

Generation and Reaction of Monocarbonyliodonium Ylides: Ester Exchange of (Z)-(β -Acetoxyvinyl)iodonium Salts with Lithium Ethoxide and Synthesis of α,β -Epoxy Ketones

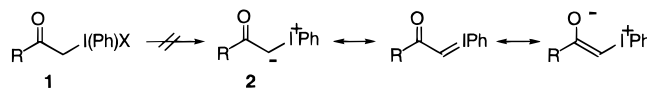
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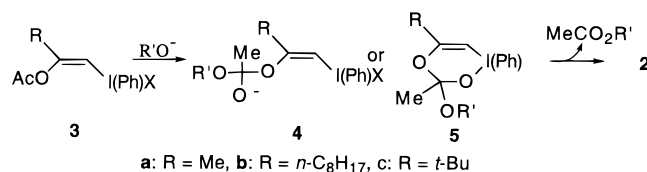
Abstract: Reported here for the first time are the generation of monocarbonyliodonium ylides and their alkylidene-transfer reactions to aldehydes yielding α,β -epoxy ketones. Exposure of (Z)-(2-acetoxy-1-decenyliodonium bromide, prepared stereoselectively by sodium acetate-catalyzed Michael addition of acetic acid to (1-decenyli)(phenyl)iodonium salt, to EtOLi in THF at -78 °C results in ester exchange to generate the monocarbonyliodonium ylide with the liberation of ethyl acetate. ¹H NMR measurements indicate that the ylide is stable up to -30 °C in THF-*d*₈ but gradually decomposes at -20 °C to 1-bromo-2-decanone. The monocarbonyliodonium ylide acts as an alkylidene-transfer agent to carbonyl compounds, and the reaction with aldehydes in THF–DMSO at -30 °C gives α,β -epoxy ketones with *E*-isomers as a major product. With an α,β -unsaturated aldehyde, selective 1,2-addition to the carbonyl group was observed. The relative rates of the alkylidene-transfer reaction of this ylide for a series of ring-substituted benzaldehydes were measured. A Hammett correlation plot with the σ constants of substituents afforded the reaction constant $\rho = 2.95$ ($r = 1.00$), which indicates that the monocarbonyliodonium ylide is moderately nucleophilic in nature.

As was pointed out by Moriarty and co-workers, generation and characterization of monocarbonyliodonium ylides represent long-standing problems in the field of hypervalent organoiodane chemistry.^{1,2} In spite of the increasing interest in and research on iodonium ylides, the chemistry of unstabilized monocarbonyliodonium ylides remains unknown.³ The most common approach for generating monocarbonyliodonium (N, P, As, Bi, S, etc.) ylides involves α -proton abstraction from (2-oxoalkyl)onium salts by a base.^{4,5} This method, however, cannot be applied for generating monocarbonyliodonium ylides (**2**); because of the very high nucleofugality of the phenyliodonio groups,⁶ (2-oxoalkyl)iodonium salts (**1**) generated from ketones by the reaction with hypervalent phenyliodanes undergo substitution reactions, instead of α -deprotonation to the ylides **2**, by a variety of nucleophilic agents. The nucleophiles include HO⁻, Br⁻, F⁻, AcOH, H₃PO₄, TsOH, TMSN₃, silyl enol ether, olefin, etc. and result in formation of the α -functionalized ketones.^{2c,7} The rhodium acetate-catalyzed decomposition of



α -diazo- β -diketones undergoes transylidation with iodoarenes, yielding stabilized iodonium ylides.^{2a,8} Attempts at transylidation of α -diazomonoketones with iodoarenes, however, result in intramolecular Wolff rearrangement.^{2a}

With these considerations in mind, we envisioned a novel strategy that involves an ester exchange reaction of (β -(acyloxy)-vinyl)iodonium salts (**3**) with alkoxide anions. It is illustrated in the following scheme. In this strategy, the acyclic (**4**) or cyclic vinylidane (**5**)⁹ is formed by nucleophilic attack of an alkoxide anion on the carbonyl group of **3**. Subsequent



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(9) Vinylidanes with similar cyclic structure have been reported. See ref 3b.

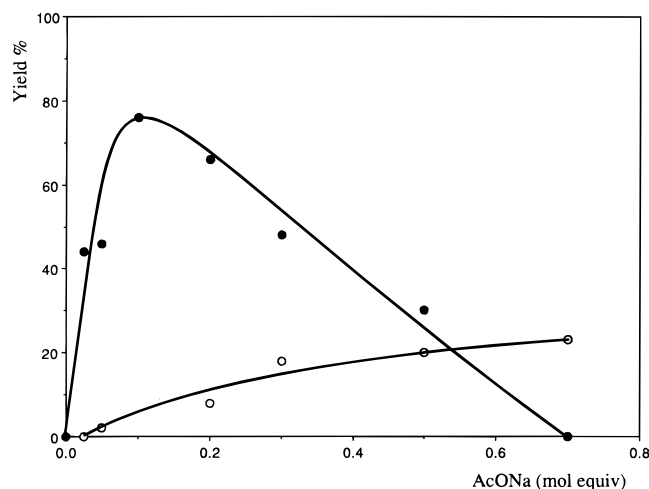
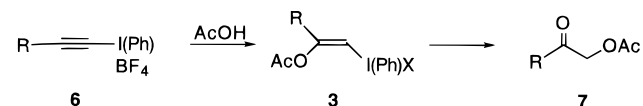


Figure 1. Plots of yields of (*Z*)-(β -acetoxyvinyl)iodonium salt **3b** ($X = \text{Br}$) (●) and 1-acetoxy-2-decanone (**7b**) (○) vs amounts of AcONa for the Michael addition of acetic acid to **6b** at room temperature.

decomposition of **4** or **5** with liberation of an ester allows direct generation of monocarbonyliodonium ylides (**2**), thereby avoiding the intermediacy of (2-oxoalkyl)iodonium salts (**1**). We now report, for the first time, a general method for generating monocarbonyliodonium ylides (**2**) from hitherto unknown (β -acetoxyvinyl)iodonium salts (**3**) and their reactions with aldehydes, thus making it possible to synthesize α,β -epoxy ketones (**12**) in high yields.

Results and Discussion

Recently, we reported that the reaction of alkynyl(phenyl)iodonium tetrafluoroborates (**6**) with acetic acid occurs at 80 °C to afford α -acetoxy ketones (**7**);¹⁰ for instance, heating a solution of (1-decynyl)(phenyl)iodonium tetrafluoroborate (**6b**) in acetic acid at 80 °C gives 1-acetoxy-2-decanone (**7b**) in 86% yield. In this reaction, the *anti* Michael addition products, (*Z*)-(β -acetoxyvinyl)iodonium salts (**3**), have been proposed to be intermediates leading to formation of the α -acetoxy ketones (**7**) but have never been isolated or characterized.¹⁰



We found that both using a catalytic amount of sodium acetate as an additive and carrying out the reaction at room temperature make it possible to isolate the intermediate Michael adduct (*Z*)-(β -acetoxyvinyl)iodonium salts (**3**). As shown in Figure 1, the Michael addition of acetic acid to **6b** yielding **3b** is highly sensitive to the amounts of the additive; reaction of **6b** with acetic acid in the presence of 0.1 equiv of sodium acetate at room temperature under nitrogen afforded **3b** ($X = \text{Br}$) stereoselectively in 76% yield (after ligand exchange with NaBr). Without addition of sodium acetate, the reaction at room temperature recovered the alkynylidonium salt **6b**. Use of larger amounts of the additive resulted in decreases in the yields of **3b**, along with the formation of considerable amounts of **7b**. The structure of **3b** was determined by spectroscopy using two-dimensional (2D) NMR techniques, i.e., ¹H, ¹H-COSY, ¹³C, ¹H-COSY, and nuclear Overhauser enhancement spectroscopy (NOESY), and fast atom bombardment (FAB) mass spectrometry. The sodium acetate-catalyzed Michael addition to (1-

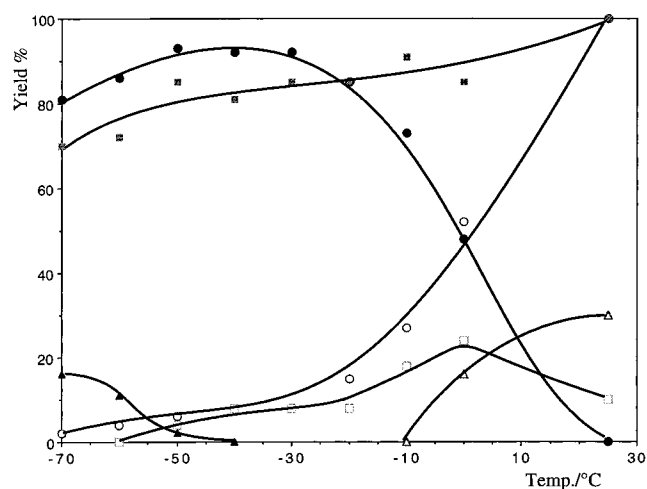
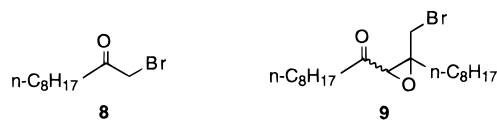


Figure 2. Temperature dependence for reaction of (*Z*)-(β -acetoxyvinyl)iodonium salt **3b** ($X = \text{Br}$) with EtOLi (1 equiv) in THF-*d*₈ under argon. Yields were determined by ¹H NMR. Symbols are as follows: (●) **2b**, (▲) **3b**, (■) AcOEt, (○) PhI, (□) **8**, and (△) **9**.

propynyl)- (**6a**) and (3,3-dimethyl-1-butynyl)iodonium salts (**6c**) similarly afforded the (*Z*)-vinylidonium salts **3a** and **3c** ($X = \text{Br}$) in 69% and 64% yields, respectively. These results provide direct evidence showing that carboxylic acids act as good Michael donors toward the alkynyl(phenyl)iodonium salts (see below).

