# Indium(III) Bromide Catalyzed Rapid Propargylation of Heteroaromatic Systems by α-Aryl-Substituted Propargyl Alcohols

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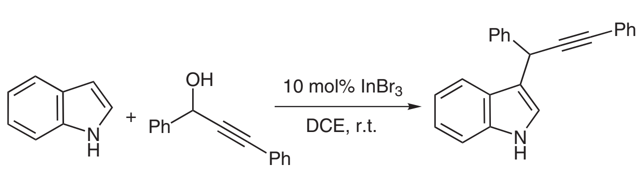
**Abstract:** A variety of heteroaromatic compounds such as indole, carbazole, pyrrole, and furan underwent smooth coupling with propargylic alcohols in the presence of 10 mol% of indium(III) bromide under mild conditions to furnish exclusively propargylated heterocycles in excellent yields and high regioselectivity. The use of indium(III) bromide makes this procedure simple, convenient, and practical. The hydroxy groups of the propargylic alcohols were simply replaced by the nucleophiles in an $S_N2'$ manner.

**Key words:** indium reagents, nucleophilic substitution, C-alkylation, propargylation

The indole nucleus is a prominent structural motif found in numerous natural products and synthetic compounds with important biological activities, and thus considerable attention has been focused toward general, flexible, and selective methods for the synthesis of highly functionalized indole derivatives.[1] Currently, the implementation of mild and selective procedures with ample functional group tolerance for the preparation of indoles is of great interest.[2–5] Nucleophilic substitution of the hydroxy group in alcohols with nucleophiles generally requires preactivation of the alcohols because of the poor leaving ability of the hydroxy group.[6] Consequently, hydroxy groups are generally transformed into the corresponding halides, carboxylates, carbonates, phosphonates, or related compounds.[7] However, such processes inevitably produce stoichiometric amounts of salt waste and, also, substitution with halides requires a stoichiometric amount of base, which limits their use in large-scale synthesis. In most cases, either a high reaction temperature is required or a promoter is added to enhance the leaving ability of the hydroxy group. Therefore, the direct catalytic substitution of alcohols by indoles with the aid of an efficient, water-tolerant, and recyclable catalyst is highly desirable. Recently, indium(III) bromide has received increasing attention as a water-tolerant green Lewis acid catalyst for organic synthesis, and has demonstrated highly chemo-, regio-, and stereoselective results.[8] Compared to conventional Lewis acids, it has the advantages of water stability, recyclability, operational simplicity, strong tolerance toward oxygen and nitrogen-containing substrates and functional groups, and that it can often be used in catalytic amounts. It has recently been utilized for the deoxygenation of activated alcohols and allylation of doubly activated alcohols.[8b,9] However, there have been no reports on the use of indium(III) bromide as catalyst for the propargylation of heteroaromatic systems by α-aryl-substituted propargyl alcohols.

In continuation of our interest in the catalytic use of indium(III) bromide,[10] the work we report herein is on a novel and efficient propargylation of heteroaromatics by α-aryl-substituted propargyl alcohols. In a preliminary study, indole (**1a**) was treated with 1,3-diphenylprop-2-yn-1-ol (**2a**) in the presence of 10 mol% of indium(III) bromide (Scheme 1). The reaction went to completion at room temperature within 15 minutes to give product **3a** in 91% yield (Scheme 1; Table 1, entry 1).



**1a** **2a** **3a**

**Scheme 1**

Encouraged by this result, we turned our attention to various other indoles (Table 1). Interestingly, 5-bromo-, 5-nitro-, and 2-phenyl-substituted indoles (**1b–d**) reacted smoothly with 1,3-diphenylprop-2-yn-1-ol (**2a**) to furnish the corresponding 3-propargylated indoles **3b–d** in excellent yields (Table 1, entries 2–4). Other propargylic alcohols such as 1-(*p*-tolyl)hept-2-yn-1-ol (**2b**) and 1-phenylhept-2-yn-1-ol (**2c**) reacted efficiently with indole (**1a**), 5-cyanoindole (**1e**), and 5-nitroindole (**1c**) at room temperature under identical conditions (Table 1, entries 5–9). In addition, the reaction with (*E*)-1,5-diphenylpent-1-en-4-yn-3-ol (**2d**) also proceeded well (Scheme 2; Table 1, entries 10 and 11). Similarly, (*E*)-1-phenylnon-1-en-4-yn-3-ol (**2e**) reacted smoothly with 5-bromoindole (**1b**) and 7-ethylindole (**1f**) (Table 1, entries 12 and 13). Pyrrole (**1g**) and furan (**1h**) gave the respective 2-propargylated pyrrole and furan derivatives **3o** and **3p** (Table 1, entries 15 and 16). Like with indole (**1a**), the propargylation of carbazole (**1i**) occurred at the C-3 position (Table 1, entry 17).

