Supplementary Information

Synthesis of 1,2-Bisalkylidenecyclopentanes from 1,6-Allenynes via Stereoselective Addition of Nucleophiles to Ruthenacyclopentenes

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Additional Information

When 1,6-allenynes 3j–l were employed (Table 1, runs 10–12), cycloisomerization products 6j–l and MeOH adduct 7l were obtained in low yields. Formation of these by-products is rationalized by b-hydride elimination from C or E followed by reductive elimination, as explained in CpRu-catalyzed enyne cycloisomerization. See: B. M. Trost and F. D. Toste, J. Am. Chem. Soc., 2000, 122, 714. These results also suggested that the reaction proceeded via ruthenacyclopentenes C and E.

![Chemical Structure](image)

Experimental Procedure and Spectral Data

General Experimental Details

All manipulations were performed under an argon atmosphere unless stated otherwise. THF, Et2O, toluene and DMF were purified under argon using The Ultimate Solvent System (Glass Counter Inc.). MeOH, EtOH, 'PrOH, and 'BuOH were distilled from sodium under argon atmosphere. AcOH was dried by azeotropic removal of water with benzene and then distilled under reduced pressure. All other solvents and reagents were purified when necessary by standard procedures. Chromatography was performed on silica gel 60 (Merck, 230–400 mesh) with the indicated solvent as eluent. IR spectra were obtained on a Perkin-Elmer FTIR 1605 spectrometer. 1H NMR (400 MHz) and 13C NMR (100 MHz) spectroscopy were carried out on a Jeol ECX400 or a Jeol ECS400 NMR spectrometer, and 1H NMR (500 MHz) and 13C NMR (125 MHz) spectroscopy were carried out on a Jeol ECA500 NMR spectrometer. Mass spectra were obtained on a Jeol JMS-100GCv mass spectrometer for EI-LRMS and EI-HRMS, and on a Jeol JMS-T100LP or a Thermo Scientific Exactive mass spectrometer for ESI-LRMS and ESI-HRMS.

General Procedure for Ruthenium-Catalyzed Reactions

**Method A (Without Acid Treatment)**

A mixture of an allenyne and Cp*RuCl(cod) (5 mol% to the allenyne) in degassed MeOH (0.1 M) was stirred at room temperature under argon atmosphere (1 atm). After removal of volatiles, the residue was purified by column chromatography on silica gel to give a product.

**Method B (With Acid Treatment)**

A mixture of an allenyne and Cp*RuCl(cod) (5 mol% to the allenyne) in degassed MeOH (0.1 M) was stirred at room temperature under argon atmosphere (1 atm). To the mixture was added 10% HCl aqueous solution at 0 °C and the mixture was stirred at room temperature for ca. 10 min. To the mixture was added saturated NaHCO3 aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was dried over Na2SO4 and concentrated. The residue was purified by column chromatography on silica gel to give a product.

**Method C (Without Acid Treatment, Table 2)**

A mixture of an allenyne, [Cp*Ru(MeCN)3]PF6 (5 mol% to the allenyne) and a nucleophile (10 equiv. to the allenyne) in degassed THF (0.1 M) was stirred at room temperature under argon...
atmosphere (1 atm). After removal of volatiles, the residue was purified by column chromatography on silica gel to give a product.

**Dimethyl (3E,4Z)-3-(2,2-dimethylpropylidene)-4-(1-methoxyethylidene)cyclopentane-1,1-dicarboxylate (4a).** According to the General Procedure (Method A), a crude product, which was obtained from 3a (19.5 mg, 70.0 µmol) and Cp*RuCl(cod) (1.3 mg, 3.4 µmol) in MeOH (0.70 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give 4a (20.4 mg, 94%) as a colorless oil. IR (neat) 1738, 1656, 1435, 1269, 1205 cm⁻¹; 1H-NMR (500 MHz, CDCl₃) δ 6.41 (t, J = 2.3 Hz, 1H), 3.72 (s, 6H), 3.60 (s, 3H), 3.09 (d, J = 2.3 Hz, 2H), 2.88 (br s, 2H), 1.90 (s, 3H), 1.13 (s, 9H); 13C-NMR (125 MHz, CDCl₃) δ 172.0 (2C), 147.1, 136.1, 133.2, 115.1, 58.2, 54.7, 52.7 (2C), 39.1, 37.8, 32.8, 30.7 (3C), 15.7; ESI-HRMS calcd for C₁₇H₂₆O₅Na 333.16725 [(M+Na)+], found 333.16748.

**Dimethyl 3-acetyl-4-neopentylcyclopent-3-ene-1,1-dicarboxylate (5a).** According to the General Procedure (Method B), a crude product, which was obtained from 3a (21.2 mg, 76.1 µmol), Cp*RuCl(cod) (1.5 mg, 3.9 µmol) in MeOH (0.76 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give 5a (24.5 mg, quant) as a colorless oil. IR (neat) 1734, 1681, 1606, 1268, 1216 cm⁻¹; 1H-NMR (400 MHz, CDCl₃) δ 3.75 (s, 6H), 3.33 (s, 2H), 3.18 (s, 2H), 2.49 (s, 2H), 2.22 (s, 3H), 0.94 (s, 9H); 13C-NMR (125 MHz, CDCl₃) δ 197.2, 171.8 (2C), 152.2, 134.0, 57.2, 53.0 (2C), 47.3, 42.2, 41.9, 33.1, 30.6, 30.3 (3C); ESI-HRMS calcd for C₁₆H₂₄O₅Na 319.15160 [(M+Na)+], found 319.15162.

**1-Acetyl-4,4-bis[(benzyloxy)methyl]-2-neopentylcyclopentene (5b).** According to the General Procedure (Method B), a crude product, which was obtained from 3b (42.6 mg, 105 µmol) and Cp*RuCl(cod) (2.0 mg, 5.3 µmol) in MeOH (1.06 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 5b (36.6 mg, 82%) as a colorless oil. IR (neat) 1678, 1604, 1227, 1100 cm⁻¹; 1H-NMR (500 MHz, CDCl₃) δ 7.36-7.26 (m, 10H), 4.53 (s, 4H), 3.44 (s, 4H), 2.60 (s, 2H), 2.49 (d, J = 6.9 Hz, 4H), 2.17 (s, 3H), 0.93 (s, 9H); 13C-NMR (125 MHz, CDCl₃) δ 198.6, 153.9, 138.5 (2C), 135.2, 128.3 (2C), 127.49 (4C), 127.47 (4C), 73.5 (2C), 73.2 (2C), 46.6, 45.1, 42.5, 40.9, 32.9, 30.6, 30.5 (3C); EI-LRMS m/z 420 (M⁺), 329, 299, 91, 57, 43; EI-HRMS calcd for C₂₈H₃₆O₃ 420.26644, found 420.26483.

**1-Acetyl-4,4-bis(hydroxymethyl)-2-neopentylcyclopentene (5c).** According to the General Procedure (Method B), a crude product, which was obtained from 3c (15.0 mg, 67.5 µmol) and Cp*RuCl(cod) (1.2 mg, 3.2 µmol) in MeOH (0.67 mL) for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt = 1/1) to give 5c (14.1 mg, 87%) as a colorless oil. IR (film, CHCl₃) 3399, 1671, 1600, 1039 cm⁻¹; 1H-NMR (400 MHz, CDCl₃) δ 3.68 (dd, J = 12.7, 10.4 Hz, 4H), 2.87 (br s, 2H), 2.56 (s, 2H), 2.48 (s, 2H), 2.43 (t, J = 2.0 Hz, 2H), 2.20 (s, 3H), 0.93 (s, 9H); 13C-NMR (125 MHz, CDCl₃) δ 198.9, 153.8, 135.2, 69.3 (2C), 46.1, 45.7, 42.7, 40.2, 32.9, 30.6, 30.5 (3C); EI-LRMS m/z 240 (M⁺), 184, 153, 57, 43; EI-HRMS calcd for C₁₄H₂₄O₃ 240.17254, found 240.17175.

