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SUPPORTING INFORMATION

Title: Intramolecular Heck Couplings and Cycloisomerizations of Bromodienes and Enynes with 1',1'-Disubstituted Methylenecyclopropane Terminators: Efficient Syntheses of [3]Dendralenes

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1-Chloro-1-(2'-propenyl)cyclopropane (8-Cl): A solution of 15.6 g (200 mmol) of DMSO in 250 mL of THF was treated with 4.00 g (100 mmol) of NaH (60% in mineral oil) and the mixture heated under reflux for 1 h, then cooled to 0 °C, treated with 35.7 g (100 mmol) of methyl-triphenylphosphonium bromide and stirred at room temp for 30 min. After addition of 11.9 g (100 mmol) of 1-acetyl-1-chlorocyclopropane (**7**-Cl) the mixture was heated under reflux for 1 h and after cooling to room temp. treated with 400 mL of water. The reaction mixture was extracted with pentane (3 × 100 mL), the combined organic phases were washed with water (3 × 100 mL) and saturated NaCl-solution and dried ($MgSO_4$). The solvent was distilled off through a 50 cm Vigreux column. Distillation of the residue gave 10.3 g (88%) of **8**-Cl as a colorless liquid, b.p. 93.5 °C. – IR (film): nu(tilde) = 3089 cm^{-1} (C=CH_2), 3033 (cPr–H), 2866, 1685, 1648 (C=C), 1141, 1027, 909, 792, 563. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.07 (m, 2 H, cPr-H), 1.10–1.27 (m, 2 H, cPr-H), 1.85 (s, 3 H, 3'-H), 4.84 (d, ^2J = 1.6 Hz, 1 H, 1'-H), 5.02 (d, ^2J = 1.6 Hz, 1 H, 1'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 19.7 (+, C-3'), 25.5 [–, C-2(3)], 45.6 (C_{quat}, C-1), 112.7 (–, C-1'), 144.6 (C_{quat}, C-2').

Dimethyl (2'-Cyclopropylidenepropyl)-(2''-bromoprop-2''-enyl)malonate (9): According to GP 1, 800 mg (6.86 mmol) of the alkene **8**-Cl, 1.80 g (7.17 mmol) of dimethyl 2'-bromoprop-2'-enylmalonate, 170 mg (7.08 mmol) of sodium hydride, 16.0 mg (37.5 μmol) of dppb and 19.7 mg (34.3 μmol, 0.5 mol%) of $Pd(dba)_2$ were stirred at 25 °C for 12 h. Work-up and chromatography on silica gel (column 5 × 20 cm, light petroleum/ether 20 : 1) yielded 1.34 g (59%) of **9** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.9–1.25 (m, 4 H, cPr-H), 1.80 (s, 3 H, 3'-H), 2.80 (s, 2 H, 1'-H), 3.18 (s, 2 H, 1''-H), 3.72 (s, 6 H, CH_3O), 5.6–5.7 (m, 2 H, 3''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.0 (–, cPr-C), 2.9 (–, cPr-C), 21.3 (+, C-3'), 34.3 (–, C-1''), 43.1 (–, C-1'), 52.6 (+, CH_3O), 57.3 (C_{quat}, C-1), 119.5 (C_{quat}, cPr-C), 121.8 (–, C-3''), 126.8 (C_{quat}, C-2'*), 127.2 (C_{quat}, *C*=CH_2*), 170.7 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 332/330 (1/1) [M^+], 251 (18) [M^+ – Br], 191 (21) [M^+ – CO_2Me – HBr], 131 (100) [M^+ – 2 CO_2Me – 2 H – Br].

Dimethyl (2'-Cyclopropylidenepropyl)(prop-2''-ynyl)malonate (10-H**):** According to GP 1, 583 mg (5.00 mmol) of the alkene **8**-Cl, 851 mg (5.00 mmol) of dimethyl propargylmalonate, 200 mg (5.00 mmol) of sodium hydride (60% in mineral oil), 47.0 mg (110 μmol) of dppb and 57.5 mg (100 μmol, 2 mol%) of $Pd(dba)_2$ were heated at 66 °C for 1 h. Work-up and chromatography on silica gel (column 2 × 20 cm, petroleum ether/ether 20 : 1) yielded 910 mg (73%) of **10**-H as a colorless oil. The spectroscopic data were identical with those reported in the literature.[11b]

Dimethyl (2'-Cyclopropylidenepropyl)malonate (11): According to GP 1, 4.00 g (34.3 mmol) of the alkene **8**-Cl, 5.95 g (45.0 mmol) of dimethyl malonate, 1.80 g (45.0 mmol) of sodium hydride (60% in mineral oil), 16.0 mg (37.5 μmol) of dppb and 19.7 mg (34.3 μmol, 0.1 mol%) of $Pd(dba)_2$ were heated at 66 °C for 12 h. Work-up and chromatography on silica gel (column 5 × 20 cm, petroleum ether/ether 20 : 1) yielded 3.06 g (42%) of **11** as a colorless oil. The spectroscopic data were identical with those reported in the literature.[11b]

Ethyl 4-Cyclopropylidenepentanoate (13): A solution of 4.64 g (10.0 mmol) of 3-bromopropyltriphenylphosphonium bromide in 50 mL of benzene was treated with 2.47 g (22.0 mmol) of KO*t*Bu, and the mixture was stirred at 70 °C for 2 h. To the suspension was added 1.44 g (10.0 mmol) of ethyl 4-oxopentanoate (**12**) in 10 mL of benzene within 10 min, and the mixture was stirred at 70 °C for an additional 4 h. After cooling to ambient temp., the mixture was added to 200 mL of pentane, treated with 10 g of Celite and filtered. After removal of the solvents in a rotatory evaporator, the

residue was subjected to chromatography on 50 g of silica gel, eluting with light petroleum → light petroleum/ether 10 : 1.

Fraction I: triphenylphosphane; R_f = 0.5 (light petroleum).

Fraction II: 958 mg (57%) of **13** as a colorless oil, R_f = 0.3 (light petroleum/ether 10 : 1). – IR (film): nu(tilde) = 2978 cm^{-1}, 2912, 1735, 1447, 1419, 1373, 1256, 1177, 1037, 995, 702, 668. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.83–0.95 (m, 2 H, cPr-H), 0.93–1.10 (m, 2 H, cPr-H), 1.23 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.77–1.81 (m, 3 H, 5-H), 2.40–2.58 (m, 4 H, 2-H, 3-H), 4.10 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.0 (–, cPr-C), 3.2 (–, cPr-C), 14.2 (+, OCH_2CH_3), 20.9 (+, CH_3), 31.7 (–, CH_2), 32.5 (–, CH_2), 60.2 (–, OCH_2CH_3), 115.7 (C_{quat}, cPr-C), 122.6 (C_{quat}, C-4), 173.7 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 292 (3) [M^+], 218 (27) [$M^+ – C_2H_5OH – C_2H_4$], 207 (76), 198 (38), 161 (63), 145 (69), 91 (61), 79 (100) [$C_6H_7^+$]. – Elemental analysis calcd (%) for $C_{10}H_{13}O_2$ (168.12): C 71.39, H 9.59; found C 71.10, H 9.79.

Ethyl 4-Bromo-2-(2'-cyclopropylidenepropyl)pent-4-enoate (14): A solution of 565 mg (4.00 mmol) of 2,2,6,6-tetramethylpiperidine (TMP) in 10 mL of THF and 2 mL of DMPU was treated at −78 °C with 2.5 mL (1.6 M in hexane, 4 mmol) of *n*BuLi, and stirred for 10 min. Then 336 mg (2.00 mmol) of the ester **13** and 1.00 g (5.00 mmol) of 2,3-dibromopropene were added, and the mixture stirred for another 145 min. The cooled suspension was treated with 5 mL of saturated NH_4Cl solution, and after warming back to room temp. aqueous work-up followed. Chromatography on silica gel (column 2 × 20 cm, light petroleum/ether 40 : 1) gave 500 mg (87%) of **14**. – IR (KBr): nu(tilde) = 3047 cm^{-1}, 2977, 2933, 2910, 1735 (C=O), 1629 (C=C), 1445, 1413, 1375, 1353, 1306, 1247, 1221, 1179, 1113, 1046, 1029, 972, 891, 855, 789, 759, 734, 665, 531. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.90–1.20 (m, 4 H, cPr-H), 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.83 (t, ^4J = 1.6 Hz, 3 H, 3'-H), 2.32 (dd, ^2J = 13.8, ^3J = 6.2 Hz, 1 H, 2'-H_A), 2.45–2.60 (m, 2 H, 3-H_A, 2'-H_B), 2.75 (ddd, ^2J = 14.6, ^3J = 9.0, ^4J = 0.8 Hz, 1 H, 3-H_B), 2.98–3.12 (m_c, 1 H, 2-H), 4.07 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 5.42 (d, ^2J = 1.7 Hz, 1 H, 5-H), 5.60 (d, ^2J = 1.7 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.0 (–, cPr-C), 3.0 (–, cPr-C), 14.2 (+, OCH_2CH_3), 20.4 (+, CH_3), 38.7 (–, CH_2), 42.3 (+, CH), 43.3 (–, CH_2), 60.4 (–, OCH_2CH_3), 118.3 (C_{quat}, cPr-C), 118.5 (–, C-5), 120.8 (C_{quat}, C-2'), 131.4 (C_{quat}, C-4), 174.7 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 273/271 (3/3) [$M^+ – CH_3$], 243/241 (7/6) [$M^+ – C_2H_5O$], 215/213 (6/7) [$M^+ – C_2H_5O_2C$], 133 (71) [$M^+ – C_2H_5O_2C – HBr$], 91 (100), 77 (61) [$C_6H_5^+$]. – Elemental analysis calcd (%) for $C_{13}H_{19}BrO_2$ (287.2): C 54.37, H 6.67; found C 54.28, H 6.53.

