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Friedel-Crafts Alkylation of Indoles with Nitroalkenes Catalyzed by Zn(II)-Thiourea Complex

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Friedel-Crafts alkylation of indoles with nitroalkenes catalyzed by a novel Zn(II)-thiourea complex has been developed. The remarkable advantages of this reaction are mild reaction conditions, simple workup procedure, high yield of products and the use of ethanol as acceptable solvent.

Keywords Friedel-Crafts alkylation, indole, nitroalkene, thiourea, catalysis

Introduction

The Friedel-Crafts reaction is powerful carbon-carbon forming processes,[1] and the Friedel-Crafts alkylation reaction of arenes with electron-deficient alkenes is one of the most important organic transformations.[2] Among the acceptors, nitroalkenes are very attractive, since the nitro moiety is a strong electron-withdrawing group that can be readily transformed into a range of different functionalities, which lead to important building blocks and products.[3] In addition, indole and many of its derivatives are found widely in variety of natural plants,[4] which can provide access to valuable precursors to compounds of biological[5] and medicinal interest,[6] such as cytotoxic, antioxidative, insecticidal activities and antibiotics in pharmaceuticals.[7] Therefore, using nitroalkenes as substrates to achieve Friedel-Crafts alkylation of indoles has been paid considerable attention since the nitro functional group is a strongly electron-withdrawing group that can be readily transformed into an amino functional group.[8]

Owing to the importance of this transformation, several efficient complexes derived from ligands and metal salts have been successfully applied in Friedel-Crafts reaction of heterocycles with electron-deficient olefins in some pioneering reports.[9] And a wide variety of metal salts such as $Yb(OTf)_3$-$Sc_2(CO_3)_3$, $CeCl_3$•$7H_2O$-NaI-SiO_2 and iodine were used for this purpose.[10] On the other hand, in recent years, small organic molecules,[11] such as thiourea, were also found to catalyze the above-mentioned reaction. However, in these pioneer reports, tedious workup procedures, severity of reaction condition, and difficulties in product isolation obstacle the simple preparation of such kinds of products, thus the Friedel-Crafts alkylation of indole needs to undergo continuous development.[12]

The research for achieving a general method for conjugative addition of indoles to nitroalkenes remains in great demand.[13] Herein we reveal a new, mild and easy procedure for the Friedel-Crafts alkylation of indole with nitroalkene in acceptable medium, catalyzed by Zn(II)-thiourea complex.

Results and Discussion

The ligand **L** (Scheme 1) was synthesized from the reaction between diamine thiourea (1.0 mmol) and 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (2.1 mmol) in ethanol in the presence of glacial acetic acid at refluxing for 5 h in 74% yields. Eventually, the imines may be crystallized from ethanol. The thione group is relatively unstable in the monomeric forms and tends to turn to the more stable thiol form by enethiolization in solution (Scheme 1).

Selection of Lewis acids

Our research began with the optimization of the model reaction (Scheme 2) between indole (**1a**) and nitroalkene (**2a**). **L** was subsequently investigated as the only catalyst in the reaction (Table 1, Entry 2). In addition, the reactivity of a variety of metal salts-ligand complexes-based catalysts, which were generated in situ from metal salts and **L**, were also evaluated as shown in

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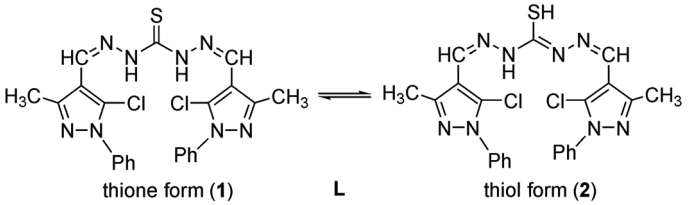
Scheme 1



Scheme 2 Friedel-Crafts alkylation of indole with nitroalkene

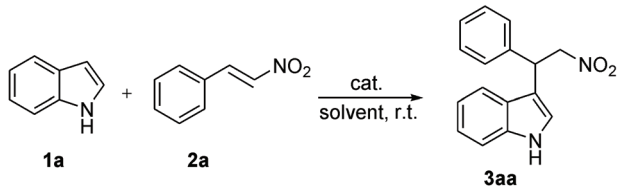


Table 1 Friedel-Crafts alkylation of indole **1a** with nitroalkene **2a** catalyzed by M-**L**[a]

