Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

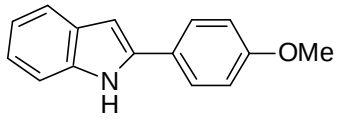
An Easy Access to Aryl- and Heteroaryl-Annulated[*a*]carbazoles Utilizing Indium Nonaflate-Catalyzed Reaction of 2-Arylindoles with Propargyl Ethers

Teruhisa Tsuchimoto, Hiromichi Matsubayashi, Masayoshi Kaneko, Eiji Shirakawa and Yusuke Kawakami

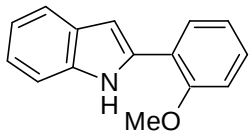
General Remarks. All manipulations were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a Varian Gemini 2000 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or a Varian INOVA 500 (^{2}H, 76 MHz; ^{13}C, 125 MHz; ^{19}F, 470 MHz) spectrometer using tetramethylsilane (^{1}H and ^{13}C), chloroform-*d* (^{2}H), or fluorotrichloromethane (^{19}F) as an internal standard. Analytical gas chromatography was performed on a Shimadzu model GC-18A instrument equipped with a capillary column of CP-SIL 5 CB (100% dimethyl polysiloxane, 30 m x 0.25 mm x 0.25 μm) using helium as carrier gas. High-resolution mass spectra were obtained with a Bruker Bio APEX 70e or a JEOL JMS-HX110A spectrometer. Elemental analyses were carried out with a Vario EL III machine. All melting points were measured with a Yanaco Micro Melting Point apparatus and uncorrected. Unless otherwise noted, reagents were commercially available and used without further purification. Dibutyl ether was distilled under nitrogen from sodium benzophenone ketyl prior to use. 2-Arylindoles **1c**–**1j** were prepared according to literature procedures.[1] 2,2'-Bis(*N*-methylindolyl) (**1k**) was prepared according to the literature procedure.[2] 4,4',5,5'-Tetramethyl-2,2'-bithiophene (**4a**) and 5,5'-diethyl-2,2'-bithiophene (**4b**) were prepared according to reported procedures.[3] 4,4',5,5'-Tetramethyl-2,2'-bifuran (**4c**) was synthesized according to the literature method.[4]

Preparation of Indium Nonafluorobutanesulfonate [In(ONf)$_3$]. In_2O_3 (597 mg, 2.15 mmol) was placed in a 50 mL two necked, round-bottomed flask equipped with a reflux condenser. To this were added H_2O (10 mL) and nonafluorobutanesulfonic acid (2.49 g, 8.30 mmol) successively, and the resulting mixture was stirred at 100 °C for 10 h. Filtration to remove the excess In_2O_3 and evaporation of H_2O gave hydrate of In(ONf)$_3$. The resulting hydrate was slowly warmed up to 150 °C over a period of 5 h under vacuum and the heating was continued for additional 10 h to give In(ONf)$_3$ (2.73 g, 97% yield) as a white powder. ^{19}F NMR (470 MHz, CD_3CN) δ –80.4, –113.6, –120.8, –125.3. Anal. Calcd for $C_{12}F_{27}InO_9S_3$: C, 14.24; S, 9.50. Found: C, 14.18; S, 9.56.

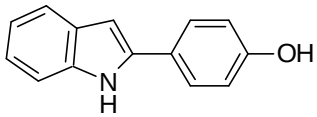
Spectral and analytical data of 2-arylindoles prepared follow.



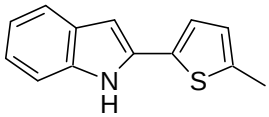
2-(4-Methoxyphenyl)-1*H*-indole (1c).[1c,5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (s, 3 H), 6.72 (dd, *J* = 2.1, 0.9 Hz, 1 H), 6.99 (dt, *J* = 9.0, 2.6 Hz, 2 H), 7.08–7.20 (m, 2 H), 7.36–7.41 (m, 1 H), 7.57–7.63 (m, 3 H), 8.25 (bs, 1 H).



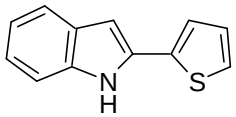
2-(2-Methoxyphenyl)-1*H*-indole (1d).[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (s, 3 H), 6.91 (dd, *J* = 2.1, 0.9 Hz, 1 H), 7.02–7.22 (m, 4 H), 7.26–7.33 (m, 1 H), 7.43 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.64 (dd, *J* = 7.8, 0.7 Hz, 1 H), 7.85 (dd, *J* = 7.7, 1.7 Hz, 1 H), 9.67 (bs, 1 H).



