JOC The Journal of Organic Chemistry

Subscriber access provided by UNIV OF NEBRASKA - LINCOLN

Note

Kinetic Resolution of Racemic and Branched Monosubstituted Allylic Acetates by a Ruthenium-Catalyzed Regioselective Allylic Etherification

Toru Shinozawa, Shou Terasaki, Shota Mizuno, and Motoi Kawatsura

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b00939 • Publication Date (Web): 08 Jun 2016

Downloaded from http://pubs.acs.org on June 14, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Kinetic Resolution of Racemic and Branched Monosubstituted Allylic Acetates by a Ruthenium-Catalyzed Regioselective Allylic Etherification

Toru Shinozawa, Shou Terasaki, Shota Mizuno, and Motoi Kawatsura*

Department of Chemistry, College of Humanities & Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

ABSTRACT: We demonstrated the kinetic resolution of racemic and branched monosubstituted allylic acetates by a ruthenium-catalyzed regioselective allylic etherification. The reaction was effectively catalyzed by the chiral ruthenium catalyst, which was generated by $[RuCl_2(p\text{-cymene})]_2$ and (*S,S*)-iPr-pybox, catalytic amount of TFA, and both the allylic etherification product and recovered allylic acetate were obtained as an enantiomerically enriched form with up to a 103 *s* value.

The synthesis of enantiomerically-enriched organic compounds is an important topic in the field of synthetic organic chemistry, and the transition metal catalyzed asymmetric allylic substitution of the allylic substrate, which possesses a leaving group at the allylic position, has been recognized as one of the most powerful methods to construct chiral carbon-carbon or chiral carbon-heteroatom bonds.[1] For example, the reaction of allylic substrates with the oxygen nucleophiles effectively provides the allylic ethers,[2-4] and those asymmetric reactions were also realized by several transition metal catalysts.[5,6] Especially, there are several types of asymmetric allylic etherfications of monosubstituted allylic compounds, but the reaction of the racemic and branched monosubstituted allylic substrates, which are easy to prepare, is a still challenging reaction system compared to the reaction of linear-type monosubstituted allylic substrates.[7] To the best our knowledge, there are only limited examples of asymmetric allylic etherification of racemic and branched monosubstituted allylic substrates. For example, Carreira[6h,7b] and Hartwig[7c] realized those asymmetric reactions by the kinetic resolution using chiral iridium catalysts. On the other hand,

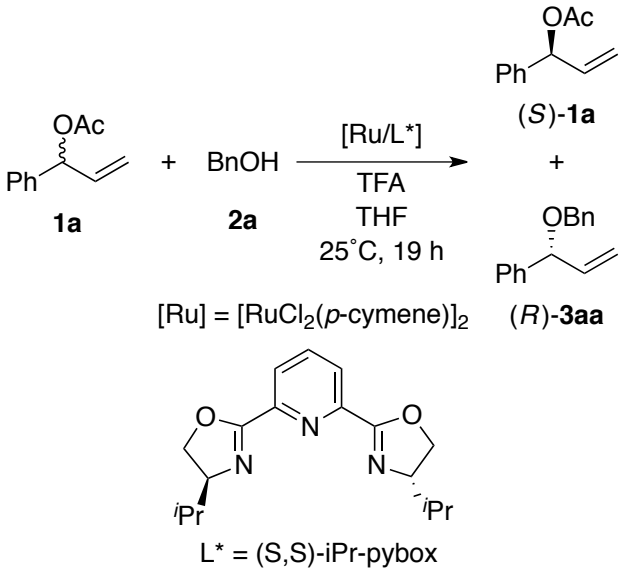
the ruthenium catalyzed asymmetric allylic substitutions of monosubstituted allylic compounds,[8,9] which include the allylic etherification,[10] have been developed by several groups over the last decade. However, these reactions were conducted using linear-type monosubstituted allylic substrates, and there is still no report about the asymmetric allylic etherification of racemic and branched monosubstituted allylic substrates. Recently, we studied several types of stereoselective ruthenium-catalyzed allylic substitutions,[9i,11] and succeeded in the intermolecular asymmetric allylic substitution of racemic and branched monosubstituted allylic substrates with amines. During the course of those ruthenium-catalyzed reactions of the racemic and branched monosubstituted allylic substrates, we examined the reaction with alcohols and revealed that the reaction provides both the starting allylic substrate and allylic etherification product with a high % ee and *s* value. We now report the kinetic resolution[6h,7b-c,12-14] of racemic and branched monosubstituted allylic acetates by a ruthenium-catalyzed allylic etherification.

We first examined the reaction of the racemic and branched allylic acetate **1a** with benzyl alcohol (**2a**) (2.0 equiv to **1a**) in the presence of 5 mol% of

$[RuCl_2(p\text{-cymene})]_2$[11b,11d,15] and 10 mol% of (*S,S*)-iPr-pybox (**L***), but the intended reaction did not proceed (Table 1, entry 1). However, when 0.5 equivalent of trifluoroacetic acid (TFA) was added to the reaction system, the intended regioselective reaction proceeded and the desired branched etherification product **3aa** was obtained in 47% isolated yield with 72% ee (*R*) (entry 2).[16] Based on this reaction, we also confirmed that the enantiomeric excess of the unreacted and recovered substrate **1a** is 92% ee (*S*), and we are convinced that kinetic resolution (*s* = 17) took place in this ruthenium-catalyzed reaction. To progress the reaction with a higher *s* value, we optimized the reaction conditions, then we found that the amounts and the ratio of ruthenium and iPr-pybox are important for determining the *s* value. For example, the reaction by two equivalents of chiral ligands to ruthenium decreased the conversion and % ee of recovered allylic substrate, but the higher s value was observed (entry 3). We also confirmed that a reduced amount of the ruthenium/ligand catalyst increased the *s* value (entries 3 and 4). Furthermore, the present reaction is also very sensitive to the amount of TFA and **2a**, and we confirmed that the use of 0.8 equivalent of TFA and 2.5 equivalents of **2a** produced the highest *s* value (*s* = 99) (entries 4-8).[17] We also

demonstrated the reaction with 1 mmol of **1a** and confirmed that the reaction proceeds without loosing *s* value (entry 9).

Table 1. Ruthenium-catalyzed Allylic Etherification of Racemic Allylic Acetate 1a with Benzylalcohol (2a)[a]



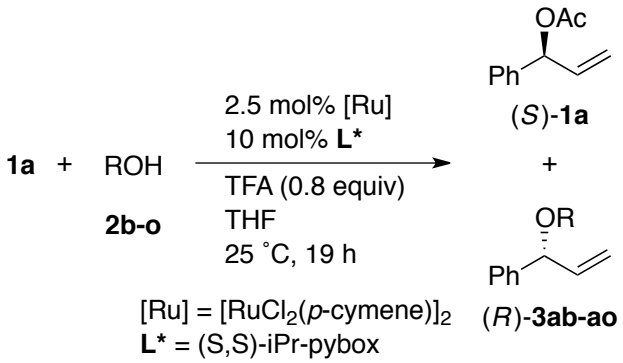
entry	[Ru] (mol%)	**L*** (mol%)	TFA (equiv)	conversion[b] (%) of **1a**	% ee[c] of recovered (*S*)-**1a**	yield[d] (%) of (*R*)-**3aa**	% ee[c] of (*R*)-**3aa**	*s*[e]
1	5.0	10	—	0	—	0	—	—
2	5.0	10	0.5	55	92	47	72	17
3	5.0	20	0.5	35	46	27	90	31
4	2.5	10	0.5	29	40	25	95	57
5	2.5	10	1.0	50	85	44	88	45
6	2.5	10	0.7	40	66	36	94	63
7[f]	2.5	10	0.7	45	73	40	94	77
8[f]	2.5	10	0.8	52	99	44	90	99
9[g]	2.5	10	0.8	53	95	48	90	99

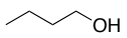
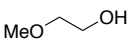
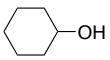
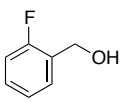
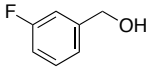
[a] Reaction conditions: **1a** (0.14 mmol), **2a** (0.28 mmol), $[RuCl_2(p\text{-cymene})]_2$, **L***, and TFA in THF at 25 ˚C for 19 h. [b] Conversion (*c*) was calculated by the following formula: c = (NMR $yield_{\mathbf{1a}}$)/[(NMR

