Radical-Mediated Three-Component Coupling of Alkenes

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Dedicated to the memory of Professor *Hanns Fischer*, whose pioneer contribution to radical chemistry remains a fantastic source of inspiration

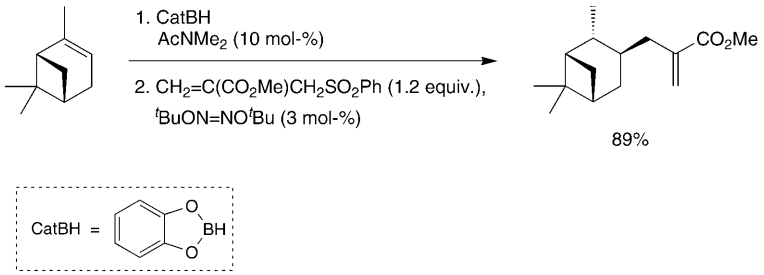
A tandem radical process involving conjugate addition to an activated alkene followed by allylation is reported. *B*-Alkylcatecholboranes, easily available *via* hydroboration of the corresponding alkenes, were used to generate the initial radicals. These radicals add efficiently to electrophilic alkenes such as phenyl vinyl sulfone, *N*-phenylmaleimide, and dialkyl fumarate. In the last step of this one-pot process, the radical adducts react with the allylic sulfones. The whole process can be considered as a unique and selective coupling of three different alkenes.

Introduction. – The spectacular development of radical chemistry in organic synthesis over the last 20 years is tightly bound to tin (Sn)-based methods [1]. However, the use of trialkyltin derivatives, which are toxic and contaminate the products even after repeated purification by column chromatography, represents a strong limitation for their application in medicinal chemistry and for the production of compounds of therapeutic importance [2]. The development of radical chain reactions under Sn-free conditions represents one of the most-important challenges in radical chemistry to extend its scopes from a research tool to a production tool. Nowadays, different Sn-free strategies are developed [3]. Among them, the use of organoboranes as radical precursors has a privileged position for the generation of alkyl radicals [4]. Recently, we have shown that *B*-alkylcatecholboranes, easily prepared by hydroboration of olefins, are so far the most-reactive and useful boron-based radical precursors [5]. This approach had led to the development of several methods for C–X (X = H, O) and C–C bond formation. For instance, a radical allylation reaction with allyl sulfones as allylating agents has been reported, as exemplified in *Scheme 1* [6][7]. The scope of this reaction is remarkably wide due to the diversity of allyl sulfones available[1]).

Radical conjugate addition–allylation processes are synthetically very useful procedures that are routinely achieved by Sn chemistry starting from halides, activated alkenes, and allylstannanes [10]. Related reactions with allylplumbanes are also known [11]. Radical addition to alkenes *via* transfer of a xanthate group, followed by allylation with allyl sulfones, has also been reported [12]. In this reaction, the two

[1]) For a review on radical allylations with allylsulfones, see [8]. See also references cited in [6] and [9].

Scheme 1. *Radical Allylation of* B-*Alkylcatecholboranes*

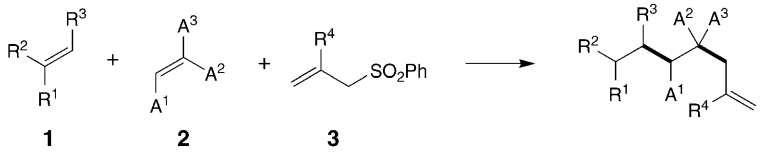


steps have to be run consecutively. An interesting Sn-free process where alkyl allyl sulfones are used as radical precursors and allylating agents is also known [9].

Herein, we report a novel one-pot tandem process involving radicals generated from organoboranes, activated alkenes, and allyl sulfones. The whole process corresponds to a unique and selective coupling of three different alkenes.

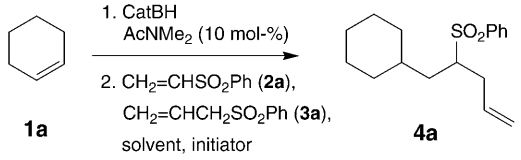
Results. – The aim of this work was to achieve the three-component coupling reaction depicted in *Scheme 2*. Three different alkenes served as starting materials, and the whole sequence was achieved by hydroboration of alkene **1** with catecholborane (CatBH), followed by conjugate addition to the activated alkene **2**, and by allylation of the radical adduct with the allyl sulfone **3**. Such a process can only work if the reactivities of the activated alkene **2** and of the allylic sulfone **3** are different. This could be easily achieved by using an electrophilic alkene **2** ($A^1 - A^3 =$ electron-withdrawing groups) to trap the initial radical, and an allylic sulfone **3** substituted at position 2 by neutral or electron-donating groups ($R^4 = H$, alkyl) to allylate the radical adduct.

Scheme 2. *Three-Component Coupling Reaction of Alkenes.* Newly formed C–C bonds are marked bold.



The optimization of the process was carried out with a model reaction involving cyclohexene (**1a**), phenyl vinyl sulfone (**2a**), and allyl phenyl sulfone (**3a**), and the results are shown in the *Table*. In CH_2Cl_2 (*Entry 1*), the coupling product **4a** was isolated in only 32% yield. Under these conditions, **3a** was entirely consumed. Variation of the nature of the initiator and of the workup procedure had no significant effect on the yield of the reaction. Using an excess (1.5 equiv.) of the allyl sulfone **3a** (*Entry 2*) gave rise to an increased yield (43%). When running the radical process in DMF at 100°, instead of CH_2Cl_2 at 25°, with a slight excess of **1a** (1.1 equiv.) and **3a** (1.6 equiv.), gave a cleaner reaction, and the desired product **4a** was isolated as a single product in 68% yield (*Entry 3*). The excess of **3a** was recovered unchanged at the end of the reaction.

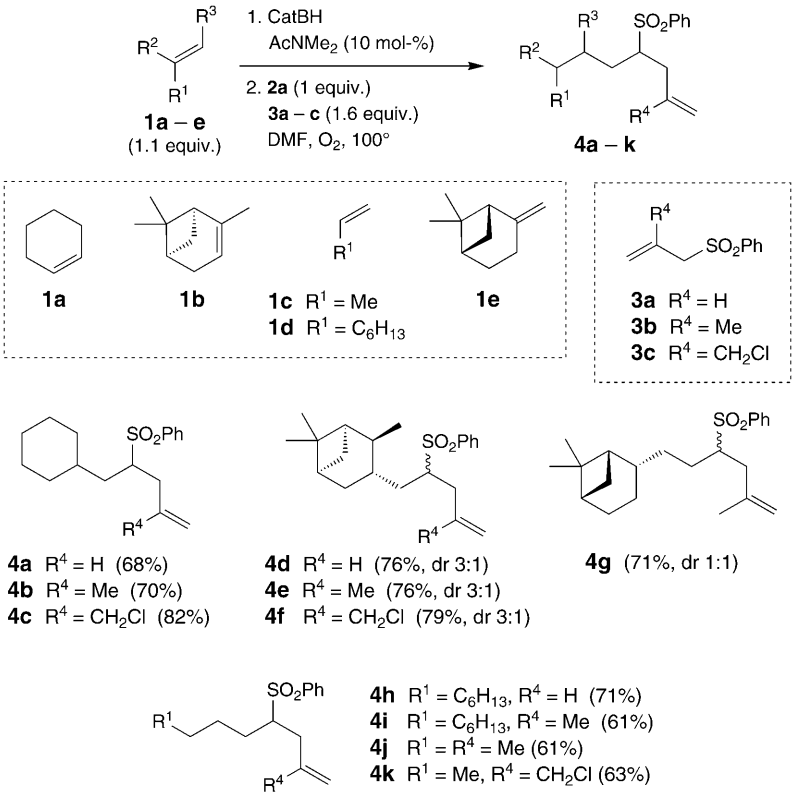
Table. *Optimization of the Three-Component Coupling Reaction*



