JOC The Journal of Organic Chemistry

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Palladium-Catalyzed Enantioselective Heteroannulation of 1,3-Dienes by Functionally Substituted Aryl Iodides

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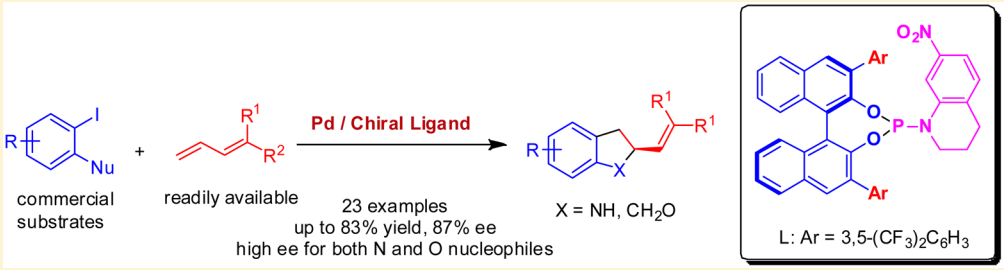
Supporting Information



ABSTRACT: The first enantioselective heteroannulation of 1,3-dienes by 2-iodoanilines and 2-iodobenzylic alcohols is described. The application of a BINOL-derived phosphoramidite ligand bearing electron-withdrawing substituents is the key to obtaining high enantioselectivity. This protocol provides an efficient way to access optically active chiral indolines and isochromans from readily available starting materials.

The development of new methods to obtain novel and valuable compounds in an efficient and stereoselective way remains a long-standing challenge for synthetic organic chemistry. Among these procedures are transition-metal-catalyzed cascade reactions featuring efficient building up complex molecules from simple and easily available substrates.[1] Palladium-catalyzed annulation of 1,3-dienes by functionally substituted aryl halides represents one of the best examples in this category.[2] In this chemistry, pioneered by Dieck[2a] and Larock,[2b] readily available iodobenzene derivatives and 1,3-dienes undergo a palladium-catalyzed tandem Heck[3]/intramolecular Tsuji−Trost allylation[4] process. This methodology provides an ideal approach to access a large range of heterocycles and all-carbon-fused cyclic compounds as shown in Figure 1b. These cyclic structures, from indolines and tetrahydroisoquinolines to dihydrobenzofurans and others are privileged structural motifs found in numerous naturally bioactive alkaloids, drugs, and pharmaceutical agents, as exemplified by oleracein A−D, tremetone, pseudoanguillosporin A, C, and so forth (Figure 1c).[5]

Despite the importance of this versatile methodology, the asymmetric version of this chemistry has not been accomplished until now, though sporadic reports concerning enantioselective tandem Heck/Tsuji−Trost reactions have been found in the last three decades. Shibasaki's group reported a Pd/BINAP-catalyzed intramolecular asymmetric Heck reaction-anion capture process and successfully utilized the methods for the synthesis of a series of natural products.[6] Employing the same catalyst, Overman and co-workers applied a catalytic intramolecular Heck reaction, followed by capture of the resulting η^3-allylpalladium intermediate by a tethered diketopiperazine as the key step in the concise total synthesis of several natural products.[7] Using amino group tethered 1,3-dienes and iodobenzenes as substrates, Helmchen reported a tandem Heck/asymmetric Tsuji−Trost reaction catalyzed by palladium with PHOX as the ligand.[8] In this reaction, besides the limitation of narrow substrate scope, it requires a ten-day reaction time to obtain up to 80% enantiomeric excess with moderate yield. Very recently, Gong reported a Pd/chiral phosphoramidite-catalyzed intermolecular Heck/asymmetric Tsuji−Trost reaction of iodobenzenes, 1,3-dienes, and sodium dialkyl malonates.[9] Back to the chemistry of Dieck and Larock,[2] the challenging part of the asymmetric version is to search for ideal ligands that are appropriate for both Heck reaction and subsequent asymmetric Tsuji−Trost reaction. Herein, we will report the first enantioselective heteroannulation of 1,3-dienes and functionally substituted aryl iodides for the synthesis optically active indolines[10] and isochromans[11] (Figure 1d).

Our study was initiated from the screening of chiral ligands for the reaction of 2-iodoaniline (**1a**) and (*E*)-1-phenylbutadiene (**2a**) in the presence of 5 mol % of $Pd(OAc)_2$ and K_2CO_3 in THF at 80 °C. The resulting reaction mixture was treated with $AcCl/Et_3N$ to convert the product into more stable Ac-protected indoline. (*R*)-BINAP, Trost ligand, and chiral phosphinooxazoline-type P, N ligand, which were frequently employed in the asymmetric Tsuji−Trost reaction and asymmetric Heck reaction, were not able to provide good results (Table 1, entries 1−3). Then, BINOL-derived chiral phosphoramidite ligands were investigated for the cascade reaction. In the presence of ligand **L4**, synthesized from