Ethyl 2-(2-Cyclopropylidenepropyl)pentynoate (15): To a solution of 1.153 g (8.16 mmol) of 2,2,6,6-tetramethylpiperidine (TMP) in 20 mL of THF and 4 mL of DMPU was added at –78 °C 3.26 mL (2.5 M solution in hexane, 8.16 mmol) of *n*BuLi, and the mixture stirred for 10 min at this temperature. Then 686 mg (4.08 mmol) of the ester **13** and 607 mg (5.10 mmol) of 2,3-dibromopropene were added at –78 °C, and the mixture stirred at this temperature for an additional 145 min. To the rapidly stirred cold suspension was added 10 mL of saturated NH_4Cl solution, and after warming to room temp., aqueous work-up as usual [addition of 20 mL of H_2O, extraction with Et_2O (2 × 20 mL), drying over $MgSO_4$] followed. Chromatography of the residue after evaporation of the solvents on 40 g of silica gel (column 2 × 20 cm, pentane/ether 30 : 1) gave 590 mg (70%) of **15**, R_f = 0.27. – IR (film): nu(tilde) = 3297 cm^{-1}, 2978, 2913, 2121, 1734, 1446, 1375, 1177, 1047, 1029, 855, 641. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.85–1.10 (m, 4 H, cPr-H), 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.79 (m_c, 3 H, 3'-H), 1.96 (t, ^4J = 2.7 Hz, 1 H, 5-H), 2.32–2.60 (m, 4 H, 3-H, 1'-H), 2.79–2.94 (m, 1 H, 2-H), 4.11 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.9 (–, cPr-C), 3.1 (–, cPr-C), 14.2 (+, OCH_2CH_3), 20.6 (+, CH_3), 20.8 (–, CH_2), 30.3 (–, CH_2), 42.8 (+, CH), 60.5 (–, OCH_2CH_3), 69.6 (C_{quat}, C-4), 80.5(+, CH), 118.2 (C_{quat}, cPr-C), 120.9 (C_{quat}, C-2'), 174.4 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 206 (1), 191 (6), 177 (8), 163 (8), 161 (8), 133 (100), 131 (28), 117 (88), 105 (66), 93 (79), 91 (95), 79 (48), 77 (51), 67 (34), 65 (20), 55 (26), 53 (28), 43 (26), 41 (62). – Elemental analysis calcd (%) for $C_{13}H_{18}O_2$ (206.28): C 75.69, H 8.80; found C 75.82, H 8.60.

Ethyl 1-Acetylcyclopropanecarboxylate (17): A mixture of 130 g (1.00 mol) of ethyl acetoacetate (**16**), 282 g (1.50 mol) of 1,2-dibromoethane and 553 g (4.00 mol) of K_2CO_3 in 1.2 L of DMSO was stirred at ambient temp. for 24 h, then added to 2 L of water and extracted with diethyl ether (5 × 300 mL). The combined organic phases were washed with water (5 × 300 mL), once with 300 mL of brine and dried ($MgSO_4$). After removal of the solvents in a rotatory evaporator, distillation under reduced pressure yielded 107 g (69%) of **17**, b.p. 125 °C (100 Torr). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.40 (s, 4 H, cPr-H), 2.40 (s, 3 H, $COCH_3$), 4.13 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 13.9 (+, OCH_2CH_3), 18.9 [–, C-2(3)], 29.7 (+, CH_3CO), 34.9 (C_{quat}, C-1), 61.1 (–, OCH_2CH_3), 170.8 (C_{quat}, CO_2), 202.9 (C_{quat}, $COCH_3$).

Ethyl 1-(1'-Cyclopropylideneethyl)cyclopropanecarboxylate (18): a) A suspension of 23.2 g (50.0 mmol) of 3-bromopropyltriphenylphosphonium bromide and 16.8 g (150 mmol) of KO*t*Bu in 100 mL of toluene was stirred at 70 °C for 2 h. A solution of 7.81 g (50.0 mmol) of the ester **17** in

10 mL of toluene was added dropwise, and the mixture was stirred for an additional 24 h. After being cooled to room temp., 10 g of Celite and 200 mL of pentane were added. After filtration, vacuum distillation at 0.1 Torr yielded 5.0 g of a colorless oil. Chromatography on silica gel (column 3 × 20 cm, light petroleum/ether 10 : 1) furnished 2.0 g (22%) of **18** as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.8–0.95 (m, 2 H, cPr-H), 0.97–1.02 (m, 4 H, cPr-H), 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.28–1.32 (m, 2 H, cPr-H), 1.92 (s, 3 H, 2'-H), 4.05 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.6 (–, cPr-C), 3.4 (–, cPr-C), 14.0 (+, OCH_2CH_3), 16.0 (–, cPr-C), 20.4 (+, C-2'), 22.6 (–, cPr-C), 29.0 (C_{quat}, C-1), 60.43 (–, OCH_2CH_3), 119.8 (C_{quat}, C=C), 122.3 (C_{quat}, C=C), 174.5 (C_{quat}, CO_2).

b) A suspension of 46.4 g (100 mmol) of 3-bromopropyltriphenylphosphonium bromide and 33.7 g (300 mmol) of KO*t*Bu in 250 mL of benzene was stirred at 70 °C for 2 h. A solution of 7.81 g (50.0 mmol) of the ester **17** in 10 mL of benzene was added dropwise, and the mixture was stirred for an additional 12 h. After being cooled to room temp., 10 g of Celite and 200 mL of pentane were added. Filtration and vacuum distillation at 0.1 Torr yielded 5.0 g of a colorless oil. Chromatography on silica gel (column 3 × 20 cm, light petroleum/ether 10 : 1) furnished 2.0 g (22%) of **18** as a colorless oil.

c) A suspension of 23.2 g (50.0 mmol) of 3-bromopropyltriphenylphosphonium bromide and 12.3 g (110 mmol) of KO*t*Bu in 200 mL of benzene was stirred at 70 °C for 2 h. A solution of 7.81 g (50.0 mmol) of the ester **17** in 10 mL of benzene was added dropwise, and the mixture was stirred for an additional 12 h. After being cooled to room temp., 10 g of Celite and 200 mL of pentane were added. Filtration and removal of the solvents in a rotatory evaporator yielded 15.0 g of a colored oil. Chromatography on silica gel (column 6 × 30 cm, pentane → pentane/ether 10 : 1) gave 4.5 g (50%) of **18** as a colorless oil.

[1'-(1''-Cyclopropylideneethyl)cyclopropyl]methanol (19): To a solution of 400 mg (10.5 mmol) of lithium aluminum hydride in 50 mL of diethyl ether was added dropwise a solution of 3.00 g (16.6 mmol) of **18** in 10 mL of diethyl ether, and the mixture was heated under reflux for 1 h. After being cooled to room temp., this mixture was treated dropwise with 5% NaOH until a colorless precipitate occurred. This was filtered off, and the filtrate concentrated in a rotatory evaporator to yield 2.30 g (100%) of **19** as a colorless oil, which was not purified any further. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55–0.60 (m, 2 H, cPr-H), 0.72–0.80 (m, 2 H, cPr-H), 0.88–0.98 (m, 2 H, cPr-H), 1.40–1.50 (m, 2 H, cPr-H), 1.75 (bs, 1 H, OH), 1.82 (s, 3 H, 2''-H), 3.57 (bs, 2 H, 1-H). – MS (70 eV, EI), *m/z* (%): 138 (1.0) [M^+], 137 (1.3) [M^+ – H], 123 (25).

