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FULL PAPER

Synthesis of *N*-Heterocycles by Reductive Cyclization of Nitroalkenes using Molybdenum Hexacarbonyl as Carbon Monoxide Surrogate

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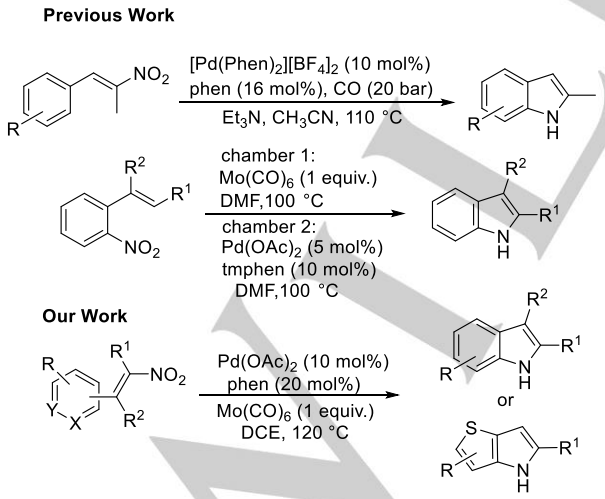
Abstract: The development of a method that uses molybdenum hexacarbonyl [$Mo(CO)_6$] as carbon monoxide (CO) surrogate for the palladium-catalyzed reductive cyclization of nitroalkenes into indoles or thienopyrroles is reported. Several types of nitroalkenes could be transformed into the desired products in excellent yields and in most case got higher yields and complete regioselectivities than those previously reported with palladium/CO system.

Introduction

N-heterocycles are widely distributed in a broad range of products, including natural alkaloids or bioactive pharmaceuticals, ligands and functional materials.[1] Pyrrole-fused aromatic rings are central to many natural and synthetic products that exhibit biological and therapeutic activities.[2] Accordingly, numerous *N*-heterocycles constructing methods have been developed in the past decades,[3] especially the research about catalytic reductive cyclization of nitroarenes by using CO as reductant.[4] However, the widespread of this method is limited by the requirement of safety measures for pressurized CO. Recently, much attention has been paid to the use of CO surrogates and it was reported that $Mo(CO)_6$ could trigger this transformation in combination with palladium catalysts.[4j, 5] Nonetheless, several synthetic steps for the preparation of the starting substrates with two *ortho*-substituted functional partners become the common limit to this synthetic strategy. The direct catalytic deoxygenative cyclization of nitroalkene has emerged as an attractive strategy for indole synthesis, the pioneered elegant studies in this field by using CO as stoichiometric reductant have been reported by Dong and Ragaini's group (Scheme 1).[6] Herein, we present a method for the palladium-catalyzed synthesis of *N*-heterocycles from nitroalkenes using $Mo(CO)_6$ as the reductant.



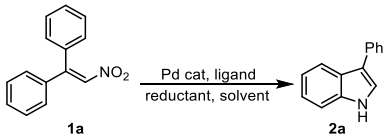
Scheme 1. Reported and current work on palladium-catalyzed reductive cyclization.

Results and Discussion

The nitroalkene **1a** was easily prepared from benzaldehyde via Wittig reaction and nitration, and initially investigated the reductant cyclization in the presence of transition-metal catalysts and reductants. At the outset, when substrate **1a** was treated with $Pd(CH_3CN)_2Cl_2$, $Mo(CO)_6$ and phenanathroline (phen) in 1,2-dichloroethan (DCE), the indole **2a** was obtained in 68% yield (Table 1, entry 1). Different reductants were investigated and it was found that other carbonyl complexes and phenyl formate could also promote this reaction but gave lower yield (Table 1, entries 2-4), which indicated that $Mo(CO)_6$ did not act only as CO surrogate. Inspired by these initial results, we further screened different palladium sources and ligands. It was found that the reaction catalyzed by $Pd(OAc)_2$ gave better yield than those catalyzed by $Pd(CH_3CN)_2Cl_2$, $[Pd(CH_3CN)_4][BF_4]_2$ and $Pd(dppf)Cl_2$ (Table 1, entries 5-7), and tmphen was less suitable for this reaction than phen (Table 1, entry 8). Solvent screening showed DCE was the optimal solvent for this reaction (Table 1, entries 9, 10). Increasing the temperature to 140 °C or reducing the catalyst loading (5% mol palladium, 10% mol ligand) were proved to be less detrimental for the reaction (Table 1, entries 11, 12).

With the optimal condition in hand, the scope of the reductive cyclization was explored. The β, β-diaryl nitroalkenes, which were synthesized from corresponding substituted benzophenones via cascade Wittig reaction/nitrification were first investigated and excellent yields were observed in most cases (Table 2). Interestingly, the diaryl nitroalkenes with either electron-donating or electron-withdrawing substituents in the *para* position of aryl ring gave higher yields (Table 2, entries 2-4), despite the substrate **1d** required longer reaction time. It's notable that substrates bearing amino and carboxyl group could not get the

Table 1. Optimization of palladium-catalyzed reductive cyclization[a]



1a 2a

Entry	Reductant	Catalyst/Ligand	Solvent	Yield[d] %
1	$Mo(CO)_6$	$Pd(CH_3CN)_2Cl_2$/phen	DCE	68
2	$Cr(CO)_6$	$Pd(CH_3CN)_2Cl_2$/phen	DCE	42
3	$W(CO)_6$	$Pd(CH_3CN)_2Cl_2$/phen	DCE	34
4	HCOOPh	$Pd(CH_3CN)_2Cl_2$/phen	DCE	43
5	$Mo(CO)_6$	$Pd(dppf)Cl_2$/phen	DCE	44
6	$Mo(CO)_6$	$[Pd(Phen)_2][BF_4]_2$/ phen	DCE	47
7	$Mo(CO)_6$	$Pd(OAc)_2$/ phen	DCE	80
8	$Mo(CO)_6$	$Pd(OAc)_2$/tmphen	DMF	72
9	$Mo(CO)_6$	$Pd(OAc)_2$/ phen	CH_3CN	62
10	$Mo(CO)_6$	$Pd(OAc)_2$/ phen	toluene	35
11[b]	$Mo(CO)_6$	$Pd(OAc)_2$/ phen	DCE	74
12[c]	$Mo(CO)_6$	$Pd(OAc)_2$/ phen	DCE	63

[a] Reaction conditions: **1a** (0.1 mmol), Reductant (0.1 mmol), Pd catalyst (10 mol %), Ligand (20 mol %), solvent (2 mL), 120 °C, 4h; [b] The reaction was carried out at 140 °C; [c] 5 mol % $Pd(OAc)_2$, 10 mol % phen used; [d] isolated yield.

