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Synthesis of Substituted 1,3-Diene Synthetic Equivalents by a Ru-Catalyzed Diyne Hydrative Cyclization

Barry M. Trost* and Xiaojun Huang[a]

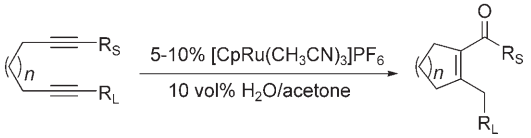
Abstract: Catalyzed by [CpRu-$(CH_3CN)_3$]PF_6, the hydrative cyclization of dipropargylic sulfone substrates provides an effective way to synthesize highly functionalized substituted 3-sulfolenes. The amount of water is crucial for the reactivity of this cycloisomerization reaction. The scope and limitations of the Ru-catalyzed cycloisomerization are discussed. A marked ketone-directing effect was observed for the first time in ruthenium-catalyzed cyclizations. A plausible mechanism for the ketone-directed cycloisomerization is also rationalized. The utility of this method was demonstrated by both sulfur dioxide extrusion of the 3-sulfolenes to afford 1,3-dienes and subsequent inter- or intramolecular Diels–Alder reactions.

Keywords: cyclization · Diels–Alder reaction · dienes · ruthenium · sulfolenes

Introduction

1,3-Butadienes are crucial cycloaddition partners and have been utilized extensively in organic synthesis. However, their chemical sensitivity sometimes makes their synthesis laborious and unpredictable, and they could be difficult to carry through multiple steps in a complex synthesis. 3-Sulfolene and its derivatives are excellent synthetic equivalents of conjugated dienes because of their enhanced stability and ease in unmasking the 1,3-diene by thermal extrusion of sulfur dioxide. Therefore, 3-sulfolenes are employed for Diels–Alder reactions in a number of complex syntheses.[1,2] Several methods for the synthesis of substituted 3-sulfolenes are reported in the literature. One approach involves the construction of the corresponding 2,5-dihydrothiophenes from functionalized precursors. However, this method usually requires multistep manipulations followed by oxidation of the 2,5-dihydrothiophenes to 3-sulfolenes.[3] Another strategy involves the formation of substituted 3-sulfolenes from other readily available 3-sulfolenes.[4] One of the most common approaches involves the addition of SO_2 to functionalized dienes,[5] a method that demands the availability of the desired functionality but is useful to convert simple 1,3-dienes into more-substituted ones. Most recently, substituted 3-sulfolenes have also been prepared by ring-closing metathesis.[6]

[CpRu] complexes (Cp = cyclopentadienyl) are known to promote several alkyne–alkyne coupling reactions.[7] Our group demonstrated that the hydrative diyne cyclization catalyzed by cyclopentadienyl-tris(acetonitrile)ruthenium(II) hexafluorophosphate ([CpRu$(CH_3CN)_3$]PF_6; **1**) is an excellent method to prepare cyclic enone systems [Eq. (1)], and



(1)

it has been used in a number of natural-product syntheses.[8] Although the hydrative diyne cyclization of substrates containing a sulfonamide group catalyzed by **1** has been documented,[8b] the chemoselectivity of this cycloisomerization reaction with respect to potential leaving groups such as sulfonyl in the propargylic position remains to be tested. Alkynes are known to be synthetically robust, and the synthesis of dipropargylic sulfone substrates from the acetylenic functionality can be quite simple.[9] Herein, we describe a novel and versatile strategy for the synthesis of highly functionalized substituted 3-sulfolenes based on **1**-catalyzed hydrative cyclization of acyclic dipropargylic sulfones [Eq. (2)]. During these studies, a unique directing effect by

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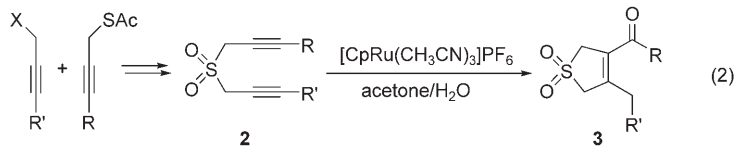


a neighboring ketone was observed for the first time in ruthenium-catalyzed cyclization reactions. We describe in detail the investigation and its successful application.[10]

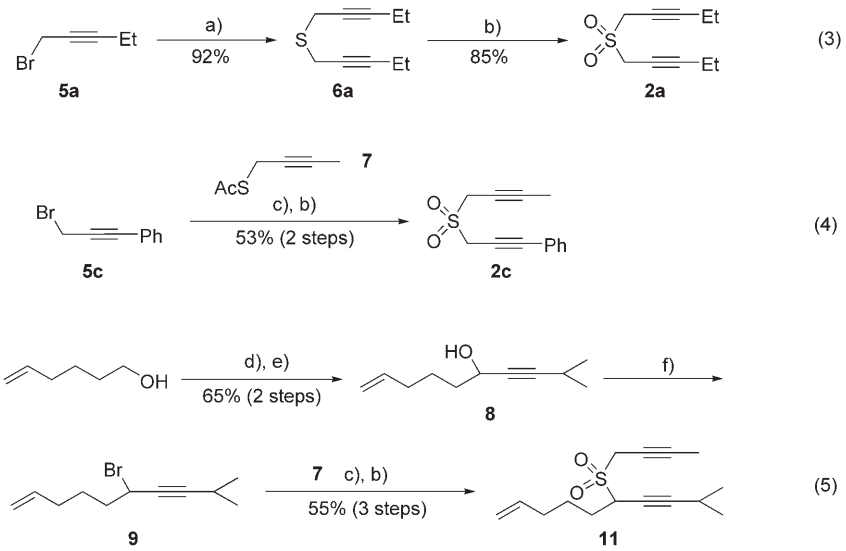
Results and Discussion

Substrate Preparation

The symmetrical dipropargylic sulfone substrates **2a**, **2b** were prepared from propargylic bromides and sodium sulfide.[9] Coupling of propargylic bromide **5a** with sodium sulfide in MeOH furnished the symmetrical linear sulfide **6a** in 95% yield. Dipropargylic sulfide **6a** was oxidized by *m*-CPBA in CH_2Cl_2 to give the corresponding sulfone **2a** in 85% yield (Scheme 1, [Eq. (3)]). The use of oxone as the oxidizing reagent (reaction in refluxing CH_2Cl_2 for several days) gave mainly the corresponding sulfoxide instead of the desired sulfone **2a**. The unsymmetrical dipropargylic sulfones **2c** and **11** were prepared from one equivalent of propargylic thioacetate (**7**) and one equivalent of propargylic bromide (**5c** or **9**) (Scheme 1, [Eq. (4)] and [Eq. (5)]).[9,11] Other unsymmetrical dipropargylic sulfone substrates were prepared in similar reaction sequences.

Reaction Optimization

Diethyl dipropargylic sulfone (**2a**) was chosen for initial examination with acetone as the solvent and a catalytic amount of **1** (Table 1). The ruthenium-catalyzed hydrative cyclization reaction proceeded very well to give 3-sulfolene **3a**. High yields were obtained when about 11 equivalents of water were added (Table 1, entry 2). These reaction conditions were used in our subsequent studies. To increase the turnover of catalyst **1**, selected additives were investigated: triphenylphosphine oxide slowed down the reaction (Table 1, entry 5), and triphenylphosphine sulfide reduced the reactivity significantly and also caused the decomposition of **2a** (Table 1, entry 6).



Scheme 1. Preparation of dipropargylic sulfone substrates. a) Na_2S, MeOH; b) *m*-CPBA, CH_2Cl_2; c) KOH, $Na_2S_2O_3$, MeOH; d) PCC, CH_2Cl_2; e) 3-methyl-1-butyne, *n*BuLi, Et_2O; f) CBr_4, Ph_3P, PhH. *m*-CPBA = *m*-chloroperbenzoic acid, PCC = pyridinium chlorochromate.

Table 1. Optimization studies of the Ru-catalyzed hydrative cyclization.[a]

Entry	Substrate	H_2O [equiv]	Additive	**3a** [%][b]
1	**2a**	55	–	80
2	**2a**	11	–	97
3	**2a**	5	–	90
4	**2a**	2	–	91
5	**2a**	55	Ph_3PO	76 (82 brsm)[c]
6	**2a**	55	Ph_3PS	17 (50 brsm)[c]

[a] All reactions were performed at 0.1 M in acetone at 60 °C with 10% **1** for 6 h. [b] Yield of isolated product. [c] brsm = based on recovered starting material.

