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Iridium-Catalyzed Asymmetric Allylic Etherification and Ring-Closing Metathesis Reaction for Enantioselective Synthesis of Chromene and 2,5-Dihydrobenzo[*b*]oxepine Derivatives

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Abstract: Iridium-catalyzed asymmetric etherifications of allylic carbonates with 2-vinylphenols and 2-allylphenols were realized. With a catalyst generated from 2 mol% of $[Ir(cod)Cl]_2$ (cod = cycloocta-1,5-diene) and 4 mol% of the phosphoramidite ligand **L2**, the etherification products were obtained in excellent *ee*s and then subjected to the ring-closing metathesis reaction providing an efficient synthesis of enantioenriched 2*H*-chromene and 2,5-dihydrobenzo[*b*]oxepine derivatives.

Keywords: allylic substitution; asymmetric catalysis; iridium; ring-closing metathesis

Introduction

Chromans and chromenes are important structural motifs that exist in numerous natural products and drug candidates possessing interesting biological activities (Figure 1).[1] Consequently, much attention has been paid to their efficient synthesis, and many synthetic methods for construction of the chroman and chromene skeletons were reported.[2,3] However, the catalytic asymmetric synthesis of chroman and 2*H*-chromene derivatives is still rare despite the importance of these compounds in enantiopure form.[4] Therefore, the highly efficient synthesis of enantiopure chroman and chromene derivatives *via* asymmetric catalysis is in great demand.

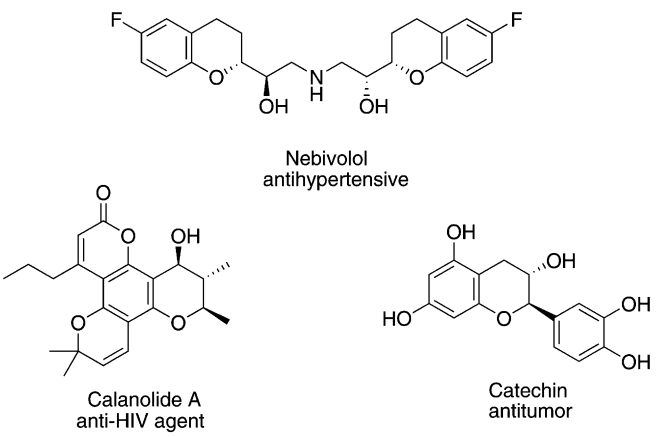
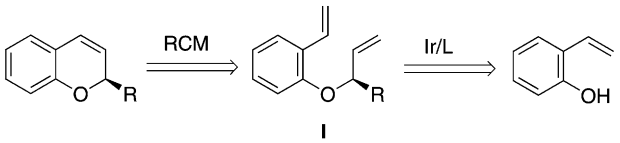


Figure 1. Selected examples of biologically active chroman and chromene derivatives.

Retrosynthetically, 2*H*-chromene derivatives could be accessed *via* the ring-closing metathesis (RCM) reaction of the ether compounds (**I**) bearing two terminal alkenes (Scheme 1). Therefore, an efficient asymmetric synthesis of the ether compounds (**I**) would represent a key to the success of the above hypothesis. We envisaged that a regio- and enantioselective allylic etherification of 2-vinylphenols would provide a straightforward access to enantioenriched ether compounds (**I**). It should be noted that the strategy combining transition metal-catalyzed allyic substitution and RCM had previously been documented in the literature.[5–9] Evans and co-workers introduced the asymmetric allylic amination/RCM strategy to



Scheme 1. A retrosynthetic analysis of enantiopure chromene derivatives.

construct the enantioenriched nitrogen-containing heterocycles in 1999.[5a] This strategy has also been utilized in Pd- and Cu-catalyzed allylic alkylations.[6,7] Target-directed synthesis *via* Ir-catalyzed allylic substitution/RCM was also extensively explored by Helmchen[8] and many others.[9]

Transition metal-catalyzed allylic substitution reactions are very powerful tools for constructing carbon-carbon and carbon-heteroatom bonds.[10] The palladium-catalyzed variant generally provides a mixture of branched and linear products, which often favors the linear substitution products with limited exceptions.[11,12] On the contrary, branched substitution products are usually favored for other transition metals such as Mo,[13] W,[14] Fe,[15] Ru,[16] Rh,[17] Ni,[18] Cu,[19] Ir.[20] For the use of substituted phenols as suitable nucleophiles in the transition metal-catalyzed allylic substitution reactions it has been documented in the literature that phenols generally proceed with *O*-allylation[21–25] with only limited examples of *C*-allylation.[26]

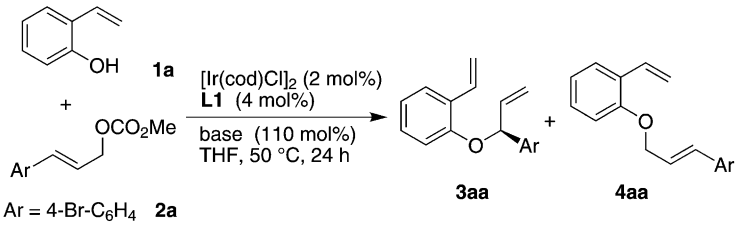
As part of our continued research interests towards Ir-catalyzed allylic substitution reaction,[27,28] we recently found that the reaction of 2-vinylanilines with allylic carbonates under the Ir-catalytic conditions proceeds *via* an allylic vinylation pathway.[28a,b] When 2-vinylphenol derivatives were tested under the same Ir-catalytic conditions, the allylic etherification reaction occurred smoothly providing the ether compounds (**I**) bearing two terminal alkenes. The products obtained here were subjected to an RCM reaction affording enantiopure 2*H*-chromene derivatives. In this paper, we report such an efficient synthesis of enantioenriched chroman and 2*H*-chromene derivatives *via* Ir-catalyzed asymmetric etherification with 2-vinylphenols and a subsequent RCM reaction. The same strategy was also applied for the synthesis of enantioenriched 2,5-dihydrobenzo[*b*]oxepines.

