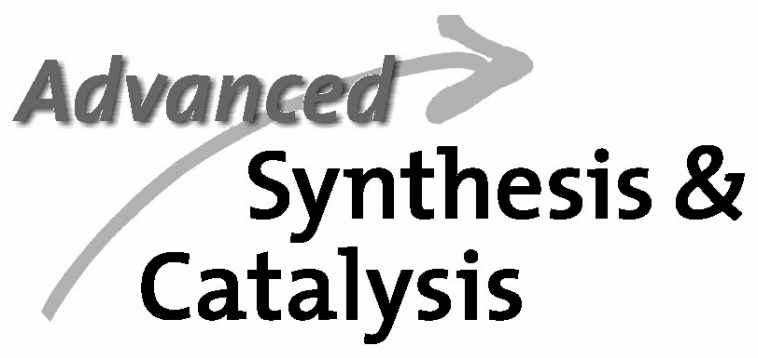

Supporting Information

Supporting Information

Suzuki-Miyaura Cross-Coupling of 2-Nitroarenediazonium Tetrafluoroborates: Synthesis of Unsymmetrical 2-Nitrobiphenyls and Highly Functionalized Carbazoles

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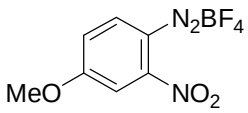
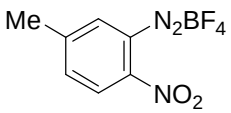
Melting points are uncorrected. All solvents and reagents were used as received from commercial sources. Analytical samples were obtained by chromatography on silica gel using an ethyl acetate-hexanes mixture as the eluent unless specified otherwise.



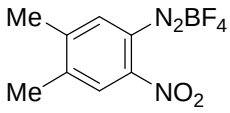
12

Preparation of 4-Methoxy-2-nitrobenzenediazonium Tetrafluoroborate (12). According to the general procedure, reaction of 4-methoxy-2-nitroaniline **11** (3.00 g, 17.8 mmol) with $BF_3{\cdot}OEt_2$ (2.71 mL, 21.4 mmol) and *tert*-butylnitrite (3.18 mL, 26.8 mmol) afforded 4.60 g (97%) of **12** as a light yellow solid: mp 82 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 4.18 (s, 3H), 7.67 (d, 1H, *J* = 8.4 Hz), 8.12 (s, 1H), 8.74 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (CD_3CN, 100 MHz) δ 97.2, 116.6, 120.6, 139.4, 148.0, 171.0.



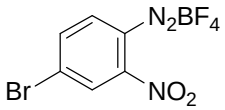
14

Preparation of 5-Methyl-2-nitrobenzenediazonium Tetrafluoroborate (14). According to the general procedure, reaction of 5-methyl-2-nitroaniline **13** (2.74 g, 18.0 mmol) with $BF_3{\cdot}OEt_2$ (2.74 mL, 21.6 mmol) and *tert*-butylnitrite (3.21 mL, 27.0 mmol) afforded 4.26 g (94%) of **14** as a tan solid: mp 80 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.64 (s, 3H), 8.29 (d, 1H, *J* = 8.6 Hz), 8.56 (d, 1H, *J* = 8.6 Hz), 8.67 (s, 1H); ^{13}C NMR (CD_3CN, 100 MHz) δ 20.7, 109.5, 128.2, 136.7, 142.9, 143.4, 150.0.



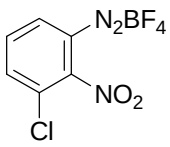
16

Preparation of 4,5-Dimethyl-2-nitrobenzenediazonium Tetrafluoroborate (16). According to the general procedure, reaction of 4,5-dimethyl-2-nitroaniline **15** (3.70 g, 22.3 mmol) with $BF_3{\cdot}OEt_2$ (3.39 mL, 26.7 mmol) and *tert*-butylnitrite (3.97 mL, 33.4 mmol) afforded 5.20 g (88%) of **16** as a tan solid: mp 95 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 2.56 (s, 3H), 2.65 (s, 3H), 8.53 (s, 1H), 8.63 (s, 1H); ^{13}C NMR (CD_3CN, 100 MHz) δ 19.4, 20.9, 105.5, 129.2, 136.3, 142.9, 148.5, 156.9.



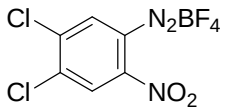
18

Preparation of 4-Bromo-2-nitrobenzenediazonium Tetrafluoroborate (18). According to the general procedure, reaction of 4-bromo-2-nitroaniline **17** (2.50 g, 11.5 mmol) with $BF_3{\cdot}OEt_2$ (1.75 mL, 13.8 mmol) and *tert*-butylnitrite (2.05 mL, 17.3 mmol) afforded 3.53 g (97%) of **18** as a tan solid: mp 130 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 8.48 (dd, 1H, *J* = 8.7 and 1.9 Hz), 8.70 (d, 1H, *J* = 8.7 Hz), 8.87 (d, 1H, *J* = 1.9 Hz); ^{13}C NMR (CD_3CN, 100 MHz) δ 109.5, 133.1, 138.0, 140.7, 141.2, 145.9.



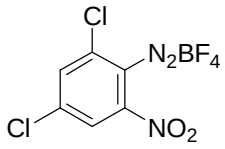
20

Preparation of 3-Chloro-2-nitrobenzenediazonium Tetrafluoroborate (20). According to the general procedure, reaction of 3-chloro-2-nitroaniline **19** (2.00 g, 11.6 mmol) with $BF_3{\cdot}OEt_2$ (1.76 mL, 13.9 mmol) and *tert*-butylnitrite (1.79 mL, 17.4 mmol) afforded 3.10 g (99%) of **20** as a tan solid: mp 129 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 8.28 (t, 1H, *J* = 8.4 Hz), 8.51 (d, 1H, *J* = 8.4 Hz), 8.86 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (CD_3CN, 100 MHz) δ 112.7, 133.4, 135.6, 136.2, 146.3.



22

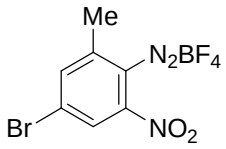
Preparation of 4,5-Dichloro-2-nitrobenzenediazonium Tetrafluoroborate (22). According to the general pro cedure, reaction of 4,5-dichloro-2-nitroaniline **21** (2.00 g, 9.66 mmol) with $BF_3{\cdot}OEt_2$ (1.47 mL, 11.6 mmol) and *tert*-butylnitrite (1.72 mL, 14.5 mmol) afforded 2.63 g (89%) of **22**[1] as a light yellow solid: mp 105 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 8.89 (s, 1H), 8.99 (s, 1H); ^{13}C NMR (CD_3CN, 100 MHz) δ 108.7, 130.2, 136.6, 141.5, 143.2, 149.2.



24

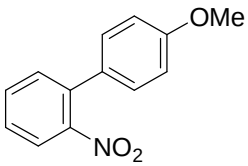
Preparation of 4,6-Dichloro-2-nitrobenzenediazonium Tetrafluoroborate (24). According to the general procedure, reaction of 4,6-dichloro-2-nitroaniline **23** (2.00 g,

9.66 mmol) with $BF_3{\cdot}OEt_2$ (1.47 mL, 11.6 mmol) and *tert*-butylnitrite (1.72 mL, 14.5 mmol) furnished 2.86 g (97%) of **24** as a yellow solid: mp 116 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 8.60 (d, 1H, *J* = 2.0 Hz), 8.81 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (CD_3CN, 100 MHz) δ 129.4, 133., 138.9, 144.2, 148.1, 151.9.



