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Supplementary Information

Transition-metal-free and organic solvent-free conversion of N-substituted 2-aminobiaryls into corresponding carbazoles *via* intramolecular oxidative radical cyclization induced by peroxodisulfate

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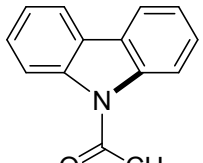
Experimental Section

General Aspects

All commercial chemicals, reagents and some precursors **A1** and **A23-A27** were used as received. All reactions were carried out in Schlenk-tubes filled with nitrogen. All reactions were carried out under nitrogen gas atmosphere using standard Schlenk techniques. All solvents and water were double-distilled and de-aerated prior to use. Reactions were monitored by analytical thin layer chromatography on silica gel with visualization under UV light. Column chromatography was carried out on silica gel using 60-120 mesh powder. NMR spectra were recorded using a 300 MHz spectrometer in deuterated solvents. IR spectra were recorded on a Nicolet Nexus FTIR spectrometer and only major peaks are reported in cm^{-1}. All melting points were measured on a PERFIT melting point apparatus and uncorrected.

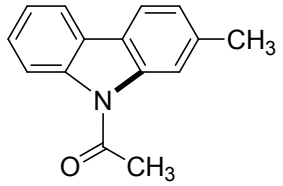
General procedure for the synthesis of N-substituted carbazoles

N-substituted 2-aminobiaryls (1.0 equiv.), $Na_2S_2O_8$ (2.0 equiv.) and TBAB (5.0 equiv.) were added into an oven-dried Schlenk-tube. The tube was evacuated and backfilled with nitrogen (3 times). Then, water (3 mL/ mmol) was injected into the tube by syringe and sealed with a Teflon lined cap. Resultant mixture was vigorously stirred under reflux for 1.5-2 h. Subsequently, the mixture was cooled and the organic matters were precipitated by saturation with NaCl and purified by recrystallization using aqueous ethanol solution. The purity of the compound was confirmed by melting point, IR and NMR measurements, vide infra.



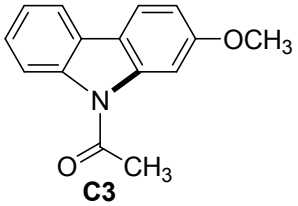
C1

1-(9H-carbazol-9-yl)ethanone (**C1**): Yield 93%; m.p. 109-111 ˚C (lit. m.p. 110-112 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 8.05-7.99 (m, 2H), 7.54-7.48 (m, 2H), 7.45-7.39 (m, 2H), 2.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 138.4, 128.0, 126.4, 124.4, 120.4, 114.9, 28.4; IR (neat, ν cm^{-1}) 3031, 2932, 1693, 1446, 1372, 1172.



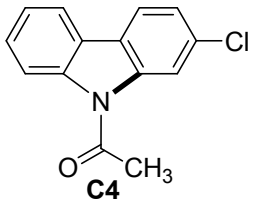
C2

1-(2-methyl-9H-carbazol-9-yl)ethanone (**C2**): Yield 86%; m.p. 85-88 ˚C (lit. m.p. 87 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 1H), 8.07 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.49-7.42 (m, 1H), 7.41-7.33 (m, 1H), 7.23 (d, J = 7.8 Hz, 1H), 2.93 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 139.3, 138.8, 137.7, 127.0, 126.8, 125.1, 124.3, 123.8, 119.9, 119.5, 116.9, 116.5, 28.1, 22.6. IR (neat, ν cm^{-1}) 3032, 2928, 1696, 1464, 1371, 1329, 1292.



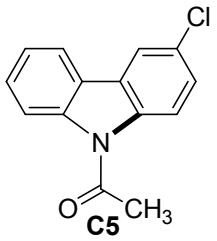
C3

1-(2-methoxy-9H-carbazol-9-yl)ethanone (**C3**): Yield 81%; m.p. 83-85 ˚C (lit. m.p. 82-84 ˚C)[3]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 1H), 7.86-7.82 (m, 2H), 7.79 (d, J = 8.6 Hz, 1H), 7.38-7.31 (m, 2H), 6.92 (dd, J = 8.6 Hz, J = 2.2 Hz, 1H), 3.86 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 159.7, 140.1, 138.5, 126.7, 125.8, 123.6, 120.2, 119.6, 119.3, 115.7, 111.4, 101.9, 55.8, 27.6; IR (neat, ν cm^{-1}) 3029, 2961, 1687, 1494, 1372, 1206, 748.



