SUPPORTING INFORMATION

Synthesis of 3-Iodoindoles by Electrophilic Cyclization of *N,N*-Dialkyl-2-(1-alkynyl)anilines

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Experiment Section

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of ethyl ether, hexanes, ethyl acetate, methylene chloride and DMF were purchased from Fisher Scientific Co. 2-Iodoaniline, phenylacetylene, 1-octyne, 1-cyclohexenyl acetylene, *tert*-butyl acetylene, 5-hexynenitrile, 5-chloro-1-hexyne, ethyl 4-(*n*-butylamino)-3-iodobenzoate and Et₃N were purchased from Aldrich Chemical Co., Inc. The palladium salts were donated by Johnson Matthey Inc. and Kawaken Fine Chemicals Co. Ltd.

Preparation of 2-Iodoanilines. 2-Iodo-4-nitroaniline,¹ 2-iodo-5-methoxyaniline¹ and ethyl 4-(*n*-butylamino)-3-iodobenzoate² were prepared according to literature procedures. The ¹H and ¹³C NMR spectral data were in good agreement with the literature data.

Ethyl 4-(*n*-butylamino)-3-iodobenzoate. This compound was obtained as a yellow oil: ¹H NMR (300 MHz, CDCl₃) δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 6.9 Hz, 3H), 1.40-1.52 (m, 2H), 1.63-1.72 (m, 2H), 3.18-3.22 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 4.61 (s, 1H), 6.49 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.33 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ

14.0, 14.6, 20.4, 31.2, 43.8, 60.7, 83.8, 108.9, 120.0, 131.7, 140.8, 150.7, 165.7; IR (neat, cm^{-1}) 3394, 2959, 2930, 2871, 1711. The product was used for the next step without further characterization.

General Procedure for Preparation of the *N,N*-Dialkyl-*o*-iodoanilines. These compounds were prepared by a procedure reported by Cadogan.³ A solution of the corresponding aniline (2.0 mmol) and iodomethane (0.85 g, 6.0 mmol) in DMF (10 ml) containing K_2CO_3 (0.55 g, 4.0 mmol) was stirred for 48 h at room temperature. Water (10 ml) was then added, and the solution was extracted with ethyl ether (3 x 10 ml). The organic extracts were washed with water (4 x 20 ml) to remove any remaining DMF, and then dried (Na_2SO_4) and the solvent was removed under reduced pressure to yield the crude product, which was further purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent.

***N,N*-Dialkyl-2-iodoanilines Prepared.**

***N,N*-Dimethyl-2-iodoaniline.** This compound was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 2.76 (s, 6H), 6.76 (t, J = 8.2 Hz, 1H), 7.08 (d, J = 9.3 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 45.2, 97.3, 120.6, 125.2, 129.2, 140.4, 155.1; IR (neat, cm^{-1}) 3002, 1944, 2830, 2783; HRMS calcd for $\text{C}_8\text{H}_{10}\text{IN}$ 246.98580. Found 246.98605.

***N,N*-Dimethyl-2-iodo-4-nitroaniline.** This compound was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 2.94 (s, 6H), 6.98 (d, J = 9.0 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 8.69 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 44.4, 90.6, 118.6, 124.8, 136.8, 160.7; IR (neat, cm^{-1}) 2947, 2871, 2843, 2794; HRMS calcd for $\text{C}_8\text{H}_9\text{IN}_2\text{O}_2$ 291.97088. Found 291.97104.

***N,N*-Dimethyl-2-iodo-5-methoxyaniline.** The compound was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 2.75 (s, 6H), 3.78 (s, 3H), 6.38 (d, J = 10.4 Hz, 1H), 6.66 (s, 1H), 7.68 (d, J = 8.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 45.0, 55.5, 85.4, 107.8, 110.0, 140.3, 156.1, 160.9; IR (neat, cm^{-1}) 2293, 2829, 2780; HRMS calcd for $\text{C}_9\text{H}_{12}\text{INO}$ 276.99637. Found 276.99697.

