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Transition-Metal Free Oxidative Alkynylation of 2-Oxindoles with Ethynylbenziodoxolone (EBX) Reagents

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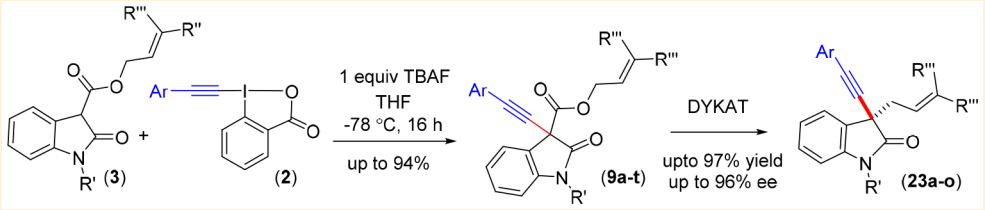
Supporting Information



ABSTRACT: We report an efficient direct alkynylations of 3-alkyl/aryl 2-oxindoles employing ethynyl-1,2-benziodoxol-3(1H)-one (EBX) to afford a wide variety of 3-alkynyl-3-alkyl/aryl 2-oxindole under transition-metal free condition. In addition to activated carbonyl compounds *viz*. 2-oxindole-3-alkylcarboxylates, this direct alkynylations protocol works efficiently on 3-alkyl/aryl 2-oxindols as well thereby widening the scope even further. Eventually, a Pd(0)-catalyzed asymmetric decarboxylative allylation of few products is shown to furnish synthetically viable enantioenriched 2-oxindoles with C-3 quaternary stereocenters.

INTRODUCTION

Owing to their interesting structural and electronic properties of alkynes, alkynylation reactions continue to be an important C−C bond-forming step in organic synthesis.[1] In this regard, 1,2-addition of terminal alkynes[1] onto carbonyls,[2a,b] imines,[2c] and 1,4-addition onto α,β-unsaturated[2d] are quite prevalent to synthesize a variety of alkynylated products. However, the alkynylation of enolates has been less explored because of obvious nucleophilic nature of terminal alkynes. This has been materialized either by reaction of haloalkynes (with an electron-withdrawing group at other end) with a carbanion nucleophile via an addition−elimination mechanism,[3] or under oxidative condition using alkynyl lead reagent as reported by Pinhey.[4] Apart from this, the use of hypervalent iodine for oxidative atom transfer reactions, in nonclassical way (*umpolung* reactivity), is emerging as a promising area, both for hetero- as well as carbon- atom transfer reactions.[5]

Seminal contributions for use of acyclic hypervalent iodine reagents (Figure 1) for alkynylation of active methylenes include Beringer's alkynyliodonium salt,[6a] Ochiai's tetrafluoroborate alkynyliodonium salts,[6b,6c] and Stang's alkynyliodonium triflates.[6d] In this regard, Waser and co-workers discovered the exceptional properties of cyclic ethynyl-1,2-benziodoxol-3(1H)-one (EBX) for the alkynylation of activated carbonyl compounds.[7] Using this ethynyl reagent, they could transfer acetylene group to a number of heteroaromatics,[8] heteroatoms[9] as well as Domino processes[10] with exceptional reactivity involving metal-catalyzed processes.[11a,b] Other reports on oxidative alkynylations include Veselý's organocatalytic alkynylation of densely functionalized monofluorinated derivatives,[11c] Maruoka's enantioselective alkynylation of cyclic β-keto esters with hypervalent iodine reagents under phase transfer catalysis,[11d] and Nachtsheim's alkynylations of azalactones.[11e]

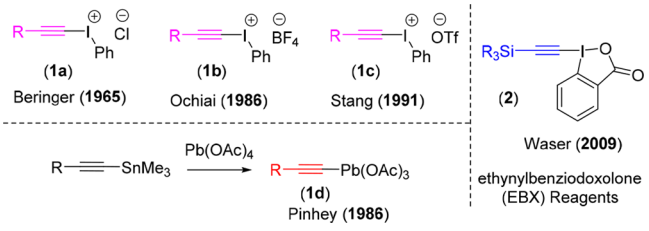


Figure 1. Hypervalent reagents used for alkynylations.

RESULTS AND DISCUSSION

Methods to install quaternary center at C-3 of the 2-oxindole core although synthetically challenging but if developed, it introduces structurally diverse family of indole alkaloids.[12,13] Despite a large number of protocols available for other functional moieties, the introduction of a privileged alkynyl group at the C3 position of oxindoles to construct an all-carbon quaternary center has scarcely been explored.[14] The nonclassical behavior (*umpolung* reactivity) with exceptional reactivity of EBX reagents, made us to consider them suitable for alkynylation of 2-oxindoles. Herein, we report a method developed for smooth alkynylation of 3-substituted-2-oxindoles

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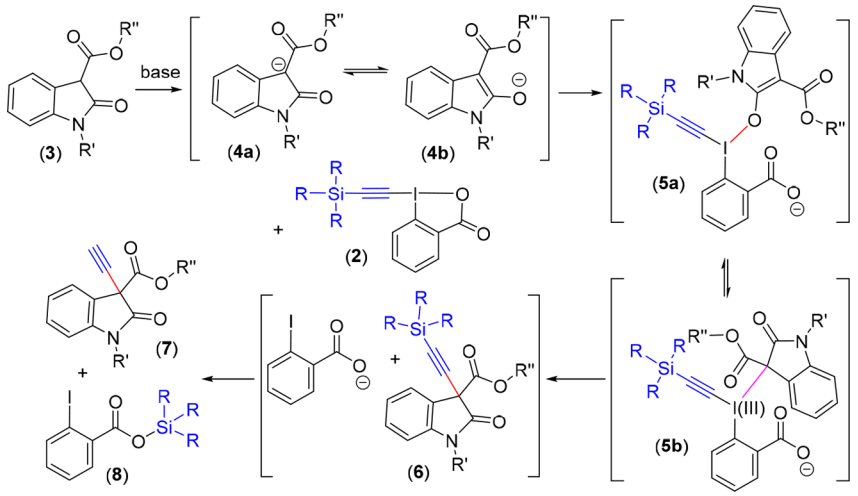
Scheme 1. Our hypothesis of Alkynylation of 2-Oxindoles



under transition metal-free condition. In addition to activated carbonyl compounds *viz.* 2-oxindole-3-alkylcarboxylates, this direct alkynylations protocol works efficiently on 3-alkyl/aryl 2-oxindols as well thereby widening the scope even further.

We hypothesized that 2-oxindole methyl-3-carboxylate **3a** could form enolate **4b** (via carbanion **4a**), which would react with TBDMS-EBX reagent **2a** to form hypervalent iodine intermediate **5a** (Scheme 1). This intermediate would then quickly form another intermediate **5b** via O−C migration, from where a reductive elimination would lead to the formation of expected product **6** and generation of 2-iodobenzoate as byproduct. Finally, removal of silyl group of **6** affords 3-ethynyl 2-oxindole **7** and byproduct **8** (Scheme 1). We envisioned that 2-oxindole 3-carboxylates having a labile proton with pK_a ∼14−15 might act as excellent substrates.

Therefore, at the outset, we choose **3a** as our model substrate to react with hypervalent iodine reagents TBDMS-EBX (**2a**), TIPS-EBX (**2b**), and TMS-EBX (**2a'**) in the presence of a variety of bases, such as NaH, Cs_2CO_3, K_2CO_3, *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG), DBU, tetrabultylammonium fluoride (TBAF), etc., at different temperature (Table 1). After exhaustive optimization, we found that oxidative ethynylation of 2-oxindole methyl-3-carboxylate **3a** can be realized in the presence of 1.0 equiv of TBAF (entry 13) at −78 °C in THF or TMG at room temperature in toluene (entry 20) to afford compound **7a** in 84 and 90%, respectively (Scheme 2).

Using standard condition, we then probed the alkynylations using silyl EBX **2a**−**c** in the presence of TMG at 25 °C to furnish terminal alkyne products **7a**−**d** in 68−90% isolated yields (Scheme 2). Further, a variety of aryl EBX (Ar-EBX) reagents were also synthesized from arylacetylenes, such as **2d**−**f**. We noticed that the Ar-EBX reagents **2d**−**f** work well in combination with TBAF at −78 °C to provide alkynes **7e**−**i** in synthetically useful yields (72−86% yields) (Scheme 2).

Further, a variety of 2-oxindole allyl-3-carboxylates were subjected to Ar-EBX reagents **2d**−**h** (Scheme 3). We assumed that these compounds might serve as the starting point of Tsuji−Trost decarboxylative allylations[15] to yield enantioenriched 3-alkynyl 2-oxindoles following a dynamic kinetic asymmetric transformations (DYKAT).[16] Hence, to test the synthetic viability of this alkynylation process, we then extended it to a variety of 2-oxindole allyl-3-carboxylates which were treated with aryl EBX reagents and the results are summarized in Scheme 3.

Rewardingly, a wide range of 2-oxindoles bearing all-carbon-quaternary centers, with ethynyl functionalities, **9a**−**t** were obtained in good yields (Scheme 3). Later, the prevalence of prenylated, reverse-prenylated, and geranylated hexahydropyrrolo[2,3-*b*]indole alkaloids,[17] exhibiting a broad spectrum of biological activities drew our attention.[18] To construct these compounds, we envisioned a direct incorporation of the prenyl, reverse-prenyl or geranylgroup at the 3-position of 2-oxindole products via Pd-catalyzed decarboxylative prenylation/reverse-prenylation/geranylations on related esters. Therefore, oxidative alkynylations were performed with a variety of substrates, which resulted products **10a**−**l** in 62−81% yields (Scheme 3).

Later, our successful alkynylations with 2-oxindole 3-carboxylates as substrates further prompted us to test *N*-Boc protected 2-oxindoles **11a**−**c**, which also fetched corresponding alkynylated products **12a**−**d** in good to excellent yields (Scheme 4). Interestingly, TBDPS-EBX **2c** afforded product **12c** in 79% yield where silyl group was intact (Scheme 4). This is probably due to bulky nature of silyl group, which is untouched in the presence of 2-iodobenzoate. The methodology was next extended to *N*-methyl protected 2-oxindoles **13a**−**e**, which resulted in a variety of products **14a**−**f** in 82−92% (Scheme 4). Since, there are abundant literature reports for indole natural products bearing 3-arylated-2-oxindole moieties,[19] we also utilized few 3-arylated 2-oxindole substrates, such as **13c**−**e**, for oxidative alkynylation reactions (Scheme 4).

Gratifyingly, subjecting the unprotected 2-oxindoles **15a**−**c** to the reaction conditions, we found that a highly chemoselective alkynylation can be achieved with Ar-EBX reagent **2d** to afford C-alkynylation products **16a**−**c** in excellent yields (Scheme 5). The latter clearly depicts soft nature of EBX reagents, which predominantly reacted at C-center nucleophile as compared to *N*-center (oxindole nitrogen) nucleophile. Exploring the oxidative alkynylation reactions to 3-substituted benzofuran-2(3*H*)-one under standard condition resulted products **18a**−**d** as well in synthetically useful yields (Scheme 5).

To our surprise, reaction of 2-methyl 3-oxindole **19a** with Ar-EBX reagent **2d** afforded complex mixture of products

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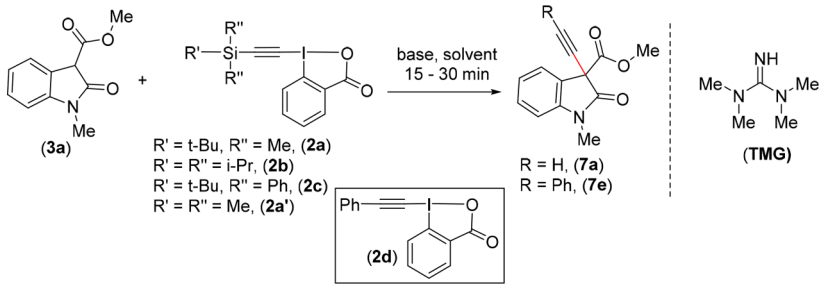
Table 1. Optimization of Oxidative Alkynes Addition of 3



entry[a]	alkyne	base	solvent	temp	time	% yield[b] (7a/7e)
1	**2a**	NaH	THF	25 °C	20 min	54 (**7a**)
2	**2b**	NaH	THF	25 °C	20 min	36 (**7a**)
3	**2c**	NaH	THF	25 °C	20 min	51 (**7a**)
4	**2b**	NaH	PhMe	25 °C	20 min	43 (**7a**)
5	**2b**	NaH	DMF	25 °C	20 min	28 (**7a**)
6	**2a**	Cs_2CO_3	THF	25 °C	20 min	60 (**7a**)
7	**2d**	K_2CO_3	xylene	25 °C	30 min	30 (**7a**)
8	**2d**	TMG	THF	25 °C	20 min	36 (**7a**)
9	**2d**	TMG	DMF	25 °C	20 min	79 (**7a**)
10	**2d**	TMG	PhMe	25 °C	20 min	74 (**7e**)
11	**2d**	DBU	PhMe	25 °C	10 min	72 (**7a**)
12	**2d**	Cs_2CO_3	PhMe	25 °C	10 min	61 (**7a**)
13	**2d**	TBAF	THF	−78 °C	16 h	84 (**7e**)
14	**2b**	33% aq. K_2CO_3	xylene	25 °C	20 min	40 (**7a**)
15	**2b**	K_2CO_3	xylene	25 °C	20 min	39 (**7a**)
16	**2c**	DBU	PhMe	25 °C	15 min	77 (**7a**)
17	**2c**	DBU	PhMe	0 °C	20 min	79 (**7a**)
18	**2c**	DBU	THF	25 °C	20 min	81 (**7a**)
19	**2c**	DBU	THF	0 °C	30 min	80 (**7a**)
20	**2a**	TMG	PhMe	25 °C	15 min	90 (**7a**)
21	**2c**	TMG	THF	25 °C	15 min	82 (**7a**)
22	**2a**	TMG	THF	25 °C	15 min	84 (**7a**)
23	**2a**	DBU	THF	25 °C	15 min	78 (**7a**)
24	**2a**	TMG	THF	25 °C	10 min	79[c] (**7a**)
25	**2b**	TMG	toluene	25 °C	20 min	57 (**7a**)
26	**2b**	TMG	DMF	25 °C	15 min	48 (**7a**)
26	**2b**	TMG	THF	25 °C	20 min	53 (**7a**)
27	**2b**	DBU	toluene	25 °C	30 min	49 (**7a**)
28	**2b**	DBU	THF	25 °C	30 min	53 (**7a**)
29	**2a'**	NaH	PhMe	25 °C	20 min	56 (**7a**)
30	**2a'**	NaH	THF	25 °C	20 min	41 (**7a**)
31	**2a'**	TMG	PhMe	25 °C	20 min	88 (**7a**)
32	**2a'**	DBU	PhMe	25 °C	20 min	82 (**7a**)
33	**2a'**	Cs_2CO_3	THF	25 °C	20 min	44 (**7a**)

[a]Reactions were carried out using 0.2 mmol of **3a** with 0.2 mmol of **2a**−**d** and **2a'** in 1 mL solvent. [b]Yields after column purification. [c]Reaction was carried out at 25 °C for 20 min.

(Scheme 6). Even, *N*-Boc 2-oxindole having no substitution did not afford product, and a byproduct arising from Ar-EBX reagent **2d** was isolated in 49% yield. Thus, 3-substitution at 2-oxindole is necessary in order to have better results from oxidative alkynylations. Next, we tried to check the possibility of one-pot direct oxidative alkynylation for the synthesis of pyrroloindoline scaffolds. Toward this direction, an attempt to synthesize pyrroloindoline **21c** via one-pot oxidative alkynylation afforded **21b** as sole product, probably indicating the soft nature of indole nitrogen (Scheme 6).

Later, we wanted to validate the mechanistic proposal shown in Scheme 1.[7a−c] Especially, given the fact that, the silyl group on EBX reagents has been demonstrated to be very sensitive to base and nucleophile.[5c] Therefore, deprotection of the silyl group before alkynylation, and not after as shown in Scheme 1, cannot be ruled out as a possible mechanism.[20] To check this, 2-oxindole **22b** was synthesized in 76% yield from **22a** by reaction with *n*-BuLi and TMSCl at −78 °C (Scheme 7). Compound **22a** was synthesized by the reaction of **13a** with TMS-EBX (**2a'**) reagent (Scheme 7).

When compound **22a** was reacted with 1 equiv of TMG and DBU, there were no products with desilylation and we found recovery of starting material **22b** in 87−89% yields (entries 1−2, Table 2). On the contrary, by treatment of **22b** with inorganic base such as KO^{t}Bu afforded terminal alkyne **22a** with TMS group cleavage (entries 3−4, Table 2). These

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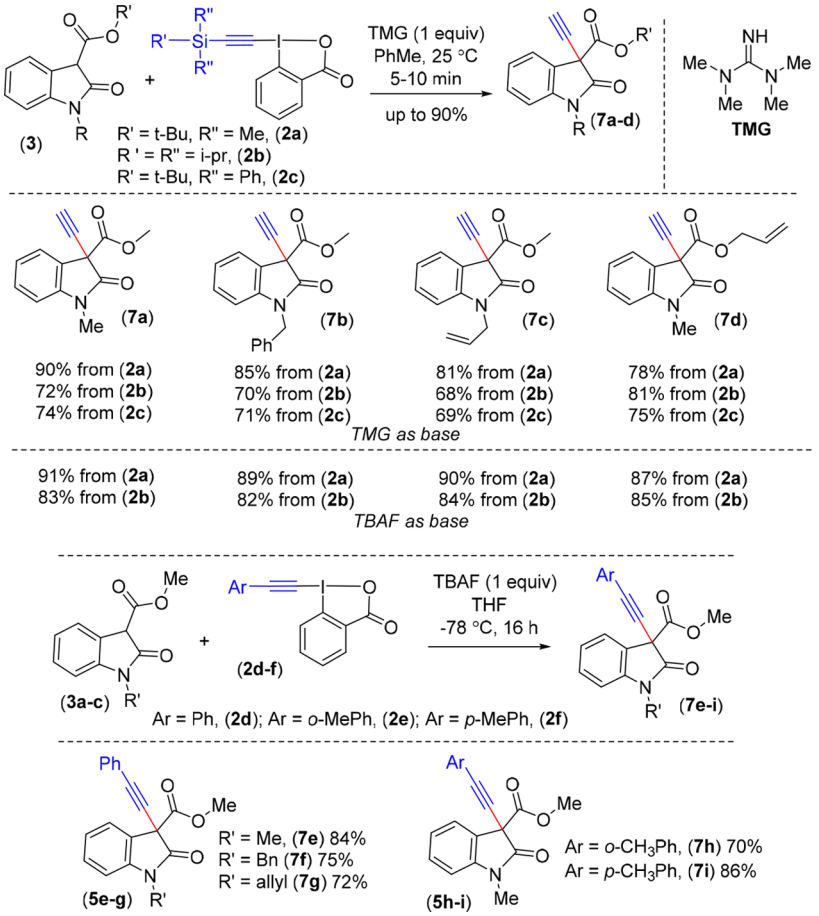
Scheme 2. Substrates Scope of Alkynylations Using EBX Reagent[a]



[a]Reactions were carried out by using 0.25 mmol of **3** with 0.275 mmol of EBX reagents **2a−c** in the presence of 0.25 mmol of TMG or TBAF under argon atmosphere. [b]Yield after column purification.

experiments clearly suggest that stoichiometric amount of byproduct 2-iodobenzoate is solely responsible for the desilyation reaction, when oxidative alkynylations were carried out in the presence of organic bases.

