Combined C-H Functionalization / C-N Bond Formation Route to Carbazoles

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Supporting Information

General. Unless otherwise noted, all reactions were carried out in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. The synthesis of carbazoles was carried out under an atmosphere of air or oxygen. Commercially available chemicals were obtained from Aldrich Chemical Co., Lancaster Synthesis, Strem Chemical, and Engelhard Industries. 2'-Bromoacetanilide (96%) was twice recrystallized from mixtures of hexanes and ethyl acetate prior to use. Anhydrous $\text{Cu}(\text{OAc})_2$ was purchased from Strem Chemical and stored in a nitrogen glovebox. All other solid reagents were used as received unless otherwise noted. Toluene was dried and purified by passing the solvent through two packed columns of activated neutral alumina and copper(II) oxide under argon prior to use.

Infrared spectra (IR) were recorded on a Perkin Elmer System 2000 FT-IR spectrophotometer, ν_{max} in cm^{-1} . Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Inova 500 instrument. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^1H CDCl_3 : δ 7.27; ^{13}C CDCl_3 : δ 77.23). ^{13}C NMR spectra were recorded with complete proton decoupling. All ^{19}F NMR spectra were reported in ppm from trichlorofluoromethane (0 ppm). Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 6890 Series GC System with a capillary column with cross-linked methyl siloxane as the stationary phase (25 m x 0.20 mm). Melting points were performed on a Mel-Temp apparatus, and were

uncorrected. Microanalyses were performed by Atlantic Microlabs, Inc. (Norcross, Georgia).

General Procedures for the Preparation of Biaryl Amide Substrates. An oven-dried disposable test tube (14 mL in volume), equipped with a screw cap, a teflon septum, and a spin bar, was cooled under vacuum and Ar. 2'-Bromoacetanilide (1.0 mmol), Pd(OAc)₂ (0.02 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.04 mmol), the appropriate boronic acid (1.5 mmol), and anhydrous K₃PO₄ (2.0 mmol) were added under air. The tube was gently shaken to mix the solid reagents. The septum-sealed tube was evacuated and refilled with Ar three times. Toluene (1.5 mL) was added via syringe. The reaction mixture was heated in an oil bath at 90 °C. Some manual swirling, or sonication, may be necessary to expedite the initiation of the reaction. After the reaction was complete, the dark solid was removed by filtration through Celite, and the Celite bed was washed with 3 x 5 mL EtOAc. In most cases, the combined filtrate was immediately concentrated, and the residue was purified by silica gel chromatography with hexanes:EtOAc mixtures. In cases where the biaryl amide and the excess boronic acid co-elute, the filtrate was diluted with EtOAc (10 mL) and washed with aqueous NaOH solution (4 x 10 mL, 1N) to remove the excess boronic acid. The combined organic phase was dried over anhydrous Na₂SO₄ before it was concentrated, and further purified by chromatography. The purified material was dried under oil-pump vacuum prior to the synthesis of carbazoles.

2-Acetamino-3'-methylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 20 min. An off-white powder was obtained after silica gel chromatography (70:30 hexanes:EtOAc), yield 0.207 g (92%, mp 79 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.16 Hz, 1H), 7.38 (m, 2H), 7.24 (d, *J* = 7.29 Hz, 2H), 7.22-7.12 (m, 4H), 2.43 (s, 3H), 2.03 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.39, 139.13, 138.26, 134.90, 132.35, 130.20, 130.18, 129.11, 128.90, 128.51, 126.33, 124.43, 121.62, 24.85, 21.68. IR (KBr plate, CDCl₃) ν 3261, 3031, 1663, 1520, 1445, 1293, 757. Anal. Calcd. for C₁₅H₁₅NO: C, 79.96; H, 6.72. Found: C, 80.05; H, 6.90.

2-Acetamino-4'-methylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 30 min. A white powder was obtained after silica gel chromatography (60:40 hexanes:EtOAc), yield 0.220 g (98%, mp 105 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.16 Hz, 1H), 7.36 (td, *J* = 7.77, 1.66 Hz, 1H), 7.29 (m, 4H), 7.24 (d, *J* = 7.55 Hz, 1H), 7.17 (m, 2H), 2.44 (s, 3H), 2.04 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.41, 138.00, 135.29, 134.96, 132.23, 130.27, 130.00, 129.28, 128.42, 124.46, 121.63, 24.85, 21.42. IR (KBr plate, CDCl₃) ν 3264, 3024, 1663, 1520, 1445, 1303, 1289, 821, 757. Anal. Calcd. for C₁₅H₁₅NO: C, 79.96; H, 6.72. Found: C, 79.73; H, 6.55.

2-Acetamino-4'-tert-butylbiphenyl. Following the general procedures, the reaction was performed on a 1.67 mmol scale at 90 °C for 4 h. A white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 4:1, 3:1, 2:1), yield 0.454 g (99%, mp 91-92 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.09 Hz, 1H), 7.51 (d, *J* = 8.09 Hz, 2H), 7.40-7.28 (m, 3H), 7.27-7.20 (m, 2H), 7.17 (t, *J* = 7.42 Hz, 1H), 2.06 (s, 3H), 1.39 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 168.45, 151.17, 135.27, 134.95, 132.14, 130.39, 129.08, 128.39, 126.24, 124.50, 121.71, 34.89, 31.54, 24.92. IR (KBr plate, CDCl₃) ν 3267, 2963, 1666, 1521, 1445, 1365, 1303, 761. Anal. Calcd. for C₁₈H₂₁NO: C, 80.85; H, 7.92. Found: C, 80.64; H, 7.87.

