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# Asymmetric synthesis of tricyclic tetralin derivatives via an intramolecular photoreaction

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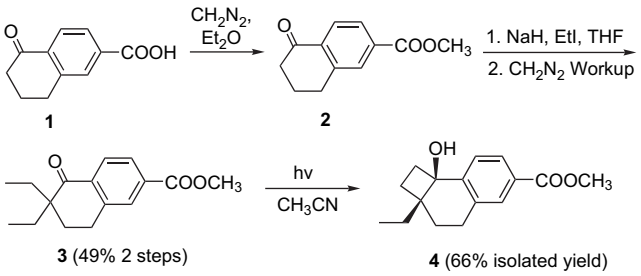
**Abstract**—An intramolecular photoreaction for the synthesis of tricyclic tetralin derivatives through a Norrish/Yang type cyclization is described. Asymmetric studies on this reaction using ionic chiral auxiliaries gave enantiomeric excesses of up to 99% at conversions of 80%, and the reaction mechanism was mapped out by a single crystal-to-single crystal reaction.


## 1. Introduction

Tricyclic tetralin derivatives are important building blocks for the synthesis of a wide variety of indole-diterpenes.[1] Synthesis of such compounds has become a challenge owing to their strained ring systems and has attracted much attention from chemists. A literature survey shows that the existing methodologies include $SmI_2$ mediated reaction,[2] radical addition reactions,[3] metal-mediated reactions,[4] and intermolecular [2+2] photoadditions.[5] Despite these advances, room still exists for developing alternative and environmentally friendly approaches to the synthesis of such compounds. As part of our interest in solid-state photochemistry,[6] we developed a new approach to the asymmetric synthesis of tricyclic tetralin derivatives via an intramolecular photoreaction. In this paper, we present what we have achieved in this regard.

## 2. Results and discussion

Our strategy for the synthesis of tricyclic tetralin compounds started from the commercially available 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid **1** (Scheme 1), which was treated with diazomethane in diethyl ether and reacted with ethyl iodide and NaH to give diethyl tetralone **3** in 49% yield (two steps from **1** to **3**). Irradiation of compound **3** in acetonitrile through Pyrex using a 450 W medium-pressure mercury lamp successfully afforded tricyclic tetralin compound **4** in 66% yield[7] via an intramolecular Norrish/Yang cylization reaction.[8] Based on 1D and 2D NMR spectra as well as IR and MS, this photoproduct was assigned the *cis*-ethyl, hydroxyl-containing structure, and the stereochemistry was further confirmed by X-ray crystallography described in the following section. Hyperchem MM3 calculations showed that the C═O···$H_\gamma$ distance is 2.71 Å, which is within the 2.72±0.2 Å range established for successful γ-hydrogen abstraction in the solid state.[9] Furthermore, the photochemical procedure converts an achiral reactant to a chiral product, which is suitable for asymmetric studies using the ionic chiral auxiliary method.




**Scheme 1**.

Next we turned to the asymmetric synthesis aspect of the work. Diethyl tetralone **3** was hydrolyzed with LiOH in THF/$H_2O$ to give carboxylic acid **5** in 98% yield (Scheme 2). The next step was to introduce internal chiral auxiliaries to compound **5** for asymmetric studies. Therefore, carboxylic acid **5** was treated with a variety of optically pure amines to form the corresponding ammonium carboxylate salts **6**. Such salts are required to crystallize in chiral space groups, which provide the asymmetric environment responsible for chiral induction. Crystals of these salts (2–5 mg) were

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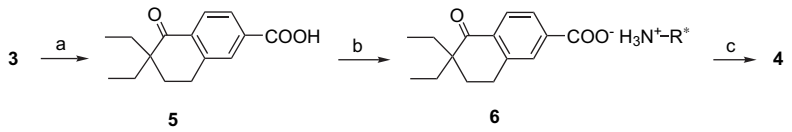


**Scheme 2**. (a) LiOH, THF/$H_2O$, 98%; (b) R*–$NH_2$; (c) *hν*, solid state, $CH_2N_2$.

crushed between two Pyrex microscope slides, sealed in polyethylene bags under nitrogen, and irradiated with a 450 W medium-pressure mercury lamp. Following photolysis, the photoproducts were treated with ethereal diazomethane, and the resulting methyl esters were analyzed by chiral HPLC to obtain the enantiomeric excess (ee) values and GC for the conversions. The results of the enantiomeric excess determinations are summarized in Table 1.