The subset of enantioenriched 2-oxindoles comprise a common structural motif in many biologically active alkaloids and therefore gained significant attention from synthetic community. Intrigued by their challenging structural arrays and impressive biological activities, we envisioned a unified approach to these targets in an asymmetric fashion. For this, we chose the well proved 2-phosphino-oxazoline (PHOX) ligands and (*S*)-**L1**-**L4**[21] and 2-phosphino-carboxamide ligands **L5**-**L8**,[21] for carrying out the Pd-catalyzed catalytic enantioselective studies. Initially, Pd(0)-catalyzed decarboxylative allylations (Table 3)[22] through a dynamic kinetic asymmetric transformation (DYKAT)[23] of allyl ester (±)-**9b**,[23] was investigated in the presence of 2.5 mol % $Pd_2(dba)_3$ in combination with 7.5 mol % ligands **L1**-**L8** in diethyl ether at 25 °C to afford product **23b** (entries 1−8). Among various ligands tested, C_2-symmetric anthracenyl based Trost ligand **L8** afforded **23b** in 63% ee with 98% yield (entry 8). Following exhaustive optimization, it was found that 2.5 mol % $Pd_2(dba)_3$ in combination with 7.5 mol % ligand **L8** in diethyl ether at −30 °C afforded product **23a** in 90% ee with 96% yield (entries 9−22, Table 3).

Under the standard condition, a number of C-alkynylated allyl-methallyl esters were subjected to catalytic enantioselective allylations in diethyl ether at −30 °C (Figure 2). To our delight, a variety of enantioenriched 2-oxindole with C-3 quaternary stereocenter could be obtained in up to 96% ee (see **23j**).

As an application of our strategy, one of the enantioenriched products **23b** was synthetically transformed into furoindoline structures[24] **25a−b** and **26** in few steps via aldehyde **24** (Scheme 8).

CONCLUSIONS

In conclusion, we developed a novel entry to direct incorporation of an alkyne functionality using EBX reagents under transition-metal free condition. The products obtained from this process are important building blocks for the synthesis of a number of pyrroloindoline alkaloids. This study not only offers a vital method for the oxidative C−C bond construction but also clearly demonstrates the potential of the modular 2-oxindole scaffolds in synthesis. We have also shown that alkynylated products derived allyl esters are good substrate for Pd(0)-catalyzed decarboxylative allylation to afford a number of enantioenriched 2-oxindole with C-3 quaternary stereogenic centers.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise stated, reactions were carried out using oven-dried glass ware with Teflon-coated magnetic stirring bars were used to stir the reactions. The syringe was used to

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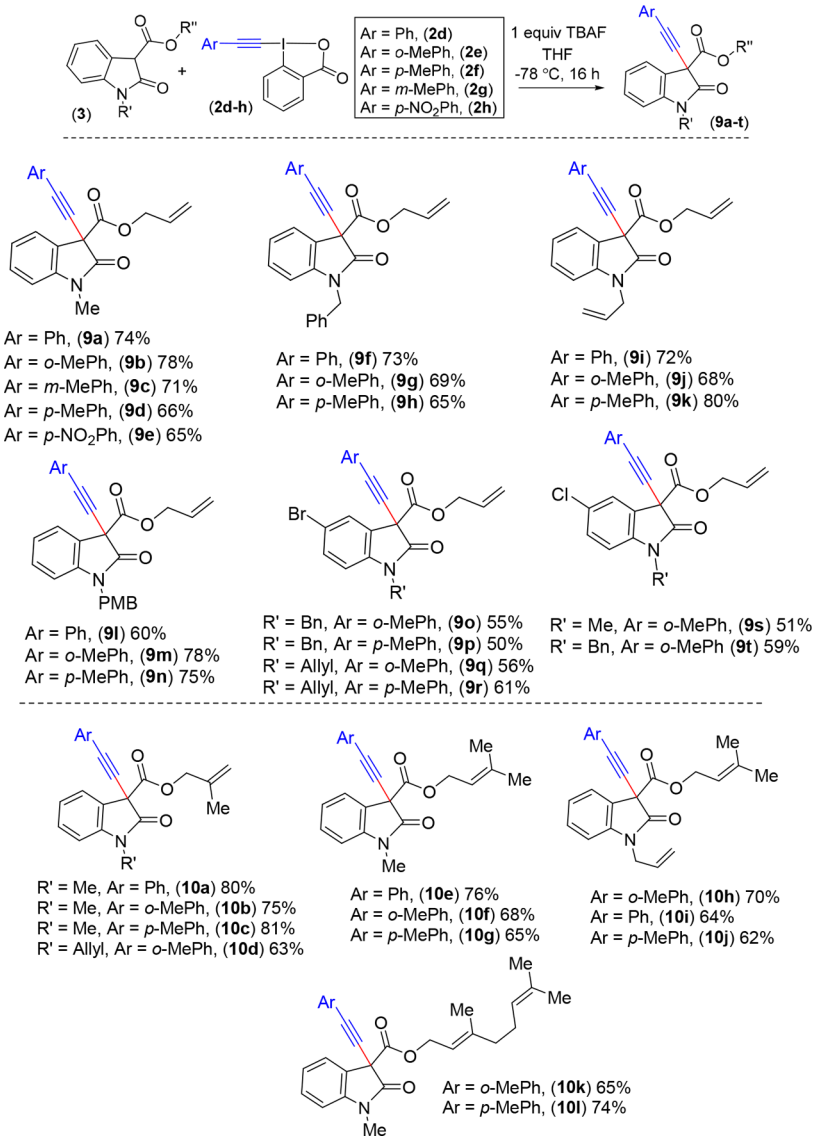
Scheme 3. Further Scope of Alkynylations Using Different Allylesters



transfer the solvents and liquid reagents. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane CH_2Cl_2) was distilled over calcium hydride. All other solvents, like nitromethane, MeOH, EtOAc, DMF, and dichloroethane (DCE), and reagents were used as received. Reaction temperatures above 25 °C were maintained by using oil bath on a magnetic stirrer. Thin layer chromatography (TLC) analysis was performed by using silica gel precoated plates (0.25 mm) 60 (F-254), Visualized by UV irradiation, yellow dip stain and other stains. Silica gel of particle size 230−400 and 100−200 mesh were used to perform flash chromatography. Digital melting point apparatus is used to record the melting points and are uncorrected. ^{1}H NMR spectra was recorded by using 400, 500, and 700 MHz spectrometers, ^{13}C NMR operating frequencies are 100, 125, and 175 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvents ($CDCl_3$) signal (δ = 7.24 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR) and (DMSO−D_6) signal (δ = 2.50 for ^{1}H NMR and δ = 39.5 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, 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 (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High-resolution mass spectrometry (HRMS) data was recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

Starting materials **3a−c**,[21b] **3f**,[21b] **3l**,[21b] **3n**,[21b] **3p**,[21b] **11a**,[21b] **13b**,[21b] **3d−e**,[16c] **3g**,[25a] **13a**,[25a] **11c**,[24a] **11b**,[25b] **15b**,[25b] **13c−d**,[25c] **13e**,[25d] **15a**,[26a] **17a**,[26b] and **17b**[26c] were synthesized following literature protocols.

*Synthesis of N-Methyl 3-(2-nitrophenyl) 2-oxindole (**13e**).* Anhydrous Cs_2CO_3 (1.96 g, 6 mmol., 1.2 equiv) was added to the solution of 1-methyl 2-oxindole (736 mg, 5 mmol., 1.0 equiv) in THF (15 mL) at 0 °C. The reaction was stirred for 10 min followed by the addition of 2-fluoro nitrobenzene (0.63 mL, 6 mmol, 1.2 equiv) at 0 °C. The reaction was stirred at room temperature for overnight. Upon completion of the reaction (as judged by running TLC), it was quenched with water (10 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were recombined and washed with brine (25 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified by column chromatography using the 30% EtOAc in hexane system as eluent to afford the desired product **13e** (1.08 g, 80% yield).

*1-Methyl-3-(2-nitrophenyl)indolin-2-one (±)-(**13e**).* The product **13e**, 80% yield as an orange gel; R_f = 0.50 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (dd, J = 8.2, 1.3 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.50 (td, J = 7.8, 1.4 Hz, 1H), 7.37 (tt, J = 7.8, 1.0 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 7.07 (t, J

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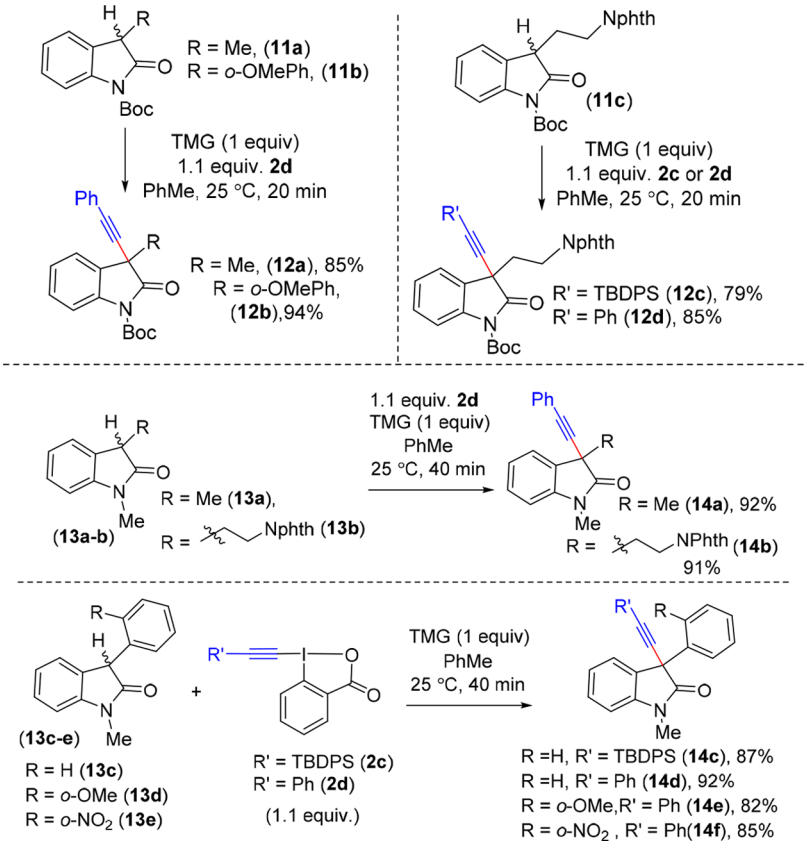
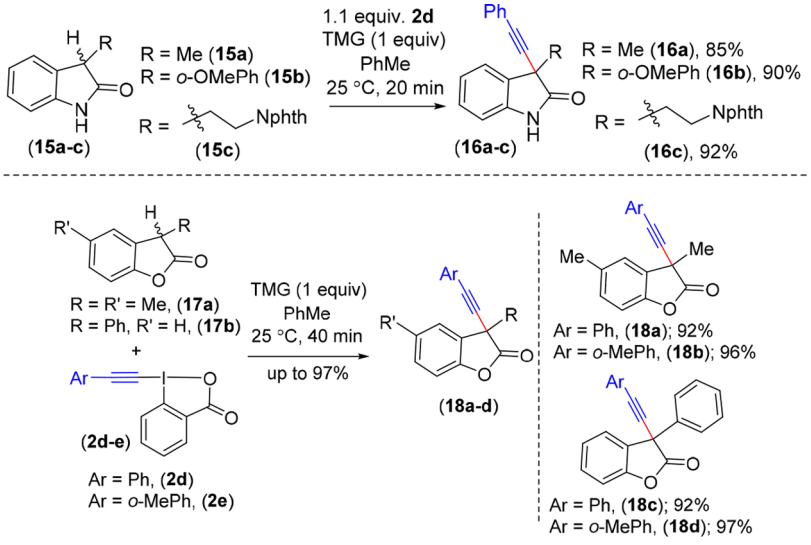
Scheme 4. Scope of Alkynylations Using *N*-Alkyl 2-Oxindoles



Scheme 5. Chemoselective Alkynylations Further Scope



= 7.5 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 3.32 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.8, 144.4, 133.5, 131.5, 128.8, 127.3, 125.6, 124.3, 122.9, 108.4, 49.2, 26.6; IR (film) υ_{max} 2997, 2959, 2850, 1782, 1662, 1610, 800 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $[C_{15}H_{12}N_2O_3 + Na]^+$: 291.0740, found: 291.0733.

Synthesis of 3-Alkynyl-2-oxoindole by General Procedure A. To the solution of 3-substituted-2-oxindole (1.0 equiv) in toluene, TMG (1.0 equiv) were added. The reaction was stirred for a few minutes followed by the addition in one portion of the hypervalent iodine reagent (EBX) (1.1 equiv). The reaction was stirred at room temperature for 15−30 min. The reaction was monitored by TLC analysis UV, iodine, cerium molybdate (Hanessian's Stain) and *p*-anisaldehyde Stain. Upon completion, the reaction was quenched with water (2 mL) and extracted with EtOAc (3 × 4 mL). The organic layers were recombined, washed with $NaHCO_3$ (1.5 mL), brine (2.5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified by column chromatography using the hexane-EtOAc system as eluent to afford the desired alkynylation product.

Synthesis of 3-Alkynyl-2-oxoindole by General Procedure B. To the solution of 3-substituted-2-oxindole (1.0 equiv) and hypervalent iodine reagent (EBX) (1.1 equiv) in dried THF was stirred at −78 °C for 5 min under nitrogen. After this period of time, TBAF (1 M in

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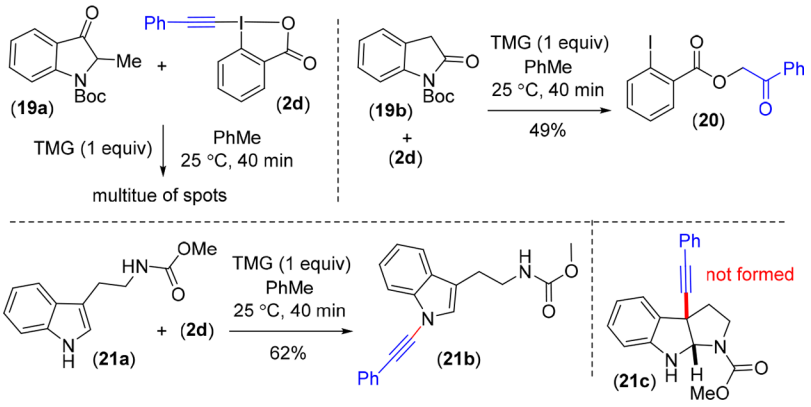
Scheme 6. Further Scopes



Scheme 7. Synthesis of TMS Protected Compound 22b

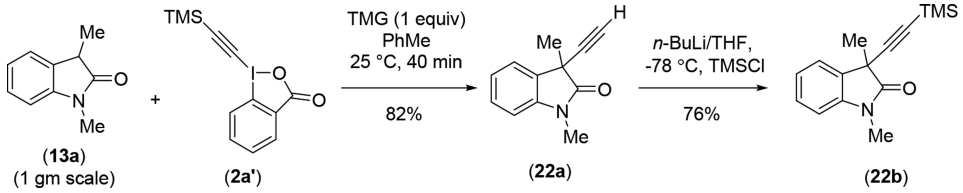
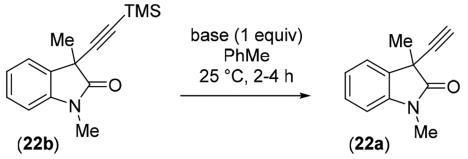


Table 2. TMS Deprotection of Compound 22b Using Various Bases



entry	base	solvent	temp	time	% yield (**22a**)	% yield (**22b**)
1.	TMG	PhMe	25 °C	4 h	00	89%
2.	DBU	PhMe	25 °C	4 h	00	87%
3.	*t*-BuOK	PhMe	25 °C	10 h	28%	34%
4.	*t*-BuOK	PhMe/MeOH (1:1)	25 °C	10 h	86%	00

THF, 1.0 equiv) was added. The reaction was stirred at −78 °C for 16 h. The reaction was monitored by TLC analysis UV, iodine, cerium molybdate (Hanessian's Stain) and *p*-anisaldehyde Stain. Upon completion, the reaction was quenched with water (2 mL) and extracted with EtOAc (3 × 5 mL). The organic layers were recombined, washed with $NaHCO_3$ (1.5 mL), brine (5.0 mL). The crude product was purified by column chromatography using the hexane-EtOAc system as eluent to afford the desired alkynylation product.

*Methyl 3-Ethynyl-1-methyl-2-oxoindoline-3-carboxylate (±)-(**7a**).* The product **7a** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (12.4 μL, 0.099 mmol), **2a** (42 mg, 0.109 mmol) and the reaction was performed for 5 min to give **7a** in 20.7 mg (0.099 mmol) as an orange solid (91% yield); mp 100−102 °C; R_f = 0.54 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 3.26 (s, 3H), 2.47 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.5, 166.3, 166.2, 143.5, 130.1, 126.5, 124.1, 123.6, 108.9, 73.2, 54.2, 54.0, 27.1; IR (film) υ_{max} 3339, 2997, 2959,1782, 1662, 1710, 800 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $[C_{13}H_{11}NO_3 + H]^+$: 230.0812, found: 230.0809.

