Reaction of Magnesium Alkylidene Carbenoids with Lithium α-Sulfonyl Carbanions: A Novel Synthesis of Tri- and Tetra-substituted Allenes from 1-Chlorovinyl *p*-Tolyl Sulfoxides and Sulfones

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Treatment of 1-chlorovinyl *p*-tolyl sulfoxides, which were synthesized from ketones and chloromethyl *p*-tolyl sulfoxide, with ethylmagnesium chloride or isopropylmagnesium chloride at below −78 °C gave magnesium alkylidene carbenoids in about 90% yields. The reaction of the generated carbenoids with lithium α-sulfonyl carbanions was found to afford tri- and tetra-substituted allenes. Both cyclic ketones and acyclic ketones were useful in this procedure. However, the 1-chlorovinyl *p*-tolyl sulfoxides derived from aldehydes gave only rearranged products, acetylenes, under the reaction conditions. The magnesium alkylidene carbenoid derived from an optically active 1-chlorovinyl *p*-tolyl sulfoxide was treated with lithium α-carbanion of 1-naphthyl phenyl sulfone; however, the obtained allene was found to be racemic. The mechanism of this reaction is also discussed.

Key words allene; magnesium alkylidene carbenoid; sulfoxide; sulfoxide-magnesium exchange; sulfone

Allenes, characterized by a 1,2-diene structure, are quite interesting and important compounds in organic and synthetic organic chemistry, and a large number of studies have been reported on their chemistry and synthesis.[1—5] Moreover, allenes have axial chirality so that unsymmetrically substituted allenes should exist in two enantiomeric forms. The allene functionality shows a high degree of reactivity toward a wide variety of reactions and many allenes are used as intermediates in synthetic pathways.[6—9]

The general methods for the synthesis of allenes are: reaction of allenyl anions with electrophiles,[3] rearrangement of propargyl derivatives,[10—12] ring-opening of cyclopropylidenes (Doering–Moor–Skattebol reaction),[13—17] reaction of propargylic derivatives with organocopper reagents,[18—21] and β-elimination of olefins.[22—27] Recently, the synthesis and reactions of chiral allenes have been received considerable attention.[28—33]

We previously reported the generation of magnesium alkylidene carbenoids **4**[34] from 1-chlorovinyl *p*-tolyl sulfoxides **3** by sulfoxide-magnesium exchange reaction and an application of the methodology to a new synthesis of tetra-substituted alkenes.[34] In continuation of our interest on the use of the magnesium alkylidene carbenoids[35] generated by the sulfoxide-metal exchange reaction[36,37] in organic synthesis, we investigated the reaction of carbenoids **4** with some carbanions and found that lithium α-sulfonyl carbanions **5** gave allenes **6** in moderate to good yields (Chart 1). This procedure offers a novel method for synthesis of tri- and tetra-substituted allenes **6** from three components, ketones **1**, chloromethyl *p*-tolyl sulfoxide **2**, and sulfones **5**, in relatively short steps. In this paper we report, in detail, the above-mentioned reaction. The scope and limitation, and the mechanism of this procedure are also discussed.[38]

Results and Discussion

Generation of Magnesium Alkylidene Carbenoids, Their Stability, and the Reaction with Lithium α-Sulfonyl Carbanions As mentioned above, we reported the generation of magnesium alkylidene carbenoids **4** from 1-chlorovinyl *p*-tolyl sulfoxides **3** with a Grignard reagent.[34] In continuation of our study on the use of the magnesium alkylidene carbenoids in new synthetic methods, we first had to reinvestigate and establish a reliable method for generation of **4** and know the stability of the carbenoids (Table 1).

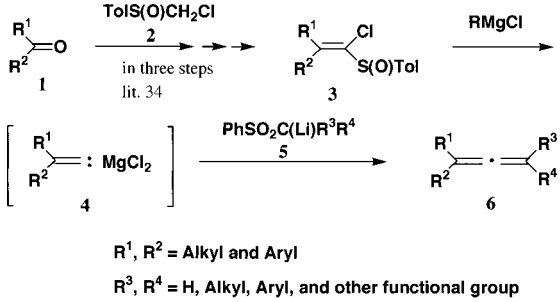
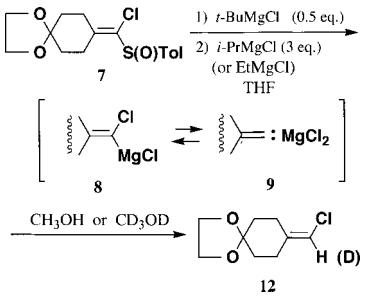


Chart 1

Table 1. Conditions for the Generation of the Magnesium Alkylidene Carbenoids (**8**, **9**) and Their Stability



Entry	Conditions	12 Yield/%
1	−78 °C 1 min	88[a]
2	−78 °C 30 min	87[a]
3	−70 °C 5 min	68
4	−65 °C 5 min	54
5	−50 °C 5 min	0[b]

a) When this reaction was quenched with CD_3OD deuterated **12** (over 90% deuterium incorporation) was obtained. *b*) A complex mixture.

