Supporting Information

Rhodium-Catalyzed Cyclization of 1,6-Enynes Triggered by Addition of Arylboronic Acids

Tomoya Miura, Masahiko Shimada, and Masahiro Murakami*

Department of Synthetic Chemistry and Biological Chemistry, Kyoto University,
Katsura, Kyoto 615-8510, Japan

General. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300 MHz and ^{13}C at 75 MHz) spectrometer using CHCl_3 (^1H , $\delta=7.26$) and CDCl_3 (^{13}C , $\delta=77.0$) as an internal standard. High resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck).

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. 1,4-Dioxane was distilled from sodium. $[\text{Rh}(\text{OH})(\text{cod})]_2$ was prepared according to the reported procedures.¹ 1,6-Enynes **1a**, **1c–1i** were prepared from dimethyl 2-(but-2-ynyl)malonate and the corresponding allyl bromides in the presence of NaH in a THF solution. (Z) or (E)-1-bromo-4-methoxybut-2-ene was prepared from the corresponding but-2-ene-1,4-diol² by methylation³ (Me_2SO_4 and NaOH in H_2O) followed by bromination (Br_2 and PPh_3 in CH_2Cl_2). (E)-1-bromo-4-methoxy-2-methylbut-2-ene was prepared from (E)-1-bromo-2-methyl-4-(tetrahydro-2-pyranyloxy)but-2-ene⁴ by removal of the O-protecting group (CSA in MeOH) followed by methylation (MeOTf and 2,6-di-*t*-butylpyridine in CH_2Cl_2). (Z)-1-Bromo-4-(*t*-butyldimethylsiloxy)but-2-ene,⁵ (Z)-4-bromobut-2-enyl acetate,⁶ and (E)-4-bromo-1,1-dimethoxybut-2-ene⁷ were prepared according to the literature. Dimethyl 2-(but-2-ynyl)-2-((Z)-4-hydroxybut-2-enyl)malonate (**1b**) was prepared from **1c** by removal of the O-protecting group (TBAF in THF/MeOH). (Z)-1-Methoxy-5,5-bis(methoxymethyl)non-2-en-7-yne (**1j**) was prepared from **1a** by the literature procedure.⁸ (Z)-5,5-Bis(phenylsulfonyl)-1-methoxynon-2-en-7-yne (**1k**) was synthesized from 5,5-bis(phenylsulfonyl)pent-2-yne and (Z)-1-bromo-4-methoxybut-2-ene according to the literature.⁹ (Z)-*N*-(but-2-ynyl)-*N*-(4-methoxybut-2-enyl)-*p*-toluenesulfonamide (**1l**) was synthesized from *N*-(but-2-ynyl)-*p*-toluenesulfonamide and (Z)-4-methoxybut-2-en-1-ol according to the literature.¹⁰

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Dimethyl 2-(but-2-ynyl)-2-((Z)-4-methoxybut-2-enyl)malonate (1a)

IR (neat): 2956, 1738, 1437, 1293, 1211, 1115 cm^{-1} ; ^1H NMR: δ = 1.75 (t, J = 2.7 Hz, 3H), 2.72 (q, J = 2.5 Hz, 2H), 2.82 (d, J = 8.1 Hz, 2H), 3.32 (s, 3H), 3.72 (s, 6H), 4.01 (d, J = 6.6 Hz, 2H), 5.30–5.41 (m, 1H), 5.64–5.75 (m, 1H); ^{13}C NMR: δ = 3.5, 23.0, 30.3, 52.7, 57.0, 58.0, 68.0, 73.3, 79.0, 125.7, 131.0, 170.4; Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_5$: C, 62.67; H, 7.51. Found: C, 62.82; H, 7.56.

Dimethyl 2-(but-2-ynyl)-2-((Z)-4-hydroxybut-2-enyl)malonate (1b)

IR (neat): 3409, 2955, 1737, 1439, 1294, 1210 cm^{-1} ; ^1H NMR: δ = 1.77 (t, J = 2.6 Hz, 3H), 2.74 (q, J = 2.5 Hz, 2H), 2.85 (dd, J = 7.8, 1.2 Hz, 2H), 3.74 (s, 6H), 4.20 (dd, J = 7.2, 1.2 Hz, 2H), 5.29–5.41 (m, 1H), 5.76–5.87 (m, 1H); ^{13}C NMR: δ = 3.5, 23.1, 30.1, 52.8, 57.0, 58.1, 73.3, 79.3, 125.4, 133.1, 170.4; HRMS (CI^+): Calcd for $\text{C}_{13}\text{H}_{19}\text{O}_5$, $\text{M}+\text{H}^+$ 255.1233. Found m/z 255.1229.

Dimethyl 2-(but-2-ynyl)-2-((Z)-4-(tert-butyldimethylsilyloxy)but-2-enyl)malonate (1c)

IR (neat): 2955, 1740, 1437, 1293, 1254, 1210 cm^{-1} ; ^1H NMR: δ = 0.07 (s, 6H), 0.89 (s, 9H), 1.75 (t, J = 2.6 Hz, 3H), 2.72 (q, J = 2.6 Hz, 2H), 2.79 (d, J = 7.8 Hz, 2H), 3.72 (s, 6H), 4.72 (dd, J = 6.3, 1.5 Hz, 2H), 5.14–5.26 (m, 1H), 5.63–5.73 (m, 1H); ^{13}C NMR: δ = -5.2, 3.5, 18.4, 22.9, 25.9, 30.3, 52.7, 57.0, 59.4, 73.3, 78.9, 122.8, 134.7, 170.4; HRMS (CI^+): Calcd for $\text{C}_{19}\text{H}_{33}\text{O}_5\text{Si}$, $\text{M}+\text{H}^+$ 369.2097. Found m/z 369.2096.