As can be seen in Table 1, the enantiomeric excess values obtained for photoproduct **4** ranged from 7.4% to 99%. For the salts studied, there was a decline in the photoproduct ee with increasing conversion, which is presumably due to the breakdown in the crystal lattice when the photoproduct replaces the reactant. Fortunately, this could be compensated by lowering the reaction temperature to −43 °C. At temperatures much below −43 °C, the solid-state photoreaction became sluggish. As expected for a well-behaved system, the use of (*S*)-(−)- and (*R*)-(+)-phenylethylamine led to the optical antipodes of photoproduct **4**.

To rationalize the enatioselective results observed in the solid state, the X-ray crystal structure of the (*S*)-(−)-1-*p*-tolylethylammonium salt was determined and is represented in Figure 1.[10] Under the influence of the chiral auxiliary, (*S*)-(−)-1-*p*-tolylethylamine, the reactant crystallized in a homochiral conformation in which the distance between the carbonyl oxygen and the γ-hydrogen Ha (O···Ha, 2.69 Å) is much closer than O···Hb (4.70 Å). As a result, bond formation between $C_1$ and Ca is favored, affording one enantiomer of photoproduct **4**. In contrast, formation of the optical antipode of the photoproduct obtained by abstraction of Hb and bonding between $C_1$ and Cb is not only unlikely on distance grounds, but following abstraction, also requires a large amplitude rotation of the aryl group, which is topochemically forbidden in the solid state. Therefore, the enantioselectivity of the reaction is governed by the homochiral conformation favorable for formation of a single enantiomer of the product.

A bonus was the finding that one of the reactions was a single crystal-to-single crystal process,[11] which allowed the crystal structures to be obtained at the beginning, mid point and the end of the reaction and an absolute configuration correlation to be established between reactant and product. In the case of the (*S*)-(−)-1-*p*-tolylethylammonium salt, the photoreaction in the solid state was found to be a single crystal-to-single crystal process, which allowed the structure of the 20% reacted crystal to be obtained.[12] Figure 2 shows an ORTEP representation of the 20% reacted crystal structure with the chiral auxiliary omitted for clarity. In this figure the gray lines belong to the reactant and the black lines belong to the photoproduct. The mixed crystal structure shown in Figure 2 proves that abstraction of the closer hydrogen (Ha) is favored over abstraction of Hb. Because the absolute configuration of the ionic chiral auxiliary is known, the absolute configurations of the reactant and the product are established, which allow us to state with certainty that abstraction of Ha led to the product with the (*R*)-configuration at $C_1$ as deduced from the crystal structure of the (*S*)-(−)-1-*p*-tolylethylammonium salt. As can be seen, there is a close correspondence in size and shape between reactant and photoproduct, a common feature of nearly all single crystal-to-single crystal transformations.

To conclude, we have developed a new and convenient approach to the synthesis of highly enantiomerically enriched tricyclic tetralin derivatives. Current efforts in our

**Table 1**. Asymmetric studies on the irradiation of salts **6** in the solid state[a]

| Amine | Temperature | Conversion[b] (%) | ee (%) | α[c] |
|---|---|---|---|---|
| (*S*)-(−)-1-*p*-Tolylethylamine | −43 °C | 100 | 98 | – |
| | Room temperature | 80 | 99 | – |
| | Room temperature | 100 | 97 | – |
| (*S*)-(−)-1-Cyclohexyl-ethylamine | −43 °C | 87 | 88 | – |
| | Room temperature | 90 | 65 | – |
| | Room temperature | 54 | 77 | – |
| (*S*)-(−)-1-Phenylethylamine | −43 °C | 51 | 86 | + |
| | Room temperature | 35 | 62 | + |
| | Room temperature | 74 | 58 | + |
| (*R*)-(+)-1-Phenylethylamine | −43 °C | 66 | 59 | – |
| | Room temperature | 44 | 56 | – |
| | Room temperature | 75 | 44 | – |
| (*R*)-(+)-β-Methylphenylethylamine | −43 °C | 23 | 21 | + |
| | Room temperature | 62 | 9.4 | + |
| | | 77 | 7.4 | + |

[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 **4** at the sodium D-line.

