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Article

Pd(0)-Catalyzed Chemoselective Deacylative Alkylations (DaA) of N-Acyl-2-oxindoles: Total Syntheses of Pyrrolidino[2,3-b]indoline Alkaloids, (±)-Deoxyeseroline and (±)-Esermethole

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Pd(0)-Catalyzed Chemoselective Deacylative Alkylations (DaA) of *N*-Acyl-2-oxindoles: Total Syntheses of Pyrrolidino[2,3-*b*]indoline Alkaloids, (±)-Deoxyeseroline and (±)-Esermethole

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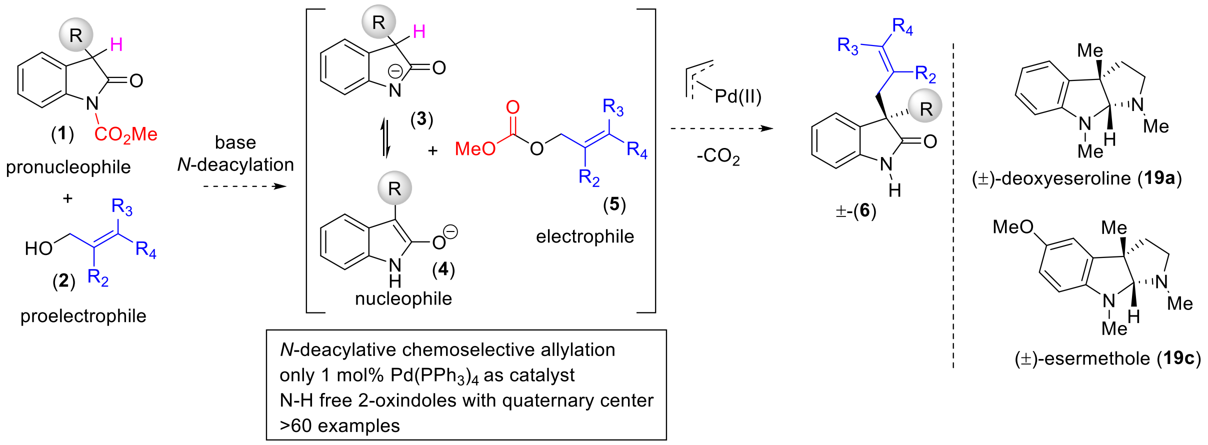
TOC GRAPHIC



ABSTRACT

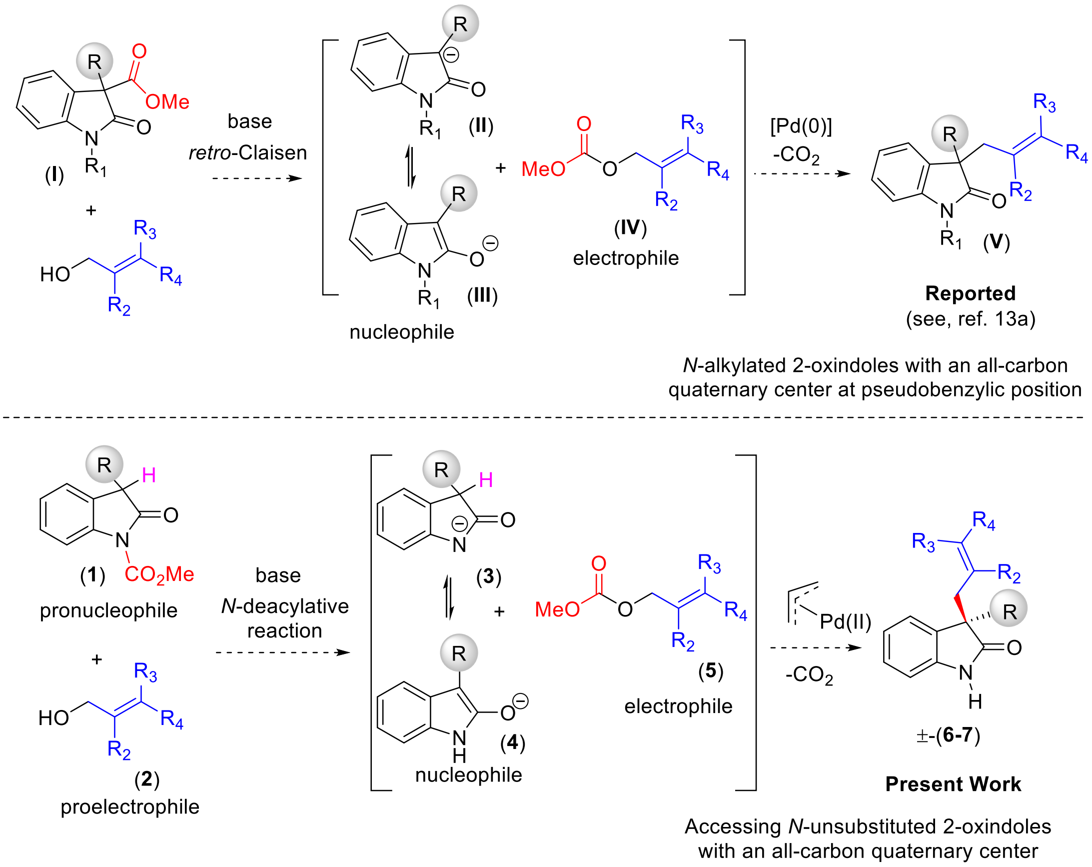
We report an efficient Pd(0)-catalyzed deacylative allylations of *N*-acyl-3-substituted 2-oxindoles *via* coupling of *in situ* generated nucleophiles (3 and 4) with allyl electrophiles, for the synthesis of a variety of 2-oxindoles with C3-quaternary centers. Gratifyingly, this alkylation process is found to be highly chemoselective in nature, where a C-C bond

formation is completely predominant over a C-N bond formation. A variety of key intermediates were synthesized utilizing aforementioned methodology.

INTRODUCTION

Palladium(0)-catalyzed decarboxylative allylation (DcA) [Tsuji-Trost allylation][1] provides opportunity for the allylation of relatively non-stabilized ketone enolates from allyl β-ketoesters or allyl enol carbonates *via* elimination of CO_2.[2, 3] Since the approach is chemically mild to produce various functionalized intermediates,[4] hence finds huge application in the total synthesis of complex natural products.[5-6] However, a major limitation of DcA reactions is that it leads to incorporation of the allyl electrophile and the nucleophile into the same reactant molecule *via* an ester linkage[6a-b] or carbonate.[6c-d] In this context, palladium(0)-catalyzed deacylative allylation (DaA) of α-nitroketone derivatives (pKa ~ 17) by Grenning and Tunge[7] opens up a unique avenue to access unsymmetrically substituted 1,6-dienes.[8, 9] Their pioneering report also suggests that a facile *retro*-Claisen activation to produce enolates (pKa ~ 18-25),[10a] and nitrile stabilized anions (pKa ~ 23)[10b] undergoes alkylations to afford diverse products.[11]

2-Oxindoles bearing an all-carbon quaternary center constitutes a prominent class of heterocycles that represent important building blocks found in a wide variety of several pharmaceuticals.[12] Recently, we have reported an efficient Pd(0)-catalyzed deacylative allylation (DaA) of 2-oxindoles sharing acyl functionality at 3-position (see, **I** in Scheme 1) with readily available allylic alcohols by employing Pd(0)-catalysis under mild reaction conditions.[13a] This reaction presumably goes through a *retro*-Claisen reaction to generate nucleophile (see, **II** and **III**) and electrophile (see, **IV**), which were reacted in the presence of catalytic Pd(0) to afford a wide variety of products with quaternary centers at the pseudobenzylic position of *N*-alkyl 2-oxindoles (see, **V**) under mild reaction conditions.[13a] Gratifyingly, the same strategy works equally well for dimeric 2-oxindole system furnishing products with vicinal quaternary center in favour of *meso*-isomer as major product. Utilizing this methodology we have reported concise total syntheses of dimeric pyrroloindoline alkaloids, *meso*-folicanthine and *meso*-chimonanthine.[13]



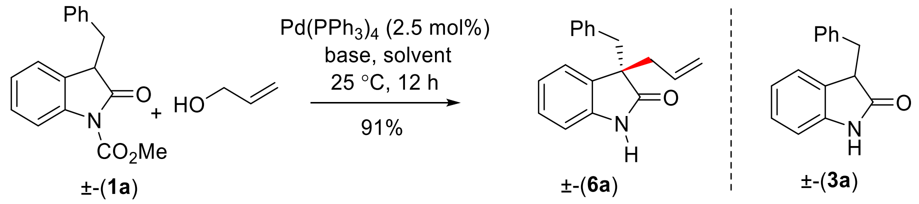
Scheme 1. Our hypothesis of *N*-deacylative alkylations (*N*-DaA).

N-Unsubstituted 2-oxindoles sharing with a quaternary centers at the pseudobenzylic position are the privileged structural scaffolds in organic synthesis. These are found to be the building blocks for the synthesis of a number of pharmaceutically important compounds and natural products. We hypothesized that an allylic alkoxide may induce a *N*-deacylation of an appropriately substituted *N*-acyl-2-oxindole **1** to form enolate **4** as active intermediate *via* anion **3** (Scheme 1). This enolate **4** would then react with Pd(II)-π-allyl complex generated *in situ* by reaction of allyl acetate and Pd(0) to furnish various 2-oxindoles with a quaternary center. However, since anion **3** and enolate **4** have several bond forming possibilities (*N*-center of anion **3** is relatively soft), a chemoselective C-C bond forming reaction would be challenging and worth testing.[13] Herein, we describe a novel strategy involving Pd(0)-catalyzed deacylative allylation of *N*-acyl-2-oxindole *via* coupling of *in situ* generated nucleophiles with allyl electrophiles (Scheme 1).

RESULTS AND DISCUSSION

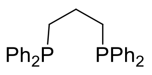
At the outset, we started optimization of deacylative allylation (DaA) with *N*-methoxycarbonyl 3-benzyl 2-oxindole (**1a**) with allyl alcohol in the presence of catalytic Pd(0) and a suitable base. Following exhaustive optimization (Table 1), we observed that deacylative alkylation (DaA) can be carried out with **1a** (0.25 mmol, 1 equiv) in the presence of either NaH (1.2 equiv) or KO^tBu (1.2 equiv) and 1 mol% $Pd(PPh_3)_4$ in toluene at room temperature, to afford the desired 2-oxindole **6a** in 91% and 89% yields, respectively (Table 1).

Table 1: Optimization of *N*-deacylative allylation (*N*-DaA) of (±)-**1a**.

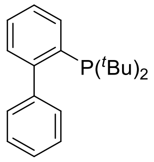


entry[a]	catalyst	base	solvent	temp	ligand	time	%[b] (6a)	% of 3a
1	$Pd_2(dba)_3$	NaH	THF	70 °C	---	4 h	44%	38%
2	$Pd_2(dba)_3$	KO^tBu	THF	70 °C	---	5 h	25%	53%
3	$Pd(OAc)_2$	NaH	THF	70 °C	PPh_3 (10 mol%)	4 h	46%	39%
4	$Pd(OAc)_2$	KO^tBu	PhMe	25 °C	PPh_3 (10 mol%)	5 h	42%	33%
5	$Pd(OAc)_2$	NaH	PhMe	25 °C	PPh_3 (10 mol%)	4 h	59%	25%
6	$Pd(OAc)_2$	NaH	PhMe	25 °C	**L1** (5 mol%)	4 h	65%	21%
7	$Pd(OAc)_2$	NaH	PhMe	25 °C	**L2** (10 mol%)	5 h	62%	14%
8	$Pd(OAc)_2$	NaH	PhMe	25 °C	**L3** (5 mol%)	6 h	79%	8%
9	$Pd(OAc)_2$	NaH	PhMe	25 °C	**L4** (5 mol%)	5 h	87%	--
10	$Pd(OAc)_2$	NaH	PhMe	25 °C	**L5** (5 mol%)	4 h	90%	--
11[c]	$Pd(PPh_3)_4$	NaH	PhMe	25 °C	---	12 h	91%	--
12[c]	$Pd(PPh_3)_4$	KO^tBu	PhMe	25 °C	---	12 h	89%	--
13[c]	$Pd(PPh_3)_4$	NaH	Et_2O	25 °C	---	14 h	62%	15%
14[c]	$Pd(PPh_3)_4$	NaH	CH_2Cl_2	25 °C	---	12 h	70%	20%
15[c]	$Pd(PPh_3)_4$	NaH	DMSO	25 °C	---	14 h	67%	17%

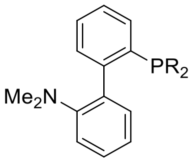
16[c]	$Pd(PPh_3)_4$	NaH	dioxane	25 °C	---	13 h	56%	21%
17[c]	$Pd(PPh_3)_4$	NaH	MeCN	25 °C	---	13 h	83%	--
18[c]	$Pd_2(dba)_3$	NaH	PhMe	25 °C	---	12 h	69%	13%
19[c]	$Pd_2(dba)_3$	NaH	DMSO	25 °C	---	12 h	65%	10%
20[c]	$Pd_2(dba)_3$	NaH	PhH	25 °C	---	12 h	65%	17%



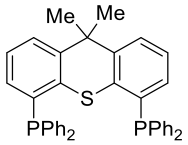
(**L1**)



(**L2**)



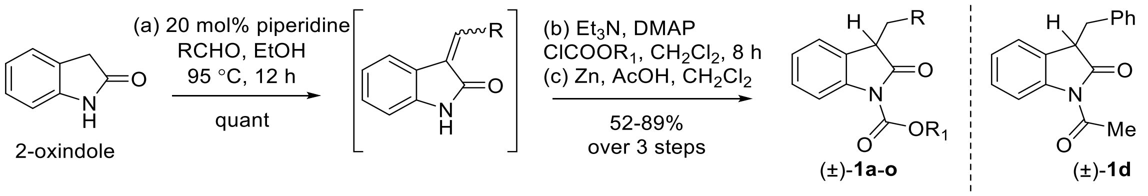
R = Ph (**L3**)
R = Cy (**L4**)



(**L5**)

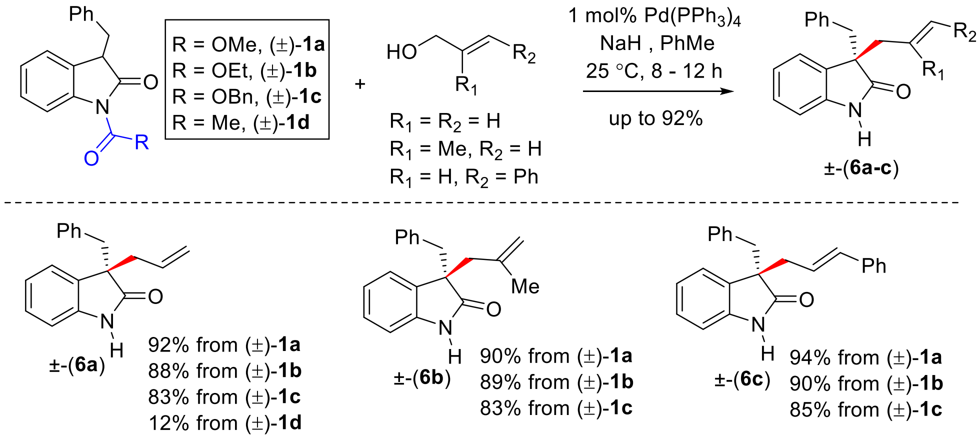
[a]reactions were carried out by using 0.25 mmol of **1a** with 0.30 mmol of allyl alcohol under argon atmosphere. [b]isolated yield after column purification. [c]1 mol% Pd-catalyst used.

This standard condition of deacylative alkylation (DaA) was applied to a variety of substrates.



Scheme 2: Synthesis of *N*-carboxymethyl 3-substituted 2-oxindoles.

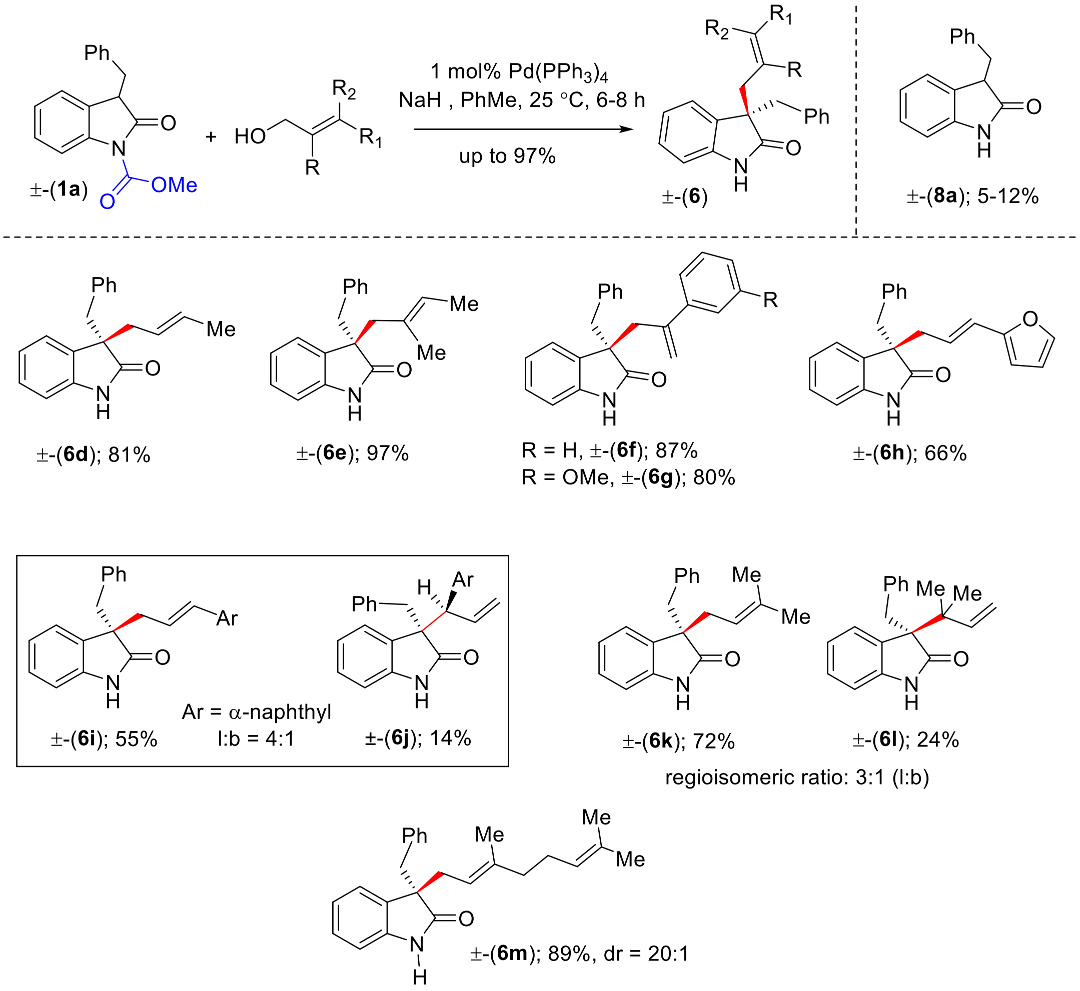
The optimization using a variety of *N*-acyl substrates **1a-d**, showed that *N*-carboxymethyl 3-substituted 2-oxindoles are good substrates for efficient DaA process (Scheme 2).



[a]reactions were carried out by using 0.25 mmol of **1a-d** with 0.30 mmol of allyl alcohol in toluene in the presence of 1 mol% Pd(PPh_3)$_4$ under argon atmosphere. [b]isolated yield after column purification.

Scheme 3: Effect of different *N*-acyl groups on *N*-DaA.[a,b]

With an optimized *N*-methoxycarbonyl as acyl group, **1a** was reacted with a variety of allyl alcohols as pro-electrophiles to afford a library of 2-oxindoles with a C3-quaternary center (Scheme 3). As obvious from scheme 2, our optimized conditions could afford a variety of products with moderate to good yields.

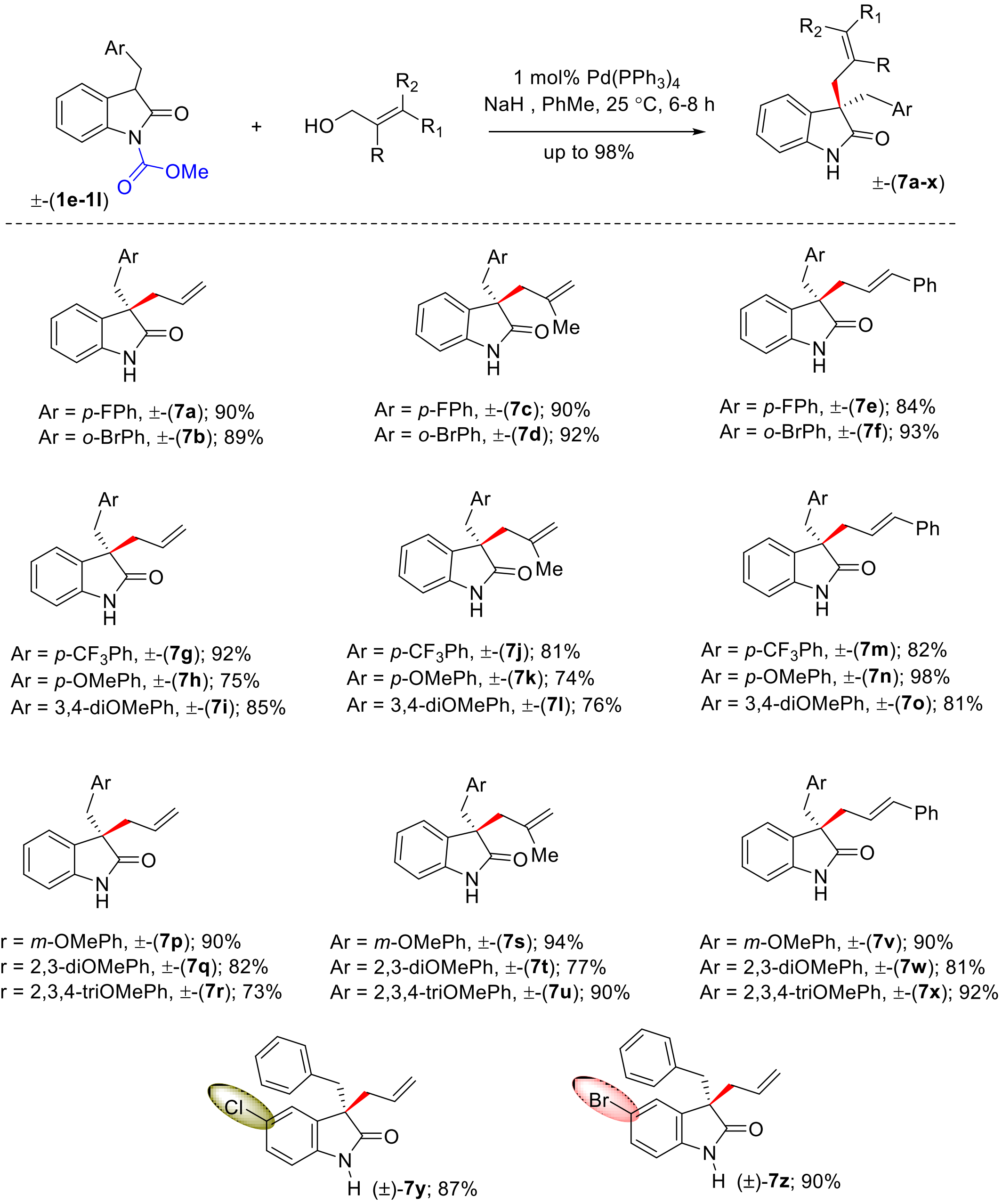


[a]reactions were carried out by using 0.25 mmol of **1a** with 0.30 mmol of substituted allyl alcohol in toluene in the presence of 1 mol% Pd(PPh$_3$)$_4$ under argon atmosphere. [b]isolated yield after silica gel column chromatography.

Scheme 4: Substrates scope of Pd(0)-catalyzed *N*-DaA.

Interestingly, crotyl, tiglyl, and cinnamyl type alcohols afforded products **6c** (Scheme 2), **6d-e**, and **6h** (Scheme 3) with complete regioselectivity, where only linear alkylations were observed. These reactions proceed through the formation of π-allyl palladium intermediates and the linear isomer was exclusively obtained as *E*-isomer (*E*:*Z* = 100:0). Aralyl alcohols furnished products **6f-g** in 80-89% isolated yields. However, cinnamyl type alcohol having a α-naphthyl as aryl group furnished in 4:1 regioselectivity in favoured of linear alkylation (see, **6i-j**, Scheme 3).