[1'-(1''-Cyclopropylideneethyl)cyclopropylmethyl](3'''-*tert*-butyldimethylsilylprop-2'''-ynyl) Ether (20-Si*t*BuMe$_2$): A two-phase system of 110 mg (796 μmol) of the alcohol **19**, 280 mg (4.99 mmol) of KOH, 410 mg (1.76 mmol) of 3-bromo-1-*tert*-butyldimethylsilylprop-1-yne and 131 mg (0.500 mmol) of tetrabutylammonium fluoride in 2 mL of water was stirred vigorously for 24 h. The solution was added to 3 mL each of water and ether and the aqueous phase extracted with diethyl ether (3 × 3 mL). The combined organic phases were washed with 2 mL of water and dried ($MgSO_4$). After removal of the solvents in a rotatory evaporator the residue was subjected to chromatography on silica gel (column 2 × 20 cm, pentane → pentane/ether 10 : 1) to give 167 mg (72%) of **20**-Si*t*BuMe$_2$ as a colorless oil, R_f = 0.4 (pentane/ether 20 : 1). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.10 [s, 6 H, $(CH_3)_2Si$], 0.95 [s, 9 H, $(CH_3)_3CSi$], 1.1–1.85 (m, 11 H, cPr-H, CH_3), 3.4–3.65 (m, 2 H, C-1), 3.91 (s, 2 H, C-1').

[1'-(1''-Cyclopropylideneethyl)cyclopropylmethyl](prop-2'''-ynyl) Ether (20-H): Variant 1, from **20**-Si*t*BuMe$_2$: To a solution of 166 mg (0.571 mmol) of the ether **20**-Si*t*BuMe$_2$ in 10 mL of THF was added 300 mg (0.951 mmol) of tetrabutylammoniumfluoride trihydrate, and the mixture stirred for 2 h. The dark colored mixture was added to 20 mL of water and extracted with pentane (5 × 10 mL). The combined organic phases were washed twice with 10 mL each of water and brine. After removal of the solvents in a rotatory evaporator, the residue was subjected to chromatography on silica gel (column 2 × 20 cm, pentane/ether 20 : 1) to give 93 mg (92%) of of **20**-H as a colorless oil.

Variant 2, from **19**: A two-phase system of 691 mg (5.00 mmol) of the alcohol **19**, 1.40 g (25.0 mmol) of KOH, 3.00 g (25.2 mmol) of propargyl bromide and 278 mg (1.00 mmol) of tetrabutylammonium chloride in 5 mL of water was stirred vigorously for 24 h. The mixture was added to 10 mL each of water and ether, the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic phases were washed with 10 mL of water and dried ($MgSO_4$). After removal of the solvents in a rotatory evaporator, the residue was subjected to chromatography on silica gel (pentane → pentane/ether 10 : 1) to give 630 mg (71%) of **20**-H as a colorless oil, R_f = 0.3 (pentane/ether 50 : 1). – IR (film): nu(tilde) = 3102 cm^{-1}, 2120 (C≡C), 1770, 1190, 700. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.55–0.60 (m, 2 H, cPr-H), 0.72–0.80 (m, 2 H, cPr-H), 0.88–0.98 (m, 2 H, cPr-H), 1.40–1.50 (m, 2 H, cPr-H), 1.85 (s, 3 H, 2''-H), 2.35 (t, ^4J = 1.4 Hz, 1 H, 3'''-H), 3.57 (bs, 2 H, 1-H), 4.17 (d, ^4J = 1.4 Hz, 2 H, 1'''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.2 (–, cPr-C), 4.1 (–, cPr-C), 19.0 (+, C-2''), 22.6 (–, cPr-C), 24.9 (C_{quat}, C-1'), 57.3 (–, C-1), 74.0 (C_{quat}, C-2'''), 75.0 (–, C-1'''), 79.9 (+, C-3'''), 116.9 (C_{quat}, C=C), 124.2 (C_{quat}, C=C). – MS (70 eV, EI), *m/z* (%): 176 (1) [M^+], 105 (100), 91 (99), 79 (82), 41 (52).

2-Bromohex-1-en-5-one (21): A solution of 6.80 g (34.0 mmol) of 2,3-dibromopropene in 5 mL of anhydrous diethyl ether was added dropwise to a suspension of ethyl sodioacetoacetate, prepared from 782 mg (34.0 mmol) of sodium and 4.42 g (34.0 mmol) of ethyl acetoaacetate (**16**) in 11 mL of anhydrous ethanol, keeping the temperature under 30 °C. After 24 h at room temp. the suspension was filtered and the solvent removed in a rotatory evaporator. The residue was purified by chromatography on silica gel (column 2 × 20 cm, pentane/ether 50 : 1) to yield 5.50 g (68%) of ethyl 2-acetyl-4-bromopent-4-enoate as a colorless oil. – IR (film): nu(tilde) = 2979 cm^{-1}, 2925, 1740 (C=O), 1717 (C=O), 1653 (C=C), 1024, 967, 745, 567. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.2 Hz, 3 H, OCH_2CH_3), 2.25 (s, 3 H, CH_3CO), 2.85 (d, ^3J = 7.0 Hz, 2 H, CH_2), 3.85 (t, ^3J = 7.0 Hz, 1 H, CH), 4.15 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH_3), 5.40 (s, 1 H, $C=CH_2$), 5.55 (s, 1 H, $C=CH_2$). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 13.9 (+, OCH_2CH_3), 29.5 (+, CH_3CO), 39.3 (–, CH_2), 57.6 (+, CH), 61.5 (–, OCH_2CH_3), 119.5 (–, CH_2=C), 129.7 (C_{quat}, C=CH_2), 168.1 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 250/248 (1/1) [M^+], 169 (75) [M^+ – Br], 43 (100) [CH_3CO^+].

A solution of 5.36 g (21.5 mmol) of ethyl 2-acetyl-4-bromopent-4-enoate in 25 mL of 5% aq. sodium hydroxide [1.25 g (31.3 mmol) NaOH in 25 mL of water] was stirred at ambient temp. for 12 h and then heated under reflux for 3 h to complete carbon dioxide removal. After cooling to room temp., the aqueous phase was extracted with diethyl ether (3 × 50 mL), the combined organic phases were dried and the solvents removed in a rotatory evaporator to yield 3.50 g (92%) of **21** as a yellowish oil which was used without further purification. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, 6-H), 2.55 (bs, 4 H, 3-H, 4-H), 5.35 (s, 1 H, 1-H), 5.05 (s, 1 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 29.9 (+, C-6), 35.5 (–, C-4), 47.2 (–, C-3), 117.3 (–, C-1), 132.7 (C_{quat}, C-2), 206.4 (C_{quat}, C-5).

5-Cyclopropylidene-2-bromohexene (22): Under an atmosphere of nitrogen 7.70 g (160 mmol) of sodium hydride (50% in mineral oil) was washed three times with pentane, before 37.1 g (79.9 mmol) of 3-bromopropyltriphenylphosphonium bromide in 150 mL of anhydrous THF was added. The mixture was heated at 66 °C, treated with 0.5 mL of ethanol and stirred at this temperature for 4 h. After slow addition of 14.2 g (80.2 mmol) of ketone **21** the mixture was stirred for an additional 12 h and then cooled to room temp. To this mixture was added 200 mL of pentane, the precipitate was collected on a filter, and the filtrate was concentrated under reduced pressure. The remaining suspension was taken up in pentane, filtered, the filtrate concentrated and subjected to chromatography on silica gel (column 4 × 20 cm, pentane) to yield 8.85 g (55%) of **22** as a

colorless liquid containing approx. 5% of 1-(2'-bromoprop-2'-enyl)-1-(1''-methylethenyl)-cyclopropane (**47**); R_f = 0.8, b.p. 100 °C (20 Torr). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.25 (m_c, 4 H, cPr-H), 1.88 (s, 3 H, 6-H), 2.45 (t, ^3J = 7.2 Hz, 2 H, 4-H), 2.65 (t, ^3J = 7.2 Hz, 2 H, 3-H), 5.40 (d, ^2J = 1.3 Hz, 1 H, 1-H), 5.80 (d, ^2J = 1.3 Hz, 1 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.4 (–, cPr-C), 3.1 (–, cPr-C), 20.7 (+, C-6), 35.2 (–, C-4), 39.6 (–, C-3), 116.1 (–, C-1), 116.5 (C_{quat}, cPr-C), 122.3 (C_{quat}, C-5), 134.6 (C_{quat}, C-2). – MS (70 eV, EI), *m/z* (%): 202/200 (0.1/0.1) [M^+], 174/172 (16/16) [$M^+ – C_2H_4$], 121 (60) [M^+ – Br], 93 (68) [$M^+ – Br – C_2H_4$], 79 (100) [$M^+ – Br – C_3H_6$].

