Coupling Reaction of Magnesium Alkylidene Carbenoids with α-Sulfonylallyllithiums: An Efficient Route to Multi-Substituted Vinylallenes

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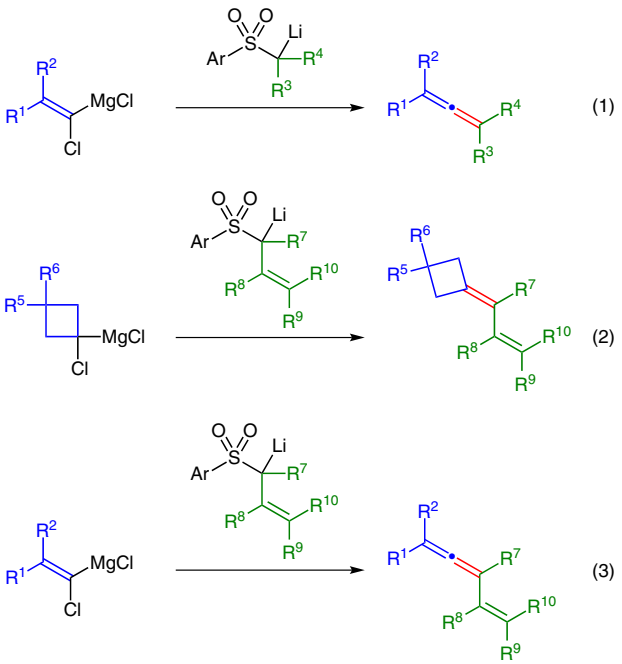
Abstract: A variety of vinylallenes were successfully synthesized from 1-chlorovinyl *p*-tolyl sulfoxides and allyl or vinyl sulfones. Allyl and vinyl sulfones served as α-sulfonylallyllithium sources were prepared from carbonyl compounds in three or four steps in good overall yields. The coupling reaction of α-sulfonylallyllithiums with magnesium alkylidene carbenoids, which were generated from 1-chlorovinyl *p*-tolyl sulfoxides and isopropylmagnesium chloride, afforded multi-substituted vinylallenes in up to 88% yield.

Key words: vinylallenes, magnesium alkylidene carbenoids, allyl sulfones, vinyl sulfones, 1-chlorovinyl *p*-tolyl sulfoxides, coupling

Vinylallenes, also referred to as 1,2,4-trienes, are a class of conjugated compounds consisting of allene and alkene units. They have attracted much attention in recent years because of their excellent synthetic utilities, especially as dienes for cycloaddition reactions.[1,2] A classical method for their synthesis is based on the S_N2' reaction of organometallic reagents with 1,4-enynes bearing a leaving group at the 3-position.[3,4] A drawback of this approach is associated with the regioselectivity of the reaction, which is caused by the presence of multiple reactive sites in the enyne substrates.[3c,e] Considering the above-mentioned limitations, there is a need for an alternative route for the preparation of vinylallenes.

Previously, we found that nucleophilic substitution proceeded at the carbenoid carbon atom of magnesium alkylidene carbenoids to give multi-substituted alkenes.[5,6] When anionic carbon nucleophiles with a leaving group on the carbanion center were used in the reaction, β-elimination of intermediates took place to give allenic compounds.[6b,c,h] For instance, the reaction of magnesium alkylidene carbenoids with α-sulfonylalkyllithiums afforded tri- and tetrasubstituted allenes in moderate yields (Scheme 1, equation 1).[6c] Meanwhile, we also found that α-sulfonylallyllithiums reacted with cyclobutylmagnesium carbenoids to give allylidenecyclobutanes (Scheme 1, equation 2).[7] If the general concept of these reactions could be extended to the reaction of magnesium alkylidene carbenoids with α-sulfonylallyllithiums, that is, if vinylidene components could be coupled with allylidene components through a double bond,[8] we reasoned that it would be an efficient route to vinylallenes (Scheme 1, equation 3). Herein, we report the synthesis of multi-substituted vinylallenes from 1-chlorovinyl sulfoxides and allyl sulfones as well as vinyl sulfones.



Scheme 1 Synthesis of multi-substituted allenes (equation 1), allylidenecyclobutanes (equation 2), and vinylallenes (equation 3) utilizing magnesium carbenoids and α-sulfonylorganolithiums

We planned to use both allyl *p*-tolyl sulfones **1** and *p*-tolyl vinyl sulfones **2** as precursors for generating α-sulfonylallyllithiums.[9] These compounds were readily prepared from aldehydes or ketones in four or less steps via the different routes presented in Scheme 2. Allyl *p*-tolyl sulfones **1** were prepared as follows (Scheme 2, equation 1). The carbonyl compounds were subjected to a Horner–Wadsworth–Emmons reaction with triethyl phosphonoacetate to give α,β-unsaturated esters. The esters were reduced with DIBAL-H to afford allylic alcohols. The

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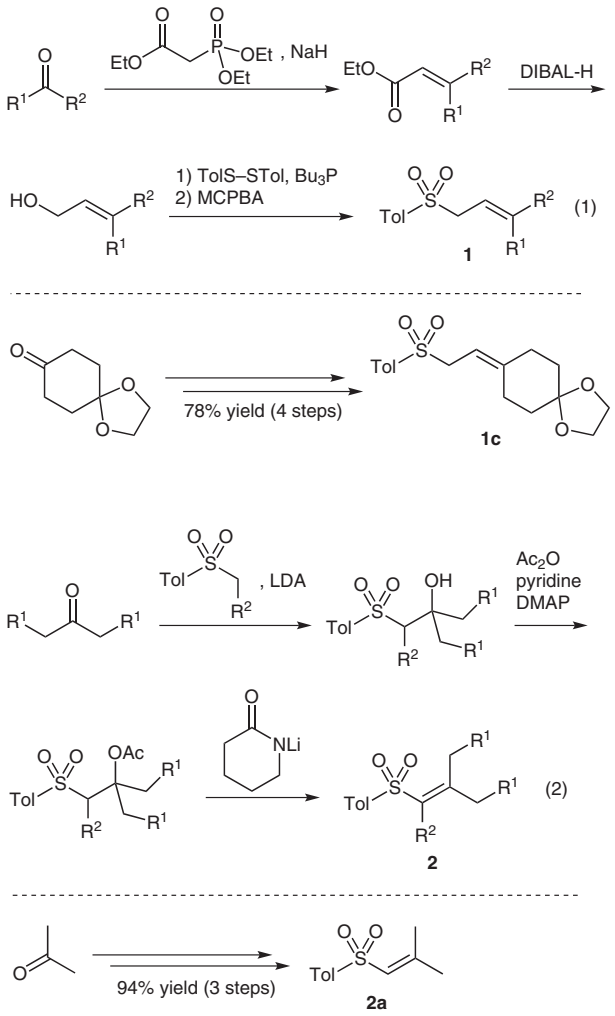
allylic alcohols were converted into the corresponding sulfides, and the sulfides were oxidized with MCPBA to furnish the requisite allyl *p*-tolyl sulfones **1**.[10] When 1,4-dioxaspiro[4.5]decan-8-one was used as the starting material, allyl *p*-tolyl sulfone **1c** was obtained in 78% overall yield. *p*-Tolyl vinyl sulfones **2** were prepared from carbonyl compounds and alkyl *p*-tolyl sulfones (Scheme 2, equation 2). Nucleophilic addition of the carbanion generated from alkyl *p*-tolyl sulfones to carbonyl compounds afforded β-hydroxyalkyl sulfones. Subsequent acetylation of the hydroxy group with acetic anhydride, followed by an elimination reaction of the resulting acetate with lithium amide, afforded the desired *p*-tolyl vinyl sulfones **2**. For example, isocrotyl *p*-tolyl sulfone (**2a**) was prepared from acetone and methyl *p*-tolyl sulfone in 94% yield over three steps.