**Dimethyl 3-neopentyl-4-propionylcyclopent-3-ene-1,1-dicarboxylate (5d).** According to the General Procedure (Method B), a crude product, which was obtained from 3d (57.1 mg, 195 µmol) and Cp*RuCl(cod) (3.7 mg, 9.7 µmol) in MeOH (1.95 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1) to give 5d (60.7 mg, quant) as a colorless oil.

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IR (neat) 1738, 1685, 1609, 1263, 1202 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.73 (s, 6H), 3.31 (br s, 2H), 3.15 (br s, 2H), 2.48 (q, \(J = 7.2\) Hz, 2H), 2.48 (s, 2H), 1.03 (t, \(J = 7.2\) Hz, 3H), 0.93 (s, 9H);
\(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 199.8, 171.8 (2C), 151.8, 133.6, 57.4, 53.0 (2C), 47.1, 42.1, 41.4, 35.7, 33.0, 30.3 (3C), 7.4; EI-LRMS \(m/z\) 310 (M\(^{+}\)), 281, 251, 197, 195, 59, 57; EI-HRMS calcd for C\(_{17}\)H\(_{26}\)O\(_5\) 310.17802, found 310.17759.

**Dimethyl 3-[(2-hydroxy)ethanoyl]-4-neopentylcyclopent-3-ene-1,1-dicarboxylate (5e).**
According to the General Procedure (Method B), a crude product, which was obtained from 3e (30.6 mg, 104 \(\mu\)mol) and Cp*RuCl(cod) (2.1 mg, 9.7 \(\mu\)mol) in MeOH (1.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 5/2) to give 5e (27.4 mg, 84%) as a colorless oil. IR (neat) 3466, 1737, 1683, 1266, 1207 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 4.29 (d, \(J = 3.4\) Hz, 2H), 3.75 (s, 6H), 4.29 (t, \(J = 3.4\) Hz, 1H), 3.25 (s, 2H), 3.21 (s, 2H), 2.58 (s, 2H), 0.96 (s, 9H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 196.4, 171.5 (2C), 157.3, 129.9, 67.8, 57.6, 53.1 (2C), 47.3, 42.8, 39.3, 33.4, 30.3 (3C); EI-LRMS \(m/z\) 312 (M\(^{+}\)), 281, 253, 221, 59, 57; EI-HRMS calcd for C\(_{16}\)H\(_{24}\)O\(_6\) 312.15729, found 312.15730.

**Dimethyl (3\(E\),4\(Z\))-3-(2,2-dimethylpropylidene)-4-[methoxy(phenyl)methylene]cyclopentane-1,1-dicarboxylate (4f).**
According to the General Procedure (Method A), a crude product, which was obtained from 3f (26.5 mg, 77.8 \(\mu\)mol) and Cp*RuCl(cod) (1.6 mg, 4.2 \(\mu\)mol) in MeOH (0.78 mL) for 16 h, was purified by column chromatography on silica gel (toluene) to give 4f (28.9 mg, quant) as a colorless oil. IR (neat) 1738, 1647, 1435, 1261 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.28 (m, 5H), 6.65 (t, \(J = 2.3\) Hz, 1H), 3.67 (s, 6H), 3.39 (s, 3H), 3.16 (d, \(J = 2.3\) Hz, 2H), 2.85 (s, 2H), 1.19 (s, 9H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.7 (2C), 149.9, 137.8, 135.9, 133.3, 128.9 (2C), 128.2 (2C), 128.0, 119.4, 58.6, 56.6, 52.7 (2C), 38.9, 38.7, 33.0, 30.6 (3C); EI-LRMS \(m/z\) 372 (M\(^{+}\)), 357, 313, 281, 77, 57; EI-HRMS calcd for C\(_{22}\)H\(_{28}\)O\(_5\) 372.19367, found 372.19303.

**Dimethyl (3\(E\),4\(Z\))-3-(2,2-dimethylpropylidene)-4-{methoxy[4-(methoxycarbonyl)phenyl]methylene}cyclopentane-1,1-dicarboxylate (4g).**
According to the General Procedure (Method A), a crude product, which was obtained from 3g (30.2 mg, 75.8 \(\mu\)mol) and Cp*RuCl(cod) (1.3 mg, 3.4 \(\mu\)mol) in MeOH (0.76 mL) for 75 h, was purified by column chromatography on silica gel (hexane/AcOEt = 9/1) to give 4g (27.3 mg, 84%) as a colorless oil. IR (neat) 1736, 1607, 1435, 1279, 1207 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.6\) Hz, 2H), 7.42 (d, \(J = 8.6\) Hz, 2H), 6.67 (t, \(J = 2.3\) Hz, 1H), 3.92 (s, 3H), 3.67 (s, 6H), 3.40 (s, 3H), 3.16 (d, \(J = 2.3\) Hz, 2H), 2.87 (s, 2H), 1.18 (s, 9H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.5 (2C), 166.7, 148.8, 140.7, 139.0, 129.53 (2C), 129.48 (2C), 128.8, 121.8, 58.6, 56.9, 52.7 (2C), 52.1, 38.7, 33.0, 30.6 (3C); EI-LRMS \(m/z\) 430 (M\(^{+}\)), 415, 373, 339, 313; EI-HRMS calcd for C\(_{24}\)H\(_{30}\)O\(_7\) 430.19915, found 430.19910.

**Dimethyl (3\(E\),4\(Z\))-3-(2,2-dimethylpropylidene)-4-{methoxy[4-(methoxy)phenyl]methylene}cyclopentane-1,1-dicarboxylate (4h).**
According to the General Procedure (Method A), a crude product, which was obtained from 3h (20.7 mg, 55.9 \(\mu\)mol) and Cp*RuCl(cod) (1.0 mg, 2.6 \(\mu\)mol) in MeOH (0.56 mL) for 5 h, was purified by column chromatography on silica gel (toluene/CH\(_2\)Cl\(_2\) = 5/1) to give 4h (18.9 mg, 84%) as a colorless oil. IR (neat) 1737, 1645, 1436, 1251, 1173 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.28-7.24 (m, 2H), 6.92-6.88 (m, 2H), 6.61 (t, \(J = 2.3\) Hz, 1H), 3.83 (s, 3H), 3.67 (s, 6H), 3.40 (s, 3H), 3.16 (d, \(J = 2.3\) Hz, 2H), 2.87 (s, 2H), 1.18 (s, 9H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 171.5 (2C), 166.7, 148.8, 140.7, 139.0, 129.53 (2C), 129.48 (2C), 128.8, 121.8, 58.6, 56.9, 52.7 (2C), 52.1, 38.7 (2C), 33.1, 30.5 (3C); EI-LRMS \(m/z\) 430 (M\(^{+}\)), 415, 373, 339, 313; EI-HRMS calcd for C\(_{22}\)H\(_{30}\)O\(_7\) 430.19915, found 430.19910.
6H), 3.39 (s, 3H), 3.15 (d, J = 2.3 Hz, 2H), 2.84 (br s, 2H), 1.18 (s, 9H); 13C-NMR (125 MHz, CDCl3) δ 171.8 (2C), 159.2, 149.7, 137.3, 133.3, 130.2 (2C), 128.2, 118.7, 113.6 (2C), 58.6, 56.5, 55.2, 52.7 (2C), 38.9, 38.8, 33.0, 30.6 (3C); EI-LRMS m/z 402 (M+), 387, 371, 345, 311, 295, 59; EI-HRMS calcd for C23H30O6 402.20424, found 402.20315.

