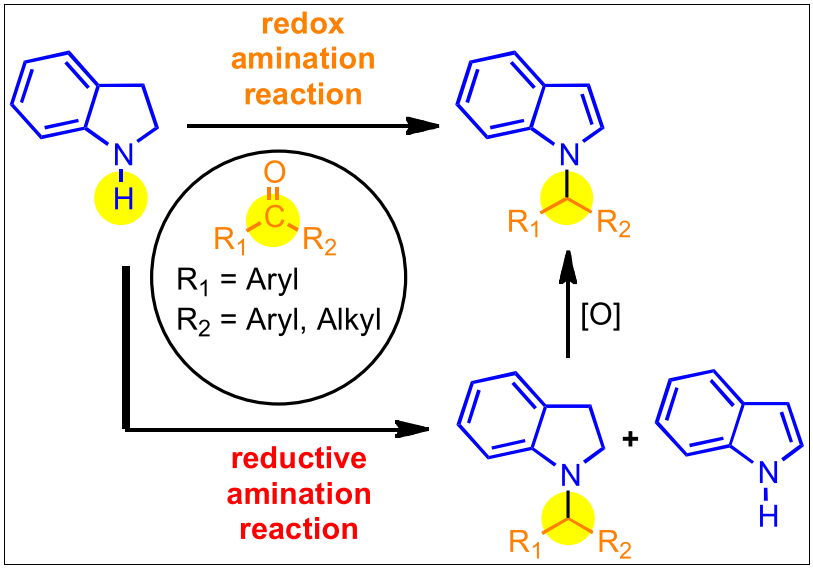
Omer Aydin,[a] Haydar Kilic,[a] Sinan Bayindir,[a,b] Esra Erdogan,[a] and Nurullah Saracoglu[a]*

[a]Department of Chemistry, Faculty of Sciences, Atatürk University, Erzurum, 25240, Turkey
[b]Department of Chemistry, Faculty of Arts and Sciences, Bingöl University, Bingöl, 12000, Turkey
*E-mail: nsarac@atauni.edu.tr

Additional Supporting Information may be found in the online version of this article.
Received February 27, 2015
DOI 10.1002/jhet.2457
Published online 13 August 2015 in Wiley Online Library (wileyonlinelibrary.com).




$Bi(NO_3)_3 \cdot 5H_2O$-Catalyzed redox amination scope and mechanistic insights of benzylic ketones with indoline are discussed. The experimental results demonstrate that the formation of *N*-alkyl-substituted indole/indoline derivatives over typically competitive redox and reductive amination processes is depending upon the reaction condition for the benzylic ketones.

*J. Heterocyclic Chem.*, **52**, 1540 (2015).

## INTRODUCTION

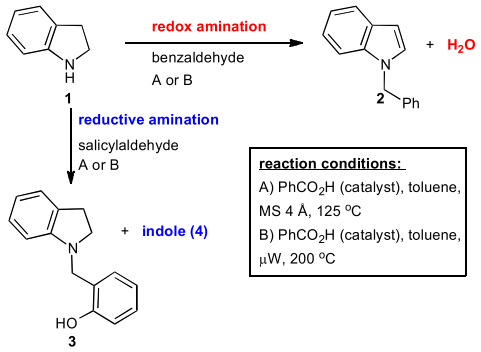
The indoles possess an important role in organic chemistry because of their significance in biological and naturally occurring molecules [1–3]. Therefore, the synthesis of functionalized indoles has become a preferred platform to develop innovative strategies [4, 5]. Recently, it has been shown that the redox amination (or isomerization) reaction is one of the most efficient routes used to obtain *N*1-substituted indoles and pyrroles [6–12]. Independently, Pan and Siedel screened the redox amination between aryl aldehydes and indolines to provide *N*-alkylindoles (Scheme 1) [13–17]. Although the redox-type amination reactions for indoline provide a one-pot reaction with a high synthetic efficiency and atom-economy and step-economy, the applications of the method have been limited to non-enolizable aldehydes. Furthermore, both groups observed reductive amination to yield *N*-alkylindolines with intermolecular hydride transfer from indoline instead of redox amination when salicylaldehydes were used as the substrate (Scheme 1).

Recently, we communicated our results to access *N*1- and excessive substituted indoles via a competitive redox and reductive amination of indoline with enolizable aliphatic ketones (Scheme 2) [18]. Here, we report on our detailed results on the bismuth nitrate-catalyzed redox amination of a wide range of benzylic ketones with indoline.

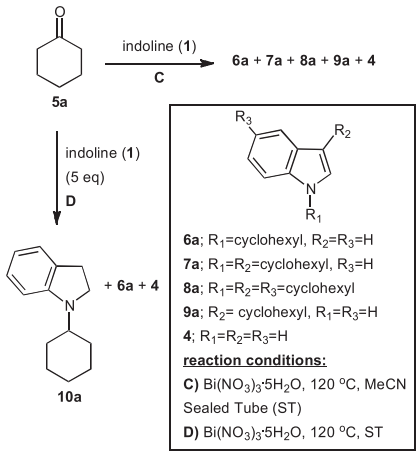
## RESULTS AND DISCUSSIONS

Under a similar protocol in connection with our initial study, we next examined the redox amination scope of indoline with aryl ketones as summarized in Table 1. Bismuth nitrate-catalyzed reactions of benzophenone (**5b**) with indoline (**1**) in a sealed tube at 120°C in acetonitrile and at 140°C without solvent a mixture of 1-benzhydrylindoline (**10b**), 1-benzhydryl-1*H*-indole (**6b**) and indole (**4**) as the redox amination product and reductive alkylation products (Entries 1 and 2 in Table 1). When 5:1 ratio of indoline to benzophenone (**5b**) was used at 120°C under solvent-free conditions the product distribution changed dramatically, and the reductive alkylation products **10b** and **4** that were accompanied by a trace amount of **6b** were observed in 66 and 27% yield,

**Scheme 1.** Reaction of aryl aldehydes and salicylaldehydes with indoline. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]




**Scheme 2.** Reaction of cyclohexanone (**5a**) with indoline.

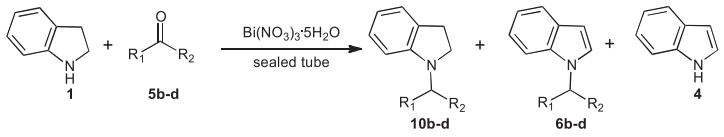



respectively. Oxidation of 1-benzhydrylindoline (**10f**) with $MnO_2$ in methylene chloride resulted in the formation of **6f** in 96% yield.

Reactions of acetophenone (**5c**) and 1-(naphthalene-2-yl)ethan-1-one (**5d**) with indoline were also examined at the same conditions, and both ketone showed similar results (Entries 4–9 in Table 1). But, the reaction setting 5:1 ratio of indoline to **5c** at 120°C under solvent-free conditions gave redox amination product as a minor product (8%), whereas the redox amination products for benzophenone and acetophenone were obtained in amounts. Compared with aliphatic ketones, the electronic nature of the ketones **5a-c** and the amounts of used indoline appeared to have an impact on reaction outcome, and reductive amination products were predominantly obtained for the first time. Based on these results, a formation mechanism of **6b** (or **6c-d**) and **10b** (or **10c-d**) was proposed in Scheme 3. It is interesting to compare the kinetic and thermodynamic control of the reaction pathways through the carbocation intermediates (Scheme 3). We suggest that iminium ions would be formed from condensation of indoline and ketone, and that these intermediates subsequently could be regenerated in the carbocation intermediates [19, 20]. The driving force for this process is the stabilization of these carbocation intermediates. While the *secondary* carbocation structure then restores the redox amination by expelling a hydrogen atom from the intermediate, the more stable *tertiary* structure due to the delocalization or resonance of the double bonds of the ring reacts to give the reductive alkylation product with indoline as reductant.

**Table 1**

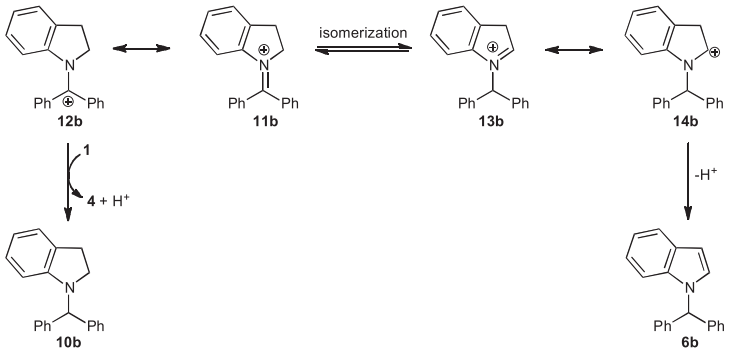
Reaction of indoline with benzylic ketones **5a-c** (1 equiv) catalyzed by $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*).




| | | | | | Product (yield%) | | |
|---|---|---|---|---|---|---|---|
| Entry | Ketone | Indoline (equiv) | Temperature (°C) | Solvent | **10** | **6** | **4** |
| 1 | **5b** $R_1 = R_2 = Ph$ | 1 | 120 | MeCN | 38 | 13 | 16 |
| 2 | | 1 | 140 | – | 18 | 56 | 6 |
| 3 | | 5 | 120 | – | 66 | Trace | 27 |
| 4 | **5c** $R_1 = Ph$, $R_2 = Me$ | 1 | 120 | MeCN | 40 | 14 | 16 |
| 5 | | 1 | 140 | – | 15 | 56 | 8 |
| 6 | | 5 | 120 | – | 58 | Trace | 31 |
| 7 | **5d** $R_1 = Np$, $R_2 = Me$ | 1 | 120 | MeCN | 52 | 14 | 24 |
| 8 | | 1 | 140 | – | 12 | 47 | 9 |
| 9 | | 5 | 120 | – | 59 | 8 | 27 |

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

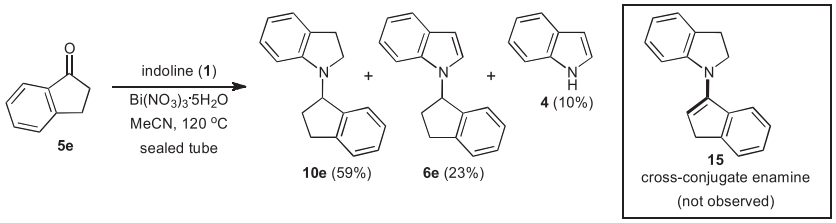
**Scheme 3.** Proposed mechanism for the formation **6a** and **10a**.




In another set of experiments, we evaluated 1-indanone (**5e**) and 2-indanone (**5f**), which are not benzylic ketones, as electrophiles in this process (Schemes 4 and 5). Treatment of a mixture of indoline and 1-indanone in acetonitrile at 120°C with bismuth nitrate catalyst afforded redox amination together with reductive amination products in proportions of 59:23:10, respectively (Scheme 4).

