Unique reactivity of Grignard reagents towards cyclopropenyl-

carboxylates-highly selective carbon-carbon bond cleavage†

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Supporting Information

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General. All solvents were distilled before use: CH_2Cl_2 was distilled over anhydrous K_2CO_3 ; THF and Et₂O were distilled from Na/benzophenone. Unless indicated otherwise, all other reagents were used as received from commercial sources. All reactions were conducted under an atmosphere of nitrogen using dried glassware. The term "concentrated under reduced pressure" refers to the removal of solvents and other volatile materials using a rotary evaporator with the water bath temperature below 40 °C, followed by removal of residual solvent under high vacuum (< 0.2 mbar).

¹H NMR spectra were recorded on a commercial instrument at 300 MHz. ¹³C NMR spectra were recorded at 75 MHz. Chemical shifts are reported in parts per million (ppm, δ). Proton spectra were calibrated to residual CHCl₃ (7.26 ppm) or TMS (0.00 ppm); carbon spectra were calibrated to CDCl₃ (77.0 ppm). Infrared (IR) spectra were recorded as films on a commercial FTIR instrument. Melting points were determined on a hot stage melting point apparatus and are uncorrected.

Ring-opening reactions of cyclopropenes with Grignard reagents.

(1) (Z)-Dimethyl 2-(1-phenylhex-1-enyl)malonate 2aa



To a dried Schlenk tube containing 1a (46.2 mg, 0.2 mmol) and 2.0 mL of THF

was added *n*-BuMgCl (2.0 M in Et₂O, 0.2 mL, 0.4 mmol) dropwise via a syringe at -70 °C. The mixture was stirred at -70 °C for 2.0 hours under N₂ atmosphere as monitored by TLC analysis and then quenched with saturated aqueous NH₄Cl (0.5 mL). Water (5 mL) was added and the mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7/1) afforded **2aa** (38.0 mg, 66%): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.15 (m, 5 H), 5.76 (t, *J* = 7.4 Hz, 1 H), 4.37 (s, 1 H), 3.71 (s, 6 H), 2.04-1.90 (m, 2 H), 1.40-1.15 (m, 4 H), 0.81 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.6, 139.2, 134.1, 132.4, 128.8, 128.1, 127.1, 59.5, 52.5, 31.5, 28.8, 22.1, 13.8; MS (EI, m/z) 290 (M⁺, 10.72), 187 (100); IR (neat, cm⁻¹) 2955, 2859, 1744, 1440, 1383, 1315, 1196, 1146, 1028; HRMS Calcd for C₁₇H₂₂O₄ (M⁺): 290.1518; Found: 290.1517.



The reaction of **1a** (0.6971 g, 3.0 mmol) and *n*-BuMgCl (2.0 M in Et₂O, 3.0 mL, 6.0 mmol) in 30 mL of THF afforded **2aa** (0.5786 g, 66%) (eluent: petroleum ether/ ethyl acetate = 7/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.18 (m, 5 H), 5.76 (t, J = 7.4 Hz, 1 H), 4.37 (s, 1 H), 3.71 (s, 6 H), 2.06-1.94 (m, 2 H), 1.42-1.18 (m, 4 H), 0.81 (t, J = 7.1 Hz, 3 H).

(2) (Z)-Dimethyl 2-(1,2-diphenylvinyl)malonate 2ab



The reaction of **1a** (46.4 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2ab** (47.8 mg, 77%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.17 (m, 5 H), 7.14-7.02 (m, 3 H), 7.00-6.88 (m, 2 H), 6.72 (s, 1 H), 4.52 (s, 1 H), 3.74 (s, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.3, 139.4, 136.0, 133.6, 132.0, 129.4, 129.0, 128.6, 127.9, 127.7, 127.2, 60.4, 52.7; MS (EI, m/z) 310 (M⁺, 27.4), 191 (100); IR (neat, cm⁻¹) 3057, 3024, 2954, 2844, 1738, 1600, 1494, 1439, 1388, 1316, 1199, 1147, 1078, 1027; HRMS Calcd for C₁₉H₁₈O₄ (M⁺): 310.1205; Found: 310.1207.

(3) (Z)-Dimethyl 2-(1-phenylbut-1-enyl)malonate 2ac



The reaction of **1a** (46.2 mg, 0.2 mmol) and EtMgCl (2.0 M in Et₂O, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2ac** (33.5 mg, 64%) (eluent: petroleum ether/ethyl acetate = 7/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.15 (m, 5 H), 5.75 (t, *J* = 7.4 Hz, 1 H), 4.38 (s, 1 H), 3.71 (s, 6 H), 2.07-1.91 (m, 2 H), 0.95 (t, *J* = 7.5 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.6, 139.1, 135.5, 132.1, 128.8, 128.1, 127.2, 59.5, 52.6, 22.6, 13.9; MS (EI, m/z) 262 (M⁺, 10.15), 203 (100); IR (neat, cm⁻¹) 2960, 2875,

1740, 1493, 1438, 1383, 1314, 1194, 1150, 1069, 1029; HRMS Calcd for C₁₅H₁₈O₄ (M⁺): 262.1205; Found: 262.1205.

(4) (Z)-Dimethyl 2-(3-methyl-1-phenylbut-1-enyl)malonate 2ad



The reaction of **1a** (46.5 mg, 0.2 mmol) and *i*-PrMgCl (2.0 M in Et₂O, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2ad** (33.7 mg, 61%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.15 (m, 5 H), 5.54 (d, *J* = 10.2 Hz, 1 H), 4.33 (s, 1 H), 3.70 (s, 6 H), 2.38-2.20 (m, 1 H), 0.93 (d, *J* = 6.6 Hz, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.5, 141.0, 139.3, 130.4, 128.7, 128.1, 127.1, 59.5, 52.5, 28.3, 22.7; MS (EI, m/z) 276 (M⁺, 5.69), 217 (100); IR (neat, cm⁻¹) 2959, 2867, 1741, 1493, 1438, 1386, 1313, 1195, 1149, 1073, 1027; HRMS: Calcd for C₁₆H₂₀O₄: 276.1362; Found: 276.1360.

(5) (Z)-Dimethyl 2-(2-cyclohexyl-1-phenylvinyl)malonate 2ae



The reaction of **1a** (46.4 mg, 0.2 mmol) and CyMgCl (2.0 M in Et₂O, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2ae** (32.3 mg, 51% yield, 66% conversion) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.13

(m, 5 H), 5.56 (d, J = 9.9 Hz, 1 H), 4.33 (s, 1 H), 3.70 (s, 6 H), 2.06-1.88 (m, 1 H), 1.75-1.47 (m, 5 H), 1.22-0.97 (m, 5 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.6, 139.6, 139.4, 130.9, 128.7, 128.1, 127.1, 59.6, 52.5, 37.8, 32.8, 25.8, 25.4; MS (EI, m/z) 316 (M⁺, 2.68), 184 (100); IR (neat, cm⁻¹) 2926, 2850, 1741, 1494, 1440, 1385, 1313, 1192, 1148, 1075, 1027; HRMS Calcd for C₁₉H₂₄O₄ (M⁺): 316.1675; Found: 316.1674.

