**A Novel X⁺(X=I, Br)-Triggered Ring-opening Coupling Reaction of Cyclopropenes
with Organic Halides.**

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Supporting Information

Typical procedure for ring-opening coupling reaction of cyclopropenes with organic halides.

(1) (*E*)-2-Allyl-2-(2'-iodovinyl)malonic acid dimethyl ester (3aa).

A mixture of cyclopropene **1a** (78 mg, 0.5 mmol), allyl iodide **2a** (168 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), Na₂CO₃ (27 mg, 50 mol%), and acetone (2 mL) was stirred under reflux for 2.5 h. After evaporation, the residue was purified by column chromatography (eluent: petroleum ether/Et₂O = 10/1) on silica gel to give **3aa** (111 mg, 69%) as a liquid. ¹H NMR (CDCl₃, 300 MHz): δ 6.93 (d, *J* = 15.3 Hz, 1 H), 6.42 (d, *J* = 15.3 Hz, 1 H), 5.72-5.56 (m, 1 H), 5.18-5.04 (m, 2 H), 3.74 (s, 6 H), 2.78 (dt, *J* = 7.5 and 1.2 Hz, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.0, 140.6, 131.6, 119.6, 79.9, 62.5, 52.9, 39.2; MS (70 eV): *m/z* (%): 325(15.34) [*M*⁺+1], 197 (100); IR (neat): 1736, 1642, 1600, 1241, 1209, 948, 927 cm⁻¹; Anal. calcd for C₁₀H₁₃IO₄: C 37.06, H 4.04. Found: C 37.32, H 4.18.

(2) (*E*)-2-Benzyl-2-(2'-iodovinyl)malonic acid dimethyl ester (3ab).

The reaction of **1a** (78 mg, 0.5 mmol), benzyl iodide **2b** (218 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na₂CO₃ (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ab** (151mg, 81%) as a liquid. ¹H NMR (CDCl₃, 300 MHz): δ 7.30-7.20 (m, 3 H), 7.10-7.02 (m, 2 H), 6.84 (d, *J* = 15.3 Hz, 1 H), 6.38 (d, *J* = 15.3 Hz, 1 H), 3.73 (s, 6 H), 3.36 (s, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.1, 141.3, 134.7, 129.9, 128.2, 127.2, 79.3, 63.8, 52.8, 42.0; MS (70 eV): *m/z* (%): 375 (4.07) [*M*⁺+1], 91 (100); IR (neat): 1736, 1600, 1496, 1445, 1435, 1271, 1198, 949 cm⁻¹; Anal. calcd for C₁₄H₁₅IO₄: C 44.94, H 4.04. Found: C 45.14, H 4.20.

(3) (*E*)-2-(2'-Iodovinyl)-2-(2''-oxo-2''-phenylethyl)malonic acid dimethyl ester (3ac).

The reaction of **1a** (78 mg, 0.5 mmol), α-iodoacetophenone **2c** (246 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na₂CO₃ (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ac** (161 mg, 80%) as colorless needles. m.p. 132-133°C (Et₂O-hexanes); ¹H NMR (CDCl₃, 300 MHz): δ 8.02-7.94 (m, 2 H), 7.64-7.56 (m, 1 H), 7.54-7.44 (m, 2 H), 7.50 (d, *J* = 15.3 Hz, 1 H), 6.35 (d, *J* = 15.3 Hz, 1 H), 3.92 (s, 2 H), 3.81 (s, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 195.4, 168.9, 141.0, 135.8, 133.7, 128.7, 128.1, 79.0, 59.8, 53.4, 44.7; MS (70 eV): *m/z* (%): 401 (0.03) [*M*⁺-1], 105 (100); IR (KBr): 1763, 1732,

1686, 1599, 1280, 1249, 959, 933 cm^{-1} ; Anal. calcd for $\text{C}_{15}\text{H}_{15}\text{IO}_5$: C 44.80, H 3.76. Found: C 44.80, H 3.74.

(4) (*E*)-2-(2'-iodovinyl)-2-(ethoxycarbonylmethyl)malonic acid dimethyl ester (3ad).