**Dimethyl (3Z,4E)-3-(2,2-dimethylpropylidene)-4-[methoxy(methoxycarbonyl)methylene]cyclopentane-1,1-dicarboxylate (4i).** According to the General Procedure (Method A), a crude product, which was obtained from 3i (28.3 mg, 87.8 µmol) and Cp*RuCl(cod) (1.8 mg, 4.8 µmol) in MeOH (0.88 mL) for 72 h, was purified by column chromatography on silica gel (hexane/AcOEt = 8/1) to give 4i (19.5 mg, 63%) as a colorless oil. IR (neat) 1738, 1634, 1436, 1268, 1202 cm⁻¹; 1H-NMR (500 MHz, CDCl3) δ 6.87 (t, J = 2.3 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 6H), 3.56 (s, 3H), 3.36 (s, 2H), 3.10 (d, J = 2.3 Hz, 2H), 1.15 (s, 9H); 13C-NMR (125 MHz, CDCl3) δ 171.6 (2C), 165.3, 145.3, 140.1, 138.7, 133.2, 58.2, 58.1, 52.8 (2C), 51.7, 38.8, 38.0, 33.4, 30.2 (3C); EI-LRMS m/z 354 (M+), 297, 59, 57; EI-HRMS calcd for C18H26O7 354.16785, found 354.16753.

**Dimethyl 3-acetyl-4-ethylcyclopent-3-ene-1,1-dicarboxylate (5j) and (E)-Dimethyl 4-ethylidene-3-vinylcyclopent-2-ene-1,1-dicarboxylate (6j).** According to the General Procedure (Method B), a crude product, which was obtained from 3j (51.0 mg, 216 µmol) and Cp*RuCl(cod) (4.2 mg, 11.1 µmol) in MeOH (2.15 mL) for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 5j (44.6 mg, 81%) as a colorless oil, and 6j (3.1 mg, 6%) as a colorless oil, respectively. 5j: IR (neat) 1737, 1683, 1435, 1263, 1201 cm⁻¹; 1H-NMR (500 MHz, CDCl3) δ 3.71 (s, 6H), 3.30-3.28 (m, 2H), 3.15 (br s, 2H), 2.51 (q, J = 7.5 Hz, 2H), 2.20 (s, 3H), 1.03 (t, J = 7.5 Hz, 3H); 13C-NMR (125 MHz, CDCl3) δ 196.5, 171.8 (2C), 155.6, 131.6, 56.5, 52.9 (2C), 44.8, 41.8, 30.2, 23.0, 12.0; EI-LRMS m/z 254 (M+), 195, 163, 152, 135, 120, 117; EI-HRMS calcd for C13H18O5 268.11542, found 268.11512. 6j: IR (film, CHCl3) 1737, 1435, 1252, 1056 cm⁻¹; 1H-NMR (500 MHz, CDCl3) δ 6.35 (dd, J = 17.6, 11.3 Hz, 1H), 6.07 (s, 1H), 5.63 (dd, J = 17.6, 1.7 Hz, 1H), 5.29 (dd, J = 11.3, 1.7 Hz, 1H), 3.75 (s, 6H), 3.17 (br s, 2H), 1.73 (d, J = 6.9 Hz, 3H); 13C-NMR (125 MHz, CDCl3) δ 171.2 (2C), 145.1, 141.4, 128.5, 127.3, 118.6, 116.0, 63.3, 52.9 (2C), 35.9, 14.8; EI-LRMS m/z 236 (M+), 177, 145, 117; EI-HRMS calcd for C13H16O4 236.10486, found 236.10446.

**Dimethyl 3-acetyl-4-propylcyclopent-3-ene-1,1-dicarboxylate (5k) and (E)-Dimethyl 4-ethylidene-3-[((E)-prop-1-enyl]cyclopent-2-ene-1,1-dicarboxylate (6k).** According to the General Procedure (Method B), a crude product, which was obtained from 3k (56.5 mg, 226 µmol) and Cp*RuCl(cod) (4.3 mg, 11.3 µmol) in MeOH (2.25 mL) for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 5k (46.8 mg, 77%) as a colorless oil, and 6k (5.1 mg, 9%) as a colorless oil, respectively. 5k: IR (neat) 1737, 1683, 1435, 1253, 1201 cm⁻¹; 1H-NMR (500 MHz, CDCl3) δ 6.53 (dd, J = 17.6, 1.7 Hz, 1H), 5.62-5.57 (m, 1H), 5.29 (dd, J = 11.3, 1.7 Hz, 1H), 3.75 (s, 6H), 3.17 (br s, 2H), 1.73 (d, J = 6.9 Hz, 3H); 13C-NMR (125 MHz, CDCl3) δ 171.2 (2C), 145.1, 141.4, 128.5, 127.3, 118.6, 116.0, 63.3, 52.9 (2C), 35.9, 14.8; EI-LRMS m/z 268 (M+), 237, 209, 177, 145, 117; EI-HRMS calcd for C14H20O5 268.13107, found 236.10464. 6k: IR (neat) 1737, 1683, 1435, 1253, 1172 cm⁻¹; 1H-NMR (500 MHz, CDCl3) δ 6.15 (dq, J = 15.5, 6.6 Hz, 1H), 6.02 (dq, J = 15.5, 1.7 Hz, 1H), 5.97 (s, 1H), 5.57 (tt, J =
2.5, 6.9 Hz, 1H), 3.74 (s, 6H), 3.16-3.14 (m, 2H), 1.81 (dd, \( J = 6.6, 1.7 \) Hz, 3H), 1.72 (d, \( J = 6.9 \) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) 171.4 (2C), 144.8, 141.8, 130.4, 125.7, 122.3, 115.6, 63.3, 52.9 (2C), 35.8, 18.7, 14.8; EI-LRMS \textit{m}/\textit{z} 250 (M\(^+\)), 191, 159, 131, 59; EI-HRMS calcd for \( \text{C}_{14}\text{H}_{18}\text{O}_4 \) 250.12051, found 250.12019.

### Dimethyl 3-acetyl-4-isobutylcyclopent-3-ene-1,1-dicarboxylate (5l), (E)-Dimethyl 4-ethylidene-3-(2-methylprop-1-enyl)cyclopent-2-ene-1,1-dicarboxylate (6l), and Dimethyl 3-(1-methoxyethyl)-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (7l).

According to the General Procedure (Method B), a crude product, which was obtained from 3l (57.8 mg, 219 \( \mu \)mol) and Cp*RuCl(cod) (4.2 mg, 11.1 \( \mu \)mol) in MeOH (2.2 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 5l (52.0 mg, 84%) as a colorless oil, 6l (3.5 mg, 6%) as a colorless oil, and 7l (2.1 mg, 3%) as a colorless oil, respectively.

5l: IR (neat) 1737, 1684, 1435, 1254, 1201 cm\(^{-1}\); \(^{1}\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) 3.73 (s, 6H), 3.33-3.32 (m, 2H), 3.14-3.13 (m, 2H), 2.42-2.39 (m, 2H), 2.23 (s, 3H), 1.85 (septet, \( J = 6.8 \) Hz, 1H), 0.88 (d, \( J = 6.8 \) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) 196.8, 171.9 (2C), 153.5, 133.1, 56.7, 53.0 (2C), 45.6, 41.9, 38.5, 30.5, 27.6, 22.5 (2C); EI-LRMS \textit{m}/\textit{z} 282 (M\(^+\)), 267, 251, 223, 191, 163, 59, 43; EI-HRMS calcd for \( \text{C}_{15}\text{H}_{22}\text{O}_5 \) 282.14672, found 282.14611.

6l: IR (neat) 1736, 1436, 1250, 1172 cm\(^{-1}\); \(^{1}\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) 5.73 (br s, 1H), 3.75 (s, 6H), 3.13-3.11 (m, 2H), 1.82 (br s, 3H), 1.80-1.78 (m, 3H), 1.71 (d, \( J = 7.0 \) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) 171.6 (2C), 144.2, 143.2, 139.8, 128.5, 116.4, 115.6, 63.8, 52.9 (2C), 35.0, 26.5, 20.1, 14.7; EI-LRMS \textit{m}/\textit{z} 264 (M\(^+\)), 205, 173, 145, 59; EI-HRMS calcd for \( \text{C}_{15}\text{H}_{20}\text{O}_4 \) 264.13616, found 264.13546.