Results and Discussion

Iridium-Catalyzed Asymmetric Allylic Etherification and Ring-Closing Metathesis Reaction for Enantioselective Synthesis of Chromene Derivatives

We began our studies by utilizing 2-vinylphenol (**1a**) and (*E*)-3-(4-bromophenyl)allyl methyl carbonate (**2a**) as the model substrates in the Ir-catalyzed allylic substitution reactions. As summarized in Table 1, with the Ir catalyst generated *in situ* from 2 mol% of $[Ir(cod)Cl]_2$ and 4 mol% of phosphoramidite **L1** (Figure 2), the reaction of **1a** and **2a** in the presence of 1.1 equiv. of K_3PO_4 in THF gave the desired branched etherification product in good yield (68%) and excellent enantioselectivity (95% *ee*) although

Table 1. Screening of various bases and additives.[a]



Entry	Base	Yield [%][b]	**3aa**/**4aa**[c]	*ee* [%][d]
1	K_3PO_4	68	86/14	95
2	DABCO	48	80/20	94
3	Cs_2CO_3	60	85/15	96
4	DBU	10	53/47	95
5	LiHMDS	36	95/5	94
6	NaHMDS	62	82/18	89
7	BSA	trace	–	–
8	Et_3N	n.r.	–	–
9	DIEA	n.r.	–	–
10[e]	Cs_2CO_3	46	89/11	93
11[f]	Cs_2CO_3	trace	–	–

[a] *Reaction conditions:* 2 mol% of $[Ir(cod)Cl]_2$, 4 mol% of **L1**, 0.2 mmol of **1a**, 0.2 mmol of **2a** and 110 mol% of base in THF (2 mL).
[b] Isolated yield of **3aa**.
[c] Determined by ^1H NMR of the crude reaction mixture.
[d] Determined by HPLC analysis.
[e] 100 mol% of CuI was used.
[f] 100 mol% of LiI was used.

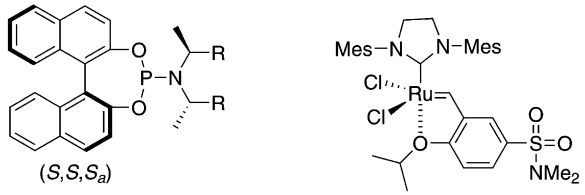


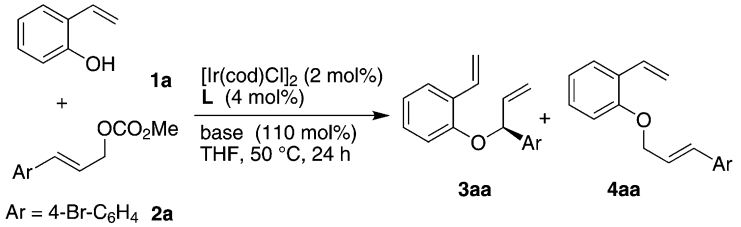
Figure 2. Phosphoramidite ligands and **Zhan-1B** catalyst.

the b (branched)/l (linear) ratio (86/14) is not satisfactory (entry 1, Table 1). These promising results encouraged us to further test different bases. Examination of bases such as DABCO, Cs_2CO_3, DBU, LiHMDS disclosed that varying the base has little effect on the enantioselectivity of the etherification product. Cs_2CO_3 is a good choice of base concerning both yield and b/l ratio (entries 2–5, Table 1). Slightly decreased yield, b/l ratio and enantioselectivity were observed when NaHMDS was employed (entry 6, Table 1). However, the reaction with BSA only gave a trace amount of product and the reaction did not occur at all with Et_3N or DIEA (entries 7–9, Table 1). Since remarkably improved regioselectivies were obtained with metal halides[29,30] as the additives in Ir-catalyzed allylic alkylation reactions, we then examined several such additives in our case. However, the reaction with CuI only led to a slightly improved b/l ratio but a decreased yield (entry 10, Table 1). The reaction with LiI was very sluggish (entry 11, Table 1).

Next, several readily available chiral phosphoramidite ligands were examined with either Cs_2CO_3 or K_3PO_4 as the base. As summarized in Table 2, the reactions with different ligands all proceeded smoothly and the combination of **L2** and Cs_2CO_3 afforded the best results (entries 1–6, Table 2). The reaction with either 0.5 equiv. or 2.0 equiv. of Cs_2CO_3 led to a decrease of both yield and enantioselectivity (entries 7 and 8, Table 2). Screening various solvents such as CH_2Cl_2, toluene, dioxane, DME, and Et_2O disclosed that THF is the best solvent for the etherification reaction (entries 3, 9–13, Table 2).

After screening the bases, additives, ligands and solvents, we established the optimal reaction conditions for the Ir-catalyzed enantioselective allylic etherification (i.e., 2 mol% of $[Ir(cod)Cl]_2$, 4 mol% of **L2**, 110 mol% of Cs_2CO_3, 0.2 mmol of **1**, 0.2 mmol of **2** in THF at 50 °C, entry 3, Table 2). In addition, we tested the subsequent RCM reaction of the etherification products. The following procedure was developed:

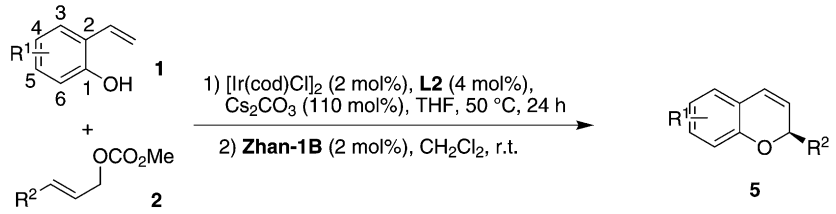
Table 2. Screening of various ligands and solvents.[a]



