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SYNTHESIS OF ALKENYL SULFONES CONTAINING NORBORNENE MOIETY†

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† Dedicated to Prof. Tohru Fukuyama on the occasion of his 70th Birthday

Abstract – Various cyclopropane containing alkenyl sulfone derivatives were synthesized starting with readily available Diels–Alder adducts.

Sulfones[1] are useful templates in organic synthesis. They are valuable substrates for Ramberg−Bäcklund reaction,[2] van Leusen reaction,[3] Julia−Lythgoe olefination.[4] In addition, they are also used as masked dienes in Diels−Alder (DA) strategy.[5] Sulfonyl groups can be manipulated in different ways and they act as good leaving groups. The sulfonyl groups also increase the acidity of hydrogen in α-position and stabilize the carbanions. Due to their versatile reactivity, they are described as "chemical chameleons".[6] Recently, we reported the synthesis of polycyclic sulfones from parent dialkenyl norbornene precursors via ring-rearrangement metathesis (RRM)[7] as a key step.[8] In connection with our major program on sulfones, we plan to study the influence of cyclopropane at 7-position of norbornene during the RRM protocol. Therefore, here, we describe a simple route to alkenyl sulfones containing cyclopropane moiety.

Our retrosynthetic approach to sulfones containing norbornene unit is shown in Figure 1. We started with the preparation of a readily available DA adduct by reacting maleic anhydride with spiro[2.4]hepta-4,6-diene in benzene at rt to afford the DA adduct in 87% yield.[9] Next, the DA adduct was reduced by following the modified procedure reported by Zhang *et al*.[10] to produce the corresponding diol **4**. In this regard, reduction of the DA adduct with $LiAlH_4$ gave exclusively the diol **4** in 79% yield. Then, the diol **4** was treated with *p*-toluenesulfonyl chloride in pyridine using the modified procedure of Polo *et al*.[11] The tosylate **3** was obtained in 75% yield. Later, treatment of the tosylate **3** with commercially available sodium sulfide ($Na_2S{\cdot}xH_2O$) in the presence of 20% Aliquat® 336 (PTC) in a mixture of toluene and water (1:1) afforded the sulfide **2** in very low yield (Scheme 1). Alternatively, when the compound **3** was treated with sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$) using 20% Aliquat® 336 in a mixture of toluene and water (1:1) the desired sulfide **2** was produced in 98% yield (Scheme 1).

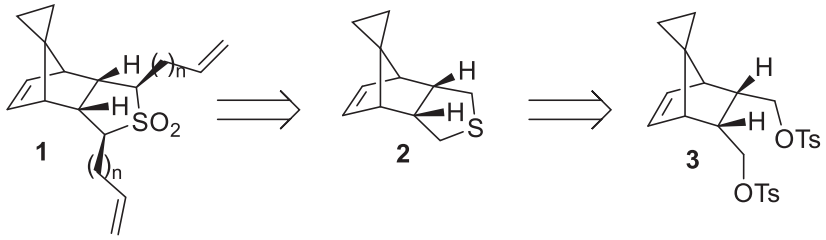
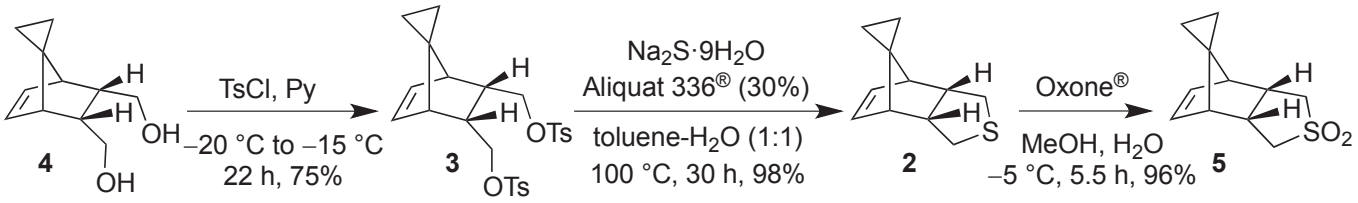


