Enantioselective Addition of Alkynes to *α,α*-Dichlorinated Aldehydes

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Supporting Information

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I. General Considerations

Reaction handling: Unless otherwise stated, all reactions were performed in flame-dried glassware under an atmosphere of N_2. Purification of products was carried out by flash column chromatography employing Fluka silica gel (pore size 60Å, 230-400 mesh particle size) and technical grade solvents as eluents with 0.3-0.5 bar pressure. Concentration of products under reduced pressure was accomplished by rotary evaporation at 35-40 °C at the required pressure. Unless otherwise noted, the yields given refer to the purified products.

Solvents and reagents: Unless otherwise stated, all chemicals and reagents were purchased from commercial suppliers and used without further purification. Zinc triflate (stored and handled in a glove box, TCI), 2,2-dichlorohexanal (Acros Organics), 2,2,4-trichlorobutanal (Acros Organics) were used as received. Toluene was dried by passage over two 4 × 36 inch columns of anhydrous neutral A-2 alumina (Macherey und Nagel; activated for >12 h at 300 °C under a flow of N_2) under an atmosphere of N_2. Triethylamine was distilled from CaH_2 under an atmosphere of dry N_2. Deuterated solvents were obtained from Armar Chemicals, Döttingen, Switzerland.

NMR Spectroscopy: NMR data was recorded on a Bruker AVIII400 and Bruker DRX400 spectrometer, both operating at 400 MHz for ^{1}H acquisitions in the indicated deuterated solvent. Chemical shifts (δ) are reported in parts per million (ppm) with the solvent resonance as internal standard (for ^{1}H–NMR $CHCl_3$ singlet at 7.26 ppm and for ^{13}C–NMR, $CDCl_3$ triplet at 77.16 ppm). The data is reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz).

IR spectroscopy: Infrared spectra were recorded on a Perkin-Elmer UATR Two spectrometer. The peaks are reported as absorption maxima (cm^{-1}).

Mass spectrometry: All analyses were performed by the mass spectrometry service of the Laboratorium für Organische Chemie at ETH Zürich. ESI measurements were carried out on Bruker maXis – ESI-Qq-TOFMS and Bruker solariX – ESI-FTICR-MS and are reported as (m/z).

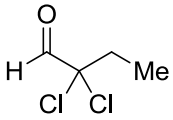
Optical Rotation: Optical rotations (α) were measured on a Jasco P-2000 polarimeter with a 10 cm path length cell. Values are reported with concentration in $mg \cdot mL^{-1}$, with c = 1.00 corresponding to 10 $mg \cdot mL^{-1}$, and solvent. The temperature (T) at which the measurement was made appears as the superscript number (/°C).

X-ray diffraction: X-ray diffraction experiments have been carried out in the Small Molecule Crystallography Center (SMoCC) at the Department of Chemistry and Applied Biosciences at ETH Zürich.

II. Synthesis and Characterization of Starting Materials

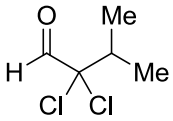
General Procedure A: Synthesis of 2,2-Dichlorinated Aldehydes. Following modified, reported procedures,[1] to the corresponding aldehyde (10.0 mmol, 1.00 equiv.) was added *t*$BuNH_2$ (1.10 mL, 1.05 equiv.) at 24 °C under ambient air. The resulting mixture was stirred at 24 °C for 20 min before it was diluted with CH_2Cl_2 (10.0 mL). $MgSO_4$ was added and the suspension was stirred for 15 min at 24 °C then filtered. The filter cake was washed with CH_2Cl_2 (2 × 5.0 mL). The solvent was removed under reduced pressure and the concentrate was dissolved in CCl_4 (8.0 mL). The flask was immersed in an ice bath and *N*-chlorosuccinimide (2.80 g, 2.10 equiv.) was added in portions over 10 min. The resulting suspension was allowed to warm to 24 °C over the course of 12 h without removing the cooling bath. The mixture was then filtered through a plug of celite and the filter cake was washed with hexane (4 × 10 mL). The solution was concentrated under reduced pressure then distilled water (8.2 mL) and conc. aq. HCl (4.6 mL) were added at 24 °C. The mixture was stirred at 24 °C under ambient air for 3 h then was partitioned in between CH_2Cl_2 (40 mL) and distilled water (40 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The combined organic phases were dried over $MgSO_4$ and concentrated (40 °C, pressure adjusted depending on the volatility of the product). The resulting 2,2-dichlorinated aldehydes were used without further purification with the exception of **2a** and **2c**, which were purified via short path distillation.

[1] (a) Verhe, R.; Dekimpe, N.; Debuyck, L.; Schamp, N. *Synthesis* **1975**, 455. (b) Nilewski, C., Deprez, N. R., Fessard, T. C., Li, D. B., Geisser, R. W. and Carreira, E. M. *Angew. Chem. Int. Ed.*, **2011**, *50*, 7940.



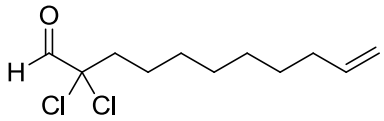
2,2-Dichlorobutanal (2a).[2] The title compound was prepared following general procedure A and purified by short path distillation.

^{1}H–NMR (300 MHz, $CDCl_3$, 298 K): δ 9.26 (s, 1H), 2.32 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); **^{13}C–NMR** (75 MHz, $CDCl_3$, 298 K): δ 185.1, 89.7, 34.2, 9.0.



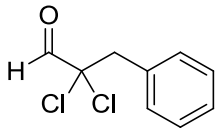
2,2-Dichloro-3-methylbutanal (2c).[2] The title compound was prepared following general procedure A and purified by short path distillation.

^{1}H–NMR (400 MHz, $CDCl_3$, 298 K): δ 9.25 (s, 1H), 2.57 (septet, *J* = 6.6 Hz, 1H), 1.15 (d, *J* = 6.6 Hz, 6H); **^{13}C–NMR** (101 MHz, $CDCl_3$, 298 K): δ 185.8, 94.5, 37.6, 17.8.



2,2-Dichloroundec-10-enal (2d). The title compound was prepared following general procedure A and was used without further purifications.

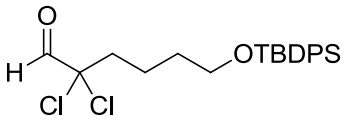
^{1}H–NMR (400 MHz, $CDCl_3$, 298 K): δ 9.24 (s, 1H), 5.86 – 5.75 (m, 1H), 5.02 – 4.91 (m, 2H), 2.29 – 2.25 (m, 2H), 2.07 – 2.01 (m, 2H), 1.66 – 1.58 (m, 2H), 1.42 – 1.25 (m, 8H); **^{13}C–NMR** (101 MHz, $CDCl_3$, 298 K): δ 185.1, 139.2, 114.4, 88.9, 40.7, 33.9, 29.2, 29.1, 29.02, 28.95, 24.6.



2,2-Dichloro-3-phenylpropanal (2e).[3] The title compound was prepared following general procedure A and was used without further purifications.

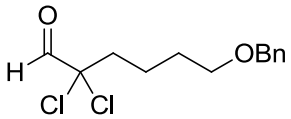
[2] De Buyck, L.; Verhé, R.; De Kimpe, N.; Courtheyn, D.; Schamp, N. *Bull. Soc. Chim. Belg.* **1980**, *89*, 441.
[3] Bellesia, F.; De Buyck, L.; Ghelfi, F.; Libertini, E.; Pagnoni, U. M.; Roncaglia, F. *Tetrahedron* **2000**, *56*, 7507.

^{1}H–NMR (400 MHz, $CDCl_3$, 298 K): δ 9.33 (s, 1H), 7.36 (s, 5H), 3.61 (s, 2H); **^{13}C–NMR** (101 MHz, $CDCl_3$, 298 K): δ 185.4, 132.7, 131.6, 128.4, 128.1, 87.5, 46.3.



6-((*Tert*-butyldiphenylsilyl)oxy)-2,2-dichlorohexanal (2f). The title compound was prepared following general procedure A and was used without further purifications.

^{1}H–NMR (400 MHz, $CDCl_3$, 298 K): δ 9.25 (s, 1H), 7.69 – 7.67 (m, 4H), 7.46 – 7.37 (m, 6H), 3.71 (t, *J* = 6.0 Hz, 2H), 2.31 – 2.27 (m, 2H), 1.83 – 1.72 (m, 2H), 1.68 – 1.61 (m, 2H), 1.07 (s, 9H); **^{13}C–NMR** (101 MHz, $CDCl_3$, 298 K): δ 185.0, 135.7, 134.0, 129.8, 127.8, 88.8, 63.3, 40.4, 31.9, 27.0, 21.2, 19.3.



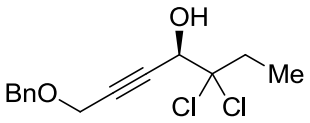
6-(Benzyloxy)-2,2-dichlorohexanal (2m). The title compound was prepared following general procedure A and was used without further purifications.

^{1}H–NMR (400 MHz, $CDCl_3$, 298 K): δ 9.24 (s, 1H), 7.39 – 7.26 (m, 5H), 4.52 (s, 2H), 3.51 (t, *J* = 5.9 Hz, 2H), 2.33 – 2.29 (m, 2H), 1.80 – 1.67 (m, 4H); **^{13}C–NMR** (101 MHz, $CDCl_3$, 298 K): δ 185.0, 138.5, 128.5, 127.8, 127.7, 88.7, 73.1, 69.8, 40.4, 29.2, 21.6.

III. Synthesis and Characterization of Products

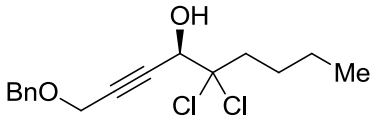
General Procedure B: Alkyne Addition to *α*,*α*-Dichlorinated Aldehydes. A 25 mL round bottom flask with a stir bar was charged with $Zn(OTf)_2$ (280 mg, 0.770 mmol, 1.10 eq) under inert atmosphere in the glovebox. Then the $Zn(OTf)_2$ was heated in an oil bath stirring for 24 h at 140 ˚C and under high vacuum. After that, it was cooled to room temperature and then was charged with (–)-*N*-Methylephedrine (151 mg, 0.840 mmol, 1.20 eq) in the glovebox. Subsequently to the flask was added dry toluene (2.0 mL) and distilled triethylamine (117 µL, 0.840 mmol, 1.20 eq). The resulting mixture was vigorously stirred at room temperature for 2.5 h

before the corresponding alkyne (0.840 mmol, 1.20 eq) was added by syringe in one portion. After 50 min of stirring the corresponding aldehyde (0.700 mmol, 1.00 eq) was added in one portion. After stirring for 12 h at room temperature the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (10 mL). The reaction mixture was poured into a separatory funnel containing diethyl ether (10 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$, concentrated in vacuo and purified by column chromatography.



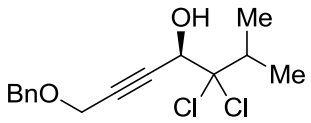
(–)-(*R*)-1-(Benzyloxy)-5,5-dichlorohept-2-yn-4-ol (3a). The product was isolated by flash chromatography (cyclohexane/EtOAc 12:1) to afford the title compound as oil (117 mg, 0.410 mmol, 65%), which solidified upon standing to an off-white solid.

TLC: R_f = 0.20 (hexane/EtOAc 10:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 5H), 4.67 (dt, *J* = 8.6, 1.7 Hz, 1H), 4.63 (s, 2H), 4.25 (d, *J* = 1.7 Hz, 2H), 2.71 (d, *J* = 8.6 Hz, 1H), 2.35 (qd, *J* = 7.2, 4.3 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 137.3, 128.6, 128.4, 128.1, 96.9, 83.7, 82.4, 71.8, 71.7, 57.3, 36.7, 9.3; **Mp**: 36–38 °C; **IR** (neat): 3386, 2942, 1455, 1057, 929, 835, 698 cm^{-1}; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{16}Cl_2O_2Na$ $[M + Na]^+$ 309.0420; found 309.0413; **Optical rotation** $[\alpha]_D^{24}$ (c = 1.2, $CHCl_3$): −0.1; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 203 nm, t_R (major) 7.2 min, t_R (minor) 6.2 min.



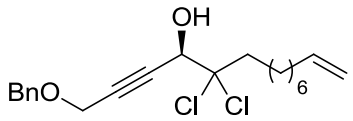
(+)-(*R*)-1-(Benzyloxy)-5,5-dichlorononon-2-yn-4-ol (3b). The product was isolated by flash chromatography (hexane/EtOAc 9:1) to afford the title compound as pale yellow oil (215 mg, 0.682 mmol, 97%).

TLC: R_f = 0.27 (hexane/EtOAc 7:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$,): δ 7.40 – 7.28 (m, 5H), 4.66 (bs, 1H), 4.63 (s, 2H), 4.25 (d, *J* = 1.7 Hz, 2H), 2.77 (s, 1H), 2.33 – 2.26 (m, 2H), 1.76 – 1.63 (m, 1H), 1.48 – 1.33 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 137.3, 128.6, 128.4, 128.1, 96.1, 83.7, 82.4, 71.8, 71.8, 57.2, 43.1, 26.9, 22.4, 14.0; **IR** (neat): 3385, 2958, 2873, 1455, 1353, 1068, 941, 741, 698 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{16}H_{20}Cl_2O_2Na$ $[M + Na]^+$ 337.0733; found 337.0735; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.71, $CHCl_3$): +2.2; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 204 nm, t_R (major) 6.3 min, t_R (minor) 5.7 min.



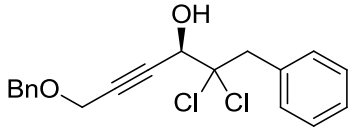
(–)-(*R*)-1-(Benzyloxy)-5,5-dichloro-6-methylhept-2-yn-4-ol (3c). The product was isolated by flash chromatography (cyclohexane/EtOAc 12:1) to afford the title compound as a colorless oil, which crystallized upon standing to colorless crystals suitable for X-ray crystallographic analysis (131 mg, 0.435 mmol, 62%). General procedure B was adapted to a scale of 1.1 mmol of the aldehyde to give the corresponding product **3c** in 59% yield and with the same enantiomeric excess.

TLC: R_f = 0.15 (cyclohexane/EtOAc 12:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 5H), 4.77 – 4.72 (m, 1H), 4.63 (s, 2H), 4.25 (d, *J* = 1.7 Hz, 2H), 2.71 – 2.60 (m, 2H), 1.18 (dd, *J* = 6.6, 1.9 Hz, 6H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 137.3, 128.6, 128.4, 128.1, 101.7, 83.5, 82.7, 71.8, 70.3, 57.3, 39.8, 18.2; **Mp**: 34–35 °C; **IR** (neat): 3384, 2976, 1455, 1354, 1061, 781, 697 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{15}H_{22}Cl_2NO_2$ $[M + NH_4]^+$ 318.1022; found 318.1019; **Optical rotation** $[\alpha]_D^{24}$ (c = 1.2, $CHCl_3$): –4.8; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 205 nm, t_R (major) 7.9 min, t_R (minor) 6.7 min.



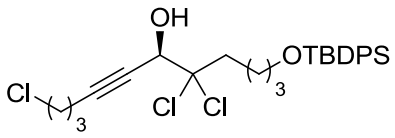
(+)-(*R*)-1-(Benzyloxy)-5,5-dichlorotetradec-13-en-2-yn-4-ol (3d). The product was isolated by flash chromatography (hexane/EtOAc 9:1) to afford the title product as yellow oil (148 mg, 0.386 mmol, 57%).

TLC: R_f = 0.32 (hexane/EtOAc 7:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$,): δ 7.37 – 7.30 (m, 5H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.00 (ddt, *J* = 17.1, 2.2, 1.6 Hz, 1H), 4.94 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.66 (dt, *J* = 8.6, 1.7 Hz, 1H), 4.63 (s, 2H), 4.25 (d, *J* = 1.7 Hz, 2H), 2.79 – 2.63 (m, 1H), 2.44 – 2.21 (m, 2H), 2.12 – 1.98 (m, 2H), 1.83 – 1.65 (m, 2H), 1.46 – 1.25 (m, 8H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 139.2, 137.3, 128.6, 128.4, 128.1, 114.4, 96.0, 83.7, 82.4, 71.84, 71.81, 57.2, 43.4, 33.9, 29.4, 29.2, 29.1, 29.0, 24.8; **IR** (neat): 3381, 2926, 2854, 1455, 1353, 1071, 1028, 995, 909, 736 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{21}H_{28}Cl_2O_2Na$ $[M + Na]^+$ 405.1359; found 405.1354; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.62, $CHCl_3$): +2.4; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 203 nm, t_R (major) 8.7 min, t_R (minor) 7.6 min.