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**Table 1** Indium(III) Bromide Catalyzed Alkylation of Heteroaromatic Systems by α-Aryl-Substituted Propargylic Alcohols

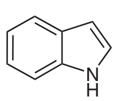
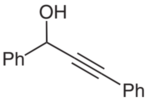
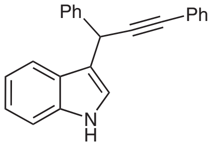
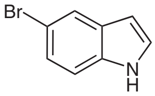
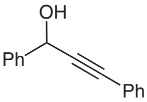
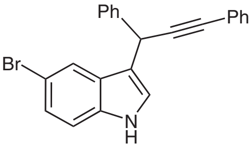
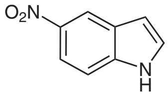
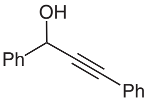
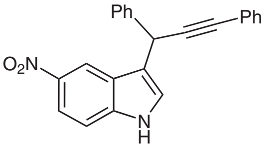
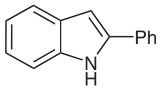
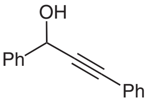
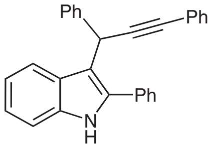
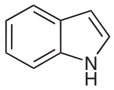
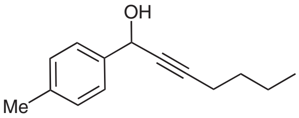
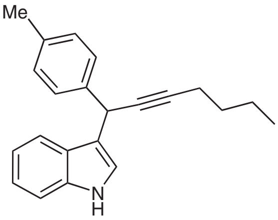
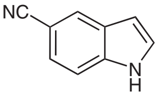
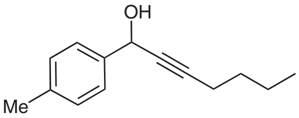
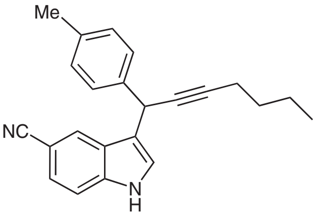
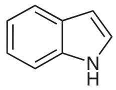
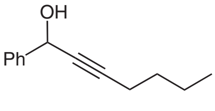
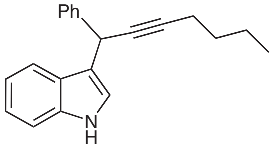
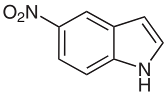
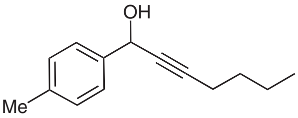
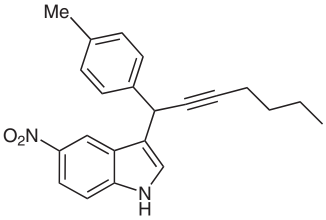
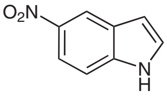
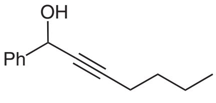
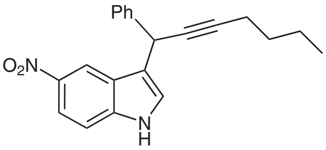
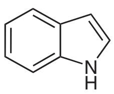
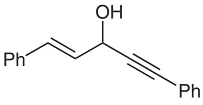
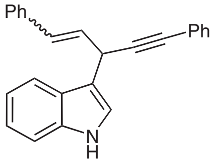
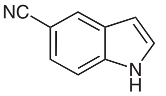
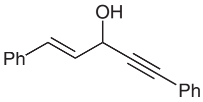
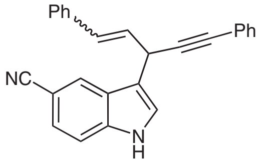
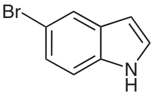
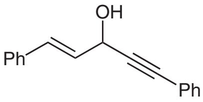
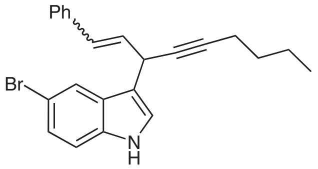
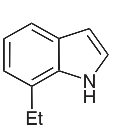
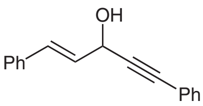
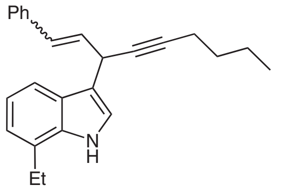
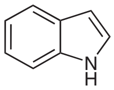
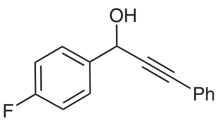
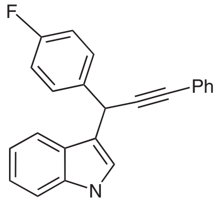
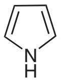
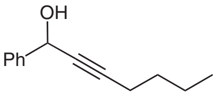
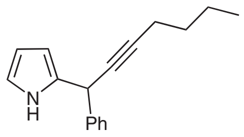
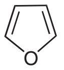
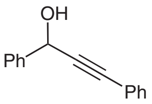
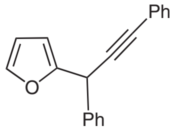
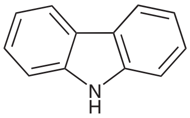
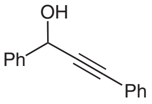
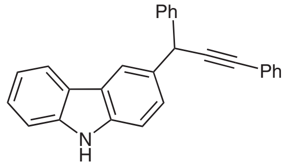
| Entry | Hetarene | 1 | Propargylic alcohol | 2 | Product[a] | 3 | Time (min) | Yield[b] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 |  | **1a** |  | **2a** |  | **3a** | 15 | 91 |
| 2 |  | **1b** |  | **2a** |  | **3b** | 25 | 93 |
| 3 |  | **1c** |  | **2a** |  | **3c** | 40 | 85 |
| 4 |  | **1d** |  | **2a** |  | **3d** | 35 | 88 |
| 5 |  | **1a** |  | **2b** |  | **3e** | 20 | 90 |
| 6 |  | **1e** |  | **2b** |  | **3f** | 35 | 87 |
| 7 |  | **1a** |  | **2c** |  | **3g** | 20 | 92 |
| 8 |  | **1c** |  | **2b** |  | **3h** | 30 | 86 |
| 9 |  | **1c** |  | **2c** |  | **3i** | 35 | 87 |

