

# **Supporting Information**

## **Title**

**Radical Cascade Reaction with 1,4-Dienes and 1,4-Enynes using 2-(Iodomethyl)cyclopropane-1,1-dicarboxylate as a Homoallyl Radical Precursor: One-step Synthesis of Bicyclo[3.3.0]octane Derivatives.**

## **Authored by**

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**Supporting Information Available.** Experimental procedures and characterization data for products **3a-3d**, **2e-2g**, **5h**. This material is available free of charge via Internet at <http://pubs.acs.org>.

## Experimental Section

Melting points were uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a 300 MHz spectrometer. In  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, chemical shifts were expressed in  $\delta$  (ppm) downfield from  $\text{CHCl}_3$  (7.26 ppm) and  $\text{CDCl}_3$  (77.0 ppm), respectively. Mass spectra were recorded by electron impact or chemical ionization. Column chromatography was performed on silica gel (75-150  $\mu\text{m}$ ). Medium-pressure liquid chromatography (MPLC) was performed on a 30 X 4 cm i. d. prepacked column (silica gel, 50  $\mu\text{m}$ ) with a UV detector.

**Preparation of dimethyl 2-(iodomethyl)cyclopropane-1,1-dicarboxylate (1) through  $\text{Ti}(\text{OR})_4$ -mediated iodocarbocyclization:**<sup>1</sup> Under Ar atmosphere, to a solution of dimethyl allylmalonate (344 mg, 2 mmol) in  $\text{CH}_2\text{Cl}_2$  (12 mL) was added  $\text{Ti}(\text{Ot-Bu})_4$  (0.8 mL, 2 mmol). After being stirred for 10 min,  $\text{I}_2$  (608 mg, 2.4 mmol) and  $\text{CuO}$  (192 mg, 2.4 mmol) were successively added, and then the mixture was stirred for 4 h. The mixture was poured into 10 %  $\text{HCl}$ , and the products were extracted with ether. The ether extracts were washed with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, dried over  $\text{MgSO}_4$ , and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 9) gave **1** (584 mg, 98 %). NMR data of **1** coincided with that reported in our previous paper.<sup>2</sup>

**Preparation of dimethyl 2-(iodomethyl)cyclopropane-1,1-dicarboxylate (1) through Beckwith's method:**<sup>3</sup> Under Ar atmosphere, to a solution of dimethyl allylmalonate (861 mg, 5 mmol) in THF (15 mL) was added to  $\text{NaH}$  (240 mg, 6 mmol) at 0 °C. After being stirred for 10 min,  $\text{I}_2$  (1.27 g, 5 mmol) was successively added, and then the mixture was refluxed for 4 h. The mixture was poured into aqueous  $\text{NH}_4\text{Cl}$  solution and the products were extracted with ether. The ether extracts were washed with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution, dried over  $\text{MgSO}_4$ , and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 9) gave **1** (994 mg, 67 %). NMR data of **1** coincided with that reported in our previous paper.<sup>2</sup>

**General procedure of radical iodine atom transfer cascade reaction of **1** with 1,4-dienes.**

Under Ar atmosphere, to a solution of dimethyl 2-iodomethylcyclopropane-1,1-dicarboxylate **1** (149 mg, 0.5 mmol), 1,4-pentadiene (0.10 mL, 1.0 mmol) and Yb(OTf)<sub>3</sub> (310 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added Et<sub>3</sub>B (0.5 mL, 1M hexane solution) at -15 °C. 20 mL of dry air was subsequently introduced with a syringe. After being stirred for 1 h at -15 °C, the mixture was poured into aqueous NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The Et<sub>2</sub>O extracts were washed with brine, dried over MgSO<sub>4</sub>, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave an inseparable mixture of *exo*-**2a** and *endo*-**2a** (*exo/endo* = 2.7). To the mixture (*exo*-**2a** and *endo*-**2a**) in DMF (4 mL) was added DBU (0.09 mL, 0.6 mmol). After being stirred for 2 h at 80 °C, the mixture was poured into aqueous NH<sub>4</sub>Cl solution and extracted with Et<sub>2</sub>O. The Et<sub>2</sub>O extracts were washed with brine, dried over MgSO<sub>4</sub>, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **3a** (93 mg, total 78 %).

**(3a*R*, 6a*S*)-Dimethyl 5-methylenehexahydro-2,2-(1H)-pentalenedicarboxylate (3a).** **3a**: colorless oil; IR (neat) 1737 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 4.82 (2H, m), 3.71 (3H, s), 3.69 (3H, s), 2.38-2.64 (6H, m), 2.01 (2H, d, *J* = 15.0 Hz), 1.75 (2H, dd, *J* = 7.0, 12.5 Hz); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ: 172.6, 172.2, 151.1, 107.0, 61.7, 52.6, 52.5, 41.8, 40.8, 39.1; MS (*m/z*) 238 (M<sup>+</sup>); Anal. Calcd for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: C, 65.53; H, 7.61. Found: C, 65.44; H, 7.64.