2-Acetamino-5-methylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 15 min. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (65:35 hexanes:EtOAc), yield 0.223 g (99%, mp 121-122 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 8.35 Hz, 1H), 7.52-7.45 (m, 2H), 7.45-7.34 (m, 3H), 7.19 (d, *J* = 8.24 Hz, 1H), 7.07 (s, 1H), 7.05 (s, 1H), 2.36 (s, 3H), 2.02 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.43, 138.55, 134.29, 132.60, 132.28, 130.84, 129.41, 129.21, 129.16, 128.05, 122.17, 24.74, 21.08. IR (KBr plate, CDCl₃) ν 3256, 3026, 2920, 1662, 1518, 1295, 701. Anal. Calcd. for C₁₅H₁₅NO: C, 79.96; H, 6.72. Found: C, 79.81; H, 6.68.

2-Acetamino-3,5-dimethylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 14 h. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 1:1, 2:3), yield 0.217 g (91%, mp 133-134 °C). ¹H NMR (500 MHz, tol-*d*₈, 105 °C) δ 7.22 (d, *J* = 7.52 Hz, 2H), 7.16 (t, *J* = 7.21 Hz, 2H), 7.09 (t, *J* = 7.52 Hz, 1H), 6.84 (s, 2H), 5.83 (s, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 1.49 (s, 3H). ¹³C NMR (125 MHz, tol-*d*₈, 105 °C) δ 168.16, 141.14, 140.48, 137.21, 136.79, 132.06, 131.05, 129.58, 128.50, 127.43, 22.14, 20.91, 18.65. IR (KBr plate, CDCl₃) ν 3248, 3027, 1652, 1524, 1291, 857, 701. Anal. Calcd. for C₁₆H₁₇NO: C, 80.29; H, 7.16. Found: C, 80.07; H, 7.27.

2-Acetamino-2'-methoxybiphenyl. Following the general procedures, the reaction was performed on a 2.5 mmol scale at 90 °C for 4 h. A white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 2:1, 1:1, 2:3), yield 0.625 g (99%, mp 74 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.09 Hz, 1H), 7.45 (s, 1H), 7.42-7.29 (m, 2H), 7.28-7.11 (m, 3H), 7.11-6.92 (m, 2H), 3.80 (s, 3H), 1.97 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.29, 156.07, 135.54, 132.17, 130.97, 130.24, 129.77, 128.29, 127.35, 124.58, 122.65, 121.70, 111.49, 55.97, 24.59. IR (KBr plate, CDCl₃) ν 3295, 1675, 1520, 1444, 1234, 1024, 754. Anal. Calcd for C₁₅H₁₅NO₂: C, 74.65; H, 6.27. Found: C, 74.41; H, 6.35.

2-Acetamino-3'-methoxybiphenyl. Following the general procedures, the reaction was performed on a 2.5 mmol scale at 90 °C for 30 min. A white powder was obtained after silica gel chromatography (50:50 hexanes:EtOAc), yield 0.591 g (98%, mp 113-114 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, *J* = 8.09 Hz, 1H), 7.38 (m, 2H), 7.30-7.10 (m, 3H), 7.05-6.80 (m, 3H), 3.84 (s, 3H), 2.03 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.43, 160.30, 139.71, 134.90, 132.06, 130.34, 130.11, 128.69, 124.43, 121.60, 121.56, 114.98, 113.81, 55.55, 24.90. IR (KBr plate, CDCl₃) ν 3267, 1664, 1586, 1522, 1442, 1303, 759. Anal. Calcd. for C₁₅H₁₅NO₂: C, 74.65; H, 6.27. Found: C, 74.32; H, 6.24.

2-Acetamino-4'-methoxybiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 2 h. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (50:50 hexanes:EtOAc), yield 0.240 g (99%, mp 132 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 8.13 Hz, 1H), 7.35 (t, *J* = 7.76 Hz, 1H), 7.30 (d, *J* = 8.59 Hz, 2H), 7.23 (d, *J* = 6.64 Hz, 1H), 7.16 (m, 2H), 7.02 (d, *J* = 8.59 Hz, 2H), 3.88 (s, 3H), 2.04 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.41, 159.51, 135.04, 132.00, 130.59, 130.41, 130.33, 128.31, 124.47, 121.67, 114.68, 55.54, 24.85. IR (KBr plate, CDCl₃) ν 3267, 1663, 1517, 1445, 1298, 1246, 1179, 1035, 834, 760. Anal. Calcd. for C₁₅H₁₅NO₂: C, 74.65; H, 6.27. Found: C, 74.72; H, 6.38.

2-Acetamino-2',4'-dimethoxybiphenyl. Following the general procedures, the reaction was performed on a 2.5 mmol scale at 90 °C for 30 min. A white powder was obtained after silica gel chromatography (50:50 hexanes:EtOAc), yield 0.670 g (99%, mp 95 °C.) ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 8.13 Hz, 1H), 7.37 (m, 2H), 7.24-7.12 (m, 3H), 6.68-6.54 (m, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 2.01 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.30, 161.22, 157.24, 135.86, 132.79, 131.22, 129.87, 128.22, 124.57, 122.41, 119.93, 105.62, 99.25, 56.06, 55.68, 24.82. IR (KBr plate, CDCl₃) ν 3306, 2937, 1683, 1519, 1446, 1304, 1208, 1159, 1030, 761. Anal. Calcd. for C₁₆H₁₇NO₃: C, 70.82; H, 6.32. Found: C, 70.88; H, 6.31.