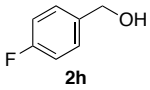
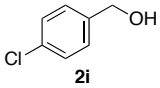
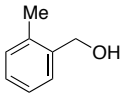
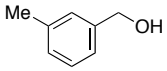
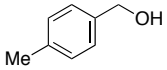
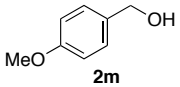
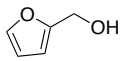
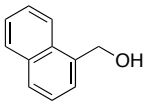
yield$_{\mathbf{1a}}$) + (NMR yield$_{\mathbf{3aa}}$)]. See Ref. 18. [c] Determined by chiral HPLC analysis. [d] Determined by ^{1}H NMR of crude materials. [e] Calculated by % ee of **3aa** (ee$_P$) and conversion (c). s = ln[1-c(1 + ee$_P$)]/ln[1-c(1-ee$_P$)], here c means conversion. See Ref. 12, and 19. [f] 0.35 mmol of **2a** was used. [g] Reaction conditions: **1a** (1.0 mmol), **2a** (2.5 equiv), [RuCl$_2$(p-cymene)]$_2$ (2.5 mol%), **L*** (10 mol%), and TFA (0.8 equiv) in THF (1.1 mL) at 25 ˚C for 19 h.

With the optimized conditions in hand, the scope of the substrates and alcohols of this kinetic resolution system was explored. We initially examined the reaction of **1a** with several alcohols, and the results are summarized in Table 2. The reactions with primary alcohols (**2b** and **2c**) provided good s values (entries 1 and 2). For example, the reaction with **2c** provided (*R*)-**3ac** in 41% yield with a 90% ee and recovered (*S*)-**1a** with an 85% ee (s = 52) (entry 1). The reaction with the secondary alcohol **2d** also exhibited a similar result (entry 3), but the reaction with cyclohexanol (**2e**) resulted in a lower s value (entry 4). Based on the result with **2a**, we further examined the reactions with several arylmethanols **2f-o**, and revealed that most of the reactions proceeded with an acceptable s value (entries 5-14). Especially, the reactions with **2j**, **2n**, and **2o** exhibited high s values (entries 9, 13, and 14), and the highest s value (s = 103) was obtained for the reaction using 1-naphthalenemethanol (**2o**) (entry 14).

Table 2. Kinetic Resolution for the Reaction of 1a with Several Alcohols 2b-o[a]



entry	2	conversion[b] (%) of 1a	% ee[c] of recovered (S)-1a	yield[d] (%) of (R)-3aa	%ee[c] of (R)-3	s[e]
1	 2b	48	84	26	91	57
2	 2c	49	85	41	90	52
3	 2d	45	78	39	92	55
4	 2e	46	83	25	87	32
5	 2f	45	77	39	92	55
6	 2g	50	93	45	89	51

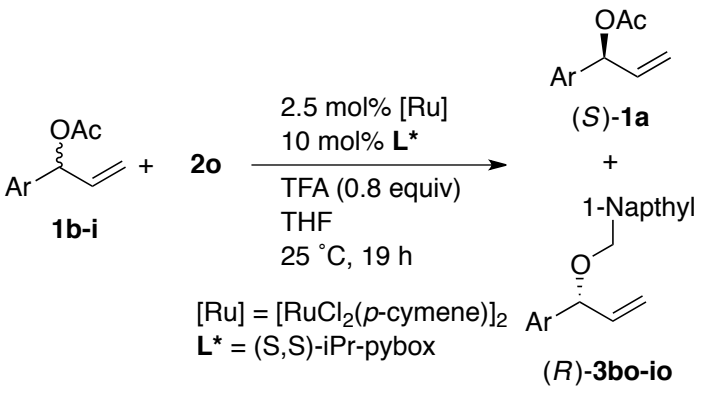
7	 **2h**	49	85	46	89	49
8	 **2i**	48	77	44	92	67
9	 **2j**	51	93	46	92	85
10	 **2k**	38	50	35	91	38
11	 **2l**	49	79	44	92	74
12	 **2m**	48	88	44	93	75
13	 **2n**	50	93	31	93	94
14	 **2o**	51	88	48	93	103

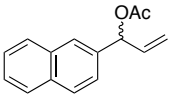
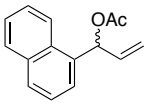
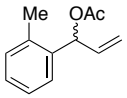
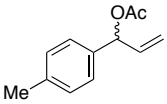
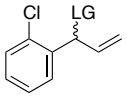
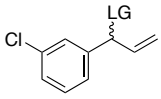
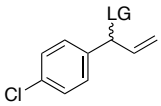
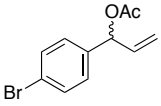
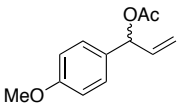
[a] Reaction conditions: **1a** (0.14 mmol), **2b-o** (0.35 mmol), 2.5 mol% of $[RuCl_2(p\text{-cymene})]_2$, 10 mol% of **L***, and TFA (0.11 mmol) in THF at 25 ˚C for 19 h. [b] Conversion (c) was calculated by the following formula: c = (NMR yield$_{\mathbf{1a}}$)/[(NMR yield$_{\mathbf{1a}}$) + (NMR yield$_{\mathbf{3aa}}$)]. See Ref. 18. [c] Determined by chiral HPLC analysis. [d] Determined by ^{1}H NMR of crude materials. [e] Calculated by % ee of **3aa** (ee_P) and conversion (c). $s = \ln[1-c(1 + ee_P)]/\ln[1-c(1-ee_P)]$, here c means conversion. See Ref. 12 and 19.

We next demonstrated the reaction of several racemic and branched allylic acetates with 1-naphthalenemethanol (**2o**). As shown in Table 3, although the reactions requires a small modification, the reactions of the allylic acetates **1b-e** with **2o** using a decreased amount of TFA to 0.5 equiv provided both the recovered allylic

acetates (*S*)-**1** and allylic substituted product (*R*)-**3** with a good enantiomeric excess and moderate to good *s* value (entries 1-4). On the other hand, we confirmed that the reactions of allylic acetates **1f-i**, which contained an electron-withdrawing group on the phenyl group, were slow and exhibited reduced *s* values even when the reaction was conducted at 40 ˚C (entries 5, 7, 9 and 11). However, better results were obtained when the leaving group of allylic esters was changed from acetates to methyl carbonates (entried 6, 8 and 10). Unfortunately, the reaction of **1j**, which possessed the *para*-methoxyphenyl group, under optimized reaction conditions was also unsuccessful; the reaction provided (*R*)-**3jo** in 24% yield with a high enantiomeric excess (94% ee), but only a trace amount of **1j** was recovered (entry 12).[20]

Table 3. Kinetic Resolution for the Reaction of Several Allylic Acetates 1b-i with 2o[a]



entry	**1**	conversion[b] (%) of **1**	% ee[c] of recovered (*S*)-**1**	yield[d] (%) of (*R*)-**3**	%ee[c] of (*R*)-**3**	*s*[e]
1[f]	 **1b**	50	80	46	93	94
2[f]	 **1c**	52	98	40	80	25
3[f]	 **1d**	50	90	41	89	51
4[f]	 **1e**	53	96	42	88	67
5[g,h]	 **1f**: LG = OAc **1f'**: LG = OCO_2Me	11	24	8	84	13
6[i]		25	28	22	93	37
7[g,j]	 **1g**: LG = OAc **1g'**: LG = OCO_2Me	11	30	8	93	31
8[k]		38	63	32	96	88
9[g,l]	 **1h**: LG = OAc **1h'**: LG = OCO_2Me	52	86	46	82	31
10[m]		51	39	45	86	38
11	 **1i**	45	49	32	92	55
12	 **1j**	—	—	24	94	—

[a] Reaction conditions: **1b-j** (0.14 mmol), **2o** (0.35 mmol), 2.5 mol% of $[RuCl_2(p\text{-cymene})]_2$, 10 mol% of **L***, and TFA (0.11 mmol) in THF at 25 ˚C for 19 h. [b] Conversion (*c*) was calculated by the following formula: c = (NMR yield$_{\mathbf{1a}}$)/[(NMR yield$_{\mathbf{1a}}$) + (NMR yield$_{\mathbf{3aa}}$)]. See Ref. 18. [c] Determined by chiral

HPLC analysis. [d] Determined by ^{1}H NMR of crude materials. [e] Calculated by % ee of **3aa** (ee_P) and conversion (c). $s = \ln[1-c(1 + ee_P)]/\ln[1-c(1-ee_P)]$, here c means conversion. See Ref. 12 and 19. [f] 0.5 equiv of TFA was used. [g] Reaction was conducted at 40 °C. [h] Reaction of **1f**. [i] Reaction of **1f'**. [j] Reaction of **1g**. [k] Reaction of **1g'**. [l] Reaction of **1h**. [m] Reaction of **1h'**.

