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Nickel-catalyzed enantioselective hydrovinylation of silyl-protected allylic alcohols: An efficient access to homoallylic alcohols with a chiral quaternary center

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Asymmetric hydrovinylation of silyl-protected allylic alcohols catalyzed by nickel complexes of chiral spiro phosphoramidite ligands was developed. A series of homoallylic alcohols with a chiral quaternary center were produced in high yields (up to 97%) and high enantioselectivities (up to 95% ee). The reaction provides an efficient method for preparing bifunctional compounds with a chiral quaternary carbon center.

asymmetric hydrovinylation, chiral spiro phosphorus ligands, functionalized olefins, chiral quaternary center

1 Introduction

Transition metal-catalyzed carbon-carbon bond formation reactions lie at the heart of organic synthesis and have drawn intensive research attention. Ni-catalyzed asymmetric hydrovinylation reaction, which uses abundantly available ethylene as a starting material to construct valuable chiral compounds, is an atom-economical carbon-carbon bond-forming reaction and has a high potential for wide applications in fine chemicals as well as pharmaceutical industry [1–3]. In the past decades, great efforts have been devoted to this field and several chiral nickel catalysts have been developed for highly selective hydrovinylation of unfunctionalized olefins including vinylarenes [4–8], α-alkylvinylarenes [9, 10], strained olefins [11], and 1,3-dienes [12, 13]. However, the hydrovinylation of functionalized olefins remains a challenge.

It is of significance that the hydrovinylation of functionalized olefin provides multi-functionalized products, which have wide applications in the synthesis of bioactive compounds. Recently, we have developed nickel-catalyzed hydrovinylation of α-ketal vinylarenes for preparing vinyl aldehydes with high yields and high chemoselectivities [14]. The asymmetric version of this reaction was also attempted by using chiral spiro phosphorus ligands; however, a very poor enantioselectivity (24% ee) was obtained. As a part of our continuous efforts on this subject, here we report the nickel-catalyzed highly enantioselective hydrovinylation of silyl-protected allylic alcohols, providing a direct protocol for the construction of homoallylic alcohols with a chiral quaternary carbon center.

2 Results and discussion

Initially, the hydrovinylation of *tert*-butyldimethyl-(2-phenylallyloxy)silane (**1a**) was performed in CH_2Cl_2 at room temperature using a nickel catalyst generated *in situ* from 2 mol% $[Ni(allyl)Br]_2$, 4 mol% (S_a,*R*,*R*)-SIPHOS-PE, and 5 mol% $NaBAr_F$ (sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate). To our delight, the hydrovinylation product **2a** was obtained with good yield (69%) and moderate ee value (41% ee) (Scheme 1). The major competitive

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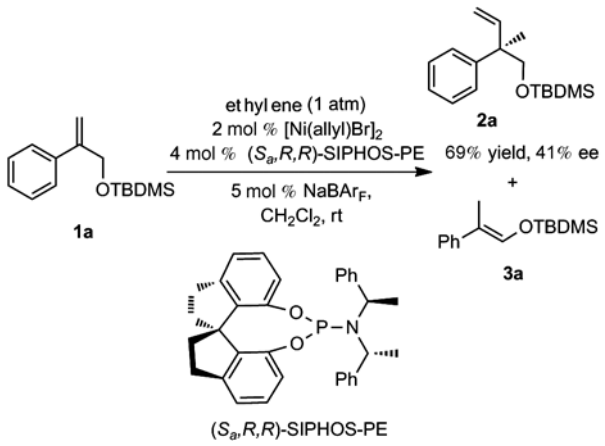


Scheme 1 The Ni-catalyzed asymmetric hydrovinylation reaction of *tert*-butyldimethyl(2-phenylallyloxy)silane. TBDMS is *tert*-butyldimethylsilyl.

side-reaction was the migration of the double bond in substrate **1a** to generate the by-product **3a**, which commonly occurs in hydrovinylation reactions.

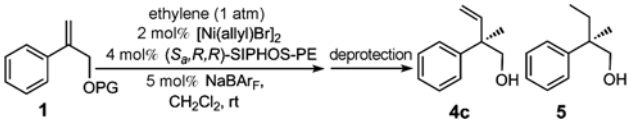
In our previous studies, we found that the coordinating property of the functional group of olefin substrates influences the reactivity and selectivity of the reaction in nickel-catalyzed hydrovinylation. A strong coordinating group occupies one of the coordinating sites of nickel and impedes the coordination of ethylene to nickel, and consequently prevents the hydrovinylation reaction. We thus believe that the choice of right protection of the functional group on olefin substrate is crucial for obtaining high reactivity, chemoselectivity, and enantioselectivity in the hydrovinylation reaction of functionalized olefins. Table 1 shows the results of hydrovinylation of the allylic alcohol with different protecting groups. The reactivity of unprotected allylic alcohol **1b** was very low, and complex products were obtained in the reaction (Table 1, entry 2). When a silyl-protecting group was introduced into the allylic alcohol substrate, the hydrovinylation reaction became applicable. Smaller silyl group TMS (trimethylsilyl) gave higher yield and higher enantioselectivity (60% ee) (entry 3); however, bulkier silyl group TIPS (tri-*iso*-propylsilyl) led to a low reactivity and low enantioselectivity (entry 4). Other protecting groups such as MOM (methoxymethyl) and benzyl were also examined, and poor enantioselectivities were obtained (entries 5 and 6).

To improve the enantioselectivity of hydrovinylation, the reaction parameters were carefully optimized. Different solvents were compared; however, none of the other solvents gave results superior to CH_2Cl_2 (Table 2, entries 2–5). Lower temperatures were found to facilitate enantioselectivity of the reaction. When the reaction temperature was decreased from room temperature to 0 °C, –40 °C and –60 °C, the enantioselectivity of the reaction was enhanced continuously from 60% ee to 81% ee (entries 6–8), albeit a longer reaction time was needed for a full conversion at low temperature. At the same time, the yield of hydrovinylation products also increased from 56% to 77% (entries 1 and 8).