The reaction of **1a** (78 mg, 0.5 mmol), α -iodoacetate **2d** (214 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na_2CO_3 (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ad** (120 mg, 65%) as an oil. ^1H NMR (CDCl_3 , 300 MHz): δ 7.09 (d, J = 15.0 Hz, 1 H), 6.44 (d, J = 15.0 Hz, 1 H), 4.12 (q, J = 7.5 Hz, 2 H), 3.78 (s, 6 H), 3.14 (s, 2 H), 1.23 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 169.4, 168.3, 140.2, 79.7, 61.1, 59.9, 53.3, 39.3, 14.0; MS (70 eV): m/z (%): 371 (20.00) [M^+ +1], 243 (100); IR (neat): 1735, 1600, 1436, 1280, 1199, 1027, 950 cm^{-1} ; Anal. calcd for $\text{C}_{11}\text{H}_{15}\text{IO}_6$: C 35.69, H 4.08. found: C 35.92, H 4.18.

(5) (*E*)-2-(2'-Iodovinyl)-2-oct-2''-ynyl-malonic acid dimethyl ester (3ae).

The reaction of **1a** (78 mg, 0.5 mmol), 1-iodooct-2-yne **2e** (236 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na_2CO_3 (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ae** (161 mg, 82%) as a liquid. ^1H NMR (CDCl_3 , 300 MHz): δ 6.97 (d, J = 15.0 Hz, 1 H), 6.48 (d, J = 15.0 Hz, 1 H), 3.79 (s, 6 H), 2.89 (t, J = 2.4 Hz, 2 H), 2.10 (tt, J = 7.5 and 2.4 Hz, 2 H), 1.50-1.40 (m, 2 H), 1.40-1.24 (m, 4 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 168.5, 140.0, 84.4, 80.1, 73.6, 62.4, 53.1, 30.8, 28.4, 25.0, 22.2, 18.5, 14.0; MS (70 eV): m/z (%): 393 (4.54) [M^+ +1], 145 (100); IR (neat): 1740, 1600, 1436, 1203, 944 cm^{-1} ; Anal. calcd for $\text{C}_{15}\text{H}_{21}\text{IO}_4$: C 45.93, H 5.40. Found: C 45.88, H 5.45.

(6) (*E*)-2-(2'-Iodovinyl)-2-(2''-methyl-allyl)malonic acid dimethyl ester (3af).

The reaction of **1a** (78 mg, 0.5 mmol), 3-iodo-2-methylpropene **2f** (182 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na_2CO_3 (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3af** (120 mg, 71%) as a liquid. ^1H NMR (CDCl_3 , 300 MHz): δ 7.03 (d, J = 15.3 Hz, 1 H), 6.39 (d, J = 15.3 Hz, 1 H), 4.83 (t, J = 1.2 Hz, 1H), 4.65 (s, 1 H), 3.72 (s, 6 H), 2.81 (s, 2 H), 1.64 (s, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 169.3, 141.0, 139.7, 115.4, 79.6, 62.0, 52.9, 43.0, 23.6; MS (70 eV): m/z (%): 339 (10.08) [M^+ +1], 151 (100); IR (neat): 1737, 1646, 1598, 1436, 1270, 1236, 1201, 1179, 951, 902 cm^{-1} ; HRMS calcd for $\text{C}_{10}\text{H}_{12}\text{IO}_3$ [M^+ -CH₃O]: 306.9831. Found: 306.9868.

(7) (*E*, *E*)-2-(2'-Iodovinyl)-5-(3''-methoxycarbonyl-prop-2''-enyl)malonic acid dimethyl ester (3ag).

The reaction of **1a** (78 mg, 0.5 mmol), methyl 4-iodocrotonate **2g** (226 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na_2CO_3 (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ag** (151 mg, 79%) as a liquid. ^1H NMR (CDCl_3 , 300 MHz): δ 6.88 (d, J = 15.3 Hz, 1 H), 6.70 (dt, J = 15.9 and 7.5 Hz, 1 H), 6.42 (d, J = 15.3 Hz, 1 H), 5.83 (dt, J = 15.9 and 1.5 Hz, 1 H), 3.71 (s, 6 H), 3.67 (s, 3 H), 2.88 (dd, J = 7.5 and 1.5 Hz, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz): δ 168.4, 165.9, 141.6, 139.8, 124.9, 80.6, 61.9, 53.1, 51.5, 37.2; MS (70 eV): m/z (%): 382 (0.74) [M^+], 255 (100); IR (neat): 1735, 1660, 1600, 1436, 1341, 1275, 1175, 983 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{IO}_6$: 381.9913. Found: 381.9938.