However, increasing the indoline content in the mixture and carrying out the reaction at 140°C exhibited similar trends. We believe that indoline reacts with 1-indanone in a way similar to its reaction with acetophenone and benzophenone. This reaction must be operating to permit both reductive amination and redox alkylation. Performing the reaction of indoline with 2-indanone under the reaction conditions at 120°C in acetonitrile led to a full conversion and formation of a new single condensation product **16** in 91% yield (Scheme 5 and Entry 1 in Table 2). However, a change in the reaction conditions produced a dramatic effect on the outcome of the reaction, resulting in the formation of products comprising condensation, redox amination, and reductive alkylation products as outlined in Table 2. These results show that full-conjugation or cross-conjugation the nitrogen atom on the enamine backbone can play an important role in controlling of the condensation products **15** and **16**. It also should be noticed that no condensation product **16** was obtained from the reaction of 2-indanone (**5f**) with excess indoline at 140°C. Therefore, we attempted to determine whether the condensation product **16** could be isomerized into redox amination product **6f**. Upon treatment of the condensation product **16** with bismuth nitrate catalyst in a sealed tube at 140°C, the expected intramolecular isomerization did not take place to give the corresponding **6f** (Scheme 5). When the product **16** was heated under the same conditions and in the presence of 8.4 m*M* of indoline (**1**), a

**Scheme 4.** Reactions of indoline (**1**, 1 equiv) with 1-indanone (**5e**) (1 equiv).




**Scheme 5.** Isomerization attempts of **16**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

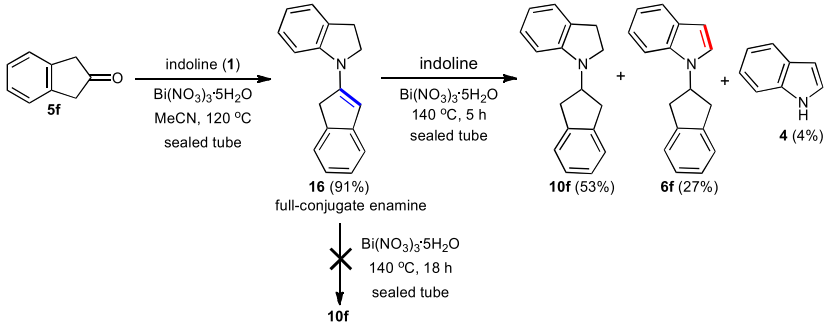


**Table 2**

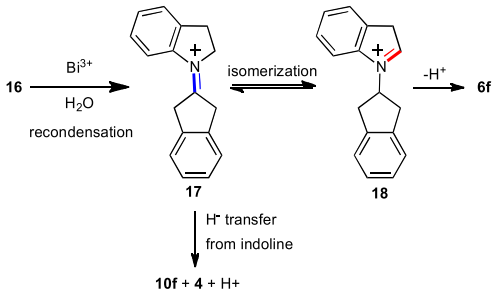
Reaction of indoline with 2-indanone (**5f**) catalyzed by $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*) in a sealed tube.

| | | | | | Product (yield%) | | | |
|---|---|---|---|---|---|---|---|---|
| Entry | Indoline: 2-indanone ratio | Solvent | Temp. (°C) | Time (h) | **16** | **10f** | **6f** | **4** |
| 1 | 1:1 | $CH_3CN$ | 120 | 1 | 91 | – | – | – |
| 2 | 1:1 | – | 140 | 5 | 61 | 8 | 10 | 4 |
| 3 | 5:1 | – | 120 | 10 | 61 | 10 | 8 | 18 |
| 4 | 5:1 | – | 140 | 3 | – | 23 | 35 | 14 |

mixture of reductive amination products **10f** and **4** and redox amination product **6f** was obtained (Scheme 5).

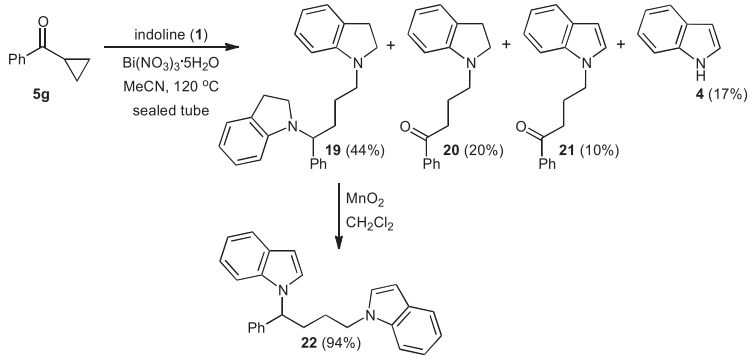
The proposed reaction pathways for the formation of **10f**, **6f**, and **4** were described in Scheme 6. This possible mechanism with Bi(III)/$H_2O$-catalyzed recondensation of the condensation product **16** to enamine ion **17**. The initially formed enamine ion **17** is converted to reductive amination products **10f** and **4,** followed by an intermolecular hydride transfer from indoline (**1**) and deprotonation steps. Then, the iminium ion **17** may undergo isomerization to the iminium ion **18**. The subsequent deprotonation forms the redox amination product **6f**. Oxidations of *N*-alkyl indolines **10e** and **10f** to indoles **6e** and **6f** were also realized by $MnO_2$ in 95% and 97% yields, respectively.

**Scheme 6.** Proposed mechanism for isomerization of **15** to **10f**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

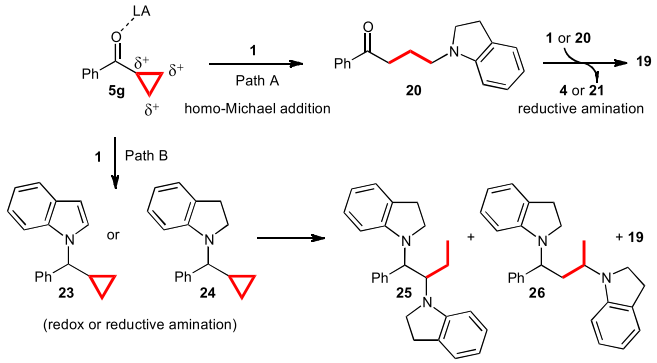



However, in order to test the effect of cyclopropyl group, the cyclopropyl phenyl ketone (**5g**) was subjected to redox amination reaction under the same reaction conditions, from which a mixture of the products, separable by chromatography, was obtained (Scheme 7). The use of an excess of indoline (**1**) resulted in a similar product mixture except for 4-(1*H*-indol-1-*yl*)-1-phenylbutan-1-one (**21**). We assume that **20** is a primary product and the others (**19**, **21**, and **4**) are secondary products, and they are formed during the reductive amination reaction of **20** under the given reaction conditions. Path A was postulated to explain these results, which begins with coordination of the catalyst with the carbonyl oxygen promoting the ring opening (Scheme 8). The subsequent nucleophilic attack of indoline to the cyclopropane ring affords the homo-Michael adduct **20**. This product could then undergo the reductive amination onto the carbonyl catalyzed by the Lewis acid to give bisindoline product **19**. During the reductive amination process, indoline (**1**) and indoline derivative **20** serve as hydride ion sources to form indole (**4**) and indole derivative **21**. We proposed the possibility of an alternative second path wherein the indoline might react with the carbonyl group to generate reductive or redox amination products transiently (Scheme 8, path B). In this situation, it is necessary to observe the formation of the most favorable cyclopropane ring-opening product(s) (**25** and **26**) as well as **19**. As a consequence, path A appears to be more favorable than path B.

**Scheme 7.** Reaction of indoline (1 equiv) with the cyclopropyl phenyl ketone (**5g**; 1 equiv).



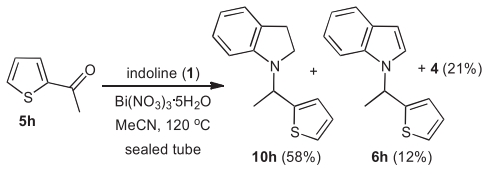
**Scheme 8.** Proposed mechanism for reaction of indoline with the cyclopropyl phenyl ketone (**5g**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



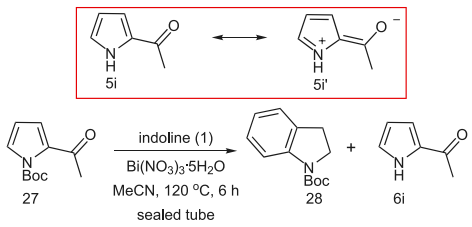

In another series of experiments, we tried to use 2-acetyl-5-membered heterocyclic (thiophene, pyrrole, and furan) ketones as an electrophile for various alkylation products. The use of 2-acetylthiophene (**5h**) in acetonitrile at 120°C resulted in the formation of corresponding products **10h**, **6h**, and **4** (Scheme 9). The reaction performed in 5 m*M* of indoline as solvent-free gave the reductive amination products **6h** and **4**. The oxidation of indoline **10h** to indole **6h** was also performed by manganese dioxide in 95% yield.

In contrast, the reaction of 2-acetylpyrrole (**5i**) failed to produce the desired compounds under the aforementioned conditions for 2-acetylthiophene (**5h**) (Scheme 10). All of these reactions only lead to the recovery of the starting material. We assume that the resonance contribution like **5i′** could decrease the susceptibility of ketone carbonyl carbon toward the nucleophilic attack. Therefore, we protected the nitrogen of 2-acetylpyrrole using di-*tert*-butyl dicarbonate in the presence of one equivalent of sodium hydride in tetrahydrofuran (THF).

**Scheme 9.** Reaction of indoline (**1**; 1 equiv) with 2-acetylthiophene (**5h**; 1 equiv).




**Scheme 10.** Reaction of indoline (**1**; 1 or 5 equiv) with *N*-Boc-2-acetylpyrrole (**5i**; 1 equiv). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

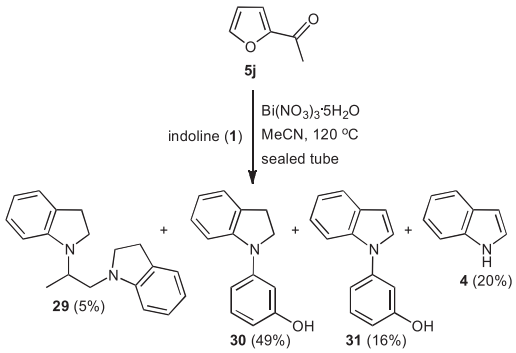



When *N*-Boc-2-acetylpyrrole (**27**) reacted with indoline as depicted in Scheme 10 (or 5 m*M* of indoline, without solvent), in all cases, a quantitative migration of the *t*-Boc protecting group at the pyrrole nitrogen to nitrogen of indoline was found (Scheme 10). We assume that the migration occurs via an intermolecular mechanism.

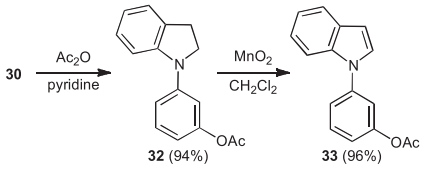
Another unexpected reaction was observed when 2-acetylfuran (**5j**) was treated with indoline at 120°C as depicted in Scheme 11. The envisioned redox amination of indoline (**1**) with **5j** under Lewis acidic conditions led to the formation of three unexpected products (**29–31**) together with indole (**4**). The repeated reaction under the same conditions in excess indoline afforded all of the products (**29**, **30**, **4**) except for indole-phenol compound **31**. Both 1,1′-(propane-1,2-*diyl*)diindoline (**29**) and 3-(indolin-1-*yl*) phenol (**30**) were then subjected to $MnO_2$-oxidation to give the corresponding indoles. But, we determined that bisindoline **29** was unstable toward the oxidation reaction. We also protected the phenolic oxygen with acetic anhydride in order to detect the free phenolic hydroxyl group of **30** (Scheme 12). Oxidation of the acetylated product **32** with $MnO_2$ was carried out in methylene chloride to give the *N*-phenyl-indole **33** (Scheme 12).

The structural analyses of the products obtained clearly show that the products do not possess a furan skeleton.