Dimethyl 2-(but-2-ynyl)-2-((Z)-4-acetoxybut-2-enyl)malonate (1d)

IR (neat): 2957, 1738, 1437, 1375, 1293, 1216 cm^{-1} ; ^1H NMR: δ = 1.74 (t, J = 2.4 Hz, 3H), 2.04 (s, 3H), 2.71 (q, J = 2.6 Hz, 2H), 2.84 (dd, J = 8.0, 0.8 Hz, 2H), 3.72 (s, 6H), 4.65 (dd, J = 6.6, 1.2 Hz, 2H), 5.36–5.49 (m, 1H), 5.64–5.76 (m, 1H); ^{13}C NMR: δ = 3.4, 20.9, 23.0, 30.2, 52.8, 56.9, 60.2, 73.0, 79.3, 127.5, 128.1, 170.2, 170.8; HRMS (CI^+): Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_6$, $\text{M}+\text{H}^+$ 297.1338. Found m/z 297.1332.

Dimethyl 2-((Z)-4-methoxybut-2-enyl)-2-(pent-2-ynyl)malonate (1e)

IR (neat): 2995, 1735, 1437, 1293, 1211, 1115 cm^{-1} ; ^1H NMR: δ = 1.09 (t, J = 7.7 Hz, 3H), 2.10 (dt, J = 7.7, 2.4 Hz, 1H), 2.15 (dt, J = 7.7, 2.4 Hz, 1H), 2.74 (t, J = 2.4 Hz, 2H), 2.80–2.86 (m, 2H), 3.33 (s, 3H), 3.73 (s, 6H), 4.00–4.06 (m, 2H), 5.31–5.42 (m, 1H), 5.65–5.76 (m, 1H); ^{13}C NMR: δ = 12.4, 14.1, 22.9, 30.3, 52.7, 57.1, 58.0, 68.0, 73.6, 85.1, 125.7, 131.0, 170.3; HRMS (CI^+): Calcd for $\text{C}_{15}\text{H}_{23}\text{O}_5$, $\text{M}+\text{H}^+$ 283.1545. Found m/z 283.1543.

Dimethyl 2-((Z)-4-methoxybut-2-enyl)-2-(3-phenylprop-2-ynyl)malonate (1f)

IR (neat): 2953, 1738, 1437, 1294, 1211, 1113 cm^{-1} ; ^1H NMR: δ = 2.83–2.91 (m, 2H), 2.98 (s, 2H), 3.25 (s, 3H), 3.74 (s, 6H), 4.01 (dd, J = 6.6, 1.5 Hz, 2H), 5.32–5.43 (m, 1H), 5.66–5.76 (m, 1H), 7.22–7.28 (m, 3H), 7.30–7.36 (m, 2H); ^{13}C NMR: δ = 23.6, 30.5, 52.9, 57.1, 58.0, 68.0, 83.6, 84.2, 123.0, 125.5, 128.0, 128.2, 131.3, 131.6, 170.2; HRMS (CI^+): Calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$, $\text{M}+\text{H}^+$ 331.1545. Found m/z 331.1544.

Dimethyl 2-(but-2-ynyl)-2-((E)-4-methoxybut-2-enyl)malonate (1g)

IR (neat): 2950, 1738, 1439, 1283, 1210, 1114 cm^{-1} ; ^1H NMR: δ = 1.76 (t, J = 2.7 Hz, 3H), 2.73 (q, J = 2.5 Hz, 2H), 2.79 (d, J = 7.2 Hz, 2H), 3.29 (s, 3H), 3.73 (s, 6H), 3.86 (d, J = 5.7 Hz, 2H), 5.45–5.58 (m, 1H), 5.62–5.74 (m, 1H); ^{13}C NMR: δ = 3.7, 23.3, 35.3, 52.9, 57.5, 57.9, 72.9, 73.4, 79.3, 127.2, 131.7, 170.6; HRMS (CI^+): Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_5$, $\text{M}+\text{H}^+$ 268.1389. Found m/z 268.1389.

Dimethyl 2-(but-2-ynyl)-2-((E)-4-methoxy-2-methylbut-2-enyl)malonate (1h)

A mixture of geometrical isomers (*E*:*Z* = 9:1)

IR (neat): 2955, 1738, 1437, 1289, 1203, 1088 cm⁻¹; ¹H NMR: *E* isomer δ = 1.59 (br s, 3H), 1.76 (t, *J* = 2.6 Hz, 3H), 2.74 (q, *J* = 2.5 Hz, 2H), 2.83 (br s, 2H), 3.31 (s, 3H), 3.73 (s, 6H), 3.92 (dd, *J* = 6.3, 0.6 Hz, 2H), 5.43–5.53 (m, 1H); ¹³C NMR: *E* isomer δ = 3.5, 17.3, 23.0, 41.4, 52.6, 57.0, 57.8, 68.8, 73.5, 79.3, 127.2, 133.9, 170.8; HRMS (CI⁺): Calcd for C₁₄H₁₉O₄, M-OMe⁺ 251.1283. Found *m/z* 251.1289.

