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

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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, Tf₂O (13.0 g, 46 mmol) was slowly added at 0 °C. The reaction was stirred at 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 NaHCO₃ and brine. The organic layer was dried over MgSO₄, 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 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.48 – 7.26 (m, 8H); ¹⁹F NMR (282 MHz, CDCl₃) δ -74.38 (s); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₄H₈O₆F₆S₂ ([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$_2$dba$_3$ (23 mg, 0.026 mmol), XantPhos (59 mg, 0.102 mmol), and K$_3$PO$_4$ (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$_3$) $\delta$ 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$_3$) $\delta$ 159.02, 141.53, 130.47, 128.73, 125.98, 123.25, 120.39, 119.78, 115.78, 115.21, 109.83, 55.75; IR (ATR, cm$^{-1}$): $\nu$ = 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$_3$) $\delta$ 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$_3$) $\delta$ 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), 1861 (vw), 1593 (s), 1576 (m), 1495 (s), 1477 (s), 1450 (s), 1362 (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 BBr₃ (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 icedcold aqueous solution of NaHCO₃. The aqueous layer was extracted with DCM three times. The organic residue was dried over MgSO₄, 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; ¹H NMR (300 MHz, CDCl₃) 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). ¹³C NMR (63 MHz, CDCl₃) 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 C₁₈H₁₄ON ([M + H]+): 260.10699; found: 260.10686; calcd. for C₁₈H₁₃ONa ([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; ¹H NMR (250 MHz, CDCl₃) δ 8.09 – 8.03 (m, 2H, ArH), 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); ¹³C NMR (63 MHz, CDCl₃) 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\(^{-1}\)): \(\nu = 3537\) (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), 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 N-(4- trifluoromethanesulfonate)carbazole (6a).**

\[
\begin{align*}
\text{N} \quad \text{OH} & \quad + \quad \text{Pyridine} \\
\text{N} \quad \text{OTf} & \quad \text{CH}_2\text{Cl}_2, 0^\circ\text{C}
\end{align*}
\]

To solution of 5a (239 mg, 0.921 mmol) in DCM was added pyridine (298 µL, 3.690 mmol) under Argon atmosphere. Then, Tf\(_2\)O (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 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) -72.65 (s); \(^13\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 147.99, 140.64, 138.12, 128.89, 126.40, 123.82, 123.19, 120.72, 120.65, 109.59; IR (ATR, cm\(^{-1}\)): \(\nu = 3063\) (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_{3}N_{3}F_{3}S ([M]^{+}): 391.04845; found: 391.04852.

\[ \text{N-(3-Trifluoromethanesulfonyl)carbazole (6b).} \]
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 °C, \[^1\text{H} \text{NMR (300 MHz, CDCl}_3 \text{)} \delta 7.97 \text{ (dt, } J = 7.7, 1.0 \text{ Hz, 2H)}, 7.50 \text{ (dd, } J = 6.4, 4.6 \text{ Hz, 2H)}, 7.38 \text{ (t, } J = 2.0 \text{ Hz, 1H}), 7.29 – 7.24 \text{ (m, 4H)}, 7.16 \text{ (ddd, } J = 9.6, 8.1, 7.2 \text{ Hz, 3H)} \]. \[^{19}\text{F} \text{NMR (282 MHz, CDCl}_3 \text{)} \delta -72.63 \text{ (s)} \]. \[^{13}\text{C} \text{NMR (75 MHz, CDCl}_3 \text{)} \delta 150.33, 140.40, 139.83, 131.53, 126.90, 126.51, 123.92, 120.90, 120.67, 120.32, 120.14, 109.56; IR (ATR, cm}^{-1} \text{): } \nu = 3072 \text{ (w), 3047 \text{ (w), 3024 \text{ (w), 1605 \text{ (m), 1585 \text{ (w), 1574 \text{ (w), 1495 \text{ (s), 1483 \text{ (s), 1454 \text{ (s), 1417 \text{ (vs), 1404 \text{ (m), 1365 \text{ (m), 1335 \text{ (m), 1315 \text{ (m), 1250 \text{ (m), 1230 \text{ (m), 1209 \text{ (vs), 1184 \text{ (s), 1163 \text{ (m), 1136 \text{ (s), 1119 \text{ (s), 1095 \text{ (s), 1084 \text{ (m), 1028 \text{ (m), 1003 \text{ (w), 984 \text{ (s), 964 \text{ (w), 924 \text{ (m), 904 \text{ (m), 877 \text{ (s), 847 \text{ (m), 798 \text{ (s), 771 \text{ (m), 764 \text{ (m), 750 \text{ (vs), 741 \text{ (s), 725 \text{ (s), 692 \text{ (s), 660 \text{ (m), 636 \text{ (m), 623 \text{ (m), 606 \text{ (s), 567 \text{ (s), 536 \text{ (m); GC-MS (EI, 70 eV): } m/z \text{ (%) = 391 (100), 258 (57), 230 (58), 228 (42), 202 (12), 69 (13); HRMS (EI): calcd. for C_{19}H_{12}O_{3}N_{3}F_{3}S ([M]^{+}): 391.04845; found: 391.04816.} \]

