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Copper(II)- and Palladium(II)-Catalyzed Enantioselective Claisen Rearrangement of Allyloxy- and Propargyloxy-Indoles to Quaternary Oxindoles and Spirocyclic Lactones

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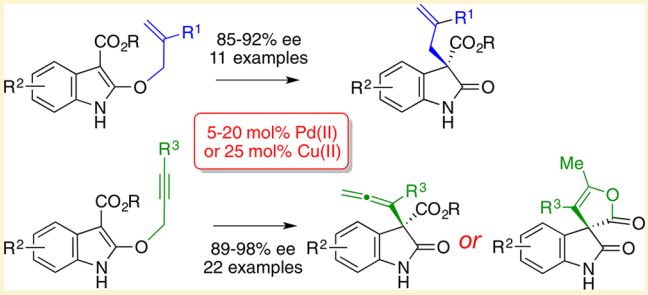
Supporting Information

ABSTRACT: In this Article, a strategy to obtain highly enantioselective catalysts for the Claisen rearrangement of allyloxy- and propargyloxy-indoles is outlined. Ultimately, copper BOX and palladium BINAP or PHOX catalysts were discovered as superior in catalyzing Claisen rearrangements of allyloxy- or proparyloxy-substituted indoles to generate oxindoles bearing allyl- or allenyl-substituted quaternary centers. This method proved to be tolerant of a broad range of functional groups. Tandem reactions of the silyl-allene products provide rapid access to a variety of spirocyclic oxindoles in one operation.



INTRODUCTION

The oxindole framework bearing a C3-quaternary stereocenter is a privileged heterocyclic motif, which is present in a large number of biologically active natural products.[1] Many of these natural products, including physostigmine,[2] flustramine B,[3] pseudophrynaminol,[4] and mollenine,[5] contain an allyl chain at the C3-position (Figure 1). This chain could easily be installed in an asymmetric fashion utilizing Claisen rearrangement methodology. Notably, syntheses have not been described for mollenine and notamides,[6] novel alkaloids derived from marine sources, which incorporate this motif.

The oxindole moiety is also a popular fragment for drug discovery, and several reports describe its incorporation into compounds with potent biological activity (Figure 1).[7−9] The apparent clinical significance of the spirocyclic quaternary center at the C3 position of oxindoles[10] has led to a demand for efficient methods for their enantioselective synthesis.[11] The topology of this moiety allows functionalization of all four faces of a tetrahedron centered on the spirocyclic center, creating an ideal environment for structural diversity.

To facilitate the synthesis of natural products and related analogues for biological evaluation and structure−activity relationships, catalytic asymmetric syntheses of oxindoles with a quaternary center have been of intense interest (Figure 2).[1e,2,11,12] For example, Overman generated such oxindoles via an asymmetric Heck reaction with very good enantioselectivity.[13] Later, Fu developed an enantioselective intramolecular acyl transfer of benzofurans and indoles, which requires an unusual carbonate.[14] Recognizing that oxindoles can be enolized readily, Trost developed an asymmetric π-allylation to yield oxindole variants.[15] For most of these methods, several steps are needed to prepare the precursors. Moreover, in all cases, *N*-masked indoles are used. Also, not all substituent combinations are available at the quaternary center. For example, ester/allyl combinations, which map onto many natural products, are not available in high enantioselectivity. By exploiting sigmatropic rearrangements, we theorized that a number of structures could be achieved that would be difficult or impossible to obtain via other routes including ester/allyl combinations, generation of two adjacent quaternary centers, and formation of allenes from the propargyl alcohols.

The Claisen rearrangement of allyl vinyl ethers is a [π^2s + σ^2s + π^2s] sigmatropic isomerization process. This transformation is a key entry to generate the γ,δ-unsaturated carbonyl moiety.[16] Despite the utility of these compounds, the development of asymmetric catalysts has proven difficult for this transformation.[17,18] As we have previously reported, we identified palladium complexes that affect the asymmetric catalytic Meerwein−Eschenmoser Claisen[18a] or Saucy−Marbet Claisen[18b] rearrangements to produce a range of oxindoles bearing a quaternary stereocenter. In this Article, we provide a complete account of our development of allyloxy or propargyloxy indoles as precursors for the generation of oxindoles and spirocylic variants bearing a tetrasubstituted stereocenter using palladium systems.

RESULTS AND DISCUSSION

We employed allyl- or propargyl-substituted indoles **3** or **4**, which were obtained from indole **1** and allylic or propargyl alcohols **2** (Scheme 1).[18,19] Although a few of these substrates were found to rearrange spontaneously at low temperatures (rt to 40 °C), care in the isolation provided indole substrates that could be stored up to a year at −20 °C.

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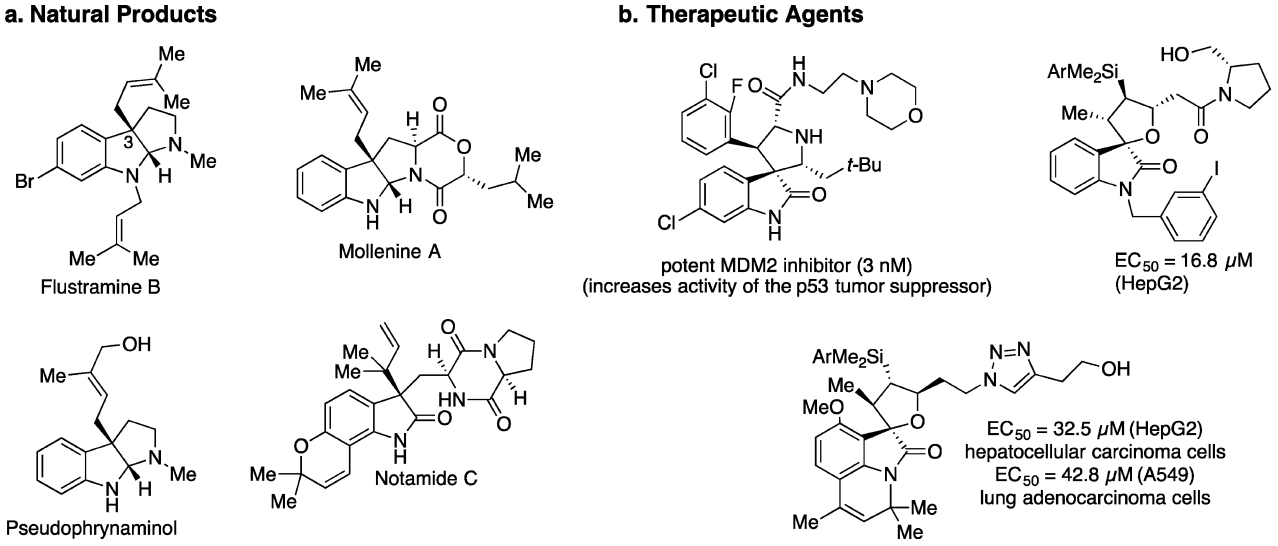


Figure 1. Natural products and pharmaceutical agents incorporating an oxindole.

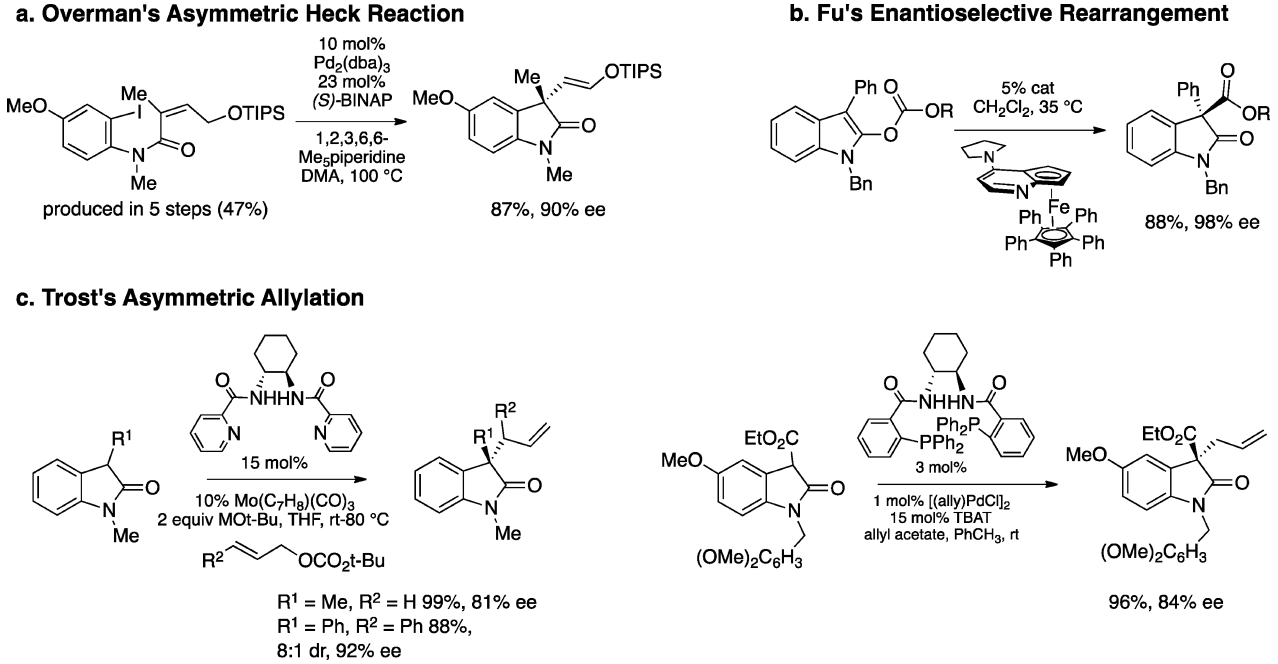
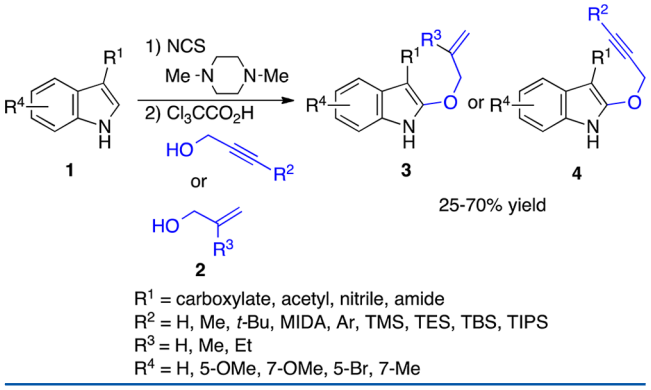
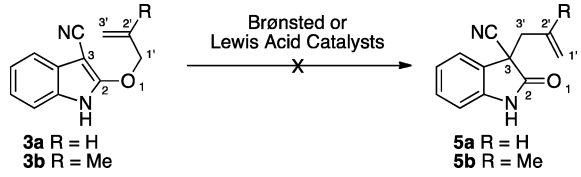


Figure 2. Catalytic asymmetric synthesis of oxindoles bearing a C3 quaternary stereocenter.

Scheme 1. Synthesis of Indole Series



Scheme 2. Claisen Rearrangement of 3-Nitrile Indole



1. Monodentate Indoles. The first substrates that were investigated bore a nitrile at the C3-position (Scheme 2) with the aim of identifying a catalyst that would activate the substrate via interaction with the ethereal oxygen. The nitrile served as an electron-withdrawing group that would decelerate the Claisen rearrangement and allow isolation of **3a** and **3b** in pure form.[20] The substituents at C2′ are known to affect the rate of the rearrangement, so both allyloxy and methallyloxy groups were incorporated. Evaluation of C3-nitrile substituents with representative Brønsted and Lewis acids revealed that these catalysts did not facilitate the Claisen rearrangement.

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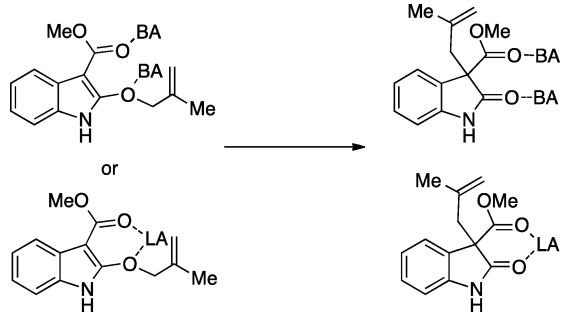
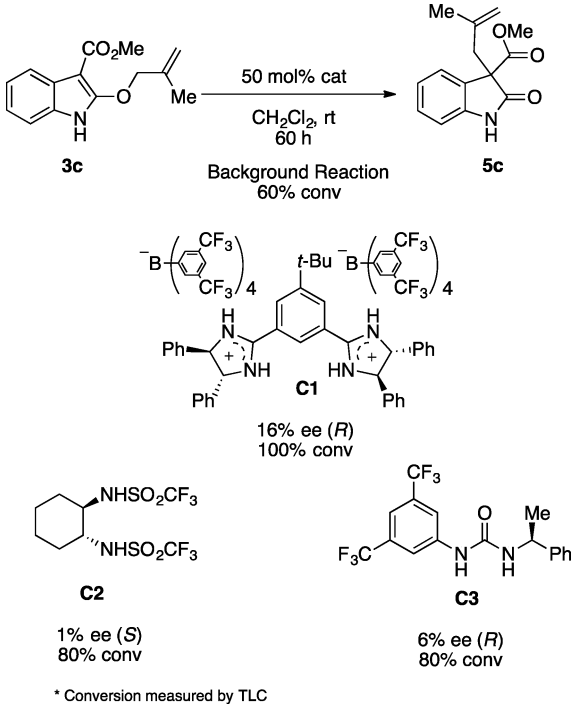
2. Bidentate Indoles. *2.1. Allyloxy Indoles.* Because of the lack of success with the monodentate substrate, an ester group was added to the C3-position. It was envisioned that either a Brønsted acid (BA) or a Lewis acid (LA) could coordinate to both the sp^3 oxygen of the allyl chain, as well as the sp^2 oxygen of a carbonyl substituent (Scheme 3), and that this double activation would accelerate the reaction.

Scheme 3. Coordination of Catalyst to a Bidentate Substrate



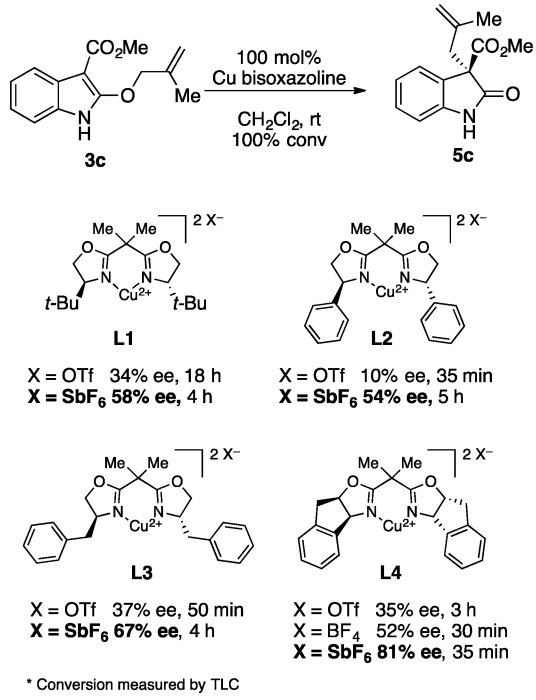
Scheme 4. Brønsted Acid Screening



Brønsted Acid Catalyst Survey. Brønsted acid catalysts were screened first (Scheme 4). Bisamidinium catalyst **C1**[21] gave complete conversion and 16% enantiomeric excess, while 80% conversion and racemic product were observed with sulfonamide **C2**. Urea **C3** also gave 80% conversion, with 6% enantiomeric excess. The low selectivity issue arises due to the competing background reaction, with 60% conversion being observed without catalyst over the same time frame.

Lewis Acid Catalyst Survey. Lewis acid catalysts, which have a much broader reactivity range, were investigated next. To diminish the background reaction and allow a gauge of the inherent selectivity of the catalysts, initial screens were conducted with stoichiometric bisoxazoline copper complexes (Scheme 5).[22] The substitution on the oxazoline portion of the ligand, as well as the counterion on the copper, both

Scheme 5. Copper Complex Counterion and Ligand Screening



dramatically affected the enantioselectivity. When copper triflate was used with the *tert*-butyl bisoxazoline ligand **L1**, only 34% ee was achieved. However, with the less-coordinating hexafluoroantimonate counterion, the selectivity increased to 58% ee. This trend was consistent regardless of the ligand used, with the hexafluoroantimonate copper complexes always giving higher enantioselectivity. Apparently, substrate binding to the Lewis acidic copper is weak; either the catalyzed reaction is quicker with the more Lewis acidic species resulting in higher enantioselectivity due to less competing thermal background reaction or the more tightly bound complex brings the asymmetric environment of the ligand into closer proximity of the reacting partners, amplifying the intrinsic asymmetric induction. Overall, the selectivity could be improved up to 81% ee with $Cu(SbF_6)_2$ and the indanol bisoxazoline **L4**.

For further optimization, a variety of solvents were evaluated (Table 1). It was necessary to use distilled solvents as trace HCl could catalyze the rearrangement.[23] Dichloromethane allowed complete conversion to product **5c** with 81% ee (entry 1). 1,2-Dichloroethane gave comparable results; however, when chloroform or toluene was used, both the selectivity and the conversion were lower (entries 2–4). Interestingly, THF gave no conversion to product either with (entry 6) or without catalyst (entry 5). Because THF appears to inhibit the background reaction that occurs in in CH_2Cl_2 at room temperature, it was thought that a small amount of THF might inhibit the background reaction while allowing the enantioselective rearrangement to proceed. Unfortunately, any amount of THF resulted in no conversion to product (entry 7). Last, acetonitrile caused decomposition of the starting material (entry 8).

With the copper complexes, the steric environment around the coordinating carbonyl proved to be an important factor to control the selectivity. Larger ester groups led to lower selectivity (Scheme 6) with the ethyl and benzyl esters **5d** and **5e** resulting in 79% ee and 73% ee, respectively. The

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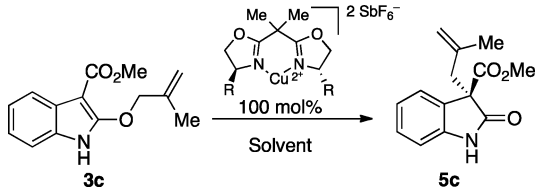
Table 1. Copper Catalyst Solvent Screening

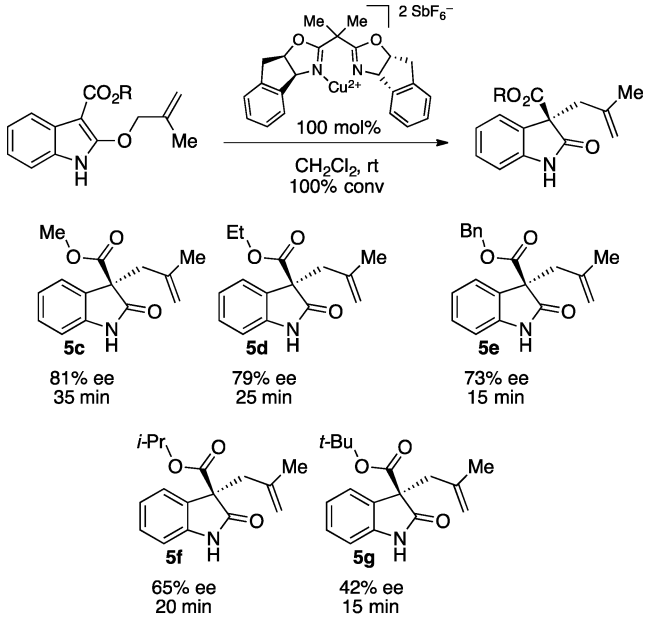


3c 5c

entry	solvent	R	conv.[a] (%)	*t*	ee (%)
1	CH_2Cl_2	indanol	100	35 min	81
2	$Cl(CH_2)_2Cl$	indanol	100	35 min	78
3	$CHCl_3$	indanol	60	4 h	69
4	$PhCH_3$	indanol	80	5 h	70
5[b]	THF		SM	18 h	NA
6	THF	*t*-Bu	SM	18 h	NA
7	2:1 CH_2Cl_2/THF	Ph	SM	18 h	NA
8	MeCN	*t*-Bu	decomp.	18 h	NA

[a]Conversion measured by TLC. [b]No catalyst was used.

Scheme 6. Substrate Scope with Copper Indanol Bisoxazoline



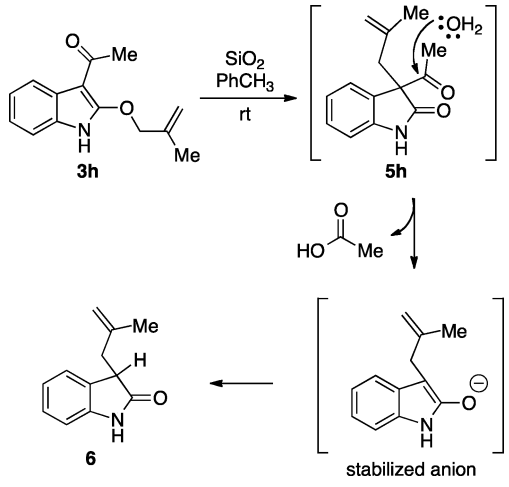
* Conversion measured by TLC

isopropyl ester **5f** decreased the selectivity further to 65% ee. The large substrate **5g**, with a *tert*-butyl ester, provided only 42% ee. Conversely, the small methyl ester **5c** gave the best result with 81% ee.

