

Supporting Information

**Rhodium-Catalyzed Reformatsky Type Reaction**

Organic Letters

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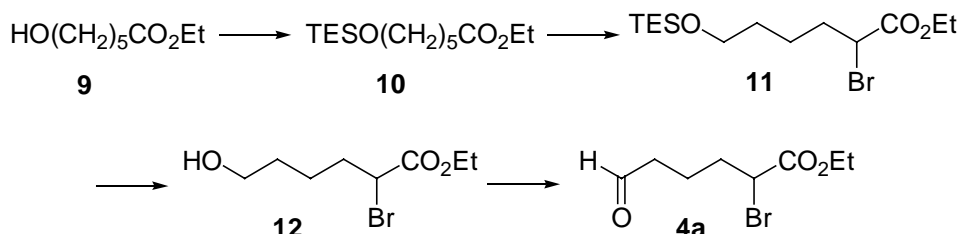
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**General Experimental Procedures.** IR spectra were recorded as thin films.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained for a solution in  $\text{CDCl}_3$ , and chemical shifts are reported on the  $\delta$ -scale from TMS as an internal standard.  $^{13}\text{C}$  multiplicities were determined with the aid of an APT sequence, separating methylene and quaternary carbons = up, from methyl and methine carbons = down.

**General procedure for the intermolecular Reformatsky type reaction:** To a stirred solution of  $\text{RhCl}(\text{PPh}_3)_3$  (5 mol%) in THF (0.2M in an  $\alpha$ -halo ester) at  $0^\circ\text{C}$  were added  $\alpha$ -halo ester **1**, a carbonyl compound **2**, and a ca. 1.0 M hexane solution of  $\text{Et}_2\text{Zn}$  (2.2 mol eq.). After stirring for 5 minutes at  $0^\circ\text{C}$ , saturated aqueous  $\text{NaHCO}_3$  was added. The reaction was filtered, and the filtrate was partitioned between  $\text{Et}_2\text{O}$  and brine. The organic extract was dried ( $\text{Na}_2\text{SO}_4$ ), and the residue was purified by column chromatography on silica gel. Spectroscopic data of all the products prepared in this manner were identical

with those reported.

Preparation of ethyl 2-bromo-6-oxohexanoate **4a** was achieved in 4 steps from ethyl 6-hydroxyhexanoate **9**.

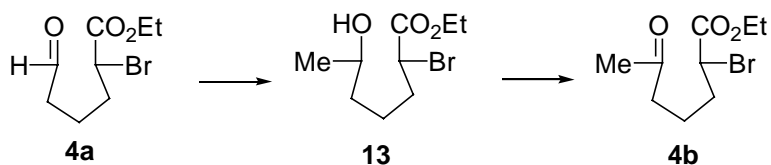


**Ethyl 6-triethylsilyloxyhexanoate 10:** To a stirred solution of ethyl 6-hydroxyhexanoate **9** (5 g, 31.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) at 0°C were added triethylamine (5.2 mL, 37.5 mmol) and chlorotriethylsilane (5.8 mL, 34.3 mmol). After stirring for 2 h at rt, the mixture was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and saturated aqueous NH<sub>4</sub>Cl and brine. The organic extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The residue was purified by bulb-to-bulb distillation (140°C, 0.5 mmHg) to provide triethylsilyl ether **10** (8.46 g, 99%) as a colorless oil. IR 2870, 2385, 1739, 1098, 745 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 0.59 (6H, q, *J* = 7.9 Hz), 0.95 (9H, t, *J* = 7.9 Hz), 1.25 (3H, t, *J* = 7.1 Hz), 1.37 – 1.70 (6H, m), 2.30 (2H, t, *J* = 7.5 Hz), 3.60 (2H, t, *J* = 6.5 Hz), 4.12 (2H, q, *J* = 7.1 Hz); <sup>13</sup>C NMR δ up: 4.4, 24.8, 25.4, 32.5, 34.3, 60.1, 62.6; down: 6.7, 14.2; HRMS (CI) calcd for C<sub>14</sub>H<sub>31</sub>O<sub>3</sub>Si (M + 1)<sup>+</sup> 275.2042, found 275.2046.

