A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles and Electrophiles for Photoinduced, Copper-Catalyzed Processes

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Supporting Information

Table of Contents

I. General Information S–1
II. Photoinduced, Copper-Catalyzed N-Arylations (Tables 1–5) S–2
III. Nucleophile Competition Experiments (Table 6) S–14
IV. Electrophile Competition Experiments (eq 2) S–14
V. Functional-Group Tolerance Experiments (Table 7) S–14
VI. Photoinduced, Copper-Catalyzed N-Alkenylations/Alkynylations (Table 8) S–15
VII. 1H NMR Spectra S–18

I. General Information

The following reagents were purchased and used as received unless otherwise specified: indole (Aldrich), 6-methoxyindole (AstaTech), 3-methylindole (Aldrich), 2-methylindole (Alfa Aesar), 7-methylindole (Aldrich), benzimidazole (Alfa Aesar), 5-methoxybenzimidazole (Aldrich), 2-methylbenzimidazole (Aldrich), imidazole (Alfa Aesar), 2-methylimidazole (Aldrich), carbazole (Aldrich; recrystallized), 3-methoxycarbazole (Matrix Scientific), iodobenzene (Aldrich), 4-iodotoluene (Aldrich), 2-iodotoluene (Aldrich), 4-iodoanisole (Aldrich), 4-iodobenzonitrile (Aldrich), 3-iodopyridine (Aldrich), bromobenzene (Avocado), 4-chlorobenzonitrile (Avocado), 1-ethyl-4-iodobenzene (Avocado), 4-bromotoluene (Aldrich), 4-chlorotoluene (Aldrich), methyl octanoate (Acros), 1-methyl-2-piperidone (Aldrich), benzylacetone (Aldrich), dicyclohexylamine (Aldrich), cyclohexylamine (Aldrich), chlorobenzene (Aldrich), trans-5-decene (Aldrich), cis-5-decene (TCI), 5-decyn (Lancaster), dibenzyl ether (Alfa Aesar), bromomethylenecyclohexane (Aldrich), CuI (Aldrich), LiOt-Bu (Alfa Aesar), and t-BuOH (Aldrich; anhydrous). CH$_3$CN was deoxygenated and dried by sparging with nitrogen followed by passage through an activated alumina column (S. G. Water) prior to use.

All coupling reactions were carried out using a Luzchem LZC–4V photoreactor at 254 nm (UVC). 1H NMR data and 13C NMR data were collected on a VARIAN 500 MHz spectrometer at ambient temperature. GC analyses were carried out on an Agilent 6890 series system with a DB-1 column (length 30 m, I.D. 0.25 mm) or an HP-5 column (length 30 m, I.D. 0.25 mm) or on an Agilent 6850 series system with a BETA DEX 120 column (length 30 m, I.D. 0.25 mm).
II. Photoinduced, Copper-Catalyzed N-Arylations (Tables 1–5)

**General Procedure.** The nitrogen heterocycle (1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), and CuI (19.0 mg, 0.10 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The test tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the test tube was evacuated and backfilled with nitrogen (three cycles). Then, CH₃CN (4.0 mL) and the aryl iodide (1.40 mmol; if the aryl iodide is a solid, then it was added immediately after the addition of CuI) were added in turn via syringe. The test tube was detached from the nitrogen manifold, and the puncture holes in the septum were covered with vacuum grease. The resulting mixture was stirred for 5 min, and then the test tube was transferred to a Luzchem LZR–4V photoreactor, where it was irradiated at 254 nm for 24 h (adequate stirring is important). Next, the mixture was passed through a long plug of silica gel (monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

Notes: (a) A Honeywell ultraviolet air treatment system (model #RUVLAMP1), available for ~$110 from retail outlets such as Amazon or The Home Depot, furnishes a comparable result: indole and iodobenzene couple in 63% yield (calibrated GC analysis) after 48 h. (b) Use of a borosilicate, rather than a quartz, test tube leads to a low yield of the C–N coupling product.

![Image](image-url)

**1-Phenyl-1H-indole (Table 1, entry 1) [16096-33-6].** The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography (hexanes). Pale-yellow oil. First run: 142 mg (73% yield). Second run: 148 mg (77% yield).

