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Indium Catalyzed Sequential Regioselective Remote C–H Indolylation and Rearrangement Reaction of Peroxyoxindole

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Abstract: Indium-catalyzed sequential remote C–H functionalization (C-6 position) and C3-indolylation of peroxyoxindole using indole is described for the synthesis of terindolinone derivatives. Whereas, *N*-substituted 3-phenyl peroxyoxindole derivatives undergoes consecutive skeletal rearrangement to generate transient carbocation, which has been trapped with indole nucleophile to generate 2-(1*H*-indol-3-yl)-4-alkyl-benzo[*b*][1,4]oxazin-3(4*H*)-one derivatives. In contrast with Indium (III) Chloride, $FeCl_3 \cdot 6H_2O$ facilitates oxidative cleavage of the peroxyoxindole (Hock cleavage) and further reaction with indole to afford biologically important trisindoline derivatives. A plausible mechanism has been proposed for these reactions with experimental evidences.

Keywords: Peroxyoxindole; Indium (III) Chloride; C–H functionalization; Trisindoline; Hock cleavage

Peroxides are an imperative functional groups in organic chemistry that can be found in many natural products and pharmaceutical drugs.[1] Since peroxide has weak oxygen-oxygen bond ($\Delta H°_{298} = 158–194\ kJ\,mol^{-1}$)[2] and low bond energy, intense application can be found as a very attractive and important intermediate in many chemical transformations and rearrangement reactions.[3] As a result of this unique bond property, organic peroxides deliver a numerous fundamental rearrangement reactions like Baeyer-Villiger,[4] Criegee,[5] Hock,[6] Kornblum-DeLaMare,[7] Smith,[8] etc. In contrast, Minisci and co-workers reported the substitution reaction of cumene peroxide with phenol.[9] Indeed, peroxides were used in multiple transformations such as oxidation reagent, radical initiator and energetic materials. However, diverse applications of these peroxides in C–C and C–X bond formation towards the chemical synthesis were scarcely studied.[10] Furthermore, synthetic application of peroxide as a coupling partner for the cross-coupling reaction has not been reported in the literature.

Remarkably, in the last decade heterocycle substituted peroxides has gained significant attention in chemical transformation.[11] As this peroxide are chemically and thermally stable, this might attribute as a coupling partner for the cross-coupling reactions and unprecedented rearrangement reactions.[12] In addition, it also exhibit various biological activities.[13] In 2017, Stoltz and co-workers have shown the reactivity of peroxyoxindole derivatives for the oxidative fragmentation and skeletal rearrangement reactions.[14a] Subsequently, we developed a Lewis acid catalyzed ring expansion of oxindole derivatives *via* skeletal rearrangement of peroxyoxindole.[14b,c] Huo and co-workers synthesized derivatives of benzoxazinone peroxides and substituted the peroxy functionality with nucleophiles in the presence of diverse metals as the catalytic system.[15]

Recently, Chen and co-workers described the synthesis of 2-indolyl-3-peroxyindolenine via acid catalysed addition of indole across the imine bond, which has been further explored for the diverse functionalization of tetrahydro-β-carbolines via oxidative coupling rearrangement.[16] Although limited investigations are available for reactions and rearrangement of peroxyoxindole derivatives, exploration of these peroxides for the newer rearrangement and chemical reactions fascinate in contemporary synthetic methodology. Apart from peroxyoxindole, indolylation of 2-oxindole and other heterocycles are also important since this heterocycle represents as core structures in many biologically active natural products and therapeutically important targets.[17] Thus, direct displacement of quaternary peroxides by indole or sequential reactions of peroxide is highly desirable in modern chemical synthesis as it deliver quaternary centre and scaffold of biologically important natural products (Figure 1).[18]