7l: IR (neat) 1737, 1435, 1259, 1199, 1087 cm\(^{-1}\); \(^{1}\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) 5.77 (br s, 1H), 4.13 (q, \( J = 6.6 \) Hz, 1H), 3.74 (s, 3H), 3.74 (s, 3H), 3.31-3.17 (m, 2H), 3.15 (s, 3H), 3.01 (br s, 2H), 1.80 (br s, 3H), 1.74 (br s, 3H), 1.22 (d, \( J = 6.6 \) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) 172.6 (2C), 136.3, 136.2, 134.5, 118.5, 72.4, 57.7, 55.8, 52.80, 52.75, 44.4, 38.1, 27.0, 20.0, 19.2; EI-LRMS \textit{m}/\textit{z} 296 (M\(^+\)), 281, 265, 204, 59; EI-HRMS calcd for \( \text{C}_{16}\text{H}_{24}\text{O}_5 \) 296.16237, found 296.16201.

### Dimethyl 3-acetyl-4-[(methoxycarbonyl)methyl]cyclopent-3-ene-1,1-dicarboxylate (5m).

According to the General Procedure (Method B), a crude product, which was obtained from 3m (69.8 mg, 249 \( \mu \)mol) and Cp*RuCl(cod) (4.8 mg, 12.6 \( \mu \)mol) in MeOH (2.5 mL) for 85 h, was purified by column chromatography on silica gel (hexane/AcOEt = 8/1) to give 5m (19.8 mg, 27%) as a colorless oil. IR (neat) 1737, 1685, 1436, 1257, 1203 cm\(^{-1}\); \(^{1}\)H-NMR (500 MHz, CDCl\(_3\)) \( \delta \) 3.76 (s, 6H), 3.68 (s, 3H), 3.65-3.63 (m, 2H), 3.39-3.38 (m, 2H), 3.27-3.25 (m, 2H), 2.23 (s, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)) \( \delta \) 196.6, 171.5 (2C), 170.1, 144.8, 134.4, 57.0, 53.1 (2C), 52.0, 52.80, 52.75, 44.4, 38.1, 27.0, 20.1, 14.7; EI-LRMS \textit{m}/\textit{z} 298 (M\(^+\)), 296.10525, found 298.10558.

### Compound 4f-D.

According to the General Procedure (Method A), a crude product, which was obtained from 3f (26.3 mg, 77.3 \( \mu \)mol) and Cp*RuCl(cod) (1.5 mg, 3.9 \( \mu \)mol) in MeOH (0.77 mL) for 44 h, was purified by column chromatography on silica gel (toluene/\( \text{CH}_2\text{Cl}_2 \) = 5/1) to give 4f-D (24.0 mg, 83%) as a colorless oil. IR (neat) 1737, 1435, 136.3, 136.2, 134.5, 118.5, 72.4, 57.7, 55.8, 52.80, 52.75, 44.4, 38.1, 27.0, 20.0, 19.2; EI-LRMS \textit{m}/\textit{z} 296 (M\(^+\)), 281, 265, 204, 59; EI-HRMS calcd for \( \text{C}_{16}\text{H}_{24}\text{O}_5 \) 296.16237, found 296.16201.
Dimethyl 3-ethyl-4-propionylcyclopent-3-en-1,1-dicarboxylate (5n). According to the General Procedure (Method B), a crude product, which was obtained from 3n (50.0 mg, 200 µmol) and Cp*RuCl(cod) (3.8 mg, 10 µmol) in MeOH (2.0 mL) for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 5n (45.9 mg, 86%) as a colorless oil. IR (neat) 1737, 1683, 1435, 1263, 1201 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 3.72 (s, 6H), 3.30 (br s, 2H), 3.13 (br s, 2H), 2.52 (q, J = 7.4 Hz, 2H), 2.48 (q, J = 7.6 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H), 1.03 (t, J = 7.6 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 199.4, 171.9 (2C), 155.3, 131.0, 56.8, 53.0 (2C), 44.6, 41.5, 35.4, 23.0, 12.0, 7.4; EI-LRMS m/z 269 [(M+H)+], 268 (M+), 209, 177, 152, 149, 59, 57; EI-HRMS calcd for C₁₄H₂₀O₅ 268.13107, found 268.13076.

Compound 4a and 5a (Table 2, run 1). According to the General Procedure (Method C), a crude product, which was obtained from 3a (28.1 mg, 101 µmol), [Cp*Ru(MeCN)₃]PF₆ (2.6 mg, 5.2 µmol), and MeOH (41 µL, 1.01 mmol) in THF (1.0 mL) for 2 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et₃N) to give 4a (27.0 mg, 86%) as a colorless oil and 5a (2.2 mg, 7%) as a colorless oil, respectively.

Dimethyl (3E,4Z)-3-(2,2-dimethylpropylidene)-4-(1-ethoxyethylidene)cyclopentane-1,1-dicarboxylate (4o). According to the General Procedure (Method C), a crude product, which was obtained from 3a (25.8 mg, 92.7 µmol), [Cp*Ru(MeCN)₃]PF₆ (2.3 mg, 4.6 µmol), and EtOH (54 µL, 0.92 mmol) in THF (0.92 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et₃N) to give 4o (22.2 mg, 74%) as a colorless oil and 5a (4.4 mg, 16%) as a colorless oil, respectively. IR (neat) 1738, 1655, 1435, 1259, 1201 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 6.53 (t, J = 2.2 Hz, 1H), 3.84 (q, J = 7.0 Hz, 2H), 3.72 (s, 6H), 3.09 (d, J = 2.2 Hz, 2H), 2.88 (br s, 2H), 1.90 (br s, 3H), 1.28 (t, J = 7.0 Hz, 3H), 1.13 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 172.0 (2C), 146.4, 136.2, 133.2, 115.5, 62.9, 58.2, 52.7 (2C), 39.1, 37.7, 32.8, 30.7 (3C), 16.2, 15.2; ESI-HRMS calcd for C₁₈H₂₉O₅ [(M+H)+] 325.20150, found 325.20155.

Dimensional 5p. According to the General Procedure (Method C), a crude product, which was obtained from 3a (27.1 mg, 97.4 µmol), [Cp*Ru(MeCN)₃]PF₆ (2.5 mg, 5.0 µmol), and iPrOH (75 µL, 0.97 mmol) in THF (0.97 mL) for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et₃N) to give 5a (1.4 mg, 5%) as a colorless oil. 4p: IR (neat) 1739, 1655, 1435, 1269, 1213 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 6.61 (t, J = 2.0 Hz, 1H), 4.24 (septet, J = 6.1 Hz, 1H), 3.71 (s, 3H), 3.71 (s, 3H), 3.07 (d, J = 2.0 Hz, 2H), 2.87 (br s, 2H), 1.85 (s, 3H), 1.20 (d, J = 6.1 Hz, 6H), 1.11 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 172.0 (2C), 144.7, 136.3, 132.8, 118.3, 69.2, 58.3, 52.7 (2C), 39.0, 37.1, 30.7 (3C), 22.6 (2C), 16.7; ESI-HRMS calcd for C₁₉H₃₁O₅ [(M+H)+] 339.21715, found 339.21695.
Dimethyl (3Z,4E)-3-(1-acetoxyethylidene)-4-(2,2-dimethylpropylidene)cyclopentane-1,1-dicarboxylate (4q). According to the General Procedure (Method C), a crude product, which was obtained from 3a (28.0 mg, 101 µmol), [Cp*Ru(MeCN)₃]PF₆ (2.7 mg, 5.4 µmol), and AcOH (57 µL, 1.00 mmol) in THF (1.0 mL) for 19 h, was purified by column chromatography on silica gel (hexane/AcOEt = 15/1 with 1% Et₃N) to give 4q (25.4 mg, 75%) as a white solid. mp: 110-112 °C; IR (film, CHCl₃) 1745, 1736, 1436, 1370 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.99 (t, J = 2.2 Hz, 1H), 3.72 (s, 6H), 3.06 (d, J = 2.2 Hz, 2H), 2.93 (br s, 2H), 2.12 (s, 3H), 1.93 (s, 3H), 1.10 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 171.5 (2C), 168.5, 139.4, 138.2, 132.2, 124.5, 57.9, 52.8 (2C), 38.6, 37.2, 32.9, 30.5 (3C), 21.0, 18.9; EI-LRMS m/z 338 (M⁺), 296, 281, 240, 181; EI-HRMS calcd for C₁₈H₂₆O₆ 338.17294, found 338.17268.