![Image](image-url)

**1-(p-Tolyl)-1H-indole (Table 1, entry 2) [167283-32-1].** The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et₂O/hexanes). Colorless oil. First run: 140 mg (68%). Second run: 143 mg (69%).
2-(4-(1H-Indol-1-yl)phenyl)propan-2-ol (Table 1, Entry 3). The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiO-t-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-(4-iodophenyl)propan-2-ol (367 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (20% EtOAc/hexanes) and purified by column chromatography on silica gel (7.5% EtOAc/hexanes→15% EtOAc/hexanes). Pale-orange solid. First run: 144 mg (57%). Second run: 143 mg (57%).

\[^1\text{H} \text{NMR}\ (500 \text{MHz, CDCl}_3) \delta 7.71−7.69 (1H), 7.67−7.62 (2H), 7.60−7.56 (1H), 7.51−7.46 (2H), 7.34 (d, 1H, J = 3.0 Hz), 7.23 (ddd, 1H, J = 8.0, 7.0, 1.0 Hz), 7.18 (ddd, 1H, J = 8.0, 7.0, 1.0 Hz), 6.69 (dd, 1H, J = 3.0, 1.0 Hz), 1.81 (br s, 1H), 1.66 (s, 6H).

\[^{13}\text{C} \text{NMR}\ (126 \text{MHz, CDCl}_3) \delta 147.5, 138.5, 136.0, 129.4, 128.1, 125.9, 124.2, 122.4, 121.2, 120.5, 110.7, 103.6, 72.6, 32.0.

\text{FT-IR}\ (\text{neat}) 3541, 3399, 3103, 3049, 2974, 2927, 2868, 1606, 1582, 1570, 1519, 1475, 1457, 1412, 1363, 1347, 1334, 1317, 1298, 1281, 1256, 1234, 1213, 1170, 1137, 1114, 1094, 1066, 1015, 955, 909, 883, 862, 840, 770, 762, 742, 720 \text{ cm}^{-1}.

\text{MS}\ (\text{ESI}) m/z (M^{+}+H) \text{calcd for C}_{17}\text{H}_{18}\text{NO: 252, found: 252}.

6-Methoxy-1-phenyl-1H-indole (Table 1, entry 4) [487058-34-4]. The title compound was synthesized according to the General Procedure from 6-methoxyindole (147 mg, 1.00 mmol), LiO-t-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→1% Et,O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH$_3$CN/water). White solid. First run: 147 mg (66%). Second run: 150 mg (67%).
6-Methoxy-1-(o-tolyl)-1H-indole (Table 1, entry 5). The title compound was synthesized according to the General Procedure from 6-methoxyindole (147 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→1% Et₂O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). Yellow oil. First run: 154 mg (65% yield). Second run: 165 mg (70% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, 1H, J = 8.5 Hz), 7.40–7.36 (m, 2H), 7.35–7.31 (m, 2H), 7.06 (d, 1H, J = 3.2 Hz), 6.82 (dd, 1H, J = 8.5, 2.2 Hz), 6.59 (d, 1H, J = 3.2 Hz), 6.50 (s, 1H), 3.76 (s, 3H), 2.09 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.8, 138.5, 137.8, 136.0, 131.4, 128.3, 128.2, 127.8, 127.0, 122.6, 121.5, 110.1, 102.5, 94.0, 55.8, 17.8.

FT-IR (neat) 3102, 3026, 2994, 2952, 2831, 1621, 1603, 1573, 1513, 1487, 1459, 1380, 1340, 1324, 1292, 1279, 1225, 1205, 1177, 1121, 1095, 1031, 927, 806, 769, 746, 720 cm⁻¹.

MS (ESI) m/z (M⁺+H) calcd for C₁₆H₁₆NO: 238, found: 238.

3-Methyl-1-phenyl-1H-indole (Table 1, entry 6) [112817-88-6]. The title compound was synthesized according to the General Procedure from 3-methylindole (131 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et₂O/hexanes). Colorless oil. First run: 152 mg (73%). Second run: 145 mg (70%).

1-(4-Methoxyphenyl)-3-methyl-1H-indole (Table 1, entry 7) [876337-56-3]. The title compound was synthesized according to the General Procedure from 3-methylindole (131 mg, 1.00
mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→2% Et₂O/hexanes). Colorless oil. First run: 138 mg (58%). Second run: 138 mg (58%).

2-Methyl-1-phenyl-1H-indole (Table 1, entry 8) [16176-77-5]. The title compound was synthesized according to the General Procedure from 2-methylindole (131 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et₂O/hexanes). Colorless oil. First run: 122 mg (59%). Second run: 124 mg (60%).

