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# Supporting Information

69451 Weinheim, Germany

# Hexasilylated Total *Carbo*-mer of Benzene

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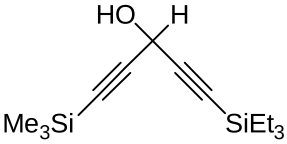
**General remarks.** THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane and dichloromethane over $P_2O_5$. Commercial solutions of EtMgBr 3 M in diethyl ether and *n*-BuLi 2.5 M in hexane were used and their effective concentration was checked by titration with 2,2,2'-trimethylpropionanilide. All other reagents were used as commercially available. All reactions were carried out under nitrogen or argon atmosphere, using schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 µm). Silica gel thin layer chromatography plates (60F254, 0.25 mm) were revealed by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used. IR: 0.1 mm $CaF_2$ cell, Perkin-Elmer GX FT-IR. $^1$H and $^{13}$C NMR: Bruker AC 200, AM 250, DPX 300 or AMX 400. X-Ray diffraction: Ipds STOE. Mass spectrometry: Quadrupolar Nermag R10-10H. Elemental analyses: Perkin-Elmer 2400 CHN (flash combustion and detection by catharometry). All IR and NMR spectra were recorded in $CDCl_3$ solutions. IR absorption frequencies *n* are in cm$^{-1}$. NMR chemical shifts *d* are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants *J* are in Hz.

**Experimental procedures and characterizations.**

**•1-triethylsilyl-5-trimethylsilylpenta-1,4-diyn-3-ol.**

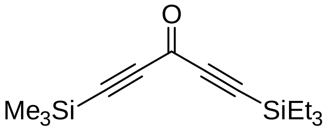


A solution of triethylsilylacetylene (2.81 g, 20 mmol) in THF (15 mL) was treated at -78 °C with *n*-butyllithium (8.0 mL, 20 mmol). The resulting mixture was stirred for 20 min. at -78 °C, then for 20 min. at RT. and a solution of trimethylsilylpropynal (2.52 g, 20 mmol) in THF (15 mL) was added at -50 °C. The mixture was allowed to warm up to RT and stirring was maintained for 1 hour. After treatment with saturated $NH_4Cl$ and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. Silica gel chromatography (heptane/ethyl acetate 9/1) afforded the expected compound as a yellow oil (4.95 g, 18.6 mmol, 93 %).

**MS** (DCI/$NH_3$): m/z (%): 301 ($M+N_2H_7$, 4); 284 ($M+NH_4$, 100); 266 ($M–H_2O+NH_4$, 15); 249 ($M–H_2O+H$, 10).

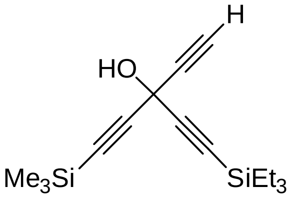
**$^1$H NMR** (CDCl$_3$): *d* = 0.17 (s, 9 H, SiC*H*$_3$); 0.60 (q, *J* = 7.9 Hz, 6 H, SiC*H*$_2$CH$_3$); 0.99 (t, *J* = 7.9 Hz, 9 H, SiCH$_2$C*H*$_3$); 2.23 (br, 1 H, O*H*); 5.08 (s, 1 H, HO-C-*H*).
**$^{13}$C{$^1$H} NMR** (CDCl$_3$): *d* = –0.47 (Si*C*H$_3$); 4.07 (Si*C*H$_2$CH$_3$); 7.24 (SiCH$_2$*C*H$_3$); 52.72 (HO-*C*-H); 86.87, 89.10 (*C*≡C-Si); 102.15, 103.31 (C≡*C*-Si).

**•1-triethylsilyl-5-trimethylsilylpenta-1,4-diyn-3-one.**



A solution of 1-triethylsilyl-5-trimethylsilylpenta-1,4-diyn-3-ol (4.12 g, 15.5 mmol) in dichloromethane at 0 °C was treated with MnO$_2$ (20.2 g, 232.6 mmol). The mixture was stirred for 30 minutes at 0 °C and then for 2 hours at RT. It was then filtered through a small pad of celite and concentrated under vacuum. Silica gel chromatography (heptane/ethyl acetate 9:1) afforded the expected ketone as an orange oil (4.01 g, 15.2 mmol, 98 %).
**MS** (DCI/NH$_3$): m/z (%): 299 (M+N$_2$H$_7$, 4); 282 (M+NH$_4$, 100); 265 (M+H, 5).
**Elemental analyses** (%): C = 63.25 (63.57); H = 9.30 (9.15).
**$^1$H NMR** (CDCl$_3$): *d* = 0.22 (s, 9H, SiC*H*$_3$); 0.66 (q, *J* = 7.8 Hz, 6H, SiC*H*$_2$); 0.99 (t, *J* = 7.8 Hz, 9H, SiCH$_2$C*H*$_3$).
**$^{13}$C{$^1$H} NMR** (CDCl$_3$): *d* = –1.00 (Si*C*H$_3$); 3.68 (Si*C*H$_2$CH$_3$); 7.20 (SiCH$_2$*C*H$_3$); 98.11, 99.24 (*C*≡C-Si); 102.62, 103.90 (C≡*C*-Si); 160.10 (*C*=O).
**$^{13}$C NMR** (CDCl$_3$): *d* = –3.88-10.21 (m, Si*C*H$_{3,}$ Si*C*H$_2$*C*H$_3$); 98.12 (s, *C*≡C-Si); 99.21 (s, *C*≡C-Si); 102.62 (s, C≡*C*-Si); 103.90 (s, C≡*C*-Si); 160.09 (s, *C*=O).
**IR** (CDCl$_3$): *n* = 2960-2877 (s, C$_{sp3}$-H); 2161 (s, C≡C); 1623 (s, C=O); 1457, 1414 (m, SiCH$_2$CH$_3$); 1253 (s, SiCH$_3$).

**•1-triethylsilyl-3-ethynyl-5-trimethylsilylpenta-1,4-diyn-3-ol (3)**



Ethynylmagnesium bromide (33.9 mL, 16.9 mmol) was added dropwise to a solution of 1-triethylsilyl-5-trimethylsilylpenta-1,4-diyn-3-one (3.44 g, 13 mmol) in THF (160 mL) at 0 °C. The resulting mixture was stirred for 30 min. at 0 °C and overnight at RT. After treatment with saturated NH$_4$Cl and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. The expected trialkynylcarbinol **3** was obtained as an oil in quantitative yield (3.78 g, 13 mmol).