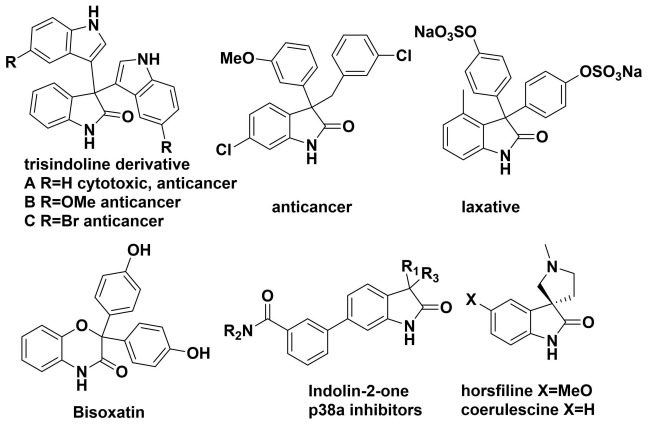
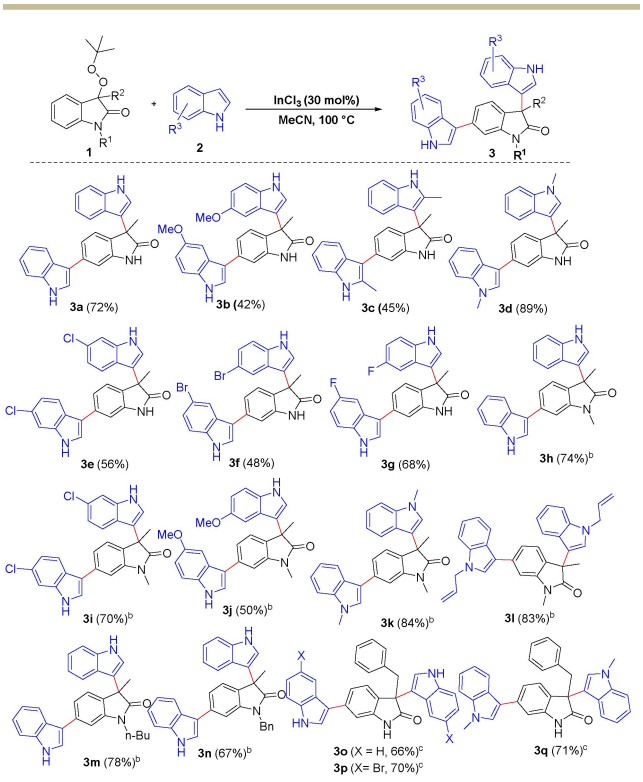


Figure 1. Representative bioactive compound having 2-oxindole core functionality.

To the best of our knowledge, there is no report for the consecutive remote C–H indolylation of peroxyoxindole and C3- indolylation of 2-oxindole by a peroxy displacement reaction. Further, there is no report for the sequential rearrangement of peroxyoxindole and incursion of the indole in the transient carbocation intermediate. For the first time, herein we report multiple new reactions promoted by a single Lewis acid-catalyst ($InCl_3$) for the remote C–H indolylation and C3-indolylation of peroxyoxindole. Whereas, by protecting N–H of the peroxyoxindole, a completely different reaction arises which led to rearrangement and indolylation of the transient carbocation. Moreover, $FeCl_3$ promotes consecutive Hock cleavage and further reaction with indole afforded biologically important trisindoline derivatives.

We commenced our reaction studies using 3-(*tert*-butylperoxy)-3-methylindolin-2-one **1a** and indole **2a**. Initially, we have performed a control experiment in the absence of catalyst, when peroxide and indole in acetonitrile are stirred at 100 °C for 24 hours, results in no reaction (Table 1, entry 1). We then accomplished the reaction using a catalytic amount of $Sn(OTf)_2$ (10 mol%), gave 48% yield of 3′-methyl-[3,3′:6′,3″-terindolin]-2′-one **3a** with deprotected peroxide **5a** in 37% as a byproduct (Table 1, entry 2). When the reaction was done with three equivalents of indole, the yield of product was improved (Table 1, entry 3). This suggests that an excess amount of indole is required for higher yield. Other catalysts such as AgOTf, $Cu(OTf)_2$, and $Pd(OAc)_2$ afford the reduced hydroxy product **6a** (Table 1, entries 5–7). Whereas $In(OTf)_3$, $Sc(OTf)_3$ and amberlyst-15 gave good yield of product 3′-methyl-[3,3′:6′,3″-terindolin]-2′-one **3a** in 66%, 55% and 50% respectively (Table 1, entries 8, 9, 10). These experiments reveal that $In(OTf)_3$ is the best catalyst for this transformation. Further, the role of solvent was also investigated, which suggested acetonitrile is a superlative solvent for this conversion (Table 1, entries 11–15). Moreover, higher catalyst loading (30 mol%) increases the yield of **3a** (Table 1, entry 16). The best-optimized condition obtained by heating the reaction mixture of 3-(*tert*-butylperoxy)-3-methylindolin-2-one (**1a**) and indole (**2a**) (3 eq.), in the presence of 30 mol% of $In(OTf)_3$ or $InCl_3$ catalyst at 100 °C for 24 hrs, which afforded product **3a** in 70% and 72% yield respectively (Table 1, entry 16 and 17). We used $InCl_3$ as a catalyst for the further reaction because it is less expensive than $In(OTf)_3$.