(6) (E)-Ethyl 3-phenyl-2-(phenylsulfonyl)oct-3-enoate 2ba



The reaction of **1b** (65.8 mg, 0.2 mmol) and *n*-BuMgCl (2.0 M in Et₂O, 0.4 mL, 0.8 mmol) in 2.0 mL of THF afforded **2ba** (41.8 mg, 54%) (eluent: petroleum ether/ethyl acetate = 7/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.88 (m, 2 H), 7.70-7.58 (m, 1 H), 7.55-7.48 (m, 2 H), 7.33-7.18 (m, 3 H), 7.13-7.07 (m, 2 H), 6.16 (t, *J* = 7.7 Hz, 1 H), 4.86 (s, 1 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 2.09-1.87 (m, 2 H), 1.34-1.07 (m, 7 H), 0.79 (t, *J* = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.0, 139.1, 139.0, 137.5, 133.9, 129.8, 128.6, 128.5, 128.2, 127.5, 127.3, 62.1, 31.2, 29.2, 22.1, 13.74, 13.70; MS (EI, m/z) 386 (M⁺, 0.02), 245 (M⁺-SO₂Ph, 100); IR (neat, cm⁻¹) 2958, 2929, 2861, 1741, 1447, 1387, 1324, 1149, 1081, 1024; HRMS Calcd for C₂₂H₂₆O₄S (M⁺): 386.1552; Found: 386.1551. Elemental analysis calcd for C₂₂H₂₆O₄S: C, 68.37; H, 6.78; S, 8.30; Found: C, 68.86; H, 7.28; S, 8.39.

(7) (E)-Ethyl 3,4-diphenyl-2-(phenylsulfonyl)but-3-enoate 2bb



The reaction of **1b** (64.9 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.4 mL, 0.8 mmol) in 2.0 mL of THF afforded **2bb** (40.0 mg, 50%) (eluent: petroleum ether/ethyl acetate = 7/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.00-7.93 (m, 2 H), 7.72-7.62 (m, 1 H), 7.57-7.47 (m, 2 H), 7.29-7.20 (m, 3 H), 7.15-7.05 (m, 5 H), 6.97 (s, 1 H), 6.90-6.80 (m, 2 H), 4.98 (s, 1 H), 4.27-4.12 (m, 2 H), 1.21 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.9, 139.6, 137.2, 135.8, 135.4, 134.1, 130.1, 129.5, 128.7, 128.3, 127.9, 127.8, 127.7, 75.9, 62.4, 13.8; MS (EI, m/z) 265 (M⁺-SO₂Ph, 79.73), 191 (100); IR (neat, cm⁻¹) 3056, 3025, 2954, 2844, 1739, 1560, 1494, 1439, 1314, 1150, 1077, 1027; Elemental analysis calcd for C₂₄H₂₂O₄S: C, 70.91; H, 5.46; S, 7.89; Found: C, 70.69; H, 5.64; S, 8.03.

(8) (Z)-Dimethyl 2-(1-(4-chlorophenyl)hex-1-enyl)malonate 2ca



The reaction of **1c** (53.2 mg, 0.2 mmol) and *n*-BuMgCl (2.0 M in Et₂O, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2ca** (40.4 mg, 62%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, *J* = 8.1 Hz, 2 H), 7.15

(d, J = 8.1 Hz, 2 H), 5.77 (t, J = 7.5 Hz, 1 H), 4.33 (s, 1 H), 3.71 (s, 6 H), 2.01-1.89 (m, 2 H), 1.40-1.14 (m, 4 H), 0.81 (t, J = 7.1 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.4, 137.4, 135.1, 133.1, 131.4, 130.4, 128.3, 59.4, 52.6, 31.4, 28.8, 22.1, 13.8; MS (EI, m/z) 326 (M⁺ (³⁷Cl), 3.92), 324 (M⁺ (³⁵Cl), 11.55), 221 (100); IR (neat, cm⁻¹) 2955, 2930, 2858, 1740, 1491, 1435, 1313, 1195, 1150, 1091, 1015; HRMS Calcd for C₁₇H₂₁³⁵ClO₄ (M⁺): 324.1128; Found: 324.1129.

(9) (Z)-Dimethyl 2-(2-phenyl-1-(p-tolyl)vinyl)malonate 2db



The reaction of **1d** (49.1 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2db** (52.8 mg, 82%): Liquid (eluent: petroleum ether/ethyl acetate = 10/1); ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.04 (m, 7 H), 7.02-6.93 (m, 2 H), 6.71 (s, 1 H), 4.53 (s, 1 H), 3.76 (s, 6 H), 2.35 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.3, 137.3, 136.3, 136.1, 133.6, 131.6, 129.3, 128.8, 127.8, 127.1, 60.5, 52.6, 21.2; MS (EI, m/z) 324 (M⁺, 27.09), 205 (100); IR (neat, cm⁻¹) 2953, 1739, 1510, 1439, 1312, 1202, 1148, 1027; HRMS Calcd for C₂₀H₂₀O₄ (M⁺): 324.1362; Found: 324.1362.

(10) (Z)-Dimethyl 2-(1-(4-nitrophenyl)-2-phenylvinyl)malonate 2eb



The reaction of **1e** (55.4 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.3 mL, 0.6 mmol) in 2.0 mL of THF afforded **2eb** (55.3 mg, 78%) (eluent: petroleum ether/ethyl acetate = 7/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.15 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.21-7.08 (m, 3 H), 6.98-6.89 (m, 2 H), 6.87 (s, 1 H), 4.54 (s, 1 H), 3.76 (s, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.9, 147.1, 146.2, 135.0, 134.5, 131.5, 130.5, 129.4, 128.2, 127.9, 123.8, 59.8, 52.9; MS (EI, m/z) 355 (M⁺, 30.58), 296 (100); IR (neat, cm⁻¹) 2954, 1737, 1597, 1519, 1435, 1347, 1312, 1282, 1151, 1108, 1017; HRMS Calcd for C₁₉H₁₇NO₆ (M⁺): 355.1056; Found: 355.1056.

(11) (E)-Dimethyl 2-(1,3-diphenylprop-1-en-2-yl)malonate 2fb



The reaction of **1f** (49.0 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2fb** (47.1 mg, 73%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.15 (m, 10 H), 6.82 (s, 1 H), 4.13 (s, 1 H), 3.81 (s, 2 H), 3.63 (s, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.5, 138.0, 136.5, 132.9, 132.0, 128.8, 128.53, 128.52, 128.3, 127.3, 126.5, 57.6, 52.6,

37.1; MS (EI, m/z) 324 (M⁺, 4.59), 91 (100); IR (neat, cm⁻¹) 3026, 2953, 1738, 1600, 1494, 1438, 1313, 1152, 1027; HRMS Calcd for C₂₀H₂₀O₄ (M⁺): 324.1362; Found: 324.1362.

(12) (E)-Dimethyl 2-(1-phenylhex-1-en-2-yl)malonate 2gb



The reaction of **1g** (42.7 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2gb** (48.3 mg, 76%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.16 (m, 5 H), 6.56 (s, 1 H), 4.21 (s, 1 H), 3.78 (s, 6 H), 2.39-2.27 (m, 2 H), 1.51-1.15 (m, 4 H), 0.86 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.7, 137.0, 134.7, 130.8, 128.6, 128.1, 126.8, 57.9, 52.6, 31.4, 30.2, 22.6, 13.8; MS (EI, m/z) 290 (M⁺, 11.4), 129 (100); IR (neat, cm⁻¹) 2957, 2866, 1739, 1438, 1314, 1194, 1147, 1028; HRMS Calcd for C₁₇H₂₂O₄ (M⁺): 290.1518; Found: 290.1517.