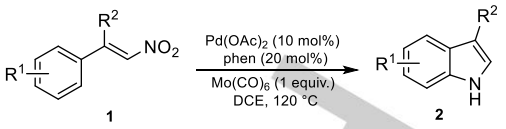
corresponding products due to their strong activity in this catalytic system (Table 2, entries 5, 6). Moreover, the α-H substituted substrates **1g**-**1i** with lower degree of conjugation of the π system were also not stable and decomposed under the optimized condition (Table 2, entries 7-9).

Subsequently, the β-phenyl-α-alkyl nitroalkenes, which could be easily prepared from aldehyde through Henry reaction, were tested for this reaction (Table 3). To our delight, it was found that this type of substrates also transformed into the desired products with medium to good yields. The decrease in yield is due to the lower reduction potential owing to the less extended system in this type substrates (Table 3, entries 1-4). Both electron-withdrawing and electron-donating groups could be present in the *para* position of aryl ring and got the similar yields. The similar inactivity of substrate with carboxyl group were observed (Table 3, entry 6). It is notable that the cyclization of **3e,** which contains a methoxyl substituent in *meta* position of phenyl ring, may in principle take place by activation of C-H bond at 2- or 4- position. Remarkably, the cyclization was selective towards the 2-position and it could be interpreted as partial coordination of the product to the metal center (Table 3, entry 5).[7]

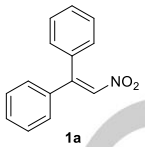
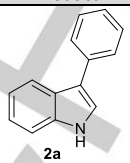
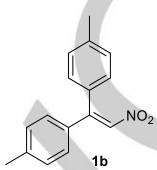
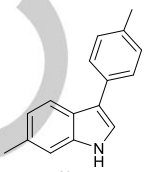
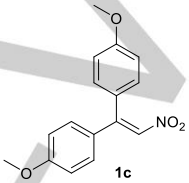
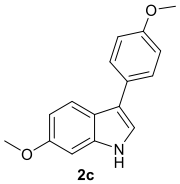
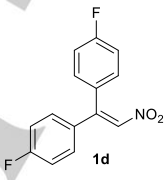
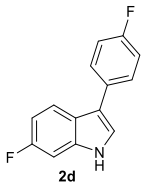
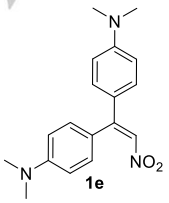
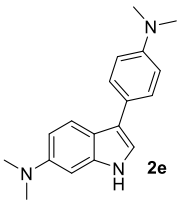
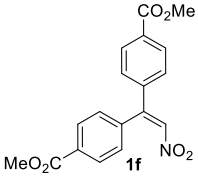
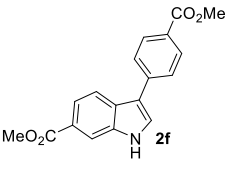
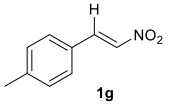
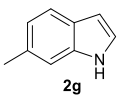
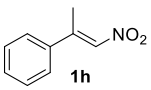
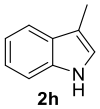
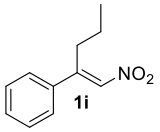
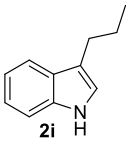
To further examine the substrate scope of this reaction, the cyclization of β-thiopenyl-α-alkyl nitroalkenes to thienopyrroles were studied (Table 3, entries 7-10). Similarly to the result of indole synthesis, the desired products were obtained through reductive cyclization under the optimized conditions in good yields. The presence of substituted groups at the alkene or thiophene ring did not affect the reactivity (Table 3, entries 8, 9). It should be noted that the good result was obtained from substrate **3j** with good yield and complete regio selectivity, which could be ascribed to the electrophilic cyclization process of the nitroso intermediate, and attack on the electron rich 2-position of the thiophene ring should be favored (Table 3, entry 10).

In addition, a series of more complicated substrates were rationally designed to study the regioselectivity of this type of reaction. As seen from Table 4, (*E*)-2-(2-nitro-alkenyl)naphthalene **5a, 5b** were subjected to the optimal

Table 2. Palladium-catalyzed reductive cyclization of β, β-diaryl nitroalkenes: Reaction scope and limitations [a]



1 2

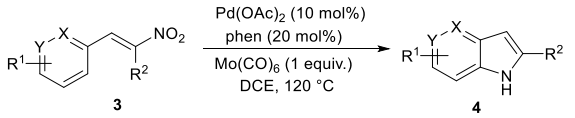
Entry	Substrate	Product	Yield[d] %
1	 1a	 2a	80
2	 1b	 2b	83
3	 1c	 2c	81
4[b]	 1d	 2d	85
5	 1e	 2e	n.d.[c]
6	 1f	 2f	n.d.[c]
7	 1g	 2g	n.d.[c]
8	 1h	 2h	n.d.[c]
9	 1i	 2i	n.d.[c]

[a] Reaction conditions: **1** (0.1 mmol), $Mo(CO)_6$ (0.1 mmol), $Pd(OAc)_2$ (10 mol %), Phen (20 mol %), DCE (2 mL), 120 °C, 4h; [b] The reaction was conducted for 12 h; [c] Not detected by GC-MS. [d] isolated yield.