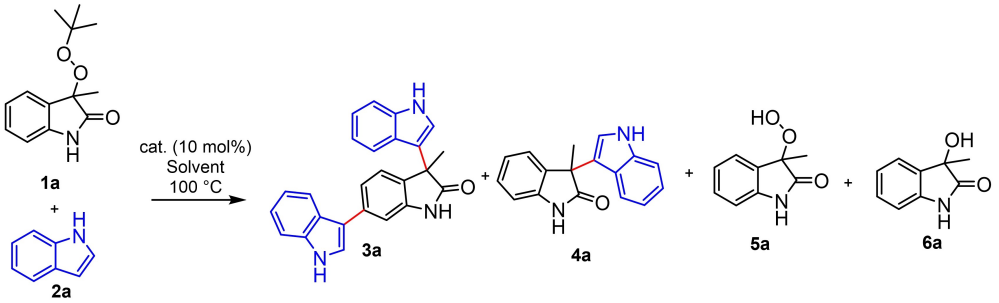
Next, these optimized conditions were applied to generalize the substrate scope for consecutive C–C bond formation with C–H functionalization of 2-oxindole at the C-6 carbon center (Scheme 1). Initially, the reaction of 3-(*tert*-butylperoxy)-3-methylindolin-2-one **1a** with optimized condition gave 3′-methyl-[3,3′:6′,3″-terindolin]-2′-one **3a** in 72% yield and the compound was well-characterized by spectroscopic techniques and X-ray analysis (see ESI Figure 1). The



[a]Reaction conditions: $InCl_3$ (30 mol%), 3-(tert-butylperoxy)-3-methylindolin-2-one **1a** (0.3 mmol), indole **2** (0.9 mmol), and acetonitrile (2 mL) were stirred at 100 °C for 24 hrs. [b]1-alkyl-3-(tert-butylperoxy)-3-methylindolin-2-one **1b** (0.3 mmol), [c]3-benzyl-3-(*tert*-butylperoxy)-indolin-2-one **1c** (0.3 mmol) used. Reported yields corresponds to isolated pure compounds.

Scheme 1. Substrate scope for sequential remote C–H functionalization and C-3 indolylation.[a]

Table 1. Optimization of reaction conditions[a]



sr. no[a]	catalyst (10 mol%)	solvent	yield **3a** (%)	yield **4a** (%)	yield **5a** (%)	yield **6a** (%)
1[b]	–	MeCN	–	–	–	–
2[b]	$Sn(OTf)_2$	MeCN	48	–	37	–
3	$Sn(OTf)_2$	MeCN	60	–	27	–
4[c]	$Sn(OTf)_2$	MeCN	57	–	38	–
5	AgOTf	MeCN	–	–	–	trace
6	$Cu(OTf)_2$	MeCN	–	–	–	45
7	$Pd(OAc)_2$	MeCN	–	–	–	42
8	$In(OTf)_3$	MeCN	66	–	–	17
9	$Sc(OTf)_3$	MeCN	55	9	15	–
10	Amberlyst-15	MeCN	50	–	35	–
11	$In(OTf)_3$	Dioxane	7	–	–	66
12	$In(OTf)_3$	Ethyl Acetate	Complicated reaction mix.			
13	$In(OTf)_3$	THF	Complicated reaction mix.			
14	$In(OTf)_3$	DMF	–	–	–	31
15	$In(OTf)_3$	Toluene	–	–	–	trace
16[d]	$In(OTf)_3$	MeCN	70	–	–	trace
17[d]	$InCl_3$	MeCN	72	–	–	trace

[a] **Reaction conditions**: [a]Catalyst (10 mol%), compound **1a** (0.3 mmol), indole **2a** (0.9 mmol), and solvent (2 mL) were stirred at 100 °C for 24 hrs.
[b] Indole **2a** (0.3 mmol).
[c] 80 °C.
[d] Catalyst (30 mol%). The mentioned yields are isolated yields.

