Six- and Eightfold Palladium-Catalyzed Cross-Coupling Reactions of Hexa- and Octabromoarenes

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General procedure for the preparation of catechol boronates 2 (GP 1): A 1 M solution of catecholborane in THF (10 mmol) was added to the respective alkyne 3 (10 mmol) at ambient temp. and the mixture heated at 70 °C for the stated time. The reaction mixture was cooled to ambient temp. and distilled in vacuo.

General procedure for the preparation of pinacol boronates 4 (GP 2): A solution of BH$_3$·SMe$_2$ (20 mmol, 10 M in dimethyl sulfide) was added dropwise to a solution of pinacol (20 mmol, 2.36 g) in CH$_2$Cl$_2$ (2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, then warmed up to ambient temp., and stirred until the evolution of hydrogen had ceased. The respective alkyne 3 (6 mmol) was slowly added with vigorous stirring at 0 °C. The reaction mixture was warmed to ambient temp. and stirred for the stated time. Then diethyl ether (150 mL), and a solution of NH$_4$Cl (250 mL) was added with stirring. The organic layer was washed quickly with a solution of NH$_4$Cl (100 mL), dried (MgSO$_4$), and the solvents were removed in vacuo. The residue was purified by flash column chromatography.

General procedure for the preparation of methyl ketones 6 (GP 3): A solution of methyllithium (1.66 M, 66 mL, 0.11 mol) in diethyl ether was added at 0 °C to a stirred solution of the respective carboxylic acid 5 (50.0 mmol) in ether (250 mL), the mixture was stirred for an additional 30 min at this temp. and for 4 h at 20 °C. The reaction mixture was poured slowly with vigorous stirring into a solution of conc. HCl (25 mL) in ice water (500 mL). The aq. layer was extracted with diethyl ether (3 × 80 mL), and the combined
organic layers were washed with NaHCO₃ solution (100 mL), dried (MgSO₄) and concentrated.

**General procedure for the preparation of terminal alkynes 3 (GP 4):** A solution of the respective methyl ketone 6 (25 mmol) in THF (30 mL) was slowly added at –78 °C to a solution of lithium diisopropylamide (LDA), freshly prepared from diisopropylamine (30 mmol) in THF (30 mL) and n-butyllithium (28 mmol) in hexane. After 1 h of stirring at this temperature, diethyl chlorophosphate (28 mmol) was added, and the mixture slowly warmed to ambient temp. and stirred for an additional 3 h. This mixture was added to a second LDA solution, prepared from diisopropylamine (50 mmol) in THF (50 mL) and nBuLi (50 mmol) at –78 °C, slowly warmed to room temp. and stirred for 12 h. Then the reaction was quenched with water (100 mL). The aq. layer was extracted with pentane (3 × 80 mL), the combined organic layers were washed with ice-cold 1 N HCl (2 × 50 mL), water (2 × 50 mL) and portions of a solution of NaHCO₃ until pH 8, dried (MgSO₄) and concentrated.

**General procedure for the preparation of alkenylstannanes 19 (GP 5):** Freshly distilled tri-n-butyltin hydride (5 mmol) and azoisobutyronitrile (0.5 mmol) were added to the respective alkyne 3 (10 mmol) in a screw-capped Pyrex bottle and were stirred at 80 °C for 24 h. Then the reaction mixture was filtered through a bed of Celite.

**2-[(E)-2-(Adamantyl)ethenyl]-1,3,2-benzodioxaborol (2b):** According to GP 1, compound 3b (570 mg, 3.56 mmol) was treated with a solution of catecholborane in THF (4 mL, 4 mmol). Twofold Kugelrohr distillation yielded 2b (956 mg, 96%) as a colorless solid. M.p. 114–118 °C; IR (KBr): ν(tilde) = 3060 cm⁻¹ (C–H), 2905, 2847 (C–H), 1632 (C=C), 1470 (CH₂), 1395, 1366, 1329, 1268, 1233, 1125, 1002, 916, 808, 738; ¹H NMR (250 MHz, CDCl₃): δ = 1.68–1.76 [m, 12 H, 2''-H, 4''-H], 2.05 (br s, 3 H, 3''-H), 5.66 (d, J = 18.4 Hz, 1 H, 1'-H), 6.92 (d, J = 18.4 Hz, 1 H, 2'-H), 7.05–7.09 (m, 2 H, Ph-H), 7.20–7.24 ppm (m, 2 H, Ph-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 28.3 (+, C-3’’), 36.8 (−, C-4’’), 37.3 (C quat, C-1’’), 41.2 (−, C-2’’*), 112.2 (+, Ph-C), 122.4 (+, Ph-C), 148.3 [C quat,
C-3a(7a)], 167.5 ppm (+, C-2'); MS (70 eV), m/z (%): 280 (20) [M]+, 136 (100), 110 (60), 92 (15), 64 (20); HRMS calcd. for C_{18}H_{21}BO_{2}: 280.1634, found 280.1634.

2-[(E)-2-(1-Methylcyclohexyl)ethenyl]-1,3,2-benzodioxaborol (2c): According to GP 1, compound 3c (1.22 g, 10.0 mmol) was treated with a solution of catecholborane in THF (10 mL, 10 mmol). Kugelrohr distillation yielded 2c (1.48 g, 61%) as a colorless oil. B.p. 140 °C/0.1 Torr; IR (film): ν(tilde) = 3053 cm$^{-1}$ (C–H), 2936, 2848, 1632 (C=C), 1472, 1369, 1331, 1236 (C–O), 1099, 1003, 807, 746; $^1$H NMR (250 MHz, CDCl$_3$): δ = 1.05 (s, 3 H, CH$_3$), 1.36–1.68 (m, 10 H, CH$_2$), 5.76 (d, $^3$J = 18.5 Hz, 1 H, 1'-H), 7.05 (d, $^3$J = 18.5 Hz, 1 H, 2'-H), 7.02–7.11 (m, 2 H, Ph-H), 7.29–7.25 ppm (m, 2 H, Ph-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): δ = 22.4 (–, CH$_2$), 26.2 (–, C-4”), 26.8 (+, CH$_3$), 37.0 (–, CH$_2$), 38.4 (C$_{quat}$, C-3’), 112.2 (+, Ph-C), 122.4 (+, Ph-C), 148.2 [C$_{quat}$, C-3a(7a)], 167.2 ppm (+, C-2'); MS (70 eV), m/z (%): 242/241 (32/8) [M]+, 160/159 (30/8), 136 (80), 110 (100), 92 (20), 64 (40); HRMS calcd. for C$_{15}$H$_{19}$BO$_2$ (242.1): 242.1478, found 242.1478.

2-[(E)-2-(1-Methylcyclopropyl)ethenyl]-1,3,2-benzodioxaborol (2d): According to GP 1, compound 3d (1.60 g, 20.0 mmol) was treated with a solution of catecholborane in THF (20 mL, 20 mmol). Twofold Kugelrohr distillation yielded 2d (1.26 g, 31%) as a colorless oil. B.p. 75 °C/0.1 Torr; IR (film): ν(tilde) = 3057 cm$^{-1}$ (C–H), 2961, 1624 (C=C), 1508, 1473, 1423, 1403, 1372, 1337, 1235 (C–O), 807, 744; $^1$H NMR (250 MHz, CDCl$_3$): δ = 0.80 (br s, 2 H, cPr-H), 0.83 (br s, 2 H, cPr-H), 1.28 (s, 3 H, CH$_3$), 5.71 (d, $^3$J = 18.1 Hz, 1 H, 1’-H), 6.54 (d, $^3$J = 18.1 Hz, 1 H, 2’-H), 7.04–7.08 (m, 2 H, Ph-H), 7.18–7.22 ppm (m, 2 H, Ph-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): δ = 16.7 (–, cPr-C), 20.0 (+, CH$_3$), 20.4 (C$_{quat}$, C-3’), 112.2 (+, Ph-C), 122.4 (+, Ph-C), 148.3 [C$_{quat}$, C-3a(7a)], 165.3 ppm (+, C-2’); MS (70 eV), m/z (%): 200/199 (64/18) [M]+, 185/184 (100/25) [M – CH$_3$]+, 144 (15), 80 (16), 67 (16); HRMS calcd. for C$_{12}$H$_{13}$BO$_2$ (200.2): 200.1008, found 200.1008.