In conclusion, we have demonstrated the kinetic resolution of racemic and branched monosubstituted allylic acetates by the ruthenium-catalyzed regioselective allylic etherification. The reaction was effectively catalyzed by the $[RuCl_2(p\text{-cymene})]_2$/(*S,S*)-iPr-pybox catalyst with catalytic amount of TFA, and provided both the enantiomerically enriched allylic etherification product and the recovered branched monosubstituted allylic acetate with a high enantiomeric excess and high s value.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under a nitrogen atmosphere. NMR spectra were recorded on a 500 MHz (for ^{1}H), 125 MHz (for ^{13}C), and 470 MHz (for ^{19}F). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and an internal C_6F_6 standard for ^{19}F NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H

and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 ˚C unless otherwise noted. The NMR yields were determined by ^{1}H NMR using an internal standard (phenanthrene). HRMS were obtained on an ESI mass spectrometer. Allylic acetates **1a-i** were prepared according to the literature, or by the reaction of corresponding allylic alcohols with acetic anhydride, in the presence of pyridine and DMAP.[21] (*S*,*S*)-iPr-pybox[22] was prepared according to the literature. All other chemicals, including $[RuCl_2(p\text{-cymene})]_2$ and trifluoroacetic acid, were purchased from commercial sources and used without further purification.

General procedure for the kinetic resolution in the ruthenium-catalyzed asymmetric allylic etherification of racemic 1-arylallyl esters with alcohols. The reaction conditions and results are shown in Tables. A Typical procedure is given for the reaction of *rac*-**1a** with **2a** (Table 1, Entry 8). To a solution of *rac*-**1a** (25 mg, 0.14 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.1 mg, 0.004 mmol), (*S*,*S*)-iPr-pybox (4.2 mg, 0.014 mmol), and TFA (12.5 mg, 0.11 mmol) in anhydrous THF (0.15 mL) was added alcohol **2a** (38 mg, 0.35 mmol). The reaction mixture was stirred at 25 ˚C for 19 h, then quenched with H_2O, and extracted with ethyl acetate (3 x 2 mL). The combined

organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The NMR yield (phenanthrene as an internal standard) of (*R*)-**3aa** was determined to be 44% by 270 MHz ^{1}H NMR of the crude materials. The crude material was chromatographed on silica gel (hexane/ethyl acetate/Et_3N = 96/4/1) to give 12 mg (38%) of (*R*)-**3aa** and 7.4 mg (30%) of (*S*)-**1a**, then enantiomeric purities were determined by HPLC using a chiral stationary phase column.

(*R*)-Benzyloxy allylbenzene ((*R*)-3aa).[6h] Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.52 (s, 2H), 4.83 (d, *J* = 7.0 Hz, 1H), 5.22 (dt, *J* = 10.3, 1.4 Hz, 1H), 5.29 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.99 (ddd, *J* = 17.0, 10.3, 7.0 Hz, 1H), 7.23–7.39 (m, 10H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 70.0, 81.9, 116.4, 126.9, 127.5, 127.6, 127.7, 128.3, 128.4, 138.4, 138.8, 140.9. IR (neat) 3063, 3030, 2859, 1496, 1454, 1388, 1304, 1199, 1065, 1028, 991, 927, 844, 737, 418 cm^{-1}. $[\alpha]_D^{22}$ +48 (*c* 0.29, $CHCl_3$) (90% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 22.8 min (minor); t_R 25.5 min (major)). **(*S*)-1a:** $[\alpha]_D^{23}$ +38 (*c* 0.16, $CHCl_3$) (99% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL

OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.3 min (minor); t_R 11.4 min (major)).

(*R*)-Butoxy allylbenzene ((*R*)-3ab).[23] Colorless oil (26% NMR yield, and 3.8 mg (20% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.4 Hz, 3H), 1.32–1.46 (m, 2H), 1.54–1.65 (m, 2H), 3.32–3.51 (m, 2H), 4.72 (d, *J* = 6.8 Hz, 1H), 5.18 (dt, *J* = 10.3, 1.4 Hz 1H), 5.25 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.94 (ddd, *J* = 17.0, 10.3, 6.8 Hz, 1H), 7.23–7.40 (m, 5H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 13.9, 19.4, 31.9, 68.4, 82.9, 115.9, 126.8, 127.5, 128.4, 139.3, 141.4. IR (neat) 3029, 2958, 2931, 1455, 1092, 924, 745, 700 cm^{-1}. $[\alpha]_D^{23}$ –77 (*c* 0.03, $CHCl_3$) (91% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 6.0 min (minor); t_R 6.5 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.3 min (minor); t_R 11.2 min (major)).

(*R*)-2-Methoxyethoxy allylbenzene ((*R*)-3ac). Colorless oil (41% NMR yield, and 6.4 mg (23% isolated yield) after silica gel chromatography). ^{1}H NMR (270

MHz, $CDCl_3$): δ 3.38 (s, 3H), 3.51–3.67 (m, 4H), 4.79 (d, *J* = 6.5 Hz, 1H), 5.19 (d, *J* = 10.3 Hz, 1H), 5.26 (d, *J* = 17.0 Hz, 1H), 5.97 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 7.23–7.41 (m, 5H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 59.1, 67.8, 72.0, 83.5, 116.4, 126.9, 127.6, 128.4, 138.9, 140.9. IR (neat) 2874, 1492, 1452, 1307, 1199, 1093, 1030, 990, 927, 844, 759, 701, 522 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{12}H_{16}O_2$ [M] 192.1150, found 192.1122. $[\alpha]_D^{23}$ –4.8 (*c* 0.42, $CHCl_3$) (90% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 13.5 min (minor); t_R 14.1 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.2 min (minor); t_R 11.1 min (major)).

(*R*)-isoPropoxy allylbenzene ((*R*)-3ad).[6h] Colorless oil (39% NMR yield, and 7.0 mg (28% isolated yield) after silica gel chromatography). ^1H NMR (270 MHz, $CDCl_3$): δ 1.15 (d, *J* = 5.9 Hz, 3H), 1.20 (d, *J* = 5.9 Hz, 3H), 3.67 (sep, *J* = 5.9 Hz, 1H), 4.86 (d, *J* = 6.8 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 5.23 (d, *J* = 17.0 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.3, 6.8 Hz, 1H), 7.22–7.41 (m, 5H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ

22.1, 22.4, 68.7, 79.9, 115.6, 126.8, 127.4, 128.3, 139.7, 141.8. IR (neat) 3063, 3028, 2972, 2931, 2872, 1493, 1452, 1372, 1303, 1174, 1122, 1081, 1056, 1028, 991, 923, 755, 700 cm^{-1}. $[\alpha]_D^{22}$ –18 (*c* 0.33, $CHCl_3$) (92% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 0.8 mL/min, 220 nm, rt, t_R 7.4 min (minor); t_R 7.9 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 9.8 min (minor); t_R 10.8 min (major)).

