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Mild Rh(III)-Catalyzed C7-Allylation of Indolines with Allylic Carbonates

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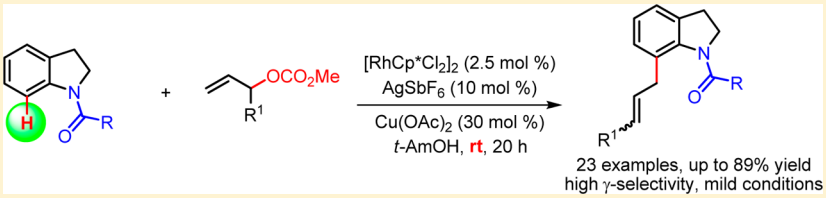
Supporting Information



ABSTRACT: The rhodium(III)-catalyzed direct allylation of indolines with allylic carbonates at room temperature is described. These transformations provide the facile and efficient construction of C7-allylated indolic scaffold.

INTRODUCTION

Transition-metal-catalyzed C−H bond functionalization has emerged as a powerful tool due to its remarkable potential for step economy and environmental sustainability.[1] With the development of catalytic C−H bond functionalization, it has become the most straightforward protocol leading to allylated molecules. For example, Oi and Inoue first reported the ruthenium-catalyzed direct allylation of 2-phenylpyridines with allylic acetates affording a regioisomeric mixture of olefins.[2] Bergman and Ellman described a single example for the Rh(III)-catalyzed allylation of a ketoxime with allyl acetate in the presence of copper oxidant to deliver a terminal alkene.[3] Glorius disclosed a beautiful protocol on the Rh(III)-catalyzed terminal allylation of benzamides and indoles with allylic carbonates.[4] In sharp contrast, Loh demonstrated the Rh(III)-catalyzed internal allylation of benzamides with allylic acetates to provide conjugated olefins.[5] Friedel−Crafts-type C−H allylations of aromatic compounds with allylic carbonates under ruthenium catalysis were also demonstrated.[6] Very recently, direct C−H allylations of electron-deficient polyfluoroarenes and heterocycles under copper and palladium catalysis were reported.[7] Moreover, Krische,[8] Ma,[9] and Cramer[10] independently described the Ir- or Rh-catalyzed allylation reactions of benzamides using allenes as allyl sources. Interestingly, Glorius has recently reported the selective and efficient Co(III)-catalyzed C−H allylation of indoles with allyl carbonates.[11] In addition, Wang demonstrated the Rh(III)-catalyzed direct C−H allylation reaction with 4-vinyl-1,3-dioxolan-2-ones to afford allylic alcohols.[12]

The indoles and indolines are ubiquitous structural motifs found in a large number of natural products with diverse and important biological activities.[13] In particular, the allylated indole or indoline alkaloids are widely distributed in terrestrial and marine organisms, especially in the genera *Penicillium* and *Aspergillus* of ascomycota, and display broad structural diversity.[14] The prevalence of allylated indoles and indolines in bioactive natural products and the versatility of olefin transformations have led to the development of many useful methods for their preparation.[15,16] Notably, the C7-allylated indoles and indolines are known as pivotal heterocyclic compounds found in a number of bioactive synthetic molecules and natural products, as shown in Figure 1.[17]

Recently, the directing group-assisted catalytic C7-functionalizations of indolines with various coupling partners were demonstrated (Scheme 1). For example, acylation,[18] arylation,[19] olefination,[20] alkylation,[21] and alkynylation[22] of indo-

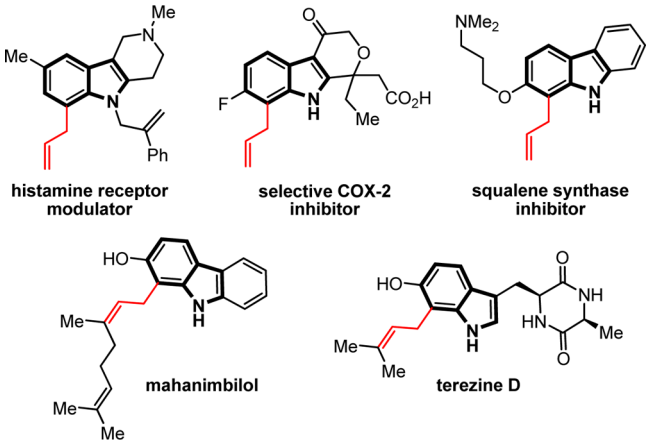


Figure 1. Selected examples for synthetic or natural C7-allylated products.

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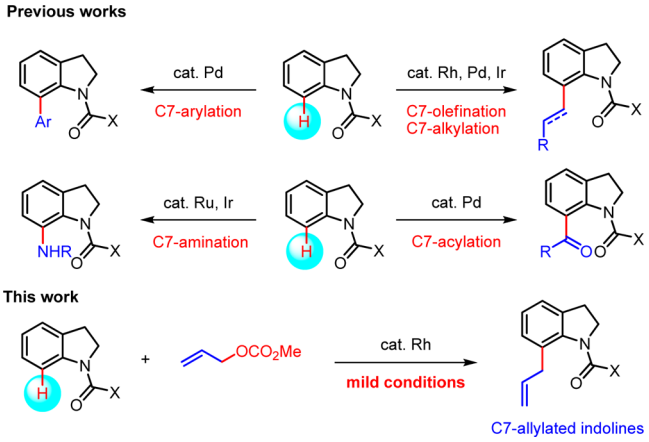
Scheme 1. Catalytic C7-Functionalization of Indolines

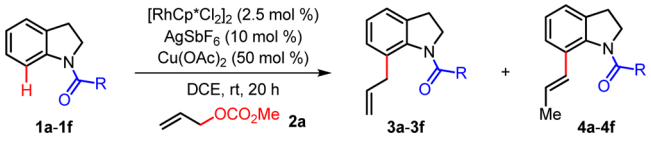


lines at the C-7 position were described under ruthenium, palladium, rhodium, iron, and iridium catalysis. In addition, Ru(II)- or Ir(III)-catalyzed C7-aminations of indolines with organic azides were reported by Zhu, Chang, and Zhou/Li, respectively.[23] Inspired by our recent study on the decarboxylative acylation of indolines at the C7-position[24] and in continuation of the catalytic C−H allylation of aromatic and α,β-unsaturated carboxamides,[25] we herein disclose the rhodium-catalyzed direct allylation and crotylation of indolines with allylic carbonates via C−H bond activation.

RESULTS AND DISCUSSION

Our study was initiated by examining the coupling of *N*-acetyl indoline (**1a**) and allyl methyl carbonate (**2a**) under rhodium catalysis (Table 1). To our delight, the cationic rhodium

Table 1. Screening of *N*-Protection Groups[a]



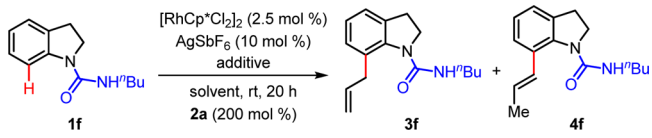
entry	R	substrate	yield (%)[b]	ratio (**3**:**4**)[c]
1	Me	**1a**	55	1.9:1
2	*t*-Bu	**1b**	37	1.4:1
3	NMe_2	**1c**	35	6.9:1
4	pyrrolidinyl	**1d**	12	3.5:1
5	NHPh	**1e**	19	10.9:1
6	NH^{n}Bu	**1f**	80	9.5:1

[a]Reaction conditions: **1a**−**1f** (0.3 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (50 mol %), DCE (1 mL) under air at room temperature for 20 h in reaction tubes. [b]Isolated yield by flash column chromatography. [c]Regioisomeric ratio between terminal and internal olefins determined by ^{1}H NMR analysis of crude reaction mixture.

complex, derived from $[Cp^*RhCl_2]_2$ and $AgSbF_6$, was found to catalyze the coupling of **1a** and **2a** in the presence of $Cu(OAc)_2$ as an additive in dichloroethane (DCE) at room temperature for 20 h to provide the C7-allylated product **3a** with a regioisomeric mixture of 1.9:1 ratio in 55% yield (Table 1, entry 1). Similarly, pivaloyl directing group **1b** displayed low level of both reactivity and selectivity (Table 1, entry 2). However, *N*,*N*-dimethylcarbamoyl indoline (**1c**) gave terminal olefin **3c** with good level of regioselectivity (6.9:1), albeit in low yield (Table 1, entry 3). Thus, we focused on the screening of other carbamoyl directing groups. Interestingly, *N*-butylindoline-1-carboxamide (**1f**), derived from indoline and *n*-butyl isocyanate, was found to be far more effective in this coupling reaction to afford our desired product **3f** with high terminal selectivity (9.5:1) in 80% yield (Table 1, entry 6).

With the optimal directing group of indolines in hand, we further optimized the reaction conditions to afford increased terminal selectivity (Table 2). Screening of solvents under

Table 2. Selected Optimization of the Reaction Conditions[a]



entry	additive (mol %)	solvent	yield (%)[b]	ratio (**3f**:**4f**)[c]
1	$Cu(OAc)_2$ (50)	DCE	80	9.5:1
2	$Cu(OAc)_2$ (50)	DMF	39	5.7:1
3	$Cu(OAc)_2$ (50)	toluene	29	7.5:1
4	$Cu(OAc)_2$ (50)	MeCN	5	1.0:1
5	$Cu(OAc)_2$ (50)	THF	74	8.9:1
6	$Cu(OAc)_2$ (50)	*t*-AmOH	84	>50:1
7	$Cu(OAc)_2{\cdot}H_2O$ (50)	*t*-AmOH	66	7.1:1
8	PivOH (50)	*t*-AmOH	5	>50:1
9	AgOAc (50)	*t*-AmOH	57	6.3:1
10	**$Cu(OAc)_2$ (30)**	***t*-AmOH**	**81**	**>50:1**
11		*t*-AmOH	NR	trace
12[d]	$Cu(OAc)_2$ (30)	*t*-AmOH	NR	0

[a]Reaction conditions: **1f** (0.3 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), additive (quantity noted), solvent (1 mL) under air at room temperature for 20 h in reaction tubes. [b]Isolated yield by flash column chromatography. [c]Regioisomeric ratio between terminal and internal olefins determined by ^{1}H NMR analysis of crude reaction mixture. [d]In the absence of $AgSbF_6$.

otherwise identical conditions revealed that *tert*-amyl alcohol (*t*-AmOH) was found to be the most effective solvent in this coupling reaction to afford terminal olefination product **3f** in high yield (84%) with excellent level of regioselectivity (>50:1), whereas other solvents such as DCE, DMF, toluene, MeCN, and THF were less effective (Table 2, entries 1−6). Further study revealed that $Cu(OAc)_2$ additive is unique in its ability to facilitate high levels of conversion and selectivity (Table 2, entries 7−9). In addition, decreasing amount of $Cu(OAc)_2$ to 30 mol % provided a comparable yield (81%) and selectivity (>50:1) (Table 2, entry 10), but no formation of **3f** was observed when either $Cu(OAc)_2$ or $AgSbF_6$ were excluded (Table 2, entries 11 and 12).