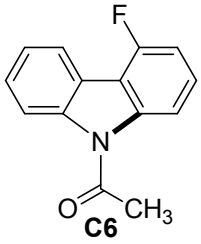
C4

1-(2-chloro-9H-carbazol-9-yl)ethanone (**C4**): Yield 89%; m.p. 110-112 ˚C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.41-7.30 (m, 2H), 2.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 139.3, 138.7, 133.3, 127.6, 125.9, 124.7, 124.4, 124.1, 120.5, 120.2, 117.1, 115.9, 27.9; IR (neat, ν cm^{-1}) 3027, 2927, 1694, 1492, 1309, 1229, 1189.



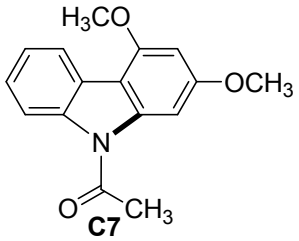
C5

1-(3-chloro-9H-carbazol-9-yl)ethanone (C5): Yield 91%; m.p. 123-124 ˚C (lit. m.p. 124-125 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 8.6 Hz, 1H), 7.94-7.85 (m, 2H), 7.53-7.45 (m, 1H), 7.44-7.35 (m, 2H), 2.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.9, 139.1, 137.2, 129.5, 128.1, 127.7, 127.4, 125.6, 123.9, 120.3, 119.7, 117.6, 116.1, 27.9; IR (neat, ν cm^{-1}) 3038, 2925, 1689, 1477, 1366, 1191.



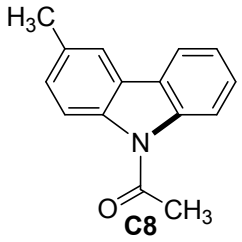
C6

1-(4-fluoro-9H-carbazol-9-yl)ethanone (**C6**): Yield 86%; m.p. 115-117 ˚C (lit. m.p. 115-116 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 8.04 (d, J = 8.4 Hz, 1H), 7.54-7.49 (m, 1H), 7.45-7.39 (m, 2H), 7.14-6.94 (m, 1H), 2.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 159.2, 157.1, 140.7, 140.5, 138.2, 128.3, 128.1, 127.7, 127.6, 124.4, 123.9, 123.8, 123.3, 123.2, 115.9, 115.1, 114.9, 112.3, 112.4, 110.2, 110.1, 27.8; IR (neat, ν cm^{-1}) 3056, 3049, 2937, 1698, 1456, 1254.



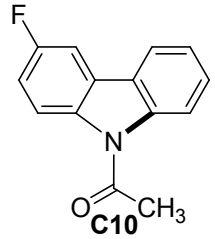
C7

1-(2,4-dimethoxy-9H-carbazol-9-yl)ethanone (**C7**): Yield 64%; m.p. 135-137 ˚C (lit. m.p. 137 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-8.21 (m, 1H), 7.97-7.81 (m, 1H), 7.56 (s, 1H), 7.36-7.33 (m, 2H), 6.52 (s, 1H), 4.01 (s, 3H), 3.97 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 160.8, 156.1, 141.0, 137.8, 126.4, 125.1, 123.9, 122.6, 115.2, 109.3, 94.9, 93.7, 56.0, 55.6, 28.1; IR (neat, ν cm^{-1}) 3040, 2962, 2943, 1698, 1457, 1288, 1218.



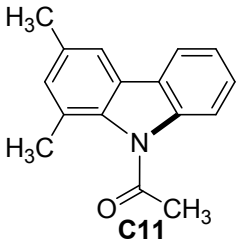
C8

1-(3-methyl-9H-carbazol-9-yl)ethanone (**C8**): Yield 88%; m.p. 110-112 ˚C (lit. m.p. 71-72 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.99-7.94 (m, 1H), 7.81 (s, 1H), 7.52-7.46 (m, 1H), 7.41-7.37 (m, 1H), 7.32 (dd, J = 8.4 Hz, J = 1.8 Hz, 1H), 2.88 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 138.2, 136.3, 132.8, 127.9, 126.5, 126.1, 125.8, 123.2, 119.5, 119.2, 115.8, 115.4, 27.2, 20.7; IR (neat, ν cm^{-1}) 3054, 2961, 2946, 1699, 1619, 1458, 1289, 1217.



