Synthesis of Carbazoles and Dibenzofurans via Cross-Coupling of *o*-Iodoanilines and *o*- Iodophenols with Silylaryl Triflates

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Supporting Information

General. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted. All yields reported represent an average of at least two independent runs. The silylaryl triflate **1a**, CsF and acetonitrile were purchased from Sigma-Aldrich Co. The 4,5-dimethyl-substituted silylaryl triflate **1b** was prepared according to a literature procedure.¹

Preparation of the starting materials: The starting materials **1**, **3**, **6**,² **8**,³ **10**,⁴ **13**,⁵ **15**, **17** were either commercially available or easily prepared using literature procedures.

***N*-(2-Iodobenzyl)methanesulfonamide (**13**).** To the solution of the *o*-iodobenzylamine (1.0 mmol) and triethylamine (1.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise methanesulfonyl chloride (1.0 mmol) at 0 °C. The reaction was stirred overnight at room temperature. The resulting solution was washed with brine (20 mL) and extracted with CH_2Cl_2 (30 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product (0.29 g) in a 93 % yield as a white solid: mp 109-111 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.84 (dd, J = 7.8, 1.2 Hz, 1H), 7.45 (dd, J = 7.5, 1.5 Hz, 1H), 7.36 (td, J = 7.5, 1.2 Hz, 1H), 7.02 (td, J = 7.8, 1.8

Hz, 1H), 4.35 (d, J = 6.6 Hz, 2H), 2.82 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 140.0, 139.1, 130.4, 130.2, 129.0, 99.1, 51.9, 41.6; IR (CDCl_3 , cm^{-1}) 3428, 1643, 1313; HRMS m/z 310.9482 (calcd $\text{C}_8\text{H}_{10}\text{INO}_2\text{S}$, 310.9477).

General procedure for the synthesis of carbazoles.

In a 4 dram vial, the silylaryl triflate **1a** or **1b** (0.275 mmol) and CsF (0.75 mmol) were added to a solution of the *o*-iodoaniline (0.25 mmol) in acetonitrile (4 mL). The solution was allowed to stir at room temperature for 10 h under air. The vial was then flushed with argon and $\text{Pd}(\text{OAc})_2$ (5 mol %, 3.1 mg) and PCy_3 (10 mol %, 7.0 mg) were added to the reaction, which was heated to 100 °C for 1 d. The resulting solution was washed with brine (20 mL) and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

Carbazole (2). The indicated compound was obtained in a 77 % yield (32 mg) as a white solid: mp 242-244 °C (lit.⁶ mp 242-247 °C). The ^1H and ^{13}C NMR spectra match the literature data:⁶ ^1H NMR (300 MHz, acetone- d_6) δ 10.32 (s, 1H), 8.13 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.40 (td, J = 8.1, 1.2 Hz, 2H), 7.19 (td, J = 8.1, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, acetone- d_6) δ 140.3, 125.7, 123.3, 120.2, 119.0, 111.1, 111.0; IR (CDCl_3 , cm^{-1}) 3416, 3070.

1,3-Dichlorocarbazole (4). The indicated compound was obtained in an 87 % yield (51 mg) as a white solid: mp 97-99 °C; ^1H NMR (300 MHz, acetone- d_6) δ 10.76 (s, 1H), 8.18-8.16 (m, 2H), 7.63-7.00 (m, 1H), 7.52-7.46 (m, 2H), 7.26 (td, J = 7.2, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, acetone- d_6) δ 141.0, 135.8, 127.4, 125.8, 124.5, 124.0, 122.5, 121.1, 120.2, 118.9, 116.4, 111.9; IR (CDCl_3 , cm^{-1}) 3450, 3409, 3075, 3056, 2917, 1567, 1442; HRMS m/z 234.9959 (calcd $\text{C}_{12}\text{H}_7\text{Cl}_2\text{N}$, 234.9955).

1,3-Dichloro-6,7-dimethylcarbazole (5). The indicated compound was obtained in an 85 % yield (56 mg) as a slightly yellow solid: mp 132-133 °C; ^1H NMR (300 MHz, acetone- d_6) δ 10.49 (s, 1H), 8.01 (d, J = 1.8 Hz, 1H), 7.87 (s, 1H), 7.39 (d, J = 1.8 Hz, 1H), 7.37 (s, 1H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, acetone- d_6) δ 139.9, 136.8, 135.7, 128.8, 125.8, 123.8, 123.7, 121.1, 120.7, 118.4, 116.2, 112.3; IR (CDCl_3 , cm^{-1}) 3446, 2965, 2919, 2855, 1637, 1565, 1452; HRMS m/z 263.0272 (calcd $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N}$, 263.0268).

N-Methylcarbazole (7). The indicated compound was obtained in an 82 % yield (37 mg) as a white solid: mp 87-88 °C (lit.⁷ mp 87 °C). The ¹H and ¹³C NMR spectra match the literature data:⁸ ¹H NMR (300 MHz, CDCl₃) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.49-7.43 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.23-7.21 (m, 2H), 3.78 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 141.0, 125.6, 122.7, 120.3, 118.8, 108.4, 29.0; IR (CDCl₃, cm⁻¹) 3050, 2938; HRMS *m/z* 181.2335 (calcd C₁₃H₁₁N, 181.2331).