To evaluate the scope and limitation of this process, the optimal reaction conditions were applied to a range of *N*-butyl carbamoyl indolines **1g**−**1t** (Table 3). In all cases, good to excellent yields and high terminal selectivity of the desired aryl C−H allylation adducts were obtained. Exceptionally, indoline **1g** with electron-rich moiety at the C4-position exhibited slightly decreased reactivity. It should be noted that C6-substituted indolines **1j** and **1k** were tolerated under current reaction conditions to afford the corresponding products in high yields and excellent level of regioselectivity. In addition, this reaction was highly compatible with C2-substituted indolines **1l**, **1q**, and **1r**. To our surprise, this reaction is only restricted to indolines. For example, *N*-methyl aniline **1s** and tetrahydroquinoline **1t** containing a *N*-butylcarbamoyl directing

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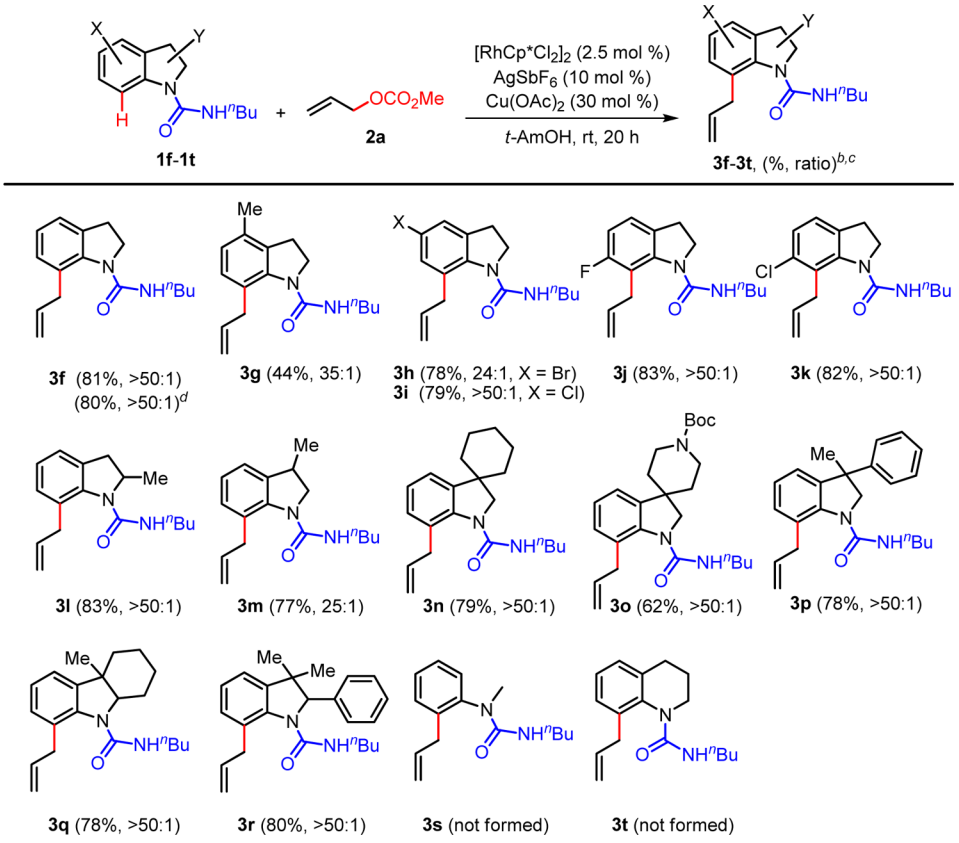
Table 3. Scope of Indolines[a]



[a]Reaction conditions: **1f**–**1t** (0.3 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (30 mol %), *t*-AmOH (1 mL) under air at room temperature for 20 h in reaction tubes. [b]Isolated yield by flash column chromatography. [c]Regioisomeric ratio between terminal and internal olefins determined by ^1H NMR analysis of crude reaction mixture. [d]Scale-up experiment (**1f**, 3 mmol).

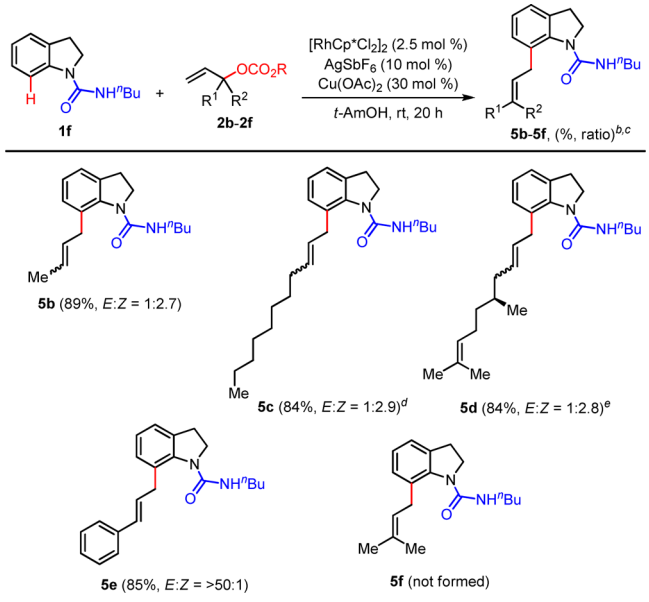
group failed to deliver the corresponding products under standard reaction condtions.

To further explore the scope and limitation of this transformation, various allylic carbonates **2b**–**2f** were screened to couple with **1f**, as shown in Table 4. The monosubstituted allyl alkyl carbonates **2b**–**2d** were smoothly coupled with **1f** to give the (*Z*)-crotylation products **5b**–**5d** as major isomers in high yields. In sharp contrast, α-phenyl-substituted allyl carbonate **2e** underwent completely *trans*-selectivity with **1f**. Notably, these reactions proceeded readily with complete γ-selectivity in case of branched allylic carbonates, and no migration of double bond on the products was observed. However, linear crotyl carbonates and β-substituted allylic carbonates did not deliver the corresponding coupling products, presumably due to the increased steric hindrance of electrophilic allylic carbonates, preventing formal S_N-type reactions with rhodacycle intermediate.[26] In addition, α,α-disubstituted allylic carbonate **2f** was found to be unreactive under the optimal reaction conditions.

To our delight, 2-vinyloxirane **2g** was also coupled with indoline **1f** to afford a mixture of allylic alcohol **5g** with 3:1 *E*/*Z* ratio in 69% yield as a result of olefin insertion and epoxide ring-opening, which is in agreement with the formal S_N-type reaction mechanism (Scheme 2).[27]

To demonstrate the synthetic utility of C7-allylated indolines, various transformations of the allylated product **3f** were conducted (Scheme 3). Intermolecular olefin metathesis between **3f** and ethyl acrylate gave α,β-unsaturated ester **6a**, which subsequently underwent aza-Michael reaction to furnish

Table 4. Scope of Allylic Carbonates[a]



[a]Reaction conditions: **1f** (0.3 mmol), **2b**–**2f** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (30 mol %), *t*-AmOH (1 mL) under air at room temperature for 20 h in reaction tubes. All cases provided the regioisomeric ratio of above 50:1 between terminal and internal olefins. [b]Isolated yield by flash column chromatography. [c]Diastereomeric ratio between *trans*- and *cis*-olefins determined by ^1H NMR analysis. [d]THF was used as a solvent. [e]40 h.

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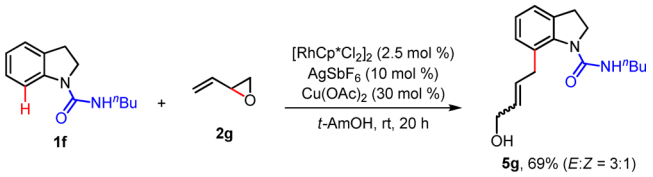
Scheme 2. Indoline Allylation with 2-Vinyloxirane



tricyclic compound **6b** in 45% yield. Interestingly, while carrying out the deprotection of *N*-butylcarbamoyl group of **3f** under standard basic conditions, we observed the deprotection as well as olefin migration of **3f** to provide free-(NH)-indoline **6c** in high yield. Subsequently this deprotected product **6c** under transfer hydrogenation conditions provided smoothly C7-olefinated indole **6d** in high yield.

