Rhodium-Catalyzed Isomerization of Unactivated Alkynes to 1,3-Dienes

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Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon.

Et_2O and THF were purified by passing through a neutral alumina column under nitrogen. DMF and 1,2-dichloroethane were distilled over CaH_2 under vacuum.

Dimethyl allylmalonate (Aldrich), methyl 2-oxocyclopentanecarboxylate (Aldrich), dimethyl methylmalonate (Aldrich), benzyl bromide (Nacalai Tesque), 1-bromo-2-pentyne (Wako Chemicals), iodoethane (TCI), 1-phenyl-1-hexyne (TCI), $LiAlH_4$ (Wako Chemicals), NaH (Kanto Chemicals; 60 wt% in mineral oil), and *n*-BuLi (Kanto Chemicals; 1.59 M solution in hexane) were used as received.

Dimethyl methyl(2-pentynyl)malonate (**1a**),[1] methyl 5,5-bis(methoxycarbonyl)-2-decen-7-ynoate (**1j**),[1] *tert*-butyl 4-ethynylpiperidine-1-carboxylate,[2] 1-benzylidene-3-oxopyrazolidin-1-ium-2-ide (**3**),[3] 2-hexyn-1-yl *p*-toluenesulfonate,[4] $[RhCl(cod)]_2$,[5] $RhH(PPh_3)_4$,[6] and (±)-binap[7] were synthesized following the literature procedures.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemicals and used as received.

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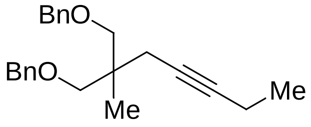
II. Synthesis of Substrates

The yields have not been optimized.

6,6-bis(benzyloxymethyl)-3-pentyne (1b)



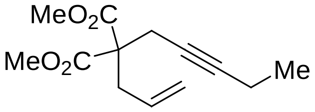
1b

A solution of dimethyl methyl(2-pentynyl)malonate (**1a**; 1.06 g, 4.99 mmol) in Et_2O (8 mL) was added to a suspension of $LiAlH_4$ (378 mg, 9.96 mmol) in Et_2O (12 mL) at 0 °C. The mixture was stirred for 9 h at room temperature and the reaction was quenched with water. The precipitate was removed by filtration, and the remaining solution was dried over $MgSO_4$, filtered, and concentrated under vacuum to afford diol as a colorless oil (775 mg, 4.96 mmol; 99% yield).

A solution of this diol in THF (10 mL) was added to a suspension of NaH (602 mg, 15.1 mmol; 60 wt% in mineral oil) in THF (15 mL)/DMF (3 mL) at 0 °C. The resulting mixture was stirred for 30 min at 0 °C and benzyl bromide (1.31 mL, 11.0 mmol) was then added to it. After stirring for 12 h at room temperature, the reaction was quenched with water and extracted with Et_2O. The organic layer was washed with NaCl (saturated, aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O/hexane = 1/30 to afford **1b** as a colorless oil (983 mg, 2.92 mmol; 59% yield).

^1H NMR ($CDCl_3$): δ 7.37-7.31 (m, 8H), 7.29-7.25 (m, 2H), 4.52 (s, 4H), 3.40 (d, $^2J_{HH}$ = 8.8 Hz, 2H), 3.36 (d, $^2J_{HH}$ = 8.9 Hz, 2H), 2.25 (t, $^5J_{HH}$ = 2.2 Hz, 2H), 2.14 (qt, $^3J_{HH}$ = 7.5 Hz and $^5J_{HH}$ = 2.4 Hz, 2H), 1.10 (t, $^3J_{HH}$ = 7.4 Hz, 3H), 1.03 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.2, 128.4, 127.52, 127.50, 83.7, 76.5, 74.5, 73.5, 39.6, 25.2, 19.7, 14.6, 12.7. HRMS (ESI) calcd for $C_{23}H_{29}O_2$ ($M+H^+$) 337.2162, found 337.2166.

Dimethyl allyl(2-pentynyl)malonate (1c) (CAS 191801-56-6)

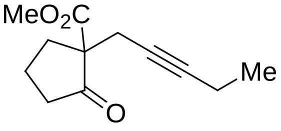


1c

Dimethyl allylmalonate (804 μL, 5.00 mmol) was added dropwise to a suspension of NaH (240 mg, 6.00 mmol; 60 wt% in mineral oil) in THF (15 mL) at 0 °C. The resulting mixture was stirred for 20 min at 0 °C and 1-bromo-2-pentyne (639 μL, 6.25 mmol) was then added to it. After stirring for 11 h at room temperature, the reaction was quenched with water and extracted with Et_2O. The organic layer was washed with NaCl (saturated, aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O / hexane = 1 / 6 to afford **1c** as a pale yellow oil (1.17 g, 4.89 mmol; 98% yield).

