Switching of Stereochemistry. Dramatic Effect of HMPA on the Stereoselectivity of the Cyclopropanation Reaction of Telluronium Allylides with α,β-Unsaturated Esters and Amides

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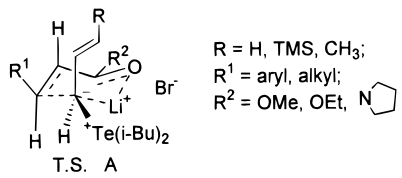
Introduction

The vinylcyclopropane is an ubiquitous structural element of a variety of biologically active compounds,[1] notably agrochemicals such as pyrethroids.[2] In addition, vinylcyclopropanes serve as diverse intermediates in organic synthesis.[3] Sequentially, the construction of the vinylcyclopropane enjoys continued development of new methods.[4] In view of the difficulty that can be associated with both the regioselective introduction of the vinyl group and the stereoselective formation of multisubstituted cyclopropane, many synthetic approaches rely on indirect routes.[5] One direct method, involving the reaction of conjugated dienes with carbenes or carbenoids, lacks generality and requires difficult manipulations.[6] Another one—the addition of an activated allylic reagent, such as vinyl-type carbene or carbinoid, to an alkene[7]—is also limited by structural requirements, and only a few examples have appeared in the literature. In our previous publications, we have shown that the telluronium allylides were readily available and reacted with α,β-unsaturated esters or ketones to provide the vinylcyclopropane derivatives in high yields with high stereoselectivity.[8] With silylated telluronium allylide as a reagent, for example, *trans*-2-((trimethylsilyl)vinyl)-*trans*-3-arylcyclopropyl esters could be synthesized with selectivity as high as >99:1 by ylide cyclopropanation of α,β-unsaturated esters.[8a] Interestingly, in some cases, the stereoselectivity of ylide cyclopropanantions of α,β-unsaturated esters or amides could be controlled by the choice of the base used for the formation of ylide. Thus, either of the two geometrical isomers of a polyfunctionalized 3-vinylcyclopropane could be obtained at will with high stereoselectivity.[8c] The mechanistic reason for this tuning has also been clarified. In brief, when $KN(SiMe_3)_3$ is used as the base, this cyclopropanation reaction is subject to thermodynamic control and *cis*-2-vinyl isomer is the major product. In the presence of lithium salts, however, the reactions maybe proceed via a chelating six-membered ring transition state, which is formed by coordination of lithium ion with carbonyl oxygen and ylidic carbanion simultaneously (Scheme 1). This coordination can change the stereochemical course of the reaction. This mechanistic insight suggested that it is possible to tune the stereoselectivity of such reactions by inhibition of the coordination in situ as shown in Scheme

Scheme 1



T.S. A

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Scheme 2

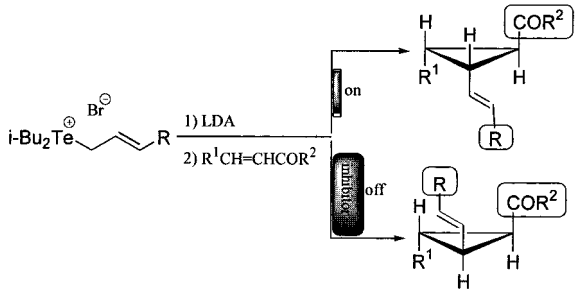
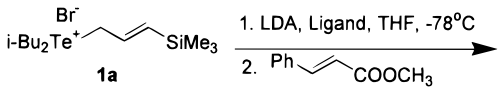
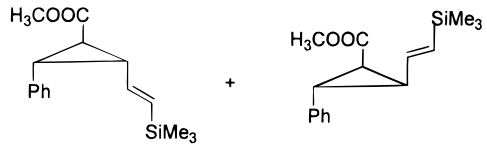


Table 1. Effects of Additives on the Stereochemistry of the Reaction of Ylide 2a with Methyl Cinnamate





4a **5a**

entry	ligand (2 equiv/Li^+)	yield (%)	**4a**:**5a**[a]
1		83	>99:1
2	HMPT	80	>99:1
3	TMEDA	80	>99:1
4	PMDETA	94	85:15
5	HMPA	73	10:90
6	12-crown-4	71	8:92

[a] The ratio of stereoisomers was determined by ^{1}H NMR and/or GC.