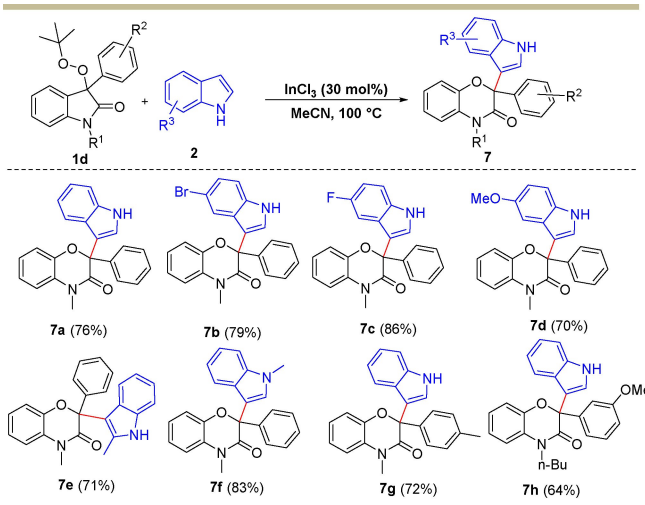
electron-donating group such as 2-methyl, 5-methoxy on indole afforded moderate to good yield of the product (**3b** and **3c**). Whereas in the case of *N*-methyl indole, the reaction proceeded smoothly and gave an 89% yield of **3d**. Electron-withdrawing substituted indoles like 6-chloro, 5-bromo, and 5-fluoro indoles were reacted well with peroxyoxindole **1a**, to deliver moderate yield of the products (**3e**–**3g**). Subsequently, the *N*-methyl peroxyoxindole **1b** provided good yields of the corresponding products (**3h**–**3l**). Furthermore, the reaction of *N*-butyl and *N*-benzyl protected peroxide afforded 78% and 67% yield of the products. The reaction also showed good results with 3-benzyl-3-(*tert*-butylperoxy)-indolin-2-one **1c** with 66%, 70% and 71% yields of the products **3o**, **3p** and **3q** respectively. However, this reaction with other hetero-arenes like pyrrole, benzofuran and imidazole were failed to give the respective products. To our delight, a gram-scale reaction was also successfully performed with 3-(*tert*-butylperoxy)-3-methylindolin-2-one **1a** and indole **2a** under optimized condition to afford 54% yield of the product **3a** along with 19% of **6a** as a byproduct.

After obtaining effective results with 3-alkyl peroxyoxindole for the construction of C–C bond by substitution of peroxide and C–H functionalization at C-6 carbon of oxindole, we turned towards the rearrangement reaction peroxyoxindole followed by indolylation to generate benzoxazinone with C–C bond formation. Recently, our group reported tin catalyzed rearrangement of peroxyoxindole for the construction of C–O bond.[14c] For the sequential rearrangement and indolylation of peroxide, 3-(*tert*-butylperoxy)-1-methyl-3-phenylindolin-2-one **1d** and 3 equivalents of indole **2a** were reacted in presence of $InCl_3$ (30 mol%) affording 2-(1*H*-indol-3-yl)-4-methyl-2-phenyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **7a** in 77% isolated yield. The spectroscopic data confirmed the product

7a. But we did not detect compound **3** in this reaction. Furthermore, we reoptimized the reaction condition and we found that 1.5 equivalents of indole was sufficient to deliver rearranged product **7a** in 76% yield. Then, we set out the substrate scope for this transformation by using various indole and 3-phenyl peroxyoxindole (Scheme 2). To our delight, the reaction of 3-(*tert*-butylperoxy)-1-methyl-3-phenylindolin-2-one **1d** with indole having an electron-withdrawing group like 5-bromo and 5-fluoro under optimized reaction conditions afforded the desired products **7b** and **7c** in excellent yield, respectively. Then, the indole bearing electron-donating functionalities such as 5-methoxy, 2-methyl provided good yields of the corresponding products (Scheme 2, **7d**–**7e**). Next, the *N*-protected indole gave 83% yield of the rearranged product **7f** and the structure of **7f** was confirmed by the X-ray analysis (see ESI figure 2). Moreover, the substitution on phenyl of 3-(*tert*-butylperoxy)-1-alkyl-3-phenylindolin-2-one gave moderate to good yield of the products (Scheme 2, **7g**–**7h**).