^1H NMR ($CDCl_3$): δ 5.62 (ddt, $^3J_{HH}$ = 17.1, 9.7, and 7.5 Hz, 1H), 5.15 (d, $^3J_{HH}$ = 17.0 Hz, 1H), 5.10 (d, $^3J_{HH}$ = 10.0 Hz, 1H), 3.72 (s, 6H), 2.78 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 2.74 (s, 2H), 2.12 (q, $^3J_{HH}$ = 7.4 Hz, 2H), 1.08 (t, $^3J_{HH}$ = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 170.7, 132.2, 119.7, 85.3, 73.7, 57.5, 52.8, 36.8, 23.2, 14.4, 12.5.

Methyl 2-oxo-1-(2-pentynyl)cyclopentanecarboxylate (1d) (CAS 68480-23-9)

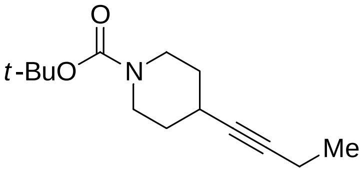


1d

Methyl 2-oxocyclopentanecarboxylate (621 μL, 5.00 mmol) was added dropwise to a suspension of NaH (240 mg, 6.00 mmol; 60 wt% in mineral oil) in THF (15 mL) at 0 °C. The resulting mixture was stirred for 12 min at 0 °C and 1-bromo-2-pentyne (639 μL, 6.25 mmol) was then added to it. After stirring for 2 h at room temperature, the reaction was quenched with water and extracted with Et_2O. The organic layer was washed with NaCl (saturated, aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O / hexane = 1 / 4 to afford **1d** as a yellow oil (654 mg, 3.14 mmol; 63% yield).

^1H NMR ($CDCl_3$): δ 3.70 (s, 3H), 2.68 (t, $^5J_{HH}$ = 2.3 Hz, 2H), 2.50-2.43 (m, 2H), 2.34-2.23 (m, 2H), 2.12 (qt, $^3J_{HH}$ = 7.5 Hz and $^5J_{HH}$ = 2.4 Hz, 2H), 2.08-2.02 (m, 2H), 1.08 (t, $^3J_{HH}$ = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 214.3, 171.3, 84.5, 74.7, 59.4, 52.9, 38.7, 32.7, 23.9, 20.0, 14.3, 12.5.

***tert*-Butyl 4-(1-butynyl)piperidine-1-carboxylate (1e)**

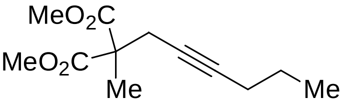


1e

n-BuLi (1.89 mL, 3.01 mmol; 1.59 M solution in hexane) was added to a solution of *tert*-butyl 4-ethynylpiperidine-1-carboxylate (628 mg, 3.00 mmol) in THF (10 mL) at –78 °C. The resulting mixture was stirred for 25 min at –78 to –55 °C and iodoethane (360 μL, 4.50 mmol) was then added to it. After stirring for 19 h at 50 °C, the reaction was diluted with NaCl (aqueous) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O/hexane = 1/4 to afford **1e** as a colorless oil (712 mg, 3.00 mmol; 100% yield).

^{1}H NMR ($CDCl_3$): δ 3.67 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 6.7 and 3.8 Hz, 2H), 3.15 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 8.5 and 3.4 Hz, 2H), 2.55-2.49 (m, 1H), 2.16 (qd, $^3J_{HH}$ = 7.4 Hz and $^5J_{HH}$ = 2.1 Hz, 2H), 1.73 (ddt, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 6.8 and 3.7 Hz, 2H), 1.51 (dtd, $^2J_{HH}$ = 13.1 Hz and $^3J_{HH}$ = 8.3 and 3.5 Hz, 2H), 1.45 (s, 9H), 1.11 (t, $^3J_{HH}$ = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 155.0, 83.3, 81.7, 79.5, 42.5, 32.0, 28.7, 27.2, 14.6, 12.6. HRMS (ESI) calcd for $C_{14}H_{23}NO_2Na$ (M+Na$^+$) 260.1621, found 260.1609.

