Supporting Information

Stereoselective Coupling Reaction of Dimethylzinc and Alkyne toward Nickelacycles

Takamichi Mori, Toshiyuki Nakamura, and Masanari Kimura

Graduate School of Science and Technology, Nagasaki University

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University

Bunkyo-machi, Nagasaki 852-8521, Japan

E-mail: masanari@nagasaki-u.ac.jp

Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel 60F₂₅₄). Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303.

Solvents and Reagents

Tetrahydrofuran, diethyl ether, and 1,4-dioxane were dried and distilled from benzophenone and sodium immediately prior to use under nitrogen atmosphere. Anhydrous toluene and dichloromethane were purchased (Aldrich) and used without further purification. $\text{Ni}(\text{acac})_2$, PPh_3 , $n\text{-Bu}_3\text{P}$, dppf [1,1'-bis(diphenylphosphino)ferrocene], 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride, and Me_2Zn (1.0 M hexane solution) (Kanto Kagaku) were purchased and used without further purification. 3-Hexyne, dimethylacetylene, bis(methoxycarbonyl)ethyne, 1-phenyl-1-butyne, phenylacetylene, trimethylsilylacetylene, bistrimethylacetylene, and diphenylacetylene (Tokyo Kasei Kogyo Co., Ltd) were purchased and distilled prior to use. Butadiene monoxide and isoprene oxide (Aldrich) were purchased and distilled prior to use. Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate was prepared according to the literature.¹

General procedure for the Pd-catalyzed coupling reaction of aldehyde with isoprene (run 6, Table 1): To a solution of $\text{Pd}(\text{OAc})_2$ (22.4 mg, 0.1 mmol) and Xantphos (57.8 mg, 0.1 mmol) in dry THF (5 mL) were successively added benzaldehyde (106 mg, 1 mmol), isoprene (400 mL, 4 mmol), and triethylborane (2 mmol, 1.0 M THF solution) via syringe under nitrogen atmosphere. The mixture was stirred at ambient temperature for 24 h. The mixture was diluted with 30 mL of EtOAc and washed with 2 N HCl, sat. NaHCO_3 , and then brine. The extract was dried (MgSO_4) and concentrated in vacuo and the residual oil was subjected to column chromatography over silica gel (hexane/EtOAc = 10/1 v/v) to give **1a** (173 mg, 99%, R_f = 0.47; hexane/ethyl acetate = 4/1 v/v).

(2E,5E)-5-Ethyl-6-methylocta-2,5-dien-1-ol (1a): (a mixture of *E*- and *Z*- isomers in a ratio of 3 : 1): IR (neat) 3319 (m), 2962 (s), 2931 (s), 2872 (s), 1655 (w), 1458 (m), 1373 (m), 1070 (m), 1004 (m), 970 (m), 792 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , *E*-isomer) δ 0.94 (t, J =

7.6 Hz, 3 H), 0.97 (t, $J = 7.6$ Hz, 3 H), 1.62 (s, 3 H), 2.03 (q, $J = 7.6$ Hz, 2 H), 2.04 (q, $J = 7.6$ Hz, 2 H), 2.75 (br m, 2 H), 4.09 (br m, 2 H), 5.62 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3 , *E*-isomer) δ 13.3, 13.6, 17.5, 24.9, 27.0, 34.7, 63.8, 127.9, 128.8, 131.2, 131.6; ^1H -NMR (400 MHz, CDCl_3 , *Z*-isomer) δ 1.58 (s, 3 H), 2.80 (d, $J = 7.3$ Hz, 2 H), 4.26 (br m, 2 H), 5.45 (dt, $J = 11.0, 7.3$ Hz, 1 H), 5.58 (dm, $J = 11.0$ Hz, 1 H); ^{13}C -NMR (100 MHz, CDCl_3 , *Z*-isomer) δ 13.2, 13.6, 17.5, 24.8, 27.1, 30.2, 58.7, 127.9, 128.8, 131.0, 131.4; High-resolution MS, calcd for $\text{C}_{11}\text{H}_{20}\text{O}$: 168.1514. Found m/z (relative intensity): 169($\text{M}^+ + 1$, 1), 168.1497 (M^+ , 8), 167 (20), 151 (27), 150 (31), 139 (100).