2-Acetamino-5-methyl-4'-methoxybiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 10 min. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (65:35 hexanes:EtOAc), yield 0.230 g (90%, mp 123-124 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 8.24 Hz, 1H), 7.29 (d, *J* = 8.49 Hz, 2H), 7.16 (d, *J* = 8.24 Hz, 1H), 7.11-6.95 (m, 4H), 3.88 (s, 3H), 2.34 (s, 3H), 2.03 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 168.40, 159.43, 134.18, 132.44, 132.24, 130.90, 130.65, 130.55, 128.83, 122.01, 114.59, 55.55, 24.76, 21.07. IR (KBr plate, CDCl₃) ν 3265, 1663, 1516, 1246, 1177, 1029, 828. Anal. Calcd. for C₁₆H₁₇NO₂: C, 75.26; H, 6.72. Found: C, 75.11; H, 6.71.

2-Acetamino-2'-fluorobiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale with boronic acid recrystallized from water at 90 °C for 10 min. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 2:1, 3:2), yield 0.214 g (94%, mp 105-106 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.16 Hz, 1H), 7.43 (t, *J* = 7.29 Hz, 2H), 7.38-7.16 (m, 5H), 7.00 (s, 1H), 2.04 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃) δ -114.49. ¹³C NMR (125 MHz, CDCl₃) δ 168.54, 160.70, 158.73, 135.43, 132.21, 132.19, 130.88, 130.43, 130.36, 129.22, 127.26, 125.72, 125.59, 125.06, 125.03, 124.91, 123.04, 116.36, 116.19, 24.62. IR (KBr plate, CDCl₃) ν 3259, 1665, 1523, 1442, 1296, 757. Anal. Calcd. for C₁₄H₁₂NOF: C, 73.33; H, 5.28. Found: C, 73.34; H, 5.36.

2-Acetamino-4'-fluorobiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 1 h. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (65:35 hexanes:EtOAc), yield 0.218 g (95%, mp 125 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 8.20 Hz, 1H), 7.42-7.31 (m, 3H), 7.25-7.13 (m, 4H), 7.02 (s, 1H), 2.04 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃) δ -114.08. ¹³C NMR (125 MHz, CDCl₃) δ 168.46, 163.67, 161.70, 134.89, 134.30, 134.27, 131.63, 131.20, 131.14, 130.33, 128.82, 124.76, 122.25, 116.38, 116.21, 24.79. IR (KBr plate, CDCl₃) ν 3259, 3039, 1663, 1515, 1446, 1222, 1159, 838, 759. Anal. Calcd. for C₁₄H₁₂NOF: C, 73.33; H, 5.28. Found: C, 73.21; H, 5.26.

2-Acetamino-5-fluorobiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 20 min. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (65:35 hexanes:EtOAc), yield 0.221 g (97%, mp 136 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.16 (m, 1H), 7.50 (m, 2H), 7.44 (t, *J* = 7.33 Hz, 1H), 7.36 (d, *J* = 7.01 Hz, 2H), 7.12-7.02 (m, 2H), 6.98 (dd, *J* = 8.93, 2.86 Hz, 1H), 2.02 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃) δ -118.14. ¹³C NMR (125 MHz, CDCl₃) δ 168.51, 160.40, 158.46,

137.37, 137.335, 134.73, 134.67, 130.88, 130.86, 129.39, 129.20, 128.61, 124.17, 124.11, 116.93, 116.75, 115.17, 115.00, 24.59. IR (KBr plate, CDCl_3) ν 3258, 3032, 1662, 1523, 1487, 1412, 1182, 768, 701. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{NOF}$: C, 73.33; H, 5.28. Found: C, 73.14; H, 5.22.

2-Acetamino-3,5-difluorobiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 14 h. An aqueous NaOH workup was performed, and the crude residue was recrystallized to give a white powder. The mother liquor was concentrated and purified by silica gel chromatography (gradient; hexanes:EtOAc, 2:1, 1:1) to give a white powder. The combined yield was 0.242 g (98%, mp 152 °C). ^1H NMR (500 MHz, CDCl_3 , 60 °C) δ 7.47-7.37 (m, 3H), 7.36-7.31 (m, 2H), 6.90 (m, 2H), 6.42 (s, 1H), 1.99 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -111.32, -114.31. ^{13}C NMR (125 MHz, CDCl_3 , 60 °C) δ 169.57, 162.52, 162.42, 160.54, 160.44, 160.03, 159.93, 158.03, 157.92, 143.01, 137.53, 129.45, 128.82, 128.80, 128.56, 119.10, 112.90, 112.72, 103.94, 103.54, 22.74. IR (KBr plate, CDCl_3) ν 3246, 3025, 1664, 1527, 1430, 1146, 1105, 1001, 767, 701. Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NOF}_2$: C, 67.99; H, 4.49. Found: C, 68.15; H, 4.50.