*Methyl 1-Benzyl-3-ethynyl-2-oxoindoline-3-carboxylate (±)-(**7b**).* The product **7b** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (11.1 μL, 0.089 mmol), **2a** (37.8 mg, 0.098 mmol) and the reaction was performed for 5 min to give **7b** in 24.2 mg (0.089 mmol) as a light orange solid (89% yield); mp 155−156 °C; R_f = 0.36 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.32−7.24 (m, 5H), 7.21 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.07 (td, *J* = 7.6, 1.0 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.10 (d, *J* = 15.8 Hz, 1H), 4.80 (d, *J* = 15.8 Hz, 1H), 3.78 (s, 3H), 2.51 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.8, 166.3, 142.6, 134.9, 130.0, 128.9, 127.8, 127.1, 126.6, 124.1, 123.6, 110.0, 73.5, 54.35, 54.1, 44.4, 29.7.; IR (film) υ_{max} 3340, 2999, 2951, 2246, 1739, 1691, 1459, 1189, 1021, 821 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $[C_{19}H_{15}NO_3 + Na]^+$: 328.0944, found: 328.0964.

*Methyl 1-Allyl-3-ethynyl-2-oxoindoline-3-carboxylate (±)-(**7c**).* The product **7c** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (16.3 μL, 0.13 mmol), **2a** (55.2 mg, 0.143 mmol) and the reaction was performed for 5 min to give **7c** in 29.7 mg (0.13 mmol) as an orange solid (90% yield); mp 75−77 °C; R_f = 0.40 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.32 (td, *J* = 7.8, 1.3 Hz, 1H), 7.10 (td, *J* = 7.6, 1.0 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.2, 5.0 Hz, 1H), 5.27−5.21 (m, 2H), 4.45 (ddt, *J* = 16.6, 5.0, 1.8 Hz, 1H), 4.28 (ddt, *J* = 16.6, 5.2, 1.7 Hz, 1H), 3.75 (s, 3H), 2.48 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.3, 166.3, 142.7, 130.4, 130.0, 126.6, 124.1, 123.6, 117.8, 109.8, 73.4, 73.2, 54.3, 54.1, 42.9; IR (film) υ_{max} 3342, 2991, 2850, 1710, 1686, 1581, 1250, 833 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $[C_{15}H_{13}NO_3 + Na]^+$: 278.0788, found: 278.0805.

*Allyl 3-Ethynyl-1-methyl-2-oxoindoline-3-carboxylate (±)-(**7d**).* The product **7d** was synthesized according to the general

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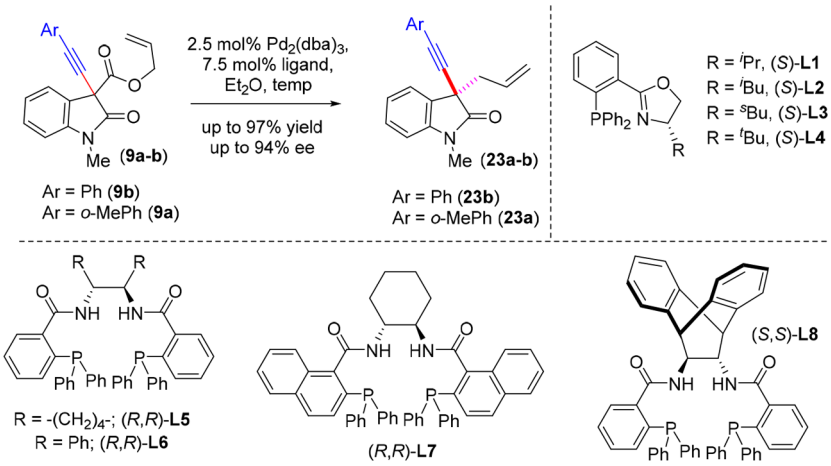
Table 3. Optimization of Catalytic Decarboxylative Allylations



entry[a]	substrate	$Pd_2(dba)_3$	ligand	solvent	temp	time	% yield (**23b**)[b]	% ee[c]
1	**9b**	2.5% mol %	7.5 mol % **L1**	Et_2O	25 °C	14 h	75%	29% ee
2	**9b**	2.5% mol %	7.5 mol % **L2**	Et_2O	25 °C	12 h	72%	24% ee
3	**9b**	2.5% mol %	7.5 mol % **L3**	Et_2O	25 °C	8 h	74%	35% ee
4	**9b**	2.5% mol %	7.5 mol % **L4**	Et_2O	25 °C	14 h	81%	37% ee
5	**9b**	2.5% mol %	7.5 mol % **L5**	Et_2O	25 °C	10 h	82%	62% ee
6	**9b**	2.5% mol %	7.5 mol % **L6**	Et_2O	25 °C	8 h	90%	26% ee
7	**9b**	2.5% mol %	7.5 mol % **L7**	Et_2O	25 °C	14 h	92%	30% ee
8	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	25 °C	10 h	98%	63% ee
9	**9b**	2.5% mol %	7.5 mol % **L8**	THF	25 °C	16 h	84%	78% ee
10	**9b**	2.5% mol %	7.5 mol % **L8**	PhMe	25 °C	10 h	74%	68% ee
11	**9b**	2.5% mol %	7.5 mol % **L8**	CH_2Cl_2	25 °C	12 h	68%	65% ee
12	**9b**	2.5% mol %	7.5 mol % **L8**	$CHCl_3$	25 °C	14 h	74%	69% ee
13	**9b**	2.5% mol %	7.5 mol % **L8**	$(CH_2Cl)_2$	25 °C	12 h	78%	63% ee
14	**9b**	2.5% mol %	7.5 mol % **L8**	$(CH_2OMe)_2$	25 °C	15 h	74%	68% ee
15	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	0 °C	11 h	99%	76% ee
16	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	−10 °C	12 h	98%	80% ee
17	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	−20 °C	15 h	99%	84% ee
18	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	−25 °C	15 h	98%	84% ee
19	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	−30 °C	17 h	97%	87% ee
20	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	−40 °C	30 h	75%	84% ee
21	**9b**	2.5% mol %	7.5 mol % **L8**	Et_2O	−40 °C	42 h	60%	ND
22	**9a**	2.5% mol %	7.5 mol % **L8**	Et_2O	−30 °C	16 h	96%	90% ee[d]

[a]Reactions were carried out using 0.04 mmol of **9a**/**9b** with in 3 mL solvent. [b]Yields after column purification. [c]ee's were determined by chiralpak IB column (4% isopropanol in *n*-hexane and 1 mL/min flow rate). [d]90% ee of product **23a**.

experimental procedure A (2.5 mL toluene) using TMG (27.1 μL, 0.216 mmol), **2a** (91.7 mg, 0.237 mmol) and the reaction was performed for 5 min to give **7d** in 48.0 mg (0.216 mmol) as a colorless oil (87% yield); R_f = 0.40 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 6.9 Hz, 1H), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.80 (ddt, *J* = 17.2, 10.7, 5.4 Hz, 1H), 5.24−5.16 (m, 2H), 4.63 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.26 (s, 3H), 2.47 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.5, 165.4, 143.5, 130.8, 130.1, 126.5, 124.1, 123.6, 118.7, 108.9, 73.3, 71.2, 67.2, 54.4, 27.1; IR (film) υ_{max} 2989, 2899, 1725, 1686, 1568, 738 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+H]$^+$ calcd for $[C_{15}H_{13}NO_3 + H]^+$: 256.0968, found: 256.0980.

*Methyl 1-Methyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**7e**).* The product **7e** was synthesized according to the general experimental procedure B (2.0 mL THF) using TBAF (97 μL, 0.097 mmol), **2d** (37.1 mg, 0.106 mmol) and the reaction was performed for 16 h to give **7e** in 25.0 mg (0.097 mmol) as a colorless oil (84% yield); R_f = 0.35 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50−7.43 (m, 3H), 7.37 (td, *J* = 7.8, 1.3 Hz, 1H), 7.28−7.23 (m, 3H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.77 (s, 3H), 3.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.7, 143.5, 132.1, 129.9, 128.7, 128.1, 127.2, 124.3, 123.5, 122.1, 108.9, 84.6, 82.1, 54.9, 53.9, 27.1; IR (film) υ_{max} 3311, 2976, 1698, 1686, 1470, 897 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for $[C_{19}H_{15}NO_3 + Na]^+$: 328.0944, found: 328.0959.

*Methyl 1-Benzyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**7f**).* The product **7f** was synthesized according to the general experimental procedure B (2.0 mL THF) using TBAF (88 μL, 0.088 mmol), **2d** (33.7 mg, 0.096 mmol) and the reaction was performed for 16 h to give **7f** in 25.4 mg (0.088 mmol) as a colorless oil (75% yield); R_f = 0.4 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (dt, *J* = 7.8, 2.0 Hz, 3H), 7.40−7.35 (m, 4H), 7.35−7.29 (m, 4H), 7.26 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.15−7.09 (m, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.19 (d, *J* = 15.8 Hz, 1H), 4.84 (d, *J* = 15.8 Hz, 1H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.3, 166.8, 142.5, 135.0, 132.19, 129.8, 128.8, 128.7, 128.1, 127.8, 127.3, 127.1, 124.2, 123.5, 122.1, 110.0, 84.9, 81.9, 55.09, 54.0, 44.4; IR (film) υ_{max} 2992, 2888, 1658, 1591, 1418, 1109, 842 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for $[C_{25}H_{19}NO_3 + Na]^+$: 404.1257, found: 404.1254.

*Methyl 1-Allyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**7g**).* The product **7g** was synthesized according to the general

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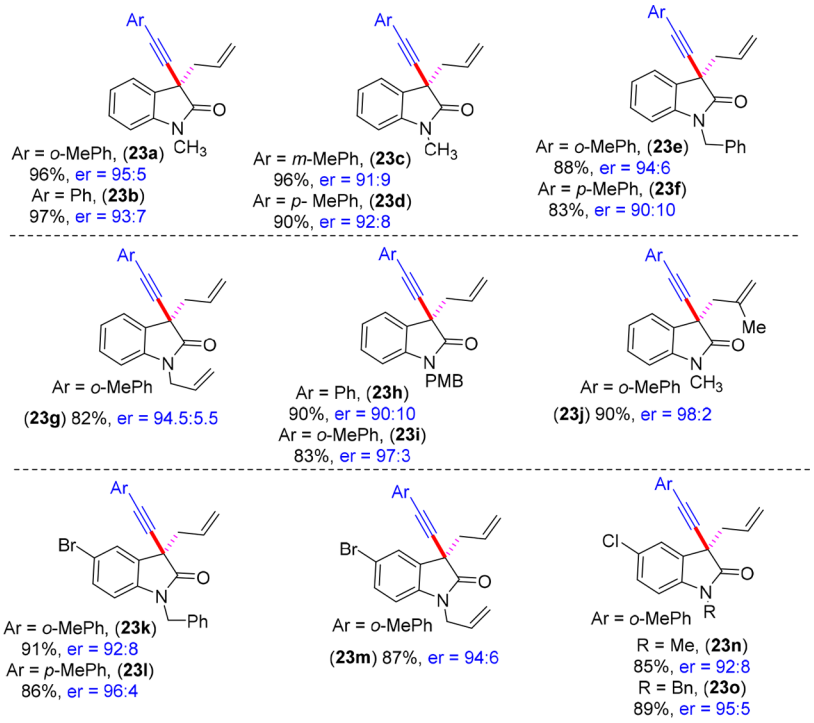
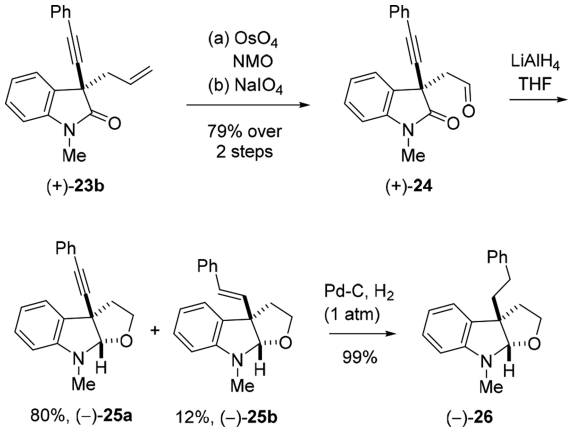


Figure 2. Substrate scope of catalytic DcA using **L8** (a–c). (a) Reactions were carried out on 0.04 mmol of substrates in 3 mL of solvent under argon atmosphere. (b) Yield after column purification. (c) ee's were determined by chiral HPLC analysis.

Scheme 8. Synthetic Manipulation of DcA Products



experimental procedure B (2.5 mL THF) using TBAF (108 μL, 0.108 mmol), **2d** (41.3 mg, 0.118 mmol) and the reaction was performed for 16 h to give **7g** in 26.0 mg (0.108 mmol) as a colorless oil (72% yield); R_f = 0.36 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54–7.47 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.33–7.27 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.97–5.82 (m, 1H), 5.36–5.23 (m, 2H), 4.58–4.48 (m, 1H), 4.38–4.30 (m, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.9, 166.8, 142.7, 132.2, 130.5, 129.8, 128.7, 128.1, 127.3, 124.3, 123.5, 122.1, 117.7, 109.8, 84.8, 82.0, 55.0, 54.0, 42.9; IR (film) υ_{max} 2989, 2878, 1758, 1655, 1489, 895, 758 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{21}H_{17}NO_3$ + Na]$^+$: 354.1101, found: 354.1108.

*Methyl 1-Methyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**7h**).* The product **7h** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (121 μL, 0.121 mmol), **2e** (48.2 mg, 0.133 mmol) and the reaction was performed for 16 h to give **7h** in 27.0 mg (0.121 mmol) as a colorless oil (70% yield); R_f = 0.36 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.43–7.32 (m, 2H), 7.23–7.10 (m, 3H), 7.13–7.03 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.77 (s, 3H), 3.29 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 166.8, 143.5, 141.1, 132.2, 129.9, 129.3, 128.7, 127.4, 125.3, 124.2, 123.5, 121.9, 108.9, 85.9, 83.8, 55.1, 53.9, 27.1, 20.6; IR (film) υ_{max} 2988, 2891, 1667, 1580, 1409, 1110, 831 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{20}H_{17}NO_3$ + Na]$^+$: 342.1101, found: 342.1122.

*Methyl 1-Methyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**7i**).* The product **7i** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (121 μL, 0.121 mmol), **2f** (48.2 mg, 0.133 mmol) and the reaction was performed for 16 h to give **7i** in 33.35 mg (0.121 mmol) as a colorless oil (86% yield); R_f = 0.38 (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 7.4 Hz, 1H), 7.34 (dd, *J* = 7.7, 5.4 Hz, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 3.77 (s, 3H), 3.27 (s, 3H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 166.8, 143.4, 138.8, 132.0, 129.9, 128.9, 127.3, 124.3, 123.5, 119.0, 108.8, 84.8, 81.3, 54.9, 53.9, 27.1, 21.5; IR (film) υ_{max} 2994, 2906, 1670, 1584, 1895, 1103, 850 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{20}H_{17}NO_3$ + Na]$^+$: 342.1101, found: 342.1118.

*Allyl 1-Methyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**9a**).* The product **9a** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (173 μL, 0.173 mmol), **2d** (66.2 mg, 0.190 mmol) and the reaction was performed for 16 h to give **9a** in 42.0 mg (0.173 mmol) as a yellow color solid (74% yield); mp 58–59 °C; R_f = 0.45 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (ddd, *J* = 14.6, 7.7, 1.7 Hz, 3H), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H), 7.26 (td, *J* = 5.8, 2.7 Hz, 3H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.6, 5.4 Hz, 1H), 5.30–5.14 (m, 2H), 4.66 (dt, *J* = 5.4, 1.5 Hz, 2H), 3.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ170.0, 165.9, 143.5, 132.1, 131.0, 130.0, 128.7, 128.1, 127.2, 124.2, 123.5, 122.1, 118.5, 108.9, 84.7, 82.0, 67.04, 55.0, 27.0.; IR (film) υ_{max} 2959, 2912, 2800,1687, 1120, 981,754 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{21}H_{17}NO_3$ + Na]$^+$: 354.1101, found: 354.1121.

*Allyl 1-Methyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9b**).* The product **9b** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (216 μL, 0.216 mmol), **2e** (86 mg, 0.237 mmol) and the reaction was performed for

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16 h to give **9b** in 58.5 mg (0.216 mmol) as a yellow color solid (78% yield); mp 60−62 °C; R_f = 0.60 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, J = 7.5, 1.3 Hz, 1H), 7.40−7.34 (m, 2H), 7.24−7.11 (m, 3H), 7.10−7.05 (m, 1H), 6.87 (d, J = 7.8 Hz, 1H), 5.83 (ddt, J = 17.3, 10.7, 5.4 Hz, 1H), 5.30−5.15 (m, 2H), 4.66 (dt, J = 5.4, 1.5 Hz, 2H), 3.28 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 166.0, 143.5, 141.1, 132.2, 131.0, 129.9, 129.3, 128.7, 127.4, 125.4, 124.2, 123.5, 121.9, 118.6, 108.9, 85.9, 83.9, 67.1, 55.3, 27.1, 20.7; IR (film) υ_{max} 2976, 2910, 1690, 1510, 1429, 890 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{22}H_{19}NO_3$ + Na]$^+$: 368.1257, found: 368.1249.

*Allyl 1-Methyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9c**).* The product **9c** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (216 μL, 0.216 mmol), **2g** (86 mg, 0.237 mmol) and the reaction was performed for 16 h to give **9c** in 53.0 mg (0.216 mmol) as a yellow color oil (71% yield); R_f = 0.60 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, J = 7.5, 1.3 Hz, 1H), 7.36 (td, J = 7.8, 1.3 Hz, 1H), 7.31−7.22 (m, 2H), 7.16−7.07 (m, 3H), 6.87 (d, J = 7.8 Hz, 1H), 5.83 (ddt, J = 17.3, 10.6, 5.4 Hz, 1H), 5.29−5.14 (m, 2H), 4.66 (dt, J = 5.4, 1.5 Hz, 2H), 3.28 (s, 3H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.0, 165.9, 143.5, 137.8, 132.8, 131.0, 129.9, 129.6, 129.2, 128.0, 127.3, 124.3, 123.5, 121.9, 118.5, 108.9, 84.9, 81.7, 67.0, 55.1, 27.1, 21.1; IR (film) υ_{max} 2982, 2920, 2891, 1416, 1139, 780 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{22}H_{19}NO_3$ + Na]$^+$: 368.1257, found: 368.1285.