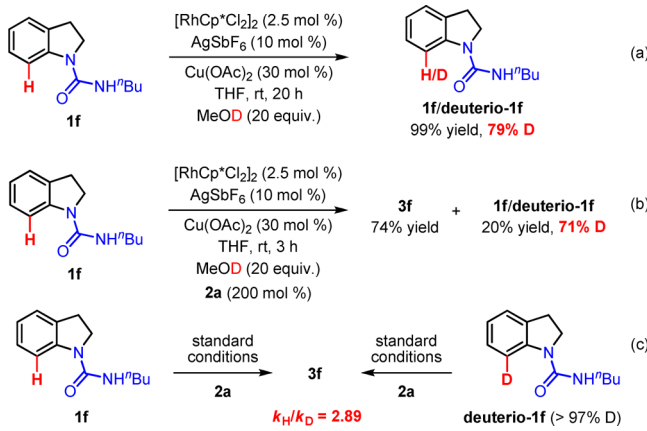
To gain mechanistic insight, the following experiments were performed (Scheme 4). A hydrogen−deuterium exchange using MeOD indicated that the cleavage of the C−H bond at the indoline C7-position was a reversible metalation−proto-(deutero)demetalation process (Scheme 4a). In the presence of allyl methyl carbonate (**2a**) and MeOD, no deuterium incorporation of product **3a** and significant deuteration (71% D) of recovered starting material was observed (Scheme 4b). Next, two parallel reactions of **1f** and **deuterio-1f** with **2a** under standard reaction conditions resulted in the kinetic isotope effect (k_H/k_D) of 2.89, thus indicating that C−H cleavage might be involved in the rate-limiting step (Scheme 4c).[28]

A proposed reaction mechanism was depicted in Scheme 5. Coordination of the carbonyl group to cationic Rh(III) catalyst and subsequent C−H cleavage delivers the cyclorhodated species **I**, which on migratory insertion of a double bond into Rh−C bond affords an eight-membered Rh(III) intermediate **II**. Further, *β*-oxygen elimination provides the product **3f** and regenerates a Rh(III) catalyst. Alternatively, coordination of allyl methyl carbonate to the cyclorhodated species **I** followed by nucleophilic substitution can not be ruled out in the catalytic cycle to afford 7-allylated product **3f**.[29]

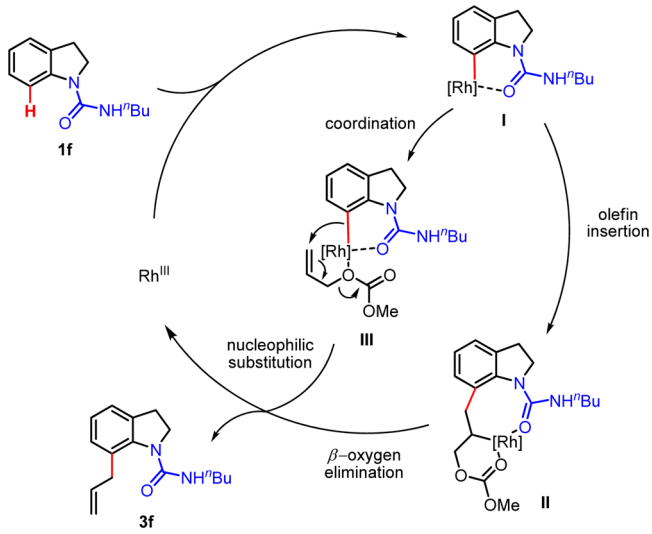
CONCLUSION

We have disclosed a highly selective C7-allylation of indolines with allylic carbonates under rhodium catalysis. These transformations have been applied to a wide range of substrates, and typically proceed with excellent levels of chemoselectivity as well as with high functional group tolerance.

Scheme 4. Mechanistic Investigations



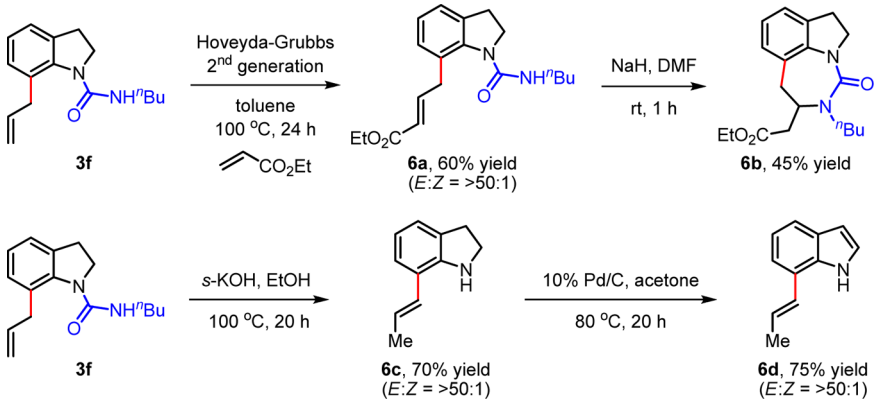
Scheme 5. Proposed Reaction Mechanism



EXPERIMENTAL SECTION

General Procedure for the Synthesis of *N*-Acyl or *N*-Carbamoyl Indolines (1a−1e). To a stirred solution of indoline (1.00 g, 8.4 mmol) and triethylamine (3.5 mL, 25.2 mmol) in CH_2Cl_2 (10 mL) was added dropwise a solution of *N*-acyl or *N*-carbamoyl chloride (12.6 mmol) in CH_2Cl_2 (7 mL) at 0 °C. The reaction mixture was stirred at this temperature for 15 min and further stirred at room temperature for 3 h. The resulting mixture was partitioned between CH_2Cl_2 and H_2O. The organic layer was dried over $MgSO_4$ and

Scheme 3. Synthetic Transformation of C7-Allylated Indolines



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concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc) to give the corresponding products **1a**–**1e**.

*1-(Indolin-1-yl)ethanone (**1a**).*[20b] 1.21 g (89%); white solid; mp = 102–104 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 1H), 7.18–7.14 (m, 2H), 6.98 (t, J = 7.4 Hz, 1H), 4.03 (t, J = 8.4 Hz, 2H), 3.18 (t, J = 8.4 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.7, 142.9, 131.0, 127.5, 124.5, 123.6, 117.0, 48.7, 28.0, 24.3.

*1-(Indolin-1-yl)-2,2-dimethylpropan-1-one (**1b**).*[23a] 1.33 g (78%); light brown solid; mp = 54–58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, J = 8.5 Hz, 1H), 7.19–7.17 (m, 2H), 7.02 (t, J = 7.0 Hz, 1H), 4.23 (t, J = 8.1 Hz, 2H), 3.14 (t, J = 8.1 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 144.7, 130.7, 127.3, 124.2, 123.6, 118.4, 49.4, 40.2, 29.3, 27.7.

*N,N-Dimethylindoline-1-carboxamide (**1c**).*[20b] 1.32 g (83%); light brown solid; mp = 57–62 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.13 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 6.90 (d, J = 7.9 Hz, 1H), 6.85 (t, J = 7.3 Hz, 1H), 3.87 (t, J = 8.2 Hz, 2H), 3.00 (t, J = 8.2 Hz, 2H), 2.91 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.3, 144.3, 131.4, 120.7, 124.8, 121.3, 113.3, 50.3, 38.1, 28.1.

*Indolin-1-yl(pyrrolidin-1-yl)methanone (**1d**).* 1.25 g (69%); light yellow solid; mp = 76–85 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.08–7.03 (m, 3H), 6.79 (t, J = 7.2 Hz, 1H), 3.85 (t, J = 8.3 Hz, 2H), 3.39–3.37 (m, 2H), 3.29–3.26 (m, 2H), 2.97 (t, J = 8.4 Hz, 2H), 1.82–1.80 (m, 2H), 1.75–1.72 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.5, 144.3, 131.1, 126.9, 124.5, 121.3, 114.7, 49.9, 48.3, 47.8, 38.2, 28.5, 25.4; IR (KBr) υ 2969, 2873, 1637, 1600, 1478, 1384, 1259, 1204, 1017, 917, 871, 730 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{16}N_2O$ $[M]^+$ 216.1263, found 216.1262.

*N-Phenylindoline-1-carboxamide (**1e**).* 1.40 g (70%); white solid; mp = 109–111 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 7.7 Hz, 2H), 7.28 (br s, 2H), 7.18–7.14 (m, 2H), 7.04 (br s, 1H), 6.93 (t, J = 6.9 Hz, 1H), 6.53 (br s, 1H), 4.01–3.94 (m, 2H), 3.16–3.13 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.4, 144.2, 138.3, 130.7, 129.0, 127.7, 124.8, 123.6, 122.3, 120.3, 115.0, 47.5, 27.9; IR (KBr) υ 3316, 3048, 2884, 1652, 1523, 1478, 1438, 1342, 1237, 1171, 1141, 1024, 732 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{14}N_2O$ $[M]^+$ 238.1106, found 238.1107.

General Procedure for the Synthesis of *N*-Butylindoline-1-carboxamides (1f–1r). To a stirred solution of indoline (1.00 g, 8.4 mmol) in CH_2Cl_2 (25 mL) were added triethylamine (3.5 mL, 25.2 mmol) and *n*-butyl isocyanate (1.25 g, 12.6 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was washed with H_2O and extracted with EtOAc. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc) to give the corresponding products **1f**–**1r**.

*N-Butylindoline-1-carboxamide (**1f**).* 1.48 g (81%); white solid; mp = 72–74 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.84 (d, J = 8.0 Hz, 1H), 7.13–7.09 (m, 2H), 6.86 (t, J = 7.4 Hz, 1H), 4.60 (br s, 1H), 3.85 (t, J = 8.4 Hz, 2H), 3.30–3.28 (m, 2H), 3.12 (t, J = 8.6 Hz, 2H), 1.54–1.50 (m, 2H), 1.38–1.33 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.1, 143.8, 130.2, 127.6, 124.5, 121.6, 114.6, 47.0, 40.3, 32.3, 27.8, 20.1, 13.8; IR (KBr) υ 3344, 2956, 2928, 2861, 1643, 1520, 1480, 1461, 1386, 1339, 1292, 1264, 1153, 1088, 1022, 930, 748 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{18}N_2O$ $[M]^+$ 218.1419, found 218.1420.

*N-Butyl-4-methylindoline-1-carboxamide (**1g**).* 1.42 g (73%); yellow sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.68 (d, J = 8.8 Hz, 1H), 6.94–6.92 (m, 2H), 4.52 (br s, 1H), 3.85 (t, J = 8.3 Hz, 2H), 3.31–3.28 (m, 2H), 3.09 (t, J = 8.5 Hz, 2H), 2.25 (s, 3H), 1.54–1.50 (m, 2H), 1.39–1.33 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.3, 141.5, 131.3, 130.6, 128.1, 125.5, 114.4, 47.3, 40.4, 32.5, 28.0, 21.0, 20.3, 14.0; IR (KBr) υ 3338, 2957, 2928, 2861, 1644, 1523, 1487, 1384, 1332, 1263, 1160, 1133, 817, 733 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{14}H_{20}N_2O$ $[M]^+$ 232.1576, found 232.1577.