26

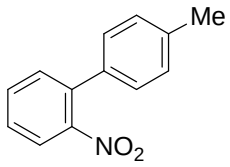
Preparation of 4-Bromo-6-methyl-2-nitrobenzenediazonium Tetrafluoroborate (26). According to the general procedure, reaction of 4-bromo-6-methyl-2-nitroaniline **25** (5.00 g, 21.6 mmol) with $BF_3{\cdot}OEt_2$ (3.29 mL, 26.0 mmol) and *tert*-butylnitrite (3.86 mL, 32.5 mmol) afforded 6.96 g (98%) of **96** as a colorless solid: mp 133 °C (decomp); ^{1}H NMR (CD_3CN, 400 MHz) δ 2.84 (s, 3H), 8.41 (s, 1H), 8.71 (s, 1H); ^{13}C NMR (CD_3CN, 100 MHz) δ 18.7, 108.5, 130.2, 138.2, 141.6, 141.7, 150.7.



28

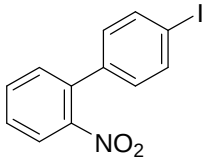
Preparation of 4-Methoxy-2-nitrobiphenyl (28). According to the general procedure, reaction of **5** (1.06 g, 4.45 mmol) and 4-methoxyphenyl boronic acid **27** in the presence of $Pd(OAc)_2$ (25 mg, 0.111 mmol) gave 720 mg (85%) of **28** as a yellow solid: mp 59-60 °C (Lit.[2] 61-62 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.84 (s, 3H), 6.97 (m, 2H), 7.27 (m, 2H), 7.44 (m, 2H), 7.58 (dd, 1H, *J* = 7.6 and 1.2 Hz), 7.80 (dd, 1H, *J* = 8.4 and 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.4, 114.3, 124.1, 127.8, 129.2, 129.6, 132.0, 132.2,

135.9, 149.5, 159.8. Anal. Calcd. For $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.91; H, 4.75; N, 5.99.



32

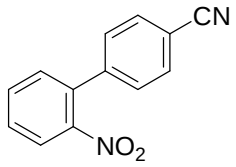
Preparation of 4'-Methyl-2-nitrobiphenyl (32). According to the general procedure, reaction of **5** (1.31 g, 4.41 mmol) and *p*-tolyl boronic acid **31** (500 mg, 3.68 mmol) in the presence of $Pd(OAc)_2$ (25 mg, 0.111 mmol) gave 729 mg (93%) of **32**[3] as an oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 3H), 7.26 (s, 4H), 7.48 (m, 2H), 7.62 (m, 1H), 7.84 (dd, 1H, *J* = 7.5 and 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 124.1, 127.9, 128.0, 129.6, 132.0, 132.3, 134.5, 136.3, 138.2, 149.4. Anal. Calcd. For $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.22; H, 5.18; N, 6.57.



34

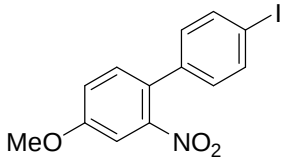
Preparation of 4'-Iodo-2-nitrobiphenyl (34). According to the general procedure, reaction of **5** (1.20 g, 4.06 mmol) and 4-iodophenyl boronic acid **33** (838 mg, 3.38 mmol) in the presence of $Pd(OAc)_2$ (23 mg, 0.101 mmol) gave 930 mg (85%) of **34** as a light yellow solid: mp 81-82 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.07 (m, 2H), 7.41 (dd, 1H, *J* = 7.6 and 1.2 Hz), 7.51 (dt, 1H, *J* = 8.0 and 1.2 Hz), 7.64 (dt, 1H, *J* = 7.6 and 1.2 Hz), 7.77 (m, 2H), 7.90 (dd, 1H, *J* = 8.0 and 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 94.4,

124.4, 128.7, 129.8, 131.8, 132.6, 135.4, 137.1, 137.9, 149.0. Anal. Calcd. For $C_{12}H_8INO_2$: C, 44.33; H, 2.48; N, 4.31. Found: C, 44.08; H, 2.41; N, 4.32.



36

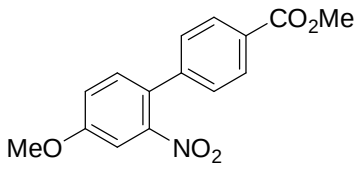
Preparation of 4'-Cyano-2-nitrobiphenyl (36). According to the general procedure, reaction of **5** (2.42 g, 8.17 mmol) and 4-cyanophenyl boronic acid **35** (1.00 g, 6.81 mmol) in the presence of $Pd(OAc)_2$ (46 mg, 0.204 mmol) gave 720 mg (85%) of **36** as a yellow solid: mp 145-146 °C (Lit.[4] 145-147 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42 (m, 3H), 7.59 (dd, 1H, *J* = 7.8 and 1.4 Hz), 7.70 (m, 3H), 7.97 (dd, 1H, *J* = 8.1 and 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 112.2, 118.5, 124.7, 128.9, 129.5, 131.8, 132.4, 133.0, 134.8, 142.6, 148.7. Anal. Calcd. For $C_{13}H_8N_2O_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.59; H, 3.57; N, 12.44.



37

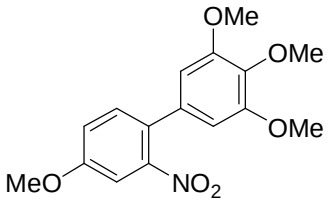
Preparation of 4'-Iodo-4-methoxy-2-nitrobiphenyl (37). According to the general procedure, reaction of **12** (1.20 g, 4.50 mmol) and 4-iodophenyl boronic acid **33** (929 mg, 3.75 mmol) in the presence of $Pd(OAc)_2$ (25 mg, 0.111 mmol) gave 1.03 g (77%) of **37** as a yellow solid: mp 124-125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.91 (s, 3H), 7.02 (d, 2H, *J* = 8.2 Hz), 7.16 (dd, 1H, *J* = 8.5 and 2.5 Hz), 7.30 (d, 1H, *J* = 8.5 Hz), 7.40 9d, 1H, *J* = 2.5 Hz), 7.43 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.1, 93.8, 109.4,

118.9, 127.6, 130.0, 132.7, 137.1, 137.8, 149.4, 159.5. Anal. Calcd. For $C_{13}H_{10}INO_3$: C, 43.97; H, 2.84; N, 3.94. Found: C, 43.86; H, 2.88; N, 3.91.



39

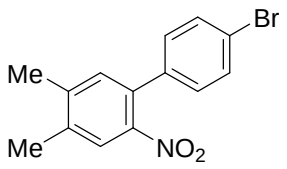
Preparation of 4'-Methoxy-2'-nitro-biphenyl-4-carboxylic acid methyl ester (39). According to the general procedure, reaction of **12** (1.96 g, 7.33 mmol) 4-methoxycarbonylphenylboronic acid **38** (1.10 g, 6.11 mmol) in the presence of $Pd(OAc)_2$ (41 mg, 0.183 mmol) gave 1.43 g (81%) of **39** as a yellow solid: mp 111-112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 3H), 3.91 (s, 3H), 7.15 (dd, 1H, *J* = 8.6 and 2.6 Hz), 7.32 (m, 3H), 7.40 (d, 1H, *J* = 2.6 Hz), 8.04 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.2, 56.0, 109.5, 118.9, 127.3, 127.7, 128.2, 129.6, 129.9, 130.2, 132.7, 142.2, 149.4, 159.7, 166.7. Anal. Calcd. For $C_{15}H_{13}NO_5$: C, 62.72; H, 4.56; N, 4.88. Found: C, 62.56; H, 4.49; N, 4.82.



