

Supporting Information for:

**Differential Scanning Calorimetry (DSC) as a Tool for Probing the Reactivity of Polyynes
Relevant to Hexadehydro-Diels–Alder (HDDA) Cascades**

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I. General Experimental

General Protocols

DSC analyses were performed using a Discovery DSC (TA Instruments) equipped with a refrigerated cooling system. Samples (3 – 6 mg) were added to TZero aluminum pans. A dry N₂ purge flowed through the cell at 50 mL min⁻¹. Pans were ramped between 40 °C and 300 °C at 2 °C min⁻¹. All analyses were carried through TA Trios software version 3.0.

NMR spectra were recorded in the indicated solvent on a Varian Inova 500 (500 MHz) or Bruker Avance 500 (500 MHz) spectrometer. "The following format is used to report the proton NMR data: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. Coupling constant analysis was informed by methods we have previously reported.^{1,2} Chemical shifts for proton spectra are referenced to TMS ($\delta = 0.00$ ppm) for spectra recorded in CDCl₃. Non-first order multiplets are identified as 'nfom'.³ Chemical shifts for ¹³C NMR spectra are referenced to CDCl₃ ($\delta = 77.16$ ppm).

"Infrared spectral data were collected on an FT-IR spectrometer (Midac Corporation Prospect 4000). Spectra were collected as thin films in attenuated total reflectance (ATR) mode on a germanium window."³

HRMS data were obtained using a Bruker BioTOF II electrospray ionization (ESI) mass spectrometer. Samples were doped with either PPG or PEG as an internal calibrant and then were introduced as a methanolic solution.

"MPLC (medium pressure liquid chromatography) was performed at 25-200 psi. Columns were hand-packed with Silasorb silica gel (18-32 μ m, 60 Å pore size). A Waters HPLC pump and R401 differential refractive index detector were used. Flash chromatography was performed on E. Merck silica gel (230-400 mesh). Thin layer chromatography was carried out on glass or plastic backed plates of silica gel. Spots were visualized by UV irradiation and/or dipping in a solution of anisaldehyde, phosphomolybdic acid, potassium permanganate, or ceric ammonium molybdate followed by heat treatment."³

"Reactions requiring anhydrous conditions were performed in flame- or oven-dried glassware under an inert atmosphere (nitrogen or argon). Anhydrous diethyl ether, toluene, THF, and methylene chloride were passed through a column of activated alumina and tapped immediately prior to use. CHCl₃ used as a medium for the HDDA reaction was ethanol-free. Reported (external) reaction temperatures are the temperature of the heating bath. HDDA initiated reactions, including those that were carried out at temperatures above the boiling point of the solvent, were typically carried out in a screw-capped vial or culture tube fitted with an inert, Teflon®-lined cap."³

Derivation of HDDA Activation Energies from Experimental Half-Lives

Rate constants (k) were determined from the experimentally measured half-lives of HDDA substrates (Equation 1). The pre-exponential factor (A) for the Arrhenius equation ($1.42 \times 10^{10} \text{ s}^{-1}$) was determined via an Arrhenius plot for the ketotriyne **11**.⁴ Activation energies were then calculated via the Arrhenius equation (see Equation 2 and the cell entry formulae from an Excel[®] spreadsheet).

	A	B	C	D	E
Row 1	Substrate	$t_{1/2}$ (h at T_{exp})	T_{exp} (K)	$k_{T_{\text{exp}}}$ (s^{-1})	E_a (kcal mol^{-1})
Row 2	11	5	353	3.85×10^{-5}	23.5

Cell D2 input: $=\text{LN}(2)/(\text{B2} * 60 * 60)$

$R = 0.00198 \text{ kcal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

Cell E2 input: $=-(0.00198 * \text{C2}) * \text{LN}(\text{D2} / (1.42\text{E}10))$

$A = 1.42 \times 10^{10} (\text{s}^{-1})$

$$(1) \quad k = 0.693 / t_{1/2} \qquad (2) \quad k = Ae^{-E_a/(RT)}$$

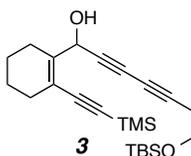
Substrate	$t_{1/2}$	E_a (kcal/mol)	DSC onset T
4	6 h @ 60 °C	22.3	82 °C
11	5 h @ 80 °C	23.5	97 °C
10	3 h @ 115 °C	25.5	109 °C
15	4 h @ 115 °C	25.7	119 °C
12	4 h @ 150 °C	28.0	152 °C
13	6 h @ 180 °C	30.4	191 °C

II. Preparation details and characterization data for all new compounds

"Procedures for preparation and spectral data are provided for i) all new compounds in the manuscript and ii) all new intermediates used in the synthetic route by which the former were made. The latter are specified by S#, since they only appear here in the Supporting Information. A reference is provided for each non-commercially available compound that is used in the syntheses and these have not been given a structure number."³

The preparation of and characterization data for those compounds that we have previously reported (namely, **3**, **4**, **5**, **10**, **S1**, **11**, **S2**, **12**, **S3**, **13**, **15**, and **16**) are reproduced here as a matter of completeness and for convenience to the reader. In each instance, that text is provided in quotations and a citation provided.

7-((*tert*-Butyldimethylsilyloxy)-1-(2-((trimethylsilyl)ethynyl)cyclohex-1-en-1-yl)hepta-2,4-diyn-1-ol (**3**)



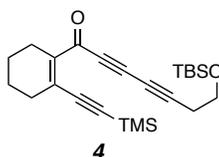
¹H NMR (500 MHz, CDCl₃): δ 5.63 (d, *J* = 5.0 Hz, 1H, CHOH), 3.74 (t, *J* = 7.0 Hz, 2H, CH₂O), 2.50 (t, *J* = 7.0 Hz, 2H, C≡CCH₂), 2.29 (br tt, *J* = 6.1, 2.4 Hz, 2H, =C-CH₂), 2.19 (br tt, *J* = 5.9, 2.4 Hz, 2H, =C-CH₂), 2.10 (d, *J* = 5.2 Hz, CHOH), 1.62 [m, 4H, CH₂(CH₂)₂CH₂], 0.89 [s, 9H, SiC(CH₃)₃], 0.19 [s, 9H, Si(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 143.7, 119.0, 103.6, 99.1, 78.8, 74.8, 70.2, 65.8, 64.6, 61.5, 30.2, 26.0, 24.0, 23.9, 22.1, 22.0, 18.5, 0.1, and -5.2.