**Scheme 11.** Reaction of indoline (**1**; 1 equiv) with 2-acetylfuran (**5j**; 1 equiv).

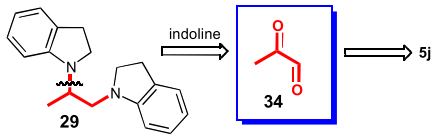


**Scheme 12.** Acetylation of phenol **30** and oxidation of **32** with $MnO_2$.



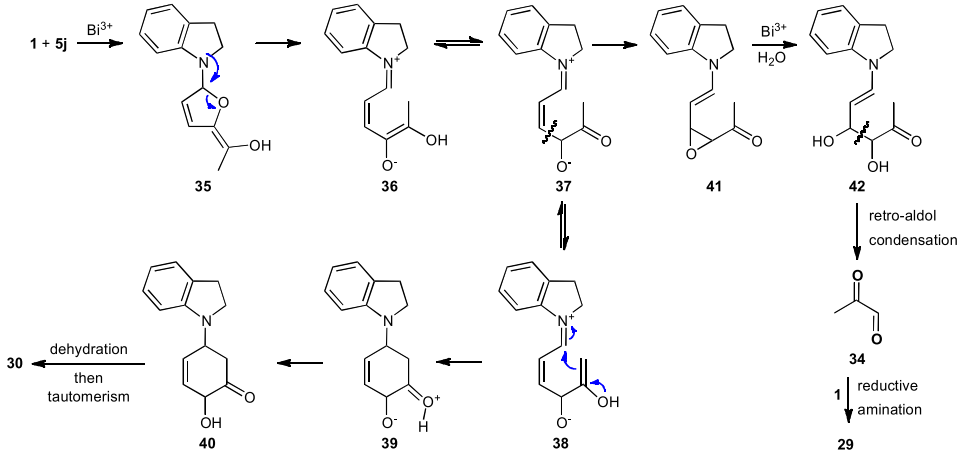

Indeed, the retrosynthetic analysis illustrated in Scheme 13 guide us that bisindoline **29** can be produced through a sequential reductive alkylation reaction between indoline and methylglyoxal (**34**). We reasoned that 2-acetylfuran (**5j**) would be unstable to yield methylglyoxal under our reaction conditions. In order to test this foresight, 2-acetylfuran was subjected to the same reaction conditions without indoline, but no transformation to methylglyoxal took place, and in each case, the starting material was recovered unchanged. Consequently, an alternative pathway was followed; one possible route is depicted in Scheme 14: the indoline (**1**) and 3-(indolin-1-*yl*)phenol (**30**), which serve as a hydride source to give indole (**4**) and 3-(1*H*-indol-1-*yl*)phenol (**31**) during the reductive alkylation process. On the basis of the results obtained, a plausible mechanism for the phenolic-type products is proposed as depicted in Scheme 14. First, the mechanism likely involves the formation of 1,6-addition product **35** (an amino acetal) by attack of indoline to the coordination of the catalyst-furan, followed by intermolecular ring opening, providing zwitterionic intermediates **36–38**. The intermolecular condensation of the enolat and iminium components built the construction of six-membered ring **39** as a precursor of the phenol ring. A sequential tautomerization–dehydration process of **40** leads to **30**.

**Scheme 13.** Retrosynthetic analysis for **29**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

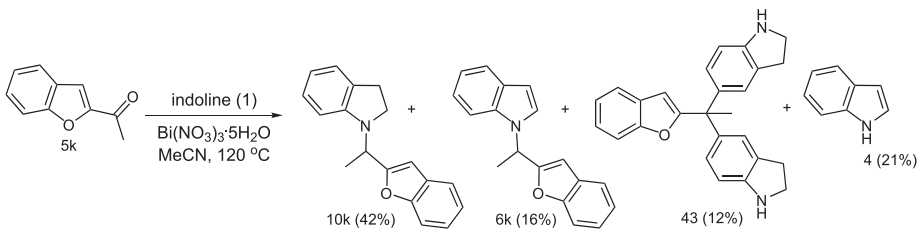



Once the formation of unexpected products was determined for 2-acetylfuran (**5j**), the chemistry was extended to 2-acetylbenzofuran (**5k**). When the 2-acetylbenzofuran (**5k**) was submitted to the same conditions, bisarylmethane **43** as a new product was formed in addition to the reductive amination products **10k**, **4**, and redox isomerization product **6k** (Scheme 15). Much to our surprise, the formation of 5,5′-bisarylmethane-type product **43** was firstly isolated in 12% yields. When the reaction was carried out with excess indoline at 120°C under solvent-free conditions, the products obtained were reductive amination products **10k**, **4**, and bisarylmethanes **43** and **44**. Although the bisarylmethanes **43** and **44** could not be separated by silica gel chromatography, both in case of the mixture of

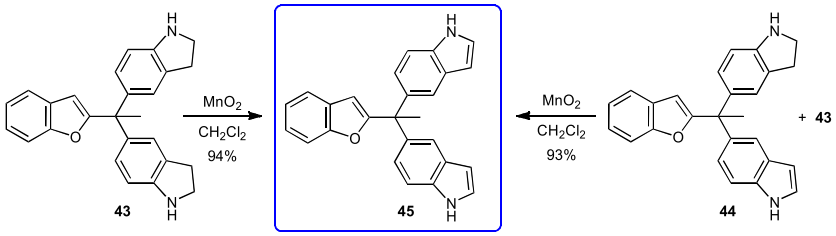
**Scheme 14.** Proposed formation mechanism for **29** and **30**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



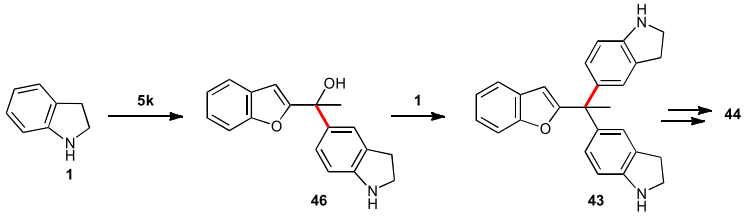

**Scheme 15.** Reaction of indoline (**1**; 1 equiv) with 2-acetylbenzofuran (**6o**; 1 equiv).



**Scheme 16.** Synthesis of **43** from **41** and a mixture of **41** and **42**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]




**Scheme 17.** Formation of **43** and **44**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]




the bisarylmethanes (**43**, **44**) and the pure **43** were oxidized with $MnO_2$ to the corresponding bis(indolyl)methane **45**, respectively (Scheme 16). We propose that the bisarylmethane **43** is formed by subsequent Friedel–Crafts C-alkylation between 2-acetylbenzofuran (**5k**) and 2 equivalent of indoline, which can react on C-5 carbon to yield the Friedel–Crafts product (Scheme 17). We postulate that indoline acts as an ambident nucleophile, and the outcome of the reaction strongly depends on the structure of the ketone moiety. Furthermore, the bisarylmethane **43** takes part in the reductive amination process to form **44** by releasing a hydride followed by a proton loss.

## CONCLUSION

In conclusion, this study elucidated for the first time a new type of the alkylation products with redox and/or reductive aminations that can occur upon treatment of indoline with a wide variety of benzylic ketones in the presence of a bismuth nitrate catalyst. The present experimental study has provided important mechanistic insights into the role of the electronic nature of the ketones on the course of the reaction. The key step for these reactions is the formation of an iminium ion from a ketone group and indoline. For the redox amination reaction, the iminium ion transforms to *N*-alkyl indoles by isomerization during the reaction sequence. Moreover, the inherent reducing power of indoline allows for an intermolecular hydride transfer to this iminium ion and opens up a new path for *N*-alkyl indolines via a (this) reductive amination protocol. Further studies aimed at examining the redox amination scope of diketones with indoline are currently in progress in our lab.

## EXPERIMENTAL

**General.** All reagents and solvents were purchased from commercial suppliers and used without further purification. Column chromatography and thin-layer chromatography (TLC) were performed using Silica gel 60 (70-230 Fluka) and Silica gel 60 HF254 (Fluka), respectively. Melting points were determined on a Buchi 539 capillary melting apparatus and uncorrected. Infrared spectra were recorded on a Mattson 1000 FT-IR spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on 400 (100) MHz Varian and Bruker spectrometers and are reported in d units with $SiMe_4$ as the internal standard. Elemental analyses were carried out on a Leco CHNS-932 instrument.

***General procedure 1 (GP1): the reaction of indoline (1; 1 equiv) with ketone (5b-k; 1 equiv) at 120°C.*** To a solution of indoline (**1**; 1.0 equiv) in MeCN (5 mL) was added ketone (**5b-k**, 1.0 equiv) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*). Reaction mixture was stirred magnetically in a sealed tube at 120°C. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with water (2 × 50 mL), and organic phase was dried over $Na_2SO_4$. The crude product was purified by silica gel column chromatograph, and isolated compounds were given according to elution sequence (EtOAc/Hexane or hexane) in general.

***General procedure 2 (GP2): the reaction of indoline (1; 1 equiv) with ketone (5b-k; 1 equiv) at 140°C.*** A mixture of indoline (**1**; 1.0 m*M*), ketone (**5b-k**, 1.0 equiv) and $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 equiv) was stirred magnetically in a sealed tube at 140°C. The reaction was monitored by TLC. After the completion of the reaction, the mixture was diluted with ethylacetate (30 mL) and washed with

water (2 × 50 mL), and organic phase was dried over $Na_2SO_4$. The crude product was purified by silica gel column chromatograph, and isolated compounds were given according to elution sequence (EtOAc/Hexane or hexane) in general.

***General procedure 3 (GP3): the reaction of indoline (1; 5 equiv) with ketone (5b-k; 1 equiv) at 120°C in solvent-free condition.*** A mixture of indoline (**1,** 5.0 equiv), ketone (**5b-k**, 1.0 equiv) and $Bi(NO_3)_3 5H_2O$ (0.1 m*M*) was stirred magnetically in a sealed tube at 120°C 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 (2 × 50 mL), and organic phase was dried over $Na_2SO_4$. The crude product was purified by silica gel column chromatograph, and isolated compounds were given according to elution sequence (EtOAc/Hexane or hexane) in general.

***General procedure for $MnO_2$ oxidation: from N-alkyl indoline (10b-k) to N-alkyl indole (6b-k).*** To a solution of *N*-alkyl indolines (**10b-k**; 1.0 equiv) in $CH_2Cl_2$ (10 mL) was added the active $MnO_2$ (10.0 equiv). The mixture was stirred at room temperature for 12 h. The reaction was monitored by TLC. After filtration, the mixture was evaporated under reduced pressure, and the compound (**7a-o**) was purified by silica gel column chromatography, and isolated compounds were given according to elution sequence (EtOAc/Hexane or hexane) in general.