2-[(E)-3’,3’-Dimethylpentenyl]-1,3,2-benzodioxaborol (2e): According to GP 1, compound 3e (962 mg, 10.0 mmol) was treated with a solution of catecholborane in THF (10 mL,
Twofold Kugelrohr distillation yielded 2e (637 mg, 29%) as a colorless oil. B.p. 60 °C/0.1 Torr; IR (film): \( \nu (\widetilde{\text{C–H}}) = 3061 \text{ cm}^{-1} \), 2961, 1635 (C=C), 1476, 1343, 1235 (C–O), 1124, 1048, 1003, 808, 737; \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 0.85 \) (t, \( ^3J = 7.3 \text{ Hz} \), 3 H, 5'-H), 1.09 [s, 6 H, C(CH\(_3\))\(_2\)], 1.42 (q, \( ^3J = 7.3 \text{ Hz} \), 2 H, 4'-H), 5.69 (d, \( ^3J = 18.4 \text{ Hz} \), 1 H, 1'-H), 6.81 (d, \( ^3J = 18.4 \text{ Hz} \), 1 H, 2'-H), 6.92–7.15 (m, 2 H, Ph-H), 7.18–7.24 ppm (m, 2 H, Ph-H); \(^13\)C NMR (62.9 MHz, CDCl\(_3\), additional DEPT): \( \delta = 8.9 \) (+, C-5'), 25.7 [+, C(CH\(_3\))\(_2\)], 34.5 (–, C-4'), 38.6 (C\(_\text{quat}\), C-3'), 112.2 (+, Ph-C), 122.4 (+, Ph-C), 148.2 [C\(_\text{quat}\), C-3a(7a)], 166.7 ppm (+, C-2'); MS (70 eV), \( m/z \) (%): 216/215 (15/4) \([M]^+\), 201/200 (16/4) \([M – \text{CH}_3]^+\), 136 (24), 110 (100), 64 (20); HRMS calcd. for C\(_{13}\)H\(_{17}\)BO\(_2\) (216.1): 216.1321, found 216.1321.

\( 2\)-(\(E\)-3',3'-Dimethyl-5'-methoxypentenyl)-1,3,2-benzodioxaborol (2h): According to GP 1, compound 3h (3.41 g, 27.0 mmol) was treated with a solution of catecholborane in THF (28 mL, 28 mmol) for 5 h. Kugelrohr distillation yielded 2h (1.79 g, 27%) as a colorless oil. B.p. 125 °C/0.1 Torr; \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 1.13 \) [s, 6 H, C(CH\(_3\))\(_2\)], 1.74 (t, \( ^3J = 7.5 \text{ Hz} \), 2 H, 4'-H), 3.33 (s, 3 H, OCH\(_3\)), 3.40 (t, \( ^3J = 7.5 \text{ Hz} \), 2 H, 5'-H), 5.74 (d, \( ^3J = 18.4 \text{ Hz} \), 1 H, 1'-H), 6.95–7.28 ppm (m, 5 H, Ph-H, 2'-H); \(^13\)C NMR (62.9 MHz, CDCl\(_3\), additional DEPT): \( \delta = 26.6 \) (+, C(CH\(_3\))\(_2\)), 37.4 (C\(_\text{quat}\), C-3'), 41.0 (–, C-4'), 58.5 (+, OCH\(_3\)), 69.8 (–, C-5'), 112.2 (+, Ph-C), 122.5 (+, Ph-C), 148.2 [C\(_\text{quat}\), C-3a(7a)], 165.7 ppm (+, C-2'); MS (70 eV), \( m/z \) (%): 246 (4) \([M]^+\), 192 (12), 136 (100); HRMS calcd. for C\(_{14}\)H\(_{19}\)BO\(_3\) (246.1): 246.1427, found 246.1427.

\( 2\)-(\(E\)-3',3'-Dimethyl-6'-methoxyhexenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f): According to GP 2, compound 3f (1.40 g, 10.0 mmol) was added to a solution of pinacolborane, prepared from pinacol (2.36 g, 20.0 mmol) and BH\(_3\)·SMe\(_2\) (2.0 ml, 20 mmol), and the mixture was stirred for 16 h at ambient temp. Flash column chromatography on silica gel [90 g, pentane/diethyl ether (5:1), column 3\( \times \)35 cm] yielded 4f (973 mg, 36%) as a colorless oil, \( R_f = 0.40 \). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 0.99 \) [s, 6 H, C(CH\(_3\))\(_2\)], 1.25 [s, 12 H, C(CH\(_3\))\(_2\)], 1.26–1.38 (m, 2 H, 4'-H), 1.41–1.53 (m, 2 H, 5'-H), 3.30 (s, 3 H, OCH\(_3\)), 3.31 (t, \( ^3J = 6.4 \text{ Hz} \), 2 H, 6'-H), 5.33 (d, \( ^3J = 18.4 \text{ Hz} \), 1 H, 1'-H), 6.54 ppm (d, \( ^3J = 18.4 \text{ Hz} \), 1 H, 2'-H); \(^13\)C NMR (62.9 MHz, CDCl\(_3\), additional DEPT): \( \delta = 24.8 \) (+, C(CH\(_3\))\(_2\)), 24.9 (–, C-4'), 26.4 (+, C(CH\(_3\))\(_2\)), 37.7 (C\(_\text{quat}\), C-3'), 38.5 (–, C-5'), 58.5 (+, OCH\(_3\)), 73.5 (–, C-6'), 83.0 [C\(_\text{quat}\), C-4(5)], 163.0 ppm (+, C-2'); MS (70 eV), \( m/z \) (%): 268 (2) \([M]^+\), 197 (18), 153 (19), 110
(21), 101 (32), 95 (50), 82 (100); HRMS calcd. for C_{15}H_{29}BO_{3} (268.2): 268.2210, found 268.2209.

1-Ethynyladamantane (3b): According to GP 4, compound 6b (1.00 g, 5.61 mmol) in THF (3 mL) was added to a solution of LDA, prepared from diisopropylamine (0.9 mL, 6.7 mmol) in THF (6 mL) and nBuLi (2.6 mL, 2.36 M, 6.1 mmol). After 1 h of stirring diethyl chlorophosphate (1.03 g, 5.97 mmol) was added and the mixture slowly warmed to room temp. The reaction mixture was added to a second portion of an LDA solution, prepared from diisopropylamine (1.5 mL, 11 mmol) in THF (10 mL) and nBuLi (5.0 mL, 2.36 M, 12 mmol). Sublimation at 60 °C/20 Torr yielded 559 mg (62%) of 3b as colorless needles. M.p. 78 °C (Lit.\textsuperscript{[1]} 83 °C); \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): \delta = 1.68 (t, \ J = 3.0 Hz, 6 H, 4-H), 1.88 (d, \ J = 3.0 Hz, 6 H, 2-H), 1.95 (br s, 3 H, 3-H), 2.09 ppm (s, 1 H, 2'-H); \textsuperscript{13}C NMR (62.9 MHz, CDCl\textsubscript{3}, additional DEPT): \delta = 27.8 (+, C-3), 29.3 (C\textsubscript{quat}, C-1), 36.3 (–, C-4*), 42.7 (–, C-2*), 66.6 (+, C-2'), 93.0 ppm (C\textsubscript{quat}, C-1'); MS (70 eV), \textit{m/z} (%): 160 (100) [\textit{M}]^+, 145 (20), 131 (15), 117 (20), 103 (20), 91 (20); C\textsubscript{12}H\textsubscript{16} (160.3).