2. Herein we reported the full details of our efforts to develop this strategy.

Results and Discussion

Hexamethylphosphoramide (HMPA) is a highly polar, aprotic solvent which coordinates well to the lithium ion. It was reported that this ability of HMPA was approximately 300 times stronger than that of tetrahydrofuran (THF).[9] HMPA is frequently used to accelerate organolithium reactions. More notable are the instances where it has been used to alter the course of selectivity, such as the regioselectivity of additions to α,*β*-unsaturated carbonyl compounds.[10] HMPA was chosen as the first additive because it is supposed to inhibit the formation of lithium-mediated transition state in situ by its strong coordinating ability with lithium ion. As expected, silylated telluronium allylide **2a**, which was generated in situ from the corresponding telluronium salt **1a** and LDA, reacted with methyl cinnamate **3a** to afford *trans*-2-vinyl-*trans*-3-substituted cyclopropyl ester **4a** in high yield with high selectivity in the absence of HMPA. The same reaction provided *cis*-2-vinyl-*trans*-3-substituted cyclopropyl ester **5a** in the presence of HMPA (Table 1). The ability of hexamethylphosphorous triamide (HMPT), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*′-pentamethyldiethylenetriamine (PMDETA) and 12-crown-4 to affect the stereochemical course were also studied. Some results are shown in Table 1. From entries 2−4 in Table 1, it can be seen that HMPT, TMEDA, and PMDETA could not alter the stereochemical course probably due to their weaker coordination with lithium ion than that of HMPA. As expected, both HMPA and 12-crown-4 could switch the stereoselectivity of this reaction.

Table 2. Effects of the Amount of HMPA on the Cyclopropanation

entry	HMPA (equiv)	yield (%)	**4a**:**5a**[a]
1[b]	2.0	73	10:90
2	0.5	83	93:7
3	1.0	82	78:22
4	2.0	78	8:92
5	3.0	81	8:92
6	4.0	80	8:92
7	6.0	71	8:92
8	10.0	56	2:98
9	20.0	44	2:98

[a] The ratio of stereoisomers was determined by ^{1}H NMR. [b] HMPA was added after formation of the ylide. As for the other entries, the telluronium salt was deprotonated by the mixture LDA and HMPA.

Further studies showed that the amount of HMPA used in this reaction also influenced the stereoselectivity and the yield (Table 2). The stereochemical course did not change when 0.5 equiv of HMPA was used. In this case, the ratio of isomer **4a** and **5a** is 93:7 (entry 2 in Table 2), which was almost the same as that of free HMPA (entry 1 in Table 1). However, the ratio of isomer **4a** and **5a** was tuned from 99:1 to 2:98 when 10 equiv of HMPA was added into the reaction system although the yield decreased (entry 8 in Table 2). It was also found that the stereoselectivity is almost independent of addition sequence of reactants. When two different addition sequences were used, similar selectivities were achieved (entries 1 and 4 in Table 2). Accordingly, the most efficient and suitable additive for tuning the stereochemistry is HMPA (2 equiv) considering the high cost of 12-crown-4.

The generality of this tuning reaction was established by investigating a variety of α,*β*- unsaturated carbonyl compounds as substrates. As shown in Table 3, when either *β*-aryl-substituted or *β*-alkyl-substituted α,*β*-unsaturated esters or amides were used, these reactions proceeded smoothly. HMPA, like a switch of stereochemistry, could play a crucial role to tune the stereoselectivity of these cyclopropanations. Moreover, the unsubstituted allylide could give the similar stereochemistry although the yield was low in the presence of HMPA (entry 16 in Table 3).