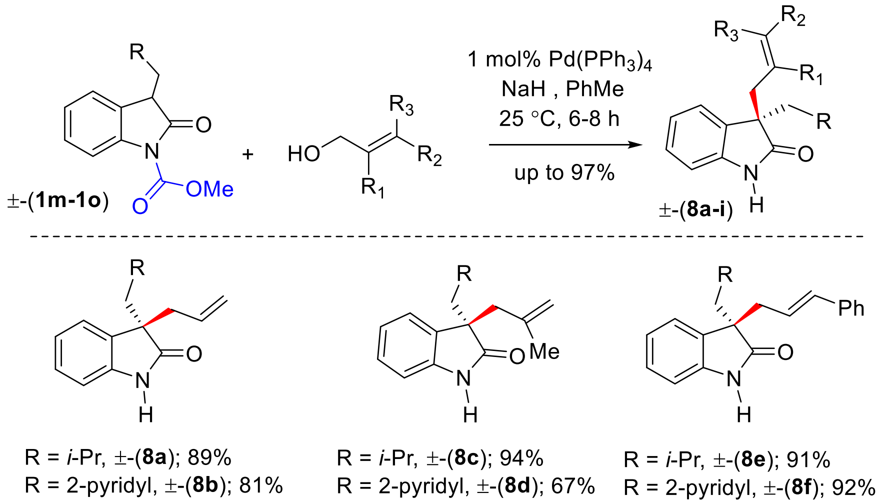
We then sought to explore our strategy to prenylated, reverse-prenylated, and geranylated hexahydropyrrolo[2,3-*b*]indole natural products.[14] To realize this we proposed a direct incorporation of the prenyl, reverseprenyl, or geranyl group at the 3-position of 2-oxindole products[15] *via* Pd-catalyzed deacylative allylation involving *retro*-Claisen activation. In case of 3,3-dimethylallyl alcohol, where **6k-l** was formed in 2:1 regioselectivity in favoured of **6k**. Gratifyingly, geranyl alcohol as a pronucleophile afforded product **6m** as a liner product as exclusive one.[16]



[a]reactions were carried out by using 0.25 mmol of **1e-l** with 0.30 mmol of substituted allyl alcohol in toluene in the presence of 1 mol% Pd(PPh_3)$_4$ under argon atmosphere. [b]isolated yield after silica gel column chromatography.

Scheme 5: Substrates scope of *N*-DaA.[a,b]

Later, a variety of 3-substution on *N*-methoxycarbonyl 2-oxindoles were reacted with allyl, methallyl, and cinnamyl alcohols as pro-electrophiles, under optimized condition of DaA (Schemes 4 and 5). These reactions afforded a variety of products in good to excellent yields, where again linear selectivities were observed in case of cinnamyl alcohol (Schemes 4 and 5).

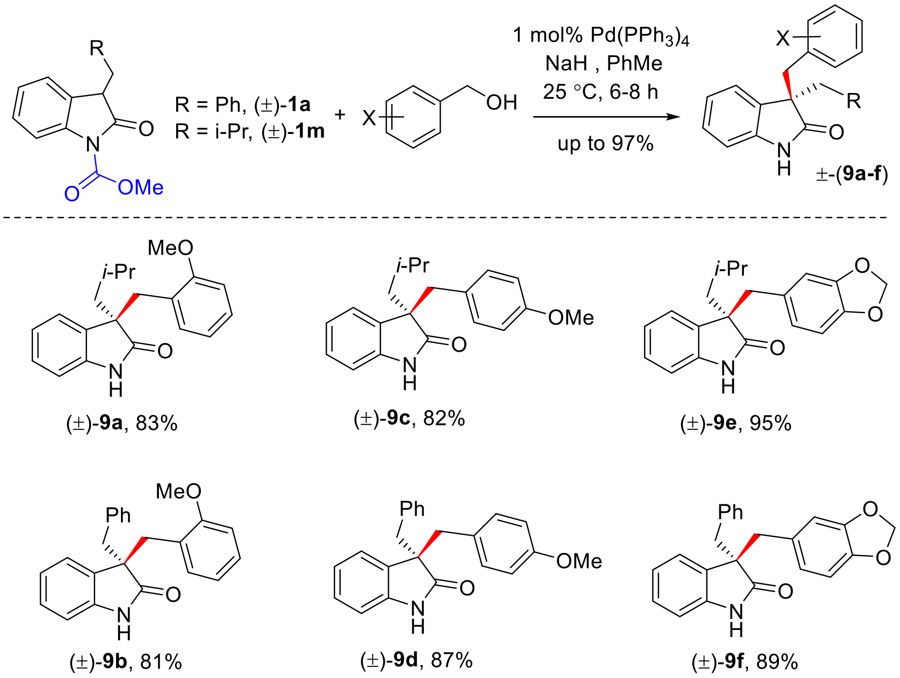


[a]reactions were carried out by using 0.25 mmol of **1m-o** with 0.30 mmol of substituted allyl alcohol in toluene in the presence of 1 mol% Pd(PPh_3)$_4$ under argon atmosphere. [b]isolated yield after silica gel column chromatography.

Scheme 6: Substrates scope of *N*-DaA.[a,b]

Further, recent reports on direct benzylation of nitriles in the presence of benzyl alcohols by Tunge[17] prompted us to explore our deacylative methodology even further.[18] The proposed catalytic cycle for these transformations invoke a cationic η^3-benzyl-palladium intermediate which is less common since aromaticity is disrupted.[19] Therefore, to demonstrate the scope of this deacylative alkylation variant subsequent investigation on direct deacylative benzylation (DaB) of *N*-methoxycarbonyl 2-oxindoles was undertaken. Impressively, a variety of 2-

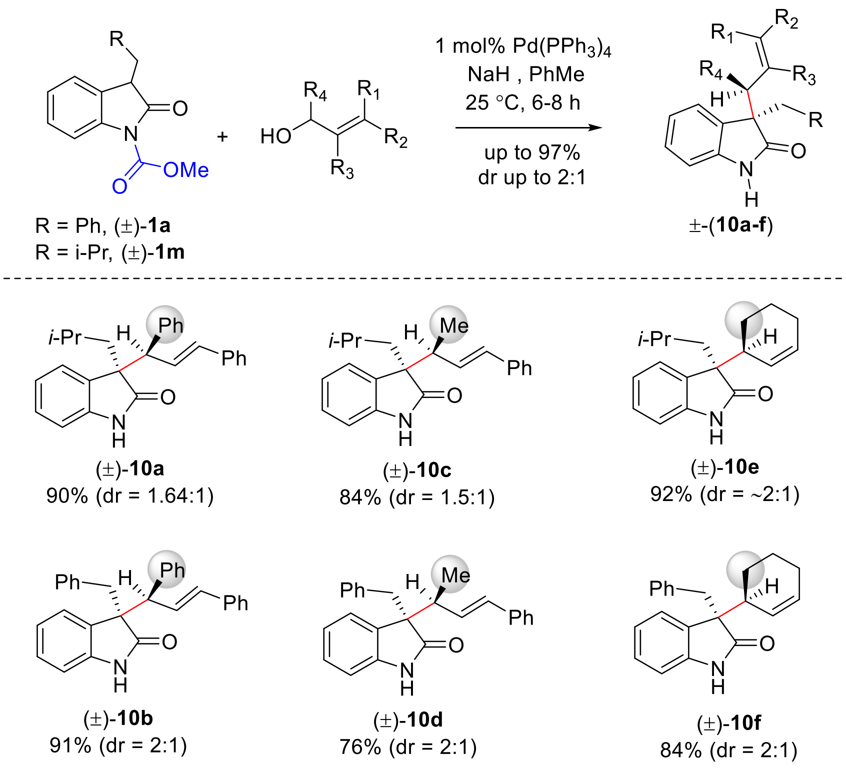
oxindoles with C3-benyl quaternary centers can be synthesized under optimized conditions (Scheme 6).



[a]reactions were carried out by using 0.25 mmol of **1a** and **1m** with 0.30 mmol of substituted benzylalcohol in toluene in the presence of 1 mol% Pd(PPh_3)$_4$ under argon atmosphere. [b]isolated yield after silica gel column chromatography.

Scheme 7: Substrates scope of Pd(0)-catalyzed *N*-DaB.[a,b]

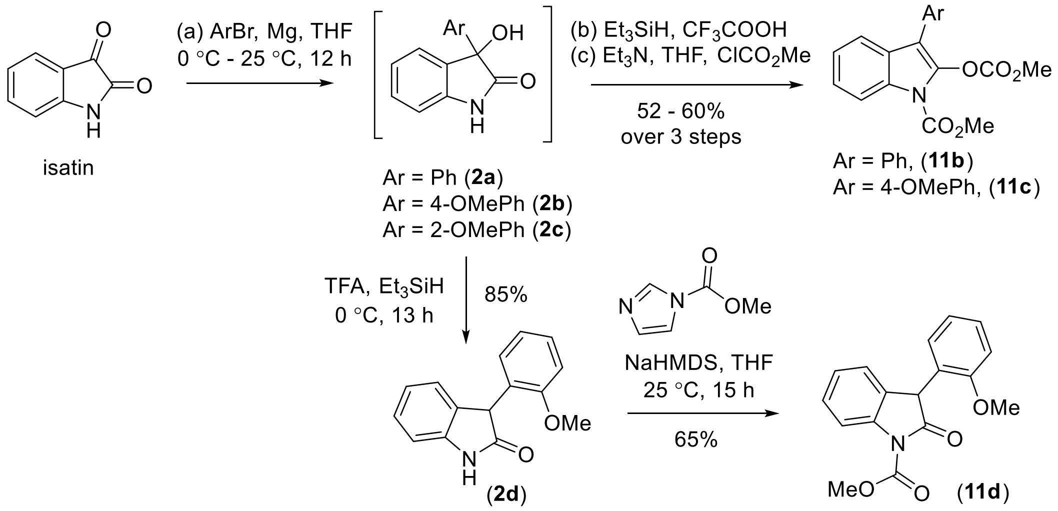
The generation of all-carbon quaternary centers is complicated by the presence of vicinal tertiary stereocenters due to increased steric demands and the introduction of requisite diastereocontrol.[20] Therefore, further utility of our approach was shown to forge vicinal tertiary, quaternary centers in 2-oxindole systems (Scheme 8). Gratifyingly, a number of such structural motifs **10a-f** can be synthesized using secondary allyl alcohols as pro-electrophiles in 76-92% yields with dr up to ~2:1 (Scheme 8).



[a] reactions were carried out by using 0.25 mmol of **1a** and **1m** with 0.30 mmol of substituted allyl alcohol in toluene in the presence of 1 mol% Pd(PPh$_3$)$_4$ under argon atmosphere. [b] isolated yield after silica gel column chromatography.

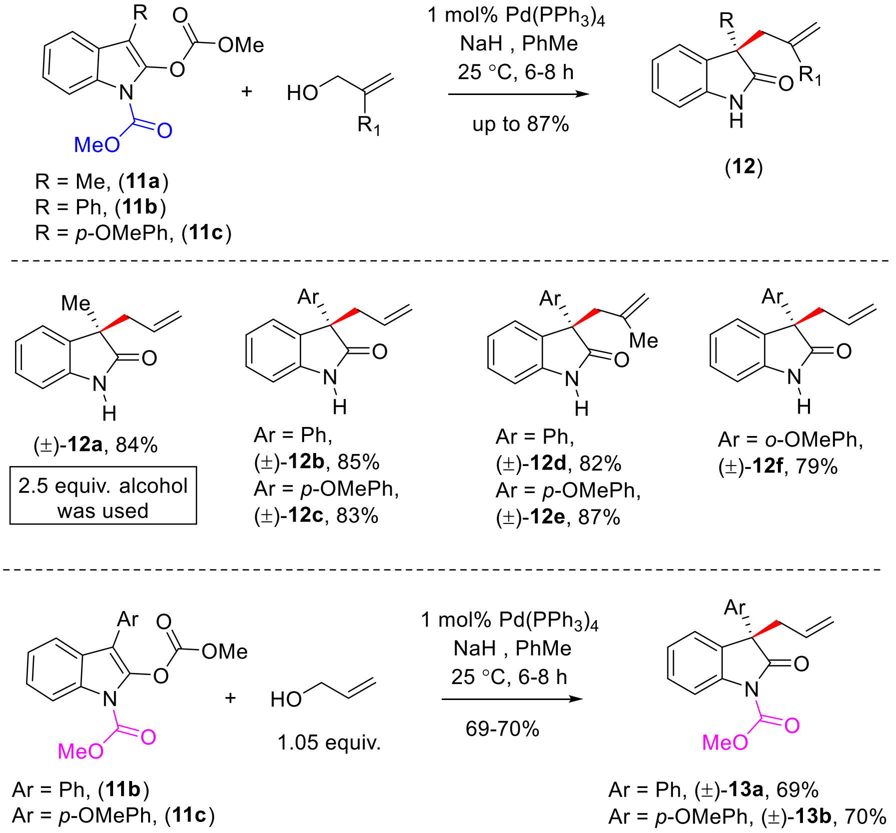
Scheme 8: Syntheses of 2-oxindoles with vicinal quaternary-tertiary centers via *N*-DaA.[a-b]

Later, synthetic versatility of our DaA was shown using *N*-acyl 2-indole methylcarbonates **11a-c**, where allylation was carried out using 2.2 equiv. of allyl alcohol to furnished products **12a-e** in good yields (Scheme 10). A variety of substrates **11b-c** were synthesized following Scheme 9. Isatin was reacted with ArMgBr at 0 ºC in tetrahydrofuran for 12 h to afford 3-aryl 3-hydroxy 2-oxindoles **2a-c**, which were reduced with triethylsilane in the presence of trifluoroacetic acid to afford 3-aryl 2-oxindoles **2d** in 85% yield (Scheme 9). Compound **2d** was reacted with imidazolyl carbonyl reagent to furnish **11d** in 65% yield. In another sequence, **2a-b** were reduced with triethylsilane in the presence of trifluoroacetic acid followed by reaction with 2 equivalent of chloromethyl formate to afford compounds **11b-c** in 52-60% yields over 3 steps (Scheme 9).



Scheme 9: Synthesis of *N*-carboxymethyl 3-substituted 2-indolyl methylcarbonates.

To our delight, a chemoselective allylation can be envisioned using 1.05 equiv. of allyl alcohol as pro-electrophile, to afford 3-aryl-3-allyl 2-oxindoles **13a-b** in synthetically useful yields (Scheme 10).

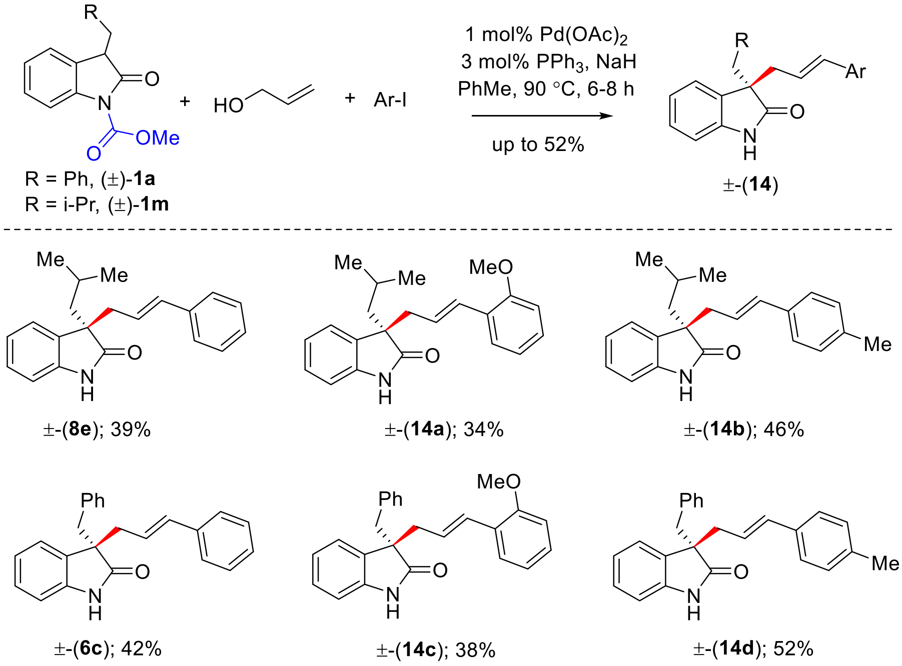


[a]reactions were carried out by using 0.25 mmol of **11a-c** with 0.625 mmol (2.5 equiv.) of allyl alcohol or methallyl alcohol [for products **12a-e**] in toluene in the presence of 1 mol% Pd(PPh_3)$_4$ under argon

atmosphere. [b]isolated yield after column purification. [c]0.263 mmol (~1.05 equiv.) of allyl alcohol was used for chemoselective allylations [for products **13a-b**].

Scheme 10: DaA of *N*-acyl-enolcarbonates **11a-c** and a chemoselective allylation for the synthesis of **13a-b**.[a-c]

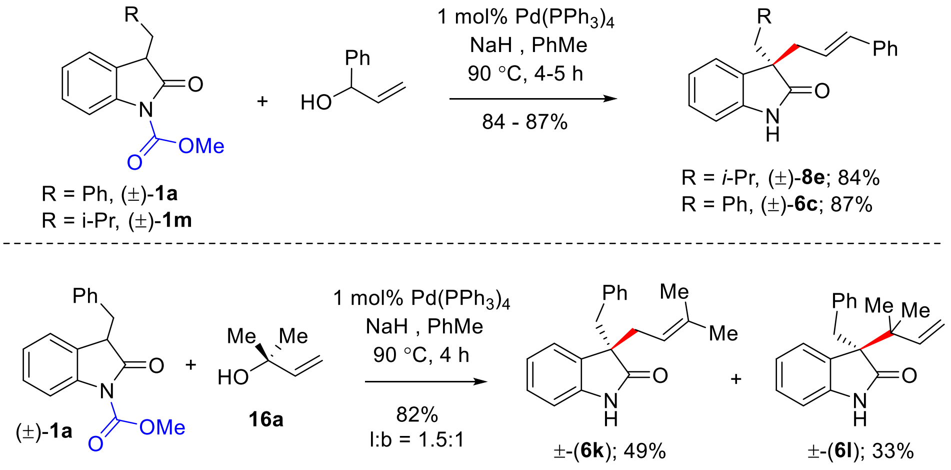
Further effort was put forward for a one-pot domino deacylative allylation-Heck reaction sequence, to afford a number of C3-cinnamylated 2-oxindoles **14a-e** and **6c** in moderate yields (Scheme 11).



[a]reactions were carried out by using 0.25 mmol of **1a** and **1m** with 0.30 mmol of allyl alcohol and 0.30 mmol of haloarenes in toluene in the presence of 1 mol% $Pd(OAc)_2$ and 3 mol% of PPh_3 at 90 ˚C under argon atmosphere. [b]isolated yield after silica gel column chromatography.

Scheme 11: Domino *N*-DaA-arylation sequence.[a,b]

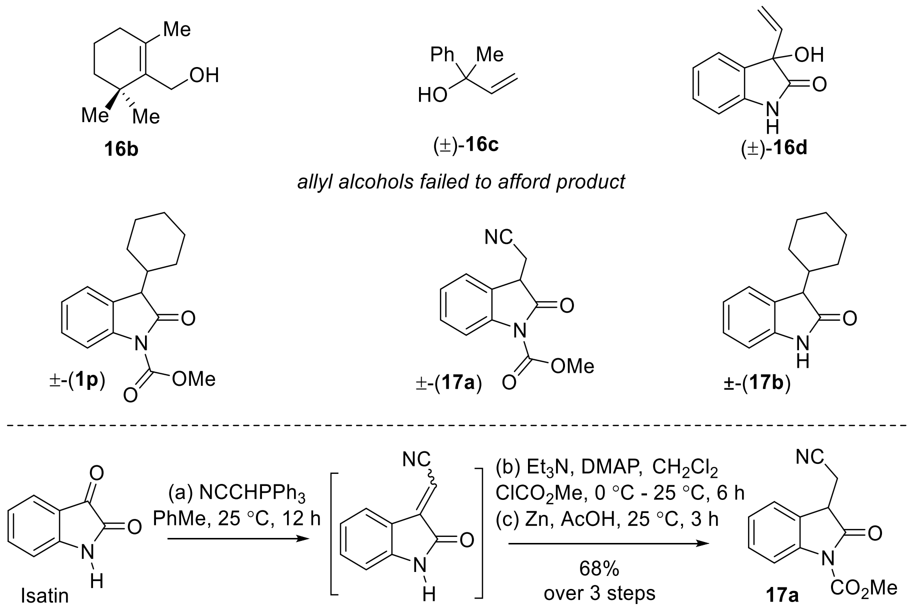
Further, it has been shown that secondary alcohol such as phenylvinylcarbinol is a good *pro*-electrophile, which afforded products **8e** and **6c** through highly regioselective DaA in 84-87% yields with linear products (Scheme 12). Interestingly, alcohol **16a** afforded products **6k** and **6l** in 82% yields with 1.5:1 (l:b) regioisomeric ratio in favor of linear product (Scheme 12).



[a]reactions were carried out by using 0.25 mmol of **1a** and **1m** with 0.30 mmol of allyl alcohols in toluene at 90 ˚C in the presence of 1 mol% $Pd(PPh_3)_4$ under argon atmosphere. [b]isolated yield after silica gel column chromatography.

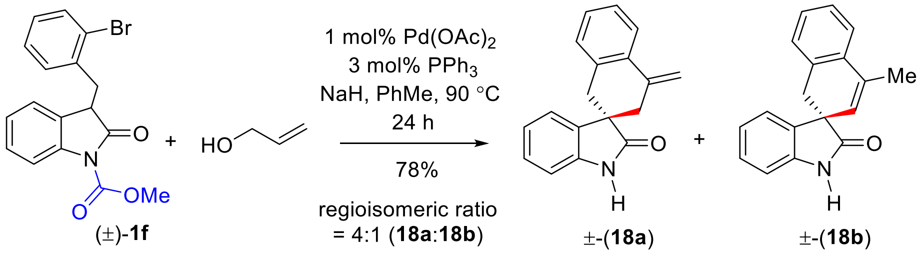
Scheme 12: Further substrate scope of *N*-DaA.[a,b]

However, to our disappointment, alcohols **16b-d** are not good substrates for the DaA reactions. We have found that *N*-methoxycarbonyl 2-oxindoles **17a** and **1p**, with different electronic and steric properties, are not suitable for DaA reaction. *N*-Methoxycarbonyl 2-oxindoles **17a** was synthesized from isatin as per reactions sequence shown in Scheme 13. In case of substrate **1p**, we encountered with deacylative protonation product (**17b** was isolated in 85% yields) as shown in Scheme 13.



Scheme 13: Substrates failed under *N*-DaA.

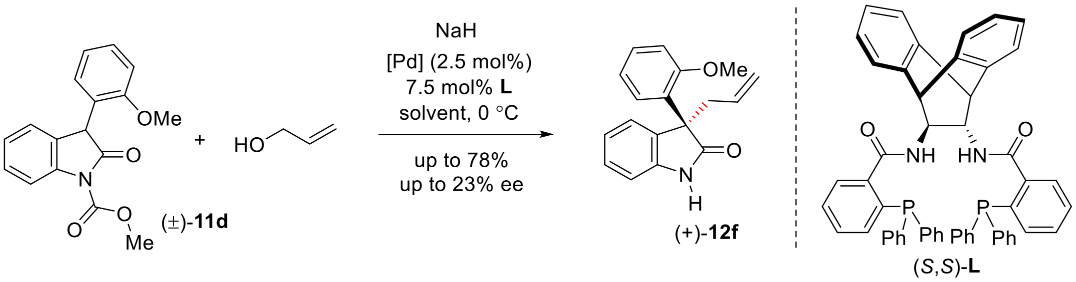
We further tested our methodology for an efficient one-pot domino Pd(0)-catalyzed DaA followed by an intramolecular Heck cyclization (Scheme 14). It was noteworthy to observe that N-H free spiro-fused 2-oxindole **18** was obtained in 75% yield under reflux.[16]



[a]reaction was carried out by using 0.25 mmol of **1f** with 0.30 mmol of allyl alcohol at 90 ˚C.

Scheme 14: An efficient one-pot *N*-deacylative allylation-Heck sequenece of **1f**.

Having successful execution of catalytic deacylative alkylations (DcA), we then procedded for the development of enantioselective version of our methodology (Scheme 15). Towards this, we have utilized *N*-acyl 2-oxindole **11d** for deacylative alkylation with allyl alcohol in the presence of 2.5 mol% $Pd_2(dba)_3$ and 7.5 mol% (*S*,*S*)-**L** under argon atmosphere. After exhaustive optimization, it was found that a maximum of 23% ee was observed when methyl *tert*-butylether was used as solvent at 0 C (entry 6).