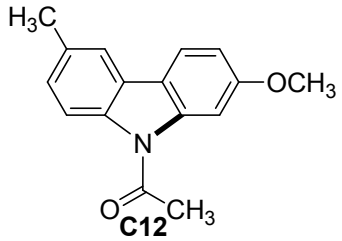
C10

1-(3-fluoro-9H-carbazol-9-yl)ethanone (**C10**): Yield 89%; m.p. 110-112 ˚C (lit. m.p. 107-108 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.8 Hz, J = 4.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.4 Hz, 1H), 7.66 (dd, J = 8.16 Hz, J = 2.8 Hz, 1H), 7.57-7.51 (m, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.22-7.16 (m, 1H), 2.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 160.2, 157.5, 138.6, 134.4, 127.3, 127.1, 126.9, 125.4, 125.3, 123.2, 119.7, 117.3, 117.2, 115.5, 114.2, 113.8, 105.5, 105.2, 27.2; IR (neat, ν cm^{-1}) 3049, 2973, 1698, 1567, 1432, 1273.

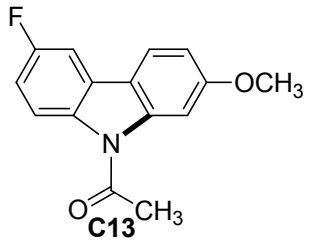


C11

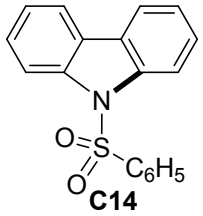
1-(1,3-dimethyl-9H-carbazol-9-yl)ethanone (**C11**): Yield 85%; m.p. 110-112 ˚C (lit. m.p. 65-66 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.59 (s, 1H), 7.47-7.41 (m, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.11 (s, 1H), 2.69 (s, 3H), 2.51 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 139.4, 136.4, 133.1, 130.5, 127.4, 126.4, 126.1, 125.5, 122.6, 119.2, 117.0, 114.0, 26.5, 20.7, 20.5; IR (neat, ν cm^{-1}) 3051, 2969, 1696, 1578, 1446, 1288.



1-(2-methoxy-6-methyl-9H-carbazol-9-yl)ethanone (**C12**): Yield 72%; m.p. 77-78 ˚C (lit. m.p. 78 ˚C)[1]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.68 (s, 2H), 7.16 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 3.93 (s, 3H), 2.85 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 159.7, 140.5, 136.7, 133.4, 127.1, 127.0, 120.3, 119.9, 119.6, 115.4, 111.6, 102.2, 55.9, 27.6, 21.4; IR (neat, ν cm^{-1}) 3059, 2917, 1688, 1428, 1371, 1321.

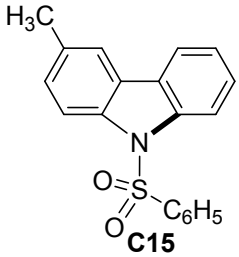


1-(6-fluoro-2-methoxy-9H-carbazol-9-yl)ethanone (**C13**): Yield 83%; m.p. 114-116 ˚C (lit. m.p. 115-116 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (dd, J = 9.0 Hz, J = 4.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 7.11 (m, 1H), 7.01 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H), 3.91 (s, 3H), 2.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0, 160.2, 159.7, 140.9, 135.0, 128.2, 120.9, 119.1, 117.1, 113.2, 111.4, 105.5, 102.1, 55.9, 27.8; IR (neat, ν cm^{-1}) 3062, 2957, 1698, 1625, 1376, 1169.



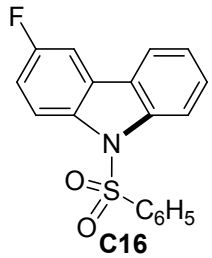
C14

9-(phenylsulfonyl)-9H-carbazole (**C14**): Yield 86%; m.p. 120-123 ˚C (lit. m.p. 120-122 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38-8.32 (m, 2H), 7.93-7.88 (m, 2H), 7.78 (dd, J = 8.4 Hz, J = 1.4 Hz, 2H), 7.53-7.47 (m, 2H), 7.48-7.43 (m, 1H), 7.39-7.32 (m, 2H), 7.31 (dd, J = 8.2 Hz, J = 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 137.9, 134.0, 129.3, 127.5, 126.4, 126.6, 124.2, 120.3, 115.1; IR (neat, ν cm^{-1}) 3027, 2924, 1439, 1378, 1177.