1-Ethynyl-1-methylcyclohexane (3c): According to GP 4, compound 6c (3.5 g, 25 mmol) in THF (3 mL) was added to an LDA solution, prepared from diisopropylamine (3.0 g, 30 mmol) in THF (30 mL) and nBuLi (18 mL, 1.6 M, 29 mmol). After 1 h of stirring, diethyl chlorophosphate (4.8 g, 28 mmol) was added, and the mixture slowly warmed to room temp. The reaction mixture was added to a second portion of an LDA solution, prepared from diisopropylamine (5.1 g, 50 mmol) in THF (50 mL) and nBuLi (31 mL, 1.6 M, 50 mmol). Distillation of the crude product yielded 3c (2.6 g, 85%). B.p. 111 °C/200 Torr (Lit.\textsuperscript{[2]} 48 °C/15 Torr); IR (film): \textit{nu}(tilde) = 3310 cm\textsuperscript{-1} (C≡C–H), 2929 (C–H), 2854, 1448, 1376, 1292, 1071, 968, 932, 627; \textsuperscript{1}H NMR (250 MHz, CDCl\textsubscript{3}): d = 1.09–1.24 (m, 2 H, 4-H), 1.21 (s, 3 H, 1-CH\textsubscript{3}), 1.51–1.78 (m, 8 H, CH\textsubscript{2}), 2.12 ppm (s, 1 H, (C≡C–H); \textsuperscript{13}C NMR (62.9 MHz, CDCl\textsubscript{3}, additional DEPT): d = 23.1 (–, C-3(5)*), 25.8 (–, C-4), 30.2 (+, CH\textsubscript{3}), 32.4 (C\textsubscript{quat}, C-1), 39.2 (–, C-2(6)*), 68.8 (C\textsubscript{quat}, C-1'), 91.3 ppm (+, C-2'); MS (70 eV), \textit{m/z} (%): 122 (5) [\textit{M}]^+, 107 (30) [\textit{M} – CH\textsubscript{3}]^+, 94 (24), 93 (100), 91 (22), 79 (62); C\textsubscript{9}H\textsubscript{14} (122.2).
1-Ethynyl-1-methylcyclopropane (3d): A suspension of KF (36 g, 0.62 mol) in a mixture of H$_2$O (22.0 mL) and DMF (250 mL) was stirred for 4 h at 20 °C. Then 1-methyl-1-(trimethylsilylethynyl)cyclopropane (8, 31.0 g, 0.204 mol) was added, and the reaction mixture was stirred at ambient temp. for 2 d. After this, all the volatile material was "bulb-to-bulb" distilled, at first under water-aspirator vacuum and 20 °C oil bath temperature, and then under further reduced pressure (0.1 Torr) with a 30 °C oil bath, the receiver flask was cooled in a dry ice/acetone bath. The content of the receiver flask was allowed to warm up to 20 °C and the product was purified by distillation at atmospheric pressure using a Fischer HMS 500 Spaltrohr (concentric cube) column. The alkyne 3d (14.1 g, 86%) was obtained as a colorless liquid with b.p. 57.3–57.9 °C and purity ≥ 98.5%. IR (film): ν̃ = 3318 cm$^{-1}$ (C=C–H), 2958, 2117 (C=C), 1255, 845, 757; $^1$H NMR (250 MHz, CDCl$_3$): δ = 0.54–0.59 (m, AA'BB', 2 H, Cpr), 0.88–0.92 (m, AA'BB', 2 H, Cpr), 1.26 (s, 3 H, CH$_3$), 1.82 ppm (s, 1 H, 2'-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): δ = 6.3 (C$_\text{quat}$, C-1), 16.1 [–, C-2(3)], 23.9 (+, CH$_3$), 63.3 (+, C-2'), 90.5 ppm (C$_\text{quat}$, C-1'); MS (EI, 70 eV), m/z (%): 80 (5) [M]$^+$, 79 (10), 66 (10), 51 (5); C$_6$H$_8$ (80.1).

3,3-Dimethylpentyne (3e): To a solution of 3,3-dimethylpentanone (9, 34.5 g, 302 mmol) in CH$_2$Cl$_2$ (300 mL) and pyridine (3 mL) was added dropwise phosphorous pentachloride (69.3 g, 333 mmol) in CH$_2$Cl$_2$ (500 mL) at 0 °C within 2 h. Then the reaction mixture was stirred for 1 h at 0–5 °C, NaHCO$_3$ (152 g, 1.81 mol) was added, and the mixture stirred at ambient temp. for 16 h. Then it was filtered through a Büchner funnel and the solid was extracted with CH$_2$Cl$_2$ (300 mL). The combined organic solutions were concentrated to about 35 mL, and this residue was added dropwise to a suspension of potassium hydroxide (533 g, 9.50 mol) in 2-ethoxyethanol (800 mL) within 2 h at an oil bath temp. of 140–150 °C. The crude product was distilled over a 30 cm Vigreux column into a cooled flask (–78 °C). Fractional distillation yielded 18.9 g (65%) of 3e as a clear liquid. B.p. 71 °C [Lit.$^{[2]}$ 71 °C]; IR (film): ν̃ = 3310 cm$^{-1}$ (C≡C–H), 2971 (C–H), 2927 (C–H), 2880, 2110 (C≡C), 1464, 1300, 1092, 668, 631; $^1$H NMR (250 MHz, CDCl$_3$): δ = 0.98 (t, $^3$J = 7.4 Hz, 3 H, 5-H),
1.18 [s, 6H, C(CH₃)₂], 1.43 (q. ³J = 7.4 Hz, 2 H, CH₂), 2.06 ppm (s, 1H, 1-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 9.5 (+, C-5), 28.6 [+ , C(CH₃)₂], 31.3 (C₂quat, C-3), 35.7 (–, C-4), 67.5 (C₂quat, C-2), 91.8 ppm (+, C-1); MS (70 eV), m/z (%): 96 (3) [M]+, 95 (4) [M – H]+, 81 (100) [M – CH₃]+, 67 (80) [M – C₂H₅]+, 41 (30); elemental analysis calcd. (%) for C₇H₁₂ (96.17): C 87.42, H 12.58; found C 87.29, H 12.59.

3,3-Dimethyl-6-methoxy-1-hexyne (3f): The alcohol 18 (3.50 g, 27.7 mmol) was added dropwise at 0 °C to a suspension of NaH (60%, 1.22 g, 30.5 mmol) in diethyl ether (20 mL), and the mixture stirred at 20 °C for 4 h. Then methyl iodide (4.33 g, 30.5 mmol) was added at 0 °C, and the mixture stirred for 20 h at 20 °C. The reaction mixture was poured into ice-cold 1 M hydrochloric acid (15 mL), the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (60 mL), dried (Na₂SO₄), and the solvent was removed in vacuo Column chromatography on silica gel [150 g, pentane/diethyl ether (20:1), column 4.5 × 30 cm] yielded 3f (2.14 g, 55%), Rf = 0.32, as a colorless liquid. IR (film): ν(tilde) = 3299 cm⁻¹ (C≡C–H), 2967, 2926, 2874, 2827, 1471, 1453, 1386, 1363, 1266, 1243, 1119, 869, 629; ¹H NMR (250 MHz, CDCl₃): δ = 1.20 [s, 6 H, C(CH₃)₂], 1.41–1.47 (m, 2 H, 4-H), 1.67–1.77 (m, 2 H, 5-H), 2.06 (s, 1 H, 1-H), 3.23 (s, 3 H, OCH₃), 3.39 ppm (t, ³J = 6.4 Hz, 2 H, 6-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 25.5 (–, C-4), 29.1 [+ , C(CH₃)₂], 30.8 (C₂quat, C-3), 39.6 (–, C-5), 58.5 (+, OCH₃), 67.9 (+, C-1), 73.0 (–, C-6), 91.6 ppm (C₂quat, C-2); elemental analysis calcd. (%) for C₉H₁₆O (140.2): C 77.09, H 11.50; found C 75.88, H 10.86.