***Reaction of indoline (1) with benzophenone (5b).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol) catalyzed the reaction of indoline (**1**; 500 mg, 4.2 m*M*) with benzophenone (**5b**; 765 mg, 4.2 m*M*) was performed at 120°C for 4 h in MeCN according to GP1. ***N*-Benzhydryl indoline (10b)** [21, 22]. 480 mg, 38%, colorless viscous liquid, eluent: EtOAc/hexane (30%), Rf = 0.81 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.36–7.24 (m, =CH, 10H), 7.07 (d, *J* = 6.2 Hz, =CH, 1H), 6.92 (t, *J* = 7.7 Hz, =CH, 1H), 6.63 (t, *J* = 7.0 Hz, =CH, 1H), 6.19 (d, *J* = 7.7 Hz, =CH, 1H), 5.55 (s, CH, 1H), 3.19 (t, *J* = 8.3 Hz, $CH_2$, 2H), 2.94 (t, *J* = 8.3 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 152.1, 141.5, 130.6 (2C), 128.7, 127.4, 127.3, 124.5, 117.7, 108.3, 66.8, 51.7, 28.5. IR (KBr, $cm^{-1}$): 2978, 2928, 2109, 1463, 1457, 1401, 1355, 1310, 1228, 1190, 1163, 1122, 1084, 979, 908, 858, 811. *Anal*. Calcd. for $C_{21}H_{19}N$: C, 88.38; H, 6.71; N, 4.91, found: C, 88.35; H, 6.67; N, 4.93. ***N*-Benzhydryl-1*H*-indole (6b)** [23, 24]. 158 mg, 13%, colorless viscous liquid, eluent: EtOAc/hexane (30%), Rf = 0.55 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.65–7.63 (m, =CH, 1H), 7.35–7.26 (m, =CH, 7H), 7.25–7.08 (m, =CH, 6H), 6.83 (d, *J* = 3.0 Hz, =CH, 2H), 6.50 (d, *J* = 1.3 Hz, =CH, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 139.9, 136.6, 128.9, 128.7, 128.4, 127.9, 126.9, 121.6, 120.9, 119.8, 110.2, 101.4, 63.7. IR (KBr, $cm^{-1}$): 3029, 2978, 2928, 2109, 1509, 1463, 1457, 1355, 1310, 1300, 1228, 1190, 1163, 1122, 979, 908, 858, 811. *Anal*. Calcd. for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94, found: C, 89.05; H, 6.04; N, 4.93. **Indole (4).** 202 mg, 16%, eluent: EtOAc/hexane (40%), Rf = 0.26 (254 nm).

***Reaction of indoline (1) with benzophenone (5b) at 140°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with benzophenone (**5b**; 765 mg, 4.2 m*M*) was performed at 140°C for 1 h in solvent-free condition according to GP2. ***N*-Benzhydryl indoline (10b).** 230 mg, 18%. ***N*-Benzhydryl-1*H*-indole (6b).** 705 mg, 56%. **Indole (4).** 70 mg, 6%.

***Reaction of indoline (1) with benzophenone (5b) at 120°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 mmol)-Catalyzed reaction of indoline (**1**; 1 g, 8.4 m*M*) with benzophenone (**5a**; 305 mg, 1.7 m*M*) was performed at 120°C for 1 h in solvent-free condition according to GP3. ***N*-Benzhydryl indoline (10b).** 465 mg, 66%. **Indole (4).** 189 mg, 27%. **Indoline (1).** 405 mg (3.5 m*M*) was recovered. ***N*-Benzhydryl-1*H*-indole (6b).** *N*-Benzhydryl-1*H*-indole (**6b**) was obtained as colorless viscous liquid (429 mg, 96%) from the oxidation of *N*-benzhydryl indoline (**10b**; 450 mg, 1.6 m*M*) with $MnO_2$ (1.37 g, 16.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***Reaction of indoline (1) with acetophenone (5c).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with acetophenone (**5c**; 504 mg, 4.2 m*M*) was performed at 120°C for 3 h in MeCN according to GP1. ***N*-(1-Phenylethyl)indoline (10c)** [21–25]. 405 mg, 40%, dark viscous liquid, eluent: EtOAc/hexane (30%), Rf = 0.72 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.4 Hz, =CH, 1H), 7.36–7.33 (m, =CH, 2H), 7.28–7.25 (m, =CH, 2H), 7.06 (d, *J* = 7.4 Hz, =CH, 1H), 7.00 (t, *J* = 7.4 Hz, =CH, 1H), 6.61 (t, *J* = 7.4 Hz, =CH, 1H), 6.36 (d, *J* = 7.4 Hz, =CH, 1H), 4.73 (q, *J* = 7.0 Hz, CH, 1H), 3.40 (dd, A part of AB system, *J* = 16.7, 8.5 Hz, $CH_2$, 1H), 3.33 (dd, A part of AB system, *J* = 16.7, 8.5 Hz, $CH_2$, 1H), 2.96 (t, *J* = 8.5 Hz, $CH_2$, 2H), 1.54 (d, *J* = 7.0 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.7, 143.2, 130.4, 128.7, 127.5, 127.4, 127.2, 124.7, 117.3, 107.5, 54.8, 48.2, 28.5, 16.8. 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 $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27, found: C, 86.11; H, 7.64; N, 6.30. ***N*-(1-Phenylethyl)-1*H*-indole (6c)** [26, 27]. 145 mg, 14%, yellow viscous liquid, eluent: EtOAc/hexane (20%), Rf = 0.53 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.1 Hz, =CH, 1H), 7.31–7.22 (m, =CH, 5H), 7.15–7.06 (m, =CH, 4H), 6.58 (d, *J* = 3.3 Hz, =CH, 1H), 5.70–5.66 (m, CH, 1H), 1.93 (d, *J* = 7.3 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 142.9, 136.3, 129,0, 128.9, 127.7, 126.1, 125.1, 121.7, 121.1, 119.8, 110.3, 101.7, 55.0, 22.0. IR (KBr, $cm^{-1}$): 2978, 2928, 2109, 1509, 1463, 1457, 1401, 1355, 1310, 1300, 1228, 1190, 1163, 1122, 1084, 979, 858, 811. *Anal*. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33, found: C, 86.86; H, 6.82; N, 6.38. **Indole (4).** 160 mg, 16%, eluent: EtOAc/hexane (40%), Rf = 0.26 (254 nm).

***Reaction of indoline (1) with acetophenone (5c) at 140°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with acetophenone (**5b**; 504 mg, 4.2 m*M*) was performed at 140°C for 1 h in solvent-free condition according to GP2. ***N*-(1-Phenylethyl)indoline (10c).** 151 mg, 15%. ***N*-(1-Phenylethyl)-1*H*-indole (6c).** 560 mg, 56%. **Indole (4).** 81 mg, 8%.

***Reaction of indoline (1) with acetophenone (5c) at 120°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 1 g, 8.4 m*M*) with acetophenone (**5c**; 202 mg, 1.7 m*M*) was performed at 120°C for 1 h in solvent-free condition according to GP3. ***N*-(1-Phenylethyl)indoline (10c).** 352 mg, 58%. **Indole (4).** 187 mg, 31%. **Indoline (1).** 510 mg (4.4 m*M*) was recovered. ***N*-(1-Phenylethyl)-1*H*-indole (6c).** *N*-(1-phenylethyl)-1*H*-indole (**6c**) was obtained as yellow viscous liquid (304 mg, 88%) from the oxidation of *N*-(1-phenylethyl)indoline (**10c**; 350 mg, 1.6 m*M*) with $MnO_2$ (1.37 g, 16 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***Reaction of indoline (1) with 1-(naphthalen-2-yl)ethan-1-one (5d).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-(naphthalen-2-*yl*) ethan-1-one (**5d**; 714 mg, 4.2 m*M*) was performed at 120°C for 8 h in MeCN according to GP1. ***N*-(1-(Naphthalen-2-*yl*)ethyl)indoline (10d).** 630 mg, 52%, gray solid, m.p. = 102–103°C (hexane), eluent: EtOAc/hexane (10%), Rf = 0.85 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.82–7.78 (m, =CH, 4H), 7.55 (dd, *J* = 8.5, 1.7 Hz, =CH, 1H), 7.48–7.42 (m, =CH, 2H), 7.05 (d, *J* = 7.4, =CH, 1H), 6.97 (t, *J* = 7.4 Hz, =CH, 1H), 6.60 (t, *J* = 7.4 Hz, =CH, 1H), 6.38 (d, *J* = 7.4 Hz, =CH, 1H), 4.83 (q, *J* = 6.9 Hz, CH, 1H), 3.38 (dd, A part of AB system, *J* = 16.8, 8.3 Hz, $CH_2$, 1H), 3.30 (dd, B part of AB system, *J* = 16.8, 8.3 Hz, $CH_2$, 1H), 2.94 (t, *J* = 8.3 Hz, $CH_2$, 2H) 1.59 (d, *J* = 6.9 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.5, 140.0, 133.4, 132.7, 130.3, 128.2, 128.0, 127.7, 127.3, 126.1, 126.1, 125.7, 125.2, 124.5, 117.2, 107.4, 54.8, 48.2, 28.3, 16.3. IR (KBr, $cm^{-1}$): 3375, 3043, 2934, 2847, 1613, 1574, 1493, 1474, 1453, 1371, 1321, 1298, 1249, 1177, 1159, 1107, 1053, 1023, 938, 883, 811. *Anal*. Calcd. for $C_{20}H_{19}N$: C, C, 87.87; H, 7.01; N, 5.12, found: C, 87.82; H, 7.11; N, 5.10. ***N*-(1-(Naphthalen-2-*yl*)ethyl)-1*H*-indole (6d).** 172 mg, 14%, pale yellow solid, m.p. = 75–76°C (hexane), eluent: EtOAc/hexane (10%), Rf = 0.73 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.92–7.84 (m, =CH, 4H), 7.75 (s, =CH, 1H), 7.61–7.57 (m, =CH, 2H), 7.44 (dd, *J* = 9.9, 4.2 Hz, =CH, 2H), 7.35 (dd, *J* = 8.5, 1.6 Hz, =CH, 2H), 7.28 (dd, *J* = 5.5, 3.5 Hz, =CH, 2H), 5.92 (q, *J* = 7.0 Hz, CH, 1H), 2.09 (d, *J* = 7.0 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.5, 136.6, 133.7, 133.1, 129.3, 129.0, 128.4, 128.1, 126.7, 126.4, 125.4, 124.8, 124.8, 121.9, 121.4, 120.1, 110.5, 102.0, 55.3, 22.0. IR (KBr, $cm^{-1}$): 3375, 3043, 2934, 2847, 1613, 1574, 1493, 1474, 1453, 1371, 1321, 1298, 1249, 1177, 1159, 1107, 1053, 1023, 938, 883, 811. *Anal*. Calcd. for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16 found: C, 88.44; H, 6.38; N, 5.12. **Indole (4).** 143 mg, 24%, eluent: EtOAc/hexane (40%), Rf = 0.26 (254 nm).

***Reaction of indoline (1) with 1-(naphthalen-2-yl)ethan-1-one (5d) at 140°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-(naphthalen-2-*yl*) ethan-1-one (**5d**; 714 mg, 4.2 m*M*) was performed at 140°C for 2 h in solvent-free condition according to GP2. ***N*-(1-(Naphthalen-2-*yl*)ethyl)indoline (10d).** 149 mg, 12%. ***N*-(1-(Naphthalen-2-*yl*)ethyl)-1*H*-indole (6d).** 567 mg, 47%. **Indole (4).** 95 mg, 9%.