International Advisory Board Member

Barry M. Trost *obtained his BA at the Univ. of Pennsylvania (1962) and PhD at the Massachusetts Institute of Technology (1965). He then moved to the Univ. of Wisconsin where he was promoted to Professor in 1969 and Vilas Research Professor in 1982. He joined the faculty at Stanford Univ. in 1987, where he is the Tamaki Professor of Humanities and Sciences. His research interests revolve around the theme of selectivity for which he has received numerous honors and awards.*

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Scope and Limitations

The success of this reaction led us to explore the scope of the ruthenium-catalyzed hydrative cycloisomerization reaction with various dipropargylic sulfones (Table 2). Unsymmetrical dipropargylic sulfone substrates demonstrated very good chemoselectivity. The addition of water usually took place at the sterically more-accessible side (Table 2, entries 3–11).[8] In general, 10% catalyst was required to achieve complete conversion for this type of reaction. The reaction was compatible with aromatic alkynes (Table 2, entry 3) as well as a number of functional groups, including free hydroxy (Table 2, entry 4), chloride (Table 2, entry 9), bromide (Table 2, entry 10), silyl ether (Table 2, entries 5 and 11) and ketone (Table 2, entries 12–15). Desilylation products were observed during ruthenium-catalyzed cyclization of silylalkynes (Table 2, entries 6 and 7). Given the efficiency of the Ru-catalyzed [5+2] cycloaddition with the same catalyst,[11] the compatibility of the cyclopropylalkyne (Table 2, entry 8) is particularly noteworthy. More interestingly, the carbonyl group can direct the addition of water to the sterically more-hindered side to form 1,4-diketone **3l** with high selectivity (Table 2, entry 12). This electronic directing effect was also observed when dipropargylic sulfone **2m**, which has a carbonyl group at the δ position, was used (Table 2, entry 13), as shown by the major product **3m** (63%) arising from the addition of water to the more-hindered side, presumably directed by the carbonyl group. The addition of Lewis acid ($Yb(OTf)_3 \cdot H_2O$) to the hydrative cyclization of substrate **2m** was tested to improve the se-

Table 2. Scope of substrates in the Ru-catalyzed synthesis of 3-sulfolenes.[a]

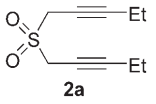
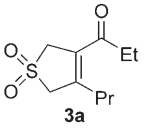
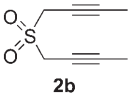
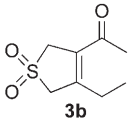
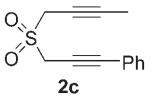
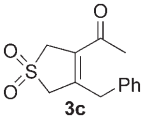
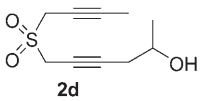
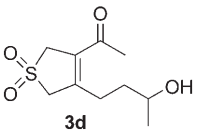
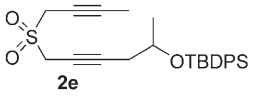
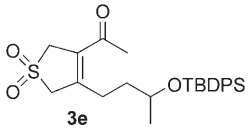
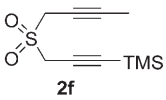
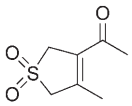
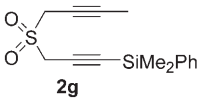
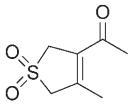
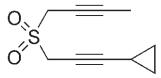
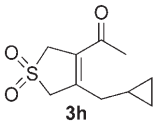
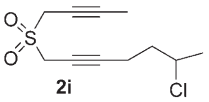
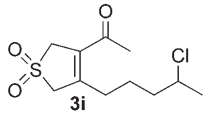
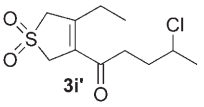
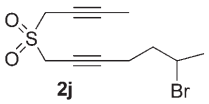
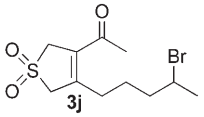
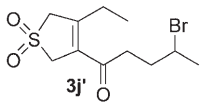
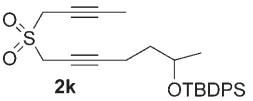
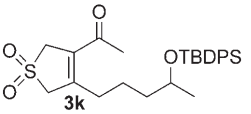
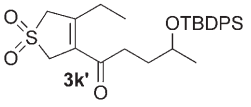
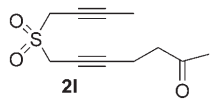
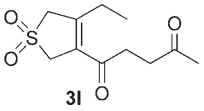
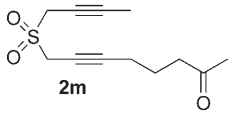
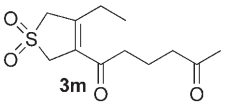
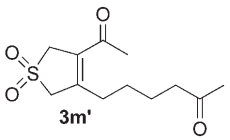
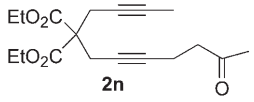
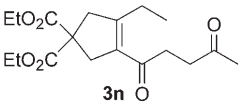
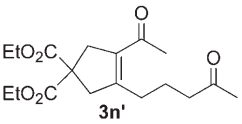
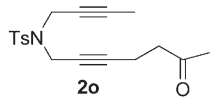
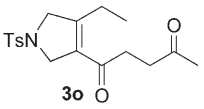
Entry	Substrate	*t* [h]	Product	Yield [%][b]
1	 **2a**	6	 **3a**	97
2	 **2b**	12	 **3b**	67
3	 **2c**	20	 **3c**	81
4	 **2d**	15[c]	 **3d**	55
5	 **2e**	24	 **3e**	84
6	 **2f**	20	 **3f**	75
7	 **2g**	20	 **3f**	80
8	 **2h**	22	 **3h**	76
9	 **2i**	4.5	 **3i**  **3i'**	76 11
10	 **2j**	1.5	 **3j**  **3j'**	60 7.8
11	 **2k**	12	 **3k**  **3k'**	64 13

Table 2. (Continued)

Entry	Substrate	*t* [h]	Product	Yield [%][b]
12		18		82
13		5.5	 	63 18
14		4	 	82 11
15		2		72

[a] The reactions were carried out with 0.1 M substrate and 10% **1** in 2 vol% water/acetone at 60 °C. [b] Yield of isolated product after chromatography. [c] 5 vol% water/acetone was used. TBDPS = *tert*-butyldiphenylsilyl, TMS = trimethylsilyl, Ts = *p*-toluenesulfonyl.

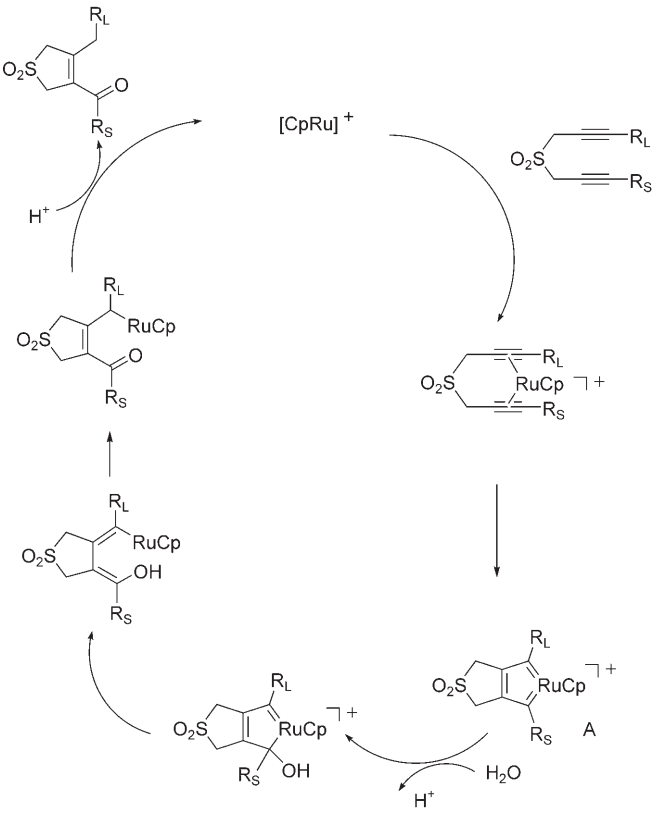
lectivity of this transformation. However, the selectivity and yield of products **3m** and **3m′** (68% for **3m**, 21% for **3m′**) were almost the same as the case without $Yb(OTf)_3 \cdot H_2O$. To further explore this interesting electronic effect, we also prepared diyne substrates **2n** and **2o** by changing the tether from sulfone to nitrogen and carbon. The carbonyl-directed cyclic-enone products (**3n**, **3o**) were formed as the major product for substrate **2n** and as the sole product for substrate **2o** (Table 2, entries 14 and 15).

Mechanistic Rationale

Scheme 2 outlines the mechanistic rationale of the hydrative diene cyclization. The regioselectivity of the hydration is determined by the attack of water on intermediate A. Preference for such an attack adjacent to R_S should be observed, and it is. It is remarkable that it only takes a β branch on R_L the size of OH (Table 2, entry 4) to give complete regioselectivity. With the sterically very small halogen atoms as a γ branch on R_L, the selectivity is still about 7:1 (Table 2, entries 9 and 10).

The most remarkable aspect of the current work is the reversal of regioselectivity by the presence of a γ-keto group in R_L (Table 2, entry 12), which appears to be general (Table 2, entries 14 and 15). While the selectivity falls somewhat when a δ-keto substrate is employed, it remains significant (≈4:1; Table 2, entry 13).