Dimethyl (3Z,4E)-3-(1-chloroethylidene)-4-(2,2-dimethylpropylidene)cyclopentane-1,1-dicarboxylate (4r). According to the General Procedure (Method C), a crude product, which was obtained from 3a (27.7 mg, 99.5 µmol), [Cp*Ru(MeCN)₃]PF₆ (2.5 mg, 5.0 µmol), and a solution of HCl in Et₂O (1.0 mL, 1.0 M, 1.0 mmol) in THF (1.0 mL) for 6 h, was purified by column chromatography on silica gel (hexane/AcOEt = 20/1 with 1% Et₃N) to give 4r (20.6 mg, 61%) as a colorless oil. IR (film, CHCl₃) 1739, 1640, 1435, 1263, 1206 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 6.66 (t, J = 2.3 Hz, 1H), 3.74 (s, 6H), 3.13 (d, J = 2.3 Hz, 2H), 2.98 (d, J = 1.1 Hz, 2H), 2.15 (br s, 3H), 1.14 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 171.5 (2C), 140.3, 132.5, 132.1, 121.1, 57.5, 52.9 (2C), 39.7, 38.7, 33.1, 30.5 (3C), 25.9; EI-LRMS m/z 314 (M⁺), 279, 278, 219, 195, 59; EI-HRMS calcd for C₁₆H₂₃ClO₄ 314.12849, found 314.12726.
Preparation of 1,6-Allenynes

A new synthetic route to 1,6-allenynes bearing dialkyl malonate moieties has been established (Scheme S1). Thus, methyl α-allenylcarboxylate 9 was easily prepared from the corresponding alcohol 8 and trimethyl orthoacetate via the Johnson-Claisen rearrangement. Next, 9 was treated with 2 equivalents of LHMDS at -78 °C, then the anion of 9 was successively reacted with methyl chloroformate and propargyl halide 10 in a one pot to give 1,6-allenylene 3.

\[
\begin{align*}
\text{cat. EtCO}_2\text{H} & \quad \text{MeC(OMe)}_3, 110 ^\circ\text{C} \\
\text{9} & \quad \text{MeO}_2\text{C} \quad \text{MeO}_2\text{C} \\
1) \text{LHMDS (2 equiv.)} & \quad 2) \text{ClCO}_2\text{Me} \\
\text{R}^2 & \quad \text{R}^2 \\
3) \text{MeC(OMe)}_3 \\
\text{10} & \quad \text{MeO}_2\text{C} \\
& \quad \text{MeO}_2\text{C} \\
& \quad \text{MeO}_2\text{C} \\
& \quad \text{MeO}_2\text{C}
\end{align*}
\]

Scheme S1. General procedure for the synthesis of 1,6-allenynes 3

\[
\begin{align*}
\text{cat. EtCO}_2\text{H} & \quad \text{MeC(OMe)}_3, 110 ^\circ\text{C} \\
\text{9} & \quad \text{MeO}_2\text{C} \quad \text{MeO}_2\text{C} \\
1) \text{LHMDS (2 equiv.)} & \quad 2) \text{ClCO}_2\text{Me} \\
\text{Bu} & \quad \text{Bu} \\
3) \text{MeC(OMe)}_3 \\
\text{10} & \quad \text{MeO}_2\text{C} \\
& \quad \text{MeO}_2\text{C} \\
& \quad \text{MeO}_2\text{C} \\
& \quad \text{MeO}_2\text{C}
\end{align*}
\]

Scheme S2. Preparation of 3a

Methyl 6,6-dimethylhepta-3,4-dienoate (9a). Into a flask equipped with a Dean-Stark trap were placed 8a (2.243 g, 20.00 mmol), trimethyl orthoacetate (15.0 mL, 120 mmol), and propanoic acid (0.30 mL, 4.02 mmol). The mixture was stirred and heated at 110 °C for 48 h and remaining trimethyl orthoacetate was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give 9a (2.840 g, 84%) as a colorless oil. IR (neat) 1968, 1737, 1435, 1229, 1061 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.27 (dt, \(J = 6.5, 7.2\) Hz, 1H), 5.18 (dt, \(J = 6.5, 2.9\) Hz, 1H), 3.69 (s, 3H), 3.02 (dd, \(J = 7.2, 2.9\) Hz, 2H), 1.02 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 202.3, 172.0, 104.2, 85.7, 51.8, 35.1, 31.8, 30.0 (3C); EI-LRMS \(m/z\) 168 (M⁺), 153, 140, 125, 111, 109, 57; EI-HRMS calcd for C₁₀H₁₆O₂ 168.11503, found 168.11467.

5,5-Bis(methoxycarbonyl)-9,9-dimethyldeca-6,7-dien-2-yne (3a). To a solution of 9a (917.7 mg, 5.455 mmol) in THF (6.4 mL) was slowly added a solution of LHMDS in THF (1.60 M, 7.1 mL, 11.4 mmol) and the mixture was stirred at the same temperature for 25 min. To the mixture was slowly added methyl chloroformate (0.42 mL, 5.44 mmol) at -78 °C, and the mixture was stirred at the same temperature for 5 min. To the mixture was slowly added 10a (1.950 g, 10.84 mmol) in THF (3.0 mL) at -78 °C, and the mixture was allowed to warm to room temperature over 1 h and stirred at the same temperature overnight. To the mixture was added saturated NH₄Cl aqueous solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed

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1. For the synthesis of 1,6-allenylene via direct coupling of malonate derivative and bromoallenes, see: V. Pardo-Rodríguez, J. Marco-Martínez, E. Buñuel and D. J. Cárdenas, Org. Lett., 2009, 11, 4548.
with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give 3a (915.3 mg, 60%) as a colorless oil.

IR (neat) 1968, 1741, 1435, 1230, 1203 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.79 (d, J = 6.3 Hz, 1H), 5.38 (d, J = 6.3 Hz, 1H), 3.74 (s, 6H), 2.89-2.79 (m, 2H), 1.73 (t, J = 2.6 Hz, 3H), 1.03 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.4, 169.8, 169.7, 107.5, 91.8, 78.5, 73.7, 58.1, 52.82, 52.80, 32.2, 29.8 (3C), 25.3, 3.5; ESI-HRMS calcd for C₁₆H₂₂O₄Na 301.1410, found 301.1407.

~ Preparation of 3b and 3c ~

5,5-Bis(hydroxymethyl)-9,9-dimethyldeca-6,7-dien-2-yne (3c). To a solution of LiAlH₄ (50.1 mg, 1.32 mmol) in Et₂O (2.7 mL) was added to a solution of 3a (118.4 mg, 425.4 µmol) in Et₂O (1.5 mL) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. The mixture was added Na₂SO₄·10H₂O/Celite® (1 to 1 mixture) at 0 °C, and the resulting mixture was stirred at room temperature overnight. The mixture was filtered, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 2/1) to give 3c (58.1 mg, 61%) as a white solid. mp; 84-86 °C; IR (film, CHCl₃) 3310, 1959, 1037 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.29 (d, J = 6.5 Hz, 1H), 5.19 (d, J = 6.5 Hz, 1H), 3.71 (s, 4H), 2.39-2.30 (m, 2H), 2.08-2.04 (br, 2H), 1.79 (t, J = 2.6 Hz, 3H), 1.05 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.5, 105.7, 94.6, 78.4, 75.4, 67.6, 67.5, 44.4, 31.7, 30.1 (3C), 23.4, 3.6; EI-LRMS m/z 207 [(M-Me)+], 191, 57; EI-HRMS calcd for C₁₃H₁₉O₂ 207.13850, found 207.13806.