**Table 1** Indium(III) Bromide Catalyzed Alkylation of Heteroaromatic Systems by α-Aryl-Substituted Propargylic Alcohols (continued)

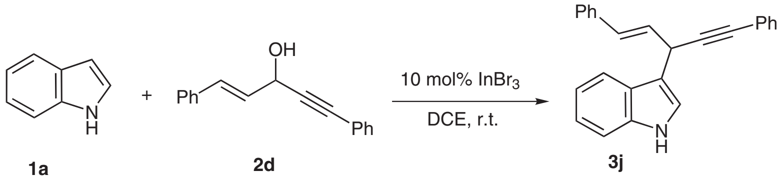
| Entry | Hetarene | 1 | Propargylic alcohol | 2 | Product[a] | 3 | Time (min) | Yield[b] (%) |
|---|---|---|---|---|---|---|---|---|
| 10 |  | **1a** |  | **2d** |  | **3j** | 30 | 86[c] |
| 11 |  | **1e** |  | **2d** |  | **3k** | 35 | 84[c] |
| 12 |  | **1b** |  | **2e** |  | **3l** | 30 | 91[c] |
| 13 |  | **1f** |  | **2e** |  | **3m** | 25 | 88[c] |
| 14 |  | **1a** |  | **2f** |  | **3n** | 35 | 92 |
| 15 |  | **1g** |  | **2c** |  | **3o** | 40 | 84 |
| 16 |  | **1h** |  | **2a** |  | **3p** | 35 | 86 |
| 17 |  | **1i** |  | **2a** |  | **3q** | 35 | 88 |

[a] All products were characterized by $^{1}H$ and $^{13}C$ NMR, IR, and mass spectroscopy.

[b] Isolated and non-optimized yield.

[c] *E*/*Z* ratio 9:1.

Interestingly, electron-deficient indoles such as 5-nitro- (**1c**) and 5-cyanoindole (**1e**) also underwent smooth alkylation with propargylic alcohols under similar reaction conditions to give the corresponding 3-substituted indoles (Table 1). In all cases, the reactions proceeded efficiently in high selectivity and were completed within 15–40 minutes. In the absence of indium(III) bromide, no reaction was observed. No addition or rearranged products were observed when secondary alcohols activated by both allylic and propargylic functionalities were used (Table 1,



**Scheme 2**

entries 10–13). The hydroxy group was simply replaced by the indole in an $S_N2'$ manner. This method is compatible with alkenyl-, alkynyl-, halo-, nitro-, cyano-, and free amino groups. Acid-sensitive substrates such as pyrrole and furan were also well tolerated under these conditions. Primary benzylic alcohols failed to react with indoles under these conditions. As solvent, 1,2-dichloroethane appeared to give the best results. All the products were characterized by $^1H$- and $^{13}C$ NMR-, IR-, and mass spectroscopy. To examine the efficacy of indium(III) bromide, this reaction was carried out with various other indium(III) salts such as indium(III) fluoride, -chloride, -perchlorate, and -triflate. Of these, indium(III) bromide was found to give the best results in terms of conversion. Alternatively, 10 mol% of bismuth(III) triflate was also equally effective for this conversion. The results presented in Table 1 illustrate the scope and generality of this process with regard to various heteroaromatic systems and secondary propargylic alcohols.