3,3-Dimethyl-5-methylthio-1-pentyne (3g): Methanethiol (3.89 g, 81.0 mmol) in methanol (30 mL) was added dropwise at −5 °C to a mixture of sodium (1.60 g, 70.0 mmol) in methanol (70 mL) in a three-necked round-bottom flask equipped with dry-ice condenser and dropping funnel. After stirring for 1 h at 15 °C, the sulfonate 15 (8.73 g, 45.9 mmol) was added at −5 °C. The reaction mixture was stirred for an additional 18 h at 20 °C, then diluted with diethyl ether (200 mL) and treated with water (100 mL). The aqueous phase was extracted with diethyl ether (2 × 100 mL), the combined organic layers were dried (Na₂SO₄), and the solvent was removed in vacuo Bulb-to-bulb distillation afforded 3g (4.38 g, 67%) as a colorless liquid. IR (film): ν(tilde) = 3295 cm⁻¹ (C≡C–H), 2971, 2917, 2869, 1470, 1448, 1364, 1244, 1200, 635 (C=S), 543; ¹H NMR (250 MHz, CDCl₃): δ = 1.22 [s, 6 H, C(CH₃)₂],
1.68 (m, 2 H, 4-H), 2.10 (s, 1 H, 1-H), 2.11 (s, 3 H, SCH₃), 2.61 ppm (m, 2 H, 5-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 15.5 (+, SCH₃), 29.0 [+ C(CH₃)₂], 30.0 (−, C-5), 31.1 (Cquat, C-3), 42.7 (−, C-4), 68.5 (+, C-1), 90.6 ppm (Cquat, C-2); MS (70 eV), m/z (%): 142 (56) [M⁺], 127 (20), 114 (20), 99 (28), 75 (100), 61 (36) [C₂H₅S⁺], 41 (36); elemental analysis calcd. (%) for C₈H₁₄S (142.3): C 67.54, H 9.92; found C 67.33, H 9.67.

3,3-Dimethyl-5-methoxy-1-pentyne (3h): The alcohol 16 (26.9 g, 240 mmol) was added dropwise to a suspension of NaH (60%, 10.4 g, 260 mmol) in diethyl ether (100 mL) and the mixture was stirred at 20 °C for 30 min. Then methyl iodide (36.9 g, 260 mmol) was added within 30 min, and the mixture stirred for an additional 40 h at 20 °C. Afterwards, it was poured into ice-cold hydrochloric acid (1 M, 100 mL), the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with brine (100 mL), dried (Na₂SO₄), and the solvent was removed by distillation through a 30 cm Vigreux column. Distillation of the residue under reduced pressure yielded 3h (24.6 g, 81%) as a colorless liquid. B.p. 70 – 72 °C/193– 195 Torr; IR (film): ν(═C–H) = 3300 cm⁻¹, 2972, 2947, 2810, 2108 (C≡C), 1451, 1364, 1210, 1120, 966, 625; ¹H NMR (250 MHz, CDCl₃): δ = 1.23 [s, 6 H, C(CH₃)₂], 1.70 (t, ³J = 7.3 Hz, 2 H, 4-H), 2.09 (s, 1 H, 1-H), 3.33 (s, 3 H, OCH₃), 3.56 ppm (t, ³J = 7.3 Hz, 2 H, 5-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 29.5 [+ C(CH₃)₂], 29.6 (Cquat, C-3), 41.9 (−, C-4), 58.6 (+, OCH₃), 68.1 (+, C-1), 70.2 (−, C-5), 91.1 ppm (Cquat, C-2); MS (70 eV), m/z (%): 125 (8) [M – H]+, 111 (100), 79 (34), 67 (42), 45 (60); MS (DCI, NH₃), m/z (%): 161 (20) [M + NH₄ + NH₃]+, 144 (100) [M + NH₄]+, 127 (42) [M + H]+; elemental analysis calcd. (%) for C₈H₁₄O (126.2): C 76.14, H 11.18; found C 75.89, H 10.96.

2-[(E)-3',3'-Dimethylbutenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a): According to GP 2, compound 3a (1.64 g, 20.0 mmol) was added to a solution of pinacolborane, prepared from pinacol (4.72 g, 40.0 mmol) and BH₃·SMe₂ (4.0 ml, 40 mmol), and the mixture was stirred for 16 h at ambient temp. Column chromatography on silica gel [120 g, pentane/diethyl ether (1:1), column 3 × 40 cm] yielded 4a (1.54 g, 37%) as a colorless solid. Rₗ = 0.70; m.p. 31 °C; IR (KBr): ν(tilde) = 2995 cm⁻¹, 1642, 1475, 1381, 1359, 1269, 1154; ¹H NMR (250 MHz, CDCl₃): δ = 1.01 [s, 9 H, C(CH₃)₃], 1.26 [s, 12 H, C(CH₃)₂], 5.34 (d, ³J = 18.3 Hz, 1 H, 1'-H), 6.63 ppm (d, ³J = 18.3 Hz, 1 H, 2'-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 24.8 [+ C(CH₃)₂], 28.8 [+ C(CH₃)₂], 35.0 (Cquat, C-3’), 83.0 (Cquat, C-4(5)),...
164.4 ppm (+, C-2'); MS (70 eV), m/z (%): 210/209 (28/7) [M]⁺, 195/194 (32/9) [M – CH₃]⁺, 153/152 (100/26) [M – C(CH₃)₃]⁺, 111 (49), 84 (58); HRMS calcd. for C₁₂H₂₃BO₂ (210.2): 210.1791, found 210.1792.

2-[(E)-3',3'-Dimethyl-1'-pentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e): According to GP 2, compound 3e (4.81 g, 50.0 mmol) was added to a solution of pinacolborane, prepared from pinacol (11.9 g, 100 mmol) and BH₃·SMe₂ (10.0 ml, 100 mmol), and the mixture was stirred for 15 h at ambient temp. Column chromatography on silica gel [100 g, pentane/diethyl ether (10:1), column 3 × 50 cm] yielded 4e (2.90 g, 26%) as a colorless solid.

Rᵣ = 0.62; IR (KBr): ν(tilde) = 2998 cm⁻¹, 1639, 1472, 1377, 1349, 1265, 1161; ¹H NMR (250 MHz, CDCl₃): δ = 0.77 [t, 3 J = 7.5 Hz, 3 H, CH₂C(H₃)]; 0.97 [s, 6 H, C(CH₃)₂], 1.27 [s, 12 H, C(CH₃)₂], 1.32 [q, 3 J = 7.5 Hz, 2 H, CH₂], 5.33 (d, 3 J = 18.3 Hz, 1 H, 1'-H), 6.54 ppm (d, 3 J = 18.3 Hz, 1 H, 2'-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 8.9 (+, C-5'), 24.8 [+ C(CH₃)₂], 25.9 [+ C(CH₃)₂], 34.5 (-, C-4'), 38.1 [C quat, C-3'], 82.9 [C quat, C-4(5)], 163.4 ppm (+, C-2'); C₁₃H₂₅BO₂: (224.2).

2-[(E)-3',3'-Dimethyl-5'-methylthiopentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g): According to GP 2, compound 3g (2.85 g, 20.0 mmol) was added to a solution of pinacolborane, prepared from pinacol (4.72 g, 40.0 mmol) and BH₃·SMe₂ (4.0 ml, 40 mmol), and the mixture was stirred for 12 h at ambient temp. Flash column chromatography on silica gel [100 g, pentane/diethyl ether (20:1), column 5 × 35 cm] yielded 4g (3.73 g, 69%) as a colorless oil.

Rᵣ = 0.35; ¹H NMR (250 MHz, CDCl₃): δ = 1.01 [s, 6 H, C(CH₃)₂], 1.26 [s, 12 H, C(CH₃)₂], 1.60 (m, 2 H, 4'-H), 2.07 (s, 3 H, SCH₃), 2.35 (m, 2 H, 5'-H), 5.34 (d, 3 J = 18.3 Hz, 1 H, 1'-H), 6.51 ppm (d, 3 J = 18.3 Hz, 1 H, 2'-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 15.5 (+, SCH₃), 24.8 [+ C(CH₃)₂], 26.3 [+ C(CH₃)₂], 29.6 (-, C-5'), 38.2 (C quat, C-3'), 41.7 (-, C-4'), 83.1 [C quat, C-4(5)], 162.0 ppm (+, C-2'); MS (70 eV), m/z (%): 271/270/269 (8/40/12) [M]⁺, 256/255/254 (14/100/25) [M – CH₃]⁺, 200 (44), 153 (50), 75 (86) [C₆H₁₅S]⁺, 41 (40); HRMS calcd. for C₁₁H₁₂BO₂S (270.2): 270.1825, found 270.1824.