IR (neat): 3420 (br), 2954, 2931, 2858, 2140, 1471, 1250, 1107, 878, 842, and 778 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₄H₃₈NaO₂Si₂⁺ [M+Na⁺] requires 437.2303; found 437.2320.³⁴

7-((*tert*-Butyldimethylsilyloxy)-1-(2-((trimethylsilyl)ethynyl)cyclohex-1-en-1-yl)hepta-2,4-diyn-1-one (**4**)



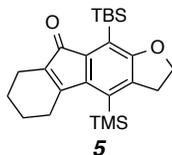
¹H NMR (500 MHz, CDCl₃): δ 3.76 (t, *J* = 7.0 Hz, 2H, CH₂O), 2.58 (t, *J* = 7.0 Hz, 2H, ≡CCH₂), 2.41 (br t, *J* = 5.4 Hz, 2H, =C-CH₂), 2.38 (br t, *J* = 5.7 Hz, 2H, =C-CH₂), 1.65–1.59 [m, 4H, CH₂(CH₂)₂CH₂], 0.89 [s, 9H, SiC(CH₃)₃], 0.23 [s, 9H, Si(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂].

^{13}C NMR (125 MHz, CDCl_3): δ 177.4, 142.4, 133.1, 107.3, 103.8, 87.7, 79.2, 73.3, 66.2, 61.1, 33.9, 26.0, 25.3, 24.3, 21.9, 21.6, 18.4, 0.0, and -5.2.

IR (neat): 2951, 2930, 2858, 2359, 2340, 2232, 2141, 1605, 1250, 1107, 842, and 779 cm^{-1} .

HRMS (ESI-TOF): Calcd for $\text{C}_{24}\text{H}_{36}\text{NaO}_2\text{Si}_2^+$ [$\text{M}+\text{Na}^+$] requires 435.2146; found 435.2151.”⁴

10-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)-2,3,5,6,7,8-hexahydro-9H-fluoreno[2,3-*b*]furan-9-one
(5)

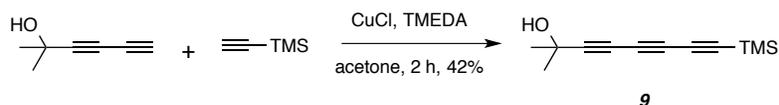


^1H NMR (500 MHz, CDCl_3): δ 4.36 (t, $J = 8.7$ Hz, 2H, CH_2O), 3.15 (t, $J = 8.7$ Hz, 2H, ArCH_2), 2.58 (tt, $J = 5.7, 2.6$ Hz, 2H, $=\text{C}-\text{CH}_2$), 2.21 (tt, $J = 6.1, 2.7$ Hz, 2H, $=\text{C}-\text{CH}_2$), 1.77–1.71 (m, 2H, $=\text{C}-\text{CH}_2\text{CH}_2$), 1.70–1.65 (m, 2H, $=\text{C}-\text{CH}_2\text{CH}_2$), 0.94 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 0.41 [s, 9H, $\text{Si}(\text{CH}_3)_3$], and 0.33 [s, 6H, $\text{Si}(\text{CH}_3)_2$].

^{13}C NMR (125 MHz, CDCl_3): δ 197.9, 164.8, 159.5, 145.4, 139.8, 133.8, 132.3, 131.1, 119.7, 69.9, 33.0, 28.0, 27.7, 23.3, 21.6, 20.1, 19.2, 4.2, and -1.3.

IR (neat): 2936, 2928, 2892, 2854, 1706, 1423, 1310, 1253, 844, and 826 cm^{-1} .

HRMS (ESI-TOF): Calcd for $\text{C}_{24}\text{H}_{36}\text{NaO}_2\text{Si}_2^+$ [$\text{M}+\text{Na}^+$] requires 435.2146; found 435.2152.”⁴

2-Methyl-8-(trimethylsilyl)octa-3,5,7-triyn-2-ol (9)

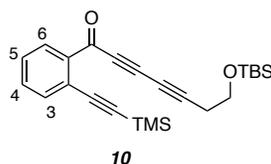
To a solution of CuCl (100 mg, 1.0 mmol) in acetone (15 mL) was added tetramethylethylenediamine (50 μ L, 0.33 mmol) and the mixture was stirred for 10 minutes at ambient temperature. Trimethylsilylacetylene (2.8 mL, 20 mmol) and 2-methylhexa-3,5-diyne-2-ol⁵ (270 mg, 2.5 mmol) in acetone (2 mL) were added dropwise over 5 minutes and the resulting solution was stirred, open to the air, for 2 h. Water was added (10 mL), and the mixture was extracted with EtOAc (3 x 20 mL), washed with brine, dried (MgSO₄), filtered, and concentrated under reduced pressure. Purification by MPLC (3:1 hexanes:EtOAc) gave **9** (215 mg, 1.1 mmol, 42%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 1.54 [s, 6H, C(CH₃)₂] and 0.21 [s, 9H, Si(CH₃)₃].

¹³C NMR (125 MHz, CDCl₃): δ 88.0, 87.8, 82.5, 67.5, 65.8, 64.1, 61.1, 31.1, and -0.4.

IR: 3300 (br), 2984, 2962, 2901, 2166, 2075, 1292, 1251, 962, 850, and 761 cm⁻¹.

GC-MS (EI) (50 °C 2 min, ramp 20 °C/min, hold 250 °C 3 min): t_r = 7.07 min; m/z : 204, 189, 171, 147, and 75.

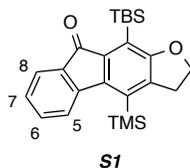
7-((*tert*-Butyldimethylsilyl)oxy)-1-(2-((trimethylsilyl)ethynyl)phenyl)hepta-2,4-diyne-1-one (10)


¹H NMR (500 MHz, CDCl₃): δ 8.00 (d, *J* = 7.8 Hz, 1H, *H*6), 7.58 (d, *J* = 7.6 Hz, 1H, *H*3), 7.49 (ddd, *J* = 7.5, 7.5 Hz, 1H, *H*4), 7.41 (t, *J* = 7.6, 7.6 Hz, 1H, *H*5), 3.80 (t, *J* = 6.8 Hz, 2H, CH₂O), 2.61 (t, *J* = 6.8 Hz, 2H, C≡CCH₂), 0.90 [s, 9H, SiC(CH₃)₃], 0.28 [s, 9H, Si(CH₃)₃], and 0.09 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 176.6, 138.4, 135.2, 132.7, 131.4, 128.4, 123.0, 102.7, 102.2, 88.4, 78.9, 72.5, 65.6, 61.0, 26.0, 24.3, 18.4, 0.0, and -5.2.