In summary, indium(III) bromide has proved to be an effective catalyst for the propargylation of heteroaromatic systems by propargylic alcohols in high yields and short reaction times with high selectivity, making it a useful and attractive process for the alkylation of heteroaromatics. The use of indium(III) bromide makes this procedure simple, convenient, and practical.

Melting points were recorded on a Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. $^1H$ and $^{13}C$ NMR spectra were recorded on Gemini-200 and Varian Bruker-300 spectrometers; samples were dissolved in $CDCl_3$ and TMS was used as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. HRMS were conducted under ESI mode.

### Propargylation of Hetarenes 1a–h by Propargyl Alcohols 2a–f; General Procedure

A mixture of hetarene **1** (1.0 mmol), propargylic alcohol **2** (1.0 mmol), and $InBr_3$ (10 mol%) in DCE (5 mL) was stirred at r.t. for the appropriate time (Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was diluted with $H_2O$ and extracted with $CH_2Cl_2$ (2 × 15 mL). The combined organic layers were dried ($Na_2SO_4$), concentrated in vacuo, and purified by column chromatography (silica gel, Merck, 100–200 mesh, EtOAc–hexane, 1:9); this afforded pure product **3**.

### 3-(1,3-Diphenylprop-2-ynyl)-1*H*-indole (3a)

Dark brown liquid.

IR (KBr): 3418, 3061, 2923, 2853, 2360, 2196, 1696, 1595, 1451, 1285, 1214, 882, 795, 755, 697 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 5.33$ (s, 1 H), 6.99 (d, $J = 1.7$ Hz, 1 H), 7.11 (d, $J = 8.4$ Hz, 1 H), 7.18–7.33 (m, 6 H), 7.39–7.47 (m, 6 H), 7.69 (d, $J = 1.7$ Hz, 1 H), 7.89 (br s, 1 H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 35.4$, 83.2, 90.5, 111.1, 116.7, 119.5, 122.1, 122.5, 123.6, 126.0, 126.7, 127.7, 127.8, 128.1, 128.4, 131.6, 136.6, 141.2.

MS (EI, 70 eV): $m/z$ (%) = 308 (100) [M + $H^+$].

HRMS: $m/z$ calcd for $C_{23}H_{18}N$: 308.1439; found: 308.1446.

### 5-Bromo-3-(1,3-diphenylprop-2-ynyl)-1*H*-indole (3b)

Brown liquid.

IR (KBr): 3425, 2924, 2855, 1453, 756, 695 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 5.35$ (s, 1 H), 7.05 (d, $J = 1.4$ Hz, 1 H), 7.14–7.36 (m, 9 H), 7.39–7.51 (m, 3 H), 7.70 (d, $J = 1.4$ Hz, 1 H), 7.97 (br s, 1 H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 31.6$, 82.1, 87.5, 111.1, 112.1, 117.5, 121.0, 121.6, 122.7, 123.5, 126.2, 128.4, 128.8, 129.1, 129.9, 130.4, 133.3, 134.4, 140.8.

MS (EI, 70 eV): $m/z$ (%) = 409 (40) [$M^+$ + Na].

HRMS: $m/z$ calcd for $C_{23}H_{16}BrNNa$: 408.0363; found: 408.0369.

### 3-(1,3-Diphenylprop-2-ynyl)-5-nitro-1*H*-indole (3c)

Yellow solid; mp 110–113 °C.

IR (KBr): 3410, 2923, 2853, 1622, 1517, 1466, 1331, 1098, 755, 695 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 5.44$ (s, 1 H), 7.19–7.37 (m, 8 H), 7.44–7.51 (m, 4 H), 8.10 (dd, $J = 2.4$, 9.4 Hz, 1 H), 8.31 (br s, 1 H), 8.63 (d, $J = 1.7$ Hz, 1 H).

$^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 31.8$, 81.2, 87.2, 111.0, 111.6, 115.0, 122.7, 123.6, 125.4, 126.9, 128.3, 128.4, 128.5, 128.7, 129.0, 134.3, 140.4, 142.8.

MS (EI, 70 eV): $m/z$ (%) = 375 (100) [$M^+$ + Na].

HRMS: $m/z$ calcd for $C_{23}H_{16}N_2O_2Na$: 375.1109; found: 375.1116.

### 3-(1,3-Diphenylprop-2-ynyl)-2-phenyl-1*H*-indole (3d)

Liquid.

IR (KBr): 3412, 2924, 2854, 1744, 1599, 1489, 1452, 756, 695 $cm^{-1}$.

$^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 5.60$ (s, 1 H), 7.08–7.58 (m, 19 H), 7.99 (br s, 1 H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 30.4$, 81.4, 87.8, 112.1, 112.8, 119.8, 121.4, 122.6, 123.0, 123.8, 125.9, 127.4, 127.8, 128.0, 128.5, 128.9, 129.2, 130.2, 131.1, 132.4, 134.2, 137.7, 142.8.