The mechanism for this reaction of telluronium allylide with α,*β*-unsaturated esters or amides in the absence of HMPA, like our previous report, is outlined in Scheme 3. A possible mechanism could be envisioned to proceed via a chelating six-membered ring transition state, which is formed by coordination of lithium ion with carbonyl oxygen and ylidic carbanion simultaneously. Transition state A might be anticipated to be more stable than transition state B because the Te(i-Bu)$_2$ group is much bulkier than the vinyl one. Thus, the formation of intermediate **6** in the initial condensation is favored over that of intermediate **7**. Following elimination leads to compound **4** as the major product. In the presence of HMPA (Scheme 4), however, HMPA might block the formation of the six-membered ring transition state

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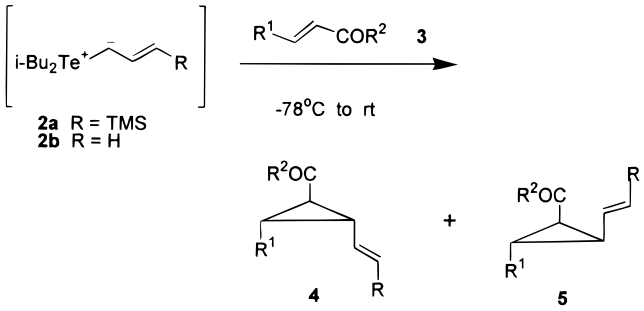
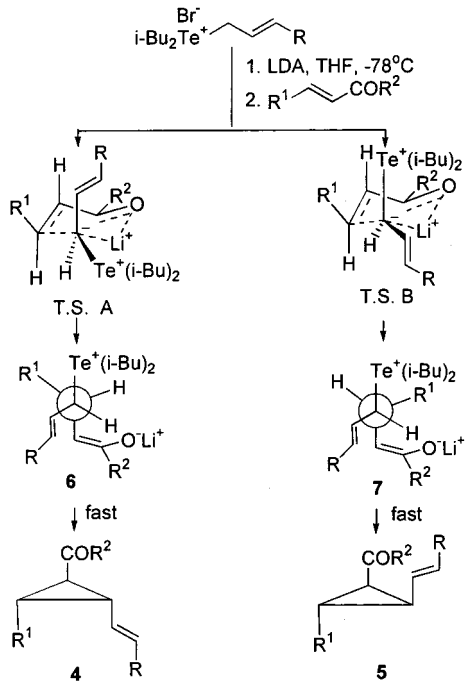
Table 3. Stereochemical Tuning of the Reaction of Telluronium Ylides 2 with α,β-Unsaturated Esters and Amides



