An Efficient Stereocontrolled Strategy in the Cyclopropanation Reactions of α,β-Unsaturated Ketones with Semistabilized Ylides: Highly Selective Synthesis of Two Geometrical Isomers of Vinyl-Substituted Cyclopropane Derivatives

Yong Tang, Yao-Zeng Huang,* Li-Xin Dai,* Jie Sun, and Wei Xia

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

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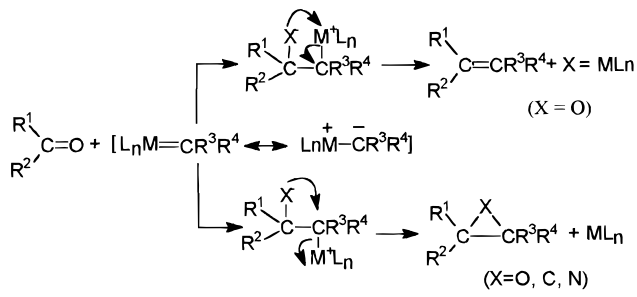
The semistabilized telluronium ylides **2a**−**e**, generated *in situ* from the corresponding telluronium salts **1a**−**e**, reacted with α,β-unsaturated ketones **6a**−**d** to afford *cis*-2-vinyl-*trans*-3-substituted cyclopropyl ketones with high stereoselectivity and in high to excellent yields. Conversely, these enones gave *trans*-2-vinyl-*trans*-3-substituted cyclopropyl ketones, when the corresponding arsonium ylides **10a**−**e** were employed. Other factors such as solvent and amount of base also influenced the stereochemistry of this reaction. A mechanistic rationale is discussed briefly.

The birth of the Wittig reaction[1] marked the entry of ylides into the arsenal of important synthetic tools. Ylides,[2] because of their effectiveness and generality, have not only become one of the most useful reagents in constructing carbon−carbon double bonds,[3] but also has been used in constructing small ring compounds such as epoxides,[4] cyclopropanes,[5] and aziridines[6] in some cases (Scheme 1). Compared to olefination, less attention has been directed toward constructing compounds with three-membered ring *via* an ylide route.

Because of the structure, an ylide can be regarded as a good nucleophile which also possesses a potential leaving group. Thus, ylides should be useful reagents for the preparation of small ring compounds by the proper choice of the heteroatom, the ligand of the ylide, as well as the reaction conditions. This concept, together with the importance of epoxides,[7] cyclopropanes,[8] and aziridines,[9] stimulated our interest in developing synthetic methods for these kinds of compounds *via* the ylide route, particularly in controlling the stereochemical path of these reactions.

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

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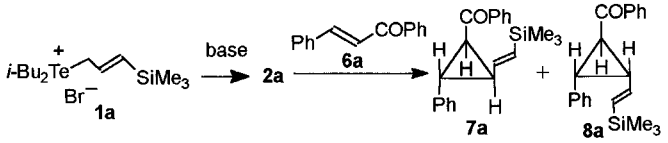
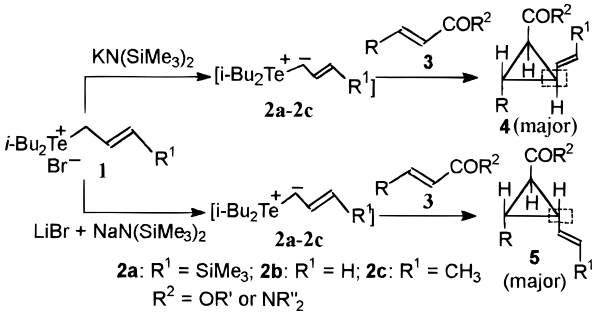
Table 1. Reaction of Silylated Telluronium Allylide (generated from 1a) with Chalcone under Different Conditions



entry	substrate	base and solvent [a]	ratio (**7**/**8**) [b]	yield (%) [c]
1	**6a**	LiBr + $NaN(SiMe_3)_2$, THF	90/10 (**7a**/**8a**)	53 [d]
2	**6a**	KDA, THF	92/8 (**7a**/**8a**)	70
3	**6a**	LTMP, THF	92/8 (**7a**/**8a**)	50 [d]
4	**6a** + Ph⁄⁄COOMe	$KN(SiMe_3)_2$, THF	96/4 (**7a**/**8a**)	78 [e]
5	**6a**	$KOBu^t$, THF	90/10 (**7a**/**8a**)	89
6	**6a**	$NaN(SiMe_3)_2$, THF	92/8 (**7a**/**8a**)	94
7	**6a**	$KN(SiMe_3)_2$, THF	>94/6 (**7a**/**8a**)	92

[a] 1 equiv. of base was used in all reactions. [b] The configuration and the ratio of stereoisomers was determined by 300 MHz ^{1}H NMR. [c] Isolated yields based on moles of substrates used. [d] About a 30% yield of epoxide was obtained. [e] No **5a** (see Scheme 2) was isolated and 15% of chalcone was recovered.