(8) (*E,E*)-2-(2'-Iodovinyl)-2-(3''-phenyl-2''-propenyl)malonic acid dimethyl ester (3ah).

The reaction of **1a** (78 mg, 0.5 mmol), *trans*-cinnamy iodide **2h** (244 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na₂CO₃ (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ah** (183 mg, 92%) as colorless needles. m.p. 80-81°C (Et₂O-hexanes); ¹H NMR (CDCl₃, 300 MHz): δ 7.40-7.20 (m, 5 H), 7.00 (d, *J* = 15.0 Hz, 1 H), 6.49 (d, *J* = 15.0 Hz, 1 H), 6.46 (d, *J* = 15.6 Hz, 1 H), 6.04 (dt, *J* = 15.6 and 7.5 Hz, 1 H), 3.75 (s, 6 H), 2.95 (d, *J* = 7.5 Hz, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 168.9, 140.6, 136.6, 134.4, 128.4, 127.4, 126.1, 122.8, 80.0, 62.7, 52.9, 38.5; MS (70 eV): *m/z* (%): 400 (0.01) [*M*⁺], 117 (100); IR (KBr): 1736, 1599, 1578, 1496, 1435, 1266, 1237, 1200, 1180, 968, 950 cm⁻¹; Anal. calcd for C₁₆H₁₇IO₄: C 48.02, H 4.28. Found: C 48.24, H 4.09.

(9) (*E*)-2-Benzyl-2-(2'-bromovinyl)malonic acid dimethyl ester (3ai).

The reaction of **1a** (78 mg, 0.5 mmol), benzyl bromide **2i** (257 mg, 1.5 mmol), LiBr (4.4 mg, 10 mol%), and Li₂CO₃ (19 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ai** (110 mg, 67%) as colorless needles. m.p. 63-64°C (Et₂O-hexanes); ¹H NMR (CDCl₃, 300 MHz): δ 7.36-7.20 (m, 3 H), 7.12-7.06 (m, 2 H), 6.50 (d, *J* = 14.1 Hz, 1 H), 6.30 (d, *J* = 14.1 Hz, 1 H), 3.75 (s, 6 H), 3.38 (s, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.3, 134.8, 133.7, 130.0, 128.3, 127.3, 109.0, 61.9, 53.0, 42.2; MS (70 eV): *m/z* (%): 247 (7.69) [*M*⁺+1-Br], 91 (100); IR (KBr): 1738, 1614, 1585, 1496, 1455, 1435, 1273, 1207, 1179, 1083, 936 cm⁻¹; Anal. calcd for C₁₄H₁₅BrO₄: C 51.40, H 4.62. Found: C 51.42, H 4.46.

(10) (*E,E*)-2-(2'-Bromovinyl)-2-(3''-phenylprop-2''-enyl)malonic acid dimethyl ester (3aj).

The reaction of **1a** (78 mg, 0.5 mmol), *trans*-cinnamyl bromide **2j** (197 mg, 1.0 mmol), LiBr (8.7 mg, 20 mol%), and Li₂CO₃ (19 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3aj** (113 mg, 64%) as colorless needles. m.p. 52-53°C (Et₂O-hexanes); ¹H NMR (CDCl₃, 300 MHz): δ 7.38-7.20 (m, 5 H), 6.65 (d, *J* = 14.1 Hz, 1 H), 6.47 (dt, *J* = 15.6 and 1.2 Hz, 1 H), 6.40 (d, *J* = 14.1 Hz, 1 H), 6.04 (dt, *J* = 15.6 and 7.2 Hz, 1 H), 3.77 (s, 6 H), 2.96 (dd, *J* = 7.2 and 1.2 Hz, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.2, 136.7, 134.5, 133.2, 128.5, 127.6, 126.2, 122.8, 109.6, 60.9, 53.0, 38.8; MS (70 eV): *m/z* (%): 354 (0.18) [*M*⁺(⁸¹Br)], 352 (0.20) [*M*⁺(⁷⁹Br)], 117 (100); IR (neat): 1737, 1616, 1600, 1496, 1436, 1268, 1239, 1209, 1181, 969, 942 cm⁻¹; Anal. calcd for C₁₆H₁₇BrO₄: C 54.41, H 4.85. Found: C 54.51, H 4.93.

