Supporting Information

Diastereoselective Construction of Cyclopent-2-enone-4-ols from Aldehydes and 1,2-Allenones Catalyzed by N-Heterocyclic Carbene

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**General:** $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AM 300 MHz spectrometer. IR spectra were recorded with a Perkin–Elmer 983G instrument. Elemental analyses were measured with a Carlo-Erba EA1110 elementary analysis instrument. Mass spectrometry was performed with an HP 5989A system. High-resolution mass spectrometry was determined with a Finnigan MAT 8430 or Bruker APEXIII instrument. 1-Ethyl-3-methylimidazolium tetrafluoroborate was purchased from J&K. Cs$_2$CO$_3$ was purchased from Energy Chemical. 1,4-Dioxane and toluene were distilled from Na/benzophenone before use. CH$_2$Cl$_2$ was distilled from CaH$_2$ before use. All liquid aldehydes were freshly distilled before use. Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers.

1,2-Allenones 2a,$^1$ 2b,$^2$ 2c,$^3$ 2e,$^4$ and 2f$^{3,5}$ were prepared according to reported literatures.
Experimental details and analytical data

1. Optimization of the reaction conditions.

Table S1 Reaction exploration

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<th>Entry</th>
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⁴ Reaction conditions: A solution of NHC precursor and Cs₂CO₃ in solvent (1 mL) was stirred at 20 °C for 10 min, then 0.8 mmol of 1a, 0.4 mmol of 2a, and solvent (1 mL) were added sequentially. The resulting mixture was then stirred at 20 °C for the time indicated in the Table. ³ Determined by NMR of the crude product using dibromomethane as the internal standard. ³ The Benzoin product was formed in 39% yield. ³ The Benzoin product was formed in 74% yield. ³ Dr was 100:0 as determined by NMR. ⁵ Dr was 95:5 as determined by NMR. ⁶ Dr was 88:12 as determined by NMR. ⁷ Dr was 100:0 as determined by NMR. ² 20 mol % of Cs₂CO₃ was used.

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**Diagram:**

1. Reaction conditions: A solution of NHC precursor and Cs₂CO₃ in solvent (1 mL) was stirred at 20 °C for 10 min, then 0.8 mmol of 1a, 0.4 mmol of 2a, and solvent (1 mL) were added sequentially. The resulting mixture was then stirred at 20 °C for the time indicated in the Table. Determined by NMR of the crude product using dibromomethane as the internal standard. The Benzoin product was formed in 39% yield. The Benzoin product was formed in 74% yield. Dr was 100:0 as determined by NMR. Dr was 95:5 as determined by NMR. Dr was 88:12 as determined by NMR. Dr was 100:0 as determined by NMR. 20 mol % of Cs₂CO₃ was used.
Table S2 Exploration of the NHCs in dioxane

![Image of reaction scheme]

<table>
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<th>Entry</th>
<th>NHC precursor</th>
<th>t (h)</th>
<th>Product yield (%)</th>
<th>Recovery of 2a (%)</th>
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<td>A1</td>
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<td>24 4 5 40%</td>
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<td>8</td>
<td>F</td>
<td>22</td>
<td>3    — — —</td>
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*a Reaction conditions: A solution of NHC precursor and Cs2CO3 in dioxane (1 mL) was stirred at 20 °C for 10 min, then 0.48 mmol of 1a, 0.4 mmol of 2a, and dioxane (1 mL) were added sequentially. The resulting mixture was then stirred at 20 °C for the time indicated in the Table. † Determined by NMR of the crude product using dibromomethane as the internal standard. ‡ Dr was 95:5 as determined by NMR.

2. Preparation of 1,2-allenyl ketones 2d

(1) 9-(Benzyloxy)nona-1,2-dien-4-one (2d) (mdk-9-109)

![Image of reaction scheme]

To a Schlenk flask were added Fe(NO3)3·9H2O (124.2 mg, 0.3 mmol), TEMPO (48.0 mg, 0.3 mmol), NaCl (17.8 mg, 0.3 mmol), and DCE (8 mL) with stirring. Then 9-(benzyloxy)nona-1,2-dien-4-ol (741.2 mg, 3 mmol) and DCE (4 mL) were added. The residual air in the reaction system was excluded by oxygen provided by a balloon.
After that, the resulting mixture was stirred at rt under oxygen provided by the balloon. After 3.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl ether (20 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (60-90 °C)/ethyl acetate = 15/1 (480 mL) to 10/1 (440 mL)) afforded 2d (527.8 mg, 72%) as a liquid: 1H NMR (300 MHz, CDCl3) δ 7.38-7.23 (m, 5H, ArH), 5.77 (t, J = 6.5 Hz, 1H, =CH), 5.22 (d, J = 6.3 Hz, 2H, =CH2), 4.49 (s, 2H, CH2), 3.46 (t, J = 6.6 Hz, 2H, CH2), 2.61 (t, J = 7.4 Hz, 2H, CH2), 1.69-1.55 (m, 4H, CH2 × 2), 1.46-1.33 (m, 2H, CH2); 13C NMR (75 MHz, CDCl3) δ 216.6, 200.8, 138.5, 128.3, 127.6, 127.5, 96.7, 79.3, 72.9, 70.1, 39.0, 29.5, 25.8, 24.3; IR (neat) ν (cm⁻¹) 3087, 3064, 3029, 2988, 2936, 2859, 2793, 1958, 1933, 1682, 1496, 1454, 1409, 1363, 1308, 1204, 1158, 1104, 1028; MS (70 ev, EI) m/z (%) 244 (M⁺, 0.43), 91 (100); Elemental analysis calcd (%) for C16H20O2: C, 78.65, H, 8.25; Found: C, 78.44; H, 8.16.