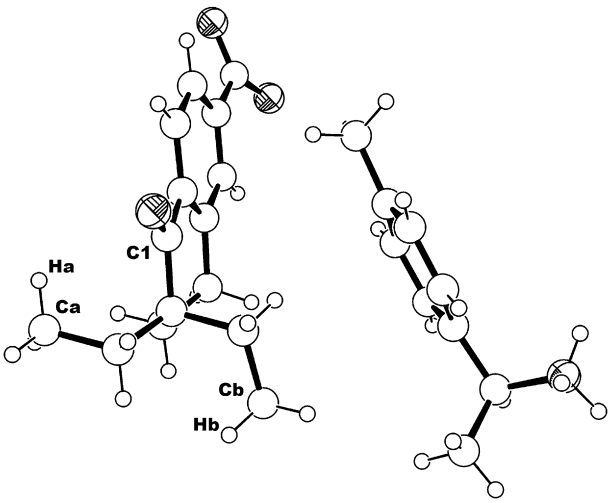


**Figure 1**. ORTEP presentation of X-ray crystal structure of (*S*)-(−)-1-*p*-tolylethylammonium salt.

lab to synthesize natural products using this approach are ongoing.

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 631948 and 631949. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

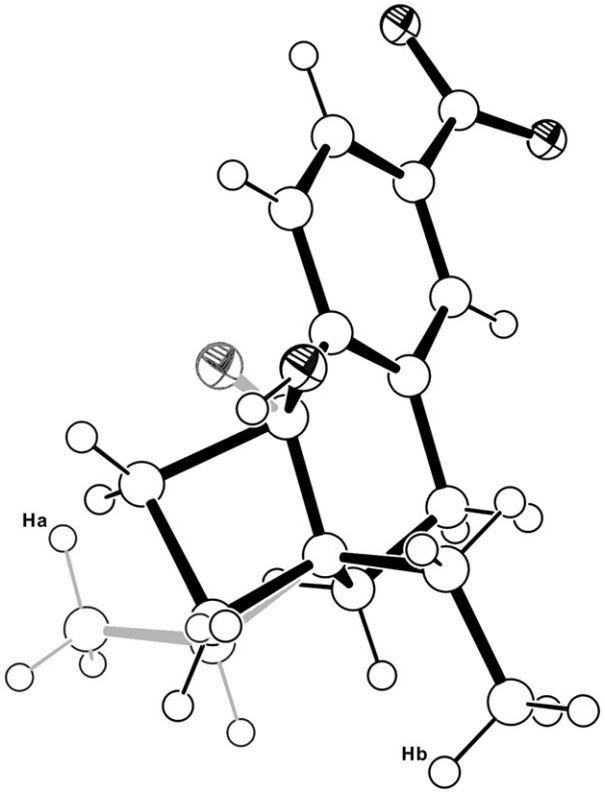


**Figure 2**. ORTEP presentation of mixed crystal containing 80% starting material and 20% product (chiral auxiliary omitted for clarity).

## 3. Experimental

### 3.1. General methods

Commercial spectral grade solvents were used for photochemical experiments unless otherwise stated. For synthetic use, tetrahydrofuran and diethyl ether were dried over the sodium ketyl of benzophenone; dichloromethane was dried over calcium hydride; acetonitrile was distilled from $P_2O_5$. Melting points were determined on a Fisher–Johns hot-stage apparatus and uncorrected. Analytical TLC was performed on 0.20 mm silica gel 60-F plates and visualized under UV light and/or by staining with phosphomolybdic acid. Infrared spectra were recorded on a Perkin–Elmer 1710 Fourier transform spectrometer. Low-resolution mass spectra were obtained from a Kratos MS 50 instrument using electron impact (EI) ionization at 70 eV. Elemental analyses were performed on a Carlo Erba CHN Model 1106 analyzer. $^1$H NMR spectra were obtained at 400 MHz on Bruker AV-400 instruments. $^{13}$C NMR spectra were recorded at 100 MHz.