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In order to remove a trace of moisture from the reaction mixture, *t*-BuMgCl (0.5 eq) was added to a solution of **7** (1 eq) in THF and after 10 min, *i*-PrMgCl or EtMgCl (3 eq) was added dropwise to the reaction mixture at the temperature shown in Table 1. It should be noted that the *t*-BuMgCl does not react at all with the vinylsulfoxide **7** even at room temperature; however, *i*-PrMgCl reacts with **7** at −78 °C even in the presence of the trace of moisture. Also note that *i*-PrMgCl and EtMgCl had been found to be equally effective in this sulfoxide–magnesium exchange reaction. The reaction was quenched with CH_3OH or CD_3OD and the yield of the produced vinylchloride **12**[34] and the rate of deuterium incorporation were measured. From these values the efficacy of the sulfoxide–magnesium exchange reaction and the stability of the generated magnesium alkylidene carbenoid (**8**, **9**) were evaluated.

As shown in entry 1, Table 1, quite rapid reaction took place within 1 min to afford the magnesium carbenoid in high yield and the protonation of the carbenoid was suppressed to less than 10%. The reaction mixture was allowed to stand at −78 °C for 30 min (entry 2). The result showed that the generated carbenoid was stable at below −78 °C for at least 30 min. When this reaction was carried out at −70 °C marked decrease of the yield of **12** was observed, and at −65 °C the yield was found to be about 50%. At −50 °C, the reaction gave a complex mixture. These results indicated that the carbenoid was fairly unstable at over −70 °C.

With a general method for the formation of the magnesium alkylidene carbenoid and the perception of its stability in hand, we next examined the reaction of the carbenoid with some carbon nucleophiles and found that the reaction with lithium α-sulfonyl carbanions gave allenes (Chart 2).

First, the magnesium alkylidene carbenoid (**8**, **9**)[34] was generated from **7** with EtMgCl as above at −78 °C and to this carbenoid a solution of the lithium α-sulfonyl carbanion **10** (3 eq) derived from benzyl phenyl sulfone with *n*-BuLi was added through a canula, and the temperature of the reaction mixture was gradually allowed to warm to room temperature. We obtained a crystalline compound which showed sharp absorption at 1954 cm^{-1} in the IR spectrum. Other spectral data showed that the product was the allene **13a**. We propose a plausible mechanism of this reaction as shown in Chart 2. First, the lithium α-sulfonyl carbanion **10** attacks the electron-deficient carbenoid carbon of **9** to give the vinyl anion **11**. As the sulfonyl group is a good leaving group, β-elimination takes place to afford the allene **13a**. This mechanism was further supported by other experiments described below.

The reaction of the magnesium alkylidene carbenoid with the lithium α-sulfonyl carbanion was found to take place

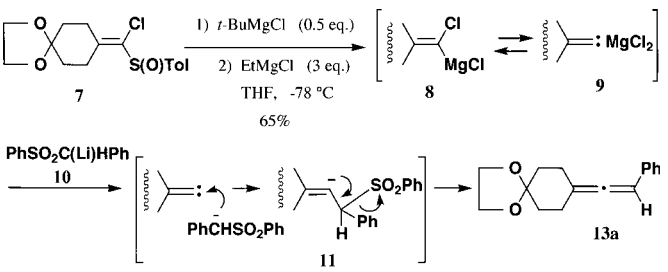


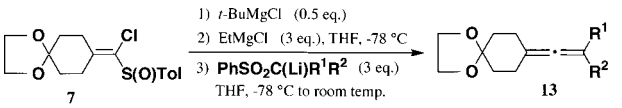
Chart 2

quite fast even at −78 °C within 10 min. However, for technical reasons, the reaction mixture was allowed to warm to room temperature and was quenched with sat. aq. NH_4Cl.

We next investigated this reaction using various kinds of sulfones, and the results are summarized in Table 2. The result in entry 1 has been described above. The results in entries 2 to 4 are quite interesting. In contrast to the result with benzyl phenyl sulfone (entry 1), the α-sulfonyl carbanion having a hydrogen or an alkyl group as R^1 gave low yield (entry 3) or a complex mixture (entries 2, 4).

