Supporting Information for

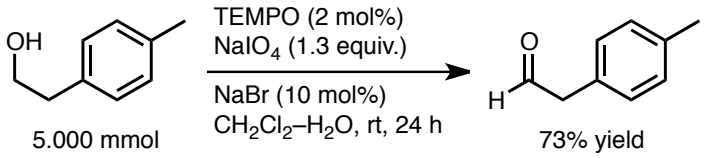
Indium-catalyzed annulation of 3-aryl- and 3-heteroarylindoles with propargyl ethers: synthesis and photoluminescent properties of aryl- and heteroaryl[*c*]carbazoles

Yuta Nagase, Hiroyuki Shirai, Masayoshi Kaneko, Eiji Shirakawa* and Teruhisa Tsuchimoto*

General Remarks. All manipulations were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance (NMR) spectra were taken on a JEOL JMN-ECA 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) or a JEOL JMN-ECA 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer using tetramethylsilane (^{1}H and ^{13}C) as an internal standard. Analytical gas chromatography (GC) was performed on a Shimadzu model GC-2014 instrument equipped with a capillary column of Inert Cap 5 (5% phenyl polysilphenylene-siloxane, 30 m x 0.25 mm x 0.25 μm) using nitrogen as carrier gas. Gas chromatography–mass spectrometry (GC–MS) analyses were performed with a Shimadzu model GCMS-QP2010 instrument equipped with a capillary column of ID-BPX5 by electron ionization at 70 eV using helium as carrier gas. Preparative recycling high-performance liquid chromatography (HPLC) was performed with JAI LC-9104 equipped with JAIGEL-GS320 column using a mixture of hexane–ethyl acetate (EtOAc) as eluent. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-9105 equipped with JAIGEL-1H and JAIGEL-2H columns using chloroform as eluent. All melting points were measured with a Yanaco Micro Melting Point apparatus and uncorrected. High-resolution mass spectra (HRMS) were measured at National Institute of Advanced Industrial Science and Technology (AIST). Elemental analyses were performed on a Vario EL III elemental analysis instrument. UV-vis absorption spectra were recorded with a JASCO V-550 spectrophotometer at room temperature. Fluorescence spectra were recorded with a JASCO FP-6500 spectrofluorometer at room temperature using an excitation wavelength of 265 nm. A solution of *p*-terphenyl in cyclohexane was used as a quantum yield standard (Φ_F = 0.87 at 265 nm excitation). Dibutyl ether (Bu_2O) was distilled under argon from sodium just prior to use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled under argon from sodium benzophenone ketyl just before use. Chlorobenzene (PhCl), toluene (PhMe), and dichloromethane (CH_2Cl_2) were distilled under argon from calcium chloride

just prior to use. Anhydrous dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich Co. LLC. and used without further purification. 3-Phenyl-1*H*-indole (**1a**)[1] and 3,3'-biindolyl[2] were synthesized according to the respective literature methods. $In(ONf)_3$ (Nf = $SO_2C_4F_9$)[3] and $In(NTf_2)_3$ (Tf = SO_2CF_3)[4] were prepared by the respective literature procedures. Unless otherwise noted, reagents were commercially available and used as received without further purification.

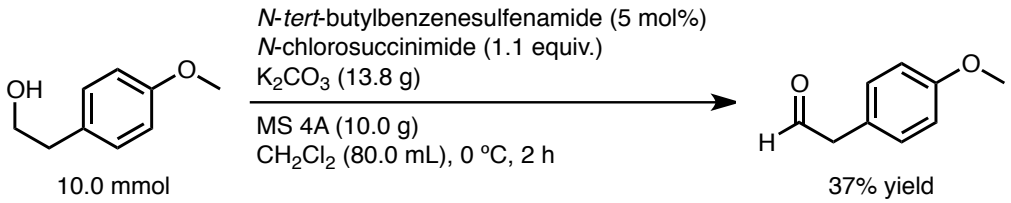
Synthesis of Arylacetaldehydes



4-Methylphenylacetaldehyde. The title compound was synthesized according to the literature method.[5] In a 100 mL Schlenk tube, 2-(4-methylphenyl)ethanol (681.0 mg, 5.000 mmol) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (15.8 mg, 0.101 mmol) were dissolved in CH_2Cl_2 (10.0 mL). To this were added an aqueous solution of $NaIO_4$ (1367 mg, 6.392 mmol) and NaBr (51.5 mg, 0.500 mmol) in H_2O (12.0 mL). After being stirred vigorously at room temperature for 24 h, the resulting solution was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layer was washed with a 10% $Na_2S_2O_3$ aqueous solution (10 mL), a saturated $NaHCO_3$ aqueous solution (10 mL) and brine (10 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) gave 4-methylphenylacetaldehyde (467.5 mg, 73% yield) as a colorless liquid. This compound has been already synthesized in literature, and its spectral and analytical data are in good

[1] For synthesis of **1a**, see: (*a*) J. G. Rodríguez, A. Lafuente and P. García-Almaraz, *J. Heterocycl. Chem.*, 2000, **37**, 1281; for spectral and analytical data of **1a**, see: (*b*) L. Joucla, N. Batail and L. Djakovitch, *Adv. Synth. Catal.*, 2010, **352**, 2929.
[2] For synthesis of 3,3'-biindolyl, see: (*a*) J. Bergman, *Acta Chim. Scand.*, 1971, **25**, 1277; for spectral and analytical data of 3,3'-biindolyl, see: (*b*) C. Ramesh, V. Kavala, C.-W. Kuo, B. R. Raju and C.-F. Yao, *Eur. J. Org. Chem.*, 2010, 3796.
[3] T. Tsuchimoto, H. Matsubayashi, M. Kaneko, E. Shirakawa and Y. Kawakami, *Angew. Chem., Int. Ed.*, 2005, **44**, 1336.
[4] (*a*) C. G. Frost, J. P. Hartley and D. Griffin, *Tetrahedron Lett.*, 2002, **43**, 4789; (*b*) M. Nakamura, K. Endo and E. Nakamura, *Adv. Synth. Catal.*, 2005, **347**, 1681.
[5] M. Lei, R.-J. Hu and Y.-G. Wang, *Tetrahedron*, 2006, **62**, 8928.

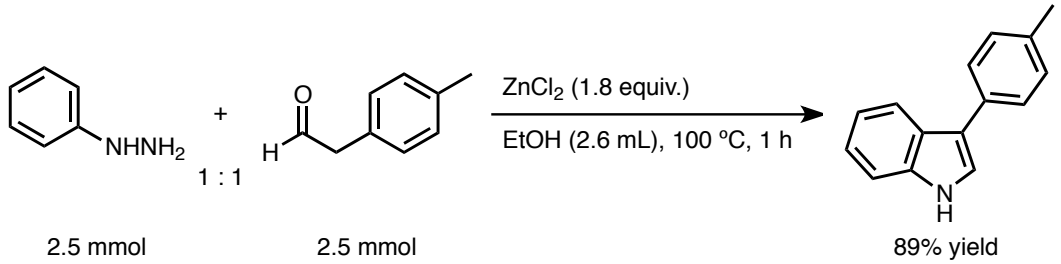
agreement with those reported in reference 6.[6] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 3.65 (d, J = 2.3 Hz, 2 H), 7.11 (d, J = 8.0 Hz, 2 H), 7.18 (d, J = 8.0 Hz, 2 H), 9.73 (t, J = 2.3 Hz, 1 H).



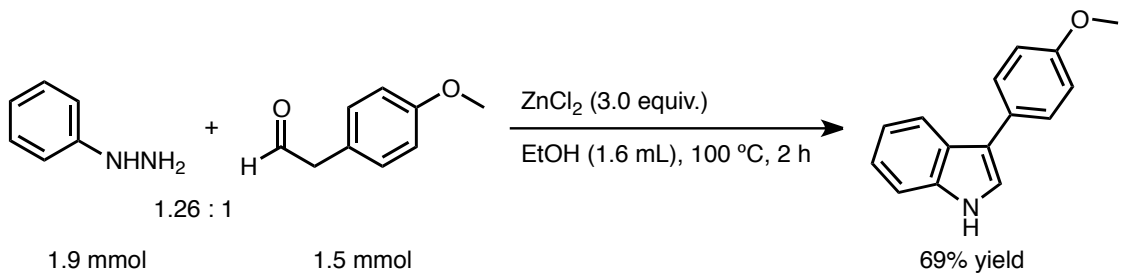
4-Methoxyphenylacetaldehyde. The title compound was synthesized according to the reported procedure.[7] A 300 mL Schlenk tube was charged with molecular sieves 4A (10.0 g), K_2CO_3 (13.8 g, 99.8 mmol), *N*-chlorosuccinimide (1.46 g, 10.9 mmol) and CH_2Cl_2 (20.0 mL). To this were successively added a solution of 2-(4-methoxyphenyl)ethanol (1.52 g, 10.0 mmol) in CH_2Cl_2 (30.0 mL) and a solution of *N-tert*-butylbenzenesulfenamide (90.7 mg, 0.500 mmol) in CH_2Cl_2 (30.0 mL) at 0 °C. After being stirred at 0 °C for 2 h, the reaction mixture was quenched with water (80 mL). The resulting solution was filtered through a pad of Celite, and the aqueous phase was extracted with CH_2Cl_2 (80 mL x 3). The combined organic layer was washed with water (80 mL) and brine (80 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) gave 4-methoxyphenylacetaldehyde (590.3 mg, 37% yield) as a colorless liquid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in reference 6.[6] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (d, J = 2.3 Hz, 2 H), 3.81 (s, 3 H), 6.89–6.93 (m, 2 H), 7.11–7.16 (m, 2 H), 9.72 (t, J = 2.1 Hz, 1 H).