5,5-Bis[(benzyloxy)methyl]-9,9-dimethyldeca-6,7-dien-2-yne (3b). To a suspension of NaH (60% dispersion in mineral oil, 15.8 mg, 395 µmol) in DMF (0.60 mL) was added a solution of 3c (25.9 mg, 117 µmol) in DMF (0.60 mL) at 0 °C, and the mixture was stirred at the same temperature for 1 h. The mixture were slowly added BnBr (41.5 µL, 349 µmol) at 0 °C, and the resulting mixture was stirred at room temperature for 11 h. To the mixture was added saturated NH₄Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 3b (46.0 mg, 98%) as a colorless oil. IR (neat) 1959, 1101, 735, 697 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 7.32-7.30 (m, 8H), 7.28-7.24 (m, 2H), 5.33 (d, J = 6.3 Hz, 1H), 5.21 (d, J = 6.3 Hz, 1H), 4.52 (d, J = 2.1 Hz, 4H), 3.49 (d, J = 4.1 Hz, 4H), 2.42-2.33 (m, 2H), 1.74 (t, J = 2.6 Hz, 3H), 1.02 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.2, 138.8 (2C), 128.2 (4C), 127.38 (2C), 127.34 (2C), 127.27 (2C), 105.1, 95.5, 77.4, 76.0, 73.3 (2C), 73.2, 72.9, 43.5, 31.7, 30.1 (3C), 24.0, 3.6; EI-LRMS m/z 387 [(M-Me)+], 349, 311, 281, 255, 91, 57; EI-HRMS calcd for C₂₇H₃₄O₂ 387.23240, found 387.23210.
~ Preparation of 3d ~

6,6-Bis(methoxycarbonyl)-2,2-dimethylundeca-3,4-dien-8-yne (3d). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9a (339.2 mg, 2.645 mmol), LHMDS in THF (1.00 M, 4.40 mL, 4.40 mmol), methyl chloroformate (159 µL, 2.06 mmol), and 10d (724 mg, 3.73 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give 3d (379.6 mg, 64%) as a colorless oil. IR (neat) 1968, 1737, 1435, 1229, 1061 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.78 (d, J = 6.3 Hz, 1H), 5.36 (d, J = 6.3 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 2.88-2.78 (m, 2H), 2.09 (tq, J = 2.5, 7.6 Hz, 2H), 1.05 (t, J = 7.6 Hz, 3H), 1.02 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.3, 169.8, 169.7, 107.5, 91.8, 84.6, 74.0, 58.1, 52.7 (2C), 32.1, 29.8 (3C), 25.3, 14.5, 12.3; EI-LRMS m/z 293 [(M+H)⁺], 233, 225, 201, 173, 59, 57; EI-HRMS calcd for C₁₇H₂₅O₄ 293.17528, found 293.17454.

~ Preparation of 3e ~

5,5-bis(methoxycarbonyl)-1-((tert-butyldimethylsilyloxy)-9,9-dimethyldeca-6,7-dien-2-yne (11). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9a (445.6 mg, 2.649 mmol), LHMDS in THF (1.00 M, 5.40 mL, 5.40 mmol), methyl chloroformate (205 µL, 2.65 mmol), and the crude 10e (819.9 mg, 3.12 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give 11 (119.1 mg, 11%) as a colorless oil. IR (neat) 1968, 1742, 1318, 1230, 1081 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.79 (d, J = 6.3 Hz, 1H), 5.37 (d, J = 6.3 Hz, 1H), 4.23 (t, J = 2.0 Hz, 2H), 3.732 (s, 3H), 3.728 (s, 3H), 2.97-2.87 (m, 2H), 1.02 (s, 9H), 0.88 (s, 9H), 0.08 (s, 6H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.4, 169.6, 169.4, 107.7, 91.7, 81.4, 79.7, 57.7, 52.9 (2C), 51.8, 32.2, 29.9 (3C), 25.8 (3C), 25.3, 18.2, -5.2 (2C); EI-LRMS m/z 351 [(M⁻⁻⁻⁻Bu)⁺], 277, 225, 57; EI-HRMS calcd for C₁₈H₂₇O₅Si 351.16277, found 351.16276.

5,5-Bis(methoxylcarbonyl)-9,9-dimethyldeca-6,7-dien-2-yn-1-ol (3e). To a solution of 11 (47.2 mg, 115 µmol) in EtOH (3.1 mL) was added 10% HCl aqueous solution (0.35 mL) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. To the mixture was added saturated NaHCO₃ aqueous solution, and the mixture was diluted with MeOH, dried over Na₂SO₄, and concentrated.

The residue was purified by column chromatography on silica gel (hexane/Et₂O = 5/3) to give 3e (32.4 mg, 95%) as a colorless oil. IR (film, CHCl₃) 3470, 1739, 1232, 1018 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.77 (d, J = 6.3 Hz, 1H), 5.39 (d, J = 6.3 Hz, 1H), 4.18 (d, J = 2.0 Hz, 2H), 3.74 (s, 3H), 2.91 (dt, J = 1.8 Hz, 2.0 Hz, 2H), 1.99 (br s, 1H), 1.02 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.4, 169.6, 169.5, 107.8, 91.6, 81.2, 80.8, 57.7, 52.94, 52.93, 51.0, 32.2, 29.8 (3C), 25.2; EI-LRMS m/z 225 [(M-C₄H₅O)+], 203, 59, 57; EI-HRMS calcd for C₁₂H₁₇O₄ 225.11268, found 225.11269.

~ Preparation of 3f ~

\[
\begin{align*}
\text{MeO}_2\text{C} & \equiv \equiv \text{Bu} \\
9a & \rightarrow \text{MeO}_2\text{C} & \equiv \equiv \text{Bu} \\
& \text{1) LHMDS (2 equiv.)} \\
& \text{2) ClCO}_2\text{Me} \\
& \text{3) Br} \\
& \text{PhI cat. Pd(PPh}_3)_4 \text{ cat. CuI} \\
& \text{Et}_3\text{N} \\
& \text{MeO}_2\text{C} & \equiv \equiv \text{Bu} \\
12 & \rightarrow \text{MeO}_2\text{C} & \equiv \equiv \text{Bu} \\
& \text{3f: 89%}
\end{align*}
\]

**Scheme S6. Preparation of 3f**

4,4-Bis(methoxylcarbonyl)-8,8-dimethylnona-5,6-diene-1-yne (12). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9a (169.2 mg, 1.006 mmol), LHMDS in THF (1.00 M, 2.00 mL, 2.00 mmol), methyl chloroformate (77 µL, 1.00 mmol), and 3-bromopropyne (95 µL, 1.07 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give 12 (92.3 mg, 35%) as a colorless oil. IR (neat) 3291, 1967, 1740, 1436, 1231, 1204 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.80 (d, J = 6.3 Hz, 1H), 5.40 (d, J = 6.3 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.88 (d, J = 2.6, 1.4 Hz, 2H), 1.98 (t, J = 2.6 Hz, 1H), 1.03 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.5, 169.4, 169.3, 107.9, 91.5, 79.2, 71.0, 57.6, 52.90, 52.88, 32.2, 29.9 (3C), 24.8; EI-LRMS m/z 264 (M⁺), 205, 173, 145, 57; EI-HRMS calcd for C₁₅H₂₀O₄ 264.13616, found 264.13557.

