Activated cyclooctenones are effective dienophiles[1]

Hsing-Jang Liu, Dan-Xiong Wang, Jeung Bea Kim, Eric N.C. Browne, and Yu Wang

Abstract: The first Diels–Alder addition of a diene to a cyclooctenone dienophile has been observed. Three activated cyclooctenone dienophiles **1**, **2**, and **3** are studied with a variety of simple and functionalized dienes. Diels–Alder adducts are produced in excellent yields under very mild Lewis acid catalyzed conditions. The usual orientation rules are followed and, as predicted, the products are formed for the most part exclusively by ester-*endo* addition. The stereoselectivity is influenced by the substitution pattern of the diene in some cases. The factors influencing the stereochemical selectivity of the addition are discussed in some detail.

Key words: 2-carbalkoxy-2-cyclooctenones, Diels–Alder reaction, six–eight fused ring system.

Résumé : On a observé la première addition de Diels–Alder d'un diène sur une cycloocténone comme diénophile. On a étudié trois diénophiles, des cycloocténones activées **1**, **2** et **3**, avec divers diènes simples et fonctionalisées. On a obtenu les adduits de Diels–Alder avec d'excellents rendements dans des conditions très douces avec des catalyseurs de Lewis. On a suivi les règles usuelles d'orientation et comme prévu, les produits obtenus sont presqu'exclusivement les résultats d'une addition *endo* d'esters. La stéréosélectivité, dans quelques cas, est influencée par le schéma de distribution des diènes. On discute des facteurs qui influencent la sélectivité stéréochimique de l'addition.

Mots clés : 2-carbalkoxy-2-cycloocténones, réaction de Diels–Alder, système à six–huit noyaux condensés.

[Traduit par la rédaction]

Introduction

Our group has continued to expand on our long-standing program of investigation into the Diels–Alder chemistry of cycloalkenone dienophiles.[5] Encouraged by recent successes in applying our discoveries of methodology in this field to the synthesis of structurally challenging and important natural products such as (+)-qinghaoshu (2), (−)-qinghaoshu IV (3), and two diterpenoids of the *cis*-clerodane family (4), we have turned our attention to the more challenging larger ring cycloalkenones as a tool for rapid assembly of less accessible polycyclic ring systems. We recently reported (1) our work on the scarcely precedented Diels–Alder addition to cycloheptenones in which the tactic of activating reactivity by the use of a 2-carbalkoxy substituent aided additions to a variety of substituted derivatives. There are no reports in the literature of intermolecular Diels–Alder additions to 2-cyclooctenones. Yet there is an increasing number of examples in the literature of complex natural products possessing the six–eight fused ring system that could result from such an addition.[6]

This provides a strong challenge for the development of this unprecedented approach and its application to synthesis. We are pleased now to report for the first time on the facile, selective, and highly efficient additions of 1,3-dienes to activated cyclooctenones.

Results and discussion

We examined three activated cyclooctenones **1**, **2**, and **3**, which were selected for their simplicity yet still would serve as probes to the regio- and stereoselectivity of the additions. As outlined in Scheme 1, the unsaturated enone ester **1** was prepared from cycloheptanone via boron trifluoride catalyzed ring expansion with ethyl diazoacetate (9), which gave a 74% yield of keto ester **4** and its enol tautomer **5** in ca. 1.6:1 ratio. This was followed by a phenylselenenylation – oxidative elimination process (10) to furnish **1** in 85% yield.

Two complementary approaches to the substituted enone ester system of **2** and **3**, summarized in Schemes 2 and 3, were

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This paper is dedicated to Professor William A. Ayer on the occasion of his 65th birthday.

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[5] See ref. 1 and the bibliography of ref. 5 therein.

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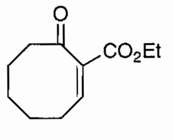
[6] For selected examples see these reports on variecolein (5), taxol (6), aleurodiscal (7), and schisanlignone (8).



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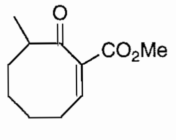

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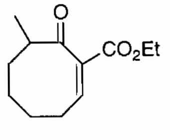

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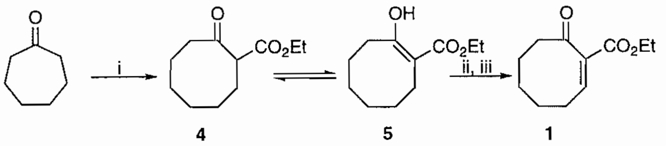
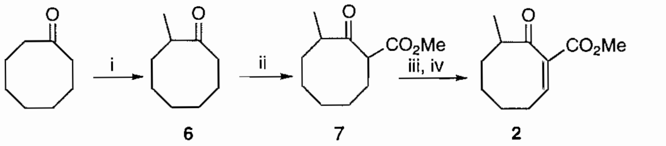
Scheme 1. The preparation of enone ester **1**.



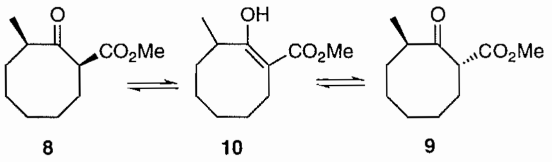
(i) N_2CHCO_2Et, $BF_3{\bullet}OEt_2$, ether, r.t., 24 h, 74%; (ii) PhSeCl, Py, CH_2Cl_2, 0°C, 1 h; (iii) H_2O_2, CH_2Cl_2, 0°C, 40 min, 85% (two steps).

Scheme 2. The preparation of enone ester **2**.



(i) LDA, THF, -78°C, 30 min; then CH_3I, r.t., 40 h, 89%; (ii) NaH, $(CH_3O)_2CO$, DME, reflux, 19 h, 85%; (iii) NaH, PhSeCl, THF, 0°C, 15 min; (iv) H_2O_2, CH_2Cl_2, 0°C → r.t., 40 min, 86% (two steps).

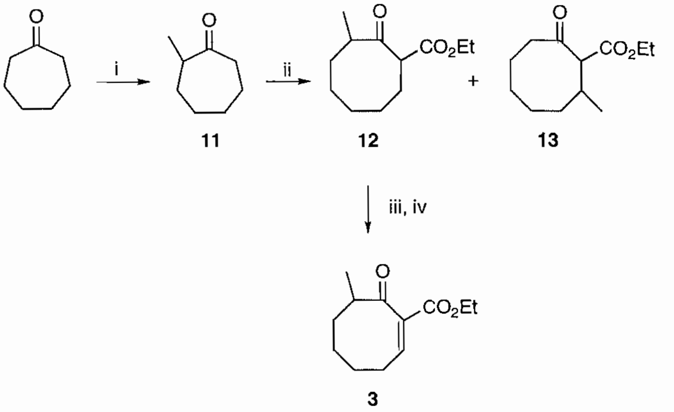
followed. α-Methylation of cyclooctanone with lithium diisopropylamide and methyl iodide (11) gave ketone **6** in 89% yield. Carbomethoxylation of **6** with dimethyl carbonate and sodium hydride (12) gave exclusively keto ester **7** in 85% yield as a mixture of two epimeric keto forms **8** and **9** and the enol tautomer **10** (4:2:3 ratio). The cross-conjugated double bond was introduced by phenylselenenylation and oxidative elimination (10) to give **2** in 86% overall yield.



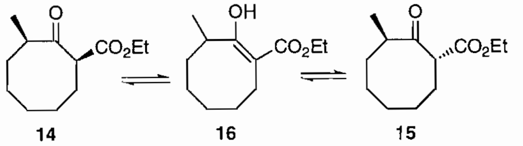
Alternatively, α-methylation of cycloheptanone by the same method used above gave ketone **11** in 70% yield. The keto ester **12** was obtained in this case by ring expansion with ethyl diazoacetate and boron trifluoride etherate (9), giving the product in 56% yield along with a significant quantity (38% yield) of the separable by-product **13**.[7] The keto ester **12** was also obtained as a mixture of epimeric ketones **14** and **15** and the enol tautomer **16** in a ratio of about 3:1:1. The same selenenylation – oxidative elimination approach used previously converted **12** to **3** in 85% yield. A bromination–dehydrobromination approach (13), used in our laboratory in other systems, was unsuccessful as treatment of **12** with *N*-bromosuccinimide gave a complex mixture of products.

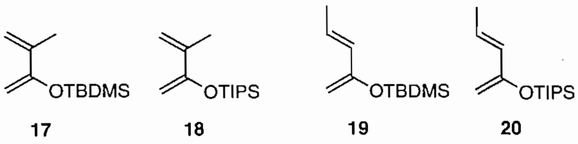
The 2-silyloxy-substituted dienes **17**–**20** used in our study were not commercially available and were prepared by the general method of Ireland and Thompson (14) using *tert*-butyldimethylsilyl chloride and triisopropylsilyl chloride to trap the enolates generated from *trans*-3-penten-2-one and 3-methyl-3-buten-2-one with lithium diisopropylamide.

Scheme 3. The preparation of enone ester **3**.



(i) LDA, THF, -78°C, 30 min; then CH_3I, r.t., 10 h, 70 %; (ii) N_2CHCO_2Et, $BF_3{\bullet}OEt_2$, ether, r.t., 24 h, 94% (**12** : **13** = 1.5 : 1); (iii) NaH, PhSeCl, THF, 0°C, 30 min; (iv) H_2O_2, CH_2Cl_2, 0°C → r.t., 40 min, 85% (two steps).





TBDMS = *t*-$BuMe_2Si$; TIPS = $(i\text{-}Pr)_3Si$

Diels–Alder reactions

The general procedures for the Diels–Alder cycloaddition were straightforward. For those catalyzed by ferric chloride, stannic chloride, or boron trifluoride etherate, the Lewis acid was simply added to an ether solution of the diene and dienophile. For zinc chloride catalyzed reaction, the Lewis acid was first flame fused and then dissolved in ether. The dienophile was then added as a solution in ether and, after stirring for 30 min to allow for complex formation, the diene was introduced. After complete consumption of the dienophile, the reaction was quenched by addition of aqueous sodium bicarbonate and worked up. The additions to unsubstituted enone ester **1** are summarized in Table 1. At −20°C, both ferric chloride and stannic chloride gave adduct **21** in high yield. Ferric chloride gave a particularly fast conversion to product. Boron trifluoride etherate and zinc chloride gave slow conversions even at higher temperature (0°C). As expected, the uncatalyzed reaction gave virtually no adduct at room temperature. Having thus determined effective conditions and catalysts for this system, we investigated a selected group of examples with simple dienes to give adducts **22** through **27**. The yields were uniformly high. The addition took place as expected with com-

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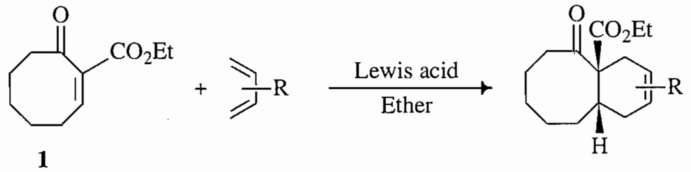
[7] The ethyl diazoacetate – boron trifluoride ring expansion has been used frequently in our laboratories and is usually much more selective than in this case.

Table 1. Diels–Alder reaction of 2-carbethoxy-2-cyclooctenone (**1**).



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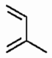
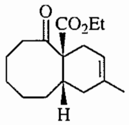
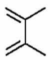
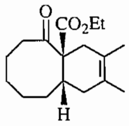
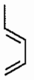
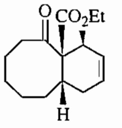
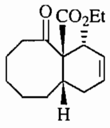
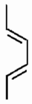
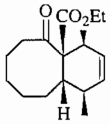
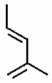
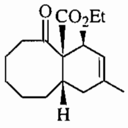
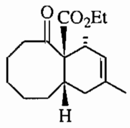
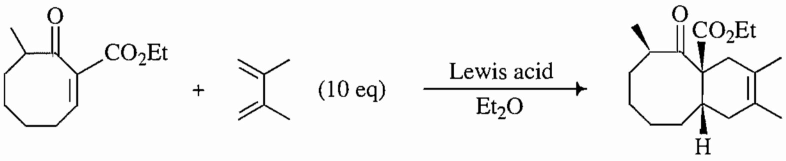
Entry	Diene (10 equiv.)	Time (h)	Temp (°C)	Product	Lewis acid[a]	Yield (%)
1		1/3	−20	 **21**	FeCl$_3$	84
		24	−20		SnCl$_4$	86
		72	0		ZnCl$_2$	16
		48	0		BF$_3$·OEt$_2$	35
		72	r.t.		—	2
2		1/3	−20	 **22**	FeCl$_3$	89
3		1/3	−20	  **23** (85:15) **24**	FeCl$_3$	80
		18	−20		SnCl$_4$	89
4		24	−20	 **25**	SnCl$_4$	95
		10	−78		FeCl$_3$	82
5		1	−20	  **26** (77:23) **27**	SnCl$_4$	83

[a]Ferric chloride, stannic chloride, and boron trifluoride etherate were used at 1 equivalent. Zinc chloride was used at 2 equivalents.