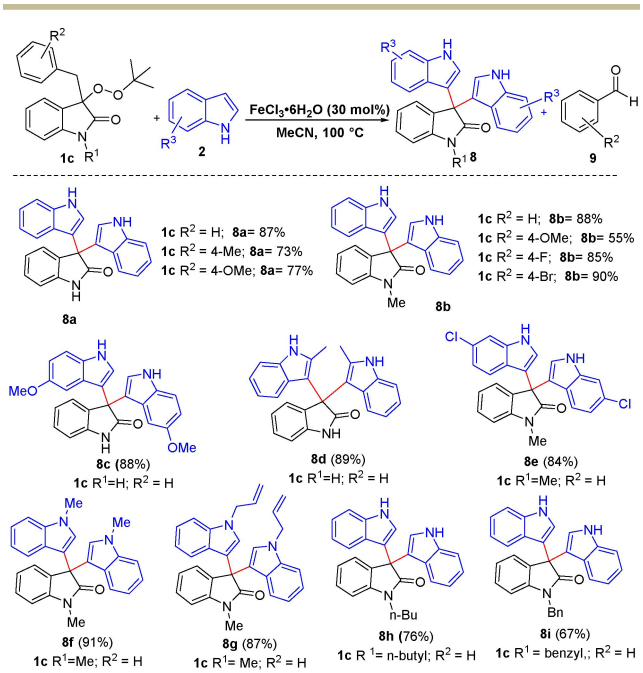
On the other hand, 3-benzyl-3-(*tert*-butylperoxy)-indolin-2-one **1c** undergoes Hock cleavage, which delivers trisindoline derivatives in the presence of indole and $FeCl_3 \cdot 6H_2O$ as a catalyst at 100 °C. Initially, we have optimized this reaction (see supporting information table-1) and we found the best optimization condition for this transformation is 3 equivalents of indole **2a** in the presence of 30 mol% Fe-catalyst at 100 °C giving 87% yield of the product **8a**. To extend the substrate scope, we studied this reaction with other substituted peroxyoxindoles. The electron-donating and electron-withdrawing substitution on the benzyl part of the peroxyoxindole result in a good to excellent yield of trisindoline derivatives **8b** (Scheme 3). Furthermore, indole having substitutions like 5-methoxy, 2-methyl, 6-chloro, *N*-methyl and *N*-allyl provided good to excellent yield of respective trisindoline products (**8c**–**8g**). This reaction was also successful with *N*-butyl and *N*-benzyl peroxyoxindole to give **8h** and **8i** in good yield, respectively.

To shed light on the mechanism, we performed the reaction of **4a** and **2a** under optimized reaction conditions, in which the desired product **3a** was not observed (Scheme 4, entry a). Furthermore, TBHP was added in the reaction of **4a** and **2a** to check the role of peroxy group on C–H functionalization, then product **3a** was not detected (Scheme 4, entry b). Next, a reaction of **5a** or **6a** with **2a** under standard condition afforded **3a**. This suggests that product **3a** can be formed from **5a** or **6a** as an intermediate (Scheme 4, entry c and d). These experiments clearly emphasize that both C–H functionalization and substitution take place simultaneously. Moreover, absence of peroxy group in 3-methyl-2-oxindole or 6-cholorooxindole results no reaction with indole in the presence/absence