3. Preparation of cyclopent-2-enone-4-ols 5aa-5ee

(1) 4-(4-Bromophenyl)-4-hydroxy-3-methyl-5-pentylcyclopent-2-enone (5aa)

Typical Procedure I: To a dry Schlenk flask was added Cs2CO3 (65.1 mg, 0.2 mmol) under N2. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (40.3 mg, 0.2 mmol),
dioxane (3.75 mL), and CH₂Cl₂ (1.25 mL) were added sequentially under N₂. The resulting mixture was stirred at rt. After 10 min, the mixture was cooled to -10 °C, 1a (226.8 mg, 1.2 mmol)/CH₂Cl₂ (1.25 mL) and 2a (152.3 mg, 1 mmol)/dioxane (3.75 mL) were added sequentially. The resulting mixture was stirred at -10 °C. After 19.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (20 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (30 °C ~ 60 °C, redistillation)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL × 2) to 3/1 (400 mL)) afforded 5aa (0.1796 g, 53%, dr > 99:1) (the dr of the crude product was 95:5 as determined via the NMR analysis) as a liquid: 

^1^H NMR (300 MHz, CDCl₃) δ 7.47 (d, J = 8.7 Hz, 2H, ArH), 7.13 (brs, 2H, ArH), 6.13 (q, J = 1.3 Hz, 1H, =CH), 2.72 (s, 1H, OH), 2.58 (dd, J₁ = 9.0 Hz, J₂ = 5.4 Hz, 1H, CH), 1.90 (d, J = 1.5 Hz, 3H, CH₃), 1.59-1.46 (m, 1H, one proton from CH₂), 1.40-0.94 (m, 6H, CH₂ × 3), 0.89-0.72 (m, 4H, CH₃ + one proton from CH₂); ^1^C NMR (75 MHz, CDCl₃) δ 206.1, 176.1, 138.4, 131.3, 130.1, 127.5, 121.6, 85.2, 61.4, 31.6, 27.1, 25.9, 22.1, 13.9, 13.6; IR (neat) ν (cm⁻¹) 3435, 2954, 2930, 2859, 1693, 1625, 1589, 1572, 1487, 1466, 1456, 1434, 1397, 1375, 1307, 1297, 1245, 1232, 1205, 1164, 1075, 1010; MS (70 ev, EI) m/z (%) 338 (M⁺(^81Br), 4.15), 336 (M⁺(^79Br), 4.56), 265 (100); HRMS calcd for C₁₇H₂₁⁷⁹BrO₂ (M⁺): 336.0725, found: 336.0728.

The following compounds were prepared according to Typical procedure I.

(2) 4-Hydroxy-3-methyl-5-pentyl-4-phenylcyclopent-2-enone (5ba) (mdk-8-065)
The reaction of 1b (127.4 mg, 1.2 mmol), 2a (153.0 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs₂CO₃ (65.3 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 11 h afforded 5ba (0.1966 g, 76%, dr = 99:1) (petroleum ether (60 °C ~ 90 °C, redistillation)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL) to 3/1 (400 mL)) (the dr of the crude product was 96:4 as determined via the NMR analysis) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.51-6.97 (m, 5H, ArH), 6.14 (q, J = 1.3 Hz, 1H, =CH), 2.81 (s, 1H, OH), 2.60 (dd, J₁ = 9.2 Hz, J₂ = 5.3 Hz, 1H, CH), 1.91 (d, J = 1.5 Hz, 3H, CH₃), 1.59-1.45 (m, 1H, one proton from CH₂), 1.38-0.91 (m, 6H, CH₂ × 3), 0.90-0.78 (m, 1H, one proton from CH₂), 0.75 (t, J = 6.8 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 206.3, 176.1, 139.2, 130.1, 128.2, 127.5, 125.5, 85.6, 61.4, 31.7, 27.1, 25.8, 22.1, 13.9, 13.7; IR (neat) ν (cm⁻¹) 3439, 3087, 3060, 3028, 2955, 2930, 2859, 1693, 1626, 1601, 1491, 1448, 1374, 1301, 1246, 1232, 1205, 1165, 1131, 1093, 1066, 1015; MS (70 ev, EI) m/z (%) 258 (M⁺, 14.47), 187 (100); Elemental analysis calcd (%) for C₁₇H₂₂O₂: C, 79.03; H, 8.58; Found: C, 79.00; H, 8.81.

(3) 4-Hydroxy-3-methyl-4-phenyl-5-propylcyclopent-2-enone (5bb) (mdk-8-080)
The reaction of 1b (127.6 mg, 1.2 mmol), 2b (124.3 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (39.9 mg, 0.2 mmol), and Cs₂CO₃ (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 15.5 h afforded 5bb (0.1461 g, 63%, dr = 99:1) (petroleum ether (30 °C ~ 60 °C)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL × 2 + 180 mL) to 3/1 (400 mL)) (the dr of the crude product was 95:5 as determined via the NMR analysis) as a liquid (solid, m. p. 79–81 °C (EtOH)): ¹H NMR (300 MHz, CDCl₃) δ 7.47-6.99 (m, 5H, ArH), 6.13 (q, J = 1.4 Hz, 1H, =CH), 3.18 (s, 1H, OH), 2.64 (dd, J₁ = 8.7 Hz, J₂ = 5.4 Hz, 1H, CH), 1.91 (d, J = 1.5 Hz, 3H, CH₃), 1.55-1.39 (m, 1H, one proton from CH₂), 1.39-1.14 (m, 2H, CH₂), 0.89-0.75 (m, 1H, one proton from CH₂), 0.69 (t, J = 7.4 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 206.7, 176.6, 139.3, 129.9, 128.2, 127.5, 125.5, 85.5, 61.1, 28.1, 20.8, 13.9, 13.7; IR (neat) ν (cm⁻¹) 3435, 3087, 3060, 3028, 2958, 2933, 2871, 1694, 1626, 1601, 1491, 1465, 1448, 1375, 1319, 1301, 1249, 1220, 1194, 1170, 1131, 1096, 1066, 1034, 1002; MS (70 ev, EI) m/z (%) 230 (M⁺, 9.35), 187 (100); HRMS calcd for C₁₅H₁₈O₂ (M⁺): 230.1307, found: 230.1310.