2-[(E)-3',3'-Dimethyl-5'-methoxypentenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h): According to GP 2, compound 3h (1.26 g, 10.0 mmol) was added to a solution of pinacolborane, prepared from pinacol (2.36 g, 20.0 mmol) and BH₃·SMe₂ (2.0 ml, 20 mmol),
and the mixture was stirred for 7 h at ambient temp. Flash column chromatography on silica gel [80 g, pentane/diethyl ether (4:1), column 2.5 × 30 cm] yielded 4h (1.73 g, 68%) as a colorless oil. Rf = 0.59; IR (film): ν(tilde) = 2982 cm⁻¹, 2935, 1641, 1447, 1381, 1325, 1220, 1169; 1H NMR (250 MHz, CDCl₃): δ = 1.01 [s, 6 H, C(CH₃)₂], 1.28 [s, 12 H, C(CH₃)₂], 1.63 (t, 3J = 7.4 Hz, 2 H, 4'-H), 3.28 (s, OCH₃), 3.32 (t, 3J = 7.4 Hz, 2 H, 5'-H), 5.34 (d, 3J = 18.4 Hz, 1 H, 1'-H), 6.76 ppm (d, 3J = 18.4 Hz, 1 H, 2'-H); 13C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 24.8 [+ , C(CH₃)₂], 26.7 [+ , C(CH₃)₂], 36.9 (C quat, C-3’), 41.1 (– , C-4’), 58.5 (– , C-5’), 69.8 (+, OCH₃), 83.0 [C quat, C-4(5)], 162.5 ppm (+, C-2’); C₁₄H₂₇BO₃ (254.2).

**Adamantyl methyl ketone (6b):** According to GP 3, methyllithium (43 mL, 88 mmol) was added to a solution of adamantanecarboxylic acid (7.46 g, 41.4 mmol) in diethyl ether (250 mL) at 0 °C, and the mixture was stirred at 20 °C for 4 h. Recrystallization from methanol/water yielded 7.13 g (97%) of colorless needles. M.p. 52–53 °C (Lit.[³] 53–54 °C); 1H NMR (250 MHz, CDCl₃): δ = 1.67–1.69 (br s, 6 H, 4 -H), 1.78 (d, 3J = 2.4 Hz, 6 H, 2-H), 2.02 (br s, 3 H, 3-H), 2.07 ppm (s, 3 H, COCH₃); 13C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 24.3 (+, COCH₃), 27.9 (+, C-3), 36.5 (–, C-4*), 38.2 (–, C-2*), 46.4 (C quat, C-1), 214.2 ppm (C quat, C=O); MS (70 eV) m/z (%): 178 (10) [M]+, 163 (1) [M – CH₃]+, 135 (100) [M – COCH₃]+, 107 (10), 93 (10); elemental analysis calcd. (%) for C₁₂H₁₈O (178.3): C 80.85, H 10.18; found C 80.74, H 10.22.

**Methyl 1-methylcyclohexyl ketone (6c):** According to GP 3, methyllithium (66 mL, 0.11 mmol) was added to a solution of 1-methylcyclohexanecarboxylic acid (7.11 g, 50.0 mmol) in diethyl ether (250 mL) at 0 °C. Distillation at reduced pressure yielded 6c (6.40 g, 91%). B.p. 84 °C/30 Torr (Lit.[⁴] 72 °C/18 Torr); the 1H NMR spectrum was identical to the reported one.[⁴]

**1-Methyl-1-(trimethylsilylethynyl)cyclopropane (8):** To a solution of 1-(trimethylsilyl)ethynylcyclopropane (7, 25.1 g, 0.182 mol) in Et₂O (200 mL) was added dropwise nBuLi (0.182 mol, 114 mL of a 1.6 M solution in hexane) at 0 °C, and the reaction mixture
was stirred at ambient temp. for 24 h. Then dimethyl sulfate (43.3 mL, 57.4 g, 0.455 mol) was added dropwise at −10 °C, the resulting solution was stirred at 10 °C and then at 20 °C for 30 min each. The reaction was quenched by adding a mixture of sat. aq. NH₄Cl and 25% aq. ammonia solutions (1:3, 250 mL), and the mixture then stirred at ambient temp. for 1 h. The aqueous phase was extracted with diethyl ether (3 × 150 mL), and the combined organic layers were washed successively with 5% aq. hydrochloric acid (250 mL), 5% aq. NaHCO₃ solution (150 mL) and H₂O (150 mL), dried (MgSO₄) and concentrated at ambient pressure. After fractional distillation under reduced pressure, 8 (22.2 g, 80%) was obtained as a colorless liquid. B.p. 80–82 °C/90 mbar; IR (film): ν(≈) = 3010 cm⁻¹, 2983, 2162 (C=C), 1305, 1250, 957, 842, 759, 731; ¹H NMR (250 MHz, CDCl₃): δ = 0.12 [s, 9 H, Si(CH₃)₃], 0.58 (m, AAB'B', 2 H, Cpr), 0.91 (m, AAB'B', 2 H, Cpr), 1.25 ppm (s, 3 H, CH₃); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 0.3 [+ , Si(CH₃)₃], 7.4 (C quat, C-1), 16.7 [−, C-2(3)], 24.1 (+, CH₃), 79.0 (C quat, C-1'), 113.2 ppm (C quat, C-2'); MS (EI, 70 eV), m/z (%): 152 (10) [M]⁺, 137 (100) [M−CH₃]⁺, 123 (6), 109 (24), 97 (17), 83 (30), 73 (96) [Si(CH₃)₃]⁺, 59 (38), 43 (34); HRMS calcd. for C₉H₁₆Si (152.3): 152.1021, found 152.1021.

3-Chloro-3-methylbutyne (11): The 2-methyl-3-butyn-2-ol (252 g, 3.00 mol) was added over 1 h to a solution of calcium chloride (167 g, 1.50 mol), copper(II) chloride (162 g, 1.20 mol) and copper bronze (1.8 g, 28 mmol) in conc. hydrochloric acid (1.3 L) at 0 °C and the mixture stirred for 1 h at this temp. After phase separation of the reaction mixture the organic layer was washed with ice-cold conc. hydrochloric acid (5 × 120 mL) and with water (3 × 100 mL), then dried over K₂CO₃. Distillation under reduced pressure with a small amount of K₂CO₃ in the flask yielded 288 g (94%) of 11 as a colorless liquid. B.p. 52–53 °C/310 Torr; IR (film): ν(tilde) = 3298 cm⁻¹ (C≡C–H), 2999, 2984, 2935, 2121 (C≡C), 1448, 1369, 1227, 1119, 946, 787; ¹H NMR (250 MHz, CDCl₃): δ = 1.87 [s, 6 H, C(CH₃)₂], 2.62 ppm (s, 1 H, 1-H); ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 34.5 [+ , C(CH₃)₂], 56.9 (C quat, C-3), 71.9 (C quat, C-2), 86.5 ppm (+, C-1); MS (70 eV), m/z (%): 89/87 (8/22) [M − CH₃]⁺, 67 (100) [M − Cl]⁺, 55 (28), 41 (24); MS (DCI, NH₃), m/z (%): 138/136 (20/74) [M + 2 NH₃]⁺, 119 (100) [M + NH₃]⁺, 102 (88) [M]⁺; elemental analysis calcd. (%) for C₅H₁₆Cl (102.6): C 58.55, H 6.88; found C 58.25, H 6.60.
Diethyl 2-(1,1-dimethyl-2-propynyl)malonate (12): Diethyl malonate (330 g, 2.06 mol) was added to a still warm solution of sodium (46.0 g, 2.00 mol) in ethanol (1.1 L) and stirred at 60 °C for 30 min. Then, chloride 11 (193 g, 1.88 mol) was added. The reaction mixture was heated and stirred for 1 h at 65 °C, 30 min at 80 °C and finally 15 h at 50 °C. The resulting suspension was filtered and concentrated. The residue was treated with ice-cold conc. hydrochloric acid (800 mL) and extracted with diethyl ether (6 × 300 mL). The combined organic layers were washed with water (2 × 300 mL) and a solution of NaHCO₃ (2 × 300 mL), dried (MgSO₄), and the solvent was removed in vacuo. Distillation under reduced pressure using a 10 cm Vigreux column yielded 12 (265 g, 62%) as a colorless liquid. B.p. 98−101 °C/2−4 Torr; IR (film): ν(tilde) = 3280 cm⁻¹ (C≡C–H), 2981, 2940, 2876, 1754 (C=O), 1735, 1466, 1369, 1231, 1096, 1040, 861; ¹H NMR (250 MHz, CDCl₃): δ = 1.24 [t, 3J = 7.1 Hz, 6 H, C(COOCH₂CH₃)₂], 1.42 [s, 6 H, C(CH₃)₂], 2.17 (s, 1 H, 5-H), 3.40 (s, 1 H, 2-H), 4.18 ppm [q, 3J = 7.1 Hz, 4 H, C(COOC₂H₃CH₃)₂]; ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 14.0 (+, C(COOCH₂CH₃)₂), 27.3 (+, C(CH₃)₂), 32.4 [C quat, C-3], 60.1 (+, C-2), 61.2 [−, C(COOCH₂CH₃)₂], 69.3 (C quat, C-4), 88.6 (+, C-5), 167.2 ppm [C quat, C(COOCH₂CH₃)₂]; MS (DCI, NH₃), m/z (%): 261 (56) [M + NH₄ + NH₃]⁺, 244 (100) [M + NH₄]⁺; elemental analysis calcd. (%) for C₁₂H₁₈O₄ (226.3): C 63.70, H 8.02; found C 63.38, H 7.81.