When (*Z*)-(β -acetoxyvinyl)iodonium salt **3b** ($X = \text{Br}$) was treated with EtOLi (1 equiv) in THF-*d*₈ at -78 °C under argon, the solution immediately turned pale yellow, and ¹H NMR showed immediate formation of the monocarbonyliodonium ylide **2b** in more than 80% yield and the byproduct, ethyl acetate, in 70% yield. The proton on the α -ylidic carbon of **2b** appeared at δ 4.85 ppm as a singlet, whose identity was determined by the disappearance of this signal when the α -deuterated vinylidonium salt **3b-*ad*** was used.^{11,12} As shown in Figure 2, the ylide **2b** is stable up to -30 °C but gradually decomposes at -20 °C, accompanied by formation of iodobenzene and α -bromo ketone **8**. At higher temperature (> -10 °C), condensation of **8** takes place to give a stereoisomeric mixture of the epoxide **9** (*E*:*Z* = 16:84).



Observation of a negative NOE between α -methine and γ -methylene protons at -70 °C suggests the preference of *cisoid* conformation in **2b**, as was observed in other monocarbonyliodonium (P, S, and As) ylides in solution¹³ and/or in solid state.¹⁴

(11) ¹H NMR spectra of ylides **2b**, **2b-*ad***, and **2c** are included as Supporting Information (Figures S1–S3).

(12) A reviewer pointed out that the lithium enolate structure **A**, instead of the monocarbonyliodonium ylide **2b**, can account for the low-temperature ¹H NMR. The cyclic structure **B** is a possible alternative. These possibilities cannot be ruled out. However, it is generally accepted that the base-induced α -proton abstraction from (2-oxoalkyl)onium (N, P, As, Bi, S, etc.) salts generates the monocarbonyliodonium ylides but not the corresponding enolates.^{4,5}



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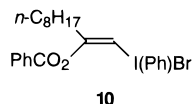
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Table 1. Synthesis of α,β -Epoxy Ketone **12** from (β -Acetoxyvinyl)iodonium Salt **3**^a

entry	3 (X)	R'CHO	12	yield (%) ^b	<i>E:Z</i>
1	3a (Br)	PhCHO	12a	51	67:33
2	3a (BF ₄)	PhCHO ^c	12a	58	60:40
3	3b (Br)	<i>p</i> -MeC ₆ H ₄ CHO	12b	80	93:7
4	3b (Br)	<i>o</i> -MeC ₆ H ₄ CHO	12c	57	96:4
5	3b (Br)	PhCHO	12d	91	95:5
6	3b (BF ₄)	PhCHO ^c	12d	77	95:5
7	3b (Br)	<i>p</i> -BrC ₆ H ₄ CHO	12e	79	96:4
8	3b (Br)	<i>p</i> -ClC ₆ H ₄ CHO	12f	78	95:5
9	3b (Br)	<i>p</i> -FC ₆ H ₄ CHO	12g	81	95:5
10	3b (Br)	<i>p</i> -NO ₂ C ₆ H ₄ CHO	12h	65	85:15
11	3b (Br)	<i>n</i> -C ₇ H ₅ CHO	12i	86	93:7
12	3b (Br)	<i>n</i> -C ₉ H ₁₉ CHO	12j	84	90:10
13	3b (Br)	Me ₂ CHCH ₂ CHO	12k	82	90:10
14	3b (Br)	Me ₂ CHCHO	12l	79	93:7
15	3b (Br)	<i>E</i> -MeCH=CHCHO	12m	67	85:15
16	3c (Br)	<i>p</i> -MeC ₆ H ₄ CHO	12n	67	83:17
17	3c (Br)	PhCHO	12o	80	89:11
18	3c (Br)	<i>p</i> -ClC ₆ H ₄ CHO	12p	92	85:15

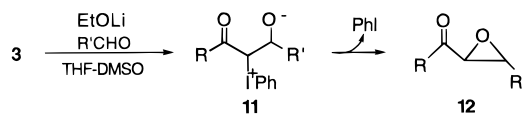
^a Unless otherwise noted, reactions were carried out using 1 equiv of EtOLi and 1.5 equiv of an aldehyde in THF–DMSO (12:1) at –30 °C for 2 h under argon. ^b Isolated yields. ^c Reactions were carried out in THF (at –78 °C → room temperature).

In fact, trapping of the ylide **2b** with benzoyl chloride in THF at –78 °C gave (*Z*)-(2-(benzoyloxy)-1-decyl)(phenyl)iodonium bromide (**10**) stereoselectively in 32% yield (after ligand exchange with NaBr).¹³ The structure of **10** was determined



by comparison of the spectral data with those of an authentic sample, prepared by sodium benzoate-catalyzed stereoselective Michael addition of benzoic acid to the alkynyliodonium salt **6b** in methanol in 58% yield.

The monocarbonyliodonium ylides (**2**), generated by the ester exchange of **3** with EtOLi, are nucleophilic in nature and undergo addition reaction with aldehydes in THF–DMSO (12:1) at –30 °C, yielding α,β -epoxy ketones **12** with *E*-isomers as a major product (Table 1). The reaction presumably proceeds via intervention of the zwitterions **11**, followed by intramolecular reductive cyclization with liberation of iodobenzene. Thus, the



iodonium ylides (**2**) act as an alkylidene-transfer agent for carbonyl compounds. Reaction of **3b** (X = Br) with EtOLi (1 equiv) in the presence of benzaldehyde (1.5 equiv) gave 91% yield of **12d** with high *E*-selectivity (entry 5).¹⁵ Other lithium alkoxides resulted in a decreased yield of **12d**: MeOLi (49%, *E:Z* = 93:7), *i*-PrOLi (82%, *E:Z* = 94:6), and *t*-BuOLi (66%, *E:Z* = 85:15). MeOLi is only sparingly soluble in THF–DMSO. The more sterically demanding nature of *i*-PrOLi and *t*-BuOLi compared to EtOLi is likely to be responsible for the decreased yields of **12d**. Use of EtONa and EtOK gave poor

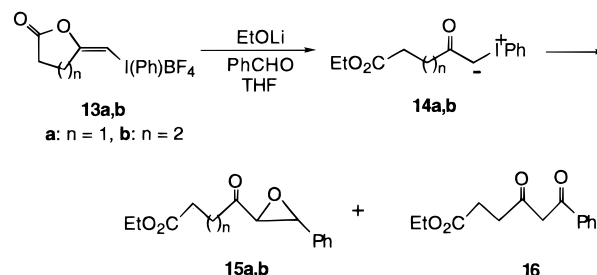
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(15) Use of an excess amount (1.5 equiv) of benzaldehyde is crucial for the high-yield synthesis of **12d**, because the ester exchange of **3b** with EtOLi competes with the nucleophilic attack on benzaldehyde leading to PhCH(OEt)OLi, which, in turn, could also act as a nucleophile for the ester exchange reaction of **3b**. In fact, a small amount of PhCH(OEt)OAc was isolated in this reaction. The reaction using 1 equiv of benzaldehyde resulted in a decreased (60%) yield of **12d**.

results. Interestingly, *n*-BuLi and LDA afforded **12d** in 69% and 46% yields, respectively.

As shown in Table 1, the ylides **2** readily undergo additions to aromatic aldehydes with electron-withdrawing and -donating substituents as well as aliphatic aldehydes to give the epoxides **12** in good yields. With an α,β -unsaturated aldehyde, selective 1,2-addition to the carbonyl group was observed, with no evidence for Michael addition yielding cyclopropanes (entry 15). The sterically demanding substrate, pivalaldehyde, did not react under our conditions. It is generally accepted that the preparatively important ylides, stabilized by an adjacent carbonyl group (RCOCH=X; X = PPh₃, AsPh₃, BiPh₃, and SME₂), react with aldehyde but not with ketones, except under forcing conditions.^{4,16,17} This also holds for the reaction of monocarbonyliodonium ylides (**2**). The reaction of ylide **2b** with diethyl ketone and benzophenone did not give any epoxide; instead, dimerization products (*E*)- and (*Z*)-10-eicosen-9,12-diones were produced (35–63%).

