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Indole synthesis: palladium-catalyzed C–H bond amination via reduction of nitroalkenes with carbon monoxide

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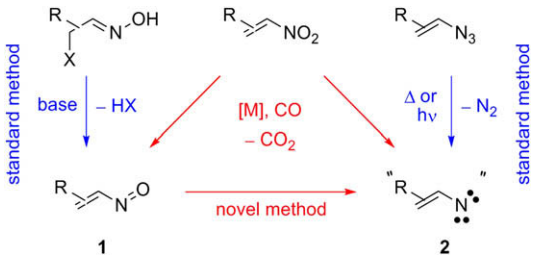
ABSTRACT

Nitroalkenes have been called 'chemical chameleons' due to their versatility in numerous synthetic transformations. Herein, we describe the first transition metal-catalyzed transformation of conjugated nitroalkenes into indoles. Under mild reaction conditions (1 atm carbon monoxide, 110 °C), palladium catalyzes the reductive cyclization of nitroalkenes to form a putative nitrosoalkene intermediate, which then rearranges to provide 3-arylindoles in high yields. Notably, this novel C–H bond amination takes advantage of carbon monoxide as an inexpensive stoichiometric reductant and produces carbon dioxide as the major byproduct.

1. Introduction

Nitrogen-containing heterocycles are among the most common structural architectures found in small-molecule therapeutics, drug candidates, and natural products.[1] Consequently, there is a strong driving force to design new and efficient strategies for making carbon–nitrogen (C–N) bonds.[1b,c] The direct amination of carbon–hydrogen (C–H) bonds has emerged as an attractive strategy for C–N bond formation.[2] In contrast to conventional methods, this strategy does not require two functionalized partners; instead, a relatively inert C–H bond is directly converted into a C–N bond. Du Bois and co-workers have pioneered elegant studies in this field by demonstrating various rhodium(II)-catalyzed C–H bond aminations using hypervalent iodine species (e.g., $PhI(OAc)_2$ and PhI=O) as stoichiometric oxidants.[2–4] Herein, we present a novel transition metal-catalyzed indole synthesis that features C–H bond amination using carbon monoxide (CO) as the terminal reductant.

The nitrosoalkene[5] (**1**) and vinylnitrene[6,7] (**2**) represent two important intermediates that have been relatively elusive and underutilized for C–N bond formation. Conventional methods for generating **1** and **2** have been limited to the use of α-halooxime[5] and vinylazide[6] precursors, respectively. It occurred to us that the reduction of nitroalkenes[8] with CO[9] would be an attractive alternative for accessing both **1** and/or **2** (Scheme 1). In contrast to the known methods, this metal-catalyzed approach would take advantage of nitroalkenes as readily available reagents for making nitrogen heterocycles, while exploiting CO as an inexpensive stoichiometric reductant. Transition metal-catalyzed reduction with CO is a well-established industrial process for making aromatic isocyanates, ureas, carbamates, and various *N*-heterocycles.[10] Remarkably, despite extensive work over the last 20 years, this methodology has been strictly limited to *nitroarene* substrates.[10–12]



Scheme 1. Metal-catalyzed reductive cyclization as a strategy for nitrosoalkene and vinylnitrene production.

In light of this challenge, we envisioned a novel C–H bond amination protocol for making indoles[12–15] starting from *nitroalkenes*[8] and CO (Scheme 2). In this metal-catalyzed process, reductive cyclization of nitroalkene **3** would form a five-membered metallacycle (**4**). Decarboxylation of metallacycle **4** would generate an η^2-bound nitrosoalkene complex (**5**),[16] which could then undergo intramolecular $4\pi+2\omega$, five-atom electrocyclization[17] to form nitronate **6**. Subsequent hydrogen shift and re-aromatization would generate *N*-hydroxyindole **7**, which is then reduced to the

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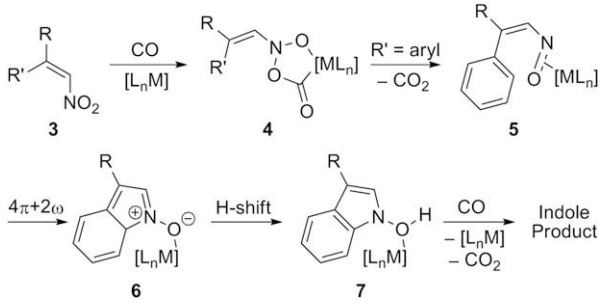
desired indole product by a second equivalent of CO.[18] Alternatively, intermediate **5** could be reduced to a vinyl metal-imido complex that undergoes C–H bond insertion to furnish the same product.[19] Notably, Russel and co-workers have reported the reductive cyclization of nitroalkenes to form indoles by using phosphites as a stoichiometric reductant.[13] Our strategy would be complimentary and advantageous to the Cadogen–Sundberg phosphite method[12a,b] because we use CO as a reductant (rather than neat phosphites) and CO_2 is a nontoxic and easily removed byproduct (in comparison to phosphite oxides). This overall transformation would be mechanistically distinct to Driver's recently reported rhodium-catalyzed indole synthesis from vinylazides.[20]

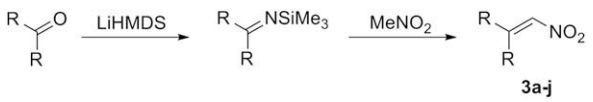


Scheme 2. Reductive cyclization of conjugated nitroalkenes to form 3-arylindoles.

