TiCl₄-catalyzed Intermolecular Hydroamination Reactions of Norbornene

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Supporting Information

Experimental Section

TiCl₄-mediated reactions were carried out on a 2 mmol scale under N₂ using pre-dried glassware. Chemicals were obtained from Aldrich, Fluka, Lancaster, and Acros, and were used without further purification. Amines were distilled under N₂, and stored over molecular sieves (4 Å). Known products were identified by comparison with independently synthesized samples (¹H- and ¹³C-NMR, GC/MS).

Representative Procedure for Hydroamination of Norbornene (1):

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(2-chloro-phenyl)-amine (3g):**

TiCl₄ (0.22 ml, 2.00 mmol) was added to a solution of norbornene (**1**) (0.188 mg, 2.00 mmol) and 2-chloroaniline (1.02 g, 8.00 mmol) (**2g**) in toluene (2 mL) under N₂. The suspension was stirred at 169 °C for 2 h in a sealed tube, after which GC/MS analysis indicated complete conversion of norbornene (**1**). CH₂Cl₂ (50 mL) and sat. aq. NaHCO₃ (20 mL) were added to the cooled reaction mixture. The separated aqueous phase was extracted with CH₂Cl₂ (2 x 75 mL). The combined organic layers were dried over MgSO₄ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et₂O, 200/1) to yield **3g** as a pale yellow oil (346 mg, 78 %).

Representative Procedure for Tosylation of Hydrofunctionalization Products:

N-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(4-fluoro-phenyl)-4-methyl-benzenesulfonamide (**3d'**):

Bicyclo[2.2.1]hept-2-yl-(4-fluoro-phenyl)-amine (**3d**) (249 mg, 1.21 mmol) and tosylchlorid (463 mg, 2.43 mmol) were stirred under N₂ in pyridine (10 mL) for 24 h at room temperature. CH₂Cl₂ (50 mL) was added to the reaction mixture. The solution was washed subsequently with aq. HCl (2 M, 2 x 50 mL), sat. aq. NaHCO₃ (50 mL) and sat. aq. NaCl (50 mL). The organic phase was dried over MgSO₄ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (*n*-pentane/Et₂O, 30/1→20/1→10/1→6/1) to yield **3d'** as a white solid (396 mg, 91 %).

N-(*exo*-Bicyclo[2.2.1]hept-2-yl)-4-methyl-*N*-phenyl-benzenesulfonamide (**3a'**).

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 20/1→10/1→6/1) yielded **3a'** (311 mg, 48 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.59 (d, 2H, *J* = 8.3 Hz), 7.30-7.24 (m, 5H), 6.99 (d, 2H, *J* = 8.1 Hz), 4.09 (dd, 1H, *J* = 8.2, 5.7 Hz), 2.43 (s, 3H), 2.27 (m, 1H), 1.72 (m, 1H), 1.55-1.05 (m, 6H), 0.90-0.65 (m, 2H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 143.0 (C), 137.5 (C), 137.2 (C), 132.4 (CH), 129.3 (CH), 128.7 (CH), 128.4 (CH), 127.7 (CH), 62.4 (CH), 41.9 (CH), 38.8 (CH₂), 35.6 (CH), 35.6 (CH₂), 28.6 (CH₂), 28.0 (CH₂), 21.5 (CH₃). IR (KBr): 2958, 2872, 1597, 1491, 1346, 1164, 1080, 791, 663 cm⁻¹. MS (EI) *m/z* (relative intensity) 341 (18) [M⁺], 247 (42), 186 (73), 155 (26), 106 (100), 91 (36), 77 (37). HR-MS (EI) *m/z* calcd for C₂₀H₂₃NO₂S 341.1449, found 341.1420. C₂₀H₂₃NO₂S (341.48) Anal. Calcd C, 70.35; H, 6.79; N, 4.10; S, 9.40. Found C, 70.49; H, 6.68; N, 4.10; S, 9.30.