IR (neat): 2956, 2929, 2857, 2234, 2145, 1648, 1297, 1251, 1108, 865, 843, and 757 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₄H₃₂NaO₂Si₂⁺ [*M*+Na⁺] requires 431.1833; found 431.1805. ”⁴

10-((*tert*-Butyldimethylsilyl)oxy)-4-(trimethylsilyl)-2,3-dihydro-9H-fluoreno[2,3-*b*]furan-9-one (S1)


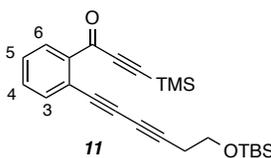
¹H NMR (500 MHz, CDCl₃): δ 7.53 (ddd, *J* = 7.2, 1.3, 0.6 Hz, 1H, *H*8), 7.50 (ddd, *J* = 7.7, 0.7, 0.7 Hz, 1H, *H*5), 7.36 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H, *H*6), 7.14 (ddd, *J* = 7.4, 7.4, 0.8 Hz, 1H, *H*7), 4.44 (t, *J* = 8.8, 2H, CH₂O), 3.25 (t, *J* = 8.8 Hz, 2H, ArCH₂), 0.98 [s, 9H, SiC(CH₃)₃], 0.50 [s, 9H, Si(CH₃)₃], and 0.38 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 194.4, 166.1, 145.6, 144.9, 141.7, 137.6, 134.9, 133.5, 132.9, 127.0, 123.9, 123.5, 120.1, 69.9, 32.7, 27.7, 19.4, 2.5, and -1.2.

IR (neat): 2953, 2895, 2853, 1715, 1292, 1254, 902, 845, 825, 763, and 752 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₄H₃₂NaO₂Si₂⁺ [*M*+Na⁺] requires 431.1833; found 431.1853.

MP: 159–162 °C”⁴

1-(2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyne-1-yl)phenyl)-3-(trimethylsilyl)prop-2-yn-1-one (11)


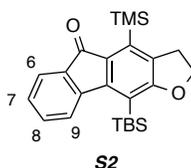
¹H NMR (500 MHz, CDCl₃): δ 8.08 (d, *J* = 7.8 Hz, 1H, *H*6), 7.60 (d, *J* = 7.6 Hz, 1H, *H*3), 7.49 (ddd, *J* = 7.6, 7.5, 1.2 Hz, 1H, *H*4), 7.44 (t, *J* = 7.7, 7.6, 1.2 Hz, 1H, *H*5), 3.79 (t, *J* = 7.2 Hz, 2H, CH₂O), 2.59 (t, *J* = 7.2 Hz, 2H, C≡CCH₂), 0.91 [s, 9H, SiC(CH₃)₃], 0.30 [s, 9H, Si(CH₃)₃], and 0.09 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 176.6, 139.2, 135.8, 132.6, 131.9, 128.6, 122.1, 101.6, 101.5, 83.9, 80.6, 73.1, 66.8, 61.5, 26.0, 24.3, 18.5, -0.5, and -5.1.

IR (neat): 2956, 2930, 2858, 2244, 2153, 1649, 1252, 1234, 1108, 1014, and 844 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₄H₃₂NaO₂Si₂⁺ [M+Na⁺] requires 431.1833; found 431.1839. ”⁴

10-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)-2,3-dihydro-5*H*-fluoreno[3,2-*b*]furan-5-one (S2)



¹H NMR (500 MHz, CDCl₃): δ 7.67 (ddd, *J* = 7.7, 0.8, 0.8 Hz, 1H, *H*9), 7.53 (ddd, *J* = 7.2, 1.3, 0.6 Hz, 1H, *H*6), 7.35 (ddd, *J* = 7.6, 7.6, 1.3 Hz, 1H, *H*8), 7.21 (ddd, *J* = 7.4, 7.4, 0.9 Hz, 1H, *H*7), 4.51 (t, *J* = 8.8 Hz, 2H, CH₂O), 3.23 (t, *J* = 8.8 Hz, 2H, CH₂CH₂O), 1.09 [s, 9H, SiC(CH₃)₃], 0.40 [s, 6H, Si(CH₃)₂], and 0.39 [s, 9H, Si(CH₃)₃].

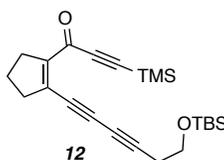
¹³C NMR (125 MHz, CDCl₃): δ 193.9, 170.6, 154.8, 144.8, 138.9, 135.5, 133.7, 132.8, 131.8, 128.4, 124.2, 123.0, 115.9, 70.7, 31.2, 28.1, 19.5, 1.6, and 0.0.

IR (neat): 2951, 2928, 2895, 2856, 1702, 1289, 1247, 843, 824 and 747 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₄H₃₂NaO₂Si₂⁺ [M+Na⁺] requires 431.1833; found 431.1832.

MP: 55–58 °C.”⁴

1-(2-(6-((*tert*-Butyldimethylsilyl)oxy)hexa-1,3-diyn-1-yl)cyclopent-1-en-1-yl)-3-(trimethylsilyl)prop-2-yn-1-one (12)



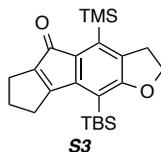
¹H NMR (500 MHz, CDCl₃): δ 3.77 (t, *J* = 7.1 Hz, 2H, CH₂OSi), 2.77–2.71 (m, 4H, CH₂CH₂CH₂), 2.59 (t, *J* = 7.1 Hz, 2H, CH₂CH₂O), 1.90 (pentet, *J* = 7.7 Hz, 2H, CH₂CH₂C=C), 0.90 [s, 9H, SiC(CH₃)₃], 0.29 [s, 9H, Si(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 173.3, 149.1, 136.9, 101.9, 100.4, 87.8, 87.3, 70.6, 66.9, 61.3, 41.0, 32.8, 26.0, 24.3, 21.8, 18.4, -0.5, and -5.1.