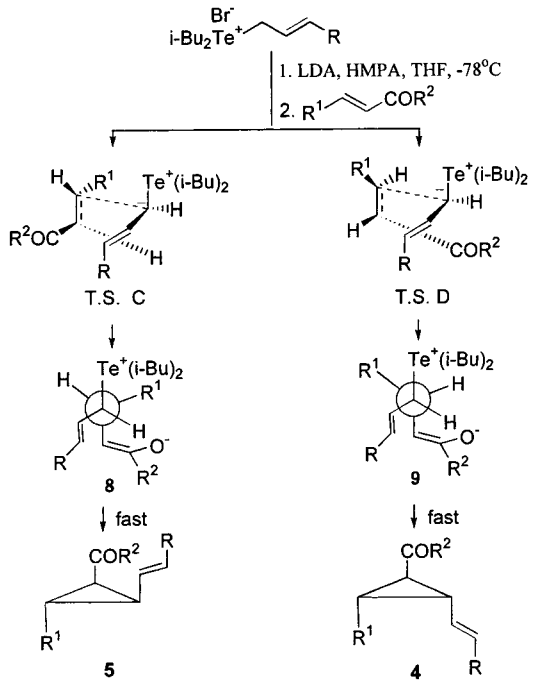
entry	2	3	R1	R2	HMPA/ LDA	yield (%)	4:5
1	2a	3a	Ph	OCH_3		83	>99:1
2	2a	3a	Ph	OCH_3	3.0	81	8:92
3	2a	3b	*p*-FC_6H_4	OCH_3		76	>99:1
4	2a	3b	*p*-FC_6H_4	OCH_3	3.0	78	7:93
5	2a	3c	*p*-$CH_3C_6H_4$	OCH_3		84	99:1
6	2a	3c	*p*-$CH_3C_6H_4$	OCH_3	3.0	73	9:91
7	2a	3d	*p*-$CH_3OC_6H_4$	OCH_3		84	>99:1
8	2a	3d	*p*-$CH_3OC_6H_4$	OCH_3	3.0	80	10:90
9	2a	3e	*o*-$CH_3OC_6H_4$	OCH_3		71	92:8
10	2a	3e	*o*-$CH_3OC_6H_4$	OCH_3	3.0	69	7:93
11	2a	3f	Ph	N		78	>99:1
12	2a	3f	Ph	N	3.0	64	<1:99
13	2a	3g	CH_3	N		78	>95:5
14	2a	3g	CH_3	N	3.0	46	8:92
15	2b	3h	Ph	OCH_3		75	98:2
16	2b	3h	Ph	OCH_3	3.0	24	10:90

Scheme 3



because of its strong ability of coordination with lithium ion. The mechanistic pathway, in this case, is similar to the well-accepted mechanism for some arsonium and sulfonium ylide cyclopropantion.[11] The ylide reacted with α,β-unsaturated carbonyl compound to form intermediates **8** and **9**. Intermediate **8** is more stable than **9** because all the sterically demanding groups are at one side in intermediate **9**. Therefore, this reaction affords compound **5** as a major product.

Scheme 4



Conclusions

The switch-like method for the stereocontrol of ylide cyclopropanation described in this paper provides a facile means for the synthesis of the two geometrical isomers of a multifunctionalized 3-vinylcyclopropane derivatives. These derivatives can undergo many chemical transformation and are useful in organic synthesis.[3] We have, therefore, developed another path for tuning the stereoselectivity in the cyclopropanation reaction of ylides with a Michael acceptor. This method is comparable with the tuning of stereochemical course by the choice of base in the reaction of some semistablized telluronium ylides with α,β-unsaturated esters or amides.[8c] Asymmetric ylide cyclopropanation reactions are now in progress in our laboratory.

Experimental Section

All reaction flasks and equipment were dried for several hours prior to use and all reactions were carried out under argon. THF was dried by distillation over sodium−benzophenone ketyl. The reagents and starting materials were purchased from commercial sources and used directly.

General Procedure. Method A. To a solution of telluronium salt (457 mg, 1.05 mmol) in THF was added LDA (1.05 mmol, made from diisopropylamine and *n*-butyllithium) at −78 °C. After 5 min of stirring, α,β-unsaturated ester or amide (0.70 mmol) in THF (2.0 mL) was added. The resulting solution was stirred for 4 h at −78 °C and then warmed to room temperature. 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 thin-layer chromatography.

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Method B is similar to method A, except the mixture of LDA and HMPA was used instead of LDA in method A.

***trans*-2-Phenyl-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (4a).**[8c] Method A: yield 83%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.4−7.3 (m, 5H), 6.00 (d, J = 18.5 Hz, 1H), 5.42 (dd, J = 8.72, 18.5 Hz, 1H), 3.85 (s, 3H), 3.06 (dd, J = 5.4, 9.6 Hz, 1H), 2.54−2.6 (m, 1H), 2.34 (t, J = 4.9 Hz, 1H), 0.02 (s, 9H).