41

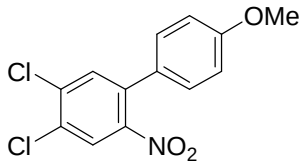
Preparation of 3,4,5,4'-Tetramethoxy-2'-nitrobiphenyl (41). According to the general procedure, reaction of **12** (1.60 g, 5.84 mmol) and 3,4,5-trimethoxyphenyl boronic acid **40** (1.03 g, 4.87 mmol) in the presence of $Pd(OAc)_2$ (33 mg, 0.146 mmol) gave 1.29 g (83%) of **41** as a colorless solid: mp 88-89 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.83 (s,

6H), 3.87 (s, 3H), 3.89 (s, 3H), 6.45 (s, 2H), 7.12 (dd, 1H, *J* = 8.5 and 2.6 Hz), 7.30 (d, 1H, *J* = 2.6 Hz), 7.35 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.0, 56.2, 61.0, 105.4, 108.9, 118.4, 128.4, 132.6, 132.7, 137.9, 149.9, 153.3, 159.2. Anal. Calcd. For $C_{16}H_{17}NO_6$: C, 60.18; H, 5.37; N, 4.39. Found: C, 59.99; H, 5.22; N, 4.33.



43

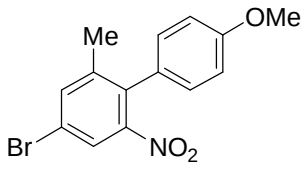
Preparation of 4'-Bromo-4,5-dimethyl-2-nitrobiphenyl (43). According to the general procedure, reaction of **16** (1.20 g, 4.52 mmol) and 4-bromophenyl boronic acid **42** (757 mg, 3.77 mmol) in the presence of $Pd(OAc)_2$ (25 mg, 0.111 mmol) gave 1.05 g (91%) of **43** as a yellow solid: mp 77-78 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.38 9s, 3H), 2.39 (s, 3H), 7.17 (m, 3H), 7.53 (m, 2H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.4, 19.8, 122.2, 125.4, 129.7, 131.7, 131.7, 132.8, 132.9, 136.9, 137.6, 142.5, 146.5. Anal. Calcd. For $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.58. Found: C, 54.72; H, 3.81; N, 4.33.



44

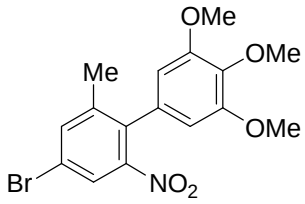
Preparation of 4,5-Dichloro-4'-methoxy-2-nitrobiphenyl (44). According to the general procedure, reaction of **22** (2.99 g, 11.21 mmol) and 4-methoxyphenyl boronic acid **27** (1.42 g, 9.34 mmol) in the presence of $Pd(OAc)_2$ (63 mg, 0.280 mmol) gave 1.89 g (78%) of **44** as a yellow solid: mp 89-90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.85 (s, 3H), 6.97 (d, 2H, *J* = 8.7 Hz), 7.23 (d, 2H, *J* = 8.7 Hz), 7.54 (s, 1H), 7.96 (s, 1H); ^{13}C

NMR ($CDCl_3$, 100 MHz) δ 55.4, 114.5, 126.0, 127.4, 127.8, 129.2, 131.9, 133.5, 135.8, 136.9, 160.3. Anal. Calcd. For $C_{13}H_9Cl_2NO_3$: C, 52.37; H, 3.04; N, 4.70. Found: C, 52.28; H, 2.99; N, 4.69.



45

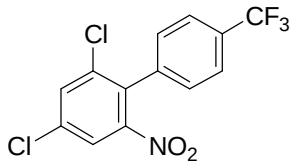
Preparation of 4-Bromo-4'-methoxy-2-methyl-6-nitrobiphenyl (45). According to the general procedure, reaction of **26** (1.20 g, 3.63 mmol) and 4-methoxyphenyl boronic acid **27** (460 mg, 3.03 mmol) in the presence of $Pd(OAc)_2$ (20 mg, 0.091 mmol) gave 750 mg (77%) of **45** as a yellow solid: mp 111-112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 3H), 3.85 (s, 3H), 6.97 (m, 2H), 7.10 (m, 2H), 7.62 (d, 1H, *J* = 1.9 Hz), 7.76 (d, 1H, *J* = 1.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.6, 55.3, 114.2, 120.7, 123.8, 126.8, 129.7, 134.1, 136.3, 141.7, 151.2, 159.6. Anal. Calcd. For $C_{14}H_{12}BrNO_3$: C, 52.20; H, 3.75; N, 4.35. Found: C, 52.02; H, 3.66; N, 4.32.



46

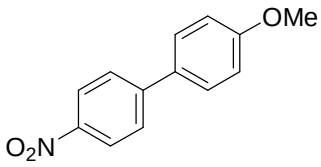
Preparation of 4-Bromo-2-methyl-3',4',5'-trimethoxy-6-nitrobiphenyl (46). According to the general procedure, reaction of **26** (1.20 g, 3.63 mmol) and 3,4,5-trimethoxyphenyl boronic acid **40** (642 mg, 3.03 mmol) in the presence of $Pd(OAc)_2$ (20 mg, 0.091 mmol) gave 660 mg (57%) of **46** as a yellow solid: mp 139-140 °C; ^{1}H NMR

($CDCl_3$, 400 MHz) δ 2.18 (s, 3H), 3.81 (s, 6H), 3.88 (s, 3H), 6.36 (s, 2H), 7.62 (s, 1H), 7.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 56.3, 61.0, 105.8, 120.9, 123.7, 130.1, 134.2, 136.3, 138.0, 141.4, 150.9, 153.5. Anal. Calcd. For $C_{16}H_{16}BrNO_5$: C, 50.28; H, 4.22; N, 3.66. Found: C, 49.99; H, 4.06; N, 3.59.



48

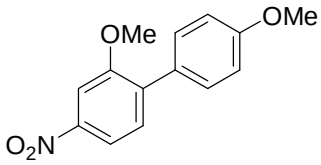
Preparation of 2,4-Dichloro-6-nitro-4'-trifluoromethylbiphenyl (48). According to the general procedure, reaction of **24** (1.31 g, 4.52 mmol) and 4-trifluoromethylphenyl boronic acid **47** (780 mg, 4.11 mmol) in the presence of $Pd(OAc)_2$ (46.1 mg, 0.205 mmol) gave 900 mg (65%) of **48** as a yellow oil: ^1H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, 2H, *J* = 8.2 Hz), 7.73 (d, 2H, *J* = 8.2 Hz), 7.77 (d, 1H, *J* = 1.9 Hz), 7.84 (d, 1H, *J* = 1.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.8, 124.0 (q, *J* = 272 Hz), 125.7 (q, *J* = 4.0 Hz), 129.4, 131.6 (q, *J* = 33 Hz), 132.3, 133.5, 135.3, 136.6, 137.0, 150.7. ^{19}F NMR ($CDCl_3$, 75 MHz) δ -63.3. Anal. Calcd. For $C_{13}H_6Cl_2F_3NO_2$: C, 46.46; H, 1.80; N, 4.17. Found: C, 46.41; H, 1.79; N, 4.12.