Ethyl 3,3-dimethyl-4-pentynoate (13): A mixture of diester 12 (113 g, 500 mmol), sodium bromide (56.6 g, 550 mmol) and water (13.5 mL, 750 mmol) in DMSO (800 mL) was heated at 190 °C for 20 h. The resulting suspension was cooled down to ambient temp., poured into ice-water (1000 mL), and the aqueous layer was extracted with pentane (5 × 300 mL). The combined organic layers were dried (Na₂SO₄), and the solvent was removed in vacuo. Distillation under reduced pressure yielded 13 (67.8 g, 88%) as a colorless liquid. B.p. 68–70 °C/10 Torr; IR (film): ν(tilde) = 3294 cm⁻¹ (C≡C–H), 2978, 2938, 2875, 1735 (C=O), 1468, 1369, 1224, 1119, 1036; ¹H NMR (250 MHz, CDCl₃): δ = 1.25 (t, 3J = 7.0 Hz, 3 H, CH₂CH₃), 1.34 [s, 6 H, C(CH₃)₂], 2.14 (s, 1 H, 5-H), 2.43 (s, 2 H, 2-H), 4.14 ppm [q, 3J = 7.0 Hz, 2 H, CH₂CH₃]; ¹³C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 14.2 (+, CH₂CH₃), 29.1 [+ C(CH₃)₂], 29.6 (C quat, C-3), 46.8 (−, C-2), 60.3 (−, CH₂CH₃), 68.3 (+, C-5), 90.0 ppm (C quat, C-4); MS (70 eV), m/z (%): 154 (10) [M]⁺, 139 (38), 125 (25), 111 (24), 109 (46), 88 (26), 81 (46), 67 (100), 41 (40); elemental analysis calcd. (%) for C₆H₁₄O₂ (154.2): C 70.10, H 9.15; found C 70.00, H 9.02.
**4,4-Dimethyl-5-hexyne-1-nitrile (14):** Sodium cyanide (4.90 g, 100 mmol) was added to the sulfonate 15 (9.56 g, 50.2 mmol) in DMSO (90 mL), the mixture was at 90 °C stirred for 30 min, and at 20 °C for an additional 19 h. Then it was diluted with diethyl ether (60 mL) and treated with water (50 mL). The aqueous layer was extracted with diethyl ether (3 × 40 mL), the combined organic layers dried (Na$_2$SO$_4$), and the solvent was removed in vacuo Bulb-to-bulb distillation gave 14 (5.56 g, 91%) as a colorless liquid. IR (film): ν(˜) = 3294 cm$^{-1}$ (C≡C–H), 2975, 2934, 2873, 2249 (C≡N), 1472, 1456, 1390, 1368, 1207, 636; $^1$H NMR (250 MHz, CDCl$_3$): δ = 1.25 [s, 6 H, C(CH$_3$)$_2$], 1.80 (m, 2 H, 3-H), 2.16 (s, 1 H, 6-H), 2.51 ppm (m, 2 H, 2-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): δ = 13.5 (–, C-2), 28.6 [+ , C(CH$_3$)$_2$], 30.9 (C$_{quat}$, C-4), 38.3 (–, C-3), 69.9 (+, C-6), 88.9 (C$_{quat}$, C-5), 119.3 ppm (C$_{quat}$, CN); MS (70 eV), m/z (%): 120 (26) [M–H]$^+$, 106 (36), 79 (42), 67 (100) [C$_6$H$_7$]$^+$; MS (DCI, NH$_3$), m/z (%): 156 (40) [M + NH$_4$ + NH$_3$]$^+$, 139 (100) [M + NH$_4$]$^+$; elemental analysis calcd. (%) for C$_8$H$_{11}$N (121.2): C 79.29, H 9.15, N 11.56; found C 79.28, H 8.90, N 11.38.

**3,3-Dimethyl-4-pentynyl) methanesulfonate (15):** Mesyl chloride (12.3 g, 107 mmol) and triethylamine (12.1 g, 120 mmol) were added at 0 °C to a solution of alcohol 16 (11.2 g, 100 mmol) in dichloromethane (180 mL), and the mixture was at this temp. stirred for 30 min. The resulting mixture was hydrolyzed with ice-cold hydrochloric acid (2 M, 200 mL), and the water layer was extracted with diethyl ether (2 × 150 mL). The combined organic layers were dried (Na$_2$SO$_4$) and the solvent was removed in vacuo Bulb-to-bulb distillation yielded 15 (18.9 g, 99%) as a colorless liquid. IR (film): ν(˜) = 3282 cm$^{-1}$ (C≡C–H), 3028, 2974, 2941, 2874, 1473, 1356 (S=O), 1176 (S=O), 1075, 959, 838; $^1$H NMR (250 MHz, CDCl$_3$): δ = 1.26 [s, 6 H, C(CH$_3$)$_2$], 1.87 (t, $^3$J = 7.3 Hz, 2 H, 2-H), 2.15 (s, 1 H, 5-H), 3.00 (s, 3 H, SCH$_3$), 4.42 ppm (t, $^3$J = 7.3 Hz, 2 H, 1-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): δ = 29.4 [+ , C(CH$_3$)$_2$], 29.6 (C$_{quat}$, 3-C), 37.3 (+, SCH$_3$), 41.2 (–, C-2), 67.7 (–, C-1), 69.3 (+, C-5), 89.5 ppm (C$_{quat}$, C-2); MS (DCI, NH$_3$), m/z (%): 398 (2) [2M + NH$_4$]$^+$, 225 (17) [M + NH$_4$ + NH$_3$]$^+$, 208 (100) [M + NH$_3$]$^+$; elemental analysis calcd. (%) for C$_8$H$_{14}$O$_3$S (190.3): C 50.50, H 7.42; found C 50.39, H 7.65.

**3,3-Dimethyl-4-pentyn-1-ol (16):** The ester 13 (74.0 g, 480 mmol) was added at 0 °C within 45 min to a suspension of LiAlH$_4$ (14.6 g, 385 mmol) in diethyl ether (450 mL), the mixture
stirred at ambient temp. for 14 h and under reflux for an additional 1 h. The reaction mixture was treated with ice-cold hydrochloric acid (2 M, 600 mL), and extracted with diethyl ether (5 × 300 mL). The combined organic layers were dried (Na₂SO₄), and the solvent was removed in vacuo. Distillation under reduced pressure yielded 16 (48.5 g, 90%) as a colorless liquid. B.p. 82–85 °C/95–100 Torr; IR (film): ν̃(O–H) = 3400 cm⁻¹ (OH), 3301 (C≡C–H), 2969, 2944, 2871, 2108 (C≡C); 1H NMR (250 MHz, CDCl₃): δ = 1.25 [s, 6 H, C(CH₃)₂], 1.72 (t, 3J = 6.7 Hz, 2 H, 2-H), 1.98 (brs, 1 H, OH), 2.15 (s, 1 H, 5-H), 3.84 ppm (t, 3J = 6.7 Hz, 2 H, 1-H); 13C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 29.3 (Cquat, C-3), 29.5 (+, C(CH₃)₂), 45.2 (–, C-2), 60.3 (–, C-1), 68.8 (+, C-5), 91.4 ppm (Cquat, C-4); MS (DCI, NH₃), m/z (%): 147 (27) [M + NH₄ + NH₃]+, 130 (100) [M + NH₄]+, 113 (23) [M + H]+; elemental analysis calcd. (%) for C₇H₁₂O (112.2): C 74.95, H 10.78; found C 74.60, H 10.74.