**MS** (DCI/$NH_3$): m/z (%): 308 (M+$NH_4$, 11); 290 (M–$H_2O$+$NH_4$, 100); 273 (M–$H_2O$+H, 6).

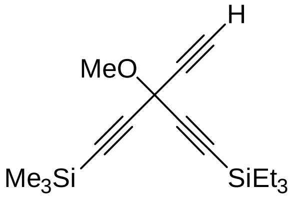
**$^1$H NMR** ($CDCl_3$): *d* = 0.18 (s, 9H, SiC*H*$_3$); 0.62 (q, *J* = 7.8 Hz, 6H, SiC*H*$_2$CH$_3$); 0.99 (t, *J* = 7.8 Hz, 9H, SiCH$_2$C*H*$_3$); 2.64 (s, 1H, ≡C*H*), 2.87 (brs, 1H, O*H*).

**RMN $^{13}$C{$^1$H}** ($CDCl_3$): *d* = –0,56 (Si*C*H$_3$); 4,04 (Si*C*H$_2$CH$_3$); 7,30 (SiCH$_2$*C*H$_3$); 54,26 (HO-*C*); 71,16 (C≡*C*-H); 81,12 (*C*≡C-H) ; 86,33 and 88,25 (*C*≡C-Si); 101,15 and 102,59 (C≡*C*-Si)

**$^{13}$C NMR** ($CDCl_3$): *d* = –3.44-10.34 (m, Si*C*H$_{3,}$ Si*C*H$_2$*C*H$_3$); 54.29 (s, *C*-OH); 71.16 (d, *J* = 256 Hz, ≡*C*-H); 81.12 (d, *J* = 50 Hz, *C*≡CH); 86.29 (s, *C*≡C-Si); 88.20 (s, *C*≡C-Si); 101.12 (s, C≡*C*-Si); 102.56 (s, C≡*C*-Si).

**IR** ($CDCl_3$): *n* = 3571 (s, OH); 3307 (s, $C_{sp}$-H); 2959-2876 (s, $C_{sp3}$-H); 2130 (w, C≡C); 1457, 1415 (m, SiCH$_2$CH$_3$); 1252 (s, SiCH$_3$).

### •1-triethylsilyl-3-ethynyl-3-methoxy-5-trimethylsilylpenta-1,4-diyne (4)



A solution of the trialkynylcarbinol **3** (3.66 g, 12.6 mmol) in THF (120 mL) was treated at –78 °C with *n*-butyllithium (5.5 mL, 12.6 mmol). After stirring for 30 minutes at –78 °C, methyl iodide (3.9 mL, 12.6 mmol) and DMSO (4.2 mL, 62.9 mmol) were added. The resulting mixture was progressively warmed up to RT, then stirred overnight at RT. After addition of diethyl ether (20 mL) and water (60 mL), the layers were separated and the organic one was washed with saturated $NH_4Cl$. The aqueous phase was extracted with diethyl ether, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Silica gel chromatography (heptane/ethyl acetate 97/3) afforded trialkynyl ether **4** as a pale yellow oil (3.56 g, 11.7 mmol, 93 %).

**MS** (DCI/$NH_3$): m/z (%): 322 (M+$NH_4$, 12); 305 (M+H, 19); 290 (M–MeOH+$NH_4$, 100); 273 (M–MeOH+H, 7).

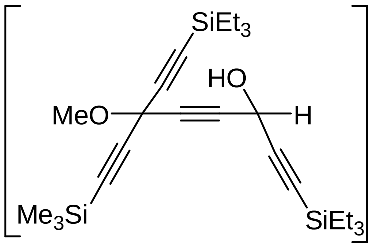
**Elemental analyses** (%): C = 67.05 (67.04); H = 9.27 (9.68).

**$^1$H NMR** ($CDCl_3$): *d* = 0.19 (s, 9H, SiC*H*$_3$); 0.63 (q, *J* = 7.8 Hz, 6H, SiC*H*$_2$CH$_3$); 0.99 (t, *J* = 7.8 Hz, 9H, SiCH$_2$C*H*$_3$); 2.62 (s, 1H, ≡C*H*); 3.48 (s, 3H, OC*H*$_3$).

**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = –0.56 (Si*C*H$_3$); 4.05 (Si*C*H$_2$CH$_3$); 7.32 (SiCH$_2$*C*H$_3$); 52.41 (C-O-*C*H$_3$); 60.67 (*C*-O-CH$_3$); 72.16 (C≡*C*-H); 79.05 (*C*≡C-H); 87.37, 89.16 (*C*≡C-Si); 99.21, 100,40 (C≡*C*-Si).

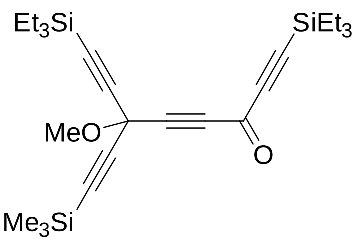
$^{13}$**C NMR** ($CDCl_3$): *d* = –3.44-10.33 (m, Si*C*H$_3$, Si*C*H$_2$*C*H$_3$); 52.41 (q, *J* = 143 Hz, C-O-*C*H$_3$); 60.70 (s, *C*-O-CH$_3$); 72.15 (d, *J* = 254 Hz, C≡*C*H); 79.06 (d, *J* = 49 Hz, *C*≡CH); 87.36 (s, *C*≡C-Si); 89.17 (d, *J* = 5.7 Hz, *C*≡C-Si); 99.20 (s, C≡*C*-Si); 100.39 (s, C≡*C*-Si).
**IR** ($CDCl_3$): *n* = 3306 (s, $C_{sp}$-H); 2959-876 (s, $C_{sp3}$-H); 2175, 2128 (w, C≡C); 1458, 1415 (m, $SiCH_2CH_3$); 1252 (s, $SiCH_3$).

**•1,8-bis(triethylsilyl)-6-(trimethylsilyl)ethynyl-6-methoxyocta-1,4,7-triyn-3-ol (6)**



A solution of trialkynyl ether **4** (1.88 g, 6.17 mmol) in THF (30 mL) was treated with ethylmagnesium bromide (2.26 mL, 6.79 mmol) at 0 °C. The resulting mixture was stirred for 30 min. at 0 °C and then for 2 h at RT. A solution of aldehyde **5** (TES-C≡C-CHO **5**, 1.25 g, 7.41 mmol) in THF (30 mL) was then added at 0 °C. The mixture was allowed to warm up to RT and stirring was maintained overnight. After treatment with saturated $NH_4Cl$ and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. The expected tetrayne **6** was obtained as a brown oil, and it was directly used in the next oxidation step without further purification.
$^{1}$**H NMR** ($CDCl_3$): *d* = 0.17 (s, 9H, SiC*H*$_3$); 0.54-0.66 (m, 12H, SiC*H*$_2$CH$_3$); 0.94-1.01 (m, 18H, SiCH$_2$C*H*$_3$); 2.41 (s, br, 1H, O*H*); 3.46 (s, 3H, OC*H*$_3$); 5.16 (s, 1H, HO-C-*H*).

