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A method for the synthesis of cyclopropanes by regiospecific and regioselective magnesium carbenoid 1,3-CH insertion as the key reactions

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ABSTRACT

Addition reaction of two geometrical isomers of 1-chlorovinyl *p*-tolyl sulfoxides, derived from unsymmetrical ketones and chloromethyl *p*-tolyl sulfoxide, with lithium enolate of *tert*-butyl acetate gave single diastereomers of the adduct, respectively. Treatment of each diastereomer with *i*-PrMgCl resulted in the formation of magnesium carbenoid. Highly regiospecific 1,3-CH insertion reaction was found to take place from each magnesium carbenoid to afford cyclopropanes. On the other hand, when the unsymmetrical ketones bearing an oxygen- or a nitrogen-functional group on the α-carbon were used in this procedure, the regioselective 1,3-CH insertion reaction proceeded mainly. Stereochemistry of the adducts, reaction mechanism, and essence of the specificity and the selectivity are discussed.

1. Introduction

Cyclopropanes are very important and interesting compounds in organic and synthetic organic chemistry, and innumerable studies have been reported concerning their chemistry, synthesis and synthetic uses.[1] Since the cyclopropane ring is highly strained, ring-opening reactions of cyclopropanes occur under the influence of a variety of chemical reagents under mild conditions with carbon–carbon or carbon–hetero atom bond-formation.[1] These properties are one of the reasons why cyclopropanes are versatile compounds in organic and synthetic organic chemistry.

We also have been interested in the synthesis of cyclopropanes by our original methods.[2] Recently, we found that the treatment of 1-chloroalkyl *p*-tolyl sulfoxides bearing a quaternary carbon at the 2-position with *i*-PrMgCl resulted in the formation of cyclopropanes in high yields via the 1,3-carbon hydrogen (1,3-CH) insertion reaction[3] of the generated magnesium carbenoid intermediates.[4] In continuation of our aforementioned chemistry, as shown in Scheme 1, we recently found that the reaction of adducts **2**, derived from 1-chlorovinyl *p*-tolyl sulfoxides **1** with lithium enolate of *tert*-butyl acetate, with *i*-PrMgCl gave cyclopropanes **4** or **5** via the 1,3-CH insertion reaction of generated magnesium carbenoid intermediates **3** with high regiospecificity.[5] In contrast to this, the reaction of adducts **7**, which were derived from 1-chlorovinyl *p*-tolyl sulfoxides **6** derived from unsymmetrical ketones bearing a heteroatom at the α-position, gave cyclopropanes **9** with high regioselectivity via the regioselective 1,3-CH insertion reaction of magnesium carbenoid intermediates **8**. In this paper we would like to report, in detail, the results described above.

2. Results and discussion

2.1. Synthesis of cyclopropanes by regiospecific magnesium carbenoid 1,3-CH insertion as the key reaction

In our previous work, we investigated the synthesis of cyclopropanes based on the magnesium carbenoid 1,3-CH insertion reaction by the use of 1-chlorovinyl *p*-tolyl sulfoxides derived from symmetrical ketones.[4b,c] As we recognized that the 1,3-CH insertion reaction of magnesium carbenoids is a new and very useful reaction in the synthesis of cyclopropanes, we further investigated this reaction with 1-chlorovinyl *p*-tolyl sulfoxides derived from unsymmetrical ketones. The representative example of this study is shown in Scheme 2.

At first, geometrical isomers *E*-**11** and *Z*-**11** were synthesized from 4-phenyl-2-butanone and chloromethyl *p*-tolyl sulfoxide **10** in three steps in high overall yields.[6b] Vinyl sulfoxide *E*-**11** was treated with lithium enolate of *tert*-butyl acetate in THF at −78 °C to afford adduct **12** in quantitative yield as a single product. The same reaction starting from *Z*-**11** again gave quantitative yield of adduct **15** as a single product. These products **12** and **15** were diastereomers to each other. The configuration of the products, **12** and **15**,

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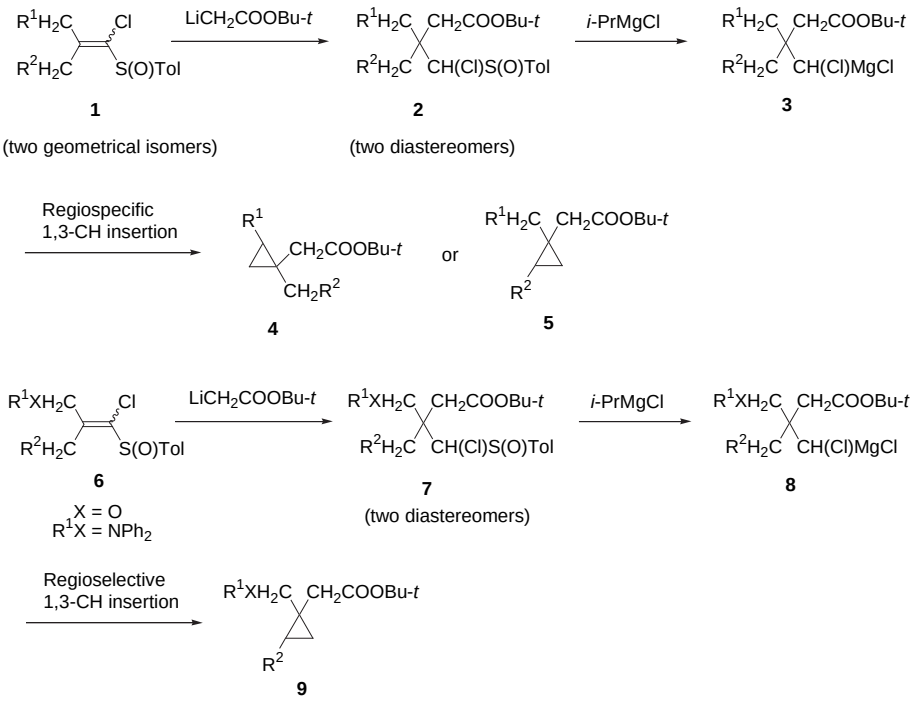
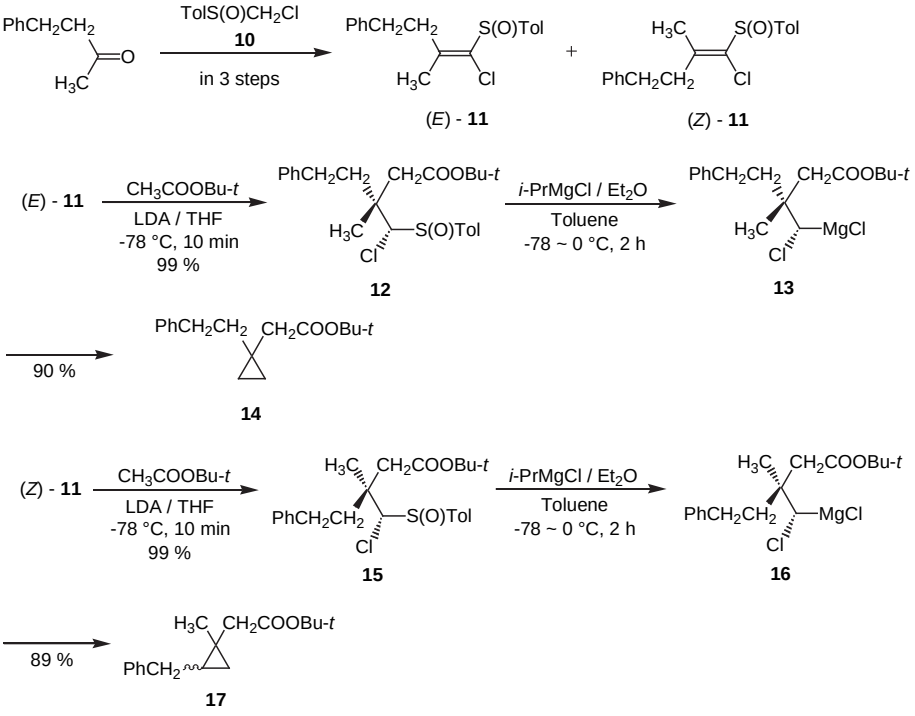


Scheme 1. Regiospecific and regioselective 1,3-CH insertion reactions.



Scheme 2. Regiospecific 1,3-CH insertion reaction.

was determined by X-ray crystallographic analysis of the corresponding carboxylic acids, as reported previously.[5]

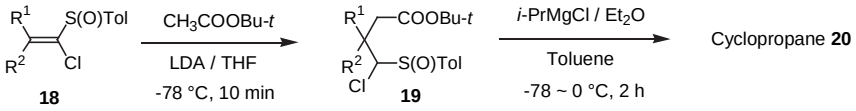
A solution of adduct **12** in THF was added to a solution of *i*-PrMgCl (ether solution; 5 equiv) in toluene at −78 °C and the temperature of the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction mixture was found to be very clean and cyclopropane **14** was obtained in 90% yield as a single product. In this case, the 1,3-CH insertion reaction of the generated magnesium carbenoid intermediate **13** took place between the carbenoid and the methyl carbon to give cyclopropane **14**. The same reaction of adduct **15** with *i*-PrMgCl gave again very clean reaction mixture and, somewhat surprisingly, we obtained cyclopropane **17** as about 10:1 mixture of two diastereomers in 89% yield. In this case, the 1,3-CH insertion reaction of the generated magnesium carbenoid intermediate **16** took place between the carbenoid and the methylene carbon of

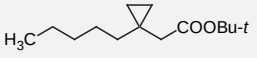
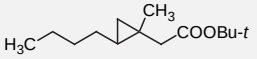
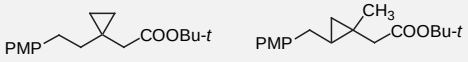
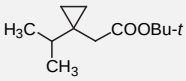
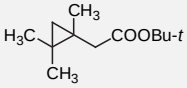
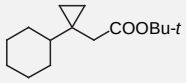
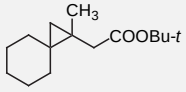
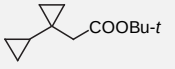
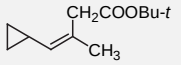
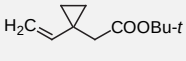
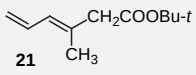
the 2-phenylethyl group to afford cyclopropanes **17**. Namely, the 1,3-CH insertion reaction of the magnesium carbenoid intermediates **13** and **16** gave cyclopropanes **14** and **17**, respectively, with perfect regiospecificity.

In order to investigate the generality, efficiency, and specificity of these reactions, we further studied this procedure starting with several unsymmetrical ketones and the results are summarized in Table 1. 2-Heptanone (entries 1 and 2), 4-(4-methoxyphenyl)-2-butanone (entry 3), 3-methyl-2-butanone (entries 4 and 5), cyclohexyl methyl ketone (entries 6 and 7), cyclopropyl methyl ketone (entries 8 and 9), and methyl vinyl ketone (entries 10 and 11) were selected as the unsymmetrical ketones. 1-Chlorovinyl *p*-tolyl sulfoxides **18** were synthesized from the above-mentioned ketones with chloromethyl *p*-tolyl sulfoxide **10** in three steps in good overall yields.[6] Each geometrical isomer of 1-chlorovinyl *p*-tolyl sulfoxides **18**, except **18c**, was separated and reacted with lithium enolate of *tert*-butyl acetate to give adduct **19** in up to 99% yield as a single diastereomer. As shown in entry 3, the geometrical isomers **18c** could not be separated and were used as a mixture to give adduct **19c** in 95% yield as a mixture of two diastereomers.

