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Palladium/ClickFerrophos-Catalyzed Asymmetric Domino Allylstannylation–Heck Reaction of *o*-Formylaryl Triflate

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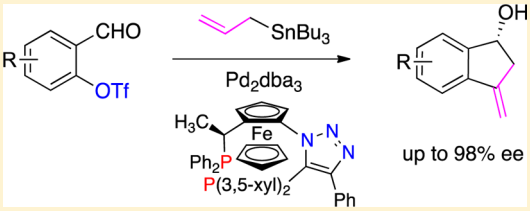
Supporting Information

ABSTRACT: Asymmetric domino allylstannylation–Heck reaction of *o*-formylaryl triflates was successively catalyzed by Pd/ClickFerrophos to give the 3-methylene-indan-1-ols in good yields with good to excellent enantioselectivities. The benefit of the reaction is that the starting *o*-formylaryl triflates are prepared from easily accessible salicylaldehyde derivatives, and the variation of the product, chiral 3-methylene-indan-1-ols, can be expanded. The reaction with 4-substituted substrates gave the corresponding 3-methylene-indan-1-ols in good yields with high enantioselectivities, whereas the reaction with 5- and 6-substituted substrates occasionally afforded the corresponding Stille coupling product in significant amounts along with the desired 3-methylene-indan-1-ols.



INTRODUCTION

Optically active indanols are important compounds owing to their biological activities and are key intermediates in the design of a number of biologically active compounds.[1] For example, the total synthesis of convulsant-active anisatin,[1a] a main component of the seeds of Japanese star anise, was achieved by using a chiral indanol as a key intermediate. Chiral indanols can be precursors of chiral indamines, which block dopamine reuptake.[1b]

Kündig et al. reported the allylation of chiral 2-chlorobenzaldehyde chromium complex followed by an intramolecular Heck reaction which gives 3-methylene-indan-1-ol chromium complex.[2] Porco et al. reported the stepwise asymmetric Hosomi reaction of 2-bromobenzaldehyde with chiral allylsilane followed by an intramolecular Heck reaction.[3] Dudding et al. recently reported the synthesis of chiral 3-methylene-indan-1-ols by a similar tandem Hosomi–Heck reaction.[4] Schmalz et al. recently reported a palladium-catalyzed domino allylstannylation–Heck reaction of 2-iodobenzaldehyde and *o*-formylaryl triflates, which led to the facile synthesis of chiral 3-methylene-1-indanols in one step.[5] The asymmetric version of this reaction was achieved by a Pd/Taniaphos complex to give chiral 3-methylene-indan-1-ol with good enantioselectivity (96% ee) and moderate yield (52%).[6] *o*-Formylphenyl triflate is able to be prepared from the trifluoromethanesulfonylation of salicylaldehyde. A variety of salicylaldehyde derivatives are easily accessible; thus, *o*-formylaryl triflates represent synthetically preferable substrates. However, the reaction with *o*-formylphenyl triflate using Pd/Taniaphos and Pd/BINAP complexes affords 70% ee and 48% ee of the product in 52% and 75% yield, respectively.[6] Therefore, improved yields and enantioselectivities with *o*-formylphenyltriflates are desirable.

We have developed ClickFerrophos ligands, which are chiral ferrocenyldiphosphine ligands possessing a 1,2,3-triazole motif[7] and sometimes work more effectively than Taniaphos ligands[8] in certain reactions. The Schmalz's domino allylstannylation–Heck reaction has attracted our interest because it successfully gives 3-methylene-indan-1-ols due to the unique activation mechanism of an aldehyde moiety and an aryl halide (triflate) by palladium(II).[5] Thus, we desired to improve the reaction with *o*-formylphenyl triflates using Pd/ClickFerrophos complexes. We have found that the complex works effectively to give 3-methylene-indan-1-ol in a good yield (up to 84% yield) with high enantioselectivity (up to 98% ee) and report the details of the reaction.