A number of chiral spiro phosphorus ligands developed in our laboratory [15] were tested in the hydrovinylation reaction of **1c** (Figure 1). Ligand (*S*$_a$,*R*,*R*)-SIPHOS-PE was found to be the best choice of ligands in terms of the yield and enantioselectivity of the reaction.

A variety of trimethyl(2-arylallyloxy)silanes were investigated in the hydrovinylation reaction under the optimal reaction conditions. All substrates with a *meta*- or *para*-substituent on the phenyl ring made the hydrovinylation reaction proceed smoothly and produce the corresponding homoallylic alcohols with a chiral quaternary carbon center in moderate to good yields (42%–97%) and good to high enantioselectivities (76%–95% ee) (Table 3, entries 1–12).

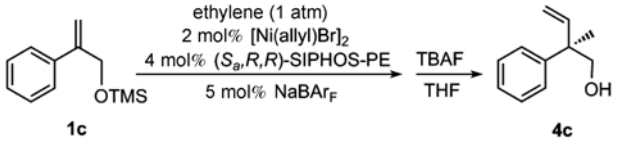
Table 1 Ni-catalyzed asymmetric hydrovinylation of allyl alcohol: protecting groups [a]



Entry	Substrate	PG	Yield of **4c** (%) [b]	ee (%) [c] of **4c**
1	**1a**	TBDMS	69	41
2	**1b**	H	ND [d]	–
3	**1c**	TMS	56	60
4	**1d**	TIPS	31	25
5	**1e**	MOM	49	–22
6	**1f**	Bn	35 [e]	20 [e]

a) Reaction conditions: $[Ni(allyl)Br]_2$ (0.01 mmol), (*S*$_a$,*R*,*R*)-SIPHOS-PE (0.02 mmol), $NaBAr_F$ (0.024 mmol), substrate (0.5 mmol), CH_2Cl_2 (2.5 mL), rt, 1 to 3 h. b) Yield for two steps. c) Determined by SFC (supercritical fluid chromatography) using a Chiralcel OJ-H column. d) Not determined. e) Date for deprotecting product **5**.

Table 2 Ni-catalyzed asymmetric hydrovinylation reaction of trimethyl (2-phenylallyloxy)silane: optimizing reaction conditions [a]



Entry	Solvent	Temp.	Time	Conv. (%) [b]	Yield (%)	ee (%)
1	CH_2Cl_2	rt	< 1 h	100	56	60
2	toluene	rt	3 h	39	5	49
3	Et_2O	rt	3 h	trace	–	–
4	$CHCl_3$	rt	4.5 h	28	10	53
5	CH_2ClCH_2Cl	rt	4.5 h	29	trace	ND
6	CH_2Cl_2	0 °C	15 min	100	59	68
7	CH_2Cl_2	–40 °C	30 min	99	78	79
8	CH_2Cl_2	–60 °C	5 h	99	77	81

a) Reaction conditions and analysis were the same as those in Table 1, entry 3. b) Determined by GC using a HP-5 column.

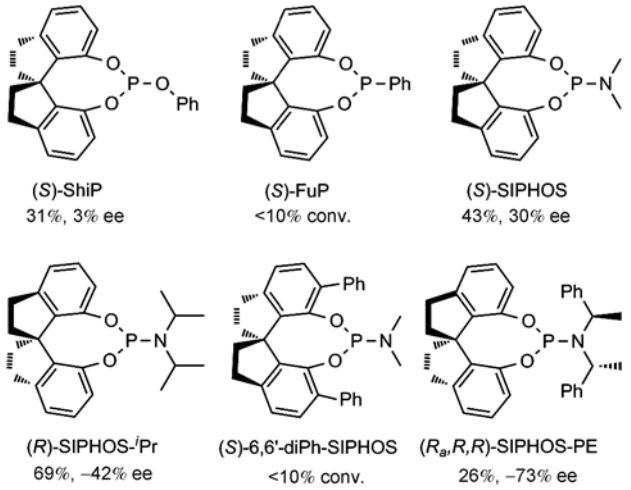
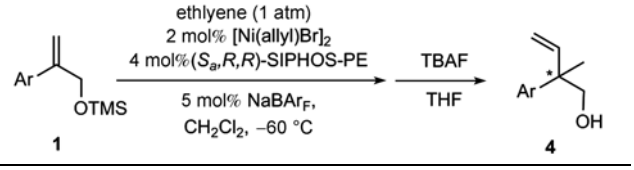
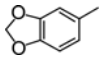


Figure 1 Ligand screening (reaction conditions were the same as those in Table 2, entry 8).

Table 3 Asymmetric hydrovinylation of trimethyl(2-arylallyloxy)silanes [a]

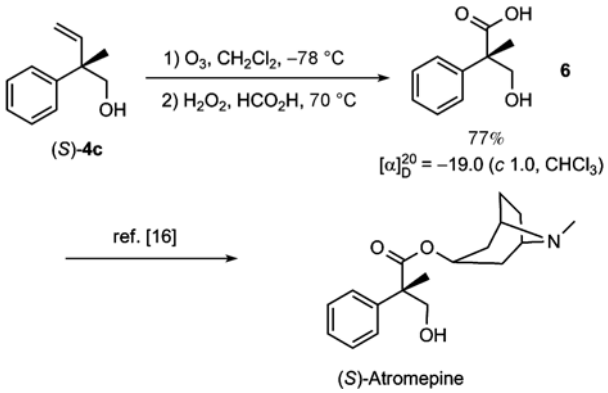


Entry	Substrate	Ar	Product	Yield (%)	ee (%)
1	**1c**	C_6H_5	**4c**	77	81 (R)
2 [b]	**1g**	4-MeC_6H_4	**4g**	91	78 (R)
3	**1h**	4-MeOC_6H_4	**4h**	97	85
4	**1i**	4-FC_6H_4	**4i**	80	94
5	**1j**	4-ClC_6H_4	**4j**	69	92
6	**1k**	4-BrC_6H_4	**4k**	62	95
7	**1l**	4-PhC_6H_4	**4l**	82	80
8	**1m**	3-MeOC_6H_4	**4m**	86	76
9	**1n**	3-FC_6H_4	**4n**	49	91
10	**1o**	3-ClC_6H_4	**4o**	42	88
11	**1p**	3-BrC_6H_4	**4p**	49	85
12	**1q**		**4q**	92	89
13	**1r**	2-naphthyl	**4r**	92	81
14	**1s**		**4s**	90	73

a) Reaction conditions and analysis were the same as those in Table 2, entry 8. The by-products were the enolsilylethers formed by migration of the double bond in substrates. b) The reaction was performed at −40 °C.