(2*E*,5*Z*)-5,6-Diphenylhepta-2,5-dien-1-ol (1b): (a mixture of *E*- and *Z*- isomers in a ratio of 2 : 1): IR (neat) 3350 (s), 3055 (s), 3020 (s), 2993 (s), 2928 (s), 2870 (m), 1717 (s), 1682 (s), 1599 (m), 1489 (s), 1443 (s), 1026 (m), 970 (m), 912 (m), 764 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , *E*-isomer) δ 2.17 (s, 3 H), 3.31 (br m, 2 H), 4.10 (br m, 2 H), 5.72 (m, 2 H), 7.00 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3 , *E*-isomer) δ 21.1, 37.9, 63.6, 125.6, 127.4, 127.5, 128.9, 129.0, 129.4, 129.5, 129.6, 134.7, 142.8, 143.1, 144.1; ^1H NMR (400 MHz, CDCl_3 , *Z*-isomer) δ 2.20 (s, 3 H), 3.34 (d, $J = 6.6$ Hz, 2 H), 4.00 (d, $J = 6.3$ Hz, 2 H), 5.57 (dt, $J = 10.2, 6.6$ Hz, 1 H), 5.72 (dt, $J = 10.2, 6.3$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , *Z*-isomer) δ 20.9, 33.5, 58.4, 125.8, 127.4, 127.5, 128.9, 129.3, 129.4, 129.5, 129.6, 135.4, 142.8, 143.1, 144.0; High-resolution MS, calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: 264.1514. Found m/z (relative intensity): 264.1440 (M^+ , 42), 263 (100), 262 (51), 246 (57).

(2*E*,5*Z*)-5,6-Bis(trimethylsilyl)hepta-2,5-dien-1-ol (1c): (a mixture of *E*- and *Z*- isomers in a ratio of 2 : 1): IR (neat) 3329 (m), 2955 (s), 2899 (m), 2864 (m), 1456 (w), 1248 (s), 1001 (m), 968 (m), 837 (s), 756 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , *E*-isomer) δ 0.06 (s, 9 H), 0.06 (s, 9 H), 1.71 (m, 3 H), 2.77 (br m, 2 H), 4.00 (br m, 2 H), 5.56 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3 , *E*-isomer) δ 0.4, 0.7, 17.6, 37.9, 63.7, 129.2, 131.9, 142.9, 144.7; ^1H NMR (400 MHz,

CDCl₃, Z-isomer) δ 2.81 (d, J = 7.6 Hz, 2 H), 4.19 (d, J = 6.3 Hz, 2 H), 5.42 (dt, J = 9.0, 7.6 Hz, 1 H), 5.48 (dt, J = 9.0, 6.3 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃, Z-isomer) δ 0.4, 0.7, 17.6, 30.3, 58.6, 130.3, 132.5, 143.3, 144.3; High-resolution MS, calcd for C₁₃H₂₈OSi₂: 256.1679. Found m/z (relative intensity): 257 (M⁺+1, 24), 256.1679 (M⁺, 100), 225 (9).

(2E,5Z)-6-methyl-5-phenylocta-2,5-dien-1-ol (1d): (a mixture of 4 isomers, a major isomer was assigned): IR (neat) 3350 (s), 3057 (m), 3020 (m), 2968 (s), 2933 (s), 2873 (s), 1717 (s), 1682 (s), 1599 (m), 1491 (s), 1441 (s), 1026 (s), 972 (m), 766 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 2E-isomer) δ 0.89 (t, J = 7.6 Hz, 3 H), 1.58 (br s, 1 H), 1.89 (q, J = 7.6 Hz, 2 H), 1.93 (s, 3 H), 2.94 (br m, 2 H), 4.14 (br m, 2 H), 5.73 (m, 2 H), 7.10 (t, J = 7.6 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃, 2E-isomer) δ 13.4, 21.0, 26.2, 33.8, 63.7, 125.8, 127.8, 127.9, 128.5, 129.3, 130.4, 130.9, 144.9; ¹H NMR (400 MHz, CDCl₃, 2Z-isomer) δ 0.90 (t, J = 7.6 Hz, 3 H), 1.31 (br s, 1 H), 1.89 (q, J = 7.6 Hz, 2 H), 1.95 (s, 3 H), 2.98 (d, J = 7.3 Hz, 2 H), 4.31 (d, J = 6.6 Hz, 2 H), 5.56 (dt, J = 10.7, 7.3 Hz, 1 H), 5.67 (dt, J = 10.7, 6.6 Hz, 1 H), 7.10 (t, J = 7.6 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 7.29 (t, J = 7.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃, 2Z-isomer) δ 13.3, 20.9, 26.1, 29.4, 58.7, 125.8, 127.9, 127.9, 128.6, 129.2, 130.4, 130.9, 144.9; High-resolution MS, calcd for C₁₅H₂₀O: 216.1514. Found m/z (relative intensity): 217 (M⁺+1, 16), 216.1496 (M⁺, 100), 214 (15), 199 (36).

