Highly Diastereoselective Synthesis of Vinylcyclopropane Derivatives with (−)-8-Phenylmenthol as Chiral Auxiliary

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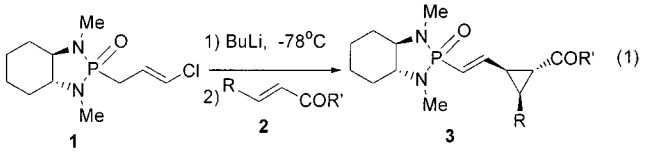
The silylated telluronium allylide **4**, generated in situ from the corresponding telluronium salt in the presence of LiTMP, reacted with (−)-8-phenylmenthyl α,β-unsaturated esters to afford *trans*-2-silylvinyl-*trans*-3-substituted cyclopropyl esters with high diastereoselectivity in high yields. The absolute configuration was determined by chemical transformation. A mechanistic rationale is proposed.

Introduction

The vinylcyclopropane derivatives are very useful intermediates in organic synthesis and ubiquitous substructures of several biologically active compounds,[1] notably agrochemicals such as pyrethroids.[2] Consequently, development of new methods for the construction of vinylcyclopropanes continues.[3] In view of the difficulty that can be associated with both the regioselective introduction of vinyl group and the stereoselective formation of multisubstituted cyclopropane, most frequently, many synthetic approaches rely on indirect routes.[4] In particular, for the preparation of optically active vinylcyclopropanes, resolution is still the best method and few direct asymmetric syntheses of vinylcyclopropanes were reported in the literatures.[5] One of the most successful examples was discovered by Hanessian's group.[6] They found that chiral chloroallylphosphonic amide such as compound **1** could run a formal [2 + 1] cycloaddition reaction to afford highly functionalized cyclopropane derivatives in high yield with excellent diastereoselectivity (eq 1). In our previous publications, we have



(1)

described that the telluronium allylides could react with α,β-unsaturated esters or ketones to provide the vinylcyclopropane derivatives in high yields with high stereoselectivity.[7] We also found that the stereoselectivity of the reaction of telluronium allylides with α,β-unsaturated esters or amides could be controlled by the choice of the base used for the formation of ylide or by the use of HMPA (Scheme 1). And thus, either of the two geometrical isomers of a polyfunctionalized 3-vinylcyclopropane could be obtained at will with high stereoselectivity.[8] In our continuing studies on the application of ylides in organic synthesis, we focused on asymmetric synthesis of vinylcyclopropane derivatives. In this paper, we wish to report a chiral auxiliary-controlled access to the optically active trimethylsilylvinylcyclopropane derivatives via ylide routes.

Results and Discussion

First, we synthesized menthyl cinnamate **6a** from (−)-menthol and cinnamic acid according to literature.[9] It could react with the silylated telluronium allylide **5**, generated in situ from the corresponding telluronium salt **4** in the presence of LiTMP, to form the cyclopropanation

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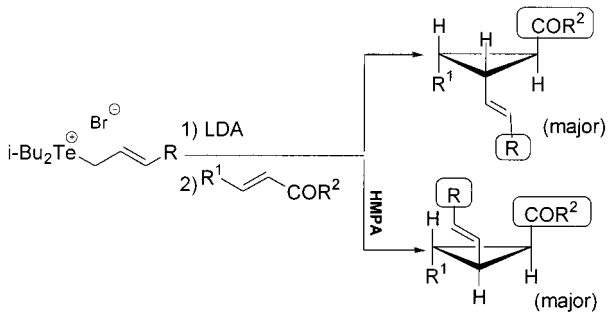
Scheme 1

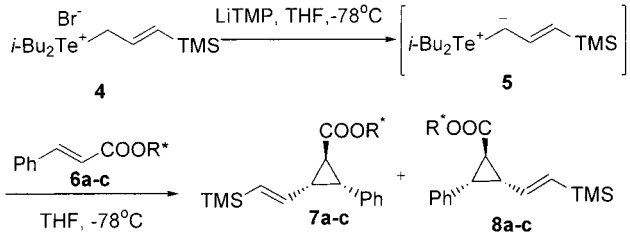


products **7a** and **8a** smoothly. Though the geometrical selectivity (cis/trans) is exclusive, the diastereoselectivity is very low and the de is only 16%.[10] Much higher stereodirecting efficiency of (−)-8-phenylmenthyl, compared to (−)-menthyl, was reported in the conjugated addition of nucleophilic reagent to α,β-unsaturated esters.[11] Thus, we chose (−)-8-phenylmenthol as the auxiliary to continue our study and hoped that the phenyl group could act as a powerful stereodirecting steric barrier to enhance the diastereoselectivity. As expected, the reaction of ylide **5** with 8-phenylmenthyl cinnamate worked well with high selectivity in good yield. The ratio of the two isomers **7b**:**8b** is up to 92:8.[12] Attempts to use more bulky 8-(2-naphthyl)menthyl instead of (−)-8-phenylmenthyl led to the same diastereodifferentiation in this reaction (Scheme 2).

Further studies showed that THF is the best solvent for this reaction, compared to *n*-hexane, ether and toluene (entries 1, 5, 6, and 7 in Table 1). Although LDA and KHMDS could be used as the base to produce ylide, the best one is LiTMP as shown in Table 1 (entries 1, 8, and 9). Lowering the reaction temperature just enhanced the diastereoselectivity a little but low yield was obtained (entries 2 and 3 in Table 1).

The good diastereoselectivities obtained with cinnamate encouraged us to further explore the cyclopropanation of other α,β-unsaturated esters. As shown in Table 2, a variety of α,β-unsaturated esters could react with silylated allylic telluronium ylide to provide silylvinylcyclopropane derivatives with high diastereoselectivity in high yields. It is worth noting that the highly optically active product could be obtained by recrystallization. For example, compound **7b/8b** (84% de) was recrystallized to afford compound **7b′/8b′** with 95% de in 57% yield.

