), 3.97 (2H, d, J = 12 Hz), 7.23-7.28 (2H, m), 7.44-7.46 (4H, m), 7.60 (2H, d, J = 8 Hz), 7.94-7.96 (4H, m), $\delta_C$ (75 MHz; CDCl$_3$) 25.6, 26.0, 30.5, 31.1, 31.6, 51.9, 61.7, 125.3, 125.7, 127.5, 128.0, 128.3, 128.4, 131.4, 133.1, 134.5, 135.1, HRMS (Cl+): calc. for C$_{28}$H$_{27}$N (MH+) 377.2144, found 377.2138.

(S)-N-benzyl-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine 20

![Structural formula of compound 20]

Prepared according to the general procedure from benzylamine (133 mg, 1.25 mmol). The title compound 20 was isolated as a colourless foam which solidified on standing (398 mg, 1.04 mmol, 92%), m.p. 82-83 °C, [α]$_D^{20}$ +304 (c 1.09, CHCl$_3$), $\nu_{\max}$(solid) /cm$^{-1}$ 3051, 2933, 2805, 2755, 1761, 1733, 1624, 1594, 1567, 1507, 1494, $\delta_H$ (300 MHz; CDCl$_3$) 3.22 (d, 2H, J = 12 Hz), 3.62 – 3.64 (m, 2H), 3.68 (d, 2H, J = 12 Hz), 7.25-7.57 (m, 13H), 7.98 (d, 4H, J = 8 Hz), $\delta_C$ (75 MHz; CDCl$_3$) 55.1, 59.6, 125.5, 125.8, 127.2, 127.6, 127.9, 128.3, 128.4, 128.5, 129.3, 131.5, 133.1, 133.2, 133.7, 135.2, 139.3, HRMS (Cl+): calc. for C$_{29}$H$_{23}$N (MH+) 386.1903, found 386.1898.
(S)-N-Phenyl-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine 21

Prepared according to the general procedure from aniline (0.12 g, 1.28 mmol). The crude product was isolated as a pale brown oil which was purified by column chromatography (1:1 petrol : EtOAc) to give the title compound 21 as pale yellow oil (446 mg, 1.20 mmol, 94%), [α]_{D}^{20} = -293 (c 1.00, CHCl₃), ν_max(solid) /cm⁻¹ 3053, 2360, 2341, 1595, 1578, 1500, 1465, 1372, δ_H (300 MHz; CDCl₃) 3.87 (d, 2H, J = 12 Hz), 4.54 (d, 2H, J = 12 Hz), 6.88 (d, 1H, J = 8 Hz), 6.95 (2H, d, J = 6 Hz), 7.28-7.37 (m, 4H), 7.45-7.56 (m, 4H), 7.61 (d, 2H, J = 9 Hz), 7.94 (d, 2H, J = 9 Hz), 7.98 (d, 2H, J = 12 Hz) δ_C (75 MHz; CDCl₃) 52.6, 115.6, 118.6, 125.8, 126.1, 127.6, 127.7, 128.5, 129.1, 129.3, 131.5, 133.4, 133.8, 134.9, HRMS (Cl+): calc. for C_{28}H_{21}N (MH+) 371.1674, found 371.1670.

(S)-N-(4-methoxyphenyl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine 22

Prepared according to the general procedure from p-anisidine (0.15 g, 1.14 mmol). The crude product was isolated as a pale yellow foam which was purified by column chromatography (1:1 petrol : EtOAc) to give the title compound 22 as yellow powder (380 mg, 0.94 mmol, 83%) m.p. 91-92 °C, [α]_{D}^{20} = -259.6 (c 1.00, CHCl₃), ν_max(solid) /cm⁻¹ 3388, 3049, 2995, 2948, 2907, 2831, 2348, 2047, 1915, 1830, 1734, 1615, 1594, 1580, δ_H (300 MHz; CDCl₃) 3.76 (s, 3H), 3.78 (d, 2H, J = 12 Hz), 4.32 (d, 2H, J = 12 Hz), 6.80-6.92 (m, 4H), 7.24-7.31 (m, 2H), 7.43-7.53 (m, 6H), 7.91 (t, J = 8 Hz), δ_C (75 MHz; CDCl₃) 53.7, 55.5, 114.4, 117.9, 125.6, 125.9, 127.5, 127.6, 128.4, 128.8, 131.4, 133.3, 133.6, 134.8, 144.4, 153.1, HRMS (Cl+): calc. for C_{29}H_{23}NO (MH+) 402.1844, found 402.1847.
(11bS)-4-amino-4-isopropyl-4,5-dihydro-3H-dinaphtho[2,1-c:1’,2’-e]azepin-4-ium tetraphenylborate 23