Entry	Equivalents			Solvent	*T* [°]	Yield of **4a**
	1a	**2a**	**3a**			[%]
1	1	1	1	CH_2Cl_2	25	32
2	1	1	1.5	CH_2Cl_2	25	43
3	1.1	1	1.6	DMF	100	68

The three-component reaction involving phenyl vinyl sulfone (**2a**) was next examined with different radicals generated from alkenes **1a**–**e** and allyl sulfones **3a**–**c** (*Scheme 3*). Good yields (68–82%) were obtained with secondary alkyl radicals generated from cyclohexenes (**4a**–**c**) and α-pinenes (**4d**–**f**). As expected, the less-nucleo-

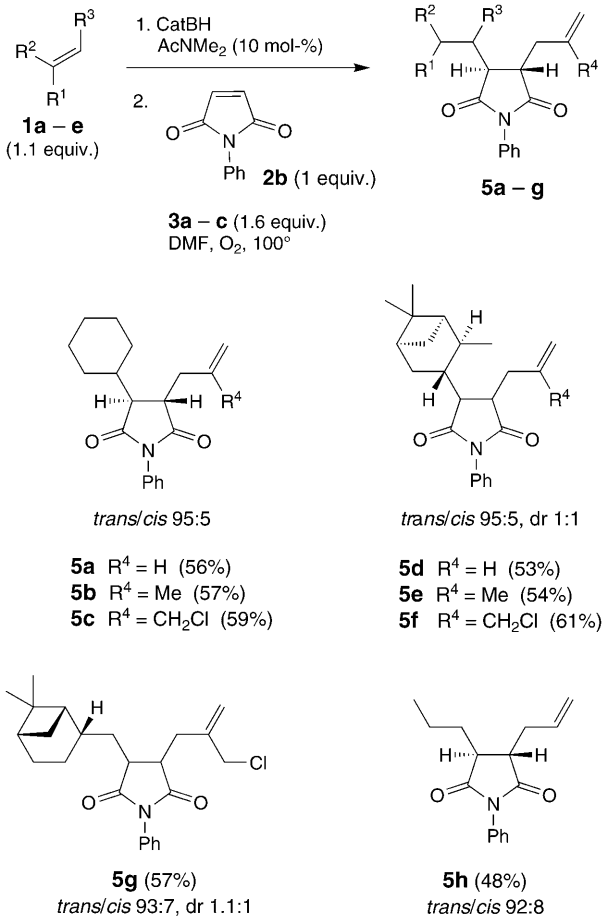
Scheme 3. *Reactions with Phenyl Vinyl Sulfone* (**2a**)



philic primary alkyl radicals gave rise to slightly lower yields (**4g**–**k**; 61–71%). The substitution at C(2) of the allyl sulfone (R^4 = H, Me, CH_2Cl) did not strongly influence the yield of the reaction. The reaction with the chloromethyl-substituted sulfone ($R^4 = ClCH_2$) is remarkable in that it involves a selective β-fragmentation of a benzenesulfonyl group in the presence of a Cl-atom. This result fits with the reported rate of β-fragmentation of a 2-benzenesulfonylalkyl radical, which proceeds 6.8 times faster than that of the 2-chloroalkyl radical [13].

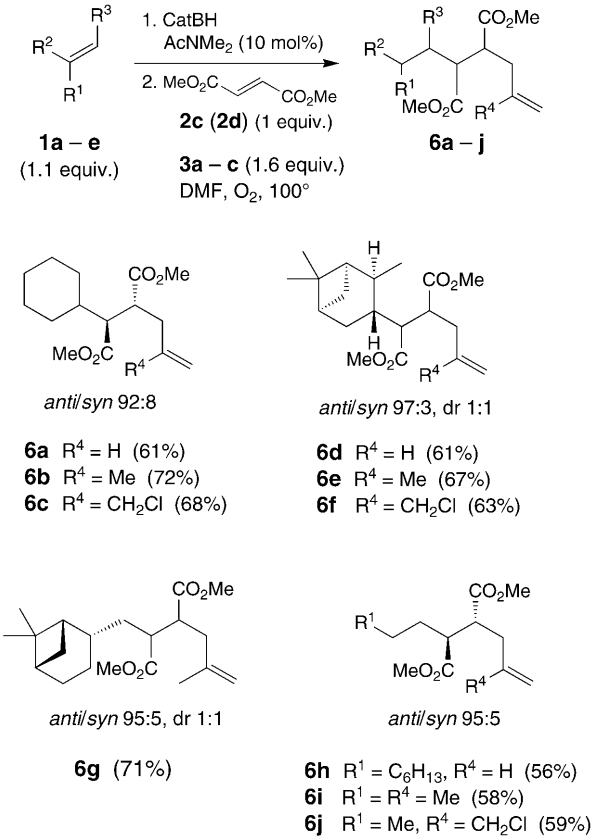
Other radical traps were also tested. Preparatively useful results were obtained with highly activated olefins such as *N*-phenylmaleimide (**2b**; *Scheme 4*) and dimethyl fumarate (**2c**; *Scheme 5*). With **2b**, all reactions were found to be *trans* stereoselective[2]), affording addition product **5** in moderate yields with secondary alkyl radicals (**5a**–**f**; 53–61%) and primary alkyl radicals (**5g**, 57%; **5h**, 48%). The formation of oligomers

Scheme 4. *Reactions with* N-*phenylmaleimide* (**2b**)



[2]) For related diastereoselective additions to maleimide derivatives, see [9] and [14].

Scheme 5. *Reactions with Dimethyl Fumarate* (**2c**). The diethyl ester **2d** was used instead of the dimethyl ester **2c** for the preparation of **6d** and **6h**.



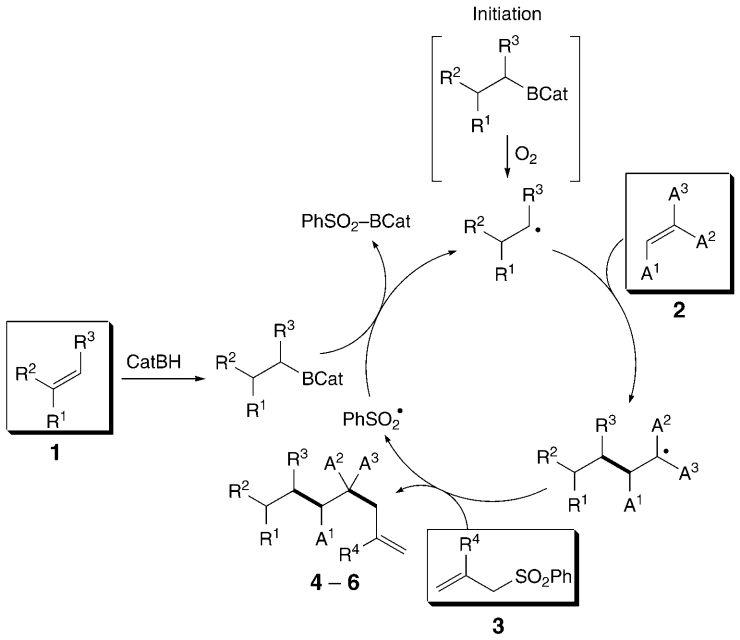
resulting from the addition of the radical adduct to another molecule of *N*-phenylmaleimide (**2b**) was detected by GC/MS analysis of the crude products and rationalizes the lower yields observed with this trap relative to the vinyl sulfone **2a**.

The reaction with dimethyl fumarate (**2c**) was investigated next. It was found to afford preferentially the *anti* isomer in moderate-to-good yields with secondary and primary alkyl radicals (*Scheme 5*)[3]). No oligomerization product was produced in this reaction. Attempts to run similar reactions with methyl acrylate afforded the addition–allylation product in low yield, together with a larger amount of oligomers.