**(3a*R*, 6a*S*)-Dimethyl 6-methyl-5-methylenehexahydro-2,2-(1H)-pentalenedicarboxylate (3b).** **2b** was prepared from **1** (149 mg, 0.5 mmol) and 3-methyl-1,4-pentadiene (0.12 mL, 1.0 mmol) in accordance with the general procedure. The subsequent treatment with DBU in CH<sub>3</sub>CN, work-up and purification of the residue by column chromatography (hexane/AcOEt = 30) gave the mixture of *exo*-**3b** and *endo*-**3b** (53 mg, total 42 %) in a ratio of *exo/endo* = 2.8. *exo*-**3b**: colorless oil; IR (neat) 1737 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 4.77 (1H, quint, *J* = 1.5 Hz), 4.73 (1H, quint, *J* = 1.5 Hz), 3.72 (3H, s), 3.70 (3H, s), 2.47-2.64 (4H, m), 2.05-2.23 (2H, m), 1.80-1.98 (2H, m), 1.61 (1H, m), 1.04 (3H, d, *J* = 6.7 Hz); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ: 172.7, 172.4, 157.0, 105.0, 62.1, 52.5, 51.1, 45.0, 40.9, 40.7, 39.5, 37.7, 35.1, 18.5. MS (*m/z*) 252 (M<sup>+</sup>); Anal. Calcd for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>: C, 66.65; H, 7.99. Found: C, 66.40; H, 8.02.

**(3a*R*, 6a*S*)-Dimethyl 5-ethylidenehexahydro-2,2-(1*H*)-pentalenedicarboxylate (3c).** **2c** was prepared from **1** (149 mg, 0.5 mmol) and 1,4-hexadiene (0.12 mL, 1.0 mmol) in accordance with the general procedure. The subsequent treatment with DBU in DMF, work-up and the purification of the residue by column chromatography (hexane/AcOEt = 30) gave **3c** (95 mg, total 75 %). **3c**: colorless oil; IR (neat) 1737  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 5.28 (1*H*, m), 3.72 (3*H*, s), 3.69 (3*H*, s), 2.24-2.64 (6*H*, m), 2.04 (2*H*, t,  $J$  = 16.8 Hz), 1.72-1.83 (2*H*, m), 1.56 (3*H*, d,  $J$  = 6.6 Hz);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 172.8, 172.4, 142.1, 116.1, 61.8, 52.5 (OMe x 2), 42.3, 41.8, 41.0, 40.4, 39.3, 34.0, 14.6; MS (*m/z*) 252 (M $^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C, 66.65; H, 7.99. Found: C, 66.62; H, 8.01.

**(3a*R*, 6a*S*)-Dimethyl 3a-methyl-5-methylenehexahydro-2,2-(1*H*)-pentalenedicarboxylate (3d).** **2d** was prepared from **1** (149 mg, 0.5 mmol) and 2-methyl-1,4-pentadiene (0.12 mL, 1.0 mmol) in accordance with the general procedure. The subsequent treatment with DBU in DMF, work-up and the purification of the residue by column chromatography (hexane/AcOEt = 30) gave **3d** (64 mg, total 51 %). **3d**: colorless oil; IR (neat) 1737  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 4.82 (2*H*, m), 3.73 (3*H*, s), 3.70 (3*H*, s), 2.56 (1*H*, ddd,  $J$  = 1.0, 7.2, 13.4 Hz), 2.50 (1*H*, m), 2.07-2.34 (6*H*, m), 1.85 (1*H*, dd,  $J$  = 9.1, 13.4 Hz), 1.06 (3*H*, s);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 173.1, 172.7, 151.3, 107.1, 60.6, 52.6 (OMe x 2), 50.0, 49.8, 47.3, 46.8, 40.8, 37.6, 27.3; MS (*m/z*) 252 (M $^+$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C, 66.65; H, 7.99. Found: C, 66.66; H, 8.03.

**General procedure of radical iodine atom transfer cascade reaction of 1 with 1,4-enynes.** Under Ar atmosphere, to a solution of dimethyl 2-iodomethylcyclopropane-1,1-dicarboxylate **1** (149 mg, 0.5 mmol), 1-undecene-4-yne (150 mg, 1.0 mmol) and  $\text{Yb}(\text{OTf})_3$  (310 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) was added  $\text{Et}_3\text{B}$  (0.5 mL, 1M hexane solution) at -15 °C. 20 mL of dry air was subsequently introduced with a syringe. After being stirred for 1 h at -15 °C, the mixture was poured into aqueous  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{Et}_2\text{O}$ . The  $\text{Et}_2\text{O}$  extracts were washed with brine, dried over  $\text{MgSO}_4$ , and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **2e** (166 mg, 74 %).