Scheme 2 Preparation of allyl sulfones **1** and vinyl sulfones **2** (Tol = 4-MeC_6H_4)

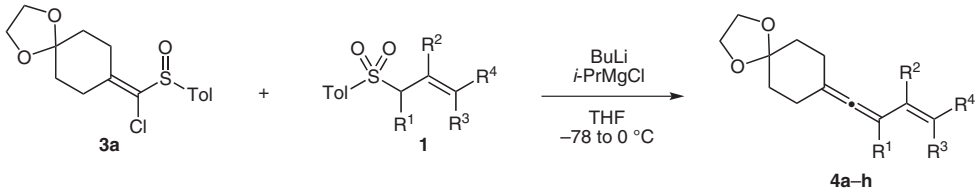
With two types of α-sulfonylallyl anion sources in hand, our attention was turned to the coupling reaction of 1-chlorovinyl *p*-tolyl sulfoxides **3** with the sulfones **1** or **2**. In a previous preliminary study, we reported that the reaction of the magnesium alkylidene carbenoid generated from the sulfoxide **3a** with the α-sulfonylallyllithium generated from allyl sulfone **1a** gave vinylallene **4a** in 51% yield (Table 1, entry 1).[6c] In this reaction, a solution of α-sulfonylallyllithium in THF was added to a solution of magnesium alkylidene carbenoid in THF through a cannula. The experimental procedure was modified for the coupling reaction to forgo these laborious cannula transfers. After several experimentations, it was found that the reaction could proceed when the magnesium alkylidene carbenoid was generated in the presence of α-sulfonylallyllithium, indicating that the order of addition of the two components was inconsequential. It was also found that using *tert*-butylmagnesium chloride as an additive improved the yield of the reaction. *tert*-Butylmagnesium chloride was not capable of reacting with the sulfoxides **3** and improved the reaction by minimizing protonation of the magnesium alkylidene carbenoid by trace water in the reaction media. By our improved protocol, the desired coupling product **4a** was obtained in 57% yield (Table 1, entry 2).

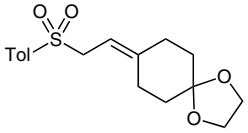
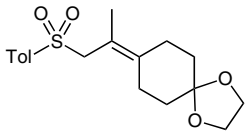
To demonstrate the extent of substrate tolerance in this reaction, various allyl sulfones **1b**–**h** were used for the coupling reaction (Table 1, entries 3–10).[11] The reaction of both acyclic and cyclic 3,3-disubstituted allyl sulfones **1b**–**d** with 1-chlorovinyl *p*-tolyl sulfoxide **3a** proceeded smoothly under the optimized conditions to give the corresponding vinylallenes **4b**–**d** in 66–88% yields (entries 3–5). When geometric isomers of cinnamyl sulfone, (*E*)-**1e** and (*Z*)-**1e**, were used in the reaction, styrylallenes (*E*)-**4e** and (*Z*)-**4e** were formed without isomerization of the C=C bond (entries 6 and 7).[12] The sulfones **1f** and **1g**, which bear a methyl group at the β-position, also reacted with the sulfoxide **3a** to furnish tri- and pentasubstituted vinylallenes **4f** and **4g** (entries 8 and 9). However, attempts to synthesize the fully substituted vinylallene **4h** were unsuccessful because of the difficulty in deprotonating the α-substituted allyl sulfone **1h** (entry 10).

The coupling reaction was applicable to a variety of magnesium alkylidene carbenoids (Table 2).[13] 1-Chlorovinyl *p*-tolyl sulfoxides **3b**–**d** having two alkyl groups including methyl, ethyl, and 2-phenylethyl groups at the β-position underwent the reaction with allyl sulfone **1c** to give the corresponding vinylallenes **4i**–**k** in 68–80% yields (Table 2, entries 1–3). The coupling reaction also took place with cyclic 1-chlorovinyl sulfoxides **3e**–**g** bearing a 5-, 8-, and 15-membered ring to afford vinylallenes **4l**–**n** in 53–85% yields (entries 4–6). When sulfoxide (*Z*)-**3h**, which has two different substituents at the β-position, was employed in the reaction, vinylallene **4o** was obtained in 63% yield, whereas the reaction with the other geometric isomer (*E*)-**3h** afforded the same product **4o** in lower yield (entries 7 and 8). Presumably, this is due to the difference in reactivity of the magnesium alkylidene carbenoids toward the α-sulfonylallyllithium.

The deprotonation of vinyl sulfones **2** was used as an alternative method for the generation of α-sulfonylallyllithiums (Table 3). In this reaction, a proton at the γ-position is abstracted by butyllithium. Considering the difficulty in deprotonating α-substituted allylsulfones (Table 1, entry

Table 1 Synthesis of Vinylallenes **4a**–**h** from Allyl Sulfones **1** and Sulfoxide **3a**



Entry	Allyl sulfone **1**	R^1	R^2	R^3	R^4	Vinylallene **4**	Yield of **4** (%)
1[a]	**1a**	H	H	H	H	**4a**	51
2[b]	**1a**	H	H	H	H	**4a**	57
3[b]	**1b**	H	H	Me	Me	**4b**	73
4[b]	**1c**					**4c**	88
5[b]	**1d**	H	H	Ph	Ph	**4d**	66
6[b]	(*E*)-**1e**	H	H	H	Ph	(*E*)-**4e**	72
7[b]	(*Z*)-**1e**	H	H	Ph	H	(*Z*)-**4e**	68
8[b]	**1f**	H	Me	H	H	**4f**	74
9[b]	**1g**					**4g**	68
10[b,c]	**1h**	Me	Me	Me	Me	**4h**	0

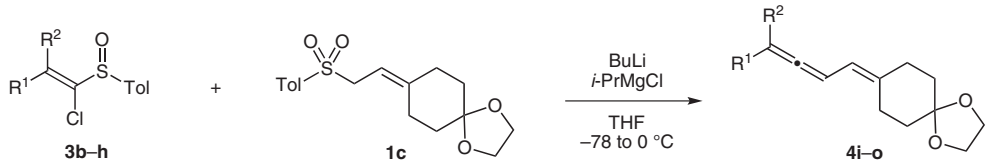
[a] A solution of α-sulfonylallyllithium in THF was added to a solution of magnesium alkylidene carbenoid in THF through a cannula.
[b] Magnesium alkylidene carbenoid was generated from sulfoxide **3a** in the presence of α-sulfonylallyllithium.
[c] *t*-BuLi was used as a base instead of BuLi.

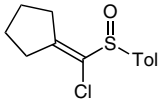
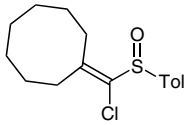
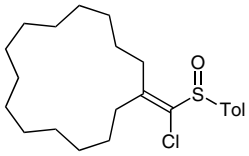
10), this method is particularly suitable for generating α-substituted α-sulfonylallyllithiums. As expected, the coupling reaction of acyclic and cyclic vinyl sulfones **2a**–**d** with sulfoxide **3a** gave a variety of vinylallenes **4f** and **4p**–**r** in 64–79% yields (Table 3, entries 1–4). Vinylallenes **4s** and **4t** bearing a substituent at the 3-position were obtained from α-substituted vinyl sulfones **2e** and **2f** in 82% and 75% yield, respectively (entries 5 and 6). Vinyl sulfone **2g** bearing a *tert*-butoxycarbonyl group at the α-position could also be used as the coupling partner, although the yield of the product **4u** was far from satisfactory due to the low nucleophilicity of the resulting carbanion (entry 7).