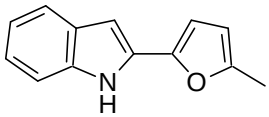
2-(4-Hydroxyphenyl)-1*H*-indole (1e).[1b] ^{1}H NMR (300 MHz, CD_3COCD_3) δ 6.71 (dd, *J* = 2.1, 0.9 Hz, 1 H), 6.91 (dt, *J* = 9.0, 2.4 Hz, 2 H), 6.97 (ddd, *J* = 7.8, 6.8, 1.2 Hz, 1 H), 6.97 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1 H), 7.33–7.38 (m, 1 H), 7.48–7.53 (m, 1 H), 7.69 (dt, *J* = 8.7, 2.5 Hz, 2 H), 8.52 (s, 1 H), 10.47 (bs, 1 H).



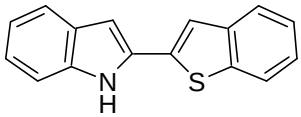
2-(5-Methylthien-2-yl)-1*H*-indole (1f). A white solid, mp 128–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (d, *J* = 1.2 Hz, 3 H), 6.64 (d, *J* = 1.8 Hz, 1 H), 6.72–6.75 (m, 1 H), 7.05 (d, *J* = 3.6 Hz, 1 H), 7.07–7.13 (m, 1 H), 7.17 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.35 (d, *J* = 8.1 Hz, 1 H), 7.55–7.59 (m, 1 H), 8.15 (bs, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.3, 99.7, 110.7, 120.41, 120.44, 122.4, 122.8, 126.1, 129.2, 132.7, 133.4, 136.5, 139.6. HRMS (ESI) Calcd for $C_{13}H_{12}NS$: M^++H, 214.0690. Found: *m*/*z* 214.0696.



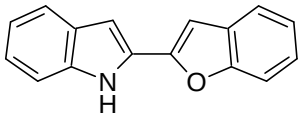
2-Thien-2-yl-1*H*-indole (1g).[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 2.3, 0.8 Hz, 1 H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1 H), 7.09–7.15 (m, 1 H), 7.20 (ddd, *J* = 8.0, 7.0, 1.5 Hz, 1 H), 7.25–7.28 (m, 1 H), 7.29 (dd, *J* = 5.3, 1.1 Hz, 1 H), 7.37 (ddt, *J* = 7.8, 1.2, 1.0 Hz, 1 H), 7.60 (ddt, *J* = 7.8, 1.2, 0.7 Hz, 1 H), 8.21 (bs, 1 H).



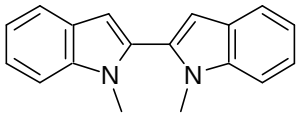
2-(5-Methylfuran-2-yl)-1*H*-indole (1h). A white solid, mp 85–86 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (d, *J* = 0.6 Hz, 3 H), 6.08 (dq, *J* = 3.3, 1.2 Hz, 1 H), 6.52 (d, *J* = 3.0 Hz, 1 H), 6.67 (dd, *J* = 2.1, 0.9 Hz, 1 H), 7.10 (td, *J* = 7.3, 1.1 Hz, 1 H), 7.17 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.34–7.39 (m, 1 H), 7.56–7.61 (m, 1 H), 8.40 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ?? ? ?97.9, 106.3, 107.8, 110.7, 120.2, 120.4, 122.1, 129.0, 129.6, 135.9, 146.0, 151.7. HRMS (ESI) Calcd for $C_{13}H_{11}NO$: M^+, 197.0840. Found: *m*/*z* 197.0833.



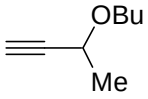
2-Benzo[*b*]thien-2-yl-1*H*-indole (1i).[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (dd, *J* = 2.0, 0.8 Hz, 1 H), 7.14 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1 H), 7.23 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1 H), 7.30–7.43 (m, 3 H), 7.47 (s, 1 H), 7.61–7.65 (m, 1 H), 7.76–7.80 (m, 1 H), 7.81–7.85 (m, 1 H), 8.36 (bs, 1 H).



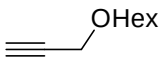
2-Benzo[*b*]furan-2-yl-1*H*-indole (1j).[6] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97–7.00 (m, 2 H), 7.15 (ddd, *J* = 7.1, 6.8, 1.2 Hz, 1 H), 7.21–7.34 (m, 3 H), 7.43 (dq, *J* = 8.1, 0.9 Hz, 1 H), 7.50–7.54 (m, 1 H), 7.57–7.62 (m, 1 H), 7.64–7.68 (m, 1 H), 8.67 (bs, 1 H).



2,2'-Bis(*N*-methylindolyl) (1k).[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.73 (s, 6 H), 6.68 (d, *J* = 0.9 Hz, 2 H), 7.20 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 2 H), 7.32 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 2 H), 7.42 (dd, *J* = 8.3, 0.9 Hz, 2 H), 7.70 (dd, *J* = 8.1, 1.0 Hz, 2 H).

