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Reaction of magnesium alkylidene carbenoids with lithium acetylides and lithium thiolates: a novel synthesis of conjugated enynes and vinyl sulfides

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Abstract—Magnesium alkylidene carbenoids were generated from 1-chlorovinyl *p*-tolyl sulfoxides with *i*-PrMgCl at −78 °C in THF or toluene via the sulfoxide–magnesium exchange reaction. Reaction of the generated magnesium alkylidene carbenoids with lithium acetylides or lithium thiolates gave conjugated enynes or vinyl sulfides, respectively, in moderate to good yields. The intermediate of this reaction was found to be the alkenyl anion and it could be trapped with some electrophiles to give tetra-substituted conjugated enynes and vinyl sulfides.

Carbenes and carbenoids are a highly reactive carbon species and are frequently used as useful intermediates in organic synthesis.[1] Alkylidene carbenes and carbenoids are a quite interesting and highly reactive carbon species.[2] The carbenoids generated from alkylhalides or alkenylhalides with alkylmetals, such as alkyllithium or a Grignard reagent by halogen–metal or hydrogen–metal exchange reaction have been known to have both nucleophilic and electrophilic nature,[3] because the carbenoids have the nature of α-halocarbanion and a carbene–metal complex at the same time.

We recently reported generation of magnesium alkylidene carbenoids **2** from 1-chlorovinyl *p*-tolyl sulfoxides **1**, which were synthesized from ketones and chloromethyl *p*-tolyl sulfoxide in three steps in high overall yield, with a Grignard reagent[4] via sulfoxide–magnesium exchange reaction.[5] The reaction of the generated magnesium alkylidene carbenoids **2** with water or benzaldehyde gave chloroolefins **3** (E=H) or the adduct **3** (E=PhCH(OH)).[4] These reactions reveal the nucleophilic nature of the magnesium alkylidene carbenoids **2** (see Scheme 1).

On the other hand, the reaction of the magnesium alkylidene carbenoids **2** with some nucleophiles (such as Grignard reagents[4b] and lithium α-sulfonyl carbanions[6]) gave the adducts, alkenylmetal **4**, from which allenes and tetra-substituted olefins **5**, were obtained.[7] These reactions reveal the electrophilic nature of the magnesium alkylidene carbenoids **2**.

In continuation of our interest in the study of the reactivity of the magnesium alkylidene carbenoids generated from 1-chlorovinyl *p*-tolyl sulfoxides with a Grignard reagent, we investigated the reaction of **2** with lithium acetylides and lithium thiolates and found that the reactions give conjugated enynes **6** and vinyl sulfides **7**, respectively, in moderate to good yields. In this paper the details of the results are reported.

1. Results and discussion

1.1. Generation of the magnesium alkylidene carbenoids and the reaction with lithium acetylides to give conjugated enynes

First, 1-chlorovinyl *p*-tolyl sulfoxide **8** was synthesized from cyclopentadecanone and chloromethyl *p*-tolyl sulfoxide.[8] The vinyl sulfoxide **8** was treated with *tert*-butylmagnesium chloride (0.13 equiv) in THF at −78 °C to remove a trace of moisture in the reaction mixture.[6] To this mixture was added isopropylmagnesium chloride (3 equiv) at −78 °C. The sulfoxide–magnesium exchange reaction took place instantaneously to afford the magnesium alkylidene carbenoid **9** in a quantitative yield.[6] To this solution of the carbenoid **9**, lithium carbanion of 1-hexyne (3 equiv), generated from 1-hexyne with *n*-butyllithium, was added through a cannula and the reaction mixture was

Keywords: Sulfoxides; Sulfoxide–magnesium exchange; Magnesium alkylidene carbenoid; Conjugated enyne; Vinyl sulfide.
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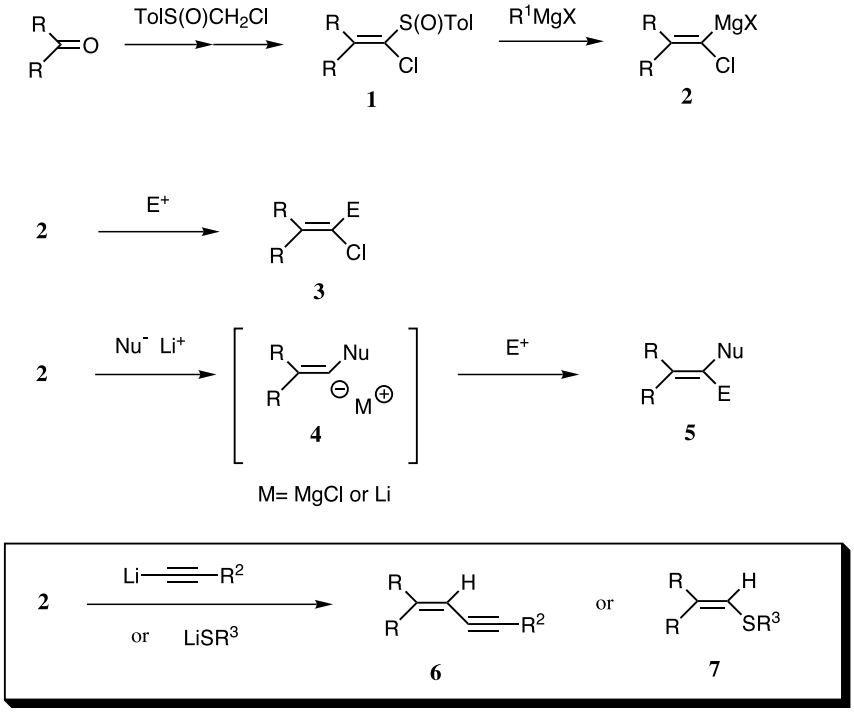
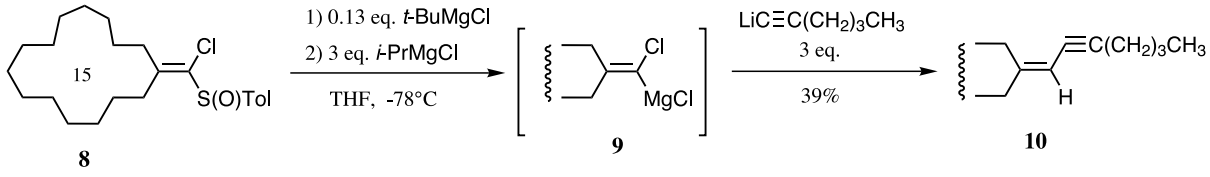


Scheme 1.



Scheme 2.

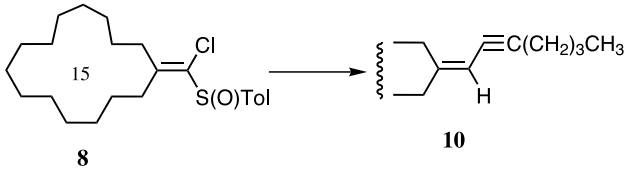
stirred and slowly allowed to warm to room temperature (Scheme 2).