7-Methyl-1-phenyl-1H-indole (Table 1, entry 9) [473918-43-3]. The title compound was synthesized according to the General Procedure from 7-methylindole (131 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et₂O/hexanes). White solid. First run: 139 mg (67%). Second run: 133 mg (64%).

1-Phenyl-1H-benzo[d]imidazole (Table 2, entry 1) [2622-60-8]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH₃CN (3.0 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by
column chromatography on silica gel (0.75% MeOH/CH₂Cl₂, then 15% → 25% EtOAc/hexanes). Yellow oil. First run: 158 mg (81%). Second run: 165 mg (85%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

![Chemical Structure](image_url)

**4-(1H-Benzol[d]imidazol-1-yl)benzonitrile (Table 2, entry 2) [25699-95-0].** The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO-t-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodobenzonitrile (321 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH₃CN (3.0 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. The product was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by column chromatography on silica gel (1% MeOH/CH₂Cl₂, then 40% → 55% EtOAc/hexanes). Yellow solid. First run: 185 mg (84%). Second run: 180 mg (82%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

![Chemical Structure](image_url)

**1-(4-Methoxyphenyl)-1H-benzol[d]imidazole (Table 2, entry 3) [2622-61-9].** The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO-t-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-idoanisole (328 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH₃CN (3.0 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by column chromatography on silica gel (1% MeOH/CH₂Cl₂, then 30% → 50% EtOAc/hexanes). Yellow solid. First run: 177 mg (79%). Second run: 164 mg (73%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.
6-Methoxy-1-phenyl-1*H*-benzo[*d*]imidazole (Table 2, entry 4) [69445-55-2]. The title compound was synthesized according to the General Procedure from 5-methoxybenzimidazole (148 mg, 1.00 mmol), LiO*-*Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% MeOH/CH$_2$Cl$_2$) and purified by column chromatography (1%→5% MeOH/CH$_2$Cl$_2$, then 20%→35% EtOAc/hexanes). Yellow solid. First run: 182 mg (81%), 6-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole/5-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole = 1.0:1. Second run: 190 mg (85%), 6-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole/5-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole = 1.1:1.

2-Methyl-1-phenyl-1*H*-benzo[*d*]imidazole (Table 2, entry 5) [1484-39-5]. The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiO*-*Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH$_2$Cl$_2$) and purified by column chromatography on silica gel (1%→5% MeOH/CH$_2$Cl$_2$, then 20%→35% ethyl acetate/hexanes). Yellow solid. First run: 169 mg (81%). Second run: 175 mg (84%). Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

2-Methyl-1-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (Table 2, entry 6) [68874-09-9]. The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiO*-*Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica (10% MeOH/CH$_2$Cl$_2$) and purified by column chromatography (1% MeOH/CH$_2$Cl$_2$, then 20% EtOAc/hexanes). Yellow solid. First run: 170 mg (76%). Second run: 166 mg (75%).
Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

![2-Methyl-1-(pyridin-3-yl)-1H-benzo[d]imidazole](image)

2-Methyl-1-(pyridin-3-yl)-1H-benzo[d]imidazole (Table 2, entry 7). The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 3-iodopyridine (287 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica (10% MeOH/CH₂Cl₂) and purified by column chromatography on silica gel (2% MeOH/CH₂Cl₂). Yellow solid. First run: 139 mg (66%). Second run: 140 mg (67%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

¹H NMR (500 MHz, CDCl₃) δ 8.78 (d, 1H, J = 3.2 Hz), 8.70 (s, 1H), 7.45 (apparent t, 2H, J = 3.2 Hz), 7.55 (dd, 1H, J = 7.9, 5.1 Hz), 7.28 (t, 1H, J = 7.8 Hz), 7.21 (t, 1H, J = 7.8 Hz), 7.10 (d, 1H, J = 8.0 Hz), 2.52 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 151.4, 150.1, 148.3, 142.8, 136.3, 134.6, 133.0, 124.5, 123.2, 123.0, 119.4, 109.6, 14.6.

FT-IR (neat) 3391, 3053, 2927, 2851, 1615, 1587, 1575, 1524, 1486, 1456, 1427, 1393, 1372, 1314, 1287, 1249, 1187, 1149, 1105, 1050, 1029, 1015, 999, 929, 878, 810, 765, 745, 712 cm⁻¹.