IR (neat): 2955, 2930, 2857, 2228, 1609, 1252, 1107, and 846 cm^{-1} .

HRMS (ESI-TOF): Calcd for $\text{C}_{23}\text{H}_{34}\text{NaO}_2\text{Si}_2^+$ [$\text{M}+\text{Na}^+$] requires 421.1990; found 421.2000. ”⁴

9-(*tert*-Butyldimethylsilyl)-4-(trimethylsilyl)-3,6,7,8-tetrahydrocyclopenta[2,3]indeno[5,6-*b*]furan-5(2H)-one (S3)



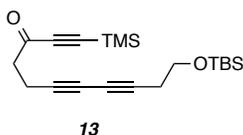
¹H NMR (500 MHz, CDCl_3): δ 4.42 (t, $J = 8.9$ Hz, 2H, CH_2O), 3.14 (t, $J = 8.9$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 2.75 (tt, $J = 6.9, 2.8$ Hz, 2H, $\text{CH}_2\text{CC}=\text{O}$), 2.41 (tt, $J = 7.3, 3.0$ Hz, 2H, $\text{CH}_2\text{C}(\text{Ar})$), 2.26 (br pentet, $J = 7.3$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.94 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 0.34 [s, 6H, $\text{Si}(\text{CH}_3)_2$], and 0.33 [s, 9H, $\text{Si}(\text{CH}_3)_3$].

¹³C NMR (125 MHz, CDCl_3): δ 193.9, 169.6, 168.3, 150.0, 145.2, 137.1, 134.7, 128.0, 116.1, 70.3, 33.1, 31.5, 27.7, 27.5, 24.5, 18.5, 1.6, and -0.2.

IR (neat):, 2952, 2928, 2895, 2855, 1698, 1497, 1375, 1301, 1247, 1111, 844, and 809 cm^{-1} .

HRMS (ESI-TOF): Calcd for $\text{C}_{23}\text{H}_{34}\text{NaO}_2\text{Si}_2^+$ [$\text{M}+\text{Na}^+$] requires 421.1990; found 421.2022.

MP: 148–153 $^\circ\text{C}$.”⁴

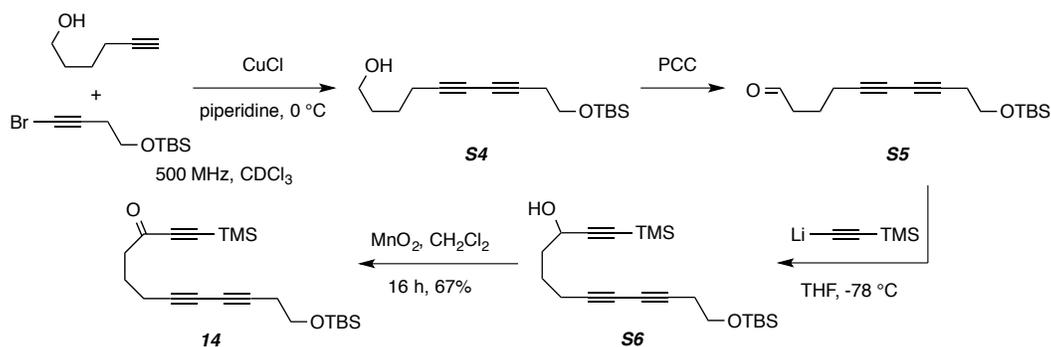
11-((*tert*-Butyldimethylsilyl)oxy)-1-(trimethylsilyl)undeca-1,6,8-triyn-3-one (13)

¹H NMR (500 MHz, CDCl₃): δ 3.72 (t, *J* = 7.1 Hz, 2H, CH₂OSi), 2.81 [br t, *J* = 7.3 Hz, 2H, CH₂CH₂C(=O)], 2.58 [br t, *J* = 7.5 Hz, 2H, CH₂CH₂C(=O)], 2.46 (tt, *J* = 7.1, 1.1 Hz, 2H, C≡CCH₂CH₂OSi), 0.89 [s, 9H, SiC(CH₃)₃], 0.25 [s, 9H, Si(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 184.8, 101.4, 99.4, 75.2, 75.1, 66.3, 66.2, 61.6, 43.7, 26.0, 23.8, 18.5, 14.0, -0.7, and -5.2.

IR (neat): 2956, 2930, 2857, 2229, 2153, 1681, 1253, 1109, and 845 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₀H₃₂NaO₂Si₂⁺ [M+Na⁺] requires 383.1833; found 383.1844.”⁴

12-((*tert*-Butyldimethylsilyloxy)-1-(trimethylsilyl)dodeca-1,7,9-triyn-3-one (14)


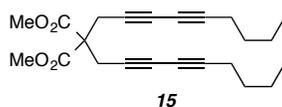
The preparation of **14** followed by direct analogy to that of **13**.⁴ Following the general Cadiot-Chodkiewicz procedure,⁴ 5-hexyn-1-ol and TBS-protected 1-bromobut-1-yn-4-ol were coupled to give diynol **S4**. The alcohol was oxidized with pyridinium chlorochromate (PCC) to provide the aldehyde **S5** [¹H NMR (500 MHz, CDCl₃): 9.80 (t, *J* = 1.2 Hz, 1H, CHO), 3.73 (t, *J* = 7.1 Hz, 2H, CH₂OSi), 2.60 (dt, *J* = 1.2, 7.2 Hz, 2H, CH₂CH₂OSi), 2.46 (tt, *J* = 7.1, 1.1, 2H, CHOCH₂), 2.34 (tt, *J* = 6.8, 1.0 Hz, 2H, CH₂CH₂CH₂C≡C), 1.85 (p, *J* = 7.0 Hz, 2H, CH₂CH₂CH₂), 0.89 [s, 9H, SiC(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂]]. The aldehyde was added to a THF solution of lithium trimethylsilylacetylide at -78 °C to give triyne **S6** [¹H NMR (500 MHz, CDCl₃): 4.38 (dt, *J* = 6.4, 5.4 Hz, 1H, CHOH), 3.73 (t, *J* = 7.2 Hz, 2H, CH₂OSi), 2.47 (tt, *J* = 7.2, 1.1 Hz, 2H, CH₂CH₂OSi), 2.32 (tt, *J* = 6.9, 1.1 Hz, 2H, CH₂C≡C), 1.79 (m, 2H, CH₂CHOH), 1.70 (m, 2H, CH₂CH₂CHOH), 0.89 [s, 9H, SiC(CH₃)₃], 0.17 [s, 9H, Si(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂]]. The triyne alcohol **S6** (60 mg, 0.16 mmol) was dissolved in CH₂Cl₂ (2.0 mL) and MnO₂ (278 mg, 3.2 mmol) was added at room temperature. After 16 h the reaction mixture was filtered through Celite® (EtOAc eluent) and concentrated to give the ketone **14** (41 mg, 0.11 mmol, 67%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 3.73 (t, *J* = 7.1 Hz, 2H, CH₂O), 2.70 (t, *J* = 7.3 Hz, CH₂C=O), 2.47 (tt, *J* = 7.1, 1.1 Hz, 2H, CH₂CH₂OSi), 2.33 (tt, *J* = 6.9, 1.1 Hz, 2H, CH₂CH₂CH₂C=O), 1.86 (tt, *J* = 7.2, 7.0 Hz, 2H, CH₂CH₂CH₂C=O), 0.90 [s, 9H, SiC(CH₃)₃], 0.25 [s, 9H, Si(CH₃)₃], and 0.07 [s, 6H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 186.8, 102.0, 98.3, 76.4, 74.9, 66.4, 66.3, 61.6, 44.0, 26.0, 23.8, 22.5, 18.6, 18.5, -0.6, and -5.1.