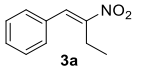
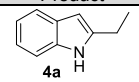
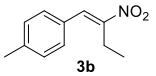
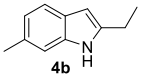
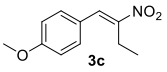
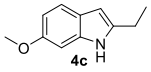
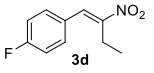
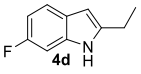
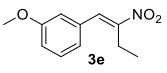
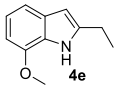
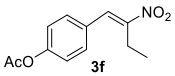
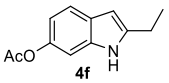
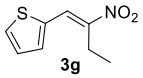
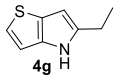
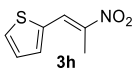
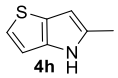
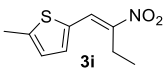
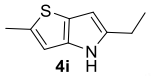
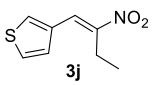
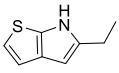
conditions, the amination of carbon-hydrogen bond was observed only at the β position of the naphthalene ring, which indicated this electrophilic substitution occurring under thermodynamic control

(Table 4, entries 1, 2).[8] In the case of (*E*)-1-(2-nitro-alkenyl)naphthalene **5c**, the complete β selectivity was also obtained and the benzo[*de*]quinoline skeleton was not detected (Table 4, entry 3).[9]

Table 3. Palladium-catalyzed reductive cyclization of β-phenyl-α-alkyl nitroalkenes: Reaction scope and limitations [a]

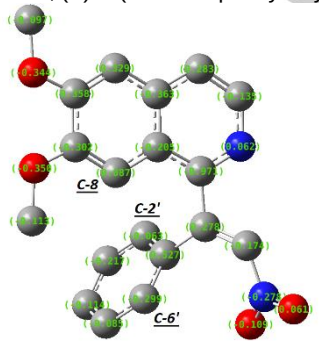


3 4

Entry	Substrate	Product	Yield[b] %
1	 3a	 4a	72
2	 3b	 4b	63
3	 3c	 4c	67
4	 3d	 4d	70
5	 3e	 4e	63
6	 3f	 4f	n.d.[c]
7	 3g	 4g	78
8	 3h	 4h	68
9	 3i	 4i	76
10	 3j	 4j	63

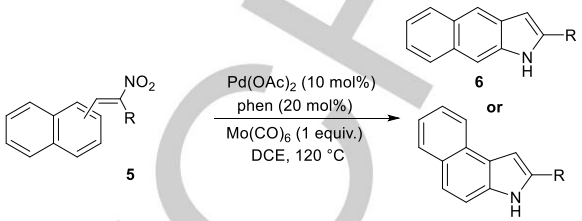
[a] Reaction conditions: **3** (0.1 mmol), $Mo(CO)_6$ (0.1 mmol), $Pd(OAc)_2$ (10 mol %), Phen (20 mol %), DCE (2 mL), 120 °C, 4h; [b] isolated yield. [c] Not detected by GC-MS.

To explore whether five- or six-membered ring-closure is favored in this reaction, (*E*)-1-(2-nitro-1-phenylvinyl)isoquinoline **7,** prepared through successive Bischer-Napieralski reaction and one-step oxidation,[10] were evaluated under the optimized conditions. To our surprise, this type diaryl nitroalkenes were all transformed into isoquinoline-indole linked *N*-biheteroarenes **8** underwent the reductive cyclization in the five-membered ring manner (Table 5). Even for the reaction of substrate **7b** (Table 5, entry 2), containing two electron-donating methoxyl groups on the isoquinoline ring and no substituent group on the phenyl ring, furnished the *N*- biheteroarenes **8b** in excellent yield and the benzo[*de*]naphthyridine **8b'** was not detected. To rationalize the observed regioselectivity of this reaction, density functional theory (DFT) calculations were conducted. The distribution of Mulliken atomic charge[11] from **7b** showed much lower electronic density on carbon 8 (0.087) of the isoquiloine ring than on carbon 2' (-0.063) and carbon 6' (-0.299) of the phenyl ring when calculated

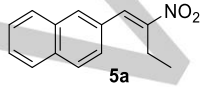
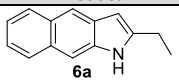
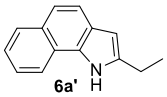
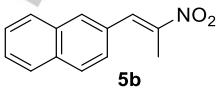
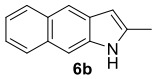
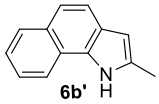
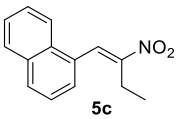
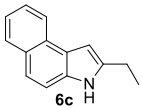
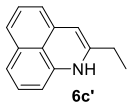


Scheme 2. Mulliken atomic charge distribution for **7b**.

