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Assembly of 3-allyl-3-ethynyl-oxindole motifs *via* palladium(II)-catalyzed quaternary allylation of 3-ethynyl-3-OBoc-oxindoles†

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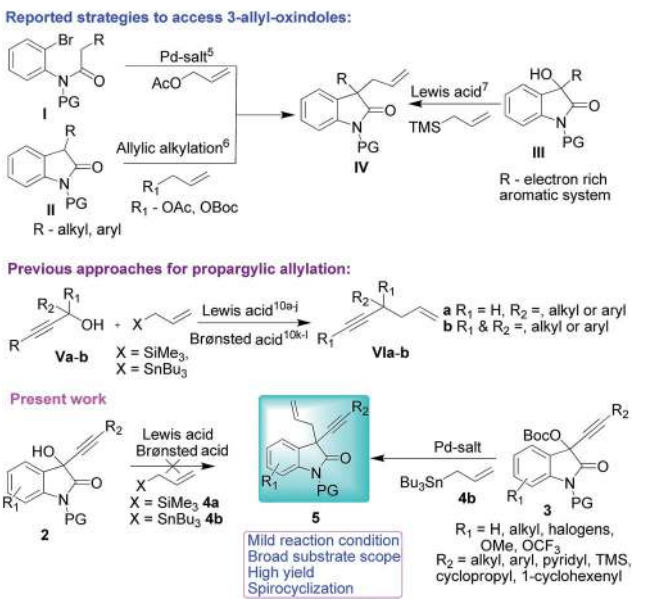
Palladium(II)-catalyzed C3-allylation of 3-ethynyl-3-OBoc oxindole derivatives was achieved for the first time to access highly functionalized 3-allyl-3-ethynyl substituted oxindole derivatives for a broad range of substrates in very good yields (up to 94%). The synthetic applications of the allylated products were explored by synthesizing five and six membered carbocyclic spirooxindoles in moderate to very good diastereoselectivities.

Introduction

The development of new synthetic strategies to access 3,3-disubstituted oxindoles remains an important task in synthetic chemistry, because of their exciting and unique applications in biology.[1] Despite the advances in organic synthesis to synthesize these motifs with diverse substitutions like N, O, S, *etc.*,[2] only a few protocols are available to construct 3,3-dicarbon substituted oxindoles.[3] Among various known 3,3-disubstituted oxindoles, introduction of allyl substitution at C3-position gained much attention, since they can eventually be exploited to synthesize various natural products and pharmaceutical lead compounds.[4] In this regard, few racemic and chiral strategies have been reported in the literature to access 3-allyl substituted oxindoles. These include arylation of amides **I**,[5] asymmetric allylic alkylation using oxindole prochiral nucleophiles[6] **II** and allylation of 3-hydroxy-oxindoles bearing electron rich aromatic ring systems **III** (Scheme 1).[7] Despite these developments, to our surprise there is no literature precedence to construct 3-allyl-3-ethynyl substituted oxindoles **5**. Furthermore, grafting allyl and ethynyl substitutions at C3-position of oxindole is highly desirable, since, ethynyl and allyl (1,5-enyne) combination is well exploited in the literature to build cyclic and complex structures.[8] We hope that, incorporating ethynyl and allyl substitutions at C3-position of oxindole would enable the structural diversification around C3-position of oxindole, which is much desired in medicinal chemistry. Apart from its synthetic utility the presence of alkyne moiety at 3-position of oxindole showed higher anti-retroviral inhibition in HIV-1 than efavirenz.[9] Hence, the identification of suitable combination of electrophile and nucleophile to access 3-allyl-3-ethynyl substituted oxindoles is of great importance.

