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Catalyst Assisted Selective Vinylation and Methylallylation of Quaternary Carbon Centre by using *tert*-Butyl Acetate

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Abstract. The $In(OTf)_3$-catalyzed α-vinylation of various hydroxy functionalized quaternary carbon centre by using isobutylene generated in situ from *tert*-butyl acetate is presented as first synthetic methodology. Moreover, *tert*-butyl acetate is non-flammable feedstock and is a readily available source for the in-situ production of vinyl substituents, demonstrated vinylation reaction with quaternary hydroxy/methoxy compounds. Moreover, an excellent selectivity for the methylallylation over the vinylation was obtained with $Ni(OTf)_2$. In case of peroxyoxindole, methylallyl functionalized 1,4-benzoxazin-3-one derivatives were formed through the sequential rearrangement of peroxyoxindole and the nucleophilic attack by isobutylene. The detailed mechanism for this reaction has been provided based on the preliminary experiments and kinetics studies.

Keywords: Methylallylation; Rearrangement; *tert*-butylacetate; Isobutylene; Lewis Acid

From the perspective of synthesis, the interconversion of functional groups at quaternary carbon centre is imperative because many natural products, drugs, and value-added products features such skeletons.[1] Efficaciously constructing a quaternary carbon centre with four substituents is most challenging in organic syntheses due to steric hindrance and marginally reactive functional groups. Thus, various approaches have been reported for the formation of different quaternary carbon centres in the past few decades.[2] In modern chemical syntheses, direct nucleophilic substitution for olefination (vinyl/allyl), which has been used in many total syntheses, at quaternary centre is a fascinating research topic because it provides many advantages such as atom economy and sustainability.[2a,3] Few methods for vinylation and allylation at the oxindole core by using prefunctionalized aliphatic alkenes were reported.[4] Funk et al. reported the C3-allylation of 3-alkyl-3-bromoindolin-2-one with allyl stannenes or allyl trimethylsilane derivatives to produce C3-allyl substituted-2-indolinones by using a stoichiometric amount of bases (Figure 1 (A-I)).[5] Subsequently, Huang et al. reported the Pd-catalyzed α-vinylation of carbonyl compounds by using bromo alkenes in the presence of LiHMDS (Figure 1 (A-II)).[6] Kozlowski et al. proposed catalytic Meerwein−Eschenmoser Claisen rearrangement for the synthesis of allyl oxindoles with a quaternary stereocentre by using Pd catalysts (Figure 1 (A-III)).[6] Kozlowski et al. proposed catalytic Meerwein−Eschenmoser Claisen rearrangement for the synthesis of allyl oxindoles with a quaternary stereocentre by using Pd catalysts (Figure 1 (A-IV)).[7] Bisai et al. provided the quaternary allyl functionalization of 3-hydroxy-3-aryl-2-oxindoles

