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HOMOCHIRAL KETALS IN ORGANIC SYNTHESIS. DIASTEREOSELECTIVE CYCLOPROPANATION OF α,β-UNSATURATED KETALS DERIVED FROM 1,4-DI-*O*-BENZYL-L-THREITOL[1]

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Abstract. 2-Cycloalken-1-one 1,4-di-*O*-benzyl-L-threitol ketals undergo efficient and diastereoselective cyclopropanation when treated with an excess of the Simmons-Smith reagent. For example, 2-cyclohexen-1-one 1,4-di-*O*-benzyl-L-threitol ketal gave in 90-98% yield a 9:1 mixture of diastereomeric cyclopropanes as established by 62.9 MHz ^{13}C NMR spectroscopy and by hydrolysis of the mixture to (1R,6S)-bicyclo[4.1.0]heptan-2-one. Sixteen other examples are presented which demonstrate the generality and predictability of the process for 2-cycloalken-1-one ketals, as well as an unfortunate lack of diastereoselectivity for α,β-unsaturated 1,4-di-*O*-benzyl-L-threitol acetals.

Time and again, cyclopropyl ketones have proven useful as synthetic intermediates.[2] Angle strain associated with the cyclopropane ring and polarization by the carbonyl impart special reactivity to these molecules. Reductive ring opening is well-known,[2d-e,3] as are ring opening reactions by both electrophilic [2f,4] and nucleophilic [2i,5] reagents. Ready conversion of the carbonyl to alcoholic functionality by reduction or by 1,2-addition makes olefins of defined geometry accessible via stereocontrolled cyclopropylcarbinol rearrangements.[2a-c,6] Wittig-type olefination provides vinyl-cyclopropanes, which rearrange thermally to cyclopentenes.[2j-k,7]

Despite their synthetic versatility, general preparations of cyclopropyl ketones are few in number. These include: direct cyclopropanation of α,β-unsaturated ketones;[8,9,10] cyclopropanation of allylic alcohols, followed by oxidation;[2d-4,8,9,11] and decomposition of diazoketones in the presence of alkenes.[2b,g,i,k,12] Fewer still are general methods for enantioselective production of cyclopropyl ketones.[13,14] These include: cyclopropanation of achiral α,β-unsaturated ketones with chirally modified cyclopropanating reagents;[15,16] and cyclopropanation of non-racemic allylic alcohols, followed by oxidation.[11,17] While the former processes are straightforward, they generally suffer from low enantioselectivities. The latter process can, in principle, provide cyclopropyl ketones possessing very high enantiomeric excesses, but depends upon prior resolution of the allylic alcohol -- an inefficient and laborious task at best! Since modern synthetic chemists frequently seek to produce a single enantiomer of a complex target structure, an efficient enantioselective synthesis of cyclopropyl ketones would render them all the more attractive as synthetic intermediates. Toward this end, we have examined the Simmons-Smith cyclopropanation[8] of a series of homochiral ene ketals and ene acetals derived from readily available 1,4-di-*O*-benzyl-L-threitol[18] and report herein a general, efficient, enantioselective synthesis of bicyclo[m.1.0]alkanones and tricyclo[m.n.1.0]-alkanones.

RESULTS

Preparations of Ene Ketals and Ene Acetals. Excepting compounds 13, 15, 17, and 27 (Table I), all required ene ketals and ene acetals were prepared by direct ketalization of the corresponding enones under standard conditions (0.5-0.9 equivalents of 1,4-di-*O*-benzyl-L-threitol, *p*-toluenesulfonic acid or pyridinum *p*-toluenesulfonate catalyst, benzene, reflux with azeotropic removal of water under argon). Ketalizations were generally slow but clean reactions. In most cases, double bond migration during ketalization was minimal. However, ketalization of 3-[(1-methyl)ethyl]-2-cyclopenten-1-one produced a 2:5 mixture of ketal 5 and an isomer, 3-[(1-methyl)ethylidine]cyclopentan-1-one 1,4-di-*O*-benzyl-L-threitol ketal 5a, which was separated chromatographically. Ketalization of 2-cycloheptен-1-one also produced a mixture (9:1) of the desired ketal 25 and its Δ3 isomer 25a which were separable by chromatography. To ensure positioning of the double bond,

compounds 13, 17, and 27 were prepared via the corresponding α-bromoketones by a two-step process: ketalization, followed by elimination.[19] Compound 15 was prepared by ketalization of 4-tosyloxycyclohexanone, followed by elimination. Yields appear in Table I.

Diastereoselective Cyclopropanations. Standard Simmons-Smith cyclopropanation[8] (400-700) mg zinc-copper couple[20]/mmol ene ketal, 3 equivalents diiodomethane, iodine catalyst, diethyl ether, reflux under argon) of the ene ketals and ene acetals listed in Table I resulted in diastereoselectivities ranging from approximately 20:1, the limit of detectability, to 1:1 as determined from 62.9-MHz ^{13}C NMR spectra of the product mixtures.[21] Chemical yields were generally good to excellent on scales ranging from 0.26-35.3 mmol. In several reactions (entries 3-6, 10, and 27), anhydrous potassium carbonate was included in the reaction mixture to neutralize developing acidity.

Diastereoselection was uniformly good for α,β-unsaturated cycloalkenone ketals 1, 3, 5, 7, 9, 11, 13, 17, 19, 25 and 27, but poor for β,γ-unsaturated cycloalkenone ketal 15. Diastereoselection was uniformly poor for α,β-unsaturated aldehyde acetals 23, 31, and 33, but better for ketals of the corresponding methyl ketones (compare 21 and 23, 29 and 31).[22]

Hydrolyses of Cyclopropane Ketals. Results of the acid-catalyzed hydrolyses of selected cyclopropane ketals are summarized in Table II. Under the conditions employed (hydrochloric acid, methanol, water, room temperature), hydrolysis was rapid and clean, providing the product cyclopropyl ketones 35-45 in good to excellent yields. In most cases the chiral auxiliary was also recovered in good to excellent yield.

The absolute stereochemistries assigned to cyclopropyl ketones 35, 36, 40, and 45 follow from their measured optical rotations and assignments previously made in the literature (Table II). The absolute stereochemistries assigned to cyclopropyl ketones 37, 38, 39, and 42 were based upon application of the Reversed Octant Rule to the CD spectra of these molecules, all of which exhibited positive Cotton effects (Table III).[17b] Although the absolute stereochemistries of cyclopropyl ketones 41, 43, and 44 remain unproven, stereochemistries for 41 and 44 were tentatively assigned in accord with the previous assignments.

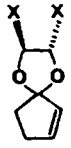
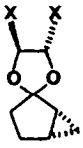
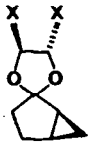
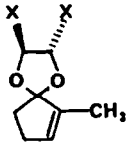
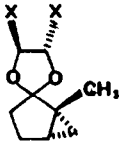
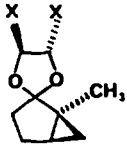
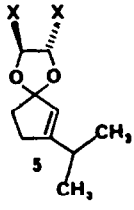
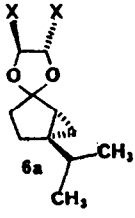
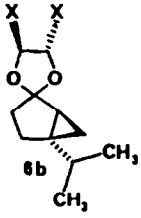
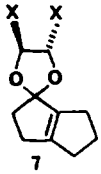
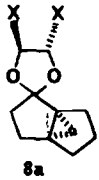
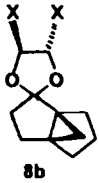
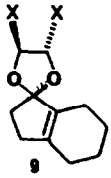
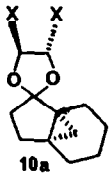
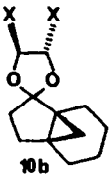
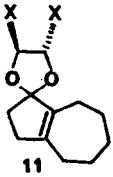
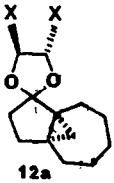
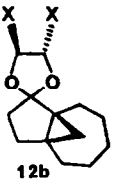
DISCUSSION