Dimethyl methyl(2-hexynyl)malonate (1g)

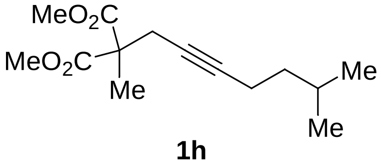


1g

Dimethyl methylmalonate (320 μL, 2.40 mmol) was added dropwise to a suspension of NaH (106 mg, 2.65 mmol; 60 wt% in mineral oil) in THF (5 mL) at 0 °C. The resulting mixture was stirred for 25 min at 0 °C and 2-hexyn-1-yl *p*-toluenesulfonate (908 mg, 3.60 mmol) was then added to it. After stirring for 12 h at room temperature, the reaction was quenched with water and extracted with Et_2O. The organic layer was washed with NaCl (saturated, aqueous), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 2/1 to afford **1g** as a colorless oil (333 mg, 1.47 mmol; 61% yield).

^{1}H NMR ($CDCl_3$): δ 3.72 (s, 6H), 2.75 (t, $^5J_{HH}$ = 2.4 Hz, 2H), 2.09 (tt, $^3J_{HH}$ = 7.0 Hz and ${}^{5}J_{HH}$ = 2.4 Hz, 2H), 1.53 (s, 3H), 1.47 (sextet, ${}^{3}J_{HH}$ = 7.2 Hz, 2H), 0.94 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 171.8, 83.6, 74.9, 53.8, 52.9, 26.5, 22.5, 20.8, 20.1, 13.5. HRMS (ESI) calcd for $C_{12}H_{18}O_4Na$ ($M+Na^+$) 249.1097, found 249.1108.

Dimethyl methyl(6-methyl-2-heptynyl)malonate (1h)

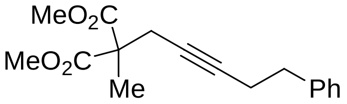


1h

This was synthesized following the procedure for compound **1g**. Colorless oil, 74% yield.

^{1}H NMR ($CDCl_3$): δ 3.73 (s, 6H), 2.75 (t, ${}^{5}J_{HH}$ = 2.4 Hz, 2H), 2.12 (tt, ${}^{3}J_{HH}$ = 7.4 Hz and ${}^{5}J_{HH}$ = 2.4 Hz, 2H), 1.70-1.59 (m, 1H), 1.53 (s, 3H), 1.34 (q, ${}^{3}J_{HH}$ = 7.2 Hz, 2H), 0.87 (d, ${}^{3}J_{HH}$ = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 171.6, 83.5, 74.4, 53.6, 52.7, 37.8, 27.1, 26.3, 22.1, 19.9, 16.6. HRMS (ESI) calcd for $C_{14}H_{22}O_4Na$ ($M+Na^+$) 277.1410, found 277.1411.

Dimethyl methyl(5-phenyl-2-pentynyl)malonate (1i)



1i

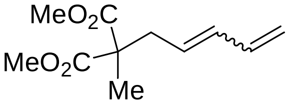
This was synthesized following the procedure for compound **1g**. Colorless oil, 100% yield.

^{1}H NMR ($CDCl_3$): δ 7.30-7.27 (m, 2H), 7.21-7.18 (m, 3H), 3.72 (s, 6H), 2.77 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 2H), 2.75 (t, ${}^{5}J_{HH}$ = 2.3 Hz, 2H), 2.43 (tt, ${}^{3}J_{HH}$ = 7.5 Hz and ${}^{5}J_{HH}$ = 2.3 Hz, 2H), 1.49 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 171.8, 140.9, 128.6, 128.5, 126.4, 82.9, 75.6, 53.7, 52.9, 35.5, 26.5, 21.0, 20.1. HRMS (ESI) calcd for $C_{17}H_{21}O_4$ ($M+H^+$) 289.1434, found 289.1429.

III. Catalytic Reactions

General Procedure for Equation 2 and Table 1.

A solution of $[RhCl(cod)]_2$ (2.5 mg, 10 μmol Rh) and (±)-binap (6.8 mg, 11 μmol) in 1,2-dichloroethane (0.3 mL) was stirred for 5 min at room temperature. Dipole **3** (34.8 mg, 0.20 mmol) and alkyne **1** (0.20 mmol) were added to it with additional 1,2-dichloroethane (0.3 mL), and the mixture was stirred for 24–72 h at 80–100 °C. After cooled to room temperature, the reaction mixture was directly passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with Et_2O / hexane to afford compound **2**.

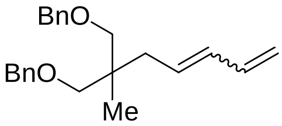


2a

Equation 1. (CAS 148876-15-7 for *E*; 148876-25-9 for *Z*) The reaction was conducted for 24 h at 80 °C. Colorless oil. 89% yield, *E* / *Z* = 77 / 23.

