Supplementary Material (ESI) for Chemical Communications

Rh(II)-Catalyzed Skeletal Reorganization of 1,6- and 1,7-Enynes Involving Selective Cleavage of C-C Triple Bonds

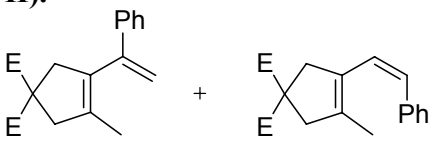
Kazusa Ota and Naoto Chatani*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

Typical Procedures. A 10-mL two-necked flask equipped with a reflux condenser connected to a N_2 line was flame-dried under the flow N_2 and cooled to room temperature. enyne (0.5 mmol), Rh(II) (0.01 mmol) were added and toluene (2.5 mL) were added via a syringe. The vessel was heated in an oil bath at 80 °C. The reaction was monitored by GC and after it was completed, the vessel was cooled. The volatile components were removed *in vacuo* and the residue was subjected to column chromatography on silica gel to give a product.

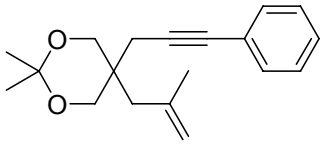
Diethyl 4-methyl-3-(1-phenylethenyl)-3-cyclopentene-1,1-dicarboxylate (2b-I) and (*Z*)-Diethyl 4-methyl-3-(2-phenylethenyl)-3-cyclopentene-1,1-dicarboxylate (2b-II).



2b-I 2b-II

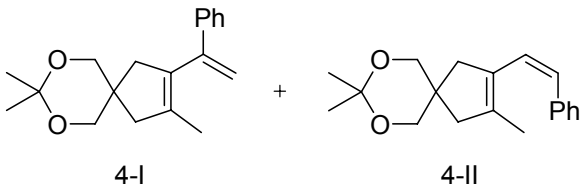
^{1}H and ^{13}C NMR were obtained from a 52:48 mixture of **2b-I** and **2b-II**. Colorless oil; R_f 0.37 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ [1.55 (s, 3H), 3.09 (s, 2H), 3.12 (s, 2H), 5.11 (d, *J*= 1.6 Hz, 1H), 5.43 (d, *J*= 1.6 Hz, 1H) (**2b-I**)], [1.63 (s, 3H), 2.90 (s, 2H), 2.96 (s, 2H), 6.16 (d, *J*= 11.9 Hz, 1H), 6.49 (d, *J*= 11.9 Hz, 1H) (**2b-II**)], [1.19-1.28 (m), 4.12-4.25 (m), 7.21-7.31 (m) (**2b-I** and/or **2b-II**)]; ^{13}C NMR ($CDCl_3$) δ [13.96, 14.83, 44.35, 46.35, 57.28, 61.31, 114.78, 126.88, 127.40, 128.15, 132.45, 134.16, 140.26, 144.73, 172.14 (**2b-I**)], [13.92, 14.32, 42.77, 45.43, 57.58, 61.40, 124.44, 126.77, 127.77, 128.72, 129.98, 130.08, 135.49, 138.02, 172.09 (**2b-II**)]; IR (neat) 3077 m, 3056 m, 2981 s, 2935 m, 2906 m, 1745 s, 1722 s, 1492 m, 1463 m, 1446 s, 1388 m, 1367 s, 1245 s, 1184 s, 1160 s, 1118 s, 1097 s, 1070 s, 1024 m, 862 m, 779 m, 700 s; MS, *m*/*z* (relative intensity, %) [328 (M^+, 40), 255 (26), 254 (100), 181 (94), 180 (20), 166 (24), 165 (30) (**2b-I**)], [328 (M^+, 21), 255 (58), 182 (21), 181 (100) (**2b-II**)]; Exact Mass Calcd for $C_{20}H_{24}O_4$: 328.1675. Found: [328.1688 (**2b-I**)] and [328.1666 (**2b-II**)]

4-(4,4-Dimethyl-[3,5]-dioxanyl)-6-methyl-1-phenylhept-6-en-1-yne (3).



Colorless oil; *Rf* 0.31 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 3H), 1.45 (s, 3H), 1.84 (s, 3H), 2.18 (s, 2H), 2.67 (s, 2H), 3.75 (s, 4H), 4.84 (s, 1H), 4.96 (dd, *J*= 1.9 Hz, 1.4 Hz, 1H), 7.27-7.30 (m, 3H) 7.38-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.42, 23.46, 25.34, 26.43, 36.53, 40.12, 67.23, 83.44, 86.86, 98.00, 115.46, 123.69, 127.58, 128.11, 131.42, 140.73; IR (neat) 3075 m, 2991 m, 2944 m, 2863 m, 1643 m, 1598 w, 1490 m, 1452 m, 1384 m, 1371 s, 1265 m, 1220 m, 1197 s, 1157 m, 1112 s, 1070 s, 1039 m, 898 m, 755 s, 732 m, 692 s, 522 m; MS, *m*/*z* (relative intensity, %) 269 (M^+-Me, 12), 195 (37), 181 (24), 167 (24), 142 (24), 141 (40), 131 (28), 129 (25), 128 (54), 117 (43), 116 (22), 115 (100), 105 (32), 103 (50), 93 (33), 91 (45), 79 (22), 77 (20), 55 (29); Exact Mass Calcd for $C_{19}H_{24}O_2$: 284.1776. Found: 284.1786.