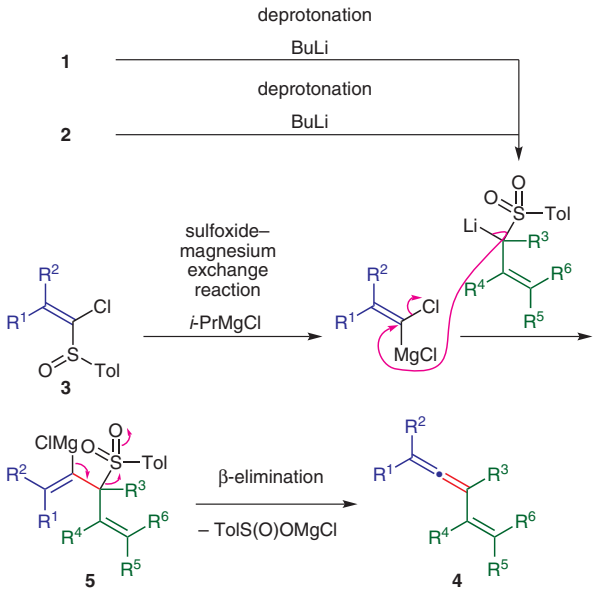
In the ^{13}C NMR spectra of vinylallenes **4**, the signals corresponding to allenic carbon atoms were observed in the range of 200 to 204 ppm, and characteristic IR absorptions of allenes **4** were observed at 1939–1952 cm^{-1}. Over short periods of time, vinylallenes **4** were sufficiently stable in air at room temperature and could be purified by column chromatography on silica gel. However, these compounds were not stable during long-term storage. For example, 88% of vinylallene **4a** decomposed after five days of storage at 25 °C. When vinylallene **4a** was kept at 40 °C, it decomposed completely within three hours. Diluted solutions of vinylallenes decomposed over longer time periods than neat samples. A solution of vinylallene **4a** in $CHCl_3$ gradually degraded, and 41% of vinylallene **4a** remained after five days of storage at 25 °C. When a solution of vinylallene **4a** was stored at 0 °C for three weeks, 65% of vinylallene **4a** could be recovered from the resulting messy sample.

A plausible mechanism for the coupling reaction is shown in Scheme 3. First, an α-sulfonylallyllithium is generated from allyl sulfone **1** or vinyl sulfone **2** and butyllithium. Once the magnesium alkylidene carbenoid has been generated from 1-chlorovinyl *p*-tolyl sulfoxide **3** and isopropylmagnesium chloride by a sulfoxides–magnesium exchange reaction,[5] nucleophilic substitution of the resulting magnesium alkylidene carbenoid with the α-sulfonylallyllithium takes place at the carbenoid carbon atom to give intermediate **5**.[14,15] Magnesium 4-methylbenzenesulfinate chloride is lost from intermediate **5** to form vinylallene **4**.

Table 2 Synthesis of Vinylallenes **4i–o** from Allyl Sulfone **1c** and Sulfoxides **3b–h**



Entry	Sulfoxide **3**	R^1	R^2	Vinylallene **4**	Yield of **4** (%)
1	**3b**	Me	Me	**4i**	78
2	**3c**	Et	Et	**4j**	68
3	**3d**	$PhCH_2CH_2$	$PhCH_2CH_2$	**4k**	80
4	**3e**			**4l**	85
5	**3f**			**4m**	67
6	**3g**			**4n**	53
7	(*E*)-**3h**	Me	n-C_5H_{11}	**4o**	49
8	(*Z*)-**3h**	n-C_5H_{11}	Me	**4o**	63

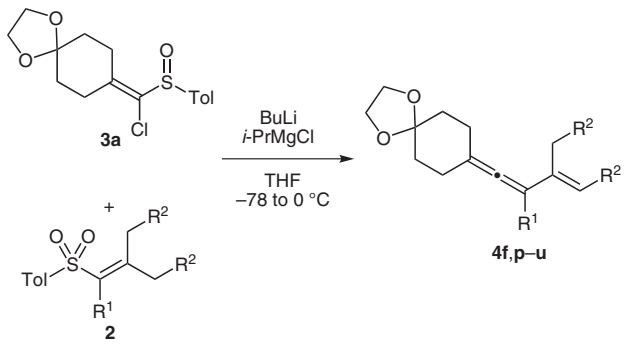


Scheme 3 A plausible mechanism for the reaction of magnesium alkylidene carbenoids with α-sulfonylallyllithiums

In summary, we have developed an efficient method for the synthesis of multi-substituted vinylallenes. The present strategy enabled us to combine two different coupling partners, the vinylidene and allylidene synthons, via the C=C bond without homocoupling products. We were able to use both allyl and vinyl sulfones as α-sulfonylallyl anion sources, which is a strength of our strategy as both classes of compounds could be readily prepared from diverse aldehydes and ketones. Further studies on the applications of magnesium alkylidene carbenoids as vinylidene building blocks are in progress and will be reported in due course.

Melting points were measured using a Yanaco MP-S3 apparatus and are uncorrected. NMR spectra were measured in a $CDCl_3$ solution with Jeol JNM-LA 300, Jeol JNM-LA 500, Bruker DPX 300, Bruker DPX 400, and Bruker AV 600 spectrometers. Mass spectra (MS) were obtained at 70 eV by direct injection with a Hitachi M-80B mass spectrometer. IR spectra were recorded on a PerkinElmer Spectrum One FTIR instrument. Silica gel 60 N (Kanto Chemical) 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. Anhyd THF was purchased from Kanto Chemical Co., Inc. and used as supplied. Toluene was distilled from CaH_2. All reactions involving air- or water-sensitive compounds were routinely conducted in glassware that had been flame-dried under a positive pressure of argon. 1-Chlorovinyl *p*-tolyl sulfoxides **3** were prepared according to the procedure

Table 3 Synthesis of Vinylallenes **4f**,**p**–**u** from Vinyl Sulfones **2** and Sulfoxide **3a**



Entry	Vinyl sulfone **2**	Vinylallene **4**	Yield of **4** (%)
1	**2a**	**4f**	74
2	**2b**	**4p**	64
3	**2c**	**4q**	68
4[a]	**2d**	**4r**	79
5	**2e**	**4s**	82
6	**2f**	**4t**	75
7[a]	**2g**	**4u**	30

[a] LDA was used as a base instead of BuLi.

described in the literature.[6a,c,e,16] Allyl *p*-tolyl sulfones **1a**,[17a] **1b**,[17b] (*E*)-**1e**,[17c] and **1f**,[17b] *p*-tolyl vinyl sulfones **2a**,[18a] **2b**,[9c] and **2e**,[18b] and vinylallene **4a**[6c] are known compounds.