Various synthetic efforts were reported in the literature for the direct addition of allyltrimethylsilane to secondary propargyl alcohols **Va** using Lewis[10a–j] or Brønsted[10k,l] acid catalysts (Scheme 1). Despite, these accomplishments in the literature, only a very few protocols are available for the allylation of tertiary propargyl alcohols **Vb** or their derivatives.[11] Moreover, there is no literature precedence on the allylic substitution of propargyl alcohol derivative in oxindole scaffold **2**. Therefore, development of a general, efficient, catalytic method for



Scheme 1 Strategies to access allylated products.

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propargylic substitution reaction comprising oxindole moiety is highly warranted.

Results and discussion

Our attempt began with the synthesis of 3-hydroxy-3-ethynylindolin-2-ones **2** by treating isatins **1** with alkynyl magnesium bromide generated *in situ* from corresponding alkyne using Grignard reaction in the absence of silver salt and pyrophoric reagent.[9,12] This is the first report which discloses the synthesis of 3-hydroxy-3-ethynylindolin-2-ones **2a–y** using *in situ* generated Grignard reagent (see ESI†).

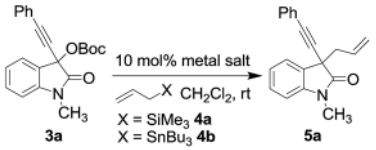
Initially, we attempted the direct allylation of 3-hydroxy-1-methyl-3-(phenylethynyl)indolin-2-one **2a** with allyltrimethylsilane/allyltributylstannane **4a**/**4b** in the presence of either Lewis acids or Brønsted acid in dichloromethane. In contrast to previous successful reports,[10] allylation failed to occur in the presence of Lewis acid/Brønsted acid. Similar results were observed when trifluoroacetic acid and $BF_3 : Et_2O$ were employed as catalysts and the allylation of **2a** did not occur even at elevated temperature under these conditions (see ESI†). It is reasonable to anticipate that, creation of cation at pseudobenzylic position in the absence of electron rich aromatic system is less favorable. Hence, we employed corresponding 3-OBoc oxindole derivative **3a** as the reactant. However, the reaction of trimethylsilane **4a** with 3-OBoc oxindole derivative **3a** afforded only negligible amount of allylated product **5a** under Lewis acid conditions (Table 1, entries 1–6). The allylation reaction between allyltributylstannane **4b** and 3-OBoc oxindole derivative **3a** afforded the desired product **5a** in 38% yield when scandium triflate was employed as a catalyst (Table 1, entry 7). Screening of other Lewis acids under identical conditions did not bring in desired results (entries 8–12). Hence, we turned our attention to palladium catalysts to achieve the allylation at pseudobenzylic position due to their demonstrated potential in C–C bond formation.[13] As a preliminary investigation, allylation reaction between allyltributylstannane **4b** and 3-OBoc oxindole derivative **3a** was carried out in the presence of 5 mol% of palladium(II) chloride and 10 mol% of PPh_3 in dichloromethane at ambient temperature. The reaction proceeded smoothly to afford the corresponding allylated product **5a** in 77% yield (Table 2, entry 1). To further improve the yield, different palladium(II) salts were screened under established conditions (Table 2, entries 2–6). The best result was obtained using allylpalladium(II) chloride dimer and the desired allylated product **5a** was isolated in 94% yield (Table 2, entry 6).

Having established the optimal reaction conditions, the influence of nitrogen protecting groups on reactivity was examined. Different N_1-substituted 3-OBoc oxindole derivatives **3a–e** were subjected to allylation under identical reaction conditions and the results are depicted in Table 3. 3-OBoc oxindoles **3b–e** which contain different protecting groups such as benzyl **3b**, *tert*-butyloxy carbonyl **3c**, allyl **3d** and propargyl **3e** rendered the desired allylated products **5b–e** with very good yields (84–90%). The presence of different N_1-protecting groups did not affect the efficiency of the reaction. Hence, the desired protecting group can be incorporated depending upon the utility of the final product. After examining the effect of protecting groups at N_1-position, the impact of having different substitutions at various position on aryl part of the oxindole moiety was studied using N_1-methyl substituted 3-OBoc-oxidole **3a**.