***trans*-2-Phenyl-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (5a).**[8c] Method B: yield 81%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.4−7.2 (m, 5H), 6.3−6.1 (m, 1H), 6.01 (d, J = 18.6 Hz, 1H), 3.80 (s, 3H), 2.87 (t, J = 5.9 Hz, 1H), 2.4−2.36 (m, 2H), 0.14 (s, 9H).

***trans*-2-(4-Fluorophenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (4b).** Method A: yield 76%; IR (film) ν/cm^{-1} 2954 (s), 1731 (vs), 1609 (m), 1442 (s), 1247 (s), 1172 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.45−7.40 (m, 2H), 7.26−7.20 (m, 2H), 6.18 (d, J = 18.5 Hz, 1H), 5.51 (dd, J = 8.7, 18.5 Hz, 1H), 4.0 (s, 3H), 3.16 (dd, J = 5.28, 9.46 Hz, 1H), 2.74−2.67 (m, 1H), 2.44 (t, J = 4.83, 1H), 0.18 (s, 9H); MS (EI, *m*/z, rel intensity) 292 (M$^+$, 1.02), 188 (47.22), 160 (58.74), 73 (100). Anal. Calcd for $C_{16}H_{21}FO_2Si$: C, 65.72; H, 7.24. Found: C, 65.95; H, 7.54.

***trans*-2-(4-Fluorophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (5b).** Method B: yield 78%; mp 82−84 °C; IR (KBr) ν/cm^{-1} 2954 (m), 1729 (vs), 1607 (m), 1514 (vs), 1170 (vs); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.32−7.10 (m, 2H), 7.1−7. 0 (m, 2H), 6.22−6.09 (m, 1H), 5.99 (d, J = 18.6 Hz, 1H), 3.78 (s, 3H), 2.84 (t, J = 5.89 Hz, 1H), 2.35−2.22 (m, 2H), 0.12 (s, 9H); MS (EI, *m*/z, rel intensity) 292 (M$^+$, 1.56), 188 (38.74), 160 (61.15), 73 (100). Anal. Calcd. for $C_{16}H_{21}FO_2Si$: C, 65.72; H, 7.24. Found: C, 66.05; H, 7.52.

***trans*-2-(4-Methylphenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (4c).** Method A: yield 84%; IR (film) ν/cm^{-1} 2953 (s), 1731 (vs), 1611 (s), 1440 (s), 1274 (s) 1169 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.14 (s, 4H), 5.94 (d, J = 18.5 Hz, 1H), 5.40 (dd, J = 8.8, 18.5 Hz, 1H), 3.79 (s, 3H), 2.96 (dd, J = 5.35, 9.6 Hz, 1H), 2.54−2.46 (m, 1H), 2.38 (s, 3H), 2.25 (t, J = 5.26 Hz, 1H), 0.0 (s, 9H); MS (EI, *m*/z, rel intensity) 288 (M$^+$, 1.16), 184 (27.03), 156 (27.85), 73 (100). Anal. Calcd for $C_{27}H_{24}O_2Si$: C, 70.79; H, 8.38. Found: C, 71.02; H, 8.46.

***trans*-2-(4-Methylphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (5c).** Method B: yield 73%; mp 79−81 °C; IR (KBr) ν/cm^{-1} 2954 (s), 1729 (vs), 1611 (s), 1444 (s), 1357 (s) 1248 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.16 (d, J = 7.53 Hz, 2H), 7.07 (d, J = 8.06 Hz, 2H), 6.24−6.11 (m, 1H), 5.98 (d, J = 18.5 Hz, 1H), 3.76 (s, 3H), 2.83 (t, J = 5.95 Hz, 1H), 2.37 (s, 3H), 2.35−2.31 (m, 2H) 0.09 (s, 9H); MS (EI, *m*/z, rel intensity) 288 (M$^+$, 1.82), 257 (5.94), 184 (31.23), 156 (63.3), 73 (100). Anal. Calcd for $C_{27}H_{24}O_2Si$: C, 70.79; H, 8.38. Found: C, 70.93; H, 8.53.

