(*E*)-(1*R*)-4(a)- and -4(e)-Methyl-2-adamantylideneacetaldehydes. AlH_3 reduction of the above mixture (0.7 g) gave the corresponding 4(a)- and 4(e)-methyl alcohols. The mixture of the alcohols (0.66 g) could not be separated into two pure isomers, and the separation was tried in the next step.

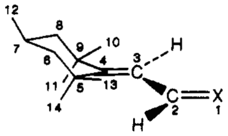
The mixture of alcohols on oxidation with MnO_2 as earlier gave the corresponding aldehydes. The mixture (0.6 g) on repeated radial chromatography separation with 20:1 hexane–ether gave the two pure isomers. However, during separation most of the product was decomposed. The less polar fraction solidified on standing to give 60 mg of 4(a)-methyl aldehyde: mp 50–54 °C; $[\alpha]^{21}{}_{\mathrm{Hg}}$ +3.49 ± 0.1° (*c* 0.26, cyclohexane); IR (CCl_4) 2917, 2852, 2750 (w), 1670, 1626, and 1608 (w) cm^{-1}; ^1H NMR 0.92 (d, *J* = 7 Hz, 3 H), 1.7–2.2 (m, 11 H), 2.27 (br s, 1 H), 3.54 (br s, 1 H), 5.8 (d, *J* = 8.3 Hz, 1 H), and 10 (d, *J* = 8.4 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ϵ 1, λ_{380} ϵ 22, λ_{362} ϵ 53, λ_{346} ϵ 66, λ_{333} ϵ 59, λ_{322} ϵ 45, λ_{310} ϵ 29, λ_{300} ϵ 18, λ_{243} ϵ 18900, λ_{239} ϵ 19000; CD (cyclohexane) $\Delta\epsilon_{380}$ −0.06, $\Delta\epsilon_{362}$ −0.15, $\Delta\epsilon_{347}$ −0.18, $\Delta\epsilon_{332}$ −0.14, $\Delta\epsilon_{320}$ −0.09, $\Delta\epsilon_{310}$ −0.05, $\Delta\epsilon_{300}$ −0.02, $\Delta\epsilon_{238}$ +1.95, and $\Delta\epsilon_{208}$ −2.57.

The polar fraction gave 26 mg of 4(e)-methyl aldehyde as a liquid: $[\alpha]^{25}{}_{\mathrm{Hg}}$ +53.45 ± 0.8° (*c* 0.23, cyclohexane); IR (CCl_4), 2900, 2850, 2740, 1675, 1630, and 1610 (w) cm^{-1}; ^1H NMR 1.13 (d, *J* = 7 Hz, 3 H), 1.63 (br d, *J* = 12.2 Hz, 2 H), 1.7–2.17 (m, 9 H), 2.25 (br s, 1 H), 3.61 (br s, 1 H), 5.8 (d, *J* = 8.4 Hz, 1 H), and 10.3 (d, 8.3 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ϵ 1, λ_{379} ϵ 21, λ_{361} ϵ 48, λ_{345} ϵ 61, λ_{332} ϵ 55, λ_{320} ϵ 43, λ_{310} ϵ 31, λ_{300} ϵ 23, λ_{242} ϵ 17600, and λ_{238} ϵ 17800; CD (cyclohexane) $\Delta\epsilon_{379}$ +0.05, $\Delta\epsilon_{360}$ +0.12, $\Delta\epsilon_{345}$ +0.14, $\Delta\epsilon_{331}$ +0.11, $\Delta\epsilon_{319}$ +0.05, $\Delta\epsilon_{300}$ −0.03, $\Delta\epsilon_{290}$ −0.04, $\Delta\epsilon_{280}$ −0.02, $\Delta\epsilon_{238}$ +2.47, and $\Delta\epsilon_{208}$ −1.38.

(*E*)-(1*R*)-4(a)-Methyl-2-adamantylidenepropene. Via an earlier procedure, methylenetriphenylphosphorane was condensed with 60 mg of methyl aldehyde. The product was isolated and purified to obtain 7 mg of methyl propene as a liquid: $[\alpha]^{19}{}_{\mathrm{Hg}}$ +14.61 ± 0.2° (*c* 0.13, cyclohexane); IR (CCl_4) 3070, 3012, 2900, 2840, 1790, 1645, and 1600 (w) cm^{-1}; ^1H NMR 0.89 (d, *J* = 7 Hz, 3 H), 1.6–2 (m, 11 H), 2.07 (br s, 1 H), 2.92 (br s, 1 H), 4.92 (dd, *J* = 2.3, 10.2 Hz, 1 H), 5.09 (dd, *J* = 2.3, 16.8 Hz, 1 H), 5.74 (d, *J* = 11 Hz, 1 H), and 6.62 (m, *J* = 10.5, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ϵ 18200, λ_{241} ϵ 27500 and λ_{234} ϵ 25500; CD (cyclohexane) $\Delta\epsilon_{249}$ +0.92; $\Delta\epsilon_{240}$ +1.51, $\Delta\epsilon_{232}$ +1.68, and $\Delta\epsilon_{194}$ −2.1; MS (EI), *m*/*e* 188 (100, $M^{\bullet+}$), 173, 159, 145, 131, 117, 105, and 91, high resolution) calcd for $C_{14}H_{20}$ 188.1565, found 188.1565.

(*E*)-(1*R*)-4(e)-Methyl-2-adamantylidenepropene. Methylenetriphenylphosphorane was condensed with methyl aldehyde (20 mg) to give after workup and purification as earlier, 9 mg (45%) of methyl propene as a liquid: $[\alpha]^{20}{}_{\mathrm{Hg}}$ +52.19 ± 0.17° (*c* 0.16, cyclohexane); IR (CCl_4) 3067, 3014, 2900, 2840, 1790, and 1650 cm^{-1}; ^1H NMR 1.07 (d, *J* = 7 Hz, 3 H), 1.5–2.2 (m, 12 H), 3.01 (br s, 1 H), 4.93 (dd, *J* = 2.3, 10.2 Hz, 1 H), 5.09 (dd, *J* = 2.2, 16.9 Hz, 1 H), 5.76 (d, *J* = 10.9 Hz, 1 H), and 6.62 (m, *J* = 10.3, 10.6, 16.9 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ϵ 18800, λ_{241} ϵ 28700, and λ_{235} ϵ 26800; CD (cyclohexane) $\Delta\epsilon_{248}$ +1.41, $\Delta\epsilon_{240}$ +2.42, $\Delta\epsilon_{232}$ +1.81, $\Delta\epsilon_{225}$ +1.34, $\Delta\epsilon_{210}$ −0.54, and $\Delta\epsilon_{190}$ +1; MS (EI), *m*/*e* 188 (100, $M^{+\bullet}$), 173, 159, 145, 131, 117, 105, 91 and 79, (high resolution) calcd for $C_{14}H_{20}$ 188.1565, found 188.1565.

MMP2 Calculations[21]



dihedral angle	X	
	CH_2	O
$C_1-C_2-C_3-C_4$	−176.68°	−169.86°
$C_2-C_3-C_4-C_5$	− 0.25°	0.85°
$C_2-C_3-C_4-C_9$	−171.46°	−171.02°
$C_3-C_4-C_5-C_{13}$	52.90°	50.27°
$C_3-C_4-C_5-C_{14}$	− 69.14°	− 72.29°
$C_3-C_4-C_9-C_{10}$	− 47.91°	− 45.16°
$C_3-C_4-C_9-C_{11}$	70.83°	73.31°
energy of conformer, kcal/mol	23.43	27.13

Acknowledgment. This work was supported by a grant from the National Science Foundation for which we are grateful.