Dimethyl 2-(but-2-ynyl)-2-((E)-4,4-dimethoxybut-2-enyl)malonate (1i)

IR (neat): 2955, 1738, 1437, 1202, 1130, 1053 cm⁻¹; ¹H NMR: δ = 1.75 (t, *J* = 2.4 Hz, 3H), 2.74 (q, *J* = 2.6 Hz, 2H), 2.82 (d, *J* = 7.2 Hz, 2H), 3.28 (s, 6H), 3.73 (s, 6H), 4.71 (d, *J* = 4.2 Hz, 1H), 5.52–5.73 (m, 2H); ¹³C NMR: δ = 3.5, 23.1, 35.0, 52.6, 52.7, 57.1, 73.0, 79.1, 102.4, 128.4, 131.6, 170.3; HRMS (CI⁺): Calcd for C₁₅H₂₃O₆, M+H⁺ 299.1495. Found *m/z* 299.1493.

(Z)-1-Methoxy-5,5-bis(methoxymethyl)non-2-en-7-yne (1j)

IR (neat): 2961, 2361, 1459, 1198, 1109 cm⁻¹; ¹H NMR: δ = 1.79 (t, *J* = 2.4 Hz, 3H), 2.11 (q, *J* = 2.7 Hz, 2H), 2.15 (d, *J* = 7.2 Hz, 2H), 3.32 (s, 6H), 3.33 (s, 3H), 4.02 (d, *J* = 5.7 Hz, 2H), 5.53–5.70 (m, 2H); ¹³C NMR: δ = 3.6, 22.2, 29.7, 42.3, 57.9, 59.2, 68.2, 74.2, 75.5, 77.3, 128.0, 129.1; HRMS (EI⁺): Calcd for C₁₃H₂₁O₂, M-OMe⁺ 209.1542. Found *m/z* 209.1542.

(Z)-5,5-Bis(phenylsulfonyl)-1-methoxynon-2-en-7-yne (1k)

IR (nujol): 1736, 1333, 1308, 1146, 1125, 1076 cm⁻¹; ¹H NMR: δ = 1.64 (t, *J* = 2.7 Hz, 3H), 3.10 (d, *J* = 6.0 Hz, 2H), 3.16 (q, *J* = 2.5 Hz, 2H), 3.33 (s, 3H), 3.97 (d, *J* = 6.0 Hz, 2H), 5.75–5.94 (m, 2H), 7.54–7.61 (m, 4H), 7.67–7.74 (m, 2H), 8.06–8.13 (m, 4H); ¹³C NMR: δ = 3.7, 20.9, 27.7, 58.3, 68.3, 70.6, 81.9, 88.9, 123.5, 128.5, 130.7, 131.5, 134.6, 136.7; HRMS (CI⁺): Calcd for C₂₂H₂₅O₅S₂, M+H⁺ 433.1143. Found *m/z* 433.1143.

(Z)-N-(-but-2-ynyl)-N-(4-methoxybut-2-enyl)-*p*-toluenesulfonamide (1l)

IR (nujol): 1597, 1444, 1340, 1161, 1094 cm⁻¹; ¹H NMR: δ = 1.55 (t, *J* = 2.4 Hz, 3H), 2.43 (s, 3H), 3.31 (s, 3H), 3.85 (d, *J* = 7.2 Hz, 2H), 3.97–4.04 (m, 4H), 5.46–5.58 (m, 1H), 5.72–5.83 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H); ¹³C NMR: δ = 3.3, 21.5, 36.4, 43.1, 58.1, 67.7, 71.8, 81.6, 126.6, 127.9, 129.3, 131.8, 136.0, 143.3; HRMS (CI⁺): Calcd for C₁₆H₂₂NO₃S, M+H⁺ 308.1320. Found *m/z* 308.1321.

Dimethyl 2-(but-2-ynyl)-2-methylmalonate (4)

IR (neat): 2955, 1736, 1437, 1252, 1206, 1150 cm⁻¹; ¹H NMR: δ = 1.52 (s, 3H), 1.75 (t, *J* = 3.0 Hz, 3H), 2.73 (q, *J* = 2.7 Hz, 2H), 3.73 (s, 6H); ¹³C NMR: δ = 3.5, 19.9, 26.2, 52.7, 53.5, 73.6, 78.8, 171.6; HRMS (CI⁺): Calcd for C₁₀H₁₄O₄, M+H⁺ 199.0970. Found *m/z* 199.0974.

General procedure for rhodium-catalyzed cyclization of 1,6-enynes (COD conditions)

To an oven-dried, N₂-purged flask was added [Rh(OH)(cod)]₂ (1.37 mg, 0.3 μ mol, 0.03 equiv of Rh) and arylboronic acid (0.4 mmol, 2.0 equiv), followed by 1 mL of 1,4-dioxane. A solution of substrate (0.2 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) was added to the reaction mixture at room temperature. After complete consumption of substrate, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and

the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the purified product.

(Z)-1,1-Dimethoxycarbonyl-3-(1-phenylethylidene)-4-vinylcyclopentane (3aa)

The Z configuration of the exo double bond was confirmed on the basis of the observed NOE shown below.

IR (neat): 2953, 1732, 1435, 1254, 1204, 1069 cm^{-1} ; ^1H NMR: δ = 1.98–2.02 (m, 3H), 2.14 (dd, J = 13.2, 6.3 Hz, 1H), 2.52 (ddd, J = 13.1, 7.9, 1.0 Hz, 1H), 3.04 (d, J = 16.8 Hz, 1H), 3.15 (dt, J = 16.5, 1.8 Hz, 1H), 3.33–3.45 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.56 (dt, J = 17.1, 1.5 Hz, 1H), 4.63 (dt, J = 10.2, 1.5 Hz, 1H), 5.37 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 7.09–7.28 (m, 5H); ^{13}C NMR: δ = 22.2, 38.9, 40.5, 45.4, 52.7, 52.9, 58.8, 113.9, 126.2, 127.8, 131.4, 136.1, 139.6, 143.5, 172.2, 172.4 (1 carbon missing); Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4$: C, 72.59; H, 7.05. Found: C, 72.78; H, 7.07.