MS (ESI) m/z (M⁺+H) calcd for C₁₃H₁₂N₃: 210, found: 210.

![1-Phenyl-1H-imidazole](image)

1-Phenyl-1H-imidazole (Table 3, entry 1) [7164-98-9]. The title compound was synthesized according to the General Procedure from imidazole (102 mg, 1.50 mmol), LiOt-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and iodosobenzene (428 mg, 2.10 mmol), except that a mixture of t-BuOH (1.5 mL) and CH₃CN (4.5 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. The reaction mixture was filtered through a plug of silica gel (1% MeOH/CH₂Cl₂) and purified by column chromatography (1% MeOH/CH₂Cl₂, then 40% → 50% EtOAc/hexanes). Pale-yellow oil. First run: 150 mg (69%). Second run: 148 mg (68%).
1-(o-Tolyl)-1H-imidazole (Table 3, entry 2) [25371-93-1]. The title compound was synthesized according to the General Procedure from imidazole (102 mg, 1.50 mmol), LiOt-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and 2-iodotoluene (458 mg, 2.10 mmol), except that a mixture of t-BuOH (1.5 mL) and CH$_3$CN (4.5 mL) was used as the solvent (t-BuOH and CH$_3$CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH$_3$CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH$_2$Cl$_2$) and purified by column chromatography (1%→3% MeOH/CH$_2$Cl$_2$, then 30%→50% EtOAc/hexanes). Yellow oil. First run: 154 mg (65%). Second run: 161 mg (68%).

2-Methyl-1-phenyl-1H-imidazole (Table 3, entry 3) [60053-07-8]. The title compound was synthesized according to the General Procedure from 2-methylimidazole (123 mg, 1.50 mmol), LiOt-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and iodobenzene (428 mg, 2.10 mmol). The reaction mixture was filtered through a plug of silica gel (10% MeOH/CH$_2$Cl$_2$) and purified by column chromatography (2% MeOH/CH$_2$Cl$_2$, then 40%→50% EtOAc/hexanes). Yellow oil. First run: 106 mg (45%). Second run: 109 mg (46%).

9-Phenyl-9H-carbazole (Table 4, entry 1) [1150-62-5]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et$_2$O/hexanes). White solid. First run: 212 mg (87%). Second run: 206 mg (85%).
4-(9H-Carbazol-9-yl)benzonitrile (Table 4, entry 2) [57103-17-0]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodobenzonitrile (321 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→2% Et2O/hexanes). Yellow solid. First run: 203 mg (76%). Second run: 209 mg (78%).

9-(4-Methoxyphenyl)-9H-carbazole (Table 4, entry 3) [19264-74-5]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et2O/hexanes). White solid. First run: 215 mg (79%). Second run: 196 mg (72%).

9-(o-Tolyl)-9H-carbazole (Table 4, entry 4) [19155-50-1]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et2O/hexanes). White solid. First run: 213 mg (83%). Second run: 204 mg (79%).
9-(Pyridin-3-yl)-9H-carbazole (Table 4, entry 5) [168127-56-8]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 3-iodopyridine (287 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (50% EtOAc/hexanes) and purified by column chromatography on silica gel (10% EtOAc/hexanes). White solid. First run: 154 mg (63%). Second run: 166 mg (68%).

3-Methoxy-9-(o-tolyl)-9H-carbazole (Table 4, entry 6). The title compound was synthesized according to the General Procedure from 3-methoxycarbazole (100 mg, 0.51 mmol), LiOt-Bu (56.8 mg, 0.71 mmol), CuI (9.7 mg, 0.051 mmol), and 2-iodotoluene (155 mg, 0.71 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography on silica gel (hexanes→1% EtOAc/hexanes). Colorless oil. First run: 110 mg (76%). Second run: 110 mg (76%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.12 (d, 1H, $J = 7.5$ Hz), 7.65 (d, 1H, $J = 2.0$ Hz), 7.50–7.33 (m, 5H), 7.27–7.23 (m, 1H), 7.06–7.01 (m, 2H), 6.96 (d, 1H, $J = 9.0$ Hz), 3.96 (s, 3H), 1.97 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 154.2, 141.8, 137.5, 136.4, 136.3, 131.6, 129.4, 128.4, 127.4, 126.0, 123.5, 123.0, 120.4, 119.2, 115.1, 110.7, 110.0, 103.4, 56.3, 17.7.