One difference between benzyl phenyl sulfone and the sulfones in entries 2 to 4 is the acidity of the hydrogen on the carbon bearing the sulfonyl group. The pK_a values of these hydrogens are estimated to be as follows[39]: $PhSO_2C\underline{H}_2Ph$ (23.4), $PhSO_2C\underline{H}_3$ (29), $PhSO_2C\underline{H}_2CH_3$ (31), $PhSO_2C\underline{H}_2SPh$ (20.3), $PhSO_2C\underline{H}_2CN$ (12.0). These values imply that some carbanion-stabilizing group plays an important role for the reaction of the α-sulfonyl carbanion with the magnesium alkylidene carbenoid. Actually, the sulfones having a carbanion-stabilizing group on the α-carbon gave the desired allenes as shown in entries 5—11, except entries 9 and 11, though the yields were variable. In the cases of entries 9 and 11, it is expected that the lithium α-sulfonyl carbanion having a phenylthio or a cyano group is too stabilized to cause the nucleophilic reaction. It is interesting to note that tetrasubstituted allenes, the synthesis of which is recognized to be

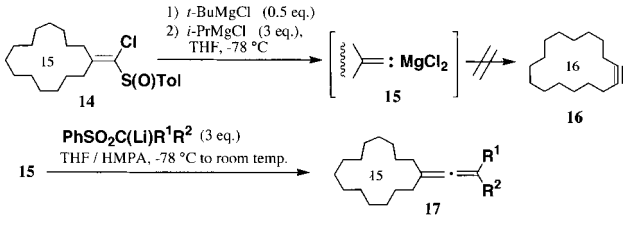
Table 2. Synthesis of Allenes **13** from 1-Chlorovinyl *p*-Tolyl Sulfoxide **7** and Various Lithium α-Sulfonyl Carbanions



Entry	Sulfone R^1	Sulfone R^2	Allene **13**	Yield %
1	Ph	H	13a	65
2	H	H	complex mixture	—
3	CH_3O-C$_6$H$_4$-CH_2CH_2	H	13b	42
4	c-C$_6$H$_{11}$	H	complex mixture	—
5	1-naphthyl	H	13c	51
6	CH_2=CH	H	13d	51
7	C_5H_{11}-C≡C	H	13e	65
8	Ph	Ph	13f	41
9	PhS	H	13g	14[a]
10	$COOCH_3$	CH_3	13h	41[b]
11	CN	H	complex mixture	—

a) The reaction was carried out in the presence of DMPU. *b*) The reaction was carried out in the presence of HMPA.

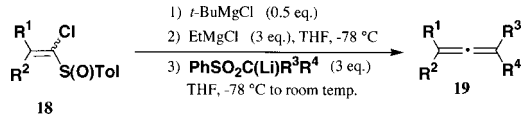
Table 3. Synthesis of Allenes **17** from 1-Chlorovinyl *p*-Tolyl Sulfoxide **14** and Various Lithium α-Sulfonyl Carbanions



Entry	Sulfone		Allene **17**	Yield
	R^1	R^2		%
1	Ph	H	**17a**	54
2		H	**17b**	56
3	Ph	Ph	**17c**	24
4	Ph	CH_3	**17d**	31
5	CH_2=CH—	H	**17e**	61[a]
6	$C_5H_{11}C{\equiv}C$—	H	**17f**	12[b]
7		CH_3	complex mixture	

a) The product of this reaction was a mixture of **17e** and chloro olefin.[34] This yield was calculated from ^{1}H-NMR. *b*) Toluene was used as a solvent and TMEDA was used as an additive.

Table 4. Synthesis of Allenes **19** from 1-Chlorovinyl *p*-Tolyl Sulfoxide **18** and Various Lithium α-Sulfonyl Carbanions



Entry	**18**		Sulfone		Allene **19**	Yield
	R^1	R^2	R^3	R^4		%
1	**18a**	Ph[a]	CH_3[a]	Ph	H	**19a**	40
2	**18a**	Ph[a]	CH_3[a]		H	**19b**	52
3	**18b**	n-C_4H_9[b]	CH_3[b]		H	**19c**	62

a) A mixture of the geometrical isomers was used. *b*) Isolated *Z*-isomer was used.