This reaction gave a somewhat complex mixture; however, we obtained interesting compound **10** as a main product in 39% yield. The product **10** showed $C_{22}H_{38}$ as the molecular formula and absorption at 2067 cm^{-1} in its IR spectrum which indicated the presence of a triple bond. ^1H NMR showed one vinyl-H (δ 5.26, singlet). From these data the structure of the product was unambiguously determined to be the conjugated enyne **10**. The chemistry of this result is quite interesting, because the carbon–carbon bond between sp^2 and sp carbons, which is recognized to be very difficult by the ionic reactions, is realized.

We next investigated improvement of the yield of the conjugated enyne **10**, and the results of the examination are summarized in Table 1. Addition of 9 equiv of DMPU or TMEDA as an additive gave disappointing results (entries 2 and 3). Addition of 9 equiv of DME was found to be effective (entry 4) and from this result it was suggested that ethers would give better yield. Use of 1,4-dioxane or cyclopentyl methyl ether (CPME) was found to be effective in this reaction and especially CPME worked to give **10** in 64% yield (entries 5 and 6). 12-Crown-4 showed some effect in this reaction (entry 7). Toluene and CPME itself did not give satisfactory results (entries 8 and 10).

With these improved conditions in hand, we investigated the generality of this reaction and the results are summarized in Table 2. The reaction was carried out under the best conditions mentioned above. Arylacetylenes gave about 40–50% yield of the enyne **11** (entries 1–3). The

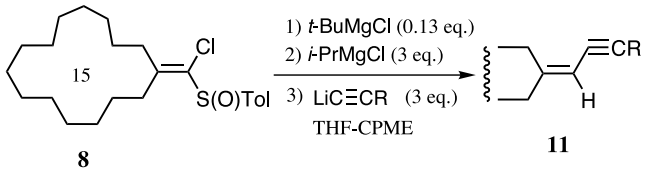
Table 1. Examination of the conditions for the synthesis of enyne **10** from 1-chlorovinyl *p*-tolyl sulfoxide **8**



Entry	Solvent	Additive	Yield of **10** (%)
1	THF	—	39
2	THF	DMPU	14
3	THF	TMEDA	28
4	THF	DME	57
5	THF	1,4-Dioxane	58
6	THF	CPME[a]	63
7	THF	12-Crown-4	50
8	Toluene	—	41
9	Toluene	DME	42
10	CPME	—	52

[a] Cyclopentyl methyl ether. Nine equivalents of CPME was added as an additive.

Table 2. Synthesis of enyne **11** from 1-chlorovinyl *p*-tolyl sulfoxide **8** with some lithium acetylides



8 **11**

Entry	Lithium acetylide		Yield of **11**[a] (%)
1	Li—	**11a**	41
2	Li—OCH$_3$	**11b**	49
3	Li—F	**11c**	38
4	Li—Si(CH$_3$)$_3$	**11d**	16
5	Li—H[b]		Complex mixture
6	ClMg—H[c]	**11e**	24

[a] Isolated yield after silica gel column chromatography.
[b] Lithium acetylide ethylenediamine complex was used.
[c] Five equivalents of ethynylmagnesium chloride was added.

arylacetylene having an electron-donating group (OCH_3) gave better yield compared with that having electron-withdrawing group (F) (entries 2 and 3). Trimethylsilylacetylene gave the desired enyne; however, the yield was found to be low. When lithium acetylide ethylenediamine complex was used as an acetylide, only a complex mixture was obtained (entry 5). However, excess ethynylmagnesium chloride gave the desired enyne **11e** in 24% yield.

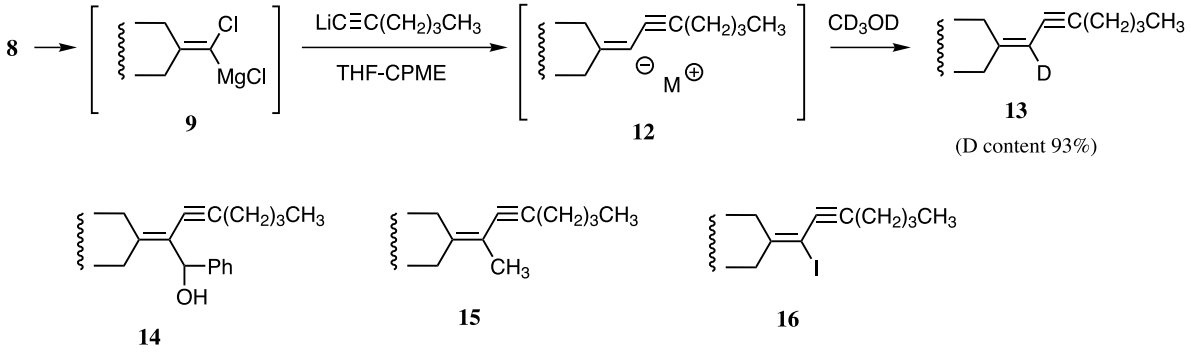
As the intermediate of this reaction is thought to be the alkenyl carbanion **12**,[4,6] we quenched this reaction with CD_3OD and the deuterated enyne **13** was obtained in 63% yield with 93% of deuterium incorporation (Scheme 3). We tried to trap the intermediate **12** with some electrophiles in the hope of getting further substituted conjugated enynes. First, to the reaction mixture was added benzaldehyde. From the tlc analysis the product was thought to be the adduct **14**; however, in the isolation process it decomposed rapidly. The reaction with iodomethane gave an inseparable mixture of the methylated product **15** and protonated product **10**. Treatment of the intermediate **12** with iodine gave the desired iodide **16** in 44% yield.

We investigated this reaction with other 1-chlorovinyl *p*-tolyl sulfoxide **17**[4b] with the lithium carbanion of 1-hexyne (Scheme 4). This reaction gave the desired enyne **19a** in 64% yield. Deuterium was incorporated by the quenching with CD_3OD and the deuterium incorporation was found to be 96%. Treatment of this reaction with iodine gave iodinated conjugated enyne **19c** in 59% yield.

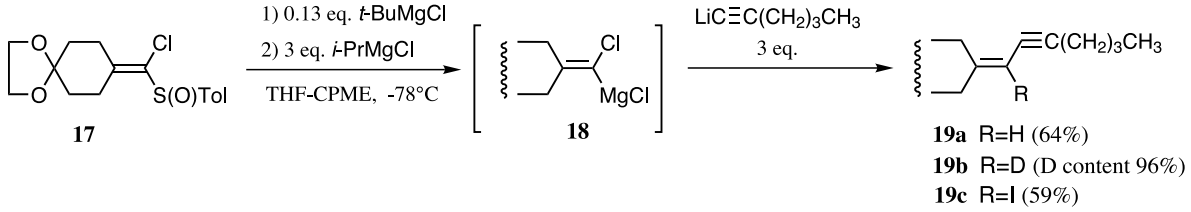
Conjugated enynes are quite interesting and important compounds in synthetic organic chemistry[9] and several methods for their synthesis have been reported.[10] Although the yields are not satisfactory, our method for the synthesis of conjugated enynes described above is fairly unique.[11]

1.2. Reaction of the magnesium alkylidene carbenoids with lithium thiolate; a novel synthesis of tri-substituted alkenyl sulfides including tetra-substituted alkenyl sulfides

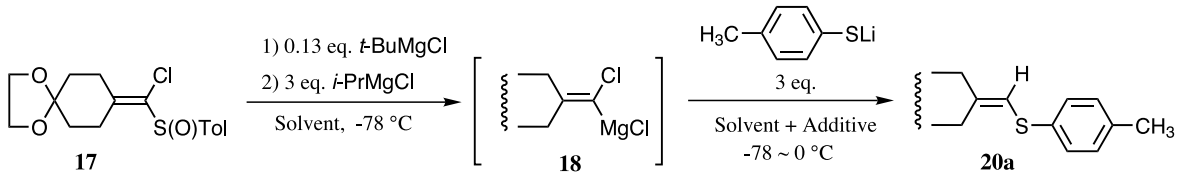
We investigated the reaction of the magnesium alkylidene carbenoid with sulfur nucleophile (Scheme 5). The magnesium alkylidene carbenoid **18** was generated from 1-chlorovinyl *p*-tolyl sulfoxide **17** as above in THF and then 3 equiv of lithium thiolate of *p*-toluenethiol, generated from the thiol with *n*-BuLi, was added. The temperature of the



Scheme 3.