***trans*-2-(4-Methoxyphenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (4d).** Method A: yield 84%; IR (film) ν/cm^{-1} 2952 (vs), 1730 (vs), 1613 (s), 1515 (s), 1441 (s) 1297 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.20 (d, J = 8.31 Hz, 2H), 6.88 (d, J = 8.75 Hz, 2H), 5.95 (d, J = 18.5 Hz, 1H), 5.38 (dd, 8.8, J = 18.6 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.95 (dd, J = 5.29, 9.5 Hz, 1H), 2.49 (dt, J = 4.5, 8.9 Hz, 1H), 2.22 (t, J = 5.19 Hz, 1H), 0.0 (s, 9H); MS (EI, *m*/z, rel intensity) 412 (M$^+$, 14.4), 169 (100), 141 (19), 77 (13). Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.07; H, 7.94. Found: C, 67.23; H, 8.19.

***trans*-2-(4-Methoxyphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (5d).** Method B: yield 80%; mp 98−100 °C; IR (KBr) ν/cm^{-1} 2953 (m), 1728 (vs), 1613 (m), 1517 (s), 1444 (s) 1248 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.07 (d, J = 8.63 Hz, 2H), 6.85 (d, J = 8.63 Hz, 2H), 6.07−6.21 (m, 1H), 5.94 (d, J = 18.5 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.78 (t, J = 5.94 Hz, 1H), 2.3−2.17 (m, 2 H), 0.09 (s, 9H); MS (EI, *m*/z, rel intensity) 304 (M$^+$, 2.19), 200 (34.02), 172 (53.76), 73 (100). Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.07; H, 7.94. Found: C, 67.10; H, 8.04.

***trans*-2-(2-Methoxyphenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (4e).** Method A: yield 71%; IR (film) ν/cm^{-1} 2953 (vs), 1731 (vs), 1611 (s), 1496 (s), 1440 (s) 1248 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.31−7.28 (m, 1H), 7.21−7.18 (m, 1H), 6.99−6.91 (m, 2H), 5.90 (d, J = 18.5 Hz, 1H), 5.39 (dd, J = 8.6, 18.5 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.02 (dd, J = 5.6, 9.6 Hz, 1H), 2.64−2.56 (m, 1H), 2.29 (dd, J = 4.5, 5.5 Hz, 1H), 0.01 (s, 9H); MS (EI, *m*/z, rel intensity) 304 (M$^+$, 1.25), 200 (14.28), 157 (17.04), 73 (100). Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.07; H, 7.94. Found: C, 67.37; H, 8.11.

***trans*-2-(2-Methoxyphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (5e).** Method B: yield 69%; mp 83−85 °C; IR (KBr) ν/cm^{-1} 2953 (vs), 1722 (vs), 1600 (s), 1499 (s), 1438 (s) 1248 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.4−7.2 (m, 1H), 7.0−6.9 (m, 3H), 6.27 (dd, J = 8.2, 18.5 Hz, 1H), 6.03 (d, J = 18.5 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.12 (t, J = 6.2 Hz, 1H), 2.4−2.3 (m, 2H), 0.15 (s, 9H); MS (EI, *m*/z, rel intensity) 304 (M$^+$, 1.23), 200 (32.18), 157 (16.7), 73 (100). Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.07; H, 7.94. Found: C, 67.46; H, 7.97.