Entry	M-Ligand	Time/h	Yield[b]/%
1		48	0
2	**L**	48	trace
3	$Zn(ClO_4)_2$	48	26
4	**L**-$Cu(ClO_4)_2$	48	56
5	**L**-$Zn(ClO_4)_2$	48	65
6	**L**-$Co(ClO_4)_2$	48	0
7	**L**-$CuCl_2$	48	trace
8	**L**-$ZnCl_2$	48	trace
9	**L**-$ZnSO_4$	48	35
10	**L**-$CuSO_4$	48	24
11	**L**-$MnAc_2$	48	21

[a] All reactions were carried out in C_2H_5OH using **L** (5 mol%), metal salt (5 mol%) or metal salts-**L** (5 mol%) as catalyst at room temperature. Indole (1 mmol), *β*-nitroalkene (0.5 mmol). [b] Isolated yield by column chromatography.

the illustrate reaction, and corresponding results were summarized in Table 1, Entries 4—11. While in the presence of Zn(II)-**L** complex, indole reacted with nitroalkene smoothly, giving the product 3-(2-nitro-1-phenyethyl)-1*H*-indole (**3aa**) in good yields, 65% (Table 1, Entry 5).

Effect of solvent and catalyst loading

With the best catalyst being identified, we next examined the solvent such as ethanol, toluene, THF, CH_2Cl_2 and so on. Ethanol is the best solvent to provide Friedel-Crafts alkylation product in high yield (up to 65%). Meanwhile, the catalyst loading also played a significant role in activity. For example, when the amount of catalyst was increased from 5 mol% to 10 mol%, 89% yield was achieved (Table 2, Entry 8). Increasing the catalyst loading from 10 mol% to 15 mol% did not result in loss in the yield (Table 2, Entry 9).

Table 2 Solvent and catalyst loading effect in the Friedel-Crafts reaction of indole with nitroalkene[a]

Entry	Cat./mol%	Solvent	Yield[b]/%
1	5%	Hexane	0
2	5%	$CHCl_3$	trace
3	5%	CH_3CN	55
4	5%	THF	53
5	5%	CH_2Cl_2	trace
6	5%	toluene	63
7	5%	CH_3CH_2OH	65
8	10%	CH_3CH_2OH	89
9	15%	CH_3CH_2OH	88

[a] All reactions were carried out using Zn(II)-thiourea complex as catalyst at room temperature. Indole (1 mmol), nitroalkene (0.5 mmol). [b] Isolated yield by column chromatography.

Catalyst characterization

The Zn(II)-thiourea complex interaction of the catalytic system was studied by XRD and FT-IR analysis. XRD spectra (Figure 1) of the **L** before and after Zn loading also showed a change. In addition, IR spectrum (Figure 2) of the complex showed a strong absorption band at 1067 cm^{-1}, which was attributed to the formation of C═N. These variations could confirm the coordination of Zn ion with the azomethine nitrogen of the imine ligand.[14]

Effect of substituent

With the optimized reaction conditions in hand, we started to investigate the substrate scope for the Friedel-Crafts alkylation of nitroalkenes and indoles. The representative results are summarized in Table 3. In

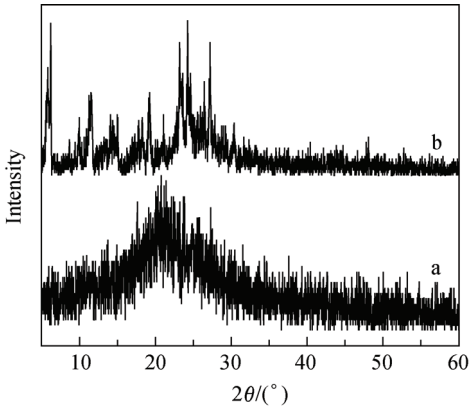


Figure 1 XRD patterns of (a) **L** and (b) Zn(II)-thiourea complex.

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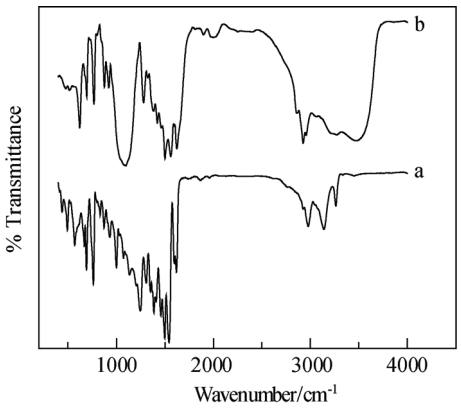

Figure 2 FT-IR spectra of (a) **L** and (b) Zn(II)-thiourea complex.