2. Results and discussion

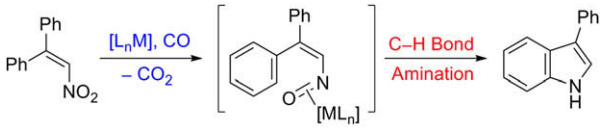
We are pleased to report that a wide range of metal salts, including those of rhodium, platinum, iron, and palladium, catalyze the desired transformation of conjugated nitroalkene **3a** to indole **8a** efficiently (Table 1). Triiron dodecacarbonyl ($Fe_3(CO)_{12}$) is an attractive catalyst (entry 5) due to its low cost, although higher temperatures and pressure were required to achieve good efficiency using Fe in comparison to Pd or Pt (see entries 4 and 7–9). Transformations with Pd display a marked ligand effect: in the absence of ligands, the desired indole product was not observed with palladium(II) diacetate ($Pd(OAc)_2$) (entry 6). Both phosphorus- and nitrogen-based ligands were examined and bidentate ligands were found to be optimal for $Pd(OAc)_2$ (entries 7 and 8). Upon further optimization,[21] the desired reductive cyclization could be achieved under mild reaction conditions with excellent efficiency: 2 mol % $Pd(OAc)_2$, 4 mol % 1,10-phenanthroline (phen), DMF,[22] 110 °C, and 1 atm of CO (99% yield, entry 9).

Given the importance of 3-arylindoles in medicinal chemistry, we prepared a number of diaryl-substituted nitroalkenes to begin exploring the scope of this method. Diaryl nitroalkenes **3a–j** were generated from their corresponding benzophenone derivatives via a straightforward two-step sequence developed in our lab and is shown in Scheme 3. Nitroalkenes containing both *para*- and *meta*-substituted phenyl groups were easily prepared. However, the analogous nitroalkenes containing *ortho*-substituted phenyl groups could not be accessed using this protocol presumably due to the increased steric hindrance, which impedes imine formation.[23]



Scheme 3. Preparation of conjugated nitroalkenes **3a–j**; LiHMDS=lithium hexamethyldisilazane.

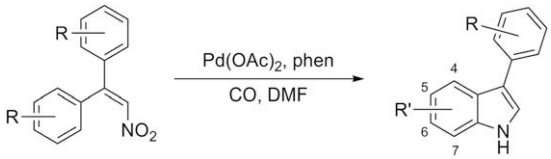
Table 1
Scope of transition-metal catalysts for nitroalkene reductive cyclization



Entry	Metal salt (mol %)	Ligand (mol %)	Yield[d] of **8a** (%)
1[a]	$NiCl_2$ (20)	phen[e] (40)	<10
2[b]	$Ru_3(CO)_{12}$ (10)	None	<10
3[b]	$Rh_6(CO)_{16}$ (10)	phen (20)	67
4[c]	$PtCl_2(PPh_3)_2$ (2)	phen (4)	69
5[a]	$Fe_3(CO)_{12}$ (10)	None	87
6[b]	$Pd(OAc)_2$ (10)	None	<1
7[b]	$Pd(OAc)_2$ (10)	dppp[f] (20)	76
8[b]	$Pd(OAc)_2$ (10)	phen (20)	78
9[c]	$Pd(OAc)_2$ (2)	phen (4)	99

[a] Conditions: CO (7 atm), DMF, 140 °C, 16 h.
[b] CO (1 atm), DMF, 100 °C, 16 h.
[c] CO (1 atm), DMF, 110 °C, 3 h.
[d] As determined by GC analysis with indole as the internal standard.
[e] phen=1,10-phenanthroline.
[f] dppp=1,3-bis(diphenylphosphino)propane.

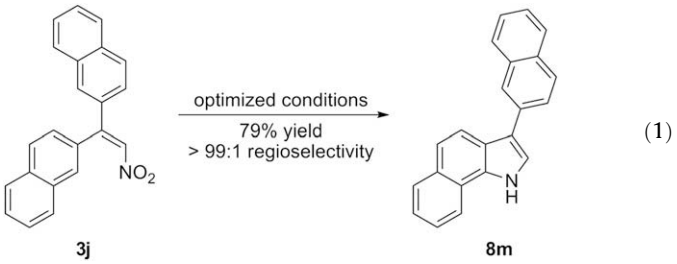
Table 2
Scope of palladium-catalyzed C–H bond amination[a]



Entry	R, nitroalkene	*T* (h)	R′, product	Yield[b] (%)
1	H (**3a**)	3	H (**8a**)	97
2	*p*-Me (**3b**)	3	6-Me (**8b**)	87
3	*p*-^{t}Bu (**3c**)	3	6-^{t}Bu (**8c**)	92
4	*p*-MeO (**3d**)	3	6-MeO (**8d**)	93
5	*m*-MeO (**3e**)	3	5-MeO (**8e**), 7-MeO (**8f**)	91[c]
6	*m*-Cl (**3f**)	6	5-Cl (**8g**), 7-Cl (**8h**)	91[d]
7	*p*-Cl (**3g**)	6	6-Cl (**8i**)	98
8	*m*-CF_3 (**3h**)	8	5-CF_3 (**8j**), 7-CF_3 (**8k**)	86[e]
9	*p*-CF_3 (**3i**)	16	6-CF_3 (**8l**)	58[f]

[a] Optimized conditions: $Pd(OAc)_2$ (2 mol %), phen (4 mol %), CO (1 atm), DMF, 110 °C.
[b] Isolated yield.
[c] Regioselectivity (based on ^{1}H NMR spectroscopy) of **8e** to **8f** is 53:47.
[d] Regioselectivity of **8g** to **8h** is 42:58.
[e] Regioselectivity of **8j** to **8k** is 51:49.
[f] Moderate yield of **8l** is attributed to significant amount of the benzophenone byproduct formation due to competing hydrolysis at long reaction times.