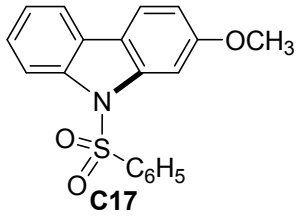
C15

3-methyl-9-(phenylsulfonyl)-9H-carbazole (**C15**): Yield 91%; m.p. 142-144 ˚C (lit. m.p. 142-145 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 7.84 (dd, J = 8.0 Hz, J = 1.0 Hz, 1H), 7.75 (dd, J = 8.2 Hz, J = 1.0 Hz, 2H), 7.62 (d, J = 1.0 Hz, 1H), 7.47-7.41 (m, 1H), 7.32-7.29 (m, 1H), 7.25-7.19 (m, 1H), 7.30-7.21 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.1, 136.6, 133.9, 133.7, 129.1, 128.8, 127.3, 126.7, 126.4, 126.6, 124.1, 120.3, 120.1, 115.4, 115.0, 21.3; IR (neat, ν cm^{-1}) 3033, 2941, 1454, 1432, 1371, 1173.



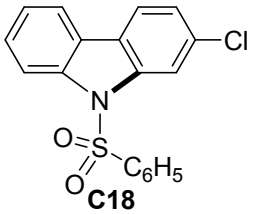
C16

3-fluoro-9-(phenylsulfonyl)-9H-carbazole (**C16**): Yield 87%; m.p. 130-132 ˚C (lit. m.p. 131-132 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 7.2 Hz, 1H), 8.18 (dd, J = 8.4 Hz, J = 3.8 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.72 (dd, J = 8.4 Hz, J = 1.6 Hz, 2H), 7.54-7.47 (m, 2H), 7.49-7.43 (m, 1H), 7.39-7.33 (m, 1H), 7.28 (dd, J = 8.4 Hz, J = 6.8 Hz, 2H), 7.24-7.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 139.4, 137.7, 134.5, 134.1, 129.1, 128.3, 127.9, 126.6, 126.1, 116.3, 115.2, 114.9, 106.3; IR (neat, ν cm^{-1}) 3036, 2924, 1596, 1443, 1377, 1169.



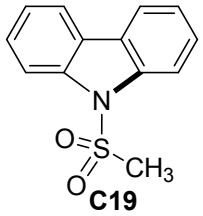
C17

2-methoxy-9-(phenylsulfonyl)-9H-carbazole (**C17**): Yield 79%; m.p. 134-136 ˚C (lit. m.p. 135-137 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (m, 1H), 7.96-7.85 (m, 3H), 7.83-7.77 (m, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.45-7.38 (m, 2H), 7.37-7.29 (m, 3H), 6.94 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 139.7, 138.4, 138.2, 134.1, 129.3, 126.4, 126.7, 126.2, 124.1, 120.3, 120.0, 119.2, 115.1, 112.2, 100.1, 56.2; IR (neat, ν cm^{-1}) 3019, 2926, 1606, 1457, 1372, 1176.



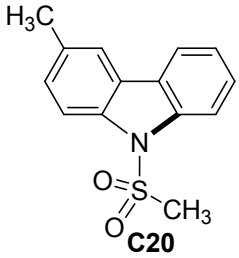
C18

2-chloro-9-(phenylsulfonyl)-9H-carbazole (**C18**): Yield 92%; m.p. 157-160 ˚C (lit. m.p. 158-159 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 2.2 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.88-7.79 (m, 4H), 7.51-7.48 (m, 2H), 7.39-7.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 138.6, 137.6, 134.3, 133.3, 129.2, 127.5, 126.7, 125.5, 125.1, 124.4, 124.5, 121.0, 120.3, 115.7, 115.3; IR (neat, ν cm^{-1}) 3021, 2924, 1598, 1453, 1417, 1174.



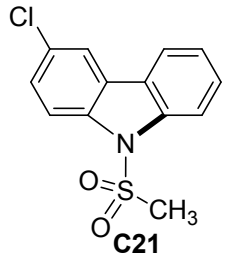
C19

9-(methylsulfonyl)-9H-carbazole (**C19**): Yield 89%; m.p. 85-88 ˚C (lit. m.p. 89 ˚C)[2]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 2H), 8.02-7.97 (m, 2H), 7.52-7.46 (m, 2H), 7.43-7.38 (m, 2H), 2.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 127.8, 126.4, 124.5, 120.4, 114.9, 38.4; IR (neat, ν cm^{-1}) 3019, 2926, 1489, 1438, 1398, 1210.