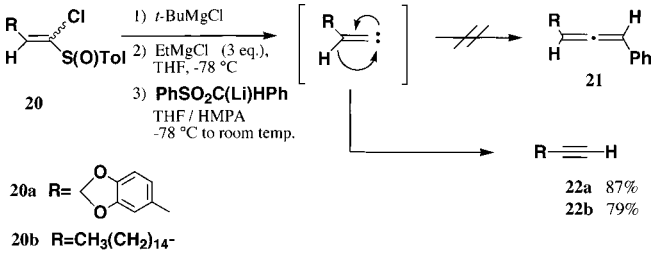


Chart 3

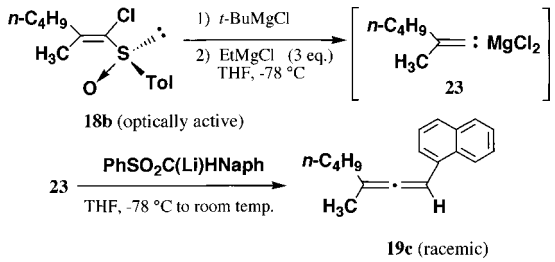


Chart 4

difficult, are also obtained by this method (entries 8, 10).

Table 3 shows the results of the reaction of 1-chlorovinyl *p*-tolyl sulfoxide **14** derived from cyclopentadecanone[34] with some sulfones. We anticipated some problem with the Fritsch–Wiechell rearrangement[40—42] of the intermediate, magnesium alkylidene carbenoid; however, **14** gave allenes **17** in similar yields and no rearranged product, cyclohexadecyne **16**, was observed. In this reaction, *i*-PrMgCl was used as the Grignard reagent and HMPA was used as an additive, except in entry 6.

Table 4 shows the results of the reaction of 1-chlorovinyl *p*-tolyl sulfoxide **18** derived from acyclic ketones (acetophenone and 2-hexanone) with some sulfones. As shown in the table, the 1-chlorovinyl *p*-tolyl sulfoxide derived from acyclic ketones gave tri-substituted allenes **19** in similar yields compared with the 1-chlorovinyl *p*-tolyl sulfoxides derived from cyclic ketones without rearranged acetylene.

The Reaction with the 1-Chlorovinyl *p*-Tolyl Sulfoxides Derived from Aldehydes and the Reaction with an Optically Active 1-Chlorovinyl *p*-Tolyl Sulfoxide Next, we studied this reaction with the 1-chlorovinyl *p*-tolyl sulfoxides (**20a**, **b**) derived from aldehydes, piperonal and hexadecanal (Chart 3). The reaction was conducted in the same way as described above, and we obtained completely different results. By this reaction, acetylenes **22a** and **22b** were obtained in good yields and the desired allenes were not observed at all. These results clearly indicated to us that the Fritsch–Wiechell rearrangement of the β-hydrogen in the magnesium alkylidene carbenoid proceeds faster than the reaction with the α-sulfonyl carbanion. From these results it was understood that we can not synthesize allenes from aldehydes by this procedure.

Finally, we investigated the feasibility of our method for asymmetric synthesis of chiral allenes starting from an optically active 1-chlorovinyl *p*-tolyl sulfoxide (Chart 4). We propose the mechanism of this allene synthesis as shown in Chart 2. If this trial would give a racemic allene, the result would give some support to the proposed mechanism. In any event, optically active 1-chlorovinyl *p*-tolyl sulfoxide **18b** was synthesized from 2-hexanone and *R*-(−)-chloromethyl *p*-tolyl sulfoxide.[43,44]

Optically pure 1-chlorovinyl *p*-tolyl sulfoxide **18b** was first treated with *t*-BuMgCl followed by three equivalents of EtMgCl at −78 °C. After 5 min, lithium α-carbanion of (1-naphthyl)methyl phenyl sulfone was added to the reaction

mixture through a canula and the temperature of the reaction mixture was slowly allowed to warm to room temperature to give the allene. The value of the specific rotation of the produced allene **19c** was found to be zero and the HPLC showed that the allene was totally racemic. From these results, this allene synthesis is quite likely to take place through the magnesium alkylidene carbenoid **23** which has no chiral information from the optical active **18b**.

Experimental

All melting points are uncorrected. ^{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. Silical gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry reagent and solvent, diisopropylamine was distilled from CaH_2 and THF was distilled from diphenylketyl. DMPU, HMPA and TMEDA were dried over $CaSO_4$ and distilled before use. Methanol and liquid N_2 were used for the cooling bath at −100 °C.