**Ethyl 2-bromo-6-hydroxyhexanoate 12:** To a stirred solution of LDA (prepared from 0.66 mL (4.7 mmol) of diisopropylamine and 3.1 mL (4.7 mmol) of 1.50M hexane solution of *n*-butyllithium in 9 mL of THF) at -78°C was added a solution of chlorotrimethylsilane (0.81 mL, 6.4 mmol) and TES-ether **10** (1 g, 3.65 mmol) in THF (9 mL). The mixture was stirred for 1 h at -78°C, after which NBS (780 mg, 4.4 mmol) was added in one portion. This mixture was stirred for 1 h at 0°C and saturated aqueous NaHCO<sub>3</sub> was added. After concentration, the residual mixture was partitioned between EtOAc and brine. The combined organic extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to provide the crude bromide **11**, which was immediately diluted with EtOH (17 mL) and stirred at 0°C. To this solution was added *p*-TsOH·H<sub>2</sub>O (64 mg, 0.34 mmol) and stirring was continued for 2 h. After addition of saturated aqueous NaHCO<sub>3</sub>, the organic phase was concentrated and partitioned between CH<sub>2</sub>Cl<sub>2</sub> and brine. The combined organic extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The residue was purified by bulb-to-bulb distillation (150°C, 0.5 mmHg) to afford alcohol **12** (797 mg, 91% for 2 steps) as a colorless oil. IR 3380, 2938, 1736, 1373, 1268, 1154, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.23 (3H, t, *J* = 7.1 Hz), 1.3 – 1.6 (4H, m), 1.88 (1H, br), 1.93 – 2.06 (2H, m), 3.58 (2H, t, *J* = 6.3 Hz), 4.17 (2H, q, *J* = 7.1 Hz), 4.18 (1H, t, *J* = 7.2 Hz); <sup>13</sup>C NMR δ up: 23.5, 31.7, 34.5, 61.9, 62.2, 169.8; down: 13.9, 45.8; HRMS (CI) calcd for C<sub>8</sub>H<sub>16</sub>O<sub>3</sub>Br (M + 1)<sup>+</sup> 239.0282, found 239.0286.

**Ethyl 2-bromo-6-oxohexanoate 4a:** To a stirred suspension of PCC (4.74 g, 22.0 mmol), sodium acetate (1.8 g, 22.0 mmol), and molecular sieves 4A (4.74 g) in CH<sub>2</sub>Cl<sub>2</sub> (17 mL) at 0°C was added a solution of alcohol **12** (3.5 g, 14.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (17 mL). After stirring for 1 h at rt, the mixture was diluted with Et<sub>2</sub>O (50 mL) and stirred vigorously for 10 min. The precipitated insoluble material was filtered off through a short silica gel column with Et<sub>2</sub>O. The filtrate was concentrated, and then purified by column chromatography on silica gel with hexane / EtOAc (3 / 1, v/v) as eluent to afford aldehyde **4a** (2.83 g, 83%) as a colorless oil. IR 2940, 1736, 1372, 1272, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.31 (3H, t, *J* = 7.1 Hz), 1.7 – 2.1 (4H, m), 2.52 (2H, dt, *J* = 1.3 and 7.3 Hz), 4.2 – 4.3 (3H, m), 9.78 (1H, t, *J* = 1.3 Hz); <sup>13</sup>C NMR δ up: 19.8, 34.0, 42.8, 62.1, 169.5; down: 13.9, 45.4, 201.2; HRMS (EI) calcd for C<sub>8</sub>H<sub>13</sub>O<sub>3</sub>Br (M)<sup>+</sup> 236.0048, found 236.0052.

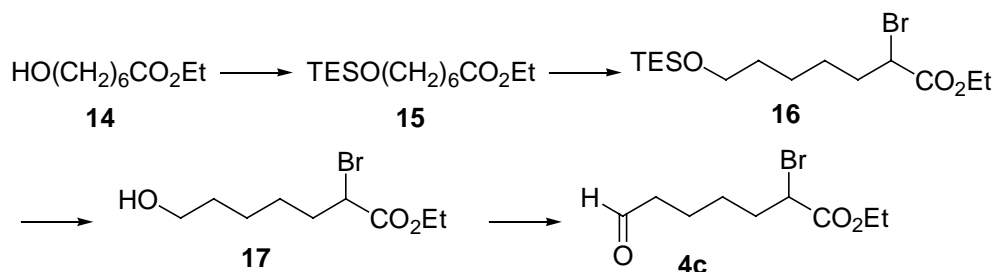
Preparation of ethyl 2-bromo-6-oxoheptanoate **4b** was achieved in 2 steps from aldehyde **4a**.