Discussion. – The conjugate addition–allylation reaction follows the mechanism depicted in *Scheme 6*. The initial alkyl radical has a nucleophilic character and, thus, reacts rapidly with the electrophilic olefin **2** to afford the corresponding radical adduct. Allylation of this radical adduct finally provides the products **4**–**6**, together with the benzenesulfonyl radical that can propagate the chain process by reaction with the *B*-

[3]) For stereoselective reactions with closely related systems, see [15].

Scheme 6. *Proposed Mechanism of the Three-Component Coupling Reaction.* Newly formed C–C bonds are marked bold.



alkylcatecholborane. Besides polar factors, a key element for the success of this radical process is that the radical adduct does not react with the alkylcatecholborane. Indeed, we have already established that radical adducts of this type ($A = CO_2R$, SO_2Ar) do not react with *B*-alkylcatecholborane to afford the corresponding enolate ($A = CO_2R$) or related species ($R = SO_2Ar$).

Conclusions. – A method for radical addition to electron-deficient unsaturated compounds, followed by allylation of the resulting intermediate radical adducts, is reported. This method is general for highly activated radical traps such as vinyl sulfones, maleimides, and fumarates, and it compares well with the well-established allyltin-mediated conjugate addition–allylation process. Since the initial radical is generated from an organoboron species obtained by hydroboration of the corresponding alkenes, the whole process represents a one-pot coupling reaction of three different alkenes.

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Experimental Part

General. Catecholborane (CatBH) was distilled under reduced pressure (b.p. 50°/50 mbar). Other reagents were obtained from commercial sources and used as received. All glassware was oven-dried at 130°, assembled hot, and allowed to cool under vacuum. Flash column chromatography (FC) was car-

ried out on *SDS* silica gel (40–63 μm), with AcOEt, cyclohexane, pentane, and *t*-BuOMe as eluents. Thin-layer chromatography (TLC) was performed on *Merck* silica gel *60 F_{254}* anal. plates; detection under UV light and/or by dipping in a soln. of $KMnO_4$ (3 g), K_2CO_3 (20 g), and 5% aq. NaOH (5 ml) in H_2O (300 ml). Melting points (m.p.) were determined in open capillaries on a *Büchi B-545* apparatus; uncorrected. IR Spectra: *Jasco FT/IR-400 plus* apparatus; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AC-300*, at 300 and 75 MHz, resp., in $CDCl_3$; chemical shifts δ in ppm rel. to residual $CHCl_3$ (δ(H) 7.26, δ(C) 77.0 ppm), coupling constants *J* in Hz. GC/MS: *Finnigan Trace GC/MS* apparatus fitted with an *Optima delta-3* (30 m). High-Resolution liquid-secondary-ion mass spectra (HR-LSI-MS): *Micromass AutospecQ*, with a Cs^+ ion beam at 20 kV, using polyethylene glycol as internal standard; in *m*/*z*.

General Procedure for the Multicomponent Reaction. Catecholborane (0.42 ml, 4 mmol) was added dropwise at 0° to a soln. of the alkene **1** (2.0 mmol) and *N*,*N*-dimethylacetamide (20.0 μl, 0.2 mmol) in CH_2Cl_2 (2 ml) under N_2 atmosphere, and the mixture was heated at reflux for 5 h. MeOH (0.08 ml, 2 mmol) was added at 0°, and the soln. was stirred for 5 min at r.t. Then, the solvent was removed by flushing with N_2. DMF (2 ml) was added to the residual *B*-alkylcatecholborane. The soln. was cooled to 0°, and the electron-deficient radical trap **2** (1.8 mmol) and the allyl sulfone **3** (3 mmol) were successively added in DMF (1 ml). The mixture was then heated at 100°, and air (180 ml, 1.5 mmol O_2) was introduced over 90 min through a needle placed just above the reaction surface. The progress of the reaction was monitored by GC/MS. At the end of the reaction, the soln. turned black. CH_2Cl_2 (50 ml) was added, and DMF was removed by washing with H_2O. The crude product was purified by FC.

{[1-(Cyclohexylmethyl)but-3-en-1-yl]sulfonyl}benzene (**4a**). Prepared from **1a** (0.164 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.357 g (68%). Colorless oil. ^1H-NMR: 7.87–7.91 (*m*, 2 H); 7.54–7.69 (*m*, 3 H); 5.67–5.81 (*m*, 1 H); 5.02–5.08 (*m*, 2 H); 3.03–3.13 (*m*, 1 H); 2.56–2.65 (*m*, 1 H); 2.24–2.34 (*m*, 1 H); 1.01–1.71 (*m*, 11 H); 0.64–0.89 (*m*, 2 H). ^{13}C-NMR: 137.9; 133.6; 133.5; 129.1; 128.9; 118.3; 61.5; 34.9; 34.8; 33.4; 33.2; 32.5; 26.3; 26.1; 25.9. EI-MS: 292 (M^+), 250, 185, 151, 109, 95, 83, 55, 41. HR-MS: 292.14954 (M^+, $C_{17}H_{24}O_2S^+$; calc. 292.14970).

{[1-(Cyclohexylmethyl)-3-methylbut-3-en-1-yl]sulfonyl}benzene (**4b**). Prepared from **1a** (0.164 g, 2 mmol), **2a** (0.302 g, 1.8 mmol), and **3b** (0.588 g, 3 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.386 g (70%). Colorless oil. ^1H-NMR: 7.87–7.90 (*m*, 2 H); 7.56–7.65 (*m*, 3 H); 4.80 (br. *s*, 1 H); 4.71 (br. *s*, 1 H); 3.17–3.21 (*m*, 1 H); 2.59 (*dd*, *J* = 13.9, 3.6, 1 H); 2.11 (*dd*, *J* = 13.9, 9.8, 1 H); 1.55–1.74 (*m*, 9 H); 1.30–1.37 (*m*, 2 H); 1.07–1.14 (*m*, 3 H); 0.73–0.76 (*m*, 2 H). ^{13}C-NMR: 140.6; 137.9; 133.6; 129.1; 129.0; 114.3; 59.7; 34.9; 34.8; 33.2; 32.9; 26.3; 26.1; 25.9; 221.7. EI-MS: 306 (M^+), 292, 264, 251, 164, 149, 121, 109, 95, 83, 55, 41. HR-MS: 306.16382 (M^+, $C_{18}H_{26}O_2S^+$; calc. 306.16535).

[[3-(Chloromethyl)-1-(cyclohexylmethyl)but-3-enyl]sulfonyl]benzene (**4c**). Prepared from **1a** (0.164 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2 cyclohexane/*t*-BuOMe 4:1). Yield: 0.503 g (82%). Colorless oil. IR: 3067, 2921, 1645, 1303, 1142, 913, 688. ^1H-NMR: 7.87–7.90 (*m*, 2 H); 7.64–7.67 (*m*, 1 H); 7.54–7.59 (*m*, 2 H); 5.99 (br. *s*, 1 H); 4.99 (br. *s*, 1 H); 3.95–4.08 (*m*, 2 H); 3.25–3.34 (*m*, 1 H); 2.72 (*dd*, *J* = 15.2, 5.5, 1 H); 2.35 (*dd*, *J* = 15.2, 7.9, 1 H); 1.61–1.78 (*m*, 6 H); 1.31–1.38 (*m*, 2 H); 1.05–1.18 (*m*, 3 H); 0.71–0.85 (*m*, 2 H). ^{13}C-NMR: 140.8; 137.6; 133.6; 129.0; 128.9; 117.9; 59.6; 47.3; 36.2; 34.7; 33.3; 33.2; 32.8; 26.2; 25.9; 25.8. EI-MS: 305 ([M – Cl]$^+$), 198, 163, 143, 109, 95, 81, 55, 41. HR-MS: 305.1575 ([M – Cl]$^+$, $C_{18}H_{25}O_2S^+$; calc. 305.1575).