(11) (*E*)-2-Allyl-2-(1'-iodomethylenepentyl)malonic acid dimethyl ester.

The reaction of **1b** (106 mg, 0.5 mmol), allyl iodide **2a** (168 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na₂CO₃ (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ba** (171 mg, 90%) as a liquid. ¹H NMR (CDCl₃, 300 MHz): δ 6.60 (s, 1 H), 5.84-5.64 (m, 1 H), 5.14-5.02 (m, 2 H), 3.71 (s, 6 H), 2.79 (dt, *J* = 6.9 and 1.2 Hz, 2 H), 2.21 (t, *J* = 7.5 Hz, 2 H); 1.48-1.20 (m, 4 H), 0.90 (t, *J* = 7.8 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.5, 144.9, 132.8, 118.9, 83.5, 65.2, 52.5, 39.1, 36.4, 29.7, 23.0, 13.7; ESI-MS: 403.1

[$M+Na^+$]; IR (neat): 1737, 1640, 1596, 1232, 1218 cm^{-1} ; HRMS calcd for $C_{14}H_{21}O_4Na$ [$M+Na^+$]: 403.0382. Found: 403.0368.

(12) (E)-2-Benzyl-2-(1'-iodomethylenepentyl)malonic acid dimethyl ester (3ba).

The reaction of **1b** (106 mg, 0.5 mmol), benzyl iodide **2b** (218 mg, 1.0 mmol), NaI (7.5 mg, 10 mol%), and Na_2CO_3 (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3bb** (213 mg, 99%) as an oil. 1H NMR ($CDCl_3$, 300 MHz): δ 7.30-7.20 (m, 3 H), 7.10-7.02 (m, 2 H), 6.55 (s, 1 H), 3.68 (s, 6 H), 3.39 (s, 2 H), 2.24 (t, $J = 7.2$ Hz, 2 H), 1.52-1.28 (m, 4 H), 0.94 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 169.3, 143.5, 135.5, 130.2, 127.9, 127.0, 85.2, 66.1, 52.4, 40.8, 36.6, 29.7, 23.0, 13.7; MS (70 eV): m/z (%): 430 (0.53) [M^++1], 77 (100); IR (neat): 1740, 1604, 1496, 1456, 1434, 1262, 1170, 1085 cm^{-1} ; HRMS calcd for $C_{18}H_{23}O_4$ [M^+-I]: 303.15964. Found: 303.15912.

(13) (E,E)-2-(1'-Bromomethylenepentyl)-2-(3''-phenyl-prop-2''-enyl)malonic acid dimethyl ester (3bj).

The reaction of **1b** (106 mg, 0.5 mmol), *trans*-cinnamyl bromide **2j** (197 mg, 1.0 mmol), LiBr (8.7 mg, 20 mol%), and Li_2CO_3 (19 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3bj** (175 mg, 86%) as an oil. 1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.18 (m, 5 H), 6.54 (s, 1 H), 6.43 (d, $J = 15.9$ Hz, 1 H), 6.16 (dt, $J = 15.9, 7.2$ Hz, 1 H), 3.72 (s, 6 H), 2.95 (d, $J = 7.2$ Hz, 2 H), 2.25 (t, $J = 8.1$ Hz, 2 H), 1.54-1.41 (m, 2 H), 1.41-1.24 (m, 2 H), 0.92 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 169.5, 140.4, 137.0, 133.9, 128.4, 127.4, 126.2, 124.2, 109.7, 65.0, 52.6, 38.2, 32.5, 29.6, 23.1, 13.7; MS (70 eV): m/z (%): 411 (1.08) [$M^+(^{81}Br)+1$], 409 [$M^+(^{79}Br)+1$], 117 (100); IR (neat): 1737, 1600, 1578, 1496, 1435, 1262, 1235, 969 cm^{-1} ; Anal. calcd for $C_{20}H_{25}BrO_4$: C 58.69, H 6.16. Found: C 58.66, H 6.18.

