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Nazarov Reactions Intercepted by (4 + 3) Cycloadditions with Oxygen-Substituted Dienes

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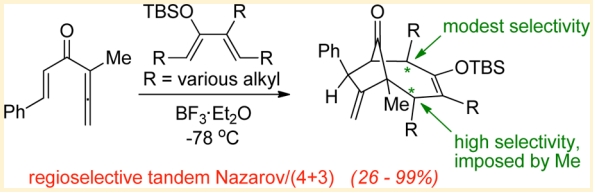
Supporting Information

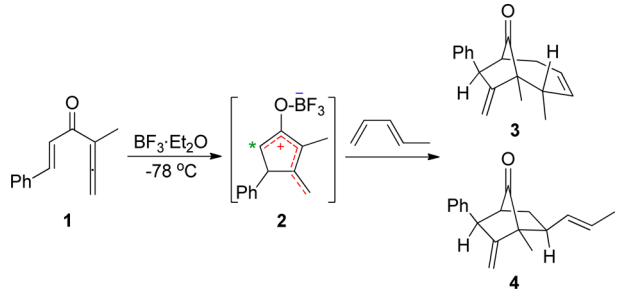
ABSTRACT: The oxyallyl cation intermediate from the Lewis acid mediated Nazarov reaction of an allenyl vinyl ketone was intercepted by acyclic, 2-silyloxy-substituted butadienes by highly regioselective (4 + 3) cycloadditions. Stereoselectivity was often modest, but in some instances steric interactions were responsible for high selectivity. The results are consistent with concerted (4 + 3) cycloadditions. In many instances, the (4 + 3) products were susceptible to fragmentation or rearrangement in the presence of the Lewis acid.



INTRODUCTION

The past decade has seen considerable development of the "interrupted" version of the thermal Nazarov reaction,[1] in which the intermediate oxyallyl cation is intercepted by a nucleophile or by further cyclization.[2] Among the most synthetically attractive modes of interception has been (4 + 3) cycloaddition.[3,4] We have shown that allenyl vinyl ketones (AVKs), e.g., **1**, are well suited as substrates for interrupted Nazarov reactions.[5−8] While the cationic intermediates (e.g., **2**) from the reactions of AVKs did react readily with acyclic dienes with a high degree of regio- and stereoselectivity, the products were often mixtures from (4 + 3) and (3 + 2) cycloaddition processes. For instance, products **3** and **4** in Scheme 1 were

Scheme 1. Nazarov Reaction of AVK 1 in the Presence of *trans*-Piperylene[6]



obtained in a ratio of 1:2.7 favoring the (3 + 2) product. Isoprene and 2,3-dimethylbutadiene both intercepted the oxyallyl cation **2** exclusively by (4 + 3) cycloaddition, although the regioselectivity with isoprene was modest (2.8:1).[6] Complete substitution of a terminus led to products that were almost exclusively the result of (3 + 2) cycloaddition.[6,8] Computational results indicated that the annular sp^2 carbon on the terminus of the π-system is the most electrophilic in oxyallyl cation **2** (with the asterisk in Scheme 1),[7] which was consistent with the regioselectivity observed in the trapping reactions.

Although a strong π-donor on the diene would be expected to control the regioselectivity of cycloaddition to the oxyallyl cation **2**, how electron donation would influence the (3 + 2) versus (4 + 3) selectivity was not known. A previous attempt to intercept the Nazarov reaction of AVK **1** with Danishefsky's diene had given only the product of Diels−Alder addition to the AVK.[6] Thus, butadiene derivatives substituted by only one oxygen function (at the 2-position) were evaluated for trapping the Nazarov reaction of an AVK. The results reported here provide valuable insights for synthesis and may contribute to a better mechanistic understanding of these complex cyclizations.

RESULTS AND DISCUSSION

The Nazarov reaction of AVK **1** in the presence of 2-[(trimethylsilyl)oxy]-1,3-butadiene[9] (**5**) was mediated by BF_3·Et_2O. The product arose regioselectively and with high facial selectivity by a tandem Nazarov/(4 + 3) cycloaddition process, but after purification on silica gel much of the material was desilylated, and so both **6** and **7** were obtained (Scheme 2). The products of the Nazarov reactions in the presence of dienes **8** and **9** were also considerably desilylated. TLC analysis of the crude reaction mixtures, before workup and chromatography, indicated the presence of both the silyl enol ethers and the ketones. Thus, some desilylation appeared to be occurring under the reaction conditions. Nevertheless, the only Nazarov products that were obtained had undergone (4 + 3) cycloaddition with the diene, and the regioselectivity was controlled completely by the silyloxy group. There were notable differences between the results with dienes **8** and **9**. The yield of (4 + 3) products (**10** + **11**) from diene **8** was only 26%, but the stereoselectivity at the methyl-bearing stereocenter was high. The methyl group (R_1) was "down" as drawn in Scheme 2,[10] and compound **12** was also isolated. With diene **9** the combined yield of Nazarov product (**13a,b** + **14a,b**) was

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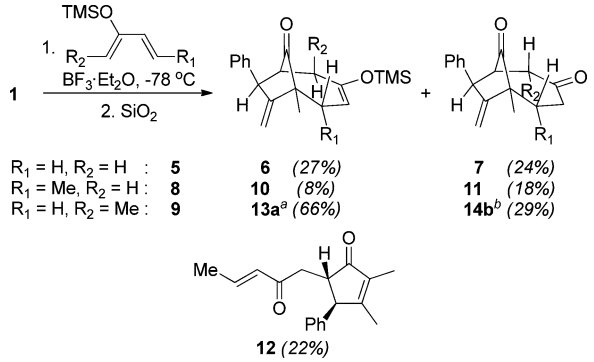
Scheme 2. Tandem Nazarov/(4 + 3) Cycloadditions of AVK 1 in the Presence of Dienes 5, 8, and 9



[a]A 5:1 ratio of methyl epimers (**13a,b**); the major epimer (**13a**) is shown. [b]A 1:1.2 ratio of methyl epimers (**14a,b**); the major epimer (**14b**) is shown.

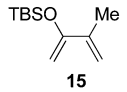
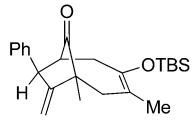
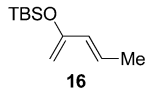
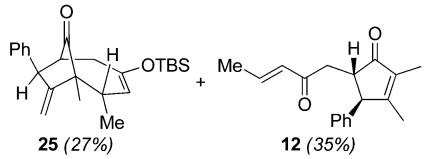
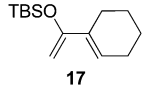
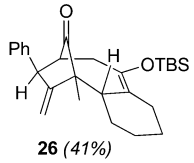
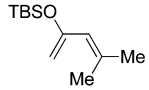
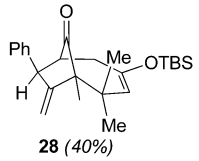
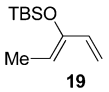
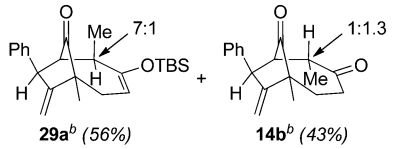
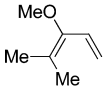
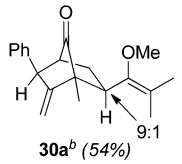
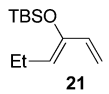
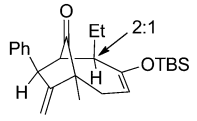
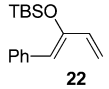
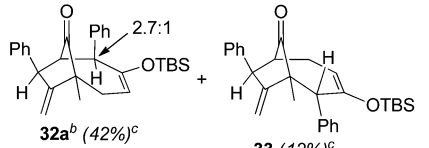
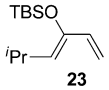
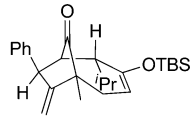
95%, but the stereoselectivity was modest at the methyl-bearing center. The methyl group (R_2) in the major epimer **13a** was "up" as drawn in Scheme 2, but the hydrolyzed product had almost equal amounts of the epimers **14a** and **14b**.

Desilylation or hydrolysis of the products from dienes **5**, **8**, and **9** had presented problems with analysis, and so dienes **15**–**23** with more robust TBS ether groups were prepared.[11] BF_3·Et_2O-mediated Nazarov reactions of AVK **1** were carried out in the presence of these dienes (Table 1). The dienes themselves, particularly those that were unsubstituted at C-1,[12] degraded quite rapidly under the reaction conditions. Cycloaddition occurred exclusively onto the face of **2** opposite the phenyl group, and the oxygen function controlled the regioselectivity. The terminus to which the oxygen donated its electron density bonded to the most electrophilic carbon of **2**, but there were two exceptional cases. In diene **20** the more electron-rich terminus (C-1) was completely substituted, and this diene trapped **2** by (3 + 2) cycloaddition to give **30a,b**. With diene **22** it appeared that the cation-stabilizing ability of the phenyl substituent competed with the oxygen function, and the (4 + 3) product **32a,b** was accompanied by a lesser amount of **33** with the regiochemistry reversed.

Dienes **16** and **17**, which bore substitution at C-4 in an *E*-geometry, with AVK **1** gave (4 + 3) products **25** and **26** very largely as one diastereomer. The structure of **25** was confirmed by X-ray crystallography. This stereoselectivity mirrored the selectivity that had been observed with the dienes without oxygen functions.[6,8] The high degree of stereoselectivity in the reactions with **16** and **17** was in contrast with examples in the literature[4a,13,14] of modest stereoselectivity in the (4 + 3) cycloadditions to oxyallyl cations. The yield of **25** was modest, but it was accompanied by a greater amount of **12**.[15] It is noteworthy that diene **18** gave the (4 + 3) product **28**. Similar dienes without the oxygen function had trapped **2** exclusively by (3 + 2) cycloaddition,[6,8] and, although the cycloadditions of **16** and **17** were highly stereoselective, **28** bore methyl groups in both the "up" and "down" orientations.