Scheme 2



In our previous publications, we have shown that some semistabilized telluronium ylides reacted readily with aldehydes and ketones to afford vinyl-substituted epoxides with *cis*-stereoselectivity.[10] This stereoselectivity was completely different from that of the corresponding sulfonium and arsonium ylides, which often gave *trans*-epoxides in the similar reactions.[4] We have also documented that silylated telluronium allylide was a good reagent for the synthesis of vinyl-subsituted cyclopropane derivatives.[11] Recently, we found that the stereoselectivity of the reaction of telluronium allylide, silylated allylide, and crotonylide with α,β-unsaturated esters and amides could be tuned by the choice of base.[12] Thus, an efficient method was developed for obtaining either of the two geometrical isomers of a polyfunctionalized vinylcyclopropane with high stereoselectivity (Scheme 2). However, the stereochemical tuning of the same reaction failed when the substrate was an α,β-unsaturated ketone. In this paper, we report another convenient and efficient method to control the stereoselectivity of the reaction of α,β-unsaturated ketones with semistabilized telluronium and arsonium ylides.

Results and Discussion

Stereochemical Control of the Reaction of Allylic Arsonium and Telluronium Ylides with α,β-Unsaturated Ketones. Contrary to the results obtained in the reaction of ylides **2a**−**c** with α,β-unsaturated esters and amides (Scheme 2), we found that the tuning of the stereochemistry failed in the cyclopropanation reaction of ylide **2a** with α,β-unsaturated ketones by simply choosing the base in the preparation of the ylide. The stereochemistry of this reaction was almost independent of added lithium salts (entries 1 *vs* 6 in Table 1). Moreover, the presence of a lithium salt reduced the yield significantly, and the product from the reaction of the ylide **2a** with chalcone **6a** was complex because of the formation of epoxides (entries 1 and 3 in Table 1). For all cases in Table 1, the major product is **7a**, in which the (trimethylsilyl)vinyl group and carbonyl group are *cis* to each other and *trans* to the phenyl group.

As shown in Table 1, although the selectivity is very high for the *cis*-isomer **7a**, we were unable to direct the reaction to product **8a** with a high *trans* ratio. In order to obtain the *trans* isomer **8a** exclusively, we tried to change the heteroatom of the ylide. From our previous experience, we found that the stereochemistry in the reaction of allylic arsonium ylides with methyl cinnamate was independent of the reaction medium and only one isomer, whose configuration is similar to that of compound **8a**,[13] was obtained. Thus, we decided to try the reaction of an arsonium ylide with α,β-unsaturated ketones in hopes of obtaining isomer **8a**. In fact, isomers **8a**−**i** were obtained in high yields with high stereoselectivity when the arsonium ylides **10a**−**e**, generated

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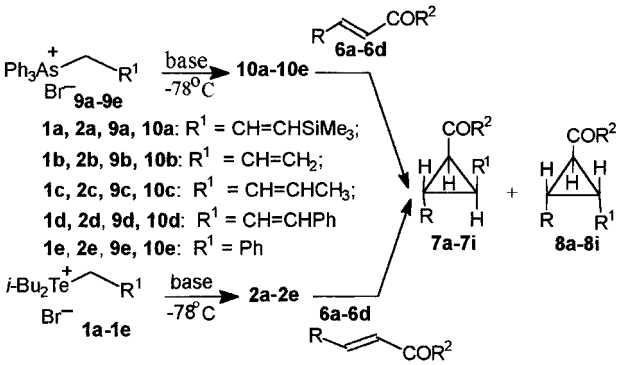
Table 2. Stereocontrolled Reactions of Enones 6 with Allylic Arsonium and Telluronium Ylides 10 and 2