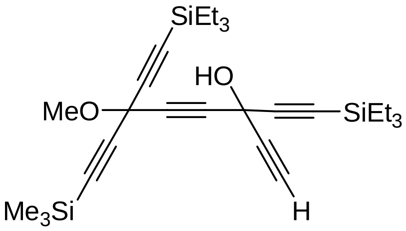
**•1,8-bis(triethylsilyl)-6-(trimethylsilyl)ethynyl-6-methoxyocta-1,4,7-triyn-3-one (7)**



A solution of the crude tetrayne **6** (see above) in dichloromethane was treated with $MnO_2$ (8.1 g, 92.6 mmol) at 0 °C. The mixture was stirred for 20 min. at 0 °C and then for 2 h at RT. It was then filtered through celite and concentrated under vacuum. Silica gel chromatography (heptane/ethyl acetate 95/5) afforded an orange oil (2.20 g) corresponding to a mixture of the expected ketone **7** and starting triyne **4** (65% total yield in **7**).
**MS** ($DCI/NH_3$): m/z (%): 488 ($M+NH_4$, 100); 471 (M+H, 5); 456 ($M-MeOH+NH_4$, 12).

**$^1$H NMR** ($CDCl_3$): *d* = 0.17 (s, 9H, SiC*H*$_3$); 0.55-0.72 (m, 12H, SiC*H*$_2$CH$_3$); 0.84-1.03 (m, 18H, SiCH$_2$C*H*$_3$); 3.47 (s, 3H, OC*H*$_3$).
**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = –0.75 (Si*C*H$_3$), 4.04, 4.10 (Si*C*H$_2$CH$_3$); 7.05, 7.14 (SiCH$_2$*C*H$_3$); 52.60 (C-O-*C*H$_3$); 61.00 (*C*-O-CH$_3$); 81.46, 85.37, 89.22, 90.94, 97.61, 98.89, 99.05, 103.56 (8 ≡*C*); 159.22 (C=O).
**$^{13}$C NMR** ($CDCl_3$): *d* = –3.59-10.12 (m, Si*C*H$_3$, Si*C*H$_2$*C*H$_3$); 52.64 (q, *J* = 144 Hz, C-O-*C*H$_3$); 61.01 (s, *C*-O-CH$_3$); 81.46, 85.34, 89.27, 90.98, 97.55, 98.82, 99.11, 103.53 (s, 8 ≡*C*); 159,22 (s, C=O).
**IR** ($CDCl_3$): *n* = 2952-2828 (s, C$_{sp3}$-H); 2221, 2152 (s, C≡C); 1634 (s, C=O); 1457, 1414 (s, SiCH$_2$CH$_3$); 1252 (m, SiCH$_3$).

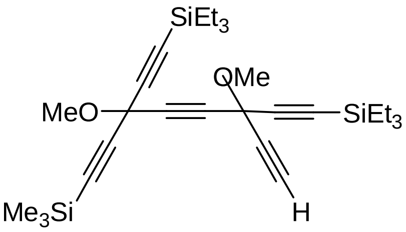
**•1,8-bis(triethylsilyl)-3-ethynyl-6-(trimethylsilyl)ethynyl-6-methoxyocta-1,4,7-triyn-3-ol (8)**



Ethynylmagnesium bromide (16.0 mL, 8.0 mmol) was added dropwise to a solution of ketone **7** (2.20 g, 4.01 mmol, containing 20 % mol. of triyne **4**) in THF (50 mL) at 0 °C. The resulting mixture was stirred 30 minutes at 0 °C and overnight at RT. After treatment with saturated $NH_4Cl$ and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. Silica gel chromatography (heptane/ethyl acetate 9/1) afforded of the expected pentayne **8** as a brown oil (1.97 g, 3.97 mmol, 99 % yield based on ketone **7**).
**MS** (DCI/$NH_3$): m/z (%): 514 (M+NH$_4$, 61); 482 (M–MeOH+NH$_4$, 100); 465 (M–MeOH+ H, 100).
**Elemental analyses** (%): C = 67.39 (67.68); H = 8.95 (8.93).
**$^1$H NMR** ($CDCl_3$): *d* = 0.17 (s, 9H, SiC*H*$_3$); 0.54 – 0.66 (m, 12H, SiC*H*$_2$CH$_3$); 0.93 – 1.01 (m, 18H, SiCH$_2$C*H*$_3$); 2.64 (d, *J* = 1.3 Hz, 1H, ≡C*H*); 3.05 (s, 1H, O*H*); 3.45 (d, *J* = 1.3 Hz, 3H, OC*H*$_3$).
**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = –0.81 (Si*C*H$_3$); 3.76, 3.84 (Si*C*H$_2$CH$_3$); 7.07 (SiCH$_2$*C*H$_3$); 52.21 (C-O-*C*H$_3$); 53.74 (*C*-OH); 60.67 (*C*-O-CH$_3$); 71.53 (C≡*C*-H); 77.63 (*C*≡C-H); 80.16, 80.58 (C-*C*≡*C*-C); 86.17, 87.51, 89.32 (*C*≡C-Si); 98.47, 99.77, 101.62 (C≡*C*-Si).
**$^{13}$C NMR** ($CDCl_3$): *d* = -4.39 – 10.85 (m, Si*C*H$_3$, Si*C*H$_2$*C*H$_3$); 52.22 (q, *J* = 144 Hz, C-O-*C*H$_3$); 53.65 (s, *C*-OH); 60.73 (s, *C*-O-CH$_3$); 71.53 (d, *J* = 256 Hz, ≡*C*-H); 77.62 (s, *C*≡C-H); 79.61, 80.59 (s,C-*C*≡*C*-C); 86.14 (d, *J* = 2.8 Hz, *C*≡C-Si); 87.48 (s, *C*≡C-Si); 89.32 (d, *J* = 2.9 Hz, *C*≡C-Si); 98.47, 99.77, 101.59 (s, C≡*C*-Si).

**IR** ($CDCl_3$): *n* = 3567 (s, OH); 3307 (s, $C_{sp}$-H); 2959-2876 (s, $C_{sp3}$-H); 2180, 2133 (w, C≡C); 1458, 1415 (m, $SiCH_2CH_3$); 1252 (s, $SiCH_3$).