2-Acetamino-2'-trifluoromethylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 30 min. A white powder was obtained after silica gel chromatography (70:30 hexanes:EtOAc), yield 0.273 g (98%, mp 101-102 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.17 (d, J = 8.16 Hz, 1H), 7.84 (d, J = 7.78 Hz, 1H), 7.65 (t, J = 7.42 Hz, 1H), 7.58 (t, J = 7.52 Hz, 1H), 7.46-7.40 (m, 1H), 7.34 (d, J = 7.29 Hz, 1H), 7.22-7.14 (m, 2H), 6.53 (s, 1H), 1.93 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -59.50. ^{13}C NMR (125 MHz, CDCl_3) δ 168.36, 136.77, 135.31, 132.42, 132.30, 130.24, 130.06, 129.29, 128.79, 126.86, 126.82, 126.78, 126.73, 125.04, 124.08, 122.86, 122.31, 24.58. IR (KBr plate, CDCl_3) ν 3285, 1669, 1522, 1442, 1315, 1172, 1126, 1115, 1035, 758. Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{NOF}_3$: C, 64.50; H, 4.33. Found: C, 64.40; H, 4.14.

2-Acetamino-4'-trifluoromethylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 30 min. A white powder was

obtained after silica gel chromatography (60:40 hexanes:EtOAc), yield 0.270 g (97%, mp 118 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.18 (d, J = 8.13 Hz, 1H), 7.75 (d, J = 7.90 Hz, 2H), 7.52 (d, J = 7.90 Hz, 2H), 7.42 (td, J = 7.19, 2.33 Hz, 1H), 7.25 (m, 2H), 6.98 (s, 1H), 2.05 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -62.73. ^{13}C NMR (125 MHz, CDCl_3) δ 168.60, 142.28, 134.62, 131.69, 130.22, 129.85, 129.36, 126.20, 126.16, 125.29, 125.17, 123.13, 123.04, 24.68. IR (KBr plate, CDCl_3) ν 3266, 1662, 1522, 1326, 1163, 1122, 1069, 765. Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{NOF}_3$: C, 64.50; H, 4.33. Found: C, 64.61; H, 4.28.

2-Acetamino-5-trifluoromethylbiphenyl. Following the general procedures, the reaction was performed on a 1 mmol scale at 90 °C for 14 h. An aqueous NaOH workup was performed prior to chromatography. A white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 2:1, 3:2), yield 0.262 g (94%, mp 132 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.53 (d, J = 8.51 Hz, 1H), 7.63 (dd, J = 8.66, 2.14 Hz, 1H), 7.54 (m, 2H), 7.51-7.46 (m, 2H), 7.39 (m, 2H), 7.29 (s, 1H), 2.06 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -62.39. ^{13}C NMR (125 MHz, CDCl_3) δ 168.56, 138.07, 136.85, 131.89, 129.69, 129.33, 128.96, 127.24, 127.21, 125.94, 125.80, 125.77, 125.74, 125.71, 125.33, 123.17, 120.98, 25.00. IR (KBr plate, CDCl_3) ν 3278, 1659, 1526, 1415, 1337, 1169, 1117, 1081, 702. Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{NOF}_3$: C, 64.50; H, 4.33. Found: C, 64.33; H, 4.34.

Representative Procedures for the Synthesis of 9-Acetylcarbazoles. An oven-dried Schlenk tube (15 mL in volume) was cooled under vacuum and Ar. The reaction was typically performed on days where the humidity of the laboratory was around 50-65%. 2-Acetaminobiphenyl (**1**, 42.3 mg, 0.2 mmol), $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01 mmol), and powdered molecular sieves (40 mg, activated 3 Å) were added under air. The tube was evacuated and refilled with Ar. Anhydrous $\text{Cu}(\text{OAc})_2$ (36.3 mg, 0.2 mmol) was loaded into the Schlenk tube in a nitrogen glovebox. Under a positive Ar pressure, toluene (2 mL) was added via syringe. The reaction mixture was sonicated and degassed under a weak vacuum and refilled with O_2 from the double manifold (the procedure was carried out three times). The sealed Schlenk tube was lowered into an oil bath at 120 °C, and stirred for 12 h. After cooling, distilled water (1 mL), ammonium hydroxide solution (3

mL, 30%), and EtOAc (2 mL) were added to the cooled reaction mixture. The organic phase was separated, and the aqueous phase was further extracted with 3 x 2 mL EtOAc. The combined organic fractions were dried over anhydrous Na₂SO₄ and filtered through Celite. The filtrate was concentrated, and the residue was purified by silica gel chromatography with 80:20 hexanes:EtOAc. The purified material was dried under oil-pump vacuum, affording an off-white powder, yield 42 mg (94%). Alternatively, on extremely dry days (relative humidity <30%), the reaction can be set up with a disposable test tube equipped with a screw cap and a teflon septum. The tube was evacuated to <50 mTorr with a 21 gauge needle and refilled with O₂ from a balloon (this was carried out three times), which was left attached afterwards with an 18 gauge needle. Toluene was added under balloon O₂ atm, and the reaction mixture was lowered into an oil bath at 120 °C up to the solvent level. The reaction was stirred for 18 to 24 h. Comparable yields to the method with Schlenk tubes were obtained.

9-Acetyl-2-methylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (93:7 hexanes:EtOAc), yield 44 mg (98%, mp 87 °C). ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 8.35 Hz, 1H), 8.08 (s, 1H), 7.97 (d, *J* = 7.65 Hz, 1H), 7.88 (d, *J* = 7.82 Hz, 1H), 7.46 (td, *J* = 7.82, 1.37 Hz, 1H), 7.38 (td, *J* = 7.48, 0.96 Hz, 1H), 7.23 (d, *J* = 7.86 Hz, 1H), 2.90 (s, 3H), 2.56 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 170.39, 139.25, 138.79, 137.83, 126.98, 126.79, 125.11, 124.22, 123.82, 119.76, 119.64, 116.94, 116.36, 28.03, 22.57. IR (KBr plate, CDCl₃) ν 1694, 1461, 1368, 1327, 1288, 767, 724. Anal. Calcd. for C₁₅H₁₃NO: C, 80.68; H, 5.87. Found: C, 80.57; H, 5.91.