(4) 5-Benzyl-4-hydroxy-3-methyl-4-phenylcyclopent-2-enone (5bc) (mdk-8-098)
The reaction of 1b (127.8 mg, 1.2 mmol), 2c (173.0 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.1 mg, 0.2 mmol), and Cs₂CO₃ (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 22 h afforded 5bc (0.1598 g, 57%, dr = 92:8) (petroleum ether (30 °C ~ 60 °C)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL) to 3/1 (600 mL)) (the dr of the crude product was 92:8 as determined via the NMR analysis) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.26 (m, 3H, ArH), 7.25-6.97 (m, 5H, ArH), 6.81-6.70 (m, 2H, ArH), [6.14 (q, J = 1.3 Hz, 0.92H), 6.12 (q, J = 1.2 Hz, 0.08H), 1H, =CH], 3.27-3.04 (m, 2H, CH₂), [2.42 (s, 0.08H), 2.30 (s, 0.83H), 1H, OH], 2.26-2.14 (m, 1H, CH), 1.90-1.82 (m, 3H, CH₃); IR (neat) ν (cm⁻¹) 3418, 3086, 3061, 3028, 2948, 2916, 2855, 1694, 1625, 1602, 1496, 1448, 1434, 1374, 1304, 1243, 1211, 1162, 1088, 1065, 1014; MS (70 ev, EI) m/z (%) 278 (M⁺, 57.11), 187 (100); Elemental analysis calcd (%) for C₁₉H₁₈O₂: C, 81.99, H, 6.52; Found: C, 81.69; H, 6.47.

(5) 5-(4-(Benzyloxy)butyl)-4-hydroxy-3-methyl-4-phenylcyclopent-2-enone (5bd)

(mdऽ-9-110)
The reaction of 1b (128.0 mg, 1.2 mmol), 2d (244.3 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.3 mg, 0.2 mmol), and Cs₂CO₃ (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 11.5 h afforded 5bd (0.2337 g, 65%, purity= 98%, dr = 99:1) (petroleum ether (60 °C – 90 °C)/ethyl acetate = 10/1 (440 mL) to 5/1 (420 mL + 600 mL) to 3/1 (400 mL)) (the dr of the crude product was 96:4 as determined via the NMR analysis) as a liquid:

ΔH NMR (300 MHz, CDCl₃) δ 7.43-6.99 (m, 10H, ArH), 6.11 (q, J = 1.4 Hz, 1H, =CH), 4.42 (s, 2H, CH₂), 3.49-3.16 (m, 3H, OH + CH₂), 2.65 (dd, J₁ = 9.0 Hz, J₂ = 5.1 Hz, 1H, CH), 1.87 (d, J = 1.2 Hz, 3H, CH₃), 1.63-1.19 (m, 5H, CH₂ × 2 + one proton from CH₂), 1.01-0.82 (m, 1H, one proton from CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 206.5, 176.8, 139.3, 138.2, 129.6, 128.2, 128.1, 127.6, 127.4, 127.36, 125.5, 85.1, 72.6, 69.9, 60.9, 25.4, 23.7, 13.6; IR (neat) ν (cm⁻¹) 3439, 3086, 3061, 3029, 2938, 2862, 2793, 1694, 1626, 1601, 1492, 1448, 1372, 1301, 1240, 1162, 1097, 1068, 1028; MS (70 ev, EI) m/z (%) 350 (M⁺, 3.28), 91 (100); HRMS calcd for C₂₃H₂₆O₃ (M⁺): 350.1882, found: 350.1878.

(6) (4R*,5S*)-4-(4-Phenylphenyl)-4-hydroxy-3-methyl-5-pentylcyclopent-2-enone (4R*,5S*-5ca) (mdk-8-068-1) and (4R*,5R*)-4-(4-Phenylphenyl)-4-hydroxy-3-methyl-5-pentylcyclopent-2-enone (4R*,5R*-5ca) (mdk-8-068-2)
The reaction of 1c (225.5 mg, 1.2 mmol), 2a (152.9 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs$_2$CO$_3$ (65.5 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 8.5 h afforded impure $4R^*,5S^*-5ca$ (18.4 mg) and pure $4R^*,5R^*-5ca$ (241.0 mg, 72%) (petroleum ether (30 °C ~ 60 °C)/ethyl acetate = 10/1 (440 mL + 400 mL) to 5/1 (480 mL + 200 mL) to 3/1 (400 mL)) (the dr of the crude product was 94:6 as determined via the NMR analysis). Further purification of the impure $4R^*,5S^*-5ca$ by column chromatography on silica gel afforded pure $4R^*,5S^*-5ca$ (8.9 mg, 3%) (DCM (400 mL)).

$4R^*,5S^*-5ca$, minor, the less polar isomer, liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.62-7.57 (m, 4H, ArH), 7.49-7.34 (m, 5H, ArH), 6.10 (q, $J = 1.3$ Hz, 1H, –CH), 2.61 (dd, $J_1 = 8.7$ Hz, $J_2 = 5.7$ Hz, 1H, CH), 2.01 (s, 1H, OH), 1.92 (d, $J = 1.5$ Hz, 3H, CH$_3$), 1.83-1.59 (m, 2H, CH$_2$), 1.51-1.32 (m, 2H, CH$_2$), 1.31-1.14 (m, 4H, CH$_2$ × 2), 0.81 (t, $J = 6.9$ Hz, 3H, CH$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 208.6, 177.2, 142.4, 140.4, 140.1, 130.5, 128.8, 127.4, 127.3, 127.0, 125.0, 82.8, 59.7, 31.8, 27.3, 26.8, 22.3, 14.1, 14.0; IR (neat) ν (cm$^{-1}$) 3444, 3057, 3029, 2954, 2927, 2857, 1694, 1626, 1600, 1486, 1435, 1405, 1374, 1298, 1263, 1213, 1195, 1180, 1133, 1076, 1007; MS (70 ev, EI) m/z (%) 334 (M$^+$, 14.35), 263 (100); HRMS calcd for C$_{23}$H$_{26}$O$_2$ (M$^+$): 334.1933, found: 334.1929.