**•1,8-bis(triethylsilyl)-3-ethynyl-6-(trimethylsilyl)ethynyl-3,6-dimethoxyocta-1,4,7-triyne (9)**



A solution of the pentayn-ol **8** (3.53 g, 7.11 mmol) in THF (150 mL) was treated with *n*-butyllithium (2.84 mL, 7.11 mmol) at –78 °C. After stirring for 30 minutes at –78 °C, methyl iodide (2.2 mL, 35.5 mmol) and DMSO (2.4 mL, 35.5 mmol) were added and the resulting mixture was progressively warmed up to RT, then stirred overnight at RT. After addition of diethyl ether (10 mL) and water (60 mL), the layers were separated and the organic one was treated with saturated $NH_4Cl$. The aqueous layer was extracted with diethyl ether, and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Silica gel chromatography (heptane/ethyl acetate 95/5) afforded the expected product **9** as a yellow oil (3.60 g, 7.05 mmol, 99 %).

**MS** (DCI/$NH_3$): m/z (%): 528 (M+$NH_4$, 100); 511 (M+H, 8); 496 (M–MeOH+$NH_4$, 40); 488 (M–$CH_3C$≡CH+$NH_4$, 8); 479 (M–MeOH+H, 25); 464 (M–2MeOH+$NH_4$, 24); 456 (M–MeOH–$CH_3C$≡CH+$NH_4$, 40).

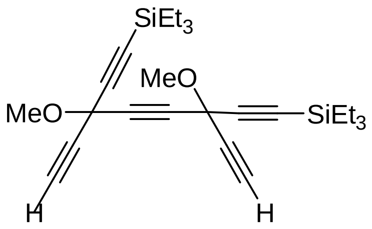
**$^1$H NMR** ($CDCl_3$): *d* = 0.16 (s, 9H, SiC*H*$_3$); 0.60 (q, *J* = 7.8 Hz, 12H, SiC*H*$_2$CH$_3$); 0.97 (t, *J* = 7.8 Hz, 18H, SiCH$_2$C*H*$_3$); 2.62 (s, 1H, ≡C*H*); 3.45 (s, 3H, OC*H*$_3$); 3.47 (s, 3H, OC*H*$_3$).

**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = –0.57 (Si*C*H$_3$); 4.03 (Si*C*H$_2$CH$_3$); 7.30 (SiCH$_2$*C*H$_3$); 52.53, 52.60 (C-O-*C*H$_3$); 60.49, 60.86 (*C*-O-CH$_3$); 72.42 (C≡*C*-H); 78.52, 78.85, 79.45 (3 C-*C*≡*C*-C, *C*≡C-H); 87.66, 87.78, 89.49 (3 *C*≡C-Si); 98.74, 99.55, 100.02 (3 C≡*C*-Si).

**$^{13}$C NMR** ($CDCl_3$): *d* = -3.43 – 10.33 (m, Si*C*H$_3$, Si*C*H$_2$*C*H$_3$); 52.52 (q, *J* = 144 Hz, C-O-*C*H$_3$); 52.56 (q, *J* = 144 Hz, C-O-*C*H$_3$); 60.42 (d, *J* = 4.4 Hz, *C*-O-CH$_3$); 60.92 (s, *C*-O-CH$_3$); 72.43 (d, *J* = 255 Hz, C≡*C*H); 78.11, 78.84, 79.45 (s, 3 C-*C*≡*C*-C, *C*≡C-H); 87.66, 87.76, 89.45 (s, 3 *C*≡C-Si); 98.74, 99.56, 100.02 (s, 3 C≡*C*-Si).

**IR** ($CDCl_3$): *n* = 3307 (m, $C_{sp}$-H); 2959-2876 (s, $C_{sp3}$-H); 2175, 2127 (w, C≡C); 1458, 1415 (m, $SiCH_2CH_3$); 1252 (s, $SiCH_3$).

**•1,8-bis(triethylsilyl)-3,6-diethynyl-3,6-dimethoxyocta-1,4,7-triyne (10a)**



A mixture of $\mathrm{K_2CO_3}$ (0.97 g, 0.70 mmol) in methanol (250 mL) was added to a solution of trisilylated pentayne **9** (3.60 g, 7.05 mmol) in methanol (100 mL) at RT. The resulting suspension was stirred 10 minutes, then saturated $\mathrm{NH_4Cl}$ (60 mL) was added and the mixture was rapidly concentrated under reduced pressure to remove methanol. After addition of diethyl ether (60 mL), the organic layer was washed twice with saturated $\mathrm{NH_4Cl}$, then the combined aqueous layers were extracted with diethyl ether. The resulting organic layers were combined and washed with brine, dried over $\mathrm{MgSO_4}$ and concentrated to dryness. Silica gel chromatography (heptane/ethyl acetate 95/5) afforded bis-terminal pentayne **10a** as a yellow oil (2.72 g, 6.21 mmol, 88 %).

**MS** (DCI/$\mathrm{NH_3}$): m/z (%): 456 (M+$\mathrm{NH_4}$, 100).

**Elemental analyses** (%): C = 71.07 (71.17); H = 8.73 (8.59).

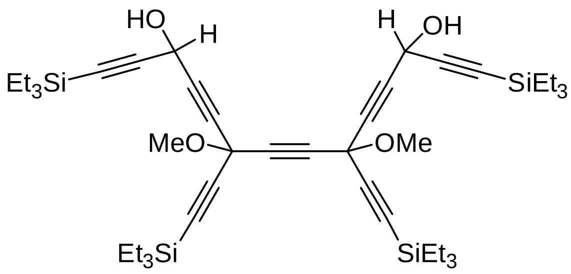
**$^1$H NMR** ($\mathrm{CDCl_3}$): *d* = 0.16 (s, 9H, $\mathrm{SiC}H_3$); 0.60 (q, *J* = 7.8 Hz, 12H, $\mathrm{SiC}H_2\mathrm{CH_3}$); 0.97 (t, *J* = 7.8 Hz, 18H, $\mathrm{SiCH_2C}H_3$); 2.62 (s, 1H, $\equiv\mathrm{C}H$); 3.45 (s, 3H, $\mathrm{OC}H_3$); 3.47 (s, 3H, $\mathrm{OC}H_3$).

**$^{13}$C{$^1$H} NMR** ($\mathrm{CDCl_3}$): *d* = 3.98 ($\mathrm{Si}C\mathrm{H_2CH_3}$); 7.30 ($\mathrm{SiCH_2}C\mathrm{H_3}$); 52.59 (C-O-$C\mathrm{H_3}$); 60.42 (*C*-O-$\mathrm{CH_3}$); 72.56 (C≡*C*-H); 78.39 (*C*≡C-H); 79.09 (C-C≡*C*-C); 87.90 (*C*≡C-Si); 99.49 (C≡*C*-Si).