1-(2-Phenylvinylidene)-4,4-ethylenedioxycyclohexane (13a) To a solution of **7** (100 mg, 0.31 mmol) in 2.5 ml of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (0.155 mmol) dropwise with stirring. After 10 min, EtMgCl (0.93 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid **9**. Benzyl phenyl sulfone (crystals, 216 mg, 0.93 mmol) was added to a solution of *n*-BuLi (1.12 mmol) in 3 ml of dry THF in another flame-dried flask at 0 °C under argon atmosphere to give yellow clear solution, and this solution was cooled to −78 °C. This solution was added to the solution of the carbenoid **9** through a canula. The temperature of the reaction mixture was gradually allowed to warm to room temperature for 2 h. The reaction was quenched with sat. aq. NH_4Cl and the whole was extracted with $CHCl_3$ and the extract was dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **13a** (49 mg, 65%) as colorless crystals; mp 73—74 °C (AcOEt–hexane). IR (KBr) 2944, 2878, 1954 (allene), 1230, 1117, 1068, 1033, 904, 698, 668 cm^{-1}; ^{1}H-NMR δ 1.81—1.85 (4H, m), 2.34—2.47 (4H, m), 3.99 (4H, s), 6.03 (1H, m), 7.15—7.31 (5H, m). MS *m/z* (%) 242 (M^+, 100), 213 (8), 197 (10), 170 (20), 156 (33), 141 (65), 128 (83). Calcd for $C_{16}H_{18}O_2$: M, 242.1305. Found: *m/z* 242.1313. *Anal.* Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.34; H, 7.42.

1-{2-[2-(4-Methoxyphenyl)ethyl]vinylidene}-4,4-ethylenedioxycyclohexane (13b) Colorless oil; IR (neat) 2949, 1966 (allene), 1612, 1513, 1246, 1118, 1078, 1034, 901 cm^{-1}; ^{1}H-NMR δ 1.70 (4H, octet, *J*=5.6 Hz), 2.20 (4H, dt, *J*=6.4, 1.9 Hz), 2.26 (2H, q, *J*=6.9 Hz), 2.65 (2H, t, *J*=7.6 Hz), 3.78 (3H, s), 3.95 (4H, s), 5.03 (1H, m), 6.82 (2H, d, *J*=8.6 Hz), 7.10 (2H, d, *J*=8.6 Hz). MS *m/z* (%) 300 (M^+, 19), 238 (11), 121 (100). Calcd for $C_{19}H_{24}O_3$: M, 300.1724. Found: *m/z* 300.1713.

1-[2-(1-Naphthyl)vinylidene]-4,4-ethylenedioxycyclohexane (13c) Colorless crystals; mp 78—79 °C (AcOEt–hexane). IR (KBr) 2954, 1949 (allene), 1437, 1231, 1083, 1031, 899, 797 cm^{-1}; ^{1}H-NMR δ 1.86 (4H, t, *J*=6.0 Hz), 2.42—2.51 (4H, m), 3.99 (4H, s), 6.71 (1H, m), 7.40—7.51 (4H, m), 7.71 (1H, d, *J*=8.3 Hz), 7.84 (1H, d, *J*=7.8 Hz), 8.25 (1H, d, *J*=8.1 Hz). MS *m/z* (%) 292 (M^+, 100), 247 (40), 230 (78), 191 (62), 178 (99). Calcd for $C_{20}H_{20}O_2$: M, 292.1462, Found: *m/z* 292.1452. *Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.21; H, 6.91.

1-(2-Ethenylvinylidene)-4,4-ethylenedioxycyclohexane (13d) Yellow oil; IR (neat) 2954, 1951 (allene), 1614, 1442, 1236, 1107, 1071, 1032, 897 cm^{-1}; ^{1}H-NMR δ 1.75 (4H, t, *J*=6.5 Hz), 2.31 (4H, m), 3.97 (4H, s), 4.94 (1H, dq, *J*=10.1, 1.6 Hz), 5.14 (1H, dq, *J*=17.1, 1.6 Hz), 5.72 (1H, d, *J*=8.3 Hz), 6.17 (1H, ddd, *J*=17.1, 10.1, 8.3 Hz). MS *m/z* (%) 192 (M^+, 9), 101 (38), 99 (100), 86 (63). Calcd for $C_{12}H_{16}O_2$: M, 192.1149. Found: *m/z* 192.1159.