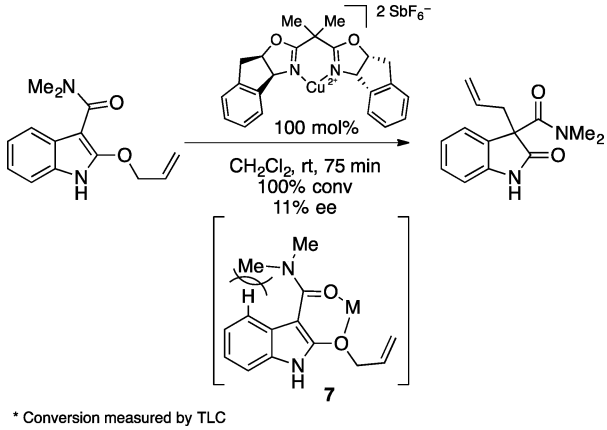
It was hypothesized that replacing the methyl ester with a methyl ketone **3h** might improve the selectivity (Scheme 7) as smaller esters afforded better enantioselectivities (Scheme 6). Unfortunately, rearranged product **5h** was not stable. The methyl ketone was cleaved, presumably via a facile retro-Claisen condensation of the more electrophilic ketone, affording only product **6**. In principle, this route to monosubstituted oxindoles such as **6** could be subject to asymmetric induction using a chiral protonation catalyst. However, this exchange of methyl ketone for an allyl was not investigated further.

Installation of an amide at the 3-position of the indole provided another possible substrate (Scheme 8). In a fashion analogous to that of the ester series, the C3-amide was

Scheme 7. Effect of Methyl Ketone at C3 Position



Scheme 8. Use of C3-Amide Derivative



* Conversion measured by TLC

generated by reaction with *N*-chlorosuccinimide and allyl alcohol. Disappointingly, copper(II) was unable to promote the rearrangement with high enantioselectivity. It appears that allylic strain (see Scheme 8) destabilizes coordination mode **7**, which is necessary for good asymmetry transfer from the catalyst to the product.

To further optimize the rearrangement of the ester substrates, a range of loadings of the copper species were investigated (Table 2). When 200 mol % loading was used, there was no improvement in enantioselectivity (entries 1,2). When the loading was lowered to 50 mol %, almost complete conversion was observed with only a small loss in enantioselectivity. Decreasing the loading to 25 mol % lowered conversion (78%) and selectivity (76% ee), indicating that thermal rearrangement was intervening during the relatively slow turnover.

Because of poor turnover with substoichiometric copper(II), additional metals were examined for superior turnover (Table 3). The bisoxazoline metal complexes were screened as stoichiometric promoters for the rearrangement with the goal of selectively stabilizing the starting material complex **3c** and destabilizing the product−metal adduct **5c**. Copper provided the highest enantioselectivities and complete conversion. Both nickel and zinc resulted in lower conversion to product, as well as lower selectivity. Interestingly, when zinc was employed, the opposite enantiomer of the product was formed, which is consistent with a change from square planar to tetrahedral coordination geometry.[24] Encouragingly, the palladium adduct exhibited reactivity at the

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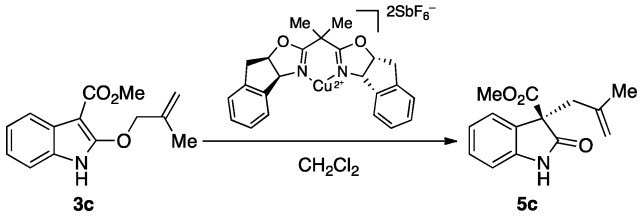
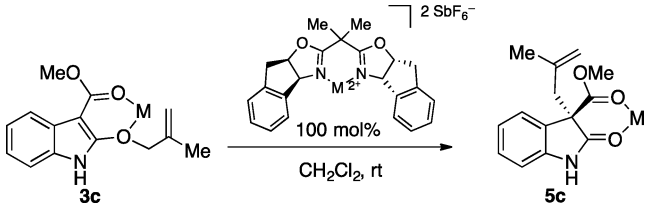
Table 2. Catalyst Loading with Copper Indanol Complex



entry	cat. loading (mol %)	T (°C)	conv.[a] (%)	t	ee (%)
1	200	10	100	10 min	82
2	100	10	90	5 h	80
3	100	rt	100	35 min	81
4	50	rt	93	2 h	77
5	25	rt	78	2.5 h	76

[a]Conversion measured by NMR.

Table 3. Metal Screening



entry	M	conv.[a] (%)	t	ee (%)
1	$CuCl_2$	100	35 min	81
2	$CuBr_2$	100	75 min	80
3	$ZnCl_2$	30	2 h	24[b]
4	$NiBr_2$	50	2 h	47
5	$PdCl_2$	100	1 h	73

[a]Conversion measured by TLC. [b]Opposite enantiomer.

same level as the copper adduct, along with moderate levels of selectivity (73% ee).

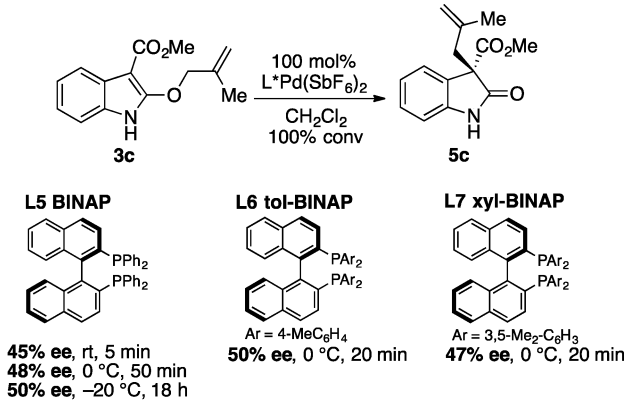
Palladium Catalysts. Attention turned to the palladium complexes because palladium can accommodate a wider array of ligands (diamines, aminophosphines, and diphosphines), offering more opportunity for catalyst optimization. A number of diphosphine ligands were screened (Scheme 9), building on the promising 73% ee with [Pd(*S*,*S*)-Ind-box]$(SbF_6)_2$. BINAP (**L5**) gave a promising 45% ee and exceedingly fast reactions (complete conversion to product in just 5 min at room temperature). Lowering the temperature only slowed the rate of conversion to product and did not increase the selectivity. More sterically encumbered ligands such as tol-BINAP (**L6**) and xylyl-BINAP (**L7**) were used without any appreciable change in the enantioselectivity. DifluoroPhos (**L8**), which has a smaller bite angle than that of BINAP, increased the selectivity to 56% ee.[25] Finally, BIPHEP (**L9**) gave moderate selectivity.

Changing the palladium counterion did little to affect the enantioselectivity. In the case of triflate or acetate, the product formed very slowly (Scheme 10). Presumably, strongly coordinating counterions inhibit the coordination of the substrate.[26]

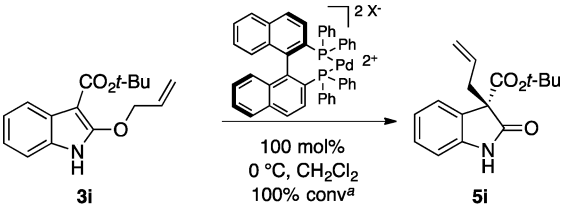
Lowering the loading to 20 mol % showed no drop in selectivity, and complete conversion to product was observed in 10 min at room temperature (Table 4). Decreasing the loading further to 5 mol % provided **5g** with the same enantioselectivity at 82% ee, and did not substantially reduce the rate.

Two proposed transition states (Figure 3), which are in accord with those computed[27] for the copper-catalyzed reactions of

Scheme 9. Initial Screening of Diphosphine Palladium Complexes



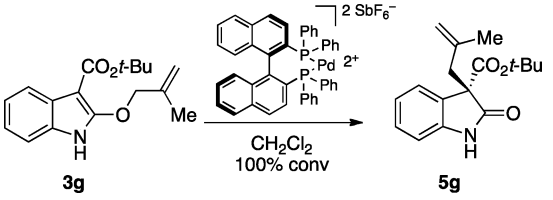
Scheme 10. Effect of Pd Counterion on Enantioselectivity



X	ee (%)
SbF_6	89
BF_4	90
ClO_4	86
OTf	84[b]
OAc	NA[c]

(a) Conversion measured by TLC
(b) 60% conversion
(c) 10% conversion

Table 4. Effect of Pd Catalyst Loading on Enantioselectivity[a]



entry	mol %	T (°C)	t (min)	ee (%)
1	100	0	10	84
2	20	rt	10	82
3	20	0	80	85
4	5	rt	80	82

[a]Conversion measured by TLC.

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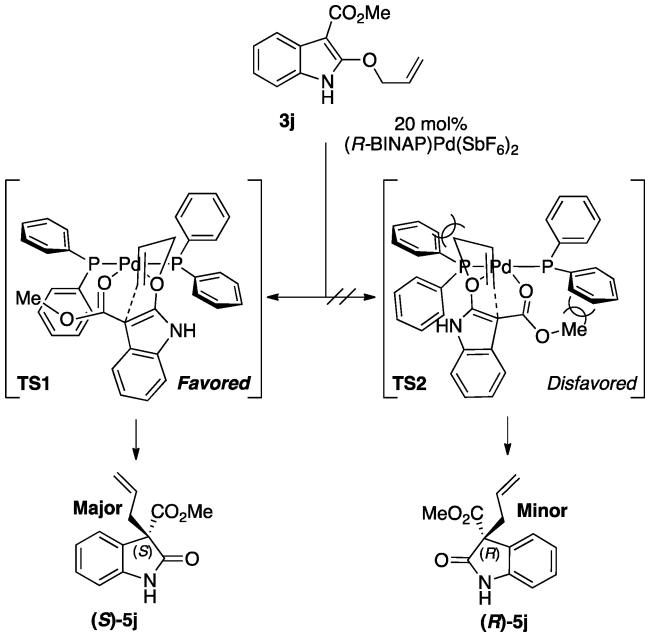


Figure 3. Stereochemical model of the Pd-BINAP-catalyzed rearrangement.

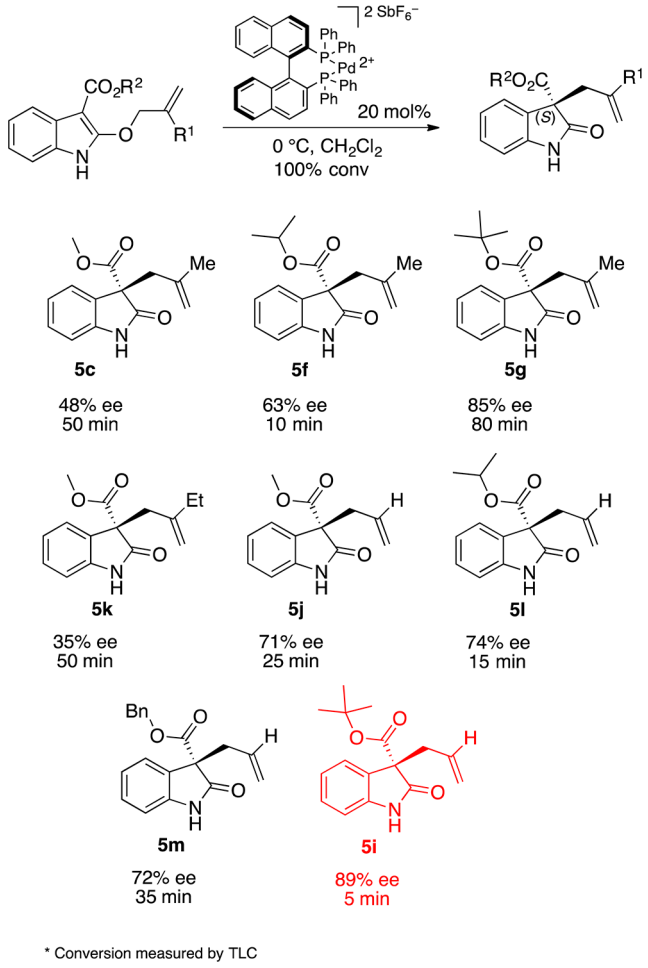
substrates containing a similar coordination array,[17a,b] illustrate the C_2-symmetric BINAP-derived catalyst coordinating to the indole starting material **3j** (the BINAP backbone is removed for clarity).[28] In **TS2**, there are steric interactions between the ester and the pseudoequatorial phenyl group, as well as between the allyl group and the pseudoequatorial phenyl group on the other phosphorus center. These interactions suggest that increasing the steric bulk of the ester might further destabilize **TS2** and increase the enantioselectivity.

To test this theory, a series of esters were screened using the palladium-BINAP catalyst (Scheme 11). Notably, the selectivity was improved when the steric bulk of the C3-ester increased, as the isopropyl and *tert*-butyl esters (**5f** and **5g**) of the methylallyl derivative furnished the product in 63% ee and 85% ee, respectively, relative to the 48% ee of the methyl ester (**5c**). Similar results were seen with both the isopropyl and the benzyl esters (**5l** and **5m**) in the allyl series. Decreasing the steric bulk at R^1 on the allyl group also improved the selectivity, in accordance with the above hypothesis. While the ethallyl derivative **5k** afforded only 35% ee, the allyl derivative **5j** provided a much higher 71% ee. The *tert*-butyl ester with allyl substitution **5i** gave the best selectivity with 89% ee. Moreover, the turnover problems observed with copper catalysts were not seen with the palladium catalysts.

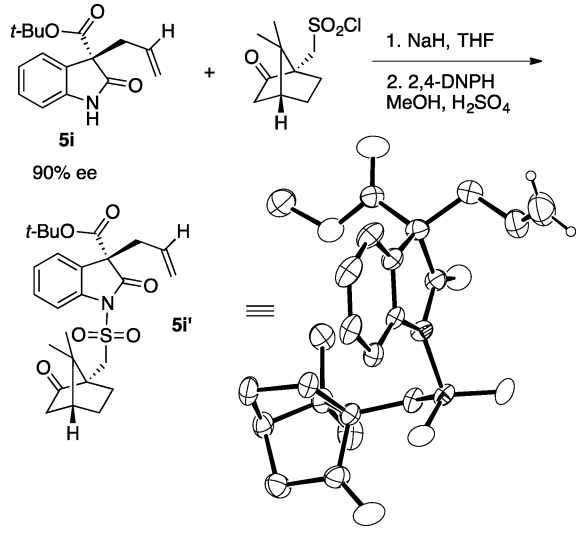
To understand how the catalyst conveys asymmetry in the reaction, it was necessary to determine the absolute configuration of the quaternary stereocenter that is formed during the course of the reaction. In an effort to obtain an X-ray crystal structure, attempts were made to synthesize a hydrazone derivative of the oxindole product over two steps by sulfonylation of the *tert*-butyl ester **5i** and condensation with 2,4-dinitrophenylhydrazine (2,4-DNPH) (Scheme 12). The transesterified methyl ester **5′i** was observed, rather than the expected hydrazone. An X-ray crystal structure was obtained showing that **5′i** was the (*S*)-configuration. All other structures were assigned by analogy from this result.

Although the goal of establishing a Meerwein−Eschenmoser Claisen rearrangement with high enantioselectivity using

Scheme 11. Substrate Scope with Palladium-BINAP Catalyst



Scheme 12. Crystal Structure of the Derivatized Oxindole



substoichiometric catalyst loadings had been achieved, the substrate scope of this reaction was limited. High enantioselectivity was only observed when unsubstituted allyl alcohol was used, with the exception of compound **5g** (Scheme 11). New ligands were investigated to further optimize the reaction with the aim of expanding the substrate scope. The phosphinooxazoline (PHOX) ligands were screened because they combine the

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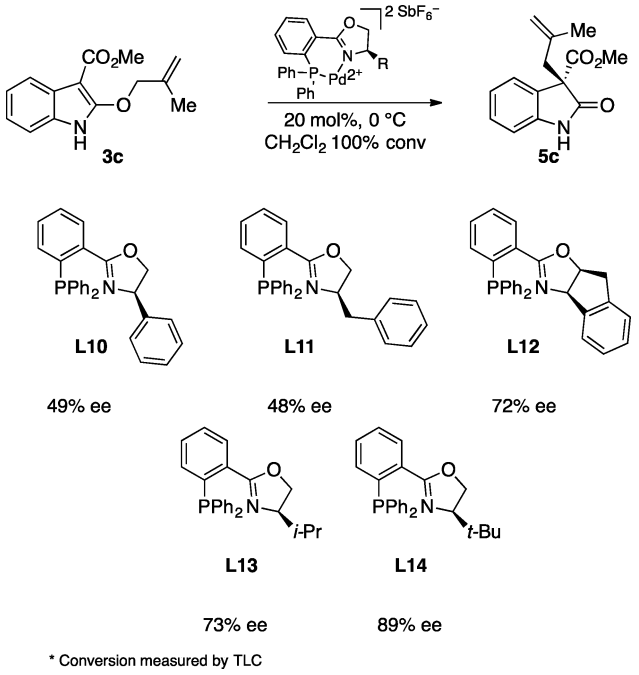
Scheme 13. Substrate Screening with PHOX Pd Catalysts



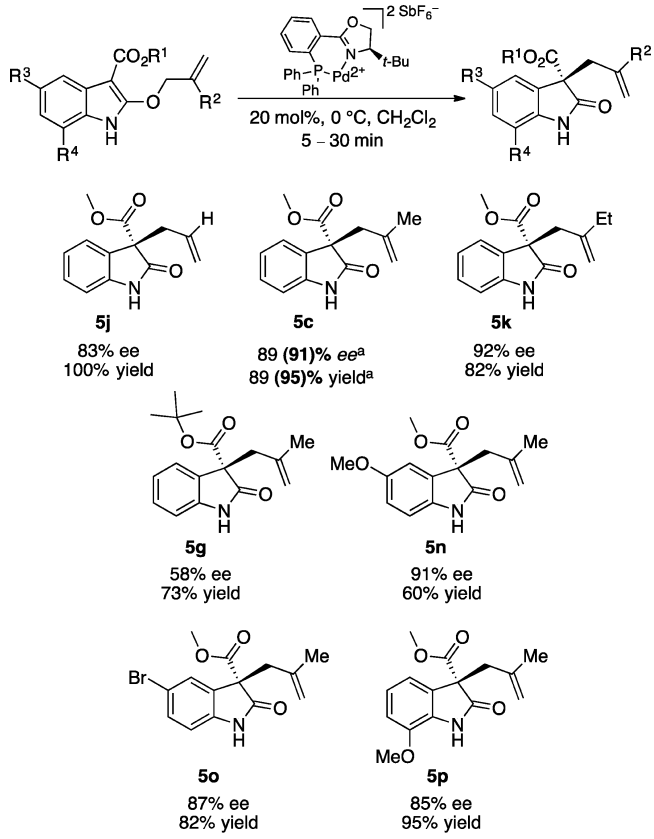
scaffolds of both the diphosphine ligands and the bisoxazoline ligands (Scheme 13). Only moderate enantioselectivities were observed with the phenyl- and benzyl-phosphinooxazoline ligands (**L10**, **L11**). Indanol ligand **L12**, as well as the isopropyl ligand **L13**, provided the product **5c** in good selectivity. The *tert*-butyl-phosphinooxazoline ligand **L14** generated the highest selectivity (89% ee).

tert-Butyl-phosphinooxazoline ligand afforded high selectivities over a range of substrates (Scheme 14). While methyl ester with allyl alcohol **5j** afforded the product in 83% ee, methyl allyl alcohol **5c** and ethyl allyl alcohol **5k** provided 89% and 92% ee, respectively. The enantioselectivity (91% ee) and yield (95%) improved when the reaction was performed on a 1 mmol scale. Contrary to results with the BINAP ligand, the use of the *tert*-butyl ester **5g** lowered both enantioselectivity and yield. Interestingly, the smaller methyl ester provided high enantioselectivity regardless of the electronics of the aromatic ring (**5n**–**5p**).

Mechanism. Because copper(II), zinc(II), nickel(II), and palladium(II) complexes all promote the Meerwein–Eschenmoser Claisen, a Lewis acid activation pathway seemed plausible.[28] With the same ligand, the selectivity of copper(II) and palladium(II) was virtually identical (Table 3, entries 1 and 5), which is consistent with the square planar coordination environments of these Lewis acids. As would be expected with a large change in coordination environment, zinc(II), which forms tetrahedral complexes, was much less selective (Table 3, entry 3). The major difference between copper(II) and palladium(II) lies in the turnover, which is ascribed to the larger size and weaker O-coordinating ability of the palladium. To determine if reduced palladium(0) was forming and causing to a π-allyl cation pathway, a deuterium atom was installed on the allyl group of the indole starting material **3q** (Scheme 15). This substrate was subjected to the reaction conditions, and only the [3,3′] rearranged product **5q** was observed by ^{1}H NMR, resulting in 80% isolated yield and 92% ee.

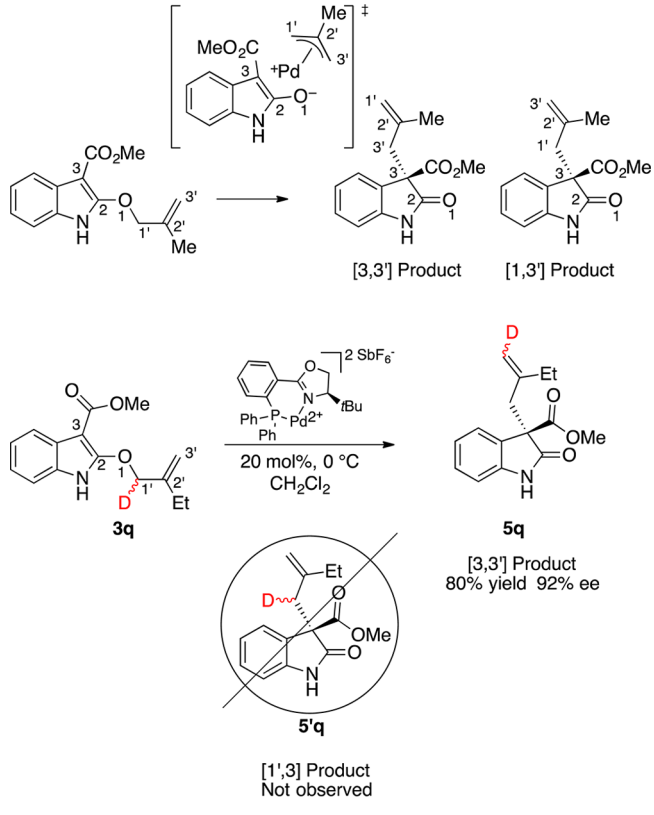
A further study of the mechanism of the formation of allyloxindole from the indole precursor was undertaken,

Scheme 14. Substrate Scope with *t*-BuPHOX Pd Catalyst



[a]Paranthetic results are from a larger scale (1 mmol) reaction.