E-isomer: ^{1}H NMR ($CDCl_3$): δ 6.27 (dt, $^3J_{HH}$ = 17.0 and 10.3 Hz, 1H), 6.08 (dd, $^3J_{HH}$ = 15.0 and 10.5 Hz, 1H), 5.54 (dt, $^3J_{HH}$ = 15.1 and 7.6 Hz, 1H), 5.12 (d, $^3J_{HH}$ = 16.7 Hz, 1H), 5.01 (d, $^3J_{HH}$ = 10.1 Hz, 1H), 3.71 (s, 6H), 2.63 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 1.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 172.2, 136.5, 135.1, 128.1, 116.4, 53.8, 52.5, 38.9, 19.9.

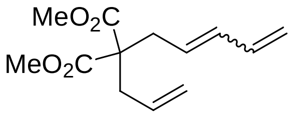
Z-isomer: ^{1}H NMR ($CDCl_3$): δ 6.61 (dt, $^3J_{HH}$ = 16.8 and 10.7 Hz, 1H), 6.12 (t, $^3J_{HH}$ = 11.0 Hz, 1H), 5.32 (dt, $^3J_{HH}$ = 10.1 and 8.2 Hz, 1H), 5.22 (d, $^3J_{HH}$ = 16.9 Hz, 1H), 5.14 (d, $^3J_{HH}$ = 10.7 Hz, 1H), 3.70 (s, 6H), 2.76 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 1.40 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 172.2, 132.9, 131.6, 125.2, 118.5, 53.7, 52.5, 33.6, 19.8.



2b

Table 1, Entry 1. The reaction was conducted for 48 h at 80 °C in the presence of 7 mol% catalyst. Colorless oil. 76% yield, *E* / *Z* = 73 / 27.

^{1}H NMR ($CDCl_3$): δ 7.37-7.27 (m, 10H), 6.69 (dt, $^3J_{HH}$ = 16.8 and 10.6 Hz, 0.27H), 6.28 (dt, $^3J_{HH}$ = 17.0 and 10.2 Hz, 0.73H), 6.10 (t, $^3J_{HH}$ = 11.0 Hz, 0.27H), 6.04 (dd, $^3J_{HH}$ = 15.1 and 10.3 Hz, 0.73H), 5.65 (dt, $^3J_{HH}$ = 15.0 and 7.8 Hz, 0.73H), 5.47 (dt, $^3J_{HH}$ = 10.1 and 8.9 Hz, 0.27H), 5.18 (dd, $^3J_{HH}$ = 17.0 Hz and $^2J_{HH}$ = 2.1 Hz, 0.27H), 5.08 (dd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 1.4 Hz, 0.73H), 5.06 (d, $^3J_{HH}$ = 10.0 Hz, 0.27H), 4.96 (dd, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 1.3 Hz, 0.73H), 4.49 (s, 2.92H), 4.48 (s, 1.08H), 3.31 (d, $^2J_{HH}$ = 8.8 Hz, 0.54H), 3.30 (d, $^{2}J_{HH}$ = 8.8 Hz, 1.46H), 3.29 (d, $^{2}J_{HH}$ = 8.7 Hz, 0.54H), 3.28 (d, $^{2}J_{HH}$ = 8.8 Hz, 1.46H), 2.27 (d, $^{3}J_{HH}$ = 8.1 Hz, 0.54H), 2.14 (d, $^{3}J_{HH}$ = 7.8 Hz, 1.46H), 0.94 (s, 0.81H), 0.92 (s, 2.19H). ^{13}C NMR ($CDCl_3$): δ 138.9, 137.2, 133.7, 132.5, 131.6, 131.0, 128.4, 128.21, 128.20, 127.7, 127.31, 127.30, 127.29, 127.26, 116.7, 114.9, 74.7, 74.6, 73.2, 73.1, 39.9, 39.7, 38.0, 32.5, 19.6, 19.5. HRMS (ESI) calcd for $C_{23}H_{29}O_2$ ($M+H^+$) 337.2162, found 337.2162.



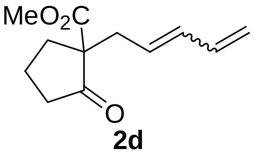
2c

Table 1, Entry 2. (CAS 355114-57-7 for *E*) The reaction was conducted for 24 h at 80 °C. Colorless oil. 84% yield, *E*/*Z* = 69/31.