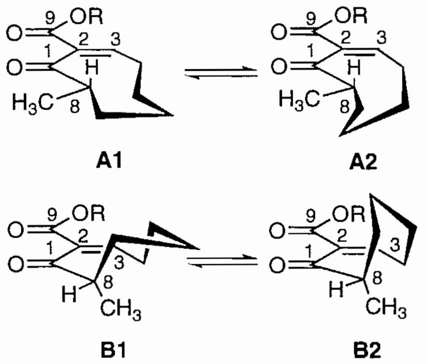
Table 2. Lewis acid catalyzed Diels–Alder reaction of enone **3** and 2,3-dimethyl-1,3-butadiene.



3 **28**

Time (h)	Temp (°C)	Lewis acid[a]	Yield (%)
0.5	−40	FeCl$_3$ (1 equiv.)	96
17	−40	SnCl$_4$ (1 equiv.)	98
101	r.t.	ZnCl$_2$ (2 equiv.)	85
52	r.t.	BF$_3$·OEt$_2$ (1 equiv.)	0

Scheme 4. The conformational equilibrium of cyclooctenones.



plete *ortho*-rule and *para*-rule selectivity and with moderate to good preference for the same ester-*endo* addition as in other systems.[5]

Initial investigations of additions to enone ester **3** are summarized in Table 2. Again ferric chloride and stannic chloride were superior and powerful catalysts. But in this sequence boron trifluoride was completely ineffective. The dienophile was recovered quantitatively. Zinc chloride did in fact produce product **28** in good yield although with a much slower rate than the first two catalysts mentioned. Thus the broader studies on Diels–Alder reactions of **2** and **3** were concentrated on examples with stannic chloride and ferric chloride. The results of these investigations are summarized in Table 3. These reactions too followed the expected regiochemical rules (15). Even for addition of the 2,3-disubstituted diene **18** the expected regio-directing dominance of the electron-donating silyloxy substituent led to complete selection in favor of the adduct **34** with none of the isomeric adduct observed. All of the adducts were formed by preferential ester-*endo* addition except for that with cyclopentadiene, which was at best only slightly selective. A significant proportion of the keto-*endo* adduct **43** was formed. This particular loss of selectivity for cyclopentadiene is not exhibited in other systems we have studied and is not readily explained. The ester-*endo* attack observed for the majority of adducts is expected on the basis of minimum steric interaction between the diene and dienophile in the transition state.

The face selectivity of the additions to the dienophiles with two different diastereotopic faces was less consistent. When the C-2 position of the diene was substituted, addition to **2** and **3** proceeded with preferential addition to the apparently less hindered face (opposite to the methyl substituent). This was expected even though reversed selectivity in favor of the apparently more hindered face had previously been observed for additions to the congener **44** (1). But where the diene had no C-2 substituent, the diene appeared to add to **3** preferentially from the more hindered methyl-substituted face. As noted for additions to **44**, the rationale for this unexpected selectivity is unclear.[8] Several of the additions (Entries 2, 5, and 8) also produced one inseparable minor isomer whose stereochemistry could not be completely assigned. It was therefore impossible to determine if these minor isomers were derived from keto-*endo* addition, which would indicate diminished preference for the established ester-*endo* orientation of addition, giving products epimeric at C-12, or from diminished face selectivity resulting in products that are epimeric at C-3.

We considered the conformational effects of the eight-membered ring on the orientations of the Diels–Alder additions. Using the report of Arshinova (16) and considering the effect of planar fragments (ketone carbonyl and double bond) as constraints on the flexibility of the ring system, we have proposed two conformations around the enone-ester system that are illustrated in Scheme 4. The conformations **A1** and **A2** would clearly present a face opposite to the methyl substituent for relatively unhindered cycloaddition to the enone. Conformations **B1** and **B2** are clearly less suited to additions at the enone double bond since the methyl substituent is pseudo-axial on one face while the remainder of the eight-membered ring occupies the other face of the system. And yet addition to the methyl-substituted face was observed. Further study and a broadened selection of examples may provide a better understanding of the complex stereochemical and conformational relationships that are expressed in this system.

Structural assignments

While the establishment of product structures has by now become fairly routine in our studies of cycloalkenone dienophiles, there are a few elements that warrant particular attention and are discussed below. For the most part, however, the structures were clearly evident on first-order examination of the spectroscopic data.

The stereochemistry of adduct **28** was confirmed by NOE experiments in which irradiation of the C-3 methyl substituent gave enhancement of the signals for the ester methyl (11%) and methylene (1%) protons and for the C-8 ring-junction proton (5%). Irradiation of the C-3 proton gave enhancement of the allylic methyls at C-10 and C-11 (1% each) and one of the C-12 protons (7%). These two results indicated that the methyl substituent was on the same face of the ring as the carbethoxy group. Similar NOE studies were run for other compounds in the series and the results of those experiments are summarized in Table 4.

Proof of the *para*-addition orientation for adduct **29** was made by an INEPT-NMR experiment and by chemical transformation. In the INEPT experiment, when the vinyl proton of **29** at δ 5.30 was irradiated the signal of the quaternary ring junction carbon at C-1 (δ 63.3 in the ^{13}C NMR APT spectrum) was observed in the corresponding INEPT ^{13}C NMR spectrum. If the adduct had the *anti-para* addition structure **45**, this irradiation should cause display of the signal for the tertiary ring junction carbon at C-8.

Chemical derivatization of **29** was achieved by photooxidation (17) to give two products **46** and **47**. In the ^{1}H NMR spectrum of the enone derivative **47** the vinyl proton was observed at δ 6.60 as a quartet of doublets (J = 1, 5.5 Hz) due to coupling with the enone methyl substituent and most importantly with the ring junction proton. In the corresponding derivative **48** of the *anti-para* product **45**, the 5.5 Hz coupling to the ring junction would be absent and the enone proton would appear only as a finely split quartet.

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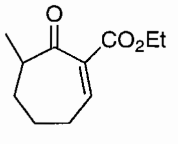
[8] It could be that the C-2 substituted diene reacts in an almost stepwise manner under pseudo-charge control, which has a different steric demand from the C-2 unsubstituted diene that should react in a more concerted manner. We thank the referee for this suggestion.

The regiochemistry of adduct **21** was confirmed in a similar manner. Photooxidation of this compound gave enone **49** as the sole product, which showed, in the ^{1}H NMR spectrum, a quartet of doublets (J = 1, 6 Hz) at δ 6.68 for the vinylic proton.



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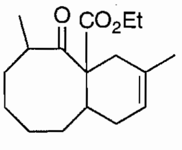

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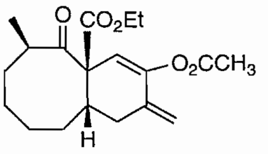

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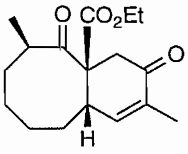
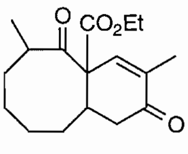


47



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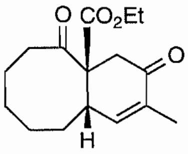


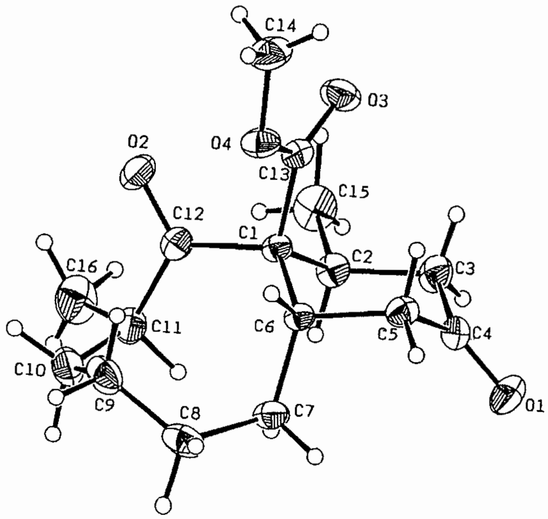
49

Adducts of **2** and **3** with diene **17** were found to be highly unstable and could not be isolated or characterized. Decomposition occurred in an NMR sample tube in deuteriobenzene within 20 min to give a complex mixture. Even at –22°C extensive decomposition was seen within 24 h. The other functionalized dienes **18**, **19**, and **20** gave stable adducts that could be purified. Nevertheless, addition of **20** to **2** gave primarily the deprotected derivative **37** and only a trace of protected enol ether **38** in which the double bond had migrated. TLC analyses showed that the silyl protecting group was eliminated in the cycloaddition reaction mixture. The structure of **37** was verified by X-ray crystallographic analysis.[9] The X-ray structure is shown in Scheme 5. The regiochemistry of compound **38** was confirmed by ^{1}H NMR decoupling experiments.

Conclusion

The Lewis acid catalyzed Diels–Alder addition of activated cyclooctenones proceeds under mild conditions in high yield and with moderate to high and predictable stereochemistry to give adducts with great potential for synthetic use. Adducts are in use in our laboratory as key intermediates in the synthesis of several natural products and further details on this work will be reported in a future publication.

Scheme 5. The three-dimensional X-ray crystallographical structure of compound **37**.



Experimental

General

Melting points were recorded on a Kofler hot stage apparatus and are not corrected. Combustion elemental analyses were performed by the microanalytical laboratory of this department. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 7199 or Nicolet MX-1 FT-IR spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker WH-200, Bruker WH-300, Bruker WH-400, or UNITY-500 using deuteriochloroform ($CDCl_3$) as solvent unless otherwise stated. The chemical shift of the deuterated solvent peak (for $CDCl_3$: δ = 7.25 ppm, for C_6D_6: δ = 7.15 ppm) was used as an internal reference. Coupling constants are reported to ±0.5 Hz. Chemical shift measurements are reported in delta (δ) units. The following abbreviations are used: s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet and br = broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker WH-300 (75 MHz) NMR spectrometer as solutions in deuteriochloroform ($CDCl_3$) as the internal standard, setting the central peak at 77.00 ppm. Carbon-13 multiplicities were derived from Carr–Purcell–Meiboom–Gill spin echo J-modulated experiments (APT or Attached Proton Test) (18). Methyl and methine groups are shown as singlets antiphase (a) with respect to the deuteriochloroform signal, whereas methylene groups, quaternary carbons, and carbonyl groups appear in phase (p) with it. Nuclear Overhauser enhancement (NOE) experiments were determined in the difference mode in which a control (undecoupled) spectrum was computer subtracted from the irradiated spectrum after Fourier transformation. Positive enhancements are defined as signals possessing an antiphase with respect to the irradiated signal. Samples for NOE measurements were deoxygenated with argon for 10 min prior to use. Two-dimensional (2D) homonuclear correlation spectrum (COSY) and proton spin decoupling experiments were performed on the Bruker WH-300 MHz NMR machine

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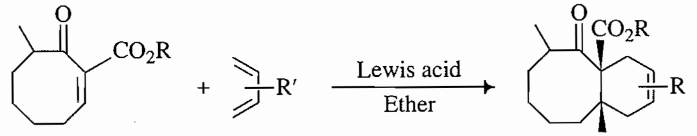
[9] X-ray crystallographic data for **37**, comprising tables of bond distances and angles, atomic parameters, and anisotropic temperature factors, have been deposited and can be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. With the exception of the anisotropic temperature factors, these data have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Table 3. Lewis acid catalyzed Diels–Alder reaction of enones **2** and **3**.



2 R = Me
3 R = Et

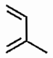
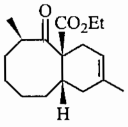
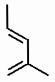
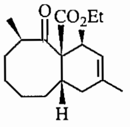
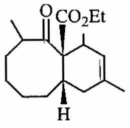
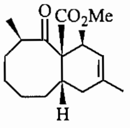
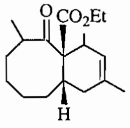
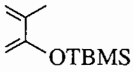
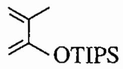
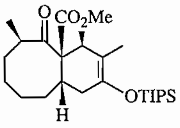
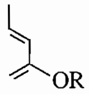
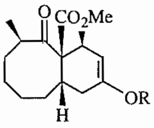
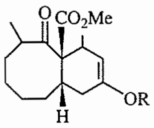
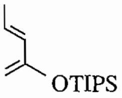
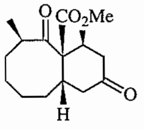
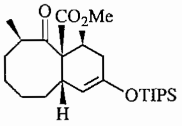
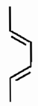
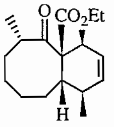
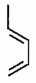
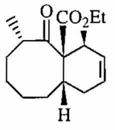
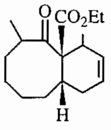
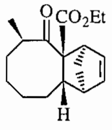
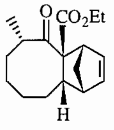
Entry	Diene	Time (h)	Temp (°C)	Product(s)	Lewis acid	Yield (%)
1	 (10 equiv.)	0.5	−40	 **29**	$FeCl_3$ (1 equiv.)	95
2	 (10 equiv.)	0.5 0.5 0.5	−40 −50 −78	  **30** (4:1) **31**	$FeCl_3$ (1 equiv.)	75 80 77
		0.5 24	−78 −78	  **32** (4:1) **33**	$FeCl_3$ (1 equiv.) $SnCl_4$ (1 equiv.)	82 80
3[a]	 (10 equiv.) **17**			Unstable		
4[a]	 (2 equiv.) **18**	4	−78	 **34**	$SnCl_4$ (1 equiv.)	90
5[a]	 **19** R = TBDMS; (10 equiv.)	1	−78	  **35** (2:1) **36**	$SnCl_4$ (1 equiv.)	89
6[a]	 **20** (2 equiv.)	1	−78	 **37**	$SnCl_4$ (1 equiv.)	98
				 **38**		Trace
7	 (10 equiv.)	5.5 2	−40 −20	 **39**	$FeCl_3$ (1 equiv.)	92 68

Table 3. (*concluded*).