***N*-(*exo*-2-Bicyclo[2.2.1]hept-2-yl-phenyl)-4-methyl-benzenesulfonamide (4a').**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 10/1→6/1) yielded **4a'** (128 mg, 20 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.63 (d, 2H, *J* = 8.3 Hz), 7.41 (m, 1H), 7.21 (d, 2H, *J* = 8.0 Hz), 7.16-7.05 (m, 3H), 6.34 (s, 1H), 2.38 (s, 3H), 2.30-2.20 (m, 2H), 2.19 (m, 1H), 1.65 (ddd, 1H, *J* = 11.6, 9.1, 2.0 Hz), 1.55-1.40 (m, 3H), 1.30-1.10 (m, 4H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 143.8 (C), 139.2 (C), 136.9 (C), 134.0 (C), 129.6 (CH), 127.2 (CH), 126.3 (CH), 125.7 (CH), 125.7 (CH), 123.5 (CH), 41.3 (CH), 40.9 (CH), 38.9 (CH₂), 36.9 (CH), 36.4 (CH₂), 30.3 (CH₂), 28.7 (CH₂), 21.5 (CH₃). IR (KBr): 3305, 3044, 2955, 2871, 1597, 1496, 1407, 1330, 1159, 1093, 930, 813, 745, 662 cm⁻¹. MS (EI) *m/z* (relative intensity) 341 (58) [M⁺], 186 (100), 157 (45), 130 (29), 118 (42), 106 (55), 91 (25). HR-MS (EI) *m/z* calcd for C₂₀H₂₃NO₂S 341.1449, found 341.1417. C₂₀H₂₃NO₂S (341.48) Anal. Calcd C, 70.35; H, 6.79; N, 4.10. Found C, 70.09; H, 6.70; N, 4.04.

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-4-methyl-*N*-(4-methyl-phenyl)-benzenesulfonamide (3b').**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 30/1→20/1→10/1) yielded **3b'** (167 mg, 24 %) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.60-7.58 (m, 2 H), 7.27-7.25 (m, 2 H), 7.10-7.08 (m, 2 H), 6.87-6.85 (m, 2 H), 4.09 (dd, *J* = 7.9, 5.5 Hz, 1 H), 2.43 (s, 3 H), 2.34 (s, 3 H), 2.34 (d, *J* = 3.0 Hz, 1 H), 2.03 (s, 1 H), 1.69 (ddd, *J* = 12.9, 8.4, 2.3 Hz, 1 H), 1.57-1.51 (m, 1 H), 1.48-1.34 (m, 2 H), 1.26-1.20 (m, 1 H), 1.11-1.05 (m, 1 H),

0.81-0.78 (m, 1 H), 0.70-0.67 (m, 1 H). ^{13}C -NMR (100 MHz, DEPT, CDCl_3): δ = 143.9 (C_q), 138.4 (C_q), 137.7 (C_q), 134.4 (C_q), 132.1 (CH), 129.4 (CH), 129.3 (CH), 127.7 (CH), 62.3 (CH), 41.9 (CH), 38.8 (CH_2), 35.7 (CH), 35.6 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 21.5 (CH_3), 21.2 (CH_3). IR (KBr): 3289, 3030, 2953, 2870, 1599, 1508, 1454, 1345, 1163, 1094, 1078 cm^{-1} . ^1H MS (EI) m/z (relative intensity) 355 (16) [M^+], 294 (12), 261 (100), 200 (52), 155 (6). HR-MS (EI) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_2\text{S}$ 355.1606, found 355.1615. $\text{C}_{20}\text{H}_{23}\text{NO}_2\text{S}$ (355.49) Anal. Calcd C, 70.95; H, 7.09; N, 3.94. Found C, 70.85; H, 6.98; N, 3.84.

***N*-(*exo*-2-Bicyclo[2.2.1]hept-2-yl-4-methylphenyl)-4-methyl-benzenesulfonamide (**4b'**).**

Purification by column chromatography (SiO_2 , *n*-pentane/ Et_2O 50/1 $\rightarrow$ 15/1 $\rightarrow$ 5/1) yielded **4b'** (145 mg, 21 %) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ = 7.64-7.61 (m, 2 H), 7.27-7.22 (m, 3 H), 6.96-6.92 (m, 2 H), 6.26 (s, br, 1 H), 2.39 (s, 3 H), 2.29 (s, 3 H), 2.29 (s, 1H), 2.25 (dd, J = 9.0, 5.9 Hz, 1 H), 2.15-2.14 (m, 1 H), 1.60 (ddd, J = 11.6, 9.9, 2.4 Hz, 1 H), 1.55-1.50 (m, 2 H), 1.49-1.46 (m, 1 H), 1.28-1.17 (m, 3 H), 1.15-1.07 (m, 1 H). ^{13}C -NMR (100 MHz, DEPT, CDCl_3): δ = δ 143.6 (C_q), 140.0 (C_q), 137.1 (C_q), 135.7 (C_q), 131.3 (C_q), 129.5 (CH), 127.2 (CH), 126.9 (CH), 126.5 (CH), 124.5 (CH), 41.2 (CH), 41.1 (CH), 39.0 (CH_2), 36.8 (CH), 36.4 (CH_2), 30.4 (CH_2), 28.7 (CH_2), 21.5 (CH_3), 21.2 (CH_3). IR (KBr): 3302, 3034, 2867, 2952, 1598, 1496, 1334, 1166, 1093, 813, 665, 552 cm^{-1} . MS (EI) m/z (relative intensity) 355 (100) [M^+], 200 (98), 171 (24), 158 (12), 144 (23), 132 (27), 120 (56), 91 (23), HR-MS (EI) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{S}$ 355.1606, found 355.1612. $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{S}$ (355.49) Anal. Calcd C, 70.95; H, 7.09; N, 3.94. Found C, 70.76; H, 6.95; N, 3.86.