A plausible mechanistic rationalization for the ketone-directing effect is depicted in Scheme 3. The ruthenium catalyst first reacts with the diyne to form a ruthenacyclopentadiene.[12] The carbonyl oxygen atom coordinates with ruthenium in the ruthenacycle to form intermediate A. This facilitates the hydration of the ketone to generate intermediate B. Subsequent ring opening (B→C→D) followed by protonation gives the observed carbonyl-directed product **3l**. This mechanism explains the results of entries 12 and 13 in Table 2. In entry 12, the six-membered ruthenacycle in intermediate A gives a completely carbonyl-directed 1,4-diketone product (**3l**). In entry 13, there is a seven-membered ruthenacycle in intermediate A. This allows water to add to the less-hindered side to form **3m′** as the minor product.



Scheme 2. A mechanistic rationale for hydrative diyne cyclization. R_S = small alkyl group, R_L = larger alkyl group.

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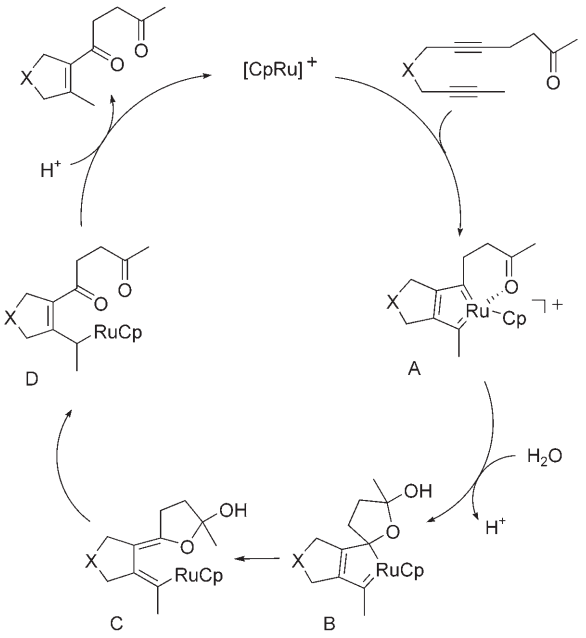


Scheme 3. A mechanistic rationale for carbonyl-directed hydrative cyclization.

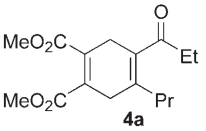
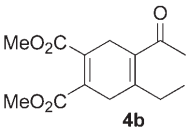
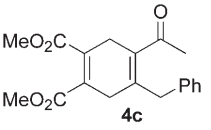
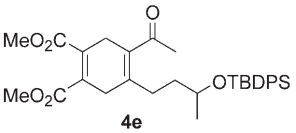
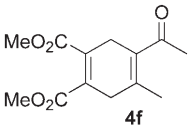
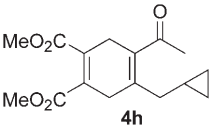
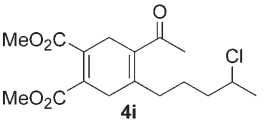
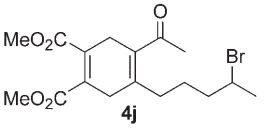
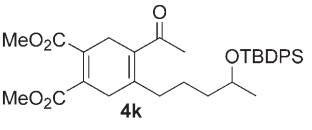
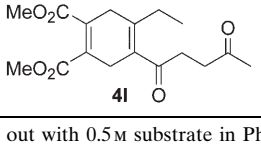
Synthetic Utility of 3-Sulfolenes

The substituted 3-sulfolenes were used efficiently as equivalents of conjugated dienes in intermolecular Diels–Alder reactions. Dimethyl acetylenedicarboxylate (DMAD) was chosen as the dienophile. The Diels–Alder adducts were isolated in high yields by heating a mixture of the sulfolenes with DMAD at 160 °C in a microwave apparatus (Table 3).[13,14] The obtained spectral data on the cyclohexa-1,4-dienes agrees with those previously reported for similar compounds.[1–6]

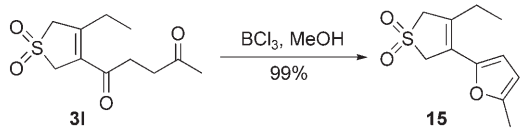
To extend the use of this method, we prepared dipropargylic sulfone **11**. Under the standard ruthenium-catalyzed cyclization conditions, sulfolene **12** was prepared in 50% yield (Scheme 4). Treatment of **12** with methyl acrylate in the presence of Grubbs II catalyst afforded *trans*-enonate **13** in moderate yield (51%; 63% based on recovered **12**).[15] Exposure of **13** in PhMe to 160 °C in a microwave for 2 h gave bicyclic enone **14** as a single diastereomer in very good yield (86%). The *trans,trans* relationship of the three contiguous stereogenic centers in the six-membered ring of **14** was established by extensive NMR spectroscopic studies, including 2D ROESY (Scheme 4).

A synthetic application of the ketone-directed addition was demonstrated by the formation of furan **15** from diketone **3l** [Eq. (6)].[16] 3-Sulfolenes can also be converted into 1,3-dienes simply by heating. Compound **3a** was transformed into 1,3-diene **16** in good yield when heated at 160 °C in a microwave apparatus [Eq. (7)].

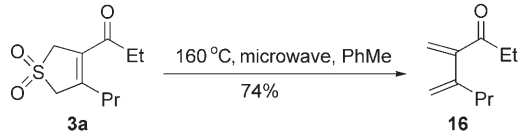
Table 3. Intermolecular Diels–Alder reactions with substituted 3-sulfolenes as 1,3-dienes.[a]

Entry	Substrate	DMAD, *t*	Product	Yield [%][b]
1	**3a**	1.5 equiv, 2 h	 **4a**	79
2	**3b**	3 equiv, 2 h	 **4b**	80
3	**3c**	2 equiv, 2 h	 **4c**	82
4	**3e**	3 equiv, 2 h	 **4e**	86
5	**3f**	3 equiv, 2 h	 **4f**	75
6	**3h**	3 equiv, 2 h	 **4h**	81
7	**3i**	3 equiv, 2 h	 **4i**	83
8	**3j**	3 equiv, 2 h	 **4j**	65
9	**3k**	3 equiv, 2 h	 **4k**	84
10	**3l**	1 equiv, 45 min	 **4l**	70

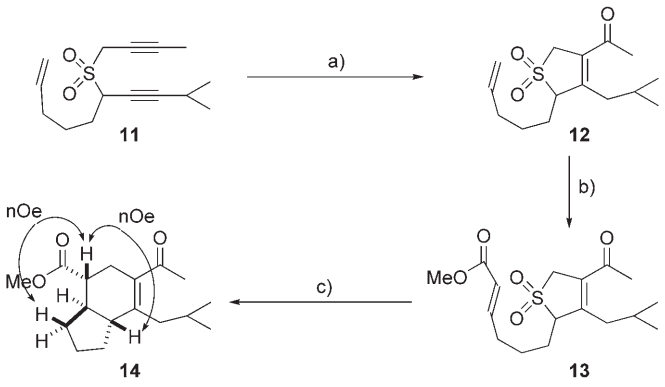
[a] The reactions were carried out with 0.5 M substrate in PhMe at 160 °C (microwave). [b] Yield of isolated product after chromatography. DMAD = dimethyl acetylenedicarboxylate.



(6)



(7)



Scheme 4. Intramolecular Diels–Alder reaction. a) **1**, acetone, H_2O, 50%; b) methyl acrylate, 5% Grubbs II catalyst, PhH, 51% (63% based on recovered starting material); c) microwave, 160°C, PhMe, 86%.

Conclusions

A general and convenient synthesis of highly functionalized 3-sulfolenes by using ruthenium-catalyzed hydrative cyclization has been described. During these studies, a unique carbonyl-directing effect was observed for the first time. This effect provided complementary regioselectivity for the synthesis of substituted 3-sulfolenes and other cyclic enones by this method. The use of 3-sulfolenes as 1,3-diene equivalents was also demonstrated by SO_2 extrusion followed by trapping with dienophiles in either inter- or intramolecular Diels–Alder reactions. The bicyclic system **14** from an intramolecular Diels–Alder reaction is a common structural motif in a number of biologically active natural products.