$4R^*,5R^*-5ca$, major, the more polar isomer, liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.64-7.51 (m, 4H, ArH), 7.50-7.19 (m, 5H, ArH), 6.17 (q, $J = 1.3$ Hz, 1H, –CH), 2.66 (s, 1H, OH), 2.63 (dd, $J_1 = 9.0$ Hz, $J_2 = 5.1$ Hz, 1H, CH), 1.95 (d, $J = 1.5$ Hz, 3H,
CH₃), 1.64-1.49 (m, 1H, one proton from CH₂), 1.41-1.19 (m, 2H, CH₂), 1.19-0.83 (m, 5H, 2 × CH₂ + one proton from CH₂), 0.74 (t, J = 7.1 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 206.9, 177.0, 140.3, 140.1, 138.3, 129.8, 128.7, 127.3, 126.9, 126.7, 126.1, 85.3, 61.4, 31.6, 27.1, 25.9, 22.0, 13.82, 13.80; IR (neat) ν (cm⁻¹) 3448, 3057, 3029, 2953, 2929, 2858, 1691, 1625, 1560, 1486, 1435, 1404, 1374, 1317, 1301, 1267, 1232, 1207, 1196, 1180, 1164, 1132, 1076, 1007; MS (70 ev, EI) m/z (%) 334 (M⁺, 18.23), 263 (100); HRMS calcd for C₂₃H₂₆O₂ (M⁺): 334.1933, found: 334.1929.

(7) 4-Hydroxy-3-methyl-5-propyl-4-((p-tolyl)cyclopent-2-enone (5db) (mdk-8-077)

The reaction of 1d (145.0 mg, 1.2 mmol), 2b (124.4 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (39.8 mg, 0.2 mmol), and Cs₂CO₃ (65.4 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 32.5 h afforded 5db (0.1612 g, 65%, purity 98%, dr = 99:1) (petroleum ether (30 °C ~ 60 °C)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 + 120 mL) to 3/1 (400 mL)) (the dr of the crude product was 94:6 as determined via the NMR analysis) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.38-6.77 (m, 4H, ArH), 6.11 (q, J = 1.3 Hz, 1H, =CH), 3.19 (s, 1H, OH), 2.63 (dd, J₁ = 8.7 Hz, J₂ = 5.4 Hz, 1H, CH), 2.34 (s, 3H, CH₃), 1.91 (d, J = 1.2 Hz, 3H, CH₃), 1.54-1.15 (m, 3H, CH₂ + one proton from CH₂), 0.93-0.76 (m, 1H, one proton from CH₂), 0.71 (t, J = 7.2 Hz, 3H, CH₃); ¹³C NMR (75 MHz,
CDCl$_3$) $\delta$ 206.8, 176.8, 137.1, 136.3, 129.7, 128.9, 125.4, 85.4, 61.0, 28.0, 20.9, 20.8, 14.0, 13.7; IR (neat) ν (cm$^{-1}$) 3443, 3051, 3024, 2958, 2932, 2871, 1693, 1625, 1511, 1465, 1434, 1409, 1375, 1316, 1300, 1286, 1248, 1220, 1193, 1170, 1131, 1111, 1078, 1038, 1021, 1008; MS (70 ev, EI) m/z (%) 244 (M$^+$, 16.88), 201 (100); HRMS calcd for C$_{16}$H$_{20}$O$_2$ (M$^+$): 244.1463, found: 244.1472.

(8) 5-Benzyl-4-hydroxy-3-methyl-4-(naphth-2-yl)cyclopent-2-enone  (5ec)

(mdk-8-106)

![Reaction schematic](image)

The reaction of 1e (191.5 mg, 1.2 mmol), 2c (173.0 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs$_2$CO$_3$ (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 13 h afforded 5ec (0.1866 g, 57%, dr = 91:9) (petroleum ether (30 °C ~ 60 °C)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL + 180 mL) to 3/1 (400 mL + 200 mL)) (the dr of the crude product was 92:8 as determined via the NMR analysis) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.92-7.59 (m, 4H, ArH), 7.59-7.40 (m, 2H, ArH), 7.20-6.90 (m, 4H, ArH), 6.81-6.57 (m, 2H, ArH), [6.20 (q, $J$ = 1.3 Hz, 0.91H), 6.17 (q, $J$ = 1.3 Hz, 0.09H), 1H, $=CH$], 3.30-3.06 (m, 2H, CH$_2$), [2.67 (s, 0.08H), 2.57 (s, 0.89H), 1H, OH], 2.22 (dd, $J_1$ = 14.4 Hz, $J_2$= 9.9 Hz, 1H, CH), 1.88 (d, $J$ = 1.2 Hz, 3H, CH$_3$); IR (neat) ν (cm$^{-1}$) 3432, 3084, 3059, 3027, 2978, 2947, 2918, 2853, 1691, 1625,
1601, 1507, 1497, 1454, 1434, 1373, 1304, 1271, 1211, 1196, 1161, 1115, 1077, 1034, 1019; MS (70 ev, EI) m/z (%) 328 (M+, 14.99), 237 (100); Elemental analysis calcd (%) for C23H20O2: C, 84.12, H, 6.14; Found: C, 83.69; H, 6.25.

(9) (4R*,5S*)-4-Hydroxy-5-isopropyl-3-methyl-4-(naphthalen-2-yl)cyclopent-2-enone (4R*,5S*-5ee) (mdk-8-115-1) and (4R*,5R*)-4-Hydroxy-5-isopropyl-3-methyl-4-(naphthalen-2-yl)cyclopent-2-enone (4R*,5R*-5ee) (mdk-8-115-2)

The reaction of 1e (191.6 mg, 1.2 mmol), 2e (124.5 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (39.9 mg, 0.2 mmol), and Cs₂CO₃ (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 22.5 h afforded 4R*,5S*-5ee (3.8 mg, 1%) and 4R*,5R*-5ee (156.3 mg, 55%) (petroleum ether (30 °C–60 °C)/ethyl acetate = 60/1 (400 mL × 2) to 10/1 (440 mL) to 5/1 (480 mL × 3) to 3/1 (400 mL)) (the dr of the crude product was 95:5 as determined via the NMR analysis).

