# Organic & Biomolecular Chemistry

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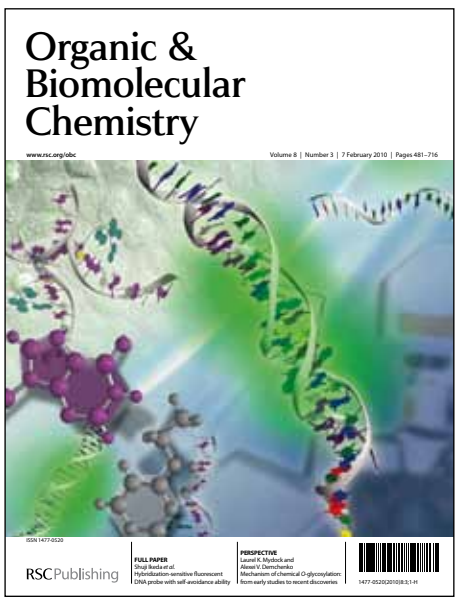


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# Acid-Catalyzed Reactions of 3-Hydroxy-2-oxindoles with Electron-rich Substrates: Synthesis of 2-Oxindoles with All-Carbon Quaternary Center†

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†This paper is dedicated to Professor Hiriyakkanavar Ila, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, India.

**Lewis acid catalyzed reaction of *in situ* generated 2*H*-indol-2-one (9) with various 2π and other electron-rich substrates has been developed. A variety of electron-rich substrates such as allyl/methallyltrimethylsilane, phenylacetylene, styrenes, acetophenone, and indoles have been used. The methodology provides a straightforward approach for the synthesis of 2-oxindoles with an all-carbon quaternary center at the pseudobenzylic position.**

The development of efficient methodologies to forge an all-carbon quaternary stereocenter[1] remains an active area in the realm of exploratory synthetic research. Towards this, methods involving catalytic reagents/conditions are comparatively more appealing and needs further exploration.[2] In this regard, 2-oxindoles bearing an all-carbon quaternary stereocenters at the C-3(a) position comprise a common structural motif in many biologically active complex cyclotryptamine alkaloids, such as idiospermuline (**1a**), calycosidine (**1b**)[3] (Figure 1) having tricyclic C(3a)-arylpyrroloindoline core (**2**) and hence, is a fascinating synthetic target to achieve. The tricyclic core **2** has been reported to be synthesized from 3-allylated-2-oxindole **3**.

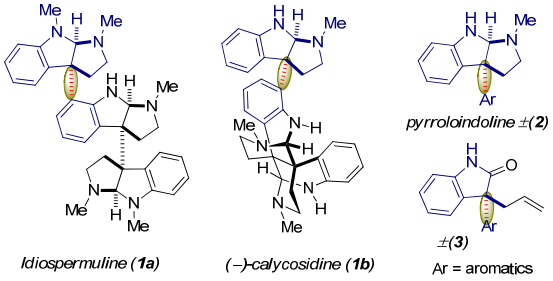


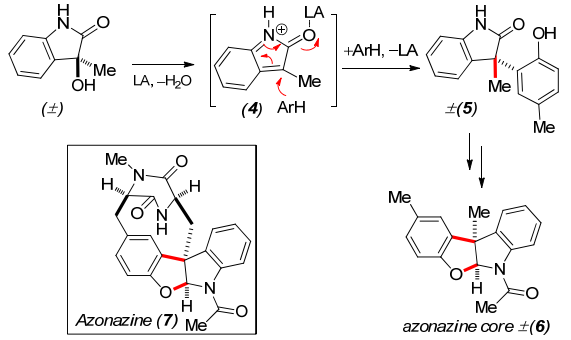

**Figure 1**. Alkaloids (**1a-b**) sharing quaternary stereocenters.

3-Hydroxy-2-oxindole especially serves as a versatile building block for the syntheses of many indole based biologically active molecules. Their ability to undergo variety of nucleophilic substitution reactions (for instance, Friedel-Crafts alkylations of aromatic compounds with 3,3-disubstituted-2-oxindole[4] as electron-deficient partner), has made them extensively used powerful synthetic tool to realize different C-C bond forming events. In 1985, Baeyer and Lazarus,[5a] for the first time, accessed symmetrical 3,3-disubstituted oxindoles starting from isatin through iterative electrophilic aromatic substitutions. In 1998, Olah and co-workers[5b] reported a general synthetic route to symmetrical 3,3-disubstituted oxindoles from isatins in superacidic triflic acid ($CF_3SO_3H$, TfOH). Following this report, Halperin,[5c] Zolotukhin,[5d] and Björkling[5e] independently reported similar approaches to a variety of symmetrical and unsymmetrically substituted 2-oxindoles. In 2006, Yadav and co-workers reported synthesis of trisindole type structures utilizing $Bi(OTf)_3$-catalyzed condensation of isatin and indoles.[5f]

In 2004, Nicolaou *et al.*[6a] demonstrated that 3-hydroxy-2-oxindole could be activated under the influence of trifluoromethane sulfonic acid leading to the formation of an all-carbon quarternary center at the pseudobenzylic (3a)-position of 2-oxindole derivative. Their pioneering work led to the efficient total synthesis of diazonamide A[6a] and related structures. Further, in 2007, Padwa and co-workers[6b-c] reported $BF_3.OEt_2$-catalyzed F-C alkylations as well as intramolecular reactions of 3-hydroxy-2-oxindoles with electron-rich 2π-systems for the synthesis of unsymmetrically substituted 2-oxindoles and spiro-oxindole derivatives. Later, Neuville and Zhu *et al.*[6d] reported trifluoroacetic acid promoted an intramolecular double F-C alkylations to access spiro-oxindoles. Recently, Zhou and coworkers studied $Hg(ClO_4)_2.3H_2O$-catalyzed[6e] F-C alkylations of electron-rich aromatics with 3-hydroxyoxindoles and $HClO_4$-catalyzed synthesis of α-quaternary esters or ketones[6f] and benzofuranones bearing a quaternary center.[6g] Very recently, Zhu and co-workers[6h] have reported a one-pot integrated Brønsted base-catalyzed trichloroacetimidation of 3-hydroxyoxindoles followed by Brønsted acid-catalyzed nucleophilic substitution reaction to access a variety of unsymmetrically substituted 2-

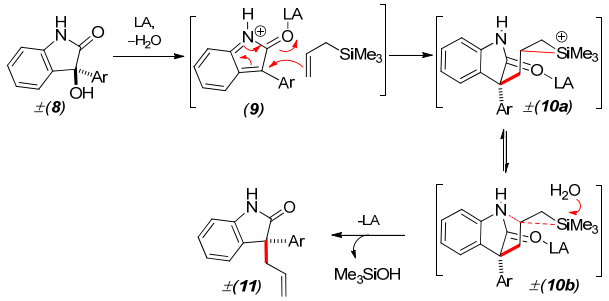
oxindoles. In addition, Lewis acid-activation strategy has also been applied in the synthesis of variety of 2-oxindoles containing heteroatom at the 3-position.[7]

Very recently, we have also shown an efficient Lewis acid catalyzed Friedel-Crafts alkylations of phenols with 3-alkyl-3-hydroxy-2-oxindole through the intermediacy of 2*H*-indol-2-one ring **4**.[8] The methodology was applied for the synthesis of tetracyclic core **6** of azonazine **7** (Scheme 1).[8] In case of 3-hydroxy-2-oxindoles, the Friedel-Crafts alkylations are known to proceed through the formation of 2*H*-indol-2-one ring (Scheme 1). Similar kind of species are also reported to be formed under base mediated elimination of 3-halo-2-oxindoles and is well utilized in the total synthesis of complex indole alkaloids *via* formal cycloaddition processes.[9,10] Continuing our efforts aiming at the studies towards total synthesis of complex indole alkaloids,[11] herein, we report a Lewis acid catalyzed *in situ* generation of 2*H*-indol-2-one ring from 3-aryl-3-hydroxy-2-oxindoles **8** and their subsequent reactions with substrates having 2π–systems to generate 2-oxindoles bearing an all-carbon quaternary center at the pseudobenzylic position.




**Scheme 1:** F-C alkylation approach to the azanozine core.

At the outset, we attempted the possibility of addition of allyltrimethylsilane onto the reactive 2*H*-indol-2-one ring **9** to affect allylation reactions. We thought that the generation of well established silyl-stabilized β-carbocation[12] intermediate **10a** by the reaction of 2*H*-indol-2-one **9** with allyltrimethylsilane (Scheme 2), could be stabilized by amide nitrogen to form intermediate **10b**. Intermediate **10b** would then afford the allylated product **11** on subsequent removal of $Me_3SiOH$.