Scheme 4.



Entry	Solvent	Additive (10 eq.)	**20a** (Yield/%)
1	THF		51
2	THF	HMPA	51
3	THF	TMEDA	48
4	THF	DME	55
5	Toluene		60
6	Toluene	DME	80

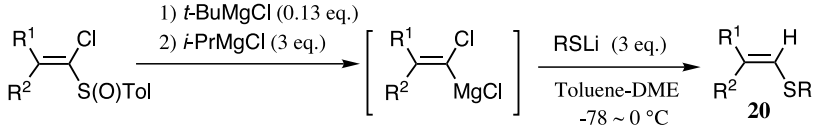
Scheme 5.

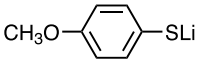
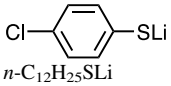
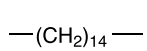
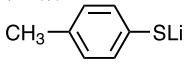
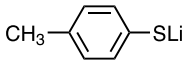
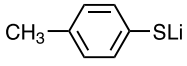
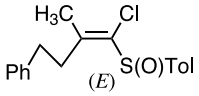
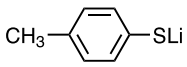
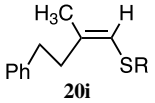
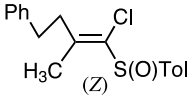
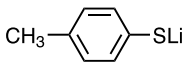
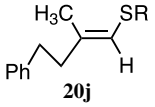
reaction mixture was slowly allowed to warm to 0 °C to give the desired vinyl sulfide **20a** in 51% yield (entry 1).

Improvement of the yield of **20a** in this reaction was investigated as shown in Scheme 5. Ten equivalents of the additive, HMPA, TMEDA or DME, were added to the THF solution and some effect was shown with DME (entry 2–4). Changing the solvent to toluene gave better yield (entry 5). Finally, toluene with 10 equiv of DME was found to be the choice for the solvent system of this reaction and 80% yield of the vinyl sulfide **20a** was obtained.

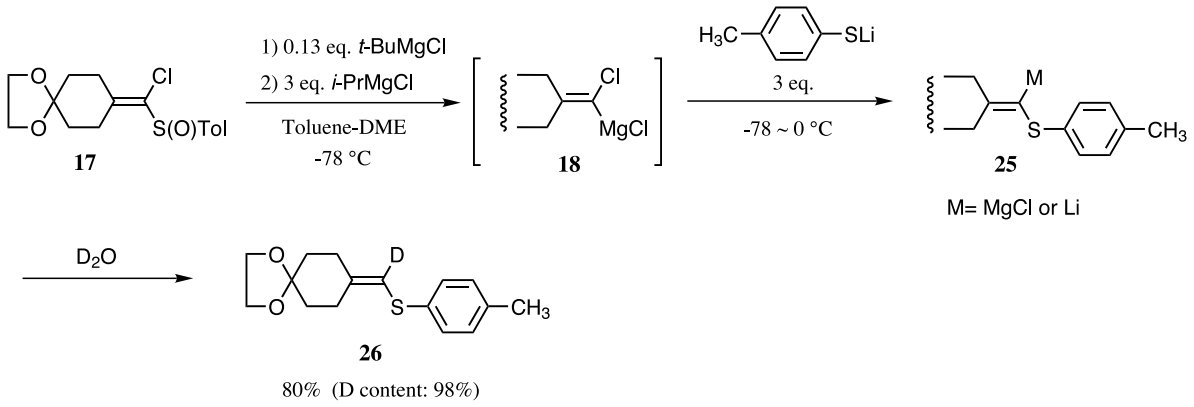
Vinyl sulfides are important compounds in organic synthesis, such as masked carbonyl compounds.[12] Several methods for synthesis of the vinyl sulfides have been reported;[13] however, synthesis of vinyl sulfide from

Table 3. Synthesis of vinyl sulfides **20** from 1-chlorovinyl *p*-tolyl sulfoxides with lithium thiolates via the magnesium alkylidene carbenoids



Entry	1-Chlorovinyl *p*-tolyl sulfoxide			RSLi	Yield of **20**[a]	
	R^1		R^2			(%)
1	**17**				**20b**	82
2		**17**			**20c**	72
3		**17**		n-$C_{12}H_{25}SLi$	**20d**	60[b]
4		**17**		$(CH_3)_3CSLi$	**20e**	39
5	**8**				**20f**	51
6	**21**	CH_3	CH_3		**20g**	77
7	**22**	Ph	Ph		**20h**	68
8	**23**	 (*E*)			 **20i**	65[c]
9	**24**	 (*Z*)			 **20j**	79[d]

[a] Isolated yield after silica gel column chromatography.
[b] THF was used as a solvent.
[c] The product was a mixture of *Z*-isomer **20i** and *E*-isomer **20j** (**20i**:**20j**=3.5:1).
[d] The product was a mixture of *E*-isomer **20j** and *Z*-isomer **20i** (**20i**:**20j**=1:5).



Scheme 6.

alkylidene carbenoid with thiolate is a unique way which has not been reported yet.

Encouraged by the results described above, we studied the generality of this reaction (Table 3). 4-Methoxybenzenethiol gave a similar yield of vinyl sulfide **20b** (entry 1); however, the benzenethiol having an electron-withdrawing group, chlorine, at the 4-position gave vinyl sulfide **20c** in slightly lower yield (entry 2). As the lithium thiolate of dodecanethiol was insoluble in toluene, the reaction with the magnesium alkylidene carbenoid was carried out in THF, and 60% yield of the vinyl sulfide **20d** was obtained (entry 3). 2-Methyl-2-propanethiol gave a somewhat lower yield of **20e** and steric hindrance was thought to be the reason for the low yield (entry 4).

This reaction was investigated using the 1-chlorovinyl *p*-tolyl sulfoxides derived from cyclopentadecanone (**8**), acetone (**21**), benzophenone (**22**) and 4-phenyl-2-butanone (**23** and **24**) with lithium *p*-toluenethiolate (Table 3, entries 5–9). As shown in Table 3, entries 5–7, 1-chlorovinyl *p*-tolyl sulfoxides **8**, **21** and **22** gave the desired vinyl sulfides (**20f**, **20g**, and **20h**) in moderate to good yields. Somewhat interestingly, the geometrical isomer *E*-vinyl sulfide **23** gave *Z*-isomer **20i** predominantly. In contrast to this, *Z*-vinyl sulfoxide **24** gave *E*-vinyl sulfide **20j** stereospecifically; however, the stereospecificity was not so high (entries 8 and 9).