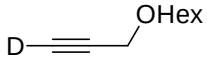


Preparation of 3-Butoxy-1-butyne (2b).[7] A 100 mL two necked round-bottomed flask was charged with a 55% dispersion of NaH (1.20 g, 50.0 mmol) in paraffin oil, which was washed with hexane (5 mL x 2). To this was added THF (30 mL) and the suspension was cooled to 0 °C. 1-Butyn-3-ol (3.50 g, 50.0 mmol) was added dropwise and the resulting solution was warmed up to room temperature. After being stirred for 1 h, 1-iodobutane (7.36 g, 40.0 mmol) was added dropwise over a period of 5 min, and the mixture was stirred for 20 h. The solution was diluted with Et_2O (50 mL) and washed with saturated NH_4Cl aqueous solution (5 mL x 2). The aqueous solution was extracted with Et_2O (10 mL x 2) and the combined organic layer was washed with saturated $NaHCO_3$ aqueous solution (5 mL) and brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by distillation (70 °C/100 mmHg) gave 3-butoxy-1-butyne (2.02 g, 40% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3 H), 1.31–1.46 (m, 2 H), 1.44 (d, *J* = 6.6 Hz, 3 H), 1.41–1.63 (m, 2 H), 2.39 (d, *J* = 2.1 Hz, 1 H), 3.37 (dt, *J* = 9.0, 6.6 Hz, 1 H), 3.72 (dt, *J* = 9.0, 6.6 Hz, 1 H), 4.13 (qd, *J* = 6.6, 2.1 Hz, 1 H).



3-Hexyloxy-1-propyne.[8] The title compound for the synthesis of 1-deuterio-3-hexyloxy-1-propyne was prepared by the reaction of propargyl alcohol with 1-iodohexane according to the above procedure and purified by column

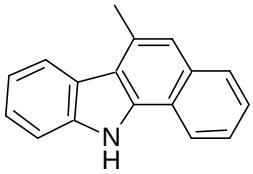
chromatography on silica gel (pentane/Et_2O = 250/1, 43% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86–0.91 (m, 3 H), 1.25–1.40 (m, 6 H), 1.51–1.64 (m, 2 H), 2.41 (t, *J* = 2.4 Hz, 1 H), 3.51 (t, *J* = 6.8 Hz, 2 H), 4.13 (d, *J* = 2.4 Hz, 2 H).



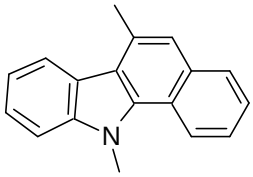
Preparation of 1-Deuterio-3-hexyloxy-1-propyne. A 50 mL two necked round-bottomed flask was charged with 3-hexyloxy-1-propyne (1.50 g, 10.7 mmol). To this was added Et_2O (20 mL) and the solution was cooled to –78 °C. Hexane solution of BuLi (1.54 M, 6.95 mL, 10.7 mmol) was added dropwise over a period of 10 min. After being stirred for 1 h at –78 °C, D_2O solution of DCl (1.6 M, 6.3 mL) was added and the mixture was slowly warmed up to room temperature. The solution was diluted with Et_2O (50 mL) and washed with saturated NH_4Cl aqueous solution (5 mL). The aqueous solution was extracted with Et_2O (10 mL x 2) and the combined organic layer was washed with brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (pentane/Et_2O = 250/1) gave 1-deuterio-3-hexyloxy-1-propyne (1.26 g, 84% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86–0.91 (m, 3 H), 1.25–1.40 (m, 6 H), 1.51–1.64 (m, 2 H), 3.51 (t, *J* = 6.8 Hz, 2 H), 4.13 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 25.8, 29.5, 31.7, 58.8, 70.3, 73.7 (t, *J* = 37.9 Hz), 79.7 (t, *J* = 7.2 Hz).

Synthesis of Aryl- and Heteroaryl-Annulated[*a*]carbazoles Utilizing $In(ONf)_3$-Catalyzed Reaction of 2-Arylindoles with Propargyl Ethers. A General Procedure. $In(ONf)_3$ (60.7 mg, 60 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 °C in vacuo for 2 h. The tube was cooled down to room temperature and filled with nitrogen. Dibutyl ether (3.0 or 9.0 mL) was added to the tube and stirred for 10 min at room temperature. To this were added a 2-arylindole (0.20 mmol) and a propargyl ether (0.22 mmol) successively, and the resulting mixture was stirred at 70 or 100 °C. After the time specified in Table 2, the mixture was

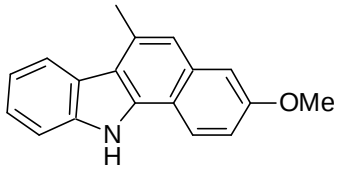
diluted with ethyl acetate (10 mL) and washed with saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel gave the corresponding aryl- or heteroaryl-annulated[*a*]carbazole. The results are summarized in Table 2.