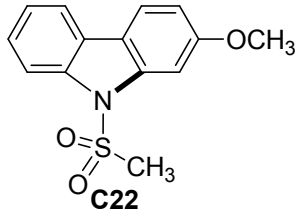
C20

3-methyl-9-(methylsulfonyl)-9H-carbazole (**C20**): Yield 94%; m.p. 122-124 ˚C (lit. m.p. 121-124 ˚C)[4]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.48-7.39 (m, 2H), 7.28 (d, J = 8.0 Hz, 1H), 2.93 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 136.4, 134.0, 128.7, 127.2, 126.4, 126.1, 124.2, 120.3, 120.1, 114.9, 114.4, 38.3, 21.2; IR (neat, ν cm^{-1}) 3016, 2926, 1484, 1441, 1382, 1219, 1154.



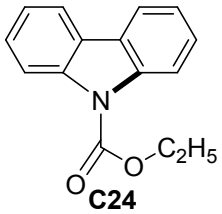
C21

3-chloro-9-(methylsulfonyl)-9H-carbazole (**C21**): Yield 85%; m.p. 146-149 ˚C (lit. m.p. 146-148 ˚C)[4]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.96-7.91 (m, 2H), 7.53-7.48 (m, 1H), 7.43-7.39 (m, 2H), 2.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 136.4, 129.8, 128.3, 127.4, 125.1, 124.2, 120.5, 120.0, 115.8, 114.7, 38.6; IR (neat, ν cm^{-1}) 3018, 2936, 1468, 1437, 1426, 1358, 1264, 1151.



C22

2-methoxy-9-(methylsulfonyl)-9H-carbazole (**C22**): Yield 81%; m.p. 114-118 ˚C (lit. m.p. 116-117 ˚C)[4]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.73-7.69 (m, 1H), 7.41-7.36 (m, 2H), 7.01 (dd, J = 8.0 Hz, J = 2.4 Hz, 1H), 3.92 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 139.4, 138.2, 126.1, 126.4, 124.2, 120.9, 119.2, 114.7, 112.6, 112.3, 99.1, 55.8, 38.5; IR (neat, ν cm^{-1}) 3015, 2968, 1496, 1457, 1438, 1427, 1356, 1268, 1164.

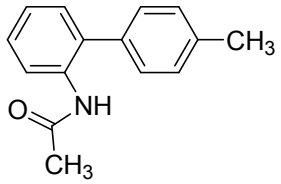


C24

Ethyl 9H-carbazole-9-carboxylate (**C24**): Yield 28%; m.p. 72-74 ˚C (lit. m.p. 73-74 ˚C)[5]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.36 (t, J = 8 Hz, 2H), 7.24 (t, J = 8 Hz, 2H), 4.52 (q, J = 6.8 Hz, 2H), 1.48 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 138.2, 127.0, 125.7, 123.1, 119.4, 116.2, 62.8, 14.3; IR (neat, ν cm^{-1}) 3032, 2944, 1742, 1446, 1367, 1209, 1171.

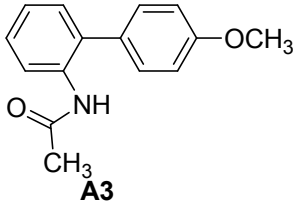
General procedure for the synthesis of 2-amidobiaryls A2-A22

The 2-amidobiaryls (**A2-A22**) were readily synthesized by utilizing the literature described method. A solution of 2-aminobiaryls (1.0 equiv.), obtained by Suzuki-cross coupling reactions, and dry pyridine (10.0 equiv.) in dry CH_2Cl_2 at 0 °C was drop wise added 3.0 equiv., of acetyl chloride (for synthesis of **A2-A13**)/benzenesulfonyl chloride (for synthesis of **A14-A18**)/ methanesulfonyl chloride (for synthesis of **A19-A22**) under nitrogen gas atmosphere. Resultant reaction mixture was stirred at room temperature for 15-18 h. Subsequently, the reaction mixture was diluted with CH_2Cl_2 and poured into saturated aqueous $NaHCO_3$ solution. The layers were separated and the organic phase was washed with water, brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated by rotary evaporation. The residue obtained was purified by silica gel column chromatography filtration to provide the desired 2-amidobiaryls. The spectroscopic characterization data were in accordance with those reported in the literature, cf. vide infra.



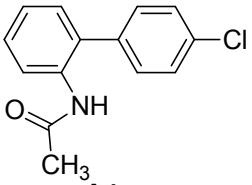
A2

N-(4'-methyl-[1,1'-biphenyl]-2-yl)acetamide (**A2**):[1] Yield 74%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 8.2 Hz, 1H), 7.42-7.33 (m, 1H), 7.31-7.26 (m, 4H), 7.25 (d, J = 7.6 Hz, 1H), 7.20-7.14 (m, 2H), 2.42 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 138.0, 135.3, 135.0, 132.4, 130.3, 130.1, 129.4, 128.3, 124.6, 121.5, 24.7, 21.4.