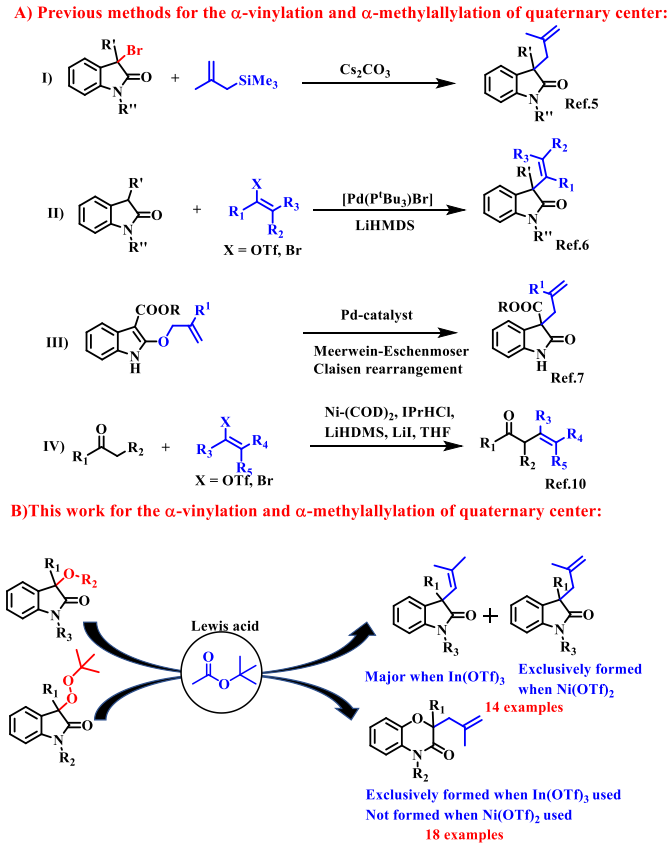


Figure 1. State of the art for the vinylation and methylallylation reaction

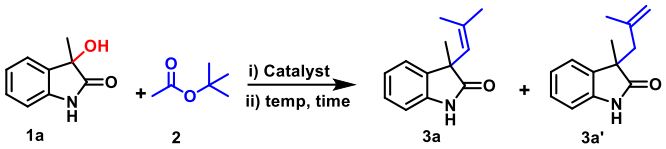
with various allyl trimethylsilane derivatives in the presence of catalytic Lewis acids.[8] Additionally, α-vinylation of cyclic amides with arylacetylenes in metal free environment was reported.[9] The Helquist research group reported the Ni-catalyzed α-vinylation of carbonyl com-pounds by using ketone enolates with alkenyl halides (Figure 1 (A-IV)).[10] The Ni-catalyzed α-vinylation of β-keto amides/esters by using hypervalent iodine salts was described.[11]

All the aforementioned procedures use prefunctionalized alkenes as a source for α-vinylation/methylallylation and require stoichiometric bases. Furthermore, these reactions involve specific basic condition that leads isomerization to be a competing reaction. However, the catalytic selective vinylation/methylallylation of a quaternary carbon centre by using isobutylene has not been reported. Although isobutylene is an inexpensive and commercially available source, its polymerization propensity under experimental condition and highly flammable property limits its reactivity as a nucleophile, which remains an unresolved problem.[12] Therefore, developing an efficient method to construct vinyl or methylallyl quaternary carbon centres by using isobutylene derivatives is highly appealing. While various approaches have been reported for the in situ generation of isobutylene[12], there is no studies reported on selective catalytic vinylation or methylallylation at the quaternary hydroxy or peroxyl functionalized carbon centre using isobutylene.

In this study, we report the Lewis acid catalyzed highly selective α-vinylation and methylallylation of quaternary 3-hydroxyoxindole or peroxyoxindole through the direct nucleophilic substitution of the hydroxy/peroxy group with in situ generated isobutylene from *tert*-butyl acetate (Figure 1B). In this reaction, the Lewis acid control the selectivity of methylallylation and vinylation. Thus, $In(OTf)_3$ catalyzed this reaction toward selective α-vinylation at the quaternary centre. The $Ni(OTf)_2$ directed this reaction exclusively for the formation of methylallylation. Moreover, this reaction with peroxyoxindole in the presence of catalytic $In(OTf)_3$ undergo sequential rearrangement and nucleophilic addition of isobutylene to synthesize selectively methylallyl functionalized 1,4-benzoxazin-3-one derivatives.

Initially, we have performed the vinylation of 3-methyl-3-hydroxyoxindole **1a** by using *tert*-butyl acetate as the isobutylene source. In the control experiment, **1a** was stirred with *tert*-butyl acetate without a catalyst at room temperature and 60 °C, no reaction was observed (Table 1, entry 1 and 2). Several Lewis acids were tested for vinylation at the C3 position of **1a**. The highly substituted alkene **3a** (31%, Saytzeff product) as a major and less substituted methylallylated compound **3a'** as a minor product (23%, Hoffmann product) was obtained when $In(OTf)_3$ was used as a catalyst at 60 °C (Table 1, entry 3). This reaction was unsuccessful when $Cu(OTf)_2$, $Mn(OTf)_2$, $FeCl_3•6H_2O$, $LiClO_4$, and $AlCl_3$ were used as catalyst (Table 1, entries 4,5,7,9, and 11). The use of other Lewis acids such as $Sn(OTf)_2$, $Mn(ClO_4)_2•xH_2O$,