IR: 2955, 2930, 2857, 2149, 1679, 1253, 1110, 846, and 778 cm⁻¹.

HR ESI-MS calcd for C₂₁H₃₄NaO₂Si₂ [M + Na]⁺ 397.1990, found 397.2007.

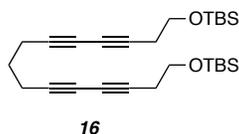
Dimethyl 2,2-di(nona-2,4-diyn-1-yl)malonate (15)


¹H NMR (500 MHz, CDCl₃): δ 3.77 (s, 6H, CO₂CH₃), 3.06 [s, 4H, CH₂C(CO₂Me)₂], 2.24 (t, *J* = 6.9 Hz, 4H, CH₂C≡C), 1.50 (br tt, *J* = 7.0, 7.0 Hz, 4H, C≡CCH₂CH₂), 1.40 (br tq, *J* = 7.0, 7.0 Hz, 4H, CH₂CH₃), and 0.91 (t, *J* = 7.3 Hz, 6H, CH₃).

¹³C NMR (125 MHz, CDCl₃): δ 169.0, 79.2, 70.7, 68.9, 65.0, 56.9, 53.5, 30.4, 24.0, 22.1, 19.1, and 13.7.

IR (neat): 2957, 2934, 2873, 2259, 1744, 1435, 1320, 1292, 1210, 1184, 1072, and 1054 cm⁻¹.

HRMS (ESI-TOF): Calcd for C₂₃H₂₈NaO₄⁺ [M+Na⁺] requires 391.1880; found 391.1885.⁶

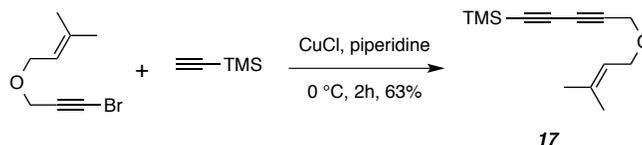
2,2,3,3,21,21,22,22-Octamethyl-4,20-dioxa-3,21-disilatricosa-7,9,14,16-tetrayne (16)


¹H NMR (500 MHz, CDCl₃): δ 3.73 (t, *J* = 7.1 Hz, 4H, CH₂OSi), 2.46 (tt, *J* = 7.1, 1.1 Hz, 4H, CH₂CH₂OSi), 2.38 (tt, *J* = 6.9, 1.1 Hz, 4H, CH₂C≡CC≡C), 1.73 (pentet, *J* = 6.9 Hz, 2H, CH₂CH₂C≡C), 0.89 [s, 18H, OSiC(CH₃)₃], and 0.07 [s, 12H, Si(CH₃)₂].

¹³C NMR (125 MHz, CDCl₃): δ 76.3, 74.8, 66.4, 66.1, 61.6, 27.2, 26.0, 23.8, 18.47, 18.45, and -5.2.

IR (neat): 2953, 2929, 2857, 1255, 1106, 838, and 776 cm⁻¹.

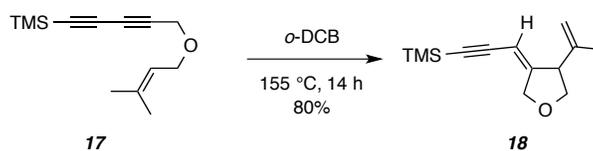
HRMS (ESI-TOF): Calcd for C₂₇H₄₄NaO₂Si₂⁺ [M+Na⁺] requires 479.2772; found 479.2790.⁴

Trimethyl(5-((3-methylbut-2-en-1-yl)oxy)penta-1,3-diyn-1-yl)silane (17)

CuCl (75 mg, 0.75 mmol) was added to a stirred solution of 1-((3-bromoprop-2-yn-1-yl)oxy)-3-methylbut-2-ene⁷ (1.0 g, 5.0 mmol) and trimethylsilylacetylene (1.4 mL, 10.0 mmol) in freshly deaerated piperidine (sparging with N₂ gas, 25 mL) at 0 °C and under an inert atmosphere. After 1 h the reaction mixture was diluted with satd. aq. NH₄Cl and extracted with EtOAc or Et₂O. The combined organic extracts were washed with brine, dried (MgSO₄), and concentrated. Purification by MPLC (hexanes:EtOAc 20:1) gave diyne **17** (693 mg, 3.2 mmol, 63%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 5.32 (t, *J* = 6.7 Hz, 1H, C=CH), 4.19 (s, 2H, C≡CCH₂), 4.05 (d, *J* = 7.1 Hz, 2H, C=CHCH₂O), 1.76 (s, 3H, CH₃C=C), 1.71 (s, 3H, CH₃C=C), and 0.20 [s, 9H, Si(CH₃)₃].

