Electronic Supplementary Material (ESI) for Organic .

Efficient Synthesis of Biscarbazoles by Palladium-Catalyzed Twofold C-N Coupling and C-H Activation Reactions

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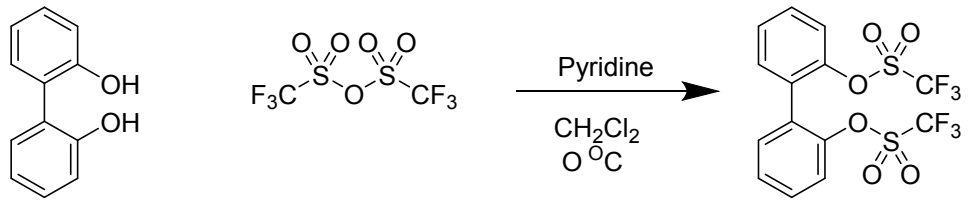
Supporting Information

Content List:

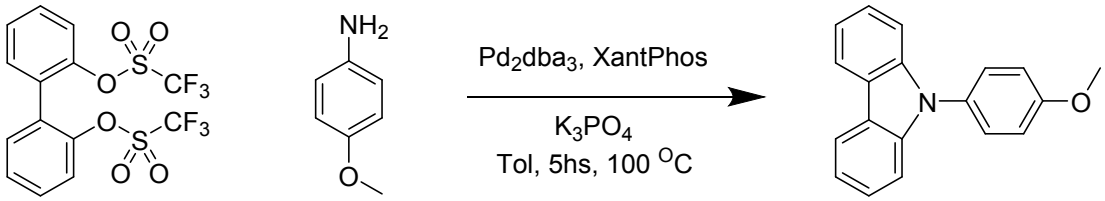
Experimental Section

Synthesis of 2,2'-biphenylylene ditriflate (1).

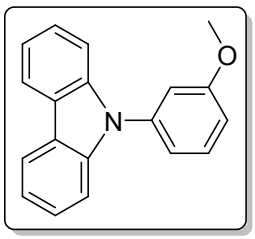


To a solution of 2,2'-dihydroxyl biphenyl (4.3 g, 23 mmol) in DCM was added pyridine (7.0 mL) under Argon atmosphere. Then, Tf_2O (13.0 g, 46 mmol) was slowly added at 0 ºC. The reaction was stirredat the same temperature for 3 h until the reaction was completed (tlc control). The reaction mixture was diluted by DCM and subsequently washed with 1M HCl, 1M $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. The colorless residue was purified by column chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **1** (9.3 g, 90 %, white solid); mp. 35-36 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.26 (m, 8H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -74.38 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.01, 132.75, 130.90, 129.55, 128.68, 118.50 (q, J = 320.1 Hz), 121.81; IR (ATR, cm^{-1}): ν = 1504 (w), 1473 (m), 1452 (w), 1439 (w), 1414 (vs), 1400 (s), 1277 (w), 1244 (s), 1201 (vs), 1165 (m), 1149 (s), 1132 (vs), 1111 (s), 1084 (s), 1045 (m), 1012 (w), 991 (w), 955 (w), 935 (w), 893 (s), 872 (vs), 779 (s), 769 (vs), 760 (s), 735 (m), 725 (s), 667 (w), 646 (w), 619 (s), 588 (s), 571 (vs); GC-MS (EI, 70 eV): m/z (%) = 450 (64), 317 (6), 184 (100), 168 (90), 156 (25), 139 (20), 128 (37), 102 (19), 69 (30); HRMS (EI): calcd. for $C_{14}H_8O_6F_6S_2$ ($[M]^+$): 449.96610; found: 449.96583.

Synthesis of *N*-(4-methoxyphenyl)carbazole (4a).

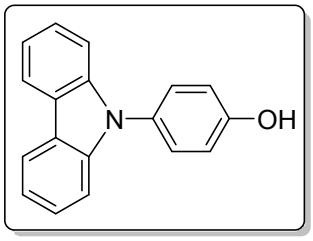


In a 50 mL dried pressure tube were added **1** (460 mg, 1.021 mmol), *p*-anisidine (151 mg, 1.226 mmol), Pd_2dba_3 (23 mg, 0.026 mmol), XantPhos (59 mg, 0.102 mmol), and K_3PO_4 (650 mg, 3.062 mmol) and the flask was backfilled with Argon 3 times. Then, the mixture was dissolved in 20 mL of toluene and, subsequently, backfilled with Argon 3 times. The reaction mixture was stirred at 100 ºC under Argon atmosphere for 5 hours (tlc control). The reaction was cooled down to ambient temperature, then the solvent was removed by evaporation *in vacuo*. The crude product was extracted with EtOAc and water several times. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ethylacetate/heptane = 1:10) to give **4a** (265 mg, 95 %) as a white solid, mp. 156-157 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 2H, ArH), 7.48 – 7.24 (m, 9H, ArH), 7.12 (d, *J* = 9.0 Hz, 2H, ArH), 3.92 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.02, 141.53, 130.47, 128.73, 125.98, 123.25, 120.39, 119.78, 115.21, 109.83, 55.75; IR (ATR, cm^{-1}): ν = 1591 (w), 1510 (s), 1479 (m), 1450 (s), 1336 (m), 1317 (m), 1246 (s), 1240 (s), 1228 (s), 1178 (s), 1147 (m), 1120 (m), 1107 (m), 1028 (s), 997 (m), 908 (m), 852 (w), 829 (s), 810 (m), 798 (m), 748 (vs), 725 (s), 698 (m), 642 (m), 621 (s), 611 (m), 584 (s), 569 (s), 532 (s); GC-MS (EI, 70 eV): m/z (%) = 273 (100), 258 (47), 230 (12), 228 (30); HRMS (EI): calcd. for $C_{19}H_{15}ON$ ([M]$^+$): 273.11482; found: 273.11474.