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[21] These calculations were made by Dr. M. Duraisamy using the facilities kindly provided by Professor N. L. Allinger at the University of Georgia.

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Syntheses and Chiroptical Properties of 4-Oxo- and 4-Methylene-2-adamantylidene Derivatives[1]

H. M. Walborsky* and S. Madhava Reddy

Dittmer Laboratories of Chemistry, Florida State University, Tallahassee, Florida 32306-3006

Received September 28, 1987

The (*Z*)- and (*E*)-(1*R*)-4-oxo- and -4-methylene-2-adamantylidene derivatives of methyl acetate, acetone, acetaldehyde, 2-ethanol, and propene have been synthesized. Their *Z* and *E* configurations have been assigned by their ^1H and ^{13}C NMR spectra. All 4-oxo compounds obey the octant rule for their n–π^* absorption. The Cotton effect for the π–π^* absorption of the 4-methylene derivatives are of the same sign as for the 4-oxo compounds.

It had been observed that when a substituent is located in an equatorial position β to the carbonyl chromophore that the Octant rule is obeyed. However, if the substituent is axially located then the Octant rule is not followed.[2] To account for this anomaly it was originally suggested that the axial substituent belonged in a back octant[3] and later it was considered as an "antioctant" configuration.[4] Recently, Lightner, and co-workers[4,5] have provided convincing evidence that the axial substituent projects into

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[1] This work was supported by a grant from the National Science Foundation to whom we are grateful.

[2] (a) Snatzke, G.; Eckhardt, G.; Ehrig, B. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 998. (b) Snatzke, G.; Eckhardt, G. *Tetrahedron* **1968** *24*, 4543; **1970**, *26*, 1143; *Chem. Ber.* **1968**, *101*, 2010. (c) Snatzke, G.; Ehrig, B.; Klein, H. *Tetrahedron* **1969**, *25*, 5601. (d) Snatzke, G.; Marguarding, D. *Chem. Ber.* **1967**, *100*, 1710. (e) Numan, H.; Troostwijk, C. B.; Wieringa, J. H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 1761.

[3] Moffitt, W.; Woodard, R. B.; Moscowitz, A.; Klyne, W.; Djerassi, C. J. *J. Am. Chem. Soc.* **1961**, *83*, 4013.

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[5] Lightner, D. A.; Bouman, T. D.; Wijekoon, W. M. D.; Hansen, A. E. *J. Am. Chem. Soc.* **1986**, *108*, 4487.

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Table I. ^1H NMR Data of Methyl 4-Oxo- and 4-Methylene-2-adamantylideneacetates 1–4[a]

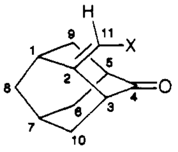
no.	compound	H_1	H_3	H_5	H_{11}
1	unsubstituted ester	2.43	4.06		5.59
2	*Z*-(1*R*)-(−)-1[b]	2.62 (−1.66)	4.80 (1.66)	2.67 (−0.01)	5.68 (0.08)
3	*E*-(1*R*)-(+)-2[c]	4.28	3.14	2.68	5.60
4	*Z*-(1*R*)-(−)-3	2.49 (−1.64)	4.70 (1.71)	2.56 (−0.01)	5.56 (−0.03)
5	*E*-(1*R*)-(+)-4	4.13	2.99	2.57	5.59

[a] Values in the parentheses: $\Delta\delta(Z-E)$. [b] NOE experiment: saturation of H_{11} proton resulted in a 13% enhancement of H_1 proton at 2.62 ppm. [c] NOE experiment: saturation of H_{11} proton gave an enhancement of 22% of H_3 proton at 3.14 ppm, and saturation of H_3 proton gave an enhancement of 28% of H_{11} olefinic proton at 5.60 ppm.

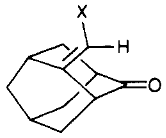
the front octant, very near to the third nodal surface, which would then be expected to show a Cotton effect, for the long wavelength n–π* carbonyl absorption, opposite to that for the equatorial isomer and thereby obey the Octant Rule.[6] We have recently had the occasion to prepare systems in which a trigonal sp^2 carbon atom is located β to the inherently dissymmetric carbonyl and exo methylene chromophores. The syntheses and chiroptical properties of these molecules are the subjects of this paper.

Syntheses. The (*Z*)- and (*E*)-(1*R*)-4-oxo-2-adamantylidene derivatives 1 and 2, where X = $COOCH_3$, $COCH_3$, CHO, and $CH{=}CH_2$ were conveniently prepared, in good yield, by pyridinium chlorochromate (PCC) oxidation[7] of the precursor 4-hydroxy compounds of known absolute configuration and whose syntheses have previously been described.[8]

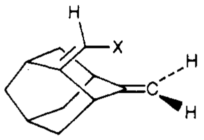
(*Z*)- and (*E*)-4-methylene (X = $COOCH_3$)[8] 3 and 4 were used as starting material for the preparation of the other derivatives (X = CH_2OH, CHO, $COCH_3$, and $CH{=}CH_2$). Aluminum hydride reduction of 3 and 4 (X = $COOCH_3$) yielded the corresponding alcohols, which upon MnO_2 oxidation gave the desired aldehydes 3 and 4 (X = CHO). The ketones 3 and 4 (X = $COCH_3$) were obtained by treating 3 and 4 (X = CHO) with methylmagnesium chloride and oxidizing the resultant allylic alcohols with MnO_2. The desired dienes were simply made by the condensation of the 3 and 4 (X = CHO) with methylenetriphenylphosphorane.



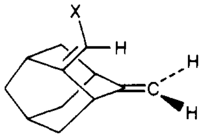
Z-(1*R*)-4-oxo-**1**



E-(1*R*)-4-oxo-**2**



Z-(1*R*)-4-methylene-**3**



E-(1*R*)-4-methylene-**4**

***E* and *Z* Configurations. ^1H NMR.** The ^1H NMR data for selected protons in 4-oxo and 4-methylene esters (1–4, X = $COOCH_3$) have been tabulated in Table I (and ^1H NMR data for other derivatives of 1–4, see the Experimental Section). The assignments of chemical shifts of H_1, H_3, and H_5 in the series of compounds were confirmed by NOE experiments. In each pair of derivatives, 1, 2 and 3, 4, the compound with one very deshielded proton H_3 and two upfield protons H_1 and H_5 is assigned the *Z* configuration and the one with two deshielded protons H_1 and H_3 and unchanged H_5 proton is assigned the *E* configuration.

Upon comparison of the chemical shifts of H_1, H_3, H_5, and H_{11} in each pair of *Z* and *E* isomers, it is noted that the H_1 proton is deshielded and the H_3 proton is shielded to the same extent. So that in the case of X = $COOCH_3$, $COCH_3$ the shielding and deshielding is in the order of 1.7 and 1 ppm for X = CHO, 0.6 ppm when X = $CH{=}CH_2$, and 0.5 ppm for X = CH_2OH. Notice that the H_5 proton remains constant for each pair of geometric isomers.

The olefinic proton H_{11} is deshielded in the order of 0.08 ppm in all the 4-oxo compounds (1 and 2) and shielded (0.02 ppm) in all the 4-methylene compounds (3 and 4) when one compares the *Z* to *E* isomer in each pair. Moreover, in comparing the *Z* isomers 1 and 3 and the *E* isomers 2 and 4, one observes that the chemical shifts of the H_1, H_3, H_5, and H_{11} protons are deshielded in the oxo compounds 1 and 2 by about 0.1 ppm with the exception of the H_{11} proton in all the 2 and 4 isomers where it remained constant. Finally, the 4-methylene protons appeared as two doublets (H_A, H_B) in all the *Z* isomers (3) and as a singlet in all the *E* isomers (4) (X = $COOCH_3$, $COCH_3$, CHO) with the exception of 4 (X = CH_2OH, $CH{=}CH_2$), where they again appeared as two doublets (see the Experimental Section).

