JOC The Journal of Organic Chemistry

Note

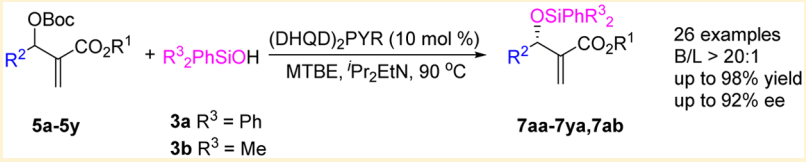
pubs.acs.org/joc

Organocatalytic Enantioselective Allylic Etherification of Morita–Baylis–Hillman Carbonates and Silanols

Hui-Li Liu, Ming-Sheng Xie,* Gui-Rong Qu, and Hai-Ming Guo*

Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China

Supporting Information

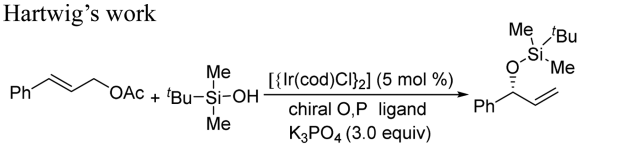


ABSTRACT: The organocatalytic asymmetric allylic etherification reaction of Morita–Baylis–Hillman carbonates and silanols was reported for the first time. With modified cinchona alkaloid $(DHQD)_2PYR$ as the catalyst, a series of aromatic, heterocyclic, or aliphatic Morita–Baylis–Hillman carbonates (25 examples) worked well with triphenylsilanol, affording the corresponding products in moderate to good yields (up to 98%), high regioselectivities (>20:1), and good enantioselectivities (up to 92%). When dimethylphenylsilanol was used as the nucleophile, the product was obtained in 60% yield and 87% ee.

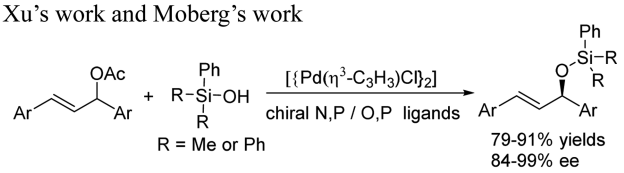
The asymmetric nucleophilic substitution reactions[1] of allylic substrates and various nucleophiles (such as C, N, O, P, S, B)[2−13] are powerful methods to construct carbon–carbon and carbon–heteroatom bonds. Among them, allylic substitutions with O-nucleophiles have received considerable attention, and many outstanding studies in asymmetric allylic etherification (AAE) have been reported in which allylic substitutions reacted with phenols,[7] benzyl alcohols,[8] aliphatic alcohols,[9] alkoxides,[10] and carboxylates[11] are general strategies to synthesize of optically pure allylic ethers. In 2009, Chen's group reported the enantioselective O-allylic alkylation of MBH carbonates using acetophenone oxime as the O nucleophile.[12] Later, Jiang's group achieved allylic hydroxylation of MBH carbonates by using H_2O as the nucleophile directly.[13] By contrast, silicon nucleophiles, such as silane and silanol, have been less studied in the asymmetric allylic substitution reactions.[14] In 2008, Carreira's group used silanolates as the water surrogates to give chiral allylic alcohols conveniently.[15] It was worth mentioning that Hartwig's group first reported one example of an asymmetric allylic substitution reaction of cinnamyl acetate catalyzed by chiral Ir complex (Scheme 1a).[16] Later, the groups of Xu[17] and Moberg[18] used triphenylsilanol and 1,3-diaryl-2-propenyl acetate to form chiral allylic etherification products catalyzed by chiral Pd complex with N,P and O,P ligands, respectively (Scheme 1b). Considering that there are few reports using triphenylsilanol as the nucleophile and no report about allylic substitution reaction of Morita–Baylis–Hillman (MBH) carbonates and silanol, we report on the use of silanol as the nucleophile to react with MBH carbonates through successive S_N2'–S_N2' reactions under chiral organocatalysts to form chiral allylic etherification products (Scheme 1c).

Scheme 1. Asymmetric Allylic Substitution Reactions with Silanol as the Nucleophile

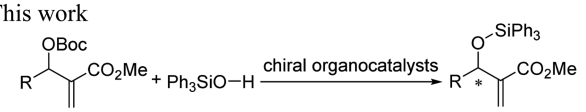
a) Hartwig's work



b) Xu's work and Moberg's work



c) This work

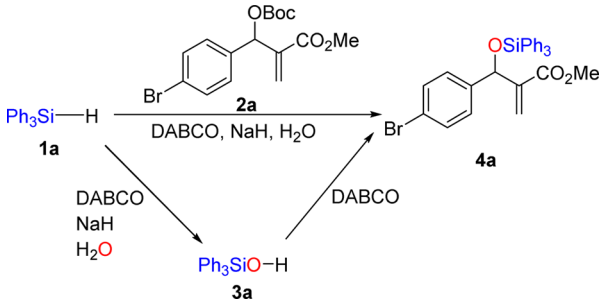


Initially, Ph_3SiH **1a** was used as the nucleophile to react with MBH carbonate **2a** in the presence of DABCO, NaH, and H_2O at room temperature, giving the etherification product **4a** in 40% yield (Scheme 2). The structure of etherification product **4a** was confirmed by X-ray diffraction. This unexpected result made us consider where the oxygen came from, so we performed a series of control experiments (see the Supporting Information for details) and found that Ph_3SiH could be

Received: August 7, 2016
Published: September 22, 2016

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035–10042

Scheme 2. Preliminary Experiments

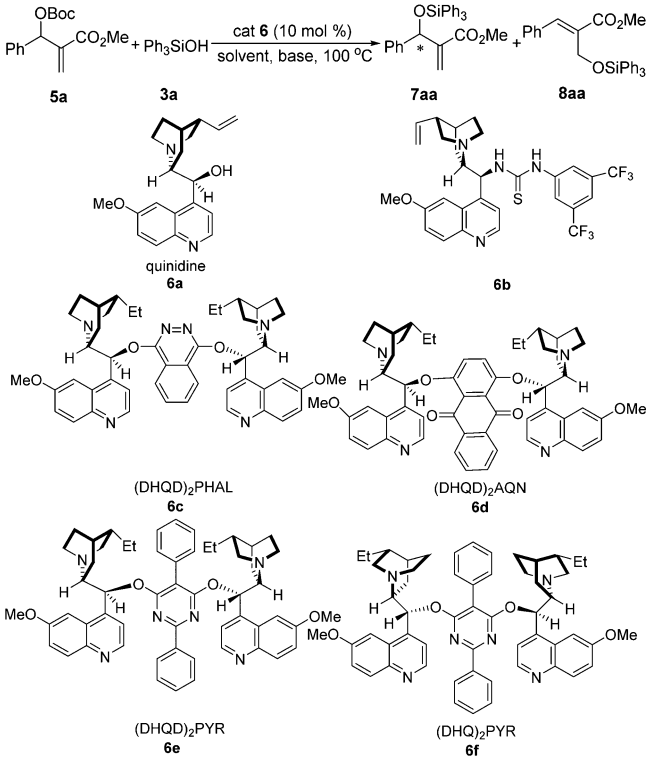


transformed into Ph_3SiOH **3a** in the presence of DABCO, NaH, and H_2O (which is the oxygen source) at room temperature, which was a new way to obtain Ph_3SiOH from Ph_3SiH.[19] Then Ph_3SiOH **3a** reacted with MBH carbonate **2a** to give the product **4a** in the presence of DABCO.

Subsequently, MBH carbonate (**5a**) and Ph_3SiOH (**3a**) were chosen as the model substrates and NaO^{t}Bu was used as the base in *tert*-butyl methyl ether (MTBE) at 100 °C. When quinidine (**6a**) was used as the catalyst, the products **7aa** and **8aa** were formed in 36% total yield and 56% ee, with poor regioselectivity in which the branch product **7aa** was the major form (Table 1, entry 1). When quinine-derived thiourea catalyst **6b** was used as the catalyst, the desired product was only obtained in 14% yield and 8% ee (Table 1, entry 2). When C_2-symmetric (bis)cinchona alkaloid derivatives such as $(DHQD)_2PHAL$ (**6c**), $(DHQD)_2AQN$ (**6d**), $(DHQD)_2PYR$ (**6e**), and $(DHQ)_2PYR$ (**6f**) were used, the ee values were improved significantly (Table 1, entries 3−6), in which $(DHQD)_2PYR$ gave the corresponding product in 52% yield, 12:1 regioselectivity, and 87% ee (Table 1, entry 5). Other bases including Cs_2CO_3, Et_3N, and $^i Pr_2EtN$ were tested (Table 1, entries 7−9), and it was found that $^i Pr_2EtN$ was the best base, affording the desired product in 80% yield, high regioselectivity (>20:1), and 89% ee (Table 1, entry 9). To further increase the yield, the substrate ratio of **5a** and **3a** was examined (Table 1, entries 9−12). The better ratio of **5a**:**3a** was 1.5:1, giving the etherification product in 88% yield, high regioselectivity (>20:1), and 89% ee (Table 1, entry 11). Switching the reaction solvent from MTBE to THF, EE, anisole, or DCM proved that MTBE was the best reaction medium for this reaction (Table 1, entries 11 vs 13−16). When the reaction was performed at a lower temperature of 90 °C, the ee value of **7aa** was improved to 90% and the yield increased from 88% to 91% (Table 1, entry 17 vs 11). By lowering the reaction temperature to 70 °C after 48 h, the ee value of **7aa** was improved to 92% along with a sharply decrease in the yield (Table 1, entry 18). When the catalyst loading was lowered from 10 to 5 mol %, the ee value could be maintained, along with lower yield (Table 1, entry 19). Therefore, the optimal reaction conditions were found to be $(DHQD)_2PYR$ (**6e**) (10 mol %) as the catalyst and $^i Pr_2EtN$ as the base in MTBE at 90 °C for 12 h.