(2E,5E)-6-Phenylhepta-2,5-dien-1-ol (1e): (a mixture of E- and Z- isomers in a ratio of 2 : 1): IR (neat) 3371 (br), 3024 (s), 2926 (s), 2872 (s), 1719 (m), 1647 (m), 1495 (s), 1447 (s), 1028 (s), 927 (s), 760 (s), 698 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 2E-isomer) δ 1.55 (br, 1 H), 2.05 (t, J = 1.0 Hz, 3 H), 2.99 (t, J = 7.0 Hz, 2 H), 4.12 (d, J = 5.3 Hz, 1 H), 4.27 (d, J = 5.3 Hz, 1 H), 5.60-5.80 (m, 3 H), 7.21 (tt, J = 7.0, 2.0 Hz, 1 H), 7.30 (td, J = 7.0, 1.5 Hz, 1 H), 7.36 (dt, J = 7.0, 1.3 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃, 2E-isomer) δ 15.8, 31.4, 63.6,

125.5, 126.6, 128.0, 128.2, 129.4, 130.7, 135.9, 143.5; ^1H NMR (400 MHz, CDCl_3 , 2Z-isomer) δ 1.55 (br, 1 H), 2.05 (t, $J = 1.0$ Hz, 3 H), 2.95 (t $J = 7.0$ Hz, 2 H), 4.12 (d, $J = 5.3$ Hz, 1 H), 4.27 (d, $J = 5.3$ Hz, 1 H), 5.60-5.80 (m, 3 H), 7.21 (tt, $J = 7.0, 2.0$ Hz, 1 H), 7.30 (td, $J = 7.0, 1.5$ Hz, 1 H), 7.36 (dt, $J = 7.0, 1.3$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , 2Z-isomer) δ 15.8, 27.3, 58.6, 125.5, 126.6, 128.0, 128.2, 128.8, 130.7, 135.6, 143.4; High-resolution MS, calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: 188.1183. Found m/z (relative intensity): 189 ($\text{M}^+ + 1$, 8), 188.1183 (M^+ , 54), 171 (13), 157 (48).

(E)-4-Phenyl-2-vinylpent-3-en-1-ol (1e'): IR (neat) 3362 (br), 3080 (s), 2928 (s), 2872 (s), 1726 (s), 1636 (m), 1597 (m), 1493 (m), 914 (m), 758 (s), 696 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.54 (s, 1 H), 2.09 (d, $J = 1.5$ Hz, 3 H), 3.38 (ddt, $J = 10.3, 9.0, 7.4$ Hz 1 H), 3.62 (d, $J = 7.4$ Hz, 2 H), 5.17 (dd, $J = 7.6, 1.5$ Hz, 1 H), 5.20 (dd, $J = 17.3, 1.5$ Hz, 1 H), 5.63 (dq, $J = 9.0, 1.5$ Hz, 1 H), 5.78 (ddd, $J = 17.3, 10.3, 7.6$ Hz, 1 H), 7.24 (tt, $J = 7.9, 2.3$ Hz, 1 H), 7.31 (td, $J = 7.9, 1.5$ Hz, 2 H), 7.39 (dt, $J = 7.9, 1.3$ Hz, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ 16.4, 46.3, 65.5, 116.5, 125.6, 125.9, 126.9, 128.1, 137.4, 138.0, 143.3; High-resolution MS, calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: 188.1183. Found m/z (relative intensity): 189 ($\text{M}^+ + 1$, 7), 188.1183 (M^+ , 46), 157 (100), 142 (76).