*Allyl 1-Methyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**9d**).* The product **9d** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (216 μL, 0.216 mmol), **2f** (86 mg, 0.237 mmol) and the reaction was performed for 16 h to give **9d** in 49.0 mg (0.216 mmol) as a yellow color oil (66% yield); R_f = 0.47 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, J = 7.5, 1.2 Hz, 1H), 7.38−7.33 (m, 3H), 7.11 (td, J = 7.6, 1.0 Hz, 1H), 7.06 (d, J = 7.9 Hz, 2H), 6.87 (d, J = 7.8 Hz, 1H), 5.83 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.25 (dq, J = 17.2, 1.6 Hz, 1H), 5.18 (dd, J = 10.5, 1.4 Hz, 1H), 4.66 (dt, J = 5.5, 1.6 Hz, 2H), 3.28 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 166.0, 143.5, 138.8, 132.0, 131.0, 129.9, 129.0 128.9, 127.3, 124.3, 123.5, 119.1, 118.5, 108.8, 84.9, 81.3, 67.0, 55.1, 27.1, 21.1; IR (film) υ_{max} 2999, 2959, 2847, 1701, 1649, 1500, 1479, 825 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{22}H_{19}NO_3$ + Na]$^+$: 368.1257, found: 368.1260.

*Methyl 1-(3-Methylbut-2-en-1-yl)-2-oxo-3-(phenylethynyl)-indoline-3-carboxylate (±)-(**9e**).* The product **9e** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (216 μL, 0.216 mmol), **2h** (93.4 mg, 0.237 mmol) and the reaction was performed for 16 h to give **9e** in 53.8 mg (0.216 mmol) as a red color oil (65% yield); R_f = 0.57 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.36−7.34 (m, 1H), 7.06−7.02 (m, 1H), 6.85 (d, J = 7.7 Hz, 2H), 5.48 (ddt, J = 17.5, 10.1, 5.8 Hz, 1H), 5.06−5.01 (m, 2H), 4.32 (ddt, J = 13.1, 5.8, 1.4 Hz, 1H), 4.21 (ddt, J = 13.0, 5.9, 1.4 Hz, 1H), 3.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.6, 166.8, 149.3, 147.1, 145.6, 145.5, 130.4, 130.2, 127.8, 126.0, 125.8, 123.5, 123.3, 119.3, 108.9, 85.0, 66.9, 66.6, 26.8. IR (film) υ_{max} 2999, 2901, 2871, 1701, 1694, 1559, 1395, 761 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for [$C_{21}H_{16}N_2O_5$ + H]$^+$: 377.1132, found: 377.1109.

*Allyl 1-Benzyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**9f**).* The product **9f** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (162 μL, 0.162 mmol), **2d** (62 mg, 0.178 mmol) and the reaction was performed for 16 h to give **9f** in 48.0 mg (0.162 mmol) as a yellow color solid (73% yield); mp 77−79 °C; R_f = 0.50 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (td, J = 4.4, 2.1 Hz, 3H), 7.33 (dd, J = 12.1, 7.0 Hz, 7H), 7.29−7.25 (m, 2H), 7.11 (t, J = 7.7 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 5.88 (td, J = 10.9, 5.3 Hz, 1H), 5.36−5.19 (m, 3H), 4.84−4.64 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.3, 165.9, 142.6, 135.0, 132.2, 130.9, 129.9, 128.8, 128.7, 128.2, 127.7, 127.3, 127.1, 124.2, 123.5, 122.1, 118.9, 110.0, 85.0, 81.9, 67.2, 55.3, 44.4; IR (film) υ_{max} 2986, 2916, 1697, 1606, 834 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for [$C_{27}H_{21}NO_3$ + H]$^+$: 408.1594, found: 408.1609.

*Allyl 1-Benzyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9g**).* The product **9g** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (162 μL, 0.162 mmol), **2e** (64.5 mg, 0.178 mmol) and the reaction was performed for 16 h to give **9g** in 47.0 mg (0.162 mmol) as a yellow color gel (69% yield); R_f = 0.47 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: δ 7.52−7.46 (m, 1H), 7.45−7.39 (m, 1H), 7.35−7.28 (m, 4H), 7.26 (d, J = 10.6 Hz, 1H), 7.23−7.14 (m, 3H), 7.08 (q, J = 7.6 Hz, 2H), 6.71 (d, J = 7.8 Hz, 1H), 5.85 (ddt, J = 16.4, 10.9, 5.6 Hz, 1H), 5.31−5.11 (m, 3H), 4.79 (d, J = 15.9 Hz, 1H), 4.74−4.63 (m, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.4, 166.0, 142.6, 141.1, 135.1, 132.2, 131.0, 129.8, 129.4, 128.8, 128.7, 127.7, 127.4, 127.1, 125.4, 124.1, 123.5, 121.9, 119.0, 110.0, 85.8, 84.1, 67.2, 55.4, 44.3, 20.7; IR (film) υ_{max} 2985, 2899, 1799, 1701, 1651, 1361, 1179, 1031, 803 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for [$C_{28}H_{23}NO_3$ + H]$^+$: 422.1751, found: 422.1771.

*Allyl 1-Benzyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**9h**).* The product **9h** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (162 μL, 0.162 mmol), **2f** (64.5 mg, 0.178 mmol) and the reaction was performed for 16 h to give **9h** in 44.0 mg (0.162 mmol) as a light yellow color solid (65% yield); mp 102−105 °C; R_f = 0.40 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (dd, J = 7.5, 1.2 Hz, 1H), 7.44−7.39 (m, 2H), 7.37−7.33 (m, 3H), 7.31 (dd, J = 5.1, 1.8 Hz, 1H), 7.28−7.22 (m, 2H), 7.14−7.08 (m, 3H), 6.73 (d, J = 7.8 Hz, 1H), 5.88 (ddt, J = 17.3, 10.8, 5.6 Hz, 1H), 5.34−5.20 (m, 3H), 4.82−4.65 (m, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.4, 166.0, 142.6, 138.8, 135.0, 132.0, 130.9, 129.8, 128.9, 128.8, 127.72, 127.4, 127.1, 124.2, 123.5, 119.0, 118.8, 109.9, 85.1, 81.2, 67.2, 55.3, 44.3, 21.5; IR (film) υ_{max} 2979, 2899, 5757, 1666, 1569, 1179 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for [$C_{28}H_{23}NO_3$ + H]$^+$: 422.1751, found: 422.1753.

*Allyl 1-Allyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**9i**).* The product **9i** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (194 μL, 0.194 mmol), **2d** (74.3 mg, 0.213 mmol) and the reaction was performed for 16 h to give **9i** in 50.0 mg (0.194 mmol) as a yellow color oil (72% yield); R_f = 0.48 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52−7.43 (m, 3H), 7.32 (td, J = 7.8, 1.3 Hz, 1H), 7.29−7.24 (m, 3H), 7.11 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 7.9 Hz, 1H), 5.84 (dddd, J = 17.5, 10.6, 7.4, 5.2 Hz, 2H), 5.30−5.16 (m, 4H), 4.66 (dq, J = 5.7, 1.8 Hz, 2H), 4.56−4.45 (m, 1H), 4.28 (ddt, J = 16.4, 5.1, 1.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.8, 165.9, 142.7, 132.2, 130.9, 130.5, 129.8, 128.7, 128.1, 127.3, 124.2, 123.4, 122.2, 118.6, 117.7, 109.8, 84.9, 82.0, 67.1, 55.1, 42.9; IR (film) υ_{max} 2989, 2911, 1739, 1700, 1680, 1410, 1111, 805 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{23}H_{19}NO_3$ + Na]$^+$: 380.1257, found: 380.1266.

*Allyl 1-Allyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9j**).* The product **9j** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (190 μL, 0.190 mmol), **2e** (75.7 mg, 0.209 mmol) and the reaction was performed for 10 min to give **9j** in 48.0 mg (0.190 mmol) as a colorless gel (68% yield); R_f = 0.34 (30% EtOAc in hexane).^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, J = 7.5, 1.3 Hz, 1H), 7.40 (dd, J = 7.7, 1.4 Hz, 1H), 7.32 (d, J = 1.3 Hz, 1H), 7.22−7.13 (m, 2H), 7.13−7.04 (m, 2H), 6.85 (d, J = 7.9 Hz, 1H), 5.84 (dddd, J = 17.2, 12.3, 10.5, 5.5 Hz, 2H), 5.33−5.12 (m, 4H), 4.69−4.65 (m, 2H), 4.55−4.42 (m, 1H), 4.30 (ddt, J = 16.6, 5.2, 1.7 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.9, 166.0, 142.7, 141.1, 132.2, 130.9, 130.5, 129.8, 129.3, 128.7, 127.4, 125.3, 124.2, 123.4, 121.9, 118.7, 117.7, 109.8, 85.8, 84.0, 67.1, 55.3, 42.8, 20.7; IR (film) υ_{max} 3002, 2926, 1756, 1713, 1541, 1181, cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{24}H_{21}NO_3$ + Na]$^+$: 394.1414, found: 394.1430.

*Allyl 1-Allyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**9k**).* The product **9k** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (194 μL, 0.194

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mmol), **2f** (77.2 mg, 0.213 mmol) and the reaction was performed for 16 h to give **9k** in 58.0 mg (0.194 mmol) as a colorless gel (80% yield); R_f = 0.40 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (dd, J = 7.4, 1.4 Hz, 1H), 7.40−7.26 (m, 3H), 7.14−7.05 (m, 3H), 6.86 (d, J = 7.8 Hz, 1H), 5.93−5.70 (m, 2H), 5.35−5.09 (m, 4H), 4.65 (q, J = 4.9, 2.1 Hz, 2H), 4.50 (ddt, J = 16.5, 4.0, 2.0 Hz, 1H), 4.31−4.21 (m, 1H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.9, 166.0, 142.7, 138.81, 132.0, 131.0, 130.5, 129.8, 128.9, 127.4, 124.2, 123.4, 119.1, 118.6, 117.7, 109.7, 85.0, 81.2, 67.0, 66.8, 55.2, 42.9, 21.5; IR (film) υ_{max} 2989, 2910, 2870, 1710, 1659, 1025, 831 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{24}H_{21}NO_3$ + Na]$^+$: 394.1414, found: 394.1414.

*Allyl 1-(4-Methoxybenzyl)-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**9l**).* The product **9l** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF (296 μL, 0.296 mmol), **2d** (113.3 mg, 0.325 mmol) and the reaction was performed for 16 h to give **9l** in 78.0 mg (0.296 mmol) as a yellow gel (60% yield); R_f = 0.45 (35% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, J = 7.5, 1.8 Hz, 3H), 7.30−7.21 (m, 6H), 7.07 (t, J = 7.6 Hz, 1H), 6.86−6.82 (m, 2H), 6.73 (d, J = 7.9 Hz, 1H), 5.84 (ddt, J = 16.4, 10.8, 5.5 Hz, 1H), 5.32−5.09 (m, 3H), 4.73−4.62 (m, 3H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.2, 166.0, 159.2, 142.7, 132.2, 131.0, 129.8, 128.7, 128.5, 128.1, 127.3, 127.1, 124.2, 123.5, 122.2, 118.8, 114.2, 110.0, 84.9, 82.0, 67.2, 55.3, 55.2, 43.9; IR (film) υ_{max} 2979, 2910, 2809, 1700,1689,1500, 1320 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{28}H_{23}NO_4$ + Na]$^+$: 460.1519, found: 460.1510.

*Allyl 1-(4-Methoxybenzyl)-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9m**).* The product **9m** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF (296 μL, 0.296 mmol), **2e** (117.9 mg, 0.325 mmol) and the reaction was performed for 16 h to give **9m** in 105.0 mg (0.296 mmol) as a red color gel (78% yield); R_f = 0.44 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49−7.45 (m, 1H), 7.43−7.41 (m, 1H), 7.28−7.24 (m, 2H), 7.24−7.14 (m, 3H), 7.12−7.05 (m, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 7.8 Hz, 1H), 5.84 (ddt, J = 16.4, 10.8, 5.6 Hz, 1H), 5.28−5.2 (m, 2H), 5.11 (d, J = 15.5 Hz, 1H), 4.75−4.66 (m, 3H), 3.76 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.3, 166.1, 159.2, 142.6, 141.1, 132.2, 131.0, 129.8, 129.4, 128.7, 128.6, 128.5, 127.4, 127.1, 125.4, 124.1, 123.4, 122.0, 118.9, 114.2, 110.0, 85.9, 84.1, 55.4, 55.3, 43.8, 20.7; IR (film) υ_{max} 2979, 2938, 2819, 1748, 1694, 1521, 1321, 891 cm^{-1}; HRMS (ESI-TOF) m/z: [M + K]$^+$ calcd for [$C_{29}H_{25}NO_4$ + K]$^+$: 490.1415, found: 490.1433.

*Allyl 1-(4-Methoxybenzyl)-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**9n**).* The product **9n** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (148 μL, 0.148 mmol), **2f** (58.9 mg, 0.162 mmol) and the reaction was performed for 16 h to give **9n** in 50.0 mg (0.148 mmol) as a yellow gel (75% yield); R_f = 0.47 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 7.9 Hz, 2H), 7.25 (t, J = 9.4 Hz, 3H), 7.07 (dd, J = 8.0, 2.5 Hz, 3H), 6.87−6.77 (m, 2H), 6.72 (d, J = 7.5 Hz, 1H), 5.84 (ddt, J = 16.2, 10.8, 5.3 Hz, 1H), 5.29−5.07 (m, 3H), 4.74−4.57 (m, 3H), 3.76 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.3, 166.1, 159.2, 142.6, 138.8, 132.1, 131.0, 130.9, 129.8, 128.9, 128.5, 127.4, 127.1, 124.2, 123.4, 118.8, 114.2, 110.0, 85.1, 81.3, 67.1, 55.3, 55.2, 43.8, 21.5; IR (film) υ_{max} 2989, 2930, 2899, 1699, 1528, 1271, 890 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{29}H_{25}NO_4$ + Na]$^+$: 474.1676, found: 474.1704.

*Allyl 1-Benzyl-5-bromo-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9o**).* The product **9o** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (129 μL, 0.129 mmol), **2e** (51.4 mg, 0.142 mmol) and the reaction was performed for 16 h to give **9o** in 35.20 mg (0.129 mmol) as a yellow oil (55% yield); R_f = 0.47 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, J = 2.0 Hz, 1H), 7.45−7.42 (m, 1H), 7.34 (dd, J = 8.4, 2.0 Hz, 1H), 7.31−7.24 (m, 6H), 7.23−7.15 (m, 2H), 7.11 (td, J = 7.4, 1.8 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 5.86 (ddd, J = 16.4, 10.8, 5.5 Hz, 1H), 5.35−5.11 (m, 3H), 4.78−4.65 (m, 3H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.8, 165.5, 141.6, 141.2, 134.6, 132.8, 132.2, 130.8, 129.4, 129.1, 128.9, 127.9, 127.4, 127.3, 127.1, 125.4, 121.6, 119.4, 116.0, 111.4, 85.0, 84.7, 67.6, 55.2, 44.4, 20.7; IR (film) υ_{max} 2930, 2847, 2246, 2254, 1744, 1699, 890 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{28}H_{22}BrNO_3$ + Na]$^+$: 522.0675, found: 522.0675.

*Allyl 1-Benzyl-5-bromo-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**9p**).* The product **9p** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (129 μL, 0.129 mmol), **2f** (51.4 mg, 0.142 mmol) and the reaction was performed for 16 h to give **9p** in 33.0 mg (0.129 mmol) as a yellow oil (50% yield); R_f = 0.47 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H), 7.35−7.25 (m, 6H), 7.10 (d, J = 7.8 Hz, 2H), 6.56 (d, J = 8.3 Hz, 1H), 5.86 (ddt, J = 16.3, 10.8, 5.6 Hz, 1H), 5.35−5.13 (m, 3H), 4.77−4.62 (m, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.8, 165.5, 141.6, 139.1, 134.6, 132.7, 132.1, 130.8, 129.1, 129.0, 128.9, 127.9, 127.4, 127.1, 119.2, 118.8, 116.0, 111.4, 85.7, 80.4, 67.5, 55.1, 44.4, 21.6; IR (film) υ_{max} 2979, 2921, 2811, 1678, 1608, 1299, 910 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{28}H_{22}BrNO_3$ + Na]$^+$: 522.0675, found: 522.0671.

*Allyl 1-Allyl-5-bromo-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9q**).* The product **9q** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (148 μL, 0.148 mmol), **2e** (58.9 mg, 0.162 mmol) and the reaction was performed for 16 h to give **9q** in 37.5 mg (0.148 mmol) as a yellow oil (56% yield); R_f = 0.45 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J = 2.0 Hz, 1H), 7.45 (dd, J = 8.3, 2.0 Hz, 1H), 7.42−7.38 (m, 1H), 7.23−7.14 (m, 2H), 7.09 (td, J = 7.4, 1.7 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.84 (dddt, J = 15.2, 10.1, 7.5, 5.3 Hz, 2H), 5.32−5.16 (m, 4H), 4.68 (tt, J = 5.5, 1.5 Hz, 2H), 4.48 (ddt, J = 16.7, 4.5, 1.9 Hz, 1H), 4.27 (ddt, J = 16.6, 5.2, 1.7 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.3, 165.4, 141.8, 141.2, 132.7, 132.2, 130.8, 130.1, 129.4, 129.1, 128.9, 127.4, 125.4, 121.6, 119.1, 117.9, 115.9, 111.2, 85.0, 84.6, 67.4, 55.1, 42.9, 20.7; IR (film) υ_{max} 2989, 2925, 2878, 1660, 842 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{24}H_{20}BrNO_3$ + Na]$^+$: 472.0519, found: 472.0530.

*Allyl 1-Allyl-5-bromo-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9r**).* The product **9r** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (148 μL, 0.148 mmol), **2f** (58.9 mg, 0.162 mmol) and the reaction was performed for 16 h to give **9r** in 41.0 mg (0.148 mmol) as a yellow gel (61% yield); R_f = 0.44 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, J = 2.0 Hz, 1H), 7.44 (dd, J = 8.3, 2.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.72 (d, J = 8.4 Hz, 1H), 5.90−5.75 (m, 2H), 5.33−5.18 (m, 4H), 4.73−4.61 (m, 2H), 4.49 (dt, J = 16.6, 2.7 Hz, 1H), 4.24 (dd, J = 16.7, 4.9 Hz, 1H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.4, 165.4, 141.7, 139.1, 132.7, 132.1, 130.8, 130.1, 129.1, 128.9, 127.5, 119.0, 118.8, 117.9, 115.9, 111.2, 85.6, 80.5, 67.3, 55.0, 42.9, 21.5; IR (film) υ_{max} 2975, 2955, 2880, 1691, 1555, 1220 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for [$C_{24}H_{20}BrNO_3$ + Na]$^+$: 472.0519, found: 472.0520.