Scheme 2



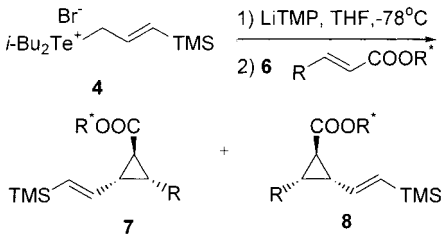
6a, 7a, 8a: R* = (-)-menthyl, 89%, **7a/8a** = 58/42
6b, 7b, 8b: R* = (-)-8-phenylmenthyl, 83%, **7b/8b** = 92/8
6c, 7c, 8c: R* = 8-(2-naphthyl)menthyl, 94%, **7c/8c** = 91/9

Table 1. Effects of Solvent, Base, and Temperature on the Cyclopropanation of 8-Phenylmenthyl Cinnamate 6b with Telluronium Allylide 5[a]

entry	**6b**:**4**:base	solvent	base	yield (%)[b]	**7b**:**8b**[c]
1	1:3:3	THF	LiTMP	83	92:8
2[d]	1:2:2	THF	LiTMP	43	91:9
3[d,e]	1:2:2	THF	LiTMP	32	93:7
4[d]	1:3:3	THF	LiTMP	59	90:10
5	1:3:3	hexane	LiTMP	trace[f]	/
6	1:3:3	ether	LiTMP	trace[f]	/
7	1:3:3	toluene	LiTMP	trace[f]	/
8	1:3:3	THF	LDA	70	91:9
9	1:3:3	THF	KHMDS	[g]	/

[a] All reactions were carried out as follows unless otherwise noted: A mixture of telluronium salt **4** and base in solvent was stirred at −78 °C for 5−10 min, then α,β-unsaturated ester **6b** was added. The resulting solution was stirred for 2 h at this temperature and then filtered rapidly through a glass funnel with a thin layer of silica gel and washed with ethyl acetate. The combined filtrate was concentrated, and the residue was purified by flash chromatography. [b]Isolated yield. [c]The ratio of **7b**:**8b** was determined by ^{1}H NMR. [d]The mixture of telluronium salt **4** and base was stirred for over 30 min before ester **6b** was added. [e]The reaction was carried out at −100 °C. [f]Most of the ester **6b** could be recovered. [g]The reaction was complicated, and small amount of 2-*cis*-trimethylsilylvinyl-3-*trans*-phenylcycloproapanecarboxylic ester was isolated.

Table 2. Asymmetric Cyclopropanation of Telluronium Salt 4 with α,β-Unsaturated Esters

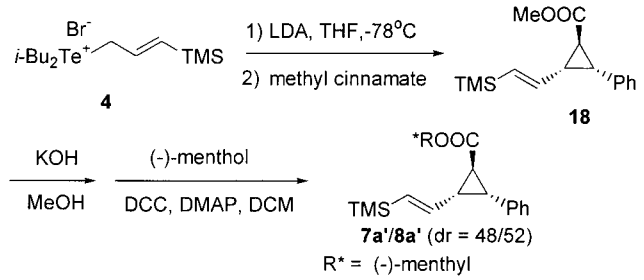


R* = (-)-8-Phenylmenthyl

entry	**6**	R	yield (%)[a]	**7**:**8**[b]
1	**6b**	Ph	83	92:8
2	**6d**	H	72	86:14
3	**6e**	*p*-ClC_6H_4	94	88:12
4	**6f**	*p*-FC_6H_4	100	90:10
5	**6g**	*p*-$CH_3C_6H_4$	89	89:11
6	**6h**	*p*-$CF_3C_6H_4$	94	88:12
7	**6i**	*p*-$CH_3OC_6H_4$	90	86:14

[a] Isolated yields. [b]The ratios of compound **7** and **8** were determined by ^{1}H NMR.

(10) The de value of **7a**/**8a** was determined by HPLC. The relative stereochemistries of compounds **7a** and **8a** were determined by chemical transformatiom as follows. Compound **18**, prepared as reported,[8b] was hydrolyzed and followed by esterification with (−)-menthol to afford **7a′**/**8a′** (dr = 48/52, determined by HPLC) which have the same ^{1}H NMR spectrum as that of compounds **7a** and **8a**. Thus, the relative stereochemistries of compounds **7a** and **8a** were assigned as described in Scheme 2.



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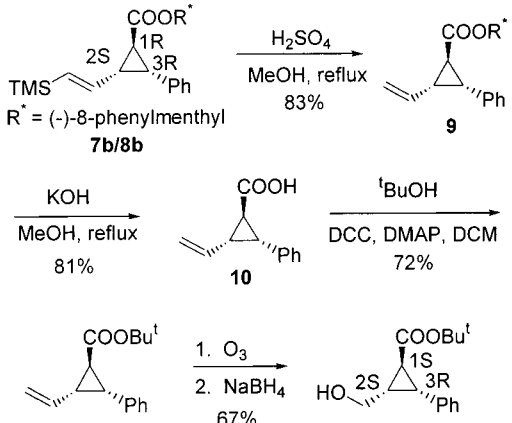
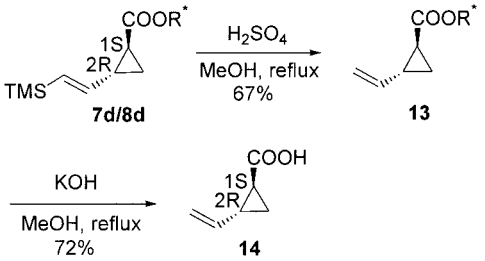
(12) The dr value of **7b**/**8b** was determined by ^{1}H NMR. The relative stereochemistries (cis/trans) were determined by similar chemical transformation as described in ref 10.

