SUPPORTING INFORMATION

Alkyne Cross Metathesis Reactions Of Extended Scope

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General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the drying agents indicated and were stored and transferred under Ar: CH_2Cl_2 (P_4O_{10}), toluene (Na/K), THF (magnesium/ anthracene). Flash chromatography: Merck silica gel (230-400 mesh). NMR: Spectra were recorded on a Bruker DPX 300 spectrometer in the solvent indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. IR: Nicolet Magna 750 FT-IR, wavenumbers in cm^{-1}. MS: Finnigan MAT 8200 (70 eV); HR-MS: Finnigan MAT 95. Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka) were used as received.

Representative Procedure for ACM: 2-(5-Chloro-pent-1-ynyl)-benzoic acid methylester: To a solution of complex **1** (57 mg, 0.092 mmol) in toluene (10 mL) and CH_2Cl_2 (300 μL) is added 2-prop-1-ynyl-benzoic acid methyl ester **6** (160 mg, 0.91 mmol) and 1,8-dichloro-oct-4-yne **2** (247 mg, 1.38 mmol) and the resulting solution is stirred at 80°C for 8 h. After evaporation of the solvent, the residue is chromatographed (first toluene, then hexanes/ethyl acetate 15:1) affording the title compound as a colorless oil (135 mg, 62 %). IR 3068, 2995, 2951, 2874, 2227, 1730, 1485, 1433, 1294, 1252, 1130, 1085, 758; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.89 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.49 (ddt, *J* = 15.2, 7.8, 1.5 Hz, 2H), 7.37 (dt, *J* = 7.5, 1.6 Hz, 1H), 3.91 (s, 3 H), 3.81 (t, *J* = 6.4 Hz, 2 H), 2.68 (t, *J* = 6.7 Hz, 2 H), 2.09 (q, *J* = 6.6 Hz, 2 H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 167.0, 134.4, 132.6, 131.9, 130.4, 127.8, 124.2, 93.9, 80.3, 52.3, 44.3, 31.8, 17.4; MS (EI) *m/z* (rel intensity) 236 (1), 201 (6), 187 (2), 174 (100), 159 (16), 143 (8), 131 (7), 115 (12); HR-MS ($C_{13}H_{13}O_2Cl$+H): *calcd*. 237.068232;

found 237.068136. Anal. *calcd*. for $C_{13}H_{13}O_2Cl$ (236.69): C, 65.97; H, 5.54; *found* C, 65.79; H, 5.46.

The following compounds have been prepared analogously:

3,3'-Bis(trifluoromethyl)-acetylene: IR 3077, 2926, 2857, 1609, 1587, 1493, 1440, 1348, 1165, 1128, 1070, 1913, 805, 694; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.85 (s, 2H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 135.2, 131.5, 129.5, 128.8, 125.7, 124.0, 122.4, 89.4; MS (EI) *m*/*z* (rel intensity) 314 (100), 295 (15), 264 (4), 245 (4), 225 (6), 194 (2), 176 (3), 169 (3), 157 (4), 147 (3), 132 (1), 99 (1), 75 (1); HR-MS ($C_{16}H_8F_6$): *calcd.* 314.053018, *found* 314.053135.

1-(5-Chloro-pent-1-ynyl)-3-trifluoromethyl-benzene: IR 3078, 2999, 2962, 2846, 2233, 1433, 1337, 1167, 1129, 1073, 902, 801, 696, 1602; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.69 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 7.6 Hz, 1H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 2.11 (quint., *J* = 6.6 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 135.2, 131.0, 129.3, 128.7, 124.8, 124.6, 124.3, 90.5, 80.3, 44.2, 31.7, 17.1; MS (EI) *m*/*z* (rel intensity) 246 (47), 227 (13), 211 (100), 191 (44), 183 (97), 142 (32), 133 (26), 115 (20), 87 (8), 75 (8), 63 (14); HR-MS ($C_{12}H_{10}F_3Cl$): *calcd.* 246.042312, *found* 246.042480. Anal. *calcd*. for $C_{12}H_{10}F_3Cl$ (246.66): C, 58.43; H, 4.09; *found* C, 58.60; H, 3.98.

4,4'-Ethynediyl-di-benzonitrile: IR 3058, 2920, 2225, 1928, 1675, 1606, 1502, 1408, 1273, 1182, 1022, 841, 553; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.61 (dd, *J* = 8.5, 1.8 Hz, 4H), 7.57 (dd, *J* = 8.5, 1.8 Hz, 4H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ132.0, 131.9, 126.8, 118.0, 112.2, 91.4; MS (EI) *m*/*z* (rel intensity) 228 (100), 201 (8), 175 (4), 151 (3), 137 (1), 100 (3), 87 (4), 74 (3), 63 (1).

4-(5-Chloro-pent-1-ynyl)-benzonitrile: IR 3091, 3059, 2960, 2926, 2227, 1604, 1501, 1291, 1177, 840, 657, 555; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.69 (s, 1H), 7.61 (d, *J* = 8.5Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 2.11 (quint., *J* = 6.6 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 132.4, 132.4, 128.9, 118.8, 111.5, 93.6, 80.4, 44.2, 31.5, 17.2; MS (EI) *m*/*z* (rel intensity) 203 (37), 168 (100), 153 (27), 140 (77), 127 (14), 113 (18), 87 (5), 75 (5), 63 (12); HR-MS ($C_{12}H_{10}NCl$): *calcd.* 203.050177, *found* 203.05025. Anal. *calcd*. for $C_{12}H_{10}NCl$ (203.67): C, 70.77; H, 4.95; N, 6.88; *found* C, 70.85; H, 4.95; N, 6.94.

Bis-(2-methoxy-phenyl)-acetylene: IR 3104, 3075, 3031, 2998, 2964, 2937, 2832, 1598, 1573, 1500, 1465, 1433, 1276, 1242, 1116, 1021, 753; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.50 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.35 (m, 1H), 6.97 (m, 2H), 3.94 (s, 3H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.3, 133.7, 130.1, 120.8, 112.9, 111.2, 90.0, 56.2; MS (EI) *m*/*z* (rel intensity) 238 (100), 223 (22), 207 (10), 195 (5), 178 (8), 165 (19), 152 (13), 131 (26), 119 (5), 89 (5), 76 (6), 63 (5); HR-MS ($C_{16}H_{14}O_2$): *calcd.* 238.099379, *found*. 238.099436.

1-(5-Chloro-pent-1-ynyl)-2-methoxy-benzene (10b): IR 3074, 3004, 2940, 2248, 1596, 1493, 1434, 1261, 1117, 1024, 755; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.36 - 7.27 (m, 2H), 6.94 - 6.9 (m, 2H), 3.87 (s, 3H), 2.64 (t, *J* = 6.7 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.97 (quint., *J* = 7.0 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): 160.5, 133.6, 129.2, 120.7, 119.8, 112.8, 111.0, 91.6, 78.8, 56.0, 25.2, 19.0, 16.4; MS (EI) *m/z* (rel intensity) 208 (100), 173 (35), 158 (31), 131 (62), 115 (67), 102 (14), 91 (35), 77 (13), 63 (15), 51 (13); HR-MS ($C_{12}H_{13}OCl$): *calcd.* 208.065493, *found* 208.065321. Anal. *calcd*. for $C_{12}H_{13}OCl$ (208.68): C, 69.07; H, 6.28; *found* C, 69.20; H, 6.24.

Bis-(2-methoxycarbonyl-phenyl)-ethyne: IR 3073, 2985, 2849, 2844, 1722, 1567, 1493, 1435, 1256, 1084, 964, 760, 696; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.99 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.72 (dd, *J* = 7.6, 1.3 Hz 1H), 7.56 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.45 (dt, *J* = 7.7, 1.4 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (CD_2Cl_2, 75 MHz): 166.8, 134.5, 132.4, 132.1, 130.7, 128.6, 124.0, 93.3, 52.5; MS (EI) *m/z* (rel intensity) 294 (10), 279 (100), 264 (24), 248 (20), 220 (17), 208 (3), 192 (2), 176 (7), 163 (10), 132 (8), 116 (4), 102 (7), 88 (9), 75 (4), 59 (2); HR-MS ($C_{18}H_{14}O_4$): *calcd.* 294.089208, *found* 294.089107. Anal. *calcd*. for $C_{18}H_{14}O_4$ (294.09): C, 73.46; H, 4.79; *found* C, 73.55; H, 4.72.

2-(5-Chloro-pent-1-ynyl)-benzoic acid methyl ester: IR 3068, 2995, 2951, 2874, 2227, 1730, 1485, 1433, 1294, 1252, 1130, 1085, 758; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.89 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.49 (ddt, *J* = 15.2, 7.8, 1.5 Hz, 2H), 7.37 (dt, *J* = 7.5, 1.6 Hz, 1H), 3.91 (s, 3 H), 3.81 (t, *J* = 6.4 Hz, 2 H), 2.68 (t, *J* = 6.7 Hz, 2H), 2.09 (quint., *J* = 6.6 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 167.0, 134.4, 132.6, 131.9, 130.4, 127.8, 124.2, 93.9, 80.3, 52.3, 44.3, 31.8, 17.4; MS (EI) *m/z* (rel intensity) 236 (1), 201 (6), 187 (2), 174 (100), 159 (16), 143 (8), 131 (7), 115 (12), 102 (6), 88 (3), 74 (2); HR-MS ($C_{13}H_{14}O_2Cl$+H): *calcd.* 237.068232, *found* 237.068136. Anal. *calcd*. for $C_{13}H_{13}O_2Cl$ (236.69): C, 65.97; H, 5.54; *found* C, 65.79; H, 5.46.

Tolan-4,4'-bis-carbaldehyde: IR 3059, 2846, 2742, 1702, 1602, 1562, 1385, 1300, 1205, 1161, 862, 827, 792; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.05 (s, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 191.6, 136.4, 132.7, 129.9, 128.9, 92.3; MS (EI) *m/z* (rel intensity) 234 (100), 205 (9), 176 (30), 151 (10), 116 (5), 102 (4), 88 (7), 75 (5), 63 (2), 51 (3); HR-MS ($C_{16}H_{10}O_2$): *calcd.* 234.068079, *found* 234.067917. Anal. *calcd*. for $C_{16}H_{10}O_2$ (234.07): C, 82.04; H, 4.30; *found* C, 82.11; H, 4.33.

4-(5-Chloro-pent-1-ynyl)-benzaldehyde: IR 2963, 2932, 2870, 2731, 2229, 1702, 1602, 1473, 1390, 1207, 1166, 829; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.05 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6.9 Hz, 2H), 2.09 (quint., *J* = 6.5 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 191.7, 135.7, 132.5, 130.3, 129.8, 93.2, 81.1, 44.2, 31.7, 17.3; MS (EI) *m/z* (rel intensity) 206 (96), 171 (59), 143 (87), 128 (91), 115 (100), 101 (6), 89 (13), 75 (11), 63 (26), 51 (14), 39 (14); HR-MS ($C_{12}H_{11}OCl$): *calcd.* 206.049843, *found* 206.049898. Anal. *calcd*. for $C_{12}H_{11}OCl$ (206.67): C, 69.74; H, 5.36; *found* C, 69.88; H, 5.43.

2-(5-Chloro-pent-1-ynyl)-thiophene: IR 3106, 2959, 2921, 2848, 2225, 1518, 1428, 1289, 1191, 1043, 851, 701; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.24 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.16 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.98 (dd, *J* = 5.2 Hz, 1H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 2.09 (quint., *J* = 6.6 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 131.6, 127.2, 126.6, 124.0, 92.7, 74.7, 44.3, 31.7, 17.4; MS (EI) *m/z* (rel intensity) 184 (62), 149 (51), 134 (22), 121 (100), 115 (42), 108 (4), 91 (86), 77 (24), 69 (12), 63 (14), 51 (10), 45 (15); Found: C, 58.40; H, 5.32. HR-MS ($C_9H_9Cl_4S$): *calcd.* 184.011351, *found* 184.011459.

1-Hex-1-ynyl-2-methoxy-benzene (10a): IR 3074, 3002, 2957, 2933, 2872, 2232, 1596, 1493, 1262, 1171, 1027, 750; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.36 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.27(dt, *J* = 8.2, 1.8 Hz, 1H), 6.90 (m, 2H), 3.87 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.65 - 1.47 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.3, 133.8, 129.2, 120.6, 113.5, 111.0, 94.8, 77.0, 56.0, 31.3, 22.4, 19.6, 13.8; MS (EI) *m/z* (rel intensity) 188 (100), 173 (45), 159 (35), 145 (30), 131 (46), 115 (52), 107 (10), 91 (34), 77 (11), 63 (9), 51 (7); HR-MS ($C_{13}H_{16}O$): *calcd.* 188.120115, *found* 188.120241. Anal. *calcd*. for $C_{13}H_{16}O$ (188.12): C, 82.94; H, 8.57; *found* C, 82.75; H, 8.65.

6-(2-Methoxy-phenyl)-hex-5-yne-nitrile (10c): IR 3074, 3004, 2940, 2837, 2248, 1596, 1493, 1434,1261, 1117, 1024, 755; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.38 (dd, *J* =7.8, 1.8 Hz, 1H), 7.30 (td, *J* =7.8, 1.8 Hz, 1H), 6.94 - 6.88 (m, 2H), 3.87 (s, 3H), 2.64 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.97 (quint., *J* = 7.0 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 160.5, 133.6, 129.7, 120.7, 119.8, 112.8, 111.0, 91.6, 78.8, 56.0, 25.2, 19.1, 16.4; MS (EI) *m/z* (rel intensity) 199 (100), 184 (7), 171 (30), 157 (13), 144 (26), 131 (22), 115 (49), 102 (9), 91 (19), 77 (8), 68 (22), 63 (11), 51 (8), 39 (9); HR-MS ($C_{13}H_{13}NO$): *calcd.* 199.099714, *found* 199.099461. Anal. *calcd*. for $C_{13}H_{13}NO$ (199.10): C, 78.36; H, 6.58; N, 7.03; *found* C, 78.30; H, 6.52; N, 7.09.

2-[6-(2-Methoxy-phenyl)-hex-5-ynyloxy]-tetrahydro-pyran (10d): IR 3073, 2941, 2868, 2792, 2233, 2051, 1596, 1493, 1464 1261, 1118, 1033, 752; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.32 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.25 (dt, *J* = 8.2, 1.8 Hz, 1H), 6.90 (m, 2H), 4.50 (t, *J* = 3.2Hz, 1H), 3.86 (s, 3H), 3.87- 3.74 (m, 2H), 3.50- 3.43 (m, 2H), 2.51 (t, *J* = 6.9Hz, 2H), 1.81 - 1.69 (m, 10H); ^{13}C NMR (CD_2Cl_2, 75 MHz): 160.3, 133.8, 129.3, 120.6, 113.5, 111.0, 99.1, 94.5, 77.2, 67.2, 62.4, 56.0, 31.2, 29.4, 26.1, 26.0, 20.0, 19.8; MS (EI) *m/z* (rel intensity) 288 (9), 257 (3), 217 (13), 204 (10), 188 (4), 172 (11), 158 (8), 145 (9), 131 (10), 115 (18), 85 (100), 67 (13), 57 (14), 41 (16); HR-MS ($C_{18}H_{24}O_3$): *calcd.* 288.172544, *found* 288.172475. Anal. *calcd*. for $C_{18}H_{24}O_3$ (288.17): C, 74.79; H, 8.39; *found* C, 74.88; H, 8.48.

(4-Benzosulfonyl-but-1-ynyl)-benzene (13): IR 3062, 2918, 2240, 1585, 1491, 1447, 1308, 1151, 1086, 759, 731, 689, 594, 528; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.95 (d, *J* = 8.1Hz, 2H), 7.7 – 7.58 (m, 3H), 7.30 (s, 5H), 3.34 (t, *J* = 7.3 Hz, 2H), 2.86 (t, *J* = 7.9 Hz, 2H) ; ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 139.1, 134.3, 131.8, 129.8, 128.6, 128.5, 123.2, 85.3, 82.5, 55.0, 14.6 ; MS (EI) *m/z* (rel intensity) 270 (2), 178 (2), 128 (100), 102 (5), 77 (11), 51 (7); HR-MS

($C_{16}H_{14}O_2S$+H): *calcd.* 271.079277, *found* 271.079062. Anal. *calcd*. for $C_{16}H_{14}O_2S$ (270.07): C, 71.08; H, 5.22; *found* C, 71.18; H, 5.29.

Hex-1-ynyl-benzene (15a): IR 3080, 3055, 2958, 2872, 2231, 1598, 1490, 1465, 1070, 912, 755, 691; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.42 – 7.39 (m, 2H), 7.36 – 7.29 (m, 3H), 2.45 (t, *J* = 6.9, 2H), 1.68 – 1.46 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 131.8, 128.6, 127.8, 124.5, 90.8, 80.7, 31.3, 22.4, 19.4, 13.8; MS (EI) *m/z* (rel intensity) 158 (33), 143 (53), 129 (59), 115 (100), 102 (17), 89 (15), 77 (8), 63 (11), 51 (8), 39 (9).

1-Hex-1-ynyl-4-methoxy-benzene (15b): IR 3002, 2957, 2934, 2232, 1596, 1493, 1464, 1262, 1120, 1027, 751; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.31 (d, *J* = 9.2 Hz, 2H), 6.81(d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.70 - 1.30 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 159.1, 132.8, 132.3, 113.9, 88.7, 80.3, 55.1, 31.0, 22.0, 19.1, 13.6; MS (EI) *m/z* (rel intensity) 188 (100), 173 (45), 159 (35), 145 (30), 131 (46), 115 (52), 107 (10), 91 (34), 77 (11), 63 (9), 51 (7).

4-(Hex-1-ynyl)-benzoic acid ethyl ester (15c): IR 2959, 2934, 2873, 2230, 1719, 1607, 1465, 1272, 1106, 858, 770, 697; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 1.67 - 1.44 (m, 4 H), 1.39 (t, *J* = 7.1 Hz, 3 H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 166.3, 131.7, 129.8, 129.6, 129.2, 94.3, 80.2, 61.4, 31.1, 22.4, 19.5, 14.5, 13.8; MS (EI) *m/z* (rel intensity) 230 (87), 215 (40), 201 (12), 185 (87), 173 (6), 157 (81), 143 (34), 129 (100), 115 (42), 101 (6), 91 (13), 77 (11), 63 (10), 29 (43); HR-MS ($C_{15}H_{18}O_2$): *calcd.* 230.130679, *found* 230.130827. Anal. *calcd*. for $C_{15}H_{18}O_2$ (230.13): C, 78.16; H, 7.82; *found* C, 78.22; H, 7.76.

1-Cyano-9-(tetrahydro-pyran-2-yloxy)-non-4-yne: IR 2942, 2867, 2247, 1454, 1352, 1201, 1137, 1120, 1076, 1034, 986, 905, 869, 814; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 4.56 (t, *J* = 3.4 Hz, 1H), 3.89 – 3.77 (m, 1H), 3.76 – 3.69 (m, 1H), 3.50 – 3.43 (m, 1H), 3.42 – 3.35 (m, 1H), 2.49 (t, *J* = 7.2 Hz, 2 H), 2.36 – 2.30 (m, 2H), 2.23 – 2.18 (m, 2H), 2.36 – 2.30 (m, 2H), 1.83 (quint., *J* = 6.9 Hz, 2 H), 1.78 – 1.53 (m, 10H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 119.8, 99.1, 82.2, 77.8, 67.2, 62.2, 31.2, 29.3, 26.2, 25.9, 25.4, 20.0, 18.8, 18.2, 16.4; MS (EI) *m/z* (rel intensity) 249 (<1), 181 (1), 166 (2), 148 (14), 131 (7), 120 (7), 101 (9), 85(100), 79 (11), 67 (12), 56 (9), 41 (17); HR-MS ($C_{15}H_{13}O_2N$+H): *calcd.* 250.180703, *found* 250.180949. Anal. *calcd*. for $C_{15}H_{23}O_2N$ (249.17): C, 72.25; H, 9.30; N, 5.62; *found* C, 72.46; H, 9.39; N, 5.72.

1-Chloro-8-cyano-4-octyne: IR 2961, 2943, 2872, 2845, 2247, 1435, 1348, 1291, 859, 650; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 3.67 (t, *J* = 6.4 Hz, 2H), 2.48 (t, *J* = 2.6 Hz, 2H), 2.39 - 2.31 (m, 4 H), 1.94 (quint., *J* = 6.4 Hz, 2H), 1.83 (quint., *J* = 6.8 Hz, 2H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 119.7, 80.3, 78.7, 44.3, 31.9, 25.2, 18.1, 16.4, 16.3; MS (EI) *m/z* (rel intensity) 169 (24), 141 (4), 132 (11), 120 (100), 106 (24), 91 (23), 79 (46), 65 (23), 51 (16), 39 (27), 27 (21); HR-MS ($C_9H_{12}NCl$): *calcd.* 169.065827, *found* 169.065657. Anal. *calcd*. for $C_9H_{12}NCl$ (169.07): C, 63.72; H, 7.13; N, 8.26; *found* C, 63.86; H, 7.18; N, 8.35.

7-[3-(*tert*-Butyl-dimethyl-silanyloxy)-5-oxo-2-(3-triethylsilanyloxy-oct-2-enyl)-cyclopentyl]-hept-5-ynoic acid methyl ester ((–)-18a). $[\alpha]_D^{20}$ = –14.6 (c = 0.78, $CHCl_3$). IR 2956, 2929, 2858, 1748, 1607, 1464, 1252, 1110, 837, 776; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 6.37 (m, 1H), 5.73 - 5.55 (m, 2H), 4.20 - 4.08 (m, 1H), 3.66 (s, 3H), 2.90 - 2.55 (m, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.35 - 2.00 (m, 7H), 1.77 (dt, *J* = 14.4, 7.2 Hz, 2H), 1.60 - 1.19 (m, 7H), 1.05 - 0.85 (m, 21H), 0.62 (q, *J* = 8.0 Hz, 6H), 0.08 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 213.9, 173.8, 137.1, 128.6, 120.2, 115.4, 81.2, 77.7, 73.4, 73.2, 53.1, 52.2, 51.7, 48.1, 39.0, 33.1, 32.3, 30.3, 25.9, 25.5, 24.6, 23.0, 18.4, 18.3, 17.1, 14.2, 7.1, 5.4, –4.5, –4.6; MS (EI) *m/z* (rel. intensity) 593 ([M^+], 3), 563 (21), 535 (85), 521 (25), 460 (8), 431 (47), 389 (65), 297 (21), 115 (30), 87 (58),75 (100), 59 (23); HR-MS ($C_{33}H_{60}O_5Si_2$ - C_4H_9): *calcd.* 535.327506, *found* 535.327411; Anal. *calcd*. for $C_{33}H_{60}O_5Si_2$ (593.00): C, 66.84; H, 10.20; *found* C, 66.52; H, 10.18.

7-[2-(3-Acetoxy-oct-1-enyl)-3-(*tert*-butyl-dimethyl-silanyloxy)-5-oxo-cyclopentyl]-hept-5-ynoic acid methyl ester ((–)-18b): $[\alpha]_D^{20}$ = –44.9 (c = 0.49, $CHCl_3$). IR 2955, 2931, 2858, 1742, 1631, 1437, 1372, 1244, 1117, 1018, 969, 839, 779; ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 5.70 - 5.55 (m, 2H), 5.40 - 5.22 (m, 1H), 4.11 (dt, *J* = 13.5, 7.2 Hz, 1H), 3.66 (s, 3H), 2.80 - 2.55 (m, 3 H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.32 -1.95 (m, 9H), 1.77 (dt, *J* = 14.3, 7.1 Hz, 2H), 1.45 -1.23 (m, 7H), 0.90 (m, 12H), 0.07 (s, 6H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 213.3, 173.8, 170.3, 132.7, 132.7, 81.3, 77.5, 74.5, 72.9, 53.1, 53.1, 52.9, 51.7, 47.9, 34.9, 33.1, 31.9, 25.9, 25.3, 24.6, 22.9, 21.4, 18.4, 18.3, 16.8, 14.1, –4.6, –4.7; MS (EI) *m/z* (rel intensity) 520 (<1), 463 (12), 403 (31), 297 (18), 275 (19), 201 (14), 117 (32), 75 (100), 55 (27), 43 (60); HR-MS ($C_{29}H_{48}O_6Si$+H): *calcd.* 521.329842, *found* 521.329390. Anal. *calcd*. for $C_{29}H_{48}O_6Si$ (520.77): C, 66.88; H, 9.29; *found* C, 66.65; H, 9.26.

Prostaglandin E_2 Methyl Ester ((–)-19). Colorless syrup. $[\alpha]_D^{20}$ = –69.2 (*c* = 0.49, CH_3OH); [Lit.[1] $[\alpha]_D^{20}$ = –71.8 (*c* = 1.31, CH_3OH)]; IR (neat) 3420, 2954, 2931, 2859, 1742, 1437, 1245, 1159, 1074, 970 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (1H, dd, *J* = 6.6, 15.3 Hz), 5.56 (1H, dd, *J* = 8.0, 15.3 Hz), 5.36 (2H, m), 4.20-3.96 (2H, m), 3.67 (3H, s), 3.15 (1H, br. s), 2.74 (1H, ddd, *J* = 0.9, 7.4, 18.5 Hz), 2.48-1.20 (20H, m), 0.89 (3H, t, *J* = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 174.2, 137.0, 131.0, 130.9, 126.5, 77.2, 77.0, 72.8, 72.1, 54.5, 53.5, 51.6, 46.1, 37.3, 33.4, 31.7, 26.6, 25.2, 25.0, 24.7, 22.6, 14.0; MS (EI) *m/z* (rel intensity) 366 ($[M]^{+\cdot}$, 0.5), 348 ($[M–H_2O]^{+\cdot}$, 21), 330 (16), 277 (32), 245 (25), 208 (79), 190 (46), 164 (86), 99 (76), 43 (100).

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[1] Johnson, C. J., Penning, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 4726.