Each adduct **19** was treated with 5 equiv of *i*-PrMgCl (ether solution) in toluene to give cyclopropane **20** in good to quantitative yield with perfect regiospecificity. It is worth noting that the 1,3-CH insertion reaction between the carbenoid and the methyl carbon took place in the adducts derived from (*E*)-1-chlorovinyl *p*-tolyl sulfoxides to give 1,1-disubstituted cyclopropanes **20** (entries 1, 3, 4, 6, 8, and 10). On the contrary, adducts **19** synthesized from (*Z*)-1-chlorovinyl *p*-tolyl sulfoxides gave tri-substituted or tetra-

Table 1
Synthesis of cyclopropanes **20** from 1-chlorovinyl *p*-tolyl sulfoxides **18** through adducts **19** by regiospecific 1,3-CH insertion of the magnesium carbenoid intermediates



Entry	**18**				**19**		**Cyclopropane 20**		
		R^1	R^2	Configuration		Yield (%)			Yield (%)
1	**18a**	Pentyl	Me	*E*	**19a**	99[a]	**20a**		88
2	**18b**	Me	Pentyl	*Z*	**19b**	95[a]	**20b**		91[c]
3	**18c**	$\begin{pmatrix}(CH_2)_2PMP \\ Me\end{pmatrix}$	$\begin{pmatrix}Me \\ (CH_2)_2PMP\end{pmatrix}$	*E*, *Z* mixture (*E*/*Z*=4:3)	**19c**	95	**20c**	 (4 : 3)	89[d]
4	**18d**	Isopropyl	Me	*E*	**19d**	70[a,b]	**20d**		99
5	**18e**	Me	Isopropyl	*Z*	**19e**	99[a]	**20e**		77
6	**18f**	Cyclohexyl	Me	*E*	**19f**	97[a]	**20f**		73
7	**18g**	Me	Cyclohexyl	*Z*	**19g**	96[a]	**20g**		77
8	**18h**	Cyclopropyl	Me	*E*	**19h**	99[a]	**20h**		99
9	**18i**	Me	Cyclopropyl	*Z*	**19i**	99[a]	**20i**		80
10	**18j**	CH_2=CH	Me	*E*	**19j**	99[a]	**20j**		62
11	**18k**	Me	CH_2=CH	*Z*	**19k**	97[a]	**21**	 **21**	56

[a] Obtained as a single diastereomer.
[b] Starting material (29%) was recovered.
[c] A 3:1 mixture of two diastereomers.
[d] Minor cyclopropane was obtained as a 6:1 mixture of two diastereomers.

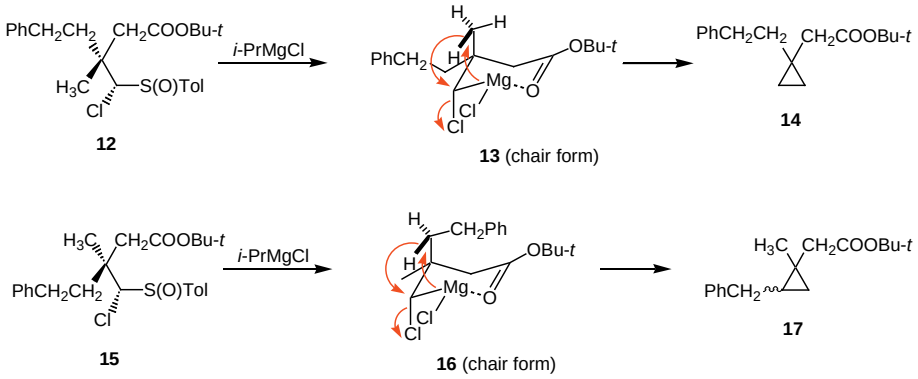
substituted cyclopropanes **20** from the 1,3-CH insertion reaction between the carbenoid and the methylene or methyne carbon (entries 2, 3, 5, and 7). Special attention should be paid to the reactions shown in entries 4–7. In these cases, the 1,3-CH insertion reaction took place between the carbenoid and the methyl or methyne carbon. As shown in Table 1, the specificity was still perfect in these cases. The result shown in entry 9 was quite interesting. The reaction of **19i** with *i*-PrMgCl did not give the expected highly strained spiro[2.2]pentane derivative. Instead, olefin **20i** was obtained in 80% yield by the 1,2-carbon–carbon (1,2-CC) insertion of the magnesium carbenoid intermediate. The result in entry 11 shows that the 1,3-CH insertion reaction of magnesium carbenoid does not take place between the carbenoid and sp^2 carbon. Only diene **21**, which was produced by the 1,2-CC insertion of the magnesium carbenoid intermediate, was obtained in 56% yield as an isolable product.

Elucidation of the origin of the regiospecificity of the 1,3-CH insertion reaction mentioned above is very important for developing these reactions to a new method for the synthesis of cyclopropanes. We proposed a plausible mechanism for these regiospecific 1,3-CH insertion reactions of magnesium carbenoids as shown in Scheme 3. Since the sulfoxide–magnesium exchange reaction[7] is known to take place with retention of the configuration of the carbon bearing a sulfinyl group,[8] treatment of adduct **12** with *i*-PrMgCl gives magnesium carbenoid **13** having R^*-configuration. The magnesium and carbonyl oxygen atom of the ester group interact to afford chair-like six-membered intermediate as shown in Scheme 3. In this intermediate, C–H bond of the methyl group attacks to the carbon bearing the chlorine atom from backside of C–Cl bond[9] to give 1,1-disubstituted cyclopropane **14**. On the other hand, the reaction of **15** with *i*-PrMgCl gave magnesium carbenoid intermediate **16**. In the chair-like six-membered intermediate (chair form **16**), the C–H bond in the backside of the C–Cl bond is on the methylene carbon. From this intermediate tri-substituted cyclopropane **17** must be obtained. As reported previously, this specificity almost disappeared when the *tert*-butoxycarbonyl group of adducts **12** and **15** was converted to trityloxymethyl group.[5]

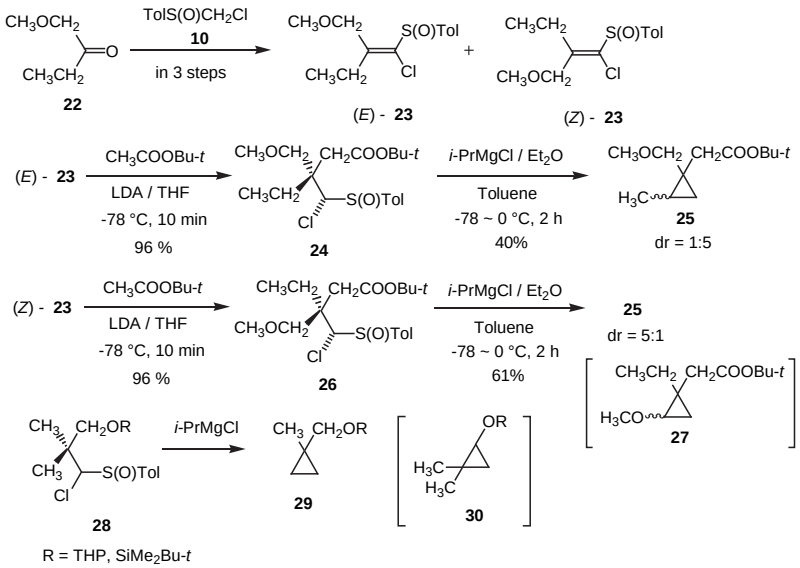
2.2. Synthesis of cyclopropanes by regioselective magnesium carbenoid 1,3-CH insertion reaction as the key reaction

Further development of the aforementioned chemistry was carried out with the unsymmetrical ketones bearing a heteroatom on the α-position. The representative results are shown in Scheme 4. At first, geometrical isomers of 1-chlorovinyl *p*-tolyl sulfoxides *E*-**23** and *Z*-**23** were synthesized from 1-methoxy-2-butanone **22** with chloromethyl *p*-tolyl sulfoxide **10** in three steps in good overall yield. The addition reaction of each vinyl sulfoxide with lithium enolate of *tert*-butyl acetate gave adduct **24** and **26**, respectively, in good yield as a single diastereomer.

Adduct **24** was treated with *i*-PrMgCl in the same way as described above and from this reaction we obtained the expected



Scheme 3. A plausible mechanism for the regiospecific 1,3-CH insertion reaction.



Scheme 4. Regioselective 1,3-CH insertion reaction of **24** and **26** with *i*-PrMgCl.

cyclopropane **25** as a mixture of two diastereomers (the ratio about 1:5 with respect to the methyl group on the cyclopropane ring) in 40% yield. In this case, as expected, the 1,3-CH insertion reaction took place between the carbenoid and the methylene carbon of the ethyl group. Next, adduct **26** was treated with *i*-PrMgCl. This reaction gave a mixture of cyclopropanes in 61% yield; however, the product was not the expected methoxycyclopropane **27** but cyclopropane **25**. In this case the ratio of the diastereomers was found to be 5:1. Obviously, the 1,3-CH insertion reaction of the magnesium carbenoid intermediate took place between the carbenoid and the methylene carbon of the ethyl group with high regioselectivity.

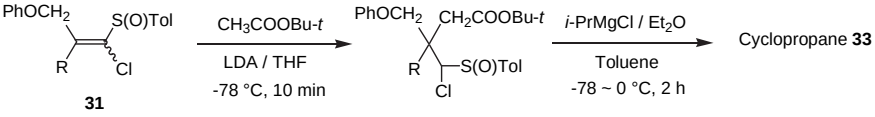
The real reason for this regioselectivity is not clear at present. However, presence of the Lewis basic oxygen atom, as the ether functional group, is thought to act as crucial role in the conformation of the magnesium carbenoid intermediates. We previously reported the 1,3-CH insertion reaction of sulfoxides bearing an alkoxymethyl group **28**. The 1,3-CH insertion reaction took place between the carbenoid carbon and the methyl carbon to give 1,1-disubstituted cyclopropane **29** in up to 97% yield without any trace of the alkoxycyclopropane **30**.[4a] The result in the presented study consistent with that in the previous investigation.[4a]

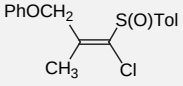
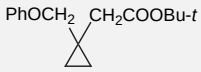
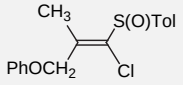
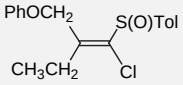
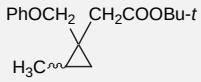
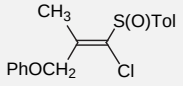
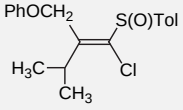
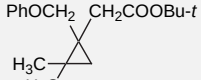
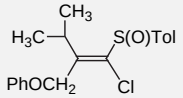
Synthesis of cyclopropanes bearing a phenoxymethyl group on the cyclopropane ring **33** starting from unsymmetrical ketones having a phenoxy group on the α-position was summarized in Table 2. 1-Chlorovinyl *p*-tolyl sulfoxides bearing a phenoxymethyl group **31** were synthesized from the corresponding ketones with chloromethyl *p*-tolyl sulfoxide **10** in good overall yields. All the addition reactions of **31** with lithium enolate of *tert*-butyl acetate smoothly proceeded to give adducts **32** in quantitative yields as single diastereomers.

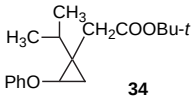
Quite different reactivity was observed between the reaction of the adducts **32a** and **32b** with *i*-PrMgCl. Thus, treatment of **32a** with *i*-PrMgCl was carried out under the same way as described above to afford the expected 1,1-disubstituted cyclopropane **33a** in 64% yield (entry 1). The same reaction of **32b** only gave a very complex mixture from which **33a** was isolated in 6% yield as only isolable product. Treatment of adducts **32c** and **32d** with *i*-PrMgCl gave the expected tri-substituted cyclopropane **33b** as a mixture of two diastereomers with high regioselectivity; however, the yields were low to moderate. The reaction of adduct **32e** with *i*-PrMgCl was found to be sluggish; however, this reaction cleanly gave the expected tetra-substituted cyclopropane **33c**. On the other hand, the reaction with **32f** gave the expected **33c** (20% yield) and the cyclopropane resulting from the 1,3-CH insertion reaction between the carbenoid and the methylene carbon of the phenoxymethyl group **34** as a main product (45%). Although the reason is not clear at present the regioselectivity was found to be low in this case.