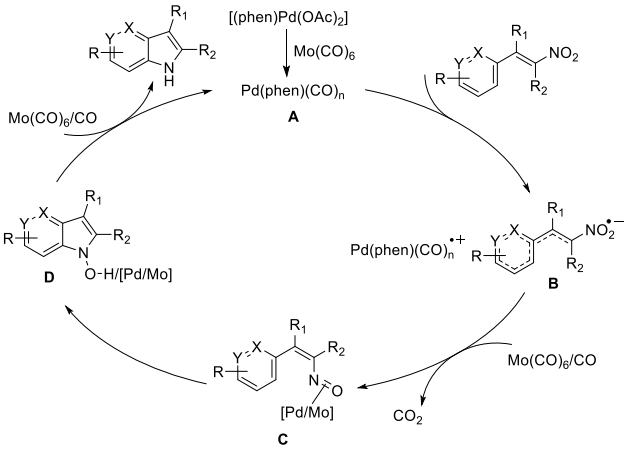
Table 4. Palladium-catalyzed reductive cyclization of nitroalkenyl naphthalenes[a]



5 6 6

Entry	Substrate	Product	Yield[b] %
1	 5a	 6a	73
		 6a'	-
2	 5b	 6b	70
		 6b'	-
3	 5c	 6c	78
		 6c'	-

[a] Reaction conditions: **5** (0.1 mmol), $Mo(CO)_6$ (0.1 mmol), $Pd(OAc)_2$ (10 mol %), Phen (20 mol %), DCE (2 mL), 120 °C, 4h; [b] isolated yield.

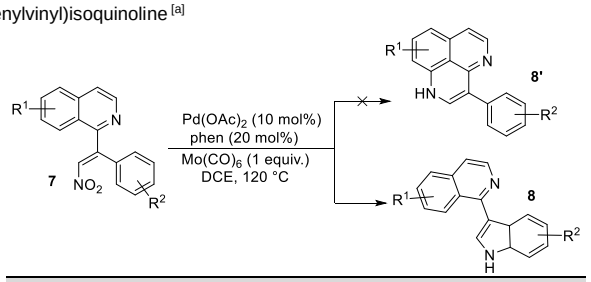


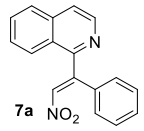
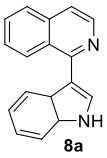
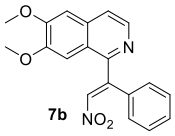
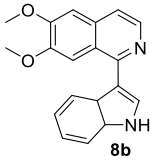
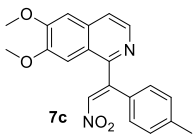
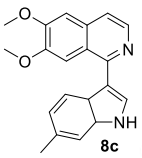
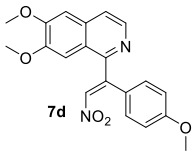
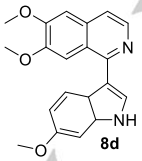
Scheme 3. Proposed reaction mechanism for the reductive cyclization of nitroalkene.

using Gaussain 09 at B3LYP/6-31G+(d, p) level of theory (Scheme 2),[12] which suggested that the electrophilic cyclization of the intermediate was favored at the phenyl ring.

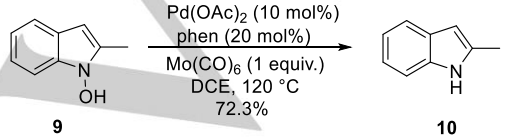
By analogy with the mechanism that previously proposed for the reductive cyclization of nitroalkenes with carbon monoxide as the reductant,[6b] we proposed the following mechanism: Firstly

Table 5. Palladium-catalyzed reductive cyclization of (2-nitro-1-phenylvinyl)isoquinoline [a]



Entry	Substrate	Product	Yield[b] %
1			76
2			73
3			78
4			81

the palladium CO complex **A** is generated through the reduction of $Pd(OAc)_2$ by $Mo(CO)_6$, which reacts with the nitroalkene underwent single-electron transfer to lead the formation of radical anion **B**. Reduction of intermediate **B** by $CO/Mo(CO)_6$ affords the nitroso intermediate **C**, which plays the role of aminating species to form the *N*-hydroxy heterocycle **D**. Eventually, the palladium catalyzed reduction of **D** by a second equivalent of CO forms the desired *N*- heterocycle product (Scheme 3). To confirm this mechanism, *N*-hydroxy heterocycle **9** was synthesized and subjected to the optimized conditions, and the expected product **10** was obtained in 72.3% yield (Scheme 4).



Scheme 4. Reduction of *N*-hydroxy heterocycle **9.**

Conclusion

In summary, we have developed an efficient and convenient method for the preparation of *N*-heterocycles from nitroalkenes by using $Mo(CO)_6$ as CO surrogates. The increased operability by avoiding the use of hazardous pressurized CO and concise synthetic approach for substrates offered more application in future studies. In most cases, the desired products could be obtained with higher regioselectivities and yields than those previously reported by using palladium/CO system. In addition, the potential of employing this method to achieve the bioactive *N*-biheteroarenes was also studied. Further efforts for mechanism studies and pharmaceutical applications of this chemistry are currently ongoing in our laboratories.

Experimental Section

General information: Unless otherwise stated, all the reactions were performed under nitrogen atmosphere. All reagents and solvents were purchased commercially (Alfa Asear, Strem, Merck and Sigma-Aldrich) and used as received. Evaporation of organic solvent was achieved by rotary evaporation with a water bath temperature below 36 °C. Thin layer chromatography (TLC) with Merck TLC silica gel 60 F254 plate was used to check reaction progress under the UV light at 254 nm. Flash column chromatography with silica gel 60 (0.010-0.063 mm) was used for product purification. ^1H and ^{13}C NMR spectra were obtained by 600 MHz Bruker Ascend 600 spectrometer. Tetramethylsilane (TMS) was used as the internal standard for the measurement of chemical shifts (δ) in ppm. Chemical shifts are reported in ppm (δ). NMR experiments were run in $CDCl_3$ as indicated, ^1H NMR spectra are referenced to the resonance from residual $CHCl_3$ at 7.26 ppm. ^{13}C NMR spectra are referenced to the central peak in the signal from $CDCl_3$ at 77.0 ppm. The multiplicities of ^1H NMR resonances are expressed by abbreviations: br s (broad singlet), s (singlet), d (doublet), t (triplet), quartet (q), m (multiplet) and combinations thereof for highly coupled systems. ^{13}C NMR spectra were run as proton decoupled experiments. ^1H and ^{13}C signals where appropriate are described by chemical shift δ (multiplicity, J (Hz), integration). HRMS (ESI) spectra were obtained using a Waters Q-Tof premierTM mass spectrometer.