RESULTS AND DISCUSSION

We first tested (*S*,*Rp*)-ClickFerrophos (**CF1**) (Figure 1) in the model reaction of *o*-formylphenyl triflate (**1**) with allyltributyltin **2**. The reaction was carried out in *N*,*N*-dimethylformamide (DMF) at 80 °C for 15 h by using 2 equiv of **2** to **1**, 2 mol % of Pd_2dba_3, and 4 mol % of the chiral ligand. GC/MS analysis of the reaction mixture showed three distinguished signals. Isolation by preparative TLC (SiO_2, hexane/ethyl acetate) followed by identification by ^1H NMR showed that three products were identified as 3-methylene-indan-1-ol (**3**) (52%), 1,2-dihydronaphthalen-1-ol (**4**) (5–6%),[9] and diallylation product **5** (40%),[10] respectively (Scheme 1). Chiral HPLC analysis of **3** showed that the ee was 96% (*R*); the absolute configuration was determined by reference to the literature[5] and further confirmed by X-ray analysis (see the Supporting Information). In this experiment, **3** was obtained to the same extent as with (*R*,*Sp*)-Taniaphos (**T1**) (52% yield). However, the enantiomeric excess (ee) was higher than that of **T1** (70% ee).[6] The nonasymmetric reaction was first reported using bis(diphenylphosphino)ferrocene (**dppf**) as an achiral ligand.

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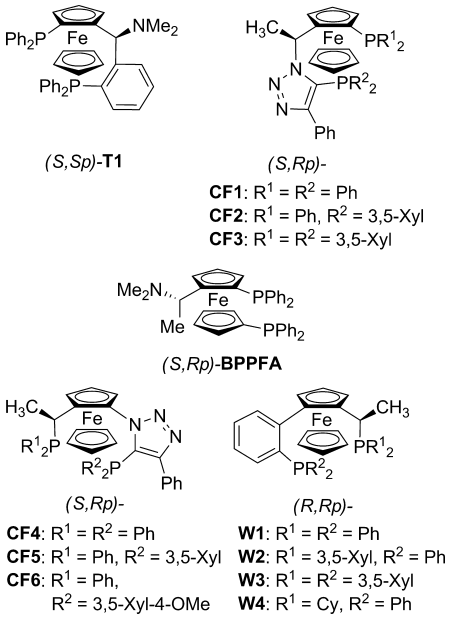
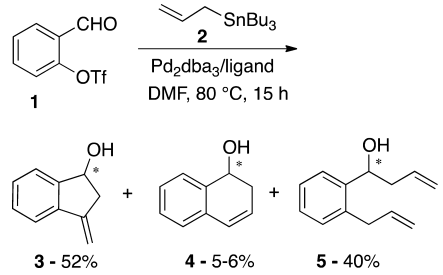


Figure 1. Chiral ferrocenyldiphosphines.

Scheme 1. Reaction of *o*-Formylphenyl Triflate 1 with Allyltributyltin

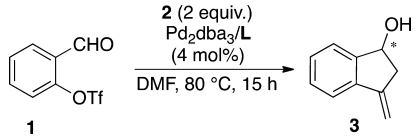


Thus, we examined **BPPFA** (Figure 1),[11] which is structurally similar to dppf bearing a chiral amine group in one of the cyclopentadienyl rings. Notably, **4** and **5** were not observed, and **3** was produced as the sole product. However, the yield (62%) and ee (41% ee) of **3** were moderate.

Encouraged by the high ee obtained with **CF1**, we optimized the phosphine substituent of (*S*,*Rp*)-configured ClickFerrophos ligands. The results of the optimization experiment are summarized in Table 1. The yield and ee of major product **3** are shown, but those of minor products **4** and **5** were not determined.