8-(2-Tosylethylidene)-1,4-dioxaspiro[4.5]decane (1c); Typical Procedure

Triethyl phosphonoacetate (3.84 g, 17.1 mmol) was added dropwise to a suspension of NaH (dispersion in paraffin liquid, 55%, 660 mg, 15 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred at 25 °C for 30 min. A soln of 1,4-dioxaspiro[4.5]decan-8-one (1.56 g, 10.0 mmol) in THF (5.0 mL) was added to the resulting soln at 0 °C, and the reaction mixture was stirred at 25 °C for 10 min. The reaction was quenched with H_2O (15 mL), and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.28 (hexane–EtOAc, 3:1)] to give ethyl 2-(1,4-dioxaspiro[4.5]decan-8-ylidene)acetate (2.25 g, 9.94 mmol, 99%) as a colorless oil. A 1.02 M soln of DIBAL-H in hexane (20.6 mL, 21.0 mmol) was added to a soln of ethyl 2-(1,4-dioxaspiro[4.5]decan-8-ylidene)acetate (2.25 g, 9.94 mmol) in toluene (20 mL) at –78 °C, and the reaction mixture was stirred at–78 °C for 5 min. The reaction was quenched with sat. aq potassium sodium tartrate (20 mL), and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.45 (hexane–EtOAc, 1:1)] to give 2-(1,4-dioxaspiro[4.5]decan-8-ylidene)ethanol (1.77 g, 9.61 mmol, 97%) as a colorless oil. Bu_3P (2.75 g, 13.6 mmol) was added to a soln of 2-(1,4-dioxaspiro[4.5]decan-8-ylidene)ethanol (1.77 g, 9.61 mmol) and $(4\text{-}MeC_6H_4S)_2$ (3.10 g, 12.6 mmol) in THF (35 mL) at 0 °C, and the reaction mixture was stirred at 25 °C for 12 h. Aq NaOH (5%, 10 mL) was added to the reaction mixture, and the mixture was extracted with toluene (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.20 (hexane–EtOAc, 10:1)] to give 8-[2-(*p*-tolylthio)ethylidene]-1,4-dioxaspiro[4.5]decane (2.64 g, 9.09 mmol, 95%) as a colorless oil. MCPBA (with approximately 25% H_2O, 2.07 g, 9.0 mmol) was added to a soln of 8-[2-(*p*-tolylthio)ethylidene]-1,4-dioxaspiro[4.5]decane (1.25 g, 4.30 mmol) in $CHCl_3$ (20 mL) at 0 °C over a period of 20 min, and the reaction mixture was stirred at 0 °C for 1 h. The reaction was quenched with sat. aq Na_2SO_3 (7.5 mL), and the mixture was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.21 (hexane–EtOAc, 2:1)] to give **1c** (1.17 g, 3.63 mmol, 84%) as colorless crystals; mp 120.1–121.0 °C.

IR (KBr): 2961, 2923, 1597, 1444, 1311, 1296, 1144, 1123, 1085, 1031, 904, 863, 812, 756, 746 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (br t, *J* = 6.7 Hz, 2 H), 1.60 (br t, *J* = 6.7 Hz, 2 H), 1.96 (br t, *J* = 6.7 Hz, 2 H), 2.24 (br t, *J* = 6.7 Hz, 2 H), 2.45 (s, 3 H), 3.80 (d, *J* = 8.0 Hz, 2 H), 3.88–3.94 (m, 4 H), 5.21 (br t, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.1 Hz, 2 H).

MS (EI): *m*/*z* (%) = 322 (M^+, 2), 167 (100), 123 (27), 105 (20), 91 (13), 86 (13).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{22}O_4S$: 322.1239; found: 322.1238.

(3-Tosylprop-1-ene-1,1-diyl)dibenzene (1d)

Yield: 2.51 g (71%); colorless crystals; mp 128.1–128.9 °C.

IR (KBr): 2967, 2923, 1595, 1490, 1445, 1314, 1290, 1226, 1167, 1133, 1084, 888, 774, 749, 709, 700, 640 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 3.90 (d, *J* = 7.9 Hz, 2 H), 6.13 (t, *J* = 7.9 Hz, 1 H), 6.67–6.73 (m, 2 H), 7.14–7.32 (m, 10 H), 7.66 (d, *J* = 8.2 Hz, 2 H).

MS (EI): *m*/*z* (%) = 348 (M^+, 1), 193 (100), 178 (15), 115 (36), 91 (14).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{22}H_{20}O_2S$: 348.1184; found: 348.1181.

(*Z*)-1-Methyl-4-[(3-phenylallyl)sulfonyl]benzene [(*Z*)-1e]

Yield: 393.3 mg (14%); colorless crystals; mp 71.6–72.2 °C.

IR (KBr): 3023, 2910, 1593, 1447, 1393, 1311, 1302, 1290, 1167, 1131, 1084, 901, 767, 698, 661 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 4.03 (d, *J* = 7.8 Hz, 2 H), 5.71 (td, *J* = 7.8, 11.4 Hz, 1 H), 6.79 (d, *J* = 11.4 Hz, 1 H), 6.99–7.02 (m, 2 H), 7.21–7.28 (m, 3 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 2 H).

MS (EI): *m*/*z* (%) = 272 (M^+, 3), 117 (100), 115 (23), 91 (12).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{16}O_2S$: 272.0871; found: 272.0869.

8-(1-Tosylpropan-2-ylidene)-1,4-dioxaspiro[4.5]decane (1g)
Yield: 2.18 g (43%); colorless crystals; mp 117.9–118.3 °C.

IR (KBr): 2957, 2890, 1595, 1448, 1311, 1303, 1287, 1147, 1116, 1085, 1030, 924, 891, 817, 742, 675 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (br t, *J* = 6.3 Hz, 2 H), 1.56–1.63 (m, 2 H), 1.78 (s, 3 H), 1.97 (br t, *J* = 6.3 Hz, 2 H), 2.28 (br t, *J* = 6.3 Hz, 2 H), 2.45 (s, 3 H), 3.89 (s, 2 H), 3.90–3.94 (m, 4 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H).

MS (EI): *m*/*z* (%) = 336 (M^+, 1), 181 (100), 137 (23), 119 (22), 99 (18), 91 (16), 86 (13).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{24}O_4S$: 336.1395; found: 336.1396.

1-[(3,4-Dimethylpent-3-en-2-yl)sulfonyl]-4-methylbenzene (1h)
Yield: 378.9 mg (15%); colorless crystals; mp 97.3–98.2 °C.

IR (KBr): 2978, 2922, 1595, 1452, 1305, 1286, 1240, 1142, 1085, 818, 729, 659 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.23–1.27 (m, 3 H), 1.49 (d, *J* = 7.0 Hz, 3 H), 1.59 (s, 3 H), 1.72 (s, 3 H), 2.44 (s, 3 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.69 (d, *J* = 8.2 Hz, 2 H).

MS (EI): *m*/*z* (%) = 252 (M^+, 1), 97 (100), 55 (23).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{20}O_2S$: 252.1184; found: 252.1183.

1-Methyl-4-[(2-methylprop-1-en-1-yl)sulfonyl]benzene (2a); Typical Procedure
A 1.65 M soln of BuLi in hexane (4.30 mL, 7.10 mmol) was added to a soln of *i*-Pr_2NH (0.720 g, 7.12 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred at 0 °C for 10 min. A soln of 1-methyl-4-(methylsulfonyl)benzene (1.02 g, 5.99 mmol) in THF (5 mL) was added dropwise to the resulting soln at –78 °C, and the mixture was stirred at –78 °C for 10 min. Acetone (0.400 g, 6.89 mmol) was added to the resulting soln at –78 °C, and the reaction mixture was stirred at –78 °C for 10 min. The reaction was quenched with sat. aq NH_4Cl (6.0 mL), and the mixture was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave crude 2-methyl-1-tosylpropan-2-ol (1.35 g) as a colorless oil. 2-Methyl-1-tosylpropan-2-ol (1.35 g) was added to a soln of Ac_2O (11.9 mL, 126 mmol) in pyridine (24.3 mL, 300 mmol) at 25 °C. DMAP (0.125 g, 1.02 mmol) was added to the resulting soln at 25 °C, and the reaction mixture was stirred at 25 °C for 12 h. After the volatile materials were removed under reduced pressure, the residue was purified by column chromatography on silica gel [R_f = 0.27 (hexane–EtOAc, 3:1)] to give 2-methyl-1-tosylpropan-2-yl acetate (1.58 g, 5.84 mmol, 97% yield for 2 steps) as colorless crystals. A 1.65 M soln of BuLi in hexane (10.6 mL, 17.5 mmol) was added to a soln of 2-piperidone (1.74 g, 17.6 mmol) in THF (40 mL) at 0 °C, and the mixture was stirred at 0 °C for 10 min. The resulting soln was added to a soln of 2-methyl-1-tosylpropan-2-yl acetate (1.58 g, 5.84 mmol) in THF (20 mL) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched with sat. aq NH_4Cl (12 mL), and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.28 (hexane–EtOAc, 3:1)] to give **2a** (1.19 g, 5.66 mmol, 97%) as colorless crystals; mp 64.5–65.0 °C (Lit.[18a] mp 62–63 °C).