The activating and directing effects of allylic and homoallylic oxygen atoms upon the course of the Simmons-Smith cyclopropanation are well-documented.[8,17,23] Chelation of zinc by oxygen can result in preferential delivery of the reagent to the closest of several double bonds and/or to a specific face of one double bond. This latter result is especially true for cycloalkenyl alcohols,[8] ethers,[8,24] and acetates.[25]

In search of a direct and general route to enantiomerically pure cyclopropyl ketones, we prepared a series of 2-cycloalken-1-one 1,4-di-O-benzyl-L-threitol ketals and subjected them to Simmons-Smith cyclopropanation. We hoped that the dissymmetric positioning of oxygen atoms in the vicinity of the double bond might result in some measure of diastereoselectivity. We were most pleased to obtain, for all 2-cycloalken-1-one 1,4-di-O-benzyl-L-threitol ketals examined, good (8:1) to excellent (20:1) diastereoselection and good to excellent chemical yields (Table I). Unsubstituted ketals 1, 13, and 25 exhibited comparable diastereoselectivities (8-9:1). Alkyl substitution on the double bond had little or no effect on the diastereoselectivity exhibited by the 2-cyclopenten-1-one system (ketals 3 and 5), but an α-methyl substituent greatly enhanced the diastereoselectivity exhibited by the 2-cyclo-hexen-1-one system (ketal 17). The greater diastereoselectivity exhibited by ketal 17 may have been due to steric destabilization of one of several possible zinc chelate structures. 3-Cyclohexen-1-one ketal 15 exhibited substantially less diastereoselectivity than 2-cyclohexen-1-one ketal 13, presumably due to the increased distance of the double bond from the site(s) of zinc chelation.

Most remarkable was the diastereoselectivity observed for 2-cyclopentadecen-1-one ketal 27. Although we anticipated less diastereoselectivity for 27 than that observed for the smaller ring 2-cycloalken-1-ones, a single cyclopropane diastereomer, 28a, was produced from 27.[26] This diastereoselectivity may be due to a conformationally-controlled exposure of one face of the olefin to the ring exterior.[27]

TABLE 1. Diastereoselective Simmons-Smith Cyclopropanation of Homochiral Ene Ketals and Ene Acetals Derived from 1,4-Bi-*O*-benzyl-L-threitol.[a]

entry	ene ketal[b]	yield, %[c,d]	$[\alpha]_D^{25}$ deg (α)[e]	cyclopropane ketals	yield, %[c]	diastereomer ratio[f]
1	 1	66	+0.23 (4.28)	 2a  2b	72	9:1
2	 3	89	-0.97 (2.38)	 4a  4b	88	9:1
3	 5	19	+8.78 (3.42)	 6a  6b	54	9:1
4	 7	21 (88)	+2.3 (0.65)	 8a  8b	78	9:1
5	 9	66 (100)	+4.3 (3.00)	 10a  10b	90	7:1
6	 11	59 (76)	+2.3 (1.71)	 12a  12b	84	9:1

[a] Reaction conditions: 400-700 mg of couple/mmol of ene ketal, 3 equiv of CH_2I_2, 0.5 M in refluxing diethyl ether, 1-24 h. [b] X = $CH_2OCH_2C_6H_5$. [c] All yields refer to isolated and purified compounds. [d] Yield based on unrecovered diol in parentheses. [e] In $CHCl_3$. [f] Determined by 62.9-MHz ^{13}C NMR.

TABLE 1, continued.

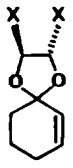
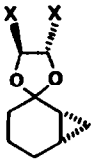
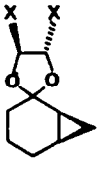
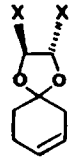
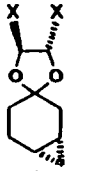
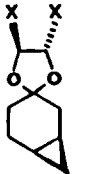
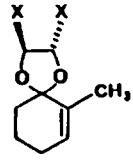
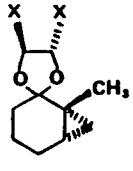
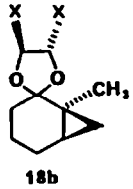
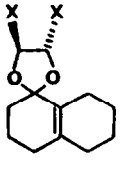
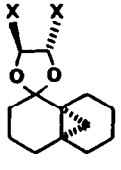
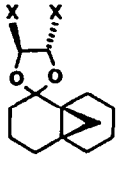
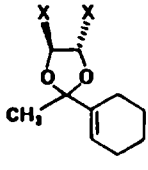
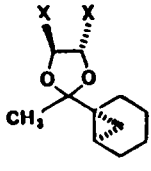
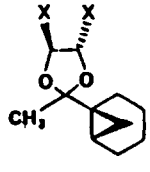
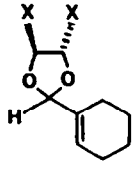
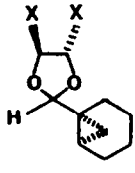
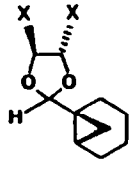
entry	ene ketal[b]	yield, %[a,d]	$[\alpha]_D^{25}$ deg (σ)[e]	cyclopropane ketals	yield, %[a]	diastereomer ratio[f]
7	 **13**	93	+9.31 (4.18)	 **14a**  **14b**	90–98	9:1
8	 **15**	86	-9.66 (3.05)	 **16a**  **16b**	88	2:1
9	 **17**	63	+14.7 (1.92)	 **18a**  **18b**	99	20:1
10	 **19**	58 (97)	+25.3 (1.18)	 **20a**  **20b**	92	7:1
11	 **21**	75	-3.41 (3.23)	 **22a**  **22b**	88	14:1
12	 **23**	46	+3.63 (2.7)	 **24a**  **24b**	70	2:1

TABLE 1, continued.

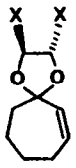
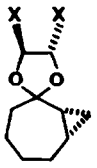
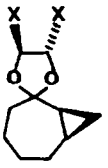
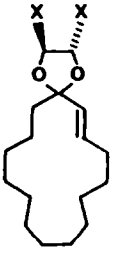
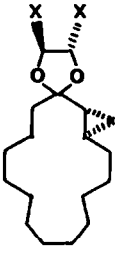
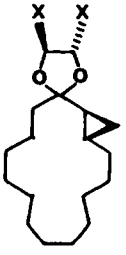
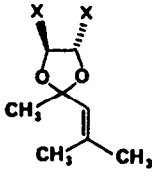
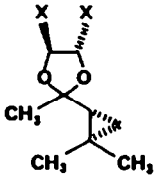
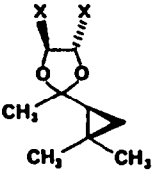
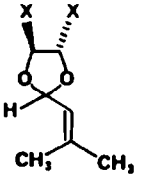
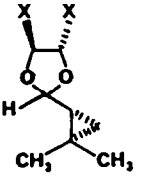
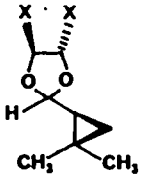
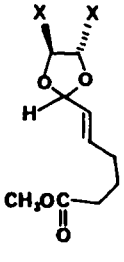
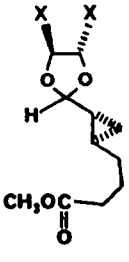
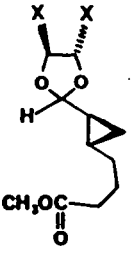
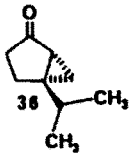
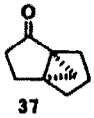
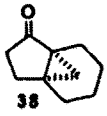
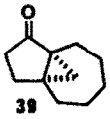
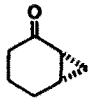
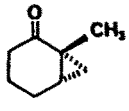
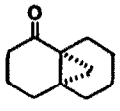
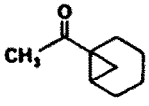
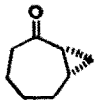
entry	ene ketal[b]	yield, %[c,d]	$[\alpha]_D^{25}$ deg (σ)[e]	cyclopropane ketals	yield, %[c]	diastereomer ratio[f]
13	 **25**	42	+1.69 (3.02)	 **26a**  **26b**	90	8:1
14	 **27**	41	-2.10 (3.04)	 **28a**  **28b**	94	20:1
15	 **29**	86	-2.46 (3.17)	 **30a**  **30b**	58	2:1
16	 **31**	70	+8.85 (5.18)	 **32a**  **32b**	94	1:1
17	 **33**	48	+5.47 (3.80)	 **34a**  **34b**	62	1:1