(*R*)-Cyclohexyloxy allylbenzene ((*R*)-3ae).[6f] Colorless oil (25% NMR yield, and 6.7 mg (22% isolated yield) after silica gel chromatography). ^1H NMR (270 MHz, $CDCl_3$): δ 1.16–1.96 (m, 10H), 3.30–3.39 (m, 1H), 4.92 (d, *J* = 6.5Hz, 1H), 5.15 (dt, *J* = 10.3, 1.5 Hz, 1H), 5.23 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.95 (ddd, *J* = 17.3, 10.3, 6.5 Hz, 1H), 7.23–7.41 (m, 5H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 24.1, 24.2, 25.8, 32.3, 32.6, 74.7, 79.5, 115.5, 126.8, 127.3, 128.3, 139.9, 142.0. IR (neat) 3062, 3028, 2931, 2856, 1639, 1493, 1450, 1341, 1302, 1259, 1198, 1080, 1027, 990, 964, 922, 844, 758, 700, 520 cm^{-1}. $[\alpha]_D^{24}$ +19 (*c* 0.43, $CHCl_3$) (87% ee). Enantiomeric purity was

determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 0.5 mL/min, 210 nm, rt, t_R 14.2 min (minor); t_R 14.8 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 11.5 min (minor); t_R 12.8 min (major)).

(*R*)-1-Fluoro-2-((1-phenylallyloxy)methyl)benzene ((*R*)-3af). Colorless oil (39% NMR yield, and 12 mg (35% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.59 (d, J = 4.6 Hz, 2H), 4.86 (d, J = 6.5 Hz, 1H), 5.24 (dt, J = 10.3, 1.4 Hz, 1H), 5.32 (dt, J = 17.0, 1.4 Hz, 1H), 5.99 (ddd, J = 17.0, 10.3, 6.5 Hz, 1H), 6.98–7.51 (m, 9H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 63.8 (d, J_{CF} = 3.9 Hz), 82.5, 115.1 (d, J_{CF} = 21.1 Hz), 116.6, 124.0 (d, J_{CF} = 3.9 Hz), 125.6 (d, J_{CF} = 14.4 Hz), 126.9, 127.7, 128.5, 129.0, 129.2, 129.9 (d, J_{CF} = 4.5 Hz), 139.7 (d, J_{CF} = 143.2 Hz), 158.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ 42.89–42.94 (m). IR(neat) 3030, 2859, 1619, 1587, 1492, 1455, 1390, 1231, 1194, 1111, 1069, 991, 928, 836, 757, 701, 516 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{16}H_{15}FNaO^+$ $[M+Na]^+$ 265.0999, found 265.1009. $[\alpha]_D^{23}$ +23 (*c* 0.44, $CHCl_3$) (92% ee). Enantiomeric purity was determined by chiral

HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 0.5 mL/min, 220 nm, rt, t_R 28.4 min (major); t_R 29.5 min (minor)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 9.5 min (minor); t_R 10.4 min (major)).

(*R*)-1-Fluoro-3-((1-phenylallyloxy)methyl)benzene ((*R*)-3ag). Colorless oil (45% NMR yield, and 14 mg (40% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.51 (s, 2H), 4.83 (d, J = 6.8Hz, 1H), 5.23 (dt, J = 10.3, 1.4 Hz, 1H), 5.30 (dt, J = 17.3, 1.4 Hz, 1H), 5.99 (ddd, J = 17.3, 10.3, 6.8 Hz, 1H), 6.92–7.40 (m, 9H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 69.3 (d, J_{CF} = 1.7 Hz), 82.3, 114.1 (d, J_{CF} = 2.2 Hz), 114.4 (d, J_{CF} = 2.8 Hz), 116.6, 122.9 (d, J_{CF} = 2.8 Hz), 126.9, 127.8, 128.5, 129.8 (d, J_{CF} = 8.4 Hz), 138.6, 140.7, 141.2 (d, J_{CF} = 7.2 Hz), 162.9 (d, J_{CF} = 245.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 48.3–48.4 (m). IR (neat) 3030, 2860, 1618, 1592, 1489, 1451, 1388, 1255, 1197, 1138, 1092, 1065, 991, 928, 867, 784, 757, 701, 522, 442 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{16}H_{16}FO^+$ $[M+H]^+$ 243.1180, found 243.1190. $[\alpha]_D^{24}$ +22 (*c* 0.55, $CHCl_3$) (89% ee). Enantiomeric purity was determined

by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 8.0 min (minor); t_R 8.8 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.5 min (minor); t_R 11.2 min (major)).

(*R*)-1-Fluoro-4-((1-phenylallyloxy)methyl)benzene ((*R*)-3ah).[5e] Colorless oil (46% NMR yield, and 15 mg (45% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.47 (s, 2H), 4.81 (d, J = 7.0 Hz, 1H), 5.22 (dt, J = 10.3, 1.4 Hz, 1H), 5.28 (dt, J = 17.3, 1.4 Hz, 1H), 5.98 (ddd, J = 17.3, 10.3, 7.0 Hz, 1H), 6.97–7.08 (m, 2H), 7.24–7.37 (m, 7H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 69.4, 82.1, 115.2 (d, J_{CF} = 21.1 Hz), 116.5, 126.9, 127.7, 128.5, 129.4 (d, J_{CF} = 8.3 Hz), 134.1 (d, J_{CF} = 3.3 Hz), 138.7, 140.8, 162.3 (d, J_{CF} = 244.8 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 46.58–46.64 (m). IR (neat) 3030, 2862, 1604, 1510, 1452, 1224, 1156, 1067, 991, 927, 824, 762, 701, 499 cm^{-1}. $[\alpha]_D^{25}$ –31 (*c* 0.59, $CHCl_3$) (89% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 11.2 min (minor); t_R

14.7 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.5 min (minor); t_R 11.5 min (major)).

(*R*)-1-Chloro-4-((1-phenylallyloxy)methyl)benzene ((*R*)-3ai).[5e] Colorless oil (44% NMR yield, and 15 mg (41% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.47 (s, 2H), 4.80 (d, *J* = 6.8 Hz, 1H), 5.22 (dt, *J* = 10.3, 1.4, Hz 1H), 5.29 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.97 (ddd, *J* = 17.0, 10.3, 6.8 Hz, 1H), 7.22–7.43 (m, 9H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 69.3, 82.1, 116.6, 126.9, 127.8, 128.4, 128.5, 128.9, 133.2, 136.9, 138.6, 140.7. IR (neat) 3063, 3029, 2858, 1640, 1600, 1492, 1452, 1408, 1383, 1341, 1295, 1199, 1088, 1015, 990, 927, 806, 761, 701, 518 cm^{-1}. $[\alpha]_D^{24}$ +31 (*c* 0.59, $CHCl_3$) (92% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 31.4 min (minor); t_R 37.7 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.5 min (minor); t_R 11.5 min (major)).

(*R*)-1-Methyl-2-((1-phenylallyloxy)methyl)benzene ((*R*)-3aj). Colorless oil (46% NMR yield, and 14 mg (42% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.30 (s, 3H), 4.50 (d, *J* = 3.5 Hz, 2H), 4.83 (d, *J* = 6.5 Hz, 1H), 5.22 (dt, *J* = 10.3, 1.4 Hz, 1H), 5.30 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.99 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 7.11–7.42 (m, 9H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 18.9, 68.6, 82.1, 116.3, 125.7, 126.9, 127.6, 127.7, 128.4, 128.5, 130.1, 136.3, 136.7, 138.9, 141.0. IR (neat) 3063, 3027, 2861, 1639, 1604, 1493, 1453, 1379, 1287, 1196, 1119, 1065, 991, 926, 842, 745, 701, 522, 434 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{17}H_{18}NaO^+$ $[M+Na]^+$ 261.1250, found 261.1226. $[\alpha]_D^{23}$ +9 (*c* 0.64, $CHCl_3$) (92% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 8.9 min (minor); t_R 11.3 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 9.8 min (minor); t_R 10.7 min (major)).

(*R*)-1-Methyl-3-((1-phenylallyloxy)methyl)benzene ((*R*)-3ak). Colorless oil (35% NMR yield, and 10 mg (30% isolated yield) after silica gel chromatography).