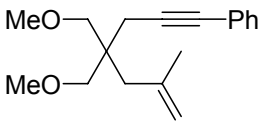
1-(4,4-Dimethyl-[3,5]-dioxanyl))-4-methyl-3-[1-(4-phenylethenyl)]-3-cyclopentene (4-I) and (*Z*)-1-(4,4-Dimethyl-[3,5]-dioxanyl))-4-methyl-3-[2-(4-phenylethenyl)]-3-cyclopentene (4-II).



4-I + 4-II

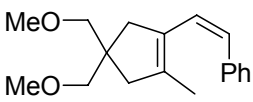
^{1}H and ^{13}C NMR were obtained from a 7:93 mixture of **4-I** and **4-II**. Colorless oil; *Rf* 0.20 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ [1.46 (s), 1.49 (s), 3.76 (s), 5.12 (d, *J*= 1.9 Hz), 5.41 (d, *J*= 1.9 Hz) (**4-I**)], [1.41 (s, 3H), 1.44 (s, 3H), 1.67 (s, 3H), 2.06 (s, 2H), 2.41 (s, 2H), 3.61 (d, *J*= 10.8 Hz, 2H), 3.67 (d, *J*= 10.8 Hz, 2H), 6.24 (d, *J*= 12.4 Hz, 2H), 6.50 (d, *J*= 12.4 Hz, 2H) (**4-II**)], [7.21-7.34 (m) (**4-I** and/or **4-II**)]; ^{13}C NMR ($CDCl_3$) δ [15.49, 23.33, 24.35, 38.89, 44.06, 46.65, 69.38, 97.70, 114.39, 126.95, 127.31, 128.19, 133.16, 135.16, 140.92, 145.91 (**4-I**)], [14.92, 21.83, 25.81, 39.45, 42.05, 46.02, 69.22, 97.62, 125.53, 126.66, 127.74, 128.73, 129.16, 130.54, 137.34, 138.42 (**4-II**)]; IR (neat) 2991 s, 2937 s, 2854 s, 1492 m, 1450 s, 1380 s, 1369 s, 1284 m, 1253 s, 1197 s, 1155 s, 1130 m, 1101 m, 1068 s, 1033 s, 933 m, 892 m, 831 s, 775 m, 732 m, 698 s, 520 m; MS, *m*/*z* (relative intensity, %) 284 (M^+, 22), 196 (20), 195 (100), 117 (35), 91 (40); Exact Mass Calcd for $C_{19}H_{24}O_2$: 284.1776. Found: 284.1784.

4,4-Bis(methoxymethyl)-6-methyl-1-phenylhept-6-en-1-yne (5).



Colorless oil; *Rf* 0.43 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 3H), 2.21 (s, 2H), 2.44 (s, 2H), 3.30 (s, 2H), 3.31 (s, 2H), 3.35 (s, 6H), 4.82 (s, 1H), 4.93 (s, 1H), 7.27-7.30 (m, 3H), 7.40-7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.42, 25.15, 38.61, 42.86, 59.14, 74.37, 82.74, 87.29, 114.95, 124.00, 127.44, 128.09, 131.42, 141.83; IR (neat) 3073 m, 2979 m, 2921 s, 2890 s, 2809 m, 1641 m, 1598 m, 1488 m, 1446 m, 1375 m, 1340 w, 1270 w, 1195 m, 1112 s, 1027 w, 989 m, 958 m, 896 m, 755 s, 692 m; MS, *m*/*z* (relative intensity, %) 273 (M^++H, 49), 272 (M^+, 0), 242 (18), 241 (100), 240 (18), 211 (10), 210 (16), 209 (95), 197 (19), 195 (24), 147 (39); Exact Mass Calcd for $C_{18}H_{25}O_2$([M+H]$^+$): 273.1855. Found: 273.1856.

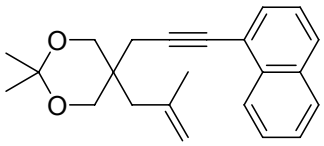
(*Z*)-4-Methyl-1,1-bis(methoxymethyl)-3-(2-phenylethenyl)-3-cyclopentene (6).