TABLE 2. Hydrolysis Products of Selected Cyclopropane 1,4-di-*O*-benzyl-L-threitol Ketals.

entry	cyclopropane ketal	product cyclopropyl ketone	yield %	$[\alpha]_D^{25}$ deg (c)	configuration	enantiomeric excess	recovered diol, %
1	**2**	 **35**	75	+12.2 (0.81)	1*R*,5*S*[a]	51	89
2	**6**	 **36**	80	+27.3 (2.34)	1*R*,5*S*[b]	80	90
3	**8**	 **37**	78	+15.2 (1.06)	3a*S*,6a*R*	--	92
4	**10**	 **38**	91	+55.4 (2.80)	3a*S*,7a*R*	--	91
5	**12**	 **39**	84	-25.9 (2.58)	3a*S*,8a*R*	--	84
6	**14**	 **40**	83	+12.7 (3.40)	1*R*,6*S*[a]	83	76
7	**18**	 **41**	81	-19.4 (0.90)	1*R*,6*S*	--	89
8	**20**	 **42**	92	+15.0 (2.01)	4a*S*,8a*R*	--	56
9	**22**	 **43**	86	-86.8 (0.37)	--	86[d]	85

[a]Ref. 17b,36. [b]Ref. 37 [c]Ref. 17a,c. [d]Ref. 17a

TABLE 2, continued.

entry	cyclopropane ketal	product cyclopropyl ketone	yield %	$[\alpha]_D^{25}$ deg (c)	configuration	enantiomeric excess	recovered diol, %
10	**26**	 **44**	75	+25.7 (0.53)	1*R*,7*S*	--	85
11	**28c**	 **45**	88	+6.0 (4.33)	1*S*,15*R*[e]	95	86

[e]Ref. 26

TABLE III. CD Spectral Data for Cyclopropyl Ketones 37, 38, 39, and 42.

cyclopropyl ketone	concentration,[a] mg/mL	λ, nm	θ,[b] deg	[θ]
37	2.08	289	+1.27	+8320
		297	+1.27	+8320
		308	+0.78	+5110
38	1.96	286	+1.26	+9660
		293	+1.27	+9730
		304	+0.70	+5360
39	1.97	286	+0.75	+6250
		294	+0.78	+6500
		305	+0.52	+4380
42	1.82	296	+0.30	+2680
		305	+0.28	+2530
		317	+0.17	+1530

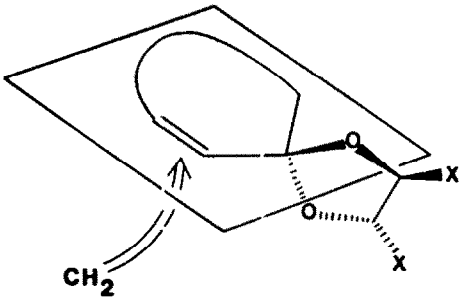
[a]In pentane. [b]At ambient temperature.

A number of natural products contain angularly methylated hydropentalene, hydroindene, hydroazulene, and hydronaphthalene ring systems. Since these systems might be derived enantioselectively from appropriate tricyclo[m.n.1.0]alkanones,[3,4] we prepared bicyclic ketals 7, 9, 11, and 19 and subjected them to Simmons-Smith cyclopropanation.[1b] The diastereoselectivities observed (7-9:1) were in keeping with our previous results with monocyclic ketals.

Hydrolyses of cyclopropane ketals 2, 6, 8, 10, 12, 14, 18, 20, 26 and 28[26] proceeded smoothly, providing the corresponding enantiomerically enriched cyclopropyl ketones in good to very good chemical yields, along with recovered 1,4-di-O-benzyl-L-threitol (Table 2). From the assigned stereochemistries of the product cyclopropyl ketones, it can be inferred that a common mode of reagent delivery is operative (Figure 1).

More disappointing were the diastereoselectivities obtained for acetals 23 (2:1), 31 (1:1), and 33 (1:1). Most interesting was the report by Yamamoto and co-workers describing asymmetric cyclopropanations of related tartrate acetals under alkylidene-transfer conditions[28] at low temperatures.[22] For α,β-unsaturated acetals, single bond rotations are permitted between the acetal and olefin. At lower temperatures, rotameric conformational freedom may be reduced, allowing for greater diastereoselection. This contention is supported by the increased diastereoselectivity observed for 21 (14:1) and 29 (2:1), since replacement of hydrogen by methyl would be expected to reduce the rotameric conformational freedom of 21 and 29 relative to 23 and 31.

Figure 1. Facial Selectivity for 2-Cycloalkene-1-one 1,4-Di-O-benzyl-L-threitol Ketals (X = $CH_2OCH_2C_6H_5$).



Conclusion

Described in this article is a general, straightforward synthetic approach for the enantioselective construction of bicyclo[n.1.0]alkan-2-ones and tricyclo[m.n.1.0]alkanones which employs a novel diastereoselective cyclopropanation process. The chemical yields and diastereoselectivities obtained thus far are generally well into the synthetically useful range, and the sense of the diastereoselection is predictable. The ready availability of both L- and D- forms of 1,4-di-O-benzylthreitol from natural and unnatural tartaric acids, respectively, makes access to either product enantiomer possible. The chiral auxilliary is also readily recoverable.

EXPERIMENTAL SECTION[29]

General Ketalization Procedure

To a well-stirred solution of the enone (1-2 equiv) in dry benzene (4-20 mL/mmol) were added 1,4-di-O-benzyl-L-threitol (1 equiv) and pyridinium p-toluenesulfonate (5-10 mol %). The mixture was heated to reflux under argon and water was removed azeotropically using a Dean-Stark trap. Progress of the reaction was monitored by TLC. Ketalization was terminated by cooling the mixture, which was then diluted with ether, washed with water, saturated sodium bicarbonate solution, saturated sodium chloride solution, dried ($MgSO_4$), and filtered. Volatiles were removed and the residue chromatographed to provide product and in some cases recovered starting materials.

General Cyclopropanation Procedure

To a well-stirred suspension of freshly prepared Zn-Cu couple (400-700 mg/mmol ene-ketal) with or without anhydrous potassium carbonate (3 molar equivalents) in freshly distilled (from P_2O_5) diethyl ether (1.7 mL/mmol ene-ketal) under argon were added a small crystal of iodine and diiodomethane (3 equivalents). After 30 min at reflux (external heating), the olefin-acetal was added as a solution in diethyl ether. Progress of the reaction was monitored by TLC and/or by HPLC. When reaction was complete, the mixture was cooled to 0°C and quenched with water or with saturated aqueous potassium carbonate (0.2 mL/mmol olefin-acetal). After stirring at room temperature for 30 min, the gray-black precipitate was removed by centrifugation or filtration and washed well with diethyl ether. The combined organic extracts were washed with saturated aqueous ammonium chloride solution, saturated aqueous sodium bicarbonate solution, saturated aqueous sodium chloride solution, dried ($MgSO_4$), filtered, and concentrated to give the crude product. Column chromatography afforded the pure product.

General Hydrolysis Procedure

To a stirred solution of the cyclopropane acetal in methanol (4.9 ml/mmol acetal) at room temperature was added 2.7 M hydrochloric acid (1 mL/mmol acetal). Progress of the reaction was monitored by TLC. When reaction was complete, the solution was poured into saturated aqueous sodium bicarbonate solution. The aqueous mixture was extracted several times with pentane, then with diethyl ether. The combined pentane extracts were dried ($MgSO_4$), filtered, and concentrated to afford a mixture of ketone and 1,4-di-O-benzyl-L-threitol. Column chromatography afforded the pure ketone as well as the diol. Additional diol was obtained from the combined diethyl ether extracts after drying ($MgSO_4$), filtration, and concentration.

2-Cyclopenten-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 1.