With the optimal conditions in hand (Table 1, entry 17), the substrate scope of the enantioselective allylic etherification reaction was examined, and the results were summarized in Scheme 3. First, different ester groups including ethyl (**5b**), *tert*-butyl (**5c**), benzyl (**5d**), 1-adamantyl (**5e**), and 2-adamantyl (**5f**) esters were tested, and the product **7aa**−**fa** could be afforded in comparable enantioselectivities (89−90% ee), while the yields ranged from 60% to 79%. When electron-withdrawing groups or electron-donating groups were the *ortho* substituents on the aromatic ring of MBH carbonates, the corresponding products **7ga**−**ka** were obtained in 90% ee, but lower yields (55−60%) were obtained for the MBH carbonates **5i**−**k** with halogen substituents on the aromatic ring. The methyl or methoxy groups (**5l**,**m**) on the *m*-position of the phenyl ring could afford the corresponding products (**7la**,**ma**) in higher ee values (91−92%), and the electron-withdrawing

Table 1. Optimization of the Reaction Conditions[a]

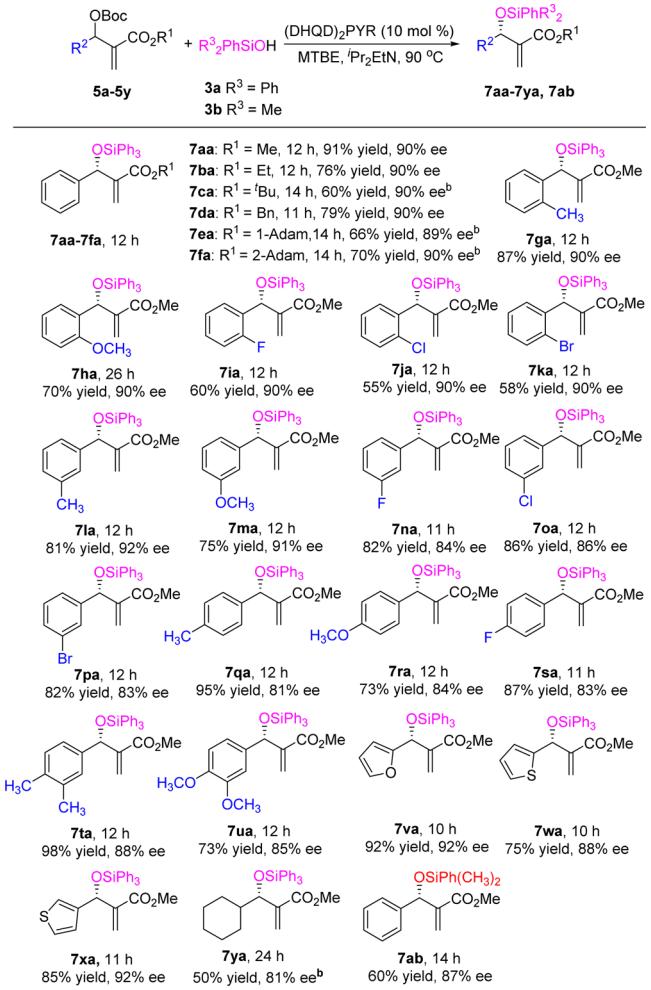


entry	cat.	5a:3a	base	solvent	yield[b] (%)	7aa/8aa[c]	ee[d] (%)
1	**6a**	1:2.5	NaO^{t}Bu	MTBE	36	4:1	56
2	**6b**	1:2.5	NaO^{t}Bu	MTBE	14	15:1	8
3	**6c**	1:2.5	NaO^{t}Bu	MTBE	52	8:1	83
4	**6d**	1:2.5	NaO^{t}Bu	MTBE	53	12:1	82
5	**6e**	1:2.5	NaO^{t}Bu	MTBE	52	12:1	87
6	**6f**	1:2.5	NaO^{t}Bu	MTBE	50	10:1	−67
7	**6e**	1:2.5	Cs_2CO_3	MTBE	75	10:1	87
8	**6e**	1:2.5	Et_3N	MTBE	74	>>20:1	54
9	**6e**	1:2.5	$^i Pr_2EtN$	MTBE	80	>20:1	89
10	**6e**	1:1	$^i Pr_2EtN$	MTBE	75	>20:1	89
11	**6e**	1.5:1	$^i Pr_2EtN$	MTBE	88	>20:1	89
12	**6e**	2:1	$^i Pr_2EtN$	MTBE	80	>20:1	89
13	**6e**	1.5:1	$^i Pr_2EtN$	THF	51	>20:1	86
14	**6e**	1.5:1	$^i Pr_2EtN$	EE	80	>20:1	89
15	**6e**	1.5:1	$^i Pr_2EtN$	anisole	51	>20:1	89
16	**6e**	1.5:1	$^i Pr_2EtN$	DCM	66	>20:1	87
17[e]	**6e**	1.5:1	$^i Pr_2EtN$	MTBE	91	>20:1	90
18[f]	**6e**	1.5:1	$^i Pr_2EtN$	MTBE	70	>20:1	92
19[g]	**6e**	1.5:1	$^i Pr_2EtN$	MTBE	74	>20:1	90

[a]Unless otherwise noted, the reaction conditions were as follows: **5a** (0.05 mmol) and **3a** (2.5 equiv) in solvent (0.5 mL) at 100 °C for 10 h. [b]Isolated yield. [c]Determined by the ^{1}H NMR spectra of the crude products. [d]The ee of **7aa** was determined by chiral HPLC analysis. [e]90 °C for 12 h. [f]70 °C for 48 h. [g]5 mol % of catalyst loading.

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035−10042

Scheme 3. Substrate Scope of Asymmetric Allylic Etherification of MBH Carbonates and Silanols[a]

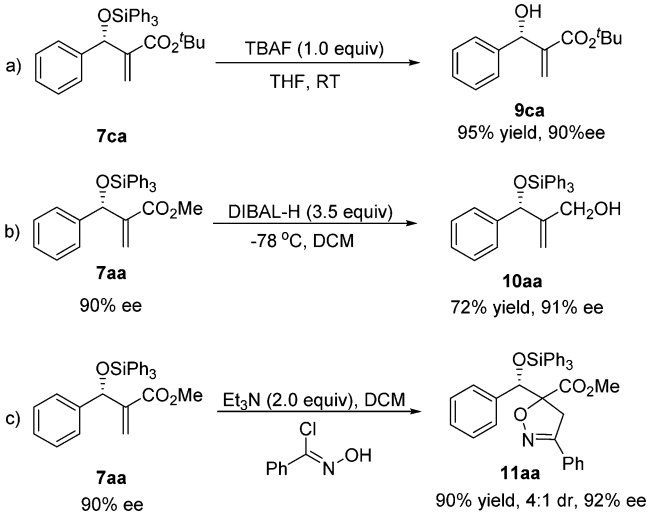


[a]Reaction conditions: **3a** (0.05 mmol), **5a**–**y** (1.5 equiv), $^{i}Pr_2EtN$ (1.0 equiv), $(DHQD)_2PYR$ (10 mol %), and MTBE (0.4 mL) in a sealed pressure tube at 90 °C. Isolated yields were reported with high regioselectivities (>20:1). The ee values were determined by chiral HPLC analysis. [b]Measured after desilylation to the corresponding alcohol **9**.

substitutions (**5n**–**p**) could give the products (**7na**–**pa**) in 83–86% ee values. Moderate enantioselectivities (81–84% ee) and moderate to good yields (73–95%) were obtained for the *para*-position substituents on the aromatic ring of MBH carbonates. Moreover, when 2-furyl-, 2-thienyl-, and 3-thienyl-substituted MBH carbonates were used as the substrates, the asymmetric allylic etherification reaction could afford the products **7va**–**xa** in 75–92% yield and 88–92% ee. In the case of aliphatic MBH carbonate (**5y**), the corresponding product (**7ya**) was obtained in 50% yield and 81% ee. When dimethylphenylsilanol (**3b**) was used as the nucleophile, the product (**7ab**) was obtained in 60% yield with 87% ee. The absolute configuration of **7ka** was determined to be *R* by X-ray crystallographic analysis (Figure 1).