Figure 1. Retrosynthetic approach to various sulfones

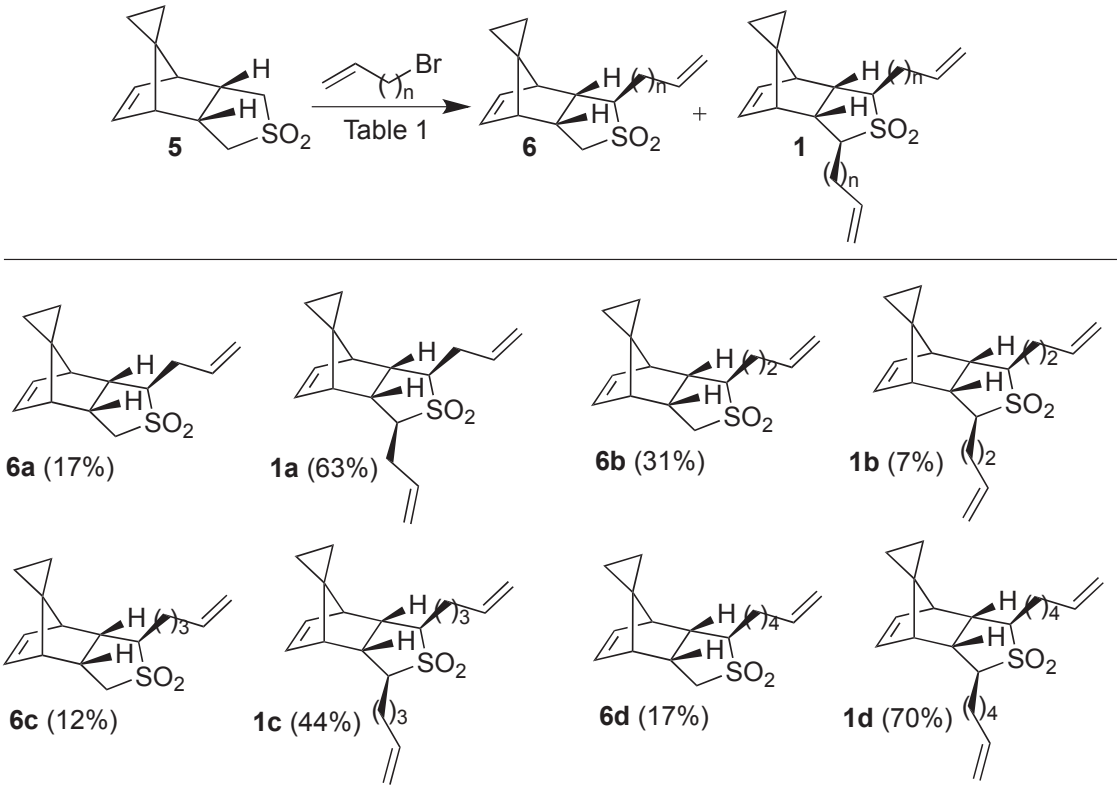


Scheme 1. Synthesis of the sulfone **5**

Our next aim was to synthesize the sulfone **5**, and in this regard, the sulfide **2** was oxidized by treatment with Oxone® in aq. MeOH to deliver the sulfone **5** (Scheme 1). After screening various reaction conditions, the reaction was carried out with 2.4 equivalents of Oxone® at –5 °C the sulfone **5** was obtained in 96% yield.

Later, our efforts were directed towards the synthesis of various dialkenyl sulfone derivatives (Scheme 2). Initially, the sufone **5** was allylated at –77 °C to rt using *n*-BuLi as a base. Here, monoallyl sulfone **6a** was obtained as a major product (42%, entry 1, Table 1) with 2.2 equivalents of allyl bromide. Nevertheless, allylation of the sulfone **5** with excess allyl bromide gave diallyl sulfone **1a** in 63% yield along with the monoallyl sulfone **6a** (17%, entry 2, Table 1). Alkenylation of **5** with 4-bromo-1-butene did not work under similar reaction conditions. Then, the sufone **5** was treated with 4-bromo-1-butene in the presence of HMPA at –71 °C to rt to get the dibutenyl sulfone **1b** (7%) and monobutenyl sulfone **6b** (31%, entry 3, Table 1). Here, the lower yield may be explained as 4-bromo-1-butene undergo elimination reaction to give more stable 1,3-butadiene (gas). When the sulfone **5** was subjected to pentenylation with 5-bromo-1-pentene at 0 °C to rt, delivered mono- and dipentenyl sulfones **6c** (12%) and **1c** (44%) respectively (entry 4, Table 1). Along similar lines, mono- and dihexenyl sulfone derivatives **6d** (17%) and **1d** (70%, entry 5, Table 1) were synthesized.