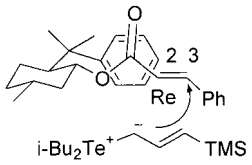
Scheme 3



Scheme 4



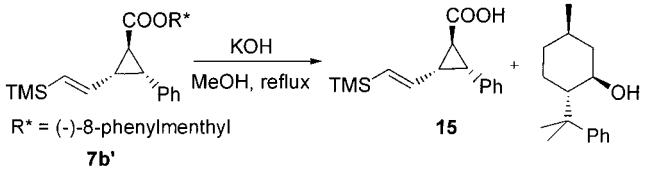
Scheme 5



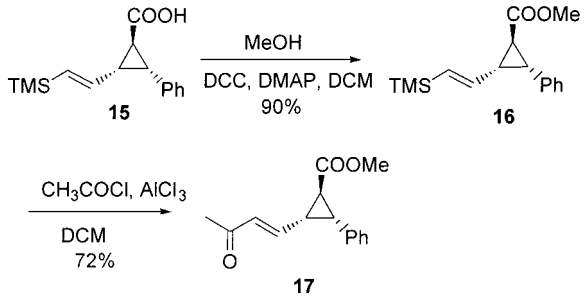
The absolute configurations of the products **7b** and **7d** were determined by chemical transformations. By treatment of compound **7b/8b** with concentrated sulfuric acid, the desilylated compound **9** was formed. Saponification of compound **9**, followed by esterification with *tert*-butyl alcohol, provided *tert*-butyl ester **11**. After one-pot ozonization and reduction of compound **11**, the known compound **12** 6 ($[\alpha]^{20}_D = -92.1°$, $c = 1.23$, $CHCl_3$) was obtained. By comparison of the rotation, the configuration of compound **12** was assigned to be 1*S*,2*S*,3*R*. Thus the configuration of compound **7b** was assigned to be 1*R*,2*S*,3*R* (Scheme 3). Cyclopropanation product **7d** was desilylated and then hydrolyzed to form 2-vinylcyclopropanecarboxylic acid **14** which has the same rotational direction ($[\alpha]^{20}_D = +107°$, $c = 0.7$, EtOH) as the known enantiomer[13] ($[\alpha]^{20}_D = +165°$, $c = 2.1$, EtOH) (Scheme 4). Thus, the absolute configuration of compound **7d** is 1*S*,2*R*.

It was well-known that there always has the π-stacking effect between the phenyl and dienyl group in (−)-8-phenylmenthyl esters of α,β-unsaturated acid.[14] As shown in Scheme 5, the phenyl group was proposed to block the Si face of the carbon−carbon double bond. The telluronium ylide attacked at C-3 on Re face, so compound **7b** was sterically preferred and formed as the major product.

Scheme 6



Scheme 7



It is worth to note that the chiral auxiliary (−)-8-phenylmenthol can be easily recovered in 92% yield by saponification (Scheme 6). Additionally, the cyclopropane derivatives prepared by the current method should be synthetically useful, because these compounds can undergo many chemical transformations. For example, compound **16** reacted with acetyl chloride to form the corresponding α,β-unsaturated ketone **17** without loss of ee (Scheme 7).

In conclusion, the synthesis of optically active vinylcyclopropane derivatives was developed by using (−)-8-phenylmenthol as the chiral auxiliary. The easy recovery of chiral auxiliary, good selectivity, and high yield make it a potentially useful method in organic synthesis. The reagent-controlled and catalytically asymmetric synthesis of vinylcyclopropane derivatives is in progress in our laboratory.

Experimental Section

All reaction flasks were dried by flame, and all reactions were carried out under argon. THF was dried by distillation over sodium−benzophenone ketyl. The reagents were purchased from commercial sources and used directly.

General Procedure for Preparation of the α,β-Unsaturated Esters.[9] To a solution of (−)-menthol (4.69 g, 30 mmol), cinnamic acid (4.89 g, 33 mmol), and DMAP (138 mg, 1.5 mmol) in dichloromethane (40 mL) at 0 °C was added DCC (7.43 g, 36 mmol) in dichloromethane (20 mL). Then, the reaction mixture was allowed to warm to room temperature. After being stirred for 10 h, the reaction mixture was passed through a short silica gel column, which was eluted with ethyl acetate. Upon removal of the solvent under vacuum, the residue was purified by column chromatrography.

Menthyl Cinnamate (6a).[15] Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.67 (d, $J = 15.9$ Hz, 1H), 7.50 (m, 2H), 7.40 (m, 3H), 6.43 (d, $J = 15.8$ Hz, 1H), 4.83 (dt, $J = 4.4$, 10.9 Hz, 1H), 0.7−2.2 (m, 9H), 0.93 (d, $J = 2.2$ Hz, 3H), 0.91 (d, $J = 2.8$ Hz, 3H), 0.79 (d, $J = 7.0$ Hz, 3H).

8-Phenylmenthyl Cinnamate (6b).[16] Yield: 55%. $[\alpha]^{20}_D = +9.9°$ (c 2.23, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.5−7.1 (m, 11H), 5.75 (d, $J = 16.0$ Hz, 1H), 4.91 (dt, $J = 4.4$,

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10.7 Hz, 1H), 2.11 (dt, J = 3.4, 12.1 Hz, 1H), 2.0−0.9 (m, 7H), 1.32 (s, 3H), 1.23 (s, 3H), 0.88 (d, J = 6.5 Hz, 3H).

8-(2-Naphthyl)menthyl Cinnamate (6c). Yield: 26% (recovered 8-(2-naphthyl)menthol, 31%). IR (KBr) ν/cm^{-1} 3078 (w), 2953 (s), 1703 (vs), 1637 (s), 1310 (s), 1176 (vs); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.5−7.1 (m, 10H), 7.02 (d, J = 16 Hz, 1H), 6.88 (d, J = 7.1 Hz, 2H), 5.25 (d, J = 16.0 Hz, 1H), 4.95 (dt, J = 4.3, 10.7 Hz, 1H), 2.26 (dt, J = 3.5, 12.0 Hz, 1H), 2.0−0.9 (m, 7H), 1,44 (s, 3H), 1.30 (s, 3H), 0.89 (d, J = 6.5 Hz, 3H); MS (EI, m/z, rel intensity) 412 (M$^+$, 14.4), 169 (100), 141 (19), 77 (13). Anal. Calcd for $C_{29}H_{32}O_2$: C, 84.43; H, 7.82. Found: C, 84.13; H, 7.85.

Ester 6d.[17] Yield: 46%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.30−7.21 (m, 4H), 7.05−7.03 (m, 1H), 5.98−5.90 (m, 1H), 5.55−5.47 (m, 2H), 4.79 (dt, J = 4.2, 10.7 Hz, 1H), 2.0−1.93 (m, 1H), 1.86−1.74 (m, 1H), 1.63−1.53 (m, 2H), 1.43−1.35 (m, 1H), 1,23 (s, 3H), 1.15 (s, 3H), 0.79 (d, J = 6.6 Hz, 3H), 1.2−0.6 (m, 3H).

Ester 6e. Yield: 52%. mp 69−71 °C; $[\alpha]^{20}_D$ = +23.9° (c 1.03, $CHCl_3$); IR (KBr) ν/cm^{-1} 3085 (w), 2952 (s), 1706 (vs), 1640 (s), 1492 (s), 1310 (s), 1187 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.5−7.0 (m, 10H), 5.68 (d, J = 16 Hz, 1H), 4.91 (dt, 4.4, 10.7 Hz, 1H), 2.2−0.8 (m, 8H), 1,32 (s, 3H), 1.22 (s, 3H), 0.89 (d, J = 6.5 Hz, 3H); MS (EI, m/z, rel intensity) 397 (M$^+$, 0.2), 215 (34.1), 119 (100), 91 (33). Anal. Calcd for $C_{25}H_{29}ClO_2$: C, 75.64; H, 7.36; Cl, 8.93. Found: C, 75.53; H, 7.31; Cl, 8.87.

