

## Synthesis of 2-Alkylidene tetrahydrofurans by Ru-catalyzed Regio- and Stereoselective Codimerization of Dihydrofurans with $\alpha,\beta$ -Unsaturated Esters

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**Materials and Methods.** All manipulations were performed under an argon atmosphere by standard Schlenk techniques. All solvents were distilled under argon over appropriate drying reagents (sodium or calcium hydride).  $[\text{RuCl}_2(\text{CO})_3]_2$ ,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{RhCl}(\text{PPh}_3)_3$ ,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ,  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{Co}_2(\text{CO})_8$  were obtained commercially, and used without further purification.  $\text{Ru}(\text{cod})(\text{cot})$ ,<sup>1</sup>  $\text{Ru}(\text{cot})(\text{dmfm})_2$ ,<sup>2</sup>  $\text{Ru}(\text{cyclooctadienyl})_2$ ,<sup>3</sup>  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ ,<sup>4</sup>  $\text{RuH}_2(\text{PPh}_3)_4$ ,<sup>5</sup>  $\text{Cp}^*\text{RuCl}(\text{cod})$ ,<sup>6</sup>  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ ,<sup>7</sup>  $\text{CpRuCl}(\text{PPh}_3)_2$ ,<sup>8</sup> 2-phenyl- or 2-(1-naphthyl)-2,3-dihydrofuran<sup>9</sup> and dimethyl fumarate- $d_2$ <sup>10</sup> were prepared as described in the literatures. 2,3-Dihydrofuran and ethyl acrylate were obtained commercially and distilled before use. The other reagents (2,5-dihydrofuran and acrylates) were obtained commercially and used without further purification.

**Physical and Analytical Measurements.** NMR spectra were recorded on a JEOL EX-400 (FT, 400MHz (<sup>1</sup>H), 100MHz (<sup>13</sup>C)) instrument. Chemical shifts ( $\delta$ ) for <sup>1</sup>H and <sup>13</sup>C are referenced to internal solvent resonance and reported relative to SiMe<sub>4</sub>. IR spectra were recorded using a Nicolet Impact 410 FT-IR spectrometer. GC-MS studies were conducted on a Shimadzu GCMS-QP5000 instrument with 70-eV electron impact ionization. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Analytical gas chromatography was performed on a Shimadzu GC-14B gas chromatograph with FID detection using a 3.2-mm i.d.  $\times$  3 m column with 2%

(w/w) silicone OV-17 liquid phase on a Chromosorb W(AW DMCS) support in 60/80 mesh. Naphthalene was used as an internal standard. Compounds **3b** and **3c** were purified on a Japan Analytical Industry Co. Ltd., Model LC-918 recycling preparative HPLC equipped with JAIGEL-1H and 2H columns (GPC) using CHCl<sub>3</sub> as an eluent, instead of flash column chromatography after Kugelrohr distillation.

**Ethyl 2-(5-phenyl-3,4,5-trihydro-2-furylidene)propanoate (3b).** The crude product was purified by Kugelrohr distillation (160 °C at 3 Torr) and HPLC to give **3b** as a colorless liquid. GC yield 39%, isolated yield 26%; IR spectrum (neat): 1785, 1454, 1381, 1175, 1140, 1117 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.32-7.19 (m, 5H), 5.31 (t, *J* = 7.3 Hz, 1H), 4.10 (q, *J* = 7.3 Hz, 2H), 3.28-3.21 (m, 1H), 3.03-2.94 (m, 1H), 2.48-2.41 (m, 1H), 2.15-1.91 (m, 1H), 1.83 (s, 3H), 1.22 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.7 (C), 169.3 (C), 140.5 (C), 128.5 (2 × CH), 127.9 (CH), 125.4 (2 × CH), 98.0 (C), 83.7 (CH), 59.6 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 31.2 (CH<sub>2</sub>), 14.6 (CH<sub>3</sub>), 11.5 (CH<sub>3</sub>); MS (EI) *m/z* 246 (M<sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>: C, 73.15; H, 7.37. Found: C, 73.32; H, 7.47.

**Ethyl 2-(5-(1-naphthyl)-3,4,5-trihydro-2-furylidene)propanoate (3c).** The crude product was purified by Kugelrohr distillation (200 °C at 1 Torr) and HPLC to give **3c** as a colorless liquid. GC yield 79%, isolated yield 65%; IR spectrum (neat): 1700, 1639, 1553, 1490, 1414, 1302 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.43-7.91 (m, 7H), 6.11 (t, *J* = 6.8 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.22 (t, *J* = 7.7 Hz, 2H), 2.74-2.66 (m, 1H), 2.19-2.11 (m, 1H), 1.99 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.8 (C), 169.3 (C), 136.1 (C), 133.6 (C), 129.8 (C), 128.9 (CH), 128.2 (CH), 126.1 (CH), 125.6 (CH), 125.3 (CH), 122.8 (CH), 121.7 (CH), 98.2 (C), 81.4 (CH), 59.7 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 30.8 (CH<sub>2</sub>), 14.6 (CH<sub>3</sub>), 11.6 (CH<sub>3</sub>); MS (EI) *m/z* 296 (M<sup>+</sup>). Anal. Calcd for C<sub>19</sub>H<sub>20</sub>O<sub>3</sub>: C, 77.00; H, 6.80. Found: C, 77.15; H, 6.85.