Entry	Diene	Time (h)	Temp (°C)	Product	Lewis acid	Yield (%)
8	 (10 equiv.)	0.4 0.5	−40 −78	 **40** (4:1)  **41**	$FeCl_3$ (1 equiv.)	68 92
9	 (10 equiv.)			 **42**  **43**		
		1	−78	2 : 1 1 : 1	$FeCl_3$ (1 equiv.)	76
		78	0 → 20		$ZnCl_2$ (2 equiv.)	91

[a]In this reaction, the diene was added to the solution of the complex of enone **2** and Lewis acid.

Table 4. NOE data for Diels–Alder adducts.

Compound	Irradiation	δ (ppm)	% Enhancement (proton)
28	$\mathrm{O{=}CCHC}\mathbf{H}_3$	1.04	11.0 ($\mathrm{CO_2CH_2C}\mathbf{H}_3$), 1.0 ($\mathrm{CO_2C}\mathbf{H}_2\mathrm{CH_3}$), 5.0 (C-8 **H**)
	$\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$	3.25	1.0 ($\mathrm{H_3CC{=}CC}\mathbf{H}_3$, 7.0 (C-12 **H**)
29	$\mathrm{O{=}CCHC}\mathbf{H}_3$	1.04	3.1 (C-8 **H**)
	$\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$	3.25	6.0 (C-12 **H**)
30	$\mathrm{O{=}CCHC}\mathbf{H}_3$	0.95	0.1 (C-8 **H**)
	$\mathrm{C{=}CHCHC}\mathbf{H}_3$	0.88	1.4 ($\mathrm{CO_2C}\mathbf{H}_2\mathrm{CH_3}$)
	C-8 **H**	2.60	1.4 ($\mathrm{CO_2C}\mathbf{H}_2\mathrm{CH_3}$), 1.5 ($\mathrm{C{=}CHCHC}\mathbf{H}_3$)
32	$\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$	2.50	1.2 ($\mathrm{C{=}CHCHC}\mathbf{H}_3$), 1.4 ($\mathrm{C{=}C}\mathbf{H}$)
	$\mathrm{C{=}CHC}\mathbf{H}\mathrm{CH_3}$	2.07	7.3 ($\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$)
	$\mathrm{C{=}CHCHC}\mathbf{H}_3$	0.90	3.6 ($\mathrm{CO_2CH_2C}\mathbf{H}_3$)
34	$\mathrm{O{=}CCHC}\mathbf{H}_3$	2.90	5.6 ($\mathrm{CO_2C}\mathbf{H}_3$)
35	$\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$	2.93	10.3 ($\mathrm{C{=}C}\mathbf{H}$)
	$\mathrm{C{=}CHCHC}\mathbf{H}_3$	1.17	3.0 ($\mathrm{CO_2C}\mathbf{H}_3$)
37	$\mathrm{O{=}CCH_2C}\mathbf{H}\mathrm{CH_3}$	2.09	11.8 ($\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$)
38	$\mathrm{O{=}CC}\mathbf{H}\mathrm{CH_3}$	2.70	10.3 ($\mathrm{CH_2C}\mathbf{H}\mathrm{CH_3}$)
39	$\mathrm{O{=}CCHC}\mathbf{H}_3$	1.15	0.5 (C-12 **H**)
	C-9 $\mathrm{C}\mathbf{H}_3$	0.95	2.0 (C-8 **H**)
40	$\mathrm{O{=}CCHC}\mathbf{H}_3$	1.08	1.0 (C-11 **H**), 2.0 (C-12 **H**)
42	$\mathrm{O{=}CCHC}\mathbf{H}_3$	1.10	1.3 ($\mathrm{CO_2C}\mathbf{H}_2\mathrm{CH_3}$), 0.3 (C-8 **H**), 1.0 (C-10 **H**)
	C-8 **H**	3.30	1.7 (C-10 **H**)
43	$\mathrm{O{=}CCHC}\mathbf{H}_3$	1.00	1.0 (C-12 **H**), 5.0 (C-11 **H**), 1.0 (C-10 **H**)
	C-12 **H**	6.23	1.0 ($\mathrm{O{=}CCHC}\mathbf{H}_3$)
	C-8 **H**	2.90	2.6 (C-13 **H**)
26	$\mathrm{C{=}CHCHC}\mathbf{H}_3$	1.02	5.8 ($\mathrm{CO_2C}\mathbf{H}_2\mathrm{CH_3}$)
	$\mathrm{C{=}CHC}\mathbf{H}\mathrm{CH_3}$	2.80	2.4 ($\mathrm{O{=}CC}\mathbf{H}\mathrm{H}$)

using the standard proton parameters. High-resolution electron impact mass spectra (HRMS) were recorded using an A.E.I. model MS-50 mass spectrometer. Chemical ionization mass spectra (CIMS) were recorded on an A.E.I. MS-12 mass spectrometer, using ammonia as the reagent gas. Spectral data are reported as *m/z* values. Bulb-to-bulb distillation was performed using a Kugelrohr distillation apparatus. Concentrations of solvent systems used in column chromatography are given by volumes.

Unless otherwise stated, all materials used were commercially available. All compounds made were racemic. With the exception of photooxidation, all reactions were carried out under a positive pressure of argon. Solvents were distilled under argon from appropriate drying agents before use. Tetrahydrofuran (THF), diethyl ether, toluene, and 1,2-dimethoxyethane (DME) were freshly distilled from solutions of sodium benzophenone ketyl. Diisopropylamine was distilled from sodium hydroxide or potassium hydroxide. Pyridine, benzene, dichloromethane, and triethylamine (TEA) were distilled from calcium hydride. Reactions requiring anhydrous conditions were performed using oven- or flame-dried glassware, assembled, and allowed to cool while being purged with argon. Argon was passed through a column of 4 Å molecular sieves, with a self-indicating silica gel (coarse grained) as the indicator. Flash chromatography was used routinely for purification and separation of product mixtures, using silica gel (Merck) of 230–400 mesh. All solvents were distilled prior to use for chromatography. Skellysolve B (Skelly B) refers to Skelly Oil Company light petroleum, bp 62–70°C. Analytical thin-layer chromatography (TLC) was carried out on aluminum sheets precoated (0.2 mm layer thickness) with silica gel 60 F_{254} (E. Merck, Darmstadt). Ultraviolet-active materials were detected by visualization under a UV lamp (254 or 350 nm). For TLC, the visualization of the chromatograms was completed by dipping in an ethanol solution of vanillin (5%, w/v) and sulfuric acid (5%, v/v), followed by careful charring on a hot plate.

2-Carbethoxycyclooctanone (4)

To a solution of cycloheptanone (1.12 g, 10 mmol) in ether (15 mL) cooled to 0°C was added boron trifluoride etherate (1.85 mL, 15 mmol). A solution of ethyl diazoacetate (1.71 g, 1.57 mL, 15 mmol) in ether (2 mL) was then added dropwise over 10 min. After 24 h at room temperature, the reaction mixture was cooled to 0°C, and a saturated aqueous solution of sodium bicarbonate was added to the mixture until the pH was raised to 7. The aqueous layer was extracted with ether (3 × 10 mL) and the organic layers were combined, washed twice with water (10 mL each), and once with saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was subjected to flash chromatography on silica gel. Elution with 5% ethyl acetate in Skelly B gave 2-carbethoxycyclooctanone (**4**) (19) (1.47 g, 74% yield). Compound **4** existed as a mixture of ketone and enol in a ratio of 1:1.56. IR ($CHCl_3$ cast): 1747 (C═O, ester, keto form), 1708 (C═O, ketone), 1644 (C═O, ester, enol form), 1613 (enol C═C) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 12.57 (s, 0.39H, **OH**, enol form), 4.20 (q, 0.78H, *J* = 7.5 Hz, OCH_2, enol form), 4.13 (q, 1.22H, *J* = 7.5 Hz, OCH_2 keto form), 3.55 (dd, 0.61H, *J* = 5, 10.5 Hz, O═CC**H**CO_2Et), 1.28 (t, 1.17H, *J* = 7.5 Hz, $OCH_2\mathbf{CH_3}$, enol form), 1.22 (t, 1.83 H, *J* = 7.5 Hz, $OCH_2\mathbf{CH_3}$ keto form); ^{13}C NMR (APT, 75 MHz in $CDCl_3$) for the keto form δ: 212.2 (p), 176.0 (p), 61.1 (p), 57.0 (a), 41.6 (p), 28.9 (p), 27.0 (p), 26.5 (p), 25.2 (p), 24.5 (p), 14.0 (a), for the enol form δ: 172.9 (p), 170.1 (p), 99.2 (p), 60.1 (p), 32.2 (p), 29.9 (p), 28.7 (p), 26.0 (p), 25.5 (p), 23.8 (p), 14.3 (a); HRMS, *m/z* (M^+) calcd. for $C_{11}H_{18}O_3$: 198.12560; found: 198.12535.

2-Carbethoxy-2-cyclooctenone (1)

At 0°C, to a solution of pyridine (0.27 mL, 3.40 mmol) and phenylselenenyl chloride (651 mg, 3.40 mmol) in dichloromethane (20 mL) was added a dichloromethane solution (5 mL) of 2-carbethoxycyclooctanone (**4**) (562 mg, 2.83 mmol) over 30 min. The mixture was stirred at 0°C for 30 min and then poured into ice-cold 2 N aqueous HCl (10 mL). The organic layer was then separated and cooled to 0°C. Aqueous hydrogen peroxide (30%, 1 mL) was added dropwise till the yellow color of the solution discharged. The mixture was stirred for 30 min and then diluted with water (10 mL). The organic layer was separated, and the aqueous layer extracted with ether (3 × 10 mL). The organic layers were combined, washed with saturated aqueous sodium bicarbonate (10 mL), water (10 mL), and saturated aqueous solution of sodium chloride (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was subjected to flash chromatography. Elution with 10% ethyl acetate in Skelly B gave enone **1** (20) (473 mg, 85% yield). IR ($CHCl_3$ cast): 1720 (C═O, ester), 1695 (C═O, ketone), 1640 (C═C) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 7.20 (t, 1H, *J* = 4.5 Hz, ═**CH**), 4.18 (m, 2H, OCH_2), 2.55 (m, 2H, O═C$\mathbf{CH_2}$), 2.38 (m, 1H, ═CHC**H**H), 1.25 (t, 3H, *J* = 7.5 Hz, $OCH_2\mathbf{CH_3}$); ^{13}C NMR (APT, 75 MHz in $CDCl_3$) δ: 208.9 (p), 164.4 (p), 146.4 (a), 131.7 (p), 61.1 (p), 44.53 (p), 30.1 (p), 29.2 (p), 22.1 (p), 21.7 (p), 14.1 (a); HRMS, *m/z* (M^+) calcd. for $C_{11}H_{16}O_3$: 196.10994; found: 196.10952. Anal. calcd. for $C_{11}H_{16}O_3$: C 67.32%, H 8.22%; found: C 67.59%, H 8.17%.