(2E,5E)-6-(Trimethylsilyl)hepta-2,5-dien-1-ol (1f): (a mixture of *E*- and *Z*- isomers in a ratio of 2 : 1): IR (neat) 3317 (br), 3009 (s), 2955 (s), 2899 (s), 1614 (m), 1404 (m), 1248 (s), 1013 (s), 970 (s), 837 (s), 750 (s), 689 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 2*E*-isomer) δ 0.01 (s, 9 H), 1.28 (s, 1 H), 1.63 (d, $J = 0.9$ Hz, 3 H), 2.84 (t, $J = 6.9$ Hz, 2 H), 4.06 (d, $J = 5.6$ Hz, 2 H), 5.62 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 2*E*-isomer) δ -2.1, 14.4, 31.2, 63.7, 128.5, 129.1, 131.0, 135.9; ^1H NMR (400 MHz, CDCl_3 , 2*Z*-isomer) 0.01 (s, 9 H), 1.28 (s, 1 H), 1.65 (d, $J = 0.9$ Hz, 3 H), 2.81 (t, $J = 6.9$ Hz, 2 H), 4.19 (d, $J = 5.6$ Hz, 2 H), 5.62 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3 , 2*Z*-isomer) δ -2.1, 14.4, 27.0, 58.6, 128.5, 129.1, 131.0,

135.9; High-resolution MS, calcd for C₁₀H₂₀OSi: 184.1283. Found *m/z* (relative intensity): 185 (M⁺+1, 16), 184.1261 (M⁺, 100), 170 (12), 169 (82), 166(34).

(*E*)-4-(Trimethylsilyl)-2-vinylpent-3-en-1-ol (1f⁺): IR (neat) 3313 (br), 3080 (m), 2955 (s), 2874 (m), 1618 (m), 1406 (m), 1248 (s), 1028 (s), 991 (m), 835 (s), 750 (s), 689 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.07 (s, 9 H), 1.43 (s, 1 H), 1.73 (d, *J* = 1.7 Hz, 3 H), 3.38 (tdd, *J* = 8.5, 7.8, 6.7 Hz, 1 H), 3.52 (d, *J* = 7.8 Hz, 2 H), 5.11 (dd, *J* = 17.6, 1.7 Hz, 1 H), 5.12 (dd, *J* = 9.8, 1.7 Hz, 1 H), 5.53 (dq, *J* = 8.5, 1.7 Hz, 1 H), 5.72 (ddd, *J* = 17.6, 9.8, 6.7 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 1.6, 15.4, 46.3, 65.6, 116.7, 136.5, 137.9, 140.9; High-resolution MS, calcd for C₁₀H₂₀OSi: 184.1283. Found *m/z* (relative intensity): 185 (M⁺+1, 16), 184.1261 (M⁺, 100), 170 (12), 169 (82), 166(34).

(2*Z*,5*E*)-5-Ethyl-2,6-dimethylocta-2,5-dien-1-ol (1g): (a mixture of *E*- and *Z*- isomers in a ratio of 1 : 2): IR (neat) 3336 (m), 2964 (s), 2934 (s), 2872 (s), 1653 (m), 1456 (s), 1375 (s), 1005 (s), 951 (w), 785 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 2*Z*-isomer) δ 0.94 (t, *J* = 7.6 Hz, 3 H), 0.96 (t, *J* = 7.6 Hz, 3 H), 1.64 (s, 3 H), 1.80 (q, *J* = 1.2 Hz, 3 H), 1.99 (q, *J* = 7.6 Hz, 2 H), 2.02 (q, *J* = 7.6 Hz, 2 H), 2.77 (d, *J* = 7.1 Hz, 2 H), 4.19 (s, 2 H), 5.31 (tq, *J* = 7.1, 1.2 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃, 2*Z*-isomer) δ 13.2, 13.6, 17.5, 21.3, 24.6, 27.1, 30.2, 61.7, 127.2, 130.5, 132.2, 133.7; ¹H NMR (400 MHz, CDCl₃, 2*E*-isomer) δ 1.64 (s, 3 H), 1.72 (s, 3 H), 2.75 (d, *J* = 6.6 Hz, 2 H), 4.00 (s, 2 H), 5.21 (t, *J* = 6.6 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃, 2*E*-isomer) δ 13.2, 13.6, 13.8, 17.6, 24.9, 27.1, 30.4, 69.1, 125.4, 130.5, 132.3, 134.2; High-resolution MS, calcd for C₁₂H₂₂O: 182.1671. Found *m/z* (relative intensity): 183 (M⁺+1, 10), 182.1669 (M⁺, 69), 164 (100).

