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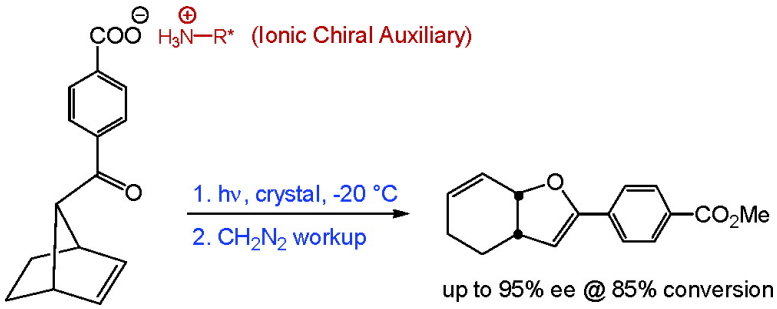

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Asymmetric Synthesis of Dihydrofurans via a Formal Retro-Claisen Photorearrangement

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Abstract: Solution-phase irradiation of a series of *syn*-7-benzoylnorbornene derivatives is shown to lead to *cis*-fused dihydrofuran derivatives in low quantum but excellent chemical yields in what is formally a retro-Claisen rearrangement. In analogy to the well-known Paterno−Büchi reaction, the first step of the rearrangement is suggested to involve $(n,\pi^*)^3$-mediated addition of the carbonyl oxygen to the norbornene double bond, producing a triplet 1,4-biradical. This intermediate, rather than closing to the oxetane, undergoes cleavage accompanied by intersystem crossing to form the dihydrofuran. To determine whether the retro-Claisen photorearrangement could be carried out enantioselectively, the 7-benzoylnorbornene reactant was equipped with a *para*-carboxylic acid substituent to which a series of optically pure amines was attached ionically via salt bridges. Irradiation of these salts in the crystalline state followed by diazomethane workup (the solid-state ionic chiral auxiliary method) was shown to afford the corresponding dihydrofuran in optical yields as high as 93% at 95% conversion. X-ray crystallography revealed that the enantioselectivity arises from crystallization of the reactant in a conformation in which the carbonyl oxygen is more favorably oriented for bond formation to one end of the norbornene double bond than the other, thus leading to a predominance of a single enantiomer.

Furans and partially reduced furans constitute a large class of naturally occurring compounds[1] that can be found in a variety of commercially important pharmaceuticals,[2] as well as in flavor and fragrance additives.[3] Consequently, efficient syntheses of such compounds have attracted considerable interest from organic chemists.[4] Among the general synthetic routes to furans are (i) regioselective introduction of substituents into simple furans[5] and (ii) cyclization reactions of appropriate acyclic precursors.[6,7] Despite these advances, room still exists for developing alternative and environmentally friendly approaches to the synthesis of such compounds. As part of a long-term interest in solid-state organic photochemistry,[8] we serendipitously discovered a new approach to the asymmetric synthesis of dihydrofurans via a novel retro-Claisen photorearrangement. In this paper, we present what we have learned to date about this unusual and interesting new reaction.

Our initial discovery in this area was made during the synthesis of a series of 7-benzoylnorbornane derivatives, which were subsequently shown to undergo diastereo- and enantioselective Yang photocyclization in the crystalline state.[9] The norbornane derivatives were synthesized via catalytic hydrogenation of the corresponding norbornenes, an example of which is keto-ester **1b** (Scheme 1). In a spirit of curiosity, compound **1b** was irradiated at >290 nm (Pyrex) in an acetonitrile solution and, to our delight, found to give a single product in 91% isolated yield. Based on its spectroscopic properties, in particular its 1D and 2D ^{1}H NMR spectra, this photoproduct was assigned the *cis*-dihydrofuran-containing structure **5b**.

The generality of this transformation, a formal retro-Claisen rearrangement, was tested by photolyzing the ketones shown in Table 1. Compounds **1a**−**1f**, all of which are expected to have lowest energy n,π^* triplet states, formed the dihydrofuran photoproduct **5** in excellent yield. In contrast, the *p*-methoxyphenyl derivative **1g**, whose lowest triplet state is undoubtedly π,π^* in nature, failed to react, and the aliphatic ketone **1h** underwent inefficient formation of oxetane **4h** upon irradiation.

The results suggest the mechanism shown in Scheme 1 in which the $(n,\pi^*)^3$ state of the ketone undergoes initial carbon−oxygen bonding to form triplet 1,4-biradical **3**. This step is

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Scheme 1

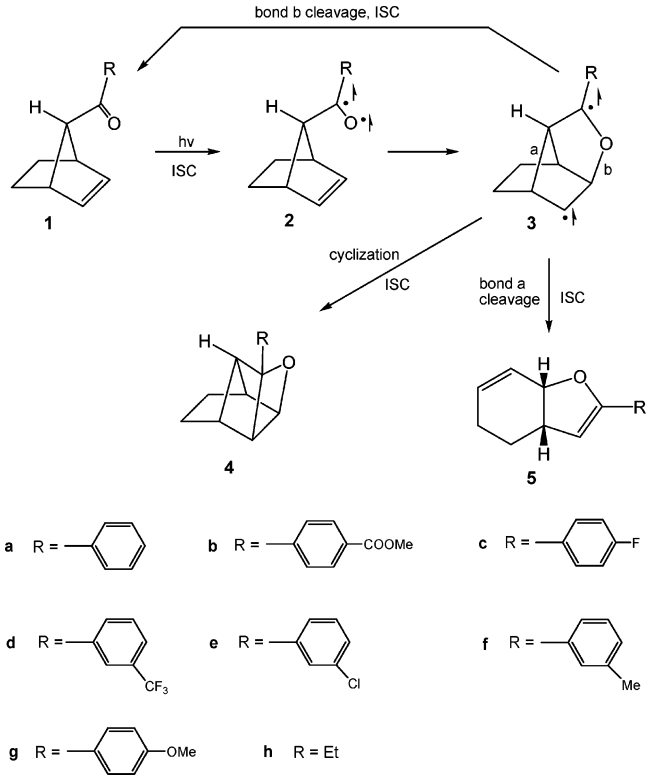


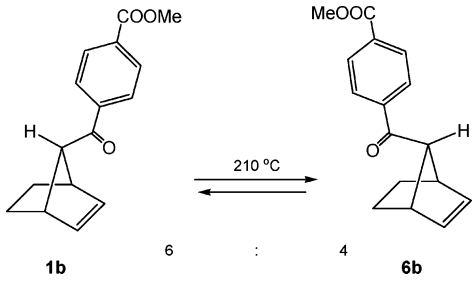
Table 1. Irradiation of Norbornenes in Acetonitrile Solution