The **CF2** ligand improved the yield of **3**, but the ee decreased. Additionally, **CF3** gave a low yield. Therefore, we tried to optimize alternative ClickFerrophos ligands, which we call ClickFerrophos II [**CF4**–**CF6** (*S*,*Rp*) configured].[6] **CF4** gave the highest ee value (96% ee), but the yield was moderate (74%). **CF6** gave the highest yield (84%) but a lower ee value (88% ee). (*R*,*Rp*)-Configured Walphos ligands, which are structurally similar to ClickFerrophos **CF4**–**CF6**, were also examined for comparison.[7] Notably, if the triazole group was replaced by the phenyl group, **W1** would correspond to the enantiomer of **CF4**. Walphos ligands gave moderate to good yields and enantioselectivities of the product, but they were not superior to ClickFerrophos **CF4**–**CF6**, despite the greater variation of the phosphine substituents. Thus, **CF5** gave a good

Table 1. Optimization of Ligand



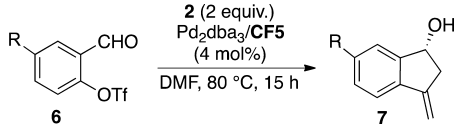
entry	L	yield (%) of **3**[a]	ee (%) (config)[b]
1	**CF1**	52	96 (*R*)
2[c]	**T1**	52	70 (*S*)
3	**BPPFA**	62	41 (*S*)
4	**CF2**	74	86 (*R*)
5	**CF3**	31	86 (*R*)
6	**CF4**	74	96 (*R*)
7	**CF5**	80	96 (*R*)
8	**CF6**	84	88 (*R*)
9	**W1**	56	86 (*S*)
10	**W2**	60	86 (*S*)
11	**W3**	73	65 (*S*)
12	**W4**	91	73 (*S*)

[a]Isolated yield. [b]Determined by chiral HPLC. [c]Data from ref 6.

yield and ee (96% ee); we examine the scope of the reaction with *o*-formyl triflate using **CF5**.

The reaction with various 4-substituted *o*-formylphenyl triflates **6** is summarized in Table 2. The major products

Table 2. Reaction with 4-Substituted *o*-Formylphenyl Triflate



entry	R in **6**	yield (%) of product[a]	ee[b] (%)
1	H, **1**	80, **3**	96
2	Me, **6a**	81, **7a**	82
3	*t*-Bu, **6b**	64, **7b**	72
4	MeO, **6c**	72, **7c**	86
5	Cl, **6d**	40, **7d**	92
6	Br, **6e**	16, **7e**; 35, **8e**	93
7[c]	Br, **6e**	48, **7e**	98
8[d]	Br, **6e**	47, **8e**	93
9	CO_2Me, **6f**	33, **7f**	74
10	NO_2, **6g**	0, **7g**	
11	MeS, **6h**	24, **7h**	31

[a]Isolated yield. [b]Determined by chiral HPLC. [c]One equivalent of **2** was used. [d]Three equivalents of **2** was used.

were the corresponding 3-methylene-indan-1-ols, and ^{1}H NMR spectra of the crude products showed the presence of small amounts (5%–10%) of 1,2-dihydronaphthalen-1-ols of which ee were not determined. Electron-donating substituents such as methyl and methoxy groups gave a good yield and ee (entries 1 and 4), but the *tert*-butyl group gave a moderate yield and ee of the corresponding 3-methylene-indan-1-ols (entries 3). The 4-chloro-substituted substrates afforded the corresponding chloro-substituted product in 40% yield with 92% ee (entry 5), whereas the 4-bromo-substituted substrates afforded a mixture of the 4-bromo-substituted product **7e** and the 4-allyl-substituted product **8e** under the usual conditions (entry 6, Scheme 2). Compound **8e** was probably produced by the Stille coupling of **7e** with the excess allyltin. When the amount of

