mL, 5.13 mmol). Workup in the usual manner and vacuum distillation gave compound **18** (0.72 g 67%): ^{1}H NMR δ 2.16 (s, 2, CH_2), 1.12 (s, 9, $(CH_3)_3$), 1.08–0.75 (m, 9, $(CH_3CH_2)_3Si$)), 0.65 (m, 6, $(CH_3CH_2)_3Si$)); GC MS, *m/z* (relative intensity) 199 ($M^+ - CH_3$, 1), 186 (9), 185 (55), 171 (2), 157 (80), 115 (100), 103 (79), 87 (38), 75 (43), 59 (13); HR MS calcd for $C_{10}H_{21}OSi$ ($M^+ - C_2H_5$) 185.1362, found 185.1364.

α-(Trimethylsilyl)acetophenone (19).[10] Treatment of α-bromoacetophenone (1.02 g, 5.13 mmol) with lithium hexamethyldisilazide, chlorotrimethylsilane, and *n*-BuLi as described above gave, after standard workup and vacuum distillation, the expected trimethylsilyl ketone (0.50 g, 51%): bp 47–50 °C (0.15 mm); ^{1}H NMR δ 8.0–7.6 (m, 2, Ar H's), 7.5–7.2 (m, 3, Ar H's), 2.73 (s, 2, CH_2), 0.07 (s, 9, $(CH_3)_3Si$); GC/MS, *m/z* (relative intensity) 192 (M^+, 25), 191 (75), 178 (16), 177 (100), 135 (54), 105 (13), 103 (13), 77 (28), 75 (76), 73 (23).

α-(Triethylsilyl)acetophenone (20). Treatment of α-bromoacetophenone (1.02 g, 5.13 mmol) with base, chlorotriethylsilane (0.86 mL, 5.13 mmol), and *n*-BuLi as described above gave the crude product. Purification by flash chromatography gave pure compound **20** (0.75 g, 62%): ^{1}H NMR δ 7.9–7.6 (m, 2, Ar H's), 7.45–7.15 (m, 3, Ar H's), 2.72 (s, 2, CH_2), 1.10–0.75 (m, 9, $(CH_3CH_2)_3Si$)), 0.61 (m, 6, $(CH_3CH_2)_3Si$)); GC/MS, *m/z* (relative intensity) 234 (M^+, 0.7), 219 (3), 206 (19), 205 (100), 177 (5), 163 (10), 135 (19), 103 (40), 77 (14), 75 (39); HR MS calcd for $C_{12}H_{17}$)OSi ($M^+ - C_2H_5$), 205.1049, found 205.1053.

Attempted Preparation of α-(Trialkylsilyl)propiophenones. The general procedure described above was applied to α-bromopropiophenone (0.78 mL, 5.10 mmol), first using chlorotrimethylsilane (0.66 mL, 5.13 mmol). After workup in the usual manner, concentration in vacuo afforded an orange oil, which was shown by GC and GC/MS to contain 1-phenylpropyne [80–83%; GC/MS, *m/z* (relative intensity) 116 (M^+, 68), 115 (100), 103 (8), 89 (7), 75 (7), 63 (6), 57 (3), 51 (2), 45 (2)] and only a trace of the desired α-(trimethylsilyl)propiophenone **21** [6–8% by GC; GC/MS, *m/z* (relative intensity) 206 (M^+, 24), 205 (71), 191 (23), 177 (44), 135 (24), 117 (30), 105 (28), 77 (27), 75 (100), 73 (63)]. With α-bromopropiophenone and chlorotriethylsilane (0.86 mL, 5.13 mmol), the analogous procedure gave primarily 1-phenylpropyne (80% by GC analysis) and only a trace of the triethylsilyl ketone **23** [(8% by GC; GC/MS, *m/z* (relative intensity) 248 (M^+, 4), 220 (5), 219 (23), 186 (20), 171 (7), 143 (34), 129 (100), 115 (29), 91 (18), 77 (7)].

Preparation of α-(Trialkylsilyl)camphors. Utilization of the general procedure given above resulted in formation of the isomeric silyl enol ether products. However, if, after addition of *n*-butyllithium to the siloxyvinyl bromide intermediate, the orange solution was stirred at room temperature for 24 h, employment of the same workup and purification conditions afforded good yields of the desired α-(trialkylsilyl)camphors as mixtures of exo and endo isomers.

α-(Trimethylsilyl)camphor (24).[10] The epimeric trimethylsilyl ketones were purified by distillation but could not be readily separated from each other: yield, 0.92 g (80%); bp 48–50 °C (0.25 mm); ^{1}H NMR (as a 1:1 mixture of epimers) δ 2.04 (d, 1)/2.00 (m, 1), 1.91 (m, 1)/1.79 (m, 1), 1.63–1.15 (m, 4), 0.84, 0.80, 0.76, 0.75, 0.73, 0.67 (all s, 3 each, CH_3's); ^{13}C NMR (as a 1:1 mixture of epimers) δ 219.0/218.6 (C-2), 57.8/57.2 (C-1), 48.3/45.9/44.7 (C-3, C-4, and C-7), 30.8/30.1/29.4/24.7 (C-5 and C-6), 20.8/19.8/19.2/18.9 (C-9 and C-10), 9.3/9.0 (C-8), −0.4/−1.3 ($Si(CH_3)_3$); GC/MS, [longer GC retention time epimer] *m/z* (relative intensity) 209 ($M^+ - CH_3$, 30), 196 (100), 195 (8), 165 (17), 154 (14), 123 (11), 108 (14), 95 (73), 73 (88), [shorter GC retention time epimer] 224 (M^+, 11), 209 (39), 197 (18), 196 (66), 181 (44), 165 (25), 119 (19), 108 (57), 95 (72), 73 (100).[10]

α-(Triethylsilyl)camphor (25). The epimeric triethylsilyl ketones were obtained in good yield (1.07 g, 78% from a 5-mmol scale reaction) and were separated by flash chromatography. Major epimer (longer retention time): ^{1}H NMR δ 2.14 (d, 1, J = 3.6 Hz), 2.02 (m, 1), 1.66–1.16 (m, 4), 0.92 (t, 9, J = 7.8 Hz, $(CH_3CH_2)_3Si$)), 0.87 (s, 3, CH_3), 0.84 (s, 3, CH_3), 0.75 (s, 3, CH_3), 0.61 (m, 6, $(CH_3CH_2)_3Si$)); ^{13}C NMR δ 219.9 (C-2), 57.6 (C-1), 46.1 (C-3, C-4, and C-8), 31.3 (C-5 or C-6), 30.5 (C-6 or C-5), 21.0 (C-9 or C-10), 20.2 (C-10 or C-9), 9.4 (C-8), 7.4 ($Si(CH_2CH_3)_3$), 4.3 ($Si(CH_2CH_3)_3$); GC/MS, *m/z* (relative intensity) 251 ($M^+ - CH_3$, 16), 239 (27), 238 (100), 237 (97), 223 (32), 135 (23), 115 (50), 103 (98), 87 (91), 75 (44). Anal. Calcd for $C_{16}H_{30}OSi$, C, 72.11; H, 11.35. Found, C, 71.82; H, 11.49. Minor epimer (shorter GC retention time): ^{1}H NMR δ 2.09 (m, 1), 1.91 (m, 1), 1.72–1.23 (m, 4), 0.98 (t, 9, J = 7.9 Hz, $(CH_3CH_2)_3Si$)), 0.95 (s, 3, CH_3), 0.87 (s, 3, CH_3), 0.83 (s, 3, CH_3), 0.68 (m, 6, $(CH_3CH_2)_3Si$)); ^{13}C NMR δ 220.3 (C-2), 58.3 (C-1), 49.0/46.4/42.5 (C-3, C-4, and C-7), 29.7 (C-5 or C-6), 25.7 (C-6 or C-5), 19.6 (C-9 or C-10), 19.3 (C-10 or C-9), 9.6 (C-8), 7.5 ($Si(CH_2CH_3)_3$), 4.1 ($Si(CH_2CH_3)_3$); GC/MS, *m/z* (relative intensity) 238 ($M^+ - C_2H_4$, 42), 237 (100), 223 (19), 135 (18), 115 (29), 103 (88), 87 (56), 75 (33), 59 (36).