(13) (E)-Dimethyl 2-(1-phenyldec-1-en-2-yl)malonate 2hb



The reaction of **1h** (53.5 mg, 0.2 mmol) and PhMgCl (2.0 M in THF, 0.2 mL, 0.4 mmol) in 2.0 mL of THF afforded **2hb** (55.8 mg, 81%) (eluent: petroleum ether/ethyl acetate = 10/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.18 (m, 5 H), 6.56 (s, 1

H), 4.21 (s, 1 H), 3.77 (s, 6 H), 2.43-2.22 (m, 2 H), 1.51-1.37 (m, 2 H) 1.37-1.12 (m, 10 H), 0.95-0.79 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.7, 137.0, 134.8, 130.8, 128.6, 128.1, 126.8, 58.0, 52.6, 31.8, 31.6, 29.5, 29.2, 29.1, 28.0, 22.6, 14.0; MS (EI, m/z) 346 (M⁺, 14.5), 129 (100); IR (neat, cm⁻¹) 3140, 3060, 3028, 2928, 2854, 1737, 1698, 1599, 1491, 1442, 1375, 1313, 1266, 1147, 1074, 1029; HRMS calcd for C₂₁H₃₀O₄ (M⁺): 346.2144; Found: 346.2145.

(14) (E)-Ethyl 3-(2-acetoxyethyl)-2-(phenylsulfonyl)oct-3-enoate 2ia



The reaction of **1i** (51.0 mg, 0.15 mmol) and *n*-BuMgCl (2.0 M in Et₂O, 0.3 mL, 0.6 mmol) in 2.0 mL of THF afforded **2ia** (27.3 mg, 46%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.86 (d, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 2 H), 5.66 (t, *J* = 7.4 Hz, 1 H), 4.58 (s, 1 H), 4.19-4.07 (m, 2 H), 4.03 (t, *J* = 7.1 Hz, 2 H), 2.77-2.59 (m, 1 H), 2.48-2.32 (m, 1 H), 2.09-1.94 (m, 5 H), 1.29-1.09 (m, 7 H), 0.84 (t, *J* = 6.6 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.8, 164.9, 140.2, 136.7, 134.0, 130.0, 128.5, 123.0, 74.7, 62.5, 62.1, 31.0, 29.8, 28.1, 22.2, 20.8, 13.8, 13.7; MS (EI, m/z) 309 (M⁺- (CH₂)₂OAc, 1.61), 255 (M⁺- SO₂Ph, 15.26), 43 (100); IR (neat, cm⁻¹) 2959, 2930, 2862, 1739, 1451, 1372, 1319, 1237, 1181, 1147, 1081, 1033; HRMS Calcd for C₁₄H₂₃O₄ (M⁺-SO₂Ph): 255.1596; Found: 255.1593. Elemental analysis calcd for C₂₀H₂₈O₆S: C, 60.58, H, 7.12, S, 8.09; Found: C, 60.93, H, 7.66, S, 7.68.

(15) (E)-Dimethyl 2-(hex-1-enyl)malonate 2ja



The reaction of **1j** (46.8 mg, 0.3 mmol) and *n*-BuMgCl (2.0 M in Et₂O, 0.3 mL, 0.6 mmol) in 2.0 mL of THF afforded **2ja**¹ (35.1 mg, 55%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.70-5.61 (m, 2 H), 4.07-3.93 (m, 1 H), 3.72 (s, 6 H), 2.07- 2.00 (m, 2 H), 1.43-1.19 (m, 4 H), 0.87 (t, *J* = 6.9 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.8, 137.2, 121.0, 55.3, 52.6, 32.0, 30.9, 22.1, 13.8; MS (EI, m/z) 214 (M⁺, 1.13), 95 (100); IR (neat, cm⁻¹) 2957, 2927, 2860, 1741, 1460, 1438, 1378, 1314, 1197, 1148, 1027.

(16) (E)-Dimethyl 2-styrylmalonate 2jb



The reaction of **1j** (46.6 mg, 0.3 mmol) and PhMgCl (2.0 M in THF, 0.3 mL, 0.6 mmol) in 2.0 mL of THF afforded **2jb** (35.7 mg, 51%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.37 (m, 2 H), 7.36-7.21 (m, 3 H), 6.59 (d, *J* = 15.9 Hz, 1 H), 6.42 (dd, *J* = 15.9 Hz, 8.9 Hz, 1 H), 4.23 (d, *J* = 9.0 Hz, 1 H), 3.78 (s, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.4, 136.0, 135.3, 128.6, 128.2, 126.6, 120.6, 55.6, 52.8; MS (EI, m/z) 234 (M⁺, 36.25), 115 (100); IR (neat, cm⁻¹) 2955, 2848, 1737, 1438, 1298, 1262, 1150, 1023; HRMS Calcd for C₁₃H₁₄O₄

(M⁺): 234.0892; Found: 234.0893.

(17) (E)-Dimethyl 2-(but-1-enyl)malonate 2jc

$$\begin{array}{cccc} MeO_2C & CO_2Me & & CO_2Me \\ & + & EtMgCl (2.0 \text{ M in Et}_2O) & \underline{THF, -70 \ ^\circ C, 2 \text{ h}} & \underline{MeO_2C} & \underline{CO_2Me} \\ & 1j & (2.0 \text{ equiv}) & 2jc (47\%) \end{array}$$

The reaction of **1**j (46.7 mg, 0.3 mmol) and EtMgCl (2.0 M in Et₂O, 0.3 mL, 0.6 mmol) in 2.0 mL of THF afforded **2**jc (26.3 mg, 47%) (eluent: petroleum ether/ethyl acetate = 8/1): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.80-5.59 (m, 2 H), 4.00 (d, *J* = 7.8 Hz, 1 H), 3.72 (s, 6 H), 2.16-2.03 (m, 2 H), 1.00 (t, *J* = 7.4 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.8, 138.6, 120.2, 55.3, 52.6, 25.4, 13.0; MS (EI, m/z) 186 (M⁺, 4.77), 127 (100); IR (neat, cm⁻¹) 2962, 1740, 1438, 1266, 1148, 1023; HRMS Calcd for C₉H₁₄O₄ (M⁺): 186.0892; Found: 186.0891.

(18) (E)-1,2-diphenyl-3-(phenylsulfonyl)prop-1-ene 4



To a solution of **2bb** (38.4 mg, 0.094 mmol) dissolved in 2 mL of the mixed solvent (MeOH: $H_2O = 1:1$) was added KOH (6.3 mg, 0.113 mmol). After stirring at rt for 10 hours as monitored by TLC, 5 mL of water and 0.1 M HCl (1 mL) were added. The mixture was extracted with ethyl ether. The organic layer was dried over anhydrous Na₂SO₄. Filtration, evaporation, and Chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) afforded **4** (23.3 mg, 74%): Solid; m.p.: 85-86 °C

(petroleum ether-ethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 2 H), 7.64-7.55 (m, 1 H), 7.53-7.43 (m, 2 H), 7.23-7.13 (m, 3 H), 7.13-6.99 (m, 5 H), 6.90-6.81 (m, 2 H), 6.49 (s, 1 H), 4.26 (s, 2 H); ¹³C NMR (CDCl₃, 75 MHz) δ 138.8, 138.6, 135.8, 135.7, 133.5, 129.13, 129.08, 129.0, 128.8, 128.6, 128.5, 128.0, 127.6, 127.5, 65.9; MS (EI, m/z) 334 (M⁺, 2.46), 115 (100); IR (KBr, cm⁻¹) 2981, 2921, 2852, 1731, 1659, 1632, 1590, 1557, 1473, 1443, 1313, 1251, 1154, 1078; HRMS Calcd for C₂₁H₁₈O₂S (M⁺): 334.1028; Found: 334.1029. Elemental analysis calcd for C₂₁H₁₈O₂S: C, 75.42; H, 5.43; S, 9.59; Found: C, 75.02; H, 5.61; S, 9.28.