4,4-Bis(methoxylcarbonyl)-8,8-dimethylnona-1-phenyl-5,6-diene-1-yne (3f). To a solution of 12 (66.0 mg, 250 µmol) and iodobenzene (31 µL, 277 µmol) in Et₃N (2.5 mL) were added CuI (8.2 mg, 43 µmol) and Pd(PPh₃)₄ (3.1 mg, 2.7 µmol), and the mixture was degassed by Freeze Pump Thaw cycle. The resulting reaction mixture was stirred at 40 °C for 12 h under argon (1 atm) and concentrated. To the mixture was added saturated NH₄Cl aqueous solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 9/1) to give 3f (75.3 mg, 89%) as a colorless oil. IR (neat) 1967, 1740, 1201 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 7.36-7.23 (m, 5H), 5.86 (d, J = 6.3 Hz, 1H), 5.41 (d, J = 6.3 Hz, 1H), 3.77 (s, 6H), 3.12 (dd, J = 17.0, 21.0 Hz, 2H), 1.05 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.5, 169.6, 169.5, 131.6 (2C), 128.1 (2C), 127.9, 123.3, 107.8, 91.8, 84.5, 83.1, 58.0, 52.90, 52.89, 32.2, 29.9 (3C), 25.9; EI-LRMS m/z 340 (M⁺), 325, 281, 249, 225, 221, 59, 57; EI-HRMS calcd for C₂₁H₂₅O₄ 340.16746, found 340.16773.
~ Preparation of 3g ~

![Scheme S7. Preparation of 3g](image)

4,4-Bis(methoxylcarbonyl)-1-(4-methoxycarbonylphenyl)-8,8-dimethylnona-5,6-diene-1-ynyl (3g). To a solution of 12 (71.7 mg, 271 μmol) and methyl p-iodobenzoate (78.1 mg, 298 μmol) in Et₃N (2.7 mL) were added CuI (8.0 mg, 42 μmol) and PdCl₂(PPh₃)₂ (1.9 mg, 2.7 μmol), and the mixture was degassed by Freeze Pump Thaw cycle. The resulting reaction mixture was stirred at 40 °C for 12 h under argon (1 atm) and concentrated. To the mixture was added saturated NH₄Cl aqueous solution, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 9/1) to give 3g (94.3 mg, 87%) as a colorless oil. IR (neat) 1967, 1740, 1727, 1276, 1201 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 5.85 (d, J = 6.3 Hz, 1H), 5.42 (d, J = 6.3 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 6H), 3.13 (dd, J = 17.0, 19.5 Hz, 2H), 1.03 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.5, 169.5, 169.4, 166.5, 131.5 (2C), 129.3, 129.2, 128.0 (2C), 107.9, 91.7, 88.2, 82.5, 57.8, 52.94, 52.93, 52.1, 32.2, 29.8 (3C), 25.8; EI-LRMS m/z 398 (M⁺), 367, 339, 307, 279, 263, 225; EI-HRMS calcd for C₂₃H₂₆O₆ 398.17294, found 398.17278.

~ Preparation of 3h ~

![Scheme S8. Preparation of 3h](image)

4,4-Bis(methoxylcarbonyl)-1-(4-methoxyphenyl)-8,8-dimethylnona-5,6-diene-1-ynyl (3h). Similar to the synthesis of 3f from 12, a crude product, which was obtained from 12 (55.5 mg, 210 μmol), p-iodoanisole (60.9 mg, 260 μmol), CuI (6.6 mg, 35 μmol), and Pd(PPh₃)₄ (2.2 mg, 1.9 μmol) in Et₃N (2.1 mL) at 40 °C for 12 h, was purified by column chromatography on silica gel (toluene) to give 3h (89.2 mg, quant) as a colorless oil. IR (neat) 1968, 1739, 1248, 1202 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 7.29-7.26 (m, 2H), 6.80-6.76 (m, 2H), 5.86 (d, J = 6.3 Hz, 1H), 5.41 (d, J = 6.3 Hz, 1H), 3.78 (s, 3H), 3.764 (s, 3H), 3.761 (s, 3H), 3.14-3.06 (m, 2H), 1.05 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.4 169.65, 169.56, 159.2, 133.0 (2C), 115.4, 113.7 (2C), 107.7, 91.8, 83.1, 82.9, 58.1, 55.2, 52.8 (2C), 32.2, 29.9 (3C), 25.9; EI-LRMS m/z 370 (M⁺), 355, 311, 279, 263, 251, 225; EI-HRMS calcd for C₂₂H₂₅O₅ 370.17802, found 370.17762.
**~ Preparation of 3i ~**

Methyl 5,5-bis(methoxycarbonyl)-9,9-dimethyldeca-6,7-dien-2-ynecarboxylate (3i). To a solution of i-Pr₂NH (237 µL, 1.68 mmol) in THF (2.0 mL) was slowly added a solution of n-BuLi in hexane (1.65 M, 1.02 mL, 1.68 mmol) at -78 °C, and the mixture was stirred at 0 °C for 30 min. To a solution of 12 (93.1 mg, 352 µmol) in THF (3.0 mL) was slowly added quarter amount of the mixture at -78 °C, and the resulting mixture was stirred at the same temperature for 1 h. The mixture was slowly added methyl chloroformate (54.5 µL, 705 µmol) at -78 °C, and the mixture was stirred at the same temperature for 30 min and allowed to warm to room temperature over 1 h and stirred at the same temperature for 8 h. To the mixture was added saturated NH₄Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10/1) to give 3i (94.3 mg, 83%) as a colorless oil. IR (neat) 1967, 1741, 1719, 1262, 1204 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.77 (d, J = 6.3 Hz, 1H), 5.43 (d, J = 6.3 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.01 (s, 2H), 1.02 (s, 9H); ¹³C-NMR (125 MHz, CDCl₃) δ 200.6, 169.0, 168.8, 153.6, 108.4, 91.2, 84.0, 74.8, 57.0, 53.14, 53.11, 52.5, 32.2, 29.8 (3C), 24.8; EI-LRMS m/z 322 (M⁺), 263, 231, 225, 203; EI-HRMS calcd for C₁₇H₂₂O₆ 322.14164, found 322.14123.

**Scheme S9. Preparation of 3i**

**~ Preparation of 3j ~**

5,5-Bis(methoxycarbonyl)nona-6,7-diene-2-yne (3j). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9j (389.1 mg, 3.084 mmol) in THF (3.3 mL), LHMDS in THF (1.00 M, 6.5 mL, 6.5 mmol), methyl chloroformate (250 µL, 3.24 mmol), and 10a (556.0 mg, 3.089 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 3j (307.7 mg, 42%) as a colorless oil. IR (neat) 1970, 1740, 1436, 1230 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.66 (dq, J = 6.6, 3.2 Hz, 1H), 5.34 (dq, J = 6.6, 6.8 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.84 (q, J = 2.6 Hz, 2H), 1.74 (t, J = 2.6 Hz, 3H), 1.68 (dd, J = 3.2, 6.8 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 204.1, 169.7, 169.6, 90.4, 89.4, 78.2, 73.6, 57.7, 52.8 (2C), 24.7, 13.6, 3.4; EI-LRMS m/z 236 (M⁺), 183, 177, 145, 117; EI-HRMS calcd for C₁₃H₁₆O₄ 236.10486, found 236.10473.

**Scheme S10. Preparation of 3j**

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**Preparation of 3k**

5,5-Bis(methoxycarbonyl)deca-6,7-dien-2-yne (3k). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9k\(^8\) (702.0 mg, 5.008 mmol) in THF (5.0 mL), LHMDS in THF (1.00 M, 10.0 mL, 10.0 mmol), methyl chloroformate (400 µL, 5.18 mmol), and 10a (903.0 mg, 5.017 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 3k (680.5 mg, 54%) as a colorless oil. IR (neat) 1967, 1740, 1436, 1228 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.69 (dt, \(J = 6.5, 3.1\) Hz, 1H), 5.40 (dt, \(J = 6.5, 6.4\) Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 2.79 (q, \(J = 2.5\) Hz, 2H), 2.00 (ddt, \(J = 3.1, 6.4, 7.1\) Hz, 2H), 1.69 (t, \(J = 2.5\) Hz, 3H), 0.96 (t, \(J = 7.1\) Hz, 3H); \(^1\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 202.8, 169.7, 169.6, 97.4, 90.6, 78.2, 73.6, 57.8, 52.7, 52.7, 24.9, 21.4, 12.9, 3.3; EI-LRMS m/z 250 (M\(^+\)), 191, 159, 131, 59; EI-HRMS calcd for C\(_{14}\)H\(_{18}\)O\(_4\) 250.12051, found 250.12033.