GC-MS (EI) (50 °C 2 min, ramp 20 °C/min, hold 250 °C 3 min): *t*₁ = 6.61 min; *m/z*: 220, 205, 190, 175, 159, 131, 83, 73, and 59 (this spectrum is essentially identical with that of **18**). *t*₂ 7.19 min; *m/z*: 219, 205, 175, 137, 121, 107, 97, 83, 73, and 53.

(Z)-Trimethyl(3-(4-(prop-1-en-2-yl)dihydrofuran-3(2H)-ylidene)prop-1-yn-1-yl)silane (18)

A solution of ether **17** (20 mg, 0.09 mmol) in *o*-DCB (0.9 mL) was heated at 155 °C. After 14 h the solution was loaded onto a column of silica and *o*-DCB was removed by initial elution with hexanes. Subsequent elution with hexanes:EtOAc (2:1) gave **18** (16 mg, 0.7 mmol, 80%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 5.40 (ddd, *J* = 2.6, 2.6, 2.6 Hz, 1H, C=CHC≡C), 4.88 (m, 1H, C=CH_aH_b), 4.87 (m, 1H, C=CH_aH_b), 4.55 (dddd, *J* = 15.3, 2.6, 1.4, 0.5 Hz, 1H, OCH_aH_bC=C), 4.49 (dddd, *J* = 15.3, 2.9, 2.4, 0.6 Hz, 1H, OCH_aH_bC=C), 4.06 (ddd, *J* = 8.8, 7.6, 0.6 Hz, 1H, OCH_aH_bCH), 3.77 (ddd, *J* = 8.7, 7.1, 0.5 Hz, 1H, OCH_aH_bCH), 3.45 (dddq, *J* = 7.7, 7.0, 2.3, 1.4, 0.7 Hz, 1H, CHC(Me)=C), 1.68 (dd, *J* = 1.5, 0.8 Hz, 3H, C=CCH₃), and 0.19 [s, 9H, Si(CH₃)₃].

¹³C NMR (125 MHz, CDCl₃): δ 158.1, 143.0, 114.5, 101.8, 101.2, 99.8, 72.7, 71.9, 52.7, 19.0, and 0.1.

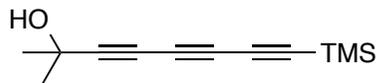
IR (neat): 2959, 2898, 2859, 2129, 1644, 1250, 1070, 844, and 759 cm^{-1} .

GC-MS (EI) (50 °C 2 min, ramp 20 °C/min, hold 250 °C 3 min): t_r = 6.56 min; m/z : 220, 205, 190, 175, 159, 131, 83, 73, and 59.

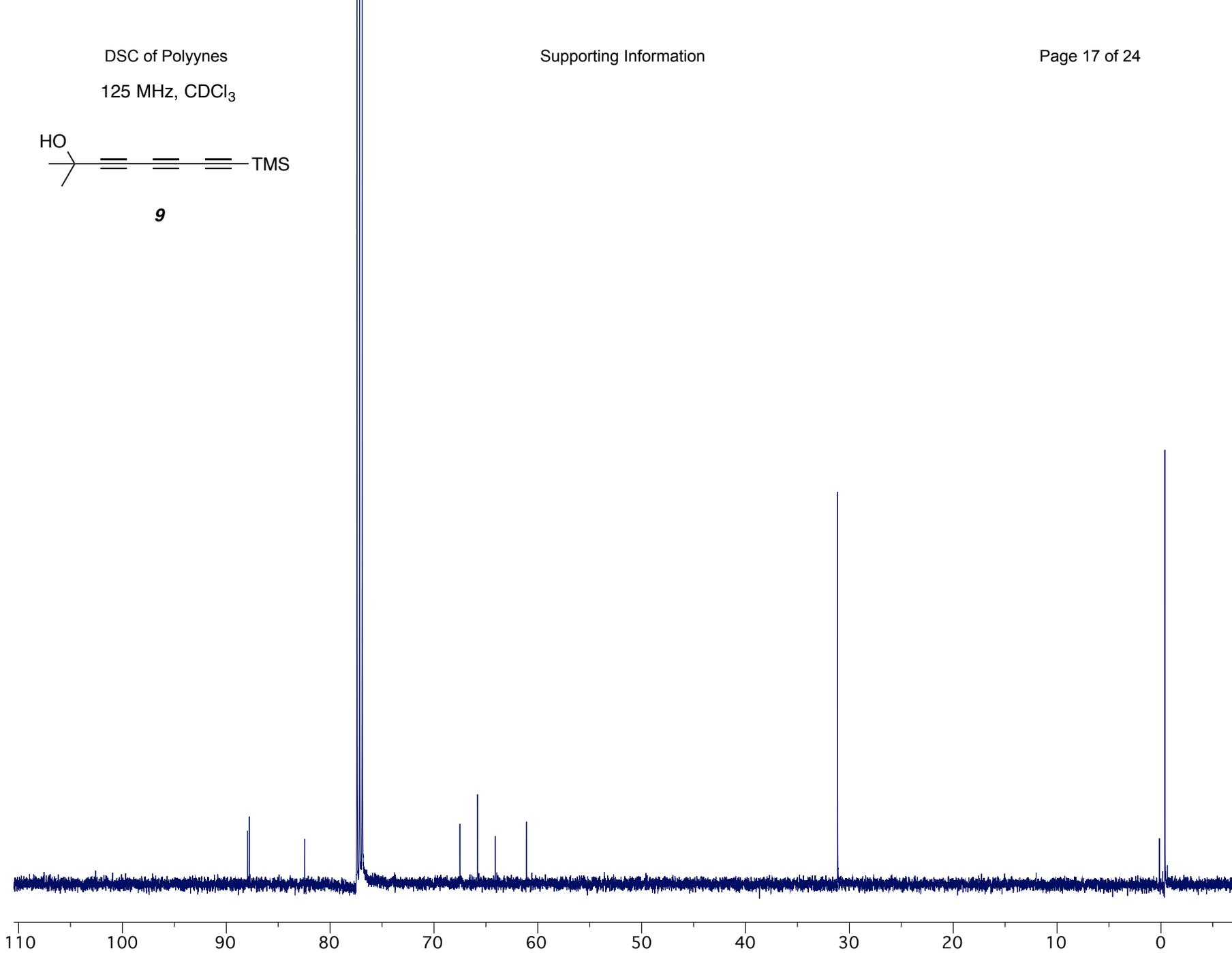
III. References for the Supporting Information

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- ² Hoye, T. R.; Zhao, H. *J. Org. Chem.* **2002**, *67*, 4014–4016.
- ³ From the Supporting Information accompanying: Niu, D.; Wang, T.; Woods, B. P.; Hoye, T. R. *Org. Lett.* **2014**, *16*, 254–257 ([doi:10.1021/ol403258c](https://doi.org/10.1021/ol403258c))
- ⁴ Woods, B. P.; Baire, B.; Hoye, T. R. *Org. Lett.* **2014**, *16*, 4578–4581.
- ⁵ Dunetz, J. R.; Danheiser, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 5776–5777.
- ⁶ Niu, D.; Wang, T.; Woods, B. P.; Hoye, T. R. *Org. Lett.* **2014**, *16*, 254–257.
- ⁷ Cho, E. J.; Kim, M.; Lee, D. *Org. Lett.* **2006**, *8*, 5413–5416.