Table 1. Optimization for the α-vinylation reaction



Entry[a]	Catalyst (mmol)	Temp (°C)	Yield (%)	
			3a	**3a'**
1	-	rt	-	-
2	-	60	-	
3	$In(OTf)_3$	60	31	23
4	$Cu(OTf)_2$	60	no Reaction	
5	$Mn(OTf)_2$	60	no Reaction	
6	$Sn(OTf)_2$	60	27	19
7	$FeCl_3•6H_2O$	60	no Reaction	
8	$Mn(ClO_4)_2•xH_2O$	60	15	13
9	$LiClO_4$	60	no Reaction	
10	$BF_3•O(C_2H_5)_2$	60	20	23
11	$AlCl_3$	60	no Reaction	
12	TfOH	60	decomposition	
13	$In(OTf)_3$	40	15	10
14	$In(OTf)_3$	rt	no Reaction	
15[b]	$In(OTf)_3$	60	42	21
16[b]	$In(OTf)_3$	80	54	27
17[b]	$In(OTf)_3$	100	49	29
18[b]	$Ni(OTf)_2$	80	-	65

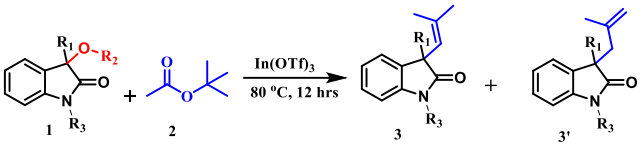
[a]All the reactions were performed using 0.12 mmol of **1a** in *tert*-butyl acetate (1.5 mL) with 10 mol% of catalyst was loaded and heated at 60 °C in a resealable vial for 12 hrs. [b]20 mol% of catalyst was loaded and heated at mentioned temperature.

and $BF_3•O(C_2H_5)_2$ resulted in poor yield of desired product (Table 1, entries 6,8 and 10). Further, no desired product was observed with triflic acid and starting material was decomposed (Table 1, entry 12). Notably, the vinylation reaction using catalyst $In(OTf)_3$ was highly efficient when used 20 mol% and the reaction yield was 63% (**3a** + **3a'**) (Table 1, entry 15). To ensure the optimal reaction conditions, reaction parameters, such as temperature and time, were carefully evaluated (Table 1, entries 15-17). The quantitative yield 81% (**3a** + **3a'**) was obtained with 20% $In(OTf)_3$ at 80 °C for 12 hrs. The better yield with $In(OTf)_3$ might be due to the higher Lewis acidity than other catalysts.

The substrate scope was explored under the optimized reaction conditions (Table 2). The derivatives of 2-oxindole featuring the substituted phenyl group were well tolerated under the developed reaction condition to acquire a substituted vinyl quaternary compound **3b** and **3c** as the major product. The phenyl group with –F and –OMe attached to the C3 position of 3-hydroxy

N-methyloxindole afforded 84% (**3d** + **3d'**) and 85% (**3f** + **3f'**) yield. Similarly, other substituted hydroxy oxindole were well tolerated under the reaction condition to provide the moderate yield of the desired products, **3e-i** and **3e'-i'**. Moreover, this reaction with hindered naphthalene substituted 2-oxindole afforded the mixture of **3j** and **3j'** in 83% yield. To determine the generality of quaternary methylallylation through nucleophilic substitution, we used C3-methoxy-substituted oxindole. Thus, the quaternary methylallylation of C3 methoxy oxindole and 1,4-benzoxazin-3-one derivatives through nucleophilic substitution afforded a satisfactory yield of substituted vinyl and methylallyl products, respectively (**3m** + **3m'**, **3l** + **3l'**and **3n** + **3n'**).