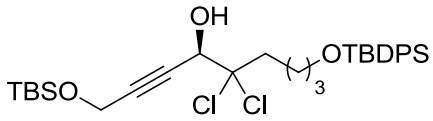
(+)-(*R*)-6-(Benzyloxy)-2,2-dichloro-1-phenylhex-4-yn-3-ol (3e). The product was isolated by flash chromatography (hexane/EtOAc 9:1) to afford the title product as yellow oil (166 mg, 0.475 mmol, 69%).

TLC: R_f = 0.29 (hexane/EtOAc 4:1; UV, $KMnO_4$); **^{1}H–NMR** (400 MHz, $CDCl_3$,): δ 7.48 – 7.40 (m, 2H), 7.38 – 7.30 (m, 8H), 4.65 (s, 2H), 4.57 (dt, *J* = 9.0, 1.7 Hz, 1H), 4.27 (d, *J* = 1.7 Hz, 2H), 3.75 – 3.51 (m, 2H), 2.86 – 2.73 (m, 1H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 137.3, 133.8, 131.5, 128.6, 128.38, 128.35, 128.1, 128.0, 94.3, 84.0, 82.6, 71.8, 70.3, 57.2, 49.0; **IR** (neat): 3372, 3032, 1496, 1456, 1070, 746, 698, 595 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{19}H_{18}Cl_2O_2Na$ $[M + Na]^+$ 371.0576; found 371.0577; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.61, $CHCl_3$): +19.9; **SFC**: Daicel Chiralpak AS-H, 3% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 204 nm, t_R (major) 23.8 min, t_R (minor) 22.9 min.



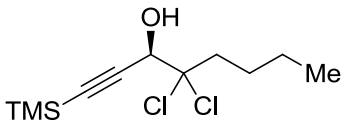
(+)-(*R*)-10-((*Tert*-butyldiphenylsilyl)oxy)-1,6,6-trichlorodec-3-yn-5-ol (3f). The product was isolated by flash chromatography (hexane/EtOAc 12:1) to afford the title product as yellow oil (207 mg, 0.394 mmol, 58%).

TLC: R_f = 0.28 (hexane/EtOAc 10:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$,): δ 7.74 – 7.56 (m, 4H), 7.46 – 7.33 (m, 6H), 4.56 (dt, *J* = 8.4, 2.0 Hz, 1H), 3.70 (t, *J* = 6.2 Hz, 2H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.59 (d, *J* = 8.4 Hz, 1H), 2.46 (td, *J* = 6.8, 1.9 Hz, 2H), 2.34 – 2.23 (m, 2H), 2.03 – 1.88 (m, 2H), 1.83 – 1.76 (m, 2H), 1.72 – 1.58 (m, 2H), 1.06 (s, 9H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 135.6, 133.9, 129.6, 127.6, 96.4, 86.4, 71.7, 63.4, 43.5, 43.0, 31.9, 30.9, 26.9, 21.3, 19.2, 16.1; **IR** (neat): 3420, 2932, 1720, 1389, 1243, 1106, 739, 701 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{27}H_{36}Cl_3O_2Si$ $[M + H]^+$ 525.1545; found 525.1542; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.51, $CHCl_3$): +2.4; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 $mL \cdot min^{-1}$, 25 °C, detection 206 nm, t_R (major) 25.4 min, t_R (minor) 21.6 min.



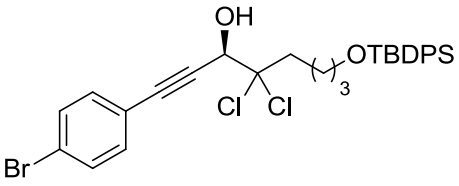
(+)-(*R*)-9,9-Dichloro-2,2,3,3,16,16-hexamethyl-15,15-diphenyl-4,14-dioxa-3,15-disilaheptadec-6-yn-8-ol (3g). The product was isolated by flash chromatography (hexane/EtOAc 12:1) to afford the title product as yellow oil (242 mg, 0.407 mmol, 58%).

TLC: R_f = 0.22 (hexane/EtOAc 20:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$,): δ 7.71 – 7.63 (m, 4H), 7.43 – 7.36 (m, 6H), 4.61 (d, *J* = 8.4 Hz, 1H), 4.38 (d, *J* = 1.7 Hz, 2H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.63 (d, *J* = 8.5 Hz, 1H), 2.33 – 2.22 (m, 2H), 1.86 – 1.74 (m, 2H), 1.68 – 1.59 (m, 2H), 1.06 (s, 9H), 0.91 (s, 9H), 0.12 (s, 6H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 135.7, 134.1, 129.7, 127.8, 96.0, 86.4, 80.3, 71.9, 63.5, 51.8, 43.1, 32.0, 29.9, 27.0, 25.9, 21.4, 19.4, –5.0; **IR** (neat): 2930, 1428, 1362, 1255, 1091, 835, 779, 701 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{31}H_{47}Cl_2O_3Si_2$ $[M + H]^+$ 593.2435; found 593.2431; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.61, $CHCl_3$): +1.9; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 mL min^{-1}, 25 °C, detection 212 nm, t_R (major) 11.8 min, t_R (minor) 10.8 min.



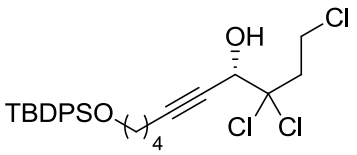
(+)-(*R*)-4,4-Dichloro-1-(trimethylsilyl)oct-1-yn-3-ol (3h). The reaction was done in 0.350 mmol scale. The product was isolated by flash chromatography (hexane/EtOAc 25:1) to afford the title product as pale oil (74.5 mg, 0.279 mmol, 80%).

TLC: R_f = 0.35 (hexane/EtOAc 20:1; $KMnO_4$); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 4.58 (d, J = 8.1 Hz, 1H), 2.75 – 2.64 (m, 1H), 2.35 – 2.20 (m, 2H), 1.68 (m, 2H), 1.48 – 1.33 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H), 0.19 (s, 9H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 100.59, 96.04, 93.16, 72.07, 43.17, 26.89, 22.38, 13.98, –0.27; **IR** (neat): 3405, 2960, 2183, 1468, 1381, 1251, 1054, 952, 933 cm^{-1}; **HRMS** (EI): *m/z* calculated for $C_{11}H_{20}Cl_2OSi$ 266.0660; found 266.0657; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.90, $CHCl_3$): +2.7.



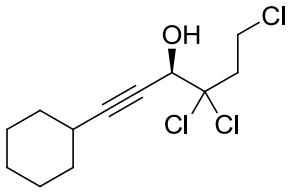
(+)-(*R*)-1-(4-Bromophenyl)-8-((*tert*-butyldiphenylsilyl)oxy)-4,4-dichlorooct-1-yn-3-ol (3i). The product was isolated by flash chromatography (hexane/EtOAc 15:1) to afford the title product as yellow oil (228 mg, 0.377 mmol, 56%).

TLC: R_f = 0.23 (hexane/EtOAc 15:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$,): δ 7.73 – 7.61 (m, 4H), 7.50 – 7.29 (m, 10H), 4.79 (d, J = 8.6 Hz, 1H), 3.71 (t, J = 6.2 Hz, 2H), 2.76 (d, J = 8.6 Hz, 1H), 2.39 – 2.30 (m, 2H), 1.91 – 1.78 (m, 2H), 1.71 – 1.61 (m, 2H), 1.06 (s, 9H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 135.7, 134.0, 133.5, 131.8, 129.7, 127.8, 123.6, 120.8, 96.1, 86.3, 85.9, 72.3, 63.5, 43.2, 32.0, 27.0, 21.5, 19.4; **IR** (neat): 3071, 2931, 1486, 1427, 1112, 1070, 937, 822, 740 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{30}H_{33}BrCl_2O_2SiNa$ $[M + Na]^+$ 625.0702; found 625.0692; **Optical rotation** $[\alpha]_D^{24}$ (c = 1.13, $CHCl_3$): +1.8; **SFC**: Daicel Chiralcell OJ-H, 10% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 208 nm, t_R (major) 40.3 min, t_R (minor) 37.3 min.



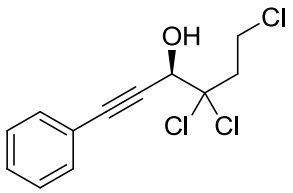
(–)-(*S*)-10-((*Tert*-butyldiphenylsilyl) oxy)-1,3,3-trichlorodec-5-yn-4-ol (3j). The reaction was conducted on a 0.291 mmol scale. The product was isolated by flash chromatography (pentane/Et_2O 14:1 to 5:1 gradient) to afford the titled compound as colorless oil (87.5 mg, 0.171 mmol, 59%).

TLC: *Rf* = 0.31 (pentane/Et_2O 5:1, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 7.69 – 7.63 (m, 4H), 7.46 – 7.34 (m, 6H), 4.59 (dt, *J* = 7.8, 1.9, 1H), 3.90 – 3.82 (m, 2H), 3.71 – 3.65 (m, 2H), 2.84 – 2.68 (m, 2H), 2.61 (d, *J* = 7.9, 1H), 2.31 – 2.23 (m, 2H), 1.72 – 1.60 (m, 4H), 1.05 (s, 9H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 135.6, 133.9, 129.6, 127.6, 92.9, 89.2, 75.4, 72.1, 63.2, 45.4, 39.2, 31.6, 26.9, 24.7, 19.2, 18.4; **IR** (thin film): 3433, 3069, 2932, 2858, 1472, 1428, 1389, 1256, 1112, 1024, 823, 702 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{26}H_{34}Cl_3O_2Si^+$ $[M+H]^+$, 511.1388; found 511.1371; **Optical rotation** $[\alpha]_D^{24}$ (c = 1.0, $CHCl_3$): –0.9.



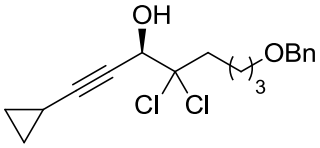
(–)-(*R*)-4,4,6-Trichloro-1-cyclohexylhex-1-yn-3-ol (3k). The reaction was done in 0.518 mmol scale. The product was isolated by flash chromatography (hexane/EtOAc 15:1) to afford the title product as slightly yellowish oil (107 mg, 0.381 mmol, 74%).

TLC: R_f = 0.21 (hexane/EtOAc 9:1, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 4.62 (dd, *J* = 7.8, 1.8, 1H), 3.90 – 3.84 (m, 2H), 2.84 – 2.71 (m, 2H), 2.66 (d, *J* = 7.8, 1H), 2.52 – 2.42 (m, 1H), 1.84 – 1.64 (m, 4H), 1.55 – 1.24 (m, 6H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 93.2, 93.0, 75.2, 72.0, 45.5, 39.3, 32.1, 28.8, 25.8, 24.5; **IR** (thin film): 3394, 2932, 2855, 1450, 1257, 1168, 1024, 717 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{12}H_{21}Cl_3NO^+$ $[M+NH_4]^+$, 300.0683; found 300.0678. **Optical rotation** $[\alpha]_D^{23}$ (c = 1.00, $CHCl_3$): –0.6.



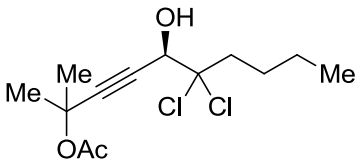
(+)-(*R*)-4,4,6-Trichloro-1-phenylhex-1-yn-3-ol (3l). The reaction was done in 0.604 mmol scale. The product was isolated by flash chromatography (pentane/Et_2O 9:1) to afford the titled compound as slightly yellowish oil (117 mg, 0.422 mmol, 70%).

TLC: *Rf* = 0.18 (pentane/Et_2O 9:1, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 7.53 – 7.46 (m, 2H), 7.41 – 7.30 (m, 3H), 4.87 (d, *J* = 7.5, 1H), 3.96 – 3.87 (m, 2H), 2.93 – 2.78 (m, 3H); **^{13}C-NMR** (101 MHz, $CDCl_3$): δ 131.9, 129.3, 128.4, 121.3, 92.6, 87.9, 83.7, 72.4, 45.5, 39.2; **IR** (thin film): 3404, 1490, 1444, 1349, 1258, 1070, 1026, 813, 699 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{12}H_{11}Cl_3NaO^+$ $[M+Na]^+$, 298.9768; found 298.9762; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.61, $CHCl_3$): +4.3.



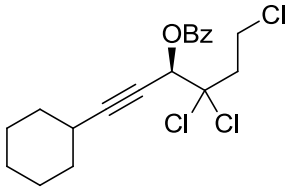
(+)-(*R*)-8-(Benzyloxy)-4,4-dichloro-1-cyclopropyloct-1-yn-3-ol (3m). The product was isolated by flash chromatography (hexane/EtOAc 9:1) to afford the title product as pale yellow oil (216 mg, 0.635 mmol, 91%).

TLC: R_f = 0.36 (hexane/EtOAc 6:1; UV, CAM); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 5H), 4.54 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.52 (s, 2H), 3.51 (t, *J* = 6.3 Hz, 2H), 2.58 (d, *J* = 8.0 Hz, 1H), 2.33 – 2.24 (m, 2H), 1.87 – 1.75 (m, 2H), 1.70 (m, 2H), 1.33 – 1.24 (m, 1H), 0.84 – 0.70 (m, 4H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 138.61, 128.54, 127.80, 127.72, 96.52, 91.74, 73.16, 72.03, 70.97, 70.04, 43.08, 29.37, 21.83, 8.52, –0.42; **IR** (thin film): 3372, 2864, 1454, 1092, 1065, 933, 814; **HRMS** (ESI): *m/z* calculated for $C_{15}H_{17}Cl_2O_2^+$ $[M+H]^+$, 299.0600; found 299.0603; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.8, $CHCl_3$): +5.9; **SFC**: Daicel Chiralpak AS-H, 5% MeOH at 100 bar, flow rate 2.0 mL·min^{-1}, 25 °C, detection 204 nm, t_R (major) 10.9 min, t_R (minor) 9.5 min.



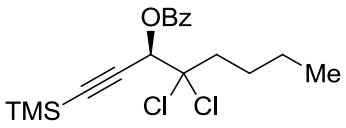
(+)-(*R*)-6,6-Dichloro-5-hydroxy-2-methyldec-3-yn-2-yl acetate (3n). The reaction was done in 0.350 mmol scale. The product was isolated by flash chromatography (hexane/EtOAc 25:1) to afford the title product as pale oil (73.4 mg, 0.249 mmol, 71%).

TLC: R_f = 0.3 (hexane/EtOAc 20:1; $KMnO_4$); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 4.61 (d, *J* = 8.1 Hz, 1H), 2.93 – 2.64 (m, 1H), 2.35 – 2.24 (m, 2H), 2.01 (s, 3H), 1.66 (m, 8H), 1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); **^{13}C–NMR** (101 MHz, $CDCl_3$): δ 169.46, 96.41, 88.57, 80.12, 71.78, 71.70, 43.28, 28.90, 28.88, 27.02, 22.49, 22.06, 14.10; **IR** (neat): 3423, 2960, 1744, 1723, 1366, 1241, 1135, 1044, 1016, 954 cm^{-1}; **HRMS** (ESI): *m/z* calculated for $C_{13}H_{20}Cl_2NaO_3$ $[M+Na]^+$ 317.0682; found 317.0684; **Optical rotation** $[\alpha]_D^{24}$ (c = 0.89, $CHCl_3$): +4.6.



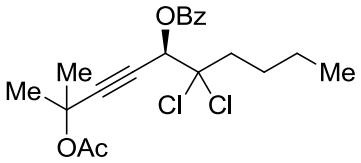
(*R*)-4,4,6-Trichloro-1-cyclohexylhex-1-yn-3-yl benzoate (BzO-3k). The product was purified by column chromatography (pentane/Et_2O 49:1) to afford benzoate as colorless oil (20 mg, 41 μmol, 62%).

TLC: *Rf* = 0.27 (pentane/Et_2O 40:1, UV, CAM); **^{1}H–NMR** (300 MHz, $CDCl_3$): δ 8.14 – 8.06 (m, 2H), 7.66 – 7.57 (m, 1H), 7.54 – 7.44 (m, 2H), 6.05 (dd, *J* = 1.8, 0.5, 1H), 3.98 – 3.88 (m, 2H), 2.91 – 2.82 (m, 2H), 2.53 – 2.41 (m, 1H), 1.84 – 1.60 (m, 4H), 1.55 – 1.21 (m, 6H); **SFC**: Daicel Chiralcel OJ-H, 100% CO_2 at 100 bar, flow rate 3 $mL \cdot min^{-1}$, 25 °C, detection 195 nm, t_R (major) = 7.9 min, t_R (minor) = 7.0 min.



(*R*)-4,4-Dichloro-1-(trimethylsilyl)oct-1-yn-3-yl benzoate (BzO-3h). The product was purified by column chromatography (hexane/EtOAc 20:1) to afford benzoate as pale yellow oil (19.5 mg, 52.1 μmol, 56%).

