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Magnesium cyclopropylidenes generated from 1-chlorocyclopropyl phenyl sulfoxides with Grignard reagents: their properties, and a sulfoxide version of the Doering–Moore–Skattebol reaction

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Abstract—Magnesium cyclopropylidenes were generated from 1-chlorocyclopropyl phenyl sulfoxides with Grignard reagents (EtMgCl or *i*-PrMgCl) in THF at −78°C in high yields by a sulfoxide–magnesium exchange reaction. The generated magnesium cyclopropylidenes were found to be stable at below −60°C for at least 3 h. It was also found that the pyramidal inversion of the magnesium carbenoid was quite slow at below −60°C. When the sulfoxide–magnesium exchange reaction was conducted with phenylmagnesium chloride at 0°C, the 1-chlorocyclopropyl phenyl sulfoxides gave allenes in good to high yields. © 2001 Elsevier Science Ltd. All rights reserved.

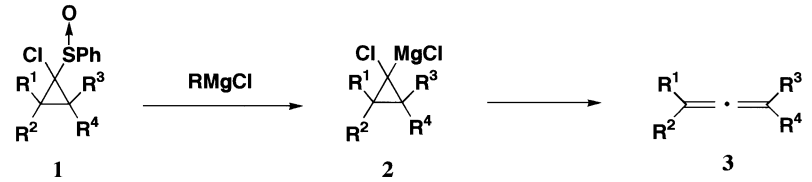
Carbenes and carbenoids have been recognized as highly reactive carbon species and are frequently used as useful intermediates in organic synthesis.[1] Cyclopropylidenes (carbenacyclopropanes) are the carbenes or carbenoids of cyclopropanes and are also known as interesting reactive intermediates. Cyclopropylidenes are usually known as the intermediates of the reaction of 1,1-dihalocyclopropanes with alkylmetals giving allenes.[2] This reaction is now called the Doering–Moore–Skattebol reaction.[3]

Recently, we reported new methods for preparing lithium and magnesium carbenoids[4] and unstable carbanions[5] by a sulfoxide–metal exchange reaction.[6] In continuation of our study on the sulfoxide–metal exchange reaction in organic synthesis, herein we report a new method for generation of magnesium cyclopropylidenes **2** from 1-chlorocyclopropyl phenyl sulfoxides **1** with Grignard reagents by the sulfoxide–magnesium exchange reaction. The properties and reactivity of the generated magnesium cyclopropylidenes **2** were investigated, and we found that at 0°C **2** were rearranged rapidly to allenes **3** in good to high yields (Scheme 1).

1. Results and discussion

1.1. Synthesis of 1-chlorocyclopropyl phenyl sulfoxides and generation of magnesium cyclopropylidenes by the sulfoxide–magnesium exchange

In this study, first of all, we selected **6** as a representative example of 1-chlorocyclopropyl phenyl sulfoxide (Scheme 2). The olefin **4**, which was synthesized from commercially available 4-(4-methoxyphenyl)-2-butanone by methylenation with the Wittig reagent, was treated with chloromethyl phenyl sulfide[7] with 50% NaOH in the presence of benzyltriethylammonium chloride (TEBACl) to give cyclopropyl phenyl sulfide **5** in 67% yield (conversion yield 94%).[8] Chlorination of the sulfide **5** with NCS[9] followed by oxidation of the sulfur with *m*-chloroperoxybenzoic acid



Scheme 1.

Keywords: sulfoxides; sulfoxide–magnesium exchange; cyclopropylidenes; allenes; Doering–Moore–Skattebol reaction.

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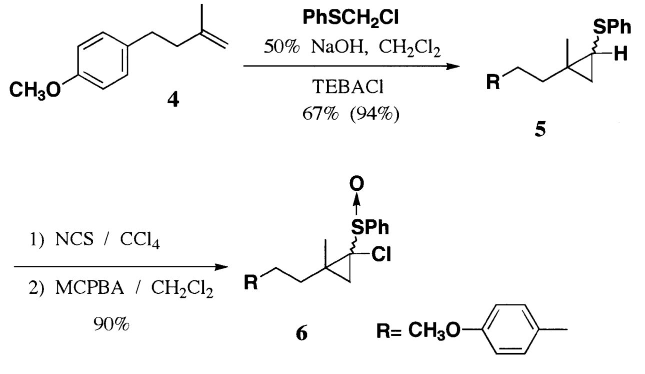


Scheme 2.

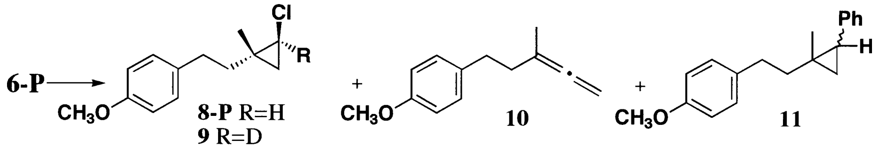
(MCPBA) gave the desired 1-chlorocyclopropyl phenyl sulfoxide **6** in 90% yield as a mixture of diastereomers.