IR ($CHCl_3$) 3019, 2920, 2865, 1497, 1454, 1363, 1135, 1079, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) 2.10-2.16 (2,m), 2.36-2.40 (2,m), 3.60-3.64 (4,m), 4.00-4.15 (2,m), 4.57 (4,br s), 5.71-5.75 (1,m), 6.04-6.09 (1,m), and 7.24-7.34 ppm (10,m); exact mass calc. for $C_{23}H_{26}O_4$, 366.18311, observed 366.18301.

(1R,5S)-Bicyclo[3.1.0]hexan-2-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 2a.
IR ($CHCl_3$) 3012, 2931, 2865, 1604, 1451, 1364, 1217, 1210, 1097, 1080, 907, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 0.42-0.61 (2,m), 1.18-2.00 (6,m), 3.51-3.71 (4,m), 3.97-4.14 (2,m), 4.53-4.60 (4,m), and 7.25-7.40 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 7.0 (CH_2), 16.2 (CH), 23.4 (CH), 24.4 (CH_2), 31.5 (CH_2), 70.5 (CH_2), 73.5 (CH_2), 77.1 (CH), 77.3 (CH), 119.8 (C), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); major diastereomer 7.0 (CH_2), 16.1 (CH), 23.1 (CH), 24.5 (CH_2), 31.4 (CH_2), 70.5 (CH_2), 73.5 (CH_2), 77.1 (CH), 77.3 (CH), 119.8 (C), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calc. for $C_{24}H_{28}O_4$, 380.19876, observed 380.20059.

2-Methyl-2-cyclopenten-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 3.
IR (neat) 3100, 3075, 3040, 2980-2820 (br), 1960 (w), 1880 (w), 1819 (w), 1744 (w), 1610 (w), 1591 (w), 1500, 1455, 1367, 1345, 1300, 1270, 1218, 1100 (br), 925, 842, 799, 730, and 691 cm^{-1}; ^1H NMR ($CDCl_3$) 1.68 (3,m), 2.04-2.11 (2,m), 2.22-2.31 (2,m), 3.60-3.66 (4,m), 3.99-4.11 (2,m), 4.57 (4,s), 5.69 (1,m), and 7.25-7.35 ppm (10,m); exact mass calculated for $C_{24}H_{28}O_4$, 380.1988, observed 380.1985.

1-Methyl-bicyclo[3.1.0]hexan-2-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 4.
IR (neat) 3080, 3040, 3020, 2940, 2879, 1500, 1456, 1378, 1335, 1300, 1216, 1185, 1100, 1030, 990, 942, 800, 734, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) 0.39 (1,dd, ^2J-5Hz, ^3J-7Hz), 0.68 (1,dd, ^2J-5z, ^3J-5Hz), 1.14-1.21 (1,m, obscured), 1.16 (3,S), 1.40-2.00 (4,m), 3.55-3.70 (4,m), 3.94-4.09 (2,m), 4.54-4.60 (4,m), and 7.25-7.35 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 14.0 (CH), 14.4 (CH_2), 22.8 (CH_3), 23.9 (C), 27.2 (CH_2), 32.8 (CH_2), 70.4 (CH_2), 70.6 (CH_2), 73.3 (CH_2), 77.8 (CH), 78.1 (CH), 120.1 (CH), 127.4 (CH), 127.5 (CH), 128.2 (CH), and 137.9 ppm (C); major diastereomer 14.0 (CH_2), 14.3 (CH), 22.8 (CH_3), 24.0 (C), 26.8 (CH_2), 32.1 (CH_2), 70.2 (CH_2), 70.6 (CH_2), 73.3 (CH_2), 76.8 (CH), 77.8 (CH), 119.9 (C), 127.4 (CH), 127.5 (CH), 128.2 (CH), and 137.9 ppm (C); exact mass calculated for $C_{25}H_{30}O_4$, 394.2144, observed 394.2142.

3-[(1-Methyl)ethyl]-2-cyclopenten-1-one Cyclic (1S,2S)-1,2-Bis[benzyloxy)methyl]ethylene Acetal 5.
IR (neat) 3090, 3065, 3035, 2965, 2930, 2870, 1650, 1499, 1405, 1383, 1368, 1355, 1319, 1286, 1253, 1208, 1136, 1100, 1030, 926, 911, 738, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) 1.04 (6,d, ^3J = 6.8 Hz), 2.13-2.21 (2,m), 2.24-2.37 (3,m), 3.60-3.63 (4,m), 4.00-4.10 (2,m), 4.57 (4,s), 5.37 (1,q, ^4J = 1.8 Hz), and 7.30-7.34 ppm (10,m); exact mass calc. for $C_{26}H_{32}O_4$ 408.2302, observed 408.2304.

(1R,5S)-5-[(1-Methyl)ethyl]bicyclo[3.1.0]hexan-2-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]-ethylene Acetal 6a.
IR ($CHCl_3$) 3012, 2952, 2925, 2865, 1451, 1384, 1364, 1347, 1317, 1100, 943, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 0.48 (1,dd, ^2J = 5.3 Hz, ^3J = 8.4 Hz), 0.57 (1,dd, ^2J = 5.3 Hz, ^3J = 3.7 Hz), 0.85 (3,d, ^3J = 6.8 Hz), 0.95 (3,d, ^3J = 6.8 Hz), 1.21-1.26 (1,m), 1.38-1.84 (5,m), 3.54-3.72 (4,m), 3.95-4.12 (2,m), 4.55-4.63 (4,m), and 7.20-7.39 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 12.1 (CH_2), 19.3 (CH_3), 19.7 (CH_3), 25.3 (C), 29.2 (CH), 31.9 (CH), 33.1 (CH_2), 33.3 (CH_2), 70.5 (CH_2), 73.4 (CH_2), 77.2 (CH) 77.3 (CH), 119.5 (C), 127.5 (CH), 128.2 (CH), and 138.1 ppm (C); major diastereomer 12.2 (CH_2), 19.3 (CH_3), 19.6 (CH_3), 25.0 (C), 28.8 (CH), 32.0 (CH), 32.8 (CH_2), 33.3 (CH_2), 70.5 (CH_2), 73.4 (CH_2), 77.2 (CH), 77.3 (CH), 119.5 (C), 127.5 (CH), 128.2 (CH), and 138.0 ppm (C); exact mass calculated for $C_{26}H_{34}O_4$ 422.2457, observed 422.2456.

2,3,5,6-Tetrahydro-1H,4H-pentalen-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 7.
IR (neat) 3190, 3165, 3132, 2920, 2860, 1495, 1451, 1370, 1301, 1170, 1105, 1029, 996, 955, 922, 737, and 699 cm^{-1}; ^1H NMR ($CDCl_3$) 2.15-2.28 (8,m), 2.48-2.56 (2,m), 3.58-3.63 (4,m), 3.96-4.08 (2,m), 4.55-4.59 (4,m), and 7.25-7.34 ppm (10,m); exact mass calculated for $C_{26}H_{30}O_4$, 406.2142, observed 406.2144.

(3aS,6aR)-2,3,5,6-Tetrahydro-3a,6a-methano-1H,4H-pentalen-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)-methyl]ethylene Acetal 8a.
IR ($CHCl_3$) 3011, 2930, 2865, 1454, 1366, 1309, 1296, 1270, 1155, 1096, 1080, 1062, 1028, 951, 699, and 668 cm^{-1}; ^1H NMR ($CDCl_3$) 0.70 (1,d, ^2J = 5.9 Hz), 0.90 (1,d, ^2J = 5.9 Hz), 1.20-2.20 (10,m), 3.48-3.78 (4,m), 3.84-4.10 (2,m), 4.48-4.70 (4,m), and 7.19-7.55 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 15.1, 23.7, 27.7, 28.2, 31.1, 38.2, 40.6, 41.2, 70.7, 70.9, 73.4, 78.4, 118.2, 127.6, 128.3,and 138.0 ppm; major diastereomer 15.1, 23.5, 28.0, 28.3, 31.0, 38.1, 40.0, 40.7, 70.3, 70.4, 73.4, 77.3, 77.4, 117.8, 127.6, 128.3, and 138.0 ppm; exact mass calculated for $C_{27}H_{32}O_4$ 420.2300, observed 420.2308.