Finally, the l,3-CH insertion reaction of magnesium carbenoid was investigated with the substrate bearing a nitrogen atom

Table 2
Synthesis of cyclopropanes bearing a phenoxymethyl group **33** from 1-chlorovinyl *p*-tolyl sulfoxides **31**



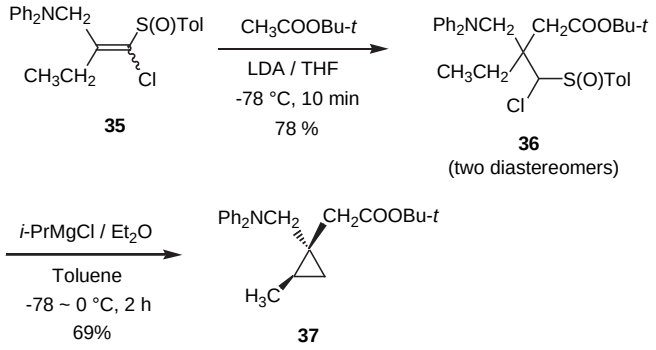
Entry	**31**			**32**		Cyclopropane **33**	
			Configuration		Yield (%)		Yield (%)
1	**31a**		*E*	**32a**	95	 **33a**	64
2	**31b**		*Z*	**32b**	96		6
3	**31c**		*E*	**32c**	96	 **33b**	63[a,b]
4	**31d**		*Z*	**32d**	97		35[a,c]
5	**31e**		*E*	**32e**	99	 **33c**	43[d]
6	**31f**		*Z*	**32f**	99		20[a,e]



34

[a] The yield was determined by ^{1}H NMR.
[b] A 7:1 mixture of two diastereomers.
[c] A 1:2 mixture of two diastereomers.
[d] The starting material was recovered in 47% yield.
[e] Cyclopropane **34** was obtained as a main product in 45% yield.

(Scheme 5). 1-Chlorovinyl *p*-tolyl sulfoxide **35** was synthesized from 1-diphenylamino-2-butanone with chloromethyl *p*-tolyl sulfoxide **10** as an inseparable mixture of two geometrical isomers. The addition reaction of the mixture of **35** with lithium enolate of *tert*-butyl acetate gave adduct **36** as an inseparable mixture of two diastereomers in 78% yield. Treatment of **36** with *i*-PrMgCl under the aforementioned conditions gave relatively clean reaction mixture and cyclopropane **37** was obtained in 69% yield as a single isomer. The structure of **37** was determined as shown in Scheme 5 by NOESY experiment; clear NOE was observed between hydrogen of the methyl group and hydrogen on the methylene carbon of *tert*-butyl acetate moiety.



Scheme 5. Synthesis of cyclopropane bearing a diphenylaminomethyl group **37** by regioselective 1,3-CH insertion reaction.

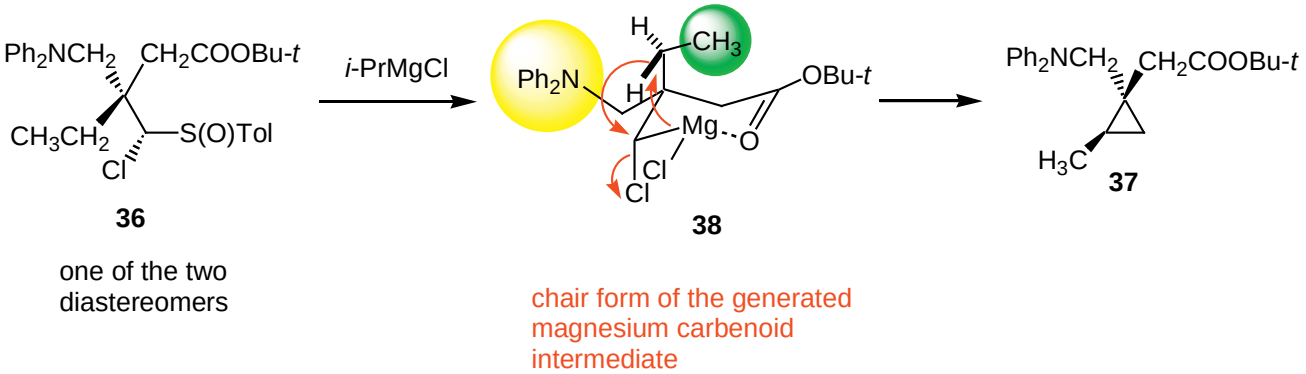
It is worth noting that since we obtained only **37** as the product, the 1,3-CH insertion reaction of the magnesium carbenoid intermediate derived from the mixture of diastereomers **36** proceeded with high regio- and stereoselectivity. The real mechanism of this region- and stereoselective reaction is still obscure; however, we could propose a plausible explanation of the selectivities as shown in Scheme 6. Similar to the magnesium carbenoid intermediate indicated in Scheme 3, the sulfoxide–magnesium exchange reaction of **36** afforded magnesium carbenoid intermediate **38**. The magnesium and carbonyl oxygen atom of the ester group interact to give chair-like six-membered intermediate in which very bulky diphenylaminomethyl group occupies equatorial position. Because of the steric repulsion of both the diphenylaminomethyl group and the ethyl group, the methyl group in the ethyl group must be moved away from the diphenylamino group, as shown in Scheme 6. From this conformation, cyclopropane **37** was obtained with high stereoselectivity.

In conclusion, we found that the 1,3-CH insertion reaction of the magnesium carbenoids generated from 1-chloroalkyl *p*-tolyl sulfoxides having an *tert*-butyl ester group, which were prepared from unsymmetrical ketones, chloromethyl *p*-tolyl sulfoxide and *tert*-butyl acetate, proceeded with complete regiospecificity when the 1-chloroalkyl *p*-tolyl sulfoxides have no heteroatom at the 3-position. The essence of the regiospecificity was demonstrated on the bases of the fixed conformation of the magnesium carbenoid intermediate. On the other hand, the reaction of 1-chlorovinyl *p*-tolyl sulfoxides prepared from unsymmetrical ketones bearing oxygen- or nitrogen-functional group at the α-position with *i*-PrMgCl, the 1,3-CH insertion reaction usually takes place with regioselectivity, though in some cases the yields were low to moderate and the selectivity is not always high. In these cases, we still find it very difficult to propose a rational transition model for explaining the selectivity. Coordination of the magnesium and the oxygen of the carbonyl group and the ether group, or the nitrogen-functional group at the same time were thought to be the reason for this complexity. The results described in this paper contribute to the regiospecific and regioselective synthesis of cyclopropanes from various ketones and to further development of the chemistry of magnesium carbenoids.

3. Experimental

3.1. General

Melting points were measured on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 500 and BRUKER UltraShield 400, 300 spectrometer. IR spectra were recorded on a Perkin–Elmer spectrum One FT-IR instrument. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion with JEOL JMS-SX102A. Silica gel 60 N (KANTO CHEMICAL) containing 0.5% fluorescence reagent 254 and a quartz column were used for column



Scheme 6. A plausible explanation for the regioselective and stereoselective formation of **37** from **36** through the 1,3-CH insertion reaction of magnesium carbenoid intermediate.

chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent and reagent, diethyl ether, and THF were distilled from diphenylketyl. Toluene, diisopropylamine, and triethylamine were distilled from CaH_2, 1,2-epoxybutane and *tert*-butyl acetate from anhydrous $CaSO_4$. Compounds (*E*)-**11**,[6b] (*Z*)-**11**,[6b] **15**,[6b] **18a**,[10] **18b**,[10] **18j**,[10] **18k**,[10] and **22**[11] are known.

*3.1.1. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methyl-5-phenylpentanoate (**12**).* *tert*-Butyl acetate (0.328 mL; 2.44 mmol) was added to a solution of LDA (2.35 mmol) in 8 mL of dry THF at −78 °C under argon atmosphere with stirring. After the solution was stirred for 10 min, a solution of vinyl sulfoxide (*E*)-**11** (150 mg; 0.47 mmol) in THF (1.4 mL) was added. The reaction mixture was stirred for 10 min and the reaction was quenched by adding satd aq NH_4Cl. The product was purified by silica gel column chromatography to afford adduct **12** (204.3 mg; 99%) as colorless oil; IR (neat) 2976, 2926, 1716 (CO), 1597, 1491, 1458, 1364, 1160, 1055 (SO), 812 cm^{-1}; ^1H NMR δ 1.42 (3H, s), 1.47 (9H, s), 2.19 (1H, dt, *J*=9.6, 5.4 Hz), 2.29 (1H, dt, *J*=9.6, 5.4 Hz), 2.42 (3H, s), 2.67 (1H, d, *J*=15.6 Hz), 2.68 (1H, dt, *J*=12.6, 5.4 Hz), 2.75 (1H, dt, *J*=12.6, 5.4 Hz), 3.07 (1H, d, *J*=15.6 Hz), 5.21 (1H, s), 7.18 (1H, m), 7.23–7.26 (2H, m), 7.28–7.31 (4H, m), 7.72 (2H, d, *J*=8.4 Hz). MS *m*/*z* (%) 434 (M^+, 0.5), 361 (13), 203 (20), 140 (100), 91 (69). Calcd for $C_{24}H_{31}ClO_3S$: M, 434.1682. Found: *m*/*z* 434.1689.

*3.1.2. tert-Butyl [1-(2-phenylethyl)cyclopropyl]acetate (**14**).* To a flame-dried flask was added dry toluene (2 mL) followed by *i*-PrMgCl (2.0 M solution in ether; 0.46 mmol; 5 equiv) at −78 °C under argon atmosphere. A solution of adduct **12** (40 mg; 0.092 mmol) in toluene (1 mL) was added to a solution of the Grignard reagent dropwise with stirring and the reaction mixture was slowly allowed to warm to 0 °C for 2 h. The reaction was quenched with satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The product was purified over silica gel column chromatography to afford cyclopropane **14** (21.5 mg; 90%) as colorless oil. IR (neat) 2978, 2931, 1725 (CO), 1603, 1455, 1467, 1314, 1256, 1141, 1017, 966, 842, 746, 699 cm^{-1}; ^1H NMR δ 0.38 (2H, m), 0.47 (2H, m), 1.47 (9H, s), 1.63 (2H, m), 2.21 (2H, s), 2.70 (2H, m), 7.14–7.20 (3H, m), 7.24–7.28 (2H, m). MS *m*/*z* (%) 260 (M^+, 3), 204 (51), 159 (12), 144 (82), 104 (37), 91 (100), 57 (78). Calcd for $C_{17}H_{24}O_2$: M, 260.1777. Found: *m*/*z* 260.1772.

*3.1.3. tert-Butyl (2-benzyl-1-methylcyclopropyl)acetate (**17**).* Colorless oil (about 10:1 mixture of two diastereomers); IR (neat) 2978, 1732 (CO), 1455, 1368, 1253, 1150, 963, 698 cm^{-1}; ^1H NMR δ 0.21 (0.1H, t, *J*=4.9 Hz), 0.34 (0.9H, t, *J*=5.1 Hz), 0.61 (0.9H, dd, *J*=8.4, 4.7 Hz), 0.71 (0.1H, dd, *J*=8.6, 4.9 Hz), 0.92 (1H, tt, *J*=8.5, 5.9 Hz), 1.14 (0.3H, s), 1.16 (2.7H, s), 1.46 (0.9H, s), 1.48 (8.1H, s), 2.13 (0.2H, d, *J*=3.9 Hz), 2.27 (1.8H, d, *J*=4.2 Hz), 2.47 (0.9H, dd, *J*=15.1, 8.5 Hz), 2.57 (0.1H, dd, *J*=15.4, 8.0 Hz), 2.80 (0.1H, dd, *J*=15.1, 6.6 Hz), 2.88 (0.9H, dd, *J*=15.1, 6.3 Hz), 7.15–7.21 (1H, m), 7.21–7.31 (4H, m). MS *m*/*z* (%) 260 (M^+, 0.1), 222 (2), 204 (49), 187 (12), 159 (13), 144 (60), 117 (34), 104 (34), 91 (78), 57 (75). Calcd for $C_{17}H_{24}O_2$: M, 260.1776. Found: *m*/*z* 260.1768.