(Z)-1,1-Dimethoxycarbonyl-3-(1-(4-fluorophenyl)ethylidene)-4-vinylcyclopentane (3ab)

IR (neat): 2955, 1733, 1603, 1509, 1435, 1260 cm^{-1} ; ^1H NMR: δ = 1.92–2.02 (m, 3H), 2.11 (dd, J = 13.2, 6.3 Hz, 1H), 2.52 (dd, J = 13.1, 8.0 Hz, 1H), 3.03 (d, J = 16.8 Hz, 1H), 3.13 (dt, J = 17.0, 1.7 Hz, 1H), 3.27–3.41 (m, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 4.55 (dt, J = 17.1, 1.4 Hz, 1H), 4.62 (d, J = 10.2 Hz, 1H), 5.34 (ddd, J = 17.1, 10.1, 7.1 Hz, 1H), 6.85–6.98 (m, 2H), 7.00–7.14 (m, 2H); ^{13}C NMR: δ = 22.3, 39.0, 40.6, 45.5, 52.7, 52.9, 58.7, 114.1, 114.6 (d, J = 20.7 Hz), 129.4 (d, J = 8.1 Hz), 130.5, 136.6, 139.3, 139.5, 161.3 (d, J = 243.2 Hz), 172.1, 172.3 (1 carbon missing); HRMS (EI^+): Calcd for $\text{C}_{19}\text{H}_{21}\text{FO}_4$, M^+ 332.1424. Found m/z 332.1423

(Z)-1,1-Dimethoxycarbonyl-3-(1-(4-nitrophenyl)ethylidene)-4-vinylcyclopentane (3ac)

IR (neat): 2953, 1734, 1541, 1509, 1456, 1340 cm^{-1} ; ^1H NMR: δ = 1.99–2.04 (m, 3H), 2.13 (dd, J = 13.2, 6.6 Hz, 1H), 2.54 (ddd, J = 13.2, 6.6, 1.1 Hz, 1H), 3.07 (d, J = 17.1 Hz, 1H), 3.16 (dt, J = 17.1, 1.8 Hz, 1H), 3.30–3.42 (m, 1H), 3.74 (s, 3H), 3.78 (s, 3H), 4.54 (dt, J = 17.1, 1.4 Hz, 1H), 4.62 (dt, J = 10.3, 1.2 Hz, 1H), 5.31 (ddd, J = 17.2, 10.0, 7.3 Hz, 1H), 7.25–7.31 (m, 2H), 8.08–8.14 (m, 2H); ^{13}C NMR: δ = 21.9, 39.3, 40.8, 45.8, 52.8, 53.0, 58.5, 114.9, 123.2, 128.9, 129.7, 139.0, 146.2, 150.4, 171.8, 172.1 (1 carbon missing); HRMS (EI^+): Calcd for $\text{C}_{19}\text{H}_{21}\text{O}_6$, M^+ 359.1369. Found m/z 359.1374.

(Z)-1,1-Dimethoxycarbonyl-3-(1-(4-methylphenyl)ethylidene)-4-vinylcyclopentane (3ad)

IR (neat): 2954, 1734, 1435, 1256, 1204, 1171 cm^{-1} ; ^1H NMR: δ = 1.98 (br s, 3H), 2.16 (dd, J = 13.2, 5.7 Hz, 1H), 2.31 (s, 3H), 2.51 (ddd, J = 13.1, 8.0, 0.9 Hz, 1H), 3.03 (d, J = 17.1 Hz, 1H), 3.15 (dt, J = 16.8, 1.8 Hz, 1H), 3.35–3.44 (m, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 4.57–4.72 (m, 2H), 5.41 (ddd, J = 17.0, 10.4, 6.5 Hz, 1H), 6.99–7.10 (m, 4H); ^{13}C NMR: δ = 21.1, 22.2, 38.9, 40.4, 45.3, 52.7, 52.9, 58.8, 114.0, 127.6, 128.5, 131.2, 135.7, 135.8, 139.7, 140.6, 172.2, 172.4; HRMS (EI^+): Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4$, M^+ 328.1675. Found m/z 328.1670.

(Z)-1,1-Dimethoxycarbonyl-3-(1-(3-methoxyphenyl)ethylidene)-4-vinylcyclopentane (3ae)

IR (neat): 2953, 1734, 1489, 1435, 1260, 1205 cm^{-1} ; ^1H NMR: δ = 1.99 (br s, 3H), 2.16 (dd, J = 13.2, 5.7 Hz, 1H), 2.51 (ddd, J = 13.1, 8.0, 0.9 Hz, 1H), 3.03 (d, J = 16.8 Hz, 1H), 3.15 (dt, J = 16.9,

1.8 Hz, 1H), 3.33–3.46 (m, 1H), 3.72 (s, 3H), 3.76 (s, 3H), 3.77 (s, 3H), 4.58–4.71 (m, 2H), 5.42 (ddd, $J = 17.1, 10.5, 6.6$ Hz, 1H), 6.65–6.78 (m, 3H), 7.16 (t, $J = 8.0$ Hz, 1H); ^{13}C NMR: $\delta = 22.1, 38.9, 40.4, 45.5, 52.7, 52.9, 55.2, 58.7, 111.6, 113.6, 114.0, 120.3, 128.8, 131.2, 136.2, 139.7, 144.9, 159.1, 172.2, 172.4$; HRMS (EI^+): Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_5$, M^+ 344.1624. Found m/z 344.1624.