As shown in Scheme 4a, the allylic etherification product **7ca** could be transformed into the corresponding alcohol **9ca** in 95% yield and 90% ee in the presence of TBAF. Thus, when Ph_3SiOH was used as the nucleophile, Ph_3SiOH could be used as the water surrogate. In the presence of the DIBAL-H,[20] the reduction of **7aa** proceeded well, affording the desired reduction product **10aa** in 72% yield and 91% ee. The 1,3-dipolar cycloaddition reaction[21] of the allylic etherification product **7aa** with chlorobenzaldoxime was performed in DCM, and the cycloadduct **11aa** was isolated in 90% yield, 4:1 dr, and 92% ee (Scheme 4c).

Scheme 4. Transformations of the Allylic Etherification Products



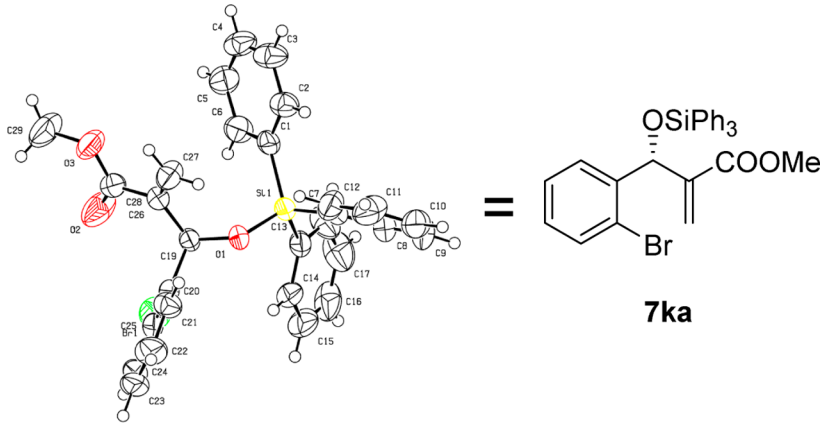
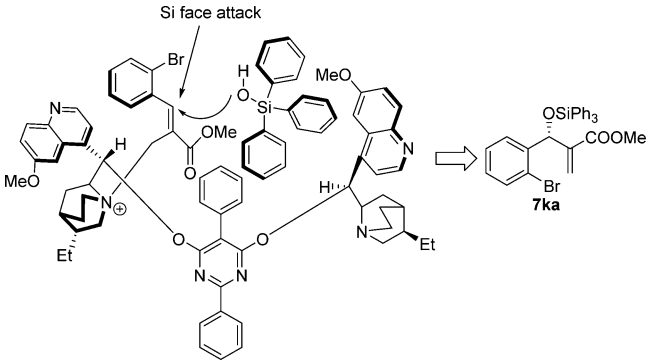


Figure 1. X-ray crystal structure (*R*)-**7ka**. The thermal ellipsoid was drawn at the 50% probability level.

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035–10042

As shown in Scheme 5, on the basis of the experimental results, we proposed a probable activation model for the formation of product (*R*)-**7ka** catalyzed by $(DHQD)_2PYR$. First, a cationic ammonium intermediate was formed from a Michael-type addition reaction of the nitrogen atom of $(DHQD)_2PYR$ with MBH carbonate **5k**. The $(DHQD)_2PYR$–MBH adduct would be preferentially formed as the *E* isomer.[22] The MBH moiety in the U-shape cleft of $(DHQD)_2PYR$ gave a sandwich-like geometry that was stabilized by the p–p stacking between the quinoline moiety and phenyl ring,[23] which effectively blocked the *Re* face of this complex. Thus, the triphenylsilanol anion was much more favorable attack from the *Si* face to afford **7ka** with the *R* configuration.

Scheme 5. Proposed Activation Model for the Formation of Product (*R*)-7ka



In conclusion, we have developed a novel and convenient chiral cinchona alkaloid $(DHQD)_2PYR$ catalyzed enantioselective allylic etherification of MBH carbonates and Ph_3SiOH with $^iPr_2EtN$ as the base in MTBE at 90 °C. A series of aromatic, heterocyclic, or aliphatic MBH carbonates (25 examples) worked well with triphenylsilanol, affording the corresponding etherification products in high regioselectivities (>20:1), moderate to good yields (58–98%), and good enantioselectivities (up to 92%). When dimethylphenylsilanol was used as the nucleophile, the product **7ba** was obtained in 60% yield and 87% ee. Thus, when Ph_3SiOH was used as the nucleophile, Ph_3SiOH could be used as the water surrogate and the chiral silicon-containing compounds could be obtained.

EXPERIMENTAL SECTION

General Methods. All of the reagents and solvents were purchased from commercial sources and used without further purification unless specified. The solvents (MTBE, THF) used in the reaction were super dry solvents purchased from commercial sources, and other solvents used in the reaction were dried by usual methods. Optical rotations were recorded with a sodium lamp of wavelength 589 nm and reported as follows: $[\alpha]^T_D$ (*c* = g/100 mL, solvent). Melting points were recorded with a micro melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on commercial instruments (600 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quartet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (150 or 100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. High-resolution mass spectra were taken with electrospray ionization (ESI) as the ionization method used for the HRMS measurement. All experiments were monitored by analytical thin-layer chromatography (TLC). Enantiomeric excesses were determined by chiral HPLC OD-H, IA, or ID columns in comparison with the authentic racemates. HPLC samples were dissolved in DCM/*n*-hexane = 1:4 unless otherwise stated. All reactions were carried out in a sealed pressure tube.

General Procedure for the Synthesis of 7aa–ya and 7ab. In a dried pressure tube equipped with a stirring bar, Ph_3SiOH (13.8 mg, 0.05 mmol), **5a–y** (0.075 mmol), $(DHQD)_2PYR$ (4.4 mg, 0.005 mmol), $^iPr_2EtN$ (8.3 μL, 0.05 mmol), and MTBE (0.4 mL) were added. The mixture was sealed and heated at 90 °C for 12 h. After completion of the reaction (as monitored by TLC), the resulting mixture was cooled to room temperature. The reaction mixture was extracted with diethyl ether. The organic layers were collected, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using V_{EA}/V_{PE} = 1:100 as eluent.

*Triphenylsilanol (**3a**).*[24] White solid; 4.8 mg, 7% yield. Mp: 150–152 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.68–7.59 (m, 6H), 7.47–7.42 (m, 3H), 7.39 (t, *J* = 7.2 Hz, 6H), 2.62 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.3, 135.1, 130.3, 128.1. HRMS: calcd for $C_{18}H_{16}OSiNa$ $[M + Na]^+$ 299.0863, found 299.0864.

*Methyl 2-((4-Bromophenyl)((triphenylsilyl)oxy)methyl)acrylate (**4a**).* White solid. Mp: 146–147 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.2 Hz, 6H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 6H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.29 (s, 1H), 6.28 (s, 1H), 5.71 (s, 1H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 142.7, 140.9, 135.5, 133.8, 131.2, 130.3, 129.2, 128.0, 124.8, 121.5, 73.2, 51.8. HRMS: calcd for $C_{29}H_{25}BrO_3SiNa$ $[M + Na]^+$ 551.0649, found 551.0658.

*Adamantan-1-yl 2-(((tert-Butoxycarbonyl)oxy)(phenyl)methyl)-acrylate (**5e**).* White solid. Mp: 119–121 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.42 (s, 1H), 6.32 (s, 1H), 5.79 (s, 1H), 2.12 (s, 3H), 2.02 (q, *J* = 11.4 Hz, 6H), 1.62–1.59 (m, 6H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.9, 152.6, 141.2, 137.9, 128.5, 128.0, 124.7, 82.6, 81.7, 76.3, 41.2, 36.2, 30.9, 27.9. HRMS: calcd for $C_{25}H_{32}O_5Na$ $[M + Na]^+$ 435.2142, found 435.2141.

*Adamantan-2-yl 2-(((tert-Butoxycarbonyl)oxy)(phenyl)methyl)-acrylate (**5f**).* White solid. Mp: 109–111 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.51 (s, 1H), 6.48 (s, 1H), 5.88 (s, 1H), 4.97–4.90 (m, 1H), 2.00–1.93 (m, 2H), 1.90 (s, 1H), 1.84–1.69 (m, 9H), 1.63 (d, *J* = 5.4 Hz, 1H), 1.53 (d, *J* = 11.4 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.5, 152.6, 140.1, 137.8, 128.6, 127.9, 126.1, 82.7, 78.2, 76.1, 37.4, 36.41, 36.37, 31.93, 31.89, 31.8, 31.7, 27.9, 27.3, 27.1. HRMS: calcd for $C_{25}H_{32}O_5Na$ $[M + Na]^+$ 435.2142, found 435.2139.