To gain insight about the role of cyclopropane on RRM process, we carried out the RRM of dialkenyl precursors with metathesis catalysts. Unfortunately, the reaction was unsuccessful due to the failure of ring-opening metathesis of cyclopropane containing norbornene double bond.



Scheme 2. Synthesis of various alkenyl sulfone derivatives

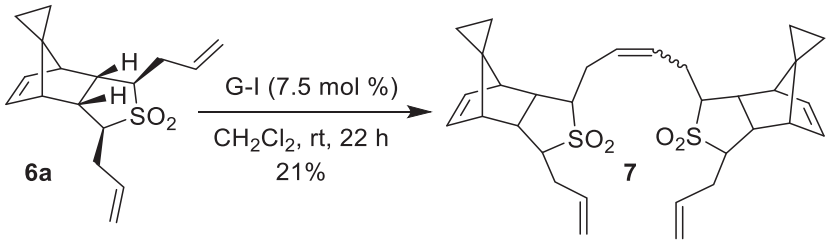
Table 1. Optimized reaction conditions to realize dialkenyl sulfones

entry	*n*	reaction conditions	**6** (yield %)	**1** (yield %)
1	1	allyl bromide (2.2 equiv), *n*-BuLi THF, −77 °C to rt, 25 h	**6a** (42)	**1a** (33)
2	1	allyl bromide (5 equiv), *n*-BuLi THF, −72 °C to rt, 34 h	**6a** (17)	**1a** (63)
3	2	4-bromo-1-butene (6 equiv), *n*-BuLi HMPA, THF −71 °C to rt, 60 h	**6b** (31[a])	**1b** (7[a])
4	3	5-bromo-1-pentene (4 equiv), *n*-BuLi HMPA, THF, 0 °C to rt, 22 h	**6c** (12)	**1c** (44)
5	4	6-bromo-1-hexene (2.8 equiv), *n*-BuLi HMPA, THF, −75 °C to rt, 22 h	**6d** (17[a])	**1d** (70[a])

[a]Isolated yield on the basis of the starting material recovered (9−36%)

Nevertheless, the diallyl compound **6a** on ring-closing metathesis (RCM) with Grubbs first-generation

(G-I) catalyst in dry CH_2Cl_2 at rt delivered cross metathesis (CM) product **7** in 21% yield (on the basis of 18% of the starting material recovered, Scheme 3). With other substrates, a complex mixture of products was observed as indicated by ^1H and ^{13}C NMR spectroscopic data.



Scheme 3. Synthesis of cross metathesis dimer **7**

In summary, we have successfully synthesized various dialkenyl sulfones containing cyclopropane moiety. Though RRM of the dialkenyl sulfones was unsuccessful, metathesis of the diallyl sulfone **6a** produced dimer product **7**. These sulfones can be further manipulated synthetically with the aid of -SO_2- functionality. All the new compounds were fully characterized by spectroscopic data.

EXPERIMENTAL

General details

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker spectrometer operated at 400 or 500 MHz for ^1H and 100.6 or 125.7 MHz for ^{13}C nuclei using tetramethylsilane (TMS) as an internal standard. The high resolution mass spectrometric (HRMS) measurements were carried out using Bruker (Maxis Impact). Infrared (IR) spectra were recorded on Nicolet Impact-400 FT IR spectrometer. Sodium sulfide nonahydrate ($Na_2S·9H_2O$) and *n*-BuLi (1.6 M solution in hexane) were purchased from Acros Organics. Dry hexamethylphosphoramide (HMPA) was prepared by stirring over CaH_2 for 1 h followed by vacuum distillation and anhydrous tetrahydrofuran (THF) was obtained by distillation over sodium benzophenone freshly prior to use.

Preparation of bis-tosylate 3

A solution of the diol **4** (500 mg, 2.77 mmol) in freshly distilled pyridine (20 mL) was cooled to −20 °C under inert atmosphere (N_2) then, was added *p*-toluenesulfonyl chloride (1.59 g, 8.32 mmol) in small portions and the suspension stirred for 30 min at −20 °C. A colorless solid started to precipitate. The suspension was stirred for 22 h at −15 °C. After completion of the reaction (TLC monitoring), cold water was added to dissolve the precipitated pyridine hydrochloride, then a new white precipitate was formed. On storage in a fridge at 4−5 °C for 2 h, the precipitation of the desired tosylate was completed. This precipitate was filtered over *Whatman filter paper* and washed with cold water. The product was dried under vacuum to give the pure compound **3** as a colorless solid (1.01 g, 75%). Mp 120.5−121.5 °C.[12] ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.75 (d, J = 8.3 Hz, 4H), 7.36 (d, J = 8.0 Hz, 4H), 5.98 (t, J = 1.9 Hz,