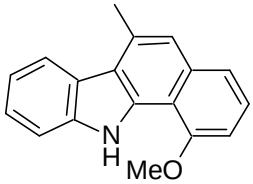
6-Methyl-11*H*-benzo[*a*]carbazole (3aa). A white solid, mp 119–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (d, *J* = 0.6 Hz, 3 H), 7.31 (td, *J* = 7.6, 0.5 Hz, 1 H), 7.40 (s, 1 H), 7.44 (td, *J* = 7.5, 0.9 Hz, 1 H), 7.48–7.54 (m, 2 H), 7.58 (d, *J* = 8.4 Hz, 1 H), 7.88–7.95 (m, 1 H), 8.03–8.09 (m, 1 H), 8.25 (d, *J* = 7.8 Hz, 1 H), 8.78 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 110.9, 118.2, 119.7, 120.0, 120.1, 120.2, 122.1, 124.4, 124.6, 124.8, 125.4, 128.1, 132.2, 132.5, 134.9, 138.6. HRMS (ESI) Calcd for $C_{17}H_{13}N$: M^+, 231.1047. Found: *m*/*z* 231.1039. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.48; H, 5.47; N, 6.15.



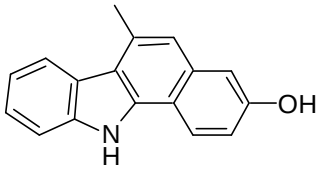
6,11-Dimethyl-11*H*-benzo[*a*]carbazole (3ba). A white solid, mp 138–139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02 (d, *J* = 0.9 Hz, 3 H), 4.43 (s, 3 H), 7.33 (ddd, *J* = 7.4, 6.8, 1.2 Hz, 1 H), 7.43 (s, 1 H), 7.48–7.57 (m, 3 H), 7.58–7.62 (m, 1 H), 7.93–8.00 (m, 1 H), 8.32 (dt, *J* = 8.1, 0.9 Hz, 1 H), 8.68–8.74 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.6, 34.1, 108.9, 118.5, 119.4, 120.6, 121.2, 122.0, 122.1, 123.5, 124.1, 124.2, 124.7, 128.5, 132.0, 133.5, 135.7, 140.8. HRMS (ESI) Calcd for $C_{18}H_{15}N$: M^+, 245.1204. Found: *m*/*z* 245.1199. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.93; H, 6.20; N, 5.89.



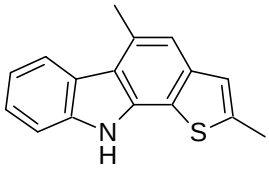
3-Methoxy-6-methyl-11*H*-benzo[*a*]carbazole (3ca). A white solid, mp 139–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (d, *J* = 1.2 Hz, 3 H), 3.96 (s, 3 H), 7.20 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.27–7.33 (m, 3 H), 7.42 (ddd, *J* = 8.0, 7.0, 1.3 Hz, 1 H), 7.58 (dt, *J* = 8.1, 0.9 Hz, 1 H), 7.99 (d, *J* = 8.7 Hz, 1 H), 8.22 (d, *J* = 7.8 Hz, 1 H), 8.73 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 55.4, 107.3, 110.8, 114.7, 116.5, 116.8, 119.3, 119.9, 121.7, 121.8, 123.9, 124.9, 132.9, 133.9, 135.3, 138.5, 157.6. HRMS (ESI) Calcd for $C_{18}H_{15}NO$: M^+, 261.1153. Found: *m*/*z* 261.1130. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.77; H, 5.46; N, 5.00.



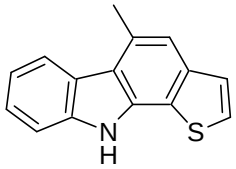
1-Methoxy-6-methyl-11*H*-benzo[*a*]carbazole (3da). A white solid, mp 154–155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.01 (d, *J* = 0.9 Hz, 3 H), 4.20 (s, 3 H), 6.93 (d, *J* = 7.5 Hz, 1 H), 7.31 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1 H), 7.36–7.38 (m, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 7.45 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1 H), 7.54 (dd, *J* = 8.4, 0.6 Hz, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 8.28 (dd, *J* = 8.0, 0.6 Hz, 1 H), 10.10 (bs, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 55.7, 103.5, 111.0, 111.7, 117.8, 119.3, 119.5, 120.5, 121.9, 123.5, 124.0, 125.3, 133.0, 134.3, 134.4, 138.0, 156.1. HRMS (ESI) Calcd for $C_{18}H_{15}NO$: M^+, 261.1153. Found: *m*/*z* 261.1131. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.86; H, 5.50; N, 5.58.