Colorless oil; *Rf* 0.43 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 3H), 2.15 (s, 2H), 2.21 (s, 2H), 3.24 (s, 4H), 3.32 (s, 6H), 6.18 (d, *J*= 12.4 Hz, 1H),

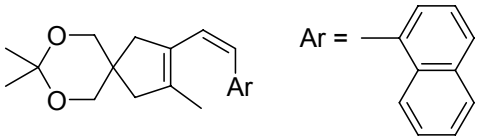
6.43 (d, *J*= 12.4 Hz, 1H), 7.22-7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.89, 41.69, 44.57, 45.15, 59.18, 76.80, 125.89, 126.57, 127.70, 128.80, 129.08, 130.99, 136.91, 138.42; IR (neat) 3056 m, 2977 m, 2919 s, 2881 s, 1639 w, 1598 w, 1492 m, 1446 s, 1384 m, 1326 m, 1199 s, 1162 m, 1112 s, 966 m, 919 w, 890 w, 775 m, 700 s; MS, *m*/*z* (relative intensity, %) 272 (M^+, 5), 195 (100), 194 (13), 165 (20), 117 (27), 91 (22); Exact Mass Calcd for $C_{18}H_{24}O_2$: 272.1776. Found: 272.1786.

4-(4,4-Dimethyl-[3,5]-dioxanyl)-6-methyl-1-(1-naphthyl)hept-6-en-1-yne (7).



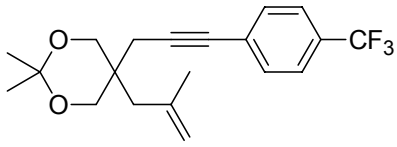
Colorless oil; *Rf* 0.42 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 6H), 1.88 (s, 3H), 2.28 (s, 2H), 2.83 (s, 2H), 3.83 (s, 4H), 4.90 (s, 1H), 4.99 (s, 1H), 7.37-7.65 (m, 4H), 7.78-7.86 (m, 2H), 8.32 (d, *J*= 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.69, 23.92, 25.41, 26.23, 36.65, 40.23, 67.31, 81.53, 91.75, 98.06, 115.56, 121.40, 125.11, 126.09, 126.15, 126.47, 127.99, 128.12, 130.21, 130.06, 133.30, 140.77; IR (neat) 3058 m, 2991 s, 2942 s, 2863 s, 1643 m, 1585 m, 1506 m, 1450 s, 1373 s, 1259 s, 1220 m, 1195 s, 1157 s, 1112 s, 1070 s, 1037 m, 896 s, 835 s, 800 s, 775 s, 522 m, 437 m; MS, *m*/*z* (relative intensity, %) 334 (M^+, 8), 245 (54), 231 (22), 219 (20), 217 (29), 215 (26), 205 (20), 203 (47), 202 (25), 193 (20), 191 (39), 189 (26), 181 (24), 179 (24), 178 (46), 166 (20), 165 (100), 164 (26), 163 (21), 153 (57), 152 (40), 93 (25), 67 (22), 55 (35); Exact Mass Calcd for $C_{23}H_{26}O_2$: 334.1933. Found: 334.1940.

(*Z*)-1-(4,4-Dimethyl-[3,5]-dioxanyl))-4-methyl-3-[2-(1-naphthyl)ethenyl]]-3-cyclopentene (8).



Colorless oil; *Rf* 0.43 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.33 (s, 3H), 1.62 (s, 2H), 1.75 (s, 3H), 2.37 (s, 2H), 3.39 (s, 4H), 4.99 (s, 1H), 7.37-7.65 (m, 4H), 7.78-7.86 (m, 2H), 6.60 (d, *J*= 12.1 Hz, 1H), 6.82 (d, *J*= 12.1 Hz, 1H), 7.25-7.27 (m, 1H), 7.38-7.50 (m, 3H), 7.76 (d, *J*= 8.1 Hz, 1H), 7.85 (dd, *J*= 6.1 Hz, 3.2 Hz, 1H), 7.97 (dd, *J*= 6.1 Hz, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.81, 20.97, 26.71, 39.26, 41.21, 46.29, 69.05, 97.43, 124.84, 125.40, 125.57, 125.68, 126.21, 126.55, 126.83, 127.20, 128.13, 130.57, 131.81, 133.08, 135.92, 139.00; IR (neat) 3056 m, 2991 s, 2937 s, 2854 s, 1637 m, 1589 m, 1506 m, 1438 m, 1380 s, 1253 s, 1197 s, 1155 s, 1130 m, 1101 m, 1068 s, 1033 m, 933 m, 831 s, 794 s, 773 s, 732 m, 518 m; MS, *m*/*z* (relative intensity, %) 334 (M^+, 86), 246 (26), 245 (100), 243 (30), 231 (34), 230 (25), 229 (25), 217 (24), 216 (28), 215 (39), 203 (24), 153 (97), 141 (30); Exact Mass Calcd for $C_{23}H_{26}O_2$: 334.1933. Found: 334.1943.

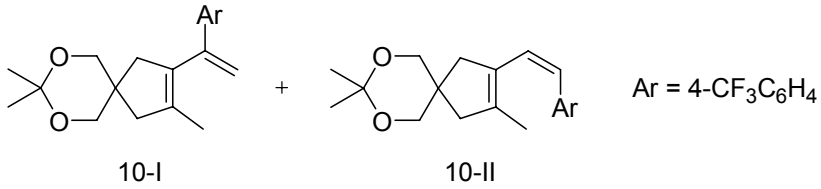
4-(4,4-Dimethyl-[3,5]-dioxanyl)-6-methyl-1-[1-(4-(trifluoromethyl)phenyl)hept-6-en-1-yne (9).