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Registry No. **6**, 3453-00-7; **7**, 10409-56-0; **8**, 814-16-4; **9**, 85234-36-2; **10**, 104464-23-5; **11**, 104464-24-6; **12**, 104487-43-6; **13**, 104464-25-7; **14**, 104464-26-8; **16**, 104464-28-0; **17**, 103230-42-8; **18**, 103230-43-9; **19**, 13735-78-9; **20**, 17718-97-7; **21**, 88257-40-3; **22**, 673-32-5; **23**, 103230-44-0; **24**, 104464-29-1; **25**, 104464-30-4; $PhCOCH_2Br$, 70-11-1; $PhCOCH(CH_3)Br$, 2114-00-3; $(CH_3)_3CCOCH_2Br$, 5469-26-1; CF_3COCH_2Br, 431-35-6; $(EtO)_2POCl$, 814-49-3; $(CF_3CH_2O)_2POCl$, 381-44-2; 3-bromocamphor, 76-29-9; camphor, 76-22-2; chlorotrimethylsilane, 75-77-4; chlorotriethylsilane, 994-30-9; camphor (trifluoroethyl enol phosphate), 104464-27-9.

Quassinoids. 2. A New Approach to the BCD Ring System

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Diels-Alder reaction of 2,6-disubstituted quinones **4** and simple dienes **5** furnished cis adducts **3** in good yields. Basic isomerization provided the *trans*-decalins **11** which were converted into the lactones **2** which are models of the BCD ring system of quassinoids.

Quassinoids are a group of related compounds isolated from plants and trees belonging to the Simaroubacae family.[1] A broad range of biological activity including antileukemic, antineoplastic, insecticidal, and antifeedant properties has led to a keen interest in these compounds and numerous accounts of synthetic efforts have been documented.[2] We have previously proposed[2a] synthetic

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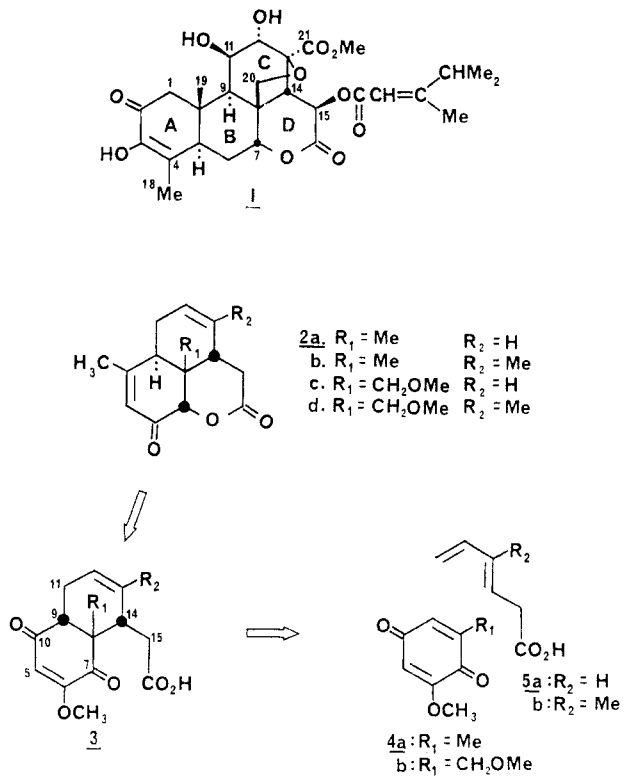
Scheme I



methololgy for and carried out the contruction of a model BCDE ring system in connection with a total synthesis of the potent antineoplastic, bruceantin (**1**) (Scheme I). In this work we present an efficient preparation of the structures **2**, from which we hope to provide a general route to a variety of quassinoids.

The essential elements of our method are an efficient and highly selective Diels–Alder reaction for construction of the BC framework; easy formation of the D ring; good control over the stereochemistry of the centers at C-7 and C-9 (the bruceantin numbering system shown in Scheme I will be used throughout this discussion); and functionalization which would permit A-ring attachment.

Results and Discussion

Quinone **4a** (Scheme II) was readily prepared by Wolff–Kishner reduction of *o*-vanillin followed by oxidation of the resulting phenol **6** with salcomine and oxygen. Quinone **4b** was obtained by selective methylation of the disodium salt of *o*-vanillyl alcohol (**7**)[2a] followed by oxidation. The preparation of diene **5a** has been previously reported.[3] Diene **5b** was prepared by treatment of the readily available aldehyde **9**[4] with diethyl (((trimethylsilyl)oxy)carbonyl)methanephosphonate anion[5] followed by reduction of the resulting chloro acid **10** with zinc and acetic acid. Traditionally, these dienes are prepared from expensive tiglic aldehyde via the Wadsworth–Emmons reaction and deconjugation (LDA, HMPA, kinetic protonation). Use of the aldehyde **9** (available from isoprene in three steps on a 100-g scale) eliminates the need for large quantities of LDA and HMPA.

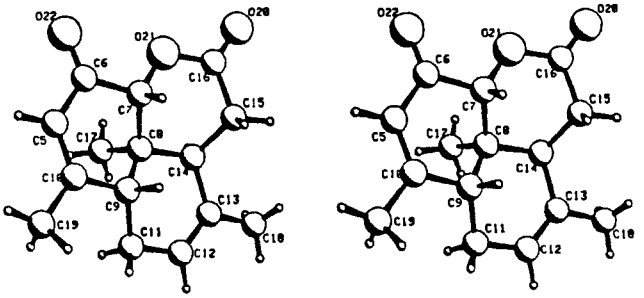


Figure 1. Computer-generated stereodrawing of the final X-ray model of the lactone **16b**.

The Diels–Alder reaction of quinones **4** (Scheme III) with dienes **5** led to the expected cis adducts **3** as crystalline solids in good yield. The adducts obtained from diene **5b** were quite unstable toward acidic reagents including themselves and mild conditions (room temperature for 5 to 10 days) were necessary to obtain cis adducts **3b** and **3d** free of significant contamination by their trans-fused isomers. Compounds **11b** and **11d** could be obtained as the only products by carrying out the reaction in refluxing benzene. The increased reactivity of **3b** and **3d** is most likely due to $A^{1,2}$ strain[6] which is introduced by the methyl group. The facile conversion of cis adducts **3** to the trans-fused **11** was welcomed since the latter structure corresponded to the natural quassinoid configuration. The method of choice for this transformation was to simply stir **3** with saturated sodium bicarbonate at room temperature for several hours. Regio- and stereoselective reduction of the *trans*-decalins **11** was then carried out with sodium borohydride at −30 °C, giving the hydroxy acids **12** as stable crystalline solids and in good yield. The stability of these compounds toward lactonization derives from the fact that the structural requirements of this system enforce a boat-like conformation in the lactone ring. Although these compounds would not lactonize under the influence of proton acids, they could be formed in the presence of dehydrating agents such as acetic anhydride to give reasonable yields of lactones **13**.

Introduction of the methyl group which was to become C-19 was straightforward. Addition of more than 3 equiv of methyllithium to hydroxy acids **12** (Scheme IV) in tetrahydrofuran at −40 °C gave a bright yellow solution of the trianion **14** which upon quenching decomposed to the hydroxy enones **15** in yields ranging from 50% to 70%. The desired BCD ring system was essentially a key step away. Namely, we needed to be able to effect epimerization of the β-hydroxy group at C-7. The hydroxy acids **15** are poor candidates for this transformation, however, because one would expect a considerable "peri" interaction between the C-15 methylene and an axially positioned C-7 hydroxyl. We therefore decided to form the D-ring first (acetic anhydride, pyridine, 25 °C) to obtain lactones **16** (see Figure 1 for an X-ray crystal diagram of compound **16b**). The lactone ring in **16** is constrained to a boat-like conformation whose inherent ring strain could now be relieved by the desired epimerization. In fact, when lactones **16** were treated with the nonnucleophilic base DBU in refluxing tetrahydrofuran, selective formation of lactones **2** was observed. Thus the requisite BCD ring in-