^{1}H NMR ($CDCl_3$): δ 6.59 (dt, $^{3}J_{HH}$ = 16.7 and 10.8 Hz, 0.31H), 6.27 (dt, $^{3}J_{HH}$ = 16.9 and 10.3 Hz, 0.69H), 6.13-6.05 (m, 1H), 5.68-5.59 (m, 1H), 5.50 (dt, $^{3}J_{HH}$ = 15.0 and 7.6 Hz, 0.69H), 5.28 (dt, $^{3}J_{HH}$ = 10.6 and 8.1 Hz, 0.31H), 5.21 (d, $^{3}J_{HH}$ = 16.8 Hz, 0.31H), 5.15-5.09 (m, 3H), 5.01 (d, $^{3}J_{HH}$ = 10.0 Hz, 0.69H), 3.71 (s, 4.14H), 3.70 (s, 1.86H), 2.78 (d, $^{3}J_{HH}$ = 7.9 Hz, 0.62H), 2.67-2.62 (m, 3.38H).

E-isomer: ^{13}C NMR ($CDCl_3$): δ 171.4, 136.8, 135.3, 132.4, 127.9, 119.5, 116.7, 58.0, 52.6, 37.3, 36.0.

Z-isomer: ^{13}C NMR ($CDCl_3$): δ 171.4, 133.1, 132.4, 131.9, 125.1, 119.6, 118.8, 58.0, 52.6, 37.2, 30.8.

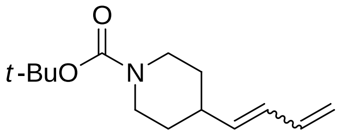


2d

Table 1, Entry 3. The reaction was conducted for 24 h at 80 °C. Colorless oil. 76% yield, *E*/*Z* = 83/17.

^{1}H NMR ($CDCl_3$): δ 6.62 (dt, $^{3}J_{HH}$ = 16.8 and 10.6 Hz, 0.17H), 6.27 (dt, $^{3}J_{HH}$ = 17.0 and 10.4 Hz, 0.83H), 6.14-6.09 (m, 0.17H), 6.09 (dd, $^{3}J_{HH}$ = 15.2 and 10.5 Hz, 0.83H), 5.54 (dt, $^{3}J_{HH}$ = 15.1 and 7.4 Hz, 0.83H), 5.32 (dt, $^{3}J_{HH}$ = 10.4 and 7.9 Hz, 0.17H), 5.23 (d, $^{3}J_{HH}$ = 16.8 Hz, 0.17H), 5.17-5.15 (m, 0.17H), 5.13 (d, $^{3}J_{HH}$ = 15.9 Hz, 0.83H), 5.02 (d, $^{3}J_{HH}$ = 10.1 Hz, 0.83H), 3.70 (s, 2.49H), 3.69 (s, 0.51H), 2.83 (ddd, $^{2}J_{HH}$ = 14.4 Hz, $^{3}J_{HH}$ =

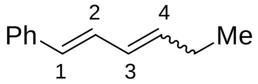
8.0 Hz, and $^{4}J_{HH}$ = 1.2 Hz, 0.17H), 2.69 (ddd, $^{2}J_{HH}$ = 14.1 Hz, $^{3}J_{HH}$ = 7.4 Hz, and $^{4}J_{HH}$ = 1.1 Hz, 0.83H), 2.53-2.36 (m, 3H), 2.26 (m, 1H), 2.03-1.87 (m, 3H). ^{13}C NMR (*E*-isomer, $CDCl_3$): δ 214.4, 171.3, 136.5, 135.1, 128.5, 116.5, 60.2, 52.5, 38.0, 36.6, 32.1, 19.5. HRMS (ESI) calcd for $C_{12}H_{16}O_3Na$ (M+Na$^+$) 231.0992, found 231.0990.



2e

Table 1, Entry 4. The reaction was conducted for 24 h at 80 °C. Colorless oil. 81% yield (contaminated with ~5% impurity), *E* / *Z* = 85 / 15.

^{1}H NMR ($CDCl_3$): δ 6.63 (dt, $^{3}J_{HH}$ = 17.0 and 10.5 Hz, 0.15H), 6.29 (dt, $^{3}J_{HH}$ = 17.0 and 10.2 Hz, 0.85H), 6.04 (dd, $^{3}J_{HH}$ = 15.4 and 10.4 Hz, 0.85H), 5.95 (t, $^{3}J_{HH}$ = 11.0 Hz, 0.15H), 5.63 (dd, $^{3}J_{HH}$ = 15.5 and 6.7 Hz, 0.85H), 5.26 (t, $^{3}J_{HH}$ = 10.0 Hz, 0.15H), 5.21 (d, $^{3}J_{HH}$ = 16.0 Hz, 0.15H), 5.12 (d, $^{3}J_{HH}$ = 15.7 Hz, 0.85H), 5.11 (d, $^{3}J_{HH}$ = 10.5 Hz, 0.15H), 5.00 (d, $^{3}J_{HH}$ = 10.1 Hz, 0.85H), 4.08 (bs, 2H), 2.73 (bs, 2H), 2.64-2.53 (m, 0.15H), 2.20-2.11 (m, 0.85H), 1.69-1.58 (m, 2H), 1.45 (s, 9H), 1.33-1.25 (m, 2H). ^{13}C NMR (*E*-isomer, $CDCl_3$): δ 154.8, 138.6, 137.1, 132.0, 115.6, 79.3, 42.7, 38.8, 31.6, 28.4. HRMS (ESI) calcd for $C_{14}H_{23}NO_2Na$ (M+Na$^+$) 260.1621, found 260.1612.