Experimental Section

General Remarks

All reactions were carried out in a flame-dried flask under dry nitrogen or argon. Dry acetone was distilled over drierite. Dry tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl or purified on an alumina column purification system. All other solvents were purified with the latter. Catalyst **1** was prepared according to the literature.[17] All solvents were HPLC grade or analytically pure. Flash chromatography employed ICN silica gel (Kieselgel 60, 230±400 mesh), analytical TLC was performed with 0.2-mm silica-coated glass plates (E. Merck, DC-Platten Kieselgel 60 F254). Infrared (IR) data were recorded on sodium chloride plates on a Perkin–Elmer Paragon 500 FTIR spectrometer. Proton and broadband decoupled ^{13}C NMR spectra were acquired at room temperature on Varian GEM 300, Inova Unity 400, or Inova Unity 500 spectrometers. Chemical shifts are reported in ppm relative to $CDCl_3$ or C_6D_6. Elemental analyses were performed by M-H-W Laboratories (USA). HRMS (EI) spectra were recorded by the Mass Spectrometer Facility of the School of Pharmacy, University of California, San Francisco (USA).1-Acetylthio-2-butyne was prepared from 2-butyne-1-ol and thiolacetic acid.[18]

Syntheses

General procedure for hydrative cyclization of dipropargylic sulfones (A): **1** (13 mg, 0.03 mmol, 10 mol%) was added under argon to a flame-dried test tube containing **2** (0.3 mmol), acetone (3 mL), and H_2O (0.06 mL). The resulting yellow-orange solution was sealed and stirred in an oil bath maintained at 60°C until all the starting material was consumed as judged by TLC. The solvent was then evaporated in vacuo, and the crude mixture was further purified by flash chromatography.

General procedure for Diels–Alder reaction of 3-sulfolenes with DMAD (B): DMAD (1.5–3 equiv) was added to a solution of **3** in PhMe (0.5 M). The mixture was sealed and stirred at 160°C under microwave irradiation for 45 min to 2 h. The solvent was then evaporated, and the crude mixture was purified by flash chromatography.

3a: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2a** (60 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 6 h provided **3a** (63 mg, 97%) after flash chromatography (EtOAc/petroleum ether=1:2). R_f=0.40 (EtOAc/petroleum ether=1:4); m.p.: 65°C; IR (thin film): $\tilde{\nu}$=2951, 2938, 2874, 1694, 1615, 1458, 1375, 1305, 1252, 1174, 1126, 919 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=4.05–4.08 (m, 2H), 3.91 (s, 2H), 2.53–2.59 (m, 2H), 2.51 (q, J=7.2 Hz, 2H), 1.44–1.55 (m, 2H), 1.08 (t, J=7.2 Hz, 3H), 0.94 ppm (t, J=7.6 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=197.8, 146.9, 129.1, 60.1, 57.3, 36.1, 32.8, 21.1, 13.9, 7.4 ppm; elemental analysis: calcd (%) for $C_{10}H_{16}O_3S$: C 55.53, H 7.46; found: C 55.54, H 7.45.

3b: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2b** (51 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 12 h provided **3b** (38 mg, 67%) after flash chromatography (EtOAc/petroleum ether=1:1). R_f=0.42 (EtOAc/petroleum ether=1:1); m.p.: 58°C; IR (thin film): $\tilde{\nu}$=2976, 2934, 1688, 1663, 1604, 1361, 1314, 1252, 1211, 1140, 927, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=4.08 (quint, J=1.2 Hz, 2H), 3.95 (quint, J=1.2 Hz, 2H), 2.63 (q of quint, J=7.6, 1.2 Hz, 2H), 2.30 (s, 3H), 1.11 ppm (t, J=7.6 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=194.7, 148.7, 129.1, 60.1, 57.6, 30.7, 24.3, 12.1 ppm; elemental analysis: calcd (%) for $C_8H_{12}O_3S$: C 51.04, H 6.43; found: C 51.30, H 6.63.

3c: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2c** (70 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 20 h provided **3c** (61 mg, 81%) after flash chromatography (EtOAc/petroleum ether=1:2). R_f=0.63 (EtOAc/petroleum ether=1:1); IR (thin film): $\tilde{\nu}$=2993, 1689, 1618, 1306, 1251, 1197, 1131, 950, 712 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=7.10–7.38 (m, 5H), 4.13 (t, J=1.5 Hz, 2H), 3.98 (s, 2H), 3.77 (s, 2H), 2.35 ppm (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=194.9, 145.2, 135.8, 129.9, 129.1, 128.6, 127.3, 60.0, 57.7, 36.6, 30.7 ppm; elemental analysis: calcd (%) for $C_{13}H_{14}O_3S$: C 62.38, H 5.64; found: C 62.15, H 5.51.

3d: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2d** (64 mg, 0.3 mmol) in acetone (3 mL) and water (0.15 mL) with a reaction time of 15 h provided **3d** (38 mg, 55%) after flash chromatography (EtOAc/petroleum ether=4:1). R_f=0.20 (EtOAc/petroleum ether=2:1); IR (thin film): $\tilde{\nu}$=3510, 2971, 2928, 1689, 1603, 1312, 1253, 1138, 847 cm^{-1}; ^1H NMR (500 MHz, C_6D_6): δ=3.39–3.47 (m, 1H), 3.13–3.28 (m, 4H), 2.44 (dt, J=13.5, 8.0 Hz, 1H), 2.06 (dt, J=13.5, 7.0 Hz, 1H), 2.02 (br s, 1H), 1.40 (s, 3H), 1.09–1.23 (m, 2H), 0.98 ppm (d, J=6.0 Hz, 3H); ^{13}C NMR (125.7 MHz, C_6D_6): δ=194.9, 147.8, 129.2, 66.2, 59.8, 57.2, 36.5, 29.8, 27.1, 23.6 ppm; elemental analysis: calcd (%) for $C_{10}H_{16}O_4S$: C 51.70, H 6.94; found: C 51.55, H 6.80.

3e: Following general procedure A, **1** (61 mg, 0.14 mmol) and **2e** (635 mg, 1.40 mmol) in acetone (14 mL) and water (0.28 mL) with a reaction time of 24 h provided **3e** (556 mg, 84%) after flash chromatography (EtOAc/petroleum ether=1:3). R_f=0.29 (EtOAc/petroleum ether=1:4); IR (thin film): $\tilde{\nu}$=2932, 2858, 1691, 1665, 1604, 1428, 1320, 1138, 1111, 1027, 739, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ=7.61–7.68 (m, 4H), 7.34–7.46 (m, 6H), 4.02 (s, 2H), 3.89 (sext, J=6.0 Hz, 1H) 3.72 (AB q, J_{AB}=17.5, $\Delta\nu_{AB}$=18.7 Hz, 2H), 2.64 (dt, J=13.5, 8.5 Hz, 1H), 2.48 (dt, J=13.5, 8.5 Hz, 1H), 2.23 (s, 3H), 1.48–1.55 (m, 2H), 1.11 (d, J=6.0 Hz, 3H), 1.04 ppm (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ=194.5, 147.5, 135.81, 135.76, 134.1, 134.0, 129.8, 129.7, 129.5, 127.7, 127.6, 68.8, 60.3, 57.5, 36.8, 30.7, 27.0, 26.9, 22.9, 19.2 ppm; elemental analysis: calcd (%) for $C_{26}H_{34}O_4SSi$: C 66.34, H 7.28; found: C 66.12, H 7.02.

3f: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2f** (69 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 20 h provided **3f** (39 mg, 75%) after flash chromatography (EtOAc/petroleum ether=1:1). R_f=0.37 (EtOAc/petroleum ether=1:1); m.p.: 72°C; IR (thin film): $\tilde{\nu}$=2968, 2922, 1688, 1608, 1427, 1361, 1312, 1220,

1139, 1098 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.05–4.08$ (m, 2H), 3.94 (q, $J = 1.3$ Hz, 2H), 2.31 (s, 3H), 2.20 ppm (tt, $J = 2.3$, 1.3 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 194.7$, 143.0, 130.0, 62.5, 57.5, 30.8, 17.8 ppm; elemental analysis: calcd (%) for $C_7H_{10}O_3S$: C 48.26, H 5.79; found: C 47.90, H 5.93.

Following general procedure A, **1** (13 mg, 0.03 mmol) and **2g** (87.5 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 20 h also provided **3f** (42 mg, 80%).

3h: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2h** (59 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 22 h provided **3h** (49 mg, 76%) after flash chromatography (EtOAc/petroleum ether = 1:2). $R_f = 0.30$ (EtOAc/petroleum ether = 1:2); IR (thin film): $\tilde{\nu} = 3080$, 3003, 2925, 1688, 1663, 1603, 1362, 1314, 1247, 1212, 1139, 933 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.04–4.10$ (m, 4H), 2.52 (d, $J = 6.8$ Hz, 2H), 2.26 (s, 3H), 0.69–0.81 (m, 1H), 0.45–0.59 (m, 2H), 0.07–0.20 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 194.8$, 147.3, 129.0, 60.4, 57.4, 35.3, 30.8, 9.2, 4.8; HRMS (EI): m/z calcd for $C_{10}H_{14}O_3S$: 214.0664; found: 214.0660.