The product **6** has three stereogenic centers and, theoretically, four diastereomers are possible. On the silica gel TLC, four products could be observed. The Rf-values of a spot of a mixture of two less polar diastereomers and that of a mixture of two more polar diastereomers are somewhat apart. We obtained the product **6** as less polar products (expressed as **6-L**; 42%) and the more polar products (expressed as **6-P**; 48%). A mixture of the two main polar isomers **6-P** was used in the following studies.

First, the α-chloro sulfoxide **6-P** was treated with 2.5 equivalents of *n*-BuLi in THF at −78°C for 5 min (a solution of **6-P** in THF was added to a solution of *n*-BuLi in THF). The starting material immediately disappeared; however, the product was a mixture of some unknown products, in which allene **8** was observed on TLC and the ^{1}H NMR spectrum (see entry 1 in Table 1). The reaction with *t*-BuLi gave a similar mixture of the products (entry 2). These results suggested that the sulfoxide–lithium exchange reaction[4] took place to give lithium cyclopropylidene. However, it was also suggested that the lithium cyclopropylidene was so reactive that several products including the allene **10** were produced.

Next, **6-P** was treated with 2.5 equivalents of EtMgCl in a similar manner as above at −78°C for 5 min to give the

Table 1. Treatment of of 1-chlorocyclopropyl phenyl sulfoxides **6-P** with 2.5 equivalents of alkylmetals under several conditions



Entry	Alkylmetal	Conditions	Electrophiles	Products (yield/%)
1	*n*-BuLi	−78°C, 5 min	H_2O	Complex mixture[a]
2	*t*-BuLi	−78°C, 5 min	H_2O	Complex mixture[a]
3	EtMgCl	−78°C, 5 min	H_2O	**8-P** (R=H, 82)
4	EtMgCl	−78°C, 5 min	CD_3OD	**9** (R=D, 77)[b]
5	*i*-PrMgCl	−78°C, 5 min	H_2O	**8-P** (R=H, 79)
6	*i*-PrMgCl	−78°C, 5 min	CD_3OD	**9** (R=D, 78)[c]
7	*i*-PrMgCl	−78°C, 1 h	CD_3OD	**9** (R=D, 80)[d]
8	*i*-PrMgCl	−78∼−60°C, 1 h	CD_3OD	**9** (R=D, 82)[d]
9	*i*-PrMgCl	−78∼−60°C, 1 h then −60°C, 3 h	CD_3OD	**9** (R=D, 81)[d]
10	PhMgCl	−78°C, 5 min	H_2O	**6-P** (89) **8-P** (R=H, trace)
11	PhMgCl	−78°C, 30 min	H_2O	**6-P** (89) **8-P** (R=H, trace)
12	PhMgCl	−78°C, 1 h	H_2O	**6-P** (90) **8-P** (R=H, trace)
13	PhMgCl	−78∼−60°C, 1 h	H_2O	**6-P** (71) **8-P** (R=H, 23)
14	PhMgCl	−78∼−60°C, 1 h then −60°C, 6 h	CD_3OD	**9** (R=D, 88)[e,f] **10** (trace) **11** (trace)
15	PhMgCl	−78∼−50°C, 1 h then −50°C, 3 h	H_2O	**8** (R=H, 84)[f] **10** (9) **11** (4)
16	PhMgCl	−78∼−50°C, 1 h then −50°C, 3 h	CD_3OD	**9** (R=D, 85)[e,f] **10** (9)
17	PhMgCl	0°C, 10 min	H_2O	**10** (82) **11** (14)
18	PhMgCl	0°C, 10 min[g]	H_2O	**8** (R=H, 5)[f] **10** (85) **11** (7)

[a] Some amount of the allene **10** was observed on TLC and ^{1}H NMR spectrum of the reaction mixture. A similar result was obtained by using 1.5 eq. RLi.

[b] D-content 91%.