Scheme 3 Friedel-Crafts alkylation of indoles with various substituted nitroalkenes

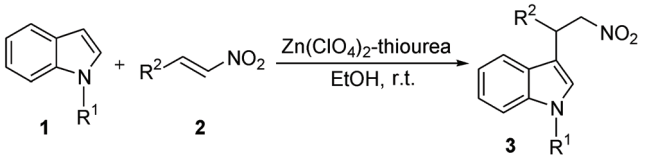

Table 3 Friedel-Crafts alkylation reaction of indoles with nitroalkenes using Zn(II)-thiourea complex[a]

Entry	R^1	R^2	*t*/h	Product	Yield[b]/%
	H (**1a**)	Ph (**2a**)	48	**3aa**	89
2	H (**1a**)	4-Cl-C_6H_4 (**2b**)	48	**3ab**	87
3	H (**1a**)	4-Br-C_6H_4 (**2c**)	48	**3ac**	90
4	H (**1a**)	2,4-Cl_2-C_6H_3 (**2d**)	48	**3ad**	94
5	H (**1a**)	2-NO_2-C_6H_4 (**2e**)	48	**3ae**	91
6	H (**1a**)	4-N(CH_3)$_2$-C_6H_4 (**2f**)	48	**3af**	92
7	H (**1a**)	2-furyl (**2g**)	48	**3ag**	80
8	H (**1a**)	4-Me-C_6H_4 (**2h**)	48	**3ah**	93
9	H (**1a**)	4-MeO-C_6H_4 (**2i**)	48	**3ai**	82
10	H (**1a**)	3-NO_2-C_6H_4 (**2j**)	48	**3aj**	95
11	CH_3 (**1b**)	4-MeO-C_6H_4 (**2i**)	48	**3bi**	81
12	CH_3 (**1b**)	Ph (**2a**)	48	**3ba**	84
13	CH_3 (**1b**)	4-N(CH_3)$_2$-C_6H_4 (**2f**)	48	**3bf**	85
14	CH_3 (**1b**)	4-Me-C_6H_4 (**2h**)	48	**3bh**	86
15	CH_3 (**1b**)	2-furyl (**2g**)	48	**3bg**	61
16	CH_2-CH_3 (**1c**)	4-N(CH_3)$_2$-C_6H_4 (**2f**)	48	**3cf**	73

[a] All reactions were carrided out using Zn(II)-thiourea (10 mol%) as catalyst in EtOH at room temperature, indoles (1 mmol), nitroalkenes (0.5 mmol). All the products were characterized by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis. [b] Isolated yield by column chromatography.

general, nitroalkenes tolerated substitutions at any position of the aromatic ring, and both electron-withdrawing and electron-donating groups were comparable. nitroalkenes containing electron-withdrawing groups on the aromatic ring had a slightly higher reaction rate than those with electron-donating groups. For example, the electron-withdrawing groups on the aromatic ring provided the highest yield with **1a**, giving 94%, 91% and 95% of **3ad**, **3ae** and **3aj** (Table 3, Entries 4—5, 10) respectively, and the electron-donating group on the aromatic ring afforded good yield with **1a**, giving 82% of **3ai**. The indole with methyl or ethyl on the 1-position also worked well with nitroalkenes, and 73%—86% yields were obtained (Table 3, Entries 11—14, 16). The moderate to good yields were afforded when nitroalkenes contained furan ring (Table 3, Entries 7, 15).

Conclusions

In conclusion, we have described an efficient protocol for the synthesis of wide range of products (**3aa**—**3cf**) in presence of thiourea-Zn(II) as catalyst in ethanol. Mild reaction condition, simple workup procedure, easy isolation are the best features in this process. Further work is in progress to extrapolate the catalytic activity of thiourea ligand to other organic transformation.

Experimental

Chemicals and apparatus

All common reagents and solvents were used as obtained from commercial suppliers without further purification. Various substituted nitroalkenes were synthesized by aldehyde and CH_3NO_2. Purification of reaction products was carried out by column chromatography using Qingdao silica gel (300—400 mesh). Analytical thin-layer chromatography (TLC) was performed on silica gel GF_{254} (Qingdao, China) with ethyl acetate and petroleum ether (60—90 ℃) and detection by UV light or iodine vapor. Melting points were recorded on an Elemental digital melting points apparatus and were uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN INOVA 400 MHz FT-NMR spectrometer, using $CDCl_3$ or DMSO as solvent and TMS as internal reference. The IR spectra were recorded on a Bruker Equinox 55 FT-IR. Elemental analyses were performed on a Thermo Flash EA1112.