Received: July 5, 2016
Published: August 26, 2016

DOI: 10.1021/acs.joc.6b01611
J. Org. Chem. 2016, 81, 9402−9408

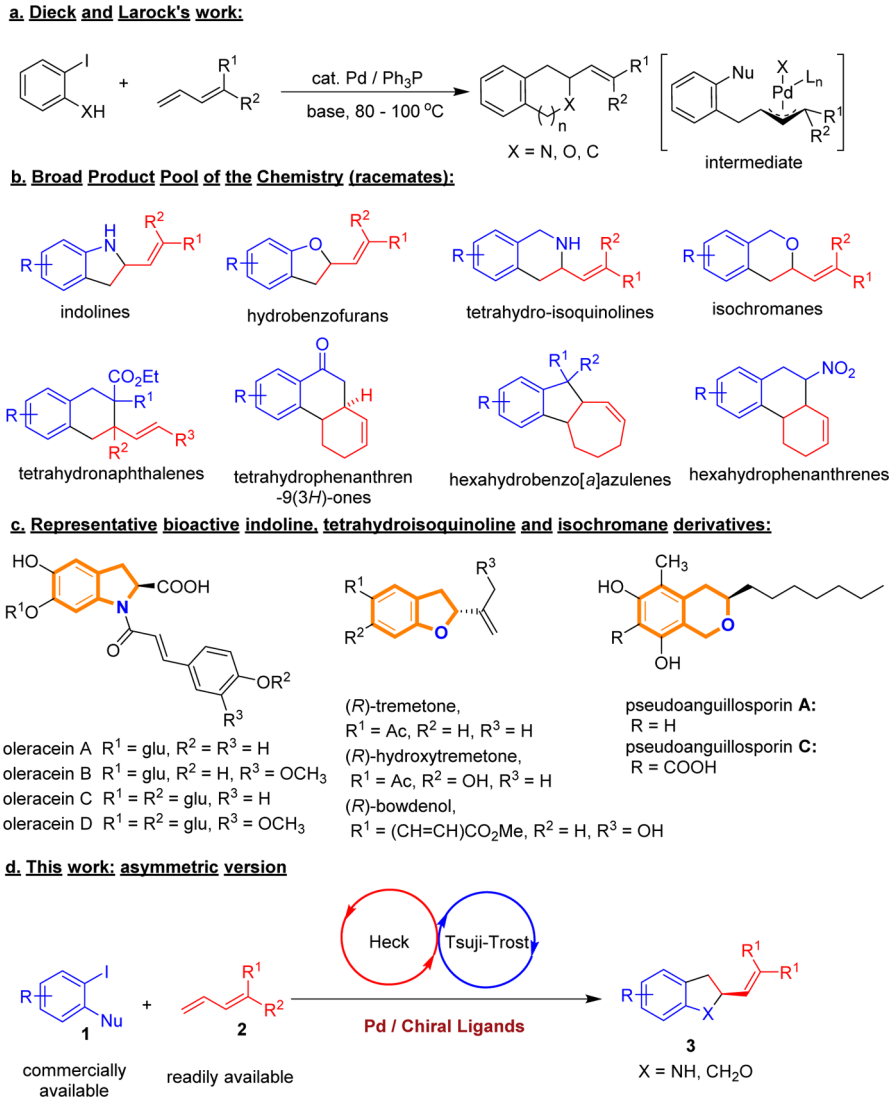


Figure 1. Palladium-catalyzed heteroannulation of 1,3-dienes and functionally substituted aryl iodides.

nonsubstituted BINOL and tetrahydroquinoline, desired product **3a** was obtained with 25% yield but without any enantiomeric excess (entry 4). Introducing electron-withdrawing 4-nitrophenyl groups at the 3,3′-positions of the binaphthyl backbone led to a drastic increase in the yield, albeit still without enantioselectivity (**L5**, entry 5). Replacing the 4-nitrophenyl group with 3,5-$(CF_3)_2C_6H_3$ greatly enhanced the enantioselectivity to 80% ee, however, with a rather poor yield (**L6**, entry 6). Further modifying the tetrahydroquinoline moiety revealed that incorporating an electron-withdrawing group at the 7-position could greatly increase the yield without considerable erosion of the enantioselectivity (entries 7−8). **L8** was identified to be the optimal ligand for the reaction, providing **3a** with 78% yield and 80% enantiomeric excess (entry 8). Noteworthily, **L8** was also the optimal ligand for the intermolecular Heck/asymmetric Tsuji−Trost reaction of iodobenzenes, 1,3-dienes, and sodium dialkyl malonates.[9] A screening of the solvents found DME (dimethoxyethane) to be the best solvent regarding both yield and enantioselectivity (entries 9−12). The reaction did not occur at all without a base. Although several bases were suitable for the reaction, proving satisfying results, $KHCO_3$ could further increase the optical yield from 82 to 83% ee (entries 13−16). Furthermore, tuning the ratio of substrates could slightly increase the enantioselectivity to 84% ee.

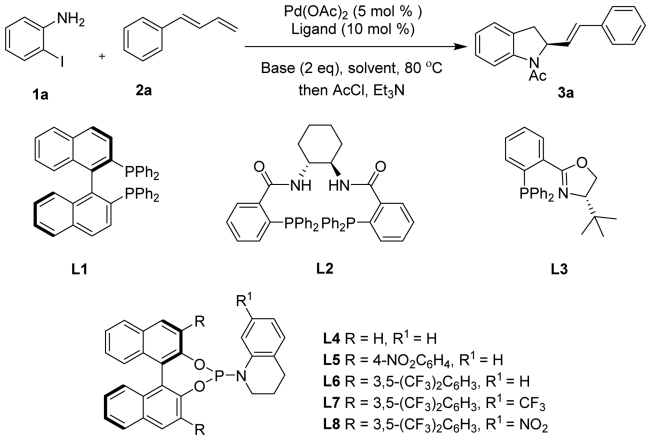
Under the optimized conditions, we next explored the generality of the cascade reaction (Scheme 1). The substrate scope of 1,3-diene was investigated by the reaction of 2-iodoaniline with various substituted 1,3-butadienes. Generally, the reactions went smoothly to give the desired indolines in high enantioselectivities ranging from 75 to 86% ee and up to 78% isolated yield (Scheme 1, **3a**−**3i**).

Arylbutadienes with either electron-withdrawing or -donating substituents were all tolerable for the protocol. The substitution pattern of arylbutadienes **2** exhibited little effect on the yield and enantioselectivity. Notably, cyclohexyl- and diphenyl-substituted 1,3-butadienes could also undergo the cascade reaction to afford the desired indolines with high enantioselectivities (80−82% ee) and moderate yields (**3h**, **3i**). Electron-deficient dienyl ester **2s** was also applicable for the reaction, providing product **3s** with 40% yield and 79% ee (eq 1).