4R*,5S*-5ee, minor, the less polar isomer, liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.95-7.91 (m, 1H, ArH), 7.89-7.79 (m, 3H, ArH), 7.54-7.46 (m, 2H, ArH), 7.28 (dd, J₁ = 8.7 Hz, J₂ = 2.1 Hz, 1H, ArH), 6.14 (q, J = 1.3 Hz, 1H, =CH), 2.60 (d, J = 4.5 Hz, 1H, CH), 2.35-2.21 (m, 2H, one proton from CH₂ + OH), 1.89 (d, J = 1.5 Hz, 3H, CH₃), 1.11 (d, J = 6.6 Hz, 3H, CH₃), 1.06 (d, J = 6.6 Hz, 3H, CH₃); ¹³C NMR (75
MHZ, CDCl3) δ 208.0, 177.1, 141.3, 133.1, 132.5, 131.7, 128.7, 128.1, 127.6, 126.5, 126.2, 123.3, 122.6, 83.6, 64.5, 27.8, 22.0, 19.8, 13.8; IR (neat) ν (cm⁻¹) 3445, 3057, 2957, 2929, 2872, 1688, 1628, 1599, 1507, 1466, 1435, 1385, 1368, 1296, 1272, 1231, 1199, 1160, 1132, 1078, 1020; MS (70 ev, EI) m/z (%) 280 (M⁺, 10.47), 237 (100); HRMS calcd for C₁₉H₂₀O₂ (M⁺): 280.1463, found: 280.1466.

4R*,5R*-5ee, major, the more polar isomer, solid, m. p. 147~149 °C (ethyl acetate): ¹H NMR (300 MHz, CDCl3) δ 8.12-7.67 (m, 4H, ArH), 7.60-6.90 (m, 3H, ArH), 6.11 (q, J = 1.3 Hz, 1H, =CH), 2.56 (s, 1H, OH), 2.52 (d, J = 8.7 Hz, 1H, CH), 1.87 (d, J = 1.2 Hz, 3H, CH₃), 1.84-1.73 (m, 1H, CH), 1.04 (d, J = 6.6 Hz, 3H, CH₃), 0.73 (d, J = 6.6 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl3) δ 205.7, 175.5, 137.3, 133.0, 132.5, 130.2, 128.2, 127.8, 127.5, 126.3, 126.2, 125.1, 123.7, 85.3, 67.4, 26.5, 21.8, 20.5, 13.3; IR (neat) ν (cm⁻¹) 3453, 3057, 2957, 2920, 2870, 1687, 1629, 1599, 1507, 1470, 1435, 1386, 1373, 1301, 1270, 1254, 1234, 1195, 1162, 1123, 1094, 1041, 1030; MS (70 ev, EI) m/z (%) 280 (M⁺, 7.79), 237 (100); Elemental analysis calcd (%) for C₁₉H₂₀O₂: C, 81.40, H, 7.19; Found: C, 81.42; H, 7.24.

(10) 4-Hydroxy-3-methyl-4-phenylspiro[4.5]dec-2-en-1-one (5bf) (mdk-9-010-4)

The reaction of 1b (126.9 mg, 1.2 mmol), 2f (150.7 mg, 1 mmol),
1-ethyl-3-methylimidazolium tetrafluoroborate (40.0 mg, 0.2 mmol), and Cs$_2$CO$_3$ (65.0 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 32 h, then at 50 °C for 14.5 h afforded (E)-3bf (0.0094 g, 4%), 4bf (0.0026 g, 1%), (Z)-3bf (0.0097 g, 4%), and 5bf (0.1281 g, 50%) (in the order of polarity in silica gel column) (petroleum ether (60 °C ~ 90 °C, redistillation)/ethyl acetate = 40/1 (400 mL) to 30/1 (480 mL × 2 + 300 mL) to 10/1 (300 mL) to 5/1 (420 mL) to 3/1 (400 mL)).

(E)-3bf, the least polar isomer, liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.83-7.77 (m, 2H, ArH), 7.64-7.57 (m, 1H, ArH), 7.53-7.45 (m, 2H, ArH), 6.51 (q, $J = 1.5$ Hz, 1H, =CH), 2.45-2.31 (m, 4H, CH$_3$ + one proton from cyclohexyl group), 1.91-1.73 (m, 4H, from cyclohexyl group), 1.71-1.60 (m, 1H, from cyclohexyl group), 1.42-1.15 (m, 5H, from cyclohexyl group); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 204.6, 198.5, 149.3, 136.1, 133.1, 130.5, 129.7, 128.5, 51.8, 28.1, 25.8, 25.5, 15.8; IR (neat) $\nu$ (cm$^{-1}$) 2929, 2853, 1688, 1660, 1612, 1596, 1448, 1263, 1156, 1143, 1001; MS (70 ev, EI) m/z (%) 256 (M$^+$, 8.01), 83 (100); HRMS calcd for C$_{17}$H$_{20}$O$_2$ (M$^+$): 256.1463, found: 256.1465.

4bf, the less polar isomer, liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87-7.80 (m, 2H, ArH), 7.57-7.50 (m, 1H, ArH), 7.48-7.40 (m, 2H, ArH), 5.89 (d, $J = 0.9$ Hz, 1H, one proton from =CH$_2$), 5.77 (s, 1H, one proton from =CH$_2$), 3.68 (d, $J = 0.3$ Hz, 2H, CH$_2$), 2.53-2.41 (m, 1H, from cyclohexyl group), 1.98-1.62 (m, 5H, from cyclohexyl group), 1.46-1.16 (m, 5H, from cyclohexyl group); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 210.9, 197.4, 142.3, 137.4, 132.2, 129.8, 128.7, 128.1, 50.7, 44.5, 28.4, 25.8, 25.6; IR (neat) $\nu$ (cm$^{-1}$) 2929, 2853, 1707, 1656, 1598, 1448, 1339, 1317, 1213, 1143, 1068; MS (70 ev, EI) m/z (%) 256 (M$^+$, 4.98), 83 (100); HRMS calcd for C$_{17}$H$_{20}$O$_2$ (M$^+$):
(Z)-3bf, the more polar isomer, liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.89-7.81 (m, 2H, ArH), 7.59-7.50 (m, 1H, ArH), 7.49-7.41 (m, 2H, ArH), 6.44 (q, $J = 1.5$ Hz, 1H, =CH), 2.42-2.29 (m, 1H, from cyclohexyl group), 2.12 (d, $J = 1.5$ Hz, 3H, CH$_3$), 1.88-1.59 (m, 5H, from cyclohexyl group), 1.33-1.09 (m, 5H, from cyclohexyl group); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 201.0, 199.4, 154.1, 134.4, 133.2, 128.7, 128.3, 125.3, 50.1, 27.9, 25.7, 25.5, 21.7; IR (neat) ν (cm$^{-1}$) 2929, 2854, 1675, 1615, 1583, 1449, 1372, 1355, 1311, 1246, 1231, 1161, 1093, 1071; MS (70 ev, EI) m/z (%) 256 (M$^+$, 7.51), 174 (100); HRMS calcd for C$_{17}$H$_{20}$O$_2$ (M$^+$): 256.1463, found: 256.1466.