^{13}C NMR. As can be seen from Table III (Experimental Section), the C-1 and C-3 carbons are affected by their location to the substituent X. In all the *Z* isomers 1 (X = $COOCH_3$, CHO, $CH{=}CH_2$), the C-3 carbon appeared at 53 ppm, and in all the *E* isomers 2 (X = $COOCH_3$, CHO, $CH{=}CH_2$), the C-1 carbon was observed at 32 ppm. The substituent X is shielding the γ-carbon that is located syn to it. A similar shielding effect is observed for the 4-methylene system 3 and 4 (X = $COOCH_3$) as shown in Table III (see the Experimental Section), entries 7 and 8. This shielding of the γ-carbon syn to the substituent X is in contrast to the effect that the substituent X has on the proton attached to it. As we have shown earlier (Table I) the effect of the substituent X on the proton is that of deshielding.

The assignment of the *Z* and *E* configurations based on the NMR studies is consistent with previous assignments made on the basis of the exciton coupling of the benzoate derivatives of the precursor alcohols.[9]

Absolute Configuration: UV and CD Data. Figures 1 and 2 show UV and CD curves for pairs of (*Z*)- and (*E*)-(1*R*)-4-oxo esters 1 and 2 (X = $COOCH_3$), respectively. All the isomers of 1 and 2 (X = $COOCH_3$, $COCH_3$, CHO, and $CH{=}CH_2$) exhibit intense n–π* absorptions at ~300 nm (ε ~500–1100) for the carbonyl in the 4-position as well as the long-wavelength π–π* absorptions, of expected intensity, for the α,β-unsaturated chromophore.

For the established absolute configuration (1*R*),[9] a positive Cotton effect is predicted for the n–π* transition for the 4-oxo derivatives 1 and 2 by the application of the

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(6) Deuterium as a substituent still presents a problem that has not been completely resolved although a rationale has been presented.[5]

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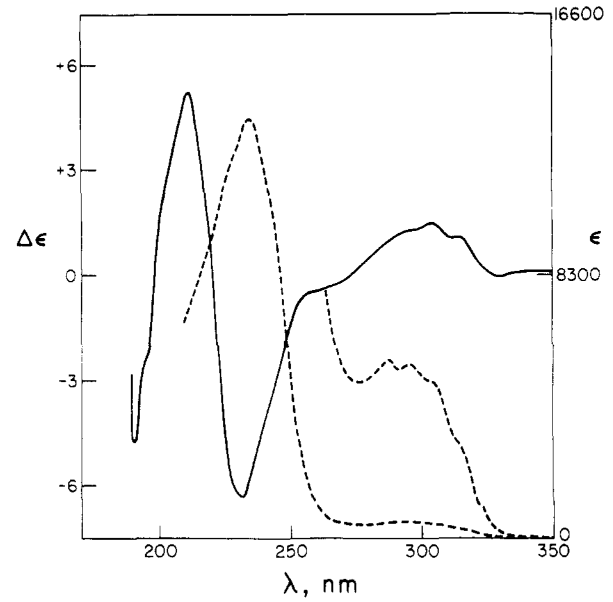

Figure 1. Circular dichroism (–) and ultraviolet (- -) spectra of 9.54×10^{-5} and UV spectrum of 9.54×10^{-4}, $\epsilon/10$, methyl (*Z*)-(1*R*)-4-oxo-2-adamantylideneacetate in CH_3CN and corrected to 100% ee.

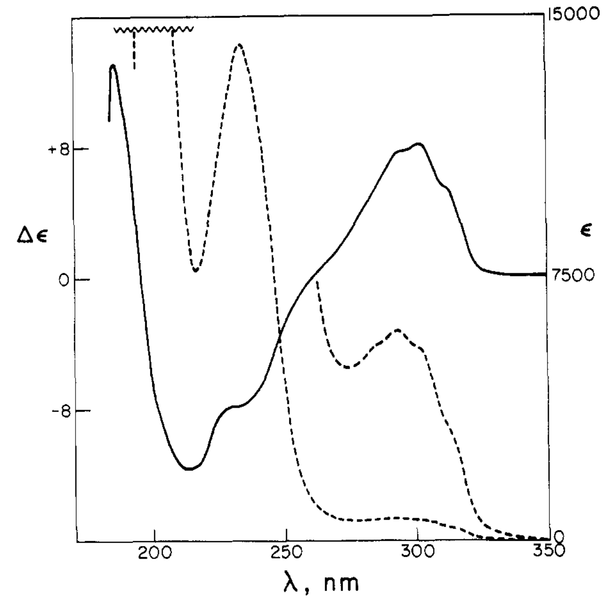

Figure 2. Circular dichroism (–) and ultraviolet (- -) spectra of 1.05×10^{-4} and UV spectrum of 1.05×10^{-3}, $\epsilon/10$, methyl (*E*)-(1*R*)-4-oxo-2-adamantylideneacetate in CH_3CN and corrected to 100% ee.

Octant Rule.[2-5] A strong positive CD at ~300 nm for the n–π^* transition in all the isomers of the 4-oxo derivatives 1 and 2 (Table II, entries 1, 2, 5, 6, 9, 10, 13, and 14) confirms the Octant Rule prediction. When comparing the intensity of the n–π^* transition in each pair of the *Z* and *E* isomers (Table II), all the *E* isomers (**2**) show more intense $\Delta\epsilon$ values (5.52–8.84) than the *Z* isomers (**1**) (0.33–1.50), with the exception of aldehydes (**1** and **2**, X = CHO), where the magnitude is of the same order (~4.5).

The π–π^* absorptions for the 4-methylene derivatives **3** and **4** (X = $COOCH_3$, $COCH_3$, CHO, and $CH{=}CH_2$) are found at ~200 nm (ϵ 9000–16000), for the 4-methylene chromophore as well as the usual long wavelength π–π^* absorptions of normal intensity for the α,β-unsaturated chromophore. All the 4-methylene isomers **3** and **4** exhibit a positive CD absorption for their π–π^* transition at ~200 nm (Table II, entries 3, 4, 7, 8, 11, and 12) and is opposite to that predicted by application of the Scott–Wrixon Octant Rule for olefins.[10]

Table II. UV and CD Data of 1–4 and Their Derivatives[a]

no.	compound	X	UV: λ, nm (ϵ)	CD:[b] Δϵ (nm)
1	*Z*-(1*R*)-(–)-**1**[c]	$COOCH_3$	304 (500)	+1.50 (304)
			295 (550)	+1.37 (295)
			288 (560)	+1.05 (288)
2	*E*-(1*R*)-(+)-**2**[c]		302 (550)	+8.71 (302)
			293 (600)	+8.32 (295)
			284 (550)	
3	*Z*-(1*R*)-(–)-**3**		197 (10800)	+15.09 (193)
4	*E*-(1*R*)-(+)-**4**		200 (9600)	*d*
5	*Z*-(1*R*)-(+)-**1**	$COCH_3$	308 (639)	+1.30 (307)
			298 (789)	+1.07 (297)
			290 (799)	+0.65 (287)
6	*E*-(1*R*)-(+)-**2**		306 (686)	+8.76 (306)
			296 (814)	+8.84 (296)
			288 (800)	+6.88 (288)
7	*Z*-(1*R*)-(–)-**3**		192 (14500)	+10.18 (200)
8	*E*-(1*R*)-(+)-**4**		192 (14500)	+8.59 (204)
9	*Z*-(1*R*)-(+)-**1**[c]	CHO	304 (925)	+4.50 (302)
			294 (980)	+4.12 (295)
			285 (1100)	
10	*E*-(1*R*)-(+)-**2**[c]		304 (587)	+4.52 (302)
			294 (710)	+4.35 (295)
			284 (716)	
11	*Z*-(1*R*)-(–)-**3**	CHO	190 (15000)	+9.49 (194)
12	*E*-(1*R*)-(+)-**4**		196 (9100)	+8.32 (203)
13	*Z*-(1*R*)-(–)-**1**	$CH{=}CH_2$	308 (570)	+0.33 (305)
			297 (630)	+0.13 (295)
			288 (570)	
14	*E*-(1*R*)-(+)-**2**		308 (800)	+5.52 (306)
			298 (889)	+5.04 (297)
			288 (838)	+3.87 (290)
15	*Z*-(1*R*)-(–)-**3**		190 (16000)	+20.53 (206)
16	*E*-(1*R*)-(–)-**4**		200 (9000)	+9.58 (206)