The spectroscopic properties of **2a** matched those reported in the literature.[18a]

1-[(Cyclopentylidenemethyl)sulfonyl]-4-methylbenzene (2c)
Yield: 1.15 g (98%); colorless crystals; mp 39.0–39.5 °C.

IR (KBr): 2960, 2876, 1633, 1597, 1417, 1329, 1312, 1287, 1147, 1086, 1031, 862, 815 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.65 (quint, *J* = 7.0 Hz, 2 H), 1.75 (quint, *J* = 7.0 Hz, 2 H), 2.40–2.45 (m, 5 H), 2.79 (br t, *J* = 6.9 Hz, 2 H), 6.25 (br s, 1 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 65.69; H, 6.80; S, 13.58.

1-[(Cyclohexylidenemethyl)sulfonyl]-4-methylbenzene (2d)
Yield: 510.4 mg (99%); colorless crystals; mp 37.0–37.6 °C.

IR (KBr): 2945, 2936, 2855, 1620, 1443, 1310, 1297, 1288, 1141, 1085, 813, 792 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.50–1.66 (m, 6 H), 2.14 (br t, *J* = 5.7 Hz, 2 H), 2.41 (s, 3 H), 2.71 (br t, *J* = 5.7 Hz, 2 H), 6.10–6.13 (m, 1 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.76 (d, *J* = 8.1 Hz, 2 H).

Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.16; H, 7.25; S, 12.81. Found: C, 66.83; H, 7.21; S, 12.78.

1-Methoxy-4-(4-methyl-3-tosylpent-3-en-1-yl)benzene (2f)
Yield: 1.58 g (54%); colorless crystals; mp 90.5–91.1 °C.

IR (KBr): 2937, 1633, 1610, 1512, 1457, 1444, 1299, 1245, 1172, 1137, 1085, 1029, 814, 692, 601 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.78 (s, 3 H), 2.13 (s, 3 H), 2.42 (s, 3 H), 2.64–2.70 (m, 2 H), 2.72–2.78 (m, 2 H), 3.79 (s, 3 H), 6.82 (d, *J* = 8.5 Hz, 2 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H).

MS (EI): *m*/*z* (%) = 344 (M^+, 16), 121 (100).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{24}O_3S$: 344.1446; found: 344.1447.

***tert*-Butyl 3-Methyl-2-tosylbut-2-enoate (2g)**
A 2.69 M soln of BuLi in hexane (3.12 mL, 8.39 mmol) was added to a soln of *i*-Pr_2NH (0.821 g, 8.11 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred at 0 °C for 10 min. A soln of *tert*-butyl 2-(*p*-tolylthio)acetate[19] (1.67 g, 7.01 mmol) in THF (15 mL) was added dropwise to the resulting soln at –78 °C, and the mixture was stirred at –78 °C for 10 min. Acetone (0.450 g, 7.75 mmol) was added to the resulting soln at –78 °C, and the reaction mixture was stirred at –78 °C for 10 min. The reaction was quenched with sat. aq NH_4Cl (6.0 mL) and the mixture was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and filtered. Removal of the solvent under reduced pressure gave crude *tert*-butyl 3-hydroxy-3-methyl-2-(*p*-tolylthio)butanoate (1.78 g) as a colorless oil. *tert*-Butyl 3-hydroxy-3-methyl-2-(*p*-tolylthio)butanoate (1.78 g) was added to a soln of Ac_2O (15.0 mL, 159 mmol) in pyridine (30.0 mL, 371 mmol) at 25 °C. DMAP (0.145 g, 1.19 mmol) was then added to the resulting soln at 25 °C, and the reaction mixture was stirred at 25 °C for 12 h. After the volatile materials were removed under reduced pressure, the residue was purified by column chromatography on silica gel [R_f = 0.20 (hexane–EtOAc, 10:1)] to give *tert*-butyl 3-acetoxy-3-methyl-2-(*p*-tolylthio)butanoate (1.31 g, 3.87 mmol, 55% yield for 2 steps) as a colorless oil. A 2.69 M soln of BuLi in hexane (7.10 mL, 19.1 mmol) was added to a soln of 2-piperidone (1.93 g, 19.5 mmol) in THF (50 mL) at 0 °C, and the mixture was stirred at 0 °C for 10 min. The resulting soln was added to a soln of *tert*-butyl 3-acetoxy-3-methyl-2-(*p*-tolylthio)butanoate (1.31 g, 3.87 mmol) in THF (30 mL) at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. The reaction was quenched with sat. aq NH_4Cl (14 mL) and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.28 (hexane–EtOAc, 20:1)] to give *tert*-butyl 3-methyl-2-(*p*-tolylthio)but-2-enoate (0.993 g, 3.57 mmol, 92%) as a colorless oil. MCPBA (with approximately 25% H_2O, 1.72 g, 7.48 mmol) was added to a soln of *tert*-butyl 3-methyl-2-(*p*-tolylthio)but-2-enoate (0.993 g, 3.57 mmol) in $CHCl_3$ (15 mL) at 0 °C over a period of 20 min, and the reaction mixture was stirred at 0 °C for 1 h. The reaction was

quenched with sat. aq Na_2SO_3 (7.5 mL), and the mixture was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.23 (hexane–EtOAc, 2:1)] to give **2g** (0.986 g, 3.18 mmol, 89%) as colorless crystals; mp 102.5–103.0 °C.

IR (KBr): 2973, 1720, 1617, 1369, 1317, 1271, 1147, 1086, 1008, 843, 806, 756, 660 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 9 H), 1.92 (s, 3 H), 2.12 (s, 3 H), 2.43 (s, 3 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H).

Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14; S, 10.33. Found: C, 61.73; H, 7.06; S, 10.36.

1-Chlorovinyl *p*-Tolyl Sulfoxides 3

1-Chlorovinyl *p*-tolyl sulfoxides **3** were prepared according to the procedure described in the literature.[6a,c,e,16] The physical and analytical data of new sulfoxides **3c**,**d** are given below.

1-[(1-Chloro-2-ethylbut-1-en-1-yl)sulfinyl]-4-methylbenzene (3c)

Yield: 438.3 mg (24%); yellow oil.

IR (neat): 2974, 2937, 2875, 1597, 1493, 1462, 1087, 1061, 877, 808 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.4 Hz, 3 H), 1.22 (t, *J* = 7.4 Hz, 3 H), 2.30–2.46 (m, 2 H), 2.41 (s, 3 H), 2.71 (qd, *J* = 7.4, 14.8 Hz, 1 H), 2.81 (qd, *J* = 7.4, 14.8 Hz, 1 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H).

MS (FAB): *m*/*z* (%) = 257 ($[M + H]^+$, 100), 239 (12).