As described above for the reaction of the magnesium alkylidene carbenoid **9** with lithium acetylides (Scheme 3), the intermediate of the reaction of the magnesium alkylidene carbenoid **18** with lithium *p*-toluenethiolate was again thought to be the alkenyl anion **25** (Scheme 6). To confirm this, the reaction was quenched with D_2O and we obtained deuterated vinyl sulfide **26** in 80% yield with 98% deuterium incorporation. If the intermediate **25** would react with other electrophiles, the reaction achieved a new method for the synthesis of fully substituted vinyl sulfides. We investigated this feasibility and the results are summarized in Table 4.

The vinylthio anion **27** was generated from **17** and lithium *p*-toluenethiolate, as described above in Scheme 6 and 7 equiv of benzaldehyde was added to the reaction mixture at 0 °C; however, not the desired adduct **28a** (see Table 4) but a complex mixture was obtained. After some investigation it was found that the reaction was best conducted at −40 °C and the adduct **28a** was obtained in 64% yield (entry 1). In the case of propanal the best yield was obtained at 0 °C; however, the yield was much lower compared with that of benzaldehyde (entry 2). All other reactions were best carried out at −40 °C.

Benzoylchloride gave the enone having a tolylsulfanyl group at the α-position **28c** in 54% yield. Ethyl chloroformate gave the desired product **28d** in only 11% yield (entry 4). The reaction with iodine gave the desired alkenyliodide **28e** in good yield. Iodomethane, styrene oxide and carbon disulfide did not react at all with the intermediate anion **27**.

To investigate the generality of this reaction, the 1-chlorovinyl *p*-tolyl sulfoxide derived from acetone **21** was treated with *i*-PrMgCl followed by lithium *p*-toluenethiolate and the generated carbanion was treated with benzaldehyde and iodine. This reaction afforded the adduct **28f** and iodide **28g** in 58 and 72% yield, respectively (entries 6 and 7). Finally, this reaction was carried out with **17** and *p*-methoxybenzenthiol followed by benzaldehyde to give **28h** in 49% yield. From the results described above, the generality of the procedure was confirmed.

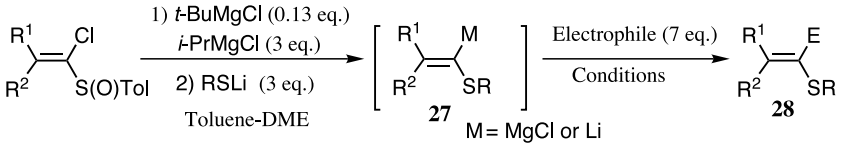
In conclusion, we have developed a new method for synthesis of conjugated enynes and vinyl sulfides by the reaction with magnesium alkylidene carbenoids and lithium acetylides or lithium thiolates in moderate to good yields. In some cases the intermediates, alkenyl anions, could be trapped with electrophiles. These reactions offer a unique and good procedure for the synthesis of highly substituted enynes and vinyl sulfides.

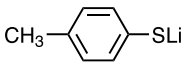
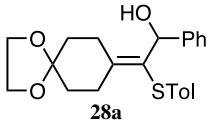
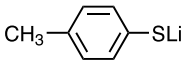
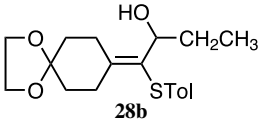
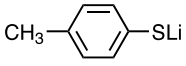
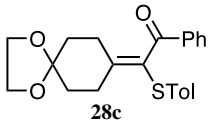
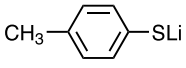
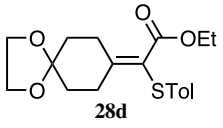
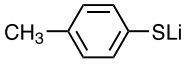
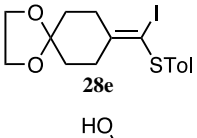
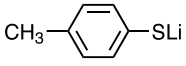
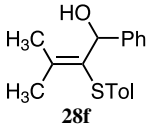
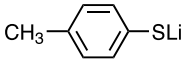
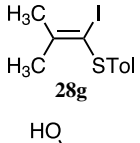
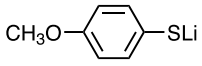
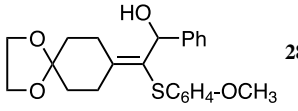
2. Experimental

2.1. General

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. Silica gel 60 (MERCK) containing 0.5% fluorescence reagent 254 and

Table 4. Synthesis of tri-substituted vinyl sulfides **28** from 1-chlorovinyl *p*-tolyl sulfoxides with lithium thiolates and electrophiles via the magnesium alkylidene carbenoids



Entry	1-Chlorovinyl *p*-tolyl sulfoxide	RSLi	Electrophile and conditions	Yield of **28**[a] (%)
1	**17**		PhCHO, −40 °C, 15 min	 **28a** 64
2	**17**		CH_3CH_2CHO, −40–0 °C, 1 h	 **28b** 39
3	**17**		PhCOCl, −40 °C, 15 min	 **28c** 54
4	**17**		ClCOOEt, −40 °C, 15 min	 **28d** 11
5	**17**		I_2, −40 °C, 15 min	 **28e** 50
6	**21**		PhCHO, −40 °C, 15 min	 **28f** 58
7	**21**		I_2, −40 °C, 15 min	 **28g** 72
8	**17**		PhCHO, −40 °C, 15 min	 **28h** 49

[a] Isolated yield after silica gel column chromatography.

a 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, DMPU, TMEDA, toluene and HMPA were distilled from CaH_2 and THF, cyclopentyl methyl ether, 1,4-dioxane and DME were distilled from diphenylketyl.

2.1.1. (Hept-2-ynylidene)cyclopentadecane (10). To a solution of **8** (100 mg; 0.25 mmol) in 20 ml of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (0.033 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (0.75 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid **9**. *n*-BuLi (0.8 mmol) was added to a solution of 1-hexyne (0.086 ml; 0.75 mmol) in 6 ml of dry THF and dry CPME (0.27 ml; 2.3 mmol) in another flame-dried flask at −78 °C under argon atmosphere to give a white muddy solution. This solution was added to a solution of the carbenoid **9** through a canula. Temperature of the reaction mixture was gradually allowed to warm to room temperature for 2 h. The reaction was quenched with satd aq NH_4Cl and the whole was extracted with hexane–AcOEt and the extract was dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column

chromatography to give **10** (48.4 mg; 64%) as a colorless oil; IR (neat) 2930, 2858, 2067 (triple bond), 1638, 1460 cm^{-1}; ^1H NMR δ 0.92 (3H, t, $J=7.2$ Hz), 1.32–1.55 (28H, m), 2.06 (2H, t, $J=7.3$ Hz), 2.28 (2H, t, $J=7.4$ Hz), 2.33 (2H, dt, $J=6.9$, 2.1 Hz), 5.26 (1H, s). MS *m/z* (%) 302 (M^+, 100), 259 (11), 245 (9), 161 (13), 147 (24), 136 (35), 121 (29), 105 (42). Calcd for $C_{22}H_{38}$: M, 302.2971. Found: *m/z* 302.2981.

