Synthesis of *N*-Alkylated Indolines and Indoles from Indoline and Aliphatic Ketones

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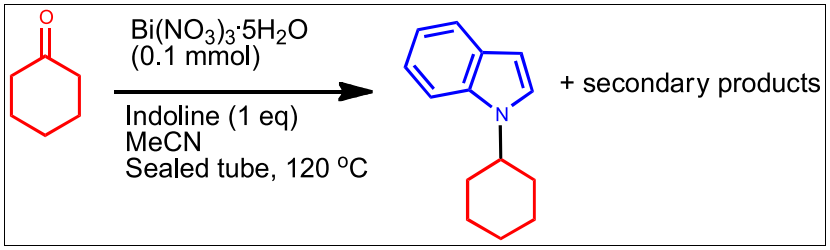

A survey of redox aminations of indoline with aliphatic ketones using bismuth nitrate as catalyst is described. A reaction of an equivalent amount of indoline and aliphatic cyclic and acyclic ketones provides a mixture of excessive alkylated indole derivatives over typically redox isomerization and reductive alkylation pathways while using of the five equivalent of indoline provides *N*-alkylated indolines as a reductive alkylation product. The desired *N*-alkyl indoles from the oxidation of *N*-alkyl indolines were obtained in excellent yields.

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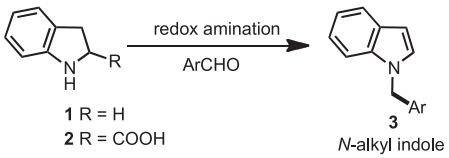
INTRODUCTION

Many natural and synthetic biologically active compounds containing indole skeletons are being used as therapeutic agents [1–5]. Therefore, a great deal of attention have been continued to develop innovative synthetic strategies for the decoration of indole cores. Indole is an electron-rich heteroaromatic system, and although various methods for its alkylation at the C3-position are well established, its C2-alkylation remains to be a difficult task [6,7]. As an alternative solution to this problem, we have developed an indirect two-step protocol for C2-alkylation, in which the first step is an alkylation of 4,7-dihydroindole as a Michael donor and the second one is the oxidation of C2-alkylated 4,7-dihydroindole [8,9]. *N*-Alkyl indoles are also found in numerous natural products and pharmaceutical compounds [10–14]. However, regioselective functionalization at the *N*-position of indoles is still unexplored [15,16]. Recently, the redox amination has become a very powerful trend in C–N bond forming reactions applied to the synthesis of *N*-alkyl pyrroles and *N*-alkyl indoles [17]. The reactions of aryl aldehydes with indoline (**1**) and 2-carboxyindoline (**2**) have been used as precursors of the *N*-alkyl indoles (Scheme 1) [18–22]. Pan and Siedel groups have reported independently on the Brønsted acid-catalyzed intermolecular redox amination of indoline with benzaldehydes (or aryl aldehydes) under reflux and microwave irradiation conditions, respectively, to yield *N*-benzyl indoles **3** [23–27]. In another set of the research of Pan group, the evaluation of salicylaldehydes as an electrophile in the standard process gave *N*-alkylindolines instead of the expected *N*-alkyl indoles.

Scheme 1. Present synthesis of *N*-alkyl indoles via redox amination.



However, the mechanism of these redox aminations is still controversial. Computational studies conducted at the second-order Møller–Plesset perturbation theory (MP2) and density functional theory levels have shown that the one-step direct 1,3-hydrogen shift, which was proposed earlier for the redox process, was not valid because of its very high activation energy requirement [28]. The results suggest that the process involving the formation of the acetic acid-assisted azomethine ylide intermediate should be the most likely process.

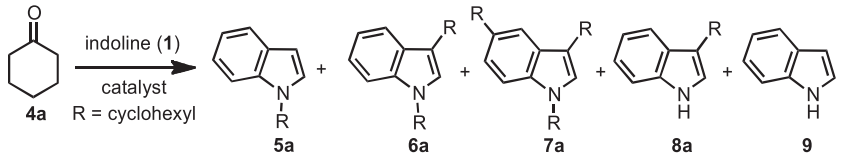
Although the previous studies to generate *N*-alkyl indoles over the redox amination process from indolines are the powerful method, they are restriction with aryl or nonenolisable aldehydes. However, the synthetic and mechanistic potentials of ketones to engage in redox amination reactions of indoline have not yet been evaluated. Here, we report on our premier results of the bismuth nitrate-catalyzed redox amination of the enolisable cyclic and acyclic ketones with indoline.