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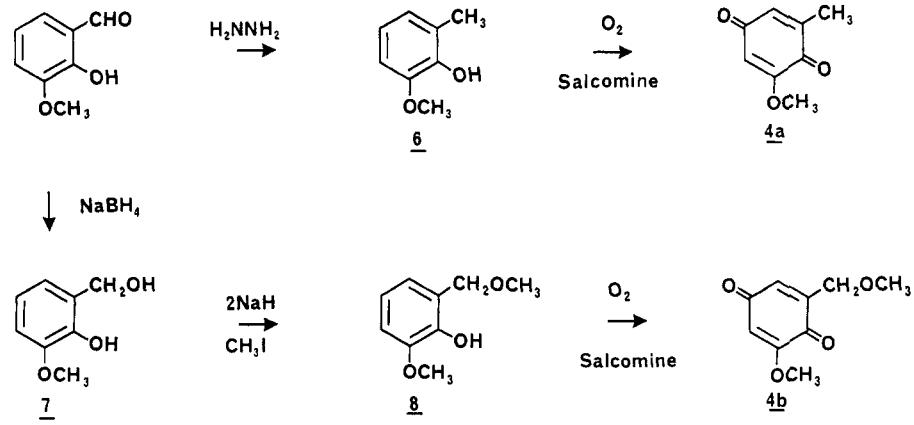
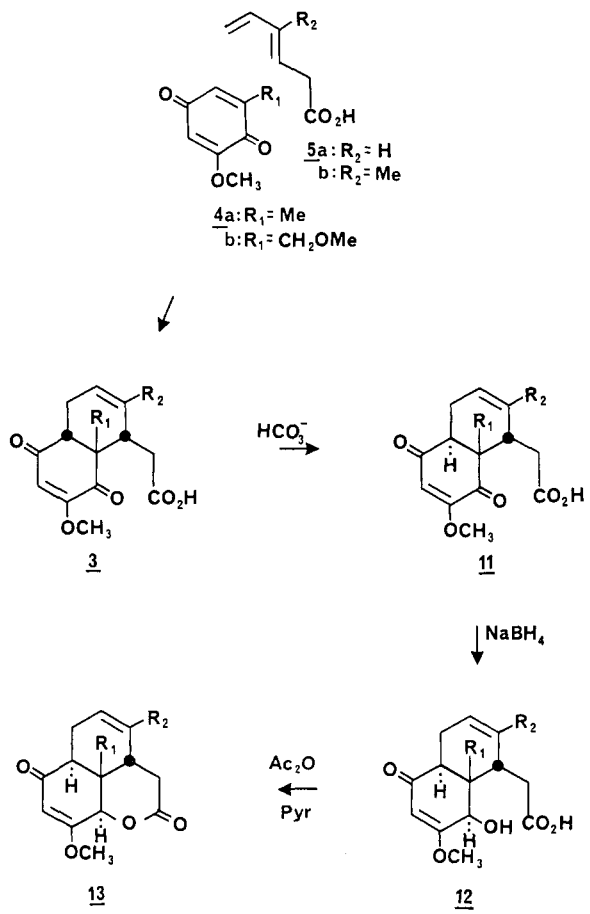
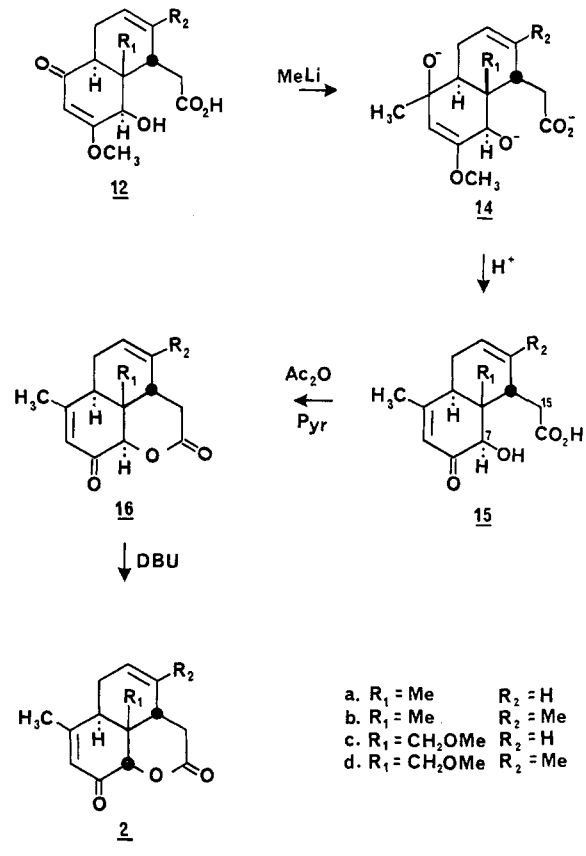
Scheme II



Scheme III



Scheme IV



termediates were prepared through a relatively short sequence and in the case of **2b** in ca. 20% overall yield (unoptimized) from the key Diels–Alder reaction.

Spectral Section

In general spectral assignments were initiated on compounds containing a C-13 methyl substituent (e.g., **2b**). In these cases H-12 was readily identified. Irradiation at H-12 decoupled the geminal pair at H-11. With this information and by performing an additional decoupling experiment H-9 was uncovered in each system. Once the spectral characteristics of the H-9, H-11 subsystem were deduced, identification of the H-14, H-15 group became straightforward. Irradiation of H-13 in the appropriate compounds simplified and identified H-14. Decoupling of H-14 then made the positions of the H-15 protons clear. All measurements of coupling constants and chemical shifts for lactones **2**, **13**, and **16** are listed in Table I and were made

Table I. 500-MHz NMR Spectral Data of Tricyclic Lactones (Taken in $CDCl_3$ Unless Otherwise Noted)

	observed proton, coupling constant (hertz)													
compd	11α	J	11β	J	9	J	14	J	15α	J	15β	J	7	J
2a	2.39–2.47 m		1.92–1.97 m		2.55 bd	12.0	2.39, 2.47 m		2.88 dd	10.7, 17.5	2.48 dd	4.9, 17.5	4.19 s	
b	2.40 bdt	17.2, 5.5	1.89–1.98 m		2.49–2.55 m		2.19 dd	6.4, 11.0	2.95 dd	11.0, 18.2	2.53 dd	6.4, 18.2	4.18 s	
c	2.39 bdt	17.6, 5.5	1.86 dddd	2.5, 12.7, 4.8, 17.6	2.65 bd	12.7	3.07 m		2.86 dd	11.7, 17.1	2.48 dd	3.6, 17.1	4.65 s	
d	2.37 bddd	4.5, 5.3, 17.3	1.83 bdd	12.0, 17.3	2.62 bd	12.0	2.83 bdd	4.5, 11.3	2.92 dd	11.3, 17.5	2.54 dd	4.5, 17.4	4.66 s	
16a	2.41 ddd	4.3, 5.4, 17.0	1.96–2.04 m		2.59 bd	12.0	2.18 m		2.51 t	14.8	2.63 dd	4.1, 14.8	4.63 s	
b	2.38 dt	17.0, 5.0	1.96–2.08 m		2.59 bd	10.7	2.0 m		2.47 t	15.0	2.83 dd	3.7, 15.0	4.66 s	
c	2.38 ddd	4.5, 5.5, 16.5	2.18 bbd	11.0, 16.5	2.68–2.78 m		2.68–2.78 m		2.52 t	14.7	2.71 dd	4.2, 14.7	4.71 s	
d	2.34 dt	16.5, 5.5	2.06–2.13 m	12.1, 16.5	2.72 bd	12.1	2.61 bd	14.5	2.47 t	14.6	2.90 dd	3.7, 14.5	4.73 s	
13a	2.50 ddd	4.4, 6.0, 17.3	2.19 bdd	11.4, 17.3	2.25 dd	4.0, 11.4	2.21 bd	14.5	2.62 t	14.5	2.68 dd	5.1, 15.1	5.06 d	1.6
b	2.46 ddd	4.3, 5.5, 17.5	2.00 bdd	11.4, 17.5	2.25 dd	4.3, 11.4	2.10 bd	14.8	2.57 t	14.8	2.88 dd	4.5, 14.9	5.09 s	
c	2.46 ddd	4.4, 6.5, 17.1	2.12 bdd	11.4, 17.1	2.36 dd	4.3, 11.4	2.83 bd	14.7	2.62 t	14.7	2.76 dd	4.9, 14.7	5.18 d	1.6
d	2.41 ddd	4.0, 5.5, 16.6	2.04–2.10 m		2.34 dd	4.0, 11.2	2.71 bd	14.5	2.57 t	14.5	2.94 dd	4.5, 14.5	5.18 s	