(2*Z*,5*Z*)-2-Methyl-5,6-diphenylhepta-2,5-dien-1-ol (1h): (a mixture of *E*- and *Z*- isomers in a ratio of 1 : 3): IR (neat) 3350 (s), 3057 (m), 3024 (s), 2968 (s), 2933 (s), 2876 (s), 1719 (s),

1701 (s), 1670 (m), 1599 (m), 1491 (s), 1437 (s), 1026 (m), 912 (m), 760 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 2Z-isomer) δ 1.55 (br s, 1 H), 1.74 (d, $J = 1.2$ Hz, 3 H), 2.20 (s, 3 H), 3.30 (d, $J = 7.6$ Hz, 2 H), 3.91 (s, 2 H), 5.31 (tq, $J = 7.6, 1.2$ Hz, 1 H), 6.92 - 7.08 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3 , 2Z-isomer) δ 20.9, 21.3, 33.8, 61.5, 124.6, 125.7, 127.4, 127.5, 128.9, 129.6, 135.2, 136.0, 143.0, 144.1; ^1H NMR (400 MHz, CDCl_3 , 2E-isomer) δ 1.63 (d, $J = 1.2$ Hz, 3 H), 2.18 (s, 3 H), 3.48 (dd, $J = 13.9, 6.8$ Hz, 1 H), 3.48 (dd, $J = 13.9, 6.8$ Hz, 1 H), 3.97 (s, 2 H), 5.41 (tq, $J = 6.8, 1.2$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , 2E-isomer) δ 13.8, 21.1, 33.8, 68.8, 123.5, 125.5, 127.4, 127.5, 129.0, 129.4, 135.2, 136.0, 143.0, 144.1; High-resolution MS, calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: 278.1671. Found m/z (relative intensity): 279 ($\text{M}^+ + 1$, 17), 278.1658 (M^+ , 73), 260 (100).

(2Z,5Z)-2-Methyl-5,6-bis(trimethylsilyl)hepta-2,5-dien-1-ol (1i): (a mixture of *E*- and *Z*-isomers in a ratio of 1 : 1): IR (neat) 3396 (br), 2955 (s), 2899 (s), 1717 (s), 1699 (s), 1437 (m), 1248 (s), 1047 (s), 1009 (s), 839 (s), 756 (s), 689 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 2Z-isomer) δ 0.14 (s, 9 H), 0.18 (s, 9 H), 1.72 (s, 3 H), 1.80 (brs, 1 H), 1.83 (s, 3 H), 2.85 (d, $J = 6.7$ Hz, 2 H), 4.19 (d, $J = 4.2$ Hz, 2 H), 5.04 (t, $J = 6.7$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , 2Z-isomer) δ 0.81, 1.46, 13.9, 18.7, 25.4, 69.1, 124.3, 133.4, 143.9, 149.8; ^1H NMR (400 MHz, CDCl_3 , 2E-isomer) δ 0.13 (s, 9 H), 0.17 (s, 9 H), 1.72 (s, 3 H), 1.80 (brs, 1 H), 1.83 (s, 3 H), 2.83 (d, $J = 6.8$ Hz, 2 H), 4.19 (d, $J = 4.2$ Hz, 2 H), 5.02 (t, $J = 6.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , 2E-isomer) δ 0.81, 1.93, 18.7, 20.2, 25.4, 61.9, 125.9, 133.5, 143.9, 151.2; High-resolution MS, calcd for $\text{C}_{14}\text{H}_{30}\text{OSi}_2$: 270.1835. Found m/z (relative intensity): 270.1812 (M^+ , 100), 269 (72), 254 (94).

Dimethyl 2-[(2E,5E)-5-ethyl-6-methylocta-2,5-dienyl]malonate (2a): (a mixture of *E*- and *Z*-isomers in a ratio of 8 : 1): IR (neat) 2959 (s), 2882 (m), 1738 (s), 1655 (w), 1437 (s), 1340 (m), 1269 (m), 1161 (m), 974 (m), 698 (w) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 2E-isomer) δ