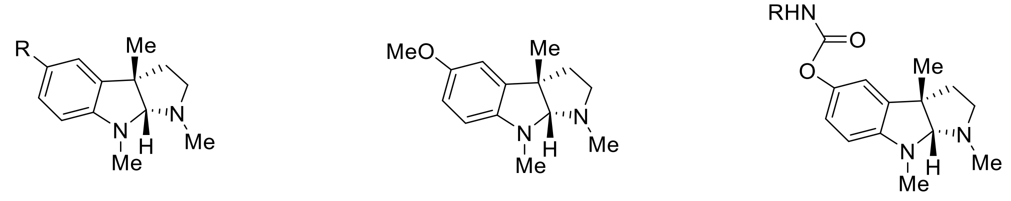


entry[a]	**catalyst**	**solvent**	**temp**	**ligand**	**time**	**%**[b] **(12f)**	**% of ee**[c] **(12f)**
1.	2.5 mol% $Pd_2(dba)_3$	THF	25 °C	7.5 mol% (*S*,*S*)-L	12 h	65%	05%
2.	2.5 mol% $Pd_2(dba)_3$	PhMe	25 °C	7.5 mol% (*S*,*S*)-L	9 h	69%	12%
3.	2.5 mol% $Pd_2(dba)_3$	Et_2O	25 °C	7.5 mol% (*S*,*S*)-L	6 h	72%	08%
4.	2.5 mol% $Pd_2(dba)_3$	MTBE	25 °C	7.5 mol% (*S*,*S*)-L	10 h	78%	20%
5.	2.5 mol% $Pd_2(dba)_3$	CH_2Cl_2	25 °C	7.5 mol% (*S*,*S*)-L	10 h	76%	10%
6.	2.5 mol% $Pd_2(dba)_3$	MTBE	0 °C	7.5 mol% (*S*,*S*)-L	12 h	72%	23%
7.	2.5 mol% $Pd_2(dba)_3$	MTBE	-10 °C	7.5 mol% (*S*,*S*)-L	24 h	52%	20%

[a] reactions were carried out by using 0.20 mmol of **11d** with 0.30 mmol of allyl alcohol in the presence of 2.5 mol% $Pd_2(dba)_3$ and 7.5 mol% (*S*,*S*)-**L** under argon atmosphere. [b] isolated yield after silica gel column chromatography. [c] ee's were determined using chiral HPLC column (OD-3).

Scheme 15: Catalytic enantioselective deacylative alkylations (DcA).

Later, the application of *N*-deacylative alkylations strategy for the synthesis of pyrrolidino[2,3-*b*]indoline was undertaken. The cyclic pyrrolidino[2,3-*b*]indoline [see; **19a-e** (Figure 1)] is the fundamental building block of cyclotryptamine alkaloids. This ring system is found exclusively in the *cis*-configuration with an all-carbon quaternary stereocenter in almost all alkaloids, presumably because of the higher level of ring strain in the *trans*-stereoisomer. They are reported to prevent the hydrolysis of acetylcholine by acetylcholinesterase at the transmitted sites of acetylcholine so as to effect the enhancement of acetylcholine, and therefore, act as an acetylcholinesterase inhibitor.[21] We envisioned that the pyrroloindoline alkaloids can be accessed from 3-allyl 3-methyl 2-oxindole **12a** (Scheme 9).



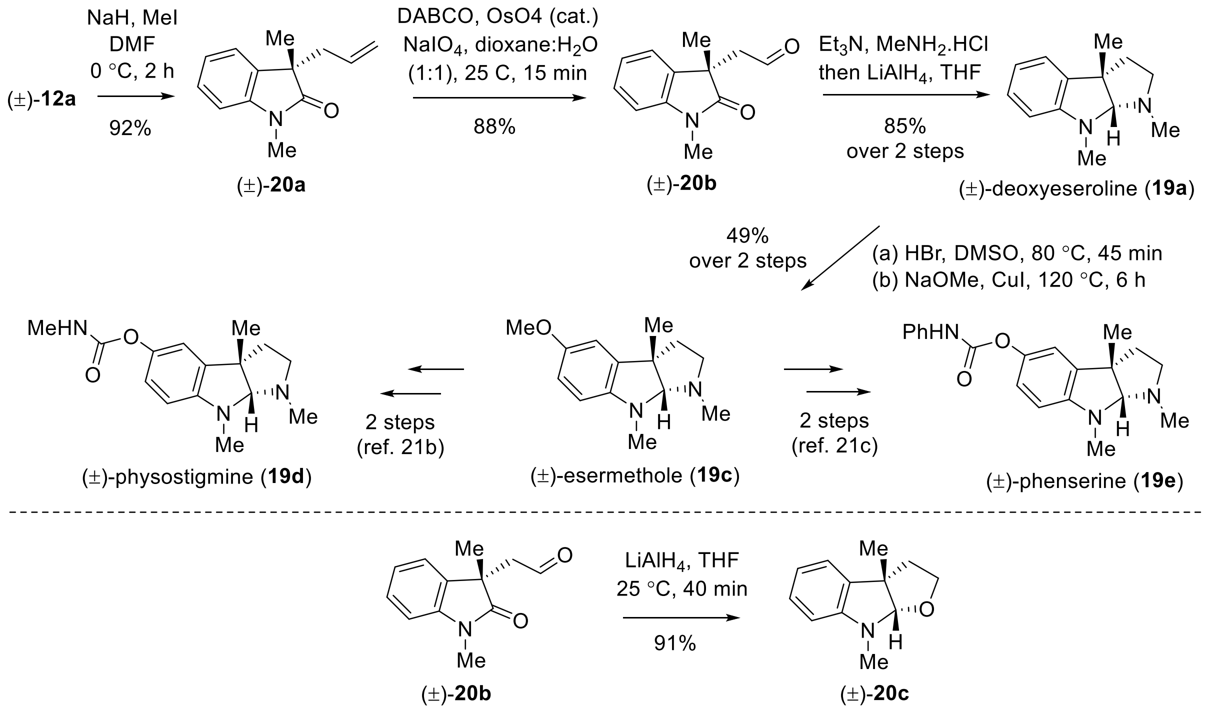
R = H, (–)-deoxyeseroline (**19a**)
R = OH, (–)-eseroline (**19b**)

(–)-esermethole (**19c**)

R = Me, (–)-physostigmine (**19d**)
R = Ph, (–)-phenserine (**19e**)

Figure 1: Representative pyrrolidino[2,3-*b*]indoline alklaoids.

Towards this end, we have elaborated (±)-**12a** for the synthesis of a variety of advanced intermediates required for formal total synthesis of cyclotryptamine alkaloids. Towards this direction, 2-oxindole (±)-**12a** was *N*-methylated using MeI in the presence of NaH to afford compound (±)-**20a** in 92% yield (Scheme 16). The olefin functionality of 2-oxindole (±)-**20a** was oxidized to afford aldehyde (±)-**20b** in 90% yield over 2 steps. Later, aldehyde (±)-**20b** was reacted with methylamine hydrochloride followed by reduction using $LiAlH_4$ to complete total synthesis of naturally occurring pyrrolidino[2,3-*b*]indoline, (±)-deoxyeseroline [(±)-**19a**] in 85% yields over 2 steps (Scheme 16).[22a] Later, total synthesis of (±)-esermethole (**19c**) was achieved from (±)-deoxyeseroline [(±)-**19a**] in two steps. Towards this, (±)-**19a** was reacted with HBr in DMSO at 80 ºC for 45 min to afford bromocompound, which was then reacted with NaOMe in the presence of Cu(I)I to complete total synthesis of (±)-esermethole (**19c**) in 49% over 2 steps.[21a]



Scheme 16: Total synthesis of (±)-deoxyeseroline (**19a**) and (±)-esermethole (**19c**).

In another sequence, aldehyde (±)-**20b** was directly transformed to furoindoline intermediate (±)-**20d** in 91% yield (Scheme 16). Since total syntheses of (±)-physostigmine [(±)-**19d**]^{22b} and (±)-phenserine [(±)-**19e**]^{22c} are known from (±)-esermethole [(±)-**19c**], our efforts culminated in total syntheses of these pyrrolidino[2,3-*b*]indoline alkaloids.

CONCLUSIONS

In summary, we have developed an efficient Pd(0)-catalyzed chemoselective *N*-deacylative alkylations (DaA) of *N*-acyl-2-oxindoles with a variety of allyl alcohols. This methodology was further extended with few benzyl alcohols to affect deacylative benzylation (DaB). A number of N-H free 2-oxindoles with C3-quaternary centers can be synthesized in synthetically useful yields under mild condition. Utilizing this strategy, total synthesis of naturally occurring pyrrolidino[2,3-*b*]indoline, (±)-deoxyeseroline [(±)-**19a**] and (±)-esermethole [(±)-**19c**] have been achieved in few steps. Further development towards the enantioselective variant of this process as well as its application in total synthesis of hexahydropyrrolo[2,3-b]indole alkaloids are under active investigation in our laboratory.

EXPERIMENTAL SECTION

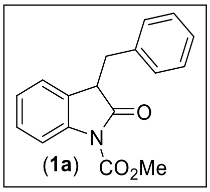
Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under an inert 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 and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperature. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silica gel of particle size 100-200 mesh was used for flash chromatography. Melting points were recorded on a digital melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded 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 ($CDCl_3$) signal ($\delta = 7.26$ for ^1H NMR and $\delta = 77.0$ for ^{13}C NMR). Data for ^1H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). 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 and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-Resolution Mass Spectrometry (HRMS) and Low-Resolution Mass Spectrometry (LRMS) data were recorded using methanol as solvent.

Synthesis of *N*-Acyl 2-Oxindoles (**1a-o**): To a stirred solution of 2-oxindole (1.50 mmol; 1.0 equiv) in EtOH (5 mL) at 25 ºC were added piperidine (30 µL, 0.30mmol, 0.20 equiv) and corresponding aldehyde (1.50 mmol; 1.0 equiv). Then the reaction mixture was stirred for 8 - 12 h on refluxing. Upon consumption of starting material (monitored by TLC) the reaction mixture was concentrated under reduced pressure.

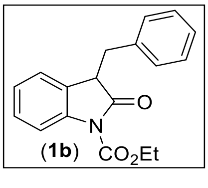
The crude material was directly dissolved in 10 mL of CH_2Cl_2. To that solution, Et_3N (0.27 mL, 2.10 mmol, 2.1 equiv) followed by DMAP (0.224 g, 2.10 mmol, 2.0 equiv) and corresponding chloroformate (0.14 mL, 2.10 mmol, 2.0 equiv) was added at 0 ºC, reaction mixture was stirred on 25 ºC. TLC analysis showed the complete consumption starting material. Then the organic layer was diluted by CH_2Cl_2 and washed with water (10 mL). The collected organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and dried by using high vacuum pump.

The crude material was dissolved in CH_3COOH (5 mL) open flask. To that Zn (1.37 g, 21.0 mmol, 20.0 equiv) and stirred over 25 °C for 4 h. Upon completation of the reaction (judged by TLC analysis), filtered through celite, and concentrated under reduced pressure. The crude reaction mixture diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ solution (10 mL), and brine. The extracted organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and dried by using high vacuum pump. The crude product was purified by flash chromatography using (20%-40% EtOAc in hexanes) mixture as eluents to afford the desired product **1a-o**.



(**1a**)

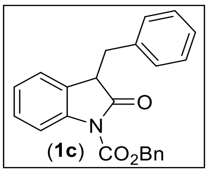
Methyl 3-benzyl-2-oxoindoline-1-carboxylate (**1a**): 82% yield over 3 steps (1.06 mmol scale) of (**1a**) as colorless solid. R_f = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.26-7.17 (m, 4H), 7.12-7.10 (m, 2H), 7.03 (td, *J* = 1.0, 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 3.96 (s, 3H), 3.83 (q, *J* = 4.5 Hz, 1H), 3.46 (dd, *J* = 4.9, 13.7 Hz, 1H), 2.99 (q, *J* = 8.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 151.4, 139.7, 137.0, 129.4, 128.4, 128.3, 127.2, 126.9, 124.4, 124.3, 115.0, 53.8, 47.5, 37.5; **IR** (film) υ_{max} 2987, 1738, 1613, 1598, 1405, 1318, 1301, 1200, 1107, 971, 775, 702cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}NO_3 + Na$ 304.0944; Found 304.0952. MP = 106-110 ºC.



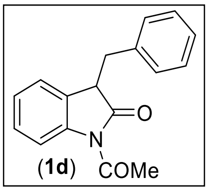
(**1b**)

Ethyl 3-benzyl-2-oxoindoline-1-carboxylate (**1b**): 60% yield over 3 steps (1.06 mmol scale) of (**1b**) as yellow gel. R_f = 0.25 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83

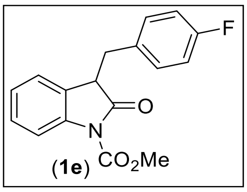
(d, *J* = 8.2 Hz, 1H), 7.30-7.22 (m, 4H), 7.18-7.15 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 4.50-4.45 (m, 2H), 3.88 (dd, *J* = 8.9, 4.6 Hz, 1H), 3.51 (dd, *J* = 13.8, 4.7 Hz, 1H), 3.02 (dd, *J* = 13.7, 8.8 Hz, 1H), 1.46 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 150.8, 139.8, 137.1, 129.4, 128.4, 128.3, 127.2, 126.9, 124.4, 124.2, 114.9, 63.3, 47.5, 37.6, 14.3; **IR** (film) υ_{max} 3015, 1842, 1798, 1641, 1495, 1381, 1332, 1201, 1105, 978, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}NO_3$ + Na 318.1101; Found 318.1100.



Benzyl 3-benzyl-2-oxoindoline-1-carboxylate (**1c**): 79% yield over 3 steps (1.06 mmol scale) of (**1c**) as light yellow gel. R_f = 0.29 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.45-7.38 (m, 4H), 7.29-7.25 (m, 3H), 7.17-7.15 (m, 2H), 7.07 (s, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.46 (s, 2H), 3.90 (dd, *J* = 8.8, 4.6 Hz, 1H), 3.55-3.47 (m, 1H), 3.04 (dd, *J* = 13.7, 8.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 150.7, 139.6, 137.1, 135.1, 129.4, 128.7, 128.5, 128.3, 128.1, 127.8, 127.2, 126.9, 124.4, 124.3, 115.0, 68.5, 47.5, 37.6; **IR** (film) υ_{max} 1938, 1716, 1695, 1608, 1498, 1431, 1350, 1209, 1001, 962, 780, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{19}NO_3$ + Na 380.1257; Found 380.1268.

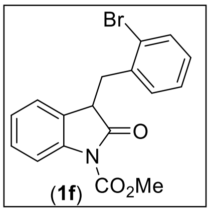


1-Acetyl-3-benzylindolin-2-one (**1d**): 73% yield over 3 steps (1.06 mmol scale) of (**1d**) as light colorless gel. R_f = 0.24 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 7.31-7.22 (m, 4H), 7.14-7.10 (m, 3H), 6.91 (d, *J* = 7.5 Hz, 1H), 3.92 (dd, *J* = 8.5, 4.7 Hz, 1H), 3.48 (dd, *J* = 13.7, 4.7 Hz, 1H), 3.09 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.65 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 170.8, 140.5, 136.8, 129.4, 128.4, 128.3, 127.4, 127.0, 124.7, 124.1, 116.4, 47.6, 37.6, 26.7.; **IR** (film) υ_{max} 3332, 2981, 1742, 1688, 1562, 1550, 1371, 908, 879, 850, 735 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}NO_2$ + Na 288.0995; Found 288.1009.



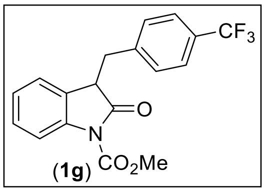
(**1e**)

Methyl 3-(4-fluorobenzyl)-2-oxoindoline-1-carboxylate (**1e**): 62% yield over 3 steps (0.15 mmol scale) of (**1e**) as yellow gel. R_f = 0.27 (30% EtOAc in hexane); ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.30 – 7.26 (m, 1H), 7.11 – 7.03 (m, 3H), 6.93 – 6.87 (m, 3H), 3.99 (s, 3H), 3.85 (dd, *J* = 8.1, 4.7 Hz, 1H), 3.41 (dd, *J* = 13.9, 4.8 Hz, 1H), 3.07 (dd, *J* = 13.9, 8.1 Hz, 1H); ^{13}**C NMR** (125 MHz $CDCl_3$) δ 175.13, 161.99 (d, *J* = 245.2 Hz), 151.46, 139.85, 132.58, 132.55, 131.07 (d, *J* = 7.9 Hz), 128.62, 126.99, 124.45 (d, *J* = 23.7 Hz), 115.48, 115.31, 115.26, 54.04, 47.71, 36.68. **IR** (film) υ_{max} 2987, 1741, 1600, 1572, 1531, 1441, 1291, 1260, 1059, 955, 907, 855, 752 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{14}NFO_3$ + H 300.1030; Found 300.1041.



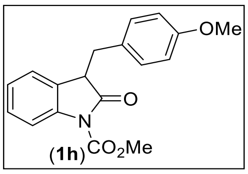
(**1f**)

Methyl 3-(2-bromobenzyl)-2-oxoindoline-1-carboxylate (**1f**): 89% yield over 3 steps (1.06 mmol scale) of (**1f**) as yellow gel. R_f = 0.27 (30% EtOAc in hexane); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.70 (brs, s, 1H), 7.29 – 7.23 (m, 2H), 7.12-7.01 (m, 3H), 6.93 – 6.84 (m, 2H), 3.96 (m, 1H), 3.62 (s, 3H), 3.47 (dd, *J* = 13.8, 9.0 Hz, 1H), 3.01 (dd, *J* = 13.7, 6.4 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 173.9, 167.8, 160.7 (d, *J* = 247.7 Hz), 154.8, 136.0, 134.4, 134.3, 132.5, 130.4 (d, *J* = 8.3 Hz), 129.5, 128.5 (d, *J* = 14.5 Hz), 115.3 (d, *J* = 21.4 Hz), 52.51, 52.5, 36.5; **IR** (film) υ_{max} 3069, 1749, 1639, 1590, 1372, 1306, 1109, 1100, 1069, 1033, 901, 889, 835, 790 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}NBrO_3$ + Na 382.0049; Found 382.0046.



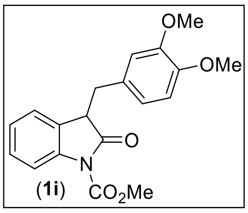
(**1g**)

Methyl 2-oxo-3-(4-(trifluoromethyl)benzyl)indoline-1-carboxylate (**1g**): 78% yield over 3 steps (1.06 mmol scale) of (**1g**) as yellow solid. R_f = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.21 (m, 3H), 7.09 (td, *J* = 7.6, 1.1 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 3.98 (s, 3H), 3.90 (dd, *J* = 8.0, 4.9 Hz, 1H), 3.47 (dd, *J* = 13.8, 4.8 Hz, 1H), 3.15 (dd, *J* = 13.8, 8.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 151.3, 141.01, 141.0, 140.9, 139.7, 129.8, 129.7, 129.2 (q, *J* = 3.8 Hz), 128.7, 126.6, 125.4 (q, *J* = 3.8 Hz), 124.5, 115.2, 53.9, 47.2, 36.9. ; **IR** (film) υ_{max} 1851, 1709, 1631, 1581, 1543, 1440, 1375, 1308, 1121, 1043, 951, 906, 751, 790 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}NF_3O_3$ + H 350.0999; Found 350.1019. MP = 87-92 ºC.



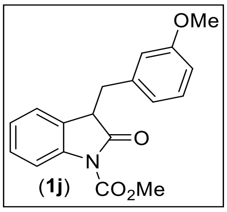
(**1h**)

Methyl 2-oxo-3-(4-(trifluoromethyl)benzyl)indoline-1-carboxylate (**1h**): 70% yield over 3 steps (1.06 mmol scale) of (**1h**) as colorless solid. R_f = 0.26 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 1.4, 7.1 Hz, 1H), 7.06 – 6.99 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 3.97 (s, 3H), 3.80 (dd, *J* = 8.5, 4.7 Hz, 1H), 3.74 (s, 3H), 3.39 (dd, *J* = 13.9, 4.6 Hz, 1H), 2.97 (dd, *J* = 13.8, 8.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 158.5, 151.4, 139.7, 130.4, 128.9, 128.3, 127.3, 124.4, 124.3, 115.0, 113.8, 55.2, 53.9, 47.8, 36.6; **IR** (film) υ_{max} 1880, 1706, 1658, 1601, 1573, 1509, 1441, 1430, 1398, 1073, 901, 855, 852, 730 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}NO_4$ + Na 236.1281; Found 334.1048. MP = 90-93 ºC.

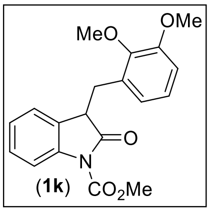


(**1i**)

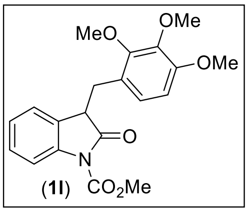
Methyl 3-(3,4-dimethoxybenzyl)-2-oxoindoline-1-carboxylate (**1i**): 88% yield over 3 steps (1.06 mmol scale) of (**1i**) as yellow gel. R_f = 0.26 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.25 (td, *J* = 1.8, 8.5 Hz 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.62 (dd, *J* = 1.8, 10.2 Hz, 1H), 6.54 (d, *J* = 13.8, 8.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 151.3, 148.6, 147.9, 139.8, 129.1, 128.3, 127.3, 124.4, 124.3, 121.7, 115.1, 112.3, 110.9, 55.8, 55.7, 53.8, 47.7, 37.1.; **IR** (film) υ_{max} 3041, 1801, 1716, 1616, 1598, 1357, 1200, 1098, 1036, 911, 901, 855, 800, 735 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{19}NO_5$ + Na 364.1155; Found 364.1145.



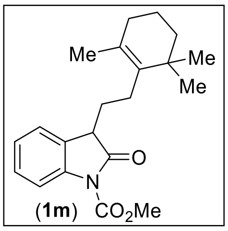
Methyl methyl 3-(3-methoxybenzyl)-2-oxoindoline-1-carboxylate (**1j**): **7**2% yield over 3 steps (1.06 mmol scale) of (**1j**) as colorless gel. R$_f$ = 0.23 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) 7.69 (brs, s, 1H), 7.28-7.25 (m, 2H), 7.17 – 7.08 (m, 2H), 6.74 – 6.70 (m, 2H), 6.62 (m, 1H), 3.99 (m, 1H),, 3.71 (s, 3H), 3.64 (s, 3H), 3.49 (dd, *J* = 13.6, 8.7 Hz, 1H), 3.01 (dd, *J* = 13.6, 6.5 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 174.1, 159.6, 154.6, 140.2, 136.1, 129.5, 128.5, 128.3, 125.1, 125.0, 121.2, 114.4, 112.3, 77.2, 55.1, 52.5, 52.4, 37.5; **IR** (film) υ_{max} 2981, 1885, 1715, 1632, 1592, 1507, 1352, 1009, 1001, 982, 903, 851, 800, 771 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{17}NO_4$ + H 312.1230; Found 312.1218.



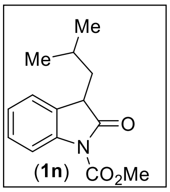
Methyl 3-(2,3-dimethoxybenzyl)-2-oxoindoline-1-carboxylate (**1k**): 53% yield over 3 steps (1.06 mmol scale) of (**1k**) as colorless solid. R$_f$ = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) 7.86 (d, *J* = 8.2 Hz, 1H), 7.23 (td, *J* = 1.4, 8.1 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.85 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.72 (dd, *J* = 1.4, 6.9 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 4.01-3.97 (m, 4H), 3.79 (s, 3H), 3.49 (dd, *J* = 13.6, 5.3 Hz, 1H), 2.87 (dd, *J* = 13.6, 9.7 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 175.5, 152.8, 151.6, 147.7, 139.5, 131.5, 128.1, 127.7, 124.6, 124.2, 123.8, 122.9, 114.8, 111.4, 60.5, 55.7, 53.8, 45.9, 32.5; **IR** (film) υ_{max} 1831, 1659, 1539, 1503, 1404, 1189, 1103, 1100, 959, 938, 889, 851, 735, 701 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{19}NO_5$ + Na 364.1155; Found 364.1178. MP = 95-100 ^{o}C.


(**1l**)

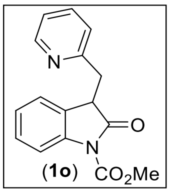
Methyl 2-oxo-3-(2,3,4-trimethoxybenzyl)indoline-1-carboxylate (**1l**): 69% yield over 3 steps (1.06 mmol scale) of (**1l**) as colorless solid. R$_f$ = 0.42 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) 7.84 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.21 (ddt, *J* = 8.9, 8.3, 1.2 Hz, 1H), 6.97 (td, *J* = 7.6, 1.1 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.65 (td, *J* = 1.3, 2.5, 7.6 Hz, 1H), 3.90 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.83 (s, 6H), 3.81 (s, 3H), 3.39 (dd, *J* = 13.7, 5.6 Hz, 1H), 2.84 (dd, *J* = 13.7, 9.2 Hz, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 175.4, 152.9, 152.2, 151.5, 142.2, 139.5, 128.0, 127.7, 125.0, 124.5, 124.1, 123.3, 114.8, 106.9, 60.7, 55.9, 53.7, 46.1, 32.3; **IR** (film) υ_{max} 3059, 1755, 1690, 1599, 1401, 1365, 1340, 1109, 1081, 991, 935, 782, 735, 701 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{21}NO_6$ + Na 394.1261; Found 394.1263. MP = 118-124 ºC.