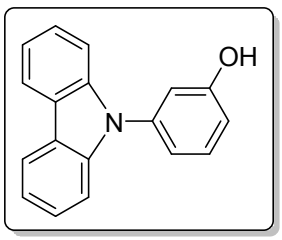


***N*-(4-Methoxyphenyl)carbazole (4b).** Prepared following the procedure given for the synthesis of **4a** using **1** (460 mg, 1.021 mmol) and *m*-anisidine (138 µL, 1.226 mmol). The crude product was separated via flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **4b** (265 mg, 95 %) as a colorless syrup; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.7, 0.6 Hz, 2H), 7.46 – 7.27 (m, 5H), 7.25 – 7.12 (m, 2H), 7.12 – 6.97 (m, 2H), 6.91 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 160.94, 140.95, 138.96, 130.66, 126.07, 123.49, 120.41, 120.04, 119.44, 113.38, 112.80, 110.04, 55.63; IR (ATR, cm^{-1}):

ν = 3051 (w), 2955 (w), 2933 (w), 2833 (w), 1927 (w), 1890 (w), 1861 (vw), 1593 (s), 1576 (m), 1495 (s), 1477 (s), 1450 (s), 1362 (m), 1335 (m), 1311 (s), 1281 (s), 1250 (s), 1227 (s), 1184 (m), 1153 (s), 1119 (m), 1099 (m), 1088 (m), 1078 (m), 1039 (s), 1003 (m), 995 (m), 984 (m), 970 (m), 918 (m), 872 (m), 845 (m), 833 (m), 825 (m), 779 (m), 744 (vs), 721 (vs), 692 (vs), 652 (m), 636 (m), 615 (m), 588 (m), 559 (m); GC-MS (EI, 70 eV): m/z (%) = 273 (100), 258 (7), 241 (5), 228 (19); HRMS (EI): calcd. for $C_{19}H_{15}ON$ ($[M]^+$): 273.11484; found: 273.11482.



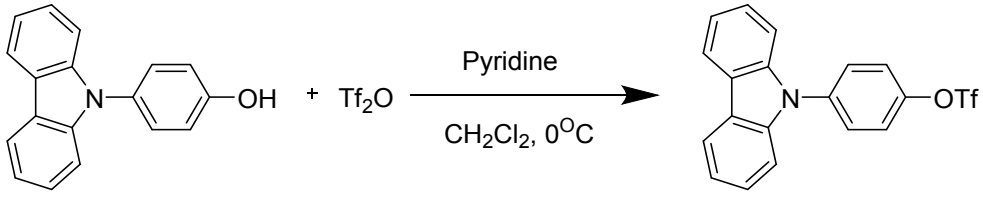
***N*-(4-Hydroxyphenyl)carbazole (5a).** To solution of **4a** (265 mg, 0.970 mmol) in DCM at -78 ºC was slowly added BBr_3 (367 µl, 3.880 mmol). The temperature was allowed to rise to ambient temperature. The reaction was controlled by TLC until the starting material completely disappeared. The reaction mixture was poured to an icecold aqueous solution of $NaHCO_3$. The aqueous layer was extracted with DCM three times. The organic residue was dried over $MgSO_4$, filtered and then the solvent was evaporated *in vacuo*. The crude product was purified over flash silica gel column chromatography (silica gel, ethylacetate/heptane = 1:10) to give **5a** (239 mg, 95 %), mp. 106-107 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H, ArH), 7.44 – 7.36 (m, 4H, ArH), 7.35 – 7.23 (m, 4H, ArH), 7.05 (d, *J* = 8.8 Hz, 2H, ArH). ^{13}C NMR (63 MHz, $CDCl_3$) δ 155.00, 141.50, 130.72, 128.99, 126.00, 123.28, 120.40, 119.82, 116.72, 109.81; IR (ATR, cm^{-1}): ν = 3196 (m), 3043 (w), 1622 (w), 1593 (m), 1512 (s), 1479 (m), 1450 (s), 1363 (m), 1335 (m), 1315 (m), 1248 (m), 1228 (s), 1219 (s), 1178 (s), 1165 (m), 1147 (m), 1099 (m), 1028 (w), 1014 (m), 1003 (w), 910 (m), 833 (s), 820 (m), 746 (vs), 723 (vs), 665 (m), 623 (s), 611 (m), 584 (s), 567 (m), 532 (m); GC-MS (EI, 70 eV): m/z (%) = 259 (100), 241 (6), 228 (10); HRMS (ESI): calcd. for $C_{18}H_{14}ON$ ($[M + H]^+$): 260.10699; found: 260.10686; calcd. for $C_{18}H_{13}ONNa$ ($[M + Na]^+$): 282.08894; found: 282.08872.



***N*-(4-Hydroxyphenyl)carbazole (5b).** Prepared, following the procedure given for the synthesis of **5a**, starting with carbazole **4b** (265 mg, 0.970 mmol) to give **5b** (231 mg, 92 %) as a colorless syrup; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.41 – 7.31 (m, 5H), 7.25 – 7.16 (m, 2H), 7.07 (ddd, *J* = 7.9, 1.9, 0.9 Hz, 1H), 6.96 (t, *J* = 2.2 Hz, 1H), 6.84 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 4.86 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 156.67,

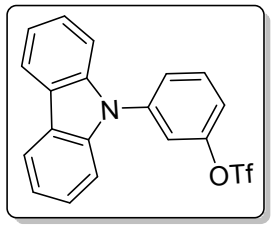
140.71, 138.99, 130.79, 125.93, 123.37, 120.26, 119.96, 119.48, 114.48, 114.06, 109.88; IR (ATR, cm^{-1}): ν = 3537 (w), 3271 (m), 3047 (w), 1599 (s), 1576 (m), 1498 (s), 1485 (m), 1471 (m), 1450 (s), 1367 (m), 1346 (m), 1335 (m), 1321 (m), 1304 (m), 1261 (m), 1252 (m), 1230 (s), 1209 (m), 1178 (m), 1165 (m), 1151 (s), 1124 (m), 991 (m), 920 (m), 872 (m), 849 (m), 781 (m), 748 (vs), 742 (vs), 719 (vs), 696 (vs), 667 (m), 636 (m), 615 (m), 584 (m), 573 (m), 557 (m); GC-MS (EI, 70 eV): m/z (%) = 259(100), 241 (4), 228 (8), 204 (4); HRMS (EI): calcd. for $C_{18}H_{13}ON$ ($[M]^+$): 259.09917; found: 259.09925.

Synthesis of of *N*-(4- trifluoromethanesulfonate)carbazole (6a).