TLC: *Rf* = 0.37 (hexane/EtOAc 40:1, UV, $KMnO_4$); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 8.20 – 7.97 (m, 2H), 7.71 – 7.57 (m, 1H), 7.54 – 7.40 (m, 2H), 6.04 (s, 1H), 2.62 – 2.24 (m, 2H), 1.83 – 1.65 (m, 2H), 1.49 – 1.34 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.19 (s, 9H); **SFC**: Daicel Chiralpak IA, 0.5% MeOH at 100 bar, flow rate 2 mL·min^{-1}, 25 °C, detection 216 nm, t_R (major) = 5.2 min, t_R (minor) = 5.7 min.



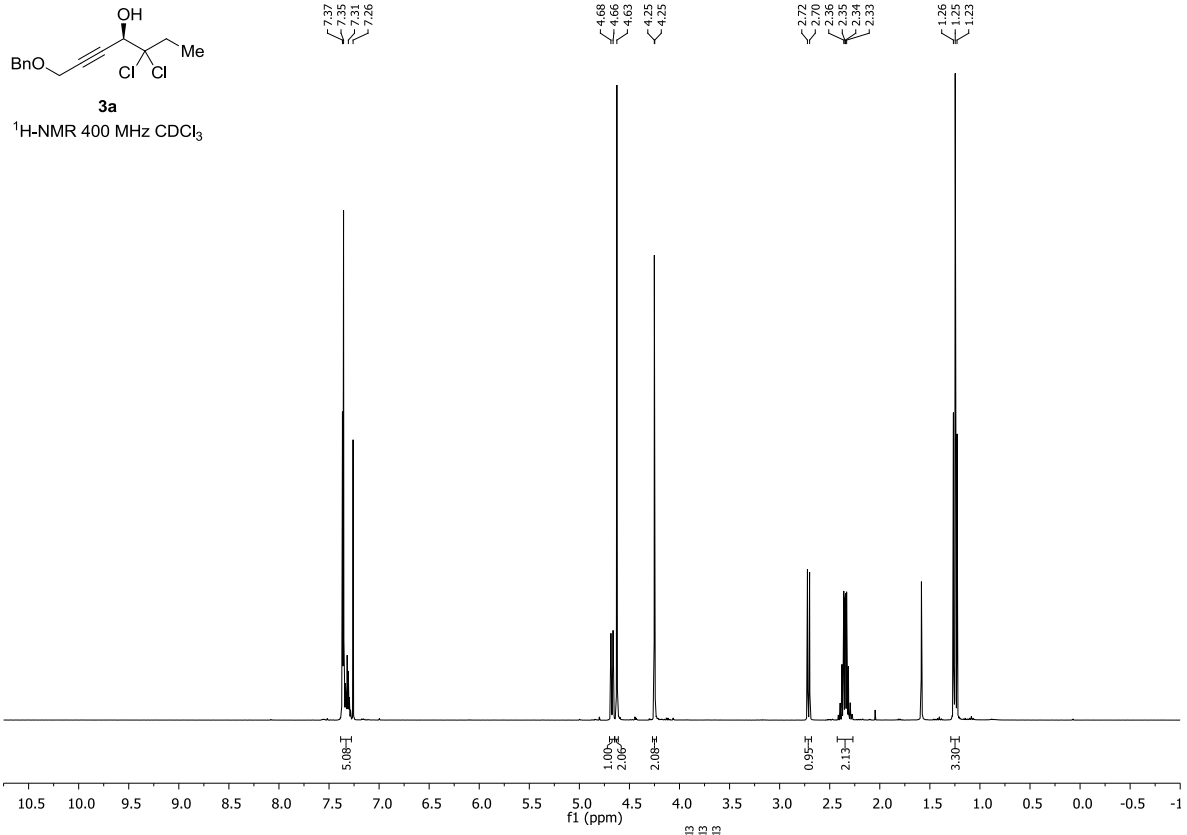
(*R*)-2-Acetoxy-6,6-dichloro-2-methyldec-3-yn-5-yl benzoate (BzO-3n). The product was purified by column chromatography (hexanes/EtOAc 49:1) to afford benzoate as colorless oil (15 mg, 38 μmol, 63%).

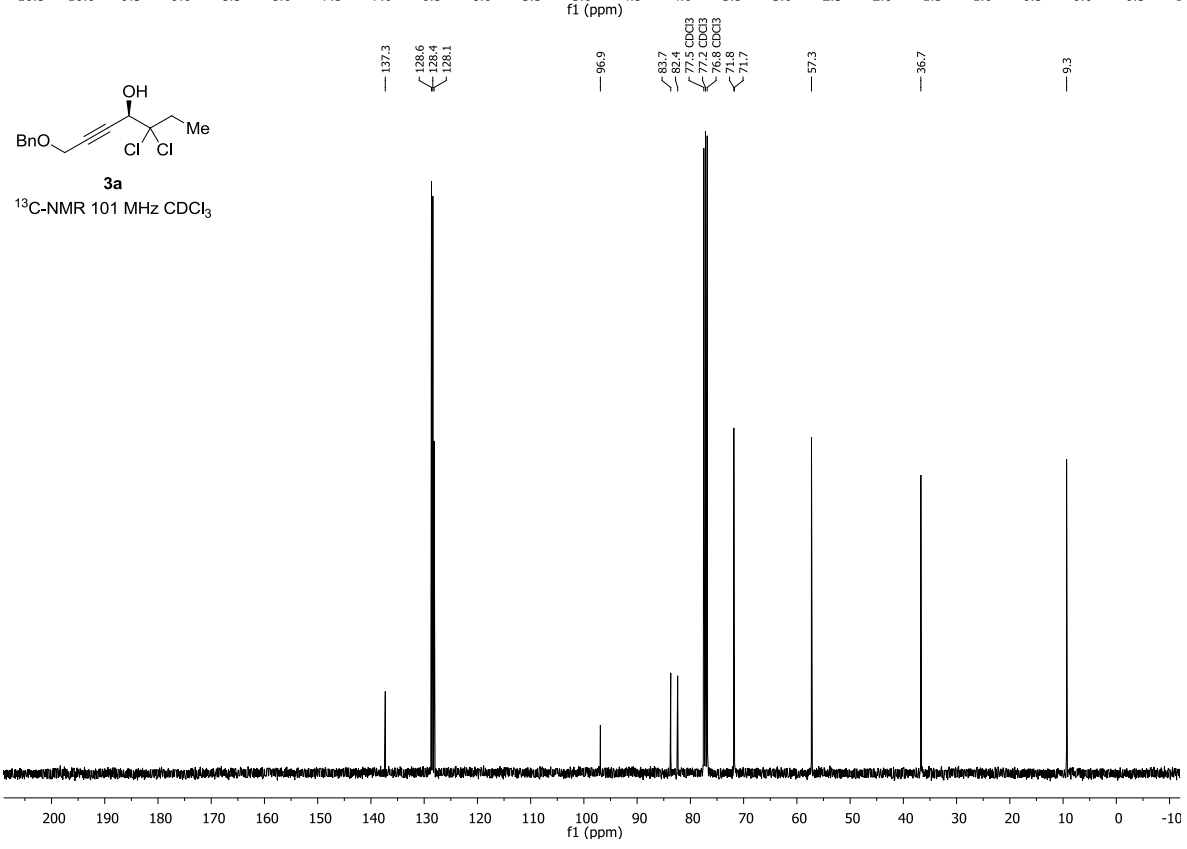
TLC: *Rf* = 0.38 (hexane/EtOAc 15:1, UV, KMnO4); **^{1}H–NMR** (400 MHz, $CDCl_3$): δ 8.17 – 8.04 (m, 2H), 7.67 – 7.54 (m, 1H), 7.54 – 7.42 (m, 2H), 6.06 (s, 1H), 2.48 – 2.31 (m, 2H), 2.00 (s, 3H), 1.79 – 1.69 (m, 2H), 1.65 (s, 3H), 1.64 (s, 3H) 1.51 – 1.36 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); **HPLC**: Dialcel Chiralpak IC-3, 99% hexane, 1% *i*PrOH, flow rate 1 mL·min^{-1}, 25 ºC, detection 230nm, t_R (major) = 6.83 min, t_R (minor) = 14.85 min.

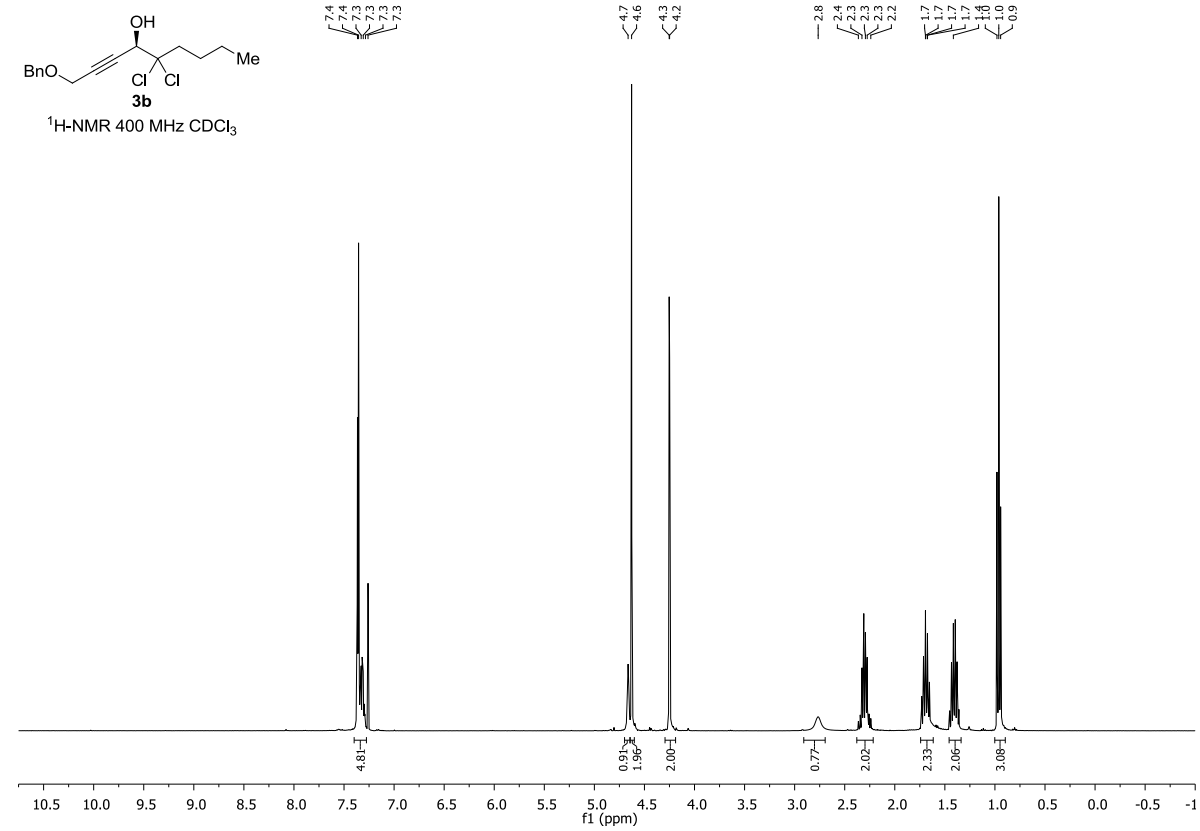
Example for a Racemic Alkyne Addition to *α,α*-Dichlorinated Aldehydes. In the glovebox, a 5 mL round bottom flask was charged with $Zn(OTf)_2$ (140 mg, 0.385 mmol, 1.10 eq), (+)-*N*-methylephedrine (37.5 mg, 0.210 mmol, 0.600 eq) and (–)-*N*-methylephedrine (37.5 mg, 0.210 mmol, 0.600 eq). To the flask was added dry toluene (1.0 mL) and triethylamine (58 μL, 0.42 mmol, 1.2 eq). The resulting mixture was vigorously stirred at room temperature for 2.5 h before the corresponding alkyne (0.350 mmol, 1.20 eq) was added via syringe in one portion. After 50 min of stirring the corresponding aldehyde (0.350 mmol, 1.00 eq) was added in one

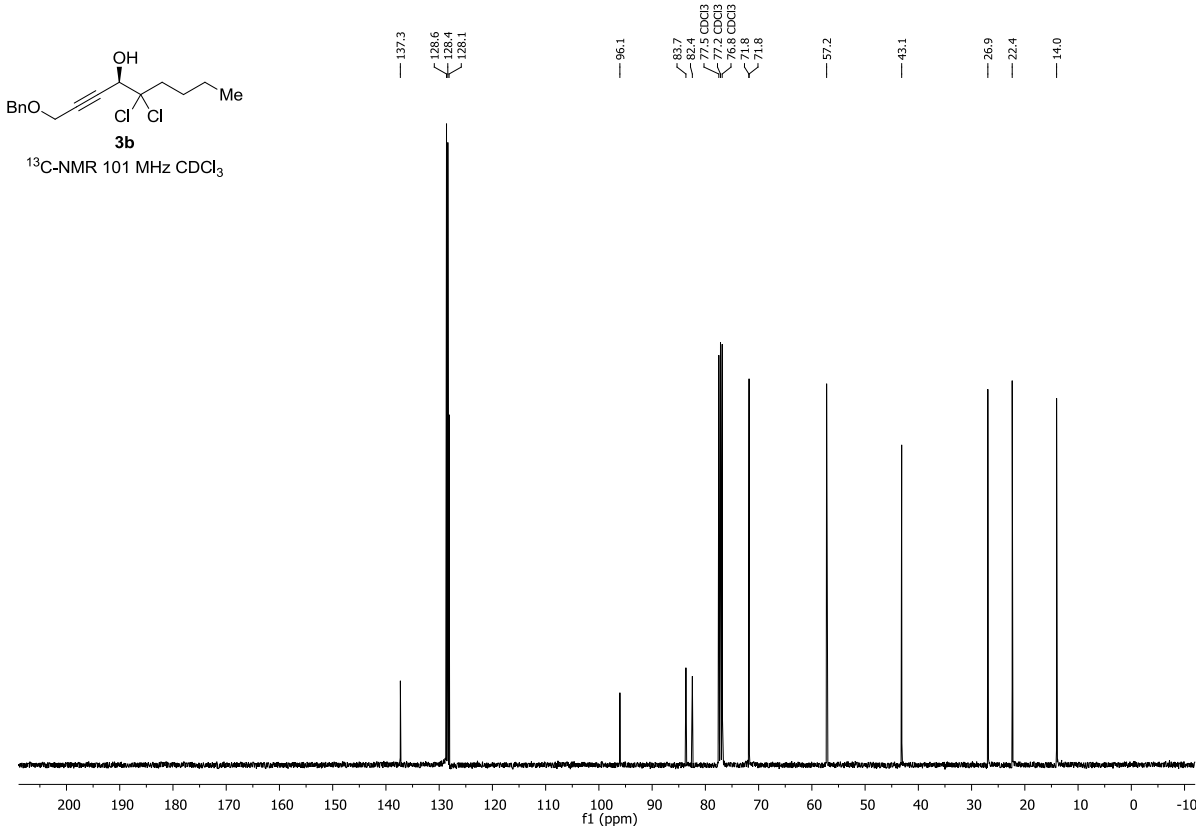
portion. After stirring for 12 h at room temperature the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (5 mL). The reaction mixture was poured into a separatory funnel containing diethyl ether (5 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous $MgSO_4$, concentrated in vacuo and purified by column chromatography.