Diene **19**, just like diene **9**, provided (4 + 3) products **29a,b** and **14a,b** in a very high combined yield from AVK **1**. However, once again, desilylation was facile and the major epimer **14b** had its methyl group "down". It is likely that the stereoselectivity of the cycloaddition was modest. Other C-1-substituted dienes **21** and **22** gave (4 + 3) products **31a,b** and **32a,b** with the epimeric substituents mainly "up", and it

Table 1. Products of the Tandem Nazarov/Cycloadditions of AVK 1 in the Presence of Dienes 15–23[a]

diene	products[a]
 **15**	 **24** *(35%)*
 **16**	 **25** *(27%)* **12** *(35%)*
 **17**	 **26** *(41%)*
 **18**	 **28** *(40%)*
 **19**	 **29a**[b] *(56%)* **14b**[b] *(43%)*
 **20**	 **30a**[b] *(54%)*
 **21**	 **31a**[b] *(34%)*
 **22**	 **32a**[b] *(42%)*[c] **33** *(12%)*[c]
 **23**	 **34** *(38%)*

[a]Reaction conditions: BF_3·Et_2O (1.1 equiv), diene (5 equiv), in CH_2Cl_2, −78 °C, 5 min; chromatography over silica gel. [b]Obtained as a mixture of epimers (**a**, **b**) at the indicated carbon. The major epimer is the one shown. The ratios of the epimers did not alter significantly during purification. [c]Yields were estimated. The product was obtained in two fractions. The first fraction (33%) was **32a**, and the second (21%) was a 1:1.3 mixture of **32b** and **33**, respectively.

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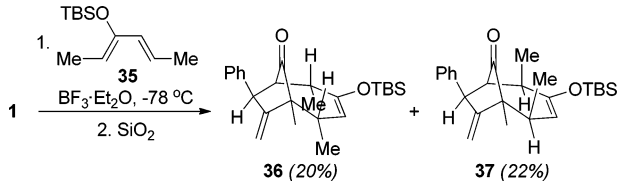
was interesting that in the minor product **33** the phenyl group was "down" as in **25** and **26**. However, diene **23** with a bulkier isopropyl substituent gave only **34**, with the substituent "down". The structure of **34** was verified by X-ray crystallography.

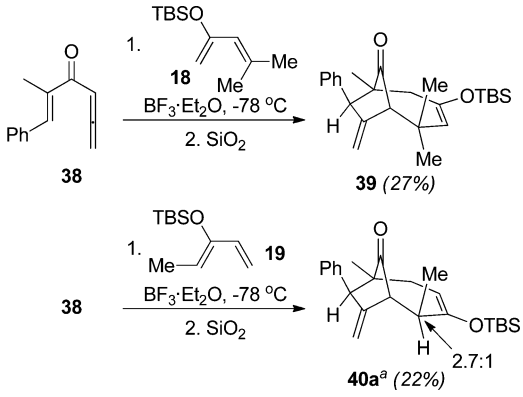
AVK **1** and $BF_3{\cdot}Et_2O$ were added to a mixture of 2 equiv each of **16** and **19**. The ^1H NMR spectrum of the crude product revealed a ratio of 1:3.5:8:2, respectively, for the trapped Nazarov products **25**/**12**/**29a**/**29b**. Therefore, although diene **19** gave a higher yield of tandem product compared to diene **16**, diene **19** reacted with the oxyallyl cation **2** only slightly more quickly than did diene **16**. The implication was that diene **35**, with substituents on both termini, would be subject roughly equally to the phenomena that controlled the development of stereochemistry at both C-1 and C-4. The result of trapping the Nazarov reaction of AVK **1** with **35** was the formation of almost equal amounts of the (4 + 3) products **36**, with both methyl groups "down", and **37**, with both methyl groups "up" (Scheme 3).

Scheme 3. Nazarov Reaction of AVK 1 in the Presence of Diene 35



AVKs **38** and **1** just differ in the position of the methyl group, but computations have shown that the most electrophilic carbon in the oxyallyl cation derived from **38** is on the same carbon as in **2**.[7] Nevertheless, **38** is much less stable than **1**, and lower yields were expected with **38**. (As such, the yields in Scheme 4 are over three steps: the oxidation of the alcohol to the ketone, base-induced isomerization to the AVK, and the tandem Nazarov/(4 + 3) cycloaddition.) Two reactions were carried out using **38**. Trapping its Nazarov reaction with diene **18** led to the (4 + 3) product **39**, which was in accord with the formation of **28**. Diene **19**, however, trapped the oxyallyl cation via (4 + 3) cycloaddition but with the regioselectivity reversed to give **40a**,**b**.

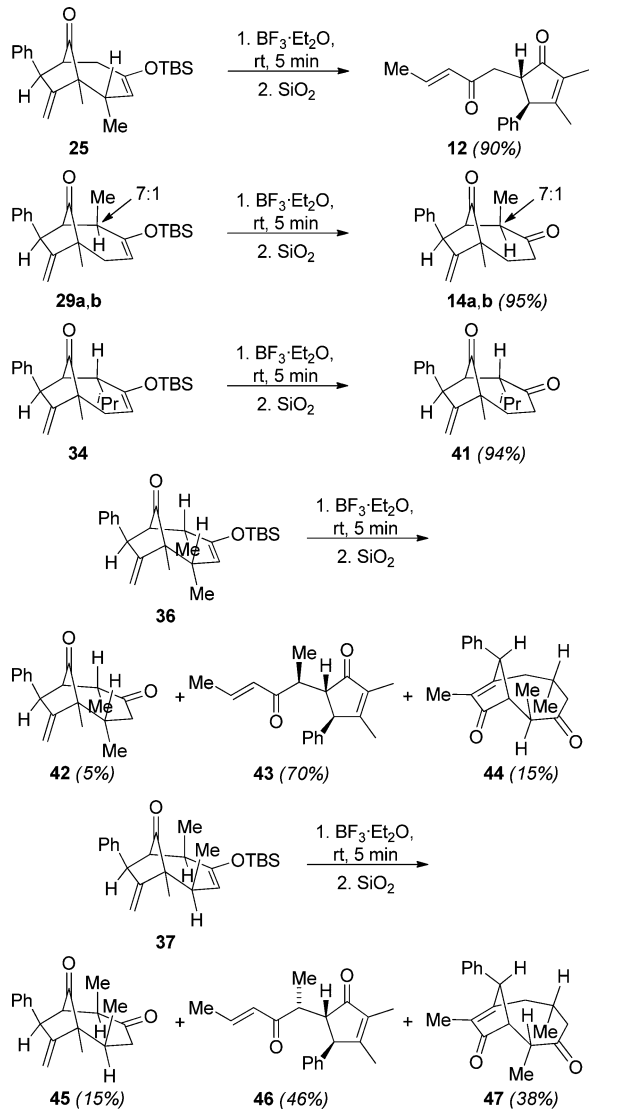
Scheme 4. Nazarov Reactions of AVK 38 in the Presence of Dienes 18 and 19



[a]Obtained as a mixture of epimers (**a**, **b**) at the indicated carbon; the major epimer (**40a**) is shown.

The appearance of **12** in the reactions of dienes **8** and **16** might be consistent with a stepwise mechanism for the (4 + 3) cycloadditions. Compound **12** would be the product if the reaction stopped after the formation of the first carbon−carbon bond, i.e., a "homologous Mukaiyama" product for which there is precedent when an oxyallyl cation is intercepted by an oxygen-substituted alkene.[6,16] However, similar compounds have been produced by the acid-mediated opening of some (3 + 2) products of unoxygenated dienes.[8,17] Thus, some (4 + 3) products from this study were treated briefly with $BF_3{\cdot}Et_2O$ at rt. The results are summarized in Scheme 5. Compound **25**, which had been initially obtained with **12**, provided the ring-opened compound **12** cleanly. Thus, the (4 + 3) product **25** has limited stability in the presence of the Lewis acid, and **12** might also have been derived from the (4 + 3) product rather than from a competing stepwise process. Obviously, the isolated yield of **25** from the original Nazarov/cycloaddition tandem process might have been reduced significantly by a

Scheme 5. Room-Temperature Treatment of (4 + 3) Cycloaddition Products with $BF_3{\cdot}Et_2O$



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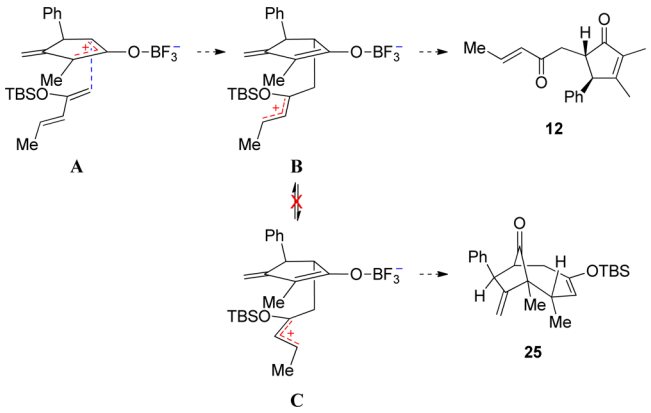
subsequent ring-opening reaction. The epimeric mixture of **29a,b** gave the desilylated products **14a,b** in very high yield, but no ring-opened product was detected. The ratio of the epimers was unaltered during desilylation, which suggested that epimerization could not have been extensive under the conditions of the initial experiments. Thus, the stereoselectivity of the (4 + 3) cycloadditions of dienes **9** and **19** was indeed modest, approximately 4:1. On the other hand, the isolated yields of (4 + 3) cycloaddition products with dienes **9** and **19** were the highest of all the dienes. Compound **34** was also desilylated without epimerization. Compounds **36** and **37** were also of limited stability in the presence of $BF_3{\cdot}Et_2O$. These compounds gave mixtures of desilylated (but not epimerized) compounds **42** and **45**, ring-opened compounds **43** and **46**, and compounds with a rearranged, bicyclo[5.2.1]decenedione framework **44** and **47**. These rearrangement products would have arisen by the same ring-opening process as the process that produced **43** and **46** but followed by reclosure onto the exocyclic double bond. This rearrangement is precedented,[6,8] but these examples show that the reclosure takes place stereoselectively forming the new chiral center with the methyl "down". In addition, these results affirm that even the rearrangement proceeds without epimerization.