(Z)-1,1-Dimethoxycarbonyl-3-(1-(3-chlorophenyl)ethylidene)-4-vinylcyclopentane (3af)

IR (neat): 2953, 1733, 1435, 1259, 1205, 1173 cm^{-1} ; ^1H NMR: $\delta = 1.97$ (br s, 3H), 2.12 (dd, $J = 13.2, 6.5$ Hz, 1H), 2.52 (dd, $J = 13.2, 7.8$ Hz, 1H), 3.04 (d, $J = 17.1$ Hz, 1H), 3.13 (dt, $J = 17.1, 1.5$ Hz, 1H), 3.30–3.43 (m, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.57 (dt, $J = 17.0, 1.4$ Hz, 1H), 4.57 (dt, $J = 9.9, 1.4$ Hz, 1H), 5.34 (ddd, $J = 17.2, 10.1, 7.1$ Hz, 1H), 6.96–7.02 (m, 1H), 7.08–7.21 (m, 3H); ^{13}C NMR: $\delta = 22.0, 39.0, 40.7, 45.6, 52.8, 52.9, 58.6, 114.4, 126.1, 126.3, 128.1, 129.1, 130.2, 133.5, 137.3, 139.3, 145.2, 172.0, 172.2$; HRMS (EI^+): Calcd for $\text{C}_{19}\text{H}_{21}\text{ClO}_4$, M^+ 348.1128. Found m/z 348.1127.

(Z)-1,1-Dimethoxycarbonyl-3-(1-(2-methylphenyl)ethylidene)-4-vinylcyclopentane (3ag)

A mixture of atropisomers (52:48)

IR (neat): 2953, 1736, 1435, 1256, 1204, 1171 cm^{-1} ; ^1H NMR: a mixture of atropisomers (1:1) $\delta = 1.89$ (br s, 1.5H), 1.91 (br s, 1.5H), 2.02 (dd, $J = 13.5, 8.1$ Hz, 0.5H), 2.10 (dd, $J = 13.2, 6.6$ Hz, 0.5H), 2.13 (s, 1.5H), 2.14 (s, 1.5H), 2.48–2.60 (m, 1H), 2.88 (q, $J = 7.5$ Hz, 0.5H), 2.98–3.17 (m, 2H), 3.23 (q, $J = 7.8$ Hz, 0.5H), 3.74 (s, 1.5H), 3.746 (s, 1.5H), 3.754 (s, 1.5H), 3.79 (s, 1.5H), 4.15–4.58 (m, 2H), 5.23 (ddd, $J = 18.3, 10.2, 8.4$ Hz, 0.5H), 5.36 (ddd, $J = 17.1, 10.2, 7.2$ Hz, 0.5H), 6.87–6.96 (m, 1H), 7.01–7.15 (m, 3H); ^{13}C NMR: a mixture of atropisomers (1:1) $\delta = 18.8, 19.6, 21.5, 22.1, 38.4, 38.6, 40.1, 40.4, 45.5, 45.8, 52.7, 52.8, 58.9, 113.2, 113.5, 125.1, 125.5, 126.4, 126.5, 128.0, 129.0, 129.6, 129.8, 131.0, 132.2, 134.0, 135.4, 135.9, 136.2, 138.2, 139.5, 142.5, 143.0, 172.1, 172.2, 172.3$ (2 carbon missing); HRMS (EI^+): Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4$, M^+ 328.1675. Found m/z 328.1671.

(Z)-1,1-Dimethoxycarbonyl-3-(1-(1-naphthyl)ethylidene)-4-vinylcyclopentane (3ah)

A mixture of atropisomers (62:38)

IR (neat): 2953, 1733, 1435, 1266, 1200, 1169 cm^{-1} ; ^1H NMR: a mixture of atropisomers (5:3) $\delta = 2.00$ –2.16 (m, 4H), 2.45 (ddd, $J = 13.2, 8.0, 1.4$ Hz, 0.625H), 2.56 (dd, $J = 13.2, 7.8$ Hz, 0.375H), 2.75–2.88 (m, 0.625H), 3.06–3.41 (m, 2.375H), 3.75 (s, 1.875H), 3.76 (s, 1.125H), 3.82 (s, 1.125H), 3.84 (s, 1.875H), 3.97–4.11 (m, 1.375H), 4.37 (ddd, $J = 10.2, 1.5, 0.9$ Hz, 0.625H), 5.00 (ddd, $J = 17.1, 10.1, 8.0$ Hz, 0.375H), 5.27 (ddd, $J = 17.2, 10.0, 7.4$ Hz, 0.625H), 7.12 (dd, $J = 7.2, 1.2$ Hz, 0.375H), 7.18 (dd, $J = 7.2, 1.2$ Hz, 0.625H), 7.32–7.49 (m, 3H), 7.67–7.87 (m, 3H); ^{13}C NMR: a mixture of atropisomers (5:3) $\delta = 22.5, 22.9, 38.8, 38.9, 40.3, 40.5, 45.8, 45.9, 52.8, 52.87, 52.90, 58.88, 58.91, 113.1, 113.4, 124.9, 125.1, 125.2, 125.31, 125.34, 125.4, 125.8, 125.9, 126.0, 126.6, 126.8, 128.0, 128.4, 129.5, 130.2, 130.9, 131.8, 133.5, 133.6, 137.6, 138.1, 138.5, 139.4, 140.9, 141.5, 172.11, 172.14, 172.2, 172.4$ (2 carbon missing); HRMS (EI^+): Calcd for $\text{C}_{23}\text{H}_{24}\text{O}_4$, M^+ 364.1675. Found m/z 364.1678.