entry	ylide	substrate	base and solvent[a]	ratio (**7**/**8**)[b]	yield (%)[c]
1	**2a**	**6a**	$KN(SiMe_3)_2$, THF	>94/6 (**7a**/**8a**)	92
2	**10a**	**6a**	LiBr + KOBu^t, THF	<1/99 (**7a**/**8a**)	94
3	**2a**	R = *p*-$CH_3C_6H_4$; R^2 = Ph (**6b**)	$KN(SiMe_3)_2$, THF	97/3 (**7b**/**8b**)	92
4	**10a**	*d*	LiBr + KOBu^t, THF	<1/99 (**7b**/**8b**)	84
5	**2a**	R = *p*-ClC_6H_4; R^2 = Ph (**6c**)	$KN(SiMe_3)_2$, THF	96/4 (**7c**/**8c**)	90
6	**10a**	*d*	LiBr + KOBu^t, THF	<1/99 (**7c**/**8c**)	85
7	**2a**	R = *p*-ClC_6H_4; R^2 = Bu^t (**6d**)	$KN(SiMe_3)_2$, THF	>99/1 (**7d**/**8d**)	80
8	**10a**	*d*	LiBr + KOBu^t, THF	<1/99 (**7d**/**8d**)	91
9	**2b**	**6a**	KOBu^t, THF	>99/1 (**7e**/**8e**)	92
11	**10b**	**6a**	LiBr + KOBu^t, THF	14/86 (**7e**/**8e**)	93
12	**10b**	**6a**	KOBu^t, THF	6:94 (**7e**/**8e**)	84
13	**2b**	**6d**	KOBu^t, THF	98/2 (**7f**/**8f**)	92
14	**10b**	**6d**	LiBr + KOBu^t, THF	4/96 (**7f**/**8f**)	86
15	**2c**	**6d**	$KN(SiMe_3)_2$, THF	85:15 (**7g**/**8g**)	91
16	**10c**	**6d**	$KN(NSiMe_3)_2$, THF	13/87 (**7g**/**8g**)	85
17	**10c**	**6d**	LiBr, KOBu^t, toluene	10/90 (**7g**/**8g**)	83
18	**2d**	**6d**	$KN(SiMe_3)_2$, THF	92:8 (**7h**/**8h**)	90
19	**10d**	**6d**	LiBr + $NaN(SiMe_3)_2$, THF	4:94 (**7h**/**8h**)	83
20	**2e**	**6d**	$KN(SiMe_3)_2$, THF	98:2 (**7i**/**8i**)	90
22	**10e**	**6d**	LiBr + $NaN(SiMe_3)_2$, THF	10:90 (**7i**/**8i**)	84
23	**2a**	**6a**	$KN(SiMe_3)_2$(2 eq), THF	55:45 (**7a**/**8a**)	29
24	**10a**	**6a**	$NaN(SiMe_3)_2$(2 eq), THF	<1:99 (**7a**/**8a**)	81

[a] 1 equiv of base was used except as mentioned. [b] The configuration and the ratio of stereoisomers were determined by 300 MHz ^{1}H NMR. [c] Isolated yields based on moles of substrates used. [d] Same as above.

from the corresponding salts **9a**−**e** *in situ*, were used instead of the corresponding telluronium ylides **2a**−**e**. Thus, we succeeded in obtaining either isomers **7** or **8** with high stereoselectivity by the choice of allylic telluronium or arsonium ylide. Some results are summarized in Table 2. From this table, the following conclusions concerning the ylide cyclopropanation of α,β-unsaturated ketones may be drawn:

1. Allylic telluronium ylides **2a**−**e** react smoothly with α,β-unsaturated ketones to give *cis*-vinylcyclopropyl ketone derivatives **7** in high yields.

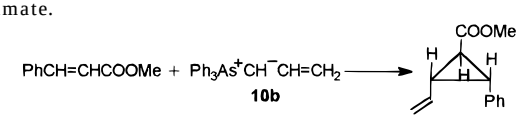
2. Like the telluronium ylides **2a**−**e**, the allylic arsonium ylides **10a**−**e** also react smoothly with α,β-unsaturated ketones to furnish cyclopropane derivatives in high yields, but with opposite stereochemistry from that of the corresponding telluronium ylides. The *trans*-vinylcyclopropyl ketone derivatives **8** were obtained preferentially.

Further experiments showed that excess $KN(SiMe_3)_2$ also has a detrimental effect on both the yield and stereoselectivity of the reaction between ylide **2a** and the α,β-unsaturated ketone (entry 23 *vs* 1 in Table 2). This result may be rationalized by a proposed mechanism (Scheme 3). Intermediates **A** and **B**, produced by addition of ylide **2a** to chalcone, might further react with the excess $KN(SiMe_3)_2$ to form the ylide anion **C**. This side-reaction stops the intramolecular substitution of **A** and **B** to form the desired product and thus lowers the yield (from 92% to 29%). Equilibration of the originally formed **C** also changed the highly selective reaction to a nonselective one (94:6 to 55:45).

Strong evidence for the proposed mechanism was obtained by using 2 equiv of chalcone with 1 equiv of salt **1a** and 2 equiv of $KN(SiMe_3)_2$. Product **11**, which derives from the further reaction of ylide anion **C** with the extra 1 equiv of chalcone, was isolated in 17% yield (Scheme 3). Therefore, in order to prepare compound **7a** in high yield and high selectivity, limiting the amount of $KN(SiMe_3)_2$ to 1 equiv is crucial. Otherwise, a mixture of **7a** and **8a** will be obtained.