2,3,4,5,6,7-Hexahydro-1H-inden-1-one Cyclic (1S,2S)-1,2-Bis[benzyloxy)methyl]ethylene Acetal 9.
IR (neat) 3062, 3029, 2924, 2855, 1496, 1452, 1385, 1365, 1304, 1295, 1245, 1205, 1186, 1151, 1084, 1026, 999, 922, 737, and 698 cm^{-1}; ^1H NMR ($CDCl_3$) 1.59-1.67 (4,m), 1.93-2.03 (4,m), 2.08 (2,br t, J-6Hz), 2.19-2.28 (2,m), 3.60-3.65 (4,m), 3.97-4.11 (2,m), 4.57 (4,s), and 7.25-7.34 ppm (10,m); exact mass calculated for $C_{27}H_{32}O_4$ 420.2300, observed 420.2307.

(3aS,7aR)-2,3,4,5,6,7-Hexahydro-3a,7a-methano-1H-inden-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)-methyl]ethylene Acetal 10a.
IR ($CHCl_3$) 3012, 2931, 2858, 1451, 1364, 1314, 1219, 1100, 1027, 950, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 0.40 (1,d, ^2J = 5.2 Hz), 0.76 (1,d, ^2J = 5.1 Hz), 0.91-1.96 (11,m), 2.14-2.28 (1,m), 3.43-3.78 (4,m), 3.92-4.10 (2,m), 4.50-4.66 (4,m), and 7.21-7.52 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 18.1, 20.8, 21.9, 22.2, 25.8, 28.8, 29.9, 31.9, 33.3, 70.5, 70.8, 73.3, 77.7, 78.3, 120.9, 127.4, 128.2, and 138.1 ppm; major diastereomer 17.9, 20.8, 22.2, 25.8, 28.8, 29.8, 31.9, 32.6, 70.1, 70.8, 73.3, 77.0, 77.6, 120.5, 127.4, 128.2, and 138.1 ppm; exact mass calculated for $C_{28}H_{34}O_4$, 434.2457, observed 434.2457.

2,3,5,6,7,8-Hexahydro-1H,4H-azulen-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 11.
IR (Neat) 3088, 3061, 3035, 2919, 2850, 1498, 1454, 1385, 1366, 1311, 1292, 1260, 1211, 1161, 1093, 1030, 1019, 978, 955, 940, 911, 738, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) 1.52-1.63 (4,m), 1.63-1.78 (2,m), 2.04 (2,br t, J = 6.5 Hz), 2.06-2.18 (4,m), 2.23-2.32 (2,m), 3.59-3.68 (4,m), 3.95-4.12 (2,m), 4.57 (2,s), 4.58 (2,s), and 7.25-7.37 ppm (10,m); exact mass calculated for $C_{28}H_{34}O_4$ 434.2457, observed 434.2455.

(3aS,8aR)-2,3,5,6,7,8-Hexahydro-3a,8a-methano-1H,4H-azulen-1-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy) methyl]ethylene Acetal 12a.
IR ($CHCl_3$) 3005, 2918, 2858, 1451, 1364, 1311, 1237, 1130, 1097, 1074, 977, 947, 907, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 0.52-0.69 (2,m), 1.03-2.17 (14,m), 3.50-3.78 (4,m), 3.90-4.10 (2,m), 4.50-4.65 (4,m), and 7.20-7.55 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 14.8, 26.8, 27.2, 27.3, 30.4, 32.1, 32.2, 33.7, 33.8, 35.8, 70.4, 70.9, 73.3, 78.1, 121.9, 127.5, 128.2, and 138.0 ppm; major diastereomer 15.4, 26.4, 27.2, 27.3, 30.4, 32.1, 32.2, 33.0, 34.0, 35.5, 70.4, 70.9, 73.3, 77.1, 77.6. 121.9, 127.5, 128.2, and 138.0 ppm; exact mass calculated for $C_{29}H_{36}O_4$ 448.2613, observed 448.2621.

2-Cyclohexen-1-one Cyclic (1S, 2S)-1,2-Bis[benzyloxy)methyl]ethylene Acetal 13.
IR ($CHCl_3$) 3058, 3005, 2932, 2865, 1648, 1491, 1451, 1394, 1364, 1231, 1174, 1127, 1104, 1074, 940, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 1.71-1.91 (4,m), 1.96-2.07 (2,m), 3.59-3.69 (4,m), 4.03-4.17 (2,m), 4.57 (4,s), 5.63 (1,dt, ^4J ~1 Hz, ^3J = 10.1 Hz), 5.93 (1,dt, ^3J = 3.9 Hz, ^3J = 10.1 Hz), and 7.24-7.38 ppm (10,m); exact mass calculated for $C_{24}H_{28}O_4$ 380.19876, observed 380.19720.

(1R, 6S)-2-Norcaranone Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 14a.
IR ($CHCl_3$) 3012, 2938, 2865, 1451, 1364, 1210, 1137, 1094, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 0.25-0.40 (1,m), 0.62-0.79 (1,m), 1.00-1.72 (7,m), 1.75-1.95 (1,m), 3.54-3.77 (4,m), 3.98-4.23 (2,m), 4.50-4.70 (4,m), and 7.18-7.45 ppm (10,m); ^{13}C NMR ($CDCl_3$) major diastereomer 9.4 (CH_2), 12.4 (CH), 19.8 (CH), 19.9 (CH_2), 22.4 (CH_2), 32.7 (CH_2), 70.6 (CH_2), 70.7 (CH_2), 73.4 (CH_2), 77.2 (CH), 77.4 (CH), 110.3 (C), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calculated for $C_{25}H_{30}O_4$, 394.21441, observed 394.21228.

3-Cyclohexen-1-one Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 15.
IR ($CHCl_3$) 3025, 3012, 2925, 2865, 1495, 1451, 1358, 1264, 1244, 1137, 1104, 1070, 1027, 907, 857, 737, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 1.72-1.90 (2,m), 2.18-2.45 (4,m) 3.60-3.68 (4,m), 4.03-4.20 (2,m), 4.57 (4,s), 5.54-5.64 (1,m), 5.66-5.76 (1,m), and 7.20-7.42 ppm (10,m); exact mass calculated for $C_{24}H_{28}O_4$, 380.19876, observed 380.19834.

3-Norcaranone Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 16.
IR ($CHCl_3$) 3012, 2925, 2865, 1495, 1451, 1361, 1137, 1090, 1027, 994, 696, and 667 cm^{-1}; ^1H NMR ($CDCl_3$) 0.09-0.20 (1,m), 0.51-0.63 (1, m), 0.80-1.02 (2, m), 1.22-1.65 (2,m), 1.70-1.93 (2,m), 2.02-2.38 (2,m), 3.49-3.70 (4,m), 3.94-4.18 (2,m), 4.52-4.64 (4,m), and 7.22-7.41 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 8.9 (CH), 9.2 (CH), 10.6 (CH_2), 21.9 (CH_2), 30.6 (CH_2), 34.9 (CH_2), 70.8 (CH_2), 70.9 (CH_2), 73.3 (CH_2), 73.5 (CH_2), 76.9 (CH), 77.2 (CH), 77.6 (CH), 109.8 (C), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); major diastereomer, 8.9 (CH), 9.2 (CH), 10.3 (CH_2), 21.7 (CH_2), 30.3 (CH_2), 34.8 (CH_2), 70.6 (CH_2), 70.7 (CH_2), 73.3 (CH_2), 73.5 (CH_2), 76.9 (CH), 77.2 (CH), 77.6 (CH), 109.6 (C), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calculated for $C_{25}H_{30}O_4$ 394.21441, observed 394.21265.

2-Methyl-2-cyclohexen-1-one Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 17.
IR ($CHCl_3$) 3012, 2932, 2865, 1495, 1451, 1364, 1264, 1211, 1174, 1130, 1100, 1077, 1024, 950, 780, 767, 733, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 1.63-2.08 (9,m), 3.57-3.71 (4,m), 3.96-4.08 (1,m), 4.09-4.19 (1,m), 4.56 (4,s), 5.68 (1,br s), and 7.20-7.40 ppm (10,m); exact mass calculated for $C_{25}H_{30}O_4$ 394.21441, observed 394.21426.