*3.1.4. 1-Chloro-2-methyl-4-(4-methoxyphenyl)-but-1-enyl p-tolyl sulfoxide (**18c**).* Colorless oil (about 4:3 mixture of two diastereomers); IR (neat) 2998, 2933, 1612, 1515, 1456, 1302, 1249, 1178, 1088, 1058 (SO), 892, 810, 753 cm^{-1}; ^1H NMR δ 2.05 (1.7H, s), 2.24 (1.3H, s), 2.39 (1.7H, s), 2.42 (1.3H, s), 2.49–2.57 (0.43H, m), 2.64–2.86 (2H, m), 2.89–2.96 (1.14H, m), 3.12–3.18 (0.43H, m), 3.78 (1.3H, s), 3.80 (1.7H, s), 6.79 (0.86H, d, *J*=8.6 Hz), 6.87 (1.14H, d, *J*=8.6 Hz), 7.06 (0.86H, d, *J*=8.6 Hz), 7.13 (1.14H, d, *J*=8.6 Hz), 7.16 (1.14H, d, *J*=8.3 Hz), 7.22 (1.14H, d, *J*=7.9 Hz), 7.29 (0.86H, d, *J*=8.0 Hz), 7.37 (0.86H, d, *J*=8.3 Hz). MS *m*/*z* (%) 348 (M^+, 3), 331 (41), 239 (3), 208 (6), 172 (11), 158 (7), 121 (100), 91 (14), 77 (10), 65 (6). Calcd for $C_{19}H_{21}ClO_2S$: M, 348.0951. Found: *m*/*z* 348.0950.

*3.1.5. (E)-1-Chloro-2,3-dimethylbut-1-enyl p-tolyl sulfoxide (**18d**).* Colorless crystals; mp 75–75.5 °C (hexane); IR (KBr) 2966, 1595, 1490, 1464, 1366, 1231, 1088, 1055 (SO), 803 cm^{-1}; ^1H NMR δ 1.16 (3H, d, *J*=6.9 Hz), 1.19 (3H, d, *J*=6.8 Hz), 1.90 (3H, s), 2.41 (3H, s), 3.83 (1H, septet, *J*=6.8 Hz), 7.32 (2H, d, *J*=8.2 Hz), 7.48 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{13}H_{17}ClOS$: C, 60.80; H, 6.67; Cl, 13.81; S, 12.49. Found: C, 60.75; H, 6.51; Cl, 13.70; S, 12.54.

*3.1.6. (Z)-1-Chloro-2,3-dimethylbut-1-enyl p-tolyl sulfoxide (**18e**).* Colorless crystals; mp 122.5–124 °C (hexane); IR (KBr) 2965, 1595, 1439, 1307, 1083, 1051 (SO), 811 cm^{-1}; ^1H NMR δ 1.02 (3H, d, *J*=6.8 Hz), 1.08 (3H, d, *J*=6.8 Hz), 2.22 (3H, s), 2.41 (3H, s), 3.18 (1H, septet, *J*=6.8 Hz), 7.31 (2H, d, *J*=8.2 Hz), 7.46 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{13}H_{17}ClOS$: C, 60.80; H, 6.67; Cl, 13.81; S, 12.49. Found: C, 60.90; H, 6.54; Cl, 13.70; S, 12.54.

*3.1.7. (E)-1-Chloro-2-cyclohexylprop-1-enyl p-tolyl sulfoxide (**18f**).* Colorless crystals; mp 74–74.5 °C (hexane–AcOEt); IR (KBr) 2926, 2853, 1594, 1489, 1445, 1088, 1060 (SO), 806 cm^{-1}; ^1H NMR δ 1.13–1.31 (1H, m), 1.32–1.58 (5H, m), 1.70–1.90 (4H, m), 1.92 (3H, s), 2.41 (3H, s), 3.43 (1H, tt, *J*=11.3, 3.6 Hz), 7.31 (2H, d, *J*=8.3 Hz), 7.47 (2H, d, *J*=8.3 Hz). Anal. Calcd for $C_{16}H_{21}ClOS$: C, 64.74; H, 7.13; Cl, 11.94; S, 10.80. Found: C, 64.88; H, 7.04; Cl, 11.79; S, 10.77.

*3.1.8. (Z)-1-Chloro-2-cyclohexylprop-1-enyl p-tolyl sulfoxide (**18g**).* Colorless crystals; mp 109.5–110.5 °C (hexane–AcOEt); IR (KBr) 2932, 2853, 1594, 1445, 1087, 1055 (SO), 879, 806 cm^{-1}; ^1H NMR δ 1.10–1.25 (1H, m), 1.25–1.40 (4H, m), 1.47–1.57 (1H, m), 1.63–1.86 (4H, m), 2.23 (3H, s), 2.41 (3H, s), 2.74–2.88 (1H, m), 7.30 (2H, d, *J*=8.3 Hz), 7.45 (2H, d, *J*=8.3 Hz). Anal. Calcd for $C_{16}H_{21}ClOS$: C, 64.74; H, 7.13; Cl, 11.94; S, 10.80. Found: C, 64.80; H, 7.01; Cl, 11.74; S, 10.78.

*3.1.9. (E)-1-Chloro-2-cyclopropylprop-1-enyl p-tolyl sulfoxide (**18h**).* Colorless crystals; mp 120–120.5 °C (hexane–AcOEt); IR (KBr) 3010, 2921, 1584, 1491, 1359, 1084, 1054 (SO), 930, 809 cm^{-1}; ^1H NMR δ 0.73–0.81 (1H, m), 0.87–1.03 (3H, m), 1.63 (3H, s), 2.42 (3H, s), 2.67 (1H, m), 7.32 (2H, d, *J*=8.0 Hz), 7.52 (2H, d, *J*=8.0 Hz). Anal. Calcd for $C_{13}H_{15}ClOS$: C, 61.29; H, 5.93; Cl, 13.92; S, 12.58. Found: C, 61.34; H, 5.84; Cl, 13.80; S, 12.55.

*3.1.10. (Z)-1-Chloro-2-cyclopropylprop-1-enyl p-tolyl sulfoxide (**18i**).* Colorless crystals; mp 131.5–132 °C (hexane–AcOEt); IR (KBr) 3013, 1581, 1447, 1266, 1083, 1050 (SO), 881, 808 cm^{-1}; ^1H NMR δ 0.73–0.80 (1H, m), 0.81–0.95 (3H, m), 1.95 (3H, s), 2.18 (1H, m), 2.42 (3H, s), 7.32 (2H, d, *J*=8.0 Hz), 7.48 (2H, d, *J*=8.0 Hz). Anal. Calcd for $C_{13}H_{15}ClOS$: C, 61.29; H, 5.93; Cl, 13.92; S, 12.58. Found: C, 61.34; H, 5.80; Cl, 13.76; S, 12.52.

*3.1.11. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methyloctanoate (**19a**).* Colorless oil; IR (neat) 2932, 1724 (CO), 1597, 1456, 1368, 1218, 1161, 1056 (SO), 812 cm^{-1}; ^1H NMR δ 0.91 (3H, t, *J*=6.6 Hz), 1.31 (3H, s), 1.31–1.41 (6H, m), 1.46 (9H, s), 1.79–1.88 (1H, m), 1.91–2.00 (1H, m), 2.42 (3H, s), 2.51 (1H, d, *J*=15.5 Hz), 3.00 (1H, d, *J*=15.5 Hz), 5.16 (1H, s), 7.30 (2H, d, *J*=8.2 Hz), 7.72 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 401 ($[M+H]^+$, 26), 345 (100), 327 (19), 205 (4), 169 (20), 140 (12), 123 (10), 109 (6), 57 (10). Calcd for $C_{21}H_{34}ClO_3S$: M, 401.1917. Found: *m*/*z* 401.1915.

*3.1.12. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methyloctanoate (**19b**).* Colorless oil; IR (neat) 2931, 1732 (CO), 1598, 1456, 1368, 1222, 1143, 1056 (SO), 812 cm^{-1}; ^1H NMR δ 0.89 (3H, t, *J*=7.0 Hz), 1.23–1.38 (6H, m), 1.42 (3H, s), 1.45 (9H, s), 1.68 (2H, dd, *J*=9.2,

6.6 Hz), 2.42 (3H, s), 2.68 (1H, d, *J*=15.6 Hz), 2.93 (1H, d, *J*=15.6 Hz), 5.07 (1H, s), 7.31 (2H, d, *J*=8.2 Hz), 7.72 (2H, d, *J*=8.2 Hz). MS (FAB) *m*/*z* (%) 401 ([M+H]$^+$, 25), 345 (100), 327 (20), 205 (4), 169 (15), 140 (11), 123 (8), 109 (6), 57 (9). Calcd for $C_{21}H_{34}ClO_3S$: M, 401.1917. Found: *m*/*z* 401.1916.

*3.1.13. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-5-(4-methoxyphenyl)-3-methylpentanoate (**19c**).* Colorless oil; IR (neat) 2977, 2934, 1723 (CO), 1613, 1515, 1463, 1368, 1247, 1156, 1054 (SO), 813 cm^{-1}; ^{1}H NMR δ 1.41 (1.3H, s), 1.47 (3.9H, s), 1.48 (5.1H, s), 1.50 (1.7H, s), 1.92–2.08 (1H, m), 2.11–2.35 (1H, m), 2.42 (1.3H, s), 2.43 (1.7H, s), 2.52–2.75 (2.43H, m), 2.82 (0.57H, d, *J*=15.8 Hz), 3.06 (0.43H, d, *J*=15.3 Hz), 3.06 (0.57H, d, *J*=15.5 Hz), 3.78 (1.3H, s), 3.79 (1.7H, s), 5.11 (0.43H, s), 5.20 (0.57H, s), 6.83 (2H, t, *J*=8.0 Hz), 7.10 (0.86H, d, *J*=8.4 Hz), 7.15 (1.14H, d, *J*=8.5 Hz), 7.31 (1.14H, d, *J*=8.0 Hz), 7.32 (0.86H, d, *J*=7.7 Hz), 7.72 (0.86H, d, *J*=7.7 Hz), 7.74 (1.14H, d, *J*=8.0 Hz). MS (FAB) *m*/*z* (%) 465 ([M+H]$^+$, 26), 409 (100), 391 (17), 269 (5), 233 (58), 173 (37), 121 (80), 57 (16). Calcd for $C_{25}H_{34}ClO_4S$: M, 465.1866. Found: *m*/*z* 465.1864.

*3.1.14. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3,4-dimethylpentanoate (**19d**).* Colorless oil; IR (neat) 2978, 1723 (CO), 1456, 1368, 1220, 1159, 1056 (SO), 812 cm^{-1}; ^{1}H NMR δ 1.03 (3H, d, *J*=6.9 Hz), 1.10 (3H, d, *J*=6.9 Hz), 1.30 (3H, s), 1.47 (9H, s), 2.42 (3H, s), 2.51 (1H, septet, *J*=6.9 Hz), 2.52 (1H, d, *J*=15.5 Hz), 2.90 (1H, d, *J*=15.5 Hz), 5.25 (1H, s), 7.31 (2H, d, *J*=8.1 Hz), 7.74 (2H, d, *J*=8.1 Hz). MS (FAB) *m*/*z* (%) 373 ([M+H]$^+$, 30), 317 (100), 299 (20), 177 (5), 141 (28), 123 (16), 91 (2), 57 (10). Calcd for $C_{19}H_{30}ClO_3S$: M, 373.1605. Found: *m*/*z* 373.1601.