The effect of halogen substitutions at different positions on aryl ring of oxindole scaffold was investigated initially. It was observed that, sterically demanding 4-Cl and 4-Br substituents are well accommodated under the catalytic conditions to afford the corresponding allylated products (**5f** and **5g**) in good yields.

The allylation reaction of 5-fluoro substituted 3-OBoc oxindole derivative **3h** proceeded to yield **5h** in 83%, whereas all other 5-halogen substituents rendered the corresponding

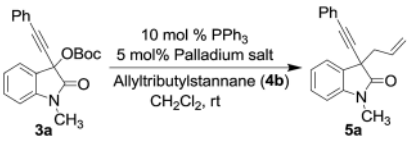
Table 1 Screening of Lewis acids and allylating agents[a]



Entry	Metal salt	Allylating agent **4**	Time (h)	Yield[b] (%)
1	$Sc(OTf)_3$	**4a**	24	<10
2	$Cu(OTf)_2$	**4a**	24	—
3	$Yb(OTf)_3$	**4a**	24	Trace
4	$FeCl_3$	**4a**	48	—
5	$SnCl_4$	**4a**	48	—
6	$TiCl_4$	**4a**	48	—
7	$Sc(OTf)_3$	**4b**	40	38
8	$Cu(OTf)_2$	**4b**	24	<10
9	$Yb(OTf)_3$	**4b**	48	21
10	$FeCl_3$	**4b**	32	26
11	$SnCl_4$	**4b**	32	30
12	$TiCl_4$	**4b**	32	19

[a] The allylation reaction was performed between **3a** (1 eq, 0.27 mmol) and **4** (2 eq) with 10 mol% of Lewis acids and 2 equiv. of allylating agents (**4a** or **4b**) in CH_2Cl_2 as a solvent at rt. [b] Isolated yield of the product.

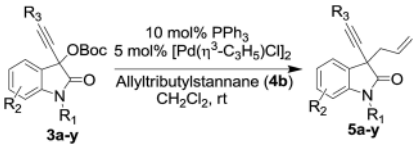
Table 2 Optimization of palladium salts[a]

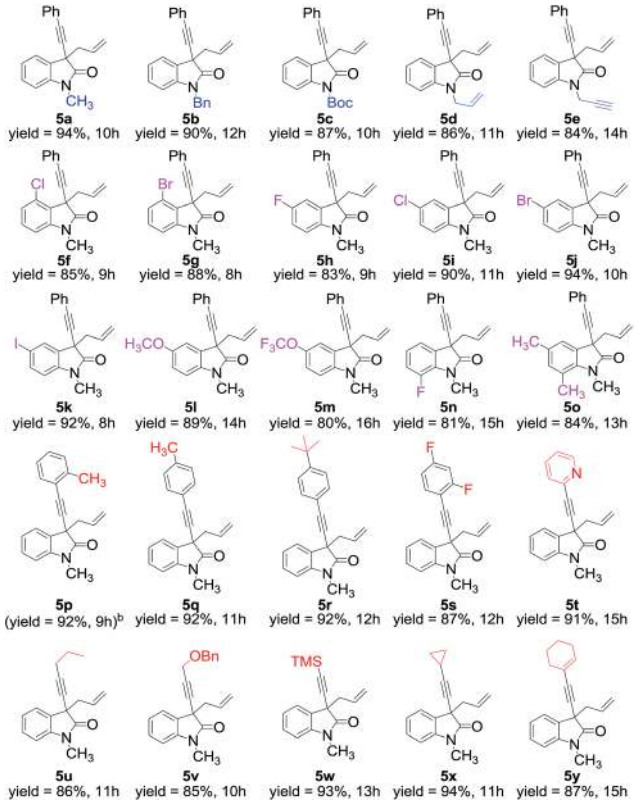


Entry	Palladium salt	Time (h)	Yield[b] (%)
1	$PdCl_2$	15	77
2	$Pd(OAc)_2$	16	72
3	$Pd(PPh_3)_2Cl_2$	14	70
4	$Pd(TFA)_2$	48	60
5	$Pd_2(dba)_3$	48	62
6	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	10	94

[a] The allylation reaction was performed between **3a** (1 eq, 0.27 mmol) and **4b** (2 eq) with 5 mol% of palladium salt and 10 mol% of PPh_3 in CH_2Cl_2 as a solvent at rt. [b] Isolated yield of the product.

