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SUPPORTING INFORMATION

Title: Facile Construction of Spirocyclopropanated Bi-, Tri- and Tetracyclic Skeletons by Novel Cascades Involving Intra- and Intermolecular Heck Reactions of 2-Bromo-1,6-enynes and Bicyclopropylidene

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Dimethyl 2-(2'-bromoallyl)malonate (**4**),[1] 2-(2'-propynyloxy)tetrahydro-2*H*-pyran (**6**-H)[2] and *N*-(2-bromoallyl)-*N*-(*p*-tosyl)amine (**10**)[3] were prepared according to literature procedures. Alcohols **2**-Cpr,[4] **2**-*t*Bu,[5] **2**-Ph,[6] **26a**,[7] **26b**[8] and **26c**[9] and their syntheses have been described before, therefore only the general procedure (GP3) is presented here.

General Procedure for the Functionalization of Terminal Alkynes with Formaldehyde (GP3): To a solution of 20.0 mmol of the respective alkyne in 50 mL of anhydrous THF was added dropwise *n*-butyllithium (22.0 mmol, 2.5 M solution in hexane) at –78 °C and the mixture was stirred at 0 °C for 1 h. After cooling down to –78 °C anhydrous paraformaldehyde (751 mg, 25.0 mmol) was added in one batch, and the reaction mixture was allowed to reach room temperature overnight under continuous stirring. Sat. NH_4Cl solution (50 mL) was added, and the aqueous layer was extracted with diethyl ether (3×70 mL). The combined ethereal phases were washed with brine (70 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by chromatography on silica gel, eluting with pentane/diethyl ether mixtures.

General Procedure for the Reaction of 2-(2'-Propynyloxy)tetrahydro-2*H*-pyran with Electrophiles (GP4): To a solution of 2-(2'-propynyloxy)tetrahydro-2*H*-pyran (1.40 g, 10.0 mmol) in 40 mL of anhydrous THF was added dropwise *n*-butyllithium (10.5 mmol, 2.5 M solution in hexane) at –78 °C, and the mixture was stirred at 0 °C for 1 h. After cooling down to –78 °C, 10.5 mmol of the respective electrophile was

added dropwise, and the reaction mixture was allowed to reach room temperature overnight under continuous stirring. Sat. NH_4Cl solution (50 mL) was added, and the aqueous layer was extracted with diethyl ether (3×50 mL). The combined ethereal phases were washed with brine (50 mL), dried over $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was purified by chromatography on silica gel, eluting with pentane/diethyl ether mixtures.

General Procedure for the Bromination of Tetrahydropyranyl Ethers (GP5): To a solution of triphenylphosphine (6.61 g, 25.2 mmol) in 60 mL of anhydrous CH_2Cl_2 was added dropwise bromine (1.28 mL, 25.0 mmol) at –10 °C. The resulting colorless suspension was stirred at this temperature for another 30 min, after which 20.0 mmol of the corresponding THP ether was added dropwise. The mixture was allowed to reach room temperature, stirred for an additional 8 h, and then poured into 50 mL of water. The aqueous layer was extracted with CH_2Cl_2 (3×50 mL), the combined organic layers washed with brine (70 mL), and dried over $MgSO_4$. The solvent was destilled off over a 20 cm vigreux column, and the residue was destilled or subjected to column chromatography on silica with pentane as eluent.

Trimethyl[3-(tetrahydro-2'*H*-2'-pyranyloxy)-1-propynyl]silane (**6**-TMS): According to **GP4**, 2-(2'-propynyloxy)tetrahydro-2*H*-pyran (**6**-H, 2.30 g, 16.4 mmol) in 60 mL of anhydrous THF was treated at –78 °C with *n*-BuLi (6.9 mL, 17.3 mmol, 2.5 M in hexane). To the resulting mixture was added dropwise chlorotrimethylsilane (1.85 g, 17.0 mmol). Column chromatography on silica gel (90 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.65) yielded **6**-TMS (3.27 g, 94%) as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.13 [s, 9 H, $Si(CH_3)_3$], 1.41–1.92 (m, 6 H, THP-H), 3.45–3.85 (m, 2 H, THP-H), 4.19 (bs, 2 H, CH_2O), 4.70–4.84 (m, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –0.25 [3 C, $Si(CH_3)_3$], 18.95 (THP-C), 25.33 (THP-C), 30.20 (THP-C), 54.75 (C-3), 61.84 (THP-C), 90.80 (C-1), 96.69 (THP-C). 101.88 (C-2). – $C_{11}H_{20}O_2Si$ (212.4). The experimental data agree with those cited in the literature.[10]

(3-Bromo-1-propynyl)trimethylsilane (**7**-TMS): According to **GP5**, PPh_3 (3.15 g, 12.0 mmol) and bromine (590 μL, 11.5 mmol) were reacted with trimethyl[3-(tetra-

hydro-2'*H*-2'-pyranyloxy)-1-propynyl]silane (**6**-TMS, 2.12 g, 9.98 mmol) in 30 mL of CH_2Cl_2 at –10 °C. Destillation at reduced pressure (44–48°C, 1 Torr) yielded **7**-TMS (1.59 g, 83%) as a colorless liquid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.15 [s, 9 H, $Si(CH_3)_3$], 3.87 (s, 2 H, CH_2Br). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = – 0.35 [3 C, $Si(CH_3)_3$], 14.60 (C-3), 92.26 (C-1), 99.95 (C-2). – $C_6H_{11}BrSi$ (191.1). The experimental data agree with those cited in the literature.[10]

***tert*-Butyldimethyl[3-(tetrahydro-2'*H*-2'-pyranyloxy)-1-propynyl]silane** (**6**-TBDMS): According to **GP4**, 2-(2'-propynyloxy)tetrahydro-2*H*-pyran (**6**-H, 5.06 g, 36.1 mmol) in 100 mL of anhydrous THF was treated at –78 °C with *n*-BuLi (15.0 mL, 37.5 mmol, 2.5 M in hexane). To the resulting mixture was added *tert*-butyldimethylchlorosilane (5.59 g, 37.1 mmol) in three separate batches. Column chromatography on silica gel (150 g, 4 × 25 cm, pentane/diethyl ether 10:1, R_f = 0.60) yielded **6**-TBDMS (7.07 g, 77%) as a colorless oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 [s, 6 H, $Si(CH_3)_2$], 0.84 [s, 9 H, $C(CH_3)_3$], 1.48–1.90 (m, 6 H, THP-H), 3.46–3.90 (m, 2 H, THP-H), 4.24 (bs, 2 H, CH_2O), 4.80–4.91 (m, 1 H, 2'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.66 [2 C, $Si(CH_3)_2$], 16.31 [3 C, $C(CH_3)_3$], 18.90 (THP-C), 25.22 (THP-C), 25.89 [$C(CH_3)_3$], 30.11 (THP-C), 54.61 (C-3), 61.85 (THP-C), 88.91 (C-1), 96.41 (THP-C). 102.09 (C-2). – $C_{14}H_{26}O_2Si$ (254.4). The experimental data agree with those cited in the literature.[11]