*3.1.15. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3,4-dimethylpentanoate (**19e**).* Colorless oil; IR (neat) 2978, 1723 (CO), 1456, 1368, 1221, 1161, 1140, 1084 (SO), 1056, 812 cm^{-1}; ^{1}H NMR δ 0.97 (3H, d, *J*=6.9 Hz), 1.01 (3H, d, *J*=6.9 Hz), 1.42 (3H, s), 1.46 (9H, s), 2.24 (1H, septet, *J*=6.9 Hz), 2.43 (3H, s), 2.60 (1H, d, *J*=16.1 Hz), 2.93 (1H, d, *J*=16.1 Hz), 5.49 (1H, s), 7.32 (2H, d, *J*=8.0 Hz), 7.79 (2H, d, *J*=8.0 Hz). MS (FAB) *m*/*z* (%) 373 ([M+H]$^+$, 31), 317 (100), 299 (22), 177 (4), 141 (20), 123 (14), 91 (2), 57 (10). Calcd for $C_{19}H_{30}ClO_3S$: M, 373.1605. Found: *m*/*z* 373.1604.

*3.1.16. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-cyclohexylbutanoate (**19f**).* Colorless crystals; mp 99–99.5 °C (hexane–AcOEt); IR (KBr) 2927, 1717 (CO), 1447, 1364, 1219, 1150, 1057 (SO), 814 cm^{-1}; ^{1}H NMR δ 1.06–1.23 (3H, m), 1.23–1.38 (2H, m), 1.31 (3H, s), 1.46 (9H, s), 1.65–1.73 (1H, m), 1.75–1.90 (3H, m), 2.00–2.14 (2H, m), 2.42 (3H, s), 2.55 (1H, d, *J*=15.4 Hz), 2.88 (1H, d, *J*=15.4 Hz), 5.26 (1H, s), 7.31 (2H, d, *J*=8.2 Hz), 7.74 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{22}H_{33}ClO_3S$: C, 63.98; H, 8.05; Cl, 8.58; S, 7.76. Found: C, 64.20; H, 8.00; Cl, 8.55; S, 7.75.

*3.1.17. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-cyclohexylbutanoate (**19g**).* Colorless crystals; mp 109–109.5 °C (hexane–AcOEt); IR (KBr) 2928, 1720 (CO), 1453, 1366, 1224, 1159, 1054 (SO), 809 cm^{-1}; ^{1}H NMR δ 1.00–1.33 (6H, m), 1.42 (3H, s), 1.46 (9H, s), 1.61–1.77 (2H, m), 1.77–1.88 (3H, m), 2.42 (3H, s), 2.58 (1H, d, *J*=16.1 Hz), 3.00 (1H, d, *J*=16.1 Hz), 5.53 (1H, s), 7.31 (2H, d, *J*=8.2 Hz), 7.79 (2H, d, *J*=8.2 Hz). Anal. Calcd for $C_{22}H_{33}ClO_3S$: C, 63.98; H, 8.05; Cl, 8.58; S, 7.76. Found: C, 64.15; H, 7.94; Cl, 8.40; S, 7.70.

*3.1.18. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-cyclopropylbutanoate (**19h**).* Colorless oil; IR (neat) 2979, 1728 (CO), 1598, 1456, 1372, 1219, 1159, 1055 (SO), 812 cm^{-1}; ^{1}H NMR δ 0.47–0.61 (4H, m), 1.06 (3H, s), 1.32–1.44 (1H, m), 1.47 (9H, s), 2.27 (1H, d, *J*=15.2 Hz), 2.43 (3H, s), 3.22 (1H, d, *J*=15.2 Hz), 5.40 (1H, s), 7.32 (2H, d, *J*=8.1 Hz), 7.75 (2H, d, *J*=8.1 Hz). MS (FAB) *m*/*z* (%) 371 ([M+H]$^+$, 25), 315 (100), 297 (19), 164 (4), 123 (18), 93 (12), 57 (12). Calcd for $C_{19}H_{28}ClO_3S$: M, 371.1448. Found: *m*/*z* 371.1446.

*3.1.19. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-cyclopropylbutanoate (**19i**).* Colorless oil; IR (neat) 2979, 1732 (CO), 1597, 1456, 1368, 1218, 1153, 1057 (SO), 812 cm^{-1}; ^{1}H NMR δ 0.33 (1H, m), 0.45 (1H, m), 0.62 (1H, m), 0.76 (1H, m), 1.13 (3H, s), 1.19–1.33 (1H, m), 1.44 (9H, s), 2.43 (3H, s), 2.63 (1H, d, *J*=15.6 Hz), 2.73 (1H, d, *J*=15.6 Hz), 5.26 (1H, s), 7.31 (2H, d, *J*=8.1 Hz), 7.74 (2H, d, *J*=8.1 Hz). MS (FAB) *m*/*z* (%) 371 ([M+H]$^+$, 31), 315 (100), 297 (13), 139 (11), 123 (10), 93 (8), 57 (9). Calcd for $C_{19}H_{28}ClO_3S$: M, 371.1448. Found: *m*/*z* 371.1445.

*3.1.20. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methylpent-4-enoate (**19j**).* Colorless oil; IR (neat) 2980, 1723 (CO), 1458, 1368, 1218, 1158, 1056 (SO), 813 cm^{-1}; ^{1}H NMR δ 1.43 (3H, s), 1.46 (9H, s), 2.42 (3H, s), 2.64 (1H, d, *J*=15.6 Hz), 3.20 (1H, d, *J*=15.6 Hz), 5.24 (1H, s), 5.25–5.36 (2H, m), 6.27 (1H, dd, *J*=17.5, 10.9 Hz), 7.31 (2H, d, *J*=8.1 Hz), 7.71 (2H, d, *J*=8.1 Hz). MS *m*/*z* (%) 356 (M$^+$, trace), 340 (0.1), 283 (17), 161 (13), 140 (100), 125 (16), 92 (12). Calcd for $C_{18}H_{25}ClO_3S$: M, 356.1213. Found: *m*/*z* 356.1211.

*3.1.21. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methylpent-4-enoate (**19k**).* Colorless oil; IR (neat) 2979, 1728 (CO), 1455, 1368, 1220, 1152, 1057 (SO), 812 cm^{-1}; ^{1}H NMR δ 1.44 (9H, s), 1.62 (3H, s), 2.42 (3H, s), 2.71 (1H, d, *J*=15.8 Hz), 2.83 (1H, d, *J*=15.8 Hz), 5.08 (1H, s), 5.24 (1H, d, *J*=17.4 Hz), 5.28 (1H, d, *J*=10.8 Hz), 6.11 (1H, dd, *J*=17.4, 10.8 Hz), 7.31 (2H, d, *J*=8.0 Hz), 7.71 (2H, d, *J*=8.0 Hz). MS *m*/*z* (%) 356 (M$^+$, trace), 340 (0.2), 283 (14), 161 (9), 140 (100), 125 (14), 92 (13). Calcd for $C_{18}H_{25}ClO_3S$: M, 356.1213. Found: *m*/*z* 356.1212.

*3.1.22. tert-Butyl (1-pentylcyclopropyl)acetate (**20a**).* Colorless oil; IR (neat) 2960, 2930, 1732 (CO), 1459, 1368, 1256, 1144, 965, 844 cm^{-1}; ^{1}H NMR δ 0.33 (2H, m), 0.41 (2H, m), 0.88 (3H, t, *J*=7.3 Hz), 1.18–1.41 (8H, m), 1.45 (9H, s), 2.10 (2H, s). MS *m*/*z* (%) 226 (M$^+$, trace), 170 (27), 153 (10), 141 (7), 110 (91), 99 (9), 83 (10), 69 (23), 57 (100). Calcd for $C_{14}H_{26}O_2$: M, 226.1933. Found: *m*/*z* 226.1922.

*3.1.23. tert-Butyl (2-butyl-1-methylcyclopropyl)acetate (**20b**).* Colorless oil (about 3:1 mixture of two diastereomers); IR (neat) 2960, 2930, 1735 (CO), 1458, 1367, 1255, 1148, 965, 844 cm^{-1}; ^{1}H NMR δ −0.03 (0.2H, t, *J*=5.0 Hz), 0.09 (0.8H, t, *J*=4.9 Hz), 0.47 (0.8H, dd, *J*=8.6, 4.5 Hz), 0.51–0.60 (1H, m), 0.61–0.69 (0.2H, m), 0.84–0.93 (3H, m), 1.10 (3H, s), 1.20–1.41 (6H, m), 1.45 (1.8H, s), 1.46 (7.2H, s), 1.98 (0.2H, d, *J*=14.2 Hz), 2.14 (0.2H, d, *J*=14.2 Hz), 2.16 (0.8H, d, *J*=15.1 Hz), 2.21 (0.8H, d, *J*=15.1 Hz). MS *m*/*z* (%) 226 (M$^+$, 0.1), 170 (44), 152 (13), 141 (1), 125 (5), 110 (100), 100 (11), 83 (11), 69 (27), 57 (84). Calcd for $C_{14}H_{26}O_2$: M, 226.1932. Found: *m*/*z* 226.1939.

*3.1.24. tert-Butyl {1-[2-(4-methoxyphenyl)ethyl]cyclopropyl}acetate and tert-butyl [2-(4-methoxybenzyl)-1-methylcyclopropyl]acetate (**20c**).* Colorless oil (about 4:3 mixture of two diastereomers); IR (neat) 2977, 2932, 1725 (CO), 1512, 1367, 1245, 1148, 1038, 821 cm^{-1}; ^{1}H NMR δ 0.32 (0.4H, t, *J*=5.2 Hz), 0.34–0.39 (1.2H, m), 0.43–0.48 (1.2H, m), 0.60 (0.4H, dd, *J*=8.5, 4.8 Hz), 0.83–0.93 (0.4H, m), 1.16 (1.2H, s), 1.46 (5.1H, s), 1.47 (3.9H, s), 1.55–1.64 (1.2H, m), 2.20 (1.2H, s), 2.26 (0.8H, d, *J*=4.7 Hz), 2.42 (0.4H, dd, *J*=15.1, 8.5 Hz), 2.60–2.67 (1.2H, m), 2.82 (0.4H, dd, *J*=15.1, 5.9 Hz), 3.77 (1.7H, s), 3.78 (1.3H, s), 6.78–6.86 (2H, m), 7.04–7.12 (1.2H, m), 7.12–7.18 (0.8H, m). MS (FAB) *m*/*z* (%) 290 ([M+H]$^+$, 20), 234 (43), 173 (19), 134 (29), 121 (100), 57 (15). Calcd for $C_{18}H_{26}O_3$: M, 290.1882. Found: *m*/*z* 290.1881.

*3.1.25. tert-Butyl (1-isopropylcyclopropyl)acetate (**20d**).* Colorless oil; IR (neat) 2964, 1728 (CO), 1463, 1368, 1256, 1144, 968, 854 cm^{-1}; ^{1}H NMR δ 0.36 (2H, dd, *J*=6.3, 4.4 Hz), 0.45 (2H, dd, *J*=6.3,

4.4 Hz), 0.90 (6H, d, *J*=6.9 Hz), 1.27 (1H, septet, *J*=6.9 Hz), 1.44 (9H, s), 2.17 (2H, s). MS *m*/*z* (%) 198 (M^+, trace), 142 (69), 125 (15), 97 (34), 83 (32), 57 (100). Calcd for $C_{12}H_{22}O_2$: M, 198.1620. Found: *m*/*z* 198.1627.

*3.1.26. tert-Butyl (1,2,2-trimethylcyclopropyl)acetate (**20e**).* Colorless oil; IR (neat) 2980, 1732 (CO), 1458, 1368, 1258, 1163, 963 cm^{-1}; ^1H NMR δ 0.17 (1H, d, *J*=4.5 Hz), 0.26 (1H, d, *J*=4.5 Hz), 1.10 (3H, s), 1.11 (3H, s), 1.15 (3H, s), 1.46 (9H, s), 2.18 (1H, d, *J*=15.6 Hz), 2.36 (1H, d, *J*=15.6 Hz). MS *m*/*z* (%) 198 (M^+, trace), 142 (85), 125 (11), 97 (40), 83 (100), 57 (78). Calcd for $C_{12}H_{22}O_2$: M, 198.1620. Found: *m*/*z* 198.1615.