1-[2-(1-Heptynyl)vinylidene]-4,4-ethylenedioxycyclohexane (13e) Yellow oil; IR (neat) 2954, 2218 (acetylene), 1955 (allene), 1442, 1241, 1115, 1067, 1032, 942 cm^{-1}; ^{1}H-NMR δ 0.90 (3H, t, *J*=7.1 Hz), 1.27—1.38 (4H, m), 1.50—1.55 (2H, m), 1.69—1.81 (4H, m), 2.27—2.36 (6H, m), 3.97 (4H, s), 5.27 (1H, m). MS *m/z* (%) 260 (M^+, 3), 153 (9), 101 (90), 99 (100). Calcd for $C_{17}H_{24}O_2$: M, 260.1777. Found: *m/z* 260.1766.

1-(2,2-Diphenylvinylidene)-4,4-ethylenedioxycyclohexane (13f) Colorless crystals; mp 106—107 °C (AcOEt–hexane). IR (KBr) 2924, 1950 (allene), 1597, 1488, 1441, 1261, 1120, 1031, 900, 775, 697 cm^{-1}; ^{1}H-NMR δ 1.85 (4H, t, *J*=6.4 Hz), 2.48 (4H, t, *J*=6.4 Hz), 3.99 (4H, s), 7.23—7.33 (10H, m). MS *m/z* (%) 318 (M^+, 97), 232 (50), 217 (100), 202 (53). Calcd for $C_{22}H_{22}O_2$: M, 318.1618. Found: *m/z* 318.1616. *Anal.* Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.85; H, 6.92.

1-(2-Phenylthiovinylidene)-4,4-ethylenedioxycyclohexane (13g) Yellow oil; IR (neat) 2952, 2881, 1953 (allene), 1583, 1439, 1118, 1088, 1032, 903, 742 cm^{-1}; ^{1}H-NMR δ 1.60—1.64 (2H, m), 1.68—1.73 (2H, m), 2.28—2.32 (4H, m), 3.94 (4H, s), 5.83 (1H, m), 7.21—7.41 (5H, m). MS *m/z* (%) 274 (M^+, 27), 165 (36), 99 (100), 86 (50). Calcd for $C_{16}H_{18}O_2S$: M, 274.1028. Found: *m/z* 274.1021.

1-(2-Methoxycarbonyl-2-methylvinylidene)-4,4-ethylenedioxycyclohexane (13h) Colorless oil; IR (neat) 2958, 1965 (allene), 1712, 1696, 1435, 1269, 1119, 1031, 939 cm^{-1}; ^{1}H-NMR δ 1.76—1.81 (4H, m), 1.85 (3H, s), 2.33—2.38 (4H, m), 3.71 (3H, s), 3.98 (4H, s). MS *m/z* (%) 238 (M^+, 42), 179 (17), 99 (45), 86 (100). Calcd for $C_{13}H_{18}O_4$: M, 238.1203. Found: *m/z* 238.1187.

(2-Phenylvinylidene)cyclopentadecane (17a) Colorless oil; IR (neat) 2929, 2857, 1946 (allene), 1598, 1460, 1216, 909, 760 cm^{-1}; ^{1}H-NMR δ 1.37—1.40 (20H, m), 1.50—1.55 (4H, m), 2.12 (4H, dt, *J*=6.8, 2.4 Hz), 6.08 (1H, m), 7.11—7.19 (1H, m), 7.24—7.31 (4H, m). MS *m/z* (%) 310 (M^+, 24), 155 (24), 144 (81), 129 (100), 91 (31). Calcd for $C_{23}H_{34}$: M, 310.2659. Found: *m/z* 310.2659.

[2-(1-Naphthyl)vinylidene]cyclopentadecane (17b) Colorless oil; IR (neat) 3057, 2928, 2856, 1944 (allene), 1460, 771 cm^{-1}; ^{1}H-NMR δ 1.37—1.43 (20H, m), 1.54—1.60 (4H, m), 2.14—2.22 (4H, m), 6.80 (1H, m), 7.42 (1H, t, *J*=7.7 Hz), 7.42—7.51 (2H, m), 7.57 (1H, d, *J*=7.2 Hz), 7.69 (1H, d, *J*=8.3 Hz), 7.83 (1H, d, *J*=7.6 Hz), 8.26 (1H, d, *J*=8.2 Hz). MS *m/z* (%) 360 (M^+, 95), 191 (50), 179 (100), 178 (99), 165 (44). Calcd for $C_{27}H_{36}$: M, 360.2814. Found: *m/z* 360.2806.