Table 3 Substrate diversity[a]





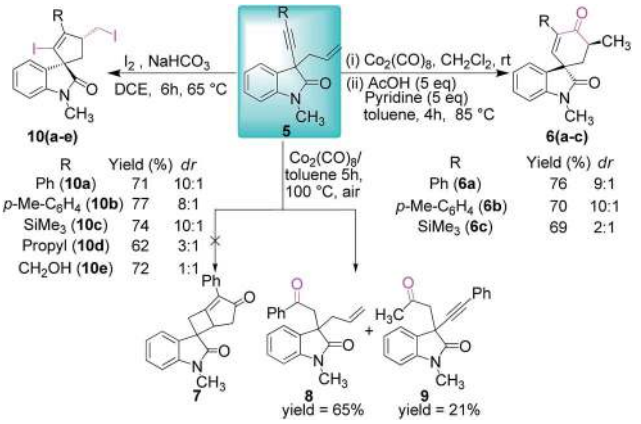
[a] The allylation reaction was performed between **3a–y** (1 eq) and allyltributylstannane **4b** (2 eq, 0.55) with 10 mol% of PPh_3, 5 mol% of ally palladium(II) chloride dimer in CH_2Cl_2 as a solvent at rt. [b] ESI.

allylated products **5i–k** in very good yields in the range of 90–94%. It is noteworthy that the presence of bromo-**5j** as well as iodo **5k** substituents did not retard the catalytic efficiency of the reaction. Incorporation of electron releasing substitution like 5-methoxy group did not affect the efficiency of the reaction and desired allylated product **5l** was isolated with 89% yield. Replacement of 5-methoxy substituent by 5-trifluoromethoxy substitution **5m** slightly affected the yield of the reaction (80%). The presence of substitutents at 7-position (7-fluoro, 5,7-dimethyl) did not hamper the catalytic efficiency and resultant allylated products (**5n** and **5o**) were isolated with better yields.

After investigating the influence of various substituents on aryl part of oxindole moiety, scope of differently substituted alkynes was explored. Grafting a methyl substitution either at *ortho*- or *para*-position of the aryl ring did not show any negative effect and corresponding allylated products (**5p** and **5q**) were obtained with similar yields (92%). Aryl part of alkyne having bulky group like *tert*-butyl at *para*-position underwent smooth allylation to afford the product **5r** in 92% yield. Presence of difluoro-substitution on aryl part of alkyne moiety did not retard the catalytic efficiency, and the respective *o*-, *p*-difluoro substituted product **5s** was isolated with 87% yield. To study the effect of presence of hetero atom, 3-(2-pyridyl ethynyl) substituted 3-OBoc-oxindole **3t** was employed as a substrate. Under the established catalytic condition, existence of pyridyl group did not pose any adverse effect to the conversion and the product **5t** was obtained with an excellent yield of 91%.