[a] Refers to n–π^* transitions in 4-oxo isomers **1** and **2** and π–π^* transitions in 4-methylene isomers **3** and **4**. [b] Data corrected to 100% ee; solvent, cyclohexane. [c] Solvent CH_3CN. [d] Peak under the next transition.

Experimental Section

For a description of the instruments, general procedures, synthesis, and spectral data of starting materials used in the following experiments, see ref 8.

Pyridinium Chlorochromate (PCC) Oxidation of Alcohols: General Procedure. A mixture of alcohol (1 equiv) and PCC (1.5 equiv) in dry CH_2Cl_2 (~25 mL for 1 g of alcohol) was stirred at room temperature under nitrogen atmosphere for 1 h. The reaction mixture was diluted with ethyl ether and filtered through silica gel with a 1:1 ether–CH_2Cl_2 solvent mixture. Solvent was removed, and the product was purified by radial chromatography with a hexane–ether mixture to obtain the corresponding pure ketone in good yield (80–90%).

Methyl (*Z*)-(1*R*)-4-Oxo-2-adamantylideneacetate. Separate PCC oxidation of the (*Z*)-(1*R*)-4(a) (53 mg, $[\alpha]^{25}{}_{Hg}$ –47.21 ± 0.71°, 84% ee) and (*Z*)-(1*R*)-4(e) (0.02 g, $[\alpha]^{25}{}_{Hg}$ +25.22 ± 0.08°, 84% ee) hydroxy esters gave the keto ester in 46 and 17 mg yield, respectively, as a crystalline solid: mp 80–86 °C; $[\alpha]^{25}{}_{Hg}$ –10.53 ± 0.8° (*c* 0.28, $CHCl_3$); IR (CCl_4) 2915, 2840, 1730, and 1650 cm^{-1}; ^1H NMR 1.8–2.23 (m, 9 H), 2.62 (br s, 1 H), 2.67 (br s, 1 H), 3.69 (s, 3 H), 4.8 (br s, 1 H), and 5.68 (s, 1 H) ppm; ^{13}C NMR see Table III; UV (CH_3CN); λ_{315} ϵ 290, λ_{304} ϵ 500, λ_{295} ϵ 550, λ_{288} ϵ 560, and λ_{234} ϵ 13300; CD (CH_3CN) $\Delta\epsilon_{314}$ +0.83, $\Delta\epsilon_{304}$ +1.26, $\Delta\epsilon_{295}$ +1.15, $\Delta\epsilon_{288}$ +0.88, $\Delta\epsilon_{260}$ –0.3, $\Delta\epsilon_{232}$ –5.47, $\Delta\epsilon_{211}$ +4.71, and $\Delta\epsilon_{192}$ –4.18. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.96; H, 7.35.

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Methyl (*E*)-(1*R*)-4-Oxo-2-adamantylideneacetate. Via the general procedure, PCC oxidation of (*E*)-(1*R*)-4(a) (0.05 g, $[\alpha]^{25}_{\mathrm{Hg}}$ +26.13 ± 0.4°, 84% ee) and (*E*)-(1*R*)-4(e) (0.04 g, $[\alpha]^{25}_{\mathrm{Hg}}$ +40.34 ± 0.26°, 84% ee) hydroxy esters in separate experiments yielded 43 and 35 mg, respectively, of the pure keto ester as a solid: mp 79–82 °C; $[\alpha]^{25}_{\mathrm{Hg}}$ +147.66 ± 0.08° (*c* 0.59, $CHCl_3$); IR (CCl_4) 2920, 2850, 1730, 1720, and 1650 cm^{-1}; ^{1}H NMR 1.8–2.3 (m, 9 H), 2.68 (br s, 1 H), 3.14 (br s, 1 H), 3.69 (s, 3 H), 4.28 (br s, 1 H), and 5.6 (s, 1 H) ppm; ^{13}C NMR see Table III; UV (CH_3CN) λ_{313} ϵ 320, λ_{302} ϵ 550, λ_{293} ϵ 600, λ_{284} ϵ 550, and λ_{234} ϵ 14 200; CD (CH_3CN) $\Delta\epsilon_{313}$ +4.83, $\Delta\epsilon_{302}$ +7.32, $\Delta\epsilon_{295}$ +6.99, $\Delta\epsilon_{270}$ +1.7, $\Delta\epsilon_{232}$ −7.11, $\Delta\epsilon_{213}$ −9.95, and $\Delta\epsilon_{185}$ +11.38. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.95; H, 7.25.

(*Z*)-(1*R*)-4-Oxo-2-adamantylideneacetaldehyde. (*Z*)-(1*R*)-4(a) (65 mg, $[\alpha]^{25}_{\mathrm{Hg}}$ −15.18 ± 0.3°, 84% ee) and (*Z*)-(1*R*)-4(e) (20 mg, $[\alpha]^{26}_{\mathrm{Hg}}$ +40.85 ± 0.28°, 84% ee) hydroxy aldehydes on oxidation with PCC gave, respectively, 55 and 17 mg of keto aldehyde as a solid: mp 100–102 °C; $[\alpha]^{26}_{\mathrm{Hg}}$ +32.06 ± 0.8° (*c* 0.3, $CHCl_3$); IR ($CHCl_3$) 2910, 2850, 1725, 1670, and 1630 cm^{-1}; ^{1}H NMR 1.8–2.35 (m, 9 H), 2.74 (br s, 2 H, H_1, H_5), 4.28 (br s, 1 H, H_3), 5.89 (d, *J* = 7.9 Hz, 1 H, H_{11}), and 9.97 (d, *J* = 7.9 Hz, 1 H) ppm; ^{13}C NMR see Table III; UV (CH_3CN) λ_{372} ϵ 20, λ_{353} ϵ 55, λ_{340} ϵ 75, λ_{316} ϵ 490, λ_{304} ϵ 925, λ_{294} ϵ 980, λ_{285} ϵ 1100, λ_{250} ϵ 16 800, and λ_{227} ϵ 7800 (*c* unknown, cyclohexane) λ_{385}, λ_{366}, λ_{349}, λ_{334}, λ_{318}, λ_{307}, λ_{296}, λ_{288}, λ_{279}, λ_{249}, λ_{242}, λ_{226}, and λ_{219}; CD (CH_3CN) $\Delta\epsilon_{368}$ −0.15, $\Delta\epsilon_{354}$ −0.26, $\Delta\epsilon_{342}$ −0.21, $\Delta\epsilon_{331}$ −0.11, $\Delta\epsilon_{313}$ +2.39, $\Delta\epsilon_{302}$ +3.78, $\Delta\epsilon_{295}$ +3.46, $\Delta\epsilon_{250}$ −2.66, $\Delta\epsilon_{245}$ −3.01, $\Delta\epsilon_{230}$ −3.28, $\Delta\epsilon_{212}$ −3.19, and $\Delta\epsilon_{193}$ −3.54, (*c* unknown, cyclohexane) $\Delta\epsilon_{414}$-, $\Delta\epsilon_{384}$-, $\Delta\epsilon_{365}$-, $\Delta\epsilon_{350}$-, $\Delta\epsilon_{315}$+, $\Delta\epsilon_{304}$+, $\Delta\epsilon_{295}$+, $\Delta\epsilon_{250}$-, $\Delta\epsilon_{243}$-, $\Delta\epsilon_{215}$-, and $\Delta\epsilon_{208}$-; MS (EI), *m*/*e* 190 (89, $M^{\bullet+}$), 162, 147, 133, 121, 119, 105, 91 (100), and 79 (high resolution) calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0977.