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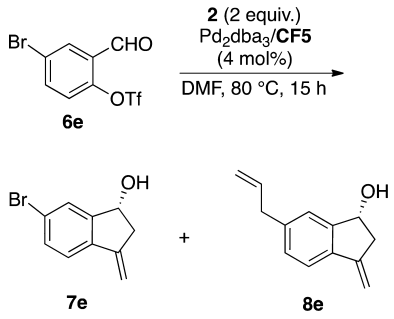
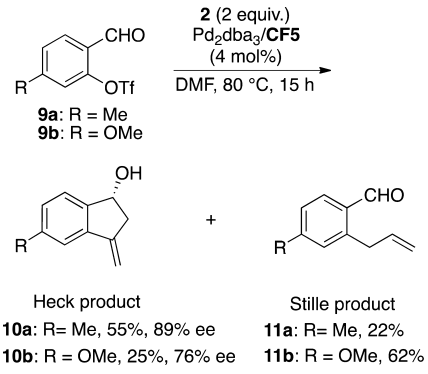
Scheme 2. Reaction with 4-Bromo-*o*-formylphenyl Triflate



allyltin was reduced to 1 equiv to **6e**, **7e** was obtained as the sole product (entry 7). Conversely, the use of 3 equiv of the allyltin gave **8e** exclusively (entry 8). Electron-withdrawing substituents such as the carbomethoxy group gave a low yield of **7f** with a moderate ee (entry 9), while the nitro substituent hardly afforded the corresponding indanol giving a complex mixture including the starting aldehyde (entry 10). The reaction with 4-methylthio-substituted *o*-formylphenyl triflate **6h** afforded the corresponding 3-methylene-indan-1-ol **7h** in low yield (24%) with low ee (31% ee) maybe due to its coordination to palladium atom (entry 11).

We also examined the scope of the reaction with 5- and 6-substituted *o*-formylphenyl triflates. The reaction with 5-methyl- and 5-methoxy-*o*-formylphenyl triflates **9a**,**b** gave the corresponding 3-methyleneindan-1-ols **10a**,**b** (Heck product) in low to moderate yields with good enantioselectivities (Scheme 3). Notably, the Stille coupling product **11a**,**b**[11] of

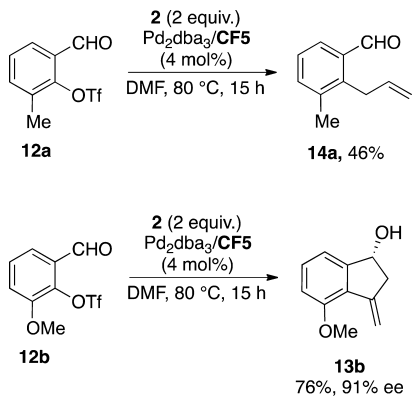
Scheme 3. Reaction with 5-Substituted *o*-Formylphenyl Triflate



the triflate with allyltin was also produced in considerable amounts; the aldehyde moiety did not undergo allylation by the allyltin.

The reaction with 6-methyl-*o*-formylphenyl triflate **12a** gave the corresponding 3-methylene-indan-1-ol **13a** and its regioisomer 1,2-dihydronaphthalen-1-ol in a very low yield (less than 5% combined). Instead, the Stille coupling product **14a** was produced in a 46% yield (Scheme 4). On the other hand, the reaction with 6-methoxy-substituted substrate **12b** gave the corresponding Heck product **13b** as the sole product in a good yield with high enantioselectivity. Here, the better yield of 3-methylene-indan-1-ols with 6-MeO-**12b** than with 5-MeO-**10b** is consistent with the results of Schmalz's non-asymmetric reaction: the position of the methoxy group affects the electrophilicity of the aldehyde group.[5]

Scheme 4. Reaction with 6-Substituted *o*-Formylphenyl Triflate



CONCLUSIONS

Pd/ClickFerrophos works as an effective catalyst for the enantioselective domino allylstannylation−Heck reaction of *o*-formylaryl triflates to give the 3-methylene-indan-1-ols in good yields with good to excellent enantioselectivities. The use of easily accessible salicylaldehyde derivatives is beneficial for the preparation of a variety of chiral 3-methyleneindan-1-ols. However, the reaction was dependent on the position of the substituent on the aryl group. The reaction with 4-substituted substrates gave the corresponding 3-methylene-indan-1-ols in good yields with high enantioselectivities, whereas the reaction with 5- and 6-substituted substrates afforded the corresponding Stille coupling products in significant amounts depending on the substituent in addition to the desired 3-methyleneindan-1-ols.