Ethyl 4-(*n*-butylmethylanino)-3-iodobenzoate. The product was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, J = 7.5 Hz, 3H), 1.30-1.40 (m, 5H), 2.78 (s, 3H), 3.03 (t, J = 9.0 Hz, 2H), 4.35 (q, J = 7.2 Hz, 2H), 7.02 (d, J = 8.4 Hz, 1H), 7.96 (dd, J = 8.4, 2.1 Hz, 1H), 8.49 (d, J = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.2, 14.6, 20.4, 29.7, 41.9, 56.1, 61.2, 95.7, 120.7, 126.2, 130.5, 142.0, 158.9, 165.4; IR (neat, cm^{-1}) 3004, 2922, 1713; HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{INO}_2$ 361.05388. Found 361.05433.

General Procedure for the Palladium-Catalyzed Formation of *N,N*-Dialkyl-2-(1-alkynyl)anilines. To a solution of Et_3N (12.5 ml), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.070 g, 2 mol %), 5 mmol of *N,N*-dialkyl-*o*-iodoaniline and 6.0 mmol of terminal acetylene (stired 5 min beforehand), CuI (0.010 g, 1 mol %) was added and stirring was continued for another 2 min before flushing with Ar. The flask was then sealed. The mixture was allowed to stir at room temperature for the desired time and the resulting solution was filtered and washed with a satd aq NaCl solution and extracted with diethyl ether (2 x 10 ml). The combined ether fractions were dried over Na_2SO_4 and concentrated under vacuum to yield the crude product. The crude product was purified by flash chromatography on silica gel using ethyl acetate/hexane as the eluent.

***N,N*-Dialkyl-2-(1-alkynyl)anilines Prepared.**

***N,N*-Dimethyl-2-(phenylethynyl)aniline (1).** The product was obtained as a yellow oil:

^1H NMR (400 MHz, CDCl_3) δ 3.01 (s, 6H), 6.88-6.94 (m, 2H), 7.25 (t, J = 6.3 Hz, 1H), 7.31-7.37 (m, 3H), 7.49 (d, J = 5.7 Hz, 1H), 7.54 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 43.8, 89.1, 95.0, 115.3, 117.2, 120.7, 124.1, 128.2, 128.5, 129.5, 131.5, 134.6, 155.0; IR (neat, cm^{-1}) 3059, 2943, 2833, 2785, 2209; HRMS calcd for $\text{C}_{16}\text{H}_{15}\text{N}$ 221.12045. Found 221.12076.

***N,N*-Dimethyl-2-(3,3-dimethyl-1-butynyl)aniline (3).** The product was obtained as a

yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.34 (s, 9H), 2.92 (s, 6H), 6.80-6.86 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 28.5, 31.2, 43.6, 78.5, 104.0, 116.2, 116.9, 120.5, 128.5, 134.5, 154.6; IR (neat, cm^{-1}) 3004, 2923, 2147; HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{N}$ 200.14392. Found 200.14417.

***N,N*-Dimethyl-2-(1-octynyl)aniline (5).** The product was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, J = 6.9 Hz, 3H), 1.29-1.34 (m, 4 H), 1.46-1.49 (m, 2H), 1.62 (q, J = 3.8 Hz, 2H), 2.47 (t, J = 7.2 Hz, 2H), 2.91 (s, 3H), 6.83-6.90 (m, 2H), 7.18 (t, J = 5.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.3, 20.1, 22.8, 28.9, 29.0, 31.6, 43.8, 79.7, 96.1, 116.8, 117.1, 120.9, 128.5, 134.5, 154.8; IR (neat, cm^{-1}) 2930, 2858, 2782, 2242; HRMS calcd for $\text{C}_{16}\text{H}_{23}\text{N}$ 229.18305. Found 229.18336.

***N,N*-Dimethyl-2-(cyclohex-1-enyl)aniline (7).** The product was obtained as a yellow oil:

^1H NMR (300 MHz, CDCl_3) δ 1.62-1.68 (m, 4H), 2.13-2.15 (m, 2H), 2.25-2.27 (m, 2H), 2.93 (s, 6H), 6.18-6.19 (m, 1H), 6.84-6.89 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.37 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.8, 22.5, 25.9, 29.3, 43.6, 86.3, 96.8, 115.9, 117.0, 120.6, 121.3, 128.8, 134.2, 134.4, 154.6; IR (neat, cm^{-1}) 2932, 2859, 2832, 2196; HRMS calcd for $\text{C}_{16}\text{H}_{19}\text{N}$ 225.15175. Found 225.15209.