Scheme 15. [3,3′] versus [1′,3] Rearrangement



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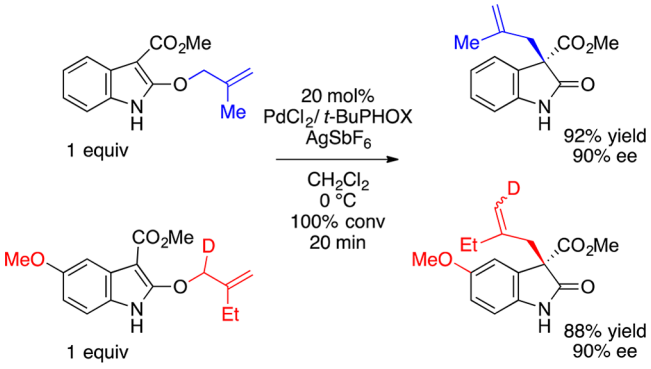
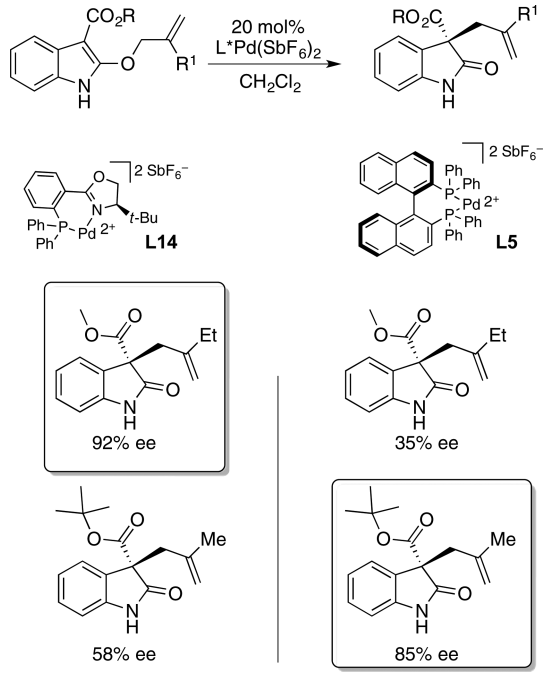
Scheme 16. Crossover Mechanism Experiment



Scheme 17. Comparison of *t*-BuPHOX Ligand with BINAP Ligand



utilizing two different substrates with unique substitution on the allyl and indole fragments (Scheme 16). If discrete π-allyl species were forming, four products arising from both allyl fragments combining with both indole fragments should be observed. There is also literature precedent for alkene activation with palladium(II) catalysts.[29] However, these cases do not possess an alternate strong coordination site for the palladium as shown in Scheme 3. If reaction via alkene coordination was occurring, substrates lacking the ester coordination group should also be viable, which is not the case (Scheme 2 and ref 29b). Finally, the Lewis acid activation[28] models explain the sense and trends in the stereochemcial induction (see Figure 3 and discussion above). Overall, the evidence supports the concerted Meerwein–Eschenmoser Claisen rearrangement illustrated in Figure 3.

In summary, the palladium-catalyzed enantioselective Meerwein–Eschenmoser Claisen rearrangement is a useful tool to give access to oxindole products bearing an allyl-substituted quaternary stereocenter. While the BINAP (**L5**) provided higher selectivities with large esters and small allyl alcohols, *tert*-butyl-phosphinooxazoline (**L14**) afforded the best selectivity with the smaller C3-methyl ester and the larger allyl alcohols (Scheme 17). The rearrangement has proven to be general, as substrates with either electron-withdrawing or electron-donating groups on the indole framework work well. In addition, catalyst loadings as low as 5 mol % can be used. The absolute configurations of the products were established through crystal structures (see the Supporting Information) and are in accord with the proposed stereochemical models.

2.2. Propargyloxy Indoles. With the goal of expanding this methodology from allyl ethers to propargyl ethers, we investigated the Saucy–Marbet rearrangement. Very few catalytic asymmetric methods of forming allenes exist,[30] as most transformations to allenes commence with enantioenriched precursors.[31] Notably, enantioenriched allenes have many potential applications.[32] In asymmetric catalysis, the transformations of propargyl vinyl ethers to provide β-substituted allenyl carbonyls remain highly challenging, as evidenced by the fact that no catalytic asymmetric Saucy–Marbet Claisen rearrangements were reported prior to our effort.[18,33] Examination of simple models revealed that the alkyne sp centers significantly perturb the sigmatropic rearrangement transition state. In addition, cylindrically symmetric alkyne gives no opportunity for facial discrimination. On the basis of the success of palladium catalysts for the transformation of allyloxy indoles to allyl oxindoles, a stereochemical model of the Pd(*t*-BuPHOX) catalyst with the propargyl substituted indoles was proposed (Figure 4). This model suggested that the ester group, which most likely coordinates to the palladium metal, could interact with larger alkyne terminal substituents, suppressing the pathways to one of the enantiomers.

Palladium Catalyst Survey. In line with this hypothesis, increasing the size of the terminal alkyne substituents did result in enhanced selectivity with the Pd(*t*-BuPHOX) catalyst (Table 5, entries 1–5). In particular, very high levels of enantioselectivity (96–98% ee) were observed with alkynes having *ortho*-substituted aryl groups at R^2. In addition, the reactivity of these compounds with the catalyst was significantly higher. For example, complete conversion to product was observed in 8 h at −15 °C with just 5 mol % catalyst loading (entries 5–9). Other alkynes with large groups, such as TMS, *tert*-butyl, and *N*-methyliminodiacetic acid (MIDA) boronates, provided lower selectivity (entries 10–12).

In an effort to improve the enantioselection of nonaryl alkynes, alternative ligands were evaluated. Trends similar to Pd(*t*-BuPHOX) catalyst (i.e., better selectivity for large substituents) were also observed with BINAP-derived complexes (Table 6). Methyl ester with propargyl alcohol **4d** afforded 4% ee (entry 2), while *tert*-butyl-substituted propargyl alcohol **4k** provided 76% ee (entry 3). Among a series of biaryl diphosphine ligands, DifluoroPHOS proved the most effective, providing *tert*-butyl-substituted allene **8k** with 90% yield and 86% ee (entry 4). Most surprising was the poor selectivity of the TMS-substituted alkyne (entry 6). A significant improvement with a return to BINAP (44% vs 77% ee, entries 6–7) suggested that trace fluoride from the DifluoroPHOS interferes with the rearrangement. While elevated temperature (rt vs 0 °C) allowed for good conversion of TBS substrates (entry 9), it also led to lower selectivity, which limited the utility of this system for large silyl-substituted terminal alkynes. However, this problem could be solved by modifying the reaction solvent. A screen of CH_2Cl_2, $C_6H_5CF_3$, THF, toluene, C_6H_5Cl, and several mixtures thereof revealed that a toluene–C_6H_5Cl mixture afforded good conversion and enantioselectivity (89% ee, entry 10) with the TBS substrate.

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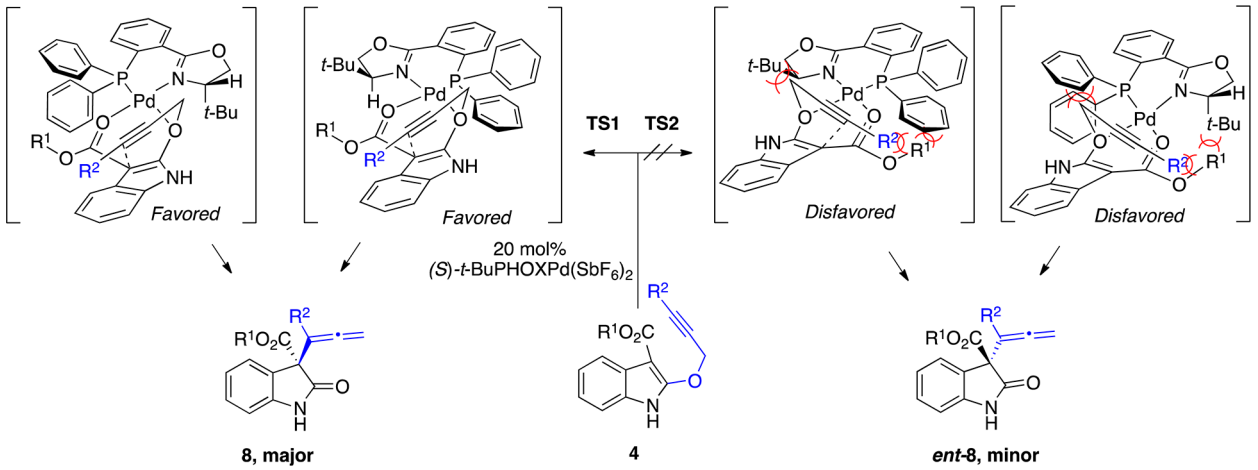
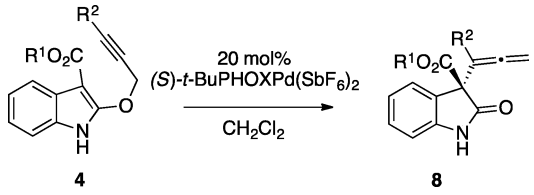


Figure 4. Proposed transition states with the *t*-BuPHOX Pd catalyst.

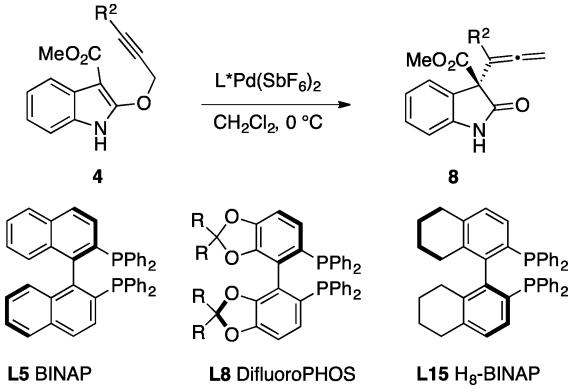
Table 5. Substrate Scope with Palladium *t*-BuPHOX



entry	4	R^1	R^2	mol % cat.	*T* (°C)	*t*	yield (%)	ee (%)
1	**a**	*t*-Bu	H	20	0	10 min	100[a]	0
2	**b**	*t*-Bu	Me	20	0	15 min	100[a]	4
3	**c**	Me	H	20	0	10 min	100[a]	14
4	**d**	Me	Me	20	0	15 min	100[a]	45
5	**e**	Me	Ph	5	−15	8 h	96	78
6	**f**	Me	*o*-MePh	5	−15	8 h	95	98
7	**g**	Me	*o*-BrPh	5	−15	8 h	93	96
8	**h**	Me	1-Nap	5	−15	8 h	95	98
9	**i**	Me	*o*-MeOPh	5	−15	8 h	90	98
10	**j**	Me	TMS	20	0	90 min	15	14
11	**k**	Me	*t*-Bu	20	0	2 d	100[a]	45
12[b]	**l**	Me	MIDA-B	20	45	2 d	60	70

[a]Conversion (%) measured by TLC. [b]MIDA boronate; see ref 34. Solvent: 1:5:5 MeCN:C_6H_5Cl:CH_2Cl_2.

Table 6. Diphosphine Ligand Screening in the Saucy−Marbet Rearrangement



entry	L	4	R^2	mol % cat.	*t*	yield (%)	ee (%)
1	**L5**	**c**	H	20	10 min	100	8
2	**L5**	**d**	Me	20	30 min	100	4
3	**L5**	**k**	*t*-Bu	20	2 d	40	76
4	**L8**	**k**	*t*-Bu	100	10 h	90	86
5	**L15**	**k**	*t*-Bu	100	10 h	90	83
6	**L8**	**j**	TMS	100	10 h	95	44
7	**L5**	**j**	TMS	100	4 h	90	77
8	**L5**	**j**	TMS	20	4 d	100	60
9	**L5**	**m**	TBS	100	14 h	100	78[a]
10	**L5**	**m**	TBS	20	5 d	90	89[b]

[a]Room temperature. [b]Reaction condition: 1:1 C_6H_5Cl:$C_6H_5CH_3$ at room temperature.

Gratifyingly, the Pd-(*R*)-BINAP complex afforded high selectivities with a range of TES- or TBS-substrates (Table 7). Both electron-withdrawing and electron-donating groups were tolerated on the indole framework. However, lower catalyst loadings translated into unacceptably long reaction times and lower enantioselectivity. To maintain the enantioselectivity for a 5 mol % catalyst reaction, we discovered that degassing of solvents was critical (Table 7, entry 4). To increase the rate of this reaction, a similar diphosphine ligand bearing an electron-withdrawing group was theorized to result in a more Lewis-acidic and reactive catalyst. BIPHEP (**L9**, entry 5) was indeed better in terms of reaction time but worse than BINAP (**L5**, entry 4) in terms of enantioselectivity. The (*R*)-configuration of the products was established through crystal structure (see the Supporting Information).

Mechanism. A further study of the mechanism of the formation of allene **8** from **4** was undertaken by utilizing two different substrates, each containing unique propargyl and indole fragments, in one reaction (Scheme 18). As was the case for the allyloxy substrates (see Scheme 16), no crossover was observed in the reaction, and the products arising from a [3,3′]-sigmatropic rearrangement were isolated in high isolated yield and enantioselectivity. This result ruled out a stepwise ionic mechanism and confirmed a concerted Saucy−Marbet Claisen rearrangement to generate the enantioenriched allenes.

Parallel Microscale Screening. The main drawback with the palladium catalysts remained the long reaction times. In an attempt to resolve this issue, a number of different metals were complexed with BINAP and examined (Table 8). Although 100 mol % catalyst was used, the reactions with Ag, Cu, Pt were very slow and resulted in decomposition (entries 1−3). Among metal complexes, Ni catalyst gave highest selectivity, but poor turnover (entries 4,5). On the other hand, the reaction

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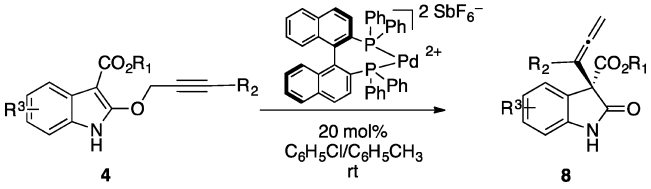
Table 7. Substrate Scope in the Saucy–Marbet Rearrangement



entry	4	R^1	R^2	R^3	t (d)	yield (%)	ee (%)
1	**n**	Me	TES	H	6	78	90
2	**m**	Me	TBS	H	5	90	89
3	**o**	Et	TBS	7-Me	5	87	90
4	**o**	Et	TBS	7-Me	10	76	90[a]
5	**o**	Et	TBS	7-Me	6	65	86[a,b]
6	**p**	Et	TBS	5-OMe	5	82	93
7	**q**	Et	TBS	7-OMe	6	91	93
8	**r**	Et	TBS	5-Br	6	85	90

[a]5 mol % L*Pd$(SbF_6)_2$. [b]BIPHEP **L9** was used.

Scheme 18. Mechanism Study

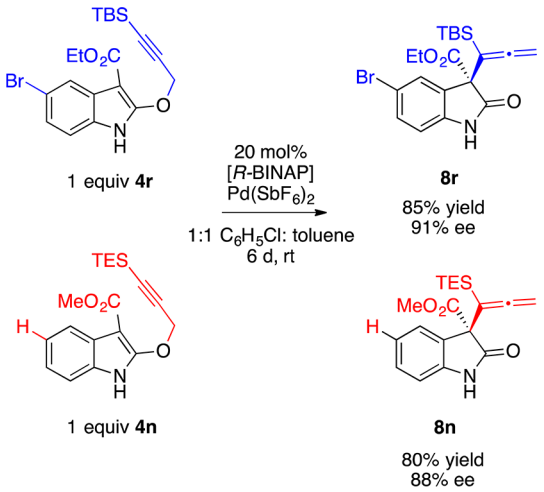
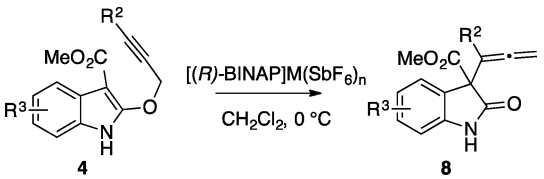


Table 8. Metal Screening



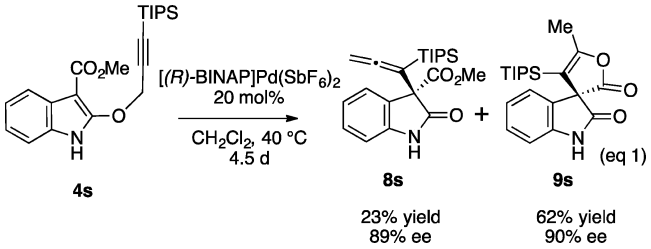
entry	M	R^2	cat. mol %	t	yield (%)	ee (%)
1	Ag(I)	*t*-Bu	100	4 d	0	NA
2	Cu(II)	*t*-Bu	100	4 d	0	NA
3	Pt(II)	*t*-Bu	100	2 d	decomp.	NA
4	Ni(II)	*t*-Bu	100	4 d	30	87
5	Ni(II)	TIPS	100	4 d	90	66[a]
6	Au(III)	TBS	20	2 h	100	60[b]

[a]Temperature: 45 °C. [b]R^3 = 5-MeO. Reaction conditions: Au(III) catalyst, C_6H_5Cl, 0 °C.

with Au(III) proceeded at a much faster rate but with modest selectivity (entry 6).[35]

Encouraged by the reactivity of the gold(III) catalyst (Table 9, entries 1 and 3), we undertook a parallel microscale screen with resources that became available at this point in the project. Using 1 mL vials with 100 μL reaction volumes at a 0.1 M concentration, 192 chiral mono- and bidentate phosphine ligands were screened in 96-well plates. A control experiment on larger scale showed that the AgCl formed during the generation of the gold catalyst did not affect the enantioselectivity; this result was crucial as it is very difficult to remove the AgCl precipitate at the microscale level. However, we were disappointed with the poor selectivity of substrates (R^2 = TBS, 0–67% ee) seen with either Au(III) or Au(I) catalysts. Use of a larger silyl group (TIPS, Table 9, entry 4) or smaller groups (TMS and Me, entries 6–8) did not result in retention of the selectivity. Unfortunately, the enantioselectivity could not be improved using different solvents (entry 3) or counteranions (entry 5). As a result, we determined that the palladium(II) catalyst is the most efficient catalyst for the Saucy–Marbet Claisen rearrangement, providing both sufficient reactivity and high enantioselectivity.

2.3. Spirocyclization with Propargyloxy Indoles. Higher temperatures (40 °C vs rt) were required when the optimized conditions using catalytic palladium were applied to the larger TIPS substrates. Under these conditions, an entirely different product, spirocyclic lactone **9s**, was observed as the major product (eq 1). Only a few examples of the racemic, saturated versions of these spirooxindoles have been reported.[7,36] Because of the broad utility of tandem reactions and the interesting structures of the spirocyclic lactones, further study of this tandem cyclization was undertaken.



To determine the cause of the cyclization, the allene was investigated as a potential intermediate (Figure 5). Notably, the cyclization is not catalyzed by Brønsted acid, and the Pd catalyst is necessary to generate the spirolactone from the allene (Figure 5). Specially, TIPS-substituted **8s** (89% ee) was isolated at lower temperature and then resubjected to the reaction conditions, resulting in full conversion to **9s** (90% ee). Hypothesizing that the spirocyclic compounds **9** arose from hydration of allenes **8** and subsequent Lewis acid-induced cyclization, β-silyl ketone **10** was generated (see below). Upon subjection of this ketone to the palladium catalyst, the spirocyclic lactone **9o** was obtained as the sole product.

We also observed that nonsilyl substrates reluctantly formed the spirolactone. The mechanism most consistent with all of the data is the formation of allene **8** followed by hydration and a palladium-catalyzed cyclization to generate lactone **9** (Scheme 19). A key component of this mechanism is carbocation intermediate **11**, which is stabilized via the β-silyl effect,[37] and explains why nonsilyl substrates cyclize slowly.

To selectively generate the allene **8** at elevated temperature (vs spirocyclic lactone **9**), efforts were directed at removing trace water and acid from the reaction mixtures (Table 10). Water absorbents such as 3 or 4 Å MS, MgO, and $MgSO_4$ were used, which stopped the cyclization process to some extent (entries 1–4). It was exciting to find that the use of 2,4,6-tri-*tert*-butylpyridine or (TMEDA)Zn$(SbF_6)_2$ prevented the cyclization entirely (entries 5 and 7).