RESULTS AND DISCUSSIONS

To optimize the redox amination feasibility between aliphatic ketones and indoline, at the start of our

Table 1

Studies on optimization for the reaction of indoline (**1**; 1 equivalent) with cyclohexanone (**6**; 1 equivalent).



			Products (yield%)				
Entry	Catalyst	Conditions	**5a**	**6a**	**7a**	**8a**	**9**
1	$Bi(NO_3)_3{\cdot}5H_2O$	rt, CH_2Cl_2	—	—	—	—	—
2		80°C, MeCN	—	—	—	—	—
3		120°C, MeCN (or PhMe)	38	13	12	13	4
4		140°C	35	15	21	15	6
5	$ZrCl_4$	rt, CH_2Cl_2	—	—	—	—	—
6		80°C, MeCN	—	—	—	—	—
7		120°C, MeCN (or PhMe)	30	21	25	3	12
8		140°C	12	26	28	15	6
9	$Zn(OTf)_2$	rt, CH_2Cl_2	—	—	—	—	—
10		80°C, MeCN	—	—	—	—	—
11		120°C, MeCN (or PhMe)	25	26	4	2	19
12		140°C	27	10	18	17	8

No reaction took place in the presence of PhCOOH or TFA as catalyst under same reaction conditions.

investigations, the reaction of indoline (**1**) with cyclohexanone (**4a**) was selected as a test reaction. In these preliminary experiments, in addition to *N*-cyclohexylindole (**5a**) as the desired product, four other compounds, which can be assumed to be secondary reaction products, were also isolated from the reaction mixture using column or thin-layer chromatography (TLC) (Table 1). The formation of the undesired products **6–9** could not be suppressed under different reaction conditions in which various Brønsted and Lewis acids such as $Bi(NO_3)_3{\cdot}5H_2O$, $ZrCl_4$, $Zn(OTf)_2$, PhCOOH, or TFA were employed as catalysts at varying temperatures and in different solvents (Table 1). Better yield for the desired product **5a** was obtained with $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) at 120°C (in sealed tube) in acetonitrile (entry 3).

Under a similar protocol, we next examined the scope of the redox amination as summarized in Table 2. Indoline and aliphatic cyclic ketones such as cyclopentanone (**4b**) and cycloheptanone (**4c**) similarly underwent the redox amination and alkylation side reactions. In most cases, the desired *N*-alkyl indoles were obtained as major products in a similar product distribution trend. However, the same reaction conditions, when applied to 2-butanone (**4d**) as an acyclic ketone, afforded a separable mixture containing five products (Scheme 2). In addition to similar alkylation products observed to cyclic ketones, *N-sec*-butylindoline (**10d**) and 1,5-di-*sec*-butylindole (**11d**) were first detected (Scheme 2).

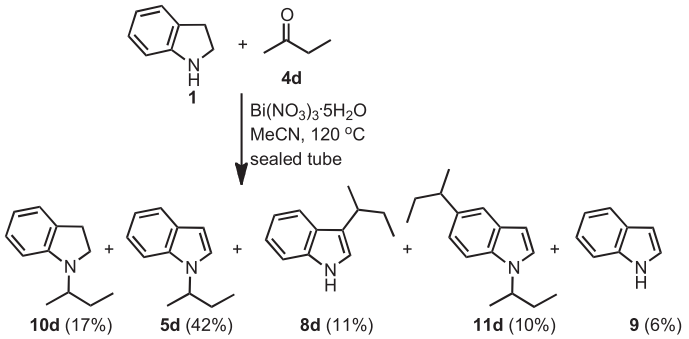
The formation of the undesired products **6–9** could not be suppressed under different reaction conditions in which various Brønsted and Lewis acids were employed as catalysts at varying temperatures and in different solvents. To probe the effect of varying ratios of starting materials on product distribution, indoline (1 equivalent) was reacted with cyclohexanone (5 equivalent) in the presence