2.1.2. (3-Phenylprop-2-ynylidene)cyclopentadecane (11a). Colorless oil; IR (neat) 2929, 2857, 2198 (triple bond), 1595, 1489, 1459, 1443, 910, 754, 690 cm^{-1}; ^1H NMR δ 1.33–1.60 (24H, m), 2.15 (2H, t, $J=7.3$ Hz), 2.40 (2H, t, $J=7.4$ Hz), 5.51 (1H, s), 7.25–7.31 (3H, m), 7.39–7.42 (2H, m). MS *m/z* (%) 322 (M^+, 100), 169 (15), 167 (26), 128 (20), 91 (16). Calcd for $C_{24}H_{34}$: M, 322.2658. Found: *m/z* 322.2653.

2.1.3. {3-(4-Methoxyphenyl)prop-2-ynylidene}cyclopentadecane (11b). Colorless oil; IR (neat) 2930, 2857, 2192 (triple bond), 1603, 1508, 1459, 1442, 1290, 1247, 1171, 1038, 830 cm^{-1}; ^1H NMR δ 1.24–1.59 (24H, m), 2.14 (2H, t, $J=7.2$ Hz), 2.38 (2H, t, $J=7.3$ Hz), 3.81 (3H, s), 5.49 (1H, s), 6.83 (2H, d, $J=8.8$ Hz), 7.34 (2H, d, $J=8.8$ Hz). MS *m/z* (%) 352 (M^+, 100), 197 (11), 185 (10), 171 (5), 145 (4) 121 (9). Calcd for $C_{25}H_{36}O$: M, 352.2685. Found: *m/z* 352.2775.

2.1.4. {3-(4-Fluorophenyl)prop-2-ynylidene}cyclopentadecane (11c). Yellow oil; IR (neat) 2930, 2858, 2199 (triple bond), 1599, 1506, 1460, 1231, 1155, 834 cm^{-1}; ^1H NMR δ 1.33–1.58 (24H, m), 2.15 (2H, t, $J=7.4$ Hz), 2.38 (2H, t, $J=7.6$ Hz), 5.49 (1H, s), 7.00 (2H, t, $J=8.6$ Hz), 7.36–7.40 (2H, m). MS *m/z* (%) 340 (M^+, 100), 185 (28), 173 (24), 146 (25), 109 (18). Calcd for $C_{24}H_{33}F$: M, 340.2609. Found: *m/z* 340.2559.

2.1.5. {3-(Trimethylsilyl)prop-2-ynylidene}cyclopentadecane (11d). Colorless oil; IR (neat) 2929, 2858, 2132 (triple bond), 1615, 1461, 1249 (C–Si), 1085, 842, 759 cm^{-1}; ^1H NMR δ 0.18 (9H, s), 1.32–1.53 (24H, m), 2.08 (2H, t, $J=7.1$ Hz), 2.32 (2H, t, $J=7.7$ Hz), 5.32 (1H, s). MS *m/z* (%) 318 (M^+, 48), 303 (47), 244 (8), 194 (7), 73 (100). Calcd for $C_{21}H_{38}Si$: M, 318.2741. Found: *m/z* 318.2751.

2.1.6. (Prop-2-ynylidene)cyclopentadecane (11e). Colorless oil; IR (neat) 3312, 2929, 2857, 2098 (triple bond), 1619, 1459, 1350, 1288, 1173 cm^{-1}; ^1H NMR δ 1.32–1.53 (24H, m), 2.10 (2H, t, $J=7.3$ Hz), 2.33 (2H, t, $J=7.4$ Hz), 3.00 (1H, d, $J=2.4$ Hz), 5.28 (1H, s). MS *m/z* (%) 246 (M^+, 28), 147 (16), 133 (30), 119 (42), 107 (63), 93 (93), 80 (100). Calcd for $C_{18}H_{30}$: M, 246.2337. Found: *m/z* 246.2347.

2.1.7. {(1-Deuterio)hept-2-ynylidene}cyclopentadecane (13). Colorless oil; IR (neat) 2930, 2858, 2238 (triple bond), 1615, 1460, 1350, 1298, 730, 710 cm^{-1}; ^1H NMR δ 0.92 (3H, t, $J=7.0$ Hz), 1.32–1.55 (28H, m), 2.06 (2H, t, $J=7.4$ Hz), 2.28 (2H, t, $J=7.4$ Hz), 2.33 (2H, t, $J=7.0$ Hz). MS *m/z* (%) 303 (M^+, 100), 260 (13), 246 (10), 150 (14), 137 (42), 134 (31), 108 (30). Calcd for $C_{22}H_{37}D$: M, 303.3034. Found: *m/z* 303.3034.

2.1.8. (1-Methylhept-2-ynylidene)cyclopentadecane (15). To a solution of **8** (100 mg; 0.25 mmol) in 20 ml of dry THF in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (0.033 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (0.75 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid **9**. *n*-BuLi (0.8 mmol) was added to a solution of 1-hexyne (0.086 ml; 0.75 mmol) in 6 ml of dry THF and CPME (0.27 ml; 2.3 mmol) in another flame-dried flask at −78 °C under argon atmosphere to give a white muddy solution. This solution was added to a solution of the carbenoid **9** through a canula. Temperature of the reaction mixture was gradually allowed to warm to −10 °C for 2 h. Iodomethane (1.75 mmol) was added dropwise to the reaction mixture. Temperature of the reaction mixture was gradually allowed to warm to room temperature for 30 min. The reaction was quenched by adding satd aq NH_4Cl and the whole was extracted with AcOEt. The product was purified by silica gel column chromatography. As this product was an inseparable mixture with **10**, only the data for ^1H NMR is reported: ^1H NMR δ 0.92 (3H, t, $J=7.0$ Hz), 1.32–1.54 (28H, m), 1.78 (3H, s), 2.06 (2H, t, $J=7.4$ Hz), 2.28 (2H, t, $J=7.1$ Hz), 2.34 (2H, t, $J=6.7$ Hz).

2.1.9. (1-Iodohept-2-ynylidene)cyclopentadecane (16). Yellow oil; IR (neat) 2929, 2858, 2208 (triple bond), 1458, 1350, 1325, 1104, 738 cm^{-1}; ^1H NMR δ 0.92 (3H, t, $J=7.0$ Hz), 1.32–1.56 (28H, m), 2.24 (2H, t, $J=7.8$ Hz), 2.38–2.43 (4H, m). MS *m/z* (%) 428 (M^+, 96), 375 (16), 301 (72), 265 (27), 225 (35), 189 (17), 149 (32), 109 (62), 81 (100). Calcd for $C_{22}H_{37}I$: M, 428.1940. Found: *m/z* 428.1941.

2.1.10. 8-(Hept-2-ynylidene)-1,4-dioxaspiro[4,5]decane (19a). Colorless oil; IR (neat) 2954, 2875, 2213 (triple bond), 1634, 1442, 1374, 1271, 1249, 1228, 1120, 1083, 1035, 945, 908, 684 cm^{-1}; ^1H NMR δ 0.92 (3H, t, $J=7.3$ Hz), 1.43 (2H, sextet, $J=7.3$ Hz), 1.52 (2H, quintet, $J=7.2$ Hz), 1.71 (4H, quintet, $J=6.7$ Hz), 2.29–2.35 (4H, m), 2.54 (2H, t, $J=6.4$ Hz), 3.97 (4H, s), 5.26 (1H, s). MS *m/z* (%) 234 (M^+, 100), 205 (20), 191 (14), 148 (15), 133 (22), 119 (20), 105 (27), 91 (38). Calcd for $C_{15}H_{22}O_2$; M, 234.1618. Found: *m/z* 234.1613.