*3.1.27. tert-Butyl (1-cyclohexylcyclopropyl)acetate (**20f**).* Colorless oil; IR (neat) 2927, 1728 (CO), 1451, 1368, 1257, 1146, 968 cm^{-1}; ^1H NMR δ 0.34–0.39 (2H, m), 0.40–0.45 (2H, m), 0.84 (1H, tt, *J*=11.8, 3.2 Hz), 0.97–1.23 (6H, m), 1.44 (9H, s), 1.63–1.78 (4H, m), 2.16 (2H, s). MS *m*/*z* (%) 238 (M^+, 0.1), 223 (1), 182 (47), 154 (11), 136 (18), 122 (100), 95 (15), 81 (26), 57 (65). Calcd for $C_{15}H_{26}O_2$: M, 238.1933. Found: *m*/*z* 238.1927.

*3.1.28. tert-Butyl (1-methylspiro[2.5]oct-1-yl)acetate (**20g**).* Colorless oil; IR (neat) 2927, 1732 (CO), 1446, 1368, 1254, 1156, 960 cm^{-1}; ^1H NMR δ 0.15 (1H, d, *J*=4.5 Hz), 0.25 (1H, d, *J*=4.5 Hz), 1.15 (3H, s), 1.23–1.62 (10H, m), 1.46 (9H, s), 2.23 (1H, d, *J*=15.7 Hz), 2.32 (1H, d, *J*=15.7 Hz). MS *m*/*z* (%) 238 (M^+, 0.1), 223 (1), 182 (65), 164 (22), 137 (14), 122 (100), 95 (17), 81 (35), 57 (33). Calcd for $C_{15}H_{26}O_2$: M, 238.1932. Found: *m*/*z* 238.1940.

*3.1.29. tert-(Butyl (1-cyclopropy)cyclopropyl)acetate (**20h**).* Colorless oil; IR (neat) 2979, 1732 (CO), 1458, 1368, 1257, 1146, 1018 cm^{-1}; ^1H NMR δ −0.04–0.01 (2H, m), 0.23–0.29 (2H, m), 0.29–0.35 (4H, m), 1.18 (1H, m), 1.47 (9H, s), 2.25 (2H, s). MS *m*/*z* (%) 196 (M^+, 0.1), 181 (1), 140 (60), 125 (15), 95 (53), 79 (25), 57 (100). Calcd for $C_{12}H_{20}O_2$: M, 196.1463. Found: *m*/*z* 196.1462.

*3.1.30. tert-Butyl 4-cyclopropyl-3-methyl-3-butenoate (**20i**).* Colorless oil; IR (neat) 2978, 1732 (CO), 1459, 1368, 1295, 1151, 951 cm^{-1}; ^1H NMR δ 0.31 (2H, dt, *J*=6.2, 4.4 Hz), 0.67–0.72 (2H, m), 1.41–1.49 (1H, m), 1.45 (9H, s), 1.75 (3H, d, *J*=1.2 Hz), 3.07 (2H, d, *J*=0.5 Hz), 4.74 (1H, br d, *J*=9.1 Hz). MS *m*/*z* (%) 196 (M^+, 0.4), 140 (67), 123 (12), 111 (28), 95 (69), 81 (17), 57 (100). Calcd for $C_{12}H_{20}O_2$: M, 196.1464. Found: *m*/*z* 196.1467.

*3.1.31. tert-Butyl (1-vinylcyclopropyl)acetate (**20j**).* Colorless oil; IR (neat) 2979, 1732 (CO), 1638, 1458, 1368, 1357, 1146, 992, 901 cm^{-1}; ^1H NMR δ 0.68–0.72 (2H, m), 0.73–0.78 (2H, m), 1.44 (9H, s), 2.33 (2H, s), 4.91 (1H, dd, *J*=10.7, 0.9 Hz), 4.96 (1H, dd, *J*=17.4, 0.9 Hz), 5.53 (1H, dd, *J*=17.4, 10.7 Hz). MS *m*/*z* (%) 182 (M^+, 2), 126 (66), 109 (21), 81 (45), 57 (100). Calcd for $C_{11}H_{18}O_2$: M, 182.1307. Found: *m*/*z* 182.1304.

*3.1.32. tert-Butyl 3-methylhexa-3,5-dienoate (**21**).* Colorless oil; IR (neat) 2979, 1731 (CO), 1368, 1253, 1151 cm^{-1}; ^1H NMR δ 1.44 (9H, s), 1.86 (3H, s), 3.08 (2H, s), 5.04 (1H, d, *J*=10.6 Hz), 5.14 (1H, d, *J*=16.9 Hz), 5.99 (1H, br d, *J*=10.8 Hz), 6.54 (1H, dt, *J*=16.7, 10.6 Hz).

*3.1.33. (E)-1-Chloro-2-methoxymethylbut-1-enyl p-tolyl sulfoxide ((E)-**23**).* Colorless oil; IR (neat) 2976, 2931, 2876, 1493, 1460, 1190, 1088, 1061 (SO), 811 cm^{-1}; ^1H NMR δ 1.08 (3H, t, *J*=7.6 Hz), 2.44 (2H, m), 2.41 (3H, s), 3.44 (3H, s), 4.31 (1H, d, *J*=11.3 Hz), 4.54 (1H, d, *J*=11.3 Hz), 7.31 (2H, d, *J*=8.2 Hz), 7.51 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 272 (M^+, 1), 255 (100), 223 (32), 139 (7), 123 (5), 97 (12), 91 (8), 79 (10), 65 (7), 45 (19). Calcd for $C_{13}H_{17}ClO_2S$: M, 272.0638. Found: *m*/*z* 272.0637.

*3.1.34. (Z)-1-Chloro-2-methoxymethylbut-1-enyl p-tolyl sulfoxide ((Z)-**23**).* Colorless oil; IR (neat) 2976, 2933, 2875, 1492, 1455, 1193, 1088, 1061 (SO), 808 cm^{-1}; ^1H NMR δ 1.23 (3H, t, *J*=7.5 Hz), 2.42 (3H, s), 2.84 (2H, m), 3.33 (3H, s), 4.19 (1H, d, *J*=14.0 Hz), 4.22 (1H, d, *J*=14.0 Hz), 7.32 (2H, d, *J*=8.2 Hz), 7.51 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 272 (M^+, 38), 255 (76), 223 (78), 187 (18), 139 (24), 123 (15), 105 (22), 97 (7), 91 (24), 65 (22), 45 (100). Calcd for $C_{13}H_{17}ClO_2S$: M, 272.0638. Found: *m*/*z* 272.0637.

*3.1.35. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methoxymethylpentanoate (**24**).* Colorless oil; IR (neat) 2980, 2929, 1720 (CO), 1456, 1392, 1367, 1216, 1151, 1113, 1083, 1050 (SO), 812, 755 cm^{-1}; ^1H NMR δ 0.98 (3H, t, *J*=7.6 Hz), 1.45 (9H, s), 1.75–1.88 (2H, m), 2.42 (3H, s), 2.73 (1H, d, *J*=15.6 Hz), 2.95 (1H, d, *J*=15.6 Hz), 3.40 (3H, s), 3.62 (1H, d, *J*=9.5 Hz), 3.81 (1H, d, *J*=9.5 Hz), 5.08 (1H, s), 7.31 (2H, d, *J*=8.2 Hz), 7.72 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 388 (M^+, 0.1), 315 (20), 193 (40), 157 (35), 140 (100), 125 (28), 91 (10), 57 (33), 45 (38). Calcd for $C_{19}H_{29}ClO_4S$: M, 388.1475. Found: *m*/*z* 388.1480.

*3.1.36. tert-Butyl (1-methoxymethyl-2-methylcyclopropyl)acetate (**25**).* Colorless oil (about 5:1 mixture of two diastereomers); IR (neat) 2978, 2929, 1732 (CO), 1455, 1367, 1255, 1148, 1111, 951, 850 cm^{-1}; ^1H NMR δ 0.13 (0.83H, t, *J*=5.3 Hz), 0.20 (0.17H, t, *J*=5.3 Hz), 0.64 (0.83H, dd, *J*=8.5, 4.9 Hz), 0.67 (0.17H, dd, *J*=8.5, 4.9 Hz), 0.76–0.92 (1H, m), 1.09 (2.5H, d, *J*=6.3 Hz), 1.11 (0.5H, d, *J*=6.3 Hz), 1.45 (1.5H, s), 1.46 (7.5H, s), 2.17 (0.17H, d, *J*=15.0 Hz), 2.27 (0.83H, d, *J*=16.0 Hz), 2.29 (0.17H, d, *J*=15.0 Hz), 2.40 (0.83H, d, *J*=16.0 Hz), 3.19 (0.83H, d, *J*=10.0 Hz), 3.30 (0.83H, d, *J*=10.0 Hz), 3.31 (2.5H, s), 3.34 (0.5H, s), 3.34 (0.17H, d, *J*=10.1 Hz), 3.46 (0.17H, d, *J*=10.1 Hz). MS *m*/*z* (%) 158 ($[M-C_4H_9]^+$, 62), 141 (22), 126 (38), 116 (73), 99 (29), 81 (33), 71 (57), 57 (100), 45 (22).

*3.1.37. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-methoxymethylpentanoate (**26**).* Colorless oil; IR (neat) 2978, 2927, 1722 (CO), 1458, 1392, 1367, 1254, 1218, 1153, 1115, 1083, 1054 (SO), 811, 755 cm^{-1}; ^1H NMR δ 1.03 (3H, t, *J*=7.6 Hz), 1.46 (9H, s), 1.97 (1H, dq, *J*=14.8, 7.4 Hz), 2.03 (1H, dq, *J*=14.8, 7.4 Hz), 2.42 (3H, s), 2.63 (1H, d, *J*=15.0 Hz), 2.96 (1H, d, *J*=15.0 Hz), 3.31 (3H, s), 3.56 (1H, d, *J*=9.3 Hz), 3.58 (1H, d, *J*=9.3 Hz), 5.22 (1H, s), 7.31 (2H, d, *J*=8.3 Hz), 7.75 (2H, d, *J*=8.3 Hz). MS *m*/*z* (%) 388 (M^+, 0.3), 315 (22), 193 (32), 184 (16), 157 (36), 140 (100), 125 (29), 91 (11), 57 (36), 45 (50). Calcd for $C_{19}H_{29}ClO_4S$: M, 388.1475. Found: *m*/*z* 388.1471.

The starting ketones for the synthesis of **31c**–**f** were synthesized as follows.

3.1.38. 1-Phenoxy-2-butanone. To a solution of phenol (2.82 g; 30 mmol) and sodium hydroxide (1.20 g; 30 mmol) in 60 mL of water at room temperature was added 1,2-epoxybutane (7.75 mL; 90 mmol) dropwise with stirring. After 2 days, the reaction was quenched with satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to afford crude alcohol. To a solution of the crude alcohol in 150 mL of DMSO in a flame-dried flask at room temperature under argon atmosphere was added Et_3N (20.9 mL; 150 mmol) dropwise with stirring. After 10 min, sulfur trioxide pyridine complex (98%, 14.6 g; 90.0 mmol) was added to the reaction mixture with stirring. After 1 h, the reaction mixture was diluted with ether and the reaction was quenched with satd aq NH_4Cl. The whole was extracted with benzene. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to afford 1-phenoxy-2-butanone (4.46 g; 90%) as colorless oil; IR (neat) 3064, 3043, 2979, 2939, 1732 (CO), 1599, 1495, 1457, 1434, 1293, 1246, 1161, 1084, 754, 691 cm^{-1}; ^1H NMR δ 1.11 (3H, t, *J*=7.3 Hz), 2.64 (2H, q, *J*=7.3 Hz),

4.56 (2H, s), 6.85–6.93 (2H, m), 6.96–7.04 (1H, m), 7.24–7.35 (2H, m).