	observed proton, coupling constant (hertz)													
compd	20	J	21	J	CH_3O (C-6)	CH_3O (C-20)	19	J	12	J	13	J	5	J
2a	0.96 s						1.95 d	1.1	5.63 bd	10.0	5.8 bdd	10.0, 5.6	5.96 q	1.1
b	0.93 s		1.69 s				1.94 d	1.2	5.46 bd	5.0			5.95 q	1.2
c	3.37 d, 3.35 d	9.4				3.21 s	1.95 bs		5.61–5.65 m		5.80–5.84 m		6.02 m	
c	3.36 d, 3.30 d	9.5	1.72 s			3.20 s	1.94 s		5.49 bd	4.5			6.01 bs	
16a	0.97 s						1.99 d	1.0	5.98–6.01 m		5.65 bd	9.9	5.99 s	
b	0.95 s		1.75 d	1.2			1.98 d	1.5	5.70 bd	4.9			5.97 q	1.5
c	3.55 d, 3.35 d	9.5				3.21 s	2.03 d	1.1	5.97–6.01 m		5.69 bd	10.3	6.03 q	1.3
d	3.45 d, 3.38 d	9.6	1.76 s			3.19 s	2.01 s		5.69 bd	5.7			6.01 s	
13a	1.02 s				3.80 s				5.99–6.01 m		5.56 bd	9.9	5.36 d	1.6
b	1.01 s		1.72 d	1.0	3.81 s				5.72–5.73 m				5.37 d	1.7
c	3.48 d, 3.43 d	9.7			3.82 s	3.22 s			5.99–6.03 m		5.62 bd	9.9	5.41 s	
d	3.49 d, 3.36 d	9.7	1.75 s		3.82 s	3.21 s			5.70–5.71 m				5.41 s	

under the assumption that the spectra were first order.

Experimental Section

General Procedures. Melting points are uncorrected. ^1H NMR spectra were recorded with Bruker 200- and 500-MHz instruments. ^{13}C NMR spectra were taken at 50 MHz. Tetramethylsilane was used as an internal standard in $CDCl_3$ except where explicitly stated otherwise. Infrared spectra were obtained on a Beckman IR-4210 instrument. Mass spectra were determined on an AE1-M59 spectrometer. Thin-layer chromatography was performed with Merck 60F-254 plates and column chromatography was carried out with Merck silica gel (230–400 mesh). Ethereal solvents were prepared by distillation over sodium with benzophenone as an indicator. The titre of all alkyllithium reagents was checked (diphenylacetic acid indicator) immediately before use. All other chemicals were used directly as obtained commercially unless otherwise noted.

X-ray measurements for lactone **16b** ($C_{15}H_{18}O_3$) were made at 114 K on a crystal with well-defined faces, about 0.3 mm on a side, on a Syntex P1 diffractometer with Mo Kα radiation (λ = 0.7107 Å), μ = 0.99 cm^{-1}. The space group was $P2_1/n$, with cell dimensions a = 7.644 (2) Å, b = 9.680 (2) Å, c = 16.496 (6) Å, and 4 molecules in the unit cell. Out of a total of 3355 observed reflections to 2θ = 50°, 1809 had $I > 3\sigma(I)$, and these were used for solution of the structure by direct methods and refinement by full-matrix least squares. All hydrogen atoms were found in a difference map and were fixed in position and not refined. The final R was 0.050 (R_w = 0.060). The molecular geometry showed no unusual features.

Lactones 2. A solution of **16a**, (0.20 g, 0.86 mmol) in 20 mL of anhydrous THF with a small amount of 1,8-diazabicyclo-[5.4.0]undec-7-ene (0.01 g, 0.06 mmol) was refluxed for 36 h, after which time the starting material was absent (as judged by thin layer chromatography). The volatiles were removed at reduced pressure and the residue was chromatographed over silical gel to give a crystalline product. One recrystallization from ethyl acetate–hexane afforded analytically pure **2a** (0.13 g, 65%). **2b** (0.20, 61%) was obtained in similar fashion. **2c** (0.045 g, 43%) and **2d** (0.046 g, 45%) were obtained by increasing the amount of DBU (0.5 equiv) and decreasing the reflux time (4 h). **2a**: mp 146–147 °C; ^{13}C NMR δ 189.53, 169.59, 162.17, 128.58, 126.04, 124.84, 83.73, 37.84, 36.87, 35.19, 33.29, 23.76, 21.75, 16.49; IR (KBr) cm^{-1} 2972 (m), 1745 (s), 1673 (s), 1613 (m), 1437 (m), 1380 (s), 1234 (s), 1179 (s), 1054 (m), 1028 (s); mass spectrum calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1101. **2b**: mp 134–136 °C; ^{13}C NMR δ 189.73, 169.55, 162.27, 134.69, 124.70, 120.33, 83.83, 42.10, 36.50, 34.48, 32.31, 24.12, 21.65, 21.65, 16.20; IR (KBr) Cm^{-1} 1750 (s),

1679 (s), 1613 (m), 1439 (m), 1380 (s), 1190 (s), 1181 (s), 1045 (s); mass spectrum calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1264. **2c**: mp 152–153 °C; ^{13}C NMR δ 188.95, 170.04, 161.69, 129.26, 125.97, 125.79, 80.08, 70.28, 59.40, 42.04, 34.50, 33.23, 32.40, 23.44, 21.83; IR (KBr) cm^{-1} 2905 (m), 1740 (s), 1669 (s), 1605 (m), 1438 (m), 1328 (m), 1225 (s), 1183 (s), 1105 (s), 1047 (s); mass spectrum calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1205. **2d**: mp 130–131 °C; ^{13}C NMR δ 189.18, 169.86, 161.60, 134.95, 125.59, 120.45, 80.16, 69.97, 59.37, 41.38, 36.30, 33.78, 31.82, 23.85, 21.65, 21.51; IR (KBr) cm^{-1} 2940 (m), 2900 (m), 1766 (s), 1698 (s), 1620 (s), 1452 (s), 1254 (s), 1100–1130 (bs), 990 (s); mass spectrum calcd for $C_{16}H_{20}O_4$ 276.1362, found 276.1357.

Diels–Alder Adducts 3. A mixture of quinone **4a** (2.74 g, 0.018 mol) and diene acid **5b** (2.73 g, 0.023 mol) in 15 mL of CH_2Cl_2 was stirred for 6–10 days in the dark. The white crystalline product was filtered and the filtrate was concentrated to give an additional crop of yellowish crystals. This was repeated until no further crystallization could be induced. The crude product was recrystallized from ethyl acetate–hexane below 30 °C to give pure **3b** (4.45 g 90%). Adducts **3a** (1.4 g, 93%), **3c** (3.7 g, 97%), and **3d** (2.1 g, 67% accompanied by 16% of **11d**) were prepared in similar fashion. **3a**: mp 130–130.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.48 (s, 3 H), 2.83 (dd, J_1 = 7 Hz, J_2 = 10 Hz, 1 H), 2.51–2.72 (m, 4), 2.93 (t, J = 7 Hz, 1 H), 3.79 (s, 3 H), 5.66 (s, 2 H), 5.90 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.15, 24.59, 35.90, 39.72, 49.68, 52.58, 56.31, 109.44, 123.97, 127.81, 160.89, 177.64, 196.45, 198.76; IR (KBr) cm^{-1} 3015, 2860, 1660, 1600, 1240, 1200, 1185; mass spectrum calcd for $C_{14}C_{16}O_5$ 264.0997, found 264.0986. **3b**: mp 90 °C dec; ^1H NMR δ 1.44 (s, 3 H), 1.71 (s, 3 H), 2.08–2.86 (m, 6 H), 3.79 (s, 3 H), 5.39 (br s, 1 H), 6.02 (s, 1 H), 8.00 (br s, 1 H); ^{13}C NMR δ 21.48, 22.29, 23.50, 34.80, 43.29, 50.10, 50.36, 55.96, 110.52, 119.29, 132.90, 161.16, 176.95, 196.33, 198.40; IR (KBr) cm^{-1} 3700–2500 (s), 1710 (s), 1660 (s), 1610 (s), 1412 (m), 1360 (s), 1235 (s), 1205 (s), 1065 (s); mass spectrum calcd for $C_{15}H_{18}O_5$ 278.1139, found 278.1158. **3c**: mp 156 °C; ^1H NMR δ 2.00–2.48 (m, 5 H), 2.79 (bd, J = 19 Hz, 1 H), 3.26 (s, 3 H), 3.37–3.43 (m, 1 H), 3.77 (s, 3 H), 3.94 (d, J = 9 Hz), 5.56–5.71 (m, 2 H), 6.00 (s, 1 H); ^{13}C NMR δ 20.80, 36.28, 36.87, 44.36, 53.77, 56.26, 59.08, 74.78, 111.71, 125.26, 126.67, 161.27, 176.40, 195.11, 198.40 IR (KBr) cm^{-1} 3600–2300 (s), 1710 (s), 1603 (s), 1466 (m), 1440 (m), 1420 (m), 1385 (m), 1353 (s), 1250 (s), 1190 (s), 1085 (s), 1056 (s), 1030 (s), 995 (m), 934 (s), 856 (s), 722 (s); mass spectrum calcd for $C_{15}H_{18}O_6$–C_2H_5O 249.0763, found 249.0782. **3d**: mp 136–137 °C; ^1H NMR δ 1.68 (s, 3 H), 2.17 (s, 1 H), 2.31 (d, J = 5 Hz, 2 H) 2.49 (d, J = 6 Hz, 1 H), 2.90 (br s, 1 H), 3.29 (s, 3 H, OCH_3), 3.37–3.44 (m, 2 H, H-9, H-30a), 3.78 (s, 3 H) 3.97 (d, J = 9 Hz), 5.42 (br s, 1 H), 6.06 (s, 1 H); ^{13}C NMR δ 20.24, 21.82, 35.46, 40.51, 43.02, 54.80, 56.02, 58.82, 74.66, 111.96, 120.44, 132.70, 161.39, 176.39, 194.70, 198.61; IR (KBr) cm^{-1} 3200, 1730, 1680, 1660, 1610; mass spectrum calcd for $C_{16}H_{20}O_6$ 308.1260, found 308.1271.