EXPERIMENTAL SECTION

General Procedure for the Domino Allylstannylation−Heck Reaction. The following provide a typical experimental procedure for the asymmetric domino allylstannylation/Heck reaction of *o*-formylaryl triflates.[6] In a 20 mL Schlenk tube containing a stirring bar were dissolved $[Pd_2(dba)_3]$ (10.0 μmol, 9.2 mg) and **CF5** (20.0 μmol, 15.6 mg) in anhydrous DMF (5.0 mL), and the solution was stirred at room temperature for 30 min under nitrogen. Then, to the Schlenk tube were added 2-formylphenyl triflate (127.1 mg, 0.50 mmol) and allyltributyltin (0.31 mL, 1.0 mmol), and the resulting mixture was stirred at 80 °C for 15 h. After cooling to room temperature, saturated aq KF (10 mL) was added, and the precipitate was filtered. The aqueous layer was extracted with three portions of AcOEt (10 mL). The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, and filtered, and solvent was evaporated by rotary evaporator. GC/MS analysis of the reaction mixture showed three distinguished signals (signal A−C); the M^+ of two of them were 146 (signal A and B), and the M^+ of the other was 189 (signal C). The products were purified by preparative TLC (silica gel, *n*-hexane/ethyl acetate = 4/1) and identified by ^{1}H NMR. Signals A and B corresponded to 3-methylene-2,3-dihydro-1*H*-indan-1-ol (**3**) and 1,2-dihydronaphthanlen-1-ol (**4**), respectively. The enantiomeric excess of **3** was determined by a chiral HPLC.

*(R)-3-Methylene-1H-indan-1-ol (**3**):*.[5,6] white-yellow solid (57.8 mg, 80%, 96% ee); mp = 64−66 °C; $[\alpha]^{26}_D$ = −9.8 (*c* 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (s, 1H), 2.66 (tdd, *J* = 2.3, 4.6, 16.9 Hz, 1H), 3.20 (tdd, *J* = 2.0, 7.3, 16.9 Hz, 1H,), 5.10 (t, 1H, *J* = 2.0 Hz), 5.27 (m, 1H), 5.53 (t, *J* = 2.3 Hz, 1H), 7.33 (m, 2H), 7.46−7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 42.4, 73.2, 104.3, 120.6, 125.0, 128.6, 128.7, 140.2, 146.3. 146.9; HPLC (Chiralpak IB, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 25.9 min (minor), t_R = 29.4 min (major). Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.33; H, 7.01.

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*1,2-Dihydronaphthalen-1-ol (**4**):*[9] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 1H), 2.57 (m, 2H), 4.75 (t, J = 5.4 Hz, 1H), 5.97 (m, 1H), 6.54 (d, J = 9.3 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.21−7.30 (m, 2H), 7.35 (d, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.5, 67.5, 125.4, 126.5, 126.9, 127.1, 127.5, 128.3, 132.7, 136.2; MS (EI) m/z 146.0.

*(R)-6-Methyl-3-methylene-1H-indan-1-ol (**7a**):* white solid (64.8 mg, 81%, 82% ee); mp = 61−62 °C; $[\alpha]^{28}_D$ = −19.3 (c 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (br s, 1H), 2.38 (s, 3H), 2.59−2.68 (m, 1H), 3.19 (tdd, J = 2.0, 7.3, 16.9 Hz, 1H), 5.02 (t, J = 2.0 Hz, 1H), 5.22 (m, 1H), 5.45 (t, J = 2.3 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.27 (m, 1H), 7.41 (d, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 42.7, 73.2, 103.2, 120.4, 125.4, 129.8, 137.6, 139.0, 146.2, 147.1; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 20.8 min (minor), t_R = 23.2 min (major). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.22; H, 7.63;