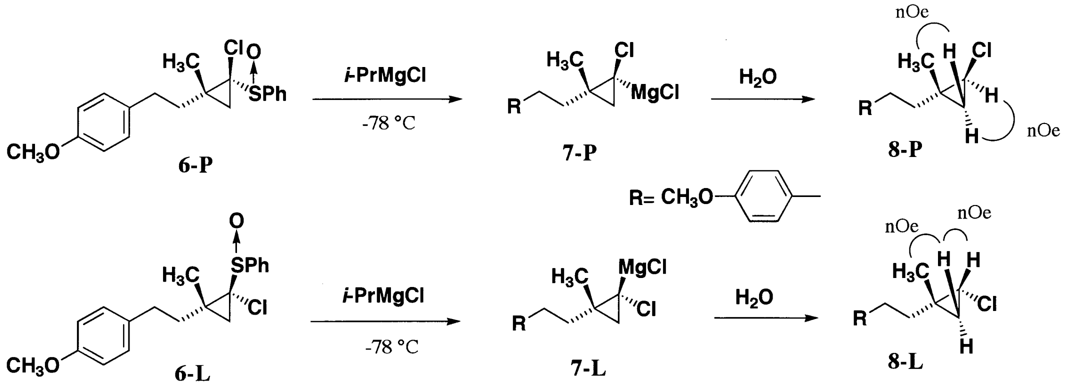
[c] D-content 93%.

[d] D-content 95–96%.

[e] D-content over 99%.

[f] A mixture of two diastereomers.

[g] 1.5 Equivalents of PhMgCl was used in this experiment.



Conditions / From	-78 °C, 5 min$^{a)}$	-78 ~ -60 °C, 1 h$^{b)}$	-78 ~ -60 °C, 1 h, then -60 °C 3 h$^{c)}$
6-P	**8-P** only$^{a)}$	**8-P** + trace of **8-L**$^{b)}$	**8-P** : **8-L** = 5 : 2$^{c, d)}$
6-L	**8-L** only	**8-L** + trace of **8-P**	**8-P** :**8-L** = 1 : 5$^{d)}$

Scheme 3. (a) The conditions and the yield, see Table 1, entry 5. (b) The conditions and the yield, see Table 1, entry 8. (c) The conditions and the yield, see Table 1, entry 9. (d) The ratio was determined by ^{1}H NMR.

desulfinylated product **8-P** in 82% yield without any trace of the starting sulfoxide **6-P** (entry 3). Even *i*-PrMgCl reacted with **6-P** at −78°C quickly to give the desulfinylated product **8-P** in good yield (entry 5). Quenching the above two reactions with CD_3OD gave the deuterated chlorocyclopropane **9** with over 90% deuterium incorporation (entries 4 and 6). These results showed that the intermediate of these reactions was the magnesium cyclopropylidene **7-P**[4b] (see Scheme 3).

Quite interestingly, even though the starting material **6-P** is a mixture of two diastereomers, the product **8-P** is a single isomer. This result implies that the diastereomers of **6-P** must be caused by the sulfoxide stereogenic center. We treated **6-L** (a mixture of two diastereomers) with *i*-PrMgCl under the same conditions to give the desulfinylated product **8-L** in the same yield. The product **8-L** was again a single isomer, which is the diastereomer of **8-P**. In order to determine the stereochemistry of **8-P** and **8-L**, NOESY spectum of both compounds was measured. From a detailed inspection of the spectra, we were able to determine the unambiguous structure of **8-P** and **8-L** as shown in Scheme 3. At the same time the stereochemistry of the 1-chlorocyclopropyl phenyl sulfoxides **6-P** and **6-L** was determined.

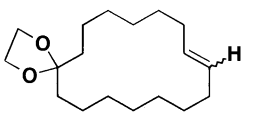
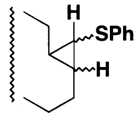
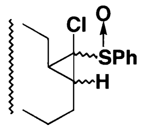
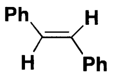
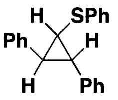
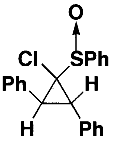
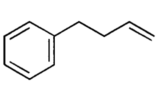
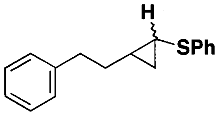
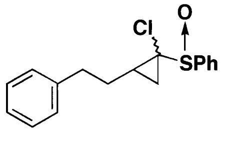
To ascertain the stability of the carbenoid **7-P**, the reaction mixture was stirred at −78°C for 1 h and the reaction was quenched with CD_3OD (Table 1, entry 7). The result was almost the same as that of entry 6. The reaction temperature was slowly allowed to warm to −60°C over 1 h (entry 8). In addition, the reaction was further left to stand at −60°C for 3 h (entry 9). Both reactions showed the same chemical yield and deuterium content within experimental error. By our study, for the first time, the magnesium cyclopropylidenes have been found to be stable at below −60°C for at least 3 h.

In detailed inspection of the ^{1}H NMR spectra of the product from the experiments in Table 1 (entrie 5, 8, and 9), especially entry 9, we noticed that the product from **6-P** was a mixture of **8-P** and **8-L** (**8-P**:**8-L**=5:2; see Scheme 3). We treated the 1-chlorocyclopropyl phenyl sulfoxide **6-L** with *i*-PrMgCl under the same conditions as for **6-P** and the results are shown in the table in Scheme 3. From the results in the table, we concluded that the configurational stability of the magnesium cyclopropylidenes **7-P** and **7-L** is high at below −60°C; however, the pyramidal inversion of the carbenoid also slowly takes place at −60°C.