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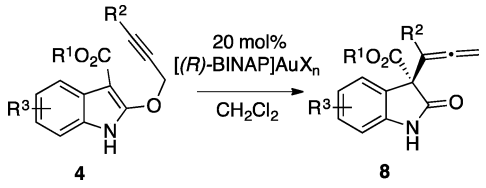
Table 9. Gold Catalyst Optimization



entry	*n*	X	R^1	R^2	R^3	*T* (°C)	*t*	conv. (%)	ee (%)
1	3	SbF_6^-	Me	TBS	5-MeO	rt	2 h	100	60
2	1	SbF_6^-	Me	TBS	5-MeO	rt	3 h	100	47
3	3	SbF_6^-	Me	TBS	5-MeO	0	6 h	100	60[a]
4	3	SbF_6^-	Me	TIPS	H	rt	18 h	100	36
5	3	BF_4^-	Me	TIPS	H	rt	14 h	50	10
6	3	SbF_6^-	*i*-Pr	TMS	H	0	1 h	100	6
7	3	SbF_6^-	Me	Me	H	0	30 min	100	3
8	1	SbF_6^-	Me	Me	H	0	30 min	100	7

[a]Solvent: C_6H_5Cl.

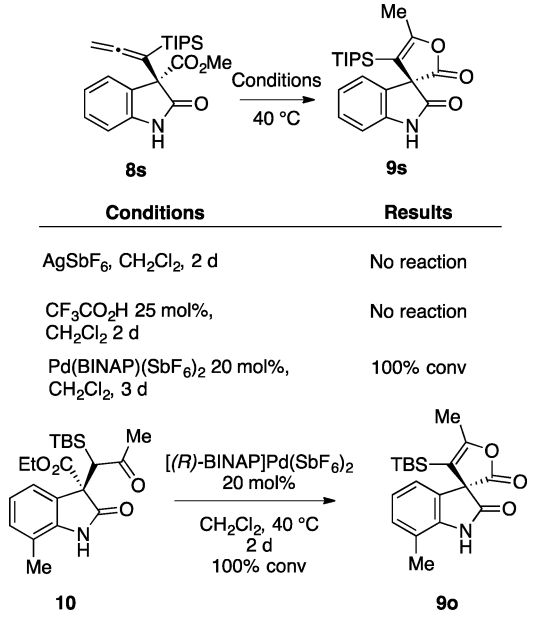
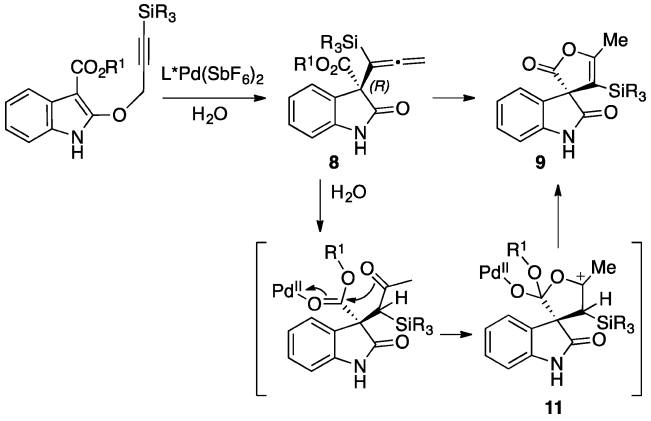


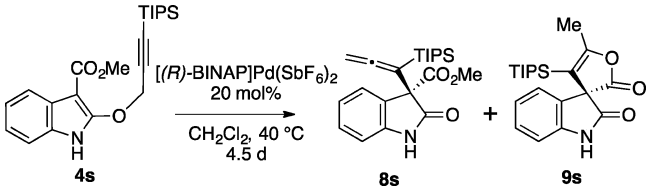
Figure 5. Formation of the spirocyclic lactone.

Scheme 19. Proposal Mechanism for the Formation of Spirocyclic Lactones



In line with the proposed mechanism (Scheme 19), addition of water shifted the reaction outcome entirely to the spirolactone **9**. A range of substrates was readily transformed to the corresponding spirooxindole lactones (Table 11). Substrates with different esters or indole substituents were well tolerated,

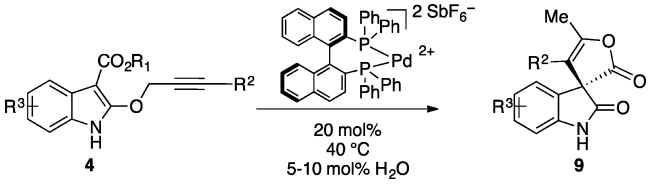
Table 10. Additives Screening



entry	additives	yield (%)	8s:9s
1	1 equiv of MgO	65	1:0.8
2	1 equiv of $MgSO_4$	85	1:4.4
3	MS 3 Å or 4 Å	0–5	NA
4	$NaHCO_3$	100	1:2.2
5[a]	10 mol % tri-*tert*-butylpyridine	80 (10 d)	1:0 (82% ee)
6	10 mol % $N(TMS)_3$	50 (10 d)	NA
7[a]	10 mol % $Zn(TMEDA)(SbF_6)_2$	55	1:0 (94% ee)

[a]30 mol % palladium catalyst.

Table 11. Tandem Rearrangement-Cyclization



entry	**4**	R^1	R^2	R^3	*t* (d)	solvent[a]	yield (%)	ee (%)
1	**s**	Me	TIPS	H	4.5	C	78[b]	90
2	**t**	Et	TIPS	H	4	C	95	90
3	**u**	CH_2CF_3	TIPS	H	4	C	90	87
4	**v**	Bn	TIPS	H	4	C	95	92
5	**w**	Et	TIPS	7-Me	6	B	93	96
6	**x**	Et	TIPS	5-OMe	5	A	81	91
7	**y**	Et	TIPS	7-OMe	6	C	90	92
8	**z**	Et	TIPS	5-Br	6	B	82	92
9[c]	**m**	Me	TBS	H	5	B	95	86

[a]Solvents: (A) CH_2Cl_2, (B) 1:1 C_6H_5Cl:$C_6H_5CH_3$, (C) C_6H_5Cl. [b]Performed with 0.5 mmol of substrate. [c]Reaction conducted at room temperature.

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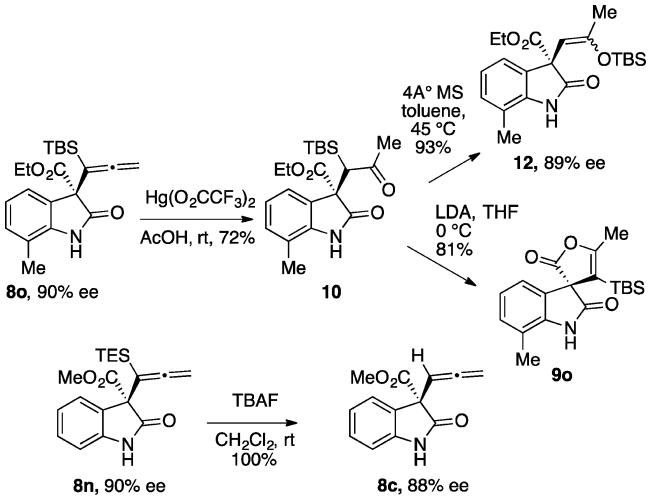
providing the lactone in good yields and enantioselectivities. Reactions on a larger scale also proceeded well (Table 11, entry 1).

The allenyl products were found to be useful in a number of transformations (Scheme 20). Hydration of the allene **8o** with $Hg(O_2CCF_3)_2$ provided α-silyl ketone **10.** This ketone could easily undergo Brook rearrangement to form silyl enol ether **12** or cylization to form lactone **9o**. The silyl group on **8n** was effectively removed by TBAF to provide the simplest congener **8c**, a compound that was not directly accessible with good selectivity via the Saucy–Marbet Claisen rearragement (see Table 5, entry 3).

Scheme 20. Transformations of Allenyl Compounds



CONCLUSION

In this Article, highly enantioselective catalytic processes are described for the Meerwein–Eschenmoser and Saucy–Marbet Claisen rearrangements using BINAP or *t*-BuPHOX palladium catalysts to construct a range of oxindoles bearing an allyl- or allenyl-substituted quaternary center. Mechanistic evidence firmly established the intermediacy of a [3,3′]-sigmatropic rearrangement versus ionic or stepwise processes. Indole substrates with functional groups at different positions can be utilized, which allow for further functionalization of the resultant oxindole products. Tandem reactions of silyl-allene indoles provide rapid access to a variety of spirocyclic oxindoles in one operation. In summary, a wide range of structurally rich chiral oxindoles is readily accessible via the catalytic transformations described herein.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all nonaqueous reactions were carried out under an atmosphere of dry N_2 in dried glassware. When necessary, solvents and reagents were dried prior to use. THF was distilled from sodium benzophenone ketyl. CH_3CN, CH_2Cl_2, TMEDA, and toluene were distilled from CaH_2. The alcohols[38] and some indole precursors[17−19,39] were prepared following the literature protocols.

When necessary, the column was prewashed with 1% Et_3N in the eluent system. Enantiomeric excesses were determined using analytical high performance liquid chromatography (HPLC) or supercritical fluid chromatography (SFC) with UV detection at 254 nm, using analytical OD, AS AD, IA, OJ-H columns (0.46 cm × 25 cm). Chemical shifts are reported in ppm from tetramethylsilane (0 ppm) or from the solvent resonance ($CDCl_3$ 7.26 ppm, THF-d_8 3.58 ppm, acetone-d_6 2.05 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants, and number of protons. Mass spectra were obtained from a TOF mass spectrometer with an ionization mode of either CI or ES. Optical rotations are reported as follows $[\alpha]^{23}_D$ (*c* g/mL × 100, solvent).

Representative Procedure (A) for Installation of an Allyl Alcohol to Indole Substrates. *Methyl 2-(2-Methylallyloxy)-1H-indole-3-carboxylate (**3c**).* To a flame-dried round-bottom flask was added methyl indole-3-carboxylate (3.0 g, 17.13 mmol). CH_2Cl_2 (15 mL) was added, and upon cooling to 0 °C, distilled 1,4-dimethylpiperazine (1.29 mL, 9.60 mmol) and recrystallized *N*-chlorosuccinimide (2.52 g, 19.02 mmol) were added. The resulting solution was stirred at 0 °C for 2 h. In a separate flame-dried round-bottom flask, methallyl alcohol (2.9 mL, 34.26 mmol) and trichloroacetic acid (0.67 g, 4.11 mmol) were dissolved in CH_2Cl_2 (15 mL). The solution was cooled to 0 °C and transferred via cannula to the indole solution. This mixture was stirred for 2 h at 0 °C, at which time the reaction mixture was concentrated under vacuum. It was then loaded onto a base-washed SiO_2 column (1% Et_3N, 24% EtOAc, 75% hexanes) and eluted with 25% EtOAc/hexanes to afford **3c** (2.5 g) in 60% yield as a white solid: mp 92−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (bs, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.23−7.14 (m, 3H), 5.18 (s, 1H), 5.05 (s, 1H), 4.81 (s, 2H), 3.93 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.5, 156.9, 141.4, 131.0, 127.2, 121.5, 121.4, 121.1, 113.1, 110.6, 89.9, 76.8, 49.9, 19.0; IR (film) 3231, 2949, 1660, 1552, 1475 cm^{-1}; HRMS (ES) *m*/*z* = 268.0949 calcd for $C_{14}H_{15}NO_3Na$ $[MNa]^+$, found 268.0957.

*2-(Allyloxy)-1H-indole-3-carbonitrile (**3a**).* Following the general procedure, compound **3b** was obtained in 38% yield. Because of the difficulty in separating compound **3a** from the indole-3-nitrile, the isolated yield was calculated from the mixture of compound **3a** and indole-3-nitrile. As the consequence, compound **3a** was only assessed by ^{1}H NMR experiment and mass spectrum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (bs, 1H), 7.55−7.53 (m, 1H), 7.26−7.14 (m, 3H), 5.54 (dd, *J* = 1.2, 17.2 Hz, 1H), 5.40 (dd, *J* = 1.1, 10.5 Hz, 1H), 5.10 (dt, *J* = 1.3, 5.5 Hz, 2H); HRMS (CI) *m*/*z* = 199.0871 calcd for $C_{12}H_{11}N_2O$ $[MH]^+$, found 199.0878.

*2-(2-Methylallyloxy)-1H-indole-3-carbonitrile (**3b**).* Following the general procedure (A), **3b** (0.056 g, 0.26 mmol) was obtained in 38% yield as a white solid: mp 104−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (bs, 1H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.24−7.18 (m, 3H), 5.20 (s, 1H), 5.10 (s, 1H), 5.03 (s, 2H), 1.89 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 157.0, 139.7, 130.1, 127.3, 121.7, 121.1, 117.4, 114.8, 113.1, 110.5, 107.7, 75.0, 18.3; IR (film) 3223, 3173, 2926, 2212, 1563, 1471 cm^{-1}; HRMS (CI) *m*/*z* = 213.1028 calcd for $C_{13}H_{13}N_2O$ $[MH]^+$, found 213.0994.

*Ethyl 2-(2-Methylallyloxy)-1H-indole-3-carboxylate (**3d**).* Following the general procedure (A), **3d** (0.06 g, 0.23 mmol) was obtained in 47% yield as beige solid: mp 90−91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (bs, 1H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.24−7.12 (m, 3H), 5.15 (s, 1H), 5.00 (s, 1H), 4.77(s, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.81 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.0, 156.8, 141.4, 131.0, 127.3, 121.4, 121.3, 121.2, 113.0, 110.5, 90.2, 76.9, 58.9, 19.1, 14.7; IR (film) 3231, 2980, 1660, 1552, 1471 cm^{-1}; HRMS (CI) *m*/*z* = 260.1287 calcd for $C_{15}H_{18}NO_3$ $[MH]^+$, found 260.1299.

*Benzyl 2-(2-Methylallyloxy)-1H-indole-3-carboxylate (**3e**).* Following the general procedure (A), **3e** (0.073 g, 0.23 mmol) was obtained in 45% yield as a brown oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (bs, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.40−7.31 (m, 4H), 7.23−7.14 (m, 4 H), 5.41 (s, 2H), 5.15 (s, 1H), 5.05 (s, 1H), 4.81 (s, 2H), 1.85 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 163.9, 157.1, 141.2, 138.4, 131.1, 128.6, 128.3, 127.9, 127.3, 121.6, 121.4, 121.1, 113.2, 109.9, 89.7, 76.7, 64.9, 19.1; IR (film) 3250, 2926, 1660, 1552, 1475, 1455 cm^{-1}; HRMS (ES) *m*/*z* = 344.1263 calcd for $C_{20}H_{19}NO_3Na$ $[MNa]^+$, found 344.1270.

*Isopropyl 2-(2-Methylallyloxy)-1H-indole-3-carboxylate (**3f**).* Following general procedure (A), **3f** (0.191 g, 0.70 mmol) was obtained in 55% yield as a white solid: mp 88−90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (bs, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.25−7.12 (m, 3H),

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5.31−5.28 (m, 1H), 5.19 (s, 1H), 5.06 (s, 1H), 4.83 (s, 2H), 1.88 (s, 3H), 1.43 (d, J = 6.2 Hz, 6H); ^{13}C NMR (90 MHz, THF-d_8) δ 163.7, 156.8, 141.4, 130.9, 127.4, 121.4, 121.3, 121.2, 113.0, 110.5, 90.5, 76.8, 65.9, 22.2, 19.1; IR (film) 3227, 2980, 2937, 1656, 1552, 1471, 1374 cm^{-1}; HRMS (ES) m/z = 296.1263 calcd for $C_{16}H_{19}NO_3Na$ [MNa]$^+$, found 296.1268.

*tert-Butyl 2-(2-Methylallyloxy)-1H-indole-3-carboxylate (**3g**).* Following the general procedure (A), **3g** (0.12 g, 0.418 mmol) was obtained in 34% yield as a pale yellow solid: mp 105−107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (bs, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.15−7.08 (m, 3H), 5.13 (s, 1H), 5.01 (s, 1H), 4.77 (s, 2H), 1.82 (s, 3H), 1.60 (s, 9H); ^{13}C NMR (90 MHz, THF-d_8) δ 163.8, 156.6, 141.0, 129.9, 127.4, 121.2 (2), 121.1, 113.1, 110.4, 91.6, 78.6, 76.8, 28.6, 19.1; IR (film) 3237, 2976, 1656, 1552, 1459, 1366 cm^{-1}; HRMS (ES) m/z = 310.1419 calcd for $C_{17}H_{21}NO_3Na$ [MNa]$^+$, found 310.1411.

*Methyl 2-(2-Methylenebutoxy)-1H-indole-3-carboxylate (**3k**).* Following the general procedure (A), **3k** (0.257 g, 0.99 mmol) was obtained in 43% yield as a yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (bs, 1H), 8.04 (d, J = 7.4 Hz, 1H), 7.26−7.15 (m, 3H), 5.23 (s, 1H), 5.09 (s, 1H), 4.89 (s, 2H), 3.93 (s, 3H), 2.23 (q, J = 7.0 Hz, 2H), 1.13 (t, J = 7.4 Hz, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 165.1, 157.5, 147.4, 131.5, 127.7, 122.0, 121.9, 121.6, 111.8, 111.1, 90.4, 76.4, 50.4, 26.6, 12.5; IR (film) 3229, 2966, 2881, 1668, 1552, 1468, 1352, 1267 cm^{-1}; HRMS (ES, negative ion) m/z = 258.1130 calcd for $C_{15}H_{16}NO_3$ [M − H]$^-$, found 258.1123.

*Methyl 2-(1-Deutero-2-methylenebutoxy)-1H-indole-3-carboxylate (**3q**).* Following the general procedure (A), **3q** (0.036 g, 0.14 mmol) was obtained in 17% yield as a yellow resin: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (bs, 1H), 8.04 (d, J = 7.2 Hz, 1H), 7.26−7.16 (m, 3H), 5.23 (t, J = 1.1 Hz, 1H), 5.09 (s, 1H), 4.86 (s, 1H), 3.91 (s, 3H), 2.23 (q, J = 7.4 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.5, 157.0, 147.0, 131.1, 127.3, 121.5, 121.4, 121.2, 111.5, 110.6, 90.0, 75.8 (t, J = 22.3 Hz), 49.9, 26.2, 12.3; IR (film) 3229, 3090, 2935, 2881, 1668, 1552, 1468, 1328, 1244 cm^{-1}; HRMS (ES) m/z = 283.1169 calcd for $C_{15}H_{16}DNO_3Na$ [MNa]$^+$, found 283.1165.

*2-(Allyloxy)-N,N-dimethyl-1H-indole-3-carboxamide (**7**).* Following the general procedure (A), compound **7** (0.145 g, 0.59 mmol) was obtained in 59% yield as a beige solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (bs, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.07 (m, 2H), 5.94 (m, 1H), 5.32 (d, J = 17.0, Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 4.65 (d, J = 5.5 Hz, 2H), 3.11 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 150.2, 132.5, 129.9, 126.3, 120.9, 120.7, 119.0, 118.6, 110.3, 91.2, 73.1, 38.6; IR (film) 3460, 3182, 3066, 2943, 2765, 1776, 1707, 1591, 1514, 1468, 1429, 1352, 1182 cm^{-1}; HRMS (ES) m/z = 245.1290 calcd for $C_{14}H_{17}N_2O_2$ [MH]$^+$, found 245.1285.

Representative Procedure (B) for Installation of an Allyl Alcohol to Indole Substrates. *Methyl 2-(Allyloxy)-1H-indole-3-carboxylate (**3j**).* To a flame-dried round-bottom flask was added methyl indole-3-carboxylate (0.30 g, 1.71 mmol). After that was dissolved in CH_2Cl_2 (4 mL) and cooled to 0 °C, 1,4-diazobicyclo[2.2.0]-octane (DABCO) (0.108 g, 0.96 mmol) was added followed by recrystallized *N*-chlorosuccinimide (0.253 g, 1.90 mmol). The resultant solution was stirred at 0 °C for 30 min, followed by addition of allyl alcohol (0.23 mL, 3.42 mmol) and methanesulfonic acid (0.016 mL, 0.24 mmol). This mixture was stirred for 30 min at 0 °C, at which time the reaction mixture was concentrated under vacuum and chromatographed on a base-washed SiO_2 column (1% Et_3N, 24% EtOAc, 75% hexanes) using 25% EtOAc/hexanes as the eluent to afford **3j** (0.224 g, 0.97 mmol) in 57% yield as an off-white oil: mp 80−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (bs, 1H), 8.05 (m, 1H), 7.22−7.18 (m, 3H), 6.13−6.05 (m, 1H), 5.49 (d, J = 17.2 Hz, 1H), 5.36 (d, J = 10.4 Hz, 1H), 4.95 (d, J = 5.7 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.7, 157.0, 133.7, 131.0, 127.3, 121.6, 121.5, 121.2, 117.8, 110.7, 90.3, 74.4, 50.0; IR (film) 3229, 2997, 2950, 1668, 1552, 1468, 1328, 1251, 1213 cm^{-1}; HRMS (ES) m/z = 254.0799 calcd for $C_{13}H_{13}NO_3Na$ [MNa]$^+$, found 254.0797.

*tert-Butyl 2-(Allyloxy)-1H-indole-3-carboxylate (**3i**).* Following the general procedure (A), **3i** (0.53 g, 1.94 mmol) was obtained in 77% yield as a white solid: mp 124−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (bs, 1H), 8.01 (d, J = 7.0 Hz, 1H), 7.25−7.13 (m, 3H), 6.15−6.02 (m, 1H), 5.46 (dd, J = 17.2, 1.4 Hz, 1H), 5.33 (dd, J = 10.4, 1.2 Hz, 1H), 4.92 (m, 2H), 1.66 (s, 9H); ^{13}C NMR (90 MHz, THF-d_8) δ 163.9, 156.7, 134.0, 130.9, 127.4, 121.4 (2), 121.3, 117.7, 110.6, 92.1, 81.6, 74.6, 28.6; IR (film) 3229, 2981, 2881, 1661, 1552, 1468, 1367, 1251, 1174, 1097 cm^{-1}; HRMS (ES) m/z = 274.1443 calcd for $C_{16}H_{20}NO_3$ [MH]$^+$, found 274.1435.