HRMS (FAB): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{18}ClOS$: 257.0767; found: 257.0765.

{3-[Chloro(*p*-tolylsulfinyl)methylene]pentane-1,5-diyl}dibenzene (3d)

Yield: 2.06 g (84%); colorless crystals; mp 66.1–67.1 °C.

IR (KBr): 3024, 2927, 1601, 1495, 1453, 1087, 1054, 889, 804, 747, 710, 695 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.62–3.00 (m, 8 H), 7.17 (d, *J* = 7.4 Hz, 2 H), 7.19–7.30 (m, 10 H), 7.33 (t, *J* = 7.4 Hz, 2 H).

MS (FAB): *m*/*z* (%) = 409 [$(M + 1)^+$, 100], 91 (19).

HRMS (FAB): *m*/*z* $[(M + 1)^+]$ calcd for $C_{25}H_{26}ClOS$: 409.1393; found: 409.1388.

8,8′-(Prop-1-ene-1,3-diylidene)bis(1,4-dioxaspiro[4.5]decane) (4c); Typical Procedure

A 1.62 M soln of BuLi in hexane (0.185 mL, 0.299 mmol) was added dropwise to a soln of **1c** (96.7 mg, 0.300 mmol) in THF (1.0 mL) at –78 °C, and the mixture was allowed to warm to –70 °C over a period of 10 min. A soln of **3a** (32.7 mg, 0.100 mmol) in THF (0.5 mL) and a 1.02 M soln of *t*-BuMgCl in THF (0.098 mL, 0.100 mmol) were added to the resulting soln at –78 °C. A 2.0 M soln of *i*-PrMgCl in THF (0.14 mL, 0.28 mmol) was added to the resulting soln at –78 °C, and the reaction mixture was allowed to warm to 0 °C over a period of 1.5 h. The reaction was quenched with sat. aq NH_4Cl (1.5 mL) and the mixture was extracted with $CHCl_3$ (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.18 (hexane–EtOAc, 10:1)] to give **4c** as colorless crystals; yield: 28.0 mg (0.0879 mmol, 88%); mp 103.3–104.4 °C.

IR (KBr): 2952, 2877, 1947 (=•=), 1435, 1271, 1239, 1119, 1078, 1031, 951, 942, 902, 817 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.66–1.78 (m, 8 H), 2.26–2.34 (m, 6 H), 2.38 (br t, *J* = 6.5 Hz, 2 H), 3.96 (s, 4 H), 3.97 (s, 4 H), 5.62 (d, *J* = 10.8 Hz, 1 H), 5.92 (d of quint, *J* = 2.1, 10.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.3 (CH_2), 28.6 (CH_2), 33.6 (CH_2), 35.2 (CH_2), 35.3 (CH_2), 35.9 (CH_2), 64.3 (CH_2), 88.3 (CH), 100.8 (C), 108.3 (C), 108.8 (C), 119.0 (CH), 138.3 (C), 201.9 (C).

MS (EI): *m*/*z* (%) = 318 (M^+, 97), 232 (86), 204 (33), 170 (56), 118 (100), 117 (28), 99 (71), 91 (28), 86 (27).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{19}H_{26}O_4$: 318.1831; found: 318.1829.

8-(4-Methylpenta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4b)

Yield: 16.1 mg (73%); colorless oil.

IR (neat): 2954, 2885, 1950 (=•=), 1718, 1441, 1377, 1240, 1217, 1111, 1067, 1032, 905, 757, 668 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.71–1.79 (m, 10 H), 2.26–2.33 (m, 4 H), 3.97 (s, 4 H), 5.60 (d of sept, *J* = 1.4, 10.7 Hz, 1 H), 5.89 (d of quint, *J* = 2.1, 10.7 Hz, 1 H).

MS (EI): *m*/*z* (%) = 220 (M^+, 2), 99 (100), 91 (11), 86 (14), 55 (16).

HRMS of compound **4b** could not be measured because of low intensity of M^+ peak.

8-(4,4-Diphenylbuta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4d)

Yield: 22.7 mg (66%); colorless crystals; mp 109.6–110.3 °C.

IR (KBr): 3020, 2951, 2882, 1946 (=•=), 1494, 1445, 1248, 1119, 1066, 1032, 906, 760, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.68–1.83 (m, 4 H), 2.25–2.41 (m, 4 H), 3.97 (s, 4 H), 5.84 (d of quint, *J* = 2.0, 11.1 Hz, 1 H), 6.53 (d, *J* = 11.1 Hz, 1 H), 7.17–7.42 (m, 10 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 28.5 (CH_2), 35.3 (CH_2), 64.36 (CH_2), 64.37 (CH_2), 91.1 (CH), 100.9 (C), 108.3 (C), 124.7 (CH), 127.1 (CH), 127.2 (CH), 127.3 (CH), 128.1 (CH), 128.3 (CH), 130.4 (CH), 139.6 (C), 140.7 (C), 142.3 (C), 203.9 (C).

MS (EI): *m*/*z* (%) = 344 (M^+, 60), 242 (84), 230 (54), 209 (95), 207 (100), 178 (55), 165 (51), 153 (99), 105 (95), 99 (91).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{24}H_{24}O_2$: 344.1776; found: 344.1779.

(*E*)-8-(4-Phenylbuta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane [(*E*)-4e]

Yield: 19.3 mg (72%); colorless oil.

IR (neat): 2951, 2882, 1947 (=•=), 1253, 1121, 1063, 1032, 961, 905, 748, 734, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.79 (t, *J* = 6.5 Hz, 4 H), 2.32–2.39 (m, 4 H), 3.98 (s, 4 H), 5.90 (d of quint, *J* = 2.0, 10.0 Hz, 1 H), 6.46 (d, *J* = 15.8 Hz, 1 H), 6.59 (dd, *J* = 10.0, 15.8 Hz, 1 H), 7.16–7.22 (m, 1 H), 7.26–7.32 (m, 2 H), 7.35–7.40 (m, 2 H).

MS (EI): *m*/*z* (%) = 268 (M^+, 100), 223 (20), 181 (18), 167 (56), 153 (45), 128 (17), 99 (47), 91 (20).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{18}H_{20}O_2$: 268.1463; found: 268.1463.

(*Z*)-8-(4-Phenylbuta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane [(*Z*)-4e]

Yield: 18.2 mg (68%); colorless oil.

IR (neat): 2951, 2881, 1948 (=•=), 1449, 1430, 1242, 1117, 1077, 1032, 904, 774, 733, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.76 (t, *J* = 6.4 Hz, 4 H), 2.30–2.38 (m, 4 H), 3.97 (s, 4 H), 6.08 (t, *J* = 11.4 Hz, 1 H), 6.24–6.32 (m, 1 H), 6.36 (dd, *J* = 0.8, 11.4 Hz, 1 H), 7.18–7.27 (m, 1 H), 7.28–7.37 (m, 4 H).

MS (EI): *m*/*z* (%) = 268 (M^+, 23), 206 (21), 181 (17), 167 (56), 154 (51), 141 (19), 128 (23), 115 (18), 99 (100), 91 (19), 86 (18).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{18}H_{20}O_2$: 268.1463; found: 268.1466.

8-(3-Methylbuta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4f)
Yield: 15.3 mg (74%); colorless oil.