The substrates **1g** and **1h**, containing an electron-donating group at the *para*-position of phenyl ring, gave higher yields (91% and 97%) and lower ee values (78% ee and 85% ee) (entries 2 and 3). While the substrates **1i**, **1j** and **1k** having an electron-withdrawing group at the *para*-position of phenyl ring gave lower yields (62%–80%) but higher ee values (92%–95% ee) (entries 4–6). The substrates with a *meta*-substituent afforded lower yields or lower enantioselectivities (entries 8–11 vs. 3–6). The substrates with 2-biphenyl (**1l**) and 3,5-dimethylenedioxyphenyl (**1q**) also provided good yields and enantioselectivities (entries 7 and 12). The *ortho* substitution on the phenyl ring of the substrate fully prohibited the reaction under standard conditions (data not shown). In addition to styrene derivatives, the substrates containing naphthyl (**1r**) and thiophenyl (**1s**) groups could also undergo the hydrovinylation reaction with high yields and good enantioselectivities (entries 13 and 14).

The double bond and hydroxyl group present in the products of asymmetric hydrovinylation provide a potential for conversion to various chiral bifunctional compounds, which are significant intermediates in the synthesis of natural products and pharmaceuticals. For example, oxidation of compound (*S*)-**4c** with ozone and hydrogen perhydroxide produced (*S*)-α-methyltropic acid (**6**), which is a key intermediate for the synthesis of chiral drug (*S*)-Atromepine (Scheme 2) [16].



Scheme 2 Asymmetric synthesis of (*S*)-α-methyltropic acid, an intermediate in the synthesis of (*S*)-Atromepine.

3 Conclusions

In conclusion, highly enantioselective nickel-catalyzed asymmetric hydrovinylation of functionalized olefins, silyl-protected allylic alcohols, was realized by using chiral spiro phosphoramidite ligands. The reaction provides a practically useful and efficient method for the construction of bifunctional compounds with a chiral quaternary carbon center.

4 Experimental

4.1 General

The reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Commercially available reagents were used as received without further purification unless otherwise noted. Ethylene (99.9%) was purchased from BAPB Gases Com-

pany, Ltd., Beijing. Anhydrous dichloromethane, DCE, chloroform and DMF were distilled from calcium hydride under nitrogen before use. Anhydrous toluene, THF and ether were distilled from sodium benzophenone ketyl under nitrogen before use. $[Ni(allyl)Br]_2$ [17], $NaBAr_F$ [18, 19] and chiral spiro phosphorous ligands [20–22] were prepared according to the previously reported procedures. Ligands ShiP, SIPHOS, and SIPHOS-PE are commercially available from Aldrich or Strem Co. The 2-arylprop-2-en-1-ol was prepared by reaction of arylmagnesium bromide and prop-2-yn-1-ol in the presence of a catalytic amount of CuI according to the previously reported procedure [23]. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) or a Bruker AV 300 spectrometer at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR) in $CDCl_3$. Chemical shifts were reported in ppm downfield from internal Me_4Si. HRMS were recorded on a VG ZAB-HS mass spectrometer with EI resource. GC analyses were performed using a Hewlett Packard Model HP 6890 Series equipped with HP-5 column. HPLC analyses were performed on a Waters 2996 chromatography. SFC analyses were performed on Agilent 1200 Series.

4.2 Preparation and analytic data of substrates

Typical procedure for preparation of trimethyl(2-arylallyloxy) silane: A mixture of 2-arylprop-2-en-1-ol (10 mmol) and pyridine (11 mmol) in THF (50 mL) was stirred at room temperature, and TMSCl (10 mmol) was added dropwise. After stirring for 1 h, the resulting suspension was filtrated. The filtrate was concentrated under vacuum and the residue was purified by chromatography (ethyl acetate/petroleum ether = 1:10, *v*/*v*) to give trimethyl(2-arylallyloxy)silane. The analysis data of trimethyl(2-arylallyloxy)silane are illustrated below.

*Trimethyl(2-phenylallyloxy)silane (**1c**)*

Colorless oil, 92% yield (from prop-2-yn-1-ol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.26 (m, 5H), 5.45 (s, 1H), 5.39 (s, 1H), 4.52 (s, 2H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 139.3, 128.6, 127.9, 126.3, 112.1, 64.6, 0.2; HRMS (EI) Calcd for $C_{12}H_{18}OSi$: 206.1127; Found 206.1144.

*Trimethyl(2-p-tolylallyloxy)silane (**1g**)*

Colorless oil, 68% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 5.25 (s, 1H), 5.18 (s, 1H), 4.34 (s, 2H), 2.19 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 137.6, 136.4, 129.3, 126.2, 111.3, 64.6, 21.4, –0.1; HRMS (EI) Calcd for $C_{13}H_{20}OSi$: 220.1283; Found 220.1284.

*(2-(4-Methoxyphenyl)allyloxy)trimethylsilane (**1h**)*

Colorless oil, 29% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 5.21 (s, 1H), 5.13 (s, 1H), 4.33 (s, 2H), 3.66 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 146.6, 131.9, 127.5, 114.1, 110.8, 64.9, 55.5, 0.0; HRMS (EI) Calcd for $C_{13}H_{20}O_2Si$: 236.1233; Found 236.1237.