Entry	L	Base	Solvent	Yield [%][b]	**3aa**/**4aa**[c]	*ee* [%][d]
1	**L1**	Cs_2CO_3	THF	60	85/15	96
2	**L1**	K_3PO_4	THF	68	86/14	95
3	**L2**	Cs_2CO_3	THF	71	93/7	94
4	**L2**	K_3PO_4	THF	69	89/11	95
5	**L3**	Cs_2CO_3	THF	57	72/28	97
6	**L3**	K_3PO_4	THF	60	72/28	92
7[e]	**L2**	Cs_2CO_3	THF	49	85/15	90
8[f]	**L2**	Cs_2CO_3	THF	60	93/7	90
9	**L2**	Cs_2CO_3	CH_2Cl_2	49	82/18	77
10	**L2**	Cs_2CO_3	toluene	53	83/17	90
11	**L2**	Cs_2CO_3	dioxane	69	90/10	94
12	**L2**	Cs_2CO_3	DME	73	91/9	95
13	**L2**	Cs_2CO_3	Et_2O	63	78/22	88

[a] *Reaction conditions:* 2 mol% of $[Ir(cod)Cl]_2$, 4 mol% of **L**, 0.2 mmol of **1a**, 0.2 mmol of **2a** and 110 mol% of base in THF (2 mL).
[b] Isolated yield of **3aa**.
[c] Determined by ^1H NMR of the crude reaction mixture.
[d] Determined by HPLC analysis.
[e] 50 mol% of Cs_2CO_3 was used.
[f] 200 mol% of Cs_2CO_3 was used.

Table 3. Ir-catalyzed allylic etherification with 2-vinylphenols/RCM reaction.[a]



Entry	**1**, R^1	**2**, R^2	Yield [%][b]	*ee* [%][c]
1	**1a**, H	**2a**, 4-Br-C_6H_4	**5aa**, 73	94
2	**1a**, H	**2b**, 4-Me-C_6H_4	**5ab**, 43	94
3	**1a**, H	**2c**, 4-MeO-C_6H_4	**5ac**, 41	86
4	**1a**, H	**2d**, 3-MeO-C_6H_4	**5ad**, 61	93
5	**1a**, H	**2e**, 3-Cl-C_6H_4	**5ae**, 62	90
6	**1a**, H	**2f**, Ph	**5af**, 68	94
7	**1a**, H	**2g**, *n*-C_3H_7	**5ag**, 52	93
8	**1b**, 4-MeO	**2f**, Ph	**5bf**, 29	89
9	**1c**, 4-Br	**2f**, Ph	**5cf**, 50	92
10	**1d**, 4-Cl	**2f**, Ph	**5df**, 42	92
11	**1d**, 4-Cl	**2h**, 4-Cl-C_6H_4	**5dh**, 39	92
12	**1e**, 6-MeO	**2c**, 4-MeO-C_6H_4	trace	-

[a] *Reaction conditions:* 1) 2 mol% of $[Ir(cod)Cl]_2$, 4 mol% of **L2**, 0.2 mmol of **1**, 0.2 mmol of **2** and 110 mol% of Cs_2CO_3 in THF (2 mL); 2) 2 mol% of **Zhan-1B** in CH_2Cl_2.
[b] Isolated yield.
[c] Determined by HPLC analysis.

upon completion of the Ir-catalyzed enantioselective allylic etherification reaction, the etherification products obtained by short silica gel column chromatography were then subjected to RCM reaction in the presence of 2 mol% of **Zhan-1B** in CH_2Cl_2 at room temperature (Figure 2).[31]

Following the above optimized procedures, the substrate scope was explored for various substituted 2-vinyphenols and allyl methyl carbonates to test the generality of this methodology. The results are summarized in Table 3. Substrates bearing either electron-donating groups (4-Me, 4-MeO, 3-MeO, entries 2–4, Table 3) or electron-withdrawing groups (4-Br, 3-Cl, entries 1 and 5, Table 3) on the phenyl ring of the cinnamyl cabonates were well tolerated and led to the corresponding 2*H*-chromene derivatives in moderate to good yields (41–73%) over two steps with excellent enantioselectivities (86–94% *ee*). Notably, aliphatic allyl methyl carbonate also worked quite well (52% yield, 93% *ee*, entry 7, Table 3). In addition, the reactions with 2-vinylphenols bearing either an electron-donating group (4-MeO, entry 8, Table 3) or electron-withdrawing groups (4-Br, 4-Cl, entries 9–11, Table 3) generally led to slightly decreased yields (29–50%) but excellent enantioselectivities (90–92% *ee*). However, when 6-MeO-2-vinylphenol was used, no reaction occurred probably due to the steric hindrance of the *ortho*-substitution (entry 12, Table 3).

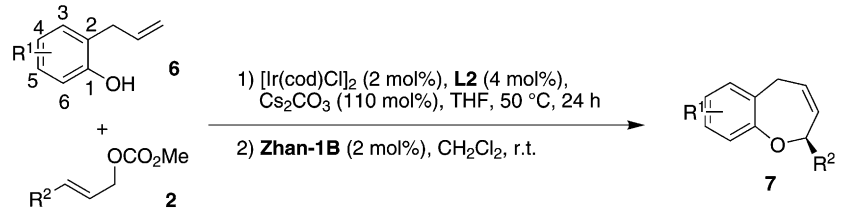
Iridium-Catalyzed Asymmetric Allylic Etherification and Ring-Closing Metathesis Reaction for Enantioselective Synthesis of 2,5-Dihydrobenzo[*b*]oxepine Derivatives

To further broaden the utility of this synthetic strategy, 2-allylphenols were also tested under the etherification/RCM conditions, which would lead to the enantioenriched 2,5-dihydrobenzo[*b*]oxepines. The results are summarized in Table 4. To our delight, following the same two-step procedures, 2,5-dihydrobenzo[*b*]oxepines could be obtained generally in a higher degree of efficiency than the chromene formation with good yields (49–82%) and excellent *ee*s (93–96%). Notably, benzo[*b*]oxepine is the structural motif of many natural products and drug candidates.[32]