(*E*)-(1*R*)-4-Oxo-2-adamantylideneacetaldehyde. By the general procedure, PCC oxidation of (*E*)-(1*R*)-4(a) (45 mg, $[\alpha]^{25}_{\mathrm{Hg}}$ +12.9 ± 0.33°, 84% ee) and (*E*)-(1*R*)-4(e) (60 mg, $[\alpha]^{26}_{\mathrm{Hg}}$ +40.41 ± 0.65°, 84% ee) hydroxy aldehydes gave 40 and 50 mg, respectively, of the pure keto aldehyde as a white crystalline solid: mp 75–80 °C; $[\alpha]^{25}_{\mathrm{Hg}}$ +143.88 ± 0.3° (*c* 0.47, $CHCl_3$); IR ($CHCl_3$) 2920, 2850, 1720, 1670, and 1640 cm^{-1}; ^{1}H NMR 1.8–2.4 (m, 9 H), 2.76 (br s, 1 H, H_5), 3.26 (br s, 1 H, H_3), 3.82 (br s, 1 H, H_1), 5.81 (d, *J* = 7.8 Hz, 1 H, H_{11}), and 9.98 (d, *J* = 7.8 Hz, 1 H) ppm; ^{13}C NMR see Table III; UV (CH_3CN) λ_{372} ϵ 15, λ_{356} ϵ 34, λ_{340} ϵ 54, λ_{316} ϵ 340, λ_{304} ϵ 587, λ_{294} ϵ 710, λ_{284} ϵ 716, λ_{246} ϵ 16 900, and λ_{226} ϵ 6800, (*c* unknown, cyclohexane) λ_{385}, λ_{366}, λ_{350}, λ_{333}, λ_{318}, λ_{306}, λ_{297}, λ_{288}, λ_{280}, λ_{240}, λ_{226}, and λ_{220}; CD (CH_3CN) $\Delta\epsilon_{370}$ +0.09, $\Delta\epsilon_{353}$ +0.46, $\Delta\epsilon_{337}$ +0.64, $\Delta\epsilon_{314}$ +2.64, $\Delta\epsilon_{302}$ +3.8, $\Delta\epsilon_{295}$ +3.66, $\Delta\epsilon_{247}$ −4.77, $\Delta\epsilon_{205}$ −4.08, and $\Delta\epsilon_{187}$ +2.78, (*c* unknown, cyclohexane) $\Delta\epsilon_{385}$+, $\Delta\epsilon_{365}$+, $\Delta\epsilon_{350}$+, $\Delta\epsilon_{333}$+, $\Delta\epsilon_{316}$+, $\Delta\epsilon_{305}$+, $\Delta\epsilon_{297}$+, $\Delta\epsilon_{242}$-, $\Delta\epsilon_{220}$-, and $\Delta\epsilon_{211}$-. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.78; H, 7.37. Found: 75.83: H, 7.47.

(*Z*)-(1*R*)-4-Oxo-2-adamantylidenepropene. PCC oxidation of (*Z*)-(1*R*)-4(a) (15 mg, $[\alpha]^{25}_{\mathrm{Hg}}$ +25.23 ± 0.31°, 84% ee) and (*Z*)-(1*R*)-4(e) (5 mg, $[\alpha]^{26}_{\mathrm{Hg}}$ +31.65 ± 1.07°, 84% ee) hydroxypropenes by use of general procedure gave 12 and 4 mg of ketone propene as a solid: mp 50–52 °C; $[\alpha]^{25}_{\mathrm{Hg}}$ −34.87 ± 0.8° (*c* 0.26, $CHCl_3$); IR (CCl_4) 3070 (w), 3030 (w), 2920, 2850, 1800 (w), 1728, and 1650 cm^{-1}; ^{1}H NMR 1.8–2.2 (m, 9 H), 2.55 (br s, 1 H, H_1), 2.64 (br s, 1 H, H_5), 3.67 (br s, 1 H, H_3), 5.04 (dd, *J* = 1.8, 9 Hz, 1 H)) 5.16 (dd, *J* = 1.8, 16.5 Hz, 1 H), 5.89 (d, *J* = 11 Hz, 1 H, H_{11}), and 6.55 (sextet, *J* = 10.4, 11, 16.5 Hz, 1 H) ppm; ^{13}C NMR see Table III; UV (cyclohexane) λ_{320} ϵ 310, λ_{308} ϵ 570, λ_{297} ϵ 630, λ_{288} ϵ 570, λ_{249} ϵ 16 600, λ_{241} ϵ 20 300, and λ_{234} ϵ 15 900, (CH_3CN) λ_{316} ϵ 460, λ_{305} ϵ 750, λ_{295} ϵ 780, ϵ_{286} ϵ 665, and λ_{241} ϵ 18 800; CD (cyclohexane) $\Delta\epsilon_{324}$ −0.05, $\Delta\epsilon_{316}$ +0.27, $\Delta\epsilon_{305}$ +0.28, $\Delta\epsilon_{295}$ +0.11, $\Delta\epsilon_{270}$ −0.05, $\Delta\epsilon_{248}$ −2, $\Delta\epsilon_{238}$ −3.63, $\Delta\epsilon_{231}$ −3.5, and $\Delta\epsilon_{197}$ +5.55, (CH_3CN) $\Delta\epsilon_{321}$ −0.095, $\Delta\epsilon_{312}$ +0.17, $\Delta\epsilon_{302}$ +0.15, $\Delta\epsilon_{292}$ +0.028, $\Delta\epsilon_{275}$ −0.034, $\Delta\epsilon_{247}$ −1.08, $\Delta\epsilon_{239}$ −2.21, $\Delta\epsilon_{231}$ −2.08, $\Delta\epsilon_{215}$ +0.35, $\Delta\epsilon_{190}$ +4.34; MS (EI), *m*/*e* 188 (100, $M^{\bullet+}$), 160, 145, 131, 117, 105, and 91 (94), (high resolution) calcd for $C_{13}H_{16}O$ 188.1201, found 188.1205.