Table 2. Substrate scope for $In(OTf)_3$ catalyzed α-vinylation reaction

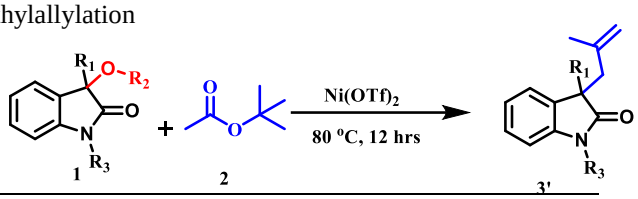


Entry[a]	Substrate **1**			Yield (%)	
	R_1	R_2	R_3	**3**	**3'**
1	**1a**: Me	H	H	**3a** (54)	**3a'** (27)
2[b]	**1b:** C_4H_9	H	H	**3b** +**3b'** (59)	
3	**1c:** 4-MeC_6H_4	H	Me	**3c** (64)	**3c'** (31)
4	**1d:** 3-FC_6H_4	H	Me	**3d** (52)	**3d'** (32)
5	**1e:** Me	H	Me	**3e** (58)	**3e'** (25)
6	**1f:** 4-$MeOC_6H_4$	H	Me	**3f** (52)	**3f'** (33)
7	**1g:** Me	H	C_4H_9	**3g** (41)	**3g'** (32)
8	**1h:** 4^{t}BuC_6H_4	H	Bn	**3h** (42)	**3h'** (39)
9[b]	**1i:** Naphthyl	H	Bn	**3i** + **3i'** (72)	
10[b]	**1j:** 4-$MeOC_6H_4$	H	Bn	**3j** + **3j'** (83)	
11	**1k:** 4-MeC_6H_4	H	BrC_8H_{14}	**3k** (53)	**3k'** (24)
12	**1l:** 3,5-F,FC_6H_3	Me	Me	**3l** (31)	**3l'** (33)
13	**1m:** 4-MeC_6H_4	Me	Me	**3c** (51)	**3c'** (42)
14[b,c]	**1n:** Me	Me	Me	**5f** + **5f'** (54)	

[a]All the reactions were performed using 0.12-0.31 mmol of **1** in *tert*-butyl acetate (1.5 mL) with 20 mol% $In(OTf)_3$ at 80 °C in a resealable vial. [b]1:1 ratio by ^{1}H-NMR, [c] **1n** = 2-methoxy-2,4-dimethyl-2H-benzo[b][1,4]oxazin-3(4H)-one.

Interestingly, exclusive selectivity on the methylallylated Hoffmann product **(3a'**) was isolated when 2-oxindole featuring –OH or –OMe substituted at the C3 position was treated with *tert*-butyl acetate in the presence of 20 mol% $Ni(OTf)_2$ as the catalyst (Table 3). Thus, this reaction of alkyl substituted hydroxy oxindole afforded the moderate yield of the quaternary methylallylated products **3a**' and **3b'** (Table 3). High yield and exclusive selectivity for **3c'** and **3d'** were observed with aryl-substituted hydroxyl oxindole (Table 3). The *N*-substituted C3-hydroxy oxindole was suitable to produce exclusively the quaternary allylated products (**3f'-m'**) in high yields (Table 3).

Table 3. Substrate scope for $Ni(OTf)_2$-catalyzed α-methylallylation

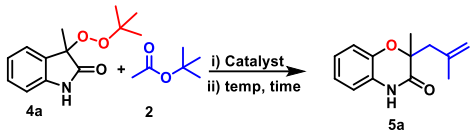


Entry[a]	Substrate **1**			Yield (%)
	R_1	R_2	R_3	**3'**
1	**1a**: Me	H	H	**3a'**:65
2[b]	**1b:** C_4H_9	H	H	**3b'**:72
3	**1c:** 4-MeC_6H_4	H	Me	**3c'**:61
4	**1d:** 3-FC_6H_4	H	Me	**3d'**:76
5	**1e:** Me	H	Me	**3e'**:70
6	**1f:** 4-$MeOC_6H_4$	H	Me	**3f'**:79
7	**1g:** Me	H	C_4H_9	**3g'**:81
8	**1h:** 4^{t}BuC_6H_4	H	Bn	**3h'**:66
9[b]	**1l:** 3,5-F,FC_6H_3	Me	Me	**3l'**:72
10[b]	**1m:** 4-MeC_6H_4	Me	Me	**3m'**:65
11	**1o :** 4-MeC_6H_4	H	allyl	**3o'**:67
12	**1p :** C_6H_5	Me	H	**3p'**:77

[a]All the reactions were conducted using 0.12-0.31 mmol of **1** in *tert*-butyl acetate (1.5 mL) with 20 mol% $Ni(OTf)_2$ at 80 °C in the resealable vial. [b]**1p** =2-methoxy-2-phenyl-2H-benzo[b][1,4]oxazin-3(4H)-one.