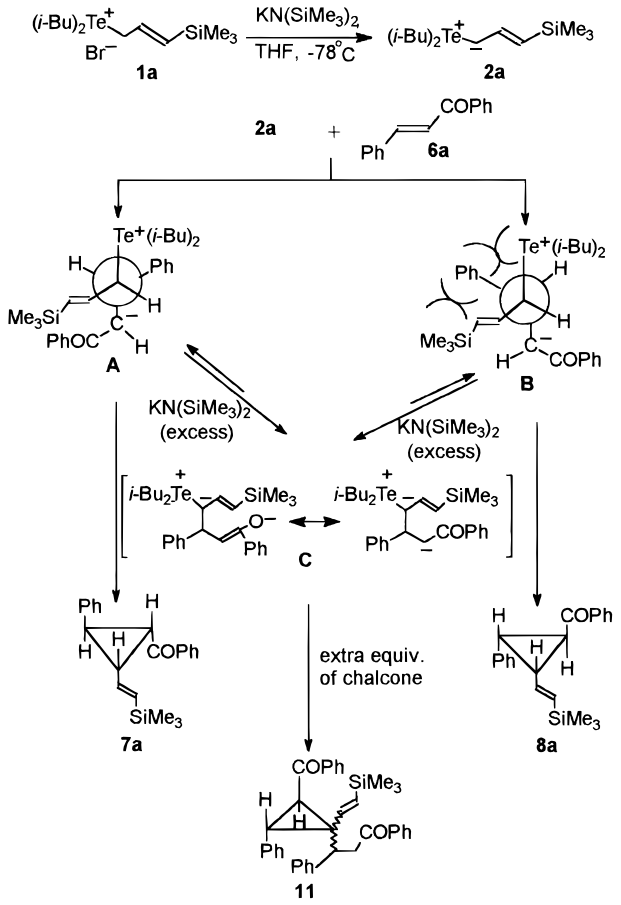
Determination of the Configuration of Cyclopropane Derivatives. The configuration of **7a** was determined by ^{1}H NMR, ^{1}H−^{1}H NOESY, shift reagent, and chemical transformation as detailed in our previous publications.[11b] It was further proved by X-ray diffraction analysis[21] (Supporting Information). In the literature, Shen et al.[14] have shown that proton chemical shifts are strongly influenced by the nature of substituents on the ring of a trisubstituted cyclopropane system; the substituent with higher electronegativity causes a downfield chemical shift. On the basis of this finding, together with

(13) Only *trans*-2-vinyl-*trans*-3-phenyl-1-(methoxycarbonyl)cyclopropane was isolated when allylic arsonium ylide **10b** reacted with methyl cinnamate.

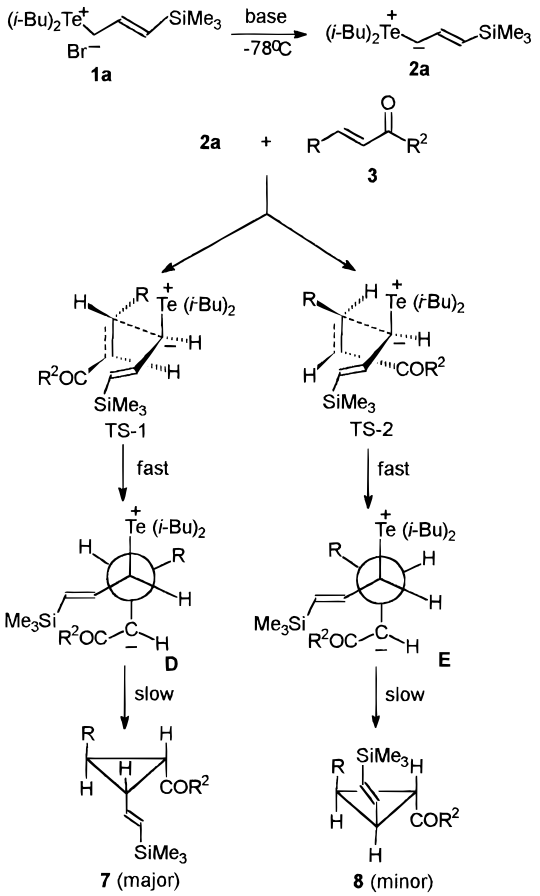


(14) Shen, Y. C.; Huang, Y. Z.; Xin, Y. K.; Xu, G. J. *Acta Chim. Sinica* **1981**, *39*, 243.

Scheme 3



Scheme 4



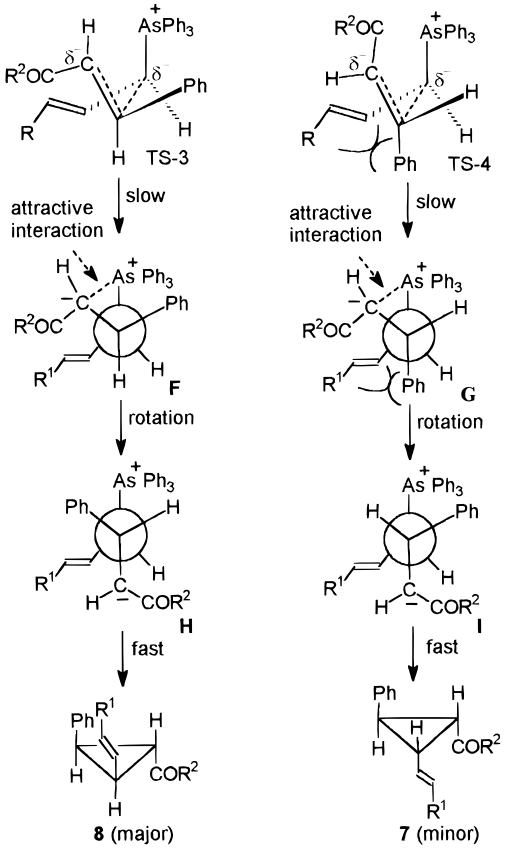
the coupling constants and coupling patterns of **7a** and **8a**, we could assign the configuration of **8a**.