0.91 (t, $J = 7.6$ Hz, 3 H), 0.96 (t, $J = 7.6$ Hz, 3 H), 1.54 (s, 3 H), 1.97 (q, $J = 7.6$ Hz, 2 H), 2.02 (q, $J = 7.6$ Hz, 2 H), 2.58 (ddd, $J = 7.8, 6.8, 1.2$ Hz, 2 H), 2.67 (d, $J = 6.1$ Hz, 2 H), 3.40 (t, $J = 7.8$ Hz, 1 H), 3.71 (s, 6 H), 5.32 (dt, $J = 15.1, 6.8$ Hz, 1 H), 5.46 (dt, $J = 15.1, 6.1, 1.2$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , 2*E*-isomer) δ 13.3, 13.6, 17.5, 24.7, 27.0, 31.9, 35.0, 52.1, 52.3, 52.7, 124.9, 127.7, 131.1, 131.8, 169.2, 172.4; ^{13}C NMR (100 MHz, CDCl_3 , 2*Z*-isomer) δ 13.2, 13.7, 17.6, 24.9, 26.9, 27.1, 30.0, 51.7, 52.4, 52.4, 124.9, 127.7, 131.1, 132.0, 169.3, 172.4; High-resolution MS, calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4$: 282.1831. Found m/z (relative intensity): 282.1829 (M^+ , 100), 253 (64), 251 (25).

Dimethyl 2-[(2*E*,5*Z*)-5,6-diphenylhepta-2,5-dienyl]malonate (2b): IR (neat) 3078 (w), 3020 (s), 2999 (m), 2953 (s), 1732 (s), 1599 (w), 1491 (m), 1435 (s), 1339 (m), 1267 (m), 1232 (m), 1198 (m), 1155 (s), 972 (w), 764 (s), 700 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.13 (s, 3 H), 2.60 (ddd, $J = 7.6, 6.8, 1.0$ Hz, 2 H), 3.23 (d, $J = 5.9$ Hz, 2 H), 3.38 (t, $J = 7.6$ Hz, 1 H), 3.69 (s, 6 H), 5.46 (dt, $J = 15.1, 6.8$ Hz, 1 H), 5.58 (dt, $J = 15.1, 5.9, 1.0$ Hz, 1 H), 6.90 - 7.06 (m, 10 H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 31.9, 38.2, 52.0, 52.3, 52.4, 125.5, 125.6, 127.3, 127.4, 128.6, 128.9, 129.4, 134.5, 134.9, 138.9, 143.3, 144.2, 169.1; High-resolution MS, calcd for $\text{C}_{24}\text{H}_{26}\text{O}_4$: 378.1831. Found m/z (relative intensity): 379 ($\text{M}^+ + 1$, 27), 378.1835 (M^+ , 100), 360 (3).

Dimethyl 2-[(2*E*,5*Z*)-5,6-bis(trimethylsilyl)hepta-2,5-dienyl]malonate (2c): IR (neat) 2957 (s), 1736 (s), 1456 (m), 1437 (m), 1340 (m), 1248 (s), 1198 (s), 1155 (s), 972 (m), 839 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.15 (s, 18 H), 1.76 (s, 3 H), 2.62 (d, $J = 6.4$ Hz, 2 H), 2.62 (t, $J = 7.5$ Hz, 2 H), 3.42 (t, $J = 7.5$ Hz, 1 H), 3.75 (s, 6 H), 5.64-5.46 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3) δ -2.1, 22.8, 32.1, 52.3, 125.5, 130.1, 143.2, 150.5, 169.3; High-resolution MS, calcd for $\text{C}_{18}\text{H}_{34}\text{O}_4\text{Si}_2$: 370.1996. Found m/z (relative intensity): 371 ($\text{M}^+ + 1$, 22), 370.2006 (M^+ , 78), 355 (100), 339 (6).