**Scheme 2:** Working hypothesis of allylation reactions.

Initially the allylation reactions were carried out using 1.5 equiv. of allyltrimethylsilane as 2π substrate with 1 equiv. of 3-hydroxy-2-oxindole **8a** (*in situ* generated 2*H*-indol-2-one **9**) in presence of $BF_3.OEt_2$ and $HClO_4$ at room temperature and the results are summarized in table 1. Among various solvents *viz.* *c*-hexane, diethylether, THF, dichloroethane, ethylacetate, xylene, DMF, benzene, toluene, and mesitylene screened (entries 1-10), dichloroethane (entry 4) was found to be reasonably good and provided 66% of **11a** when 20 mol% of $BF_3.OEt_2$ was used as catalyst. This encouraged us to carry out the reactions in other chlorinated solvents such as dichloromethane and chloroform. We found that, 20 mol% of $BF_3.OEt_2$ afforded products in 68% and 94% yields in dichloromethane and chloroform, respectively (entries 11 and 12).

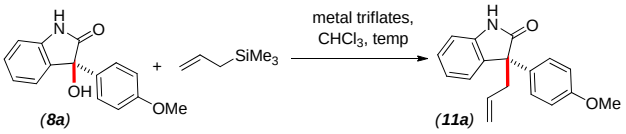
**Table 1:** Optimization of $BF_3.OEt_2/HClO_4$-catalyzed allylation reactions.


| entry | cat. (mol%) | solvent | temp. | time | yield[a,b] | 8a[c] |
|---|---|---|---|---|---|---|
| 1. | 20 mol% $BF_3.OEt_2$ | *c*-hexane | 25 °C | 10 h | 21% | 48% |
| 2. | 20 mol% $BF_3.OEt_2$ | $Et_2O$ | 25 °C | 7 h | 10% | 72% |
| 3. | 20 mol% $BF_3.OEt_2$ | THF | 25 °C | 9 h | 08% | 81% |
| 4. | 20 mol% $BF_3.OEt_2$ | DCE | 25 °C | 3 h | 66% | 12% |
| 5. | 20 mol% $BF_3.OEt_2$ | EtOAc | 25 °C | 10 h | traces | 90% |
| 6. | 20 mol% $BF_3.OEt_2$ | xylene | 25 °C | 8 h | 14% | 64% |
| 7. | 20 mol% $BF_3.OEt_2$ | DMF | 25 °C | 12 h | traces | 82% |
| 8. | 20 mol% $BF_3.OEt_2$ | benzene | 25 °C | 5 h | 39% | 40% |
| 9. | 20 mol% $BF_3.OEt_2$ | toluene | 25 °C | 4 h | 42% | 34% |
| 10. | 20 mol% $BF_3.OEt_2$ | mesitylene | 25 °C | 5 h | 33% | 40% |
| 11. | 20 mol% $BF_3.OEt_2$ | $CH_2Cl_2$ | 25 °C | 2 h | 68% | 21% |
| 12. | 20 mol% $BF_3.OEt_2$ | $CHCl_3$ | 25 °C | 2 h | 94% | -- |
| 13. | 10 mol% $BF_3.OEt_2$ | $CH_2Cl_2$ | 25 °C | 3 h | 62% | 11% |
| **14.** | **10 mol% $BF_3.OEt_2$** | **$CHCl_3$** | **25 °C** | **3 h** | **93%** | **--** |
| 15. | 5 mol% $BF_3.OEt_2$ | $CHCl_3$ | 25 °C | 5 h | 60% | 17% |
| 16. | 5 mol% $BF_3.OEt_2$ | $CHCl_3$ | 40 °C | 2 h | 71% | 08% |
| 17. | 20 mol% $HClO_4$ | $CHCl_3$ | 25 °C | 0.5 h | 95% | -- |
| 18. | 20 mol% $HClO_4$ | $CH_2Cl_2$ | 25 °C | 0.5 h | 89% | -- |
| **19.** | **10 mol% $HClO_4$** | **$CHCl_3$** | **25 °C** | **0.5 h** | **91%** | **--** |
| 20. | 10 mol% $HClO_4$ | $CH_2Cl_2$ | 25 °C | 0.5 h | 86% | -- |
| 21. | 5 mol% $HClO_4$ | $CHCl_3$ | 25 °C | 1 h | 82% | -- |
| 22. | 5 mol% $HClO_4$ | $CHCl_3$ | 40 °C | 0.5 h | 85% | -- |
| 23. | 5 mol% $HClO_4$ | $CH_2Cl_2$ | 25 °C | 1 h | 76% | -- |
| 24. | 10 mol% $BF_3.OEt_2$ | $CH_3CN$ | 25 °C | 2 h | 49% | 32% |
| 25. | 10 mol% $HClO_4$ | $CH_3CN$ | 25 °C | 1 h | 54% | --[d] |

[a]reactions were carried out on a 0.5 mmol of **8a** with 0.75 mmol of allyl/methallylsilane in 2.5 mL of solvent. [b]isolated yields after column chromatography. [c]isolated starting materials. [d]decomposition of the rest of the mass balance.

Interestingly, 10 mol% of $BF_3.OEt_2$ also afforded products **11a** in 93% yields in chloroform (entry 14). However, on further decrease in catalyst loading to 5 mol%, the yield of the reaction dropped down to 60% (entry 15). On the other hand, 10 mol% of $HClO_4$ afforded products in 89% and 91% yields in dichloromethane and chloroform, respectively (entries 18 and 19), whereas, 5 mol% of $HClO_4$ afforded products in 82-85% yields (entries 21 and 22). We found that acetonitrile[13] was not a good choice as solvent and afforded products in 49-54% yields when the reactions were carried out at room temperature in the presence of 10 mol% of $BF_3.OEt_2$ and $HClO_4$, respectively. Thus, we decided to carry out the allylation reactions in the presence of 10 mol% of each $BF_3.OEt_2$ and $HClO_4$ as catalysts in chloroform at room temperature.

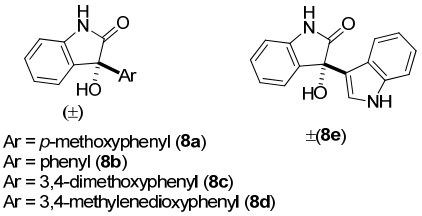
**Table 2:** Optimization using metal-triflates.




| entry | Lewis acid | eqiuv.[a] | temp. | time | yield[b] |
|---|---|---|---|---|---|
| 1. | $Sc(OTf)_3$ | 20 mol% | 25 °C | 12 h | 10%[c] |
| 2. | $Zn(OTf)_2$ | 20 mol% | 25 °C | 12 h | traces[c] |
| 3. | Ag(OTf) | 20 mol% | 25 °C | 16 h | 09% |
| 4. | Cu(OTf) | 20 mol% | 25 °C | 12 h | 15% |
| 5. | $Ce(OTf)_3$ | 20 mol% | 25 °C | 12 h | 40% |
| 6. | $Sn(OTf)_2$ | 20 mol% | 25 °C | 4 h | 89% |
| **7.** | **$Sn(OTf)_2$** | **10 mol%** | **25 °C** | **8 h** | **88%[d]** |
| 8. | $Sn(OTf)_2$ | 10 mol% | 45 °C | 0.5 h | 60% |
| 9. | $Bi(OTf)_3$ | 20 mol% | 25 °C | 4 h | 85% |
| **10.** | **$Bi(OTf)_3$** | **10 mol%** | **25 °C** | **6 h** | **80%[e]** |
| 11. | $Bi(OTf)_3$ | 10 mol% | 45 °C | 0.5 h | 62% |
| 12. | $Cu(OTf)_2$ | 20 mol% | 25 °C | 2 h | 70% |
| **13.** | **$Cu(OTf)_2$** | **10 mol%** | **25 °C** | **4 h** | **66%[f]** |
| 14. | $Yb(OTf)_3$ | 20 mol% | 25 °C | 12 h | traces[c] |
| 15. | $In(OTf)_3$ | 20 mol% | 25 °C | 1.5 h | 80% |
| **16.** | **$In(OTf)_3$** | **10 mol%** | **25 °C** | **2 h** | **75%[g]** |