Colorless oil; *Rf* 0.43 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 3H), 1.45 (s, 3H), 2.15 (s, 2H), 2.72 (s, 2H), 3.71 (d, *J*= 11.6 Hz, 2H), 3.77 (d, *J*= 11.6 Hz, 2H), 4.83 (s, 1H), 4.97 (s, 1H), 7.49 (d, *J*= 8.5 Hz, 2H), 7.54 (d, *J*= 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.93, 23.41, 25.24, 26.75, 36.55, 40.20, 67.18, 82.28, 89.91, 98.04, 115.54, 123.85 (q, *J*= 270.9 Hz), 125.02 (q, *J*= 3.7 Hz), 127.50 (q, *J*= 1.3 Hz), 129.33 (q, *J*= 32.3 Hz), 131.62, 140.48; IR (neat) 3075 m, 2992 s, 2942 m, 2865 m, 2223 m, 1643 m, 1616 s, 1452 m, 1373 s, 1324 s, 1267 s, 1197 s, 1166 s, 1130 s, 1068 s, 1039 m, 1018 s, 900 m, 842 s, 732 w, 715 w, 597 m, 522 m; MS, *m*/*z* (relative intensity, %) 352 (M^+, 4), 337 (49), 277 (51), 263 (79), 249 (81), 238 (51), 236 (32), 235 (49), 227 (50), 210 (57), 209 (55),

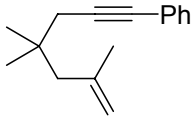
185 (34), 183 (100), 171 (38), 165 (39), 159 (33), 141 (33), 105 (30), 93 (61), 43 (73); Elemental Analysis Calcd for $C_{20}H_{23}F_3O_2$: C, 68.17; H, 6.58; F, 16.17. Found: C, 68.17; H, 6.58; F, 16.17.

1-(4,4-Dimethyl-[3,5]-dioxanyl))-4-methyl-3-{1-[4-(trifluoromethyl)phenyl]ethenyl}-3-cyclopentene (10-I) and (*Z*)-1-(4,4-Dimethyl-[3,5]-dioxanyl))-4-methyl-3-{2-[4-(trifluoromethyl)phenylethenyl]}-3-cyclopentene (10-II).



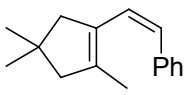
Colorless oil; *Rf* 0.43 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ [1.41 (s), 1.44 (s), 1.49 (s), 2.39 (s), 3.72 (s), 5.17 (s), 5.41 (s) (**10-I**)], [1.36 (s, 3H), 1.40 (s, 3H), 2.03 (s, 2H), 2.33 (s, 2H), 3.57 (d, *J*= 11.2 Hz, 2H), 3.62 (d, *J*= 11.2 Hz, 2H), 6.30 (d, *J*= 12.7 Hz, 1H), 6.44 (d, *J*= 12.7 Hz, 1H), 7.30 (d, *J*= 8.4 Hz, 2H), 7.52 (d, *J*= 8.4 Hz, 2H) (**10-II**)]; ^{13}C NMR ($CDCl_3$) δ [15.78, 23.65, 23.96, 38.91, 44.05, 46.55, 69.30, 97.76, 116.22, 125.19 (q, *J*= 3.7 Hz), 126.51, 127.25, 132.50, 135.94, 144.62, 144.86 (**10-I**)], [14.97, 22.46, 25.10, 39.55, 42.27, 45.83, 69.13, 97.71, 124.22 (q, *J*= 271.2 Hz), 124.69 (q, *J*= 3.9 Hz), 127.37, 127.52, 128.58 (q, *J*= 32.5 Hz), 130.17, 138.61, 142.11 (q, *J*= 1.5 Hz) (**10-II**)]; IR (neat) 2992 m, 2938 m, 2910 m, 2856 m ,1616 m, 1440 m, 1382 s, 1371 s, 1324 s, 1251 m, 1199 s, 1164 s, 1126 s, 1066 s, 1035 m, 1018 m, 875 m, 831 s, 730 m, 607 m, 520 m; MS, *m*/*z* (relative intensity, %) [352 (M^+, 21), 337 (67), 277 (100), 263 (69), 249 (43), 171 (62) (**10-I**)], [352 (M^+, 21), 337 (12), 277 (26), 264 (24), 263 (100) (**10-II**)]; Exact Mass Calcd for $C_{20}H_{23}F_3O_2$: 352.1650. Found: [352.1661 (**10-I**)] and [352.1667 (**10-II**)].

4,4,6-Trimethyl-1-phenylhept-6-en-1-yne (11).