*Isopropyl 2-(Allyloxy)-1H-indole-3-carboxylate (**3l**).* Following the general procedure (B), **3l** (0.15 g, 0.59 mmol) was obtained in 80% yield as an off-white oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (bs, 1H), 8.05 (d, J = 7.0 Hz, 1H), 7.25−7.19 (m, 3H), 6.18−6.05 (m, 1H), 5.49 (ddd, J = 1.4, 2.9, 17.2 Hz, 1H), 5.36 (ddd, 1.4, 2.9, 10.4 Hz, 1H), 5.35 (septet, J = 6.3 Hz, 1H), 4.96 (ddd, J = 1.3, 2.7, 5.7 Hz, 2H), 1.42 (d, J = 6.3 Hz, 6H); ^{13}C NMR (90 MHz, THF-d_8) δ 163.9, 156.9, 133.8, 131.5, 127.4, 121.5 (2), 121.3, 117.7, 110.7, 90.9, 74.4, 66.2, 22.3; IR (film) 3229, 2981, 2935, 1738, 1661, 1552, 1468, 1375, 1244, 1097 cm^{-1}; HRMS (ES) m/z = 260.1287 calcd for $C_{15}H_{18}NO_3$ [MH]$^+$, found 260.1281.

*Benzyl 2-(Allyloxy)-1H-indole-3-carboxylate (**3m**).* Following the general procedure (B), **3m** (0.121 g, 0.39 mmol) was obtained in 66% yield as a yellow oil: ^{1}H NMR (360 MHz, THF-d_8) δ 10.87 (bs, 1H), 8.07 (m, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.37−7.20 (m, 4H), 7.11−7.06 (m, 2H), 6.14−6.04 (m, 1H), 5.45 (dd, J = 1.6, 17.2 Hz, 1H), 5.39 (s, 2H), 5.24 (dd, J = 1.3, 10.5 Hz), 4.92 (m, 2H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.1, 157.2, 138.4, 133.5, 131.2, 128.7, 128.2, 128.0, 127.3, 121.7, 121.6, 121.2, 118.0, 110.8, 90.1, 74.2, 64.9; IR (film) 3229, 3090, 3035, 2950, 2881, 1661, 1552, 1460, 1352, 1259, 1213 cm^{-1}; HRMS (ES) m/z = 308.1287 calcd for $C_{19}H_{18}NO_3$ [MH]$^+$, found 308.1285.

*Methyl 2-(2-Methylallyloxy)-5-methoxy-1H-indole-3-carboxylate (**3n**).* Following the general procedure (B), **3n** (0.03 g, 0.11 mmol) was obtained in 22% yield as an off-white oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (bs, 1H), 7.59 (m, 1H), 7.10 (d, J = 8.6 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 5.19 (s, 1H), 5.06 (s, 1H), 4.79 (s, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.6, 157.1, 156.3, 141.5, 128.2, 125.6, 113.1, 111.2, 110.1, 104.2, 90.2, 76.8, 55.4, 49.9, 19.1; IR (film) 3244, 2950, 1668, 1591, 1552, 1468, 1352, 1274, 1205 cm^{-1}; HRMS (ES) m/z = 298.1055 calcd for $C_{15}H_{17}NO_4Na$ [MNa]$^+$, found 298.1066.

*Methyl 2-(2-Methylallyloxy)-5-bromo-1H-indole-3-carboxylate (**3o**).* Following the general procedure (B), **3o** (0.07 g, 0.22 mmol) was obtained in 55% yield as an off-white oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (bs, 1H), 8.17 (d, J = 2.0 Hz, 1H), 7.26 (m, 1H), 7.09 (d, J = 8.5 Hz, 1H), 5.20 (s, 1H), 5.10 (s, 1H), 4.85 (s, 2H), 3.93 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.2, 157.6, 141.1, 134.6, 129.1, 124.3, 123.5, 115.1, 113.4, 112.4, 89.7, 76.8, 50.7, 19.1; IR (film) 3221, 2950, 1668, 1552, 1483, 1352, 1251, 1213 cm^{-1}; HRMS (ES) m/z = 346.0055 calcd for $C_{14}H_{14}BrNO_3Na$ [MNa]$^+$, found 346.0045.

*Methyl 2-(2-Methylallyloxy)-7-methoxy-1H-indole-3-carboxylate (**3p**).* Following general procedure (B), **3p** (0.086 g, 0.31 mmol) was obtained in 43% yield as a white resin: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (bs, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.66 (d, J = 7.9 Hz, 1H), 5.21 (s, 1H), 5.08 (s, 1H), 4.83 (s, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (90 MHz, THF-d_8) δ 164.0, 156.0, 145.4, 141.1, 127.5, 121.9, 121.3, 113.5, 112.6, 101.9, 90.5, 77.0, 54.6, 49.3, 18.6; IR (film) 3221, 1950, 2842, 1668, 1552, 1475, 1367, 1282, 1220 cm^{-1}; HRMS (ES) m/z = 298.1055 calcd for $C_{15}H_{17}NO_4Na$ [MNa]$^+$, found 298.1057.

Representative Procedure for Installation of a Propargyl Alcohol to Indole Substrates. *Methyl 2-((4,4-Dimethylpent-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4k**).* To a solution of methyl indole-3-carboxylate (200 mg, 1.14 mmol) in CH_2Cl_2 (10 mL) cooled to 0 °C was added 1,4-dimethylpiperazine (0.085 mL, 0.64 mmol), followed by recrystallized *N*-chlorosuccinimide (167 mg, 1.26 mmol). The resultant solution was stirred at 0 °C for 3 h. A solution of the propargyl alcohol (127 mg, 1.14 mmol) and trichloroacetic acid (45 mg, 0.27 mmol) in CH_2Cl_2 (1 mL) at 0 °C was transferred via cannula to the indole solution. This mixture was stirred for 12 h at 0 °C, at which time the reaction mixture was concentrated and

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chromatographed on a base-washed SiO_2 column using 15% ethyl ether/hexane to afford **4k** (131 mg, 0.456 mmol) in 40% yield as a white resin: ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.55 (bs, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.26−7.16 (m, 3H), 5.03 (s, 2H), 3.92 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 165.1, 155.8, 129.8, 126.1, 122.33, 122.3, 121.31, 110.5, 99.3, 91.4, 73.1, 62.0, 51.1, 30.8, 27.8; IR (film) 3236, 2974, 2873, 2248, 1668, 1552, 1468, 1352, 1267, 1205, 1104 cm^{-1}; HRMS (ES) m/z = 308.1263 calcd for $C_{17}H_{19}NO_3Na$ $[MNa]^+$, found 308.1259.

*tert-Butyl 2-(Prop-2-yn-1-yloxy)-1H-indole-3-carboxylate (**4a**).* Following the general procedure, compound **4a** was obtained as a white solid in 30% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (bs, 1H), 8.03 (d, J = 7.0 Hz, 1H), 7.30−7.17 (m, 3H), 5.07 (d, J = 2.5 Hz, 2H), 2.58 (t, J = 2.5 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 155.1, 129.7, 126.0, 122.4, 122.2, 121.5, 110.8, 93.5, 80.5, 78.3, 77.4, 61.7, 28.8; IR (film) 3283, 2974, 2124, 1653, 1552, 1468, 1367, 1328, 167, 1213, 1174, 1097 cm^{-1}; HRMS (ES) m/z = 294.1106 calcd for $C_{16}H_{17}NO_3Na$ $[MNa]^+$, found 294.1104.

*tert-Butyl 2-(But-2-yn-1-yloxy)-1H-indole-3-carboxylate (**4b**).* Following the general procedure, compound **4b** was obtained as a white solid in 44% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (bs, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.26−7.15 (m, 3H), 5.02 (q, J = 2.4 Hz, 2H), 1.86 (t, J = 2.4 Hz, 3H), 1.65 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 155.6 129.7, 126.2, 122.1, 121.4, 110.6, 100.2, 92.9, 86.2, 80.2, 73.8, 62.0, 28.9, 3.9; IR (film) 3221, 2974, 2927, 2240, 1661, 1552, 1468, 1352, 1213, 1174, 1097 cm^{-1}; HRMS (ES) m/z = 308.1263 calcd for $C_{17}H_{19}NO_3Na$ $[MNa]^+$, found 308.1266.

*Methyl 2-(Prop-2-yn-1-yloxy)-1H-indole-3-carboxylate (**4c**).* Following the general procedure, compound **4c** was obtained as a white resin in 45% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (bs, 1H), 8.05 (d, J = 7.0 Hz, 1H), 7.30−7.19 (m, 3H), 5.13 (d, J = 2.5 Hz, 2H), 3.93 (s, 3H), 2.62 (t, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 155.4, 129.8, 125.9, 122.6, 122.4, 121.3, 110.9, 91.7, 78.0, 77.6, 61.7, 51.23; IR (film) 3283, 2950, 2132, 1676, 1552, 1468, 1344, 1267, 1205, 1104 cm^{-1}; HRMS (ES) m/z = 252.0637 calcd for $C_{13}H_{11}NO_3Na$ $[MNa]^+$, found 252.0634.

*Methyl 2-(But-2-yn-1-yloxy)-1H-indole-3-carboxylate (**4d**).* Following the general procedure, compound **4d** was obtained as a white resin in 47% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (bs, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.26−7.15 (m, 3H), 5.04 (q, J = 2.5 Hz, 2H), 3.92(S, 3H), 1.87 (t, J = 2.4 Hz, 5H); ^{13}C NMR (125 MHz, THF-d_8) δ 163.5, 155.3, 129.9, 126.0, 120.7, 120.5, 120.3, 109.8, 90.0, 83.5, 73.3, 60.9, 49.0, 1.8; IR (film) 3229, 2950, 2240, 1668, 1552, 1468, 1344, 1267, 1213, 1097 cm^{-1}; HRMS (ES) m/z = 244.0974 calcd for $C_{14}H_{14}NO_3$ $[MH]^+$, found 244.0963.

*Methyl 2-((3-Phenylprop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4e**).* Following the general procedure, compound **4e** was obtained as a colorless oil in 28% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (bs, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.36−7.19 (m, 8H), 5.29 (s, 2H), 3.95 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 155.7, 132.0, 129.9, 129.2, 128.6, 126.0, 122.4, 122.3, 121.9, 121.3, 110.9, 91.5, 89.3, 83.1, 62.4, 51.2; IR (film) 3233, 2950, 2235, 1670, 1550, 1468, 1345, 1205, 1103, 1018 cm^{-1}; HRMS (ES) m/z = 328.0950 calcd for $C_{19}H_{15}NO_3Na$ $[MNa]^+$, found 328.0948.

*Methyl 2-((3-(o-Tolyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4f**).* Following the general procedure, compound **4f** was obtained as a colorless oil in 31% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (bs, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.27−7.14 (m, 5H), 7.10 (t, J = 6.5 Hz, 1H), 5.36 (s, 2H), 3.94 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 155.7, 140.7, 132.4, 129.8, 129.7, 129.3, 126.0, 125.8, 122.5, 122.3, 121.6, 121.3, 110.7, 91.7, 88.3, 86.8, 62.4, 51.2, 20.7; IR (film) 3227, 2949, 2221, 1671, 1551, 1472, 1343, 1210, 1101, 1010 cm^{-1}; HRMS (ES) m/z = 320.1287 calcd for $C_{20}H_{18}NO_3$ $[MH]^+$, found 320.1281.

*Methyl 2-((3-(2-Bromophenyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4g**).* Following the general procedure, compound **4g** was obtained as a colorless resin in 15% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (bs, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.28−7.16 (m, 5H), 5.31 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 155.6, 133.9, 132.6, 130.5, 130.0, 127.4, 125.9, 125.7, 123.9, 122.4, 122.3, 121.3, 110.8, 91.5, 87.9, 87.6, 61.9, 51.2; IR (film) 3253, 2954, 2233, 1671, 1550, 1466, 1344, 1204, 1104, 1017 cm^{-1}; HRMS (ES) m/z = 406.0055 calcd for $C_{19}H_{14}NO_3NaBr$ $[MNa]^+$, found 406.0051.

*Methyl 2-((3-(Naphthalen-1-yl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4h**).* Following the general procedure, compound **4h** was obtained as a colorless resin in 17% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (bs, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.82 (t, J = 8.5 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.46 (t, J = 7.0 Hz, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.29−7.19 (m, 5H), 5.51 (s, 2H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 155.6, 133.3, 133.2, 130.9, 129.9, 129.7, 128.4, 127.2, 126.7, 126.1, 125.9, 125.2, 122.5, 122.3, 121.4, 119.5, 110.9, 92.0, 87.9, 87.5, 62.6, 51.2; IR (film) 3245, 3061, 2225, 1671, 1549, 1466, 1333, 1205, 1102 cm^{-1}; HRMS (ES) m/z = 378.1106 calcd for $C_{23}H_{17}NO_3Na$ $[MNa]^+$, found 378.1106.

*Methyl 2-((3-(2-Methoxyphenyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4i**).* Following the general procedure, compound **4i** was obtained in 15% yield. Because of the difficulty in separating compound **4i** from the methylindole-3-carboxylate and the instability of this material at ambient temperature, the isolated yield was calculated from the mixture of compound **4i** and methylindole-3-carboxylate (1.4:1). As a consequence, compound **4i** was only assessed by ^{1}H NMR experiment and mass spectrum. ^{1}H NMR (500 MHz, THF-d_8) δ 7.99−7.97 (m, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.21−7.05 (m, 4H), 6.90 (d, J = 7.8 Hz, 1H), 6.81 (t, J = 8.3 Hz, 1H), 5.36 (s, 2H), 3.82 (s, 3H), 3.68 (s, 3H); HRMS (ES) m/z = 358.1055 calcd for $C_{20}H_{17}NO_4Na$ $[MNa]^+$, found 358.1055.

*Methyl 2-((3-(Trimethylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4j**).* Following the general procedure, compound **4j** was obtained as a white resin in 26% yield: ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.48 (bs, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.27−7.17 (m, 3H), 5.06 (s, 2H), 3.93 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 165.0, 155.3, 129.7, 126.0, 122.6, 122.4, 121.5, 110.6, 99.5, 95.7, 91.8, 62.5, 51.2, −0.2; IR (film) 3236, 2958, 2186, 1668, 1552, 1468, 1344, 1251, 1205, 1104, 1035 cm^{-1}; HRMS (ES) m/z = 324.1032 calcd for $C_{16}H_{19}NO_3NaSi$ $[MNa]^+$, found 324.1041.

*8-(3-((3-(Methoxycarbonyl)-1H-indol-2-yl)oxy)prop-1-yn-1-yl)-4-methyl-2,6-dioxohexahydro-[1,3,2]oxazaborolo[2,3-b][1,3,2]-oxazaborol-4-ium-8-uide (**4l**).* Following the general procedure, to a solution of methyl indole-3-carboxylate (61 mg, 0.35 mmol) in CH_2Cl_2 (2 mL) cooled to 0 °C was added 1,4-dimethylpiperazine (0.026 mL, 0.20 mmol), followed by recrystallized *N*-chlorosuccinimide (58 mg, 0.44 mmol). The resultant solution was stirred at 0 °C for 3 h. A solution of the propargyl alcohol (30 mg, 0.14 mmol) and trichloroacetic acid (14 mg, 0.08 mmol) in THF (0.5 mL) at 0 °C was transferred via cannula to the indole solution. This mixture was stirred for 12 h at 0 °C, at which time the reaction mixture was concentrated and chromatographed on a base-washed SiO_2 column using 80% ethyl acetate/hexane to afford **4l** (46 mg, 0.12 mmol) in 90% yield as a white resin; ^{1}H NMR (500 MHz, acetone-d_6) δ 7.99−7.97 (m, 1H), 7.33−7.91 (m, 1H), 7.16−7.11 (m, 2H), 5.21 (s, 2H), 4.21 (d, J = 17.0 Hz, 2H), 3.94 (d, J = 17.0 Hz, 2H), 3.84 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 168.4, 165.1, 156.3, 131.2, 127.1, 122.7, 122.4, 121.6, 111.8, 91.7, 62.27, 62.25, 50.8, 48.2. The ^{13}C NMR signals for two alkynyl carbons were not seen in accord with prior reports;[40] IR (film) 3222, 2945, 2200, 1773, 1694, 1562, 1469, 1350, 1271, 1113, 1034 cm^{-1}; HRMS (ES) m/z = 407.1027 calcd for $C_{18}H_{17}BN_2O_7Na$ $[MNa]^+$, found 407.1033.

*Methyl 2-((3-(tert-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4m**).* Following the general procedure, compound **4m** was obtained as a white solid in 43% yield: mp 128−129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (bs, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.26−7.17 (m, 3H), 5.07 (s, 2H), 3.94 (s, 3H), 0.86 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 155.5, 129.8, 125.9, 122.4, 122.3, 121.3, 110.7, 100.0, 94.1, 91.6, 62.1, 51.2, 26.1, 16.5, −4.7; IR (film) 3190, 2958, 2858, 2186, 1661, 1552, 1468, 1259, 1097, 1027 cm^{-1}; HRMS (ES) m/z = 344.1682 calcd for $C_{19}H_{26}NO_3Si$ $[MH]^+$, found 344.1690.

*Ethyl 2-((3-(tert-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)-7-methoxy-1H-indole-3-carboxylate (**4n**).* Following the general procedure, compound **4n** was obtained as a white solid in 50% yield: mp 98−99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (bs, 1H), 8.06 (d, J = 7.5 Hz, 1H), 7.26−7.16 (m, 3H), 5.07 (s, 2H), 3.94 (s, 3H), 0.93 (t, J = 8 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 155.6, 129.9, 125.9, 122.4, 122.3, 121.2, 110.7, 100.4, 93.3, 91.5, 62.1, 51.4, 7.46, 4.21; IR (film) 3259, 2958, 2881, 2186, 1668, 1552, 1468, 1205, 1104, 1012 cm^{-1}; HRMS (ES) m/z = 344.1682 calcd for $C_{19}H_{26}NO_3Si$ $[MH]^+$, found 344.1699.

*Ethyl 2-((3-(tert-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)-7-methyl-1H-indole-3-carboxylate (**4o**).* Following the general procedure, compound **4o** was obtained as a white solid in 31% yield: mp 117−118 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (bs, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.15 (dd, J = 8.0, 7.0 Hz, 1H), 7.00 (d, J = 7.0 Hz, 1H), 5.08 (s, 2H), 4.40 (q, J = 7 Hz, 2H), 2.41 (s, 3H), 1.45 (t, J = 7 Hz, 3H), 0.87 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 155.4, 129.2, 125.6, 123.2, 122.4, 119.7, 119.2, 100.3, 93.7, 92.5, 62.4, 59.8, 26.1, 16.5 (2C), 14.8, −4.8; IR (film) 3229, 2958, 2858, 2186, 1668, 1552, 1468, 1274, 1213, 1097 cm^{-1}; HRMS (ES) m/z = 370.1838 calcd for $C_{21}H_{28}NO_4Si$ $[M - H]^-$, found 370.1855.

*Ethyl 2-((3-(tert-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)-5-methoxy-1H-indole-3-carboxylate (**4p**).* Following the general procedure, compound **4p** was obtained as a white solid in 39% yield: mp 145−146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (bs, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.10 (d, J = 9.0 Hz, 1H), 6.82 (dd, J = 2.0, 9.0 Hz, 1H), 5.05 (s, 2H), 4.39 (q, J = 7.0 Hz, 2H), 3.87 (s, 3H), 1.44 (t, J = 7.0 Hz, 3H), 0.87 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 156.0, 155.5, 126.9, 124.3, 111.8, 111.4, 104.2, 100.2, 94.0, 92.2, 62.4, 59.8, 55.9, 26.1, 16.6, 14.8, −4.7; IR (film) 3213, 2935, 2858, 2186, 1653, 1468, 1352, 1205, 1166, 1104, 1043 cm^{-1}; HRMS (ES) m/z = 388.1944 calcd for $C_{21}H_{30}NO_4Si$ $[MH]^+$, found 388.1934.

*Ethyl 2-((3-(tert-Butyldimethylsilyl)prop-2-yn-1-yl)oxy)-7-methoxy-1H-indole-3-carboxylate (**4q**).* Following the general procedure, compound **4q** was obtained as a white solid in 16% yield: mp 107−108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (bs, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.12 (dd, J = 8.0, 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.03 (s, 2H), 4.37 (q, J = 7.5 Hz, 2H), 3.90 (s, 3H), 1.41 (t, J = 7.5 Hz, 3H), 0.86 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 154.9, 145.4, 127.1, 122.6, 119.8, 114.0, 102.8, 100.2, 94.2, 92.5, 62.1, 59.8, 55.5, 26.1, 16.5, 14.8, −4.8; IR (film) 3244, 2935, 2858, 2186, 1676, 1552, 1468, 1282, 1027 cm^{-1}; HRMS (ES) m/z = 386.1788 calcd for $C_{21}H_{28}NO_4Si$ $[M - H]^-$, found 386.1796.