Quinone 4a. Oxygen was bubbled rapidly into a stirring solution of 125.3 g (0.907 mol) of phenol **6**, 11.3 g (36.3 mmol) of salcomine,[9] and dry dimethylformamide (1.0 L) for 18 h. The mixture was poured onto ice and crude **4a** was collected by filtration. The filtate was continuously extracted with diethyl ether for 24 h to afford additional crude product. The two batches were combined and recrystallized from ethanol to afford 114.3 g (83%) of quinone **4a**, identical in all respects with a sample obtained via Fremy's salt oxidation.[10]

Quinone 4b. A solution of *o*-vanillyl methyl ether (**8**) (9.40 g, 0.056 mol) in dry dimethylformamide (96 mL) was stirred with salcomine (0.93 g, 0.003 mol) for 3 days with a slow stream of oxygen bubbled through. The crystalline solid deposited during this period was separated and the dark filtrate poured into ice when a brown solid was thrown out of solution. The latter was filtered, washed with water, and dried. The solid materials were combined and purified by repeated recrystallization from methanol to give 4.77 g of bright yellow crystalline needles: mp 137–138 °C. The aqueous fraction was extracted with methylene chloride (4 × 50 mL). The CH_2Cl_2 extract was washed with brine and dried (Na_2SO_4). The CH_2Cl_2 was removed and the residual DMF was distilled off under high vacuum. The resulting black residue was extracted with ether. From the ether extract was obtained a further crop of bright yellow crystals: weight = 2.74 g; total yield of quinone **4b** = 7.52 g (74%); ^1H NMR δ 6.72 (s, 1 H), 5.91 (s, 1 H), 4.32 (s, 2 H), 3.82 (s, 3 H), 3.46 (s, 3 H); ^{13}C NMR δ 55.95, 58.73, 67.17, 106.98, 131.57, 143.08, 158.29, 181.04, 186.78; IR (KBr) cm^{-1} 1640, 1590; mass spectrum calculated for $C_9H_{10}O_4$ 182.0579, found 182.0578.

Diene Acid 5b.[11] The chloro acid **10** (2.6 g, 0.016 mol) was dissolved in glacial acetic acid (32 mL) and zinc dust (10.4 g) added under N_2. The reaction mixture was stirred overnight at room temperature. The zinc was filtered and the acetic acid distilled off under high vacuum. The remaining gum was diluted with water (100 mL) and extracted with methylene chloride (4 × 50 mL). The organic phase was washed with brine and dried ($MgSO_4$). The methylene chloride was evaporated and the remaining yellow oil distilled under high vacuum. A colorless oil, bp 110 °C (0.17 mmHg), was collected: 1.02 g, 50%; ^1H NMR (60 MHz) δ 1.70 (s, 3 H), 3.23 (d, J = 6 Hz, 2 H), 5.01 (d, J = 6 Hz, 1 H), 5.25 (d, J = 10 Hz, 1 H), 5.70 (t, J = 7 Hz, 1 H), 6.51 (dd, J = 9, 10 Hz, 1 H).

Phenol 6.[12] A stirring solution of 200.0 g (1.31 mol) of *o*-vanillin, 133.3 g (2.63 mol) of hydrazine hydrate, and triethylene glycol (1.0 L) was heated at 110 °C for 10 min, after which 455.6 g (8.12 mol) of potassium hydroxide was added. The mixture was then heated to 150 °C for 12 h. After cooling, water (4.0 L) was added. The mixture was extracted with chloroform (4 × 1 L). The combined organic layers were washed with brine (1 L), dried (Na_2SO_4), and concentrated under reduced pressure to afford a brown liquid. Distillation (115 °C at 25 mmHg) gave 172.3 g (95%) of phenol **6** as white crystals: ^1H NMR (60 MHz, $CDCl_3$) δ 2.1 (s, 3 H), 3.85 (s, 3 H), 5.6–5.8 (br s, 1 H), 6.8 (br s, 3 H).

***o*-Vanillyl Methyl Ether (8).** Sodium hydride (0.72 g, 0.15 mol, 50% suspension in oil) was weighed into a three-necked, round-bottomed flask (500 mL). It was washed twice with dry benzene and then with dry THF and finally covered with THF (350 mL). The flask was stoppered with rubber septa and flushed with N_2. *o*-Vanillyl alcohol (11.629 g, 0.0755 mol) dissolved in dry THF (100 mL) was added under N_2 when a vigorous evolution of gas occurred and a greyish white solid came out of solution. Methyl iodide (4.70 mL, 0.0755 mol) was added and the reation mixture stirred overnight. The solution was filtered from the white solid which separated out and the solvent removed. The residue was distributed between ether and water (350 mL:100 mL). The aqueous fraction was extracted with ether (4 × 50 mL). The combined ether extract was washed with water and dried (Na_2SO_4). The ether was evaporated off leaving a pale brown oil (1.619 g). The aqueous fraction was acidified with 10% HCl and extracted with ether. From this ether extract was obtained 12.154 g of pale brown oil. TLC indicated that oils from both ether extracts contained essentially the same compound. These were combined and distilled under high vacuum, giving a colorless oil: bp 128–130 °C (0.18 mmHg); weight = 11.46 g (90.4%); ^1H NMR δ 3.42 (s, 3 H), 3.88 (s, 3 H), 6.30 (br s, 1 H), 6.84 (t, J = 5 Hz, 3 H); ^{13}C NMR δ 55.38, 57.48, 69.43, 110.06, 118.98, 120.79, 123.40 143.76, 146.49; IR (neat) cm^{-1} 3380, 2920, 2810, 1470, 1430, 1270, 1060; mass spectrum calcd for $C_9C_{12}O_3$ 168.0787, found 168.0786.

Chloro Acid 10. *n*-Butyllithium (6.7 mmol, 4.2 mL, 1.6 M in hexane) was added dropwise over a period of 10 min to a water cooled solution of diethyl ((trimethylsiloxy)carbonyl)methanephosphonate (1.80 g, 6.7 mmol) in dry tetrahydrofuran (25 mL). The solution was allowed to stir for 6 h after which time a solution of the aldehyde **9** (0.40 g, 3.4 mmol) in dry tetrahydrofuran (10 mL) was added over 2 min. After stirring for 90 min, the THF was evaporated at reduced pressure, H_2O (20 mL) was added, and the resulting mixture was extracted with ether (2 × 25 mL). The organic layer was dried over $MgSO_4$ and evaporated to give off-white crystals which were recrystallized from hexane–ethyl acetate to give pure **10** (0.39 g, 71%): mp 132–133 °C; ^1H NMR δ 1.90 s, 4.21 (d, J = 7.9 Hz), 5.96 (d, J = 15.7 Hz), 6.08 (br t, J = 7.9 Hz), 7.40 (d, J = 15.7 Hz); ^{13}C NMR δ 12.00, 39.44, 118.26, 134.89, 136.69, 149.74, 172.22; IR (KBr) cm^{-1} 3360–2260 (m), 1705 (s), 1634 (m), 1438 (m), 1337 (m), 1305 (s), 1269 (m), 998 (s); mass

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spectrum calcd for $C_7H_9O_2Cl$ 160.0292, found 160.0289.