Ester 6f. Yield: 63.5%. mp 76−78 °C; $[\alpha]^{20}_D$ = +7.3° (c 1.07, $CHCl_3$); IR (KBr) ν/cm^{-1} 3085 (w), 2953 (s), 1706 (vs), 1641 (s), 1602 (s), 1510 (s), 1313 (s), 1179 (vs). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.5−7.0 (m, 10H), 5.65 (d, J = 16.0 Hz, 1H), 4.91 (dt, J = 4.33, 10.7 Hz, 1H), 2.12 (dt, J = 3.46, 12.0 Hz, 1H), 2.0−1.90 (m, 1H), 1.85−1.75 (m, 1H), 1.75−1.65 (m, 1H), 1.60−1.45 (m, 1H), 1.32 (s, 3H), 1.22 (s, 3H), 0.88 (d, J = 6.5 Hz, 3H), 1.3−0.8 (m, 3H); MS (EI, m/z, rel intensity) 381 (M$^+$, 0.46), 215 (53), 119 (100), 105 (42), 91 (26). Anal. Calcd for $C_{25}H_{29}FO_2$: C 78.92; H, 7.68. Found: C, 79.38; H, 7.90.

Ester 6g. Yield: 56%. $[\alpha]^{20}_D$ = +23.7° (c 1.34, $CHCl_3$); IR (film) ν/cm^{-1} 3087 (w), 2952 (s), 1705 (vs), 1635 (vs), 1608 (vs), 1309 (vs), 1270 (vs), 1093 (s). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.5−7.0 (m, 10H), 5.72 (d, J = 16 Hz, 1H), 4.92 (dt, J = 6.4, 10.7 Hz, 1H), 2.36 (s, 3H), 2.10 (dt, J = 3.4, 12.1 Hz, 1H), 1.98−1.91 (m, 1H), 1.80−1.60 (m, 2H), 1.60−1.40 (m, 1H), 1,32 (s, 3H), 1.23 (s, 3H), 1.3−0.8 (m, 3H), 0.87 (d, J = 6.5 Hz, 3H); MS (EI, m/z, rel intensity) 376 (M$^+$, 0.14), 214 (9.66), 162 (22), 119 (100), 91 (48). Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.94; H, 8.56. Found: C, 83.05; H, 8.58.

Ester 6h. Yield: 67.5%. mp 82−84 °C; $[\alpha]^{20}_D$ = +7.5° (c 1.07, $CHCl_3$); IR (KBr) ν/cm^{-1} 3085 (w), 2963 (s), 1706 (vs), 1644 (s), 1366 (s), 1336 (s), 1282 (s), 1192 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.4−7.0 (m, 6H), 5.75 (d, J = 16 Hz, 1H), 4.92 (dt, J = 4.4, 10.7 Hz, 1H), 2.3−2.0 (m, 1H), 2.0−1.8 (m, 2H), 1.8−1.7 (m, 1H), 1.60−1.40 (m, 1H), 1.32 (s, 3H), 1.22 (s, 3H), 1.3−0.8 (m, 3H), 0.89 (d, J = 6.5 Hz, 3H); MS (EI, m/z, rel intensity) 411 (M$^+$ − 19, 0.39), 214 (3.14), 199 (12), 119 (100), 105 (3.5), 91 (21). Anal. Calcd for $C_{26}H_{29}F_3O_2$: C, 72.54; H, 6.79. Found: C, 72.67; H, 6.92.

Ester 6i. Yield: 51.6%. mp 88−90 °C; $[\alpha]^{20}_D$ = +33.8° (c 1.02, $CHCl_3$); IR (KBr) ν/cm^{-1} 3080 (w), 2953 (m), 1702 (s), 1636 (m), 1604 (s), 1512 (s), 1172 (vs); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.5−7.0 (m, 8H), 6.88 (d, J = 8.8 Hz, 2H), 5.65 (d, J = 16 Hz, 1H), 4.90 (dt, J = 4.3, 10.8 Hz, 1H), 3.84 (s, 3H), 2.0−0.8 (m, 7H), 1.40 (dt, J = 3.4, 12.1 Hz, 1H), 1.32 (s, 3H), 1.22 (s, 3H), 0.88 (d, J = 6.5 Hz, 3H); MS (EI, m/z, rel intensity) 392 (M$^+$, 14.7), 178 (94), 161 (69), 119 (100), 91 (50). Anal. Calcd for $C_{26}H_{32}O_3$: C, 79.56; H, 8.22. Found: C, 79.53; H, 8.28.

General Procedure for Cyclopropanation Reaction via Telluronium Ylide. To a solution of telluronium salt **4** (544 mg, 1.25 mmol) in THF (2 mL) was added LiTMP (1.25 mmol, made from 2,2,6,6-tetramethylpiperidine and n-butyllithium in situ) at −78 °C. After stirring for 3−5 min, the α,β-unsaturated ester **6** (0.418 mmol) in THF (1 mL) was added. The resulting solution was stirring for 4 h at −78 °C, and then several drops of water were added to quench the reactions. The reaction mixture was passed through a short silica gel column, which was eluted with ethyl acetate. After concentration of the elution, the residue was purified by preparative thin-layer chromatography.

Cyclopropane Derivative 7a. Yield: 89%. **7a/8a** = 58/42;10 IR (film) ν/cm^{-1} 3063 (w), 2957 (s), 1722 (vs), 1613 (m), 1174 (s); ^{1}H NMR for **7a** and **8a** (300 MHz, $CDCl_3$, TMS) δ 7.6−7.4 (m, 5H), 6.15 (d, J = 18.6 Hz, 1H), 5.59 (dd, J = 8.7, 18.6 Hz, 1H), 5.01 (dt, J = 6.8, 10.8 Hz, 1H), 3.25−3.15 (m, 1H), 2.75−2.65 (m, 1H), 2.50 (t, J = 4.7 Hz, 1H), 2.5−1.0 (m, 9H), 1.20 (d, J = 3.2 Hz, 3H), 1.18 (d, J = 3.1 Hz, 3H), 1.06 (d, J = 7.0 Hz, 3H), 0.18 (s, 9H); MS (EI, m/z, rel intensity) 399 (M$^+$, 0.39), 383 (5.0), 261 (22.5), 139 (35), 83 (100). Anal. Calcd for $C_{25}H_{38}O_2Si$: C, 75.33; H, 9.61. Found: C, 74.93; H, 9.52.