**Ethyl 2-bromo-6-hydroxyheptanoate 13:** To a stirred solution of aldehyde **4a** (500 mg, 2.1 mmol) in THF (10 mL) at 0°C was added a solution of MeTi(O<sup>i</sup>Pr)<sub>3</sub><sup>1</sup> (prepared from 4.2 mL (4.2 mmol) of 1.0M hexane solution of ClTi(O<sup>i</sup>Pr)<sub>3</sub> and 3.7 mL (4.2 mmol) of 1.14M Et<sub>2</sub>O solution of MeLi in 8 mL of THF). After stirring for 30 min at 0°C, saturated aqueous NH<sub>4</sub>Cl was added. After filtration of the precipitate through a pad of Celite, the filtrate was concentrated. The residual mixture was partitioned between EtOAc and brine. The combined organic extract was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The residue was purified by column chromatography on silica gel with hexane / EtOAc (3 / 1, v/v) as eluent to afford alcohol **13** (426 mg, 80%) as a colorless oil. IR 2295, 2966, 1738, 1375, 1272, 1153 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.20 (3H, d, *J* = 6.3 Hz), 1.30 (3H, t, *J* = 7.1 Hz), 1.39 – 1.62 (4H, m), 1.92 – 2.13 (2H, m), 3.80 (1H, dt, *J* = 6.3 and 12.0 Hz), 4.23 (2H, q, *J* = 7.1 Hz), 4.25 (1H, t, *J* = 7.1 Hz); <sup>13</sup>C NMR δ up: 23.5, 34.6, 38.1, 61.9, 169.8; down: 13.8, 23.4, 45.8, 67.4; HRMS (CI) calcd for C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>Br (M + 1)<sup>+</sup> 253.0439, found 253.0446.

**Ethyl 2-bromo-6-oxoheptanoate 4b:** To a stirred solution of alcohol **13** (420 mg, 1.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (8 mL) was added portionwise Dess-Martin periodinane<sup>2</sup> (1.06 g, 2.5 mmol). After stirring for 3 h at rt, Et<sub>2</sub>O (20 mL) was added and stirring was continued for 10 min. The precipitate formed was filtered off, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel with hexane / EtOAc (4 / 1, v/v) as eluent to afford ketone **4b** (414 mg, 99%) as a colorless oil. IR 2983, 1716, 1738, 1372, 1255, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.30 (3H, t, *J* = 7.1 Hz), 1.60 – 2.14 (4H, m), 2.15 (3H, s), 2.50 (2H, t, *J* = 7.1 Hz), 4.21 (1H, t, *J* = 7.3 Hz), 4.23 (2H, q, *J* = 7.1 Hz); <sup>13</sup>C NMR δ up: 21.2, 33.9, 42.3, 61.8, 169.4, 207.6; down: 13.8, 29.7, 45.5; HRMS (CI) calcd for C<sub>9</sub>H<sub>16</sub>O<sub>3</sub>Br (M + 1)<sup>+</sup> 251.0282, found 251.0281.

Preparation of ethyl 2-bromo-7-oxoheptanoate **4c** was achieved in 4 steps from ethyl 7-hydroxyhexanoate **14**.<sup>3</sup>



**Ethyl 7-triethylsilyloxyheptanoate 15:** The silyl ether **15** (9.33 g, 98%) was synthesized from **14** by the same procedure as for the preparation of the silyl ether **10**. IR 2955, 1738, 1098, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 0.59 (6H, q, *J* = 7.9 Hz), 0.96 (9H, t, *J* = 7.9 Hz), 1.25 (3H, t, *J* = 7.1 Hz), 1.31 – 1.68 (8H, m), 2.29 (2H, t, *J* = 7.5 Hz), 3.59 (2H, t, *J* = 6.6 Hz), 4.12 (2H, q, *J* = 7.1 Hz); <sup>13</sup>C NMR δ up: 4.4, 24.9, 25.5, 28.9, 32.7, 34.3, 60.1, 62.8, 173.8; down: 6.7, 14.2; HRMS (EI) calcd for C<sub>15</sub>H<sub>32</sub>O<sub>3</sub>Si (M)<sup>+</sup> 288.2121, found 288.2136.