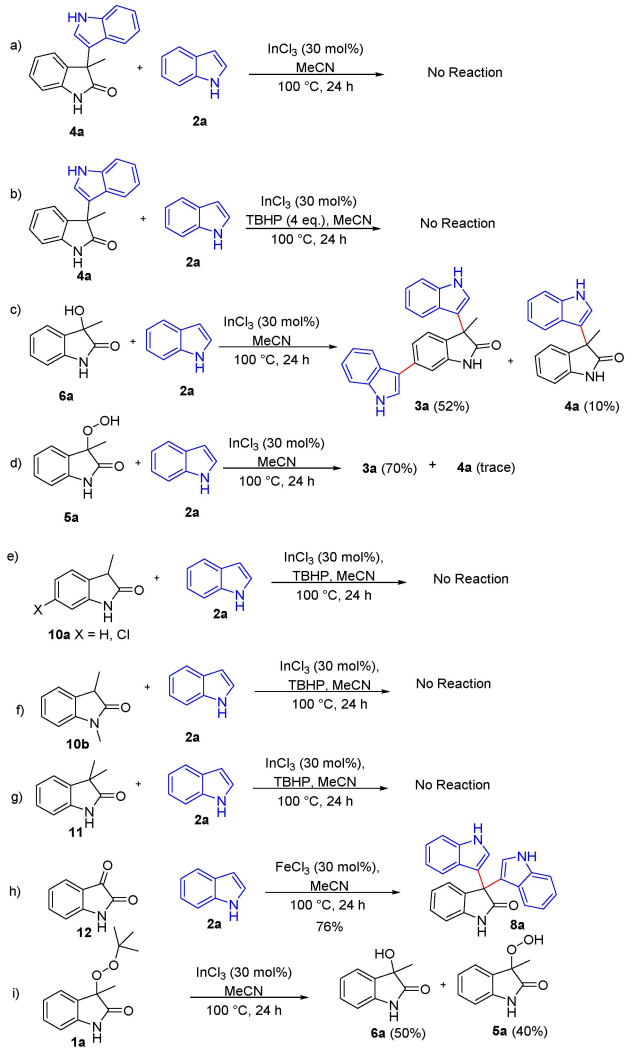
[a]Reaction conditions: $InCl_3$ (30 mol%), 3-(*tert*-butylperoxy)-1-methyl-3-phenylindolin-2-one **1d** (0.2 mmol), indole **2** (0.3 mmol), and acetonitrile (2 mL) were stirred at 100 °C for 24 hrs. Reported yields corresponds to isolated pure compounds

Scheme 2. Substrate scope for sequential rearrangement and indolylation of peroxyoxindole.[a]

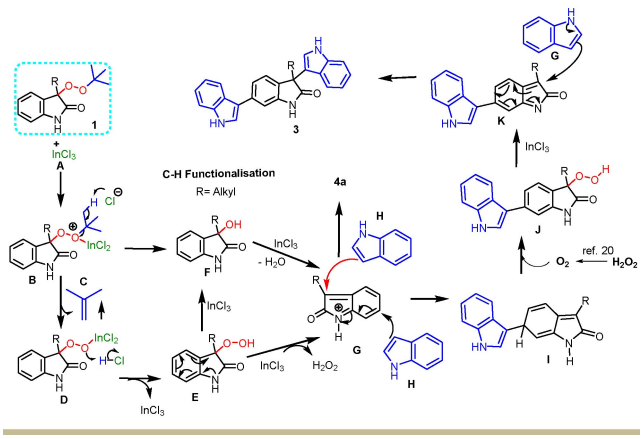


[a]Reaction conditions: $FeCl_3 \cdot 6H_2O$ (30 mol%), compound **1c** (0.2 mmol), indole **2** (0.6 mmol), and acetonitrile (2 mL) were stirred at 100 °C for 24 hrs. Reported yields corresponds to isolated pure compounds

Scheme 3. Synthesis of trisindoline via sequential Hock cleavage and indolylation.[a]



Scheme 4. Experiments for mechanisms studies.