**$^{13}$C NMR** ($\mathrm{CDCl_3}$): *d* = 3.99 (t, *J* = 118 Hz, $\mathrm{Si}C\mathrm{H_2CH_3}$); 7.30 (q, *J* = 126 Hz, $\mathrm{SiCH_2}C\mathrm{H_3}$); 52.61 (q, *J* = 144 Hz, C-O-$C\mathrm{H_3}$); 60.44 (s, *C*-O-$\mathrm{CH_3}$); 72.55 (d, *J* = 255 Hz, C≡*C*H); 78.37 (d, *J* = 49 Hz, *C*≡C-H); 79.09 (s, C-C≡*C*-C); 87.90 (s, *C*≡C-Si); 99.48 (s, C≡*C*-Si).

**IR** ($\mathrm{CDCl_3}$): *n* = 3307 (s, $\mathrm{C}_{sp}$-H); 2959-2876 (s, $\mathrm{C}_{sp3}$-H); 2127 (w, C≡C); 1458, 1415 (m, $\mathrm{SiCH_2CH_3}$).

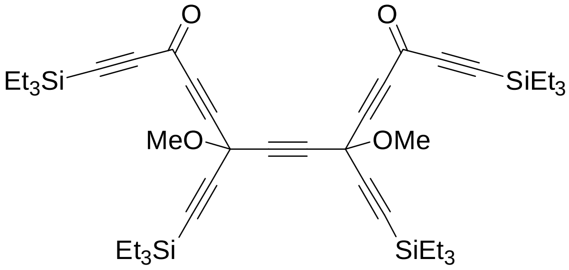
### •1,14-bis(triethylsilyl)-6,9-bis(triethylsilylethynyl)-6,9-dimethoxytetradeca-1,4,7,10,13-pentayn-3,12-ol (11)



A solution of the bis-terminal pentayne **10a** (1.20 g, 2.74 mmol) in THF (50 mL) was treated with ethylmagnesium bromide (1.92 mL, 5.75 mmol) at 0 °C. The resulting mixture was stirred 30 for min. at 0 °C, then for 2 h at RT, and a solution of aldehyde **5** (TES-C≡C-CHO, 1.01 g, 6.03 mmol) in THF (10 mL) was added at 0 °C. The mixture was allowed to warm up to RT and stirring was maintained overnight. After treatment with saturated $NH_4Cl$ and extraction with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. The expected heptayne **11** was obtained as a brown oil and was directly oxidized without further purification.

**$^1$H NMR** ($CDCl_3$): *d* = 0.55-0.66 (m, 24H, SiC$H_2$CH$_3$); 0.94-1.02 (m, 36H, SiCH$_2$C$H_3$); 2.41 (brs, 2H, O*H*); 3.47 (s, 6H, OC$H_3$); 5.16 (s, 2H, HO-C-*H*).

### •1,14-bis(triethylsilyl)-6,9-bis(triethylsilylethynyl)-6,9-dimethoxytetradeca-1,4,7,10,13-pentayn-3,12-dione (13)



A solution of the crude heptayne **11** in dichloromethane was treated with $MnO_2$ (7.15 g, 82.1 mmol) at 0 °C . The mixture was stirred for 20 min. at 0 °C, then for 2 h at RT. It was filtered through celite and concentrated under vacuum. Silica gel chromatography (heptane/ethyl acetate 95/5) afforded diketone **13** as a brown oil (1.47 g, 1.91 mmol, 70 %).

**MS** (DCI/$NH_3$): m/z (%): 788 (M+$NH_4$, 100).

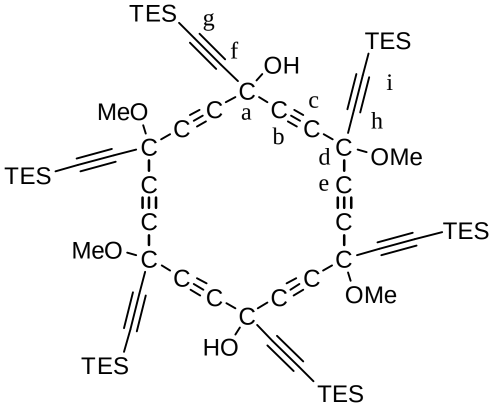
**Elemental analyses** (%): C = 68.51 (67.81); H = 8.62 (8.76).

**$^1$H NMR** ($CDCl_3$): *d* = 0.58-0.73 (m, 24H, SiC$H_2$CH$_3$); 0.94-1.03 (m, 36H, SiCH$_2$C$H_3$); 3.50 (s, 6H, OC$H_3$).

**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = 3.65, 3.93 (Si*C*H$_2$CH$_3$); 7.22, 7.31 (SiCH$_2$*C*H$_3$); 53.10 (C-O-*C*H$_3$); 60.69 (*C*-O-CH$_3$); 78.82, 81.88, 83.92, 90.43, 97.38, 99.53, 103.35 (7 ≡*C*); 159.26 (C=O).

**IR** ($CDCl_3$): *n* = 2959-2877 (s, $C_{sp3}$-H); 2220, 2152 (m, C≡C); 1634 (s, C=O); 1458, 1415 (m, SiCH$_2$CH$_3$).

### •1,4,7,10,13,16-hexa(triethylsilylethynyl)-4,7,13,16-tetramethoxycyclooctadeca-2,5,8,11,14,17-hexayn-1,10-diol (15)



A solution of bis-terminal pentayne **10a** (0.677 g, 1.545 mmol) in THF (50 mL) was treated with ethylmagnesium bromide (1.03 mL, 3.09 mmol) at 0 °C. The mixture was stirred for 30 min. at 0 °C, then for 2 h at RT, and a solution of the diketone **13** (1.190 g, 1.545 mmol) in THF (150 mL) was added at 0 °C. After refluxing for 60 h at 65 °C, the mixture was treated with saturated $NH_4Cl$. The aqueous layer was extracted with diethyl ether and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated to dryness. Two silica gel chromatographies (heptane/ethyl acetate 9/1 and 93/7) afforded four fractions of [6]pericyclyne **15** (0.629 g, 0.52 mmol, 34 %). The collected fractions were analyzed separately.

**Fraction 1:** 109 mg, brown oil.

**MS** (DCI/$NH_3$): m/z (%): 1227 (M+$NH_4$, 100).

**$^1$H NMR** ($CDCl_3$): *d* = 0.56 – 0.67 (m, 36H, $\mathrm{SiC}H_2\mathrm{CH_3}$); 0.94 – 1.02 (m, 54H, $\mathrm{SiCH_2C}H_3$); 2.99, 3.10 (2H, O*H*); 3.48, 3.50 (12H, $\mathrm{OC}H_3$).