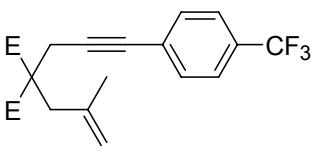
Colorless oil; *Rf* 0.28 (hexane); ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 6H), 1.83 (s, 3H), 2.12 (s, 2H), 2.32 (s, 2H), 4.74 (s, 1H), 4.90 (s, 1H), 7.27 (m, 3H), 7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.40, 27.62, 32.84, 34.85, 48.66, 82.55, 88.67, 114.38, 124.05, 127.37, 128.08, 131.40, 143.11; IR (neat) 3073 m, 2962 s, 2919 s, 1716 m, 1641 m, 1598 m, 1488 s, 1465 s, 1444 s, 1380 m, 1369 m, 1324 m, 1255 m, 1184 m, 1068 m, 1029 w, 894 s, 755 s, 692 s, 526 m; MS, *m*/*z* (relative intensity, %) 212 (M^+, 52), 91 (100); Exact Mass Calcd for $C_{16}H_{20}$: 212.1565. Found: 212.1559.

(*Z*)-1,1,4-Trimethyl-3-(2-phenylethenyl)-3-cyclopentene (12).



Colorless oil; *Rf* 0.54 (hexane); ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 6H), 1.64 (s, 3H), 2.05 (s, 2H), 2.14 (s, 2H), 6.25 (d, *J*= 11.8 Hz, 1H), 6.43 (d, *J*= 11.8 Hz, 1H), 7.20-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.19, 29.68, 37.03, 50.32, 53.40, 126.14, 126.34, 127.53, 128.25, 128.83, 131.62, 138.19, 138.55; IR (neat) 3029 m, 2952 s, 2865 s, 1706 m, 1600 m, 1494 m, 1450 s, 1380 m, 1363 m, 1315 m, 1268 m, 1207 m, 1170 m, 1070 m, 968 m, 835 m, 748 s, 696 s; MS, *m*/*z* (relative intensity, %) 212 (M^+, 73), 197 (86), 155 (29), 141 (56), 128 (22), 121 (23), 115 (29), 105 (34), 91 (100), 77 (23); Exact Mass Calcd for $C_{16}H_{20}$: 212.1565. Found: 212.1562.

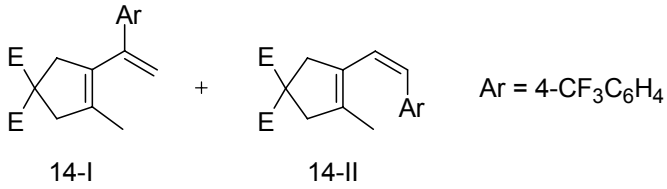
Diethyl 2-(2-methyl-2-propenyl)-2-{3-[4-(trifluoromethyl)phenyl]-2-propynyl}malonate (13).



Colorless oil; *Rf* 0.40 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.27 (t, *J*= 7.2 Hz, 6H), 1.70 (s, 3H), 2.89 (s, 2H), 3.07 (s, 2H), 4.16-4.29 (m, 4H), 4.88

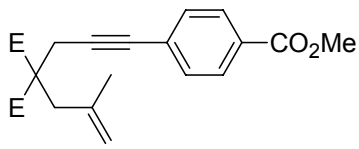
(s, 1H), 4.93 (d, *J*= 1.4 Hz, 1H), 7.46 (d, *J*= 4.2 Hz, 2H), 7.53 (d, *J*= 4.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 23.27, 23.55, 39.70, 56.54, 61.66, 82.45, 87.68, 116.17, 123.78 (q, *J*= 271.3 Hz), 125.99 (q, *J*= 3.9 Hz), 126.97 (q, *J*= 1.1 Hz), 129.55 (q, *J*= 32.5 Hz), 131.67, 139.81, 169.90; IR (neat) 3077 m, 2983 m, 2938 m, 1737 s, 1644 m, 1616 m, 1463 m, 1446 m, 1403 m , 1367 m, 1324 s, 1299 s, 1276 s, 1238 s, 1207 s, 1184 s, 1168 s, 1128 s, 1105 s, 1068 s, 1018 s, 904 m, 844 s, 705 w, 678 w, 597 m, 553 w, 520 w; MS, *m*/*z* (relative intensity, %) 322 (M^+-CO_2Et, 16), 321 (26), 293 (20), 292 (50), 276 (25), 249 (100); Exact Mass Calcd for $C_{21}H_{23}F_3O_4$: 396.1548. Found: 396.1546.

Diethyl 4-methyl-3-{1-[4-(trifluoromethyl)phenyl]ethenyl}-3-cyclopentene-1,1-dicarboxylate (14-I) and (*Z*)-Diethyl 4-methyl-3-{2-[4-(trifluoromethyl)phenyl]ethenyl}-3-cyclopentene-1,1-dicarboxylate (14-II).