***N*-(exo-Bicyclo[2.2.1]hept-2-yl)-*N*-(2,4,6-trimethyl-phenyl)-4-methyl-benzenesulfonamide (**3c'**).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 20/1→15/1) yielded **3c'** (276 mg, 60 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.64 (d, 2 H, *J* = 8.2 Hz), 7.27 (d, 2 H, *J* = 8.2 Hz), 6.85 (s, 1H), 6.83 (s, 1H), 3.93 (dd, 1 H, *J* = 7.0, 6.2 Hz), 2.42 (s, 3H), 2.37 (m, 1H), 2.26 (s, 3H), 2.09 (m, 1H), 2.07 (s, 3H), 1.92 (s, 3H), 1.71 (m, 1H), 1.60-1.40 (m, 3H), 1.30-0.95 (m, 4H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 142.9 (C), 140.2 (C), 138.3 (C), 137.6 (C), 132.9 (CH), 129.7 (CH), 127.9 (CH), 127.3 (CH), 63.9 (CH), 42.9 (CH), 38.9 (CH₂), 37.8 (CH), 37.8 (CH₂), 28.4 (CH₂), 27.9 (CH₂), 21.5 (CH₃), 20.9 (CH₃), 19.8 (CH₃). IR (KBr): 2953, 2871, 1599, 1344, 1161, 1093, 898, 678 cm⁻¹. MS (EI) *m/z* (relative intensity) 383 ([M⁺] 14), 228 (100), 148 (19), 146 (32). HR-MS (EI) *m/z* calcd for C₂₃H₂₉NSO₂ 383.1919, found 383.1922. Anal. Calcd C, 72.02; H, 7.62; N, 3.65. Found C, 71.23; H, 7.57; N, 3.58.

***N*-(exo-Bicyclo[2.2.1]hept-2-yl)-*N*-(4-fluoro-phenyl)-4-methyl-benzenesulfonamide (**3d'**).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 20/1→10/1→6/1) yielded **3d'** (396 mg, 56 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.57 (d, 2H, *J* = 8.3 Hz), 7.26 (d, 2H, *J* = 8.0 Hz), 7.00-6.90 (m, 4H), 4.09 (dd, 1H, *J* = 7.8, 5.0 Hz), 2.42 (s, 3H), 2.23 (m, 1H), 2.05 (m, 1H), 1.70-1.05 (m, 6H), 0.82 (md, 1H, *J* = 10.2 Hz), 0.68 (md, 1H, *J* = 10.2 Hz). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 162.3 (CF, d, *J* = 249.1 Hz), 143.2 (C), 137.1

(C), 133.9 (CH, d, $J = 8.7$ Hz), 133.0 (C, d, $J = 3.2$ Hz), 129.4 (CH), 127.6 (CH), 115.6 (CH, d, $J = 22.6$ Hz), 62.3 (CH), 41.8 (CH), 38.8 (CH₂), 35.6 (CH), 35.6 (CH₂), 28.6 (CH₂), 27.9 (CH₂), 21.5 (CH₃). ¹⁹F-NMR (376 MHz, CDCl₃): $\delta = -111.4$ (m). IR (KBr): 3075, 2957, 2873, 1599, 1476, 1335, 1152, 1094, 1078, 841, 678 cm⁻¹. MS (EI) m/z (relative intensity) 359 (23) [M⁺], 265 (100), 204 (53), 155 (17), 124 (25). HR-MS (EI) m/z calcd for C₂₀H₂₂NFO₂S 359.1355, found 359.1351. C₂₀H₂₂NFO₂S (359.46) Anal. Calcd C, 66.83; H, 6.17; N, 3.90. Found C, 66.55; H, 6.15; N, 3.84.