*(2-(4-Fluorophenyl)allyloxy)trimethylsilane (**1i**)*

Colorless oil, 60% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, J = 8.8 and 5.6 Hz, 2H), 7.04 (t, J = 8.8 Hz, 2H), 5.43 (s, 1H), 5.42 (s, 1H), 4.53 (s, 2H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 161.4, 146.2, 135.3, 128.0, 127.9, 115.4, 115.2, 112.2, 64.7, –0.3; HRMS (EI) Calcd for $C_{12}H_{17}FOSi$: 224.1033; Found 224.1032.

*(2-(4-Chlorophenyl)allyloxy)trimethylsilane (**1j**)*

Colorless oil, 34% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22–7.13 (m, 4H), 5.28 (s, 1H), 5.23 (s, 1H), 4.32 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 137.6, 133.7, 128.6, 127.6, 112.9, 64.5, –0.2; HRMS (EI) Calcd for $C_{12}H_{17}ClOSi$: 240.0737; Found 240.0741.

*(2-(4-Bromophenyl)allyloxy)trimethylsilane (**1k**)*

Colorless oil, 47% yield (from prop-2-yn-1-ol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 5.40 (s, 1H), 4.48 (s, 2H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 139.1, 131.6, 128.0, 121.9, 113.0, 64.5, –0.2; HRMS (EI) Calcd for $C_{12}H_{17}BrOSi$: 284.0232; Found 284.0235.

*(2-(4-Biphenyl)allyloxy)trimethylsilane (**1l**)*

White solid (mp: 58–60 °C), 41% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.30 (m, 9H), 5.52 (s, 1H), 5.44 (s, 1H), 4.56 (s, 2H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 141.0, 140.8, 138.2, 129.1, 127.7, 127.3, 127.2, 126.8, 112.3, 64.7, 0.0; HRMS (EI) Calcd for $C_{18}H_{22}OSi$: 282.1440; Found 282.1433.

*(2-(3-Methoxyphenyl)allyloxy)trimethylsilane (**1m**)*

Colorless oil, 34% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–6.90 (m, 4H), 5.55 (s, 1H), 5.50 (s, 1H), 4.60 (s, 2H), 3.86 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 147.3, 141.1, 129.7, 119.0, 113.4, 112.6, 112.5, 64.8, 55.5, 0.0; HRMS (EI) Calcd for $C_{13}H_{20}O_2Si$: 236.1233; Found 236.1234.

*(2-(3-Fluorophenyl)allyloxy)trimethylsilane (**1n**)*

Colorless oil, 56% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12–6.75 (m, 4H), 5.29 (s, 1H), 5.25 (s, 1H), 4.31 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 161.8, 146.4, 142.0, 141.9, 130.3, 130.2, 122.2, 115.1, 114.8, 113.7, 113.5, 64.7, 0.0; HRMS (EI)

Calcd for $C_{12}H_{17}FOSi$: 224.1033; Found 224.1034.

*(2-(3-Chlorophenyl)allyloxy)trimethylsilane (**1o**)*

Colorless oil, 49% yield (from prop-2-yn-1-ol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.26 (m, 4H), 5.47 (s, 1H), 5.42 (s, 1H), 4.78 (s, 2H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 141.4, 134.7, 130.0, 128.1, 126.7, 124.7, 113.6, 64.7, 0.0; HRMS (EI) Calcd for $C_{12}H_{17}ClOSi$: 240.0737; Found 240.0738.

*(2-(3-Bromophenyl)allyloxy)trimethylsilane (**1p**)*

Colorless oil, 33% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–6.99 (m, 4H), 5.28 (s, 1H), 5.24 (s, 1H), 4.30 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 141.6, 131.0, 130.2, 129.6, 125.1, 123.0, 113.7, 64.6, 0.0; HRMS (EI) Calcd for $C_{12}H_{17}BrOSi$: 284.0232; Found 284.0234.

*(2-(Benzo[d][1,3]dioxol-5-yl)allyloxy)trimethylsilane (**1q**)*

Colorless oil, 32% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78–6.57 (m, 3H), 5.74 (s, 2H), 5.18 (s, 1H), 5.13 (s, 1H), 4.28 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 147.6, 146.7, 133.7, 119.9, 111.5, 108.4, 107.1, 101.4, 65.0, 0.0; HRMS (EI) Calcd for $C_{13}H_{18}O_3Si$: 250.1025; Found 250.1058.

*Trimethyl(2-(naphthalen-2-yl)allyloxy)silane (**1r**)*

Yellow oil, 74% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83–7.39 (m, 7H), 5.61 (s, 1H), 5.51 (s, 1H), 4.64 (s, 2H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 136.5, 133.7, 133.3, 128.5, 128.2, 127.9, 126.5, 126.2, 124.9, 124.8, 112.9, 64.8, 0.0; HRMS (EI) Calcd for $C_{16}H_{20}OSi$: 256.1283; Found 256.1290.

*Trimethyl(2-(thiophen-2-yl)allyloxy)silane (**1s**)*

Colorless oil, 32% yield (from prop-2-yn-1-ol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04–6.84 (m, 3H), 5.39 (s, 1H), 5.18 (s, 1H), 4.37 (s, 2H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 141.0, 127.6, 124.6, 123.6, 111.0, 64.7, 0.0; HRMS (EI) Calcd for $C_{10}H_{16}OSSi$: 212.0691; Found 212.0697.

*tert-Butyldimethyl(2-phenylallyloxy)silane (**1a**)*

The mixture of 2-phenylprop-2-en-1-ol (2.4 g, 18 mmol) and imidazole (13.6 g, 203 mmol) in dry DMF (40 mL) was stirred at room temperature, and TBDMSCl (3.0 g, 20 mmol) was added dropwise. After stirring for 20 h, the resulting solution was poured to 200 mL water and extracted with CH_2Cl_2 three times. The organic layer was washed by cold hydrochloric acid (1 M), saturated $NaHCO_3$ solution and brine. After dried over anhydrous Na_2SO_4, the solution was concentrated under vacuum and the residue was purified by chromatography (ethyl acetate/petroleum ether = 1:10, *v/v*) to give *tert*-butyldimethyl(2-phenylallyloxy)silane (4.2 g, 95% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5H), 5.43 (d, J = 1.6 Hz, 1H), 5.41 (d, J = 2.0 Hz, 1H), 4.54 (s, 2H), 0.95 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 139.3, 128.4, 127.8, 126.2, 111.5, 64.9, 26.1, 18.5, 0.0; HRMS (EI) Calcd for $C_{11}H_{15}OSi$ (M–C_4H_9): 191.0892; Found 191.0897.