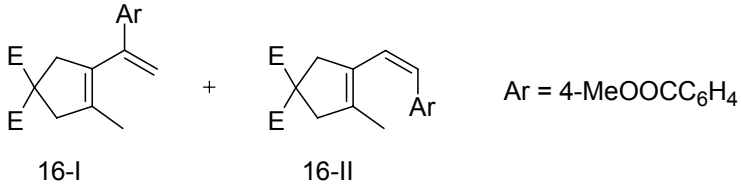
^{1}H and ^{13}C NMR were obtained from a 9:91 mixture of **14-I** and **14-II**. Colorless oil; *Rf* 0.37 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ [3.10 (s), 5.21 (s), 5.49 (s) (**14-I**)], [1.61 (s, 3H), 2.86 (s, 1H), 2.97 (s, 1H), 6.26 (d, *J*= 12.4 Hz, 1H), 6.48 (d, *J*= 12.4 Hz, 1H), 7.34 (d, *J*= 8.4 Hz, 2H), 7.53 (d, *J*= 8.4 Hz, 2H) (**14-II**)], [1.19-1.28 (m), 4.13-4.23 (m) (**14-I** and/or **14-II**)]; ^{13}C NMR ($CDCl_3$) δ [13.96, 14.92, 44.25, 46.37, 57.26, 61.51, 116.66, 125.18 (q, *J*= 3.9 Hz), 127.23, 131.78, 135.02, 143.92 (q, *J*= 1.7 Hz), 172.06 (**14-I**)], [13.89, 14.39, 42.81 , 45.46, 57.54, 61.44, 124.20 (q, *J*= 271.6 Hz), 124.75 (q, *J*= 3.9 Hz), 126.46, 128.60, 128.66 (q, *J*= 32 Hz), 128.96, 129.50, 136.68, 141.70 (q, *J*= 1.6 Hz), 171.98 (**14-II**)]; IR (neat) 2983 m, 2937 m, 2910 m, 1733 s, 1616 m, 1463 m, 1444 m, 1367 m, 1326 s, 1257 s, 1164 s, 1124 s, 1068 s, 1018 m, 863 m, 829 w, 605 w; MS, *m*/*z* (relative intensity, %) [396 (M^+, 24), 323 (34), 322 (100), 277 (23), 250 (27), 249 (87), 165 (24) (**14-I**)], [396 (M^+, 19), 323 (24), 322 (100), 249 (71) (**14-II**)]; Exact Mass Calcd for $C_{21}H_{23}F_3O_4$: 396.1548. Found: [396.1524 (**14-I**)] and [396.1565 (**14-II**)]

Diethyl 2-(2-methyl-2-propenyl)-2-{3-[4-(methoxycarbonyl)phenyl]-2-propynyl}malonate (15).



Colorless oil; *Rf* 0.23 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.27 (t, *J*= 7.0 Hz, 6H), 1.70 (s, 3H), 2.90 (s, 1H), 3.07 (s, 1H), 3.91 (s, 3H), 4.17 (m, 4H), 4.89 (s, 1H), 4.94 (s, 1H), 7.42 (d, *J*= 8.6 Hz, 2H), 7.95 (d, *J*= 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.09, 23.33, 23.64, 39.70, 52.16, 56.57, 61.67, 83.05, 88.20, 116.19, 127.88, 129.14, 129.25, 131.36, 139.83, 166.31, 169.92; IR (neat) 2981 s, 2908 m, 1725 s, 1644 m, 1606 m, 1560 w, 1506 w, 1438 s, 1403 m, 1369 m, 1276 s, 1241 s, 1205 s, 1184 s, 1108 s, 1074 s, 904 m, 860 m, 769 m, 696 m, 557 w, 532 w; MS, *m*/*z* (relative intensity, %) 386 (M^+, 6), 355 (15), 313 (22), 312 (55), 285 (21), 283 (49), 281 (62), 280 (25), 267 (36), 253 (28), 239 (100), 207 (23), 181 (26), 180 (34), 179 (30), 173 (29), 165 (30), 163 (48), 149 (47); Exact Mass Calcd for $C_{22}H_{26}O_6$: 386.1729. Found: 386.1723.

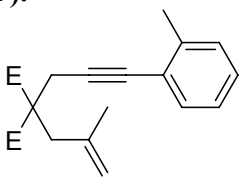
Diethyl 4-methyl-3-{1-[4-(methoxycarbonyl)phenyl]ethenyl}-3-cyclopentene-1,1-dicarboxylate (16-I) and (*Z*)-Diethyl 4-methyl-3-{2-[4-(methoxycarbonyl)phenyl]ethenyl}-3-cyclopentene-1,1-dicarboxylate (16-II).



^{1}H and ^{13}C NMR were obtained from a 13:87 mixture of **16-I** and **16-II**. Colorless oil; *Rf* 0.23 (hexane/EtOAc = 5/1); ^{1}H