We then moved on to examine the scope of the other substrate **1** by the reaction of a variety of commercially available substituted 2-iodoanilines with 1-phenylbutadiene **2a**

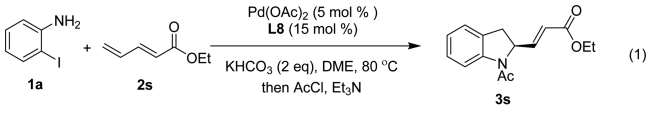
DOI: 10.1021/acs.joc.6b01611
J. Org. Chem. 2016, 81, 9402−9408

Table 1. Optimization of the Reaction Conditions[a]



entry	ligand	solvent	base	conversion (%)	yield (%)[b]	ee (%)[c]
1[d]	**L1**	THF	K_2CO_3	50	18	4
2[d]	**L2**	THF	K_2CO_3	<5	trace	4
3	**L3**	THF	K_2CO_3	<5	trace	7
4	**L4**	THF	K_2CO_3	45	25	0
5	**L5**	THF	K_2CO_3	>95	80	0
6	**L6**	THF	K_2CO_3	58	34	80
7	**L7**	THF	K_2CO_3	>95	82	70
8	**L8**	THF	K_2CO_3	>95	78	80
9	**L8**	2-Me-THF	K_2CO_3	>95	85	79
10	**L8**	^{t}BuOMe	K_2CO_3	59	28	79
11	**L8**	1,4-dioxane	K_2CO_3	70	58	27
12	**L8**	DME	K_2CO_3	>95	88	82
13	**L8**	DME	Na_2CO_3	88	54	82
14	**L8**	DME	K_3PO_4	>95	80	82
15	**L8**	DME	DIPEA	>95	70	82
16	**L8**	DME	$KHCO_3$	>95	85	83
17[e]	**L8**	DME	$KHCO_3$	>95	85	83
18[f]	**L8**	DME	$KHCO_3$	>95	77	84

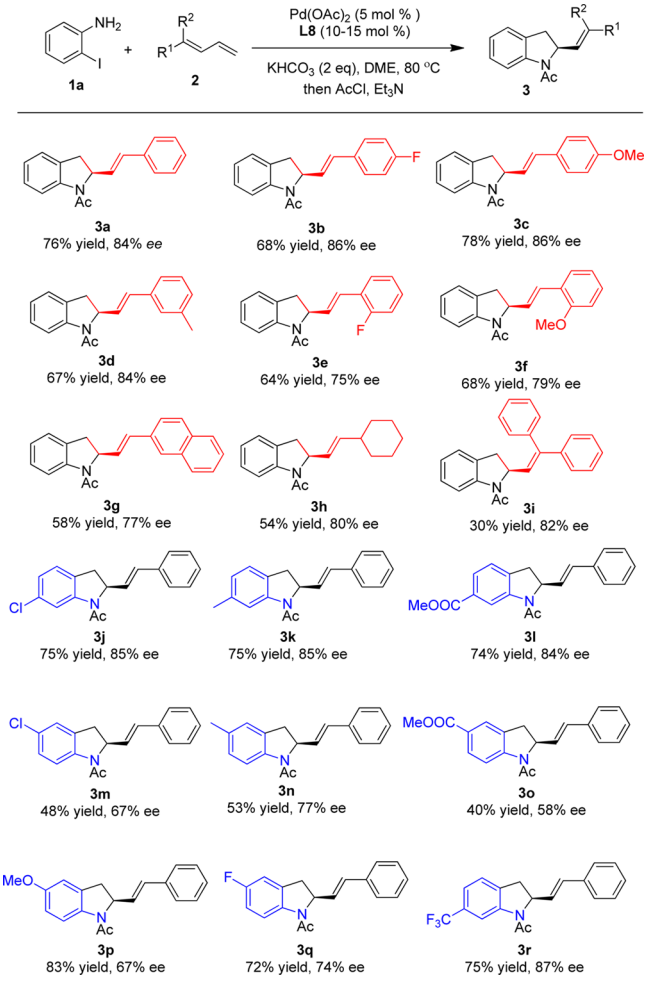
[a]Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (5 mol %), **L** (10 mol %), **2a** (1.1 equiv), solvent (1 mL), 80 °C, 15 h, under Ar. [b]On the basis of ^{1}H NMR analysis of the crude reaction mixture using trimethylbenzene-1,3,5-tricarboxylate as an internal standard. [c]Determined by HPLC. [d]Using 5 mol % ligand. [e]Reaction carried out with **1a** (0.1 mmol) and **2a** (0.2 mmol). [f]Reaction carried out with **1a** (0.2 mmol) and **2a** (0.1 mmol).



40% yield, 79% ee

(**3j**–**3r**). Notably, the position of the substituent on the benzene ring of 2-iodoanilines exhibited significant effect on both enantioselectivity and yield. It could be concluded that 5-substituted 2-iodoanilines provided much higher yield and stereoselectivity than those with substituents at 4-position (**3j**, **3k**, **3l** vs **3m**, **3n**, **3o**, respectively). Generally, 5-substituted 2-iodoanilines provided the corresponding indolines with high enantioselectivities (84–87% ee) and good yields (74–75%), whereas 4-substituted substrates gave much poorer results (40–83% yield, 58–77% ee). On the other hand, the electronic property of the substituents showed an obscure influence on the outcome of the reaction.

Scheme 1. Scope of 1,3-Dienes[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.1 mmol), $Pd(OAc)_2$ (5 mol %), **L8** (15 mol %), DME (1.0 mL), 80 °C, 15 h, under Ar; 15 mol % ligand was used to obtain stable and repeatable results except for **3a**.

In the meantime, we altered the nucleophile from *o*-iodolanilines to *o*-iodobenzyl alcohol under the same reaction conditions. To our delight, upon the reaction with several arylbutadienes, chiral isochromans could also be obtained with high enantioselectivities and moderate yields (Scheme 2, **5a**–**5d**).