**Ethyl 2-bromo-7-hydroxyheptanoate 17:** The bromoalcohol **17** (3.38 g, 81% for 2 steps) was synthesized from **15** via **16**, by the same procedure as for the preparation of **12**. IR 3360, 2936, 1739, 1270, 1154 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.30 (3H, t, *J* = 7.1 Hz), 1.32 – 1.63 (6H, m), 1.91 (1H, br), 1.97 – 2.11 (2H, m), 3.63 (2H, t, *J* =

<sup>1</sup> Reetz, M. T.; Westermann, J.; Steinbach, R.; Wenderoth, B.; Peter, R.; Ostarek, R.; Maus, S. *Chem. Ber.* **1985**, *118*, 1421.

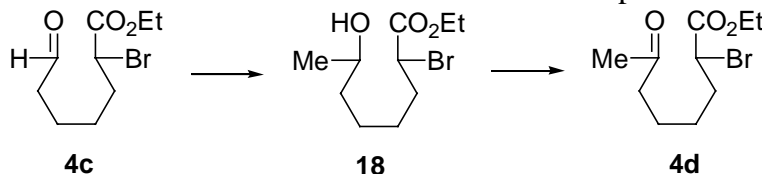
<sup>2</sup> (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156. (b) Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.

<sup>3</sup> Ballini, R.; Marcantoni, E.; Petrini, M. *Synth. Commun.* **1991**, *21*, 1075.

6.4 Hz), 4.21 (1H, t,  $J = 7.1$  Hz), 4.23 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 24.9, 26.9, 32.2, 34.7, 61.9, 62.4, 169.8; down: 13.9, 45.9; HRMS (CI) calcd for  $\text{C}_9\text{H}_{18}\text{O}_3\text{Br}$  ( $M + 1$ ) $^+$  253.0439, found 253.0401.

**Ethyl 2-bromo-7-oxoheptanoate 4c:** The aldehyde **4c** (2.27 g, 70%) was synthesized from **17** by the same procedure as for the preparation of the aldehyde **4a**. IR 2939, 1735, 1264, 1155  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.30 (3H, t,  $J = 7.1$  Hz), 1.37 – 1.74 (4H, m), 1.96 – 2.14 (2H, m), 2.48 (2H, dt,  $J = 1.5$  and 7.3 Hz), 4.21 (1H, dd,  $J = 6.9$  and 7.9 Hz), 4.23 (2H, q,  $J = 7.1$  Hz), 9.77 (1H, t,  $J = 1.5$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 21.1, 26.7, 34.5, 43.3, 61.9, 169.6; down: 13.9, 45.6, 201.8; HRMS (CI) calcd for  $\text{C}_9\text{H}_{16}\text{O}_3\text{Br}$  ( $M + 1$ ) $^+$  251.0282, found 251.0255.

Preparation of ethyl 2-bromo-7-oxooctanoate **4d** was achieved in 2 steps from aldehyde **4c**.



**Ethyl 2-bromo-7-hydroxyoctanoate 18:** The alcohol **18** (780 mg, 99%) was synthesized from **4c** by the same procedure as for the preparation of the alcohol **13**. IR 3375, 2935, 1739, 1373, 1264, 1153, 1030  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.19 (3H, d,  $J = 6.3$  Hz), 1.30 (3H, t,  $J = 7.1$  Hz), 1.34 – 1.54 (6H, m), 1.78 (1H, br s), 1.94 – 2.10 (2H, m), 3.79 (1H, dq,  $J = 6.1$  Hz), 4.21 (1H, dd,  $J = 6.9$  and 7.8 Hz), 4.23 (2H, q,  $J = 7.1$  Hz),  $^{13}\text{C}$  NMR  $\delta$  up: 24.9, 27.1, 34.7, 38.8, 61.8, 169.8; down: 13.9, 23.4, 45.9, 67.7; HRMS (CI) calcd for  $\text{C}_{10}\text{H}_{20}\text{O}_3\text{Br}$  ( $M + 1$ ) $^+$  267.0595, found 267.0565.