MS (EI, 70 eV): $m/z$ (%) = 406 (70) [$M^+$ + Na].

HRMS: $m/z$ calcd for $C_{29}H_{21}NNa$: 406.1571; found: 406.1588.

### 3-[1-(4-Tolyl)hept-2-ynyl]-1*H*-indole (3e)

Liquid.

IR (KBr): 3417, 3051, 2956, 2927, 2863, 1613, 1510, 1456, 1421, 1344, 1093, 772, 742 $cm^{-1}$.

$^1$H NMR (300 MHz, CDCl$_3$): δ = 0.91 (t, $J$ = 6.7 Hz, 3 H), 1.36–1.57 (m, 4 H), 2.24 (dt, $J$ = 2.2, 6.7 Hz, 2 H), 2.30 (s, 3 H), 5.09 (s, 1 H), 6.93–7.10 (m, 6 H), 7.18–7.28 (m, 2 H), 7.44 (d, $J$ = 8.3 Hz, 1 H), 7.81 (br s, 1 H).

$^{13}$C NMR (50 MHz, CDCl$_3$): δ = 13.4, 19.6, 22.3, 32.2, 33.2, 75.4, 79.7, 111.2, 113.1, 118.9, 120.6, 122.4, 123.5, 126.4, 128.9, 129.0, 129.8, 137.2, 141.2.

MS (EI, 70 eV): *m/z* (%) = 324 (90) [M$^+$ + Na].

HRMS: *m/z* calcd for C$_{22}$H$_{23}$NNa: 324.1728; found: 324.1736.

**3-[1-(4-Tolyl)hept-2-ynyl]-1*H*-indole-5-carbonitrile (3f)**
Dark brown liquid.

IR (KBr): 3330, 2957, 2929, 2865, 2221, 1617, 1510, 1467, 1430, 1355, 1093, 805, 769 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 0.92 (t, $J$ = 7.5 Hz, 3 H), 1.36–1.57 (m, 4 H), 2.25 (dt, $J$ = 2.2, 7.5 Hz, 2 H), 2.32 (s, 3 H), 5.08 (s, 1 H), 7.02–7.16 (m, 3 H), 7.23–7.29 (m, 2 H), 7.31–7.40 (m, 2 H), 7.87 (s, 1 H), 8.50 (br s, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 13.7, 19.5, 22.0, 25.1, 30.9, 33.9, 78.7, 83.8, 102.2, 111.0, 113.8, 116.2, 123.9, 124.6, 126.6, 128.7, 129.2, 129.9, 136.6, 140.1, 142.2.

MS (EI, 70 eV): *m/z* (%) = 349 (100) [M$^+$ + Na].

HRMS: *m/z* calcd for C$_{23}$H$_{22}$N$_2$Na: 349.1680; found: 349.1688.

**3-(1-Phenylhept-2-ynyl)-1*H*-indole (3g)**
Yellow liquid.

IR (KBr): 3416, 2925, 2856, 1454, 1339, 1091, 742, 700 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 0.88 (t, $J$ = 6.7 Hz, 3 H), 1.18–1.58 (m, 4 H), 2.24 (dt, $J$ = 1.5, 6.7 Hz, 2 H), 5.28 (s, 1 H), 6.94–7.49 (m, 10 H), 7.87 (br s, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 13.5, 18.5, 22.0, 30.9, 34.7, 79.7, 84.3, 111.0, 117.1, 117.8, 120.6, 125.2, 125.5, 126.9, 127.6, 128.5, 139.6, 141.0, 141.6.

MS (EI, 70 eV): *m/z* (%) = 310 (100) [M$^+$ + Na].

HRMS: *m/z* calcd for C$_{21}$H$_{21}$NNa: 310.1571; found: 310.1577.

**5-Nitro-3-[1-(4-tolyl)hept-2-ynyl]-1*H*-indole (3h)**
Yellow solid; mp 175–177 °C.

IR (neat): 3325, 2928, 2860, 1508, 1454, 1319, 1229, 1089, 740, 677 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 0.91 (t, $J$ = 7.5 Hz, 3 H), 1.39–1.60 (m, 4 H), 2.26 (dt, $J$ = 2.2, 7.5 Hz, 2 H), 2.33 (s, 3 H), 5.13 (s, 1 H), 7.07–7.12 (m, 2 H), 7.24–7.34 (m, 4 H), 8.06 (dd, $J$ = 2.2, 9.0 Hz, 1 H), 8.25 (br s, 1 H), 8.54 (d, $J$ = 2.2 Hz, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 13.5, 18.6, 21.0, 22.0, 30.9, 34.4, 80.6, 84.1, 111.1, 117.2, 117.8, 120.7, 125.5, 127.5, 129.3, 136.6, 138.1, 139.7, 141.6.

MS (EI, 70 eV): *m/z* (%) = 369 (100) [M$^+$ + Na].