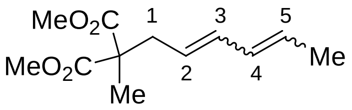
2f

Table 1, Entry 5. (CAS 39491-62-8 for (1*E*,3*E*); 39491-61-7 for (1*E*,3*Z*)) The reaction was conducted for 36 h at 100 °C. Colorless oil. 73% yield, (1*E*,3*E*) / (1*E*,3*Z*) = 71 / 29.

E-isomer: ^{1}H NMR ($CDCl_3$): δ 7.37 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H), 7.29 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.19 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.76 (dd, $^{3}J_{HH}$ = 15.7 and 10.3 Hz, 1H), 6.45 (d, $^{3}J_{HH}$ = 15.7 Hz, 1H), 6.21 (dd, $^{3}J_{HH}$ = 15.1 and 10.4 Hz, 1H), 5.67 (dt, $^{3}J_{HH}$ = 15.1 and 6.7 Hz, 1H), 2.17 (quint, $^{3}J_{HH}$ = 7.1 Hz, 2H), 1.05 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H).

Z-isomer: ^{1}H NMR ($CDCl_3$): δ 7.41 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H), 7.34-7.31 (m, 2H), 7.21 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 7.04 (dd, $^{3}J_{HH}$ = 15.7 and 11.1 Hz, 1H), 6.52 (d, $^{3}J_{HH}$ = 15.7 Hz, 1H), 6.13 (t, $^{3}J_{HH}$ = 10.8 Hz, 1H), 5.53 (dt, $^{3}J_{HH}$ = 10.6 and 7.6 Hz, 1H), 2.17 (quint of d, $^{3}J_{HH}$ = 7.6 Hz and $^{4}J_{HH}$ = 1.5 Hz, 2H), 1.05 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H).

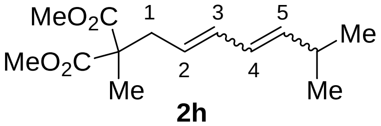
^{13}C NMR (CDCl$_3$): δ 137.7, 137.4, 134.8, 131.2, 129.9, 129.53, 129.45, 128.54, 128.51, 128.1, 127.3, 127.0, 126.3, 126.1, 124.3, 25.9, 21.3, 14.3, 13.5.



2g

Table 1, Entry 6. (CAS 198876-11-3 for (2*E*,4*E*)) The reaction was conducted for 61 h at 100 °C. Colorless oil. 84% yield, (2*E*,4*E*) / (2*E*,4*Z*) / (2*Z*,4*E*) / (2*Z*,4*Z*) = 49 / 35 / 8 / 8.

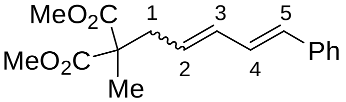
^{1}H NMR (CDCl$_3$): δ 6.43-6.22 (m, 0.24H), 6.37 (dd, $^3J_{HH}$ = 14.9 and 11.1 Hz, 0.35H), 6.09-5.92 (m, 1.41H), 5.71 (dq, $^3J_{HH}$ = 15.2 and 7.1 Hz, 0.08H), 5.61 (dq, $^3J_{HH}$ = 14.1 and 6.8 Hz, 0.49H), 5.60-5.54 (m, 0.08H), 5.49 (dt, $^3J_{HH}$ = 15.0 and 7.6 Hz, 0.35H), 5.42 (dq, $^3J_{HH}$ = 10.9 and 7.2 Hz, 0.35H), 5.37 (dt, $^3J_{HH}$ = 13.9 and 7.7 Hz, 0.49H), 5.31 (dt, $^3J_{HH}$ = 10.4 and 8.3 Hz, 0.08H), 5.14 (dt, $^3J_{HH}$ = 10.4 and 8.3 Hz, 0.08H), 3.72-3.70 (m, 6H), 2.75 (d, $^3J_{HH}$ = 7.4 Hz, 0.16H), 2.73 (d, $^3J_{HH}$ = 7.4 Hz, 0.16H), 2.66 (d, $^3J_{HH}$ = 7.6 Hz, 0.70H), 2.60 (d, $^3J_{HH}$ = 7.6 Hz, 0.98H), 1.77-1.71 (m, 3H), 1.40 (s, 0.48H), 1.39 (s, 1.05H), 1.37 (s, 1.47H). ^{13}C NMR (2*E* isomers, CDCl$_3$): δ 172.58, 172.55, 134.9, 131.3, 129.8, 129.1, 128.9, 127.2, 125.9, 124.7, 54.12, 54.09, 52.68, 52.66, 39.5, 39.2, 20.14, 20.08, 18.2, 13.5.