Hex-1-yn-5-one (23-H): a) Two-Step Variant: A solution of 39.3 g (330 mmol) of propargyl bromide in 20 mL of anhydrous ethanol was added dropwise with stirring to a suspension of ethyl sodioacetoacetate prepared from 7.30 g (318 mmol) of sodium and 43.0 g (330 mmol) of ethyl acetoacetate (**16**) in 100 mL of anhydrous ethanol, keeping the temperature under 30 °C. After having been stirred for 24 h at ambient temp. the suspension was filtered and the solvent removed in a rotatory evaporator. The residue was washed with 50 mL each of water and ether, and the aqueous phase extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed twice with 15 mL each of saturated NaCl solution, dried ($MgSO_4$) and fractionated.

Fraction I: Mixture of 6.0 g of ethyl acetoacetate and 6.0 g (11%) of ethyl 2-acetylpent-4-ynoate, b.p. 120–130 °C (40 Torr).

Fraction II: 26.5 g (48%) of ethyl 2-acetylpent-4-ynoate as a colorless liquid, b.p. 135–145 °C/40 Torr. – IR (film): nu(tilde) = 3208 cm^{-1}, 3027, 2910, 1750–1717 (C=O, CO_2), 1650 (C=O), 1426, 1123, 1019, 856, 650, 547. – ^{1}H NMR (250 MHz, $CDCl_3$): (keto/enol-tautomer: keto/enol 5 : 1) keto form: δ = 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 2.30 (s, 3 H, CH_3CO), 2.68 (m, 2 H, 3-H), 2.94 (dd, ^4J = 2.5, ^4J = 5.6 Hz, 1 H, 5-H), 3.68 (t, ^3J = 7.5 Hz, 1 H, 2-H), 4.21 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (+, OCH_2CH_3), 17.4 (–, C-3), 29.4 (+, CH_3CO), 58.3 (+, C-2), 61.8 (–, OCH_2CH_3), 70.2 (C_{quat}, C-4), 80.4 (+, C-5), 168.0 (C_{quat}, CO_2), 200.9 (C_{quat}, $COCH_3$). – Enol form: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.62 [s, 3 H, $CH_3C(OH)C$], 2.68 (m, 2 H, 3-H), 2.94 (dd, ^4J = 2.5, ^4J = 5.6 Hz, 1 H, 5-H), 4.21 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 12.8 (s, 1 H, OH). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (+, OCH_2CH_3), 21.8 (–, C-3), 26.0 [+, $CH_3C(OH)C$], 62.3 (–, OCH_2CH_3), 71.8 (C_{quat}, C-4), 78.6 (+, C-5), 169.2 (C_{quat}, CO_2), 173.4 (C_{quat}, C=), 176.5 (C_{quat}, C=).

A solution of 6.10 g (36.3 mmol) of ethyl 2-acetylpent-4-ynoate in 28.8 mL (36.0 mmol) of 5% aq. sodium hydroxide was stirred at ambient temp. for 12 h and then heated under reflux for 6 h. Extraction with diethyl ether (3 × 50 mL), drying of the combined organic phases over $MgSO_4$ and

distillation over a 20 cm Vigreux column yielded 2.00 g (57%) of **23**-H as a colorless liquid, b.p. 142 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.94 (t, ^4J = 2.6 Hz, 1 H, 1-H), 2.17 (s, 3 H, 6-H), 2.44 (dt, ^3J = 7.2, ^4J = 2.6 Hz, 2 H, 3-H), 2.69 (t, ^3J = 7.2 Hz, 2 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 12.7 (–, C-3), 29.6 (+, C-6), 41.9 (–, C-4), 77.1 (C_{quat}, C-2), 82.8 (+, C-1), 206.0 (C_{quat}, C-5). – MS (70 eV, EI), *m/z* (%): 95 (100) [M^+ – H], 81 (77) [$M^+ – CH_3$], 53 (16) [$M^+ – CH_3CO$].

b) One-Step Variant: In a mixture of 176 g (1.35 mol) of ethyl acetoacetate and 300 mL of anhydrous ethanol 25.2 g (1.10 mol) of sodium was dissolved. Propargyl bromide (119 g, 1.0 mol) was added dropwise at 0 °C within 20 min. The mixture was stirred at ambient temp. for 3 h and then at 60 °C for 4 h. Then, the sodium bromide was filtered off, and the solvent removed under vacuum in a rotatory evaporator. To the residue was added 400 mL (1.00 mol) of 10% aq. sodium hydroxide, and the mixture was stirred at ambient temp. for 2 h and at 60 °C for 3 h. The mixture was cooled to ambient temperature acidified with conc. hydrochloric acid to a pH of 4 and extracted with diethyl ether (4 × 150 mL). The organic phase was washed with 300 mL each of saturated sodium hydrogen carbonate solution and water, then dried over $MgSO_4$. The ether was distilled off in a rotatory evaporator, and the residue fractionated over a 10 cm Vigreux column to yield 49.6 g (52%) of **23**-H as a colorless liquid, b.p. 65 °C (40 Torr).

In additional 15.1 g (0.09 mol, 9%) of ethyl 2-acetylpent-4-ynoate was recovered as a colorless liquid, b.p. 115 °C (40 Torr).

5-Cyclopropylidenehex-1-yne (24-H): a) Wittig Olefination of 23-H: A suspension of 9.30 g (20.0 mmol) of 3-bromopropyltriphenylphosphonium bromide and 6.72 g (59.9 mmol) of KO*t*Bu in 50 mL of benzene was stirred at 70 °C for 2 h. A solution of 1.92 g (20.0 mmol) of hex-1-yn-5-one (**23**-H) in 10 mL of benzene was added dropwise, and the mixture was stirred at 70 °C for an additional 3 h. After cooling down to ambient temperature, the mixture was added to a mixture of 1 mL of ethanol and 200 mL of pentane, then filtered. The solvent was distilled off over a 20 cm Vigreux column and the brown residue short-path distilled at 100 Torr to yield 200 mg (8%) of **24**-H, contaminated with benzene.

b) Wittig Olefination of 23-SiMe$_3$: Under a nitrogen atmosphere a mixture of 6.00 g (250 mmol) of sodium hydride and 46.4 g (100 mmol) of 3-bromopropyltriphenylphosphonium bromide in 150 mL of anhydrous THF was heated under reflux for 1 h. After dropwise addition of 0.5 mL of ethanol, the mixture was heated for 4 h, and 17.8 g (100 mmol) of **23**-$SiMe_3$ in 30 mL of anhydrous THF was added slowly. The reaction mixture was heated under reflux for 16 h. To the cooled mixture was added 50 g of Celite. The mixture was diluted with 700 mL of pentane, filtered and the residue washed with pentane. The solvent mixture was removed in a rotatory evaporator, and the

procedure was repeated twice. Distillation over a 10 cm Vigreux column yielded 4.80 g (42%) of **24**-H as a colorless liquid, b.p. 50 °C (20 Torr). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.16 (m_c, 4 H, cPr-H), 1.90 (t, ^4J = 1.6 Hz, 3 H, 6-H), 1.98 (t, ^4J = 1.2 Hz, 1 H, 1-H), 2.42–2.47 (m_c, 4 H, 3-H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.3 (–, cPr-C), 3.1 (–, cPr-C), 17.1 (–, C-3), 21.3 (+, C-6), 35.7 (–, C-4), 68.0 (+, C-1), 84.8 (C_{quat}, C-2), 116.5 (C_{quat}, cPr-C), 122.5 (C_{quat}, C-5).

2-Methyl-2-(but-3'-ynyl)-1,3-dioxolane (25-H): To a solution of 38.9 g (405 mmol) of hex-1-yn-5-one (**23**-H) and 29.8 g (480 mmol) of ethylene glycol in 100 mL of chloroform was added 100 mg (0.581 mmol) of *p*-toluenesulfonic acid. The flask was attached to a Dean-Stark trap, and the mixture was heated under reflux for 12 h, until no water could be recovered any more. After the mixture had cooled down, it was washed with 100 mL each of diluted NaOH solution and water, then dried over K_2CO_3. The solvent was distilled off, and the product fractionated from added solid K_2CO_3 over a 10 cm Vigreux column at 30 Torr to yield 47.7 g (84%) of **25**-H as a colorless liquid, b.p. 72 °C. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.89–1.95 (m, 3 H, CH_2, CH), 2.17–2.32 (m, 2 H, CH_2), 3.87–3.99 [m_c, 4 H, 4(5)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 13.3 (+, CH_3), 23.8 (–, C-1'), 38.0 (–, C-2'), 64.8 [–, C-4(5)], 67.9 (+, C-4'), 84.3 (C_{quat}, C-3'), 109.0 (C_{quat}, C-2). – MS (70 eV, EI), *m/z* (%): 125 (32) [$M^+ - CH_3$], 87 (100), 43 (42). – $C_8H_{12}O_2$ (140.2): calcd C 68.55, H 8.63; found C 68.51, H 8.81.