As the chemical yield and the deuterium incorporation of the sulfoxide–magnesium exchange reaction of **6** with EtMgCl and *i*-PrMgCl were not satisfactory, we investigated this reaction further with other Grignard reagents. Treatment of **6-P** with PhMgCl in THF at −78°C for 5 min gave mainly the starting material with a trace of chlorocyclopropane **8-P** (Table 1, entry 10). Entries 10, 11 and 12 show that **6-P** hardly reacts with PhMgCl at −78°C. The reaction temperature was then allowed to warm to −60°C for 1 h, and we found that **6-P** reacted with PhMgCl to give the desulfinylated product **8-P** in 23% yield (entry 13). This result indicated that the sulfoxide–metal exchange reaction of **6-P** with PhMgCl took place at about −60°C. The reaction mixture was further stirred at −60°C for 6 h, and then the reaction was quenched with CD_3OD (entry 14). The chemical yield of the obtained cyclopropane **9** was quite high and the deuterium incorporation was found to be perfect.

The reaction mixture was further allowed to warm to −50°C (entries 15 and 16). These experiments gave the chlorocyclopropanes **8** and **9**; however, the formation of allene **10** was observed in 9% yield. From these experiments described above, we concluded that the produced magnesium cyclopropylidene **7-P** slowly rearranges to give allene

Table 2. Synthesis of 1-chlorocyclopropyl phenyl sulfoxides from olefins through cyclopropyl phenyl sulfides

Entry	Olefin	Cyclopropyl Phenyl Sulfide	1-Chlorocyclopropyl Phenyl Sulfoxide
		Yield / %	Yield / %
1	 (*E*/*Z* mixture)	 **12** 65 (93)[a)]	 **15** 94
2		 **13** 88 (96)[a)]	 **16** 99
3		 **14** 63 (93)[a)]	 **17** 99

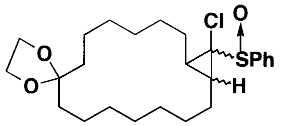
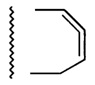
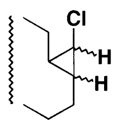
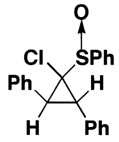
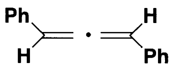
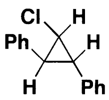
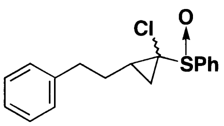
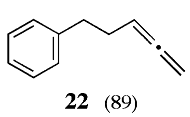
[a] The yield in parentheses is the conversion yield.

at above −50°C. As the chemical yield and deuterium incorporation of the cyclopropane **9** was better when PhMgCl was used instead of EtMgCl or *i*-PrMgCl, we used PhMgCl throughout the studies described below. When this reaction was carried out at 0°C, the allene **10** was obtained in good yield (entries 17 and 18). The magnesiumcyclopropylidenes have been thought to be the intermediates of the reaction of dibromocyclopropanes with magnesium to give allenes. The results described above further support this assumption. It is interesting to note that in these cases phenylated cyclopropane **11** was obtained in low yield.

1.2. A synthesis of allenes from olefins via a sulfoxide version of the Doering–Moore–Skattebol reaction

To extend the chemistry described above to a new method for the synthesis of allenes from olefins with one-carbon

Table 3. Reaction of 1-chlorocyclopropyl phenyl sulfoxides with 2.5 equivalents of PhMgCl under several conditions

Entry	1-Chlorocyclopropyl Phenyl Sulfoxide	Conditions	Products (Yield / %)	
1	 **15**	-78 °C - -30 °C, 70 min	 **18** (25)	 **19** (47)
2		0 °C, 10 min	**18** (82)	**19** (trace)
3	 **16**	-78 °C - -30 °C, 70 min	 **20** (26)	 **21** (65)
4		0 °C, 10 min	**20** (89)	**21** (trace)
5	 **17**	0 °C, 10 min	 **22** (89)	

elongation, three 1-chlorocyclopropyl phenyl sulfoxides were synthesized from the corresponding olefins in good overall yields. As shown in Table 2, cyclohexadecenone derivatives, *trans*-stilbene, and 4-phenyl-1-butene gave the desired cyclopropyl phenyl sulfides **12–14** in good yields. The chlorination and the oxidation of the sulfides gave the 1-chlorocyclopropyl phenyl sulfoxides **15–17** in almost quantitative yields without any problem.