Table 2

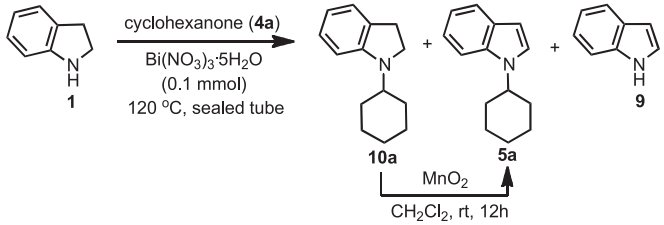
The reaction of indoline (**1**, 1 equivalent) with ketones **4b–c** (1 equivalent) catalyzed by $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol).

Entry	Ketone **4**	Product (yield%)					
1	Cyclopentanone (**4b**)	**5b**	**6b**	**7b**	**8b**	**9**	R = cyclopentyl
		50	Not isolated	—	—	17	
2	Cycloheptanone (**4c**)	**5c**	**6c**	**7c**	**8c**	**9**	R = cycloheptyl
		39	13	10	26	3	

Scheme 2. Reaction of indoline (**1**; 1 equivalent) with 2-butanone (**4d**; 1 equivalent).



Scheme 3. The reaction of indoline (**1**; 5 equivalent) with cyclohexanone (**4a**; 1 equivalent).



of $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) at 120°C in acetonitrile. In this reaction, no *N*-alkyl indole **5a** formation was observed. This is possible because of the increased reactivity of *N*-alkylation product **5a**, allowing for its complete conversion into 1,3-dialkyl and 1,3,5-trialkylation products.

Alternatively, when 5 : 1 equivalent ratio of indoline to cyclohexanone was used under the same reaction conditions, the product portfolio changed considerably, as shown in Scheme 3, and the formation of *N*-cyclohexylindoline (**10a**) as a reductive alkylation product first was observed in a high yield. It was found that no other alkylation products were formed, and only a trace amount of **5a** could be identified. The improved method was also applied to the reaction of the other ketones (except for acetone), and the observed similar results are summarized in Table 3. However, we noticed that *N*-alkyl indolines **10a–d** easily tend to oxidize to the corresponding indole compounds either on standing or during the purification. Therefore, *N*-alkyl indolines **10a–d** were aromatized with MnO_2.

A plausible mechanism for the reaction of indoline with cyclohexanone is shown in Scheme 4. The mechanism for the formation of *N*-cyclohexylindole (**5a**) involves subsequent condensation and final isomerization of indoline with cyclohexanone in the presence of bismuth nitrate. According to the experimental results, we proposed a reductive alkylation mechanism based on the formation of iminium ion for the formation of the other products. As depicted in Scheme 4, in the presence of a Lewis acid, the direct substitution of cyclohexanone with *N*-cyclohexylindole (**5a**) produces 1-(1-cyclohexylindo-lin-3-*yl*)cyclohexanol, which is subsequently converted to the iminium ion **12** by eliminating H_2O. Intermolecular

Table 3

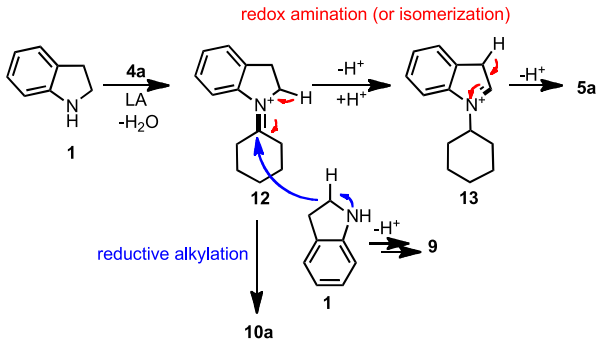
The reaction of excess indoline (**1**; 5 equivalent) with ketones **4a–d** (1 equivalent) catalyzed by $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol).