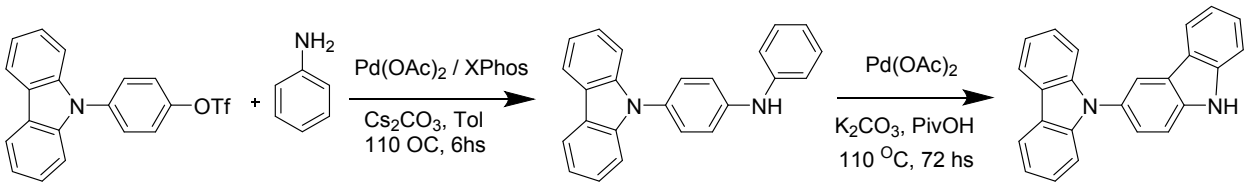
To solution of **5a** (239 mg, 0.921 mmol) in DCM was added pyridine (298 µL, 3.690 mmol) under Argon atmosphere. Then, Tf_2O (234 µL, 1.383 mmol) was dropwise added at 0 °C. The reaction mixture was stirred at the same temperature for 3 h until all starting material disappeared (controlled by tlc). The reaction mixture was diluted by DCM and subsequently washed with 1M HCl, 1M $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. The colorless residue was purified by column chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **6a** (310 mg, 86 %) as a white solid, mp. 112 - 114 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 1H), 7.72 – 7.65 (m, 1H), 7.57 – 7.50 (m, 1H), 7.48 – 7.36 (m, 2H), 7.36 – 7.29 (m, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.65 (s); ^{13}C NMR (63 MHz, $CDCl_3$) δ 147.99, 140.64, 138.12, 128.89, 126.40, 123.82, 123.19, 120.72, 120.65, 109.59; IR (ATR, cm^{-1}): ν = 3063 (w), 2924 (w), 1593 (w), 1504 (s), 1477 (m), 1452 (s), 1421 (s), 1412 (s), 1365 (w), 1335 (m), 1315 (m), 1248 (m), 1228 (s), 1215 (vs), 1167 (m), 1134 (vs), 1101 (m), 1026 (w), 1016 (m), 1001 (w), 916 (m), 887 (vs), 841 (s), 820 (m), 787 (m), 764 (w), 752 (vs), 725 (s), 696 (s), 644 (m), 619 (s), 611 (vs), 602 (vs), 573 (s), 565 (m), 530 (s); GC-MS (EI, 70 eV): m/z (%) = 391 (51), 259 (20), 258 (100),

230 (15), 228 (28), 69 (9); HRMS (EI): calcd. for $C_{19}H_{12}O_3NF_3S$ ([M]$^+$): 391.04845; found: 391.04852.



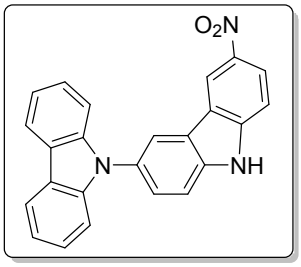
***N*-(3-Trifluoromethanesulfonate)carbazole (6b).** Prepared, following the procedure given for the synthesis of **6a**, from carbazole **5b** (231 mg, 0.891 mmol) to give **6b** (328 mg, 94 %) as a white solid, mp. 76-78 ºC, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.50 (dd, *J* = 6.4, 4.6 Hz, 2H), 7.38 (t, *J* = 2.0 Hz, 1H), 7.29 – 7.24 (m, 4H), 7.16 (ddd, *J* = 9.6, 8.1, 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.63 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.33, 140.40, 139.83, 131.53, 126.90, 126.51, 123.92, 120.90, 120.67, 120.32, 120.14, 109.56; IR (ATR, cm^{-1}): ν = 3072 (w), 3047 (w), 3024 (w), 1605 (m), 1585 (w), 1574 (w), 1495 (s), 1483 (s), 1454 (s), 1417 (vs), 1404 (m), 1365 (m), 1335 (m), 1315 (m), 1250 (m), 1230 (m), 1209 (vs), 1184 (s), 1163 (m), 1136 (s), 1119 (s), 1095 (s), 1084 (m), 1028 (m), 1003 (w), 984 (s), 964 (w), 924 (m), 904 (m), 877 (s), 847 (m), 798 (s), 771 (m), 764 (m), 750 (vs), 741 (s), 725 (s), 692 (s), 660 (m), 636 (m), 623 (m), 606 (s), 567 (s), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 391 (100), 258 (57), 230 (58), 228 (42), 202 (12), 69 (13); HRMS (EI): calcd. for $C_{19}H_{12}O_3NF_3S$ ([M]$^+$): 391.04845; found: 391.04816.

Typical procedure for the synthesis of biscarbazoles 3a-j and 7a-j.

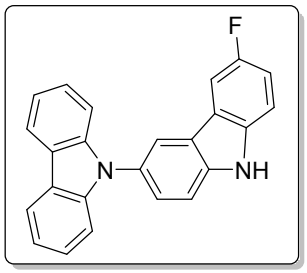


9*H*-3,9'-Biscarbazole (3a). Cesium carbonate (125 mg, 0.383 mmol) was added to a pressure tube charged with $Pd(OAc)_2$ (3 mg, 0.013 ammol) and XPhos (12 mg, 0.026 mmol) under argon atmosphere. Compound **6a** (100 mg, 0.256 mmol) and aniline (26 µL, 0.281 mmol) was added to the mixture and the tube was backfilled with argon several times. The mixture was stirred at 110 °C in anhydrous toluene (5 mL) for 6 hours. After cooling, the reaction mixture was diluted with dichloromethane (10 mL), filtered through a celite pad, and washed with dichloromethane (20 mL). The filtrate was concentrated *in vacuo*. Pivalic acid was added to the filtrate charged with

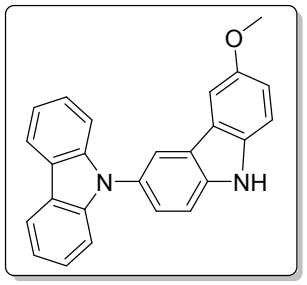
$Pd(OAc)_2$ (3 mg, 0.013 mmol) and potassium carbonate (35 mg, 0.256 mmol). The mixture was stirred at 110 °C under air atmosphere for 72 hours (controlled by tlc). The solution was then cooled to room temperature, diluted with DCM and washed with a saturated aqueous solution of sodium carbonate, dried over Magnesium sulfate, filtered and evaporated in *vacuo*. The product was purified by flash chromatography (silica gel, ethylacetate/heptanes = 1:10) to yield **3a** (73 mg, 86%) as a white solid; mp. 211-212 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 10.4, 3.9 Hz, 4H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.07 (m, 12H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 142.06, 140.30, 138.71, 129.56, 126.71, 125.99, 125.58, 124.50, 123.21, 123.14, 120.72, 120.40, 120.05, 119.71, 111.73, 111.05, 109.99; IR (ATR, cm^{-1}): ν = 3394 (m), 3076 (w), 3051 (m), 3020 (w), 2926 (w), 1595 (m), 1574 (m), 1495 (m), 1485 (m), 1475 (s), 1462 (s), 1448 (s), 1346 (m), 1333 (m), 1311 (s), 1273 (m), 1230 (s), 1203 (m), 1163 (m), 1149 (m), 1126 (m), 1117 (m), 1097 (m), 1024 (m), 1011 (m), 1003 (m), 957 (m), 926 (m), 918 (m), 845 (m), 820 (s), 742 (vs), 733 (s), 719 (vs), 660 (m), 650 (s), 631 (m), 615 (m), 580 (m), 571 (s); GC-MS (EI, 70 eV): m/z (%) = 332 (100), 166 (14), 139 (4); HRMS (EI): calcd. for $C_{24}H_{16}N_2$ ($[M]^+$): 332.13080; found: 332.13072.