49

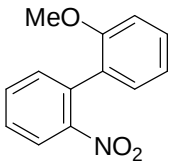
Preparation of 4-Methoxy-4-nitrobiphenyl (49). According to the general procedure, reaction of **8** (1.68 g, 7.11 mmol) and 4-methoxyphenyl boronic acid **27** (900 mg, 5.92 mmol) in the presence of $Pd(OAc)_2$ (40 mg, 0.178 mmol) gave 950 mg (70%) of **49** as a

yellow solid: mp 107-108 °C (Lit.[5] 107-108 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.87 (s, 3H), 7.02 (d, 2H, *J* = 8.5 Hz), 7.57 (d, 2H, *J* = 8.5 Hz), 7.67 (d, 2H, *J* = 8.7 Hz), 8.25 (d, 2H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.5, 114.7, 124.2, 127.1, 128.6, 131.1, 146.6, 147.2, 160.6. Anal. Calcd. For $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.13; H, 4.85; N, 6.09.



51

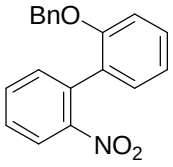
Preparation of 2,4'-Dimethoxy-4-nitrobiphenyl (51). According to the general procedure, reaction of **50** (1.29 g, 4.82 mmol) and 4-methoxyphenyl boronic acid **27** (610 mg, 4.01 mmol) in the presence of $Pd(OAc)_2$ (27 mg, 0.120 mmol) gave 920 mg (88%) of **51** as a yellow solid: mp 119-120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.87 (s, 3H), 3.93 (s, 3H), 7.00 (d, 2H, *J* = 8.7 Hz), 7.44 (d, 1H, *J* = 8.3 Hz), 7.51 (d, 2H, *J* = 8.7 Hz), 7.82 (d, 1H, *J* = 2.2 Hz), 7.90 (dd, 1H, *J* = 8.3 and 2.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.4, 56.1, 106.3, 113.9, 116.2, 128.7, 130.6, 130.7, 137.2, 147.7, 156.8, 159.8. Anal. Calcd. For $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.96; H, 5.11; N, 5.44.



57

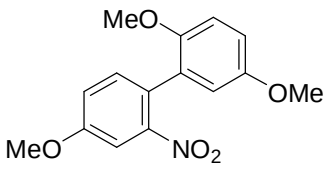
Preparation of 2'-Methoxy-2-nitrobiphenyl (57). According to the general procedure, reaction of **5** (1.20 g, 5.11 mmol) and 2-methoxyphenyl boronic acid **54** (706 mg, 4.65 mmol) in the presence of $Pd(OAc)_2$ (31.3 mg, 0.139 mmol) gave 905 mg (85%) of **57** as a

yellow solid: mp 80-81 °C (Lit.[6] 80-83 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.66 (s, 3H), 6.89 (d, 1H, *J* = 8.2 Hz), 7.14 (t, 1H, *J* = 7.5 Hz), 7.36 (dd, 1H, *J* = 7.5 and 1.6 Hz), 7.41-7.52 (m, 3H), 7.67 (t, 1H, *J* = 7.5 Hz), 7.97 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.2, 110.7, 121.3, 123.9, 127.1, 128.0, 129.7, 129.9, 132.5, 132.8, 133.1, 149.8, 156.0. Anal. Calcd. For $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.89; H, 4.76; N, 5.99.



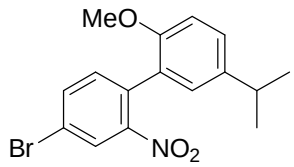
59

Preparation of 2'-Benzyloxy-2-nitrobiphenyl (59) According to the general procedure, reaction of **5** (1.00 g, 5.11 mmol) and 2-benzyloxyphenyl boronic acid **58** (875 mg, 3.84 mmol) in the presence of $Pd(OAc)_2$ (26 mg, 0.115 mmol) gave 1.00 mg (85%) of **59** as a light yellow solid: mp 80-81 °C (Lit.[7] 80-83 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.06 (s, 2H), 7.00 (d, 1H, *J* = 8.2 Hz), 7.15 (t, 1H, *J* = 7.5 Hz), 7.28-7.51 (m, 11H), 7.66 (t, 1H, *J* = 7.5 Hz), 8.01 (d, 1H, *J* = 8.2 hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.5, 112.6, 121.5, 124.0, 126.0, 127.7, 127.9, 128.1, 128.5, 129.8, 129.9, 132.7, 132.8, 133.5, 136.8, 149.6, 155.2. Anal. Calcd. For $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.31; H, 4.66; N, 4.35.



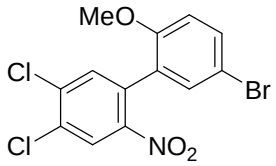
61

Preparation of 4-Bromo-2',5'-dimethoxy-2-nitrobiphenyl (61). According to the general procedure, reaction of **18** (958 g, 3.03 mmol) and 2,5-dimethoxyphenyl boronic acid **60** (460 mg, 2.53 mmol) in the presence of $Pd(OAc)_2$ (17 mg, 0.076 mmol) gave 720 mg (84%) of **61** as a bright yellow solid: mp 121-122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.65 (s, 3H), 3.82 (s, 3H), 6.84 (m, 2H), 6.90 (dd, 1H, *J* = 8.5 and 1.4 Hz), 7.29 (d, 1H, *J* = 8.2 Hz), 7.76 (d, 1H, *J* = 8.2 Hz), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.7, 55.9, 111.7, 114.3, 115.3, 121.3, 126.8, 127.0, 131.9, 133.7, 135.8, 150.0, 154.1. Anal. Calcd. For $C_{14}H_{12}BrNO_4$: C, 49.73; H, 3.58; N, 4.14. Found: C, 49.81; H, 3.59; N, 4.14.



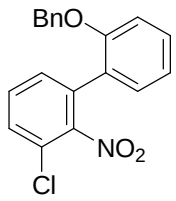
63

Preparation of 4-Bromo-5'-isopropyl-2'-methoxy-2-nitrobiphenyl (63). According to the general procedure, reaction of **18** (1.20 g, 3.80 mmol) and 5-isopropyl-2-methoxyphenyl boronic acid **62** (615 mg, 3.17 mmol) in the presence of $Pd(OAc)_2$ (21 mg, 0.095 mmol) gave 990 mg (89%) of **63** as a yellow solid: mp 66-67 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (d, 6H, *J* = 6.9 Hz), 2.94 (m, 1H), 3.69 (s, 3H), 6.85 (d, 1H, *J* = 8.5 Hz), 7.15 (d, 1H, *J* = 2.1 Hz), 7.25 (dd, 1H, *J* = 8.5 and 2.1 Hz), 7.32 (d, 1H, *J* = 8.2 Hz), 7.75 (dd, 1H, *J* =8.2 and 2.0 Hz), 8.08 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2, 33.3, 55.2, 110.7, 121.0, 125.6, 126.9, 127.7, 127.9, 129.8, 132.4, 133.9, 135.6, 141.8, 153.9. Anal. Calcd. For $C_{16}H_{16}BrNO_3$: C, 54.87; H, 4.61; N, 4.00. Found: C, 55.03; H, 4.66; N, 3.99.