Cyclopropane Derivative 7b. Yield: 83%. **7b/8b** = 92:8;[12] IR (film) ν/cm^{-1} 3089 (w), 2955 (s), 1718 (vs), 1611 (m), 1248 (s), 1174 (s), 860 (s). ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.1(m, 10H), 5.89 (d, J = 18.6 Hz, 1H), 5.34 (dd, J = 8.7, 18.5 Hz, 1H), 4.95 (dt, J = 4.4, 10.8 Hz, 1H), 2.92 (dd, J = 9.7, 5.3 Hz, 0.92H, **7b**-PhC*H*), 2.65 (dd, J = 9.8, 5.5 Hz, 0.08H, **8b**-PhC*H*), 2.36 (dt, J = 8.9, 4.5 Hz, 1H), 1.89 (dd, J = 5.1, 4.8 Hz, 1H), 2.2−0.9 (m, 8H), 1.46 (s, 3H), 1.35 (s, 3H), 0.99 (d, J = 6.8 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 172.0, 151.2, 142.0, 136.0, 132.9, 129.0, 128.0, 127.9, 126.5, 125.3, 125.2, 75.1, 50.6, 41.9, 39.8, 34.6, 34.0, 32.0, 31.3, 27.4, 27.1, 26.8, 26.3, 21.8, −1.4; MS (EI, m/z, rel intensity) 460 (M$^+$ − 15, 0.35), 215 (3.93), 119 (52), 105 (100), 91 (26). Anal. Calcd for $C_{31}H_{42}O_2Si$: C, 78.43; H, 8.92. Found: C, 78.08; H, 8.53.

Cyclopropane Derivative 7c. Yield: 94%. **7c/8c** = 90:10; IR (KBr) ν/cm^{-1} 3057 (w), 2955 (s), 1713 (vs), 1630 (m), 1175 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 8.0−7.8 (m, 12H), 5.92 (d, J = 18.5 Hz, 0.10H, **8c**-TMSC*H*=), 5.80 (d, J = 18.6 Hz, 0.90H, **7c**-TMSC*H*=), 5.25 (dd, J = 18.6, 8.7 Hz, 1H), 5.05 (dt, J = 4.3, 10.7 Hz, 1H), 2.93 (dd, J = 9.6, 5.4 Hz, 0.90H, **7c**-PhC*H*), 2.60 (dd, J = 9.6, 5.4 Hz, 0.10H, **8c**-PhC*H*), 2.4−1.0 (m, 10H), 1,62 (s, 3H), 1.48 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 172.1, 148.8, 142.0, 135.9, 133.4, 132.7, 131.5, 129.0, 128.04, 127.98, 127.5, 127.3, 126.4, 125.8, 125.2, 124.8, 123.3, 75.3, 50.2, 41.9, 40.2, 34.6, 33.9, 31.9, 31.4, 27.3, 27.2, 27.0, 26.4, 21.8, −1.4; MS (EI, m/z, rel intensity) 526 (M$^+$, 5), 265 (35), 169 (100), 141 (40). Anal. Calcd for $C_{35}H_{44}O_2Si$: C, 84.10; H, 8.45. Found: C, 80.12; H, 8.52.

Cyclopropane Derivative 7d. Yield: 72%. **7d/8d** = 86:14; IR (film) ν/cm^{-1} 3060 (w), 2955 (s), 1716 (vs), 1607 (m), 1513(s), 1176 (s); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.3−7.1 (m, 4H), 7.1−7.0 (m, 1H), 5.76 (d, J = 18.5 Hz, 0.14H, 7d-TMSC*H*=), 5.68 (d, J = 18.5 Hz, 0.86H, **8d**-TMSC*H*=), 5.38 (dd, J = 8.3, 18.5 Hz, 1H), 4.78 (dt, J = 6.2, 10.6 Hz, 1H), 2.1−1.9 (m, 1H), 1.9−1.75 (m, 2H), 1.7−1.6 (m, 2H), 1.50−1.32 (m, 2H), 1,27 (s, 3H), 1.21 (s, 3H), 0.84 (d, J = 6.5 Hz, 3H), 1.3−0.7 (m, 5H), 0.0 (s, 9H); MS (EI, m/z, rel intensity) 384 (M$^+$ − 15, 0.96), 215 (7.05), 119 (100), 91 (29). Anal. Calcd for $C_{25}H_{38}O_2Si$: C, 75.32; H, 9.61. Found: C, 75.54; H, 9.88.

Cyclopropane Derivative 7e. Yield: 94%. **7e/8e** = 88:12; IR (film) ν/cm^{-1} 3090 (w), 2955 (s), 2923 (s), 1716 (vs), 1600 (w), 1495 (s), 1174 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.3−7.2 (m, 6H), 7.2−7.0 (m, 3H), 5,85 (d, J = 18.5 Hz, 1H), 5.29 (dd, J = 8.5, 18.5 Hz, 1H), 4.94 (dt, J = 4.3, 10.8 Hz, 1H), 2.83 (dd, J = 9.6, 5.3 Hz, 0.88H, **7e**-p-ClC_6H_4CH), 2.56 (dd, J = 9.6, 5.4 Hz, 0.12H, **8e**-p-ClC_6H_4CH), 2.33 (dt, J = 9.2, 4.6 Hz, 1H), 2.19 (dt, J = 3.5, 18.1 Hz, 1H), 2.05−1.95 (m, 1H), 1.85−1.65 (m, 2H), 1.6−1.4 (m, 1H), 1.43 (s, 3H), 1.32 (s, 3H), 0.95 (d, J = 6.5 Hz, 3H), 1.4−0.9 (m, 4H), 0.0 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 171.5, 151.2, 141.2, 134.5, 133.4, 132.2, 130.3, 128.0, 127.9, 125.2, 125.0, 75.0, 50.4, 41.7, 40.0, 34.5, 33.8, 31.2, 31.0, 27.5, 27.2, 26.6, 25.6, 21.7, −1.4; MS (EI, m/z, rel intensity) 494 (M$^+$ − 15, 0.35), 215 (6.32), 119 (80), 105

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(100), 91 (33). Anal. Calcd for $C_{31}H_{41}ClO_2Si$: C, 73.12; H, 8.05; Cl, 6.96. Found: C, 73.00; H, 8.43; Cl, 7.12.