Mechanistic studies and synthetic applications

(1) Deuterated (E)-ethyl 3,4-diphenyl-2-(phenylsulfonyl)but-3-enoate 2bb-d



To a dried Schlenk tube were added **1b** (65.8 mg, 0.2 mmol) and 2.0 mL of THF under N₂ atmosphere. Then PhMgCl (2.0 M in THF, 0.4 mL, 0.8 mmol) was added dropwise via a syringe at -30 °C. The mixture was stirred at -30 °C for 2.0 hours and then a solution of AcOD (98.2 mg, 1.6 mmol) in 0.5 mL of THF was added via a syringe. After being stirred at -30 °C for 0.5 hour, the temperature was raised to rt naturally and the mixture was stirred for another 0.5 hour. Then 3 mL of D₂O was added, the mixture was extracted with Et₂O (5 mL x 3), dried over anhydrous Na₂SO₄, filtrated, and evaporated. ¹H NMR (300 MHz, CDCl₃) analysis of the crude product

showed $\geq 92\%$ D-incorporation at the C-1 position. Chromatography on silica gel (eluent: petroleum ether/ethyl acetate =7/1) afforded **2bb**-*d* (38.2 mg, 46%): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, *J* = 7.8 Hz, 2 H), 7.71-7.62 (m, 1 H), 7.57-7.47 (m, 2 H), 7.31-7.17 (m, 3 H), 7.17-7.03 (m, 5 H), 6.98 (s, 0.08 H), 6.91-6.80 (m, 2 H), 4.97 (s, 0.29 H), 4.26-4.12 (m, 2 H), 1.21 (t, *J* = 7.2 Hz, 3 H); MS (crude product) (EI, m/z) 267 (M⁺- SO₂Ph, 56.07), 193 (100); HRMS (crude product) Calcd for C₁₈H₁₅D₂O₂ (M⁺- SO₂Ph): 267.1354; Found: 267.1356.

(2) (E)-Dimethyl 2-(2-iodo-3-methyl-1-phenylbut-1-enyl)malonate 5a



To a dried Schlenk tube were added **1a** (69.5 mg, 0.3 mmol) and 3.0 mL of THF under Ar atmosphere. Then *i*-PrMgCl (2.0 M in Et₂O, 0.33 mL, 0.66 mmol) was added dropwise via a syringe at -70 °C. After being stirred at -70 °C for 2.0 hours, a solution of I₂ (153.0 mg, 0.6 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -70 °C for another 0.5 h, then at rt for 3.5 h by removing the cooling bath. A saturated aqueous solution of Na₂S₂O₃ (0.5 mL) and 5 mL of water were added sequentially, and the mixture was extracted with Et₂O (5 mL x 3), and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) afforded **5a** (47.3 mg of pure product and 13.2 mg of a mixed product with 55% of purity, 45% combined yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.20 (m, 5 H), 4.96 (s, 1 H), 3.58 (s, 6 H),

2.03 (heptet, J = 6.6 Hz, 1 H), 0.90 (d, J = 6.6 Hz, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.8, 138.0, 136.2, 129.8, 128.6, 128.1, 127.7, 65.8, 52.5, 35.9, 23.7; MS (EI, m/z) 275 (M⁺- I, 78.21), 183 (100); IR (neat, cm⁻¹) 2964, 2929, 1738, 1602, 1490, 1459, 1434, 1363, 1304, 1257, 1194, 1149, 1123, 1072, 1030; HRMS Calcd for C₁₆H₁₉O₄ (M⁺- I): 275.1283; Found: 275.1281.

(3) (Z)-Dimethyl 2-(2-isopropyl-1-phenylpenta-1,4-dienyl)malonate 6a



To a dried Schlenk tube were added **1a** (69.2 mg, 0.3 mmol) and 3.0 mL of THF under Ar atmosphere. Then *i*-PrMgCl (2.0 M in Et₂O, 0.33 mL, 0.66 mmol) was added dropwise via a syringe at -70 °C. After being stirred at -70 °C for 2.0 hours, a solution of allyl bromide (73.6 mg, 0.6 mmol) and CuCN (2.6 mg, 0.03 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -70 °C for another 0.5 h and then at rt for 3.0 h by removing the cooling bath. A saturated aqueous solution of NH₄Cl (0.5 mL) and 5 mL of water were added sequentially. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded **6a** (54.3 mg contaminated with the protonolysis product **2ad**, molar ratio: 93/7 (**6a/2ad**), 54% yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.18 (m, 5 H), 5.89-5.74 (m, 1 H), 5.25-5.05 (m, 2 H), 4.75 (s, 1 H), 3.55 (s, 6 H), 2.87 (dt, *J* = 6.0 Hz and 1.7 Hz, 2 H), 2.50 (heptet, *J* = 6.8 Hz, 1 H), 0.88 (d, *J* = 6.6 Hz, 6 H); ¹³C

NMR (CDCl₃, 75 MHz) δ 168.9, 145.0, 139.3, 135.8, 129.6, 129.4, 127.7, 126.9, 115.7, 55.6, 52.1, 32.2, 31.1, 20.6; MS (EI, m/z) 316 (M⁺, 1.31), 184 (100); IR (neat, cm⁻¹) 2958, 2870, 1736, 1636, 1492, 1435, 1363, 1306, 1264, 1239, 1193, 1147, 1072, 1026; HRMS Calcd for C₁₉H₂₄O₄ (M⁺): 316.1675; Found: 316.1677.

(4) (Z)-Dimethyl 2-(2,3-dimethyl-1-phenylbut-1-enyl)malonate 7a



To a dried Schlenk tube were added **1a** (69.8 mg, 0.3 mmol) and 3.0 mL of THF under Ar atmosphere. Then *i*-PrMgCl (2.0 M in Et₂O, 0.33 mL, 0.66 mmol) was added dropwise via a syringe at -70 °C. After being stirred at -70 °C for 2.0 hours, a solution of MeI (129.7 mg, 0.9 mmol) and CuCN (2.7 mg, 0.03 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -70 °C for another 0.5 h and then at rt for 3.5 h by removing the cooling bath. A saturated aqueous solution of NH₄Cl (0.5 mL) and 5 mL of water were added sequentially. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded **7a** (57.1 mg contaminated with the protonolysis product **2ad**, molar ratio: 94/6 (**7a/2ad**), 62% yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.16 (m, 5 H), 4.66 (s, 1 H), 3.57 (s, 6 H), 2.47 (heptet, *J* = 6.9 Hz, 1 H), 1.65 (s, 3 H), 0.88 (d, *J* = 6.9 Hz, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.9, 144.0, 139.9, 129.4, 127.7, 126.7, 126.3, 56.2, 52.2, 31.8, 20.4, 12.2; MS (EI, m/z) 290 (M⁺, 8.41), 59 (100); IR

(neat, cm⁻¹) 2959, 2870, 1736, 1491, 1434, 1362, 1308, 1265, 1241, 1194, 1146, 1071, 1029; HRMS Calcd for C₁₇H₂₂O₄ (M⁺): 290.1518; Found: 290.1518.