(Z)-1,1-Dimethoxycarbonyl-3-(1-phenylpropylidene)-4-vinylcyclopentane (3ea)

IR (neat): 2957, 1738, 1435, 1262, 1204, 1171 cm^{-1} ; ^1H NMR: $\delta = 0.91$ (t, $J = 7.5$ Hz, 3H), 2.08 (dd, $J = 12.9, 6.0$ Hz, 1H), 2.20–2.48 (m, 2H), 2.53 (dd, $J = 13.2, 8.1$ Hz, 1H), 3.09 (s, 2H), 3.31 (q, $J = 7.0$ Hz, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 4.48 (dt, $J = 16.8, 1.5$ Hz, 1H), 4.59 (dt, $J = 9.9, 1.8$ Hz, 1H), 5.35 (ddd, $J = 17.1, 10.5, 6.9$ Hz, 1H), 7.03–7.08 (m, 2H), 7.16–7.27 (m, 3H); ^{13}C NMR: $\delta = 12.5, 29.2, 38.1, 40.0, 45.0, 52.7, 52.8, 58.9, 113.6, 126.2, 127.7, 128.5, 135.3, 138.4, 139.5, 142.0, 172.1$.

172.3; HRMS (EI⁺): Calcd for C₂₀H₂₄O₄, M⁺ 328.1675. Found m/z 328.1674.

1,1-Dimethoxycarbonyl-3-(diphenylmethylene)-4-vinylcyclopentane (3fa)

IR (neat): 2953, 1734, 1267, 1206, 1167, 1075 cm⁻¹; ¹H NMR: δ = 2.08 (dd, *J* = 13.2, 7.2 Hz, 1H), 2.66 (ddd, *J* = 12.9, 8.1, 1.8 Hz, 1H), 2.94 (dd, *J* = 12.9, 8.1, 1.8 Hz, 1H), 3.24 (dd, *J* = 16.5, 2.4 Hz, 1H), 3.68–3.75 (m, 1H), 3.70 (s, 3H), 3.72 (s, 3H), 4.57 (dt, *J* = 17.1, 1.2 Hz, 1H), 4.66 (dt, *J* = 10.2, 1.2 Hz, 1H), 5.48 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 7.08–7.32 (m, 10H); ¹³C NMR: δ = 39.7, 40.3, 45.4, 52.8, 59.2, 114.0, 126.56, 126.62, 128.0, 129.0, 129.3, 138.1, 138.9, 139.3, 141.8, 142.6, 171.9, 172.0 (1 carbon missing); HRMS (EI⁺): Calcd for C₂₄H₂₄O₄, M⁺ 376.1675. Found m/z 376.1674.

(Z)-1,1-Dimethoxycarbonyl-3-(1-phenylethylidene)-4-methyl-4-vinylcyclopentane (3ha)

IR (neat): 2953, 1740, 1435, 1256, 1204, 1170 cm⁻¹; ¹H NMR: δ = 0.79 (s, 3H), 1.92–1.98 (m, 3H), 2.25 (d, *J* = 13.5, 1H), 2.47 (dd, *J* = 13.4, 1.1 Hz, 1H), 3.16 (dd, *J* = 17.4, 1.2 Hz, 1H), 3.31 (dt, *J* = 17.6, 1.3 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.69 (dd, *J* = 10.5, 1.2 Hz, 1H), 4.76 (dt, *J* = 17.4, 1.2 Hz, 1H), 5.58 (dd, *J* = 17.4, 10.8 Hz, 1H), 7.02–7.09 (m, 2H), 7.12–7.25 (m, 3H); ¹³C NMR: δ = 24.4, 25.3, 40.3, 49.1, 49.3, 52.7, 52.9, 57.1, 111.1, 126.1, 127.4, 128.5, 131.1, 138.7, 143.6, 145.5, 172.3, 172.8; HRMS (EI⁺): Calcd for C₂₀H₂₄O₄, M⁺ 328.1675. Found m/z 328.1667.

(Z)-1,1-Dimethoxycarbonyl-3-(1-phenylethylidene)-4-(formylmethyl)cyclopentane (3ia)

IR (neat): 2955, 2728, 1722, 1435, 1261, 1203 cm⁻¹; ¹H NMR: δ = 1.91 (dd, *J* = 13.5, 7.7 Hz, 1H), 1.97 (br s, 3H), 2.04 (ddd, *J* = 17.7, 9.3, 2.1 Hz, 1H), 2.11 (ddd, *J* = 17.4, 4.2, 1.2 Hz, 1H), 2.68 (ddd, *J* = 13.4, 8.3, 1.6 Hz, 1H), 3.01 (dt, *J* = 16.7, 1.9 Hz, 1H), 3.13 (d, *J* = 16.5 Hz, 1H), 3.29–3.43 (m, 1H), 3.75 (s, 3H), 3.78 (s, 3H), 7.09–7.14 (m, 2H), 7.17–7.25 (m, 1H), 7.26–7.34 (m, 2H), 9.32–9.34 (m, 1H); ¹³C NMR: δ = 22.6, 35.0, 39.3, 40.0, 47.8, 52.85, 52.91, 58.8, 126.8, 127.5, 128.5, 131.0, 136.5, 143.2, 172.0, 172.1, 201.3; HRMS (CI⁺): Calcd for C₁₉H₂₃O₅, M+H⁺ 331.1545. Found m/z 331.1547.