IR (neat): 2950, 2881, 1952 (=•=), 1619, 1441, 1271, 1235, 1117, 1072, 1033, 951, 943, 903, 881 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.68–1.85 (m, 7 H), 2.29–2.36 (m, 4 H), 3.97 (s, 4 H), 4.79–4.82 (m, 1 H), 4.87–4.90 (m, 1 H), 5.79–5.83 (m, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.6 (CH_3), 28.6 (CH_2), 35.4 (CH_2), 64.32 (CH_2), 64.35 (CH_2), 96.0 (CH), 102.8 (C), 108.2 (C), 112.7 (CH_2), 140.1 (C), 200.5 (C).

MS (EI): *m*/*z* (%) = 206 (M^+, 100), 191 (14), 187 (14), 161 (17), 119 (24), 105 (57), 99 (77), 92 (19), 91 (53), 86 (43), 79 (14), 77 (18).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{13}H_{18}O_2$: 206.1307; found: 206.1309.

8,8′-(But-1-ene-1,3-diylidene)bis(1,4-dioxaspiro[4.5]decane) (4g)
Yield: 22.7 mg (68%); colorless oil.

IR (neat): 2950, 2882, 1948 (=•=), 1442, 1271, 1246, 1228, 1119, 1069, 1033, 943, 909, 732 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.65–1.81 (m, 11 H), 2.29–2.36 (m, 4 H), 2.37–2.46 (m, 4 H), 3.96–3.98 (m, 8 H), 6.20 (quint, *J* = 1.9 Hz, 1 H).

MS (EI): *m*/*z* (%) = 332 (M^+, 38), 246 (14), 218 (21), 184 (19), 132 (45), 101 (24), 99 (100), 86 (26).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{28}O_4$: 332.1988; found: 332.1981.

8-(4-Methylpenta-2,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4i)
Yield: 17.2 mg (78%); colorless oil.

IR (neat): 2949, 2881, 1949 (=•=), 1444, 1363, 1272, 1226, 1123, 1105, 1076, 1035, 945, 906, 681 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.68–1.73 (m, 10 H), 2.29 (br t, *J* = 6.5 Hz, 2 H), 2.38 (br t, *J* = 6.6 Hz, 2 H), 3.97 (s, 4 H), 5.61 (d, *J* = 10.9 Hz, 1 H), 5.84–5.90 (d of sept, *J* = 2.7 Hz, 1 H).

MS (EI): *m*/*z* (%) = 220 (M^+, 20), 134 (46), 119 (100), 99 (26), 91 (31).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{20}O_2$: 220.1463; found: 220.1462.

8-(4-Ethylhexa-2,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4j)
Yield: 16.8 mg (68%); colorless oil.

IR (neat): 2963, 2878, 1942 (=•=), 1454, 1272, 1225, 1123, 1106, 1078, 1035, 945, 906, 824, 733, 680 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 6 H), 1.67–1.74 (m, 4 H), 1.99 (dq, *J* = 2.9, 7.4 Hz, 4 H), 2.29 (br t, *J* = 6.4 Hz, 2 H), 2.39 (br t, *J* = 6.4 Hz, 2 H), 3.97 (s, 4 H), 5.61 (d, *J* = 10.8 Hz, 1 H), 6.05 (d of quint, *J* = 2.9, 10.8 Hz, 1 H).

MS (EI): *m*/*z* (%) = 248 (M^+, 20), 162 (27), 133 (100), 105 (22), 99 (19), 91 (19).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{24}O_2$: 248.1776; found: 248.1773.

8-(4-Phenethyl-6-phenylhexa-2,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4k)
Yield: 32.1 mg (80%); colorless oil.

IR (neat): 3026, 2947, 2884, 1943 (=•=), 1603, 1496, 1453, 1271, 1224, 1121, 1099, 1074, 1034, 907, 735, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.66–1.74 (m, 4 H), 2.23–2.40 (m, 8 H), 2.72 (t, *J* = 7.9 Hz, 4 H), 3.97 (s, 4 H), 5.41 (d, *J* = 10.9 Hz, 1 H), 6.01 (d of quint, *J* = 2.8, 10.9 Hz, 1 H), 7.13–7.20 (m, 6 H), 7.22–7.30 (m, 4 H).

MS (EI): *m*/*z* (%) = 400 (M^+, 56), 309 (46), 247 (62), 209 (37), 169 (30), 105 (29), 99 (28), 91 (100).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{28}H_{32}O_2$: 400.2402; found: 400.2405.

8-(3-Cyclopentylideneallylidene)-1,4-dioxaspiro[4.5]decane (4l)
Yield: 21.3 mg (85%); colorless oil.

IR (neat): 2952, 2876, 1946 (=•=), 1436, 1272, 1121, 1096, 1035, 945, 906, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.65–1.73 (m, 8 H), 2.25–2.33 (m, 2 H), 2.33–2.43 (m, 6 H), 3.97 (s, 4 H), 5.64 (d, *J* = 10.9 Hz, 1 H), 5.98 (d of quint, *J* = 3.9, 10.9 Hz, 1 H).

MS (EI): *m*/*z* (%) = 246 (M^+, 53), 160 (100), 145 (39), 131 (42), 118 (66), 117 (69), 99 (49), 92 (50), 91 (48).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{22}O_2$: 246.1620; found: 246.1618.

8-(3-Cyclooctylideneallylidene)-1,4-dioxaspiro[4.5]decane (4m)
Yield: 19.3 mg (67%); colorless oil.

IR (neat): 2928, 2854, 1939 (=•=), 1698, 1445, 1271, 1227, 1122, 1105, 1081, 1035, 946, 908, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.49–1.74 (m, 14 H), 2.14–2.22 (m, 4 H), 2.29 (br t, *J* = 6.6 Hz, 2 H), 2.39 (br t, *J* = 6.4 Hz, 2 H), 3.97 (s, 4 H), 5.64 (br d, *J* = 10.9 Hz, 1 H), 5.91 (d of quint, *J* = 2.0, 10.9 Hz, 1 H).

MS (EI): *m*/*z* (%) = 288 (M^+, 50), 202 (100), 131 (36), 118 (52), 117 (54), 99 (63), 92 (68), 91 (45).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{19}H_{28}O_2$: 288.2089; found: 288.2086.

8-(3-Cyclopentadecylideneallylidene)-1,4-dioxaspiro[4.5]decane (4n)
Yield: 20.6 mg (53%); colorless oil.

IR (neat): 2929, 2856, 1942 (=•=), 1459, 1444, 1271, 1224, 1122, 1100, 1075, 1035, 945, 907, 734 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.52 (m, 24 H), 1.67–1.74 (m, 4 H), 2.00 (dt, *J* = 2.4, 6.7 Hz, 4 H), 2.29 (br t, *J* = 6.3 Hz, 2 H), 2.38 (br t, *J* = 6.3 Hz, 2 H), 3.97 (s, 4 H), 5.61 (br d, *J* = 10.9 Hz, 1 H), 5.94 (d of quint, *J* = 2.4, 10.9 Hz, 1 H).

MS (EI): *m*/*z* (%) = 386 (M^+, 100), 300 (92), 99 (95).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{26}H_{42}O_2$: 386.3185; found: 386.3182.

8-(4-Methylnona-2,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4o)
Yield: 13.6 mg (49%, Table 2, entry 7), 17.6 mg (63%, Table 2, entry 8); colorless oil.

IR (neat): 2954, 2930, 2875, 1946 (=•=), 1443, 1272, 1218, 1123, 1108, 1074, 1035, 945, 906, 758, 682 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (br t, *J* = 7.0 Hz, 3 H), 1.24–1.36 (m, 4 H), 1.36–1.48 (m, 2 H), 1.67–1.73 (m, 7 H), 1.96 (dt, *J* = 2.7, 6.7 Hz, 2 H), 2.29 (br t, *J* = 6.7 Hz, 2 H), 2.38 (br t, *J* = 6.7 Hz, 2 H), 3.97 (s, 4 H), 5.60 (br d, *J* = 10.8 Hz, 1 H), 5.91 (d of sext, *J* = 2.7, 10.8 Hz, 1 H).