3i and **3i′**: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2i** (74 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 4.5 h provided **3i** (60 mg, 76%) and **3i′** (9 mg, 11%) after flash chromatography (EtOAc/petroleum ether = 1:2). **3i**: $R_f = 0.59$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu} = 2973$, 2929, 1689, 1663, 1604, 1315, 1251, 1138, 929 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.08$ (s, 2H), 3.97–4.05 (m, 1H), 3.94 (s, 2H), 2.58–2.66 (m, 2H), 2.28 (s, 3H), 1.52–1.79 (m, 4H), 1.49 ppm (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 194.7$, 147.0, 129.5, 60.2, 58.0, 57.5, 39.5, 30.7, 30.2, 25.3, 24.7 ppm; elemental analysis: calcd (%) for $C_{11}H_{17}ClO_3S$: C 49.90, H 6.47; found: C 49.78, H 6.58. **3i′**: $R_f = 0.67$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu} = 2975$, 2929, 1689, 1604, 1460, 1381, 1316, 1251, 1165, 1139, 926 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.02–4.13$ (m, 3H), 3.95 (s, 2H), 2.68–2.78 (m, 2H), 2.63 (q, $J = 7.5$ Hz, 2H), 2.10–2.18 (m, 1H), 1.81–1.91 (m, 1H), 1.53 (d, $J = 6.5$ Hz, 3H), 1.11 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 196.2$, 149.0, 128.5, 60.0, 57.8, 57.4, 39.7, 33.6, 25.6, 24.5, 12.1 ppm; elemental analysis: calcd (%) for $C_{11}H_{17}ClO_3S$: C 49.90, H 6.47; found: C 49.95, H 6.28.

3j and **3j′**: Following general procedure A, **1** (22 mg, 0.05 mmol) and **2j** (146 mg, 0.5 mmol) in acetone (5 mL) and water (0.1 mL) with a reaction time of 1.5 h provided **3j** (92 mg, 60%) and **3j′** (12 mg, 7.8%) after flash chromatography (EtOAc/petroleum ether = 1:2). **3j**: $R_f = 0.55$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu} = 2968$, 2925, 1720, 1689, 1664, 1603, 1315, 1230, 1138 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.07–4.14$ (m, 3H), 3.95 (s, 2H), 2.63 (t, $J = 7.0$ Hz, 2H), 2.29 (s, 3H), 1.55–1.85 (m, 4H), 1.69 ppm (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta =$ 194.7, 147.0, 129.6, 60.2, 57.5, 50.7, 40.3, 30.8, 30.0, 26.4, 25.9 ppm; HRMS (EI): m/z calcd for $C_{11}H_{17}BrO$: 246.0442 $[M-SO_2]^+$; found: 246.0431. **3j′**: $R_f = 0.67$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\nu = 2967$, 2927, 1723, 1689, 1661, 1603, 1462, 1381, 1316, 1138, 925 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.11–4.19$ (m, 1H), 4.12 (s, 2H), 3.95 (s, 2H), 2.68–2.81 (m, 2H), 2.63 (q, $J = 7.5$ Hz, 2H), 2.12–2.22 (m, 1H), 1.90–2.03 (m, 1H), 1.73 (d, $J = 7.0$ Hz, 3H), 1.12 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 196.0$, 149.1, 128.5, 60.0, 57.4, 50.7, 41.0, 34.3, 26.7, 24.5, 12.1 ppm; HRMS (EI): m/z calcd for $C_{11}H_{16}O_3S$: 228.0820 $[M-HBr]^+$; found: 228.0819.

3k and **3k′**: Following general procedure A, **1** (22 mg, 0.05 mmol) and **2k** (233 mg, 0.5 mmol) in acetone (5 mL) and water (0.1 mL) with a reaction time of 12 h provided **3k** (154 mg, 64%) and **3k′** (31 mg, 13%) after flash chromatography (EtOAc/petroleum ether = 1:4–1:3). **3k**: $R_f = 0.23$ (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu} = 2964$, 2858, 1691, 1603, 1428, 1319, 1138, 1111, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.61–7.68$ (m, 4H), 7.33–7.44 (m, 6H), 4.04 (s, 2H), 3.84 (sext, $J = 6.0$ Hz, 1H), 3.78 (AB q, $J_{AB} = 18.0$, $\Delta\nu_{AB} = 13.5$ Hz, 2H), 2.40–2.52 (m, 2H), 2.24 (s, 3H), 1.25–1.52 (m, 4H), 1.08 (d, $J = 6.0$ Hz, 3H), 1.03 ppm (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 194.6$, 147.4, 135.83, 135.79, 134.4, 134.3, 129.62, 129.55, 129.52, 127.6, 127.5, 68.9, 60.2, 57.5, 38.9, 30.9, 30.7, 27.0, 23.5, 23.3, 19.2 ppm; elemental analysis: calcd (%) for $C_{27}H_{36}O_4SSi$: C 66.90, H 7.49; found: C 67.06, H 7.63. **3k′**: $R_f = 0.36$ (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu} = 2965$, 2858, 1691, 1604, 1428, 1319, 1138, 1111, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.58–7.72$ (m, 4H), 7.30–7.48 (m, 6H), 3.81–3.98 (m, 5H), 2.48–2.58 (m, 3H), 2.34–2.43 (m, 1H), 1.62–1.79 (m, 2H), 1.09 (d, $J = 6.0$ Hz, 3H), 1.05 (t, $J = 7.5$ Hz, 3H), 1.03 ppm (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 197.1$, 148.2, 135.84, 135.77, 134.2, 134.1, 129.8, 129.7, 128.5, 127.7, 127.6, 68.5, 59.9, 57.3, 38.9, 32.6, 27.0, 24.3, 23.6, 19.3, 12.1 ppm.

3l: Following general procedure A, **1** (4.5 mg, 0.01 mmol) and **2l** (22.7 mg, 0.1 mmol) in acetone (1 mL) and water (0.02 mL) with a reaction time of 18 h provided **3l** (20 mg, 82%) after flash chromatography (EtOAc/petroleum ether = 1:1). $R_f = 0.43$ (EtOAc/petroleum ether = 1:1); m.p.: 67 °C; IR (thin film): $\tilde{\nu} = 2975$, 2924, 1715, 1688, 1604, 1363, 1314, 1252, 1160, 1138, 919 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 4.13$ (t, $J = 1.2$ Hz, 2H), 3.94 (s, 2H), 2.69–2.81 (m, 4H), 2.60 (q, $J = 7.6$ Hz, 2H), 2.19 (s, 3H), 1.09 ppm (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 206.6$, 195.8, 148.5, 128.4, 59.9, 57.4, 37.0, 36.2, 29.8, 24.4, 12.1 ppm; elemental analysis: calcd (%) for $C_{11}H_{16}O_4S$: C 54.08, H 6.60; found: C 54.30, H 6.84.

3m and **3m′**: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2m** (72 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 5.5 h provided **3m** (49 mg, 63%) and **3m′** (14 mg, 18%) after flash chromatography (EtOAc/petroleum ether = 1:1). **3m**: $R_f = 0.43$ (EtOAc/petroleum ether = 1:1); m.p.: 80 °C; IR (thin film): $\tilde{\nu} = 2978$, 2926, 1707, 1680, 1606, 1376, 1309, 1251, 1159, 1106, 932 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.07$ (t, $J = 1.0$ Hz, 2H), 3.92 (s, 2H), 2.60 (q, $J = 7.5$ Hz, 2H), 2.53 (t, $J = 7.0$ Hz, 2H), 2.48 (t, $J = 7.0$ Hz, 2H), 2.11 (s, 3H), 1.84 (quint, $J = 7.0$ Hz, 2H), 1.08 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 208.1$, 196.7, 148.7, 128.7, 59.8, 57.3, 42.0, 41.5, 29.9, 24.4, 17.3, 12.1 ppm; elemental analysis: calcd (%) for $C_{12}H_{18}O_4S$: C 55.79, H 7.02; found: C 56.02, H 6.69. **3m′**: $R_f = 0.37$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu} = 2932$, 1714, 1689, 1662, 1603, 1410, 1362, 1313, 1252, 1136, 1089, 930 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.07$ (s, 2H), 3.94 (s, 2H), 2.61 (t, $J = 7.5$ Hz, 2H), 2.46 (t, $J = 7.5$ Hz, 2H), 2.28 (s, 3H), 2.12 (s, 3H), 1.59 (quint, $J = 7.5$ Hz, 2H), 1.41–1.50 ppm (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 208.3$, 194.7, 147.3, 129.5, 60.2, 57.5, 42.8, 30.8, 30.7, 30.0, 27.1, 23.1 ppm; elemental analysis: calcd (%) for $C_{12}H_{18}O_4S$: C 55.79, H 7.02; found: C 55.60, H 6.89.