Cyclic (*E*)-(β -(acyloxy)vinyl)iodonium salts (**13**), prepared by iodine(III)-induced lactonization of 4- and 5-alkynoic acids,¹⁸ can also generate a functionalized monocarbonyliodonium ylide (**14**); thus, reaction of **13a** with EtOLi in the presence of benzaldehyde gives a mixture of the epoxide **15a** (*E:Z* = 63:37, 35%) and 1,3-diketone **16** (19%), in both of which the lactone functionalities were converted to ethyl esters. Similarly, ester exchange of the enol lactone **13b**, followed by alkylidene transfer to benzaldehyde, afforded the epoxide **15b** (*E:Z* = 62:38) in 54% yield.



The relative rates of the alkylidene-transfer reaction of **2b** for a series of ring-substituted benzaldehydes were measured in THF–DMSO at –30 °C, in which a mixture of two competing benzaldehydes, each in 15-fold excess, was used. Electron-withdrawing *m*- and *p*-Cl groups increase the rate of the reaction, and the relative rates are as follows: *m*-ClC₆H₄CHO (11.7) > *p*-ClC₆H₄CHO (4.7) > PhCHO (1.0) > *p*-MeC₆H₄CHO (0.30). A Hammett correlation plot with the σ constants of substituents in the aromatic ring afforded the reaction constant $\rho = 2.95$ ($r = 1.00$), which indicates moderate nucleophilicity of the monocarbonyliodonium ylide **2b**.

Bases such as *tert*-amines and *t*-BuOK abstract α -vinylic hydrogens of vinyl(phenyl)iodonium salts, generating vinyl-iodonium ylides or alkylidenecarbenes, depending on the nature of the substituents on the vinylic carbons.^{3bc,19} Therefore, an alternative process should be considered—one involving α -vinylic proton abstraction of (*Z*)-(β -acetoxyvinyl)iodonium salt **3** with EtOLi, yielding the vinyl-iodonium ylides, which, in turn,

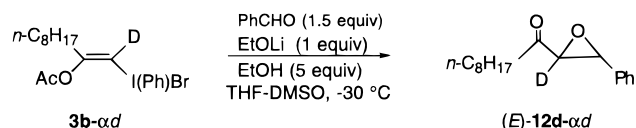
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react with aldehydes to give the epoxide **12**. The following results, however, clearly indicate that this α -proton abstraction does not occur; the α -deuterated iodonium salt **3b-*ad***, on treatment with EtOLi in the presence of benzaldehyde (1.5 equiv) and ethanol (5 equiv), afforded the epoxide (*E*)-**12d-*ad*** (71%), in which 95% of the deuterium is retained. Under these



conditions, the α -proton abstraction mechanism predicts loss of most of the deuterium because of kinetic deuterium isotope effects on protonation from ethanol. Very interestingly, similar retention of deuterium (more than 94%) in (*E*)-**12d-*ad*** was also observed when *n*-BuLi or LDA (in the presence of 5 equiv of *i*-Pr₂NH) was used instead of EtOLi. Thus, the proposed ester exchange mechanism, leading to generation of the monocarbonyliodonium ylides (**2**), by the reaction with EtOLi is further supported. These results also imply that the intermediate iodonium ylide **2b** survives, even in the presence of a large excess of ethanol, and reacts with aldehydes. It has been reported that the phenyliodonio group raises the CH acidity of malonic esters by 8 orders of magnitude.²⁰ Based on these data, the acidity (pK_a) of α -methylene protons of (2-oxoalkyl)-iodonium salts (**1**) is calculated to be 12, more acidic than ethanol ($pK_a = 18$).

Our results provide evidence for the generation of monocarbonyliodonium ylides, which we have begun to characterize, and offer proof of the concept that our ester exchange methodology is generally applicable for generation of these ylides.

Experimental Section

General Information. IR spectra were recorded on JASCO IRA-1 and Perkin Elmer 1720 FT-IR spectrometers. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a JEOL JNM-FX 200 or JNM-GX 400 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from internal Me₄Si. Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230–400 mesh) was used for flash chromatography. Melting points were determined with a Yanaco micromelting points apparatus and are uncorrected. Acetic acid was distilled in the presence of a small amount of acetic anhydride. Dichloromethane and dimethyl sulfoxide were dried over CaH₂ and distilled under argon. BF₃·Et₂O was distilled from CaH₂ under argon. THF was distilled from sodium benzophenone ketyl under argon.

Substrates. 1-Alkynyl(phenyl)iodonium tetrafluoroborates (**6**) were prepared by a BF₃-catalyzed silicon-iodonium exchange reaction of (1-alkynyl)trimethylsilanes with iodosylbenzene.²¹

General Procedure for Michael Addition of Acetic Acid to (1-Alkynyl)(phenyl)iodonium Tetrafluoroborates (6**). A Typical Example: Synthesis of (*Z*)-(2-Acetoxy-1-decenyloxy)(phenyl)iodonium Bromide (**3b**, X = Br).** To a mixture of (1-decenyloxy)(phenyl)iodonium tetrafluoroborate (**6b**, 44 mg, 0.10 mmol) and sodium acetate (0.8 mg, 0.01 mmol) was added acetic acid (3 mL) at room temperature under argon, and the solution was stirred for 2 days. The solvent was evaporated under reduced pressure. After addition of water, the mixture was extracted with dichloromethane two times. The combined organic extracts were vigorously shaken with a saturated aqueous NaBr solution three times. The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane by decanting at -78 °C. Recrystallization from dichlo-

romethane–hexane gave the iodonium bromide **3b** (X = Br, 36 mg, 76%) as colorless needles: mp 160–162 °C; IR (KBr) 2927, 2855, 1762, 1639, 1472, 1439, 1371, 1187, 1109, 740 cm⁻¹; ¹H NMR (CDCl₃) δ 8.04 (br d, *J* = 8.3 Hz, 2H), 7.53 (br t, *J* = 7.3 Hz, 1H), 7.39 (br dd, *J* = 8.3, 7.3 Hz, 2H), 6.39 (s, 1H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.19 (s, 3H), 1.57–1.20 (m, 12H), 0.87 (t, *J* = 6.5 Hz, 3H); ¹³C NMR (THF-*d*₈) δ 167.7 (s), 161.5 (s), 135.3 (d), 131.5 (d), 130.9 (d), 122.7 (s), 96.8 (d), 34.1 (t), 32.8 (t), 30.1 (t), 30.1 (t), 29.7 (t), 27.3 (t), 23.5 (t), 20.8 (q), 14.4 (q); FAB MS *m/z* 401 [(M – Br)⁺]; HRMS (FAB) calcd for C₁₈H₂₆O₂I [(M – Br)⁺] 401.0978, found 401.0977. Anal. Calcd for C₁₈H₂₆O₂Br: C, 44.93; H, 5.45. Found: C, 44.73; H, 5.35.

Synthesis of (*Z*)-(2-Acetoxy-1-propenyl)(phenyl)iodonium Bromide (3a**, X = Br).** According to the general procedure, (1-propenyl)(phenyl)iodonium tetrafluoroborate (**6a**, 100 mg, 0.30 mmol) was treated with sodium acetate (17 mg, 0.30 mmol) in acetic acid (10 mL) at room temperature for 3.2 h under argon. Recrystallization from dichloromethane–diethyl ether gave the iodonium bromide **3a** (X = Br, 80 mg, 69%) as a white powder: mp 176–179 °C; IR (KBr) 3047, 1763, 1637, 1472, 1446, 1362, 1190, 1119, 992, 931, 736 cm⁻¹; ¹H NMR (CDCl₃) δ 8.03 (br d, *J* = 8.6 Hz, 2H), 7.52 (br t, *J* = 7.4 Hz, 1H), 7.39 (br dd, *J* = 8.6, 7.4 Hz, 2H), 6.42 (q, *J* = 0.9 Hz, 1H), 2.27 (d, *J* = 0.9 Hz, 3H), 2.14 (s, 3H); FAB MS *m/z* 303 [(M – Br)⁺]. Anal. Calcd for C₁₁H₁₂O₂Br: C, 34.49; H, 3.16. Found: C, 34.37; H, 3.10.

Synthesis of (*Z*)-(2-Acetoxy-3,3-dimethyl-1-butenyl)(phenyl)iodonium Bromide (3c**, X = Br).** According to the general procedure, (3,3-dimethyl-1-butenyl)(phenyl)iodonium tetrafluoroborate (**6c**, 342 mg, 0.92 mmol) was treated with sodium acetate (23 mg, 0.28 mmol) in acetic acid (30 mL) at room temperature for 25 h under argon. Recrystallization from dichloromethane–hexane gave the iodonium bromide **3c** (X = Br, 250 mg, 64%) as colorless needles: mp 167–169 °C; IR (KBr) 3035, 2975, 1763, 1610, 1446, 1369, 1173, 1064 cm⁻¹; ¹H NMR (CDCl₃) δ 8.10 (br d, *J* = 8.0 Hz, 2H), 7.57 (br t, *J* = 7.3 Hz, 1H), 7.43 (br dd, *J* = 8.0, 7.3 Hz, 2H), 6.46 (s, 1H), 2.37 (s, 3H), 1.15 (s, 9H); FAB MS *m/z* 345 [(M – Br)⁺]. Anal. Calcd for C₁₄H₁₈O₂Br: C, 39.56; H, 4.27. Found: C, 39.35; H, 4.22.