6-Nitro-9*H*-3,9'-biscarbazole (3b). The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 4-nitroaniline (39 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:3) to yield **3b** (96 mg, 95 %) as a red solid; mp. 306-308 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.35 (s, 2H), 9.32 (d, *J* = 2.2 Hz, 3H), 8.72 (d, *J* = 1.8 Hz, 3H), 8.39 – 8.22 (m, 9H), 7.87 (d, *J* = 8.5 Hz, 3H), 7.79 – 7.65 (m, 6H), 7.37 (dqd, *J* = 9.0, 6.8, 1.3 Hz, 18H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 144.00, 140.97, 140.13, 140.10, 129.42, 126.29, 126.14, 123.68, 122.49, 122.09, 121.71, 120.43, 120.34, 119.76, 118.33, 113.27, 111.50, 109.70; IR (ATR, cm^{-1}): ν = 3307 (m), 2955 (w), 2922 (w), 2850 (w), 1608 (m), 1585 (m), 1495 (s), 1475 (s), 1448 (s), 1315 (s), 1308 (s), 1288 (s), 1228 (s), 1200 (s), 1163 (s), 1147 (m), 1128 (s), 1103 (m), 1078 (s), 1030 (m), 1016 (m), 889 (m), 852 (m), 823 (s), 816 (s), 748 (vs), 741 (s), 731 (s), 721 (vs), 683 (s), 654 (s), 640 (s), 625 (s), 613 (s), 590 (s), 567 (s), 557 (s), 528 (s); GC-MS (EI, 70 eV): m/z (%) = 329 (51), 314 (16), 114 (14), 73 (33), 60 (45), 44 (100); HRMS (ESI): calcd. for $C_{24}H_{16}O_2N_3$ ($[M + H]^+$): 378.1237; found: 378.12327; calcd. for $C_{24}H_{15}O_2N_3Na$ ($[M + Na]^+$): 400.10565; found: 400.10522.

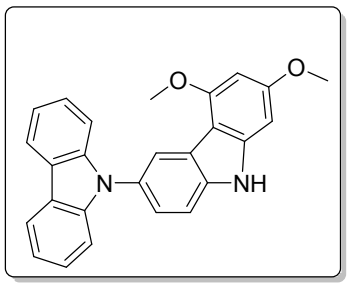


6-Fluoro-9*H*-3,9'-bicarbazole (3c). The product was prepared following general procedure using compound **6a** (100 mg, 0.256 mmol) and 4-fluoroaniline (27 µL, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3c** (90 mg, 63 %) as a red solid; mp. 238-240 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.62 (s, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 2H), 8.06 (dd, *J* = 9.4, 2.6 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.57 (dt, *J* = 8.6, 3.5 Hz, 2H), 7.42 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.37 – 7.22 (m, 5H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.47 (d, *J* = 232.6 Hz), 141.23, 139.92, 136.95, 127.70, 126.08, 125.30, 123.19 (d, *J* = 4.2 Hz), 122.69 (d, *J* = 10.1 Hz), 122.35, 120.40, 119.71, 119.59, 113.95 (d, *J* = 25.6 Hz), 112.51, 112.18 (d, *J* = 9.1 Hz), 109.64, 106.35 (d, *J* = 23.9 Hz); IR (ATR, cm^{-1}): ν = 3394 (m), 3053 (w), 2953 (w), 2920 (w), 2850 (w), 1587 (m), 1574 (m), 1495 (s), 1466 (s), 1448 (s), 1315 (m), 1284 (m), 1244 (m), 1228 (s), 1171 (m), 1151 (s), 1140 (m), 1124 (m), 1115 (m), 850 (m), 812 (s), 752 (vs), 744 (s), 721 (s), 656 (s), 646 (s), 615 (m), 596 (m), 575 (s), 565 (s), 544 (s), 532 (m); GC-MS (EI, 70 eV): m/z (%) = 350 (100), 174 (15); HRMS (ESI): calcd. for $C_{24}H_{16}FN_2$ ([M + H]$^+$): 351.1292; found: 351.12844; calcd. for $C_{24}H_{15}OFN_2Na$ ([M + Na]$^+$): 373.11115; found: 373.11065.

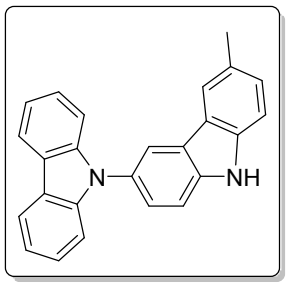


6-Methoxy-9*H*-3,9'-biscarbazole (3d). The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and *p*-anisidine (35 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **3d** (93 mg, 53 %) as a white solid; mp. 256-257 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.46 (s, 1H), 8.31 (dd, *J* = 28.0, 4.8 Hz, 3H), 7.75 (dd, *J* = 27.7, 5.5 Hz, 2H), 7.40 (dddd, *J* = 44.2, 15.9, 8.1, 1.5 Hz, 8H), 7.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 153.17, 141.32, 139.54, 135.31, 127.23, 126.06, 124.45, 123.48, 122.64, 122.33, 120.40, 119.52, 119.29, 115.66, 112.20, 111.95, 109.68, 103.39, 55.56; IR (ATR, cm^{-1}): ν = 3417 (m), 3045 (w), 2928 (w), 2829 (m), 1622 (m), 1589 (s), 1581 (s), 1574 (s), 1497 (s), 1470 (m), 1464 (m), 1450 (s), 1435 (m), 1360 (s), 1335 (m), 1313 (m), 1294 (s), 1232 (s), 1201 (s), 1173 (m), 1151 (m), 1140 (m), 1032 (m), 808 (m), 773 (s), 752 (vs), 727 (s), 656 (m), 648 (m), 617 (m), 607 (m), 569 (s),

528 (m); GC-MS (EI, 70 eV): m/z (%) = 362 (100), 347 (26), 319 (16), 290 (5), 174 (14); HRMS (ESI): calcd. for $C_{25}H_{17}N_2O$ ([M - H]$^-$): 361.13464; found: 361.13557.