*Allyl 5-Chloro-1-methyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9s**).* The product **9s** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (188 μL, 0.188 mmol), **2e** (74.9 mg, 0.206 mmol) and the reaction was performed for 16 h to give **9s** in 36.5 mg (0.188 mmol) as a yellow gel (51% yield); R_f = 0.35 (15% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J = 2.1 Hz, 1H), 7.40 (ddd, J = 19.2, 8.1, 1.8 Hz, 2H), 7.28 (s, 1H), 7.23−7.19 (m, 1H), 7.12 (td, J = 7.3, 1.6 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.89 (ddt, J = 17.2, 10.8, 5.5 Hz, 1H), 5.36−5.23 (m, 2H), 4.72 (dt, J = 5.6, 1.5 Hz, 2H), 3.31 (s, 3H), 2.47(s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 169.6, 165.4, 142.1, 141.1, 132.2, 130.8, 129.9, 129.4, 128.9, 128.9, 125.4, 124.7, 121.6, 119.0, 109.8, 100.0, 85.0, 84.4, 67.4, 55.5, 27.2, 20.7; IR (film) υ_{max} 2977, 2900, 1756, 1665, 981, cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for [$C_{22}H_{18}ClNO_3$ + H]$^+$: 380.1048, found: 380.1037.

*Allyl 1-Benzyl-5-chloro-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**9t**).* The product **9t** was synthesized according to the

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general experimental procedure B (2.5 mL THF) using TBAF (146 μL, 0.146 mmol), **2a** (58.1 mg, 0.160 mmol) and the reaction was performed for 16 h to give **9t** in 39.20 mg (0.146 mmol) as a yellow gel (59% yield); R_f = 0.50 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.50(d, *J* = 2.1 Hz, 1H), 7.46(dd, *J* = 7.6, 1.3 Hz, 1H), 7.40−7.30 (m, 5H), 7.30−7.26 (m, 1H), 7.25−7.21 (m, 2H), 7.14 (td, *J* = 7.4, 1.6 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.90 (ddt, *J* = 17.3, 10.5, 5.7 Hz, 1H), 5.38−5.16 (m, 3H), 4.85−4.67 (m, 3H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 169.9, 165.5, 141.1, 141.1, 134.6, 132.2, 130.8, 129.8, 129.4, 128.9, 128.8, 128.7, 127.9, 127.0, 125.4, 124.6, 121.6, 119.3, 110.9, 85.0, 84.6, 67.5, 55.3, 44.5, 20.7; IR (film) υ_{max} 2990, 2888, 1700, 1555, 901 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{28}H_{22}ClNO_3$ + Na]$^+$: 478.1180, found: 478.1162.

*2-Methallyl 1-Methyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**10a**).* The product **10a** was synthesized according to the general experimental procedure B (2.5 mL THF) using TBAF (101 μL, 0.101 mmol), **2d** (38.6 mg, 0.111 mmol) and the reaction was performed for 16 h to give **10a** in 28.0 mg (0.101 mmol) as a colorless gel (80% yield); R_f = 0.50 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51−7.42 (m, 3H), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H), 7.27 (dtd, *J* = 7.4, 5.8, 5.4, 1.8 Hz, 3H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.88 (dt, *J* = 9.3, 1.4 Hz, 2H), 4.64−4.51 (m, 2H), 3.28 (s, 3H), 1.65 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.0, 165.8, 143.5, 138.9, 132.1, 130.0, 128.7, 128.1, 127.2, 124.3, 123.5, 122.2, 113.3, 108.9, 84.8, 82.0, 69.6, 55.1, 27.1, 19.2; IR (film) υ_{max} 2986, 2897,1739, 1667, 1250 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{22}H_{19}NO_3$ + Na]$^+$: 368.1257, found: 368.1282.

*2-Methallyl 1-Methyl-2-oxo-3-(o-tolylethynyl) indoline-3-carboxylate (±)-(**10b**).* The product **10b** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (203 μL, 0.203 mmol), **2e** (80.8 mg, 0.223 mmol) and the reaction was performed for 16 h to give **10b** in 55.0 mg (0.203 mmol) as a yellow oil (75% yield); R_f = 0.42 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.38−7.32 (m, 3H), 7.13−7.05 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.89−4.86 (m, 2H), 4.62−4.52 (m, 2H), 3.27 (s, 3H), 2.30 (s, 3H), 1.65 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 165.9, 143.5, 138.9, 138.8, 132.0, 129.9, 129.8, 128.9, 127.4, 125.9, 124.3, 123.5, 119.1, 113.2, 108.8, 84.9, 81.3, 69.6, 55.2, 27.0, 21.5, 19.2; IR (film) υ_{max} 2994, 2946, 1700, 1626, 1120, 813 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{23}H_{21}NO_3$ + Na]$^+$: 382.1414, found: 382.1428.

*2-Methallyl 1-Methyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**10c**).* The product **10c** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (203 μL, 0.203 mmol), **2f** (80.8 mg, 0.223 mmol) and the reaction was performed for 16 h to give **10c** in 59.0 mg (0.203 mmol) as a light yellow gel (81% yield); R_f = 0.40 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.42−7.32 (m, 2H), 7.20−7.06 (m, 4H), 6.87 (d, *J* = 7.8 Hz, 1H), 4.93−4.83 (m, 2H), 4.64−4.50 (m, 2H), 3.28 (s, 3H), 2.43 (s, 3H), 1.65 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 165.9, 143.6, 141.0, 138.9, 132.2, 129.9, 129.3, 128.7, 125.4, 124.1, 123.5, 113.4, 108.9, 85.9, 83.9, 69.6, 55.3, 27.1, 20.7, 19.2; IR (film) υ_{max} 2958, 2917, 1686, 1422, 1336, 781 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{23}H_{21}NO_3$ + Na]$^+$: 382.1414, found: 382.1430.

*2-Methylallyl 1-Allyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**10d**).* The product **10d** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (184 μL, 0.184 mmol), **2e** (73.3 mg, 0.202 mmol) and the reaction was performed for 16 h to give **10d** in 45.0 mg (0.184 mmol) as a light yellow gel (63% yield); R_f = 0.47 (30% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.36 (td, *J* = 7.8, 1.3 Hz, 1H), 7.25−7.18 (m, 2H), 7.13 (dtd, *J* = 13.9, 7.5, 1.3 Hz, 2H), 6.92−6.88 (m, 1H), 5.90 (ddt, *J* = 17.2, 10.2, 5.0 Hz, 1H), 5.34−5.23 (m, 2H), 4.91 (dp, *J* = 8.6, 1.2 Hz, 2H), 4.67−4.59 (m, 2H), 4.55 (ddt, *J* = 16.6, 4.8, 1.8 Hz, 1H), 4.33 (ddt, *J* = 16.5, 5.1, 1.7 Hz, 1H), 2.47 (s, 3H), 1.68 (t, *J* = 1.1 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 169.9, 166.1, 142.7, 141.1, 138.9, 132.2, 130.5, 129.8, 129.3, 128.7, 127.5, 125.4, 124.1, 123.4, 121.9, 117.7, 113.6, 109.8, 85.8, 84.0, 69.7, 55.4, 42.9, 20.7, 19.2; IR (film) υ_{max} 2985, 2954, 2870, 1685, 1310 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{25}H_{23}NO_3$ + Na]$^+$: 408.1570, found: 408.1583.

*3-Methyl But-2-en-1-yl 1-methyl-2-oxo-3-(phenylethynyl)-indoline-3-carboxylate (±)-(**10e**).* The product **10e** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF (308 μL, 0.308 mmol), **2d** (117.9 mg, 0.338 mmol) and the reaction was performed for 16 h to give **10e** in 83.9 mg (0.308 mmol) as a yellow oil (76% yield); R_f = 0.59 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51−7.41 (m, 3H), 7.36 (td, *J* = 7.8, 1.2 Hz, 1H), 7.26 (td, *J* = 7.2, 6.7, 2.9 Hz, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.31−5.21 (m, 1H), 4.65 (dd, *J* = 7.4, 3.1 Hz, 2H), 3.27 (s, 3H), 1.70 (s, 3H), 1.62 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1, 166.1, 143.5, 140.1, 132.1, 129.8, 128.6, 128.1, 127.4, 124.2, 123.4, 122.3, 117.6, 108.8, 84.5, 82.3, 63.9, 55.1, 27.1, 25.7, 18.1. IR (film) υ_{max} 2999, 2926, 1701, 1656, 1519, 1189, 737 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{23}H_{21}NO_3$ + Na]$^+$: 382.1414, found: 382.1426.

*3-Methyl But-2-en-1-yl 1-methyl-2-oxo-3-(o-tolylethynyl)-indoline-3-carboxylate (±)-(**10f**).* The product **10f** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF (308 μL, 0.308 mmol), **2e** (122.7 mg, 0.338 mmol) and the reaction was performed for 16 h to give **10f** in 78.0 mg (0.308 mmol) as a light yellow gel (68% yield); R_f = 0.59 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.4 Hz, 1H), 7.40−7.32 (m, 2H), 7.22−7.14 (m, 2H), 7.13−7.04 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.32−5.23 (m, 1H), 4.66 (d, *J* = 7.1 Hz, 2H), 3.27 (s, 3H), 2.42 (s, 3H), 1.70 (s, 3H), 1.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.2, 166.3, 143.5, 141.1, 140.1, 132.1, 129.8, 129.3, 128.6, 127.5, 125.3, 124.2, 123.4, 122.0, 117.6, 108.8, 86.1, 83.7, 63.9, 55.3, 27.1, 25.7, 20.6, 18.1; IR (film) υ_{max} 2958, 2900, 2877, 1698, 1589, 1310,1035 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{24}H_{23}NO_3$ + Na]$^+$: 396.1570, found: 396.1575.

*3-Methyl But-2-en-1-yl 1-methyl-2-oxo-3-(p-tolylethynyl)-indoline-3-carboxylate (±)-(**10g**).* The product **10g** was synthesized according to the general experimental procedure B (3.5 mL THF) using TBAF (308 μL, 0.308 mmol), **2f** (122.7 mg, 0.338 mmol) and the reaction was performed for 16 h to give **10g** in 75.0 mg (0.308 mmol) as a light yellow gel (65% yield); R_f = 0.49 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.4 Hz, 1H), 7.40−7.28 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.30−5.22 (m, 1H), 4.64 (dd, *J* = 7.3, 3.1 Hz, 2H), 3.27 (s, 3H), 2.30 (s, 3H), 1.69 (s, 3H), 1.62 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.25, 166.23, 143.49, 140.01, 138.72, 132.02, 129.76, 128.85, 127.47, 124.24, 123.39, 119.16, 117.66, 108.77, 84.65, 81.54, 63.90, 55.14, 27.05, 25.73, 21.50, 18.11; IR (film) υ_{max} 2969, 2910, 2812, 1659, 1211, 731 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{24}H_{23}NO_3$ + Na]$^+$: 396.1570, found: 396.1578.

*3-Methyl But-2-en-1-yl 1-allyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**10h**).* The product **10h** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF (350 μL, 0.350 mmol), **2e** (139.4 mg, 0.385 mmol) and the reaction was performed for 16 h to give **10h** in 97.5 mg (0.350 mmol) as a yellow gel (70% yield); R_f = 0.50 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.22−7.13 (m, 2H), 7.12−7.04 (m, 2H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.85 (ddd, *J* = 12.3, 10.4, 5.2 Hz, 1H), 5.33−5.15 (m, 4H), 4.71−4.57 (m, 2H), 4.51 (ddt, *J* = 16.8, 4.2, 1.9 Hz, 1H), 4.32−4.20 (m, 1H), 2.43 (s, 3H), 1.69 (s, 3H), 1.60 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.3, 142.7, 141.1, 140.4, 132.1, 130.5, 129.7, 129.3, 128.6, 127.6, 125.3, 124.1, 123.3, 122.0, 117.5, 117.5, 109.67, 86.1, 83.9, 63.8, 55.4, 42.8, 25.7, 20.6, 18.1; IR (film) υ_{max} 2989, 2950, 2872, 1752, 1679, 1541, 1351 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{26}H_{25}NO_3$ + Na]$^+$: 422.1727, found: 422.1747.

*3-Methyl But-2-en-1-yl 1-allyl-2-oxo-3-(phenylethynyl)indoline-3-carboxylate (±)-(**10i**).* The product **10i** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF

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(350 μL, 0.350 mmol), **2d** (134 mg, 0.385 mmol) and the reaction was performed for 16 h to give **10i** in 85.0 mg (0.350 mmol) as a light yellow gel (64% yield); R_f = 0.45 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05−7.95 (m, 1H), 7.48−7.44 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.20−7.16 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.85 (ddt, *J* = 17.3, 10.1, 4.9 Hz, 1H), 5.29−5.20 (m, 3H), 4.76−4.56 (m, 2H), 4.54−4.43 (m, 1H), 4.25 (dd, *J* = 16.7, 5.1 Hz, 1H), 1.69 (s, 3H), 1.60 (s, 3H; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.1, 142.7, 141.4, 140.3, 134.0, 132.2, 130.5, 129.7, 128.9, 128.6, 128.1, 124.2, 123.3, 117.5, 109.7, 84.7, 82.2, 63.8, 55.24, 42.8, 25.7, 18.1; IR (film) υ_{max} 2960, 2986, 2810, 1656, 1342, 1201 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{25}H_{23}NO_3$ + Na]$^+$: 408.1570, found: 408.1585.

*3-Methyl But-2-en-1-yl 1-allyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**10j**).* The product **10j** was synthesized according to the general experimental procedure B (4.0 mL THF) using TBAF (139.4 μL, 0.385 mmol), **2f** (350 mg, 0.350 mmol) and the reaction was performed for 16 h to give **10j** in 86.0 mg (0.350 mmol) as a yellow gel (62% yield); R_f = 0.45 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 3H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.85 (ddd, *J* = 12.5, 10.4, 5.2 Hz, 1H), 5.29−5.19 (m, 3H), 4.69−4.56 (m, 2H), 4.54−4.47 (m, 1H), 4.32−4.19 (m, 1H), 2.31 (s, 3H), 1.69 (s, 3H), 1.60 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 170.1,166.2,142.7,140.3, 138.7, 132.1, 130.5, 129.6, 128.9, 127.5, 124.2, 123.3, 119.2, 117.5, 117.5, 109.7, 84.9, 81.4, 63.8,55.3, 42.8, 25.7, 21.5, 18.1; IR (film) υ_{max} 2988, 2922, 2819, 1741, 1691, 1202 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{26}H_{25}NO_3$ + Na]$^+$: 422.1727, found: 422.1731.

*(E)-3,7-Dimethyl octa-2,6-dien-1-yl 1-methyl-2-oxo-3-(o-tolylethynyl)indoline-3-carboxylate (±)-(**10k**).* The product **10k** was synthesized according to the general experimental procedure B (3.0 mL THF) using TBAF (152 μL, 0.152 mmol), **2e** (60.5 mg, 0.167 mmol) and the reaction was performed for 16 h to give **10k** in 44.0 mg (0.152 mmol) as a brownish gel (65% yield); R_f = 0.55 (25% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.40−7.32 (m, 2H), 7.20−7.14 (m, 2H), 7.08 (dtd, *J* = 14.7, 7.4, 1.4 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 5.32−5.21 (m, 1H), 5.07−4.96 (m, 1H), 4.68 (d, *J* = 7.1 Hz, 2H), 3.28 (s, 3H), 2.42 (s, 3H), 2.07−1.92 (m, 4H), 1.65 (d, *J* = 1.5 Hz, 3H), 1.62 (d, *J* = 1.3 Hz, 3H), 1.57 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.2, 166.2, 143.5, 143.5, 141.1, 132.1, 131.8, 129.8, 129.3, 128.6, 127.5, 125.3, 124.1, 123.7, 123.4, 122.0, 117.3, 108.8, 86.1, 83.7, 63.8, 55.3, 39.5, 27.0, 26.3, 25.7, 20.6, 17.7, 16.5; IR (film) υ_{max} 2986, 2931, 2890, 2811, 1666, 1271 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{29}H_{31}NO_3$ + Na]$^+$: 464.2196, found: 464.2181.

*(E)-3,7-Dimethyl octa-2,6-dien-1-yl 1-methyl-2-oxo-3-(p-tolylethynyl)indoline-3-carboxylate (±)-(**10l**).* The product **10l** was synthesized according to the general experimental procedure B (2.0 mL THF) using TBAF (76 μL, 0.076 mmol), **2f** (30.3 mg, 0.083 mmol) and the reaction was performed for 16 h to give **10l** in 25.0 mg (0.076 mmol) as a light brownish gel (74% yield); R_f = 0.35 (15% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.37−7.30 (m, 3H), 7.12−7.04 (m, 3H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.26 (ddd, *J* = 8.4, 6.6, 1.6 Hz, 1H), 5.08−4.98 (m, 1H), 4.67 (d, *J* = 7.0 Hz, 2H), 3.27 (s, 3H), 2.30 (s, 3H), 2.00 (qt, *J* = 8.2, 5.9, 4.4 Hz, 4H), 1.65 (s, 3H), 1.61 (s, 3H), 1.57 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 170.3, 166.2, 143.5, 143.4, 138.7, 132.0, 131.8, 129.8, 128.8, 127.5, 124.2, 123.7, 123.4, 119.2, 117.4, 108.8, 84.7, 81.5, 63.8, 55.2, 39.5, 27.0, 26.3, 25.7, 21.5, 17.7, 16.5; IR (film) υ_{max} 2975, 2944, 2844, 2849, 1669, 1511, 1255, 855, 740 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{29}H_{31}NO_3$ + Na]$^+$: 464.2196, found: 464.2193.

*tert-Butyl 3-methyl-2-oxo-3-(phenylethynyl)indoline-1-carboxylate (±)-(**12a**).* The product **12a** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (23.8 μL, 0.190 mmol), **2d** (72.7 mg, 0.209 mmol) and the reaction was performed for 10 min to give **12a** in 56.0 mg (0.190 mmol) as a white solid (85% yield); MP 88−90 °C; R_f = 0.34 (5% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.2 Hz, 1H), 7.41 (ddd, *J* = 14.7, 7.5, 2.0 Hz, 3H), 7.33 (td, *J* = 7.9, 1.4 Hz, 1H), 7.28−7.25 (m, 2H), 7.23 (d, *J* = 14.1 Hz, 2H), 1.78 (s, 3H), 1.64 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 174.0, 149.2, 138.2, 131.9, 131.2, 130.5, 128.8, 128.1, 125.0, 123.4, 122.4, 115.3, 87.2, 84.7, 83.1, 44.1, 28.0, 26.7; IR (film) υ_{max} 3010, 2922, 2360, 1711, 1610, 1512, 1351, 744 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{22}H_{21}NO_3$ + Na]$^+$: 370.1414, found: 370.1415.