6-(2-*N,N*-Dimethylaminophenyl)-5-hexynenitrile (9). The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.97 (t, J = 7.2 Hz, 2H), 2.57 (t, J = 7.2 Hz, 2H), 2.67 (t, J = 6.8 Hz, 2H), 2.90 (s, 6H), 6.87 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.3, 19.1, 24.9, 43.8, 81.6, 92.3, 115.9, 117.3, 119.4, 121.0, 129.1, 134.4, 155.0; IR (neat, cm^{-1}) 3061, 2942, 2834, 2785, 2247; HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2$ 212.13135. Found 212.13172.

***N,N*-Dimethyl-2-(5-chloro-1-pentynyl)aniline (11).** The product was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 2.04-2.11 (m, 2H), 2.68 (t, J = 6.8 Hz, 2H), 2.91 (s, 6H), 3.74 (t, J = 6.3 Hz, 2H), 6.84-6.92 (m, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 17.6, 31.7, 43.8, 44.0, 80.8, 93.6, 116.3, 117.3, 121.0, 128.9, 134.5, 154.9; IR (neat, cm^{-1}) 2943, 2832, 2784, 2259; HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{ClN}$ 221.69713. Found 221.69754.

***N,N*-Dimethyl-4-nitro-2-(phenylethynyl)aniline (13).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 3.26 (s, 6H), 6.78 (d, J = 9.2 Hz, 1H), 7.36-7.38 (m, 3H), 7.50-7.52 (m, 2H), 8.06 (dd, J = 9.2, 2.4 Hz, 1H), 8.35 (d, J = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 42.7, 87.7, 95.3, 110.4, 114.7, 123.0, 125.1, 128.6, 128.7, 131.1, 131.4, 138.5, 157.5; IR (neat, cm^{-1}) 2954, 2917, 2849, 2133; HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2$ 266.10553. Found 266.10592.

***N,N*-Dimethyl-4-nitro-2-(1-octynyl)aniline (15).** The product was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, J = 6.8 Hz, 3H), 1.30-1.34 (m, 4H), 1.43-1.48 (m, 2H), 1.62 (q, J = 7.2 Hz, 2H), 2.45 (t, J = 7.1 Hz, 2H), 3.15 (s, 6H), 6.73 (d, J = 9.3 Hz, 1H), 7.99 (dd, J = 9.3, 2.7 Hz, 1H), 8.20 (d, J = 2.7 Hz, 1H); ^{13}C NMR (75 MHz,

CDCl₃) δ 14.2, 19.9, 22.7, 28.7, 28.9, 31.5, 42.8, 78.7, 97.3, 112.4, 114.9, 124.5, 131.4, 138.9, 158.0; IR (neat, cm⁻¹) 2930, 2857, 2806, 2224; HRMS calcd for C₁₆H₂₂N₂O₂ 274.16813. Found 274.16830.

***N,N*-Dimethyl-2-(cyclohex-1-enylethynyl)-5-methoxyaniline (17).** The product was obtained as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 1.59-1.68 (m, 4H), 2.12-2.14 (m, 2H), 2.22-2.24 (m, 2H), 2.92 (s, 6H), 3.78 (s, 3H), 6.13-6.15 (m, 1H), 6.38-6.41 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.8, 22.6, 25.9, 29.4, 43.4, 55.3, 86.2, 95.3, 103.8, 105.2, 108.3, 121.4, 133.6, 135.3, 156.0, 160.3; IR (neat, cm⁻¹) 2932, 2834, 2786, 2194; HRMS calcd for C₁₇H₂₁NO 255.16231. Found 255.16270.

Ethyl 4-*n*-butylmethylamino-3-(phenylethynyl)benzoate (19). The product was obtained as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 0.87 (t, *J* = 7.4 Hz, 3H), 1.25-1.31 (m, 2H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.63-1.69 (m, 2H), 3.02 (s, 3H), 3.54 (t, *J* = 7.8 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 1H), 7.31-7.35 (m, 3H), 7.49-7.51 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 8.15 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 14.6, 20.4, 30.1, 39.8, 54.9, 60.7, 89.0, 94.2, 111.7, 115.8, 120.5, 123.8, 128.2, 128.5, 130.8, 131.3, 137.1, 156.6, 166.2; IR (neat, cm⁻¹) 2957, 2929, 2870, 2203; HRMS calcd for C₂₂H₂₅NO₂ 335.18853. Found 335.18887.