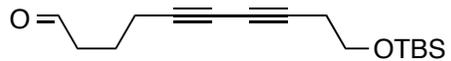
125 MHz, CDCl₃



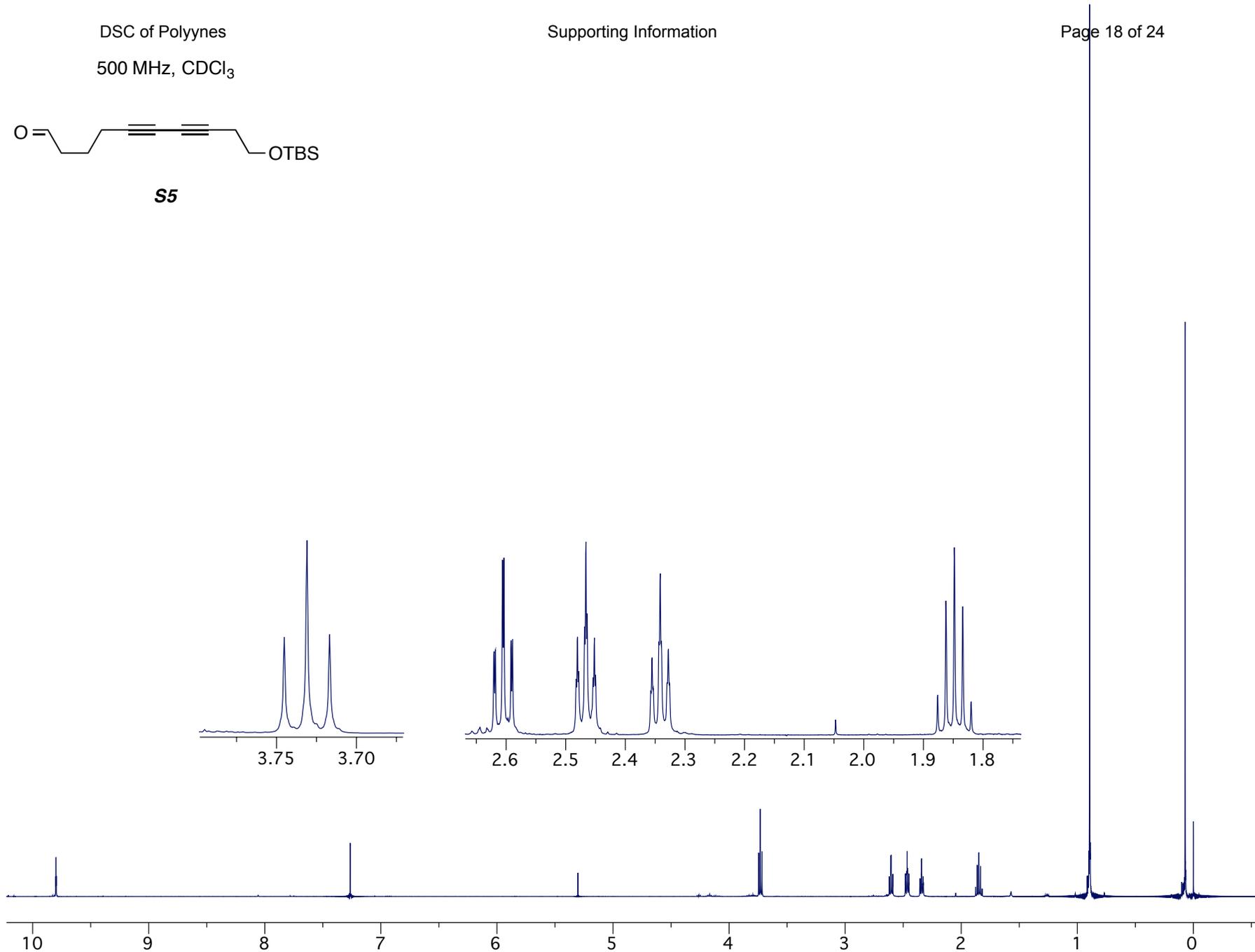
9



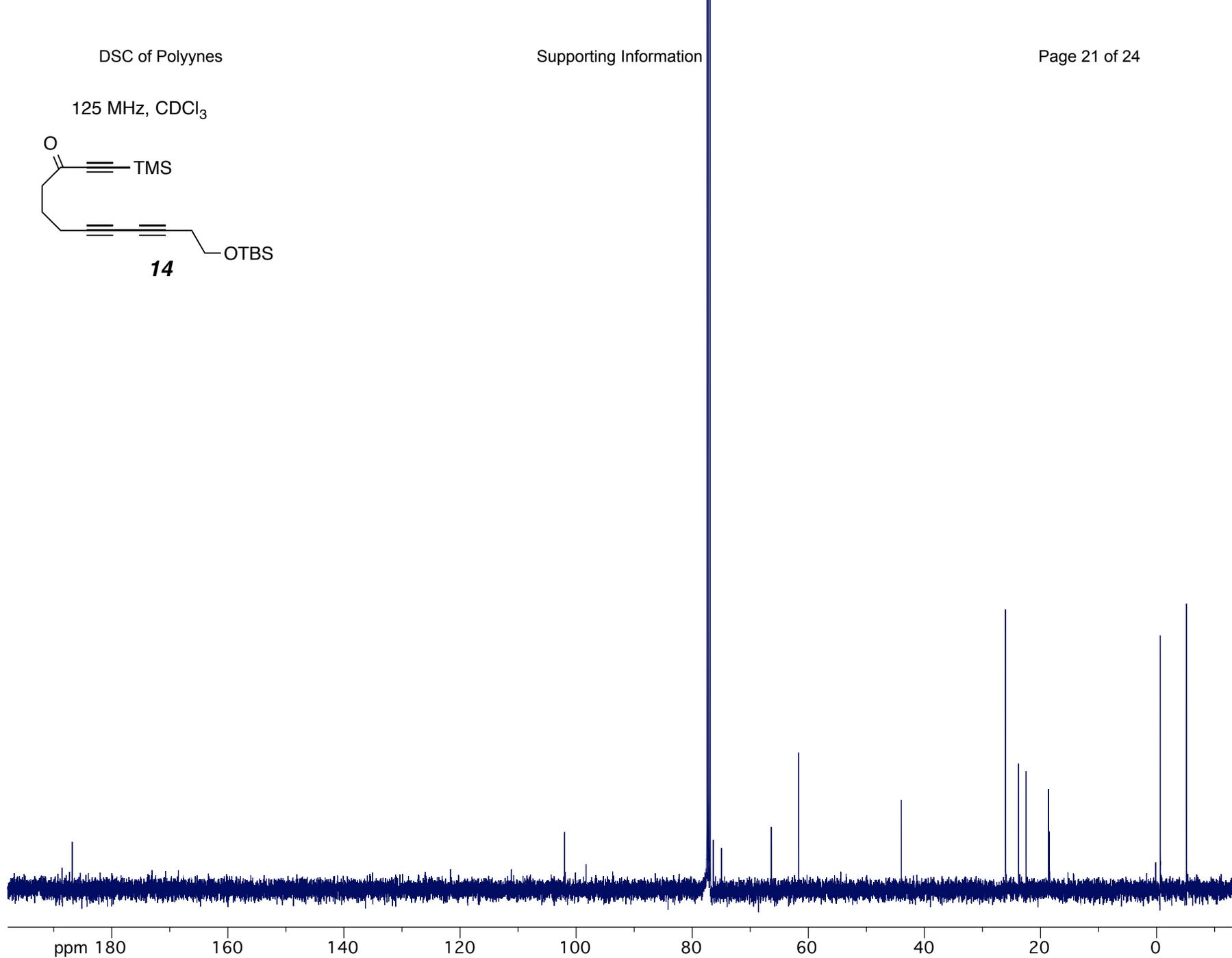
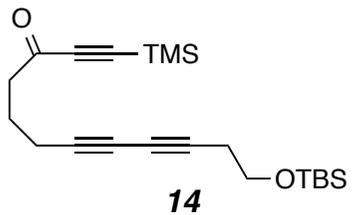
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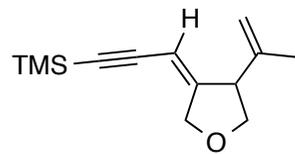