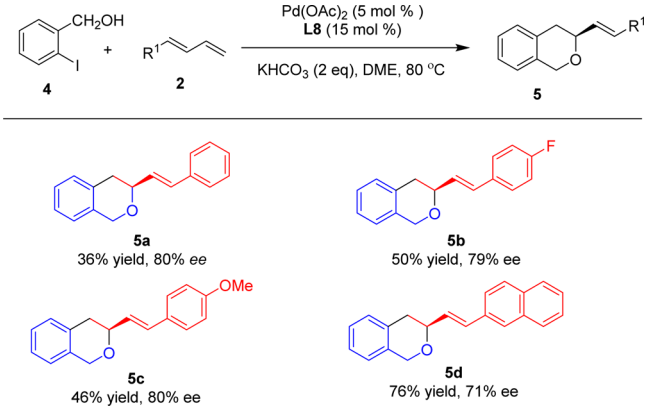
In summary, we have developed, to the best of our knowledge, the first palladium-catalyzed enantioselective heteroannulation of 1,3-dienes by 2-iodoanilines and 2-iodobenzylic alcohols. The employment of a BINOL-derived phosphoramidite ligand bearing electron-withdrawing substituents is crucial for the stereocontrol of the reaction. With the same ligand, both 2-iodoanilines and 2-iodobenzyl alcohol were well tolerated for this cascade reaction. This protocol provides an efficient way to access optically active chiral indolines and isochromans from readily available starting materials.

EXPERIMENTAL SECTION

General Method. NMR spectra were recorded on a 400 MHz spectrometer. HRMS spectra were recorded on a TOF-Q mass spectrometer. The enantiomeric excess of the compounds was determined by chiral HPLC using racemic compounds as references. All solvents were purified and dried according to standard methods

DOI: 10.1021/acs.joc.6b01611
J. Org. Chem. 2016, 81, 9402–9408

Scheme 2. Synthesis of Isochromanes[a]



[a]Reaction conditions: **4** (0.2 mmol), **2** (0.1 mmol), $Pd(OAc)_2$ (5 mol %), **L8** (15 mol %), DME (1.0 mL), 80 °C, 48 h, under Ar.

prior to use, unless stated otherwise. For the synthesis procedure and determination of the absolute configuration, see the Supporting Information.

General Reaction Procedures. To a flame-dried and Ar-purged Schlenk tube (10 mL) were added $Pd(OAc)_2$ (0.05 equiv), phosphoramidite **L8** (0.15 equiv), potassium bicarbonate (2.0 equiv), 2-iodoaniline (2.0 equiv), and a stir bar. The Schlenk tube was then evacuated and filled with argon. This cycle was repeated three times and followed by addition of aryl butadiene (0.1 mmol) and DME (1 mL) via syringe. The mixture was stirred at 80 °C for 15 h and was then cooled to 0 °C. To the reaction mixture at 0 °C was slowly added Et_3N (15 equiv) and acetyl chloride (10 equiv). The resulting mixture was stirred at room temperature for 30 min and then filtered through silica gel and washed with ethyl acetate. The organic phase was concentrated in vacuo. The product was purified by column chromatography on silica gel (eluent, PE/EA = 10:1 or PE/*t*-BuOH = 20:1).

Characterization of Products 3 and 5. *(S,E)-1-(2-Styrylindolin-1-yl)ethanone (**3a**).* Colorless oil. Yield: 76%, 20.0 mg. $[\alpha]_D^{20}$ −56.0 (*c* 0.16, $CHCl_3$). Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 13.35 min (minor), t_R = 14.90 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.4 Hz, 1H), 7.34−7.15 (m, 7H), 7.09−6.98 (m, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.02−4.92 (m, 1H), 3.59 (dd, *J* = 14.5, 10.2 Hz, 1H), 2.92 (d, *J* = 15.9 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 142.3, 135.8, 130.6, 129.5, 128.6, 128.4, 128.0, 127.6, 126.5, 124.7, 123.9, 117.5, 62.2, 36.1, 23.9. IR (KBr) γ 2955, 2921, 2850, 1658, 1460, 1396, 1021, 755, 694 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{18}ON$: 264.1383; observed: 264.1378. For the absolute configuration determination process of **3a**, see the Supporting Information.

*(S,E)-1-(2-(4-Fluorostyryl)indolin-1-yl)ethanone (**3b**).* Colorless oil. Yield: 68%, 19.1 mg. $[\alpha]_D^{20}$ −45.6 (*c* 0.15, $CHCl_3$). Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 13.29 min (minor), t_R = 14.98 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.6 Hz, 1H), 7.30−7.15 (m, 4H), 7.04 (dd, *J* = 8.2, 7.5 Hz, 1H), 6.97 (t, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.08−4.84 (m, 1H), 3.75−3.33 (m, 1H), 2.91 (d, *J* = 15.9 Hz, 1H), 2.26 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 162.5 (d, *J* = 247.6 Hz), 142.3, 132.0, 129.5, 129.3, 128.2, 128.0 (d, *J* = 8.1 Hz), 127.7, 124.8, 123.9, 117.5, 115.5 (d, *J* = 21.6 Hz), 62.1, 36.1, 23.9. IR (KBr) γ 2955, 2921, 2851, 1659, 1460, 1379, 1226, 1091, 1020, 756 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{17}ONF$: 282.1289; observed: 282.1282.

*(S,E)-1-(2-(4-Methoxystyryl)indolin-1-yl)ethanone (**3c**).* Colorless oil. Yield: 78%, 22.8 mg. $[\alpha]_D^{20}$ −56.6 (*c* 0.24, $CHCl_3$). Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 20.50 min (minor), t_R = 22.65 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.8 Hz, 1H), 7.27−7.14 (m, 4H), 7.03 (td, *J* = 7.5, 0.7 Hz, 1H), 6.88−6.72 (m, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.05 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.03−4.80 (m, 1H), 3.77 (s, 3H), 3.56 (dd, *J* = 14.7, 9.9 Hz, 1H), 2.90 (d, *J* = 15.9 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 159.5, 142.4, 130.0, 129.7, 128.5, 127.7, 127.6, 126.2, 124.7, 123.8, 117.4, 114.0, 62.3, 55.2, 36.2, 23.9. IR (KBr) γ 2955, 2922, 2852, 1658, 1510, 1460, 1395, 1249, 1027 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{19}H_{20}O_2N$: 294.1489; observed: 294.1483.