*(1*R*,2*S*,3*S*,5*R*)-2,6,6-Trimethyl-3-[2-(phenylsulfonyl)pent-4-en-1-yl]bicyclo[3.1.1]heptane* (**4d**). Prepared from **1b** (0.272 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.474 g (76%; dr 3:1)[4]). Colorless oil. ^1H-NMR: 7.81–7.87 (*m*, 2 H); 7.42–7.56 (*m*, 3 H); 5.59–5.79 (*m*, 1 H); 4.97–5.06 (*m*, 2 H); 2.98–3.07 (*m*, 1 H); 2.64–2.73 (*m*, 2 H); 2.32–2.59 (*m*, 2 H); 1.92–2.08 (*m*, 2 H); 1.63–1.76 (*m*, 3 H); 1.41–1.47 (*m*, 1 H); 1.06–1.17 (*m*, 4 H); 0.74–0.90 (*m*, 6 H); 0.61 (*d*, *J* = 9.9, 1 H). ^{13}C-NMR: 138.3; 137.8; 133.6; 133.5; 129.1; 128.9; 118.9; 61.7; 47.9; 43.9; 41.7; 38.7; 34.2; 34.0; 33.9; 33.4; 33.2; 32..5; 28.0; 22.9; 21.4. EI-MS: 347 (M^+), 332, 292, 266, 238, 205, 150, 137, 107, 93, 83. HR-MS: 346.19620 (M^+, $C_{21}H_{30}O_2S^+$; 346.19665).

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[4]) The term 'dr' refers to diastereoisomer ratio.

*(1*R*,2*S*,3*S*,5*R*)-2,6,6-Trimethyl-3-[4-methyl-2-(phenylsulfonyl)pent-4-en-1-yl]bicyclo[3.1.1]heptane* (**4e**). Prepared from **1b** (0.272 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.493 g (76%; dr 3:1). Colorless oil. IR: 3076, 2901, 1646, 1330, 1142, 894. ^{1}H-NMR (one isomer): 7.88–7.93 (*m*, 2 H); 7.63–7.65 (*m*, 1 H); 7.54–7.59 (*m*, 2 H); 4.73–4.87 (*m*, 2 H); 3.17–3.26 (*m*, 1 H); 2.65–2.74 (*m*, 1 H); 2.20–2.26 (*m*, 1 H); 2.01–2.08 (*m*, 2 H); 1.77–1.94 (*m*, 3 H); 1.70–1.74 (*m*, 1 H); 1.68 (br. *s*, 3 H); 1.31–1.47 (*m*, 3 H); 1.17–1.23 (*m*, 1 H); 1.14 (*s*, 3 H); 0.89 (*d*, *J* = 8.3, 3 H); 0.63 (*s*, 3 H); 0.59 (*d*, *J* = 9.4, 1 H). ^{13}C-NMR: 140.4; 138.9; 133.8; 129.3; 129.2; 115.2; 60.3; 48.2; 44.2; 42.0; 39.0; 38.8; 38.6; 33.9; 33.1; 28.3; 27.1; 22.9; 21.9; 21.4. EI-MS: 360 (M^+), 345, 219, 163, 107, 93, 81, 55, 41. HR-ES-TOF-MS: 383.2020 ($[M+Na]^+$, $C_{22}H_{32}NaO_2S^+$; calc. 383.2020).

*(1*R*,2*S*,3*S*,5*R*)-3-[4-(Chloromethyl)-2-(phenylsulfonyl)pent-4-en-1-yl]-2,6,6-trimethylbicyclo[3.1.1]-heptane* (**4f**). Prepared from **1b** (0.272 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1): Yield: 0.561 g (79%; dr 3:1). Colorless oil. IR: 3071, 2901, 1643, 1303, 1142, 915, 689. ^{1}H-NMR: 7.87–7.90 (*m*, 2 H); 7.63–7.68 (*m*, 1 H); 7.54–7.59 (*m*, 2 H); 5.23 (br. *s*, 1 H); 4.99 (br. *s*, 1 H); 3.97 (*d*, *J* = 6.4, 2 H); 3.25–3.29 (*m*, 1 H); 2.85 (*dd*, *J* = 14.6, 3.9, 2 H); 2.19–2.23 (*m*, 2 H); 1.94–1.98 (*m*, 2 H); 1.79–1.85 (*m*, 2 H); 1.63–1.69 (*m*, 2 H); 1.36–1.40 (*m*, 2 H); 1.10 (*s*, 3 H); 0.93 (*d*, *J* = 7.2, 3 H); 0.80 (*s*, 3 H); 0.53 (*d*, *J* = 9.5, 1 H). ^{13}C-NMR: 140.3; 138.2; 133.7; 129.1; 128.8; 118.5; 60.0; 47.9; 47.3; 43.9; 41.7; 39.4; 38.5; 34.3; 33.9; 33.8; 33.1; 28.0; 22.7; 21.2. EI-MS: 359 ($[M-Cl]^+$), 252, 209, 163, 143, 93, 77, 55, 41. HR-MS: 359.2034 ($[M-Cl]^+$, $C_{22}H_{31}O_2S^+$; calc. 359.2044).

*(1*S*,2*S*,5*S*)-6,6-Dimethyl-2-[5-methyl-3-(phenylsulfonyl)hex-5-en-1-yl]bicyclo[3.1.1]heptane* (**4g**). Prepared from **1e** (0.272 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.460 g (71%; *trans*/*cis* 95:5). Colorless oil. IR: 3080, 2911, 1647, 1303, 1143, 891. ^{1}H-NMR: 7.88–7.91 (*m*, 2 H); 7.63–7.68 (*m*, 1 H); 7.43–7.59 (*m*, 2 H); 4.87 (br. *s*, 1 H); 4.73 (br. *s*, 1 H); 3.02–3.06 (*m*, 1 H); 2.57–2.63 (*m*, 1 H); 2.16–2.29 (*m*, 2 H); 1.72–1.91 (*m*, 6 H); 1.65 (br. *s*, 3 H); 1.42–1.56 (*m*, 3 H); 1.15–1.25 (*m*, 2 H); 1.13 (*s*, 3 H); 1.90 (*s*, 3 H); 0.77–0.79 (*m*, 1 H). ^{13}C-NMR: 140.7; 138.1; 133.5; 129.1; 128.1; 114.1; 62.6; 46.1; 45.9; 41.5; 38.6; 37.0; 36.8; 34.8; 33.6; 28.1; 26.3; 23.2; 22.1; 21.7. EI-MS: 360 (M^+), 345, 305, 279, 163, 107, 81, 55, 41. HR-ESI-TOF-MS: 361.2201 ($[M+H]^+$, $C_{22}H_{33}O_2S^+$; calc. 361.2201).

[(1-Prop-2-en-1-yldecyl)sulfonyl]benzene (**4h**). Prepared from **1d** (0.224 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 9:1). Yield: 0.412 g (71%). Colorless oil. ^{1}H-NMR: 7.86–7.90 (*m*, 2 H); 7.55–7.65 (*m*, 3 H); 5.66–5.79 (*m*, 1 H); 5.01–5.08 (*m*, 2 H); 2.94–3.02 (*m*, 1 H); 2.54–2.64 (*m*, 1 H); 2.29–2.39 (*m*, 1 H); 1.76–1.88 (*m*, 1 H); 1.49–1.65 (*m*, 1 H); 1.20–1.45 (*m*, 14 H); 0.86 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 138.1; 133.6; 133.5; 129.0; 128.9; 118.2; 64.1; 32.4; 31.8; 29.4; 29.2; 27.2; 26.6; 14.1. EI-MS: 322 (M^+), 250, 222, 180, 143, 111, 97, 83, 69, 57. HR-MS: 322.19653 (M^+, $C_{19}H_{30}O_2S^+$; calc. 322.19665).