***Reaction of indoline (1) with 1-(naphthalen-2-yl)ethan-1-one (5d) at 120°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 1.5 g, 12.6 m*M*) with 1-(naphthalen-2-*yl*)ethan-1-one (**5d**; 429 mg, 2.5 m*M*) was performed at 120°C for 3 h in solvent-free condition according to GP3. ***N*-(1-(naphthalen-2-*yl*)ethyl)indoline (10d).** 605 mg, 59%. ***N*-(1-(Naphthalen-2-*yl*)ethyl)-1*H*-indole (6d).** 83 mg, 8%. **Indole (4).** 276 mg, 27%. **Indoline (1).** 852 mg (7.3 m*M*) was recovered. ***N*-(1-(Naphthalen-2-*yl*)ethyl)-1*H*-indole (6d).** *N*-(1-(Naphthalen-2-*yl*)ethyl)-1*H*-indole (**6d**) was obtained as pale yellow solid (270 mg, 97%, m.p. = 75–76°C (hexane)) from the oxidation of *N*-(1-(naphthalen-2-*yl*)ethyl) indoline (**10d**; 280 mg, 1.0 m*M*) with $MnO_2$ (890 g, 10.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***Reaction of indoline (1) with 1-indanone (5e).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-indanone (**5e**; 555 mg, 4.2 m*M*) was performed at 120°C for 2 h in MeCN according to GP1. **1-(2,3-Dihydro-1*H*-inden-1-*yl*)indoline (10e).** 415 mg, 59%, white solid, m.p. = 98–99°C ($CH_2Cl_2$/hexane), eluent: EtOAc/hexane (20%), Rf = 0.69 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.36–7.25 (m, =CH, 3H), 7.24–7.19 (m, =CH, 1H), 7.18–7.03 (m, =CH, 2H), 6.64 (t, *J* = 7.5 Hz, =CH, 1H), 6.53 (d, *J* = 7.5 Hz, =CH, 1H), 5.30 (t, *J* = 8.0 Hz, CH, 1H), 3.24 (dd, *J* = 17.5, 8.0 Hz, $CH_2$, 1H), 3.14 (dd, *J* = 16.5, 8.0 Hz, $CH_2$, 1H), 3.04–2.86 (m, $CH_2$, 4H), 2.39–2.31 (m, $CH_2$, 1H), 2.12–2.02 (m, $CH_2$, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.6, 143.7, 142.1, 130.4, 127.6, 127.3, 126.3, 125.0, 124.9, 124.5, 117.3, 107.3, 61.1, 47.7, 30.6, 28.2, 27.0. IR (KBr, $cm^{-1}$): 2948, 2851, 1605, 1483, 1458, 1255, 1022, 938, 883, 811. *Anal*. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95, found: C, 86.81; H, 7.31; N, 5.93. **1-(2,3-Dihydro-1*H*-inden-1-*yl*)-1*H*-indole (6e).** 246 mg, 23%, pale yellow solid, m.p. = 63–64°C ($CH_2Cl_2$/hexane), eluent: EtOAc/hexane (20%), Rf = 0.38 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.7 Hz, =CH, 1H), 7.37–7.29 (m, =CH, 3H), 7.21–7.17 (m, =CH, 2H), 7.14–7.09 (m, =CH, 2H), 6.91 (d, *J* = 3.2 Hz, =CH, 1H), 6.48 (d, *J* = 3.2 Hz, =CH, 1H), 6.01 (t, *J* = 7.4 Hz, CH, 1H), 3.18–3.11 (m, $CH_2$, 1H), 3.06–2.98 (m, $CH_2$, 1H), 2.75–2.67 (m, $CH_2$, 1H), 2.30–2.11 (m, $CH_2$, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 143.8, 141.8, 136.3, 129.2, 128.7, 127.2, 126.1, 125.3, 125.2,

121.5, 121.3, 119.7, 110.0, 101.7, 61.3, 33.9, 30.7. IR (KBr, $cm^{-1}$): 3027, 2948, 2851, 1605, 1483, 1458, 1255, 1022, 938, 883, 811. *Anal*. Calcd. for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00, found: C, 87.47; H, 6.51; N, 5.97. **Indole (4).** 110 mg, 10%, eluent: EtOAc/hexane (40%), Rf = 0.31 (254 nm).

***Reaction of indoline (1) with 1-indanone (5e) at 140°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*) catalyzed the reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-indanone (**5e**; 555 mg, 4.2 m*M*) was performed at 140°C for 1 h in solvent-free condition according to GP2. **1-(2,3-Dihydro-1*H*-inden-1-*yl*)indoline (10e):** 206 mg, 20%. **1-(2,3-Dihydro-1*H*-inden-1-*yl*)-1*H*-indole (6e).** 565 mg, 54%. **Indole (4).** 80 mg, 8%.

***Reaction of indoline (1) with 1-indanone (5e) at 120°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 1 g, 8.4 m*M*) with 1-indanone (**5e**; 221 mg, 1.7 m*M*) was performed at 120°C for 1 h in solvent-free condition according to GP3. **1-(2,3-Dihydro-1*H*-inden-1-*yl*)indoline (10e).** 385 mg, 62%. **Indole (4).** 184 mg, 29%. **Indoline (1).** 430 mg (3.7 m*M*) was recovered. **1-(2,3-Dihydro-1*H*-inden-1-*yl*)-1*H*-indole (6e).** 1-(2,3-Dihydro-1*H*-inden-1-yl)-1*H*-indole (**6e**) was obtained as pale yellow solid (329 mg, 95%) from the reaction of 1-(2,3-dihydro-1*H*-inden-1-*yl*)indoline (**10e**; 350 mg, 1.5 m*M*) with $MnO_2$ (1.29 g, 15.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***Reaction of indoline (1) with 2-indanone (5f) at 120°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 2-indanone (**5f**; 555 mg, 4.2 m*M*) was performed at 120°C for 1 h in MeCN according to GP1. **1-(1*H*-Inden-2-*yl*)indoline (15).** 961 mg, 91%, pale brown solid, m.p. = 117–118°C ($CH_2Cl_2$/hexane), eluent: EtOAc/hexane (20%), Rf = 0.67 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.0 Hz, =CH, 1H), 7.26–7.13 (m, =CH, 5H), 7.02–6.99 (m, =CH, 1H), 6.86–6.82 (m, =CH, 1H), 5.83 (s, =CH, 1H), 3.97 (t, *J* = 8.9 Hz, $CH_2$, 2H), 3.82 (s, $CH_2$, 2H), 3.22 (t, *J* = 8.9 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.2, 146.0, 145.8, 137.2, 131.4, 127.8, 127.1, 125.3, 123.2, 121.3, 119.6, 118.1, 109.8, 102.6, 51.1, 39.1, 27.9. IR (KBr, $cm^{-1}$): 3303, 3029, 1657, 1523, 1450, 1337, 1250, 1207, 1126, 1018, 938, 883, 811. *Anal*. Calcd. for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00, found: C, 87.55; H, 6.41; N, 6.04.

***Reaction of indoline (1) with 2-indanone (5f) at 140°C.*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 2-indanone (**5f**; 555 mg, 4.2 m*M*) was performed at 140°C for 5 h in solvent-free condition according to GP2. **1-(1*H*-Inden-2-*yl*)indoline (16).** 642 mg, 61%. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)indoline (10f).** 85 mg, 8%, pale yellow solid, m.p. = 175–176°C ($CH_2Cl_2$/hexane), eluent: EtOAc/hexane (20%), Rf = 0.67 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.24–7.22 (m, =CH, 2H), 7.19–7.16 (m, =CH, 2H), 7.09–7.05 (m, =CH, 2H), 6.66 (t, *J* = 7.7 Hz, =CH, 1H), 6.55 (d, *J* = 7.7 Hz, =CH, 1H), 4.55–4.50 (m, CH, 1H), 3.25–7.17 (m, $CH_2$, 4H), 3.07 (dd, *J* = 16.1, 6.2 Hz, $CH_2$, 2H), 2.90 (t, *J* = 8.1 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.4, 141.6, 130.6, 127.3, 126.6, 126.5, 124.4, 117.6, 107.5, 56.7, 48.3, 35.3, 28.4. IR (KBr, $cm^{-1}$): 3303, 3029, 1657, 1523, 1450, 1337, 1250, 1207, 1126, 1018, 1199, 938, 883, 811. *Anal*. Calcd. for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95, found: C, 86.71; H, 7.23; N, 5.98. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)-1*H*-indole (6f).** 106 mg, 10%, white solid, m.p. = 107–108°C ($CH_2Cl_2$/hexane), eluent: EtOAc/hexane (20%), Rf = 0.41 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.7 Hz, =CH, 1H), 7.41 (d, *J* = 8.4 Hz, =CH, 1H), 7.31–7.20 (m, =CH, 5H), 7.12 (t, *J* = 7.7 Hz, =CH, 1H), 7.07 (d, *J* = 3.3 Hz, =CH, 1H), 6.45 (d, *J* = 3.3 Hz, =CH, 1H), 5.38–5.32 (m, CH, 1H), 3.55 (dd, *J* = 16.5, 7.7 Hz, $CH_2$, 2H), 3.33 (dd, *J* = 16.5, 5.6 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.7, 135.8, 128.8, 127.1, 124.8, 124.7, 121.4, 121.1, 119.5, 109.6, 101.5, 56.0, 39.8. IR (KBr, $cm^{-1}$): 3018, 2919, 2848, 2605, 1480, 1450, 1445, 1249, 1199, 938, 883, 811. *Anal*. Calcd. for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00, found: C, 87.57; H, 6.45; N, 5.97. **Indole (4).** 40 mg, 4%, eluent: EtOAc/hexane (40%), Rf = 0.31 (254 nm).

***Reaction of indoline (1) with 1-(1H-inden-2-yl)indoline (15).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 1.0 g, 8.4 m*M*) with 1-(1*H*-inden-2-*yl*)indoline (**16**; 391 mg, 1.7 m*M*) was performed at 140°C for 5 h in solvent-free condition according to GP2. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)indoline (10f).** 280 mg, 53%. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)-1*H*-indole (6f):** 143 mg, 27%. **Indole (4).** 40 mg, 4%.

***Reaction of indoline (1) with 2-indanone (5f).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 1.0 g, 8.4 m*M*) with 2-indanone (**5f**; 221 mg, 1.7 m*M*) was performed at 140°C for 3 h in solvent-free condition according to GP2. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)indoline (10f).** 143 mg, 23%. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)-1*H*-indole (6f).** 216 mg, 35%. **Indole (4).** 87 mg, 14%. **Indoline (1).** 610 mg (5.2 m*M*) was recovered. **1-(2,3-Dihydro-1*H*-inden-2-*yl*)-1*H*-indole (6f).** 1-(2,3-Dihydro-1*H*-inden-2-*yl*)-1*H*-indole (**6f**) was obtained as white solid (192 mg, 97%) from the oxidation of 1-(2,3-dihydro-1*H*-inden-2-*yl*)indoline (**10f**; 200 mg, 0.9 m*M*) with $MnO_2$ (740 mg, 9.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***Reaction of indoline (1) with 1-cyclopropylethan-1-one (5g).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-cyclopropylethan-1-one (**5g**; 613 mg, 4.2 m*M*) was performed at 120°C for 8 h in MeCN according to GP1. **1,1′-(1-Phenylbutane-1,4-diyl)diindoline (19).** 492 mg, 44%, yellow viscous liquid, eluent: EtOAc/hexane (10%), Rf = 0.74 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.47–7.40 (m, =CH, 4H), 7.35 (t, *J* = 6.9 Hz, =CH, 1H), 7.19–7.12 (m, =CH, 4H), 6.76 (t, *J* = 7.6 Hz, =CH, 1H), 6.69 (t, *J* = 7.6 Hz, =CH, 1H), 6.62 (d, *J* = 7.6 Hz, =CH, 1H), 6.56 (d, *J* = 7.6 Hz, = CH, 1H), 4.77 (t, *J* = 7.6 Hz, CH, 1H), 3.62–3.55