5bf, the most polar isomer, liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.72-6.67 (m, 5H, ArH), 6.13 (q, $J = 1.4$ Hz, 1H, =CH), 2.51 (brs, 1H, OH), 1.92 (d, $J = 1.5$ Hz, 3H, CH$_3$), 1.85-1.40 (m, 6H, from cyclohexyl group), 1.38-1.06 (m, 3H, from cyclohexyl group), 0.91-0.78 (m, 1H, from cyclohexyl group); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 210.5, 173.9, 140.6, 129.6, 128.0, 127.4, 125.9, 87.5, 56.3, 32.9, 30.0, 25.4, 22.4, 21.6, 14.1; IR (neat) ν (cm$^{-1}$) 3462, 3085, 3058, 3027, 2933, 2861, 1686, 1631, 1600, 1490, 1449, 1374, 1361, 1310, 1266, 1226, 1194, 1147, 1127, 1105, 1069, 1031; MS (70 ev, EI) m/z (%) 256 (M$^+$, 77.01), 151 (100); HRMS calcd for C$_{17}$H$_{20}$O$_2$ (M$^+$): 256.1463, found: 256.1459.

(11) 9-Hydroxy-8-vinylideneicosan-7-one (6fa) (mdk-10-039)

The reaction of 1f (221.0 mg, 1.2 mmol), 2a (152.3 mg, 1 mmol),
1-ethyl-3-methylimidazolium tetrafluoroborate (40.3 mg, 0.2 mmol), and Cs$_2$CO$_3$ (65.1 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 22 h afforded 6fa (0.0192 g, 6%) (petroleum ether (60 °C ~ 90 °C)/ethyl acetate = 15/1 (300 mL) to 10/1 (300 mL)) (58% of 1f and 39% of 2a were recovered, respectively, as determined via NMR analysis) as a liquid: $^1$H NMR (300 MHz, CDCl$_3$) δ 5.32 (d, $J$ = 1.8 Hz, 2H, =CH$_2$), 4.49-4.38 (m, 1H, CH), 3.12 (d, $J$ = 5.4 Hz, 1H, OH), 2.65 (dd, $J_1$ = 7.8 Hz, $J_2$ = 6.9 Hz, 2H, CH$_2$), 1.65-1.52 (m, 4H, CH$_2$ × 2), 1.36-1.19 (m, 24H, CH$_2$ × 12), 0.88 (t, $J$ = 6.8 Hz, 6H, CH$_3$ × 2); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 214.5, 203.2, 110.7, 81.2, 68.8, 39.8, 35.1, 31.9, 31.5, 29.7, 29.63, 29.62, 29.58, 29.4, 29.3, 28.8, 25.8, 24.7, 22.7, 22.5, 14.1, 14.0; IR (neat) ν (cm$^{-1}$) 3472, 2955, 2924, 2854, 1958, 1931, 1673, 1466, 1405, 1378, 1278, 1234, 1177, 1080, 1019; MS (70 ev, El) m/z (%) 336 (M$^+$, 1.87), 43 (100); HRMS calcd for C$_{22}$H$_{40}$O$_2$ (M$^+$): 336.3028, found: 336.3026.

4. Mechanistic studies

(1) Preparation of (E)-3ba and (Z)-3ba (mdk-10-022)

\[ \text{To a dry Schlenk flask was added Cs}_2\text{CO}_3 (97.8 mg, 0.3 mmol) under N}_2. \text{ Then 1-ethyl-3-methylimidazolium tetrafluoroborate (60.9 mg, 0.3 mmol) and toluene (7.5 mL) were added sequentially under N}_2. \text{ The resulting mixture was stirred at rt. After 10 min, the mixture was cooled to 20 °C, 1b (636.4 mg, 6 mmol)/toluene (4.5 mL) } \]
and 2a (456.0 mg, 3 mmol)/toluene (3 mL) were added sequentially. Then the resulting mixture was stirred at 20 °C. After 22.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl acetate (20 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (60 °C ~ 90 °C)/ethyl acetate = 80/1 (400 mL × 4) to 40/1 (400 mL × 2) to 20/1 (420 mL × 2)) afforded (E)-3ba (0.2137 g, 27%, purity = 98%) and (Z)-3ba (0.0265 g, 3%, purity = 80%)

(E)-3ba, the less polar isomer, liquid: ¹H NMR (600 MHz, CDCl₃) δ 7.83-7.76 (m, 2H, ArH), 7.62-7.57 (m, 1H, ArH), 7.51-7.45 (m, 2H, ArH), 6.45 (q, J = 1.2 Hz, 1H, =CH), 2.51 (t, J = 7.5 Hz, 2H, CH₂), 2.36 (d, J = 1.2 Hz, 3H, CH₃), 1.64-1.57 (m, 2H, CH₂), 1.34-1.23 (m, 6H, CH₂ × 3), 0.88 (t, J = 6.9 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 201.7, 198.4, 148.8, 135.9, 133.1, 130.8, 129.7, 128.5, 44.8, 31.5, 28.7, 23.7, 22.4, 15.7, 14.0; IR (neat) ν (cm⁻¹) 3061, 3027, 2956, 2929, 2857, 1694, 1661, 1615, 1597, 1448, 1405, 1377, 1361, 1316, 1265, 1209, 1179, 1155, 1130, 1075, 1031, 1003; MS (70 ev, EI) m/z (%) 258 (M⁺, 38.90), 105 (100); HRMS calcd for C₁₇H₂₂O₂ (M⁺): 258.1620, found: 258.1621.