Subsequently, we studied this reaction with peroxide functionalised 2-oxindole derivatives to acquire quaternary methylallyl functionalized 1,4-benzoxazin-3-one (**5**). A model reaction was studied for the optimal condition (Table 4). This reaction did not afford any product in the absence of Lewis acid at room and high temperature (Table 4, entry 1 and 2). We have screened several Lewis acids, such as $FeCl_3$, $Fe(OTf)_2$, $Mn(OTf)_2$, $Sn(OTf)_2$, $Ni(OTf)_2$, and $Cu(OTf)_2$ (Table 4, entries 3–8). However, none of these catalyst provided satisfactory results. Interestingly, the exclusive selectivity for methylallylation was observed when 30% $In(OTf)_3$ used as a catalyst at 60 °C and afforded 52% yield of **5a** (Table 4, entry 9). This reaction afforded 85% yield of **5a** after 24 h (Table 3, entry 11). The yield was decreased when temperature increased to 80 °C, and **4a** decomposed when reaction temperature was 100 °C (Table 4, entries 12, 13). Moreover, Bronsted acid failed to provide **5a** (Table 4, entries 14,15).

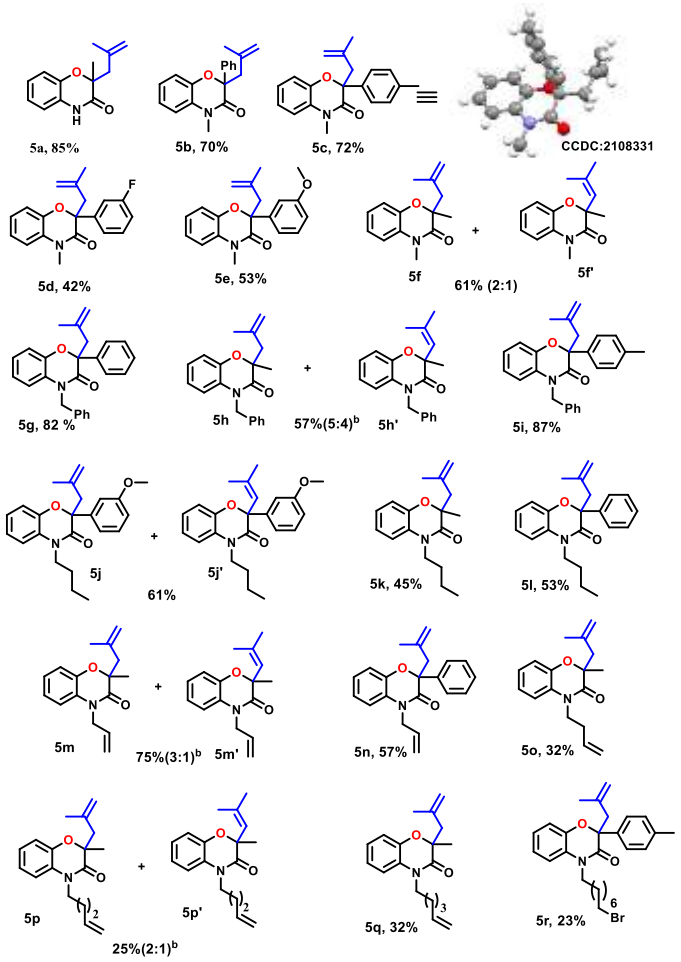
Table 4. Optimization of reaction condition with peroxyoxindole



Entry	Catalyst	Temp (°C)	Time (hrs)	Yield of **5a** (%)
1	-	rt	16	no reaction
2	-	60	16	no reaction
3[b]	$FeCl_3$	60	16	0
4	$Mn(OTf)_2$	60	16	no reaction
5	$Sn(OTf)_2$	60	16	45
6	$Fe(OTf)_2$	60	16	0
7	$Ni(OTF)_2$	60	16	no reaction
8	$Cu(OTf)_2$	60	16	no reaction
9	$In(OTf)_3$	60	16	52
10[b]	$In(OTf)_3$	rt	16	0
11[c]	$In(OTf)_3$	60	24	85
12	$In(OTf)_3$	80	24	47
13	$In(OTf)_3$	100	24	decomposition
14[d]	Amberlyst®-15	60	24	10
15	TFA	60	24	decomposition

[a]Reaction condition: All the reactions were performed using 0.21 mmol of **4a** in *tert*-butyl acetate (1.5 mL) with 30 mol% catalyst at a specific temperature in the resealable vial. [b]No expected product was obtained. [c]63% of product **5a** was obtained with 20 mol% $In(OTf)_3$; [d]w/w ratio of 2:1 was used for substrate : Amberlyst®-15.