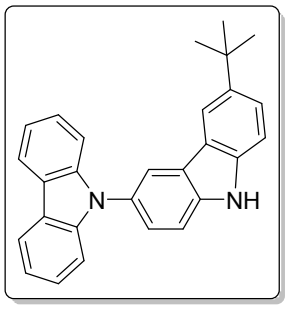


5,7-Dimethoxy-9*H*-3,9'-biscarbazole (3e). The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 3,5-dimethoxyaniline (43 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:4) to yield **3e** (100 mg, 50 %) as a white solid; mp. 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 2.0 Hz, 1H), 8.26 – 8.15 (m, 2H), 8.09 (s, 1H), 7.50 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.46 – 7.34 (m, 5H), 7.34 – 7.25 (m, 3H), 6.56 (d, *J* = 1.9 Hz, 1H), 6.34 (d, *J* = 1.9 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.97, 156.90, 142.35, 142.24, 137.96, 129.65, 125.89, 124.09, 123.44, 123.09, 121.42, 120.30, 119.49, 110.65, 110.20, 106.90, 91.59, 87.00, 55.85, 55.52; IR (ATR, cm^{-1}): ν = 3400 (w), 2918 (w), 2839 (w), 1633 (m), 1622 (m), 1614 (m), 1591 (m), 1495 (s), 1464 (s), 1450 (s), 1435 (m), 1335 (m), 1329 (m), 1315 (m), 1290 (s), 1230 (s), 1209 (s), 1196 (s), 1149 (s), 1120 (s), 1099 (m), 1049 (m), 918 (m), 806 (s), 750 (vs), 723 (s), 656 (s), 642 (m), 557 (m); GC-MS (EI, 70 eV): m/z (%) = 392 (100), 334 (22), 196 (12), 167 (7), 140 (22); HRMS (ESI): calcd. for $C_{26}H_{21}N_2O_2$ ([M + H]$^+$): 393.15975; found: 393.1595; calcd. for $C_{26}H_{20}N_2O_2Na$ ([M + Na]$^+$): 415.1417; found: 415.14155.

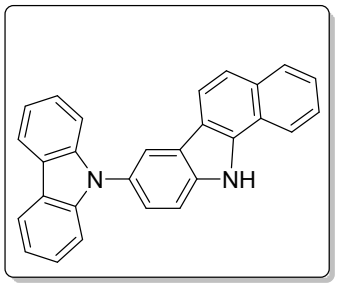


6-Methyl-9*H*-3,9'-biscarbazole (3g). The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and *p*-toluidine (30 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3g** (89 mg, 34 %) as a white solid; mp. 231-232 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 3H), 7.76 (d, *J* = 0.7 Hz, 1H), 7.46 (ddd, *J* = 10.4, 8.5, 1.2 Hz, 2H), 7.39 – 7.14 (m, 9H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.08, 139.05, 138.57, 129.45, 129.38, 128.09, 125.96, 125.39, 124.38, 123.36, 123.21, 120.59, 120.38, 119.67, 119.60, 111.69, 110.73, 110.01, 21.56; IR (ATR, cm^{-1}): ν = 3410 (m), 3057 (w), 2916 (w), 2852 (w), 2831 (w), 1593 (m), 1583 (m), 1574 (m), 1497 (s), 1479 (m), 1464 (s), 1452 (s), 1358 (m), 1338 (m), 1317 (m), 1296 (m), 1277 (m), 1242 (m), 1230 (s), 1153 (m), 820 (s), 806 (m), 748 (vs), 723 (vs), 658 (m), 646 (m), 575 (s), 540

(m), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 346 (100), 173 (9); HRMS (ESI): calcd. for $C_{25}H_{19}N_2$ ([M + H]$^+$): 347.15428; found: 347.15337; calcd. for $C_{25}H_{18}N_2Na$ ([M + Na]$^+$): 369.13622; found: 369.13578.

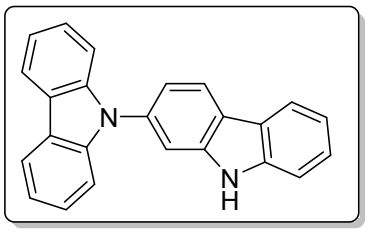


***6-(tert*-Butyl)-*9H*-3,9'-bicarbazole (3h).** The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 4-(*tert*-butyl)aniline (45 µL, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3h** (99 mg, 70 %) as a white solid; mp. 183-185 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.28 – 7.87 (m, 4H), 7.60 – 7.05 (m, 10H), 1.34 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 143.20, 142.16, 139.18, 138.43, 129.36, 125.94, 125.36, 124.80, 123.20, 122.90, 120.39, 119.65, 116.72, 111.67, 110.57, 110.02, 34.86, 32.06; IR (ATR, cm^{-1}): ν = 3408 (m), 3045 (w), 2953 (m), 2862 (w), 1622 (m), 1614 (m), 1595 (m), 1574 (m), 1495 (s), 1470 (s), 1450 (s), 1362 (m), 1335 (m), 1315 (m), 1294 (m), 1281 (m), 1242 (m), 1230 (s), 1201 (m), 1163 (m), 1138 (m), 1117 (m), 808 (s), 746 (vs), 723 (vs), 661 (m), 648 (m), 627 (vs), 577 (m), 546 (m), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 388 (100), 373 (63), 332 (10), 207 (9), 187 (13), 173 (24); HRMS (ESI): calcd. for $C_{28}H_{25}N_2$ ([M + H]$^+$): 389.20123; found: 389.20074;

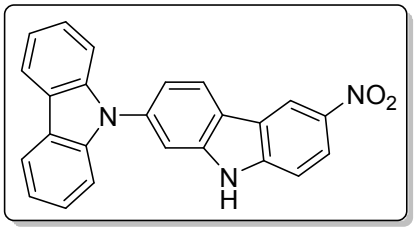


8-(9*H*-Carbazol-9-yl)-11*H*-benzo[*a*]carbazole (3j). The product was prepared following the general procedure using compound **6a** (100 mg, 0.256 mmol) and 2-aminonaphthalene (40 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **3j** (98 mg, 42 %) as a white solid; mp. 220-222 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.18 (d, *J* = 1.9 Hz, 1H), 8.11 (dd, *J* = 4.3, 3.4 Hz, 3H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.34 (dd, *J* = 4.4, 0.8 Hz, 4H), 7.25 – 7.19 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.95, 137.57, 135.86, 132.74, 130.05, 129.21, 125.86, 125.68, 125.21, 124.52, 123.13, 121.15, 120.80, 120.55, 120.28, 119.60, 119.24, 119.12, 118.30, 112.11, 109.90; IR (ATR, cm^{-1}): ν = 3417 (w), 3045 (w), 2918 (w), 2848 (w), 1593 (m), 1514 (m), 1495 (s), 1477 (m), 1464 (m), 1450 (s), 1417 (m), 1385 (m), 1358 (m), 1335 (m), 1313 (m), 1304 (m), 1281 (m), 1230 (s), 1205 (m), 1169 (m),

1157 (m), 1146 (m), 1117 (m), 1105 (m), 806 (s), 748 (vs), 723 (s), 687 (m), 650 (m), 604 (m), 565 (m), 550 (m); GC-MS (EI, 70 eV): m/z (%) = 382 (100), 216 (6), 190 (25); HRMS (ESI): calcd. for $C_{28}H_{19}N_2$ ([M + H]$^+$): 383.15428; found: 383.15362; calcd. for $C_{28}H_{18}N_2Na$ ([M + Na]$^+$): 405.13622; found: 405.13638.