Cyclopropane Derivative 7f. Yield: 100%. **7f/8f** = 90:10; IR (film) ν/cm^{-1} 3056 (w), 2955 (s), 2924 (m), 1717 (vs), 1607 (m), 1513 (s), 1176 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.38 (d, J = 7.8 Hz, 2H), 7.32−7.26 (m, 2H), 7.17−7.01 (m, 5H), 5,89 (d, J = 18.6 Hz, 1H), 5.28 (dd, J = 8.6, 18.6 Hz, 1H), 4.95 (dt, J = 4.3, 10.7 Hz, 1H), 2.86 (dd, J = 9.5, 5.3 Hz, 0.90H, **7f**-*p*-FC_6H_4CH), 2.58 (dd, J = 9.7, 5.5 Hz, 0.10H, **8f**-*p*-FC_6H_4CH), 2.40−2.28 (m, 1H), 2.2−2.1 (m, 1H), 2.04−1.95 (m, 1H), 1.72 (t, J = 4.9, 1H), 1.75−1.65 (m, 2H), 1,65−1.5 (m, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 0.96 (d, J = 6.4 Hz, 3H), 1.5−0.9 (m, 3H), 0.0 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 171.8, 161.6 (d, $^1J_{CF}$ = 244.0 Hz), 151.3, 141.7, 133.3, 131.7 (d, $^4J_{CF}$ = 3.2 Hz), 130.6 (d, $^3J_{CF}$ = 7.9 Hz), 128.0, 125.4, 125.1, 114.8 (d, $^2J_{CF}$ = 21.0 Hz), 75.1, 50.5, 41.9, 39.8, 34.6, 33.8, 31.3, 31.1, 27.5, 27.3, 26.8, 26.1, 21.8, −1.4; MS (EI, m/z, rel intensity) 477 (M^+ − 15, 0.21), 215 (5.41), 119 (73), 105 (100), 91 (33). Anal. Calcd for $C_{31}H_{41}FO_2Si$: C, 75.56; H, 8.39. Found: C, 75.52; H, 8.18.

Cyclopropane Derivative 7g. Yield: 89%. **7g/8g** = 89:11; IR (film) ν/cm^{-1} 3050 (w), 2954 (s), 2923 (m), 1717 (vs), 1610 (m), 1173 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.39−7.26 (m, 4H), 7.18−7.01 (m, 5H), 5.88 (d, J = 18.6 Hz, 1H), 5.31 (dd, J = 8.7, 18.6 Hz, 1H), 4.94 (dt, J = 4.3, 10.7 Hz, 1H), 2.87 (dd, J = 9.5, 5.4 Hz, 0.89H, **7g**-*p*-$CH_3C_6H_4CH$), 2.63 (dd, J = 9.4, 5.2 Hz, 0.11H, **8g**-*p*-$CH_3C_6H_4CH$), 2.40 (s, 3H), 2.30−2.28 (m, 2H), 2.16−2.0 (m, 2H), 1.85 (t, J = 4.9, 1H), 1.70 (br d, J = 11.6, 2H), 1.65−1.5 (m, 1H), 1.45 (s, 3H), 1.34 (s, 3H), 0.95 (d, J = 6.4 Hz, 3H), 1.5−0.9 (m, 2H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 172.0, 151.1, 142.2, 135.9, 132.9, 132.6, 128.9, 128.6, 127.9, 125.3, 125.1, 75.0, 50.5, 41.8, 39.8, 34.6, 34.1, 31.7, 31.3, 27.5, 26.9, 26.8, 26.4, 21.8, 21.0, −1.4; MS (EI, m/z, rel intensity) 474 (M^+ − 15, 0.13), 216 (3.38), 119 (62), 105 (100), 91 (35). Anal. Calcd for $C_{32}H_{44}O_2Si$: C, 78.63; H, 9.07. Found: C, 78.65; H, 9.15.

Cyclopropane Derivative 7h. Yield: 94%. **7h/8h** = 88:12; IR (film) ν/cm^{-1} 3080 (w), 2955 (s), 2925 (s), 1717 (vs), 1618 (s), 1325 (vs), 1166 (s), 1127 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 8.2 Hz, 2H), 7.5−7.2 (m, 6H), 7.13 (t, J = 8.2 Hz, 1H), 5.89 (d, J = 18.5 Hz, 1H), 5.31 (dd, J = 8.3, 18.5 Hz, 1H), 4.99 (dt, J = 4.3, 10.7 Hz, 1H), 2.92 (dd, J = 9.7, 5.4 Hz, 0.88H, **7h**-*p*-$CF_3C_6H_4CH$), 2.61 (dd, J = 9.9, 5.7 Hz, 0.12H, **8h**-*p*-$CF_3C_6H_4CH$), 2.4−2.3 (m, 1H), 2.25−2.1 (m, 1H), 2.1−2.0 (m, 1H), 1.9−1.7 (m, 3H), 1.7−1.5 (m, 1H), 1.45 (s, 3H), 1.33 (s, 3H), 0.98 (d, J = 6.4 Hz, 3H), 1.5−1.0 (m, 3H), 0.01 (s, 9H); ^{13}C NMR of **7h′** (recrystallized, de = 100%), (75 MHz, $CDCl_3$ TMS) δ 171.6, 151.4, 140.8, 140.4, 134.2, 129.4, 128.8 (q, $^2J_{CF}$ = 32.0 Hz), 125.4, 125.2, 124.9 (q, $^3J_{CF}$ = 3.8 Hz), 124.4 (q, $^1J_{CF}$ = 270.0 Hz), 75.3, 50.5, 41.9, 39.8, 34.6, 34.1, 31.5, 31.4, 27.8, 27.3, 26.7, 25.6, 21.8, −1.5; MS (EI, m/z, rel intensity) 524 (M^+ − 15, 0.12), 215 (7.6), 119 (68), 105 (100), 91 (42). Anal. Calcd for $C_{32}H_{41}F_3O_2Si$: C, 70.81; H, 7.61. Found: C, 71.11; H, 7.70.