The mechanism of (4 + 3) cycloaddition has been the subject of some debate.[18] The formation of (4 + 3) products can only take place with a diene in its *s-cis* conformation. A transition state **A** (illustrated with AVK **1** and diene **16** in Scheme 6)

Scheme 6. Reaction of AVK 1 with *s-trans* Diene 16



represents the initial carbon−carbon bond formation for a stepwise process with a diene in its *s-trans* conformation. This can only lead to an allylic cation **B**, but in order to cyclize to the (4 + 3) cycloaddition product **25** the allylic cation would need to isomerize to **C**.[19] This isomerization would not be feasible during the course of a 5 min reaction in an aprotic solvent at −78 °C. On the other hand, **12** and products of (3 + 2) cycloaddition could arise from **B** without isomerization. Thus, unless the initial carbon−carbon bond-forming process was reversible, reaction of the oxyallyl cation **2** with any diene in its *s-trans* conformation could not lead to a (4 + 3) cycloaddition product. Competitive reactions of *s-trans* dienes might be a significant factor in the generally modest yields of (4 + 3) cycloaddition products.

The most plausible reason why almost every diene in this study, even diene **18** for which the *s-trans* conformation would be much favored over the *s-cis*, gave a product derived from the diene in its *s-cis* conformation is that these (4 + 3) cycloadditions are concerted. The stereoselectivity and, in one instance, the regioselectivity can be explained by invoking an asynchronous transition state in which the shorter incipient bond *a* is the one from the electron-rich terminus of the diene to the most electrophilic carbon of the oxyallyl cation. Diagrams of some representative transitions states are shown in Figure 1. A concerted cycloaddition could take place via a

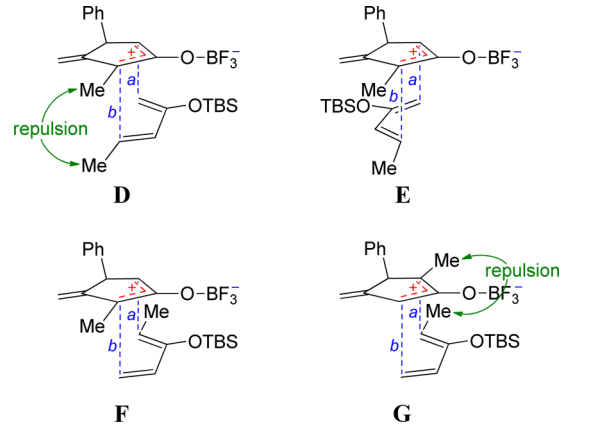


Figure 1. Representations of transition states for concerted but asynchronous (4 + 3) cycloadditions: *a* is a shorter incipient bond than *b*. **D** is a compact transition state for **2** with diene **16**; **E** is an extended transition state for **2** with diene **16**; **F** is a compact transition state for **2** with diene **19**; **G** is an unfavored (compact) transition state for the oxyallyl cation from **38** with diene **19**.

compact **D** or an extended transition state **E**, illustrated for the concerted cycloaddition of **2** with diene **16**. In this instance, the energy of **E** must be lower than of **D** since the observed (4 + 3) product was **25**, and so it is suggested that the stereoselectivity might be the result of a greater steric interaction between the methyl groups in **D** than in **E**. (Computational data would be required to corroborate this suggestion.) A steric interaction between the methyl groups in either transition state might have lowered the proportion of concerted (4 + 3) cycloaddition in favor of a stepwise reaction that would have given compound **12**. Note that the stereochemistry of the product **32** would have been controlled by a similar methyl−phenyl interaction. The oxyallyl cation **2** with diene **19** gave **29a,b** with a small stereochemical bias. In this instance, the methyl groups cannot interact sterically, and the transition state energy for the (4 + 3) cycloaddition would be lower, leading to the high yield of (4 + 3) products. In addition, the difference in the transition-state energies between the compact and the extended geometries is not large without a significant steric interaction between substituents on the termini of the diene and on the α positions of the oxyallyl cations. In fact, that **29a**, with the methyl "up", was the slightly favored isomer indicates that in the absence of significant steric interactions the compact transition state **F** is slightly favored over the extended transition state. Dienes **21** and **22** reacted with stereoselectivities as with **19**, but the result with diene **23** might have reflected a hydrogen−isopropyl interaction that was now significant at the transition state of the (4 + 3) cycloaddition that led to **34**. Why the methyl−methyl interaction is more inhibiting in **G** than in **D** is due to the asynchronous transition state, i.e., the methyls would be closer in **G** than in **D**.

The trapping of **2** with diene **35** was a process in which the methyl substituents on the diene would have acted in

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opposition. The methyl group at C-1 of the diene would have favored the compact transition state, but in this geometry the methyl group at C-4 of the diene would have inhibited a (4 + 3) cycloaddition. On the other hand, the extended transition state, which would have been disfavored by the methyl at C-1 of the diene, would be the favored geometry at C-4 of the diene. Thus, it is reasonable that the reaction took place in low yield but gave the products of the extended and the compact transition states, i.e., **36** and **37**, in essentially equal amounts.

Repositioning the α methyl group of the AVK, as in AVK **38**, led to a dramatic difference in the reactivity. In this instance, the regioselectivity was reversed, and **40a,b** was the (4 + 3) product. This is consistent with a large steric interaction between the methyl groups in transition state **G** (and in the corresponding extended transition state), but with the opposite regioselectivity there was no methyl−methyl interaction, and the approximately 3:1 ratio of epimers reflected a small bias in favor of a compact transition state.

CONCLUSIONS

The $BF_3{\cdot}Et_2O$-mediated Nazarov reaction of the AVK **1** generates a cyclic oxyallyl cation intermediate that can be intercepted by cycloaddition with an oxygen-substituted diene. Unlike interception with hydrocarbon dienes which react by (3 + 2) and (4 + 3) cycloadditions, the more electron-rich dienes used in this study give the products of (4 + 3) cycloadditions only, except when steric hindrance in the (4 + 3) process would be very high. However, several factors conspire to reduce the yields of the (4 + 3) products. The dienes themselves are unstable under the reaction conditions, the (4 + 3) products can undergo Lewis acid-mediated ring cleavage, and any reaction of the diene in its *s-trans* conformation would lead to an intermediate that cannot cyclize to the (4 + 3) product.

In spite of the generally modest yields, some important features of these (4 + 3) cycloadditions have been revealed. The regioselectivity is generally very high, with the more electron-rich terminus of the diene reacting with the more electrophilic carbon of the oxyallyl cation. The (4 + 3) cycloaddition is a concerted reaction, with the compact transition state having a somewhat lower energy barrier than that of the extended transition state. This leads in some instances to poor stereoselectivity. However, steric interactions can influence this selectivity and examples of high selectivity are now known. A computational study related to (4 + 3) cycloaddition is now underway in our laboratories.

EXPERIMENTAL SECTION

General Considerations. Reactions were carried out using oven-dried Teflon-coated magnetic stir bars in oven-dried glassware (150 °C), sealed with rubber septa under a positive nitrogen atmosphere. Elevated temperatures were maintained using a silicone oil bath controlled with a thermostat device. Temperatures of 0 and −78 °C were achieved using ice/water and ethyl acetate/liquid nitrogen, respectively. Concentration in vacuo was achieved using a rotary evaporator (22 mmHg) with residual solvent being removed under high vacuum (5 mmHg). Commercially available reagents were used without further purification. Tetrahydrofuran (THF) was distilled over sodium benzophenone under a dry nitrogen atmosphere. CH_2Cl_2 was distilled over calcium hydride under a dry nitrogen atmosphere. Thin-layer chromatography (TLC) was performed using 250 μm aluminum-backed F_{254} silica gel plates. The plates were visualized by ultraviolet light (254 nm) and treated with *o*-vanillin or potassium permanganate stains followed by heating on a hot plate. Flash chromatography was carried out on 230−400 mesh (40−63 μm) silica gel.

Melting points (uncorrected) were acquired using a Fisher-Johns apparatus. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the solvent peak (for $CDCl_3$, ^{1}H NMR: 7.26 ppm, ^{13}C NMR: 77.16 ppm). Positive-ion high-resolution mass spectra (HRMS) were obtained using APCI or ESI on a TOF mass spectrometer. Infrared (IR) spectra were recorded on an FT instrument. Samples were prepared as thin films on a NaCl plate. Structures were determined using ^{1}H and ^{13}C NMR spectra, including two- dimensional NMR experiments (COSY, HSQC and HMBC). Relative stereochemistry was assigned using one-dimensional NOE experiments.[20]

Procedure for Dienes 5, 8, and 9. On the basis of the work by Jung and McCombs,[9] a solution of α,β-unsaturated ketone (50 mmol) in anhydrous DMF (3.5 mL) and a solution of Me_3SiCl (62 mmol) in DMF (3.5 mL) were both added dropwise over a period of 30 min to a heated (84 °C) solution of Et_3N (62 mmol) in DMF (30 mL). Heating was continued overnight (14 h). The solution was then allowed to attain rt before workup. The solution was diluted with pentane (50 mL) and washed with cold 5% aqueous $NaHCO_3$ (150 mL). The aqueous layer was re-extracted with pentane (2 × 50 mL), and the combined organic extracts were washed with distilled water (50 mL), dried over Na_2SO_4, and concentrated under vacuum. The residue was distilled under reduced pressure.

*2-[(Trimethylsilyl)oxy]-1,3-butadiene (**5**).* 3-Buten-2-one (4.1 mL, 50 mmol), Me_3SiCl (7.9 mL, 62 mmol), and Et_3N (8.6 mL, 62 mmol) gave **5** (2.6 g, 37%) as a colorless liquid: bp 33−35 °C (22 mmHg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (dd, J = 16.9, 10.5 Hz, 1H), 5.47 (dd, J = 16.9, 1.5 Hz, 1H), 5.08 (br d, J = 10.5 Hz, 1H), 4.35 (s, 1H), 4.34 (s, 1H), 0.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.9, 134.6, 114.6, 96.5, 0.7 (3C). These data match those in the literature.[9]

*(E)-2-[(Trimethylsilyl)oxy]-1,3-pentadiene (**8**).* 3-Penten-2-one (4.9 mL, 50 mmol), Me_3SiCl (7.9 mL, 62 mmol), and Et_3N (8.6 mL, 62 mmol) gave **8** (3.3 g, 42%) as a colorless liquid: bp 36−37 °C (22 mmHg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96 (dq, J = 15.1, 6.4 Hz, 1H), 5.90 (d, J = 15.3 Hz, 1H), 4.20 (s, 2H), 1.76 (d, J = 6.4 Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 129.1 126.7, 93.8, 17.7, 0.2 (3C). These data match those in the literature.[21]

*(Z)-3-[(Trimethylsilyl)oxy]-1,3-pentadiene (**9**).* 1-Penten-3-one (4.9 mL, 50 mmol), Me_3SiCl (7.9 mL, 62 mmol), and Et_3N (8.6 mL, 62 mmol) gave **9** (1.7 g, 21%) as a colorless liquid: bp 41−42 °C (22 mmHg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.17 (dd, J = 17.1, 10.6 Hz, 1H), 5.24 (br d, J = 17.0 Hz, 1H), 4.93 (br d, J = 10.1 Hz, 1H), 4.87 (q, J = 7.0 Hz, 1H), 1.64 (d, J = 7.0 Hz, 3H), 0.21 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 135.6, 111.5, 110.4, 11.7, 0.8 (3C). These data match those in the literature.[22]

Procedure for Dienes 15−19. On the basis of the work of Jung and Nishimura,[11] a solution of α,β-unsaturated ketone (10 mmol) in THF (40 mL) was cooled to 0 °C. Et_3N (25 mmol) was added, followed by the slow addition of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) (11 mmol). The solution was stirred at 0 °C until the reaction was complete, as evidenced by TLC. The solution was then diluted with pentane (80 mL) and washed with saturated aqueous $NaHCO_3$ (25 mL), water (2 × 25 mL), and brine (25 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography (2% Et_3N in pentane).