**Ethyl 2-bromo-7-oxooctanoate 4d:** The ketone **4d** (743 mg, 97%) was synthesized from **18** by the same procedure as for the preparation of the alcohol **4b**. IR 2940, 1739, 1717, 1370, 1264, 1157  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.30 (3H, t,  $J = 7.1$  Hz), 1.35 – 1.67 (4H, m), 1.97 – 2.13 (2H, m), 2.14 (3H, s), 2.46 (2H, t,  $J = 7.1$  Hz), 4.21 (1H, dd,  $J = 6.9$  and 7.8 Hz), 4.23 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 22.7, 26.6, 34.5, 43.0, 61.9, 169.6, 208.3; down: 13.8, 29.8, 45.7; HRMS (CI) calcd for  $\text{C}_{10}\text{H}_{18}\text{O}_3\text{Br}$  ( $M + 1$ ) $^+$  265.0439, found 265.0425.

**The intramolecular Reformatsky type reaction: Preparation of  $\beta$ -hydroxy esters 5a and 6a:** To a stirred solution of  $\text{RhCl}(\text{PPh}_3)_3$  (37 mg, 0.04 mmol) in THF (10 mL) at  $0^\circ\text{C}$  was added a solution of aldehyde **4a** (190 mg, 0.8 mmol) in THF (6 mL). After stirring for 5 min, a 1.02M hexane solution of  $\text{Et}_2\text{Zn}$  (1.73 mL, 1.76 mmol) was added dropwise over 5 min. This mixture was stirred at  $0^\circ\text{C}$  for 5 min, and saturated aqueous  $\text{NaHCO}_3$  was added to the mixture. After filtration of the precipitate, the filtrate was concentrated. The residual mixture was partitioned between  $\text{Et}_2\text{O}$  and brine. The combined organic extract was dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was purified by column chromatography on silica gel with hexane /  $\text{EtOAc}$  (2 / 1, v/v) as eluent. The first fraction gave the *cis*-hydroxy ester **5a**<sup>4</sup> (80 mg, 63%) as a colorless oil. IR 3460, 2970, 1735, 1190, 1034  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.28 (3H, t,  $J = 7.1$  Hz), 1.58 – 2.07 (6H, m), 2.68 (2H, dt,  $J = 4.5$  and 9.7 Hz), 3.16 (1H, d,  $J = 2.8$  Hz), 4.19 (2H, q,  $J = 7.1$  Hz), 4.44 (1H, dt,  $J = 2.8$  and 4.5 Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 22.0, 26.3, 33.9, 60.6, 174.9; down: 14.1, 49.5, 73.6; HRMS (EI) calcd for  $\text{C}_6\text{H}_9\text{O}_3$  ( $M - \text{Et}(29)$ ) $^+$  129.0552, found 129.0548. The second fraction gave the *trans*-hydroxy ester **6a**<sup>5</sup> (6 mg, 5%) as a colorless oil. IR 3540, 2960, 1733, 1188, 1037  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.28 (3H, t,  $J = 7.1$  Hz), 1.58 – 2.11 (7H, m), 2.66 (1H, dt,  $J = 6.4$  and 8.6 Hz), 4.17 (2H, q,  $J = 7.1$  Hz), 4.38 (1H, q,  $J = 6.4$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 21.9, 27.0, 34.1, 60.6, 174.9; down: 14.2, 52.6, 76.3; HRMS (EI) calcd for  $\text{C}_6\text{H}_9\text{O}_3$  ( $M - \text{Et}(29)$ ) $^+$  129.0552, found 129.0524.

<sup>4</sup> Seebach, D.; Roggo, S.; Maetzke, T.; Braunschweiger, H.; Cercus, J.; Krieger, M. *Helv. Chim. Acta* **1987**, *70*, 1605.