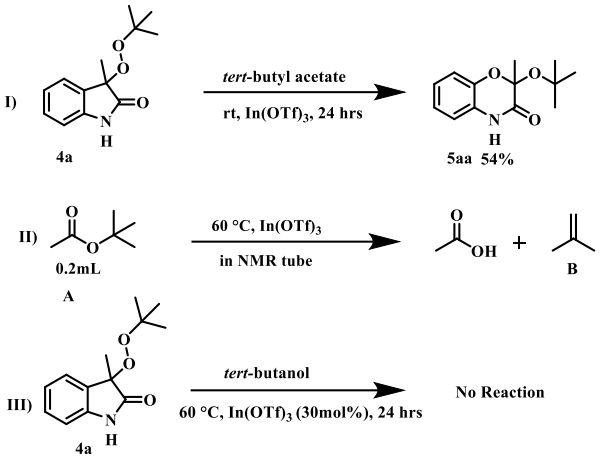
Subsequently, we explored the substrate scope for this methylallyl functionalization with various C3-alkylated peroxyoxindole (Scheme 1). Thus, *N*-protected C3-substituted peroxyoxindole, where the phenyl group had $–CH_3$, –F, and –OMe, afforded a good yield of the respective methylallyl substituted products **5b–e** in 42-72% yields. Further, the structure of product **5c** is confirmed by X-ray structure (see SI, Figure S9). The *N*-benzyl protected peroxy-oxindoles were also undergo successful methylallylation reaction to provide a good yield of the rearranged products, **5g**–**5h**. The decrease in yield was observed for C3-substituted *N*-butyl peroxyoxindole derivatives (**5j**-**5l**). This reaction was tolerant to allyl functionality to afford 75% yield of a mixture of Hoffmann and Saytzeff product, **5m** and **5m'** (ratio 3:1, Scheme 1). The C3-phenyl *N*-allyl substituted peroxyoxindole afforded selectively **5n** in 57% yield. The yield decreased with increasing the carbon chain of N-substitution of peroxyoxindole, i.e *N*-allyl, *N*-butene, *N*-pentene, *N*-hexene, *N*-(8-bromooctyl) substituted peroxyoxindole afforded desired **5o**–**5r**, respectively.



Reaction condition: All reactions were carried out at 0.15-0.21 mmol (50 mg) of **4** in *tert*-butyl acetate (1.5mL) using 30 mol % of $In(OTf)_3$ at 60 °C in the resealable tube for 24 hrs; [b]NMR conversion.

Scheme 1. Substrate scope for the sequential rearrangement and methylallylation reaction

To understand the reaction pathway, a control experiment was performed with *tert*-butyl acetate, **4a** and $In(OTf)_3$ at room temperature (Scheme 2 (I)) resulted attacking of *tert*-butyloxy group at C3-position of 1,4-benzoxazine moiety. This indicate that heating is required for the generation of isobutylene. Further, the reaction was performed in the NMR tube with *tert*-butyl acetate and $In(OTf)_3$ at 60 °C (Scheme 2 (II)). This experiment was confirmed the in situ generation of isobutylene by NMR analysis (SI, Figure S4-S7). Furthermore, the reaction of **4a** with *tert*-butanol resulted no reaction (Scheme 2 (III)), indicating that *tert*-butanol might coordinate with the Lewis acid, which diminishes reactivity of Lewis acid.



Scheme 2. Preliminary experiment for the mechanistic study

The reaction kinetics was studied by varying the catalyst and peroxide **4a** concentration. Moreover, this kinetic study helps to understand the effect of various component on the sequential rearrangement and methylallytion reaction for the formation of **5a** by the initial rate method. Initially, the rate order for the formation of **5a** was determined by measuring the initial rate of the reaction at different concentrations of **4a**. The various concentrations of **4a** (0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.4 M) were reacted with 0.03 M of $In(OTf)_3$ catalyst (see SI, Table S1, Figure S2). This indicate that the rate of the reaction increases upon increasing the concentration of **4a** and a slope 0.985 was obtained from the plot of log(rate) versus log(concentration of **4a**) (Figure 3a).