*tert-Butyl 3-(2-methoxyphenyl)-2-oxo-3-(phenylethynyl)-indoline-1-carboxylate (±)-(**12b**).* The product **12b** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (11 μL, 0.088 mmol), **2d** (33.7 mg, 0.096 mmol) and the reaction was performed for 10 min to give **12b** in 36.5 mg (0.088 mmol) as a white solid (94% yield), mp 137−139 °C; R_f = 0.26 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.49−7.47 (m, 2H), 7.30 (td, *J* = 5.5, 2.6 Hz, 5H), 7.11−7.02 (m, 3H), 6.78 (dd, *J* = 8.2, 1.1 Hz, 1H), 3.48 (s, 3H), 1.68 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.8, 156.1, 149.7, 139.5, 132.0, 130.9, 129.9, 129.8, 128.6, 128.4, 128.2, 127.4, 124.7, 123.5, 122.4, 121.1, 114.8, 112.2, 87.0, 85.6, 84.2, 55.7, 51.9, 28.2; IR (film) υ_{max} 3158, 2960, 2079, 1712, 1681, 771 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{28}H_{25}NO_4$ + Na]$^+$: 462.1676, found: 462.1664.

*tert-Butyl 3-((tert-butyldiphenylsilyl)ethynyl)-3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-oxoindoline-1-carboxylate (±)-(**12c**).* The product **12c** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (12.3 μL, 0.098 mmol), **2c** (55 mg, 0.107 mmol) and the reaction was performed for 10 min to give **12c** in 52.0 mg (0.098 mmol) as a clear oil (79% yield); R_f = 0.36 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.2 Hz, 1H), 7.73 (dq, *J* = 8.3, 3.3, 2.5 Hz, 6H), 7.64 (td, *J* = 5.2, 2.1 Hz, 2H), 7.42 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.37−7.31 (m, 6H), 7.20 (td, *J* = 7.9, 1.4 Hz, 1H), 7.08 (td, *J* = 7.6, 1.1 Hz, 1H), 4.01 (ddd, *J* = 13.9, 8.5, 6.9 Hz, 1H), 3.87 (ddd, *J* = 14.0, 8.6, 5.4 Hz, 1H), 2.68−2.53 (m, 2H), 1.65 (s, 9H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 171.7, 167.7, 149.0, 138.9, 135.6 (d, *J* = 2.0 Hz), 133.8, 132.8 (d, *J* = 3.0 Hz), 132.0, 129.5, 129.1, 128.3, 127.7, 124.9, 123.5, 123.1, 115.6, 105.5, 84.8, 47.5, 37.0, 28.1, 27.0, 18.7; IR (film) υ_{max} 3421, 2979, 2851, 1777, 1720, 1654, 1235 cm^{-1}.

*tert-Butyl 3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-2-oxo-3-(phenylethynyl)indoline-1-carboxylate (±)-(**12d**).* The product **12d** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (15.4 μL, 0.123 mmol), **2d** (47.1 mg, 0.135 mmol) and the reaction was performed for 10 min to give **12d** in 53.0 mg (0.123 mmol) as a light yellow solid (85% yield), mp 120−122 °C; R_f = 0.35 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.62 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.48 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.26−7.19 (m, 4H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 4.04 (dt, *J* = 14.0, 7.6 Hz, 1H), 3.89 (ddd, *J* = 13.8, 8.2, 5.2 Hz, 1H), 2.64 (dt, *J* = 13.7, 7.8 Hz, 1H), 2.46 (ddd, *J* = 13.5, 8.0, 5.2 Hz, 1H), 1.63 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.4, 167.9, 149.0, 138.8, 133.8, 133.9, 132.0, 131.9, 129.0, 128.8, 128.5, 128.2, 128.1, 125.0, 123.8, 123.1, 122.2, 115.5, 85.4, 84.7, 84.5, 46.9, 36.7, 33.9, 28.1; IR (film) υ_{max} 3142, 2965, 2187, 1717, 1680, 1644 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{31}H_{26}N_2O_5$+ Na]$^+$: 529.1734, found: 529.1745.

*1,3-Dimethyl-3-(phenylethynyl)indolin-2-one (±)-(**14a**).* The product **14a** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (27.2 μL, 0.217 mmol), **2d** (83.1 mg, 0.238 mmol) and the reaction was performed for 10 min to give **14a** in 51.0 mg (0.217 mmol) as a white solid (92% yield), mp 65−67 °C; R_f = 0.42 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43−7.39 (m, 3H), 7.30 (td, *J* = 7.8, 1.3 Hz, 1H), 7.24 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 1.74 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 175.9, 142.4, 132.5, 131.9, 128.7, 128.3, 128.1, 123.4, 123.2, 122.7, 108.5, 87.6, 82.4, 43.5, 26.7, 25.7; IR (film) υ_{max} 3111, 2979, 2268, 1705, 1611, 814 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{18}H_{15}NO$ + Na]$^+$: 284.1046, found: 284.1065.

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*2-(2-(1-Methyl-2-oxo-3-(phenylethynyl)indolin-3-yl)ethyl)-isoindoline-1,3-dione (±)-(**14b**).* The product **14b** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (9.8 μL, 0.078 mmol), **2d** (29.8 mg, 0.085 mmol) and the reaction was performed for 10 min to give **14b** in 29.50 mg (0.078 mmol) as a colorless gel (91% yield); R_f = 0.45 (40% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.60 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.42 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.34 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.24−7.18 (m, 3H), 7.12 (td, *J* = 7.7, 1.3 Hz, 1H), 6.91 (td, *J* = 7.6, 1.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.04−3.98 (m, 1H), 3.79 (ddd, *J* = 14.2, 7.5, 5.1 Hz, 1H), 3.23 (s, 3H), 2.70 (dt, *J* = 13.8, 7.7 Hz, 1H), 2.46 (ddd, *J* = 13.8, 7.2, 5.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 174.2, 167.9, 142.8, 133.8, 133.7, 132.0, 131.9, 129.8, 128.7, 128.3, 128.1, 123.7, 123.1, 123.0, 122.9 122.5, 108.7; IR (film) υ_{max} 2981, 1749, 1711, 1610, 1371, 1039 cm^{-1}.

*3-((tert-Butyldiphenylsilyl)ethynyl)-1-methyl-3-phenylindolin-2-one (±)-(**14c**).* The product **14c** was synthesized according to the general experimental procedure A (2.5 mL toluene) using TMG (19.7 μL, 0.157 mmol), **2c** (88.1 mg, 0.172 mmol) and the reaction was performed for 10 min to give **14c** in 67.0 mg (0.157 mmol) as a light yellow solid (87% yield), mp 93−95 °C; R_f = 0.45 (40% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (ddd, *J* = 7.2, 3.0, 1.7 Hz, 4H), 7.48−7.46 (m, 2H), 7.40−7.29 (m, 11H), 7.17−7.13 (m, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.27 (s, 3H), 1.09 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.7, 143.3, 138.3, 135.6 (d, *J* = 1.4 Hz), 133.1 (d, *J* = 3.3 Hz), 131.5, 129.5, 129.2, 128.8, 128.0, 127.7, 126.9, 125.0, 123.5, 108.7, 106.8, 84.8, 53.5, 29.7, 27.1, 18.8; IR (film) υ_{max} 3102, 2989, 2987, 2152, 1749, 1576 cm^{-1}.

*1-Methyl-3-phenyl-3-(phenylethynyl)indolin-2-one (±)-(**14d**).* The product **14d** was synthesized according to the general experimental procedure A (2.5 mL toluene) using TMG (19.7 μL, 0.157 mmol), **2d** (60.1 mg, 0.172 mmol) and the reaction was performed for 12 min to give **14d** in 46.0 mg (0.157 mmol) as a white solid (92% yield), mp 144−146 °C; R_f = 0.35 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53−7.47 (m, 4H), 7.40−7.28 (m, 8H), 7.15 (td, *J* = 7.6, 1.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 174.3, 143.1, 138.4, 131.9, 131.8, 129.1, 128.7, 128.4, 128.1, 127.9, 126.8, 124.9, 123.5, 122.5, 108.6, 86.5, 84.3, 52.8, 26.9; IR (film) υ_{max} 3060, 2929, 2248, 1734, 780 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+H]$^+$ calcd for [$C_{23}H_{17}NO$ + H]$^+$: 324.1383, found: 324.1405.[27a]

*3-(2-Methoxyphenyl)-1-methyl-3-(phenylethynyl)indolin-2-one (±)-(**14e**).* The product **14e** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (12.8 μL, 0.102 mmol), **2d** (39 mg, 0.112 mmol) and the reaction was performed for 10 min to give **14e** in 29.5 mg (0.102 mmol) as a white solid (82% yield), mp 147−149 °C; R_f = 0.35 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.49−7.47 (m, 2H), 7.32−7.25 (m, 5H), 7.09 (td, *J* = 7.6, 1.1 Hz, 1H), 7.04 (d, *J* = 6.1 Hz, 1H), 7.00−6.96 (m, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.78−6.75 (m, 1H), 3.43 (s, 3H), 3.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 175.3, 156.4, 143.7, 132.0, 130.2, 129.6, 128.4, 128.30, 128.2, 123.3, 122.9, 121.0,120.9, 112.1, 107.8, 86.0, 85.8, 55.9, 51.3, 27.0; IR (film) υ_{max} 3067, 2955, 2859, 1731, 1150 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+H]$^+$ calcd for [$C_{24}H_{19}NO_2$ + H]$^+$: 354.1489, found: 354.1502.[27a]

*1-Methyl-3-(2-nitrophenyl)-3-(phenylethynyl)indolin-2-one (±)-(**14f**).* The product **14f** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (18.7 μL, 0.149 mmol), **2d** (57 mg, 0.164 mmol) and the reaction was performed for 15 min to give **14f** in 48.02 mg (0.149 mmol) as a yellow solid (85% yield); mp 139−140 °C; R_f = 0.44 (20% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.78−7.71 (m, 2H), 7.51 (td, *J* = 7.8, 1.4 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.36−7.25 (m, 4H), 7.02 (dd, *J* = 6.9, 1.3 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 3.37 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.4, 148.4, 144.1, 133.4, 132.9, 132.0, 130.7, 129.6, 129.4, 129.4, 128.9, 128.3, 125.2, 123.2, 122.8, 122.0, 108.8, 86.1, 85.7, 52.3, 27.2; IR (film) υ_{max} 3115, 2916, 1700, 1644, 1487, 1356, 1216, 1178, 939, 726 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+H]$^+$ calcd for [$C_{23}H_{16}N_2O_3$ + H]$^+$: 369.1234, found: 369.1226.

*3-Methyl-3-(phenylethynyl)indolin-2-one (±)-(**16a**).* The product **16a** was synthesized according to the general experimental procedure A (2.5 mL toluene) using TMG (25 μL, 0.20 mmol), **2d** (76.6 mg, 0.22 mmol) and the reaction was performed for 20 min to give **16a** in 41.50 mg (0.20 mmol) as a white solid (85% yield); mp 72−74 °C; R_f = 0.31 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.58 (d, *J* = 9.5 Hz, 1H), 7.46−7.35 (m, 3H), 7.29−7.19 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 1.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 179.1, 139.8, 133.0, 131.9, 128.7, 128.3, 128.1, 123.6, 123.2, 122.7, 110.6, 87.3, 82.7, 44.1, 25.7; IR (film) υ_{max} 3219, 2981, 2079, 1729, 1689 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M +Na]$^+$ calcd for [$C_{17}H_{13}NO$ + Na]$^+$: 270.0889, found: 270.0886.

*3-(2-Methoxyphenyl)-3-(phenylethynyl)indolin-2-one (±)-(**16b**).* The product **16b** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (15.7 μL, 0.125 mmol), **2d** (47.8 mg, 0.137 mmol) and the reaction was performed for 35 min to give **16b** in 38.0 mg (0.125 mmol) as a colorless gel (90% yield); R_f = 0.25 (40% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (s, 1H), 8.15 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.49−7.46 (m, 2H), 7.34−7.26 (m, 4H), 7.20−7.15 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01−6.99 (m, 1H), 6.95−6.91 (m, 2H), 6.81−6.78 (m, 1H), 3.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 177.7, 156.5, 140.8, 132.8, 132.0, 130.2, 129.7, 128.5, 128.2, 128.2, 126.6, 123.5, 122.8, 122.6, 121.0, 112.2, 109.7, 86.0, 85.9, 55.6, 51.8; IR (film) υ_{max} 3200, 2962, 2083, 1725, 1661, 778 cm^{-1}.

*2-[2-(2-Oxo-3-(phenylethynyl)indolin-3-yl)ethyl] isoindoline-1,3-dione (±)-(**16c**).* The product **16c** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (12.3 μL, 0.098 mmol), **2d** (37.5 mg, 0.107 mmol) and the reaction was performed for 25 min to give **16c** in 36.5 mg (0.098 mmol) as a white solid (92% yield), mp 180−182 °C; R_f = 0.21 (40% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (s, 1H), 7.79−7.68 (m, 2H), 7.63−7.54 (m, 2H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 6.8 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 3H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.06 (dt, *J* = 14.5, 7.4 Hz, 1H), 3.88 (ddd, *J* = 13.9, 8.1, 5.5 Hz, 1H), 2.65 (dt, *J* = 14.6, 7.6 Hz, 1H), 2.48 (dt, *J* = 13.7, 6.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 176.9, 168.0, 140.1, 133.8, 132.0, 131.9, 130.4, 128.9, 128.3, 128.1,128.0, 124.1, 123.1, 123.1, 122.4, 110.7, 85.6, 84.0, 46.7, 35.9, 34.0; IR (film) υ_{max} 3257, 3065, 2973, 2927, 1772, 1707, 1629 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+H]$^+$ calcd for [$C_{26}H_{18}N_2O_3$ + H]$^+$: 407.1390, found: 407.1402.

*3,5-Dimethyl-3-(phenylethynyl)benzofuran-2(3H)-one (±)-(**18a**).* The product **18a** was synthesized according to the general experimental procedure A (2.0 mL toluene), the reaction was performed in 37.30 mg (0.154 mmol) with TMG (19.3 μL, 0.154 mmol), **2d** (59 mg, 0.169 mmol) for 15 min to give **18a** in 92% yield as a colorless oil, R_f = 0.40 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43−7.40 (m, 2H), 7.30−7.23 (m, 4H), 7.13 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 2.37 (s, 3H), 1.84 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 175.5, 150.0, 134.7, 131.9, 130.6, 124.0, 128.7, 128.2, 124.1, 122.1, 110.8, 85.9, 83.6, 42.3, 26.6, 21.2; IR (film) υ_{max} 3001, 2989, 1807, 1735, 1479, 1251, 830 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: [M+Na]$^+$ calcd for [$C_{18}H_{14}O_2$ + Na]$^+$: 285.0886, found: 285.0879.

*3,5-Dimethyl-3-(o-tolylethynyl)benzofuran-2(3H)-one (±)-(**18b**).* The product **18b** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (19.3 μL, 0.154 mmol), **2e** (61.3 mg, 0.169 mmol) and the reaction was performed for 15 min to give **18b** in 40.80 mg (0.154 mmol) as a colorless oil (96% yield); R_f = 0.40 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.28−7.24 (m, 2H), 7.22−7.20 (m, 1H), 7.19−7.12 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H), 2.41 (s, 3H), 1.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 175.5, 150.0, 140.6, 134.7, 132.0, 130.7, 129.9, 129.4, 128.7, 125.5, 124.0, 121.8, 110.8, 89.9, 82.6, 42.4, 26.7, 21.2, 20.6; IR (film) υ_{max} 3029, 2921, 1851, 1720, 1300, 1035, 831 cm^{-1}.

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*3-Phenyl-3-(phenylethynyl)benzofuran-2(3H)-one (±)-(**18c**).* The product **18c** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (17.5 μL, 0.140 mmol), **2d** (53.6 mg, 0.154 mmol) and the reaction was performed for 15 min to give **18c** in 41.0 mg (0.140 mmol) as a white solid (92% yield), mp 75−77 °C; R_f = 0.51 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (t, *J* = 7.1 Hz, 4H), 7.40−7.29 (m, 7H), 7.24 (q, *J* = 7.7, 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.2, 152.9, 137.3, 132.0, 130.23, 130.0, 129.0, 128.9, 128.6, 128.3, 126.8, 125.3, 125.2, 121.9, 111.2, 85.7, 84.7, 51.4; IR (film) υ_{max} 3111, 2929, 2249, 1800, 879 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $[C_{22}H_{14}O_2 + Na]^+$: 333.0886, found: 333.0896.

*3-Phenyl-3-(o-tolylethynyl)benzofuran-2(3H)-one (±)-(**18d**).* The product **18d** was synthesized according to the general experimental procedure A (2.0 mL toluene) using TMG (15 μL, 0.120 mmol), **2e** (47.8 mg, 0.132 mmol) and the reaction was performed for 15 min to give **18d** in 37.30 mg (0.120 mmol) as a white solid (97% yield), mp 67−69 °C; R_f = 0.51 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57−7.48 (m, 2H), 7.52−7.41 (m, 2H), 7.43−7.34 (m, 4H), 7.31−7.23 (m, 3H), 7.26−7.19 (m, 1H), 7.16 (td, *J* = 7.4, 1.7 Hz, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 173.2, 152.9, 140.8, 137.4, 132.2, 130.0, 129.5, 129.15, 129.0, 128.9, 128.6, 126.9, 125.6, 125.3, 125.2, 121.69, 111.3, 88.7, 84.8, 49.8, 20.8; IR (film) υ_{max} 2958, 2855, 1721, 1681 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $[C_{23}H_{16}O_2 + Na]^+$: 347.1043, found: 347.1031.