2-Methyl-2-(4'-trimethylsilylbut-3'-ynyl)-1,3-dioxolane (25-SiMe$_3$): To a solution of 47.7 g (340 mmol) of **25**-H in 400 mL of anhydrous ether, kept under an atmosphere of nitrogen at –60 °C, was added within 60 min 157 mL (370 mmol) of a 2.36 M *n*-butyllithium solution in hexane. After stirring for an additional 1 h, 44.5 g (410 mmol) of trimethylchlorosilane was added at the same temperature. The reaction mixture was slowly warmed to ambient temp. and 400 mL of saturated NH_4Cl solution was added. The aqueous phase was extracted with diethyl ether (4 × 150 mL), the combined organic phases were washed with 100 mL of brine and dried ($MgSO_4$). The solvent was removed in a rotatory evaporator, and the residue was fractionated over a 10 cm Vigreux column to yield 40.3 g (56%) of **25**-SiMe$_3$ as a colorless liquid, b.p. 92 °C (30 Torr). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 1.30 (s, 3 H, CH_3), 1.88 (t, ^3J = 8 Hz, 2 H, 1'-H), 2.30 (t, ^3J = 8 Hz, 2 H, 2'-H), 3.87–3.94 [m, 4 H, 4(5)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.1 [+, $Si(CH_3)_3$], 14.8 (+, CH_3), 23.8 (–, C-2'), 38.1 (–, C-1'), 64.7 [–, C-4(5)], 84.1 (C_{quat}, C-3'), 107.1 (C_{quat}, C-4'), 109.0 (C_{quat}, C-2). – MS (70 eV, EI), *m/z* (%): 197 (17) [$M^+ - CH_3$], 87 (100) [$H_3CC(O_2C_2H_4)^+$], 73 (16) [$(CH_3)_3Si^+$], 43 (23) [CH_3CO^+].

6-Trimethylsilylhex-5-yn-2-one (23-SiMe$_3$): To a suspension of 90 g of silica gel in 160 mL of dichloromethane was added 14 mL of a 10% (16 mmol) solution of oxalic acid, and the mixture was stirred until the aqueous phase had been absorbed completely by the silica gel. Then 30.0 g (141 mmol) of **25**-SiMe$_3$ was added, and the mixture stirred at ambient temp. for 5 h, then it was neutralized by addition of 3.0 g $NaHCO_3$. After 5 min the silica gel was filtered off and washed with dichloromethane (3 × 50 mL). The solvent was removed in a rotatory evaporator at ambient temp. and a pressure of 400 Torr. The residue was fractionated over a 10 cm Vigreux column to yield 18.1 g (76%) of **23**-SiMe$_3$ as a colorless liquid, b.p. 81 °C (25 Torr). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.17 [s, 9 H, Si(CH_3)$_3$], 2.15 (s, 3 H, 1-H), 2.31–2.82 (m, 4 H, 3-H, 4-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.1 [+, Si(CH_3)$_3$], 12.4 (–, C-4), 29.1 (+, C-1), 43.2 (–, C-3), 75.1 (C_{quat}, C-5), 84.6 (C_{quat}, C-6), 205.2 (C_{quat}, C-2).

Diethyl 3'-Oxobutylmalonate (27): A solution of sodium ethanolate in ethanol, prepared from 400 mg of sodium (17.4 mmol) and 50 mL of anhydrous ethanol, was treated with 48.0 g (300 mmol) of diethyl malonate and the mixture stirred for 10 min. After being cooled to 0 °C, 21.0 g (300 mmol) of freshly distilled butenone (**26**) in 130 mL of anhydrous ethanol was added dropwise within 3 h and the mixture stirred for an additional 12 h at ambient temp. After removal of the solvents by distillation at 60 °C through a 30 cm column packed with glass turnings, the residue was added to 100 mL of brine, the aqueous phase extracted with diethyl ether (3 × 100 mL) and the combined organic phases dried ($MgSO_4$). Distillation gave, besides of diethyl malonate 54.78 g (79%) of **27** as a colorless oil, b.p. 120 °C (0.01 Torr). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 6 H, CH_3), 2.13 (s, 3 H, 4'-H), 2.15 (dt, ^3J = 7.3 Hz, 2 H, CH_2), 2.53 (t, ^3J = 7.3 Hz, 2 H, CH_2), 3.38 (t, ^3J = 7.3 Hz, 1 H, CH), 4.45 (q, ^3J = 7.1 Hz, 4 H, CH_2O). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 13.7 (+, OCH_2CH_3), 22.1 (+, C-4'), 29.5 (–, C-1'*), 40.0 (–, C-2'*), 50.3 (+, C-1), 61.0 (–, OCH_2CH_3), 168.7 (C_{quat}, CO), 206.7 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 230 (21) [M^+], 185 (54) [$M^+ - C_2H_5O$], 160 (100) [$CH_2(CO_2C_2H_5)^+$], 139 (78). – Elemental analysis calcd (%) for $C_{11}H_{18}O_5$ (230.3): C 57.38, H 7.88; found C 57.58, H 7.60.

Diethyl (3'-Cyclopropylidenebutyl)(2''-propynyl)malonate (28-H): To a solution of 39.3 g (155 mmol) of the malonate **29** in 300 mL of anhydrous THF was added with stirring 3.6 g of NaH (60% in mineral oil), and the mixture was stirred, until the evolution of hydrogen ceased (~10 min), 21.3 ml (197 mmol) of propargyl bromide (80% in Toluene) was added, and the mixture was stirred for an additional 60 min. The mixture was washed with water (200 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed in a rotatory evaporator to give 29.3 g (65%) of **28**-H

as a light yellow oil. For subsequent reactions, aliquots of this crude product were purified by column chromatography on silica gel (petroleum ether/ether 10 : 1), R_f = 0.2. – IR (film): nu(tilde) = 3301 cm^{-1} (C≡C–H), 3024, 2852, 1773, 1734 (C=O), 1447, 1369, 1269, 1096, 1036, 739, 705, 651, 518. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.83–1.03 (m_c, 4 H, cPr-H), 1.25 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 1.81 (s, 3 H, 4'-H), 1.99–2.14 (m, 2 H, 1'-H), 2.05 (t, ^4J = 2.6 Hz, 1 H, 3"-H), 2.18–2.35 (m, 2 H, 2'-H), 2.85 (d, ^4J = 2.6 Hz, 2 H, 1"-H), 4.19 (q, ^3J = 7.1 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.5 (–, cPr-C), 2.7 (–, cPr-C), 14.0 (+, OCH_2CH_3), 20.4 (–, CH_2), 22.5 (+, CH_3), 29.8 (–, CH_2), 31.0 (–, CH_2), 56.5 (C_{quat}, C-1), 61.4 (–, OCH_2CH_3), 71.1 (C_{quat}, C-2"), 78.9 (+, C-3"), 116.2 (C_{quat}, cPr-C), 122.9 (C_{quat}, C-3'), 170.0 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 292 (3) [M^+], 218 (27) [$M^+ – C_2H_5OH – C_2H_4$], 207 (76), 198 (38), 161 (63), 145 (69), 91 (61), 79 (100) [$C_6H_7^+$]. – Elemental analysis calcd (%) for $C_{17}H_{24}O_4$ (292.4): C 69.84, H 8.27; found C 69.61, H 8.04.

Diethyl (3'-Cyclopropylidenebutyl)malonate (29): To a solution of 111 g (0.238 mol) of 3-bromopropyltriphenylphosphonium bromide in 350 mL of anhydrous benzene was added 58.75 g (0.524 mol) of KO*t*Bu and the mixture stirred at 70 °C for 2 h. To this suspension was added with stirring 50.0 g (0.238 mol) of the malonic ester **27** in 50 mL of anhydrous benzene within 30 min and the mixture was stirred at 70 °C for an additional 4 h. After being cooled to room temp. the mixture was added to 600 mL of pentane and filtered. After removal of the solvents in a rotatory evaporator the residue was subjected to chromatography on 300 g of silica gel (petroleum ether → petroleum ether/ether 10 : 1).

Fraction I: triphenylphosphane; R_f = 0.5 (petroleum ether).

Fraction II: 39.32 g (65%) of **29** as a colorless oil; R_f = 0.3 (petroleum ether/ether 10 : 1). – IR (film): nu(tilde) = 3024 cm^{-1}, 2951, 2960, 2852, 1734 (C=O), 1448, 1370, 1156, 1032, 862, 738, 545. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90–1.05 (m_c, 4 H, cPr-H), 1.25 (t, ^3J = 7.2 Hz, 6 H, OCH_2CH_3), 1.78 (s, 3 H, 4'-H), 2.00–2.20 (m, 4 H, 1'-H, 2'-H), 3.28 (t, ^3J = 7.2 Hz, 1 H, 1-H), 4.17 (q, ^3J = 7.2 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.6 (–, CH_2), 2.8 (–, CH_2), 14.0 (+, OCH_2CH_3), 20.3 (+, C-4'), 26.6 (–, C-1'*), 34.1 (–, C-2'*), 51.4 (+, C-1), 61.2 (–, OCH_2CH_3), 116.8 (C_{quat}, C-3'), 122.5 (C_{quat}, cPr-C), 169.5 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 254 (1) [M^+], 209 (14) [$M^+ – C_2H_5O$], 180 (46) [$M^+ – C_2H_5OH – C_2H_4$], 163 (21), 135 (43) [$M^+ – C_2H_5O_2C – C_2H_5OH$], 107 (64) [$M^+ – C_2H_5O_2C – C_2H_5OH – C_2H_4$], 79 (100) [$C_6H_7^+$]. – Elemental analysis calcd (%) for $C_{14}H_{22}O_4$ (254.3): C 66.12, H 8.72; found C 65.82, H 8.48.