Transformations of the Products

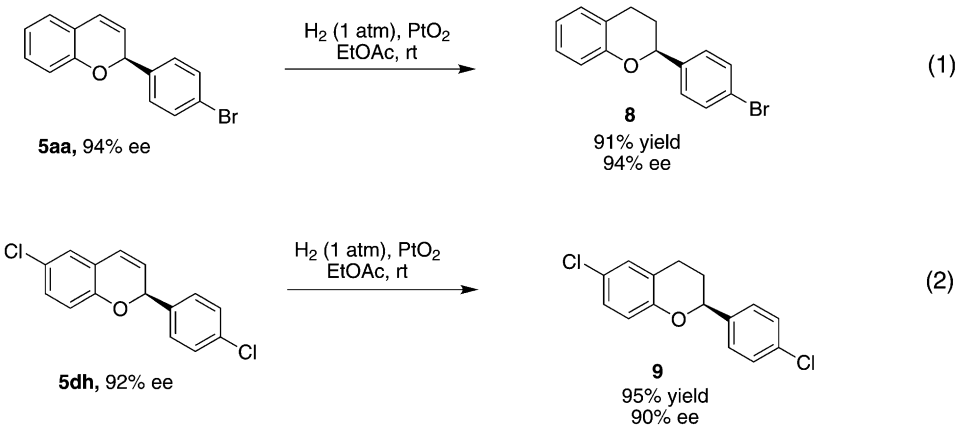
The application of the products obtained with the current methodology has been explored. With the enantioenriched chromenes in hand, the chroman scaffold could be easily obtained by hydrogenation with PtO_2 in ethyl acetate at room temperature [Eq. (1) and Eq. (2)]. The absolute configuration of **5aa** was assigned to be (*S*) by comparing the optical rotation of the hydrogenated product **8**.[33] It should be noted that the hydrogenation product **9** is an inhibitor of rhinovirus

Table 4. Ir-catalyzed etherification with 2-allylphenols/RCM reaction.[a]



Entry	**6**, R^1	**2**, R^2	Yield [%][b]	*ee* [%][c]
1	**6a**, H	**2a**, 4-Br-C_6H_4	**7aa**, 82	96
2	**6a**, H	**2b**, 4-Me-C_6H_4	**7ab**, 63	94
3	**6a**, H	**2c**, 4-MeO-C_6H_4	**7ac**, 67	95
4	**6a**, H	**2d**, 3-MeO-C_6H_4	**7ad**, 74	95
5	**6a**, H	**2e**, 3-Cl-C_6H_4	**7ae**, 61	96
6	**6a**, H	**2f**, Ph	**7af**, 81	94
7	**6a**, H	**2g**, *n*-C_3H_7	**7ag**, 70	94
8	**6a**, H	**2h**, 4-Cl-C_6H_4	**7ah**, 49	95
9	**6b**, 4-MeO	**2f**, Ph	**7bf**, 70	95
10	**6c**, 4-Cl	**2f**, Ph	**7cf**, 69	93

[a] *Reaction conditions:* 1) 2 mol% of $[Ir(cod)Cl]_2$, 4 mol% of **L2**, 0.2 mmol of **6**, 0.2 mmol of **2** and 110 mol% of Cs_2CO_3 in THF (2 mL); 2) 2 mol% of **Zhan-1B** in CH_2Cl_2.
[b] Isolated yield.
[c] Determined by HPLC analysis.



(BW683C).[34] The hydrogenation reactions generally proceed in excellent yields (91–95%) without notable loss of the enantiomeric purity.

Conclusions

In summary, we have successfully developed an efficient method for the synthesis of enantioenriched 2*H*-chromene and 2,5-dihydrobenzo[*b*]oxepine derivatives by employing Ir-catalyzed asymmetric allylic etherification and a subsequent RCM reaction. The current methodology features high enantioselectivity and ready availability of the starting materials, which make it particularly attractive in organic synthesis.

Experimental Section

General Procedure for the Ir-Catalyzed Allylic Etherification Reaction with 2-Vinylphenols/RCM Reaction

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), phosphoramidite ligand **L2** (5.1 mg, 0.008 mmol, 4 mol%), THF (0.5 mL) and *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 0.5 h, and the color of the solution changed from orange to light yellow. Then the reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. To the same flask, 2-vinylphenol derivative **1** (0.20 mmol), allylic carbonate **2** (0.2 mmol), Cs_2CO_3 (71.5 mg, 0.22 mmol) and THF (2 mL) were added. The re-

action mixture was stirred at 50 °C for 24 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered through celite and washed with EtOAc. The solvents were removed under reduced pressure. Then the crude residue was purified by silica gel column chromatography to give the products (branched products **3** and linear products **4**).

To a solution of the above products in CH_2Cl_2 (3 mL) was added **Zhan-1B** catalyst (2.9 mg, 0.004 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired products **5**.

3aa: Colorless oil; yield: 71%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 99/1, $v = 0.6$ mL min^{-1}, $\lambda =$ 254 nm, t(minor) = 12.00 min, t(major) = 13.47 min]; $[\alpha]_D^{20}$: +69.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.25–5.30 (m, 2H), 5.34 (d, $J = 17.2$ Hz, 1H), 5.60 (d, $J =$ 5.6 Hz, 1H), 5.75 (dd, $J = 17.6$, 1.2 Hz, 1H), 6.06 (ddd, $J =$ 16.4, 10.4, 6.0 Hz, 1H), 6.78 (d, $J = 8.4$ Hz, 1H), 6.92 (t, $J =$ 7.6 Hz, 1H), 7.09–7.18 (m, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 80.6, 114.4, 114.5, 116.9, 121.3, 121.7, 126.5, 127.7, 128.3, 128.5, 131.5, 131.8, 137.5, 139.2, 154.6. IR (thin film): $\nu_{max} =$ 3085, 1900, 1626, 1598, 1485, 1454, 1291, 1234, 1106, 1072, 1011, 993, 931, 813, 749 cm^{-1}; MS (EI): $m/z = 314$ (M^+); HR-MS (EI): $m/z = 314.0301$, calcd. for $C_{17}H_{15}OBr$ (M^+): 314.0306..