9-(Methylsulfonyl)carbazole (9). The indicated compound was obtained in an 85 % yield (52 mg) as a white solid: mp 98-99 °C (lit.⁹ mp 101 °C). The ¹H NMR spectrum matches the literature data:⁶ ¹H NMR (300 MHz, CDCl₃) δ 8.16 (d, *J* = 7.2, 2H), 8.02-7.99 (m, 2H), 7.52-7.39 (m, 4H), 2.97 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 138.6, 127.8, 126.5, 124.4, 120.4, 114.9, 38.9; IR (CDCl₃, cm⁻¹) 3060, 3027, 2929, 1441; HRMS *m/z* 245.0515 (calcd C₁₃H₁₁NO₂S, 245.0510).

Ethyl 2,3-dimethylcarbazole-9-carboxylate (11). The indicated compound was obtained in an 85 % yield (57 mg) as a slightly yellow solid: mp 81-82 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.26 (d, *J* = 7.2 Hz, 1H), 8.11 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.71 (s, 1H), 7.43-7.39 (m, 1H), 7.35-7.32 (m, 1H), 4.59 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.56 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 152.7, 138.4, 137.2, 136.5, 132.1, 126.7, 126.3, 124.1, 123.3, 120.3, 119.4, 117.2, 116.5, 63.1, 21.2, 20.2, 14.7; IR (CDCl₃, cm⁻¹) 3061, 2980, 2920, 1727, 1451; HRMS *m/z* 267.1263 (calcd C₁₇H₁₇NO₂, 267.1259).

Ethyl carbazole-9-carboxylate (12). The indicated compound was obtained in an 85 % yield (51 mg) as a slightly yellow solid: mp 73-74 °C. The ¹H NMR spectrum matches the literature data:¹⁰ ¹H NMR (300 MHz, CDCl₃) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.49-7.43 (m, 2H), 7.34 (td, *J* = 7.5, 0.9 Hz, 2H), 4.58 (q, *J* = 7.2 Hz, 2H), 1.55 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 152.7, 138.5, 127.4, 126.1, 123.5, 119.8, 116.5, 63.3, 14.7; IR (CDCl₃, cm⁻¹) 3057, 3043, 2983, 2933, 1731, 1444; HRMS *m/z* 239.0949 (calcd C₁₅H₁₃NO₂, 239.0946).

5,6-Dihydro-5-(methylsulfonyl)phenanthridine (14). The indicated compound was obtained in an 85 % yield (43 mg) as a slightly yellow solid: mp 73-74 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.86-7.79 (m, 2H), 7.71-7.68 (m, 1H), 7.46-7.30 (m, 5H), 4.83 (s, 2H), 2.26 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 136.0, 132.3, 131.5, 129.9, 129.1, 129.0,

128.8, 128.1, 127.8, 126.3, 124.3, 123.9, 49.7, 37.9; IR (CDCl₃, cm⁻¹) 3067, 3025, 2927, 2853, 1491, 1342; HRMS m/z 259.0072 (calcd C₁₄H₁₃NO₂S, 259.0067).

General procedure for the synthesis of dibenzofurans.

In a 4 dram vial, the silylaryl triflate **1a** or **1b** (0.3 mmol) and CsF (0.875 mmol) were added to a solution of the *o*-iodophenol (0.25 mmol) in acetonitrile (4 mL). The rest of the procedure is the same as the synthesis of the carbazoles.

Dibenzofuran (16). The indicated compound was obtained in a 70 % yield (30 mg) as a white solid: mp 80-82 °C (lit.¹¹ mp 81-82 °C). The ¹H NMR spectrum matches the literature data:¹¹ ¹H NMR (300 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.8, 0.6 Hz, 2H), 7.62(d, *J* = 8.1 Hz, 2H), 7.49 (td, *J* = 7.5, 1.5 Hz, 2H), 7.37 (td, *J* = 7.8, 0.9 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 156.4, 127.4, 124.5, 122.9, 120.9, 111.9.

Methyl dibenzofuran-2-carboxylate (18). The indicated compound was obtained in an 80 % yield (45 mg) as a slightly yellow solid: mp 75-77 °C. The ¹H NMR spectrum matches the literature data:¹² ¹H NMR (300 MHz, CDCl₃) δ 8.68 (d, *J* = 1.5 Hz, 1H), 8.17 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.99 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.60-7.56 (m, 2H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 0.9 Hz, 1H), 3.97 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 167.2, 159.1, 157.0, 129.1, 128.1, 125.2, 124.6, 123.9, 123.5, 123.1, 121.2, 112.1, 111.7, 52.4; IR (CDCl₃, cm⁻¹) 3081, 3027, 2950, 2917, 2863, 1718, 1436, 1307; HRMS m/z 226.0633 (calcd C₁₄H₁₀O₃, 226.0629).

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