(m, $CH_2$, 1H), 3.40–3.34 (m, $CH_2$, 3H), 3.21 (t, $J$ = 7.1 Hz, $CH_2$, 2H), 3.10–3.00 (m, $CH_2$, 4H), 2.26–2.19 (m, $CH_2$, 2H), 1.90–1.72 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.1, 151.9, 140.8, 130.4, 129.9, 128.7, 128.2, 127.7, 127.6 (2C), 124.9, 124.8, 117.8, 116.9, 107.3, 106.8, 59.1, 53.5, 49.6, 47.3, 29.3, 28.9, 28.5, 25.2. IR (KBr, $cm^{-1}$): 3046, 3025, 2946, 2843, 1606, 1488, 1472, 1459, 1388, 1329, 1304, 1259, 1156, 1023, 915, 864, 815. *Anal*. Calcd. for $C_{26}H_{28}N_2$: C, 84.74; H, 7.66; N, 7.60, found: C, 84.74; H, 7.58; N, 7.49. **4-(Indolin-1-*yl*)-1-phenylbutan-1-one (20).** 220 mg, 20%, dark brown viscous liquid, eluent: EtOAc/hexane (10%), Rf = 0.68 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, $J$ = 7.5 Hz, =CH, 2H), 7.54 (t, $J$ = 7.5 Hz, =CH, 1H), 7.44 (t, $J$ = 7.5 Hz, =CH, 2H), 7.04 (t, $J$ = 7.7 Hz, =CH, 2H), 6.63 (t, $J$ = 7.7 Hz, =CH, 1H), 6.47 (d, $J$ = 7.7 Hz, =CH, 1H), 3.33 (t, $J$ = 8.3 Hz, $CH_2$, 2H), 3.15 (t, $J$ = 7.0 Hz, $CH_2$, 2H), 3.09 (t, $J$ = 7.0 Hz, $CH_2$, 2H), 2.94 (t, $J$ = 8.3 Hz, $CH_2$, 2H), 2.10–2.03 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 200.1, 152.9, 137.2, 133.2, 130.2, 128.8, 128.3, 127.5, 124.6, 117.8, 107.2, 53.4, 49.0, 36.0, 28.8, 22.4. IR (KBr, $cm^{-1}$): 3054, 2949, 2816, 1684, 1606, 1489, 1459, 1449, 1366, 1317, 1270, 1247, 1209, 1015, 1001, 868, 814. *Anal*. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28, found: C, 81.42; H, 7.24; N, 5.30. **4-(1*H*-Indol-1-*yl*)-1-phenylbutan-1-one (21).** 115 mg, 10%, brown solid, m.p. = 74–78°C (hexane), eluent: EtOAc/hexane (10%), Rf = 0.31 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.95 (bd, $J$ = 7.3 Hz, =CH, 2H), 7.81 (d, $J$ = 7.7 Hz, =CH, 1H), 7.62–7.61 (m, =CH, 1H), 7.52–7.48 (m, =CH, 3H), 7.38–7.34 (m, =CH, 1H), 7.30–7.26 (m, =CH, 1H), 7.18 (bd, $J$ = 2.9 Hz, =CH, 1H), 6.66–6.65 (m, =CH, 1H), 4.27 (t, $J$ = 6.9 Hz, $CH_2$, 2H), 2.92 (t, $J$ = 6.9 Hz, $CH_2$, 2H), 2.34 (p, $J$ = 6.9, $CH_2$, 2H) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.5, 136.9 (2C), 136.2, 133.4, 128.9, 128.2, 128.1, 121.8, 121.2, 119.6, 109.7, 101.5, 45.6, 35.2, 24.7. IR (KBr, $cm^{-1}$): 3053, 2947, 2824, 1678, 1606, 1499, 1459, 1447, 1356, 1311, 1280, 1239, 1209, 1017, 976, 867, 811. *Anal*. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32, found: C, 82.22; H, 6.44; N, 5.30. **Indole (4).** 188 mg, 17%, eluent: EtOAc/hexane (20%), Rf = 0.26 (254 nm).

***Reaction of indoline (1) with 1-cyclopropylethan-1-one (5g).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 1.5 g, 12.6 m*M*) with 1-cyclopropylethan-1-one (**5g**; 613 mg, 4.2 m*M*) was performed at 120°C for 8 h in solvent-free condition. **1,1′-(1-Phenylbutane-1,4-diyl) diindoline (19).** 390 mg, 41%. **4-(Indolin-1-yl)-1-phenylbutan-1-one (20).** 214 mg, 22%. **Indole (4).** 285 mg, 30%. **Indoline (1).** 858 mg (7.3 m*M*) was recovered.

***1,1′-(1-Phenylbutane-1,4-diyl) bis-1H-indole (22).*** 1,1′-(1-Phenylbutane-1,4-diyl) bis-1*H*-indole (**22**) was obtained as yellow viscous liquid (94 mg, 94%, eluent: EtOAc/hexane (10%), Rf = 0.62 (254 nm)) from the oxidation of 1,1′-(1-phenylbutane-1,4-*diyl*) diindoline (**19**; 100 mg, 0.3 m*M*) with $MnO_2$ (260 mg, 3.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure. **1,1′-(1-Phenylbutane-1,4-*diyl*) bis-1*H*-indole (22).** $^1$H NMR (400 MHz, $CDCl_3$): δ 7.63–7.59 (m, =CH, 2H), 7.20–7.12 (m, =CH, 6H), 7.10–7.04 (m, =CH, 4H), 7.02 (dd, $J$ = 7.5, 1.6 Hz, =CH, 2H), 6.94 (d, $J$ = 3.1 Hz, =CH, 1H), 6.52 (d, $J$ = 3.1 Hz, =CH, 1H), 6.46 (d, $J$ = 3.1 Hz, =CH, 1H), 5.29 (dd, $J$ = 9.4, 6.8 Hz, CH, 1H), 4.02 (t, $J$ = 6.8 Hz, $CH_2$, 2H), 2.32–2.12 (m, $CH_2$, 2H), 1.84–1.73 (m, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.3 (2C), 136.6, 136.2, 129.0 (2C), 128.9, 128.0, 126.6, 125.0, 122.0, 121.9, 121.4, 121.3, 120.0, 119.7, 110.1, 109.6, 102.5, 101.7, 59.4, 46.1, 32.8, 27.6. IR (KBr, $cm^{-1}$): 3048, 3021, 2957, 2834, 1606, 1474, 1452, 1437, 1392, 1329, 1308, 1262, 1171, 1019, 932, 871, 811. *Anal*. Calcd. for $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69, found: C, 85.56; H, 6.72; N, 7.80.

***Reaction of indoline (1) with 2-acetylthiophene (5h).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 2-acetylthiophene (**5h**; 529 mg, 4.2 m*M*) was performed at 120°C for 6 h in MeCN according to GP1. ***N*-(1-(Thiophen-2-*yl*) ethyl) indoline (10h).** 596 mg, 58%, dark brown viscous liquid, eluent: EtOAc/hexane (10%), Rf = 0.81 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.17 (t, $J$ = 3.4 Hz, =CH, 1H), 7.02–7.06 (m, =CH, 2H), 6.92–6.95 (m, =CH, 2H), 6.63 (t, $J$ = 7.6 Hz, =CH, 1H), 6.51 (d, $J$ = 7.6 Hz, =CH, 1H), 5.02 (q, $J$ = 6.9 Hz, CH, 1H), 3.38 (dd, A part of AB system, $J$ = 16.9, 8.5 Hz, $CH_2$, 1H), 3.27 (dd, B part of AB system, $J$ = 16.9, 8.5 Hz, $CH_2$, 1H), 2.92 (t, $J$ = 8.5 Hz, $CH_2$, 2H), 1.60 (d, $J$ = 6.9 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 150.7, 146.4, 130.3, 127.2, 126.4, 124.6, 124.3, 124.2, 117.6, 107.7, 50.5, 47.0, 28.1, 17.0. IR (KBr, $cm^{-1}$): 3070, 3042, 2974, 2845, 1606, 1486, 1459, 1385, 1328, 1302, 1256, 1235, 1184, 1024, 850, 831. *Anal.* Calcd. for $C_{14}H_{15}NS$: C, 73.32; H, 6.59; N, 6.11; S, 13.98, found: C, 73.32; H, 6.65; N, 6.20; S, 13.94. ***N*-(1-(Thiophen-2-*yl*) ethyl)-1*H*-indole (6h).** 125 mg, 12%, dark yellow viscous liquid, eluent: EtOAc/hexane (10%), Rf = 0.77 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.64 (t, $J$ = 7.7 Hz, =CH, 1H), 7.37 (d, $J$ = 7.7 Hz, =CH, 1H), 7.21–7.17 (m, =CH, 2H), 7.11 (t, $J$ = 7.7 Hz, =CH, 1H), 6.92 (dd, $J$ = 5.1, 3.7 Hz, =CH, 1H), 6.87 (d, $J$ = 3.7 Hz, =CH, 1H), 6.54 (d, $J$ = 3.3 Hz, =CH, 1H), 5.92 (q, $J$ = 7.0 Hz, CH, 1H), 1.97 (d, $J$ = 7.0 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.1 (2C), 128.7, 126.7, 124.8, 124.7, 124.4, 121.5, 121.1, 119.6, 109.6, 102.0, 50.7, 22.2. IR (KBr, $cm^{-1}$): 3082, 3028, 2972, 2839, 1605, 1479, 1452, 1384, 1332, 1309, 1256, 1232, 1184, 1023, 882, 824. *Anal.* Calcd. for $C_{14}H_{13}NS$: C, 73.97; H, 5.76; N, 6.16; S, 14.11, found: C, 73.88; H, 5.72; N, 6.24; S, 14.13. **Indole (4).** 212 mg, 21%, eluent: EtOAc/hexane (20%), Rf = 0.26 (254 nm).

***Reaction of indoline (1) with 2-acetylthiophene (5h).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*) catalyzed the reaction of indoline (**1**; 1.5 g, 12.6 m*M*) with 2-acetylthiophene (**5h**; 318 mg, 2.5 m*M*) was performed at 120°C for 2 h in solvent-free condition according to GP3. ***N*-(1-(Thiophen-2-*yl*) ethyl) indoline (10h).** 542 mg, 59%. **Indole (4):** 285 mg, 31%. **Indoline (1).** 872 mg (7.5 m*M*) was recovered. ***N*-(1-(Thiophen-2-*yl*) ethyl)-1*H*-indole (6h).** *N*-(1-(Thiophen-2-*yl*) ethyl)-1*H*-indole (**6h**) was obtained as dark yellow viscous liquid (235 mg, 95%) from the oxidation of *N*-(1-(thiophen-2-*yl*) ethyl) indoline (**10h**; 250 mg, 1.1 m*M*) with $MnO_2$ (948 mg, 11.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***N-Boc-2-acetylpyrrole (27)* [28].** To a solution of 2-acetylpyrrole (**5i**; 500 mg, 4.6 m*M*) and di-*tert*-butyl dicarbonate (1.1 g, 5.0 m*M*) in freshly distilled THF (50 mL) was added slowly NaH (0.314 g, 2.8 m*M*) in freshly distilled THF (50 mL). The mixture was stirred at room temperature for 1 h. Then the reaction mixture was solved with EtOAc (3 × 30 mL) and the organic phase was washed with $NH_4Cl$ (5%, 3 × 30 mL) and dried over $Na_2SO_4$. The crude product (958 mg) was purified on silica gel column (25 g) with EtOAc/hexane (13%) to yield *N*-Boc-2-acetylpyrrole (**27**; 912 mg, 95%, colorless viscous liquid, Rf = 0.52 (254 nm)). ***N*-Boc-2-acetylpyrrole (27).** $^1$H NMR (400 MHz, $CDCl_3$): δ 7.24–7.23 (m, =CH, 1H), 6.78 (dd, *J* = 3.6, 1.6 Hz, =CH, 1H), 6.08 (t, *J* = 3.6 Hz, =CH, 1H), 2.36 (s, $CH_3$, 3H), 1.50 (s, $CH_3$, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 188.3, 148.9, 134.1, 127.8, 121.1, 109.9, 84.7, 27.8, 27.4. IR (KBr, $cm^{-1}$): 3150, 2982, 2936, 2906, 1749, 1618,1544, 1477, 1442, 1390, 1372, 1339, 1300, 1251, 1166, 1126, 1066, 1016, 894, 846.