<sup>5</sup> Fang, C.; Ogawa, T.; Suemune, H.; Sakai, K. *Tetrahedron: Asym.* **1991**, *2*, 389.

**$\beta$ -Hydroxy esters 5b and 6b:** The reaction was performed on 0.55 mmol scale of ketone **4b** to give **5b** (59%) and **6b** (5%).

**5b:** IR 3500, 2970, 1713, 1375, 1181  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.29 (3H, t,  $J = 7.1$  Hz), 1.39 (3H, s), 1.56 – 2.13 (6H, m), 2.53 (1H, t,  $J = 9.6$  Hz), 3.36 (1H, br s), 4.19 (2H, q,  $J = 7.1$  Hz). NOE was observed between C1-H and C2-Me.  $^{13}\text{C}$  NMR  $\delta$  up: 21.8, 28.2, 40.4, 60.5, 79.7, 175.2; down: 14.2, 26.7, 53.1; HRMS (EI) calcd for  $\text{C}_9\text{H}_{16}\text{O}_3$  (M) $^+$  172.1099, found 172.1077.

**6b:** IR 3460, 2970, 1730, 1375, 1164  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.25 (3H, s), 1.29 (3H, t,  $J = 7.1$  Hz), 1.63 – 2.17 (6H, m), 2.21 (1H, br), 2.77 (1H, t,  $J = 8.7$  Hz), 4.18 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 21.0, 26.0, 40.3, 60.4, 80.7, 173.9; down: 14.3, 24.4, 55.7; HRMS (EI) calcd for  $\text{C}_9\text{H}_{16}\text{O}_3$  (M) $^+$  172.1099, found 172.1077.

**$\beta$ -Hydroxy esters 5c and 6c:** The reaction was performed on 1.39 mmol scale of aldehyde **4c** to give **5c** (41%) and **6c** (33%)<sup>6</sup>.

**5c:** IR 3510, 2935, 1720, 1180, 1039  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.27 (3H, t,  $J = 7.1$  Hz), 1.29 – 1.97 (8H, m), 2.47 (1H, dt,  $J = 3.5$  and 11.0 Hz), 3.29 (1H, br s), 4.14 – 4.18 (1H, br), 4.17 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 19.9, 23.8, 24.7, 60.4, 175.7; down: 14.0, 46.6, 66.5; HRMS (EI) calcd for  $\text{C}_9\text{H}_{16}\text{O}_3$  (M) $^+$  172.1099, found 172.1095.

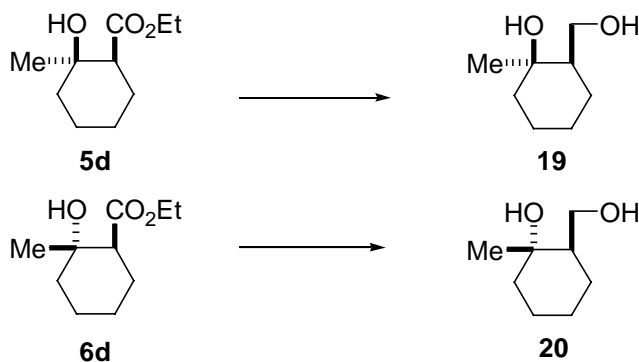
**5c:** IR 3446, 2936, 1732, 1180  $\text{cm}^{-1}$ ; 1.18 – 1.44 (4H, m), 1.27 (3H, t,  $J = 7.1$  Hz), 1.69 – 1.80 (2H, m), 1.99 – 2.08 (2H, m), 2.25 (1H, ddd,  $J = 4.0, 9.9,$  and 12.2 Hz), 3.06 (1H, br s), 3.76 (1H, dt,  $J = 4.6$  and 9.9 Hz), 4.17 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 24.2, 24.9, 28.0, 33.6, 60.5, 175.2; down: 14.1, 51.3, 70.8; HRMS (EI) calcd for  $\text{C}_9\text{H}_{16}\text{O}_3$  (M) $^+$  172.1099, found 172.1095.

**$\beta$ -Hydroxy esters 5d and 6d:** The reaction was performed on 1.0 mmol scale of ketone **4d** to give **5d** (65%) and **6d** (26%).