Synthesis of 3-(4-methylphenyl)-1*H*-indole and 3-(4-methoxyphenyl)-1*H*-indole. 3-(4-Methylphenyl)-1*H*-indole and 3-(4-methoxyphenyl)-1*H*-indole were synthesized according to the same procedure as for the synthesis of **1a**.[1] Their spectral and analytical data are as follows:

[6] A. D. Chowdhury, R. Ray and G. K. Lahiri, *Chem. Commun.*, 2012, **48**, 5497.
[7] T. Mukaiyama, J. Matsuo, D. Iida and H. Kitagawa, *Chem. Lett.*, 2001, **30**, 846.

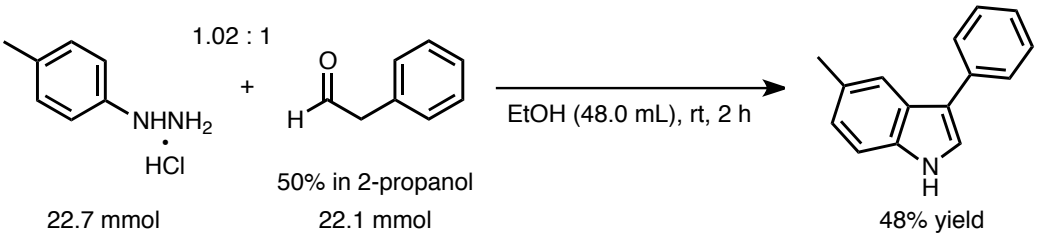


3-(4-Methylphenyl)-1*H*-indole. The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in reference 8.[8] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3 H), 7.19 (t, *J* = 7.4 Hz 1 H), 7.22–7.29 (m, 3 H), 7.34 (d, *J* = 2.3 Hz, 1 H), 7.43 (d, *J* = 8.1 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 8.19 (bs, 1 H).

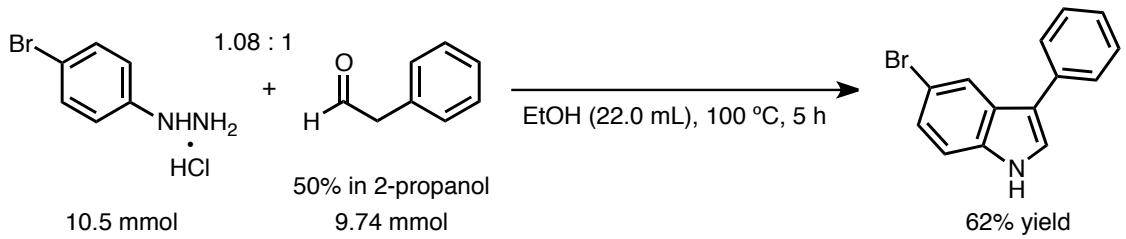


3-(4-Methoxyphenyl)-1*H*-indole. The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in reference 9.[9] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3 H), 7.01 (d, *J* = 8.6 Hz, 2 H), 7.19 (td, *J* = 6.9, 1.1 Hz, 1 H), 7.22–7.28 (m, 1 H), 7.31 (d, *J* = 2.3 Hz, 1 H), 7.43 (dd, *J* = 8.0, 0.6 Hz, 1 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 8.19 (bs, 1 H).

[8] A. V. Sadovoy, A. E. Kovrov, G. A. Golubeva and L. A. Sviridova, *Chem. Heterocycl. Comp.*, 2011, **46**, 1215.
[9] L. Ackermann, M. Dell'Acqua, S. Fenner, R. Vicente and R. Sandmann, *Org. Lett.*, 2011, **13**, 2358.

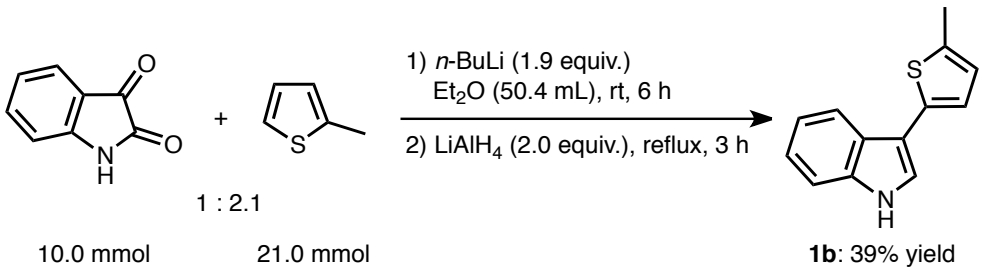


Synthesis of 5-Methyl-3-phenyl-1*H*-indole. 5-Methyl-3-phenyl-1*H*-indole was synthesized according to the following modified literature procedure.[1] Under an argon atmosphere, 4-methylphenylhydrazine hydrochloride (2.77 g, 22.7 mmol), a 50% 2-propanol solution of phenylacetaldehyde (5.30 g, 22.1 mmol) and EtOH (48.0 mL) were placed in a 300 mL Schlenk tube, the mixture in which was stirred at room temperature for 2 h. The resulting solution was filtered, and the solvent was removed under reduced pressure. To this was added a 4% HCl aqueous solution (40 mL), and the aqueous phase was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was washed with brine (20 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) gave 5-methyl-3-phenyl-1*H*-indole (2.19 g, 48% yield) as a white solid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in reference 10.[10] Therefore, only ^{1}H NMR data measured in $CDCl_3$ and also in DMSO-d_6 are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (s, 3 H), 7.08 (dd, J = 8.3, 1.5 Hz, 1 H), 7.29 (tt, J = 7.5, 1.3 Hz, 1 H), 7.31–7.35 (m, 2 H), 7.45 (tt, J = 7.7, 1.8 Hz, 2 H), 7.64–7.69 (m, 2 H), 7.73 (d, J = 1.7 Hz, 1 H), 8.14 (bs, 1 H); ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.79 (s, 3 H), 6.81 (dd, J = 8.7, 2.3 Hz, 1 H), 7.22 (t, J = 7.3 Hz, 1 H), 7.30 (d, J = 1.8 Hz, 1 H), 7.35 (d, J = 8.7 Hz, 1 H), 7.43 (t, J = 7.6 Hz, 2 H), 7.62 (d, J = 2.3 Hz, 1 H), 7.67 (d, J = 7.3 Hz, 2 H), 11.21 (bs, 1 H).



[10] (*a*) A. A. Lamar and K. M. Nicholas, *Tetrahedron*, 2009, **65**, 3829; (*b*) N. Batail, V. Dufaud and L. Djakovitch, *Tetrahedron Lett.*, 2011, **52**, 1916.

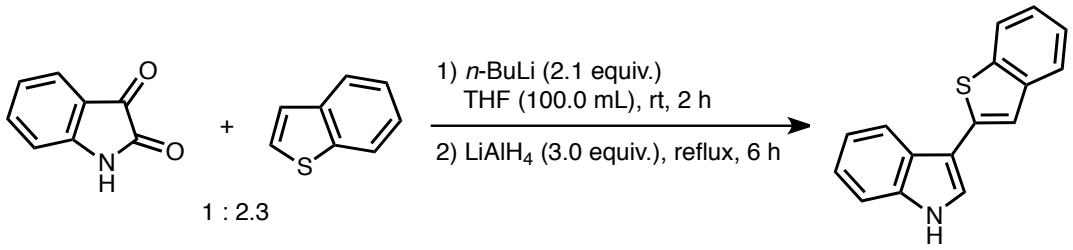
Synthesis of 5-Bromo-3-phenyl-1*H*-indole. 5-Bromo-3-phenyl-1*H*-indole was synthesized according to the following modified literature procedure.[1] Under an argon atmosphere, 4-bromophenylhydrazine hydrochloride (2.35 g, 10.5 mmol), a 50% 2-propanol solution of phenylacetaldehyde (1.17 g, 9.74 mmol) and EtOH (22.0 mL) were placed in a 300 mL Schlenk tube, the mixture in which was stirred at 100 ºC for 5 h. The resulting solution was filtered, and the solvent was removed under reduced pressure. To this was added a 4% HCl aqueous solution (20 mL), and the aqueous phase was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layer was washed with brine (10 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) gave 5-bromo-3-phenyl-1*H*-indole (1.63 g, 62% yield) as a white solid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in reference 11.[11] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.36 (m, 3 H), 7.36 (d, *J* = 2.8 Hz, 1 H), 7.46 (tt, *J* = 7.7, 1.7 Hz, 2 H), 7.58–7.64 (m, 2 H), 8.05 (d, *J* = 1.4 Hz, 1 H), 8.26 (bs, 1 H).