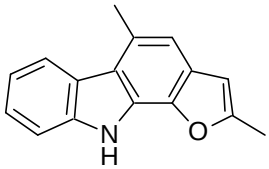
3-Hydroxy-6-methyl-11*H*-benzo[*a*]carbazole (3ea). A white solid, mp 180–182 °C. ^{1}H NMR (300 MHz, CD_3COCD_3) δ 2.91 (d, *J* = 0.9 Hz, 3 H), 7.14 (dd, *J* = 8.7, 2.4 Hz, 1 H), 7.16–7.22 (m, 2 H), 7.27 (d, *J* = 2.1 Hz, 1 H), 7.32 (ddd, *J* = 15.3, 7.7, 1.2 Hz, 1 H), 7.57 (dt, *J* = 7.8, 0.9 Hz, 1 H), 8.16 (dd, *J* = 8.0, 0.5 Hz, 1 H), 8.28 (d, *J* = 9.0 Hz, 1 H), 8.53 (bs, 1 H), 11.1 (bs, 1 H); ^{13}C NMR (125 MHz, CD_3COCD_3) δ 21.4, 111.0, 111.9, 115.8, 116.7, 117.1, 119.3, 120.3, 122.3, 123.8, 124.4, 125.6, 133.4, 135.5, 137.0, 140.0, 156.3. HRMS (ESI) Calcd for $C_{17}H_{13}NO$: M^+, 247.0996. Found: *m*/*z* 247.0987. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.19; H, 5.48; N, 5.50.



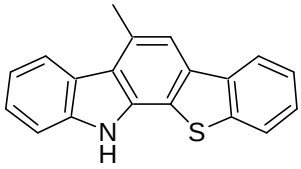
2,5-Dimethyl-10*H*-thieno[2,3-*a*]carbazole (3fa). A white solid, mp 169–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.65 (d, *J* = 1.2 Hz, 3 H), 2.94 (d, *J* = 0.6 Hz, 3 H), 7.08 (q, *J* = 1.2 Hz, 1 H), 7.28 (ddd, *J* = 8.0, 7.1, 0.9, 1 H), 7.32 (d, *J* = 0.6 Hz, 1 H), 7.40 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1 H), 7.52 (dt, *J* = 8.4, 0.6 Hz, 1 H), 8.18–8.21 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.1, 21.0, 110.7, 115.9, 118.0, 119.5, 119.9, 122.1, 122.9, 124.2, 124.9, 130.2, 133.7, 138.9, 139.0, 139.8. HRMS (ESI) Calcd for $C_{16}H_{13}NS$: M^+, 251.0768. Found: *m*/*z* 251.0759. Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.53; H, 5.10; N, 5.23; S, 12.91.



5-Methyl-10*H*-thieno[2,3-*a*]carbazole (3ga). A white solid, mp 167–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (d, *J* = 0.9 Hz, 3 H), 7.30 (ddd, *J* = 7.9, 7.1, 0.9 Hz, 1 H), 7.40–7.47 (m, 3 H), 7.48 (q, *J* = 0.9 Hz, 1 H), 7.55 (dt, *J* = 8.2, 0.9 Hz, 1 H), 8.21–8.25 (m, 1 H), 8.34 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 110.8, 116.5, 118.4, 120.0, 120.1, 122.2, 124.0, 124.6, 124.7, 125.0, 130.4, 133.9, 139.0, 139.1. HRMS (ESI) $C_{15}H_{11}NS$: M^+, 237.0612. Found: *m*/*z* 237.0588. Anal. Calcd for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; N, 5.90; S, 13.51. Found: C, 75.92; H, 4.38; N, 5.89; S, 13.83.

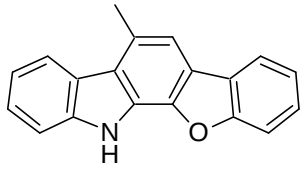


2,5-Dimethyl-10*H*-furo[2,3-*a*]carbazole (3ha). A white solid, mp 121–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (d, *J* = 0.9 Hz, 3 H), 2.92 (s, 3 H), 6.47 (t, *J* = 0.9 Hz, 1 H), 7.09 (s, 1 H), 7.24–7.30 (m, 1 H), 7.37–7.43 (m, 1 H), 7.52 (d, *J* = 8.4 Hz, 1 H), 8.20 (d, *J* = 7.5 Hz, 1 H), 8.37 (bs, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.0, 103.6, 110.7, 112.6, 119.1, 119.8, 122.0, 124.37, 124.42, 125.1, 127.2, 128.0, 139.02, 139.09, 154.5. HRMS (ESI) Calcd for $C_{16}H_{13}NO$: M^+, 235.0996. Found: *m*/*z* 235.0995. Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.63; H, 5.33; N, 5.87.