{[1-(2-Methylprop-2-en-1-yl)decyl]sulfonyl}benzene (**4i**). Prepared from **1d** (0.224 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.393 g (65%). Colorless oil. ^{1}H-NMR: 7.88–7.91 (*m*, 2 H); 7.52–7.66 (*m*, 3 H); 4.80 (br. *s*, 1 H); 4.72 (br. *s*, 1 H); 3.08–3.13 (*m*, 1 H); 2.58 (*dd*, *J* = 14.3, 3.3, 1 H); 2.20 (*dd*, *J* = 14.3, 9.9, 1 H); 1.77–1.83 (*m*, 1 H); 1.58–1.63 (*m*, 4 H); 1.20–1.45 (*m*, 14 H); 0.87 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 140.7; 138.0; 133.6; 133.5; 129.1; 129.0; 114.0; 62.4; 37.0; 31.8; 29.5; 29.4; 29.2; 28.0; 26.9; 26.6; 22.6; 14.1. EI-MS: 336 (M^+), 322, 281, 194, 143, 111, 97, 83, 69, 57. HR-MS: 336.21255 (M^+, $C_{20}H_{32}O_2S^+$; calc. 336.21230).

{[1-(2-Methylprop-2-en-1-yl)pentyl]sulfonyl}benzene (**4j**). Prepared from *B*-propylcatecholborane (0.324 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.292 g (61%). Colorless oil. IR: 3082, 2956, 1647, 1302, 1143, 894. ^{1}H-NMR: 7.87–7.90 (*m*, 2 H); 7.63–7.65 (*m*, 1 H); 7.56–7.58 (*m*, 2 H); 4.80 (br. *s*, 1 H); 4.71 (br. *s*, 1 H); 3.05–3.13 (*m*, 1 H); 2.58 (*dd*, *J* = 14.4, 3.6, 1 H); 2.14–2.19 (*m*, 1 H); 1.77–1.83 (*m*, 1 H); 1.62 (br. *s*, 3 H); 1.55–1.59 (*m*, 1 H); 1.33–1.39 (*m*, 2 H); 1.20–1.26 (*m*, 2 H); 0.83 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR: 140.5; 137.9; 133.5; 129.0; 128.7; 113.9; 62.3; 36.9; 28.9; 27.6; 22.5; 21.6; 13.5. EI-MS: 265 ($[M-1]^+$), 158, 143, 123, 81, 77, 41. HR-ESI-TOF-MS: 267.1418 ($[M+H]^+$, $C_{15}H_{23}O_2S^+$; calc. 267.1418).

({1-[2-(Chloromethyl)prop-2-en-1-yl]pentyl}sulfonyl)benzene (**4k**). From *B*-propylcatecholborane (0.324 g, 2.0 mmol), **2a** (0.302 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 4:1). Yield: 0.341 g (63%). Colorless oil. IR: 3064, 2956, 1640, 1301, 1142, 914, 668. ^{1}H-NMR: 7.87–7.90 (*m*, 2 H); 7.64–7.66 (*m*, 1 H); 7.54–7.59 (*m*, 2 H); 5.21 (br. *s*, 1 H); 5.0 (br. *s*, 1 H); 4.01 (*dd*, *J* = 20.8, 12.1, 1 H); 3.15–3.21 (*m*, 1 H); 2.70 (*dd*, *J* = 15.3, 5.1, 1 H); 2.41 (*dd*, *J* = 15.3, 8.6, 1 H); 1.50–1.54 (*m*, 1 H); 1.40–1.43 (*m*, 1 H); 1.36–1.38 (*m*, 2 H); 1.21–1.26 (*m*, 2 H); 0.84 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 140.8; 137.8; 133.7; 129.1; 128.9; 117.9; 62.2; 47.4; 32.5; 28.9; 28.0; 22.5; 13.6. EI-MS: 265 ($[M-Cl]^+$), 158, 143, 123, 81, 77, 41. HR-MS: 265.1260 ($[M-Cl]^+$, $C_{15}H_{21}O_2S^+$; calc. 265.1262).

*(3*RS*,4*RS*)-3-Cyclohexyl-1-phenyl-4-(prop-2-en-1-yl)pyrrolidine-2,5-dione* (**5a**). Prepared from **1a** (0.164 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.299 g (56%). Colorless powder. M.p. 81–82°. IR: 3093, 2920, 1698, 1641, 911. ^{1}H-NMR: 7.43–7.47 (*m*, 2 H); 7.37–7.41 (*m*, 1 H); 7.23–7.26 (*m*, 2 H); 5.70–5.79 (*m*, 1 H); 5.17–5.23 (*m*, 2 H); 2.81–2.86 (*m*, 1 H); 2.67 (*dd*, *J* = 3.8, 3.8, 1 H); 2.57–2.59 (*m*, 2 H); 1.98–2.03 (*m*, 1 H); 1.71–1.83 (*m*, 5 H); 1.08–1.27 (*m*, 5 H). ^{13}C-NMR: 178.1; 177.9; 132.9; 131.9; 129.1; 128.5; 126.5; 119.6; 50.2; 42.5; 39.8; 36.1; 30.4; 28.5; 26.3; 26.1; 26.0. EI-MS: 297 (M^+), 215, 174, 119, 77, 55, 41. HR-MS: 297.17288 (M^+, $C_{19}H_{23}NO_2^+$; calc. 297.17255).

*(3*RS*,4*RS*)-3-Cyclohexyl-4-(2-methylprop-2-en-1-yl)-1-phenylpyrrolidine-2,5-dione* (**5b**). Prepared from **1a** (0.164 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.319 g (57%). Colorless powder. M.p. 116–117°. IR: 3060, 2911, 1698, 1652, 911. ^{1}H-NMR: 7.40–7.44 (*m*, 2 H); 7.35–7.38 (*m*, 1 H); 7.24–2.27 (*m*, 2 H); 4.91–4.92 (*m*, 1 H); 4.80–4.81 (*m*, 1 H); 2.82–2.86 (*m*, 1 H); 2.68 (*dd*, *J* = 3.7, 3.6, 1 H); 2.61 (br. *dd*, *J* = 13.1, 4.8, 1 H); 2.40 (*ddd*, *J* = 13.7, 8.8, 0.6, 1 H); 1.89–1.98 (*m*, 1 H); 1.77 (br. *s*, 3 H); 1.59–1.81 (*m*, 5 H); 1.02–1.35 (*m*, 5 H). ^{13}C-NMR: 178.6; 178.0; 141.2; 132.0; 129.1; 128.5; 126.4; 115.0; 50.1; 41.6; 40.5; 40.1; 29.9; 28.8; 26.3; 26.1; 25.9; 22.2. EI-MS: 311 (M^+), 256, 229, 174, 77, 55, 41. HR-MS: 311.18852 (M^+, $C_{20}H_{25}NO_2^+$; calc. 311.18845).

*(3*RS*,4*RS*)-3-[2-(Chloromethyl)prop-2-en-1-yl]-4-cyclohexyl-1-phenylpyrrolidine-2,5-dione* (**5c**). Prepared from **1a** (0.164 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.367 g (59%). Colorless crystalline solid. M.p 114–115°. IR: 3098, 2924, 1701, 1648, 939, 671. ^{1}H-NMR: 7.40–7.45 (*m*, 2 H); 7.35–7.38 (*m*, 1 H); 7.24–7.28 (*m*, 2 H); 5.31 (br. *s*, 1 H); 5.09 (br. *s*, 1 H); 4.12 (*ddd*, *J* = 12, 0.9, 2 H); 2.90–2.94 (*m*, 1 H); 2.60–2.68 (*m*, 3 H); 1.94–1.99 (*m*, 1 H); 1.71–1.83 (*m*, 5 H); 1.20–1.33 (*m*, 5 H). ^{13}C-NMR: 177.8; 177.5; 141.2; 131.8; 129.1; 128.5; 126.4; 118.5; 51.2; 47.6; 41.5; 40.0; 36.0; 30.0; 28.8; 26.3; 26.1; 25.9. EI-MS: 345 (M^+), 310, 228, 174, 81, 77, 67, 55, 41. HR-MS: 345.14955 (M^+, $C_{20}H_{24}ClNO_2^+$; calc. 345.14893).