General Procedure for Synthesis of N-Heterocycles. In an oven-dried tube (15ml), $Pd(OAc)_2$ (10 mol%), 1,10 -phenanthroline (phen) (20 mol%) and $Mo(CO)_6$ (0.1 mmol) was added. Then under the nitrogen atmosphere, the nitroalkene(0.1 mmol) dissolved in the DCE (2 ml) was added using laboratory syringe. Then the tube was heated in 120 °C for 2h with the monitoring of TLC. The reaction was cooled to room temperature and concentrated in vacuo to give the crude residue. The crude reaction mixture was purified with silica gel column chromatography with petroleum ether/ ethyl acetate as the eluent to get the indole.

2, 2-diphenyl-1-nitroethylene (1a). ^1H NMR (600 MHz, Chloroform-d) δ 7.48 – 7.41 (m, 5H), 7.39 (t, J = 7.7 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.23 (dd, J = 7.7, 1.6 Hz, 2H). ^{13}C NMR (151 MHz,

Chloroform-d) δ 150.4, 137.0, 135.5, 134.4, 130.9, 129.3, 128.9 (2C), 128.8 (2C), 128.8 (2C), 128.5 (2C).

2, 2-di(4-methylphenyl)-1-nitroethylene (1b). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.41 (s, 1H), 7.24 (d, J = 7.8 Hz, 2H), 7.19 (s, 4H), 7.12 (d, J = 7.7 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 150.9, 141.4, 139.4, 134.5, 133.5, 132.7, 129.5 (2C), 129.1 (2C), 129.0 (2C), 128.9 (2C), 21.4, 21.3.

2, 2-di(4-methoxyphenyl)-1-nitroethylene (1c). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.36 (s, 1H), 7.24 (dd, J = 9.3, 2.5 Hz, 2H), 7.16 (dd, J = 9.1, 2.4 Hz, 2H), 6.94 (dd, J = 9.2, 2.4 Hz, 2H), 6.89 (dd, J = 9.4, 2.4 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 162.0, 160.6, 150.8, 132.3, 131.0 (2C), 130.9 (2C), 129.8, 127.7, 114.2 (2C), 113.8 (2C), 55.4, 55.3.

2, 2-di(4-fluorophenyl)-1-nitroethylene (1d). ^{1}H NMR (600 MHz, Methylene Chloride-d2) δ 7.43 (s, 1H), 7.32 – 7.28 (m, 2H), 7.26–7.20 (m, 2H), 7.18 – 7.08 (m, 4H). ^{13}C NMR (151 MHz, Methylene Chloride-d2) δ 165.7, 164.5, 164.0, 162.9, 148.8, 134.9, 133.5, 133.5, 131.9, 131.8, 131.5 (d, 3 Hz, C-F), 131.4 (d, 3 Hz, C-F), 116.5 (d, 90 Hz, C-F), 116.1 (d, 90 Hz, C-F).

(E)- 2- phenyl-1-ethyl-1-nitroethylene (3a). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.03 (s, 1H), 7.44 (m, 5H), 2.87 (q, J = 7.4 Hz, 2H), 1.28 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 153.3, 133.1, 132.3, 129.9, 129.6 (2C), 129.0 (2C), 20.7, 12.5.

(E)- 2- (4-methylphenyl)-1-ethyl-1-nitroethylene (3b). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.00 (s, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.88 (q, J = 7.4 Hz, 2H), 2.40 (s, 3H), 1.28 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 152.4, 140.5, 133.2, 129.7 (2C), 129.7 (2C), 21.4, 20.7, 12.4.

(E)- 2- (4-methoxyphenyl)-1-ethyl-1-nitroethylene (3c). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.01 (s, 1H), 7.41 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 9 Hz, 2H), 3.86 (s, 3H), 2.89 (q, J = 7.4 Hz, 2H), 1.28 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 161.1, 151.2, 133.2, 131.8 (2C), 124.6, 114.5 (2C), 55.4, 20.8, 12.3.

(E)- 2- (4-fluorophenyl)-1-ethyl-1-nitroethylene (3d). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (s, 1H), 7.42 (ddd, J = 8.6, 5.0, 2.4 Hz, 2H), 7.18 – 7.12 (m, 2H), 2.85 (q, J = 7.4 Hz, 2H), 1.27 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 164.3, 162.6, 153.0, 131.9, 131.7 (d, JC-F =34.2 Hz), 128.4, 128.4, 116.3 (d, JC-F =27 Hz), 20.6, 12.4.

(E)- 2- (3-methoxyphenyl)-1-ethyl-1-nitroethylene (3e). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.98 (s, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.97 (dd, J = 8.3, 2.3 Hz, 1H), 6.94 – 6.92 (m, 1H), 3.84 (s, 3H), 2.87 (q, J = 7.4 Hz, 2H), 1.28 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 159.8, 153.5, 133.6, 133.0, 130.0, 121.9, 115.4, 115.1, 55.3, 20.8, 12.5.

(E)- 2- thiophenyl-1-ethyl-1-nitroethylene (3f). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.24 (s, 1H), 7.63 (d, J = 5.1 Hz, 1H), 7.42 (d, J = 3.6 Hz, 1H), 7.18 (dd, J = 5.1, 3.7 Hz, 1H), 3.02 (q, J = 7.4 Hz, 2H), 1.27 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 149.9, 134.9, 134.7, 131.7, 128.2, 126.7, 21.4, 11.6.

(E)- 2- thiophenyl-1-methyl-1-nitroethylene (3g). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.29 (s, 1H), 7.64 (d, J = 5.0 Hz, 1H), 7.43 (s, 1H), 7.19 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 144.3 , 135.1 , 134.7 , 131.7 , 128.1 , 127.2 , 14.2 .