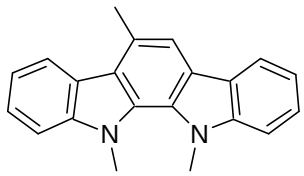


5-Methyl-12*H*-benzothieno[2,3-*a*]carbazole (3ia). A white solid, mp 205–206 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.04 (d, *J* = 0.9 Hz, 3 H), 7.32 (ddd, *J* =

8.0, 7.0, 0.9 Hz, 1 H), 7.44–7.48 (m, 2 H), 7.50 (ddd, *J* = 7.8, 7.0, 0.9 Hz, 1 H), 7.56 (dt, *J* = 8.0, 0.9 Hz, 1 H), 7.82 (q, *J* = 0.9 Hz, 1 H), 7.92 (ddd, *J* = 7.8, 6.3, 0.9 Hz, 1 H), 8.21–8.27 (m, 2 H), 8.30 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.1, 110.8, 110.9, 114.6, 119.0, 120.2, 120.7, 121.8, 122.5, 123.1, 124.6, 125.2, 126.1, 130.5, 134.0, 134.2, 136.6, 139.0, 139.5. HRMS (ESI) $C_{19}H_{13}NS$: M^+, 287.0768. Found: *m*/*z* 287.0786. Anal. Calcd for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; N, 4.87; S, 11.16. Found: C, 79.28; H, 4.30; N, 4.51; S, 11.28.

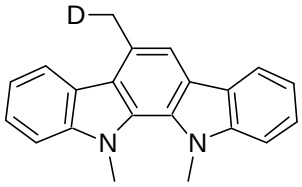


5-Methyl-12*H*-benzofuro[2,3-*a*]carbazole (3ja). A white solid, mp 168–169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ3.01 (d, *J* = 0.6 Hz, 3 H), 7.29–7.51 (m, 4 H), 7.56–7.66 (m, 3 H), 7.98–8.02 (m, 1 H), 8.27 (d, *J* = 7.5 Hz, 1 H), 8.56 (bs, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 111.0, 111.6, 112.5, 120.1, 120.5, 121.5, 122.3, 122.4, 122.9, 124.6, 124.7, 125.3, 125.4, 126.2, 128.4, 139.6, 140.5, 156.3. HRMS (ESI) $C_{19}H_{13}NO$: M^+, 271.0996. Found: *m*/*z* 271.0978. Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.05; H, 4.47; N, 4.90.

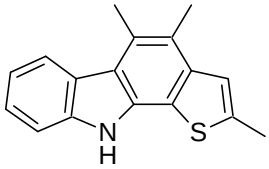


5,11,12-Trimethyl-11*H*,12*H*-indolo[2,3-*a*]carbazole (3ka). A white solid, mp 188–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02 (d, *J* = 0.9 Hz, 3 H), 4.16 (s, 3 H), 4.21 (s, 3 H), 7.26–7.36 (m, 2 H), 7.48–7.54 (m, 4 H), 7.72 (q, *J* = 0.9 Hz, 1 H), 8.12 (dt, *J* = 7.8, 0.9 Hz, 1 H), 8.29 (dt, *J* = 7.5, 0.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ21.3, 36.3, 36.6, 109.9, 110.2, 113.6, 119.8, 119.91, 119.94, 122.1, 122.3, 123.5, 124.7, 125.0, 125.3, 125.69, 125.72, 128.5, 130.0, 143.8, 144.3. HRMS (ESI)

Calcd for $C_{21}H_{18}N_2$: M^+, 298.1469. Found: *m*/*z* 298.1487. Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.77; H, 5.88; N, 9.72.

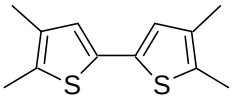


5-Monodeuteriomethyl-11,12-dimethyl-11*H*,12*H*-indolo[2,3-*a*]carbazole (3ka-*d*). A white solid, mp 188–189 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.01 (td, *J* = 2.1, 0.8 Hz, 3 H), 4.15 (s, 3 H), 4.20 (s, 3 H), 7.26–7.37 (m, 2 H), 7.48–7.54 (m, 4 H), 7.73 (t, *J* = 0.9 Hz, 1 H), 8.12 (dt, *J* = 7.8, 0.9 Hz, 1 H), 8.29 (dt, *J* = 7.5, 0.9 Hz, 1 H); ^{2}H NMR (76 MHz, $CHCl_3$) δ 3.03 (s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0 (t, *J* = 19.7 Hz), 36.3, 36.6, 109.8, 110.2, 113.6, 119.8, 119.87, 119.90, 122.1, 122.2, 123.5, 124.7, 125.0, 125.2, 125.67, 125.70, 128.5, 130.0, 143.8, 144.3. HRMS (ESI) Calcd for $C_{21}H_{17}DN_2$: M^+, 299.1531. Found: *m*/*z* 299.1515.