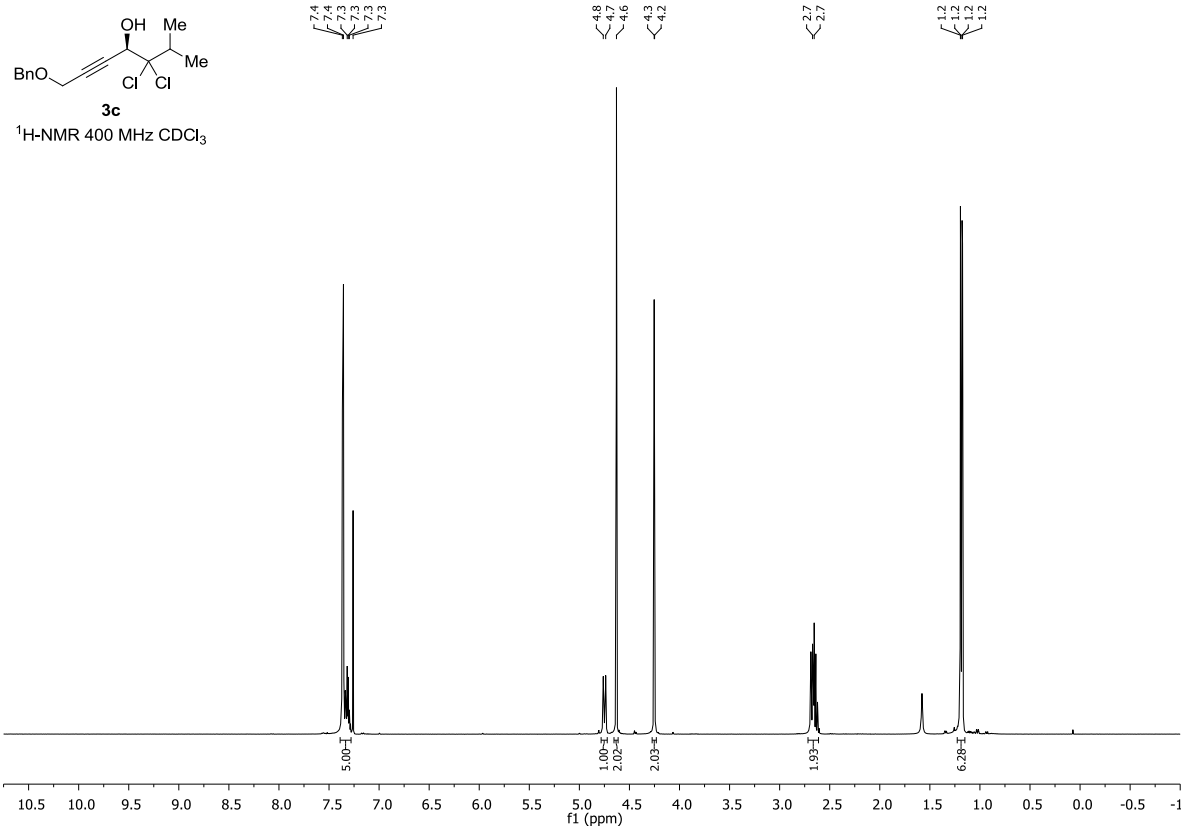
IV. NMR Spectra






OH
BnO
Cl
Cl
Me
3b
^{1}H-NMR 400 MHz $CDCl_3$
7.4
7.4
7.3
7.3
7.3
7.3
4.7
4.6
4.3
4.2
2.8
2.4
2.3
2.3
2.3
2.2
1.7
1.7
1.7
1.7
1.4
1.4
1.0
0.9
4.81
0.91
1.96
2.00
0.77
2.02
2.33
2.06
3.08
f1 (ppm)


OH
BnO
Cl
Cl
Me
3b
^{13}C-NMR 101 MHz $CDCl_3$
137.3
128.6
128.4
128.1
96.1
83.7
82.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
71.8
71.8
57.2
43.1
26.9
22.4
14.0
f1 (ppm)


OH
Me
Me
BnO
Cl
Cl
3c
1H-NMR 400 MHz CDCl3
7.4
7.4
7.3
7.3
7.3
7.3
4.8
4.7
4.6
4.3
4.2
2.7
2.7
1.2
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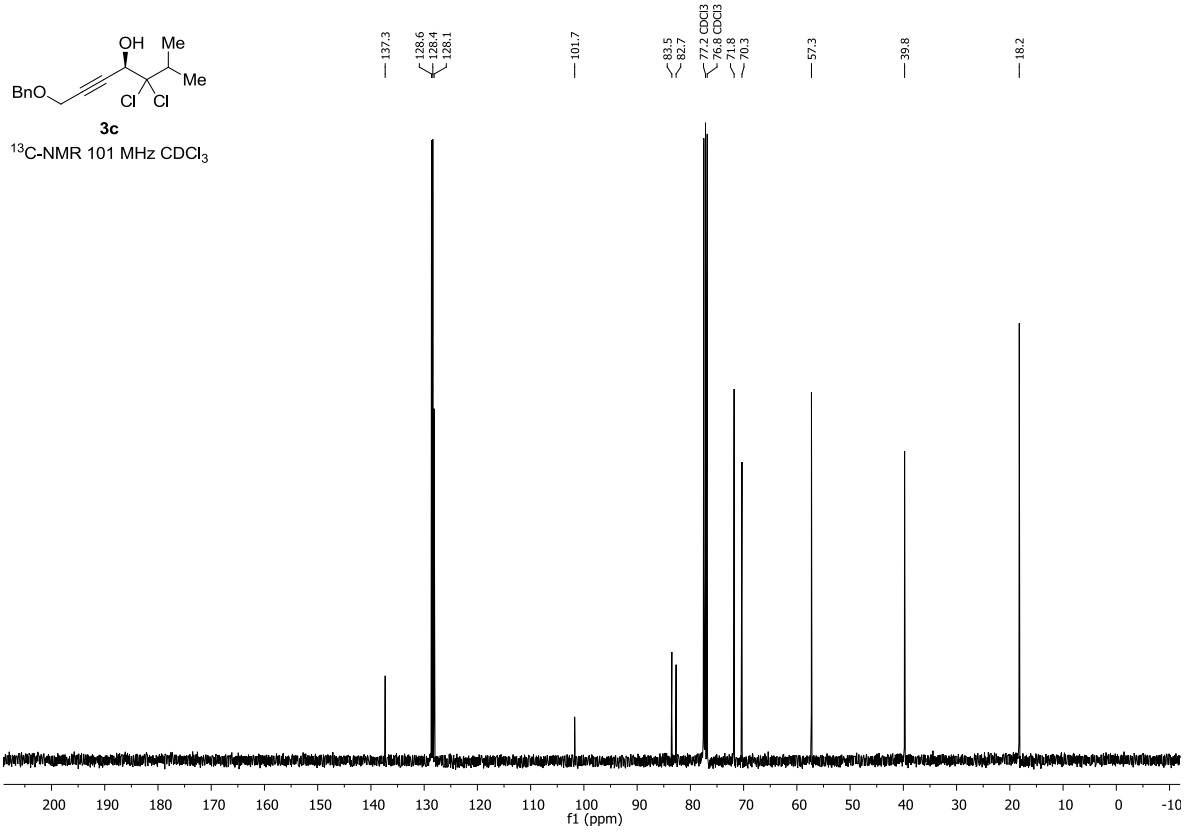
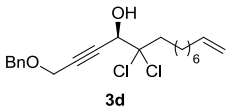
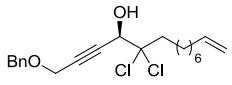
1.00
2.02
2.03
1.93
6.28
f1 (ppm)


OH
Me
Me
BnO
Cl
Cl
3c
13C-NMR 101 MHz CDCl3
137.3
128.6
128.4
128.1
101.7
83.5
82.7
77.2 CDCl3
76.8 CDCl3
71.8
70.3
57.3
39.8
18.2
f1 (ppm)