Reductive cyclization of diaryl nitroalkenes bearing various substituents affords 3-arylindoles in good to excellent yields (Table 2). The amination of more electron-rich aromatic rings occurred faster than that of electron-poor aromatic rings: substrates bearing H-, Me-, ^{t}Bu-, and MeO-substituent underwent reductive cyclization in high yield (87–97%) within 3 h (entries 1–5), while nitroalkenes bearing electron-withdrawing groups such as Cl and CF_3 required longer reaction times (6–16 h, entries 6–9). Nitroalkenes containing *meta*-substituted phenyl groups gave both regioisomers of the indole products (i.e., the 5- and 7-substituted indoles were formed). However, reductive cyclization of a 2-naphthyl substrate (**3j**) produced benzo[*g*]indole (**8m**) as the exclusive product (Eq. 1); the regiochemistry shown was confirmed by single crystal X-ray analysis (Fig. 1).[24]



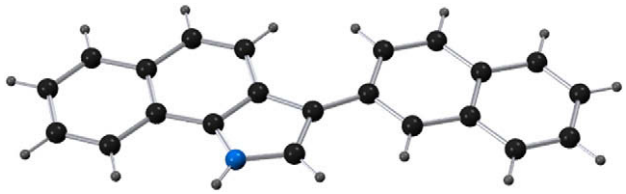


Figure 1. POV-ray drawing of **8m**. C, black; N, blue; H, gray.

3. Conclusions

In summary, we have developed a new synthesis of indoles via the reductive cyclization of conjugated nitroalkenes. While further development is warranted, this metal-catalyzed C–N bond forming strategy is attractive because a functionalized coupling partner (e.g., aryl halide or triflate)[1b,c] is not required. Using mild reaction conditions, the amination of both electron-rich and electron-deficient aromatic sp^2 C–H bonds is possible. Expanded scope and mechanistic studies are underway.

4. Experimental section

4.1. General

Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, or Oakwood Products, Inc. and were purified prior to use following the guidelines of Perrin and Armarego.[25] Nitrogen, argon, and carbon monoxide were purchased from BOC Gases and used as-received. All reactions were carried out under nitrogen or argon atmosphere unless otherwise indicated. Reactions were monitored using thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates. Visualization of the developed chromatogram was performed under UV light or $KMnO_4$ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on any of the three instruments: a Varian Mercury 300, a Varian Mercury 400, or a Varian NMR 400. NMR spectra were internally referenced to residual protio solvent signals. Data for ^1H NMR data are reported as follows: chemical shift (δ shift), multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets, dt=doublet of triplets, dq=doublet of quartets, ddd=doublet of doublet of doublets), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm). Mass spectra (MS) were recorded on a Sciex QStar Mass Spectrometer. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21/FTIR-8400S system and are reported in terms of frequency of absorption (cm^{-1}). Melting point ranges were determined on a Fisher–Johns Melting Point Apparatus. Column chromatography was performed using Silicycle Silia-P Flash Silica Gel using either glass columns or a Biotage SP1® System. Solvents were purchased from Caledon Laboratories Ltd and were purified according to standard procedures.[25] Reductive cyclization reactions were all performed in a Biotage Endeavor® Catalyst Screening System.

4.2. Typical experimental procedure for the preparation of 3

According to the modified procedures of Gosselin et al.[26] and Charles,[27] to a cold (0 °C) solution of the substituted benzophenone in THF was added a 1.0 M solution of lithium hexamethyldisilazane (LiHMDS) in THF. After 4–24 h at ambient temperature, the reaction mixture was concentrated in vacuo. To the crude material was added nitromethane ($MeNO_2$) and the resulting mixture was sonicated for 5–15 min. The precipitate was filtered off and the filtrate was heated at reflux until the trimethylsilylimine was consumed (1–3 days) as determined by TLC analysis (10% ethyl acetate in hexanes). The yellow reaction solution was concentrated in vacuo and the resulting residue was purified by silica gel chromatography with a solvent gradient of 1–20% ethyl acetate (EtOAc) in hexanes to afford the title compounds.

*4.2.1. 2,2-Diphenyl-1-nitroethylene (**3a**)*

A solution of benzophenone imine (4.00 mL, 23.9 mmol) in $MeNO_2$ was heated to reflux. After 3 days, the resulting mixture was concentrated in vacuo. The resulting residue was purified by silica gel column chromatography to afford **7e** as a yellow solid (5.23 g, 23.2 mmol) in 97% yield: mp 86–87 °C; IR (neat) 3109, 3061, 1618, 1593, 1573, 1506, 1485, 1440, 1390, 1346, 1330, 1240, 1186, 1155, 1072, 1030, 993, 921, 858, 842, 767, 744, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51–7.35 (m, 7H), 7.34–7.21 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 137.0, 135.5, 134.3, 130.8, 129.2, 128.8, 128.8, 128.7, 128.4; LRMS (EI) *m*/*z* 225 (M); HRMS (EI) exact mass calcd for ($C_{14}H_{11}NO_2$) requires *m*/*z* 225.0790, found *m*/*z* 225.0788.

*4.2.2. 2,2-Di(4-methylphenyl)-1-nitroethylene (**3b**)*

Prepared according to the general procedure for **3** from 4,4′-dimethylbenzophenone (2.52 g, 12.0 mmol), LiHMDS (24.0 mL, 24.0 mmol), and $MeNO_2$ (50 mL) to provide the title compound as a yellow solid (0.20 g, 0.8 mmol) in 7% yield: mp 110–111 °C; IR (neat) 3107, 2918, 2854, 1599, 1564, 1512, 1496, 1406, 1328, 1246, 1213, 1190, 1112, 1035, 1020, 995, 910, 852, 815, 790, 731, 711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.23 (d, *J*=7.8 Hz, 2H), 7.18 (s, 4H), 7.11 (d, *J*=8.1 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.4, 139.4, 134.5, 133.5, 132.7, 129.5, 129.1, 129.0, 128.9, 21.4, 21.3; LRMS (EI) *m*/*z* 253 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}NO_2$) requires *m*/*z* 253.1103, found *m*/*z* 253.1104.