(3-Bromo-1-propynyl)-*tert*-butyldimethylsilane (**7**-TBDMS): According to **GP5**, triphenylphosphine (3.30 g, 12.6 mmol) and bromine (640 µL, 12.5 mmol) were reacted with *tert*-butyldimethyl[3-(tetrahydro-2'*H*-2'-pyranyloxy)-1-propynyl]silane (**6**-TBDMS, 2.54 g, 9.98 mmol) in 30 mL of CH_2Cl_2 at –10 °C. Column chromatography on silica gel (80 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.90) yielded **7**-TBDMS (1.68 g, 72%) as a colorless liquid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.17 [s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $C(CH_3)_3$], 3.84 (s, 2 H, CH_2Br). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –4.86 [2 C, $Si(CH_3)_2$], 14.70 (C-3), 16.54 [$C(CH_3)_3$], 25.97 [3 C, $C(CH_3)_3$], 90.83 (C-1), 100.54 (C-2). – $C_9H_{17}BrSi$ (233.2). The experimental data agree with those cited in the literature.[11]

Dimethyl[3'-(tetrahydro-2''*H*-2''-pyranyloxy-1'-propynyl)]-2-thienylsilane (**6**-ThDMS): According to **GP4**, 2-(2'-propynyloxy)tetrahydro-2*H*-pyran (**6**-H, 2.72 g, 19.4 mmol) in 50 mL of anhydrous THF was treated with *n*-BuLi (7.96 mL, 19.9 mmol, 2.5 M in hexane) at –78 °C, and the mixture subsequently reacted with 2-thienyldimethylchlorosilane (3.52 g, 19.9 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.50) yielded **6**-ThDMS (4.13 g, 76%) as a colorless oil. – IR (film): nu(tilde) = 3100 cm^{-1}, 2943, 2869, 2852, 2177, 1465, 1440, 1406, 1342, 1325, 1251, 1215, 1201, 1120, 1080, 1062, 997, 902, 813, 783, 709, 680. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.16 (s, 3 H, $SiCH_3$), 0.52 (s, 3 H, $SiCH_3$), 1.51–1.80 (m, 6 H, THP-H), 3.40–3.54 (m, 2 H, THP-H), 3.78–3.91 (m, 2 H, CH_2O), 4.89 (t, *J* = 1.5 Hz, 1 H, 2'-H), 7.21 (dd, ^3J = 4.6, ^3J = 3.1 Hz, 1 H, thienyl-H), 7.38 (d, ^3J = 3.1 Hz, 1 H, thienyl-H), 7.64 (d, ^3J = 4.6 Hz, 1 H, thienyl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.09 [2 C, $Si(CH_3)_2$], 18.92 (THP-C), 25.29 (THP-C), 30.15 (THP-C), 54.67 (C-3'), 61.87 (THP-C), 88.37 (C-1'), 96.54 (THP-C), 103.36 (C-2'), 128.14 (thienyl-C), 131.32 (thienyl-C), 135.26 (thienyl-C), 136.01 (thienyl-C). – MS (EI, 70 eV), *m/z* (%): 280 (4) [M^+], 196 (43) [M^+ – THP], 179 (100) [M^+ – THP – H_2O], 141 (61), 103 (60). – HRMS: Calcd. for $C_{14}H_{20}O_2SSi$: 280.0953, correct mass.

3-Bromo-1-propynyl(dimethyl)2-thienylsilane (**7**-ThDMS): According to **GP5**, PPh_3 (2.78 g, 10.6 mmol) und bromine (545 µL, 10.6 mmol) were reacted with dimethyl[3'-(tetrahydro-2"*H*-2"-pyranyloxy-1'-propynyl)]-2-thienylsilane (**6**-ThDMS) (2.38 g, 8.49 mmol) in 25 mL of CH_2Cl_2 at –10 °C. Column chromatography on silica gel (60 g, 3 × 30 cm, pentane, R_f = 0.95) yielded **7**-ThDMS (1.52 g, 69%) as a pale yellow liquid. – IR (film): nu(tilde) = 3103 cm^{-1}, 3060, 2947, 2868, 2181, 1496, 1406, 1352, 1325, 1253, 1205, 1126, 1037, 997, 966, 812, 783, 711, 680, 619. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.14 (s, 3 H, $SiCH_3$), 0.53 (s, 3 H, $SiCH_3$), 3.92 (s, 2 H, CH_2Br), 7.21 (dd, ^3J = 4.5, ^3J = 3.0 Hz, 1 H, thienyl-H), 7.38 (d, ^3J = 3.0 Hz, 1 H, thienyl-H), 7.64 (d, ^3J = 4.5 Hz, 1 H, thienyl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = –0.11 [2 C, $Si(CH_3)_2$], 14.31 (C-3), 89.69 (C-1), 101.56 (C-2), 128.22 (thienyl-C), 131.53 (thienyl-C), 135.43 (thienyl-C). One thienyl signal was not detected. – MS (EI, 70 eV), *m/z* (%): 260/258 (90/86) [M^+], 245/243 (100/96) [M^+ – CH_3], 217/215

(60/53), 179 (80) [M^+ – Br], 139 (77), 121 (78), 97 (80). – HRMS: Calcd. for $C_9H_{11}BrSSi$: 257.9534, correct mass.

2-(9'-Decene-2'-ynyloxy)tetrahydro-2*H*-pyran (**6**-Hept): According to **GP4**, 2-(2'-propynyloxy)tetrahydro-2*H*-pyran (**6**-H, 3.95 g, 28.2 mmol) in 100 mL of anhydrous THF was first treated with *n*-BuLi (11.8 mL, 29.5 mmol, 2.5 M in hexane) at –78 °C, and the mixture subsequently reacted with 7-bromo-1-heptene (5.14 g, 29.0 mmol) and HMPA (5.22 g, 29.1 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.45) yielded **6**-Hept (3.93 g, 59%) as a colorless oil. – IR (film): nu(tilde) = 2935 cm^{-1}, 2856, 2842, 2227, 1641, 1454, 1440, 1346, 1263, 1201, 1116, 1024, 972, 904, 871, 815. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.89 (m, 12 H, 5'-H, 6'-H, 7'-H, THP-H), 1.91–2.10 (m, 2 H, 4'-H*), 2.12–2.26 (m, 2 H, 8'-H*), 3.41–3.58 (m, 1 H, THP-H), 3.73–3.89 (m, 1 H, THP-H), 4.09–4.32 (m, 2 H, CH_2O), 4.74–5.07 (m, 3 H, 10'-H, THP-H), 5.79 (m_c, 1 H, 9'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.72 (–, THP-C), 19.07 (–, C-4') 25.29 (–, THP-C), 28.27 (–, C-5'*), 28.34 (–, C-6'*), 28.39 (–, C-7'*), 30.24 (–, THP-C), 33.58 (–, C-8'), 54.67 (–, C-1'), 61.91 (–, THP-C), 75.73 (C_{quat}, C-2'), 86.54 (C_{quat}, C-3'), 96.52 (+, THP-C), 114.36 (–, C-10'), 138.79 (+, C-9'). – MS (EI, 70 eV), *m/z* (%): 235 (1) [M^+ – H], 193 (4), 152 (19), 141 (61), 135 (24), 93 (85), 85 (94), 55 (100). – $C_{15}H_{24}O_2$ (236.4).