4aa: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.69$ (dd, $J = 5.6$, 1.6 Hz, 2H), 5.28 (dd, $J = 11.2$, 1.2 Hz, 1H), 5.76 (dd, $J =$ 18.0, 1.6 Hz, 1H), 6.41 (dt, $J = 16.0$, 5.6 Hz, 1H), 6.66 (d, $J =$ 16.0 Hz, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 7.12 (dd, $J = 18.0$, 11.2 Hz, 1H), 7.20–7.28 (m, 3H), 7.43–7.47 (m, 2H), 7.48–7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.8, 112.4, 114.5, 121.0, 121.6, 125.4, 126.5, 127.1, 128.1, 128.8, 131.3, 131.5, 131.7, 135.4, 155.6; IR (thin film): $\nu_{max} = 2856$, 1625, 1596, 1486, 1447, 1236, 1108, 1071, 1008, 972, 909, 752 cm^{-1}; MS (EI): $m/z = 314$ (M^+); HR-MS (EI): $m/z = 314.0308$, calcd. for $C_{17}H_{15}OBr$ (M^+): 314.0306.

5aa: Colorless oil; yield: 73%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 99/1, $v = 1.0$ mL min^{-1}, $\lambda =$ 254 nm, t(minor) = 17.68 min, t(major) = 20.12 min]; $[\alpha]_D^{20}$: −215.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.75 (dd, $J = 10.0$, 3.2 Hz, 1H), 5.85–5.86 (m, 1H), 6.53 (dd, $J = 10.0$, 2.0 Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 6.86 (t, $J =$ 7.2 Hz, 1H), 7.00 (dd, $J = 7.2$, 2.0 Hz, 1H), 7.10 (t, $J =$ 8.0 Hz, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 76.2$, 116.0, 121.1, 121.3, 122.3, 124.1, 124.4, 126.6, 128.7, 129.6, 131.7, 139.7, 152.8; IR (thin film): $\nu_{max} = 3044$, 2926, 1738, 1630, 1604, 1589, 1263, 1228, 1205, 1114, 1011, 958, 824, 798, 753 cm^{-1}; MS (EI): $m/z = 285$ (M^+); HR-MS (EI): $m/z = 285.9995$, calcd. for $C_{15}H_{11}OBr$ (M^+): 285.9993.

5ab:[35] Colorless oil; yield: 43%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 18.72 min, t(major) = 32.50 min]; $[\alpha]_D^{20}$: −192.0 (*c* 0.89, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) $\delta =$ 2.34 (s, 3H), 5.78 (dd, $J = 9.9$, 3.6 Hz, 1H), 5.87–5.88 (m, 1H), 6.53 (d, $J = 9.9$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 6.85 (t, $J = 7.5$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 1H), 7.09 (t, $J =$ 7.8 Hz, 1H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H).

5ac:[36] Colorless oil; yield: 41%; 86% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 28.80 min, t(major) = 35.26 min]; $[\alpha]_D^{20}$: −126.5 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 3.80 (s, 3H), 5.78 (dd, $J = 9.9$, 3.3 Hz, 1H), 5.86–5.87 (m, 1H), 6.54 (dd, $J = 9.9$, 1.5 Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.83–6.90 (m, 3H), 7.01 (d, $J = 7.5$ Hz, 1H), 7.09 (t, $J =$ 7.8 Hz, 1H), 7.38 (d, $J = 8.4$ Hz, 2H).

5ad: Colorless oil; yield: 61%; 93% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 5.04 min, t(major) = 5.57 min]; $[\alpha]_D^{20}$: −154.6 (*c* 1.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 3.79 (s, 3H), 5.78 (dd, $J = 10.0$, 3.2 Hz, 1H), 5.88–5.89 (m, 1H), 6.50–6.53 (m, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 6.84–6.88 (m, 2H), 6.99–7.04 (m, 3H), 7.08–7.14 (m, 1H), 7.23–7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.2$, 77.0, 112.5, 113.8, 116.0, 119.2, 121.2, 121.3, 124.0, 124.8, 126.6, 129.4, 129.7, 142.4, 153.1, 159.8; IR (thin film): $\nu_{max} = 3041$, 2937, 2834, 1733, 1601, 1487, 1455, 1272, 1040, 778, 753, 699 cm^{-1}; MS (EI): $m/z = 238$ (M^+); HR-MS (EI): $m/z = 238.0998$, calcd. for $C_{16}H_{14}O_2$ (M^+): 238.0994.

5ae: Colorless oil; yield: 62%; 90% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 4.37 min, t(major) = 4.86 min]; $[\alpha]_D^{20}$: −222.2 (*c* 1.30, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.77 (dd, $J = 10.0$, 3.6 Hz, 1H), 5.88–5.90 (m, 1H), 6.55 (d, $J = 9.6$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 6.88 (t, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 9.6$ Hz, 1H), 7.29–7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 76.3$, 116.0, 121.1, 121.4, 124.0, 124.4, 125.1, 126.7, 127.2, 128.4, 129.6, 129.9, 134.5, 142.8, 152.8; IR (thin film): $\nu_{max} = 2959$, 1738, 1693, 1485, 1350, 1229, 1113, 1078, 775 cm^{-1}; MS (EI): $m/z =$ 242 (M^+); HR-MS (EI): $m/z = 242.0500$, calcd. for $C_{15}H_{11}OCl$ (M^+): 242.0498.

5af:[37] Colorless oil; yield: 68%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v = 0.6$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 29.13 min, t(major) = 32.45 min]; $[\alpha]_D^{20}$: −144.2 (*c* 0.66, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 5.80 (dd, $J = 9.6$, 3.3 Hz, 1H), 5.91–5.93 (m, 1H), 6.53 (dd, $J = 9.6$, 1.2 Hz, 1H), 6.89 (d, $J = 8.1$ Hz, 1H), 6.86 (t, $J =$ 8.1 Hz, 1H), 7.01 (d, $J = 7.8$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 7.32–7.47 (m, 5H).