**(3a*R*, 6a*S*)-Dimethyl 5-(1-iodoheptylidene)hexahydro-2,2-(1*H*)-pentalenedicarboxylate (2e).** **2e**: colorless oil; IR (neat) 1738  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 3.71 (3*H*, s), 3.70 (3*H*, s), 2.72 (1*H*, m), 2.44-2.59 (5*H*, m), 2.37 (2*H*, t,  $J$  = 7.2 Hz), 2.19-2.27 (2*H*, m), 1.87-1.97 (2*H*, m), 1.46

(2H, m), 1.21-1.34 (6H, m), 0.87 (3H, t,  $J$  = 6.8 Hz);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 172.8, 172.5, 147.2, 98.8, 61.7, 52.7 (OMe x 2), 46.4, 44.9, 42.2, 41.7, 40.2, 40.2, 36.3, 31.7, 29.2, 28.0, 22.6, 14.0; MS ( $m/z$ ) 448 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{19}\text{H}_{29}\text{IO}_4$ : C, 50.90; H, 6.52. Found: C, 51.05; H, 6.57.

**(3a*R* , 6a*S* )-Dimethyl 5-[iodo(phenyl)methylene]hexahydro-2,2-(1H)-pentaledicarboxylate (2f).** **2f** was prepared from **1** (149 mg, 0.5 mmol) and 1-phenyl-4-pentene-yne (142 mg, 1.0 mmol) in accordance with the general procedure. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **2f** (156 mg, 71 %). **2f**: colorless oil; IR (neat)  $1734\text{ cm}^{-1}$ ;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.27-7.30 (4H, m), 7.21 (1H, m), 3.73 (3H, s), 3.72 (3H, s), 2.37-2.80 (7H, m), 2.20 (1H, dd,  $J$  = 2.7, 16.9 Hz), 2.03 (1H, dd,  $J$  = 6.4, 13.4 Hz), 1.86 (1H, dd,  $J$  = 6.4, 13.4 Hz);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 172.5, 172.3, 151.0, 143.7, 128.7, 128.0, 127.4, 90.5, 61.6, 52.6 (OMe x 2), 46.9, 44.9, 42.0, 40.4, 40.0, 37.8; MS ( $m/z$ ) 440 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{IO}_4$ : C, 51.83; H, 4.81. Found: C, 51.59; H, 4.84.

**(3a*R* , 6a*S*)-Dimethyl 5-{2-[*tert*-butyldiphenylsilyl]oxy}-1-iodoethylidene}hexahydro-2,2-(1H)-pentaledicarboxylate (2g).** **2g** was prepared from **1** (149 mg, 0.5 mmol) and 1-*tert*-butyldiphenylsiloxy-5-hexene-2-yne (335 mg, 1.0 mmol) in accordance with the general procedure. Purification of the residue by column chromatography (hexane/AcOEt = 30) gave **2g** (231 mg, 73 %). **2g**: colorless oil; IR (neat)  $1736\text{ cm}^{-1}$ ;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.69-7.76 (4H, m), 7.35-7.48 (6H, m), 4.25 (2H, s), 3.72 (3H, s), 3.71 (3H, s), 2.46-2.65 (4H, m), 2.41 (1H, dd,  $J$  = 7.4, 13.7 Hz), 2.15-2.30 (2H, m), 1.90-2.02 (2H, m), 1.82 (1H, dd,  $J$  = 7.0, 13.7 Hz), 1.08 (9H, s);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 172.7, 172.4, 150.0, 135.7, 133.4, 129.7, 127.6, 97.3, 68.0, 68.0, 61.7, 52.7 (OMe x 2), 46.2, 44.9, 41.9, 40.0, 36.4, 26.8, 19.3; MS ( $m/z$ ) 575 ( $\text{M}^+-t\text{-Bu}$ ); Anal. Calcd for  $\text{C}_{30}\text{H}_{37}\text{IO}_5\text{Si}$ : C, 56.96; H, 5.90. Found: C, 56.66; H, 5.91.

**Dimethyl 3-(3-butenyl)-4-methylene-1,1-cyclopentenedicarboxylate (5h).** **4h** was prepared from **1** (149 mg, 0.5 mmol) and 1,5-hexadiene (0.12 mL, 1.0 mmol) in accordance with the general procedure (using 1,4-diene). The subsequent treatment with DBU in DMF, work-up and the purification of the residue by column chromatography (hexane/AcOEt = 30) gave **5h** (85 mg, total 67 %). **5h**: colorless oil; IR (neat)  $1738\text{ cm}^{-1}$ ;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 5.81 (1H, tdd,  $J$  = 6.5, 10.2, 17.8 Hz), 4.92-5.07 (3H, m), 4.83 (1H, q,  $J$  = 2.3 Hz), 3.73 (3H, s), 3.72 (3H, s), 3.03 (1H, brd,  $J$  = 16.6 Hz), 2.93 (1H, qd,  $J$  = 2.2, 16.6 Hz), 2.45-2.67 (2H, m), 1.98-2.22 (2H, m), 1.69-1.84

(2H, m), 1.37 (1H, m);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ )  $\delta$ : 172.1 (C=O x 2), 151.8, 138.3, 114.6, 106.2, 58.2, 52.7 (OMe x 2), 41.7, 40.8, 39.7, 33.2, 31.6; MS ( $m/z$ ) 193 ( $\text{M}^+ \text{-CO}_2\text{Me}$ ); Anal. Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C, 66.65; H, 7.99. Found: C, 66.65; H, 8.04.

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