FT-IR (neat) 3050, 2993, 2932, 2830, 1627, 1600, 1580, 1498, 1485, 1462, 1438, 1381, 1329, 1329, 1285, 1254, 1236, 1206, 1179, 1167, 1149, 1119, 1098, 1035, 943, 912, 860, 847, 806, 764, 746, 720 cm$^{-1}$.

MS (ESI) $m/z$ (M$^+$) calcd for C$_{20}$H$_{17}$NO: 287, found: 287.

1-Fluoro-9-(o-tolyl)-9H-carbazole (Table 4, entry 7). The title compound was synthesized according to the General Procedure from 1-fluorocarbazole (100 mg, 0.54 mmol), LiOt-Bu (60.5 mg, 0.76 mmol), CuI (10.3 mg, 0.054 mmol), and 2-iodotoluene (165 mg, 0.76 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column
chromatography on silica gel (hexanes→1% Et₂O/hexanes). Pale-yellow oil. First run: 111 mg (75%). Second run: 110 mg (74%).

¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, 1H, J = 8.0 Hz), 7.93 (d, 1H, J = 7.5 Hz), 7.47–7.34 (m, 5H), 7.30 (t, 1H, J = 7.5 Hz), 7.18 (td, 1H, J = 8.0, 4.0 Hz), 7.10 (dd, 1H, J = 12.0, 7.5 Hz), 7.01 (d, 1H, J = 8.5 Hz), 2.01 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.6 (d, JₙC = 245.8 Hz), 141.9, 137.4, 137.3, 131.1, 129.0, 128.9, 128.7 (d, JₙC = 8.7 Hz), 127.0 (d, JₙC = 4.8 Hz), 126.9, 126.7, 123.0 (d, JₙC = 2.9 Hz), 120.5, 120.2, 119.8 (d, JₙC = 6.8 Hz), 116.2 (d, JₙC = 3.9 Hz), 112.1 (d, JₙC = 17.3 Hz), 110.3, 17.5.

FT-IR (neat) 3058, 2955, 2924, 1635, 1602, 1577, 1498, 1455, 1435, 1381, 1354, 1339, 1316, 1290, 1248, 1184, 1154, 1116, 1081, 1053, 1014, 951, 884, 787, 745, 733, 722 cm⁻¹.

MS (EI) m/z (M⁺) calcd for C₁₉H₁₄FN: 275, found: 275.

1-Phenyl-1H-indole (Table 5, entry 1) [16096-33-6]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and bromobenzene (220 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% EtOAc/hexanes) and purified by column chromatography (hexanes). Pale-yellow oil. First run: 115 mg (60% yield). Second run: 122 mg (63% yield).

1-Phenyl-1H-benzo[d]imidazole (Table 5, entry 2) [2622-60-8]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and bromobenzene (220 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH₃CN (3.0 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. Reaction time: 48 h. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by normal-phase column chromatography on silica gel (0.75% MeOH/CH₂Cl₂) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). Yellow oil. First run: 118 mg (61%). Second run: 125 mg (64%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.
4-(9H-Carbazol-9-yl)benzonitrile (Table 5, entry 3) [57103-17-0]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-chlorobenzonitrile (193 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (20% EtOAc/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→2% Et₂O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH₃CN/water). Yellow solid. First run: 192 mg (72%). Second run: 194 mg (72%).

4-(1H-Benz[d]imidazol-1-yl)benzonitrile (Table 5, entry 4) [25699-95-0]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiOt-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-chlorobenzonitrile (193 mg, 1.40 mmol), except that a mixture of t-BuOH (1.0 mL) and CH₃CN (3.0 mL) was used as the solvent (t-BuOH and CH₃CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH₃CN. Reaction time: 48 h. The product was filtered through a plug of silica gel (5% MeOH/CH₂Cl₂) and purified by column chromatography on silica gel (1% MeOH/CH₂Cl₂, then 40%→55% EtOAc/hexanes). Yellow solid. First run: 131 mg (60%). Second run: 135 mg (62%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.
III. Nucleophile Competition Experiments (Table 6)

Procedure. Both of the nitrogen heterocycles (0.40 mmol each) and LiOt-Bu (32.0 mg, 0.40 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz tube was transferred to a glovebox, where t-BuOH (0.40 mL) and CH$_3$CN (0.40 mL) were added. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH$_3$CN (0.80 mL, 0.050 M) was added, followed by iodobenzene (114 mg, 0.56 mmol) and dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The quartz test tube was capped with a rubber septum and transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm (adequate stirring is important). The ratio of products was determined by GC analysis after 2 h.