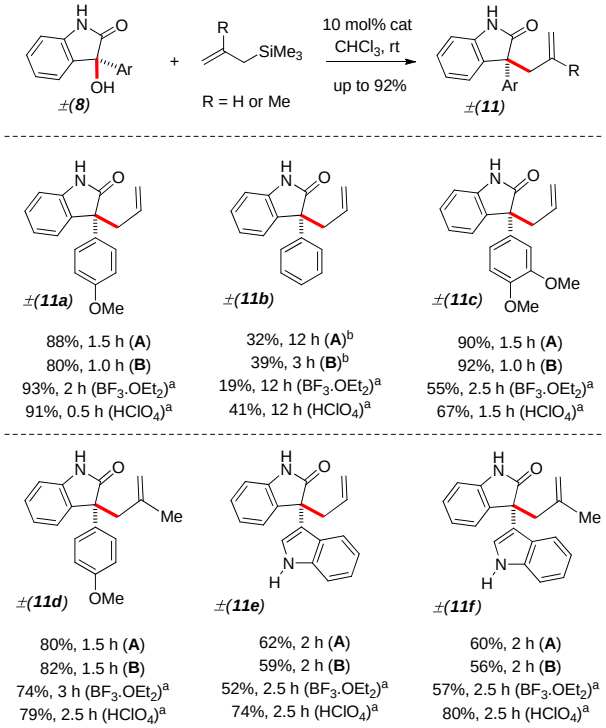
[a]Reactions were carried out on a 1.0 mmol of **8a** with 3.0 mmol of allyltrimethylsilane in 5 mL of $CHCl_3$. [b]Isolated yields after column chromatography. [c]Starting materials were isolated in most of the cases. [d]condition **A**: 10 mol% $Sn(OTf)_2$; [e]condition **B**: 10 mol% $Bi(OTf)_3$; [f]condition **C**: 10 mol% $Cu(OTf)_2$; [g]condition **D**: 10 mol% $In(OTf)_3$

Next, we screened the reaction in the presence of a variety of metal triflates and the results are shown in table 2. It was found that 20 mol% of metal triflates such as $Sc(OTf)_3$, $Zn(OTf)_2$, Ag(I)OTf, Cu(I)OTf, $Ce(OTf)_3$, and $Yb(OTf)_3$ were inefficient in providing **11a** in good yields (entries 1-5 and 14). After exhaustive optimization (table 2), we found that 10 mol% $Sn(OTf)_2$ (condition **A**), $Bi(OTf)_3$ (condition **B**), $Cu(OTf)_2$ (condition **C**), and $In(OTf)_3$ (condition **D**) each resulted in the formation of allylated 2-oxindole derivatives **11a** in 88%, 80%, 66%, and 75% yields, respectively, at room temperature (entries 7, 10, 13, and 16).




Ar = *p*-methoxyphenyl (**8a**)
Ar = phenyl (**8b**)
Ar = 3,4-dimethoxyphenyl (**8c**)
Ar = 3,4-methylenedioxyphenyl (**8d**)

**Figure 2**. 3-Hydroxy-3-aryl-2-oxindoles used in this study.



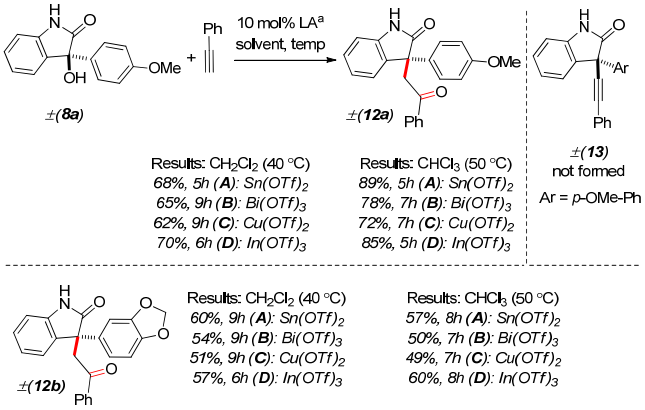

Reactions were carried out on a 1.0 mmol of **8** with 3.0 mmol of silane reagent in 5 mL of $CHCl_3$. [a]10 mol% of catalysts and 1.5 mmol of silane reagent were used. [b]starting materials were recovered for rest of the mass balance. condition **A**: 10 mol% $Sn(OTf)_2$; condition **B**: 10 mol% $Bi(OTf)_3$.

**Figure 3:** Reactions of 3-hydroxy-2-oxindoles with allyl/methallyl trimethylsilane.

Having the optimized condition in hand, various 3-hydroxy-2-oxindoles (**8a-e**, Figure 2) were reacted with allylsilane/methallyl trimethylsilane in chloroform in the presence of 10 mol% of $Sn(OTf)_2$ (condition **A**), $Bi(OTf)_3$ (condition **B**), and 10 mol% of each $BF_3.OEt_2$ and $HClO_4$ as catalysts to furnish various 2-oxindole moeities bearing an all-carbon quaternary stereocenters at 3-position. To our delight, these reactions worked without event to generate desired allylated/methallylated products **11a-f** in moderate to excellent yields (Figure 3), except in the case of substrate **8b** which afforded only 19-41% of allylated

product **11b**. This led us to a conclusion that, in order to achieve better yields, the substrates must contain electron-donating group. 2-Oxindoles of the type **11a-d** are known to be potential intermediates for the synthesis of C-(3a)-arylpyrroloindoline **2**, a common structural motif present in many complex alkaloids (see, **1a-b** in figure 1).[14] We believe that, the 2-oxindoles **11e-f** could serve as an advanced intermediate for the synthesis of bis-indole based alkaloids.[15]

The outcome of the allylation chemistry of the *in situ* generated **9** encouraged us to check the addition of terminal alkyne to the reactive 2*H*-indol-2-one **9** (Scheme 3). To our delight, on subjecting 3-hydroxy-2-oxindole **8a** with phenylacetylene in presence of Lewis acids such as 10 mol% each of $Sn(OTf)_2$ (condition **A**), $Bi(OTf)_3$ (condition **B**), $Cu(OTf)_2$ (condition **C**) and $In(OTf)_3$ (condition **D**) in refluxing dichloromethane, we could achieve **12a** in 68%, 65%, 62%, and 70% yields, respectively (Scheme 3). We also found similar efficiencies when the reactions were conducted in refluxing chloroform. Notably, there were no traces of phenylacetylene addition product **13** being formed. The methodology was further extended to substrate **8d** which led to the formation of **12b** (up to 60% yields) in almost similar efficiency (Scheme 3). The single crystal X-ray analysis of products **12a** and **12b** unambiguously proved the formation of 2-oxindoles having an all-carbon quaternary center at the pseudobenzylic position.

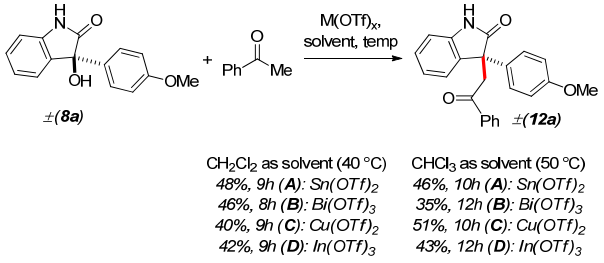



X-ray of **12a** (CCDC 933799) X-ray of **12b** (CCDC 933800)

Reactions were carried out on a 1.0 mmol of **8a** with 3.0 mmol of phenylacetylene in 5 mL of solvent. [a]10 mol% Lewis acids were used in all cases.

**Scheme 3:** Lewis acid catalyzed phenylacetylene addition to **±8a**.

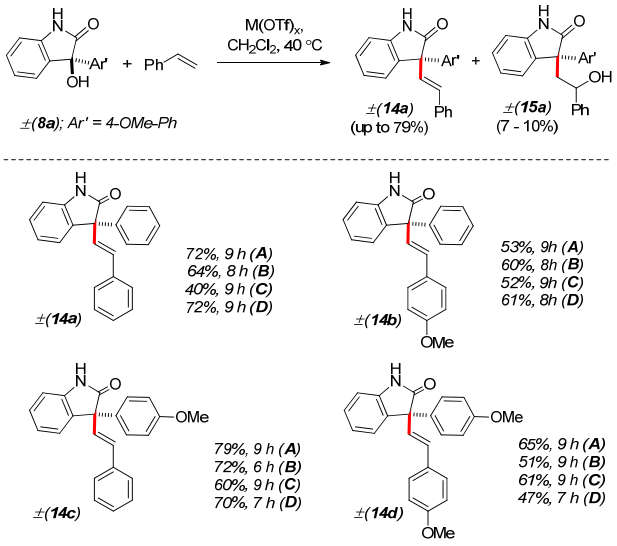
Further, we envisioned that similar 2-oxindole **12a** could be achieved from a reaction of 3-hydroxy-2-oxindole **8a** with acetophenone in the presence of Lewis acids. Noticeably, 10 mol% each of $Sn(OTf)_2$ (condition **A**), $Bi(OTf)_3$ (condition **B**), $Cu(OTf)_2$ (condition **C**) and $In(OTf)_3$ (condition **D**) in refluxing dichloromethane, afforded 2-oxindole **12a** in 48%, 46%, 40%, and 42% yields, respectively (Scheme 4). Similar efficiencies were observed when the reactions were carried out in refluxing chloroform (up to 51% yields of **12a**). This study suggests that an unmasked ketone can be added to the 3-aryl-3-hydroxy-2-oxindole under the influence of Lewis acid, *via* the keto-enol tautomerization.