**3.1.1. Methyl 2,2-diethyl-1-tetralone-6-carboxylate.** Methyl 1-tetralone-6-carboxylate (1.98 g, 9.7 mmol) prepared from the methyl esterification of 1-tetralone-6-carboxylic acid was dissolved in 75 mL of dry THF.[13] To this stirred solution, NaH (1.3 g, 60% dispersion in mineral oil, 32.5 mmol) was added at 0 °C under nitrogen. After being stirred for 10 min, ethyl iodide (2.32 mL) was added and then the mixture was stirred at room temperature for 2 days. The reaction mixture was cooled to 0 °C, quenched with 1 N HCl, and extracted with diethyl ether. The ether extract was washed with saturated $Na_2S_2O_3$ aqueous solution, water, brine, dried over $MgSO_4$, and filtered. The filtrate was evaporated in vacuo to afford a crude product, which was treated with $CH_2N_2$, and then purified by column chromatography on silica gel with pet ether–diethyl ether (20:1) to give the ester **3** as an oil (1.16 g, 49% yield). *$^1$H NMR* (400 MHz, $CDCl_3$): $\delta$ 8.06 (d, $J$=8.0 Hz, 1H), 7.89 (d, $J$=8.3 Hz, 1H), 7.88 (s, 1H), 3.91 (s, 3H), 3.00 (t, $J$=6.3 Hz, 2H), 2.02 (t, $J$=6.3 Hz, 2H), 1.67–1.69 (m, 2H), 1.59–1.61 (m, 2H), 0.83 (t, $J$=7.5 Hz, 6H). *$^{13}$C NMR* (100 MHz, $CDCl_3$): $\delta$ 201.5 (+), 166.5 (+), 143.0 (+), 135.2 (+), 133.5 (+), 130.1 (−), 128.0 (−), 127.9 (−), 52.4 (−), 48.0 (+), 29.9 (+), 26.2 (+)×2, 24.9 (+), 8.1 (−)×2. *IR* (NaCl) $\nu_{max}$: 2969, 2940, 1727, 1684, 1437, 1280, 1097, 907, 752 cm$^{-1}$. *LRMS* (EI): 260 [M$^+$], 245, 232 (100), 203, 189, 176, 148, 117, 103, 89, 77, 55. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.48; H, 7.88.

**3.1.2. Irradiation of compound 3 in acetonitrile.** The solution of **3** (70 mg, 0.27 mmol) in acetonitrile (30 mL) was purged with $N_2$ for 15 min and irradiated with 450 W medium-pressure mercury lamp under $N_2$ for 8 h. After irradiation, the solvent was removed in vacuo and the residue was purified by chromatography with pet ether–diethyl ether (8:1) to give photoproduct **4** (46 mg, 66%) and the cleavage product (6 mg, 10%) as colorless oils.

Photoproduct **4**: *$^1$H NMR* (400 MHz, $C_6D_6$): $\delta$ 8.10 (d, $J$=8.1 Hz, 1H), 8.00 (s, 1H), 7.62 (d, $J$=8.1 Hz, 1H), 3.55 (s, 3H), 2.44–2.46 (m, 2H), 2.19–2.20 (m, 1H), 1.82–1.83

(m, 1H), 1.68–1.69 (m, 1H), 1.38–1.40 (m, 2H), 1.26–1.28 (m, 2H), 1.02–1.04 (m, 1H), 0.76 (t, $J$=7.5 Hz, 3H). *$^{13}$C NMR* (100 MHz, $C_6D_6$): $\delta$ 166.9 (+), 148.7 (+), 137.0 (+), 129.9 (−), 128.9 (+), 126.8 (−)×2, 73.9 (+), 51.5 (−), 46.6 (+), 35.7 (+), 27.8 (+), 27.6 (+), 27.0 (+), 21.1 (+), 8.1 (−). *IR* (NaCl) $\nu_{max}$: 3480, 2944, 2356, 1718, 1703, 1437, 1289, 1113, 773 cm$^{-1}$. *LRMS* (EI): 260 [M$^+$], 232(100), 217, 203, 177, 144, 115, 91, 77, 59. Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.33; H, 7.79.