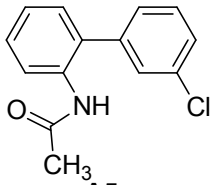
A3

N-(4'-methoxy-[1,1'-biphenyl]-2-yl)acetamide (A3):[3] Yield 89%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.2 Hz, 1H), 7.34-7.22 (m, 3H), 7.21-7.13 (m, 3H), 7.01 (d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 159.5, 134.8, 131.9, 130.4, 130.4, 130.2, 128.0, 124.2, 121.4, 114.3, 55.2, 24.4.



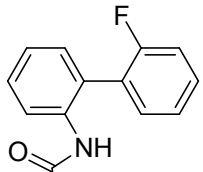
A4

N-(4'-chloro-[1,1'-biphenyl]-2-yl)acetamide (**A4**):[6] Yield 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.2 Hz, 1H), 7.45-7.38 (m, 2H), 7.39-7.31 (m, 1H), 7.30-7.24 (m, 2H), 7.20-7.16 (m, 2H), 7.01 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 136.6, 134.6, 134.1, 131.4, 130.6, 129.9, 129.2, 128.5, 124.6, 122.3, 24.5.



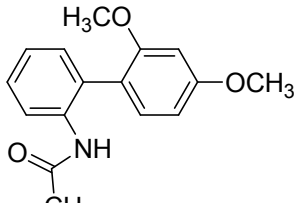
A5

N-(3'-chloro-[1,1'-biphenyl]-2-yl)acetamide (**A5**):[2] Yield 76%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.0 Hz, 1H), 7.45-7.37 (m, 4H), 7.28-7.16 (m, 3H), 7.08 (s, 1H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 140.3, 135.2, 134.9, 131.2, 130.4, 130.2, 129.6, 129.2, 128.3, 127.6, 124.9, 122.7, 24.7.



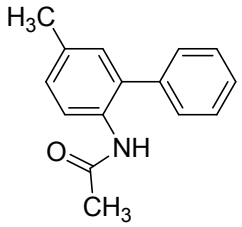
A6

N-(2'-fluoro-[1,1'-biphenyl]-2-yl)acetamide (**A6**):[1] Yield 68%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 8.2 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.39-7.18 (m, 5H), 7.04 (s, 1H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 160.6, 158.6, 135.5, 132.3, 132.3, 130.9, 130.5, 130.6, 129.4, 127.4, 125.8, 125.7, 125.2, 125.0, 124.9, 123.1, 116.5, 116.2, 24.6.



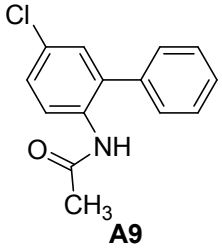
A7

N-(2',4'-dimethoxy-[1,1'-biphenyl]-2-yl)acetamide (**A7**):[1] Yield 69%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.2 Hz, 1H), 7.38-7.29 (m, 2H), 7.25-7.11 (m, 3H), 6.69-6.54 (m, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 161.2, 157.3, 135.9, 132.8, 131.4, 129.8, 128.3, 124.7, 122.4, 119.9, 105.7, 99.4, 56.1, 55.8, 24.7.



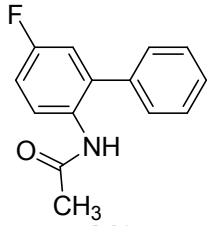
A8

N-(5-methyl-[1,1'-biphenyl]-2-yl)acetamide (**A8**):[1] Yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 1H), 7.53-7.47 (m, 2H), 7.45-7.32 (m, 3H), 7.21 (d, J = 8.3 Hz, 1H), 7.09 (s, 1H), 7.06 (s, 1H), 2.36 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 138.6, 134.4, 132.6, 132.4, 130.9, 129.6, 129.3, 129.1, 128.1, 122.2, 24.7, 21.2.



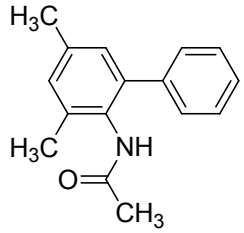
A9

N-(5-chloro-[1,1'-biphenyl]-2-yl)acetamide (**A9**):[3] Yield 73%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 8.6 Hz, 1H), 7.47-7.24 (m, 3H), 7.31-7.26 (m, 3H), 7.21 (d, J = 2.4 Hz, 1H), 7.09 (s, 1H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 136.6, 133.7, 133.4, 129.9, 129.3, 129.2, 129.0, 128.5, 128.2, 122.9, 24.4.