1-Methyl-2-norcaranone Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 18.
IR ($CHCl_3$) 3005, 2938, 2865, 1491, 1451, 1364, 1250, 1217, 1191, 1144, 1091, 1027, 967, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 0.42-0.50 (1,m), 0.51-0.60 (1,m), 0.92-1.05 (1,m), 1.07 (3,s), 1.14-1.72 (5,m), 1.85-2.02 (1,m), 3.56-3.65 (2,m), 3.67-3.75 (2,m), 3.94-4.06 (1,m), 4.11-4.21 (1,m), 4.52-4.65 (4,m), and 7.20-7.40 ppm (10,m); ^{13}C NMR ($CDCl_3$) 19.4 (CH_2), 19.9 (CH_3), 21.0 (C), 21.6 (CH), 22.2 (CH_2), 22.3 (CH_2), 31.6 (CH_2), 70.4 (CH_2), 71.0 (CH_2), 73.4 (CH_2), 73.5 (CH_2), 78.3 (CH), 112.7 (C), 127.5 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calculated for $C_{26}H_{32}O_4$ 408.23006, observed 408.22855.

3,4,5,6,7,8-Hexahydronaphthalen-1(2H)-one Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 19.[16]

(4aS, 8aR)-3,4,5,6,7,8-Hexahydro-4a,8a-methanonaphthalen-1(2H)-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 20.[16]

1-Cyclohexen-1-yl Methyl Ketone Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 21.
IR ($CHCl_3$) 3020, 2940, 2870, 1500, 1455, 1370, and 1080 cm^{-1}; ^1H NMR ($CDCl_3$) 1.60 (3,s), 1.46-1.62 (4,m), 1.93-2.05 (4,m), 3.45-3.64 (4,m), 3.87-3.95 (1,m), 4.02-4.17 (1,m), 4.54-4.60 (4,m), 5.87 (1,m) and 7.24-7.34 ppm (10,m); exact mass calculated for $C_{26}H_{32}O_4$, 408.23006, observed 408.22937.

Methyl 1-Norcaryl Ketone Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 22.
IR ($CHCl_3$) 3012, 2932, 2858, 1451, 1371, 1080, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 0.11 (1,dd, ^2J = 4.2 Hz, ^3J = 5.8 Hz), 0.71 (1,dd, ^2J = 4.2 Hz, ^3J = 9.7 Hz), 1.05-1.34 (5,m), 1.37 (3,s), 1.49-1.85 (3,m), 1.91-2.06 (1,m), 3.55-3.66 (4,m), 3.88 (1,dt, ^3J = 4.8, 8.2 Hz), 4.07 (1,dt, ^3J = 4.9, 8.2 Hz), 4.53-4.60 (4,m), and 7.23-7.38 ppm (10,m); ^{13}C NMR ($CDCl_3$) 13.9 (CH_2), 14.6 (CH), 21.0 (C), 22.0 (CH_2), 23.3 (CH_2), 23.4 (CH_3), 25.9 (CH_2), 26.1 (CH_2), 70.3 (CH_2), 70.7 (CH_2), 73.4 (CH_2), 77.4 (CH), 78.1 (CH), 112.5 (C), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calculated for $C_{27}H_{34}O_4$ 422.24571, observed 422.24585.

1-Cyclohexene Carboxaldehyde Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 23.
IR (neat) 3090, 3065, 3035, 3005, 2930, 2860, 1499, 1457, 1369, 1301, 1190, 1136, 1095, 1075, 1046, 1030, 975, 925, 840, 802, 738, and 699 cm^{-1}; ^1H NMR ($CDCl_3$) 1.55-1.62 (4,m), 2.03-2.06 (4,m), 3.58-3.66 (4,m), 3.99-4.16 (2,m), 4.57 (4,s), 5.29 (1,s), 5.91 (1, br m), and 7.25-7.35 ppm (10,m); exact mass calculated for $C_{25}H_{30}O_4$ 394.2144, observed 394.2129.

1-Norcarylcarboxaldehyde Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 24.
IR ($CHCl_3$) 3015, 2935, 2865, 1732, 1454, 1365, 1117, 1098, 1078, 995, 910, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.31 (1,dd, ^2J = 5.0 Hz, ^3J = 5.6 Hz), 0.64 (1,dd, ^2J = 4.7 Hz, ^3J = 9.4 Hz), 0.81-2.10 (9,m), 3.51-3.72 (4,m), 3.92-4.11 (2,m), 4.37 and 4.38 (1,s, diastereotopic protons), 4.55-4.63 (4,m), and 7.21-7.30 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 13.7 (CH_2), 14.4 (CH), 20.2 (C), 21.0 (CH_2), 21.6 (CH_2), 22.7 (CH_2), 23.1 (CH_2), 70.4 (CH_2), 70.6 (CH_2), 73.4 (CH_2), 77.6 (CH), 77.9 (CH), 111.0 (CH), 127.6 (CH), 128.4 (CH), and 138.1 ppm (C); major diastereomer 13.8 (CH_2), 14.3 (CH), 20.2 (C), 21.0 (CH_2), 21.6 (CH_2), 22.8 (CH_2), 23.1 (CH_2), 70.4 (CH_2), 70.5 (CH_2), 73.4 (CH_2), 77.4 (CH), 77.8 (CH), 110.9 (CH), 127.6 (CH), 128.4 (CH), and 138.1 ppm (C); exact mass calculated for $C_{26}H_{32}O_4$ 408.2300, observed 408.2283.

2-Cyclohepten-1-one Cyclic (1S, 2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 25.
IR ($CHCl_3$) 3012, 2931, 2858, 1494, 1451, 1364, 1230, 1097, 980, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 1.57-1.69 (2,m), 1.71-1.82 (2,m), 1.86-1.96 (2,m), 2.13-2.23 (2,m), 3.57-3.70 (4,m), 4.00-4.11 (2,m), 4.58 (4,s), 5.69 (1,d, ^3J = 12 Hz), 5.79-5.90 (1,m), and 7.25-7.38 ppm (10,m); exact mass calculated for $C_{25}H_{30}O_4$ 394.21441, observed 394.21344.

Bicyclo[5.1.0]octan-2-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 26.
IR ($CHCl_3$) 3020, 2930, 2870, 1455, 1370, 1135, 1095, 1010, 970, 917, 900, and 800 cm^{-1}; ^1H NMR ($CDCl_3$) 0.40-0.48 (1,m), 0.53-0.67 (1,m), 0.79-0.97 (1,m), 1.08-1.67 (6,m), 1.73-2.14 (3,m),3.58-3.72 (4,m), 3.92-4.12 (2,m), 4.53-4.64 (4,m), and 7.22-7.38 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 8.0 (CH_2), 14.0 (CH), 24.0 (CH_2), 24.7 (CH), 27.1 (CH_2), 28.7 (CH_2), 39.3 (CH_2), 70.7 (CH_2), 70.9 (CH_2), 73.4 (CH_2), 77.9 (CH), 78.4 (CH), 112.3 (C), 127.6 (CH), 127.7 (CH), 128.3 (CH), and 138.2 ppm (C); major diastereomer 9.7 (CH_2), 15.0 (CH), 24.3 (CH), 24.5 (CH_2), 27.8 (CH_2), 29.5 (CH_2), 40.7 (CH_2), 70.7 (CH_2), 70.9 (CH_2), 73.4 (CH_2), 77.9 (CH), 78.4 (CH), 111.7 (C), 127.6 (CH), 127.7 (CH), 128.3 (CH), and 138.2 ppm (C); exact mass calculated for $C_{26}H_{32}O_4$ 408.23006, observed 408.22977.