*5-Bromo-N-butylindoline-1-carboxamide (**1h**).* 1.74 g (70%); light yellow solid; mp = 159–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 7.3 Hz, 1H), 7.27–7.24 (m, 2H), 4.52 (br s, 1H), 3.90 (t, J = 7.8 Hz, 2H), 3.33 (s, 2H), 3.17 (t, J = 7.9 Hz, 2H), 1.61–1.51 (m, 2H), 1.45–1.33 (m, 2H), 0.96 (t, J = 6.6 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.8, 143.0, 132.2, 130.4, 127.4, 116.1, 113.8, 47.0, 40.2, 32.2, 27.5, 20.1, 13.8; IR (KBr) υ 3343, 2956, 2928, 2871, 2176, 1645, 1519, 1468, 1327, 1298, 1253, 1154, 1090, 817, 734 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{17}BrN_2O$ $[M]^+$ 296.0524, found 296.0522.

*N-Butyl-5-chloroindoline-1-carboxamide (**1i**).* 1.44 g (68%); light yellow solid; mp = 87–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 8.1 Hz, 1H), 7.43 (s, 1H), 7.29–7.26 (m, 1H), 4.68 (br s, 1H), 4.07 (t, J = 8.9 Hz, 2H), 3.49–3.47 (m, 2H), 3.33 (t, J = 8.4 Hz, 2H), 1.77–1.68 (m, 2H), 1.62–1.50 (m, 2H), 1.15–1.10 (m, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.9, 142.5, 131.8, 127.4, 126.4, 124.5, 115.6, 47.1, 40.2, 32.2, 27.6, 20.1, 13.8; IR (KBr) υ 3340, 2957, 2930, 2872, 1645, 1519, 1471, 1328, 1252, 1154, 1091, 874, 819, 733 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{17}ClN_2O$ $[M]^+$ 252.1029, found 252.1034.

*N-Butyl-6-fluoroindoline-1-carboxamide (**1j**).* 1.29 g (65%); white solid; mp = 114–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.6 Hz, 1H), 7.00 (t, J = 7.9 Hz, 1H), 6.59–6.53 (m, 1H), 4.53 (br s, 1H), 3.91 (t, J = 9.0 Hz, 2H), 3.34–3.28 (m, 2H), 3.12 (t, J = 8.5 Hz, 2H), 1.59–1.50 (m, 2H), 1.44–1.32 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 239.5 Hz), 154.8, 145.1 (d, J_{C-F} = 12.0 Hz), 125.1 (d, J_{C-F} = 2.5 Hz), 124.5 (d, J_{C-F} = 10.3 Hz), 107.8 (d, J_{C-F} = 22.5 Hz), 103.0 (d, J_{C-F} = 29.7 Hz), 47.8, 40.2, 32.2, 27.1, 20.1, 13.8; IR (KBr) υ 3338, 2954, 2931, 2870, 1643, 1530, 1490, 1390, 1300, 1263, 1160, 1079, 856, 786, 738 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{17}FN_2O$ $[M]^+$ 236.1325, found 236.1329.

*N-Butyl-6-chloroindoline-1-carboxamide (**1k**).* 1.29 g (61%); light yellow solid; mp = 83–85 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 4.51 (br s, 1H), 3.89 (t, J = 8.4 Hz, 2H), 3.31 (t, J = 6.8 Hz, 2H), 3.12 (t, J = 8.4 Hz, 2H), 1.60–1.50 (m, 2H), 1.44–1.32 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.8, 145.0, 133.3, 124.9, 121.5, 115.2, 47.5, 40.3, 32.3, 27.4, 20.1, 13.8; IR (KBr) υ 3340, 2956, 2926, 2857, 1644, 1532, 1479, 1420, 1382, 1341, 1296, 1265, 1181, 1095, 988, 861, 789, 737 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{17}ClN_2O$ $[M]^+$ 252.1029, found 252.1030.

*N-Butyl-2-methylindoline-1-carboxamide (**1l**).* 1.46 g (75%); white solid; mp = 105–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 6.91 (t, J = 7.2 Hz, 1H), 4.74 (br s, 1H), 4.44–4.34 (m, 1H), 3.42–3.33 (m, 3H), 2.60 (d, J = 15.8 Hz, 1H), 1.61–1.51 (m, 2H), 1.45–1.33 (m, 2H), 1.30 (d, J = 6.3 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.7, 142.4, 129.9, 127.5, 125.2, 121.9, 114.7, 55.2, 40.2, 36.3, 32.3, 21.0, 20.2, 13.8; IR (KBr) υ 3310, 2960, 2927, 2859, 1633, 1517, 1477, 1456, 1371, 1289, 1220, 1152, 1085, 1022, 933, 858, 753 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{14}H_{20}N_2O$ $[M]^+$ 232.1576, found 232.1574.

*N-Butyl-3-methylindoline-1-carboxamide (**1m**).* 1.26 g (65%); white solid; mp = 89–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.19–7.10 (m, 2H), 6.19 (td, J = 7.8 Hz, 1H), 4.58 (br s, 1H), 4.05 (t, J = 8.2 Hz, 1H), 3.51–3.39 (m, 2H), 3.32 (t, J = 7.0 Hz, 2H), 1.60–1.51 (m, 2H), 1.54–1.32 (m, 5H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.1, 143.2, 135.4, 127.7, 123.4, 121.7, 114.5, 55.2, 40.2, 34.6, 32.3, 20.3, 20.1, 13.8; IR (KBr) υ 3338, 2957, 2927, 2870, 1643, 1520, 1478, 1461, 1342, 1288, 1153, 1090, 1022, 930, 747 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{14}H_{20}N_2O$ $[M]^+$ 232.1576, found 232.1576.

*N-Butylspiro[cyclohexane-1,3′-indoline]-1′-carboxamide (**1n**).* 1.68 g (70%); white solid; mp = 144–145 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.0 Hz, 1H), 7.19–7.08 (m, 2H), 6.92 (t, J = 8.2 Hz, 1H), 4.61 (br s, 1H), 3.69 (s, 2H), 3.34 (t, J = 7.1 Hz, 2H), 1.76–1.53 (m, 8H), 1.44–1.33 (m, 6H), 0.96 (t, J = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.1, 142.6, 139.6, 127.9, 122.3, 121.7, 114.5, 57.5, 44.4, 40.3, 37.3, 32.3, 25.3, 23.0, 20.1, 13.8; IR (KBr) υ 3349, 2924, 2848, 1639, 1521, 1477, 1459, 1335, 1301, 1276, 1192, 1095, 1020, 936, 888, 750 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{26}N_2O$ $[M]^+$ 286.2045, found 286.2039.

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*tert-Butyl 1-(Butylcarbamoyl)spiro[indoline-3,4′-piperidine]-1′-carboxylate (**1o**).* 0.356 g (23%); light yellow sticky solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 1H), 7.19 (td, J = 8.6, 1.3 Hz, 1H), 7.08 (d, J = 7.4 Hz, 1H), 6.94 (td, J = 7.8, 0.9 Hz, 1H), 4.68 (br s, 1H), 4.14−4.10 (m, 2H), 3.76 (s, 2H), 3.37−3.30 (m, 2H), 2.86 (t, J = 12.8 Hz, 2H), 1.88−1.78 (m, 2H), 1.66−1.36 (m, 15H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.0, 154.8, 142.7, 137.8, 128.4, 122.5, 122.0, 114.4, 79.8, 56.6, 42.7, 40.3, 36.5, 32.3, 29.7, 28.4, 20.1, 13.8; IR (KBr) υ 3325, 2925, 2847, 1638, 1520, 1477, 1456, 1341, 1279, 1220, 1152, 1095, 933, 754 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{33}N_3O_3$ $[M]^+$ 387.2522, found 387.2521.

*N-Butyl-3-methyl-3-phenylindoline-1-carboxamide (**1p**).* 1.68 g (65%); light yellow solid; mp = 94−96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.1 Hz, 1H), 7.32−7.19 (m, 6H), 6.94−6.93 (m, 2H), 4.51 (br s, 1H), 4.00 (d, J = 9.0 Hz, 1H), 3.88 (d, J = 9.1 Hz, 1H), 3.34−3.28 (m, 2H), 1.75 (s, 3H), 1.58−1.48 (m, 2H), 1.43−1.30 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.9, 147.0, 143.1, 138.6, 128.4, 128.1, 126.6, 126.4, 123.9, 122.1, 114.7, 64.1, 47.8, 40.2, 32.2, 27.2, 20.1, 13.8; IR (KBr) υ 3338, 2958, 2929, 2871, 1644, 1520, 1478, 1337, 1264, 1154, 1023, 734 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{24}N_2O$ $[M]^+$ 308.1889, found 308.1902.

*N-Butyl-4a-methyl-2,3,4,4a-tetrahydro-1H-carbazole-9(9aH)-carboxamide (**1q**).* 1.32 g (55%); white solid; mp = 164−166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.9 Hz, 1H), 7.17 (td, J = 8.1, 1.3 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.95 (td, J = 7.8, 0.8 Hz, 1H), 4.77 (br s, 1H), 3.81−3.76 (m, 1H), 3.34 (s, 2H), 2.24−2.18 (m, 1H), 2.11−2.06 (m, 1H), 1.61−1.50 (m, 5H), 1.45−1.33 (m, 2H), 1.25−1.17 (m, 3H), 1.12 (s, 3H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.1, 141.6, 138.6, 127.5, 122.2, 121.8, 115.2, 67.3, 43.6, 40.2, 32.4, 32.3, 31.0, 28.3, 22.3, 21.8, 20.2, 13.8; IR (KBr) υ 3323, 2925, 2854, 1634, 1532, 1473, 1387, 1285, 1197, 1119, 1022, 928, 844, 749 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{26}N_2O$ $[M]^+$ 286.2045, found 286.2041.

*N-Butyl-3,3-dimethyl-2-phenylindoline-1-carboxamide (**1r**).* 1.35 g (50%); white solid; mp = 137−139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.33−7.28 (m, 3H), 7.24−7.20 (m, 1H), 7.16−7.13 (m, 2H), 7.06−6.95 (m, 2H), 4.71 (s, 1H), 4.30 (br s, 1H), 3.24−3.00 (m, 2H), 1.43 (s, 3H), 1.29−1.19 (m, 2H), 1.06−0.93 (m, 2H), 0.85 (s, 3H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.4, 143.1, 138.7, 138.2, 128.9, 128.3, 128.0, 126.6, 122.2, 122.1, 114.8, 45.4, 39.9, 32.6, 31.7, 24.2, 19.6, 13.6; IR (KBr) υ 3369, 2958, 2928, 2869, 1643, 1515, 1476, 1453, 1377, 1284, 1152, 1121, 1024, 939, 888, 826, 747 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{26}N_2O$ $[M]^+$ 322.2045, found 322.2039.