2.1.11. 8-(1-Deuteriohept-2-ynylidene)-1,4-dioxaspiro-[4,5]decane (19b). Colorless oil; IR (neat) 2954, 2875, 2237 (triple bond), 1626, 1443, 1365, 1239, 1121, 1084, 1035, 942, 903, 664 cm^{-1}; ^1H NMR δ 0.92 (3H, t, $J=7.3$ Hz), 1.39–1.46 (2H, m), 1.42 (2H, sextet, $J=7.3$ Hz), 1.52 (2H, quintet, $J=7.2$ Hz), 1.70 (4H, quintet, $J=6.4$ Hz), 2.32 (4H, quintet, $J=6.6$ Hz), 2.54 (2H, t, $J=6.4$ Hz), 3.97 (4H, s). MS *m/z* (%) 235 (M^+, 100), 206 (22), 192 (17), 149 (17), 134 (26), 120 (26), 106 (32), 92 (40). Calcd for $C_{15}H_{21}DO_2$: M, 235.1680, Found: *m/z* 235.1674.

2.1.12. 8-(1-Iodohept-2-ynylidene)-1,4-dioxaspiro[4,5]-decane (19c). Yellow oil; IR (neat) 2956, 2875, 2208 (triple bond), 1678, 1633, 1435, 1366, 1277, 1236, 1218, 1121, 1083, 1034, 944, 908, 804 cm^{-1}; ^1H NMR δ 0.92 (3H, t, $J=7.3$ Hz), 1.39–1.47 (2H, m), 1.51–1.55 (2H, m), 1.68 (4H, quintet, $J=6.6$ Hz), 2.41 (2H, t, $J=7.0$ Hz), 2.54 (2H, t, $J=6.4$ Hz), 2.70 (2H, t, $J=6.4$ Hz), 3.97 (4H, s). MS *m/z* (%) 360 (M^+, 100), 322 (11), 233 (24), 232 (14), 195

(19), 189 (33), 151 (17), 147 (16), 105 (22). Calcd for $C_{15}H_{21}O_2I$: M, 360.0586. Found: *m/z* 360.0579.

2.1.13. 8-{(*p*-Tolylsulfanyl)methylene}-1,4-dioxaspiro-[4.5]decane (20a). To a solution of **17** (65.4 mg; 0.2 mmol) in 6 ml of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added *t*-BuMgCl (0.025 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (0.60 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid **18**. *n*-BuLi (0.66 mmol) was added to a solution of *p*-toluenethiol (74.5 mg; 0.6 mmol) in 6 ml of dry toluene and dry DME (0.21 ml; 2 mmol) in another flame-dried flask at −78 °C under argon atmosphere to give the thiolate anion. This solution was added to a solution of the carbenoid **18** through a canula. Temperature of the reaction mixture was gradually allowed to warm to 0 °C for 2 h. The reaction was quenched by satd aq NH_4Cl and the whole was extracted with $CHCl_3$. The organic layer was washed once with water and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel column chromatography to give **20a** (44.2 mg; 80%) as a colorless oil; IR (neat) 2948, 2880, 1492, 1120, 1085, 1034, 908, 805 cm^{-1}; ^1H NMR δ 1.71–1.76 (4H, m), 2.32 (3H, s), 2.40 (2H, t, J=6.4 Hz), 2.53 (2H, t, J=6.6 Hz), 3.98 (4H, s), 5.92 (1H, s), 7.10 (2H, d, J=8.0 Hz), 7.21 (2H, d, J=8.3 Hz). MS *m/z* (%) 276 (M^+, 100), 215 (12), 153 (63), 109 (27), 99 (17), 91 (17). Calcd for $C_{16}H_{20}O_2S$: M, 276.1183. Found: *m/z* 276.1179.

2.1.14. 8-{(4-Methoxyphenylsulfanyl)methylene}-1,4-dioxaspiro[4.5]decane (20b). Colorless oil; IR (neat) 2949, 2883, 1593, 1494, 1287, 1245, 1120, 1084, 1033, 908, 825, 757 cm^{-1}; ^1H NMR δ 1.73 (4H, t, J=6.5 Hz), 2.37 (2H, t, J=6.5 Hz), 2.52 (2H, t, J=6.5 Hz), 3.79 (3H, s), 3.98 (4H, s), 5.87 (1H, s), 6.85 (2H, d, J=8.9 Hz), 7.29 (2H, d, J=8.9 Hz). MS *m/z* (%) 292 (M^+, 100), 231 (12), 153 (50), 139 (27), 109 (27). Calcd for $C_{16}H_{20}O_3S$: M, 292.1132. Found: *m/z* 292.1138.

2.1.15. 8-{(4-Chlorophenylsulfanyl)methylene}-1,4-dioxaspiro[4.5]decane (20c). Colorless needles; mp 50.5–51.5 °C (hexane); IR (KBr) 2954, 2877, 1622, 1473, 1132, 1118, 1089, 1029, 913, 812, 682 cm^{-1}; ^1H NMR δ 1.72 (2H, t, J=6.7 Hz), 1.76 (2H, t, J=6.6 Hz), 2.43 (2H, t, J=6.6 Hz), 2.53 (2H, t, J=6.6 Hz), 3.98 (4H, s), 5.91 (1H, s), 7.21 (2H, d, J=8.6 Hz), 7.25 (2H, d, J=8.6 Hz). Anal. Calcd for $C_{15}H_{17}ClO_2S$: C, 60.70; H, 5.77; Cl, 11.94; S, 10.80. Found: C, 60.82; H, 5.74; Cl, 11.87; S, 10.88%.

2.1.16. 8-{(Dodecylsulfanyl)methylene}-1,4-dioxaspiro-[4.5]decane (20d). Colorless oil; IR (neat) 2926, 2854, 1120, 1085, 1035, 908 cm^{-1}; ^1H NMR δ 0.88 (3H, t, J=7.0 Hz), 1.22–1.32 (16H, m), 1.36–1.39 (2H, m), 1.60 (2H, t, J=7.5 Hz), 1.68 (4H, t, J=6.4 Hz), 2.30 (2H, t, J=6.4 Hz), 2.40 (2H, t, J=6.6 Hz), 2.62 (2H, t, J=7.3 Hz), 3.97 (4H, s), 5.66 (1H, s). MS *m/z* (%) 354 (M^+, 81), 293 (16), 185 (77), 153 (100), 99 (34). Calcd for $C_{21}H_{38}O_2S$: M, 354.2590. Found: *m/z* 354.2581.

2.1.17. 8-{(*tert*-Butylsulfanyl)methylene}-1,4-dioxaspiro-[4.5]decane (20e). Colorless oil; IR (neat) 2955, 2881, 1457, 1364, 1270, 1120, 1085, 1035, 909 cm^{-1}; ^1H NMR δ 1.33 (9H, s), 1.67 (2H, t, J=6.6 Hz), 1.70 (2H, t, J=6.4 Hz), 2.36 (2H, t, J=6.4 Hz), 2.48 (2H, t, J=6.6 Hz), 3.97 (4H, s), 5.87 (1H, s). MS *m/z* (%) 242 (M^+, 52), 186 (63), 153 (100), 124 (18), 99 (25), 86 (40), 57, (39). Calcd for $C_{13}H_{22}O_2S$: M, 242.1339. Found: *m/z* 242.1340.