*4.2.3. 2,2-Di(4-tert-butylphenyl)-1-nitroethylene (**3c**)*

Prepared according to the general procedure for **3** from 4,4′-bis(*tert*-butyl)benzophenone (1.02 g, 3.5 mmol), LiHMDS (7.0 mL, 7.0 mmol), and $MeNO_2$ (40 mL) to provide the title compound as a yellow solid (0.93 g, 2.7 mmol) in 80% yield: mp 124–126 °C; IR (neat) 2958, 2902, 2864, 1595, 1506, 1471, 1463, 1406, 1338, 1265, 1201, 1111, 1024, 993, 916, 833, 810 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J*=7.9 Hz, 3H), 7.40 (d, *J*=8.6 Hz, 2H), 7.23 (d, *J*=8.6 Hz, 2H), 7.16 (d, *J*=8.4 Hz, 2H), 1.36 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 152.4, 150.8, 134.4, 133.6, 132.5, 128.8, 128.7, 125.8, 125.3, 34.9, 34.8, 31.3, 31.1; LRMS (EI) *m*/*z* 337 (M); HRMS (EI) exact mass calcd for ($C_{22}H_{27}NO_2$) requires *m*/*z* 337.2042, found *m*/*z* 337.2041.

*4.2.4. 2,2-Di(4-methoxyphenyl)-1-nitroethylene (**3d**)*

Prepared according to the general procedure for **3** from 4,4′-dimethoxybenzophenone (2.92 g, 12.0 mmol), LiHMDS (24.0 mL, 24.0 mmol), and $MeNO_2$ (50 mL) to provide the title compound as a yellow solid (1.75 g, 5.0 mmol) in 51% yield: mp 113–114 °C; IR (neat) 3099, 2964, 2931, 2902, 2837, 1618, 1595, 1575, 1506, 1458, 1448, 1440, 1415, 1332, 1311, 1286, 1244, 1172, 1157, 1120, 1107, 1022, 993, 908, 856, 825, 806, 792 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.23 (d, *J*=9.0 Hz, 2H), 7.16 (d, *J*=8.9 Hz, 2H), 6.94 (d,

J=8.9 Hz, 2H), 6.89 (d, J=9.0 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 160.6, 150.7, 132.3, 132.2, 130.9, 129.8, 127.7, 114.2, 113.9, 55.5, 55.3; LRMS (EI) m/z 285 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}NO_4$) requires m/z 285.1001, found m/z 285.1003.

4.2.5. 2,2-Di(3-methoxyphenyl)-1-nitroethylene (**3e**)

Prepared according to the general procedure for **3** from 3,3′-dimethoxybenzophenone (1.58 g, 6.5 mmol), LiHMDS (13.0 mL, 13.0 mmol), and $MeNO_2$ (70 mL) to provide the title compound as a yellow oil (1.73 g, 6.1 mmol) in 93% yield: IR (neat) 3090, 2999, 2939, 2835, 1593, 1577, 1516, 1487, 1463, 1454, 1431, 1338, 1288, 1265, 1251, 1242, 1211, 1176, 1130, 1049, 1006, 875, 783, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.38–7.24 (m, 2H), 7.01–6.95 (m, 2H), 6.89 (ddd, J=7.7, 1.7, and 0.9 Hz, 1H), 6.82–6.79 (m, 2H), 6.74 (dd, J=2.4 and 1.6 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.5, 149.9, 138.1, 136.6, 134.5, 129.8, 129.5, 121.2, 120.9, 116.1, 114.7, 114.5, 114.2, 55.3, 55.2; LRMS (EI) m/z 285 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}NO_4$) requires m/z 285.1001, found m/z 285.1008.

4.2.6. 2,2-Di(3-chlorophenyl)-1-nitroethylene (**3f**)

Prepared according to the general procedure for **3** from 3,3′-dichlorobenzophenone (3.00 g, 12.0 mmol), LiHMDS (24.0 mL, 24.0 mmol), and $MeNO_2$ (50 mL) to provide the title compound as a yellow oil (3.13 g, 10.6 mmol) in 87% yield: IR (neat) 3105, 3066, 2951, 2848, 1616, 1593, 1564, 1517, 1471, 1409, 1340, 1242, 1161, 1099, 1082, 997, 937, 885, 823, 792 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.41–7.32 (m, 3H), 7.26 (t, J=1.9 Hz, 1H), 7.20 (t, J=1.8 Hz, 1H), 7.16 (ddd, J=7.8, 1.7, and 1.1 Hz, 1H), 7.12 (dt, J=7.5 and 2.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 138.1, 136.5, 135.5, 135.2, 134.7, 131.1, 130.3, 130.0, 129.7, 128.6, 128.5, 126.8, 126.7; LRMS (EI) m/z 293 (M); HRMS (EI) exact mass calcd for ($C_{14}H_9Cl_2NO_2$) requires m/z 293.0010, found m/z 293.0006.