Mechanism

The mechanism for the reaction of telluronium allylide with α,β-unsaturated ketones, which may be similar to the well-accepted mechanism[15] for some arsonium and sulfonium ylide cyclopropanations, is outlined in Schemes 4 and 5. In order to clarify this mechanism, we further examined the reaction, as follows. When chalcone **6a** was used as the reactant and $KN(SiMe_3)_2$ was the base, we found that the color of ylide **2a** faded immediately at −78 °C. Subsequent quenching with water afforded **7a** in 37% yield, which is much lower than that (92% yield) obtained by raising the temperature from −78 °C to room temperature and then quenching (entry 7 in Table 1). Also, chalcone was recovered in 55% yield in the former case. This experiment suggested that the rate-determining step in the reaction of ylide **2a** with α,β-unsaturated ketones is the second step, i.e., the displacement reaction of the telluronium group. If the first step is reversible, there may be time to allow the unstable intermediate **E** to equilibrate with intermediate **D** irrespective of the initial ratio of **D** and **E** during the addition step (Scheme 4). Thus, the product distribution would be determined by the cyclization of **D** *vs* **E** with the former being favored on steric grounds.

With the arsonium ylide **10a**, the addition reaction is irreversible. Both TS-3 and TS-4 benefit from electrostatic attraction, but the former should be preferred on steric grounds. Thus, intermediate **H**, though less stable,

Scheme 5



(15) (a) Bestmann, H. J.; Seng, D.-C. F. *Angew. Chem.* **1962**, *74*, 154. (b) Tsuge, O.; Shinkai, P. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3514. (c) Greenberg, F. H.; Schulman, E. M. *J. Org. Chem.* **1993**, *58*, 5853. (d) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 138.

would be formed in greater amount. This kind of electrostatic attraction would also be present with the Te(Bu-*i*)$_2$ system, but in the Te system, the addition step is a reversible fast step, so the rate-determining step, the cyclization step, would determine the stereochemical outcome of the product. This argument was further supported by the following experiment: When 1 equiv of chalcone was added to the deep-red solution of ylide **10a** at −78 °C, the color of ylide **10a** completely disappeared and we isolated **8a** in 72% yield by subsequent quenching with water. When we allowed the reaction mixture to warm up slowly to room temperature before quenching, the yield of **8a** was 70%. The similar yields obtained under the two conditions showed that the elimination reaction of **H** and **I** in the reaction of ylide **10a** with α,β-unsaturated ketones might be the faster step. So the reaction of arsonium ylide **10a** with α,β-unsaturated ketones affords **8a** as the major product.

Conclusions

We have developed a facile and practical synthetic method for the synthesis of two geometrical isomers of vinylcyclopropyl ketone derivatives with high stereoselectivity. These derivatives can undergo many chemical transformations and are useful in organic synthesis.[16] We have, therefore, provided another path for controlling stereoselectivity in the cyclopropanation reaction of ylides with Michael acceptors, comparable with the tuning of the stereochemical path in the reaction of some semistabilized telluronium ylides with α,β-unsaturated esters and amides.[12] Asymmetric ylide cyclopropanation reactions and applications of this method to organic synthsis are now under investigation in our laboratory.

Experimental Section

All reactions were carried out under N_2. All solvents for the reactions were purified before use. Sodium bis(trimethylsilyl)amide and potassium hydride were purchased from Aldrich and Fluka, respectively, and were used directly without further purification. Potassium bis(trimethylsilyl)-amide,[17] telluronium salts **1a**−**e** and arsonium salts **9a**−**e** were prepared as described in references 18 and 19, respectively.

General Procedures. Condition A: A solution of base (0.75 mmol) in THF (0.75 mL) was added dropwise to a solution of telluronium or arsonium salt (0.75 mmol) + LiBr (0.75 mmol) in 6.5 mL of solvent at −78 °C under N_2. The mixture was stirred for 5 min, and then the α,β-unsaturated compound (0.5 mmol) in solvent (1 mL) was added. The reaction mixture was allowed to warm to room temperature after the reaction was completed. Usual workup and flash chromatography gave the pure product. **Condition B:** Similar to condition A, only there was no lithium salt addition.

1-Benzoyl-*trans*-2-phenyl-*cis*-3-[(trimethylsilyl)vinyl]-cyclopropane (7a).[11b,20] For substrate **6a**, using telluronium salt **1a** and under condition B, 92%. δ (C_6D_6/TMS, 300 MHz) 0.09 (s, 9 H), 2.43 (d of t, *J* = 6.3, 8.9 Hz, 1 H), 2.95 (dd, *J* = 5.7, 8.9 Hz, 1 H), 3.46 (t, *J* = 5.9 Hz, 1 H), 5.95 (d, *J* = 18.6 Hz, 1 H), 6.45 (dd, *J* = 8.9, 18.6 Hz, 1 H), 6.96 (m, 8 H), 7.83 (d, *J* = 7.2 Hz, 2 H).