2H), 3.79 (dd, J = 9.4, 6.2 Hz, 2H), 3.62–3.58 (m, 2H), 2.72–2.66 (m, 2H), 2.47 (s, 6H), 2.27 (br s, 2H), 0.47–0.44 (m, 2H), 0.36–0.32 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 145.2, 135.5, 132.9, 130.1, 128.0, 69.9, 50.5, 44.6, 41.7, 21.9, 7.5, 6.1; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{25}H_{28}O_6S_2Na$ $[M+Na]^+$: 511.1220, found: 511.1219.

Synthesis of sulfide 2

A mixture of tosylate **3** (3.00 g, 6.26 mmol), $Na_2S{\cdot}9H_2O$ (12.03 g, 50.08 mmol), and Aliquat® 336 (759 mg, 1.88 mmol) in a mixed solvent of toluene (45 mL) and water (45 mL) was stirred for 5 min. Then, the reaction mixture was refluxed at 100 °C for 30 h. After completion of the reaction (TLC monitoring), the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography using 1% EtOAc in petroleum ether to obtain the cyclic sulfide **2** (1.10 g, 98%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.26 (t, J = 1.9 Hz, 2H), 3.38–3.33 (m, 2H), 2.70 (dd, J = 11.6, 7.6 Hz, 2H), 2.49–2.44 (m, 2H), 2.14 (t, J = 1.5 Hz, 2H), 0.47–0.38 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 137.3, 54.6, 51.0, 50.8, 34.2, 7.9, 6.5; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{11}H_{14}SK$ $[M+K]^+$: 217.0448, found: 217.0445.

Synthesis of sulfone 5

To a stirred solution of sulfide **2** (1.10 g, 6.17 mmol) in MeOH (40 mL) at −5 °C, was added a solution of Oxone® (4.55 g, 14.81 mmol) in water (40 mL). Then, the reaction mixture became milky white suspension. This suspension was stirred at the same temperature for 5.5 h. After completion of the reaction (TLC monitoring), the solvent was removed under reduced pressure. The resulting residue was extracted with $CHCl_3$ (3 × 30 mL). The combined organic extracts were washed with brine (2 × 10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (30% EtOAc–petroleum ether) to obtain the required sulfone **5** (1.25 g, 96%) as a colorless solid. Mp 170−171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.34 (t, J = 2.0 Hz, 2H), 3.15–3.07 (m, 4H), 2.40–2.35 (m, 4H), 0.58–0.54 (m, 2H), 0.48–0.44 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) = 136.8, 52.5, 50.4, 45.6, 40.1, 7.7, 6.0; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{11}H_{14}NaO_2S$ $[M+Na]^+$: 233.0607, found: 233.0607; IR (neat): υ_{max} = 3054, 2978, 1404, 1296, 1138, 765 cm^{-1}.

Synthesis of allyl sulfones 6a and 1a

A solution of sulfone **5** (300 mg, 1.43 mmol) in anhydrous THF (15 mL) under inert atmosphere (N_2) was cooled to −72 °C. To this solution *n*-BuLi (0.50 mL, 3.4 equiv, 1.6 M solution in hexane) was added dropwise, and the reaction mixture was stirred for 20 min. Next, allyl bromide (0.06 mL, 0.76 mmol) was added at the same temperature (−72 °C). Then, the resulting reaction mixture was allowed to attain rt, and

the stirring was continued for 33 h at rt. After completion of the reaction (TLC monitoring), the reaction mixture was quenched with water (2 mL), and the solvent was removed under reduced pressure. The residue was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (2 × 10 mL), and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave the crude product, which was purified by silica gel column chromatography (10% EtOAc–petroleum ether) to furnish the diallyl sulfone **1a** (260 mg, 63%) as a colorless crystalline solid. Further elution with 15% EtOAc–petroleum ether delivered the mono-allyl sulfone **6a** (60 mg, 17%) as a yellow liquid.