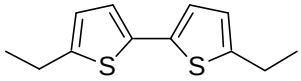


2,4,5-Trimethyl-10*H*-thieno[2,3-*a*]carbazole (3fb). A white solid, mp 176–178 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64 (s, 3 H), 2.68 (d, *J* = 1.2 Hz, 3 H), 2.90 (s, 3 H), 7.21 (q, *J* = 1.2 Hz, 1 H), 7.23–7.29 (m, 1 H), 7.39 (ddd, *J* = 8.1, 7.0, 0.9 Hz, 1 H), 7.50 (dt, *J* = 8.1, 0.9 Hz, 1 H), 8.11 (bs, 1 H), 8.25–8.29 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.8, 16.2, 16.4, 110.7, 118.5, 119.1, 119.7, 121.5, 122.3, 122.4, 124.3, 125.0, 127.6, 132.2, 138.3, 139.2, 139.8. HRMS (ESI) Calcd for $C_{17}H_{15}NS$: M^+, 265.0924. Found: *m*/*z* 265.0904. Anal. Calcd for $C_{17}H_{15}NS$: C, 76.94; H, 5.70; N, 5.28; S, 12.08. Found: C, 76.96; H, 5.32; N, 5.31; S, 11.69.

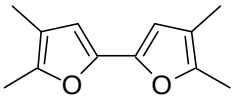
Spectral and analytical data of bithiophenes and a bifuran prepared follow.



4,4',5,5'-Tetramethyl-2,2'-bithiophene (4a). A white solid, mp 104–105 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 6 H), 2.31 (s, 6 H), 6.75 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 13.5, 125.7, 131.3, 132.9, 133.6. HRMS (ESI) Calcd for $C_{12}H_{14}S_2$: M^+, 222.0536. Found: *m*/*z* 222.0529.



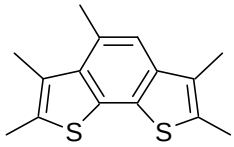
5,5'-Diethyl-2,2'-bithiophene (4b). A pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.5 Hz, 6 H), 2.82 (qd, *J* = 7.5, 1.2 Hz, 4 H), 6.67 (dt, *J* = 3.6, 1.1 Hz, 2 H), 6.90 (d, *J* = 3.3 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.8, 23.5, 122.7, 123.9, 135.2, 146.2. HRMS (ESI) Calcd for $C_{12}H_{14}S_2$: M^+, 222.0536. Found: *m*/*z* 222.0530.



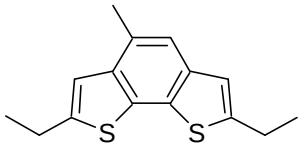
4,4',5,5'-Tetramethyl-2,2'-bifuran (4c). A white solid, mp 50–51 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 6 H), 2.23 (s, 6 H), 6.22 (s, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.9, 11.4, 107.3, 115.6, 144.0, 146.4. HRMS (ESI) Calcd for $C_{12}H_{14}O_2$: M^+, 190.0993. Found: *m*/*z* 190.0985.

Synthesis of Benzodithiophenes or a Benzodifuran Utilizing In(ONf)$_3$-Catalyzed Reaction of Bithiophenes or a Bifuran with Methyl Propargyl Ether. A General Procedure. In(ONf)$_3$ (60.7 mg, 60 μmol) was placed in a 20 mL Schlenk tube, which was heated at 150 °C in vacuo for 2 h. The tube was cooled down to room temperature and filled with nitrogen. Dibutyl ether (1.0 mL) was added to the tube and stirred for 10 min at room temperature. To this were added a bithiophene or a

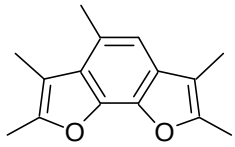
bifuran (0.20 mmol) and methyl propargyl ether (15.4 mg, 0.22 mmol) successively, and the resulting mixture was stirred at 70 or 90 °C. After the time specified in Scheme 2, the mixture was diluted with ethyl acetate (10 mL) and washed with saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous sodium sulfate. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel gave the corresponding benzodithiophenes or a benzodifuran. The results are summarized in Scheme 2.



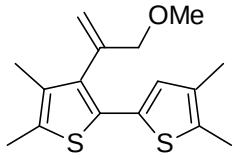
2,3,4,6,7-Pentamethylbenzo[2,1-*b*:3,4-*b'*]dithiophene (4aa). A white solid, mp 137–139 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.29 (d, *J* = 0.9 Hz, 3 H), 2.47 (d, *J* = 0.9 Hz, 3 H), 2.48 (d, *J* = 0.9 Hz, 3 H), 2.54 (d, *J* = 0.9 Hz, 3 H), 2.83 (d, *J* = 0.9 Hz, 3 H), 7.22 (q, *J* = 0.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.7, 13.7, 14.1, 15.4, 22.2, 120.1, 127.4, 129.3, 129.5, 130.6, 131.4, 131.6, 136.4, 137.5. HRMS (ESI) Calcd for $C_{15}H_{16}S_2$: M^+, 260.0693. Found: *m*/*z* 260.0698. Anal. Calcd for $C_{15}H_{16}S_2$: C, 69.18; H, 6.91; S, 24.63. Found: C, 68.96; H, 6.88, S, 24.85.