3n and **3n′**: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2n** (96 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 4 h provided **3n** (83 mg, 82%) and **3n′** (11.5 mg, 11%) after flash chromatography (EtOAc/petroleum ether = 1:2). **3n**: $R_f = 0.58$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu} = 2981$, 1732, 1681, 1656, 1619, 1366, 1258, 1189, 1073, 861 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.16$ (q, $J = 7.5$ Hz, 4H), 3.31 (t, $J = 1.5$ Hz, 2H), 3.12 (s, 2H), 2.71–2.76 (m, 2H), 2.66–2.70 (m, 2H), 2.50 (q, $J = 7.5$ Hz, 2H), 2.17 (s, 3H), 1.21 (t, $J = 7.5$ Hz, 6H), 1.01 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 207.3$, 196.9, 171.4, 156.4, 130.7, 61.8, 56.8, 44.6, 41.3, 36.6, 36.0, 30.0, 23.1, 13.9, 12.0 ppm; elemental analysis: calcd (%) for $C_{18}H_{26}O_6$: C 63.89, H 7.74; found: C 63.94, H 7.68. **3n′**: $R_f = 0.47$ (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu} = 2983$, 1732, 1682, 1655, 1618, 1422, 1366, 1259, 1187, 1073, 1018, 861 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 4.18$ (q, $J = 7.0$ Hz, 4H), 3.30 (t, $J = 1.5$ Hz, 2H), 3.12 (s, 2H), 2.49 (t, $J = 7.5$ Hz, 2H), 2.44 (t, $J = 7.5$ Hz, 2H), 2.21 (s, 3H), 2.11 (s, 3H), 1.72 (quint, $J = 7.5$ Hz, 2H), 1.24 ppm (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta =$ 208.5, 196.8, 171.4, 153.7, 132.6, 61.9, 56.8, 44.9, 42.8, 41.8, 30.3, 29.9, 28.8, 21.6, 14.0 ppm; HRMS (EI): m/z calcd for $C_{18}H_{26}O_6$: 338.1729; found: 338.1720.

3o: Following general procedure A, **1** (13 mg, 0.03 mmol) and **2o** (100 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 2 h provided **3o** (75 mg, 72%) after flash chromatography (EtOAc/petroleum ether = 2:3). $R_f = 0.45$ (EtOAc/petroleum ether = 1:1); m.p.: 117 °C; IR (thin film): $\tilde{\nu} = 2976$, 2910, 1715, 1682, 1622, 1597, 1393, 1337, 1162, 1114, 843, 674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 4.35 (t, $J = 4.0$ Hz, 2H), 4.19 (t, $J = 4.0$ Hz, 2H), 2.61–2.72 (m, 4H), 2.47 (q, $J = 7.6$ Hz, 2H), 2.41 (s, 3H), 2.16 (s, 3H), 0.98 ppm (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 206.9$, 194.8, 152.5, 143.9, 133.4, 129.9, 129.0, 127.4, 58.0, 55.3, 36.4, 35.8, 29.9, 21.51, 21.45, 12.0 ppm; elemental analysis: calcd (%) for $C_{18}H_{23}NO_4S$: C 61.87, H 6.63; found: C 62.06, H 6.82.

4a: Following general procedure B, **3a** (55.5 mg, 0.257 mmol) and DMAD (47.5 μL, 0.386 mmol) in PhMe (0.51 mL) with a reaction time of 2 h provided **4a** (60 mg, 79%) after flash chromatography (EtOAc/petroleum ether = 1:2). R_f = 0.33 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 2957, 2874, 1726, 1693, 1628, 1436, 1274, 1202, 1076, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.764 (s, 3H), 3.761 (s, 3H), 3.21 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.52 (q, J = 7.2 Hz, 2H), 2.14 (t, J = 7.2 Hz, 2H), 1.44 (sext, J = 7.2 Hz, 2H), 1.06 (t, J = 7.2 Hz, 3H), 0.89 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 205.5, 167.8, 167.7, 138.1, 131.9, 131.7, 129.0, 52.38, 52.35, 35.8, 35.0, 32.5, 29.5, 21.4, 14.0, 7.8 ppm; elemental analysis: calcd (%) for $C_{16}H_{22}O_5$: C 65.29, H 7.53; found: C 65.14, H 7.44.

4b: Following general procedure B, **3b** (50.5 mg, 0.268 mmol) and DMAD (0.1 mL, 0.8 mmol) in PhMe (0.54 mL) with a reaction time of 2 h provided **4b** (57 mg, 79%) after flash chromatography (EtOAc/petroleum ether = 1:4). R_f = 0.61 (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu}$ = 2954, 2877, 1726, 1692, 1624, 1436, 1356, 1274, 1196, 1075, 941, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 6H), 3.22 (t, J = 7.6 Hz, 2H), 3.08 (t, J = 7.6 Hz, 2H), 2.26 (q, J = 7.6 Hz, 2H), 2.25 (s, 3H), 1.05 ppm (t, J = 7.6 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 201.7, 167.7, 167.6, 141.5, 132.0, 131.5, 128.4, 52.38, 52.36, 32.5, 29.9, 29.7, 27.0, 12.7 ppm; elemental analysis: calcd (%) for $C_{14}H_{18}O_5$: C 63.15, H 6.81; found: C 62.99, H 6.68.

4c: Following general procedure B, **3c** (61 mg, 0.244 mmol) and DMAD (60 μL, 0.49 mmol) in PhMe (0.5 mL) with a reaction time of 2 h provided **4c** (66 mg, 82%) after flash chromatography (EtOAc/petroleum ether = 1:3). R_f = 0.17 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 2953, 1725, 1693, 1631, 1435, 1281, 1074, 1052, 759, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.32 (m, 5H), 3.77 (s, 3H), 3.71 (s, 3H), 3.61 (s, 2H), 3.31 (t, J = 7.6 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.32 ppm (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 202.1, 167.6, 167.5, 137.8, 136.8, 132.0, 131.0, 130.5, 128.7, 128.6, 126.6, 52.4, 52.3, 39.1, 32.4, 29.8, 29.6 ppm; HRMS (EI): m/z calcd for $C_{19}H_{20}O_5$: 328.1311; found: 328.1294.

4e: Following general procedure B, **3e** (235 mg, 0.50 mmol) and DMAD (0.18 mL, 1.5 mmol) in PhMe (1.0 mL) with a reaction time of 2 h provided **4e** (236 mg, 86%) after flash chromatography (EtOAc/petroleum ether = 1:4). R_f = 0.36 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 2953, 2858, 1732, 1694, 1622, 1590, 1429, 1356, 1282, 1111, 1057, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62–7.69 (m, 4H), 7.31–7.43 (m, 6H), 3.86 (sext, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.19 (t, J = 7.6 Hz, 2H), 2.96 (t, J = 7.6 Hz, 2H), 2.08–2.32 (m, 2H), 2.19 (s, 3H), 1.44–1.60 (m, 2H), 1.08 (d, J = 6.0 Hz, 3H), 1.03 ppm (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 201.5, 167.7, 167.6, 140.2, 135.83, 135.81, 134.5, 134.3, 131.9, 131.5, 129.6, 129.5, 128.7, 127.5, 127.4, 69.3, 52.4, 52.3, 37.5, 33.0, 29.9, 29.8, 29.7, 27.0, 22.9, 19.2 ppm; elemental analysis: calcd (%) for $C_{32}H_{40}O_6Si$: C 70.04, H 7.35; found: C 70.86, H 7.18.

4f: Following general procedure B, **3f** (87 mg, 0.50 mmol) and DMAD (0.18 mL, 1.5 mmol) in PhMe (1.0 mL) with a reaction time of 2 h provided **4f** (94 mg, 75%) after flash chromatography (EtOAc/petroleum ether = 1:3). R_f = 0.53 (EtOAc/petroleum ether = 1:1); m.p.: 58 °C; IR (thin film): $\tilde{\nu}$ = 2954, 1724, 1692, 1436, 1283, 1075 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3H), 3.76 (s, 3H), 3.24 (t, J = 7.6 Hz, 2H), 3.08 (t, J = 7.6 Hz, 2H), 2.27 (s, 3H), 1.94 ppm (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 201.4, 167.8, 167.5, 137.2, 132.5, 130.9, 128.6, 52.39, 52.36, 35.4, 30.1, 29.7, 20.7 ppm; elemental analysis: calcd (%) for $C_{13}H_{16}O_5$: C 61.90, H 6.39; found: C 61.92, H 6.22.

4h: Following general procedure B, **3h** (108 mg, 0.50 mmol) and DMAD (0.18 mL, 1.5 mmol) in PhMe (1.0 mL) with a reaction time of 2 h provided **4h** (118 mg, 81%) after flash chromatography (EtOAc/petroleum ether = 1:3). R_f = 0.55 (EtOAc/petroleum ether = 1:2); IR (thin film): $\tilde{\nu}$ = 3002, 2953, 1725, 1692, 1628, 1435, 1279, 1075 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.774 (s, 3H), 3.767 (s, 3H), 3.15–3.28 (m, 4H), 2.25 (s, 3H), 2.16 (d, J = 7.2 Hz, 2H), 0.71–0.83 (m, 1H), 0.38–0.52 (m, 2H), 0.04–0.17 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 202.3, 167.9, 167.6, 139.0, 132.2, 131.2, 129.0, 52.4, 37.9, 32.9, 29.9, 29.5, 9.7, 4.7 ppm; elemental analysis: calcd (%) for $C_{16}H_{20}O_5$: C 65.74, H 6.90; found: C 65.82, H 6.79.