S5



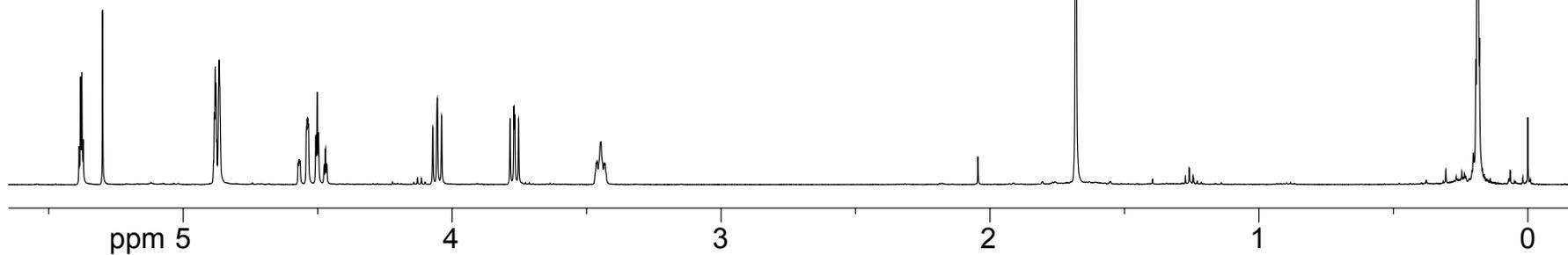
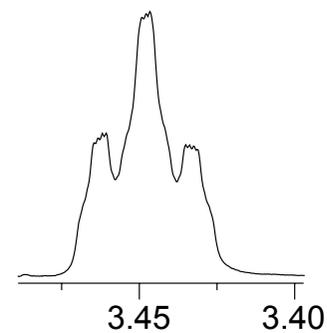
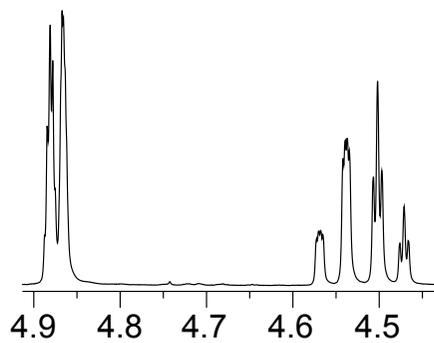
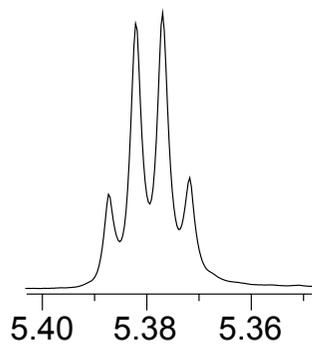
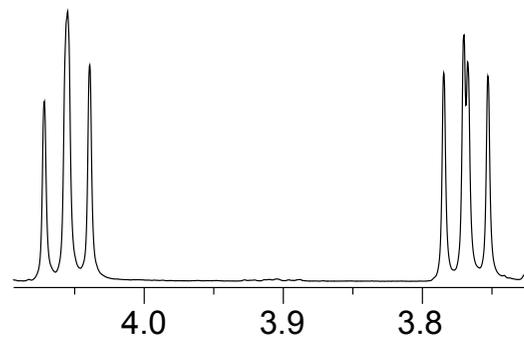
125 MHz, CDCl₃



500 MHz, CDCl₃



18



125 MHz, CDCl₃