compound	time (h)	conv. (%)	isolated yield of product **5** (%)
1a	1.3	54	96
	4.4	97	91
1b	1.4	53	98
	4.5	98	91
1c	1.4	51	94
	5.0	99	89
1d	1.4	47	94
	6.5	93	87
1e	1.6	44	89
	7.5	89	83
1f	1.6	31	90
	8.0	87	76
1g	20	a	a
1h	0.5	5.0	**4h**[b]

[a] Trace amounts of several unidentified products formed according to GC. [b] Identified by NMR as a mixture with starting material **1h**. Prolonged irradiation led to the formation of several additional unidentified byproducts.

identical to the first step of the triplet-mediated Paterno-Büchi reaction. Biradical **3** has three possible fates: (1) intersystem crossing accompanied by cleavage of carbon−oxygen bond b to regenerate ketone **1**, (2) intersystem crossing accompanied by biradical closure to form oxetane **4**, and (3) intersystem crossing accompanied by cleavage of carbon−carbon bond a to produce dihydrofuran derivative **5**. To get an indication of the importance of pathway 1 (regeneration of starting ketone), a quantum yield determination was carried out. In benzene, using valerophenone actinometry, the quantum yield for formation of dihydrofuran **5b** from ketone **1b** was found to be 0.021, a value that suggests that reversion to starting material plays a significant role in the partitioning of biradical **3**. Another possible reason for the low quantum yield is intramolecular charge-transfer quenching of the triplet excited state. In 1975, Morrison,

Scheme 2



Wagner, and co-workers showed that such a process is operative in the photochemistry of two γ,δ-unsaturated phenyl ketones (1-phenyl-4-hexene-1-one and 1-phenyl-2-ethyl-4-pentene-1-one).[10] Ketones of general structure **1** are also γ,δ-unsaturated aryl ketones, and it seems likely that quenching is occurring in these cases as well.

Based on the product distribution, it is evident that path 3 (cleavage of bond a) is favored over path 2 (biradical closure), which makes sense given the high strain energy of the oxetane.[11] Only in the case of aliphatic ketone **1h** was oxetane formation observed, a reaction that is most likely singlet-mediated.[12] The failure of *p*-methoxyphenyl ketone **1g** to react is also consistent with the proposed mechanism. Such ketones have lowest π,π^* triplet excited states, which are known to form oxetanes inefficiently.[13] Because the retro-Claisen and oxetane-forming reactions share the same first step, it is not surprising that neither is formed in the case of reactant **1g**.

Thermal retro-Claisen rearrangements have been investigated by Boeckman and others,[14] and it was therefore of interest to determine whether the **1** to **5** transformation could be initiated thermally. However, as shown in Scheme 2, heating ketone **1b** at 210 °C for 52 h produced a 6:4 mixture of **1b** and its epimer **6b**. The same mixture was formed when pure ketone **6b** was thermolyzed. This reaction most likely takes place through formation of the corresponding enol, although a mechanism involving carbon−carbon bond rupture, rotation, and reclosure cannot be ruled out completely.

The retro-Claisen photorearrangement of ketone **1** to dihydrofuran derivative **5** is suitable for asymmetric induction studies, because it converts an achiral reactant to a chiral product, and it was therefore decided to apply the solid-state ionic chiral auxiliary approach to this problem.[15] To this end, keto-acid **1i** (Scheme 3) was prepared and treated with a variety of optically pure amines to form the corresponding ammonium carboxylate salts **1j** (Table 2). Such salts are required to crystallize in chiral space groups, which provide the asymmetric environment responsible for chiral induction. Crystals of the

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(11) The difference in strain energy between oxetane **4b** and compound **5b** calculated by molecular mechanics is 107.44 kcal/mol. The calculations were performed using the HyperChem/ChemPlus software package (version 5.11/2.0).
(12) As a general rule, aliphatic aldehydes and ketones undergo stereospecific oxetane formation through their $(n,\pi^*)^1$ excited states. See, for example: Arnold, D. R.; Hinman, R. L.; Glick, A. H. *Tetrahedron Lett.* **1964**, 1425. Yang, N. C.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1277.
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(15) Scheffer, J. R. *Can. J. Chem.* **2001**, *79*, 349.

Scheme 3

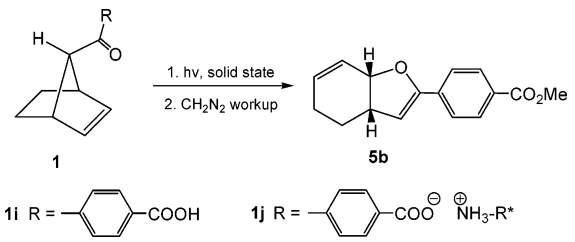

Table 2. Asymmetric Induction in the Irradiation of Salts **1j** in the Crystalline State[a]

amine	temp	conversion (%)[b]	ee (%)	α[c]
(*S*)-(−)-1-*p*-tolylethylamine	−20 °C	95	93	+
	room temp	68	90	+
	room temp	97	75	+
(*R*)-(−)-1-aminoindan	−20 °C	47	91	−
	room temp	53	91	−
	room temp	89	88	−
(*R*)-(+)-1-phenylethylamine	−20 °C	100	71	+
	room temp	59	90	+
	room temp	90	57	+
(*S*)-(−)-1-phenylethylamine	−20 °C	68	80	−
	room temp	72	72	−
	room temp	100	62	−
L-prolinamide	−20 °C	85	95	+
	room temp	72	53	+
	room temp	86	35	+
(1*S*,2*R*)-(−)-*cis*-1-amino-indanol	−20 °C	43	74	+
	room temp	83	71	+
	room temp	90	37	+
(*S*)-(−)-1-cyclohexyl-ethylamine	−20 °C	74	60	−
	room temp	60	58	−
	room temp	82	57	−
(1*R*,2*R*)-(−)-2-amino-1-phenyl-1,3-propanediol	−20 °C	59	28	−
	room temp	60	43	−
	room temp	77	42	−