***Reaction of indoline (1) with N-Boc-2-acetylpyrrole (27).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with *N*-Boc-2-acetylpyrrole (**27**; 878 mg, 4.2 m*M*) was performed at 120°C for 6 h in MeCN according to GP1. ***tert*-Butyl indoline-1-carboxylate (28)** [27–30]**.** 615 mg, 45%, yellow viscous liquid, eluent: EtOAc/hexane (10%), Rf = 0.71 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.85 (bs, =CH, 0.7H), 7.45 (bs, =CH, 0.3H), 7.16–7.11 (m, =CH, 2H), 6.95–6.88 (m, *J* = 7.4, 1.0 Hz, =CH, 2H), 3.97–3.94 (m, =CH, 2H), 3.08 (t, *J* = 8.7 Hz, 2H), 1.58 (s, $CH_3$, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 127.6, 124.9, 122.3, 114.9, 47.8, 28.7, 27.6. IR (KBr, $cm^{-1}$): 3042, 2938, 2850, 1769, 1606, 1498, 1462, 1368, 1298, 1288, 1069, 1013, 979, 924, 887, 817. *Anal*. Calcd. for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39, found: C, 71.33; H, 7.72; N, 6.34.

***Reaction of indoline (1) with 1-(furan-2-yl) ethan-1-one (5j).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-(furan-2-*yl*) ethan-1-one (**5j**; 462 mg, 4.2 m*M*) was performed at 120°C for 8 h in MeCN according to GP1. **1,1′-(Propane-1,2-diyl) diindole (29).** 45 mg, 5%, dark yellow viscous liquid, eluent: EtOAc/hexane (15%), Rf = 0.73 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.13–7.02 (m, =CH, 4H), 6.67–6.59 (m, =CH, 2H), 6.49–6.44 (m, =CH, 2H), 4.00–3.91 (m, CH, 1H), 3.52–3.32 (m, $CH_2$, 4H), 3.24 (dd, A part of AB system, *J* = 13.5, 6.7 Hz, $CH_2$, 1H), 3.13 (dd, B part of AB system, *J* = 13.4, 6.0 Hz, $CH_2$, 1H), 2.99–2.94 (m, $CH_2$, 4H), 1.21 (d, *J* = 6.7 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 152.9, 151.4, 130.1, 129.8, 127.5 (2C), 124.7 (2C), 117.5, 117.0, 106.6, 106.4, 54.1, 53.2, 49.6, 46.3, 28.9, 28.5, 14.1. IR (KBr, $cm^{-1}$): 3439, 3315, 2930, 1734, 1690, 1620, 1548, 1469, 1401, 1345, 1315, 1266, 1217, 1161, 1119, 917, 898, 849. *Anal*. Calcd. for $C_{19}H_{22}N_2$: C, 81.97; H, 7.97; N, 10.06, found: 81.88; H, 7.92; N, 10.11. **3-(Indolin-1-*yl*) phenol (30).** 475 mg, 49%, brown viscous liquid, eluent: EtOAc/hexane (15%), Rf = 0.65 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.25–7.21 (m, =CH, 3H), 7.11–7.05 (m, =CH, 2H), 6.99–6.94 (m, =CH, 1H), 6.87–6.83 (m, =CH, 1H), 6.36 (bs, OH, 1H), 6.34 (d, *J* = 7.7 Hz, =CH, 1H), 3.74 (t, *J* = 8.1 Hz, $CH_2$, 2H), 3.19 (t, *J* = 8.1 Hz, $CH_2$, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.5, 151.3, 132.8, 130.9, 128.1, 127.7, 125.0, 124.9, 121.3, 120.1, 115.3, 109.9, 56.0, 29.4. IR (KBr, $cm^{-1}$): 3421, 3046, 2955, 2929, 2849, 1603, 1496, 1459, 1366, 1288, 1262, 1227, 1186, 1174, 1151, 1113, 1055, 1036, 1026, 927, 872, 820. *Anal*. Calcd. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63, found: C, 79.58; H, 6.31; N, 6.50. **3-(1*H*-Indol-1-*yl*) phenol (31).** 152 mg, 16%, black viscous liquid, eluent: EtOAc/hexane (15%), Rf = 0.56 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 7.0, 1.5 Hz, =CH, 1H), 7.37 (t, *J* = 7.7 Hz, =CH, 1H), 7.30–7.01 (m, =CH, 6H), 7.05 (t, *J* = 7.7 Hz, =CH, 1H), 6.75 (d, *J* = 3.3 Hz, =CH, 1H), 5.00 (bs, OH, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.7, 136.8, 130.0, 129.1, 128.8, 128.5, 126.0, 123.1, 121.5, 121.4, 121.0, 117.1, 110.7, 104.6. IR (KBr, $cm^{-1}$): 3480, 3051, 2925, 2854, 1705, 1593, 1515, 1499, 1455, 1332, 1309, 1291, 1230, 1214, 1188, 1137, 1116, 1098, 1061, 1033, 1012, 957, 937, 883, 854, 824. *Anal*. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69, found: C, 80.43; H, 5.42; N, 6.57. **Indole (4).** 188 mg, 20%, eluent: EtOAc/hexane (20%), Rf = 0.26 (254 nm).

***3-(1H-Indol-1-yl) phenol (31).*** 3-(1*H*-Indol-1-*yl*) phenol (**31**) was obtained as pale brown viscous liquid (279 mg, 94%) from the oxidation of 3-(indolin-1-*yl*) phenol (**30**; brown viscous liquid, 300 mg, 1.4 m*M*) with $MnO_2$ (1.23 g, 14.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***3-(Indolin-1-yl) phenyl acetate (32).*** To a solution of 3-(indolin-1-*yl*) phenol (**30**; 300 mg, 1.42 m*M*) in pyridine (5 mL) was added 0.4 mL (4.3 m*M*) of $Ac_2O$. The mixture was stirred at room temperature for 12 h. The reaction was monitored by TLC. Then the mixture was solved with EtOAc (3 × 30 mL) and the organic phase was washed with $H_2O$ (3 × 30 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure. 3-(Indolin-1-*yl*) phenyl acetate (**32**; 338 mg, black viscous

liquid, 94%, eluent: EtOAc/hexane (20%), Rf = 0.52 (254 nm)) was purified on a silica gel column chromatograph with EtOAc/hexane. **3-(Indolin-1-*yl*) phenyl acetate (32).** $^1$H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 8.2, 0.9 Hz, =CH, 1H), 7.30–7.26 (m, =CH, 1H), 7.24–7.18 (m, =CH, 3H), 7.07 (t, *J* = 7.6 Hz, =CH, 1H), 6.77 (t, *J* = 7.6 Hz, =CH, 1H), 6.52 (d, *J* = 7.6 Hz, =CH, 1H), 3.91 (t, *J* = 8.5 Hz, $CH_2$, 2H), 3.16 (t, *J* = 8.5 Hz, $CH_2$, 2H), 2.06 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.2, 148.7, 145.8, 137.3, 130.5, 127.2, 127.1, 125.3, 124.8, 124.4, 123.8, 118.8, 109.4, 54.0, 29.1, 21.0. IR (KBr, $cm^{-1}$): 3028, 2933, 2850, 1769, 1597, 1498, 1462, 1368, 1331, 1316, 1298, 1263, 1108, 1093, 1043, 1010, 938, 903, 817. *Anal*. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53, found: C, 75.79; H, 5.86; N, 5.52.

***3-(1H-Indol-1-yl) phenyl acetate (33).*** 3-(1*H*-Indol-1-*yl*) phenyl acetate (**32**) was obtained as pale brown viscous liquid (286 mg, 96%, eluent: EtOAc/hexane (15%), Rf = 0.44 (254 nm)) from the oxidation of 3-(indolin-1-*yl*) phenyl acetate (**32**; 300 mg, 1.2 m*M*) with $MnO_2$ (1 g, 12.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure. **3-(1*H*-Indol-1-*yl*) phenyl acetate (33).** $^1$H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.7 Hz, =CH, 1H), 7.46 (dd, *J* = 7.7, 1.7 Hz, =CH, 1H), 7.42–7.38 (m, =CH, 1H), 7.36–7.32 (m, =CH, 1H), 7.23 (dd, *J* = 7.7, 1.2 Hz, =CH, 1H), 7.22–7.11 (m, =CH, 4H), 6.64 (d, *J* = 3.2 Hz, =CH, 1H), 1.82 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.9, 146.2, 136.7, 132.3, 128.9, 128.8, 128.7, 128.5, 127.2, 124.2, 122.6, 121.1, 120.6, 111.0, 103.8, 20.6. IR (KBr, $cm^{-1}$): 3106, 3066, 2926, 2853, 1768, 1605, 1518, 1500, 1476, 1459, 1369, 1333, 1308, 1268, 1238, 1188, 1137, 1101, 1064, 1038, 947, 906, 866, 820. *Anal*. Calcd. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57, found: C, 76.52; H, 5.26; N, 5.45.