(5) (E)-Dimethyl 2-(2-cyclohexyl-2-iodo-1-phenylvinyl)malonate 5b



To a dried Schlenk tube were added 1a (46.5 mg, 0.2 mmol) and 2.0 mL of THF under Ar atmosphere. Then CyMgCl (2.0 M in Et₂O, 0.2 mL, 0.4 mmol) was added dropwise via a syringe at -70 °C. After being stirred at -70 °C for 2.0 hours, a solution of I₂ (102.2 mg, 0.4 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -70 °C for another 1.0 h and then at rt for 4.0 h by removing the cooling bath. A saturated aqueous solution of Na₂S₂O₃ (0.5 mL) and 5 mL of water were added sequentially. The mixture was extracted with Et_2O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 9/1) afforded **5b** (48.6 mg, 55%): Liquid; ¹H NMR (300 MHz, CDCl₃) & 7.35-7.18 (m, 5 H), 4.96 (s, 1 H), 3.57 (s, 6 H), 1.74-1.60 (m, 3 H), 1.58-1.31 (m, 5 H), 1.19-1.01 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.8, 138.2, 136.6, 128.6, 128.1, 127.7, 127.3, 65.9, 52.5, 45.8, 33.6, 25.4, 25.1; MS (EI, m/z) 315 (M⁺- I, 87.55), 183 (100); IR (neat, cm⁻¹) 2928, 2853, 1739, 1601, 1491, 1434, 1305, 1236, 1194, 1149, 1098, 1074, 1027; HRMS Calcd for C₁₉H₂₃O₄ (M⁺- I): 315.1596; Found: 315.1601.

(6) (*Z*)-Dimethyl 2-(2-cyclohexyl-1-phenylpenta-1,4-dienyl)malonate **6b**



To a dried Schlenk tube were added 1a (69.6 mg, 0.3 mmol) and 3.0 mL of THF under Ar atmosphere. Then CyMgCl (2.0 M in Et₂O, 0.33 mL, 0.66 mmol) was added dropwise via a syringe at -70 °C. After being stirred at -70 °C for 2.0 hours, a solution of allyl bromide (74.0 mg, 0.6 mmol) and CuCN (2.7 mg, 0.03 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -70 °C for another 0.5 h and then at rt for 3.0 h by removing the cooling bath. A saturated aqueous solution of NH₄Cl (0.5 mL) and 5 mL of water were added sequentially. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded **6b** (56.6 mg contaminated with the protonolysis product **2ae**, molar ratio: 93/7 (**6b/2ae**), 49% yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.18 (m, 5 H), 5.87-5.71 (m, 1 H), 5.23-5.03 (m, 2 H), 4.73 (s, 1 H), 3.55 (s, 6 H), 2.93-2.84 (m, 2 H), 2.12 (tt, J = 11.9 Hz and 3.3 Hz, 1 H), 1.67-1.38 (m, 5 H), 1.34-1.16 (m, 2 H), 1.16-0.82 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 168.9, 144.6, 139.3, 135.7, 129.8, 129.6, 127.7, 126.8, 115.7, 55.6, 52.1, 43.1, 32.3, 30.6, 26.0, 25.9; MS (EI, m/z) 356 $(M^+, 1.81), 91 (100); IR (neat, cm^{-1}) 2927, 2852, 1736, 1435, 1312, 1264, 1242, 1194,$ 1148, 1072, 1029; HRMS Calcd for C₂₂H₂₈O₄ (M⁺): 356.1988; Found: 356.1989.

(7) (Z)-Dimethyl 2-(2-cyclohexyl-1-phenylprop-1-enyl)malonate 7b



To a dried Schlenk tube were added **1a** (69.6 mg, 0.3 mmol) and 3.0 mL of THF under Ar atmosphere. Then CyMgCl (2.0 M in Et₂O, 0.33 mL, 0.66 mmol) was added dropwise via a syringe at -70 °C. After being stirred at -70 °C for 2.0 hours, a solution of MeI (132.3 mg, 0.9 mmol) and CuCN (2.7 mg, 0.03 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -70 °C for another 0.5 h and then at rt for 3.5 h by removing the cooling bath. A saturated aqueous solution of NH₄Cl (0.5 mL) and 5 mL of water were added sequentially. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded 7b (59.1 mg contaminated with the protonolysis product 2ae, molar ratio: 92/8 (**7b/2ae**), 55% yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.14 (m, 5 H), 4.66 (s, 1 H), 3.57 (s, 6 H), 2.08 (tt, J = 11.7 Hz and 3.5 Hz, 1 H), 1.69-1.40 (m, 8 H), 1.35-1.19 (m, 2 H), 1.14-0.89 (m, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.0, 143.6, 139.9, 129.4, 127.7, 126.7, 56.3, 52.2, 42.9, 30.5, 26.0, 25.9, 13.8; MS (EI, m/z) 330 $(M^+, 8.19)$, 198 (100); IR (neat, cm⁻¹) 2926, 2852, 1737, 1491, 1434, 1309, 1264, 1243, 1194, 1147, 1073, 1022; HRMS Calcd for C₂₀H₂₆O₄ (M⁺): 330.1831; Found: 330.1832.

(8) (Z)-Ethyl 4-iodo-3,4-diphenyl-2-(phenylsulfonyl)but-3-enoate 5c



To a dried Schlenk tube were added 1b (97.6 mg, 0.3 mmol) and 4.0 mL of THF under N₂ atmosphere. Then PhMgCl (2.0 M in THF, 0.6 mL, 1.2 mmol) was added dropwise via a syringe at -30 °C. After being stirred at -30 °C for 2.0 hours, a solution of I₂ (381 mg, 1.5 mmol) in 2.0 mL of THF was added dropwise. The mixture was stirred at -30 °C for another 0.5 h and then at rt for 0.5 h by removing the cooling bath. A saturated aqueous solution of Na₂S₂O₃ (0.5 mL) and 5 mL of water were added. The mixture was extracted with Et₂O and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) afforded **5c** (88.6 mg, 56%): Solid; mp 129-130 °C (petroleum ether/ethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 8.11-8.01 (m, 2 H), 7.71-7.63 (m, 1 H), 7.63-7.50 (m, 2 H), 7.24-7.17 (m, 2 H), 7.14-6.97 (m, 8 H), 5.94 (s, 1 H), 4.17-3.99 (m, 2 H), 1.09 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.6, 144.0, 139.7, 137.5, 134.9, 134.0, 130.8, 129.4, 128.97, 128.95, 127.8, 127.7, 127.6, 127.5, 114.7, 81.8, 62.4, 13.7; MS (EI, m/z) 405 (M⁺- I, 2.01), 391 (M⁺-SO₂Ph, 4.16), 77 (100); IR (KBr, cm⁻¹) 3060, 2981, 2923, 2853, 1733, 1580, 1488, 1444, 1371, 1330, 1258, 1150, 1078, 1024; Elemental analysis calcd for C₂₄H₂₁IO₄S: C, 54.14; H, 3.98; S, 6.02; Found: C, 54.43; H, 3.87; S, 5.83.