*2-[(tert-Butyldimethylsilyl)oxy]-3-methyl-1,3-butadiene (**15**).* 3-Methyl-3-buten-2-one (1.0 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and Et_3N (3.5 mL, 25 mmol) were stirred for 1 h at 0 °C to give **15** (0.34 g, 17%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.43 (narrow m, 1H), 4.96 (narrow m, 1H), 4.47 (narrow m, 1H), 4.32 (narrow m, 1H), 1.87 (s, 3H), 0.97 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 140.0, 113.8, 92.9, 26.0 (3C), 19.8, 18.4, −4.6 (2C). These data match those in the literature.[23]

*(E)-2-[(tert-Butyldimethylsilyl)oxy]-1,3-pentadiene (**16**).* 3-Penten-2-one (0.98 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and Et_3N (3.5 mL, 25 mmol) were stirred for 1 h at 0 °C to give **16** (1.50 g, 73%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00 (dq, J = 15.1, 6.7 Hz, 1H), 5.89 (dq, J = 15.1, 1.5 Hz, 1H), 4.19 (s, 1H), 4.18 (s, 1H), 1.77−1.75 (m, 3H), 0.97 (s, 9H), 0.17 (s, 6H); ^{13}C NMR

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(126 MHz, $CDCl_3$) δ 155.2, 129.3, 126.5, 93.6, 26.0 (3C), 18.4, 17.8, −4.5 (2C). These data match those in the literature.[11]

*1-[(tert-Butyldimethylsilyl)oxy]-1-(1-cyclohexenyl)ethene (**17**).* 1-Acetyl-1-cyclohexene (1.3 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and Et_3N (3.5 mL, 25 mmol) were stirred for 2 h at 0 °C to give **17** (2.15 g, 90%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.26−6.24 (narrow m, 1H), 4.34 (s, 1H), 4.18 (s, 1H), 2.14−2.12 (narrow m, 4H), 1.68−1.57 (m, 4H), 0.97 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 133.3, 125.5, 89.6, 26.0 (3C), 25.6, 25.1, 22.9, 22.3, 18.5, −4.5 (2C). These data match those in the literature.[11]

*2-[(tert-Butyldimethylsilyl)oxy]-4-methyl-1,3-pentadiene (**18**).* 4-Methyl-3-penten-2-one (1.1 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and Et_3N (3.5 mL, 25 mmol) were stirred for 1 h at 0 °C to give **18** (1.95 g, 90%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (s, 1H), 4.30 (s, 1H), 4.16 (s, 1H), 1.89 (s, 3H), 1.77 (s, 3H), 0.94 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8, 136.8, 123.3, 95.0, 27.1, 26.0 (3C), 20.0, 18.5, −4.3 (2C). These data match those in the literature.[24]

*(Z)-3-[(tert-Butyldimethylsilyl)oxy]-1,3-pentadiene (**19**).* 1-Penten-3-one (1.0 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and Et_3N (3.5 mL, 25 mmol) were stirred for 1 h at 0 °C to give **19** (1.16 g, 59%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 (dd, J = 17.1, 10.8 Hz, 1H), 5.27 (d, J = 17.1 Hz, 1H), 4.94 (d, J = 10.8 Hz, 1H), 4.87 (q, J = 7.1 Hz, 1H), 1.64 (d, J = 7.1 Hz, 3H), 1.01 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 135.7, 111.8, 110.3, 25.9 (3C), 18.3, 12.0, −2.8, −3.5. These data match those in the literature.[25]

Procedure for 3-Methoxy-4-methyl-1,3-pentadiene (20). A solution of dimethyl 1-methoxyallylphosphonate (1.7 g, 9.6 mmol) in THF (5 mL) was added to a solution of LDA (11.5 mmol) in THF (20 mL) at −78 °C and the mixture stirred for 30 min. A solution of acetone (0.74 mL, 9.6 mmol) in THF (5 mL) was added to the mixture. The mixture was allowed to warm slowly to rt over 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (25 mL), and the mixture was extracted with Et_2O (25 mL). The organic layer was washed with brine (25 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography (10% Et_2O in pentane) to give **20** (0.30 g, 28%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.46 (dd, J = 17.1, 10.8 Hz, 1H), 5.33 (d, J = 17.0 Hz, 1H), 5.04 (dd, J = 10.8, 0.4 Hz, 1H), 3.52 (s, 3H), 1.77 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 127.9, 122.0, 112.3, 59.0, 18.5, 18.0. These data match those in the literature.[26]

Procedure for Dienes 21−23 and 35. On the basis of the work by Carreño et al.,[25] a solution of α,β-unsaturated ketone (10 mmol) and TBSOTf (11 mmol) in THF (80 mL) was cooled to −78 °C. A 1 M solution of potassium bis(trimethylsilyl)amide ($KN(SiMe_3)_2$) in THF (10 mmol) was slowly added. The solution was stirred at −78 °C for 30 min and then allowed to warm to rt with stirring for 1 h. Saturated aqueous $NaHCO_3$ (80 mL) was added, and the mixture was extracted with Et_2O (80 mL). The organic solution was washed with brine (80 mL), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography (2% Et_3N in pentane).

*(Z)-3-[(tert-Butyldimethylsilyl)oxy]-1,3-hexadiene (**21**).* 1-Hexen-3-one (1.2 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and $KN(SiMe_3)_2$ (10 mL, 10 mmol) gave **21** (1.59 g, 75%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.14 (dd, J = 17.2, 10.8 Hz, 1H), 5.28 (dd, J = 17.1, 1.0 Hz, 1H), 4.94 (dd, J = 10.8, 0.8 Hz, 1H), 4.76 (t, J = 7.2 Hz, 1H), 2.12 (quintet, J = 7.4 Hz, 2H), 1.00 (s, 9H), 0.96 (t, J = 7.5 Hz, 3H), 0.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 135.9, 118.0, 112.0, 26.2 (3C), 19.5, 18.6, 14.2, −3.5 (2C); IR (thin film) 1255, 1050, 839, 780 cm^{-1}; HRMS (APCI) calcd for $[C_{12}H_{25}OSi]^+$ 213.1669, found 213.1663.

*2-[(tert-Butyldimethylsilyl)oxy]-1-phenyl-1,3-butadiene (**22**).* 1-Phenylbut-3-en-2-one[27] (1.46 g, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and $KN(SiMe_3)_2$ (10 mL, 10 mmol) gave a 1:1 mixture of *E*:*Z* isomers of **22**[28] (1.30 g, 50%) as a colorless liquid. For the *Z*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 6.31 (dd, J = 17.1, 10.7 Hz, 1H), 5.78 (s, 1H), 5.48 (d, J = 17.1 Hz, 1H), 5.13 (d, J = 10.7 Hz, 1H), 0.99 (s, 9H), −0.12 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 136.5, 136.3, 129.3 (2C), 128.0 (2C), 126.4, 114.6, 114.5, 26.1 (3C), 18.5, −3.6 (2C). For the *E*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.17 (m, 5H), 6.68 (dd, J = 16.9, 10.7 Hz, 1H), 6.01 (s, 1H), 5.67 (d, J = 16.9 Hz, 1H), 5.18 (d, J = 10.7 Hz, 1H), 1.01 (s, 9H), 0.23 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 136.6, 131.2, 129.4 (2C), 128.3 (2C), 126.3, 116.5, 113.8, 26.1 (3C), 18.6, −4.2 (2C). For the mixture of isomers: IR (thin film) 1630, 1472, 1362, 1254, 1085, 839, 781 cm^{-1}; HRMS (ESI) calcd for $[C_{16}H_{25}OSi]^+$ 261.1669, found 261.1680.

*(Z)-3-[(tert-Butyldimethylsilyl)oxy]-5-methyl-1,3-hexadiene (**23**).* 5-Methylhex-1-en-3-one[29] (1.12 g, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and $KN(SiMe_3)_2$ (10 mL, 10 mmol) gave **23** (2.08 g, 92%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10 (dd, J = 17.1, 10.8 Hz, 1H), 5.26 (d, J = 17.1 Hz, 1H), 4.93 (d, J = 10.8 Hz, 1H), 4.60 (d, J = 9.7 Hz, 1H), 2.75−2.65 (m, 1H), 0.98 (s, 9H), 0.94 (d, J = 7.3 Hz, 6H), 0.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 136.1, 123.5, 112.2, 26.2 (3C), 25.1, 23.1 (2C), 18.6, −3.6 (2C); IR (thin film): 1253, 1053, 844 cm^{-1}; HRMS (ESI) calcd for $[C_{13}H_{26}OSiNa]^+$ 249.1645, found 249.1653.

*(2Z,4E)-3-[(tert-Butyldimethylsilyl)oxy]-2,4-hexadiene (**35**).* 4-Hexen-3-one (1.1 mL, 10 mmol), TBSOTf (2.5 mL, 11 mmol), and $KN(SiMe_3)_2$ (10 mL, 10 mmol) gave **35** (1.06 g, 50%) as a colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 (br d, J = 15.4, 1H), 5.74 (dq, J = 15.4, 6.6 Hz, 1H), 4.72 (q, J = 7.0 Hz, 1H), 1.73 (d, J = 6.6 Hz, 3H), 1.61 (d, J = 7.0 Hz, 3H), 1.00 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 130.0, 123.5, 107.1, 26.1 (3C), 18.6, 17.8, 11.8, −3.5 (2C); IR (thin film) 1255, 1073, 837 cm^{-1}; HRMS (ESI) calcd for $[C_{12}H_{25}OSi]^+$ 213.1669, found 213.1667.