Synthesis of 3-(5-Methylthiophen-2-yl)-1*H*-indole (1b). Compound **1b** was synthesized according to the literature method.[2a] Under an argon atmosphere, 2-methylthiophene (2.06 g, 21.0 mmol) and Et_2O (15.2 mL) were placed in a 300 mL two-necked round-bottomed flask equipped with a dropping funnel and a dimroth condenser attached to a three-way stopcock. To this was slowly added *n*-BuLi (11.5 mL, 19.0 mmol, 1.56 M in hexane) cooled to 0 °C through the dropping funnel, and the resulting solution was stirred at 0 °C for 1.5 h. After being warmed to room temperature, a solution of isatin (1.47 g, 10.0 mmol) in Et_2O (35.2 mL) was added in five portions through the dropping funnel, and the mixture was stirred at room temperature for 6 h.

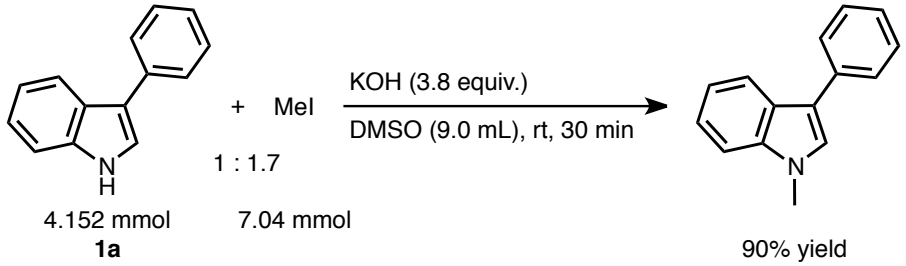
[11] R. J. Phipps, N. P. Grimster and M. J. Gaunt, *J. Am. Chem. Soc.*, 2008, **130**, 8172.

$LiAlH_4$ (763.9 mg, 20.12 mmol) was then added, and the resulting mixture was heated to reflux for 3 h. After being cooled to room temperature, the mixture was treated carefully with water (1.0 mL) to decompose excess $LiAlH_4$. The resulting suspension was filtered, and the filtrate was extracted with Et_2O (20 mL x 3). The combined organic layer was washed with brine (15 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 5/1) and further purification by recycling GPC gave 3-(5-methylthiophen-2-yl)-1*H*-indole (847.9 mg, 39% yield) as a white solid, mp 82–83 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (d, J = 0.9 Hz, 3 H), 6.73–6.78 (m, 1 H), 7.06 (d, J = 3.7 Hz, 1 H), 7.20 (td, J = 7.4, 1.1 Hz, 1 H), 7.25 (td, J = 7.6, 1.2 Hz, 1 H), 7.36 (d, J = 2.3 Hz, 1 H), 7.40 (dd, J = 7.6, 1.2 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1 H), 8.15 (bs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 111.3, 112.3, 120.0, 120.4, 121.4, 122.5, 122.6, 125.5, 125.6, 135.3, 136.4, 137.0. HRMS (EI) Calcd for $C_{13}H_{11}NS$: M^+, 213.0607. Found: *m*/*z* 213.0608.



Synthesis of 3-(Benzo[*b*]thiophen-2-yl)-1*H*-indole (1d). Compound **1d** was synthesized according to the literature method.[2a] Under an argon atmosphere, benzo[*b*]thiophene (6.18 g, 46.0 mmol) and THF (30.0 mL) were placed in a 500 mL two-necked round-bottomed flask equipped with a dropping funnel and a dimroth condenser attached to a three-way stopcock. To this was slowly added *n*-BuLi (25.0 mL, 42.0 mmol, 1.65 M in hexane) cooled to –18 ºC through the dropping funnel, and the resulting solution was stirred at –18 °C for 6 h. After being warmed to room temperature, a THF (70.0 mL) solution of isatin (2.94 g, 20.0 mmol) was added in five portions through the dropping funnel, and the mixture was stirred at room temperature for 2 h. $LiAlH_4$ (2.28 g, 60.0 mmol) was then added, and the resulting mixture was heated to reflux for 6 h. After being cooled to room temperature, the mixture was treated carefully with water (3.0 mL) to decompose excess $LiAlH_4$. The resulting suspension was filtered, and the filtrate

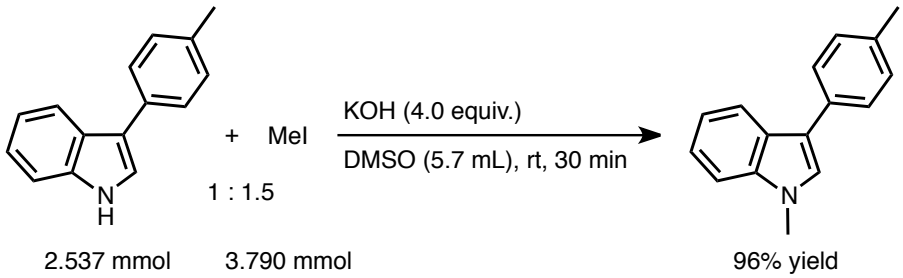
was extracted with Et_2O (60 mL x 3). The combined organic layer was washed with brine (30 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 10/1) gave 3-(benzo[*b*]thiophen-2-yl)-1*H*-indole (1.24 g, 24% yield) as a white solid, mp 155–156 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.32 (m, 3 H), 7.35 (td, *J* = 7.6, 0.8 Hz, 1 H), 7.45 (dd, *J* = 6.9, 1.7 Hz, 1 H), 7.53 (s, 1 H), 7.55 (d, *J* = 2.3 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 8.09 (dd, *J* = 6.9, 1.7 Hz, 1 H), 8.29 (bs, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.5, 112.1, 118.5, 120.1, 120.9, 122.0, 122.8, 122.95, 122.99, 123.5, 124.3, 125.4, 136.6, 138.0, 138.4, 140.9. HRMS (EI) Calcd for $C_{16}H_{11}NS$: M^+, 249.0607. Found: *m*/*z* 249.0603.



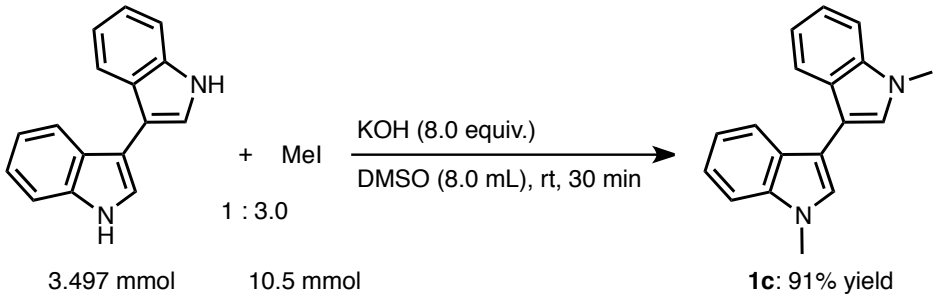
Synthesis of 1-Methyl-3-phenyl-1*H*-indole. Under an argon atmosphere, potassium hydroxide (913.5 mg, 16.28 mmol) and anhydrous DMSO (9.0 mL) were placed in a 50 mL Schlenk tube, which was immersed in a water bath at 22 ºC. To this was added 3-phenyl-1*H*-indole (**1a**; 802.5 mg, 4.152 mmol), and the mixture was stirred for 1 h. Iodomethane (1.00 g, 7.04 mmol) was added dropwise to the tube, and the resulting mixture was further stirred for 30 min. To this was added water (5 mL), and the aqueous phase was extracted with Et_2O (40 mL x 3). The combined organic layer was washed with water (10 mL x 5) and brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 35/1) gave 1-methyl-3-phenyl-1*H*-indole (775.8 mg, 90% yield) as a white solid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in references 11 and 12.[11,12] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3 H), 7.19 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.23 (s, 1 H), 7.24–7.31 (m, 2 H), 7.36 (dt, *J* =

[12] B. Join, T. Yamamoto and K. Itami, *Angew. Chem., Int. Ed.*, 2009, **48**, 3644.

8.3, 0.9 Hz, 1 H), 7.43 (tt, *J* = 7.7, 1.7 Hz, 2 H), 7.63–7.68 (m, 2 H), 7.94 (dd, *J* = 6.9, 0.9 Hz, 1 H).

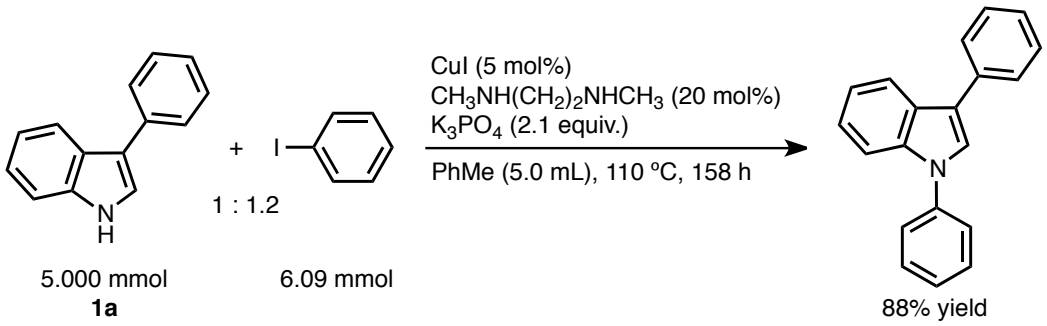


Synthesis of 1-Methyl-3-(4-methylphenyl)-1*H*-indole. Under an argon atmosphere, potassium hydroxide (561.0 mg, 10.00 mmol) and anhydrous DMSO (5.7 mL) were placed in a 50 mL Schlenk tube, which was immersed in a water bath at 22 ºC. To this was added 3-(4-methylphenyl)-1*H*-indole (526.0 mg, 2.537 mmol), and then the mixture was stirred for 1 h. Iodomethane (538.0 mg, 3.790 mmol) was added dropwise to the tube, and the resulting mixture was further stirred for 30 min. To this was added water (5 mL), and the aqueous phase was extracted with Et_2O (30 mL x 3). The combined organic layer was washed with water (5 mL x 5) and brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 7/1) gave 1-methyl-3-(4-methylphenyl)-1*H*-indole (543.4 mg, 96% yield) as a white solid. This compound has been already synthesized in literature, and its spectral and analytical data are in good agreement with those reported in references 11 and 13.[11,13] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 3.83 (s, 3 H), 7.18 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.20 (s, 1 H), 7.22–7.30 (m, 3 H), 7.36 (dd, *J* = 7.5, 1.2 Hz, 1 H), 7.55 (ddd, *J* = 8.0, 2.3, 1.8 Hz, 2 H), 7.92 (dt, *J* = 8.0, 1.2 Hz, 1 H).