Typical Procedure for the C7-Allylation of *N*-Butylindoline-1-carboxamides (3a−3t and 5b−5f). To an oven-dried sealed tube charged with *N*-butylindoline-1-carboxamide (**1f**) (65.5 mg, 0.3 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 10 mol %), and $Cu(OAc)_2$ (16.3 mg, 30 mol %) in *t*-AmOH (1 mL) was added allyl methyl carbonate (**2a**) (69.7 mg, 0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at room temperature for 20 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 7:1) to afford 62.8 mg of **3f** in 81% yield.

*1-(7-Allylindolin-1-yl)ethanone (**3a**).* 33.0 mg (55%); light yellow sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.07−7.02 (m, 3H), 5.86 (ddt, J = 17.0, 10.1, 6.7 Hz, 1H), 5.07−5.01 (m, 2H), 4.03 (s, 2H), 3.42 (d, J = 6.3 Hz, 2H), 3.00 (t, J = 7.2 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 141.1, 136.8, 134.7, 129.0, 125.5, 125.0, 122.4, 116.0, 51.3, 38.4, 30.1, 23.9; IR (KBr) υ 2915, 1993, 1658, 1591, 1429, 1379, 1327, 1234, 1186, 1105, 968, 914, 847, 760, 730 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{13}H_{15}NO$ $[M]^+$ 201.1154, found 201.1151.

*1-(7-Allylindolin-1-yl)-2,2-dimethylpropan-1-one (**3b**).* 26.7 mg (37%); light yellow sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.08−7.07 (m, 1H), 7.04−7.01 (m, 2H), 5.82 (ddt, J = 17.0, 10.0, 6.7 Hz, 1H), 5.08−5.01 (m, 2H), 4.08 (t, J = 7.3 Hz, 2H), 3.28 (d, J = 6.7 Hz, 2H), 3.00 (t, J = 7.3 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 178.2, 143.0, 136.7, 134.5, 131.6, 128.5, 125.2, 122.3, 116.1, 51.3, 40.1, 38.3, 31.3, 28.7; IR (KBr) υ 2963, 1967, 1648, 1587, 1430, 1347, 1322, 1265, 1183, 1149, 1088, 966, 903, 730 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{21}NO$ $[M]^+$ 243.1623, found 243.1622.

*7-Allyl-N,N-dimethylindoline-1-carboxamide (**3c**).* 24.2 mg (35%); light brown sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.02 (d, J = 7.2 Hz, 1H), 6.97 (d, J = 7.1 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 5.82 (ddt, J = 17.0, 10.0, 6.8 Hz, 1H), 5.08−5.00 (m, 2H), 3.88−3.84 (m, 2H), 3.27 (d, J = 6.8 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H), 2.95 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.3, 143.6, 136.5, 133.6, 131.5, 128.3, 123.7, 122.4, 116.0, 52.9, 50.5, 38.3, 37.4, 30.6; IR (KBr) υ 2924, 2010, 1650, 1482, 1451, 1377, 1292, 1258, 1166, 1062, 1006, 911, 731 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{14}H_{18}N_2O$ $[M]^+$ 230.1419, found 230.1424.

*(7-Allylindolin-1-yl)(pyrrolidin-1-yl)methanone (**3d**).* 9.1 mg (12%); light yellow sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.98 (d, J = 6.9 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 5.75 (ddt, J = 16.9, 10.0, 6.8 Hz, 1H), 5.02−4.92 (m, 2H), 3.87 (t, J = 8.2 Hz, 1H), 3.82 (t, J = 8.0 Hz, 1H), 3.39−3.36 (m, 4H), 3.27 (d, J = 6.7 Hz, 2H), 3.02−2.97 (m, 2H), 1.83−1.81 (m, 4H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.3, 143.5, 136.9, 131.4, 128.6, 123.6, 122.5, 115.8, 52.2, 50.2, 48.0, 37.8, 30.6, 28.7, 25.7; IR (KBr) υ 2874, 1966, 1644, 1592, 1452, 1383, 1285, 1254, 1196, 1124, 1048, 994, 912, 853, 753 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{20}N_2O$ $[M]^+$ 256.1576, found 256.1573.

*7-Allyl-N-phenylindoline-1-carboxamide (**3e**).* 15.9 mg (19%); light yellow solid; mp = 178−179 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 (d, J = 8.6, 1.1 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.13−7.02 (m, 4H), 6.54 (s, 1H), 5.87 (ddt, J = 16.9, 10.2, 6.5 Hz, 1H), 5.08−5.04 (m, 2H), 4.16 (t, J = 7.2 Hz, 2H), 3.41 (d, J = 6.5 Hz, 2H), 3.03 (t, J = 7.6 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.3, 141.5, 138.5, 136.3, 135.6, 129.3, 129.2, 129.0, 125.2, 123.5, 123.3, 119.6, 116.8, 52.0, 36.9, 30.2; IR (KBr) υ 3263, 3051, 2926, 1998, 1650, 1594, 1525, 1479, 1439, 1343, 1315, 1240, 1141, 1025, 916, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{18}H_{18}N_2O$ $[M]^+$ 278.1419, found 278.1422.

*7-Allyl-N-butylindoline-1-carboxamide (**3f**).* 65.0 mg (81%); light brown solid; mp = 77−81 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.06 (d, J = 7.1 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 5.90 (ddt, J = 17.0, 10.1, 6.4 Hz, 1H), 5.10−5.06 (m, 2H), 4.70 (br s, 1H), 4.06 (t, J = 7.6 Hz, 2H), 3.37 (t, J = 6.4 Hz, 2H), 3.25−3.22 (m, 2H), 2.96 (t, J = 7.7 Hz, 2H), 1.49−1.45 (m, 2H), 1.34−1.29 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.3, 142.2, 136.8, 135.5, 129.1, 128.7, 124.6, 123.0, 116.3, 51.9, 40.7, 36.9, 32.4, 30.1, 20.3, 14.0; IR (KBr) υ 3313, 3051, 2929, 1993, 1642, 1522, 1482, 1450, 1311, 1248, 1187, 1152, 1086, 912, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{22}N_2O$ $[M]^+$ 258.1732, found 258.1735.

*7-Allyl-N-butyl-4-methylindoline-1-carboxamide (**3g**).* 41.3 mg (44%); brown solid; mp = 89−92 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.82 (s, 1H), 5.91 (ddt, J = 17.0, 10.1, 6.4 Hz, 1H), 5.10−5.06 (m, 2H), 4.71 (br s, 1H), 4.05 (t, J = 7.6 Hz, 2H), 3.33 (d, J = 6.3 Hz, 2H), 3.23−3.20 (m, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.64 (s, 3H), 1.47−1.43 (m, 2H), 1.33−1.28 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.5, 139.9, 136.8, 135.8, 134.3, 129.4, 128.3, 123.9, 116.3, 52.0, 40.7, 36.7, 32.4, 30.1, 21.1, 20.2, 13.9; IR (KBr) υ 3314, 3076, 2927, 1975, 1639, 1527, 1474, 1316, 1244, 1191, 1124, 1080, 994, 909, 854, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{24}N_2O$ $[M]^+$ 272.1889, found 272.1885.

*7-Allyl-5-bromo-N-butylindoline-1-carboxamide (**3h**).* 77.0 mg (78%); brown solid; mp = 126−130 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.12 (s, 1H), 5.84 (ddt, J = 16.8, 10.2, 6.5 Hz, 1H), 5.10−5.07 (m, 2H), 4.68 (br s, 1H), 4.01 (t, J = 7.7 Hz, 2H), 3.31 (d, J = 6.5 Hz, 2H), 3.23−3.20 (m, 2H), 2.95 (t, J = 7.7 Hz, 2H), 1.48−1.44 (m, 2H), 1.34−1.28 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.8, 141.4, 136.9, 135.8, 131.4, 130.7, 125.7, 116.9, 116.8, 51.7, 40.6, 36.7, 32.2, 29.7, 20.0, 13.8; IR (KBr) υ 3308, 3066, 2929, 1995, 1640, 1530, 1454, 1422, 1307, 1244, 1187,

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1091, 993, 912, 853, 736 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{21}BrN_2O$ $[M]^+$ 336.0837, found 336.0833.

7-Allyl-N-butyl-5-chloroindoline-1-carboxamide (**3i**). 69.4 mg (79%); light yellow solid; mp = 112−117 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.99 (s, 1H), 5.85 (ddt, J = 17.5, 10.3, 6.5 Hz, 1H), 5.11−5.08 (m, 2H), 4.62 (t, J = 5.1 Hz, 1H), 4.04 (t, J = 7.7 Hz, 2H), 3.32 (d, J = 6.5 Hz, 2H), 3.25−3.22 (m, 2H), 2.96 (t, J = 7.7 Hz, 2H), 1.49−1.45 (m, 2H), 1.35−1.29 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.1, 141.0, 136.8, 136.0, 130.4, 129.5, 128.7, 123.0, 117.0, 52.0, 40.8, 36.9, 32.4, 30.0, 20.2, 13.9; IR (KBr) υ 3297, 3065, 2928, 1991, 1639, 1531, 1456, 1424, 1308, 1254, 1188, 1145, 1092, 992, 913, 857, 736 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{21}ClN_2O$ $[M]^+$ 292.1342, found 292.1335.

7-Allyl-N-butyl-6-fluoroindoline-1-carboxamide (**3j**). 68.7 mg (83%); light yellow solid; mp = 76−81 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 6.97 (t, J = 7.2 Hz, 1H), 6.68 (t, J = 9.9 Hz, 1H), 5.90 (ddt, J = 16.8, 10.2, 5.8 Hz, 1H), 4.99−4.96 (m, 2H), 4.83 (br s, 1H), 4.05 (t, J = 7.7 Hz, 2H), 3.41 (d, J = 5.8 Hz, 2H), 3.21−3.18 (m, 2H), 2.89 (t, J = 7.5 Hz, 2H), 1.47−1.42 (m, 2H), 1.32−1.26 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 160.6 (d, J_{C-F} = 240.9 Hz), 156.8, 143.6 (d, J_{C-F} = 7.6 Hz), 135.3, 130.4, 123.0 (d, J_{C-F} = 10.2 Hz), 116.7 (d, J_{C-F} = 20.1 Hz), 115.2, 110.5 (d, J_{C-F} = 23.9 Hz), 52.5, 40.5, 32.1, 30.5, 30.4, 29.3, 20.0, 13.7; IR (KBr) υ 3310, 3071, 2930, 1967, 1644, 1525, 1470, 1309, 1240, 1215, 1139, 1113, 992, 910, 802, 735 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{21}FN_2O$ $[M]^+$ 276.1638, found 276.1636.