Diels-Alder Adducts 11. 3d (0.51 g, 2.0 mmol) was dissolved in 10.0 mL of saturated aqueous sodium bicarbonate and allowed to stand overnight. Upon acidification (pH 2) of the reaction mixture with 10% HCl, a colorless precipitate was obtained (0.48 g). The mixture was cooled to 0 °C, filtered, and washed with 10 mL of ice-cold H_2O, air-dried, and then dried under high vacuum. The aqueous phase was evaporated and the residue extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried and evaporated to give a white solid (0.015 g). The crude solids were crystallized from ethyl acetate to give white crystals of **11d** (0.465 g, 91%). Trans adducts **11a** (0.36 g, 94%) and **11c** (0.61 g, 85%) were obtained similarly. **11a**: mp 200–201 °C; ^{1}H NMR δ 1.24 (s, 3 H), 2.11 (dd, J = 10, 15 Hz, 1 H), 2.24–2.58 (m), 2.75 (dd, J = 4, 15 Hz, 1 H), 2.96 (dd, J = 6, 11 Hz, 1 H), 3.80 (s, 3 H), 5.72–5.90 (m, 2 H), 6.00 (s, 1 H); ^{13}C NMR δ 21.89, 22.65, 37.63, 37.87, 44.85, 49.76, 56.19, 111.50, 125.04, 127.40, 159.93, 177.27, 196.89, 198.04; IR (KBr) cm^{-1} 1700 (s), 1662 (s), 1600 (s); mass spectrum calcd for $C_{14}H_{16}O_5$ 264.0997, found 264.0995. **11b**: mp 238–239 °C; ^{1}H NMR (Me_2SO-d_6) δ 0.98 (s, 3 H), 1.63 (s, 3 H), 1.97–2.30 (m, 3 H), 2.62–2.68 (br s, 1 H), 3.03–3.20 (m, partially obscured by H_2O peak, 2 H), 3.33 (s, 3 H), 5.30 (br s, 1 H), 6.07 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 21.57, 22.73, 39.85, 40.25, 42.23, 44.12, 50.99, 56.65, 112.04, 117.87, 135.54, 160.25, 174.00, 197.22, 198.61; IR (KBr) cm^{-1} 1595 (s), 1661 (s), 1716 (s), 2800–3600 (m); mass spectrum calcd for $C_{15}H_{18}O_5$ 278.1139, found 278.1150. **11c**: mp 164 °C; ^{1}H NMR δ 2.03–2.35 (m, 2 H), 2.49–2.53 (m, 1 H), 2.64 (dd, J = 4, 15 Hz, 1 H), 2.85–2.98 (m, 2 H), 3.14 (s, 3 H), 3.34 (d, J = 9 Hz, 1 H), 3.62 (d, J = 9 Hz, 1 H), 3.76 (s, 3 H), 5.80 (m, 2 H), 6.06 (s, 1 H); ^{13}C NMR δ 22.79, 34.74, 37.00, 43.59, 54.74, 56.02, 59.19, 76.27, 113.31, 126.01, 127.63, 161.63, 177.10, 196.29, 197.07; IR (KBr) cm^{-1} 3300–2400 (s), 1720 (s), 1675 (s), 1610 (s), 1410 (m), 1346 (s), 1280 (s), 1250 (s), 1200 (s), 1175 (s), 1112 (s), 1052 (m), 868 (m), 845 (s), 702 (m); mass spectrum calcd for $C_{15}H_{18}O_6$–C_2H_5O 249.0763, found 249.0772. **11d**: mp 196–197 °C; ^{1}H NMR ($CDCl_3$/Me_2SO-d_6) δ 1.74 (s, 3 H), 2.18 (s, 1 H), 2.24–2.29 (m, 2 H), 2.59 (d, J = 2 Hz, 1 H), 2.82–2.99 (m, 2 H), 3.12 (s, 3 H), 3.27 (d, J = 9 Hz, 1 H), 3.56 (d, J = 9 Hz, 1 H), 3.76 (s, 3 H), 5.43 (br s, 1 H), 6.04 (s, 1 H); ^{13}C NMR ($CDCl_3$/Me_2SO) δ 20.26, 20.68, 35.62, 36.83, 41.10, 53.84, 54.12, 57.18, 74.18, 113.37, 117.71, 133.75, 159.88, 171.77, 194.18, 195.12; IR (KBr) cm^{-1} 2960 (s), 1700 9s), 1670 (s), 1630 (s), 1600 (s); mass spectrum calcd for $C_{16}H_{20}O_6$ 308.1260, found 308.1254.

Diels-Alder Adduct 11b. A stirring solution of 2.00 g (13.8 mmol) of quinone **4a** in 3.30 g (26.2 mmol) of acid **5b** and benzene (2.5 mL) was heated at 60 °C under an atmosphere of nitrogen for 6 h. The product was thoroughly washed with diethyl ether (100 mL) to afford 2.00 g of **11b**. Concentration of the filtrate under reduced pressure followed by trituration with diethyl ether gave an additional 0.98 g of adduct; total yield 2.98 g (78%).

Hydroxy Acids 12. Sodium borohydride (0.06 g, 1.6 mmol) was added in two equal portions to a stirred solution of Diels–Alder adduct **11d** (0.38 g, 1.5 mmol) in 50 mL of methanol at −30 °C. The solution was stirred for 30 min at −30 °C and then allowed to warm to 25 °C. It was then acidified (pH 2) with 10% HCl and the methanol evaporated. The residue was dissolved in 10 mL of H_2O, saturated with solid NaCl, and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried and evaporated to give a white solid (0.377 g). The crude product was recrystallized from ethyl acetate/hexane to give pure **12d** (0.36 g, 95%). Hydroxy acids **12a** (0.29 g, 94%), **12b** (0.16 g, 92%), and **12c** (0.32 g, 89%) were obtained similarly. **12a**: mp 192–192.5 °C; ^{1}H NMR δ 1.00 (s, 3 H), 2.11–2.85 (m, 6 H), 3.79 (d, J = 0.5 Hz, 3 H), 4.59 (s, 1 H), 5.37 (s, 1 H), 5.71–5.82 (m, 2 H); ^{13}C NMR ($CDCl_3$/Me_2SO-d_6) δ 13.24, 22.49, 36.49, 38.41, 42.58, 43.47, 56.01, 70.30, 80.22, 99.95, 124.95, 127.49, 174.85, 175.10, 198.61; IR (KBr) cm^{-1} 3390 (s), 3200–2400 (m), 1692 (s), 1628 (s), 1597 (s), 1380 (s), 1362 (s), 1250 (s), 1225 (s), 1186 (s), 1020 (s), 877 (s), 830 (m), 705 (m); mass spectrum calcd for $C_{14}H_{18}O_5$ 266.1154, found 266.1153. **12b**: mp 209–210 °C; ^{1}H NMR δ 0.98 (s, 3 H), 1.77 (s, 3 H), 2.04–2.23 (m, 1 H), 2.32–2.64 (m, 5 H), 3.78 (s, 3 H), 4.67 (d, J = 1.4 Hz, 1 H), 5.38 (d, J = 1.4 Hz, 1 H), 5.43 (br s, 1 H); ^{13}C NMR ($CDCl_3$/Me_2SO-d_6) δ 12.88, 22.22, 22.50, 34.87, 42.08, 42.61, 43.41, 55.78, 70.01, 100.03, 119.71, 133.32, 174.67, 176.27, 198.46; IR (KBr) cm^{-1} 3418 (s), 3200–2300 (s), 1700 (s), 1628 (s), 1600 (s), 1448 (m), 1357 (s), 1313 (s), 1240 (s), 1183 (s), 1131 (s), 1040 (s), 828 (s); mass spectrum calcd for $C_{15}H_{20}O_5$ 280.1311, found 280.1307. **12c**: mp 153 °C; ^{1}H NMR δ 1.87–2.05 (m, 1 H), 2.27–2.57 (m, 3 H), 3.00 (dd, J = 5, 14 Hz, 1 H), 3.28 (s, 3 H), 3.19–3.28 (m, 1 H), 3.55 (d, J = 9 Hz, 1 H), 3.75 (d, J = 9 Hz, 1 H), 3.82 (s, 3 H), 4.64 (br s, 1 H), 5.41 (s, 1 H), 5.83 (br s, 2 H); ^{13}C NMR δ 22.44, 33.80, 36.26, 43.29, 45.33, 56.43, 59.51, 72.55, 73.04, 99.93, 125.95, 127.12, 176.29, 176.98, 197.60; IR (KBr) cm^{-1} 3435 (m), 3300–2400 (m), 1713 (s), 1642 (s), 1600 (s), 1429 (m), 1365 (m), 1348 (m), 1252 (s), 1235 (s), 1201 (s), 1109 (s), 1023 (s), 888 (m), 834 (m), 724 (m); mass spectrum calcd for $C_{15}H_{20}O_6$–H_2O 278.1154, found 278.1157. **12d**: R_f (silica gel, ethyl acetate/methanol, 9:1/v:v) 0.29 ^{1}H NMR δ 1.76 (s, 3 H), 1.85–2.01 (m, 1 H), 2.29–2.65 (m, 4 H), 2.93–2.99 (m, 1 H), 3.19 (s, 3 H), 3.47 (d, J = 10 Hz, 1 H), 3.63 (d, J = 10 Hz, 1 H), 3.74 (s, 3 H), 4.79 (s, 1 H), 5.35 (d, J = 1 Hz, 1 H), 5.43 (br s, 1 H); ^{13}C NMR δ 22.47, 22.70, 35.10, 39.12, 42.39, 46.60, 56.35, 59.50, 72.23, 72.95, 100.10, 120.99, 133.35, 176.05, 177.21, 197.99; IR (film) cm^{-1} 3423 (m), 3300–2400 (s), 1712 (s), 1650 (s), 1601 (s), 1442 (s), 1361 (s), 1227 (s), 1195 (s), 1102 (s), 1030 (m), 730 (m); mass spectrum calcd for $C_{16}H_{22}O_6$–C_2H_5O 265.1076, found 265.1081.