*Methyl (S)-2-(Phenyl((triphenylsilyl)oxy)methyl)acrylate (**7aa**).* White solid; 20.4 mg, 91% yield; 90% ee. $[\alpha]^{25}_D$ = +83.2 (*c* 0.67, DCM). Mp: 101–104 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.2 Hz, 6H), 7.40 (t, *J* = 7.2 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 6H), 7.23–7.15 (m, 5H), 6.28 (s, 1H), 6.26 (s, 1H), 5.77 (s, 1H), 3.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 143.3, 141.8, 135.6, 134.1, 130.1, 128.1, 127.9, 127.6, 127.4, 124.6, 73.9, 51.7. HRMS: calcd for $C_{29}H_{26}O_3SiNa$ $[M + Na]^+$ 473.1543, found 473.1547. The ee was determined by HPLC (ID, MTBE/*n*-hexane = 2/98, flow rate 0.6 mL/min, λ = 250 nm, t_{major} = 17.6 min, t_{minor} = 22.6 min).

*Ethyl (S)-2-(Phenyl((triphenylsilyl)oxy)methyl)acrylate (**7ba**).* White solid; 17.6 mg, 76% yield; 90% ee. $[\alpha]^{25}_D$ = +53.5 (*c* 0.67, DCM). Mp: 102–104 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.2 Hz, 6H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 6H), 7.24–7.15 (m, 5H), 6.29 (s, 1H), 6.26 (s, 1H), 5.78 (s, 1H), 4.10–3.93 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.7, 143.5, 141.9, 135.6, 134.1, 130.1, 128.1, 127.9, 127.53, 127.47, 124.4, 73.9, 60.6, 14.1. HRMS: calcd for $C_{30}H_{28}O_3SiNa$ $[M + Na]^+$ 487.1700, found 487.1710. The ee was determined by HPLC (ID, MTBE/*n*-hexane = 2/98, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 8.6 min, t_{minor} = 10.6 min).

*tert-Butyl (S)-2-(Phenyl((triphenylsilyl)oxy)methyl)acrylate (**7ca**).* Colorless oil; 14.8 mg, 60% yield; 90% ee (measured after desilylation

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035–10042

to the corresponding alcohol **9ca**). $[\alpha]^{25}_{D}$ = +99.6 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 6.6 Hz, 6H), 7.40 (t, *J* = 7.2 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 6H), 7.22−7.15 (m, 5H), 6.21 (s, 1H), 6.18 (s, 1H), 5.72 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 144.8, 142.0, 135.6, 134.2, 130.1, 128.0, 127.9, 127.5, 127.4, 123.6, 80.9, 74.1, 28.0. HRMS: calcd for $C_{32}H_{32}O_3SiNa$ $[M + Na]^+$ 515.2013, found 515.2017.

*Benzyl (S)-2-(Phenyl((triphenylsilyl)oxy)methyl)acrylate (**7da**).* Colorless oil; 20.8 mg, 79% yield; 90% ee. $[\alpha]^{25}_{D}$ = +63.0 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.2 Hz, 6H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.37−7.27 (m, 9H), 7.23−7.17 (m, 5H), 7.14 (dd, *J* = 6.6, 3.6 Hz, 2H), 6.35 (s, 1H), 6.30 (s, 1H), 5.81 (s, 1H), 5.06 (d, *J* = 12.6, 1H), 4.95 (d, *J* = 12.6, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.5, 143.2, 141.7, 135.9, 135.6, 134.0, 130.1, 128.5, 128.1, 128.0, 127.9, 127.6, 127.5, 125.0, 73.9, 66.3. HRMS: calcd for $C_{35}H_{30}O_3SiNa$ $[M + Na]^+$ 549.1856, found 549.1870. The ee was determined by HPLC (IA, 2-propanol/*n*-hexane = 3/97, flow rate 0.5 mL/min, λ = 250 nm, t_{major} = 11.3 min, t_{minor} = 17.6 min).

*Adamantan-1-yl 2-((S)-Phenyl((triphenylsilyl)oxy)methyl)acrylate (**7ea**).* Colorless oil; 18.8 mg, 66% yield; 89% ee (measured after desilylation to the corresponding alcohol **9ea**). $[\alpha]^{25}_{D}$ = +69.4 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 6.6 Hz, 6H), 7.40 (t, *J* = 7.2 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 6H), 7.24−7.11 (m, 5H), 6.21 (s, 1H), 6.18 (s, 1H), 5.72 (s, 1H), 2.08 (s, 3H), 1.91 (q, *J* = 11.4 Hz, 6H), 1.61−1.56 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.6, 144.8, 142.1, 135.6, 134.2, 130.1, 128.0, 127.9, 127.5, 127.4, 123.6, 81.0, 74.1, 41.2, 36.3, 30.9. HRMS: calcd for $C_{38}H_{38}O_3SiNa$ $[M + Na]^+$ 593.2482, found 593.2491.

*Adamantan-2-yl 2-((S)-Phenyl((triphenylsilyl)oxy)methyl)acrylate (**7fa**).* Colorless oil; 20 mg, 70% yield; 90% ee (measured after desilylation to the corresponding alcohol **9fa**). $[\alpha]^{25}_{D}$ = +52.7 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 6.6 Hz, 6H), 7.40 (t, *J* = 7.2 Hz, 3H), 7.32 (t, *J* = 7.2 Hz, 6H), 7.25−7.12 (m, 5H), 6.34 (s, 1H), 6.27 (s, 1H), 5.80 (s, 1H), 4.80−4.76 (m, 1H), 1.84−1.65 (m, 12H), 1.43 (d, *J* = 12.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.0, 143.8, 141.9, 135.6, 134.1, 130.1, 128.2, 127.9, 127.6, 127.5, 124.4, 100.1, 77.5, 74.0, 37.5, 36.3, 31.84, 31.76, 31.73, 27.3, 27.1. HRMS: calcd for $C_{38}H_{38}O_3SiNa$ $[M + Na]^+$ 593.2482, found 593.2491.

*Methyl (S)-2-(o-Tolyl((triphenylsilyl)oxy)methyl)acrylate (**7ga**).* White solid; 20.2 mg, 87% yield; 90% ee. $[\alpha]^{25}_{D}$ = +80.6 (*c* 0.67, DCM). Mp: 102−105 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.2 Hz, 6H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 6H), 7.19−7.09 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.31 (s, 1H), 6.07 (s, 1H), 6.00 (s, 1H), 3.53 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.5, 143.0, 139.4, 135.8, 135.6, 134.2, 130.3, 130.1, 128.2, 127.9, 127.5, 125.9, 125.4, 70.7, 51.7, 18.9. HRMS: calcd for $C_{30}H_{28}O_3SiNa$ $[M + Na]^+$ 487.1700, found 487.1705. The ee was determined by HPLC (ID, MTBE/*n*-hexane = 2/98, flow rate 0.5 mL/min, λ = 250 nm, t_{major} = 18.5 min, t_{minor} = 20.7 min).

*Methyl (S)-2-((2-Methoxyphenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ha**).* Colorless oil; 16.8 mg, 70% yield; 90% ee. $[\alpha]^{25}_{D}$ = +40.1 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.6 Hz, 6H), 7.46 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 3H), 7.31 (t, *J* = 7.2 Hz, 6H), 7.23−7.15 (m,1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.32 (s, 1H), 6.29 (s, 1H), 6.09 (s, 1H), 3.53 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.4, 156.4, 143.0, 135.6, 134.6, 130.2, 129.9, 128.8, 128.2, 127.7, 125.4, 120.4, 110.4, 67.4, 55.0, 51.6. HRMS: calcd for $C_{30}H_{28}O_4SiNa$ $[M + Na]^+$ 503.1649, found 503.1654. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 5/95, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 5.6 min, t_{minor} = 13.1 min).

*Methyl (R)-2-((2-Fluorophenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ia**).* White solid; 14.0 mg, 60% yield; 90% ee. $[\alpha]^{25}_{D}$ = +77.9 (*c* 0.67, DCM). Mp: 114−116 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 6H), 7.41 (t, *J* = 7.2 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 6H), 7.16 (dd, *J* = 13.8, 6.6 Hz), 7.04 (t, *J* = 7.2 Hz, 1H), 6.83 (t, *J* = 9.0 Hz, 1H), 6.39 (s, 1H), 6.27 (s, 1H), 6.10 (s, 1H), 3.56 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 160.0 (d, J_{C-F} = 247.5 Hz), 142.1, 135.5, 133.9, 130.2, 129.33 (d, J_{C-F} = 6.0 Hz), 129.29 (d, J_{C-F} = 1.5 Hz), 128.9 (d, J_{C-F} = 12.0 Hz), 127.9, 125.7, 123.9 (d, J_{C-F} = 3.0 Hz), 115.3 (d, J_{C-F} = 22.5 Hz), 67.6 (d, J_{C-F} = 1.5 Hz), 51.7. HRMS: calcd for $C_{29}H_{25}FO_3SiNa$ $[M + Na]^+$ 491.1449, found 491.1456. The ee was determined by HPLC (ID, MTBE/*n*-hexane = 3/97, flow rate 0.9 mL/min, λ = 250 nm, t_{major} = 12.2 min, t_{minor} = 17.4 min).