Reactions were carried out on a 1.0 mmol of **8a** with 3.0 mmol of acetophenone in 5 mL of solvent and 10 mol% Lewis acids were used in all cases.

**Scheme 4:** Reactions of **±8a** with acetophenone.

Next, we tested the possibility of the reactions of 3-hydroxy-2-oxindoles **8a-b** with styrene as 2π substrates in the presence of Lewis acids.




Reactions were carried out on a 1.0 mmol of **8a** with 5.0 mmol of styrenes in 5 mL of $CH_2Cl_2$. condition **A**: 10 mol% $Sn(OTf)_2$; condition **B**: 10 mol% $Bi(OTf)_3$; condition **C**: 10 mol% $Cu(OTf)_2$; condition **D**: 10 mol% $In(OTf)_3$.

**Scheme 5:** Reactions of 3-hydroxy-2-oxindoles with styrene.

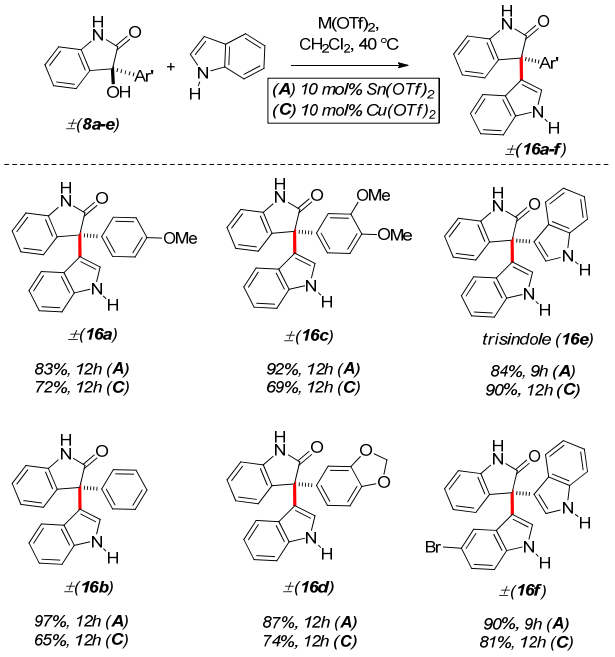
Interestingly, on subjecting styrene with 3-hydroxy-2-oxindole **8a** in the presence of Lewis acids such as 10 mol% each of $Sn(OTf)_2$ (condition **A**), $Bi(OTf)_3$ (condition



**B**), $Cu(OTf)_2$ (condition **C**) and $In(OTf)_3$ (condition **D**) in refluxing dichloromethane,[16] afforded 2-oxindole **14a** in 72%, 64%, 40%, and 72% yields, respectively (Scheme 5) along with 7-10% of **15a**. These reactions were found to be quite general to afford products **14a-d** in moderate to good yields (Scheme 5). Interestingly, the 2-oxindoles of the type **14** were also found to be potential intermediates for various complex alkaloids shown in figure 1.[15]

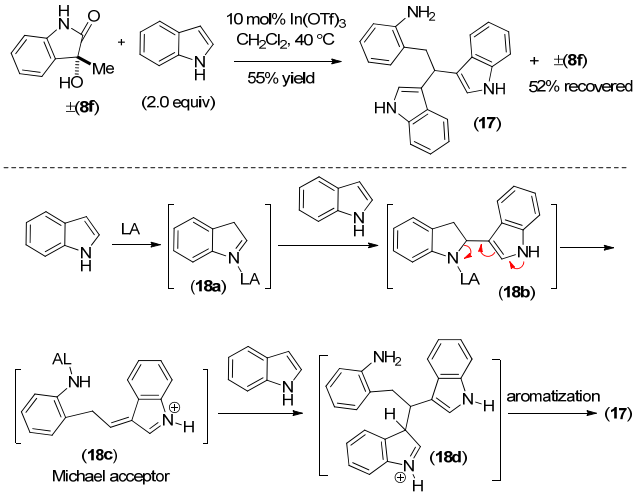
Further, encouraged by the precedence of cesium carbonate promoted reaction of 3-halo-2-oxindoles with 3-substituted indoles by Funk et al. in the synthesis of perophoramidine,[9a] we then looked into the possibility of a Lewis-acid catalyzed reaction of 3-hydroxy-2-oxindoles with indole (Scheme 6). We found that, 10 mol% of $Sn(OTf)_2$ (condition **A**) and $Cu(OTf)_2$ (condition **C**) can afforded various trisindoles (**16a-f**) in good to excellent yields.[17] In the event, we have shown an efficient synthesis of trisindole **16e** (Scheme 6), a metabolite from *vibrio sp.* isolated from a sponge,[18] in 84-90% yields.

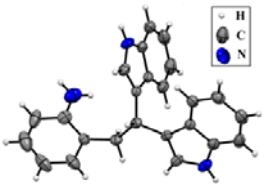



Reactions were carried out on a 1.0 mmol of **8** with 2.0 mmol of indoles in 5 mL of $CH_2Cl_2$. condition **A**: 10 mol% $Sn(OTf)_2$; condition **C**: 10 mol% $Cu(OTf)_2$.

**Scheme 6:** Reactions of 3-hydroxy-2-oxindoles with indole.

However, to our surprise, when 3-hydroxy 3-methyl 2-oxindole **8f** was reacted with 2 equiv of indole under the influence of 10 mol% $In(OTf)_3$, the reaction led to the formation of unusual product **17** in 55% yield along with 52% of recovered 2-oxindole **8f** (Scheme 7). This clearly demonstrates the high reactivity of 3-aryl-3-hydroxy-2-oxindole **8a-e** (Figure 2) as compared to 3-alkyl-3-hydroxy-2-oxindole such as **8f**. We speculated that, because of low reactivity of ±(**8f**), indole could be activated in the presence of $In(OTf)_3$ to form an intermediate (**18a**) which then reacts with second equiv of indole to afford Michael acceptor **18c** *via* the intermediacy of **18b**. At this point, third equiv of indole could add to the Michael acceptor **18c**, which upon subsequent rearomatization could furnish product **17**.[19] The unusual product was confirmed by X-ray analysis (Scheme 7). Literature report revealed that, synthesis of compound of the type **17** has been reported *via* $InCl_3$-catalyzed self-addition.[19a]



X-ray structure of **17** (CCDC 950651)

**Scheme 7:** Reaction of 3-hydroxy 3-methyl 2-oxindole (**8f**) with indole.

In summary, an efficient Lewis acid-catalyzed reactions of 3-hydroxy-3-aryl-2-oxindoles **±8** with a variety of electron rich substrates such as phenylacetylene, allyltrimethylsilane, styrene, and indole has been developed. A wide variety of 2-oxindoles bearing an all-carbon quaternary center at the pseudobenzylic position have been synthesized utilizing our methodologies. Further efforts toward the development of enantioslective approaches as well as application of this methodology in the synthesis of architecturally interesting indole alkaloids are currently in progress in our laboratory.

## Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled over sodium/benzophenone ketyl. Dichloromethane ($CH_2Cl_2$), toluene, and benzene were

distilled over calcium hydride. All other solvents such as DMSO, DMF, dioxane and reagents such as bromoarenes, isatins, electron-rich arenes etc. were used as received, unless otherwise noted. Thin layer chromatography was performed using Merck Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silicagel from Merck (particle size 100-200 mesh) was used for flash chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (AN ISO 9001:2000) and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on Bruker 400, 500 MHz spectrometers with $^{13}$C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for $^1$H NMR and δ = 77.0 for $^{13}$C NMR). Data for $^1$H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) from PerkinElmer spectrometer and are reported in frequency of absorption (cm$^{-1}$). Only selected IR absorbencies are reported. High resolution mass spectral data were obtained from the Central Instrumentation Facility (CIF) at the Indian Institute of Science Education and Research (IISER) Bhopal.

**Caution**! $HClO_4$ is a powerful oxidizing agent. Although the use of 70% aqueous solution of $HClO_4$ (only shows strong acid features and no oxidizing properties) as the catalyst could reduce the potential danger associated with $HClO_4$, still special care should be taken while carrying out the reaction. For more information, please follow: http://en.wikipedia.org/wiki/Perchloric_acid.