(9) (E)-Ethyl 3,4-diphenyl-2-(phenylsulfonyl)hepta-3,6-dienoate 6c



To a dried Schlenk tube were added 1b (163.6 mg, 0.5 mmol) and 5.0 mL of THF at -30 °C under N₂ atmosphere. Then PhMgCl (2.0 M in THF, 1.0 mL, 2.0 mmol) was added dropwise via a syringe. After being stirred at -30 °C for 2.0 hours, a solution of CuCN (4.5 mg, 0.05 mmol, 10 mol%) and allyl bromide (178.0 mg, 1.5 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -30 °C for 30 minutes then to rt for another 3.5 hours by removing the cooling bath. The reaction then was quenched with 0.5 mL of a saturated aqueous solution of NH₄Cl followed by the addition of 5 mL of water. The resulting mixture was extracted with Et₂O (5 ml x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) followed by recrystallization (solvent: petroleum) ether/diethyl ether) afforded 6c (99.4 mg, 49%): Solid; m.p.: 121-122 °C (petroleum ether/diethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, J = 7.5 Hz, 2 H), 7.63 (t, J =7.4 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 2 H), 7.12-6.89 (m, 10 H), 5.82-5.67 (m, 1 H), 5.43 (s, 1 H), 5.18- 4.97 (m, 2 H), 4.04 (q, J = 7.1 Hz, 2 H), 3.57-3.32 (m, 2 H), 1.11 (t, J = 7.1 Hz, 3 H). ¹³C NMR (CDCl₃, 75 MHz) δ 164.9, 148.1, 141.6, 139.4, 134.1, 133.8, 130.6, 129.4, 128.83, 128.80, 127.4, 127.3, 127.0, 126.6, 126.4, 116.9, 73.6, 62.1, 39.6, 13.6; MS (EI, m/z) 305 (M⁺-SO₂Ph, 15.26), 77 (100); IR (KBr, cm⁻¹) 3059, 2977, 2924, 1742, 1488, 1443, 1365, 1307, 1269, 1144, 1076, 1022; Elemental analysis calcd for C₂₇H₂₆O₄S: C, 72.62; H, 5.87; S, 7.18; Found: C, 72.30; H, 5.91; S, 7.37.



(10) (Z)-Ethyl 4-ethyl-3-phenyl-2-(phenylsulfonyl)hepta-3,6-dienoate 6d

To a dried Schlenk tube were added 1b (49.3 mg, 0.15 mmol) and 2.0 mL of THF at -30 °C under Ar atmosphere. Then EtMgCl (2.0 M in Et₂O, 0.3 mL, 0.6 mmol) was added dropwise via a syringe. After being stirred at -30 °C for 2.0 hours, a solution of CuCN (1.4 mg, 0.015 mmol) and allyl iodide (128.0 mg, 0.75 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -30 °C for 0.5 h then at rt for another 3.0 hours by removing the cooling bath. The reaction then was quenched with 0.5 mL of a saturated aqueous solution of NH₄Cl and 5 mL of water. The resulting mixture was extracted with Et₂O (5 ml x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7/1) afforded **6d** (35.4 mg contaminated with the protonolysis product, molar ratio: 93/7, 55% yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.93 (d, J = 7.8 Hz, 2 H), 7.63 (t, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.5 Hz, 2 H), 7.34-7.21 (m, 3 H), 7.20-7.07 (m, 2 H), 5.93-5.76 (m, 1 H), 5.30-5.07 (m, 3 H), 4.02-3.85 (m, 2 H), 3.12 (dd, J = 15.9 Hz and 5.1 Hz, 1 H), 2.90 (dd, J = 15.8 Hz and 5.3 Hz, 1 H), 1.95-1.78 (m, 2 H), 1.04 (t, J = 7.2 Hz, 3 H), 0.87 (t, J = 7.4 Hz, 3 H). ¹³C NMR (CDCl₃, 75 MHz) & 164.8, 149.5, 139.4, 138.9, 134.9, 133.7, 129.9, 129.4, 128.8, 127.8, 127.2, 124.4, 116.6, 73.0, 61.9, 35.6, 27.2, 13.6, 12.8; MS (EI, m/z) 257 $(M^+-SO_2Ph, 50.53), 77 (100);$ IR (neat, cm⁻¹) 3061, 2973, 2934, 2873, 1735, 1635,

1492, 1446, 1369, 1326, 1146, 1083, 1026; HRMS calcd for C₁₇H₂₁O₂ (M⁺-SO₂Ph): 257.1542; Found: 257.1543.

(11) (E)-Ethyl 4-methyl-3-phenyl-2-(phenylsulfonyl)oct-3-enoate 7c



To a dried Schlenk tube were added 1b (49.0 mg, 0.15 mmol) and 2.0 mL of THF at -30 °C under Ar atmosphere, then *n*-BuMgCl (2.0 M in Et₂O, 0.3 mL, 0.6 mmol) was added dropwise via a syringe. The mixture was stirred at -30 °C for 2.0 hours and then a solution of CuCN (1.3 mg, 0.015 mmol, 10 mol%) and MeI (128.6 mg, 0.9 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -30 °C for 0.5 h and then stirred at rt for another 3.0 hours by removing the cooling bath. The reaction was quenched with 0.5 mL of a saturated aqueous solution of NH₄Cl, and then 5 mL of water was added. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7/1) afforded 7c (31.2 mg, 52%): Solid; m.p.: 102-103 °C (petroleum ether/ethyl ether); ¹H NMR (300 MHz, CDCl₃) δ 7.95 (d, J = 7.5 Hz, 2 H), 7.63 (t, J = 7.4 Hz, 1 H), 7.51 (t, J = 7.5 Hz, 2 H), 7.30-7.18 (m, 3) H), 7.16-7.03 (m, 2 H), 5.22 (s, 1 H), 4.04-3.86 (m, 2 H), 1.93-1.75 (m, 5 H), 1.37-1.22 (m, 2 H), 1.21-0.98 (m, 5 H), 0.74 (t, J = 7.2 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) & 165.0, 147.1, 139.5, 139.4, 133.7, 130.0, 129.5, 128.8, 127.7, 127.0, 123.2, 73.7, 61.9, 36.3, 30.2, 22.4, 19.1, 13.8, 13.6; MS (EI, m/z) 259 (M⁺-SO₂Ph, 47.46), 77

(100); IR (KBr, cm⁻¹) 2959, 2930, 2872, 1713, 1447, 1370, 1326, 1280, 1249, 1149, 1086, 1073, 1022. Elemental analysis calcd for C₂₃H₂₈O₄S: C, 68.97; H, 7.05; S, 8.01; Found: C, 68.93; H, 7.40; S, 7.80.

(12) (Z)-Ethyl 4-(2-methylallyl)-3-phenyl-2-(phenylsulfonyl)oct-3-enoate 6e



To a dried Schlenk tube were added 1b (49.7 mg, 0.15 mmol) and 2.0 mL of THF at -30 °C under Ar atmosphere. n-BuMgCl (2.0 M in Et₂O, 0.3 mL, 0.6 mmol) was added dropwise via a syringe. After being stirred at -30 °C for 2.0 hours, a solution of CuCN (1.3 mg, 0.015 mmol) and 3-bromo-2-methylprop-1-ene (61.2 mg, 0.45 mmol) in 1.0 mL of THF was added dropwise. The mixture was stirred at -30 °C for 0.5 h and then stirred at rt for another 4.0 hours by removing the cooling bath. The reaction was quenched with 0.5 mL of a saturated aqueous solution of NH₄Cl, and then 5 mL of water was added. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) afforded **6e** (43.0 mg contaminated with the protonolysis product **2ba**, molar ratio: 94/6 (**6e/2ba**), 62% yield): Liquid; ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta 7.93 \text{ (d, } J = 8.1 \text{ Hz}, 2 \text{ H}), 7.63 \text{ (t, } J = 7.1 \text{ Hz}, 1 \text{ H}), 7.51 \text{ (t, } J = 7.1 \text{ Hz}, 1 \text{ Hz}, 1 \text{ Hz}), 7.51 \text{ (t, } J = 7.1 \text{ Hz}, 1 \text{ Hz}), 7.51 \text{ (t, } J = 7.1 \text{ Hz}, 1 \text{ Hz}), 7.51 \text{ (t, } J = 7.1 \text{ Hz}, 1 \text{ Hz}), 7.5$ 7.7 Hz, 2 H), 7.32-7.23 (m, 3 H), 7.22-7.15 (m, 2 H), 5.31 (s, 1 H), 4.86 (d, J = 9.3 Hz, 2 H), 3.98-3.81 (m, 2 H), 3.10 (d, J = 16.5 Hz, 1 H), 2.76 (d, J = 16.5 Hz, 1 H), 1.92-1.73 (m, 5 H), 1.36-1.22 (m, 2 H), 1.18-1.05 (m, 2 H), 1.01 (t, J = 7.1 Hz, 3 H),