Procedure for Compounds 6, 7, 10−14, 24−34, and 36−40. $BF_3{\cdot}OEt_2$ (0.44 mmol) was added to a solution of the allenyl vinyl ketone[5a,7] (0.40 mmol) and the diene (2.0 mmol) in CH_2Cl_2 (40 mL) at −78 °C. The solution was stirred for 5 min, and then saturated aqueous $NaHCO_3$ (40 mL) was added at −78 °C. After the solution was warmed to rt, the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic solutions were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (5% Et_2O in pentane).

(1R,6S*,7S*)-1-Methyl-8-methylene-7-phenyl-4-[(trimethylsilyl)-oxy]bicyclo[4.2.1]non-3-en-9-one (**6**) and (1R*,6S*,7S*)-1-Methyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione (**7**).* AVK **1** (70 mg, 0.40 mmol), **5** (0.28 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **6** (35 mg, 27%) and **7** (24 mg, 24%) as colorless oils. For **6**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.26 (m, 2H), 7.19 (tt, J = 7.4, 1.5 Hz, 1H), 7.04−7.02 (m, 2H), 5.09 (d, J = 2.4 Hz, 1H), 4.96 (dt, J = 7.4, 2.5 Hz, 1H), 4.86 (d, J = 2.1 Hz, 1H), 3.80 (q, J = 2.1 Hz, 1H), 2.70−2.68 (m, 1H), 2.57−2.52 (m, 1H), 2.38−2.30 (m, 2H), 2.15 (dd, J = 15.8, 7.4 Hz, 1H), 1.30 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.0, 157.7, 149.1, 146.3, 128.9 (2C), 127.5 (2C), 126.6, 110.0, 106.9, 54.7, 53.5, 52.0, 42.6, 37.3, 21.2, 0.5 (3C); IR (thin film) 1750 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{26}O_2SiNa]^+$ 349.1594, found 349.1581. For **7**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.07 (d, J = 7.4 Hz, 2H), 5.25 (d, J = 1.9 Hz, 1H), 5.12 (d, J = 1.7 Hz, 1H), 3.87 (q, J = 1.8 Hz, 1H), 2.86−2.84 (m 1H), 2.78 (dd, J = 15.1, 5.8 Hz, 1H), 2.68−2.62 (m, 1H), 2.60−2.52 (m, 2H), 1.95−1.90 (m, 1H), 1.87−1.82 (m, 1H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.2, 209.4, 156.1, 145.0, 129.1 (2C), 127.1 (2C), 127.0, 113.0, 54.0, 53.0, 51.3, 45.5, 41.3, 40.0, 22.3; IR (thin film) 1743, 1704 cm^{-1}; HRMS (ESI) calcd for $[C_{17}H_{18}O_2Na]^+$ 277.1199, found 277.1196.

(1R,2R*,6S*,7S*)-1,2-Dimethyl-8-methylene-7-phenyl-4-[(trimethylsilyl)oxy]bicyclo[4.2.1]non-3-en-9-one (**10**), (1R*,2R*,6S*,7S*)-1,2-Dimethyl-8-methylene-7-phenylbicyclo-[4.2.1]nonane-4,9-dione (**11**), and (4R*,5R*)-2,3-Dimethyl-5-((E)-2-oxopent-3-en-1-yl)-4-phenylcyclopent-2-enone (**12**).* AVK **1** (70 mg, 0.40 mmol), **8** (0.31 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **10** (11 mg, 8%), **11** (19 mg, 18%), and **12** (24 mg, 22%) as colorless oils. For **10**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.27 (m, 2H), 7.23−7.20 (m, 1H), 7.08−7.06 (m, 2H), 5.00 (d, J = 2.9 Hz,

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1H), 4.79−4.78 (m, 2H), 3.71 (q, J = 3.2 Hz, 1H), 2.65 (q, J = 4.2 Hz, 1H), 2.62−2.58 (m, 1H), 2.38−2.32 (m, 2H), 1.24 (s, 3H), 1.07 (d, J = 7.1 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.8, 154.2, 147.2, 145.6, 128.9 (2C), 128.2 (2C), 126.7, 115.5, 112.5, 58.4, 53.3, 52.2, 40.8, 37.8, 19.5, 17.7, 0.5 (3C); IR (thin film) 1747 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{28}O_2SiNa]^+$ 363.1751, found 363.1754. For **11**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32−7.28 (m, 2H), 7.25−7.21 (m, 1H), 7.07−7.05 (m, 2H), 5.16 (d, J = 2.8 Hz, 1H), 5.05 (d, J = 2.4 Hz, 1H), 3.87 (q, J = 2.7 Hz, 1H), 2.85−2.78 (m, 2H), 2.61−2.51 (m, 3H), 1.26 (s, 3H), 1.04 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz $CDCl_3$) δ 220.7, 208.5, 152.8, 146.0, 129.1 (2C), 127.7 (2C), 127.0, 115.4, 58.1, 54.0, 51.5, 50.4, 46.2, 40.7, 19.9, 16.2; IR (thin film) 1744, 1712 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{20}O_2Na]^+$ 291.1356, found 291.1348. For **12**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.3 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.6 Hz, 2H), 6.82 (dq, J = 15.5, 6.9 Hz, 1H), 6.08 (d, J = 15.8 Hz, 1H), 3.56 (s, 1H), 3.04 (dd, J = 16.9, 3.7 Hz, 1H), 2.80 (dd, J = 16.9, 7.8 Hz, 1H), 2.58 (t, J = 3.9 Hz, 1H), 1.86 (d, J = 6.8 Hz, 3H), 1.82 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 198.1, 169.8, 143.3, 141.6, 136.4, 131.6, 129.0 (2C), 127.9 (2C), 127.2, 56.0, 51.9, 40.3, 18.4, 15.6, 8.6; IR (thin film): 1700, 1648 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{20}O_2Na]^+$ 291.1356, found 291.1352.

(1R,5S*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenyl-4-[(trimethylsilyl)oxy]bicyclo[4.2.1]non-3-en-9-one* (**13a**), *(1R*,5R*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenyl-4-[(trimethylsilyl)oxy]bicyclo[4.2.1]non-3-en-9-one* (**13b**), *(1R*,5S*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenylbicyclo-[4.2.1]nonane-4,9-dione* (**14a**), *and (1R*,5R*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione* (**14b**). AVK **1** (70 mg, 0.40 mmol), **9** (0.31 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave a 5:1 mixture of **13a** and **13b** (89 mg, 66%) and a 1:1.2 mixture of **14a** and **14b** (31 mg, 29%) as colorless oils. For **13a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 5.13 (d, J = 2.0 Hz, 1H), 4.90 (d, J = 1.2 Hz, 1H), 4.85 (dd, J = 7.7, 1.9 Hz, 1H), 3.80 (s, 1H), 2.54−2.52 (m, 2H), 2.33 (d, J = 16.0 Hz, 1H), 2.13 (dd, J = 15.9, 7.7 Hz, 1H), 1.32 (s, 3H), 1.20 (d, J = 6.4 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.7, 157.5, 154.2, 146.6, 128.9 (2C), 127.4 (2C), 126.5, 109.8, 104.4, 59.7, 54.2, 53.0, 42.9, 41.6, 21.2, 17.6, 0.7 (3C). For **13b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 7.8 Hz, 2H), 5.09 (d, J = 2.4 Hz, 1H), 4.98−4.97 (m, 1H), 4.76 (d, J = 1.7 Hz, 1H), 3.93 (d, J = 2.5 Hz, 1H), 2.72−2.71 (m, 1H), 2.64 (t, J = 3.3 Hz, 1H), 2.31−2.28 (m, 1H), 2.20−2.15 (m, 1H), 1.34 (s, 3H), 1.23 (d, J = 7.2 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.4, 158.4, 151.6, 146.5, 128.9 (2C), 128.0 (2C), 126.4, 109.4, 106.2, 60.8, 54.9, 48.6, 42.0, 39.4, 20.1, 17.5, 0.4 (3C). For **13a** and **13b**: IR (thin film) 1741 cm^{-1}; HRMS (ESI) calcd for $[C_{21}H_{28}O_2SiNa]^+$ 363.1751, found 363.1747. For **14a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2H), 7.23−7.18 (m, 1H), 7.07−7.04 (m, 2H), 5.22 (d, J = 2.2 Hz, 1H), 5.08 (d, J = 2.0 Hz, 1H), 3.96 (q, J = 2.1 Hz, 1H), 2.69−2.50 (m, 4H), 1.98−1.80 (m, 2H), 1.27 (s, 3H), 1.25 (d, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.8, 211.6, 156.2, 145.4, 129.1 (2C), 127.1 (2C), 126.9, 112.5, 58.3, 54.4, 54.2, 50.4, 40.6, 38.8, 22.1, 16.5. For **14b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2H), 7.23−7.18 (m, 1H), 7.07−7.04 (m, 2H), 5.21 (d, J = 2.2 Hz, 1H), 5.00 (d, J = 1.9 Hz, 1H), 3.81 (q, J = 2.1 Hz, 1H), 2.90 (qd, J = 6.8, 4.6 Hz, 1H), 2.69−2.50 (m, 3H), 1.98−1.80 (m, 2H), 1.31 (s, 3H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.0, 211.2, 156.6, 145.1, 129.0 (2C), 127.3 (2C), 126.8, 112.7, 57.9, 53.2, 47.1, 46.9, 40.7, 40.5, 22.5, 13.9. For **14a** and **14b**: IR (thin film) 1743, 1745, 1711, 1709 cm^{-1}; HRMS (ESI) calcd for $[C_{18}H_{20}O_2Na]^+$ 291.1356, found 291.1346.