***Reaction of indoline (1) with 1-(benzofuran-2-yl) ethan-1-one (5k).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*)-Catalyzed reaction of indoline (**1**; 500 mg, 4.2 m*M*) with 1-(benzofuran-2-*yl*) ethan-1-one (**5k**; 672 mg, 4.2 m*M*) was performed at 120°C for 20 h in MeCN according to GP1. **1-(1-(Benzofuran-2-*yl*) ethyl) indoline (10k).** 497 mg, 42%, yellow solid, m.p. = 112–113°C (hexane), eluent: EtOAc/hexane (15%), Rf = 0.76 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 7.8, 1.0 Hz, =CH, 1H), 7.50 (d, *J* = 8.1 Hz, =CH, 1H), 7.31–7.22 (m, =CH, 2H), 7.12 (t, *J* = 7.0 Hz, =CH, 2H), 6. 71 (t, *J* = 7.0 Hz, =CH, 1H), 6.64–6.60 (m, =CH, 2H), 5.02 (q, *J* = 7.0 Hz, CH, 1H), 3.57 (dd, A part of AB system, *J* = 16.9, 8.5 Hz, $CH_2$, 1H), 3.38 (dd, B part of AB system, *J* = 16.9, 8.5 Hz, $CH_2$, 1H), 3.01 (t, *J* = 8.5 Hz, $CH_2$, 2H), 1.68 (d, *J* = 7.0 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 158.3, 155.0, 150.9, 130.4, 128.5, 127.5, 124.8, 124.1, 122.9, 121.0, 117.9, 111.5, 107.7, 103.9, 49.4, 47.8, 28.4, 15.0. IR (KBr, $cm^{-1}$): 3374, 2978, 2934, 2847, 1613, 1574, 1493, 1474, 1453, 1371, 1321, 1249, 1177, 1159, 1107, 1053, 1023, 938, 883, 811. *Anal*. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32, found: C, 82.03; H, 6.58; N, 5.29. **1-(1-(Benzofuran-2-*yl*) methyl)-1*H*-indole (6k).** 186 mg, 16%, dark yellow viscous liquid, eluent: EtOAc/hexane (15%), Rf = 0.73 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.7 Hz, =CH, 1H), 7.61 (dd, *J* = 7.9, 1.0 Hz, =CH, 1H), 7.55 (d, *J* = 8.1 Hz, =CH, 2H) 7.40–7.27 (m, =CH, 5H), 6.72 (d, J = 2.9 Hz, =CH, 1H), 6.58 (s, =CH, 1H), 5.92 (q, *J* = 7.1 Hz, CH, 1H), 2.08 (d, *J* = 7.1 Hz, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 157.5, 155.3, 136.2, 129.1, 128.3, 125.3, 124.7, 123.2, 122.1, 121.5, 121.4, 120.1, 111.7, 109.9, 103.8, 102.6, 49.8, 19.5. IR (KBr, $cm^{-1}$): 3374, 2978, 2934, 2847, 1613, 1574, 1493, 1474, 1453, 1371, 1321, 1249, 1177, 1159, 1107, 1053, 1023, 938, 883, 811. *Anal*. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36, found: C, 82.63; H, 5.72; N, 5.34. **5,5′-(1-(Benzofuran-2-*yl*) ethane-1,1-*diyl*) diindoline (43).** 143 mg, 12%, brown viscous liquid, eluent: EtOAc/hexane (15%), Rf = 0.73 (254 nm). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.44–7.38 (m, =CH, 2H), 7.20–7.12 (m, =CH, 2H), 6.94 (s, =CH, 2H), 6.83 (dd, *J* = 8.2, 1.8 Hz, =CH, 2H), 6.51 (d, *J* = 8.2 Hz, =CH, 2H), 6.22 (s, =CH, 1H), 3.60 (bs, NH, 2H), 3.47 (t, *J* = 8.3 Hz, $CH_2$, 4H), 2.92 (t, *J* = 8.3 Hz, $CH_2$, 4H), 2.09 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.6, 155.2, 150.2, 137.9, 129.5, 128.9, 127.3, 124.7, 123.6, 122.7, 120.8, 111.5, 109.0, 104.8, 49.2, 47.8, 30.2, 28.5. IR (KBr, $cm^{-1}$): 3380, 2930, 2857, 1615, 1547, 1495, 1455, 1345, 1252, 1111, 1051, 934, 884, 808. *Anal*. Calcd. for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36; N, 7.36, found: C, 82.08; H, 6.43; N, 7.28. **Indole (4).** 231 mg (21%), eluent: EtOAc/hexane (20%), Rf = 0.26 (254 nm).

***Reaction of indoline (1) with 1-(benzofuran-2-yl) ethan-1-one (5k).*** $Bi(NO_3)_3{\cdot}5H_2O$ (0.1 m*M*) catalyzed the reaction of indoline (**1**; 1.5 g, 12.6 m*M*) with 1-(benzofuran-2-*yl*)ethan-1-one (**5k**; 403 mg, 2.5 m*M*) was performed at 120°C for 20 h in solvent-free condition according to GP3. **1-(1-(Benzofuran-2-*yl*) ethyl) indoline (10k).** 553 mg; 55%. **Indole (4).** 282 mg, 28%. 868 mg (7.4 m*M*) of **indoline** (**1**) was recovered. A mixture of 5,5′-(1-(benzofuran-2-*yl*) ethane-1,1-diyl)diindoline **(43)** and 5-(1-(benzofuran-2-yl)-1-(indolin-5-yl)ethyl)-1*H*-indole **(44):** 95 mg, 10%, ratio of **43**:**44** according to $^1$H NMR is 2:3, brown viscous liquid, eluent: 20% EtOAc/hexane.

***1-(1-(Benzofuran-2-yl) methyl)-1H-indole (6k).*** 1-(1-(Benzofuran-2-*yl*) methyl)-1*H*-indole (**6k**) was obtained as dark yellow viscous liquid (238 mg, 96%) from the oxidation of 1-(1-(benzofuran-2-*yl*) ethyl) indoline (**10k**; 250 mg, 1.0 m*M*) with $MnO_2$ (825 mg, 10.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

***5,5′-(1-(Benzofuran-2-yl)ethane-1,1-diyl)bis(1H-indole) (45).*** 5,5′-(1-(Benzofuran-2-*yl*)ethane-1,1-diyl)bis(1*H*-indole) (**45**) was obtained as yellow viscous liquid (112 mg, 94%, eluent: EtOAc/hexane (15%), Rf = 0.10

(254 nm)) from the oxidation of 5,5′-(1-(benzofuran-2-*yl*) ethane-1,1-diyl)diindoline (**43**; 120 mg, 0.3 m*M*) with $MnO_2$ (274 mg, 3.0 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure. **5,5′-(1-(Benzofuran-2-*yl*)ethane-1,1-diyl)bis(1*H*-indole) (45).** $^1$H NMR (400 MHz, $CDCl_3$): δ 8.03 (bs, NH, 2H), 7.49–7.44 (m, =CH, 4H), 7.28–7.12 (m, =CH, 8H), 6.48–6.46 (m, = CH, 2H), 6.29 (s, CH, 1H), 2.35 (s, $CH_3$, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 165.7, 155.2, 139.1, 134.6, 128.9, 127.7, 124.6, 123.5, 123.4, 122.6, 120.8, 120.1, 111.6, 110.7, 105.1, 103.2, 50.1, 28.9. IR (KBr, $cm^{-1}$): 3415, 2925, 2846, 1625, 1546, 1469, 1454, 1415, 1343, 1319, 1251, 1094, 935, 885, 805. *Anal.* Calcd. for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44, found: C, 82.86; H, 5.41; N, 7.53.

***Oxidation of a mixture of 5,5′-(1-(benzofuran-2-yl)ethane-1,1-diyl)diindoline (43) and 5-(1-(benzofuran-2-yl)-1-(indolin-5-yl)ethyl)-1H-indole (44).*** 5,5′-(1-(Benzofuran-2-*yl*)ethane-1,1-*diyl*)bis(1*H*-indole) (**45**) was obtained as yellow viscous liquid (83 mg, 93%) from the oxidation of a mixture of 5,5′-(1-(benzofuran-2-*yl*)ethane-1,1-diyl)diindoline (**43**): 5-(1-(benzofuran-2-*yl*)-1-(indolin-5-yl)ethyl)-1*H*-indole (**44**) (96 mg, 2: 3 ratio) with $MnO_2$ (250 mg, 2.9 m*M*) in $CH_2Cl_2$ at room temperature for 12 h according to general procedure.

**Acknowledgments.** Authors are indebted to The Scientific and Technical Research Council of Turkey (TUBITAK, grant no. TBAG-112T600), Department of Chemistry at Ataturk University for their financial support for this study.

## REFERENCES AND NOTES

[1] Kaushik, N. K.; Kaushik, N.; Attri, P.; Kumar, N.; Kim, C. H.; Verma, A. K.; Choi, E. H. Molecules 2013, 18, 6620.
[2] O'Connor, S. E.; Maresh, J. J. Nat Prod Rep 2006, 23, 532.
[3] Sharma, V.; Kumar, P.; Pathak, D. J. Heterocyclic Chem 2010, 47, 491.
[4] Gribble, G. W. J. Chem Soc, Perkin Trans 1 2000, 1045.
[5] Humphrey, G. R.; Kuethe, J. T. Chem Rev 2006, 106, 2875.
[6] Pan, S. C.; Beilstein J. Org Chem 2012, 8, 1374.
[7] Pahadi, N. K.; Paley, M.; Jana, R.; Waetzig, S. R.; Tunge, J. A. J Am Chem Soc 2009, 131, 16626.
[8] Zou, Z. Q.; Deng, Z. J.; Yu, X. H.; Zhang, M. M.; Zhao, S. H.; Luo, T.; Yin, X.; Xu, H.; Wang, W. Sci China Chem 2012, 55, 43.
[9] Oda, M.; Fukuchi, Y.; Ito, S.; Thanh, N. C.; Kuroda, S. Tetrahedron Lett 2007, 48, 9159.
[10] Cook, A. G.; Switek, K. A.; Cutler, K. A.; Witt, A. M. Lett Org Chem 2004, 1, 1.
[11] Kumar, A. V.; Rao, K. R. Tetrahedron Lett 2011, 52, 3237.
[12] Xue, X.; Yu, A.; Cai, Y.; Cheng, J. P. Org Lett 2011, 13, 6054.
[13] Mao, H.; Wang, S.; Yu, P.; Lu, H.; Xu, R.; Pan, Y. J. Org Chem 2011, 76, 1167.
[14] Mao, H.; Xu, R.; Wan, J.; Jiang, Z.; Sun, C.; Pan, Y. Chem Eur J 2010, 16, 13352.
[15] Deb, I.; Das, D.; Seidel, D. Org Lett 2011, 13, 812.
[16] Zhang, C.; Seidel, D. J. Am Chem Soc 2010, 132, 1798.
[17] Deb, I.; Coiro, D. J.; Seidel, D. Chem Commun 2011, 47, 6473.
[18] Bayindir, S.; Erdogan, E.; Kilic, H.; Aydin, O.; Saracoglu, N. J Heterocyclic Chem 2015, DOI: 10.1002/jhet.2337.
[19] Zheng, L.; Yang, F.; Dang, Q.; Bai, X. Org Lett 2008, 10, 889.
[20] Mahato, S.; Haque, M. A.; Dwari, S.; Jana, C. K. RSC Adv 2014, 4, 46214.
[21] Viswanathan, R.; Prabhakaran, E. N.; Plotkin, M. A.; Johnston, J. N. J. Am Chem Soc 2003, 125, 163.
[22] Johnston, J. N.; Plotkin, M. A.; Viswanathan, R.; Prabhakaran, E. N. Org Lett 2001, 3, 1009.
[23] Wales, S. M.; Walker, M. M.; Johnson, J. S. Org Lett 2013, 15, 2558.
[24] Sun, N.; Hong, L.; Huang, F.; Ren, H.; Mo, W.; Hu, B.; Shen, Z.; Hu, X. Tetrahedron 2013, 69, 3927.
[25] Liu, X. Y.; Guo, Z.; Dong, S. S.; Li, X. H.; Che, C. M. Chem Eur J 2011, 17, 12932.
[26] Fletcher, A. J.; Bax, M. N.; Willis, M. C. Chem Commun 2007, 45, 4764.
[27] Karchava, A. V.; Shuleva, I. S.; Ovcharenko, A. A.; Yurovskaya, M. A. Chem Heterocycl Compd 2010, 46, 291.
[28] Landge, K. P.; Jang, K. S.; Lee, S. Y.; Chi, D. Y. J. Org Chem 2012, 77, 5705.
[29] Damien, C.; Bernard, F.; Fabienne, F. Org Biomol Chem 2012, 10, 6587.
[30] Diep, V.; Dannenberg, J. J.; Franck, R. W. J. Org Chem 2003, 68, 7907.