Dimethyl 2-((2*E*,5*E*)-5-ethyl-6-phenylhepta-2,5-dienyl)malonate (2d): (a mixture of *E*- and *Z*- isomers in a ratio of 3 : 1): IR (neat) 3020 (m), 2959 (s), 2934 (s), 1738 (s), 1491 (m), 1437 (s), 1232 (s), 1153 (s), 1026 (m), 970 (m), 768 (s), 704 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, (*E*)-) δ 0.86 (t, *J* = 7.4 Hz, 3 H), 1.85 (q, *J* = 7.4 Hz, 2 H), 1.90 (s, 3 H), 2.63 (td, *J* = 7.3, 1.2 Hz, 2 H), 2.85 (d, *J* = 6.2 Hz, 2 H), 3.44 (t, *J* = 7.3 Hz, 1 H), 3.72 (s, 6 H), 5.46 (dt, *J* = 15.4, 7.3, 1.5 Hz, 1 H), 5.57 (dt, *J* = 15.4, 6.2, 1.5 Hz, 1 H), 7.09 (dd, *J* = 7.5, 1.4 Hz, 2 H), 7.19 (tt, *J* = 7.5, 1.4 Hz, 1 H), 7.29 (td, *J* = 7.5, 1.4 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, (*E*)-) δ 13.4, 20.9, 26.1, 31.9, 34.1, 52.0, 52.3, 125.5, 125.7, 127.7, 127.9, 128.5, 131.2, 134.5, 145.0, 169.2; ¹H NMR (400 MHz, CDCl₃, (*Z*)-) δ 0.90 (t, *J* = 7.4 Hz, 3 H), 1.75 (s, 3 H), 1.91 (q, *J* = 7.4 Hz, 2 H), 2.55 (td, *J* = 7.3, 1.2 Hz, 2 H), 2.98 (d, *J* = 6.2 Hz, 2 H), 3.35 (t, *J* = 7.3 Hz, 1 H), 3.69 (s, 6 H), 5.32 (dt, *J* = 15.4, 7.3, 1.5 Hz, 1 H), 5.45 (dt, *J* = 15.4, 6.2, 1.5 Hz, 1 H), 7.03 (dd, *J* = 7.5, 1.4 Hz, 2 H), 7.19 (tt, *J* = 7.5, 1.4 Hz, 1 H), 7.27 (td, *J* = 7.5, 1.4 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃, (*Z*)-) δ 13.2, 17.0, 28.5, 31.8, 37.9, 52.0, 52.3, 125.4, 125.7, 127.9, 128.5, 130.7, 131.9, 134.4, 143.8, 169.2; High-resolution MS, calcd for C₂₀H₂₆O₄: 330.1831. Found *m/z* (relative intensity): 371 (M⁺+1, 23), 330.1832 (M⁺, 100), 315 (2), 301 (4), 299 (4).

Dimethyl 2-[(2*E*,5*E*)-6-methyl-5-(trimethylsilyl)hepta-2,5-dienyl]malonate (2e): IR (neat) 2955 (s), 1740 (s), 1612 (w), 1437 (m), 1340 (w), 1248 (m), 1155 (m), 972 (w), 856 (m), 837 (m), 756 (w), 689 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9 H), 1.62 (d, *J* = 1.2 Hz, 3 H), 1.74 (q, *J* = 1.2 Hz, 3 H), 2.58 (ddd, *J* = 1.2, 6.8, 7.6 Hz, 2 H), 2.76 (d, *J* = 6.3 Hz, 2 H), 3.41 (t, *J* = 7.6 Hz, 1 H), 3.71 (s, 6 H), 5.34 (dt, *J* = 15.1, 6.8 Hz, 1 H), 5.46 (dt, *J* = 15.1, 6.3, 1.2 Hz, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 0.40, 17.4, 22.9, 26.8, 31.9, 38.1, 52.0, 52.3, 125.5, 127.6, 130.6, 143.2, 169.2; High-resolution MS, calcd for C₁₆H₂₈O₄Si: 312.1757. Found *m/z* (relative intensity): 313 (M⁺+22), 312.1743 (M⁺, 100), 297 (81).

Dimethyl 2-[(2E,5Z)-6,8-diphenylocta-2,5-dien-7-ynyl]malonate (3f): IR (neat) 3028 (s), 2953 (s), 2843 (m), 1738 (s), 1597 (m), 1489 (s), 1435 (s), 1155 (s), 1028 (s), 970 (m), 914 (m), 758 (s), 692 (s) cm^{-1} ; ^1H NMR (400MHz, CDCl_3) δ 2.63 (td, $J = 7.6, 1.0$ Hz, 2 H), 3.25 (td, $J = 6.9, 1.0$ Hz, 2 H), 3.43 (t, $J = 7.6$ Hz, 1 H), 3.71 (s, 6 H), 5.53 (dtt, $J = 15.4, 6.9, 1.3$ Hz, 1 H), 5.65 (dtt, $J = 15.4, 7.6, 1.3$ Hz, 1 H), 6.37 (t, $J = 7.6$ Hz, 1 H), 7.27-7.37 (m, 6 H), 7.50-7.55 (m, 2 H), 7.62-7.65 (m, 2 H); ^{13}C NMR (100MHz, CDCl_3) δ 31.9, 34.4, 51.8, 52.4, 86.4, 95.5, 123.3, 124.1, 125.9, 126.8, 127.5, 128.2, 130.4, 131.4, 135.2, 137.9, 169.1; High-resolution MS, calcd for $\text{C}_{25}\text{H}_{24}\text{O}_4$: 388.1675. Found m/z (relative intensity): 389 ($\text{M}^+ + 1$, 28), 388.1689 (M^+ , 100), 373 (6), 357 (92), 329 (22).