**5d:** IR 3517, 2935, 1710, 1375, 1188  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.20 (3H, s), 1.15 – 1.31 (2H, m), 1.28 (3H, t,  $J = 7.1$  Hz), 1.44 – 1.51 (1H, m), 1.66 – 1.90 (5H, m), 2.28 (1H, dd,  $J = 3.9$  and 12.0 Hz), 3.68 (1H, d,  $J = 2.5$  Hz), 4.18 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 21.0, 24.9, 25.9, 38.1, 60.5, 68.7, 176.7; down: 14.1, 29.4, 51.2; MS (EI) found 186 (M) $^+$ .

**6d:** IR 3505, 2935, 1732, 1375, 1186  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.21 (3H, s), 1.29 (3H, t,  $J = 7.1$  Hz), 1.23 – 1.82 (7H, m), 1.93 – 2.01 (1H, m), 2.43 (1H, dd,  $J = 4.1$  and 12.2 Hz), 3.60 (1H, br s), 4.19 (2H, q,  $J = 7.1$  Hz);  $^{13}\text{C}$  NMR  $\delta$  up: 23.1, 25.0, 25.8, 40.2, 60.6, 71.3, 174.4; down: 14.2, 22.4, 53.0; HRMS (EI) calcd for  $\text{C}_{10}\text{H}_{17}\text{O}_2$  (M – OH(17)) $^+$  169.1228, found 169.1229.

The relative stereochemistries of **5d** and **6d** were determined by conversion to the known alcohols **19** and **20** as follows:



<sup>6</sup> Wittmann, G.; Göndös, G.; Bartók, M. *Helv. Chim. Acta* **1990**, 73, 635.

**cis-Diol 19:** To a stirred suspension of LAH (92 mg, 2.42 mmol) in THF (2 mL) was added a solution of ester **5d** (90 mg, 0.48 mmol) in THF (2 mL). After stirring for 30 min at 0°C, the mixture was diluted with Et<sub>2</sub>O (10 mL), and then a 10% aqueous solution of NaOH (2 mL) was added dropwise over 10 min. After filtration of the precipitate, the filtrate was concentrated. The residue was purified by column chromatography on silica gel with pentane / Et<sub>2</sub>O (1 / 5, v/v) as eluent to afford diol **19** (63 mg, 90%) as a colorless oil. IR 3340, 2930, 1445, 1010, 935 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 1.32 (3H, s), 1.19 – 1.92 (9H, m), 3.31 (1H, br), 3.62 (1H, dd, *J* = 2.6 and 10.6 Hz), 3.64 (1H, br), 4.10 (1H, dd, *J* = 3.0 and 10.6 Hz); <sup>13</sup>C NMR (BCM) δ 21.9, 25.5, 25.6, 28.9, 39.9, 45.6, 64.7, 72.7; HRMS (EI) calcd for C<sub>8</sub>H<sub>14</sub>O (M<sup>+</sup> - 18) 126.1045, found 126.1049; calcd for C<sub>8</sub>H<sub>17</sub>O<sub>2</sub> (M + 1)<sup>+</sup> 145.1228, found 145.1228.

**trans-Diol 20:** The reaction was performed on 0.24 mmol scale of ester **6d** to afford diol **20** (30 mg, 86%). IR 3350, 2928, 1446, 1140, 1020, 981 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 0.82 – 0.99 (1H, m), 1.23 (3H, s), 1.24 – 1.82 (8H, m), 3.27 (1H, br), 3.44 (1H, br), 3.56 (1H, dd, *J* = 4.6 and 10.6 Hz), 3.72 (1H, t, *J* = 10.6 Hz); <sup>13</sup>C NMR (BCM) δ 20.3, 23.5, 25.4, 26.4, 40.1, 47.9, 65.9, 74.3; HRMS (EI) calcd for C<sub>8</sub>H<sub>17</sub>O<sub>2</sub> (M + 1)<sup>+</sup> 145.1228, found 145.1211. <sup>1</sup>H NMR of the synthesized compound was identical with those reported.<sup>7</sup>

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<sup>7</sup> Pelter, A.; Vaughan-Williams, G. F.; Rosser, R. M. *Tetrahedron*, **1993**, *49*, 3007.