***N*-(2-*exo*-Bicyclo[2.2.1]hept-2-yl-4-fluoro-phenyl)-4-methyl-benzenesulfonamide (**4d'**).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 10/1→6/1) yielded **4d'** (77 mg, 12 %) as a white solid. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.59$ (d, 2H, $J = 8.4$ Hz), 7.31 (dd, 1H, $J = 8.8, 5.3$ Hz), 7.23 (d, 2H, $J = 8.0$ Hz), 6.87 (dd, 1H, $J = 10.3, 2.8$ Hz), 6.81 (ddd, 1H, $J = 8.8, 8.0, 2.8$ Hz), 6.26 (s, 1H), 2.40 (s, 3H), 2.29 (m, 1H), 2.23 (m, 1H), 2.08 (m, 1H), 1.70-1.45 (m, 4H), 1.30-1.00 (m, 4H). ¹³C-NMR (150 MHz, DEPT, CDCl₃): $\delta = 161.0$ (CF, d, $J = 245.4$ Hz), 143.9 (C), 143.7 (C, d, $J = 7.1$ Hz), 136.7 (C), 136.6 (C), 129.6 (CH), 127.1 (CH), 127.0 (CH, d, $J = 8.8$ Hz), 113.5 (CH, d, $J = 24.1$ Hz), 113.3 (CH, d, $J = 22.8$ Hz), 41.3 (CH), 41.2 (CH), 39.0 (CH₂), 36.7 (CH), 36.4 (CH₂), 30.2 (CH₂), 28.5 (CH₂), 21.5 (CH₃). ¹⁹F-NMR (375 MHz, CDCl₃): $\delta = -113.7$ (m). IR (KBr): 3301, 2953, 2871, 1598, 1492, 1404, 1333, 1164, 1094, 668 cm⁻¹. MS (EI) m/z (relative intensity) 359 (100) [M⁺], 204 (96), 175 (25), 124 (37), 91 (8). HR-MS (EI) m/z calcd for C₂₀H₂₂NFO₂S 359.1355, found 359.1360. C₂₀H₂₂NFO₂S (359.46) Anal. Calcd C, 66.83; H, 6.17; N, 3.90. Found C, 66.61; H, 6.10; N, 3.84.

***N*-(exo-Bicyclo[2.2.1]hept-2-yl)-*N*-(2-fluoro-phenyl)-amine (3e).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 200/1→100) yielded **3e** (330 mg, 80 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.00-6.92 (m, 2 H), 6.69-6.57 (m, 2 H), 3.77 (s, br, 1 H), 3.25 (dd, *J* = 7.3, 3.1 Hz, 1 H), 2.31 (s, 2 H), 1.85 (ddd, *J* = 12.8, 7.6, 2.5 Hz, 1 H), 1.62-1.47 (m, 3 H), 1.30-1.15 (m, 4 H). ¹³C-NMR (100 MHz, DEPT, CDCl₃): δ = 151.6 (d, *J* = 238 Hz, C), 136.1 (d, *J* = 11.4 Hz, C), 124.5 (d, *J* = 3.8 Hz, CH), 116.0 (d, *J* = 6.9 Hz, CH), 114.2 (d, *J* = 18.3 Hz, CH), 112.6 (d, *J* = 3.8 Hz, CH), 56.4 (CH), 41.3 (CH), 41.0 (CH₂), 35.6 (CH), 35.3 (CH₂), 28.4 (CH₂), 26.4 (CH₂). ¹⁹F-NMR (375 MHz, CDCl₃): δ = -135.7 (m). IR (KBr): 3433, 3069, 3046, 2954, 2872, 1621, 1513, 1454, 1336, 1253, 1190, 738 cm⁻¹. MS (EI) *m/z* (relative intensity) 205 ([M⁺] 100), 176 (13), 164 (7), 150 (19), 137 (30), 124 (22), 111 (45), 94 (7), 79 (7). HR-MS (EI) *m/z* calcd for C₁₃H₁₆NF 205.1267, found 205.1264.