10-Bromo-1-decene-8-yne (**7**-Hept): According to **GP5**, PPh_3 (4.72 g, 18.0 mmol) and bromine (900 µL, 17.5 mmol) were reacted with 2-(9-decene-2-ynyloxy)tetrahydro-2*H*-pyran (**6**-Hept, 3.90 g, 16.5 mmol) in 40 mL of CH_2Cl_2 at –10 °C. Column chromatography on silica gel (60 g, 3 × 30 cm, pentane, R_f = 0.90) yielded **7**-Hept (2.34 g, 66%) as a colorless oil. – IR (film): nu(tilde) = 3076 cm^{-1}, 2931, 2856, 2233, 1639, 1456, 1429, 1328, 1209, 993, 912, 609. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25–1.59 (m, 6 H, 4-H, 5-H, 6-H), 1.95–2.15 (m, 2 H, 3-H*), 2.17–2.30 (m, 2 H, 7-H*), 3.93 (t, ^5J = 2.5 Hz, 2 H, CH_2Br), 4.89–5.07 (m, 2 H, 1-H), 5.80 (m_c, 1 H, 2-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.72 (–, C-10), 18.87 (–, C-7), 28.17 (–, C-4*), 28.41 (–, C-5*), 28.32 (–, C-6*), 33.56 (–, C-3), 75.29 (C_{quat}, C-9), 88.15 (C_{quat}, C-8), 114.36 (–, C-1), 138.79 (+, C-2). – MS (EI, 70 eV), *m/z* (%): 215/213 (<1/<1) [M^+ – H], 135 (42) [M^+ – Br], 119 (60), 93 (91), 79 (86), 55 (100). – $C_{10}H_{15}Br$ (215.1).

General Procedure for the Alkylation of Malonic Ester Derivatives with Alkylbromides or in situ prepared Alkylmesylates (GP 6): *Variant A*: To a suspension of sodium hydride (680 mg, 17.0 mmol, 60% suspension in paraffin oil) in 50 mL of anhydrous THF was slowly added 15.0 mmol of the respective malonic ester derivative at room temperature. After the gas evolution had ceased the reaction mixture was stirred at this temperature for an additional 1 h. Subsequently, 15.0 mmol of the alkyl bromide was added dropwise, and the mixture was stirred at room temperature for 4–16 h. The resulting suspension was slowly poured onto 50 mL of ice water, and the aqueous layer extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the crude product was purified by chromatography on silica gel, eluting with pentane/diethyl ether mixtures.

Variant B: To a solution of 25.0 mmol of a propargylic alcohol and triethylamine (5.06 g, 50.0 mmol, 2.00 equiv.) in 100 mL of diethyl ether was slowly added mesyl chloride (3.09 g, 27.0 mmol) at 0 °C. After stirring for 1 h at this temperature, the voluminous precipitate was filtered off through a pad of celite (5 cm) and the solvent was removed *in vacuo*. The crude mesylate was directly added dropwise to a solution of 25.0 mmol of sodium malonate in 70 mL of THF, freshly prepared according to variant A. Work up was identical to variant A.

Dimethyl 2-(2'-bromoallyl)-2-(3''-cyclopropyl-2''-propynyl)malonate (**5**-Cpr): According to **GP6**, variant B, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 5.40 g, 21.5 mmol) in 70 mL of THF was treated with NaH (920 mg, 23.0 mmol, 60% suspension in paraffin oil) and the mixture was subsequently reacted with the mesylate freshly prepared from 3-cyclopropyl-2-propyn-1-ol (**2**-Cpr, 2.11 g, 21.9 mmol), triethylamine (4.45 g, 44.0 mmol) and mesyl chloride (2.52 g, 22.0 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.45) yielded **5**-Cpr (5.66 g, 80%) as a colorless oil. – IR (film): nu(tilde) = 3094 cm^{-1}, 3008, 2853, 2846, 2253, 1740, 1626, 1436, 1360, 1325, 1291, 1254, 1218, 1149, 1070, 1049, 1035, 975, 953, 901, 849, 815, 770. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.49–0.59 (m, 2 H, Cpr-H), 0.63–0.76 (m, 2 H, Cpr-H), 1.05–1.22 (m, 1 H, Cpr-C), 2.81 (d, ^5J = 2.0 Hz, 2 H, 1''-H), 3.23 (bs, 2 H, 1'-H), 3.72 (s, 6 H,

OCH_3), 5.58 (d, ^2J = 1.7 Hz, 1 H, 3'-H), 5.75–5.78 (m, 1 H, 3'-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = –0.35 (+, Cpr-C), 8.34 (–, 2 C, Cpr-C), 22.74 (–, C-1''), 43.14 (–, C-1'), 53.13 (+, 2 C, OCH_3), 56.53 (–, C-2), 69.42 (–, C-2''), 87.74 (–, C-3''), 122.77 (–, C-3'), 126.55 (–, C-2'), 169.95 (–, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 678/676/674 (24/44/22) [2 M + NH_4^+], 348/346 (52/52) [M + NH_4^+], 331/329 (100/98) [M + H^+]. – $C_{14}H_{17}BrO_4$ (329.2): calcd. C 51.08, H 5.21; found C 51.32, H 5.20.