(**1m**)

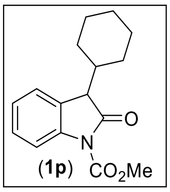
Methyl 2-oxo-3-(2,3,4-trimethoxybenzyl)indoline-1-carboxylate (**1m**): 69% yield over 3 steps (1.06 mmol scale) of (**1m**) as colorless gel. R$_f$ = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) 8.00 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.45-7.37 (m, 1H), 7.32 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.23 (td, *J* = 7.6, 2.4 Hz, 1H), 6.00-5.85 (m, 2H), 4.02 (brs, s, 3H), 3.71 (s, 3H), 1.96-1.92 (m, 2H), 1.63 (s, 3H), 1.60-1.51 (m, 2H), 1.40 (m, 2H), 0.91 (s, 3H), 0.89 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 170.6, 168.7, 151.4, 139.6, 136.0, 132.6, 129.5, 127.5, 125.0, 124.6, 115.6, 62.1, 54.1, 53.3, 39.2, 33.9, 32.6, 28.6, 28.5, 21.3, 19.1; **IR** (film) υ_{max} 2905, 1715, 1621, 1452, 1406, 1392, 1355, 1209, 1155, 1109, 1088, 980, 901, 845, 701 cm^{-1}. HRMS (ESI-TOF) m/z: [M – H]$^-$ Calcd for $C_{21}H_{27}NO_3$ - H 340.1907; Found 340.1900.


(**1n**)

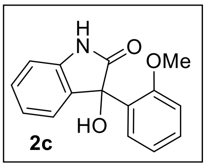
Methyl 3-isobutyl-2-oxoindoline-1-carboxylate (**1n**): 70% yield over 3 steps (1.06 mmol scale) of (**1n**) as green gel. R_f = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.34-7.24 (m, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.14 (td, *J* = 7.5, 1.1 Hz, 1H), 3.99 (s, 3H), 3.57 (t, *J* = 7.0 Hz, 1H), 2.05-1.95 (m, 1H), 1.89-1.82 (m, 1H), 1.74-1.67 (m, 1H), 0.94 (dd, *J* = 9.1, 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 151.6, 139.5, 128.5, 128.1, 124.5, 123.9, 115.1, 53.8, 44.2, 40.8, 25.1, 22.6, 22.3; **IR** (film) υ_{max} 2068, 1685, 1613, 1414, 1272, 1200, 906, 903, 853, 817, 710, 702 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_3$ + Na 270.1101; Found 270.1098.



Methyl 2-oxo-3-(pyridin-2-ylmethyl)indoline-1-carboxylate (**1o**): 57% yield over 3 steps (1.06 mmol scale) of (**10**) as durty color solid. R_f = 0.30 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) 8.50 (dt, *J* = 4.9, 1.5 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.1 (dd, *J* = 7.7, 5.0 Hz, 2H), 7.00 (td, *J* = 7.6, 1.1 Hz, 1H), 6.80 (d, *J* = 7.4 Hz, 1H), 4.26 (dd, *J* = 7.9, 5.4 Hz, 1H), 4.01 (s, 3H), 3.56 (dd, *J* = 14.7, 5.4 Hz, 1H), 3.27 (dd, *J* = 14.7, 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.7, 157.2, 151.7, 149.3, 139.7, 136.4, 128.2, 127.7, 124.4, 123.9, 121.9, 114.9, 99.9, 53.9, 45.3, 39.1; **IR** (film) υ_{max} 2939, 1652, 1518, 1503, 1489, 1436, 1415, 1238, 1216, 1209, 1151, 1109, 982, 933, 735 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{14}N_2O_3$ + H 283.1077; Found 283.1054. MP = 84-89 °C.



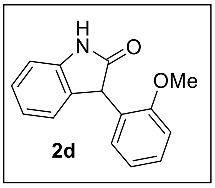
Methyl 2-oxo-3-(pyridin-2-ylmethyl)indoline-1-carboxylate (**1p**): 67% yield over 3 steps (1.06 mmol scale) of (**1p**) as pale yellow gel (dr = 1.9:1). R_f = 0.29 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.99 (dd, *J* = 8.0, 6.6 Hz, 1H for minor isomer), 7.92 (d, *J* = 8.1 Hz, 1H for major isomer), 7.69 (d, *J* = 7.8 Hz, 1H for minor isomer), 7.33-7.28 (m, 2H for major isomer & 2H for minor isomer), 7.19 (dd, *J* = 8.8, 6.3 Hz, 1H for major isomer), 4.04-4.03 (m, 3H for major isomer & 4H for minor isomer), 3.49 (d, *J* = 3.4 Hz, 1H for major isomer), 2.20-2.10 (m, 1H for major isomer & 1H for minor isomer), 1.90-1.83 (m, 1H for major isomer), 1.80-1.77 (m, 1H for major isomer & 1H for minor isomer), 1.75-1.70 (m, 2H for major isomer & 2H for minor isomer), 1.68-1.63 (m, 2H for major isomer & 3H for minor isomer), 1.60-1.57 (m, 1H for major isomer & 2H for minor isomer), 1.41-1.31 (m, 1H for major isomer), 1.29-1.21 (m, 2H for major isomer & 2H for minor isomer); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6 (2C), 151.5 (2C), 140.1 (2C), 128.1 (2C), 127.1 (2C), 124.4 (2C), 124.2 (2C), 114.9 (2C), 53.8 (2C), 51.9 (2C), 42.3 (2C), 29.7 (2C), 28.7 (2C), 26.6 (2C), 26.3 (2C), 25.9 (2C); **IR** (film) υ_{max} 2872, 1619, 1495, 1482, 1376, 1313, 1260, 1173, 905, 896, 731, 702 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{19}NO_3$ + Na 296.1257; Found 296.1236.



2c

3-Hydroxy-3-(2-methoxyphenyl)indolin-2-one: The compound (**2c**) was obtained as yellow solid (6.8 mmol scale; 1.5 g of product; 87% yield). R_f = 0.38 (50% EtOAc in hexane); **^{1}H NMR** (500 MHz, DMSO-d_6) δ = 10.28 (s, 1H), 7.87 (dd, *J*=7.7, 1.8, 1H), 7.28 (td, *J*=7.7, 1.8, 1H), 7.17 (td, *J*=7.5, 1.8, 1H), 7.06 (td, *J*=7.6, 1.1, 1H), 6.88 – 6.87 (m, 1H), 6.87 – 6.78 (m, 3H), 6.44 (s, 1H), 3.40 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ = 178.9, 156.0, 143.4, 133.5, 130.9, 129.2, 129.1, 127.3, 124.0, 121.6, 120.7, 112.2, 109.5, 75.4, 56.0; **IR** (film) 3656, 3458, 2326, 2250, 1715, 1580, 1421, 1380, 1214, 1104, 981, 890, 700 cm-1; **HRMS** (ESI) m/z $[M + Na]^+$ Calcd for $[C_{15}H_{13}NO_3 + Na]^+$ 278.0788; Found 278.0761.

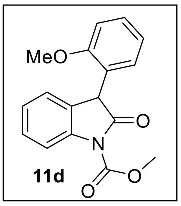
P**rocedure for the synthesis of 2-oxindole** (**2d**): In an oven-dried round-bottom flask was charged with compound 3-hydroxy 2-oxindole (±)-**2c** (1.0 equiv) in dichloromethane (15 ml) under argon atmosphere at RT. To this solution triethyl silane (5.0 equiv.) and TFA (6.0 equiv) was added at 0 ºC and stirring was continued for 13 h. After completion of the reaction (judged by TLC analysis under UV and I_2 stain) 5% (w/v) aqueous solution of sodium citrate was added drop wise to neutralize the mixture. The organic layer was separated and aqueous layer was washed with CH_2Cl_2 (2 X 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography with *n*-Hexane-EtOAc (6:4) to afford products (**2d**) as yellow solid.



2d

3-(2-Methoxyphenyl)indolin-2-one: The compound (**2d**) was obtained as orange yellow solid (3.9 mmol scale; 796 mg of product; 85% yield). R_f = 0.40 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.71 (s, 1H), 7.31 (td, *J* = 7.9, 1.8, 1H), 7.20 – 7.28 (m, 2H), 7.04 (d, *J*=7.4, 1H), 6.98 – 6.91 (m, 4H), 4.97 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 180.1, 157.5, 141.8, 130.5, 130.2, 129.0, 127.8, 125.7, 124.2, 122.3, 121.0, 111.5, 109.8, 55.7, 48.6; **IR** (film) 3766, 3358, 2926, 2550, 1719, 1480, 1411, 1310, 1114, 1004, 901, 790, 600 cm-1; **HRMS** (ESI) m/z $[M + Na]^+$ Calcd for $[C_{15}H_{13}NO_2 + Na]^+$ 262.0834; Found 262.0846.

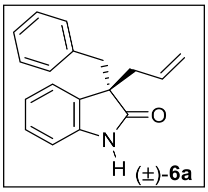
Procedure for acylation of 2-oxindole (**11d**): 2-Oxindole **2d** (1.0 equiv) was dissolved in anhydrous THF (2 mL) and then NaHMDS (1.1 equiv.) in THF (1 mL) was added at room temperature, the resulting solution was stirred for 10 min and a solution of imidazole carbamate (1.1 equiv.) in THF (0.5 mL) was added dropwise. The mixture was then allowed to stir until complete consumption of oxindole was observed by TLC. The crude product was concentrated in vacuo and purified by flash chromatography using a mixture of EtOAc and n-hexanes as eluent.



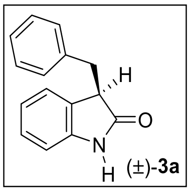
11d

Methyl 3-(2-methoxyphenyl)-2-oxoindoline-1-carboxylate (11d): The compound (**15a**) was obtained as orange yellow solid (0.42 mmol scale; 60 mg of product; 49% yield). R_f = 0.40 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J*=8.2, 1H), 7.37 – 7.29 (m, 2H), 7.23 – 7.17 (m, 1H), 7.12 (td, *J*=7.5, 1.0, 1H), 7.05 (dt, *J*=7.5, 1.4, 1H), 6.98 (td, *J*=7.5, 1.1, 1H), 6.90 (dd, *J*=8.3, 1.0, 1H), 4.92 (s, 1H), 4.06 (s, 3H), 3.68 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 174.5, 157.1, 151.8, 139.7, 130.7, 129.4, 128.4, 128.1, 125.8, 124.6, 123.9, 121.0, 114.7, 111.7, 55.8, 53.8, 53.8; **IR** (film) 3886, 3438, 2933, 2600, 1720, 1520, 1421, 1380, 1234, 1104, 981, 700, 620 cm-1; **HRMS** (ESI) m/z $[M + Na]^+$ Calcd for $[C_{17}H_{15}NO_4 + Na]^+$ 320.0893; Found 320.0886.

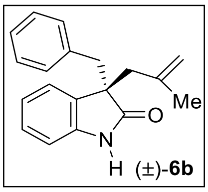
General Procedure for Deacylative Allylation of *N*-Moc-2-oxindole: A flame-dried 10 mL Schlenk flask equipped with a stir bar was charged with NaH (1.2 equiv of 0.26, 8 mg) and $Pd(PPh_3)_4$ (1.0 mol %, 0.001 mmol, 1.0 mg). To above flask 2 mL of dry toluene was added, and allyl alcohol (0.30 mmol, 17 µL) followed by *N*-Moc-2-oxindole **1a** (0.25 mmol) was added in that order. The vessel was capped and wrapped in parafilm, and the system was completely sealed over argon and allowed to react for 2 - 12 h. After the allotted reaction time as determined by TLC (2 - 12 h), the reaction mixture was diluted with 5% EtOAc in hexanes and subjected to silica gel chromatography (5% - 30% EtOAc in Hexanes) to yield the pure product.



(±)**-3-Allyl-3-benzylindolin-2-one** (**6a**): Compound **6a** was isolated in 92% yield (60.5 mg; 0.25 mmol) as yellow gel; R_f = 0.24 (20% EtOAc in hexane); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.28 (d, *J* = 1.3 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.09-7.04 (m, 2H), 6.91 (dt, *J* = 7.7, 1.6 Hz, 2H), 6.69 (d, *J* = 7.7 Hz, 1H), 5.54-5.43 (m, 1H), 5.06 (dt, *J* = 17.0, 1.7 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 3.19 (d, *J* = 13.1 Hz, 1H), 3.10 (d, *J* = 13.1 Hz, 1H), 2.78-2.64 (m, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 181.4, 140.9, 135.8, 132.2, 131.2, 130.0, 127.9, 127.7, 126.5, 124.1, 121.9, 118.9, 109.7, 54.9, 43.1, 41.6; **IR** (film) υ_{max} 2180, 1695, 1615, 1435, 1401, 1339, 1310, 1009, 982, 931, 780, 735, 706 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}NO + Na$ 286.1202; Found 286.1198.

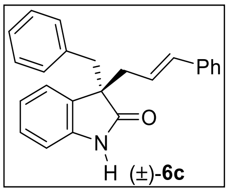


(±)**-(*E*)-3-Benzyl-3-(3-(p-tolyl)allyl)indolin-2-one** (**3a**): Compound **3a** was isolated as yellow gel; R_f = 0.24 (40% EtOAc in hexane); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.84 (brs, s, 1H), 7.24-7.20 (m, 3H), 7.18-7.13 (m, 3H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 1H), 3.74 (dd, *J* = 9.2 Hz, 4.6, 1H), 3.49 (dd, *J* = 13.7, 4.6 Hz, 1H), 2.93 (dd, *J* = 13.7, 9.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.7, 141.5, 137.8, 129.4, 128.9, 128.4, 127.9, 126.7, 124.9, 122.0, 109.7, 47.6, 36.7; **IR** (film) υ_{max} 1718, 1641, 1593, 1557, 1537, 1500, 1412, 1005, 981, 886, 823, 724, 703 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ $C_{15}H_{13}NO$ + Na 248.0889; Found 246.0905.



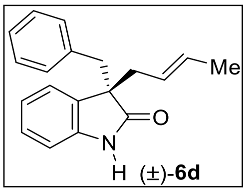
(±)-**6b**

(±)-3-Benzyl-3-(2-methylallyl)indolin-2-one (**6b**): Compound **6b** was isolated in 90% yield (62.4 mg; 0.25 mmol) as colorless solid; R_f = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.14 – 7.07 (m, 2H), 7.08 – 6.95 (m, 4H), 6.98 – 6.86 (m, 2H), 6.70 (d, *J* = 7.6 Hz, 1H), 4.56 (d, *J* = 1.8 Hz, 2H), 3.14 (d, *J* = 13.0 Hz, 1H), 3.05 (d, *J* = 13.0 Hz, 1H), 2.87 (d, *J* = 13.5 Hz, 1H), 2.62 (d, *J* = 13.5 Hz, 1H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.8, 141.2, 140.9, 135.6, 131.3, 130.1, 127.9, 127.6, 126.6, 124.6, 121.7, 114.7, 109.7, 55.2, 44.7, 44.6, 23.8; **IR** (film) υ_{max} 2832, 1814, 1643, 1491, 1432, 1316, 1128, 1123, 1101, 1009, 939, 735, 702 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{19}NO$ + Na 300.1359; Found 300.1373. MP = 80-84 ºC.



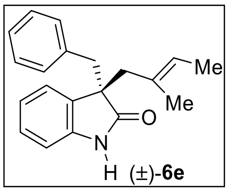
(±)-**6c**

(±)-3-Benzyl-3-cinnamylindolin-2-one (**6c**): Compound **6c** was isolated in 94% yield (79.7 mg; 0.25 mmol) as yellow gel; R_f = 0.41 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.26-7.14 (m, 5H), 7.11 (td, *J* = 7.8, 1.4 Hz, 1H), 7.06-7.00 (m, 3H), 6.91 (dd, *J* = 7.4, 2.2 Hz, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.41-6.37 (m, 1H), 5..93-5.86 (m, 1H), 3.20 (d, *J* = 13.1 Hz, 1H), 3.12 (d, *J* = 13.1 Hz, 1H), 2.88 – 2.74 (m, 2H); **^{13} C NMR** (100 MHz, $CDCl_3$) δ 180.9, 140.8, 137.2, 135.9, 133.9, 130.0, 128.6, 128.4, 127.9, 127.7, 126.5, 126.2, 124.2, 123.8, 122.0, 109.7, 63.7, 55.1, 42.9, 40.9; **IR** (film) υ_{max} 1873, 1632, 1493, 1413, 1383, 1352, 1196, 1121, 939, 919, 781, 730 cm^{-1}. **HRMS** (ESI) m/z 362.1534 [M+Na]$^+$; calculated for [$C_{24}H_{21}NO$ + Na]$^+$: 362.1515. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{21}NO$ + Na 362.1515; Found 362.1534.



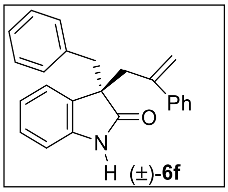
(±)-**6d**

(±)-(E)-3-Benzyl-3-(but-2-en-1-yl)indolin-2-one (**6d**): Compound **6d** was isolated in 81% yield (56.2 mg; 0.25 mmol) as yellow gel; R_f = 0.31 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 7a1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.04-6.99 (m, 4H), 6.88-6.86 (m, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 5.50-5.42 (m, 1H), 5.13-5.05 (m, 1H), 3.13 (d, *J* = 13.1 Hz, 1H), 3.03 (d, *J* = 13.1 Hz, 1H), 2.67-2.51 (m, 2H), 1.48 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.9, 140.7, 136.0, 131.5, 129.9, 129.7, 127.7, 127.6, 126.4, 124.4, 124.2, 121.9, 109.3, 55.1, 43.0, 40.6, 17.9; **IR** (film) υ_{max} 3012, 1739, 1628, 1452, 1431, 1401, 1293, 1260, 1209, 985, 903, 783, 731, 703 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{19}NO$ + Na 300.1359; Found 300.1369.



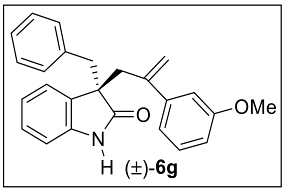
(±)-**6e**

(±)-(E)-3-Benzyl-3-(2-methylbut-2-en-1-yl)indolin-2-one (**6e**): Compound **6e** was isolated in 97% yield (70.6 mg; 0.25 mmol)as yellow gel; R_f = 0.28 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (brs, s, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 7.10-6.96 (m, 5H), 6.87-6.85 (m, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 5.17 (q, *J* = 6.9 Hz, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 3.02 (d, *J* = 13.0 Hz, 1H), 2.81 (d, *J* = 13.3 Hz, 1H), 2.57 (d, *J* = 13.3 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.8, 140.6, 135.9, 131.4, 130.9, 130.1, 127.6, 127.5, 126.4, 124.9, 123.6, 121.6, 109.2, 55.5, 47.1, 44.4, 17.0, 13.5; **IR** (film) υ_{max} 2937, 1742, 1613, 1592, 1541, 1317, 1303, 1288, 1203, 951, 903, 735 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{21}NO$ + Na 314.1515; Found 314.1513.



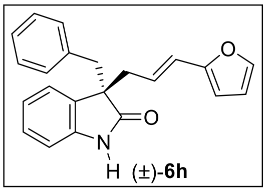
(±)-**6f**

(±)-3-Benzyl-3-(2-phenylallyl)indolin-2-one (**6f**): Compound **6f** was isolated in 87% yield (150.0 mg; 0.53 mmol) as colorless gel; R_f = 0.26 (30% EtOAc in hexane); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.94 (s, 1H), 7.14 (dt, *J* = 6.0, 2.5 Hz, 3H), 7.10 – 7.05 (m, 3H), 7.00 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.90 (td, *J* = 7.6, 1.3 Hz, 1H), 6.80 – 6.76 (m, 2H), 6.67 (td, *J* = 7.5, 1.1 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 4.98 (d, *J* = 1.8 Hz, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 3.17 (d, *J* = 13.8 Hz, 1H), 3.09 (d, *J* = 5.1 Hz, 1H), 3.07 (d, *J* = 4.3 Hz, 1H), 3.02 (d, *J* = 12.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 179.3, 144.6, 141.9, 141.7, 136.2, 130.2, 129.7, 127.6, 127.3, 127.3, 126.9, 126.1, 126.0, 124.8, 120.4, 116.1, 108.6, 54.7, 43.2, 41.7; **IR** (film) υ_{max} 1816, 1703, 1639, 1599, 1580, 1507, 1433, 1299, 1207, 1001, 958, 931, 755 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{21}NO$ + H 340.1696; Found 340.1695.



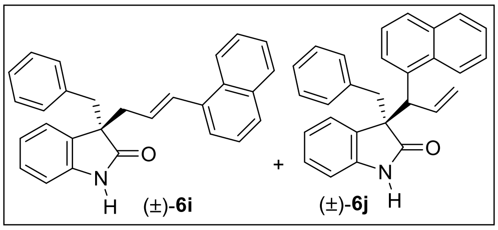
(±)-**6g**

(±)-3-Benzyl-3-(2-(3-methoxyphenyl)allyl)indolin-2-one (**6g**): Compound **6g** was isolated in 80% yield (73.8 mg; 0.25 mmol) as yellow gel; R_f = 0.42 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (brs, s, 1H), 7.04-6.96 (m, 5H), 6.86-6.83 (m, 3H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.64 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.54 (d, *J* = 7.7 Hz, 1H), 6.47 (t, *J* = 2.0 Hz, 1H), 4.97 (dd, *J* = 20.4, 1.6 Hz, 2H), 3.67 (s, 3H), 3.28 (d, *J* = 13.7 Hz, 1H), 3.13 (t, *J* = 13.1 Hz, 2H), 3.03 (d, *J* = 13.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.2, 158.9, 145.0, 143.7, 141.0, 135.7, 130.4, 130.1, 128.7, 127.6, 127.6, 126.5, 125.2, 121.4, 119.1, 117.1, 112.9, 112.1, 109.3, 55.5, 55.1, 43.9, 42.7; **IR** (film) υ_{max} 1672, 1601, 1591, 1572, 1541, 1372, 1311, 1269, 1222, 903, 872, 731, 728 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{23}NO_2$ + Na 392.1621; Found 392.1645.



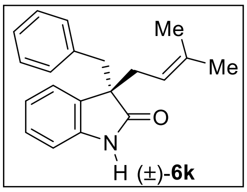
(±)-**6h**

(±)-**(E)-3-Benzyl-3-(3-(furan-2-yl)allyl)indolin-2-one** (**6h**): Compound **6h** was isolated in 66% yield (150.0 mg; 0.53 mmol) as colorless gel; R$_f$ = 0.39 (40% EtOAc in hexane); **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 10.14 (s, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.37 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.07 – 7.02 (m, 4H), 6.97 (td, *J* = 7.5, 1.1 Hz, 1H), 6.85 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.38 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.25 – 6.18 (m, 2H), 5.62 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.15 – 3.04 (m, 2H), 2.81 – 2.74 (m, 1H), 2.72 – 2.65 (m, 1H); **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 179.4, 151.8, 142.2, 141.9, 136.4, 130.9, 129.6, 127.7, 127.5, 126.2, 124.0, 122.7, 121.5, 121.1, 111.4, 109.0, 107.6, 54.4, 42.2, 40.6; **IR** (film) υ_{max} 3028, 1816, 1733, 1640, 1536, 1473, 1428, 1415, 1313, 1288, 941, 938, 732, 741 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{19}NO_2$ + Na 352.1308; Found 352.1324.