The tolerability of alkyl substitution on alkyne moiety was also examined under the optimized conditions. No significant reduction in the yield was observed for substrates **3u** and **3v** which contain linear aliphatic groups like propyl and $-CH_2OBn$. Trimethylsilyl and cyclopropyl substituted alkynes (**3w** and **3x**) were subjected for similar transformation. They were found to be ideal substrates under established protocol to afford the corresponding allylated products (**5w** and **5x**) in excellent yields (93 and 94%). The presence of double bond in cyclohexenyl substitued alkyne moiety altered neither the pathway nor the efficiency of the reaction. The corresponding product **5y** was isolated in good yield (87%). We were delighted to observe that the presence of substitutions like electron-rich and halogen functionalities either at aryl part of oxindole ring or aryl part of alkyne moiety was well tolerated under our established conditions. In addition, replacement of aryl part of alkyne moiety by heteroaryl as well as reactive alkyl substituents did not exert any negative effect on the yield. Scalability of the reaction was evaluated by performing the transformation in 3 gram scale and the expected product **5a** was isolated with 87% yield. Thus, we newly developed a palladium(II)-catalyzed C3-allylation of 3-ethynyl-3-OBoc oxindole derivatives **3a–y** to construct highly functionalized 3-allyl-3-ethynyl-oxindole scaffolds **5a–y**.

To the best of our knowledge, there is no literature precedence of grafting allyl and ethynyl substitutions at C3-position of oxindole. After achieving the synthesis of the same, we wanted to explore application of these intermediates **5** in constructing novel carbocyclic spirooxindoles (Scheme 2). The intermolecular addition reaction between alkyne and alkene is promoted by alkyne–$[Co_2(CO)_6]$ complex.[14] We employed similar strategy to achieve the intramolecular cyclization between alkyne and alkene by generating active acyl cobalt species from alkyne–$[Co_2(CO)_6]$ complex, which further underwent intramolecular addition with alkene to afford the corresponding spirooxindole cyclohexenone **6a** in very good diastereoselectivity (9 : 1). The observed *syn*-selectivity for compound **6a** is in accordance with XRD data (see ESI†). Under the established conditions, 4-methyl phenyl as well as trimethyl silyl substituted cyclohexenones **6b** and **6c** were synthesized successfully with diastereomeric ratio of 10 : 1 and 2 : 1 respectively. Substrates which possess propargylic hydrogens *e.g.* **5u** afforded a mixture of unidentified inseparable products (cyclised and oxidized products). Hence, the developed catalytic conditions suits well to construct a library of functionalized spiro-4-cyclohexenones **6a–c** from aromatic alkynes as well as alkynes which lacks propargylic hydrogens (**6c**). Pauson–Khand[15] reaction condition was applied to synthesize a spirobicyclic system from compound **5a**. Due to ring strain, the



Scheme 2 Applications of 3-allyl-1-methyl-3-(phenylethynyl)indolin-2-one (**5a**).

four membered ring formation was not observed **7**. Hence, we performed the reaction under the open atmospheric condition to obtain linear carbonylated products (**8** and **9**).

Next, the intramolecular cyclization reaction of compound **5a** under metal free condition was carried out using I_2. Treatment of molecular iodine with compound **5a** in dichloroethane at 65 °C, furnished the five-membered 2-iodo-4-iodomethyl spiro cyclopentene **10a** in good yield (71%) and diasteroselectivity (10 : 1). We were pleased to observe that under the optimized conditions, substrates with a range of substitutions including aromatic, trimethylsilyl, aliphatic and hydroxy group underwent smooth cyclization to afford corresponding spiro cyclized products **10b–e** in good yields. The stereochemical information was obtained compound **10b** from single crystal XRD data and found to be *syn* with respect to quaternary and tertiary stereocenter (see ESI†). Thus, we have successfully disclosed two unprecedented intramolecular spiro-carbocyclizations with and without metal catalyst. The protocol described here will pave a way to synthesize a library of new spiro-carbocyclic compounds to unravel the hidden truth of cellular processes.

Conclusions

To conclude, we established a novel synthetic strategy to access 3-allyl-3-ethynyl substituted oxindole derivatives in very good yields. We employed allylpalladium(II) chloride dimer with PPh_3 as a catalyst, to achieve the nucleophilic allylic substitution at pseudobenzylic position with a broad substrate scope. The synthetic utilities of the allylated product were demonstrated with three different applications including the assembly of five and six membered spiro-oxindole carbocyclic scaffolds.

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