Next, these 1-chlorocyclopropyl phenyl sulfoxides **15–17** were treated with 2.5 equivalents of PhMgCl (Table 3). When the reaction was quenched at below −30°C considerable amounts of chlorocyclopropanes **19** and **21** were obtained. These results show that the rearrangement of the carbenoids to the allenes was somewhat slow at below −30°C (entries 1 and 3). Treatment of these three sulfoxides with PhMgCl at 0°C for 10 min gave the desired allenes **18**, **20**, and **22** in good to high yields (entries 2, 4, and 5).

In conclusion, we were able to generate, for the first time, the magnesium cyclopropylidenes from 1-chlorocyclopropyl phenyl sulfoxides by the sulfoxide–magnesium exchange. The carbenoids were found to be stable at below −60°C for several hours. By this chemistry a new and reliable strategy for the synthesis of allenes from olefins was established.

2. Experimental

2.1. General

^{1}H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from benzophenone ketyl.

2.1.1. 1-(2-(4-Methoxyphenyl)ethyl)-1-methyl-2-(phenylsulfenyl)cyclopropane (5). A 50% aqueous NaOH solution (5 ml) was added to a solution of **4** (1.56 g, 8.85 mmol) and chloromethyl phenyl sulfide (1.82 g, 11.5 mmol) and benzyltriethylammonium chloride (203 mg, 0.89 mmol) in CH_2Cl_2 (3 ml) and the solution was vigorously stirred at room temperature for 24 h. The reaction was quenched by adding saturated aqueous NH_4Cl and the solution was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was evaporated to give an oil, which was purified by silica gel column chromatography to afford 1.77 g (66%, conversion yield 94%) of **5** and 462 mg (30%) of the starting olefin **4**. **5**: Colorless oil (about 5:1 diastereomeric mixture); IR (neat) 1513, 1245, 1037, 738 cm^{-1}; ^{1}H NMR δ 0.51 (1H, t, *J*=5.0 Hz), 1.00 (1H, dd, *J*=8.4, 5.0 Hz), 1.27 (2.5H, s), 1.29 (0.5H, s), 1.51 (1H, m), 1.81 (1H, m), 2.09 (1H, dd, *J*=8.4, 5.0 Hz), 2.57–2.76 (2H, m), 3.76 (0.5H, s), 3.79 (2.5H, s), 6.77–7.31 (9H, m). MS *m/z* (%) 298 (M^+, 23), 189 (44), 135 (20), 121 (100). Calcd for $C_{19}H_{22}OS$: M, 298.1390. Found: *m/z* 298.1397.

2.1.2. 8,8-Ethylenedioxy-17-(phenylsulfenyl)bicyclo[14.1.0]heptadecane (12). Colorless oil (*E,Z*, *endo,exo* mixture): IR (neat) 2925, 2854, 1585, 1479, 1457, 1439, 1077 cm^{-1}; ^{1}H NMR δ 0.67–1.08 (2H, m), 1.19–1.75 (25H, m), 1.97–2.08 (2H, m), 3.86–3.94 (4H, m), 7.10 (1H, t, *J*=7.4 Hz), 7.24–7.34 (4H, m). MS *m/z* (%) 402 (M^+, 79), 293 (100), 99 (50). Calcd for $C_{25}H_{38}O_2S$: M, 402.2592. Found: *m/z* 402.2604.

2.1.3. *trans*-2,3-Diphenyl-1-(phenylsulfenyl)cyclopropane (13). Colorless oil: IR (neat) 1600, 1582, 1496, 1478, 1093, 1026, 757, 732, 698 cm^{-1}; ^{1}H NMR δ 2.70 (1H, t, *J*=5.5 Hz), 2.94 (1H, dd, *J*=8.3, 5.5 Hz), 2.97 (1H, dd, *J*=8.3, 5.5 Hz), 7.06–7.37 (15H, m). MS *m/z* (%) 302 (M^+, 0.2), 193 (100), 178(18), 115 (69). Calcd for $C_{21}H_{18}S$: M, 302.1128. Found: *m/z* 302.1118.

2.1.4. 1-(2-Phenylethyl)-2-(phenylsulfenyl)cyclopropane (14). Colorless oil (single isomer): IR (neat) 1584, 1495, 1479, 1438, 1283, 1089, 1026, 739, 699 cm^{-1}; ^{1}H NMR δ 0.39 (1H, dt, *J*=6.1, 5.0 Hz), 1.19–1.32 (2H, m), 1.78(1H, m), 1.90 (1H, m), 2.33 (1H, dt, *J*=7.7, 5.0 Hz), 2.67 (2H, t, *J*=7.8 Hz) 7.10–7.37 (10H, m). MS *m/z* (%) 254 (M^+, 30), 145 (50), 144 (48), 109 (22), 91 (100). Calcd for $C_{17}H_{18}S$: M, 254.1127. Found: *m/z* 254.1127.