2-Methylcyclooctanone (6)

Diisopropylamine (2.62 mL, 0.02 mol) was dissolved in 12.5 mL of THF and cooled to 0°C while stirring. A solution of *n*-butyllithium (1.6 M in THF, 12.5 mL) was added dropwise over 20 min and the mixture was cooled to −78°C. A solution of cyclooctanone (1.26 g, 0.01 mol) in 5 mL of THF was added dropwise over 30 min. The solution was stirred at −78°C for 30 min followed by rapid addition of methyl iodide (1.24 mL, 0.02 mol). After 5 min, the reaction mixture was allowed to warm to room temperature and was stirred for 40 h. The reaction mixture was quenched with 25 mL of water and the aqueous layer was extracted three times with ether (10 mL each). The organic layers were combined, washed twice with water (10 mL each) and once with saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude was subjected to flash chromatography on silica gel, eluting with 2.5% ethyl acetate in Skelly B, to give 2-methylcyclooctanone (**6**) (21, 22) (0.86 g, 89% yield based on consumed starting material) along with 30% recovery of the starting material. IR ($CHCl_3$ cast): 1701 (C═O), 1376 (CH_3) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 2.55 (m, 1H, **CH**CH_3), 2.35 (m, 2H, $\mathbf{CH_2}$C═O), 1.00 (d, 3H, *J* = 7 Hz, $\mathbf{CH_3}$); ^{13}C NMR (APT, 75 MHz in $CDCl_3$) δ: 220.3 (p), 45.3 (a), 40.4 (p), 33.2 (p), 26.4 (p), 26.0

(p), 25.2 (p), 24.1 (p), 6.9 (a); HRMS, *m/z* (M^+) calcd. for $C_9H_{16}O$: 140.12012; found: 140.11977.

2-Methylcycloheptanone (11)
The title compound (23) was prepared from cycloheptanone (5.0 g, 44.6 mmol) in 70% yield using the same procedure as described above.

2-Carbomethoxy-8-methylcyclooctanone (7)
To a suspension of sodium hydride (8.57 g, 0.214 mol, 60% in oil) in 60 mL of DME was added predried dimethyl carbonate (32.17 g, 0.357 mol). The mixture was heated to reflux with stirring. A solution of 2-methylcyclooctanone (**6**) (10 g, 0.0714 mol) in 20 mL of DME was added dropwise and the reaction mixture was refluxed for 19 h, then cooled to 0°C. A 10% aqueous solution of acetic acid was added with stirring until the pH was acidic. The mixture was separated and the aqueous layer was extracted three times with ether (30 mL each). The organic layers were combined, washed with water (30 mL), saturated aqueous solution of sodium bicarbonate (30 mL), water (30 mL), and saturated aqueous solution of sodium chloride (30 mL), dried over magnesium sulfate, filtered, and concentrated. Flash chromatography of the residue on silica gel, eluting with 2.5% ethyl acetate in Skelly B, gave the ß-keto ester **7** (12.0 g, 85% yield) as a colorless oil. This compound was a mixture of two keto forms and an enol form (4:2:3 ratio). IR ($CHCl_3$, cast): 1749 (C=O, ester), 1707 (C=O, ketone), 1640 (C=O, ester, enol form), 1609 (C=C, enol form), 1365 (CH_3) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 13.47 (d, 0.33H, *J* = 1.5 Hz, **OH**, enol form), 3.46 (dd, 0.22H, *J* = 5, 10.5 Hz, OCC**H**CO_2Me, minor keto form), 3.29 (dd, 0.45H, *J* = 3, 15.5 Hz, OCC**H**CO_2Me, major keto form), 3.36 (s, 1.35H, O$\mathbf{CH_3}$, ester, major keto form), 3.31 (s, 0.66H, O$\mathbf{CH_3}$, ester, minor keto form), 3.25 (s, 0.99H, O$\mathbf{CH_3}$, ester, enol form), 1.55 (d, 1.35H, *J* = 7 Hz, $\mathbf{CH_3}$, major keto form), 1.06 (d, 0.99H, *J* = 7 Hz, $\mathbf{CH_3}$, enol form), 1.01 (d, 0.66H, *J* = 7 Hz, $\mathbf{CH_3}$, minor keto form); ^{13}C NMR (75 MHz in $CDCl_3$) for the major keto form, δ: 213.1 (p), 178.5 (p), 56.2 (a), 51.1 (a), 45.2 (a), 37.9 (p), 31.3 (p), 28.2 (p), 26.1 (p), 24.5 (p), 19.1 (a). The following minor ^{13}C NMR signals were observed for the other two isomers: 212.4 (p), 173.8 (p), 170.5 (p), 170.3 (p), 99.6 (p), 54.9 (a), 51.6 (a), 51.5 (a), 46.3 (p), 34.8 (p), 34.4 (a), 31.4 (p), 30.1 (p), 27.4 (p), 26.2 (p), 25.6 (p), 25.0 (p), 24.4 (p), 17.0 (a), 13.9 (a); HRMS, *m/z* (M^+) calcd. for $C_{11}H_{18}O_3$: 198.12560; found: 198.12635. Anal. calcd. for $C_{11}H_{18}O_3$: C 66.64%, H 9.15%; found: C 66.90%, H 9.15%.

2-Carbethoxy-8-methylcyclooctanone (12) and 2-carbethoxy-3-methylcyclooctanone (13)
To a solution of 2-methylcycloheptanone (**11**) (2.56 g, 0.02 mol) in 50 mL of dry ether cooled to 0°C was added boron trifluoride etherate (3.94 mL, 0.032 mol). A solution of ethyl diazoacetate (3.31 mL, 0.032 mol) in 5 mL of dry ether was then added dropwise over 10 min followed by warming to room temperature. After 24 h, the reaction mixture was cooled to 0°C and a saturated aqueous solution of sodium bicarbonate was added to the mixture until the pH was raised to 7. The aqueous layer was extracted three times with ether (10 mL each) and the organic layers were combined, washed twice with water (10 mL each) and once with saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was subjected to flash chromatography on silica gel. Elution with 5% ethyl acetate in Skelly B gave first 2-carbethoxy-8-methylcyclooctanone (**12**) (2.4 g, 56% yield) and then 2-carbethoxy-3-methylcyclooctanone (**13**) (1.6 g, 38% yield). Compound **12** was a mixture of two keto forms and an enol form (3:1:1 ratio). IR ($CHCl_3$ cast): 1747 (C=O, ester), 1708 (C=O, ketone), 1638 (C=O, ester, enol form), 1610 (C=C, enol form) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 12.89 (d, 0.22H, *J* = 1.5 Hz, **OH**, enol form), 4.19 (q, 0.44H, *J* = 7 Hz, O$\mathbf{CH_2}$, enol form), 4.15–4.05 (m, 1.56H, O$\mathbf{CH_2}$, two keto forms), 3.85 (dd, 0.2H, *J* = 4, 11 Hz, COC**H**CO_2Et, minor keto form), 3.50 (dd, 0.58H, *J* = 3.5, 12 Hz, COC**H**CO_2Et, major keto form), 1.95 (t, 0.6H, *J* = 7 Hz, $OCH_2\mathbf{CH_3}$, minor keto form), 1.28 (t, 0.66H, *J* = 7 Hz, $OCH_2\mathbf{CH_3}$, enol form), 1.21 (t, 1.74H, *J* = 7 Hz, $OCH_2\mathbf{CH_3}$, major keto form), 1.12 (d, 0.66H, *J* = 7 Hz, $\mathbf{CH_3}$, enol form), 1.11 (d, 1.74H, *J* = 7 Hz, $\mathbf{CH_3}$, major keto form), 0.95 (d, 0.6H, *J* = 7 Hz, $\mathbf{CH_3}$, minor keto form); ^{13}C NMR (75 MHz in $CDCl_3$) for the major keto form, δ: 215.0 (p), 170.24 (p) 61.1 (p), 56.4 (a), 45.1 (a), 35.0 (p), 28.5 (p), 25.9 (p), 25.6 (p), 24.2 (p), 19.0 (a), 14.0 (a). The following minor ^{13}C NMR signals were observed for the other two isomers: 213.7 (p), 177.9 (p), 170.15 (p), 99.6 (p), 60.9 (p), 60.1 (p), 55.0 (a), 46.4 (a), 37.7 (p), 34.1 (a), 31.3 (p), 30.9 (p), 30.2 (p), 27.2 (p), 26.0 (p), 24.7 (p), 24.5 (p), 24.4 (p), 16.7 (a), 14.3 (a), 13.7 (a); HRMS, *m/z* (M^+) calcd. for $C_{12}H_{20}O_3$: 212.14125; found: 212.14087. Compound **13** existed completely in the keto form: IR ($CHCl_3$, cast): 1745 (C=O, ester), 1705 (C=O, ketone), 1385 (CH_3) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 4.10 (m, 2H, O$\mathbf{CH_2}$), 3.30 (d, 1H, *J* = 11 Hz, COC**H**CO_2Et), 2.75–2.56 (m, 1H, C**H**HC=O), 2.54–2.23 (m, 1H, CH**H**C=O), 1.20 (t, 3H, *J* = 7 Hz, $OCH_2\mathbf{CH_3}$), 0.95 (d, 3H, *J* = 7 Hz, $\mathbf{CH_3}$); ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ: 211.0 (p), 169.4 (p), 64.7 (a), 61.1 (p), 42.0 (p), 34.7 (a), 34.5 (p), 27.3 (p), 25.6 (p), 23.6 (p), 20.7 (a), 14.1 (a); HRMS, *m/z* (M^+) calcd. for $C_{12}H_{20}O_3$: 212.14125; found: 212.14058.

2-Carbomethoxy-8-methyl-2-cyclooctenone (2)
Sodium hydride (1.02 g, 60% in oil, 25.3 mmol) was suspended in 10 mL of THF with stirring and cooled to 0°C. A solution of 2-carbomethoxy-8-methylcyclooctanone (**7**) (1.0 g, 5.05 mmol) in 5 mL of THF was added dropwise to the suspension over 15 min. When formation of the sodium enolate was complete and hydrogen gas evolution had ceased, a thick suspension developed. Stirring and cooling were continued for 20 min. Then a solution of phenylselenenyl chloride (4.86 g, 25.3 mmol) in 10 mL of THF was added. The reaction mixture was stirred at 0°C for another 15 min, then poured into a solution of ether and aqueous saturated sodium bicarbonate. The aqueous layer was extracted three times with ether (10 mL each). All the organic layers were combined, washed with water twice (10 mL each) and saturated aqueous sodium chloride solution once (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was dissolved in 20 mL of dichloromethane. The solution was stirred at 0°C and aqueous hydrogen peroxide (30%, 2 mL) was added dropwise to the solution. When oxidation was complete, as indicated by the discharge of the yellow color of the solution, the reaction mixture was warmed to room temperature with vigorous stirring for 20 min and then cooled again to 0°C. After 15 min, the suspension of benzeneselenenic acid

was filtered off. The filtrate was washed once with 10 mL of saturated aqueous solution of sodium bicarbonate, twice with water (10 mL each), and once with saturated aqueous solution of sodium chloride (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was subjected to flash chromatography on silica gel. Elution with 10% ethyl acetate in Skelly B gave 2-carbomethoxy-8-methyl-2-cyclooctenone (**2**) (0.86 g, 86% yield) as a colorless oil. IR ($CHCl_3$ cast): 1723 (C=O, ester), 1695 (C=O, ketone), 1640 (C=C), 1379 (α-CH_3), 1365 (OCH_3) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 7.18 (t, 1H, *J* = 4.5 Hz, =$\mathbf{CH}$), 3.68 (s, 3H, $O\mathbf{CH_3}$), 2.60 (m, 1H, $\mathbf{CH}CH_3$), 2.34 (m, 2H, =$CH\mathbf{CH_2}$), 1.10 (d, 3H, *J* = 7 Hz, $\mathbf{CH_3}$); ^{13}C NMR (APT, 75 MHz in $CDCl_3$) δ: 211.0 (p), 165.0 (p), 147.0 (a), 131.4 (p), 52.2 (a), 47.5 (a), 30.2 (p), 29.7 (p), 26.0 (p), 21.5 (p), 15.3 (a); HRMS, *m/z* (M^+) calcd. for $C_{11}H_{16}O_3$: 196.10984; found: 196.11022. Anal. calcd. for $C_{11}H_{16}O_3$: C 67.32%, H 8.22%; found: C 67.23%, H 8.31%.

2-Carbethoxy-8-methyl-2-cyclooctenone (3)

This compound was prepared from keto ester **12** (500 mg, 2.36 mmol) in 85% yield using the phenylselenenylation – oxidative elimination process described above. IR ($CHCl_3$ cast): 1720 (C=O, ester), 1696 (C=O, ketone), 1639 (C=C), 1378 (α-CH_3), 1369 (CH_3, ester) cm^{-1}; ^1H NMR (300 MHz in $CDCl_3$) δ: 7.18 (t, 1H, *J* = 4.5 Hz, =$\mathbf{CH}$), 4.27 (m, 2H, $O\mathbf{CH_2}$), 2.60 (m, 1H, $\mathbf{CH}CH_3$), 2.35 (m, 2H, $\mathbf{CH_2}CH$=), 1.23 (t, 3H, *J* = 7 Hz, $OCH_2\mathbf{CH_3}$), 1.14 (d, 3H, *J* = 7 Hz, $\mathbf{CH_3}$); ^{13}C NMR (APT, 75 MHz in $CDCl_3$) δ: 211.0 (p), 164.6 (p), 146.0 (a), 131.9 (p), 61.1 (p), 47.7 (a), 30.2 (p), 29.9 (p), 26.1 (p), 21.6 (p), 15.6 (a), 14.1 (a); HRMS, *m/z* (M^+) calcd. for $C_{12}H_{18}O_3$: 210.12560; found: 21.12554. Anal. calcd. for $C_{12}H_{18}O_3$: C 68.55%, H 8.63%; found: C 68.45%, H 8.50%.