(1R,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,3-dimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one* (**24**). AVK **1** (70 mg, 0.40 mmol), **15** (0.40 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **24** (54 mg, 35%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.25 (m, 2H), 7.20−7.17 (m, 1H), 7.03−7.01 (m, 2H), 5.08 (d, J = 2.4 Hz, 1H), 4.85 (d, J = 2.1 Hz, 1H), 3.80 (q, J = 2.0 Hz, 1H), 2.66−2.59 (m, 2H), 2.46 (dd, J = 16.4, 5.7 Hz, 1H), 2.40 (br d, J = 15.6 Hz, 1H), 2.04 (d, J = 15.6 Hz, 1H), 1.64 (br s, 3H), 1.28 (s, 3H), 0.96 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.5, 157.2, 146.3, 142.3, 128.9 (2C), 127.4 (2C), 126.5, 113.9, 109.7, 54.1, 53.8, 51.5, 38.7, 26.1 (3C), 21.0, 20.9, 18.4, −3.4, −3.6; IR (thin film): 1737 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{34}O_2SiNa]^+$ 405.2220, found 405.2229.

(1R,2R*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,2-dimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one* (**25**) *and (4R*,5R*)-2,3-Dimethyl-5-((E)-2-oxopent-3-en-1-yl)-4-phenylcyclopent-2-enone* (**12**). AVK **1** (70 mg, 0.40 mmol), **16** (0.40 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) were stirred for 5 min at −78 °C to give **25** (41 mg, 27%) as a colorless solid and **12** (37 mg, 35%) as a colorless oil. For **25**: mp 93−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.28 (m, 2H), 7.23−7.20 (m, 1H), 7.09−7.07 (m, 2H), 4.99 (d, J = 2.9 Hz, 1H), 4.79 (d, J = 2.5 Hz, 1H), 4.78 (t, J = 2.5 Hz, 1H), 3.72 (q, J = 3.2 Hz, 1H), 2.66 (q, J = 4.2 Hz, 1H), 2.63−2.58 (m, 1H), 2.38−2.32 (m, 2H), 1.24 (s, 3H), 1.08 (d, J = 7.1 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.6, 154.2, 147.4, 145.5, 128.8 (2C), 128.2 (2C), 126.6, 115.1, 112.4, 58.4, 53.1, 52.2, 40.9, 37.7, 25.8 (3C), 19.5, 18.1, 17.7, −4.1, −4.3; IR (thin film) 1734 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{34}O_2SiNa]^+$ 405.2220, found 405.2204.

(1R,2R*,10S*,11S*)-8-[(tert-Butyldimethylsilyl)oxy]-1-methyl-12-methylene-11-phenyltricyclo[8.*^{2,7}*2.1]tridec-7-en-13-one* (**26**). AVK **1** (70 mg, 0.40 mmol), **17** (0.48 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **26** (69 mg, 41%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.25 (m, 2H), 7.19−7.17 (m, 1H), 7.05−7.02 (m, 2H), 5.07 (d, J = 2.2 Hz, 1H), 4.90 (d, J = 2.0 Hz, 1H), 3.80 (q, J = 1.7 Hz, 1H), 3.09−3.06 (m, 1H), 2.67−2.62 (m, 2H), 2.49−2.45 (m, 1H), 2.08−2.05 (m, 2H), 1.84 (br d, J = 12.6 Hz, 1H), 1.73 (br d, J = 12.6 Hz, 1H), 1.42−1.38 (m, 2H), 1.27 (s, 3H), 1.26−1.22 (m, 1H), 1.07−0.99 (m, 1H), 0.95 (s, 9H), 0.15 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.9, 159.9, 146.5, 138.1, 128.9 (2C), 127.1 (2C), 126.5, 123.6, 109.5, 58.4, 55.4, 53.5, 52.3, 38.4, 32.6, 30.8, 28.8, 27.7, 26.1 (3C), 20.8, 18.5, −3.4, −3.5; IR (thin film) 1729 cm^{-1}; HRMS (ESI) calcd for $[C_{27}H_{39}O_2Si]^+$ 423.2714, found 423.2699.

(1R,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,2,2-trimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one* (**28**). AVK **1** (70 mg, 0.40 mmol), **18** (0.42 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **28** (63 mg, 40%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 7.8 Hz, 2H), 5.04 (d, J = 2.7 Hz, 1H), 4.85−4.82 (m, 2H), 3.75 (q, J = 2.6 Hz, 1H), 2.62−2.57 (m, 2H), 2.35 (dd, J = 17.8, 6.2 Hz, 1H), 1.22 (s, 3H), 1.12 (s, 3H), 1.01 (s, 3H), 0.93 (s, 9H), 0.16 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.9, 157.0, 146.6, 146.3, 128.8 (2C), 128.1 (2C), 126.5, 121.8, 113.3, 60.0, 53.6, 51.8, 40.6, 37.5, 26.3, 26.0, 25.9 (3C), 18.2, 17.1, −3.9, −4.3; IR (thin film) 1740 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{36}O_2SiNa]^+$ 419.2377, found 419.2369.

(1R,5S*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,5-dimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one* (**29a**), *(1R*,5R*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,5-dimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one* (**29b**), *(1R*,5S*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenylbicyclo-[4.2.1]nonane-4,9-dione* (**14a**), *and (1R*,5R*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione* (**14b**). AVK **1** (70 mg, 0.40 mmol), **19** (0.40 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave a 7:1 mixture of **29a** and **29b** (86 mg, 56%) and a 1:1.2 mixture of **14a** and **14b** (46 mg, 43%) as colorless oils. For **29a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.25 (m, 2H), 7.21−7.17 (m, 1H), 7.03−7.02 (m, 2H), 5.09 (d, J = 2.5 Hz, 1H), 4.85 (d, J = 2.1 Hz, 1H), 4.79 (dd, J = 7.6, 2.4 Hz, 1H), 3.75 (t, J = 2.1 Hz, 1H), 2.51−2.47 (m, 2H), 2.31−2.27 (m, 1H), 2.09 (dd, J = 16.0, 7.7 Hz, 1H), 1.28 (s, 3H), 1.17 (d, J = 6.8 Hz, 3H), 0.94 (s, 9H), 0.20 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.9, 157.5, 154.2, 146.5, 128.9 (2C), 127.4 (2C), 126.5, 109.8, 104.2, 59.7, 54.2, 53.0, 42.9, 41.7, 25.8 (3C), 21.2, 18.1, 17.6, −4.1, −4.2. For **29b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27−7.24 (m, 2H), 7.19−7.16 (m, 1H), 7.04−7.02 (m, 2H), 5.07 (d, J = 2.3 Hz, 1H), 5.05 (dd, J = 7.2, 2.4 Hz, 1H), 4.88 (d, J = 2.0 Hz, 1H), 3.77 (d, J = 1.8 Hz, 1H), 2.64 (dd, J = 7.8, 3.2 Hz, 1H), 2.56−2.52 (m, 1H), 2.36−2.32 (m, 1H), 2.28−2.24 (m, 1H), 1.29 (s, 3H), 0.97 (d, J = 6.9 Hz, 3H), 0.93 (s, 9H), 0.15 (s,

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3H), 0.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.3, 162.2, 159.7, 147.6, 128.9 (2C), 127.2 (2C), 126.5, 114.4, 109.7, 56.8, 53.7, 51.9, 46.4, 36.7, 25.9 (3C), 20.2, 18.2, 17.1, −4.0, −4.4. For **29a** and **29b**: IR (thin film) 1737 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{34}O_2SiNa]^+$ 405.2220, found 405.2203.

(1R,2S*,4S*,5S*)-2-(1-Methoxy-2-methylprop-1-en-1-yl)-1-methyl-6-methylene-5-phenylbicyclo[2.2.1]heptan-7-one (**30a**) and (1R*,2R*,4S*,5S*)-2-(1-Methoxy-2-methylprop-1-en-1-yl)-1-methyl-6-methylene-5-phenylbicyclo[2.2.1]heptan-7-one (**30b**).* AVK **1** (70 mg, 0.40 mmol), **20** (0.52 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave a 9:1 mixture of **30a** and **30b** (64 mg, 54%) as a colorless oil. For **30a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.1 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 5.10 (d, J = 2.0 Hz, 1H), 4.81 (s, 1H), 3.78 (s, 1H), 3.55 (s, 3H), 3.04 (dd, J = 10.3, 5.1 Hz, 1H), 2.30 (d, J = 4.7 Hz, 1H), 2.24 (dt, J = 12.4, 5.0 Hz, 1H), 1.96 (dd, J = 12.2, 10.7 Hz, 1H), 1.71 (s, 3H), 1.64 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.0, 153.3, 150.7, 143.3, 128.6 (2C), 127.5 (2C), 126.7, 117.0, 107.9, 61.3, 52.9, 51.9, 48.1, 43.4, 28.7, 19.7, 18.7, 9.4. For **30b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.8 Hz, 2H), 4.95 (d, J = 2.6 Hz, 1H), 4.77 (d, J = 2.1 Hz, 1H), 3.83 (s, 1H), 3.59 (s, 3H), 3.13 (dd, J = 10.8, 6.5 Hz, 1H), 2.17−2.08 (m, 2H), 1.95 (d, J = 10.4 Hz, 1H), 1.76 (s, 3H), 1.66 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 150.4, 149.8, 143.9, 128.7 (2C), 127.7 (2C), 126.7, 119.1, 109.6, 61.9, 55.1, 52.9, 48.2, 41.3, 28.1, 20.1, 19.3, 11.4. For **30a** and **30b**: IR (thin film) 1777, 1767 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{24}O_2Na]^+$ 319.1669, found 319.1670.