**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = 3.80 ($\mathrm{Si}C\mathrm{H_2CH_3}$); 7.15 ($\mathrm{SiCH_2}C\mathrm{H_3}$); 52.60 (O-$C\mathrm{H_3}$); 53.97 ($C_a$); 60.35, 60.45 ($C_d$); 77.74, 77.79 ($C_b$, $C_c$ or $C_e$); 78.55, 79.04 ($C_b$, $C_c$ or $C_e$); 80.72 ($C_b$, $C_c$ or $C_e$); 87.21 ($C_f$); 88.16, 88.40 ($C_h$); 98.59, 98.96 ($C_i$); 100.64, 100.87 ($C_g$).

**IR** ($CDCl_3$): *n* = 3566 (w, OH); 2958 – 2876 (s, $C_{sp3}$-H); 1457, 1415 (m, $SiCH_2CH_3$); 1056 (s, CO).

**Fraction 2:** 260 mg, brown oil.

**MS** (MNBA FAB>0): m/z (%): [$MNa^+$] = 1232.

**LSIMS H**igh **R**esolution [$MNa^+$] = 1231.63628 (Theo: 1231.63463).

**$^1$H NMR** ($CDCl_3$): *d* = 0.57 – 0.67 (m, 36H, $\mathrm{SiC}H_2\mathrm{CH_3}$); 0.95 – 1.02 (m, 54H, $\mathrm{SiCH_2C}H_3$); 2.99, 3.05 (2H, O*H*); 3.485, 3.489, 3.494 (12H, $\mathrm{OC}H_3$).

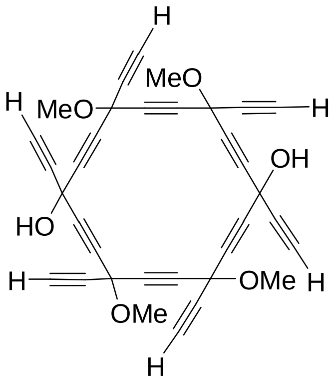
**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = 3.80 ($\mathrm{Si}C\mathrm{H_2CH_3}$); 7.13 ($\mathrm{SiCH_2}C\mathrm{H_3}$); 52.56 (O-$C\mathrm{H_3}$); 53.98, 54.02 ($C_a$); 60.35, 60.45 ($C_d$); 77.40, 77.65, 77.74, 77.80 ($C_b$, $C_c$ or $C_e$); 78.40, 78.50, 78.59, 79.06, 79.13 ($C_b$, $C_c$ or $C_e$); 80.14, 80.31, 80.63, 80.76 ($C_b$, $C_c$ or $C_e$); 87.19 ($C_f$); 88.13, 88.20, 88.37 ($C_h$); 98.44, 98.61, 98.76, 98.96 ($C_i$); 100.58, 100.72, 100.81 ($C_g$).

**IR** ($CDCl_3$): *n* = 3566 (w, OH); 2958 – 2876 (s, $C_{sp3}$-H); 1457, 1415 (m, $SiCH_2CH_3$); 1058 (s, CO).

**Fraction 3:** 80 mg, white powder.
**$^1$H NMR** ($CDCl_3$): *d* = 0.55 – 0.68 (m, 36H, $SiCH_2CH_3$); 0.94 – 1.03 (m, 54H, $SiCH_2CH_3$); 3.09, 3.10 (2H, O*H*); 3.49, 3.49 (12H, $OCH_3$).
**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = 3.80 ($SiCH_2CH_3$); 7.18 ($SiCH_2CH_3$); 52.56 (O-$CH_3$); 54.00 ($C_a$); 60.47 ($C_d$); 77.65 ($C_b$, $C_c$ or $C_e$); 78.38, 78.55 ($C_b$, $C_c$ or $C_e$); 80.31, 80.91 ($C_b$, $C_c$ or $C_e$); 87.12 ($C_f$); 88.28, 88.42 ($C_h$); 98.39, 98.72 ($C_i$); 100.69 ($C_g$).

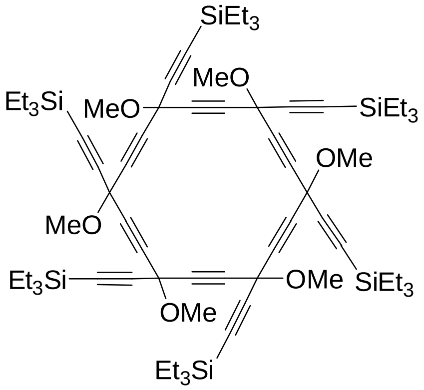
**Fraction 4:** 180 mg, brown oil.
**MS** (DCI/$NH_3$): m/z (%): 1227 (M+$NH_4$, 100).
**$^1$H NMR** ($CDCl_3$): *d* = 0.56 – 0.67 (m, 36H, $SiCH_2CH_3$); 0.95 – 1.03 (m, 54H, $SiCH_2CH_3$); 3.05, 3.06, 3.10, 3.12 (2H, O*H*); 3.48 – 3.50 (m, 12H, $OCH_3$).

**•1,4,7,10,13,16-hexaethynyl-4,7,13,16-tetramethoxycyclooctadeca-2,5,8,11,14,17-hexayn-1,10-diol (16)**



A solution of **15** (64 mg, 0.052 mmol) in methanol (5 mL) was added to a suspension of $K_2CO_3$ (56 mg, 0.42 mmol) in a 1/1 THF/methanol mixture (30 mL) at RT which was then stirred for 24 h at RT. After evaporation to dryness, diethyl ether and saturated $NH_4Cl$ were added and after separation, the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Because of its instability, the crude product **16** could only be partly characterized .
**MS** (DCI/$NH_3$): m/z (%): 542 (M+$NH_4$, 20); 490 (M-$2C_2H_2$+$NH_4$, 100).
**$^1$H NMR** ($CDCl_3$): *d* = 2.71 (m, 6H, ≡C*H*); 3.52 (m, 12H, $OCH_3$).
**IR** ($CDCl_3$): *n* = 3306 (s, $C_{sp}$-H).

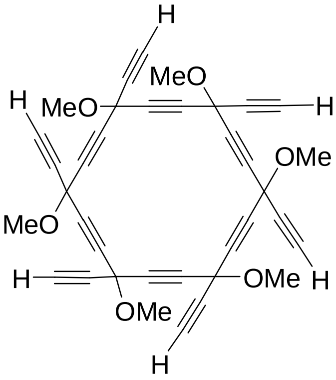
**•1,4,7,10,13,16-hexa(triethylsilylethynyl)-1,4,7,10,13,16-hexamethoxycyclooctadeca-2,5,8,11,14,17-hexayne (2b)**



A solution of **15** (92 mg, 0.076 mmol) in THF (15 mL) was treated at -78 °C by *n*-butyllithium (0.067 mL, 0.167 mmol). After stirring for 30 minutes at –78 °C, methyl iodide (0.047 mL, 0.76 mmol) and DMSO (0.050 mL, 0.76 mmol) were added. The resulting mixture was progressively warmed up to RT, then stirred overnight at RT. After addition of diethyl ether (15 mL) and water (30 mL), the organic layer was separated and washed with saturated $NH_4Cl$. The aqueous phase was extracted with diethyl ether, the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to dryness. Silica gel chromatography (heptane/ethyl acetate 95/5) afforded the expected compound **2b** as a brown oil (64 mg, 0.052 mmol, 68 %).

**MS** (DCI/$NH_3$): m/z (%): 1255 (M+$NH_4$, 100).
**$^1$H NMR** ($CDCl_3$): *d* = 0.60 (q, *J* = 7.8 Hz, 36H, $SiCH_2CH_3$); 0.97 (t, *J* = 7.8 Hz, 54H, $SiCH_2CH_3$); 3.48, 3.49 (18H, $OCH_3$).
**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = 3.98 ($SiCH_2CH_3$); 7.30 ($SiCH_2CH_3$); 52.76 (O-$CH_3$); 60.49, 60.58 (*C*-O-$CH_3$); 78.62, 79.15, 79.20, 79.29, 79.39 (C-*C*≡*C*-C); 88.00, 88.19 (*C*≡C-Si); 99.06, 99.39 (C≡*C*-Si).
**IR** ($CDCl_3$): *n* = 2959 – 2876 (s, $C_{sp3}$-H); 1458, 1415 (m, $SiCH_2CH_3$); 1058 (s, CO).

- **1,4,7,10,13,16-hexaethynyl-1,4,7,10,13,16-hexamethoxycyclooctadeca-2,5,8,11,14,17-hexayne (2a)**



A solution of **2b** (64 mg, 0.05 mmol) in methanol (5 mL) was added to a $K_2CO_3$ suspension (56 mg, 0.42 mmol) in a 1/1 THF/methanol mixture (30 mL) at RT. The resulting mixture was then stirred at RT for 24 h. After evaporation to dryness, diethyl ether and saturated $NH_4Cl$ were added, and the aqueous layer was separated and extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. Silica gel chromatography afforded **2a** as a white powder (27 mg, 0.049 mmol, 94 %).

**MS** (DCI/$NH_3$): m/z (%): 570 (M+$NH_4$, 100).

**LSIMS H**igh **R**esolution [$MNa^+$] = 575.14653 (Theo : 575.14706).

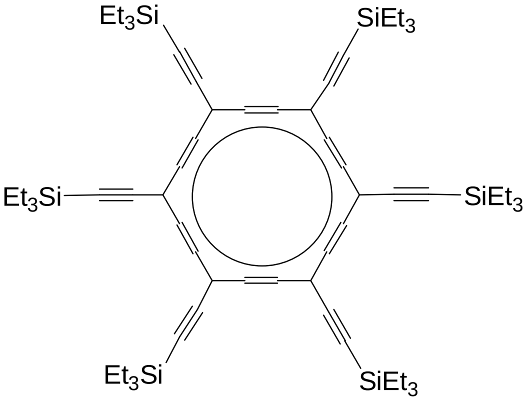
**$^1$H NMR** ($CDCl_3$): $d$ = 2.70 (m, 6H, ≡C*H*); 3.51 (m, 18H, OC$H_3$).

**$^{13}$C{$^1$H} NMR** ($CD_3CO$ $CD_3$): $d$ = 57.43 (O-*C*$H_3$); 64.98, 65.06 (*C*-O-$CH_3$); 80.64 (C≡*C*-H); 81.82, 81.98 (C-*C*≡*C*-C); 83.82, 83.89, 84.04 (*C*≡C-H).

**IR** ($CDCl_3$): $n$ = 3306 (s, $C_{sp}$-H); 2937, 2830 (s, $C_{sp3}$-H); 2127 (w, C≡C); 1223 (s); 1175(s) ; 1066 (s).

**Decomposition temperature:** 154 °C.

- **3,6,9,12,15,18-hexa[(triethylsilyl)ethynyl]-1,2,4,5,7,8,10,11,13,14,16,17-dodecadehydro [18]annulene (1a)**



$Co_2(CO)_8$ (68 mg, 0.198 mmol) was added to a solution of **15** (120 mg, 0.099 mmol) in diethyl ether (20 mL) at 0 °C. After stirring for 30 minutes at 0 °C, $SnCl_2$ (188 mg, 0.99 mmol) and etheral 2 M HCl (7.43 mL, 14.85 mmol) were added at –78 °C and the reaction mixture was progressively warmed up to RT. After stirring for 30 minutes at RT, the mixture was directly filtered through silica gel and eluted with $CHCl_3$. All the coloured fractions were combined and evaporated to dryness. Diethyl ether (30 mL) and water (20 mL) were then added. The organic layer was washed with saturated $NH_4Cl$ and the resulting aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was dissolved in a 1/1 diethyl ether/acetone mixture (20 mL), and CAN (326 mg, 0.594 mmol) was added at RT. The resulting suspension was stirred for 30 minutes at RT, and diethyl ether (50 mL) and saturated $NH_4Cl$ (20 mL) were then added. The aqueous layer was extracted with diethyl ether and the combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated to dryness. The crude product was deposited onto a preparative TLC plate and eluted with heptane, thus affording **1a** as a red-orange oil (13 mg, 0.012 mmol, 12 %).

**MS** (MALDI-TOF >0, $CHCl_3$, matrix : 1,8-dihydroxyanthrone, adduct : NaI): m/z: $[M+Na]^+$ = 1074.47.

**$^1$H NMR** ($CDCl_3$): *d* = 1.02 (q, *J* = 8 Hz, 36H, $SiCH_2CH_3$); 1.35 (t, *J* = 8 Hz, 54H, $SiCH_2CH_3$).

**$^{13}$C{$^1$H} NMR** ($CDCl_3$): *d* = 4.47 ($SiCH_2CH_3$); 7.72 ($SiCH_2CH_3$); 86.51, 104.45, 104.90, 118.55.

**IR** ($CDCl_3$): *d* = 2959 – 2856 (s, $C_{sp3}$-H); 1461, 1414 (m, $SiCH_2CH_3$).

**UV** ($CHCl_3$): $l_{max}$ (nm) (A) = 458 (1.10); 499 (0.32); 517 (0.16).

### Crystal structure information for $2b_1$.

Data were collected at 180 K on a Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-K? radiation (? = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters have been obtained by means of a least-squares refinement performed on a set of 1606 well measured reflections. The structure has been solved by Direct Methods, and refined by means of least-squares procedures on F. A disorder was observed for $O\text{-}CH_3$ groups, the carbon atom linked to the oxygen atoms O(1) is distributed over two sites (C(6) and C(7)). Carbon atom C(8) of the $CH_2Cl_2$ molecule is disordered over 6 positions generated by the symmetry with 1/6 occupancy and was refined isotropically. Other atoms, excluding hydrogen atoms, were refined anisotropically. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter. A weighting scheme of the form $w=w'[1-–((||F_0|–|F_c||)/6?\ (F_0))^2]^2$ with $w'=1/?\ {}_rA_rT_r(X)$ with coefficients 4.76, 0.49 and 3.03 for a Chebychev series for which $X = F_c/F_c(max)$ was used. All the data are contained in CCDC 632362, available free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