(Z)-1,1-Bis(methoxymethyl)-3-(1-phenylethylidene)-4-vinylcyclopentane (3ja)

IR (neat): 2975, 1458, 1447, 1198, 1109 cm⁻¹; ¹H NMR: δ = 1.45 (dd, *J* = 13.2, 6.3 Hz, 1H), 1.80 (ddd, *J* = 13.2, 8.7, 0.9 Hz, 1H), 1.98 (br s, 3H), 2.26 (dt, *J* = 16.2, 1.8 Hz, 1H), 2.43 (d, *J* = 16.5 Hz, 1H), 3.24 (d, *J* = 9.3 Hz, 1H), 3.28 (d, *J* = 9.0 Hz, 1H), 3.32–3.36 (m, 3H), 3.36 (s, 3H), 3.38 (s, 3H), 4.47–4.59 (m, 2H), 5.43 (ddd, *J* = 17.4, 10.2, 7.2 Hz, 1H), 7.11–7.29 (m, 5H); ¹³C NMR: δ = 22.3, 37.7, 38.4, 44.9, 46.4, 59.3, 59.4, 75.5, 77.0, 112.4, 125.9, 127.7, 128.0, 130.6, 139.0, 141.6, 144.1; HRMS (EI⁺): Calcd for C₁₉H₂₆O₂, M⁺ 286.1933. Found m/z 286.1928.

(Z)-1,1-Bis(phenylsulfonyl)-3-(1-phenylethylidene)-4-vinylcyclopentane (3ka)

IR (nujol): 2361, 1330, 1314, 1148, 1080 cm⁻¹; ¹H NMR: δ = 1.89 (s, 3H), 2.53 (dd, *J* = 15.3, 7.2 Hz, 1H), 2.77 (ddd, *J* = 15.2, 8.5, 1.6 Hz, 1H), 3.09 (d, *J* = 18.3 Hz, 1H), 3.57 (dt, *J* = 18.0, 2.2 Hz, 1H), 3.58–3.70 (m, 1H), 4.33 (d, *J* = 16.8 Hz, 1H), 4.53 (d, *J* = 10.2 Hz, 1H), 5.33 (ddd, *J* = 17.0, 10.1, 8.3 Hz, 1H), 7.01–7.05 (m, 2H), 7.15–7.29 (m, 3H), 7.58–7.66 (m, 4H), 7.70–7.79 (m, 2H), 8.06–8.13 (m, 4H); ¹³C NMR: δ = 22.7, 36.3, 37.6, 45.9, 92.5, 114.2, 126.6, 127.8, 128.0, 128.7, 128.8, 131.00, 131.06, 132.5, 134.3, 134.5, 134.7, 136.1, 137.2, 138.7, 142.6; HRMS (CI⁺): Calcd for C₂₇H₂₇O₄S₂, M+H⁺ 479.1351. Found m/z 479.1354.

(E)-3-(1-Phenylethylidene)-1-(*p*-toluenesulfonyl)-4-vinylpyrrolidine (3la)

IR (neat): 2984, 1599, 1495, 1338, 1163, 1096 cm⁻¹; ¹H NMR: δ = 1.91 (br s, 3H), 2.46 (s, 3H), 3.17

(dd, $J = 9.3, 6.6$ Hz, 1H), 3.23–3.33 (m, 1H), 3.26 (dd, $J = 9.2, 2.3$ Hz, 1H), 3.85 (d, $J = 14.1$ Hz, 1H), 4.01 (dt, $J = 14.0, 1.4$ Hz, 1H), 4.63 (dt, $J = 17.1, 1.4$ Hz, 1H), 4.76 (dt, $J = 10.1, 1.1$ Hz, 1H), 5.53 (ddd, $J = 17.0, 10.0, 7.0$ Hz, 1H), 7.04–7.11 (m, 2H), 7.16–7.29 (m, 3H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.71–7.78 (m, 2H); ^{13}C NMR: $\delta = 21.6, 21.8, 45.2, 50.5, 53.8, 115.0, 126.8, 127.4, 127.9, 128.0, 129.6, 131.7, 132.8, 132.9, 137.5, 142.2, 143.6$; HRMS (CI^+): Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{NS}$, $\text{M}+\text{H}^+$ 354.1528. Found m/z 354.1525.

Dimethyl 2-((*E*)-3-phenylbut-2-enyl)-2-methylmalonate (5)

IR (neat): 2953, 1736, 1435, 1244, 1204, 1111 cm^{-1} ; ^1H NMR: $\delta = 1.47$ (s, 3H), 2.05 (br s, 3H), 2.80 (d, $J = 7.5$ Hz, 2H), 3.74 (s, 6H), 5.61 (tq, $J = 7.8, 1.5$ Hz, 1H), 7.19–7.37 (m, 5H); ^{13}C NMR: $\delta = 16.2, 20.0, 34.8, 52.6, 53.9, 121.7, 125.8, 126.9, 128.1, 138.7, 143.6, 172.5$; HRMS (EI^+): Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4$, M^+ 276.1362. Found m/z 276.1362.

Rhodium-catalyzed asymmetric cyclization of 1,6-enynes 1a

To an oven-dried, N_2 -purged flask was added $[\text{Rh}(\text{OH})((R)\text{-BINAP})]_2$ (7.4 mg, 0.5 μmol , 0.05 equiv of Rh) and phenylboronic acid (**2a**) (121 mg, 1.0 mmol, 5.0 equiv), followed by 1 mL of 1,4-dioxane. A solution of substrate **1a** (0.2 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) was added to the reaction mixture at room temperature. After 14 h, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate=5:1) to give the product **3aa**.

The ee was determined on a Daicel Chiralpak OD-H column with hexane:isopropanol=93:7, flow rate=0.6 mL/min. Retention times: 8.04 min, 9.47 min. 97% ee. $[\alpha]_D^{23} +58.6$ (c 0.945, CHCl_3).