General Procedure for Iodocyclization. To a solution of 0.25 mmol of the *N,N*-dialkyl-2-(1-alkynyl)aniline and 3 ml of CH₂Cl₂, 2 equivs of I₂ dissolved in 2 ml of CH₂Cl₂ was added gradually. The reaction mixture was flushed with Ar and allowed to stir at room temperature for the desired time. The excess I₂ was removed by washing with a satd aq soln of Na₂S₂O₃. The aqueous solution was then extracted by diethyl ether (2 x 10 ml). The combined ether layers were dried over anhydrous Na₂SO₄ and concentrated under a

vacuum to yield the crude product, which was purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.

3-Iodoindoles Prepared.

***N*-Methyl-3-iodo-2-phenylindole (2).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 3.63 (s, 3H), 7.21-7.28 (m, 3H), 7.43-7.51 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 32.2, 59.0, 110.0, 120.9, 121.6, 123.1, 128.6, 129.0, 130.5, 131.1, 131.8, 137.9, 141.9; IR (neat, cm^{-1}) 3054, 2937; HRMS calcd for $\text{C}_{15}\text{H}_{12}\text{IN}$ 333.00145. Found 333.00194.

***N*-Methyl-2-*t*-butyl-3-iodoindole (4).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.67 (s, 9H), 3.92 (s, 3H), 7.16-7.25 (m, 3H), 7.52 (t, $J = 6.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 30.4, 32.4, 34.7, 54.5, 109.0, 120.5, 122.4, 122.8, 131.6, 138.6, 144.4; IR (neat, cm^{-1}) 3004, 2966, 2922; HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{IN}$ 312.02492. Found 312.02515.

***N*-Methyl-2-*n*-hexyl-3-iodoindole (6).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.30-1.43 (m, 6H), 1.56-1.59 (m, 2H), 2.82 (t, $J = 8.0$ Hz, 2H), 3.70 (s, 3H), 7.12-7.20 (m, 3H), 7.37 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3, 22.8, 27.3, 29.2, 29.5, 30.8, 31.8, 57.9, 109.4, 120.4, 120.7, 122.1, 130.2, 137.6, 142.0; IR (neat, cm^{-1}) 3053, 2926, 2855; HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{IN}$ 341.06405. Found 341.06452.

***N*-Methyl-2-(cyclohex-1-enyl)-3-iodoindole (8).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.73-1.76 (m, 2H), 1.81-1.84 (m, 2H), 2.22-2.30 (m, 4H), 3.68 (s, 3H), 5.88-5.90 (m, 1H), 7.17-7.19 (m, 1H), 7.22-7.24 (m, 2H), 7.41 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.1, 22.9, 25.7, 29.4, 31.5, 57.0, 109.7,

120.5, 121.2, 122.4, 130.0, 130.3, 133.8, 137.3, 144.4; IR (neat, cm^{-1}) 2921, 2850;

HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{IN}$ 337.03275. Found 337.03300.

4-(*N*-Methyl-3-iodoindol-2-yl)butanenitrile (10). The product was obtained as a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 1.99 (q, $J = 7.4$ Hz, 2H), 2.42 (t, $J = 7.1$ Hz, 2H), 3.02 (t, $J = 7.5$ Hz, 2H), 3.77 (s, 3H), 7.17-7.21 (m, 1H), 7.24-7.26 (m, 2H), 7.38 (d, $J = 7.7$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.8, 25.4, 26.0, 30.9, 59.3, 109.6, 119.5, 120.8, 121.0, 122.8, 130.0, 137.8, 138.8; IR (neat, cm^{-1}) 2935, 2869, 2246; HRMS calcd for $\text{C}_{13}\text{H}_{13}\text{IN}_2$ 324.01235. Found 324.01269.

***N*-Methyl-2-(3-chloropropyl)-3-iodoindole (12).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 2.04-2.11 (m, 2H), 3.02 (t, $J = 7.6$ Hz, 2H), 3.60 (t, $J = 7.8$ Hz, 2H), 3.76 (s, 3H), 7.14-7.18 (m, 1H), 7.22-7.23 (m, 2H), 7.38 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 24.6, 30.9, 32.3, 44.4, 58.6, 109.6, 120.6, 120.8, 122.5, 130.1, 137.7, 140.0; IR (neat, cm^{-1}) 2956, 2928, 2869; HRMS calcd for $\text{C}_{12}\text{H}_{13}\text{ClIN}$ 333.57813. Found 333.57851.