*(R)-(6-tert-Butyl)-3-methylene-1H-indan-1-ol (**7b**):* brown oil (78.9 mg, 78%, 72% ee); $[\alpha]^{26}_D$ = −22.3 (c 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 9H), 1.95 (br s, 1H), 2.61−2.65 (m, 1H), 3.14−3.20 (m, 1H), 5.03 (t, J = 2.0 Hz, 1H), 5.23 (m, 1H,), 5.46 (t, J = 2.3 Hz, 1H), 7.35−7.50 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 31.4, 34.9, 42.8, 73.5, 103.4, 120.2, 121.5, 126.3, 137.6, 146.1, 146.8, 152.4; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 12.9 min (minor), t_R = 14.0 min (major). Anal. Calcd for $C_{14}H_{18}O$: 83.12; H, 8.97. Found: 83.08; H, 9.04.

*(R)-6-Methoxy-3-methylene-1H-indan-1-ol (**7c**):*[5] white solid (65.2 mg, 74%, 86% ee); mp = 64−66 °C; $[\alpha]^{26}_D$ = −20.3 (c 0.09, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (br s, 1H), 2.64 (tdd, J = 2.3, 3.9, 16.8, 1H), 3.19 (tdd, J = 2.0, 6.7, 16.8 Hz, 1H), 3.82 (s, 3H), 4.95 (t, J = 2.0 Hz, 1H), 5.21 (m, 1H) 5.35 (t, J = 2.2 Hz, 1H), 6.88 (dd, J = 2.4, 8.4 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 7.42 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 43.0, 55.4, 73.3, 101.9, 108.5, 116.3, 121.7, 133.0, 145.7, 148.6, 160.6; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 46.8 min (minor), t_R = 50.6 min (major). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.65; H, 6.88.

*(R)-6-Chloro-3-methylene-1H-indan-1-ol (**7d**):* white solid (37.8 mg, 42%, 92% ee); mp = 96−98 °C; $[\alpha]^{26}_D$ = −12.6 (c 0.11, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (br, 1H), 2.67 (tdd, J = 2.3, 4.7, 16.9 Hz, 1H), 3.21 (tdd, J = 2.0, 7.3, 16.9 Hz, 1H), 5.11 (t, 1H, J = 2.0 Hz), 5.24 (m, 1H), 5.50 (t, J = 2.3 Hz, 1H), 7.29, (d, J = 8.3 Hz, 1H), 7.44 (d, J = 8.3 Hz, 1H), 7.46 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 42.4, 72.7, 104.8, 121.7, 125.1, 129.0, 134.3, 138.5, 145.0, 148.3; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 31.8 min (minor), t_R = 35.8 min (major). Anal. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02. Found: C, 66.14; H, 4.88.

*(R)-6-Bromo-3-methylene-1H-indan-1-ol (**7e**).* The title compound was obtained as a sole product by use of 0.5 mmol of allyltributyltin: white solid (54.1 mg, 48%, 98% ee); mp = 106−107 °C; $[\alpha]^{25}_D$ = −36.7 (c 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (br, 1H), 2.56−2.67 (m, 1H), 3.16−3.22 (m, 1H), 5.10 (t, J = 2.0 Hz, 1H), 5.22 (m, 1H), 5.50 (t, J = 2.4 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.60 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 42.4, 72.7, 105.0, 122.4, 125.9, 128.2, 131.8, 139.0, 145.0, 148.6; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 17.7 min (minor), t_R = 19.2 min (major). Anal. Calcd for $C_{10}H_9BrO$: C, 53.36; H, 4.03. Found: C, 53.14; H, 4.13. The solid recrystallized from hexane/chloroform was suitable for X-ray analysis. CCDC 1000292.