**General procedure for the synthesis of 3-hydroxy-2oxindoles ±(8a-d):**[20] A flame-dried round-bottom flask was charged with isatin (5 mmol, 1.0 equiv.) in anhydrous THF (20 mL) and the round bottom flask was placed at 0 ºC. To this reaction mixture aryl Grignard reagent (12.5 mmol, 2.5 equiv.) was added drop-wise *via* a syringe. The reaction was slowly allowed to warm up to room temperature (1 h) and stirring was continued for 4-5 hours. Upon completion of the reaction (judged by TLC), the reaction mixture was quenched at 0 ºC with saturated aqueous $NH_4Cl$ (5 mL). The whole mixture was filtered through a celite-bed and washed with diethyl ether. The organic layer was evaporated under reduced pressure and the crude mixture was purified by a silica-gel column chromatography.

**(±)-3-Hydroxy-3-(4-methoxyphenyl)indolin-2-one ±(8a)**: 79% yield, $R_f$ = 0.51 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, 0.1mL DMSO-$D_6$, 0.5 mL $CDCl_3$) δ 10.33 (s, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.11 (d, *J* = 7.08 Hz, 1H), 6.97 (t, *J* = 7.24 Hz, 1H), 6.88 (t, *J* = 6.52 Hz, 1H), 6.52 (s, 1H), 3.72 (s, 3H), [3.38 ($H_2O$) in DMSO-$D_6$], 2.51 (DMSO); **$^{13}$C NMR** (100 MHz, 0.1mL DMSO-$D_6$, in 0.5 mL $CDCl_3$) δ 179.1, 159.1, 142.3, 134.2, 133.9, 129.6, 127.3, 125.2, 122.4, 113.9, 110.2, 77.3, 55.5; **IR** (film) $\upsilon_{max}$ 3253, 2918, 1724, 1510, 1253, 1177, 1105, 1034 cm$^{-1}$; **HRMS** (ESI) m/z 278.0802 [(M + Na)$^+$; calculated for [$C_{15}H_{13}NO_3$ + Na]$^+$: 278.0788]; **MP** 188-190 ºC.

**(±)-3-Hydroxy-3-phenylindolin-2-one ±(8b):** 87% yield, $R_f$ = 0.54 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, 0.1 mL DMSO-$d_6$, 0.5 mL $CDCl_3$) δ: 10.05 (br, s, 1H), 7.32-7.38 (m, 2H), 7.08-7.27 (m, 5H), 6.83-6.95 (m, 2H), 6.36 (br, s, 1H); **$^{13}$C NMR** (100 MHz, 0.1mL DMSO-$d_6$, in 0.5 mL $CDCl_3$) δ: 179.4, 142.1, 141.5, 133.7, 129.3, 128.2, 127.6, 125.8, 125.0, 122.3, 110.3; **IR** (film) $\upsilon_{max}$ 3292, 2918, 1700, 1617, 1472, 1325, 757 cm$^{-1}$; **HRMS** (ESI) m/z 248.0658 [(M + Na)$^+$; calculated for [$C_{14}H_{11}NO_2$ + Na]$^+$: 248.0682]; **MP** 207-209 ºC.

**(±)-3-(3,4-Dimethoxyphenyl)-3-hydroxyindolin-2-one ±(8c):** 83% yield, $R_f$ = 0.44 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, 0.1 mL DMSO-$D_6$, 0.5 mL $CDCl_3$) δ 9.55 (s, 1H), 7.03-7.09 (m, 3H), 6.86 (t, *J* = 7.92 Hz, 1H), 6.72-6.77 (m, 1H), 6.59-6.62 (m, 2H), 6.53 (s, 1H), 3.7 (br, s, 3H), 3.67 (br, s, 3H); **$^{13}$C NMR** (100 MHz, 0.1mL DMSO-$D_6$, in 0.5 mL $CDCl_3$) δ 179.6, 148.7, 148.5, 141.6, 133.4, 133.1, 129.2, 125.0, 122.4, 118.0, 110.7, 110.3, 109.4, 77.6, 55.8; **IR** (film) $\upsilon_{max}$ 3321, 1716, 1274, 1188, 1110, 922, 747, 628 cm$^{-1}$; **HRMS** (ESI) m/z 304.1345 [(M + $NH_4$)$^+$; calculated for [$C_{16}H_{15}NO_4$ + $NH_4$]$^+$: 304.1339]; **MP** 146-148 ºC.

**(±)-3-(Benzo[d][1,3]dioxol-5-yl)-3-hydroxyindolin-2-one ±(8d):** 74% yield, $R_f$ = 0.49 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, 0.1mL DMSO-$D_6$, 0.5 mL $CDCl_3$) δ 9.96 (s, 1H), 7.12-7.17 (m, 2H), 6.92 (m, 2H), 6.83 (d, *J* = 7.72 Hz, 1H), 6.72-6.74 (m, 1H), 6.63 (d, *J* = 8.12 Hz, 1H), 6.28 (s, 1H), 5.86 (d, *J* = 2.88 Hz, 1H), 3.07 (1H, exchangeable); **$^{13}$C NMR** (100 MHz, 0.1mL DMSO-$D_6$, in 0.5 mL $CDCl_3$) δ 179.3, 147.6, 147.1, 142.0, 135.3, 133.5, 129.3, 125.0, 122.3, 119.1, 110.2, 107.8, 106.8, 101.0, 77.5; **IR** (film) $\upsilon_{max}$ 3385, 2917, 1713, 1698, 1608, 1462, 1244, 1175, 1107, 1031 cm$^{-1}$; **HRMS** (ESI) m/z 292.0590 [(M + Na)$^+$; calculated for [$C_{15}H_{11}NO_4$ + Na]$^+$: 292.0580]; **MP** 228-231 ºC.

**General procedure of allylations/methallylation of ±8**. A flame-dried round-bottom flask was charged with **±8** (1.0 mmol) in chloroform (6.0 mL) at room temperature. To this reaction mixture was added 10 mol% Lewis acid followed by the addition of allyl/methallytrimethylsilanes (1.5 mmol). The reaction mixture was stirred and the progress of the reaction monitored by TLC (approx. 2 h). After the completion of the reaction, 3 mL of saturated bicarbonate solution was added to the reaction mixtures and extracted three times with dichloromethane (3 X 5 mL). The organic layers were collected and dried over anhydrous $MgSO_4$ and concentrated in vacuum. The crude

product was purified over silica gel by column chromatography using ethylacetate in petroleum ether as eluents.

**(±)-3-Allyl-3-(4-methoxyphenyl)indolin-2-one** ±(**11a**): $R_f$ = 0.75 (40% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.97 (br, s, 1H), 7.32 (d, *J* = 8.32 Hz, 2H), 7.25 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 7.68 Hz, 1H), 6.87 (d, *J* = 8.32 Hz, 2H), 5.48 (m, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 10.08 Hz, 1H), 3.79 (s, 3H), 3.04 (m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 180.9, 158.8, 141.1, 132.6, 132.4, 131.4, 128.2, 128.1, 125.3, 122.4, 119.2, 114.0, 110.1, 56.3, 55.2, 41.7; **IR** (film) $\upsilon_{max}$ 3236, 3078, 2932, 2835, 1701, 1616, 1512, 1470, 1292, 1250, 1184, 1034, 922, 745 $cm^{-1}$; **HRMS** (ESI) m/z 280.1330 $[(M + H)^+$; calculated for $[C_{18}H_{18}NO_2]^+$: 280.1332]; **MP** 92-95 ºC.

**3-Allyl-3-phenylindolin-2-one** ±(**11b**): Colorless gel, $R_f$ = 0.78 (40% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.32 (br, s, 1H), 7.40-7.42 (m, 2H), 7.32-7.36 (m, 2H), 7.26-7.29 (m, 2H), 7.23-7.25 (m, 1H), 7.11 (td, *J* = 7.56, 1.04 Hz, 1H), 6.96 (m, 1H), 5.45 - 5.54 (m, 1H), 5.06 - 5.12 (m, 1H), 4.96 - 4.99 (m, 1H), 3.03 - 3.13 (m, 2H), 1.25 - 1.45 (hexane); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 180.2, 140.8, 139.4, 132.4, 132.2, 128.6, 128.2, 127.4, 127.0, 125.4, 122.5, 119.4, 110.0, 57.0, 41.0; **IR** (film) $\upsilon_{max}$ 3247, 3075, 2928, 1695, 1617,1514, 1465, 1184, 748 $cm^{-1}$.