Dimethyl 2-(2'-bromoallyl)-2-(4'',4''-dimethyl-2''-pentynyl)malonate (**5**-*t*Bu): According to **GP6**, *variant B*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 4.52 g, 18.0 mmol) in 60 mL of THF was treated with NaH (816 mg, 20.4 mmol, 60% suspension in paraffin oil) and the mixture subsequently reacted with the mesylate freshly prepared from 4,4-dimethyl-2-pentyn-1-ol (**2**-*t*Bu, 2.18 g, 19.4 mmol), triethylamine (4.05 g, 40.0 mmol) and mesyl chloride (2.52 g, 22.0 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.45) yielded **5**-*t*Bu (4.54 g, 73%) as a colorless oil. – IR (film): nu(tilde) = 2968 cm^{-1}, 2903, 2867, 2843, 2242, 1740, 1626, 1457, 1436, 1363, 1326, 1292, 1267, 1253, 1217, 1151, 1113, 1075, 1061, 1041, 976, 953, 933, 898, 852, 739. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 [s, 9 H, $C(CH_3)_3$], 2.83 (s, 2 H, 1''), 3.26 (s, 2 H, 1'-H), 3.74 (s, 6 H, OCH_3), 5.60 (d, ^2J = 1.5 Hz, 1 H, 3'-H), 5.78–5.81 (m, 1 H, 3'-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 22.33 (–, C-1'') 27.33 [–, $C(CH_3)_3$], 31.04 [+, 3 C, $C(CH_3)_3$], 42.90 (–, C-1'), 52.83 (+, 2 C, OCH_3), 56.40 (–, C-2), 72.71 (–, C-2''), 93.07 (–, C-3''), 122.43 (–, C-3'), 126.41 (–, C-2'), 169.75 (–, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 364/362 (100/98) [M + NH_4^+], 347/345 (12/12) [M + H^+]. – $C_{15}H_{21}BrO_4$ (345.2): calcd. C 52.19, H 6.13; found C 52.29, H 5.85.

Dimethyl 2-(2'-bromoallyl)-2-(3''-phenyl-2''-propynyl)malonate (**5**-Ph): According to **GP6**, *variant B*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 4.12 g, 16.4 mmol) in 50 mL of THF was treated with NaH (716 mg, 17.9 mmol, 60% suspension in paraffin oil) and the mixture subsequently reacted with the mesylate freshly prepared from 3-phenyl-2-propyn-1-ol (**2**-Ph, 2.41 g, 18.2 mmol), triethylamine (3.85 g, 38.0 mmol) and mesyl chloride (2.18 g, 19.0 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.40)

yielded **5**-Ph (4.73 g, 79%) as a colorless oil, which turned black-green upon prolonged storage. – IR (film): nu(tilde) = 3002 cm^{-1}, 2953, 2842, 1740, 1626, 1598, 1572, 1491, 1435, 1327, 1292, 1250, 1218, 1150, 1070, 1044, 1029, 987, 973, 947, 901, 849, 817, 758, 692. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.14 (s, 2 H, 1"), 3.36 (s, 2 H, 1'-H), 3.78 (s, 6 H, OCH_3), 5.64 (d, ^{2}J = 1.5 Hz, 1 H, 3'-H), 5.85–5.87 (m, 1 H, 3'-H), 7.25–7.40 (m, 5 H, aryl-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 23.11 (–, C-1"), 43.09 (–, C-1'), 53.04 (+, 2 C, OCH_3), 56.27 (–, C-2), 83.97 (–, C-3"), 122.78 (–, C-3'), 122.89 (+, aryl-C), 126.21 (–, C-2'), 128.11 (+, 2 C, aryl-C), 128.21 (+, 2 C, aryl-C), 131.55 (–, aryl-C), 169.60 (–, 2 C, C=O). Signal of C-2" not detected. – MS (200 eV, DCI, NH_3), *m/z* (%): 750/748/746 (5/10/5) [2 M + NH_4^+], 384/382 (100/99) [M + NH_4^+], 367/365 (47/48) [M + H^+]. – $C_{17}H_{17}BrO_4$ (365.2): calcd. C 55.91, H 4.69; found C 55.82, H 4.73.

Dimethyl 2-(2'-bromoallyl)-2-[3''-trimethylsilyl-2''-propynyl]malonate (**5**-TMS): According to **GP6**, *variant A*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 2.01 g, 8.01 mmol) in 40 mL of THF was treated with NaH (400 mg, 10.0 mmol, 60% suspension in paraffin oil) and the mixture subsequently reacted with 3-bromo-1-propynyl(trimethyl)silane (**7**-TMS, 1.53 g, 8.00 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.40) yielded **5**-TMS (2.40 g, 83%) as a colorless oil. – IR (film): nu(tilde) = 2954 cm^{-1}, 2898, 2842, 2179, 1743, 1625, 1436, 1321, 1290, 1251, 1218, 1182, 1028, 910, 846, 734, 644. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.12 [s, 9 H, $Si(CH_3)_3$], 2.91 (s, 2 H, 1"-H), 3.27 (s, 2 H, 1'-H), 3.74 (s, 6 H, OCH_3), 5.60 (d, ^{2}J = 1.6 Hz, 1 H, 3'-H), 5.78–5.80 (m, 1 H, 3'-H). – ^{13}C NMR (50.4 MHz, $CDCl_3$, APT): δ = 0.15 [+, 3 C, $Si(CH_3)_3$], 23.47 (–, C-1"), 42.90 (–, C-1'), 52.93 (+, 2 C, OCH_3), 56.06 (–, C-2), 89.00 (–, C-3"), 101.00 (–, C-2"), 122.66 (–, C-3'), 126.18 (–, C-2'), 169.43 (–, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 380/378 (100/92) [M + NH_4^+], 363/361 (31/26) [M + H^+]. – $C_{14}H_{21}BrO_4Si$ (361.3): calcd. C 46.54, H 5.86; found C 46.40, H 5.77.

Dimethyl 2-(2'-bromoallyl)-2-[3''-*tert*-butyl(dimethyl)silyl-2''-propynyl]malonate (**5**-TBDMS): According to **GP6**, *variant A*, a solution of dimethyl 2-(2'-bromoallyl)-malonate (**4**, 7.03 g, 28.0 mmol) in 90 mL of THF was treated with NaH (1.25 g, 31.3 mmol, 60% suspension in paraffin oil) and the mixture subsequently reacted with 3-

bromo-1-propynyl(*tert*-butyldimethyl)silane (**7**-TBDMS, 6.81 g, 29.2 mmol). Column chromatography on silica gel (150 g, 4 × 25 cm, pentane/diethyl ether 10:1, R_f = 0.40) yielded **5**-TBDMS (9.51 g, 84%) as a colorless oil. – IR (film): nu(tilde) = 2930 cm^{-1}, 2896, 2857, 2178, 1745, 1626, 1471, 1463, 1436, 1362, 1322, 1290, 1251, 1218, 1152, 1072, 1026, 975, 939, 899, 839, 826, 777, 682, 629. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 [s, 6 H, $Si(CH_3)_2$], 0.84 [s, 9 H, $C(CH_3)_3$], 2.88 (s, 2 H, 1''-H), 3.23 (s, 2 H, 1'-H), 3.68 (s, 6 H, OCH_3), 5.55 (d, ^2J = 1.7 Hz, 1 H, 3'-H), 5.73–5.76 (m, 1 H, 3'-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = –4.64 [+, 2 C, $Si(CH_3)_2$], 16.36 [–, *C*$(CH_3)_3$], 23.55 (–, C-1''), 25.95 [+, 3 C, C(*C*$H_3)_3$], 42.93 (–, C-1'), 52.96 (+, 2 C, OCH_3), 56.11 (–, C-2), 87.13 (–, C-3''), 101.49 (–, C-2''), 122.65 (–, C-3'), 126.23 (–, C-2'), 169.43 (–, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 422/420 (100/95) [M + NH_4^+], 405/403 (25/24) [M + H^+]. – $C_{17}H_{27}BrO_4Si$ (403.4): calcd. C 50.62, H 6.75; found C 50.82, H 6.67.