Lactones 13. Hydroxy acid **12d** (0.30 g, 1.1 mmol) was dissolved in a solution of acetic anhydride (5.0 mL, 53.0 mmol) and pyridine (2.0 mL, 25.0 mmol) and stirred for 45 min. The volatiles were evaporated under vacuum and the residue was filtered through 2.0 g of silica gel with ethyl acetate eluent. Evaporation of the solvent gave a light yellow solid which was recrystallized from ethyl acetate–hexane to give **13d** as colorless crystals (0.21 g, 76%). If the reaction time was increased to 12 h the yields became lower. Lactones **13a** (0.04 g, 43%), **13b** (0.08 g, 51%), and **13c** (0.19 g, 33%) were obtained in this manner. **13a**: mp 202 °C; ^{13}C NMR δ 17.14, 20.17, 35.10, 39.00, 40.87, 50.53, 56.61, 79.59, 80.40, 101.01, 126.22, 128.22, 169.97, 171.36, 196.45; IR (KBr) cm^{-1} 2972 (w), 2950 (w), 2950 (w), 1764 (s), 1752 (s), 1662 (s), 1602 (s), 1385 (s), 1250 (s), 1220 (s), 1122 (s), 1064 (s), 1050 (s), 1022 (m), 727 (m); mass spectrum calcd for $C_{14}H_{16}O_4$ 248.1049, found 248.1048. **13b**: mp 200–201 °C; ^{13}C NMR δ 17.15, 20.51, 21.14, 33.46, 41.01, 42.72, 50.45, 56.61, 79.65, 100.99, 123.46, 131.45, 170.03, 171.63, 196.57; IR (KBr) cm^{-1} 2970 (m), 2935 (m), 1740 (s), 1650 (s), 1595 (s), 1455 (m), 1388 (s), 1250 (s), 1229 (s), 1174 (s), 1121 (s), 1054 (s), 820 (m), 732 (m); mass spectrum calcd for $C_{15}H_{18}O_5$ 262.1205, found 262.1209. **13c**: mp 178–180 °C; ^{13}C NMR δ 21.15, 33.27, 35.07, 44.92, 50.09, 56.69, 59.44, 72.43, 77.53, 78.94, 101.36, 126.78, 128.05, 169.19, 171.07, 195.95; IR (KBr) cm^{-1} 2930 (m), 2892 (m), 1752 (s), 1656 (s), 1604 (s), 1448 (m), 1390 (s), 1250 (s), 1107 (s), 1007 (s); mass spectrum calcd for $C_{15}H_{18}O_5$ 278.1154, found 278.1148. **13d**: mp 206–208 °C; ^{13}C NMR δ 21.19, 21.34, 33.50, 36.87, 45.01 49.95, 56.68, 59.43, 72.34, 79.08, 101.24, 123.26, 132.05, 169.32, 171.30, 195.97; IR (KBr) cm^{-1} 2940 (m), 1736 (s), 1652 (s), 1593 (s), 1442 (m), 1370 (s), 1282 (s), 1250 (s), 1228 (s), 1115 (s), 1101 (s), 1039 (s), 932 (m), 822 (m); mass spectrum calcd for $C_{16}H_{20}O_5$ 292.1311, found 292.1322.

Hydroxy Acids 15. A solution of hydroxy acid **12d** (0.37 g, 1.3 mmol) dissolved in 20 mL of THF was added dropwise over 10 min to a stirred solution of methyllithium (4.7 mL, 1.6 M in ether, 7.5 mmol) and 50 mL of THF at −40 °C. The mixture was stirred for an additional 30 min and then canulated into 25 mL of rapidly stirred ice-cold H_2O. The basic solution was extracted with ethyl acetate (2 × 25 mL). The aqueous layer was acidified (pH 3) with 10% HCl, saturated with solid NaCl, and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried and evaporated to give an oil consisting of two major components, **15d** and **12d** (35:4). **15d** separated as white crystals (0.22 g). The remaining oil was chromatographed (silica gel: ethyl acetate/acetic acid/MeOH) to give an additional 0.034 g. Recrystallization from ethyl acetate afforded pure **15d** (0.25 g, 71%). **15a–c** were obtained in a similar manner (0.41 g, 58%), (0.22 g, 55%), (0.13 g, 50%), respectively. **15a**: mp 158–159 °C; ^{1}H NMR δ 0.84 (s, 3 H), 1.87–2.05 (m, 1 H), 1.96 (s, 3 H), 2.25–2.63 (m, 3 H), 2.95 (dd, J = 4, 14 Hz, 1 H), 4.11 (s, 1 H), 5.81–5.88 (m, 2 H), 5.99 (d, J = 1 Hz, 1 H); ^{13}C NMR δ 11.84, 21.52, 25.10, 36.35, 38.70, 39.39, 43.53, 76.49, 123.44, 125.39, 128.43, 162.75, 178.14, 199.17; IR (KBr) cm^{-1} 3380 (s), 2960 (s), 1695 (s), 1637 (s), 1414 (m), 1365 (m), 1248 (s), 1155 (s), 1095 (m); mass spectrum calcd for $C_{14}H_{18}O_4$ 250.1205, found 250.1209. **15b**: mp 143–144 °C; ^{1}H NMR δ 0.81 (s, 3 H), 1.78 (s, 3 H), 1.94 (s, 3 H), 1.80–2.00 (m, 1 H), 2.34–2.63 (m, 4 H), 2.71 (dd, J = 8, 16 Hz, 1 H), 4.27 (s, 1 H), 5.42–5.44 (br