(2,2-Diphenylvinylidene)cyclopentadecane (17c) Colorless crystals; mp 48—49 °C (hexane). IR (KBr) 3058, 2928, 2856, 1942 (allene), 1598, 1491, 1455, 767, 695 cm^{-1}; ^{1}H-NMR δ 1.25—1.35 (20H, m), 1.53—1.56 (4H, m), 2.18 (4H, t, *J*=7.0 Hz), 7.21—7.47 (10H, m). MS *m/z* (%) 386 (M^+, 60), 246 (10), 217 (30), 205 (100). Calcd for $C_{29}H_{38}$: M, 386.2972. Found: *m/z* 386.2980. *Anal.* Calcd for $C_{29}H_{38}$: C, 90.09; H, 9.91. Found: C, 89.76; H, 10.02.

(2-Methyl-2-phenylvinylidene)cyclopentadecane (17d) Colorless oil; IR (neat) 2929, 2856, 1946 (allene), 1492, 1459, 1444, 758, 692 cm^{-1}; ^{1}H-NMR δ 1.36—1.54 (24H, m), 2.04—2.16 (4H, m), 2.08 (3H, s), 7.16 (1H, t, *J*=7.5 Hz), 7.30 (2H, t, *J*=7.5 Hz), 7.40 (2H, d, *J*=7.5 Hz). MS *m/z* (%) 324 (M^+, 49), 309 (7), 156 (38), 143 (100). Calcd for $C_{24}H_{36}$: M, 324.2815. Found: *m/z* 324.2817.

(2-Ethenylvinylidene)cyclopentadecane (17e) Colorless oil; IR (neat) 2928, 2857, 1944 (allene), 1614, 1459, 987, 893 cm^{-1}; ^{1}H-NMR δ 1.33—1.48 (24H, m), 1.99—2.07 (4H, m), 4.91 (1H, d, *J*=10.1 Hz), 5.13 (1H, d, *J*=17.1 Hz), 5.77 (1H, d, *J*=10.4 Hz), 6.17 (1H, ddd, *J*=17.1, 10.4, 10.1 Hz). MS *m/z* (%) 260 (M^+, 11), 105 (22), 94 (100). Calcd for $C_{19}H_{32}$: M, 260.2502. Found: *m/z* 260.2503.

[2-(1-Heptynyl)vinylidene]cyclopentadecane (17f) Yellow oil; IR (neat) 2857, 2232 (acetylene), 1942 (allene), 1461, 727 cm^{-1}; ^{1}H-NMR δ 0.90 (3H, t, *J*=7.0 Hz), 1.32—1.55 (30H, m), 2.02 (4H, dt, *J*=10.7, 2.5 Hz), 2.28 (2H, dt, *J*=7.1, 2.1 Hz), 5.29 (1H, m). MS *m/z* (%) 328 (M^+, 7), 224 (36), 72 (77), 55 (99), 41 (100). Calcd for $C_{24}H_{40}$: M, 328.3130. Found: *m/z* 328.3132.

1,3-Diphenyl-1,2-butadiene (19a) Colorless oil; IR (neat) 3027, 1936 (allene), 1597, 1493, 1449, 762, 693 cm^{-1}; ^{1}H-NMR δ 2.23 (3H, d, *J*=2.9 Hz), 6.47 (1H, q, *J*=2.9 Hz), 7.10—7.47 (10H, m). MS *m/z* (%) 206 (M^+, 100), 191 (99), 179 (94), 123 (69), 105 (82), 77 (79). Calcd for $C_{16}H_{14}$: M, 206.1094. Found: *m/z* 206.1095.

1-(1-Naphthyl)-3-phenyl-1,2-propadiene (19b) Yellow oil; IR (neat) 3059, 2922, 1935 (allene), 1493, 774, 693 cm^{-1}; ^{1}H-NMR δ 2.28 (3H, d, *J*=2.6 Hz), 7.17 (1H, d, *J*=2.6 Hz), 7.21—7.88 (11H, m), 8.29 (1H, d, *J*=7.9 Hz). MS *m/z* (%) 256 (M^+, 61), 241 (100), 239 (44), 179 (25). Calcd for $C_{20}H_{16}$: M, 256.1251. Found: *m/z* 256.1253.

1-(1-Naphthyl)-3-methyl-1,2-heptadiene (19c) Colorless oil; IR (neat) 2956, 2929, 1950 (allene), 1591, 1510, 1465, 771 cm^{-1}; ^{1}H-NMR δ 0.89 (3H, t, *J*=7.4 Hz), 1.34—1.41 (2H, m), 1.46—1.56 (2H, m), 1.86 (3H, d, *J*=2.8 Hz), 2.08—2.18 (2H, m), 6.73 (1H, m), 7.40—7.53 (4H, m), 7.69 (1H, d, *J*=8.3 Hz), 7.83 (1H, d, *J*=8.0 Hz), 8.25 (1H, d, *J*=8.3 Hz). MS *m/z* (%) 236 (M^+, 38), 193 (60), 179 (100). Calcd for $C_{18}H_{20}$: M, 236.1563. Found: *m/z* 236.1558.