General procedure for preparation of product

To a solution of nitroalkenes (0.5 mmol) in ethanol (5 mL), indole (1 mmol) was added followed by thiourea ligand (10 mol%) and metal salt (10 mol%) at room temperature. The reaction mixture was stirred continuously. After complete conversion as indicated by TLC, the solution was diluted with saturated sodium chloride solution and extracted with ethyl acetate (5 mL×3), dried by $MgSO_4$, then solvent was removed under reduced pressure to give a crude product which was purified by column chromatography on silica gel (ethyl acetate/petroleum ether 1∶5) to furnish the products **3aa**—**3cf**.

Spectral data for compounds

1,1'-[(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazol-4-ylmethylene)-amino]-thiourea Yellow powder; m.p. 236—238 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.55 (s, 3H), 2.68 (s, 3H), 7.44—7.68 (m, 10H, Ar-H), 8.01 (s, 1H), 8.05 (s, 1H), 10.19 (s, 1H), 10.64 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.78, 112.9, 125.1, 127.5, 128.8, 129.4, 135.3, 137.4, 148.6, 177.7; IR (KBr) ν: 3260, 3134, 2960, 1620, 1543, 1500, 1385, 1004, 763 cm^{-1}. Anal. calcd for $C_{23}H_{20}Cl_2N_8S$: C 54.01, H 3.94, N 21.91; found C 54.11, H 3.95, N 21.94.

3-(2-Nitro-1-phenyl-ethyl)-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.95 (dd, J=8.4, 12.4 Hz, 1H), 5.07 (dd, J=8.0, 12.4 Hz, 1H), 5.20 (t, J=8.0 Hz, 1H), 7.03—7.46 (m, 10H, Ar-H), 8.11 (brs, NH); IR (KBr) ν: 3660, 3421, 2927, 1602, 1550, 1457, 1378, 1103, 745 cm^{-1}. Anal. calcd for $C_{16}H_{14}N_2O_2$: C 72.16, H 3.30, N 10.52; found C 72.21, H 3.24, N 10.59.

3-[1-(4-Chloro-phenyl)-2-nitro-ethyl]-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.91 (dd, J=8.8, 12.4 Hz, 1H), 5.05 (dd, J=7.2, 12.4 Hz, 1H), 5.17 (t, J=8.0 Hz, 1H), 7.01—7.42 (m, 9H, Ar-H), 8.10 (brs, NH); IR (KBr) ν: 3420, 3059, 2921, 1620, 1549, 1458, 1378, 1092, 746 cm^{-1}. Anal. calcd for $C_{16}H_{13}ClN_2O_2$: C 63.90, H 4.36, N 9.32; found C 63.93, H 4.30, N 9.39.

3-[1-(4-Bromo-phenyl)-2-nitro-ethyl]-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.91 (dd, J=8.8, 12.4 Hz, 1H), 5.05 (dd, J=7.6, 12.4 Hz, 1H), 5.05 (t, J=8.0 Hz, 1H), 7.01—7.46 (m, 9H, Ar-H), 8.11 (brs, NH); IR (KBr) ν: 3421, 3058, 2919, 1620, 1551, 1488, 1378, 1104, 745 cm^{-1}. Anal. calcd for $C_{16}H_{13}BrN_2O_2$: C 55.67, H 3.80, N 8.12; found C 55.55, H 3.88, N 8.20.

3-[1-(2,4-Dichloro-phenyl)-2-nitro-ethyl]-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.93 (dd, J=7.2, 12.8 Hz, 1H), 4.99 (dd, J=8.4, 12.8 Hz, 1H), 5.69 (t, J=8.0 Hz, 1H), 7.04—7.47 (m, 8H, Ar-H), 8.13 (brs, NH); IR (KBr) ν: 3419, 3060, 2923, 1620, 1551, 1469, 1378, 1103, 745 cm^{-1}. Anal. calcd for $C_{16}H_{12}Cl_2N_2O_2$: C 57.33, H 3.61, N 8.36; found C 57.29, H 3.77, N 8.19.