HRMS: *m/z* calcd for C$_{22}$H$_{22}$N$_2$O$_2$Na: 369.1578; found: 369.1589.

**5-Nitro-3-(1-phenylhept-2-ynyl)-1*H*-indole (3i)**
Yellow solid; mp 169–171 °C.

IR (KBr): 3439, 3309, 2957, 2925, 2854, 2362, 1625, 1515, 1456, 1324, 1209, 1083, 730, 697 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 0.91 (t, $J$ = 7.3 Hz, 3 H), 1.34–1.62 (m, 4 H), 2.26 (dt, $J$ = 2.2, 6.6 Hz, 2 H), 5.20 (s, 1 H), 7.16–7.33 (m, 4 H), 7.38–7.48 (m, 3 H), 7.95 (dd, $J$ = 2.2, 8.8 Hz, 1 H), 8.46 (d, $J$ = 2.2 Hz, 1 H), 11.2 (br s, 1 H).

$^{13}$C NMR (CDCl$_3$, 300 MHz): δ = 13.5, 18.5, 22.0, 30.9, 34.7, 79.7, 84.3, 111.0, 117.1, 117.8, 120.6, 125.2, 125.5, 126.9, 127.6, 128.5, 139.6, 141.0, 141.6.

MS (EI, 70 eV): *m/z* (%) = 333 (100) [M + H$^+$].

HRMS: *m/z* calcd for C$_{21}$H$_{21}$N$_2$O$_2$: 333.1603; found: 333.1609.

**3-[(*E*)-3-Phenyl-1-(2-phenylethynyl)allyl]-1*H*-indole (3j)**
Brown liquid.

IR (KBr): 3421, 2923, 2853, 1596, 1489, 1455, 1416, 1337, 1218, 1095, 958, 747, 695 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 4.96 (d, $J$ = 7.2 Hz, 1 H), 5.58 (dd, $J$ = 1.4, 16.0 Hz, 1 H), 6.62 (dd, $J$ = 7.2, 16.0 Hz, 1 H), 6.75 (d, $J$ = 2.1 Hz, 1 H), 6.87–7.37 (m, 14 H), 7.81 (br s, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 34.6, 83.9, 90.6, 111.1, 112.2, 118.9, 120.1, 121.0, 122.1, 122.7, 123.6, 126.3, 127.6, 128.4, 128.9, 129.5, 130.0, 131.1, 133.2, 136.6, 141.1.

MS (EI, 70 eV): *m/z* (%) = 334 (80) [M + H$^+$].

HRMS: *m/z* calcd for C$_{25}$H$_{20}$N: 334.1595; found: 334.1601.

**3-[(*E*)-3-Phenyl-1-(2-phenylethynyl)allyl]-1*H*-indole-5-carbonitrile (3k)**
Yellow liquid.

IR (KBr): 3416, 2922, 2853, 2220, 1618, 1436, 1356, 8.5, 756, 694 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 4.97 (d, $J$ = 6.7 Hz, 1 H), 5.65 (dd, $J$ = 1.5, 15.8 Hz, 1 H), 6.37 (dd, $J$ = 6.7, 15.8 Hz, 1 H), 7.02 (d, $J$ = 1.5 Hz, 1 H), 7.16–7.49 (m, 12 H), 8.13 (s, 1 H), 8.33 (m, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 34.6, 83.9, 90.6, 102.2, 111.1, 112.2, 116.0, 122.1, 122.7, 123.0, 124.1, 126.1, 126.9, 127.8, 128.4, 128.9, 129.4, 129.7, 131.1, 133.3, 136.6, 142.2.

MS (EI, 70 eV): *m/z* (%) = 359 (100) [M + H$^+$].

HRMS: *m/z* calcd for C$_{26}$H$_{19}$N$_2$: 359.1548; found: 359.1555.

**5-Bromo-3-{1-[(*E*)-2-phenylvinyl]hept-2-ynyl}-1*H*-indole (3l)**
Liquid.

IR (KBr): 3425, 2923, 2853, 1457, 1215, 1097, 958, 794 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 0.91 (t, $J$ = 7.5 Hz, 3 H), 1.34–1.51 (m, 4 H), 2.21–2.30 (m, 2 H), 4.88 (d, $J$ = 6.8 Hz, 1 H), 5.38 (dd, $J$ = 1.5, 15.8 Hz, 1 H), 6.43 (dd, $J$ = 7.5, 15.8 Hz, 1 H), 7.09–7.37 (m, 9 H), 7.94 (br s, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 13.5, 18.5, 22.0, 30.9, 34.7, 79.7, 84.3, 111.0, 114.1, 118.6, 121.2, 121.9, 122.6, 123.5, 126.4, 128.2, 129.0, 130.8, 131.6, 136.6, 137.9.

MS (EI, 70 eV): *m/z* (%) = 314 (50) [M + H$^+$].