[a] Samples were irradiated through Pyrex using a 450-W Hanovia medium-pressure mercury lamp. [b] Conversion % based on GC. [c] Sign of rotation of major enantiomer of photoproduct **5b** at the sodium D-line.

salts (2−5 mg) were crushed between two Pyrex microscope slides, sealed in polyethylene bags under nitrogen, and irradiated with a 450 W medium-pressure mercury lamp.[16] Following photolysis, the samples were treated with ethereal diazomethane (caution), and the resulting methyl esters were analyzed by chiral HPLC to obtain the enantiomeric excess (ee) values and by GC for the extent of conversion. As in solution, dihydrofuran compound **5b** was the sole GC-detectable photoproduct in the solid state. The results of the enantiomeric excess determinations are summarized in Table 2.

As can be seen from the data in Table 2, the enantiomeric excess values obtained for photoproduct **5b** in the solid state ranged from 28% to 95%. As expected for a well-behaved system, the use of (*R*)-(+)- and (*S*)-(−)-1-phenylethylamine as chiral auxiliaries led to the optical antipodes of dihydrofuran **5b**. For the salts studied, there was a decline in photoproduct ee with increasing conversion, which is presumably due to the breakdown in order of the crystal lattice as product replaces starting material. This could be compensated to a certain extent by performing the photolyses at −20 °C, which had a particularly strong effect in the case of the L-prolinamide salt.

(16) Although not studied in the present instance, previous work from our group has shown that the solid-state ionic chiral auxiliary procedure can be carried out on scales as high as 500 mg and presumably even higher. For an example, see: Scheffer, J. R.; Wang, K. *Synthesis* **2001**, 1253.

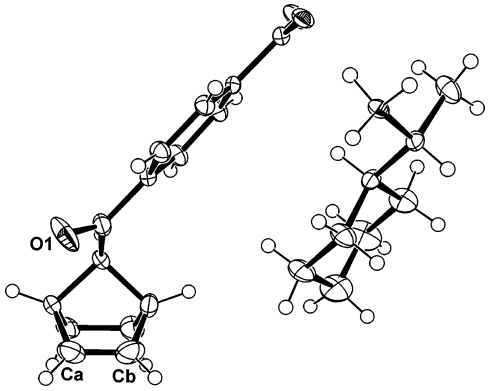

Figure 1. ORTEP representation of the X-ray crystal structure of the (*S*)-(−)-1-cyclohexylethylamine salt of keto-acid **1i** with 50% probability thermal ellipsoids.

Interestingly, lowering the photolysis temperature in the case of the (1*R*,2*R*)-(−)-2-amino1-phenyl-1,3-propanediol salt actually decreased the ee slightly. At temperatures much below −20 °C, the solid-state photoreaction became impracticably slow.

To rationalize the enantioselectivity observed in the solid state, the X-ray crystal structure of the (*S*)-(−)-1-cyclohexylethylamine salt was determined and is presented in Figure 1. Under the influence of the ionic chiral auxiliary, the carboxylate reactant crystallizes in a homochiral conformation in which the carbonyl oxygen is significantly closer to C_a (2.95 Å) than to C_b (3.29 Å). In addition, the n-orbital on oxygen, assumed to lie in the plane of the carbonyl group, can be seen to be more favorably oriented for bond formation with C_a than C_b.[17] As a result, the C_a−O bond is formed preferentially, affording a 1,4-biradical that leads to one enantiomer of the final photoproduct. The optical antipode of the photoproduct results from C_b−O bond formation, which requires a large amplitude rotation of the pendant aryl group that is topochemically and geometrically disfavored in the crystalline state. The enantioselectivity is therefore the result of preorganization of the reactant in a homochiral conformation favorable for the formation of a single enantiomer of the product.

In summary, the present study reports a convenient approach to the synthesis of highly enantiomerically enriched dihydrofuran compounds via a novel retro-Claisen photorearrangement. We are continuing to explore the scope and generality of this interesting and unusual transformation.

Experimental Section

Synthesis of the Weinreb Amide of Bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxylate. The known carboxylic acid, bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxylate,[18] was converted to its Weinreb amide by the general procedure reported by Jones et al.,[19,20] mp 64 °C (ether/pet ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (m, 2H), 3.64 (s, 3H), 3.15 (d, J = 1.5 Hz, 2H), 3.08 (s, 3H), 2.52 (s, 1H), 1.72 (m, 2H), 1.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3 (+), 132.4 (−), 62.3 (−), 62.3 (−), 60.9 (−), 44.3 (−), 24.8 (+). IR (KBr) ν_{max}: 1646, 1479, 1387, 1175, 974, 877, 718, 511 cm^{-1}. LRMS (EI): 181 [M$^+$], 121, 103, 93,

(17) A rough estimate of the orientation of the n-orbital with respect to C_a and C_b is given by the magnitude of the dihedral angle formed by the oxygen atom, the carbonyl carbon, the α-carbon atom, and C_a or C_b. This angle is −34.8° for C_a and −67.8° for C_b.
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79, 77, 65. Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.31; H, 8.33; N, 7.70.