[13] I. A. Kashulin and I. E. Nifant'ev, *J. Org. Chem.*, 2004, **69**, 5476.

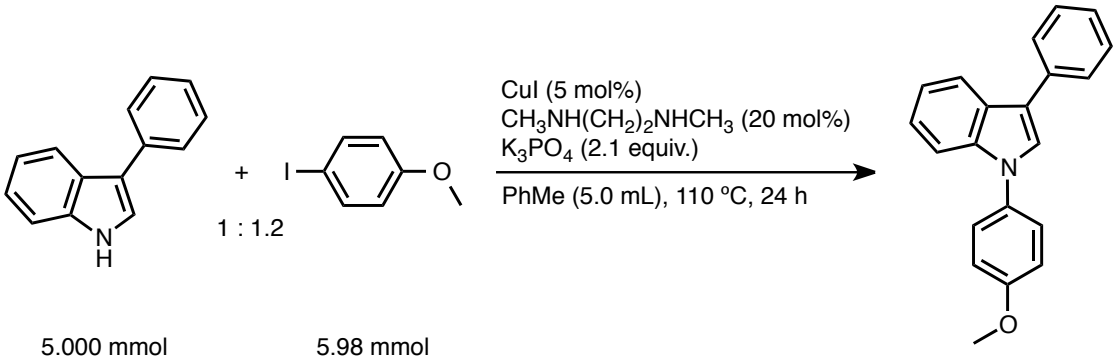
Synthesis of 1,1'-Dimethyl-3,3'-biindolyl (1c). Under an argon atmosphere, potassium hydroxide (1.57 g, 27.9 mmol) and anhydrous DMSO (8.0 mL) were placed in a 50 mL Schlenk tube, which was immersed in a water bath at 22 ºC. To this was added 3,3'-biindolyl[2] (812.4 mg, 3.497 mmol), and then the mixture was stirred for 1 h. Iodomethane (1.50 g, 10.5 mmol) was added dropwise to the tube, and the resulting mixture was further stirred for 30 min. To this was added water (5 mL), and the aqueous phase was extracted with Et_2O (40 mL x 3). The combined organic layer was washed with water (8 mL x 5) and brine (5 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 7/1) gave 1,1'-dimethyl-3,3'-biindolyl (**1c**; 837.3 mg, 91% yield) as a white solid, mp 186–187 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 6 H), 7.16 (ddd, *J* = 8.1, 6.8, 1.0 Hz, 2 H), 7.28 (ddd, *J* = 8.2, 6.9, 0.9 Hz, 2 H), 7.31 (s, 2 H), 7.38 (ddd, *J* = 8.3, 1.4, 0.9 Hz, 2 H), 7.83 (dt, *J* = 7.8, 0.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.8, 109.3, 109.5, 119.2, 120.3, 121.8, 126.0, 127.2, 137.1. Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 83.06; H, 6.18; N, 10.74.



Synthesis of 1,3-Diphenyl-1*H*-indole. 1,3-Diphenyl-1*H*-indole was synthesized according to the literature method.[14] Into a 50 mL Schlenk tube was placed CuI (47.6 mg, 0.249 mmol), 3-phenyl-1*H*-indole (**1a**; 966.2 mg, 5.000 mmol) and K_3PO_4 (2.22 g, 10.4 mmol), and then the tube was evacuated and filled with argon. Iodobenzene (1.24 g, 6.09 mmol), *N*,*N*'-dimethylethylenediamine (88.2 mg, 1.00 mmol) and PhMe (5.0 mL) were added successively to the tube, and the mixture was stirred at 110 °C for 158 h. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 30/1) gave 1,3-diphenyl-1*H*-indole (1433.9 mg, 88% yield) as a white solid. This compound has been already synthesized in

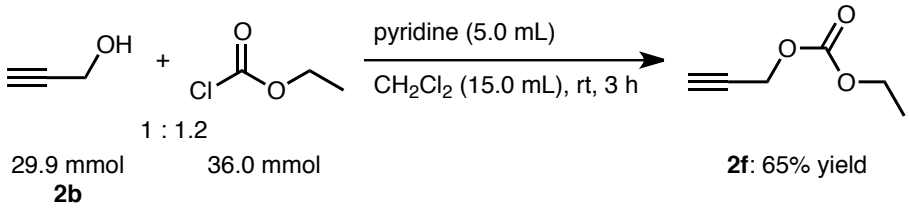
[14] J. C. Antilla, A. Klapars and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 11684.

literature, and its spectral and analytical data are in good agreement with those reported in reference 15.[15] Therefore, only ^{1}H NMR data are provided here. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.30 (m, 2 H), 7.32 (tdd, *J* = 7.4, 1.7, 1.1 Hz, 1 H), 7.39 (tt, *J* = 6.7, 1.9 Hz, 1 H), 7.47 (tt, *J* = 7.7, 1.7 Hz, 2 H), 7.51 (s, 1 H), 7.52–7.59 (m, 4 H), 7.61 (dd, *J* = 7.2, 1.4 Hz, 1 H), 7.69–7.74 (m, 2 H), 7.99 (ddd, *J* = 7.7, 1.7, 0.9 Hz, 1 H).

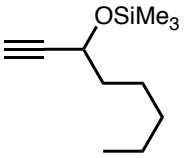


Synthesis of 1-(4-Methoxyphenyl)-3-phenyl-1*H*-indole. 1-(4-Methoxyphenyl)-3-phenyl-1*H*-indole was synthesized according to the literature method.[14] Into a 50 mL Schlenk tube was placed CuI (47.6 mg, 0.249 mmol), 3-phenyl-1*H*-indole (**1a**; 966.2 mg, 5.000 mmol) and K_3PO_4 (2.22 g, 10.4 mmol), and then the tube was evacuated and filled with argon. 4-Methoxyiodobenzene (1.40 g, 5.98 mmol), *N*,*N*-dimethylethylenediamine (88.2 mg, 1.00 mmol) and PhMe (5.0 mL) were added successively to the tube, and the mixture was stirred at 110 °C for 24 h. Filtration through a pad of Celite and evaporation of the solvent followed by column chromatography on silica gel (hexane/EtOAc = 15/1) gave 1-(4-methoxyphenyl)-3-pheny-1*H*-lindole (1440.0 mg, 82% yield) as a white solid, mp 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3 H), 7.05 (dt, *J* = 9.6, 3.2 Hz, 2 H), 7.19–7.28 (m, 2 H), 7.30 (tt, *J* = 7.5, 1.4 Hz, 1 H), 7.41–7.52 (m, 6 H), 7.67–7.74 (m, 2 H), 7.95–8.02 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.6, 110.7, 114.8, 118.4, 120.0, 120.6, 122.6, 125.9, 126.1, 126.7, 127.5, 128.8, 132.4, 135.2, 137.1, 158.4 (One carbon signal is missing due to overlapping). HRMS (EI) Calcd for $C_{21}H_{17}NO$: M^+, 299.1305. Found: *m*/*z* 299.1298.

[15] T. Gehrmann, J. L. Fillol, S. A. Scholl, H. Wadepohl and L. H. Gade, *Angew. Chem., Int. Ed.*, 2011, **50**, 5757.



Synthesis of Ethyl prop-2-yn-1-yl carbonate (2f). Under an argon atmosphere, propargyl alcohol (**2b**; 1.68 g, 29.9 mmol), pyridine (5.0 mL) and CH_2Cl_2 (15.0 mL) were placed in a 50 mL Schlenk tube, to which was added dropwise ethyl chloroformate (3.91 g, 36.0 mmol) at 0 ºC. After being stirred at room temperature for 3 h, the reaction mixture was quenched with water (5 mL), and the aqueous phase was extracted with Et_2O (40 mL x 3). The combined organic layer was washed with brine (15 mL) and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by short-path distillation under reduced pressure (72 ºC/30 mmHg) gave ethyl prop-2-yn-1-yl carbonate (**2f**; 2.50 g, 65% yield) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 3 H), 2.53 (t, J = 2.3 Hz, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 4.73 (d, J = 2.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 55.1, 64.6, 75.6, 77.1, 154.5. Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.14; H, 6.28.