		Product (yield%)		
Entry	Ketone **4**	**10**	**9**	**5**
1	**a**	58	33	Trace
2	**b**	57	35	Trace
3	**c**	59	31	Trace
4	**d**	54	35	Trace

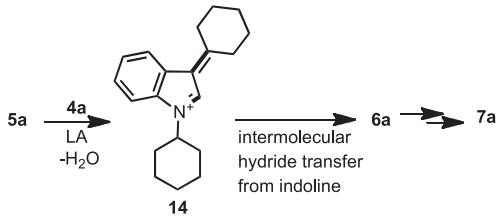
hydride transfer from another indoline to the iminium ion **12** led to *N*-alkylation product **10a**. On the other hand, the deprotonation of the iminium ion generated from indoline results in the formation of indole (**9**). Similarly, a mechanism to 1,3-alkylation could also be suggested for the formation of both 1,3,5-alkylation and 3-alkylation products (**6a**, **7a**) (Scheme 5).

Attempts to extend this reaction to acetone failed to give any of the desired alkylation product under the usual reaction condition. Therefore, we changed the amount of catalyst and performed the reaction without any solvent. The reaction of indoline (4.2 mmol) with acetone (42 mmol) in the presence of $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) at 120°C in a sealed tube led to *N*-alkylindole (**5e**), 1,3-dialkyl indole **6e**, and indole (**9**). Additionally, we found that heating of indoline (1 equivalent) with acetone (10 equivalent) in the presence of 10 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ yielded pyrrolo[3,2,1-*ij*]quinolines (**15** and **16**) as a result of chain reaction (Scheme 6). This reaction may proceed via an intermolecular aldol-type reaction

Scheme 4. Proposed mechanism for Lewis acid (LA)-promoted redox isomerization and reductive alkylation products **5a**, **10a**. [Color figure can be viewed in the online issue,which is available at wileyonlinelibrary.com.]



Scheme 5. Formation of the reductive alkylation products **6a**, **7a** as secondary product.



between acetone and the iminium intermediate **17** followed by an intramolecular Friedel–Crafts alkylation of the resulting ketone **18** and the pyrrolo[3,2,1-*ij*]quinoline skeleton are formed (Scheme 7). In the next step of the reaction sequence, a Lewis acid-catalyzed dehydration of the alcohol occurs cationic types (Scheme 7). Finally, the tetra-quinoline and dihydropyrrolo-quinoline **22** and **23** undergoes a dehydrogenation to provide Friedel–Crafts-type alkylation in the same reaction vessel resulting in the corresponding indole.

CONCLUSIONS

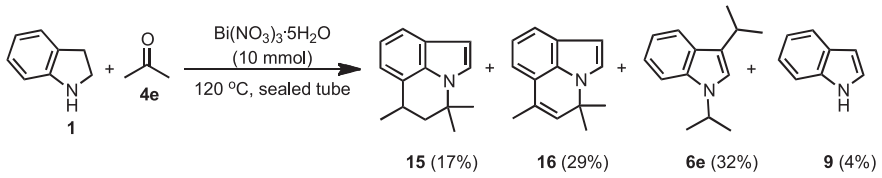
In summary, we have first reported bismuth nitrate-catalyzed redox aminations of indoline with aliphatic ketones. A possible formation mechanism for the products is described. Further studies aimed at examining the redox amination scope of benzylic ketones with indoline are in progress.

EXPERIMENTAL SECTION

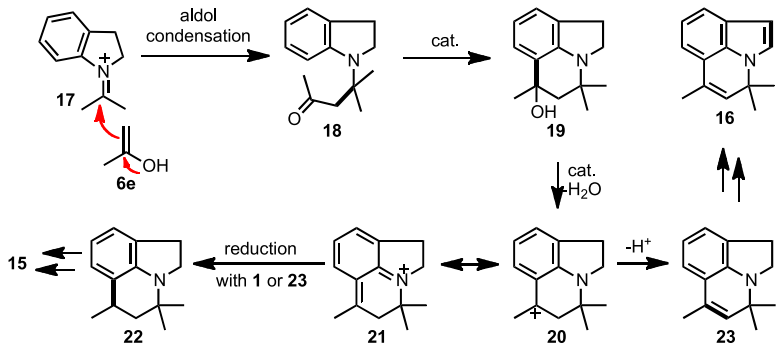
Representative procedure (RP1): reaction of indoline (1; 1 equivalent) with cyclohexanone (4a; 1 equivalent). To a solution of indoline (**1**; 500 mg; 4.2 mmol) in MeCN (5 mL) was added cyclohexanone (**4a**; 412 mg, 4.2 mmol) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol, 48 mg). Reaction mixture was stirred magnetically in a sealed tube at 120°C for 3 h. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with water (3 × 30 mL), and organic phase was dried over Na_2SO_4. The crude product (830 mg) was purified by silica gel column chromatograph (25 g), and isolated compounds was given according to elution sequence.