Michael Addition of Benzoic Acid to (1-Decenyloxy)(phenyl)iodonium Tetrafluoroborate (6b**).** To a solution of (1-decenyloxy)iodonium salt **6b** (100 mg, 0.23 mmol) and benzoic acid (572 mg, 4.68 mmol) in methanol (6 mL) was added sodium benzoate (3.2 mg, 0.023 mmol) at room temperature under argon, and the solution was stirred for 2 days. After addition of water, the mixture was extracted with dichloromethane two times. The organic layer was filtered and concentrated under aspirator vacuum. The solid residue was washed several times with a large amount of hexane by decanting to remove benzoic acid and then dissolved in dichloromethane. The solution was vigorously shaken with a saturated aqueous NaBr solution four times. The organic layer was filtered and then concentrated under aspirator vacuum, and the solid residue was washed several times with hexane by decanting at -78 °C. Recrystallization from dichloromethane–hexane gave (*Z*)-(2-(benzoyloxy)-1-decenyloxy)(phenyl)iodonium bromide (**10**, 73 mg, 58%) as colorless leaflets: mp 118–120 °C; IR (KBr) 3047, 3028, 2922, 2853, 1741, 1634, 1600, 1451, 1267, 1231, 1059 cm⁻¹; ¹H NMR (CDCl₃) δ 8.02 (br d, *J* = 8.3 Hz, 2H), 7.92 (br d, *J* = 7.5 Hz, 2H), 7.66 (br t, *J* = 7.2 Hz, 1H), 7.54–7.37 (m, 3H), 7.32–7.20 (m, 2H), 6.55 (s, 1H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.80–1.50 (m, 2H), 1.42–1.20 (m, 10H), 0.85 (t, *J* = 6.8 Hz, 3H); FAB MS *m/z* 463 [(M – Br)⁺]. Anal. Calcd for C₂₃H₂₈O₂Br·¹/₃H₂O: C, 50.29; H, 5.26. Found: C, 50.26; H, 5.13.

Generation and Decomposition of the Monocarbonyliodonium Ylides **2b.** To a solution of (*Z*)-(2-acetoxy-1-decenyloxy)iodonium bromide **3b** (X = Br, 5.5 mg, 0.011 mmol) in THF-*d*₈ (0.75 mL) in an NMR tube containing a small glass rod was added a 0.14 M THF-*d*₈ solution of EtOLi (0.083 mL, 0.011 mmol), prepared by the reaction of EtOH with *n*-BuLi (1.6 M in hexane) in THF-*d*₈ at 0 °C for 20 min, at -78 °C under argon. ¹H NMR spectra were measured over the temperature range from -78 to 25 °C at 10 °C intervals. The yields of the products, the monocarbonyliodonium ylide **2b**, ethyl acetate, iodobenzene, the α -bromo ketone **8**, and the epoxide **9** (*E*:*Z* = 16:84), were determined by ¹H NMR and are shown in Figure 2.

2b: ¹H NMR (THF-*d*₈ at -78 °C) δ 8.19 (d, *J* = 6.8 Hz, 2H), 7.40–7.34 (m, 3H), 4.85 (s, 1H), 2.31 (br t, *J* = 6.6 Hz, 2H), 1.67–1.15 (m,

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12H), 0.90 (br t, $J = 6.1$ Hz, 3H); ^{13}C NMR (THF- d_8 at -78 °C) δ 183.5 (s), 130.9 (d), 130.6 (d), 129.8 (d), 116.6 (s), 52.3 (d), 38.7 (t), 33.3 (t), 31.2 (t), 31.1 (t), 30.9 (t), 29.0 (t), 24.1 (t), 14.9 (q). Because the ^{13}C signal of the ylidic carbon of **2b** is broad, the chemical shift (δ 52.3) was determined by generating the ^{13}C -enriched monocarbonyliodonium ylide from (Z)-(2-acetoxy-1-decenyl- ^{13}C)(phenyl)iodonium bromide (99% enriched). A large $^1J_{\text{C-H}}$ value (193 Hz) of the ylidic carbon indicates sp^2 hybridization.

Pure samples of **8** and **9** were isolated by preparative TLC (50% dichloromethane in hexane) from a large scale reaction of **3b**.

8: 22 colorless oil; IR (CHCl₃) 2930, 2850, 1710, 1600 cm^{-1} ; ^1H NMR (CDCl₃) δ 3.88 (s, 2H), 2.65 (t, $J = 7.0$ Hz, 2H), 1.61–1.54 (m, 2H), 1.32–1.24 (m, 10H), 0.88 (t, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl₃) δ 202.3 (s), 39.9 (t), 34.3 (t), 31.8 (t), 29.3 (t), 29.10 (t), 29.05 (t), 23.9 (t), 22.6 (t), 14.1 (q); MS m/z (relative intensity) 236 (0.4), 234 (0.4, M^+), 155 (7), 141 (100), 85 (48), 83 (76), 57 (39); HRMS calcd for C₁₀H₁₉OBr (M^+) 234.0619, found 234.0620. Anal. Calcd for C₁₀H₁₉OBr: C, 51.08; H, 8.14. Found: C, 50.96; H, 8.03.

(E)-9: colorless oil; ^1H NMR (CDCl₃) δ 3.57 (s, 1H), 3.53 (d, $J = 10.8$ Hz, 1H), 3.34 (d, $J = 10.8$ Hz, 1H), 2.54 (t, $J = 7.1$ Hz, 2H), 1.75–0.80 (m, 32H); MS m/z (relative intensity) 390 (1), 388 (1, M^+), 295 (60), 141 (100), 57 (39).

(Z)-9: colorless oil; IR (CHCl₃) 2915, 2845, 1715, 1600, 1455, 1400 cm^{-1} ; ^1H NMR (CDCl₃) δ 3.62 (s, 1H), 3.47 (d, $J = 10.7$ Hz, 1H), 3.29 (d, $J = 10.7$ Hz, 1H), 2.61 (dt, $J = 17.1, 7.3$ Hz, 1H), 2.58 (dt, $J = 17.1, 7.3$ Hz, 1H), 2.04 (dt, $J = 15.1, 7.3$ Hz, 1H), 1.78 (dt, $J = 15.1, 7.3$ Hz, 1H), 1.65 (quint, $J = 7.3$ Hz, 2H), 1.47–1.20 (m, 22H), 0.89 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl₃) δ 204.6, 65.3, 64.0, 41.8, 32.9, 31.8, 30.3, 29.3, 29.2, 29.1, 24.2, 23.3, 22.6, 14.1; MS m/z (relative intensity) 390 (1), 388 (1, M^+), 295 (26), 141 (100), 92 (64), 57 (42); HRMS calcd for C₂₀H₃₇OBr (M^+) 388.1977, found 388.1975. The stereochemistry of **9** was determined by NOESY.

Reaction of the Iodonium Ylide 2b with Benzoyl Chloride. To a stirred solution of the iodonium bromide **3b** ($\text{X} = \text{Br}$, 30 mg, 0.062 mmol) in THF (6 mL) was added a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol), prepared by the reaction of EtOH with *n*-BuLi (1.6 M in hexane) in THF at 0 °C for 20 min, at -78 °C under argon. The solution immediately turned pale yellow. After being stirred for 0.5 h, a solution of benzoyl chloride (13 mg, 0.094 mmol) in THF (0.1 mL) was added dropwise at -78 °C, and the mixture was stirred for 1 h. After addition of dichloromethane (15 mL), the solution was shaken with a saturated aqueous NaBr solution three times using a separatory funnel, washed with water, and filtered. Concentration under an aspirator vacuum gave an oil, which was washed several times with hexane by decanting at -78 °C to give a mixture of the iodonium bromides **3b** (20%) and **10** (32%).

General Procedure for Synthesis of α,β -Epoxy Ketone 12. A **Typical Example (Table 1, Entry 5): 1,2-Epoxy-1-phenylundecan-3-one (12d).** To a stirred solution of (Z)-(2-acetoxy-1-decenyl)iodonium bromide **3b** ($\text{X} = \text{Br}$, 30 mg, 0.062 mmol) and benzaldehyde (9.9 mg, 0.094 mmol) in THF–DMSO (12:1, 6.5 mL) was added a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at -30 °C under argon. The solution immediately turned pale yellow. After being stirred for 2 h, the mixture was quenched with water and extracted with diethyl ether. The organic phase was washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Preparative TLC (10% ethyl acetate in hexane) of the crude mixture gave (*E*)-**12d** (14.2 mg, 88%) and (*Z*)-**12d** (0.7 mg), which was contaminated with a small amount of impurity. Pure (*Z*)-**12d** was obtained by repeated preparative TLC. The *E*:*Z* ratio of **12d** was determined to be 95:5 by ^1H NMR of the crude reaction mixture.