Note: Reactions with benzimidazole were quickly transferred to the photoreactor before they became heterogeneous.

IV. Electrophile Competition Experiments (eq 2)

Procedure. Indole (46.9 mg, 0.40 mmol) and LiOt-Bu (44.8 mg, 0.56 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz tube was transferred to a glovebox, where CH$_3$CN (0.80 mL), 1-ethyl-4-iodobenzene (130 mg, 0.56 mmol), and the aryl bromide or chloride (0.56 mmol) were added in turn. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH$_3$CN (0.80 mL, 0.050 M) was added, followed by dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The quartz test tube was capped with a rubber septum and transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm (adequate stirring is important). The ratio of products was determined by GC analysis after 1 h.

V. Functional-Group Tolerance Experiments (Table 7)

Procedure. Indole (46.9 mg, 0.40 mmol) and LiOt-Bu (44.8 mg, 0.56 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz test tube was transferred to a glovebox, where CH$_3$CN (0.80 mL) and the additive (0.40 mmol) were added in turn. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH$_3$CN (0.80 mL, 0.050 M) was added, followed by iodobenzene (114 mg, 0.56 mmol) and dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The reaction mixture was stirred for 3 min, and then an aliquot was taken for a t = 0 time point. Next, the quartz test tube was capped with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm for 24 h (adequate stirring is important). The yield of product and the percent recovery of the additive were determined by GC analysis.
VI. Photoinduced, Copper-Catalyzed N-Alkenylations/Alkynylation (Table 8)

**General Procedure.** The nitrogen heterocycle (0.50 mmol) and LiOt-Bu (83.0 mg, 1.04 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The quartz tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was evacuated and backfilled with nitrogen (3 cycles). Then, CH₃CN (4.0 mL) was added, and the mixture was stirred for 10 min. Next, a solution of CuI in CH₃CN (500 µL, 0.10 M) was added via syringe, and the mixture was stirred for 10 min. A 4-mL oven-dried vial was charged with the alkenyl iodide (0.85 mmol), closed with a septum cap, and evacuated and backfilled with nitrogen (3 cycles). The alkenyl iodide was transferred to the quartz tube via syringe. The vial was rinsed with CH₃CN (0.50 mL), and the washing was transferred to the quartz tube. The test tube was detached from the nitrogen manifold, and the puncture holes in the septum were covered with vacuum grease. The mixture was stirred for 10 min, and then the test tube was transferred to a Luzchem LZC-4V photoreactor, where it was irradiated at 254 nm for 12 h (adequate stirring is important). Next, the reaction mixture was passed through a plug of silica gel (10% EtOAc/hexanes; monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

Note: For the N-alkynylation process (Table 8, entry 5), the same procedure was employed, except that the reaction mixture was irradiated for 24 h.

![9-((4-(tert-Butyl)cyclohexylidene)methyl)-9H-carbazole](image)

**9-((4-(tert-Butyl)cyclohexylidene)methyl)-9H-carbazole (Table 8, entry 1).** The title compound was synthesized according to the General Procedure from carbazole (84 mg, 0.50 mmol) and 1-(iodomethylidene)-4-tert-butyl-cyclohexane (237 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 138 mg (87%). Second run: 131 mg (83%).

$^1$H NMR (500 MHz, CDCl₃) δ 8.11 (d, 2H, $J = 7.7$ Hz), 7.46 (t, 2H, $J = 7.7$ Hz), 7.40–7.21 (m, 4H), 6.45 (s, 1H), 2.75–2.62 (m, 1H), 2.36–2.25 (m, 2H), 2.11–2.03 (m, 1H), 1.89–1.70 (m, 2H), 1.35–1.20 (m, 2H), 1.08–0.96 (m, 1H), 0.89 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl₃) δ 144.6, 140.9, 125.6, 122.9, 120.1, 119.3, 114.1, 110.0, 48.1, 33.2, 32.5, 29.2, 28.9, 28.1, 27.6.

FT-IR (neat) 3054, 2986, 2305, 1479, 1457, 1422, 1265, 896 cm⁻¹.