(*E*)-(1*R*)-4-Oxo-2-adamantylidenepropene. (*E*)-(1*R*)-4(a) (7 mg, $[\alpha]^{26}_{\mathrm{Hg}}$ +16.76 ± 3.3°, 84% ee) and (*E*)-(1*R*)-4(e) (10 mg, $[\alpha]^{26}_{\mathrm{Hg}}$ +29.44 ± 1.67°, 84% ee) hydroxypropenes were treated with PCC separately to give after purification ketopropene (6 and 8 mg, respectively) as a semisolid: $[\alpha]^{26}_{\mathrm{Hg}}$ +79.26 ± 2.73° (*c* 0.04, $CHCl_3$); IR ($CHCl_3$) 1720, 1650, and 1600 cm^{-1}; ^{1}H NMR 1.8–2.2 (m, 9 H), 2.64 (br s, 1 H, H_5), 3.07 (br s, 1 H, H_3), 3.16 (br s, 1 H, H_1), 5.04 (dd, *J* = 1.8, 10.2 Hz, 1 H), 5.17 (dd, *J* = 1.8, 16.78 Hz, 1 H), 5.79 (d, *J* = 10.96 Hz, 1 H, H_{11}), and 6.51 (sextet, *J* =

Table III. ^{13}C NMR Data Assignment of Carbon Resonances in 1–4 and Their Derivatives[a]

no.	compound	X	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12[b]	others
1	adamantane[c]		28.5	37.8	28.5	37.8	28.5	37.8	28.5	37.8	37.8	37.8			
2	2-adamantanone[c]		46.9	216.6	46.9	39.2	27.6	36.3	27.6	39.2	39.2	39.2			
			(18.4)[d]	(178.8)	(18.4)	(1.4)	(−0.9)	(−1.5)	(−0.9)	(1.4)	(1.4)	(1.4)			
3	2-adamantylidenemethane[c]		39.1	158.2	39.1	39.7	28.3	37.3	28.3	39.7	39.7	39.7	100.6		
			(10.6)[e]	(120.4)	(10.6)	(1.9)	(−0.2)	(−0.5)	(−0.2)	(1.9)	(1.9)	(1.9)			
4	unsubstituted ester	$COOCH_3$	32.6	172.0	41.0	39.9	27.7	36.6	27.7	38.9	38.9	39.9	108.0	167.0	50.3 (OCH_3)
5	*Z*-(1*R*)-(−)-1		39.8	166.4	53.2	212.9	45.9	36.3[g]	27.5	38.9[g]	42.8	39.1	111.5	164.0	51.1 (OCH_3)
			(40.1)[f]	(173.4)	(51.0)	(217.7)	(46.1)	(38.0)	(26.8)	(38.4)	(41.3)	(40.3)			
6	*E*-(1*R*)-(+)-2		31.7	166.7	60.4	212.6	46.0	37.8[g]	27.4	36.0[g]	39.0	43.4	111.4	164.9	51.1 (OCH_3)
			(31.7)[f]	(173.4)	(59.4)	(218.7)	(46.1)	(38.0)	(26.8)	(37.4)	(40.3)	(41.3)			
7	*Z*-(1*R*)-(−)-3		40.7	166.8	43.4	155.3	38.1	38.6	27.9	39.7	41.6	40.3	108.2	170.1	50.5 (OCH_3), 103.4 ($C{=}CH_2$)
			(40.8)[f]	(173.9)	(43.2)	(159.3)	(38.3)	(38.5)	(27.5)	(39.4)	(41.8)	(40.8)			
8	*E*-(1*R*)-(+)-4		32.4	167.2	52.0	155.9	38.1	38.6	27.9	38.7	39.4	42.6	108.4	170.4	50.7 (OCH_3), 102.5 ($C{=}CH_2$)
			(32.4)[f]	(173.9)	(51.6)	(160.3)	(38.3)	(38.5)	(27.5)	(38.4)	(40.8)	(41.8)			
9	*Z*-(1*R*)-(+)-1	CHO	39.8	167.9	53.1	211.1	45.8	36.0[g]	27.5	38.5[g]	43.1	38.8	123.3	189.2	
10	*E*-(1*R*)-(+)-2	CHO	32.1	168.0	60.1	211.0	45.9	38.2[g]	27.5	36.1[g]	38.8	43.4	123.1	187.3	
11	*Z*-(1*R*)-(−)-1	$CH{=}CH_2$	39.2	146.0	52.8	214.0	46.6	37.9[g]	28.0	38.3[g]	41.8	39.2	121.8	131.3	116.7 ($CH{=}CH_2$)
12	*E*-(1*R*)-(+)-2		31.7	142.1	59.7	213.7	46.5	37.3	27.9	37.3	39.1	42.3	121.6	131.7	116.7 ($CH{=}CH_2$)

[a] Assignment of carbon resonances are based on the (i) off-resonance or DEPT sequence spectra, (ii) selective proton decoupled off-resonance spectra, carried out in methyl esters (entries 4–6), and (iii) comparison with the calculated shieldings (values in the parentheses, entries 5–8). [b] C-12 = X = $COOCH_3$, CHO, $CH{=}CH_2$. [c] Data taken from ref 11. [d] $\Delta\delta(2-1)$. [e] $\Delta\delta(3-1)$. [f] Calculated shieldings, obtained by adding substituent induced shifts (SIS) (entries 2 and 3, values in the parentheses) in a suitable way to the shifts taken from the ^{13}C NMR spectrum of methyl 2-adamantylideneacetate (entry 4). [g] Assignment could be interchanged.

10.6, 16.78 Hz, 1 H) ppm; ^{13}C NMR see Table III; UV (cyclohexane) λ_{319} ϵ 464, λ_{308} ϵ 800, λ_{298} ϵ 889, λ_{288} ϵ 838, λ_{250} ϵ 20 000, λ_{241} ϵ 23 200, and λ_{234} ϵ 17 000, (CH_3CN) λ_{316} ϵ 560, λ_{304} ϵ 890, λ_{295} ϵ 918, λ_{286} ϵ 790, λ_{249} ϵ 17 500, λ_{241} ϵ 21 400, and ϵ_{234} ϵ 17 700; CD (cyclohexane) $\Delta\epsilon_{317}$ +3.05, $\Delta\epsilon_{306}$ +4.64, $\Delta\epsilon_{297}$ +4.24, $\Delta\epsilon_{290}$ +3.25, $\Delta\epsilon_{270}$ +0.93, $\Delta\epsilon_{247}$ −7.3, $\Delta\epsilon_{239}$ −9.55, $\Delta\epsilon_{232}$ −6.83, $\Delta\epsilon_{215}$ −1.46, and $\Delta\epsilon_{200}$ +5.44, (CH_3CN) $\Delta\epsilon_{313}$ +3.18, $\Delta\epsilon_{302}$ +4.47, $\Delta\epsilon_{293}$ +3.99, $\Delta\epsilon_{270}$ +0.93, $\Delta\epsilon_{247}$ −7.73, $\Delta\epsilon_{239}$ −8.94, $\Delta\epsilon_{232}$ −5.48, $\Delta\epsilon_{215}$ +0.72, and $\Delta\epsilon_{196}$ +0.48; MS (EI), *m/e* 188 (88, $M^{\bullet+}$), 160, 145, 131, 117, 105, and 91 (100), (high resolution) calcd for $C_{13}H_{16}O$ 188.1201, found 188.1223.

***(Z)*-(1*R*)-4-Oxo-2-adamantylideneacetone.** Via the general procedure, (*Z*)-(1*R*)-4(a) (25 mg, $[\alpha]^{24}_{\mathrm{Hg}}$ −212.07 ± 1.67°, 92% ee), and (*Z*)–(1*R*)–4(e) (20 mg, $[\alpha]^{26}_{\mathrm{Hg}}$ +16.6 ± 1.4°, 92% ee) hydroxy methyl ketones were treated with PCC in separate experiments to yield, respectively, 20 and 17 mg of pure ketone acetone as a solid: mp 87–90 °C; $[\alpha]^{24}_{\mathrm{Hg}}$ +58.76 ± 0.61° (*c* 0.24, cyclohexane); IR (CCl_4) 2920, 2850, 1730, 1695, and 1620 cm^{-1}; ^{1}H NMR 1.8–2.3 (m, 9 H), 2.17 (s, 3 H), 2.53 (br s, 1 H, H_1), 2.66 (br s, 1 H, H_5), 4.79 (br s, 1 H, H_3), and 6.04 (s, 1 H, H_{11}) ppm; UV (cyclohexane) λ_{340} ϵ 80, λ_{321} ϵ 350, λ_{308} ϵ 639, λ_{298} ϵ 789, λ_{290} ϵ 799, ϵ_{256} ϵ 9700, λ_{249} ϵ 11 200, λ_{234} ϵ 7000, λ_{226} ϵ 6400, and λ_{218} ϵ 5200; CD (cyclohexane) $\Delta\epsilon_{340}$ +0.2, $\Delta\epsilon_{319}$ +0.9, $\Delta\epsilon_{307}$ +1.2, $\Delta\epsilon_{297}$ +0.99, $\Delta\epsilon_{287}$ +0.6, $\Delta\epsilon_{257}$ −1.43, $\Delta\epsilon_{247}$ −2.43, $\Delta\epsilon_{222}$ +11.05, and $\Delta\epsilon_{200}$ −4.99; MS (EI), *m/e* 204 (100, $M^{\bullet+}$), 189, 176, 161, 147, 133, 117, 108, and 91, (high resolution) calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1150.