5ag:[38] Colorless oil; yield: 52%; 93% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 99/1, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 5.67 min, t(major) = 6.65 min]; $[\alpha]_D^{20}$: −176.2 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.95 (t, $J = 7.6$ Hz, 3H), 1.43–1.85 (m, 4H), 4.84–4.86 (m, 1H), 5.87 (dd, $J = 4.8$, 3.2 Hz, 1H), 6.38 (d, $J = 10.0$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.83 (t, $J = 7.2$ Hz, 1H), 6.95 (d, $J =$ 7.6 Hz, 1H), 7.09 (t, $J = 9.2$ Hz, 1H).

5bf:[39] Colorless oil; yield: 29%; 89% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 70/30, $v = 1.0$ mL min^{-1}, $\lambda =$ 254 nm, t(minor) = 32.62 min, t(major) = 44.26 min]; $[\alpha]_D^{20}$: −224.8 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 3.76 (s, 3H), 5.83–5.88 (m, 2H), 6.49–6.75 (m, 4H), 7.26–7.46 (m, 5H).

5cf:[37] Colorless oil; yield: 50%; 92% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 70/30, $v = 1.0$ mL·min^{-1}, $\lambda =$ 230 nm, t(minor) = 16.55 min, t(major) = 19.48 min]; $[\alpha]_D^{20}$: −151.4 (*c* 1.30, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.84 (dd, $J = 10.0$, 3.6 Hz, 1H), 5.90–5.92 (m, 1H), 6.47 (dd, $J = 9.6$, 1.6 Hz, 1H), 6.66 (d, $J = 8.0$ Hz, 1H), 7.12 (d, $J =$

2.4 Hz, 1H), 7.18 (dd, $J=8.8$, 2.8 Hz, 1H), 7.33–7.43 (m, 5H).

5df:[37] Colorless oil; yield: 42%; 92% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 97/3, v = 1.0 mL min^{-1}, $\lambda=$ 230 nm, t(minor) = 20.75 min, t(major) = 23.18 min]; $[\alpha]_D^{20}$: −243.1 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 5.83–5.92 (m, 2H), 6.48 (d, $J=9.9$ Hz, 1H), 6.71 (d, $J=$ 9.0 Hz, 1H), 6.99 (d, $J=2.7$ Hz, 1H), 7.04 (dd, $J=8.4$, 2.4 Hz, 1H), 7.33–7.44 (m, 5H).

5dh:[40] Colorless oil; yield: 39%; 92% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 70/30, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(minor) = 8.03 min, t(major) = 10.55 min]; $[\alpha]_D^{20}$: −145.2 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 5.80–5.88 (m, 2H), 6.49 (d, $J=9.9$ Hz, 1H), 6.70 (d, $J=$ 8.4 Hz, 1H), 6.99–7.07 (m, 2H), 7.34–7.36 (m, 2H).

General Procedure for the Ir-Catalyzed Allylic Etherification with 2-Allylphenols/RCM Reaction

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), phosphoramidite ligand **L2** (5.1 mg, 0.008 mmol, 4 mol%), THF (0.5 mL) and *n*-propylamine (0.5 mL). The reaction mixture was heated at 50 °C for 0.5 h, and the color of the solution changed from orange to light yellow. Then the reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. To the same flask, 2-vinylphenol derivative **6** (0.20 mmol), allylic carbonate **2** (0.2 mmol), Cs_2CO_3 (71.5 mg, 0.22 mmol) and THF (2 mL) were added. The reaction mixture was stirred at 50 °C for 24 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered through celite and washed with EtOAc. The solvents were removed under reduced pressure. Then the crude residue was purified by silica gel column chromatography to give the products.

To a solution of the above products in CH_2Cl_2 (3 mL) was added **Zhan-1B** catalyst (2.9 mg, 0.004 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 4 h. Then the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography to afford the desired products **7**.

7aa: Colorless oil; yield: 82%; 96% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 95/5, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(major) = 11.22 min, t(minor) = 19.52 min]; $[[\alpha]_D^{20}$: −77.3 (*c* 2.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 3.32 (dd, $J=16.8$, 6.8 Hz, 1H), 3.80 (dd, $J=16.8$, 4.0 Hz, 1H), 5.47–5.52 (m, 2H), 5.98–6.04 (m, 1H), 6.85 (d, $J=$ 9.2 Hz, 1H), 7.01 (t, $J=8.4$ Hz, 1H), 7.11 (t, $J=8.0$ Hz, 2H), 7.27 (t, $J=8.8$ Hz, 2H), 7.47–7.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=31.4$, 81.6, 122.1, 122.5, 124.1, 126.7, 127.7, 128.5, 129.4, 129.7, 131.5, 136.2, 139.3, 156.6; IR (thin film): $\nu_{max}=$3022, 1585, 1488, 1453, 1425, 1263, 1231, 1102, 1011, 965, 789 cm^{-1}; MS (EI): $m/z=300$ (M^+); HR-MS (EI): $m/z=300.0149$, calcd for $C_{16}H_{13}OBr$ (M^+): 300.0150; anal. calcd. for $C_{16}H_{13}OBr$: C 63.81, H 4.35; found: C 63.92, H 4.65.

7ab: Colorless oil; yield: 63%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 85/15, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(major) = 11.76 min, t(minor) = 24.53 min]; $[\alpha]_D^{20}$: −128.6 (*c* 0.86, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 2.35 (s, 3H), 3.29 (dd, $J=16.8$, 6.8 Hz, 1H), 3.81–3.86 (m, 1H), 5.48–5.56 (m, 2H), 5.96–6.02 (m, 1H), 6.87–6.90 (m, 1H), 7.00 (t, $J=8.8$ Hz, 1H), 7.11 (t, $J=7.2$ Hz, 2H), 7.17 (d, $J=8.4$ Hz, 2H), 7.31 (d, $J=8.4$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.2$, 31.4, 82.3, 122.6, 123.9, 126.1, 127.6, 127.7, 128.4, 129.1, 130.5, 136.5, 137.4, 137.9, 157.0; IR (thin film): $\nu_{max}=$3407, 3023, 2921, 1605, 1514, 1488, 1232, 968, 799 cm^{-1}; MS (EI): $m/z=236$ (M^+); HR-MS (EI): $m/z=236.1206$, calcd. for $C_{17}H_{16}O$ (M^+): 236.1201.