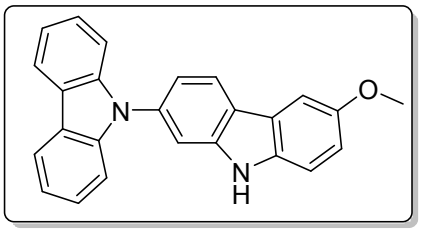


9*H*-2,9'-Biscarbazole (7a). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and aniline (26 μL, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7a** (65 mg, 77 %) as a white solid; mp. 298-300 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 10.61 (s, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.29 – 8.20 (m, 3H), 7.78 – 7.72 (m, 1H), 7.61 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.50 – 7.38 (m, 6H), 7.33 – 7.23 (m, 3H); ^{13}C NMR (63 MHz, acetone-d_6) δ 142.28, 141.82, 141.72, 135.91, 126.95, 126.89, 124.14, 123.66, 123.52, 122.23, 121.18, 121.11, 120.72, 120.28, 118.82, 112.02, 110.76, 110.47; IR (ATR, cm^{-1}): ν = 3414 (m), 3053 (w), 2926 (w), 1603 (m), 1489 (m), 1460 (m), 1450 (s), 1441 (s), 1362 (m), 1336 (m), 1321 (m), 1230 (s), 1201 (m), 1157 (m), 1095 (m), 999 (m), 978 (m), 937 (m), 918 (m), 849 (m), 818 (m), 752 (s), 742 (s), 723 (vs), 663 (s), 631 (m), 615 (m), 565 (s); GC-MS (EI, 70 eV): m/z (%) = 332 (100), 166 (16); HRMS (EI): calcd. for $C_{24}H_{16}N_2$ ([M]$^+$): 332.13080; found: 332.13106.

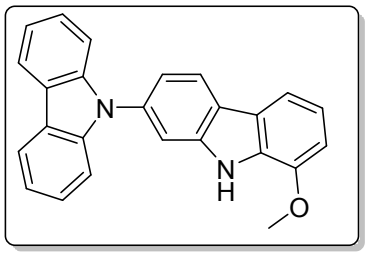


6-Nitro-9*H*-2,9'-biscarbazole (7b). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-nitroaniline (39 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:3) to yield **7b** (61 mg, 63 %) as a red solid; mp. 310-312 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.25 (s, 1H), 9.29 (d, *J* = 2.3 Hz, 1H), 8.66 (d, *J* = 8.3 Hz, 1H), 8.36 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.28 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 1.5 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.57 – 7.39 (m, 5H), 7.39 – 7.25 (m, 2H) ; ^{13}C NMR (63 MHz, DMSO-d_6) δ 144.02, 141.82, 140.47, 140.28, 135.81, 126.29, 122.92, 122.76, 121.97, 121.82, 121.56, 120.54, 120.10, 119.04, 117.68, 111.45, 110.14, 109.76; IR (ATR, cm^{-1}): ν = 3348 (m), 3059 (w), 2916 (w), 1610 (s), 1593 (m), 1583 (m), 1506 (s), 1477 (s), 1464 (m), 1450 (s), 1365 (m), 1331 (s), 1319 (s), 1309 (s), 1279 (s), 1248 (s), 1228 (s), 1196 (m),

1159 (s), 1124 (s), 1099 (s), 1084 (s), 1028 (m), 1014 (m), 1003 (m), 982 (m), 916 (m), 893 (m), 866 (m), 849 (m), 841 (m), 823 (s), 748 (vs), 725 (vs), 692 (s), 663 (s), 636 (m), 627 (m), 615 (m), 584 (s), 573 (s), 565 (s), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 377 (100), 331 (34), 281 (4), 189 (8), 173 (26); HRMS (ESI): calcd. for $C_{24}H_{15}O_2N_3Na$ ([M + Na]$^+$): 400.10565; found: 400.10564.

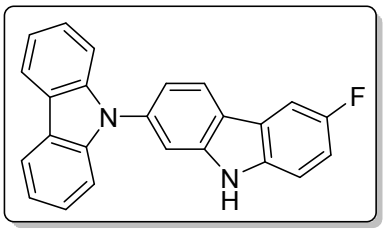


6-Methoxy-9*H*-2,9'-biscarbazole (7c). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and *p*-anisidine (35 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **7c** (47 mg, 51 %) as a white solid; mp. 225-227 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 10.42 (s, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.27 – 8.20 (m, 2H), 7.80 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 1.5 Hz, 1H), 7.56 – 7.25 (m, 9H), 7.12 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (63 MHz, acetone-d_6) δ 155.14, 142.32, 142.25, 136.59, 135.74, 126.86, 124.11, 123.56, 122.28, 121.10, 120.69, 118.31, 116.35, 112.71, 110.76, 110.48, 103.79, 56.15; IR (ATR, cm^{-1}): ν = 3415 (m), 3053 (w), 2993 (w), 1608 (m), 1589 (m), 1489 (s), 1471 (m), 1462 (m), 1448 (s), 1427 (s), 1335 (m), 1319 (m), 1308 (m), 1288 (s), 1252 (m), 1225 (s), 1217 (s), 1201 (s), 1169 (s), 1159 (s), 1126 (m), 1115 (m), 1095 (m), 1030 (s), 1012 (m), 1003 (m), 980 (m), 914 (m), 906 (m), 895 (m), 860 (m), 850 (m), 837 (s), 822 (m), 804 (vs), 775 (m), 754 (vs), 744 (vs), 725 (vs), 708 (s), 663 (s), 652 (m), 615 (m), 606 (s), 588 (m), 565 (m), 553 (m), 528 (s); GC-MS (EI, 70 eV): m/z (%) = 362 (100), 347 (21), 330 (14), 290 (6), 207 (6), 159 (68), 145 (29), 133 (15); HRMS (EI): calcd. for $C_{25}H_{18}N_2O$ ([M]$^+$): 362.14136; found: 362.14150.