9-Acetyl-2-*tert*-butylcarbazole. Following the general procedures, a light yellow viscous oil was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 10:1, 9:1), yield 51 mg (96%). ¹H NMR (500 MHz, CDCl₃) δ 8.35 (s, 1H), 8.16 (d, *J* = 8.27 Hz, 1H), 7.97 (d, *J* = 7.67 Hz, 1H), 7.92 (d, *J* = 8.17 Hz, 1H), 7.50-7.42 (m, 2H), 7.38 (t, *J* = 7.47 Hz, 1H), 2.90 (s, 3H), 1.46 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 170.37, 151.30, 139.24, 138.99, 126.97, 126.69, 124.13, 123.79, 121.61, 119.85, 119.37, 116.26,

113.46, 35.63, 31.93, 28.02. IR (KBr plate, CDCl_3) ν 2962, 1695, 1367, 1327, 1286, 1234, 747, 726. Anal. Calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}$: C, 81.46; H, 7.22. Found: C, 81.58; H, 7.31.

9-Acetyl-3-methylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (93:7 hexanes:EtOAc), yield 41 mg (92%, mp 71-72 °C) when the substrate was 2-acetamino-5-methylbiphenyl. The same compound was obtained as the major product when the substrate was 2-acetamino-3'-methylbiphenyl, yield 36 mg (81%). ^1H NMR (500 MHz, CDCl_3) δ 8.23 (d, J = 8.39 Hz, 1H), 8.07 (d, J = 8.39 Hz, 1H), 7.97 (dt, J = 7.78, 0.69 Hz, 1H), 7.79 (s, 1H), 7.48 (td, J = 7.82, 1.33 Hz, 1H), 7.38 (t, J = 7.48 Hz, 1H), 7.29 (d, J = 8.51 Hz, 1H), 2.88 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.17, 139.07, 136.93, 133.54, 128.62, 127.42, 126.77, 126.61, 123.81, 120.18, 119.92, 116.54, 116.10, 27.93, 21.45. IR (KBr plate, CDCl_3) ν 3018, 1690, 1452, 1369, 1301, 748. Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}$: C, 80.68; H, 5.87. Found: C, 80.44; H, 5.93.

9-Acetyl-1,3-dimethylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (95:5 hexanes:EtOAc), yield 45 mg (95%, mp 65-66 °C). ^1H NMR (500 MHz, CDCl_3) δ 7.95 (m, 2H), 7.64 (s, 1H), 7.44 (t, J = 7.77 Hz, 1H), 7.36 (t, J = 7.48 Hz, 1H), 7.13 (s, 1H), 2.70 (s, 3H), 2.50 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.95, 140.24, 137.36, 134.06, 131.48, 128.18, 127.13, 126.89, 126.22, 123.49, 120.13, 117.72, 114.75, 27.22, 21.45, 21.38. IR (KBr plate, CDCl_3) ν 2925, 1702, 1433, 1363, 1273, 1212, 748. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}$: C, 80.97; H, 6.38. Found: C, 81.14; H, 6.28.

9-Acetyl-1-methoxycarbazole. Following the general procedures, this minor product from several experiments was combined and purified by silica gel chromatography (85:15 hexanes:EtOAc). Removal of solvents by rotary evaporation gave a colorless oil, yield 12 mg. ^1H NMR (500 MHz, CDCl_3) δ 8.30 (d, J = 8.35 Hz, 1H), 7.96 (d, J = 7.67 Hz, 1H), 7.65 (d, J = 7.70 Hz, 1H), 7.48 (t, J = 7.80 Hz, 1H), 7.40-7.34 (m, 2H), 7.02 (d, J = 8.01 Hz, 1H), 4.01 (s, 3H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.16, 148.24, 140.36, 129.32, 128.06, 127.85, 125.45, 124.80, 123.45, 119.92, 115.30, 112.96,

109.50, 55.88, 27.45. IR (KBr plate, CDCl_3) ν 1700, 1585, 1450, 1423, 1325, 1266, 1224, 1016, 751.

9-Acetyl-2-methoxycarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (80:20 hexanes:EtOAc), yield 47 mg (97%, mp 82 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, J = 8.08 Hz, 1H), 7.91 (m, 2H), 7.86 (d, J = 8.51 Hz, 1H), 7.39 (m, 2H), 6.99 (dd, J = 8.50, 2.21 Hz, 1H), 3.94 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.42, 159.96, 140.27, 138.60, 126.88, 126.09, 123.88, 120.39, 119.91, 119.37, 115.93, 111.58, 102.15, 55.97, 27.97. IR (KBr plate, CDCl_3) ν 1693, 1463, 1369, 1327, 1200, 1041, 763, 747. Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.28; H, 5.48. Found: C, 75.50; H, 5.52.