**tert-Butyl 2-(3,4,5-trihydro-2-furylidene)propanoate (3d).** The crude product was purified by

flash column chromatography (ethyl acetate/hexane = 1/1) and Kugelrohr distillation (120 °C at 10 Torr) to give **3d** as a colorless liquid. GC yield 72%, isolated yield 55%; IR spectrum (neat): 1693, 1639, 1455, 1366  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.18 (t,  $J = 6.8$  Hz, 2H), 3.01 (t,  $J = 7.0$  Hz, 2H), 2.09-2.02 (m, 2H), 1.78 (s, 3H), 1.48 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  169.0 (C), 168.7 (C), 99.1 (C), 79.0 (C), 71.0 ( $\text{CH}_2$ ), 30.9 ( $\text{CH}_2$ ), 28.5 ( $3 \times \text{CH}_3$ ), 24.7 ( $\text{CH}_2$ ), 11.7 ( $\text{CH}_3$ ); MS (EI)  $m/z$  198 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{11}\text{H}_{18}\text{O}_3$ : C, 66.64; H, 9.15. Found: C, 66.85; H, 9.06.

**Methyl 3-phenyl-2-(3,4,5-trihydro-2-furylidene)propanoate (3e).** The crude product was purified by flash column chromatography (ethyl acetate/hexane = 1/3) and Kugelrohr distillation (150 °C at 5 Torr) to give **3e** as a colorless liquid. GC yield 44%, isolated yield 19%; IR spectrum (neat): 1698, 1633, 1494, 1436  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.26-7.21 (m, 5H), 4.25 (t,  $J = 7.1$  Hz, 2H), 3.67 (s, 2H), 3.66 (s, 3H), 3.12 (t,  $J = 7.8$  Hz, 2H), 2.14-2.07 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  171.7 (C), 169.2 (C), 141.7 (C), 128.3 ( $2 \times \text{CH}$ ), 127.9 ( $2 \times \text{CH}$ ), 125.4 (CH), 101.7 (C), 71.6 ( $\text{CH}_2$ ), 51.0 ( $\text{CH}_3$ ), 31.8 ( $\text{CH}_2$ ), 31.2 ( $\text{CH}_2$ ), 24.4 ( $\text{CH}_2$ ); MS (EI)  $m/z$  232 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_3$ : C, 72.39; H, 6.94. Found: C, 72.46; H, 6.96.

**Methyl 2-(3,4,5-trihydro-2-furylidene)butanoate (3f).** The crude product was purified by flash column chromatography (ethyl acetate/hexane = 1/3) and Kugelrohr distillation (110 °C at 10 Torr) to give **3f** as a colorless liquid. Isolated yield 11%; IR spectrum (neat): 1740, 1632, 1434, 1374  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.14 (t,  $J = 7.0$  Hz, 2H), 3.70 (s, 3H), 3.06 (t,  $J = 7.8$  Hz, 2H), 2.32 (q,  $J = 7.3$  Hz, 2H), 2.11-2.03 (m, 2H), 0.99 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  170.4 (C), 169.5 (C), 104.1 (C), 71.3 ( $\text{CH}_2$ ), 50.8 ( $\text{CH}_3$ ), 31.0 ( $\text{CH}_2$ ), 24.4 ( $\text{CH}_2$ ), 19.5 ( $\text{CH}_2$ ), 13.9 ( $\text{CH}_3$ ); MS (EI)  $m/z$  170 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_9\text{H}_{14}\text{O}_3$ : C, 63.51; H, 8.29. Found: C, 63.25; H, 8.28.

**Dimethyl 2-(3,4,5-trihydro-2-furylidene)butane-1,4-dioate (3g).** The crude product was purified by flash column chromatography (ethyl acetate/hexane = 1/1) and Kugelrohr distillation (130 °C at 10

Torr) to give **3g** as a colorless liquid. GC yield 64%, isolated yield 55%; IR spectrum (neat): 1747, 1714, 1644, 1435, 1376  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  4.25 (t,  $J = 7.1$  Hz, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.37 (s, 2H), 3.15 (t,  $J = 7.8$  Hz, 2H), 2.15-2.09 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  173.0 (C), 172.5 (C), 168.4 (C), 95.8 (C), 72.0 ( $\text{CH}_2$ ), 51.7 ( $\text{CH}_3$ ), 51.1 ( $\text{CH}_3$ ), 31.6 ( $\text{CH}_2$ ), 31.1 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_2$ ); MS (EI)  $m/z$  214 ( $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_5$ : C, 56.07; H, 6.59. Found: C, 56.36; H, 6.61.

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