7-Allyl-N-butyl-6-chloroindoline-1-carboxamide (**3k**). 77.0 mg (82%); light yellow solid; mp = 87−93 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.05 (d, J = 7.9 Hz, 1H), 6.99 (d, J = 7.9 Hz, 1H), 5.87 (ddt, J = 17.1, 10.1, 5.8 Hz, 1H), 5.01−4.99 (m, 1H), 4.96−4.93 (m, 1H), 4.78 (br s, 1H), 4.06 (t, J = 7.7 Hz, 2H), 3.55 (d, J = 7.4 Hz, 2H), 3.22−3.19 (m, 2H), 2.91 (t, J = 7.7 Hz, 2H), 1.47−1.43 (m, 2H), 1.32−1.27 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.1, 144.1, 134.8, 134.4, 134.0, 127.1, 125.7, 123.5, 115.5, 52.6, 40.6, 34.2, 32.1, 29.7, 20.0, 13.8; IR (KBr) υ 3313, 3055, 2956, 1963, 1647, 1527, 1445, 1427, 1331, 1303, 1265, 1190, 1087, 990, 912, 801, 733 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{16}H_{21}ClN_2O$ $[M]^+$ 292.1342, found 292.1344.

7-Allyl-N-butyl-2-methylindoline-1-carboxamide (**3l**). 68.1 mg (83%); light yellow sticky solid; ^1H NMR (700 MHz, $CDCl_3$) δ 7.05 (d, J = 7.0 Hz, 1H), 7.00 (d, J = 7.4 Hz, 1H), 6.97 (t, J = 7.3 Hz, 1H), 5.91−5.85 (m, 1H), 5.06−5.03 (m, 2H), 4.70 (br s, 1H), 4.64−4.60 (m, 1H), 3.43−3.40 (m, 1H), 3.36−3.28 (m, 2H), 3.27−3.17 (m, 2H), 2.36 (d, J = 6.6 Hz, 1H), 1.48−1.43 (m, 2H), 1.32−1.28 (m, 2H), 1.17 (d, J = 6.7 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.7, 140.5, 136.6, 134.2, 129.1, 128.8, 124.4, 123.4, 115.9, 58.6, 40.4, 36.9, 36.7, 32.2, 21.7, 20.1, 13.8; IR (KBr) υ 3348, 2957, 1969, 1641, 1513, 1445, 1377, 1357, 1298, 1264, 1190, 1108, 1075, 994, 910, 735 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{24}N_2O$ $[M]^+$ 272.1889, found 272.1885.

7-Allyl-N-butyl-3-methylindoline-1-carboxamide (**3m**). 62.6 mg (77%); light yellow solid; mp = 72−76 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.02−6.98 (m, 3H), 5.90 (ddt, J = 16.8, 10.1, 6.3 Hz, 1H), 5.09−5.05 (m, 2H), 4.81 (br s, 1H), 4.22 (t, J = 8.8 Hz, 1H), 3.55−3.52 (m, 1H), 3.36 (d, J = 6.3 Hz, 2H), 3.30−3.17 (m, 3H), 1.47−1.43 (m, 2H), 1.32−1.27 (m, 2H), 1.20 (d, J = 6.8 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.3, 141.7, 140.4, 136.6, 128.9, 128.5, 124.6, 121.5, 116.1, 59.5, 40.5, 36.6, 36.5, 32.2, 20.0, 18.4, 13.8; IR (KBr) υ 3312, 2958, 1959, 1641, 1524, 1443, 1321, 1300, 1243, 1144, 1089, 1059, 993, 910, 735 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{24}N_2O$ $[M]^+$ 272.1889, found 272.1886.

7′-Allyl-N-butylspiro[cyclohexane-1,3′-indoline]-1′-carboxamide (**3n**). 77.0 mg (79%); light yellow solid; mp = 140−146 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.03−6.98 (m, 3H), 5.90 (ddt, J = 17.0, 10.1, 6.4 Hz, 1H), 5.11−5.06 (m, 2H), 4.79 (br s, 1H), 3.89 (s, 2H), 3.36 (d, J = 6.4 Hz, 2H), 3.24−3.21 (m, 2H), 1.71−1.67 (m, 4H), 1.56−1.50 (m, 4H), 1.47−1.43 (m, 2H), 1.41−1.35 (m, 2H), 1.32−1.26 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.6, 144.4, 141.3, 136.5, 129.0, 128.5, 124.7, 120.5, 116.1, 61.3, 46.0, 40.5, 36.4, 35.6, 32.2, 25.6, 23.2, 20.2, 13.8; IR (KBr) υ 3349, 2927, 1994, 1642, 1518, 1442, 1311, 1242, 1146, 1065, 994, 907, 735 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{21}H_{30}N_2O$ $[M]^+$ 326.2358, found 326.2359.

tert-Butyl 7-Allyl-1-(butylcarbamoyl)spiro[indoline-3,4′-piperidine]-1′-carboxylate (**3o**). 79.9 mg (62%); light brown sticky solid; ^1H NMR (700 MHz, $CDCl_3$) δ 7.08−7.04 (m, 2H), 7.00−6.97 (m, 1H), 5.92 (ddt, J = 16.6, 10.2, 6.3 Hz, 1H), 5.11−5.09 (m, 2H), 4.77 (br s, 1H), 4.14−3.97 (m, 5H), 3.36 (d, J = 6.3 Hz, 2H), 3.24−3.21 (m, 2H), 2.88 (br s, 2H), 1.74 (br s, 2H), 1.54−1.46 (m, 3H), 1.45 (s, 9H), 1.32−1.25 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.4, 154.8, 142.7, 141.3, 136.3, 129.6, 128.7, 125.1, 120.7, 116.4, 79.7, 60.2, 44.4, 40.5, 36.2, 32.2, 28.4, 25.1, 20.0, 13.7; IR (KBr) υ 3312, 2929, 1967, 1668, 1525, 1424, 1365, 1237, 1169, 1144, 1091, 969, 911, 862, 732 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{25}H_{37}N_3O_3$ $[M]^+$ 427.2835, found 427.2833.

7-Allyl-N-butyl-3-methyl-3-phenylindoline-1-carboxamide (**3p**). 81.8 mg (78%); light brown solid; mp = 79−83 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.27−7.22 (m, 4H), 7.18 (t, J = 8.4 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 7.2 Hz, 1H), 5.98 (ddt, J = 17.0, 10.1, 6.4 Hz, 1H), 5.16−5.11 (m, 2H), 4.81 (br s, 1H), 4.30 (d, J = 10.8 Hz, 1H), 3.99 (d, J = 10.7 Hz, 1H), 3.43 (d, J = 6.5 Hz, 2H), 3.21−3.12 (m, 2H), 1.65 (s, 3H), 1.37−1.32 (m, 2H), 1.22−1.17 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.3, 145.8, 143.4, 141.9, 136.5, 129.3, 129.0, 128.3, 126.6, 126.5, 125.1, 122.2, 116.3, 67.2, 49.8, 40.3, 36.5, 32.2, 25.5, 19.9, 13.8; IR (KBr) υ 3312, 2958, 2929, 2010, 1644, 1524, 1441, 1317, 1263, 1068, 1029, 912, 758, 735 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{23}H_{28}N_2O$ $[M]^+$ 348.2202, found 348.2204.

8-Allyl-N-butyl-4a-methyl-2,3,4,4a-tetrahydro-1H-carbazole-9-(9aH)-carboxamide (**3q**). 76.1 mg (78%); light yellow solid; mp = 94−101 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.05−7.02 (m, 2H), 6.94 (dd, J = 6.8, 1.6 Hz, 1H), 5.89 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 5.08−5.05 (m, 2H), 4.70 (t, J = 5.3 Hz, 1H), 4.13−4.10 (m, 1H), 3.44−3.28 (m, 2H), 3.25−3.23 (m, 2H), 2.19−2.16 (m, 1H), 2.03−1.99 (m, 1H), 1.53−1.23 (m, 10H), 1.08 (s, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.5, 142.9, 140.9, 136.7, 130.0, 129.2, 125.2, 120.3, 116.1, 70.7, 45.6, 40.6, 36.4, 33.3, 32.5, 30.6, 30.0, 23.6, 22.2, 20.2, 13.9; IR (KBr) υ 3288, 2926, 1994, 1638, 1524, 1436, 1304, 1264, 1187, 1146, 1083, 993, 911, 757, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{21}H_{30}N_2O$ $[M]^+$ 326.2358, found 326.2359.

7-Allyl-N-butyl-3,3-dimethyl-2-phenylindoline-1-carboxamide (**3r**). 87.3 mg (80%); yellow sticky solid; ^1H NMR (700 MHz, $CDCl_3$) δ 7.26−7.23 (m, 3H), 7.11 (d, J = 7.7 Hz, 1H), 7.06−7.03 (m, 3H), 6.91 (dd, J = 7.2, 1.1 Hz, 1H), 5.98 (ddt, J = 16.9, 10.0, 6.7 Hz, 1H), 5.17−5.08 (m, 2H), 4.94 (s, 1H), 4.54 (t, J = 5.3 Hz, 1H), 3.61 (dd, J = 15.8, 6.6 Hz, 1H), 3.46 (dd, J = 15.8, 6.7 Hz, 1H), 3.30−3.26 (m, 1H), 3.21−3.16 (m, 1H), 1.48−1.43 (m, 2H), 1.42 (s, 3H), 1.31−1.25 (m, 2H), 0.89 (t, J = 7.3 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.0, 142.0, 141.2, 140.0, 136.8, 129.4, 128.4, 128.1, 127.7, 126.8, 124.5, 120.5, 116.2, 78.4, 46.3, 40.3, 37.4, 32.5, 32.1, 22.9, 19.9, 13.7; IR (KBr) υ 3346, 2957, 2928, 2007, 1945, 1659, 1505, 1439, 1362, 1290, 1246, 1203, 1138, 1072, 994, 910, 751 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{24}H_{30}N_2O$ $[M]^+$ 362.2358, found 362.2368.