Synthesis of Keto-Ester 1b. Methyl 4-iodobenzoate (0.365 g, 1.39 mmol) was dissolved in THF (50 mL) and cooled to −40 °C. Isopropylmagnesium chloride (0.73 mL, 2 M, 1.46 mmol) was added, and the solution was stirred for 1 h. A solution of the Weinreb amide prepared above (0.24 g, 1.31 mmol) in THF (10 mL) was added, and the mixture was stirred for 2 h, gradually warmed to −20 °C, stirred for 2 h, and finally stirred overnight at room temperature. The reaction was quenched by addition of a saturated solution of ammonium chloride (25 mL), followed by removal of THF in vacuo and its replacement with diethyl ether (25 mL). The ethereal solution was washed with 10% HCl (2 × 15 mL) and water (3 × 20 mL) before being dried over magnesium sulfate. Removal of the solvent in vacuo gave a yellow oil, which was purified by chromatography (10% ether/pet ether) to give a white solid (0.101 g, 30%), mp 128−129 °C (ether/pet ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (m, 2H), 7.85 (m, 2H), 5.95 (t, J = 1.8 Hz, 2H), 3.91 (s, 3H), 3.25 (m, 2H), 3.21 (brs, 1H), 1.91 (m, 2H), 1.11 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2 (+), 166.2 (+), 146.6 (+), 133.3 (+), 132.7 (−), 129.6 (−), 127.9 (−), 67.7 (−), 52.4 (−), 45.2 (−), 25.1 (+). IR (KBr) ν_{max}: 3061, 2958, 1716, 1405, 1116, 873, 770, 696 cm^{-1}. LRMS (EI): 256 [M$^+$], 197, 179, 164, 135, 103, 91, 77. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.15; H, 6.36.

Synthesis of Carboxylic Acid 1i. 4-Iodobenzoic acid (1.30 g, 5.24 mmol) was dissolved in THF (50 mL) under nitrogen and cooled to −30 °C. Isopropylmagnesium chloride (5.25 mL, 2 M, 10.5 mmol) was added dropwise, and the resulting solution was stirred for 1 h. On addition of the second Grignard equivalent, a light brown precipitate began to form. The Weinreb amide prepared above (0.99 g, 5.47 mmol) in THF (5 mL) was added dropwise, and the resulting mixture was gradually warmed to −20 °C and stirred for 4 h during which time the precipitate dissolved. The solution was allowed to stir at room temperature overnight and then quenched with saturated ammonium chloride. After acidification with 10% HCl, the THF was replaced by ether and extracted with 10% HCl and water. The organic layer was then washed with saturated sodium bicarbonate (3 × 50 mL), and the combined aqueous portions were acidified with concentrated HCl causing acid **1i** to precipitate. The suspended precipitate was washed with ether (2 × 50 mL), and the organic portions were washed with water (3 × 50 mL) before being dried over magnesium sulfate. Removal of the solvent gave an off-white solid composed of the desired acid and benzoic acid that was purified by recrystallization from methanol to give pure acid **1i** as a white solid (0.58 g, 44%), mp 242 °C (methanol). ^{1}H NMR (400 MHz, DMSO): δ 8.01 (m, 2H), 7.90 (m, 2H), 5.89 (t, J = 1.8 Hz, 2H), 3.39 (brs, 1H), 3.15 (m, 2H), 1.92 (m, 2H), 0.98 (m, 2H). ^{13}C NMR (100 MHz, DMSO): δ 198.9 (+), 166.6 (+), 140.0 (+), 134.0 (+), 132.8 (−), 129.5 (−), 128.0 (−), 67.2 (−), 44.6 (−), 24.7 (+). IR (KBr) ν_{max}: 3200−2700 (br), 2988, 2550, 1572, 1408, 1216, 1037, 985, 874, 786, 712 cm^{-1}. LRMS (EI): 242 [M$^+$], 227, 197, 179, 150, 149, 91, 77, 65, 50. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.35; H, 5.77.

General Procedure for Synthesis of Ketones 1a and 1c−h. To a solution of the Weinreb amide prepared above (100 mg, 0.55 mmol) in 3 mL of THF was added 3 equiv of the appropriate freshly prepared Grignard reagent in THF. The mixture was refluxed until the amide was consumed (checked by TLC), cooled to room temperature, poured into 30 mL of 10% HCl, stirred for 30 min, and extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed with water (2 × 30 mL) and dried over magnesium sulfate. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (ether/pet ether) to give ketones **1a** and **1c−h**.

Ketone 1a. Yield 90%, mp 61 °C (ether/pet ether). ^{1}H NMR (400 MHz, CD_3CN): δ 7.82 (m, 2H), 7.55 (m, 1H), 7.44 (m, 2H), 5.88 (m, 2H), 3.31 (brs, 1H), 3.18 (d, J = 1.4 Hz, 2H), 1.93 (m, 2H), 1.04 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 200.0 (+), 138.3 (+), 133.6 (−), 133.4 (−), 129.4 (−), 128.8 (−), 68.2 (−), 46.0 (−), 25.6 (+). IR (KBr) ν_{max}: 2977, 2812, 1679, 1375, 1217, 1008, 861, 761, 687 cm^{-1}. LRMS (EI): 198 [M$^+$], 183, 120, 105, 91, 77, 51. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.77; H, 7.13.

Ketone 1c. Yield 88%, oil. ^{1}H NMR (400 MHz, CD_3CN): δ 7.89 (m, 2H), 7.17 (m, 2H), 5.89 (m, 2H), 3.28 (brs, 1H), 3.17 (d, J = 1.2 Hz, 2H), 1.92 (m, 2H), 1.04 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 198.7 (+), 134.9 (+), 133.6 (−), 131.7 (−), 128.7 (+), 116.2 (−), 68.1 (−), 46.1 (−), 25.6 (−). IR (neat) ν_{max}: 2987, 2863, 1673, 1436, 1216, 1014, 873, 770, 696 cm^{-1}. LRMS (EI): 216 [M$^+$], 201, 159, 138, 123, 95, 75, 51. HRMS (EI) calcd for $C_{14}H_{13}FO$: 216.2508. Found: 216.2510.