**3-Allyl-3-(3,4-dimethoxyphenyl)indolin-2-one** ±(**11c**): Colorless gel, $R_f$ = 0.63 (40% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.79 (br, s, 1H), 7.25 (m, 2H), 7.09 (td, *J* = 7.56, 0.96 Hz, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.95 (m, 1H), 6.90 (dd, *J* = 8.44, 2.2 Hz, 1H), 6.80 (d, *J* = 8.52 Hz, 1H), 5.48 (m, 1H), 5.07 (dd, *J* = 17.07, 1.79 Hz, 1H), 4.96 (dd, *J* = 10.27, 1.83 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.03 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 180.7, 148.9, 148.4, 141.0, 140.9, 132.3, 131.8, 128.2, 125.3, 122.4, 119.4, 119.3, 111.0, 110.6, 110.1, 56.5, 55.9, 55.8, 41.9 ; IR (film) $\upsilon_{max}$ 3290, 3213, 2932, 2835, 1713, 1620, 1516, 1470, 1258, 1234, 1146, 1026, 741 $cm^{-1}$; **HRMS** (ESI) m/z 310.1447 $[(M+H)^+$; calculated for $[C_{19}H_{20}NO_3]^+$: 310.1438].

**(±)-3-(4-methoxyphenyl)-3-(2-methylallyl)indolin-2-one** ±(**11d**): Colorless solid, $R_f$ = 0.75 (40% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 9.00 (br, 1H), 7.34 (m, 2H), 7.21-7.28 (m, 2H), 7.09 (td, *J* = 7.52, 1 Hz, 1H), 6.95-6.96 (m, 1H), 6.86 (m, 2H), 4.63-4.68 (m, 2H), 3.79 (s, 3H), 3.24 (d, *J* = 13.24 Hz, 1H), 2.92 (d, *J* = 13.28 Hz, 1H), 1.41 (br, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 181.4, 158.8, 141.2, 140.9, 132.5, 128.3, 128.1, 128.0, 125.9, 122.2, 115.3, 113.9, 110.2, 56.5, 55.3, 45.2, 23.7; **IR** (film) $\upsilon_{max}$ 3248, 3078, 2928, 1694, 1616, 1512, 1470, 1443, 1292, 1184, 1034, 748 $cm^{-1}$; **HRMS** (ESI) m/z 316.1308 $[(M + Na)^+$; calculated for $[C_{19}H_{19}NO_2 + Na]^+$: 316.1349]; **MP** 85-90 ºC.

**(±)-3-allyl-3-(1H-indol-3-yl)indolin-2-one** ±(**11e**): $R_f$ = 0.65 (50% EtOAc in hexane). **$^1$H NMR** (400 MHz, DMSO) δ: 8.22 (brs, 1H), 8.14 (brs, 1H), 7.29 (d, *J* = 8.32 Hz, 1H), 7.23 (m, 1H), 7.07-7.14 (m, 4H), 6.99 (t, *J* = 7.48 Hz, 1H), 6.88-6.94 (m, 2H), 5.47-5.58 (m, 1H), 5.09 (d, *J* = 16.96 Hz, 1H), 4.95 (d, *J* = 10.08 Hz, 1H), 3.06-3.21 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 180.4, 140.7, 136.8, 132.9, 132.1, 128.1, 125.5, 124.9, 123.0, 122.6, 122.2, 120.2, 119.7, 119.3, 114.8, 111.3, 109.7, 52.9, 40.7; IR (film) $\upsilon_{max}$ 3273, 2926, 2855, 1699, 1621, 1471, 1352, 1225, 1182, 923, 741 $cm^{-1}$; **HRMS** (ESI) m/z 289.1349 $[(M + H)^+$; calculated for $[C_{19}H_{17}N_2O]^+$: 289.1335].

**(±)-3-(1H-indol-3-yl)-3-(2-methylallyl)indolin-2-one** ±(**11f**): $R_f$ = 0.66 (50% EtOAc in hexane). **$^1$H NMR** (400 MHz, DMSO-$D_6$) δ: 10.98 (s, 1H), 10.47 (s, 1H), 7.28 (m, 2H), 7.16 (t, *J* = 7.52 Hz, 1H), 7.04 (d, *J* = 7.24 Hz, 1H), 6.95 (t, *J* = 7.32 Hz, 1H), 6.87 (m, 3H), 6.73 (t, *J* = 7.48 Hz, 1H), 4.59 (s, 1H), 4.52 (s, 1H), 3.36 (DMSO), 3.16 (d, *J* = 12.88 Hz, 1H), 2.98 (d, *J* = 12.88 Hz, 1H), 1.33 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 180.0, 142.7, 141.2, 137.1, 133.7, 128.3, 125.5, 125.2, 123.8, 121.8, 121.4, 119.7, 118.9, 115.6, 115.2, 112.0, 109.7, 52.9, 43.5, 24.3;IR (film) $\upsilon_{max}$ 3247, 2922, 1708, 1618, 1472, 1329, 1225, 1171, 1105, 1020, 900, 822, 745 $cm^{-1}$; **HRMS** (ESI) m/z 303.1504 $[(M + H)^+$; calculated for $[C_{20}H_{19}N_2O]^+$: 303.1492].

**General procedure for the phenyl acetylene addition to ±8.** A flame-dried round-bottom flask was charged with **±8** (1.0 mmol, 1.0 equiv.) in dichloromethane or chloroform (6 mL) under inert atmosphere. To this reaction mixture, 10 mol % Lewis acid was added at room temperature followed by the addition of 3 equiv. of phenyl acetylene. Finally, the reaction mixture was reflux at 40-50 ºC for indicated time. Upon completion of the reaction (judged by the TLC), the reaction mixture was cooled to room temperature and diluted with 15 mL of dichloromethane and then it was extracted with 5 mL of saturated sodium bicarbonate. The organic layers were dried over sodium sulphate and the crude materials were purified by flash chromatography using EtOAc and petroleum ether to afford products ±(**12a-b**).

**(±)-3-(4-methoxyphenyl)-3-(2-oxo-2-phenylethyl) indolin-2-one** ±(**12a**): $R_f$ = 0.42 (30% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 7.98 (s, 1H), 7.90 (m, 2H), 7.56 (tt, *J* = 6.8, 1.2 Hz, 1H), 7.43 (m, 2H), 7.38 (m, 2H), 7.23-7.27 (m, 2H), 7.03 (td, *J*= 7.52, 0.96 Hz, 1H), 6.98 (d, *J* = 7.64 Hz, 1H), 6.85-6.89 (m, 2H), 4.13 (ABq, *J* = 18 Hz, 2H), 3.79 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 195.9, 180.6, 159.0, 141.7, 136.3, 133.3, 132.4, 131.3, 128.6, 128.0, 127.9, 124.3, 122.2, 114.1, 110.1, 55.3, 52.9, 46.9; **IR** (film) $\upsilon_{max}$ 2925, 1706, 1616, 1471, 1254, 1184, 1106, 1033, 752 $cm^{-1}$; **HRMS** (ESI) m/z 358.1440]; $[(M + H)^+$; calculated for $[C_{23}H_{20}NO_3]^+$: 358.1438]; **MP** 140-143 ºC.

**(±)-3-(benzo[d][1,3]dioxol-5-yl)-3-(2-oxo-2-phenylethyl) indolin-2-one ±(12b)**: $R_f$ = 0.51 (50% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.02 (brs, 1H), 7.85 (d, *J* = 7.36 Hz, 2H), 7.52 (t, *J* = 7.41 Hz, 1H), 7.39 (t, *J* = 7.80 Hz, 2H), 7.20 (m, 2H), 6.97 (td, *J* = 14.38, 7.59 Hz, 3H), 6.84 (dd, *J* = 8.27, 1.88 Hz, 1H), 6.71 (d, *J* = 8.21 Hz, 1H), 5.91 (s, 2H), 4.09 (ABq, *J* = 18 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 195.8, 180.4, 148.0, 147.1, 141.7, 136.3, 133.4, 133.1, 132.2, 128.6, 128.4, 128.0, 124.4, 122.3, 120.2, 110.2, 108.2, 107.6, 101.2, 53.2, 46.9; **IR** (film) $\upsilon_{max}$ 3229, 2928, 1716, 1608, 1509, 1472, 1253, 1024, 755 $cm^{-1}$; **HRMS** (ESI) m/z 372.1246]; $[(M + H)^+$; calculated for $[C_{23}H_{18}NO_4]^+$: 372.1230].