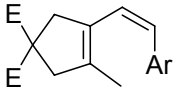
NMR ($CDCl_3$) δ [1.52 (s), 3.10 (s), 3.91 (s), 5.20 (s), 5.51 (s) (**16-I**)], [1.60 (s, 3H), 2.89 (s, 2H), 2.97 (s, 2H), 3.91 (s, 3H), 6.24 (d, *J*= 12.4 Hz, 1H), 6.49 (d, *J*= 12.4 Hz, 1H), 7.30 (d, *J*= 8.0 Hz, 2H), 7.95 (d, *J*= 8.0 Hz, 2H) (**16-II**)], [1.19-1.28 (m), 4.13-4.25 (m) (**16-I** and/or **16-II**)]; ^{13}C NMR ($CDCl_3$) δ [14.13, 15.13, 44.36, 46.46, 52.11, 57.30, 61.58, 116.57, 126.86, 128.19, 129.29, 131.74, 134.80, 143.93, 144.90, 166.80, 171.96 (**16-I**)], [14.08, 14.60, 42.87, 45.59, 52.06, 57.64, 61.52, 126.28, 128.62, 128.96, 129.10, 129.51, 129.56, 136.58, 142.77, 166.83, 171.87 (**16-II**)]; IR (neat) 2981 m, 2952 m, 2908 m, 1725 s, 1606 m, 1436 m, 1388 w, 1367 m, 1280 s, 1255 s, 1182 s, 1110 m, 1070 m, 1018 m, 968 w, 863 m, 781 m, 703 w; MS, *m*/*z* (relative intensity, %) [386 (M^+, 81), 313 (44), 312 (76), 281 (85), 280 (34), 267 (30), 253 (26), 240 (27), 239 (100), 207 (21), 181 (20), 180 (34), 179 (33), 165 (58), 149 (58), 105 (21) (**16-I**)], [386 (M^+, 32), 313 (26), 312 (100), 239 (35), 179 (29), 165 (25) (**16-II**)]; Exact Mass Calcd for $C_{22}H_{26}O_6$: 386.1729. Found: [386.1733 (**16-I**)] and [386.1744 (**16-II**)].

Diethyl 2-(2-methyl-2-propenyl)-2-[3-(2-methylphenyl)-2-propynyl]malonate (17).



Colorless oil; *Rf* 0.43 (hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$) δ 1.27 (t, *J*= 7.3 Hz, 6H), 1.72 (s, 3H), 2.39 (s, 3H), 2.92 (s, 2H), 3.11 (s, 2H), 4.16-4.28 (m, 4H), 4.90 (brs, 1H), 4.93 (brs, 1H), 7.08-7.19 (m, 3H), 7.34 (d, *J*= 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.54, 21.25, 23.87, 24.21, 40.03, 57.19, 62.00, 82.94, 88.99, 116.49, 123.44, 125.72, 128.19, 129.61, 132.32, 140.30, 140.43, 170.47; IR (neat) 3073 m, 2981 s, 2937 m, 1735 s, 1644 m, 1484 m, 1450 m, 1369 m, 1326 m, 1297 s, 1274 s, 1205 s, 1184 s, 1095 m, 1074 s, 1020 m, 902 m, 862 m, 759 s, 715 w, 553 w; MS, *m*/*z* (relative intensity, %) 342 (M^+, 1), 269 (27), 268 (27), 239 (44), 223 (24), 195 (98), 180 (26), 179 (24), 165 (20), 129 (28), 128 (53), 127 (23), 119 (27), 115 (34), 105 (100); Exact Mass Calcd for $C_{21}H_{26}O_4$: 342.1831. Found: 342.1835.

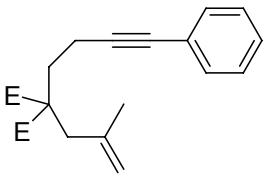
(*Z*)-Diethyl 4-methyl-3-[2-(2-methylphenyl)ethenyl]-3-cyclopentene-1,1-dicarboxylate (18).



Ar = 2-MeC_6H_4

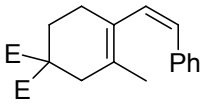
Colorless oil; *Rf* 0.29 (hexane/EtOAc = 5/1); ^1H NMR ($CDCl_3$) δ 1.18 (t, *J*= 7.1 Hz, 6H), 1.69 (s, 3H), 2.25 (s, 3H), 2.64 (s, 2H), 2.93 (s, 2H), 4.12 (q, *J*= 7.1 Hz, 4H), 6.31 (d, *J*= 12.2 Hz, 1H), 6.47 (d, *J*= 12.2 Hz, 1H), 7.07-7.14 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.36, 14.48, 20.41, 42.87, 45.86, 58.01, 61.69, 124.87, 125.45, 127.52, 129.14, 129.75, 129.84, 130.65, 136.37, 136.65, 138.19, 172.53; IR (neat) 2981 m, 2935 w, 2908 w, 1733 s, 1446 w, 1253 s, 1184 m, 1118 w, 1097 w, 1072 m, 1020 w, 862 w, 744 w; MS, *m*/*z* (relative intensity, %) 342 (M^+, 49), 269 (22), 268 (81), 195 (100), 194 (25), 179 (27), 165 (24); Exact Mass Calcd for $C_{20}H_{26}O_6$: 342.1831. Found: 342.1836.

Diethyl 2-(2-methyl-2-propenyl)-2-(4-phenyl-3-butynyl)malonate (19).