Ketone 1d. Yield 64%, oil. ^{1}H NMR (400 MHz, CD_3CN): δ 8.06 (m, 2H), 7.84 (m, 1H), 7.62 (m, 1H), 5.87 (m, 2H), 3.35 (brs, 1H), 3.18 (d, J = 1.6 Hz, 2H), 1.92 (m, 2H), 1.03 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 199.2 (+), 139.0 (+), 133.7 (−), 132.7 (−), 131.4 (+), 130.6 (−), 129.8 (−), 123.7 (+), 125.3 (−), 68.2 (−), 46.04 (−), 25.6 (+). IR (neat) ν_{max}: 2937, 2815, 1679, 1347, 1219, 997, 864, 753, 677, 593 cm^{-1}. LRMS (EI): 266 [M$^+$], 251, 225, 188, 173, 145, 93, 77, 51. HRMS (EI) calcd for $C_{15}H_{13}F_3O$: 266.2583. Found: 266.2586.

Ketone 1e. Yield 78%, oil. ^{1}H NMR (400 MHz, CD_3CN): δ 7.76 (m, 2H), 7.52 (m, 1H), 7.42 (m, 1H), 5.88 (m, 2H), 3.26 (brs, 1H), 3.16 (d, J = 1.4 Hz, 2H), 1.92 (m, 2H), 1.01 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 199.0 (+), 140.0 (+), 135.2 (+), 133.6 (−), 133.2 (−), 131.2 (−), 128.5 (−), 127.4 (−), 68.2(−), 46.0 (−), 25.6 (+). IR (neat) ν_{max}: 2969, 2779, 1643, 1412, 1216, 997, 861, 685, 597 cm^{-1}. LRMS (EI): 234 [M$^+$, {^{37}Cl}], 232 [M$^+$, {^{35}Cl}], 217, 179, 154, 139, 111, 75, 51. HRMS (EI) calcd for $C_{14}H_{13}ClO$: 232.0654 {^{35}Cl}, 234.0673 {^{37}Cl}. Found: 232.0655 {^{35}Cl}, 234.0673 {^{37}Cl}.

Ketone 1f. Yield 83%, mp 73 °C (ether/pet ether). ^{1}H NMR (400 MHz, CD_3CN): δ 7.62 (m, 2H), 7.34 (m, 2H), 5.88 (m, 2H), 3.27 (brs, 1H), 3.17 (d, J = 1.2 Hz, 2H), 2.36 (s, 3H), 1.92 (m, 2H), 1.03 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 200.3 (+), 139.4 (+), 138.4 (+), 134.1 (−), 133.7 (−), 129.3 (−), 129.2 (−), 126.1 (−), 68.3 (−), 46.1 (−), 25.7 (+), 21.4 (−). IR (KBr) ν_{max}: 2979, 2814, 1681, 1345, 1219, 998, 867, 749, 673, 598 cm^{-1}. LRMS (EI): 212 [M$^+$], 197, 179, 134, 119, 91, 65, 51. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.77; H, 7.61.

Ketone 1g. Yield 73%, mp 76 °C (ether/pet ether). ^{1}H NMR (400 MHz, CD_3CN): δ 7.82 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 5.88 (d, J = 1.4 Hz, 2H), 3.83 (s, 3H), 3.25 (brs, 1H), 3.17 (brs, 2H), 1.92 (m, 2H), 1.01 (m, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 198.4 (+), 164.0 (+), 133.6 (−), 131.3 (+), 131.2 (−), 114.5 (−), 68.1 (−), 56.2 (−), 46.2 (−), 25.7 (+). IR (KBr) ν_{max}: 2930, 2834, 1673, 1356, 1207, 997, 867, 753, 677, 591 cm^{-1}. LRMS (EI): 228 [M$^+$], 213, 185, 150, 135, 107, 92, 77, 63. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.89; H, 7.09.

Ketone 1h. Yield 91%, oil. ^{1}H NMR (400 MHz, C_6D_6): δ 5.76 (m, 2H), 2.96 (d, J = 1.6 Hz, 2H), 1.95 (q, 2H), 1.84 (brs, 1H), 1.42 (m, 2H), 0.93 (m, 2H), 0.80 (m, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 208.2 (+), 133.4 (−), 70.2(−), 44.1 (−), 35.2 (+), 25.2 (+), 7.7 (−). IR (neat) ν_{max}: 2922, 2813, 1672, 1217, 677, 591 cm^{-1}. LRMS (EI): 150 [M$^+$], 135, 121, 93, 72, 57. HRMS (EI) calcd for $C_{10}H_{14}O$: 150.1045. Found: 105.1043.

Irradiation of Keto-Ester 1b in Acetonitrile. Keto-ester **1b** (100 mg, 0.39 mmol) was dissolved in acetonitrile (50 mL) and purged with nitrogen for 15 min. The solution was then irradiated through Pyrex with a 450 W medium-pressure mercury lamp for 3 h before the acetonitrile was removed in vacuo. The residue was purified by silica gel column chromatography (10% ether/pet ether) to give compound **5b** as a white solid (91 mg, 91%), mp 58 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.10 (m, 2H), 7.62 (m, 2H), 5.99 (m, 1H), 5.87 (t, J = 1.8 Hz, 1H), 5.21 (d, J = 2.8 Hz, 1H), 4.68 (d, J = 8.8 Hz, 1H), 3.47 (s, 3H), 2.63 (m, 1H), 1.77 (m, 1H), 1.45 (m, 2H), 1.23 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 166.3 (+), 155.4 (+), 135.8 (+), 132.7 (−), 130.3

(+), 129.9 (−), 125.4 (−), 125.2 (−), 103.4 (−), 77.2 (−), 51.5 (−), 41.4 (−), 26.0 (+), 23.2 (+). IR (KBr) ν_{max}: 1716, 1679, 1225, 1219, 873, 770, 696 cm^{-1}. LRMS (EI): 256 [M$^+$], 241, 197, 178, 163, 147, 91. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.81; H, 6.33.

General Procedure for Irradiation of Ketones 1a and 1c−g in Acetonitrile Solution. The solutions of ketones **1a** and **1c−g** (80 mg) in acetonitrile (40 mL) were purged with nitrogen for 15 min and then irradiated through Pyrex with a 450 W medium-pressure mercury lamp for 1.3−20 h. The solvent was removed in vacuo and the residues were purified by silica gel chromatography (ether/pet ether) to give dihydrofurans **5a** and **5c−g**.