***N*-Methyl-3-iodo-5-nitro-2-phenylindole (14).** The compound was obtained as pale yellow crystals, which decompose at 125 °C: ^1H NMR (300 MHz, CDCl_3) δ 3.74 (s, 3H), 7.36 (d, $J = 9.0$ Hz, 1H), 7.46-7.59 (m, 2H), 7.53-7.57 (m, 3H), 8.19 (dd, $J = 9.0, 2.4$ Hz, 1H), 8.45 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.6, 32.7, 61.3, 110.2, 118.6, 119.0, 128.9, 129.8, 130.2, 130.7, 130.9, 140.9, 142.7, 145.4; IR (neat, cm^{-1}) 2924, 2852; HRMS calcd for $\text{C}_{15}\text{H}_{11}\text{IN}_2\text{O}_2$ 378.01168. Found 378.01242.

***N*-Methyl-2-*n*-hexyl-3-iodo-5-nitroindole (16).** The product was obtained as a pale yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, $J = 7.1$ Hz, 3H), 1.31-1.37 (m, 4H), 1.39-1.46 (m, 2H), 1.57-1.64 (m, 2H), 2.87 (t, $J = 7.5$ Hz, 2H), 3.81 (s, 3H), 7.25 (d, $J = 8.4$ Hz,

1H), 8.09 (dd, $J = 9.0, 2.4$ Hz, 1H), 8.32 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.3, 16.6, 22.8, 27.6, 29.3, 31.4, 31.7, 60.3, 109.5, 117.8, 118.0, 130.0, 140.8, 142.4, 145.9; IR (neat, cm^{-1}) 3004, 2964, 2923; HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{IN}_2\text{O}_2$ 386.04913. Found 386.04988.

***N*-Methyl-2-(1-cyclohexenyl)-3-iodo-6-methoxyindole (18).** The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 1.72-1.75 (m, 2H), 1.79-1.82 (m, 2H), 2.22-2.26 (m, 4H), 3.61 (s, 3H), 3.86 (s, 3H), 5.87 (s, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 6.82 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.27 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.1, 22.9, 25.7, 29.5, 31.5, 56.0, 56.5, 93.4, 110.1, 121.8, 124.6, 130.0, 133.7, 137.8, 143.5, 157.0; IR (neat, cm^{-1}) 2925, 2855; HRMS calcd for $\text{C}_{16}\text{H}_{18}\text{INO}$ 367.06332. Found 367.06396.

Ethyl 1-*n*-butyl-3-iodo-2-phenylindole-5-carboxylate (20). The product was obtained as a yellow oil: ^1H NMR (400 MHz, CDCl_3) δ 0.67 (t, $J = 7.2$ Hz, 3H), 1.02-1.07 (m, 2H), 1.36 (t, $J = 7.0$ Hz, 3H), 1.47-1.51 (m, 2H), 4.00 (t, $J = 7.2$ Hz, 2H), 4.34 (t, $J = 7.0$ Hz, 2H), 7.25 (d, $J = 8.8$ Hz, 1H), 7.34-7.43 (m, 5H), 7.91 (d, $J = 8.4$ Hz, 1H), 8.17 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.7, 14.7, 20.0, 32.2, 45.2, 60.9, 61.2, 110.1, 123.2, 124.2, 124.5, 128.7, 129.3, 130.3, 130.9, 131.7, 139.6, 143.3, 167.6; IR (neat, cm^{-1}) 3058, 2959, 2932, 2872, 1709; HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{INO}_2$ 447.06953. Found 447.07000.

Ethyl 3-iodo-1-methyl-2-phenylindole-5-carboxylate (21). The product was obtained as a pale yellow solid: mp 103-105 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 1.38 (t, $J = 7.2$ Hz, 3H), 3.62 (s, 3H), 4.36 (q, $J = 7.2$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 1H), 7.38-7.48 (m, 5H), 7.94 (d, $J = 8.8$ Hz, 1H), 8.18 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.7, 32.4, 60.6, 61.0, 109.8, 123.3, 124.4, 124.5, 128.7, 129.3, 130.2, 131.0, 131.3, 140.5, 143.4, 167.6;

IR (neat, cm^{-1}) 2978, 2933, 1705; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{INO}_2$ 405.02258. Found 405.02306.