4.2.7. 2,2-Di(4-chlorophenyl)-1-nitroethylene (**3g**)

Prepared according to the general procedure for **3** from 4,4′-dichlorobenzophenone (3.03 g, 12.0 mmol), LiHMDS (24.0 mL, 24.0 mmol), and $MeNO_2$ (55 mL) to provide the title compound as a yellow solid (1.47 g, 5.0 mmol) in 41% yield: mp 122–124 °C; IR (neat) 3092, 3066, 2922, 2850, 1612, 1583, 1560, 1519, 1485, 1452, 1400, 1327, 1298, 1265, 1238, 1176, 1153, 1089, 1053, 1012, 993, 972, 956, 939, 908, 844, 829, 819, 773, 754, 721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.35 (m, 5H), 7.21 (d, J=8.7 Hz, 2H), 7.15 (d, J=8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 137.5, 135.8, 135.0, 134.6, 133.4, 130.2, 130.1, 129.3, 129.0; LRMS (EI) m/z 293 (M); HRMS (EI) exact mass calcd for ($C_{14}H_9Cl_2NO_2$) requires m/z 293.0010, found m/z 293.0002.

4.2.8. 2,2-Di(3-trifluoromethylphenyl)-1-nitroethylene (**3h**)

Prepared according to the general procedure for **3** from 3,3′-bis(trifluoromethyl)benzophenone (3.18 g, 10.0 mmol), LiHMDS (20.0 mL, 20.0 mmol), and $MeNO_2$ (40 mL) to provide the title compound as a yellow oil (2.72 g, 7.5 mmol) in 74% yield: IR (neat) 3109, 3072, 1622, 1523, 1435, 1342, 1330, 1305, 1276, 1236, 1168, 1153, 1126, 1097, 1076, 943, 808 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J=7.6 Hz, 2H), 7.62–7.52 (m, 3H), 7.48–7.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 137.1, 136.1, 135.4, 132.1, 132.0, 131.8 (q, J=32.9 and 33.0 Hz, CF_3), 131.4 (q, J=32.8 and 32.9 Hz, CF_3), 129.8, 129.4, 127.8 (q, J=3.5 and 3.5 Hz), 126.5 (q, J=3.7 and 3.7 Hz), 125.5 (q, J=3.9 and 4.0 Hz), 125.1 (q, J=3.8 and 3.8 Hz), 124.9 (d, J=18.5 Hz), 122.1 (d, J=18.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.1, −63.3; LRMS (EI) m/z 361 (M); HRMS (EI) exact mass calcd for ($C_{16}H_9F_6NO_2$) requires m/z 361.0537, found m/z 361.0554.

4.2.9. 2,2-Di(4-trifluoromethylphenyl)-1-nitroethylene (**3i**)

Prepared according to the general procedure for **3** from 4,4′-bis(trifluoromethyl)benzophenone (1.27 g, 4.0 mmol), LiHMDS (10.0 mL, 10.0 mmol), and $MeNO_2$ (50 mL) to provide the title compound as a yellow solid (1.15 g, 3.2 mmol) in 79% yield: mp 91–92 °C; IR (neat) 3107, 3078, 2927, 2854, 1625, 1608, 1571, 1527, 1510, 1409, 1317, 1240, 1163, 1138, 1114, 1107, 1064, 1016, 995, 977, 964, 912, 835, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J=8.2 Hz, 2H), 7.68 (d, J=8.3 Hz, 2H), 7.49 (s, 1H), 7.40 (d, J=8.2 Hz, 2H), 7.36 (d, J=8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 139.6, 138.4, 136.2, 132.9 (q, J=33.1 and 33.1 Hz, CF_3), 131.6 (q, J=33.1 and 33.1 Hz, CF_3), 129.1, 129.0, 126.1 (q, J=3.8 and 3.8 Hz), 125.8 (q, J=3.8 and 3.8 Hz), 125.4 (d, J=16.6 Hz), 121.8 (d, J=16.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.3, −63.5; LRMS (EI) m/z 342 (M−19); HRMS (EI) exact mass calcd for ($C_{16}H_9F_5NO_2$)$^+$ requires m/z 342.0553, found m/z 342.0574.

4.2.10. 2,2-Di(2-naphthyl)-1-nitroethylene (**3j**)

Prepared according to the general procedure for **3** from di-2-naphthalenylmethanone (0.57 g, 2.0 mmol), LiHMDS (4.0 mL, 4.0 mmol), and $MeNO_2$ (25 mL) to provide the title compound as a yellow solid (0.47 g, 1.45 mmol) in 60% yield: mp 122–124 °C; IR (neat) 2935, 1740, 1600, 1585, 1561, 1493, 1469, 1324, 1276, 1261, 1238, 1219, 1188, 1130, 1002, 962, 902, 867, 833, 820, 803, 751, 706 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J=8.6 Hz, 1H), 7.92 (d, J=7.4 Hz, 1H), 7.90–7.80 (m, 3H), 7.80–7.73 (m, 3H), 7.65 (s, 1H), 7.62–7.48 (m, 4H), 7.43 (dd, J=8.7 and 1.8 Hz, 1H), 7.39 (dd, J=8.7 and 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 134.7, 134.4, 134.2, 133.4, 133.0, 132.9, 132.8, 130.1, 128.7, 128.7, 128.6, 128.6, 128.4, 128.2, 127.8, 127.6, 127.1, 126.9, 126.5, 126.3, 125.0; LRMS (EI) m/z 325 (M); HRMS (EI) exact mass calcd for ($C_{22}H_{15}NO_2$) requires m/z 325.1103, found m/z 325.1107.

4.3. Typical experimental procedure for the preparation of 8

According to a modified procedure of Smitrovich and Davies,[11a] an Endeavor® glass liner was successively charged with nitroalkene and a solution of $Pd(OAc)_2$ (2 mol %) and 1,10-phenanthroline (phen) (4 mol %) in DMF. After the liner was inserted into the Endeavor® pressure reactor, the reactor was sealed and purged three times with CO. The reactor was pressurized with CO (1 atm) and heated at 110 °C for 3–16 h. The red reaction mixture was cooled to ambient temperature and concentrated. The resulting residue was purified by silica gel chromatography with a solvent gradient of 1–20% EtOAc in hexanes to afford the title compounds.