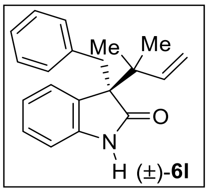


(±)-**6i** (±)-**6j**

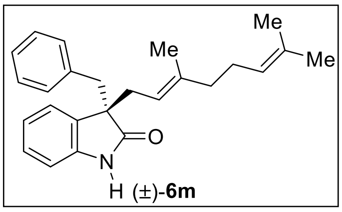
(±)-**(E)-3-Benzyl-3-(3-(naphthalen-1-yl)allyl)indolin-2-one** (**6i**) & (±)-**3-Benzyl-3-(1-(naphthalen-1-yl)allyl)indolin-2-one** (**6j**): Compound **6i** & **6j** were isolated in 69% yield (67.2 mg; 0.25 mmol) as colorless foam (ratio of **6i**:**6j** = 4:1); R$_f$ = 0.36 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (brs, s, 1H for major isomer), 8.32 (brs, s, 1H for minor isomer), 7.79 (t, *J* = 8.6 Hz, 1H for major isomer), 7.74-7.64 (m, 2H for major isomer & 2H for minor isomer), 7.08-6.99 (m, 4H for major isomer & 4H for minor isomer), 6.97-6.89 (m, 2H for major isomer & 2H for minor isomer), 6.87-6.77 (m, 3H for minor isomer), 6.69 7.1 (s, 1H for major isomer), 7.46-7.44 (m, 1H for major isomer), 7.42-7.39 (m, 1H for major isomer & 1H for minor isomer), 7.37-7.31 (m, 1H for major isomer & 1H for minor isomer), 7.24-7.22 (m, 1H for major isomer & 1H for minor isomer), 7.13 (t, *J* = 7.4 Hz, 1H for major isomer & 1H for minor isomer), 7.08-6.99 (m, 4H for major isomer & 4H for minor isomer), 6.97-6.89 (m, 2H for major isomer & 2H for minor isomer), 6.87-6.77 (m, 3H for minor isomer), 6.69 (d, *J* = 7.4 Hz, 1H for major isomer), 6.54 (d, *J* = 16.9 Hz, 1H for minor isomer), 4.94 (d, *J* = 9.3 Hz, 1H for minor isomer), 4.16-4.06 (m, 2H for minor isomer), 3.49-3.45 (m, 1H for minor isomer), 3.26-3.13 (m, 2H for major isomer), 2.91-2.81 (m, 2H for major isomer); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 188.5, 181.2, 141.4, 140.9, 137.0, 135.9, 135.9, 135.7, 134.6, 134.1, 133.5, 133.1, 132.8, 132.5, 131.3, 130.0, 130.0, 129.9, 129.5, 128.4, 128.0, 128.0, 127.9, 127.8, 127.72, 127.73, 127.2, 127.61, 127.4, 126.6, 126.3, 126.2, 126.0, 125.9, 125.8, 125.7, 125.6, 124.2, 124.2, 123.5, 122.1, 121.5, 118.3, 109.8, 109.6, 60.5, 59.1, 57.2, 55.3, 42.9, 42.3, 41.0; **IR** (film) υ_{max} 3021, 2899, 1731, 1608, 1499, 1493, 1455, 1421, 1377, 1313, 1218, 966, 905, 888, 812, 739 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{28}H_{23}NO$ + H 390.1852; Found 390.1850.



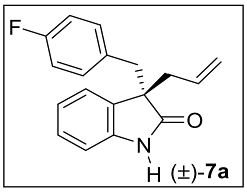
(±)-3-Benzyl-3-(3-methylbut-2-en-1-yl)indolin-2-one (**6k**): Compound **6k** was isolated in 64% yield (46.6 mg; 0.25 mmol) as colorless gel; R$_f$ = 0.28 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.70 (brs, s, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.09 (td, *J* = 7.6, 1.3 Hz, 1H), 7.04-6.97 (m, 4H), 6.89- 6.86 (m, 2H), 6.63 (d, *J* = 7.7 Hz, 1H), 4.87-4.83 (m, 1H), 3.16 (d, *J* = 13.1 Hz, 1H), 3.07 (d, *J* = 13.1 Hz, 1H), 2.70-2.55 (m, 2H), 1.54 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 181.0, 140.7, 136.1, 135.3, 131.7, 129.9, 127.7, 127.6, 126.4, 124.2, 121.8, 117.8, 109.2, 55.1, 42.9, 36.0, 25.9, 18.1; **IR** (film) υ_{max} 1742, 1639, 1578, 1552, 1413, 1320, 1309, 1288, 1201, 988, 971, 902, 739, 712 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{21}NO$ + Na 314.1515; Found 314.1529.



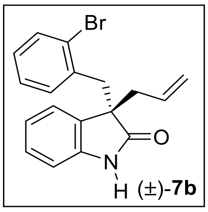
(±)-3-Benzyl-3-(2-methylbut-3-en-2-yl)indolin-2-one (**6k**): Compound **6k** was isolated in 33% yield (24.0 mg; 0.25 mmol) as colorless gel; R$_f$ = 0.30 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.43 (s, 1H), 7.38 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.11 (td, *J* = 7.7, 1.2 Hz, 1H), 7.00 (td, *J* = 7.6, 1.1 Hz, 1H), 6.98-6.91 (m, 3H), 6.88-6.83 (m, 2H), 6.65 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.25 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.18 (dd, *J* = 10.8, 1.3 Hz, 1H), 5.10 (dd, *J* = 17.4, 1.3 Hz, 1H), 3.44 (d, *J* = 13.0 Hz, 1H), 3.09 (d, *J* = 13.0 Hz, 1H), 1.29 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 180.7, 143.7, 141.5, 136.6, 130.3, 130.1, 127.7, 127.5, 126.5, 126.0, 121.0, 113.8, 109.1, 60.4, 42.1, 37.6, 22.6, 22.2; **IR** (film) υ_{max} 2812, 1628, 1593, 1573, 1501, 1414, 1398, 1084, 1033, 999, 753 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{21}NO + Na$ 314.1515; Found 314.1519.



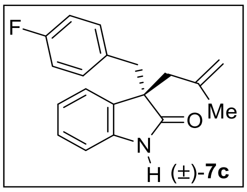
(±)-(E)-3-Benzyl-3-(3,7-dimethylocta-2,6-dien-1-yl)indolin-2-one (**6m**): Compound **6m** was isolated in 89% yield (150.0 mg; 0.53 mmol) as colorless gel; R$_f$ = 0.34 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.07 (s, 1H), 7.32 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.06 – 7.00 (m, 4H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 – 6.81 (m, 2H), 6.57 – 6.52 (m, 1H), 4.91 – 4.87 (m, 1H), 4.79 – 4.73 (m, 1H), 3.10 (d, *J* = 13.0 Hz, 1H), 3.02 (d, *J* = 13.0 Hz, 1H), 2.58 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.50 – 2.44 (m, 1H), 1.87 – 1.74 (m, 4H), 1.58 (s, 3H), 1.48 (s, 3H), .47 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 179.9, 142.0, 137.4, 136.6, 131.3, 130.6, 129.6, 127.4, 126.1, 124.0, 123.8, 120.8, 118.2, 108.7, 54.4, 41.9, 36.0, 26.0, 25.4, 17.5, 16.1. **IR** (film) υ_{max} 3013, 1749, 1620, 1455, 1432, 1366, 1315, 1275, 1089, 1035, 990, 920, 735 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}NO + H$ 360.2322; Found 360.2350.



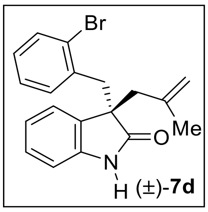
(±)-3-Allyl-3-(4-fluorobenzyl)indolin-2-one (**7a**): Compound **7a** was isolated in 90 % yield (150.0 mg; 0.53 mmol) as colorless gel; R$_f$ = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.15 (s, 1H), 7.35 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.06 (td, *J* = 7.6, 1.1 Hz, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 – 6.83 (m, 4H), 6.59 (dt, *J* = 7.7, 0.8 Hz, 1H), 5.36 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 4.96 (ddd, *J* = 17.1, 2.4, 1.3 Hz, 1H), 4.88 (dd, *J* = 10.1, 2.2 Hz, 1H), 3.09 (d, *J* = 13.1 Hz, 1H), 3.01 (d, *J* = 13.1 Hz, 1H), 2.62 (ddt, *J* = 13.5, 6.9, 1.2 Hz, 1H), 2.55 (ddt, *J* = 13.4, 7.6, 1.1 Hz, 1H); **^{13}C NMR** (126 MHz, DMSO-d_6) δ 179.4, 160.8 (d, *J* = 242.1 Hz), 141.9, 132.7, 132.5, 132.5, 132.2, 131.3 (d, *J* = 7.9 Hz), 130.7, 127.7, 124.1, 121.1, 118.4, 114.1 (d, *J* = 21.1 Hz), 109.0, 54.1, 41.4, 41.2; **IR** (film) υ_{max} 2793, 1733, 1638, 1491, 1472, 1433, 1333, 1308, 1272, 1248, 1190, 1130, 1008, 1005, 958, 943, 739, 706 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}NFO$ + H 282.1289; Found 282.1310.



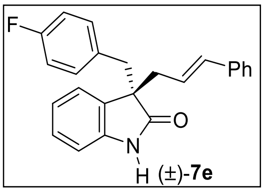
(±)-3-Allyl-3-(2-bromobenzyl)indolin-2-one (**7b**): Compound **7b** was isolated in 89% yield (76.1 mg; 0.25 mmol) as yellow solid; R_f = 0.26 (20% EtOAc in hexane); 1H NMR (400 MHz, CDCl3) 8.95 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.12 (q, J = 7.7, 7.1 Hz, 3H), 7.01 (t, J = 7.5 Hz, 1H), 6.96-6.90 (m, 2H), 6.77 (d, J = 7.7 Hz, 1H), 5.46-5.35 (m, 1H), 5.02 (dd, J = 17.0, 1.9 Hz, 1H), 4.89 (dd, J = 10.1, 1.9 Hz, 1H), 3.46 (d, J = 13.9 Hz, 2H), 3.32 (d, J = 13.9 Hz, 1H), 2.79-2.66 (m, 2H); 13C NMR (100 MHz, CDCl3) δ 181.7, 140.7, 136.1, 132.8, 131.9, 131.1, 130.6, 128.2, 127.9, 126.9, 125.8, 124.9, 121.9, 54.5, 41.7, 41.0; **IR** (film) υ_{max} 2966, 2851, 1700, 1601, 1480, 1391, 1002, 935, 924, 700 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}B_rNO$ + H 342.0488; Found 342.0479. MP = 106-109 ºC.



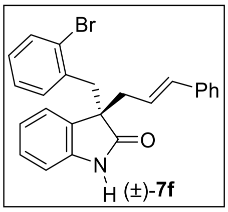
(±)-3-(4-Fluorobenzyl)-3-(2-methylallyl)indolin-2-one (**7c**): Compound **7c** was isolated in 90% yield (66.5 mg; 0.25 mmol) as colorless gel; R_f = 0.25 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 29.2 Hz, 1H), 7.19-7.07 (m, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.81-6.77 (m, 2H), 6.69-6.65 (m, 3H), 4.55 (d, *J* = 3.7 Hz, 2H), 3.11 (d, *J* = 13.1 Hz, 1H), 2.99 (d, *J* = 13.1 Hz, 1H), 2.83 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 13.4 Hz, 1H), 1.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.4, 161.7 (d, *J* = 244.8 Hz), 141.0, 140.7, 131.4 (d, *J* = 8.0 Hz), 131.3 (d, *J* = 3.3 Hz), 131.1, 127.9, 124.4, 121.9, 114.4 (d, *J* = 21.1 Hz), 109.7, 55.2, 44.7, 43.9, 23.7; **IR** (film) υ_{max} 2800, 2750, 1750, 1628, 1445, 1381, 990, 930, 789, 731 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NFO$ + H 296.1445; Found 296.1470.



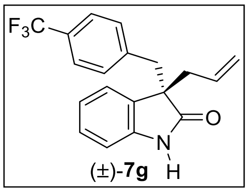
(±)**-3-(2-Bromobenzyl)-3-(2-methylallyl)indolin-2-one** (**7d**): Compound **7d** was isolated in 92% yield (81.9 mg; 0.25 mmol) as colorless gel; R_f = 0.29 (30% EtOAc in hexane); ^{1}**H NMR** (400 MHz, $CDCl_3$) 8.97 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.12-7.09 (m, 3H), 7.02 (td, *J* = 1.3, 7.5 Hz, 1H), 6.93 (td, *J* = 7.6, 2.6 Hz, 2H), 6.75 (d, *J* = 7.7 Hz, 1H), 4.56 (d, *J* = 4.5 Hz, 2H), 3.43 (d, *J* = 13.7 Hz, 1H), 3.31 (d, *J* = 13.7 Hz, 1H), 2.90 (d, *J* = 13.4 Hz, 1H), 2.67 (d, *J* = 13.3 Hz, 1H), 1.33 (s, 3H).; ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 181.9, 140.8, 140.6, 135.9, 132.8, 131.3, 130.6, 128.3, 127.9, 126.9, 125.9, 125.4, 121.7, 114.9, 109.6, 54.8, 44.7, 42.5, 23.8.; **IR** (film) υ_{max} 2922, 2851, 1713, 1620, 995, 920, 789 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}NBrO + H$ 356.0645; Found 356.0641.



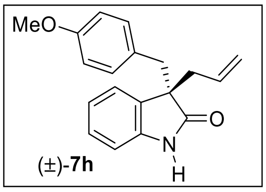
(±)**-3-Cinnamyl-3-(4-fluorobenzyl)indolin-2-one** (**7e**): Compound **7e** was isolated in 84% yield (75.1 mg; 0.25 mmol) as colorless solid; R_f = 0.24 (20% EtOAc in hexane); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.24-7.15 (m, 7H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.87-6.84 (m, , 2H), 6.72-6.66 (m, 3H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.96-5.88 (m, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 3.08 (d, *J* = 13.3, 1H), 2.79 (d, *J* = 7.6 Hz, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 181.2, 161.7 (d, *J* = 244.7 Hz), 140.9, 137.1, 134.1, 131.6 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 7.8 Hz), 131.1, 128.5, 128.1, 127.3, 126.2, 124.1, 123.6, 122.2, 114.5 (d, *J* = 21.1 Hz), 109.9, 55.3, 42.0, 40.9; **IR** (film) υ_{max} 2850, 2751, 1780, 1620, 1440, 1385, 992, 931, 780, 725 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}NFO + H$ 358.1602; Found 358.1620. MP = 152-155 ºC.



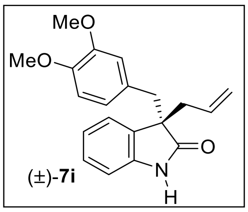
(±)-3-(2-Bromobenzyl)-3-cinnamylindolin-2-one (**7f**): Compound **7f** was isolated in 93% yield (97.3 mg; 0.25 mmol) as light yellow solid; R_f = 0.31 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.22-7.09 (m, 8H), 7.03-6.90 (m, 3H), 6.73 (dd, *J* = 7.8, 3.7 Hz, 1H), 6.38 (d, *J* =15.7 Hz, 1H), 5.87-5.79 (m, 1H), 3.51 (d, *J* = 13.9 Hz, 1H), 3.37 (d, *J* = 13.9 Hz, 1H), 2.86 (m, 2H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.3, 140.5, 137.2, 136.1, 134.2, 132.8, 131.1, 130.6, 128.4, 128.2, 128.1, 127.3, 126.9, 126.2, 125.8, 125.0, 123.5, 122.0, 109.6, 54.7, 40.9, 40.9; **IR** (film) υ_{max} 3105, 2755, 1700, 1650, 1442, 1391, 1005, 990, 921, 789 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{20}NBrO$ + H 418.0801; Found 418.0813. MP = 158-161 ºC.



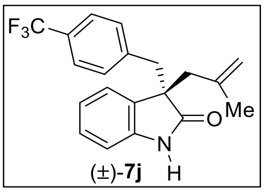
(±)-3-Allyl-3-(4-(trifluoromethyl)benzyl)indolin-2-one (**7g**): Compound **7g** was isolated in 92% yield (76.2 mg; 0.25 mmol) as yellow gel; R_f = 0.27 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 5.48-5.38 (m, 1H), 5.01 (dd, *J* = 1.8, 7.0 Hz, 1H), 4.87 (d, *J* = 10.1 Hz, 1H), 3.21 (d, *J* = 13.1 Hz, 1H), 3.10 (d, *J* = 13.1 Hz, 1H), 2.72-2.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.8, 140.8, 139.9, 131.8, 130.7, 130.2, 128.8 (q, *J* = 32.2 Hz), 128.2, 124.6 (q, *J* = 3.8 Hz), 123.9, 122.8, 122.2, 119.2, 109.8, 54.8, 42.6, 41.8; **IR** (film) υ_{max} 3105, 2851, 1790, 1621, 1432, 1380, 900, 850, 780, 735, 690 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{16}NF_3O$ + H 332.1257; Found 332.1256.



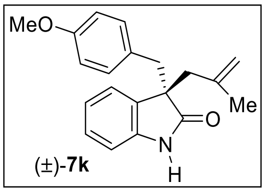
(±)-3-Allyl-3-(4-methoxybenzyl)indolin-2-one (**7h**): Compound **7h** was isolated in 75% yield (55.0 mg; 0.25 mmol) as colorless gel; R_f = 0.32 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.15-7.10 (m, 2H), 7.02 (td, *J* = 1.0, 7.8 Hz, 1H), 6.80-6.76 (m, 2H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.54-6.51 (m, 2H), 5.46-5.36 (m, 1H), 5.00 (dd, *J* = 17.0, 1.9 Hz, 1H), 4.84 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.62 (s, 3H), 3.08 (d, *J* = 13.3 Hz, 1H), 3.00 (d, *J* = 13.3 Hz, 1H), 2.71-2.58 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6, 158.1, 141.1, 132.2, 131.5, 130.9, 127.9, 127.8, 124.0, 121.9, 118.8, 113.1, 109.7, 55.1, 54.9, 42.3, 41.5; **IR** (film) υ_{max} 2750, 2100, 1701, 1680, 1490, 1480, 1405, 1378, 1352, 1255, 1120, 900, 981, 750 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}NO_2$ + Na 316.1308; Found 316.1301.



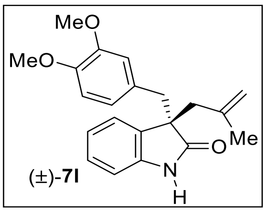
(±)-3-allyl-3-(3,4-dimethoxybenzyl)indolin-2-one (**7i**): Compound **7i** was isolated in 85% yield (68.7 mg; 0.25 mmol) as colorless gel; R$_f$ = 0.32 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.48 (s, 2H), 6.22 (s, 1H), 5.45-5.36 (m, 1H), 4.98 (dd, *J* = 17.0, 1.9 Hz, 1H), 4.84 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.65 (s, 3H), 3.48 (s, 3H), 3.06 (d, *J* = 13.2, 1H), 2.99 (d, *J* = 13.3 Hz, 1H), 2.69-2.58 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.4, 147.7, 147.5, 141.3, 132.2, 131.6, 128.3, 127.9, 123.9, 122.2, 121.8, 118.8, 112.9, 110.4, 109.8, 55.5, 55.4, 55.1, 42.8, 41.5; **IR** (film) υ_{max} 2750, 2100, 1701, 1680, 1490, 1480, 1405, 1378, 1352, 1255, 1120, 900, 981, 750 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}NO_3$ + H 324.1594; Found 324.1606.



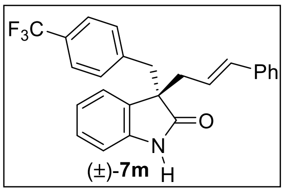
(±)-3-(2-Methylallyl)-3-(4-(trifluoromethyl)benzyl)indolin-2-one (**7j**): Compound **7j** was isolated in 81% yield (69.9 mg; 0.25 mmol) as colorless solid; R$_f$ = 0.25 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 4.57 (d, *J* = 6.8 Hz, 2H), 3.19 (d, *J* = 12.9 Hz, 1H), 3.07 (d, *J* = 12.9 Hz, 1H), 2.85 (d, *J* = 13.4 Hz, 1H), 2.61 (d, *J* = 13.4 Hz, 1H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.8, 140.9, 140.5, 139.7, 130.7, 130.3, 125.5, 128.8 (q, *J* = 32.3 Hz), 128.2, 124.5 (q, *J* = 3.8 Hz), 124.4, 122.0, 114.9, 109.8, 55.0, 44.9, 44.3, 23.7; **IR** (film) υ_{max} 3310, 2805, 2800, 2305, 1716, 1685, 1430, 1351, 901, 852, 795, 730 cm^{-1}. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{20}H_{18}NF_3O$ + H 346.1413; Found 346.1422. MP = 142-145 ºC.



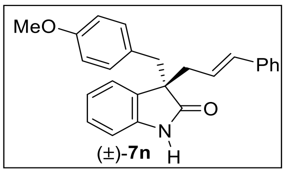
(±)-3-(4-Methoxybenzyl)-3-(2-methylallyl)indolin-2-one (**7k**): Compound **7k** was isolated in 74% yield (56.9 mg; 0.25 mmol) as colorless solid; R$_f$ = 0.30 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.18 – 7.08 (m, 2H), 7.05 – 6.95 (m, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 6.60 – 6.51 (d, *J* = 7.4 Hz, 2H), 4.56 (m, 2H), 3.65 (s, 3H), 3.06 (d, *J* = 13.2 Hz, 1H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.83 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 13.5 Hz, 1H), 1.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.2, 158.2, 140.9, 140.9, 131.4, 131.1, 127.8, 127.7, 124.6, 121.8, 114.6, 112.9, 109.5, 55.2, 55.0, 44.6, 44.0, 23.7; **IR** (film) υ_{max} 3050, 2816, 1785, 1623, 1491, 1477, 1379, 1291, 1151, 900, 881, 735 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{21}NO_2$ + Na 330.1465; Found 330.1474. MP = 153-155 ºC.



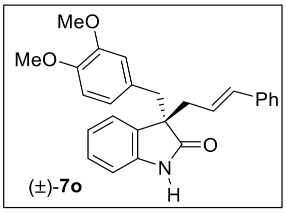
(±)-3-Allyl-3-(3,4-dimethoxybenzyl)indolin-2-one (**7l**): Compound **7l** was isolated in 76% yield (64.1 mg; 0.25 mmol) as colorless gel; R$_f$ = 0.32 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.99 – 6.95 (m, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 6.43 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.15 (d, *J* = 1.9 Hz, 1H), 4.57 – 4.48 (m, 2H), 3.67 (s, 3H), 3.47 (s, 3H), 3.02 (d, *J* = 13.1 Hz, 1H), 2.93 (d, *J* = 13.1 Hz, 1H), 2.79 (d, *J* = 13.5 Hz, 1H), 2.57 (s, 1H), 1.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.9, 147.7, 147.5, 141.1, 140.9, 131.5, 127.9, 127.8, 124.5, 122.3, 121.7, 114.6, 112.9, 110.3, 109.6, 55.6, 55.5, 55.3, 44.6, 29.7, 23.7; **IR** (film) υ_{max} 3052, 2792, 1781, 1653, 1485, 1473, 1373, 1285, 1001, 979, 852, 730 cm^{-1}. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{23}NO_3$ + Na 360.1570; Found 360.1577.


(±)-**7m**

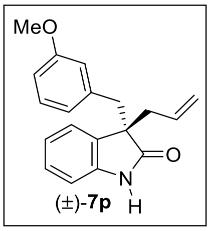
(±)-3-Cinnamyl-3-(4-(trifluoromethyl)benzyl)indolin-2-one (**7m**): Compound **7m** was in 82% yield (83.5 mg; 0.25 mmol) isolated as colorless solid; R*f* = 0.28 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.29-7.23 (m, 3H), 7.21-7.12 (m, 6H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.94-5.86 (m, 1H), 3.26 (d, *J* = 13.1 Hz, 1H), 3.15 (d, *J* = 13.1 Hz, 1H), 2.80 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.4, 140.6, 140.0, 137.0, 134.3, 130.7, 130.3, 128.8 (q, *J* = 31.1 Hz), 128.5, 128.3, 127.4, 126.2, 124.6 (q, *J* = 3.7 Hz), 124.0, 123.3, 122.8, 122.3, 109.9, 54.9, 42.5, 41.1; **IR** (film) υ_{max} 3251, 2896, 2793, 1715, 1646, 1443, 1048, 958, 753 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{20}F_3NO$ + H 408.1570; Found 408.1588. MP = 148-150 ºC.


(±)-**7n**

(±)-3-Cinnamyl-3-(4-methoxybenzyl)indolin-2-one (**7n**): Compound **7n** was isolated in 98% yield (90.5 mg; 0.25 mmol) as yellow gel; R*f* = 0.31 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.22-7.09 (m, 7H), 7.03 (td, *J* = 7.5, 1.1 Hz, 1H), 6.82-6.79 (m, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.59-6.55 (m, 2H), 6.37 (d, *J* = 15.7 Hz, 1H), 5.92-5.84 (m, 1H), 3.65 (s, 3H), 3.14 (d, *J* = 13.3 Hz, 1H), 3.06 (d, *J* = 13.3 Hz, 1H), 2.83-2.73 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.7, 158.2, 140.7, 137.2, 133.9, 131.4, 130.9, 128.4, 127.9, 127.9, 127.2, 126.2, 124.2, 123.9, 122.0, 113.1, 109.6, 55.2, 55.0, 42.2, 40.8; **IR** (film) υ_{max} 2285, 1852, 1719, 1601, 1442, 1081, 920 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}NO_2$ + Na 392.1621; Found 392.1628.