Diethyl (3'-Cyclopropylidenebutyl)(2''-bromo-2''-propenyl)malonate (30): To a solution of 7.70 g (28.69 mmol) of the malonate **29** in 150 mL of anhydrous THF was added with stirring 1.15 g of NaH (60% in mineral oil), and the mixture was stirred until the evolution of hydrogen ceased (~30 min). Then 6.02 g (30.12 mmol) of 2,3-dibromopropene was added, and the mixture was stirred for an additional 60 min. After aqueous work-up as usual [200 mL of H_2O, extraction with Et_2O (2 × 100 mL), drying over $MgSO_4$] the solvent was removed in a rotatory evaporator, and the residue was subjected to chromatography on 160 g of silica gel (column 4.5 × 20 cm, pentane/ether 10 : 1) to yield 7.67 g (72%) of **30** (R_f = 0.21) as a colorless oil. – IR (film): nu(tilde) = 3028 cm^{-1}, 2876, 2856, 1778, 1734, 1625, 1447, 1368, 1314, 1122, 1022, 898, 859, 560, 525. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87–1.04 (m, 4 H, cPr-H), 1.24 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 1.75–1.80 (m, 3 H, 4'-H), 1.95–2.22 (m, 4 H, 1'-H, 2'-H), 3.16 (d, ^4J = 0.8 Hz, 2 H, 1''-H), 4.10–4.23 (m, 4 H, OCH_2CH_3), 5.55 (d, ^2J = 1.6 Hz, 1 H, 3''-H), 5.65 (dt, ^2J = 1.6 Hz, ^4J = 1.6 Hz, 1 H, 3''-H) – ^{13}C NMR (75.0 MHz, $CDCl_3$, DEPT): δ = 1.6 (–, cPr-C), 2.8 (–, cPr-C), 14.0 (+, OCH_2CH_3), 20.5 (+, CH_3), 29.4 (–, CH_2), 31.1 (–, CH_2), 42.7 (–, CH_2), 56.8 (C_{quat}, C-1), 61.4 (–, OCH_2CH_3), 71.1 (C_{quat}, C-2''), 78.9 (+, CH), 116.2 (C_{quat}, cPr-C), 121.5 (C_{quat}, C-3''), 122.9 (C_{quat}, C-3'), 127.5 (C_{quat}, C-2''), 170.6 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 374/372 (0.5/0.5) [M^+], 280/278 (11/11), 247 (9), 219 (28), 207 (50), 199 (47), 79 (100).

Diethyl (3'-Cyclopropylidenebutyl)(5''-trimethylsilylpent-4''-ynyl)malonate (32-SiMe$_3$): To a solution of 333 mg (1.31 mmol) of diethyl (3'-cyclopropylidenebutyl)malonate (**29**) in 10 mL of anhydrous THF was added 80.0 mg (2.00 mmol) of NaH (60% in mineral oil) and the mixture stirred for 30 min. After addition of 500 mg (1.88 mmol) of **35**-I stirring was continued for 18 h. After addition of 30 mL each of water and diethyl ether the organic phase was washed with 10 mL each of water and brine. After removal of the solvent in a rotatory evaporator the crude product was purified by flash chromatography (column 2 × 20 cm, petroleum ether/ether = 20 : 1) to yield 450 mg (87%) of **32**-$SiMe_3$ as a colorless oil, R_f = 0.32. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 9 H, $Si(CH_3)_3$], 0.80–0.95 (m_c, 4 H, cPr-H), 1.19 (t, ^3J = 7.2 Hz, 6 H, OCH_2CH_3), 1.33–1.44 (m, 2 H, 2''-H), 1.75 (t, ^3J = 1.4 Hz, 3 H, 4'-H), 1.90–2.11 (m, 6 H, 1'-H, 2'-H, 2''-H), 2.19 (t, ^3J = 7.1 Hz, 2 H, 3''-H), 4.12 (t, ^3J = 7.2 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = –0.08 [+, $Si(CH_3)_3$], 1.3 (–, CH_2), 2.6 (–, CH_2), 13.9 (+, OCH_2CH_3), 20.0 (–, C-2''), 20.4 (+, C-4'), 23.3 (–, C-1'), 26.7 (–, C-1''), 30.1 (–, C-3''), 31.2 (–, C-2'), 56.9 (C_{quat}, C-1), 60.8 (–, OCH_2CH_3), 84.7 (C_{quat}, C-5''), 106.4 (C_{quat}, C-4''), 115.8 (C_{quat}, cPr-C), 122.3 (C_{quat}, C-3'), 171.4 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 392 (1.7) [M^+], 363 (3) [$M^+ - CH_2CH_3$], 283 (48), 73 (100) [$Si(CH_3)_3^+$]. – $C_{22}H_{36}O_4Si$ (392.6): calcd C 67.30, H 9.24; found C 67.19, H 9.13.

Diethyl (3'-Cyclopropylidenebutyl)(pent-4''-ynyl)malonate (32-H): To a solution of 340 mg (0.866 mmol) of malonate **32**-$SiMe_3$ in 10 mL of THF was added 316 mg (1.00 mmol) of tetra-butylammonium fluoride trihydrate, and the mixture was stirred for 3 h (TLC control). To this mixture were added 30 mL each of diethyl ether and water, the organic phase was extracted with diethyl ether (3 × 20 mL), the combined organic phases were washed twice with 10 mL each of water and brine, then dried ($MgSO_4$). After removal of the solvent in a rotatory evaporator the residue was purified by flash chromatography on silica gel (column 2 × 20 cm, petroleum ether/ether 20 : 1). The first fraction furnished 268 mg (97%) of **32**-H as a colorless oil, $R_f = 0.28$. – IR (film): nu(tilde) = 3360 cm^{-1} (C≡C–H), 3273, 2978, 2935, 2872, 2120 (C≡C), 1772, 1734 (C=O), 1457, 1368, 1177, 1095, 1027, 860, 668, 560. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.86–0.94 (m_c, 4 H, cPr-H), 1.19 (t, ^3J = 7.2 Hz, 6 H, OCH_2CH_3), 1.33–1.43 (m, 2 H, 2''-H), 1.73 (s, 3 H, 4'-H), 1.98–2.03 (m, 7 H, 1'-H, 2'-H, 1''-H, 5''-H), 2.14 (dt, ^4J = 1.4, ^3J = 7.1 Hz, 2 H, 3''-H), 4.12 (t, ^3J = 7.2 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.3 (–, cPr-C), 2.6 (–, cPr-C), 13.9 (+, OCH_2CH_3), 18.5 (–, C-2''), 20.4 (+, C-4'), 23.2 (–, C-1'), 26.7 (–, C-1''), 30.3 (–, C-3''), 31.2 (–, C-2'), 56.9 (C_{quat}, C-1), 60.9 (–, OCH_2CH_3), 68.6 (+, C-5''), 83.5 (C_{quat}, C-4''), 115.8 (C_{quat}, cPr-C), 123.0 (C_{quat}, C-3'), 171.3 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 320 (6) [M^+], 291 (2) [$M^+ - C_2H_5$], 275 (5) [$M^+ - C_2H_5O$], 247 (6), 201 (18), 173 (32), 152 (57), 79 (100). – $C_{19}H_{28}O_4$ (320.4): calcd C 71.21, H 8.81; found C 71.00, H 8.53.