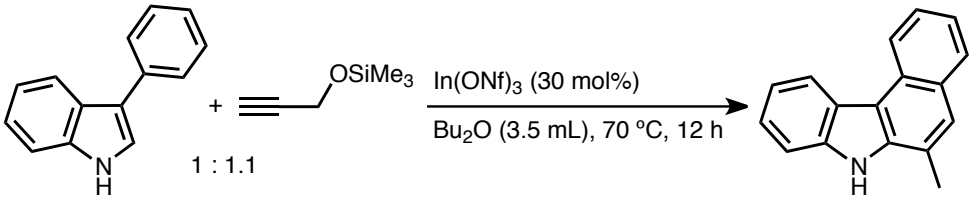


Synthesis of 3-Trimethylsilyloxy-1-octyne. 3-Trimethylsilyloxy-1-octyne as a colorless liquid was synthesized according to the reported procedure.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.89 (t, J = 6.9 Hz, 3 H), 1.23–1.36 (m, 4 H), 1.36–1.48 (m, 2 H), 1.61–1.73 (m, 2 H), 2.39 (d, J = 2.3 Hz, 1 H), 4.32 (td, J = 6.6, 2.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.1, 14.0, 22.6, 24.8, 31.4, 38.5, 62.5, 72.0, 85.6. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.83; H, 10.76.

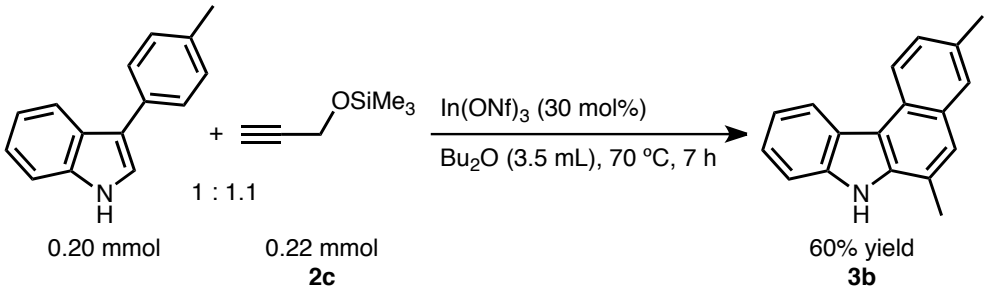
Synthesis of Aryl- and Heteroaryl[*c*]carbazoles Utilizing Indium-Catalyzed Annulation of 3-Aryl- and 3-Heteroarylindoles with Propargyl Ethers. A General

[16] J. Schwartz, D. B. Carr, R. T. Hansen and F. M. Dayrit, *J. Org. Chem.*, 1980, **45**, 3053.

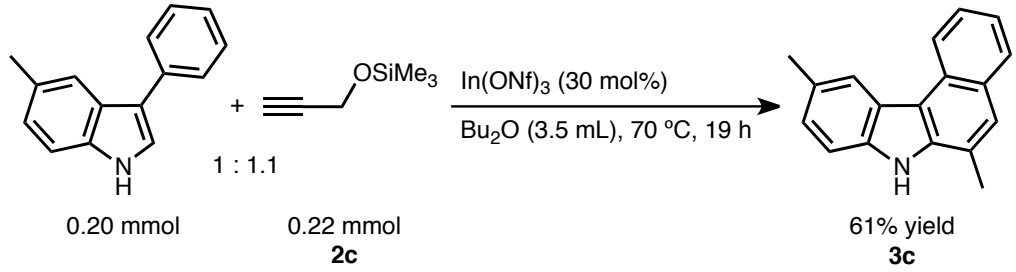
Procedure for Table 2 and Equations 1–3. $In(ONf)_3$ [(40.4 mg, 20.0 μmol) or (60.7 mg, 60.0 μmol)] was placed in a 20 or 50 mL Schlenk tube, which was heated at 150 °C in vacuo for 2 h. The tube was cooled down to room temperature and filled with argon. Bu_2O (3.5 or 7.5 mL) or PhCl (3.5 mL) was added to the tube and then the mixture was stirred at room temperature for 10 min. To this were added 3-(hetero)arylindole (0.200 mmol) and propargyl ether (0.220 or 0.260 mmol) successively, and the resulting mixture was stirred at 70, 85, 100 or 110 °C. After the time specified in Table 2 and Equations 1–3, the mixture was diluted with EtOAc (10 mL) and washed with a saturated $NaHCO_3$ aqueous solution (1 mL) and brine (1 mL), and then dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent followed by column chromatography on silica gel using hexane–EtOAc as eluent gave the corresponding (hetero)aryl[*c*]carbazoles. In case that purity of **3** or **4** is insufficient, further purification was performed with recycling HPLC or GPC. Products **3** and **4** synthesized here were fully characterized by ^1H and ^{13}C NMR spectroscopy, and elemental analysis or HRMS.



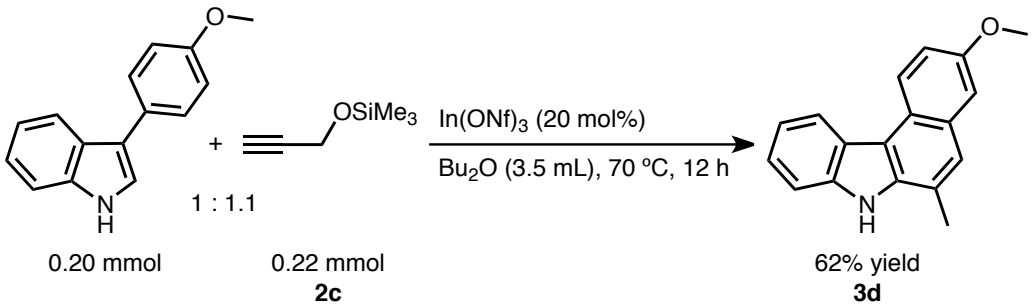
6-Methyl-7*H*-benzo[*c*]carbazole (3a). The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 154–155 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 2.68 (d, J = 0.9 Hz, 3 H), 7.38 (ddd, J = 8.3, 6.9, 0.9 Hz 1 H), 7.448 (tdd, J = 7.6, 1.4, 0.9 Hz, 1 H), 7.449 (s, 1 H), 7.59 (ddd, J = 7.9, 1.3, 0.8 Hz, 1 H), 7.62–7.69 (m, 2 H), 7.93 (d, J = 8.2 Hz, 1 H), 8.35 (bs, 1 H), 8.56 (dd, J = 8.2, 0.5 Hz, 1 H), 8.74 (dd, J = 8.2, 0.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.3, 111.2, 115.0, 120.3, 121.4, 122.1, 122.98, 123.03, 124.2, 124.4, 126.0, 126.5, 128.4, 128.8, 129.6, 137.3, 138.3. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.51; H, 5.88; N, 6.04.



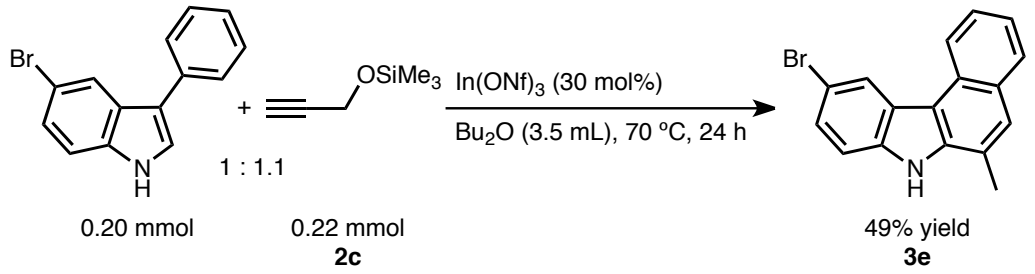
3,6-Dimethyl-7*H*-benzo[*c*]carbazole (3b). The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 176–177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3 H), 2.70 (d, *J* = 0.9 Hz, 3 H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.44 (td, *J* = 7.6, 1.1 Hz, 1 H), 7.49 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.58 (s, 1 H), 7.60 (dt, *J* = 7.8, 0.9 Hz, 1 H), 7.71 (s, 1 H), 8.33 (bs, 1 H), 8.54 (dd, *J* = 7.8, 0.9 Hz, 1 H), 8.64 (dd, *J* = 8.2, 0.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 21.8, 110.8, 114.7, 121.5, 122.0, 122.8, 123.0, 124.6, 125.6, 125.9, 126.3, 128.4, 128.8, 129.47, 129.52, 136.5, 137.6. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.91; H, 5.77; N, 5.74.



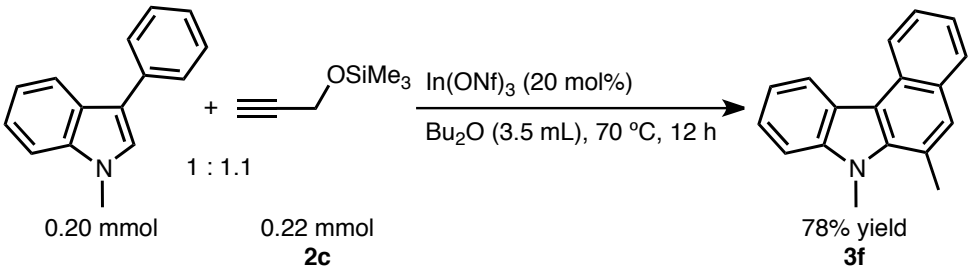
6,10-Dimethyl-7*H*-benzo[*c*]carbazole (3c). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 181–182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.63 (s, 3 H), 2.70 (d, *J* = 1.2 Hz, 3 H), 7.28 (dd, *J* = 8.6, 1.2 Hz, 1 H), 7.44 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.50 (dd, *J* = 8.0, 0.6 Hz, 1 H), 7.61–7.68 (m, 2 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 8.28 (bs, 1 H), 8.36 (s, 1 H), 8.75 (dd, *J* = 8.0, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.3, 21.8, 110.8, 114.7, 121.5, 122.0, 122.8, 123.0, 124.7, 125.6, 125.9, 126.3, 128.4, 128.9, 129.5, 129.6, 136.6, 137.6. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.02; H, 5.80; N, 5.74.