MS (EI): *m*/*z* (%) = 276 (M^+, 13), 220 (33), 190 (18), 158 (16), 133 (15), 119 (100), 105 (23), 99 (24), 91 (27).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{28}O_2$: 276.2089; found: 276.2091.

8-(3-Methylbuta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4f); Typical Procedure

A 1.59 M soln of BuLi in hexane (0.190 mL, 0.302 mmol) was added dropwise to a soln of **2a** (63.1 mg, 0.300 mmol) in THF (1.0 mL) at –78 °C, and the mixture was allowed to warm to –55 °C over a period of 20 min. A soln of **3a** (32.7 mg, 0.100 mmol) in THF (0.5 mL) and a 1.02 M soln of *t*-BuMgCl in THF (0.098 mL, 0.100 mmol) were added to the resulting soln at –78 °C. A 2.0 M soln of *i*-PrMgCl in THF (0.14 mL, 0.28 mmol) was added to the resulting soln at –78 °C, and the reaction mixture was allowed to warm to 0 °C over a period of 1.5 h. The reaction was quenched with sat. aq NH_4Cl (1.5 mL) and the mixture was extracted with $CHCl_3$ (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel [R_f = 0.35 (hexane–EtOAc, 10:1)] to give **4f** as a colorless oil; yield: 15.3 mg (0.0742 mmol, 74%).

For spectral properties, see above.

(*Z*)-8-(3-Ethylpenta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4p)

The geometry of the double bond of vinylallene **4p** was determined by NOESY spectrum.

Yield: 14.3 mg (64%); colorless oil.

IR (neat): 2953, 2880, 1950 (=•=), 1718, 1442, 1273, 1241, 1118, 1075, 1033, 951, 943, 903 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3 H), 1.64–1.85 (m, 7 H), 2.03–2.12 (m, 2 H), 2.30–2.36 (m, 4 H), 3.97 (s, 4 H), 5.28–5.36 (m, 1 H), 6.00–6.04 (m, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.3 (CH_3), 13.8 (CH_3), 28.2 (CH_2), 28.6 (CH_2), 35.4 (CH_2), 64.3 (CH_2), 64.4 (CH_2), 89.1 (CH), 101.9 (C), 108.4 (C), 120.5 (CH), 136.1 (C), 200.4 (C).

MS (EI): *m*/*z* (%) = 234 (M$^+$, 24), 189 (26), 120 (34), 119 (37), 105 (36), 99 (100), 91 (53), 87 (51), 77 (26).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{15}H_{22}O_2$: 234.1620; found: 234.1621.

8-[2-(Cyclopent-1-en-1-yl)vinylidene]-1,4-dioxaspiro[4.5]decane (4q)

Yield: 15.8 mg (68%); colorless oil.

IR (neat): 2951, 2885, 1952 (=•=), 1441, 1252, 1113, 1068, 1033, 952, 904, 757, 734 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69–1.82 (m, 4 H), 1.88 (m, 2 H), 2.27–2.35 (m, 6 H), 2.36–2.45 (m, 2 H), 3.97 (s, 4 H), 5.60 (quint, *J* = 2.2, 1 H), 5.93 (br s, 1 H).

MS (EI): *m*/*z* (%) = 232 (M$^+$, 7), 99 (37), 86 (60), 85 (66), 84 (94), 83 (100).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{15}H_{20}O_2$: 232.1463; found: 232.1461.

8-[2-(Cyclohex-1-en-1-yl)vinylidene]-1,4-dioxaspiro[4.5]decane (4r)

Yield: 19.5 mg (79%); colorless oil.

IR (neat): 2929, 2882, 1952 (=•=), 1437, 1234, 1114, 1068, 1033, 951, 943, 904, 758, 734 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54–1.70 (m, 4 H), 1.70–1.84 (m, 4 H), 1.96–2.04 (m, 2 H), 2.05–2.13 (m, 2 H), 2.30 (dt, *J* = 1.7, 6.3 Hz, 4 H), 3.97 (s, 4 H), 5.61–5.65 (m, 1 H), 5.72 (br s, 1 H).

MS (EI): *m*/*z* (%) = 246 (M$^+$, 20), 99 (57), 86 (61), 85 (66), 84 (96), 83 (100).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{22}O_2$: 246.1620; found: 246.1620.

8-(2,3-Dimethylbuta-1,3-dien-1-ylidene)-1,4-dioxaspiro[4.5]decane (4s)

Ethyl *p*-tolyl sulfone was used as the starting material instead of methyl *p*-tolyl sulfone for the synthesis of vinyl sulfone **2e** required for the preparation of **4s**.

Yield: 18.1 mg (82%); colorless oil.

IR (neat): 2949, 2881, 1951 (=•=), 1619, 1442, 1266, 1200, 1120, 1086, 1034, 943, 926, 896, 878 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.68–1.80 (m, 4 H), 1.82 (s, 3 H), 1.84 (s, 3 H), 2.29 (t, *J* = 6.4 Hz, 4 H), 3.97 (s, 4 H), 4.866 (s, 1 H), 4.869 (s, 1 H).

MS (EI): *m*/*z* (%) = 220 (M$^+$, 96), 159 (27), 133 (28), 119 (49), 105 (32), 99 (100), 91 (44), 86 (58).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_{20}O_2$: 220.1463; found: 220.1466.

8-[2-(4-Methoxyphenethyl)-3-methylbuta-1,3-dien-1-ylidene]-1,4-dioxaspiro[4.5]decane (4t)

3-(*p*-Methoxyphenyl)propyl *p*-tolyl sulfone was used as the starting material instead of methyl *p*-tolyl sulfone for the synthesis of vinyl sulfone **2f** required for the preparation of **4t**.

Yield: 25.4 mg (75%); colorless oil.

IR (neat): 2948, 2883, 1949 (=•=), 1614, 1513, 1442, 1247, 1178, 1120, 1079, 1035, 902, 824, 756, 734 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (t, *J* = 6.4 Hz, 4 H), 1.81 (s, 3 H), 2.18–2.25 (m, 4 H), 2.45 (br t, *J* = 7.7 Hz, 2 H), 2.70 (br t, *J* = 7.7 Hz, 2 H), 3.78 (s, 3 H), 3.96 (s, 4 H), 4.86–4.89 (m, 1 H), 4.94 (br s, 1 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H).

MS (EI): *m*/*z* (%) = 340 (M$^+$, 67), 295 (12), 121 (100), 101 (15), 99 (24).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{22}H_{28}O_3$: 340.2038; found: 340.2034.

***tert*-Butyl 2-(1,4-Dioxaspiro[4.5]decan-8-ylidenemethylene)-3-methylbut-3-enoate (4u)**

Yield: 9.1 mg (30%); colorless oil.

IR (neat): 3011, 2954, 2884, 1949 (=•=), 1713 (C=O), 1368, 1247, 1161, 1120, 1082, 1065, 1033, 907, 757 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 9 H), 1.76–1.83 (m, 7 H), 2.36–2.43 (m, 4 H), 3.98 (s, 4 H), 5.06–5.09 (m, 1 H), 5.46–5.48 (m, 1 H).

MS (EI): *m*/*z* (%) = 306 (M$^+$, 1), 250 (99), 235 (22), 205 (42), 161 (27), 143 (32), 112 (40), 99 (34), 86 (39), 57 (100).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{26}O_4$: 306.1831; found: 306.1831.

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