(E)- 2- (2-methyl-thiophenyl)-1-ethyl-1-nitroethylene (3h). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.17 (s, 1H), 7.24 (d, J = 3.6 Hz, 1H), 6.88 – 6.81 (m, 1H), 2.98 (q, J = 7.4 Hz, 2H), 2.57 (s, 3H), 1.24 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 148.5, 147.9, 135.9, 132.6, 127.3, 126.7, 21.3, 15.8, 11.7.

(E)-3-(2-nitrobut-1-en-1-yl)thiophene (3i). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.02 (s, 1H), 7.61 – 7.58 (m, 1H), 7.44 (dd, J = 5.1, 2.9 Hz, 1H), 7.26 (dd, J = 4.6, 1.6 Hz, 1H), 2.92 (q, J = 7.4 Hz, 2H), 1.28 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 151.6, 133.4, 129.9, 127.8, 127.2, 127.0, 21.0, 12.1.

(E)- 2- naphthalenyl-1-ethyl-1-nitroethylene (5a). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.19 (s, 1H), 7.95 – 7.85 (m, 4H), 7.60 – 7.53 (m, 2H), 7.51 (dd, J = 8.5, 1.6 Hz, 1H), 2.96 (q, J = 7.4 Hz, 2H), 1.35 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 153.4, 133.6, 133.3, 133.1, 130.3, 129.8, 128.8, 128.5, 127.8, 127.6, 126.9, 126.0, 20.9, 12.6.

(E)- 2- naphthalenyl-1-methyl-1-nitroethylene (5b). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.25 (s, 1H), 7.96 – 7.83 (m, 5H), 7.60 – 7.54 (m, 2H), 7.52 (d, J = 8.5 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 147.8 , 133.7 , 133.6 , 133.0 , 130.5 , 129.8 , 128.6 , 128.5 , 127.8 , 127.6 , 126.9 , 126.4 , 14.2 .

(E)-1-(2-nitrobut-1-en-1-yl)naphthalene (5c). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.5 (s, 1H), 8.0 – 7.9 (m, 3H), 7.6 – 7.5 (m, 2H), 7.6 – 7.5 (m, 1H), 7.4 (d, J = 7.1 Hz, 1H), 2.8 (q, J = 7.4 Hz, 2H), 1.2 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 154.9, 133.4, 131.5, 131.4, 130.1, 129.8, 128.7, 127.0, 126.6, 126.4, 125.2, 124.1, 20.9, 12.8.

(E)-1-(2-nitro-1-phenylvinyl)isoquinoline (7a). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.63 (dd, J = 5.8, 2.6 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 2.6 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 5.6 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.40 – 7.32 (m, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 155.5 , 147.7 , 142.0 , 136.8 , 136.2 , 134.4 , 131.4 , 130.8 , 129.3(2C) , 128.2 , 128.0(2C) , 127.4 , 126.7 , 125.3 , 121.2 .

(E)-6,7-dimethoxy-1-(2-nitro-1-phenylvinyl)isoquinoline (7b). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.48 (d, J = 5.6 Hz, 1H), 7.81 (s, 1H), 7.62 (d, J = 5.7 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.40 – 7.34 (m, 4H), 7.15 (s, 1H), 6.94 (s, 1H), 4.04 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 153.4 , 152.4 , 151.0 , 147.4 , 140.7 , 136.8 , 134.5 , 133.5 , 131.4 , 129.3(2C) , 128.1(2C) , 122.6, 120.1 , 105.3 , 103.1 , 77.2 , 56.2 , 55.9 .

(E)-6,7-dimethoxy-1-(2-nitro-1-(p-tolyl)vinyl)isoquinoline (7c). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.47 (d, J = 5.6 Hz, 1H), 7.81 (s, 1H), 7.61 (d, J = 5.7 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 3H), 6.93 (s, 1H), 4.04 (s, 3H), 3.80 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 153.5 , 152.6 , 151.0 , 142.2 , 140.6 , 136.1 , 133.4 , 131.6 , 130.0(2C) , 128.1(2C) , 122.7 , 120.0 , 105.3 , 103.2 , 77.2 , 56.2 , 55.9 , 21.4 .

(E)-6,7-dimethoxy-1-(1-(4-methoxyphenyl)-2-nitrovinyl)isoquinoline (7d). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.47 (d, J = 5.6 Hz, 1H), 7.81 (s, 1H), 7.61 (d, J = 5.6 Hz, 1H), 7.27 (d, J = 9.0 Hz, 2H), 7.14 (s, 1H), 6.93 (s, 1H), 6.87 (d, J = 9.0 Hz, 2H), 4.04 (s, 3H), 3.81 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 162.4 , 153.4 , 152.9 , 150.9 , 140.9 , 134.9 , 133.3 , 129.9(2C) , 126.6 , 122.7 , 119.9 , 114.8(2C) , 105.3 , 103.2 , 56.2 , 56.0 , 55.5 .

Characterization Data for N-Heterocycles 3-phenylindole (2a). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.13 (s, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.73 (d, J = 7.9 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.43 (d, J = 8.1 Hz, 1H), 7.39 – 7.22 (m, 5H) ^{13}C NMR (151 MHz, Chloroform-d) δ 136.6, 135.5, 128.7 (2C), 127.4 (2C), 125.9, 125.7, 122.4, 121.8, 120.3, 119.8, 118.2, 111.4. HRMS (ESI): calcd. for [M+H]$^{+}$, 194.0891; found 194.1038.

6-methyl-3-p-tolylindole (2b). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.02 (s, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.21 (s, 1H), 7.05 (d, J = 8.1 Hz, 1H), 2.51 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 137.1, 135.4, 132.7, 132.1, 129.4 (2C), 127.2 (2C), 123.6, 121.9, 120.8, 119.5, 118.0, 111.2, 21.6, 21.1. HRMS (ESI): calcd. for [M+H]$^{+}$, 222.1204; found 222.1279.