(14) (E)-2-Allyl-2-(benzenesulfonyl)-3-(iodomethylene)heptanoic acid ethyl ester.

The reaction of **1c** (154 mg, 0.5 mmol), allyl iodide **2a** (336 mg, 2.0 mmol), NaI (15 mg, 20 mol%), and Na_2CO_3 (27 mg, 50 mol%) in 2 mL of acetone under reflux afforded **3ca** (131 mg, 64%) as an oil. 1H NMR ($CDCl_3$, 300 MHz): δ 7.85-7.80 (m, 2 H), 7.66-7.58 (m, 1 H), 7.55-7.44 (m, 2 H), 6.57 (s, 1 H), 6.00-5.84 (m, 1 H), 5.24-5.12 (m, 2 H), 4.28-4.12 (m, 2 H), 3.28 (dd, $J = 14.7$ and 6.0 Hz, 1 H), 3.00 (dd, $J = 14.7$ and 7.8 Hz, 1 H), 2.14-1.96 (m, 2 H), 1.34-1.16 (m, 4 H), 1.26 (t, $J = 7.2$ Hz, 3 H), 0.82 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 166.6, 142.0, 136.5, 133.9, 132.0, 131.4, 128.2, 119.7, 89.5, 81.7, 62.3, 37.0, 36.5, 29.3, 22.8, 13.7, 13.6; MS (70 eV): m/z (%): 477 (0.35) [M^++1], 335 (100); IR (neat): 1736, 1639, 1584, 1466, 1488, 1310, 1212, 1150, 1080, 923 cm^{-1} ; Anal. calcd for $C_{19}H_{25}IO_4S$: C 47.90, H 5.29. Found: C 47.78, H 5.32.

Synthetic transformations of 3aa.

(1) (E)-2-Allyl-2-styrylmalonic acid dimethyl ester (4aa).

A mixture of **3aa** (81 mg, 0.25 mmol), phenylboronic acid (61 mg, 0.5 mmol), $Pd(PPh_3)_4$ (14 mg, 5 mol%), Na_2CO_3 (2 M, 0.3 mL), CH_3OH (0.1 mL) and toluene (2 mL) was refluxed under Ar for 5 h. After extraction with ether, the combined extracts were washed with H_2O and saturated NaCl successively. After drying over $MgSO_4$, filtration, and evaporation, the residue was purified by column chromatography on silica gel to

afford **4aa** (49 mg, 72 %) as an oil. ¹H NMR (CDCl₃, 300 MHz): δ 7.46-7.39 (m, 2 H), 7.38-7.24 (m, 3 H), 6.70 (d, *J* = 16.5 Hz, 1 H), 6.52 (d, *J* = 16.5 Hz, 1 H), 5.80-5.66 (m, 1 H), 5.18-5.06 (m, 2 H), 3.77 (s, 6 H), 2.94 (dt, *J* = 7.2 and 1.2 Hz, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 170.5, 136.3, 132.2, 131.8, 128.5, 128.0, 126.5, 125.7, 119.1, 59.6, 52.7, 40.0; MS (70 eV): *m/z* (%): 274 (1.19) [*M*⁺], 173 (100); IR (neat): 1735, 1642, 1601, 1579, 1497, 1436, 1232, 1208, 967 cm⁻¹; HRMS calcd for C₁₆H₁₈O₄: 274.1205. Found: 274.1515.

(2) (*E*)-2-Allyl-2-(4'-phenylbut-1'-en-3'-ynyl)malonic acid dimethyl ester (5aa).

A mixture of **3aa** (81 mg, 0.25 mmol), phenylacetylene (51 mg, 0.5 mmol), PdCl₂(PPh₃)₂ (8.8 mg, 5 mol%), CuI (4.8 mg, 10 mol%), K₂CO₃ (69 mg, 0.5 mmol), and CH₃CN (2 mL) was stirred at rt under Ar for 6 h. Evaporation and purification by column chromatography on silica gel afforded **5aa** (68 mg, 91%) as colorless needles. m.p. 73-74°C (Et₂O-hexanes). ¹H NMR (CDCl₃, 300 MHz): δ 7.50-7.40 (m, 2 H), 7.36-7.28 (m, 3 H), 6.62 (d, *J* = 16.5 Hz, 1 H), 5.87 (d, *J* = 16.5 Hz, 1 H), 5.76-5.60 (m, 1 H), 5.18-5.08 (m, 2 H), 3.75 (s, 6 H), 2.86 (d, *J* = 7.2 Hz, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.7, 138.4, 131.7, 131.4, 128.33, 128.25, 122.9, 119.4, 112.6, 91.4, 86.8, 59.9, 52.8, 39.6; MS (70 eV): *m/z* (%): 298 (11.13) [*M*⁺], 179 (100); IR (KBr): 1750, 1729, 1641, 1232, 1210, 963, 923 cm⁻¹; Anal. calcd for C₁₈H₁₈O₄: C 72.47, H 6.08. Found: C 72.57, H 6.31.