Monoallyl sulfone 6a: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.31 (d, J = 1.2 Hz, 2H), 5.87–5.76 (m, 1H), 5.22 (d, J = 17.1 Hz, 1H), 5.14 (d, J = 10.2 Hz, 1H), 3.19 (dd, J = 13.3, 8.4 Hz, 1H), 3.01–2.92 (m, 1H), 2.77–2.69 (m, 1H), 2.63 (td, J = 9.5, 3.6 Hz, 1H), 2.45–2.40 (m, 2H), 2.39–2.34 (m, 3H), 0.56–0.51 (m, 2H), 0.46–0.42 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 137.2, 136.6, 133.5, 118.6, 61.8, 52,4, 50.8, 50.5, 47.2, 45.7, 38.4, 30.5, 7.7, 6.0; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{14}H_{18}NaO_2S$ $[M+Na]^+$: 273.0920, found: 273.0920; IR (neat): υ_{max} = 3020, 2972, 1440, 1304, 1217, 1131, 758 cm^{-1}.

Diallyl sulfone 1a: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.28 (t, J = 2.0 Hz, 2H), 5.86–5.77 (m, 2H), 5.21 (dd, J = 16.9, 0.8 Hz, 2H), 5.13 (d, J = 10.1 Hz, 2H), 2.76–2.73 (m, 2H), 2.54–2.51 (m, 2H), 2.45–2.38 (m, 4H), 2.34 (t, J = 1.6 Hz, 2H), 0.53–0.50 (m, 2H), 0.43–0.40 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) = 136.8 (d), 133.6 (d), 118.5 (t), 61.8 (d), 50.9 (d), 45.8 (d), 45.8 (s), 30.7 (t), 7.8 (t), 6.0 (t); HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{17}H_{22}NaO_2S$ $[M+Na]^+$: 313.1233, found: 313.1233; IR (neat): υ_{max} = 2935, 1642, 1439, 1305, 1135 cm^{-1}.

Synthesis of butenyl sulfones 6b and 1b

A solution of sulfone **5** (500 mg, 2.38 mmol) in anhydrous THF (20 mL) under inert atmosphere (N_2) was cooled to −71 °C. To this solution, *n*-BuLi (4.46 mL, 3.0 equiv, 1.6 M solution in hexane) was added dropwise, and the reaction mixture was stirred at −71 °C for 30 min. Next, HMPA (1.24 mL, 7.13 mmol) was added slowly followed by 4-bromo-1-butene (1.45 mL, 14.26 mmol), and continued the stirring at the same temperature for 1 h. Then, the reaction mixture was brought gradually to rt, and continued the stirring for another 59 h. After completion of the reaction (TLC monitoring), the reaction mixture was quenched with water (2 mL), and removed the solvent under reduced pressure. The residue was extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with brine (2 × 10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (5% EtOAc–petroleum ether) to give the dibutenyl sulfone **1b** (36 mg, 7%, on the basis of 20% of the starting material recovered) as a colorless liquid, and further elution with 8% EtOAc–petroleum ether delivered monobutenyl sulfone **6b** (154 mg, 31%, on the basis of 20% of the starting material recovered) as a pale yellow liquid.

Monobutenyl sulfone 6b: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.29 (t, J = 1.6 Hz, 2H), 5.82–5.71 (m, 1H), 5.11–5.02 (m, 2H), 3.16 (dd, J = 13.2, 8.4 Hz, 1H), 2.99–2.91 (m, 1H), 2.59 (td, J = 10.0, 3.6 Hz, 1H), 2.41–2.33 (m, 4H), 2.32–2.19 (m, 2H), 2.12–2.03 (m, 1H), 1.81–1.72 (m, 1H), 0.56–0.51 (m, 2H), 0.47–0.41 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 137.1 (d), 137.0 (d), 136.5 (d), 116.3 (t), 61.3 (d), 52.4 (t), 50.7 (d), 50.4 (d), 47.4 (d), 45.7 (s), 38.4 (d), 30.8 (t), 25.5 (t), 7.7 (t), 6.0 (t); HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{15}H_{20}NaO_2S$ $[M+Na]^+$: 287.1076, found: 287.1075; IR (neat): υ_{max} = 3068, 2967, 1641, 1452, 1303, 1138, 914 cm^{-1}

Dibutenyl sulfone 1b: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.26 (s, 2H), 5.82–5.72 (m, 2H), 5.10–5.02 (m, 4H), 2.51–2.46 (m, 2H), 2.42–2.18 (m, 8H), 2.14–2.05 (m, 2H), 1.82–1.73 (m, 2H), 0.55–0.51 (m, 2H), 0.44–0.41 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ (ppm) = 137.0 (d), 136.8 (d), 116.2 (t), 61.3 (d), 50.7 (d), 46.0 (d), 45.7 (s), 30.8 (t), 25.7 (t), 7.7 (t), 6.0 (t); HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{19}H_{26}NaO_2S$ $[M+Na]^+$: 341.1546, found: 341.1549; IR (neat): υ_{max} = 3070, 2976, 1640, 1453, 1298, 1136, 912 cm^{-1}.