3.1.39. 3-Methyl-1-phenoxy-2-butanone. To a solution of *N,O*-dimethylhydroxylamine hydrochloride (98%, 2.99 g; 30 mmol) and Et_3N (5 mL; 36 mmol) in 100 mL of THF was added phenoxyacetyl chloride (98%, 4.97 mL; 36 mmol) dropwise with stirring at 0 °C. The reaction mixture was stirred at 0 °C for 5 min and at room temperature for overnight. The reaction was quenched with satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated and the residue was roughly purified by silica gel column chromatography to afford the Weinreb amide. To a solution of the Weinreb amide in 100 mL dry THF in a flame-dried flask at 0 °C under argon atmosphere was added a solution of *i*-PrMgCl (2.0 M solution in THF; 30 mL; 60 mmol) dropwise with stirring. The reaction mixture was stirred at 0 °C for 5 min and at room temperature for 10 min. A solution of *i*-PrMgCl (2.0 M solution in THF; 7.5 mL; 15 mmol) was added again to the reaction mixture with stirring. After 20 min, the reaction was quenched with satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to afford 3-methyl-1-phenoxy-2-butanone (4.46 g; 90%) as colorless oil; IR (neat) 2973, 1731 (CO), 1717, 1600, 1496, 1245, 754 cm^{-1}; ^1H NMR δ 1.16 (6H, d, J=6.9 Hz), 2.96 (1H, septet, J=6.9 Hz), 4.64 (2H, s), 6.85–6.93 (2H, m), 6.95–7.05 (1H, m), 7.24–7.35 (2H, m).

*3.1.40. (E)-1-Chloro-2-phenoxymethyl-1-propenyl p-tolyl sulfoxide (**31a**).* Colorless crystals; mp 105.5–106.5 °C (hexane–AcOEt); IR (KBr) 3055, 2947, 1599, 1498, 1241, 1085, 1055 (SO), 1016, 806, 749 cm^{-1}; ^1H NMR δ 2.15 (3H, s), 2.41 (3H, s), 4.89 (1H, d, J=11.1 Hz), 5.20 (1H, d, J=11.1 Hz), 6.95–7.08 (3H, m), 7.28–7.39 (4H, m), 7.46–7.53 (2H, m). MS *m*/*z* (%) 320 (M^+, 4), 303 (100), 267 (22), 209 (26), 191 (11), 179 (30), 143 (34), 123 (20), 91 (11). Calcd for $C_{17}H_{17}ClO_2S$: M, 320.0638. Found: *m*/*z* 320.0641.

*3.1.41. (Z)-1-Chloro-2-phenoxymethyl-1-propenyl p-tolyl sulfoxide (**31b**).* Colorless crystals; mp 93.0–93.5 °C (hexane–AcOEt); IR (KBr) 2924, 1598, 1494, 1226, 1208, 1086, 1054 (SO), 1013, 804, 748, 687 cm^{-1}; ^1H NMR δ 2.36 (3H, s), 2.43 (3H, s), 4.75 (1H, d, J=14.2 Hz), 4.85 (1H, d, J=14.2 Hz), 6.79–6.87 (2H, m), 6.94–7.03 (1H, m), 7.22–7.35 (4H, m), 7.42–7.49 (2H, m). MS *m*/*z* (%) 320 (M^+, 21), 303 (61), 191 (43), 179 (97), 143 (100), 123 (83), 107 (33), 91 (21). Calcd for $C_{17}H_{17}ClO_2S$: M, 320.0638. Found: *m*/*z* 320.0639.

*3.1.42. (E)-1-Chloro-2-phenoxymethylbut-1-enyl p-tolyl sulfoxide (**31c**).* Colorless crystals; mp 94.5–95.0 °C (hexane–AcOEt); IR (KBr) 2976, 2937, 1596, 1586, 1497, 1237, 1085, 1055 (SO), 1034, 807, 752 cm^{-1}; ^1H NMR δ 1.14 (3H, t, J=7.6 Hz), 2.41 (3H, s), 2.54 (2H, q, J=7.6 Hz), 4.85 (1H, d, J=10.8 Hz), 5.21 (1H, d, J=10.8 Hz), 6.95–7.08 (3H, m), 7.28–7.39 (4H, m), 7.48–7.56 (2H, m). Anal. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.58. Found: C, 64.55; H, 5.61; Cl, 10.56; S, 9.55.

*3.1.43. (Z)-1-Chloro-2-phenoxymethylbut-1-enyl p-tolyl sulfoxide (**31d**).* Colorless crystals; mp 90.0–90.5 °C (hexane–AcOEt); IR (KBr) 2976, 2943, 1596, 1493, 1204, 1089, 1056 (SO), 1041, 802, 751 cm^{-1}; ^1H NMR δ 1.28 (3H, t, J=7.5 Hz), 2.43 (3H, s), 2.75–3.00 (2H, m), 4.81 (1H, d, J=14.1 Hz), 4.89 (1H, d, J=14.1 Hz), 6.80–6.89 (2H, m), 6.94–7.03 (1H, m), 7.21–7.37 (4H, m), 7.45–7.53 (2H, m). Anal. Calcd for $C_{18}H_{19}ClO_2S$: C, 64.56; H, 5.72; Cl, 10.59; S, 9.58. Found: C, 64.54; H, 5.60; Cl, 10.57; S, 9.60.

*3.1.44. (E)-1-Chloro-3-methyl-2-phenoxymethylbut-1-enyl p-tolyl sulfoxide (**31e**).* Colorless crystals; mp 132.0–132.5 °C (hexane–AcOEt); IR (KBr) 2969, 1598, 1498, 1230, 1084, 1058 (SO), 1014, 813, 757 cm^{-1}; ^1H NMR δ 1.13 (3H, d, J=6.9 Hz), 1.15 (3H, d, J=6.9 Hz), 2.42 (3H, s), 3.24 (1H, septet, J=6.9 Hz), 4.70 (1H, d, J=10.1 Hz), 5.17 (1H, d, J=10.1 Hz), 6.94–7.09 (3H, m), 7.29–7.40 (4H, m), 7.58–7.66 (2H, m). Anal. Calcd for $C_{19}H_{21}ClO_2S$: C, 65.41; H, 6.07; Cl, 10.16; S, 9.19. Found: C, 65.48; H, 5.91; Cl, 10.12; S, 9.26.

*3.1.45. (Z)-1-Chloro-3-methyl-2-phenoxymethylbut-1-enyl p-tolyl sulfoxide (**31f**).* Colorless crystals; mp 88–89 °C (hexane–AcOEt); IR (KBr) 2977, 2960, 1596, 1494, 1200, 1088, 1055 (SO), 1035, 800, 752 cm^{-1}; ^1H NMR δ 1.28 (3H, d, J=6.9 Hz), 1.32 (3H, d, J=6.9 Hz), 2.43 (3H, s), 3.83 (1H, septet, J=6.9 Hz), 4.71 (1H, d, J=11.4 Hz), 4.79 (1H, d, J=11.4 Hz), 6.84–6.93 (2H, m), 6.93–7.02 (1H, m), 7.22–7.38 (4H, m), 7.49–7.57 (2H, m). Anal. Calcd for $C_{19}H_{21}ClO_2S$: C, 65.41; H, 6.07; Cl, 10.16; S, 9.19. Found: C, 65.49; H, 5.84; Cl, 10.05; S, 9.12.

*3.1.46. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-phenoxymethylbutanoate (**32a**).* Colorless oil; IR (neat) 2978, 2932, 1723 (CO), 1599, 1496, 1470, 1366, 1244, 1149, 1081, 1054(SO), 812, 754, 691 cm^{-1}; ^1H NMR δ 1.40 (9H, s), 1.50 (3H, s), 2.42 (3H, s), 2.69 (1H, d, J=15.8 Hz), 3.09 (1H, d, J=15.8 Hz), 4.25 (1H, d, J=9.2 Hz), 4.47 (1H, d, J=9.2 Hz), 5.17 (1H, s), 6.91–7.02 (3H, m), 7.22–7.36 (4H, m), 7.68–7.75 (2H, m). MS *m*/*z* (%) 436 (M^+, 0.3), 363 (21), 241 (24), 205 (30), 196 (9), 140 (100), 123 (10), 107 (54), 94 (12), 77 (14), 57 (31). Calcd for $C_{23}H_{29}ClO_4S$: M, 436.1475. Found: *m*/*z* 436.1470.

*3.1.47. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-phenoxymethylbutanoate (**32b**).* Colorless oil; IR (neat) 2977, 2931, 1723 (CO), 1599, 1496, 1471, 1392, 1367, 1302, 1243, 1138, 1081, 1055 (SO), 811, 754, 691 cm^{-1}; ^1H NMR δ 1.39 (9H, s), 1.53 (3H, s), 2.43 (3H, s), 3.01 (1H, d, J=15.5 Hz), 3.11 (1H, d, J=15.5 Hz), 4.11 (1H, d, J=9.0 Hz), 4.22 (1H, d, J=9.0 Hz), 5.18 (1H, s), 6.87–6.99 (3H, m), 7.22–7.36 (4H, m), 7.70–7.76 (2H, m). MS *m*/*z* (%) 436 (M^+, 0.8), 363 (25), 241 (20), 205 (25), 196 (11), 140 (100), 123 (8), 107 (64), 94 (10), 77 (15), 57 (29). Calcd for $C_{23}H_{29}ClO_4S$: M, 436.1475. Found: *m*/*z* 436.1469.

*3.1.48. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-phenoxymethylpentanoate (**32c**).* Colorless oil; IR (neat) 2976, 1723 (CO), 1599, 1496, 1367, 1243, 1146, 1081, 1056 (SO), 754 cm^{-1}; ^1H NMR δ 1.05 (3H, t, J=7.6 Hz), 1.41 (9H, s), 1.95 (2H, q, J=7.6 Hz), 2.42 (3H, s), 2.91 (1H, d, J=16.2 Hz), 3.18 (1H, d, J=16.2 Hz), 4.26 (1H, d, J=9.5 Hz), 4.39 (1H, d, J=9.5 Hz), 5.14 (1H, s), 6.92–7.05 (3H, m), 7.23–7.36 (4H, m), 7.68–7.76 (2H, m). MS *m*/*z* (%) 450 (M^+, 0.03), 377 (20), 255 (26), 237 (12), 219 (26), 195 (6), 159 (23), 140 (100), 125 (19), 107 (58), 94 (15), 77 (18), 57 (41). Calcd for $C_{24}H_{31}ClO_4S$: M, 450.1632. Found: *m*/*z* 450.1630.

*3.1.49. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-phenoxymethylpentanoate (**32d**).* Colorless oil; IR (neat) 2977, 1724 (CO), 1599, 1497, 1367, 1243, 1156, 1081, 1055 (SO), 754 cm^{-1}; ^1H NMR δ 1.11 (3H, t, J=7.5 Hz), 1.40 (9H, s), 2.03–2.27 (2H, m), 2.43 (3H, s), 2.85 (1H, d, J=15.6 Hz), 3.07 (1H, d, J=15.6 Hz), 4.16 (1H, d, J=9.3 Hz), 4.25 (1H, d, J=9.3 Hz), 5.32 (1H, s), 6.89–7.00 (3H, m), 7.22–7.37 (4H, m), 7.70–7.78 (2H, m). MS *m*/*z* (%) 450 (M^+, 0.2), 377 (25), 255 (27), 237 (8), 219 (30), 196 (8), 159 (21), 140 (100), 125 (20), 107 (66), 94 (15), 77 (20), 57 (41). Calcd for $C_{24}H_{31}ClO_4S$: M, 450.1632. Found: *m*/*z* 450.1632.