1-Benzoyl-*trans*-2-phenyl-*trans*-3-[(trimethylsilyl)vinyl]-cyclopropane (8a). For substrate **6a**, using arsonium salt **9a** and under condition A, 94%. δ ($CDCl_3$/TMS, 300 MHz) 0.05 (s, 9 H), 2.75 (m, 1 H), 3.26 (m, 2 H), 5.50 (dd, *J* = 8.9, 18.5 Hz, 1 H), 5.95 (d, *J* = 18.5 Hz, 1 H), 7.30 (m, 5 H), 7.54 (m, 3 H), 8.07 (dd, *J* = 1.6, 8.2 Hz, 2 H); δ (C_6D_6/TMS, 300 MHz) 0.03 (s, 9 H), 2.91 (ddd, *J* = 4.4, 8.8, 9.0 Hz, 1 H), 3.24 (dd, *J* = 4.7, 5.9 Hz, 1 H), 3.36 (dd, *J* = 5.2, 9.3 Hz, 1 H), 5.67 (dd, *J* = 8.8, 18.5 Hz, 1 H), 5.89 (d, *J* = 18.5 Hz, 1 H), 7.10 (m, 8 H), 8.05 (m, 2 H).

1-Benzoyl-*trans*-2-(4-methylphenyl)-*cis*-3-[(trimethylsilyl)vinyl]cyclopropane (7b).[11b,20] For substrate **6b**, using telluronium salt **1a** and under condition B, 92%. δ (C_6D_6/TMS, 300 MHz) 0.07 (s, 9 H), 2.08 (s, 3 H), 2.50 (d of t, *J* = 6.4 Hz, *J* = 8.9 Hz, 1 H), 3.08 (dd, *J* = 5.4 Hz, *J* = 8.9 Hz, 1 H), 3.40 (t, *J* = 5.9 Hz, 1 H), 6.00 (d, *J* = 18.5 Hz, 1 H), 6.53 (dd, *J* = 8.5, 18.5 Hz, 1 H), 7.06 (m, 7 H), 7.91 (d, *J* = 8.2, 2 H).

1-Benzoyl-*trans*-2-(4-methylphenyl)-*trans*-3-[(trimethylsilyl)vinyl]cyclopropane (8b). For substrate **6b**, using arsonium salt **9a** and under condition A, 84%. δ ($CDCl_3$/TMS, 300 MHz) −0.03 (s, 9 H), 2.36 (s, 3 H), 2.70 (m, 1 H), 3.19 (m, 2 H), 5.51 (dd, *J* = 8.5, 18.5 Hz, 1 H), 5.92 (d, *J* = 18.5 Hz, 1 H), 7.13 (m, 4 H), 7.53 (m, 3 H), 8.05 (dd, *J* = 1.6, 8.7 Hz, 2 H).

1-Benzoyl-*trans*-2-(4-chlorophenyl)-*cis*-3-[(trimethylsilyl)vinyl]cyclopropane (7c).[11b,20] For substrate **6c**, using telluronium salt **1a** and under condition B, 90%. δ (C_6D_6/TMS, 300 MHz) 0.04 (s, 9 H), 2.35 (d of t, *J* = 6.3, 8.9 Hz, 1 H), 2.85 (dd, *J* = 5.7, 9.3 Hz, 1 H), 3.15 (t, *J* = 5.9 Hz, 1 H), 5.95 (d, *J* = 18.6 Hz, 1 H), 6.38 (dd, *J* = 8.9, 18.6 Hz, 1 H), 6.55 (d, *J* = 8.7 Hz, 2 H), 7.08 (m, 5 H) and 7.85 (m, 2 H).

1-Benzoyl-*trans*-2-(4-chlorophenyl)-*trans*-3-[(trimethylsilyl)vinyl]cyclopropane (8c). For substrate **6c**, using arsonium salt **9a** and under condition A, 85%. δ ($CDCl_3$/TMS, 300 MHz) 0.04 (s, 9 H), 2.78 (m, 1 H), 3.30 (m, 2 H), 5.55 (d, *J* = 8.5, 18.5 Hz, 1 H), 5.98 (d, *J* = 18.5 Hz, 1 H), 7.30 (m, 4 H), 7.56 (m, 3 H), 8.12 (m, 2 H).