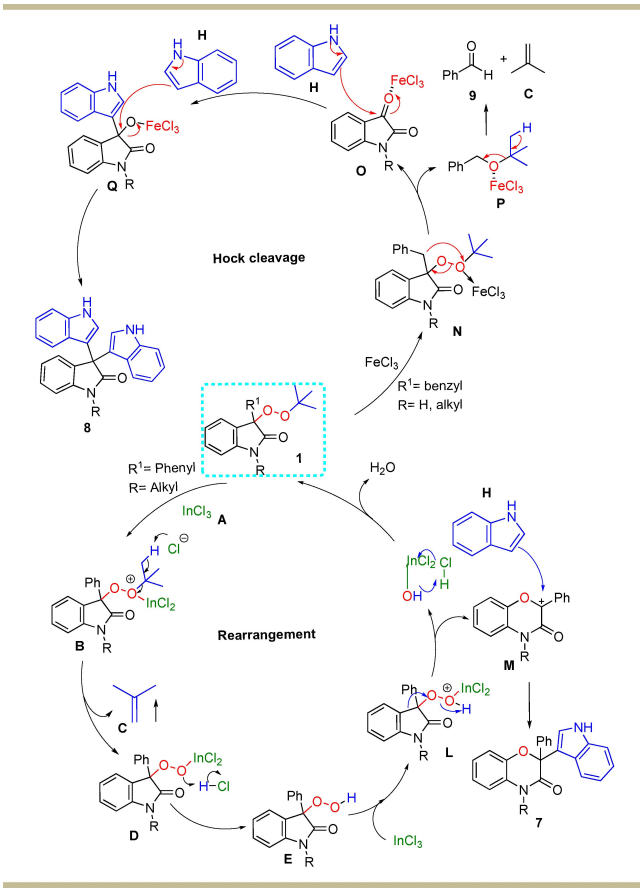


Scheme 5. Plausible mechanism for sequential remote C–H functionalization and C-3 indolylation.

of external the oxidant TBHP. This indicates that peroxide functionality is crucial for the C–H functionalization (Scheme 4, entry e). Similarly, dimethyl substituted 2-oxindole or 3,3-dimethyl-2-oxindole under the same condition resulted no reaction (Scheme 4, entry f, g). Furthermore, in absence of indole, peroxyoxindole gave product **5 a** and **6 a** (Scheme 4, entry i). From this, it was clear that the peroxy functionality (O–O–R) plays a vital role for the formation of product **3**.

Based on experimental observation and previous literature reports[9,14b,c,19] plausible mechanism for $InCl_3$ catalyzed synthesis 3′-methyl-[3,3′:6′,3″-terindolin]-2′-one **3** is illustrated in scheme 5. Initially, In(III) coordinates with peroxide **1** to form **B**. Then **B** undergoes deprotonation produce complex **D** with the liberation of isobutylene **C**.[14b,c] The formation of isobutylene is confirmed by ^{1}H-NMR and GC-MS spectra. Subsequently, protonation of intermediate **D** and elimination of $InCl_3$ generate complex **E**.[14b,c] Furthermore, intermediate **G** can be formed from intermediate **E** by elimination of H_2O_2,[9] which is facilitated by the tautomerism involved with free N–H of the peroxyindole in the presence of Lewis acid, $InCl_3$. Alternatively, intermediate **G** can also be formed via the intermediate **F** by elimination of water assisted by $InCl_3$. Also, this intermediate **G** is confirmed by HRMS analysis (see ESI, figure 3). According to literature reports,[19] C-6 carbon of intermediate **G** has the highest positive charge density than C-3. Hence indole attack at C-6 carbon of complex **G** to afford dearomatised complex **I**. Further, O_2 might be generated in-situ from H_2O_2 under the experimental condition.[20] Then, aromatization and peroxidation of the complex **I** in the presence of H_2O_2 or O_2 led the intermediate **J**. Further, the intermediate **J** can be transformed into the intermediate **K** in the presence of $InCl_3$. Finally, second indole attacks on C-3 of the intermediate **K** led to the desired product **3**. The product **4** is formed by the direct indole attack on the C3 position of the intermediate **G**.

The proposed mechanistic steps for rearrangement reaction are similar to that of the substitution of peroxide (Scheme 6). However, in the case of rearrangement, complex **D** undergoes protonation to afford intermediate **E**. Further coordination of **E** with $InCl_3$ furnished the Indium chelated complex **L**. Next, ring expansion led to carbocation intermediate **M** with regeneration of catalyst **A**.[14b,c] This might be due to resonance effect of phenyl ring which donate the electron to the reactive center. This facilitate the ring expansion via C3–C4 carbon shift on to oxygen to form the intermediate **M**. This carbocation **M** is trapped by indole **H** to afford rearranged product **7**.