Dihydrofuran 5a. Yield 91%, mp 56 °C (ether/pet ether). ^{1}H NMR (400 MHz, CD_3CN): δ 7.54 (m, 2H), 7.32 (m, 3H), 6.13 (m, 1H), 5.96 (m, 1H), 5.51 (d, J = 2.8 Hz, 1H), 4.78 (d, J = 8.2 Hz, 1H), 3.00 (m, 1H), 2.12 (m, 1H), 1.89 (m, 2H), 1.29 (m, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ 154.0 (+), 133.9 (−), 132.2 (+), 129.2 (−), 129.1 (−), 125.7 (−), 125.6 (−), 102.0 (−), 77.7 (−), 41.7 (−), 26.6 (+), 23.6 (+). IR (KBr) ν_{max}: 1731, 1671, 1193, 1207, 893, 761, 689 cm^{-1}. LRMS (EI): 198 [M$^+$], 183, 141, 120, 105, 91, 77, 51. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.92; H, 7.07.

Dihydrofuran 5c. Yield 89%, oil. ^{1}H NMR (400 MHz, CD_3CN): δ 7.16 (m, 2H), 7.07 (m, 2H), 6.12 (m, 1H), 5.95 (m, 1H), 5.46 (d, J = 2.8 Hz, 1H), 4.80 (d, J = 8.8 Hz, 1H), 3.01 (m, 1H), 2.06 (m, 1H), 1.89 (m, 2H), 1.28 (m, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ 155.1 (+), 134.8 (+), 134.0 (−), 128.7 (+), 127.8 (−), 127.7 (−), 125.5 (−), 116.1 (−), 115.9 (−), 101.8 (−), 77.8 (−), 41.7 (−), 26.6 (+), 23.6 (+). IR (neat) ν_{max}: 1809, 1702, 1224, 1201, 879, 789, 654 cm^{-1}. LRMS (EI): 216 [M$^+$], 201, 183, 138, 95, 77, 51. HRMS (EI) calcd for $C_{14}H_{13}FO$: 216.2508. Found: 216.2511.

Dihydrofuran 5d. Yield 87%, oil. ^{1}H NMR (400 MHz, CD_3CN): δ 7.75 (m, 2H), 7.57 (m, 1H), 7.48 (m, 1H), 6.12 (m, 1H), 5.94 (m, 1H), 5.62 (d, J = 2.8 Hz, 1H), 4.80 (d, J = 8.8 Hz, 1H), 3.02 (m, 1H), 2.05 (m, 1H), 1.86 (m, 2H), 1.25 (m, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ 153.7 (+), 134.2 (−), 131.1 (+), 130.9 (+), 129.4 (−), 126.0 (+), 125.6 (−), 125.4 (−), 122.3 (−), 104.2 (−), 78.0 (−), 41.8 (−), 26.5 (+), 23.6 (+). IR (neat) ν_{max}: 1789, 1643, 1221, 1208, 897, 767, 657 cm^{-1}. LRMS (EI): 266 [M$^+$], 251, 238, 188, 173, 145, 91, 77, 51. HRMS (EI) calcd for $C_{15}H_{13}F_3O$: 266.2583. Found: 266.2584.

Dihydrofuran 5e. Yield 83%, oil. ^{1}H NMR (400 MHz, CD_3CN): δ 7.52 (m, 3H), 7.40 (m, 1H), 6.13 (m, 1H), 5.94 (m, 1H), 5.55 (d, J = 2.8 Hz, 1H), 4.80 (d, J = 8.8 Hz, 1H), 3.01 (m, 1H), 2.14 (m, 1H), 1.79 (m, 2H), 1.25 (m, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ 154.7 (+), 134.2 (+), 137.1 (+), 134.1 (−), 130.9 (−), 128.9 (−), 125.5 (−), 125.4 (−), 124.2 (−), 77.9 (−), 41.8 (−), 26.5 (+), 23.6 (+). IR (neat) ν_{max}: 1717, 1679, 1224, 1218, 863, 769, 679 cm^{-1}. LRMS (EI): 234 [M$^+$, {^{37}Cl}], 232 [M$^+$, {^{35}Cl}], 217, 178, 154, 139, 111, 91, 77, 51. HRMS (EI) calcd for $C_{14}H_{13}ClO$: 232.0654 {^{35}Cl}, 234.0673 {^{37}Cl}. Found: 232.0655 {^{35}Cl}, 234.0672 {^{37}Cl}.

Dihydrofuran 5f. Yield 76%, mp 67 °C (ether/pet ether). ^{1}H NMR (400 MHz, CD_3CN): δ 7.34 (m, 2H), 7.20 (m, 1H), 7.10 (m, 1H), 6.11 (m, 1H), 5.95 (m, 1H), 5.46 (d, J = 2.8 Hz, 1H), 4.78 (d, J = 8.0 Hz, 1H), 2.99 (m, 1H), 2.30 (s, 3H), 2.06 (m, 1H), 1.87 (m, 2H), 1.27 (m, 1H). ^{13}C NMR (100 MHz, CD_3CN): δ 153.7 (+), 138.9 (+), 133.9 (−), 132.2 (+), 129.9 (−), 129.2 (−), 126.3 (−), 125.7 (−), 122.9 (−), 101.9 (−), 77.7 (−), 41.7 (−), 26.7 (+), 25.0 (+), 21.3 (−). IR (KBr) ν_{max}: 1717, 1658, 1224, 1203, 873, 790, 676 cm^{-1}. LRMS (EI): 212 [M$^+$], 197, 165, 134, 119, 91, 77, 65. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.81; H, 7.66.