65

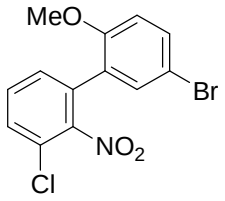
Preparation of 5'-Bromo-4,5-dichloro-2'-methoxy-2-nitrobiphenyl (65). According to the general procedure, reaction of **22** (1.06 g, 4.45 mmol) and 5-bromo-2-methoxyphenyl boronic acid **64** (755 mg, 3.27 mmol) in the presence of $Pd(OAc)_2$ (22 mg, 0.098 mmol) gave 1.00 g (81%) of **65** as a yellow solid: mp 142-143 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (s, 3H), 6.79 (d, 1H, *J* = 8.8 Hz), 7.40 (s, 1H), 7.48 (d, 1H, *J* = 8.8 Hz), 7.50 (s, 1H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 112.5, 113.4, 126.1, 127.1, 131.5, 131.9, 132.7, 133.2, 133.7, 147.7, 155.1. Anal. Calcd. For $C_{13}H_8BrCl_2NO_3$: C, 41.41; H, 2.14; N, 3.72. Found: C, 41.11; H, 2.08; N, 3.69.



66

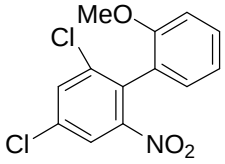
Preparation of 2'-Benzyloxy-3-chloro-2-nitrobiphenyl (66). According to the general procedure, reaction of **20** (1.20 g, 4.43 mmol) and 2-benzyloxyphenyl boronic acid **58** (841 mg, 3.69 mmol) in the presence of $Pd(OAc)_2$ (25 mg, 0.111 mmol) gave 900 mg (72%) of **66** as a colorless solid: mp 76-77 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.08 (s, 2H), 7.02 (m, 2H), 7.23-7.39 (m, 8H), 7.46 (m, 1H), 7.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.5, 113.2, 121.2, 125.0, 125.3, 126.9, 127.8, 128.6, 129.6, 130.5, 130.6, 130.8,

133.7, 136.9, 155.7. Anal. Calcd. For $C_{19}H_{14}ClNO_3$: C, 67.16; H, 4.15; N, 4.12. Found: C, 66.93; H, 4.03; N, 4.10.



67

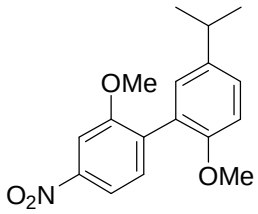
Preparation of 5'-Bromo-3-chloro-2'-methoxy-2-nitrobiphenyl (67). According to the general procedure, reaction of **20** (1.20 g, 4.42 mmol) and 5-bromo-2-methoxyphenyl boronic acid **64** (851 mg, 3.69 mmol) in the presence of $Pd(OAc)_2$ (25 mg, 0.111 mmol) gave 600 mg (48%) of **67** as a light yellow solid: mp 150-151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71 (s, 3H), 6.81 (d, 1H, *J* = 8.8 Hz), 7.29 (dd, 1H, *J* = 7.6 and 1.5 Hz); 7.34 (d, 1H, *J* = 2.4 Hz), 7.46-7.50 (m, 2H), 7.54 (dd, 1H, *J* = 8.1 and 1.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 112.7, 112.9, 125.7, 126.6, 130.1, 130.3, 130.9, 132.5, 133.0, 133.2, 149.1, 155.6. Anal. Calcd. For $C_{13}H_9BrClNO_3$: C, 45.58; H, 2.65; N, 4.09. Found: C, 45.22; H, 2.43; N, 3.88.



68

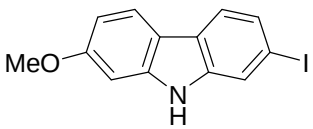
Preparation of 2,4-Dichloro-2',5'-dimethoxy-6-nitrobiphenyl (68). According to the general procedure, reaction of **24** (924 mg, 3.02 mmol) and 2,5-dimethoxyphenyl boronic acid **60** (500 mg, 2.75 mmol) in the presence of $Pd(OAc)_2$ (19 mg, 0.082 mmol) gave 193 mg (23%) of **68** as an orange solid: mp 89-90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.69 (s,

3H), 3.79 (s, 3H), 6.73 (d, 1H, *J* = 2.9 Hz), 6.90 (d, 1H, *J* = 9.0 Hz), 6.96 (dd, 1H, *J* = 9.0 and 2.9 Hz), 7.73 (d, 1H, *J* = 2.0 Hz), 7.83 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.8, 56.1, 112.1, 115.2, 116.1, 123.0, 123.4, 133.4, 134.2, 137.1, 150.5, 151.1, 153.6. Anal. Calcd. For $C_{14}H_{11}Cl_2NO_4$: C, 51.24; H, 3.38; N, 4.27. Found: C, 51.15; H, 3.35; N, 4.26.



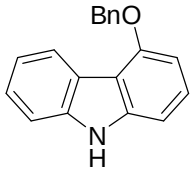
71

Preparation of 5'-Isopropyl-2,2'-dimethoxy-4-nitrobiphenyl (71). According to the general procedure, reaction of Fast Red B **50** (1.65 g, 6.18 mmol) and 2-methoxy-5-isopropyl boronic acid **62** (1.00 g, 5.15 mmol) in the presence of $Pd(OAc)_2$ (35 mg, 0.155 mmol) gave 1.40 g (90%) of **71** as a yellow solid: mp 71-72 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30 (d, 6H, *J* = 7.0 Hz), 2.95 (m, 1H), 3.79 (s, 3H), 3.90 (s, 3H), 6.97 (d, 1H, *J* = 8.5 Hz), 7.12 (d, 1H, *J* = 2.3 Hz), 7.28 (dd, 1H, *J* = 8.5 and 2.3 Hz), 7.43 (d, 1H, *J* = 8.3 Hz), 7.85 (d, 1H, *J* = 2.2 Hz), 7.91 (dd, 1H, *J* = 8.3 and 2.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2, 33.3, 55.9, 56.2, 106.0, 111.2, 115.6, 125.5, 127.5, 129.2, 132.0, 135.5, 140.9, 148.2, 155.0, 157.6. Anal. Calcd. For $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.88; H, 6.41; N, 4.67.



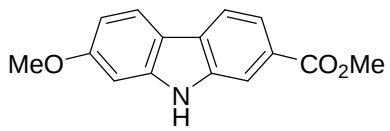
74

Preparation of 2-Iodo-7-methoxy-9*H*-carbazole (74). According to the general procedure, treatment of **37** (370 mg, 1.04 mmol) with triethylphosphite under microwave irradiation afforded 240 mg (71%) of **74** as a colorless solid: mp 275 °C (decomp); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.80 (s, 3H), 6.75 (dd, 1H, *J* = 8.4 and 1.8 Hz), 6.95 (s, 1H), 7.36 (dd, 1H, *J* = 8.0 and 1.3 Hz), 7.75 (m, 2H), 7.92 (d, 1H, *J* = 8.4 Hz), 11.1 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 89.0, 95.1, 108.8, 116.1, 119.6, 121.7, 121.8, 127.7, 127.4, 141.6, 159.5. Anal. Calcd. For $C_{13}H_{10}INO$: C, 48.32; H, 3.12; N, 4.33. Found: C, 47.92; H, 3.89; N, 3.97.