Cleavage product: *$^1$H NMR* (400 MHz, $CDCl_3$): $\delta$ 8.02 (d, $J$=8.5 Hz, 1H), 7.87–7.89 (m, 2H), 3.90 (s, 3H), 3.00–3.02 (m, 2H), 2.40–2.41 (m, 1H), 2.22–2.23 (m, 1H), 1.94–1.95 (m, 1H), 1.86–1.87 (m, 1H), 1.53–1.55 (m, 1H), 0.97 (t, $J$=7.5 Hz, 3H). *$^{13}$C NMR* (100 MHz, $CDCl_3$): $\delta$ 199.7 (+), 166.4 (+), 143.8 (+), 135.5 (+), 133.6 (+), 130.1 (−), 127.5 (−), 127.3 (−), 52.4 (−), 49.0 (−), 28.3 (+), 27.5 (+), 22.3 (+), 11.3 (−). *IR* (NaCl) $\nu_{max}$: 2954, 2873, 1725, 1687, 1437, 1282, 906, 746 cm$^{-1}$. *LRMS* (EI): 232 [M$^+$], 217, 204 (100), 176, 145, 117, 89, 77, 63. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 71.99; H, 7.08.

**3.1.3. 2,2-Diethyl-1-tetralone-6-carboxylic acid.** To a solution of keto-ester **3** (839 mg, 3.22 mmol) in THF (26 mL) and $H_2O$ (13 mL) was added LiOH (1.2 g, 50 mmol). The mixture was stirred at room temperature for 4 h and then diethyl ether (40 mL) was added. The organic layer was washed with water (3×25 mL) and the aqueous layers were combined and acidified with concd HCl. The solution was then extracted with diethyl ether (4×40 mL) and the combined organic layer was washed with water (3×20 mL) and dried over $MgSO_4$. Removal of solvent in vacuo gave a white solid, which was recrystallized from methanol to afford keto-acid **5** as a white solid (778 mg, 98% yield), mp 168–169 °C. *$^1$H NMR* (400 MHz, $CDCl_3$): $\delta$ 8.10 (d, $J$=8.0 Hz, 1H), 7.97 (d, $J$=8.9 Hz, 1H), 7.96 (s, 1H), 3.02 (t, $J$=6.3 Hz, 2H), 2.03 (t, $J$=6.3 Hz, 2H), 1.68–1.70 (m, 2H), 1.58–1.60 (m, 2H), 0.83 (t, $J$=7.4 Hz, 6H). *$^{13}$C NMR* (100 MHz, $CDCl_3$): $\delta$ 201.5 (+), 171.5 (+), 143.1 (+), 135.8 (+), 132.6 (+), 130.7 (−), 128.1 (−), 127.9 (−), 48.0 (+), 29.8 (+), 26.2 (+)×2, 24.9 (+), 8.1 (−)×2. *IR* (KBr) $\nu_{max}$: 3864, 2969, 2560, 1684, 1435, 1307, 1220, 907, 759 cm$^{-1}$. *LRMS* (ESI): 247 [M$^+$−1], 214, 168, 142, 111, 83, 63. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.29; H, 7.38.

### 3.2. General procedure for synthesis of salts 6

To a solution of keto-acid **5** (80 mg, 32.5 mmol) in diethyl ether (5 mL) was added an equivalent of optically pure amine. Upon the addition, the precipitate formed immediately. The resulting suspension was filtered by suction to give the salt, which was then recrystallized from methanol.

**3.2.1. (*S*)-(−)-1-Phenylethylammonium and (*R*)-(+)-1-phenylethylammonium salts.** Mp 153–155 °C (methanol). *$^1$H NMR* (400 MHz, $CD_3OD$): $\delta$ 7.87 (d, $J$=8.6 Hz, 1H), 7.74 (m, 2H), 7.41–7.31 (m, 5H), 4.38 (q, $J$=6.9 Hz, 1H), 2.97 (t, $J$=6.3 Hz, 2H), 1.99 (t, $J$=6.3 Hz, 2H), 1.65–1.66 (m, 2H), 1.56 (d, $J$=6.8 Hz, 3H), 1.52–1.54 (m, 2H), 0.79 (t, $J$=7.4 Hz, 6H). *$^{13}$C NMR* (100 MHz, $CD_3OD$): $\delta$ 202.8 (+), 173.0 (+), 143.3 (+), 142.2 (+), 138.9 (+), 133.1 (+), 129.5 (−), 129.0 (−)×2, 128.8 (−), 126.9 (−)×2, 126.4 (−)×2, 51.1 (−), 47.8 (+), 30.0 (+), 26.3 (+)×2, 24.8 (+), 19.7 (−), 7.3 (−)×2. IR (KBr) $\nu_{max}$: 3437, 2969, 2688, 2176, 1647, 1620, 1526, 1386, 1221, 909, 762 cm$^{-1}$. *LRMS* (ESI): 368 [M$^+$+1], 269, 122, 105. Anal. Calcd for $C_{23}H_{29}NO_3$: C, 75.17; H, 7.95; N, 3.81. Found: C, 75.38; H, 8.10; N, 3.63.