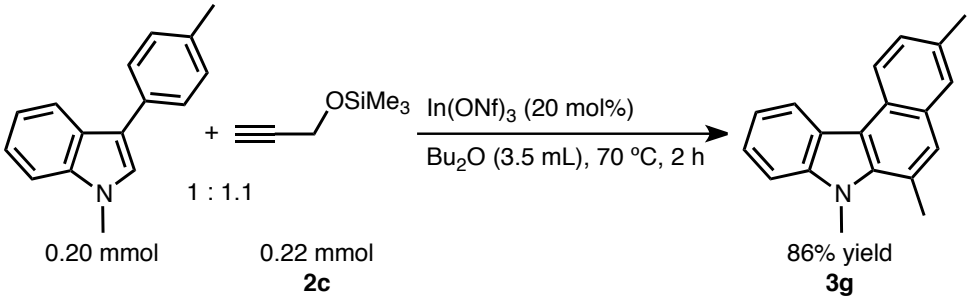
3-Methoxy-6-methyl-7*H*-benzo[*c*]carbazole (3d). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 140–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.67 (d, *J* = 0.6 Hz, 3 H), 3.95 (s, 3 H), 7.28–7.38 (m, 3 H), 7.43 (td, *J* = 7.7, 1.2 Hz, 1 H), 7.53–7.60 (m, 2 H), 8.27 (bs, 1 H), 8.51 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.65 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.3, 55.4, 107.8, 111.2, 115.3, 117.40, 117.41, 120.1, 121.9, 123.7, 124.2, 124.41, 124.42, 125.6, 130.6, 136.1, 138.4, 155.5. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.88; H, 5.54; N, 5.40.



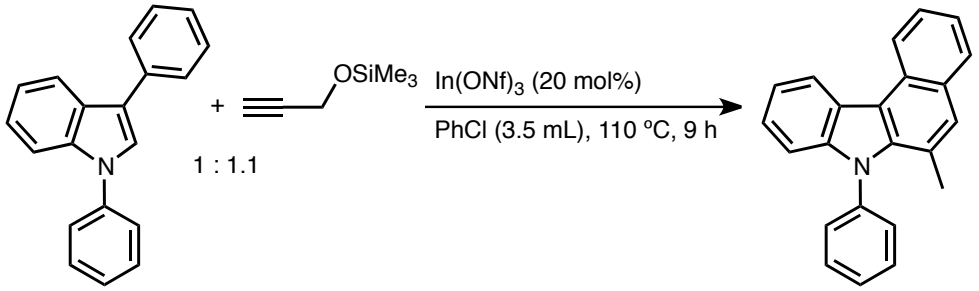
10-Bromo-6-methyl-7*H*-benzo[*c*]carbazole (3e). The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 181–182 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (s, 3 H), 7.44–7.50 (m, 2 H), 7.53 (ddd, *J* = 8.6, 1.7, 0.6 Hz, 1 H), 7.62–7.71 (m, 2 H), 7.93 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.38 (bs, 1 H), 8.63 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.67 (d, *J* = 1.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 112.5, 113.3, 114.2, 121.3, 122.8, 123.4, 124.6, 126.1, 126.4, 126.9, 127.3, 128.51, 128.54, 129.6, 136.8, 137.9. Anal. Calcd for $C_{17}H_{12}BrN$: C, 65.83; H, 3.90; N, 4.52. Found: C, 65.79; H, 3.51; N, 4.57.



6,7-Dimethyl-7*H*-benzo[*c*]carbazole (3f). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 10/1). A white solid, mp 156–157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.01 (d, *J* = 1.1 Hz, 3 H), 4.27 (s, 3 H), 7.38 (td, *J* = 6.9, 1.1 Hz, 1 H), 7.43 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.51 (td, *J* = 7.8, 1.1 Hz, 1 H), 7.55 (dd, *J* = 8.0, 0.6 Hz, 1 H), 7.60 (d, *J* = 1.1 Hz, 1 H), 7.64 (ddd, *J* = 8.6, 6.9, 1.1 Hz, 1 H), 7.90 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.61 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.79 (dd, *J* = 8.0, 0.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 32.6, 109.2, 115.7, 119.8, 122.0, 122.3, 122.9, 122.9, 123.5, 124.0, 126.1, 128.1, 128.92, 128.98, 129.1, 138.2, 140.6. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.88; H, 6.25; N, 5.72.

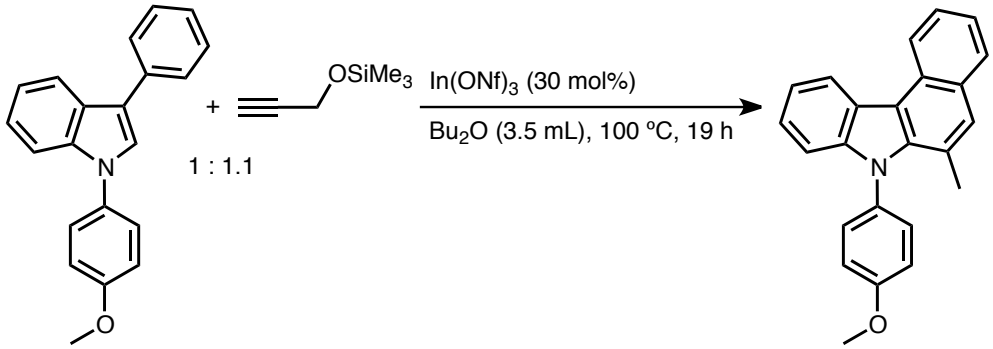


3,6,7-Trimethyl-7*H*-benzo[*c*]carbazole (3g). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 10/1). A white solid, mp 167–168 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.55 (s, 3 H), 2.97 (d, *J* = 1.2 Hz, 3 H), 4.22 (s, 3 H), 7.36 (ddd, *J* = 8.3, 6.6, 1.1 Hz, 1 H), 7.44–7.54 (m, 4 H), 7.66 (s, 1 H), 8.57 (d, *J* = 8.0 Hz, 1 H), 8.67 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.50, 21.53, 32.5, 109.1, 115.7, 119.6, 121.9, 122.2, 122.7, 123.4, 123.8, 126.9, 127.3, 128.1, 128.4, 129.3, 132.2, 137.7, 140.6. Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.09; H, 6.61; N, 5.38.



0.20 mmol 0.22 mmol **2c** 51% yield **3h**

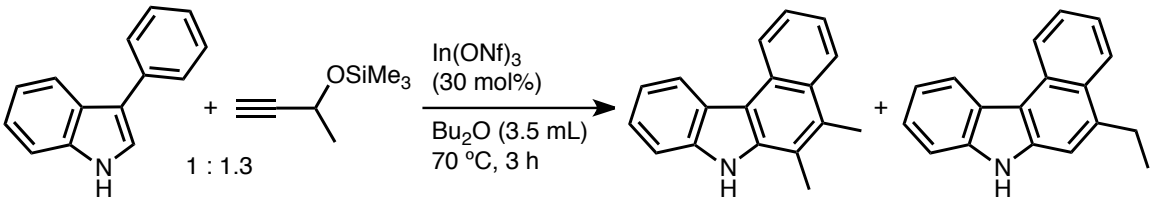
6-Methyl-7-phenyl-7*H*-benzo[*c*]carbazole (3h). The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 119–120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (d, *J* = 1.2 Hz, 3 H), 7.14 (dd, *J* = 7.2, 1.4 Hz, 1 H), 7.35–7.43 (m, 2 H), 7.44–7.52 (m, 3 H), 7.53–7.61 (m, 4 H), 7.67 (ddd, *J* = 8.3, 6.6, 1.1 Hz, 1 H), 7.92 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.64 (dd, *J* = 6.9, 1.2 Hz, 1 H), 8.85 (dd, *J* = 8.6, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 110.7, 116.1, 120.5, 121.8, 123.00, 123.04, 123.2, 123.5, 124.2, 126.1, 128.1, 128.66, 128.70, 128.9, 129.2, 129.4, 129.8, 138.4, 139.7, 142.1. Anal. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56. Found: C, 90.26; H, 5.66; N, 4.58.