6-methoxy-3-(4-methoxyphenyl)-1H-indole (2c). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.08 (s, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 2.4 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 2.2 Hz, 1H), 6.86 (dd, J = 8.7, 2.3 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 158.3, 156.8, 137.6, 128.6 (2C), 128.4, 120.6, 120.6, 120.0, 118.2, 114.5 (2C), 110.3, 95.0, 55.9, 55.6. HRMS (ESI): calcd. for [M+H]$^{+}$, 253.1103; found 253.1181.

6-fluoro-3-(4-fluorophenyl)-1H-indole (2d). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.18 (s, 1H), 7.77 (dd, J = 8.7, 5.3 Hz, 1H), 7.58 (ddd, J = 8.4, 5.2, 2.5 Hz, 2H), 7.28 (s, 1H), 7.15 (t, J = 8.7 Hz, 2H), 7.11 (dd, J = 9.4, 2.2 Hz, 1H), 6.97 (td, J = 9.1, 2.3 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 162.4, 160.9 (d, JC-F =61.2 Hz), 159.3, 136.5 (d, JC-F =49.2 Hz), 131.1 (d, JC-F =12.6 Hz), 128.9 (d, JC-F =31.2 Hz), 122.4, 121.7 (d, JC-F =39.6 Hz), 120.4 (d, JC-F =39.6 Hz), 117.6, 115.7 (d, JC-F =84.6 Hz), 109.2 (d, JC-F =24.5 Hz), 97.7 , 97.6. HRMS (ESI): calcd. for [M+H]$^{+}$, 230.0703; found 230.0782.

2-ethyl-1H-indole (4a). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.85 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.32 – 7.29 (m, 1H), 7.15 – 7.11 (m, 1H), 7.10 – 7.07 (m, 1H), 6.28 – 6.25 (m, 1H), 2.84 – 2.77 (m, 2H), 1.36 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 141.3, 135.8, 128.8, 120.9, 119.7, 119.6, 110.2, 98.7, 21.4, 13.2. HRMS (ESI): calcd. for [M+H]$^{+}$, 146.0891; found 146.0968.

2-ethyl-6-methyl-1H-indole (4b). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.72 (d, J = 23.7 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.09 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.18 (s, 1H), 2.77 (q, J = 7.5 Hz, 2H), 2.44 (s, 3H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 140.6, 136.3, 130.6, 126.5, 121.2, 119.4, 110.3, 98.4, 21.7, 21.4, 13.2. HRMS (ESI): calcd. for [M+H]$^{+}$, 160.1048; found 160.1127.

2-ethyl-6-methoxy-1H-indole (4c). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.76 (s, 1H), 7.40 (d, J = 8.5 Hz, 1H), 6.81 (s, 1H), 6.76 (d, J = 8.5 Hz, 1H), 6.17 (s, 1H), 3.84 (s, 3H), 2.75 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 155.7 , 140.2 , 136.5 , 123.0 , 120.2 , 109.0 , 98.3 , 94.5 , 55.7 , 21.4 , 13.2 . HRMS (ESI): calcd. for [M+H]$^{+}$, 176.0997; found 176.1078.

2-ethyl-6-fluoro-1H-indole (4d). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.84 (s, 1H), 7.42 (dd, J = 8.6, 5.4 Hz, 1H), 6.98 (dd, J = 9.6, 2.1 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.21 (s, 1H), 2.77 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 160.1, 158.5, 141.7 (d, JC-F =3.0 Hz), 135.7 (d, JC-F =12.1 Hz), 125.2, 120.3 (d, JC-F =10.6 Hz), 108.1 (d, JC-F =6.0 Hz), 98.6, 96.8 (d, JC-F =24.7 Hz), 21.4, 13.1. HRMS (ESI): calcd. for [M+H]$^{+}$, 164.0797; found 164.0874.

2-ethyl-7-methoxy-1H-indole (4e). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.10 (s, 1H), 7.14 (d, J = 7.9 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 6.22 (d, J = 1.2 Hz, 1H), 3.95 (s, 3H), 2.79 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 145.5, 140.9, 130.0, 126.0, 119.8, 112.7, 101.1, 99.0, 55.3, 21.4, 13.4. HRMS (ESI): calcd. for [M+H]$^{+}$, 176.0997; found 176.1079.

5-ethyl-4H-thieno[3,2-b]pyrrole (4f). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.83 (s, 1H), 7.19 (d, J = 5.1 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.77 (d, J = 3.4 Hz, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 137.4, 130.4, 126.6, 126.1, 124.2, 113.1, 19.5, 14.5. HRMS (ESI): calcd. for [M+H]$^{+}$, 152.0456; found 152.0539.

5-methyl-4H-thieno[3,2-b]pyrrole (4g). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (s, 1H), 7.20 (d, J = 5.1 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.78 (d, J = 3.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 137.4 , 126.7 , 126.0 , 124.3 , 124.1 , 113.9 , 12.0 . HRMS (ESI): calcd. for [M+H]$^{+}$, 138.0299; found 138.0465.

5-ethyl-2-methyl-4H-thieno[3,2-b]pyrrole (4h). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.83 (s, 1H), 6.58 (s, 1H), 6.08 (s, 1H), 2.72 (q, J = 7.6 Hz, 2H), 2.51 (s, 3H), 1.28 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 138.1, 136.6, 121.8, 109.3, 97.7, 29.7, 21.7, 16.4, 13.8. HRMS (ESI): calcd. for [M+H]$^{+}$, 166.0612; found 166.0684.

5-ethyl-6H-thieno[2,3-b]pyrrole (4i). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.01 (s, 1H), 6.94 (d, J = 5.2 Hz, 1H), 6.78 (d, J = 5.2 Hz, 1H), 6.19 – 6.15 (m, 1H), 2.74 (q, J = 7.5 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 141.1, 131.9, 131.1, 128.5, 125.9, 122.8, 117.5, 116.9, 97.8, 44.0, 35.2, 21.8, 13.7. HRMS (ESI): calcd. for [M+H]$^{+}$, 152.0456; found 152.0531.