^{1}H NMR (270 MHz, $CDCl_3$): δ 2.34 (s, 3H), 4.48 (s, 2H), 4.83 (d, *J* = 6.5 Hz, 1H), 5.22 (dt, *J* = 10.3, 1.4 Hz, 1H), 5.29 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.99 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 7.07–7.42 (m, 9H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 21.4, 70.1, 82.0, 116.4, 124.7, 127.0, 127.6, 128.22, 128.23, 128.41, 128.43, 137.9, 138.3, 138.9, 141.0. IR (neat) 3028, 2922, 2860, 1640, 1609, 1491, 1452, 1384, 1305, 1197, 1156, 1067, 990, 926, 843, 759, 700, 522, 431 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{17}H_{18}NaO^+$ $[M+Na]^+$ 261.1250, found 261.1248. $[\alpha]_D^{33}$ +13 (*c* 0.62, $CHCl_3$) (91% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 8.9 min (minor); t_R 11.0 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 9.8 min (minor); t_R 10.7 min (major)).

(*R*)-1-Methyl-4-((1-phenylallyloxy)methyl)benzene ((*R*)-3al).[5e] Colorless oil (44% NMR yield, and 14 mg (42% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.34 (s, 3H), 4.48 (s, 2H), 4.81 (d, *J* = 6.8Hz, 1H), 5.21 (dt, *J* = 10.3, 1.4 Hz, 1H), 5.27 (dt, *J* = 17.8, 1.4 Hz, 1H), 5.97 (ddd, *J* = 17.8, 10.3, 6.8

Hz, 1H), 7.13–7.36 (m, 9H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 21.1, 69.9, 81.7, 116.3, 126.9, 127.6, 127.8, 128.4, 129.0, 135.3, 137.1, 138.9, 141.0. IR (neat) 3027, 2860, 1517, 1492, 1452, 1385, 1304, 1200, 1066, 1021, 991, 926, 840, 802, 759, 701, 484 cm^{-1}. $[\alpha]_D^{33}$ +6 (*c* 0.65, $CHCl_3$) (92% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 11.7 min (minor); t_R 16.0 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.3 min (minor); t_R 11.2 min (major)).

(*R*)-1-Methoxy-4-((1-phenylallyloxy)methyl)benzene ((*R*)-3am).[5e]

Colorless oil (44% NMR yield, and 14 mg (39% isolated yield) after silica gel chromatography). ^1H NMR (270 MHz, $CDCl_3$): δ 3.80 (s, 3H), 4.45 (s, 2H), 4.81 (d, *J* = 7.0 Hz, 1H), 5.21 (dt, *J* = 10.5, 1.4 Hz, 1H), 5.27 (dt, *J* = 17.0, 1.4 Hz, 1H), 5.98 (ddd, *J* = 17.0, 10.5, 7.0 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.31–7.42 (m, 5H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 55.3, 69.7, 81.6, 113.7, 116.4, 127.0, 127.6, 128.4, 129.3, 130.5, 138.9, 141.0, 159.1. IR (neat) 3029, 2934, 2836, 1613,

1586, 1514, 1454, 1419, 1387, 1302, 1248, 1173, 1063, 1036, 991, 926, 821, 759, 701, 517 cm^{-1}. $[\alpha]_D^{24}$ +8 (*c* 0.49, $CHCl_3$) (93% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 23.6 min (minor); t_R 30.9 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.2 min (minor); t_R 11.1 min (major)).

(*R*)-2-(((Phenylallyl)oxy)methyl)furan ((*R*)-3an). Colorless oil (31% NMR yield, and 9.3 mg (31% isolated yield) after silica gel chromatography). ^1H NMR (270 MHz, $CDCl_3$): δ 4.46 (s, 2H), 4.84 (d, *J* = 7.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 5.28 (d, *J* = 16.7 Hz, 1H), 5.97 (ddd, *J* = 16.7, 10.0, 7.0 Hz, 1H), 6.28–6.34 (m, 2H), 7.25–7.42 (m, 6H). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ 62.1, 81.7, 109.3, 110.2, 116.8, 127.0, 127.7, 128.5, 138.5, 140.6, 142.7, 151.8. IR (neat) 3029, 2857, 1503, 1452, 1341, 1225, 1150, 1060, 1015, 993, 923, 885, 813, 740, 701, 600 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{14}H_{14}O_2$ [M] 214.0994, found 214.1015. $[\alpha]_D^{33}$ –44 (*c* 0.18, $CHCl_3$) (93% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel

CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 14.1 min (minor); t_R 15.9 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 12.0 min (minor); t_R 12.6 min (major)).

(*R*)-2-(((Phenylallyl)oxy)methyl)naphthalene ((*R*)-3ao). Colorless oil (48% NMR yield, and 17 mg (44% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.92 (d, *J* = 6.8 Hz, 1H), 4.96 (s, 2H), 5.25 (d, *J* = 10.5 Hz, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 6.03 (ddd, *J* = 17.0, 10.5, 6.8 Hz, 1H), 7.27–7.51 (m, 9H), 7.79–7.87 (m, 2H), 8.07–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 68.6, 82.1, 116.7, 124.0, 125.2, 125.7, 126.1, 126.3, 127.0, 127.7, 128.4, 128.5, 131.7, 133.7, 133.8, 138.8, 140.9. IR (neat) 3060, 2857, 1598, 1509, 1452, 1387, 1231, 1167, 1064, 927, 793, 776, 701 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{20}H_{18}NaO^+$ $[M+Na]^+$ 297.1250, found 297.1271. $[\alpha]_D^{27}$ +8 (*c* 0.48, $CHCl_3$) (93% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL AD-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 7.7 min (minor); t_R 8.2 min (major)). **(*S*)-1a:** Enantiomeric purity was determined by chiral HPLC using a

Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 10.5 min (minor); t_R 11.5 min (major)).

(*R*)-1-(((1-(Naphthalen-2-yl)allyl)oxy)methyl)naphthalene ((*R*)-3bo).

Colorless oil (46% NMR yield, and 19 mg (42% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.00 (s, 2H), 5.09 (d, *J* = 6.5 Hz, 1H), 5.28 (d, *J* = 10.3 Hz, 1H), 5.36 (d, *J* = 17.0 Hz, 1H), 6.10 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 7.41–7.53 (m, 7H), 7.80–7.87 (m, 6H), 8.09–8.12 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 68.7, 82.1, 116.8, 124.1, 125.0, 125.2, 125.7, 125.9, 126.0, 126.09, 126.1 126.4, 127.7, 127.9, 128.0, 128.3, 128.5, 128.51, 133.1, 133.3, 133.7, 133.8, 138.3, 138.8. IR (neat) 3047, 2998, 2923, 2872, 1931, 1734, 1636, 1598, 1509, 1481, 1441, 1421, 1381, 1365, 1307, 1291, 1278, 1268, 1244, 1227, 1171, 1156, 1124, 1083, 1036, 990, 948, 933, 901, 863, 822, 803, 781, 752, 700, 648, 624, 603, 548, 515, 504, 476, 434, 418, 402 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{24}H_{20}NaO^+$ $[M+Na]^+$ 347.1406, found 347.1435. $[\alpha]_D^{30}$ –44 (*c* 0.09, $CHCl_3$) (93% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL AD-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 6.4 min (minor); t_R 6.8

min (major)). **(*S*)-1b:** $[\alpha]_D^{23}$ +62 (*c* 0.29, $CHCl_3$) (80% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 16.5 min (minor); t_R 19.9 min (major)).

(*R*)-1-(((1-(Naphthalen-1-yl)allyl)oxy)methyl)naphthalene ((*R*)-3co). Colorless oil (48% NMR yield, and 17 mg (37% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 5.00 (d, *J* = 5.7 Hz, 2H), 5.24 (d, *J* = 10.3 Hz, 1H), 5.35 (d, *J* = 17.3 Hz, 1H), 5.60 (d, *J* = 5.7 Hz, 1H), 6.22 (ddd, *J* = 17.3, 10.3, 5.7 Hz, 1H), 7.39–7.52 (m, 7H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.79–7.94 (m, 4H), 8.06–8.08 (m, 1H), 8.18 (d, *J* = 8.1 Hz, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 68.8, 80.3, 116.7, 124.1, 124.2, 125.2, 125.3, 125.4, 125.5, 125.6, 125.7, 125.8, 126.0, 126.4, 128.4, 128.5, 128.7, 131.0, 131.7, 133.7, 133.8, 134.0, 136.2, 138.3. IR (neat) 3048, 2857, 1597, 1509, 1395, 1167, 1063, 926, 777, 418 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{24}H_{20}NaO^+$ $[M+Na]^+$ 347.1406, found 347.1435. $[\alpha]_D^{30}$ +28 (*c* 0.58, $CHCl_3$) (84% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 5.5 min (minor); t_R 6.7 min (major)). **(*S*)-1c:** $[\alpha]_D^{24}$ –18 (*c* 0.22, $CHCl_3$) (98% ee).

Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL AD-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 14.7 min (minor); t_R 16.0 min (major)).

(*R*)-1-(((1-(*o*-Tolyl)allyl)oxy)methyl)naphthalene ((*R*)-3do). Colorless oil (54% NMR yield, and 21 mg (52% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.26 (s, 3H), 4.94 (s, 2H), 5.11 (d, J = 6.2 Hz, 1H), 5.21 (d, J = 9.5 Hz, 1H), 5.23 (d, J = 17.0 Hz, 1H), 6.00 (ddd, J = 17.0, 9.5, 6.2 Hz, 1H), 7.14–7.27 (m, 3H), 7.39–7.53 (m, 5H), 7.78–7.87 (m, 2H), 8.07–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 19.2, 68.5, 79.1, 116.5, 124.0, 125.2, 125.7, 126.0, 126.2, 126.3, 126.8, 127.5, 128.4, 128.5, 130.5, 131.7, 133.7, 133.9, 135.8, 137.9, 138.6. IR (neat) 3048, 2862, 1598, 1510, 1488, 1459, 1384, 1231, 1166, 1065, 991, 927, 793, 777, 756, 727, 456 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{21}H_{21}O^+$ $[M+H]^+$ 289.1587, found 289.1589. $[\alpha]_D^{26}$ +55 (*c* 0.55, $CHCl_3$) (89% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 13.2 min (minor); t_R 14.9 min (major)). **(*S*)-1d:** $[\alpha]_D^{24}$ –129 (*c* 0.14, $CHCl_3$) (96% ee). Enantiomeric purity was determined by chiral

HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 6.6 min (minor); t_R 7.6 min (major)).

(*R*)-1-(((1-(*p*-Tolyl)allyl)oxy)methyl)naphthalene ((*R*)-3eo). Colorless oil (59% NMR yield, and 21 mg (52% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.35 (s, 3H), 4.89 (d, J = 6.2 Hz, 1H), 4.94 (s, 2H), 5.22 (d, J = 10.0 Hz, 1H), 5.30 (d, J = 17.3 Hz, 1H), 6.02 (ddd, J = 17.3, 10.0, 6.2 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 7.27 (m, 2H), 7.40–7.51 (m, 4H), 7.79–7.87 (m, 2H), 8.07–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 21.2, 68.5, 82.0, 116.4, 124.1, 125.2, 125.7, 126.0, 126.3, 127.0, 128.4, 128.5, 129.2, 131.7, 133.7, 133.9, 137.4, 137.9, 139.0. IR (neat) 3048, 2923, 2859, 1511, 1065, 926, 793, 776, 527 cm^{-1}. $[\alpha]_D^{30}$ +61 (*c* 0.36, $CHCl_3$) (88% ee). HRMS (ESI): *m/z*: calcd for $C_{21}H_{21}O^+$ $[M+H]^+$ 289.1587, found 289.1594. Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 18.1 min (minor); t_R 19.3 min (major)). **(*S*)-1e:** $[\alpha]_D^{24}$ –224 (*c* 0.17, $CHCl_3$) (97% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL

OJ-H (hexane/2-propanol = 49/1, flow: 1.0 mL/min, 220 nm, rt, t_R 9.9 min (minor); t_R 13.0 min (major)).

(*R*)-1-(((1-(2-Chlorophenyl)allyl)oxy)methyl)naphthalene ((*R*)-3fo).

Colorless oil (22% NMR yield, and 8.6 mg (20% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.97 (s, 2H), 5.23 (d, *J* = 10.3 Hz, 1H), 5.35 (d, *J* = 17.0 Hz, 1H), 5.44 (d, *J* = 5.9 Hz, 1H), 5.97 (ddd, *J* = 17.0, 10.3, 5.9 Hz, 1H), 7.20–7.55 (m, 7H), 7.60 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.79–7.88 (m, 2H), 8.06–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 69.0, 78.3, 116.8, 124.0, 125.3, 125.7, 126.1, 126.3, 127.2, 128.2, 128.5, 128.51, 128.7, 129.4, 131.6, 133.0, 133.6, 133.7, 137.0, 138.4. IR (neat) 3062, 1510, 1471, 1440, 1046, 928, 793, 777 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{20}H_{17}ClNaO^+$ $[M+Na]^+$ 331.0860, found 331.0886. $[\alpha]_D^{27}$ +34 (*c* 0.12, $CHCl_3$) (93% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 13.6 min (miner); t_R 15.1 min (major)). **(*S*)-1f':** $[\alpha]_D^{28}$ –20 (*c* 0.20, $CHCl_3$) (28% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel

CHIRALCEL OJ-H (hexane/2-propanol = 999/1, flow: 1.0 mL/min, 220 nm, rt, t_R 18.0 min (major); t_R 20.1 min (minor)).

(*R*)-1-(((1-(3-Chlorophenyl)allyl)oxy)methyl)naphthalene ((*R*)-3go). Colorless oil (32% NMR yield, and 11 mg (25% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.88 (d, J = 6.5, 1H), 4.97 (d, J = 6.2 Hz, 2H), 5.28 (d, J = 9.5 Hz, 1H), 5.33 (d, J = 16.5 Hz, 1H), 5.97 (ddd, J = 16.5, 9.5, 6.5 Hz, 1H), 7.22–7.31 (m, 3H), 7.38–7.55 (m, 5H), 7.80–7.88 (m, 2H), 8.07–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 68.7, 81.4, 117.4, 124.0, 125.1, 125.2, 125.8, 126.2, 126.4, 127.1, 127.8, 128.5, 128.6, 129.7, 131.7, 133.4, 133.7, 134.4, 138.2, 143.1. IR (neat) 3062, 1742, 1597, 1575, 1510, 1475, 1428, 1231, 1196, 1167, 1066, 930, 777, 736, 695 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{20}H_{17}ClO$ [M] 308.0968, found 308.0957. $[\alpha]_D^{28}$ +89 (*c* 0.11, $CHCl_3$) (96% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 14.8 min (minor); t_R 15.6 min (major)). **(*S*)-1g':** $[\alpha]_D^{28}$ +14 (*c* 0.14, $CHCl_3$) (63% ee). Enantiomeric purity was determined by chiral HPLC using a

Daicel CHIRALPAK AD-H (hexane/2-propanol = 99/1, flow: 1.0 mL/min, 220 nm, rt, t_R 7.6 min (minor); t_R 9.8 min (major)).

(*R*)-1-(((1-(4-Chlorophenyl)allyl)oxy)methyl)naphthalene ((*R*)-3ho). Colorless oil (45% NMR yield, and 17 mg (39% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.88 (d, *J* = 6.8 Hz, 1H), 4.96 (d, *J* = 6.2 Hz, 2H), 5.27 (d, *J* = 6.8 Hz, 1H), 5.32 (d, *J* = 14.0 Hz, 1H), 5.97 (ddd, *J* = 17.3, 10.3, 6.5 Hz, 1H), 7.32–7.54 (m, 8H), 7.80–7.88 (m, 2H), 8.06–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 68.7, 81.3, 117.2, 124.0, 125.2, 125.8, 126.1, 126.4, 128.4, 128.5, 128.6, 131.7, 133.5, 133.7, 138.4, 139.4. IR (neat) 2860, 1489, 1090, 1014, 929, 793, 776, 527 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{20}H_{17}ClNaO^+$ $[M+Na]^+$ 331.0860, found 331.0887. $[\alpha]_D^{28}$ +30 (*c* 0.13, $CHCl_3$) (86% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 15.1 min (major); t_R 16.0 min (minor)). **(*S*)-1h':** $[\alpha]_D^{28}$ –42 (*c* 0.14, $CHCl_3$) (98% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALPAK AD-H (hexane/2-propanol = 99/1, flow: 1.0 mL/min, 220 nm, rt, t_R 7.6 min (minor); t_R 9.8 min (major)).