(E)-Cyclopentadec-2-en-1-one Cyclic (1S,2S)-1,2-Bis[benzyloxy)methyl]ethylene Acetal 27.[26]
IR ($CHCl_3$) 3012, 2925, 2851, 1494, 1451, 1364, 1264, 1097, 977, 907 and 677 cm^{-1}; ^1H NMR ($CDCl_3$) 1.11-1.49 (20,m), 1.63-1.77 (2,m), 1.98-2.12 (2,m), 3.47-3.68 (4,m), 3.92-4.06 (2,m), 4.52-4.62 (4,m), 5.42 (1,dt, ^3J = 15.6 Hz, ^4J = 1.1 Hz), 5.72 (1,dt, ^3J = 15.6 Hz, ^3J = 7.1 Hz), and 7.20-7.39 ppm (10,m); exact mass calculated for $C_{33}H_{46}O_4$ 506.3396, observed 506.3386.

(1R,15R)-Bicyclo[13.1.0]hexadecan-2-one Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 28a.[26]
IR ($CHCl_3$) 3005, 2925, 2851, 1451, 1361, 1137, 1087 and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 0.13-0.23 (1,m), 0.52-0.62 (1,m), 0.66-0.95 (2,m), 1.12-1.89 (24,m), 3.51-3.70 (4,m), 3.80-3.89 (1,m), 3.95-4.08 (1,m), 4.53 (2,s), 4.57 (2,s), and 7.20-7.40 ppm (10,m); ^{13}C NMR ($CDCl_3$) 8.8 (CH_2), 16.4 (CH), 22.3 (CH_2), 25.6 (CH), 25.8 (CH_2), 26.2 (CH_2, 26.3 (CH_2, 26.4 (CH_2), 26.6 (CH_2), 27.1 (CH_2), 27.3 (CH_2), 27.4 (CH_2), 29.1 (CH_2), 33.7 (CH_2), 40.3 (CH_2), 70.8 (CH_2), 70.9 (CH_2), 73.4 (CH_2), 73.5 (CH_2), 77.1 (CH), 78.8 (CH), 111.7 (C), 127.5 (CH), 127.6 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calculated for $C_{34}H_{48}O_4$ 520.3552, observed 520.3544.

4-Methyl-3-penten-2-one Cyclec (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 29.
IR ($CHCl_3$) 3005, 2965, 2925, 2865, 1648, 1642, 1492, 1451, 1368, 1317, 1238, 1134, 1096, 1024, 910, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 1.50 (3,s), 1.65 (3,d, ^4J = 1.4 Hz), 1.78 (3,d, ^4J = 1.7 Hz), 3.45-3.68 (4,m), 3.92-4.08 (2,m), 4.08-4.65 (4,m), 5.30 (1,q ^4J = 1.3 Hz), and 7.21-7.40 ppm (10,m); exact mass calculated for $C_{24}H_{30}O_4$ 382.2144, observed 382.2138.

Methyl 2,2-Dimethylcylopropyl Ketone Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 30. IR ($CHCl_3$) 3005, 2931, 2865, 1494, 1451, 1371, 1237, 1090, 1023 and 907 cm^{-1}; ^1H NMR ($CDCl_3$) 0.31-0.47 (2,m), 0.88-1.00 (1,m), 1.03 (3,s), 1.17 and 1.18 (3,s, diastereotopic methyls), 1.45 and 1.47 (3,s, diastereotopic methyls), 3.53-3.69 (4,m), 3.85-3.96 (1,m), 3.99-4.12 (1,m), 4.51-4.63 (4,m), and 7.21-7.41 ppm (10,m); ^{13}C NMR ($CDCl_3$) minor diastereomer 15.8 (CH_2), 16.3 (C), 19.3 (CH), 27.4 (CH_3), 28.2 (CH_3), 32.7 (CH_3), 70.3 (CH_2), 70.6 (CH_2), 73.4 (CH_2), 77.2 (CH), 77.9 (CH), 110.1 (C), 127.6 (CH), 127.7 (CH), 128.3 (CH), and 138.1 ppm (C); major diastereomer 15.3 (CH_2), 16.4 (C), 19.4 (CH), 27.4 (CH_3), 28.0 (CH_3), 32.9 (CH_3), 70.8 (CH_2), 70.9 (CH_2), 73.4 (CH_2), 76.4 (CH), 110.3 (C), 127.6 (CH), 127.7 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calc. for $C_{25}H_{32}O_4$ 396.2300, observed 396.2290.

3-Methylcrotonaldehyde Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 31. IR ($CHCl_3$) 3012, 2912, 2858, 1678, 1495, 1447, 1378, 1364, 1207, 1157, 1071, 1027, 960, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 1.74 (6,br s), 3.56-3.70 (4,m), 3.99-4.17 (2,m), 4.57 (4,s), 5.25 (1,br d, ^3J = 7.5 Hz), 5.70 (1,d ^3J = 7.5 Hz), and 7.24-7.34 ppm (10,m); exact mass calc. for $C_{23}H_{28}O_4$ 368.19876, observed 368.19681.

2,2-Dimethylcyclopropane Carboxaldehyde Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 32. IR ($CHCl_3$) 3065, 3032, 3012, 2952, 2925, 2865, 1495, 1451, 1210, 1127, 1091, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 0.37-0.43 (1,m), 0.56-0.64 (1,m), 0.79-0.91 (1,m), 1.06 and 1.07 (3,s), 1.12 and 1.14 (3,s), 3.55-3.72 (4,m), 3.99-4.13 (2,H), 4.52-4.60 (4,m), 4.64 and 4.67 (1,d, ^3J = 7.9 Hz and 7.7 Hz), and 7.22-7.38 ppm (10,m); ^{13}C NMR ($CDCl_3$) 15.6 (CH_2), 17.5 and 17.7 (C), 20.4 (CH), 26.3, 26.5, and 27.0 (CH_3), 70.4 and 70.7 (CH_2), 73.4 (CH_2), 77.4 and 77.9 (CH), 106.7 and 106.8 (CH), 127.4 (CH), 127.5 (CH), 127.6 (CH), 127.7 (CH), 128.3 (CH), and 138.1 ppm (C); exact mass calculated for $C_{24}H_{30}O_4$ 382.21441, observed 383.21243.

Methyl (E)-6-Formyl-5-hexenoate Cyclic (1S,2S)-1,2-Bis[(benzyloxy)methyl]ethylene Acetal 33. IR ($CHCl_3$) 3019, 2945, 2865, 1728, 1678, 1491, 1454, 1438, 1364, 1231, 1147, 1101, 1067, 1027, 967, and 697 cm^{-1}; ^1H NMR ($CDCl_3$) 1.73 (2, apparent quintet, ^3J = 7.3 Hz), 2.10 (2,ddt, ^3J = 7.3 Hz, ^3J = 6.6 Hz, ^4J = 1.3 Hz), 2.31 (2,t, ^3J = 7.3 Hz), 3.55-3.70 (4,m), 3.65 (3,s), 4.00-4.18 (2,m), 4.57 (4,s), 5.36 (1,d, ^3J = 6.7 Hz), 5.51 (1,ddt, ^3J = 15.5 Hz, ^3J = 6.7 Hz, ^4J = 1.3 Hz), 5.89 (1, dt, ^3J = 15.5 Hz, ^3J = 6.6 Hz), and 7.24-7.35 ppm (10, m); exact mass calculated for $C_{26}H_{32}O_6$ 440.219891, observed 440.217896.

Methyl 2-Formylcyclopropanebutyrate Cyclic (1S, 2S)-1,2-Bis-[(benzyloxy)methyl]ethylene Acetal 34. IR ($CHCl_3$) 3012, 2925, 2865, 1728, 1451, 1437, 1364, 1241, 1097, and 696 cm^{-1}; ^1H NMR ($CDCl_3$) 0.30-0.42 (1,m), 0.55-0.68 (1,m), 0.71-0.95 (2,m), 1.08-1.50 (3,m), 1.63-1.85 (2,m), 2.35 (2,br t, ^3J = 7.5 Hz), 3.46-3.78 (7,m), 3.90-4.20 (2,m), 4.46-4.70 (4,m), and 7.15-7.45 ppm (10,m); ^{13}C NMR ($CDCl_3$) 8.3 (CH_2), 14.8 (CH), 20.9 (CH), 24.7 (CH_2), 32.5 (CH_2), 33.6 (CH_2), 51.4 (CH_3), 70.3 (CH_2), 70.6 (CH_2), 73.4 (CH_2), 73.5 (CH_2), 77.5 (CH), 77.8 (CH), 107.2 (CH), 127.5 (CH), 127.6 (CH), 128.4 (CH), 138.0 (C), and 174.1 ppm (C); exact mass calculated for $C_{27}H_{34}O_6$ 454.23554, observed 454.23303.