(E)-7-(But-2-enyl)-N-butylindoline-1-carboxamide and (Z)-7-(But-2-enyl)-N-butylindoline-1-carboxamide (**5b**). 72.6 mg (89%); brown solid; mp = 85−89 °C; *E*:*Z* ratio = 1:2.7; ^1H NMR (700 MHz, $CDCl_3$) *E*-isomer, δ 7.05 (d, J = 7.0 Hz, 1H), 7.02 (t, J = 7.1 Hz, 1H), 6.99−6.96 (m, 1H), 5.60−5.45 (m, 2H), 4.70 (br s, 1H), 4.08−4.05 (m, 2H), 3.54 (d, J = 7.0 Hz, 2H), 3.26−3.21 (m, 2H), 2.96−2.93 (m, 2H), 1.67−1.66 (m, 3H), 1.50−1.43 (m, 2H), 1.35−1.28 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); *Z*-isomer, δ 7.05 (d, J = 7.0 Hz, 1H), 7.02 (t, J = 7.1 Hz, 1H), 6.99−6.96 (m, 1H), 5.60−5.45 (m, 2H), 4.74 (br s, 1H), 4.08−4.05 (m, 2H), 3.28 (br s, 2H), 3.26−3.21 (m, 2H), 2.96−2.93 (m, 2H), 1.67−1.66 (m, 3H), 1.50−1.43 (m, 2H), 1.35−1.28 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) *E*-isomer, δ 157.4, 142.2, 135.4, 129.5, 129.2, 128.4, 125.8, 124.8, 122.7, 51.9, 40.7, 35.5, 32.4, 30.2, 20.3, 18.1, 13.9; *Z*-isomer, δ 157.3, 142.1, 135.6, 130.2, 129.1, 128.6, 126.9, 124.6, 122.8, 51.9, 40.7, 35.5, 32.4, 30.1, 20.3, 18.1, 13.9; IR (KBr) υ 3312, 2956, 2928, 2011, 1641, 1525, 1449,

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1308, 1248, 1188, 1152, 1089, 966, 847, 757 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{24}N_2O$ $[M]^+$ 272.1889, found 272.1884.

*(E)-N-Butyl-7-(undec-2-enyl)indoline-1-carboxamide (**5c**).* 93.7 mg (84%); orange sticky solid; *E*:*Z* ratio = 1:2.9; ^1H NMR (700 MHz, $CDCl_3$) *E*-isomer, δ 7.06−7.01 (m, 2H), 6.98−6.96 (m, 1H), 5.53−5.41 (m, 2H), 4.70 (br s, 1H), 4.07 (t, J = 7.6 Hz, 2H), 3.34 (d, J = 7.0 Hz, 2H), 3.26−3.21 (m, 2H), 2.96−2.93 (m, 2H), 2.10−2.07 (m, 2H), 1.50−1.44 (m, 2H), 1.40−1.06 (m, 14H), 0.91 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H); *Z*-isomer, δ 7.06−7.01 (m, 2H), 6.98−6.96 (m, 1H), 5.53−5.41 (m, 2H), 4.74 (br s, 1H), 4.07 (t, J = 7.6 Hz, 2H), 3.29 (d, J = 5.3 Hz, 2H), 3.26−3.21 (m, 2H), 2.96−2.93 (m, 2H), 2.00−1.98 (m, 2H), 1.50−1.44 (m, 2H), 1.40−1.06 (m, 14H), 0.89 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) *E*-isomer, δ 157.4, 142.1, 135.3, 132.0, 130.3, 128.6, 127.3, 124.7, 122.7, 51.9, 40.7, 35.5, 32.4, 32.0, 30.2, 29.8, 29.7, 29.5, 29.4, 27.5, 22.8, 20.3, 13.9; *Z*-isomer, δ 157.3, 142.1, 135.5, 132.7, 129.6, 129.0, 127.8, 124.6, 122.8, 51.9, 40.7, 35.5, 32.7, 32.0, 30.1, 29.8, 29.6, 29.5, 29.4, 27.5, 22.8, 20.3, 14.2; IR (KBr) υ 3313, 2923, 2853, 1966, 1644, 1527, 1450, 1313, 1249, 1188, 969, 850, 763, 735 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{24}H_{38}N_2O$ $[M]^+$ 370.2984, found 370.2980.

*(S,E)-N-Butyl-7-(5,9-dimethyldeca-2,8-dienyl)indoline-1-carboxamide and (S,Z)-N-Butyl-7-(5,9-dimethyldeca-2,8-dienyl)indoline-1-carboxamide (**5d**).* 96.7 mg (84%); orange sticky solid; *E*:*Z* ratio = 1:2.8; ^1H NMR (700 MHz, $CDCl_3$) *E*-isomer, δ 7.06−7.02 (m, 2H), 6.97 (t, J = 7.4 Hz, 1H), 5.53−5.44 (m, 2H), 5.08−5.05 (m, 1H), 4.67 (t, J = 5.6 Hz, 1H), 4.08−4.05 (m, 2H), 3.34 (d, J = 5.8 Hz, 2H), 3.26−3.22 (m, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.11−1.82 (m, 4H), 1.66 (s, 3H), 1.57 (s, 3H), 1.50−1.44 (m, 3H), 1.37−1.29 (m, 3H), 1.16−1.08 (m, 1H), 0.91−0.85 (m, 6H); *Z*-isomer, δ 7.06−7.02 (m, 2H), 6.97 (t, J = 7.4 Hz, 1H), 5.53−5.44 (m, 2H), 5.08−5.05 (m, 1H), 4.70 (t, J = 5.5 Hz, 1H), 4.08−4.05 (m, 2H), 3.31 (d, J = 4.6 Hz, 2H), 3.26−3.22 (m, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.11−1.82 (m, 4H), 1.66 (s, 3H), 1.57 (s, 3H), 1.50−1.44 (m, 3H), 1.37−1.29 (m, 3H), 1.16−1.08 (m, 1H), 0.91−0.85 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) *E*-isomer, δ 157.3, 142.1, 135.5, 131.3, 131.2, 130.5, 129.8, 129.1, 129.0, 128.6, 128.1, 125.1, 125.0, 124.8, 124.6, 122.8, 122.7, 51.9, 40.8, 36.9, 34.8, 33.2, 32.5, 30.4, 25.8, 20.3, 19.7, 17.8, 14.0; *Z*-isomer, δ 157.3, 142.1, 135.5, 131.2, 130.5, 129.8, 129.1, 128.6, 125.0, 124.6, 122.8, 51.9, 40.1, 36.8, 35.7, 34.8, 32.9, 32.5, 30.4, 30.1, 25.9, 25.7, 20.3, 19.6, 17.8, 14.0; IR (KBr) υ 3315, 2925, 1975, 1643, 1527, 1449, 1312, 1249, 1188, 1089, 970, 847, 762, 737 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{25}H_{38}N_2O$ $[M]^+$ 382.2984, found 382.2982.

*N-Butyl-7-cinnamylindoline-1-carboxamide (**5e**).* 85.3 mg (85%); light yellow solid; mp = 121−123 °C; *E*:*Z* ratio = 50>:1; ^1H NMR (700 MHz, $CDCl_3$) *E*-isomer, δ 7.32 (t, J = 8.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.19−7.16 (m, 1H), 7.09−7.08 (m, 2H), 6.99 (t, J = 7.5 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H), 6.28 (dt, J = 15.8, 6.7 Hz, 1H), 4.67 (br s, 1H), 4.07 (t, J = 7.8 Hz, 2H), 3.55 (dd, J = 6.7, 1.2 Hz, 2H), 3.25−3.22 (m, 2H), 2.99 (t, J = 7.7 Hz, 2H), 1.47−1.42 (m, 2H), 1.32−1.26 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) *E*-isomer, δ 157.4, 142.3, 137.7, 135.4, 131.6, 129.3, 129.1, 128.7, 128.6, 127.3, 126.3, 124.7, 123.1, 51.9, 40.9, 36.3, 32.5, 30.2, 20.3, 14.0; IR (KBr) υ 3312, 2926, 1996, 1641, 1525, 1449, 1311, 1247, 1188, 963, 752, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{22}H_{26}N_2O$ $[M]^+$ 334.2045, found 334.2039.

Experimental Procedure and Characterization for the C7-Allylation of Indoline with 2-Vinyloxirane. To an oven-dried sealed tube charged with *N*-butylindoline-1-carboxamide (**1f**) (65.5 mg, 0.3 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 10 mol %), and $Cu(OAc)_2$ (16.3 mg, 30 mol %) in *t*-AmOH (1 mL) was added 2-vinyloxirane (**2g**) (42.1 mg, 0.6 mmol, 200 mol %). The reaction mixture was allowed to stir at room temperature for 20 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 1:1) to afford 59.6 mg of **5g** in 69% yield.

*N-Butyl-7-(4-hydroxybut-2-enyl)indoline-1-carboxamide (**5g**).* Brown sticky solid; *E*:*Z* ratio = 3:1; ^1H NMR (700 MHz, $CDCl_3$) *E*-isomer, δ 7.07−7.00 (m, 2H), 6.97 (t, J = 7.3 Hz, 1H), 5.77−5.67 (m, 2H), 4.66 (br s, 1H), 4.08 (d, J = 5.6 Hz, 2H), 4.04 (t, J = 7.7 Hz, 2H), 3.38 (d, J = 6.1 Hz, 2H), 3.27−3.23 (m, 2H), 2.97 (t, J = 7.7 Hz, 2H), 1.65 (br s, 1H), 1.52−1.45 (m, 2H), 1.37−1.29 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); *Z*-isomer, δ 7.07−7.00 (m, 2H), 6.97 (t, J = 7.3 Hz, 1H), 5.62−5.58 (m, 2H), 4.62 (br s, 1H), 4.17 (d, J = 7.0 Hz, 2H), 4.01 (t, J = 7.7 Hz, 2H), 3.43 (d, J = 7.1 Hz, 2H), 3.27−3.23 (m, 2H), 3.00 (t, J = 7.7 Hz, 2H), 1.65 (br s, 1H), 1.52−1.45 (m, 2H), 1.37−1.29 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) *E*-isomer, δ 157.4, 142.1, 135.4, 130.7, 129.6, 129.1, 128.8, 124.6, 123.1, 63.7, 58.4, 51.9, 40.8, 35.7, 32.4, 30.1, 20.3, 14.0; *Z*-isomer, δ 157.6, 141.9, 134.8, 130.9, 129.6, 129.0, 128.8, 124.7, 122.8, 63.7, 58.4, 51.8, 40.8, 35.7, 32.4, 30.1, 20.3, 14.0; IR (KBr) υ 3313, 2929, 2870, 1946, 1642, 1523, 1450, 1314, 1249, 1187, 1091, 972, 905, 762, 731 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{17}H_{24}N_2O_2$ $[M]^+$ 288.1838, found 288.1837.