(Z)-3ba, the more polar isomer, liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.90-7.83 (m, 2H, ArH), 7.60-7.52 (m, 1H, ArH), 7.50-7.40 (m, 2H, ArH), 6.37 (q, J = 1.5 Hz, 1H, =CH), 2.44 (t, J = 7.4 Hz, 2H, CH₂), 2.12 (d, J = 1.5 Hz, 3H, CH₃), 1.56-1.43 (m, 2H, CH₂), 1.28-1.13 (m, 6H, CH₂ × 3), 0.84 (t, J = 6.8 Hz, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 199.4, 198.5, 153.7, 134.4, 133.3, 128.7, 128.3, 126.1, 42.9, 31.5, 28.7, 23.6, 22.4, 21.6, 14.0; IR (neat) ν (cm⁻¹) 2955, 2929, 2857, 1674, 1615, 1583,
1449, 1405, 1370, 1239, 1159, 1123, 1076; MS (70 ev, El) m/z (%) 258 (M⁺, 6.39), 105 (100); HRMS calcd for C₁₇H₂₂O₂ (M⁺): 258.1620, found: 258.1623.

(2) Reactions of (E)-3ba and (Z)-3ba in the presence of Cs₂CO₃ respectively

To a dry Schlenk tube was added Cs₂CO₃ (13.2 mg, 0.04 mmol) under N₂. Then dioxane (0.75 mL) and CH₂Cl₂ (0.25 mL) were added sequentially under N₂. The mixture was cooled to -10 °C, (E)-3ba (51.5 mg, 0.2 mmol, purity = 98%), CH₂Cl₂ (0.25 mL), and dioxane (0.75 mL) were added sequentially. The resulting mixture was stirred at -10 °C. After 12 h, the reaction mixture was filtrated through a short column of silica gel (eluent: ethyl acetate (15 mL×3)), evaporated, and analyzed by NMR with 7 μL of CH₂Br₂ as the internal standard. As a result, 93% of (E)-3ba was recovered and 5ba was not formed.

Following the procedure for eq (1), the reaction of (Z)-3ba (26.0 mg, 0.08 mmol, purity = 80%) and Cs₂CO₃ (5.3 mg, 0.016 mmol) in dioxane (0.6 mL) and CH₂Cl₂ (0.2 mL) at -10 °C for 9 h afforded 81% recovery of (Z)-3ba without the formation of 5ba as determined by NMR analysis.
Reactions of (E)-3ba and (Z)-3ba in the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate and Cs₂CO₃ respectively

To a dry Schlenk tube was added Cs₂CO₃ (13.1 mg, 0.04 mmol) under N₂. Then 1-ethyl-3-methylimidazolium tetrafluoroborate (8.0 mg, 0.04 mmol), dioxane (0.75 mL), and CH₂Cl₂ (0.25 mL) were added sequentially under N₂. The resulting mixture was stirred at rt. After 10 min, the mixture was cooled to -10 °C, (E)-3ba (52.3 mg, 0.2 mmol, purity = 98%), CH₂Cl₂ (0.25 mL), and dioxane (0.75 mL) were added sequentially. The resulting mixture was stirred at -10 °C. After 12 h, the reaction mixture was filtrated through a short column of silica gel (eluent: ethyl acetate (15 mL×3)), evaporated, and analyzed by NMR with 7 μL of CH₂Br₂ as the internal standard. As a result, 95% of (E)-3ba was recovered and the formation of 5ba was not observed.

Following the procedure for eq (3), the reaction of (Z)-3ba (20.8 mg, 0.064 mmol, purity = 80%), 1-ethyl-3-methylimidazolium tetrafluoroborate (2.7 mg, 0.0128 mmol), Cs₂CO₃ (4.3 mg, 0.0128 mmol) in dioxane (0.48 mL), and CH₂Cl₂ (0.16 mL) at -10 °C for 13 h afforded 34% of 5ba, 3% of 4ba, and 41% recovery of (Z)-3ba as
determined by NMR analysis.

5. Preparation of \((E)-3\text{aa}, \, 4\text{aa}, \, \text{and} \, (Z)-3\text{aa} \, (\text{mdk-}10-084)\)

![Chemical Reaction Diagram]

To a dry Schlenk flask was added Cs\(_2\)CO\(_3\) (12.9 mg, 0.04 mmol) under N\(_2\). Then 1-butyl-3-methylimidazolium tetrafluoroborate (9.1 mg, 0.04 mmol) and toluene (1 mL) were added sequentially under N\(_2\). The resulting mixture was stirred at 20 °C. After 10 min, 1\(a\) (151.6 mg, 0.8 mmol), 2\(a\) (60.5 mg, 0.4 mmol), and toluene (1 mL) were added sequentially. Then the resulting mixture was stirred at 20 °C. After 22.5 h, the reaction was complete as monitored by TLC. Filtration through a short column of silica gel (eluent: ethyl ether (10 mL×3)), evaporation, and column chromatography on silica gel (petroleum ether (60 °C ~ 90 °C, redistillation)/ethyl acetate = 80/1 (400 mL × 2) to 60/1 (420 mL) to 40/1 (400 mL) to 20/1 (420 mL)) afforded \((E)-3\text{aa} \, (0.0442 g, 33\%), \, 4\text{aa} \, (0.0048 g, 3\%, \, \text{purity} = 83\%), \, \text{and} \, (Z)-3\text{aa} \, (0.0042 g, 3\%, \, \text{purity} = 66\%) \, \text{(in the order of polarity in silica gel column)}\)