*1-Phenyl-3-(prop-2-en-1-yl)-4-[(1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]pyrrolidine-2,5-dione* (**5d**). Prepared from **1b** (0.272 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.335 g (53%; dr 1:1). Colorless oil. IR: 3095, 2903, 1706, 1646, 689. ^{1}H-NMR (one isomer): 7.43–7.47 (*m*, 2 H); 7.38–7.44 (*m*, 1 H); 7.23–7.27 (*m*, 2 H); 5.71–5.84 (*m*, 1 H); 5.18–5.25 (*m*, 2 H), 2.83–2.97 (*m*, 2 H); 2.57–2.65 (*m*, 2 H); 2.36–2.44 (*m*, 2 H); 2.05–2.11 (*m*, 1 H); 1.92–1.96 (*m*, 1 H); 1.77–1.83 (*m*, 2 H); 1.27–1.33 (*m*, 1 H); 1.22 (*s*, 3 H); 1.09 (*d*, *J* = 7.0, 3 H); 1.05 (*s*, 3 H); 0.75 (*d*, *J* = 9.9, 1 H). ^{13}C-NMR (two diastereoisomers): 178.5; 178.0; 177.9; 133.0; 132.9; 132.0; 131.9; 129.1; 128.6; 128.5; 126.5; 126.4; 119.7; 119.6; 48.6; 47.9; 47.7; 47.6; 43.9; 42.7; 41.3; 41.2; 39.9; 39.4; 39.3; 38.9; 38.6; 38.4; 36.6; 35.7; 34.4; 32.9; 31.1; 29.0; 28.3; 28.2; 23.0; 22.7; 21.3; 20.6. EI-MS: 351 (M^+), 215, 174, 136, 77, 55, 41. HR-MS: 351.21982 (M^+, $C_{23}H_{29}NO_2^+$; calc. 351.21945).

*3-(2-Methylprop-2-en-1-yl)-1-phenyl-4-[(1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]pyrrolidine-2,5-dione* (**5e**). Prepared from **1b** (0.272 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.335 g (54%; dr 1:1). Colorless oil. IR: 1390, 2904, 1705, 1657, 896. ^{1}H-NMR (one isomer): 7.40–7.44 (*m*, 2 H); 7.31–7.35 (*m*, 1 H); 7.24–7.28 (*m*, 2 H); 4.80–4.89 (*m*, 2 H); 2.80–2.92 (*m*, 2 H); 2.56–2.64 (*m*, 1 H); 2.44–2.50 (*m*, 1 H); 2.33–2.39 (*m*, 1 H); 2.10–2.26 (*m*, 2 H); 1.89–1.93 (*m*, 1 H); 1.76 (*d*, *J* = 5.9, 3 H); 1.73–1.75 (*m*, 1 H); 1.35–1.47 (*m*, 2 H); 1.19 (*s*, 3 H); 1.04 (*d*, *J* = 11.1, 3 H), 1.0 (*s*, 3 H); 0.70 (*d*, *J* = 10.0, 1 H). ^{13}C-NMR (two diastereoisomers): 178.8; 178.6; 178.3; 178.0; 141.1; 141.1; 131.9; 131.9; 129.1; 129.1; 128.5; 128.4; 126.4; 126.3; 115.3; 115.0; 48.8; 48.0; 47.9; 47.7; 42.4; 41.7; 41.2; 40.8; 40.1; 39.8; 39.4; 39.3; 39.1; 38.6;

38.4; 34.4; 32.8; 30.7; 28.9; 28.3; 28.2; 26.8; 22.9; 22.7; 22.2; 21.8; 21.1; 20.7. EI-MS: 365 (M^+), 229, 174, 136, 93, 77, 55, 41. HR-MS: 365.23548 (M^+, $C_{24}H_{31}NO_2^+$; calc. 365.23560).

*3-[2-(Chloromethyl)prop-2-en-1-yl]-1-phenyl-4-[(1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]pyrrolidine-2,5-dione* (**5f**). Prepared from **1b** (0.272 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.439 g (61%; dr 1:1). Colorless oil. IR: 3091, 2904, 1704, 1650, 909, 690. ^{1}H-NMR (one isomer): 7.44–7.49 (*m*, 2 H); 7.35–7.38 (*m*, 1 H); 7.24–7.27 (*m*, 2 H); 5.17 (br. *s*, 1 H); 5.12 (br. *s*, 1 H); 4.11–4.17 (*m*, 2 H); 2.97–3.03 (*m*, 1 H); 2.84–2.89 (*m*, 1 H); 2.69–2.73 (*m*, 1 H); 2.56–2.61 (*m*, 1 H); 2.31–2.41 (*m*, 3 H); 1.94–1.98 (*m*, 1 H); 1.78–1.83 (*m*, 1 H); 1.48–1.52 (*m*, 2 H); 1.22 (*s*, 3 H); 1.09 (*d*, *J* = 7.0, 3 H); 1.03 (*s*, 3 H); 0.77(*d*, *J* = 10.0, 1 H). ^{13}C-NMR (two diastereoisomers): 178.1; 177.9; 177.6; 141.1; 131.9; 131.8; 129.1; 128.6; 128.5; 126.4; 126.3; 118.7; 118.6; 53.4; 49.3; 48.7; 47.9; 47.7; 47.5; 47.4; 42.5; 41.5; 41.3; 41.2; 39.9; 39.4; 39.3; 39.0; 38.6; 38.4; 36.4; 35.7; 34.4; 32.8; 30.7; 29.0; 28.3; 28.2; 26.8; 22.9; 22.7; 21.1; 20.7. EI-MS: 364 ([M – Cl]$^+$), 228, 174, 136, 91, 77, 55, 41. HR-MS: 399.19650 (M^+, $C_{24}H_{30}ClNO_2^+$; calc. 399.19608).

*3-[2-(Chloromethyl)prop-2-en-1-yl]-4-{[(1*S*,2*S*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl}-1-phenylpyrrolidine-2,5-dione* (**5g**). Prepared from **1e** (0.272 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.410 g (57%; dr 49:44:4:3). Colorless oil. IR: 3090, 2907, 1705, 1654, 908, 689. ^{1}H-NMR: (one isomer) 7.44–7.49 (*m*, 2 H); 7.38–7.41 (*m*, 1 H); 7.24–7.27 (*m*, 2 H); 5.33 (br. *s*, 1 H); 5.11 (br. *s*, 1 H); 4.09–4.12 (*m*, 2 H); 2.72–2.86 (*m*, 4 H); 2.31–2.37 (*m*, 2 H); 1.85–2.0 (*m*, 6 H); 1.51–1.55 (*m*, 2 H); 1.19 (*s*, 3 H); 1.03 (*s*, 3 H); 0.89–0.92 (*m*, 1 H). ^{13}C-NMR: 178.4; 177.5; 141.2; 131.9; 129.1; 128.5; 126.3; 118.3; 47.5; 46.4; 44.8; 43.7; 41.4; 39.8; 38.7; 38.2; 35.4; 33.6; 28.1; 26.3; 23.2; 22.4. EI-MS: 399 (M^+), 364, 310, 228, 174, 137, 77, 41. HR-MS: 399.19635 ($C_{24}H_{30}ClNO_2^+$; calc. 399.19650).