(1R, 5S)-Bicyclo[3.1.0]hexan-2-one 35.[17b,36] IR ($CHCl_3$) 3000, 2960, 2930, 2875, 1720, 1460, 1380, 1315, 1305, 1185, 1145, 1105, 990, 925, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) 0.85-0.96 (1,m), 1.08-1.32 (2,m), 1.68-1.82 (1,m), and 1.88-2.25 ppm (4,m).

(+)-Sabina Ketone 36.[37] IR ($CHCl_3$) 3007, 2963, 2876, 1720, 1466, 1386, 1366, 1298, 1265, 1184, 1021, 953, 907, and 650 cm^{-1}; ^1H NMR ($CDCl_3$) 0.94 (3,d, ^3J = 6.9 Hz), 0.99 (3,d, ^3J = 6.8 Hz), 1.07 (1,dd, ^2J = 4.6 Hz, ^3J = 3.1 Hz), 1.18 (1,dd, ^2J = 4.6 Hz, ^3J = 9.0 Hz), 1.50-1.69 (2,m), 1.93-2.05 (2,m), and 2.08-2.25 ppm (2,m); exact mass calculated for $C_9H_{14}O$ 138.1045, observed 138.1042.

(3aS, 6aR)-2,3,5,6-Tetrahydro-3a,6a-methano-1H,4H-pentalen-1-one 37. IR ($CHCl_3$) 3011, 2944, 2872, 1703, 1455, 1418, 1367, 1289, 1272, 1252, 1233, 1197, 1126, 1065, 1055, 1038, 1023, 984, 886, 865, and 666 cm^{-1}; ^1H NMR ($CDCl_3$) 1.15-2.21 (10,m), 2.23-2.40 (1,m), and 2.45-2.65 ppm (1,m); ^{13}C NMR ($CDCl_3$) 22.6, 23.3, 27.0, 31.1, 39.0, 43.8, 46.7, and 212.8 ppm; mass spectrum (70 eV) m/z (rel. intensity) 137(3), 136(31), 121(2), 108(10), 95(8), 94(99), 93(24), 91(13), 79(100), 77(19); exact mass calculated for $C_9H_{12}O$ 136.0888, observed 136.0889.

(3aS, 7aR)-2,3,4,5,6,7-Hexahydro-3a,7a-methano-1H-inden-1-one 38[38]. IR ($CHCl_3$) 3013, 2937, 2867, 1706, 1454, 1416, 1379, 1312, 1260, 1184, 1152, 1132, 1104, 1079, 1049, 1024, 1006, 862, 699, and 666 cm^{-1}; ^1H NMR ($CDCl_3$) 0.96-1.30 (4,m), 1.31-1.55 (3,m), 1.59-1.91 (2,m), 1.96-2.27 (4,m), and 2.29-2.42 ppm (1,m); ^{13}C NMR ($CDCl_3$) 20.2, 21.7, 21.8, 24.9, 29.6, 29.9, 32.9, 33.1, 36.4, and 215.4 ppm; mass spectrum (70 eV) m/z (rel. intensity) 151(4), 150(42), 135(3), 122(5), 121(3), 108(100), 107(10), 93(73), 91(20), 80(20), 79(58); exact mass calculated for $C_{10}H_{14}O$ 150.1045, observed 150.1044.

(3aS, 8aR)-2,3,5,6,7,8-Hexahydro-3a,8a-methano-1H,4H-azulen-1-one 39.[38] IR ($CHCl_3$) 3015, 2925, 2851, 1706, 1455, 1373, 1234, 1077, 1056, 1029, 968, 833,and 668 cm^{-1}; ^1H NMR ($CDCl_3$) 1.14 (2,s), 1.18-1.36 (3,m), 1.38-1.75 (5,m), 1.83-2.25 (5,m) and 2.42-2.60 ppm (1,m); ^{13}C NMR ($CDCl_3$) 26.2, 26.8, 27.1, 28.3, 32.4, 33.3, 35.2, 38.0, 42.6, and 215.6 ppm; mass spectrum (70 eV) m/z (rel. intensity) 165(10), 164(82), 149(9), 136(12), 135(10), 123(10), 122(100), 121(16), 108(9), 107(67), 105(8), 94(52), 93(90), 91(31), 81(24), 80(32), 79(87), 77(28), 68(16), 67(33); exact mass calculated for $C_{11}H_{16}O$ 164.1201, observed 164.1201.

(1R, 6S)-2-Norcaranone 40.[17a,c] IR ($CHCl_3$) 3005, 2938, 2858, 1681, 1474, 1448, 1347, 1321, 1244, 1214, 1067, 960, 930, 873, 823, and 663 cm^{-1}; ^1H NMR ($CDCl_3$) 1.02-1.16 (1,m), 1.17-1.28 (1,m), 1.50-1.81 (4,m), 1.83-2.14 (3,m) and 2.22-2.37 ppm (1,m).

(-)-1-Methyl-2-norcaranone 41.
IR ($CHCl_3$) 3012, 2965, 2932, 2865, 1671, 1451, 1357, 1234, 1214, 1124, 1097, 907, 820, 723, and 666 cm^{-1}; ^1H NMR ($CDCl_3$) 0.79 (1, dd, J = 5.1 Hz, J = 7.9 Hz), 1.14 (3,s), 1.29 (1, t, J = 5.5 Hz), 1.42-1.52 (1,m), 1.56-1.68 (2,m), 1.80-2.08 (3,m), and 2.23 ppm (1, dt, ^3J = 5.1 Hz, ^2J = 18.0 Hz); mass spectrum (70 eV) m/z (rel. intensity) 124(9), 109(3), 96(11), 95(11), 83(3), 82(23), 81(48), 79(9), 69(45), 68(78), 67(100); exact mass calculated for $C_8H_{12}O$, 124.0888, observed 124.0893.

(4aS,8aR)-3,4,5,6,7,8-Hexahydro-4a,8a-methanonaphthalen-1(2H)-one 42.[1b,39]

(-)-Methyl Norcaryl Ketone 43.[17a]
IR ($CHCl_3$) 3012, 2932, 2859, 1675, 1447, 1384, 1354, 1274, 1238, 1211, 1164, 907, and 830 cm^{-1}; ^1H NMR ($CDCl_3$) 0.71 (1,dd, J = 4.3 Hz, J = 6.8 Hz), 1.12-1.38 (5,m), 1.54-1.78 (3,m), 1.81-1.97 (1,m), 2.03 (3,s), and 2.32-2.55 ppm (1,m); mass spectrum (70 eV) m/z (rel. intensity) 139(9), 138(100), 137(7), 123(54), 109(23), 95(19), 67(18); exact mass calculated for $C_9H_{14}O$ 138.1045, observed 138.1050.

(+)-Bicyclo[5.1.0]octan-2-one 44.
IR ($CHCl_3$) 3005, 2925, 2858, 1650, 1661, 1451, 1364, 1060, 1000, 868 and 706 cm^{-1}; ^1H NMR ($CDCl_3$) 0.97-1.32 (4,m), 1.36-1.79 (4,m), 1.82-1.98 (2,m), and 2.27-2.43 ppm (2,m); mass spectrum (70 eV) m/z (rel. intensity) 125(2), 124(32), 123(8), 121(3), 113(6), 111(17), 110(6), 109(12), 99(9), 98(8), 97(36), 95(31), 91(34), 85(37), 84(13), 83(40), 82(20), 81(52), 80(57), 79(16), 71(56), 70(25), 69(100), 68(35), 67(62); exact mass calculated for $C_8H_{12}O$ 124.0888, observed 124.0892.

(1S, 15S)-Bicyclo[13.1.0]hexadecan-2-one 45.[26]

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