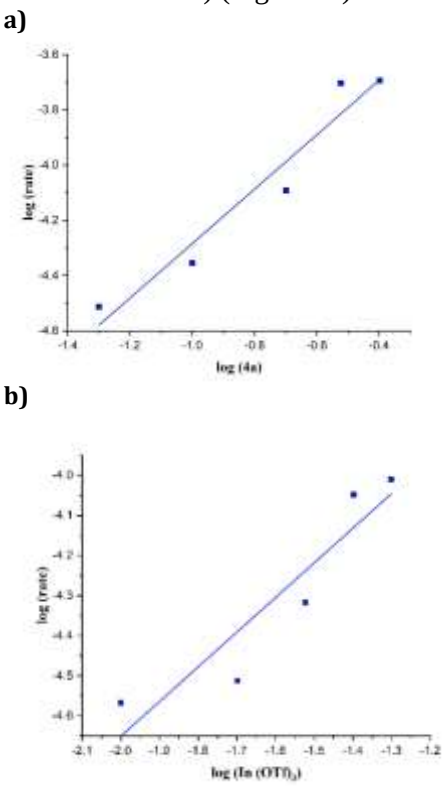
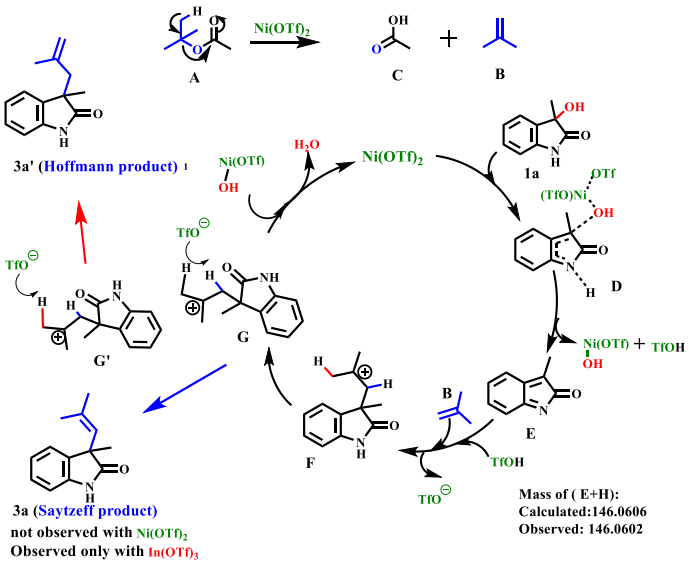


Figure 3. (a) Plot of log (rate) versus log (concn. **4a**). (b) Plot of log (rate) versus log($In(OTf)_3$)

Thus, this sequential rearrangement and substitution reaction to form **5a** majorly depends upon the concentration of compound **4a**. Notably, increasing in the rate was observed upon increasing the loading of $In(OTf)_3$ catalyst (see SI, Table S2, Figure S3) and 0.863 slope was obtained (Figure 3b). This highlights that the reaction is positive order with respect to the catalyst $In(OTf)_3$, and involves multiple steps. From the positive rate order with respect to the peroxide **4a** and $In(OTf)_3$, the activation of the peroxide **4a** by the catalyst might be the crucial step in the catalytic cycle.

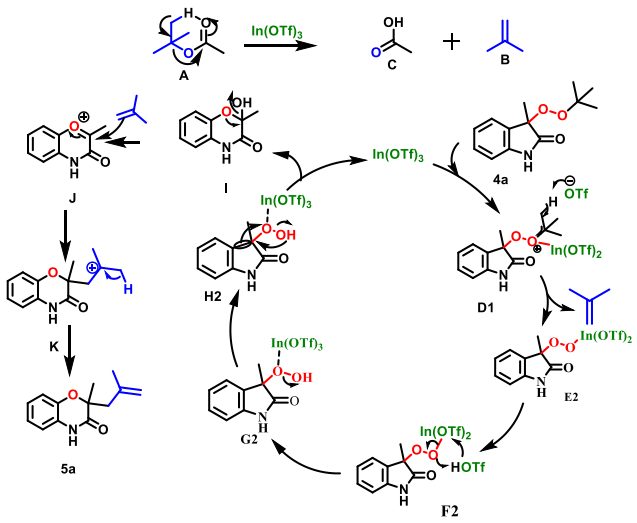
Based on the experimental studies and previous reports,[8,12] we have proposed the mechanism for the formation of product **3**. The catalytic cycle (Scheme 3) begins through the coordination of $Ni(OTf)_2$ with the oxygen of C3-hydroxy-3-methyloxindole (**1a**) to give transition state **D**. The lone pair on the nitrogen of **D** undergoes electronic conjugation to form the intermediate **E** with the formation of triflic acid in the reaction medium. Further, the formation of intermediate **E** is confirmed by HRMS (see the SI, Figure S126). The mass of (**E** +H) is 146.0602. The intermediate **E** is attacked by isobutylene to form the intermediate **F**. Finally, OTf^- abstracts terminal hydrogen via **G'** to obtain the desired product **3a'**. A similar catalytic cycle occurs in the presence of In(OTf)3 to form the mixture of Hoffmann and Saytzeff product.