***(E)*-(1*R*)-4-Oxo-2-adamantylideneacetone.** By use of the general procedure, (*E*)-(1*R*)-4(a) (40 mg, $[\alpha]^{24}_{\mathrm{Hg}}$ +38.52 ± 0.82°, 92% ee) and (*E*)-(1*R*)-4(e) (30 mg, $[\alpha]^{25}_{\mathrm{Hg}}$ +43.88 ± 0.1°, 92% ee) hydroxy methyl ketones on PCC oxidation gave 34 and 24 mg of ketoacetone as a solid: $[\alpha]^{24}_{\mathrm{Hg}}$ +147.24 ± 0.94° (*c* 0.22, cyclohexane); IR (CCl_4) 2924, 2856, 1723, 1685, and 1612 cm^{-1}; ^{1}H NMR 1.7–2.3 (m, 9 H), 2.18 (s, 3 H), 2.68 (br s, 1 H, H_5), 3.06 (br s, 1 H, H_3), 4.27 (br s, 1 H, H_1), and 5.97 (s, 1 H, H_{11}) ppm; UV (cyclohexane) λ_{346} ϵ 63, λ_{318} ϵ 371, λ_{306} ϵ 686, λ_{296} ϵ 814, λ_{288} ϵ 800, λ_{255} ϵ 9500, ϵ_{248} ϵ 10 800, ϵ_{224} ϵ 4400, and λ_{216} ϵ 3900; CD (cyclohexane) $\Delta\epsilon_{346}$ −0.046, $\Delta\epsilon_{317}$ +4.38, $\Delta\epsilon_{306}$ +8.06, $\Delta\epsilon_{296}$ +8.14, $\Delta\epsilon_{288}$ +6.33, $\Delta\epsilon_{250}$ −6.67, $\Delta\epsilon_{220}$ −8.66, and $\Delta\epsilon_{194}$ +4.03; MS (EI), *m/e* 204 (100, $M^{\bullet+}$), 189, 176, 161, 147, 133, 117, 108, 91, and 79, (high resolution) calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1150.

***(Z)*-(1*R*)-4-Methylene-2-adamantylideneacetaldehyde.** AlH_3 reduction of methyl (*Z*)-(1*R*)-4-methylene-2-adamantylideneacetate (0.3 g, $[\alpha]^{24}_{\mathrm{Hg}}$ −104.38 ± 0.76°, 92% ee) was carried out via an earlier procedure[8] to give after workup methylene alcohol as a liquid: IR (film) 3300 (broad), 3040, 2900 (m), and 1650 cm^{-1}; ^{1}H NMR 1.16 (br s, 1 H, OH), 1.7–2.03 (m, 9 H), 2.44 (br s, 1 H, H_1), 2.56 (br s, 1 H, H_5), 3.46 (br s, 1 H, H_3), 4.14, 4.16 (2 d, *J* = 7.03, 6.99 Hz, 2 H), 4.51 (d, *J* = 1.92 Hz, 1 H), 4.56 (d, *J* = 1.91 Hz, 1 H), and 5.33 (t, *J* = 7.09 Hz, 1 H, H_{11}) ppm.

The above alcohol in 30 mL of hexane was treated with active MnO_2 (3 g) for 3 h. Filtration and purification yielded 0.22 g (85%) of methylene aldehdye as a low-melting solid: mp 34 °C; $[\alpha]^{25}_{\mathrm{Hg}}$ −66.25 ± 0.95° (*c* 0.22, cyclohexane); IR (CCl_4) 3055, 2900, 2840, 1785 (w), 1675, 1655, 1630, and 1610 cm^{-1}; ^{1}H NMR 1.7–2.2 (m, 9 H), 2.6 (br s, 1 H, H_1), 2.63 (br s, 1 H, H_5), 4.19 (br s, 1 H, H_3), 4.64 (d, *J* = 1.4 Hz, 1 H), 4.67 (d, *J* = 1.4 Hz, 1 H), 5.78 (d, *J* = 8 Hz, 1 H, H_{11}), and 10.06 (d, *J* = 8 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ϵ 1.6, λ_{380} ϵ 23, λ_{361} ϵ 52, λ_{345} ϵ 66, λ_{332} ϵ 58, λ_{320} ϵ 44, λ_{310} ϵ 30, λ_{300} ϵ 19, λ_{240} ϵ 18 000, λ_{236} ϵ 19 300, and λ_{190} ϵ 15 000; CD (cyclohexane) $\Delta\epsilon_{380}$ +0.1, $\Delta\epsilon_{362}$ +0.31, $\Delta\epsilon_{346}$ +0.4, $\Delta\epsilon_{332}$ +0.34, $\Delta\epsilon_{320}$ +0.21, $\Delta\epsilon_{308}$ +0.12, $\Delta\epsilon_{300}$ +0.06, $\Delta\epsilon_{244}$ −8.73, $\Delta\epsilon_{217}$ +1.49, and $\Delta\epsilon_{194}$ +8.73. Anal. Calcd for $C_{13}H_{16}O$: C, 82.98; H, 8.51. Found: C, 82.95; H, 8.62.

***(Z)*-(1*R*)-4-Methylene-2-adamantylidenepropene.** By use of an earlier procedure,[8] 0.1 g of methylene aldehyde was condensed with methylenetriphenylphosphorane. The product after workup was purified by radial chromatography (two times) to yield 76 mg (77%) of methylene propene as a liquid: $[\alpha]^{25}_{\mathrm{Hg}}$ −91.8 ± 1.31° (*c* 0.16, cyclohexane); IR (CCl_4) 3070, 3050, 3015, 2960, 2900, 2840, 1780 (w), and 1650 cm^{-1}; ^{1}H NMR 1.7–2.1 (m, 9 H), 2.43 (br s, 1 H, H_1), 2.56 (br s, 1 H, H_5), 3.59 (br s, 1 H, H_3), 4.51 (d, *J* = 1.9 Hz, 1 H), 4.56 (d, *J* = 1.9 Hz, 1 H), 4.97 (dd, *J* = 1.9, 10.07 Hz, 1 H), 5.11 (dd, *J* = 1.9, 17.08 Hz, 1 H), 5.75 (d, *J* = 10.98 Hz, 1 H, H_{11}), and 6.64 (m, *J* = 10.5, 10.6, 16.8 Hz, 1 H) ppm; UV (cyclohexane) λ_{249} ϵ 19 800, λ_{241} ϵ 29 700, λ_{235} ϵ 26 700, and λ_{190} ϵ 16 000; CD (cyclohexane) $\Delta\epsilon_{250}$ −7.24, $\Delta\epsilon_{240}$ −12, and $\Delta\epsilon_{206}$ +18.89. Anal. Calcd for $C_{14}H_{18}$: C, 90.32; H, 9.68. Found: C, 90.33; H, 9.66.