***trans*-2-Phenyl-*trans*-3-((trimethylsilyl)vinyl)-1-((1-pyrrolidinyl)carbonyl)cyclopropane (4f).** Method A: yield 78%; mp 116−118 °C; IR (KBr) ν/cm^{-1} 2948 (s), 1623 (vs), 1452 (s), 1396 (m), 985 (m); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.38−7.25 (m, 5H), 5.94 (d, J = 18.5 Hz, 1H), 5.48 (dd, J = 8.9, 18.5 Hz, 1H), 3.78 (br, 2H), 3.6 (br, 2H), 3.05 (dd, J = 5.4, 9.4 Hz, 1H), 2.59 (dt, J = 4.6, 8.5 Hz, 1H), 2.33 (t, J = 4.6 Hz, 1H), 2.12−2.05 (m, 2H), 2.1−2.0 (m, 2H), 0.01 (s, 9H); MS (EI, *m*/z, rel intensity) 313 (M$^+$, 2.61), 298 (4.31), 222 (13.23), 98 (100). Anal. Calcd for $C_{19}H_{27}NOSi$: C, 72.79; H, 8.68, N 4.47. Found: C, 72.76; H, 8.59, N 4.39.

***trans*-2-Phenyl-*cis*-3-((trimethylsilyl)vinyl)-1-((1-pyrrolidinyl)carbonyl)cyclopropane (5f).** Method B: yield 64%; mp 72−74 °C; IR (KBr) ν/cm^{-1} 2951 (m), 1632 (vs), 1447 (s), 1246 (m), 856 (s); ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.23−7.06 (m, 5H), 5.96 (dd, J = 6.8, 18.5 Hz, 1H), 5.80 (d, J = 18.6 Hz, 1H), 3.57−3.40 (m, 4H), 2.85 (t, J = 5.7 Hz, 1H), 2.24−2.14 (m, 2H), 1.95−1.75 (m, 4H), 0.01 (s, 9H); MS (EI, *m*/z, rel intensity) 313 (M$^+$, 3.0), 293 (6.25), 222 (20.1), 98 (100). Anal. Calcd for $C_{19}H_{27}NOSi$: C, 72.79; H, 8.68, N 4.47. Found: C, 72.76; H, 8.62, N 4.44.

***trans*-2-Methyl-*trans*-3-((trimethylsilyl)vinyl)-1-((1-pyrrolidinyl)carbonyl)cyclopropane (4 g).** Method A: yield 78%; IR (film) ν/cm^{-1} 1632 (s), 1465 (m), 1249 (m), 854 (s); ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 5.88−5.73 (m, 2H), 3.59 (dt, J = 1.6, 7.0 Hz, 2H), 3.45 (t, J = 6.7 Hz, 2H), 2.18−2.14 (m, 1H), 1.99−1.94 (m, 2H), 1.89−1.83 (m, 2H), 1.75−1.60 (m, 1H), 1.50 (t, J = 4.7 Hz, 1H), 1.14 (d, J = 6.5 Hz, 3H), 0.05 (s, 9H).

***trans*-2-Methyl-*cis*-3-((trimethylsilyl)vinyl)-1-((1-pyrrolidinyl)carbonyl)cyclopropane (5g).** Method B: yield 46%; IR (film) ν/cm^{-1} 1630 (s), 1435 (s), 1238 (s), 840 (m); ^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ 5.78 (br, 2H), 3.53−3.40 (m, 4H), 1.97−1.67 (m, 5H), 1.65 (br, 2H), 1.12 (d, J = 6 Hz, 3H), 0.01 (s, 9H).

***trans*-2-Phenyl-*trans*-3-vinyl-1-(methoxycarbonyl)cyclopropane (4h).**[8c] Method A: yield 75%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.32−7.19 (m, 5H), 5.30−5.0 (m, 3H), 3.74 (s, 3H), 2.94 (dd, J = 5.4, 9.6 Hz, 1H), 2.43 (m, 1H), 2.20 (t, J = 5.0 Hz, 1H).

***trans*-2-Phenyl-*cis*-3-vinyl-1-(methoxycarbonyl)cyclopropane (5h).**[8c] Method B: yield 24%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS) δ 7.32−7.0 (m, 5H), 6.03−5.91 (m, 1H), 5.29 (dd, J = 1.4, 17 Hz, 1H) 5.12 (dd, J =1.5, 10 Hz, 1H), 3.72 (s, 1H) 2.76 (t, J = 5.9 Hz, 1H). 2.33−2.20 (m, 2H).

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