*Methyl (R)-2-((2-Chlorophenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ja**).* White solid; 13.3 mg, 55% yield; 90% ee. $[\alpha]^{25}_{D}$ = −14.9 (*c* 0.67, DCM). Mp: 120−123 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 6H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 6H), 7.24−7.17 (m, 2H), 7.14 (t, *J* = 7.2 Hz 1H), 6.34 (s, 1H), 6.23 (s, 1H), 5.98 (s, 1H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 142.1, 139.1, 135.6, 133.9, 133.01, 130.1, 129.5, 129.3, 128.8, 127.9, 126.8, 126.5, 70.4, 51.7. HRMS: calcd for $C_{29}H_{25}ClO_3SiNa$ $[M + Na]^+$ 507.1154, found 507.1158. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 5/95, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 5.4 min, t_{minor} = 9.9 min).

*Methyl (R)-2-((2-Bromophenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ka**).* White solid; 15.3 mg, 58% yield; 90% ee. $[\alpha]^{25}_{D}$ = +3.5 (*c* 0.67, DCM). Mp: 122−125 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 6H), 7.42−7.35 (m, 4H), 7.32 (t, *J* = 7.2 Hz, 6H), 7.25−7.23 (m, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.32 (s, 1H), 6.18 (s, 1H), 5.89 (s, 1H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 142.2, 140.7, 135.6, 134.0, 132.6, 130.1, 129.8, 129.1, 127.9, 127.4, 126.7, 123.3, 72.8, 51.8. HRMS: calcd for $C_{29}H_{25}BrO_3SiNa$ $[M + Na]^+$ 551.0649, found 551.0654. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 5/95, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 5.3 min, t_{minor} = 11.6 min).

*Methyl (S)-2-(m-Tolyl((triphenylsilyl)oxy)methyl)acrylate (**7la**).* White solid; 18.8 mg, 81% yield; 92% ee. $[\alpha]^{25}_{D}$ = +72.4 (*c* 0.67, DCM). Mp: 81−83 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 6H), 7.41 (t, *J* = 7.2 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 6H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.95 (s, 1H), 6.30 (s, 1H), 6.27 (s, 1H), 5.75 (s, 1H), 3.57 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 143.2, 141.6, 137.5, 135.6, 134.1, 130.1, 128.3, 128.0, 127.8, 124.6, 124.5, 73.9, 51.7, 21.5. HRMS: calcd for $C_{30}H_{28}O_3SiNa$ $[M + Na]^+$ 487.1700, found 487.1708. The ee was determined by HPLC (ID, MTBE/*n*-hexane = 2/98, flow rate 0.6 mL/min, λ = 250 nm, t_{major} = 18.1 min, t_{minor} = 23.0 min).

*Methyl (S)-2-((3-Methoxyphenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ma**).* Colorless oil; 18.0 mg, 75% yield; 91% ee. $[\alpha]^{25}_{D}$ = +100.1 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 6H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.34 (t, *J* = 7.2 Hz, 6H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 6.74 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.30 (s, 1H), 6.25 (s, 1H), 5.78 (s, 1H), 3.70 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 159.4, 143.4, 143.2, 135.6, 134.1, 130.1, 129.1, 127.9, 124.8, 119.8, 113.5, 112.6, 73.7, 55.2, 51.7. HRMS: calcd for $C_{30}H_{28}O_4SiNa$ $[M + Na]^+$ 503.1649, found 503.1656. The ee was determined by HPLC (OD-H, 2-proprnol/*n*-hexane = 3/97, flow rate 0.5 mL/min, λ = 250 nm, t_{major} = 9.2 min, t_{minor} = 10.8 min).

*Methyl (S)-2-((3-Fluorophenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7na**).* White solid; 19.2 mg, 82% yield; 84% ee. $[\alpha]^{25}_{D}$ = +81.8 (*c* 0.67, DCM). Mp: 96−98 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.8 Hz, 6H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.33 (t, *J* = 7.2 Hz, 6H), 7.13 (dd, *J* = 13.8, 7.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 9.6 Hz, 1H), 6.86 (td, *J* = 8.4, 1.8 Hz, 1H), 6.31 (s, 1H), 6.28 (s, 1H), 5.75 (s, 1H), 3.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 162.7 (d, J_{C-F} = 244.5 Hz), 144.5 (d, J_{C-F} = 6.0 Hz), 142.8, 135.5, 133.8, 130.3, 129.5 (d, J_{C-F} = 7.5 Hz), 128.0, 125.1, 123.0 (d, J_{C-F} = 3.0 Hz), 114.5 (d, J_{C-F} = 21.0 Hz), 114.2 (d, J_{C-F} = 22.5 Hz), 73.2 (d, J_{C-F} = 1.5 Hz), 51.8. HRMS: calcd for $C_{29}H_{25}FO_3SiNa$ $[M + Na]^+$ 491.1449, found 491.1452. The ee was determined by HPLC (ID, MTBEl/*n*-hexane = 2/98, flow rate 0.6 mL/min, λ = 250 nm, t_{major} = 16.5 min, t_{minor} = 20.2 min).

*(S)-2-((3-Chlorophenyl)((triphenylsilyl)oxy)methyl)acrylate (**7oa**).* White solid; 20.8 mg, 86% yield; 86% ee. $[\alpha]^{25}_{D}$ = +93.6 (*c* 0.67, DCM). Mp: 81−83 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, *J* =

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035−10042

7.8 Hz, 6H), 7.42 (t, J = 7.2 Hz, 3H), 7.34 (t, J = 7.2 Hz, 6H), 7.21–7.02 (m, 4H), 6.33 (s, 1H), 6.30 (s, 1H), 5.72 (s, 1H), 3.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 143.9, 142.7, 135.5, 133.9, 133.7, 130.3, 129.4, 128.0, 127.7, 127.6, 125.6, 125.1, 73.2, 51.8. HRMS: calcd for $C_{29}H_{25}ClO_3SiNa$ $[M + Na]^+$ 507.1154, found 507.1160. The ee was determined by HPLC (ID, MTBE/n-hexane = 2/98, flow rate 1.0 mL/min, λ = 250 nm, t_{major} = 9.8 min, t_{minor} = 11.7 min).

*Methyl (S)-2-((3-Bromophenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7pa**).* Colorless oil; 21.6 mg, 82% yield; 83% ee. $[\alpha]^{25}_D$ = +71.2 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, J = 7.2 Hz, 6H), 7.42 (t, J = 7.2 Hz, 3H), 7.34 (t, J = 7.2 Hz, 6H), 7.32–7.27 (m, 2H), 7.13 (d, J = 7.8 Hz, 1H), 7.04 (t, J = 7.2 Hz, 1H), 6.33 (s, 1H), 6.31 (s, 1H), 5.71 (s, 1H), 3.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 144.1, 142.6, 135.5, 133.7, 130.7, 130.6, 130.3, 129.7, 128.0, 126.1, 125.1, 122.1, 73.2, 51.8. HRMS: calcd for $C_{29}H_{25}BrO_3SiNa$ $[M + Na]^+$ 551.0649, found 551.0654. The ee was determined by HPLC (ID, MTBE/n-hexane = 2/98, flow rate 0.6 mL/min, λ = 250 nm, t_{major} = 16.0 min, t_{minor} = 18.5 min).

*Methyl (S)-2-(p-Tolyl((triphenylsilyl)oxy)methyl)acrylate (**7qa**).* White solid; 22.0 mg, 95% yield; 81% ee. $[\alpha]^{25}_D$ = +92.1 (c 0.67, DCM). Mp: 78–80 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, J = 7.8 Hz, 6H), 7.42 (t, J = 7.2 Hz, 3H), 7.33 (t, J = 7.2 Hz, 6H), 7.12 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 6.28 (s, 1H), 6.26 (s, 1H), 5.77 (s, 1H), 3.56 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 143.3, 138.8, 137.2, 135.6, 134.1, 130.1, 128.8, 127.9, 127.4, 124.4, 73.7, 51.7, 21.3. HRMS: calcd for $C_{30}H_{28}O_3SiNa$ $[M + Na]^+$ 487.1700, found 487.1707. The ee was determined by HPLC (ID, 2-propanol/n-hexane = 3/97, flow rate 0.5 mL/min, λ = 250 nm, t_{major} = 9.2 min, t_{minor} = 10.2 min).