(*R*)-1-(((1-(4-Bromophenyl)allyl)oxy)methyl)naphthalene ((*R*)-3io).

Colorless oil (32% NMR yield, and 13 mg (26% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.86 (d, *J* = 6.8 Hz, 1H), 4.96 (d, *J* = 6.2 Hz, 2H), 5.27 (d, *J* = 9.7 Hz, 1H), 5.32 (d, *J* = 13.8 Hz, 1H), 5.96 (ddd, *J* = 13.8, 9.7, 6.8 Hz, 1H), 7.21–7.27 (m, 2H), 7.40–7.54 (m, 6H), 7.80–7.88 (m, 2H), 8.06–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 68.7, 81.3, 117.2, 121.5, 124.0, 125.2, 125.8, 126.1, 126.4, 128.5, 128.6, 128.7, 131.5, 131.7, 133.5, 133.7, 138.3, 140.0. IR (neat) 3047, 2859, 1591, 1510, 1395, 1167, 928, 719, 525 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{20}H_{18}BrO^{+}$ $[M+H]^{+}$ 353.0536, found 353.0539. $[\alpha]_D^{24}$ +52 (*c* 0.27, $CHCl_3$) (91% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 16.0 min (major); t_R 17.2 min (minor)). **(*S*)-1i:** $[\alpha]_D^{23}$ +5 (*c* 0.38, $CHCl_3$) (53% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 499/1, flow: 1.0 mL/min, 220 nm, rt, t_R 13.7 min (minor); t_R 14.8 min (major)).

(*R*)-1-(((1-(4-Methoxyphenyl)allyl)oxy)methyl)naphthalene ((*R*)-3jo). Colorless oil (24% NMR yield, and 9.4 mg (22% isolated yield) after silica gel chromatography). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.81 (s, 3H) 4.87 (d, *J* = 6.8 Hz, 1H), 4.94 (s, 2H), 5.22 (dt, *J* = 10.5, 1.4 Hz, 1H), 5.28 (dt, *J* = 17.3, 1.4 Hz, 1H), 6.02 (ddd, *J* = 17.3, 10.5, 6.8 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.39–7.53 (m, 4H), 7.78–7.87 (m, 2H), 8.06–8.10 (m, 1H). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): δ 55.3, 68.4, 81.6, 113.9, 116.2, 124.1, 125.2, 125.7, 126.0, 126.3, 128.3, 128.4, 128.5, 131.8, 133.0, 133.7, 134.0, 139.0, 159.2. IR (neat) 2929, 1738, 1610, 1511, 1464, 1303, 1247, 1173, 1036, 926, 777 cm^{-1}. HRMS (ESI): *m/z*: calcd for $C_{21}H_{21}O_2^+$ $[M+H]^+$ 305.1536, found 305.1529. $[\alpha]_D^{27}$ +7 (*c* 0.30, $CHCl_3$) (94% ee). Enantiomeric purity was determined by chiral HPLC using a Daicel CHIRALCEL OJ-H (hexane/2-propanol = 9/1, flow: 0.5 mL/min, 220 nm, rt, t_R 17.4 min (minor); t_R 21.2 min (major)).

1-(((3-(4-Methoxyphenyl)allyl)oxy)methyl)naphthalene (4jo). White solid (21% NMR yield, and 8.6 mg (20% isolated yield) after silica gel chromatography). Mp 61–64 °C. ^{1}H NMR (270 MHz, $CDCl_3$): 3.80 (s, 3H), 4.25 (d,

J = 6.2 Hz, 2H), 5.01 (s, 2H), 6.23 (dt, *J* = 15.9, 6.2 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.41–7.56 (m, 4H), 7.80–7.88 (m, 2H), 8.14 (d, *J* = 7.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (67.5 Mz, $CDCl_3$): δ 55.3, 70.4, 71.0, 114.0, 123.8, 124.0, 125.2, 125.7, 126.2, 126.5, 127.7, 128.5, 128.6, 129.5, 131.8, 132.4, 133.7, 133.8, 159.3. IR (KBr) 3008, 2954, 2836, 1657, 1606, 1510, 1464, 1420, 1362, 1335, 1305, 1252, 1175, 1160, 1128, 1110, 1129, 970, 838, 796, 772, 550, 524, 404. HRMS (ESI): *m/z*: calcd for $C_{21}H_{21}O_2^+$ $[M+H]^+$ 305.1536, found 305.1533.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of NMR (^{1}H, ^{19}F and ^{13}C) and HPLC charts for all products.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kawatsur@chs.nihon-u.ac.jp

Notes

The authors declare no competing financial interest.

REFERENCES

1. (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422. (b) Lu, Z.; Ma, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 258–297.

2. For selected examples of Pd-catalyzed allylic etherification of allyl compounds, See: (a) Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc., Jpn.* **1972**, *45*, 230–236. (b) Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769–1772. (c) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* **1985**, *26*, 5615–5618. (d) Goux, C.; Lhoste, P.; Sinou, D. *Synlett* **1992**, 725–727. (e) Cacchi, S.; Fabrizi, G.; Moro, L. *Synlett* **1998**, 741–745. (f) Nay, B.; Peyrat, J.-F.; Vercauteren, J. *Eur. J. Org. Chem.* **1999**, 2231–2234. (g) Massacret, M.; Lhoste, P.; Lakhmiri, R.; Parella, T.; Sinou, D. *Eur. J. Org. Chem.* **1999**, 2665–2673.

3. (a) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2000**, *122*, 5012–5013. (b)

Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2002**, *124*, 7882–7883.

4. (a) Mbaye, M. D.; Demerseman, B.; Renaud, J.-L.; Toupet, L.; Bruneau, C. *Angew. Chem. Int. Ed.* **2003**, *42*, 5066–5068. (b) Mbaye, M. D.; Demerseman, B.; Renaud, J.-L.; Toupet, L.; Bruneau, C. *Adv. Synth. Catal.* **2004**, *346*, 835–841. (c) Hermatschweiler, R.; Fernández, I.; Pregosin, P. S.; Breher, F. *Organometallics* **2006**, *25*, 1440–1447.

5. (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, *120*, 9074–9075. (b) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 11262–11263. (c) Trost, B. M.; Tang, W. *J. Am. Chem. Soc.* **2002**, *124*, 14542–14543. (d) Lam, F. L.; Au-Yeung, T. T.-L.; Kwong, F. Y.; Zhou, Z.; Wong, K. Y.; Chan, A. S. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 1280–1283. (e) Fang, P.; Ding, C.-H.; Hou, X.-L.; Dai, L.-X. *Tetrahedron: Asymmetry* **2010**, *21*, 1176–1178. (f) Zang, Y.; Ojima, I. *J. Org. Chem.* **2013**, *78*, 4013–4018. (g) Ye, F.; Zheng, Z.-J.; Li, L.; Yang, K.-F.; Xia, C.-G.; Xu, L.-W. *Chem. Eur. J.* **2013**, *19*, 15452–15457.

6. (a) López, F.; Ohmura, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 3426–3427. (b) Shu, C.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2004**, *43*, 4794–4797. (c)

Leitner, A.; Shu, C.; Hartwig, J. F. *Org. Lett.* **2005**, *7*, 1093–1096. (d) Shekhar, S.; Trantow, B.; Leitner, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 11770–11771. (e) Kimura, M.; Uozumi, Y. *J. Org. Chem*. **2007**, *72*, 707–714. (f) Ueno, S.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2008**, *47*, 1928–1931. (g) Lyothier, I.; Defieber, C.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2006**, *45*, 6204–6207. (h) Roggen, M.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 5568–5571. (i) He, H.; Ye, K.-Y.; Wu, Q.-F.; Dai, L.-X. You, S.-L. *Adv. Synth. Catal.* **2012**, *354*, 1084–1094.

7. (a) Trost, B. M.; Fraisse, P. L.; Ball, Z. T. *Angew. Chem. Int. Ed.* **2002**, *41*, 1059–1061. (b) Fischer, C.; Defieber, C.; Suzuki, T.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, *126*, 1628–1629. (c) Stanley, L. M.; Bai, C.; Ueda, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 8918–8920.