*Triisopropyl(2-phenylallyloxy)silane (**1d**)*

Compound **1d** was prepared from 2-phenylprop-2-en-1-ol and TIPSCl by the same procedure as that for **1a**. Pale yellow oil, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5H), 5.49 (s, 1H), 5.44 (s, 1H), 4.61 (s, 2H), 1.20–1.09 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 139.3, 128.4, 127.7, 126.0, 111.1, 64.9, 18.2, 12.2; HRMS (EI) Calcd for $C_{15}H_{23}OSi$ (M–C_3H_7): 247.1518; Found 247.1513.

*1-(1-(Methoxymethoxy)prop-2-en-2-yl)benzene (**1e**)*

Under nitrogen atmosphere, 2-phenylprop-2-en-1-ol (1.9 g, 14 mmol) was added to the suspension of NaH (0.36 g, 15 mmol) in dry THF (50 mL). After stirring for 4 h at room temperature, the system turned to brown. The $MeOCH_2Cl$ (1.4 g, 17 mmol) was added dropwise. After stirring overnight, the resulting suspension was poured to 100 mL water and extracted with ether three times. The organic layer was washed by brine and dried over anhydrous Na_2SO_4. After filtration and concentration under vacuum, the residue was purified by chromatography (ethyl acetate/petroleum ether = 1:10, *v/v*) to give 1-(1-(methoxymethoxy)prop-2-en-2-yl)-benzene (2.1 g, 85% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.8 Hz, 2H), 7.36–7.29 (m, 3H), 5.54 (s, 1H), 5.37 (s, 1H), 4.70 (s, 2H), 4.47 (s, 2H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.2, 138.9, 128.4, 127.8, 126.1, 114.3, 95.5, 68.9, 55.3; HRMS (EI) Calcd for $C_{11}H_{14}O_2$: 178.0994; Found 178.0995.

*1-((2-Phenylallyloxy)methyl)benzene (**1f**)[24]*

Compound **1f** was prepared from 2-phenylprop-2-en-1-ol, NaH and BnCl by the similar procedure as that for **1e**. Colorless oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.36–7.29 (m, 8H), 5.56 (s, 1H), 5.38 (s, 1H), 4.57 (s, 2H), 4.42 (s, 2H).

4.3 General procedure for asymmetric Ni-catalyzed hydrovinylation

Under nitrogen atmosphere, $[Ni(allyl)Br]_2$ (10 μmol), chiral phosphorus ligand (20 μmol) and distilled CH_2Cl_2 (2.5 mL) were introduced into a Schlenk tube equipped with a stirring bar. The mixture was stirred at room temperature for 1 min and transferred to another Schlenk tube containing NaBArF (24 μmol). The resulting mixture was stirred for 3 min at room temperature and then cooled to the desired temperature. The inert atmosphere in the Schlenk tube was replaced by ethylene three times and the trimethyl-(2-arylallyloxy) silane (0.5 mmol) was introduced. The reaction mixture was

stirred for specified time (monitored by GC). After the reaction was completed, the mixture was concentrated under reduced pressure. The residue was resolved by THF (5 mL), and TBAF (50 mg) was added to the solution. The mixture was stirred at room temperature until the deprotecting reaction finished. Finally, the resulting mixture was chromatographed on silica gel column to give the pure product. The analysis data of the products are illustrated below.

*(2R)-2-Methyl-2-phenylbut-3-en-1-ol (**4c**) [25]*

Colorless oil, 77% yield, 81% ee, $[\alpha]_D^{20} = -18.1$ (*c* 1.9, ethanol). The absolute configuration of **4c** was determined to be *R* (see *S* compound **6**). SFC condition: Chiralcel OJ-H column, sc CO_2/*i*-PrOH = 90:10, flow rate = 2.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 5.19 min for *S* enantiomer, t_R = 5.58 min for *R* enantiomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4H), 7.25–7.21 (m, 1H), 6.07 (dd, *J* = 17.7 and 11.1 Hz, 1H), 5.26 (dd, *J* = 10.8 and 1.2 Hz, 1H), 5.15 (dd, *J* = 17.7 and 1.2 Hz, 1H), 3.78 (d, *J* = 3.6 Hz, 2H), 1.46 (s, 1H), 1.42 (s, 3H).

*(2R)-2-Methyl-2-p-tolylbut-3-en-1-ol (**4g**)* [26]

Colorless oil, 91% yield, 78% ee, $[\alpha]_D^{20} = -10.4$ (*c* 1.25, $CHCl_3$). The absolute configuration of **4g** was determined to be *R* by comparison of the [α] value of **4g** with reported data; *R*-enriched **4g** (uncertain ee value): $[\alpha]_D^{20} = -2.4$ (*c* 1.2, $CHCl_3$) [26]. SFC condition: Chiralcel OJ-H column, sc CO_2/*i*-PrOH = 90:10, flow rate = 2.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 4.89 min for *S* isomer, t_R = 5.48 min for *R* isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.07 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.25 (dd, *J* = 10.8 and 0.9 Hz, 1H), 5.14 (dd, *J* = 17.7 and 0.9 Hz, 1H), 3.77 (d, *J* = 5.7 Hz, 2H), 2.33 (s, 3H), 1.55 (s, 1H), 1.41 (s, 3H).

*2-(4-Methoxyphenyl)-2-methylbut-3-en-1-ol (**4h**)* [27]

Colorless oil, 97% yield, 85% ee, $[\alpha]_D^{20} = -21.0$ (*c* 1.5, ethanol). SFC condition: Chiralcel OJ-H column, sc CO_2/*i*-PrOH = 90:10, flow rate = 2.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 6.56 min for the minor isomer, t_R = 7.08 min for the major isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 12.0 Hz, 2H), 6.87 (d, *J* = 11.7 Hz, 2H), 6.05 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.23 (dd, *J* = 10.8 and 1.2 Hz, 1H), 5.12 (dd, *J* = 17.7 and 1.2 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 2H), 1.45 (s, 1H), 1.40 (s, 3H).