***N*-(2-exo-Bicyclo[2.2.1]hept-2-yl)-2-fluoro-phenyl-amine (4e).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 200/1→100/1) yielded **4e** (10 mg, 2 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 6.92 (d, *J* = 8.5 Hz, 1 H), 6.87-6.82 (m, 1 H), 6.66 (ddd, *J* = 9.7, 8.5, 5.9 Hz, 1 H), 3.68 (s, br, 2 H), 2.60 (dd, *J* = 8.7, 5.5 Hz, 1 H), 2.46 (d, *J* = 3.4 Hz, 1 H), 2.38 (s, 1 H), 1.82 (ddd, *J* = 11.6, 9.2, 2.3 Hz, 1 H), 1.71-1.52 (m, 4 H), 1.43-1.21 (m, 3 H). ¹³C-NMR (100 MHz, DEPT, CDCl₃): δ = 151.9 (d, *J* = 237 Hz,

C), 134.0 (d, $J = 3.1$ Hz, C), 132.2 (d, $J = 11.5$ Hz, C), 120.5 (d, $J = 2.3$ Hz, CH), 117.3 (d, $J = 7.6$ Hz, CH), 112.1 (d, $J = 19.0$ Hz, CH), 42.0 (d, $J = 2.3$ Hz, CH), 40.6 (CH), 37.8 (CH₂), 36.8 (CH), 36.3 (CH₂), 30.2 (CH₂), 29.2 (CH₂). ¹⁹F-NMR (375 MHz, CDCl₃): $\delta = -134.3$ (dd, $J = 9.7, 5.9$ Hz). IR (KBr): 3400, 2955, 2925, 2854, 1738, 1630, 1476, 1377, 1262, 1216, 1093, 1021, 799 cm⁻¹. MS (EI) m/z (relative intensity) 205 ([M⁺] 78), 176 (15), 162 (14), 148 (14), 137 (60), 124 (100), 111 (10), 77 (6). HR-MS (EI) m/z calcd for C₁₃H₁₆NF 205.1267, found 205.1268.

***N*-(exo-Bicyclo[2.2.1]hept-2-yl)-*N*-(4-chloro-phenyl)-4-methyl-benzenesulfonamide (3f).**

Purification by column chromatography (SiO₂, n-pentane/Et₂O 30/1→20/1→10/1→6/1) yielded **3f** (570 mg, 67 %) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.55$ (d, $J = 8.4$ Hz, 2 H), 7.25 (d, $J = 8.4$ Hz, 4 H), 6.90 (d, $J = 8.4$ Hz, 2 H), 4.05 (dd, $J = 7.9, 5.1$ Hz, 1 H), 2.42 (s, 3 H), 2.23 (m, 1 H), 2.05 (m, 1 H), 1.80-1.00 (m, 6 H), 0.82 (d, $J = 9.9$ Hz, 1 H), 0.69 (d, $J = 9.9$ Hz, 1 H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): $\delta = 143.3$ (C), 137.0 (C), 135.8 (C), 134.4 (C), 133.5 (CH), 129.4 (CH), 128.9 (CH), 127.6 (CH), 62.5 (CH), 41.8 (CH), 38.8 (CH₂), 35.6 (CH), 35.6 (CH₂), 28.5 (CH₂), 27.9 (CH₂), 21.5 (CH₃). IR (KBr): 3091, 2959, 2873, 1487, 1345, 1158, 1092, 1078, 721, 667, 596, 589, 548 cm⁻¹. MS (EI) m/z (relative intensity) 375 ([M⁺] 12), 281 (100), 220 (47), 155 (20), 140 (30), 91 (8). HR-MS (EI) m/z calcd for C₂₀H₂₂NSClO₂ 375.1060, found 375.1058. Anal. Calcd C, 63.90; H, 5.90; N, 3.73. Found C, 63.89; H, 5.93; N, 3.61.