(1R,5S*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-5-ethyl-1-methyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one (**31a**) and (1R*,5R*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-5-ethyl-1-methyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one (**31b**).* AVK **1** (70 mg, 0.40 mmol), **21** (0.42 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave a 2:1 mixture of **31a** and **31b** (54 mg, 34%) as a colorless oil. For **31a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 7.3 Hz, 2H), 5.09 (d, J = 2.3 Hz, 1H), 4.86 (d, J = 2.0 Hz, 1H), 4.81 (dd, J = 8.2, 2.3 Hz, 1H), 3.72 (d, J = 1.9 Hz, 1H), 2.69 (dd, J = 5.3, 1.8 Hz, 1H), 2.29−2.25 (m, 2H), 2.06 (dd, J = 15.9, 8.2 Hz, 1H), 1.64−1.62 (m, 1H), 1.48−1.35 (m, 1H), 1.27 (s, 3H), 0.99 (t, J = 7.4 Hz, 3H), 0.95 (s, 9H), 0.22 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.0, 157.5, 154.3, 146.7, 128.9 (2C), 127.4 (2C), 126.5, 109.8, 104.1, 56.2, 54.4, 52.8, 50.3, 41.3, 25.8 (3C), 24.5, 21.0, 18.1, 12.6, −4.1, −4.3. For **31b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.07 (d, J = 7.3 Hz, 2H), 5.03 (d, J = 2.7 Hz, 1H), 4.92−4.89 (m, 1H), 4.63 (d, J = 2.3 Hz, 1H), 3.90 (q, J = 3.0 Hz, 1H), 2.81 (t, J = 3.9 Hz, 1H), 2.42−2.39 (m, 1H), 2.29−2.25 (m, 1H), 2.19−2.14 (m, 2H), 1.48−1.35 (m, 1H), 1.30 (s, 3H), 0.94 (s, 9H), 0.67 (t, J = 7.4 Hz, 3H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.4, 158.8, 151.5, 145.9, 128.8 (2C), 128.1 (2C), 126.4, 108.9, 105.9, 55.9, 55.5, 48.4, 46.8, 41.8, 26.0 (3C), 22.3, 19.9, 18.4, 11.9, −4.1, −4.4. For **31a** and **31b**: IR (thin film) 1743 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{36}O_2SiNa]^+$ 419.2377, found 419.2382.

(1R,5S*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1-methyl-8-methylene-5,7-diphenylbicyclo[4.2.1]non-3-en-9-one (**32a**), (1R*,5R*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1-methyl-8-methylene-5,7-diphenylbicyclo[4.2.1]non-3-en-9-one (**32b**), and (1R*,2R*,6S*,7S*)-3-[(tert-Butyldimethylsilyl)oxy]-1-methyl-8-methylene-2,7-diphenylbicyclo[4.2.1]non-3-en-9-one (**33**).* AVK **1** (70 mg, 0.40 mmol), **22** (0.52 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **32a** (59 mg, 33%) and a 1.3:1 mixture of **32b** and **33** (37 mg, 21%) as colorless oils. For **32a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.17 (m, 6H), 7.05 (d, J = 7.3 Hz, 4H), 5.14 (d, J = 2.3 Hz, 1H), 5.07 (dd, J = 7.9, 2.3 Hz, 1H), 4.92 (d, J = 2.0 Hz, 1H), 3.97 (d, J = 2.0 Hz, 1H), 3.74 (d, J = 4.7 Hz, 1H), 2.75 (dd, J = 4.8, 2.0 Hz, 1H), 2.51 (d, J = 16.1 Hz, 1H), 2.23 (dd, J = 16.1, 7.9 Hz, 1H), 1.28 (s, 3H), 0.75 (s, 9H), 0.13 (s, 3H), −0.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 217.8, 157.2, 151.7, 146.4, 139.3, 128.9 (2C), 128.45 (2C), 128.37 (2C), 127.39 (2C), 127.21, 126.6, 110.2, 106.5, 60.7, 54.8, 54.3, 53.2, 41.7, 25.6 (3C), 21.4, 18.0, −4.1, −4.7; IR (thin film) 1744 cm^{-1}; HRMS (ESI) calcd for $[C_{29}H_{36}O_2SiNa]^+$ 467.2377, found 467.2381. For **32b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.02 (m, 8H), 6.52 (d, J = 6.5 Hz, 2H), 5.15 (d, J = 2.4 Hz, 1H), 5.08−5.07 (m, 1H), 4.82 (d, J = 2.0 Hz, 1H), 4.10 (d, J = 2.4 Hz, 1H), 3.92−3.91 (m, 1H), 2.78 (dd, J = 5.0, 3.1 Hz, 1H), 2.43 (dt, J = 16.5, 3.3 Hz, 1H), 2.33 (dd, J = 17.9, 5.3 Hz, 1H), 1.35 (s, 3H), 0.58 (s, 9H), 0.05 (s, 3H), −0.10 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.8, 157.5, 148.4, 145.8, 140.0, 129.8 (2C), 128.4 (2C), 128.1 (2C), 127.0, 126.6, 126.0 (2C), 109.8, 108.6, 61.6, 54.6, 50.7, 47.5, 42.8, 25.4 (3C), 21.0, 17.8, −4.1, −5.1. For **33**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.02 (m, 10H), 5.02−5.01 (m, 1H), 4.54 (d, J = 2.5 Hz, 1H), 4.15 (d, J = 3.0 Hz, 1H), 3.92−3.91 (m, 1H), 3.35 (d, J = 1.8 Hz, 1H), 2.84 (q, J = 4.3 Hz, 1H), 2.71−2.66 (m, 1H), 2.52−2.48 (m, 1H), 1.19 (s, 3H), 0.51 (s, 9H), −0.02 (s, 3H), −0.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.3, 153.3, 150.1, 145.1, 137.9, 128.8 (2C), 128.6 (2C), 127.5 (2C), 127.0, 126.7, 126.5 (2C), 114.6, 106.3, 57.7, 56.6, 55.8, 52.4, 32.2, 25.3 (3C), 21.4, 17.8, −4.4, −4.8. For **32b** and **33**: IR (thin film) 1745 cm^{-1}; HRMS (ESI) calcd for $[C_{29}H_{37}O_2Si]^+$ 445.2557, found 445.2556.

(1R,5R*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1-methyl-8-methylene-7-phenyl-5-isopropylbicyclo[4.2.1]non-3-en-9-one (**34**).* AVK **1** (70 mg, 0.40 mmol), **23** (0.45 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **34** (62 mg, 38%) as a colorless solid: mp 168−169 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 7.3 Hz, 2H), 4.99−4.96 (m, 2H), 4.61 (d, J = 2.2 Hz, 1H), 3.74 (q, J = 2.4 Hz, 1H), 2.74 (br s, 1H), 2.46−2.41 (m, 1H), 2.39 (br s, 1H), 2.15−2.05 (m, 2H), 1.26 (s, 3H), 0.95 (s, 9H), 0.89 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H), 0.21 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 223.0, 159.1, 153.4, 146.2, 128.7 (2C), 128.2 (2C), 126.3, 109.0, 104.4, 56.1, 54.4, 51.3, 49.7, 41.2, 28.5, 26.1 (3C), 21.9, 19.9, 19.6, 18.4, −4.1, −4.4; IR (thin film) 1737 cm^{-1}; HRMS (ESI) calcd for $[C_{26}H_{38}O_2SiNa]^+$ 433.2533, found 433.2533.

(1R,2R*,5R*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,2,5-trimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one (**36**) and (1R*,2S*,5S*,6S*,7S*)-4-[(tert-Butyldimethylsilyl)oxy]-1,2,5-trimethyl-8-methylene-7-phenylbicyclo[4.2.1]non-3-en-9-one (**37**).* AVK **1** (70 mg, 0.40 mmol), **35** (0.42 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave a mixture of **36** (32 mg, 20%) and **37** (35 mg, 22%) as colorless oils. For **36**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.0 Hz, 1H), 7.10 (d, J = 7.8 Hz, 2H), 4.93 (d, J = 2.7 Hz, 1H), 4.73 (s, 1H), 4.63 (d, J = 1.8 Hz, 1H), 3.78 (t, J = 2.2 Hz, 1H), 2.76−2.74 (m, 1H), 2.64 (t, J = 4.6 Hz, 1H), 2.30−2.26 (m, 1H), 1.23 (s, 3H), 1.12 (d, J = 7.1 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H), 0.93 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.4, 154.8, 150.0, 145.5, 128.8 (2C), 128.7 (2C), 126.5, 113.9, 111.6, 59.7, 58.4, 49.0, 40.6, 40.2, 26.0 (3C), 18.7, 18.3, 18.0, 17.1, −4.1, −4.4. For **37**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H), 5.06 (d, J = 1.5 Hz, 1H), 4.89 (d, J = 7.2 Hz, 1H), 4.86 (s, 1H), 3.73 (s, 1H), 2.46−2.44 (m, 2H), 2.22 (quintet, J = 7.0 Hz, 1H), 1.29 (s, 3H), 1.16 (d, J = 6.6 Hz, 3H), 0.98 (d, J = 6.9 Hz, 3H), 0.95 (s, 9H), 0.21 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.5, 159.6, 152.5, 146.9, 128.9 (2C), 127.2 (2C), 126.4, 112.1, 109.5, 59.9, 56.5, 53.0, 46.1, 42.9, 25.9 (3C), 20.3, 18.4, 18.2, 17.8, −3.9, −4.2. For **36** and **37**: IR (thin film) 1740 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{36}O_2SiNa]^+$ 419.2377, found 419.2362.

(1R,6S*,8R*)-4-[(tert-Butyldimethylsilyl)oxy]-1,5,5-trimethyl-7-methylene-8-phenylbicyclo[4.2.1]non-3-en-9-one (**39**).* AVK **38** (70 mg, 0.40 mmol), **18** (0.40 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **39** (43 mg, 27%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 7.3 Hz, 2H), 5.15 (d, J = 2.5 Hz, 1H), 4.90 (s, 1H), 4.83 (d, J = 1.9 Hz, 1H), 3.95 (d, J = 1.7 Hz, 1H), 2.81 (s, 1H), 2.31 (dd, J = 16.8, 2.3 Hz, 1H), 2.17 (d, J = 16.8 Hz, 1H), 1.25 (s, 3H), 1.17 (s, 3H), 0.94 (s, 9H), 0.63 (s, 3H), 0.17 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.3, 149.5, 146.7, 143.1, 130.1, 128.2 (2C), 126.7 (2C), 118.8, 114.4, 65.9, 57.2, 51.1, 47.7, 38.9, 30.6, 29.2, 25.9 (3C), 21.0, 18.2, −4.0, −4.3; IR (thin film): 1742 cm^{-1}; HRMS (ESI) calcd for $[C_{25}H_{36}O_2SiNa]^+$ 419.2377, found 419.2371.

