Supporting Information

Stereoselective Coupling Reaction of Dimethylzinc and Alkyne toward Nickelacycles

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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. Ni(acac)₂, PPh₃, *n*-Bu₃P, dppe [1,1'-bis(diphenylphosphino)ferrocene], 1,3-bis(2,6-di-isopropylphenyl)imidazolium chloride, and Me₂Zn (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 Ni-Catalyzed Three-Component Connection Reaction of Alkyne, Vinyloxacyclopropane and Me₂Zn (entry 1, Table 1): To a solution of Ni(acac)₂ (25.7 mg, 0.1 mmol) in dry THF (3 mL) were successively added butadiene monoxide (70.1 mg, 1 mmol), 3-hexyne (82.0 mg, 1 mmol), and dimethylzinc (1.2 mmol, 1.0 M hexane 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. NaHCO₃, and then brine. The extract was dried (MgSO₄) and concentrated in vacuo and the residual oil was subjected to column chromatography over silica gel (hexane/EtOAc = 4/1 v/v) to give **1a** (155.0 mg, 92%, *R*_f = 0.35; hexane/ethyl acetate = 4/1 v/v). **(2*E*,5*E*)-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, CDCl₃, *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, CDCl_3 , *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); ^{13}C NMR (100 MHz, CDCl_3 , *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 $\text{C}_{13}\text{H}_{28}\text{OSi}_2$: 256.1679. Found m/z (relative intensity): 257 ($\text{M}^+ + 1$, 24), 256.1679 (M^+ , 100), 225 (9).

(2*E*,5*Z*)-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, CDCl_3 , 2*E*-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); ^{13}C NMR (100 MHz, CDCl_3 , 2*E*-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, CDCl_3 , 2*Z*-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); ^{13}C NMR (100 MHz, CDCl_3 , 2*Z*-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 $\text{C}_{15}\text{H}_{20}\text{O}$: 216.1514. Found m/z (relative intensity): 217 ($\text{M}^+ + 1$, 16), 216.1496 (M^+ , 100), 214 (15), 199 (36).

(2*E*,5*E*)-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, CDCl_3 , 2*E*-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); ^{13}C NMR (100 MHz, CDCl_3 , 2*E*-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 $\text{C}_{10}\text{H}_{20}\text{OSi}$: 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, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) δ 1.6, 15.4, 46.3, 65.6, 116.7, 136.5, 137.9, 140.9; High-resolution MS, calcd for $\text{C}_{10}\text{H}_{20}\text{OSi}$: 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, CDCl_3 , 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); ^{13}C NMR (100 MHz, CDCl_3 , 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, CDCl_3 , 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); ^{13}C NMR (100 MHz, CDCl_3 , 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 $\text{C}_{12}\text{H}_{22}\text{O}$: 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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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 C₂₀H₂₂O: 278.1671. Found m/z (relative intensity): 279 (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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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 C₁₄H₃₀OSi₂: 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, CDCl₃, 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 (dtt, $J = 15.1, 6.1, 1.2$ 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 (dtt, $J = 15.1, 5.9, 1.0$ 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-[(2*E*,5*Z*)-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-[(2*E*,5*E*)-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 C₁₅H₂₆O₄Si: 298.1600. Found *m/z* (relative intensity): 299 (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

1b

S15

1d

815

S19

le

S20

1e

δ / ppm

0 1 2 3 4 5 6 7

S24

δ / ppm

0 1 2 3 4 5 6 7

92S

TMS

1.8

S27

S31

7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
 δ / ppm

S32

2a

S34

2a

S35

2b

935

2b

S37

2d

S41

2e

S42

2e

S43

S45