General procedure for the preparation of trialkylsilyloxy substituted 1,3-butadienes 17–20

Diisopropylamine (0.25 mL, 1.8 mmol) was dissolved in 5 mL of THF and cooled to 0°C with stirring. A solution of *n*-butyllithium (1.6 M in THF, 1.2 mL, 1.9 mmol) was added dropwise over 20 min. The resulting lithium diisopropylamide solution was then cooled to −78°C followed by dropwise addition of a solution of the corresponding substituted methyl vinyl ketone (100 mg, 1.2 mmol) in 5 mL of THF over 30 min. The solution was stirred at −78°C for 30 min followed by rapid addition of the corresponding trialkylsilyl chloride (1.8 mmol). The reaction mixture was allowed to warm to room temperature after 15 min and stirred at room temperature for 40 h. The reaction mixture was quenched with 10 mL of water and the aqueous layer was extracted three times with Skelly B (10 mL each). The organic solutions were combined, washed twice with water (10 mL each) and once with saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude yellow oil was purified by bulb-to-bulb distillation to give the product.

*2-*tert*-Butyldimethylsilyloxy-3-methyl-1,3-butadiene (17)*

This compound was prepared in an improved yield of 92% yield from 3-methyl-3-buten-2-one using *tert*-butyldimethylsilyl chloride as the trapping reagent according to the reported procedure (14, 24).

2-Triisopropylsilyloxy-3-methyl-1,3-butadiene (18)

The title compound was prepared from 3-methyl-3-buten-2-one using triisopropylsilyl chloride as the trapping reagent. Bulb-to-bulb distillation of the crude product at 80°C/0.2 Torr (1 Torr = 133.3 Pa) gave the desired diene **18** in 70% yield. IR (hexane cast): 1590 (C=C-O), 1384 (CH_3), 1023, 819 (Si-O-C) cm^{-1}; ^1H NMR (300 MHz in C_6D_6) δ: 5.70 (ddd, 1H, *J* = 0.5, 0.5, 2.5 Hz, $C\mathbf{H}H{=}C(CH_3)$), 5.00 (s, br, $CH\mathbf{H}{=}C(CH_3)$), 4.45 (s, 1H, $C\mathbf{H}H{=}C(OTIPS)$), 4.35 (s, 1H, $CH\mathbf{H}{=}C$-(OTIPS)), 1.75 (s, 3H, $\mathbf{CH_3}C$=), 1.13–1.11 (m, 21H, **CH**, $\mathbf{CH_3}$ on TIPS); ^{13}C NMR (75 MHz in C_6D_6) δ: 157.2 (p), 140.2 (p), 113.9 (p), 91.7 (p), 19.9 (a), 18.3 (6C, a), 13.2 (3C, a); HRMS, *m/z* (M^+) calcd. for $C_{14}H_{28}OSi$: 240.19095; found: 240.18995.

trans-*2-*tert*-Butyldimethylsilyloxy-1,3-pentadiene (19)*

Diene **19** was prepared from *trans*-3-penten-2-one using *tert*-butyldimethylsilyl chloride as the trapping reagent. Bulb-to-bulb distillation of the crude product and collecting the fraction at 70°C/0.5 Torr gave the diene in 85% yield. IR (neat film): 1657 and 1641 (C=C, conjugated), 1593 (C=C-O), 1023, 826 (Si-O-C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.17 (qd, 1H, *J* = 7, 14 Hz, $CH_3\mathbf{CH}{=}CH$), 5.88 (qd, 1H, *J* = 2, 14 Hz, $CH_3CH{=}\mathbf{CH}$), 4.29 (s, 1H, =$CH\mathbf{H}$), 4.22 (s, 1H, =$\mathbf{C}HH$), 1.58 (dd, 3H, *J* = 2, 7 Hz, $\mathbf{CH_3}CH$=), 0.99 (s, br, 9H, $(\mathbf{CH_3})_3C$), 0.15 (s, br, 6H, 2 $\mathbf{CH_3}$); ^{13}C NMR (APT, 75 MHz, C_6D_6) δ: 155.4 (p), 129.8 (a), 126.0 (a), 93.4 (p), 25.8 (3C, a), 18.3 (p), 17.3 (a), −4.7 (2C, a); HRMS, *m/z* (M^+) calcd. for $C_{14}H_{28}OSi$: 240.19095; found: 240.18995.

trans-*2-Triisopropylsilyloxy-1,3-pentadiene (20)*

The title compound was prepared from 3-penten-2-one using triisopropylsilyl chloride as the trapping reagent. The crude product was purified by bulb-to-bulb distillation. Diene **20** was collected at 40°C/0.5 Torr in 90% yield. ^1H NMR (300 MHz, C_6D_6) δ: 6.25 (qd, 1H, *J* = 7, 14 Hz, $CH_3\mathbf{CH}{=}CH$), 5.88 (qd, 1H, *J* = 2, 14 Hz, $CH_3CH{=}\mathbf{CH}$), 4.29 (s, br, 1H, $\mathbf{H}HC$=), 4.19 (s, br, 1H, $H\mathbf{H}C$=), 1.60 (dd, 3H, *J* = 2, 7 Hz, =$CH\mathbf{CH_3}$), 1.13 (m, 3H, 3 $Si\mathbf{CH}(CH_3)_2$), 1.02 (d, 18H, *J* = 6.5 Hz, 3 $CH(\mathbf{CH_3})_2$); ^{13}C NMR (300 MHz, C_6D_6) δ: 155.8 (p), 130.0 (a), 126.1 (a), 92.8 (p), 18.3 (a), 17.9 (6C, a), 12.6 (3C, a); HRMS, *m/z* (M^+) calcd. for $C_{14}H_{28}OSi$: 240.19095; found: 240.18994.

General procedure for $FeCl_3$, $SnCl_4$, and $BF_3{\cdot}OEt_2$ catalyzed Diels–Alder reactions

To an ethereal solution (3 mL) of enone (0.24 mmol) was added the diene (2.4 mmol). Lewis acid (0.24 mmol) was then added and the resulting solution was stirred. The progress of the reaction was monitored by TLC. Upon completion, a saturated aqueous sodium bicarbonate solution was added. The ether layer was separated and the aqueous layer was extracted three times with ether (10 mL each). The combined ether solutions were washed with water (10 mL) and saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by flash chromatography (ethyl acetate – Skelly B) to give the desired adduct(s). Yield, time, and temperature of each reaction are shown in Tables 1, 2, and 3. When more than one product was obtained, products are presented in order of elution from flash chromatography.

General procedure for ZnCl$_2$ catalyzed Diels–Alder reactions

Zinc chloride (0.48 mmol) was fused in a reaction flask under an argon atmosphere and dissolved in dry ether (3 mL). A solution of enone (0.24 mmol) in dry ether (1 mL) was added. After stirring at room temperature for 30 min, diene (2.4 mmol) was then added. The resulting mixture was stirred at room temperature. The reaction was monitored with TLC and upon completion was quenched with saturated aqueous sodium bicarbonate solution. The ether layer was separated and the aqueous layer was extracted three times with ether (10 mL each). The combined ether solutions were washed with saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by flash chromatography (ethyl acetate – Skelly B) to give the desired adduct(s). Yields and reaction conditions are shown in Tables 1, 2, and 3.

(1S*, 8S*)-1-Carbethoxy-10-methylbicyclo[6.4.0]dodec-10-en-2-one (**21**): IR (CHCl$_3$ cast): 1738 (C═O, ester), 1705 (C═O, ketone) cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 5.18 (m, 1H, ═C**H**), 4.10 (m, 2H, OC**H**$_2$), 3.15 (m, 1H, C**H**, C-8), 3.11 (dm, 1H, J = 12 Hz, CH**H**C═O), 2.80 (ddd, 1H, J = 1.5, 5.5, 18.5 Hz, C**H**H, C-12), 2.54 (dm, 1H, J = 18 Hz, C**H**H, C-9), 2.16 (dddd, 1H, J = 2, 4, 7, 18.5 Hz, CH**H**, C-12), 2.08 (ddd, 1H, J = 3.5, 5, 12 Hz, C**H**HC═O), 1.58 (s, br, 3H, ═CC**H**$_3$), 1.18 (t, 3H, J = 7 Hz, OCH$_2$C**H**$_3$); ^{13}C (APT, 75 MHz, CDCl$_3$) δ: 212.3 (p), 170.6 (p), 131.6 (p), 118.5 (a), 63.34 (p), 61.5 (p), 37.2 (p), 36.4 (p), 32.8 (a), 32.6 (p), 29.8 (p), 26.2 (p), 25.09 (p), 24.2 (p), 23.4 (a), 14.0 (a); HRMS, m/z (M$^+$) calcd. for $C_{16}H_{24}O_3$: 264.17255; found: 264.17239.

(1S*, 8S*)-1-Carbethoxy-10,11-dimethylbicyclo[6.4.0]dodec-10-en-2-one (**22**): IR (CHCl$_3$ cast): 1738 (C═O, ester), 1705 (C═O, ketone) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ: 4.10 (m, 2H, OC**H**$_2$), 3.18 (m, 1H, C**H**HC═O), 3.12 (m, 1H, C**H**, ring junction), 2.70 (d, 1H, J = 18 Hz, C**H**H, C-12), 2.55 (d, 1H, J = 18 Hz, C**H**H, C-9), 2.20 (d, 1H, J = 18 Hz, CH**H**, C-12), 2.10 (m, 1H, CH**H**C═O), 1.65 (s, br, 3H, ═CC**H**$_3$), 1.55 (s, br, 3H, ═CC**H**$_3$), 1.15 (t, 3H, J = 7 Hz, OCH$_2$C**H**$_3$); ^{13}C (APT, 75 MHz, CDCl$_3$) δ: 212.7 (p), 170.6 (p), 123.3 (p), 122.8 (p), 64.1 (p), 61.4 (p), 38.0 (p), 37.2(p), 33.0 (a), 33.6 (p), 30.7 (p), 29.8 (p), 26.3 (p), 24.3 (p), 19.1 (a), 18.8 (a), 14.0 (a); HRMS, m/z (M$^+$) calcd. for $C_{17}H_{26}O_3$: 278.18820; found: 278.18844.

(1S*, 8S*, 12S*)-1-Carbethoxy-12-methylbycyclo[6.4.0.]-dodec-10-en-2-one (23) and (1S*, 8S*, 12R*)-1-carbethoxy-12-methylbicyclo[6.4.0]dodec-10-en-2-one (**24**)

The products **23** and **24** were obtained as an inseparable mixture in an 85:15 ratio. For the mixture: IR (CHCl$_3$ cast): 1736 (C═O, ester), 1702 (C═O, ketone) cm^{-1}; HRMS, m/z (M$^+$) calcd. for $C_{16}H_{24}O_2$: 264.17255; found: 264.17258. Anal. calcd. for $C_{16}H_{24}O_2$: C 72.69%, H 9.15%; found: C 72.56%, 9.34%. For the major isomer **23**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.50–5.60 (m, 2H, C**H**═C**H**), 4.15 (m, 2H, OC**H**$_2$), 3.00–3.10 (m, 2H, C**H** ring junction, and CH**H**C═O), 2.96 (q, 1H, J = 7.5 Hz, CH$_3$C**H**CH═), 2.40 (m, 1H, C**H**HCH═), 2.15 (ddd, 1H, J = 7.5, 8, 13 Hz, C**H**HC═O), 1.90–1.30 (m, 7H, 3 C**H**$_2$ and CH**H**CH═), 1.25 (t, 3H, J = 7 Hz, OCH$_2$C**H**$_3$), 1.15 (d, 3H, J = 7.5 Hz, C**H**$_3$CHCH═); ^{13}C NMR (APT, 75 MHz, CDCl$_3$) δ: 210.9 (p), 171.8 (p), 131.3 (a), 123.4 (a), 65.4 (p), 61.6 (p), 40.9 (p), 35.0 (a), 34.5 (a), 32.4 (p), 30.2 (p), 27.5 (p), 27.3 (p), 23.3 (p), 16.6 (a), 13.9 (a). For the minor isomer **24**: ^{1}H NMR δ: 1.07 (d, 3H, J = 7 Hz, C**H**$_3$); ^{13}C NMR δ: 211.1 (p), 130.1 (a), 123.6 (a), 63.4 (p), 60.6 (p), 40.3 (p), 32.2 (a), 32.1 (p), 31.8 (p), 29.8 (a), 27.3 (p), 26.2 (p), 24.0 (p), 18.0 (a), 14.1 (a).