4.3.1. 3-Phenylindole (**8a**)

Prepared according to the general procedure for **8** from 2,2-diphenyl-1-nitroethylene (67.4 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (55.7 mg, 0.29 mmol) in 96% yield: ^{1}H and ^{13}C NMR data for **8a** matched those reported in the literature.[28]

4.3.2. 6-Methyl-3-p-tolylindole (**8b**)

Prepared according to the general procedure for **8** from 2,2-di(4-methylphenyl)-1-nitroethylene (76.0 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (61.6 mg, 0.28 mmol) in 87% yield: mp 113–114 °C; IR (neat) 3398, 3024, 2960, 2935, 2914, 2856, 1548, 1454, 1390, 1328, 1263, 1240, 1145, 1109, 1099, 1033, 1001, 966, 935, 860, 821, 804, 792, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (br s, 1H, NH), 7.85 (d, J=8.2 Hz, 1H), 7.60 (d, J=8.1 Hz, 2H), 7.29 (d, J=8.1 Hz, 2H), 7.25 (d, J=2.4 Hz, 1H), 7.20 (s, 1H), 7.06 (d, J=8.3 Hz, 1H), 2.52 (s, 3H), 2.44 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 137.1, 135.4, 132.7, 132.1, 129.4, 127.2, 123.6, 121.9, 120.8, 119.4, 118.0, 111.3, 21.6, 21.1; LRMS (EI) *m*/*z* 221 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}N$) requires *m*/*z* 221.1204, found *m*/*z* 221.1199.

*4.3.3. 6-tert-Butyl-3-(4-tert-butylphenyl)indole (**8c**)*

Prepared according to the general procedure for **8** from 2,2-di(4-*tert*-butylphenyl)-1-nitroethylene (0.101 g, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (83.5 mg, 0.27 mmol) in 91% yield: mp 174–175 °C; IR (neat) 3423, 3379, 3109, 3080, 3032, 2949, 2900, 2862, 1610, 1546, 1456, 1386, 1359, 1269, 1246, 1197, 1101, 962, 854, 839, 796, 786, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (br s, 1H, NH), 7.95 (d, *J*=8.6 Hz, 1H), 7.68 (d, *J*=8.2 Hz, 2H), 7.54 (d, *J*=8.3 Hz, 2H), 7.44 (s, 1H), 7.34 (d, *J*=8.5 Hz, 1H), 7.29 (d, *J*=2.4 Hz, 1H), 1.47 (s, 9H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 145.7, 136.8, 132.9, 126.9, 125.6, 123.5, 121.3, 119.4, 118.5, 117.8, 107.6, 34.7, 34.5, 31.8, 31.4; LRMS (EI) *m*/*z* 305 (M); HRMS (EI) exact mass calcd for ($C_{22}H_{27}N$) requires *m*/*z* 305.2144, found *m*/*z* 305.2136.

*4.3.4. 6-Methoxy-3-(4-methoxyphenyl)indole (**8d**)*

Prepared according to the general procedure for **8** from 2,2-di(4-methoxyphenyl)-1-nitroethylene (85.7 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (72.7 mg, 0.29 mmol) in 93% yield: mp 144–145 °C; IR (neat) 3412, 3012, 2953, 2929, 2904, 2837, 2360, 1735, 1627, 1543, 1498, 1450, 1438, 1390, 1334, 1311, 1288, 1265, 1182, 1163, 1151, 1114, 1103, 1028, 956, 827, 788, 748, 719, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (br s, 1H, NH), 7.80 (d, *J*=8.7 Hz, 1H), 7.60 (d, *J*=8.7 Hz, 2H), 7.15 (d, *J*=2.4 Hz, 1H), 7.03 (d, *J*=8.7 Hz, 2H), 6.89 (dd, *J*=8.7 and 2.3 Hz, 1H), 6.85 (d, *J*=2.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 156.5, 137.3, 128.3, 128.2, 120.3, 120.2, 119.9, 117.7, 114.2, 110.1, 94.7, 55.6, 55.3; LRMS (EI) *m*/*z* 253 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}NO_2$) requires *m*/*z* 253.1103, found *m*/*z* 253.1101.

*4.3.5. 5-Methoxy-3-(3-methoxyphenyl)indole (**8e**)*

Prepared according to the general procedure for **8** from 2,2-di(3-methoxyphenyl)-1-nitroethylene (84.6 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as a light-brown oil (35.0 mg, 0.14 mmol) in 43% yield: IR (neat) 3406, 2993, 2933, 2904, 2829, 1600, 1583, 1541, 1477, 1454, 1436, 1411, 1321, 1298, 1278, 1215, 1172, 1111, 1033, 987, 921, 840, 794, 783 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (br s, 1H, NH), 7.42–7.35 (m, 2H), 7.31 (m, 1H), 7.27 (d, *J*=5.4 Hz, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 6.92 (dd, *J*=8.8 and 2.4 Hz, 1H), 6.86 (dd, *J*=8.2 and 2.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.7, 137.1, 131.7, 129.8, 126.1, 122.7, 119.9, 117.9, 113.0, 112.7, 112.1, 111.3, 101.6, 55.9, 55.2; LRMS (EI) *m*/*z* 253 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}NO_2$) requires *m*/*z* 253.1103, found *m*/*z* 253.1091.