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*cis*-3-[(trimethylsilyl)vinyl]cyclopropane (7d). For substrate **6d**, using telluronium salt **1a** and under condition B, 80%. δ ($CDCl_3$/TMS, 300 MHz) 0.05 (s, 9 H), 1.16 (m, 9 H), 2.34 (m, 1 H), 2.72 (dd, *J* = 5.5, 9.2 Hz, 1 H), 2.91 (dd, *J* = 5.9, 5.9 Hz, 1 H), 5.86 (m, 2 H), 7.04 (d, *J* = 9.0 Hz, 2 H), 7.25 (d, *J* = 9.0 Hz, 2 H); MS *m*/*z* 336 (5), 335 (7), 334 (11), 319 (3), 249 (6), (9), 73 (58), 57 (100), (35), 59 (11). HRMS Calcd for $C_{19}H_{27}$-ClOSi: 334.1558. Found: 334.1539.

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*trans*-3-[(trimethylsilyl)vinyl]cyclopropane (8d). For substrate **6d**, using arsonium salt **9a** and under condition A, 91%. δ ($CDCl_3$/TMS, 300 MHz) 0.02 (s, 9 H), 1.28 (s, 9 H), 2.45 (m, 1 H), 2.74 (dd, *J* = 4.9, 5.0 Hz, 1 H), 2.95 (dd, *J* = 5.4, 9.3 Hz, 1 H), 5.42 (dd, *J* = 8.6, 18.5 Hz, 1 H), 5.93 (d, *J* = 18.5 Hz, 1 H), 7.13 (d, *J* = 8.5 Hz, 2 H), 7.32 (d, *J* = 8.5 Hz, 2H).

1-Benzoyl-*trans*-2-phenyl-*cis*-3-vinylcyclopropane (7e).[11b,20] For substrate **6a**, using telluronium salt **1b** and under condition B, 92%. δ ($CDCl_3$/TMS, 300 MHz) 2.60 (ddd, *J* = 5.7, 8.3, 8.9 Hz, 1 H), 3.19 (dd, *J* = 5.7, 6.2 Hz, 1 H), 3.28 (dd, *J* = 5.5, 8.9 Hz, 1 H), 5.06 (dd, *J* = 1.7, 10.3 Hz, 1 H), 5.30 (dd, *J* = 1.7, 14.6 Hz, 1 H), 5.90 (ddd, *J* = 1.7, 10.3, 14.6 Hz, 1 H), 7.23 (m, 4 H), 7.55 (m, 4 H), 8.02 (m, 2 H).

1-Benzoyl-*trans*-2-phenyl-*trans*-3-vinylcyclopropane (8e). For substrate **6a**, using arsonium salt **9b** and under condition B, 84%. δ ($CDCl_3$/TMS, 300 MHz) 2.60 (m, 1 H), 3.20 (m, 2 H), 5.06 (m, 1 H), 5.34 (m, 2 H), 7.21 (m, 4 H), 7.55 (m, 4 H), 8.05 (m, 2 H).

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*cis*-3-vinylcyclopropane (7f). For substrate **6d**, using telluronium salt **1b** and under condition B, 92%. δ ($CHCl_3$/TMS, 300 MHz) 1.16 (s, 9 H), 2.30 (ddd, *J* = 5.5, 9.1, 9.2 Hz, 1 H), 2.73 (dd, *J*

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= 5.5, 9.2 Hz, 1 H), 2.88 (dd, *J* = 5.5, 5.5 Hz, 1 H), 5.02 (dd, *J* = 1.6, 10.3 Hz, 1 H), 5.22 (dd, *J* = 1.7, 17.0 Hz, 1 H), 5.73 (m, 1 H), 7.03 (dd, *J* = 8.4 Hz, 2 H), 7.23(d, *J* = 8.4 Hz, 2 H); MS *m/z* 263 (1), 205 (2), 177 (14), 142 (26), 141 (24), 115 (13), 57 (100), 43 (1). Anal. Calcd for $C_{16}H_{19}ClO$: C, 73.13; H, 7.29. Found: C, 72.90; H, 7.13.

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*trans*-3-vinylcyclopropane (8f). For substrate **6d**, using arsonium salt **9b** and under condition A, 86%. δ ($CDCl_3$/TMS, 300 MHz) 1.27 (s, 9 H), 2.34 (m, 1 H), 2.64 (dd, *J* = 5.2 Hz, 1 H), 2.88 (dd, *J* = 5.3, 9.4 Hz, 1 H), 5.05 (m, 1 H), 5.25 (m, 2 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H).

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*trans*-3-propenylcyclopropane (7g). For substrate **6d**, using telluronium salt **1c** and under condition B, 91%. δ ($CHCl_3$/TMS, 300 MHz) 1.10 (s, 9 H), 1.57 (dd, *J* = 1.6, 6.3 Hz, 3 H), 2.14 (m, 1 H), 2.55 (dd, *J* = 5.5, 9.1 Hz, 1 H), 2.64 (dd, *J* = 5.9, 6.1 Hz, 1 H), 5.38 (m, 1 H), 5.51 (m, 1 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H); MS *m/z* 276 (1), 219 (2), 191 (51), 165 (33), 141 (14), 85 (19), 57 (100), 43 (2). HRMS Calcd for $C_{17}H_{21}ClO$: 276.1281. Found: 276.1276.