Dimethyl 2-bromotetradeca-1,13-diene-6-yne-4,4-dicarboxylate (**5**-Hept): According to **GP6**, *variant A*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 2.06 g, 8.20 mmol) in 40 mL of THF was treated with NaH (400 mg, 10.0 mmol, 60% suspension in paraffin oil) and the mixture subsequently reacted with 10-bromo-1-decene-8-yne (**7**-Hept, 1.82 g, 8.46 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.45) yielded **5**-Hept (2.08 g, 66%) as a colorless oil. – IR (film): nu(tilde) = 2931 cm^{-1}, 2856, 2233, 1737, 1641, 1625, 1454, 1434, 1326, 1290, 1217, 1201, 1184, 1153, 1070, 904, 850. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.49 (m, 6 H, 9-H, 10-H, 11-H), 1.91–2.14 (m, 4 H, 8-H, 12-H), 2.82 (s, 2 H, 5-H), 3.22 (s, 2 H, 3-H), 3.69 (s, 6 H, OCH_3), 4.82–5.03 (m, 2 H, 14-H), 5.57 (d, ^2J = 1.5 Hz, 1 H, 1-H), 5.63–5.88 (m, 2 H, 1-H, 13-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 18.39 (–, C-8), 22.40 (–, C-5), 28.07 (–, C-9*), 28.23 (–, C-10*), 28.57 (–, C-11*), 33.51 (–, C-12), 42.79 (–, C-3), 52.72 (+, 2 C, OCH_3), 56.12 (C_{quat}, C-4), 73.97 (C_{quat}, C-6), 84.08 (C_{quat}, C-7), 114.24 (–, C-14), 122.24 (–, C-1), 126.26 (C_{quat}, C-2), 138.66 (+, C-13), 169.56 (C_{quat}, 2 C, C=O). – MS (EI, 70 eV), *m/z* (%): 385/383 (2/2) [M^+ – H], 371/369 (20/18) [M^+ – CH_3], 327/325 (59/61) [M^+ – CO_2CH_3], 305 (100) [M^+ – Br], 254 (51), 213 (19), 185 (31), 163 (29), 91 (23). – $C_{18}H_{25}BrO_4$ (385.3): calcd. C 56.11, H 6.54; found C 55.96, H 6.53.

[3'-(2''-Bromoallyloxy)-1'-propynyl]benzene (**9**-Ph): To a solution of 3-phenyl-2-propyn-1-ol (**2**-Ph, 1.32 g, 9.99 mmol) in 15 mL of CH_2Cl_2 was added in sequence cetyltrimethylammonium bromide (182 mg, 501 μmol, 5 mol%), sodium hydroxide solution (15 mL, 50% in water) and 2,3-dibromopropene (**8**, 2.00 g, 10.0 mmol). The mixture was stirred vigorously at room temperature for 24 h, then diluted with CH_2Cl_2 (50 mL) and the resulting mixture was added to water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3×50 mL), the combined organic layers were washed with brine (100 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to leave a residue of about 10 mL, to which diethyl ether (50 mL) was added. The precipitated CETAB was filtered off, and the filtrate concentrated *in vacuo*. Column chromatography on silica gel (100 g, 4×25 cm, pentane/diethyl ether 10:1, $R_f = 0.80$) yielded **9**-Ph (1.73 g, 69%) as a colorless oil. – IR (film): nu(tilde) = 3100 cm^{-1}, 3080, 3056, 3034, 2947, 2898, 2852, 2240, 1953, 1882, 1806, 1640, 1598, 1571, 1490, 1442, 1355, 1256, 1247, 1160, 1085, 1030, 968, 902, 757, 691, 669. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.28 (s, 2 H, 3'), 4.44 (s, 2 H, 1''-H), 5.66–5.70 (m, 1 H, 3''-H), 5.98–6.01 (m, 1 H, 3''-H), 7.30–7.37 (m, 2 H, aryl-H), 7.32–7.51 (m, 3 H, aryl-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 58.16 (–, C-3'), 73.65 (–, C-1''), 84.45 (–, C-2'), 87.16 (–, C-1'), 118.81 (–, C-3''), 122.64 (–, aryl-C), 128.58 (+, aryl-C), 128.85 (+, 2 C, aryl-C), 128.91 (–, C-2''), 132.00 (+, 2 C, aryl-C). – MS (200 eV, DCI, NH_3), *m/z* (%): 522/520/518 (22/44/21) [2 M + NH_4^+], 287/285 (58/58) [M + NH_4^+ + NH_3], 270/268 (97/100) [M + NH_4^+]. – $C_{12}H_{11}BrO$ (251.1): calcd. C 57.39, H 4.42; found C 57.40, H 4.48.

[3-(2'-Bromoallyloxy)-1-propynyl](*tert*-butyl)dimethylsilane (**9**-TBDMS): A solution of 3-[*tert*-butyl(dimethyl)silyl]-2-propyn-1-ol (**2**-TBDMS, 1.70 g, 9.98 mmol) in 10 mL of anhydrous THF was slowly added to a suspension of NaH (516 mg, 12.9 mmol, 60% suspension in paraffin oil) in 50 mL of THF and the mixture was stirred at room temperature for 1 h. Then the mixture was cooled down to 0 °C, 2,3-dibromopropene (**8**, 2.00 g, 10.0 mmol) was slowly added, and the resulting mixture stirred overnight, while letting it warm to room temperature. Saturated NH_4Cl solution (50 mL) was added, the aqueous phase was extracted with diethyl ether (3×50 mL), and the combined ethereal phases were washed with brine (100 mL). After drying over $MgSO_4$ the solvent was removed *in vacuo*, and the

residue subjected to column chromatography on silica gel (60 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.75) to give **9**-TBDMS (2.23 g, 77%) as a colorless oil. – IR (film): nu(tilde) = 2954 cm^{-1}, 2929, 2897, 2857, 2174, 1724, 1670, 1641, 1471, 1463, 1442, 1410, 1390, 1362, 1352, 1251, 1215, 1162, 1090, 1037, 1000, 939, 900, 840, 826, 812, 777, 684, 621. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 [s, 6 H, $Si(CH_3)_2$], 0.94 [s, 9 H, $C(CH_3)_3$], 4.21 (s, 4 H, 3-H, 1'-H), 5.63–5.66 (m, 1 H, 3'-H), 5.91–5.96 (m, 1 H, 3'-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = –4.73 [+, 2 C, $Si(CH_3)$], 16.66 [–, $C(CH_3)_3$], 26.00 [+, 3 C, $C(CH_3)_3$], 57.77 (–, C-3), 73.07 (–, C-1'), 90.62 (–, C-1), 101.10 (–, C-2), 118.64 (–, C-3'), 128.61 (–, C-2'). – MS (200 eV, DCI, NH_3), *m/z* (%): 325/323 (18/17) [M + NH_4^+ + NH_3], 308/306 (98/100) [M + NH_4^+]. – $C_{12}H_{21}BrOSi$ (289.3): calcd. C 49.82, H 7.32; found C 49.61, H 7.14.