4,4-Dimethyl-5-hexynoic acid (17): To a solution of nitrile 14 (4.88 g, 40.3 mmol) in ethanol (3 mL), was added a solution of sodium hydroxide (25%, 14 mL), and the mixture heated at 100 °C for 17 h. The resulting mixture was acidified with H₂SO₄ and extracted with diethyl ether (4 × 70 mL). The combined organic layers were dried (CaCl₂), and the solvent was removed in vacuo. Bulb-to-bulb distillation afforded 17 (5.31 g, 94%) as a colorless liquid. 1H NMR (250 MHz, CDCl₃): δ = 1.26 [s, 6 H, C(CH₃)₂], 1.74 (m, 2 H, 3-H), 2.12 (s, 1 H, 6-H), 2.56 (m, 2 H, 2-H), 9.55 ppm (brs, 1 H, COOH); 13C NMR (62.9 MHz, CDCl₃, additional DEPT): δ = 28.9 (+, C(CH₃)₂), 30.5 (–, C-3), 30.6 (Cquat, C-4), 37.3 (–, C-2), 68.9 (+, C-6), 90.2 (Cquat, C-5), 180.2 ppm (Cquat, COOH); MS (70 eV), m/z (%): 139 (26) [M–H]+, 125 (22), 98 (30), 67 (100), 41 (42); MS (DCI, NH₃), m/z (%) 175 (40) [M + NH₄ + NH₃]+, 158 (100) [M + NH₄]+; elemental analysis calcd. (%) for C₈H₁₂O₂ (140.2): C 68.55, H 8.63; found C 68.34, H 8.63.

4,4-Dimethyl-5-hexyn-1-ol (18): The acid 17 (4.91 g, 35 mmol) was added slowly at 0 °C to a suspension of LiAlH₄ (1.18 g, 31.1 mmol) in diethyl ether (40 mL). The reaction mixture was heated under reflux for 1 h and afterwards stirred for 18 h at 20 °C. Then it was treated with 2 M hydrochloric acid (40 mL), and the aqueous phase was extracted with diethyl ether (5 × 30 mL). The combined organic layers were dried (Na₂SO₄), and the solvent was removed in vacuo. Bulb-to-bulb distillation gave 18 (4.31 g, 98%) as a colorless liquid. IR (film): ν̃(O–H) = 3400 cm⁻¹ (O–H), 3301 (C≡C–H), 2969, 2944, 2871, 2108 (C≡C), 1471, 1455,
$^1$H NMR (250 MHz, CDCl$_3$): $\delta = 1.21$ [s, 6 H, C(CH$_3$)$_2$], 1.42–1.49 (m, 2 H, 3-H), 1.69–1.76 (m, 2 H, 2-H), 2.03 (brs, 1 H, OH), 2.08 (s, 1 H, 6-H), 3.67 ppm (t, $^3$$J = 6.5$ Hz, 2 H, l-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): $\delta = 28.6$ (–, C-3), 29.1 [+, C(CH$_3$)$_2$], 30.7 (Cquat, C-4), 39.2 (–, C-2), 63.2 (–, C-1), 67.9 (+, C-6), 91.6 ppm (Cquat, C-5); MS (DCI, NH$_3$), $m/z$ (%): 161 (10) [$M + NH_4 + NH_3]^+$, 144 (100) [$M + NH_4]^+$, 127 (15) [$M + H]^+$. C$_8$H$_{14}$O (126.2).

1-(tert-Butyl)-2-(tri-n-butylstannyl)ethene (19a): According to GP 5, 3,3-dimethylbutyne (10.80 g, 131.5 mmol) was treated with tri-n-butyltin hydride (24.25 g, 83.32 mmol) and azoisobutyronitrile (0.66 g, 4.0 mmol). Distillation yielded 19a (22.52 g, 72%) as a colorless liquid. B.p. 82 °C (0.001 Torr); $^1$H NMR indicates a $E$/$Z$ ratio of 9:1; IR (film): $\nu$(tilde) = 2957 cm$^{-1}$, 2927, 2871, 1593, 1463, 1377, 1360, 1072, 993; $^1$H NMR (250 MHz, CDCl$_3$): (E)-19a: $\delta = 0.83–0.97$ (m, 6 H, CH$_2$), 0.89 (t, $J = 7.2$ Hz, 9 H, CH$_3$), 1.00 [s, 9 H, C(CH$_3$)$_3$], 1.26–1.38 (m, 6 H, CH$_2$), 1.44–1.56 (m, 6 H, CH$_2$), 5.72–6.03 ppm [ABX system, $J_{AB} = 19.6$, $^2$$J$(117/119Sn-H) = 70.2, $^3$$J$(117/119Sn-H) = 85.1 Hz, 2 H, 1-H, 2-H]; (Z)-19a: $\delta = 0.83–0.97$ (m, 6 H, CH$_2$), 0.89 (t, $J = 7.2$ Hz, 9 H, CH$_3$), 1.00 [s, 9 H, C(CH$_3$)$_3$], 1.26–1.38 (m, 6 H, CH$_2$), 1.44–1.56 (m, 6 H, CH$_2$), 5.56 (d, $J = 14.3$ Hz, 1 H, 2-H), 6.64 ppm (d, $J = 14.3$ Hz, 1 H, 1-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): (E)-19a: $\delta = 9.4$ (–, CH$_2$), 13.7 (+, CH$_3$), 27.2 (–, CH$_2$), 29.1 (–, CH$_2$), 29.2 [+; C(CH$_3$)$_3$], 35.9 [Cquat, C(CH$_3$)$_3$], 119.7 (+, C-1), 160.0 ppm (+, C-2); MS (70 eV), $m/z$ (%): 317/315/313 (100/75/45) [$M – C_4H_9]^+$, 261/259/257 (55/40/25) [$M – C_4H_9 – C_4H_8]^+$, 203 (60), 120 (20), 41 (25); elemental analysis calcd. (%) for C$_{18}$H$_{38}$Sn (373.2): C 57.93, H 10.26; found C 59.02, H 10.14.

1-Adamantyl-2-(tri-n-butylstannyl)ethene (19b): According to GP 5 1-adamantylethylene (503 mg, 3.14 mmol) was treated with tri-n-butyltin hydride (789 mg, 2.71 mmol) and azoisobutyronitrile (34 mg, 0.21 mmol). Distillation yielded 19b (1.11 g, 91%) as a colorless liquid. B.p. 160 °C (0.001 Torr); the $^1$H NMR spectrum indicated an $E$/$Z$ ratio of 9:1; IR (film): nu(tilde) = 2955 cm$^{-1}$, 2906, 2847, 1593, 1452, 1376, 1197, 1071, 992; $^1$H NMR (250 MHz, CDCl$_3$): (E)-19b: $\delta = 0.82–0.99$ (m, 6 H, CH$_2$), 0.85 (t, $J = 7.3$ Hz, 9 H, CH$_3$), 1.26–1.34 (m, 6 H, CH$_2$), 1.45–1.52 (m, 6 H, CH$_2$), 1.57 (d, $J = 2.6$ Hz, 6 H, 2'-H), 1.67–1.70
(m, 6 H, 4’-H), 1.98 (brs, 3 H, 3’-H), 5.39–5.59 ppm [ABX system, $J_{AB} = 19.4$, $^3J^{(117/119)}\text{Sn-H}) = 72.8$, $^2J^{(117/119)}\text{Sn-H}) = 78.4$ Hz, 2 H, 1-H, 2-H]; (Z)-19b: $\delta = 0.82$–0.99 (m, 6 H, CH$_3$), 0.85 (t, $J = 7.3$ Hz, 9 H, CH$_3$), 1.26–1.34 (m, 6 H, CH$_2$), 1.45–1.52 (m, 6 H, CH$_2$), 1.57 (d, $J = 2.6$ Hz, 6 H, 2’-H), 1.67–1.70 (m, 6 H, 4’-H), 1.98 (brs, 3 H, 3’-H), 5.56 (d, $J = 14.0$ Hz, 1 H, 2-H), 6.46 ppm (d, $J = 14.0$ Hz, 1 H, 1-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): (E)-19b: $\delta = 9.4$ (–, CH$_2$), 13.7 (+, CH$_3$), 27.2 (–, CH$_2$), 28.6 (+, C-3’), 29.1 (–, CH$_2$), 37.0 (–, C-4’), 37.1 (C$_{quat}$, C-1’), 42.0 (–, C-2’), 119.7 (+, C-1), 160.4 ppm (+, C-2); MS (70 eV), $m/z$ (%): 395/393/391 (65/48/30) [M – C$_4$H$_9$]$^+$, 339/337/335 (20/15/10) [M – C$_4$H$_9$ – C$_4$H$_8$]$^+$, 281/279/277 (50/38/23) [M – C$_4$H$_9$ – C$_4$H$_8$ – C$_4$H$_{10}$]$^+$, 135 (100) [adamantyl]$^+$; C$_{22}$H$_{44}$Sn (451.3).