2,7-Diethyl-4-methylbenzo[2,1-*b*:3,4-*b'*]dithiophene (4ba). A pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.7 Hz, 3 H), 1.41 (t, *J* = 7.7 Hz, 3 H), 2.61 (d, *J* = 0.9 Hz, 3 H), 2.90–3.01 (m, 4 H), 6.99 (t, *J* = 1.2 Hz, 1 H), 7.11 (t, *J* = 1.2 Hz, 1 H), 7.36 (d, *J* = 0.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5, 15.6, 19.7, 23.9, 24.1, 119.0, 119.7, 120.3, 128.7, 130.2, 132.2, 137.0, 137.3, 145.6, 145.8. HRMS (ESI) Calcd for $C_{15}H_{16}S_2$: M^+, 260.0693. Found: *m*/*z* 260.0699. Anal. Calcd for $C_{15}H_{16}S_2$: C, 69.18; H, 6.91; S, 24.63. Found: C, 68.81; H, 6.84, S, 25.03.



2,3,4,6,7-Pentamethylbenzo[2,1-*b*:3,4-*b'*]difuran (4ca). A white solid, mp 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (q, *J* = 0.9 Hz, 3 H), 2.34 (q, *J* = 0.9 Hz, 3 H), 2.40 (m, 6 H), 2.68 (d, *J* = 0.9 Hz, 3 H), 6.90 (q, *J* = 0.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.2, 10.7, 11.6, 11.8, 19.5, 110.2, 111.2, 113.6, 124.9, 125.5, 127.3, 137.0, 138.1, 148.9, 149.2. HRMS (ESI) Calcd for $C_{15}H_{16}O_2$: M^+, 228.1149. Found: *m*/*z* 228.1138. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.72; H, 6.86.



3-(3-Methoxy-1-propen-2-yl)-4,4',5,5'-tetramethyl-2,2'-bithiophene (6). A pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (d, *J* = 0.6 Hz, 3 H), 2.08 (s, 3 H), 2.29 (s, 3 H), 2.32 (d, *J* = 0.6 Hz, 3 H), 3.39 (s, 3 H), 3.92 (t, *J* = 1.7 Hz, 2 H), 5.18 (q, *J* = 1.7 Hz, 1 H), 5.63 (q, *J* = 1.9 Hz, 1 H), 6.81 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.5, 12.8, 13.2, 13.4, 58.6, 74.3, 116.8, 127.9, 129.2, 130.9, 131.5, 132.6, 133.1, 133.7, 136.8, 142.4. HRMS (ESI) Calcd for $C_{16}H_{20}OS_2Na$: M^++Na, 315.0852. Found: *m*/*z* 315.0854. Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89; S, 21.93. Found: C, 65.44; H, 6.49; S, 22.01.

References

[1] a) R. L. Shriner, W. C. Ashley, E. Welch, *Org. Synth. Coll. Vol. 3* **1955**, 725–727; b) K. C. Joshi, R. Jain, S. Garg, *J. Indian Chem. Soc.* **1985**, *62*, 388–390; c) J. Slätt, J. Bergman, *Tetrahedron* **2002**, *58*, 9187–9191.

[2] U. Pindur, Y.-S. Kim, D. Schollmeyer, *J. Heterocyclic. Chem.* **1994**, *31*, 377–386.

[3] a) M. Kumada, K. Tamao, K. Sumitani, *Org. Synth. Coll. Vol. 6* **1988**, 407–411; b) G. Engelmann, G. Kossmehl, J. Heinze, P. Tschuncky, W. Jugelt, H.-P. Welzel, *J. Chem. Soc., Perkin Trans. 2* **1998**, 169–175 and references therein.

[4] M. J. Arco, M. H. Trarnmell, J. D. White, *J. Org. Chem.* **1976**, *41*, 2075–2083.

[5] S. Cacchi, G. Fabrizi, L. M. Parisi, *Org. Lett.* **2003**, *5*, 3843–3846.

[6] R. L. Hudkins, J. L. Diebold, F. D. Marsh, *J. Org. Chem.* **1995**, *60*, 6218–6220.

[7] M. R. Kulibekov, *Doklady-Akademiya Nauk Azerbaidzhanskoi SSR* **1964**, *20*, 15–21.

[8] V. I. Nikitin, E. M. Glazunera, I. M. Potiva, I. Voropaeva, *J. Org. Chem. (USSR)* **1995**, *60*, 6218–6220.