s, 1 H), 5.96–5.98 (m, 1 H); ^{13}C NMR δ 11.93, 21.49, 22.68, 25.41, 35.37, 38.68, 43.95, 44.12, 76.49, 120.13, 123.41, 135.15, 162.72, 178.26, 199.08; IR (KBr) cm^{-1} 3390 (s), 3220–2400 (s), 1700 (s), 1670 (s), 1443 (s), 1380 (m), 1212 (s), 1104 (m); mass spectrum calcd for $C_{15}H_{20}O_4$ 264.1362, found 264.1360. **15c**: mp 153–154 °C; ^{1}H NMR δ 1.93 (s, 3 H), 1.88–1.97 (m, 1 H), 2.33 (dd, J = 11, 14 Hz, 1 H), 2.44 (m, 1 H), 2.69–2.84 (m, 2 H), 3.01 (dd, J = 4.5, 14 Hz, 1 H), 3.15 (s, 3 H), 3.49 (d, J = 10 H, 1 H), 3.58 (d, J = 10 Hz, 1 H), 4.18 (s, 1 H), 5.81–5.94 (m, 2 H), 5.95 (br s, 1 H); ^{13}C NMR δ 21.43, 25.31, 34.93, 36.22, 38.85, 47.45, 59.30, 72.31, 76.51, 124.65, 126.24, 128.67, 159.67, 177.74, 198.55; IR (KBr) cm^{-1} 3440 (m), 3240–2400 (m), 1708 (s), 1698 (s), 1265 (s), 1170 (s), 1106 (s); mass spectrum calcd for $C_{15}H_{20}O_5$–C_2H_5O 235.0971, found 235.0978. **15d**: mp 137–139 °C; ^{1}H NMR δ 1.79 (s, 3 H), 1.91 (s, 3 H), 1.74–1.96 (m, 1 H), 2.35–2.54 (m, 2 H), 2.66–2.78 (m, 3 H), 3.12 (s, 3 H), 3.46 (d, J = 10 Hz, 1 H), 3.56 (d, J = 10 Hz, 1 H), 4.36 (s, 1 H), 5.47 (d, J = 2 Hz, 1 H), 5.93 (m, 1 H); ^{13}C NMR δ 21.34, 22.55, 25.53, 35.35, 38.19, 40.21, 48.21, 59.33, 72.53, 76.26, 120.90, 124.54, 135.43, 159.72, 177.41, 198.58; IR (KBr) cm^{-1} 3380 (m), 3260–2440 (s), 1728 (s), 1665 (s), 1625 (m), 1442 (m), 1415 (m), 1383 (m), 1215 (s), 1197 (s), 1109 (s); mass spectrum calcd for $C_{16}H_{22}O_5$–C_2H_5O 249.1127, found 249.1140.

Lactones 16 (Method A). Hydroxy acid **15d** (0.17 g, 0.72 mmol) was dissolved in a solution of acetic anhydride (2.5 mL, 26.5 mmol) and pyridine (1.0 mL, 12.4 mmol) and stirred for 1 h after which time the volatiles were evaporated under high vacuum. The crude solid was chromatographed (silica gel, ethyl acetate/hexane) to give **16d** as white crystals (0.12 g, 76%). Lactone **16c** was obtained in the same manner (0.53 g, 56%). Lactones **16a** (0.072 g, 32%) and **16b** (0.045 g, 34%) were obtained when the reaction time was increased to 12 h. **16a**: mp 140–141 °C; ^{13}C NMR δ 15.43, 21.46, 22.90, 35.13, 39.48, 41.54, 44.25, 85.19, 125.86, 126.64, 127.72, 160.20, 171.32, 190.55; IR (KBr) cm^{-1} 2990 (m), 2950 (m), 2900 (w), 2865 (s), 1765 (s), 1700 (s), 1616 (m), 1440 (m), 1384 (m), 1252 (s), 1238 (s), 1120 (s), 1072 (s), 874 (m); mass spectrum calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1090. **16b**: mp 288–289 °C; ^{13}C NMR δ 13.8, 21.3, 24.1, 23.2, 33.3, 41.4, 43.3, 44.1, 85.1, 122.9, 125.6, 132.0, 164.0, 171.6, 190.7; IR (KBr) cm^{-1} 1236 (s), 1660 (s), 1750 (s); mass spectrum calcd for $C_{15}H_{18}O_3$ 246.1256, found 246.1257. **16c**: mp 155 °C dec; ^{13}C NMR δ 21.49, 24.16, 34.30, 35.13, 44.06, 46.31, 59.50, 71.57, 84.47, 126.07, 127.55, 128.03, 160.18, 171.01, 189.80; IR (KBr) cm^{-1} 2890 (m), 1755 (s), 1687 (s), 1608 (m), 1432 (m), 1254 (s), 1113 (s), 736 (m), 725 (m); mass spectrum calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1208. **16d**: mp 150 °C dec; ^{13}C NMR δ 21.40, 21.52, 24.42, 33.45, 37.94, 44.03, 46.19, 59.50, 71.48, 84.59, 123.23, 126.04, 133.02, 160.01, 171.21, 189.92; IR (KBr) cm^{-1} 2920 (m), 2880 (m), 1752 (s), 1683 (s), 1609 (m), 1442 (m), 1239 (s), 1110 (s); mass spectrum calcd for $C_{16}H_{20}O_4$ 276.1362, found 276.1358.

Lactones 16 (Method B). To a stirring solution of 692.0 mg (2.47 mmol) of Diels–Alder adduct **11b** at −20 °C in anhydrous methanol (25 mL) under an atmosphere of nitrogen was added 130 mg (3.44 mmol) of sodium borohydride in ca. 25-mg portions over 10 min. The mixture was stirred an additional 25 min after which water (5 mL) was added dropwise, followed by 5% HCl (5 mL). The mixture was diluted with water (40 mL) and then extracted with ethyl acetate (3 × 35 mL). The combined organic layers were washed with brine (40 mL), dried (Na_2SO_4), and concentrated to afford 693 mg of hydroxy acid **12b** as a white solid: ^{1}H NMR (60 MHz, Me_2SO-d_6) δ 0.63 (s, 3 H), 1.5 (s, 3 H), 1.8–2.6 (m obscured by solvent/water peaks), 3.5 (s, 3 H), 4.45 (s, 1 H), 4.95–5.15 (m, 2 H). Crude **12b** was used without purification. To a stirring solution of 693.0 mg of **12b** in THF (50 mL) at −35 °C under an atmosphere of nitrogen was added 4.4 mL (7.54 mmol) of 1.7 M methyllithium over 5 min. The mixture was stirred an additional 20 min and then saturated $NaHCO_3$ (10.0 mL) was added dropwise with rapid stirring. The mixture was warmed to −10 °C and then acidified to pH 5 with 2% HCl (as shown by pH paper). The aqueous layer was extracted with ethyl acetate (2 × 25 mL). The combined organic layers were washed with brine (50 mL), dried (Na_2SO_4), and concentrated under reduced pressure to afford 700 mg of **15b** as a yellow oil. Crude enone **15b** was then stirred with 0.5 mL (3.19 mmol) of diisopropylcarbodiimide and 0.5 mL of pyridine in CH_2Cl_3 (9.0 mL) for 16.5 h. The mixture was filtered and diluted with ethyl acetate (35 mL), and the organic layer was washed with water (5 × 15 mL) and brine (20 mL), dried (Na_2SO_4), and concentrated to afford 540.1 mg of a yellow solid. Recrystallization from ethyl acetate gave **16b** as white crystals (0.28 g, 46%).

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Registry No. **2a**, 104199-02-2; **2b**, 104199-03-3; **2c**, 104199-04-4; **2d**, 104319-34-8; **3a**, 104199-07-7; **3b**, 104199-08-8; **3c**, 104199-09-9; **3d**, 104265-19-2; **4a**, 611-68-7; **4b**, 104199-06-6; **5a**, 29949-29-9; **5b**, 87668-09-5; **6**, 2896-67-5; **7**, 4383-05-5; **8**, 104199-12-4; **9**, 3330-25-4; **10**, 104199-13-5; **11a**, 104199-15-7; **11b**, 104199-11-3; **11c**, 104199-16-8; **11d**, 104199-10-2; **12a**, 104199-17-9; **12b**, 104199-18-0; **12c**, 104199-19-1; **12d**, 104199-20-4; **13a**, 104199-21-5; **13b**, 104199-22-6; **13c**, 104199-23-7; **13d**, 104199-24-8; **15a**, 104199-25-9; **15b**, 104293-66-5; **15c**, 104199-26-0; **15d**, 104199-27-1; **16a**, 104265-16-9; **16b**, 104265-17-0; **16c**, 104265-18-1; **16d**, 104199-05-5; $(EtO)_2P(O)$=CHCOOTMS, 66130-90-3; *o*-vanillin, 148-53-8.

Supplementary Material Available: Position and displacement parameters for compound **16b** (Table 1); bond distances, bond angles, and torsion angles for compound **16b** (Table 2) (4 pages). Ordering information is given on any current masthead page.