4i: Following general procedure B, **3i** (58 mg, 0.219 mmol) and DMAD (81 μL, 0.66 mmol) in PhMe (0.5 mL) with a reaction time of 2 h provided **4i** (62.5 mg, 83%) after flash chromatography (EtOAc/petroleum ether = 1:2). R_f = 0.57 (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu}$ = 2953, 1727, 1693, 1625, 1436, 1280, 1075, 914, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.01 (sext, J = 6.5 Hz, 1H), 3.776 (s, 3H), 3.775 (s, 3H), 3.25 (t, J = 8.0 Hz, 2H), 3.09 (t, J = 8.0 Hz, 2H), 2.17–2.31 (m, 2H), 2.25 (s, 3H), 1.50–1.78 (m, 4H), 1.49 ppm (d, J = 6.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 201.5, 167.7, 167.5, 140.0, 131.9, 131.4, 129.0, 58.4, 52.44, 52.41, 39.9, 33.2, 33.0, 29.79, 29.76, 25.3, 25.2 ppm; elemental analysis: calcd (%) for $C_{17}H_{23}ClO_5$: C 59.56, H 6.76; found: C 59.33, H 6.79.

4j: Following general procedure B, **3j** (80 mg, 0.259 mmol) and DMAD (95 μL, 0.77 mmol) in PhMe (0.52 mL) with a reaction time of 2 h provided **4j** (65 mg, 65%) after flash chromatography (EtOAc/petroleum ether = 1:2). R_f = 0.68 (EtOAc/petroleum ether = 1:1); IR (thin film): $\tilde{\nu}$ = 2952, 1725, 1692, 1625, 1435, 1279, 1075 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.06–4.15 (m, 1H), 3.777 (s, 3H), 3.775 (s, 3H), 3.25 (t, J = 7.5 Hz, 2H), 3.10 (t, J = 7.5 Hz, 2H), 2.18–2.31 (m, 2H), 2.25 (s, 3H), 1.50–1.86 (m, 4H), 1.69 ppm (d, J = 6.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 201.4, 167.7, 167.5, 139.9, 131.9, 131.4, 129.0, 52.44, 52.42, 51.3, 40.7, 33.1, 33.0, 29.80, 29.76, 26.4, 26.3 ppm; elemental analysis: calcd (%) for $C_{17}H_{23}BrO_5$: C 52.72, H 5.99; found: C 52.94, H 6.10.

4k: Following general procedure B, **3k** (121 mg, 0.25 mmol) and DMAD (90 μL, 0.73 mmol) in PhMe (0.5 mL) with a reaction time of 2 h provided **4k** (118 mg, 84%) after flash chromatography (EtOAc/petroleum ether = 1:4). R_f = 0.35 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 2952, 2858, 1727, 1694, 1429, 1277, 1111, 1074, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.67 (m, 4H), 7.31–7.42 (m, 6H), 3.82 (sext, J = 6.0 Hz, 1H), 3.78 (s, 6H), 3.20 (t, J = 8.0 Hz, 2H), 2.99 (t, J = 8.0 Hz, 2H), 2.20 (s, 3H), 2.02–2.18 (m, 2H), 1.30–1.48 (m, 4H), 1.05 (d, J = 6.0 Hz, 3H), 1.02 ppm (s, 9H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 201.8, 167.8, 167.6, 139.7, 135.84, 135.81, 134.7, 134.4, 132.0, 131.4, 129.5, 129.4, 128.9, 127.5, 127.4, 69.2, 52.41, 52.35, 39.2, 33.7, 32.7, 29.9, 29.7, 27.0, 23.7, 23.2, 19.2 ppm.

4l: Following general procedure B, **3l** (61.5 mg, 0.25 mmol) and DMAD (31 μL, 0.25 mmol) in PhMe (0.5 mL) with a reaction time of 45 min provided **4l** (56.5 mg, 70%) after flash chromatography (EtOAc/petroleum ether = 2:3). R_f = 0.43 (EtOAc/petroleum ether = 1:1); m.p.: 63 °C; IR (thin film): $\tilde{\nu}$ = 2955, 1732, 1693, 1629, 1436, 1356, 1272, 1203, 1157, 1074, 1034, 938, 770 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.770 (s, 3H), 3.768 (s, 3H), 3.27 (t, J = 8.0 Hz, 2H), 3.08 (t, J = 8.0 Hz, 2H), 2.71–2.79 (m, 4H), 2.21 (q, J = 7.5 Hz, 2H), 2.19 (s, 3H), 1.04 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 207.1, 202.5, 167.73, 167.71, 141.1, 131.9, 131.6, 128.0, 52.39, 52.37, 36.9, 35.3, 32.3, 29.9, 29.5, 27.0, 12.7 ppm; elemental analysis: calcd (%) for $C_{17}H_{22}O_6$: C 63.34, H 6.88; found: C 63.60, H 6.73.

8: PCC (6.46 g, 30.0 mmol) and 4-Å molecular sieves (5 g) were added to a stirred and cooled (0 °C) solution of 5-hexene-1-ol (2.4 mL, 20.0 mmol) in CH_2Cl_2 (200 mL). The ice bath was removed, and stirring was continued for 5 h. The mixture was diluted with Et_2O, filtered through a pad of silica gel, and rinsed with Et_2O. The solvent was removed in vacuo to give the crude aldehyde (2 g), which was used in the next step without purification. BuLi (2.5 M in hexane, 8.0 mL, 20 mmol) was added to a stirred and cooled (−78 °C) solution of 3-methyl-1-butyne (2.25 mL, 22 mmol) in Et_2O (40 mL). After 15 min, a solution of the above aldehyde (2 g, ≈20 mmol) in Et_2O (10 mL) was added to the reaction mixture. Stirring was continued overnight (12 h), and the reaction mixture reached room temperature. The mixture was cooled to 0 °C and quenched with ice water, then extracted with Et_2O. The organic phase was washed with brine and dried (Na_2SO_4). Flash chromatography of the residue over silica gel (EtOAc/petroleum ether = 1:6) gave **8** (2.15 g, 65%, two steps) as a colorless oil. R_f = 0.53 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 3355, 3077, 2971, 2935, 2870, 2241, 1641, 1460, 1384, 1320, 1184, 1068, 1018, 911 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.78 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H), 4.86–5.06 (m, 2H), 4.32 (dt, J = 1.8, 6.6 Hz, 1H), 2.54 (d of sept, J = 1.8, 6.9 Hz, 1H), 1.99–2.12 (m, 2H), 1.88–1.95 (m, 1H), 1.42–1.74, (m, 4H), 1.12 ppm (d, J = 6.9 Hz, 6H);

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.5, 114.6, 91.0, 80.3, 62.4, 37.5, 33.3, 24.4, 22.9, 20.4 ppm; elemental analysis: calcd (%) for $C_{11}H_{18}O$: C 79.46, H 10.91; found: C 79.24, H 10.77.

9: The procedure for the preparation of **5d** was followed, using **8** (1.94 g, 11.7 mmol), CBr_4 (3.88 g, 11.7 mmol), Ph_3P (3.07 g, 11.7 mmol) and PhH (20 mL), and a reaction time of 20 h. Bromide **9** (3.3 g) was used as crude in the next step. R_f = 0.95 (EtOAc/petroleum ether = 1:10); IR (thin film): $\tilde{\nu}$ = 3077, 2972, 2934, 2869, 2237, 1641, 1458, 1320, 1216, 1146, 992, 912, 735, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (ddt, J = 16.8, 10.2, 6.6 Hz, 1H), 4.90–5.07 (m, 2H), 4.53 (dt, J = 6.6, 2.1 Hz, 1H), 2.59 (d of sept, J = 2.1, 6.9 Hz, 1H), 1.88–2.14 (m, 4H), 1.50–1.67 (m, 2H), 1.14 ppm (d, J = 6.9 Hz, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 138.0, 115.0, 93.6, 78.5, 39.5, 38.4, 32.7, 26.5, 22.68, 22.66, 20.6 ppm.

10: The procedure for the preparation of **6c** was followed, using **7**[18] (0.689 g, 5.37 mmol), **9** (1.50 g, ≈5.37 mmol, half the material from the above reaction), $Na_2S_2O_3$ (12 mg, 0.076 mmol), KOH (300 mg, 5.35 mmol), and MeOH (10 mL), and a reaction time of 20 h. Product **10** (1.45 g) was used as crude in the next step.