*2-(4-Fluorophenyl)-2-methylbut-3-en-1-ol (**4i**)*

Colorless oil, 80% yield, 94% ee, $[\alpha]_D^{20} = -16.7$ (*c* 1.6, ethanol). HPLC condition: Chiralcel OJ-H column, *n*-hexane/*i*-propanol = 95:5, flow rate = 0.8 mL/min, wavelength = 220 nm, t_R = 22.22 min for the major isomer, t_R = 24.17 min for the minor isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.7 and 5.4 Hz, 2H), 6.93 (t, *J* = 8.4 Hz, 2H), 5.95 (dd, *J* = 17.7 and 11.1 Hz, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 5.04 (d, *J* = 18.0 Hz, 1H), 3.67 (s, 2H), 1.45 (s, 1H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 159.9, 143.5, 140.3, 140.2, 128.6, 128.5, 115.2, 115.0, 114.7, 70.0, 46.5, 22.8; HRMS (EI) Calcd for $C_{11}H_{13}FO$: 180.0950; Found 180.0950.

*2-(4-Chlorophenyl)-2-methylbut-3-en-1-ol (**4j**)*

Colorless oil, 69% yield, 92% ee, $[\alpha]_D^{20} = -20.6$ (*c* 0.65, ethanol). HPLC condition: Chiralcel OJ-H column, *n*-hexane/*i*-propanol = 97:3, flow rate = 0.8 mL/min, wavelength = 220 nm, t_R = 23.32 min for major isomer, t_R = 24.79 min for the minor isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.6 Hz, 4H), 6.03 (dd, *J* = 17.6 and 10.8 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 17.6 Hz, 1H), 3.76 (s, 2H), 1.43 (s, 1H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 132.4, 128.5, 128.4, 115.1, 69.8, 46.7, 22.7; HRMS (EI) Calcd for $C_{11}H_{13}ClO$: 196.0655; Found 196.0654.

*2-(4-Bromophenyl)-2-methylbut-3-en-1-ol (**4k**)*

Colorless oil, 62% yield, 95% ee, $[\alpha]_D^{20} = -20.1$ (*c* 1.0, ethanol). HPLC condition: Chiralcel OJ-H column, *n*-hexane/*i*-propanol = 98:2, flow rate = 0.7 mL/min, wavelength = 220 nm, t_R = 25.97 min for the major isomer, t_R = 27.59 min for the minor isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.01 (dd, *J* = 18.0 and 10.8 Hz, 1H), 5.26 (d, *J* = 10.8 Hz, 1H), 5.12 (d, *J* = 17.6 Hz, 1H), 3.74 (s, 2H), 1.45 (s, 1H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.3, 131.7, 129.1, 120.7, 115.3, 70.0, 47.0, 22.9; HRMS (EI) Calcd for $C_{11}H_{13}BrO$: 240.0150; Found 240.0150.

*2-(4-Biphenyl)-2-methylbut-3-en-1-ol (**4l**)*

White solid (mp: 43–45 °C), 82% yield, 80% ee, $[\alpha]_D^{20} = -26.6$ (*c* 1.35, ethanol). SFC condition: Chiralcel OD-H column, sc CO_2/*i*-PrOH = 80:20, flow rate = 2.0 mL/min, wavelength = 254 nm, pressure = 100 bar, t_R = 7.19 min for the major isomer, t_R = 8.02 min for the minor isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.33 (m, 9H), 6.11 (dd, *J* = 17.6 and 10.8 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 17.6 Hz, 1H), 3.84 (d, *J* = 6.4 Hz, 2H), 1.57 (s, 1H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 143.6, 140.8, 139.4, 128.9, 127.4, 127.3, 127.2, 127.1, 114.7, 70.1, 46.8, 22.7; HRMS (EI) Calcd for $C_{17}H_{18}O$: 238.1358; Found 238.1358.

*2-(3-Methoxyphenyl)-2-methylbut-3-en-1-ol (**4m**)*

Colorless oil, 86% yield, 76% ee, $[\alpha]_D^{20} = -17.2$ (*c* 2.25, ethanol). HPLC condition: Chiralcel OJ-H column, *n*-hexane/*i*-propanol = 90:10, flow rate = 0.8 mL/min, wavelength = 220 nm, t_R = 19.57 min for the minor isomer, t_R = 21.20 min for the major isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 1H), 6.87–6.68 (m, 3H), 5.98 (dd, *J* = 17.4 and 10.8 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 5.07 (d, *J* = 17.4 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 2H), 1.43 (s, 1H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 146.5, 143.7, 129.6,

119.4, 114.7, 113.8, 111.5, 70.2, 55.4, 47.2, 22.8; HRMS (EI) Calcd for $C_{12}H_{16}O_2$: 192.1150; Found 192.1150.

*2-(3-Fluorophenyl)-2-methylbut-3-en-1-ol (**4n**)*

Colorless oil, 49% yield, 91% ee, $[\alpha]_D^{20} = -17.5$ (*c* 0.85, ethanol). SFC condition: Chiralpak AD-H column, sc CO_2/*i*-PrOH = 95:5, flow rate = 2.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 7.55 min for the minor isomer, t_R = 8.54 min for the major isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.19 (m, 1H), 7.07–6.97 (m, 2H), 6.86 (t, *J* = 8.1 Hz 1H), 5.97 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.21 (d, *J* = 10.8 Hz, 1H), 5.08 (d, *J* = 17.7 Hz, 1H), 3.70 (s, 2H), 1.34 (s, 3H), 1.32 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 161.3, 143.0, 129.9, 129.7, 122.5, 115.1, 114.4, 114.1, 113.5, 113.2, 69.8, 47.0, 22.6; HRMS (EI) Calcd for $C_{11}H_{13}FO$: 180.0950; Found 180.0955.