3-[2-Nitro-1-(2-nitro-phenyl)-2-nitro-ethyl]-1*H*-indole[9] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.24 (dd, J=8.4, 13.2 Hz, 1H), 5.29 (dd, J=7.2, 13.2 Hz, 1H), 6.04 (t, J=8.0 Hz, 1H), 7.18—7.68 (m, 9H, Ar-H), 8.35 (brs, NH); IR (KBr) ν: 3421, 3062, 2923, 1620, 1551, 1459, 1355, 1106, 745 cm^{-1}. Anal. calcd for $C_{16}H_{13}N_3O_4$: C 61.73, H 4.21, N 13.50; found C 61.57, H 4.22, N 13.57.

{4-[1-(1*H*-Indol-3-yl)-2-nitro-ethyl]-phenyl}-dimethylamine[3a] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.92 (s, 6H), 4.88 (dd, J=8.0, 12.0 Hz, 1H), 5.03 (dd, J=8.0, 12.0 Hz, 1H), 5.10 (t, J=8.0 Hz, 1H), 6.66—7.47 (m, 9H, Ar-H), 8.05 (brs, NH); IR (KBr) ν: 3429, 3062, 2913, 1544, 1520, 1456, 1379, 1104, 741 cm^{-1}. Anal. calcd for $C_{18}H_{19}N_3O_2$: C 69.88, H 6.19, N 13.58; found C 69.92, H 6.24, N 13.52.

3-(1-Furan-2-yl-2-nitro-ethyl)-1H-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.91 (dd, J=7.6, 12.4 Hz, 1H), 5.05 (dd, J=8.0, 12.0 Hz, 1H), 5.24 (t, J=8.0 Hz, 1H), 6.16—6.18 (m, 1H), 6.30—6.32 (m, 1H), 7.09—7.56 (m, 6H, Ar-H), 8.11 (brs, NH); IR (KBr) ν: 3420, 3058, 2919, 1620, 1555, 1458, 1378, 1013, 743 cm^{-1}. Anal. calcd for $C_{14}H_{12}N_2O_3$: C 65.62, H 4.72, N 10.93; found C 65.54, H 4.85, N 11.03.

3-(2-Nitro-1-*p*-tolylethyl)-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.30 (s, 1H), 4.90 (dd, J=8.4, 12.4 Hz, 1H), 5.03 (dd, J=7.6, 12.4 Hz, 1H), 5.14 (t, J=8.0 Hz, 1H), 6.98—7.45 (m, 9H, Ar-H), 8.04 (brs, NH); IR (KBr) ν: 3421, 3054, 2921, 1549, 1551, 1458, 1379, 1101, 745 cm^{-1}. Anal. calcd for $C_{17}H_{16}N_2O_2$: C 72.84, H 5.75, N 9.99; found C 72.74, H 5.73, N 10.04.

3-[1-(4-Methoxy-phenyl)-2-nitro-ethyl]-1*H*-indole[2b] White powder; m.p. 149—150 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.77 (s, 3H), 4.90 (dd, J=8.4, 12.0 Hz, 1H), 5.05 (dd, J=7.6, 12.0 Hz, 1H), 5.14 (t, J=8.0 Hz, 1H), 6.83—7.44 (m, 9H, Ar-H), 8.02 (brs, NH); IR (KBr) ν: 3409, 3056, 2926, 1549, 1510, 1457, 1246, 1180, 748 cm^{-1}. Anal. calcd for $C_{17}H_{16}N_2O_3$: C 68.91, H 5.44, N 9.45; found C 69.01, H 5.48, N 9.53.

3-[2-Nitro-1-(3-nitro-phenyl)-ethyl]-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.99 (dd, J=8.8, 12.8 Hz, 1H), 5.11 (dd, J=6.8, 12.8 Hz, 1H), 5.30 (t, J=7.2 Hz, 1H), 7.07—8.14 (m, 9H, Ar-H), 8.22 (brs, NH); IR (KBr) ν: 3419, 3063, 2921, 1553, 1526, 1378, 1350, 1101, 748 cm^{-1}. Anal. calcd for $C_{16}H_{13}N_3O_4$: C 61.73, H 4.21, N 13.50; found C 61.77, H 4.19, N 13.61.