(E)-12d: colorless needles; mp 167–168 °C (recrystallized from methanol); IR (CHCl₃) 2925, 2850, 1710, 1455, 1410 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.38–7.26 (m, 5H), 3.96 (d, $J = 2.0$ Hz, 1H), 3.51 (d, $J = 2.0$ Hz, 1H), 2.54 (dt, $J = 17.5, 8.0$ Hz, 1H), 2.43 (dt, $J = 17.5, 8.0$ Hz, 1H), 1.63–1.59 (m, 2H), 1.33–1.26 (m, 10H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (CDCl₃) δ 206.1 (s), 135.3 (s), 129.0 (d), 128.7 (d), 125.7 (d), 63.1 (d), 58.0 (d), 37.8 (t), 31.8 (t), 29.3 (t), 29.2 (t), 29.1 (t), 23.1 (t), 22.6 (t), 14.1 (q); MS m/z (relative intensity) 260 (59, M^+), 141 (41), 120 (100), 91 (55), 57 (68); HRMS calcd for

C₁₇H₂₄O₂ (M^+) 260.1776, found 260.1780. Anal. Calcd for C₁₇H₂₄O₂: C, 77.09; H, 9.32. Found: C, 77.14; H, 9.34.

(Z)-12d: pale yellow oil; IR (CHCl₃) 2920, 2850, 1705, 1600, 1450, 1400 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.37–7.26 (m, 5H), 4.33 (d, $J = 5.0$ Hz, 1H), 3.83 (d, $J = 5.0$ Hz, 1H), 2.21 (ddd, $J = 17.6, 7.8, 6.3$ Hz, 1H), 2.09 (ddd, $J = 17.6, 7.8, 6.3$ Hz, 1H), 1.48–0.91 (m, 12H), 0.86 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl₃) δ 205.1 (s), 133.1 (s), 128.5 (d), 128.3 (d), 126.6 (d), 61.1 (d), 57.9 (d), 40.3 (t), 31.7 (t), 29.1 (t), 29.0 (t), 28.8 (t), 22.6 (t), 14.1 (q); MS m/z (relative intensity) 260 (44, M^+), 175 (7), 162 (11), 104 (40), 90 (100), 41 (34); HRMS calcd for C₁₇H₂₄O₂ (M^+) 260.1776, found 260.1785. Anal. Calcd for C₁₇H₂₄O₂: C, 77.09; H, 9.32. Found: C, 77.01; H, 9.41.

(E)-1,2-Epoxy-1-phenylbutan-3-one ((E)-12a): colorless leaflets; mp 40–41.5 °C (recrystallized from methanol, lit.²³ mp 44–45 °C); IR (CHCl₃) 2900, 1705, 1405, 1355 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.39–7.25 (m, 5H), 4.01 (d, $J = 1.7$ Hz, 1H), 3.50 (d, $J = 1.7$ Hz, 1H), 2.20 (s, 3H); MS m/z (relative intensity) 162 (32, M^+), 120 (42), 91 (100), 43 (72); HRMS calcd for C₁₀H₁₀O₂ (M^+) 162.0681, found 162.0687.

(Z)-1,2-Epoxy-1-phenylbutan-3-one ((Z)-12a): pale yellow oil; IR (CHCl₃) 2900, 2840, 1710, 1600 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.38–7.25 (m, 5H), 4.34 (d, $J = 4.9$ Hz, 1H), 3.81 (d, $J = 4.9$ Hz, 1H), 1.84 (s, 3H); MS m/z (relative intensity) 162 (39, M^+), 120 (40), 91 (100), 43 (68); HRMS calcd for C₁₀H₁₀O₂ (M^+) 162.0681, found 162.0692.

(E)-1,2-Epoxy-1-(4-methylphenyl)undecan-3-one ((E)-12b): colorless needles; mp 60–61 °C (recrystallized from methanol); IR (KBr) 2921, 2851, 1709, 1468, 1397, 1380, 1112, 826 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.17 (br s, 4H), 3.93 (d, $J = 2.0$ Hz, 1H), 3.51 (d, $J = 2.0$ Hz, 1H), 2.57 (dt, $J = 17.3, 7.6$ Hz, 1H), 2.37 (dt, $J = 17.3, 7.6$ Hz, 1H), 2.36 (s, 3H), 1.75–1.52 (m, 2H), 1.41–1.19 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 274 (69, M^+), 237 (2), 167 (47), 134 (97), 118 (100), 105 (96), 71 (89); HRMS calcd for C₁₈H₂₆O₂ (M^+) 274.1933, found 274.1939. Anal. Calcd for C₁₈H₂₆O₂: C, 77.52; H, 9.58. Found: C, 77.66; H, 9.93.

(Z)-1,2-Epoxy-1-(4-methylphenyl)undecan-3-one ((Z)-12b): pale yellow oil; IR (CHCl₃) 2920, 2850, 1820, 1705, 1600, 1465 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.24 (br d, $J = 8.3$ Hz, 2H), 7.13 (br d, $J = 8.3$ Hz, 2H), 4.29 (d, $J = 4.9$ Hz, 1H), 3.81 (d, $J = 4.9$ Hz, 1H), 2.21 (ddd, $J = 16.5, 7.8, 6.5$ Hz, 1H), 2.10 (ddd, $J = 16.5, 7.8, 6.5$ Hz, 1H), 1.50–0.90 (m, 12H), 0.86 (t, $J = 6.5$ Hz, 3H); MS m/z (relative intensity) 274 (31, M^+), 161 (15), 134 (39), 105 (100), 41 (43); HRMS calcd for C₁₈H₂₆O₂ (M^+) 274.1933, found 274.1937.

(E)-1,2-Epoxy-1-(2-methylphenyl)undecan-3-one ((E)-12c): colorless oil; IR (CHCl₃) 2920, 2845, 1705, 1455, 1405 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.26–7.15 (m, 4H), 4.10 (d, $J = 2.0$ Hz, 1H), 3.41 (d, $J = 2.0$ Hz, 1H), 2.56 (dt, $J = 17.3, 6.7$ Hz, 1H), 2.46 (dt, $J = 17.3, 6.7$ Hz, 1H), 2.37 (s, 3H), 1.75–1.56 (m, 2H), 1.38–1.19 (m, 10H), 0.88 (t, $J = 6.3$ Hz, 3H); MS m/z (relative intensity) 274 (69, M^+), 134 (100), 105 (72), 57 (51); HRMS calcd for C₁₈H₂₆O₂ (M^+) 274.1933, found 274.1940.

(Z)-1,2-Epoxy-1-(2-methylphenyl)undecan-3-one ((Z)-12c): colorless oil; IR (CHCl₃) 2920, 2845, 1700, 1460, 1275 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.26–7.06 (m, 4H), 4.27 (d, $J = 4.9$ Hz, 1H), 3.82 (d, $J = 4.9$ Hz, 1H), 2.31 (s, 3H), 2.31–2.16 (m, 1H), 2.05–1.85 (m, 1H), 1.70–0.80 (m, 12H), 0.86 (t, $J = 7.1$ Hz, 3H); MS m/z (relative intensity) 274 (77, M^+), 145 (41), 119 (39), 105 (100); HRMS calcd for C₁₈H₂₆O₂ (M^+) 274.1933, found 274.1924.

(E)-1-(4-Bromophenyl)-1,2-epoxyundecan-3-one ((E)-12e): colorless leaflets; mp 61–62 °C (recrystallized from methanol–dichloromethane); IR (KBr) 2927, 2849, 1708, 1491, 1470, 1439, 836 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.50 (br d, $J = 8.3$ Hz, 2H), 7.16 (br d, $J = 8.3$ Hz, 2H), 3.94 (d, $J = 1.8$ Hz, 1H), 3.47 (d, $J = 1.8$ Hz, 1H), 2.54 (dt, $J = 17.6, 7.6$ Hz, 1H), 2.42 (dt, $J = 17.6, 7.3$ Hz, 1H), 1.74–1.53 (m, 2H), 1.43–1.15 (m, 10H), 0.88 (t, $J = 6.4$ Hz, 3H); MS m/z (relative intensity) 340 (18), 338 (20, M^+), 198 (35), 169 (37), 141 (63), 71 (100); HRMS calcd for C₁₇H₂₃O₂Br (M^+) 338.0881, found 338.0886. Anal. Calcd for C₁₇H₂₃O₂Br: C, 60.18; H, 6.83. Found: C, 59.95; H, 6.80.

(Z)-1-(4-Bromophenyl)-1,2-epoxyundecan-3-one ((Z)-12e): colorless oil; IR (CHCl₃) 2915, 2845, 1715, 1495, 1070, 1015 cm^{-1} ; ^1H NMR (CDCl₃) δ 7.47 (br d, $J = 8.6$ Hz, 2H), 7.24 (br d, $J = 8.6$ Hz,

2H), 4.27 (d, $J = 4.9$ Hz, 1H), 3.86 (d, $J = 4.9$ Hz, 1H), 2.22 (dt, $J = 17.0, 7.3$ Hz, 1H), 2.15 (dt, $J = 17.0, 7.3$ Hz, 1H), 1.55–0.90 (m, 12H), 0.87 (t, $J = 6.7$ Hz, 3H); MS m/z (relative intensity) 340 (13), 338 (12, M^+), 178 (27), 169 (52), 89 (100), 71 (85); HRMS calcd for $C_{17}H_{23}O_2Br$ (M^+) 338.0881, found 338.0890.