Cyclopropane Derivative 7i. Yield: 90%. **7i/8i** = 86:14; IR (film) ν/cm^{-1} 3090 (w), 2953 (s), 1717 (vs), 1612 (s), 1515 (s), 1248 (s), 1173 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.39−7.28 (m, 4H), 7.2−7.1 (m, 3H), 6.90 (d, J = 8.6 Hz, 2H), 5.88 (d, J = 18.6 Hz, 1H), 5.34 (dd, J = 8.7, 18.5 Hz, 1H), 4.94 (dt, J = 4.3, 10.7 Hz, 1H), 3.86 (s, 3H), 2.85 (dd, J = 9.5, 5.3 Hz, 0.86H, **7i**-*p*-$CH_3OC_6H_4CH$), 2.60 (dd, J = 9.4, 5.1 Hz, 0.14H, **8i**-*p*-$CH_3OC_6H_4CH$), 2.37−2.28 (m, 1H), 2.2−1.95 (m, 2H), 1.8 (t, J = 4.8 Hz, 1H), 1.7−1.67 (m, 2H), 1.6−1.5 (m, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 1.5−1.0 (m, 3H), 0.95 (d, J = 6.4 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$ TMS) δ 172.1, 158.2, 151.1, 142.3, 132.6, 130.1, 128.0, 127.9, 125.3, 125.1, 113.4, 76.6, 55.1, 50.5, 41.8, 39.8, 34.6, 34.0, 31.3, 27.6, 26.9, 26.8, 26.5, 21.8, −1.4; MS (EI, m/z, rel intensity) 474 (M^+ − 31, 0.11), 289 (7.3), 246 (14), 119 (68), 105 (100), 91 (42). Anal. Calcd for $C_{32}H_{44}O_3Si$: C, 76.14; H, 8.78. Found: C, 75.98; H, 8.63.

Determination the Absolute Configuration of 7b

Preparation of Ester 9. A solution of **7b** (805 mg, 1.70 mmol) and concentrated sufuric acid (0.2 mL) in methyl alcohol (30 mL) was refluxed for 25 h. The resulting solution was concentrated, and water (20 mL) was added. The mixture was extracted with ether, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography to afford a colorless oil 570 mg (83%). IR (film) ν/cm^{-1} 3088 (w), 2956 (s), 1716 (vs), 1278 (m), 1189 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.0 (m, 10H), 5.2−4.9 (m, 3H), 4.85 (dt, J = 10.7, 4.4 Hz, 1H), 2.82 (dd, J = 9.7, 5.5 Hz, 1H), 2.23 (dt, J = 4.9, 3.8 Hz, 1H), 2.1−2.0 (m, 1H), 2.0−1.9 (m, 1H), 1.75 (t, J = 5.0 Hz, 1H), 1.36 (s, 3H), 1.25 (s, 3H), 0.90 (s, 3H), 1.7−0.9 (m, 6H); MS (EI, m/z, rel intensity) 283 (M^+ − 119, 2.49), 119 (76.63), 105 (100), 91 (33). Anal. Calcd for $C_{28}H_{34}O2$: C, 83.54; H, 8.51. Found: C, 83.58; H, 8.48.

Preparation of Acid 10. A solution of **9** (535 mg, 1.33 mmol) and potassium hydroxide (1.49 g, 26.6 mmol) in methyl alcohol (15 mL) was refluxed for 2 h. The resulting mixture was concentrated, and then water (20 mL) was added. The residue was acidified with 10% HCl and extracted with ethyl acetate, and then the combined extraction was dried and concentrated. The residue was purified by column chromatography to give acid **10**. Yield: 96%. mp 74−76 °C; $[\alpha]^{20}D$ = +5.7° (c = 0.91, $CHCl_3$); IR (film) ν/cm^{-1} 3000 (s, br), 1695 (vs), 1459 (m), 699 (m); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.1 (m, 5H), 5.4−5.0 (m, 3H), 3.01 (dd, J = 9.6, 5.3 Hz, 1H), 2.52 (dt, J = 9.4, 4.5 Hz, 1H), 2.21 (t, J = 4.9 Hz, 1H); MS (EI, m/z, rel intensity) 171 (13.86), 143 (67.07), 135 (62.85), 115 (19.48), 57 (100). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.58; H, 6.42. Found: C, 76.50; H, 6.50.

Preparation of Ester 11. To a solution of *tert*-butyl alcohol (170 mg, 2.3 mmol), acid **10** (216 mg, 1.15 mmol), and DMAP (140 mg, 1.15 mmol) in dichloromethane (8 mL) at 0 °C was added DCC (474 mg, 2.3 mmol) in dichloromethane (4 mL). The reaction mixture was allowed to warm to room temperature and was stirred for 10 h. The reaction mixture was passed through a short silica gel column, which was eluted with ethyl acetate. Upon removal of the solvent under vacuum, the residue was purified by column chromatography. Yield: 72%. $[\alpha]^{20}_D$ = +7.2° (c = 1.14, $CHCl_3$); IR (film) ν/cm^{-1} 2980 (m), 2120 (w), 1720 (vs), 1285 (m), 1151 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.1 (m, 5H), 5.3−4.9 (m, 3H), 2.85 (dd, J = 9.6, 5.4 Hz, 1H), 2.37 (dt, J = 8.8, 4.8 Hz, 1H), 2.14 (t, J = 4.9 Hz, 1H), 1.49 (s, 9H); MS (EI, m/z, rel intensity) 243 (M^+ − 1, 1.44), 143 (18.84), 119 (79.93), 105 (100). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 79.13; H, 8.01.

Preparation of 12.[6] A solution of **11** (137 mg, 0.56 mmol) in a mixed solvent of methyl alcohol/dichloromethane (1:1, 16 mL) was treated with a stream of O_3 in −78 °C until starting material could not be detected by TLC analysis (about 30 min). The reaction mixture was flushed with argon to remove residual O_3, and then $NaBH_4$ (25 mg, 0.67 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred 6 h. The reaction mixture was passed through a short silica gel column, which was eluted with ethyl acetate. Purification by silica gel chromatography provided 94 mg (67%) of the alcohol. $[\alpha]^{20}_D$ = −92° (c = 1.23, $CHCl_3$), (ref:[6] $[\alpha]^{20}_D$ = +122.1°, c = 1.23, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.1 (m, 5H), 3.55 (m, 1H), 3.4 (m, 1H), 2.82 (dd, J = 8.6, 5.9 Hz, 1H), 2.05 (m, 2H), 1.48 (s, 9H).