Diethyl [4'-(Prop-2''-ynyloxy)but-2'-ynyl](3'''-cyclopropylidenebutyl)malonate (33-H): To a solution of 74.5 mg (293 μmol) of diethyl (3'-cyclopropylidenebutyl)malonate (**29**) in 5 mL of THF was added 20 mg (0.50 mmol) of NaH (60% in mineral oil), and the mixture was stirred for 30 min. After addition of 117 mg (500 μmol) of the iodide **37**-I the mixture was stirred for an additional 2 h. After addition of 10 mL of water, the mixture was extracted with diethyl ether (3 × 10 mL), the combined organic phases were washed twice with 5 mL each of water and brine and dried ($MgSO_4$). After removal of the solvents the residue was subjected to chromatograpy on silica gel (column 1 × 20 cm, light petroleum/ether 20 : 1) and gave 90 mg (85%) of **33**-H as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88–1.15 (m, 4 H, cPr-H), 1.20 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 1.76 (t, ^4J = 1.5 Hz, 3 H, 4'''-H), 1.99–2.10 (m, 2 H, 1'''-H), 2.16–2.23 (m, 2 H, 2'''-H), 2.39 (t, ^4J = 2.3 Hz, 1 H, 3''-H), 2.84 (t, ^4J = 2.1 Hz, 2 H, 1'-H), 4.10–4.18 (m, 8 H, OCH_2CH_3, 1''-H, 4'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.4 (–, cPr-C), 2.6 (–, cPr-C), 13.9 (+, OCH_2CH_3), 20.3 (–, C-1'''), 22.8 (+, C-4'''), 29.9 (–, C-2'''), 30.9 (–, C-1'), 55.8 (C_{quat}, C-1), 56.0 (–,

CH_2O), 56.5 (–, CH_2O), 61.3 (–, OCH_2CH_3), 74.6 (C_{quat}, C≡C), 77.8 (+, C-3''), 78.8 (C_{quat}, C≡C), 82.0 (C_{quat}, C≡C), 116.1 (C_{quat}, cPr-C), 122.8 (C_{quat}, C-3'''), 170.1 (C_{quat}, CO).

4-(Prop-2'-ynyloxy)but-2-yn-1-ol (37-OH) and 1,4-Bis(prop-2'-ynyloxy)but-2-yne (37-OProp): A two-phase system of 8.61 g (100 mmol) of but-2-yne-1,4-diol (**36**), 11.9 g (100 mmol) of propargyl bromide and 5.61 g (100 mmol) of KOH in 50 mL of water was vigorously stirred at ambient temp. for 4 h. The emulsion was diluted with 100 mL each of water and ether, the aqueous phase extracted with diethyl ether (3 × 50 mL), the combined organic phases were washed with water (3 × 30 mL) and brine, then dried ($MgSO_4$), and the solvent was removed in a rotatory evaporator. Chromatography on silica gel (column 3 × 20 cm, light petroleum/ether 10 : 1) gave two fractions.

Fraction I: 2.00 g (25%) of **37**-OProp as a colorless oil; R_f = 0.9. – IR (film): nu(tilde) = 3320 cm^{-1} (C≡C–H), 3026, 2856 (CH_2), 2777, 2118 (C≡C), 1443, 1356, 1264, 1247, 1171, 1011, 987, 887, 710, 683, 586. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (t, ^4J = 2.3 Hz, 2 H, 3'-H), 4.19 (d, ^4J = 2.3 Hz, 4 H, 1'-H), 4.25 [s, 4 H, 1(4)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 56.3 (–, CH_2O), 56.5 (–, CH_2O), 74.9 (+, C-3'), 78.7 (C_{quat}, C-2'), 81.9 [C_{quat}, C-2(3)]. – MS (70 eV, EI), *m/z* (%): 161 (0.1) [M^+ – H], 131 (4), 77 (100).

Fraction II: 4.80 g (39%) of **37**-OH as a colorless oil; R_f = 0.3. – IR (film): nu(tilde) = 3557 cm^{-1} (OH), 3320 (C≡C–H), 3084, 2995, 2813, 2773, 2120 (C≡C), 1718, 1444, 1287, 1176, 914, 722, 522. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (t, ^4J = 2.3 Hz, 1 H, 3'-H), 3.45 (bs, 1 H, OH), 4.15–4.30 (m, 6 H, CH_2). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 50.3 (–, C-1), 56.2 (–, CH_2O), 56.5 (–, CH_2O), 75.1 (+, C-3'), 78.6 (C_{quat}, C-2'), 80.0 (C_{quat}, C≡C), 85.3 (C_{quat}, C≡C). – MS (70 eV, EI), *m/z* (%): 124 (0.1) [M^+], 123 (3) [M^+ – H], 93 (25) [M^+ – CH_3O], 66 (100).

4-Iodobut-2-ynyl Prop-2-ynyl Ether (37-I): To a solution of the propargyl alcohol **37**-OH (1.29 g, 10.4 mmol), triphenylphosphine (4.72 g, 18.0 mmol) and imidazole (1.29 g, 18.9 mmol) in diethyl ether (20 mL) and acetonitrile (14 mL) was added iodine (5.08 g, 20.0 mmol) in small portions at 0 °C, and the mixture was stirred for 1 h. Ether (200 mL) was added, and the mixture was washed with 20% $Na_2S_2O_3$ solution (~50 mL), until no further change of color occurred. After drying ($MgSO_4$) the solution was concentrated on a rotatory evaporator, and the residue subjected to column chromatography (column 3 × 20 cm) on silica gel, eluting with light petroleum/ether, 10 : 1, to give 2.25 g (92%) of **37**-I as a colorless oil which slowly turned brown upon standing at ambient temparature. – IR (film): nu(tilde) = 3320 cm^{-1} (C≡C–H), 3026, 2778, 2120 (C≡C), 1457, 1377, 723. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (t, ^4J = 2.4 Hz, 1 H, 3'-H), 3.69 (t, ^5J = 2.2 Hz, 2 H, 4-

H), 4.19 (d, ^4J = 2.4 Hz, 2 H, 1'-H), 4.23 (t, ^5J = 2.2 Hz, 2 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = –19.39 (–, C-4), 56.43 (–, CH_2), 56.77 (–, CH_2), 75.01 (+, C-3'), 78.74 (C_{quat}, C≡C), 80.24 (C_{quat}, C≡C), 83.68 (C_{quat}, C≡C). – MS (70 eV, EI), *m/z* (%): 183 (41), 127 (89) [I^+], 77 (100). – C_7H_7IO (234.0).

Dimethyl [4'-(Prop-2''-ynyloxy)but-2'-ynyl](2'''-cyclopropylidenepropyl)malonate (38-H): According to GP 2, a solution of 764 mg (3.60 mmol) of dimethyl (2'-cyclopropylidenepropyl)-malonate (**11**) in 20 mL of THF was treated with 200 mg (5.00 mmol) of NaH (60% in mineral oil), and the mixture stirred for 30 min. After addition of 850 mg (3.63 mmol) of the iodide **37**-I, stirring was continued for 2 h, then 10 mL of water was added, and the mixture was extracted with diethyl ether (3 × 10 mL), the combined organic phases were washed twice with 5 mL each of water and brine, then dried ($MgSO_4$). After removal of the solvents, the residue was subjected to chromatography on silica gel (column 3 × 20 cm, light petroleum/ether 20 : 1 → 10 : 1) to give 750 mg (66%) of **38**-H as a colorless oil. R_f = 0.3 (light petroleum/ether, 10:1). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.00–1.16 (m, 4 H, cPr-H), 1.69 (t, ^4J = 1.5 Hz, 3 H, 3'''-H), 2.41 (t, ^4J = 2.3 Hz, 1 H, 3''-H), 2.78 (s, 2 H, 1'-H), 2.94 (bs, 2 H, 1'''-H), 3.70 (s, 6 H, OCH_3), 4.18 (bs, 4 H, 1''-H, 4'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.5 (–, cPr-C), 3.6 (–, cPr-C), 21.2 (+, C-3'''), 23.0 (–, C-1'), 38.8 (–, C-1'''), 52.5 (+, OCH_3), 55.8 (–, CH_2O), 56.6 (–, CH_2O), 56.7 (C_{quat}, C-1), 74.7 (C_{quat}, C≡C), 77.5 (+, C-3''), 78.9 (C_{quat}, C≡C), 82.6 (C_{quat}, C≡C), 118.5 (C_{quat}, cPr-C), 122.3 (C_{quat}, C-2'''), 170.7 (C_{quat}, CO).

5-Trimethylsilylpent-4-yn-1-ol (35-OH): A mixture of 6.10 g (26.7 mmol) of 5-trimethylsilyl-1-trimethylsilyloxy-4-pentyne (**35**-$OSiMe_3$), 4.47 g (41.1 mmol) of chlorotrimethylsilane and 6.15 g (41.0 mmol) of sodium iodide in 10 mL of acetonitrile was heated at 75 °C for 2 h. Then the reaction mixture was added to an ice cold saturated $NaHCO_3$ solution and the free iodine removed by addition of sodium hydrogensulfite. The reaction mixture was extracted with diethyl ether (3 × 30 mL), the combined organic phases were washed with 20 mL each of water and brine, dried (Na_2SO_4) and evaporated under reduced pressure to dryness. Column chromatography on 150 g of silica gel (column 4.5 × 20 cm, pentane/ether 3 : 1) yielded 2.88 g (69%) of **35**-OH as a colorless oil. – IR (film): nu(tilde) = 3538 cm^{-1} (O–H), 3165, 2992, 2826, 2176 (C≡C), 1431, 1250, 1079 (C–O), 1071, 801, 701, 645, 537. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 1.79 (tt, ^3J = 6.8, ^3J = 6.8 Hz, 2 H, 2-H), 2.25 (s, 1 H, OH), 2.35 (t, ^3J = 6.8 Hz, 2 H, 3-H), 3.78 (t, ^3J = 6.8 Hz, 2 H, 1-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = –0.01 [+, $Si(CH_3)$], 16.4 (–, C-

2), 31.1 (–, C-3), 61.5 (–, C-1), 85.0 (C_{quat}, C-5), 106.7 (C_{quat}, C-4). – MS (70 eV, EI), *m/z* (%): 156 (4) [M^+], 141 (22) [$M^+ – CH_3$], 85 (100) [$M^+ – SiMe_3 + 2$ H], 73 (62) [$SiMe_3^+$].