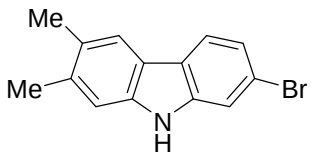
75

Preparation of 4-Benzyloxy-9*H*-carbazole (75). According to the general procedure, treatment of **59** (425 mg, 1.39 mmol) with triethylphosphite under microwave irradiation afforded 240 mg (63%) of **75** as a colorless solid: mp 178-179 °C (Lit.[8] 180 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.40 (s, 2H), 6.18 (d, 1H, *J* = 8.0 Hz), 7.01 (d, 1H, *J* = 8.0 Hz), 7.32-7.41 (m, 3H), 7.45-7.54 (m, 4H), 7.67 (d, 2H, *J* = 8.0 Hz), 7.85 (br s, 1H), 8.47 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.1, 101.8, 104.0, 110.2, 113.0, 119.9, 122.8, 123.3, 125.1, 126.8, 127.6, 128.1, 129.8, 137.6, 138.9, 141.2, 155.4. Anal. Calcd. For $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12. Found: C, 83.61; H, 5.59; N, 5.16.



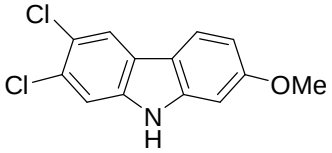
76

Preparation of 7-Methoxy-9*H*-carbazole2-carboxylic acid methyl ester (76). According to the general procedure, treatment of **39** (730 mg, 2.54 mmol) with triethylphosphite under microwave irradiation afforded 400 mg (62%) of **76** as a colorless solid: mp 219-220 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.83 (s, 3H), 3.85 (s, 3H), 6.79 (dd, 1H, J = 8.6 and 2.2 Hz), 7.00 (d, 1H, J = 2.2 Hz), 7.71 (dd, 1H, J = 8.0 and 1.4 Hz), 8.02 (m, 3H), 11.4 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 52.4, 55.8, 95.0, 109.4, 112.4, 115.9, 119.5, 120.0, 122.4, 125.3, 127.1, 139.5, 143.2, 160.1, 167.5. Anal. Calcd. For $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.49; H, 5.02; N, 5.41.



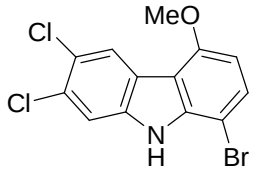
77

Preparation of 7-Bromo-2,3-dimethyl-9*H*-carbazole (77). According to the general procedure, treatment of **43** (400 mg, 1.31 mmol) with triethylphosphite under microwave irradiation afforded 210 mg (59%) of **77** as a colorless solid: mp 286-287 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.32 (s, 3H), 2.33 (s, 3H), 7.18 (d, 1H, J = 8.2 Hz), 7.24 (s, 1H), 7.55 (s, 1H), 7.82 (s, 1H), 7.91 (d, 1H, J = 8.2 Hz), 11.10 (br s, 1H);); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 20.2, 20.9, 112.1, 113.8, 117.8, 120.4, 121.0, 121.4, 121.9, 122.1, 127.7, 135.4, 139.3, 141.1. Anal. Calcd. For $C_{14}H_{12}BrN$: C, 61.33; H, 4.41; N, 5.11. Found: C, 62.98; H, 4.31; N, 4.97.



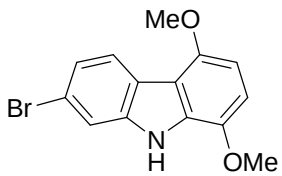
78

Preparation of 2,3-Dichloro-7-methoxy-9*H*-carbazole (78). According to the general procedure, treatment of **44** (250 mg, 0.663 mmol) with triethylphosphite under microwave irradiation afforded 167 mg (73%) of **78** as a colorless solid: mp 206-207 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.85 (s, 3H), 6.82 (d, 1H), 7.01 (s, 1H), 7.65 (s, 1H), 8.04 (d, 1H, J = 7.8 Hz), 8.29 (s, 1H), 11.35 (br s, 1H);); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.8, 95.2, 109.3, 112.5, 115.3, 121.1, 121.3, 122.2, 123.5, 126.4, 139.2, 142.6, 159.8. Anal. Calcd. For $C_{13}H_9Cl_2NO$: C, 58.67; H, 3.41; N, 5.26. Found: C, 58.43; H, 3.11; N, 5.19.



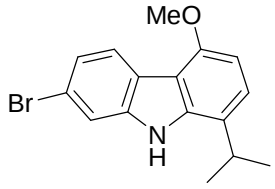
79

Preparation of 1-Bromo-6,7-dichloro-4-methoxy-9*H*-carbazole (79). According to the general procedure, treatment of **65** (250 mg, 0.663 mmol) with triethylphosphite under microwave irradiation afforded 167 mg (73%) of **79** as a colorless solid: mp 201-202 °C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.99 (s, 3H), 6.68 (d, 1H, J = 8.4 Hz), 7.52 (d, 1H, J = 8.4 Hz), 7.65 (s, 1H), 8.15 (s, 1H), 11.62 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 56.4, 95.2, 103.0, 112.1, 113.1, 122.1, 122.4, 123.5, 127.9, 130.3, 138.5, 140.2, 155.5. Anal. Calcd. For $C_{13}H_8BrCl_2NO$: C, 45.26; H, 2.34; N, 4.06. Found: C, 44.92; H, 2.12; N, 3.89.



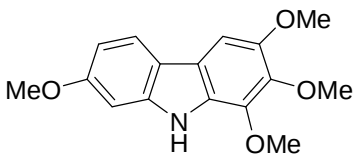
80

Preparation of 7-Bromo-1,4-dimethoxy-9*H*-carbazole (80). According to the general procedure, treatment of **61** (350 mg, 1.04 mmol) with triethylphosphite under microwave irradiation afforded 270 mg (85%) of **80** as a colorless solid: mp 95-96 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.96 (s, 3H), 4.02 (s, 3H), 6.53 (d, 1H, *J* = 8.5 Hz), 6.79 (d, 1H, *J* = 8.5 Hz), 7.36 (dd, 1H, *J* = 8.4 and 1.4 Hz), 7.52 (d, 1H, *J* = 1.4 Hz), 8.17 (d, 1H, *J* = 8.4 Hz), 8.26 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.7, 56.1, 99.8, 106.7, 113.4, 113.5, 118.6, 122.1, 122.9, 124.2, 131.0, 139.4, 140.1, 150.3. Anal. Calcd. For $C_{14}H_{12}BrNO_2$: C, 54.92; H, 3.95; N, 4.58. Found: C, 54.89; H, 3.91; N, 4.58.



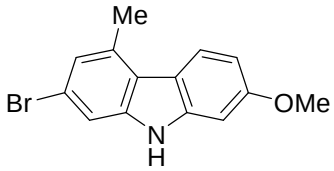
81

Preparation of 7-Bromo-1-isopropyl-4-methoxy-9*H*-carbazole (81). According to the general procedure, treatment of **63** (400 mg, 1.14 mmol) with triethylphosphite under microwave irradiation afforded 312 mg (86%) of **81** as a colorless solid: mp 110-111 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (d, 6H, *J* = 6.9 Hz), 3.21 (m, 1H), 4.06 (s, 3H), 6.68 (d, 1H, *J* = 8.2 Hz), 7.25 (d, 1H, *J* = 8.2 Hz), 7.36 (dd, 1H, *J* = 8.3 and 1.7 Hz), 7.57 (d, 1H, *J* = 1.7 Hz), 8.01 (br s, 1H), 8.19 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.0, 28.9, 55.5, 100.9, 112.0, 113.1, 118.3, 122.2, 122.9, 123.0, 123.5, 124.3, 138.9, 139.5, 154.4. Anal. Calcd. For $C_{16}H_{16}BrNO$: C, 60.39; H, 5.07; N, 4.40. Found: C, 60.27; H, 4.99; N, 4.39.