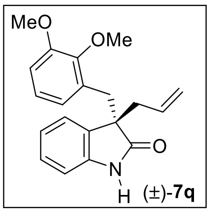

(±)-**7o**

(±)-3-Cinnamyl-3-(3,4-dimethoxybenzyl)indolin-2-one (**7o**): Compound **7o** was isolated in 81% yield (150.0 mg; 0.53 mmol) as yellow foam; R_f = 0.35 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.24 – 7.18 (m, 4H), 7.18 (q, *J* = 1.6 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.12 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.06 (td, *J* = 7.5, 1.2 Hz, 1H), 6.68 – 6.64 (m, 1H), 6.58 – 6.52 (m, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.28 (d, *J* = 1.9 Hz, 1H), 5.93 (dt, *J* = 15.4, 7.5 Hz, 1H), 3.72 (s, 3H), 3.55 (s, 3H), 3.15 (d, *J* = 13.3 Hz, 1H), 3.08 (d, *J* = 13.3 Hz, 1H), 2.83 – 2.79 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 180.6, 147.8, 147.5, 140.9, 137.1, 133.9, 131.5, 128.4, 128.3, 127.9, 127.2, 126.2, 124.1, 123.8, 122.1, 121.9, 112.9, 110.4, 109.7, 55.6, 55.4, 55.3, 42.7, 40.7; **IR** (film) υ_{max} 2942, 2201, 1715, 1642, 1412, 1301, 1255, 905, 982, 742 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}NO_3$ + H 400.1907; Found 400.1926.



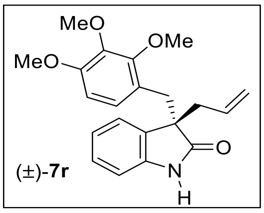
(±)-**7p**

(±)-3-Allyl-3-(3-methoxybenzyl)indolin-2-one (**7p**): Compound **7p** was isolated in 90% yield (66.0 mg; 0.25 mmol) as yellow gel; R_f = 0.25 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.12 (td, *J* = 7.7, 1.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.37 (t, *J* = 2.0 Hz, 1H), 5.50-5.40 (m, 1H), 5.02 (dd, *J* = 16.9, 1.9 Hz, 1H), 4.90 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.53 (s, 3H), 3.12 (d, *J* = 13.1 Hz, 1H), 3.04 (d, *J* = 13.1 Hz, 1H), 2.73-2.60 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.9, 158.8, 140.9, 137.32, 132.2, 131.3, 128.6, 127.9, 124.2, 122.5, 121.9, 118.9, 114.9, 112.7, 109.6, 54.9, 54.8, 43.1, 41.7; **IR** (film) υ_{max} 3019, 2855, 1742, 1618, 1402, 1395, 1318, 1105, 942, 845, 752 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}NO_2$ + H 294.1489; Found 294.1495.



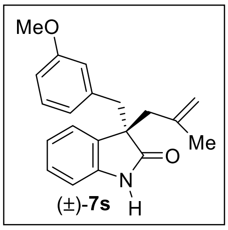
(±)-**7q**

(±)-3-Allyl-3-(2,3-dimethoxybenzyl)indolin-2-one (**7q**): Compound **7q** was isolated in 82% yield (66.3 mg; 0.25 mmol) as yellow gel; R_f = 0.29 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.09 -7.01 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.78-6.70 (m, 2H), 6.66 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.58 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.43-5.33 (m, 1H), 4.98 (dd, *J* = 17.0, 1.9 Hz, 1H), 4.86 (dd, *J* = 10.1, 2.0 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.30 (d, *J* = 13.4 Hz, 1H), 3.09 (d, *J* = 13.4 Hz, 1H), 2.77-2.58 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6, 152.4, 147.7, 140.6, 132.4, 131.4, 130.3, 128.2, 127.6, 124.8, 123.1, 121.9, 118.7, 111.1, 109.2, 60.5, 55.7, 54.3, 41.9, 35.4; **IR** (film) υ_{max} 2890, 2305, 1850, 1685, 1400, 1351, 1305, 1250, 900, 980, 755 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}NO_3$ + H 324.1594; Found 324.1613.



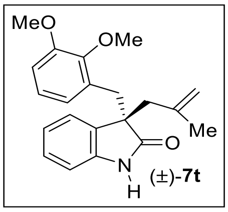
(±)-**7r**

(±)-3-Allyl-3-(2,3,4-trimethoxybenzyl)indolin-2-one (**7r**): Compound **7r** was isolated in 73% yield (150.0 mg; 0.53 mmol) as yellow gel; R_f = 0.29 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.10 – 7.06 (m, 2H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.39 (d, *J* = 8.6 Hz, 1H), 5.41 (dddd, *J* = 17.0, 10.2, 7.7, 6.8 Hz, 1H), 5.04 – 4.96 (m, 1H), 4.88 (ddd, *J* = 10.2, 2.1, 1.1 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.65 (s, 3H), 3.22 (d, *J* = 13.5 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H), 2.73 (ddt, *J* = 13.5, 7.7, 1.0 Hz, 1H), 2.62 (ddt, *J* = 13.5, 6.8, 1.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.5, 152.3, 152.1, 141.6, 140.5, 132.5, 131.4, 127.5, 125.1, 124.9, 122.2, 121.7, 118.7, 109.1, 106.3, 55.8, 54.6, 41.6, 35.3; **IR** (film) υ_{max} 2752, 1801, 1743, 1648, 1445, 1352, 1149, 849, 845, 701 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO_4$ + Na 376.1519; Found 324.1539.



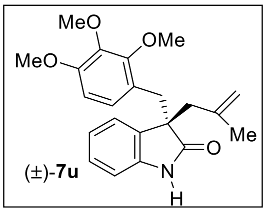
(±)-**7s**

(±)**-3-Allyl-3-(2-methoxybenzyl)indolin-2-one** (**7s**): Compound **7s** was isolated in 94% yield (72.2 mg; 0.25 mmol) as colorless solid; R_f = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.15 (t, *J* = 7.0 Hz, 1H), 7.10 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.93 (t, *J* =7.9 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.35 (t, *J* = 2.0 Hz, 1H), 4.57 (dd, *J* = 4.3, 2.3 Hz, 2H), 3.53 (s, 3H), 3.11 (d, *J* = 13.0 Hz, 1H), 3.02 (d, *J* = 12.9 Hz, 1H), 2.84 (d, *J* = 13.5 Hz, 1H), 2.61 (d, *J* = 13.5 Hz, 1H), 1.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.4, 158.8, 141.1, 140.9, 137.1, 131.3, 128.5, 127.9, 124.6, 122.6, 121.7, 114.9, 114.7, 112.9, 109.7, 55.1, 54.9, 44.8, 44.7, 23.7; **IR** (film) υ_{max} 3218, 1895, 1740, 1619, 1452, 1349, 1142, 1010, 982, 851, 701 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}NO_2$ + H 308.1645; Found 308.1666. MP = 158-162 ºC.



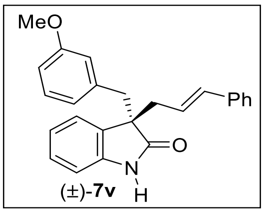
(±)-**7t**

(±)**-3-(2,3-Dimethoxybenzyl)-3-(2-methylallyl)indolin-2-one** (**7t**): Compound **7t** was isolated in 77% yield (65.0 mg; 0.25 mmol) as yellow gel; R_f = 0.26 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.08-7.01 (m, 2H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.67 (dd, *J* = 8.2 Hz, 1.5, 1H), 6.56 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.53 (dd, *J* = 1.8, 5.7 Hz, 2H), 3.74 (s, 3H), 3.70 (s, 3H), 3.28 (d, *J* = 13.3 Hz, 1H), 3.06 (d, *J* = 13.2 Hz, 1H), 2.88 (d, *J* = 13.4 Hz, 1H), 2.60 (d, *J* = 13.5 Hz, 1H), 1.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.0, 152.4, 147.8, 141.0, 140.8, 131.5, 130.1, 127.6, 125.2, 123.2, 122.9, 121.6, 114.6, 111.1, 109.3, 60.5, 55.7, 54.7, 44.8, 36.8, 23.8; **IR** (film) υ_{max} 3052, 2792, 1781, 1653, 1485, 1473, 1373, 1285, 1001, 979, 852, 730 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}NO_3$ + H 338.1751; Found 338.1729.

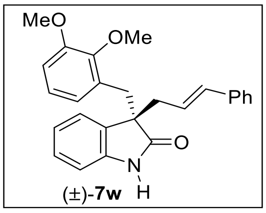


(±)-**7u**

(±)-3-(2-Methylallyl)-3-(2,3,4-trimethoxybenzyl)indolin-2-one (**7u**): Compound **7u** was in 90% yield (82.7 mg; 0.25 mmol) isolated as yellow solid; R_f = 0.32 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 1H), 6.36 (d, *J* = 8.6 Hz, 1H), 4.52 (s, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H), 3.18 (d, *J* = 13.3 Hz, 1H), 3.00 (d, *J* = 13.3 Hz, 1H), 2.85 (d, *J* = 13.5 Hz, 1H), 2.59 (d, *J* = 13.5 Hz, 1H), 1.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.4, 152.3, 152.2, 141.6, 141.1, 131.5, 127.5, 125.3, 125.2, 122.0, 121.4, 114.5, 109.3, 106.3, 60.6, 60.5, 55.7, 54.9, 44.6, 36.9, 29.7, 23.7; **IR** (film) υ_{max} 2042, 1872, 1718, 1641, 1540, 1515, 1312, 1121, 958, 931, 849, 702 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}NO_4$ + H 368.1856; Found 368.1878. MP = 147-153 ºC.

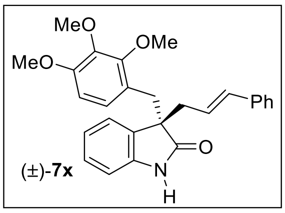


(±)-3-Cinnamyl-3-(3-methoxybenzyl)indolin-2-one (**7v**): Compound **7v** was isolated in 90% yield (83.1 mg; 0.25 mmol) as colorless gel; R_f = 0.24 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.24-7.15 (m, 6H), 7.11 (dd, *J* = 7.7 Hz, 1.3, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.46-6.33 (m, 2H), 5.96-5.88 (m, 1H), 3.53 (s, 3H), 3.19 (d, *J* = 13.1 Hz, 1H), 3.11 (d, *J* = 13.1 Hz, 1H), 2.82-2.76 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.0, 158.9, 140.9, 137.4, 137.2, 134.0, 131.3, 128.7, 128.4, 127.9, 127.3, 126.2, 124.21, 123.8, 122.5, 121.9, 114.9, 112.8, 109.8, 55.1, 54.9, 42.9, 40.9; **IR** (film) υ_{max} 1943, 1651, 1458, 1401, 1392, 1386, 1280, 1142, 1001, 982, 884, 851, 800 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{23}NO_2$ + H 370.1802; Found 370.1782.

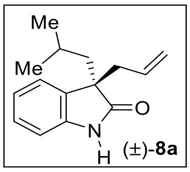


(±)-3-Cinnamyl-3-(2,3-dimethoxybenzyl)indolin-2-one (**7w**): Compound **7w** was isolated in 81% yield (80.8 mg; 0.25 mmol) as yellow gel; R_f = 0.31 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.18-7.09 (m, 6H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.93 (t,

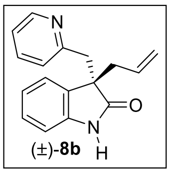
J = 7.5 Hz, 1H), 6.77-6.70 (m, 2H), 6.65-6.60 (m, 2H), 6.35 (d, J = 15.7 Hz, 1H), 5.86-5.78 (m, 1H), 3.72 (s, 6H), 3.36 (d, J = 13.4 Hz, 1H), 3.15 (d, J = 13.4 Hz, 1H), 2.90-2.75 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.9, 152.4, 147.7, 140.7, 137.3, 133.8, 131.5, 130.4, 128.3, 127.7, 127.1, 126.2, 124.7, 124.1, 123.1, 123.1, 121.9, 111.1, 109.5, 60.1, 55.3, 54.2, 41.3, 35.3; **IR** (film) υ_{max} 2872, 1700, 1602, 1552, 1305, 1301, 952, 782, 735 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}NO_3$ + H 400.1927; Found 400.1927.



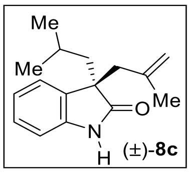
(±)-3-Cinnamyl-3-(2,3,4-trimethoxybenzyl)indolin-2-one (**7x**): Compound **7x** was isolated in 92% yield (98.7 mg; 0.25 mmol) as yellow gel; R_f = 0.26 (40% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.19-7.10 (m, 6H), 7.08-7.03 (m, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.70 (dd, J = 8.2, 3.9 Hz, 2H), 6.37-6.34 (m, 2H), 5.87-5.80 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.27 (d, J = 13.5 Hz, 1H), 3.09 (d, J = 13.5 Hz, 1H), 2.92-2.68 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.9, 152.3, 152.2, 141.6, 140.7, 137.3, 133.7, 131.5, 128.4, 127.6, 127.1, 126.1, 125.1, 124.9, 124.2, 122.4, 121.7, 109.4, 106.4, 60.7, 60.6, 55.8, 54.9, 40.9, 35.2; **IR** (film) υ_{max} 3081, 1742, 1691, 1485, 1392, 1281, 945, 920, 895, 700, 696 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{27}NO_4$ + H 430.2013; Found 430.2008.



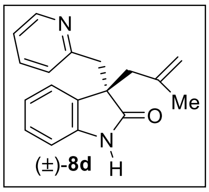
(±)-3-Allyl-3-isobutylindolin-2-one (**8a**): Compound **8a** was isolated in 89% yield (51.0 mg; 0.25 mmol) as yellow gel; R_f = 0.31 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.19-7.10 (m, 6H), 7.08-7.03 (m, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.70 (dd, J = 8.2, 3.9 Hz, 2H), 6.37-6.34 (m, 2H), 5.87-5.80 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.27 (d, J = 13.5 Hz, 1H), 3.09 (d, J = 13.5 Hz, 1H), 2.92-2.68 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.1, 141.1, 132.4, 132.0, 127.7, 123.6, 122.1, 118.8, 109.9, 53.2, 45.3, 44.1, 25.5, 24.2, 23.1; **IR** (film) υ_{max} 2085, 1742, 1615, 1412, 1402, 1392, 1105, 1001, 982, 732, 691cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}NO$ + H 230.1539; Found 230.1552.



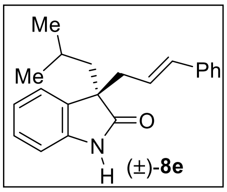
(±)-3-Allyl-3-(pyridin-2-ylmethyl)indolin-2-one (**8b**): Compound **8b** was isolated in 81% yield (150.0 mg; 0.53 mmol) as colorless gel; R$_f$ = 0.24 (50% EtOAc in hexane); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.21 (s, 1H), 8.27 – 8.22 (m, 1H), 7.49 (td, *J* = 7.7, 1.9 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.93 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.83 (td, *J* = 7.5, 1.0 Hz, 1H), 6.64 – 6.59 (m, 1H), 5.36 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 4.99 – 4.92 (m, 1H), 4.88 (dd, *J* = 10.1, 2.2 Hz, 1H), 3.26 – 3.18 (m, 2H), 2.64 – 2.60 (m, 1H), 2.56 – 2.51 (m, 1H); ^{13}C **NMR** (125 MHz, DMSO-d_6) δ 179.6, 157.0, 148.4, 141.9, 135.7, 132.6, 131.0, 127.4, 124.1, 123.7, 121.4, 120.8, 118.5, 108.8, 52.6, 43.8, 41.8; **IR** (film) υ_{max} 3085, 2895, 1782, 1615, 1492, 1385, 1281, 1100, 1091, 985, 752, 736 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{17}H_{16}N_2O$ + H 265.1335; Found 265.1344.



(±)-3-Isobutyl-3-(2-methylallyl)indolin-2-one (**8c**): Compound **8c** was isolated in 94% yield (57.2 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.33 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 9.52 (s, 1H), 7.18-7.11 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 4.57-4.46 (m, 2H), 2.66 (d, *J* = 13.1 Hz, 1H), 2.42 (d, *J* = 13.0 Hz, 1H), 1.93 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.77 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.36-1.29 (m, 4H), 0.72 (d, *J* = 6.6 Hz, 3H), 0.58 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$) δ 183.2, 141.4, 140.6, 132.5, 127.7, 123.9, 121.9, 114.8, 109.9, 53.7, 47.4, 47.0, 25.2, 24.3, 23.8, 23.3; **IR** (film) υ_{max} 2935, 1801, 1622, 1548, 1541, 1378, 1201, 900, 882, 751, 701 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{21}NO$ + Na 266.1515; Found 266.1523.

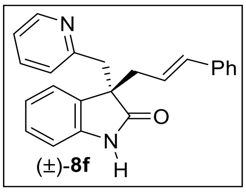


(±)-3-(2-Methylallyl)-3-(pyridin-2-ylmethyl)indolin-2-one (**8d**): Compound **8d** was isolated in 67% yield (66.6 mg; 0.25 mmol) as yellow gel; R_f = 0.28 (50% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.66-7.56 (m, 1H), 7.52-7.41 (m, 1H), 7.36-7.31 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.03 (td, *J* =7.8, 2.7 Hz, 1H), 6.94-6.87 (m, 2H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.55 (s, 2H), 3.39 (d, *J* = 13.1 Hz, 1H), 3.25 (d, *J* = 13.1 Hz, 1H), 2.85 (d, *J* = 13.4 Hz, 1H), 2.65 (d, *J* = 13.4 Hz, 1H), 1.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.8, 156.5, 148.5, 140.7, 135.9, 132.1, 131.0, 127.8, 124.7, 124.1, 121.7, 121.6, 114.9, 109.6, 54.3, 46.0, 45.0, 23.8; **IR** (film) υ_{max} 1715, 1642, 1452, 1440, 1300, 1281, 1176, 900, 882, 751 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}N_2O$ + H 279.1492; Found 279.1480.



(±)-**8e**

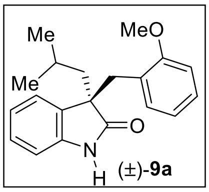
(±)-3-Cinnamyl-3-isobutylindolin-2-one (**8e**): Compound **8e** was isolated in 91% yield (69.5 mg; 0.25 mmol) as yellow gel; R_f = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.26-7.09 (m, 7H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.30 (d, *J* = 15.7 Hz, 1H), 5.86 (dt, *J* = 15.4, 7.5 Hz, 1H), 2.59 (d, *J* = 7.6 Hz, 2H), 1.98-1.92 (m, 2H), 1.40-1.27 (m, 1H), 0.70 (d, *J* = 6.7 Hz, 3H), 0.62 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.8, 140.9, 137.2, 133.9, 132.4, 128.4, 127.8, 127.2, 126.2, 123.8, 123.7, 122.2, 109.9, 53.4, 44.9, 43.3, 25.5, 24.2, 23.0; **IR** (film) υ_{max} 3025, 2897, 2752, 1758, 1612, 1305, 1158, 959, 758 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}NO$ + Na 328.1672; Found 328.1684.



(±)-**8f**

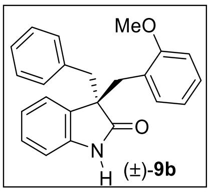
(±)-3-Cinnamyl-3-(pyridin-2-ylmethyl)indolin-2-one (**8f**): Compound **8f** was isolated in 92% yield (82.5 mg; 0.25 mmol) as colorless gel; R_f = 0.26 (50% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$-*d*) δ 8.17 (s, 1H), 7.63 – 7.35 (m, 1H), 7.29 – 7.24 (m, 1H), 7.14 – 7.06 (m, 6H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.87 (dt, *J* = 7.4, 3.4 Hz, 2H), 6.82 (dt, *J* = 8.4, 4.3 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 5.85 (dt, *J* = 15.3, 7.5 Hz, 1H), 3.42

(d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 13.5 Hz, 1H), 2.75 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.4, 156.9, 148.8, 140.9, 137.2, 135.9, 134.1, 131.1, 128.5, 127.9, 127.3, 126.3, 124.4, 124.0, 123.7, 122.0, 121.5, 109.6, 54.2, 44.5, 41.4; **IR** (film) υ_{max} 3181, 2958, 1742, 1691, 1041, 982, 768, 735 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}N_2O$ + H 341.1648; Found 341.1659.



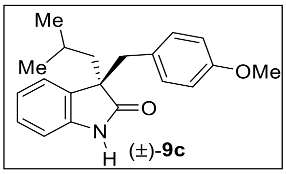
(±)-**9a**

(±)-3-Isobutyl-3-(2-methoxybenzyl)indolin-2-one (**9a**): Compound **9a** was isolated in 83% yield (64.2 mg; 0.25 mmol) as yellow gel; R_f = 0.25 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.20-8.68 (brs, 1H), 7.32-7.28 (m, 2H), 7.10-7.05 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 4.72 (s, 3H), 3.88 (d, *J* = 1.4 Hz, 4H), 2.12-1.99 (m, 1H), 0.76 (m, 3H), 0.77-0.63 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.1, 157.4, 140.8, 131.5, 129.1, 128.9, 128.7, 127.3, 121.1, 120.7, 119.7, 110.2, 109.9, 61.9, 55.3, 45.3, 38.2, 25.5, 24.3, 23.2; **IR** (film) υ_{max} 2975, 1840, 1712, 1600, 1352, 1285, 1005, 981, 975, 850, 693 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}NO_2$ + H 310.1802; Found 310.1831



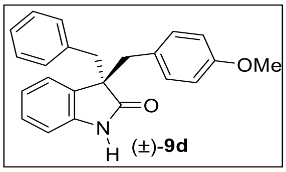
(±)-**9b**

(±)-3-Benzyl-3-(2-methoxybenzyl)indolin-2-one (**9b**): Compound **9b** was isolated in 81% yield (69.5 mg; 0.25 mmol) as yellow gel; R_f = 0.24 (30% EtOAc in hexane); **1H NMR** (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.4 Hz, 1H), 7.16 – 7.13 (m, 1H), 7.10 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.06 – 7.02 (m, 3H), 7.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.94 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.93 – 6.90 (m, 2H), 6.76 (td, *J* = 7.4, 1.1 Hz, 1H), 6.69 – 6.65 (m, 1H), 6.48 (dt, *J* = 7.6, 0.8 Hz, 1H), 3.62 (s, 3H), 3.53 (d, *J* = 13.3 Hz, 1H), 3.38 (d, *J* = 13.1 Hz, 1H), 3.18 (dd, *J* = 13.2, 7.7 Hz, 2H). **13C NMR** (125 MHz, $CDCl_3$) δ 181.1, 157.4, 140.4, 136.2, 131.5, 130.8, 130.0, 127.9, 127.6, 127.4, 126.3, 125.4, 124.8, 121.0, 119.9, 110.0, 108.9, 56.3, 54.7, 43.2, 36.1.**IR** (film) υ_{max} 1791, 1620, 1492, 1490, 1310, 1255, 1051, 981, 752, 735, 671 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{23}H_{21}NO_2$ + Na 366.1465; Found 366.1470.



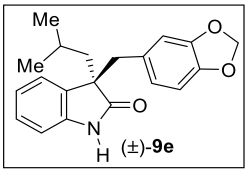
(±)-**9c**

(±)-3-Isobutyl-3-(4-methoxybenzyl)indolin-2-one (9c): Compound **9c** was in 82% yield (150 mg; 0.50 mmol) isolated as yellow gel; Rf = 0.31 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ = 7.24 (t, *J*=8.7, 1H), 7.06 (t, *J*=7.6, 1H), 6.95 (t, *J*=7.5, 1H), 6.63 (dd, *J*=15.9, 7.9, 3H), 6.53 (d, *J*=8.2, 2H), 3.57 (s, 3H), 2.88 (dd, *J*=13.0, 7.9, 2H), 1.90 – 1.75 (m, 2H), 1.18 (dt, *J*=13.9, 7.0, 1H), 0.64 (d, *J*=6.6, 3H), 0.54 (d, *J*=6.7, 3H); **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ 181.3, 158.0, 142.2, 132.0, 131.1, 128.5, 128.4, 128.0, 124.5, 121.7, 113.9, 113.1, 109.5, 55.2, 54.6, 46.0, 44.3, 25.5, 24.4, 23.4; **IR** (film) υ_{max} 3005, 2998, 1815, 1710, 1645, 1432, 1135, 1001, 932, 855 cm^{-1}; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{20}H_{23}NO_2$ + Na 332.1621; Found 332.1641.



(±)-**9d**

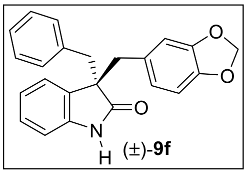
(±)-3-benzyl-3-(4-methoxybenzyl)indolin-2-one (**9d**): Compound **9d** was isolated in 87% yield (74.7 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.32 (40% EtOAc in hexane); **^{1}H NMR** (500 MHz, CDCl$_3$) δ 8.25 (d, *J* = 14.4 Hz, 1H), 7.18 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.09-7.03 (m, 5H), 6.96 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.62-6.57 (m, 2H), 6.55-6.49 (m, 1H), 3.66 (s, 3H), 3.31 (d, *J* = 13.1 Hz, 1H), 3.26 (d, *J* = 13.3 Hz, 1H), 3.17 (dd, *J* = 15.7, 13.2 Hz, 2H); **^{13}C NMR** (125 MHz, CDCl$_3$) δ 181.0, 158.1, 140.9, 135.9, 131.1, 130.9, 130.1, 127.9, 127.8, 127.7, 126.5, 124.7, 121.6, 113.1, 109.6, 56.6, 54.9, 43.3, 42.6; **IR** (film) υ_{max} 1748, 1691, 1632, 1415, 1392, 1051, 982, 931, 645 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{23}H_{21}NO_2$ + H 344.1634; Found 344.1645.