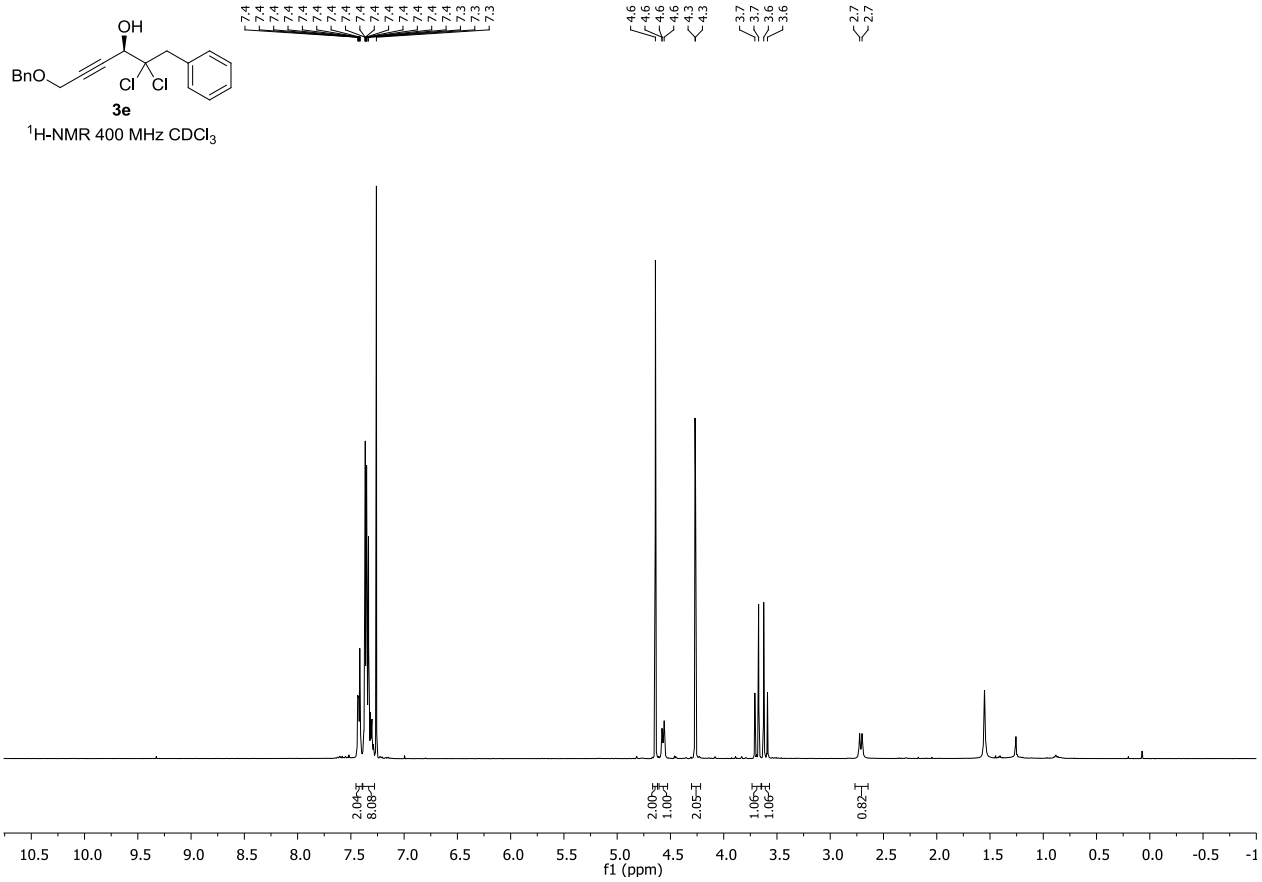
3d

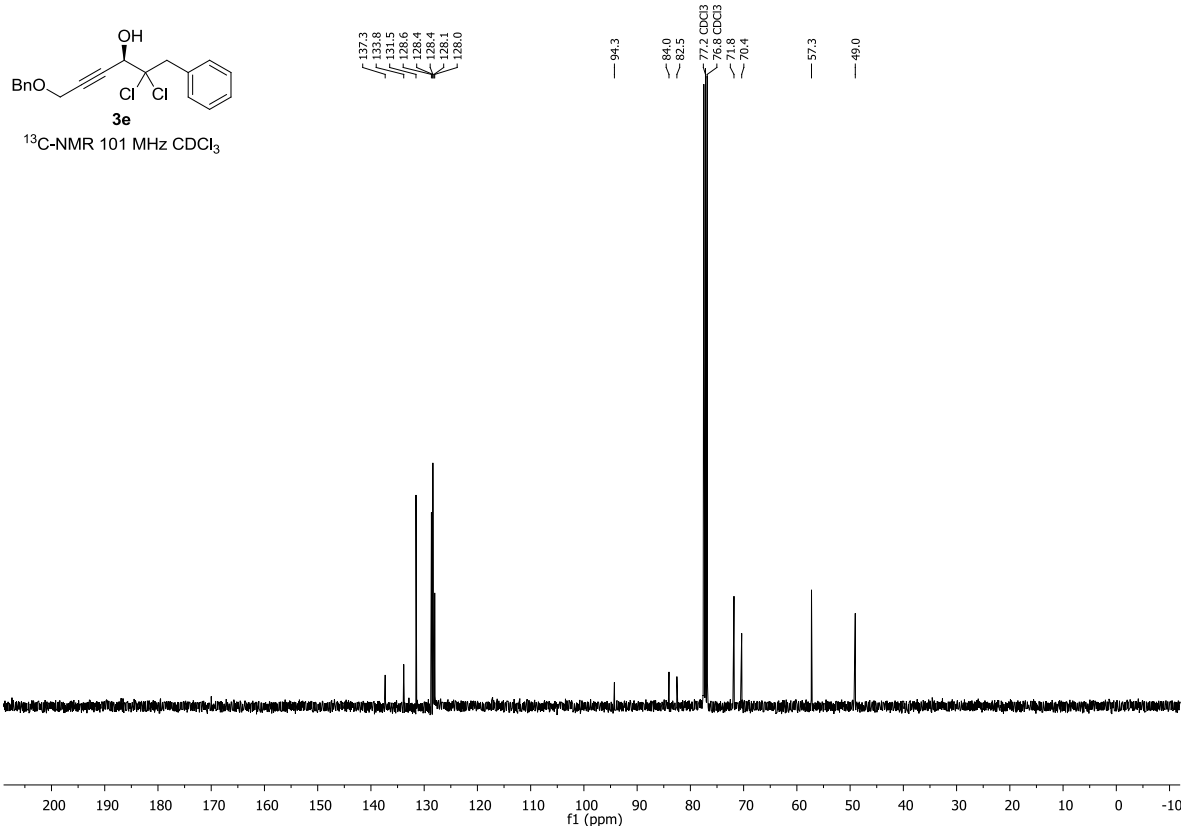
^{1}H-NMR 400 MHz $CDCl_3$

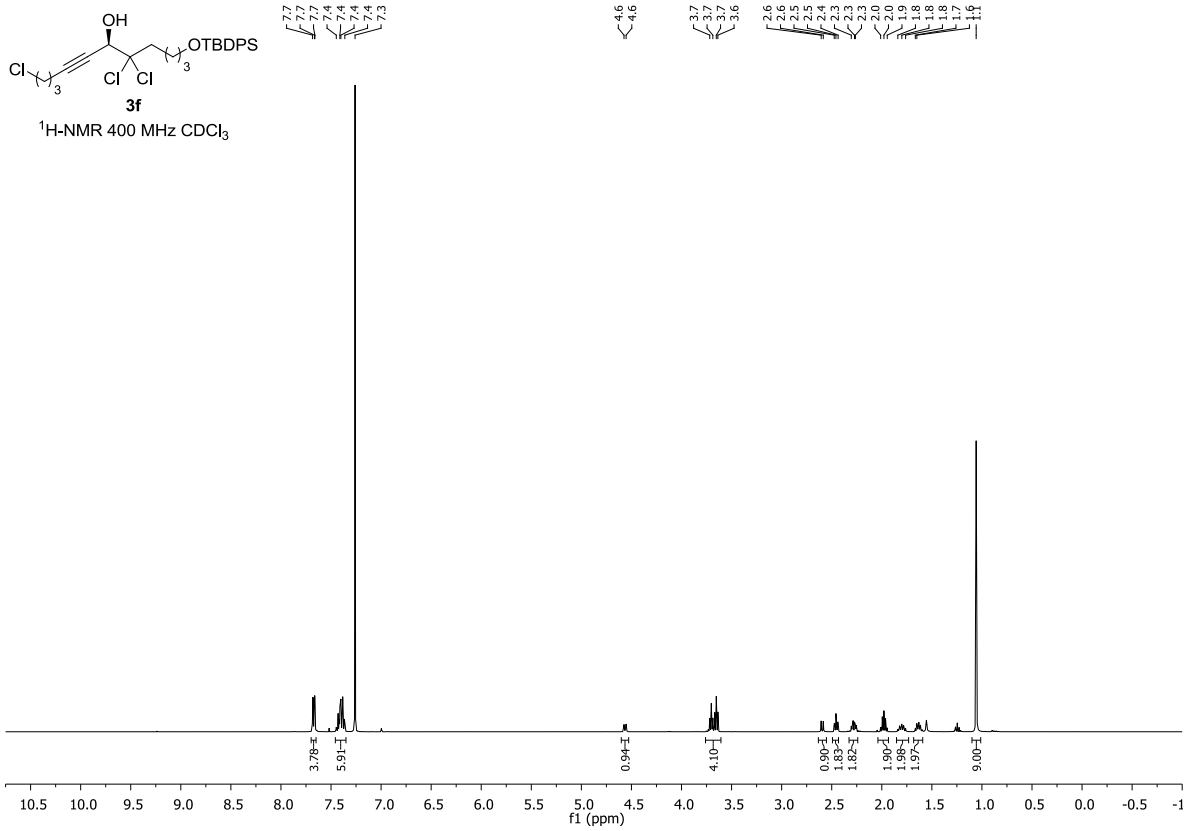


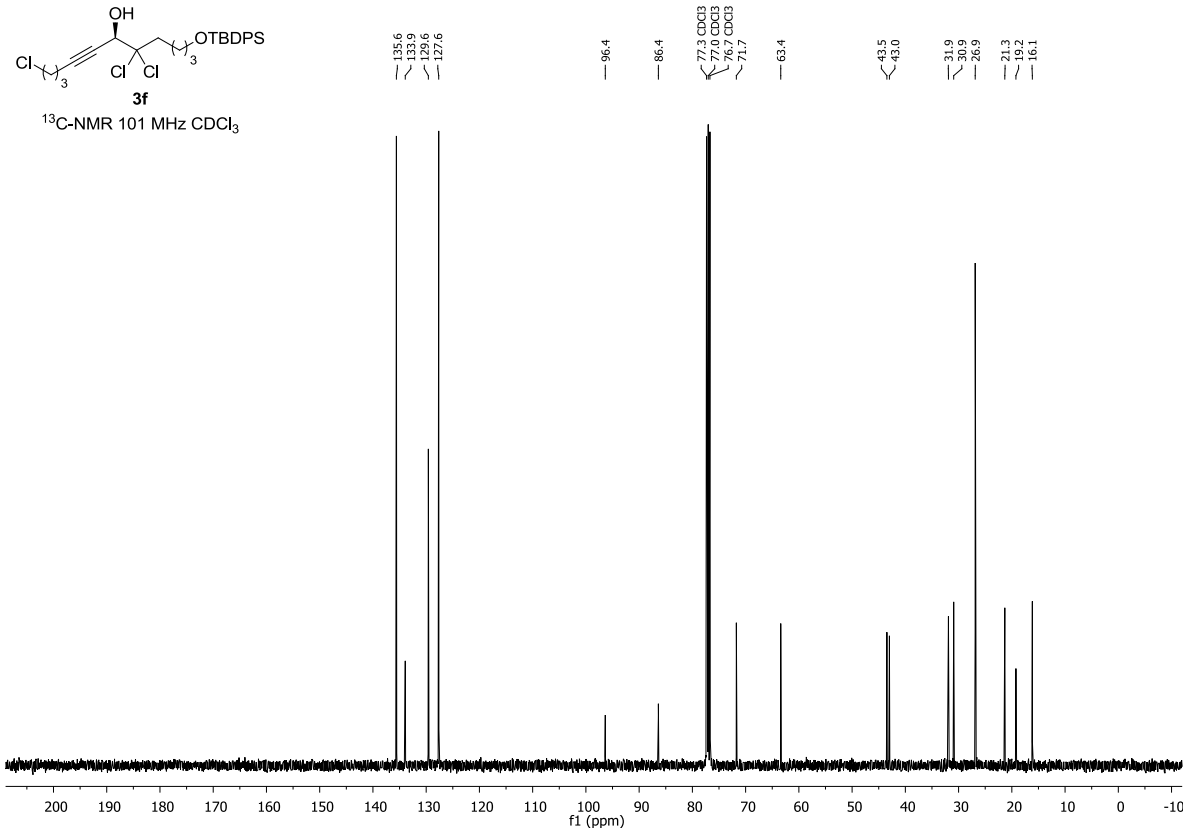
3d

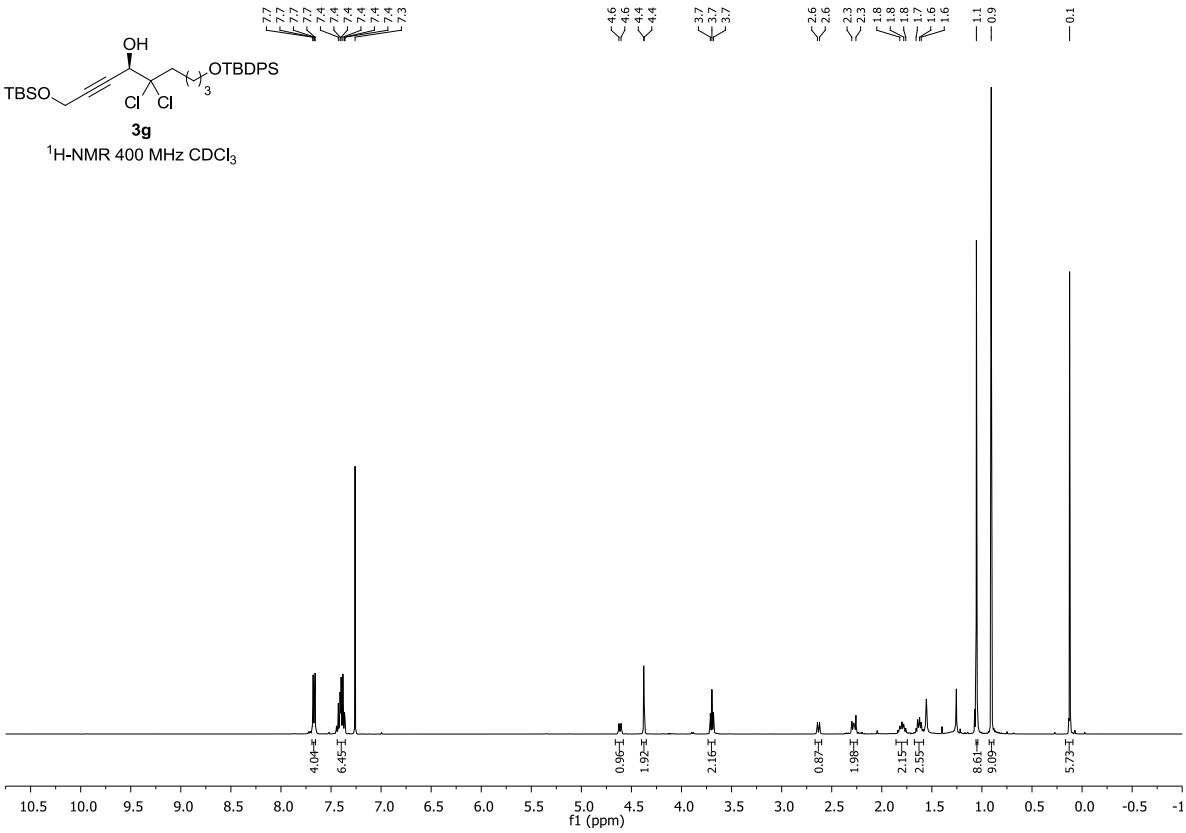
^{13}C-NMR 101 MHz $CDCl_3$

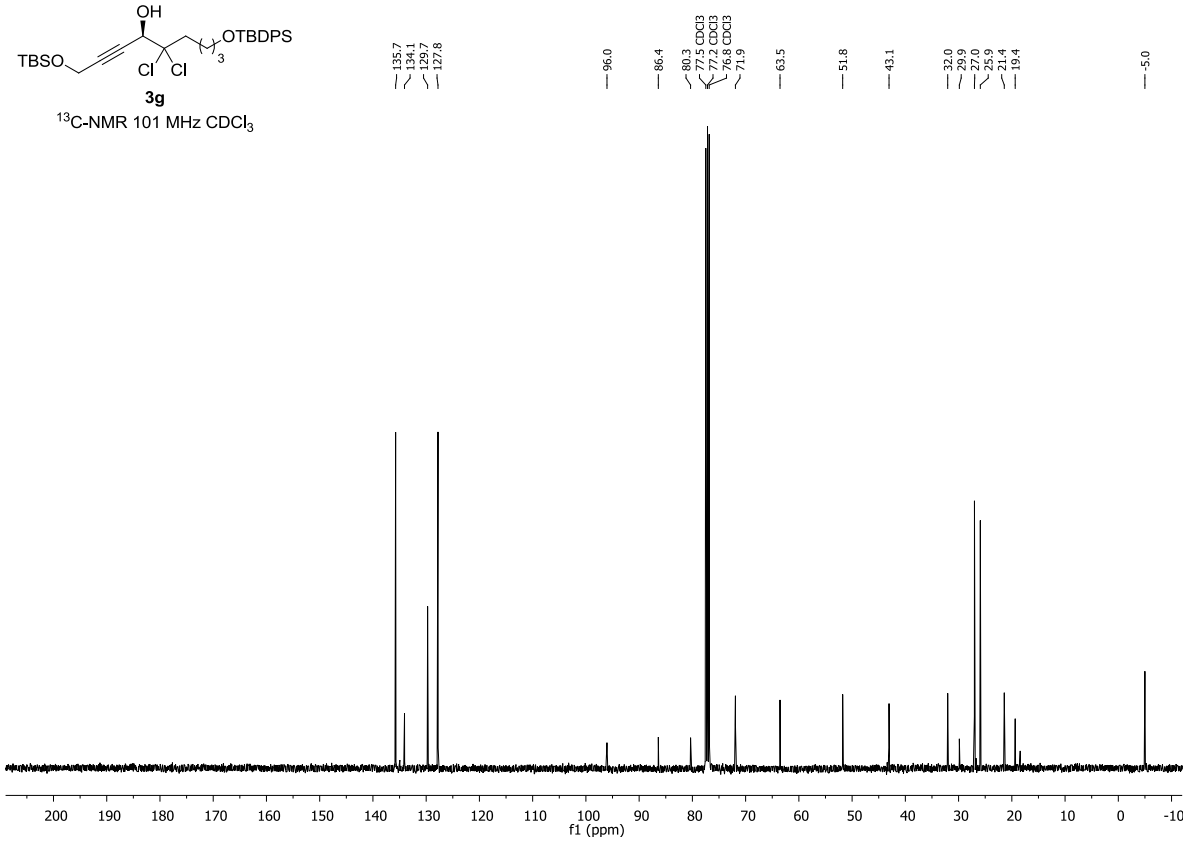

OH
BnO
Cl
Cl
3e
1H-NMR 400 MHz CDCl3
f1 (ppm)

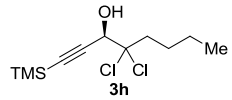

OH
BnO
Cl
Cl
3e
13C-NMR 101 MHz CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)


OH
OTBDPS
Cl
Cl Cl
3
3
3f
1H-NMR 400 MHz CDCl3
7.7
7.7
7.7
7.4
7.4
7.4
7.4
7.3
4.6
4.6
3.7
3.7
3.7
3.6
2.6
2.6
2.5
2.5
2.4
2.3
2.3
2.3
2.0
2.0
1.9
1.8
1.8
1.8
1.7
1.6
3.78
5.91
0.94
4.10
0.90
1.83
1.82
1.90
1.98
1.97
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


OH
OTBDPS
Cl
Cl Cl
3
3
3f
13C-NMR 101 MHz CDCl3
135.6
133.9
129.6
127.6
96.4
86.4
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
71.7
63.4
43.5
43.0
31.9
30.9
26.9
21.3
19.2
16.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

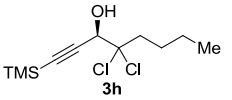

OH
TBSO
OTBDPS
3
Cl Cl
3g
1H-NMR 400 MHz CDCl3
f1 (ppm)


OH
TBSO
OTBDPS
3
Cl Cl
3g
13C-NMR 101 MHz CDCl3
f1 (ppm)