*Methyl (S)-2-((4-Methoxyphenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ra**).* Colorless oil; 17.5 mg, 73% yield; 84% ee. $[\alpha]^{25}_D$ = +109.9 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, J = 7.8 Hz, 6H), 7.41 (t, J = 7.2 Hz, 3H), 7.33 (t, J = 7.2 Hz, 6H), 7.12 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 6.28 (s, 1H), 6.27 (s, 1H), 5.74 (s, 1H), 3.77 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 159.0, 143.3, 135.5, 134.1, 133.9, 130.1, 128.7, 127.9, 124.1, 113.4, 73.4, 55.3, 51.7. HRMS: calcd for $C_{30}H_{28}O_4SiNa$ $[M + Na]^+$ 503.1649, found 503.1659. The ee was determined by HPLC (ID, 2-propanol/n-hexane = 3/97, flow rate 0.5 mL/min, λ = 250 nm, t_{major} = 11.5 min, t_{minor} = 13.0 min).

*Methyl (S)-2-((4-Fluorophenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7sa**).* White solid; 20.4 mg, 87% yield; 83% ee. $[\alpha]^{25}_D$ = +69.5 (c 0.67, DCM). Mp: 69–72 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, J = 7.8 Hz, 6H), 7.42 (t, J = 7.2 Hz, 3H), 7.34 (t, J = 7.2 Hz, 6H), 7.16 (dd, J = 7.8, 5.4 Hz, 2H), 6.86 (t, J = 8.4 Hz, 2H), 6.31 (s, 2H), 5.76 (s, 1H), 3.58 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 162.2 (d, J_{C-F} = 244.5 Hz), 143.1, 137.7 (d, J_{C-F} = 3.0 Hz), 135.5, 133.9, 130.2, 129.1 (d, J_{C-F} = 7.5 Hz), 127.9, 124.5, 114.9 (d, J_{C-F} = 21 Hz), 73.2, 51.7. HRMS: calcd for $C_{29}H_{25}FO_3SiNa$ $[M + Na]^+$ 491.1449, found 491.1465. The ee was determined by HPLC (ID, 2-propanol/n-hexane = 3/97, flow rate 0.5 mL/min, λ = 250 nm, t_{minor} = 8.8 min, t_{major} = 9.8 min).

*Methyl (S)-2-((3,4-Dimethylphenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ta**).* White solid; 23.4 mg, 98% yield; 88% ee. $[\alpha]^{25}_D$ = +100.7 (c 0.67, DCM). Mp: 104–106 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, J = 7.8 Hz, 6H), 7.40 (t, J = 7.2 Hz, 3H), 7.31 (t, J = 7.2 Hz, 6H), 6.95 (t, J = 7.8 Hz, 2H), 6.88 (s, 1H), 6.27 (s, 1H), 6.24 (s, 1H), 5.72 (s, 1H), 3.55 (s, 3H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.2, 143.3, 139.1, 136.1, 135.8, 135.6, 135.3, 134.2, 130.0, 129.3, 128.9, 127.8, 124.9, 124.4, 73.8, 51.7, 19.8, 19.6. HRMS: calcd for $C_{31}H_{30}O_3SiNa$ $[M + Na]^+$ 501.1856, found 501.1867. The ee was determined by HPLC (ID, MTBE/n-hexane = 2/98, flow rate 1.0 mL/min, λ = 250 nm, t_{major} = 7.7 min, t_{minor} = 9.9 min).

*Methyl (S)-2-((3,4-Dimethoxyphenyl)((triphenylsilyl)oxy)methyl)-acrylate (**7ua**).* Colorless oil; 18.6 mg, 73% yield; 85% ee. $[\alpha]^{25}_D$ = +127.4 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, J = 7.8 Hz, 6H), 7.40 (t, J = 7.2 Hz, 3H), 7.32 (t, J = 7.2 Hz, 6H), 6.74–6.65 (m, 3H), 6.28 (s, 1H), 6.24 (s, 1H), 5.73 (s, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.57 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.3, 148.5, 148.4, 143.3, 135.6, 134.3, 134.2, 130.1, 127.9, 124.2, 119.9, 110.8, 110.7, 73.8, 55.9, 55.8, 51.7. HRMS: calcd for $C_{31}H_{30}O_5SiNa$ $[M + Na]^+$ 533.1755, found 533.1769. The ee was determined by HPLC (ID, MTBE/n-hexane = 1/99, flow rate 0.5 mL/min, λ = 250 nm, t_{major} = 26.1 min, t_{minor} = 30.9 min).

*Methyl (R)-2-(Furan-2-yl((triphenylsilyl)oxy)methyl)acrylate (**7va**).* Colorless oil; 20.2 mg, 92% yield; 92% ee. $[\alpha]^{25}_D$ = +117.6 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 7.8 Hz, 6H), 7.42 (t, J = 7.2 Hz, 3H), 7.35 (t, J = 7.2 Hz, 6H), 7.24 (s, 1H), 6.40 (s, 1H), 6.32 (s, 1H), 6.23–6.17 (m, 1H), 6.00 (d, J = 2.4 Hz, 1H), 5.82 (s, 1H), 3.60 (s, 3H). ^{13}C NMR (150 MHz, $(CD_3)_2CO$): δ 166.0, 154.9, 143.3, 141.5, 136.2, 134.7, 131.1, 128.8, 126.2, 111.1, 108.8, 67.8, 52.0. HRMS: calcd for $C_{27}H_{24}O_4SiNa$ $[M + Na]^+$ 463.1336, found 463.1343. The ee was determined by HPLC (ID, MTBE/n-hexane = 1.5/98.5, flow rate 0.9 mL/min, λ = 250 nm, t_{major} = 13.6 min, t_{minor} = 17.3 min).

*Methyl (R)-2-(Thiophene-2-yl((triphenylsilyl)oxy)methyl)acrylate (**7wa**).* Colorless oil; 17.1 mg, 75% yield; 88% ee. $[\alpha]^{25}_D$ = +101.1 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J = 7.2 Hz, 6H), 7.43 (t, J = 7.2 Hz, 3H), 7.35 (t, J = 7.2 Hz, 6H), 7.16 (d, J = 5.4 Hz, 1H), 6.81 (t, J = 4.2 Hz, 1H), 6.72 (d, J = 3.0 Hz, 1H), 6.31 (s, 2H), 6.07 (s, 1H), 3.61 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 146.2, 142.9, 135.6, 133.8, 130.2, 127.9, 126.4, 125.4, 125.1, 125.0, 69.3, 51.8. HRMS: calcd for $C_{27}H_{24}O_3SSiNa$ $[M + Na]^+$ 479.1108, found 479.1114. The ee was determined by HPLC (ID, MTBE/n-hexane = 3/97, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 13.9 min, t_{minor} = 16.3 min).

*Methyl (R)-2-(Thiophene-3-yl((triphenylsilyl)oxy)methyl)acrylate (**7xa**).* White solid; 19.4 mg, 85% yield; 92% ee. $[\alpha]^{25}_D$ = +56.9 (c 0.67, DCM). Mp: 66–68 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 7.8 Hz, 6H), 7.43 (t, J = 7.2 Hz, 3H), 7.35 (t, J = 7.2 Hz, 6H), 7.14 (dd, J = 4.2, 3.0 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 4.8 Hz, 1H), 6.30 (s, 1H), 6.27 (s, 1H), 5.91 (s, 1H), 3.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1, 143.1, 142.9, 135.5, 134.0, 130.2, 127.9, 126.6, 125.3, 124.6, 122.5, 69.7, 51.7. HRMS: calcd for $C_{27}H_{24}O_3SSiNa$ $[M + Na]^+$ 479.1108, found 479.1117. The ee was determined by HPLC (ID, MTBE/n-hexane = 3/97, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 14.1 min, t_{minor} = 17.0 min).

*Methyl (S)-2-(Cyclohexyl((triphenylsilyl)oxy)methyl)acrylate (**7ya**).* Colorless oil; 13.4 mg, 50% yield; 81% ee. $[\alpha]^{25}_D$ = +20.9 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, J = 7.2 Hz, 6H), 7.42 (t, J = 7.2 Hz, 3H), 7.36 (t, J = 7.2 Hz, 6H), 6.18 (s, 1H), 5.85 (s, 1H), 4.71 (d, J = 4.8 Hz, 1H), 3.62 (s, 3H), 1.79 (d, J = 12.6 Hz, 1H), 1.73–1.57 (m, 3H), 1.55–1.50 (m, 1H), 1.46 (d, J = 12.6 Hz, 1H), 1.18–0.93 (m, 5H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 141.9, 135.8, 134.6, 130.0, 127.8, 126.7, 75.5, 51.7, 44.0, 29.4, 27.6, 26.6, 26.5, 26.4. HRMS: calcd for $C_{29}H_{32}O_3SiNa$ $[M + Na]^+$ 479.2013, found 479.2020.

*Methyl (S)-2-((((Dimethyl(phenyl)silyl)oxy)(phenyl)methyl)acrylate (**7ab**).* Colorless oil; 9.8 mg, 60% yield; 87% ee. $[\alpha]^{25}_D$ = +76.7 (c 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52–7.46 (m, 2H), 7.40–7.31 (m, 3H), 7.30–7.24 (m, 4H), 7.23–7.20 (m, 1H), 6.29 (s, 1H), 6.08 (s, 1H), 5.62 (s, 1H), 3.63 (s, 3H), 0.292 (s, 1H), 0.287 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.4, 143.5, 142.2, 137.7, 133.6, 129.7, 128.2, 127.9, 127.7, 127.4, 124.6, 73.1, 51.8, −1.0, −1.2. HRMS: calcd for $C_{19}H_{22}O_3SiNa$ $[M + Na]^+$ 349.1230, found 349.1236. The ee was determined by HPLC (OD-H, MTBE/n-hexane = 1/99, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 11.6 min, t_{minor} = 18.3 min).