*(R)-6-Allyl-3-methylene-1H-indan-1-ol (**8e**).* The title compound was obtained as a sole product by use of 1.5 mmol of allyltributyltin: yellow oil (44.0 mg, 47%, 93% ee); $[\alpha]^{25}_D$ = −31.4 (c 0.32, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (br, 1H), 2.60−2.67 (m, 1H), 3.17 (dd, J = 4.7, 16.9 Hz, 1H), 3.40 (d, J = 7.3 Hz, 2H), 5.04−5.12 (m, 3H), 5.19−5.22 (m, 1H), 5.46 (t, 1H, J = 2.3 Hz), 5.89−6.02 (m, 1H), 7.15 (d, J = 7.9 Hz, 1H), 7.28 (s, 1H), 7.43 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 40.2, 42.7, 73.2, 103.6, 116.1, 120.6, 125.0, 129.4, 137.1, 138.3, 141.2, 146.1, 147.2; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 20.2 min (minor), t_R = 22.6 min (major). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.87; H, 7.48;

*(R)-6-Carbomethoxy-3-methylene-1H-indan-1-ol (**7f**):* white solid (33.7 mg, 33%, 74% ee); mp = 82−83 °C; $[\alpha]^{25}_D$ = −5.1 (c 0.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (br, 1H), 2.67−2.77 (m, 1H), 3.18−3.26 (m, 1H), 3.92, (s, 3H), 5.22 (s, 1H), 5.30 (m, 1H), 5.64 (s, 1H), 7.55 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 42.4, 52.2, 72.8, 107.2, 120.5, 126.6, 130.2, 130.4, 144.6, 145.5, 147.0, 166.8; HPLC (Chiralpak IB, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min) t_R = 32.2 min (major), t_R = 36.4 min (minor). Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found C, 70.48; H, 6.18.

*(R)-3-Methylene-6-(methylthio)-1H-indan-1-ol (**7h**):* pale yellow solid (23.1 mg, 24%, 31% ee); mp = 50−51 °C; $[\alpha]^{25}_D$ = −14.3 (c 0.12, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (br, 1H), 2.07 (s, 3H), 2.64 (tdd, J = 2.3, 3.9, 16.7, 1H), 3.18 (tdd, J = 2.0, 7.0, 16.7 Hz, 1H), 5.04 (t, J = 2.0 Hz, 1H), 5.21 (m, 1H) 5.45 (t, J = 2.3 Hz, 1H), 7.20 (dd, J = 1.4, 8.2 Hz, 1H), 7.32 (s, 1H), 7.40 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 15.8, 42.6, 73.2, 103.7, 120.9, 122.2, 127.2, 137.3, 139.5, 145.6, 147.6; HPLC (Chiralpak IB, n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min) t_R = 19.0 min (minor), t_R = 23.2 min (major). Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.46; H, 5.94.

The reaction with 5-methyl-2-formylphenyl triflate (**9a**) gave a mixture of **10a** and **11a**.

*(R)-5-Methyl-3-methylene-1H-indan-1-ol (**10a**):* white solid (44.0 mg, 55%, 89% ee); mp = 83−84 °C; $[\alpha]^{26}_D$ = +6.5 (c 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (br s, 1H), 2.38 (s, 1H), 2.55−2.69 (m, 1H), 3.20 (tdd, J = 2.0, 7.2, 16.9 Hz, 1H), 5.06 (t, J = 2.0 Hz, 1H), 5.21 (m, 1H), 5.49 (t, J = 2.4 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.34 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 42.8, 73.1, 103.9, 120.9, 124.8, 130.0, 138.6, 140.3, 144.3, 146.3; HPLC (Chiralpak IB, n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 51.5 min (minor), t_R = 54.2 min (major). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.35; H, 7.44.