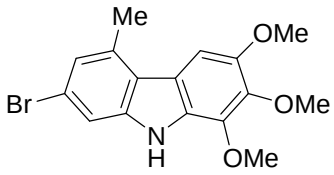
82

Preparation of 1,2,3,7-Tetramethoxy-9*H*-carbazole (82). According to the general procedure, treatment of **41** (460 mg, 1.44 mmol) with triethylphosphite under microwave irradiation afforded 273 mg (66%) of **82** as a colorless solid: mp 164-165 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.87 (s, 3H), 3.99 (s, 6H), 4.11 (s, 3H), 6.83 (dd, 1H, *J* = 8.5 and 2.1 Hz), 6.89 (d, 1H, *J* = 2.1 Hz), 7.23 (s, 1H), 7.82 (d, 1H, *J* = 8.5 Hz), 8.12 (br s, 1H);); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 56.8, 61.2, 61.5, 95.0, 97.7, 108.2, 117.8, 118.9, 120.6, 127.9, 138.6, 140.0, 141.1, 148.8, 158.7. Anal. Calcd. For $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.90; H, 5.95; N, 4.87.



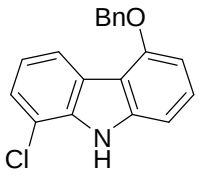
83

Preparation of 2-Bromo-7-methoxy-4-methyl-9*H*-carbazole (83). According to the general procedure, treatment of **45** (400 mg, 1.24 mmol) with triethylphosphite under microwave irradiation afforded 300 mg (83%) of **83** as a colorless solid: mp 149-150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.77 (s, 3H), 3.89 (s, 3H), 6.80 (d, 1H, *J* = 2.3 Hz), 6.89 (dd, 1H, *J* = 8.7 and 2.3 Hz), 7.13 (m, 1H), 7.26 (m, 1H), 7.77 (br s, 1H), 7.96 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.4, 55.7, 94.7, 108.7, 111.0, 117.3, 117.7, 121.1, 123.2, 124.0, 133.8, 140.2, 141.0, 158.9. Anal. Calcd. For $C_{14}H_{12}BrNO$: C, 57.95; H, 4.17; N, 4.83. Found: C, 58.01; H, 4.22; N, 4.85.



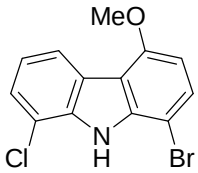
84

Preparation of 7-Bromo-5-methyl-1,2,3-trimethoxy-9*H*-carbazole (84). According to the general procedure, treatment of **46** (330 mg, 0.863 mmol) with triethylphosphite under microwave irradiation afforded 256 mg (85%) of **84** as a colorless solid: mp 173-174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.80 (s, 3H), 4.00 (s, 6H), 4.12 (s, 3H), 7.09 (s, 1H), 7.36 (s, 1H), 7.40 (s, 1H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 57.0, 61.3, 61.5, 100.7, 111.5, 118.4, 118.7, 121.5, 123.7, 128.4, 134.2, 138.4, 140.4, 140.9, 148.8. Anal. Calcd. For $C_{16}H_{16}BrNO_3$: C, 54.87; H, 4.61; N, 4.00. Found: C, 54.79; H, 4.55; N, 3.98.



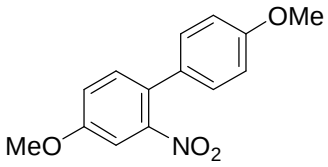
85

Preparation of 5-Benzyloxy-1-chloro-9*H*-carbazole (85). According to the general procedure, treatment of **66** (300 mg, 0.883 mmol) with triethylphosphite under microwave irradiation afforded 170 mg (63%) of **85** as a colorless solid: mp 87-88 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.35 (s, 2H), 6.79 (d, 1H, *J* = 8.0 Hz), 7.12 (d, 1H, *J* = 8.1 Hz), 7.18 (t, 1H, *J* = 8.1 Hz), 7.37-7.50 (m, 5H), 7.60 (d, 2H, *J* = 7.5 Hz), 8.24 (d, 1H, *J* = 7.5 Hz), 8.30 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 70.0, 102.0, 104.0, 113.1, 115.3, 120.4, 121.5, 124.1, 124.2, 127.3, 127.4, 127.9, 128.6, 135.9, 137.1, 140.7, 155.3. Anal. Calcd. For $C_{19}H_{14}ClNO$: C, 74.15; H, 4.58; N, 4.55. Found: C, 74.17; H, 4.59; N, 4.56.



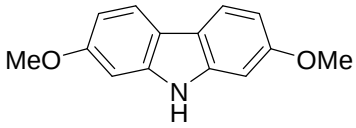
86

Preparation of 1-Bromo-8-chloro-4-methoxy-9*H*-carbazole (86). According to the general procedure, treatment of **67** (290 mg, 0.847 mmol) with triethylphosphite under microwave irradiation afforded 108 mg (41%) of **86** as a colorless solid: mp 89-90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.02 (s, 3H), 6.53 (d, 1H, *J* = 8.5 Hz), 7.19 (t, 1H, *J* = 7.8 Hz), 7.41 (d, 1H, *J* = 7.8 Hz), 7.44 (d, 1H, *J* = 8.5 Hz), 8.14 (d, 1H, *J* = 7.8 Hz), 8.30 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.6, 95.4, 102.4, 115.8, 121.0, 121.8, 124.6, 129.1, 132.5, 135.4, 138.7, 155.6. Anal. Calcd. For $C_{13}H_9BrClNO$: C, 50.27; H, 2.92; N, 4.51. Found: C, 49.89; H, 2.71; N, 4.33.



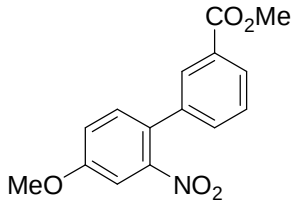
87

Preparation of 4,4'-Dimethoxy-2-nitrobiphenyl (87). According to the general procedure, reaction of **12** (2.99 g, 11.21 mmol) and 4-methoxyphenyl boronic acid **27** (1.42 g, 9.34 mmol) in the presence of $Pd(OAc)_2$ (63 mg, 0.28 mmol) gave 1.89 g (78%) of **87** as a light yellow solid: mp 137-138 °C (lit.[9] 136-138 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.82 (s, 3H), 3.89 9s, 3H), 6.94 (m, 2H), 7.13 (dd, 1H, *J* = 8.7 and 2.6 Hz), 7.22 (m, 2H), 7.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.4, 56.0, 109.0, 114.2, 118.6, 128.3, 129.3, 129.5, 132.8, 149.8, 158.9, 159.5. Anal. Calcd. For $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.77; H, 5.01; N, 5.39.



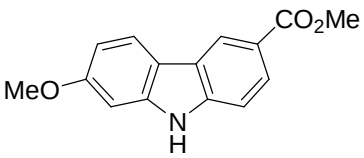
88

Preparation of 2,7-Dimethoxy-9*H*-carbazole (clavsine-V) (88). According to the general procedure, treatment of **87** (1.20 g, 4.63 mmol) with triethylphosphite under microwave irradiation afforded 852 mg (81%) of **88** as a colorless solid: mp 271-272 °C (Lit.[9] 272-273 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.78 (s, 3H), 7.69 (dd, 2H, J = 8.5 and 2.0 Hz), 6.91 (d, 2H, J = 2.0 Hz), 7.79 (d, 2H, J = 8.5 Hz), 10.91 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 55.7, 95.2, 107.8, 117.0, 120.4, 141.6, 158.1. Anal. Calcd. For $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.01; H, 5.78; N, 6.14.