HRMS: *m/z* calcd for C$_{23}$H$_{24}$N: 314.1908; found: 314.1912.

**7-Ethyl-3-{1-[(*E*)-2-phenylvinyl]hept-2-ynyl}-1*H*-indole (3m)**
Liquid.

IR (KBr): 3419, 2958, 2924, 2854, 2211, 1625, 1452, 1262, 751, 698 cm$^{-1}$.

$^1$H NMR (200 MHz, CDCl$_3$): δ = 0.83–0.98 (m, 5 H), 1.36 (dt, $J$ = 1.5, 7.5 Hz, 3 H), 1.49 (m, 2 H), 2.27 (m, 2 H), 2.80 (m, 2 H), 4.70 (d, $J$ = 6.0 Hz, 1 H), 6.33 (dd, $J$ = 6.0, 15.6 Hz, 1 H), 6.72 (d, $J$ = 15.6 Hz, 1 H), 6.97 (m, 2 H), 7.10–7.39 (m, 6 H), 7.50 (d, $J$ = 7.5 Hz, 1 H), 7.86 (br s, 1 H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ = 13.5, 14.2, 18.8, 22.0, 28.1, 31.2, 34.7, 79.7, 84.3, 111.0, 117.1, 117.8, 122.2, 123.0, 123.8, 125.5, 126.4, 127.3, 128.0, 129.9, 131.6, 136.8, 140.1.

MS (EI, 70 eV): *m/z* (%) = 342 (100) [M + H$^+$].

HRMS: *m*/*z* calcd for $C_{25}H_{28}N$: 342.2221; found: 342.2230.

**3-[1-(4-Fluorophenyl)-3-phenylprop-2-ynyl]-1*H*-indole (3n)**
Brown liquid.

IR (KBr): 3416, 3056, 2923, 2853, 1601, 1503, 1453, 1222, 1156, 1093, 846, 746, 692 cm$^{-1}$.

$^{1}$H NMR (200 MHz, $CDCl_3$): δ = 5.38 (s, 1 H), 6.93–7.03 (m, 3 H), 7.08–7.16 (m, 2 H), 7.21–7.35 (m, 4 H), 7.38–7.50 (m, 5 H), 7.91 (br s, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 13.4, 19.6, 22.5, 32.2, 34.6, 79.4, 84.2, 111.0, 112.1, 115.4, 119.6, 121.1, 123.3, 124.1, 128.8, 131.5, 138.9, 141.6, 163.3.

MS (EI, 70 eV): *m*/*z* (%) = 348 (60) [M$^+$ + Na].

HRMS: *m*/*z* calcd for $C_{23}H_{16}FNNa$: 348.1164; found: 348.1173.

**2-(1-Phenylhept-2-ynyl)-1*H*-pyrrole (3o)**
Dark brown liquid.

IR (KBr): 3429, 2957, 2926, 2855, 1490, 1455, 1026, 717 cm$^{-1}$.

$^{1}$H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.1 Hz, 3 H), 1.38–1.60 (m, 4 H), 2.27 (dt, *J* = 2.4, 6.9 Hz, 2 H), 4.97 (m, 1 H), 5.87 (m, 1 H), 6.04 (dd, *J* = 2.8, 3.2 Hz, 1 H), 6.60 (m, 1 H), 7.16–7.34 (m, 5 H), 8.00 (br s, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 13.2, 18.2, 21.7, 30.6, 36.3, 78.6, 84.1, 105.6, 108.2, 116.5, 126.6, 127.2, 128.2, 131.0, 140.5.

MS (EI, 70 eV): *m*/*z* (%) = 238 (100) [M + H$^+$].

HRMS: *m*/*z* calcd for $C_{17}H_{20}N$: 238.1595; found: 238.1604.

**2-(1,3-Diphenylprop-2-ynyl)furan (3p)**
Pale brown liquid.

IR (KBr): 2923, 2853, 2361, 1596, 1492, 1177, 1071, 1009, 753, 725, 692 cm$^{-1}$.

$^{1}$H NMR (200 MHz, $CDCl_3$): δ = 5.20 (s, 1 H), 6.23 (m, 2 H), 7.20–7.35 (m, 7 H), 7.40–7.47 (m, 4 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 35.5, 85.6, 93.3, 107.5, 110.6, 123.3, 126.5, 127.4, 128.0, 128.8, 129.5, 133.5, 143.9, 146.8, 154.1.

MS (EI, 70 eV): *m*/*z* (%) = 281 (100) [M$^+$ + Na].

HRMS: *m*/*z* calcd for $C_{19}H_{14}ONa$: 281.0942; found: 281.0951.

**3-(1,3-Diphenylprop-2-ynyl)-9*H*-carbazole (3q)**
Dark brown liquid.

IR (KBr): 3420, 2947, 2926, 2855, 1480, 1455, 1026, 720 cm$^{-1}$.