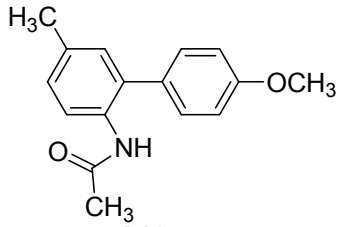
A10

N-(5-fluoro-[1,1'-biphenyl]-2-yl)acetamide (**A10**):[1] Yield 69%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17-8.15 (m, 1H), 7.52-7.47 (m, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.0 Hz, 2H), 7.13-7.02 (m, 2H), 7.01-6.96 (m, 1H), 2.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 160.5, 158.6, 137.4, 137.3, 134.7, 134.6, 130.9, 130.7, 129.4, 129.2, 128.7, 124.2, 124.1, 117.0, 116.8, 115.2, 115.0, 24.6.



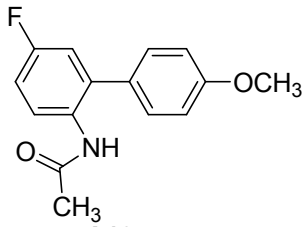
A11

N-(3,5-dimethyl-[1,1'-biphenyl]-2-yl)acetamide (**A11**):[1] Yield 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.82 (s, 2H), 5.83 (s, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 141.2, 140.6, 137.1, 136.9, 132.1, 131.1, 129.7, 128.5, 127.4, 22.1, 20.9, 18.7.



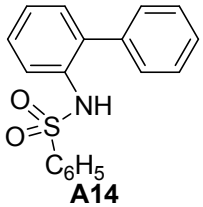
A12

N-(4'-methoxy-5-methyl-[1,1'-biphenyl]-2-yl)acetamide (**A12**):[1] Yield 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, J = 8.2 Hz, 1H), 7.28 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.2 Hz, 1H), 7.13-6.94 (m, 4H), 3.87 (s, 3H), 2.36 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 159.5, 134.2, 132.5, 132.2, 130.9, 130.8, 130.6, 128.8, 122.0, 114.7, 55.6, 24.7, 21.0.



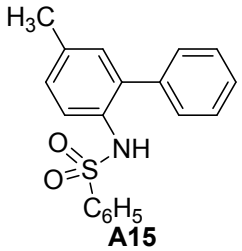
A13

N-(5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)acetamide (**A13**):[2] Yield 76%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16-8.14 (m, 1H), 7.29-7.25 (m, 2H), 7.08-7.01 (m, 4H), 6.96-6.93 (m, 1H), 3.86 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 159.8, 159.6, 159.4, 134.5, 134.4, 131.0, 130.5, 129.4, 123.9, 123.85, 116.9, 116.8, 114.8, 114.7, 55.5, 24.6.



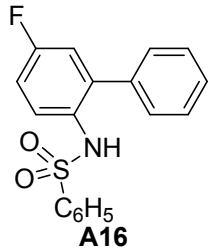
A14

N-([1,1'-biphenyl]-2-yl)benzenesulfonamide (**A14**):[2] Yield 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2 Hz, 1H), 7.57-7.50 (m, 3H), 7.41-7.29 (m, 6H), 7.15-7.13 (m, 1H), 7.11-7.09 (m, 1H), 6.82-6.78 (m, 2H), 6.59 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 137.2, 134.1, 133.6, 132.9, 130.3, 129.1, 128.9, 128.7, 128.6, 128.1, 127.2, 125.1, 121.8.



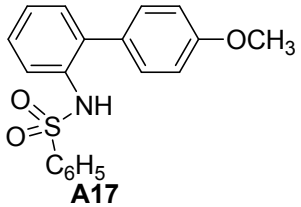
A15

N-(5-methyl-[1,1'-biphenyl]-2-yl)benzenesulfonamide (**A15**):[2] Yield 87%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 1H), 7.54-7.48 (m, 3H), 7.38-7.32 (m, 2H), 7.32-7.25 (m, 3H), 7.15-7.12 (m, 1H), 6.87 (s, 1H), 6.77-6.73 (m, 2H), 6.51 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 137.3, 134.9, 134.3, 132.7, 130.8, 130.7, 129.1, 128.9, 128.7, 127.8, 127.2, 122.1, 20.9.