Determination of the Absolute Configuration of 7d

Preparation of Ester 13. A solution of **7d** (235 mg, 0.589 mmol) and concentrated sufuric acid (0.07 mL) in methyl alcohol (15 mL) was refluxed for 23 h. After concentration, to the residue was added water (10 mL). The resulting mixture was extracted with ether, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography to give **13**. Yield: 67%. IR (film) ν/cm^{-1} 3088 (w), 2956 (s), 1718 (vs), 1394(s), 1178 (s), 700 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.30−7.20 (m, 4H), 7.15−7.05 (m, 1H), 5.4−5.2 (m, 1H), 5.1−5.0 (m, 1H), 5.0−4.9 (m, 1H), 4.78 (dt, J = 10.7, 4.4 Hz, 1H), 2.1−1.9 (m, 1H), 1.9−0.7 (m, 11H), 1.31 (s, 3H), 1.20 (s, 3H), 0.86 (d, J = 6.5 Hz, 3H); MS (EI, m/z, rel intensity) 326 (M^+, 0.37), 214 (10.0), 119 (100), 91 (20). Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.86; H, 9.36.

Preparation of Acid 14.[13] A solution of **13** (114 mg, 0.35 mmol) and potassium hydroxide (393 mg, 7.0 mmol) in methyl alcohol (5 mL) was refluxed for 10 h. After concentration, to

the residue was added water (10 mL). The resulting mixture was acidified with 10% HCl and extracted with ethyl acetate. The extraction was dried over Na_2SO_4. After concentration, the residue was purified by column chromatography. Yield: 72%. $[\alpha]^{20}_D = +107°$ ($c = 0.7$, EtOH), (ref:[11] $[\alpha]^{20}_D = 165°$, $c =$ 2.0, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 5.5−5.3 (m, 1H), 5.18 (d, $J = 16.0$ Hz, 1H), 5.02 (d, $J = 10.0$ Hz, 1H), 2.2−2.0 (m, 1H), 1.7−1.6 (m, 1H), 15−1.4 (m, 1H), 1.1−1.0 (m, 1H).

Some Chemical Transformations of the ((Trimethylsilyl)vinyl)cyclopropane Derivative 7b′

(1*R*,2*R*,3*S*)-2-Phenyl-3-((trimethylsilyl)vinyl)cyclopropanecaboxylic Acid (15). A solution of **7b′** (de = 95%, recrystallization of **7b** from ethyl alcohol, 203 mg, 0.428 mmol) and potassium hydroxide (482 mg, 26.6 mmol) in methyl alcohol (10 mL) was refluxed for 5 h. After concentration, to the residue was added water (12 mL). The resulting mixture was acidified with 10% HCl and extracted with ethyl acetate. The extraction was dried and concentrated. The residue was purified by column chromatograph to give (−)-8-phenylmenthol (94 mg, 92%) and acid **15**. Yield: 84%. mp 116−118 °C; $[\alpha]^{20}_D = +62°$ ($c = 1.0$, $CHCl_3$); IR (film) ν/cm^{-1} 3207 (s, br), 1714 (vs), 1615 (m), 1440 (s), 1177 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.2 (m, 5H), 5.99 (d, $J = 18.5$ Hz, 1H), 5.37 (dd, $J = 18.5$, 8.8 Hz, 1H), 3.08 (dd, $J = 9.6$, 5.3 Hz, 1H), 2.60 (dt, $J = 9.2$, 4.4 Hz, 1H), 2.31 (t, $J = 4.9$ Hz, 1H), 0.08 (s, 9H); MS (EI, m/z, rel intensity) 260 (M^+, 3.90), 245 (41.87), 227 (17.64), 170 (39.44), 142 (100). Anal. Calcd for $C_{15}H_{20}O_2Si$: C, 69.18; H, 7.74. Found: C, 69.01; H, 7.36.

Methyl (1*R*,2*R*,3*S*)-2-Phenyl-3-((trimethylsilyl)vinyl)-cyclopropanecarboxylate (16).[8b] To a solution of acid 15 (76 mg, 0.292 mmol), methyl alcohol (18 mg, 0.58 mmol), and DMAP (36 mg, 0.20 mmol) in dichloromethane (4 mL) at 0 °C was added DCC (120 mg, 0.58 mmol) in dichloromethane (2 mL). Then, the reaction mixture was allowed to warm to room temperature. After stirring for 10 h, the reaction mixture was passed through a short silica gel column, which was eluted with ethyl acetate. Upon removal of the solvent under vacuum, the residue was purified by column chromatrography. Yield: 90%. 94.9% ee (determined by HPLC: OD-H, *n*-hexane/2-PrOH = 200/1, 1 mL/min; $t_R = 12.2$ min (minor), 13.4 min (major)). $[\alpha]^{20}_D = +64°$ ($c = 1.17$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.2 (m, 5H), 5.97 (d, $J = 18.5$ Hz, 1H), 5.38 (dd, $J = 18.5$, 8.8 Hz, 1H), 3.82 (s, 3H), 3.03 (dd, $J = 9.6$, 5.4 Hz, 1H), 2.54 (dt, $J = 9.0$, 4.6 Hz, 1H), 2.32 (t, $J = 4.9$ Hz, 1H), 0.08 (s, 9H).

Methyl (1*R*,2*R*,3*S*)-2-(2-Acylvinyl)-3-phenylcyclopropanecarboxylate (17). A solution of **16** (50 mg, 0.18 mmol) in 15 mL of dichloromethane was added over 1 h to a stirred mixture of acetyl chloride (72 mg, 0.91 mmol) and aluminum chloride (121 mg, 0.91 mmol) in 8 mL of dichlormethane at 0 °C. The mixture was stirred for an additional 15 min and poured into 20 mL of saturated sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane (3 × 20 mL), and the combined organic layers were washed with saturated sodium bicarbonate solution, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography to give 32 mg (72%) of the unsaturated ketone **17**, 94.3% ee (determined by HPLC: OD-H, *n*-hexane/2-PrOH = 95/5, 0.8 mL/min; $t_R = 19.8$ min (major), 22.7 min (minor)). $[\alpha]^{20}_D = +114.6°$ ($c = 1.0$, $CHCl_3$); IR (film) ν/cm^{-1} 3031 (w), 2954 (w), 1733 (vs), 1671 (vs), 1444 (s), 1174 (s); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.4−7.2 (m, 5H), 6,28 (d, $J = 15.8$ Hz, 1H), 6.05 (dd, $J = 15.8$, 10.1 Hz, 1H), 3.77 (s, 3H), 3.16 (dd, $J = 9.3$, 5.6 Hz, 1H), 2.55 (dt, $J = 9.8$, 3.9 Hz, 1H), 2.42 (t, $J = 4.5$ Hz, 1H), 2.05 (s, 3H); MS (EI, m/z, rel intensity) 245 (M^+, 3.23), 244 (1.59), 185 (32.32), 169 (20.34), 115 (34.89), 43 (100). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.77; H, 6.65.

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