(E)-1-(4-Chlorophenyl)-1,2-epoxyundecan-3-one ((E)-12f): colorless leaflets; mp 64–65 °C (recrystallized from methanol); IR (KBr) 2922, 2850, 1708, 1496, 1471, 1438, 1096, 838 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.35 (br d, $J = 8.5$ Hz, 2H), 7.22 (br d, $J = 8.5$ Hz, 2H), 3.95 (d, $J = 1.7$ Hz, 1H), 3.47 (d, $J = 1.7$ Hz, 1H), 2.54 (dt, $J = 17.6, 7.6$ Hz, 1H), 2.44 (dt, $J = 17.6, 7.6$ Hz, 1H), 1.73–1.50 (m, 2H), 1.44–1.15 (m, 10H), 0.88 (t, $J = 6.3$ Hz, 3H); MS m/z (relative intensity) 296 (12), 294 (41, M^+), 209 (9), 154 (75), 138 (66), 125 (67), 89 (100), 81 (77); HRMS calcd for $C_{17}H_{23}O_2Cl$ (M^+) 294.1387, found 294.1390. Anal. Calcd for $C_{17}H_{23}O_2Cl \cdot \frac{1}{3}H_2O$: C, 67.88; H, 7.93. Found: C, 67.65; H, 7.64.

(Z)-1-(4-Chlorophenyl)-1,2-epoxyundecan-3-one ((Z)-12f): colorless oil; IR ($CHCl_3$) 2915, 2845, 1715, 1490, 1090 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.31 (br s, 4H), 4.29 (d, $J = 4.9$ Hz, 1H), 3.86 (d, $J = 4.9$ Hz, 1H), 2.22 (dt, $J = 17.2, 7.6$ Hz, 1H), 2.15 (dt, $J = 17.2, 7.6$ Hz, 1H), 1.51–0.90 (m, 12H), 0.86 (t, $J = 6.7$ Hz, 3H); MS m/z (relative intensity) 296 (8), 294 (21, M^+), 209 (6), 161 (20), 125 (100), 89 (91), 71 (92); HRMS calcd for $C_{17}H_{23}O_2Cl$ (M^+) 294.1387, found 294.1400.

(E)-1,2-Epoxy-1-(4-fluorophenyl)undecan-3-one ((E)-12g): colorless leaflets; mp 51–52 °C (recrystallized from methanol); IR (KBr) 2957, 2922, 2850, 1709, 1610, 1518, 1466, 1248, 839 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.26 (br dd, $J = 8.5$ Hz, $J_{HF} = 5.4$ Hz, 2H), 7.06 (br t, $J = 8.5$ Hz, $J_{HF} = 8.5$ Hz, 2H), 3.96 (d, $J = 1.7$ Hz, 1H), 3.48 (d, $J = 1.7$ Hz, 1H), 2.55 (dt, $J = 17.3, 7.1$ Hz, 1H), 2.43 (dt, $J = 17.3, 7.1$ Hz, 1H), 1.76–1.51 (m, 2H), 1.46–1.19 (m, 10H), 0.88 (t, $J = 6.2$ Hz, 3H); MS m/z (relative intensity) 278 (18, M^+), 180 (10), 138 (93), 109 (100), 71 (88), 57 (80); HRMS calcd for $C_{17}H_{23}O_2F$ (M^+) 278.1682, found 278.1679. Anal. Calcd for $C_{17}H_{23}O_2F$: C, 73.35; H, 8.33. Found: C, 73.24; H, 8.35.

(Z)-1,2-Epoxy-1-(4-fluorophenyl)undecan-3-one ((Z)-12g): colorless oil; IR ($CHCl_3$) 2920, 2845, 1710, 1605, 1505 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.35 (br dd, $J = 8.6$ Hz, $J_{HF} = 5.6$ Hz, 2H), 7.02 (br t, $J = 8.6$ Hz, $J_{HF} = 8.6$ Hz, 2H), 4.29 (d, $J = 4.7$ Hz, 1H), 3.84 (d, $J = 4.7$ Hz, 1H), 2.23–2.12 (m, 2H), 1.47–0.89 (m, 12H), 0.86 (t, $J = 6.7$ Hz, 3H); MS m/z (relative intensity) 278 (16, M^+), 180 (12), 138 (17), 122 (48), 109 (100), 71 (45), 57 (53); HRMS calcd for $C_{17}H_{23}O_2F$ (M^+) 278.1682, found 278.1661.

(E)-1,2-Epoxy-1-(4-nitrophenyl)undecan-3-one ((E)-12h): colorless needles; mp 37–38 °C (recrystallized from dichloromethane–hexane); IR (KBr) 2923, 2853, 1722, 1604, 1526, 1469, 1437, 1350, 1108, 853, 752 cm^{-1} ; 1H NMR ($CDCl_3$) δ 8.24 (br d, $J = 8.8$ Hz, 2H), 7.46 (br d, $J = 8.8$ Hz, 2H), 4.09 (d, $J = 1.7$ Hz, 1H), 3.50 (d, $J = 1.7$ Hz, 1H), 2.72 (dt, $J = 17.6, 7.3$ Hz, 1H), 2.46 (dt, $J = 17.6, 7.3$ Hz, 1H), 1.78–1.52 (m, 2H), 1.41–1.18 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 305 (48, M^+), 165 (18), 141 (100), 71 (77), 57 (95), 43 (66); HRMS calcd for $C_{17}H_{23}O_4N$ (M^+) 305.1627, found 305.1637. Anal. Calcd for $C_{17}H_{23}O_4N$: C, 66.86; H, 7.59; N, 4.59. Found: C, 66.66; H, 7.49; N, 4.52.

(Z)-1,2-Epoxy-1-(4-nitrophenyl)undecan-3-one ((Z)-12h): colorless oil; IR ($CHCl_3$) 2920, 2845, 1720, 1600, 1520, 1350, 850 cm^{-1} ; 1H NMR ($CDCl_3$) δ 8.21 (br d, $J = 8.6$ Hz, 2H), 7.57 (br d, $J = 8.6$ Hz, 2H), 4.42 (d, $J = 4.9$ Hz, 1H), 3.99 (d, $J = 4.9$ Hz, 1H), 2.24 (t, $J = 7.2$ Hz, 2H), 1.40–0.90 (m, 12H), 0.85 (t, $J = 6.7$ Hz, 3H); MS m/z (relative intensity) 305 (100, M^+), 165 (19), 149 (27), 97 (36), 57 (65), 43 (67); HRMS calcd for $C_{17}H_{23}O_4N$ (M^+) 305.1627, found 305.1618.

(E)-3,4-Epoxytridecan-5-one ((E)-12i): colorless oil; IR ($CHCl_3$) 2915, 2845, 1700, 1455, 1375, 870 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.23 (d, $J = 2.0$ Hz, 1H), 3.04 (dt, $J = 2.0, 5.4$ Hz, 1H), 2.43 (dt, $J = 17.3, 7.3$ Hz, 1H), 2.28 (dt, $J = 17.3, 7.3$ Hz, 1H), 1.78–1.46 (m, 4H), 1.38–1.16 (m, 10H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 212 (14, M^+), 183 (44), 141 (100), 71 (77), 57 (98); HRMS calcd for $C_{13}H_{24}O_2$ (M^+) 212.1776, found 212.1790.

(Z)-3,4-Epoxytridecan-5-one ((Z)-12i): pale yellow oil; IR ($CHCl_3$) 2920, 2840, 1715, 1455 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.60 (d, $J = 4.9$ Hz, 1H), 3.17 (dt, $J = 4.9, 6.1$ Hz, 1H), 2.52 (t, $J = 7.3$ Hz, 2H), 1.71–1.15 (m, 14H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz,

3H); MS m/z (relative intensity) 212 (16, M^+), 183 (39), 141 (58), 71 (82), 57 (100); HRMS calcd for $C_{13}H_{24}O_2$ (M^+) 212.1776, found 212.1777.

(E)-10,11-Epoxyeicosan-9-one ((E)-12j): white powder; mp 40–40.5 °C (recrystallized from methanol); IR (KBr) 2921, 2851, 1716, 1467, 1404, 1379, 882, 855, 726 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.21 (d, $J = 2.0$ Hz, 1H), 3.03 (dt, $J = 2.0, 5.3$ Hz, 1H), 2.42 (dt, $J = 17.3, 7.3$ Hz, 1H), 2.28 (dt, $J = 17.3, 7.3$ Hz, 1H), 1.70–1.15 (m, 28H), 1.00–0.79 (6H); MS m/z (relative intensity) 310 (25, M^+), 183 (42), 141 (100), 71 (63), 57 (81), 43 (66); HRMS calcd for $C_{20}H_{38}O_2$ (M^+) 310.2872, found 310.2865. Anal. Calcd for $C_{20}H_{38}O_2$: C, 77.36; H, 12.33. Found: C, 77.17; H, 12.34.