*4.3.6. 7-Methoxy-3-(3-methoxyphenyl)indole (**8f**)*

Prepared according to the general procedure for **8** from 2,2-di(3-methoxyphenyl)-1-nitroethylene (84.6 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as a pink solid (39.2 mg, 0.16 mmol) in 48% yield: mp 72–74 °C; IR (neat) 3404, 2966, 2933, 2854, 1625, 1604, 1577, 1498, 1477, 1444, 1431, 1413, 1369, 1346, 1332, 1265, 1249, 1220, 1168, 1149, 1101, 1091, 1074, 1058, 1037, 989, 925, 873, 815, 777, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (br s, 1H, NH), 7.58 (d, *J*=8.2 Hz, 1H), 7.40–7.34 (m, 2H), 7.29 (d, *J*=7.6 Hz, 1H), 7.25 (s, 1H), 7.13 (t, *J*=7.9 Hz, 1H), 6.86 (dd, *J*=8.2 and 2.5 Hz, 1H), 6.72 (d, *J*=7.7 Hz, 1H), 3.99 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 146.2, 137.1, 129.7, 127.2, 126.9, 121.4, 120.7, 119.9, 118.6, 113.0, 112.5, 111.4, 102.1, 55.3, 55.2; LRMS (EI) *m*/*z* 253 (M); HRMS (EI) exact mass calcd for ($C_{16}H_{15}NO_2$) requires *m*/*z* 253.1103, found *m*/*z* 253.1093.

*4.3.7. 5-Chloro-3-(3-chlorophenyl)indole (**8g**)*

Prepared according to the general procedure for **8** from 2,2-di(3-chlorophenyl)-1-nitroethylene (89.0 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as a light-brown oil (31.9 mg, 0.12 mmol) in 40% yield: IR (neat) 3435, 3118, 3062, 2924, 2852, 1597, 1571, 1541, 1460, 1398, 1342, 1286, 1238, 1095, 989, 891, 796, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (br s, 1H, NH), 7.87 (d, *J*=2.0 Hz, 1H), 7.58 (t, *J*=1.8 Hz, 1H), 7.50 (dt, *J*=7.7 and 2.8 Hz, 1H), 7.40–7.33 (m, 3H), 7.30–7.27 (m, 1H), 7.22 (dd, *J*=8.7 and 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.9, 134.6, 130.0, 127.2, 126.5, 126.4, 126.2, 125.4, 123.4, 123.0, 119.0, 116.8, 112.5; LRMS (EI) *m*/*z* 261 (M); HRMS (EI) exact mass calcd for ($C_{14}H_9Cl_2N$) requires *m*/*z* 261.0112, found *m*/*z* 261.0110.

*4.3.8. 7-Chloro-3-(3-chlorophenyl)indole (**8h**)*

Prepared according to the general procedure for **8** from 2,2-di(3-chlorophenyl)-1-nitroethylene (89.0 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (42.4 mg, 0.16 mmol) in 51% yield: mp 95–97 °C; IR (neat) 3414, 3390, 3120, 3072, 2926, 2854, 2358, 1589, 1570, 1554, 1537, 1490, 1469, 1433, 1390, 1342, 1298, 1269, 1249, 1211, 1170, 1134, 1111, 1080, 1051, 997, 891, 877, 837, 819, 783, 761, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.51 (br s, 1H, NH), 7.81 (d, *J*=7.9 Hz, 1H), 7.64 (s, 1H), 7.53 (d, *J*=7.8 Hz, 1H), 7.42–7.35 (m, 2H), 7.30–7.27 (m, 2H), 7.16 (t, *J*=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 134.6, 133.9, 130.0, 127.3, 126.8, 126.3, 125.5, 122.6, 122.0, 121.3, 118.2, 118.1, 116.9; LRMS (EI) *m*/*z* 261 (M); HRMS (EI) exact mass calcd for ($C_{14}H_9Cl_2N$) requires *m*/*z* 261.0112, found *m*/*z* 261.0101.

*4.3.9. 6-Chloro-3-(4-chlorophenyl)indole (**8i**)*

Prepared according to the general procedure for **8** from 2,2-di(4-chlorophenyl)-1-nitroethylene (88.2 mg, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (77.7 mg, 0.30 mmol) in 98% yield: mp 142–144 °C; IR (neat) 3435, 3064, 2922, 2852, 1595, 1539, 1485, 1452, 1444, 1413, 1382, 1327, 1290, 1255, 1222, 1147, 1107, 1087, 1062, 1008, 958, 900, 837, 812, 798, 785, 742, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (br s, 1H, NH), 7.77 (d, *J*=8.6 Hz, 1H), 7.55 (d, *J*=8.5 Hz, 2H), 7.42–7.39 (m, 3H), 7.33 (d, *J*=2.6 Hz, 1H), 7.18 (dd, *J*=8.6 and 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 133.4, 131.9, 128.9, 128.5, 128.4, 124.1, 122.3, 121.2, 120.4, 117.3, 111.4; LRMS (EI) *m*/*z* 261 (M); HRMS (EI) exact mass calcd for ($C_{14}H_{19}Cl_2N$) requires *m*/*z* 261.0112, found *m*/*z* 261.0103.

*4.3.10. 5-Trifluoromethyl-3-(3-trifluoromethylphenyl)indole (**8j**)*

Prepared according to the general procedure for **8** from 2,2-di(3-trifluoromethylphenyl)-1-nitroethylene (0.108 g, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (47.0 mg, 0.14 mmol) in 45% yield: mp 75–77 °C; IR (neat) 3485, 2922, 1612, 1543, 1481, 1425, 1317, 1292, 1271, 1259, 1242, 1155, 1143, 1087, 1070, 1055, 999, 981, 943, 898, 877, 810, 796, 777, 756, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (br s, 1H, NH), 8.16 (s, 1H), 7.87–7.82 (m, 2H), 7.66–7.58 (m, 2H), 7.53 (s, 2H), 7.51 (d, *J*=2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.3, 131.3 (q, *J*=32.2 and 32.2 Hz, CF_3), 130.7, 129.4, 126.5, 125.6, 124.9, 124.2 (q, *J*=3.9 and 3.8 Hz), 123.8, 123.2 (q, *J*=31.9

and 32.1 Hz, CF_3), 123.1 (q, J=3.8 and 3.9 Hz), 119.6 (q, J=3.4 and 3.5 Hz), 118.1, 117.1 (q, J=4.3 and 4.2 Hz), 111.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ −60.8, −63.0; LRMS (EI) m/z 329 (M); HRMS (EI) exact mass calcd for ($C_{16}H_9F_6N$) requires m/z 329.0639, found m/z 329.0637.