*(S,E)-1-(2-(3-Methylstyryl)indolin-1-yl)ethanone (**3d**).* Colorless oil. Yield: 67%, 18.6 mg. $[\alpha]_D^{20}$ −54.4 (*c* 0.26, $CHCl_3$). Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 11.06 min (minor), t_R = 13.04 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.0 Hz, 1H), 7.25−6.99 (m, 7H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.10−4.84 (m, 1H), 3.59 (dd, *J* = 15.0, 10.1 Hz, 1H), 2.92 (d, *J* = 15.9 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 142.4, 138.2, 135.8, 130.7, 129.6, 128.8, 128.5, 128.2, 127.6, 127.1, 124.7, 123.9, 123.7, 117.5, 62.3, 36.2, 23.9, 21.3. IR (KBr) γ 2954, 2921, 2851, 1660, 1460, 1395, 1021, 756 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{19}H_{20}ON$: 278.1539; observed: 278.1535.

*(S,E)-1-(2-(2-Fluorostyryl)indolin-1-yl)ethanone (**3e**).* Colorless oil. Yield: 64%, 18.0 mg. $[\alpha]_D^{20}$ −37.8 (*c* 0.28, $CHCl_3$). Enantiomeric excess: 75%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 11.37 min (minor), t_R = 19.42 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.7 Hz, 1H), 7.35 (td, *J* = 7.7, 1.6 Hz, 1H), 7.25−7.12 (m, 3H), 7.10−6.94 (m, 3H), 6.66 (d, *J* = 16.1 Hz, 1H), 6.29 (dd, *J* = 16.1, 7.3 Hz, 1H), 5.07−4.88 (m, 1H), 3.60 (dd, *J* = 14.6, 10.3 Hz, 1H), 2.92 (d, *J* = 16.0 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 160.3 (d, *J* = 249.8 Hz), 142.3, 131.1 (d, *J* = 3.9 Hz), 129.5, 129.3 (d, *J* = 8.4 Hz), 127.7, 127.5 (d, *J* = 3.6 Hz), 124.7, 124.1 (d, *J* = 2.5 Hz), 123.9, 123.7 (d, *J* = 12.7 Hz), 123.3 (d, *J* = 2.1 Hz), 117.5, 115.8 (d, *J* = 22.1 Hz), 62.5, 36.1, 23.9. IR (KBr) γ 2955, 2922, 2851, 1660, 1482, 1460, 1395, 756 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{17}ONF$: 282.1289; observed: 282.1283.

*(S,E)-1-(2-(2-Methoxystyryl)indolin-1-yl)ethanone (**3f**).* Colorless oil. Yield: 68%, 19.9 mg. $[\alpha]_D^{20}$ −19.7 (*c* 0.20, $CHCl_3$). Enantiomeric excess: 79%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 13.20 min (minor), t_R = 15.06 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.8 Hz, 1H), 7.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24−7.11 (m, 3H), 7.08−6.96 (m, 1H), 6.92−6.80 (m, 3H), 6.21 (dd, *J* = 16.0, 7.8 Hz, 1H), 5.12−4.78 (m, 1H), 3.81 (s, 3H), 3.58 (dd, *J* = 15.5, 10.0 Hz, 1H), 2.92 (d, *J* = 16.0 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 156.8, 142.4, 129.8, 129.1, 129.0, 127.5, 126.9, 125.9, 124.8, 124.7, 123.7, 120.6, 117.5, 110.9, 62.9, 55.4, 36.3, 24.0. IR (KBr) γ 2955, 2920, 2850, 1657, 1461, 1395, 1247, 1023, 754 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{19}H_{20}O_2N$: 294.1489; observed: 294.1484.

*(S,E)-1-(2-(2-(Naphthalen-2-yl)vinyl)indolin-1-yl)ethanone (**3g**).* Colorless oil. Yield: 58%, 18.1 mg. $[\alpha]_D^{20}$ +17.9 (*c* 0.07, $CHCl_3$). Enantiomeric excess: 77%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 16.88 min (minor), t_R = 18.51 min (major). ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 6.8 Hz, 1H), 7.84−7.63 (m, 4H), 7.54−7.36 (m, 3H), 7.27−7.16 (m, 2H), 7.05 (td, *J* = 7.4, 0.9 Hz, 1H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.10−4.91 (m, 1H), 3.60 (dd, *J* = 14.7, 10.1 Hz, 1H), 2.95 (d, *J* = 15.9 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 142.4, 133.4, 133.2, 133.1, 130.7, 129.6, 128.7, 128.3, 127.9, 127.7, 127.6, 126.7, 126.4, 126.1, 124.8, 123.9, 123.3, 117.5, 62.3, 36.2, 23.9. IR (KBr) γ 2955, 2921, 2850, 1459, 1376, 1093, 1022, 756 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{22}H_{20}ON$: 314.1539; observed: 314.1534.