(Z)-10,11-Epoxyeicosan-9-one ((Z)-12j): colorless leaflets; mp 33–34 °C (recrystallized from methanol–dichloromethane); IR ($CHCl_3$) 2920, 2850, 1715, 1460, 1375 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.58 (d, $J = 4.9$ Hz, 1H), 3.20 (q, $J = 4.9$ Hz, 1H), 2.52 (t, $J = 7.3$ Hz, 2H), 1.70–1.15 (m, 28H), 0.95–0.80 (6H); MS m/z (relative intensity) 310 (76, M^+), 183 (42), 141 (91), 95 (28), 71 (70), 57 (100), 43 (98); HRMS calcd for $C_{20}H_{38}O_2$ (M^+) 310.2872, found 310.2882. Anal. Calcd for $C_{20}H_{38}O_2 \cdot \frac{1}{4}H_2O$: C, 76.25; H, 12.31. Found: C, 76.63; H, 12.21.

(E)-4,5-Epoxy-2-methyltetradecan-6-one ((E)-12k): pale yellow oil; IR ($CHCl_3$) 2950, 2925, 2845, 1705, 1460, 1365, 985 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.19 (d, $J = 2.0$ Hz, 1H), 3.05 (dt, $J = 2.0, 5.9$ Hz, 1H), 2.43 (dt, $J = 17.3, 7.5$ Hz, 1H), 2.29 (dt, $J = 17.3, 7.5$ Hz, 1H), 1.85 (nonet, $J = 6.6$ Hz, 1H), 1.67–1.44 (m, 4H), 1.35–1.17 (m, 10H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 240 (11, M^+), 183 (46), 141 (75), 71 (80), 57 (100); HRMS calcd for $C_{15}H_{28}O_2$ (M^+) 240.2089, found 240.2112.

(Z)-4,5-Epoxy-2-methyltetradecan-6-one ((Z)-12k): colorless oil; IR ($CHCl_3$) 2920, 2850, 1710, 1460, 1370 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.57 (d, $J = 4.6$ Hz, 1H), 3.24 (dt, $J = 4.6, 5.3$ Hz, 1H), 2.52 (t, $J = 7.3$ Hz, 2H), 1.91–1.53 (m, 3H), 1.49–1.18 (m, 12H), 0.99 (d, $J = 6.6$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 3H), 0.88 (t, $J = 6.6$ Hz, 3H); MS m/z (relative intensity) 240 (50, M^+), 183 (84), 141 (93), 99 (46), 85 (41), 71 (87), 57 (100); HRMS calcd for $C_{15}H_{28}O_2$ (M^+) 240.2089, found 240.2097.

(E)-3,4-Epoxy-2-methyltridecan-5-one ((E)-12l): colorless oil; IR ($CHCl_3$) 2930, 2850, 1705, 1465, 1375, 890 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.26 (d, $J = 1.7$ Hz, 1H), 2.85 (dd, $J = 1.7, 6.6$ Hz, 1H), 2.43 (dt, $J = 16.6, 7.6$ Hz, 1H), 2.28 (dt, $J = 16.6, 7.6$ Hz, 1H), 1.78–1.51 (m, 2H), 1.43–1.10 (m, 11H), 1.05 (d, $J = 6.8$ Hz, 3H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 226 (5, M^+), 183 (68), 141 (68), 71 (80), 57 (100); HRMS calcd for $C_{14}H_{26}O_2$ (M^+) 226.1933, found 226.1945.

(Z)-3,4-Epoxy-2-methyltridecan-5-one ((Z)-12l): pale yellow oil; IR ($CHCl_3$) 2920, 2840, 1700, 1455 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.60 (d, $J = 4.9$ Hz, 1H), 2.89 (dd, $J = 4.9, 9.3$ Hz, 1H), 2.53 (t, $J = 7.3$ Hz, 2H), 1.71–1.51 (m, 2H), 1.48–1.20 (m, 11H), 1.13 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 226 (16, M^+), 225 (14), 183 (52), 141 (37), 85 (100), 71 (67), 57 (92); HRMS calcd for $C_{14}H_{26}O_2$ (M^+) 226.1933, found 226.1917.

(E,E)-4,5-Epoxy-2-tetradecen-6-one ((E,E)-12m): colorless oil; IR ($CHCl_3$) 2920, 2845, 1710, 1450, 1360 cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.03 (dq, $J = 15.4, 6.6$ Hz, 1H), 5.19 (ddq, $J = 15.4, 8.1, 1.7$ Hz, 1H), 3.42 (dd, $J = 1.9, 8.1$ Hz, 1H), 3.37 (d, $J = 1.9$ Hz, 1H), 2.45 (dt, $J = 17.3, 7.3$ Hz, 1H), 2.32 (dt, $J = 17.3, 7.3$ Hz, 1H), 1.78 (dd, $J = 6.6, 1.7$ Hz, 3H), 1.70–1.52 (m, 2H), 1.41–1.18 (m, 10H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 224 (15, M^+), 172 (20), 146 (84), 99 (38), 84 (100), 71 (84), 57 (99); HRMS calcd for $C_{14}H_{24}O_2$ (M^+) 224.1776, found 224.1762.

(Z,E)-4,5-Epoxy-2-tetradecen-6-one ((Z,E)-12m): colorless oil; IR ($CHCl_3$) 2920, 2840, 1715 cm^{-1} ; 1H NMR ($CDCl_3$) δ 6.06 (dq, $J = 15.4, 6.6$ Hz, 1H), 5.22 (ddq, $J = 15.4, 8.6, 1.5$ Hz, 1H), 3.75 (d, $J = 4.9$ Hz, 1H), 3.63 (dd, $J = 4.9, 8.6$ Hz, 1H), 2.51 (t, $J = 7.3$ Hz, 2H), 1.74 (dd, $J = 6.6, 1.5$ Hz, 3H), 1.70–1.18 (m, 12H), 0.88 (t, $J = 6.8$ Hz, 3H); MS m/z (relative intensity) 224 (6, M^+), 183 (2), 172 (3), 141 (14), 84 (85), 49 (100); HRMS calcd for $C_{14}H_{24}O_2$ (M^+) 224.1776, found 224.1791.

(E)-4,4-Dimethyl-1,2-epoxy-1-(4-methylphenyl)pentan-3-one ((E)-12n): colorless needles; mp 56–59 °C (recrystallized from

methanol, lit.²⁴ mp 60–61 °C; IR (KBr) 2963, 1708, 1478, 1397, 1075, 806 cm⁻¹; ¹H NMR (CDCl₃) δ 7.19 (br s, 4H), 3.85 (d, *J* = 1.7 Hz, 1H), 3.82 (d, *J* = 1.7 Hz, 1H), 2.36 (s, 3H), 1.23 (s, 9H); MS *m/z* (relative intensity) 218 (51, M⁺), 134 (41), 105 (67), 83 (100), 57 (85).

(Z)-4,4-Dimethyl-1,2-epoxy-1-(4-methylphenyl)pentan-3-one ((Z)-12n):²⁴ colorless crystals; IR (CHCl₃) 2940, 1705, 1470, 1360, 990 cm⁻¹; ¹H NMR (CDCl₃) δ 7.22 (br d, *J* = 8.2 Hz, 2H), 7.11 (br d, *J* = 8.2 Hz, 2H), 4.30 (d, *J* = 4.7 Hz, 1H), 4.20 (d, *J* = 4.7 Hz, 1H), 2.31 (s, 3H), 0.99 (s, 9H); MS *m/z* (relative intensity) 218 (55, M⁺), 203 (5), 105 (100), 57 (91).

(E)-4,4-Dimethyl-1,2-epoxy-1-phenylpentan-3-one ((E)-12o): colorless leaflets; mp 67–69 °C (recrystallized from methanol, lit.²⁵ mp 70–71 °C); IR (KBr) 3032, 2977, 1709, 1458, 1092, 882 cm⁻¹; ¹H NMR (CDCl₃) δ 7.40–7.26 (m, 5H), 3.86 (s, 2H), 1.24 (s, 9H); MS *m/z* (relative intensity) 204 (44, M⁺), 120 (38), 91 (56), 57 (100). Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.89. Found: C, 76.13; H, 7.91.

(Z)-4,4-Dimethyl-1,2-epoxy-1-phenylpentan-3-one ((Z)-12o):²⁴ colorless crystals; IR (CHCl₃) 2945, 1705, 1475 cm⁻¹; ¹H NMR (CDCl₃) δ 7.33–7.26 (m, 5H), 4.36 (d, *J* = 4.9 Hz, 1H), 4.22 (d, *J* = 4.9 Hz, 1H), 0.98 (s, 9H); MS *m/z* (relative intensity) 204 (31, M⁺), 176 (24), 91 (51), 57 (100).