4.3.11. 7-Trifluoromethyl-3-(3-trifluoromethylphenyl)indole (**8k**)

Prepared according to the general procedure for **8** from 2,2-di(3-trifluoromethylphenyl)-1-nitroethylene (0.108 g, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as a yellow oil (41.1 mg, 0.12 mmol) in 41% yield: IR (neat) 3493, 2929, 2856, 1718, 1618, 1591, 1554, 1442, 1355, 1328, 1311, 1251, 1215, 1165, 1120, 1074, 1002, 900, 800, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (br s, 1H, NH), 8.06 (d, J=8.1 Hz, 1H), 7.89 (s, 1H), 7.85–7.78 (m, 1H), 7.59 (d, J=5.0 Hz, 2H), 7.56 (d, J=7.4 Hz, 1H), 7.49 (d, J=2.6 Hz, 1H), 7.30 (t, J=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 132.1, 131.3 (q, J=32.0 and 32.0 Hz, CF_3), 130.8, 129.3, 127.0, 125.9 (d, J=66.8 Hz), 124.3 (q, J=3.7 and 3.8 Hz), 123.4, 123.3, 123.2 (d, J=67.4 Hz), 123.1 (q, J=3.8 and 3.8 Hz), 120.3 (q, J=4.5 and 4.5 Hz), 120.1, 117.6, 113.9 (q, J=33.0 and 33.1 Hz, CF_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ −65.5, −67.8; LRMS (EI) m/z 329 (M); HRMS (EI) exact mass calcd for ($C_{16}H_9F_6N$) requires m/z 329.0639, found m/z 329.0623.

4.3.12. 6-Trifluoromethyl-3-(4-trifluoromethylphenyl)indole (**8l**)

Prepared according to the general procedure for **8** from 2,2-di(4-trifluoromethylphenyl)-1-nitroethylene (0.107 g, 0.30 mmol), $Pd(OAc)_2$ (1.38 mg, 0.006 mmol), phen (2.24 mg, 0.012 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (61.1 mg, 0.19 mmol) in 58% yield: mp 86–87 °C; IR (neat) 3487, 3412, 3126, 2922, 2850, 1618, 1581, 1554, 1510, 1502, 1456, 1425, 1398, 1355, 1323, 1313, 1303, 1273, 1224, 1166, 1151, 1099, 1064, 1053, 1012, 964, 912, 871, 846, 817, 794, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (br s, 1H, NH), 7.99 (d, J=8.5 Hz, 1H), 7.78–7.70 (m, 5H), 7.57 (d, J=2.6 Hz, 1H), 7.47 (dd, J=8.5 and 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 135.6, 128.4, 128.3 (q, J=32.4 and 32.4 Hz, CF_3), 127.7, 127.5, 126.0 (d, J=59.0 Hz), 125.9 (q, J=3.7 and 3.8 Hz), 125.0 (q, J=31.8 and 31.9 Hz, CF_3), 124.9, 123.3 (d, J=59.6 Hz), 120.0, 117.5 (q, J=3.5 and 3.6 Hz), 109.2 (q, J=4.4 and 4.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.2, −62.7; LRMS (EI) m/z 329 (M); HRMS (EI) exact mass calcd for ($C_{16}H_9F_6N$) requires m/z 329.0639, found m/z 329.0626.

4.3.13. 3-(2-Naphthyl)benzo[g]indole (**8m**)

repared according to the general procedure for **8** from 2,2-di(2-naphthyl)-1-nitroethylene (0.161 g, 0.50 mmol), $Pd(OAc)_2$ (2.20 mg, 0.010 mmol), phen (3.60 mg, 0.020 mmol), and DMF (1.5 mL) to provide the title compound as an off-white solid (116.0 mg, 0.40 mmol) in 79% yield: mp 276–278 °C; IR (neat) 3413, 3392, 2930, 1719, 1628, 1596, 1536, 1521, 1465, 1450, 1423, 1386, 1275, 1246, 1225, 1131, 1111, 1027, 950, 926, 887, 858, 819, 794, 738 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 12.36 (s, 1H, NH), 8.44 (d, J=8.2 Hz, 1H), 8.28 (s, 1H), 8.15 (d, J=8.7 Hz, 1H), 8.04–7.89 (m, 6H), 7.63–7.42 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 133.6, 133.3, 131.5, 131.3, 129.6, 128.2, 128.1, 127.6, 127.4, 126.2, 126.1, 125.4, 125.0, 123.8, 122.1, 122.0, 120.7, 120.6, 120.4, 119.5, 117.5; LRMS (EI) m/z 293 (M); HRMS (EI) exact mass calcd for ($C_{22}H_{15}N$) requires m/z 293.1204, found m/z 293.1202.

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Supplementary data

^1H, ^{13}C, and ^{19}F NMR spectra of compounds **3a**–**3j** and **8a**–**8m** and X-ray crystallographic data of **8m** are found in the Supplementary data, along with experimental procedures and characterization data for the new substituted-benzophenone derivatives. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.11.034.

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