Experimental Procedure and Characterization for Olefin Metathesis of 3f. To an oven-dried sealed tube charged with 7-allyl-*N*-butylindoline-1-carboxamide (**3f**) (51.6 mg, 0.2 mmol, 100 mol %) in toluene (1 mL) were added Hoveyda−Grubbs second generation catalyst (8.4 mg, 5 mol %) and ethyl acrylate (60.0 mg, 0.6 mmol, 300 mol %) at room temperature. The reaction mixture was allowed to stir at 100 °C for 24 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 5:1) to afford 40.0 mg of **6a** in 60% yield.

*(E)-Ethyl 4-(1-(Butylcarbamoyl)indolin-7-yl)but-2-enoate (**6a**).* Light brown sticky solid; *E*:*Z* ratio = 50>:1; ^1H NMR (700 MHz, $CDCl_3$) δ 7.07 (d, J = 6.7 Hz, 1H), 7.01−6.94 (m, 3H), 5.81 (d, J = 15.5 Hz, 1H), 4.59 (t, J = 5.3 Hz, 1H), 4.15−4.12 (m, 2H), 4.02 (t, J = 7.8 Hz, 2H), 3.56 (d, J = 6.7 Hz, 2H), 3.25−3.22 (m, 2H), 3.00 (t, J = 7.7 Hz, 2H), 1.49−1.45 (m, 2H), 1.35−1.30 (m, 2H), 1.25−1.22 (m, 3H), 0.90 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.7, 157.1, 147.1, 142.3, 135.0, 129.2, 127.1, 124.6, 123.3, 122.5, 60.3, 51.7, 40.8, 35.9, 32.4, 30.1, 29.8, 20.2, 14.4, 13.9; IR (KBr) υ 3328, 2927, 2975, 1715, 1646, 1523, 1459, 1306, 1263, 1187, 1154, 1042, 983, 905, 845, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{19}H_{26}N_2O_3$ $[M]^+$ 330.1943, found 330.1943.

Experimental Procedure and Characterization for the Intramolecular Cyclization of 6a. To a stirred solution of (*E*)-ethyl 4-(1-(butylcarbamoyl)indolin-7-yl)but-2-enoate (**6a**) (44.4 mg, 0.13 mmol, 100 mol %) in DMF (2 mL) was added NaH (7.8 mg, 0.19 mmol, 150 mol %, 60% dispersion in mineral oil) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. The reaction mixture was quenched and partitioned between EtOAc and H_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 6:1) to afford 18.6 mg of **6b** in 45% yield.

*Ethyl 3-Butyl-4-oxo-1,2,3,4,6,7-hexahydro-[1,3]diazepino[6,7,1-hi]indole-2-carboxylate (**6b**).* Light brown sticky solid; ^1H NMR (700 MHz, $CDCl_3$) δ 7.02 (d, J = 7.0 Hz, 1H), 6.83−6.79 (m, 2H), 4.19 (q, J = 10.8 Hz, 1H), 4.17−4.11 (m, 1H), 4.09−4.05 (m, 2H), 3.74−3.70 (m, 1H), 3.29−3.25 (m, 1H), 3.10 (dd, J = 16.1, 2.5 Hz, 1H), 3.03−2.96 (m, 3H), 2.66−2.65 (m, 1H), 2.36−2.35 (m, 1H), 1.62−1.49 (m, 3H), 1.34−1.29 (m, 2H), 1.18 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 171.6, 156.1, 140.3, 132.5, 129.3, 123.9, 121.8, 120.3, 61.0, 53.2, 51.9, 50.0, 38.1, 36.8, 30.6, 26.7, 20.4, 14.3; IR (KBr) υ 2925, 1730, 1628, 1460, 1423, 1366, 1351, 1307, 1239, 1176, 1106, 1029, 930, 853, 734 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{19}H_{26}N_2O_3$ $[M]^+$ 330.1943, found 330.1944.

General Procedure and Characterization for the Deprotection and Olefin Migration of 3f. To an oven-dried sealed tube charged with 7-allyl-*N*-butylindoline-1-carboxamide (**3f**) (51.6 mg, 0.2 mmol, 100 mol %) in EtOH (2 mL) was added aqueous *s*-KOH solution (1 mL) at room temperature. The reaction mixture was stirred for 20 h at 100 °C and cooled to 0 °C. The reaction mixture was neutralized with aqueous *s*-NH_4Cl solution, and partitioned between EtOAc and H_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column

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chromatography (silica gel, *n*-hexanes/EtOAc = 15:1) to afford 22.3 mg of **6c** in 70% yield.

*(E)-7-(Prop-1-enyl)indoline (**6c**).* Brown sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.02 (d, J = 7.7 Hz, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.34 (dd, J = 15.8, 1.6 Hz, 1H), 6.10 (dq, J = 15.7, 6.5 Hz, 1H), 3.57 (t, J = 8.4 Hz, 2H), 3.03 (t, J = 8.4 Hz, 1H), 1.86 (dd, J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 147.7, 130.3, 127.6, 126.6, 125.2, 123.1, 121.2, 119.9, 47.3, 30.0, 19.1; IR (KBr) υ 3363, 2921, 2850, 1731, 1647, 1590, 1433, 1373, 1333, 1248, 1056, 962, 749 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{11}H_{13}N$ $[M]^+$ 159.1048, found 159.1046.

General Procedure and Characterization for Oxidation of 6c. To an oven-dried sealed tube charged with **6c** (47.8 mg, 0.3 mmol, 100 mol %) in acetone (1 mL) was added 10% Pd/C (8.8 mg) at room temperature. The reaction mixture was stirred for 20 h at 80 °C and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 20:1) to afford 35.4 mg of **6d** in 75% yield.

*(E)-7-(Prop-1-enyl)-1H-indole (**6d**).* Yellow sticky solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.32 (br s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.22−7.20 (m, 1H), 7.18 (d, J = 7.2 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.68 (dd, J = 15.7, 6.6 Hz, 1H), 6.57−6.56 (m, 1H), 6.32−6.27 (m, 1H), 1.98 (dd, J = 8.4 Hz, 1H), 1.86 (dd, J = 6.6, 1.7 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 133.5, 128.3, 127.5, 127.0, 124.0, 121.9, 120.1, 119.9, 119.5, 103.1, 18.9; IR (KBr) υ 3376, 2922, 2848, 1593, 1434, 1248, 1195, 1056, 961, 748 cm^{-1}; HRMS (quadrupole, EI) m/z calcd for $C_{11}H_{11}N$ $[M]^+$ 157.0891, found 157.0891.

Experimental Procedure and Characterization of H/D Exchange Experiment without 2a. To an oven-dried sealed tube charged with *N*-butylindoline-1-carboxamide (**1f**) (65.5 mg, 0.3 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 10 mol %), and $Cu(OAc)_2$ (16.3 mg, 30 mol %) in THF (1 mL) was added MeOD (20 equiv). The reaction mixture was allowed to stir at room temperature for 20 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 8:1) to afford 64.8 mg of **1f**/**deuterio-1f** (79% D incorporation) in 99% yield.

*N-Butylindoline-1-carboxamide (**1f**) and N-Butyl-7-deuterioindoline-1-carboxamide (**deuterio-1f**).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 0.21H), 7.12−7.07 (m, 2H), 6.85 (t, J = 7.3 Hz, 1H), 4.69 (br s, 1H), 3.83 (t, J = 8.5 Hz, 2H), 3.31−3.24 (m, 2H), 3.10 (t, J = 8.5 Hz, 2H), 1.56−1.47 (m, 2H), 1.40−1.28 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H).

Experimental Procedure and Characterization of H/D Exchange Experiment with 2a. To an oven-dried sealed tube charged with *N*-butylindoline-1-carboxamide (**1f**) (65.5 mg, 0.3 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 10 mol %), and $Cu(OAc)_2$ (16.3 mg, 30 mol %) in THF (1 mL) were added allyl methyl carbonate (**2a**) (69.7 mg, 0.6 mmol, 200 mol %) and MeOD (20 equiv). The reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, *n*-hexanes/EtOAc = 8:1 to 6:1) to afford 57.3 mg of **3f** (74% yield) and 13.2 mg of **1f**/**deuterio-1f** (71% D incorporation, 20% yield), respectively.

Kinetic Isotope Effect (KIE) Experiment. To an oven-dried sealed tube charged with **1f** (32.8 mg, 0.15 mmol, 50 mol %), $[RhCp^*Cl_2]_2$ (4.6 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 10 mol %), and $Cu(OAc)_2$ (16.3 mg, 30 mol %) in *t*-AmOH (1 mL) were added allyl methyl carbonate (**2a**) (69.7 mg, 0.6 mmol, 200 mol %) and tetradecane (59.5 mg, 0.3 mmol) as an internal standard. In another reaction tube, **deuterio-1f** (32.9 mg, 0.15 mmol, 50 mol %, >99% D) was used instead of **1f**. The two reactions were allowed to stir at room temperature. An aliquot of each reaction mixture was taken at the time of 10, 20, 30, 40, and 50 min. The relative yield of each product was determined by GC−MS (tetradecane as an internal standard). A kinetic isotope effect value (k_H/k_D) of 2.89 was observed (see the Supporting Information for details).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed kinetic isotope effect (KIE) experiment and ^{1}H NMR and ^{13}C NMR copies of all 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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