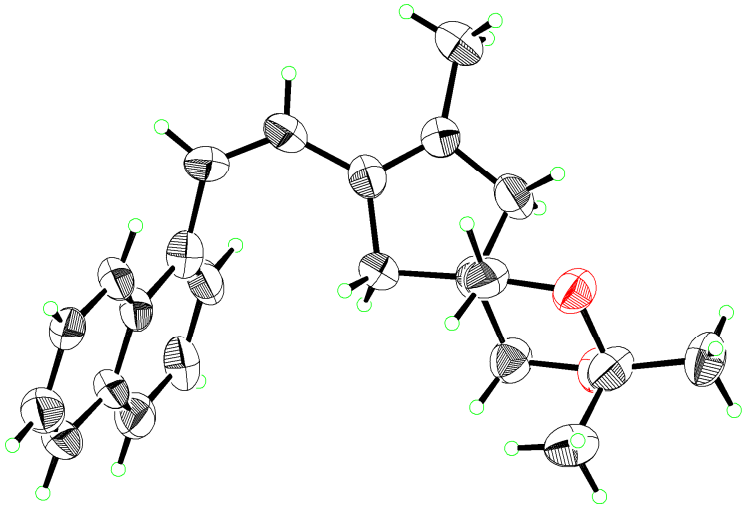
Colorless oil; *Rf* 0.31 (hexane/EtOAc = 3/1); ^1H NMR ($CDCl_3$) δ 1.26 (t, *J*= 7.0 Hz, 6H), 1.69 (s, 3H), 2.22-2.90 (m, 2H), 2.36-2.43 (m, 2H), 2.77 (s, 2H), 4.19 (q, *J*= 7.0 Hz, 4H), 4.79 (s, 1H), 4.90 (s, 1H), 7.28-7.29 (m, 3H), 7.38-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.10, 15.07, 23.26, 31.67, 40.47, 56.41, 61.41, 80.82, 88.86, 115.76, 123.61, 127.53, 128.06, 131.40, 140.25, 170.97; IR (neat) 3075 w, 2981 m, 2908 m, 1731 s, 1490 m, 1444 m, 1369 m, 1299 m, 1263 m, 1234 m, 1199 s, 1184 s, 1089 m, 1070 m, 1024 m, 902 m, 863 w, 757 m, 694 m; MS, *m*/*z* (relative intensity, %) 342 (M^+, 0.8), 214 (41), 195 (23), 128 (30), 122 (100), 115 (34); Exact Mass Calcd for $C_{21}H_{26}O_4$: 342.1831. Found: 342.1827.

(*Z*)-Diethyl 3-methyl-4-(2-phenylethenyl)-3-cyclohexene-1,1-dicarboxylate (20).



Colorless oil; *Rf* 0.43 (hexane/EtOAc = 5/1); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, *J*= 7.0 Hz, 6H), 1.58 (s, 3H), 2.08-2.15 (m, 4H), 2.51 (s, 2H), 4.20 (q, *J*= 7.0 Hz, 4H), 6.05 (d, *J*= 11.9 Hz, 1H), 6.34 (d, *J*= 11.9 Hz, 1H), 7.23-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.14, 20.11, 25.55, 27.73, 36.22, 53.52, 61.26, 126.73, 126.98, 127.21, 128.00, 128.24, 129.34, 130.46, 137.62, 171.39; IR (neat) 2981 s, 2935 m, 2906 m, 1731 s, 1492 m, 1446 m, 1388 m, 1367 m, 1326 m, 1295 s, 1253 s, 1174 s, 1116 s, 1083 s, 1045 m, 1024 m, 860 w, 781 m, 696 m; MS, *m*/*z* (relative intensity, %) 342 (M^+, 30), 269 (25), 268 (100), 195 (29), 91 (25); Exact Mass Calcd for $C_{21}H_{26}O_4$: 342.1831. Found: 342.1832.

X-ray Crystallographic Structure Analysis.



ORTEP drawing of **8**. The atoms are drawn as 25% probability ellipsoids. Four crystallographically independent molecules are observed in the unit cell. Other independent molecules were omitted for clarify.

X-ray crystallography was performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54187 Å). The data were collected at 298 K using ω scan in the θ range of 3.4–71.59 deg. The structure of **8** was solved by SHELXL97 program. [1] All H atoms were located at ideal positions and refined as riding on their parent atoms with U_{iso} (H) = 1.2–1.5 U_{eq} (C) and with C–H = 0.93 Å for **8**.

Crystal data for 8 (CCDC 678098)**:** $C_{23}H_{26}O_2$, M = 334.44, colorless platelet, monoclinic, space group $P2_1$ / c (#14), a = 11.0122 (8) Å, b = 42.512 (3) Å, c = 16.7649 (12) Å, α = 90 °, β = 101.821 (3)°, γ = 90 °, V = 7682.1 (9) Å^3, T = 298 K, Z = 16, D_c = 1.157 g cm^{-1}, μ = 0.561 cm^{-1}, crystal dimensions 0.08 × 0.07 × 0.02 mm^3, 120789 reflections collected, 14755 unique (R_{int} = 0.258) which were used in all calculations. R_1 = 0.125, wR_2 = 0.255for $I > 2\sigma$ (I), R_1 = 0.424, wR_2 = 0.424, $GOOF$ = 0.85 for all data.

1) Sheldrick, G. M. *SHELXL97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.