Rhodium-catalyzed domino cyclization of enediyne

(*Z*)-5,5,10,10-tetramethoxycarbonyl-1-methoxytetradeca-2-ene-7,12-diyne (6)

A solution of dimethyl 2-(but-2-ynyl)malonate (553 mg, 3.0 mmol) in THF (5 mL) was added slowly to a suspension of NaH (dry 95%, 78 mg, 3.1 mmol) in THF (12 mL) at 0 $^\circ\text{C}$, and the mixture was stirred at room temperature for 1 h. The resulting solution was added dropwise for 2 h at -10 $^\circ\text{C}$ to a solution of 1,4-dibromo-2-butyne¹¹ (708 mg, 3.3 mmol) in THF (5 mL), and the resulting mixture was stirred at room temperature for an additional 1 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried with MgSO_4 , filtered and concentrated. The crude oil was purified by silica gel chromatography (hexane:ethyl acetate=5:1~3:1) to give dimethyl 2-(4-bromobut-2-ynyl)-2-(but-2-ynyl)malonate (582 mg, 1.8 mmol, 62% yield) as a viscous oil; ^1H NMR: $\delta = 1.76$ (t, $J = 2.7$ Hz, 3H), 2.90 (q, $J = 2.7$ Hz, 2H), 3.03 (t, $J = 2.4$ Hz, 2H), 3.76 (s, 6H), 3.86 (t, $J = 2.4$ Hz, 2H).

A solution of dimethyl 2-((*Z*)-4-methoxybut-2-enyl)malonate (412 mg, 1.9 mmol) in THF (5 mL) was added slowly to a suspension of NaH (dry 95%, 75 mg, 3.0 mmol) in THF (5 mL) at 0 $^\circ\text{C}$, and the mixture was stirred at room temperature for 1 h. A solution of dimethyl 2-(4-bromobut-2-ynyl)-2-(but-2-ynyl)malonate (582 mg, 1.8 mmol) in THF (5 mL) was added dropwise via syringe, and the mixture was stirred at room temperature for 1 h. Water was added slowly to quench the reaction, and the reaction mixture was extracted with ethyl acetate. The combined organic extracts

¹¹ Machinek, R.; Lüttke, W. *Synthesis* **1975**, 255.

were washed with brine, dried with MgSO_4 , filtered and concentrated. The crude oil was purified by silica gel chromatography (hexane:ethyl acetate=3:1) to give **6** (701 mg, 1.8 mmol, 85% yield) as a viscous oil.

IR (neat): 2957, 1739, 1437, 1329, 1294, 1239 cm^{-1} ; ^1H NMR: δ = 1.74 (t, J = 2.6 Hz, 3H), 2.75 (t, J = 2.4 Hz, 2H), 2.78 (d, J = 7.8 Hz, 2H), 2.87 (q, J = 2.5 Hz, 2H), 2.93 (t, J = 2.3 Hz, 2H), 3.34 (s, 3H), 3.73 (s, 6H), 3.74 (s, 6H), 4.01 (dd, J = 6.6, 1.5 Hz, 2H), 5.28–5.40 (m, 1H), 5.64–5.75 (m, 1H); ^{13}C NMR: δ = 3.5, 22.88, 22.93, 30.2, 52.8, 52.9, 56.7, 56.9, 58.0, 67.9, 72.9, 77.7, 77.8, 79.1, 125.5, 128.3, 131.1, 169.3, 170.1; HRMS (CI^+): Calcd for $\text{C}_{23}\text{H}_{31}\text{O}_9$, $\text{M}+\text{H}^+$ 451.1968. Found m/z 451.1979.

(Z)-1,1-dimethoxycarbonyl-3-[3,3-dimethoxycarbonyl-5-((Z)-1-phenylethylidene)-cyclopentylidene]-4-vinylcyclopentane (7)

To an oven-dried, N_2 -purged flask was added $[\text{Rh}(\text{OH})(\text{cod})]_2$ (1.70 mg, 0.37 μmol , 0.06 equiv of Rh) and phenylboronic acid (59.7 mg, 0.49 mmol, 4.0 equiv), followed by 1.0 mL of 1,4-dioxane. A solution of enediyne **6** (55.6 mg, 0.12 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL) was added to the reaction mixture at room temperature. After 18 h, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate=3:1) to give **7** (32.5 mg, 0.066 mmol, 53% yield).

The Z and Z configuration of two double bonds was confirmed on the basis of the observed NOEs shown below.

6

IR (neat): 2955, 1732, 1435, 1270, 1204, 1063 cm^{-1} ; ^1H NMR: δ = 1.39–1.52 (m, 1H), 1.82 (dd, J = 12.9, 9.3 Hz, 1H), 1.97 (br s, 3H), 2.14 (ddd, J = 12.7, 8.3, 1.7 Hz, 1H), 2.72–2.82 (m, 1H), 2.82–2.98 (m, 3H), 3.01–3.11 (m, 2H), 3.64 (s, 3H), 3.65 (s, 3H), 3.74 (s, 3H), 3.76 (s, 3H), 4.61 (dt, J = 17.3, 1.7 Hz, 1H), 4.79 (dt, J = 10.5, 1.5 Hz, 1H), 5.35 (ddd, J = 17.2, 10.6, 6.5 Hz, 1H), 7.08–7.16 (m, 3H), 7.18–7.25 (m, 2H); ^{13}C NMR: δ = 21.3, 39.1, 39.4, 40.9, 41.2, 44.0, 52.59, 52.64, 52.8, 52.9, 56.6, 58.4, 113.4, 126.2, 127.9, 128.0, 130.6, 131.7, 132.5, 135.6, 139.3, 143.8, 171.1, 171.8, 172.1, 172.3; HRMS (CI^+): Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_8$, M^+ 496.2097. Found m/z 496.2095.