2h

Table 1, Entry 7. The reaction was conducted for 72 h at 100 °C. Colorless oil. 87% yield, (2*E*,4*E*) / (2*E*,4*Z*) / (2*Z*,4*E*) = 84 / 9 / 7.

^{1}H NMR (CDCl$_3$): δ 6.35 (dd, $^3J_{HH}$ = 15.4 and 11.6 Hz, 0.09H), 6.23 (dd, $^3J_{HH}$ = 15.3 and 11.1 Hz, 0.07H), 6.09-6.04 (m, 0.09 H), 6.03 (dd, $^3J_{HH}$ = 15.0 and 10.4 Hz, 0.84H), 5.93 (dd, $^3J_{HH}$ = 15.3 and 10.4 Hz, 0.84H), 5.80 (t, $^3J_{HH}$ = 10.9 Hz, 0.07H), 5.67 (dd, $^3J_{HH}$ = 14.9 and 6.3 Hz, 0.07H), 5.58 (dd, $^3J_{HH}$ = 15.1 and 6.6 Hz, 0.84H), 5.49 (dt, $^3J_{HH}$ = 15.3 and 6.9 Hz, 0.09H), 5.40 (dt, $^3J_{HH}$ = 14.9 and 7.5 Hz, 0.84H), 5.18 (t, $^3J_{HH}$ = 10.0 Hz, 0.09H), 5.16 (dt, $^3J_{HH}$ = 10.8 and 7.9 Hz, 0.07H), 3.71 (s, 5.58H), 3.70 (s, 0.42H), 2.75 (d, $^3J_{HH}$ = 7.9 Hz, 0.18H), 2.65 (d, $^3J_{HH}$ = 7.5 Hz, 0.14H), 2.61 (d, $^3J_{HH}$ = 7.6 Hz, 1.68H), 2.36-2.25 (m 1H), 1.41 (s, 0.27H), 1.39 (s, 0.21H), 1.38 (s, 2.52H), 1.00 (d, $^3J_{HH}$ = 6.8 Hz, 0.42H), 0.98 (d, ${}^3J_{HH}$ = 6.8 Hz, 5.04H), 0.96 (d, ${}^3J_{HH}$ = 6.7 Hz, 0.54H). ^{13}C NMR ((2*E*,4*E*)-isomer, $CDCl_3$): δ 172.4, 141.2, 134.9, 126.8, 124.9, 53.9, 52.5, 39.0, 30.9, 22.2, 19.9. HRMS (ESI) calcd for $C_{14}H_{22}O_4Na$ (M+Na$^+$) 277.1410, found 277.1400.



2i

Table 1, Entry 8. (CAS 148876-13-5 for (2*E*,4*E*); 148876-21-5 for (2*Z*,4*E*)) The reaction was conducted for 48 h at 100 °C. Colorless oil. 83% yield, (2*E*,4*E*) / (2*Z*,4*E*) = 81 / 19.

(2*E*,4*E*)-isomer: ^{1}H NMR ($CDCl_3$): δ 7.37 (d, ${}^3J_{HH}$ = 7.2 Hz, 2H), 7.30 (t, ${}^3J_{HH}$ = 7.7 Hz, 2H), 7.21 (t, ${}^3J_{HH}$ = 7.3 Hz, 1H), 6.73 (dd, ${}^3J_{HH}$ = 15.6 and 10.5 Hz, 1H), 6.48 (d, ${}^3J_{HH}$ = 15.6 Hz, 1H), 6.27 (dd, ${}^3J_{HH}$ = 15.0 and 10.5 Hz, 1H), 5.67 (dt, ${}^3J_{HH}$ = 15.0 and 7.5 Hz, 1H), 3.74 (s, 6H), 2.70 (d, ${}^3J_{HH}$ = 7.7 Hz, 2H), 1.43 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 172.3, 137.2, 134.7, 131.7, 128.6, 128.3, 127.7, 126.4, 126.3, 53.9, 52.5, 39.3, 20.0.