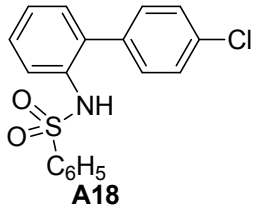
A16

N-(5-fluoro-[1,1'-biphenyl]-2-yl)benzenesulfonamide (**A16**):[2] Yield 72%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.50-7.45 (m, 2H), 7.39-7.27 (m, 5H), 7.08-7.03 (m, 1H), 6.82-6.80 (m, 1H), 6.74-6.70 (m, 2H), 6.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 158.6, 138.6, 137.0, 136.9, 136.1, 132.8, 129.4, 129.3, 128.9, 128.5, 128.2, 126.8, 124.9, 124.7, 116.9, 116.7, 115.3, 115.1.



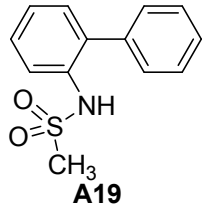
A17

N-(4'-methoxy-[1,1'-biphenyl]-2-yl)benzenesulfonamide (**A17**):[2] Yield 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 1H), 7.59-7.56 (m, 2H), 7.55-7.51 (m, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.30-7.28 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.07-7.04 (m, 1H), 6.86-6.82 (m, 2H), 6.76-6.70 (m, 2H), 6.57 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 139.2, 133.8, 133.6, 132.8, 130.4, 130.1, 129.2, 128.9, 128.3, 127.1, 125.0, 121.3, 114.5, 55.2.



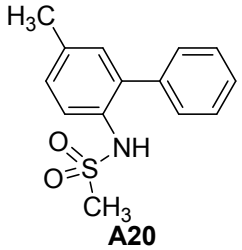
A18

N-(4'-chloro-[1,1'-biphenyl]-2-yl)benzenesulfonamide (**A18**):[2] Yield 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.66 (m, 1H), 7.58-7.50 (m, 3H), 7.38 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.27-7.25 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.05-7.03 (m, 1H), 6.75-6.72 (m, 2H), 6.42 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 135.5, 134.2, 133.4, 133.3, 132.9, 130.2, 129.2, 129.0, 128.9, 127.1, 125.3, 122.2.



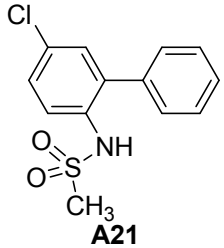
A19

N-([1,1'-biphenyl]-2-yl)methanesulfonamide (**A19**):[2] Yield 88%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 1H), 7.51-7.48 (m, 1H), 7.46-7.37 (m, 2H), 7.33-7.31 (m, 2H), 7.29-7.26 (m, 1H), 6.51 (s, 1H), 2.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 134.8, 134.1, 131.1, 130.9, 129.3, 129.2, 128.7, 128.1, 121.3, 39.5.



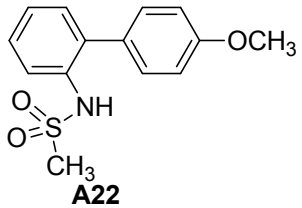
A20

N-(5-methyl-[1,1'-biphenyl]-2-yl)methanesulfonamide (**A20**):[4] Yield 81%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 8.4 Hz, 1H), 7.11 (s, 1H), 6.42 (s, 1H), 2.78 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 135.1, 133.9, 131.2, 131.1, 129.6, 129.3, 128.8, 128.2, 121.2, 39.4, 20.6.



A21

N-(5-chloro-[1,1'-biphenyl]-2-yl)methanesulfonamide (**A21**):[4] Yield 78%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 9.2 Hz, 1H), 7.54-7.41 (m, 3H), 7.38-7.34 (m, 1H), 7.33-7.26 (m, 3H), 6.44 (s, 1H), 2.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 134.9, 132.6, 130.7, 130.4, 129.6, 129.0, 128.9, 128.8, 121.6, 39.7.



A22

N-(4'-methoxy-[1,1'-biphenyl]-2-yl)methanesulfonamide (**A22**):[4] Yield 86%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.63 (m, 1H), 7.39-7.35 (m, 1H), 7.28-7.20 (m, 4H), 7.03 (d, J = 8.4 Hz, 2H), 6.52 (s, 1H), 3.84 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 134.1, 132.9, 130.8, 130.3, 129.4, 128.8, 124.8, 119.9, 114.8, 55.4, 39.5.

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