0.72 (t, J = 7.4 Hz, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.7, 148.6, 142.4, 139.4, 138.6, 133.7, 130.2, 129.4, 128.8, 127.7, 127.2, 125.3, 112.1, 72.9, 61.8, 39.5, 34.1, 30.7, 22.8, 22.6, 13.7, 13.6; MS (EI, m/z) 299 (M⁺-SO₂Ph, 10.84), 77 (100); IR (neat, cm⁻¹) 2958, 2930, 2861, 1747, 1446, 1368, 1327, 1310, 1240, 1147, 1083, 1024. HRMS Calcd for C₂₀H₂₇O₂ (M⁺-SO₂Ph): 299.2011; Found: 299.2011.

(13) (Z)-Ethyl 3,4-diphenyl-2-(phenylsulfonyl)hepta-3,5,6-trienoate 8a



To a dried Schlenk tube were added **1b** (65.4 mg, 0.2 mmol) and 2.0 mL of THF at -30 °C under N₂ atmosphere. *n*-BuMgCl (2.0 M in Et₂O, 0.4 mL, 0.8 mmol) was added dropwise via a syringe. After being stirred at -30 °C for 2.0 hours, then a solution of CuCN (1.8 mg, 0.02 mmol, 10 mol%) and propargyl bromide (72.3 mg, 0.6 mmol) in 0.5 mL of THF was added dropwise. The mixture was stirred at -30 °C for 0.5 h and then stirred at 0 °C for another 3.5 hours by removing the cooling bath. The reaction was quenched with 0.5 mL of a saturated aqueous solution of NH₄Cl, and then 5 mL of water was added. The mixture was extracted with Et₂O (5 mL x 3) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) afforded **8a** (47.3 mg, 56% yield, 86% purity): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.2 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 3 H), 7.30-7.20 (m, 3 H), 7.10-7.00 (m, 2 H), 6.28 (t, *J* = 6.6 Hz, 1 H), 5.25 (s, 1 H), 5.07-4.90 (m, 2 H), 4.09-3.87 (m, 2 H),

2.04-1.91 (m, 2 H), 1.38-1.20 (m, 3 H), 1.07 (t, J = 7.2 Hz, 3 H), 0.70 (t, J = 7.2 Hz, 3 H). ¹³C NMR (CDCl₃, 75 MHz) δ 211.7, 164.8, 142.6, 139.8, 138.9, 133.9, 129.6, 129.4, 128.9, 127.9, 127.2, 123.9, 91.9, 77.9, 73.6, 62.1, 31.9, 31.6, 22.5, 13.6; MS (EI, m/z) 424 (M⁺, 3.02), 77 (100); IR (neat, cm⁻¹) 3280, 3061, 2960, 2932, 2864, 1934, 1732, 1603, 1487, 1448, 1371, 1324, 1151, 1081, 1027. HRMS Calcd for C₂₅H₂₈O₄S (M⁺): 424.1708; Found: 424.1701.

(14) (E)-Dimethyl 2-(2-isopropyl-1-phenylpenta-1,4-dienyl)-2-(prop-2-ynyl)malonate9a



To a dried Schlenk flask were added NaH (188.1 mg, 60% powder moistened with oil, 112.9 mg, 4.7 mmol) and 15 mL of DMF, then **6a** (821.6 mg, 93% purity, 764.0 mg, 2.4 mmol) in 20 mL of DMF was added dropwise in 10 min. After being stirred at rt for another 0.5 h, a solution of propargyl bromide (1.5351 g, 13.0 mmol) in 5 mL of DMF was added dropwise. The mixture was stirred at rt for 10 min and then heated at a 75 °C oil bath for another 5.5 h. The resulting mixture was quenched with 100 mL of water. The mixture was extracted with Et₂O (30 mL x 4). The organic layer was washed with 1 M HCl (20 mL x 2) followed by 20 mL of a saturated aqueous solution of NaCl and dried over anhydrous MgSO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded

25.7 mg of **6a** (25.7 mg, 3%) and **9a** (756.5 mg, 91%): Liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.20 (m, 3 H), 7.15 (d, J = 6.8 Hz, 2 H), 5.90-5.74 (m, 1 H), 5.16-5.00 (m, 2 H), 3.63 (s, 6 H), 2.97 (d, J = 6.0 Hz, 2 H), 2.74 (s, 2 H), 2.37 (heptet, J = 6.8 Hz, 1 H), 2.07-1.99 (bs, 1 H), 0.87 (d, J = 6.4 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ 170.6, 145.3, 140.4, 137.2, 132.2, 129.5, 127.8, 126.8, 115.8, 80.6, 70.6, 62.6, 52.6, 33.7, 33.2, 27.5, 21.2; MS (EI, m/z) 354 (M⁺, 0.99), 41 (100); IR (neat, cm⁻¹) 2953, 1734, 1203, 1181, 1065, 1001. HRMS Calcd for C₂₂H₂₆O₄ (M⁺): 354.1831; Found: 354.1833.

(15) (E)-Dimethyl 2-(2-isopropyl-1-phenylpenta-1,4-dienyl)-2-methylmalonate 9b



To a dried Schlenk tube were added NaH (18.0 mg, 60% powder moistened with oil, 10.8 mg, 0.45 mmol), 1 mL of DMF, a solution of **6a** (78.8 mg, 93% purity, 73.3 mg, 0.23 mmol) in 1 mL of DMF. After being stirred at rt for 0.5 h, a solution of methyl iodide (178.2 mg, 1.25 mmol) in 1 mL of DMF was added. After being stirred at 40 °C for another 11 h, the mixture was quenched with 10 mL of water and extracted with Et_2O (5 mL x 4). The organic layer was washed with 1 M HCl (5 mL x 2) followed by 5 mL of a saturated aqueous solution of NaCl and dried over anhydrous MgSO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded **9b** (71.7 mg contaminated with the

(*E*)-dimethyl 2-methyl-2-(3-methyl-1-phenylbut-1-enyl)malonate, molar ratio: 95/5, 89% yield): Liquid; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.18 (m, 3 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 5.87-5.73 (m, 1 H), 5.14-4.99 (m, 2 H), 3.58 (s, 6 H), 2.91 (d, *J* = 5.6 Hz, 2 H), 2.37 (heptet, *J* = 6.8 Hz, 1 H), 1.50 (s, 3 H), 0.87 (d, *J* = 6.8 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ 172.4, 143.9, 141.0, 137.6, 134.3, 129.3, 127.7, 126.5, 115.6, 59.4, 52.5, 33.51, 33.47, 24.2, 21.3; MS (EI, m/z) 330 (M⁺, 1.15), 115 (100); IR (neat, cm⁻¹) 2953, 1729, 1488, 1455, 1434, 1378, 1362, 1244, 1134, 1105, 1030. HRMS Calcd for C₂₀H₂₆O₄ (M⁺): 330.1831; Found: 330.1832.