(2*Z*,4*E*)-isomer: ^{1}H NMR ($CDCl_3$): δ 7.42 (d, ${}^3J_{HH}$ = 7.1 Hz, 2H), 7.32 (t, ${}^3J_{HH}$ = 7.4 Hz, 2H), 7.21 (t, ${}^3J_{HH}$ = 7.4 Hz, 1H), 7.04 (dd, ${}^3J_{HH}$ = 16.6 and 11.1 Hz, 1H), 6.56 (d, ${}^3J_{HH}$ = 15.5 Hz, 1H), 6.30 (t, ${}^3J_{HH}$ = 10.9 Hz, 1H), 5.40 (dt, ${}^3J_{HH}$ = 9.5 and 8.0 Hz, 1H), 3.71 (s, 6H), 2.88 (d, ${}^3J_{HH}$ = 8.0 Hz, 2H), 1.46 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 172.3, 137.2, 133.7, 132.5, 128.6, 127.7, 125.3, 123.6, 53.9, 52.6, 33.9, 19.9.

Procedure for Equation 3.

A solution of $[RhCl(cod)]_2$ (2.5 mg, 10 μmol Rh) and (±)-binap (6.8 mg, 11 μmol) in 1,2-dichloroethane (0.3 mL) was stirred for 10 min at room temperature. Dipole **3** (10.5 mg, 60 μmol) and alkyne **1a** (42.5 mg, 0.20 mmol) were added to it with additional 1,2-dichloroethane (0.3 mL), and the mixture was stirred for 43 h at 80 °C. After cooled to room temperature, the reaction mixture was directly passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with Et_2O / hexane = 1 / 5 to afford compound **2a** as a colorless oil (37.0 mg, 0.174 mmol; 87% yield, *E* / *Z* = 76 / 24).

Procedure for Equation 4.

A solution of $RhH(PPh_3)_4$ (18.5 mg, 16.0 μmol Rh) and alkyne **1a** (42.5 mg, 0.20 mmol) in 1,2-dichloroethane (0.6 mL) was stirred for 76 h at 100 °C using a teflonsealed Schlenk tube. After cooled to room temperature, the reaction mixture was directly passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was chromatographed on silica gel with Et_2O/hexane = 1/5 to afford compound **2a** as a pale yellow oil (34.3 mg, 0.161 mmol; 81% yield, E/Z = 78/22).

Procedure for Equation 5.

A solution of $[RhCl(cod)]_2$ (2.5 mg, 10 μmol Rh) and (±)-binap (6.8 mg, 11 μmol) in 1,2-dichloroethane (0.3 mL) was stirred for 10 min at room temperature. Dipole **3** (34.8 mg, 0.20 mmol) and alkyne **1j** (59.3 mg, 0.20 mmol) were added to it with additional 1,2-dichloroethane (0.3 mL), and the mixture was stirred for 63 h at 100 °C. After cooled to room temperature, the reaction mixture was directly passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with Et_2O/hexane = 1/2 to afford compound **4** with diene **2j** (**4**/**2j** = 96/4) as a colorless oil (46.0 mg, 0.155 mmol; 75% yield of **4**, mixture of two diastereomers in 69/31).

^{1}H NMR ($CDCl_3$): δ 5.77 (d, $^3J_{HH}$ = 9.9 Hz, 0.69H), 5.72-5.65 (m, 0.62H), 5.63 (ddd, $^3J_{HH}$ = 9.9, 6.3, and 3.1 Hz, 0.69H), 3.73 (s, 0.93H), 3.72 (s, 2.07H), 3.714 (s, 2.07H), 3.707 (s, 0.93H), 3.70 (s, 2.07H), 3.69 (s, 0.93H), 2.64-2.35 (m, 5H), 2.28-2.10 (m, 1.38H), 2.08 (dd, $^2J_{HH}$ = 14.2 Hz and $^3J_{HH}$ = 5.3 Hz, 0.31H), 1.94 (dd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 10.6 Hz, 0.31H), 1.87 (t, J_{HH} = 12.3 Hz, 0.69H), 1.79-1.72 (m, 0.62H), 1.73 (t, J_{HH} = 12.7 Hz, 0.69H). HRMS (ESI) calcd for $C_{15}H_{21}O_6$ (M+H$^+$) 297.1333, found 297.1329.

Major diastereomer: ^{13}C NMR ($CDCl_3$): δ 175.2, 173.2, 172.9, 127.9, 126.7, 58.2, 52.97, 52.96, 51.8, 44.9, 44.7, 43.6, 38.5, 37.9, 29.7.

Minor diastereomer: ^{13}C NMR ($CDCl_3$): δ 175.9, 173.0, 172.7, 128.7, 125.2, 59.4, 53.0, 52.9, 51.9, 43.6, 42.1, 40.2, 38.5, 38.4, 27.1.