2.1.5. 1-Chloro-2-(2-(4-methoxypheny)ethyl)-2-methyl-1-(phenylsulfinyl)cyclopropane (6). A solution of **5** (567 mg, 1.9 mmol) in CCl_4 (8 ml) was stirred with *N*-chlorosuccinimmide (NCS) (330 mg, 2.47 mmol) at room temperature for 20 h. The precipitate was filtered off and the solvent was evaporated to give an oil. To a solution of the oil in CH_2Cl_2 (10 ml) was added *m*-chloroperbenzoic acid (515 mg, 2.09 mmol) at −50°C. The reaction mixture was stirred and allowed to warm to −30°C for over 1 h. After being stirred for 30 min at −30°C the reaction was quenched by adding 5% NaOH and the solution was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was evaporated to give an oil, which was purified by silica gel column chromatography to afford 280 mg (42%) of less polar products **6-L**, and 319 mg (48%) of more polar products **6-P**. **6-L:** Colorless oil (a mixture of two diastereomers): IR (neat) 1513, 1244, 1088, 1059, 1036 (SO), 747 cm^{-1}; ^{1}H NMR δ 1.14 (0.5H, d, *J*=7.0 Hz), 1.23 (0.5H, d, *J*=7.0 Hz), 1.42 (1.5H, s), 1.45 (0.5H, d, *J*=7.0 Hz), 1.48 (1.5H, s), 1.90 (0.5H, d, *J*=7.0 Hz), 2.04–2.26 (2H, m), 2.70–3.00 (2H, m), 3.80 (3H, s), 6.84–6.87 (2H, m), 7.14–7.19 (2H, m), 7.50–7.53 (3H, m), 7.64∼7.67 (2H, m). MS *m/z* (%) 348 (M^+, 2), 331 (14), 121 (100). Calcd for $C_{19}H_{21}ClO_2S$: M, 348.0951. Found: *m/z* 348.0962. **6-P:** Colorless oil (a mixture of two diastereomers): IR (neat) 1513, 1244, 1094, 1057, 1036 (SO), 750 cm^{-1}; ^{1}H NMR δ 1.15 (0.3H, d, *J*=7.0 Hz), 1.36 (0.7H, d, *J*=7.0 Hz), 1.51 (0.3H, d, *J*=7.0 Hz), 1.65 (2H, s), 1.69 (1H, s), 1.73–1.87 (1H, m), 1.89 (0.7H, d, *J*=7.0 Hz), 1.94–2.03 (1H, m), 2.42–2.83 (2H, m), 3.76 (2H, s), 3.78(1H, s), 6.78–6.82 (2H, m), 7.01–7.10 (2H, m), 7.52–7.56 (3H, m), 7.67–7.71 (2H, m). MS *m/z* (%) 348 (M^+, 2), 187 (9), 121 (100). Calcd for $C_{19}H_{21}ClO_2S$: M, 348.0948. Found: *m/z* 348.0944.

2.1.6. 17-Chloro-8,8-ethylenedioxy-17-(phenylsulfinyl)bicyclo[14.1.0]heptadecane (15). Colorless amorphous

(*E*,*Z*, *endo*,*exo* mixture): IR (neat) 1455, 1444, 1088, 1058 (SO) cm^{-1}; ^{1}H NMR δ 1.18–2.31 (28H, m), 3.90–3.94 (4H, m), 7.51–7.71 (5H, m). MS *m/z* (%) 452 (M$^+$, 3), 327 (100), 291 (9). Calcd for $C_{25}H_{37}ClO_3S$: M, 452.2152. Found: *m/z* 452.2163.

2.1.7. 1-Chloro-2,3-diphenyl-1-(phenylsulfinyl)cyclopropane (16). Colorless amorphous (about 1:1 mixture of two diastereomers): IR (neat) 1603, 1498, 1445, 1090, 1056 (SO), 755, 697 cm^{-1}; ^{1}H NMR δ 3.34 (0.5H, d, *J*=9.0 Hz), 3.40 (0.5H, d, *J*=8.3 Hz), 3.55 (0.5H, d, *J*=8.3 Hz), 4.07 (0.5H, d, *J*=9.0 Hz), 6.98–7.75 (15H, m). MS *m/z* (%) 353 (M$^+$, 0.2), 227 (32), 191 (74), 149 (100). Calcd for $C_{21}H_{18}ClOS$: M, 353.0766. Found: *m/z* 353.0758.