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*trans*-3-propenylcyclopropane (8g). For substrate **6d**, using arsonium salt **9c** and under condition A, 83%. δ ($CHCl_3$/TMS, 300 MHz) 1.15 (s, 9 H), 1.55 (dd, *J* = 1.4, 6.4 Hz, 3 H), 2.25 (ddd, *J* = 4.5, 9.2, 9.2 Hz, 1 H), 2.51 (dd, *J* = 4.8, 5.1 Hz, 1 H), 2.78 (t, *J* = 5.1, 9.2 Hz, 1 H), 4.8 (m, 1 H), 5.67 (m, 1 H), 7.05 (d, *J* = 8.3, 2 H), 7.25 (d, *J* = 8.3 Hz, 2 H).

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*cis*-3-(2-phenylvinyl)cyclopropane (7h). For substrate **6d**, using telluronium salt **1d** and under condition B, 90%. δ (C_6D_6/TMS, 300 MHz) 1.16 (s, 9 H), 2.46 (m, 1 H), 2.84 (dd, *J* = 5.6, 9.1 Hz, 1 H), 2.94 (dd, *J* = 5.8, 6.0 Hz, 1 H), 6.23 (dd, *J* = 9.4, 15.9 Hz, 1 H), 6.60 (d, *J* = 15.9 Hz, 1 H), 7.24 (m, 9 H). MS *m/z* 338 (0.2), 253 (76), 218 (18), 202 (11), 125 (22), 115 (14), 91 (19), 85(12), 57(100). Anal. Calcd for $C_{22}H_{23}ClO$: C, 77.98; H, 6.98. Found: C, 78.12; H, 6.84.

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*trans*-3-(2-phenylvinyl)cyclopropane (8h). For substrate **6d**, using arsonium salt **9d** and under condition A, 83%. δ (C_6D_6/TMS, 300 MHz) 1.24 (s, 9 H), 2.45 (ddd, *J* = 4.9, 9.2, 9.4 Hz, 1 H), 2..67 (dd, *J* = 4.7, 5.4 Hz, 1 H), 2.98 (dd, *J* = 5.4, 9.2 Hz, 1 H), 5.50 (dd, *J* = 9.7, 15.8 Hz, 1 H), 6.57 (d, *J* = 15.8 Hz, 1 H), 7.21 (m, 9 H).

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*cis*-3-phenylcyclopropane (7i). For substrate **6d**, using telluronium salt **1e** and under condition B, 90%. δ (C_6D_6/TMS, 300 MHz) 1.06 (s, 9 H), 2.88 (dd, *J* = 5.3, 9.2 Hz, 1 H), 3.01 (dd, *J* = 7.1, 9.4 Hz, 1 H), 3.30 (dd, *J* = 5.1, 7.0 Hz, 1 H), 7.24 (m, 9 H). MS *m/z* 312 (0.7), 255 (5), 227 (42), 192 (20), 165 (19), 149 (16), 115 (22), 91 (9), 85 (23), 57 (100). Anal. Calcd for $C_{20}H_{21}ClO$: C, 76.78; H, 6.77. Found: C, 76.76; H, 6.96.

1-(*tert*-Butylcarbonyl)-*trans*-2-(4-chlorophenyl)-*trans*-3-phenylcyclopropane (8i). For substrate **6d**, using arsonium salt **9e** and under condition A, 84%. δ ($CDCl_3$/TMS, 300 MHz) 1.35 (s, 9 H), 3.00 (m, 3 H), 7.21 (m, 9 H).

Capture of the Ylide Anion C. A solution of potassium bis(trimethylsilyl)amide (1.2 mmol) in THF (1.2 mL) was added dropwise to a solution of telluronium **1a** (0.6 mmol) in 6 mL of solvent at −78 °C under N_2 and subsequently was added 208 mg of chalcone. The mixture was stirred for 5 min and quenched with 1 mL of water. Usual workup and flash chromatography gave the product **11** with 17% yield. Compound **11**: δ ($CHCl_3$/TMS, 300 MHz) 0.15 (s, 9 H), 3.03 (d, *J* = 6.9 Hz, 1 H), 3.10 (d, *J* = 6.6 Hz, 1 H), 3.61 (dd, *J* = 3.6, 17.8 Hz, 1 H), 3.82 (dd, *J* = 10.10, 17.90 Hz, 1 H), 4.05 (dd, *J* = 3.60, 9.90 Hz, 1 H), 6.27 (d, *J* = 18.50 Hz, 1 H),), 6.44 (dd, *J* = 6.0, 18.5 Hz, 1 H), 7.10−7.60 (m, 18 H), 8.00 (d, *J* = 8.0 Hz, 2 H); MS *m/z* 528 (2), 409 (6), 319 (38), 105 (100), 91 (8), 73 (45), 59 (7). HRMS Calcd for $C_{36}H_{36}O_2Si$: 528.2484. Found: 528.2437.

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Supporting Information Available: Copies of NMR spectra to indicate purity of new compounds (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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