*(3*RS*,4*RS*)-1-Phenyl-3-(prop-2-en-1-yl)-4-propylpyrrolidine-2,5-dione* (**5h**). Prepared from *B*-propylcatecholborane (0.324 g, 2.0 mmol), **2b** (0.311 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.222 g (48%). Colorless powder. M.p. 80–81°. IR: 3068, 2930, 1697, 927. ^{1}H-NMR: 7.29–7.41 (*m*, 3 H); 7.24–7.28 (*m*, 2 H); 5.71–5.84 (*m*, 1 H); 5.17–5.23 (*m*, 2 H); 2.71–3.78 (*m*, 2 H); 2.60–2.63 (*m*, 2 H); 1.87–1.95 (*m*, 1 H); 1.69–1.73 (*m*, 1 H); 1.48–1.52 (*m*, 2 H); 1.0 (*t*, *J* = 7.3, 3 H). ^{13}C-NMR: 178.4; 177.8; 133.0; 131.9; 129.1; 128.5; 126.4; 119.5; 45.5; 44.4; 35.4; 33.5; 19.9; 13.9. EI-MS: 257 (M^+), 215, 174, 125, 81, 77, 67, 41. HR-MS: 257.14157 (M^+, $C_{16}H_{19}NO_2^+$; calc. 257.14157).

*Dimethyl (2*RS*,3*SR*)-2-Cyclohexyl-3-(prop-2-en-1-yl)butanedioate* (**6a**). Prepared from **1a** (0.164 g, 2.0 mmol), **2c** (0.259 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.290 g (61%). Colorless powder. M.p. 38–39°. ^{1}H-NMR: 5.66–5.73 (*m*, 1 H); 4.97–5.05 (*m*, 2 H); 3.67 (br. *s*, 6 H); 2.91 (*dt*, *J* = 4.1, 10.0, 1 H); 2.62 (*dd*, *J* = 10.0, 5.8, 1 H); 2.19–2.30 (*m*, 2 H); 1.65–1.75 (*m*, 5 H); 1.42–1.46 (*m*, 1 H); 1.07–1.19 (*m*, 5 H). ^{13}C-NMR: 174.3; 173.4; 134.8; 116.9; 53.1; 51.5; 51.2; 45.3; 38.7; 34.7; 31.5; 29.0; 26.5; 26.3; 26.2. EI-MS: 268 (M^+), 237, 177, 155, 113, 95, 81, 67, 55. HR-MS: 268.16751 (M^+, $C_{15}H_{24}O_4^+$; calc. 268.16746).

*Dimethyl (2*RS*,3*SR*)-2-Cyclohexyl-3-(2-methylprop-2-en-1-yl)butanedioate* (**6b**). Prepared from **1a** (0.164 g, 2.0 mmol), **2c** (0.259 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.203 g (72%). Colorless powder. M.p. 79–80°. IR: 3015, 2923, 1718, 1649, 916. ^{1}H-NMR: 4.71 (*s*, 1 H); 4.67 (*s*, 1 H); 3.67 (*s*, 3 H); 3.65 (*s*, 3 H); 3.02–3.07 (*m*, 1 H); 2.61 (*dd*, *J* = 9.8, 5.7, 1 H); 2.32 (*dd*, *J* = 13.8, 11.5, 1 H); 2.05 (*dd*, *J* = 13.8, 3.4, 1 H); 1.63–1.75 (*m*, 8 H); 1.42–1.47 (*m*, 1 H); 0.95–1.19 (*m*, 5 H). ^{13}C-NMR: 174.4; 173.4; 142.6; 112.2; 53.6; 51.4; 51.2; 44.3; 38.9; 38.8; 31.6; 29.0; 26.5; 26.4; 26.2; 22. EI-MS: 282 (M^+), 250, 222, 156, 95, 81, 55, 41. HR-MS: 282.18311(M^+, $C_{16}H_{26}O_4^+$; calc. 282.18314).

*Dimethyl (2*RS*,3*SR*)-2-[2-(Chloromethyl)prop-2-en-1-yl]-3-cyclohexylbutanedioate* (**6c**). Prepared from **1a** (0.164 g, 2.0 mmol), **2c** (0.259 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.387 g (68%). Colorless crystalline solid. M.p. 42–43°. IR: 2925, 1719, 1645, 916, 749. ^{1}H-NMR: 5.13 (*s*, 1 H); 4.96 (*s*, 1 H); 4.03 (*dd*, *J* = 23.5, 11.8, 2 H); 3.68 (*s*, 3 H); 3.65 (*s*, 3 H); 2.91 (*dt*, *J* = 9.9, 5.0, 1 H); 2.62 (*dd*, *J* = 9.9, 6.0, 1 H); 2.36–2.46 (*m*, 2 H); 1.63–1.75 (*m*, 5 H); 1.42–1.48 (*m*, 1 H); 0.96–1.20 (*m*, 5 H). ^{13}C-NMR: 174.1; 173.1; 142.3; 116.4; 53.6; 51.6; 51.3; 47.4; 44.1; 38.7; 33.8; 31.5; 29.2; 26.4; 26.3; 26.2. EI-MS: 316 ([M – Cl]$^+$), 249, 202, 156, 113, 79, 55, 41. HR-MS: 281.17499 ([M – Cl]$^+$, $C_{16}H_{25}O_4^+$; calc. 281.17529).

*Dimethyl 2-(Prop-2-en-1-yl)-3-[(1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]butanedioate* (**6d**). Prepared from **1b** (0.272 g, 2.0 mmol), **2d** (0.309 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.354 g (61%; *anti*/*syn* 97:3, dr 1:1). Colorless oil. ^{1}H-NMR (one isomer): 5.68–5.74 (*m*, 1 H); 4.97–5.05 (*m*, 2 H); 4.12–4.15 (*m*, 4 H); 2.73–2.88 (*m*, 2 H); 1.68–2.36 (*m*, 9 H); 1.21–1.31 (*m*, 6 H); 1.16 (*s*, 3 H); 0.94–1.03 (*m*, 6 H); 0.61 (*d*, *J* = 9.9, 1 H). ^{13}C-NMR: 173.9; 173.8; 173.2; 172.8; 135.2; 134.8; 116.9; 116.8; 60.4; 60.2; 55.2; 51.8; 48.8; 47.6; 46.3; 46.1; 41.4; 41.3; 39.7; 38.6; 38.3; 37.5; 36.5; 35.3; 34.3; 33.3; 32.6; 28.1; 27.7; 27.6; 23.2; 22.8; 22.7; 20.9; 14.4; 14.3; 14.2. EI-MS: 350 (M^+), 305, 276, 263, 223, 173, 127, 93, 81, 67, 55. HR-MS: 350.24591 (M^+, $C_{21}H_{34}O_4^+$; calc. 350.24571).

*Dimethyl 2-(2-Methylprop-2-en-1-yl)-3-[(1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]butanedioate* (**6e**). Prepared from **1b** (0.272 g, 2.0 mmol), **2c** (0.259 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.405 g (67%; *anti*/*syn* 97:3, dr 1:1). Colorless oil. IR: 3090, 2948, 1727, 1652, 893. ^{1}H-NMR: 4.72 (*s*, 1 H); 4.68 (*s*, 1 H); 3.69 (*s*, 3 H); 3.66 (*s*, 3 H); 3.06–3.14 (*m*, 1 H); 2.82 (*dd*, *J* = 10.8, 3.8, 1 H); 2.21–2.31 (*m*, 2 H); 1.97–2.07 (*m*, 3 H); 1.85–1.91 (*m*, 3 H); 1.72 (br. *s*, 3 H); 1.54 (br. *s*, 2 H); 1.17 (*s*, 3 H); 0.97 (*d*, *J* = 6.7, 3 H); 0.95 (*s*, 3 H); 0.48 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR: 174.4; 173.3; 142.6; 112.3; 52.4; 51.4; 51.2; 47.6; 45.4; 41.4; 39.8; 39.7; 38.8; 37.8; 33.4; 28.1; 27.6; 22.9; 22.0; 20.8. EI-MS: 305 ($[M-2\ Me]^+$), 249, 209, 200, 168, 145, 93, 81, 67, 55, 41. HR-ESI-TOF-MS: 359.2198 ($[M+Na]^+$, $C_{20}H_{32}NaO_4^+$; calc. 359.2198).