Synthesis of pentenyl sulfones 6c and 1c

A solution of sulfone **5** (200 mg, 0.95 mmol) in anhydrous THF (10 mL) under inert atmosphere (N_2) was cooled to 0 °C. To this solution *n*-BuLi (1.80 mL, 3.0 equiv, 1.6 M solution in hexane) was added dropwise, and the reaction mixture was stirred for 30 min. Next, HMPA (0.50 mL, 1.90 mmol) was added slowly followed by 5-bromo-1-pentene (0.44 mL, 3.80 mmol). Then, the resulting reaction mixture was allowed to attain rt, and the stirring was continued at rt for 22 h. After completion of the reaction (TLC monitoring), the reaction mixture was quenched with water (2 mL), and the solvent was removed under reduced pressure. The residue was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (2 × 10 mL), and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave the crude product, which was purified by silica gel column chromatography (8% EtOAc–petroleum ether) to furnish the dipentenyl sulfone **1c** (146 mg, 44%) as a colorless liquid. Further elution with 15% EtOAc–petroleum ether delivered the monopentenyl sulfone **6c** (32 mg, 12%) as a liquid.

Monopentenyl sulfone 6c: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.32 (s, 2H), 5.82–5.75 (m, 1H), 5.04–4.98 (m, 2H), 3.19–3.14 (m, 1H), 2.94 (br s, 1H), 2.62–2.57 (m, 1H), 2.45–2.27 (m, 4H), 2.10–2.04 (m, 2H), 1.98–1.93 (m, 1H), 1.71–1.65 (m, 1H), 1.62–1.59 (m, 2H), 0.56–1.50 (m, 2H), 0.46–1.42 (m, 2H), ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) = 137.8, 137.0, 136.7, 115.5, 62.1, 52.4, 50.8, 50.4, 47.5, 45.7, 38.3, 33.7, 26.3, 25.7, 7.7, 6.0; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{16}H_{22}NaO_2S$ $[M+Na]^+$: 301.1233, found: 301.1231; IR (neat): υ_{max} = 3071, 2935, 2861, 1641, 1461, 1296, 1132 914 cm^{-1}.

Dipentenyl sulfone 1c: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.29 (t, J = 1.8 Hz, 2H), 5.80–5.72 (m, 2H), 5.00 (dd, J = 17.1, 1.6 Hz, 2H), 4.96 (d, J = 10.2 Hz, 2H), 2.47–2.43 (m, 2H), 2.36–2.32 (m, 4H),

2.10–2.06 (m, 4H), 1.98–1.91 (m, 2H), 1.71–1.64 (m, 2H), 1.61–1.54 (m, 4H), 0.52–0.49 (m, 2H), 0.42–0.39 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) = 137.8 (d), 136.7 (d), 115.4 (t), 62.0 (d), 50.7 (d), 45.9 (d), 45.8 (s), 33.6 (t), 26.3 (t), 25.8 (t), 7.7 (t), 6.0 (t); HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{21}H_{30}NaO_2S$ $[M+Na]^+$: 369.1859, found: 369.1851; IR (neat): υ_{max} = 3066, 2935, 2864, 1640, 1458, 1291, 1133, 912 cm^{-1}.

Synthesis of hexenyl sulfones 6d and 1d

A solution of sulfone **5** (200 mg, 0.95 mmol) in anhydrous THF (13 mL) under inert atmosphere (N_2) was cooled to −75 °C. To this solution, *n*-BuLi (1.43 mL, 2.4 equiv, 1.6 M solution in hexane) was added dropwise, and the reaction mixture was stirred at −75 °C for 30 min. Next, HMPA (0.33 mL, 1.90 mmol) was added slowly followed by 6-bromo-1-hexene (0.35 mL, 2.66 mmol), and continued the stirring at the same temperature for 1 h. Then, the reaction mixture was brought gradually to rt, and continued the stirring for another 21 h. After completion of the reaction (TLC monitoring), the reaction mixture was quenched with water (2 mL), and removed the solvent under reduced pressure. The residue was extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine (2 × 10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography (7% EtOAc–petroleum ether) to give the dihexenyl sulfone **1d** (227 mg, 70%, on the basis of 9% of the starting material recovered) as a colorless liquid and further elution with 15% EtOAc–petroleum ether delivered monohexenyl sulfone **6d** (32 mg, 17%, on the basis of 9% of the starting material recovered) as a pale yellow liquid.