***N*-(2-*exo*-Bicyclo[2.2.1]hept-2-yl-4-chloro-phenyl)-4-methyl-benzenesulfonamide (**4f'**).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 4/1) yielded **4f'** (70 mg, 8 %) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 2.4 Hz, 1 H), 7.06 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.31 (s, 1 H), 2.37 (s, 3 H), 2.28 (m, 1 H), 2.21 (dd, *J* = 8.7, 5.7 Hz, 1 H), 2.12 (m, 1 H), 1.70-1.45 (m, 4 H), 1.30-1.05 (m, 4 H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 144.0 (C), 141.5 (C), 136.6 (C), 132.6 (C), 131.4 (C), 129.7 (CH), 127.1 (CH), 126.4 (CH), 126.1 (CH), 125.1 (CH), 41.3 (CH), 40.9 (CH), 38.9 (CH₂), 36.8 (CH), 36.4 (CH₂), 30.2 (CH₂), 28.6 (CH₂), 21.5 (CH₃). IR (KBr): 3305, 2951, 2871, 1484, 1334, 1166, 1093, 903, 812, 666 cm⁻¹. MS (EI) *m/z* (relative intensity) 375 ([M⁺] 79), 220 (90), 191 (39), 184 (30), 178 (12), 164 (34), 152 (38), 140 (100), 117 (51), 91 (46). HR-MS (EI) *m/z* calcd for C₂₀H₂₂NSClO₂ 375.1060, found 375.1067. Anal. Calcd C, 63.90; H, 5.90; N, 3.73. Found C, 63.92; H, 5.86; N, 3.69.

***N*-(2-*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(2-chloro-phenyl)-amine (**3g**).**

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.23 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.13 (ddd, 1H, *J* = 7.9, 7.9, 1.4 Hz), 6.65 (dd, 1H, *J* = 7.9, 1.4 Hz), 6.60 (ddd, 1H, *J* = 7.9, 7.9, 1.4 Hz), 4.18 (s, 1H), 3.28 (m, 1H), 2.35-2.20 (m, 2H), 1.87 (ddd, 1H, *J* = 12.8, 7.6, 2.4 Hz), 1.65-1.45 (m, 3H), 1.35-1.10 (m, 4H). ¹³C-NMR (75 MHz, DEPT, CD₂Cl₂): δ = 143.6 (C), 129.0 (CH), 127.8 (CH), 118.9 (C), 116.7 (CH), 112.0 (CH), 56.5 (CH), 41.4 (CH), 41.0 (CH₂), 35.8 (CH), 35.3 (CH₂), 28.5 (CH₂), 26.3 (CH₂). IR (KBr): 3420, 3069, 2954, 2870, 1598, 1510, 1326, 1034, 739 cm⁻¹.

MS (EI) m/z (relative intensity) 221 (55) [M^+], 166 (21), 153 (53), 127 (100), 67 (46). HR-MS (EI) m/z calcd for $C_{13}H_{16}NCl$ 221.0971, found 221.0972.

3h

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(2-bromo-phenyl)-amine (3h).**

Purification by column chromatography (SiO_2 , n -pentane/ Et_2O 100/1) yielded **3h** (429 mg, 81 %) as a colorless oil. 1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (dd, 1H, J = 7.8, 1.5 Hz), 7.08 (ddd, 1H, J = 8.1, 7.3, 1.5 Hz), 6.53 (dd, 1H, J = 8.1, 1.5 Hz), 6.46 (ddd, 1H, J = 7.8, 7.3, 1.5 Hz), 4.14 (s, 1H), 3.18 (dd, 1H, J = 7.0, 2.8 Hz), 2.30-2.20 (m, 2H), 1.70 (m, 1H), 1.60-1.45 (m, 3H), 1.30-1.10 (m, 4H). ^{13}C -NMR (75 MHz, DEPT, $CDCl_3$): δ = 144.3 (C), 132.3 (CH), 128.3 (CH), 117.3 (C), 112.0 (CH), 109.7 (CH), 56.6 (CH), 41.1 (CH), 41.0 (CH_2), 35.6 (CH), 35.4 (CH_2), 28.4 (CH_2), 26.3 (CH_2). IR (KBr): 3410, 3067, 2953, 2870, 1595, 1506, 1325, 1018, 739 cm^{-1} . MS (EI) m/z (relative intensity) 267 ($[M^+, ^{81}Br]$ 97), 265 ($[M^+, ^{79}Br]$ 100), 199 (57), 197 (57), 171 (63), 130 (31), 95 (17). HR-MS (EI) m/z calcd for $C_{13}H_{16}N^{79}Br$ 265.0466, found 265.0468.