**3.2.2. (*R*)-(−)-1-Cyclohexylethylammonium salt.** Mp 139–141 °C (methanol). *$^1$H NMR* (400 MHz, $CD_3OD$): $\delta$ 7.79 (d, $J$=8.5 Hz, 1H), 7.66 (m, 2H), 2.93 (m, 1H), 2.90 (t, $J$=6.3 Hz, 2H), 1.91 (t, $J$=6.3 Hz, 2H), 1.62–1.65 (m, 5H), 1.58–1.60 (m, 2H), 1.48–1.50 (m, 2H), 1.36–1.38 (m, 1H), 1.11–1.12 (m, 3H), 1.10 (d, $J$=6.8 Hz, 3H), 0.92–0.93 (m, 2H), 0.71 (t, $J$=7.5 Hz, 6H). *$^{13}$C NMR* (100 MHz, $CD_3OD$): $\delta$ 204.0 (+), 174.3 (+), 144.4 (+), 143.6 (+), 134.2 (+), 130.6 (−), 128.1 (−)×2, 53.6 (−), 48.8 (+), 42.7 (−), 31.3 (+), 30.0 (+), 28.8 (+), 27.5 (+)×2, 27.3 (+), 27.1 (+), 27.0 (+), 26.0 (+), 16.0 (−), 8.5 (−)×2. *IR* (KBr) $\nu_{max}$: 3437, 2932, 2674, 2161, 1672, 1629, 1520, 1373, 1219, 912, 777, 758 cm$^{-1}$. *LRMS* (ESI): 374 [M$^+$+1], 341, 280, 248, 128, 111, 69. Anal. Calcd for $C_{23}H_{35}NO_3$: C, 73.96; H, 9.44; N, 3.75. Found: C, 74.26; H, 9.48; N, 3.68.

**3.2.3. (*R*)-(+)-β-Methylphenethylammonium salt.** Mp 111–112 °C (methanol). *$^1$H NMR* (400 MHz, $CD_3OD$): $\delta$ 7.81 (d, $J$=8.5 Hz, 1H), 7.68–7.69 (m, 2H), 7.22–7.23 (m, 2H), 7.16–7.18 (m, 3H), 2.99 (d, $J$=7.0 Hz, 2H), 2.93–2.95 (m, 1H), 2.90 (t, $J$=6.3 Hz, 2H), 1.92 (t, $J$=6.3 Hz, 2H), 1.59–1.60 (m, 2H), 1.46–1.48 (m, 2H), 1.20 (d, $J$=6.8 Hz, 3H), 0.72 (t, $J$=7.3 Hz, 6H). *$^{13}$C NMR* (100 MHz, $CD_3OD$): $\delta$ 203.9 (+), 174.2 (+), 144.4 (+), 143.4 (+)×2, 134.2 (+), 130.7 (−), 130.1 (−)×2, 128.5 (−), 128.2 (−)×2, 128.1 (−)×2, 49.1 (+), 46.9 (+), 39.8 (−), 31.2 (+), 27.5 (+)×2, 26.0 (+), 19.9 (−), 8.5 (−)×2. *IR* (KBr) $\nu_{max}$: 3478, 2969, 2671, 2172, 1673, 1630, 1520, 1381, 1219, 909, 780, 762 cm$^{-1}$. *LRMS* (ESI): 382 [M$^+$+1], 349, 271, 136, 119, 91. Anal. Calcd for $C_{24}H_{31}NO_3$: C, 75.56; H, 8.19; N, 3.67. Found: C, 75.61; H, 8.23; N, 3.59.