\((E)-3\text{aa}, \, \text{the less polar isomer, liquid:} \, ^1\text{H NMR (600 MHz, CDCl}_3\text{)} \, \delta \, 7.69-7.65 \, (\text{m, 2H, ArH}), \, 7.64-7.61 \, (\text{m, 2H, ArH}), \, 6.42 \, (\text{q,} \, J = 1.2 \, \text{Hz, 1H, =CH}), \, 2.51 \, (\text{t,} \, J = 7.5 \, \text{Hz, 2H, CH}_2\)), \, 2.34 \, (\text{d,} \, J = 1.2 \, \text{Hz, 3H, CH}_3\)), \, 1.64-1.57 \, (\text{m, 2H, CH}_2\)), \, 1.34-1.24 \, (\text{m, 6H, CH}_2 \times 3) \), \, 0.88 \, (\text{t,} \, J = 6.9 \, \text{Hz, 3H, CH}_3\)); \, ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)} \, \delta \, 201.6, \, \ldots
197.4, 148.4, 134.7, 131.9, 131.1, 128.3, 44.8, 31.5, 28.8, 23.7, 22.4, 15.6, 14.0; IR (neat) ν (cm\(^{-1}\)) 2955, 2929, 2857, 1694, 1667, 1661, 1615, 1585, 1567, 1481, 1464, 1456, 1396, 1378, 1304, 1261, 1177, 1155, 1130, 1109, 1069, 1008; MS (70 ev, EI) m/z (%) 338 (M\(^+\)(\(^{81}\)Br), 12.47), 336 (M\(^+\)(\(^{79}\)Br), 12.56), 113 (100); HRMS calcd for C\(_{17}\)H\(_{21}\)\(^{79}\)BrO\(_2\) (M\(^+\)): 336.0725, found: 336.0718.

4aa, the “middle” isomer, liquid: \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.74-7.68 (m, 2H, ArH), 7.62-7.56 (m, 2H, ArH), 5.90 (s, 1H, one proton from =CH\(_2\)), 5.72 (s, 1H, one proton from =CH\(_2\)), 3.63 (s, 2H, CH\(_2\)), 2.51 (t, \(J = 7.5\) Hz, 2H, CH\(_2\)), 1.64-1.51 (m, 2H, CH\(_2\)), 1.36-1.19 (m, 6H, CH\(_2\) × 3), 0.87 (t, \(J = 6.8\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 207.9, 196.3, 142.0, 136.0, 131.5, 131.3, 128.6, 127.3, 46.5, 42.7, 31.6, 28.8, 23.6, 22.5, 14.0; IR (neat) ν (cm\(^{-1}\)) 2955, 2929, 2857, 1715, 1660, 1585, 1483, 1466, 1397, 1338, 1215, 1174, 1127, 1069, 1012; MS (70 ev, EI) m/z (%) 338 (M\(^+\)(\(^{81}\)Br), 15.50), 336 (M\(^+\)(\(^{79}\)Br), 14.57), 43 (100); HRMS calcd for C\(_{17}\)H\(_{21}\)\(^{79}\)BrO\(_2\) (M\(^+\)): 336.0725, found: 336.0729.

(Z)-3aa, the more polar isomer, liquid: \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.76-7.68 (m, 2H, ArH), 7.63-7.54 (m, 2H, ArH), 6.37 (q, \(J = 1.6\) Hz, 1H, =CH), 2.44 (t, \(J = 7.4\) Hz, 2H, CH\(_2\)), 2.10 (d, \(J = 1.2\) Hz, 3H, CH\(_3\)), 1.56-1.44 (m, 2H, CH\(_2\)), 1.35-1.15 (m, 6H, CH\(_2\) × 3), 0.85 (t, \(J = 6.8\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ 198.5, 198.3, 153.1, 133.3, 132.1, 129.7, 128.4, 126.3, 42.9, 31.5, 28.8, 23.5, 22.4, 21.5, 14.0; IR (neat) ν (cm\(^{-1}\)) 2954, 2928, 2857, 1674, 1616, 1585, 1483, 1441, 1394, 1370, 1244, 1158, 1070, 1010; MS (70 ev, EI) m/z (%) 338 (M\(^+\)(\(^{81}\)Br), 9.91), 336 (M\(^+\)(\(^{79}\)Br), 9.01), 183 (100); HRMS calcd for C\(_{17}\)H\(_{21}\)\(^{79}\)BrO\(_2\) (M\(^+\)): 336.0725, found: 336.0733.
6. The deuterium-labeling experiment (mdk-10-125)

The reaction of 1b-D* (129.0 mg, 1.2 mmol, >99% D), 2a (152.5 mg, 1 mmol), 1-ethyl-3-methylimidazolium tetrafluoroborate (40.6 mg, 0.2 mmol), and Cs₂CO₃ (65.3 mg, 0.2 mmol) in dioxane (7.5 mL) and dichloromethane (2.5 mL) at -10 °C for 22 h afforded 5ba-D (184.5 mg, 71%, dr = 99:1) (petroleum ether (60 °C ~ 90 °C, redistillation)/ethyl acetate = 10/1 (440 mL) to 5/1 (480 mL)) (the dr of the crude product was 96:4 as determined via the NMR analysis) as a liquid: ¹H NMR (300 MHz, CDCl₃) δ 7.50-6.92 (m, 5H, ArH), 1.59-1.44 (m, 1H, one proton from CH₂), 1.39-0.90 (m, 6H, CH₂ × 3), 0.90-0.69 (m, 4H, one proton from CH₂ + CH₃); the following signal is discernible for 5ba: [6.14 (q, J = 1.5 Hz, 0.80H), 6.07 (q, J = 1.2 Hz, 0.01H), 0.81H, =CH], 2.81 (s, 0.88H, OH), 2.60 (dd, J₁ = 8.9 Hz, J₂ = 5.3 Hz, 0.84H, CH), 1.93-1.86 (m, 2.66H, CH₃); IR (neat) ν (cm⁻¹) 3432, 3087, 3060, 3028, 2955, 2931, 2860, 1694, 1625, 1602, 1492, 1448, 1375, 1317, 1247, 1233, 1205, 1176, 1127, 1099, 1067; MS (70 ev, EI) m/z (%) 259 (M⁺(D), 10.08), 258 (M⁺, 12.72), 187 (100); HRMS calcd for C₁₇H₂₁DO₂ (M⁺): 259.1683, found: 259.1681.
References:


