Supplementary Material (ESI) for Chemical Communications
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A platinum-catalyzed annulation reaction leading to medium-sized rings

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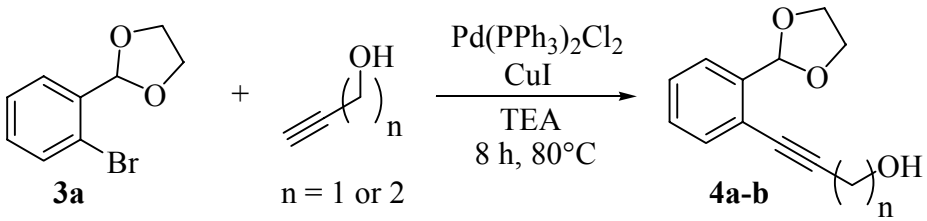
Supplementary Material

1. Preparation of 4a-b



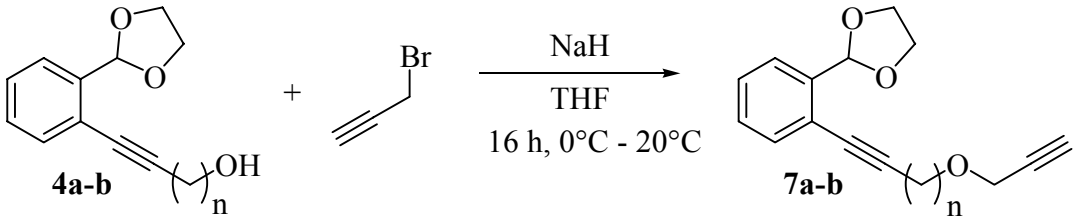
In a screw-capped flask 609 mg (10.8 mmol) of alkynol, 2.07 g (9.00 mmol) of dioxolane **3a**, 126 mg (0.18 mmol, 2 mol%) of $PdCl_2(PPh_3)_2$ and 34.0 mg (0.18 mmol, 2 mol%) of CuI were suspended in 40 ml of triethylamine. The mixture was heated under stirring at 80°C for 8 h. After evaporation of the solvents the pure products were isolated by flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate: **4a** (2:1; R_f = 0.23; **4b** (1:1; R_f = 0.31).

3-(2-[1,3]Dioxolan-2-yl)phenyl-2-propyn-1-ol (4a): (550 mg, 2.70 mmol, 30%) as colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.93 ppm (s, 1H, -OH), 3.74-4.19 (m, 4H, H-2'), 4.52 (s, 2H, H-3''), 6.19 (s, 1H, H-1'), 7.31-7.37 (m, 2H, H-Ar), 7.44-7.49 (m, 1H, H-Ar), 7.55-7.59 (m, 1H, H-Ar).

4-(2-[1,3]Dioxolan-2-yl)phenyl-3-butyn-1-ol (4b): (562 mg, 2.58 mmol, 33%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 2885 cm^{-1} (m), 2230 (w), 1698 (w), 1683 (w), 1649 (w), 1557 (w), 1541 (w), 1508 (w), 1488 (w), 1473 (w), 1456 (w), 1396 (m), 1338 (w), 1198 (w), 1116 (m), 1071 (s), 1038 (m), 961 (m), 943 (s), 903 (w), 845 (w), 761 (s), 669 (w); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 252 nm (4.14), 242 (4.18), 207 (4.58); ^{1}H NMR (400 MHz, acetone-d_6): δ = 2.63 ppm (t, *J* = 6.8 Hz, 2H, H-3''), 3.74 (q, *J* = 6.6 Hz, 2H, H-4''), 3.91 (t, *J* = 5.8 Hz, 1H, -OH), 3.97-4.03 (m, 2H, H-2'), 4.08-4.14 (m, 2H, H-2'), 6.13 (s, 1H H-1'), 7.32-7.35 (m, 2H, H-4 and H-5), 7.40 (m, 1H, H-3), 7.54 (m, 1H, H-6); ^{13}C NMR {^{1}H} (100 MHz, acetone-d_6): δ = 24.57 ppm (C-3''), 61.49 (C-4''), 66.10 (C-2'), 79.52 (C-1''), 93.36 (C-2''), 102.53 (C-1'), 124.14 (C-2), 127.19 (C-6), 128.50 (C-5), 129.66 (C-4), 132.94 (C-3), 140.55 (C-1); MS (70

eV, EI): *m/z* (%) = 218 [M^+] (26), 188 (62), 173 (29), 162 (27), 144 (85), 131 (50), 115 (100), 105 (17), 89 (20), 77 (19), 73 (34), 63 (17), 51 (12); Anal. Calcd for $C_{13}H_{14}O_3 \cdot H_2O$: C, 68.74; H, 6.29. Found: C, 69.00; H, 6.23.

2. Preparation of 7a-b



n = 1 or 2

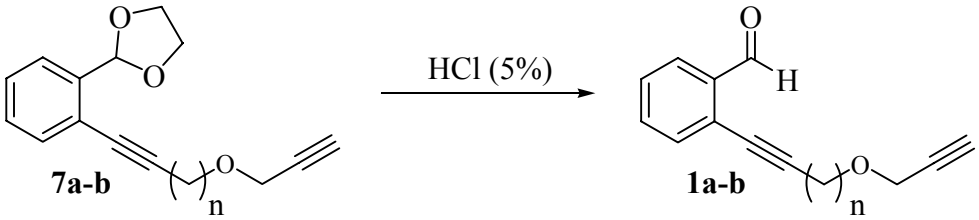
To a suspension of 120 mg (3.00 mmol, 60%) NaH in 15 ml of THF 2.65 mmol of alkynylol **4a-b** in 9 ml of THF were added dropwise. The mixture was stirred for 1 h at room temperature. A solution of 447 mg (3.00 mmol) propargyl bromide (80% in toluene) in 5 ml of THF were added at 0°C. TThe mixture was warmed up to room temperature and was stirred over night. 20 ml of brine were added and the organic layer was seperated. The aqueous layer was extracted three times with 20 ml of MTBE. The organic extract was washed with brine and dried over sodium sulfate. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate: **7a** (4:1) R_f = 0.30; **7b** (4:1) R_f = 0.32) gave product **7a-b**:

2-[2-(3-Prop-2-ynyloxy-1-propynyl)-phenyl]-[1,3]dioxolane (7a): 426 mg (1.76 mmol, 66%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3287 cm^{-1} (m), 3067 (w), 2955 (w), 2889 (m), 2855 (m), 2683 (w), 2328 (w), 2235 (w), 2116 (w), 1731 (m), 1602 (w), 1572 (w), 1486 (m), 1450 (m), 1394 (m), 1347 (m), 1246 (m), 1199 (m), 1118 (s), 1079 (vs), 1042 (m), 1028 (m), 969 (m), 943 (s), 884 (w), 845 (w), 764 (s); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 285 nm (2.61), 237 (3.87), 213 (3.82); ^{1}H NMR (400 MHz, acetone-d_6): δ = 2.99 ppm (t, *J* = 2.5 Hz; 1H, H-6''), 3.99-4.03 (dd, *J* = 10.6, 3.0 Hz, 2H, H-2'), 4.13-4.16 (dd, *J* = 10.6, 3.0 Hz, 2H, H-2'), 4.35 (d, *J* = 2.5 Hz, 2H, H-4''), 4.52 (s, 2H, H-3''), 6.11 (s, 1H, H-1'), 7.36-7.44 (m, 2H, H-5 and H-4), 7.49 (dd, *J* = 7.0, 1.5 Hz, 1H, H-3), 7.59 (d, *J* = 7.0 Hz, 1H, H-6); ^{13}C NMR {^{1}H} (100 MHz, acetone-d_6): δ = 56.88 ppm (C-4''), 57.56 (C-3''), 66.20 (C-2'), 76.47 (C-6''), 80.14 (C-5''), 84.58 (C-1''), 90.18 (C-2''), 102.51 (C-1'), 122.72 (C-2), 127.38 (C-6), 129.53 (C-5), 129.86 (C-4), 133.24 (C-3), 140.84 (C-1); MS (70 eV, EI): *m/z* (%) = 242 [M^+] (5),

241 (10), 185 (18), 169 (25), 157 (35), 141 (42), 129 (44), 115 (100), 103 (33), 89 (24), 77 (39), 73 (64), 63 (26), 59 (10), 51 (22); Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.25; H, 6.13.

2-[2-(4-Prop-2-ynyloxy-1-butynyl)-phenyl]-[1,3]dioxolane (7b): 399 mg (1.56 mmol, 59%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3275 cm^{-1} (w), 2875 (w), 2096 (w), 1716 (m), 1697 (m), 1649 (w), 1594 (w), 1557 (w), 1541 (w), 1508 (w), 1474 (w), 1456 (w), 1396 (w), 1338 (w), 1245 (w), 1097 (s), 1072 (s), 946 (m), 762 (s), 669 (m); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 320 nm (2.68), 274 (3.19), 239 (3.95), 213 (3.91); ^{1}H NMR (400 MHz, acetone-d_6): δ = 2.72 ppm (t, *J* = 6.8 Hz, 2H, H3''), 2.94 (t, *J* = 2.5 Hz, 1H, H-7''), 3.73 (t, *J* = 6.8 Hz, 2H, H-4''), 3.99-4.04 (m, 2H, H-2'), 4.09-4.15 (m, 2H, H-2'), 4.23 (d, *J* = 2.5 Hz, 2H, H-5''), 6.13 (s, 1H, H1'), 7.33-7.36 (m, 2H, H-4 and H-5), 7.41 (m, 1H, H-3), 7.55 (m, 1H, H-6); ^{13}C NMR {^{1}H} (100 MHz, acetone-d_6): δ = 21.21 ppm (C-3''), 58.46 (C-5''), 66.14 (C-2'), 68.68 (C-4''), 75.93 (C-7''), 79.35 (C-1''), 80.76 (C-6''), 92.60 (C-2''), 102.52 (C-1'), 124.03 (C-2), 127.34 (C-6), 128.70 (C-5), 129.71 (C-4), 132.99 (C-3), 140.57 (C-1); MS (70 eV, EI): *m/z* (%) = 255 [M^+] (3), 183 (19), 173 (13), 158 (26), 143 (43), 129 (32), 115 (100), 105 (11), 89 (27), 77 (16), 73 (22), 69 (33), 63 (17), 53 (15); Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.52; H, 6.50.

3. Preparation of 1a-b



n = 1 or 2

In a 50 ml flask 1.32 mmol of **7a-b** were dissolved in 10 ml of THF. At 0°C 3.4 ml (5%) of a aqueous solution of HCl were added dropwise. After 16h of stirring at room temperature 15 ml of ethyl acetate and 15 ml of water were added. The organic phase was separated and the aqueous layer was extracted two times with 10 ml of ethyl acetate. The organic extract was washed with brine and dried over sodium sulfate. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ ethyl acetate: **1a** (8:1) R_f = 0.30; **1b** (8:1) R_f = 0.29) gave products **1a-b**:

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2-(3-Prop-2-ynyloxy-1-propynyl)-benzaldehyde (1a): 214 mg (1.08 mmol, 82%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3293 cm^{-1} (s), 2851 (s), 2745 (m), 2330 (w), 2118 (w), 1697 (vs), 1594 (s), 1566 (w), 1477 (s), 1449 (s), 1389 (s), 1348 (s, br), 1275 (m), 1244 (s), 1194 (s), 1161 (w), 1081 (s, br), 967 (w), 932 (w), 886 (w), 825 (m) 763 (s); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 316 nm (3.38), 308 (3.56), 248(3.87), 236(3.87); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 ppm (t, *J* = 2.5 Hz, 1H, H-6''), 4.33 (d, *J* = 2.5 Hz, 2H, H-4''), 4.55 (s, 2H, H-3''), 7.45 (m, 1H, H-5), 7.53-7.57 (m, 2H, H-3 and H-4), 7.90 (d, *J* = 7.6 Hz, 1H, H-6), 10.49 (s, 1H, -CHO); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 56.93 ppm (C-4''), 57.26 (C-3''), 76.85 (C-6''), 78.75 (C-5''), 82.55 (C-1''), 91.39 (C-2''), 125.87 (C-2), 127.45 (C-6), 129.11 (C-5), 133.64 (C-3), 133.88 (C-4), 136.20 (C-1), 191.53 (C-1'); MS (70 eV, EI): *m/z* (%) = 197 [M^+] (4), 168 (100), 155 (10), 139 (38), 115 (78), 103 (40), 89 (22), 77 (45), 63 (30), 51 (28); Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.60; H, 5.48.

2-(4-Prop-2-ynyloxy-1-butynyl)-benzaldehyde (1b): 217 mg, (1.02 mmol, 77%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3287 cm^{-1} (m), 2865 (w), 2730 (w), 2240 (w), 2115 (w), 1693 (s), 1653 (w), 1594 (m), 1541 (w), 1475 (w), 1450 (w), 1389 (w), 1357 (w), 1272 (w), 1242 (w), 1192 (m), 1099 (s), 1014 (w), 949 (w), 823 (m), 762 (s), 669 (m), 636 (s); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 319 nm (3.45), 308 (3.50), 252 (3.92), 236 (3.93); ^{1}HNMR (400 MHz, $CDCl_3$): δ = 2.46 ppm (t, *J* = 2.5 Hz, 1H, H-7'), 2.79 (t, *J* = 6.8 Hz, 2H, H-3'), 3.77 (t, *J* = 6.6 Hz, 2H, H-4'), 4.23 (d, *J* = 2.2 Hz, 2H, H-5'), 7.40 (m, 1H, H-5), 7.51-7.52 (m, 2H, H-3 and H-4), 7.88 (d, *J* = 7.8 Hz, 1H, H-6), 10.54 (s, 1H, -CHO); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 21.06 ppm (C-3'), 58.40 (C-5'), 67.93 (C-4'), 74.92 (C-7'), 77.54 (C-1'), 79.50 (C-6'), 94.35 (C-2'), 127.15 (C-6), 127.46 (C-2), 128.33 (C-5), 133.78 (C-3), 134.08 (C-4), 136.30 (C-1), 192.21 (-CHO); MS (70 eV, EI): *m/z* (%) = 211 [M^+] (4), 182 (25), 158 (35), 153 (14), 143 (35), 128 (21), 115 (100), 89 (19), 69 (19), 63 (15); Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.24; H, 5.72.

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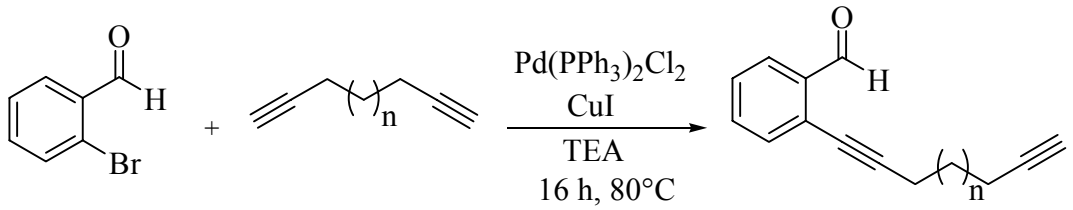
4. Preparation of 1c-f



3 **5c-f** : n = 2-4 or 10 **1c-f** : n = 2-4 or 10

In a screw capped flask 8.00 mmol of bisalkyne **5c-f**, 740 mg (4.00 mmol) of 2-bromobenzaldehyde (**3**), 56.0 mg (0.08 mmol, 2 mol%) of $PdCl_2(PPh_3)_2$ and 15.0 mg (0.08 mmol, 2 mol%) of CuI were suspended in 40 ml of triethylamine. The mixture was heated under stirring at 80°C for 16 h. The suspension was filtered through a short silica pad with ethyl acetate as eluent. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate: **1c** (30:1) R_f = 0.20; **1d** (20:1) R_f = 0.35; **1e** (30:1) R_f = 0.23; **1f** (40:1) R_f = 0.27) gave products **1c-f**:

2-Octa-1,7-diynyl-benzaldehyde (1c): 520 mg (2.48 mmol, 62 %) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3294 cm^{-1} (m), 2943 (s), 2864 (w), 2746 (w), 2228 (w), 2116 (w), 1851 (w), 1774 (m), 1694 (vs), 1595 (s), 1475 (m), 1450 (m), 1388 (m), 1243 (m), 1192 (m), 900 (m), 824 (m), 762 (s), 713 (m); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 318 nm (3.34), 308 (3.43), 244 (3.70);^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70-1.81 ppm (m, 4H, H-4' and H-5'), 1.98 (t, *J* = 2.6 Hz, 1H, H-8'), 2.27 (td, *J* = 6.7, 2.8 Hz, 2H, H-6'), 2.53 (t, *J* = 6.8 Hz, 2H, H-3'), 7.38 (m, 1H, H-5), 7.49-7.52 (m, 2H, H-3 and H-4), 7.88 (d, *J* = 7.6 Hz, 1H, H-6), 10.53 (s, 1H, -CHO); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 18.14 ppm (C-6'), 19.32 (C-3'), 27.60 (-CH_2-), 27.77 (-CH_2-), 68.86 (C-8'), 76.67 (C-1'), 84.04 (C-7'), 97.55 (C-2'), 127.15 (C-6), 127.87 (C-2), 128.11 (C-5), 133.48 (C-3), 133.81 (C-4), 136.18 (C-1), 192.21 (-CHO); MS (70 eV, EI): *m/z* (%) = 209 [M^+] (37), 195 (24), 181 (79), 167 (33), 154 (34), 144 (38), 128 (42), 115 (100), 104 (18), 89 (21), 77 (19), 59 (23); Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.73; H, 6.68.

2-Nona-1,8-diynyl-benzaldehyde (1d): 466 mg (2.08 mmol, 52%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3296 cm^{-1} (m), 2939 (s), 2861 (w), 2745 (w), 2229 (w), 2116 (w), 1696 (vs), 1652 (w), 1595 (s), 1476 (m), 1451 (m), 1431 (m), 1388 (m), 1295 (w), 1273 (m), 1243 (m), 1192 (m), 825 (m), 764 (s); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 320 nm (3.34), 308 (3.44), 248 (3.73); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58-1.63 ppm (m, 4H, H-5' and H-6'), 1.66 (m, 2H, H-4'), 1.97 (t, *J* '= 2.5 Hz, 1H, H-9'), 2.23 (m, 2H, H-7'), 2.51 (t, *J* = 6.8 Hz, 2H, H-3'),

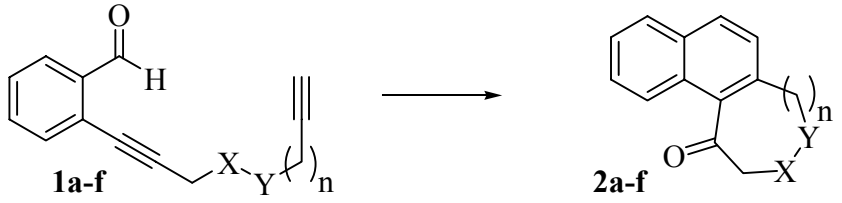
7.38 (m, 1H, H-5), 7.51 (m, 2H, H-3 and H-4), 7.88 (d, *J* = 7.6 Hz, 1H, H-6), 10.54 (s, 1H, -CHO); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 18.46 ppm (C-7'), 19.67 (C-3'), 28.07 (-CH_2-), 28.14 (-CH_2-), 28.16 (-CH_2-), 68.62 (C-9'), 76.74 (C-1'), 84.42 (C-8'), 97.90 (C-2'), 127.12 (C-6), 127.99 (C-2), 128.06 (C-5), 133.48 (C-3), 133.80 (C-4), 136.19 (C-1), 192.25 (-CHO); MS (70 eV, EI): *m/z* (%) = 223 [M^+] (11), 209 (12), 195 (60), 181 (50), 167 (31), 157 (28), 144 (100), 128 (39), 115 (100), 102 (10), 89 (22), 77 (15), 59 (15); Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.38; H, 7.13.

2-Deca-1,9-diynyl-benzaldehyde (1e): 695 mg (2.92 mmol, 73%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3299 cm^{-1} (m), 2938 (s), 2860 (w), 2746 (w), 2228 (w), 2116 (w), 1776 (w), 1697 (vs), 1595 (s), 1476 (m), 1451 (m), 1388 (m), 1273 (m), 1244 (m), 1193 (m), 901 (w), 825 (m), 764 (s); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 252 nm (3.41); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46-1.49 ppm (m, 4H, H-5' and H-6'), 1.55 (m, 2H, H-7'), 1.64 (m, 2H, H-4'), 1.94 (t, *J* = 1.8 Hz, 1H, H-10'), 2.19 (2H, td, *J* = 4.8, 1.8 Hz, H-8'), 2.48 (t, *J* = 4.8 Hz, 2H, H-3'), 7.36 (m, 1H, H-5), 7.48-7.52 (m, 2H, H-3 and H-4), 7.86 (d, *J* = 7.6 Hz, 1H, H-6), 10.52 (s, 1H, -CHO); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 18.45 ppm (C-8'), 19.65 (C-3'), 28.29 (-CH_2-), 28.28 (-CH_2-), 28.48 (-CH_2-), 28.54 (-CH_2-), 68.41 (C-10'), 76.58 (C-1'), 84.59 (C-9'), 98.07 (C-2'), 127.05 (C-6), 127.99 (C-2 and C-5), 133.41 (C-3), 133.79 (C-4), 136.11 (C-1), 192.25 (-CHO); MS (70 eV, EI): *m/z* (%) = 237 [M^+] (3), 223 (4), 209 (8), 195 (15), 181 (18), 167 (13), 157 (35), 144 (100), 128 (39), 115 (63), 95 (4), 89 (12), 77 (10), 63 (10), 55 (13); Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 6.71. Found: C, 85.29; H, 7.90.

2-Hexadeca-1,15-diynyl-benzaldehyde (1f): 799 mg (2.48 mmol, 62%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3305 cm^{-1} (m), 2924 (s), 2851 (s), 2742 (w), 2227 (w), 2116 (w), 1696 (s), 1594 (m), 1475 (m), 1465 (m), 1386 (w), 1272 (w), 1243 (m), 1191 (m), 1158 (m), 824 (w), 762 (m); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 320 nm (3.46), 308 (3.48), 256 (3.95), 236 (3.97); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28-1.56 ppm (m, 16H, H-5', H-6', H-7', H-8', H-9', H-10', H-11', H-12' and H-13'), 1.64 (m, 2H, H-4'), 1.93 (t, *J* = 2.8 Hz, 1H, H-16'), 2.18 (2H, td, *J* = 7.1, 2.8 Hz, H-14'), 2.48 (t, *J* = 7.1 Hz, 2H, H-3'), 7.38 (m, 1H, H-5), 7.49-7.52 (m, 2H, H-3 and H-4), 7.88 (d, *J* = 7.6 Hz, 1H, H-6), 10.54 (s, 1H, -CHO); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 18.56 ppm (C-14'), 19.77 (C-3'), 28.67 (-CH_2-), 28.70 (-CH_2-), 28.92 (-CH_2-), 29.14 (-CH_2-), 29.27 (-CH_2-), 29.64 (-CH_2-), 29.72 (-CH_2-), 29.73 (-CH_2-), 68.17 (C-16'), 76.51 (C-1'), 84.96 (C-15'), 98.40 (C-2'), 127.09 (C-6), 128.00 (C-5), 128.14 (C-2), 133.45 (C-3), 133.81 (C-4), 136.20 (C-1), 192.34 (-CHO); MS (70 eV, EI): *m/z* (%) = 322 [M^+] (4),

211 (4), 197 (17), 185 (23), 171 (11), 157 (35), 144 (100), 131 (15), 115 (29), 91 (4), 81 (6), 67 (8), 55 (12); Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.36%; H, 9.51.

5. Preparation of 2a-f



1a : X = O, Y = CH_2, n = 0
1b : X = CH_2, Y = O, n = 1
1c-f : X = CH_2, Y = CH_2, n = 1-3 or 9

In a screw-capped flask 0.50 mmol of **1b-f** (0.20 mmol **1a**) and 4.0 mg (15 μmol) [2 mg, 7 μmol in case of **1a**] of $PtCl_2$ were dissolved in 20 ml (10 ml) of toluene. The mixture was stirred at 140°C for a certain time (see table 1) and after cooling to room temperature it was filtered through a short silica pad (eluent: ethyl acetate). Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate: **2a** (8:1), R_f = 0.23; **2b** (2:1), R_f = 0.39; **2c** (40:1), R_f = 0.18; **2d** (20:1), R_f = 0.28; **2e** (30:1), R_f = 0.20; **2f** (40:1), R_f = 0.28) gave product **2a-f**:

1*H*-Benzo[*f*]isochroman-4-one (2a): 27 mg (0.14 mmol, 67%) as colorless crystals (m.p.: 100-102°C): IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (m), 2854 (m), 2822 (m), 1728 (w), 1663 (vs), 1622 (w), 1596 (m), 1515 (w), 1465 (w), 1444 (m), 1417 (w), 1394 (w), 1359 (w), 1347 (m), 1331 (m), 1295 (w), 1239 (s), 1221 (s), 1170 (w), 1156 (w), 1128 (w), 1116 (s), 1048 (m), 956 (s), 934 (w), 878 (w), 814 (vs), 786 (w), 756 (vs), 689 (w), 616 (w); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 316 nm (3.57), 308 (3.65), 244 (4.03), 222 (4.08); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 ppm (s, 2H, H-3), 5.04 (s, 2H, H-1), 7.28 (d, *J* = 8.5 Hz, 1H, H-10), 7.57 (td, *J* = 7.5, 1.0 Hz, 1H, H-7), 7.69 (td, *J* = 8.0, 1.0 Hz, 1H, H-6), 7.86 (d, *J* = 8.0 Hz, 1H, H-8), 8.05 (d, *J* = 8.5 Hz, 1H, H-9), 9.43 (d, *J* = 9.0 Hz, 1H, H-5); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 69.12 ppm (C-1), 73.33 (C-3), 122.16 (C-10), 124.07 (C-4a), 126.73 (C-5 and C-7), 128.67 (C-8), 129.75 (C-6), 130.90 (C-4b), 133.18 (C-8a), 135.72 (C-9), 144.26 (C-10a), 195.51 (C-4); MS (70 eV, EI): *m/z* (%) = 198 [M^+] (64), 182 (36), 180 (35), 168 (89), 145 (10), 140 (100), 112 (15), 103 (14), 89 (10), 84 (21), 74 (17), 70 (22), 59 (75); Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.48; H, 5.38.

2,3-Dihydronaphto-[2,1-c]-oxepin-1(5*H*)-one (2b): 89 mg (0.42 mmol, 89%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3050 cm^{-1} (w), 2955 (w), 2864 (w), 1684 (s), 1595 (w), 1508 (w), 1466 (w), 1428 (w), 1340 (w), 1284 (w), 1228 (m), 1185 (s), 1164 (s), 1125 (s), 1093 (s), 1034 (m), 973 (m), 889 (w), 868 (w), 842 (w), 816 (s), 786 (m), 753 (s), 670 (w); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 298 nm (3.72), 235 (3.99); ^1H NMR (400 MHz, $CDCl_3$): δ = 3.14 ppm (t, *J* = 6.3 Hz, 2H, H-2), 4.11 (t, *J* = 6.1 Hz, 2H, H-3), 5.02 (s, 2H, H-5), 7.30 (d, *J* = 8.3 Hz, 1H, H-6), 7.49-7.58 (m, 2H H-9 and H-10), 7.85 (dd, *J* = 7.8, 0.5 Hz, 1H, H-8), 7.90 (d, *J* = 8.3 Hz, 1H, H-7), 8.30 (d, *J* = 8.6 Hz, 1H, H-11); ^{13}C NMR {^1H} (100 MHz, $CDCl_3$): δ = 46.16 ppm (C-2), 66.06 (C-3), 72.47 (C-5), 125.19 (C-6), 125.31 (C-11), 126.52 (C-9), 128.02 (C-10), 128.32 (C-8), 129.93 (C-11a), 131.46 (C-7), 133.37 (C-7a), 135.83 (C-11b), 137.00 (C-5a), 204.51 (C-1); MS (70 eV, EI): *m/z* (%) = 212 [M^+] (43), 184 (45), 155 (100), 139 (14), 127 (41), 115 (4), 91 (3), 76 (8), 63 (6), 51 (4); Anal. Calcd for $C_{14}H_{12}O_2$: C. 79.22; H, 5.70. Found: C, 79.19; H, 5.96.

7,8,9,10-Tetrahydro-cyclohepta[a]naphthalen-11-one (1c): 100 mg (0.48 mmol, 95%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3050 cm^{-1} (w), 2935 (s), 1676 (vs), 1593 (w), 1507 (m), 1429 (w), 1338 (w), 1214 (m), 1170 (w), 1115 (m), 1048 (w), 941 (m), 924 (w), 866 (w), 815 (s), 769 (m), 748 (s), 678 (w); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 297 nm (3.76), 237 (4.03); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.83 ppm (m, 2H, H-9), 1.88 (m, 2H, H-8), 2.76 (m, 2H, H-10), 2.97 (m, 2H, H-7), 7.27 (d, 1H, *J* = 8.3 Hz, H-6), 7.46 (m, 1H, H-2), 7.50 (m, 1H, H-3), 7.83 (d, 1H, *J* = 8.8 Hz, H-4), 7.84 (d, 1H, *J* = 8.8 Hz, H-5), 8.06 (dd, 1H, *J* = 8.7, 0.8 Hz, H-1); ^{13}C NMR {^1H} (100 MHz, $CDCl_3$): δ = 22.11 ppm (C-9), 24.78 (C-8), 35.59 (C-7), 42.22 (C-10), 124.60 (C-1), 125.36 (C-2), 127.15 (C-3), 127.18 (C-6), 127.92 (C-4), 129.47 (C-4a), 130.70 (C-5), 132.43 (C-11b), 136.51 (C-6a), 209.97 (C-11); MS (70 eV, EI): *m/z* (%) = 210 [M^+] (100), 182 (49), 167 (11), 154 (36), 141 (33), 127 (8), 115 (8), 103 (6), 89 (5), 76 (7), 63 (5), 59 (24).

8,9,10,11-Tetrahydro-7*H*-cycloocta[a]naphthalen-12-one (1d): 90 mg (0.40 mmol, 80%) as colorless oil: IR (NaCl): $\tilde{\nu}$ = 3051 cm^{-1} (w), 2931 (s), 2855 (m), 1693 (vs), 1596 (w), 1507 (m), 1449 (m), 1407 (w), 1340 (w), 1306 (w), 1280 (w), 1255 (w), 1215 (m), 1199 (m), 1104 (w), 1028 (w), 1003 (w), 908 (w), 863 (w), 819 (m), 747 (w), 680 (m); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 320 nm (2.69), 279 (3.69), 231 (3.91); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.63 ppm (m, 2H, H-9), 1.75 (m, 2H, H-10) 1.84 (m, 2H, H-8), 2.81-2.87 (m, 4H, H-7 and H-11), 7.28 (d, 1H, *J* = 8.3 Hz, H-6), 7.43-7.49 (m, 2H, H-2 and H-3), 7.55 (m, 1H, H-4), 7.79 (d, 1H, *J* = 8.6 Hz, H-5), 7.83 (m, 1H, H-1); ^{13}C NMR {^1H} (100 MHz, $CDCl_3$): δ = 23.99 ppm

(C-10), 27.93 (C-9), 29.07 (C-8), 32.68 (C-7), 48.50 (C-11), 124.14 (C-4), 125.65 (C-2), 126.96 (C-3), 127.75 (C-6), 128.36 (C-1), 128.76 (C-12b), 128.99 (C-5), 132.07 (C-4a), 136.05 (C-6a), 137.64 (C-12a), 214.12 (C-12); MS (70 eV, EI): *m/z* (%) = 224 [M^+] (44), 195 (5), 181 (100), 168 (9), 153 (11), 140 (17), 127 (3), 115 (5), 59 (9).

7,8,9,10,11,12-Hexahydro-cyclonona[a]naphthalen-13-one (1e): 15 mg (63 µmol,, 13%) as colorless crystals (m.p.: 66°C): IR (KBr): $\tilde{\nu}$ = 3048 cm^{-1} (w), 2927 (s), 2876 (m), 2849 (m), 1691 (vs), 1594 (w), 1507 (w), 1473 (m), 1457 (m), 1384 (w), 1331 (w), 1309 (w), 1270 (w), 1241 (w), 1213 (m), 1179 (m), 1145 (w), 1106 (m), 1061 (w), 1024 (w), 995 (w), 971 (w), 861 (w), 818 (s), 805 (m), 792 (w), 749 (s), 671 (w); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 279 nm (2.57), 226 (3.44); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.33 ppm (m, 2H, H-9), 1.55 (m, 2H, H-10), 1.75 (m, 2H, H-8) 1.91 (m, 2H, H-11), 2.87 ("dd", *J* = 6.6 Hz, 2H, H-7), 2.95 ("dd", *J* = 6.3 Hz, 2H, H-12), 7.27 (d, 1H, *J* = 7.3 Hz, H-6), 7.44-7.48 (m, 2H, H-2 and H-3), 7.55 (m, 1H, H-4), 7.79 (d, 1H, *J* = 8.3 Hz, H-5), 7.84 (m, 1H, H-1); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 22.22 ppm (C-9), 24.81 (C-11), 26.27 (C-10), 29.03 (C-8), 31.61 (C-7), 43.56 (C-12), 124.43 (C-4), 125.68 (C-2), 126.87 (C-3), 128.00 (C-6), 128.47 (C-1), 128.67 (C-13b), 129.03 (C-5), 132.02 (C-4a), 134.34 (C-6a), 140.54 (C-13a), 214.38 (C-13); MS (70 eV, EI): *m/z* (%) = 228 [M^+] (45), 195 (17), 181 (100), 165 (9), 154 (17), 141 (15), 127 (4), 115 (7), 59 (6).

7,8,9,10,11,12,13,14,15,16,17,18-Dodecahydro-cyclopentadeca[a]naphthalen-19-one (1f): 9 mg (3 µmol, 5%) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21-1.45 ppm (m, 16H, -CH_2-), 1.78 (m, 4H, -CH_2-), 2.85 (t, *J* = 6.6 Hz, 2H, -CH_2-), 3.03 (t, *J* = 7.6 Hz, 2H, H-7), 7.49-7.53 (m, 2H, H-18), 7.74-7.75 (m, 2H, H-Ar), 7.81 (dd, *J* = 7.7, 2.3 Hz, 1H, H-Ar), 8.52 (dd, 1H, *J* = 8.2, 2.5 Hz, H-Ar); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 25.22 ppm (-CH_2-), 26.58 (-CH_2-), 26.85 (-CH_2-), 26.91 (-CH_2-), 26.95 (-CH_2-), 27.11 (-CH_2-), 27.27 (-CH_2-), 27.78 (-CH_2-), 29.85 (-CH_2-), 34.78 (C-7), 42.13 (C-18), 126.52 (C-Ar), 127.10 (C-Ar), 128.11 (C-Ar), 128.30 (C-Ar), 129.14 (C-Ar), 129.66 (C-Ar), 131.68 (C-Ar), 134.55 (C-Ar), 136.16 (C-Ar), 138.74 (C-Ar), 205.97 (C=O); MS (70 eV, EI): *m/z* (%) = 322 [M^+] (100), 195 (7), 169 (12), 155 (8), 141 (22), 115 (5), 108 (10), 95 (7), 91 (29), 81 (8), 67 (6), 55 (12).

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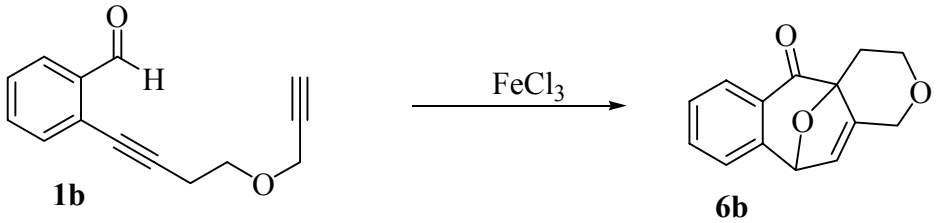
6. Preparation of 12,16-Dioxa-tetracyclo-[7.6.1.0^{2,7}.0^{9,14}]-hexadeca-2,4,6,14-tetraen-8-one (6b)



1b **6b**

70 mg of bisalkynylether **1b** (0.33 mmol) were dissolved in 5 ml of dichloromethane. To this solution 120 mg of $FeCl_3$ (0.47 mmol) were added and the suspension was stirred for 2h at room temperature. 10 ml (5%) of an aqueous solution of $NaHCO_3$ were added and the organic phase was seperated and the aqueous layer was extracted two times with 10 ml of CH_2Cl_2. The organic extract was washed with brine and dried over sodium sulfate. Evaporation of the solvents and flash chromatography of the residue (SiO_2, petroleum ether/ethyl acetate: **6b** (3:1) R_f = 0.33) gave product **6b**: 10 mg (44 µmol, 13%) as colorless crystals (m.p.: 138°C): IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1} (m), 3069 (w), 2960 (m), 2929 (m), 2876 (m), 2857 (w), 1697 (vs), 1597 (s), 1469 (w), 1448 (m), 1427 (w), 1383 (m), 1350 (w), 1326 (w), 1299 (s), 1271 (m), 1236 (m), 1211 (s), 1202 (s), 1157 (s), 1124 (m), 1096 (m), 1083 (s), 1054 (m), 1004 (m), 991 (s), 973 (m), 951 (s), 913 (s), 884 (m), 824 (m), 816 (m), 774 (s), 762 (s), 702 (m), 687 (m), 675 (w), 631 (m); UV-VIS (c = CH_3CN) λ_{max} (log ε) : 298 nm (3.10), 264 (3.67), 219 (4.13); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 ppm (dt, *J* = 12.9, 5.5 Hz, 1H, H-4), 2.53 (d, *J* = 12.9 Hz, 1H, H-4), 3.85 (dt, *J* = 12.3, 2.3 Hz, 1H, H-3), 4.01 (dd, *J* = 14.4, 2.0 Hz, 1H, H-1), 4.12 (dd, *J* = 12.0, 5.6 Hz, 1H, H-3), 4.58 (d, *J* = 14.4 Hz, 1H, H-1), 5.54 (d, *J* = 2.0 Hz, 1H, H-10), 6.53 (t, *J* = 2.0 Hz, 1H, H-11), 7.11 (d, *J* = 7.2, 1.2 Hz, 1H, H-9), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H, H-7), 7.42 (td, *J* = 7.2, 1.5 Hz, 1H, H-8), 7.94 (dd, *J* = 7.5, 1.3 Hz, 1H, H-6); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ = 32.49 ppm (C-4), 65.14 (C-1), 65.53 (C-3), 82.27 (C-10), 88.45 (C-4a), 122.00 (C-9), 128.38 (C-5a), 128.40 (C-6), 128.52 (C-7), 132.49 (C-11), 133.02 (C-8), 138.69 (C-11a), 145.61 (C-9a), 192.92 (C-5); MS (70 eV, EI): *m/z* (%) = 228 [M$^+$] (100), 200 (5), 170 (13), 156 (94), 141 (9), 128 (79), 115 (25), 102 (12), 89 (6) 77 (10), 63 (10), 55 (19), 51 (11).