7ac: Colorless oil; yield: 67%; 95% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(major) = 26.40 min, t(minor) = 40.10 min]; $[\alpha]_D^{20}$: −110.4 (*c* 0.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 3.33 (dd, $J=16.8$, 6.4 Hz, 1H), 3.76–3.80 (m, 1H), 3.80 (s, 3H), 5.50–5.55 (m, 2H), 5.97–6.03 (m, 1H), 6.84–6.89 (m, 3H), 6.99 (t, $J=7.6$ Hz, 1H), 7.08–7.11 (m, 2H), 7.32 (d, $J=$ 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.4$, 55.3, 82.0, 113.7, 122.7, 123.9, 126.2, 127.6, 128.4, 129.2, 130.4, 132.5, 136.5, 156.8, 159.5; IR (thin film): $\nu_{max}=$3400, 2933, 2836, 1610, 1512, 1248, 1175, 1055, 801, 776 cm^{-1}; MS (EI): $m/z=252$ (M^+); HR-MS (EI): $m/z=252.1154$, calcd. for $C_{17}H_{16}O_2$ (M^+): 252.1150; anal. calcd. for $C_{17}H_{16}O_2$: C 80.93, H 6.39; found: C 80.90, H 6.35.

7ad: Colorless oil; yield: 74%; 95% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(major) = 22.31 min, t(minor) = 32.57 min]; $[\alpha]_D^{20}$: −131.9 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 3.27 (dd, $J=16.8$, 6.8 Hz, 1H), 3.80 (S, 3H), 3.83–3.89 (m, 1H), 5.47–5.57 (m, 2H), 5.96–6.02 (m, 1H), 6.87 (dd, 8.0, 2.8 Hz, 1H), 6.92 (d, $J=8.0$ Hz, 1H), 6.98–7.03 (m, 3H), 7.10–7.14 (m, 2H), 7.24–7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.4$, 55.2, 82.3, 113.0, 113.8, 119.9, 122.5, 124.0, 126.2, 127.7, 128.4, 129.4, 130.4, 136.3, 142.0, 157.0, 159.7; IR (thin film): $\nu_{max}=$3395, 2936, 2834, 1600, 1488, 1454, 1266, 1232, 1197, 1048, 886, 767 cm^{-1}; MS (EI): $m/z=252$ (M^+); HR-MS (EI): $m/z=252.1155$, calcd for $C_{17}H_{16}O_2$ (M^+): 252.1150.

7ae: Colorless oil; yield: 61%; 96% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(major) = 10.27 min, t(minor) = 11.24 min]; $[\alpha]_D^{20}$: −126.2 (*c* 0.94, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 3.26 (dd, $J=16.8$, 6.8 Hz, 1H), 3.82–3.89 (m, 1H), 5.46–5.53 (m, 2H), 5.98–6.04 (m, 1H), 6.91 (d, $J=7.6$ Hz, 1H), 7.02 (t, $J=8.0$ Hz, 1H), 7.11–7.15 (m, 2H), 7.28–7.29 (m, 3H), 7.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.4$, 81.7, 122.4, 124.2, 125.7, 126.8, 127.8, 128.2, 128.6, 129.6, 129.7, 134.3, 136.2, 142.4, 156.8; IR (thin film): $\nu_{max}=$3023, 1598, 1488, 1298, 1232, 1078, 946, 785, 692 cm^{-1}; MS (EI): $m/z=256$ (M^+); HR-MS (EI): $m/z=256.0653$, calcd. for $C_{16}H_{13}OCl$ (M^+): 256.0655; anal. calcd. for $C_{16}H_{13}OCl$: C 74.85, H 5.10; found: C 74.87, H 5.06.

7af: Colorless oil; yield: 81%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v=1.0$ mL min^{-1}, $\lambda=$ 230 nm, t(minor) = 17.72 min, t(major) = 19.32 min]; $[\alpha]_D^{20}$: −102.6 (*c* 1.02, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=$ 3.28 (dd, $J=16.8$, 6.8 Hz, 1H), 3.86 (d, $J=16.8$ Hz, 1H), 5.52–5.57 (m, 2H), 5.97–6.02 (m, 1H), 6.89 (d, $J=8.0$ Hz, 1H), 7.01 (d, $J=7.2$ Hz, 1H), 7.09–7.13 (m, 2H), 7.29–7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=31.4$, 82.4, 122.5, 124.0, 126.2, 127.7, 128.1, 128.3, 128.4, 130.4, 136.4, 140.4, 157.0; IR (thin film): $\nu_{max}=$3023, 1598, 1488, 1298, 1232, 1078, 946, 785, 692 cm^{-1}); MS (EI): $m/z=222$ (M^+); HR-MS (EI): $m/z=222.1039$, calcd. for $C_{16}H_{14}O$ (M^+): 222.1045;

anal. calcd. for $C_{16}H_{14}O$: C 86.45, H 6.35; found: C 86.25, H 6.46.

7ag: Colorless oil; yield: 70%; 94% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 90/10, $v = 0.6$ mL min^{-1}, $\lambda =$ 220 nm, t(minor) = 7.70 min, t(major) = 8.71 min]; $[\alpha]_D^{20}$: +4.4 (*c* 0.82, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ (t, $J = 7.2$ Hz, 3H), 1.56–1.81 (m, 4H), 3.10 (dd, $J = 16.8$, 7.2 Hz, 1H), 3.78 (d, $J = 19.2$ Hz, 1H), 4.41–4.42 (m, 1H), 5.40 (d, $J = 11.2$ Hz, 1H), 5.80–5.85 (m, 1H), 6.97–7.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.9$, 18.8, 31.6, 38.1, 80.1, 121.9, 123.6, 125.7, 127.7, 128.6, 131.5, 136.0, 157.7; IR (thin film): $\nu_{max} = 3390$, 2958, 2930, 1645, 1487, 1452, 1253, 1233, 1109, 980 cm^{-1}; MS (EI): $m/z = 188$ (M^+); HR-MS (EI): $m/z = 188.1205$, calcd. for $C_{13}H_{16}O$ (M^+): 188.1201.