***(Z)*-(1*R*)-4-Methylene-2-adamantylideneacetone.** CH_3MgCl was added[8] to a cooled solution of methylene aldehyde (0.1 g) in THF. The reaction mixture on workup gave the corresponding methyl carbinols in 3:2 ratio (^{1}H NMR). The methyl carbinols in hexane was oxidized with active MnO_2 to obtain 72 mg (67%) of the title compound as a liquid: $[\alpha]^{25}_{\mathrm{Hg}}$ −114.28 ± 0.39° (*c* 0.23, cyclohexane); IR (CCl_4) 3057, 2960, 2900, 2840, 1790 (w), 1690, 1655, 1646, and 1617 cm^{-1}; ^{1}H NMR 1.8–2.1 (m, 9 H), 2.17 (s, 3 H), 2.41 (br s, 1 H, H_1) 2.55 (br s, 1 H, H_5), 4.56 (d, *J* = 1.89 Hz, 1 H), 4.67 (br s, H_3, d, *J* = 1.9 Hz, 2 H), and 5.93 (s, 1 H, H_{11}) ppm; UV (cyclohexane) λ_{330} ϵ 70, λ_{240} ϵ 14 800, and λ_{192} ϵ 14 500; CD (cyclohexane) $\Delta\epsilon_{348}$ −0.14, $\Delta\epsilon_{250}$ −7.32, and $\Delta\epsilon_{200}$ +9.37. Anal. Calcd for $C_{14}H_{18}O$: C, 83.17; H, 8.91. Found: C, 83.31; H, 9.02.

***(E)*-(1*R*)-4-Methylene-2-adamantylideneacetaldehyde.** Methyl (*E*)-(1*R*)-4-methylene-2-adamantylideneacetate (0.3 g, $[\alpha]^{24}_{\mathrm{Hg}}$ +55.3 ± 0.08°, 92% ee) was reduced with AlH_3 (see ref 8 for procedure) to give after workup 0.24 g of methylene alcohol as a viscous liquid: IR (film) 3300, (broad), 3050, 2900, 2840, 1665, and 1650 cm^{-1}; ^{1}H NMR 1.18 (br s, 1 H, OH), 1.6–2.1 (m, 9 H), 2.56 (br s, 1 H, H_5), 2.94 (br s, 2 H, H_1, H_3), 4.11 (d, *J* = 7 Hz, 2 H), 4.508 (d, *J* = 2 Hz, 1 H), 4.538 (d, *J* = 2.04 Hz, 1 H), and 5.35 (t, *J* = 7 Hz, 1 H, H_{11}) ppm. The methylene alcohol in 30 mL of hexane was stirred with active MnO_2 (3 g) for 3 h. Usual workup and purification of the crude product gave 0.22 g (85%) of methylene aldehyde as a liquid: $[\alpha]^{25}_{\mathrm{Hg}}$ +65.5 ± 0.32° (*c* 0.33, cyclohexane); IR (CCl_4) 3050, 2908, 2840, 1675, 1657, 1630, and 1610 cm^{-1}; ^{1}H NMR 1.7–2.2 (m, 9 H), 2.64 (br s, 1 H, H_5), 3.1 (br s, 1 H, H_3), 3.69 (br s, 1 H, H_1), 4.62 (s, 2 H), 5.8 (d, *J* = 8 Hz, 1 H, H_{11}), and 9.99 (d, *J* = 8 Hz, 1 H) ppm; UV (cyclohexane) λ_{400} ϵ 2, λ_{380} ϵ 27, λ_{363} ϵ 63, λ_{347} ϵ 78, λ_{333} ϵ 70, λ_{321} ϵ 52, λ_{310} ϵ 35, λ_{300} ϵ 22, λ_{238} ϵ 18,100, and λ_{196} ϵ 9100; CD (cyclohexane) $\Delta\epsilon_{400}$ −0.02, $\Delta\epsilon_{381}$ +0.13, $\Delta\epsilon_{364}$ +0.35, $\Delta\epsilon_{347}$ +0.42, $\Delta\epsilon_{333}$ +0.33, $\Delta\epsilon_{321}$ +0.2, $\Delta\epsilon_{311}$ +0.11, $\Delta\epsilon_{299}$ +0.05, $\Delta\epsilon_{252}$ −1.27, $\Delta\epsilon_{225}$ +5.87, and $\Delta\epsilon_{203}$ +7.66. Anal. Calcd for $C_{13}H_{16}O$: C, 82.98; H, 8.51. Found: C, 82.94; H, 8.41.

***(E)*-(1*R*)-4-Methylene-2-adamantylidenepropene.** Via an earlier procedure,[8] methylenetriphenylphosphorane was condensed with 80 mg of methylene aldehyde. The product was isolated and purified to give 50 mg (63%) of methylenepropene as a liquid: $[\alpha]^{24}_{\mathrm{Hg}}$ −5.12 ± 0.45° (*c* 0.25, cyclohexane); IR (CCl_4) 3060, 3020, 2960, 2900, 2840, 1790, and 1650 cm^{-1}; ^{1}H NMR 1.7–2.1 (m, 9 H), 2.56 (br s, 1 H, H_5), 2.94 (br s, 1 H, H_3), 3.07 (br s, 1 H, H_1), 4.5 (d, *J* = 1.92 Hz, 1 H), 4.53 (d, *J* = 1.98 Hz, 1 H), 4.95 (dd, *J* = 1.96, 9.75 Hz, 1 H), 5.11 (dd, *J* = 1.9, 16.55 Hz, 1 H), 5.77 (d, *J* = 10.94 Hz, 1 H, H_{11}), and 6.57 (m, *J* = 10.5, 10.6, 16.8 Hz, 1 H) ppm; UV (cyclohexane) λ_{250} ϵ 20 800, λ_{242} ϵ 30 800, λ_{236} ϵ 27 700, and λ_{200} ϵ 9100; CD (cyclohexane) $\Delta\epsilon_{252}$ −1,83, $\Delta\epsilon_{244}$ −2.57, $\Delta\epsilon_{237}$ −3.3, and $\Delta\epsilon_{206}$ +8.82. Anal. Calcd for $C_{14}H_{18}$: C, 90.32; H, 9.68. Found: C, 90.26; H, 9.66.

***(E)*-(1*R*)-4-Methylene-2-adamantylideneacetone.** To a cooled and stirred solution of 0.07 g of methylene aldehyde was added CH_3MgCl.[8] Workup gave the corresponding methyl carbinols in the ratio of 1:1 (^{1}H NMR). Active MnO_2 oxidation of the methyl carbinols in hexane as earlier yielded after purification 52 mg (69%) of methyleneacetone as a liquid: $[\alpha]^{24}_{\mathrm{Hg}}$ +24.1 ± 0.58° (*c* 0.22, cyclohexane); IR (CCl_4) 3053, 3020, 2960, 2900, 2840, 1685, 1650, and 1615 cm^{-1}; ^{1}H NMR 1.6–2.1 (m, 9 H), 2.17 (s 3 H), 2.57 (br s, 1 H, H_5), 2.91 (br s, 1 H, H_3), 4.13 (br s, 1 H, H_1), 4.56 (s, 2 H), and 5.96 (s, 1 H, H_{11}) ppm; UV (cyclohexane) λ_{332} ϵ 96, λ_{240} ϵ 16 200, and λ_{192} ϵ 14 500; CD (cyclohexane) $\Delta\epsilon_{337}$ −0.87, $\Delta\epsilon_{230}$ +8.18, and $\Delta\epsilon_{204}$ +7.91. Anal. Calcd for $C_{14}H_{18}O$: C, 83.17; H, 8.91. Found: C, 83.2; H, 9.01.