9-Acetyl-3-methoxycarbazole. Following the general procedures, a light yellow viscous oil was obtained after silica gel chromatography (85:15 hexanes:EtOAc), yield 19 mg (40%). ^1H NMR (500 MHz, CDCl_3) δ 8.15 (m, 2H), 7.94 (d, J = 7.66 Hz, 1H), 7.47 (t, J = 7.84 Hz, 1H), 7.43 (d, J = 2.67 Hz, 1H), 7.37 (t, J = 7.48 Hz, 1H), 7.05 (dd, J = 9.08, 2.50 Hz, 1H), 3.94 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 169.86, 156.59, 139.25, 133.26, 127.60, 127.57, 126.60, 123.67, 120.02, 117.47, 116.43, 115.00, 103.32, 55.94, 27.82. IR (KBr plate, CDCl_3) ν 1686, 1490, 1456, 1371, 1303, 1203, 1035, 748. Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.28; H, 5.48. Found: C, 75.51; H, 5.60.

9-Acetyl-4-methoxycarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 10:1, 9:1, 8:1), yield 40 mg (84%, mp 106-107 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.33 (d, J = 7.70 Hz, 1H), 8.19 (d, J = 8.24 Hz, 1H), 7.76 (d, J = 8.24 Hz, 1H), 7.44 (td, J = 7.78, 1.26 Hz, 1H), 7.41-7.34 (m, 2H), 6.83 (d, J = 8.12 Hz, 1H), 4.05 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.40, 155.80, 139.91, 137.99, 127.98, 126.40, 125.77, 123.80, 123.34, 115.69, 115.38, 108.79, 105.02, 55.66, 27.94. IR (KBr plate, CDCl_3) ν 2966, 2937, 1695, 1598, 1432, 1369, 1274, 1208, 1098, 788, 753, 719. Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.28; H, 5.48. Found: C, 75.42; H, 5.44.

9-Acetyl-2,4-dimethoxycarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (85:15 hexanes:EtOAc), yield 46 mg (86%, mp 137 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.23 (m, 1H), 7.99 (m, 1H), 7.57 (s, 1H), 7.34 (m, 2H), 6.50 (s, 1H), 4.04 (s, 3H), 3.93 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.64, 160.93, 156.12, 140.99, 137.76, 126.29, 125.07, 123.90, 122.52, 115.15, 109.29, 94.95, 93.86, 56.02, 55.77, 28.05. IR (KBr plate, CDCl_3) ν 2960, 2940, 1699, 1617, 1598, 1456, 1429, 1288, 1218, 1112, 826, 747. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 71.35; H, 5.62. Found: C, 71.48; H, 5.58.

9-Acetyl-2-methoxy-6-methylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (90:10 hexanes:EtOAc), yield 45 mg (89%, mp 78 °C). ^1H NMR (500 MHz, CDCl_3) δ 7.94 (s, 1H), 7.90 (d, J = 8.39 Hz, 1H), 7.82 (d, J = 8.55 Hz, 1H), 7.69 (s, 2H), 7.21 (d, J = 8.47 Hz, 1H), 6.98 (d, J = 8.39 Hz, 1H), 3.93 (s, 3H), 2.85 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 170.30, 159.88, 140.52, 136.71, 133.53, 127.10, 127.04, 120.25, 119.92, 119.60, 115.59, 111.53, 102.25, 55.97, 27.90, 21.43. IR (KBr plate, CDCl_3) ν 2918, 1689, 1426, 1369, 1315, 809. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_2$: C, 75.86; H, 5.97. Found: C, 76.03; H, 5.88.

9-Acetyl-2-trifluoromethylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 7:1, 6:1, 5:1), yield 52 mg (94%, mp 125 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.68 (s, 1H), 8.10 (m, 3H), 7.67 (d, J = 7.63 Hz, 1H), 7.58 (t, J = 7.86 Hz, 1H), 7.46 (t, J = 7.44 Hz, 1H), 2.94 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -61.53. ^{13}C NMR (125 MHz, CDCl_3) δ 170.03, 139.23, 138.24, 129.39, 129.14, 128.99, 128.98, 128.88, 128.64, 125.72, 125.38, 124.11, 123.55, 120.78, 120.75, 120.72, 120.69, 119.98, 115.94, 114.21, 114.17, 114.14, 114.11, 27.83. IR (KBr plate, CDCl_3) ν 1718, 1369, 1320, 1277, 1110, 749, 725. Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{NOF}_3$: C, 64.98; H, 3.64. Found: C, 64.94; H, 3.59.

9-Acetyl-3-trifluoromethylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 8:1, 7:1), yield 50 mg (90%, mp 79-81 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.43 (d, J = 8.73

Hz, 1H), 8.25 (s, 1H), 8.13 (d, $J = 8.43$ Hz, 1H), 8.05 (d, $J = 7.70$ Hz, 1H), 7.73 (d, $J = 8.77$ Hz, 1H), 7.56 (t, $J = 7.86$ Hz, 1H), 7.45 (t, $J = 7.52$ Hz, 1H), 2.92 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -61.57. ^{13}C NMR (125 MHz, CDCl_3) δ 170.23, 140.59, 139.10, 128.42, 126.46, 126.25, 125.99, 125.73, 125.70, 124.42, 124.39, 124.37, 124.34, 124.25, 123.56, 120.49, 117.22, 117.19, 117.16, 117.12, 116.92, 116.13, 27.94. IR (KBr plate, CDCl_3) ν 2925, 1701, 1332, 1272, 1116, 1063, 749. Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{NOF}_3$: C, 64.98; H, 3.64. Found: C, 65.38; H, 3.68.