Dimethyl 2-[(2E,5E)-6,8-bis(trimethylsilyl)octa-2,5-dien-7-ynyl]malonate (3g): IR (neat) 3003 (m), 2957 (s), 2899 (s), 2847(m), 2127 (s), 1738 (s), 1582 (m), 1435 (s), 1250 (s), 1155 (s), 970 (m), 841 (s), 758 (m), 698 (m) cm^{-1} ; ^1H NMR (400MHz, CDCl_3) δ 0.13 (s, 9 H), 0.18 (s, 9 H), 2.60 (td, $J = 7.6, 0.9$ Hz, 2 H), 3.06 (td, $J = 6.8, 1.0$ Hz 2 H), 3.42 (t, $J = 7.6$ Hz, 1 H), 3.72 (s, 6 H), 5.42 (dt, $J = 15.3, 7.6$ Hz, 1 H), 5.53 (dt, $J = 15.3, 6.8$ Hz, 1 H), 6.00 (t, $J = 6.8$ Hz, 1 H); ^{13}C NMR (100MHz, CDCl_3) δ -2.0, 0.3, 32.0, 35.8, 51.9, 52.4, 102.8, 104.1, 125.7, 126.7, 130.5, 148.7, 169.2; High-resolution MS, calcd for $\text{C}_{19}\text{H}_{32}\text{O}_4\text{Si}_2$: 380.1841. Found m/z (relative intensity): 381 ($\text{M}^+ + 1$, 31), 380.1841 (M^+ , 100), 365 (44), 349 (8).

Dimethyl 2-[(E)-4-(trimethylsilyl)-2-vinylpent-3-enyl]malonate (2'g): IR (neat) 3074 (m), 3003 (m), 2955 (s), 2855 (s), 1740 (s), 1616 (m), 1437 (s), 1248 (s), 1157 (s), 1024 (m), 837 (s), 752 (m), 691 (m) cm^{-1} ; ^1H NMR (400MHz, CDCl_3) δ 0.05 (s, 9 H), 1.65 (d, $J = 1.7$ Hz, 3 H), 1.96 (t, $J = 7.4$ Hz 1 H), 2.02 (t, $J = 7.4$ Hz, 1 H), 3.14 (dtd, $J = 8.7, 7.4, 7.2$ Hz, 1 H), 3.38 (t, $J = 7.4$ Hz, 1 H), 3.72 (s, 3 H), 3.73 (s, 3 H), 4.99 (dd, $J = 17.3, 1.3$ Hz, 1 H), 5.00 (dd, $J = 10.0, 1.3$ Hz, 1 H), 5.45 (dq, $J = 8.7, 1.7$ Hz, 2 H), 5.64 (ddd, $J = 17.3, 10.0, 7.2$ Hz, 1 H);

^{13}C NMR (100MHz, CDCl_3) δ -2.1, 14.6, 33.6, 40.5, 49.5, 52.4, 114.5, 138.3, 138.8, 139.5, 169.7, 169.7; High-resolution MS, calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4\text{Si}$: 298.1600. Found m/z (relative intensity): 299 ($\text{M}^+ + 1$, 18), 298.1591 (M^+ , 45), 283 (100), 267 (64).

Reference

[1] Parsons, A. T.; Campbell, M. J.; Johnson, J. S. *Org. Lett.* **2008**, *10*, 2541.

1a

S12

1b

S14

12.87

2.00

1.77

2.33

4.03

PPM 0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0

1b

S15

1d

815

S19

1e

S24

δ / ppm

0 1 2 3 4 5 6 7

TMS

1.8

7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

δ / ppm

2a

S34

2a

S35

2b

S36

2b

S37

2c

2e

S42

2e

S43

S45