**3.2.4. (*S*)-(−)-1-*p*-Tolylethylammonium salt.** Mp 159–161 °C (methanol). *$^1$H NMR* (400 MHz, $CD_3OD$): $\delta$ 7.75 (d, $J$=8.5 Hz, 1H), 7.62–7.63 (m, 2H), 7.15 (d, $J$=8.1 Hz, 2H), 7.04 (d, $J$=8.0 Hz, 2H), 4.22 (q, $J$=6.8 Hz, 1H), 2.84 (t, $J$=6.3 Hz, 2H), 2.16 (s, 3H), 1.86 (t, $J$=6.3 Hz, 2H), 1.52–1.53 (m, 2H), 1.43 (d, $J$=6.9 Hz, 3H), 1.40–1.41 (m, 2H), 0.67 (t, $J$=7.4 Hz, 6H). *$^{13}$C NMR* (100 MHz, $CD_3OD$): $\delta$ 203.9 (+), 174.2 (+), 144.4 (+), 143.4 (+), 140.1 (+), 137.0 (+), 134.2 (+), 130.8 (−), 130.7 (−)×2, 128.1 (−)×2, 127.6 (−)×2, 52.0 (−), 48.8 (+), 31.2 (+), 27.5 (+)×2, 26.0 (+), 21.2 (−), 20.9 (−), 8.5 (−)×2. *IR* (KBr) $\nu_{max}$: 3467, 2917, 2675, 2152, 1675, 1624, 1530, 1382, 1219, 912, 818, 756 cm$^{-1}$. *LRMS* (ESI): 382 [M$^+$+1], 359, 349, 271, 136, 119. Anal. Calcd for $C_{24}H_{31}NO_3$: C, 75.76; H, 8.19; N, 3.67. Found: C, 75.71; H, 8.20; N, 3.56.

### 3.3. Irradiation of (*S*)-(−)-1-phenylethylammonium salts 6 in the solid state

The salt crystals (2–5 mg) were crushed between two Pyrex microscope slides and sealed in a polyethylene bag under a positive pressure of nitrogen. The sample was irradiated

at −43 °C or room temperature for 6.5–70 h 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 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. The residue was then submitted to HPLC analysis to give the enantiomeric excesses and GC analysis to give the conversions.

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7. The ratio of Norrish type II cyclization and cleavage product is 6.5:1 based on GC analysis.
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10. Crystal data for (*S*)-(−)-1-*p*-tolylethylamine salt of keto-acid **5**: $C_{24}H_{31}N_1O_3$, $M$=381.50, orthorhombic, $a$=6.7040(10), $b$=11.729(2), $c$=27.072(6) Å, $V$=2128.7(7) Å$^3$, $T$=173 K, space group $P2_12_12_1$ (no. 19), $Z$=4, $\mu$(Mo K$\alpha$)=0.078 mm$^{-1}$, 4012 reflections measured, 269 unique ($R_{int}$=0.053), which were used in all calculations. The final $wR(F^2)$ was 0.114 (all data). Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 631948.
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12. Crystal data for (*S*)-(−)-1-*p*-tolylethylamine salt of keto-acid **5** irradiated to 20% conversion: $C_{24}H_{31}N_1O_3$, $M$=381.50, orthorhombic, $a$=6.7157(6), $b$=11.7170(10), $c$=26.856(3) Å, $V$=2113.2(4) Å$^3$, $T$=173 K, space group $P2_12_12_1$ (no. 19), $Z$=4, $\mu$(Mo K$\alpha$)=0.078 mm$^{-1}$, 4001 reflections measured, 273 unique ($R_{int}$=0.072), which were used in all calculations. The final $wR(F^2)$ was 0.172 (all data). Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 631949.
13. Methyl 1-tetralone-6-carboxylate was prepared as following: 1-tetralone-6-carboxylic acid (2.0 g, 10.5 mmol) dissolved in 80 mL diethyl ether was added with ethereal diazomethane at 0 °C until the solution turned to yellow. The resulted solution was filtered on a silica gel column and rinsed with diethyl ether. The solvent was then removed in vacuo to give a colorless oil as methyl 1-tetralone-6-carboxylate, which was used in next steps without further purifications.