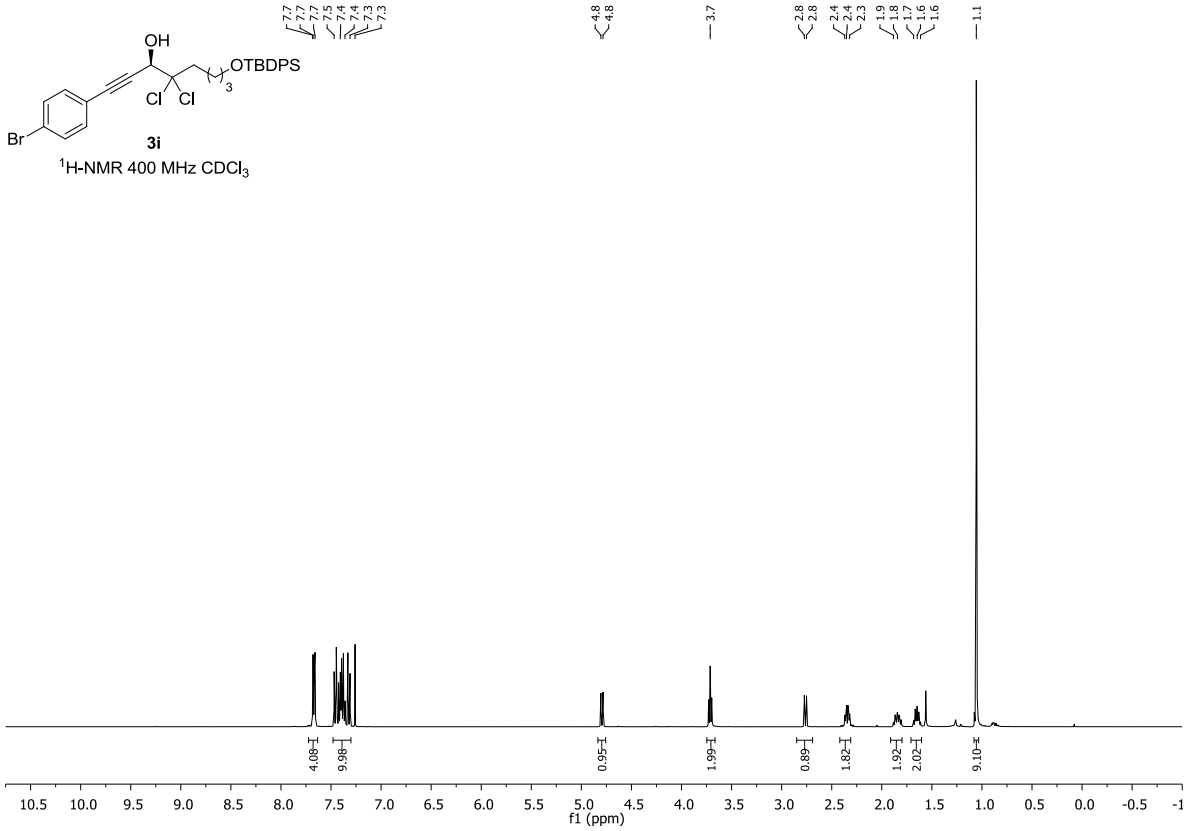
3h

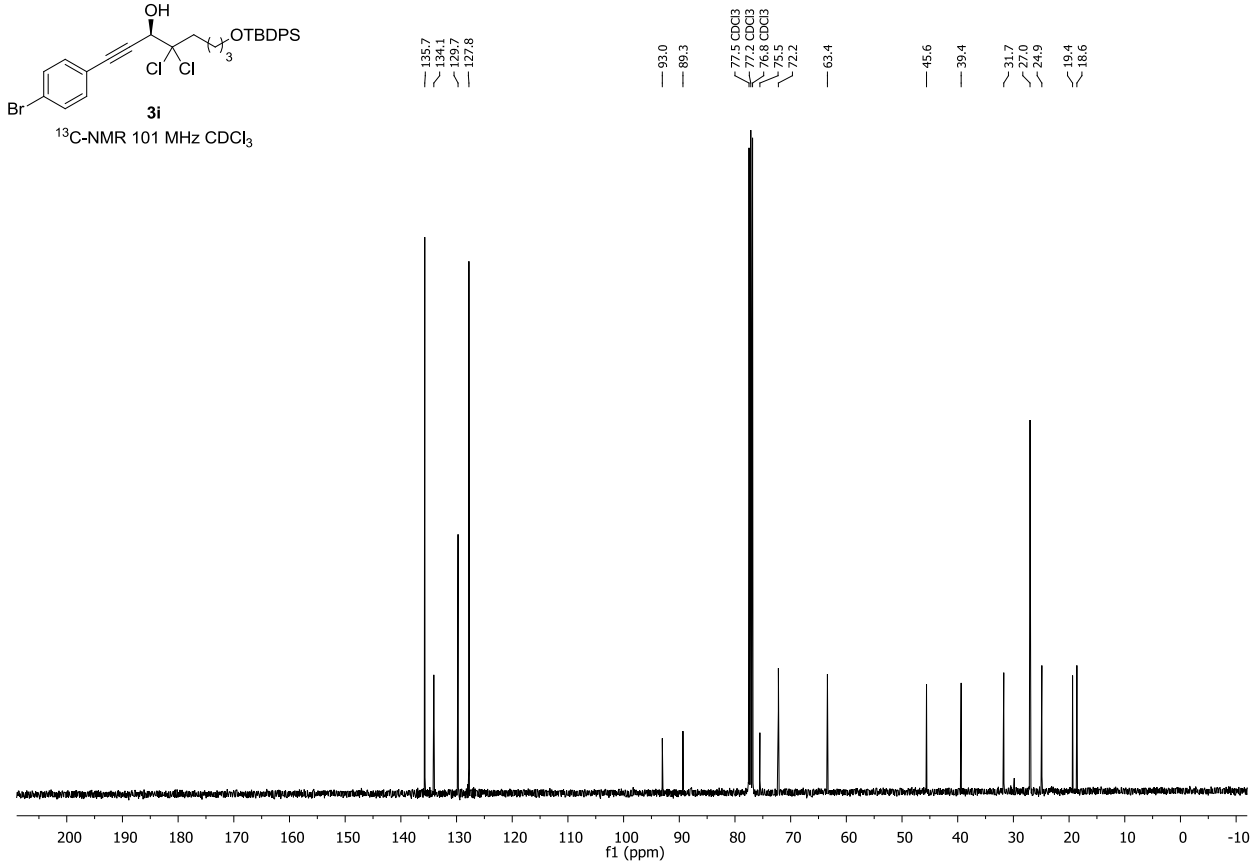
^{1}H-NMR 400 MHz $CDCl_3$

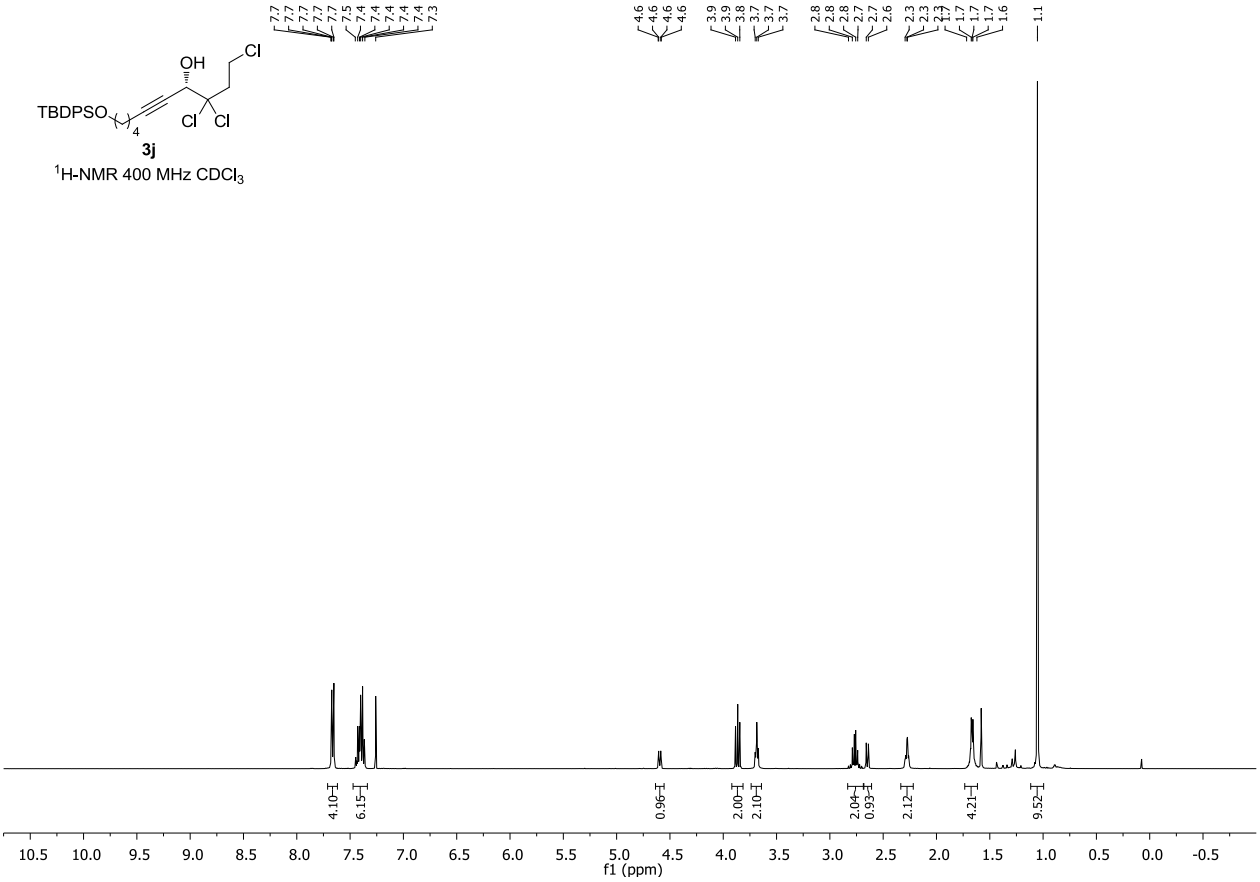


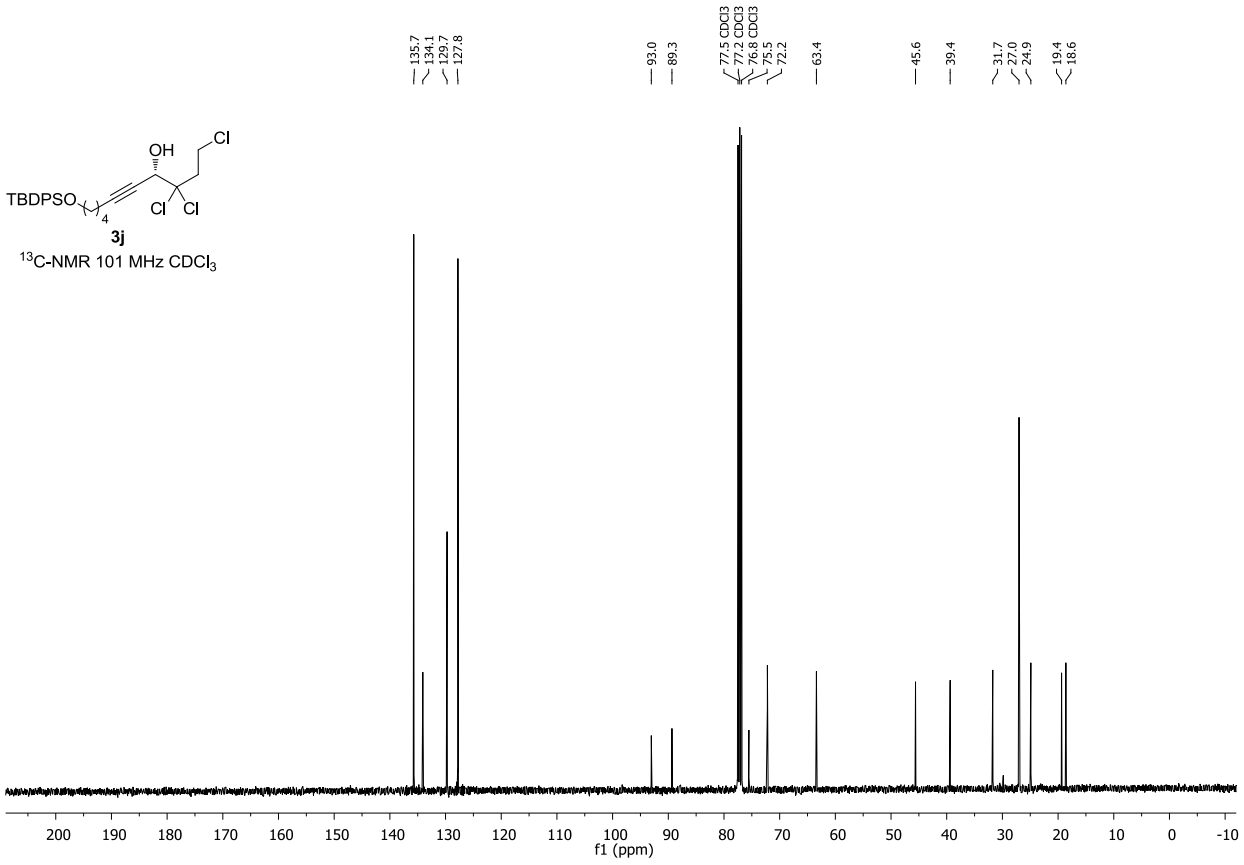
3h

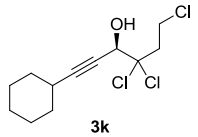
^{13}C-NMR 101 MHz $CDCl_3$


OH
OTBDPS
3
Cl
Cl
Br
3i
1H-NMR 400 MHz CDCl3
7.7
7.7
7.7
7.5
7.4
7.4
7.3
7.3
4.8
4.8
3.7
2.8
2.8
2.4
2.4
2.3
1.9
1.8
1.7
1.6
1.6
1.1
4.08
9.98
0.95
1.99
0.89
1.82
1.92
2.02
9.10
f1 (ppm)


OH
OTBDPS
3
Cl
Cl
Br
3i
13C-NMR 101 MHz CDCl3
135.7
134.1
129.7
127.8
93.0
89.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
75.5
72.2
63.4
45.6
39.4
31.7
27.0
24.9
19.4
18.6
f1 (ppm)

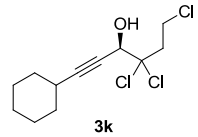

OH
Cl
TBDPSO
Cl
Cl
4
3j
1H-NMR 400 MHz CDCl3
7.7
7.7
7.7
7.7
7.7
7.5
7.4
7.4
7.4
7.4
7.4
7.3
4.6
4.6
4.6
4.6
3.9
3.9
3.8
3.7
3.7
3.7
2.8
2.8
2.8
2.7
2.7
2.6
2.3
2.3
2.3
2.3
1.7
1.7
1.7
1.6
1.1
4.10
6.15
0.96
2.00
2.10
2.04
0.93
2.12
4.21
9.52
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OH
Cl
TBDPSO
Cl
Cl
4
3j
13C-NMR 101 MHz CDCl3
135.7
134.1
129.7
127.8
93.0
89.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
75.5
72.2
63.4
45.6
39.4
31.7
27.0
24.9
19.4
18.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