(1R,5R*,6S*,8R*)-4-[(tert-Butyldimethylsilyl)oxy]-1,5-dimethyl-7-methylene-8-phenylbicyclo[4.2.1]non-3-en-9-one (**40a**) and*

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(1R,5S*,6S*,8R*)-4-[(tert-butyldimethylsilyl)oxy]-1,5-dimethyl-7-methylene-8-phenylbicyclo[4.2.1]non-3-en-9-one (**40b**).* AVK **38** (70 mg, 0.40 mmol), **19** (0.40 g, 2.0 mmol), and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave a 2.7:1 mixture of **40a** and **40b** (34 mg, 22%) as a colorless oil. For **40a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.22 (m, 2H), 7.18−7.15 (m, 1H), 6.96−6.93 (m, 2H), 5.16 (s, 1H), 4.93 (s, 1H), 4.80 (dd, J = 5.7, 4.6 Hz, 1H), 3.78 (s, 1H), 3.05 (dd, J = 5.7, 1.0 Hz, 1H), 2.47 (quintet, J = 6.7 Hz, 1H), 2.24−2.19 (m, 2H), 1.24 (d, J = 7.1 Hz, 3H), 0.92 (s, 9H), 0.66 (s, 3H), 0.14 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 219.8, 155.3, 152.2, 144.5, 128.9, 128.4 (2C), 126.5 (2C), 111.6, 102.9, 57.9, 56.8, 54.4, 44.9, 41.5, 26.0 (3C), 20.4, 18.1, 16.7, −4.11, −4.15. For **40b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.22 (m, 2H), 7.18−7.15 (m, 1H), 6.96−6.93 (m, 2H), 5.18 (s, 1H), 4.91−4.90 (m, 2H), 3.72 (s, 1H), 3.08 (s, 1H), 2.71−2.69 (m, 1H), 2.24−2.19 (m, 1H), 2.15−2.11 (m, 1H), 1.33 (d, J = 7.3 Hz, 3H), 0.93 (s, 9H), 0.67 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 222.2, 154.2, 149.6, 144.3, 129.4, 129.0 (2C), 128.3 (2C), 113.6, 102.7, 59.2, 58.1, 54.6, 41.4, 40.4, 25.8 (3C), 19.9, 18.4, 17.9, −4.23 (2C). For **40a** and **40b**: IR (thin film) 1742 cm^{-1}; HRMS (ESI) calcd for $[C_{24}H_{34}O_2SiNa]^+$ 405.2220, found 405.2217.

Procedure for Compounds 41−47. $BF_3{\cdot}OEt_2$ (1.1 equiv) was added to a solution of a Nazarov product in CH_2Cl_2 (0.1 M) at rt. The solution was stirred for 5 min before saturated aqueous $NaHCO_3$ (40 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic solutions were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (15% Et_2O in pentane).

(4R,5R*)-2,3-Dimethyl-5-((E)-2-oxopent-3-en-1-yl)-4-phenylcyclopent-2-enone (**12**).* Compound **25** (41 mg, 0.11 mmol) and $BF_3{\cdot}OEt_2$ (0.01 mL, 0.12 mmol) gave **12** (29 mg, 90%) as a colorless oil.

(1R,5S*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione (**14a**) and (1R*,5R*,6S*,7S*)-1,5-Dimethyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione (**14b**).* A 7:1 mixture of **29a** and **29b** (86 mg, 0.22 mmol) and $BF_3{\cdot}OEt_2$ (0.03 mL, 0.25 mmol) gave a 7:1 mixture of **14a** and **14b** (57 mg, 95%) as a colorless oil.

(1R,5R*,6S*,7S*)-1-Methyl-8-methylene-7-phenyl-5-isopropylbicyclo[4.2.1]nonane-4,9-dione (**41**).* Compound **34** (62 mg, 0.40 mmol) and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **41** (42 mg, 94%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.26 (m, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.2 Hz, 2H), 5.16 (d, J = 2.1 Hz, 1H), 4.95 (d, J = 1.8 Hz, 1H), 3.88 (d, J = 2.0 Hz, 1H), 2.88 (dd, J = 5.1, 2.4 Hz, 1H), 2.57−2.53 (m, 1H), 2.47−2.41 (m, 2H), 2.25−2.22 (m, 1H), 1.94−1.87 (m, 2H), 1.30 (s, 3H), 0.91 (d, J = 6.5 Hz, 3H), 0.77 (d, J = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 221.7, 210.8, 157.6, 146.0, 129.1 (2C), 127.3 (2C), 126.8, 112.4, 59.8, 54.4, 53.8, 47.2, 41.3, 40.5, 26.1, 22.3, 21.9, 20.4; IR (thin film) 1742, 1708 cm^{-1}; HRMS (ESI) calcd for $[C_{20}H_{24}O_2Na]^+$ 319.1669, found 319.1667.

(1R,2R*,5R*,6S*,7S*)-1,2,5-Trimethyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione (**42**), (4R*,5R*)-2,3-Dimethyl-5-((S*,E)-3-oxohex-4-en-2-yl)-4-phenylcyclopent-2-enone (**43**), and (1R*,2S*,5S*,10R*)-2,5,8-Trimethyl-10-phenylbicyclo[5.2.1]dec-7-ene-3,9-dione (**44**).* Compound **36** (32 mg, 0.40 mmol) and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **42** (1 mg, 5%), **43** (16 mg, 70%), and **44** (3 mg, 15%) as colorless oils. For **42**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, J = 7.1 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.5 Hz, 2H), 5.10 (s, 1H), 4.93 (s, 1H), 3.71−3.70 (m, 1H), 2.95−2.93 (m, 1H), 2.65−2.59 (m, 2H), 2.39−2.36 (m, 1H), 2.04−2.00 (m, 1H), 1.29 (s, 3H), 1.17 (d, J = 6.9 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.7, 210.7, 153.1, 146.3, 129.0 (2C), 128.0 (2C), 126.8, 115.2, 57.9, 57.6, 48.5, 48.1, 47.8, 40.3, 20.7, 16.6, 14.4; IR (thin film): 1740, 1708 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2Na]^+$: 305.1512, found: 305.1500. For **43**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.3 Hz, 2H), 7.23 (t, J = 7.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 2H), 6.85 (dq, J = 14.8, 7.3 Hz, 1H), 6.11 (d, J = 15.5 Hz, 1H), 3.86 (s, 1H), 2.51−2.41 (m, 2H), 1.85 (d, J = 6.9 Hz, 3H), 1.75 (s, 6H), 1.17 (d, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 201.5, 170.7, 143.5, 142.4, 136.4, 130.5, 129.0 (2C), 127.9 (2C), 127.1, 58.4, 53.0, 44.5, 18.4, 15.6, 15.5, 8.4; IR (thin film) 1710, 1650 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2Na]^+$ 305.1512, found 305.1507. For **44**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 7.9 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 3.96 (s, 1H), 2.87−2.83 (m, 1H), 2.68−2.59 (m, 4H), 2.42 (dd, J = 11.8, 4.4 Hz, 1H), 2.06−2.02 (m, 1H), 1.79 (s, 3H), 1.31 (d, J = 7.0 Hz, 3H), 1.23 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.1, 210.2, 175.8, 141.0, 135.7, 129.1 (2C), 127.4, 127.2 (2C), 64.6, 54.1, 53.5, 45.7, 35.9, 35.0, 23.7, 17.5, 9.4; IR (thin film) 1705, 1640 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2Na]^+$ 305.1512, found 305.1498.

(1R,2S*,5S*,6S*,7S*)-1,2,5-Trimethyl-8-methylene-7-phenylbicyclo[4.2.1]nonane-4,9-dione (**45**), (4R*,5R*)-2,3-Dimethyl-5-((R*,E)-3-oxohex-4-en-2-yl)-4-phenylcyclopent-2-enone (**46**), and (1R*,2R*,5S*,10R*)-2,5,8-Trimethyl-10-phenylbicyclo[5.2.1]dec-7-ene-3,9-dione (**47**).* Compound **37** (35 mg, 0.40 mmol) and $BF_3{\cdot}OEt_2$ (0.05 mL, 0.44 mmol) gave **45** (4 mg, 15%), **46** (11 mg, 46%), and **47** (9 mg, 38%) as colorless oils. For **45**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 7.7 Hz, 2H), 5.24 (s, 1H), 5.10 (s, 1H), 4.00 (s, 1H), 3.00−2.97 (m, 1H), 2.63−2.62 (m, 2H), 2.43−2.39 (m, 1H), 2.00−1.97 (m, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 0.96 (d, J = 7.0 Hz, 3H); ^{13}C NMR discernible signals (126 MHz, $CDCl_3$) δ 146.0, 129.1 (2C), 127.1 (2C), 126.9, 112.2, 58.7, 57.3, 54.8, 50.4, 44.3, 20.4, 16.5; IR (thin film): 1737, 1704 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2Na]^+$ 305.1512, found 305.1506. For **46**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26−7.24 (m, 2H), 7.20−7.17 (m, 1H), 6.99 (d, J = 7.8 Hz, 2H), 6.73 (dq, J = 14.9, 7.3 Hz, 1H), 6.01 (d, J = 15.6 Hz, 1H), 3.57 (s, 1H), 3.38−3.33 (m, 1H), 2.67 (s, 1H), 1.80 (s, 3H), 1.79 (s, 3H), 1.70 (d, J = 6.9 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9, 201.4, 171.5, 142.9, 141.4, 137.2, 130.0, 128.8 (2C), 128.0 (2C), 127.0, 56.6, 51.5, 44.0, 18.2, 15.6, 10.8, 8.4; IR (thin film) 1702, 1649 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2Na]^+$ 305.1512, found 305.1513. For **47**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 6.9 Hz, 1H), 7.14 (d, J = 7.7 Hz, 2H), 4.31 (s, 1H), 3.27 (dd, J = 6.6, 3.9 Hz, 1H), 3.01 (dd, J = 14.0, 3.3 Hz, 1H), 2.85 (d, J = 3.7 Hz, 1H), 2.74 (dt, J = 7.0, 3.6 Hz, 1H), 2.64−2.60 (m, 1H), 2.52 (dd, J = 12.5, 3.8 Hz, 1H), 2.17 (dd, J = 14.0, 7.1 Hz, 1H), 1.68 (s, 3H), 1.28 (d, J = 7.0 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.1, 208.4, 173.5, 141.0, 135.2, 129.1 (2C), 127.5, 127.2 (2C), 65.4, 58.5, 53.3, 48.2, 35.3, 34.2, 22.7, 14.6, 9.4; IR (thin film) 1703, 1641 cm^{-1}; HRMS (ESI) calcd for $[C_{19}H_{22}O_2Na]^+$ 305.1512, found 305.1499.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra, NOE data, and the ORTEPs and the CIFs for the X-ray analyses of **25** and **34**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00914.

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Notes

The authors declare no competing financial interest.

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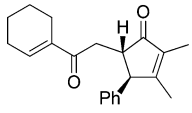

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