2.1.8. 1-Chloro-2-(2-phenylethyl)-1-(phenylsulfinyl)cyclopropane (17). Colorless oil (a mixture of diastereomers): IR (neat) 1496, 1444, 1089, 1056 (SO), 747, 698 cm^{-1}; ^{1}H NMR δ 1.02–1.04 (1H, m), 1.63–1.70 (1H, m), 1.64–1.95 (4H, m), 2.35–2.46 (2H, m), 7.07–7.30 (5H, m), 7.50–7.71 (5H, m). MS *m/z* (%) 304 (M$^+$, 1.7), 143 (16), 126 (25), 91 (100). Calcd for $C_{17}H_{17}ClOS$: M, 304.0688. Found: *m/z* 304.0688.

2.1.9. (1*S,2*S**)-1-Chloro-2-(2-(4-methoxyphenyl)ethyl)-2-methylcyclopropane (8-P).** A solution of **6-P** (70 mg, 0.2 mmol) in 1 ml of dry THF was added dropwise with stirring to a solution of *i*-PrMgCl (2.0 mol/l in THF, 0.25 ml, 0.5 mmol) in dry THF (1 ml) in a flame-dried flask at −78°C. After being stirred for 5 min, the reaction was quenched by adding saturated aqueous NH_4Cl and the solution was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and the solvent was evaporated to give an oil, which was purified by silica gel column chromatography to afford 36.7 mg (82%) of **8-P**. Colorless oil: IR(neat) 1612, 1513, 1463, 1301, 1247, 1176, 1038, 821 cm^{-1}; ^{1}H NMR δ 0.58 (1H, dd, *J*=6.1, 4.0 Hz), 0.86 (1H, dd, *J*=7.4, 6.1 Hz), 1.12 (3H, s), 1.71–1.77 (1H, m), 1.80–1.86 (1H, m), 2.61–2.67 (1H, m), 2.74–2.80 (1H, m), 2.92 (1H, dd, *J*=7.4, 4.0 Hz), 3.79 (3H, s), 6.83 (2H, d, *J*=8.6 Hz), 7.13 (2H, d, *J*=8.6 Hz). MS *m/z* (%) 224 (M$^+$, 10), 121 (100). Calcd for $C_{13}H_{17}ClO$: M, 224.0966. Found: *m/z* 224.0956.

2.1.10. (1*R,2*S**)-1-Chloro-2-(2-(4-methoxyphenyl)ethyl)-2-methylcyclopropane (8-L).** Colorless oil: IR (neat) 1612, 1513, 1455, 1301, 1246, 1177, 1037, 820 cm^{-1}; ^{1}H NMR δ 0.55 (1H, dd, *J*=6.1, 4.0 Hz), 0.86 (1H, dd, *J*=7.7, 6.1 Hz), 1.29 (3H, s), 1.49–1.53 (2H, m), 2.63 (2H, t, *J*=8.2 Hz), 2.84 (1H, dd, *J*=7.7, 4.0 Hz), 3.78(3H, s), 6.81 (2H, d, *J*=8.4 Hz), 7.06 (2H, d, *J*=8.4 Hz). MS *m/z* (%) 224 (M$^+$, 9), 121(100). Calcd for $C_{13}H_{17}ClO$: M, 224.0967. Found: *m/z* 224.0968.

2.1.11. (1*S,2*S**)-1-Chloro-1-deuterio-2-(2-(4-methoxyphenyl)ethyl)-2-methylcyclopropane (9).** Colorless oil: IR (neat) 1612, 1513, 1465, 1301, 1244, 1176, 1037, 820 cm^{-1}; ^{1}H NMR δ 0.58 (1H, d, *J*=6.1 Hz), 0.85 (1H, d, *J*=6.1 Hz), 1.12 (3H, s), 1.71–1.77 (1H, m), 1.80–1.86 (1H, m), 2.61–2.67 (1H, m), 2.74–2.80 (1H, m), 3.79 (3H, s), 6.83 (2H, d, *J*=8.6 Hz), 7.13 (2H, d, *J*=8.6 Hz). MS *m/z* (%) 225 (M$^+$, 10), 121 (100). Calcd for $C_{13}H_{16}DClO$: M, 225.1030. Found: *m/z* 225.1035.