*Methyl (E)-3-Phenyl-2-(((triphenylsilyl)oxy)methyl)acrylate (**8aa**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.67 (d, J = 7.2 Hz, 6H), 7.54 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.2 Hz, 3H), 7.38 (t, J = 7.2 Hz, 6H), 7.32 (t, J = 7.2 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 4.64 (s, 2H), 3.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 168.2, 143.8, 135.6, 134.9, 134.2, 130.7, 130.2, 130.0, 129.3, 128.6, 128.0, 58.5, 52.0. HRMS: calcd for $C_{29}H_{26}O_3SiNa$ $[M + Na]^+$ 473.1543, found 473.1546.

Procedure of the Products 7ca, 7ea, 7fa, and 7ya Desilylated to the Corresponding Alcohols. The compound **7ca**, **7ea**, **7fa**, or **7ya** was desilylated by addition of tetrabutylammonium fluoride (1.0

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035–10042

equiv) in THF.[16] The mixture was stirred at room temperature. After the completion of the reaction (as monitored by TLC), the mixture was quenched by addition of 10 mL of H_2O. The aqueous layer was extracted three times with EtOAc, and the organic layers were dried over Na_2SO_4. The solvents were removed in vacuo to give the crude mixture. The crude product was purified by flash column chromatography using $V_{DCM}/V_{EA}/V_{PE}$ = 10:4:40 as the eluent to afford the allylic product. Enantiomeric excess was determined by HPLC with a chiral stationary phase.

*tert-Butyl (S)-2-(Hydroxy(phenyl)methyl)acrylate (**9ca**).*[25] Colorless oil; 11.1 mg, 95% yield; 90% ee. $[\alpha]^{25}_D$ = +38.6 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38−7.33 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.26 (s, 1H), 5.72 (s, 1H), 5.50 (d, *J* = 5.4 Hz, 1H), 3.07 (d, *J* = 6.0 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 143.5, 141.7, 128.5, 127.8, 126.7, 125.5, 81.8, 73.8, 28.1. HRMS: calcd for $C_{14}H_{18}O_3Na$ $[M + Na]^+$ 257.1148, found 257.1152. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 5/95, flow rate 0.6 mL/min, λ = 250 nm, t_{major} = 11.3 min, t_{minor} = 12.5 min).

*Adamantan-1-yl 2-((S)-Hydroxy(phenyl)methyl)acrylate (**9ea**).* White solid; 15.0 mg, 96% yield; 89% ee. $[\alpha]^{25}_D$ = +9.2 (*c* 0.67, DCM). Mp: 100−103 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.33 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.26 (s, 1H), 5.71 (s, 1H), 5.49 (d, *J* = 6.0 Hz, 1H), 3.12 (d, *J* = 6.0 Hz, 1H), 2.14 (s, 3H), 2.09−1.98 (m, 6H), 1.66−1.61 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.5, 143.5, 141.8, 128.5, 127.8, 126.6, 125.6, 82.0, 73.8, 41.3, 36.2, 30.9. HRMS: calcd for $C_{20}H_{24}O_3Na$ $[M + Na]^+$ 335.1618, found 335.1620. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 5/95, flow rate 0.9 mL/min, λ = 250 nm, t_{major} = 8.5 min, t_{minor} = 10.2 min).

*Adamantan-2-yl 2-((S)-Hydroxy(phenyl)methyl)acrylate (**9fa**).* White solid; 15.3 mg, 98% yield; 90% ee. $[\alpha]^{25}_D$ = −39.5 (*c* 0.67, DCM). Mp: 74−76 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.42 (s, 1H), 5.83 (s, 1H), 5.58 (d, *J* = 6.0 Hz, 1H), 5.01−4.91(m, 1H), 3.08 (d, *J* = 6.0 Hz, 1H), 1.95 (d, *J* = 18.6 Hz, 2H), 1.88 (d, *J* = 12.6 Hz, 1H), 1.85−1.77 (m, 5H), 1.76−1.70 (m, 4H), 1.52 (t, *J* = 10.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8, 142.6, 141.6, 128.6, 127.9, 126.7, 126.1, 78.1, 73.7, 37.4, 36.4, 31.95, 31.93, 31.91, 31.88, 27.3, 27.0. HRMS: calcd for $C_{20}H_{24}O_3Na$ $[M + Na]^+$ 335.1618, found 335.1618. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 7.0 min, t_{minor} = 8.5 min).

*Methyl (S)-2-(Cyclohexyl((triphenylsilyl)oxy)methyl)acrylate (**9ya**).*[26] Colorless oil; 9.3 mg, 94% yield; 81% ee. $[\alpha]^{25}_D$ = −4.36 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.25 (s, 1H), 5.72 (s, 1H), 4.06 (t, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 2.53 (d, *J* = 7.8 Hz, 1H), 1.97 (d, *J* = 13.2 Hz, 1H), 1.81−1.62 (m, 3H), 1.59−1.49 (m, 2H), 1.23−1.09 (m, 3H), 1.03−0.92 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.3, 141.0, 126.4, 77.6, 52.0, 42.5, 30.1, 28.5, 26.5, 26.2, 26.1. HRMS: calcd for $C_{11}H_{18}O_3Na$ $[M + Na]^+$ 221.1145, found 221.1146. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 10/90, flow rate 0.8 mL/min, λ = 250 nm, t_{minor} = 5.8 min, t_{major} = 6.3 min).

Procedure for the Reduction of Product 10aa. DIBAL-H (1.0 M in PhMe, 0.12 mL, 0.12 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **7aa** (0.015 g, 0.033 mmol) in DCM (0.5 mL).[19] Stirring at −78 °C was continued for 2.5 h, and then MeOH (0.5 mL) was added. The cooling bath was removed, and a saturated aqueous solution of Rochelle's salt was added. The mixture was then extracted with ether. The combined organic extracts were washed with brine, dried (Na_2SO_4), and evaporated. The crude material was purified by column chromatography on silica gel (eluting with Pet/EtOAc = 1/10 mixture) to give the desired product **10aa**.

*(S)-2-(Phenyl((triphenylsilyl)oxy)methyl)prop-2-en-1-ol (**10aa**).* Colorless oil; 10.0 mg, 72% yield; 91% ee. $[\alpha]^{25}_D$ = +32.7 (*c* 0.67, DCM). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 6.6 Hz, 6H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.34 (t, *J* = 7.2 Hz, 6H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.25−7.18 (m, 3H), 5.48 (s, 1H), 5.25 (s, 1H), 5.11 (s, 1H), 4.06 (d, *J* = 13.8 Hz, 1H), 3.87 (d, *J* = 13.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.1, 141.9, 135.6, 134.0, 130.2, 128.3, 127.9, 127.5, 126.5, 112.0, 77.7, 62.9. HRMS: calcd for $C_{28}H_{26}O_2SiNa$ $[M + Na]^+$ 445.1594, found 445.1591. The ee was determined by HPLC (OD-H, 2-propanol/*n*-hexane = 5/95, flow rate 0.8 mL/min, λ = 250 nm, t_{major} = 9.1 min, t_{minor} = 10.6 min).

Procedure for the Synthesis of Cycloadduct 11aa. TEA (27 μL, 0.2 mmol) was added to a solution of chlorobenzaldoxime (30.3 mg, 0.2 mmol) in anhydrous DCM (0.5 mL) at 0 °C.[20] After the solution was stirred for 10 min, a solution of **7aa** (45 mg, 0.1 mmol) in anhydrous DCM was added dropwise. The mixture was stirred at room temperature for 12 h, the reaction was quenched with water (5 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc. The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated. Flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) afforded the diastereomerically pure product **11aa**.

*Methyl 3-Phenyl-5-((S)-phenyl((triphenylsilyl)oxy)methyl)-4,5-dihydroisoxazole-5-carboxylate (**11aa**).* White solid; 51.2 mg, 90% yield; 92% ee. $[\alpha]^{25}_D$ = +78.6 (*c* 0.67, DCM). Mp: 124−127 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ (major diastereomer) 7.62−7.59 (m, 2H), 7.50−7.47 (m, 6H), 7.40−7.34 (m, 6H), 7.30−7.28 (m, 1H), 7.26−7.22 (m, 6H), 7.20−7.18 (m, 4H), 5.44 (s, 1H), 3.82 (d. *J* = 16.8 Hz, 1H), 3.72 (d. *J* = 16.8 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (major diastereomer) 170.6, 156.6, 137.7, 135.8, 133.6, 130.3, 130.1, 129.2, 128.7, 128.6, 128.3, 127.9, 127.8, 127.0, 94.0, 76.9, 52.8, 37.8. HRMS: calcd for $C_{36}H_{31}NO_4SiNa$ $[M + Na]^+$ 592.1915, found 592.1909. The ee was determined by HPLC (ID, 2-propanol/*n*-hexane = 5/95, flow rate 0.8 mL/min, λ = 250 nm, t_{minor} = 17.1 min, t_{major} = 26.0 min).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01931.