DOI: 10.1021/acs.joc.6b01611
J. Org. Chem. 2016, 81, 9402−9408

*(S,E)-1-(2-(2-Cyclohexylvinyl)indolin-1-yl)ethanone (**3h**).* Colorless oil. Yield: 54%, 14.5 mg. $[\alpha]_D^{20}$ −12.4 (*c* 0.26, $CHCl_3$). Enantiomeric excess: 80%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 10.33 min (minor), t_R = 12.10 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, *J* = 12.9 Hz, 1H), 7.24−7.10 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.57 (dd, *J* = 15.5, 6.4 Hz, 1H), 5.41 (dd, *J* = 15.6, 7.3 Hz, 1H), 4.73 (t, *J* = 8.0 Hz, 1H), 3.50 (dd, *J* = 15.6, 9.9 Hz, 1H), 2.80 (d, *J* = 15.9 Hz, 1H), 2.22 (s, 3H), 1.99−1.85 (m, 1H), 1.75−1.55 (m, 4H). 1.38−0.86 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 142.4, 138.0, 129.8, 127.5, 126.6, 124.6, 123.7, 117.4, 62.4, 40.0, 36.3, 32.7, 32.6, 26.0, 25.9, 23.9. IR (KBr) γ 2954, 2923, 2852, 1662, 1459, 1396, 1022, 755 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{24}ON$: 270.1852; observed: 270.1849.

*(S)-1-(2-(2,2-Diphenylvinyl)indolin-1-yl)ethanone (**3i**).* Colorless oil. Yield: 30%, 10.1 mg. $[\alpha]_D^{20}$ −143.5 (*c* 0.12, $CHCl_3$). Enantiomeric excess: 82%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 11.07 min (major), t_R = 12.59 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.3 Hz, 1H), 7.53−7.35 (m, 3H), 7.26−7.14 (m, 9H), 7.03 (td, *J* = 7.4, 1.0 Hz, 1H), 6.14 (d, *J* = 9.5 Hz, 1H), 4.84 (t, *J* = 8.6 Hz, 1H), 3.59 (dd, *J* = 15.2, 10.1 Hz, 1H), 3.09 (d, *J* = 15.8 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 142.7, 142.2, 140.8, 138.7, 129.8, 129.7, 128.6, 128.3, 128.2, 128.0, 127.9, 127.7, 127.4, 124.6, 123.8, 117.5, 59.3, 37.0, 23.7. IR (KBr) γ 2955, 2921, 2851, 1460, 1378, 1093, 1023, 762 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{24}H_{22}ON$: 340.1696; observed: 340.1687.

*(S,E)-1-(6-Chloro-2-styrylindolin-1-yl)ethanone (**3j**).* Colorless oil. Yield: 75%, 22.3 mg. $[\alpha]_D^{20}$ −64.7 (*c* 0.10, $CHCl_3$). Enantiomeric excess: 85%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 10.72 min (minor), t_R = 12.30 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.34−7.23 (m, 5H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.09−4.88 (m, 1H), 3.52 (dd, *J* = 15.7, 9.8 Hz, 1H), 2.87 (d, *J* = 16.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 143.3, 135.6, 133.1, 130.8, 128.6, 128.1, 128.0, 127.9, 126.5, 125.4, 123.8, 117.7, 62.7, 35.6, 23.8. IR (KBr) γ 2955, 2921, 2851, 1664, 1474, 1418, 1390, 1093, 1022 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{17}ONCl$: 298.0993; observed: 298.0987.

*(S,E)-1-(6-Methyl-2-styrylindolin-1-yl)ethanone (**3k**).* Colorless oil. Yield: 75%, 20.9 mg. $[\alpha]_D^{20}$ −72.9 (*c* 0.14, $CHCl_3$). Enantiomeric excess: 85%, determined by HPLC (CHIRALPAK IC-H, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 10.47 min (minor), t_R = 11.67 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.33−7.19 (m, 5H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.02−4.86 (m, 1H), 3.52 (dd, *J* = 14.5, 10.2 Hz, 1H), 2.85 (d, *J* = 15.8 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 142.4, 137.5, 135.9, 130.4, 128.6, 128.5, 128.0, 126.6, 126.4, 124.6, 124.3, 118.2, 62.5, 35.8, 23.9, 21.6. IR (KBr) γ 2955, 2921, 2850, 1658, 1460, 1378, 1022, 755 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{19}H_{20}ON$: 278.1539; observed: 278.1534.

*(S,E)-Methyl 1-Acetyl-2-styrylindoline-6-carboxylate (**3l**).* Colorless oil. Yield: 74%, 23.8 mg. $[\alpha]_D^{20}$ −97.8 (*c* 0.50, $CHCl_3$). Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 56.31 min (minor), t_R = 61.99 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 7.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.32−7.20 (m, 6H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.14−4.92 (m, 1H), 3.91 (s, 3H), 3.62 (dd, *J* = 15.0, 9.6 Hz, 1H), 2.97 (d, *J* = 16.6 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 167.0, 142.5, 135.7, 134.9, 130.8, 130.0, 128.6, 128.2, 127.9, 126.5, 125.9, 124.6, 118.2, 62.3, 52.1, 36.2, 23.9. IR (KBr) γ 2922, 1717, 1663, 1433, 1392, 1277, 1088, 758 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for$C_{20}H_{20}O_3N$: 322.1438; observed: 322.1434.

*(S,E)-1-(5-Chloro-2-styrylindolin-1-yl)ethanone (**3m**).* Colorless oil. Yield: 48%, 14.3 mg. $[\alpha]_D^{20}$ +7.6 (*c* 0.18, $CHCl_3$). Enantiomeric excess: 67%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 16.81 min (minor), t_R = 18.29 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.7 Hz, 1H), 7.32−7.11 (m, 7H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.1 Hz, 1H), 5.04−4.82 (m, 1H), 3.54 (dd, *J* = 15.6, 9.9 Hz, 1H), 2.87 (d, *J* = 16.2 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 141.0, 135.6, 131.5, 130.8, 128.7, 128.6, 128.4, 128.1, 127.8, 127.5, 126.5, 124.9, 118.3, 62.3, 35.9, 23.8. IR (KBr) γ 2955, 2921, 2851, 1661, 1468, 1392, 1091, 1021 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{17}ONCl$: 298.0993; observed: 298.0989.