2-ethyl-1H-benzo[f]indole (6a). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.59 (s, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.53 – 7.48 (M, 2H), 7.43 – 7.37 (m, 1H), 6.41(s, 1H), 2.91 (q, J = 7.6 Hz, 2H), 1.42 (t, J = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 139.4, 129.9, 128.9, 125.2, 124.6, 123.2, 121.4, 120.3 (2C), 119.0, 100.5 (2C), 21.5, 13.5. HRMS (ESI): calcd. for [M+H]$^{+}$, 196.1048; found 196.1132.

2-methyl-1H-benzo[f]indole (6b). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.58 (s, 1H), 7.92 (dd, J = 14.1, 8.2 Hz, 2H), 7.64 (d, J = 8.5 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 6.37 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 133.0 , 130.1 , 129.8 , 128.9 , 125.2 , 124.8 , 123.2 , 121.3 , 120.3 , 120.2 , 119.0 , 102.1 , 13.8 . HRMS (ESI): calcd. for $[M+H]^+$, 182.0891; found 182.1036.

2-ethyl-3H-benzo[e]indole (6c). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.19 (d, J = 7.9 Hz, 2H), 7.89 (d, J = 8.1 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.46 (d, J = 8.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 6.80 (s, 1H), 2.89 (q, J = 7.5 Hz, 2H), 1.41 (td, J = 7.6, 1.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 139.4, 131.8, 129.1, 128.4, 127.8, 125.4, 123.5, 123.0, 122.9, 121.7, 112.3, 98.2, 21.5, 13.5. HRMS (ESI): calcd. for $[M+H]^+$, 196.1048; found 196.1124.

1-(1H-indol-3-yl)isoquinoline (8a). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.28 (d, J = 7.4 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.92 (s, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 7.9 Hz, 2H), 7.54 – 7.46 (m, 3H), 7.46 – 7.41 (m, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 141.8 , 134.0 , 133.7 , 130.0(2C) , 129.4 , 128.7 (2C) , 127.8 , 127.4 , 127.3 , 127.2 , 126.6 , 125.1 , 123.4 , 116.8 , 112.5 . HRMS (ESI): calcd. for $[M+H]^+$, 245.1000; found 245.1206.

1-(1H-indol-3-yl)-6,7-dimethoxyisoquinoline (8b). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.22 (d, J = 7.3 Hz, 1H), 7.91 (s, 1H), 7.58 (d, J = 7.9 Hz, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.07 (s, 1H), 6.93 (d, J = 7.3 Hz, 1H), 3.98 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 149.7 , 149.1 , 141.4 , 134.3 , 133.7 , 130.3(2C) , 128.5(2C) , 127.3 , 125.0 , 124.1 , 119.3 , 115.1 , 111.8 , 107.6 , 104.7 , 55.9 , 55.6 . HRMS (ESI): calcd. for $[M+H]^+$, 305.1212; found 305.1414.

6, 7-dimethoxy-1-(6-methyl-1H-indol-3-yl)isoquinoline (8c). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.21 (d, J = 7.3 Hz, 1H), 7.88 (s, 1H), 7.47 (d, J = 7.8 Hz, 3H), 7.30 (d, J = 7.7 Hz, 2H), 7.07 (s, 1H), 6.92 (d, J = 7.3 Hz, 1H), 3.98 (s, 3H), 3.61 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 149.6 , 149.1 , 141.5 , 137.0 , 133.6 , 131.2 , 130.2(2C) , 129.1(2C) , 125.1 , 124.0 , 119.5 , 115.0 , 111.7 , 107.5 , 104.8 , 55.9 , 55.6 , 21.3 . HRMS (ESI): calcd. for $[M+H]^+$, 319.1368; found 319.1573.

6, 7-dimethoxy-1-(6-methoxy-1H-indol-3-yl)isoquinoline (8d). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.21 (d, J = 7.3 Hz, 1H), 7.87 (s, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.44 (s, 1H), 7.07 (s, 1H), 7.03 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 7.3 Hz, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.62 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 159.0 , 149.6 , 149.1 , 141.4 , 133.7 , 131.5(2C) , 126.4 , 125.1 , 124.0 , 119.5 , 114.6 , 113.9(2C) , 111.7 , 107.6 , 104.6 , 55.9 , 55.7 , 55.4 . HRMS (ESI): calcd. for $[M+H]^+$, 335.1317; found 335.1527.

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Keywords: Nitroalkenes • *N*-Heterocycles • Molybdenum Hexacarbonyl • Reductive Cyclization

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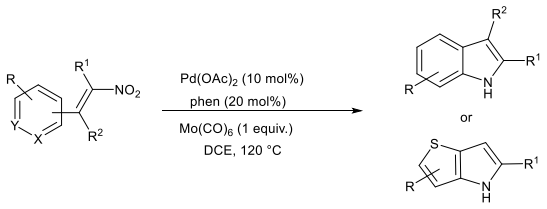

The development of a method that uses molybdenum hexacarbonyl [$Mo(CO)_6$] as carbon monoxide (CO) surrogate for the palladium-catalyzed reductive cyclization of nitroalkenes into indoles or thienopyrroles is reported. Several types of nitroalkenes could be transformed into the desired products in excellent yields and in most case got higher yields and complete regioselectivities than those previously reported with palladium/CO system.

Key Topic* Nitroalkenes • *N*-Heterocycles • Molybdenum Hexacarbonyl • Reductive Cyclization

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Page No. – Page No.

Synthesis of *N*-Heterocycles by Reductive Cyclization of Nitroalkenes using Molybdenum Hexacarbonyl as Carbon Monoxide Surrogate