(E)-Dimethyl 2-methyl-2-(3-methyl-1-phenylbut-1-enyl)malonate



To a dried Schlenk tube were added NaH (14.6 mg, 60% powder moistened with oil, 8.8 mg, 0.36 mmol) and 1 mL of DMF. Then a solution of **2ad** (55.6 mg, 0.20 mmol) in 1 mL of DMF was added. The mixture was stirred at rt for 0.5 h, which was followed by the addition of a solution of methyl iodide (142.7 mg, 1.00 mmol) in 1 mL of DMF. After being stirred at rt for another 11 h, the reaction was quenched with 15 mL of water. The resulting mixture was extracted with Et₂O (5 mL x 3). The combined organic layer was washed sequentially with 1 M HCl (5 mL), 5 mL of water, and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded (*E*)-dimethyl

2-methyl-2-(3-methyl-1-phenylbut-1-enyl)malonate (38.9 mg, 67%): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.21 (m, 3 H), 7.16-7.08 (m, 2 H), 5.43 (d, *J* = 9.6 Hz, 1 H), 3.69 (s, 6 H), 2.13-1.94 (m, 1 H), 1.48 (s, 3 H), 0.87 (d, *J* = 6.9 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ 172.0, 139.1, 138.3, 135.9, 129.6, 127.7, 126.9, 60.5, 52.4, 28.5, 22.5, 21.9; MS (EI, m/z) 290 (M⁺, 1.31), 59 (100); IR (neat, cm⁻¹) 2955, 2868, 1731, 1600, 1574, 1493, 1455, 1377, 1256, 1175, 1143, 1109, 1075, 1032. HRMS Calcd for C₁₇H₂₂O₄ (M⁺): 290.1518; Found: 290.1519.

(16) (E)-Dimethyl 2-allyl-2-(2-isopropyl-1-phenylpenta-1,4-dienyl)malonate 9c



To a dried Schlenk tube were added NaH (18.0 mg, 60% powder moistened with oil, 10.8 mg, 0.45 mmol) and 1 mL of DMF. Then a solution of 6a (79.2 mg, 93% purity, 73.7 mg, 0.23 mmol) in 1 mL of DMF was added. After being stirred at rt for 0.5 h, a solution of allyl bromide (181.3 mg, 1.5 mmol) in 1 mL of DMF was added. The mixture was stirred at rt for 0.5 h and then at 75 °C for another 7 h. The mixture was quenched with 20 mL of water and extracted with Et₂O (15 mL x 3). The organic layer was washed with 1 M HCl (10 mL) followed by a saturated aqueous solution of NaCl (10 mL x 2) and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded 9c (73.5)with (*E*)-dimethyl contaminated the mg

2-allyl-2-(3-methyl-1-phenylbut-1-enyl)malonate, molar ratio: 95/5, 84% yield): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.19 (m, 3 H), 7.11 (d, *J* = 7.2 Hz, 2 H), 5.89-5.68 (m, 2 H), 5.14-4.83 (m, 4 H), 3.64 (s, 6 H), 3.01 (d, *J* = 6.0 Hz, 2 H), 2.42 (d, *J* = 6.9 Hz, 2 H), 2.35 (heptet, *J* = 6.9 Hz, 1 H), 0.86 (d, *J* = 6.6 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ 171.2, 144.8, 140.8, 137.3, 134.0, 133.4, 129.5, 127.8, 126.6, 118.0, 115.5, 62.7, 52.2, 42.5, 33.7, 33.4, 21.3; MS (EI, m/z) 356 (M⁺, 0.19), 41 (100); IR (neat, cm⁻¹) 3078, 2952, 2871, 1730, 1638, 1488, 1434, 1362, 1291, 1209, 1126, 1072, 1033. HRMS Calcd for C₂₂H₂₈O₄ (M⁺): 356.1988; Found: 356.1987.

(E)-Dimethyl 2-allyl-2-(3-methyl-1-phenylbut-1-enyl)malonate



To a dried Schlenk tube were added NaH (14.8 mg, 60% powder moistened with oil, 8.9 mg, 0.37 mmol) and 1 mL of DMF. Then a solution of **2ad** (55.9 mg, 0.20 mmol) in 1 mL of DMF was added. The mixture was stirred at rt for 32 min, which was followed by the addition of a solution of allyl bromide (120.7 mg, 1.00 mmol) in 1 mL of DMF. After being stirred at rt for 0.5 h and at 50 °C for another 5 h, the resulting mixture was quenched with 15 mL of water and extracted with Et₂O (5 mL x 4). The combined organic layer was washed sequentially with 1 M HCl (5 mL), a saturated aqueous solution of NaCl (5 mL), and dried over anhydrous Na₂SO₄. Filtration, evaporation, and chromatography on silica gel (eluent: petroleum

ether/ethyl acetate = 20/1) afforded (*E*)-dimethyl 2-allyl-2-(3-methyl-1-phenylbut-1-enyl)malonate (62.9 mg, 98%): Liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.21 (m, 3 H), 7.13-7.04 (m, 2 H), 5.89-5.73 (m, 1 H), 5.64 (d, *J* = 9.9 Hz, 1 H), 5.08-4.97 (m, 2 H), 3.66 (s, 6 H), 2.65 (d, *J* = 6.9 Hz, 2 H), 2.13-1.95 (m, 1 H), 0.88 (d, *J* = 6.6 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ 170.7,140.6, 138.2, 134.3, 133.8, 129.4, 127.8, 127.0, 118.2, 64.4, 52.1, 40.0, 28.6, 22.5; MS (EI, m/z) 316 (M⁺, 2.04), 41 (100); IR (neat, cm⁻¹) 2955, 2868, 1734, 1640, 1600, 1574, 1493, 1435, 1384, 1363, 1282, 1237, 1212, 1135, 1075, 1038. HRMS Calcd for C₁₉H₂₄O₄ (M⁺): 316.1675; Found: 316.1679.

(17) (2*E*,5*Z*)-Dimethyl 3-isopropyl-2-phenylcyclohepta-2,5-diene-1,1-dicarboxylate10



To a dried Schlenk tube equipped with a reflux condenser were added Grubbs II catalyst (12.5 mg, 0.015 mmol), **9c** (106.9 mg, 0.3 mmol), and 3 mL of CH₂Cl₂ under Ar atmosphere, the mixture was stirred at 40 °C for 15.5 h. Then the reaction was stopped. Evaporation and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded **10** (80.7 mg, 82%): Solid; m.p.: 97-98 °C (petroleum ether/ethyl ether); ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.16 (m, 3 H), 7.12 (d, *J* = 7.2 Hz, 2 H), 5.66-5.54 (m, 2 H), 3.42 (s, 6 H), 2.98 (s, 2 H), 2.80 (s, 2 H), 2.34 (heptet, *J*

= 6.8 Hz, 1 H), 0.84 (d, J = 6.8 Hz, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ 170.8, 145.8, 141.2, 133.0, 129.4, 127.6, 126.7, 126.5, 125.8, 64.4, 52.2, 34.1, 33.2, 26.9, 19.9; MS (EI, m/z) 328 (M⁺, 1.96), 145 (100); IR (KBr, cm⁻¹) 3016, 2961, 2869, 1733, 1488, 1430, 1364, 1267, 1245, 1222, 1194, 1170, 1118, 1086, 1049, 1008. Elemental analysis calcd for C₂₀H₂₄O₄: C, 73.15; H, 7.37; Found: C, 73.03; H, 7.68.

Reference:

1. Sadao, T.; Koichi, M.; Takashi, S.; Akira, T. J. Org. Chem. 1986, 51, 4944.

¹H NMR and ¹³C NMR spectra



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