MS (EI) m/z (M⁺) calcd for C₂₃H₂₇N: 317, found: 317.
9-(4-(tert-Butyl)cyclohex-1-en-1-yl)-9H-carbazole (Table 8, entry 2). The title compound was synthesized according to the General Procedure from carbazole (84 mg, 0.50 mmol) and 4-tert-butyl-1-iodo-1-cyclohexene (225 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 114 mg (75%). Second run: 114 mg (75%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.11 (d, 2H, $J = 7.7$ Hz), 7.46–7.36 (m, 4H), 7.28–7.19 (m, 2H), 6.10–6.06 (m, 1H), 2.50–2.36 (m, 3H), 2.24–2.12 (m, 1H), 2.10–2.00 (m, 1H), 1.65–1.50 (m, 2H), 1.00 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.4, 134.3, 128.3, 125.6, 122.9, 120.2, 119.1, 109.8, 44.0, 32.4, 28.5, 27.3, 26.6, 24.4.

FT-IR (neat) 3054, 2987, 2305, 1452, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{22}$H$_{25}$N: 303, found: 303.

1-((4-(tert-Butyl)cyclohexylidene)methyl)-1H-indole (Table 8, entry 3). The title compound was synthesized according to the General Procedure from indole (59 mg, 0.50 mmol) and 1-(iodomethylidene)-4-tert-butyl-cyclohexane (237 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 100 mg (75%). Second run: 99 mg (74%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.65 (d, 1H, $J = 7.8$ Hz), 7.32 (d, 1H, $J = 8.3$ Hz), 7.27–7.21 (m, 1H), 7.18–7.12 (m, 1H), 7.11–7.08 (m, 1H), 6.58–6.53 (m, 2H), 2.66–2.48 (m, 2H), 2.26–2.15 (m, 1H), 2.05–1.97 (m, 1H), 1.91–1.79 (m, 2H), 1.31–1.15 (m, 2H), 1.10–0.97 (m, 1H), 0.89 (s, 9H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.7, 136.6, 128.5, 128.1, 121.7, 120.7, 119.7, 116.4, 110.3, 101.8, 48.1, 33.4, 32.5, 29.0, 28.4, 28.2, 27.6.

FT-IR (neat) 3054, 2986, 2305, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{19}$H$_{23}$N: 267, found: 267.
1-(Cyclohexylidenemethyl)-1H-indole (Table 8, entry 4). The title compound was synthesized according to the General Procedure from indole (59 mg, 0.50 mmol) and bromomethylenecyclohexane (155 mg, 0.85 mmol). Reaction time: 48 h. The product was purified by column chromatography (hexanes). Colorless oil. First run: 58 mg (55%). Second run: 60 mg (57%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (d, 1H, $J = 7.8$ Hz), 7.34 (d, 1H, $J = 8.2$ Hz), 7.29–7.23 (m, 1H), 7.20–7.15 (m, 1H), 7.13–7.09 (m, 1H), 6.61–6.57 (m, 2H), 2.38–2.32 (m, 2H), 2.24–2.18 (m, 2H), 1.78–1.70 (m, 2H), 1.70–1.63 (m, 2H), 1.60–1.52 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.1, 136.6, 128.5, 128.1, 121.7, 120.7, 119.7, 116.8, 110.3, 101.8, 33.4, 28.5, 28.3, 27.4, 26.5.

FT-IR (neat) 2934, 2956, 2253, 1674, 1511, 1475, 1462, 1377, 1319, 1234, 1088, 907 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{15}$H$_{17}$N: 211, found: 211.

9-((Triisopropylsilyl)ethynyl)-9H-carbazole (Table 8, entry 5). The title compound was synthesized according to the General Procedure from carbazole (84 mg, 0.50 mmol) and 2-bromo-1-triisopropylsilyl acetylene (222 mg, 0.85 mmol). The product was purified by column chromatography (hexanes). White solid. First run: 109 mg (63%). Second run: 107 mg (62%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.02 (d, 2H, $J = 7.7$ Hz), 7.64 (d, 2H, $J = 8.1$ Hz), 7.53 (t, 2H, $J = 7.7$ Hz), 7.34 (t, 2H, $J = 7.7$ Hz), 1.31–1.14 (m, 21H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.5, 126.7, 123.3, 122.0, 120.3, 111.4, 92.6, 72.8, 18.8, 11.4.

FT-IR (neat) 3054, 2986, 2305, 2178, 1422, 1265, 896 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{23}$H$_{29}$NSi: 347, found: 347.
VII. 1H NMR Spectra

(Table 1, entry 1)