*3.1.50. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-4-methyl-3-phenoxymethylpentanoate (**32e**).* Colorless oil; IR (neat) 2976, 1725 (CO), 1242, 1144, 1057 (SO), 753 cm^{-1}; ^1H NMR δ 1.12 (3H, d, J=6.9 Hz), 1.13 (3H, d, J=6.9 Hz), 1.41 (9H, s), 2.48 (1H, septet, J=6.9 Hz), 2.42 (3H, s), 2.81 (1H, d, J=16.3 Hz), 3.23 (1H, d, J=16.3 Hz), 4.34 (1H, d, J=9.7 Hz), 4.40 (1H, d, J=9.7 Hz), 5.50 (1H, s), 6.92–7.03 (3H, m), 7.24–7.35 (4H, m), 7.77 (2H, d, J=8.2 Hz). MS

m/*z* (%) 464 (M^+, 0.3), 391 (19), 269 (43), 233 (28), 140 (100), 123 (10), 107 (54), 94 (19), 77 (15), 57 (42). Calcd for $C_{25}H_{33}ClO_4S$: M, 464.1788. Found: *m*/*z* 464.1785.

*3.1.51. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-4-methyl-3-phenoxymethylpentanoate (**32f**).* Colorless oil; IR (neat) 2977, 1723 (CO), 1599, 1497, 1242, 1154, 1082, 1055 (SO), 754 cm^{-1}; ^1H NMR δ 1.15 (3H, d, *J*=6.9 Hz), 1.21 (3H, d, *J*=6.9 Hz), 1.41 (9H, s), 2.42 (3H, s), 2.76 (1H, d, *J*=15.7 Hz), 2.85 (1H, septet, *J*=6.9 Hz), 2.98 (1H, d, *J*=15.7 Hz), 4.18 (1H, d, *J*=9.6 Hz), 4.37 (1H, d, *J*=9.6 Hz), 5.52 (1H, s), 6.91–7.00 (3H, m), 7.24–7.34 (4H, m), 7.73 (2H, d, *J*=8.2 Hz). MS *m*/*z* (%) 464 (M^+, 0.4), 391 (21), 269 (48), 233 (30), 140 (100), 123 (11), 107 (54), 94 (19), 77 (16), 57 (46). Calcd for $C_{25}H_{33}ClO_4S$: M, 464.1788. Found: *m*/*z* 464.1795.

*3.1.52. tert-Butyl (1-phenoxymethylcyclopropyl)acetate (**33a**).* Colorless oil; IR (neat) 2978, 2930, 1731 (CO), 1600, 1587, 1497, 1367, 1243, 1148, 1034, 753, 691 cm^{-1}; ^1H NMR δ 0.58–0.69 (4H, m), 1.42 (9H, s), 2.41 (2H, s), 3.86 (2H, s), 6.86–6.96 (3H, m), 7.22–7.31 (2H, m). MS *m*/*z* (%) 262 (M^+, 6), 234 (5), 206 (10), 189 (16), 169 (3), 147 (10), 133 (8), 113 (24), 107 (4), 94 (100), 77 (9), 71 (10), 67 (10), 57 (36). Calcd for $C_{16}H_{22}O_3$: M, 262.1569. Found: *m*/*z* 262.1571.

*3.1.53. tert-Butyl (2-methyl-1-phenoxymethylcyclopropyl)acetate (**33b**).* Colorless oil (about 7:1 mixture of two diastereomers); IR (neat) 2976, 2931, 1730 (CO), 1600, 1497, 1367, 1243, 1149, 1032, 753, 691 cm^{-1}; ^1H NMR δ 0.23 (0.88H, t, *J*=5.3 Hz), 0.34 (0.12H, t, *J*=5.4 Hz), 0.74–0.84 (1H, m), 0.85–1.04 (1H, m), 1.13 (2.63H, d, *J*=6.3 Hz), 1.15 (0.37H, d, *J*=6.4 Hz), 1.42 (9H, s), 2.23 (0.12H, d, *J*=15.5 Hz), 2.34 (0.88H, d, *J*=16.6 Hz), 2.51 (0.12H, d, *J*=15.5 Hz), 2.61 (0.88H, d, *J*=16.6 Hz), 3.68 (0.88H, d, *J*=9.4 Hz), 3.83 (0.12H, d, *J*=9.8 Hz), 3.98 (0.88H, d, *J*=9.4 Hz), 4.14 (0.12H, d, *J*=9.8 Hz), 6.85–7.03 (3H, m), 7.21–7.32 (2H, m). MS *m*/*z* (%) 276 (M^+, 5), 220 (14), 203 (13), 161 (10), 127 (74), 109 (15), 94 (100), 85 (37), 57 (29). Calcd for $C_{17}H_{24}O_3$: M, 276.1725. Found: *m*/*z* 276.1727.

*3.1.54. tert-Butyl (2,2-dimethyl-1-phenoxymethylcyclopropyl)acetate (**33c**).* Colorless crystals, mp 54.5–55 °C (pentane); IR (KBr) 2977, 1730 (CO), 1602, 1502, 1471, 1367, 1241, 1212, 1156, 1136, 1010, 754 cm^{-1}; ^1H NMR δ 0.46 (1H, d, *J*=5.0 Hz), 0.58 (1H, d, *J*=5.0 Hz), 1.18 (3H, s), 1.20 (3H, s), 1.42 (9H, s), 2.44 (1H, d, *J*=16.6 Hz), 2.65 (1H, d, *J*=16.6 Hz), 4.03 (2H, s), 6.86–6.96 (3H, m), 7.22–7.32 (2H, m). MS *m*/*z* (%) 290 (M^+, 1), 234 (8), 217 (7), 195 (5), 141 (100), 123 (57), 94 (72), 81 (12), 77 (7), 57 (32). Calcd for $C_{18}H_{26}O_3$: M, 290.1882. Found: *m*/*z* 290.1881.

*3.1.55. tert-Butyl (1-isopropyl-2-phenoxycyclopropyl)acetate (**34**).* Colorless oil; IR (neat) 2966, 2932, 1728 (CO), 1600, 1494, 1367, 1239, 1147, 752 cm^{-1}; ^1H NMR δ 0.91–1.04 (9H, m), 1.43 (9H, s), 2.27 (1H, d, *J*=16.0 Hz), 2.47 (1H, dd, *J*=16.0, 0.94 Hz), 3.49 (1H, dd, *J*=6.1, 3.9 Hz), 6.90–7.07 (3H, m), 7.23–7.32 (2H, m). MS *m*/*z* (%) 290 (M^+, 1), 234 (56), 217 (17), 191 (100), 141 (38), 131 (70), 123 (17), 94 (55), 57 (26). Calcd for $C_{18}H_{26}O_3$: M, 290.1882. Found: *m*/*z* 290.1888.

3.2. 1-Diphenylamino-2-butanone, the starting material for the synthesis of 35 was synthesized as follows

To a solution of diphenylamine (11.8 g; 60 mmol) in 100 mL of dry THF in a flame-dried flask at 0 °C under argon atmosphere was added a solution of *n*-BuLi (1.59 M solution in hexane, 38 mL; 60 mmol) dropwise with stirring. After 5 min, 1,2-epoxybutane (2.58 mL; 30 mmol) was added to the reaction mixture dropwise at 0 °C and the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with satd aq NH_4Cl. The whole was extracted with $CHCl_3$. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to afford an aminoalcohol (5.74 g; 79%). To a solution of the aminoalcohol (2.41 g; 10 mmol) in 50 mL of DMSO in a flame-dried flask at room temperature under argon atmosphere was added Et_3N (6.97 mL; 50 mmol) dropwise with stirring. After 10 min, sulfur trioxide pyridine complex (98%, 4.87 g; 30 mmol) was added to the reaction mixture with stirring. After 1 h, the reaction mixture was diluted with ether and the reaction was quenched with satd aq NH_4Cl. The whole was extracted with benzene. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by silica gel column chromatography to afford 1-diphenylamino-2-butanone (2.26 g; 94%) as colorless amorphous; IR (KBr) 2982, 1722 (CO), 1591, 1492, 1458, 1365, 1264, 1216, 1105, 752, 693 cm^{-1}; ^1H NMR δ 1.05 (3H, t, *J*=7.3 Hz), 2.54 (1H, q, *J*=7.3 Hz), 4.43 (2H, s), 6.90–7.04 (6H, m), 7.20–7.33 (4H, m).

*3.2.1. N-[3-Chloro-2-ethyl-3-(p-tolylsulfinyl)-2-propenyl] N,N-diphenylamine (**35**).* Yellow oil (about 1:1 mixture of two diastereomers); IR (neat) 2975, 1589, 1495, 1244, 1087, 1058 (SO), 751, 966 cm^{-1}; ^1H NMR δ 1.07 (1.5H, t, *J*=7.5 Hz), 1.13 (1.5H, t, *J*=7.5 Hz), 2.39 (1.5H, s), 2.44 (1.5H, s), 2.50 (1H, q, *J*=7.5 Hz), 2.75 (0.5H, dq, *J*=13.7, 7.5 Hz), 2.87 (0.5H, dq, *J*=13.7, 7.5 Hz), 4.58 (0.5H, d, *J*=16.9 Hz), 4.72 (0.5H, d, *J*=16.9 Hz), 4.90 (0.5H, d, *J*=16.0 Hz), 5.08 (0.5H, d, *J*=16.0 Hz), 6.88–7.10 (6H, m), 7.10–7.44 (8H, m). MS *m*/*z* (%) 409 (M^+, 16), 392 (100), 356 (23), 268 (66), 182 (81), 167 (25), 139 (11), 104 (16), 91 (10), 77 (28). Calcd for $C_{24}H_{24}ClNOS$: M, 409.1267. Found: *m*/*z* 409.1265.

*3.2.2. tert-Butyl 3-[chloro(p-tolylsulfinyl)methyl]-3-[(diphenylamino)-methyl]pentanoate (**36**).* Yellow oil (about 2:1 mixture of two diastereomers); IR (neat) 2978, 1723 (CO), 1589, 1494, 1368, 1245, 1217, 1154, 1052 (SO), 753, 702 cm^{-1}; ^1H NMR δ 0.99 (1H, t, *J*=7.6 Hz), 1.07 (2H, t, *J*=7.6 Hz), 1.24 (6H, s), 1.38 (3H, s), 1.97–2.14 (0.67H, m), 1.97–2.37 (1.33H, m), 2.42 (3H, s), 2.65 (0.67H, d, *J*=17.9 Hz), 2.74 (0.33H, d, *J*=17.3 Hz), 2.76 (0.67H, d, *J*=17.9 Hz), 3.07 (0.33H, d, *J*=17.3 Hz), 4.18 (0.33H, d, *J*=15.4 Hz), 4.44 (0.33H, d, *J*=15.4 Hz), 4.55 (0.67H, d, *J*=15.5 Hz), 4.74 (0.67H, d, *J*=15.5 Hz), 5.18 (0.67H, s), 5.44 (0.33H, s), 6.93–7.15 (6H, m), 7.22–7.34 (6H, m), 7.63–7.73 (2H, m). MS *m*/*z* (%) 525 (M^+, 2), 452 (2), 294 (4), 182 (100), 139 (3), 104 (4), 77 (5). Calcd for $C_{30}H_{36}ClNO_3S$: M, 525.2104. Found: *m*/*z* 525.2111.

*3.2.3. tert-Butyl {1-[(Diphenylamino)methyl]-2-methylcyclopropyl} acetate (**37**).* Yellow oil; IR (neat) 2978, 2930, 1728 (CO), 1590, 1498, 1367, 1239, 1211, 1147, 747, 698 cm^{-1}; ^1H NMR δ −0.05 (1H, t, *J*=5.4 Hz), 0.46 (1H, dd, *J*=8.8, 4.9 Hz), 0.51–0.63 (1H, m), 0.91 (3H, d, *J*=6.2 Hz), 1.48 (9H, s), 2.38 (2H, s), 3.74 (1H, d, *J*=14.8 Hz), 3.93 (1H, d, *J*=14.8 Hz), 6.90–7.02 (6H, m), 7.19–7.30 (4H, m). MS *m*/*z* (%) 351 (M^+, 68), 295 (16), 278 (15), 208 (13), 196 (20), 182 (65), 169 (100), 127 (11), 104 (12), 85 (15), 77 (14), 57 (13). Calcd for $C_{23}H_{29}NO_2$: M, 351.2198. Found: *m*/*z* 351.2199.

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