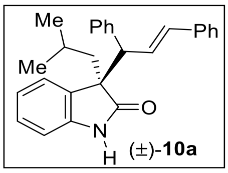
(±)-**9e**

(±)-3-(Benzo[d][1,3]dioxol-5-ylmethyl)-3-isobutylindolin-2-one (**9e**): Compound **9e** was isolated in 95% yield (76.8 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.28 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, CDCl$_3$) δ 9.20 (s, 1H), 7.22 (dd, *J* = 10.6, 7.6 Hz, 2H), 7.06-

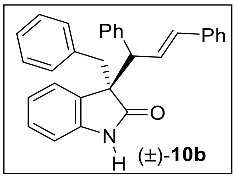
7.00 (m, 1H), 6.92-6.88 (m, 2H), 6.83-6.77 (m, 2H), 5.93 (d, *J* = 1.5 Hz, 2H), 4.59 (s, 2H), 2.09-2.01 (m, 1H), 1.91-1.84 (m, 1H), 1.73-1.66 (m, 1H), 1.02 (dd, *J* = 6.7, 1.5 Hz, 3H), 0.97 (d, *J* = 1.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.5, 147.8, 146.9, 141.6, 134.9, 130.3, 127.7, 124.3, 122.1, 120.5, 109.9, 108.2, 107.9, 100.9, 65.0, 44.4, 39.9, 25.3, 22.9, 22.1; **IR** (film) υ_{max} 3010, 1718, 1602, 1451, 1369, 1281, 1100, 901, 900, 856, 731 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{20}H_{21}NO_3$ + H 324.1594; Found 324.1618.



(±)-3-(Benzo[d][1,3]dioxol-5-ylmethyl)-3-benzylindolin-2-one (**9f**): Compound **9f** was isolated in 84% yield (100 mg; 0.28 mmol) as colorless gel; R_f = 0.32 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) 7.22 – 7.19 (m, 1H), 7.11 – 7.02 (m, 5H), 6.96 – 6.93 (m, 2H), 6.55 – 6.50 (m, 2H), 6.45 – 6.41 (m, 2H), 5.83 (d, *J* = 0.8 Hz, 2H), 3.28 (t, *J* = 13.7 Hz, 2H), 3.14 (dd, *J* = 26.0, 13.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.8, 147.8, 147.0, 146.9, 146.1, 135.8, 130.1, 127.7, 126.5, 124.6, 123.3, 121.7, 120.5, 110.4, 108.2, 107.9, 107.6, 100.9, 65.1, 56.6, 43.4; **IR** (film) υ_{max} 2741, 1849, 1715, 1632, 1432, 1391, 1105, 902, 788 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{23}H_{19}NO_3$ + Na 380.1257; Found 380.1263.

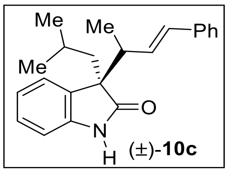


(±)-3-((E)-1,3-Diphenylallyl)-3-isobutylindolin-2-one (**10a**): Compound **10a** was isolated in 90% yield (85.8 mg; 0.25 mmol) as yellow gel (dr = 1.64:1); R_f = 0.27 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H for minor isomer), 8.41 (s, 1H for major isomer), 7.43 (d, *J* = 7.6 Hz, 1H for major isomer and 2H for minor isomer), 7.38-7.32 (m, 2H for major isomer and 2H for minor isomer), 7.29-7.20 (m, 3H for major isomer and 3H for minor isomer), 7.19- 7.09 (m, 4H for major isomer and 4H for minor isomer), 7.04-6.95 (m, 3H for major isomer and 2H for minor isomer), 6.77-6.68 (m, 2H for major isomer and 2H for minor isomer), 6.66-6.47 (m, 1H for major isomer and 1H for minor isomer), 3.79 (dd, *J* = 13.6, 9.4 Hz, 2H for major isomer), 2.15-1.94 (m, 1H for major isomer and 2 H for minor isomer), 1.96 (dd, *J* = 14.0, 7.1 Hz, 2H for minor isomer), 1.69 (dd, *J* = 14.2, 5.4 Hz, 1H for major isomer), 0.72 (d, *J* = 6.6 Hz, 3H for major isomer), 0.68 (d, *J* = 6.7 Hz, 3H for minor isomer), 0.59 (d, *J* = 6.8 Hz, 3H for major isomer), 0.56 (d, *J* = 6.8 Hz, 3H for minor isomer); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.1, 181.7, 141.8, 141.3, 139.4, 138.7, 137.3, 137.2, 133.5, 132.6, 130.9, 130.4, 129.3, 128.6, 128.4, 128.4, 128.2, 127.9, 127.8, 127.7, 127.7, 127.60, 127.4, 127.3, 126.8, 126.8, 126.5, 126.4, 125.0, 124.9, 121.9, 121.7, 109.9, 109.6, 58.0, 57.8, 57.7, 57.3, 44.4, 44.2, 25.6, 25.5, 24.4, 24.3, 23.4, 23.2; **IR** (film) υ_{max} 3315, 1816, 1742, 1685, 1601, 1482, 1315, 1117, 1061, 982, 980, 942, 901, 845, 848, 700 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{27}H_{27}NO + Na$ 404.1985; Found 404.1981.

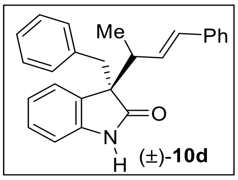


(±)-**10b**

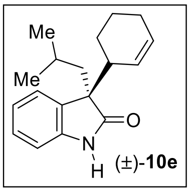
(±)-3-Benzyl-3-((E)-1,3-diphenylallyl)indolin-2-one (**10b**): Compound **10b** was isolated in 91% yield (94.5 mg; 0.25 mmol) as yellow gel (dr = 2.0:1); R_f = 0.29 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.57 (s, 1H for minor isomer), 7.56 (s, 1H for major isomer), 7.47 (d, *J* = 7.3 Hz, 1H for major isomer and 1H for minor isomer), 7.36 (t, *J* = 7.6 Hz, 2H for major isomer and 1H for minor isomer), 7.31-7.27 (m, 3H for major isomer), 7.25-7.22 (m, 2H for major isomer and 4H for minor isomer), 7.20-7.15 (m, 2H for major isomer and 2H for minor isomer), 7.13-7.10 (m, 2H for major isomer and 1H for minor isomer), 7.05-7.03 (m, 2H for major isomer and 1H for minor isomer), 6.98-6.93 (m,, 2H for major isomer and 4H for minor isomer), 6.88-6.85 (m, 3H for major isomer and 2H for minor isomer), 6.83-6.80 (m, 1H for major isomer and 2H for minor isomer), 6.76 (d, *J* = 9.4 Hz, 1H for minor isomer), 6.72-6.55 (m, 2H for major isomer and 1H for minor isomer), 6.46-6.44 (m, 1H for minor isomer), 6.40-6.38 (m, 1H for major isomer), 4.07 (dd, *J* = 16.1, 9.3 Hz, 2H for major isomer), 3.44 (d, *J* = 13.1 Hz, 1H for minor isomer), 3.34 (d, *J* = 8.0 Hz, 1H for major isomer and 2H for minor isomer), 2.91 (d, *J* = 13.1 Hz, 1H for minor isomer); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.8, 179.3, 141.3, 140.9, 139.5, 138.9, 137.2, 137.1, 136.0, 135.9, 133.7, 132.9, 130.3, 130.0, 130.0, 129.8, 129.5, 129.4, 128.9, 128.6, 128.5, 128.4, 128.2, 127.9, 127.9, 127.7, 127.7, 127.6, 127.5, 127.4, 127.4, 126.9, 126.9, 126.5, 126.5, 126.3, 125.4, 125.1, 121.8, 121.5, 109.5, 109.2, 59.7, 59.2, 56.8, 56.5, 42.3, 42.2; **IR** (film) υ_{max} 3062, 2895, 2742, 1810, 1800, 1715, 1703, 1691, 1642, 1352, 1181, 1092, 1091, 856, 852, 755, 735 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ $C_{30}H_{25}NO$ + Na 438.1828; Found 438.1830.


(±)-**10c**

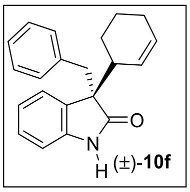
(±)-3-Isobutyl-3-((E)-4-phenylbut-3-en-2-yl)indolin-2-one (**10c**): Compound **10c** was isolated in 84% yield (67.1 mg; 0.25 mmol) as colorless gel (dr = 1.5:1); R_f = 0.26 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.46 (brs, s, 1H for major isomer & 1H for minor isomer), 7.44 (d, *J* = 8.0 Hz, 1H for major isomer and 2H for minor isomer), 7.40-7.36 (m, 2H for major isomer), 7.32-7.22 (m, 2H for major isomer and 4H for minor isomer), 7.19 (d, *J* = 7.4 Hz, 1H for major isomer and 1H for minor isomer), 7.08 (t, *J* = 7.5 Hz, 1H for major isomer and 2H for minor isomer), 7.01 (d, *J* = 7.7 Hz, 2H for major isomer), 6.50 (d, *J* = 15.8 Hz, 1H for major isomer and 1H for minor isomer), 6.29 (d, *J* = 9.2 Hz, 1H for major isomer), 6.25 (d, *J* = 9.2 Hz, 1H for minor isomer), 2.86-2.78 (m, 1H for major isomer and 1H for minor isomer), 2.00-1.92 (m, 2H for major isomer and 2H for minor isomer), 1.35-1.29 (m, 1H for major isomer and 1H for minor isomer), 0.86 (d, *J* = 6.7 Hz, 3H for major isomer and 3H for minor isomer), 0.78 (d, *J* = 6.5 Hz, 3H for major isomer and 3H for minor isomer), 0.57 (d, *J* = 6.6 Hz, 3H for major isomer and 3H for minor isomer).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.3 (2C), 141.8 (2C), 137.4 (2C), 132.0 (2C), 130.8 (2C), 130.4 (2C), 128.6 (2C), 128.4 (2C), 128.3, 127.8 (2C), 127.4 (2C), 126.3 (2C), 124.7 (2C), 122.0 (2C), 109.9 (2C), 56.7 (2C), 45.6 (2C), 44.8 (2C), 25.5 (2C), 24.2 (2C), 23.5 (2C), 15.1 (2C); **IR** (film) υ_{max} 2879, 1989, 1703, 1642, 1591, 1385, 1301, 1151, 1106, 1019, 985, 901, 738 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ $C_{22}H_{25}NO$ + H 320.2009; Found 320.2029.


(±)-**10d**

(±)-3-Benzyl-3-((E)-4-phenylbut-3-en-2-yl)indolin-2-one (**10d**): Compound **10d** was isolated in 76% yield (67.2 mg; 0.25 mmol) as colorless foam (dr = 2.0:1); R_f = 0.29 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.72 (s, 1H for major isomer and 1H for minor isomer), 7.34-7.31 (m, 2H for major isomer and 2H for minor isomer), 7.28-7.24 (m, 3H for major isomer and 2H for minor isomer), 7.20-7.15 (m, 1H for major isomer and 2H for minor isomer), 7.12 (td, *J*=7.6, 1.4, 2H for major isomer), 7.10-7.04 (m, 2H for minor isomer), 7.00-6.93 (m, 3H for major isomer and 3H for minor isomer), 6.85-6.83 (m, 2H for major isomer and 2H for minor isomer), 6.60 (d, *J*=7.5, 1H for major isomer and 1H for minor isomer), 6.48 (d, *J*=15.7, 1H for major isomer and 1H for minor isomer), 6.30 (d, *J*=9.4, 1H for major isomer), 6.26 (d, *J*=9.4, 1H for minor isomer), 3.29 (d, *J*=13.0, 1H for major isomer and 1H for minor isomer), 3.08 (d, *J*=13.1, 1H for major isomer and 1H for minor isomer), 3.10-2.88 (m, 1H for major isomer and 1H for minor isomer), 1.10 (d, *J*=6.9, 3H for major isomer and 3H for minor isomer); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.2 (2C), 141.1 (2C), 137.4 (2C), 136.2 (2C), 131.3 (2C), 131.0 (2C), 130.9 (2C), 129.9 (2C), 128.5 (2C), 127.9 (2C), 127.6 (2C), 127.2 (2C), 126.4 (2C), 126.2 (2C), 124.0 (2C), 121.9 (2C), 109.3 (2C), 58.4 (2C), 45.5 (2C), 41.9 (2C), 16.1 (2C); **IR** (film) υ_{max} 3062, 2895, 2742, 1810, 1800, 1715, 1703, 1691, 1642, 1352, 1181, 1092, 1091, 856, 852, 755, 735 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{25}H_{23}NO + H$ 354.1852; Found 354.1873.



(±)-3-(Cyclohex-2-en-1-yl)-3-isobutylindolin-2-one (**10e**): Compound **10e** was isolated in 92% yield (62.0 mg; 0.25 mmol) as colorless gel (dr = 2.0:1); R_f = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.36 (s, 1H for minor isomer), 9.24 (s, 1H for major isomer), 7.23-7.18 (m, 2H for major isomer), 7.17 -7.12 (m, 2H for minor isomer), 7.01 (q, *J* = 8.0 Hz, 1H for major isomer and 1H for minor isomer), 6.94 (t, *J* = 7.0 Hz, 1H for major isomer and 1H for minor isomer), 5.86-5.79 (m, 1H for major isomer), 5.76 (d, *J* = 10.9 Hz, 1H for major isomer), 5.63 (dt, *J* = 10.2, 3.3 Hz, 1H for minor isomer), 5.53 (d, *J* = 10.5 Hz, 1H for minor isomer), 2.66-2.61 (m, 1H for major isomer and 1H for minor isomer), 2.04 (d, *J* = 6.5 Hz, 1H for minor isomer), 2.01 (d, *J* = 6.4 Hz, 1H for major isomer), 1.97 (d, *J* = 6.7 Hz, 1H for minor isomer), 1.94-1.89 (m, 1H for major isomer and 1H for minor isomer), 1.57- 1.50 (m, 1H for major isomer and 1H for minor isomer), 1.42 (dd, *J* = 14.7, 5.1 Hz, 1H for major isomer and 1H for minor isomer), 1.38-1.35 (m, 1H for major isomer and 1H for minor isomer), 1.33-1.29 (m, 1H for major isomer), 0.76 (t, *J* = 6.2 Hz, 3H for major isomer and 3H for minor isomer), 0.58 (t, *J* = 6.0 Hz, 3H for major isomer and 3H for minor isomer); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.9 (2C), 141.5, 141.4, 132.3, 131.8, 130.8, 129.4 , 127.54, 127.52, 126.4, 125.9, 124.5, 124.2, 121.9, 121.8, 109.8, 109.4, 56.0, 55.9, 44.9, 44.2, 43.6, 43.1, 25.5, 25.4, 25.1, 25.0, 24.2, 24.2, 23.8 (2C), 23.5, 23.4, 22.5, 21.8; **IR** (film) υ_{max} 2752, 1881, 1719, 1609, 1431, 1387, 1111, 998, 851, 835, 750, 735 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ $C_{18}H_{23}NO$ + Na 292.1672; Found 292.1696.



(±)-**10f**

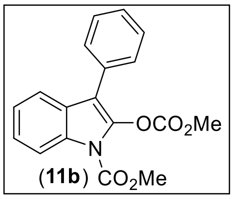
(±)-3-Benzyl-3-(-cyclohex-2-en-1-yl)indolin-2-one (**10f**): Compound **10f** was isolated in 84% yield (63.7 mg; 0.25 mmol) as colorless gel (dr = 2.0:1); R_f = 0.26 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (brs, s, 1H for major isomer and 1H for minor isomer), 7.30 (dd, *J* = 10.1, 7.3 Hz, 1H for major isomer and 1H for minor isomer), 7.10 (t, *J* = 7.6 Hz, 1H for major isomer and 1H for minor isomer), 7.02-6.93 (m, 4H for major isomer and 4H for minor isomer), 6.83-6.79 (m, 2H for major isomer and 2H for minor isomer), 6.61 (dd, *J* = 10.1, 7.7 Hz, 1H for major isomer and 1H for minor isomer), 5.93-5.87 (m, 2H for major isomer), 5.65-5.61 (m, 1H for minor isomer), 5.47 (dt, *J* = 10.4, 2.0 Hz, 1H for minor isomer), 3.29 (d, *J*=12.8, 1H for major isomer), 3.26-3.16 (m, 1H for major isomer and 2H for minor isomer), 2.89-2.81 (m, 1H for major isomer and 1H for minor isomer), 1.96-1.69 (m, 3H for major isomer and 3H for minor isomer), 1.63- 1.42 (m, 2H for major isomer and 3H for minor isomer), 1.08-0.98 (m, 1H for major isomer); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.6, 180.5, 141.1, 140.9, 136.1, 135.9, 131.1, 131.0, 130.7, 129.9, 129.9, 129.3, 127.7, 127.6, 127.5, 127.5, 126.7, 126.3, 125.8 (2C), 124.8, 124.6, 121.9, 121.8, 109.3, 109.0, 58.1, 58.0, 43.2, 42.8, 41.4, 40.7, 25.1, 25.1, 24.6, 24.6, 22.5, 21.7; **IR** (film) υ_{max} 2951, 1732, 1618, 1517, 1491, 1452, 1389, 1300, 1205, 900, 882, 855, 762, 705, 691 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ $C_{21}H_{21}NO$ + Na 326.1515; Found 326.1535.

For the synthesis of compounds **11a**, see reference 13a.

To a stirred mixture of ArBr (11.55 mmol; 2.1 equiv) and Mg turnings (334 mg, 13.75 mmol, 2.5 equiv) in THF (20 mL) was added pinch of iodine and above mixture was stirred till color of the solution change to colorless. Above reaction mixture was stirred for 4 h on 25 ºC. In another flame dried round-bottom flask, isatin (800 mg, 5.50 mmol, 1.0 equiv) taken in dry THF and early solution was added to it via cannula at 0 ºC and stirred on 25 ºC. Upon consumption of starting material (monitored by TLC) the reaction mixture was diluted by water (10 mL) and extracted by EtOAc, organic layer washed by saturated brine (10 mL). The collected organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and dried by using high vacuum pump.

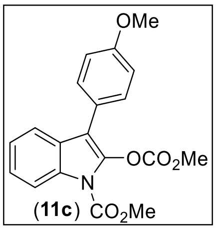
In an oven-dried round-bottom flask was charged with crude product in DCM under nitrogen atmosphere at 0 ºC. Triethyl silane (1.13 g; 16.5 mmol; 3.0 equiv.) was adeed to the solution. To that reaction mixture TFA (3.2 g; 27.5 mmol; 5.0 equiv) was added drop-wise over a period of 5 minutes at 0 ºC and stirring was continued for 12 h. Upon completion of the reaction (Judged by TLC analysis) 5% (w/v) aqueous solution of sodium citrate was added drop wise to make the pH 5 of the mixture. The organic layer was separated and aqueous layer was washed with CH_2Cl_2 (2 X 30 mL). The combined organic layer were dried over anhydrous sodium sulphate and concentrated under reduced pressure to afford the desired product, which was used for next step without further purification.

In an oven-dried round-bottom flask was charged with crude product in dry THF under nitrogen atmosphere at 0 ºC. Then Triethyl amine (2.1 mL; 16.5 mmol; 3.0 equiv.) was adeed to the solution. After 5 minutes of stirring methyl chloroformate (0.92 mL; 12.10 mmol; 2.2 equiv.) was added drop-wise over a period of 2 minutes at 0 ºC and stirring was continued. Upon completion of the reaction (judged by TLC analysis) diluted with EtOAc (100 mL) and quenched with H_2O. The whole reaction mixture was taken in a separetory funnel to separate the organic layer. The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure. The crude mixture was purified by column chromatography using EtOAc and hexane mixture as eluent to afford the desired product (**11**)

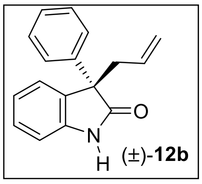


(**11b**)

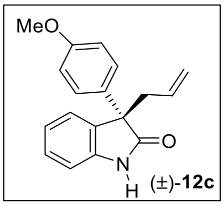
Methyl 2-((methoxycarbonyl)oxy)-3-phenyl-1H-indole-1-carboxylate (**11b**): 60% yield over 3 steps (5.50 mmol scale) of (**11b**) as colorless solid. R_f = 0.30 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) 8.11 (d, J = 8.3 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.58 – 7.54 (m, 2H), 7.47 (dd, J = 8.4 Hz, 6.7, 2H), 7.41 – 7.34 (m, 2H), 7.32 – 7.26 (m, 1H), 4.05 (s, 3H), 3.93 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 150.8, 136.9, 131.9, 130.5, 129.0, 128.8, 127.7, 126.5, 125.0, 123.8, 119.8, 115.5, 110.9, 56.3, 53.9; **IR** (film) υ_{max} 3058, 1839, 1718, 1610, 1482, 1439, 1414, 1293, 1258, 1216, 1203, 980, 914, 902, 855, 849, 800, 715 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_5$ + Na 348.0842; Found 348.0856. MP = 114-117 ºC.



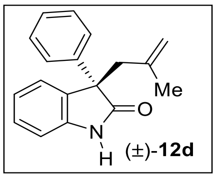
Methyl 2-((methoxycarbonyl)oxy)-3-(4-methoxyphenyl)-1H-indole-1-carboxylate (**11c**): 52% yield over 3 steps (5.50 mmol scale) of (**11c**) as colorless solid. R_f = 0.34 (30% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) 8.10 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.36 (td, *J* = 1.4, 7.2 Hz, 1H), 7.28 (td, *J* = 1.2, 7.4 Hz, 1H), 7.05 – 6.91 (m, 2H), 4.04 (s, 3H), 3.92 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 153.2, 150.8, 136.7, 131.9, 130.2, 126.8, 124.9, 123.7, 122.7, 119.7, 115.5, 114.3, 110.6, 56.2, 55.3, 53.9; **IR** (film) υ_{max} 3086, 1819, 1743, 1623, 1433, 1429, 1373, 1311, 1284, 1263, 906, 888, 821, 735 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{17}NO_6$ + Na 378.0948; Found 378.0931. MP = 97-100 ºC.



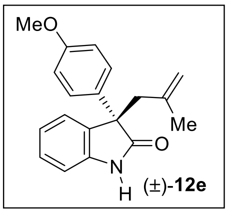
(±)-3-Allyl-3-phenylindolin-2-one (**12b**): Compound **12b** was isolated in 85% yield (52.9 mg; 0.25 mmol) as colorless gel; R_f = 0.31 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 10.8, 6.5 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 5.57-5.45 (m, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 3.17-3.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.1, 141.2, 139.4, 132.5, 132.3, 128.6, 128.2, 127.4, 127.1, 125.3, 122.5, 119.4, 110.3, 57.1, 41.6; **IR** (film) υ_{max} 3093, 1753, 1682, 1601, 1493, 1476, 1318, 1303, 1287, 1156, 1098, 853, 735, 706 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{17}H_{15}NO$ + H 250.1226; Found 250.1219.



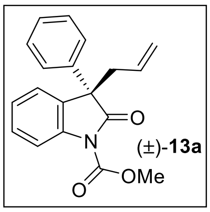
(±)-3-Allyl-3-(4-methoxyphenyl)indolin-2-one (**12c**): Compound **12c** was isolated in 83% yield (58.0 mg; 0.25 mmol) as colorless gel; R$_f$ = 0.29 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.02 (brs, 1H), 7.29-7.17 (m, 4H), 7.05 (t, *J*= 7.36 Hz, 1H), 6.91 (d, *J*= 7.73 Hz, 1H), 6.83 (d, *J*= 8.85, 2H), 5.50-5.40 (m, 1H), 5.04 (d, *J*= 17 Hz, 1H), 4.92 (d, *J*= 10.06 Hz, 1H), 3.75 (s, 3H), 3.05-2.96 (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) υ_{max} 1841, 1733, 1639, 1591, 1532, 1481, 1444, 1261, 1200, 1181, 1103, 1061, 982, 907, 701, 693 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{18}H_{17}NO_2$ + H 280.1332; Found 280.1347.