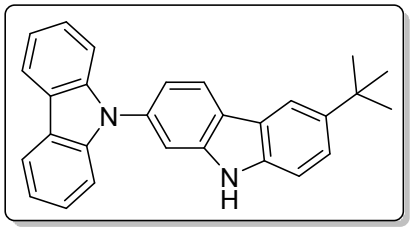


8-Methoxy-9*H*-2,9'-biscarbazole (7d). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and *o*-anisidine (32 µL, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **7d** (75 mg, 81 %) as a white solid; mp. 269-270 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 2H), 8.19 (ddd, *J* = 9.5, 7.7, 4.7 Hz, 6H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 1.4 Hz, 2H), 7.51 – 7.37 (m, 10H), 7.34 – 7.20 (m, 9H), 7.01 – 6.94 (m, 2H), 4.05 (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 145.75, 141.38, 139.72,

135.26, 130.49, 125.88, 123.92, 123.26, 123.04, 121.61, 120.37, 120.25, 119.76, 118.83, 112.86, 109.93, 109.70, 106.29, 55.58; IR (ATR, cm^{-1}): ν = 3412 (m), 3055 (w), 2931 (w), 2839 (w), 1614 (w), 1579 (m), 1504 (m), 1450 (s), 1433 (s), 1381 (m), 1365 (m), 1335 (m), 1323 (m), 1313 (m), 1306 (m), 1269 (m), 1259 (m), 1240 (m), 1230 (s), 1188 (w), 1155 (m), 1093 (m), 1063 (w), 1016 (s), 980 (w), 931 (w), 918 (m), 893 (w), 868 (w), 847 (m), 823 (m), 781 (m), 746 (vs), 723 (s), 685 (m), 665 (m), 617 (m), 577 (m), 563 (m), 555 (m), 536 (m); GC-MS (EI, 70 eV): m/z (%) = 362 (100), 347 (7), 319 (27), 181 (7), 159 (10); HRMS (ESI): calcd. for $C_{25}H_{19}N_2O$ ($[M + H]^+$): 363.14919; found: 363.14883; calcd. for $C_{25}H_{18}N_2O$ Na ($[M + Na]^+$): 385.13113; found: 385.13157.

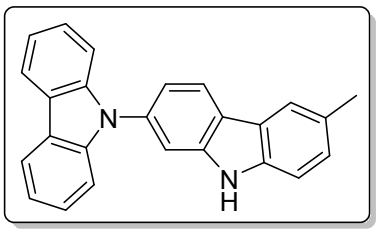


6-Fluoro-9*H*-2,9'-biscarbazole (7e). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-fluoroaniline (27 µL, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7e** (56 mg, 63 %) as a white solid; mp. 274-276 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 2H), 8.08 (dd, *J* = 9.4, 2.6 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.57 (dd, *J* = 8.9, 4.4 Hz, 1H), 7.49 – 7.24 (m, 8H); ^{19}F NMR (282 MHz, DMSO-d_6) δ -124.46 (s); ^{13}C NMR (63 MHz, DMSO) δ 156.61 (d, *J* = 232.4 Hz), 141.35, 140.55, 136.91, 134.71, 126.17, 122.61, 122.53 (d, *J* = 10.4 Hz), 122.09, 121.55 (d, *J* = 4.2 Hz), 120.47, 119.89, 117.28, 113.61 (d, *J* = 25.1 Hz), 112.08 (d, *J* = 9.3 Hz), 109.72, 109.40, 105.98 (d, *J* = 23.8 Hz); IR (ATR, cm^{-1}): ν = 3412 (m), 3051 (w), 2918 (w), 1610 (m), 1593 (m), 1585 (m), 1487 (m), 1464 (m), 1450 (s), 1362 (m), 1336 (m), 1317 (m), 1282 (m), 1271 (m), 1248 (m), 1230 (s), 1169 (s), 1157 (s), 1122 (m), 1111 (m), 1095 (m), 1053 (m), 1024 (m), 1014 (m), 999 (m), 978 (m), 935 (m), 912 (m), 860 (m), 849 (m), 816 (s), 800 (m), 779 (m), 750 (vs), 723 (vs), 710 (s), 663 (s), 654 (m), 638 (m), 615 (m), 594 (s), 575 (m), 563 (s), 540 (m), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 350 (100), 175 (11), 157 (6); HRMS (EI): calcd. for $C_{24}H_{15}FN_2$ ($[M]^+$): 350.12138; found: 350.12096.

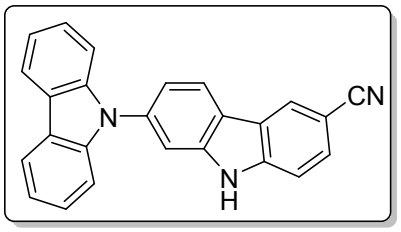


6-(*tert*-Butyl)-9*H*-2,9'-biscarbazole (7g). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-(*tert*-butyl)aniline (45 µL, 0.281

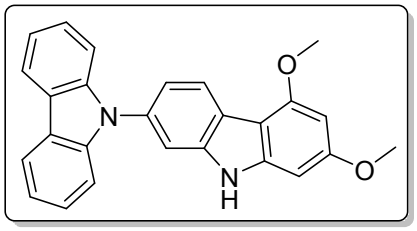
mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7g** (60 mg, 60 %) as a white solid; mp. 238-239 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.36 (s, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.26 (dd, *J* = 13.1, 4.6 Hz, 3H), 7.67 (d, *J* = 1.6 Hz, 1H), 7.62 – 7.40 (m, 6H), 7.38 – 7.26 (m, *J* = 11.4, 6.7, 2.9 Hz, 3H), 1.45 (s, 10H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 141.59, 140.71, 140.67, 138.62, 133.89, 126.18, 123.85, 122.62, 122.17, 121.84, 121.42, 120.50, 119.86, 117.00, 116.33, 110.65, 109.74, 109.07, 34.45, 31.87; IR (ATR, cm^{-1}): ν = 3400 (m), 3080 (w), 3051 (w), 3020 (w), 2956 (m), 2899 (w), 2866 (w), 1608 (m), 1500 (m), 1477 (m), 1462 (m), 1450 (s), 1429 (m), 1381 (w), 1363 (m), 1331 (m), 1313 (m), 1294 (m), 1279 (w), 1255 (m), 1246 (m), 1232 (s), 1207 (w), 1155 (m), 1140 (m), 1117 (w), 980 (w), 928 (w), 918 (w), 889 (w), 839 (m), 812 (s), 746 (vs), 723 (s), 702 (w), 665 (s), 634 (s), 615 (m), 565 (m); GC-MS (EI, 70 eV): m/z (%) = 388 (100), 373 (79), 332 (13), 207 (12), 187 (16), 172 (32), 41 (10); HRMS (EI): calcd. for $C_{28}H_{24}N_2$ ([M]$^+$): 388.19340; found: 388.19264.