0.20 mmol 0.22 mmol **2c** 53% yield **3i**

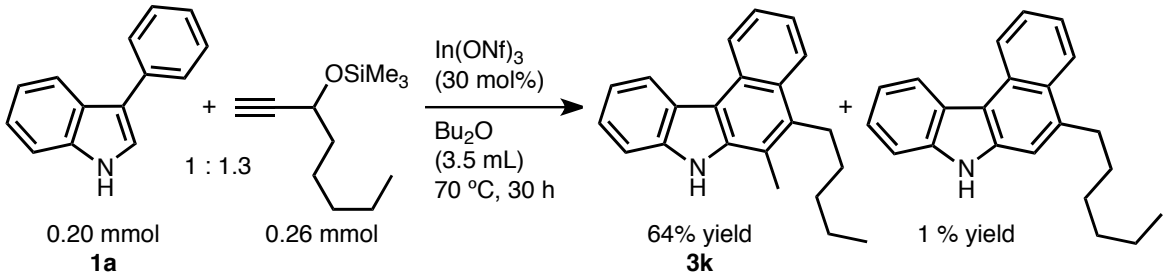
7-(4-Methoxyphenyl)-6-methyl-7*H*-benzo[*c*]carbazole (3i). The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 15/1). A white solid, mp 154–155 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.17 (d, *J* = 0.6 Hz, 3 H), 3.94 (s, 3 H), 7.07 (dt, *J* = 9.5, 2.6 Hz, 2 H), 7.13 (dd, *J* = 6.9, 2.3 Hz, 1 H), 7.35–7.42 (m, 4 H), 7.46 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.56 (d, *J* = 0.6 Hz, 1 H), 7.66 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 8.63 (dd, *J* = 6.6, 2.0 Hz, 1H), 8.84 (dd, *J* = 8.0, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 55.6, 110.8, 114.3,

115.9, 120.4, 121.8, 123.0, 123.05, 123.10, 123.4, 124.2, 126.0, 128.1, 128.6, 128.9, 129.4, 130.8, 132.2, 138.5, 142.4, 159.7. Anal. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.51; H, 5.89; N, 4.15.



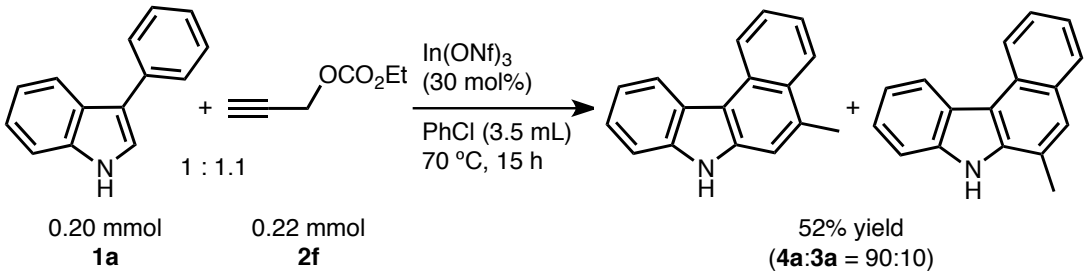
5,6-Dimethyl-7*H*-benzo[*c*]carbazole (3j). The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 216–217 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.68 (s, 3 H), 2.78 (s, 3 H), 7.37 (td, *J* = 7.4, 0.6 Hz, 1 H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.51 (ddd, *J* = 8.6, 6.9, 1.2 Hz, 1 H), 7.59 (dd, *J* = 8.0, 0.6 Hz, 1 H), 7.66 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1 H), 8.19 (dd, *J* = 8.6, 0.6 Hz, 1 H), 8.33 (bs, 1 H), 8.54 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.79 (dd, *J* = 8.0, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 15.1, 111.0, 113.3, 119.1, 120.2, 121.9, 122.9, 123.5, 123.8, 124.7, 125.1, 125.6, 128.9, 129.0, 130.1, 137.6, 138.1. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 87.97; H, 5.99; N, 5.70.

5-Ethyl-7*H*-benzo[*c*]carbazole. The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 107–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, *J* = 7.6 Hz, 3 H), 3.24 (qd, *J* = 7.6, 0.6 Hz, 2 H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.42 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.47 (d, *J* = 0.5 Hz, 1 H), 7.48–7.56 (m, 2 H), 7.70 (td, *J* = 6.9, 1.4 Hz, 1 H), 8.20 (dd, *J* = 8.7, 0.5 Hz, 1 H), 8.30 (bs, 1 H), 8.53 (dd, *J* = 7.9, 0.9 Hz, 1 H), 8.81 (dd, *J* = 8.7, 0.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 26.6, 111.0, 111.4, 114.1, 120.1, 121.7, 122.9, 123.86, 123.94, 124.2, 124.9, 126.4, 127.8, 130.5, 137.1, 138.3, 139.9. HRMS (EI) Calcd for $C_{18}H_{15}N$: M^+, 245.1199. Found: *m*/*z* 245.1193.

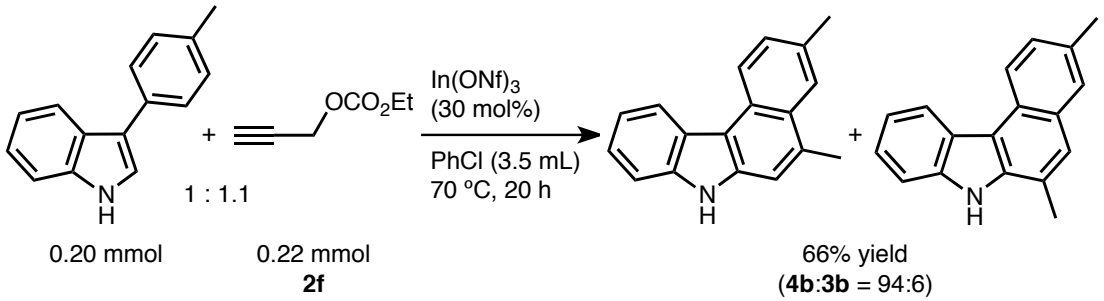


6-Methyl-5-pentyl-7*H*-benzo[*c*]carbazole (3k). The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 144–145 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.5 Hz, 3 H), 1.43 (sext, *J* = 7.5 Hz, 2 H), 1.48–1.57 (m, 2 H), 1.66–1.76 (m, 2 H), 2.68 (s, 3 H), 3.23 (t, *J* = 8.0 Hz, 2 H), 7.37 (td, *J* = 7.4, 0.6 Hz, 1 H), 7.42 (td, *J* = 7.4, 0.6 Hz, 1 H), 7.50 (ddd, *J* = 8.6, 6.9, 1.2 Hz, 1 H), 7.60 (d, *J* = 8.1 Hz, 1 H), 7.66 (td, *J* = 7.5, 0.6 Hz, 1 H), 8.19 (d, *J* = 8.6 Hz, 1 H), 8.35 (bs, 1 H), 8.54 (d, *J* = 8.0 Hz, 1 H), 8.79 (dd, *J* = 8.0, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.2, 22.7, 29.0, 30.5, 32.4, 111.0, 113.4, 118.7, 120.2, 121.9, 122.9, 123.7, 123.8, 124.6, 125.1, 125.5, 128.1, 129.2, 135.2, 137.6, 138.2. Anal. Calcd for $C_{22}H_{23}N$: C, 87.66; H, 7.69; N, 4.65. Found: C, 87.99; H, 7.99; N, 4.72.

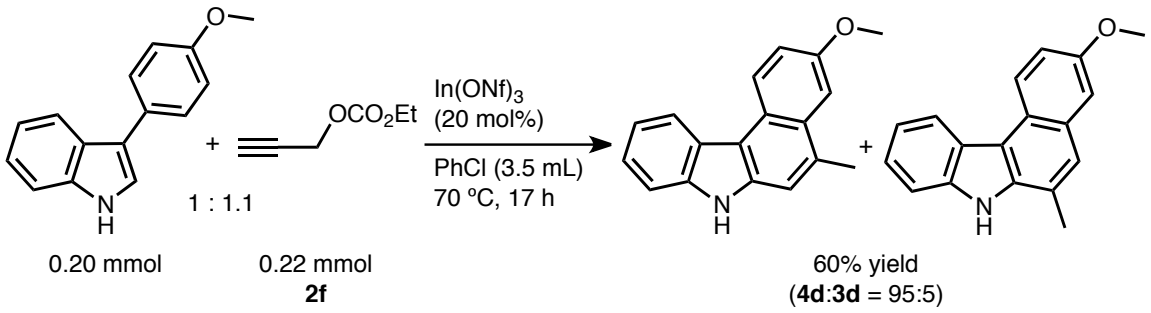
5-(1-Hexyl)-7*H*-benzo[*c*]carbazole. The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 3 H), 1.27–1.41 (m, 4 H), 1.48 (quint, *J* = 7.3 Hz, 2 H), 1.81 (quint, *J* = 7.6 Hz, 2 H), 3.17 (t, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 6.9 Hz, 1 H), 7.39–7.46 (m, 2 H), 7.47–7.55 (m, 2 H), 7.69 (td, *J* = 7.6, 0.8 Hz, 1 H), 8.18 (d, *J* = 8.2 Hz, 1 H), 8.26 (bs, 1 H), 8.52 (d, *J* = 7.8 Hz, 1 H), 8.80 (d, *J* = 8.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 29.6, 30.9, 31.8, 34.0, 111.0, 112.4, 114.1, 120.1, 121.7, 122.8, 123.8, 123.9, 124.1, 125.1, 126.4, 127.8, 130.5, 137.0, 138.3, 138.6. HRMS (EI) Calcd for $C_{22}H_{23}N$: M^+, 301.1825. Found: *m*/*z* 301.1844.