(1S*, 8S*, 9R*, 12S*)-1-Carbethoxy-9,12-dimethylbicyclo-[6.4.0]dodec-10-en-2-one (**25**): IR (CHCl$_3$, cast): 1738 (C═O, ester), 1697 (C═O, ketone) cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.60 (ddd, 1H, J = 3, 5, 10 Hz, ═C**H**, C-11), 5.20 (ddd, 1H, J = 1, 2, 10 Hz, ═C**H**, C-10), 4.10 (m, 2H, OC**H**$_2$), 3.30 (m, 2H, C**H**, C-12 and CH**H**C═O), 3.10 (m, 1H, C**H** ring junction), 2.60 (m, 1H, C**H**, C-9), 2.22 (m, 1H, C**H**HC═O), 1.20 (t, 3H, J = 7 Hz, OCH$_2$C**H**$_3$), 1.15 (d, 3H, J = 7.5, C**H**$_3$CHCH═), 1.00 (d, 3H, J = 7.5 Hz, ═CHCHC**H**$_3$); ^{13}C NMR (APT, 75 MHz, CDCl$_3$), δ: 211.8 (p), 171.0 (p), 131.9 (a), 127.9 (a), 68.0 (p), 61.9 (p), 39.2 (p), 38.1 (a), 32.5 (a), 31.7 (a), 30.4 (p), 27.2 (p), 27.1 (p), 25.2 (p), 18.0 (a), 17.0 (a), 13.9 (a); HRMS, m/z (M$^+$) calcd. for $C_{17}H_{26}O_3$: 278.18800; found: 278.18800. Anal. calcd. for $C_{17}H_{26}O_3$: C 73.33%, H 9.41%; found: C 73.44%, H 9.78%.

(1S*, 8S*, 12S*)-1-Carbethoxy-10,12-dimethylbicyclo-[6.4.0]dodec-10-en-2-one (**26**) and (1S*, 8S*, 12R*)-1-carbethoxy-10,12-dimethylbicyclo[6.4.0]dodec-10-en-2-one (**27**)

The two isomeric products were obtained as an inseparable 77:23 mixture. For the mixture: IR (CHCl$_3$ cast): 3058 (═CH), 1738 (C═O, ester), 1704 (C═O, ketone) cm^{-1}; HRMS, m/z (M$^+$) calcd. for $C_{17}H_{26}O_3$: 278.18820; found: 278.18587. For the major isomer **26**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.06 (s, br, 1H, ═C**H**), 4.20–4.00 (m, 2H, OC**H**$_2$), 3.05–2.95 (m, 2H, C**H** ring junction and HC**H**C═O), 2.80 (m, 1H, C**H**, C-12), 2.28–2.10 (m, 2H, C**H**$_2$, C-9), 1.68 (s, 3H, C**H**$_3$C═), 1.20 (t, 3H, J = 7.5 Hz, OCH$_2$C**H**$_3$), 1.02 (d, 3H, J = 7 Hz, C**H**$_3$CH); ^{13}C NMR (APT, 75 MHz, CDCl$_3$) δ: 211.1 (p), 170.7 (p), 130.7 (p), 124.2 (a), 63.3 (p), 60.5 (p), 40.2 (p), 36.6 (p), 32.8 (a), 32.1 (p), 30.0 (a), 27.6 (p), 26.2 (p), 24.0 (p), 23.5 (a), 18.3 (a), 14.1 (a). For the minor isomer **27**: ^{1}H NMR (300 MHz, CDCl$_3$) δ: 5.26 (s, br, ═C**H**), 2.75–2.65 (m, 2H, C**H**, ring junction and C**H**, C-12), 2.40 (m, 1H, C**H**HC═O), 1.65 (s, 3H, ═CC**H**$_3$), 1.10 (d, 3H, J = 7 Hz, CHC**H**$_3$); ^{13}C NMR (APT, 75 NHz, CDCl$_3$) δ: 210.8 (p), 172.1 (p), 130.5 (p), 125.4 (a), 65.0 (p), 61.5 (p), 41.2 (p), 35.6 (a), 35.1 (a), 34.9 (p), 29.8 (p), 27.6 (p), 27.0 (p), 23.0 (p), 16.9 (a), 14.0 (a).

General procedure for the SnCl$_4$ catalyzed Diels–Alder reaction of trialkylsilyloxy substituted dienes 17–20

Stannic chloride (0.24 mmol) was added to an ether solution (3 mL) of enone **2** (0.24 mmol) at −78°C and stirred for a period of time to allow for the formation of the complex of stannic chloride and the dienophile **2**. Then an ether solution (1 mL) of diene (0.48 mmol for dienes **18** and **20**, 2.4 mmol for dienes **17** and **19**) was added and the reaction was monitored by TLC. Upon completion of the reaction, saturated aqueous sodium bicarbonate solution was added. The ether layer was separated and the aqueous layer was extracted three times with ether (10 mL each). The combined ether solutions were washed with water (10 mL) and saturated aqueous sodium chloride solution (10 mL), dried over anhydrous magnesium sulfate, and concentrated. The crude product was purified by flash chromatography to give the desired product(s). Yields of products and individual reaction conditions are shown in Table 3.

(1S, 3R*, 8S*)-1-Carbethoxy-3,10,11-trimethylbicyclo-[6.4.0]dodec-10-en-2-one (28)*: IR ($CHCl_3$, cast): 1737 (C═O, ester), 1695 (C═O, ketone), 1374 (CH_3) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.15 (m, 2H, OC**H**$_2$), 3.25 (m, 1H, CH$_3$C**H**C═O), 2.66 (m, 2H, ═CC**H**$_2$, C-9), 2.59 (s, 2H, C**H**$_2$C=, C-12), 1.63 (s, br, 3H, ═CC**H**$_3$), 1.54 (s, br, 3H, ═CC**H**$_3$), 1.21 (t, 3H, *J* = 7 Hz, OCH$_2$C**H**$_3$), 1.04 (d, 3H, *J* = 7 Hz, CHC**H**$_3$); ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ: 216.8 (p), 172.2 (p), 124.0 (p), 121.7 (p), 64.4 (p), 60.9 (p), 42.1 (a), 40.0 (p), 36.50 (a), 36.45 (p), 32.4 (p), 31.9 (p), 26.5 (p), 25.8 (p), 19.4 (a), 19.04 (a), 19.03 (a), 14.1 (a); HRMS, *m/z* (M$^+$) calcd. for $C_{18}H_{28}O_3$: 292.20386; found: 292.20349. Anal. calcd. for $C_{18}H_{28}O_3$: C 73.93%, H 9.65%; found: C 74.02%, H 9.42%.

(1S, 3R*, 8S*)-1-Carbethoxy-3,10-dimethylbicyclo-[6.4.0]-dodec-10-en-2-one (29)*: IR ($CHCl_3$, cast): 1695 (C═O, ketone), 1737 (C═O, ester) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.33 (m, 1H, ═C**H**), 4.17 (m, 2H, OC**H**$_2$), 3.25 (m, 1H, C**H**CH$_3$), 2.82–2.50 (m, 4H, C**H**$_2$CH═C(CH$_3$)C**H**$_2$), 1.60 (s, 3H, C**H**$_3$C═), 1.23 (t, 3H, OCH$_2$C**H**$_3$), 1.04 (d, 3H, *J* = 6.5 Hz, C**H**$_3$); ^{13}C NMR (APT, 75 MHz in $CDCl_3$) δ: 216.9 (p), 172.2 (p), 132.4 (p), 116.9 (a), 63.3 (p), 61.0 (p), 42.1 (a), 38.4 (p), 36.6 (p), 36.5 (a), 32.4 (p), 26.4 (p), 26.3 (p), 25.9 (p), 23.6 (a), 19.3 (a), 14.0 (a); HRMS, *m/z* (M$^+$) calcd. for $C_{17}H_{26}O_3$: 278.18820; found: 278.18771. Anal. calcd. for $C_{17}H_{26}O_3$: C 73.35%, H 9.41%; found: C 73.35%, H 9.59%. INPET: irr. H at δ 5.33 (4946 Hz), found C signals from ^{13}C NMR at δ 63.3 (**C**, ring juction), 38.4 (═CH**C**H$_2$), 26.3 (═C(CH$_3$)**C**H$_2$), 23.7 (═C**C**H$_3$); irr. H at δ 3.25 (4337.4 Hz), found C signals from ^{13}C NMR at δ 217.0 (**C**═O ketone), 36.6 (**C**H$_2$CH(CH$_3$)), 25.9(**C**H$_2$), 19.3 (CH**C**H$_3$); irr. H at δ 1.04 (3679.3 Hz) found C signals from ^{13}C NMR at δ 217.0 (**C**═O ketone), 42.1 (**C**H(CH$_3$)).

(1R, 3R*, 8S*, 12S*)-1-Carbethoxy-3,10,12-trimethylbicyclo[6.4.0]dodec-10-en-2-one (30) and diastereomer 31*

In this Diels–Alder reaction, an inseparable mixture of **30** and **31** was obtained in a ratio of 4:1. For the mixture: IR ($CHCl_3$, cast): 1723 (C═O, ester), 1696 (C═O, ketone) cm^{-1}; HRMS, *m/z* (M$^+$) calcd. for $C_{18}H_{28}O_3$: 292.20386; found: 292.20374. Anal. calcd. for $C_{18}H_{28}O_3$: C 73.93%, H 9.65%; found: C 73.90%, H 9.69%. For the major isomer **30**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.08 (m, 1H, ═C**H**), 4.15 (m, 2H, OC**H**$_2$), 2.85 (m, 1H, CH$_3$**CH**CH═), 2.60 (m, 1H, **CH**, ring junction), 2.55 (m, 1H, C**H**C═O), 2.29 (dd, 1H, *J* = 6, 18 Hz, CH**H**C═), 2.05 (dd, 1H, *J* = 6, 18 Hz, C**H**HC═), 1.60 (s, 3H, ═CC**H**$_3$), 1.20 (t, 3H, *J* = 7 Hz, OCH$_2$C**H**$_3$), 0.95 (d, 3H, *J* = 6.5 Hz, C**H**$_3$CHC═O), 0.88 (d, 3H, *J* = 7.5 Hz, C**H**$_3$CHCH═); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 214.3 (p), 173.5 (p), 132.2 (p), 125.0 (a), 65.3 (p), 60.9 (p), 45.2 (a), 38.8 (a), 38.4 (a), 34.7 (p), 33.5 (p), 31.2 (p), 26.0 (p), 23.3 (a), 21.0 (p), 18.9 (a), 17.9 (a), 14.1 (a). For the minor isomer **31**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.18 (s, br, ═C**H**), 1.26 (t, 3H, *J* = 7 Hz, OCH$_2$C**H**$_3$), 1.19 (d, 3H, *J* = 7 Hz, C**H**$_3$), 1.12 (d, 3H, *J* = 7 Hz, C**H**$_3$); ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ: 171.9 (p), 131.4 (p), 124.3 (a), 65.8 (p), 60.4 (p), 41.8 (a), 38.6 (p), 37.0 (a), 36.1 (p), 31.6 (a), 31.2 (p), 26.2 (p), 25.0 (p), 23.3 (a), 20.0 (a), 18.9 (a), 16.1 (a).

(1R, 3R*, 8S*, 12S*)-1-Carbomethoxy-3,10,12-trimethylbicyclo[6.4.0]dodec-10-en-2-one (32) and diastereomer 33*

For the mixture of **32** and **33**: IR ($CHCl_3$, cast): 1733 (C═O, ester), 1699 (C═O, ketone) cm^{-1}; HRMS, *m/z* (M$^+$) calcd. for $C_{17}H_{26}O_3$: 278.18820; found: 278.18799. Anal. calcd. for $C_{17}H_{26}O_3$: C 73.35%, H 9.42%; found: C 73.46%; H 9.35%. For the major isomer **32**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.13 (m, 1H, ═C**H**), 3.72 (s, 3H, OC**H**$_3$), 2.84 (m, 1H, CH$_3$**CH**CH═), 2.60 (m, 1H, **CH**, ring junction), 2.50 (m, 1H, C**H**C═O), 2.30 (dd, 1H, *J* = 10.5, 19 Hz, CH**H**C═), 2.07 (dd, 1H, *J* = 8, 19 Hz, C**H**HC═), 1.67 (s, 3H, ═CC**H**$_3$), 0.98 (d, 3H, *J* = 6.5 Hz, C**H**$_3$CHC═O), 0.90 (d, 3H, *J* = 7.0 Hz, C**H**$_3$CHCH═); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 214.2 (p), 174.1 (p), 132.2 (p), 125.0 (a), 65.4 (p), 51.9 (a), 45.2 (a), 38.8 (a), 38.46 (a), 34.7 (p), 33.5 (p), 31.0 (p), 26.0 (p), 22.8 (a), 21.1 (p), 18.8 (a), 17.9 (a). For the minor isomer **33**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.18 (s, br, ═C**H**), 3.67 (s, 3H, OC**H**$_3$), 3.13 (m, 1H, ═CH**CH**CH$_3$), 2.97 (m, 1H, C**H**C═O), 1.15 (d, 3H, *J* = 7.5 Hz, C**H**$_3$CHC═O), 1.09 (d, 3H, *J* = 7.5 Hz, C**H**$_3$CHCH═); ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ: 131.3 (p), 124.3 (a), 66.8 (p), 51.5 (a), 41.9 (a), 38.54 (p), 36.6 (a), 36.0 (p), 31.7 (a), 26.1 (p), 24.7 (p), 23.4 (a), 19.9 (a), 18.0 (a).