3i

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(2,4-dibromo-phenyl)-amine (3i).**

Purification by column chromatography (SiO_2 , n -pentane/ Et_2O 200/1 $\rightarrow$ 50/1) yielded **3i** (570 mg, 83 %) as a colorless oil. 1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, J = 2.2 Hz, 1 H), 7.24 (dd, J = 8.8, 2.2 Hz, 1 H), 6.45 (d, J = 8.8 Hz, 1 H), 4.22 (s, br, 1 H), 3.22 (dd, J = 7.3, 2.9 Hz, 1 H), 2.32 (s, 1 H), 2.27 (d, J = 3.0 Hz, 1 H), 1.85 (ddd, J = 13.1, 7.5, 2.5 Hz, 1 H), 1.64-

1.47 (m, 3 H), 1.31-1.13 (m, 4 H). ^{13}C -NMR (75 MHz, DEPT, CDCl_3): δ = 143.3 (C), 134.2 (CH), 131.1 (CH), 113.1 (CH), 110.0 (C), 107.7 (C), 56.8 (CH), 41.1 (CH), 40.9 (CH_2), 35.6 (CH), 35.4 (CH_2), 28.4 (CH_2), 26.3 (CH_2). IR (KBr): 3411, 3068, 2954, 2911, 2870, 1588, 1495, 1475, 1454, 1387, 1323, 1305, 1264, 798 cm^{-1} . MS (EI) m/z (relative intensity) 347 ($[\text{M}^+, ^{81}\text{Br}, ^{81}\text{Br}]$ 51), 345 ($[\text{M}^+, ^{79}\text{Br}, ^{81}\text{Br}]$ 100), 343 ($[\text{M}^+, ^{79}\text{Br}, ^{79}\text{Br}]$ 52), 316 (17), 292 (14), 290 (29), 288 (16), 279 (40), 277 (81), 275 (43), 264 (38), 262 (30), 253 (47), 251 (91), 249 (45), 210 (20), 117 (20), 95 (20), 67 (18). HR-MS (EI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{N}^{79}\text{Br}_2$ 342.9571, found 342.9573.

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(3,5-bis(trifluoromethyl)-phenyl)-amine (**3j**).**

Purification by column chromatography (SiO_2 , *n*-pentane/ Et_2O 200/1) yielded **3j** (535 mg, 83 %) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ = 7.11 (s, 1 H), 6.87 (s, 2 H), 4.01 (d, J = 5.1 Hz, 1 H), 3.29-3.24 (m, 1 H), 2.34 (s, 1 H), 2.26 (d, J = 3.1 Hz, 1 H), 1.88 (ddd, 1 H, J = 12.9, 7.5, 2.3 Hz), 1.66-1.42 (m, 3 H), 1.31-1.15 (m, 4 H). ^{13}C -NMR (75 MHz, DEPT, CDCl_3): δ = 148.0 (C), 132.3 (q, J = 32.6 Hz, C), 123.6 (q, J = 272.6 Hz, C), 112.0 (q, J = 2.9 Hz, CH), 109.6 (sept, J = 4.0 Hz, CH), 56.4 (CH), 41.3 (CH), 40.9 (CH_2), 35.7 (CH), 35.5 (CH_2), 28.3 (CH_2), 26.3 (CH_2). ^{19}F -NMR (375 MHz, CDCl_3): δ = δ -63.4 (s). IR (KBr): 3440, 2959, 2877, 1622, 1516, 1474, 1429, 1395, 1278, 1175, 1131, 861 cm^{-1} . MS (EI) m/z (relative intensity) 323 ($[\text{M}^+]$ 23), 268 (19), 255 (30), 242 (49), 229 (13), 94 (39), 79 (24), 67 (21), 58 (30), 43 (100). HR-MS (EI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{NF}_6$ 323.1109, found 323.1108.

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(3,5-bis(trifluoromethyl)-phenyl)-4-methylbenzenesulfonamide (**3j'**).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 50/1→30/1) yielded **3j'** (260 mg, 54 %) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.84 (s, 1 H), 7.52-7.49 (m, 2 H), 7.39 (s, 2 H), 7.32-7.29 (m, 2 H), 3.98 (dd, *J* = 8.3, 4.2 Hz, 1 H), 2.45 (s, 3 H), 2.31 (d, *J* = 3.6 Hz, 1 H), 2.12 (s, 1 H), 1.72 (ddd, *J* = 13.1, 8.2, 2.2 Hz, 1 H), 1.56-1.37 (m, 3 H), 1.26-1.19 (m, 1 H), 1.15-1.07 (m, 1 H), 0.95-0.91 (m, 1 H), 0.77-0.73 (m, 1 H). ¹³C-NMR (75 MHz, DEPT, CDCl₃): δ = 144.2 (C), 139.9 (C), 135.7 (C), 132.1 (q, *J* = 33.9 Hz, C), 132.3 (q, *J* = 3.0 Hz, CH), 129.7 (CH), 127.8 (CH), 122.7 (q, *J* = 273 Hz, C), 122.1 (q, *J* = 3.8 Hz, CH), 63.0 (CH), 41.8 (CH), 39.2 (CH₂), 35.8 (CH), 35.6 (CH₂), 28.3 (CH₂), 27.9 (CH₂), 21.5 (CH₃). ¹⁹F-NMR (375 MHz, CDCl₃): δ = δ -61.9 (s). IR (KBr): 3436, 2968, 2876, 1362, 1279, 1188, 1167, 1138, 1092, 1082, 713, 683, 665 cm⁻¹. MS (EI) *m/z* (relative intensity) 477 ([M⁺] 9), 322 (80), 242 (100), 213 (19), 155 (28), 95 (20), 91 (42), 81 (13), 67 (16). HR-MS (EI) *m/z* calcd for C₂₂H₂₁NSO₂F₆ 477.1196, found 477.1215. Anal. Calcd C, 55.34; H, 4.43; N, 2.93. Found C, 55.23; H, 4.37; N, 2.87.