| | |
|---|---|
| Formula | $C_{37}H_{26}Cl_2O_6$ ($C_{36}H_{24}O_6$, $CH_2Cl_2$) |
| Crystal Class | Trigonal |

|  |  |  |  |
|---|---|---|---|
| Space Group | R –3 |  |  |
| a (Å) | 21.479(5) | alpha | 90 |
| b (Å) | 21.479(5) | beta | 90 |
| c (Å) | 6.560(5) | gamma | 120 |
| Volume (Å$^3$) | 2621(2) |  |  |
| Z | 3 |  |  |
| Radiation type | Mo Kα |  |  |
| Wavelength (Å) | 0.71073 |  |  |
| Density | 1.21 |  |  |
| M (g.mol$^{-1}$) | 637.51 |  |  |
| µ (mm$^{-1}$) | 0.228 |  |  |
| Temperature (K) | 180 |  |  |
| Size (mm) | 0.25x 0.30x 0.50 |  |  |
| Colour | colourless |  |  |
| Shape | block |  |  |
| Cell from | 1606 Reflections |  |  |
| Diffractometer type | XCALIBUR |  |  |
| Scan type | PHI-OMEGA |  |  |
| Reflections measured | 27634 |  |  |
| Independent reflections | 1952 |  |  |
| Rint | 0.02 |  |  |
| Theta max | 32.20 |  |  |
| Hmin, Hmax | –31 31 |  |  |
| Kmin, Kmax | –31 31 |  |  |
| Lmin, Lmax | –9 9 |  |  |
| Refinement | on F |  |  |
| R-factor | 0.0720 |  |  |
| Weighted R-factor | 0.0834 |  |  |
| Delta Rho min | –0.42 |  |  |
| Delta Rho max | 0.48 |  |  |
| Reflections used | 747 |  |  |
| sigma(I) limit | 2.00 |  |  |
| Number of parameters | 70 |  |  |
| Goodness of fit | 1.127 |  |  |

```
Atom coordinates and Uiso or Ueq:
=================================
Atom       x/a         y/b           z/c     U(equiv)      Occ
C(1)    0.20322(18)  0.04772(19)  0.4053(5)   0.0356
C(2)    0.14666(19) -0.0243(2)    0.4724(5)   0.0352
C(3)    0.10255(19) -0.0825(2)    0.5291(5)   0.0345
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C(4)    0.2101(2)    0.0483(2)    0.1821(6)   0.0485
C(5)    0.2165(4)    0.0497(4)    0.0060(8)   0.0975
C(6)    0.3288(4)    0.1228(4)    0.4329(12)  0.0638      0.6000
C(7)    0.3086(6)    0.0301(6)    0.4860(19)  0.0668      0.4000
O(1)    0.26801(14)  0.06250(17)  0.5058(5)   0.0579
Cl(1)   0.0000       0.0000       0.2212(4)   0.1027

Atom       x/a         y/b          z/c       U(iso)       Occ
C(8)   -0.015(4)     0.029(3)    -0.011(6)    0.066(8)    0.1667
H(51)   0.2213       0.0517      -0.1464      0.099(12)
H(61)   0.3730       0.1303       0.5092      0.099(12)   0.6000
H(62)   0.3245       0.1667       0.4496      0.099(12)   0.6000
H(63)   0.3361       0.1166       0.2839      0.099(12)   0.6000
H(71)   0.3526       0.0551       0.5846      0.099(12)   0.4000
H(72)   0.2818      -0.0214       0.5248      0.099(12)   0.4000
H(73)   0.3288       0.0360       0.3462      0.099(12)   0.4000

Thermal parameters:
===================
Atom      u(11)      u(22)      u(33)        u(23)       u(13)       u(12)
C(1)  0.0334(18)  0.046(2)   0.0307(14)   0.0021(15)  0.0023(14) 0.0222(17)
C(2)  0.0360(18)  0.044(2)   0.0313(15)  -0.0038(15) -0.0027(14) 0.0246(18)
C(3)  0.0381(19)  0.040(2)   0.0318(15)  -0.0021(14) -0.0028(14) 0.0242(18)
C(4)  0.064(3)    0.054(2)   0.0355(17)   0.0078(17)  0.0096(17) 0.035(2)
C(5)  0.153(6)    0.122(5)   0.044(3)     0.011(3)    0.007(3)   0.089(5)
C(6)  0.0632(16)  0.0632(16) 0.0632(16)  -0.0027(16) -0.0027(16) 0.0303(16)
C(7)  0.0662(16)  0.0662(16) 0.0662(16)  -0.0027(16) -0.0027(16) 0.0317(16)
O(1)  0.0371(15)  0.081(2)   0.0559(16)   0.0189(15)  0.0031(12) 0.0300(15)
Cl(1) 0.1298(16)  0.1298(16) 0.0484(12)   0.0000      0.0000     0.0649(8)

Distances and angles:
=====================
   C(1)  - C(2)      1.478(5)
   C(1)  - C(3)      1.479(5)
   C(1)  - C(4)      1.471(5)
   C(1)  - O(1)      1.425(4)
   C(2)  - C(3)      1.188(5)
   C(4)  - C(5)      1.162(6)
   C(6)  - O(1)      1.386(7)
   C(7)  - O(1)      1.366(8)
   Cl(1) - C(8)      1.73(3)
   Cl(1) - C(8')     1.60(4)

  C(2)  - C(1)  - C(3)    109.9(3)
  C(2)  - C(1)  - C(4)    109.4(3)
  C(3)  - C(1)  - C(4)    110.4(3)
  C(2)  - C(1)  - O(1)    107.2(3)
  C(3)  - C(1)  - O(1)    107.8(3)
  C(4)  - C(1)  - O(1)    112.0(3)
  C(1)  - C(2)  - C(3)    178.3(4)
  C(1)  - C(3)  - C(2)    178.6(3)
  C(1)  - C(4)  - C(5)    179.0(6)
  C(1)  - O(1)  - C(6)    114.1(4)
  C(1)  - O(1)  - C(7)    130.0(6)
  Cl(1) - C(8)  - Cl(1') 121.0(14)
```