9-Acetyl-4-trifluoromethylcarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 8:1, 7:1), yield 47 mg (84%, mp 96 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.66 (d, $J = 8.47$ Hz, 1H), 8.34 (d, $J = 8.09$ Hz, 1H), 8.13 (d, $J = 8.51$ Hz, 1H), 7.73 (d, $J = 7.63$ Hz, 1H), 7.57 (t, $J = 8.11$ Hz, 2H), 7.46 (t, $J = 7.69$ Hz, 1H), 2.93 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -62.04. ^{13}C NMR (125 MHz, CDCl_3) δ 170.30, 140.39, 139.03, 128.38, 127.84, 126.78, 125.67, 124.22, 124.03, 123.99, 123.94, 123.90, 123.60, 123.51, 123.24, 123.13, 123.11, 122.98, 121.57, 121.52, 121.47, 121.42, 121.35, 120.34, 115.52, 28.27. IR (KBr plate, CDCl_3) ν 1692, 1429, 1368, 1318, 1174, 1115, 1027, 801, 725. Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{NOF}_3$: C, 64.98; H, 3.64. Found: C, 64.77; H, 3.67.

9-Acetyl-2-fluorocarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (93:7 hexanes:EtOAc), yield 40 mg (89%, mp 101-102 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.12-8.05 (m, 2H), 7.96 (d, $J = 7.74$ Hz, 1H), 7.94-7.89 (m, 1H), 7.47 (t, $J = 7.81$ Hz, 1H), 7.40 (t, $J = 7.23$ Hz, 1H), 7.14 (td, $J = 8.64, 2.29$ Hz, 1H), 2.89 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -112.75. ^{13}C NMR (125 MHz, CDCl_3) δ 170.18, 163.56, 161.63, 139.55, 139.45, 138.97, 127.06, 127.06, 126.18, 124.08, 122.65, 122.64, 120.65, 120.57, 119.91, 115.99, 111.87, 111.68, 104.86, 104.62, 27.87. IR (KBr plate, CDCl_3) ν 3131, 3059, 1698, 1592, 1460, 1368, 1331, 749. Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{NOF}$: C, 73.98; H, 4.44. Found: C, 74.19; H, 4.38.

9-Acetyl-3-fluorocarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (90:10 hexanes:EtOAc), yield 43 mg (95%,

mp 107-108 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.31 (m, 1H), 8.10 (d, $J = 8.31$ Hz, 1H), 7.96 (d, $J = 7.67$ Hz, 1H), 7.63 (dd, $J = 8.15, 2.69$ Hz, 1H), 7.52 (t, $J = 7.85$ Hz, 1H), 7.41 (t, $J = 7.48$ Hz, 1H), 7.20 (td, $J = 8.97, 2.62$ Hz, 1H), 2.89 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -119.01. ^{13}C NMR (125 MHz, CDCl_3) δ 169.98, 160.77, 158.85, 139.32, 135.21, 128.12, 127.87, 127.79, 126.12, 126.09, 123.91, 120.47, 118.05, 117.99, 116.21, 114.94, 114.75, 106.14, 105.95, 27.89. IR (KBr plate, CDCl_3) ν 3059, 1690, 1484, 1370, 1309, 1170, 749. Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{NOF}$: C, 73.98; H, 4.44. Found: C, 74.07; H, 4.43.

9-Acetyl-4-fluorocarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 9:1, 8:1), yield 35 mg (77%, mp 115-116 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.18 (d, 8.05 Hz, 2H), 8.05 (d, $J = 8.40$ Hz, 1H), 7.52 (td, $J = 7.89, 1.34$ Hz, 1H), 7.46-7.39 (m, 2H), 7.10 (td, $J = 8.89, 0.61$ Hz, 1H), 2.90 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -119.61. ^{13}C NMR (125 MHz, CDCl_3) δ 170.29, 159.14, 157.16, 140.70, 140.63, 138.35, 128.19, 128.13, 127.66, 127.65, 124.32, 123.92, 123.90, 123.28, 123.24, 116.01, 115.09, 114.94, 112.38, 112.35, 110.26, 110.12, 27.98. IR (KBr plate, CDCl_3) ν 3059, 1698, 1447, 1316, 1300, 1253, 1229, 783, 750, 713. Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{NOF}$: C, 73.98; H, 4.44. Found: C, 73.70; H, 4.63.

9-Acetyl-1,3-difluorocarbazole. Following the general procedures, an off-white powder was obtained after silica gel chromatography (gradient; hexanes:EtOAc, 100:1, 100:2), yield 45 mg (93%, mp 75-77 °C). ^1H NMR (500 MHz, CDCl_3) δ 8.38 (d, $J = 8.43$ Hz, 1H), 7.92 (d, $J = 7.74$ Hz, 1H), 7.59-7.49 (m, 2H), 7.41 (t, $J = 7.54$ Hz, 1H), 7.40 (t, $J = 7.23$ Hz, 1H), 7.01 (td, $J = 10.53, 2.37$ Hz, 1H), 2.71 (dd, $J = 6.67, 0.61$ Hz, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -113.31, -115.90. ^{13}C NMR (125 MHz, CDCl_3) δ 170.87, 160.54, 160.45, 158.59, 158.51, 150.98, 150.88, 148.98, 148.88, 140.95, 131.12, 131.09, 131.04, 131.00, 129.25, 124.91, 124.89, 124.88, 124.86, 124.16, 120.19, 116.41, 103.40, 103.20, 103.18, 102.97, 102.76, 102.73, 102.57, 102.54, 76.98, 26.58, 26.45. IR (KBr plate, CDCl_3) ν 3066, 1705, 1634, 1595, 1496, 1445, 1426, 1285, 1149, 748. Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{NOF}_2$: C, 68.55; H, 3.70. Found: C, 68.82; H, 3.83.