3-[1-(3-Methoxy-phenyl)-2-nitro-ethyl]-1-methyl-1*H*-indole[3a] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.72 (s, 3H), 3.75 (s, 3H), 4.89 (dd, J=8.4, 12.4 Hz, 1H), 5.03 (dd, J=7.6, 12.4 Hz, 1H), 5.13 (t, J=8.0 Hz, 1H), 6.83—7.45 (m, 9H, Ar-H); IR (KBr) ν: 3052, 2930, 1551, 1511, 1468, 1376, 1249, 1178, 743 cm^{-1}. Anal. calcd for $C_{18}H_{18}N_2O_3$: C 69.66, H 5.85, N 9.03; found C 69.57, H 5.79, N 9.02.

1-Methyl-3-(2-nitro-1-phenyl-ethyl)-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 4.93 (dd, J=8.4, 12.4 Hz, 1H), 5.05 (dd, J=8.4, 12.4 Hz, 1H), 5.19 (t, J=4.4 Hz, 1H), 7.05—7.46 (m, 9H, Ar-H); IR (KBr) ν: 3058, 2927, 1552, 1475, 1337, 1332, 1248, 1132, 744 cm^{-1}. Anal. calcd for $C_{17}H_{16}N_2O_2$: C 77.84, H 5.75, N 9.99; found C 77.87, H 5.69, N 9.87.

{4-1-[1-(3-Ethyl-1*H*-indole-3-yl)-2-nitro-ethyl]-1-phenyl}-dimethyl-amine Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.91 (s, 6H), 3.69 (s, 3H), 4.91(dd, J=8.0, 12.4 Hz, 1H), 5.05 (dd, J=7.6, 12.4 Hz, 1H), 5.12 (t, J=7.6 Hz, 1H), 6.76—7.46 (m, 9H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 32.9, 40.5, 40.8, 79.9, 109.4, 112.7, 113.5, 119.1, 119.3, 122.0, 126.3, 126.7, 128.4, 137.2, 149.8; IR (KBr) ν: 3049, 2915, 1614, 1550, 1522, 1377, 1131, 1063, 742 cm^{-1}. Anal. calcd for $C_{19}H_{21}N_3O_2$: C 70.57, H 6.55, N 12.99; found C 70.55, H 6.59, N 12.91.

1-Methyl-3-(2-nitro-1-*p*-tolyl-ethyl)-1*H*-indole[2b] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.30 (s, 3H), 3.72 (s, 3H), 4.89 (dd, J=8.8, 12.4 Hz, 1H), 5.02 (dd, J=8.0, 12.4 Hz, 1H), 5.13 (t, J=8.0 Hz, 1H), 6.84—7.46 (m, 9H, Ar-H); IR (KBr) ν: 3054, 2919, 1615, 1553, 1475,

1377, 1013, 916, 741 cm^{-1}. Anal. calcd for $C_{18}H_{18}N_2O_2$: C 73.45, H 6.16, N 9.52; found C 73.47, H 6.13, N 9.58.

3-(1-Furan-2-yl-2-nitro-ethyl)-1-methyl-1*H*-indole Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.72 (s, 3H), 4.85 (dd, J=7.2, 12.4 Hz, 1H), 5.02 (dd, J=8.0, 12.4 Hz, 1H), 5.23 (t, J=8.0 Hz, 1H), 6.14—6.16 (m, 1H), 6.29—6.31 (m, 1H), 6.96—7.55 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 32.7, 41.2, 79.7, 109.6, 113.0, 119.1, 119.3, 122.2, 126.4, 126.6, 127.7, 129.6, 136.5, 137.1, 137.3; IR (KBr) v: 3024, 2962, 1552, 1474, 1377, 1261, 1090, 1016, 742 cm^{-1}. Anal. calcd for $C_{15}H_{14}N_2O_3$: C 66.66, H 5.22, N 10.36; found C 66.73, H 5.29, N 10.41.

{4-[1-(1-Ethyl-1*H*-indol-3-yl)-2-nitro-ethyl]-phenyl-dimethyl-amine[9] Oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.43 (t, J=7.2 Hz, 3H), 2.92 (s, 6H), 3.72 (q, J=7.2 Hz, 2H), 4.87 (dd, J=8.4, 12.0 Hz, 1H), 5.02 (dd, J=7.6, 12.0 Hz, 1H), 5.07 (q, J=8.0 Hz, 1H), 6.66—7.48 (m, 9H, Ar-H); IR (KBr) v: 2977, 2921, 1551, 1522, 1470, 1378, 1353, 1162, 742 cm^{-1}. Anal. calcd for $C_{20}H_{23}N_3O_2$: C 71.19, H 6.87, N 12.45; found C 71.23, H 6.89, N 12.38.

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