Monohexenyl sulfone 6d: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.33–6.01 (m, 2H), 5.82–5.74 (m, 1H), 5.00 (dq, *J* = 17.1, 0.6 Hz, 1H), 4.94 (dt, *J* = 10.1, 0.9 Hz, 1H), 3.16 (dd, *J* = 13.2, 8.4 Hz, 1H), 2.98–2.92 (m, 1H), 2.58 (td, *J* = 10.2, 3.6 Hz, 1H), 2.38–2.32 (m, 4H), 2.07 (q, *J* = 7.0 Hz, 2H), 1.98–1.91 (m, 1H), 1.71–1.64 (m, 2H), 1.54–1.47 (m, 1H), 1.45–1.40 (m, 2H), 0.55–0.52 (m, 2H), 0.47–0.42 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) = 138.6, 137.0, 136.6, 114.9, 62.2, 52,4, 50.8, 50.4, 47.5, 45.7, 38.3, 33.5, 28.9, 26.5, 26.1, 7.7, 6.0; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{17}H_{24}NaO_2S$ $[M+Na]^+$: 315.1389, found: 315.1391; IR (neat): υ_{max} = 3061, 2931, 1639, 1461, 1299, 1137 cm^{-1}.

Dihexenyl sulfone 1d: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 6.30 (t, *J* = 1.9 Hz, 2H), 5.83–5.75 (m, 2H), 5.00 (dq, *J* = 17.1, 1.6 Hz, 2H), 4.96–4.94 (m, 2H), 2.49–2.45 (m, 2H), 2.37–2.33 (m, 4H), 2.07 (q, *J* =.6.9 Hz, 4H), 2.00–1.93 (m, 2H), 1.72–1.64 (m, 2H), 1.56–1.47 (m, 4H), 1.46–1.40 (m, 4H), 0.55–0.52 (m, 2H), 0.46–0.41 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ (ppm) = 138.6, 136.8, 114.9, 62.2, 50.9, 46.1, 45.9, 33.5, 28.9, 26.6, 26.3, 7.8, 6.1; HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{23}H_{34}NaO_2S$ $[M+Na]^+$: 397.2172, found: 397.2173; IR (neat): υ_{max} = 3071, 2932, 1639, 1458, 1296, 1134 cm^{-1}.

Synthesis of cross metathesis (CM) product 7

A solution of the diallyl sulfone **6a** (30 mg, 0.10 mmol) in dry CH_2Cl_2 (14 mL) was degassed with nitrogen for 15 min. Next, G-I catalyst (4.25 mg, 7.50 mol%) was added at rt under ethylene atmosphere, and the resulting reaction mixture was stirred at rt for 22 h. It was realized (TLC monitoring) that even prolonged reaction time did not help to consume the starting material completely. Then, the reaction mixture was filtered through the sintered glass funnel, and the solvent was removed. The crude product was purified by silica gel column chromatography (25% EtOAc–petroleum ether) to afford the cross metathesis (CM) compound **7** (10 mg, 21%, on the basis of 18% of the starting material recovered) as a solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.33–6.28 (m, 4H), 5.87–5.76 (m, 2H), 5.68–5.66 (m, 1H), 5.62–5.58 (m, 1H), 5.21 (d, J = 16.9 Hz, 2H), 5.13 (d, J = 10.0 Hz, 2H), 2.76–2.69 (m, 4H), 2.56–2.33 (m, 16H), 0.56–0.39 (m, 8H); HRMS (ESI, Q-ToF) *m/z*: calculated for $C_{32}H_{40}NaO_4S_2$ $[M+Na]^+$: 575.2260, found: 575.2259; IR (neat): υ_{max} = 2924, 1641, 1439, 1304, 1134 cm^{-1}.