N-Methyl-2-phenyl-3-(phenylethynyl)indole (22). This indole was prepared by the following procedure. Into a well mixed Et_3N solution (5 ml) containing 5.0 mmol of 3-iodo-2-phenylindole, 6.0 mmol of phenylacetylene and $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol %), CuI (2.5 mol %) was added and the flask was flushed with Ar, sealed and allowed to stir at room temperature for 2 h. The resulting precipitate was filtered off and washed with ethyl ether (10 ml). The combined ether layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford a yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 3.69 (s, 3H), 7.21-7.32 (m, 6H), 7.41-7.44 (m, 3H), 7.49 (t, $J = 7.2$ Hz, 2H), 7.65 (dd, $J = 10.8, 2.0$ Hz, 2H), 7.85 (dd, $J = 10.4, 2.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 31.8, 84.5, 91.9, 110.0, 120.2, 121.0, 123.1, 124.7, 127.4, 128.1, 128.4, 128.5, 128.7, 129.0, 130.4, 131.0, 131.3, 137.4, 144.0; IR (neat, cm^{-1}) 3004, 2962, 2923, 2204; HRMS calcd for $\text{C}_{23}\text{H}_{17}\text{N}$ 307.13610. Found 307.13698.

N-Methyl-2,3-diphenylindole (23). This indole was prepared according to a literature procedure.⁴ Into 10 ml of a 2:1 DMF/ H_2O solution containing 5.0 mmol of 3-iodo-2-phenylindole and 5.0 mmol of Na_2CO_3 , 1.25 mmol of NaBPh_4 were added and the reaction mixture was stirred for 2 min. $\text{Pd}(\text{OAc})_2$ (5 mol %) was then added and the flask was flushed with Ar, sealed and allowed to stir at 100 $^\circ\text{C}$ for 2 h. The resulting reaction mixture was extracted with ethyl ether (2 x 10 ml). The combined ether layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford a white solid.

Recrystallization afforded a 92 % yield of a crystalline solid. The product was obtained as white needles: mp 136-137 $^\circ\text{C}$, lit¹⁶ mp 137-138 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 3.67

(s, 3H), 7.16-7.39 (m, 13H), 7.80 (d, J = 10.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 31.1, 109.8, 115.3, 119.8, 120.4, 122.4, 125.7, 127.2, 128.2, 128.4, 128.6, 130.1, 131.4, 132.1, 135.4, 137.5, 137.9; IR (neat, cm^{-1}) 3058, 2923, 2849; HRMS calcd for $\text{C}_{21}\text{H}_{17}\text{N}$ 283.13610. Found 283.13690.

***n*-Butyl (2E)-3-[1-methyl-2-phenylindol-3-yl]propenoate (24).** This indole was prepared by the following procedure.⁵ Into 1 ml of DMF containing 0.25 mmol of 3-iodo-2-phenylindole, 0.25 mmol of Na_2CO_3 and 0.25 mmol of *n*- Bu_4NCl , 0.525 mmol of *n*-butyl acrylate were added and the reaction mixture was stirred for 2 min. $\text{Pd}(\text{OAc})_2$ (5 mol %) was then added and the flask was flushed with Ar, sealed and allowed to stir at 80 °C for 24 h. The resulting reaction mixture was extracted with ethyl ether (2 x 10 ml). The combined ether layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to afford a pale yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 0.94 (t, J = 7.5 Hz, 3H), 1.37-1.44 (m, 2H), 1.62-1.67 (m, 2H), 3.61 (s, 3H), 4.15 (t, J = 6.6 Hz, 2H), 6.48 (d, J = 15.9 Hz, 1H), 7.32-7.40 (m, 5H), 7.50-7.53 (m, 3H), 7.72 (d, J = 16.2 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 19.4, 31.1, 31.3, 64.0, 110.2, 110.6, 113.1, 120.9, 121.9, 123.2, 125.8, 128.8, 129.4, 130.2, 131.1, 138.1, 139.0, 145.6, 168.8; IR (neat, cm^{-1}) 3004, 2963, 2925, 1711; HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_2$ 333.17288. Found 333.17370.

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