*Dimethyl 2-[2-(Chloromethyl)prop-2-en-1-yl]-3-[(1*R*,2*S*,3*R*,5*R*)-2,6,6-trimethylbicyclo[3.1.1]hept-3-yl]butanedioate* (**6f**). Prepared from **1b** (0.272 g, 2.0 mmol), **2c** (0.259 g, 1.8 mmol), and **3c** (0.690 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.420 g (63%; *anti*/*syn* 97:3, dr 1:1). Colorless oil. ^{1}H-NMR: 5.14 (br. *s*, 1 H); 4.97 (br. *s*, 1 H); 4.0–4.08 (*m*, 2 H); 3.69 (*s*, 3 H); 3.66 (*s*, 3 H); 3.06–3.12 (*m*, 1 H); 2.83 (*dd*, *J* = 10.8, 4.0, 1 H); 2.38–2.42 (*m*, 2 H); 2.19–2.25 (*m*, 1 H); 1.99–2.07 (*m*, 2 H); 1.76–1.84 (*m*, 3 H); 1.71–1.75 (*m*, 1 H); 1.17 (*s*, 3 H); 1.0 (*d*, *J* = 6.8, 3 H); 0.94 (*s*, 3 H); 0.47 (*d*, *J* = 9.7, 1 H). ^{13}C-NMR: 174.1; 172.9; 142.3; 116.4; 52.4; 51.6; 51.4; 47.6; 47.4; 45.2; 41.3; 39.7; 38.8; 37.8; 34.8; 33.4; 28.1; 27.6; 22.9; 20.8. EI-MS: 335 ($[M-Cl]^+$), 249, 209, 145, 93, 55, 41. HR-ESI-TOF-MS: 371.1989 ($[M+H]^+$, $C_{20}H_{32}ClO_4^+$; calc. 371.1989).

*Dimethyl 2-{[(1*S*,2*S*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]methyl}-3-(2-methylprop-2-en-1-yl)butanedioate* (**6g**). Prepared from **1e** (0.272 g, 2.0 mmol), **2c** (0.259 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.369 g (61%; *anti*/*syn* 95:5, dr 1:1). Colorless oil. IR: 3088, 2909, 1732, 1642, 893. ^{1}H-NMR: 4.73 (*s*, 1 H); 4.67 (*s*, 1 H); 3.68 (*s*, 3 H); 3.65 (*s*, 3 H); 2.81–2.87 (*m*, 1 H); 2.67–2.73 (*m*, 1 H); 2.27–2.35 (*m*, 3 H); 1.83–2.01 (*m*, 4 H); 1.70 (br. *s*, 3 H); 1.45–1.49 (*m*, 2 H); 1.35–1.39 (*m*, 2 H); 1.17 (*s*, 3 H); 0.94 (*s*, 3 H); 0.77–0.81 (*m*, 1 H). ^{13}C-NMR: 174.9; 173.9; 142.4; 112.5; 51.5; 47.3; 46.4; 44.3; 41.4; 39.3; 39.1; 38.7; 37.8; 33.7; 28.1; 26.3; 23.0; 22.7; 21.9; 21.2. EI-MS: 336 (M^+), 240, 200, 133, 91, 81, 67, 41. HR-ESI-TOF-MS: 337.2378 ($[M+H]^+$, $C_{20}H_{33}O_4^+$; calc. 337.2378).

*Dimethyl (2*RS*,3*SR*)-2-Octyl-3-prop-2-en-1-ylbutanedioate* (**6h**). Prepared from **1d** (0.224 g, 2.0 mmol), **2d** (0.309 g, 1.8 mmol), and **3a** (0.546 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.300 g (56%). Colorless oil. ^{1}H-NMR (major isomers): 5.63–5.69 (*m*, 1 H); 4.96–5.01 (*m*, 2 H); 4.07–4.16 (*m*, 4 H); 2.56–2.68 (*m*, 2 H); 2.16–2.31 (*m*, 2 H); 1.55–1.59 (*m*, 1 H); 1.21–1.39 (*m*, 19 H); 0.82–0.93 (*m*, 3 H). ^{13}C-NMR: 174.0; 173.4; 134.7; 117.0; 60.3; 48.4; 34.9; 31.7; 30.5; 29.3; 29.1; 27.1; 22.6; 14.2. EI-MS: 326 (M^+), 281, 253, 207, 200, 127, 95, 67, 55, 43. HR-MS: 226.24567 (M^+, $C_{19}H_{34}O_4^+$; calc. 226.24571).

*Dimethyl (2*RS*,3*SR*)-2-(2-Methylprop-2-en-1-yl)-3-propylbutanedioate* (**6i**). Prepared from *B*-propylcatecholborane (0.324 g, 2.0 mmol), **2c** (0.309 g, 1.8 mmol), and **3b** (0.588 g, 3.0 mmol); purified by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.252 g (58%). Colorless oil. ^{1}H-NMR (major isomers): 4.72 (*s*, 1 H); 4.67 (*s*, 1 H); 3.68 (*s*, 3 H); 3.65 (*s*, 3 H); 2.91 (*dt*, *J* = 10.0, 4.5, 1 H); 2.63 (*dt*, *J* = 10.0, 3.0, 1 H), 2.33 (*dd*, *J* = 13.7, 10.5, 1 H); 2.05 (*dd*, *J* = 13.7, 4.3, 1 H); 1.70 (br. *s*, 3 H); 1.55–1.65 (*m*, 1 H); 1.19–1.33 (*m*, 3 H); 0.87 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR: 174.6; 174.1; 142.3; 112.4; 51.5; 51.43; 47.8; 46.8; 39.1; 32.7; 21.9; 20.5; 13.7. EI-MS: 242 (M^+), 210, 182, 151, 127, 87, 81, 55, 41. HR-MS: 242.1559 (M^+, $C_{13}H_{22}O_4^+$; calc. 242.1518).

*Dimethyl (2*RS*,3*SR*)-2-[2-(Chloromethyl)prop-2-en-1-yl]-3-propylbutanedioate* (**6j**). Prepared from *B*-propylcatecholborane (0.324 g, 2.0 mmol), **2c** (0.309 g, 1.8 mmol), and **3c** (0.690g, 3.0 mmol); purified

by FC (SiO_2; cyclohexane/*t*-BuOMe 7:3). Yield: 0.293 g (59%). Colorless oil. IR: 3095, 2955, 1730, 1643, 913, 749. ^{1}H-NMR: 5.14 (br. *s*, 1 H); 4.97 (br. *s*, 1 H); 4.06 (*ddd*, *J* = 21.1, 12.0, 0.8, 2 H); 3.71 (*s*, 3 H); 3.65 (*s*, 3 H); 2.87–2.95 (*m*, 1 H); 2.65 (*dt*, *J* = 6.8, 6.6, 1 H), 2.31–2.49 (*m*, 2 H); 1.60–1.64 (*m*, 1 H); 1.21–1.42 (*m*, 3 H); 0.86 (*t*, *J* = 7.6, 3 H). ^{13}C-NMR: 174.2; 173.7; 142.1; 116.6; 51.6; 47.9; 47.4; 46.6; 34.2; 32.6; 20.5; 13.8. EI-MS: 241($[M-Cl]^+$); 209, 185, 149, 121, 87, 55, 41. HR-MS: 241.1439 ($[M-Cl]^+$, $C_{13}H_{21}O_4^+$; calc. 241.1439).

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