2.1.12. 3-Methyl-5-(4-methoxyphenyl)-1,2-pentadiene (10). A solution of **6-P** (70 mg, 0.2 mmol) in 1 ml of dry THF was added to a solution of PhMgCl (2.0 mol/l in THF, 0.25 ml, 0.5 mmol) in 1 ml of dry THF at 0°C. The reaction mixture was stirred at 0°C for 10 min, then the reaction was quenched with saturated aqueous NH_4Cl and the whole was extracted with ethyl acetate. The extract was dried over $MgSO_4$ and the solvent was evaporated to give an oil, which was purified on silica gel column chromatography to give **10** (31 mg, 82%) and **11** (7.7 mg, 14%). **10**: Colorless oil: IR (neat) 1959 (allene), 1612, 1513, 1246, 1177, 1038 cm^{-1}; ^{1}H NMR δ 1.71 (3H, t, *J*=3.1 Hz), 2.17–2.22 (2H, m), 2.65–2.69 (2H, m), 3.78(3H, s), 4.61 (2H, sextet, *J*=3.2 Hz), 6.82 (2H, d, *J*=8.8 Hz), 7.11 (2H, d, *J*=8.8 Hz). MS *m/z* (%) 188 (M$^+$, 26), 173 (25), 121 (100). Calcd for $C_{13}H_{16}O$: M, 188.1199. Found: *m/z* 188.1195. 1-(2-(4-Methoxyphenyl)ethyl)-1-methyl-2-phenylcyclopropane **11:** Colorless oil (about 1:1 mixture of two diastereomers): IR (neat) 1612, 1512, 1455, 1300, 1245, 1177, 1037 cm^{-1}; ^{1}H NMR δ 0.74–0.90 (2H, m), 0.83 (1.5H, s), 1.25–1.32 (1H, m), 1.28 (1.5H, s), 1.57–1.80 (1H, m), 1.89–1.97 (1H, m), 2.36–2.49 (1H, m), 2.73 (1H, m), 3.73 (1.5H, s), 3.80 (1.5H, s), 6.68–6.85 (3H, m), 7.10–7.28 (6H, m). MS *m/z* (%) 266 (M$^+$, 25), 161 (23), 131 (12), 121 (100). Calcd for $C_{19}H_{22}O$: M, 266.1668. Found: *m/z* 266.1660.

2.1.13. 10,10-Ethylenedioxy-1,2-cycloheptadecadiene (18). Colorless oil: IR (neat) 1961 (allene), 1456, 1121, 1076 cm^{-1}; ^{1}H NMR δ 1.25–1.58 (22H, m), 1.85–2.10 (4H, m), 3.91 (4H, s), 5.03–5.15 (2H, m). MS *m/z* (%) 292 (M$^+$, 10), 209 (12), 155 (25), 99 (100). Calcd for $C_{19}H_{32}O_2$: M, 292.2401. Found: *m/z* 292.2407.

2.1.14. 17-Chloro-8,8-Ethylenedioxybicyclo[14.1.0]heptadecane (19). Colorless oil (*E*,*Z*, *endo*,*exo* mixture): IR (neat) 1459, 1351, 1272, 1199, 1127, 1077 cm^{-1}; ^{1}H NMR δ 0.67–0.75 (2H, m), 1.09–2.54 (26H, m), 2.83–2.87 (1H, m), 3.91–3.92 (4H, m). MS m/z (%) 328 (M$^+$, 1.5), 293 (22), 292 (22), 99 (100). Calcd for $C_{19}H_{33}ClO_2$: M, 328.2166. Found: *m/z* 328.2160.

2.1.15. 1,3-Diphenyl-1,2-propadiene (20). Colorless oil: IR(neat) 1936 (allene), 1596, 1492, 1450, 1256, 1072, 1028, 793, 758, 720 cm^{-1}; ^{1}H NMR δ 6.58 (2H, s), 7.20–7.36 (10H, m). MS *m/z* (%) 192 (M$^+$, 100), 191 (80), 115 (15), 77 (27). Calcd for $C_{15}H_{12}$: M, 192.0938. Found: *m/z* 192.0949.

2.1.16. 1-Chloro-2,3-diphenylcyclopropane (21). Colorless oil: IR (neat) 1601, 1496, 1450, 1293, 1027, 758, 742, 697 cm^{-1}; ^{1}H NMR δ 2.70–2.76 (2H, m), 3.60 (1H, dd, *J*=7.4, 4.4 Hz), 7.20–7.40 (10H, m). MS *m/z* (%) 228 (M$^+$, 0.3), 193 (100), 115 (77), 91 (19). Calcd for $C_{15}H_{13}Cl$: M, 228.0705. Found: *m/z* 228.0700.

2.1.17. 5-Phenyl-1,2-pentadiene (22). Colorless oil: IR (neat) 1955 (allene), 1603, 1496, 1454, 843, 698 cm^{-1}; ^{1}H NMR δ 2.22–2.35 (2H, m), 2.73 (2H, t, *J*=7.8 Hz), 4.66 (1H, t, *J*=3.2 Hz), 4.68 (1H, t, *J*=3.2 Hz), 5.15 (1H, quint, *J*=6.6 Hz), 7.17–7.30 (5H, m). MS *m/z* (%) 144 (M$^+$, 35), 129 (79), 91 (100). Calcd for $C_{11}H_{12}$: M, 144.0938. Found: *m/z* 144.0930.

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