*Ethyl 5-Bromo-2-((3-(tert-butyldimethylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4r**).* Following the general procedure, compound **4r** was obtained as a light gray solid in 28% yield: mp 155−156 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (bs, 1H), 8.15 (d, J = 2.0 Hz, 1H), 7.25 (dd, J = 8.5, 2.0 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 5.05 (s, 2H), 4.37 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7 Hz, 3H), 0.82 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 155.9, 128.4, 127.7, 125.3, 124.1, 115.7, 112.1, 99.7, 94.4, 91.8, 62.2, 60.1, 26.1, 16.5, 14.8, −4.8; IR (film) 3221, 2958, 2858, 2186, 1668, 1552, 1475, 1328, 1251, 1205, 1104, 1027 cm^{-1}; HRMS (ES) m/z = 458.0763 calcd for $C_{20}H_{26}BrNO_3SiNa$ $[MNa]^+$, found 458.0781.

*Methyl 2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4s**).* Following the general procedure, compound **4s** was obtained as a white solid in 59% yield: mp 92−93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (bs, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.27−7.17 (m, 3H), 5.12 (s, 2H), 3.97 (s, 3H), 1.12−0.88 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 155.6, 130.1, 125.9, 122.12, 122.07, 121.0, 110.8, 100.8, 91.9, 91.2, 61.6, 51.1, 18.5, 11.1; IR (film) 3259, 2950, 2866, 2178, 1668, 1552, 1460, 1344, 1274, 1205, 1104, 1020 cm^{-1}; HRMS (ES) m/z = 386.2151 calcd for $C_{22}H_{32}$ NO_3Si $[MH]^+$, found 386.2137.

*Ethyl 2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4t**).* Following the general procedure, compound **4t** was obtained as a white solid in 40% yield: mp 93−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.03 (bs, 1H), 8.05 (d, J = 7.5 Hz, 1H), 7.24−7.17 (m, 3H), 5.11 (s, 2H), 4.41 (q, J = 7 Hz, 2H), 1.45 (t, J = 7 Hz, 3H), 1.09−0.86 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 155.5, 129.9, 125.9, 122.2, 122.1, 121.2, 110.6, 101.1, 92.0, 91.7, 61.9, 59.8, 18.6, 14.7, 11.1; IR (film) 3244, 2943, 2866, 2178, 1668, 1552, 1460, 1375, 1274, 1205, 1097, 1020 cm^{-1}; HRMS (ES) m/z = 422.2127 calcd for $C_{23}H_{33}NO_3SiNa$ $[MNa]^+$, found 422.2125.

*2,2,2-Trifluoroethyl 2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4u**).* Following the general procedure, compound **4u** was obtained as a white solid in 26% yield: mp 97−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (bs, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.29−7.21 (m, 3H), 5.08 (s, 2H), 4.73 (q, J = 8.5 Hz, 2H), 1.06−0.98 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 156.6, 129.9, 125.5, 123.8 (q, J = 275.1 Hz, 1C), 122.9, 122.8, 121.2, 110.7, 100.6, 93.1, 90.1, 61.8, 59.9 (q, J = 35 Hz, 1C), 18.6, 11.2; IR (film) 3267, 2950, 2873, 2178, 1684, 1552, 1460, 1282, 1166, 1104, 1022 cm^{-1}; HRMS (ES) m/z = 476.1845 calcd for $C_{23}H_{30}F_3NO_3SiNa$ $[MNa]^+$, found 476.1849.

*Benzyl 2-((3-(Triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4v**).* Following the general procedure, compound **4v** was obtained as a white resin in 16% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (bs, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.40−7.31 (m, 3H), 7.21−7.15 (m, 3H), 5.40 (s, 2H), 5.09 (s, 2H), 1.05−0.95 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 155.7, 137.0, 129.7, 128.7, 128.2, 128.1, 125.9, 122.4, 122.3, 121.5, 110.5, 101.2, 92.4, 91.7, 65.6, 62.1, 18.6, 11.2; IR (film) 3259, 2946, 2865, 2173, 1670, 1550, 1461, 1343, 1203, 1090, 1021 cm^{-1}; HRMS (ES) m/z = 484.2284 calcd for $C_{28}H_{35}NO_3NaSi$ $[MNa]^+$, found 484.2292.

*Ethyl 7-Methyl-2-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4w**).* Following the general procedure, compound **4w** was obtained as a white solid in 18% yield: mp 104−105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (bs, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.13 (dd, J = 7.8, 5.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 5.14 (s, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H), 1.08−0.93 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 155.3, 129.1, 125.7, 123.2, 122.4, 119.6, 119.2, 101.4, 92.7, 91.8, 62.4, 59.8, 18.7, 16.5, 14.8, 11.4; IR (film) 3229, 2943, 2866, 2178, 1668, 1552, 1468, 1313, 1274, 1213, 1097, 1020 cm^{-1}; HRMS (ES) m/z = 436.2284 calcd for $C_{24}H_{35}NO_3SiNa$ $[MNa]^+$, found 436.2271.

*Ethyl 5-Methoxy-2-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4x**).* Following the general procedure, compound **4x** was obtained as a white solid in 12% yield: mp 109−111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (bs, 1H), 7.59 (d, J = 2.5 Hz, 1H), 7.08 (d, J = 8.5 Hz, 1H), 6.81 (dd, J = 8.5, 2.5 Hz, 1H), 5.08 (s, 2H), 4.39 (q, J = 7.5 Hz, 2H), 3.87 (s, 3H), 1.44 (t, J = 7.5 Hz, 3H), 1.08−0.97 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 155.9, 155.6, 127.0, 124.4, 111.7, 111.3, 104.2, 101.3, 92.2, 92.1, 62.1, 59.8, 55.9, 18.7, 14.8, 11.1; IR (film) 3205, 2943, 2866, 2178, 1653, 1483, 1352, 1282, 1205, 1166, 1035 cm^{-1}; HRMS (ES) m/z = 452.2233 calcd for $C_{24}H_{35}NO_4SiNa$ $[MNa]^+$, found 452.2234.

*Ethyl 7-Methoxy-2-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4y**).* Following the general procedure, compound **4y** was obtained as a colorless oil in 31% yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (bs, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.13 (dd, J = 8.5, 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.09 (s, 2H), 4.39 (q, J = 7.0 Hz, 2H), 3.91 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H), 1.10−0.94 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 154.6, 145.1, 126.9, 122.3, 119.5, 113.7, 102.5, 100.9, 92.2, 92.0, 61.8, 59.5, 55.1, 18.8, 14.5, 10.9; IR (film) 3244, 2943, 2866, 2178, 1676, 1552, 1468, 1367, 1282, 1213, 1097, 1020 cm^{-1}; HRMS (ES) m/z = 452.2233 calcd for $C_{24}H_{35}NO_4SiNa$ $[MNa]^+$, found 452.2234.

*Ethyl 5-Bromo-2-((3-(triisopropylsilyl)prop-2-yn-1-yl)oxy)-1H-indole-3-carboxylate (**4z**).* Following the general procedure, compound **4z** was obtained as a light gray solid in 28% yield: mp 119−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (bs, 1H), 8.16 (d, J = 2.0 Hz, 1H), 7.26 (dd, J = 8.5, 2.0 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 5.10 (s, 2H), 4.40 (q, J = 7.0 Hz, 2H), 1.44 (t, J = 7 Hz, 3H), 1.07−0.93 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 155.9, 128.4, 127.7, 125.2, 124.0, 115.7, 112.1, 100.7, 92.6, 91.7, 61.9, 60.1, 18.6, 14.7, 11.2; IR (film) 3229, 2943, 2866, 2178, 1668, 1552, 1468, 1328, 1251, 1205, 1097, 1027 cm^{-1}; HRMS (ES) m/z = 500.1233 calcd for $C_{23}H_{32}BrNO_3SiNa$ $[MNa]^+$, found 500.1226.

General Procedure for the Racemic Claisen Rearrangement. *3-Allyl-2-oxoindoline-3-carbonitrile (**5a**).* To a solution of **3a** (0.015 g, 0.081 mmol) in CH_2Cl_2 (0.50 mL) was added SiO_2 (0.02 g, 0.32 mmol). The resulting solution was allowed to stir at room temperature until the starting material was consumed (2 days). The reaction mixture was filtered to remove the SiO_2 and then concentrated under vacuum to afford the rearranged product **5a** (0.014 g, 0.075 mmol) as a white resin in 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (bs, 1H), 7.41−7.35 (m, 2H), 7.17 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 5.77−5.69 (m, 1H), 5.24 (d, J = 10.5 Hz, 1H), 5.21 (d, J = 17.2 Hz, 1H), 3.04 (dd, J = 6.4, 13.6 Hz, 1H), 2.82 (dd, J = 8.1, 13.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 140.0, 130.4, 128.8, 125.3, 124.7, 123.7, 122.2, 116.4, 110.9, 46.9, 41.1, 22.7; IR (film) 3262, 2922, 2247, 1725, 1621, 1475 cm^{-1}; HRMS (CI) m/z = 199.0871 calcd for $C_{12}H_{10}N_2O$ $[MH]^+$, found 199.0866; CSP HPLC (Chiralpak AD, 1.0 mL/min, 95:5 hexanes:*i*-PrOH): t_R(*ent*-**1**) = 15.5 min, t_R(*ent*-**2**) = 18.3 min.

*3-(2-Methylallyl)-2-oxoindoline-3-carbonitrile (**5b**).* Following the general procedure, **5b** (0.011 g, 0.052 mmol) was obtained as a white resin in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (bs, 1H), 7.34−7.25 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 4.86 (t, J = 1.5 Hz, 1H), 4.68 (s, 1H), 2.92 (d, J = 13.5 Hz, 1H), 2.79 (d, J = 13.5 Hz, 1H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 140.6, 137.6, 130.2, 125.0, 123.2, 117.9, 117.2, 110.7, 64.4, 46.6, 44.0, 23.4; IR (film) 3250, 2926, 2856, 2227, 1729, 1621, 1475 cm^{-1}; HRMS (CI): m/z = 213.1028 calcd for $C_{13}H_{13}N_2O$ $[MH]^+$, found 213.1041; CSP HPLC (Chiralpak AD, 1.0 mL/min, 95:5 hexanes:*i*-PrOH): t_R(*ent*-**1**) = 13.9 min, t_R(*ent*-**2**) = 16.1 min.

*3-(2-Methylallyl)indolin-2-one (**6**).* Following the general procedure, compound **6** was obtained as a white resin: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (bs, 1H), 7.23 (m, 2H), 7.00 (dt, J = 0.5, 7.5 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 4.91 (s, 1H), 4.79 (s, 1H), 3.60 (dd, J = 4.5, 9.5 Hz, 1H), 2.83 (dd, J = 4.0, 14.5 Hz, 1H), 2.41 (dd, J = 10.0, 14.0 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.7, 141.8, 141.1, 129.5, 127.9, 124.9, 122.1, 113.6, 109.5, 43.9, 38.9, 22.2; IR (film) 3213, 3082, 2935, 1707, 1622, 1468, 1336, 1228 cm^{-1}; HRMS (ES) m/z = 210.0895 calcd for $C_{12}H_{13}NONa$ $[MNa]^+$, found 210.0879.

Typical Experimental Procedure for the Asymmetric Meerwein−Eschenmoser Claisen Rearrangement. *(S)-Methyl 3-(2-Methylallyl)-2-oxoindoline-3-carboxylate (**5c**).* To a solution of Pd(*t*-BuPHOX)Cl_2 (0.004 g, 0.008 mmol) in CH_2Cl_2 (0.5 mL) was added, via cannula, a solution of $AgSbF_6$ (0.005 g, 0.014 mmol) in CH_2Cl_2 (0.50 mL). The resulting solution was stirred in the absence of light for 3 h, and filtered through a PTFE filter to remove the precipitated AgCl. The resulting clear yellow solution was cooled to 0 °C, followed by addition of **3c** (0.009 g, 0.038 mmol) in CH_2Cl_2 (1.0 mL) via cannula. The reaction mixture was stirred at 0 °C until the starting material was completely consumed, as determined by TLC. Filtration through a plug of SiO_2 (5 mm × 2 cm) with 25% EtOAc/hexanes and concentration of the solution under vacuum yielded **5c** (0.008 g, 0.033 mmol) in 89% yield as a white resin: $[\alpha]^{23}_D$ +79.25 (*c* 0.40, 89% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (bs, 1H), 7.27−7.26 (m, 2H), 7.05 (t, J = 7.9, 1H), 6.94 (d, J = 7.7 Hz, 1H), 4.65 (s, 1H), 4.63 (s, 1H), 3.69 (s, 3H), 3.06 (s, 2H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 169.6, 141.3, 139.4, 129.1, 128.3, 124.4, 122.6, 115.7, 110.1, 59.9, 53.1, 41.2, 23.6; IR (film) 3250, 2953, 1741, 1702, 1621, 1475 cm^{-1}; HRMS (CI) m/z = 246.1130 calcd for $C_{14}H_{16}NO_3$ $[MH]^+$, found 246.1136; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 16.5 min, $t_R(S)$ = 20.3 min.

*(R)-Ethyl 3-(2-Methylallyl)-2-oxoindoline-3-carboxylate (**5d**).* Following the general procedure, using Cu(Ind-BOX **L7**)$(SbF_6)_2$ catalyst, compound **5d** was obtained as a white resin in 100% yield: $[\alpha]^{23}_D$ −48.44 (*c* 0.45, 79% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 7.28−7.19 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 4.67 (d, J = 16.6 Hz, 2H), 4.17 (m, 2H), 3.07 (d, J = 16.8 Hz, 1H), 3.03 (d, J = 16.8 Hz, 1H), 1.42 (s, 3H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 169.1, 141.2, 139.6, 129.0, 128.5, 124.4, 122.6, 115.6, 109.8, 62.1, 59.9, 41.0, 23.7, 11.9; IR (film) 3250, 2980, 2922, 2853, 1718, 1621, 1475 cm^{-1}; HRMS (ES) m/z = 282.1106 calcd for $C_{15}H_{17}NO_3Na$ $[MNa]^+$, found 282.1115; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 13.0 min, $t_R(S)$ = 20.0 min.

*(R)-Benzyl 3-(2-Methylallyl)-2-oxoindoline-3-carboxylate (**5e**).* Following the general procedure, using Cu(Ind-BOX **L7**)$(SbF_6)_2$ catalyst, compound **5e** was obtained as a pale yellow resin in 73% yield: $[\alpha]^{23}_D$ −22.00 (*c* 0.55, 73% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (bs, 1H), 7.25−7.13 (m, 7H), 7.02 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 5.12 (s, 2H), 4.66 (s, 1H), 4.62 (s, 1H), 3.07 (d, J = 19.5 Hz, 1H), 3.03 (d, J = 19.5 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 168.9, 141.3, 139.4, 135.3, 129.1, 128.4, 128.2, 128.1, 127.4, 124.4, 122.6, 115.7, 110.0, 67.3, 60.0, 40.9, 23.7; IR (film) 3242, 2926, 2856, 1718, 1621, 1471 cm^{-1}; HRMS (ES) m/z = 344.1263 calcd for $C_{20}H_{19}NO_3Na$ $[MNa]^+$, found 344.1264; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 17.8 min, $t_R(S)$ = 27.8 min.

*(R)-Isopropyl 3-(2-Methylallyl)-2-oxoindoline-3-carboxylate (**5f**).* Following the general procedure, using Cu(Ind-BOX **L7**)$(SbF_6)_2$ catalyst, compound **5f** was obtained as white resin in 100% yield: $[\alpha]^{23}_D$ −22.00 (*c* 0.2, 65% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (bs, 1H), 7.25−7.21 (m, 2H), 7.03 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 5.02−4.97 (m, 1H), 4.65 (s, 1H), 4.62 (s, 1H), 3.04 (d, J = 18.5 Hz, 1H), 3.01 (d, J = 18.5 Hz, 1H), 1.41 (s, 3H), 1.21 (d, J = 6.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 168.5, 141.2, 139.7, 128.9, 128.6, 124.2, 122.5, 115.5, 109.7, 69.7, 60.1, 40.9, 23.7, 21.4, 21.3; IR (film) 3250, 2984, 1733, 1621, 1475 cm^{-1}; HRMS (ES) m/z = 296.1263 calcd for $C_{16}H_{19}NO_3Na$ $[MNa]^+$, found 296.1264; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 7.7 min, $t_R(S)$ = 11.8 min.

*(S)-tert-Butyl 3-(2-Methylallyl)-2-oxoindoline-3-carboxylate (**5g**).* Following the general procedure, using Pd(BINAP)$(SbF_6)_2$ catalyst, compound **5g** was obtained as a white resin in 100% yield: $[\alpha]^{23}_D$ +66.89 (*c* 0.90, 85% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (bs, 1H), 7.23 (m, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.7 Hz, 1H), 4.61 (s, 2H), 3.04 (d, J = 13.9 Hz, 1H), 2.97 (d, J = 13.9 Hz, 1H), 1.38 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) 175.6, 167.9, 141.1, 139.9, 129.0, 128.8, 124.1, 122.4, 115.3, 109.6, 82.5, 60.7, 40.8, 27.7, 23.7; IR (film) 3262, 2980, 2930, 1733, 1621, 1475 cm^{-1}; HRMS (ES) m/z = 310.1419 calcd for $C_{17}H_{21}NO_3Na$ $[MNa]^+$, found 310.1416; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 6.1 min, $t_R(S)$ = 9.2 min.

*(S)-tert-Butyl 3-Allyl-2-oxoindoline-3-carboxylate (**5i**).* Following the general procedure, using Pd(BINAP)$(SbF_6)_2$ catalyst, compound **5i** was obtained as a white resin in 60% yield: $[\alpha]^{23}_D$ +106.5 (*c* 0.30, 89% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (bs, 1H), 7.26−7.23 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 5.50 (m, 1H), 5.06 (d, J = 17.0 Hz, 1H), 4.94 (d, J = 10.1 Hz, 1H), 2.98−2.90 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 167.7, 141.2, 131.2, 128.8, 128.7, 123.7, 122.6, 119.5, 109.7, 82.5, 60.5, 38.2, 27.7; IR (film) 3252, 3090, 2981, 2927, 1722, 1622, 1475, 1251, 1159 cm^{-1}; HRMS (CI) m/z = 274.1443 calcd for $C_{16}H_{20}NO_3$ $[MH]^+$, found 274.1459; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 7.2 min, $t_R(S)$ = 8.8 min.

*(S)-Methyl 3-Allyl-2-oxoindoline-3-carboxylate (**5j**).* Following the general procedure, compound **5j** was obtained as a white resin in 100% yield: $[\alpha]^{23}_D$ +51.30 (*c* 0.50, 83% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (bs, 1H), 7.28−7.25 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.9 Hz, 1H), 5.49−5.41 (m, 1H), 5.08 (dd, J = 1.2, 17.0 Hz, 1H), 4.97 (d, J = 10.1 Hz, 1H), 3.71 (s, 3H), 3.04 (dd, J = 6.7, 13.8 Hz, 1H), 2.97 (dd, J = 7.9, 13.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 169.3, 141.1, 130.8, 129.1, 128.0, 124.0, 122.8, 120.0, 110.0, 59.6, 53.1, 38.4; IR (film) 3252, 3090, 2958, 2858, 1715, 1622, 1475, 1437, 1336, 1236 cm^{-1}; HRMS (ES) m/z = 254.0793 calcd for $C_{13}H_{13}NO_3Na$ $[MNa]^+$, found 254.0791; CSP HPLC (Chiralpak AD, 1.0 mL/min, 95.5 hexanes:*i*-PrOH): $t_R(S)$ = 18.4 min, $t_R(R)$ = 20.6 min.

*(S)-Methyl 3-(2-Methylenebutyl)-2-oxoindoline-3-carboxylate (**5k**).* Following the general procedure, compound **5k** was obtained as a white resin in 82% yield: $[\alpha]^{23}_D$ +59.00 (*c* 0.45, 92% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (bs, 1H), 7.28−7.23 (m, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 7.7 Hz, 1H), 4.66 (t, J = 1.4 Hz, 1H), 4.64 (s, 1H), 3.69 (s, 3H), 3.08 (d, J = 16.7 Hz, 1H),

3.05 (d, J = 16.8 Hz, 1H), 1.68 (q, J = 7.4 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 169.7, 145.0, 141.3, 129.1, 128.3, 124.4, 122.6, 113.2, 110.0, 60.0, 53.1, 39.5, 29.7, 12.3; IR (film) 3275, 2927, 2858, 1715, 1622, 1444, 1236 cm^{-1}; HRMS (CI) m/z = 260.1287 calcd for $C_{15}H_{18}NO_3$ $[MH]^+$, found 260.1287; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 13.6 min, $t_R(S)$ = 15.8 min.

*(S)-Isopropyl 3-Allyl-2-oxoindoline-3-carboxylate (**5l**).* Following the general procedure, using Pd(BINAP)$(SbF_6)_2$ catalyst, compound **5l** was obtained as a white resin in 91% yield: $[\alpha]^{23}_D$ +44.20 (c 0.50, 74% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (bs, 1H), 7.25−7.23 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 5.50−5.41 (m, 1H), 5.07 (d, J = 17.0 Hz, 1H), 5.02 (m, 1H), 5.00 (d, J = 10.1 Hz, 1H), 3.01 (dd, J = 6.7, 13.8 Hz, 1H), 2.95 (dd, J = 7.8, 13.8, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 168.3, 141.1, 131.0, 128.9, 128.4, 123.9, 122.7, 119.8, 109.8, 69.7, 59.8, 38.3, 21.5, 21.3; IR (film) 3252, 3090, 2981, 2927, 2858, 1722, 1622, 1468, 1236 cm^{-1}; HRMS (ES) m/z = 282.1106 calcd for $C_{15}H_{17}NO_3Na$ $[MNa]^+$, found 282.1091; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 11.8 min, $t_R(S)$ = 14.9 min.