*2-Allyl-4-methylbenzaldehyde (**11a**):* yellow oil (18.0 mg, 22%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.80 (d, J = 6.3 Hz, 2H), 4.99 (dd, J = 1.5, 17.0 Hz, 1H), 5.08 (dd, J = 1.5, 10.1 Hz, 1H), 6.02 (tdd, J = 6.2, 10.1, 17.0 Hz, 1H), 7.10 (s, 1H), 7.20 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 10.19 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.6, 55.3, 111.8, 116.2, 116.4, 127.3, 134.4, 136.5, 144.8, 163.8, 190.7. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.65; H, 7.24.

The reaction with 5-methoxy-2-formylphenyl triflate (**9b**) gave a mixture of **10b** and **11b**.

*(R)-5-Methoxy-3-methylene-1H-indan-1-ol (**10b**):*[5] white solid (22.0 mg, 25%, 76% ee); mp = 66−68 °C; $[\alpha]^{26}_D$ = −14.2 (c 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (br, 1H), 2.65−2.69 (m, 1H), 3.20 (tdd, J = 2.0, 7.1, 17.0 Hz, 1H), 3.84 (s, 3H), 5.09 (t, J = 2.0 Hz, 1H), 5.21 (m, 1H), 5.49 (t, J = 2.4 Hz, 1H), 6.89 (dd, J = 2.4, 8.4 Hz, 1H), 6.98 (d, 1H, J = 2.4 Hz), 7.37 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 43.1, 55.5, 72.9, 104.2, 104.4, 116.4, 126.0, 139.6, 141.8, 146.4, 160.6; HPLC (Chiralpak IB, n-hexane/2-propanol = 98/1, flow rate = 1.0 mL/min) t_R = 14.0 min (minor), t_R = 22.3 min (major). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.62; H, 6.91.

*2-Allyl-4-methoxybenzaldehyde (**11b**):*[12] yellow oil (54.6 mg, 62%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (d, J = 5.2 Hz, 2H), 3.88 (s, 3H), 5.02 (dd, 1H, J = 1.5 Hz, 17.0 Hz), 5.10 (dd, 1H, J = 1.5 Hz, 10.1 Hz), 6.02 (tdd, J = 6.3, 10.1, 17.0 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.88 (dd J = 2.4 Hz, 8.6 Hz, 1H,), 7.81 (d, J = 8.6 Hz, 1H), 10.1 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 36.6, 55.3, 111.8, 116.2, 116.4, 127.3, 134.4, 136.5, 144.8, 163.8, 190.7. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.22; H, 7.01.

*(R)-4-Methoxy-3-methylene-1H-indan-1-ol (**13b**):*[5] white solid (67.1 mg, 76%, 91% ee); mp = 93−94 °C; $[\alpha]^{29}_D$ = +22.3 (c 0.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86 (br, 1H), 2.65 (tdd, J = 2.2, 3.7, 16.6 Hz, 1H), 3.17 (tdd, J = 2.0, 7.3, 16.6 Hz, 1H), 3.91 (s, 3H), 5.20−5.23 (m, 2H), 5.91 (dd, J = 2.1 Hz, 3.7 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 7.3 Hz, 1H), 7.27 (t, 1H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 43.3, 55.2, 73.3, 109.1, 110.3, 116.8, 129.9, 144.6, 149.5, 156.9, two carbon peaks overlap on each other. HPLC

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(Chiralpak IB, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min) t_R = 31.2 min (minor), t_R = 33.5 min (major). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.22; H, 7.04.

*2-Allyl-3-methylbenzaldehyde (**14a**):* white solid (36.8 mg, 46%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 3.84 (td, J = 1.8, 5.5 Hz, 2H), 4.84 (dd, J = 1.7, 10.2 Hz, 1H), 5.05 (dd, J = 1.7, 17.1 Hz, 1H), 6.00 (tdd, J = 5.5, 10.2, 17.1 Hz, 1H), 7.30 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 6.7 Hz, 1H), 10.25 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.2, 31.6, 115.8, 126.5, 129.2, 135.8, 135.9, 138.2, 140.0, 192.7. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.79; H, 7.27.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra and chiral HPLC for 3-methyleneindan-1-ols and X-ray data for **7e** (CIF). 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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