(1S, 3R*, 8S*)-1-Carbomethoxy-10-triisopropylsilyloxy-3,11-dimethylbicyclo[6.4.0]dodec-10-en-2-one (34)*

In this reaction, the solution of dienophile **2** and stannic chloride was stirred for 20 min at −78°C and then the diene **18** was added dropwise. The adduct **34** was obtained as the only isomer in 90% yield. IR ($CHCl_3$, cast): 1744 (C═O, ester), 1696 (C═O, ketone), 1658 (C═C) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ: 3.40 (s, 3H, OC**H**$_3$), 3.05 (d, br, 1H, *J* = 18 Hz, C**H**HC(OTIPS)═), 2.95–2.85 (m, 2H, **CH**CH$_3$ and **CH** ring junction), 2.83 (d, 1H, *J* = 18 Hz, C**H**HC(CH$_3$)═), 2.64 (d, br, 1H, *J* = 18 Hz, CH**H**C(CH$_3$)═), 1.77 (s, 3H, ═CC**H**$_3$), 1.73 (d, 1H, *J* = 18 Hz, CH**H**C(OTIPS)═), 1.25–1.00 (m, 26H, 3 Si**CH**(C**H**$_3$)$_2$, 2 C**H**$_2$ and C**H**H), 0.97 (d, 3H, *J* = 7.5 Hz, C**H**$_3$); ^{13}C NMR (APT, 75 MHz, C_6D_6) δ: 215.1 (p), 172.1 (p). 142.2 (p), 106.8 (p), 63.8 (p), 51.9 (a), 42.0 (a), 39.0 (p), 37.9 (a), 36.5 (p), 32.6 (p), 31.3 (p), 26.3 (p), 26.1 (p), 19.5 (a), 18.3 (a, 6C), 16.6 (a), 14.2 (a), 13.5 (a, 3C); HRMS, *m/z* (M$^+$) calcd. for $C_{25}H_{44}O_4Si$: 436.30090; found: 436.30084. Anal. calcd. for $C_{25}H_{44}O_4Si$: C 68.76%, H 10.16%; found: C 68.87%, H 10.30%.

(1R, 3R*, 8S*, 12S*)-10-*tert*-Butyldimethylsilyloxy-1-carbomethoxy-3,12-dimethylbicyclo[6.4.0]dodec-10-en-2-one (35) and diastereomer 36*

In this reaction, the solution of enone **2** and stannic chloride was stirred for 20 min at −78°C and then diene **19** was added. The mixture of **35** and **36** was obtained in 89% yield as an inseparable mixture of two isomers in a ratio of 2:1. For the mixture: IR ($CHCl_3$, cast): 1730 (C═O, ester), 1694 (C═O, ketone) cm^{-1}; HRMS, *m/z* (M$^+$) calcd. for $C_{22}H_{30}O_4Si$: 394.25294; found: 394.25318. For the major isomer **35**: ^{1}H NMR (300 MHz, C_6D_6) δ: 4.72 (s, br, 1H, ═C**H**), 3.32 (s, 3H, OC**H**$_3$), 3.15 (m, 1H, CH$_3$C**H**CH═), 2.93 (m, 1H, CH$_3$C**H**C═O), 2.30 (dddd, 1H, *J* = 1.5, 3, 9.5, 18 Hz, CH**H**, C-9), 2.10 (dddd, 1H, *J* = 1.5, 3, 7.5, 18 Hz, C**H**H, C-9), 1.27

(d, 3H, J = 7 Hz, $\mathrm{C\mathbf{H}_3CHC{=}O}$), 1.17 (d, 3H, J = 7.5 Hz, $\mathrm{C\mathbf{H}_3CHCH{=}}$), 1.00 (s, 9H, $\mathrm{SiC(C\mathbf{H}_3)_3}$), 0.19 (m, 6H, 2 $\mathrm{SiC\mathbf{H}_3}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{C_6D_6}$) δ: 211.8 (p), 173.4 (p), 148.6 (p), 107.7 (a), 65.4 (p), 51.4 (a), 46.9 (a), 41.4 (a), 39.0 (p), 38,8 (a), 33.6 (p), 31.4 (p), 26.7 (p), 26.5 (a), 25.9 (a, 3C), 21.3 (p), 19.8 (a), 18.8 (a), 18.2 (p), 14.3 (a). For the minor isomer **36**: ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$) δ: 4.78 (s, br, 1H, $\mathrm{{=}C\mathbf{H}}$), 3.39 (s, 3H, $\mathrm{OC\mathbf{H}_3}$), 2.83 (m, 1H, $\mathrm{CH_3C\mathbf{H}CH{=}}$), 2.55 (m, 1H, $\mathrm{CH_3C\mathbf{H}C{=}O}$), 1.15 (d, 3H, J = 7.5 Hz, $\mathrm{C\mathbf{H}_3CHC{=}O}$), 0.99 (s, 9H, $\mathrm{SiC(C\mathbf{H}_3)_3}$), 0.18 (s, 6H, 2 $\mathrm{SiC\mathbf{H}_3}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{C_6D_6}$) δ: 215.3 (p), 171.8 (p), 108.2 (a), 67.0 (p), 51.2 (a), 36.5 (p), 37.8 (a), 33.7 (p), 32.3 (p), 31.2 (p), 30.9 (a), 26.0 (a, 3C), 24.9 (p), 22.8 (p), 19.9 (a), 18.9 (a), 14.6 (a), 11.6 (a).

(1R, 3R*, 8S*, 12S*)-1-Carbomethoxy-3,12-dimethylbicyclo[6.4.0]dodecane-2,10-dione (37) and (1R*, 3R*, 8S*, 12S*)-1-carbomethoxy-10-triisopropylsilyloxy-3,12-dimethylbicyclo[6.4.0]dodec-9-en-2-one (38)*

In this reaction, the solution of enone **2** and stannic chloride was stirred for 1 h at −78°C and then diene **20** was added. Ketone **38** (1% yield) and dione **37** (98% yield) were separated by flash chromatography. Compound **38**: IR ($\mathrm{CHCl_3}$, cast): 1739 (C=O, ester), 1694 (C=O, ketone), 1674 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$) δ: 4.92 (dd, 1H, J = 1, 6 Hz, $\mathrm{{=}C\mathbf{H}}$), 3.50 (s, 3H, $\mathrm{OC\mathbf{H}_3}$), 3.20 (m, br, 1H, **CH**, ring junction), 2.70 (m, 1H, $\mathrm{CH_3C\mathbf{H}C{=}O}$), 2.47 (dd, br, 1H, J = 10, 16 Hz, $\mathrm{C\mathbf{H}HCOTIPS}$), 2.20 (m, 2H, $\mathrm{CH\mathbf{H}COTIPS}$, $\mathrm{C\mathbf{H}CH_3}$), 1.22 (d, 3H, J = 6.5 Hz, $\mathrm{CHC\mathbf{H}_3}$), 1.02 (d, 3H, J = 6 Hz, $\mathrm{C\mathbf{H}_3CHCO}$), 1.11 (s, br, 18H, 3 $\mathrm{SiCH(C\mathbf{H}_3)_2}$), 1.08 (m, 3H, 3 $\mathrm{SiC\mathbf{H}(CH_3)_2}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{C_6D_6}$) δ: 215.9 (p), 171.7 (p), 149.2 (p), 109.1 (a), 68.4 (p), 51.3 (a), 40.5 (a), 38.9 (a), 37.8 (p), 37.0 (p), 31.2 (p), 29.3 (a), 28.2 (p), 23.6 (p), 20.2 (a), 18.2 (a, 6C), 18.1 (a), 13.0 (a, 3C); HRMS, *m/z* ($\mathrm{M^+}$) calcd. for $\mathrm{C_{25}H_{44}O_4Si}$: 436.30090; found: 436.30074. Compound **37**, mp 106–107°C (hexane): IR ($\mathrm{CHCl_3}$, cast): 1733 (C=O, ester), 1695 (C=O, ketone) cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$) δ: 3.42 (s, 3H, $\mathrm{OC\mathbf{H}_3}$), 2.73 (m, 1H, $\mathrm{CH_3C\mathbf{H}C{=}O}$), 2.40 (dd, 1H, J = 14, 14 Hz, $\mathrm{C\mathbf{H}HC{=}O}$), 2.27 (dd, 1H, J = 5.5, 14 Hz, $\mathrm{CH\mathbf{H}C{=}O}$), 2.18 (ddd, 1H, J = 2, 4.5, 14 Hz, $\mathrm{CH\mathbf{H}C{=}O}$), 2.09 (m, 1H, $\mathrm{C\mathbf{H}CH_3}$), 1.90 (ddd, 1H, J = 2.5, 2.5, 14 Hz, $\mathrm{C\mathbf{H}HC{=}O}$), 1.02 (d, 3H, J = 6.5 Hz, $\mathrm{C\mathbf{H}_3CHCO}$), 0.90 (d, 3H, J = 6.5 Hz, $\mathrm{C\mathbf{H}_3CH}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{C_6D_6}$) δ: 214.5 (p), 206.6 (p), 171.8 (p), 68.9 (p), 51.5 (a), 48.6 (p), 46.7 (p), 40.7 (a), 39.9 (a), 37.0 (p), 33.3 (a), 28.5 (p), 27.1 (p), 23.1 (p), 19.9 (a), 18.4(a); HRMS, *m/z* ($\mathrm{M^+}$) calcd. for $\mathrm{C_{16}H_{24}O_3}$: 280.16745; found: 280.16707. Anal. calcd. for $\mathrm{C_{16}H_{24}O_3}$: C 68.55%, H 8.63%; found: C 68.72%, H 8.89%.

(1R, 3S*, 8S*, 9R*, 12S*)-1-Carbethoxy-3,9,12-trimethylbicyclo[6.4.0]dodec-10-en-2-one (**39**)*: IR ($\mathrm{CHCl_3}$, cast): 3012 (=CH), 1741 (C=O, ester), 1714 (C=O, ketone), 1684 (C=C) cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 5.56 (ddd, 1H, J = 3, 4, 10 Hz, $\mathrm{{=}C\mathbf{H}}$), 5.21 (ddd, 1H, J = 1, 2, 10 Hz, $\mathrm{{=}C\mathbf{H}}$), 4.15 (m, 2H, $\mathrm{OC\mathbf{H}_2}$), 3.25 (m, 1H, $\mathrm{C\mathbf{H}CH{=}}$), 3.15 (dt, 1H, J = 5, 10 Hz, **CH**, ring junction), 2.81 (qdd, 1H, J = 3, 7, 11 Hz, $\mathrm{CH_3C\mathbf{H}CO}$), 2.30 (m, 2H, $\mathrm{C\mathbf{H}CH{=}}$ and $\mathrm{CH\mathbf{H}}$, C-7), 1.4–1.9 (m, 7H, 3 $\mathrm{C\mathbf{H}_2}$ and $\mathrm{C\mathbf{H}H}$, C-7), 1.22 (t, 3H, J = 7 Hz, $\mathrm{OCH_2C\mathbf{H}_3}$), 1.15 (d, 3H, J = 7 Hz, $\mathrm{C\mathbf{H}_3CHCO}$), 1.08 (d, 3H, J = 7 Hz, $\mathrm{C\mathbf{H}_3CHCH{=}}$), 0.95 (d, 3H, J = 7 Hz, $\mathrm{C\mathbf{H}_3CHCH{=}}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{CDCl_3}$) δ: 214.0 (p), 172.7 (p), 131.5 (a), 128.1 (a), 69.4 (p), 61.5 (p), 49.5 (a), 39.9 (a), 33.4 (a), 32.8 (p), 32.5 (p), 27.0 (p), 25.9 (p), 24.9 (p), 21.1 (a), 18.3 (p), 17.8 (a), 14.0 (a); HRMS, *m/z* ($\mathrm{M^+}$) calcd. for $\mathrm{C_{18}H_{28}O_3}$: 292.20386; found: 292.20308. Anal. calcd. for $\mathrm{C_{18}H_{28}O_3}$: C 73.93%, H 9.65%; found: C 73.87%, H 9.64%.