11: The procedure for the preparation of **2a** was followed, using **10** (1.45 g, ≈5.37 mmol), *m*-CPBA (2.5 g, 10 mmol), and CH_2Cl_2 (50 mL), and a reaction time of 4 h. Flash chromatography of the crude product over silica gel (EtOAc/petroleum ether = 1:6) gave **11** (0.786 g, 55% over two steps). R_f = 0.52 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 3077, 2972, 2925, 2871, 2243, 1641, 1461, 1329, 1254, 1129, 915, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (ddt, J = 17.2, 10.4, 6.8 Hz, 1H), 5.02 (dq, J = 17.2, 1.6 Hz, 1H), 4.94 (ddt, J = 10.4, 2.0, 1.2 Hz, 1H), 4.18 (dq, J = 16.8, 2.4 Hz, 1H), 4.07 (ddd, J = 10.4, 4.0, 2.0 Hz, 1H), 3.80 (dq, J = 16.8, 2.4 Hz, 1H), 2.60 (d of sept, J = 2.0, 6.8 Hz, 1H), 1.98–2.18 (m, 3H), 1.87 (t, J = 2.4 Hz, 3H), 1.67–1.90 (m, 2H), 1.46–1.61 (m, 1H), 1.16 ppm (d, J = 6.8 Hz, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 137.5, 115.2, 94.8, 84.1, 71.0, 66.0, 54.3, 42.8, 32.9, 26.0, 25.8, 22.4, 20.5, 3.8 ppm; elemental analysis: calcd (%) for $C_{15}H_{22}O_2S$: C 67.63, H 8.32; found: C 67.80, H 8.37.

12: Following general procedure A, **1** (13 mg, 0.03 mmol) and **11** (80 mg, 0.3 mmol) in acetone (3 mL) and water (0.06 mL) with a reaction time of 24 h provided **12** (43 mg, 50%) after flash chromatography (EtOAc/petroleum ether = 1:4). R_f = 0.33 (EtOAc/petroleum ether = 1:4); IR (thin film): $\tilde{\nu}$ = 2959, 2871, 1690, 1641, 1597, 1465, 1360, 1311, 1208, 1137, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.75 (ddt, J = 16.8, 10.0, 6.8 Hz, 1H), 4.95–5.06 (m, 2H), 3.98 (AB q, J_{AB} = 16.4, $\Delta\nu_{AB}$ = 43.8 Hz, 2H), 3.71 (dd, J = 8.8, 3.6 Hz, 1H), 2.96 (dd, J = 13.6, 9.6 Hz, 1H), 2.28 (s, 3H), 204–2.18 (m, 2H), 1.51–2.02 (m, 6H), 0.98 (d, J = 6.4 Hz, 3H), 0.87 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 195.5, 150.9, 137.4, 129.5, 115.6, 68.2, 55.8, 37.5, 33.3, 31.0, 28.0, 27.6, 25.4, 23.2, 21.7 ppm; elemental analysis: calcd (%) for $C_{15}H_{24}O_3S$: C 63.34, H 8.51; found: C 63.51, H 8.33.

13: Grubbs II catalyst (4 mg, 0.0047 mmol) was added to a stirred solution of **12** (27.5 mg, 0.0967 mmol) and methyl acrylate (17.5 μL, 0.19 mmol) in PhH (1 mL). Stirring was continued for 3 days, and solvent was evaporated. Flash chromatography of the residue over silica gel (EtOAc/petroleum ether = 1:4–1:2) gave **12** (5 mg) as well as **13** (17 mg, 51%). R_f = 0.34 (EtOAc/petroleum ether = 1:2); IR (thin film): $\tilde{\nu}$ = 2957, 1721, 1690, 1657, 1597, 1438, 1311, 1205, 1136 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.90 (dt, J = 15.5, 7.0 Hz, 1H), 5.84 (dt, J = 15.5, 1.5 Hz, 1H), 4.05 (d, J = 16.0 Hz, 1H), 3.93 (d, J = 16.0, 1H), 3.71 (s, 3H), 3.70 (dd, J = 9.5, 3.5 Hz, 1H), 2.96 (dd, J = 14.0, 9.5 Hz, 1H), 2.29 (s, 3H), 2.20–2.33 (m, 2H), 1.74–2.00 (m, 5H), 1.58–1.70 (m, 1H), 0.98 (d, J = 6.5 Hz, 3H), 0.87 ppm (d, J = 6.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 195.5, 166.8, 150.3, 147.5, 129.7, 121.9, 68.1, 55.8, 51.5, 37.5, 31.7, 30.9, 28.0, 27.6, 24.7, 23.2, 21.6 ppm; HRMS (EI): m/z calcd for $C_{16}H_{22}O_4S$: 310.1239 $[M-MeOH]^+$; found: 310.1234.

14: Ester **13** (17 mg, 0.05 mmol) in PhMe (1 mL) was sealed and stirred at 160 °C under microwave irradiation for 2 h. The solvent was evaporated, and the crude mixture was purified by flash chromatography (EtOAc/petroleum ether = 1:8) to give **14** (12 mg, 86%). R_f = 0.42 (EtOAc/petroleum ether = 1:4); m.p.: 71 °C; IR (thin film): $\tilde{\nu}$ = 2957, 2871, 1730, 1682, 1626, 1439, 1352, 1270, 1172 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.67 (s, 3H), 2.39–2.66 (m, 3H), 2.22 (s, 3H), 2.12–2.28 (m, 1H), 1.87–2.05 (m, 3H), 1.55–1.86 (m, 5H), 1.16–1.37 (m, 2H), 0.89 (d, J = 6.5 Hz, 3H), 0.78 ppm (d, J = 7.0 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 205.3, 175.5, 142.4, 133.6, 51.6, 47.3, 45.1, 44.7, 40.4, 31.7, 30.3, 28.2, 27.7, 27.3, 23.5, 21.7, 21.4 ppm; HRMS (EI): m/z calcd for $C_{17}H_{26}O_3$: 278.1882; found: 278.1882.

15: BCl_3 (1.0 M in heptane, 0.15 mL, 0.15 mmol) was added dropwise to a stilled solution of **3l** (36.0 mg, 0.147 mmol) in MeOH (3 mL). The mixture was placed into an oil bath at 60 °C, and stirring was continued for 2 h. The mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl. The mixture was evaporated, extracted with EtOAc, dried (Na_2SO_4), and evaporated again. Flash chromatography of the residue over silica gel (EtOAc/petroleum ether = 2:5), gave **15** (33 mg, 99%) as a white solid. R_f = 0.70 (EtOAc/petroleum ether = 1:1); m.p.: 68 °C; IR (thin film): $\tilde{\nu}$ = 2970, 2927, 1724, 1595, 1523, 1460, 1314, 1250, 1134, 1028, 789 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.17 (d, J = 3.0 Hz, 1H), 6.01 (d, J = 3.0 Hz, 1H), 4.07 (s, 2H), 3.92 (s, 2H), 2.57 (q, J = 7.5 Hz, 2H), 2.29 (s, 3H), 1.10 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 152.8, 147.3, 130.8, 118.7, 111.1, 107.4, 59.3, 57.6, 23.7, 13.6, 11.9 ppm; elemental analysis: calcd (%) for $C_{11}H_{14}O_3S$: C 58.38, H 6.24; found: C 58.52, H 6.44.

16: 3-Sulfolene **3a** (54 mg, 0.25 mmol) in PhMe (1 mL) was sealed and stirred at 160 °C under microwave irradiation for 90 min. The solvent was evaporated, and the crude mixture was purified by flash chromatography (EtOAc/petroleum ether = 1:20) to give **16** (28 mg, 74%). R_f = 0.52 (EtOAc/petroleum ether = 1:10); IR (thin film): $\tilde{\nu}$ = 2961, 2874, 1686, 1630, 1590, 1459, 1378, 1098, 905, 734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.67 (s, 1H), 5.56 (s, 1H), 5.01 (s, 1H), 4.94 (s, 1H), 2.66 (q, J = 7.2 Hz, 2H), 2.17 (t, J = 7.2 Hz, 2H), 1.38 (sext, J = 7.2 Hz, 2H), 1.08 (t, J = 7.2 Hz, 3H), 0.87 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 204.2, 150.9, 146.2, 120.5, 115.1, 36.8, 33.2, 21.1, 13.6, 8.3 ppm; HRMS (EI): m/z calcd for $C_{20}H_{32}O_2$: 304.2402 $[2M]^+$; found: 304.2398.

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[18] Preparation of **7**: DIAD was added to a stirred and cooled (0 °C) solution of Ph_3P (13.32 g, 50.8 mmol) in PhH (250 mL). After 15 min, a solution of 2-butyne-1-ol (3.8 mL, 50.8 mmol) and thiolacetic acid (3.6 mL, 50.4 mmol) in PhH (50 mL) was added. The cooling bath was removed, and stirring was continued for 5 h. The solvent was then evaporated in vacuo. Flash chromatography of the residue over silica gel gave **7** (5.6 g, 87 %) as a colorless oil. $R_f = 0.64$ (EtOAC/petroleum ether = 1:10); IR (thin film): $\tilde{\nu}$ = 2959, 2920, 2855, 2237, 1698, 1434, 1354, 1243, 1136, 1107, 959, 627 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 3.59 (q, J = 2.4 Hz, 2H), 2.32 (s, 3H), 1.77 ppm (t, J = 2.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): 194.4, 78.8, 73.4, 30.1, 18.2, 3.6 ppm.

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