*2-(3-Chlorophenyl)-2-methylbut-3-en-1-ol (**4o**)*

Colorless oil, 42% yield, 88% ee, $[\alpha]_D^{20} = -15.7$ (*c* 0.75, ethanol). SFC condition: Chiralpak AD-H column, sc CO_2/*i*-PrOH = 95:5, flow rate = 2.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 11.32 min for the minor isomer, t_R = 12.27 min for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.22 (m, 4H), 6.03 (dd, *J* = 17.6 and 10.8 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 5.16 (d, *J* = 17.6 Hz, 1H), 3.77 (s, 2H), 1.48 (s, 1H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.9, 142.9, 134.4, 129.6, 127.4, 126.7, 125.2, 125.1, 115.2, 69.8, 47.0, 22.6; HRMS (EI) Calcd for $C_{11}H_{13}ClO$: 196.0655; Found 196.0654.

*2-(3-Bromophenyl)-2-methylbut-3-en-1-ol (**4p**)*

Colorless oil, 49% yield, 85% ee, $[\alpha]_D^{20} = -14.0$ (*c* 1.85, ethanol) SFC condition: Chiralpak AD-H column, sc CO_2/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 30.64 min for the minor isomer, t_R = 32.77 min for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.19 (m, 4H), 6.02 (dd, *J* = 17.6 and 10.8 Hz, 1H), 5.29 (dd, *J* = 10.8 and 0.8 Hz, 1H), 5.16 (dd, *J* = 17.6 and 0.8 Hz, 1H), 3.76 (d, *J* = 5.2 Hz, 2H), 1.47 (s, 1H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.1, 142.9, 130.3, 130.0, 129.7, 125.6, 122.7, 115.3, 69.8, 47.0, 22.6; HRMS (EI) Calcd for $C_{11}H_{13}BrO$: 240.0150; Found 240.0150.

*2-(Benzo[d][1,3]dioxol-5-yl)-2-methylbut-3-en-1-ol (**4q**)*

Colorless oil, 92% yield, 89% ee, $[\alpha]_D^{20} = -22.0$ (*c* 0.5, ethanol). HPLC condition: Chiralcel OJ-H column, *n*-hexane/*i*-propanol = 90:10, flow rate = 0.8 mL/min, wavelength = 220 nm, t_R = 21.64 min for the minor isomer, t_R = 22.88 min for the major isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77–6.66 (m, 3H), 5.93 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.83 (s, 2H), 5.14 (d, *J* = 10.8 Hz, 1H), 5.03 (d, *J* = 17.7 Hz, 1H), 3.62 (s, 2H), 1.61 (s, 1H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 146.0, 143.7, 138.5, 120.0, 114.3, 108.0, 107.8, 101.0, 70.1, 46.7, 22.9; HRMS (EI) Calcd for $C_{12}H_{14}O_3$: 206.0943; Found 206.0945.

*2-Methyl-2-(naphthalen-2-yl)but-3-en-1-ol (**4r**)*

Offwhite solid (mp: 40–42 °C), 92% yield, 81% ee, $[\alpha]_D^{20} = -29.0$ (*c* 1.0, ethanol). ee value of **4r** was determined by converting the alcohol to the corresponding benzoate and analyzing the ester on chiral HPLC. HPLC condition: Chiralcel OJ column, *n*-hexane/*i*-propanol = 90:10, flow rate = 0.8 mL/min, wavelength = 254 nm, t_R = 12.73 min for the minor isomer, t_R = 28.63 min for the major isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68–7.65 (m, 4H), 7.35–7.31 (m, 3H), 6.00 (dd, *J* = 17.7 and 10.8 Hz, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 5.03 (d, *J* = 17.7 Hz, 1H), 3.70 (s, 2H), 1.55 (s, 1H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 142.0, 133.5, 132.2, 128.1, 127.5, 126.1, 125.9, 125.7 125.5, 114.9, 69.9, 47.2, 22.8; HRMS (EI) Calcd for $C_{15}H_{16}O$: 212.1201; Found 212.1206.

*2-methyl-2-(thiophen-2-yl)but-3-en-1-ol (**4s**)*

Colorless oil, 90% yield, 73% ee, $[\alpha]_D^{20} = -26.6$ (*c* 1.7, ethanol). SFC condition: Chiralcel OJ-H column, sc CO_2/*i*-PrOH = 95:5, flow rate = 2.0 mL/min, wavelength = 220 nm, pressure = 100 bar, t_R = 23.11 min for the minor isomer, t_R = 24.20 min for the major isomer. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 4.8 Hz, 1H), 6.90–6.81 (m, 2H), 6.01 (dd, *J* = 17.4 and 10.8 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 5.07 (d, *J* = 17.4 Hz, 1H), 3.61 (s, 2H), 1.79 (s, 1H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 142.9, 126.8, 124.0, 114.7, 71.1, 45.9, 23.5; HRMS (EI) Calcd for $C_9H_{12}OS$: 168.0609; Found 168.0604.

4.4 Preparation of (*S*)-α-methyltropic acid (6) [16]

(*S*)-α-Methyltropic acid was synthesized by the same method as that used in the previous paper [14]. Yield: 77%, dark brown oil. $[\alpha]_D^{20} = -19.0$ (*c* 1.0, $CHCl_3$) ($[\alpha]_D^{25} = -19.4$ (*c* 1.65, $CHCl_3$) for *S*-enriched **6**) [28]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 5H), 4.10 (d, *J* = 11.6 Hz, 1H), 3.65 (d, *J* = 11.2 Hz, 1H), 1.68 (s, 3H).