*2-Oxo-2-phenylethyl 2-iodobenzoate (**20**).* The product **20** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (13.4 μL, 0.107 mmol), **2d** (41 mg, 0.117 mmol) and the reaction was performed for 35 min to give **20** in 19.5 mg (0.107 mmol) as a yellow gel (49% yield); R_f = 0.37 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (ddd, *J* = 13.2, 7.9, 1.5 Hz, 2H), 7.96 (dt, *J* = 7.1, 1.4 Hz, 2H), 7.64−7.60 (m, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 5.58 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 191.70, 165.77, 141.43, 134.20, 134.08, 134.00, 133.06, 131.69, 128.94, 128.01, 127.83; IR (film) υ_{max} 2985, 2910, 1755, 1689 cm^{-1}.[27b]

*Methyl (2-(1-(Phenylethynyl)-1H-indol-3-yl)ethyl)carbamate (±)-(**21b**).* The product **21b** was synthesized according to the general experimental procedure A (1.5 mL toluene) using TMG (13.4 μL, 0.107 mmol), **2d** (41 mg, 0.117 mmol) and the reaction was performed for 35 min to give **21b** in 21.0 mg (0.107 mmol) as a yellow solid (62% yield); mp 69−70 °C; R_f = 0.37 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (t, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.39 (q, *J* = 7.0, 6.5 Hz, 4H), 7.29−7.26 (m, 1H), 7.14 (s, 1H), 4.84 (s, 1H), 3.71 (s, 3H), 3.56 (d, *J* = 6.7 Hz, 2H), 2.99 (t, *J* = 6.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 157.0, 138.6, 131.3, 128.5, 128.0, 127.6, 126.2, 123.9, 122.7, 121.8, 119.23, 116.1, 111.5, 80.7, 70.7, 52.1, 40.8, 25.7; IR (film) υ_{max} 2977, 2855, 1700, 1559, 1451 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+Na]^+$ calcd for $[C_{20}H_{18}N_2O_2 + Na]^+$: 341.1260, found: 341.1284.

*Synthesis of 1,3-Dimethyl-3-((trimethylsilyl)-ethynyl)-indolin-2-one (**22b**).* To the solution of 3-substituted-2-oxindole (1.0 g, 6.2 mmol, 1.0 equiv) in toluene (15 mL), TMG (0.78 mL, 6.2 mmol, 1.0 equiv) were added. The reaction was stirred for a 5 min followed by the addition in one portion of the hypervalent iodine reagent (EBX) (2.79 g, 8.1 mmol, 1.3 equiv). The reaction was stirred at room temperature for 35 min. The reaction was monitored by TLC analysis UV, Hanessian's Stain. Upon completion, the reaction was quenched with water (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were recombined, washed with $NaHCO_3$ (1.5 mL), brine (2.5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified by column chromatography using the hexane-EtOAc system as eluent to afford the desired alkynylation product **22a** in 941 mg (82% yield).

To a solution of alkynylated compound **22a** (93 mg, 0.5 mmol, 1.0 equiv) in dry THF (5 mL) was added slowly *n*-BuLi (0.47 mL, 1.6 M in hexane, 1.5 equiv) at −78 °C. After stirring for 1 h at −78 °C, chlorotrimethylsilane (0.23 mL, 2.5 mmol, 5.0 equiv) was added and continued stirring for 2 h. Then aqueous saturated NH_4Cl (5 mL) was added to quench the reaction and extracted with EtOAc (3 × 5 mL). The organic layer was washed with brine, dried over Na_2SO_4, after that solution was concentrated and purified by column chromatography to afford the product (97.8 mg, 76% yield).

*3-Ethynyl-1,3-dimethylindolin-2-one (±)-(**22a**).* The reaction was performed for 40 min to afford 82% yield, as a colorless oil; R_f = 0.55 (30% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.34 (td, *J* = 7.8, 1.1 Hz, 1H), 7.14 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.27 (d, *J* = 1.1 Hz, 3H), 2.32 (d, *J* = 0.8 Hz, 1H), 1.71 (d, *J* = 1.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 175.6, 142.4, 131.8, 128.8, 123.2, 108.5, 82.4, 70.7, 42.7, 26.7, 25.5; IR (film) υ_{max} 3303, 2897, 2743, 2775, 2150, 1771, 1682, 832 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $[C_{12}H_{11}NO + H]^+$: 186.0913, found: 186.0906.

*1,3-Dimethyl-3-((trimethylsilyl)ethynyl)indolin-2-one (±)-(**22b**).* The reaction was performed for 2 h to give **22b** in 97.8 mg (0.5 mmol) as a light yellow oil (76% yield); R_f = 0.45 (20% EtOAc in hexane). ^{1}H NMR (500 MHz, Chloroform-d) δ: 7.38 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.86 (dt, *J* = 7.8, 0.7 Hz, 1H), 3.25 (s, 3H), 1.67 (s, 3H), 0.16 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 175.7, 142.3, 132.4, 128.6, 123.3, 123.2, 108.4, 103.5, 87.0, 43.8, 26.7, 26.95, −0.04; IR (film) υ_{max} 2914, 2897, 2753, 2701, 2158, 1743, 1671, 1665, 1508 cm^{-1}. HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $[C_{15}H_{19}NOSi + H]^+$: 258.1309, found: 258.1290.

General Experimental Procedure C for Catalytic Enantioselective Decarboxylative Allylations. In an oven-dried sealed tube, Et_2O was degassed by using nitrogen balloon at room temperature over a period of 15 min. 2.5 mol % of $Pd_2(dba)_3$ and 7.5 mol % of ligand were added to it and stirring was continued for 20 min to make the complex mixture. After that reaction mixture was cooled to −30 °C. In another vessel ester (±)-**9** (0.06 mmol; 1.0 equiv) were dissolved in dry degassed Et_2O solvent then the resulting solution was added dropwise to the complex solution and stirring was continued for specified time at same temperature. 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 (**23**).

*3-Allyl-1-methyl-3-(o-tolylethynyl)indolin-2-one (+)-(**23a**).* The product **23a** was synthesized according to the general experimental procedure C (6.5 mL Et_2O) using $Pd_2(dba)_3$ (2 mg, 0.002 mmol), $\mathbf{L_8}$ (5.8 mg, 0.006 mmol) and the reaction was performed for 27 h to give **23a** in 25.0 mg (0.087 mmol) as a yellow gel (96% yield); R_f = 0.37 (10% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (ddd, *J* = 10.8, 7.4, 1.2 Hz, 2H), 7.30 (td, *J* = 7.8, 1.3 Hz, 1H), 7.17−7.14 (m, 2H), 7.08 (dtd, *J* = 12.1, 7.0, 6.5, 1.7 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.82−5.72 (m, 1H), 5.16−5.02 (m, 2H), 3.23 (s, 3H), 2.97−2.92 (m, 1H), 2.71 (dd, *J* = 13.4, 8.2 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.8, 142.8, 140.5, 132.1, 131.6, 130.4, 129.3, 128.7, 128.3, 125.4, 124.1, 122.9, 122.5, 119.8, 108.3, 90.4, 82.6, 47.9, 43.3, 26.6, 20.8; IR (film) υ_{max} 2958, 2927, 2801, 1690, 1457 cm^{-1}; HRMS (ESI-TOF) *m*/*z*: $[M+H]^+$ calcd for $[C_{21}H_{19}NO + H]^+$: 302.1539, found: 302.1546. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 4/96; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 6.10 min, t_R major = 7.97 min. $[\alpha]_D^{24.8}$ = +15.2 (*c* = 0.11, MeOH for er = 94.9:5.1)

*3-Allyl-1-methyl-3-(phenylethynyl)indolin-2-one (+)-(**23b**).* The product **23b** was synthesized according to the general experimental procedure C (9.5 mL Et_2O) using $Pd_2(dba)_3$ (2.9 mg, 0.003 mmol), $\mathbf{L_8}$ (7.7 mg, 0.009 mmol) and the reaction was performed for 24 h to give **23b** in 35.20 mg (0.127 mmol) as a yellow oil (97% yield), R_f = 0.37 (10% EtOAc in hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (ddd, *J* = 8.1, 5.1, 1.6 Hz, 3H), 7.31 (td, *J* = 7.8, 1.3 Hz, 1H), 7.25 (dd, *J* = 5.5, 1.9 Hz, 3H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 5.73 (dddd, *J* = 17.8, 9.6, 8.2, 6.4 Hz, 1H), 5.10−5.06 (m, 2H), 3.23 (s, 3H), 2.93 (ddt, *J* = 13.4, 6.4, 1.3 Hz, 1H), 2.70 (dd, *J* = 13.4, 8.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.8, 142.8, 132.0, 131.8, 130.3, 128.8, 128.2, 124.3, 124.0, 122.7, 119.8, 108.5, 86.4, 83.6, 47.6, 43.1, 26.8; IR (film) υ_{max} 2994, 2915, 1695,

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1591, 995 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{20}H_{17}NO + Na]^+$: 310.1202, found: 310.1212. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 4/96; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 6.47 min, t_R major = 7.69 min. $[\alpha]_D^{25.0}$ = +19.2 (c = 0.1, MeOH for er = 93.3:6.7)

*3-Allyl-1-methyl-3-(m-tolylethynyl)indolin-2-one (+)-(**23c**).* The product **23c** was synthesized according to the general experimental procedure C (4.7 mL Et_2O) using $Pd_2(dba)_3$ (1.5 mg, 0.001 mmol), L_8 (3.8 mg, 0.004 mmol) and the reaction was performed for 21 h to give **23c** in 18.3 mg (0.063 mmol) as a light yellow gel (96% yield); R_f = 0.25 (10% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (dd, J = 7.4, 1.3 Hz, 1H), 7.31 (td, J = 7.8, 1.3 Hz, 1H), 7.25−7.20 (m, 2H), 7.19−7.12 (m, 1H), 7.11−7.05 (m, 2H), 6.84 (d, J = 7.8 Hz, 1H), 5.73 (dddd, J = 17.7, 9.7, 8.2, 6.4 Hz, 1H), 5.13−5.01 (m, 2H), 3.23 (s, 3H), 2.92 (ddt, J = 13.4, 6.4, 1.3 Hz, 1H), 2.69 (dd, J = 13.4, 8.2 Hz, 1H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.8, 142.8, 137.8, 132.6, 131.5, 130.3, 129.1, 129.0, 128.7, 128.0, 124.2, 122.9, 122.5, 119.8, 108.3, 85.9, 83.8, 47.6 43.1, 26.6, 21.1; IR (film) υ_{max} 2978, 2907, 2861, 1690, 1457, 1231, 1002, 696 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{21}H_{19}NO + Na]^+$: 324.1359, found: 324.1360. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 5.55 min, t_R major = 6.47 min. $[\alpha]_D^{23.0}$ = +12.09 (c = 0.09, MeOH for er = 91.0:8.9).

*3-Allyl-1-methyl-3-(p-tolylethynyl)indolin-2-one (+)-(**23d**).* The product **23d** was synthesized according to the general experimental procedure C (5.4 mL Et_2O) using $Pd_2(dba)_3$ (1.6 mg, 0.0018 mmol), L_8 (4.3 mg, 0.005 mmol) and the reaction was performed for 18 h to give **23d** in 18.9 mg (0.072 mmol) as a yellow oil (90% yield); R_f = 0.50 (20% EtOAc in hexane. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43−7.35 (m, 1H), 7.32−7.22 (m, 3H), 7.15−6.98 (m, 3H), 6.83 (d, J = 7.8 Hz, 1H), 5.81−5.65 (m, 1H), 5.14−5.00 (m, 2H), 3.22 (s, 3H), 2.99−2.87 (m, 1H), 2.70 (dd, J = 13.4, 8.2 Hz, 1H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.9, 142.8, 138.3, 131.8, 131.6, 130.4, 128.9, 128.7, 124.2, 122.9, 119.8, 119.6, 108.3, 85.6, 83.8, 47.6, 43.2, 26.6, 21.4.; IR (film) υ_{max} 2987, 2900, 2851, 1669 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{21}H_{19}NO + H]^+$: 302.1539, found: 302.1550. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD H column; solvent: hexane/2-propanol = 4/96; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 10.81 min, t_R major = 16.16 min. $[\alpha]_D^{24.9}$ = +10.3 (c = 0.106, MeOH for er = 92.1:7.9)

*3-Allyl-1-benzyl-3-(o-tolylethynyl)indolin-2-one (+)-(**23e**).* The product **23e** was synthesized according to the general experimental procedure C (3.5 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.8 mg, 0.003 mmol), the reaction was performed for 20 h to give **23e** in 15.6 mg (0.047 mmol) as a brownish white solid (88% yield); MP 73−75 °C; R_f = 0.37 (10% EtOAc in hexane. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 7.1 Hz, 2H), 7.30 (d, J = 4.3 Hz, 3H), 7.25 (d, J = 6.5 Hz, 2H), 7.21−7.14 (m, 3H), 7.12−7.02 (m, 2H), 6.72 (d, J = 7.8 Hz, 1H), 5.75 (dddd, J = 16.7, 10.1, 8.3, 6.2 Hz, 1H), 5.18−4.96 (m, 3H), 4.83 (d, J = 15.7 Hz, 1H), 3.01 (ddt, J = 13.4, 6.2, 1.4 Hz, 1H), 2.81 (dd, J = 13.4, 8.3 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.9, 141.9, 140.6, 135.6, 132.1, 131.6, 130.4, 129.3, 128.8, 128.6, 128.3, 127.6, 127.3, 125.4, 124.2, 122.9, 122.5, 120.0, 109.4, 90.5, 82.6, 47.9, 44.1, 43.3, 20.7; IR (film) υ_{max} 2979, 2911, 1691, 1611, 1211 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{27}H_{23}NO + H]^+$: 378.1852, found: 378.1877. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 5.76 min, t_R major = 9.20 min. $[\alpha]_D^{22.3}$ = +30.0 (c = 0.1, MeOH for er = 93.7:6.3).

*3-Allyl-1-benzyl-3-(p-tolylethynyl)indolin-2-one (+)-(**23f**).* The product **23f** was synthesized according to the general experimental procedure C (3.5 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.8 mg, 0.003 mmol) and the reaction was performed for 18 h to give **23f** in 14.7 mg (0.047 mmol) as a light yellow oil (83% yield), R_f = 0.52 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 7.4, 1.2 Hz, 1H), 7.34−7.27 (m, 6H), 7.25 (d, J = 6.5 Hz, 1H), 7.18 (td, J = 7.8, 1.3 Hz, 1H), 7.07 (dd, J = 8.2, 2.5 Hz, 3H), 6.71 (d, J = 7.8 Hz, 1H), 5.79−5.64 (m, 1H), 5.16−5.01 (m, 3H), 4.79 (d, J = 15.7 Hz, 1H), 3.05−2.92 (m, 1H), 2.80 (dd, J = 13.4, 8.3 Hz, 1H), 2.32 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.0, 141.9, 138.4, 135.6, 131.8, 131.6, 130.4, 128.9, 128.8, 128.6, 127.6, 127.3, 124.2, 122.9, 120.0, 119.6, 109.3, 85.7, 83.8, 47.7, 44.1, 43.3, 21.5.; IR (film) υ_{max} 2968, 2850, 1709, 1601 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{27}H_{23}NO + H]^+$: 378.1852, found: 378.1874. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 7.25 min, t_R major = 8.44 min. $[\alpha]_D^{24.0}$ = +16.0 (c = 0.1, MeOH for er = 90.1:9.9)

*1,3-Diallyl-3-(o-tolylethynyl)indolin-2-one (+)-(**23g**).* The product **23g** was synthesized according to the general experimental procedure C (4.1 mL Et_2O) using $Pd_2(dba)_3$ (1.2 mg, 0.001 mmol), L_8 (3.2 mg, 0.004 mmol) and the reaction was performed for 18 h to give **23g** in 14.40 mg (0.054 mmol) as a light yellow oil (82% yield); R_f = 0.55 (20% EtOAc in hexane. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (dd, J = 14.1, 7.5 Hz, 2H), 7.27 (dd, J = 7.8, 1.3 Hz, 1H), 7.19−7.12 (m, 2H), 7.07 (q, J = 7.6 Hz, 2H), 6.83 (d, J = 7.8 Hz, 1H), 5.91−5.65 (m, 2H), 5.32−5.17 (m, 2H), 5.14−5.01 (m, 2H), 4.45 (ddt, J = 16.4, 4.8, 1.9 Hz, 1H), 4.27 (ddt, J = 16.3, 5.5, 1.7 Hz, 1H), 2.96 (dd, J = 13.4, 6.4 Hz, 1H), 2.76 (dd, J = 13.4, 8.2 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.5, 142.0, 140.5, 133., 131.5, 131.2, 130.36, 129.3, 128.5, 128.3, 125.3, 124.1, 122.8, 122.5, 120.0, 117.6, 109.2, 90.4, 82.6, 47.8, 43.3, 42.6, 20.7; IR (film) υ_{max} 2991, 2905, 1680, 1579, 901 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{23}H_{21}NO + H]^+$: 328.1696, found: 328.1706. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak AD H column; solvent: hexane/2-propanol = 4/96; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 7.41 min, t_R major = 8.93 min. $[\alpha]_D^{24.9}$ = +18.0 (c = 0.1, MeOH for er = 94.6:5.4)

*3-Allyl-1-(4-methoxybenzyl)-3-(phenylethynyl)indolin-2-one (+)-(**23h**).* The product **23h** was synthesized according to the general experimental procedure C (3.4 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.7 mg, 0.003 mmol) and the reaction was performed for 20 h to give **23h** in 16.20 mg (0.045 mmol) as a light yellow oil (90% yield); R_f = 0.58 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48−7.44 (m, 2H), 7.43 (dd, J = 7.5, 1.3 Hz, 1H), 7.32−7.27 (m, 5H), 7.23 (td, J = 7.8, 1.3 Hz, 1H), 7.09 (td, J = 7.5, 1.0 Hz, 1H), 6.89−6.85 (m, 2H), 6.78 (dt, J = 7.9, 0.7 Hz, 1H), 5.74 (dddd, J = 16.6, 10.1, 8.3, 6.2 Hz, 1H), 5.19−5.08 (m, 2H), 5.04 (d, J = 15.4 Hz, 1H), 4.77 (d, J = 15.4 Hz, 1H), 3.80 (s, 3H), 3.02 (ddt, J = 13.4, 6.2, 1.4 Hz, 1H), 2.86−2.78 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.8, 159.1, 142.0, 132.0, 131.5, 130.3, 128.8, 128.6, 128.3, 128.1, 127.7, 124.2, 122.9, 122.7, 120.0, 114.2, 109.4, 86.5, 83.7, 55.3, 47.7, 43.7, 43.2; IR (film) υ_{max} 2999, 2911, 1701, 1678, 1501 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{27}H_{23}NO_2 + Na]^+$: 416.1621, found: 416.1645. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 9.69 min, t_R major = 21.17 min. $[\alpha]_D^{23.7}$ = +20.36 (c = 0.093, MeOH for er = 90.1:9.2)