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REFERENCES

1. (a) N. S. Simpkins, *Sulphones in Organic Synthesis*, Pergamon Press, Oxford, U.K., 1993; (b) A.-N. R. Alba, X. Companyo, and R. Rios, *Chem. Soc. Rev.*, 2010, **39**, 2018; (c) J.-E. Bäckvall, R. Chinchilla, C. Nájera, and M. Yus, *Chem. Rev.*, 1998, **98**, 2291; (d) D. C. Meadows and J. Gervay-Hague, *Med. Res. Rev.*, 2006, **26**, 793; (e) J. L. García Ruano, J. Alemán, A. Parra, and L. Marzo, *Eur. J. Org. Chem.*, 2014, **2014**, 1577; (f) D. A. Alonso, M. Fuensanta, C. Nájera, and M. Varea, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2005, **180**, 1119; (g) M. Wang, S. Chen, and X. Jiang, *Org. Lett.*, 2017, **19**, 4916; (h) A. S. Deeming, C. J. Russell, A. J. Hennessy, and M. C. Willis, *Org. Lett.*, 2014, **16**, 150.
2. (a) Z. Wang, Ramberg-Bäcklund Reaction, in *Comprehensive Organic Name Reactions and Reagents*, John Wiley & Sons, Inc., Hoboken, NJ, 2010, vol. 3, p 2298; (b) J. E. Harvey and M. J. Bartlett, *Chem. N.Z.*, 2010, **74**, 63; (c) L. J. Baird, M. S. M. Timmer, P. H. Teesdale-Spittle, and J. E. Harvey, *J. Org. Chem.*, 2009, **74**, 2271.
3. (a) O. H. Oldenziel, D. van Leusen, and A. M. van Leusen, *J. Org. Chem.*, 1977, **42**, 3114; (b) S. Kotha and V. R. Shah, *Synthesis*, 2007, 3653.

4. (a) M. Julia and J.-M. Paris, *Tetrahedron Lett.*, 1973, **14**, 4833; (b) S. E. Kelly, Alkene Synthesis, in *Comprehensive Organic Synthesis*, ed. by B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 1, p 792; (c) Z. Wang, Julia Olefination, in *Comprehensive Organic Name Reactions and Reagents*, John Wiley & Sons, Inc., Hoboken, NJ, 2010, vol. 2, p 1576.
5. (a) P. Metz, M. Fleischer, and R. Fröhlich, *Tetrahedron*, 1995, **51**, 711; (b) G. Barbarella, M. Cinquini, and S. Colonna, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1646; (c) S. Kotha and P. Khedkar, *J. Org. Chem.*, 2009, **74**, 5667; (d) S. Kotha and V. Bandi, *Heterocycles*, 2015, **90**, 226.
6. (a) D. Zheng and J. Wu, *Sulfur Dioxide Insertion Reactions for Organic Synthesis, SpringerBriefs in Molecular Science* Springer Singapore, 2017; (b) S. Kotha and A. K. Ghosh, *Indian J. Chem.*, 2006, **45B**, 227; (c) S. Kotha, P. Khedkar, and A. K. Ghosh, *Eur. J. Org. Chem.*, 2005, 3581; (d) S. Kotha, D. Kashinath, and P. Khedkar, *Synthesis*, 2007, 3357; (e) S. Kotha and P. Khedkar, *J. Org. Chem.*, 2009, **74**, 5667.
7. (a) N. Holub and S. Blechert, *Chem. Asian J.*, 2007, **2**, 1064; (b) S. Kotha and O. Ravikumar, *Eur. J. Org. Chem.*, 2016, 3900; (c) S. Kotha and O. Ravikumar, *Beilstein J. Org. Chem.*, 2015, **11**, 1259; (d) S. Kotha and O. Ravikumar, *Eur. J. Org. Chem.*, 2014, 5582.
8. (a) S. Kotha and R. Gunta, *Beilstein J. Org. Chem.*, 2015, **11**, 1373; (b) S. Kotha and R. Gunta, *Acta Cryst., Sect. E*, 2014, **70**, o1163.
9. B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 1958, 646.
10. M. J. Zhang, D. L. Flynn, and P. R. Hanson, *J. Org. Chem.*, 2007, **72**, 3194.
11. E. Polo, F. Forlini, V. Bertolasi, A. C. Boccia, and M. C. Sacchi, *Adv. Synth. Catal.*, 2008, **350**, 1544.
12. D. N. Butler and R. A. Snow, *Can. J. Chem.*, 1972, **50**, 795.