Scheme 3. Plausible catalytic pathway

Next, from the preliminary experiments (Scheme 2), kinetic analyses, and literature reports[13], a plausible mechanism is proposed for the formation of **5** (Scheme 4). Initially, *tert*-butyl acetate undergoes ester pyrolysis to produce isobutylene (**B**). The catalytic cycle starts with the coordination of $In(OTf)_3$ with peroxyoxindole **4a** to give transition state **D1**. The proton abstraction from transition state **D1** led to the formation of intermediate **E2** with the liberation of iso-

butylene gas. The intermediate **G2** formed after the protonation of intermediate **E2** followed by coordination of regenerated $In(OTf)_3$ from transition state **F2**. Then, aryl bond migrates to oxygen attached to the C3 carbon of peroxy group and simultaneously, attack of –OH to form the intermediate **I**. The intermediate **I** in the presence of $In(OTf)_3$ generates the intermediate **J**. Subsequently, intermediate **J** is attacked by the isobutylene to form the intermediate **K**. Finally, proton abstraction from **K** results in the desired product **5a** (Hoffmann product).



Scheme 4. Plausible mechanism for methylallyl functionalization through peroxyoxindole rearrangement

In summary, in this paper we have reported for the first time for the highly selective quaternary α-vinylation and methylallylation of hydroxy groups and peroxides by using *tert*-butyl acetate in the presence of catalytic $In(OTf)_3$ and $Ni(OTf)_2$. Moreover, $In(OTf)_3$ selectively promotes the quaternary α-vinylation of hydroxyl oxindole. Exclusive selectivity was obtained for methylallylation of hydroxy oxindole by using catalytic $Ni(OTf)_2$. However, this reaction with peroxyoxindole afforded sequential rearrangement and quaternary methyl allylation by using catalytic $In(OTf)_3$. Kinetic studies revealed that both the concentration of reactants and catalysts play a vital role in these reactions. From the experimental evidances and previous studies, plausible mechanisms were proposed for the methylallylation of hydroxy oxindole and peroxyoxindole. The detailed studies on the selectivity for this reaction under investigation using DFT studies and will be reported in due course.

Experimental Section

General procedure for methylallylation of C3-hydroxy-3-alkylated oxindole: The *tert*-butyl acetate (1.5 mL) was added to the 20 mL resealable vial containing 3-substituted-3-hydroxy oxindole (50 mg, 1 equiv.). Then, 20 mol% of $In(OTf)_3$ or $Ni(OTf)_2$ was added to the vial. Finally, the vial was sealed with aluminium cap with septum. Further, the solution was heated at 80 °C for 12 h. After the completion of the reaction, the volatile components were evaporated under vacuum. The residue was purified by 100-200 mesh silica gel column chromatography to afford desired product **3**.

General procedure for methylallylation of C3-peroxide-3-alkylated oxindole: The *tert*-butyl acetate (1.5 mL) was added to the 20 mL resealable vial containing 3-substituted-3-*tert*-butylperoxyoxindole (50 mg, 1 equiv.). Then, 30 mol% of $In(OTf)_3$ was added to the vial. Finally, the vial was sealed with aluminum cap with septum. Further, the solution was heated at 60 °C for 24 hours. After the completion of the reaction the volatile components were evaporated under vacuum. The residue was purified by 100-200 mesh silica gel column chromatography to afford desired product **5**.

Acknowledgements

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Catalyst Assisted Selective Vinylation and Methylallylation of Quaternary Carbon Centre by using *tert*-Butyl acetate

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