Additional Characterization Details of Regioisomeric Carbazoles in Table 3. The regioselectivity of entries 9 and 10 were determined from GC analyses of the unpurified mixtures. The identity of the major regioisomer of entry 9 in Table 3 was confirmed by both the ^1H splitting pattern and a 2D gCOSY experiment. The splitting pattern of the minor regioisomer is consistent with the proposed structure. Both regioisomers have the same molecular ion (m/z [M^+] = 239) in GC/MS. The identity of the major regioisomer of entry 10 in Table 3 was confirmed by comparing its ^1H NMR with an authentic sample prepared as in entry 2 in Table 2, for which there is no ambiguity. The ^1H splitting pattern is consistent with the assigned structure. Both the major and the minor regioisomers have the same molecular ion (m/z [M^+] = 223) in GC/MS.

Representative Procedures for the Preparation of Substituted 2'-Bromoacetanilides.

An oven-dried round flask was cooled under vacuum and Ar. Commercially available aniline (~ 0.5 mmol) and EtOAc (1.0 mL) were loaded. Neat acetyl chloride (2.2 equiv) was added dropwise at ambient temperature, and a precipitate was formed. The reaction was heated to 80 $^\circ\text{C}$ and stirred until the precipitate was completely dissolved (ca. 30 min). The reaction mixture was cooled to 0 $^\circ\text{C}$, and saturated NaHCO_3 solution (2 mL) was added slowly. The reaction mixture was stirred for 10 min before it was extracted with EtOAc (3 x 2 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 , and EtOAc was removed *in vacuo*. The dried crude material was pure enough for the Suzuki-Miyaura coupling reaction. The compounds could be further purified by recrystallization from hexanes and EtOAc mixtures.

2'-Bromo-4'-trifluoromethylacetanilide. The reaction was performed on a 3.78 mmol scale. A white powder was obtained after drying under oil-pump vacuum, yield 1.06 g (99%, mp 146 $^\circ\text{C}$). ^1H NMR (500 MHz, CDCl_3) δ 8.56 (d, J = 8.70 Hz, 1H), 7.81 (s, 1H), 7.75 (s, 1H), 7.58 (d, J = 8.64 Hz, 1H), 2.29 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -62.65. ^{13}C NMR (125 MHz, CDCl_3) δ 168.65, 138.93, 129.54, 129.51, 129.48, 129.44, 127.32, 127.05, 126.78, 126.54, 125.81, 125.78, 125.75, 125.72, 124.38, 122.22, 121.34,

120.05, 112.64, 25.14. IR (KBr plate, CDCl_3) ν 3292, 1667, 1394, 1165, 1140, 1116, 891, 836. Anal. Calcd. for $\text{C}_9\text{H}_7\text{NOBrF}_3$: C, 38.44; H, 2.51. Found: C, 38.21; H, 2.46.

2'-Bromo-4',6'-difluoroacetanilide. The reaction was performed on a 25 mmol scale. A white powder was obtained after drying under oil-pump vacuum, yield 6.05 g (97%, mp 156-157 °C). ^1H NMR (500 MHz, CDCl_3 , mixture of rotamers) δ 7.20 (d, $J = 5.57$ Hz, 1H), 6.92 (t, $J = 7.94$ Hz, 1H), 6.74 (s, 1H), 6.50 (s, 1H), 2.25 (s, 3H), 1.91 (s, 3H). ^{19}F NMR (282 MHz, CDCl_3) δ -109.21, -109.94, -110.02, -110.04. ^{13}C NMR (125 MHz, CDCl_3) δ 168.90, 162.19, 162.09, 160.18, 160.08, 159.65, 159.54, 157.62, 157.51, 123.14, 123.07, 121.23, 121.14, 116.01, 115.81, 104.76, 104.55, 104.35, 23.22. IR (KBr plate, CDCl_3) ν 3239, 1670, 1527, 1482, 1425, 1115, 850. Anal. Calcd. for $\text{C}_8\text{H}_6\text{NOBrF}_2$: C, 38.56; H, 2.43. Found: C, 38.27; H, 2.39.

2'-Bromo-4',6'-dimethylacetanilide. The reaction was performed on a 10.7 mmol scale. An off-white powder was obtained after recrystallization, yield 2.17 g (84%, mp 196 °C). ^1H NMR (500 MHz, CDCl_3 , mixture of rotamers) δ 7.35 (s, 1H), 7.27 (s, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 6.93 (s, 1H), 6.69 (s, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.27, 168.96, 140.06, 138.77, 138.61, 138.06, 132.57, 131.59, 131.54, 131.06, 130.90, 130.77, 124.87, 122.14, 23.41, 20.95, 20.88, 20.42, 19.28, 19.26. IR (KBr plate, CDCl_3) ν 3236, 3030, 1657, 1534, 1300, 862, 708. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{NOBr}$: C, 49.79; H, 5.02. Found: C, 49.57; H, 5.05.

STANDARD PROTON PARAMETERS
Solvent: CDCl₃
Ambient temperature
INNOVA-500 "rocky"
PULSE SEQUENCE
Relax. delay 10.000 sec
Pulse 90.0 degrees
Acq. time 3.200 sec
Width 10000.0 Hz
Observed H1 500.2312701 MHz
DATA PROCESSING
FT size 524288
Total time 3 minutes