1-(3,5-Di-tert-butylphenyl)-2-(tri-n-butylstannyl)ethene (19k): According to GP 5, compound 3k (1.504 g, 7.017 mmol) was treated with tri-n-butyltin hydride (2.036 g, 6.995 mmol) and azoisobutyronitrile (70 mg, 0.43 mmol). Distillation yielded 19k (1.500 g, 42%) as a pale green oil. B.p. 160 °C (0.001 Torr); the $^1$H NMR spectrum indicated an $E$/Z ratio of 5:1; IR (film): $\tilde{\nu}$ (tilde) = 2958 cm$^{-1}$, 2926, 2870, 1577, 1463, 1420, 1362, 1248, 1200, 985, 877, 704; $^1$H NMR (250 MHz, CDCl$_3$): (E)-19k: $\delta = 0.80$–1.00 (m, 15 H, CH$_2$ and CH$_3$), 1.30–1.46 [m, 24 H, C(CH$_3$)$_3$ and CH$_2$], 1.49–1.62 (m, 6 H, CH$_2$), 6.71–7.01 [ABX system, $J_{AB} = 19.8$, $^2J^{(117/119)}\text{Sn-H}) = 67$, $^3J^{(117/119)}\text{Sn-H}) = 69$ Hz, 2 H, 1-H, 2-H], 7.29 (d, $J = 1.7$ Hz, 2 H, Ph-H), 7.34 ppm (t, $J = 1.7$ Hz, 1 H, Ph-H); (Z)-19k: $\delta = 0.80$–1.00 (m, 15 H, CH$_2$ and CH$_3$), 1.30–1.46 [m, 24 H, C(CH$_3$)$_3$ and CH$_2$], 1.49–1.62 (m, 6 H, CH$_2$), 6.15 (d, $J = 13.8$ Hz, 1 H, 2-H), 7.08 (d, $J = 1.6$ Hz, 2 H, Ph-H), 7.13 (brs, 1 H, Ph-H), 7.66 ppm (d, $J = 13.8$ Hz, 1 H, 1-H); $^{13}$C NMR (62.9 MHz, CDCl$_3$, additional DEPT): (E)-19k: $\delta = 9.6$ (–, CH$_2$), 13.7 (+, CH$_3$), 27.3 (–, CH$_2$), 29.1 (–, CH$_2$), 31.5 [+; C(CH$_3$)$_3$], 34.8 [C$_{quat}$, C(CH$_3$)$_3$], 120.3 (+, C-2’), 121.9 (+, C-4’), 128.3 (+, C-1), 138.1 (C$_{quat}$, C-1’), 147.0 (+, C-2), 150.8 ppm [C$_{quat}$, C-3’(5’)]; MS (70 eV), $m/z$ (%): 449/447/445 (100/75/47) [M – C$_4$H$_9$]$^+$, 393/391/389 (10/7/5) [M – C$_4$H$_9$ – C$_4$H$_8$]$^+$, 335/333/331 (25/18/12) [M – C$_4$H$_9$ – C$_4$H$_8$ – C$_4$H$_{10}$]$^+$, 57 (10) [C$_4$H$_3$]$^+$; elemental analysis calcd. (%) for C$_{28}$H$_{50}$Sn (505.4): C 66.54, H 9.97; found C 65.48, H 9.82.
Hexakis-[(E)-(3,3-dimethyl-1-butenyl)]benzene (1a): Variant 2: According to GP 6, hexabromobenzene (552 mg, 1.00 mmol) was treated with 2a (1.33 g, 6.55 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (211 mg, 300 µmol) and powdered cesium fluoride (2.73 g, 18.0 mmol) in THF/toluene (1:1, 40 mL) for 24 h. Column chromatography on silica gel (50 g, pentane, column 2.5 × 40 cm) yielded 1a (29 mg, 5%).

Variant 3: According to GP 6, hexabromobenzene (552 mg, 1.00 mmol) was treated with 2a (1.33 g, 6.60 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (211 mg, 300 µmol) and powdered Ba(OH)$_2$·8 H$_2$O (5.43 g, 17.2 mmol) in THF/toluene (1:1, 50 mL) for 24 h. Column chromatography on silica gel (50 g, pentane, column 2.5 × 40 cm) yielded 126 mg (22%) of 1a, and 44 mg (9%), $R_f = 0.45$, of pentakis[(E)-3',3'-dimethyl-1'-butenyl]benzene (21a) as a colorless solid. M.p. 149 °C; $^1$H NMR (250 MHz, CDCl$_3$): δ = 1.12 (br s, 45 H, CH$_3$), 5.64 (d, $^3J = 18.1$ Hz, 2 H, 2'-H), 5.67 (d, $^3J = 18.2$ Hz, 1 H, 2'-H), 6.06 (d, $^3J = 18.0$ Hz, 2 H, 2'-H), 6.18 (d, $^3J = 18.2$ Hz, 1 H, 1'-H), 6.23 (d, $^3J = 18.1$ Hz, 2 H, 1'-H), 6.56 (d, $^3J = 18.0$ Hz, 2 H, 1'-H), 7.40 ppm (s, 1 H, Ph-H); MS (70 eV), m/z (%): 489/488 (22/58) [M]$^+$, 406 (25), 376/375 (25/100), 293 (24), 57 (60).

Variant 4: According to GP 6, hexabromobenzene (983 mg, 1.78 mmol) was treated with 2a (2.479 g, 12.21 mmol) in the presence of trans-di(µ-acetato)bis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (119 mg, 0.127 mmol) and powdered sodium hydroxide (1.345 g, 33.63 mmol) in toluene (50 mL) for 24 h at 90 °C. Column chromatography on silica gel (100 g, pentane, column 5 × 50 cm) yielded 1a (249 mg, 24%).

Variant 5: According to GP 6, hexabromobenzene (378 mg, 685 µmol) was treated with 4a (950 mg, 4.52 mmol) in the presence of dichlorobis(triphenylphosphine)palladium (144 mg, 206 µmol) and powdered sodium hydroxide (488 mg, 12.2 mmol) in THF/toluene (1:1, 40 mL) for 24 h. Column chromatography on silica gel (50 g, pentane, column 2.5 × 40 cm) yielded 1a (178 mg, 45%) and 21a (128 mg, 38%).

Variant 6: According to GP 7, hexabromobenzene (748 mg, 1.36 mmol) was treated with 19a (5.417 g, 14.51 mmol) in the presence of trans-di(µ-acetato)bis[2-(di-o-tolylphosphino)benzyl]dipalladium(II) (88 mg, 94 µmol) at 120 °C for 4 d. Column chromatography on
silica gel (50 g, petroleum ether, column 3×30 cm), and subsequent recrystallization from hexane yielded \textit{1a} (275 mg, 35%).