**Experimental procedure for the acetophenone addition to ±8**. A flame-dried round-bottom flask was charged with **±8** (1.0 mmol, 1.0 equiv.) in dichloromethane or chloroform (6 mL) under inert atmosphere. To this reaction mixture, 10 mol % Lewis acid was added at room temperature followed by the addition of (3.0 mmol, 3.0 equiv.) of acetophenone. Then the reaction mixture was reflux at 40-50 ºC for 8-9 h. Upon completion of the reaction (judged by running TLC), the reaction mixture was cooled to room temperature and diluted with 15 mL of dichloromethane and extracted with 5 mL of saturated sodium bicarbonate. The organic layers were dried over anhydrous $Na_2SO_4$ and the crude materials were purified by flash chromatography using EtOAc and petroleum to afford compound ±(**12a**).

**General procedure for the reaction of ±8 with styrene.** A flame-dried round-bottom flask was charged with **±8** (1.0 mmol, 1.0 equiv.) in dichloromethane (6 mL) under inert atmosphere. To this reaction mixture, 10 mol % Lewis acid was added followed by the addition of 5 equiv. of styrene. Finally, the reaction mixture was reflux at 40 ºC for 6-9 h. Upon completion of the reaction (monitored by running TLC), the reaction mixture was cooled to room temperature and diluted with 15 mL of dichloromethane and extracted with 5 mL of saturated sodium bicarbonate. The organic layers were dried over sodium sulphate and the crude materials were purified by flash chromatography to afford ±(**14**) and trace amount of compound ±(**15**).

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**(±)-3-phenyl-3-styrylindolin-2-one ±(14a)**: $R_f$ = 0.71 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.91 (brs, 1H), 7.40-7.44 (m, 2H), 7.36-7.40 (m, 3H), 7.30-7.32 (m, 3H), 7.24 (m, 2H), 7.23 (m, 1H), 7.12 (td, *J* = 7.52, 0.92 Hz, 1H), 7.03 (d, *J* = 7.72 Hz, 1H), 6.74 (d, *J* = 16.04 Hz, 1H), 6.59 (d, *J* = 16.08 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 178.9, 140.3, 140.2, 136.4, 132.4, 131.9, 128.8, 128.7, 128.6, 128.4, 127.9, 127.6, 127.5, 126.7, 125.9, 122.9, 110.3, 60.1; **IR** (film) $\upsilon_{max}$ 3214, 2925, 1715, 1472, 1326, 1208, 971, 748 $cm^{-1}$; **LRMS** (ESI) m/z 312.1378]; $[(M + H)^+$; calculated for $[C_{22}H_{18}NO]^+$: 312.1383]; **MP** 179-182 ºC.

**(±)-3-(4-methoxystyryl)-3-phenylindolin-2-one ±(14b)**: $R_f$ = 0.40 (30% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 7.90 (brs, 1H), 7.25-7.35 (m, 8H), 7.19 (d, *J* = 7.20 Hz, 1H), 7.08 (m, 1H), 6.97 (d, J = 7.72 Hz, 1H), 6.82 (d, *J* = 8.72 Hz, 2H), 6.51 (ABq, *J* = 16.08 Hz, 2H), 3.78 (S, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 178.8, 159.5, 140.2, 140.1, 132.5, 131.3, 129.2, 128.7, 128.3, 127.9, 127.6, 127.5, 126.5, 126.0, 122.9, 114.0, 110.1, 60.0, 55.3; **IR** (film) $\upsilon_{max}$ 3246, 2926, 1708, 1618, 1510, 1472, 1248, 1176, 1034, 753 $cm^{-1}$; **LRMS** (ESI) m/z 342.1543]; $[(M + H)^+$; calculated for $[C_{23}H_{20}NO_2]^+$: 342.1489].

**(±)-3-(4-methoxyphenyl)-3-styrylindolin-2-one ±(14c)**: $R_f$ = 0.60 (30% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 7.83 (brs, 1H), 7.36 (m, 2H), 7.26-7.29 (m, 4H), 7.20 (m, 2H), 7.09 (t, *J* = 7.44 Hz, 1H), 6.95 (d, *J* = 7.72 Hz,1H), 6.84 (d, *J* = 8.84 Hz, 2H), 6.63 (d, *J* = 16.08 Hz, 1H), 6.53 (d, *J* = 16.08 Hz,1H), 3.76 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 178.8, 159.1, 140.2, 136.5, 132.5, 131.9, 131.6, 129.0, 128.7, 128.6, 128.3, 127.9, 126.6, 125.9, 122.9, 114.2, 110.2, 59.4, 55.3; **IR** (film) $\upsilon_{max}$ 3112, 2924, 1713, 1615, 1472, 1251, 1034, 971, 746 $cm^{-1}$; **HRMS** (ESI) m/z 342.1481]; $[(M + H)^+$; calculated for $[C_{23}H_{20}NO_2]^+$: 342.1489]; **MP** 181-184 ºC.

**(±)-3-(4-methoxyphenyl)-3-(4-methoxystyryl)indolin-2-one ±(14d)**: $R_f$ = 0.58 (30% EtOAc in hexane), yellowish gel. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.33 (brs, 1H), 7.25-7.16 (m, 5H), 7.12 (d, *J*=7.36 Hz, 1H), 7.01 (t, *J* = 7.52 Hz, 1H), 6.90 (d, *J* = 7.68 Hz, 1H), 6.78-6.74 (m, 4H), 6.39-6.45 (ABq, *J* = 16.13, 1H), 3.71 (s, 3H), 3.69 (s, 3H) ; **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 179.4, 159.4, 159.0, 140.2, 132.8, 132.2, 131.0, 129.2, 128.7, 128.2, 127.9, 126.8, 125.8, 122.8, 114.1, 113.9, 110.3, 59.4, 55.3; **IR** (film) $\upsilon_{max}$ 3111, 2920, 1712, 1610, 1465, 1248, 1000, 968, 742 $cm^{-1}$; **HRMS** (ESI) m/z 372.1611]; $[(M + H)^+$; calculated for $[C_{24}H_{22}NO_3]^+$: 372.1594].

**(±)3-(2-hydroxy-2-phenylethyl)-3-(4-methoxyphenyl) indolin-2-one ±(15a)**: $R_f$ = 0.25 (50% EtOAc in hexane), yellowish gel. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.89 (s, 1H), 7.23 (m, 8H), 7.09 (t, *J*=7.52 Hz, 2H), 6.95 (d, *J* = 7.68 Hz, 1H), 6.78 (d, *J* = 8.68 Hz, 2H), 4.36 (d, *J* = 9.92, 1H), 3.72 (s, 3H), 3.66 (m, 1H), 3.03 (m, 1H), 2.46 (d, *J* = 13.04 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 182.2, 158.8, 144.7, 142.1, 132.8, 132.1, 128.4, 128.3, 127.9, 127.3, 125.5, 125.0, 122.4, 113.9, 110.7, 71.6, 55.3, 55.2, 47.1; **IR** (film) $\upsilon_{max}$ 3368, 2926, 1715, 1617, 1509, 1251, 1185, 1035, 755 $cm^{-1}$; **LRMS** (ESI) m/z 358.1478; $[(M + H)^+$; calculated for $[C_{23}H_{22}NO_3]^+$: 358.1438].

**General Procedure for the reaction of ±8 with indoles.** A flame-dried round-bottom flask was charged with **±8** (1.0 mmol, 1.0 equiv.) in dichloromethane (6 mL) under inert atmosphere. To this reaction mixture, 10 mol % Lewis acid was added at room temperature followed by the addition of 2 equiv. of indole. Finally, the reaction mixture was reflux at 40 ºC for 6-9 h. Upon completion of the

reaction, the reaction mixture was cooled to room temperature and diluted with 15 mL of dichloromethane and then it was extracted with 5 mL of saturated sodium bicarbonate. The organic layers were dried over sodium sulphate and the crude materials were purified by flash chromatography using EtOAc and petroleum ether to afford compound ±(**16a-f**).

**(±)-3-(1H-indol-3-yl)-3-(4-methoxyphenyl)indolin-2-one ±(16a)**: $R_f$ = 0.48 (50% EtOAc in hexane), colorless solid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 9.20 (brs, 1H), 8.25 (brs, 1H), 7.25 (d, *J* = 8.52 Hz, 3H), 7.21 (d, *J* = 8.28 Hz, 2H), 7.09 (m, 2H), 6.93 (q, *J* = 7.12, 2H), 6.76 (m, 4H), 3.71 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 180.9, 158.8, 140.1, 137.1, 134.7, 132.2, 129.1, 128.0, 125.8, 125.5, 124.3, 122.7, 122.1, 121.5, 119.5, 116.1, 113.9, 111.5, 110.4, 57.6, 55.2; **IR** (film) $\upsilon_{max}$ 3334, 2933, 1715, 1695, 1682, 1616, 1506, 1472, 1250, 1180, 1101, 826, 744 $cm^{-1}$; **HRMS** (ESI) m/z 355.1452]; $[(M + H)^+$; calculated for $[C_{23}H_{19}N_2O_2]^+$: 355.1441]; **MP** 118-121 ºC.