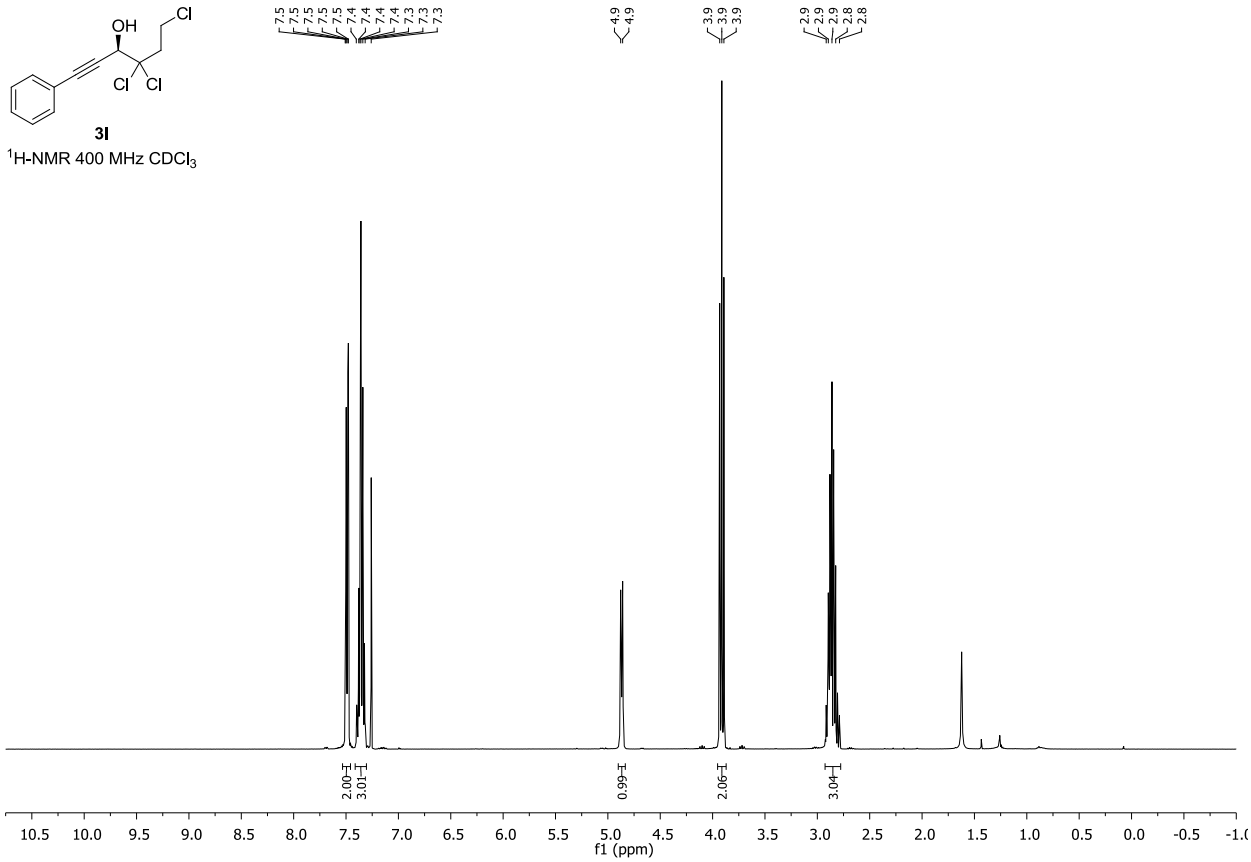
3k

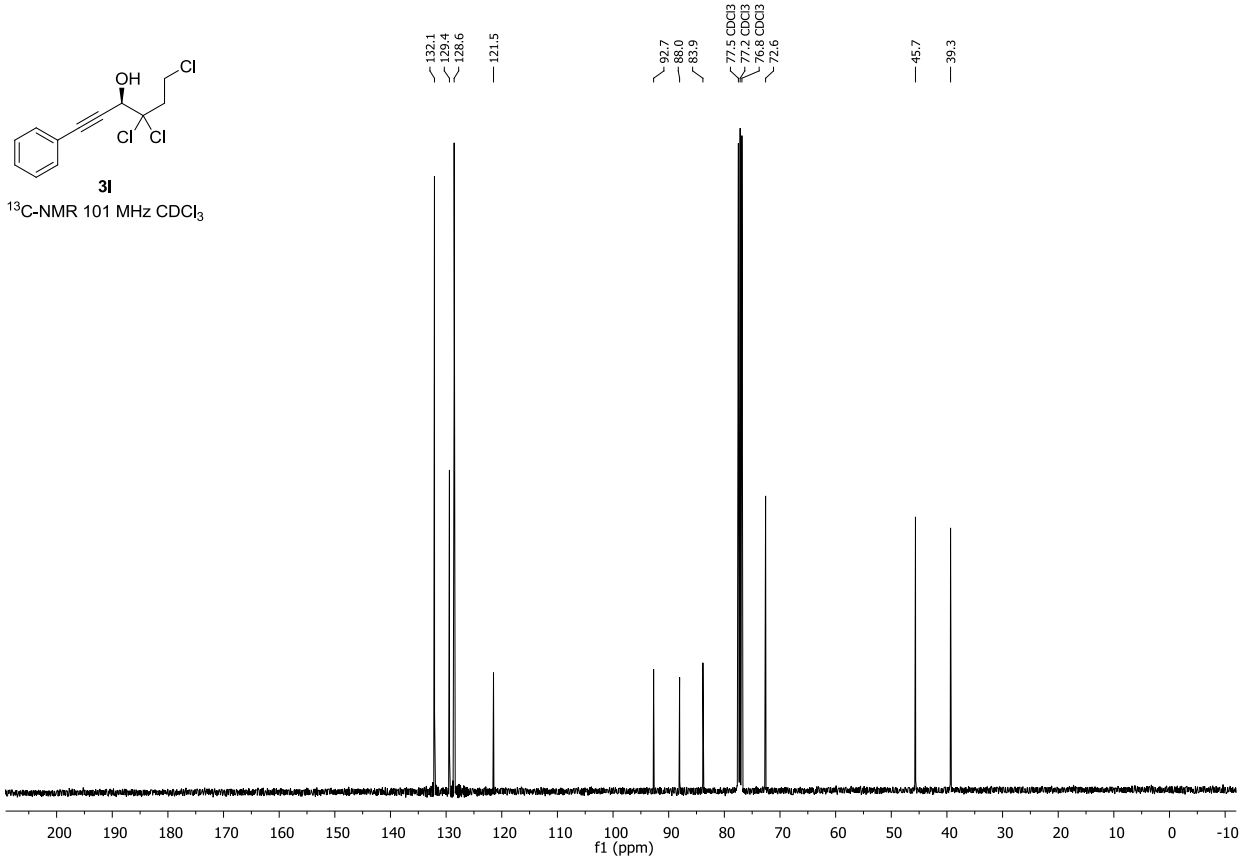
^{1}H-NMR 400 MHz $CDCl_3$

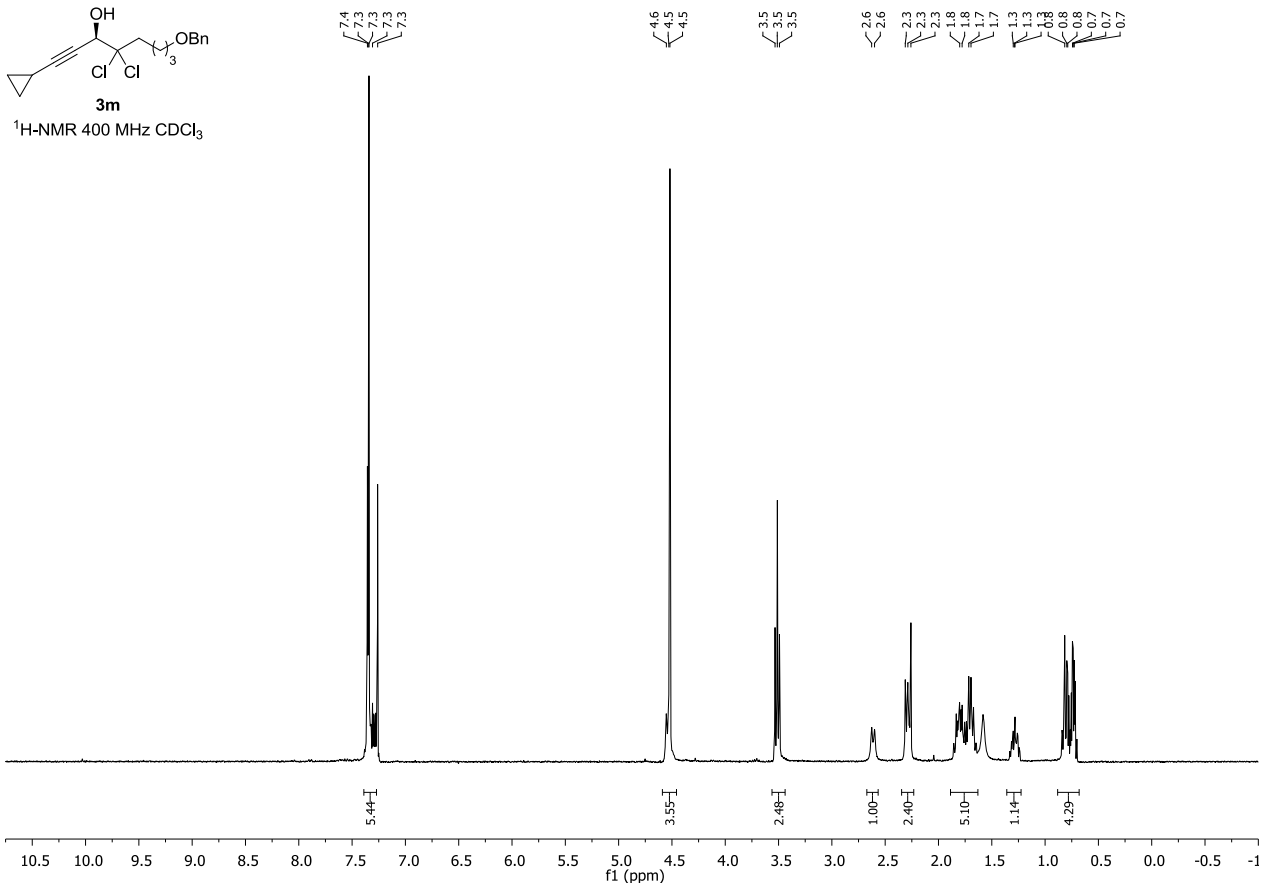


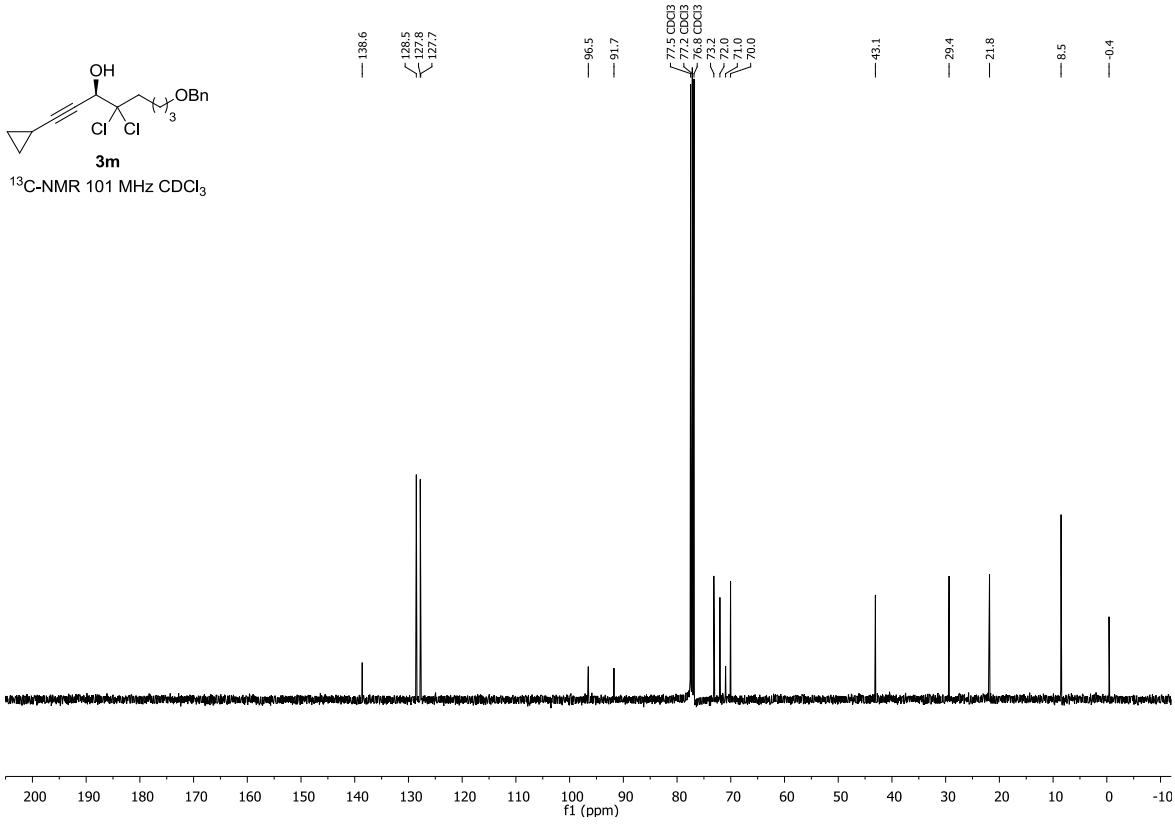
3k

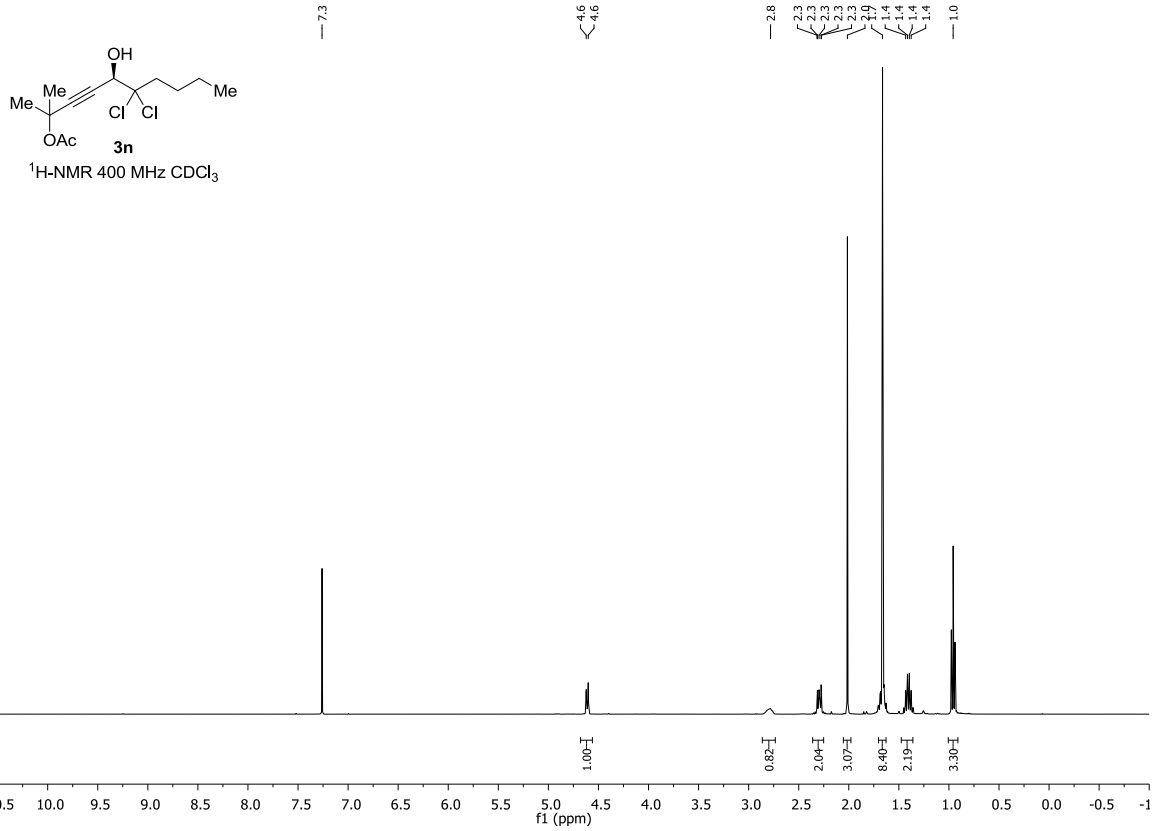
^{13}C-NMR 101 MHz $CDCl_3$

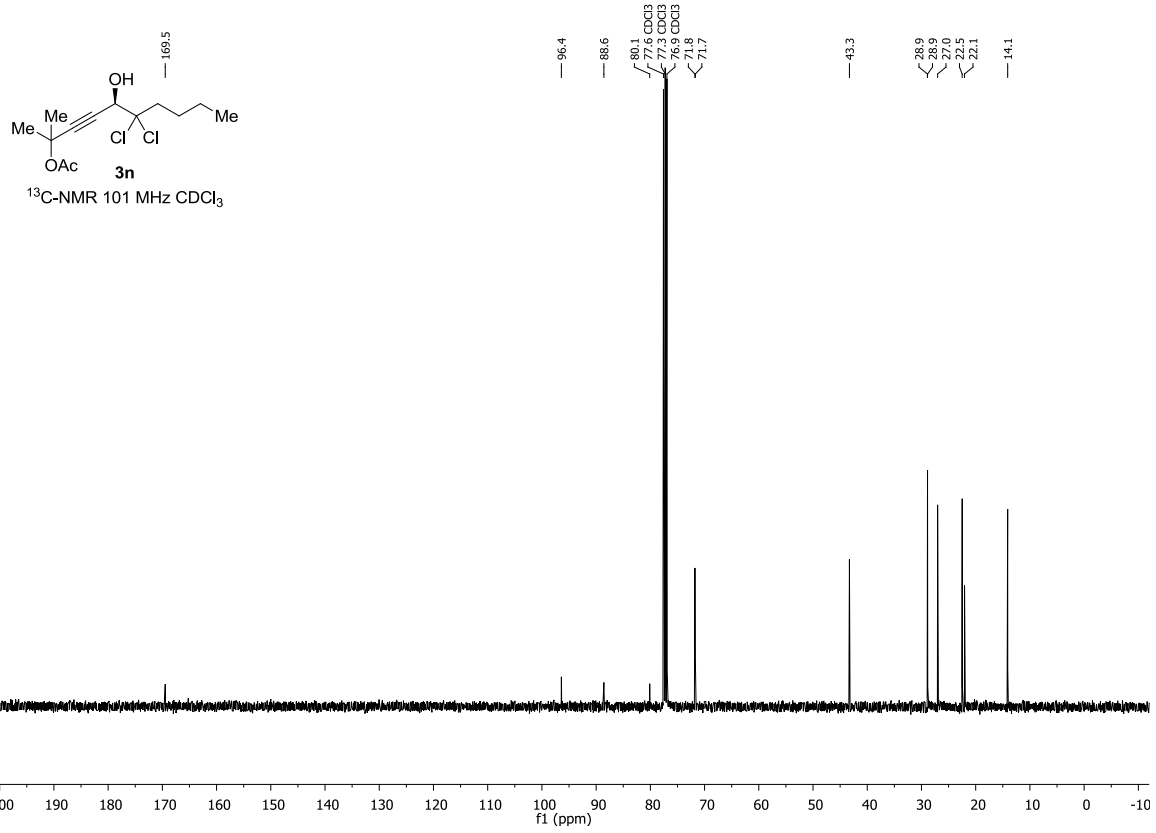

OH
Cl
Cl
Cl
3l
1H-NMR 400 MHz CDCl3
7.5
7.5
7.5
7.5
7.5
7.4
7.4
7.4
7.4
7.3
7.3
7.3
4.9
4.9
3.9
3.9
3.9
2.9
2.9
2.9
2.8
2.8
2.00
3.01
0.99
2.06
3.04
f1 (ppm)


OH
Cl
Cl
Cl
3l
13C-NMR 101 MHz CDCl3
132.1
129.4
128.6
121.5
92.7
88.0
83.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
72.6
45.7
39.3
f1 (ppm)

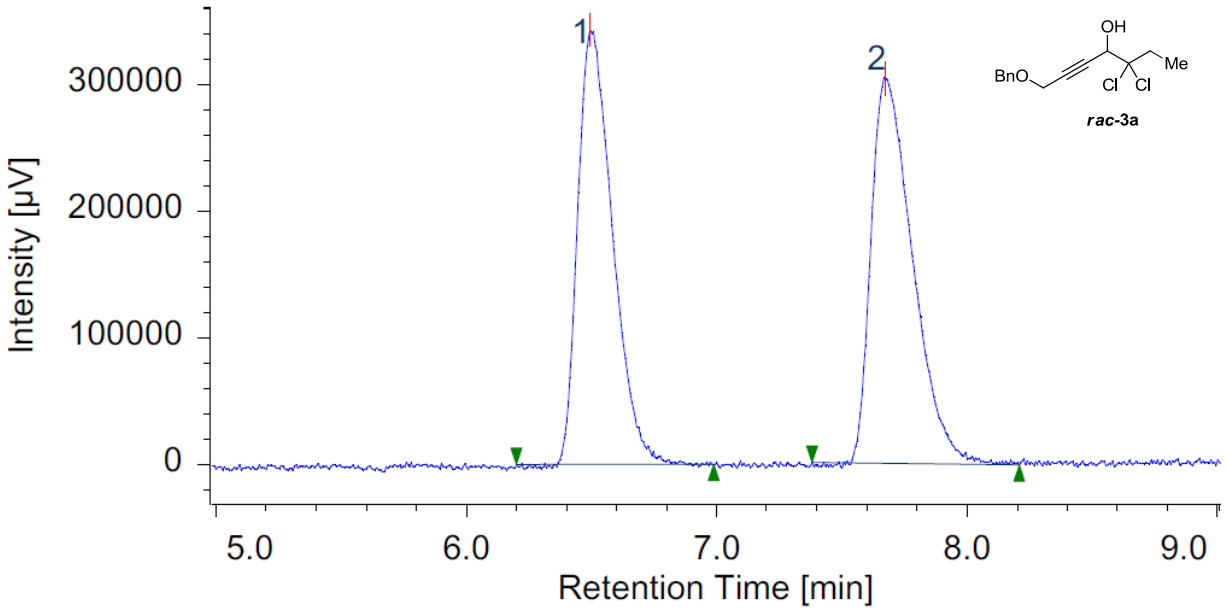

OH
OBn
3
Cl
Cl
3m
1H-NMR 400 MHz CDCl3
7.4
7.3
7.3
7.3
7.3
4.6
4.5
4.5
3.5
3.5
3.5
2.6
2.6
2.3
2.3
2.3
1.8
1.8
1.7
1.7
1.3
1.3
1.3
0.8
0.8
0.7
0.7
0.7
5.44
3.55
2.48
1.00
2.40
5.10
1.14
4.29
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


OH
OBn
3
Cl
Cl
3m
13C-NMR 101 MHz CDCl3
138.6
128.5
127.8
127.7
96.5
91.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
73.2
72.0
71.0
70.0
43.1
29.4
21.8
8.5
-0.4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

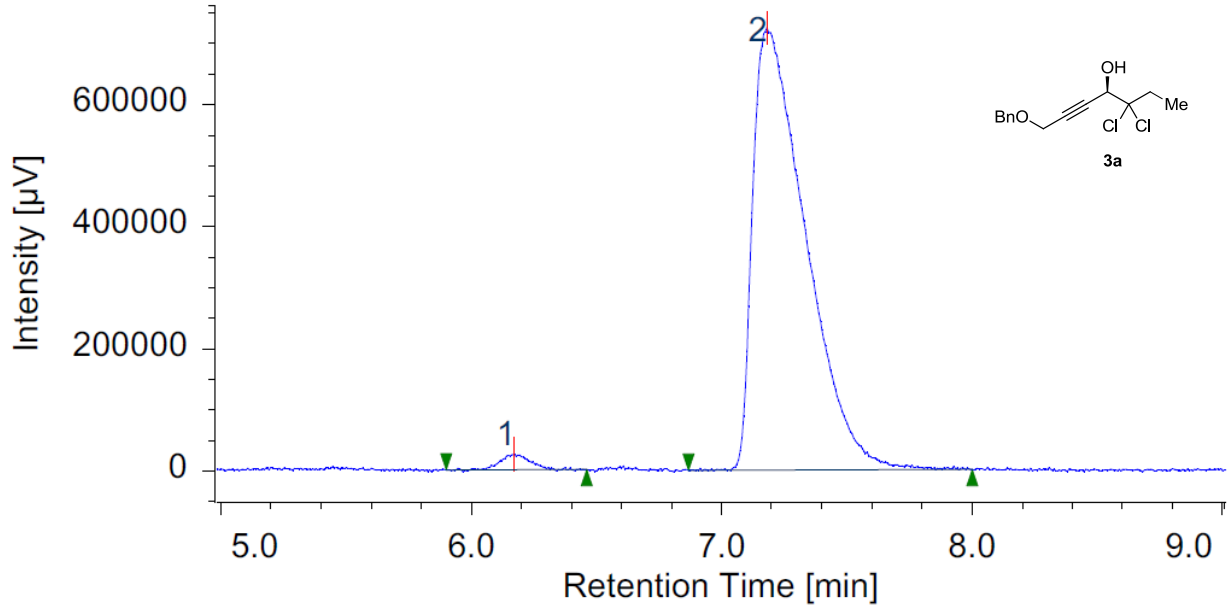

OH
Me
Me
Cl
Cl
Me
OAc
3n
^{1}H-NMR 400 MHz $CDCl_3$
7.3
4.6
4.6
2.8
2.3
2.3
2.3
2.3
2.3
1.4
1.4
1.4
1.4
1.0
1.00
0.82
2.04
3.07
8.40
2.19
3.30
f1 (ppm)