2.1.18. {(*p*-Tolylsulfanyl)methylene}cyclopentadecane (20f). Colorless oil; IR (neat) 2928, 2857, 1492, 1459, 1216, 1092, 803, 759 cm^{-1}; ^1H NMR δ 1.25–1.52 (24H, m), 2.16 (2H, t, J=7.6 Hz), 2.27 (2H, t, J=7.7 Hz), 2.31 (3H, s), 5.90 (1H, s), 7.09 (2H, d, J=7.9 Hz), 7.20 (2H, d, J=7.9 Hz). MS *m/z* (%) 344 (M^+, 100), 124 (15), 95 (8), 69 (10), 55 (14). Calcd for $C_{23}H_{36}S$: M, 344.2535. Found: *m/z* 344.2529.

2.1.19. 2-Methylpropenyl *p*-tolyl sulfide (20g). Colorless oil; IR (neat) 2967, 2910, 2727, 1892, 1492, 1440, 1372, 1302, 1171, 1091, 1062, 1017, 857, 804 cm^{-1}; ^1H NMR δ 1.86, 1.87, 2.31 (each 3H, s), 5.88 (1H, s), 7.09, 7.20 (each 2H, d, J=8.3 Hz). MS *m/z* (%) 178 (M^+, 100), 163 (31), 135 (13), 105 (13), 91 (21). Calcd for $C_{11}H_{14}S$: M, 178.0815. Found: *m/z* 178.0806.

2.1.20. 2,2-Diphenylethenyl *p*-tolyl sulfide (20h). Colorless needles; mp 84–85 °C, (AcOEt–hexane); IR (KBr) 3027, 1583, 1491, 1442, 816, 807, 775, 754, 701, 693 cm^{-1}; ^1H NMR δ 2.34 (3H, s), 6.82 (1H, s), 7.14–7.44 (14H, m). Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00; S, 10.60. Found: C, 83.28; H, 5.96; S, 10.73%.

2.1.21. (*Z*)-2-Methyl-4-phenyl-1-(*p*-tolylsulfanyl)-1-butene (20i). Colorless oil; IR (neat) 3026, 2922, 1604, 1493, 1454, 1376, 1091, 1032, 1017, 804, 743, 698 cm^{-1}; ^1H NMR δ 1.86 (3H, d, J=1.2 Hz), 2.31 (3H, s), 2.59 (2H, dd, J=8.3, 7.6 Hz), 2.76 (2H, dd, J=8.6, 7.3 Hz), 5.91 (1H, d, J=1.2 Hz), 7.08 (2H, d, J=8.0 Hz), 7.15–7.20 (3H, m), 7.23–7.24 (2H, m), 7.27–7.30 (2H, m). MS *m/z* (%) 268 (M^+, 70), 177 (100), 149 (39), 144 (53), 129 (19), 91 (36). Calcd for $C_{18}H_{20}S$: M, 268.1284. Found: *m/z* 268.1283.

2.1.22. (*E*)-2-Methyl-4-phenyl-1-(*p*-tolylsulfanyl)-1-butene (20j). Colorless oil; IR (neat) 3026, 2921, 1601, 1493, 1454, 1376, 1091, 1030, 1017, 805, 745, 699 cm^{-1}; ^1H NMR δ 1.88 (3H, s), 2.30 (3H, s), 2.47 (2H, t, J=7.8 Hz), 2.79 (2H, t, J=7.8 Hz), 5.83 (1H, s), 7.05 (4H, s), 7.18–7.23 (3H, m), 7.29 (2H, t, J=7.6 Hz). MS *m/z* (%) 268 (M^+, 58), 177 (100), 149 (31), 144 (48), 129 (19), 91 (38). Calcd for $C_{18}H_{20}S$: M, 268.1284. Found: *m/z* 268.1277.

2.1.23. 8-(Deuterio-*p*-tolylsulfanylmethylene)-1,4-dioxaspiro[4.5]decane (26). Colorless oil; IR (neat) 2949, 2880, 1492, 1440, 1364, 1274, 1226, 1122, 1087, 1034, 929, 899, 806 cm^{-1}; ^1H NMR δ 1.73 (4H, quintet, J=6.1 Hz), 2.31 (3H, s), 2.40 (2H, t, J=6.4 Hz), 2.53 (2H, t, J=6.6 Hz), 3.98 (4H, s), 7.10 (2H, d, J=8.3 Hz), 7.21 (2H, d, J=8.3 Hz). MS *m/z* (%) 277 (M^+, 100), 216 (14), 154 (60), 110 (27). Calcd for $C_{16}H_{19}DO_2S$: M, 277.1245. Found: *m/z* 277.1242.

2.1.24. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-1-phenyl-2-(*p*-tolylsulfanyl)ethanol (28a). To a solution of **17** (98.1 mg; 0.3 mmol) in 12 ml of dry toluene in a flame-dried flask at −78 °C under argon atmosphere was added

t-BuMgCl (0.04 mmol) dropwise with stirring. After 10 min, *i*-PrMgCl (0.9 mmol) was added dropwise to the reaction mixture at −78 °C to give the magnesium alkylidene carbenoid **18**. *n*-BuLi (0.96 mmol) was added to a solution of *p*-toluenethiol (112 mg; 0.9 mmol) in 9 ml of dry toluene and dry DME (0.31 ml; 3 mmol) in another flame-dried flask at −78 °C under argon atmosphere to give thiolate anion. This solution was added to the solution of the carbenoid **18** through a canula. Temperature of the reaction mixture was gradually allowed to warm to −40 °C for 1 h. Benzaldehyde (2.1 mmol) was added dropwise to the reaction mixture. After 15 min, the reaction was quenched by satd aq NH_4Cl. The whole was extracted with $CHCl_3$ and the organic layer was washed once with water and dried over $MgSO_4$. After removal of the solvent, the product was purified by silica gel flash column chromatography to give **28a** (73.4 mg; 64%) as a colorless oil; IR (neat) 3460 (OH), 2953, 2884, 1601, 1492, 1449, 1226, 1123, 1084, 1034, 944, 908, 806, 754, 700, 662 cm^{-1}; ^1H NMR δ 1.60–1.67 (2H, m), 1.76–1.86 (2H, m), 2.26 (3H, s), 2.61–2.66 (1H, m), 2.72–2.77 (3H, m), 2.89 (1H, d, J=9.8 Hz, OH), 3.97 (4H, s), 5.97 (1H, d, J=9.8 Hz), 6.99 (2H, d, J=8.3 Hz), 7.04 (2H, d, J=8.3 Hz), 7.23 (1H, t, J=7.2 Hz), 7.29 (2H, t, J=7.2 Hz), 7.34 (2H, d, J=7.2 Hz). MS *m/z* (%) 382 (M^+, 98), 364 (27), 189 (37), 155 (100), 105 (39), 99 (48), 91 (44), 77 (33). Calcd for $C_{23}H_{26}O_3S$: M, 382.1601. Found: *m/z* 382.1608.