*3-Allyl-1-(4-methoxybenzyl)-3-(o-tolylethynyl)indolin-2-one (+)-(**23i**).* The product **23i** was synthesized according to the general experimental procedure C (3.0 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.4 mg, 0.003 mmol) and the reaction was performed for 20 h to give **23i** in 13.70 mg (0.04 mmol) as a yellow oil (83% yield); R_f = 0.50 (20% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42−7.35 (m, 2H), 7.27−7.22 (m, 2H), 7.21−7.13 (m, 3H), 7.11−7.01 (m, 2H), 6.86−6.78 (m, 2H), 6.74 (d, J = 7.8 Hz, 1H), 5.81−5.66 (m, 1H), 5.16−5.03 (m, 2H), 4.97 (d, J = 15.5 Hz, 1H), 4.77 (d, J = 15.5 Hz, 1H), 3.76 (s, 3H), 2.99 (dd, J = 13.4, 6.3 Hz, 1H), 2.79 (dd, J = 13.4, 8.3 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.9, 159.1, 142.0, 140.6, 132.1, 131.6, 130.4,

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129.3, 128.8, 128.6, 128.3, 127.7, 125.4, 124.2, 122.9, 122.5, 120.0, 114.1, 109.4, 90.5, 82.6, 55.3, 47.9, 43.6, 43.3, 20.8; IR (film) υ_{max} 2978, 2961,, 1689, 1509, 814 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{28}H_{25}NO_2 + H]^+$: 408.1958, found: 408.1966. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 8.54 min, t_R major = 27.59 min. $[\alpha]_D^{21.0}$ = +46.23 (*c* = 0.093, MeOH for er = 96.8:3.2)

*1-Methyl-3-(2-methylallyl)-3-(o-tolylethynyl)indolin-2-one (+)-(**23j**).* The product **23j** was synthesized according to the general experimental procedure C (5.4 mL Et_2O) using $Pd_2(dba)_3$ (1.6 mg, 0.0018 mmol), L_8 (4.3 mg, 0.005 mmol) and the reaction was performed for 19 h to give **23j** in 20.50 mg (0.072 mmol) as a yellow oil (90% yield); R_f = 0.27 (10% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.39 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.32−7.25 (m, 3H), 7.10−7.02 (m, 3H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.75 (p, *J* = 1.6 Hz, 1H), 4.60 (d, *J* = 2.1 Hz, 1H), 3.22 (s, 3H), 2.90 (d, *J* = 13.2 Hz, 1H), 2.81 (d, *J* = 13.2 Hz, 1H), 2.30 (s, 3H), 1.60 (s, 3H; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 175.1, 142.9, 139.9, 138.3, 131.7, 130.4, 128.9,128.7, 128.6, 124.6, 122.7, 119.7, 116.1, 108.2, 86.4, 83.3, 47.6, 46.2, 26.6, 23.9, 21.5; IR (film) υ_{max} 2999, 2969, 1712, 1620, 1530, 881 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{21}NO + H]^+$: 316.1696, found: 316.1716. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 5.16 min, t_R major = 8.13 min. $[\alpha]_D^{21.9}$ = +30.05 (*c* = 0.1, MeOH for er = 98.4:1.6)

*3-Allyl-1-benzyl-5-bromo-3-(o-tolylethynyl)indolin-2-one (+)-(**23k**).* The product **23k** was synthesized according to the general experimental procedure C (3.0 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.4 mg, 0.003 mmol) and the reaction was performed for 19 h to give **23k** in 16.70 mg (0.040 mmol) as a brawn yellow oil (91% yield); R_f = 0.26 (10% EtOAc in hexane). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 2.0 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.37−7.33 (m, 3H), 7.32−7.28 (m, 3H), 7.26−7.20 (m, 2H), 7.14 (td, *J* = 7.3, 1.8 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.78 (dddd, *J* = 16.7, 10.2, 8.4, 6.3 Hz, 1H), 5.22−5.14 (m, 2H), 5.05 (d, *J* = 15.7 Hz, 1H), 4.86 (d, *J* = 15.7 Hz, 1H), 3.03 (ddt, *J* = 13.5, 6.3, 1.4 Hz, 1H), 2.85 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 174.4, 141.0, 140.6, 135.1, 132.3, 132.1, 131.5, 131.1, 129.4, 128.9, 128.5, 127.9, 127.4, 127.3, 125.5, 122.2, 120.6, 115.6, 110.9, 89.6, 83.2, 47.9, 44.2, 43.2, 20.8. IR (film) υ_{max} 3213, 2865, 2821, 1650, 1210, 814 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{22}BrNO + H]^+$: 456.0958, found: 456.0958. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 7.66 min, t_R major = 13.40 min; $[\alpha]_D^{24.0}$ = +85.0 (*c* = 0.1, MeOH for er = 92.2:7.8)

*3-Allyl-1-benzyl-5-bromo-3-(p-tolylethynyl)indolin-2-one (+)-(**23l**).* The product **23l** was synthesized according to the general experimental procedure C (3.3 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.7 mg, 0.003 mmol) and the reaction was performed for 20 h to give **23l** in 17.20 mg (0.044 mmol) as a light yellow oil (86% yield); R_f = 0.26 (10% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ: 5.73 (dddd, *J* = 16.6, 10.1, 8.3, 6.2 Hz, 1H), 5.21−5.03 (m, 3H), 4.81 (d, *J* = 15.7 Hz, 1H), 3.00 (ddt, *J* = 13.4, 6.2, 1.4 Hz, 1H), 2.83 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 174.4, 141.0, 138.6, 135.1, 132.3, 131.9, 131.5, 131.1, 128.9, 128.9, 127.8, 127.4, 127.3, 120.5, 119.3, 115.6, 110.8, 84.8, 84.4, 47.7, 44.2, 43.2, 21.5; IR (film) υ_{max} 2998, 2930, 2845, 1680, 1351, 814 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{22}BrNO + H]^+$: 456.0958, found: 456.0969. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IC 3 column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 7.23 min, t_R major = 9.52 min; $[\alpha]_D^{24.5}$ = +51.0 (*c* = 0.1, MeOH for er 4.2:95.8).

*1,3-Diallyl-5-bromo-3-(o-tolylethynyl)indolin-2-one (+)-(**23m**).* The product **23m** was synthesized according to the general experimental procedure C (4.1 mL Et_2O) using $Pd_2(dba)_3$ (1.2 mg, 0.001 mmol), L_8 (3.2 mg, 0.004 mmol) and the reaction was performed for 24 h to give **23m** in 19.60 mg (0.055 mmol) as a yellow oil (87% yield); R_f = 0.37 (10% EtOAc in hexane. ^1H NMR (500 MHz, $CDCl_3$) δ7.55 (d, *J* = 2.0 Hz, 1H), 7.45−7.39 (m, 2H), 7.25−7.17 (m, 2H), 7.12 (td, *J* = 7.3, 1.8 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.84 (ddt, *J* = 16.1, 10.5, 5.3 Hz, 1H), 5.75 (ddt, *J* = 16.9, 10.4, 4.2 Hz, 1H), 5.32−5.21 (m, 2H), 5.20−5.10 (m, 2H), 4.47 (ddt, *J* = 16.5, 4.8, 1.9 Hz, 1H), 4.29 (ddt, *J* = 16.4, 5.4, 1.7 Hz, 1H), 2.98 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.80 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 173.9, 141.1, 140.6, 132.3, 132.1, 131.5, 131.0, 130.8, 129.4, 128.5, 127.4, 125.4, 122.1, 120.5, 117.9, 115.5, 110.8, 89.5, 83.1, 47.8, 43.2, 42.7, 20.8; IR (film) υ_{max} 2988, 2901, 2853, 1699 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{20}BrNO + H]^+$: 464.0801, found: 406.0784. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak OD H column; solvent: hexane/2-propanol = 10/90; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 4.47 min, t_R major = 7.62 min; $[\alpha]_D^{24.0}$ = +67.0 (*c* = 0.1, MeOH for er = 94.2:5.8).

*3-Allyl-5-chloro-1-methyl-3-(o-tolylethynyl)indolin-2-one (+)-(**23n**).* The product **23n** was synthesized according to the general experimental procedure C (3.9 mL Et_2O) using $Pd_2(dba)_3$ (1.2 mg, 0.001 mmol), L_8 (3.2 mg, 0.004 mmol) and the reaction was performed for 22 h to give **23n** in 15.10 mg (0.052 mmol) as a yellow oil (85% yield); R_f = 0.37 (10% EtOAc in hexane. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36 (q, *J* = 2.9, 1.9 Hz, 2H), 7.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.19−7.13 (m, 2H), 7.07 (td, *J* = 7.2, 2.0 Hz, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 5.73 (dddd, *J* = 16.7, 11.0, 8.2, 6.4 Hz, 1H), 5.15−5.05 (m, 2H), 3.22 (s, 3H), 2.92 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.69 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.8, 142.8, 137.8, 132.6, 131.6, 130.3, 129.2, 129.0, 128.7, 128.0, 124.2, 122.9, 122.5, 119.8, 108.3, 86.0, 83.8, 47.6, 43.1, 26.6, 21.2; IR (film) υ_{max} 2977, 2851, 1690, 1639, 1351 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{21}H_{18}ClNO + H]^+$: 336.1150, found: 336.1144. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IB column; solvent: hexane/2-propanol = 2/98; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 6.40 min, t_R major = 7.58 min; $[\alpha]_D^{24.0}$ = +20.36 (*c* = 0.093, MeOH for er = 92.5:7.5).

*3-Allyl-1-benzyl-5-chloro-3-(o-tolylethynyl)indolin-2-one (+)-(**23o**).* The product **23o** was synthesized according to the general experimental procedure C (3.6 mL Et_2O) using $Pd_2(dba)_3$ (1 mg, 0.001 mmol), L_8 (2.9 mg, 0.003 mmol) and the reaction was performed for 24 h to give **23o** in 17.6 mg (0.048 mmol) as a yellow oil (89% yield); R_f = 0.30 (10% EtOAc in hexane). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.41−7.35 (m, 2H), 7.29 (dt, *J* = 13.1, 7.6 Hz, 5H), 7.21−7.12 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 5.81−5.64 (m, 1H), 5.19−5.07 (m, 2H), 5.01 (d, *J* = 15.8 Hz, 1H), 4.82 (d, *J* = 15.7 Hz, 1H), 2.98 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.79 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 174.5, 140.6, 140.4, 135.1, 132.1, 132.0, 131.0, 129.4, 128.8, 128.6, 128.5, 128.3, 127.8, 127.3, 125.4, 124.6, 122.1, 120.5, 110.3, 89.5, 83.1, 47.9, 44.2, 43.2, 20.7.IR (film) υ_{max} 2978, 2920, 1701, 1650, 1351, 981 cm^{-1}; HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{22}ClNO + H]^+$: 412.1463, found: 412.1485. Enantiomeric excess of pure compound was determined via HPLC analysis using a Chiralpak IC 3 column; solvent: hexane/2-propanol = 2/98; flow rate: 1.0 mL/min; detection: at 254 nm): t_R minor = 7.79 min, t_R major = 9.36 min; $[\alpha]_D^{24.0}$ = +44.0 (*c* = 0.1, MeOH for er = 95.2:4.8).

*Synthesis of (+)-(**24**).* To a stirred solution of compound (+)-**23b** (200 mg, 0.70 mmol; 1.0 equiv) in CH_2Cl_2 (10 mL) at room temperature, *N*-methyl morpholine-*N*-oxide (448 mg, 3.83 mmol; 5.5 equiv) and catalytic OsO_4 (50 μL, 4% solution in water) were added. Then the reaction mixture was allowed to stir at room temperature. Upon completion of starting material (monitored by TLC), the reaction mixture was quenched with saturated Na_2SO_3 and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was concentrated under reduced pressure. The crude material was directly

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dissolved in 6 mL THF: H2O (2:1) mixture. To that reaction mixture, $NaIO_4$ (814 mg, 0.87 mmol; 5.5 equiv) was added at 0 °C and stirred for 2h. The reaction mixture was diluted with EtOAc (15 mL) and water (10 mL) and organic layers were separated. The extracted organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using the hexane-EtOAc system as eluent to afford the desired product.

*2-(1-Methyl-2-oxo-3-(phenylethynyl)indolin-3-yl)acetaldehyde (+)-(**24**).* The reaction was performed for (3h + 2h) to give **24** in 155.0 mg (0.70 mmol) as a color less oil (79% yield); R_f = 0.57 (40% EtOAc in hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.96 (t, J = 1.8 Hz, 1H), 7.46−7.37 (m, 3H), 7.36 (dd, J = 7.8, 1.3 Hz, 1H), 7.35−7.24 (m, 3H), 7.15 (td, J = 7.5, 1.0 Hz, 1H), 6.93 (dt, J = 7.8, 0.7 Hz, 1H), 3.32 (s, 3H), 3.23−3.10 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.4, 174.0, 143.0, 131.9, 129.5, 129.3, 128.7, 128.2, 123.6, 123.4, 122.0, 108.8, 85.0, 85.0, 50.3, 43.9, 26.9; IR (film) υ_{max} 2988, 2890, 2799, 1706, 1611, 1310 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $[C_{19}H_{15}NO_2 + H]^+$: 290.1176, found: 290.1188. $[\alpha]_D^{23.8}$ = +11.25 (c = 0.1066, MeOH)

*Synthesis of (+)-**25a−b**.* Compound (+)-**24** (101 mg, 0.35 mmol, 1.0 equiv) and dissolved in dry THF under N_2 atmosphere in a flame-dried round-bottom flask. The reaction was treated with $LiAlH_4$ (66 mg, 1.73 mmol, 5 equiv) at rt to stir for 40 min. Upon completion of the reaction excess of $LiAlH_4$ was quenched by ethyl acetate at 0 °C treated with slow and dropwise addition of water and $NaHCO_3$ solution until clear organic layer formed. The organic layer was separated with separatory funnel. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography.

*8-Methyl-3a-(phenylethynyl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (−)-(**25a**).* The reaction was performed for 40 min to give **25a** in 77.00 mg (0.35 mmol) as a colorless oil (80% yield); R_f = 0.40 (5% EtOAc in hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46−7.42 (m, 2H), 7.31 (dd, J = 4.0, 2.5 Hz, 4H), 7.20 (td, J = 7.7, 1.2 Hz, 1H), 6.78 (td, J = 7.5, 1.0 Hz, 1H), 6.45 (d, J = 7.8 Hz, 1H), 5.65 (s, 1H), 4.13 (ddd, J = 9.0, 7.3, 1.7 Hz, 1H), 3.59 (ddd, J = 11.0, 8.8, 5.1 Hz, 1H), 2.99 (s, 3H), 2.66 (td, J = 11.5, 7.3 Hz, 1H), 2.45 (ddd, J = 12.1, 5.1, 1.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 150.1, 131.7, 130.5, 129.0, 128.2, 128.0, 123.8, 123.2, 117.9, 105.4, 104.9, 91.2, 82.5, 67.0, 50.3, 43.15, 31.11; IR (film) υ_{max} 2979, 2895, 2799, 1650, 1722, 1666, 1489 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $[C_{19}H_{17}NO + H]^+$: 276.1383, found: 276.1410. $[\alpha]_D^{24.6}$ = (−)-63.00 (c = 0.2, MeOH).

*8-Methyl-3a-((E)-styryl)-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]-indole (−)-(**25b**).* 12.00 mg (0.35 mmol) as a colorless oil (12% yield); R_f = 0.37 (5% EtOAc in hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40−7.34 (m, 2H), 7.34−7.28 (m, 2H), 7.28−7.22 (m, 1H), 7.21 (dd, J = 7.6, 1.2 Hz, 1H), 7.12 (dd, J = 7.3, 1.2 Hz, 1H), 6.77 (td, J = 7.4, 0.9 Hz, 1H), 6.46 (d, J = 5.3 Hz, 2H), 5.31 (s, 1H), 4.10 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 3.56 (ddd, J = 11.4, 8.5, 4.8 Hz, 1H), 2.98 (s, 3H), 2.47 (td, J = 11.6, 7.2 Hz, 1H), 2.35−2.26 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 151.3, 136.9, 132.4, 131.0, 129.6, 128.6, 128.5, 127.4, 126.3, 124.4, 117.6, 105.4, 105.0, 103.9, 67.9, 59.1, 40.4, 30.9; IR (film) υ_{max} 2988, 2890, 2770, 1679, 1587, 1478 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $[C_{19}H_{19}NO + H]^+$: 278.1539, found: 278.1546. $[\alpha]_D^{24.6}$ = (−)-46.55 (c = 0.116, MeOH).

*Synthesis of (−)-(**26**).* In an oven-dried round-bottom flask, the compound **25a** (34.97 mg, 0.127 mmol, 1.0 equiv) was taken in MeOH (5 mL) under argon atmosphere. To this reaction mixture Pd on C (0.013 mmol; 0.1 equiv) was added portion wise and it was stirred for another 10 min at room temperature under argon atmosphere. Then the reaction mixture was stirred for 10 h under H_2 (g) balloon. Upon completion of the reactions, (TLC showed complete **25a** consumption of starting material) the reaction mixture was filtered through Celite and concentrated in a rotary evaporator under vacuum. The crude products were purified by column chromatography and afforded (−)-(**26**).

*8-Methyl-3a-phenethyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]-indole (−)-**26**.* The reaction was performed for 10 h to give **26** in 35.20 mg (0.127 mmol) as a colorless oil (99% yield); R_f = 0.37 (5% EtOAc in hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (t, J = 7.4 Hz, 2H), 7.30−7.14 (m, 5H), 6.82 (t, J = 7.4 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 5.25 (s, 1H), 4.10−3.98 (m, 1H), 3.60−3.49 (m, 1H), 3.00 (s, 2H), 2.67 (td, J = 12.8, 5.7 Hz, 1H), 2.55 (td, J = 13.4, 12.8, 4.7 Hz, 1H), 2.34−2.09 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 151.4, 142.1, 132.3, 128.4, 128.4, 125.9, 123.1, 117.4, 105.0, 102.9, 67.0, 56.6, 40.9, 40.4, 32.0, 30.8; IR (film) υ_{max} 2970, 2929, 2851, 1660, 1145 cm^{-1}; $[\alpha]_D^{25.0}$ = (−)-41.22 (c = 0.1, MeOH). HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $[C_{19}H_{21}NO + H]^+$: 280.1696, found: 280.1699.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b02797.

Copies of ^{1}H, ^{13}C NMR spectra, HRMS for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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