7ah: Colorless oil; yield: 49%; 95% *ee* [Daicel Chiralpak IC, hexane/2-propanol = 99/1, $v = 0.6$ mL min^{-1}, $\lambda = 220$ nm, t(major) = 7.51 min, t(minor) = 8.00 min]; $[\alpha]_D^{20}$: −12.6 (*c* 0.60, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.41$ (d, $J =$ 6.8 Hz, 3H), 3.18 (dd, $J = 16.8$, 6.8 Hz, 1H), 3.71 (dd, $J =$ 16.8, 6.4 Hz, 1H), 4.60–4.63 (m, 1H), 5.37–5.41 (m, 1H), 5.78–5.84 (m, 1H), 6.98–7.19 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.0$, 31.4, 76.3, 122.2, 123.7, 125.2, 127.6, 128.6, 132.3, 136.1, 157.2; IR (thin film): $\nu_{max} = 2962$, 1454, 1412, 1260, 1094, 802 cm^{-1}; MS (EI): $m/z = 160$ (M^+); HR-MS (EI): $m/z = 160.0886$, calcd for $C_{11}H_{12}O$ (M^+): 160.0888.

7bf: Colorless oil; yield: 70%; 95% *ee* [Daicel Chiralpak IC, hexane/2-propanol = 90/10, $v = 1.0$ mL min^{-1}, $\lambda = 230$ nm, t(major) = 5.29 min, t(minor) = 6.17 min]; $[\alpha]_D^{20}$: −120.1 (*c* 0.73, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.22$ (dd, $J =$ 16.5, 6.9 Hz, 1H), 3.76 (s, 3H), 3.84 (d, $J = 16.5$ Hz, 1H), 5.46–5.56 (m, 2H), 5.95–6.03 (m, 1H), 6.60–6.67 (m, 2H), 6.82 (d, $J = 8.4$ Hz, 1H), 7.32–7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 31.5$, 55.5, 82.7, 111.7, 114.0, 122.9, 125.9, 127.7, 128.1, 128.4, 130.5, 137.5, 140.4, 150.6, 155.7; IR (thin film): $\nu_{max} = 2962$, 1454, 1412, 1260, 1094, 802 cm^{-1}; MS (EI): $m/z = 252$ (M^+); HR-MS (EI): $m/z = 252.1154$, calcd. for $C_{17}H_{16}O_2$ (M^+): 252.1150.

7cf: Colorless oil; yield: 69%; 93% *ee* [Daicel Chiralcel OD-H, hexane/2-propanol = 90/10, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(major) = 4.57 min, t(minor) = 4.86 min]; $[\alpha]_D^{20}$: −124.0 (*c* 0.67, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 3.29 (dd, $J = 16.5$, 6.0 Hz, 1H), 3.77 (d, $J = 18.9$ Hz, 1H), 5.51–5.58 (m, 2H), 5.95–6.03 (m, 1H), 6.77 (d, $J = 8.1$ Hz, 1H), 7.04–7.11 (m, 2H), 7.35–7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 31.0$, 82.4, 123.8, 125.6, 127.4, 127.8, 128.3, 128.5, 128.8, 130.3, 138.1, 139.7, 155.3; IR (thin film): $\nu_{max} = 3028$, 2927, 2852, 1655, 1482, 1452, 1426, 1239, 1173, 1056, 1027, 1002, 879, 821 cm^{-1}; MS (EI): $m/z = 256$ (M^+); HR-MS (EI): $m/z = 256.0653$, calcd. for $C_{16}H_{13}OCl$ (M^+): 256.0655..

General Procedure for the Hydrogenation of 5

To a solution of **5aa** (28.6 mg, 0.10 mmol) in EtOAc (2 mL) was added 10% PtO_2 (2.3 mg, 0.01 mmol) under an argon atmosphere. Then the reactor was charged with 1 atm of H_2 and the reaction mixture was stirred at room temperature. After **5aa** had been fully consumed (monitored by TLC), the reaction mixture was filtered through a celite pad. After removal of the solvent, the residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 150/1) to give **8** as yellow solid; yield: 26.2 mg (91%); 94% *ee* [Daicel Chiralpak AS-H, hexane/2-propanol = 99.75/0.25, $v =$ 0.6 mL min^{-1}, $\lambda = 254$ nm, t(minor) = 12.46 min, t(major) = 13.33 min]; $[\alpha]_D^{20}$: −18.7 (*c* 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.02$–2.25 (m, 2H), 2.79 (dt, $J = 16.2$, 4.8 Hz, 1H), 3.00 (ddd, $J = 16.8$, 10.5, 5.4 Hz, 1H), 5.06 (dd, $J = 9.9$, 2.4 Hz, 1H), 6.85–6.93 (m, 2H), 7.08–7.15 (m, 2H), 7.29–7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 25.1$, 29.9, 77.7, 116.9, 120.3, 121.8, 126.0, 127.3, 127.8, 128.5, 129.5, 141.7, 155.1. m.p.: 62–64 °C.

9:[34] Starting from product **5dh** by following the general procedure; colorless oil; yield: 95%; 90% *ee* [Daicel Chiralcel OJ-H, hexane/2-propanol = 70/30, $v = 1.0$ mL min^{-1}, $\lambda =$ 230 nm, t(minor) = 6.87 min, t(major) = 10.78 min]; $[\alpha]_D^{20}$: −3.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.98$–2.07 (m, 1H), 2.14–2.23 (m, 1H), 2.71–2.79 (m, 1H), 2.90–3.01 (m, 1H), 5.01 (dd, $J = 9.9$, 2.4 Hz, 1H), 6.81–6.91 (m, 3H), 7.31–7.40 (m, 4H).

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