(1R, 3S*, 8S*, 12S*)-1-Carbethoxy-3,12-dimethylbicyclo[6.4.0]dodec-10-en-2-one (**40**) and diastereomer **41***

Compound **40** and its diastereomer **41** were obtained as an inseparable mixture in a ratio of 4:1. For the mixture: IR ($\mathrm{CHCl_3}$, cast): 3022 (=CH), 1735 (C=O, ester), 1695 (C=O, ketone) cm^{-1}; HRMS, *m/z* ($\mathrm{M^+}$) calcd. for $\mathrm{C_{17}H_{26}O_3}$: 278.39497; found: 278.39497. Anal. calcd. for $\mathrm{C_{17}H_{26}O_3}$: C 73.35%, H 9.41%; found: C 73.38%, H 9.40%. For the major isomer **40**: ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 5.70 (ddd, 1H, J = 3.5, 7, 10 Hz, $\mathrm{C\mathbf{H}{=}}$), 5.46 (ddd, 1H, J = 2, 4.5, 10 Hz, $\mathrm{C\mathbf{H}{=}}$), 4.24 (m, 2H, $\mathrm{OC\mathbf{H}_2}$), 2.87 (m, 1H, $\mathrm{CH_3C\mathbf{H}CH{=}}$), 2.60 (m, 2H, **CH**, ring junction, and $\mathrm{CH_3C\mathbf{H}CO}$), 2.30 (m, 1H, $\mathrm{CH\mathbf{H}CH{=}}$), 2.15 (m, 1H, $\mathrm{C\mathbf{H}HCH{=}}$), 1.25 (t, 3H, J = 7 Hz, $\mathrm{OCH_2C\mathbf{H}_3}$), 1.08 (d, 3H, J = 7.5 Hz, $\mathrm{C\mathbf{H}_3CHC{=}O}$), 0.98 (d, 3H, J = 7.5 Hz, $\mathrm{C\mathbf{H}_3CHCH{=}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 213.9 (p), 173.3 (p), 130.6 (a), 124.8 (a), 65.2 (p), 61.0 (p), 45.9 (a), 38.2 (a), 38.0 (a), 34.1 (p), 30.1 (p), 28.8 (p), 26.3 (p), 21.0 (p), 19.4 (a), 17.2 (a), 14.1 (a). For the minor isomer **41**: ^{1}H NMR (500 MHz in $\mathrm{CDCl_3}$) δ: 5.58 (m, 1H, =CH), 5.49 (ddd, 1H, J = 2, 4.5, 10 Hz, =CH), 4.18 (m, 2H, $\mathrm{OC\mathbf{H}_2}$), 2.54 (m, 1H, $\mathrm{CH\mathbf{H}CH{=}}$), 1.28 (t, 3H, J = 7.5 Hz, $\mathrm{OCH_2C\mathbf{H}_3}$), 1.22 (d, 3H, J = 7.5 Hz, $\mathrm{C\mathbf{H}_3}$), 1.14 (d, 3H, J = 6.5 Hz, $\mathrm{C\mathbf{H}_3}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 213.9 (p), 171.8 (p), 130.2 (a), 124.1 (a), 65.2 (p), 60.5 (p), 41.9 (a), 40.4 (a), 36.2 (a), 33.6 (p), 31.1 (p), 29.7 (p), 26.0 (p), 24.8 (p), 20.0 (a), 18.0 (a), 14.1 (a).

(1R, 2R*, 4R*, 9S*, 10S*)-2-Carbethoxy-4-methyltricyclo[8.2.1.0^{2,9}]tridec-11-en-3-one (**42**) and (1S*, 2R*, 4S*, 9S*, 10R*)-2-carbethoxy-4-methyltricyclo-[8.2.1.0^{2,9}]tridec-11-en-3- one (**43**)*

For compound **42**: IR ($\mathrm{CHCl_3}$, cast): 3064 (=CH), 1735 (C=O, ester), 1689 (C=O, ketone) cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 6.35 (dd, 1H, J = 3, 5.5 Hz, $\mathrm{{=}C\mathbf{H}}$, C-11), 5.93 (dd, 1H, J = 3, 5.5 Hz, $\mathrm{{=}C\mathbf{H}}$, C-12), 4.15 (qd, 1H, J = 7.5, 11 Hz, $\mathrm{OC\mathbf{H}H}$), 3.98 (qd, 1H, J = 7.5, 11 Hz, $\mathrm{OCH\mathbf{H}}$), 3.30 (s, br, 1H, **CH**, ring junction), 2.49–2.60 (m, 3H, $\mathrm{{=}CHC\mathbf{H}}$, $\mathrm{C\mathbf{H}CH_3}$, $\mathrm{CHCH\mathbf{H}}$), 2.00 (dddd, 1H, J = 1, 11, 11, 15 Hz, $\mathrm{C\mathbf{H}CH{=}}$), 1.24 (t, 3H, J = 7.5 Hz, $\mathrm{OCH_2C\mathbf{H}_3}$), 1.10 (d, 3H, J = 7 Hz, $\mathrm{C\mathbf{H}_3}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{CDCl_3}$) δ: 213.3 (p), 172.2 (p), 141.1 (a), 135.5 (a), 60.8 (p), 68.7 (p), 54.1 (a), 53.8 (a), 51.8 (a) 49.1 (a), 47.0 (p), 33.4 (p), 31.4 (p), 31.2 (p), 29.7 (p), 21.9 (a), 13.9 (a); HRMS, *m/z* ($\mathrm{M^+}$) calcd. for $\mathrm{C_{17}H_{24}O_3}$: 276.17255; found: 276.17267. Anal. calcd. for $\mathrm{C_{17}H_{24}O_3}$: C 73.88%, H 8.75%; found: C 73.69%, H 8.92%. For compound **43**: IR ($\mathrm{CHCl_3}$, cast): 3010 (=CH), 1736 (C=O, ester), 1690 (C=O, ketone) cm^{-1}; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 6.32 (dd, 1H, J = 3, 5.5 Hz, $\mathrm{{=}C\mathbf{H}}$, C-11), 6.25 (ddd, 1H, J = 0.5, 3, 5.5 Hz, $\mathrm{{=}C\mathbf{H}}$, C-12), 4.20 (m, 2H, $\mathrm{OC\mathbf{H}_2}$), 3.37 (s, 1H, $\mathrm{C\mathbf{H}CH{=}}$), 2.90 (ddd, 1H, J = 3, 3, 12 Hz, **CH**, ring junction), 2.80 (m, 2H, $\mathrm{C\mathbf{H}CH{=}}$ and $\mathrm{C\mathbf{H}CH_3}$), 1.25 (t, 3H, J = 7 Hz, $\mathrm{OCH_2C\mathbf{H}_3}$), 1.00 (d, 3H, J = 7 Hz, $\mathrm{C\mathbf{H}_3}$); ^{13}C NMR (APT, 75 MHz, $\mathrm{CDCl_3}$) δ: 215.6 (p), 174.0 (p), 137.7 (a), 135.3 (a), 71.3 (p), 61.3 (p), 54.5 (a), 49.9 (a), 49.2 (a), 49.1 (p), 45.8 (a), 33.9 (p), 31.3 (p), 28.3 (p), 25.4 (p), 19.7 (a), 14.0 (a); HRMS, *m/z* (M^+) calcd. for $C_{17}H_{24}O_3$: 276.17255; found: 276.17242. Anal. calcd. for $C_{17}H_{24}O_3$: C 73.88%, H 8.75%; found: C 74.20%, H 8.90%.

(1R, 3R*, 8S*)-11-Acetoxy-1-carbethoxy-3-methyl-10-methylenebicyclo[6.4.0]dodec-11-en-2-one (**46**) and (1S*, 3R*, 8S*)-1-carbethoxy-3,10-dimethylbicyclo-[6.4.0]dodec-9-ene-2,11-dione (**47**)*

A gentle stream of oxygen was bubbled through a solution of the Diels–Alder adduct **29** (50 mg, 0.18 mmol), acetic anhydride (0.025 mL, 0.27 mmol), pyridine (0.021 mL, 0.27 mmol), 5,10,15,20-tetraphenyl-21*H*, 23*H*-porphine (5 mg), and 4-dimethylaminopyridine (catalytic amount) in 40 mL of carbon tetrachloride for 20 min. The bubbling was continued while the solution was irradiated with two 200-W tungsten light bulbs for 35 h. After turning off the light, bubbling was continued for another 19 h. The solution was diluted with 20 mL of ether and then washed with saturated aqueous sodium bicarbonate (15 mL), aqueous 1 M HCl (15 mL), and saturated aqueous sodium chloride solution (10 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and concentrated to give the crude product. This crude product was subjected to flash chromatography. Elution with 5% ethyl acetate in Skelly-B gave first the compound **46** (16.3 mg, 31% yield) and then compound **47** (7 mg, 13% yield). For compound **46**: IR (CH_2Cl_2, cast): 1767 (C=O, acetate), 1761 (C=O, ketone), 1744 (C=O, ester), 1682 (C=C, endocyclic), 1678 (C=C, exocyclic) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 5.70 (s, 1H, =C**H**), 5.10 (m, 1H, =CH**H**), 4.95 (s, 1H, =C**H**H), 4.18 (m, 2H, $OC\mathbf{H}_2$), 3.12 (m, 1H, $\mathbf{CH}CH_3$), 2.80 (dddd, 1H, *J* = 2, 2, 4, 15 Hz, $C\mathbf{H}HC{=}CH_2$), 2.70 (m, 1H, C**H**, ring junction), 2.30 (s, 3H, $CO\mathbf{CH}_3$), 2.20 (dd, 1H, *J* = 3, 15 Hz, $CH\mathbf{H}C{=}CH_2$), 1.20 (t, 3H, *J* = 7 Hz, $OCH_2\mathbf{CH}_3$), 0.90 (d, 3H, *J* = 7 Hz, $\mathbf{CH}_3$); ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ: 215.5 (p), 170.4 (p), 169.0 (p), 147.0 (p), 134.7 (p), 114.0 (a), 111.6 (p), 65.5 (p), 61.5 (p), 42.2 (a), 41.3 (a), 38.1 (p), 34.4 (p), 29.8 (p), 29.5 (p), 28.7 (p), 24.9 (p), 20.8 (a), 19.1 (a); HRMS, *m/z* (M^+) calcd. for $C_{19}H_{26}O_5$: 334.17801; found: 334.17771. For compound **47**: IR ($CHCl_3$, cast): 1738 (C=O, ester), 1698 (C=O, ketone), 1682 (C=O, enone) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.60 (dq, 1H, *J* = 1, 5.5 Hz, =C**H**), 4.15 (m, 2H, $OC\mathbf{H}_2$), 3.40 (m, 1H, C**H**CH=), 3.15 (m, 1H, $C\mathbf{H}CH_3$), 3.05 (s, br, 2H, $\mathbf{CH}_2CO$), 1.72 (d, 3H, *J* = 1 Hz, $=C\mathbf{CH}_3$), 1.19 (t, 3H, *J* = 7 Hz, $OCH_2\mathbf{CH}_3$), 1.09 (d, 3H, *J* = 7 Hz, $\mathbf{CH}_3$); ^{13}C NMR (APT 75 MHz, $CDCl_3$) δ: 213.0 (p), 195.2 (p), 171.1 (p), 148.1 (a), 133.3 (p), 64.5 (p), 61.9 (p), 42.2 (a), 41.6 (a), 38.3 (p), 35.5 (p), 27.9 (p), 26.5 (p), 26.1 (p), 19.5 (a), 15.5 (a), 14.0 (a); HRMS, *m/z* (M^+) calcd. for $C_{17}H_{24}O_4$: 292.16745; found: 292.16791.

(1S, 8S*)-1-Carbethoxy-10-methylbicyclo[6.4.0]dodec-9-ene-2,11-dione (**49**)*

This compound was prepared from adduct **21** in 31% yield using the photooxidation process described above. IR ($CHCl_3$ cast): 1733 (C=O, ester), 1708 (C=O, ketone), 1680 (C=O, conjugated ketone) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 6.68 (dd, 1H, *J* = 1, 6 Hz, =C**H**), 4.13 (m, 2H, $OC\mathbf{H}_2$), 3.70 (m, 1H, C**H**, ring junction), 3.13 (dd, 1H, *J* = 1, 18 Hz, C**H**HC=O, C-12), 3.04 (ddd, 1H, *J* = 4, 12, 13 Hz, C**H**HC=O, C-3), 2.69 (d, 1H, *J* = 18 Hz, CH**H**C=O, C-12), 2.21 (ddd, 1H, *J* = 4, 5.5, 13 Hz, CH**H**C=O, C-3), 1.57 (s, 3H, $=C\mathbf{H}_3$), 1.17 (t, 3H, *J* = 7 Hz, $OCH_2\mathbf{CH}_3$); ^{13}C NMR (APT, 75 MHz $CDCl_3$) δ: 208.4 (p), 196.5 (p), 170.4 (p), 147.0 (a), 134.7 (p), 65.9 (p), 62.3 (p), 38.8 (a), 37.3 (p), 30.2 (p), 29.8 (p), 28.0 (p), 26.1 (p), 25.0 (p), 15.5 (a), 13.9 (a); HRMS, *m/z* (M^+) calcd. for $C_{16}H_{22}O_4$: 278.15179; found: 278.15197.

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