(3) (*E*)-2-Allyl-2-(hex-1'-enyl)malonic acid dimethyl ester (6aa).

To a solution of anhydrous ZnBr₂ (270 mg, 1.2 mmol) in 2 mL of THF was added dropwise 0.63 mL of BuLi (1.6 M in hexanes, 1.0 mmol) at 0°C. After stirring for 5 min, Pd(PPh₃)₄ (29 mg, 5 mol%) and **3aa** (162 mg, 0.5 mmol) were added and the mixture was stirred for another 1 h. H₂O (5 mL) was added and the reaction mixture was extracted by ether. After drying over MgSO₄, filtration, and evaporation, the residue was purified by column chromatography on silica gel to afford **6aa** (100 mg, 79%) as a liquid. ¹H NMR (CDCl₃, 300 MHz): δ 5.88 (dt, *J* = 15.9 and 1.2 Hz, 1 H), 5.72-5.50 (m, 2 H), 5.10-5.00 (m, 2 H), 3.71 (s, 6 H), 2.76 (dt, *J* = 8.0 and 1.2 Hz, 2 H), 2.12-2.02 (m, 2 H), 1.38-1.22 (m, 4 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 170.8, 133.3, 132.5, 125.8, 118.6, 59.3, 52.4, 39.9, 32.3, 31.0, 22.0, 13.8; MS (70 eV): *m/z* (%): 255 (5.71) [*M*⁺+1], 254 (2.99) [*M*⁺], 213 (100); IR (neat): 1737, 1642, 1233, 1205, 970 cm⁻¹; HRMS calcd for C₁₁H₁₇O₄ [*M*⁺-C₃H₅]: 213.1127. Found: 213.1128.

(4) (*E,E*)-2-Allyl-2-(4'-methoxycarbonylbuta-1',3'-dienyl)malonic acid dimethyl ester (7aa).

A mixture of **3aa** (162 mg, 0.5 mmol), acrylic acid methyl ester (86 mg, 1.0 mmol), Pd(PPh₃)₄ (29 mg, 5 mol%), K₂CO₃ (138 mg, 1.0 mmol) and CH₃CN (5 mL) was stirred at 70°C under Ar for 24 h. After evaporation, the residue was purified by column chromatography on silica gel to afford **7aa** (113 mg, 79%) as colorless needles. m.p. 41-42°C (Et₂O-hexanes). ¹H NMR (CDCl₃, 300 MHz): δ 7.25 (dd, *J* = 15.3 and 10.8 Hz, 1 H), 6.46 (d, *J* = 15.9 Hz, 1 H); 6.23 (dd, *J* = 15.9 and 10.8 Hz, 1 H), 5.87 (d, *J* = 15.3 Hz, 1 H), 5.66-5.50 (m, 1 H), 5.10-5.00 (m, 2 H), 3.704 (s, 6 H), 3.697 (s, 3 H), 2.80 (d, *J* = 7.2 Hz, 2 H); ¹³C NMR (CDCl₃, 75.4 MHz): δ 169.6, 166.9, 143.5, 137.6, 131.6, 129.7,

122.1, 119.4, 59.8, 52.8, 51.5, 39.7; MS (70 eV): m/z (%): 282 (1.16) [M^+], 59 (100); IR (neat): 1737, 1729, 1643, 1616, 1436, 1232, 1210, 1144, 1000 cm^{-1} ; Anal. calcd for $\text{C}_{14}\text{H}_{18}\text{O}_6$: C 59.57, H 6.43. Found: C 59.32, H 6.59.