*(S,E)-1-(5-Methyl-2-styrylindolin-1-yl)ethanone (**3n**).* Colorless oil. Yield: 53%, 14.9 mg. $[\alpha]_D^{20}$ −29.1 (*c* 0.14, $CHCl_3$). Enantiomeric excess: 77%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 13.26 min (minor), t_R = 16.14 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 1H), 7.33−7.20 (m, 5H), 7.10−6.89 (m, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.93 (t, *J* = 7.3 Hz, 1H), 3.54 (dd, *J* = 15.4, 9.9 Hz, 1H), 2.85 (d, *J* = 15.9 Hz, 1H), 2.30 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 140.1, 135.8, 133.5, 130.4, 129.6, 128.6, 128.5, 128.0, 128.0, 126.4, 125.4, 117.2, 62.2, 36.1, 23.8, 20.9. IR (KBr) γ 2955, 2921, 2851, 1460, 1378, 1093, 1022, 761 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{19}H_{20}ON$: 278.1539; observed: 278.1535.

*(S,E)-Methyl 1-Acetyl-2-styrylindoline-5-carboxylate (**3o**).* Colorless oil. Yield: 40%, 12.8 mg. $[\alpha]_D^{20}$ +24.0 (*c* 0.28, $CHCl_3$). Enantiomeric excess: 58%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 21.70 min (major), t_R = 24.53 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38−8.14 (m, 1H), 7.98−7.93 (m, 1H), 7.86 (s, 1H), 7.36−7.20 (m, 5H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.25−4.91 (m, 1H), 3.89 (s, 3H), 3.61 (dd, *J* = 15.6, 10.0 Hz, 1H), 2.97 (d, *J* = 16.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 166.7, 146.2, 135.6, 131.0, 130.3, 129.8, 128.7, 128.2, 127.9, 126.5, 126.3, 125.6, 116.7, 62.6, 51.9, 35.7, 24.1. IR (KBr) γ 2955, 2922, 2851, 1716, 1669, 1448, 1382, 1261, 1212 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{20}H_{20}O_3N$: 322.1438; observed: 322.1429.

*(S,E)-1-(5-Methoxy-2-styrylindolin-1-yl)ethanone (**3p**).* Brown oil. Yield: 83%, 24.3 mg. $[\alpha]_D^{20}$ −28.7 (*c* 0.44, $CHCl_3$). Enantiomeric excess: 67%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 21.55 min (minor), t_R = 24.83 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 1H), 7.34−7.20 (m, 5H), 6.86−6.67 (m, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.97 (t, *J* = 8.1 Hz, 1H), 3.78 (s, 3H), 3.59 (dd, *J* = 16.0, 9.7 Hz, 1H), 2.89 (d, *J* = 16.1 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 156.5, 136.1, 135.8, 131.2, 130.5, 128.6, 128.3, 128.1, 126.5, 118.1, 112.1, 111.0, 62.4, 55.6, 36.3, 23.7. IR (KBr) γ 2956, 2924, 2852, 1652, 1487, 1460, 1395, 1272, 1192, 1033 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{19}H_{20}O_2N$: 294.1489; observed: 294.1486.

*(S,E)-1-(5-Fluoro-2-styrylindolin-1-yl)ethanone (**3q**).* Colorless oil. Yield: 72%, 20.2 mg. $[\alpha]_D^{20}$ −52.5 (*c* 0.34, $CHCl_3$). Enantiomeric excess: 74%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 50.12 min (minor), t_R = 54.70 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 4.7 Hz, 1H), 7.34−7.21 (m, 5H), 7.00−6.72 (m, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.9, 7.1 Hz, 1H), 4.98 (t, *J* = 7.6 Hz, 1H), 3.57 (dd, *J* = 15.9, 9.8 Hz, 1H), 2.89 (d, *J* = 16.2 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 159.4 (d, *J* = 242.4 Hz), 138.5, 135.7, 131.6 (d, *J* = 8.3 Hz), 130.8, 128.6, 128.1, 128.0, 126.5, 118.2 (d, *J* = 7.8 Hz), 113.9 (d, *J* = 22.6 Hz), 112.0 (d, *J* = 24.0 Hz),111.9, 62.4, 36.0, 23.7. IR (KBr) γ 2955, 2924, 1659, 1481, 1393, 1356, 1259, 1180, 751 cm^{-1}. HRMS (ESI) *m*/*z* (M + H)$^+$ calcd for $C_{18}H_{17}ONF$: 282.1289; observed: 282.1285.

*(S,E)-1-(2-Styryl-6-(trifluoromethyl)indolin-1-yl)ethanone (**3r**).* Brown oil. Yield: 75%, 24.8 mg. $[\alpha]_D^{20}$ −57.5 (*c* 0.48, $CHCl_3$).

DOI: 10.1021/acs.joc.6b01611
J. Org. Chem. 2016, 81, 9402−9408

Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 27.32 min (minor), t_R = 29.43 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.35−7.23 (m, 7H), 6.51 (d, J = 15.9 Hz, 1H), 6.19 (dd, J = 15.9, 7.1 Hz, 1H), 5.14−4.89 (m, 1H), 3.62 (dd, J = 16.0, 10.0 Hz, 1H), 2.98 (d, J = 16.5 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 142.8, 135.5, 133.5, 131.1, 130.2 (q, J = 32.0 Hz), 128.7, 128.3, 127.7, 126.5, 124.9, 124.2 (q, J = 272.4 Hz), 120.9 (q, J = 3.8 Hz), 114.4, 62.4, 36.1, 23.9. IR (KBr) γ 2955, 2922, 2852, 1667, 1438, 1395, 1324, 1290, 1162, 1122, 1060, 1022, 751 cm^{-1}. HRMS (ESI) m/z (M + H)$^+$ calcd for $C_{19}H_{17}ONF_3$: 332.1257; observed: 332.1251.