(S)-N-Isopropyl-2,7-dihydro-dinaphtho[2,1-c;1’,2’-e]azepine (1.0 g, 2.96 mmol) was dissolved in DCM (30 mL). DppONH2 (758 mg, 3.25 mmol) was added as a solid in a single portion and the resulting white slurry was stirred overnight at room temperature (TLC indicated complete consumption of the starting material). The mixture was filtered through a pad of Celite and concentrated in vacuo to give the hydrazinium diphenylphosphinate as a hygroscopic yellow foam. The crude compound was re dissolved in a minimum amount of DCM and a saturated solution of sodium tetraphenylborate (1.11 g, 3.25 mmol) in MeCN was added. Copious precipitation of a colourless solid ensued. The title compound 23 was isolated via filtration as a colourless powder (1.53 g, 2.28 mmol, 77%), [α]$_D^{20}$ +160.8° (c 0.99, CHCl$_3$), m.p. 217-219 °C (decomp.); ν$_{max}$ (DCM) /cm$^{-1}$ 3326, 3255, 3054, 2984, 1595, 1579, 1478, 1427, 1265; δ$_H$ (500 MHz; CD$_2$Cl$_2$) 1.09 (d, 3H, J = 6 Hz), 1.24 (d, 3H, J = 6 Hz), 2.98 (br s, 2H), 3.18 (d, 1H, J = 13 Hz), 3.30 (septet, 1H, J = 6 Hz), 3.56 (d, 1H, J = 12 Hz), 3.72 (d, 1H, J = 12 Hz), 4.05 (d, 1H, J = 13 Hz), 6.79 (t, 4H, J = 7 Hz), 6.93 (t, 8H, J = 7 Hz), 7.28-7.38 (m, 9H), 7.39-7.53 (m, 5H), 7.61-7.72 (m, 2H), 8.02-8.20 (m, 4H); δ$_C$ (125 MHz; CD$_2$Cl$_2$) 16.6, 16.8, 65.3, 65.6, 66.5, 122.1 (4C, para in ´BPh$_4$), 125.3, 125.9 (8C, m, meta in ´BPh$_4$), 126.2, 126.4, 127.38, 127.41, 127.5, 127.7, 127.8, 127.9, 128.0, 128.6, 128.8, 130.4, 130.7, 131.3, 131.4, 134.6, 134.8, 134.8, 136.0 (8C, s, ortho in ´BPh$_4$), 136.3, 138.6, 163.9 (q, 4C, J = 49 Hz, ipso in ´BPh$_4$), HRMS (Cl+): calc. for C$_{25}$H$_{25}$N$_2$+ 353.2012, found 353.2014
(S)-6-isopropyl-1,11-dimethyl-6,7-dihydro-5H-dibeno[c,e]azepine 24

Prepared according to the general procedure using (S)-6,6'-dimethyl-2,2'-bis(bromomethyl)biphenyl and isopropylamine (53 mg, 0.90 mmol, 1.1 eq). The title compound 24 was isolated as a colourless foam (0.18 g, 0.68 mmol, 82%), [α]_{D}^{20} + 28.8 (c 1.00, CHCl₃), ν_{max}(solid) /cm⁻¹, 2959, 2920, 2800, 1593, 1454, 1377, 1360, 1326, 1236, 1209, 1163, δₜ (400 MHz; CDCl₃) 1.10 (d, J = 6 Hz, 3H), 1.24 (d, J = 6 Hz, 3H), 2.19 (s, 6H), 2.53 (septet, J = 6 Hz, 1H), 3.01 (d, J = 12 Hz, 2H), 3.73 (d, J = 12 Hz, 2H), 7.15-7.19 (m, 2H), 7.24-7.26 (m, 4H), δₜ (75 MHz; CDCl₃) 19.7, 21.0, 21.8, 52.0, 126.6, 127.2, 129.5, 135.2, 135.7, 138.6, HRMS (CI+): calc. for C₁₉H₂₃N (MH⁺) 265.1825, found 265.1824.

(S)-4-isopropyl-4,5,8,9,10,11,12,13,14,15-decahydro-3H-dinaphtho[2,1-c:1',2'-e]azepine 25

Prepared according to the general procedure using (S)-2,2'-bis(bromomethyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene (1.0 g, 2.23 mmol, 1.0 eq) and isopropylamine (0.33 mL, 2.42 mmol, 1.1 eq.). The title compound 25 was isolated as a colourless foam in sufficient purity to be used without further purification (0.79 g, 92%), [α]_{D}^{20} -136.70 (c 1.03, CHCl₃), ν_{max}(solid) /cm⁻¹, 2927, 2858, 1449, 1378, 1325, 1212, 1162, 1125, 1064, 1024, 908, 869, 829, 811, 731, 638; δₜ (400 MHz; CDCl₃) 1.08 (d, 3H, J = 6 Hz), 1.21 (d, 3H, J = 6 Hz), 1.51-1.61 (m, 2H), 1.74-1.85 (m, 6H), 2.23 (dt, 2H, J = 11, 6 Hz), 2.53 (septet, 1H), 2.66-2.72 (m, 2H), 2.84 (dt, 4H, J = 11, 7 Hz), 2.92 (2H, d, J = 12 Hz), 3.65 (d, 2H, J = 12 Hz), 7.04 (d, 2H, J = 8 Hz), 7.08 (d, 2H, J = 8 Hz); δₜ (75 MHz; CDCl₃) 21.2, 22.7, 22.8, 27.6, 29.4, 51.7, 51.8, 126.3, 128.0, 132.4, 135.5, 136.7, 138.3, HRMS (CI+): calc. for C₂₅H₃₁N (MH⁺) 346.2529, found 346.2533