Irradiation of Ketone 1h. A solution of ketone **1h** (30 mg) in C_6D_6 (3 mL) was purged with nitrogen for 5 min and then irradiated with a 450 W medium-pressure mercury lamp equipped with a quartz filter for 0.5 h. The solution was then analyzed directly by NMR to obtain the spectral data for oxetane **5h**. ^{1}H NMR (400 MHz, C_6D_6): δ 4.14 (brs, 1H), 2.88 (m, 1H), 2.71 (brs, 1H), 2.61 (m, 1H), 2.52 (m, 1H), 1.70 (m, 2H), 1.35 (m, 2H), 0.94 (m, 2H), 0.82 (m, 3H). ^{13}C NMR (100 MHz, C_6D_6): δ 92.8 (+), 80.9 (−), 52.6 (−), 52.5 (−), 49.3 (−), 36.4 (−), 25.2 (+), 24.6 (+), 23.7 (+), 9.1 (−). GCMS (EI): 150 [M$^+$], 135, 121, 108, 91, 79, 57.

General Procedure for the Preparation of Salts 1j. To keto-acid **1i** (80 mg, 0.33 mmol) in 5 mL of diethyl ether was added 1 equiv of optically pure amine. Upon addition, a precipitate formed immediately. The resulting suspension was suction-filtered to give the salt, which was recrystallized from methanol.

(*S*)-(−)-1-*p*-Tolylethylamine Salt. Mp 189−191 °C (methanol). ^{1}H NMR (400 MHz, CD_3OD): δ 7.84 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.78 (m, 2H), 4.27 (m, 1H), 3.25 (brs, 1H), 3.18 (m, 1H), 3.09 (brs, 2H), 2.21 (s, 3H), 1.85 (m, 2H), 3.06 (d, J = 6.8 Hz, 3H), 0.96 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 202.0 (+), 174.0 (+), 140.2 (+), 139.8 (+), 136.9 (+), 133.3 (+), 133.8 (−), 130.8 (−), 130.2 (−), 128.7 (−), 127.6 (−), 68.9 (−), 52.0 (−), 46.5 (−), 25.9 (+), 21.1 (−), 20.8 (−). IR (KBr) ν_{max}: 2945, 1677, 1516, 1091, 879, 779, 696, 517 cm^{-1}. LRMS (ESI): 378 [M$^+$ + 1], 360, 281, 243, 192. Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; N, 3.71. Found: C, 76.67; H, 7.24; N, 3.65.

(*R*)-(−)-1-Aminoindan Salt. Mp 173−177 °C (methanol). ^{1}H NMR (400 MHz, CD_3OD): δ 7.90 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.19 (m, 3H), 5.80 (d, J = 1.6 Hz, 2H), 4.67 (m, 1H), 3.27 (brs, 1H), 3.19 (m, 2H), 3.05 (m, 3H), 2.88 (m, 1H), 2.48 (m, 1H), 1.98 (m, 1H), 1.87 (m, 2H), 0.99 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 201.9 (+), 173.1 (+), 145.4 (+), 141.6 (+), 140.2 (+), 139.8 (+), 133.8 (−), 130.7 (−), 130.3 (−), 128.7 (−), 128.2 (−), 126.4 (−), 125.5 (−), 69.0 (−), 56.9 (−), 46.5 (−), 31.6 (+), 31.0 (+), 25.9 (+). IR (KBr) ν_{max}: 2978, 1691, 1573, 1291, 1013, 719, 687, 517 cm^{-1}. LRMS (ESI): 376 [M$^+$ + 1], 298, 267, 265, 243, 192, 179. Anal. Calcd for $C_{24}H_{25}NO_3$: C, 76.77; H, 6.71; N, 3.73. Found: C, 76.86; H, 6.63; N, 3.64.

(*R*)-(+)-1-Phenylethylamine and (*S*)-(−)-1-Phenylethylamine Salts. Mp 187−189 °C (methanol). ^{1}H NMR (400 MHz, CD_3OD): δ 7.93 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.37 (m, 2H), 7.30 (m, 1H), 5.89 (s, 2H), 4.32 (q, J = 6.7 Hz, 1H), 3.37 (s, 1H), 3.15 (s, 2H), 1.93 (d, J = 7.2 Hz, 2H), 1.46 (d, J = 6.8 Hz, 2H), 0.96 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 198.9 (+), 168.3 (+), 142.0 (+), 141.8 (+), 137.7 (+), 132.7 (−), 129.0 (−), 128.4 (−), 127.6 (−), 127.3 (−), 126.5 (−), 67.1 (−), 49.9 (−), 44.7 (−), 24.7 (+), 22.1 (−). IR (KBr) ν_{max}: 2942, 1677, 1387, 1291, 1091, 879, 826, 709, 696, 536 cm^{-1}. LRMS (ESI): 364 [M$^+$ + 1], 348, 297, 265, 243, 173. Anal. Calcd for $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 76.23; H, 6.99; N, 3.74.

L-Prolinamide Salt. Mp 171−173 °C (methanol). ^{1}H NMR (400 MHz, CD_3OD): δ 7.88 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 5.80 (m, 2H), 4.13 (m, 1H), 3.21 (m, 4H), 3.11 (brs, 2H), 2.32 (m, 1H), 1.92 (m, 5H), 0.99 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 202.0 (+), 173.3 (+), 172.4 (+), 141.7 (+), 140.2 (+), 133.8 (−), 130.3 (−), 128.8 (−), 68.9 (−), 61.0 (−), 47.3 (+), 46.5 (−), 31.2 (+), 25.9 (+), 25.3 (+). IR (KBr) ν_{max}: 2951, 1637, 1521, 1224, 1087, 865, 773, 697, 552 cm^{-1}. LRMS (ESI): 357 [M$^+$ + 1], 297, 265, 229, 209, 137. Anal. Calcd for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86. Found: C, 64.88; H, 6.99; N, 7.57. Anal. Calcd for $C_{20}H_{24}N_2O_4 \cdot 0.75H_2O$: C, 64.94; H, 6.95; N, 7.57.