*(S)-Benzyl 3-Allyl-2-oxoindoline-3-carboxylate (**5m**).* Following the general procedure, using Pd(BINAP)$(SbF_6)_2$ catalyst, compound **5m** was obtained as a white resin in 74% yield: $[\alpha]^{23}_D$ +51.38 (c 0.40, 72% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (bs, 1H), 7.28−7.22 (m, 5H), 7.17−7.16 (m, 2H), 7.05 (td, J = 7.5, 0.9 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 5.50−5.41 (m, 1H), 5.16 (d, J = 15.5 Hz, 1H), 5.14 (d, J = 15.6 Hz, 1H), 5.08 (dd, J = 1.4, 16.9 Hz, 1H), 4.96 (dd, J = 1.7, 10.1 Hz, 1H), 3.05 (dd, J = 6.7, 13.9 Hz, 1H), 2.99 (dd, J = 7.9, 13.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 168.6, 141.2, 135.3, 130.8, 129.1, 128.4, 128.1, 128.0, 127.4, 124.0, 122.7, 120.0, 110.0, 67.3, 59.7, 38.2; IR (film) 3259, 3066, 2927, 1715, 1622, 1468, 1336 cm^{-1}; HRMS (ES) m/z = 308.1263 calcd for $C_{19}H_{18}NO_3$ $[MH]^+$, found 308.1273; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 20.7 min, $t_R(S)$ = 29.7 min.

*(S)-Methyl 5-Methoxy-3-(2-methylallyl)-2-oxoindoline-3-carboxylate (**5n**).* Following the general procedure, compound **5n** was obtained as a white resin in 60% yield: $[\alpha]^{23}_D$ +40.83 (c 0.30, 91% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (bs, 1H), 6.88 (s, 1H), 6.80 (m, 2H), 4.70 (s, 1H), 4.65 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 3.05 (d, J = 19.5 Hz, 1H), 3.02 (d, J = 19.4 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 169.6, 155.9, 139.4, 134.5, 129.5, 115.7, 113.9, 111.3, 110.3, 60.2, 55.8, 53.2, 41.2, 23.7; IR (film) 3259, 2927, 2858, 1715, 1607, 1491, 1444, 1236 cm^{-1}; HRMS (ES) m/z = 276.1236 calcd for $C_{15}H_{18}NO_4$ $[MH]^+$, found 276.1248; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 20.7 min, $t_R(S)$ = 23.8 min.

*(S)-Methyl 5-Bromo-3-(2-methylallyl)-2-oxoindoline-3-carboxylate (**5o**).* Following the general procedure, compound **5o** was obtained as a white resin in 82% yield: $[\alpha]^{23}_D$ +38.67 (c 0.45, 87% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 7.40 (m, 2H), 6.80 (d, J = 8.7 Hz, 1H), 4.70 (s, 1H), 4.63 (s, 1H), 3.72 (s, 3H), 3.05 (d, J = 19.8 Hz, 1H), 3.02 (d, J = 19.8 Hz, 1H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 168.9, 140.2, 139.0, 132.0, 130.2, 127.7, 116.1, 115.2, 111.4, 59.9, 53.4, 41.2, 23.7; IR (film) 3252, 2958, 2858, 1738, 1614, 1475, 1228 cm^{-1}; HRMS (ES) m/z = 324.0235 calcd for $C_{14}H_{15}BrNO_3$ $[MH]^+$, found 324.0240; CSP HPLC (Chiralpak AS, 1.0 mL/min, 92.5:7.5 hexanes:*i*-PrOH): $t_R(R)$ = 15.1 min, $t_R(S)$ = 25.5 min.

*(S)-Methyl 7-Methoxy-3-(2-methylallyl)-2-oxoindoline-3-carboxylate (**5p**).* Following the general procedure, compound **5p** was obtained as a white resin in 95% yield: $[\alpha]^{23}_D$ +82.78 (c 0.450, 85% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (bs, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 4.67 (s, 1H), 4.64 (s, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.04 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 169.6, 143.8, 139.5, 130.1, 128.9, 123.1, 116.6, 115.6, 111.3, 60.5, 55.6, 53.1, 41.0, 23.7; IR (film) 3229, 3090, 2958, 2850, 1715, 1622, 1498, 1228 cm^{-1}; HRMS (ES) m/z = 298.1055 calcd for $C_{15}H_{17}NO_4Na$ $[MNa]^+$, found 298.1057; CSP HPLC (Chiralpak AS, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 21.3 min, $t_R(S)$ = 27.0 min.

*(S)-Methyl 3-(2-(Deuteromethylene)butyl)-2-oxoindoline-3-carboxylate (**5q**).* Following the general procedure, compound **5q** was obtained as a white resin in 80% yield: $[\alpha]^{23}_D$ +43.13 (c 0.40, 92% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (bs, 1H), 7.32−7.24 (m, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 4.63 (s, 0.5 H, *Z*-deutero), 4.62 (s, 0.5 H, *E*-deutero), 3.70 (s, 3H), 3.07 (d, J = 16.3 Hz, 1H), 3.04 (d, J = 16.2 Hz, 1H), 1.68 (q, J = 7.3 Hz, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 169.9, 145.1, 141.4, 129.3, 128.6, 124.7, 122.8, 113.1 (t, J^1_{CD} = 23.6 Hz), 110.1, 60.2, 53.4, 39.7, 29.9, 12.5; IR (film) 3252, 3090, 2981, 2935, 1715, 1622, 1475, 1375, 1251, 1159 cm^{-1}; HRMS (ES) m/z = 283.1169 calcd for $C_{15}H_{16}DNO_3Na$ $[MNa]^+$, found 283.1173; CSP HPLC (Chiralpak OD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(R)$ = 13.6 min, $t_R(S)$ = 15.8 min.

General Procedure for Preparing Catalysts. *Pd[(R)-BINAP](SbF$_6$)$_2$.* To a flask of Pd[(*R*)-BINAP]Cl_2 (4 mg, 0.005 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of $AgSbF_6$ (3.3 mg, 0.0095 mmol) in CH_2Cl_2 (0.5 mL). The resulting solution was stirred in the absence of light for 3 h, and filtered through a PTFE filter to remove the precipitated AgCl. The resulting clear yellow solution was concentrated to afford Pd[(*R*)-BINAP]$(SbF_6)_2$ as a yellow solid in 100% yield.

Pd[(S)-t-BuPHOX](SbF$_6$)$_2$. To a flask of Pd[(*S*)-*t*-BuPHOX]Cl_2 (2.8 mg, 0.005 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of $AgSbF_6$ (3.3 mg, 0.0095 mmol) in CH_2Cl_2 (0.5 mL). The resulting solution was stirred in the absence of light for 3 h, and filtered through a PTFE filter to remove the precipitated AgCl. The resulting clear yellow solution was concentrated to afford Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ as a light yellow solid in 100% yield.

Typical Procedure for the Asymmetric Saucy−Marbet Claisen Rearrangement. *(R)-Ethyl 3-(1-(tert-Butyldimethylsilyl)-propa-1,2-dien-1-yl)-5-methoxy-2-oxoindoline-3-carboxylate (**8p**).* To a solution of the Pd[(*R*)-BINAP]$(SbF_6)_2$ complex (12 mg, 0.01 mmol, 20 mol %) in C_6H_5Cl (1 mL) was added a solution of **4p** (19.4 mg, 0.05 mmol) in toluene (1 mL) at ambient temperature. The resulting solution was stirred in the absence of light at room temperature until the starting material was completely consumed, as determined by TLC. Filtration through a plug of SiO_2 (5 mm × 2 cm) with ethyl ether, concentration of the solution, and purification by column chromatography using 50% ethyl ether/hexane afforded **8p** as a white resin in 82% yield: mp 136−137 °C; $[\alpha]^{23}_D$ +158.18 (c 0.17, 93% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (bs, 1H), 6.89 (d, J = 2.0 Hz, 1H), 6.79−6.74 (m, 2H), 4.60 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.22 (qd, J = 7.5, 11.0 Hz, 1H), 4.13 (qd, J = 7.5, 11.0 Hz, 1H), 3.78 (s, 3H), 1.23 (t, J = 7.5 Hz, 3H), 0.92 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.5, 174.8, 168.8, 155.7, 134.3, 129.7, 114.5, 113.2, 110.2, 100.2, 93.6, 74.1, 62.4, 56.1, 27.6, 19.4, 14.2, −4.0, −4.2; IR (film) 3252, 2958, 2858, 1931, 1746, 1622, 1468, 1259, 1089, 1027 cm^{-1}; HRMS (ES) m/z = 386.1788 calcd for $C_{21}H_{28}NO_4Si$ $[M - H]^-$, found 386.1776; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 14.0 min, $t_R(2)$ = 21.6 min.

*(S)-tert-Butyl 2-Oxo-3-(propa-1,2-dien-1-yl)indoline-3-carboxylate (**8a**).* Following the general procedure, using Pd(*t*-BuPHOX)$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent, compound **8a** was obtained as a white solid in 100% yield: mp 140−141 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (bs, 1H), 7.31−7.24 (m, 2H) 7.04 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 5.79 (t, J = 6.5 Hz, 1H) 4.87 (dd, 11.5, 6.5 Hz, 1H), 4.77 (dd, 11.5, 6.5 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 175.3, 167.1, 141.3, 129.2, 128.5, 125.0, 122.7, 110.3, 89.2, 83.3, 79.3, 60.2, 27.9; IR (film) 3221, 2927, 2858, 1962, 1668, 1738, 1622, 1468, 1259, 1159 cm^{-1}; HRMS (ES) m/z = 294.1106 calcd for $C_{16}H_{17}NO_3Na$ $[MNa]^+$, found 294.1100; CSP HPLC (Chiralpak AS, 1.0 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 18.3 min, $t_R(2)$ = 26.8 min.

*(S)-tert-Butyl 3-(Buta-2,3-dien-2-yl)-2-oxoindoline-3-carboxylate (**8b**).* Following the general procedure, using Pd(*t*-BuPHOX)$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent at 0 °C, compound **8b** was

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obtained as a white solid in 100% yield: mp 119−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (bs, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.24 (td, J = 7.5, 1.0 Hz, 1H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 4.77 (dq, J = 10.5, 3.0 Hz, 1H), 4.59 (dq, J = 10.5, 3.0 Hz, 1H), 1.90 (t, J = 3 Hz, 3H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.8, 175.3, 166.9, 141.3, 129.2, 128.0, 125.9, 122.4, 110.2, 97.6, 83.1, 77.8, 63.2, 27.9, 15.6; IR (film) 3213, 2927, 2858, 1962, 1738, 1622, 1475, 1259 cm^{-1}; HRMS (ES) m/z = 308.1263 calcd for $C_{17}H_{19}NO_3Na$ [MNa]$^+$, found 308.1263; CSP HPLC (Chiralpak AS, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(1)$ = 17.6 min, $t_R(2)$ = 21.9 min.

*(S)-Methyl 2-Oxo-3-(propa-1,2-dien-1-yl)indoline-3-carboxylate (**8c**).* Following the general procedure, using Pd[(*S*)-*t*-BuPHOX]-$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent at 0 °C, compound **8c** was obtained as a white solid in 100% yield: mp 128−129 °C; $[\alpha]^{23}_D$ +2.85 (*c* 0.175, 14% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (bs, 1H), 7.30−7.26 (m, 2H) 7.06 (td, J = 7.5, 1.0 Hz, 1H), 6.95 (d, J = 7.5, 1H), 5.82 (t, J = 6.5 Hz, 1H), 4.91 (dd, J = 11.5, 6.5 Hz, 1H), 4.79 (dd, J = 11.5, 6.5 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 174.9, 168.8, 141.1, 129.5, 127.8, 125.4, 122.9, 110.5, 83.1, 79.7, 59.2, 53.7; IR (film) 3252, 2935, 2889, 1962, 1746, 1475, 1244, 1189 cm^{-1}; HRMS (ES) m/z = 230.0817 calcd for $C_{13}H_{12}NO_3$ [MH]$^+$, found 230.0818; CSP HPLC (Chiralpak AD, 0.75 mL/min, 92.5:7.5 hexanes:*i*-PrOH): $t_R(1)$ = 20.5 min, $t_R(2)$ = 22.5 min.

*(S)-Methyl 3-(Buta-2,3-dien-2-yl)-2-oxoindoline-3-carboxylate (**8d**).* Following the general procedure, using Pd[(*S*)-*t*-BuPHOX]-$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent at 0 °C, compound **8d** was obtained as a white solid in 100% yield: $[\alpha]^{23}_D$ +26.67 (*c* 0.075, 45% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (bs, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.26 (td, J = 7.5, 1.5 Hz, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 4.80 (dq, J = 11.0, 3.0 Hz, 1H), 4.64 (dd, J = 11.5, 3.0 Hz, 1H), 3.75 (s, 3H), 1.89 (t, J = 3.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.9, 173.9, 168.5, 140.8, 129.5, 127.6, 126.4, 122.8, 109.9, 97.5, 78.1, 62.4, 53.5, 15.5; IR (film) 3252, 3066, 2935, 2858, 1962, 1738, 1622, 1475, 1437, 1236, 1189 cm^{-1}; HRMS (ES) m/z = 244.0974 calcd for $C_{14}H_{14}NO_3$ [MH]$^+$, found 244.0962; CSP HPLC (Chiralpak AD, 1.0 mL/min, 96.5:3.5 hexanes:*i*-PrOH): $t_R(1)$ = 23.7 min, $t_R(2)$ = 26.7 min.

*(S)-Methyl 2-Oxo-3-(1-phenylpropa-1,2-dien-1-yl)indoline-3-carboxylate (**8e**).* Following the general procedure, the reaction with 5 mol % Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent was conducted at −78 °C and slowly warmed to −15 °C. Compound **8e** was obtained as a white solid in 96% yield: mp 149−150 °C; $[\alpha]^{23}_D$ +98.57 (*c* 0.14, 78% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.21 (bs, 1H), 7.42−7.39 (m, 2H), 7.36 (d, J = 7.5, Hz, 1H), 7.26−7.17 (m, 4H), 7.02 (td, J = 7.6, 1.0 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 5.11 (d, J = 12.5 Hz, 1H), 5.02 (d, J = 12.5 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.0, 175.0, 168.6, 141.2, 133.9, 129.6, 128.4, 127.96, 127.91, 127.5, 126.3, 122.9, 110.5, 104.9, 80.3, 62.8, 53.5; IR (film) 3283, 3073, 2934, 1941, 1740, 1612, 1477, 1236, 1029 cm^{-1}; HRMS (ES) m/z = 328.0950 calcd for $C_{19}H_{15}NO_3Na$ [MNa]$^+$, found 328.0944; CSP HPLC (Chiralpak IA, 1.0 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 16.47 min, $t_R(2)$ = 26.69 min.

*(S)-Methyl 2-Oxo-3-(1-(o-tolyl)propa-1,2-dien-1-yl)indoline-3-carboxylate (**8f**).* Following the general procedure, the reaction with 5 mol % Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent was conducted at −78 °C and slowly warmed to −15 °C. Compound **8f** was obtained as a white solid in 95% yield: mp 140−141 °C ; $[\alpha]^{23}_D$ +58.50 (*c* 0.4, 98% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (bs, 1H), 7.22−7.18 (m, 3H), 7.10−7.09 (m, 2H), 7.03−7.00 (m, 1H), 6.95 (t, J = 7.5, Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 4.98 (d, J = 12.0 Hz, 1H), 4.95 (d, J = 12.0 Hz, 1H), 3.71 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 174.4, 168.3, 141.1, 137.7, 133.5, 130.4, 129.5, 128.7, 127.9, 127.5, 126.4, 125.8, 122.7, 110.2, 101.2, 78.4, 63.6, 53.4, 20.2; IR (film) 3268, 2954, 1949, 1742, 1613, 1477, 1235, 1106 cm^{-1}; HRMS (ES) m/z = 342.1106 calcd for $C_{20}H_{17}NO_3Na$ [MNa]$^+$, found 342.1105; CSP HPLC (Chiralpak IA, 1.0 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 10.65 min, $t_R(2)$ = 14.33 min.

*(S)-Methyl 3-(1-(2-Bromophenyl)propa-1,2-dien-1-yl)-2-oxoindoline-3-carboxylate (**8g**).* Following the general procedure, the reaction with 5 mol % Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent was conducted at −78 °C and slowly warmed to −15 °C. Compound **8g** was obtained as a white resin in 93% yield: $[\alpha]^{23}_D$ +44.44 (*c* 0.315, 96% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (bs, 1H), 7.55 (dd, J = 7.7, 1.6 Hz, 1H), 7.48 (dd, J = 8.0, 1.2 Hz, 1H), 7.26−7.14 (m, 3H), 7.06 (td, J = 7.5, 1.7 Hz, 1H), 6.94 (t, J = 7.7 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 5.07 (d, J = 12.0 Hz, 1H), 5.02 (d, J = 12.0 Hz, 1H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 174.7, 168.4, 141.4, 135.2, 132.9, 130.6, 129.6, 129.4, 127.4, 127.1, 126.5, 125.9, 122.6, 110.3, 101.9, 79.8, 62.5, 53.4; IR (film) 3272, 3062, 2954, 1951, 1742, 1614, 1474, 1235, 1029 cm^{-1}; HRMS (ES) m/z = 406.0055 calcd for $C_{19}H_{14}NO_3NaBr$ [MNa]$^+$, found 406.0052; CSP HPLC (Chiralpak IA, 1.0 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 15.07 min, $t_R(2)$ = 19.92 min.

*(S)-Methyl 3-(1-(Naphthalen-1-yl)propa-1,2-dien-1-yl)-2-oxoindoline-3-carboxylate (**8h**).* Following the general procedure, the reaction with 5 mol % Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent was conducted at −78 °C and slowly warmed to −15 °C. Compound **8h** was obtained as a white solid in 95% yield: decomposed at 197 °C; $[\alpha]^{23}_D$ +59.22 (*c* 0.07, 98% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (bs, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 7.5 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.44−7.37 (m, 3H), 7.30−7.20 (m, 2H), 7.11 (td, J = 7.7, 1.2 Hz, 1H), 6.83 (td, J = 7.7, 1.0 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 5.07 (d, J = 12.0 Hz, 1H), 5.04 (d, J = 12.0 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 174.6, 168.4, 141.1, 133.8, 132.4, 131.7, 129.5, 128.5, 128.3, 127.3, 126.6, 126.4, 126.1, 125.87, 125.86, 125.2, 122.6, 110.3, 100.1, 78.7, 63.9, 53.5; IR (film) 3262, 3061, 2934, 1950, 1740, 1613, 1474, 1235, 1029 cm^{-1}; HRMS (ES) m/z = 378.1106 calcd for $C_{23}H_{17}NO_3Na$ [MNa]$^+$, found 378.1109; CSP HPLC (Chiralpak IA, 1.0 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 14.3 min, $t_R(2)$ = 17.9 min.

*(S)-Methyl 3-(1-(2-Methoxyphenyl)propa-1,2-dien-1-yl)-2-oxoindoline-3-carboxylate (**8i**).* Following the general procedure, the reaction of a mixture of compound **4i** and methylindole-3-carboxylate (1.4:1) with 5 mol % Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent was conducted at −78 °C and slowly warmed to −15 °C. Compound **8i** was obtained as a colorless resin in 90% yield: $[\alpha]^{23}_D$ +14.25 (*c* 0.035, 98% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (bs, 1H), 7.32 (dd, J = 7.5, 1.7 Hz, 1H), 7.17−7.11 (m, 2H), 6.97 (d, J = 7.8 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 6.81−6.76 (m, 2H), 6.55 (d, J = 8.2 Hz, 1H), 5.15 (d, J = 11.5 Hz, 1H), 5.12 (d, J = 12.0 Hz, 1H), 3.73 (s, 3H), 3.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.7, 174.6, 169.0, 156.7, 141.2, 131.2, 129.4, 129.0, 127.4, 126.5, 124.0, 122.0, 120.6, 110.3, 109.2, 100.4, 78.4, 62.6, 54.7, 53.5; IR (film) 3226, 2924, 2857, 1940, 1745, 1617, 1472, 1227, 1024 cm^{-1}; HRMS (ES) m/z = 358.1055 calcd for $C_{20}H_{17}NO_4Na$ [MNa]$^+$, found 358.1063; CSP HPLC (Chiralpak IA, 1.0 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 22.93 min, $t_R(2)$ = 28.84 min.

*(R)-Methyl 2-Oxo-3-(1-(trimethylsilyl)propa-1,2-dien-1-yl)-indoline-3-carboxylate (**8j**).* Following the general procedure, using 100 mol % Pd[(*R*)-BINAP]$(SbF_6)_2$ and CH_2Cl_2 as the solvent at 0 °C, compound **8j** was obtained as a white solid in 90% yield: $[\alpha]^{23}_D$ +48.33 (*c* 0.06, 77% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (bs, 1H), 7.31 (ddd, J = 7.5, 1.0, 0.5 Hz, 1H), 7.26 (td, J = 7.5, 1.0 Hz, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.87 (ddd, J = 7.5, 1.0, 0.5 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 3.72 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.3, 174.9, 169.2, 140.7, 129.5, 128.3, 126.6, 122.6, 109.9, 95.4, 73.3, 61.7, 53.3, −0.1; IR (film) 3275, 2958, 2858, 1931, 1746, 1622, 1475, 1244 cm^{-1}; HRMS (ES) m/z = 324.1032 calcd for $C_{16}H_{19}NO_3NaSi$ [MNa]$^+$, found 324.1021; CSP HPLC (Chiralpak AD, 0.75 mL/min, 92.5:7.5 hexanes:*i*-PrOH): $t_R(1)$ = 12.6 min, $t_R(2)$ = 19.4 min.