1,3,5-Tricyclohexyl-1H-indole (7a). 115 mg, 12%, white solid, mp = 145–146°C (hexane), eluent: hexane, R_f = 0.88 (254 nm). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.46 (s, Ar–H, 1H), 7.27 (d, A part of AB system, J = 8.6 Hz, Ar–H, 1H), 7.07 (d, B part of AB system, J = 8.6 Hz, Ar–H, 1H), 6.94 (s, Ar–H, 1H), 4.17 (p, J = 5.8 Hz, CH, 1H), 2.84–2.82 (m, CH, 1H), 2.63 (p, J = 5.8 Hz, CH, 1H), 2.13–2.10

Scheme 6. Reaction of indoline (**1**; 1 equivalent) with acetone (**4e**; 10 equivalent).



Scheme 7. Proposed formation mechanism for pyrrolo[3,2,1-*ij*]quinolines **15** and **16**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(m, CH_2, 4H), 1.97–1.86 (m, CH_2, 10H), 1.80–1.65 (m, CH_2, 2H), 1.59–1.47 (m, CH_2, 10H), 1.44–1.27 (m, CH_2, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 138.6, 134.7, 127.2, 121.6, 120.7, 119.8, 116.9, 109.3, 55.1, 45.1, 35.8, 35.5, 34.5, 33.8, 27.5, 27.3, 26.9, 26.6, 26.3, 26.0. IR (KBr, cm^{-1}): 3374, 2924, 2852, 1672, 1631, 1607, 1437, 1397, 1359, 1322, 1270, 1255, 1456, 1439, 1397, 1356, 1206, 1323, 1163, 1122, 1084, 979, 908, 858, 811. *Anal*. Calcd for $C_{26}H_{37}N$: C, 85.89; H, 10.26; N, 3.85, found: C, 85.87; H, 10.21; N, 3.93.

N-Cyclohexyl-1H-indole (5a) *[29,30].* 345 mg, 38%, colorless liquid, eluent: hexane, R_f = 0.82 (254 nm). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.8 Hz, Ar–H, 1H), 7.42 (d, J = 7.8 Hz, Ar–H, 1H), 7.26–7.21 (m, Ar–H, 2H), 7.13 (t, J = 7.8 Hz, Ar–H, 1H), 6.54 (d, J = 3.3 Hz, Ar–H, 1H), 4.29–4.23 (m, CH, 1H), 2.19–2.16 (m, CH_2, 2H), 1.99–1.90 (m, CH_2, 2H), 1.84–1.76 (m, CH_2, 2H), 1.73–1.48 (m, CH_2, 2H), 1.38–1.30 (m, CH_2, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 135.8, 128.8, 124.3, 121.3, 121.2, 119.5, 109.7, 101.3, 55.4, 33.8, 26.3, 25.9. IR (KBr, cm^{-1}): 2921, 2851, 1627, 1456, 1439, 1397, 1356, 1206, 1323, 1163, 1122, 1084, 979, 908, 858, 811. *Anal*. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03, found: C, 84.31; H, 8.58; N, 6.98.

***1,3-Dicyclohexyl-1H-indole (6a)*.** 122 mg, 13%, colorless liquid, eluent: hexane, R_f = 0.65 (254 nm). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.7 Hz, Ar–H, 1H), 7.47 (d, J = 7.7 Hz, Ar–H, 1H), 7.30 (t, J = 7.7 Hz, Ar–H, 1H), 7.25 (t, J = 7.7 Hz, Ar–H, 1H), 7.10 (s, Ar–H, 1H), 4.32–4.24 (m, CH, 1H), 2.97–2.95 (m, CH, 1H), 2.29–2.23 (m, CH_2, 4H), 2.09–1.80 (m, CH_2, 8H), 1.77–1.61 (m, CH_2, 6H), 1.58–1.37 (m, CH, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 136.3, 127.4, 121.4, 121.9, 119.8, 119.7, 118.6, 109.7, 55.2, 35.9, 34.6, 33.8, 27.4, 26.9, 26.4, 26.1. IR (KBr, cm^{-1}): 3029, 2978, 2928, 2109, 1509, 1463, 1457, 1401, 1355, 1310, 1300, 1228, 1190, 1163, 1122, 1084, 979, 908, 858, 811. *Anal*. Calcd for $C_{20}H_{27}N$: C, 85.35; H, 9.67; N, 4.98, found: C, 85.37; H, 9.64; N, 4.93.