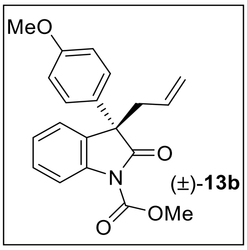
(±)-3-(2-methylallyl)-3-phenylindolin-2-one (**12d**): Compound **12d** was isolated in 82% yield (54.0 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.26-7.20 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 4.67-4.54 (m, 2H), 3.26 (d, *J* = 13.3 Hz, 1H), 2.95 (d, *J* = 13.3 Hz, 1H), 1.39 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 181.3, 141.3, 140.8, 140.4, 132.4, 128.6, 128.2, 127.4, 126.8, 125.9, 122.2, 115.4, 110.3, 57.3, 45.1, 23.7; **IR** (film) υ_{max} 2652, 1841, 1713, 1642, 1592, 1401, 1205, 1009, 850, 751 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{18}H_{17}NO$ + H 264.1383; Found 264.1404.



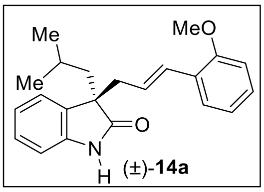
(±)-3-(4-Methoxyphenyl)-3-(2-methylallyl)indolin-2-one (**12e**): Compound **12e** was isolated in 87% yield (63.8 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.24 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 7.33-7.29 (m, 2H), 7.24-7.18 (m, 2H), 7.07-7.03 (m, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.85-6.81 (m, 2H), 4.64-4.61 (m, 2H), 3.75 (s, 3H), 3.22 (d, *J* = 13.3 Hz, 1H), 2.90 (d, *J* = 13.3 Hz, 1H), 1.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6, 158.8, 141.4, 140.9, 132.5, 132.4, 128.1, 127.9, 125.8, 122.2, 115.3, 113.9, 110.3, 56.6, 55.3, 45.2, 23.7; **IR** (film) υ_{max} 3019, 1810, 1705, 1621, 1328, 1141, 1001, 781, 755, 739 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{19}H_{19}NO_2$ + H 294.1489; Found 294.1499.



(±)-**Methyl-3-allyl-2-oxo-3-phenylindoline-1-carboxylate** (**13a**): Compound **13a** was isolated in 69% yield (53.0 mg; 0.25 mmol) as yellow gel; R_f = 0.28 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.41-7.35 (m, 1H), 7.34-7.22 (m, 7H), 5.46-5.23 (m, 1H), 5.07 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.96 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.96 (s, 3H), 3.17 (dd, *J* = 13.6, 8.1 Hz, 1H), 3.01 (dd, *J* = 13.6, 6.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.3, 151.5, 139.5, 139.1, 131.7, 130.4, 128.7, 128.7, 127.8, 127.1, 125.1, 124.8, 120.1, 115.3, 56.9, 53.9, 42.5; **IR** (film) υ_{max} 1816, 1700, 1610, 1598, 1491, 1317, 1005, 991, 941, 800, 706 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{19}H_{17}NO_3$ + Na 330.1101; Found 330.1128.

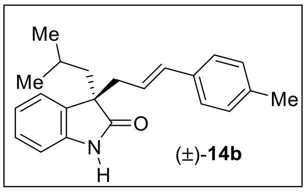


(±)-**Methyl-3-allyl-3-(4-methoxyphenyl)-2-oxoindoline-1-carboxylate** (**13b**): Compound **13b** was isolated in 70% yield (59.0 mg; 0.25 mmol) as colorless gel; R_f = 0.30 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.39-7.34 (m, 1H), 7.25-7.20 (m, 4H), 6.83-6.81 (m, 2H), 5.43-5.33 (m, 1H), 5.05 (dd, *J* = 17.0, 1.8 Hz, 1H), 4.95 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.96 (s, 3H), 3.75 (s, 3H), 3.12 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.99-2.94 (m, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.5, 159.1, 151.6, 139.4, 131.8, 131.2, 130.6, 128.6, 128.3, 125.1, 124.8, 119.9, 115.3, 114.0, 56.2, 55.3, 53.9, 42.6; **IR** (film) υ_{max} 3305, 1742, 1701, 1618, 1597, 1315, 1106, 981, 945, 785, 730 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{20}H_{19}NO_4$ + Na 360.1206; Found 360.1223.



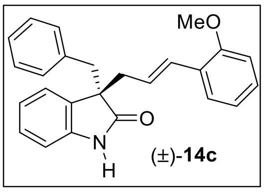
(±)-14a

(±)-(*E*)-3-Isobutyl-3-(3-(2-methoxyphenyl)allyl)indolin-2-one (**14a**): Compound **14a** was isolated in 34% yield (28.5 mg; 0.25 mmol) as yellow gel; R_f = 0.27 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.21 (d, *J* = 7.7 Hz, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.68 (d, *J* = 15.8 Hz, 1H), 5.97-5.89 (m, 1H), 3.75 (s, 3H), 2.71-2.62 (m, 2H), 2.02 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.91 (dd, *J* = 13.9, 5.4 Hz, 1H), 1.47-1.36 (m, 1H), 0.77 (dd, *J* = 6.7, 1.4 Hz, 3H), 0.67 (dd, *J* = 6.7, 1.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.2, 156.4, 141.1, 132.6, 128.7, 128.6, 128.2, 127.7, 126.8, 126.5, 124.5, 123.9, 122.1, 120.6, 110.9, 109.9, 53.5, 44.9, 43.7, 25.6, 24.2, 23.1; **IR** (film) υ_{max} 1719, 1698, 1608, 1498, 1403, 1115, 1101, 958, 913, 705, 701 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{22}H_{25}NO_2$ + H 336.1958; Found 336.1985.



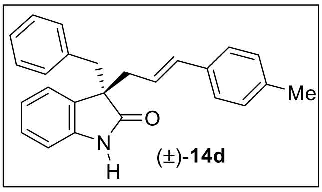
(±)-14b

(±)-(*E*)-3-Isobutyl-3-(3-(p-tolyl)allyl)indolin-2-one (**14b**): Compound **14b** was isolated in 46% yield (36.7 mg; 0.25 mmol) as colorless gel; R_f = 0.30 (20% EtOAc in hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.24-7.18 (m, 2H), 7.10-7.07 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 5.89-5.81 (m, 1H), 2.62-2.58 (m, 2H), 2.31 (s, 3H), 1.99 (dd, *J* = 13.9, 7.6 Hz, 1H), 1.88 (dd, *J* = 14.0, 5.4 Hz, 1H), 1.42-1.86 (m, 1H), 0.75-0.67 (m, 3H), 0.65 (dd, *J* = 6.7, 1.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.8, 140.9, 136.9, 134.5, 133.7, 132.4, 129.1, 128.4, 126.1, 123.8, 122.6, 122.1, 109.9, 53.5, 44.9, 43.3, 25.5, 24.2, 23.1, 21.1; **IR** (film) υ_{max} 2889, 1715, 1642, 1598, 1208, 1145, 966, 872, 800, 735 cm^{-1}. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ $C_{22}H_{25}NO$ + H 320.2009; Found 320.2030.



(±)-**14c**

(±)-(*E*)-3-Benzyl-3-(3-(2-methoxyphenyl)allyl)indolin-2-one (**14c**): Compound **14c** was isolated in 38% yield (35.1 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.24 (20% EtOAc in hexane); ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.60 (s, 1H), 7.24-7.09 (m, 4H), 7.05-7.00 (m, 4H), 6.93 (d, *J* = 6.8 Hz, 2H), 6.83-6.68 (m, 4H), 5.99-5.91 (m, 1H), 3.73 (s, 3H), 3.22 (d, *J* = 13.1 Hz, 1H), 3.14 (d, *J* = 13.2 Hz, 1H), 2.83 (d, *J* = 7.5 Hz, 2H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 181.4, 156.5, 140.9, 136.1, 131.4, 130.1, 128.8, 128.3, 127.8, 127.7, 126.8, 126.5, 126.5, 124.6, 124.4, 121.9, 120.6, 110.9, 109.7, 55.5, 55.2, 42.8, 41.3; **IR** (film) υ$_{max}$ 2813, 1714, 1608, 1491, 1435, 1395, 1298, 1108, 988, 861, 721 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ $C_{25}H_{23}NO_2$ + H 370.1802; Found 370.1824.



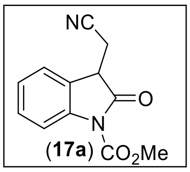
(±)-**14d**

(±)-(*E*)-3-Benzyl-3-(3-(p-tolyl)allyl)indolin-2-one (**14d**): Compound **14d** was isolated in 52% yield (46.0 mg; 0.25 mmol) as yellow gel; R$_f$ = 0.26 (20% EtOAc in hexane); ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.74 (brs, s, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.18-7.06 (m, 9H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.97-5.89 (m, 1H), 3.26 (d, *J* = 12.9 Hz, 1H), 3.18 (d, *J* = 13.2 Hz, 1H), 2.85 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 181.5, 140.9, 137.0, 135.9, 134.5, 133.9, 131.4, 130.1, 129.2, 127.9, 127.7, 126.5, 126.2, 124.3, 122.8, 121.9, 109.8, 55.2, 42.9, 40.9, 21.2; **IR** (film) υ$_{max}$ 2987, 1841, 1701, 1618, 1451, 1350, 1191, 1168, 980, 914, 735, 732 cm^{-1}. **HRMS** (ESI-TOF) m/z: [M + H]$^+$ $C_{25}H_{23}NO$ + H 354.1852; Found 354.1879.

Synthesis of *N*-Acyl 2-Oxindole 17a: To a stirred mixture of isatin (10.0 mmol; 1.0 equiv) in PhMe (20 mL) was added stabilized witting salt (10.0 mmol; 1.05 equiv.) and above mixture was stirred till color of the solution change. Above reaction mixture was stirred for 12 h on 25 ºC. Upon consumption of starting material (monitored by TLC) the reaction mixture was concentrated under reduced pressure and dried by using high vacuum pump.

The crude material was directly dissolved in 10 mL of CH_2Cl_2. To that solution, Et_3N (2.7 mL, 21.0 mmol, 2.1 equiv) followed by DMAP (2.64 g, 20.0 mmol, 2.0 equiv) and corresponding chloroformate (1.5 mL, 20.0 mmol, 2.0 equiv) was added at 0 ºC, reaction mixture was stirred on 25 ºC. TLC analysis showed the complete consumption starting material. Then the organic layer was diluted by CH_2Cl_2 and washed with water (10 mL). The collected organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and dried by using high vacuum pump.

The crude material was dissolved in CH_3COOH (5 mL) open flask. To that Zn (1.37 g, 21.0 mmol, 20.0 equiv) and stirred over 25 °C for 4 h. Upon completation of the reaction (judged by TLC analysis), filtered through celite, and concentrated under reduced pressure. The crude reaction mixture diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ solution (10 mL), and brine. The extracted organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and dried by using high vacuum pump. The crude product was purified by flash chromatography using (20%-40% EtOAc in hexanes) mixture as eluents to afford the desired product **17**.



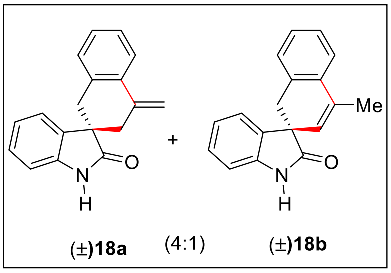
(**17a**)

Methyl 3-(cyanomethyl)-2-oxoindoline-1-carboxylate (**17a**): 70% yield over 3 steps (1.36 mmol scale) of (**17**) as orange gel. R_f = 0.28 (30% EtOAc in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.37 – 7.33 (m, 1H), 7.22 – 7.20 (m, 1H), 3.96 (s, 3H), 3.83 – 3.77 (m, 1H), 3.07 (dd, *J* = 16.9, 4.7 Hz, 1H), 2.73 (dd, *J* = 16.9, 8.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.63, 151.10, 139.81, 129.96, 125.53, 124.54, 124.12, 116.71, 115.74, 54.33, 42.23, 19.62. **IR** (film) υ_{max} 2891, 2261, 2113, 2105, 1643, 1608, 1491, 1435, 1361, 1245, 1215, 1008, 1003, 945, 913, 716, 705 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{10}N_2O_3$ + Na 253.0584; Found 253.0597.

Synthesis of Spiro 2-Oxindole 18a-b:

An oven dried 10 mL Schlenk flask equipped with a stir bar was charged with NaH (1.2 equiv of 0.71 mmol, 17 mg) and $Pd(OAc)_2$ (1.0 mol %, 0.005 mmol, 1.3 mg). To above flask 2 mL of dry toluene was added, and allyl alcohol (1.2 equiv, 0.71 mmol, 49 µL) followed by

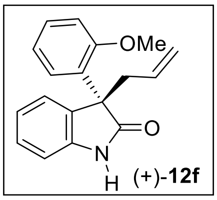
N-Moc-2-oxindole 1f (1.0 equiv, 0.59 mmol) was added in that order. The vessel was capped and wrapped in parafilm, and the system was completely sealed over argon and allowed to react for 24 h at 90 °C. Completion of reaction confirmed by TLC then reaction mixture was diluted with 5% EtOAc in hexanes and subjected to silica gel chromatography (5% - 30% EtOAc in Hexanes) to yield the pure product.



(±)-4'-methylene-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (18a) & (±)-4'-methylene-3',4'-dihydro-1'H-spiro[indoline-3,2'-naphthalen]-2-one (18b): Compound **18a** & **18b** were isolated in 71% combine yield(67.2 mg; 0.25 mmol) as colorless foam (ratio of **18a:18b** = 4:1); R*f* = 0.31 (20% EtOAc in hexane); ^{1}H NMR (500 MHz, DMSO-d6) δ 7.82 (dd, J = 7.7, 1.6 Hz, 4H for major isomer), 7.37 – 7.35 (m, 1H for minor isomer), 7.30 – 7.27 (m, 2H for minor isomer), 7.26 – 7.23 (m, 4H for major isomer), 7.23 – 7.17 (m, 4H for major isomer), 7.14 (d, J = 1.3 Hz, 2H for minor isomer), 7.13 – 7.10 (m, 8H for major isomer), 6.91 (d, J = 7.7 Hz, 4H for major isomer), 6.86 (d, J = 7.8 Hz, 1H for minor isomer), 6.72 (d, J = 1.1 Hz, 1H for minor isomer), 6.70 (dd, J = 7.6, 1.1 Hz, 4H for major isomer), 6.51 (d, J = 1.1 Hz, 1H for minor isomer), 6.49 (dd, J = 7.6, 1.2 Hz, 4H for major isomer), 5.78 (d, J = 1.9 Hz, 4H for major isomer), 5.53 (s, 1H for minor isomer), 4.97 (d, J = 1.9 Hz, 4H for major isomer), 3.22 (d, J = 16.7 Hz, 4H for major isomer), 2.83 (d, J = 14.4 Hz, 4H for major isomer), 2.77 (d, J = 7.4 Hz, 1H for major isomer), 2.73 (d, J = 18.8 Hz, 1H for minor isomer), 2.65 (dd, J = 16.7, 2.2 Hz, 4H for major isomer), 2.36 (dd, J = 14.4, 2.2 Hz, 4H for major isomer), 2.05 (s, 3H for minor isomer); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 181.3, 180.7, 141.2, 140.7, 139.2, 134.4, 134.3, 133.8, 133.6, 133.3, 133.1, 132.9, 130.1, 128.9, 128.9, 128.5, 128.4, 128.2, 127.6, 127.2, 124.9, 124.1, 124.9, 123.6, 123.4, 122.2, 121.8, 112.5, 110.2, 110.1, 50.0, 47.4, 37.4, 37.3, 19.3. IR (film) υmax 1841, 1658, 1491, 1473, 1468, 1373, 1318, 1263, 1207, 931, 908, 733, 721 cm-^{1}. **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ $C_{18}H_{15}NO$ + Na 284.1046; Found 284.1071.

Procedure for catalytic Enantioselective deacylative alkylation: In an oven-dried sealed tube charged with solvent (2.0 mL) and degassed by using nitrogen balloon at room temperature over a period of 5 minutes, followed by 2.5 mol% of $Pd_2(dba)_3$ and 7.5 mol% of (*S*,*S*)-**L** were added to it and stirring was continued for 15 minutes to make the complex mixture. In another vessel carbonate **11d** (40 mg, 0.13 mmol; 1.0 equiv.) and allyl alcohol (13.4 μL; 0.20 mmol; 1.5 equiv.) were dissolved in dry degassed (2.0 mL) solvent and then purged with N_2 for 5 minutes at 25 ºC. Afterward, NaH [60% suspension in mineral oil] (8.8 mg; 0.22 mmol; 2.0 equiv.) was added at once then the resulting solution was added drop-wise to the complex solution and stirring was continued for 10 h at 25 ºC. After complete consumption of starting material (monitored by TLC) the reaction mixture was concentrated and purified by column chromatography to afford the desired enantioenriched compound.

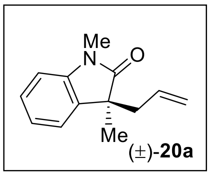
Enantiometric excess of pure compound was determined via HPLC analysis using a Chiralpak OD-3 column; solvent: hexane/2-propanol = 80/20; flow rate: 1.00 mL/min; detection: at 254 nm): t_R major = 9.38 min, t_R minor = 6.29 min. $[\alpha]_D^{24.0}$ = +30.8 (c = 0.1, $CHCl_3$ for 23% ee).



(+)-**12f**

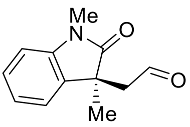
(+)-5-Methoxy-1,3-dimethyl-3-(2-methylallyl)indolin-2-one (**12f**): Yield 78%. The product was obtained as yellowish oil, R_f = 0.42 (40% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.30 (ddd, *J* = 8.1, 7.4, 1.8 Hz, 1H), 7.16 (td, *J* = 7.6, 1.3 Hz, 1H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 2H), 6.83 (dd, *J* = 8.1, 1.2 Hz, 1H), 5.51 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.08 (m, 1H), 4.97 (m, 1H), 3.49 (s, 3H), 3.10 – 2.99 (m, 2H); 13C NMR (125 MHz, $CDCl_3$) δ 181.7, 157.2, 141.5, 134.0, 131.7, 129.3, 128.8, 127.5, 127.4, 122.9, 122.0, 120.9, 119.2, 112.4, 108.9, 55.6, 54.3, 40.7, 29.7; IR (film) υ_{max} 2940, 2897, 1700, 1650, 1499, 1370, 1041, 777 cm-1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}NO + H$ 280.1332; Found 280.1321; MP = 114-117 ºC.

***N*-Methylation of 2-oxindole 12a**: A flame-dried 10 mL Schlenk flask equipped with a stir bar was charged with NaH (1.2 equiv of 0.26, 8 mg) and (±)-**19a** in 3 mL of dry DMF. To this solution was added MeI in one portion at 0 ºC. After completion of the reaction as determined by TLC (2 h), the reaction mixture was diluted with water and 10 mL EtOAc. The reaction was then extracted with EtOAc (10 mL X 2). All the organic extracts were evaporate under reduced pressure and the crude materials were purified via silica gel chromatography (5% - 30% EtOAc in hexanes) to yield the pure product.



(±)-**20a**

(*S*)-3-Allyl-1,3-dimethylindolin-2-one (±)-**20a**: 92% yield. The product was obtained as colorless gel, R*f* = 0.33 (10% EtOAc in hexane). ^{1}**H NMR** (500 MHz $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.22 (ddd, *J* = 7.5, 1.3, 0.6 Hz, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (dt, *J* = 7.7, 0.8 Hz, 1H), 5.47 (dddd, *J* = 17.0, 10.1, 7.6, 7.0 Hz, 1H), 5.04 – 4.97 (m, 1H), 4.94 (ddt, *J* = 10.1, 1.8, 0.9 Hz, 1H), 3.22 (s, 3H), 2.59 – 2.49 (m, 2H), 1.39 (s, 3H); 13C NMR (125 MHz, $CDCl_3$) δ 180.2, 143.2, 133.6, 132.6, 127.8, 122.9, 122.3, 118.6, 107.9, 48.5, 42.5, 26.1, 22.7; IR (film) υ_{max} 2929, 1722, 1658, 1614, 1590, 1522, 1490, 1470, 1340, 1244, 1044, 814 cm-1.

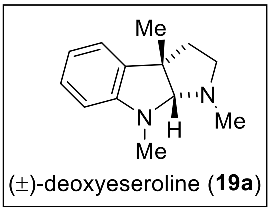


(±)-**20b**

General Procedure for (*S*)-2-(1,3-dimethyl-2-oxoindolin-3-yl)acetaldehyde (20b): To a solution of alkene (**20a**) in dioxane:water were added DABCO (5.0 equiv.), $NaIO_4$ (10.0 equiv) and OsO_4 (0.1 equiv) sequentially, and the resulting reaction mixture was stirred for 8 h at rt. Completion of reaction was confirmed by TLC then diluted with EtOAc (10 mL) and saturated $Na_2S_2O_3$ were added and separated. Combined organic layers were dried over brine and Na_2SO_4 and then concentrated on low and high vacuum. Further purification done by silica gel column chromatography to afford pure aldehyde.

(*S*)-2-(1,3-Dimethyl-2-oxoindolin-3-yl)acetaldehyde (±)-**20b**: Yield 80%.The product was obtained as yellowish oil, R_f = 0.23 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ

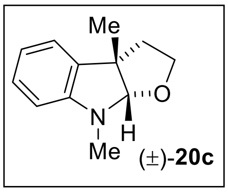
9.52 (dd, *J* = 1.9, 1.3 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.19 (ddd, *J* = 7.3, 1.3, 0.6 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (dt, *J* = 7.9, 0.8 Hz, 1H), 3.27 (s, 3H), 2.98 (dd, *J* = 6.1, 1.6 Hz, 2H), 1.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.8, 179.6, 143.2, 132.8, 128.3, 122.7, 122.4, 108.4, 50.6, 45.0, 26.4, 24.0; IR (film) υ_{max} 2988, 1722, 1691, 1487, 1220, 981 cm^{-1}.



(±)-deoxyeseroline (**19a**)

(3a*R*,8a*S*)-1,3a,8-Trimethyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole **(±)-19a**: Yield 75%.The product was obtained as yellowish gel, R_f = 0.10 (EtOAc in hexane). 1H NMR (400 MHz, $CDCl_3$) δ 7.13 (td, *J* = 7.6, 1.3 Hz, 1H), 7.05 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.73 (td, *J* = 7.4, 1.0 Hz, 1H), 6.46 (dd, *J* = 7.9, 0.9 Hz, 1H), 4.15 (s, 1H), 2.99 (s, 3H), 2.81 – 2.74 (m, 1H), 2.72 – 2.66 (m, 1H), 2.05 – 1.96 (m, 2H), 1.50 (s, 3H); 13C NMR (100 MHz, $CDCl_3$) δ 151.9, 136.7, 127.7, 122.2, 117.5, 106.6, 97.6, 53.3, 52.7, 40.9, 38.5, 36.3, 29.7, 27.4.; IR (film) υ_{max} 2944, 2890, 1544, 1450, 1322, 1053, 888 cm-1. HRMS (ESI) m/z 203.1520 [M + H]+; calculated for $[C_{18}H_{17}NO_2]^+$: 203.1543.

Synthesis of Furoindolne (±)-20c from aldehyde 20b: In a flame-dried round-bottom flask, aldehyde **20b** (0.32 mmol, 1 equiv) was taken in dry THF (8 mL) under inert atmosphere at 25 °C. To this reaction mixture was added $LiAlH_4$ (1.64 mmol, 5.0 equiv) portion wise over 5 min, and the reaction mixture was allowed to stir vigorously at 25 °C for 40 min. Upon completion of the reaction as judged by TLC analysis, the reaction mixture was quenched by consecutive addition of EtOAc (5 mL) and saturated aqueous $NaHCO_3$ solution. Then the mixture was filtered through a Celite pad and washed with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (5 - 10% EtOAc in hexane as eluents) to afford Furoindolne **(±)-20c**.



(±)-**20c**

(3a*R*,8a*R*)-3a,8-Dimethyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (±)-**20c**: Yield 89%.The product was obtained as colorless gel, R_f = 0.45 (20% EtOAc in hexane). **1H NMR** (400 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.6, 1.3 Hz, 1H), 7.09 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.73 (td, *J* = 7.3, 1.0 Hz, 1H), 6.42 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.12 (d, *J* = 0.6 Hz, 1H), 4.00 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 3.51 (ddd, *J* = 11.1, 8.6, 5.2 Hz, 1H), 2.98 (s, 3H), 2.18 (ddd, *J* = 11.8, 5.2, 1.6 Hz, 1H), 2.10 (ddd, *J* = 11.9, 11.1, 7.3 Hz, 1H), 1.52 (s, 3H); **13C NMR** (100 MHz, $CDCl_3$) δ 150.5, 134.5, 128.1, 122.5, 117.3, 105.0, 67.3, 52.3, 41.8, 30.9, 24.8; IR (film) υ_{max} 2950, 2877, 1391, 1310, 1222, 1041, 910 cm-1. HRMS (ESI) m/z 190.1204 [M + H]+; calculated for $[C_{18}H_{17}NO_2]$+: 190.1226.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, ^{13}C NMR spectra, HRMS for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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