**Preparation of 3l**

Methyl 6-methylhepta-3,4-dienoate (9l). Similar to the synthesis of 9a from 8a, a crude product, which was obtained from 8l (3.886 g, 39.60 mmol), trimethyl orthoacetate (15.0 mL, 120 mmol), and propanoic acid (0.30 mL, 4.0 mmol) at 110 °C for 6 h, was purified by column chromatography on silica gel (hexane/AcOEt = 30/1) to give 9l (1.735 mg, 28%) as a colorless oil. IR (neat) 1965, 1743, 1437, 1246, 1032 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.27-5.22 (m, 1H), 5.21-5.16 (m, 1H), 3.68 (s, 3H), 3.01 (dd, \(J = 7.4, 2.9\) Hz, 2H), 2.33-2.22 (m, 1H), 0.98 (dd, \(J = 6.9, 1.1\) Hz, 6H); \(^1\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 203.5, 172.0, 99.6, 85.1, 51.8, 35.0, 27.7, 22.32, 22.28; EI-LRMS m/z 154 (M\(^+\)), 139, 123, 111, 95, 59, 43; EI-HRMS calcd for C\(_9\)H\(_{14}\)O\(_2\) 154.09938, found 154.09972.

5,5-Bis(methoxycarbonyl)-9-methyldeca-6,7-dien-2-yne (3l). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9l (773.4 mg, 5.015 mmol) in THF (5.0 mL), LHMDS in THF (1.00 M, 10.0 mL, 10.0 mmol), methyl chloroformate (400 µL, 5.18 mmol), and 10a (903.5 mg, 5.020 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 3l (719.4 mg, 54%) as a colorless oil. IR (neat) 1967, 1740, 1436, 1227 cm\(^{-1}\); \(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.76 (dd, \(J = 6.3, 2.9\) Hz, 1H), 5.38 (dd, \(J = 6.3, 6.0\) Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.84-2.82 (m, 2H), 2.35-2.28 (m, 1H), 1.72 (dd, \(J = 2.6, 2.6\) Hz, 3H), 0.99 (dd, \(J = 6.9, 1.1\) Hz, 6H); \(^1\)C-NMR (125 MHz, CDCl\(_3\)) \(\delta\) 201.6, 169.7, 169.6, 103.0, 91.2, 78.3, 73.6, 57.9,

52.74, 52.72, 27.9, 25.1, 22.2, 22.0, 3.4; EI-LRMS m/z 264 (M‘), 205, 173, 145, 59; EI-HRMS calcd for C_{15}H_{20}O_{4} 264.13616, found 264.13591.

~ Preparation of 3m ~

Scheme S13. Preparation of 3m

3,3-Bis(methoxycarbonyl)hept-5-ynoic acid (14). To a suspension of NaH (60% dispersion in mineral oil, 823.3 mg, 20.58 mmol) and NaI (276.1 mg, 1.842 mmol) in THF (56 mL) was slowly added a solution of 13 (3.017 g, 16.38 mmol) in THF (8 mL) at 0 °C, and the mixture was stirred at room temperature for 5 min. To the mixture was added tert-butyl chloroacetate (2.93 mL, 20.5 mmol) at 0 °C, and the resulting mixture was stirred at room temperature overnight. To the mixture was added saturated NH₄Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with water and brine, dried over Na₂SO₄, and concentrated. The residue was roughly purified by short column chromatography on silica gel (hexane/AcOEt = 12/1) to give a crude tert-butyl ester (4.260 g) as a yellow oil. To a solution of the crude tert-butyl ester (4.260 g) in CH₂Cl₂ (50 mL) was added TFA (11.0 mL, 143 mmol) at room temperature, and the mixture was stirred at the same temperature for 18 h. After removal of the solvent and TFA, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 10/1) to give 14 (1.847 g, in 2 steps 47%) as a white solid. mp; 119-121 °C; IR (film, CHCl₃) 1740, 1714, 1438 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 10.95 (br s, 1H), 3.74 (s, 6H), 3.22 (s, 2H), 2.94 (q, J = 2.6 Hz, 2H), 1.75 (t, J = 2.6 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 176.6, 169.4 (2C), 79.8, 72.9, 54.8, 53.1 (2C), 36.6, 23.9, 3.5; EI-LRMS m/z 242 (M‘), 224, 196, 183, 151, 123, 59, 53; EI-HRMS calcd for C₁₁H₁₄O₆ 242.07904, found 242.07878.

Methyl 5,5-bis(methoxycarbonyl)nona-2,3-dien-8-ynecarboxylate (3m). To a solution of 14 (459.9 mg, 1.727 mmol) in CH₂Cl₂ (3.4 mL) was slowly added oxalyl chloride (165 µL, 1.92 mmol) at room temperature, and the mixture was stirred at 35 °C for 2.5 h. After removal of the volatiles, the resulting crude acyl chloride was diluted with CH₂Cl₂ (3.4 mL) and added slowly to a stirred solution of Ph₃P=CHCO₂Me (698.2 mg, 2.088 mmol) and Et₃N (290 µL, 2.081 mmol) in CH₂Cl₂ (2.8 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and concentrated. The crude product was purified by column chromatography on silica gel (hexane/AcOEt = 5/1) to give 3m (290.8 mg, in 2 steps 60%) as a colorless oil. IR (neat) 1971, 1741, 1725 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 6.24 (d, J = 6.3 Hz, 1H), 5.80 (d, J = 6.3 Hz, 1H), 3.76 (s, 6H), 3.71 (s, 3H), 2.92-2.83 (m, 2H), 1.73 (t, J = 2.6 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 211.2, 168.5 (2C), 165.3, 94.5, 91.6, 79.3, 72.7, 57.6, 53.2 (2C), 52.2, 25.3, 3.5; EI-LRMS m/z 280(M‘), 227, 221, 189, 161; EI-HRMS calcd for C₁₄H₁₄O₆ 280.09469, found 280.09512.

~ Preparation of 3n ~

6,6-Bis(methoxycarbonyl)deca-7,8-3-yne (3n). Similar to the synthesis of 3a from 9a, a crude product, which was obtained from 9j (379.3 mg, 3.01 mmol) in THF (3.3 mL), LHMDS in THF (1.00 M, 6.6 mL, 6.6 mmol), methyl chloroformate (239 μL, 3.09 mmol), and 10d (1.086 g, 5.60 mmol), was purified by column chromatography on silica gel (hexane/AcOEt = 20/1) to give 3n (327.6 mg, 44%) as a colorless oil. IR (neat) 1970, 1741, 1436, 1231, 1061 cm⁻¹; ¹H-NMR (500 MHz, CDCl₃) δ 5.65 (dq, J = 6.5, 3.3 Hz, 1H), 5.32 (dq, J = 6.5, 7.0 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.83 (t, J = 2.5 Hz, 2H), 2.09 (tq, J = 2.5, 7.5 Hz, 2H), 1.66 (dd, J = 7.0, 3.3 Hz, 3H), 1.05 (t, J = 7.5 Hz, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 204.1, 169.74, 169.68, 90.4, 89.4, 84.4, 73.9, 57.8, 52.80, 52.78, 24.8, 14.1, 13.7, 12.3; EI-LRMS m/z 251 [(M+H)⁺], 191, 183, 159, 131, 59; EI-HRMS calcd for C₁₄H₁₉O₄ 251.12833, found 251.12735.