6-Methyl-9*H*-2,9'-biscarbazole (7h). The product was prepared following general procedure using compound **6b** (100 mg, 0.256 mmol) and *p*-toluidine (31 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:10) to yield **7h** (45 mg, 51 %) as a white solid; mp. 287-289 °C; ^{1}H NMR (250 MHz, DMSO-d_6) δ 11.36 (s, 2H), 8.29 (dd, *J* = 14.4, 8.0 Hz, 7H), 8.01 (s, 2H), 7.64 (d, *J* = 1.6 Hz, 2H), 7.45 (dd, *J* = 8.4, 3.6 Hz, 11H), 7.40 – 7.20 (m, 10H), 2.49 (s, 1H); ^{13}C NMR (63 MHz, DMSO-d_6) δ 140.70, 140.64, 138.77, 134.06, 127.79, 127.38, 126.23, 122.65, 122.27, 121.75, 121.44, 120.53, 120.17, 119.91, 117.11, 110.95, 109.81, 109.15, 21.18; IR (ATR, cm^{-1}): ν = 3417 (m), 3047 (w), 2916 (w), 2850 (w), 1608 (m), 1595 (m), 1504 (m), 1489 (m), 1477 (m), 1450 (s), 1377 (m), 1362 (m), 1335 (m), 1315 (m), 1304 (m), 1294 (m), 1277 (m), 1244 (m), 1230 (s), 1174 (m), 1155 (m), 1146 (m), 1134 (m), 1120 (m), 1095 (m), 1039 (m), 1024 (m), 980 (m), 935 (m), 916 (m), 876 (m), 860 (m), 847 (m), 818 (m), 804 (s), 750 (vs), 723 (vs), 663 (s), 654 (m), 638 (m), 615 (m), 584 (s), 563 (s), 532 (m); GC-MS (EI, 70 eV): m/z (%) = 346 (100), 330 (9), 173 (9); HRMS (EI): calcd. for $C_{25}H_{18}N_2$ ([M]$^+$): 346.14645; found: 346.14639.



9*H*-[2,9'-Biscarbazole]-6-carbonitrile (7i). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 4-aminobenzonitrile (33 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:5) to yield **7i** (19 mg, 21 %) as a white solid; mp. 297-299 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.06 (s, 1H), 8.83 (d, *J* = 1.1 Hz, 1H), 8.52 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 2H), 7.85 – 7.77 (m, 2H), 7.77 – 7.69 (m, 1H), 7.55 – 7.38 (m, 5H), 7.38 – 7.25 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.47, 141.05, 140.52, 135.54, 128.98, 126.29, 125.91, 122.74, 122.49, 122.37, 121.00, 120.56, 120.48, 120.08, 118.74, 112.35, 109.86, 109.77, 100.84; IR (ATR, cm^{-1}): ν = 3284 (w), 3059 (w), 2918 (w), 2848 (w), 2229 (m), 1603 (s), 1477 (s), 1450 (s), 1435 (m), 1396 (m), 1365 (m), 1335 (s), 1319 (m), 1308 (m), 1288 (m), 1254 (s), 1228 (s), 1200 (m), 1155 (m), 1146 (m), 1132 (m), 1120 (m), 1097 (m), 1016 (m), 1003 (m), 914 (m), 899 (m), 885 (m), 847 (m), 816 (s), 810 (s), 748 (vs), 723 (s), 663 (m), 629 (s), 615 (s), 592 (m), 575 (m), 563 (m), 544 (m), 528 (m); GC-MS (EI, 70 eV): m/z (%) = 357 (100), 281 (9), 253 (8), 207 (29), 191 (15), 178 (48), 164 (15), 97 (10); HRMS (EI): calcd. for $C_{25}H_{15}N_3$ ([M]$^+$): 357.12605; found: 357.12555.



5,7-Dimethoxy-9*H*-2,9'-bicarbazole (7j). The product was prepared following the general procedure using compound **6b** (100 mg, 0.256 mmol) and 3,5-dimethoxyaniline (43 mg, 0.281 mmol). The product was purified by flash chromatography (silica gel, ethylacetate/heptane = 1:4) to yield **7j** (47 mg, 47 %) as a white solid; mp. 282-284 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.39 (dd, *J* = 11.6, 8.0 Hz, 3H), 6.73 (d, *J* = 1.6 Hz, 1H), 6.66 – 6.51 (m, 4H), 6.48 – 6.37 (m, 3H), 5.82 (d, *J* = 1.8 Hz, 1H), 5.55 (d, *J* = 1.8 Hz, 1H), 3.18 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (63 MHz, DMSO-d_6) δ 160.12, 156.02, 142.54, 140.72, 139.47, 132.01, 126.09, 122.48, 121.97, 121.46, 120.42, 119.72, 117.48, 109.68, 108.47, 105.32, 90.99, 87.21, 55.48, 55.42; IR (ATR, cm^{-1}): ν = 3398 (s), 3003 (w), 2968 (w), 2933 (m), 2918 (m), 2839 (m), 1628 (m), 1606 (s), 1585 (s), 1574 (m), 1514 (m), 1502 (m), 1477 (m), 1446 (s), 1427 (s), 1360 (m), 1333 (m), 1315 (s), 1306 (s), 1279 (s), 1234 (s), 1223 (m), 1205 (s), 1198 (s), 1147 (s), 1124 (s), 1117

(s), 1095 (m), 1049 (s), 1020 (m), 1011 (m), 997 (m), 991 (m), 980 (m), 947 (m), 933 (m), 920 (m), 874 (m), 850 (m), 820 (m), 804 (vs), 789 (m), 756 (vs), 744 (s), 727 (vs), 690 (m), 665 (s), 644 (m), 633 (m), 615 (m), 598 (m), 582 (m), 569 (m), 550 (m); GC-MS (EI, 70 eV): m/z (%) = 392 (100), 377 (17), 349 (6), 334 (22), 196 (10); HRMS (ESI): calcd. for $C_{26}H_{21}N_2O_2$ ($[M + H]^+$): 393.15975; found: 393.15893; calcd. for $C_{26}H_{21}N_2O_2Na$ ($[M + Na]^+$): 415.1417; found: 415.14089.