***N*-(2'-Bromoallyl)-*N*-{3''-phenyl-2''-propynyl}-4-methylbenzenesulfonamide** (**11**-Ph): *N*-(2-Bromoallyl)-*N*-(*p*-tosyl)amine (**10**, 2.61 g, 8.99 mmol) was added in small portions to a suspension of NaH (380 mg, 9.50 mmol, 60% suspension in paraffin oil) in 50 mL of anhydrous THF at 0 °C. The resulting suspension was stirred at 0 °C for 1 h, after which (3-bromo-1-propynyl)benzene (**7**-Ph, 1.76 g, 9.02 mmol) was added dropwise. The mixture was allowed to reach room temperature, and stirring was continued for 24 h. Ice-cold water (50 mL) was carefully added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were washed with brine (50 mL). The solvent was removed *in vacuo* and the residue subjected to column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.35) to give **11**-Ph (2.80 g, 77%) as a yellow oil, which solidified upon storage in a freezer. – IR (film): nu(tilde) = 3063 cm^{-1}, 2923, 2853, 2243, 1630, 1598, 1490, 1442, 1400, 1352, 1253, 1164, 1093, 1071, 899, 815, 758, 691, 660. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 4.18 (s, 2 H, 1'*), 4.38 (s, 2 H, 1''*-H), 5.70 (bs, 1 H, 3'-H), 5.99 (bs, 1 H, 3'-H), 7.07 (d, ^3J = 9.0 Hz, 2 H, aryl-H), 7.19–7.39 (m, 5 H, aryl-H), 7.76 (d, ^3J = 9.0 Hz, 2 H, aryl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.42 (+, CH_3), 37.04 (–, C-1''), 54.17 (–, C-1'), 81.06 (–, C-2''), 86.03 (–, C-3''), 120.35 (–, C-3'), 121.85 (C_{quat}, aryl-C), 126.97 (C_{quat}, C-2'), 127.72 (+, aryl-C), 128.12 (+, 2 C, aryl-C), 128.52 (+, 2 C, aryl-C), 129.62 (+, 2 C, aryl-C), 131.45 (+, 2 C, aryl-C), 135.77 (C_{quat}, aryl-C), 143.82 (C_{quat}, aryl-C). – MS (200 eV, DCI, NH_3), *m/z* (%): 828/826/824 (17/32/15) [2 M + NH_4^+], 440/438 (44/43) [M +

$NH_4^+ + NH_3$], 423/421 (98/100) [M + NH_4^+]. – $C_{19}H_{18}BrNO_2S$ (404.3): calcd. C 56.44, H 4.49; found C 56.69, H 4.70.

***N*-(2'-Bromoallyl)-*N*-{3''-[*tert*-butyl(dimethyl)silyl]-2''-propynyl}-4-methyl-1-benzenesulfonamide** (**11**-TBDMS): *N*-(2-Bromoallyl)-*N*-(*p*-tosyl)amine (**10**, 1.89 g, 6.51 mmol) was added in small portions to a suspension of NaH (276 mg, 6.90 mmol, 60% suspension in paraffin oil) of NaH in 40 mL of anhydrous THF at 0 °C. The resulting suspension was stirred at 0 °C for 1 h, then 3-bromo-1-propynyl(*tert*-butyl)dimethylsilane (**7**-TBDMS, 1.53 g, 6.56 mmol) was added dropwise. The mixture was allowed to reach room temperature and stirring was continued for 18 h. Ice-cold water (50 mL) was carefully added and the aqueous phase was extracted with CH_2Cl_2 (3×50 mL) and the combined organic layers were washed with brine (50 mL). The solvent was removed *in vacuo*, and the residue subjected to column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether 10:1, $R_f = 0.30$) to give **11**-TBDMS (2.19 g, 76%) as a colorless oil, which solidified upon storage in a freezer. – IR (film): nu(tilde) = 2953 cm^{-1}, 2928, 2894, 2857, 2176, 1630, 1598, 1495, 1471, 1463, 1435, 1406, 1355, 1306, 1250, 1185, 1165, 1094, 1073, 1002, 925, 901, 840, 828, 813, 777, 706, 682, 664, 609. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = –0.13 [s, 6 H, $Si(CH_3)_2$], 0.77 [s, 9 H, $C(CH_3)_3$], 2.41 (s, 3 H, CH_3), 4.07 (s, 2 H, 1'*), 4.16 (s, 2 H, 1"*-H), 5.67 (bs, 1 H, 3'-H), 5.92–5.95 (m, 1 H, 3'-H), 7.28 (d, ^3J = 9.0 Hz, 2 H, aryl-H), 7.72 (d, ^3J = 9.0 Hz, 2 H, aryl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = –4.94 [+, 2 C, $Si(CH_3)_2$], 16.17 [C_{quat}, $C(CH_3)_3$], 21.52 (+, CH_3), 25.80 [+, 3 C, $C(CH_3)_3$], 36.97 (–, C-1''), 53.72 (–, C-1'), 89.90 (–, C-3''), 97.84 (–, C-2''), 120.32 (–, C-3'), 126.83 (C_{quat}, C-2'), 127.54 (+, 2 C, aryl-C), 129.68 (+, 2 C, aryl-C), 135.89 (C_{quat}, aryl-C), 143.65 (C_{quat}, aryl-C). – MS (200 eV, DCI, NH_3), *m/z* (%): 904/902/900 (32/43/19) [2 M + NH_4^+], 478/476 (17/15) [M + NH_4^+ + NH_3], 461/459 (100/87) [M + NH_4^+]. – $C_{19}H_{28}BrNO_2SSi$ (442.5): calcd. C 51.57, H 6.38; found C 51.89, H 6.17.