3-Cyclohexyl-1H-indole (8a) *[31–34].* 115 mg, 13%, white solid, mp = 170–171°C (hexane), eluent: hexane, R_f = 0.31 (254 nm). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (bs, NH, 1H), 7.66 (d, J = 7.8 Hz, Ar–H, 1H), 7.35 (d, J = 7.8 Hz, Ar–H, 1H), 7.18 (t, J = 7.8 Hz, Ar–H, 1H), 7.10 (t, J = 7.8 Hz, Ar–H, 1H), 6.95 (s, Ar–H, 1H), 2.85–2.81 (m, CH, 1H), 2.15–2.05 (m, CH_2, 2H), 1.86–1.76 (m, CH_2, 3H), 1.55–1.42 (m, CH_2, 3H), 1.33–1.26 (m, CH_2, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 136.6, 127.0, 123.5, 122.0, 119.6 (2C), 119.2, 111.3, 35.6, 34.2, 27.2, 26.7. IR (KBr, cm^{-1}): 3402, 2921, 2851, 1627, 1456, 1439, 1355, 1323, 1163, 1122, 1084, 1052, 979, 908, 858, 811. *Anal*. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03, found: C, 84.33; H, 8.57; N, 6.98.

***Indole (9)*.** 35 mg, 4%, eluent: EtOAc/hexane (40%), R_f = 0.26 (254 nm).

Representative procedure (RP2): The reaction of indoline (1; 5 equivalent) with cyclohexanone (**4a**; 1 equivalent) at 120°C in solvent-free condition. A mixture of indoline (**1**, 1.00 g, 8.4 mmol), cyclohexanone (**4a**, 165 mg, 1.7 mmol), and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol, 48 mg) was stirred magnetically in a sealed tube at 120°C for 1 h under solvent-free condition. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with water (3 × 30 mL), and organic phase was dried over Na_2SO_4. The crude product (1.15 g) was purified by silica gel column chromatograph (25 g), and isolated compounds was given according to elution sequence.

N-Cyclohexylindoline (10a) *[35].* 332 mg, 58%, colorless liquid, eluent: hexane, R_f = 0.91 (254 nm). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.05–7.02 (m, Ar–H, 2H), 6.58 (t, J = 7.7 Hz, Ar–H, 1H), 6.40 (d, J = 7.7 Hz, Ar–H, 1H), 3.40–3.36 (m, CH, CH_2, 3H), 2.94 (t, J = 8.4 Hz, CH_2, 2H), 1.86–1.84 (m, CH_2, 4H), 1.71–1.68 (m, CH_2, 2H), 1.39–1.33 (m, CH_2, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.2, 130.1, 127.2, 124.3, 116.5, 106.8, 54.6, 46.7, 28.7, 28.3, 26.1, 26.0. IR (KBr, cm^{-1}): 2921, 2851, 1627, 1456, 1439, 1397, 1356, 1206, 1323, 1163, 1122, 1084, 979, 908, 858, 811. *Anal*. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96, found: C, 83.47; H, 9.51; N, 6.92.

***Indole (9)*.** 187 mg, 33%.

***Indoline (1)*.** 300 mg (2.6 mmol) was recovered.

Representative procedure (RP3): *N-Cyclohexyl-1H-indole* (5a). To a solution of *N*-cyclohexylindoline (**10a**; 300 mg, 1.5 mmol) in CH_2Cl_2 (10 mL) was added the active MnO_2 (1.50 g, 15 mmol). The mixture was stirred at rt for 12 h. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with water (3 × 30 mL), and organic phase was dried over Na_2SO_4. *N*-Cyclohexyl-1*H*-indole (**5a**) was eluted on silica gel column chromatography (25 g) using hexane as colorless liquid (289 mg, 97%).

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