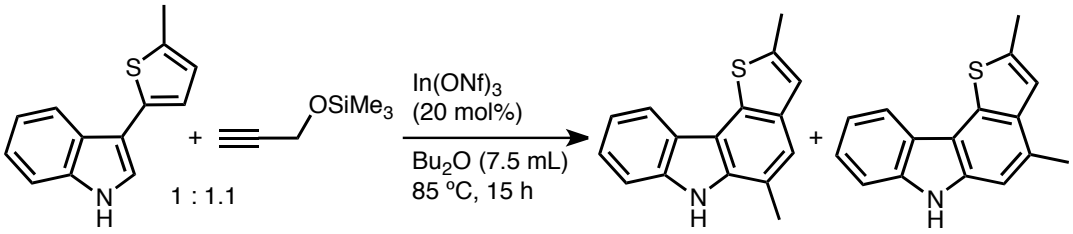
5-Methyl-7*H*-benzo[*c*]carbazole (4a). The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 201–202 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.84 (d, *J* = 1.2 Hz, 3 H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1 H), 7.43 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.49 (d, *J* = 1.2 Hz, 1 H), 7.53 (ddd *J* = 8.6, 6.9, 1.2 Hz, 1 H), 7.56 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.72 (ddd, *J* = 8.4, 6.7, 1.3 Hz, 1 H), 8.15 (dd, *J* = 8.6, 1.2 Hz, 1 H), 8.33 (bs, 1 H), 8.54 (dd, *J* = 8.6, 0.6 Hz, 1 H), 8.80 (dd, *J* = 8.0, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 111.0, 113.2, 114.0, 120.1, 121.7, 122.9, 123.7, 123.8, 124.1, 125.3, 126.6, 128.6, 130.1, 133.8, 137.0, 138.2. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.51; H, 5.88; N, 6.04.



3,5-Dimethyl-7*H*-benzo[*c*]carbazole (4b). The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 222–223 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.61 (s, 3 H), 2.81 (d, *J* = 0.6 Hz, 3 H), 7.35 (ddd, *J* = 7.5, 6.9, 0.6 Hz, 1 H), 7.41 (ddd, *J* = 7.5, 6.9, 0.6 Hz, 1 H), 7.46 (d, *J* = 0.6 Hz, 1 H), 7.52–7.58 (m, 2 H), 7.91 (s, 1 H), 8.28 (bs, 1 H), 8.51 (d, *J* = 8.0 Hz, 1 H), 8.69 (dd, *J* = 8.6, 0.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 21.9, 111.0, 113.2, 114.1, 120.0, 121.6, 123.6, 123.7, 124.1, 124.7, 128.1, 128.5, 128.8, 132.2, 133.3, 136.5, 138.2. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.18; H, 6.03; N, 5.70.

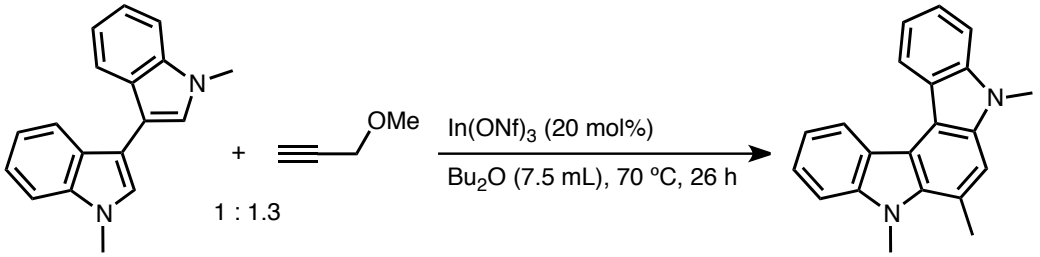


3-Methoxy-5-methyl-7*H*-benzo[*c*]carbazole (4d). The title compound was isolated by recycling GPC after column chromatography on silica gel (hexane/EtOAc = 5/1). A white solid, mp 209–210 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.80 (d, *J* = 1.2 Hz, 3 H), 4.00 (s, 3 H), 7.35 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1 H), 7.38–7.44 (m, 2 H), 7.47 (dd, *J* = 2.9, 0.6 Hz, 1 H), 7.50 (d, *J* = 1.2 Hz, 1 H), 7.55 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.28 (bs, 1 H), 8.49 (dd, *J* = 8.0, 0.6 Hz, 1 H), 8.73 (dd, *J* = 9.2, 0.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 55.4, 105.7, 111.0, 113.7, 114.4, 117.5, 120.0, 121.6, 123.86, 123.94, 125.07, 125.12, 129.7, 132.6, 135.8, 138.3, 155.5. Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.71; H, 5.43; N, 5.39.



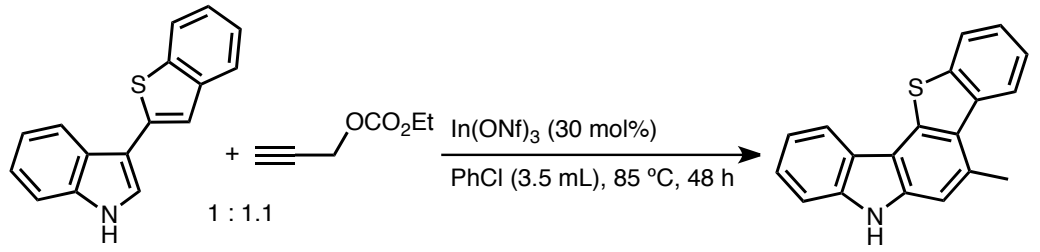
2,5-Dimethyl-6*H*-thieno[3,2-*c*]carbazole (3l). The title compound was isolated by recycling HPLC after column chromatography on silica gel (hexane/EtOAc = 7/1). A white solid, mp 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (d, *J* = 0.9 Hz, 3 H), 2.67 (d, *J* = 1.4 Hz, 3 H), 7.06 (dd, *J* = 2.5, 1.1 Hz, 1 H), 7.34 (td, *J* = 7.1, 0.9 Hz, 1 H), 7.43 (ddd, *J* = 8.3, 6.9, 0.9 Hz, 1 H), 7.51 (tt, *J* = 4.1, 0.9 Hz, 2 H), 8.07 (bs, 1 H), 8.13 (d, *J* = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 17.0, 110.7, 116.0, 117.5, 119.9, 120.8, 121.5, 121.6, 122.8, 125.0, 130.3, 134.4, 136.3, 136.8, 138.8. Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.00; H, 5.16; N, 5.58; S, 12.83.

2,4-Dimethyl-6*H*-thieno[3,2-*c*]carbazole (4l). The title compound was isolated by recycling HPLC column chromatography on silica gel (hexane/EtOAc = 7/1). A white solid, mp 184–185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.695 (s, 3 H), 2.698 (s, 3 H), 7.14–7.20 (m, 2 H), 7.32 (ddd, *J* = 8.0, 6.6, 1.1 Hz, 1 H), 7.38–7.47 (m, 2 H), 8.06 (bs, 1 H), 8.10 (ddd, *J* = 7.8, 1.8, 0.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.2, 20.5, 108.8, 110.5, 114.8, 119.7, 120.2, 121.0, 122.5, 124.7, 130.4, 132.3, 133.9, 136.4, 136.9, 138.7. HRMS (EI) Calcd for $C_{16}H_{13}NS$: M^+, 251.0763. Found: *m*/*z* 251.0760.



0.20 mmol **1c** 0.26 mmol **2a** **3m**: 40% yield

5,8-Dihydro-5,6,8-trimethylindolo[2,3-*c*]carbazole (3m). The title compound was isolated by column chromatography on silica gel (hexane/EtOAc = 7/1). A white solid, mp 262–263 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.09 (s, 3 H), 3.95 (s, 3 H), 4.25 (s, 3 H), 7.31 (s, 1 H), 7.34–7.40 (m, 2 H), 7.48–7.57 (m, 4 H), 8.85 (d, *J* = 8.0 Hz, 1 H), 8.90 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.0, 29.3, 33.0, 108.4, 108.7, 110.4, 114.5, 117.7, 118.2, 118.4, 119.8, 122.5, 122.6, 123.25, 123.30, 124.3, 124.8, 135.3, 136.3, 140.7, 141.7. Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.63; H, 5.87; N, 9.39.



0.20 mmol **1d** 0.22 mmol **2f** 34% yield **4n**

7-Methyl-5*H*-benzo[*b*]thieno[3,2-*c*]carbazole (4n). The title compound was isolated by recycling GPC column chromatography on silica gel (hexane/EtOAc = 7/1). A white solid, mp 178–179 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.68 (d, *J* = 0.6 Hz, 3 H), 7.32 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.36 (td, *J* = 7.7, 1.5 Hz, 1 H), 7.43 (tt, *J* = 7.6, 1.2 Hz, 2 H), 7.54 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.90 (dd, *J* = 8.6, 1.2 Hz, 1 H), 7.99 (d, *J* = 0.6 Hz, 1 H), 8.10–8.18 (m, 2 H), 8.38 (bs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 110.8, 116.4, 117.5, 119.5, 120.2, 120.7, 121.6, 122.96, 122.99, 124.4, 125.0, 125.5, 128.7, 130.4, 136.1, 138.2, 138.7, 139.0. Anal. Calcd for $C_{19}H_{13}NS$: C, 79.41; H, 4.56; N, 4.87; S, 11.16. Found: C, 79.03; H, 4.54; N, 4.87; S, 11.17.