Control experiments, HPLC spectral for racemic and enantiomerically enriched compounds, and NMR spectra for all new compounds (PDF)

X-ray data for compounds **4a** (CIF)

X-ray data for compounds **7ka** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: xiemingsheng@htu.edu.cn.

*E-mail: ghm@htu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (Nos. 21372066, 21472037, and 21402041), the National Basic Research Program of China (973 Program, No. 2014CB560713), the Plan for Scientific Innovation Talent of Henan Province (164200510008), Henan Normal University National Outstanding Youth Cultivation Fund (14JR003), China Postdoctoral Science Foundation funded project (2016M592293), and Program for Innovative Research Team in Science and Technology in University of Henan Province (15IRTSTHN003).

■ REFERENCES

(1) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (c) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (d) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258. (e) Hartwig, J. F.; Stanley, L. M. *Acc. Chem. Res.* **2010**, *43*, 1461. (f) Liu, T.-Y.; Xie, M.; Chen, Y.-C. *Chem. Soc. Rev.* **2012**, *41*, 4101.

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035−10042

(2) Examples of carbon nucleophiles: (a) Huang, X.; Peng, J.; Dong, L.; Chen, Y.-C. *Chem. Commun.* **2012**, *48*, 2439. (b) Nishimine, T.; Taira, H.; Tokunaga, E.; Shiro, M.; Shibata, N. *Angew. Chem., Int. Ed.* **2016**, *55*, 359. (c) Tong, G.; Zhu, B.; Lee, R.; Yang, W.; Tan, D.; Yang, C.; Han, Z.; Yan, L.; Huang, K.-W.; Jiang, Z. *J. Org. Chem.* **2013**, *78*, 5067 and references cited therein.
(3) Examples of nitrogen nucleophiles: (a) Cui, H.-L.; Feng, X.; Peng, J.; Lei, J.; Jiang, K.; Chen, Y.-C. *Angew. Chem., Int. Ed.* **2009**, *48*, 5737. (b) Wang, X.; Guo, P.; Han, Z.; Wang, X.; Wang, Z.; Ding, K. *J. Am. Chem. Soc.* **2014**, *136*, 405. (c) Huang, J.-R.; Cui, H.-L.; Lei, J.; Sun, X.-H.; Chen, Y.-C. *Chem. Commun.* **2011**, *47*, 4784. (d) Ye, K.-Y.; Cheng, Q.; Zhuo, C.-X.; Dai, L.-X.; You, S.-L. *Angew. Chem., Int. Ed.* **2016**, *55*, 8113 and references cited therein.
(4) Examples of phosphorus nucleophiles: (a) Kalyva, M.; Zografos, A. L.; Kapourani, E.; Giambazolias, E.; Devel, L.; Papakyriakou, A.; Dive, V.; Lazarou, Y. G.; Georgiadis, D. *Chem. - Eur. J.* **2015**, *21*, 3278. (b) Deng, H.-P.; Shi, M. *Eur. J. Org. Chem.* **2012**, *2012*, 183. (c) Sun, W.; Hong, L.; Liu, C.; Wang, R. *Org. Lett.* **2010**, *12*, 3914.
(5) Examples of sulfur nucleophiles: (a) Liu, X.-W.; Han, W.-Y.; Liu, X.-L.; Zhou, Y.; Zhang, X.-M.; Yuan, W.-C. *Tetrahedron* **2014**, *70*, 9191. (b) Lin, A.; Mao, H.; Zhu, X.; Ge, H.; Tan, R.; Zhu, C.; Cheng, Y. *Adv. Synth. Catal.* **2011**, *353*, 3301. (c) Xu, Q.-L.; Dai, L.-X.; You, S.-L. *Org. Lett.* **2010**, *12*, 800.
(6) Example of boron nucleophile: Ramachandran, P. V.; Pratihar, D.; Biswas, D.; Srivastava, A.; Reddy, M. V. R. *Org. Lett.* **2004**, *6*, 481.
(7) (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 4545. (b) Kim, J. N.; Lee, H. J.; Gong, J. H. *Tetrahedron Lett.* **2002**, *43*, 9141. (c) Kimura, M.; Uozumi, Y. *J. Org. Chem.* **2007**, *72*, 707.
(8) (a) 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. (b) Kato, M.; Nakamura, T.; Ogata, K.; Fukuzawa, S. *Eur. J. Org. Chem.* **2009**, *2009*, 5232.
(9) (a) Kim, H.; Lee, C. *Org. Lett.* **2002**, *4*, 4369. (b) Haight, A. R.; Stoner, E. J.; Peterson, M. J.; Grover, V. K. *J. Org. Chem.* **2003**, *68*, 8092. (c) Kim, H.; Lee, C. *Org. Lett.* **2002**, *4*, 4369.
(10) López, F.; Ohmura, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 3426.
(11) Qu, J.; Roßberg, L.; Helmchen, G. *J. Am. Chem. Soc.* **2014**, *136*, 1272.
(12) Hu, Z.-K.; Cui, H.-L.; Jiang, K.; Chen, Y.-C. *Sci. China, Ser. B: Chem.* **2009**, *52*, 1309.
(13) Zhu, B.; Yan, L.; Pan, Y.; Lee, R.; Liu, H.; Han, Z.; Huang, K.-W.; Tan, C.-K.; Jiang, Z. *J. Org. Chem.* **2011**, *76*, 6894.
(14) (a) Han, Z.-Y.; Chen, D.-F.; Wang, Y.-Y.; Guo, R.; Wang, P.-S.; Wang, C.; Gong, L.-Z. *J. Am. Chem. Soc.* **2012**, *134*, 6532. (b) Shintani, R.; Maciver, E. E.; Tamakuni, F.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 16955. (c) Lee, K.-S.; Katsoulis, D.; Choi, J. *ACS Catal.* **2016**, *6*, 1493.
(15) Lyothier, I.; Defieber, C.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6204.
(16) Ueno, S.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2008**, *47*, 1928.
(17) Ye, F.; Zheng, Z.-J.; Li, L.; Yang, K.-F.; Xia, C.-G.; Xu, L.-W. *Chem. - Eur. J.* **2013**, *19*, 15452.
(18) Bellini, R.; Magre, M.; Biosca, M.; Norrby, P.-O.; Pàmies, O.; Diéguez, M.; Moberg, C. *ACS Catal.* **2016**, *6*, 1701.
(19) (a) Kikukawa, Y.; Kuroda, Y.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 2434. (b) John, J.; Gravel, E.; Hagège, A.; Li, H.; Gacoin, T.; Doris, E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7533. (c) Limnios, D.; Kokotos, C. G. *ACS Catal.* **2013**, *3*, 2239. (d) Kim, S. M.; Jeon, M.; Kim, K. W.; Park, J.; Lee, I. S. *J. Am. Chem. Soc.* **2013**, *135*, 15714.
(20) Ma, S.; Gao, W. *J. Org. Chem.* **2002**, *67*, 6104.
(21) (a) Zhang, S.-J.; Cui, H.-L.; Jiang, K.; Li, R.; Ding, Z.-Y.; Chen, Y.-C. *Eur. J. Org. Chem.* **2009**, *2009*, 5804. (b) Lian, X.; Guo, S.; Wang, G.; Lin, L.; Liu, X.; Feng, X. *J. Org. Chem.* **2014**, *79*, 7703.
(22) Baidya, M.; Remennikov, G. Y.; Mayer, P.; Mayr, H. *Chem. - Eur. J.* **2010**, *16*, 1365.
(23) (a) Ogawa, S.; Shibata, N.; Inagaki, J.; Nakamura, S.; Toru, T.; Shiro, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8666. (b) Furukawa, T.; Kawazoe, J.; Zhang, W.; Nishimine, T.; Tokunaga, E.; Matsumoto, T.; Shiro, M.; Shibata, N. *Angew. Chem., Int. Ed.* **2011**, *50*, 9684.
(24) Sawama, Y.; Masuda, M.; Yasukawa, N.; Nakatani, R.; Nishimura, S.; Shibata, K.; Yamada, T.; Monguchi, Y.; Suzuka, H.; Takagi, Y.; Sajiki, H. *J. Org. Chem.* **2016**, *81*, 4190.
(25) Yang, K.-S.; Lee, W.-D.; Pan, J.-F.; Chen, K. *J. Org. Chem.* **2003**, *68*, 915.
(26) Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219.

DOI: 10.1021/acs.joc.6b01931
J. Org. Chem. 2016, 81, 10035−10042