***N*-(*exo*-Bicyclo[2.2.1]hept-2-yl)-*N*-(2-cyano-phenyl)-amine (**3k**).**

Purification by column chromatography (SiO₂, *n*-pentane/Et₂O 200/1→50/1→30/1) yielded **3k** (200 mg, 47 %) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ = 7.30-7.20 (m, 2H),

6.55 (d, 1H, $J = 6.4$ Hz), 6.52 (d, 1H, $J = 8.3$ Hz), 4.29 (brs, 1H), 3.19 (m, 1H), 2.23 (m, 1H), 2.19 (m, 1H), 1.76 (m, 1H), 1.55-1.30 (m, 3H), 1.25-1.05 (m, 4H). ^{13}C -NMR (75 MHz, DEPT, CDCl_3): $\delta = 149.5$ (C), 134.0 (CH), 132.7 (CH), 117.9 (C), 116.1 (CH), 111.3 (CH), 95.6 (C), 56.2 (CH), 41.2 (CH), 40.9 (CH_2), 35.6 (CH), 35.3 (CH_2), 28.3 (CH_2), 26.2 (CH_2). IR (KBr): 3413, 3370, 2954, 2871, 2212, 1576, 1511, 1462, 1330, 748 cm^{-1} . MS (EI) m/z (relative intensity) 212 ($[\text{M}^+]$ 100), 157 (33), 144 (51), 118 (32), 94 (47). HR-MS (EI) m/z calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2$ 212.1314, found 212.1309.

4m

exo-2-[2'-N-(Phenylamino)phenyl]norbornane (4m)

Purification by column chromatography (SiO_2 , n -pentane/ Et_2O 500/1 $\rightarrow$ 250/1) yielded **4m** (328 mg, 62 %) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.33$ -7.24 (m, 4H), 7.14 (ddd, $J = 7.4, 7.4, 1.1$ Hz, 1H), 7.02-6.94 (m, 3H), 6.91 (t, $J = 7.4$ Hz, 1H), 5.42 (s, 1H), 2.80 (dd, $J = 8.7, 5.5$ Hz, 1H), 2.52 (s, 1H), 2.39 (s, 1H), 1.85 (ddd, $J = 11.5, 9.0, 2.1$ Hz, 1H), 1.74-1.53 (m, 4H), 1.41-1.29 (m, 3H). ^{13}C -NMR (75 MHz, DEPT, CDCl_3): $\delta = 144.2$ (C), 140.7 (C), 137.4 (C), 129.3 (CH), 126.0 (CH), 125.8 (CH), 121.8 (CH), 120.3 (CH), 119.5 (C), 117.4 (CH), 42.0 (CH), 40.8 (CH), 38.8 (CH_2), 37.0 (CH), 36.4 (CH_2), 30.3 (CH_2), 29.1 (CH_2). MS (EI) m/z (relative intensity) 263 ($[\text{M}^+]$ 100), 234 (17), 206 (12), 194 (20), 182 (55), 167 (13), 91 (7), 77 (8). These values match those reported in the literature.¹

References

- 1 Brunet, J.-J; Commenges, G; Neibecker, D.; Rosenberg, L. *J. Organomet. Chem.* **1994**, 469, 221.

3b'

3b'

4b'

4b'

3e

3e

4e

4e

3 g

3h

3 i

3i

3k

4.3

3.2

2.0

1.0

1.0

0.9

1.9

1.8

3k

4m