*(S)-Methyl 3-(4,4-Dimethylpenta-1,2-dien-3-yl)-2-oxoindoline-3-carboxylate (**8k**).* Following the general procedure, using Pd-(difluoroPHOX)$(SbF_6)_2$ catalyst and CH_2Cl_2 as the solvent at 0 °C, compound **8k** was obtained as a white solid in 100% yield: $[\alpha]^{23}_D$ +51.20 (*c* 0.08, 86% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (bs, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.27 (td, J = 7.5, 1.0 Hz, 1H),

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7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 4.94 (d, J = 11.0 Hz, 1H), 4.81 (d, J = 11.0 Hz, 1H), 3.71 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.7, 174.6, 168.8, 140.5, 129.5, 128.1, 128.0, 122.6, 110.7, 109.8, 79.3, 63.8, 53.5, 34.8, 31.1; IR (film) 3252, 2958, 1946, 1746, 1622, 1475, 1228 cm^{-1}; HRMS (ES) m/z = 308.1263 for $C_{17}H_{19}NO_3Na$ $[MNa]^+$, found 308.1255; CSP HPLC (Chiralpak AD, 0.75 mL/min, 92.5:7.5 hexanes:*i*-PrOH): $t_R(1)$ = 15.4 min, $t_R(2)$ = 24.3 min.

*(S)-Methyl 3-(1-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)propa-1,2-dien-1-yl)-2-oxoindoline-3-carboxylate (**8l**).* Following the general procedure, the reaction with 20 mol % Pd[(*S*)-*t*-BuPHOX]$(SbF_6)_2$ catalyst and MeCN:C_6H_5Cl:CH_2Cl_2 (1:5:5) as the solvent was conducted at 45 °C for 2 days. Compound **8l** was obtained as a white solid in 60% yield: decomposed at 164 °C, $[\alpha]^{23}_D$ +5.73 (*c* 0.035, 70% ee, MeCN); ^{1}H NMR (500 MHz, acetone-d_6) δ 9.59 (bs, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.30 (d, J = 17.5 Hz, 1H), 4.21 (s, 2H), 4.07 (d, J = 17.5 Hz, 1H), 3.66 (s, 3H), 3.13 (s, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 212.4, 174.6, 169.4, 168.3, 167.7, 141.9, 129.3, 128.9, 125.9, 122.0, 109.7, 109.6, 74.5, 63.8, 63.7, 61.4, 52.3, 48.3; IR (film) 3208, 2960, 1944, 1743, 1617, 1464, 1244, 1042 cm^{-1}; HRMS (ES) m/z = 407.1027 calcd for $C_{18}H_{17}N_2O_7NaB$ $[MNa]^+$, found 407.1060; CSP SFC (Chiralpak IA, gradient 20−35% MeOH in CO_2, 2−4 mL/min, 12 MPa): $t_R(1)$ = 7.94 min, $t_R(2)$ = 8.24 min.

*(R)-Methyl 2-Oxo-3-(1-(triethylsilyl)propa-1,2-dien-1-yl)indoline-3-carboxylate (**8n**).* Following the general procedure, compound **8n** was obtained as a white solid in 78% yield: $[\alpha]^{23}_D$ +81.00 (*c* 0.05, 90% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (bs, 1H), 7.34 (dd, J = 7.5, 0.5 Hz, 1H), 7.25 (td, J = 8.0, 1.5 Hz, 1H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 3.72 (s, 3H), 0.89 (t, J = 8.0 Hz, 9H), 0.67−0.54 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 175.8, 169.2, 141.1, 129.4, 128.4, 126.5, 122.5, 110.2, 92.2, 72.9, 62.0, 53.2, 7.5, 4.1; IR (film) 3259, 2958, 2881, 1931, 1738, 1622, 1468, 1328, 1236, 1104 cm^{-1}; HRMS (ES) m/z = 342.1525 calcd for $C_{19}H_{24}NO_3Si$ $[M - H]^-$, found 342.1537; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 14.6 min, $t_R(2)$ = 18.4 min.

*(R)-Methyl 3-(1-(tert-Butyldimethylsilyl)propa-1,2-dien-1-yl)-2-oxoindoline-3-carboxylate (**8m**).* Following the general procedure, compound **8m** was obtained as a white solid in 90% yield: mp 132−133 °C; $[\alpha]^{23}_D$ +128.57 (*c* 0.07, 89% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (bs, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.22 (td, J = 7.5, 1.0 Hz, 1H), 7.01 (td, J = 7.5, 1.0 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 4.56 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 3.69 (s, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.6, 174.6, 169.3, 140.8, 129.4, 128.5, 126.8, 122.6, 109.7, 93.8, 74.0, 62.3, 53.2, 27.6, 19.4, −4.15, −4.18; IR (film) 3252, 2958, 2858, 1931, 1746, 1622, 1468, 1259, 1089, 1027 cm^{-1}; HRMS (ES) m/z = 366.1501 calcd for $C_{19}H_{25}NO_3SiNa$ $[MNa]^+$, found 366.1494; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 6.1 min, $t_R(2)$ = 11.0 min.

*(R)-Ethyl 3-(1-(tert-Butyldimethylsilyl)propa-1,2-dien-1-yl)-7-methyl-2-oxoindoline-3-carboxylate (**8o**).* Following the general procedure using 5 mol % Pd[(*R*)-BINAP]$(SbF_6)_2$ as the catalyst, compound **8o** was obtained as a white solid in 76% yield: mp 135−136 °C; $[\alpha]^{23}_D$ +137.43 (*c* 0.35, 90% ee, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (bs, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.93 (dd, J = 7.5, 7.5 Hz, 1H), 4.55 (d, J = 11.5 Hz, 1H), 4.36 (d, J = 11.5 Hz, 1H), 4.23 (qd, J = 7.0, 11.0 Hz, 1H), 4.11 (qd, J = 7.0, 11.0 Hz, 1H), 2.31 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H), 0.94 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.3, 176.4, 169.2, 140.2, 130.6, 128.2, 123.6, 122.2, 119.7, 93.6, 74.0, 62.8, 62.2, 27.7, 19.4, 16.7, 14.2, −4.0, −4.1; IR (film) 3198, 2935, 2858, 1931, 1715, 1630, 1468, 1228, 1050 cm^{-1}; HRMS (ES) m/z = 370.1838 calcd for $C_{21}H_{28}NO_3Si$ $[M - H]^-$, found 370.1825; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 12.3 min, $t_R(2)$ = 13.8 min.

*(R)-Ethyl 3-(1-(tert-Butyldimethylsilyl)propa-1,2-dien-1-yl)-7-methoxy-2-oxoindoline-3-carboxylate (**8q**).* Following the general procedure, compound **8q** was obtained as a white solid in 91% yield: $[\alpha]^{23}_D$ +172.80 (*c* 0.13, 93% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (bs, 1H), 6.98 (dd, J = 7.5, 7.5 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 6.81 (d, J = 7.5 Hz, 1H), 4.55 (d, J = 12.0 Hz, 1H), 4.37 (d, J = 12.0 Hz, 1H), 4.20 (qd, J = 7.0, 11.0 Hz, 1H), 4.10 (qd, J = 7.0, 11.0 Hz, 1H), 3.86 (s, 3H), 1.22 (t, J = 7.0 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 174.0, 168.9, 143.8, 129.9, 129.2, 122.7, 118.7, 111.5, 100.2, 93.5, 73.9, 62.3, 55.9, 27.6, 19.4, 14.2, −4.1, −4.2; IR (film) 3205, 2935, 2858, 1931, 1722, 1630, 1498, 1282, 1236, 1043 cm^{-1}; HRMS (ES) m/z = 388.1944 calcd for $C_{21}H_{30}NO_4Si$ $[MH]^+$, found 388.1954; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 11.5 min, $t_R(2)$ = 25.2 min.

*(R)-Ethyl 5-Bromo-3-(1-(tert-butyldimethylsilyl)propa-1,2-dien-1-yl)-2-oxoindoline-3-carboxylate (**8r**).* Following the general procedure, compound **8r** was obtained as a white solid in 85% yield: mp 133−134 °C; $[\alpha]^{23}_D$ +130.43 (*c* 0.12, 90% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (bs, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.36 (dd, J = 8.5, 2.0 Hz, 1H) 6.77 (d, J = 8.5 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 12.0 Hz, 1H), 4.23 (qd, J = 7.0, 10.5 Hz, 1H), 4.15 (qd, J = 7.0, 10.5 Hz, 1H), 1.25 (t, J = 7.0 Hz, 3H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.4, 175.4, 168.3, 140.1, 132.2, 130.4, 129.5, 115.0, 111.6, 93.3, 74.5, 62.7, 62.5, 27.5, 19.3, 14.2, −4.1, −4.2; IR (film) 3275, 2935, 2858, 1931, 1738, 1614, 1475, 1298, 1236, 1043 cm^{-1}; HRMS (ES) m/z = 458.0756 calcd for $C_{20}H_{26}BrNO_3SiNa$ $[MNa]^+$, found 458.0779; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 9.2 min, $t_R(2)$ = 22.3 min.

*(R)-4-(tert-Butyldimethylsilyl)-5-methyl-2H-spiro[furan-3,3′-indoline]-2,2′-dione (**9m**).* Following the general procedure, the reaction mixture was stirred at ambient temperature using C_6H_5Cl:$C_6H_5CH_3$ (1:1) as the solvent until the starting material was completely consumed, as determined by TLC (in 84 h). Next, 5 mol % H_2O was added, and the mixture was stirred at 40 °C for 36 h. Filtration through a plug of SiO_2 (5 mm × 2 cm) with ethyl ether, concentration of the solution, and purification by column chromatography using 50% ethyl ether/hexane afforded **9m** as a white resin in 95% yield: $[\alpha]^{23}_D$ +21.66 (*c* 0.06, 86% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (bs, 1H), 7.31−7.26 (m, 1H), 7.06−6.93 (m, 2H), 6.92 (d, J = 7.5 Hz, 1H), 2.27 (s, 3H), 0.82 (s, 9H), −0.07 (s, 3H), −0.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 173.6 163.2, 141.7, 130.2, 127.7, 124.8, 123.4, 110.8, 110.4, 66.5, 27.2, 18.2, 16.4, −4.92, −4.96; IR (film) 3251, 2955, 2870, 1797, 1718, 1624, 1473, 1167, 995 cm^{-1}; HRMS (ES) m/z = 352.1345 calcd for $C_{18}H_{23}NO_3SiNa$ $[MNa]^+$, found 352.1337; CSP HPLC (Chiralpak IA, 1 mL/min, 90:10 hexanes:*i*-PrOH): $t_R(1)$ = 6.3 min, $t_R(2)$ = 10.0 min.

*(R)-5-Methyl-4-(triisopropylsilyl)-2H-spiro[furan-3,3′-indoline]-2,2′-dione (**9s**).* Following the general procedure using 5 mol % H_2O and C_6H_5Cl as the solvent at 40 °C, compound **9s** was obtained as a white solid in 78% yield: mp 202−203 °C; $[\alpha]^{23}_D$ + 112.00 (*c* 0.025, 92% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.93 (bs, 1H), 7.27 (dd, J = 8.0, 1.0 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 7.03 (dd, J = 7.5, 1.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 2.28 (s, 3H), 1.03−1.01 (m, 12H), 0.89−0.87 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 174.1, 163.0, 142.0, 130.3, 127.9, 124.8, 123.3, 110.9, 109.3, 67.6, 19.2, 18.9, 16.6, 12.5; IR (film) 3236, 2950, 2873, 1800, 1715, 1622, 1468, 1220, 1166 cm^{-1}; HRMS (ES) m/z = 370.1839 calcd for $C_{21}H_{28}NO_3Si$ $[M - H]^-$, found 370.1807; CSP HPLC (Chiralpak IA, 1 mL/min, 98:2 hexanes:*i*-PrOH): $t_R(1)$ = 15.3 min, $t_R(2)$ = 39.0 min.

*(R)-5,7′-Dimethyl-4-(triisopropylsilyl)-2H-spiro[furan-3,3′-indoline]-2,2′-dione (**9w**).* Following the general procedure using 5 mol % H_2O and C_6H_5Cl:$C_6H_5CH_3$ (1:1) as the solvent at 40 °C, compound **9w** was obtained as a white solid in 93% yield: mp 239−240 °C; $[\alpha]^{23}_D$ +73.53 (*c* 0.34, 96% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (bs, 1H), 7.09 (d, J = 7.5 Hz, 1H), 6.95 (dd, J = 7.5, 7.5 Hz, 1H), 6.90 (d, J = 7.5 Hz, 1H), 2.27 (s, 6H), 1.05−0.99 (m, 12H), 0.91−0.86 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 173.6, 162.9, 140.5, 131.5, 127.5, 123.3, 122.2, 120.1, 109.3, 66.9, 19.2, 18.9, 16.68, 16.65, 12.6; IR (film) 3198, 2950, 2873, 1800, 1715, 1622, 1468, 1220, 1159, 1027 cm^{-1}; HRMS (ES) m/z = 384.1995 calcd for

$C_{22}H_{30}NO_3Si$ [M − H]$^-$, found 384.1985; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 8.9 min, $t_R(2)$ = 13.4 min.

*(R)-5′-Methoxy-5-methyl-4-(triisopropylsilyl)-2H-spiro[furan-3,3′-indoline]-2,2′-dione (**9x**).* Following the general procedure using 5 mol % H_2O and CH_2Cl_2 as the solvent at 40 °C, compound **9x** was obtained as a white solid in 81% yield: mp 147−148 °C; $[\alpha]^{23}_D$ +60.00 (*c* 0.05, 91% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (bs, 1H), 6.83 (d, *J* = 1.5 Hz, 2H), 6.67 (s, 1H), 3.74 (s, 3H), 2.28 (s, 3H), 1.08−1.00 (m, 12H), 0.94−0.89 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 172.9, 163.2, 156.4, 134.9, 128.9, 115.6, 111.4, 111.2, 109.3, 66.9, 56.0, 19.2, 18.9, 16.7, 12.6; IR (film) 3252, 2950, 2873, 1800, 1715, 1622, 1491, 1298, 1205, 1159, 1081, 1027 cm^{-1}; HRMS (ES) *m*/*z* = 424.1920 calcd for $C_{22}H_{31}NO_4SiNa$ [MNa]$^+$, found 424.1910; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 11.0 min, $t_R(2)$ = 27.0 min.

*(R)-7′-Methoxy-5-methyl-4-(triisopropylsilyl)-2H-spiro[furan-3,3′-indoline]-2,2′-dione (**9y**).* Following the general procedure using 5 mol % H_2O and C_6H_5Cl as the solvent at 40 °C, compound **9y** was obtained as a white solid in 90% yield: mp 237−238 °C; $[\alpha]^{23}_D$ +64.00 (*c* 0.4, 92% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (bs, 1H), 7.00 (dd, *J* = 8.0, 7.5 Hz, 1H), 6.86 (d, *J* = 8.0, Hz, 1H), 6.71 (d, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 2.26 (s, 3H), 1.05−0.99 (m, 12H), 0.91−0.87 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 172.2, 163.0, 144.4, 130.7, 128.5, 123.9, 116.9, 112.4, 109.1, 67.0, 56.0, 19.2, 18.9, 16.7, 12.6; IR (film) 3198, 2950, 2873, 1800, 1715, 1630, 1498, 1460, 1290, 1159, 1066, 1004 cm^{-1}; HRMS (ES) *m*/*z* = 400.1944 calcd for $C_{22}H_{30}NO_4Si$ [M − H]$^-$, found 400.1935; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 19.5 min, $t_R(2)$ = 22.9 min.

*(R)-5′-Bromo-5-methyl-4-(triisopropylsilyl)-2H-spiro[furan-3,3′-indoline]-2,2′-dione (**9z**).* Following the general procedure using 10 mol % H_2O and C_6H_5Cl:$C_6H_5CH_3$ (1:1) at 40 °C, compound **9z** was obtained as a white solid in 82% yield: mp 180−181 °C; $[\alpha]^{23}_D$ +70.66 (*c* 0.15, 92% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (bs, 1H), 7.41 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 2.28 (s, 3H), 1.03 (d, *J* = 6.0 Hz, 9H), 1.00 (qq, *J* = 6.0, 7.0 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 173.5 163.7, 140.9, 133.1, 129.8, 128.2, 115.8, 112.3, 108.9, 66.5, 19.1, 18.9, 16.7, 12.5; IR (film) 3252, 2950, 2873, 1800, 1722, 1622, 1475, 1383, 1228, 1166 cm^{-1}; HRMS (ES) *m*/*z* = 448.0944 calcd for $C_{21}H_{27}BrNO_3Si$ [M − H]$^-$, found 448.0936; CSP HPLC (Chiralpak IA, 1 mL/min, 95:5 hexanes:*i*-PrOH): $t_R(1)$ = 8.1 min, $t_R(2)$ = 21.7 min.

*Ethyl 3-(1-(tert-Butyldimethylsilyl)-2-oxopropyl)-7-methyl-2-oxoindoline-3-carboxylate (**10**).* To a flask of **8o** (35 mg, 0.1 mmol) and $(CF_3CO_2)_2Hg$ (40 mg, 0.1 mmol) were added AcOH (0.5 mL) and H_2O (0.3 mL). The reaction solution was stirred at room temperature. After 45 min, the mixture was cooled to 0 °C, diluted with ethyl acetate, and quenched with saturated aqueous $Na_2S_2O_3$. The mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash column chromatography (40% ethyl acetate/hexane) to afford **10** as a white solid in 72% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.24 (bs, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.94 (dd, *J* = 7.5, 7.8 Hz, 1H), 4.12 (qd, *J* = 10.5, 7.0 Hz, 1H), 4.10 (qd, *J* = 10.5, 7.0 Hz, 1H), 3.58 (s, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.82 (s, 9H), 0.06 (s, 3H), −0.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 177.4, 170.2, 140.0, 131.1, 128.5, 122.8, 121.7, 119.7, 62.7, 60.8, 49.7, 31.3, 27.2, 18.2, 16.5, 14.0, −5.0, −5.5; IR (film) 3213, 2966, 2866, 1737, 1715, 1661, 1468, 1259, 1213, 1027 cm^{-1}; HRMS (ES) *m*/*z* = 390.2101 calcd for $C_{21}H_{33}NO_4Si$ [MH]$^+$, found 390.2109.

*Ethyl 3-(2-((tert-Butyldimethylsilyl)oxy)prop-1-en-1-yl)-7-methyl-2-oxoindoline-3-carboxylate (**12**).* To a flask of **10** (10 mg, 0.026 mmol) in toluene (1 mL) was added 4 Å MS (30 mg). The mixture was stirred for 12 h at 45 °C and filtered through a plug of Celite. The solution was concentrated in vacuo to afford **12** as a white solid in 93% yield: $[\alpha]^{23}_D$ +176.57 (*c* 0.175, 89% ee, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (bs, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.94 (dd, *J* = 7.5, 8.0 Hz, 1H), 5.25 (s, 1H), 4.17 (qd, *J* = 10.5, 7.0 Hz, 1H), 4.13 (qd, *J* = 10.5, 7.0 Hz, 1H), 2.28 (s, 3H), 1.47 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.91 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.6, 169.5, 154.9, 139.8, 130.8, 130.4, 123.2, 121.8, 119.4, 105.1, 62.4, 59.8, 25.8, 19.7, 18.2, 16.7, 14.1, −4.2, −4.3; IR (film) 3229, 2927, 2858, 1746, 1715, 1661, 1460, 1383, 1228, 1089, 1043 cm^{-1}; HRMS (ES) *m*/*z* = 388.1944 calcd for $C_{21}H_{30}NO_4Si$ [M − H]$^-$, found 388.1941; CSP HPLC (Chiralpak IA, 0.75 mL/min, 92.5:7.5 hexanes:*i*-PrOH): $t_R(1)$ = 7.9 min, $t_R(2)$ = 9.6 min.

*N-Camphorsulfonyl Derivative of **5i** (**5′i**).* To a solution of 60% NaH in oil (0. 003 g, 0.13 mmol) in THF (2 mL) at 0 °C was added **5i** (0.018 g, 0.07 mmol). After being stirred for 5 min, camphorsulfonyl chloride (0.0180 g, 0.07 mmol) was added, and the mixture was warmed to rt. After 2 h, H_2O was added, and the aqueous layer was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under vacuum to give the camphorsulfonyl derivative in 47% yield as a white solid (0.015 g, 0.03 mmol), which was used without further purification.

The camphorsulfonyl derivative (0.015 g, 0.03 mmol) was treated with a solution of 2,4-dinitrophenylhydrazine (0.26 mL, 0.12 M) in 1:1 H_2SO_4/MeOH. The resulting solution was allowed to stir for 10 min, then cooled to 0 °C, whereupon formation of crystals was observed after 24 h. Instead of obtaining the expected hydrazone, the transesterified methyl ester product was observed. The configuration obtained from the crystal structure was used to establish the absolute stereochemistry of **5i**. The remaining compounds were assigned by analogy.

Cyclization of 10 To Form 9o. To a solution of **10** (21 mg, 0.053 mmol) in THF was added a solution of LDA in THF (0.065 mmol). The reaction mixture was stirred for 4 h at 0 °C and quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with diethyl ether, and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash column chromatography (15% ethyl acetate/hexane) to afford **9o** as a white solid in 81% yield.

Protodesilation of 8n To Form 8c. To a solution of **8n** (10 mg, 0.029 mmol) in CH_2Cl_2 was added a solution of TBAF in THF (0.073 mmol). The reaction mixture was stirred for 24 h at room temperature and quenched with saturated aqueous NH_4Cl. The aqueous layer was extracted with diethyl ether, and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash column chromatography (20% ethyl acetate/hexane) to afford **8c** as a white solid in 100% yield.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization data including ^{1}H and ^{13}C NMR spectra. X-ray crystallographic information for select compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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