Dimethyl 2-(2'-bromoallyl)-2-[3''-tributylstannyl-2''-propynyl]malonate (**5**-$SnBu_3$): To a solution of dimethyl 2-(2'-bromoallyl)-2-(2"-propynyl)malonate (**5**-H, 3.38 g, 11.7 mmol) in 30 mL of anhydrous THF was slowly added at –78 °C *n*-BuLi (4.80 mL, 12.0 mmol, 2.5 M in hexane). The solution was stirred at this temperature

for 3 h, then tri(*n*-butyl)chlorostannane (3.74 g, 11.5 mmol) was added dropwise. The reaction mixture was allowed to reach room temperature overnight, was then added to 30 mL of sat. NH_4Cl solution, and the aqueous phase was extracted with diethyl ether (3×50 mL). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether 10:1, $R_f = 0.40$) yielded **5**-Sn (4.54 g, 67%) as a colorless liquid with a disgusting smell. – IR (film): nu(tilde) = 2955 cm^{-1}, 2928, 2872, 2854, 2153, 1745, 1626, 1457, 1435, 1377, 1322, 1290, 1251, 1217, 1200, 1152, 1116, 1072, 1046, 1008, 976, 961, 898, 849, 672. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 7.1 Hz, 9 H, *n*Bu-CH_3), 1.20–1.70 (m, 18 H, *n*Bu-CH_2), 2.94 (s, 2 H, 1''-H), 3.30 (s, 2 H, 1'-H), 3.73 (s, 6 H, OCH_3), 5.60 (d, ^2J = 1.5 Hz, 1 H, 3'-H), 5.82–5.85 (m, 1 H, 3'-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 10.96 (–, 3 C, $SnCH_2$), 13.59 (+, 3 C, CH_3), 23.79 (–, C-1''), 26.03 (–, 3 C, *n*Bu-CH_2), 28.81 (–, 3 C, *n*Bu-CH_2), 42.80 (–, C-1'), 53.79 (+, 2 C, OCH_3), 56.17 (–, C-2), 86.63 (–, C-3''), 104.77 (–, C-2''), 122.50 (–, C-2'), 126.33 (–, C-3'), 169.54 (–, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 581/580/579/578/577/576/575 (<1/1/3/1/2/1/<1) [M + H^+], 308 (100). – $C_{23}H_{39}BrO_4Sn$ (578.1).

Dimethyl 2-(2'-bromoallyl)-2-{3''-[(2'''-thienyl)dimethylsilyl]-2''-propynyl}-malonate (**5**-ThDMS): According to **GP6**, *variant A*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 4.52 g, 18.0 mmol) in 60 mL of THF was treated with NaH (792 mg, 19.8 mmol, 60% suspension in paraffin oil), and the mixture subsequently reacted with 3-bromo-1-propynyl(dimethyl)-2-thienylsilane (**7**-ThDMS, 4.72 g, 18.2 mmol). Column chromatography on silica gel (100 g, 3×30 cm, pentane/diethyl ether 10:1, $R_f = 0.40$) yielded **5**-ThDMS (5.72 g, 74%) as a yellowish oil. – IR (film): nu(tilde) = 3105 cm^{-1}, 3002, 2954, 2900, 2842, 2181, 1741, 1626, 1499, 1435, 1406, 1325, 1290, 1252, 1216, 1151, 1085, 1072, 1028, 997, 975, 902, 838, 815, 783, 712, 682, 634. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.43 [s, 6 H, $Si(CH_3)_2$], 2.98 (s, 2 H, 1''-H), 3.31 (s, 2 H, 1'-H), 3.73 (s, 6 H, OCH_3), 5.59 (d, ^2J = 1.5 Hz, 1 H, 3'-H), 5.76–5.79 (m, 1 H, 3'-H), 7.19 (dd, ^3J = 4.6, ^3J = 3.2 Hz, 1 H, thienyl-H), 7.33 (d, ^3J = 3.2 Hz, 1 H, thienyl-H), 7.62 (d, ^3J = 4.6 Hz, 1 H, thienyl-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$, APT): δ = 0.21 [+, 2 C, $Si(CH_3)_2$], 23.61 (–, C-1''), 42.97 (–, C-1'), 53.02 (+, 2 C, OCH_3), 56.04 (–, C-2), 86.66 (–, C-3''), 103.01 (–, C-2''), 122.88 (–, C-3'), 126.08

(–, C-2'), 128.20 (+, thienyl-C), 131.31 (+, 2 C, thienyl-C), 135.11 (–, thienyl-C), 169.39 (–, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 878/876/874 (1/2/1) [2 M + NH_4^+], 448/446 (100/90) [M + NH_4^+]. – $C_{17}H_{21}BrO_4SSi$ (429.4): calcd. C 47.55, H 4.93; found C 47.32, H 4.66.

Dimethyl 2-(2'-bromoallyl)-2-(4''-methyl-4''-penten-2''-ynyl)malonate (**28a**): According to **GP6**, *variant B*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 3.41 g, 13.6 mmol) in 50 mL of THF was treated with NaH (568 mg, 14.2 mmol, 60% suspension in paraffin oil) and the mixture subsequently reacted with the mesylate freshly prepared from 4-methyl-4-penten-2-yn-1-ol (**26a**, 1.35 g, 14.0 mmol), triethylamine (2.83 g, 28.0 mmol) and mesyl chloride (1.60 g, 14.0 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.50) gave **28a** (3.09 g, 69%) as an unstable yellowish oil, which turned dark-orange quickly. – IR (film): nu(tilde) = 3058 cm^{-1}, 2954, 2252, 1734, 1435, 1372, 1267, 1203, 1168, 1073, 965, 894, 737, 703. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.81 (bs, 3 H, CH_3), 2.99 (bs, 2 H, 1''-H), 3.26 (bs, 2 H, 1'-H), 3.73 (s, 6 H, OCH_3), 5.13–5.16 (m, 1 H, 5''-H), 5.17 (bs, 1 H, 5''-H), 5.60 (d, ^2J = 1.5 Hz, 1 H, 3'-H), 5.78 (bs, 1 H, 3'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.74 (–, C-1''), 23.44 (+, C=C*C*H_3), 42.97 (–, C-1'), 52.90 (+, 2 C, OCH_3), 56.14 (C_{quat}, C-2), 82.82 (C_{quat}, C-2''), 85.38 (C_{quat}, C-3''), 121.44 (–, C-5''), 122.77 (–, C-3'), 126.17 (C_{quat} , C-4''*), 126.55 (C_{quat}, C-2'*), 169.51 (–, 2 C, C=O). – MS (EI, 70 eV), *m/z* (%): 330/328 (<1/1), 326 (32), 298 (24), 267 (36), 238 (45), 207 (26) [M^+ – C_3H_4Br – H_2], 179 (21), 83 (100). – $C_{14}H_{17}BrO_4$ (329.2).