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1 Jolly PW, Wilke G. in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 2 (Eds. Cornils B, Herrmann WA.), New York: Wiley-VCH, 1996. 1024–1048
2 Goossen LJ. Asymmetric hydrovinylation: New perspectives through use of modular ligand systems. *Angew Chem Int Ed*, 2002, 41: 3775–3778
3 RajanBabu TV. Asymmetric hydrovinylation reaction. *Chem Rev,* 2003, 103: 2845–2860
4 Wilke G, Monkiewicz J. DOS 3 618 169, priority 30.05.1986; *Chem. Abstr.* 1988, 109: 6735
5 Park H, RajanBabu TV. Tunable ligands for asymmetric catalysis:

Readily available carbohydrate-derived diarylphosphinites induce high selectivity in the hydrovinylation of styrene derivatives. *J Am Chem Soc*, 2002, 124: 734–735
6 Franciò G, Faraone F, Leitner W. Highly enantioselective nickel-catalyzed hydrovinylation with chiral phosphoramidite ligands. *J Am Chem Soc,* 2002, 124: 736–737
7 Zhang A, RajanBabu TV. Fine-tuning monophosphine ligands for enhanced enantioselectivity. Influence of chiral hemilabile pendant groups. *Org Lett*, 2004, 6: 1515–1517
8 Smith CR, RajanBabu TV. Efficient, selective, and green: Catalyst tuning for highly enantioselective reactions of ethylene. *Org Lett*, 2008, 10: 1657–1659
9 Shi W-J, Zhang Q, Xie J-H, Zhu S-F, Hou G-H, Zhou Q-L. Highly enantioselective hydrovinylation of α-alkyl vinylarenes. An approach to the construction of all-carbon quaternary stereocenters. *J Am Chem Soc*, 2006, 128: 2780–2781
10 Zhang A, RajanBabu TV. All-carbon quaternary centers via catalytic asymmetric hydrovinylation. New approaches to the exocyclic side chain stereochemistry problem. *J Am Chem Soc*, 2006, 128: 5620–5621
11 Kumareswaran R, Nandi M, RajanBabu TV. Hydrovinylation of norbornene. Ligand-dependent selectivity and asymmetric variations. *Org Lett*, 2003, 5: 4345–4348
12 Zhang A, RajanBabu TV. Hydrovinylation of 1,3-dienes: A new protocol, an asymmetric variation, and a potential solution to the exocyclic side chain stereochemistry problem. *J Am Chem Soc*, 2006, 128: 54–55
13 Saha B, Smith CR, RajanBabu TV. Ligand tuning in asymmetric hydrovinylation of 1,3-dienes: A stereoselective route to either steroid-C_{20}(*S*) or -C_{20} (*R*) derivatives. *J Am Chem Soc*, 2008, 130: 9000–9005
14 Zhang Q, Zhu S-F, Qiao X-C, Wang L-X, Zhou Q-L. Nickel-catalyzed highly selective hydrovinylation of α-ketals of vinylarenes. *Adv Synth Catal*, 2008, 350: 1507–1510
15 Xie J-H, Zhou Q-L. Chiral diphosphine and monodentate phosphorous ligands on a spiro scaffold for transition-metal-catalyzed asymmetric reactions. *Acc Chem Res*, 2008, 41: 581–593
16 Melone G, Vecchi A, Pagani G, Testa E. Tropine DL-α-methyltropate (methyltropine) and its optical antipodes. *J Org Chem*, 1960, 25: 859–861
17 Wilke G. π-Allyl nickel compounds and their preparation. US3422128, 1969
18 Nishida H, Takada N, Yoshimura M, Sonoda T, Kobayashi H. Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Highly lipophilic stable anionic agent for solvent-extraction cations. *Bull Chem Soc Jpn*, 1984, 57: 2600–2604
19 Brookhart M, Grant B, Volpe AF Jr. $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$: A convenient reagent for generation and stabilization of cationic, highly electrophilic organometallic complexes. *Organometallics*, 1992, 11: 3920–3922
20 Zhou H, Wang W-H, Fu Y, Xie J-H, Shi W-J, Wang L-X, Zhou Q-L. Highly enantioselective copper-catalyzed conjugate addition of diethylzinc to enones using chiral spiro phosphoramidites as ligands. *J Org Chem*, 2003, 68: 1582–1584
21 Shi W-J, Wang L-X, Fu Y, Zhu S-F, Zhou Q-L. Highly regioselective asymmetric copper-catalyzed allylic alkylation with dialkylzinc using monodentate chiral spiro phosphoramidite and phosphite ligands. *Tetrahedron: Asymmetry*, 2003, 14: 3867–3872
22 Yang Y, Zhu S-F, Duan H-F, Zhou C-Y, Wang L-X, Zhou Q-L. Asymmetric reductive coupling of dienes and aldehydes catalyzed by nickel complexes of spiro phosphoramidites: Highly enantioselective synthesis of chiral bishomoallylic alcohols. *J Am Chem Soc* 2007, 129: 2248–2249
23 Duboudin JG, Jousseaume B, Saux A. Reactifs de grignard vinyliques γ fonctionnels: I. Reactivite des organomagnesiens vis-a-vis d'alcools α acetyleniques en presence d'halogenures cuivreux. *J Organomet Chem*, 1979, 168: 1–11
24 Barluenga J, Fañanás FJ, Sanz R, Marcos C, Ignacio J M. 2-Arylallyl as a new protecting group for amines, amides and alcohols. *Chem Commun*, 2005, 933–935
25 Tueting DR, Echavarren AM, Stille JK. Palladium catalyzed coupling of organostannanes with vinyl epoxides. *Tetrahedron*, 1989, 45: 979–992
26 Fadel A, Canet JL, Salaün J. Asymmetric construction of quaternary carbons from chiral malonates: total synthesis of (+)-epilaurene and (–)-isolaurene. *Tetrahedron: Asymmetry*, 1993, 4: 27–30
27 Fadel A, Vandromme L. Total synthesis of (-)-sporochnol A, the fish deterrent from a chiral malonate. *Tetrahedron: Asymmetry*, 1999, 10: 1153–1162
28 Imao D, Itoi A, Yamazaki A, Shirakura M, Ohtoshi R, Ogata K, Ohmori Y, Ohta T, Ito Y. Easy access to esters with a benzylic quaternary carbon center from diallyl malonates by palladium-catalyzed decarboxylative allylation. *J Org Chem*, 2007, 72, 1652–1658