**(±)-3-(1H-indol-3-yl)-3-phenylindolin-2-one ±(16b)**: $R_f$ = 0.54 (30% EtOAc in hexane), colorless solid . **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.90 (s, 1H), 8.14 (s, 1H), 7.35 (m 2H), 7.26 (m, 5H), 7.24 (CDCl3), 7.19 (d, *J* = 8.08 Hz, 1H), 7.15 (t, *J* = 7.40 Hz, 1H), 7.09 (t, *J* = 7.32 Hz, 1H), 6.93 (m, 2H), 6.84 (d, *J* = 7.28 Hz, 1H), 6.79 (s, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 180.3, 140.2, 140.1, 137.1, 134.4, 128.5, 128.1, 127.9, 127.4, 125.8, 125.6, 124.4, 124.3, 122.7, 122.2, 121.6, 119.6, 119.5, 116.0, 111.4, 110.3, 58.2; **IR** (film) $\upsilon_{max}$ 3308, 2926, 1706, 1618, 1472, 1334, 1264, 1102,741 $cm^{-1}$; **HRMS** (ESI) m/z 347.1161]; $[(M + Na)^+$; calculated for $[C_{22}H_{16}N_2O + Na]^+$: 347.1155]; **MP** 148-151 ºC.

**(±)-3-(3,4-dimethoxyphenyl)-3-(1H-indol-3-yl)indolin-2-one ±(16c)**: $R_f$ = 0.40 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.70 (s, 1H), 8.21 (s, 12H), 7.26 (m, 2H), 7.09 (t, *J* = 7.60 Hz, 1h), 6.96 (m, 2H), 6.92 (m, 2H), 6.84 (m, 2H), 6.73 (d, *J* = 8.44 Hz, 1H), 3.81 (s, 3H), 3.63 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 180.3, 148.8, 148.4, 140.0, 137.0, 134.5, 132.4, 128.1, 125.8, 125.7, 124.2, 122.7, 122.2, 121.3, 120.3, 119.6, 116.4, 111.7, 111.3, 110.8, 110.2, 57.6, 55.9, 55.8; **IR** (film) $\upsilon_{max}$ 3334, 1699, 1505, 1249, 1101, 1034, 826, 744$cm^{-1}$; **HRMS** (ESI) m/z 385.1574]; $[(M + H)^+$; calculated for $[C_{24}H_{21}N_2O_3]^+$: 385.1547]; **MP** 145-149 ºC.

**(±)-3-(benzo[d][1,3]dioxol-5-yl)-3-(1H-indol-3-yl)indolin-2-one ±(16d)**: $R_f$ = 0.54 (50% EtOAc in hexane), yellowish solid. **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.89 (brs, 1H), 8.13 (s, 1H), 7.28 (d *J* = 7.92 Hz, 2H), 7.08-7.17 (m, 2H), 6.95 (t, *J* = 7.52 Hz, 2H), 6.78-6.86 (m, 4H), 6.67 (d, *J* = 8.12 Hz,1H), 5.86 (d, *J* = 2.56 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 180.3, 147.8, 146.9, 140.0, 137.1, 134.4, 134.0, 128.1, 125.7, 125.5, 124.2, 122.7, 122.2, 121.6, 121.2, 119.6, 116.1, 111.4, 110.3, 108.0, 101.1, 57.8, 29.7; **IR** (film) $\upsilon_{max}$ 3404, 2924, 1703, 1474, 1240, 1038, 743 $cm^{-1}$; **HRMS** (ESI) m/z 391.1058]; $[(M + Na)^+$; calculated for $[C_{23}H_{16}N_2O_3 + Na]^+$: 391.1053]; **MP** 159-163ºC.

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**1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16e)**: $R_f$ = 0.50 (50% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 8.13 (s, 1H), 8.02 (brs, 2H), 7.33 (d, *J* = 7.8 Hz, 3H), 7.28 (d, *J* = 8.12 Hz, 2H), 7.20 (t, *J* = 7.56 Hz, 2H), 7.10 (t, *J* = 7.40 Hz, 2H), 6.89-6.96 (m, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 179.5, 139.9, 137.0, 134.5, 128.1, 125.9, 125.6, 124.4, 122.7, 122.1, 121.3, 119.5, 115.2, 111.3, 109.9, 53.1; **IR** (film) $\upsilon_{max}$ 3402, 2923, 1697, 1614, 1470, 1334, 1098, 1014, 741$cm^{-1}$ ; **HRMS** (ESI) m/z 364.1434]; $[(M + H)^+$; calculated for $[C_{24}H_{18}N_3O]^+$: 364.1444]; **MP** 282-285 ºC.

**(±)-5-bromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one ±(16f)**: $R_f$ = 0.52 (50% EtOAc in hexane),colorless gel. **$^1$H NMR** (400 MHz, in 0.4 mL $CDCl_3$ and 0.1 mL DMSO-$D_6$) δ: 9.82 (s, 1H), 9.57 (s, 1H), 9.52 (s, 1H), 7.39 (br, 1H), 7.24 ($CDCl_3$), 7.14-7.20 (m, 2H), 7.04-7.11 (m, 3H), 6.97 (dd, *J* = 8.56, 1.68 Hz, 1H), 6.91 (t, *J* = 7.68 Hz, 1H), 6.86 (d, *J* = 7.64 Hz, 1H), 6.78 (m, 3H), 6.71 (t, *J* = 7.68 Hz, 1H), 2.52 (DMSO-$D_6$); **$^{13}$C NMR** (100 MHz in 0.4 mL $CDCl_3$ and 0.1 mL DMSO-$D_6$) δ: 179.5, 141.0, 137.1, 135.9, 134.3, 127.9, 127.7, 125.9, 125.8, 125.2, 124.6, 124.1, 123.62, 123.60, 121.9, 121.4, 120.9, 118.8, 114.6, 113.0, 112.0, 111.5, 109.9, 52.9; **IR** (film) $\upsilon_{max}$ 3412, 1664, 1472, 1026, 826, 765 $cm^{-1}$; **HRMS** (ESI) m/z 464.0348]; $[(M + Na)^+$; calculated for $[C_{24}H_{16}BrN_3O + Na]^+$: 464.0369].

**2-(2,2-di(1H-indol-3-yl)ethyl)aniline (17)**:[19] The product was obtained as yellow crystalline solid [263 mg, 75% (condition A)], $R_f$ = 0.60 (50% EtOAc in hexane). **$^1$H NMR** (400 MHz, $CDCl_3$) δ: 7.89 (brs, 2H), 7.47 (d *J* = 7.95 Hz, 2H), 7.30 (d, *J* = 8.10 Hz, 2H), 7.12 (t, *J* = 7.66 Hz, 2H), 6.98-6.97 (m, 6H), 6.61 (t, *J* = 7.41 Hz, 1H), 6.54 (d, *J* = 7.78 Hz, 1H), 4.84 (t, *J* = 7.29 Hz, 1H), 3.41 (d, *J* = 7.34 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ: 144.7, 136.6, 130.3, 126.9, 126.8, 125.9, 121.8, 119.7, 119.6, 119.1, 118.7, 115.7, 111.0, 37.1, 34.5; **IR** (film) $\upsilon_{max}$ 3412, 2924, 2854, 1619, 1456, 1339, 1265, 1096, 743 $cm^{-1}$; **HRMS** (ESI) m/z 350.1649; $[M - H]^+$; calculated for $[C_{24}H_{21}N_3 - H]^+$: 350.1652; **MP** 288-291ºC.

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## Notes and References

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17. Reactions of **±8a** with indole in the presence of 10 mol% each $Sn(OTf)_2$ (condition **A**), and $Cu(OTf)_2$ (condition **C**) in chloroform at 50 ºC (12h) afforded **±16a** in 58% and 60% yields, respectively.

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# GRAPHICAL ABSTRACTS

## Acid-Catalyzed Reactions of 3-Hydroxy-2-oxindoles with Electron-rich Substrates: Synthesis of 2-Oxindoles with All-Carbon Quaternary Center†

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Lewis acid-catalyzed reaction of 3-hydroxy-2-oxindoles **±8** with various 2π electron-rich substrates has been investigated. The methodology provides a straightforward approach to the 2-oxindoles sharing an all-carbon quaternary centers in good yields.