Dimethyl 2-(2'-bromoallyl)-2-[3''-(1'''-cyclohexenyl)-2''-propynyl]malonate (**28b**): According to **GP6**, *variant B*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 4.02 g, 16.0 mmol) in 50 mL of THF was treated with NaH (724 mg, 18.1 mmol, 60% suspension in paraffin oil), and the mixture subsequently reacted with the mesylate freshly prepared from 3-(1'-cyclohexenyl)-2-propyn-1-ol (**26b**, 2.44 g, 17.9 mmol), triethylamine (3.64 g, 36.0 mmol) and mesyl chloride (2.06 g, 18.0 mmol). Column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.50) gave **28b** (4.20 g, 71%) as a yellowish oil. – IR (film): nu(tilde) = 3024 cm^{-1}, 2929, 2858, 2244, 1742, 1626, 1436, 1325, 1291, 1252, 1217,

1150, 1070, 1043, 975, 955, 899, 847, 801. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48–1.66 (m, 4 H, 4'''-H, 5'''-H), 1.98–2.13 (m, 4 H, 3'''-H, 6'''-H), 2.99 (s, 2 H, 1''-H), 3.28 (s, 2 H, 1'-H), 3.74 (s, 6 H, OCH_3), 5.61 (d, ^{2}J = 1.5 Hz, 1 H, 3'-H), 5.80–5.83 (m, 1 H, 3'-H), 5.96–6.02 (m, 1 H, 2'''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 21.34 (–, C-3'''*), 22.74 (–, C-1''*), 22.91 (–, C-4'''*), 25.38 (–, C-5'''), 29.21 (–, C-6'''), 42.91 (–, C-1'), 52.87 (+, 2 C, OCH_3), 56.15 (C_{quat}, C-2), 80.68 (C_{quat}, C-2''), 85.95 (C_{quat}, C-3''), 120.44 (C_{quat}, C-1'''), 122.61 (–, C-3'), 126.18 (C_{quat}, C-2'), 134.26 (+, C-2'''), 169.59 (C_{quat}, 2 C, C=O). – MS (200 eV, DCI, NH_3), *m/z* (%): 758/756/754 (1/2/1) [2 M + NH_4^+], 388/386 (100/90) [M + NH_4^+], 371/369 (95/95) [M + H^+]. – $C_{17}H_{21}BrO_4$ (369.3).

Dimethyl 2-(2'-bromoallyl)-2-[(*E*)-5''-methoxy-4''-penten-2''-ynyl]malonate (**28c**): According to **GP6**, *variant B*, a solution of dimethyl 2-(2'-bromoallyl)malonate (**4**, 1.56 g, 6.21 mmol) in 20 mL of THF was treated with NaH (280 mg, 7.00 mmol, 60% suspension in paraffin oil), and the mixture subsequently reacted with the mesylate freshly prepared from (*E*)-5-methoxy-4-penten-2-yn-1-ol (**26c**, 785 mg, 7.00 mmol), triethylamine (1.47 g, 14.5 mmol) and mesyl chloride (802 mg, 7.00 mmol). The mesylate could **not** completely be freed from solvent, otherwise rapid polymerization occurred. Rapid column chromatography on silica gel (100 g, 3 × 30 cm, pentane/diethyl ether 10:1, R_f = 0.40) gave **28c** (813 mg, 38%) as an unstable orange oil. – IR (film): nu(tilde) = 3003 cm^{-1}, 2955, 2844, 2217, 1739, 1670, 1626, 1436, 1387, 1325, 1292, 1219, 1149, 1069, 973, 912, 850, 733, 665, 649. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.05 (d, ^{5}J = 2.4 Hz, 2 H, 1''-H), 3.31 (bs, 2 H, 1'-H), 3.72 (s, 3 H, OCH_3), 3.75 (s, 6 H, OCH_3), 4.40–4.46 (dt, ^{3}J = 6.4, ^{5}J = 2.4 Hz, 1 H, 4''-H), 5.61 (d, ^{2}J = 1.5 Hz, 1 H, 3'-H), 5.93 (bs, 1 H, 3'-H), 6.21 (d, ^{3}J = 6.4 Hz, 1 H, 5''-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 22.26 (–, C-1''), 42.74 (–, C-1'), 52.90 (+, OCH_3), 53.14 (+, 2 C, OCH_3), 55.70 (C_{quat}, C-2), 81.61 (C_{quat}, C-3''), 82.91 (C_{quat}, C-2''), 91.62 (+, C-4''), 123.15 (–, C-3'), 125.43 (C_{quat} , C-2'), 156.99 (+, C-5''), 168.64 (–, C=O), 169.28 (–, C=O). – MS (EI, 70 eV), *m/z* (%): 346/344 (1/1) [M^+], 265 (9) [M^+ – Br], 237 (17), 171 (100), 139 (28), 111 (30), 73 (95). – $C_{14}H_{17}BrO_5$ (345.2).

[1] M. D. Bailey, T. Halmos, D. Adamson, J. Bordeleau, C. Grand-Maitre, *Tetrahedron: Asymmetry* **1999**, *10*, 3285–3295.

[2] D. C. Billington, W. J. Kerr, P. L. Pauson, *J. Organomet. Chem.* **1987**, *328*, 223–227.

[3] C.W. Lee, K. S. Oh, K. S. Kim, K. H. Ahn, *Org. Lett.* **2000**, *2*, 1213–1216.

[4] A. B. Charette, C. Molinaro, C. Brochu, *J. Am. Chem. Soc.* **2000**, *123*, 12168–12175.

[5] T. Konoike, T. Hayashi, Y. Araki, *Tetrahedron: Asymmetry* **1994**, *5*, 1559–1566.

[6] I. E. Dolgi, K. N. Shavrin, S. V. Pavlycheva, *Izv. Akad. Nauk SSSR* **1985**, *9*, 2146–2147.

[7] T. Laird, W. D. Ollis, I. O. Sutherland, *J. Chem. Soc. Perkin Trans. I* **1980**, *9*, 2033–2048.

[8] A. L. Hurley, M. E. Welker, C. S. Day, *J. Organomet. Chem.* **2000**, *598*, 150–159.

[9] A. Dornow, F. Ische, *Chem. Ber.* **1956**, *89*, 880–883.

[10] N. L. Hungerford, W. Kitching, *J. Chem. Soc. Perkin Trans. I* **1998**, *11*, 1839–1858.

[11] D. Bom, D. P. Curran, S. Kruszewski, S. G. Zimmer, J. T. Strode, G. Kohlhagen, W. Du, A. J. Chavan, K. A. Fraley, A. L. Bingcang, L. J. Latus, Y. Pommier, T. G. Burke, *J. Med. Chem.* **2000**, *43*, 3970–3980.