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

\[ \text{9H-3,9'-Biscarbazole (3a).} \]
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 \textit{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$_3$) $\delta$ 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$_3$) $\delta$ 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$^{-1}$): $\nu$ = 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-9H-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$_6$) $\delta$ 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$_6$) $\delta$ 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$^{-1}$): $\nu$ = 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$_2$N$_3$ ([M + H]$^+$): 378.1237; found: 378.1237; calcd. for C$_{24}$H$_{15}$O$_2$N$_3$Na ([M + Na]$^+$): 400.10565; found: 400.10522.
6-Fluoro-9H-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\(_6\)) \(\delta\) 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). \(^1\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 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\(^{-1}\)): \(\nu = 3394\) (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), 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\(_2\)Na ([M + Na]\(^+\)): 373.11115; found: 373.11065.

6-Methoxy-9H-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\(_6\)) \(\delta\) 11.46 (s, 1H), 8.31 (dd, \(J = 27.7, 5.5\) Hz, 2H), 7.40 (ddddd, \(J = 44.2, 15.9, 8.1, 1.5\) Hz, 8H), 7.08 (dd, \(J = 8.8, 2.5\) Hz, 1H), 3.81 (s, 3H); \(^1\)C NMR (75 MHz, DMSO-d\(_6\)) \(\delta\) 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\(^{-1}\)): \(\nu = 3417\) (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),
5.7-Dimethoxy-9H-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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(^{-1}\)): \(\nu = 3400\) (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\(_2\)O\(_2\) ([M + H]\(^+\)): 393.15975; found: 393.1595; calcd. for C\(_{26}\)H\(_{20}\)N\(_2\)O\(_2\)Na ([M + Na]\(^+\)): 415.1417; found: 415.14155.

6-Methyl-9H-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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(^{-1}\)): \(\nu = 3410\) (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), 478 (s), 462 (s), 414 (s), 382 (s), 360 (s), 342 (s), 320 (s).
(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$_2$Na ([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$_3$) $\delta$ 8.28 – 7.87 (m, 4H), 7.60 – 7.05 (m, 10H), 1.34 (s, 9H); $^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 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$^{-1}$): $\nu$ = 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-(9H-Carbazol-9-yl)-11H-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$_3$) $\delta$ 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$_3$) $\delta$ 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$^{-1}$): $\nu$ = 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_{2}Na ([M + Na]^{+}): 405.13622; found: 405.13638.

9H-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\(_6\)) \(\delta\) 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\(_6\)) \(\delta\) 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\(^{-1}\)): \(\nu\) = 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-9H-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\(_6\)) \(\delta\) 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\(_6\)) \(\delta\) 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\(^{-1}\)): \(\nu\) = 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), 1178 (m), 1157 (m), 1105 (m), 1058 (m), 1042 (s), 1017 (m), 949 (m), 870 (m), 849 (m), 806 (s), 752 (s), 742 (s), 723 (vs), 694 (m), 646 (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-Methoxy-9H-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; 1H NMR (300 MHz, acetone-\text{d}_6) \delta 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); 13C NMR (63 MHz, acetone-\text{d}_6) \delta 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\(^{-1}\)): \(\nu = 3415\) (m), 3053 (w), 2993 (w), 1608 (m), 1589 (m), 1548 (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 (69), 145 (29), 133 (15); HRMS (EI): calcd. for C\(_{25}\)H\(_{18}\)N\(_2\)O ([M]\(^+\)): 362.14136; found: 362.14150.

8-Methoxy-9H-2,9'-biscarbazole (7d). The product was prepared following the general procedure using compound 6b (100 mg, 0.256 mmol) and o-anisidine (32 \(\mu\)L, 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; 1H NMR (300 MHz, CDCl\(_3\)) \delta 8.40 (s, 2H), 8.19 (dd, 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); 13C NMR (63 MHz, CDCl\(_3\)) \delta 145.75, 141.38, 139.72,
135.26, 130.49, 125.88, 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 (s), 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), 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 C₂₅H₁₉N₂O ([M + H]⁺): 363.14919; found: 363.14883; calcd. for C₂₅H₁₈N₂O Na ([M + Na]⁺): 385.13113; found: 385.13157.

6-Fluoro-9H-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; ¹H NMR (300 MHz, DMSO-d₆) 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); ¹⁹F NMR (282 MHz, DMSO-d₆) δ -124.46 (s); ¹³C 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 C₂₅H₁₉FN₂ ([M⁺]): 350.12138; found: 350.12096.

6-(tert-Butyl)-9H-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; ^1H 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); ^13C 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-9H-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; ^1H 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); ^13C 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.
**9H-[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$_6$) $\delta$ 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$_6$) $\delta$ 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$^{-1}$): $\nu$ = 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), 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]$^+$): 357.1265; found: 357.1255.

**5,7-Dimethoxy-9H-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$_6$) $\delta$ 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$_6$) $\delta$ 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$^{-1}$): $\nu$ = 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_{2}O_{2} ([M + H]^+): 393.15975; found: 393.15893; calcd. for C_{26}H_{21}N_{2}O_{2}Na ([M + Na]^+): 415.1417; found: 415.14089.