8. (a) Bruneau, C.; Renaud, J.-L.; Demerseman, B. *Pure Appl. Chem.* **2008**, *80*, 861–871. (b) Bruneau, C.; Achard, M. *Cood. Chem. Rev.* **2012**, *256*, 525–536. (c) Kitamura, M.; Miyata, K.; Seki, T.; Vatmurge, N.; Tanaka, S. *Pure Appl. Chem.* **2013**, *85*, 1121–1132.

9. (a) Onitsuka, K.; Kameyama, C.; Sasai, H. *Chem. Lett.* **2009**, *38*, 444–445. (b) Tanaka, S.; Seki, T.; Kitamura, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 8948–8951. (c) Kanbayashi, N.; Onitsuka, K. *J. Am. Chem. Soc.* **2010**, *132*, 1206–1207. (d) Miyata, K.; Kutsuna, H.; Kawakami, S.; Kitamura, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 4649–4653. (e) Seki, T.; Tanaka, S.; Kitamura, M. *Org. Lett.* **2012**, *14*, 608–611. (f) Takii, K.; Kanbayashi, N.; Onitsuka, K. *Chem. Commun.* **2012**, *48*, 3872–3874. (g) Kanbayashi, N.; Takenaka, K.; Okamura, T.; Onitsuka, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 4897–4901. (h) Kanbayashi, N.; Hosoda, K.; Kato, M.; Takii, K.; Okamura, T.; Onitsuka, K. *Chem. Commun.* **2015**, *51*, 10895–10898. (i) Kawatsura, M.; Uchida, K.; Terasaki, S.; Tsuji, H.; Minakawa, M.; Itoh, T. *Org. Lett.* **2014**, *16*, 1470–1473. (j) Suzuki, Y.; Seki, T.; Tanaka, S.; Kitamura, M. *J. Am. Chem. Soc.* **2015**, *137*, 9539–9542.

10. (a) Mbaye, M. D.; Renaud, J.-L.; Demerseman, B.; Bruneau, C. *Chem. Commun.* **2004**, 1870–1871. (b) Bruneau, C.; Renaud, J.-L.; Demerseman, B. *Chem. Eur. J.* **2006**, *12*, 5178–5187. (c) Onitsuka, K.; Okuda, H.; Sasai, H. *Angew. Chem. Int. Ed.* **2008**, *47*, 1454–1457. (d) Saporita, M.; Bottari, G.; Bruno, G.; Drommi, D.;

Faraone, F. *J. Mol. Catal. A: Chem.* **2009**, *309*, 159–165. (e) Sahli, Z.; Derrien, N.; Pascal, S.; Demerseman, B.; Roisnel, T.; Barrière, F.; Achard, M.; Bruneau, C. *Dalton Trans.* **2011**, *40*, 5625–5630. (f) Kanbayashi, N.; Onitsuka, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 5197–5199. (g) Trost, B. M.; Rao, M.; Dieskau, A. P. *J. Am. Chem. Soc.* **2013**, *135*, 18697–18704.

11. (a) Kawatsura, M.; Ata, F.; Wada, S.; Hayase, S.; Uno, H.; Itoh, T. *Chem. Commun.* **2007**, 298–300. (b) Kawatsura, M.; Ata, F.; Hayase, S.; Itoh, T. *Chem. Commun.* **2007**, 4283–4285. (c) Kawatsura, M.; Ata, F.; Hirakawa, T.; Hayase, S.; Itoh, T. *Tetrahedron Lett.* **2008**, *49*, 4873–4875. (d) Kawatsura, M.; Sato, M.; Tsuji, H.; Ata, F.; Itoh, T. *J. Org. Chem.* **2011**, *76*, 5485–5488.

12. For reviews, see: (a) Keith, J. M.; Larrow, J. F.; Jacobsen, E. N. *Adv. Synth. Catal.* **2001**, *343*, 5–26. (b) Robinson, D. E. J. E.; Bull, S. D. *Tetrahedron: Asymmetry* **2003**, *14*, 1407–1446. (c) Vedejs, E.; Jure, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 3974–4001. (d) Pellissier, H. *Adv. Synth. Catal.* **2011**, *353*, 1613–1666

13. Selected example of kinetic resolution in the allylic substitution of racemic and branched allylic compounds, see: (a) Hughes, D. L.; Palucki, M.; Yasuda, N.;

Reamer, R. A.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 2762–2768. (b) Qu, J.; Robberg, L.; Helmchen, G. *J. Am. Chem. Soc.* **2014**, *136*, 1272–1275. (c) Breitler, S.; Carreira, E. M. *J. Am. Chem. Soc.* **2015**, *137*, 5296–5299.

14. Onitsuka reported the kinetic resolution in the ruthenium-catalyzed allylic alkylation of allylic carbonates, see: Onitsuka, K.; Matsushima, Y.; Takahashi, S. *Organometallics* **2005**, *24*, 6472–6474.

15. (a) Bayer, A.; Kazmaier, U. *Org. Lett.* **2010**, *12*, 4960–4963. (b) Bayer, A.; Kazmaier, U. *Chem. Eur. J.* **2014**, *20*, 10484–10491. (c) Bayer, A.; Kazmaier, U. *J. Org. Chem.* **2014**, *79*, 8491–8497. (d) Bayer, A.; Kazmaier, U. *J. Org. Chem.* **2014**, *79*, 8498–8504. (e) Servatius, P.; Kazmaier, U. *Synlett* **2015**, *26*, 2001–2005.

16. It is not clear why TFA exhibited the positive effect for the present reaction system, see: Zaitsev, A. B.; Caldwell, H. F.; Pregosin, P. S.; Weiros, L. F. *Chem. Eur. J.* **2009**, *15*, 6468–6477.

17. Reactions using other chiral pybox analogues, instead of (*S,S*)-iPr-pybox exhibited low conversion and/or decreased *s* values.

18. Kano, T.; Sasaki, K.; Maruoka, K. *Org. Lett.* **2005**, *7*, 1347–1349.

19. (a) Chen, C.-S.; Fujimoto, Y.; Girdaukas, G.; Sih, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 7294–7299. (b) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249–330.

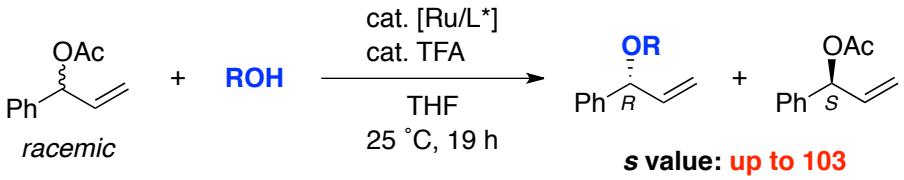
20. We also examined the reaction of alkyl group substituted racemic and branched monosubstituted allylic acetates or phenols, but those reactions resulted in no reaction.

21. (a) Lehann, J.; Lloyd-Jone, G. C. *Tetrahedron* **1995**, *51*, 8863–8874. (b) Štambaský, J.; Malkov, A. V.; Kočovský, P. *J. Org. Chem.* **2008**, *73*, 9148–9150. (c) Kadnikova, E. N.; Tharkor, V. A. *Tetrahedron: Asymmetry* **2008**, *19*, 1053–1058. (d) Ward, Y. D.; Villanueva, L. A.; Allred, G. D.; Payne, S. C.; Semones, M. A.; Liebeskind, L. S. *Organometallics* **1995**, *14*, 4132–4156. (e) Peiran, C.; Peng, X. *Tetrahedron Lett.* **2011**, *52*, 5758–5760. (f) Marion, N.; Gealageas, R.; Nolan, S. P. *Org. Lett.* **2007**, *9*, 2653–2656.

22. Cornejo, A.; Fraile, J. M.; García, J. I.; Gil, M. J.; Martínez-Merino, V.; Mayoral, J. A.; Pires, E.; Villalba, I. *Synlett* **2005**, *15*, 2321–2324.

23. Barbro, M.; Cadaura, S.; Dughera, S.; Venturello, P. *Synthesis* **2008**, 1379–1388.

Graphical Abstract



***s* value: up to 103**

[Ru] = $[RuCl_2(p\text{-cymene})]_2$, L* = (*S*,*S*)-iPr-pybox