$^{1}$H NMR (300 MHz, $CDCl_3$): δ = 5.35 (s, 1 H), 7.11–7.38 (m, 12 H), 7.40–7.53 (m, 3 H), 7.89–8.11 (m, 3 H).

MS (EI, 70 eV): *m*/*z* (%) = 380 (100) [M$^+$ + Na].

HRMS: *m*/*z* calcd for $C_{27}H_{19}NNa$: 380.1415; found: 380.1422.

## References

(1) (a) Sundberg, R. J. *Indoles*; Academic Press: New York, **1996**, 7. (b) Faulkner, D. J. *Nat. Prod., Rep.* **2001**, *18*, 1. (c) Ninomiya, I. *J. Nat. Prod.* **1992**, *55*, 541. (d) Gribble, G. W. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1045.

(2) (a) Sundberg, R. J. In *Comprehensive Heterocyclic Chemistry II*, Vol. 2; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V.; Bird, C. W., Eds.; Pergamon: Oxford, **1996**, 207. (b) Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2491. (c) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893. (d) Tois, J.; Franzen, R.; Koskinen, A. *Tetrahedron* **2003**, *59*, 5395.

(3) (a) Cacchi, S.; Fabrici, G. *Chem. Rev.* **2005**, *105*, 2873. (b) Bandini, M.; Melloni, A.; Tommasi, S.; Umani-Ronchi, A. *Synlett* **2005**, 1199. (c) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875.

(4) (a) Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 550. (b) Austin, J. F.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 1172. (c) Jensen, K. B.; Thorhange, J.; Hazel, R. G.; Jorgensen, K. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 160.

(5) (a) Srivastava, N.; Banik, B. K. *J. Org. Chem.* **2003**, *68*, 2109. (b) Bartoli, G.; Bartolacci, M.; Bosco, M.; Foglia, G.; Giuliani, A.; Marcantoni, E.; Sambri, L.; Torregiani, E. *J. Org. Chem.* **2003**, *68*, 4594.

(6) (a) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, 2921. (b) Ma, S.; Yu, S.; Peng, Z.; Guo, H. *J. Org. Chem.* **2006**, *71*, 9865. (c) Yadav, J. S.; Reddy, B. V. S.; Basak, A. K.; Narsaiah, A. V.; Prabhakar, A.; Jagadeesh, B. *Tetrahedron Lett.* **2005**, *46*, 639.

(7) (a) Westermaier, M.; Mayr, H. *Org. Lett.* **2006**, *8*, 4791. (b) Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Org. Lett.* **2004**, *6*, 3199. (c) De la Herrán, G.; Segura, A.; Csáky, A. G. *Org. Lett.* **2007**, *9*, 961. (d) Liu, Z.; Liu, L.; Shafiq, Z.; Wu, Y. C.; Wang, D.; Chen, Y. J. *Tetrahedron Lett.* **2007**, *48*, 3963.

(8) (a) Zhang, Z.-H. *Synlett* **2005**, 711. (b) Sakai, N.; Hirasawa, M.; Konakahara, T. *Tetrahedron Lett.* **2005**, *46*, 6407. (c) Agnusdei, M.; Bandini, M.; Melloni, A.; Umani-Ronchi, A. *J. Org. Chem.* **2003**, *68*, 7126. (d) Huang, J.-M.; Wong, C.-M.; Xu, F.-X.; Loh, T.-P. *Tetrahedron Lett.* **2007**, *48*, 3375. (e) Harada, S.; Takita, R.; Ohshima, T.; Matsunaga, S.; Shibasaki, M. *Chem. Commun.* **2007**, 948.

(9) Sang, H. K.; Shin, C.; Ae, N. P.; Hun, Y. K.; Moon, H. C.; Bong, Y. C.; Yong, S. C. *Synthesis* **2004**, 1581.

(10) (a) Yadav, J. S.; Reddy, B. V. S.; Rao, K. V.; Raj, K. S.; Prasad, A. R.; Kumar, S. K.; Kunwar, A. C.; Jayaprakash, P. J.; Jagannath, B. *Angew. Chem. Int. Ed.* **2003**, *42*, 5198. (b) Yadav, J. S.; Reddy, B. V. S.; Kumar, G. M. *Synlett* **2001**, 1781. (c) Yadav, J. S.; Reddy, B. V. S.; Baishya, G. *Synlett* **2003**, 396. (d) Yadav, J. S.; Reddy, B. V. S.; Krishna, A. D.; Swamy, T. *Tetrahedron Lett.* **2003**, *44*, 6055. (e) Yadav, J. S.; Reddy, B. V. S.; Swamy, T. *Synthesis* **2004**, 106. (f) Yadav, J. S.; Reddy, B. V. S.; Gakul, B. *Green Chem.* **2003**, *5*, 264. (g) Yadav, J. S.; Reddy, B. V. S.; Reddy, M. S.; Parimala, G. *Synthesis* **2003**, 2390.