(1*S*,2*R*)-(−)-*cis*-1-Aminoindanol Salt. Mp 175−178 °C (methanol). ^{1}H NMR (400 MHz, CD_3OD): δ 7.86 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.2 Hz, 1H), 7.20 (m, 3H), 5.78 (d, J = 1.4 Hz, 2H), 4.59 (m, 1H), 4.44 (d, J = 6.0 Hz, 1H), 3.26 (brs, 1H), 3.19 (m, 2H), 3.09 (m, 3H), 2.91 (m, 1H), 1.86 (m, 2H), 0.98 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD): δ 202.0 (+), 173.9 (+), 142.8 (+), 142.7 (+), 139.9 (+), 138.2 (+), 133.8 (−), 130.9 (−), 130.3 (−), 128.7 (−), 128.4 (−), 126.7 (−), 126.2 (−), 71.9 (−), 69.0 (−), 58.6 (−), 46.5 (−), 40.1 (+), 25.9 (+). IR (KBr) ν_{max}: 3300, 2968, 1689, 1574, 1293, 1201, 1013, 773, 689, 573 cm^{-1}. LRMS (ESI): 392 [M$^+$

+ 1], 300, 299, 265, 150. Anal. Calcd for $C_{24}H_{25}NO_4$: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.62; H, 6.47; N, 3.48.

(*S*)-(−)-1-Cyclohexylethylamine Salt. Mp 189−191 °C (methanol). ^{1}H NMR (400 MHz, DMSO): δ 7.91 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 5.88 (d, J = 1.7 Hz, 2H), 3.36 (s, 1H), 3.14 (brs, 2H), 2.96 (q, J = 6.4 Hz, 1H), 1.92 (m, 2H), 1.70 (m, 2H), 1.68 (brs, 2H), 1.59 (m, 1H), 1.45 (m, 1H), 1.12 (d, J = 6.7 Hz, 3H), 1.11 (m, 3H), 0.97 (m, 2H), 0.96 (m, 2H). ^{13}C NMR (100 MHz, DMSO): δ 198.9, 168.5, 143.1, 137.2, 132.7, 128.9, 127.1, 67.1, 50.7, 49.7, 41.1, 28.6, 27.0, 25.7, 25.6, 25.5, 24.7, 15.8. IR (KBr) ν_{max}: 2929, 1681, 1377, 1350, 1192, 1060, 1032, 985, 816, 781, 553 cm^{-1}. LRMS (ESI): 370 [M^+ + 1], 313, 277, 243, 139. Anal. Calcd for $C_{23}H_{31}NO_3$: C, 74.76; H, 8.46; N, 3.79. Found: C, 75.01; H, 8.46; N, 3.81.

(1*R*,2*R*)-(−)-2-Amino-1-phenyl-1,3-propanediol Salt. Mp 147−150 °C (methanol). ^{1}H NMR (400 MHz, DMSO): δ 7.96 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.38 (m, 4H), 7.29 (m, 1H), 5.89 (t, J = 1.6 Hz, 2H), 4.65 (d, J = 8.6 Hz, 1H), 3.38 (m, 2H), 3.22 (dd, J = 11.7, 5.7 Hz, 1H), 3.15 (brs, 2H), 3.07 (m, 1H), 1.93 (m, 2H), 0.98 (m, 2H). ^{13}C NMR (100 MHz, DMSO): δ 198.9, 169.2, 142.3, 141.3, 137.8, 132.7, 129.1, 128.1, 127.5, 127.3, 126.8, 71.1, 67.1, 59.3, 58.6, 44.7, 24.7. IR (KBr) ν_{max}: 1680, 1584, 1531, 1293, 1040, 837, 780, 700, 543 cm^{-1}. LRMS (ESI): 410 [M^+ + 1], 373, 279, 253, 177. Anal. Calcd for $C_{23}H_{31}NO_3$: C, 70.40; H, 6.65; N, 3.42. Found: C, 70.34; H, 6.66; N, 3.67.

General Procedure for Solid-State Irradiation of Chiral Salts 1j. The salt (2−5 mg) was crushed between two Pyrex microscope slides and sealed in a polyethylene bag under a positive pressure of nitrogen. The sample was irradiated from both sides with a 450 W medium-pressure mercury lamp. After irradiation, the salt crystals were suspended in an excess of ethereal diazomethane solution (caution: poisonous and explosive) and allowed to stand until dissolution was complete. Ether and excess diazomethane were removed in vacuo, and the residue was taken up in methylene chloride and passed through a short plug of silica gel to remove the chiral auxiliary. This afforded furan **5b** as a colorless solid, which was then submitted to HPLC analysis (Chiralcel OJ column with eluting solution of hexanes: 2-propanol = 90:10) to give the enantiomeric excesses, and GC analysis (HP-35 column) to give the conversions.

Thermal Reaction of Ketone 1b. Ketone **1b** (40 mg, 0.16 mmol) was placed in a sealed tube and heated at 210 °C in a sand bath for 52 h. The reaction mixture was separated on a silica gel column to afford starting material (23 mg) and the isomeric product **6b** (16 mg), mp 113−115 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.00 (m, 2H), 7.67 (m, 2H), 5.89 (t, J = 1.8 Hz, 2H), 3.45 (s, 3H), 2.92 (d, J = 1.6 Hz, 2H), 2.19 (m, 1H), 1.85 (m, 2H), 0.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1 (+), 165.9 (+), 140.0 (+), 136.0 (+), 133.8 (−), 129.9 (−), 128.3(−), 65.5 (−), 51.8 (−), 44.4 (−), 22.6(+). IR (KBr) ν_{max}: 3059, 2948, 1716, 1400, 1106, 874, 770, 696 cm^{-1}. LRMS (EI): 256 [M^+], 241, 225, 178, 163, 135, 93, 77. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.13; H, 6.36.

Quantum Yield Determination. The quantum yield for formation of furan **5b** in benzene was determined using valerophenone actinometry (Φ = 0.33)[21] and a merry-go-round apparatus[22] according to the standard procedure used in our group.[23] *n*-Tetradecane and *n*-nonadecane were used as internal standards for valerophenone and furan **5b**, respectively. Quantum yields were determined at varying conversions and plotted against conversion; the reported quantum yield of 0.021 represents the value extrapolated to 0% conversion.

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Supporting Information Available: Crystallographic data for the (*S*)-(−)-1-cyclohexylethylamine salt of keto-acid **1i** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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