5-Iodo-1-trimethylsilylpent-1-yne (35-I): Variant 1, from 5-Trimethylsilylpent-4-yn-1-ol (35-OH): To a solution of 0.800 g (5.12 mmol) of the alcohol **35**-OH, 2.36 g (9.00 mmol) of triphenylphosphane and 647 mg (9.50 mmol) of imidazol in 10 mL of diethyl ether and 7 mL of acetonitrile was added 2.54 g (10.0 mmol) of iodine at 0 °C within 10 min, and the mixture was stirred at this temperature for an additional 2 h, then diluted with 100 mL of diethyl ether and washed with saturated sodium thiosulfate solution until the organic phase had decolorized. The organic phase was dried ($MgSO_4$) and the solvent removed in a rotatory evaporator. Chromatography on silica gel (column 2 × 20 cm, pentane) gave 1.10 g (81%) of **35**-I as a colorless oil; $R_f = 0.34$. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 [s, 9 H, $Si(CH_3)$], 1.95 (tt, ^3J = 6.8, ^3J = 6.8 Hz, 2 H, 4-H), 2.32 (t, ^3J = 6.8 Hz, 2 H, 3-H), 3.25 (t, ^3J = 6.8 Hz, 2 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 0.1 [+, $Si(CH_3)_3$], 5.0 (–, C-5), 20.8 (–, C-4), 32.0 (–, C-3), 85.7 (C_{quat}, C-2*), 104.7 (C_{quat}, C-1*).

Variant 2, from 5-Trimethylsilylpent-4-ynyl Tosylate (35-OTs): A suspension of 1.55 g (4.99 mmol) of the tosylate **35**-OTs and 3.00 g (20.0 mmol) of sodium iodide in 10 mL of acetone was stirred at ambient temp. for 24 h. The solution was diluted with 50 mL of diethyl ether and filtered. The filtrate was washed with saturated sodium thiosulfate solution until the organic phase had decolorized. The organic phase was dried ($MgSO_4$) and the solvent removed in a rotatory evaporator. Chromatography on silica gel (column 2 × 20 cm, pentane) gave 1.22 g (92%) of **35**-I as a colorless oil.

Variant 3, from 5-Chloro-1-trimethylsilylpent-1-yne (35-Cl): A suspension of 3.00 g (17.2 mmol) of the chloride **35**-Cl and 12.9 g (86.1 mmol) of sodium iodide in 50 mL of acetone was stirred at ambient temp. for 24 h. The solution was diluted with 200 mL of diethyl ether and filtered. The filtrate was washed with saturated sodium thiosulfate solution until the organic phase had decolorized. The organic phase was dried ($MgSO_4$) and the solvent removed in a rotatory evaporator. Chromatography on silica gel (column 3 × 20 cm, pentane) gave 4.1 g (90%) of **35**-I as a colorless oil.

Diethyl (3'-Cyclobutylidenebutyl)malonate (39): To a solution of 23.9 g (50.0 mmol) of 4-bromobutyltriphenylphosphonium bromide in 250 mL of anhydrous benzene was added 14.0 g (125 mmol) of KO*t*Bu, and the mixture stirred at 70 °C for 2 h. To this suspension was added 11.5 g (49.9 mmol) of diethyl 3'-oxobutylmalonate (**27**) in 50 mL of benzene within 10 min, and the

mixture stirred at 70 °C for an additional 4 h. After being cooled to room temp. the mixture was added to 200 mL of pentane, treated with 10 g of Celite and filtered. After removal of the solvents in a rotatory evaporator the residue was subjected to chromatography on 200 g of silica gel (light petroleum → light petroleum/ether 10 : 1). – Fraction I: triphenylphosphine, $R_f = 0.5$ (light petroleum). – Fraction II: 8.72 g (65%) of **39** as a colorless oil; $R_f = 0.3$ (light petroleum/ether 10 : 1). – IR (film): nu(tilde) = 3030 cm^{-1}, 2820, 1734 (C=O), 1448, 1030, 861, 525. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.2 Hz, 6 H, OCH_2CH_3), 1.41 (s, 3 H, 4'-H), 1.78–1.96 (m, 6 H, 1'-H, 2'-H, *c*Bu-H), 2.52 (bs, 4 H, *c*Bu-H), 3.22 (t, ^3J = 7.0 Hz, 1 H, 1-H), 4.12 (t, ^3J = 7.2 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 14.0 (+, OCH_2CH_3), 15.2 (+, C-4'), 15.8 (–, *c*Bu-C), 26.6 (–, C-1'*), 28.9 (–, C-2'*), 29.1 (–, *c*Bu-C*), 29.9 (–, *c*Bu-C*), 51.3 (+, C-1), 61.1 (–, OCH_2CH_3), 123.9 (C_{quat}, C-3'), 134.6 (C_{quat}, *c*Bu-C), 169.5 (C_{quat}, CO). – MS (70 eV, EI), *m/z* (%): 268 (5) [M^+], 240 (6), 222 (10) [$M^+ - C_2H_5OH$], 194 (7) [$M^+ - C_2H_5OH - CO$], 173 (21), 149 (13) [$M^+ - C_2H_5O_2C - C_2H_5OH$], 121 (13) [$M^+ - C_2H_5O_2C - C_2H_5OH - CO$], 108 (78), 93 (100) [$C_7H_9^+$]. – Elemental analysis calcd (%) for $C_{15}H_{24}O_4$ (268.4): C 67.14, H 9.01; found C 66.94, H 8.80.

Diethyl (3'-Cyclobutylidenebutyl)(prop-2''-ynyl)malonate (40): According to GP 2, a solution of 536 mg (2.00 mmol) of the malonate **39** in 10 mL of THF was treated with NaH (60% in mineral oil) until no more evolution of hydrogen was observed. After stirring for an additional 10 min, 238 mg (2.00 mmol) of propargyl bromide was added, and the mixture was stirred for an additional 60 min. The solvent was removed in a rotatory evaporator, and the residue subjected to chromatography on silica gel (column 2 × 20 cm, light petroleum/ether 10 : 1) to yield 535 mg (87%) of **40** as a colorless oil. R_f = 0.32 (light petroleum/ether, 10:1) – IR (film): nu(tilde) = 3360 cm^{-1} (C≡C–H), 3276, 2978, 2933, 2583, 1734 (C=O), 1448, 1368, 1188, 1089, 1030, 860, 738, 667, 531. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3), 1.49 (t, ^4J = 1.6 Hz, 3 H, 4'-H), 1.74 (t, ^3J = 7.9 Hz, 2 H, 1'-H), 1.87 (qui, ^3J = 8.0 Hz, 2 H, *c*Bu-H), 2.00 (t, ^4J = 2.7 Hz, 1 H, 3''-H), 1.21 (tq, ^3J = 7.9, ^4J = 1.6 Hz, 2 H, 2'-H), 2.59 (bt, ^3J = 8.0 Hz, 4 H, *c*Bu-H), 2.84 (d, ^4J = 2.7 Hz, 2 H, 1''-H), 4.20 (q, ^3J = 7.1 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (75.0 MHz, $CDCl_3$, APT): δ = 14.1 (+, OCH_2CH_3), 15.6 (+, C-4'), 15.8 (–, *c*Bu-C), 22.5 (–, C-1''), 26.9 (–, C-1'*), 28.9 (–, C-2'*), 29.2 (–, *c*Bu-C*), 30.0 (–, *c*Bu-C*), 56.6 (–, C-1), 61.6 (–, OCH_2CH_3), 71.2 (+, C-3''), 79.0 (–, C-2''), 124.5 (–, C-3'), 133.9 (–, *c*Bu-C), 170.3 (–, CO). – MS (70 eV, EI), *m/z* (%): 292 (2), 232 (3) [$M^+ - H - C_2H_5CO_2$], 198 (100), 93 (14) [$C_6H_7^+$]. – Elemental analysis calcd (%) for $C_{18}H_{26}O_4$ (306.4): C 70.56, H 8.56; found C 70.41, H 8.35.