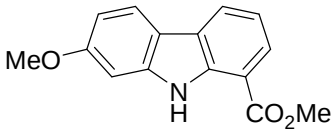


90

Preparation of 4'-Methoxy-2'-nitro-biphenyl-3-carboxylic acid methyl ester (90). According to the general procedure, reaction of **12** (1.91 g, 7.13 mmol) and 5-bromo-2-methoxyphenyl boronic acid **89** (1.07 g, 5.95 mmol) in the presence of $Pd(OAc)_2$ (40 mg, 0.178 mmol) gave 1.25 g (73%) of **90** as a yellow solid: mp 116-117 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.91 (s, 3H), 3.92 (s, 3H), 7.17 (dd, 1H, J = 8.6 and 2.6 Hz), 7.33 (d, 1H, J = 8.6 Hz), 7.45 (m, 3H), 7.98 (s, 1H), 8.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.3, 56.0, 109.4, 119.0, 127.9, 128.7, 129.0, 129.3, 130.7, 132.6, 132.9, 137.9, 149.5, 159.5, 166.7. Anal. Calcd. For $C_{15}H_{13}NO_5$: C, 62.72; H, 4.56; N, 4.88. Found: C, 62.81; H, 4.66; N, 4.90.



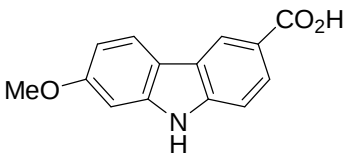
91



92

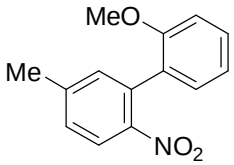
Reductive cyclization of 90. According to the general procedure, treatment of **90** (600 mg, 2.09 mmol) with triethylphosphite under microwave irradiation was followed by silica gel chromatography using 10% EtOAc/hexane. The first product to elute from the column (155 mg, 29%) was identified as **7-methoxy-9*H*-carbazole-1-carboxylic acid methyl ester (92)** and was obtained as a colorless solid: mp 132-133 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.91 (s, 3H), 4.02 (s, 3H), 7.89 (dd, 1H, *J* = 8.6 and 2.2 Hz), 6.98 (d, 1H, *J* = 2.2 Hz), 7.22 (t, 1H, *J* = 7.6 Hz), 7.94 (d, 1H, *J* = 8.6 Hz), 7.99 (d, 1H, *J* = 7.6 Hz), 8.15 (d, 1H, *J* = 7.6 Hz), 10.5 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.0, 55.7, 95.0, 109.0, 111.4, 116.3, 118.6, 121.2, 124.5, 124.9, 126.0, 140.3, 141.1, 159.7, 168.0. Anal. Calcd. For $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.79; H, 5.33; N, 5.55.

The second product to elute from the column (220 mg, 41%) was identified as **7-methoxy-9*H*-carbazole-3-carboxylic acid methyl ester (clausine C) (91)** and was obtained as a colorless solid: mp 194-195 °C (Lit.[10] 195-197 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.87 (s, 3H), 3.89 (s, 3H), 6.84 (dd, 1H, *J* = 8.6 and 2.1 Hz), 7.04 (d, 1H, *J* = 2.1 Hz), 7.51 (d, 1H, *J* = 8.5 Hz), 7.95 (dd, 1H, *J* = 8.5 and 1.5 Hz), 8.12 (d, 1H, *J* = 8.6 Hz), 8.67 (d, 1H, *J* = 1.5 Hz), 11.6 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 52.2, 55.8, 95.4, 109.2, 110.9, 116.6, 120.4, 121.8, 122.0, 123.0, 126.0, 142.3, 143.2, 159.6, 167.5. Anal. Calcd. For $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.29; H, 4.96; N, 5.33.



93

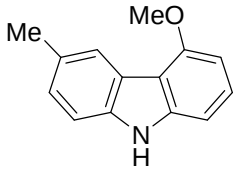
Preparation of 7-Methoxy-9*H*-carbazole-3-carboxylic acid (clausine N) (93). To a mixture of **91** (76 mg, 0.298 mmol) in 2 mL of MeOH and 0.5 mL of THF was added 2 N NaOH (0.75 mL, 1.49 mmol). After stirring for 8 h at rt the mixture was concentrated to remove MeOH and THF. The resulting aqueous solution was diluted with 10 mL of EtOAc and acidified with conc. HCl to pH = 1. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to give 66.1 mg (92%) of **93** as a colorless solid: mp 216-217 °C (Lit.[11] 215-218 °C); ^{1}H NMR (acetone-d_6, 400 MHz) δ 3.85 (s, 3H), 6.80 (dd, 1H, J = 8.6 and 2.0 Hz), 7.08 (d, 1H, J = 2.0 Hz), 7.49 (d, 1H, J = 8.5 Hz), 8.04 (d, 1H, J = 8.5 and 1.6 Hz), 8.08 (d, 1H, J = 8.6 Hz), 8.71 (s, 1H), 10.5 (br s, 1H); ^{13}C NMR (acetone-d_6, 100 MHz) δ 55.0, 95.0, 108.9, 110.1, 116.8, 121.2, 121.7, 123.2, 126.1, 142.2, 143.0, 159.8, 167.8. Anal. Calcd. For $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found: C, 69.66; H, 4.58; N, 5.79.



94

Preparation of 2'-Methoxy-5-methyl-2-nitrobiphenyl (94). According to the general procedure, reaction of **14** (3.00 g, 11.96 mmol) and 2-methoxyphenyl boronic acid **54** (1.514 g, 9.96 mmol) in the presence of $Pd(OAc)_2$ (67 mg, 0.299 mmol) gave 1.96 g (81%) of **94** as a light yellow solid: mp 84-85 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.47 (s,

3H), 3.72 (s, 3H), 6.92 (d, 1H, *J* = 8.3 Hz), 7.09 (m, 1H), 7.21 (s, 1H), 7.27 (m, 1H), 7.31 (dd, 1H, *J* = 7.5 and 1.7 Hz), 7.39 (m, 1H), 7.87 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 55.3, 110.7, 121.2, 124.1, 127.5, 128.6, 129.6, 129.7, 133.1, 133.2, 143.8, 147.6, 156.0. Anal. Calcd. For $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.33; H, 5.41; N, 5.77.



95

Preparation of 5-Methoxy-3-methyl-9*H*-carbazole (Glycoborine) (95). According to the general procedure, treatment of **94** (330 mg, 1.36 mmol) with triethylphosphite under microwave irradiation afforded 235 mg (82%) of **95** as a colorless solid: mp 154-156 °C (Lit.[12] 155-156 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.52 (s, 3H), 4.06 (s, 3H), 6.65 (d, 1H, *J* = 7.9 Hz), 7.00 (d, 1H, *J* = 7.9 Hz), 7.19 (d, 1H, *J* = 7.9 Hz), 7.25 (d, 1H, *J* = 7.9 Hz), 7.30 (t, 1H, *J* = 7.9 Hz), 7.91 (br s, 1H), 8.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 55.4, 100.2, 103.6, 109.6, 112.5, 122.9, 123.0, 126.3, 126.4, 128.9, 137.0, 141.3, 156.3. Anal. Calcd. For $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.49; H, 6.22; N, 6.61.

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