2.1.25. 1-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-1-(*p*-tolylsulfanyl)-2-butanol (28b). Colorless oil; IR (neat) 3468 (OH), 2959, 2877, 1492, 1123, 1085, 1034, 910, 805 cm^{-1}; ^1H NMR δ 0.87 (3H, t, J=6.2 Hz), 1.45–1.53 (1H, m), 1.57–1.65 (3H, m), 1.68–1.83 (2H, m), 2.23 (1H, d, J=10.1 Hz, OH), 2.28 (3H, s), 2.54–2.73 (4H, m), 3.96 (4H, s), 4.66 (1H, dt, J=10.1, 7.2 Hz), 7.04 (2H, d, J=8.0 Hz), 7.21 (2H, t, J=8.0 Hz). MS *m/z* (%) 334 (M^+, 100), 243 (18), 230 (21), 215 (22), 193 (20), 107 (19), 99 (18). Calcd for $C_{19}H_{26}O_3S$: M, 334.1602. Found: *m/z* 334.1602.

2.1.26. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-1-phenyl-2-(*p*-tolylsulfanyl)ethanone (28c). Colorless needles; mp 104.5–105.5 °C, (AcOEt–hexane); IR (KBr) 2964, 2898, 1662 (CO), 1492, 1448, 1208, 1089, 1028, 916, 809, 707 cm^{-1}; ^1H NMR δ 1.72 (2H, t, J=6.6 Hz), 1.86 (2H, t, J=6.6 Hz), 2.26 (3H, s), 2.40 (2H, t, J=6.4 Hz), 2.90 (2H, t, J=6.6 Hz), 3.95–4.01 (4H, m), 7.01 (2H, d, J=7.6 Hz), 7.13 (2H, d, J=8.3 Hz), 7.40 (2H, t, J=7.8 Hz), 7.52 (1H, tt, J=7.4, 1.4 Hz), 7.79 (2H, dd, J=8.5, 1.4 Hz). MS *m/z* (%) 380 (M^+, 95), 257 (100), 213 (53), 189 (32), 105 (92), 77 (55). Calcd for $C_{23}H_{24}O_3S$: M, 380.1446. Found: *m/z* 380.1441. Anal. Calcd for $C_{23}H_{24}O_3S$: C, 72.60; H, 6.36; S, 8.43. Found: C, 72.59; H, 6.36; S, 8.36%.

2.1.27. (1,4-Dioxaspiro[4.5]dec-8-ylidene)-(*p*-tolylsulfanyl)acetic acid ethyl ester (28d). Colorless oil; IR (neat) 2983, 1733 (CO), 1493, 1374, 1246, 1090, 1045, 916, 757 cm^{-1}; ^1H NMR δ 1.07 (3H, t, J=7.2 Hz), 1.77 (2H, t, J=6.6 Hz), 1.80 (2H, t, J=6.6 Hz), 2.30 (3H, s), 2.64 (2H, t, J=6.6 Hz), 2.79 (2H, t, J=6.6 Hz), 3.98 (4H, s), 4.04 (2H, q, J=7.0 Hz), 7.07 (2H, d, J=8.0 Hz), 7.20 (2H, d, J=8.0 Hz). MS *m/z* (%) 348 (M^+, 86), 303 (33), 302 (100), 225 (59), 183 (33), 179 (63), 119 (35). Calcd for $C_{19}H_{24}O_4S$: M, 348.1395. Found: *m/z* 348.1397.

2.1.28. 8-{Iodo-(*p*-tolylsulfanyl)methylene}-1,4-dioxaspiro[4.5]decane (28e). Colorless needles; mp 106–107 °C (AcOEt–hexane); IR (KBr) 2937, 2870, 1490, 1214, 1123, 1084, 1033, 906, 805 cm^{-1}; ^1H NMR δ 1.69 (2H, t, J=6.6 Hz), 1.78 (2H, t, J=6.6 Hz), 2.33 (3H, s), 2.69 (2H, t, J=6.6 Hz), 2.90 (2H, t, J=6.6 Hz), 3.99 (4H, s), 7.16 (4H, s). MS *m/z* (%) 402 (M^+, 35), 275 (100), 189 (55), 155 (58), 135 (21), 99 (44). Calcd for $C_{16}H_{19}IO_2S$: M, 402.0150. Found: *m/z* 402.0144. Anal. Calcd for $C_{16}H_{19}IO_2S$: C, 47.77; H, 4.76; I, 31.55; S, 7.97. Found: C, 47.81; H, 4.60; I, 31.71; S, 7.59%.

2.1.29. 3-Methyl-1-phenyl-2-(*p*-tolylsulfanyl)but-2-en-1-ol (28f). Colorless oil; IR (neat) 3437 (OH), 2922, 1622, 1600, 1492, 1449, 1017, 805, 700 cm^{-1}; ^1H NMR δ 1.99 (3H, s), 2.11 (3H, s), 2.27 (3H, s), 2.80 (1H, d, J=10.1 Hz, OH), 5.94 (1H, d, J=10.1 Hz), 7.00 (2H, d, J=8.6 Hz), 7.04 (2H, d, J=8.6 Hz), 7.23 (1H, t, J=7.2 Hz), 7.30 (2H, t, J=7.6 Hz), 7.36 (2H, d, J=7.7 Hz). MS *m/z* (%) 284 (M^+, 100), 178 (27), 177 (35), 162 (33), 144 (29), 143 (78), 77 (32). Calcd for $C_{18}H_{20}OS$: M, 284.1233. Found: *m/z* 284.1230.

2.1.30. 1-Iodo-2-methylpropenyl *p*-tolyl sulfide (28g). Colorless needles; mp 44–45 °C, (AcOEt–hexane); IR (KBr) 2908, 1489, 1204, 1183, 1071, 1016, 866, 803 cm^{-1}; ^1H NMR δ 2.10 (3H, s), 2.17 (3H, s), 2.33 (3H, s), 7.15 (4H, s). MS *m/z* (%) 304 (M^+, 39), 177 (100), 162 (38), 143 (60), 129 (18). Calcd for $C_{11}H_{13}IS$: M, 303.9782. Found: *m/z* 303.9771.

2.1.31. 2-(1,4-Dioxaspiro[4.5]dec-8-ylidene)-2-(4-methoxyphenylsulfanyl)-1-phenylethanol (28h). Colorless oil; IR (neat) 3461 (OH), 2952, 1594, 1493, 1449, 1244, 1122, 1033, 755 cm^{-1}; ^1H NMR δ 1.59–1.70 (2H, m), 1.74–1.84 (2H, m), 2.65–2.80 (4H, m), 2.92 (1H, d, J=9.8 Hz, OH), 3.75 (3H, s), 3.95–3.98 (4H, m), 5.96 (1H, d, J=9.8 Hz), 6.72 (2H, dt, J=9.6, 2.7 Hz), 7.08 (2H, dt, J=9.6, 2.7 Hz), 7.22 (1H, t, J=7.2 Hz), 7.29 (2H, t, J=6.7 Hz), 7.33 (2H, d, J=7.4 Hz). MS *m/z* (%) 398 (M^+, 100), 290 (8), 241 (10), 205 (26), 155 (24). Calcd for $C_{23}H_{26}O_4S$: M, 398.1549. Found: *m/z* 398.1543.

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