*(S,E)-Ethyl 3-(1-Acetylindolin-2-yl)acrylate (**3s**).*[12] Yellow oil. Yield: 40%, 10.3 mg. $[\alpha]_D^{20}$ −77.1 (c 0.14, $CHCl_3$). Enantiomeric excess: 79%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.97 min (minor), t_R = 20.55 min (major). ^{1}H NMR (400 MHz, DMSO) δ 8.04 (d, J = 7.0 Hz, 1H), 7.30−7.12 (m, 2H), 7.03 (t, J = 7.5 Hz, 1H), 6.88 (dd, J = 15.5, 5.1 Hz, 1H), 5.77 (dd, J = 15.7, 1.0 Hz, 1H), 5.29 (dd, J = 9.6, 5.5 Hz, 1H), 4.08 (q, J = 7.1 Hz, 2H), 3.53 (dd, J = 16.4, 9.3 Hz, 1H), 2.89 (d, J = 16.2 Hz, 1H), 2.12 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.52, 165.14, 146.97, 142.04, 129.61, 127.30, 125.12, 123.76, 120.02, 116.44, 60.23, 59.78, 39.52, 34.22, 23.40, 14.00.

*(S,E)-3-Styrylisochroman (**5a**).* Colorless oil. Yield: 36%, 8.5 mg. $[\alpha]_D^{20}$ −91.0 (c 0.13, $CHCl_3$). Enantiomeric excess: 80%, determined by HPLC (CHIRALCEL OD-H, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.70 min (minor), t_R = 11.47 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.27−7.14 (m, 4H), 7.07−6.98 (m, 1H), 6.72 (d, J = 16.0 Hz, 1H), 6.36 (dd, J = 16.0, 5.9 Hz, 1H), 5.01−4.84 (m, 2H), 4.46−4.31 (m, 1H), 2.96 (dd, J = 16.2, 10.4 Hz, 1H), 2.87 (dd, J = 16.2, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 134.5, 132.9, 131.0, 129.4, 128.8, 128.5, 127.7, 126.5, 126.5, 126.1, 124.2, 75.1, 68.0, 34.2. IR (KBr) γ 2955, 2921, 2851, 1460, 1377, 1271, 1023, 750 cm^{-1}. HRMS (ESI) m/z (M + H)$^+$ calcd for $C_{17}H_{17}O$: 237.1274; observed: 237.1272.

*(S,E)-3-(4-Fluorostyryl)isochroman (**5b**).* Colorless oil. Yield: 50%, 12.7 mg. $[\alpha]_D^{20}$ −102.0 (c 0.20, $CHCl_3$). Enantiomeric excess: 79%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.16 min (minor), t_R = 6.05 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−6.96 (m, 8H), 6.68 (d, J = 16.0 Hz, 1H), 6.27 (dd, J = 15.9, 5.4 Hz, 1H), 5.01−4.81 (m, 2H), 4.44−4.27 (m, 1H), 3.02−2.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ162.4 (d, J = 246.9 Hz), 134.4, 132.9, 132.8, 129.8, 129.2 (d, J = 2.2 Hz), 128.8, 128.0 (d, J = 8.0 Hz), 126.5, 126.2, 124.2, 115.5 (d, J = 21.6 Hz), 75.0, 68.0, 34.2. IR (KBr) γ 2922, 2849, 1507, 1276, 1261, 1227, 1088, 965, 748 cm^{-1}. HRMS (ESI) m/z (M + H)$^+$ calcd for $C_{17}H_{16}OF$: 255.1180; observed: 255.1176.

*(S,E)-3-(4-Methoxystyryl)isochroman (**5c**).* Colorless oil. Yield: 46%, 12.2 mg. $[\alpha]_D^{20}$ −39.2 (c 0.24, $CHCl_3$). Enantiomeric excess: 80%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.36 min (minor), t_R = 8.18 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.4 Hz, 2H), 7.22−7.09 (m, 3H), 7.07−6.95 (m, 1H), 6.86 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 16.0 Hz, 1H), 6.22 (dd, J = 16.0, 6.0 Hz, 1H), 5.00−4.81 (m, 2H), 4.41−4.27 (m, 1H), 3.81 (s, 3H), 3.05−2.74 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 134.5, 133.1, 130.7, 129.4, 128.8, 127.7, 127.2, 126.4, 126.1, 124.23, 114.0, 75.3, 68.0, 55.3, 34.3. IR (KBr) γ 2922, 2849, 1507, 1276, 1261, 1227, 1088, 748 cm^{-1}. HRMS (ESI) m/z (M + H)$^+$ calcd for $C_{18}H_{19}O_2$: 267.1380; observed: 267.1380.

*(S,E)-3-(2-(Naphthalen-2-yl)vinyl)isochroman (**5d**).* Colorless oil. Yield: 76%, 21.7 mg. $[\alpha]_D^{20}$ −63.3 (c 0.45, $CHCl_3$). Enantiomeric excess: 71%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70:30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.32 min (minor), t_R = 7.01 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.72 (m, 4H), 7.63 (dd, J = 8.6, 1.4 Hz, 1H), 7.49−7.36 (m, 2H), 7.22−7.12 (m, 3H), 7.07−6.99 (m, 1H), 6.87 (d, J = 16.0 Hz, 1H), 6.48 (dd, J = 16.0, 5.9 Hz, 1H), 5.03−4.86 (m, 2H), 4.49−4.34 (m, 1H), 3.08−2.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 134.2, 133.6, 133.1, 133.0, 131.1, 129.8, 128.9, 128.2, 128.0, 127.7, 126.6, 126.5, 126.3, 126.2, 125.9, 124.2, 123.5, 75.2, 68.1, 34.3. IR (KBr) γ 2922, 2849, 1507, 1276, 1261, 1227, 1088, 748 cm^{-1}. HRMS (ESI) m/z (M + H)$^+$ calcd for $C_{21}H_{19}O$: 287.1430; observed: 287.1429.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01611.

Complete description of methods and additional results, spectroscopic data for all new compounds, and synthesis procedures for substrates (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the NSFC (21502183) and the Fundamental Research Funds for the Central Universities (WK2060190041).

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