(E)-1-(4-Chlorophenyl)-4,4-dimethyl-1,2-epoxypentan-3-one ((E)-12p): colorless plates; mp 68.5–70 °C (recrystallized from methanol, lit.²⁴ mp 66–67 °C); IR (KBr) 2974, 1708, 1495, 1430, 1367, 1092, 891 cm⁻¹; ¹H NMR (CDCl₃) δ 7.36 (br d, *J* = 8.8 Hz, 2H), 7.24 (br d, *J* = 8.8 Hz, 2H), 3.84 (d, *J* = 2.0 Hz, 1H), 3.81 (d, *J* = 2.0 Hz, 1H), 1.24 (s, 9H); MS *m/z* (relative intensity) 240 (7), 238 (21, M⁺), 125 (33), 83 (35), 57 (100). Anal. Calcd for C₁₃H₁₅O₂Cl: C, 65.41; H, 6.33. Found: C, 65.45; H, 6.41.

(Z)-1-(4-Chlorophenyl)-4,4-dimethyl-1,2-epoxypentan-3-one ((Z)-12p):²⁴ colorless crystals; IR (KBr) 2971, 1709, 1493, 1475, 1371, 1090, 994, 824 cm⁻¹; ¹H NMR (CDCl₃) δ 7.30 (s, 4H), 4.30 (d, *J* = 4.9 Hz, 1H), 4.23 (d, *J* = 4.9 Hz, 1H), 1.00 (s, 9H); MS *m/z* (relative intensity) 240 (6), 238 (24, M⁺), 125 (33), 83 (47), 57 (100).

Reaction of the Cyclic (E)-β-(Acyloxy)vinyl(phenyl)iodonium Salt 13a with Benzaldehyde. To a stirred solution of the iodonium salt **13a** (30 mg, 0.077 mmol) and benzaldehyde (12 mg, 0.12 mmol) in THF (6 mL) was added a 0.43 M THF solution of EtOLi (0.27 mL, 0.12 mmol) at –78 °C under argon. After being stirred for 1 h at –78 °C, the reaction mixture was allowed to warm to room temperature during 8 h, quenched with water, and extracted with diethyl ether. Repeated preparative TLC (40% ethyl acetate in hexane) gave (*E*)- and (*Z*)-ethyl 5,6-epoxy-4-oxo-6-phenylhexanoate (**15a**) (6.7 mg, 35%, *E*:*Z* = 63:37) and ethyl 4,6-dioxo-6-phenylhexanoate (**16**) (3.7 mg, 19%).

(E)-15a: colorless oil; IR (CHCl₃) 2970, 2910, 1720, 1600, 1405, 1375, 1345, 1160 cm⁻¹; ¹H NMR (CDCl₃) δ 7.41–7.26 (m, 5H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.10 (d, *J* = 1.7 Hz, 1H), 3.56 (d, *J* = 1.7 Hz, 1H), 2.84–2.52 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H); MS *m/z* (relative intensity) 248 (84, M⁺), 203 (41), 101 (100), 91 (87); HRMS calcd for C₁₄H₁₆O₄ (M⁺) 248.1049, found 248.1062.

(Z)-15a: colorless oil; IR (CHCl₃) 2975, 1720, 1375, 1175 cm⁻¹; ¹H NMR (CDCl₃) δ 7.38–7.26 (m, 5H), 4.35 (d, *J* = 4.9 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.89 (d, *J* = 4.9 Hz, 1H), 2.64–2.26 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H); MS *m/z* (relative intensity) 248 (57, M⁺), 203 (35), 101 (69), 91 (100); HRMS calcd for C₁₄H₁₆O₄ (M⁺) 248.1049, found 248.1049.

16: pale yellow oil (a 7:1 equilibrium mixture of enol and 1,3-diketone); IR (CHCl₃) 3650, 2960, 1720, 1670, 1600, 1570, 1260, 1135 cm⁻¹; ¹H NMR (CDCl₃) δ 15.76 (br s, enol), 7.95 (br d, *J* = 8.0 Hz, 1,3-diketone), 7.86 (br d, *J* = 7.4 Hz, enol), 7.62–7.39 (m, 3H), 6.21 (s, enol), 4.17 (q, *J* = 7.1 Hz, enol), 4.16 (s, 1,3-diketone), 4.12 (q, *J*

= 7.1 Hz, 1,3-diketone), 2.94–2.59 (m, 4H), 1.31–1.20 (3H); MS *m/z* (relative intensity) 248 (36, M⁺), 203 (30), 160 (48), 147 (100), 105 (71), 69 (39); HRMS calcd for C₁₄H₁₆O₄ (M⁺) 248.1049, found 248.1051.

Reaction of the Cyclic (E)-β-(Acyloxy)vinyl(phenyl)iodonium Salt 13b with Benzaldehyde. The iodonium salt **13b** (25 mg, 0.062 mmol) was treated with EtOLi (0.094 mmol) and benzaldehyde (10 mg, 0.094 mmol) in THF (6 mL) under argon. Preparative TLC (15% ethyl acetate in hexane) gave (*E*)- and (*Z*)-ethyl 6,7-epoxy-5-oxo-7-phenylheptanoate (**15b**) (8.9 mg, 54%, *E*:*Z* = 62:38).

(E)-15b: colorless oil; IR (CHCl₃) 2965, 1720, 1455, 1405, 1375, 1185, 1095, 1020, 890 cm⁻¹; ¹H NMR (CDCl₃) δ 7.42–7.26 (m, 5H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.99 (d, *J* = 1.7 Hz, 1H), 3.52 (d, *J* = 1.7 Hz, 1H), 2.62 (dt, *J* = 17.6, 7.3 Hz, 1H), 2.55 (dt, *J* = 17.6, 7.3 Hz, 1H), 2.37 (t, *J* = 7.3 Hz, 2H), 1.96 (quint, *J* = 7.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); MS *m/z* (relative intensity) 262 (86, M⁺), 217 (95), 216 (94), 188 (80), 143 (100), 115 (76), 87 (67); HRMS calcd for C₁₅H₁₈O₄ (M⁺) 262.1205, found 262.1216.

(Z)-15b: colorless oil; IR (CHCl₃) 2990, 1725, 1455, 1400, 1375, 1200, 1020 cm⁻¹; ¹H NMR (CDCl₃) δ 7.39–7.26 (m, 5H), 4.34 (d, *J* = 4.9 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.84 (d, *J* = 4.9 Hz, 1H), 2.30 (dt, *J* = 17.8, 6.8 Hz, 1H), 2.16 (dt, *J* = 17.6, 6.8 Hz, 1H), 1.99 (t, *J* = 7.2 Hz, 2H), 1.61 (tt, *J* = 7.2, 6.8 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); MS *m/z* (relative intensity) 262 (36, M⁺), 217 (37), 216 (29), 184 (30), 143 (100), 105 (65), 91 (43); HRMS calcd for C₁₅H₁₈O₄ (M⁺) 262.1205, found 262.1214.

General Procedure for the Competition Experiments. To a stirred solution of the iodonium bromide **3b** (X = Br, 30 mg, 0.062 mmol), benzaldehyde (99 mg, 0.94 mmol), and a substituted benzaldehyde (0.94 mmol) in THF–DMSO (12:1, 6.5 mL) was added a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at –30 °C under argon. The reaction was allowed to proceed at –30 °C for 2 h. The yields of the epoxides **12** were determined by ¹H NMR of the crude reaction mixture and by isolation with repeated preparative TLC.

Reaction of 3b-*ad* with Benzaldehyde. A. EtOLi in the Presence of EtOH. The α-deuterated vinyliodonium bromide **3b-*ad*** (X = Br, >99% D) was prepared from **6b** by Michael addition of AcOD according to the general procedure. To a stirred solution of **3b-*ad*** (X = Br, 30 mg, 0.062 mmol) and benzaldehyde (9.9 mg, 0.094 mmol) in THF–DMSO (12:1, 6.5 mL) were added EtOH (14 mg, 0.31 mmol) and a 0.43 M THF solution of EtOLi (0.14 mL, 0.062 mmol) at –30 °C under argon. The reaction was allowed to proceed at –30 °C for 2 h. Preparative TLC (10% ethyl acetate in hexane) of the crude mixture gave (*E*)-**12d-*ad*** (95% D) in 71% yield.

B. *i*-Pr₂NLi in the Presence of *i*-Pr₂NH. To a stirred solution of **3b-*ad*** (X = Br, 30 mg, 0.062 mmol) and benzaldehyde (9.9 mg, 0.094 mmol) in THF–DMSO (12:1, 6.5 mL) were added *i*-Pr₂NH (31 mg, 0.31 mmol) and a 0.42 M THF solution of *i*-Pr₂NLi (0.15 mL, 0.062 mmol), prepared by the reaction of *i*-Pr₂NH with *n*-BuLi (1.6 M in hexane) in THF at 0 °C for 50 min, at –30 °C under argon. The reaction was allowed to proceed at –30 °C for 2 h. Preparative TLC of the crude mixture gave (*E*)-**12d-*ad*** (94% D) in 31% yield.

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Supporting Information Available: Experimental procedures not provided in the Experimental Section and figures (5 pages). See any current masthead page for ordering and Internet access instructions.

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