Scheme 6. Plausible mechanism for rearrangement and Hock cleavage.

Interestingly, based on previous literature reports, the possible reaction mechanism for the Hock cleavage product **8** and byproduct **9** is shown in Scheme 6.[9],[14c][16] In this case, iron (III) chloride chelates with the peroxy (O–O) bond of **1** to produce complex **N**. The migration of benzyl group on the oxygen of peroxy (O–O) will generate isatin **O** and (*tert*-butoxymethyl)benzene **P**. Then benzaldehyde **9** is formed as a cleaved product from **P** with the elimination of isobutylene. Next, iron (III) is coordinate with a carbonyl of isatin followed by indole attack to generate complex **Q**. Finally, another molecule of indole **H** is reacting with complex **Q** to afford the desired product **8**. Moreover, a reaction of isatin with excess of indole in the presence of 30 mol% of $FeCl_3$ afforded the product **8** (Scheme 4, entry h), support for the proposed mechanism (Scheme 6).

In conclusion, the substituents on peroxyoxindole delivered diverse reactions with indole in the presence of Lewis acid as a catalyst. Thus, a sequential double indolylation of peroxyoxindole via remote C–H functionalization and C3-peroxy substitution for the synthesis of terindolinone was achieved by inexpensive $InCl_3$ as a catalyst. Moreover, N–H protected 3-phenyl peroxyoxindole undergoes sequential rearrangement afforded 2-(1*H*-indol-3-yl)-4-methyl-2-phenyl-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one. Whereas in the case of $FeCl_3 \cdot 6H_2O$, 3-benzyl-3-(*tert*-butylperoxy)-indolin-2-one undergoes oxidative (hock) cleavage followed by indolylation delivers biologically active trisindoline derivatives. All the reactions were supported with a significant number of examples in 42–91% yields and the products were completely characterized by spectroscopic data. The mechanism was justified with the experimental evidences and based on the previous literature reports.

Experimental Section

General experimental procedure for the synthesis of 3′-alkyl-[3,3′:6′,3″-terindolin]-2′-one (3): In a 20 mL re-sealable vial was added $InCl_3$ (0.09 mmol, 30 mol%), acetonitrile 2 mL, peroxy compound (0.3 mmol, 1 equivalent) and finally indole (0.9 mmol 3 equivalent). The tube was sealed with a cap using crimper. The reaction mixture was heated at 100 °C in a preheated oil bath for 24 hrs. After 24 hrs added DCM and a volatile component was evaporated using a vacuum and residue was directly purified using silica gel chromatography (EtOAc: hexane = 20:80 to 50:50).

General experimental procedure for the rearrangement reaction product (7): In a 20 mL re-sealable vial was added $InCl_3$ (0.06 mmol, 30 mol%), acetonitrile 2 mL, peroxy compound (0.2 mmol, 1 equivalent) and finally indole (0.3 mmol 1.5 equivalent). The tube was sealed with a cap using crimper. The reaction mixture was heated at 100 °C in a preheated oil bath for 24 hrs. After 24 hrs added DCM and a volatile component was evaporated using a vacuum and residue was directly purified using silica gel chromatography (EtOAc: hexane = 15:85 to 30:70).

General experimental procedure for synthesis of trisindoline (8) via Hock-rearrangement/cleavage: In a 20 mL re-sealable vial (equipped with rubber septum and N_2 balloon) was added $FeCl_3 \cdot 6H_2O$ (0.06 mmol, 30 mol%), acetonitrile 2 mL, peroxy compound (0.3 mmol, 1 equivalent) and finally indole (0.9 mmol 3 equivalent). The tube was sealed with a cap using crimper. The reaction mixture was heated at 100 °C in a preheated oil bath for 24 hrs. After 24 hrs added DCM and a volatile component was evaporated using a vacuum and residue was directly purified using silica gel chromatography (EtOAc: hexane = 20:80 to 50:50).

The X-ray crystal structure: Crystallographic data are deposited with the Cambridge Crystallographic Data Centre (CCDC) under the following accession numbers: **3 a** (2054406) and **7 f** (2060053). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif/.

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Indium Catalyzed Sequential Regioselective Remote C–H Indolylation and Rearrangement Reaction of Peroxyoxindole

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