1-Chloro-2-(2,3-methylenedioxyphenyl)-1-(*p*-tolylsulfinyl)-1-ethene (20a) A solution of **2** (944 mg, 5 mmol) in dry THF (13 ml) was added dropwise to a solution of LDA (5.2 mmol) in 13 ml of THF at −78 °C. The

solution was stirred at −78 °C for 30 min, then a solution of piperonal (826 mg; 5.5 mmol) in 5 ml of THF was added. The reaction mixture was stirred for 30 min and the reaction was quenched with sat. aq. NH_4Cl. The whole was extracted with diethyl ether. The organic layer was washed once with sat. aq. NH_4Cl and the organic layer was dried over $MgSO_4$. The solution was evaporated to leave colorless crystals. The product was purified by column chromatography to give chloro alcohol (1649 mg, 97.4%).

Triethylamine (1.17 ml, 8.4 mmol) and mesyl chloride (0.65 ml, 8.4 mmol) were added to a solution of the chloro alcohol (1355 mg, 4 mmol) in dry CH_2Cl_2 (21 ml) at 0 °C. The solution was stirred for 30 min, and then DBU was added to the solution and the solution was stirred for 30 min at room temperature and the reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with Et_2O–benzene. The organic layer was washed with sat. aq. NH_4Cl and dried over $MgSO_4$. The product was isolated by flash chromatography to give **20a** (1.03 g, 80%) as colorless crystals (about 2 : 1 mixture of two isomers); IR (KBr) 2921, 1622, 1505, 1489, 1447, 1262, 1092, 1083 (SO), 1043, 926, 807 cm^{-1}; ^{1}H-NMR δ 2.42 (3H, s), 6.00, 6.04 (total 2H, each s), 6.84—7.63 (8H, m). MS *m/z* (%) 320 (M^+, 15), 272 (22), 180 (77), 140 (100), 92 (22). Calcd for $C_{16}H_{13}ClO_3S$: M, 320.0273. Found: *m/z* 320.0282. *Anal.* Calcd for $C_{16}H_{13}ClO_3S$: C, 59.91; H, 4.08; S, 10.02; Cl, 11.05. Found: C, 59.96; H, 3.84; S, 10.07; Cl, 11.43.

1-Chloro-1-(*p*-tolylsulfinyl)-1-heptadecene (20b) Colorless oil (about 5 : 4 mixture of two isomers); IR (neat) 2924, 2853, 1466, 1090 (SO), 1064 (SO), 1016, 807 cm^{-1}; ^{1}H-NMR δ 0.88 (3H, t, *J*=6.9 Hz), 1.26—1.57 (26H, m), 2.33 (1H, m), 2.41 (3H, s), 2.53—2.75 (1H, m), 6.30 (0.44H, t, *J*=8.1 Hz, (*E*)-conf.), 6.77 (0.56H, t, *J*=7.3 Hz (*Z*)-conf.), 7.26—7.56 (4H, m). MS *m/z* (%) 410 (M^+, 14), 393 (100), 197 (28), 140 (35). Calcd for $C_{24}H_{39}ClOS$: M, 410.2410. Found: *m/z* 410.2438.

(2,3-Methylenedioxyphenyl)ethyne (22a) Colorless oil; IR (neat) 3294, 2103 (acetylene), 1505, 1488, 1246, 1039, 921 cm^{-1}; ^{1}H-NMR δ 2.96 (1H, s), 5.97 (2H, s), 6.76—7.05 (3H, m). MS *m/z* (%) 146 (M^+, 100), 145 (67), 88 (17), 62 (26). Calcd for $C_9H_6O_2$: M, 146.0367. Found: *m/z* 146.0363.

1-Heptadecyne (22b) Colorless oil; IR (neat) 3314, 2120 (acetylene), 1466, 629 cm^{-1}; ^{1}H-NMR δ 0.88 (3H, t, *J*=6.7 Hz), 1.25—1.40 (24H, m), 1.49—1.55 (2H, m), 1.93 (1H, t, *J*=2.4 Hz), 2.16—2.19 (2H, m). MS *m/z* (%) 236 (M^+, 0.3), 194 (2), 166 (3), 137 (5), 96 (78), 81 (100). Calcd for $C_{17}H_{32}$: M, 236.2504. *m/z* 236.2495.

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