OH
Me
Me
Cl
Cl
Me
OAc
3n
^{13}C-NMR 101 MHz $CDCl_3$
169.5
96.4
88.6
80.1
77.6 CDCl3
77.3 CDCl3
76.9 CDCl3
71.8
71.7
43.3
28.9
28.9
27.0
22.5
22.1
14.1
f1 (ppm)

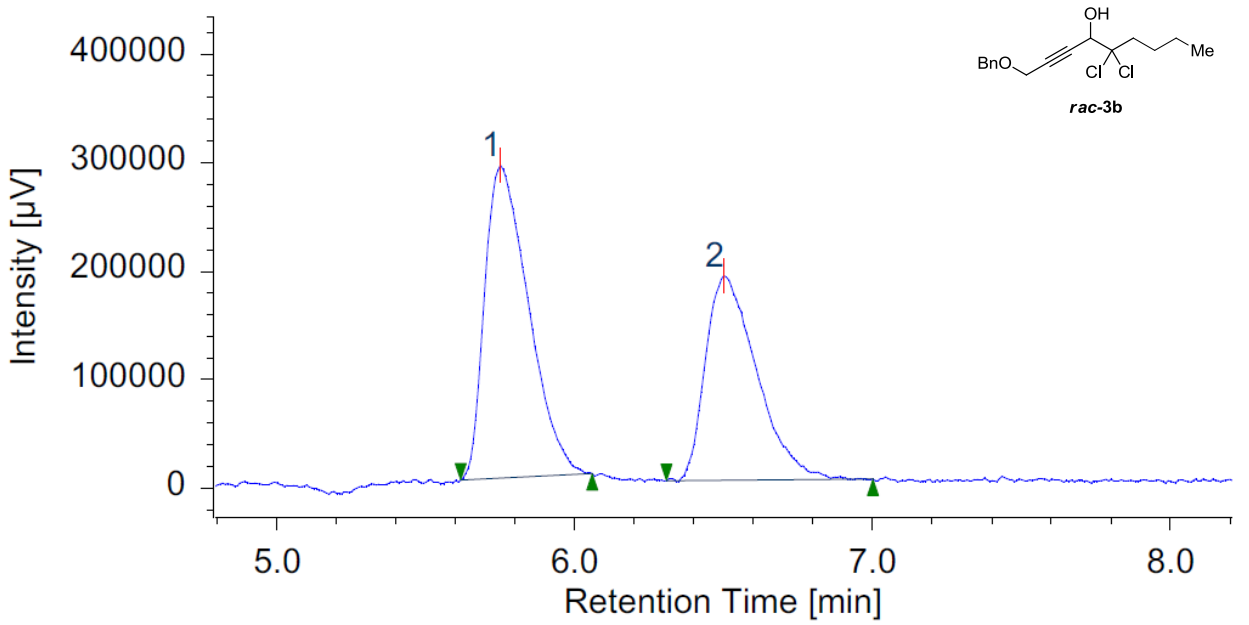
V. SFC & HPLC traces



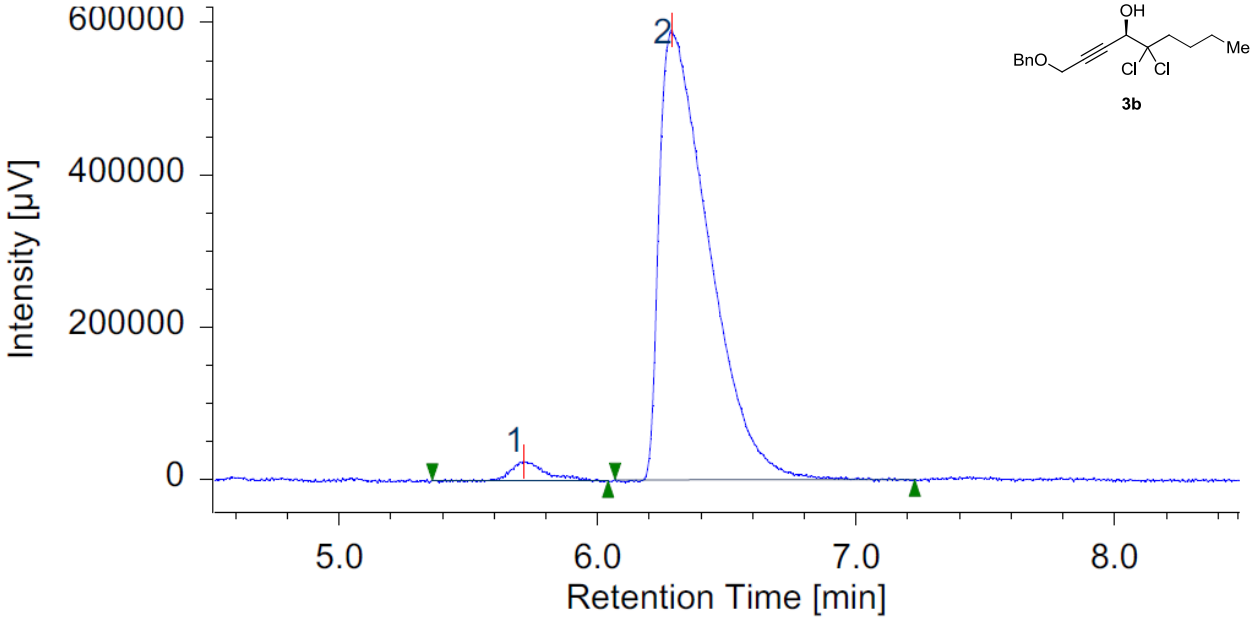
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	6.493	3299274	342827	48.339	53.076
2	Unknown	9	7.673	3526072	303093	51.661	46.924



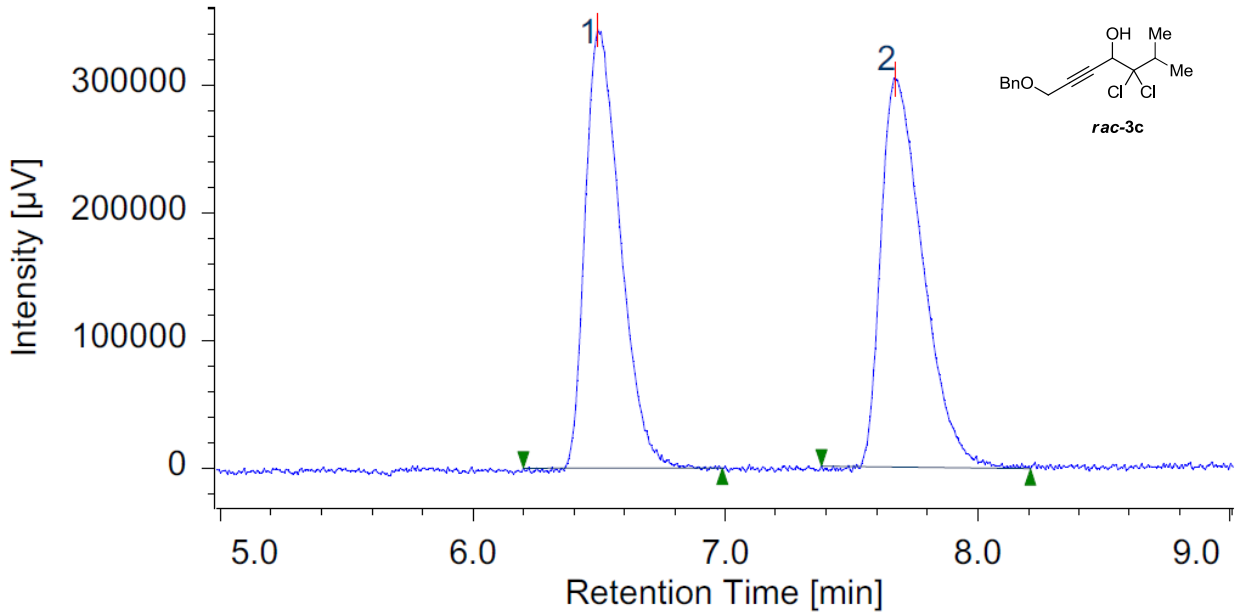
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	6.173	219505	25530	2.025	3.405
2	Unknown	9	7.180	10621114	724241	97.975	96.595



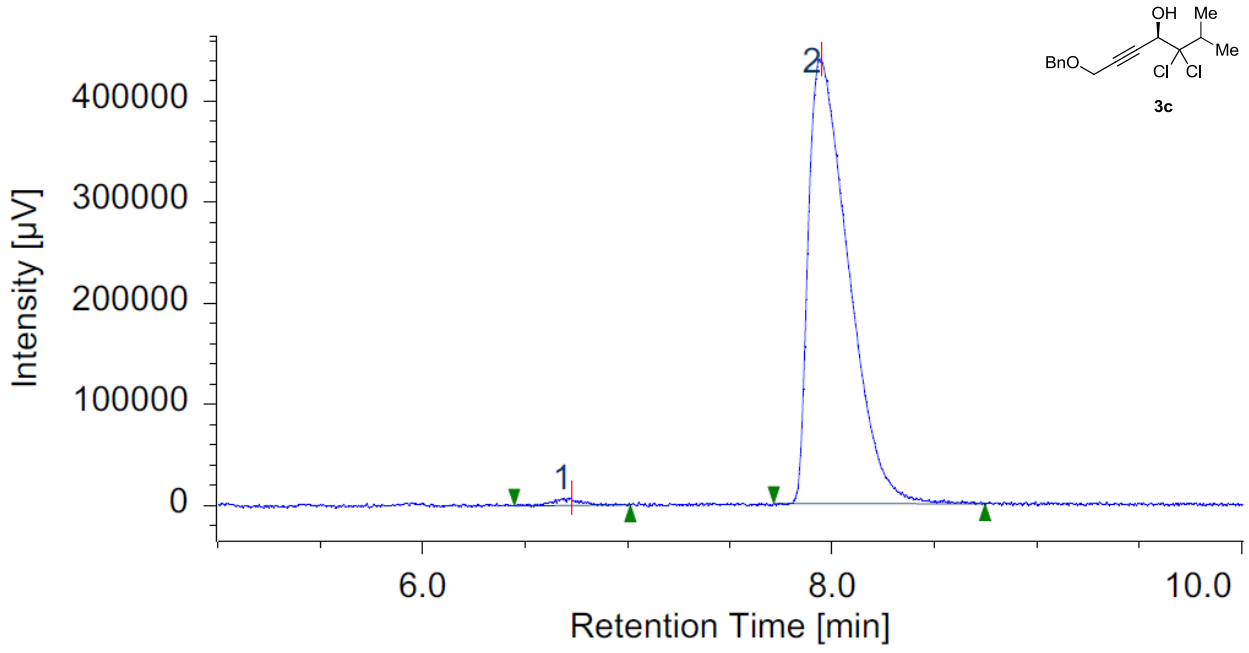
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	1	5.750	3046640	290754	58.245	60.872
2	Unknown	1	6.500	2184054	186896	41.755	39.128



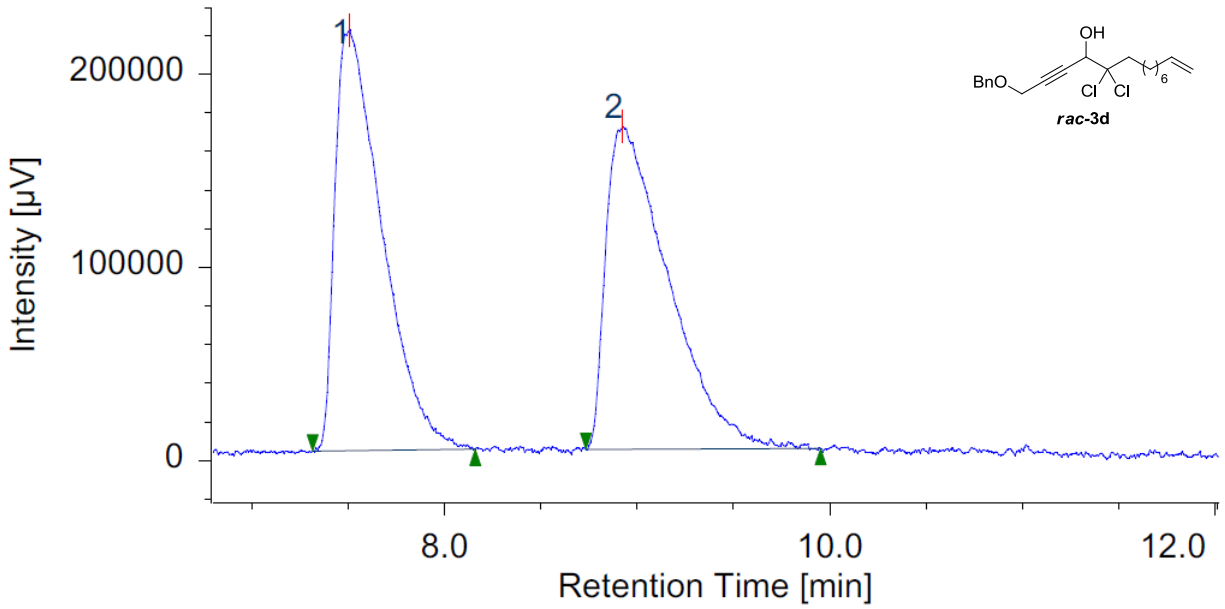
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	5.713	238808	25447	2.968	4.130
2	Unknown	9	6.287	7807081	590664	97.032	95.870



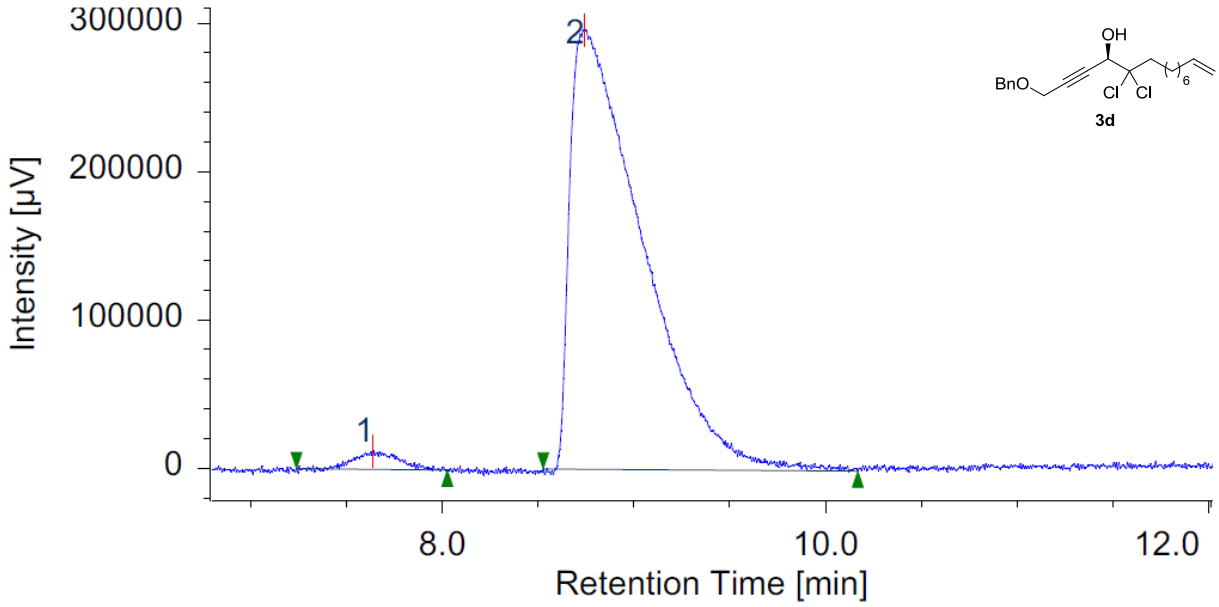
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	7.007	4638098	433899	47.464	54.123
2	Unknown	9	8.453	5133796	367785	52.536	45.877



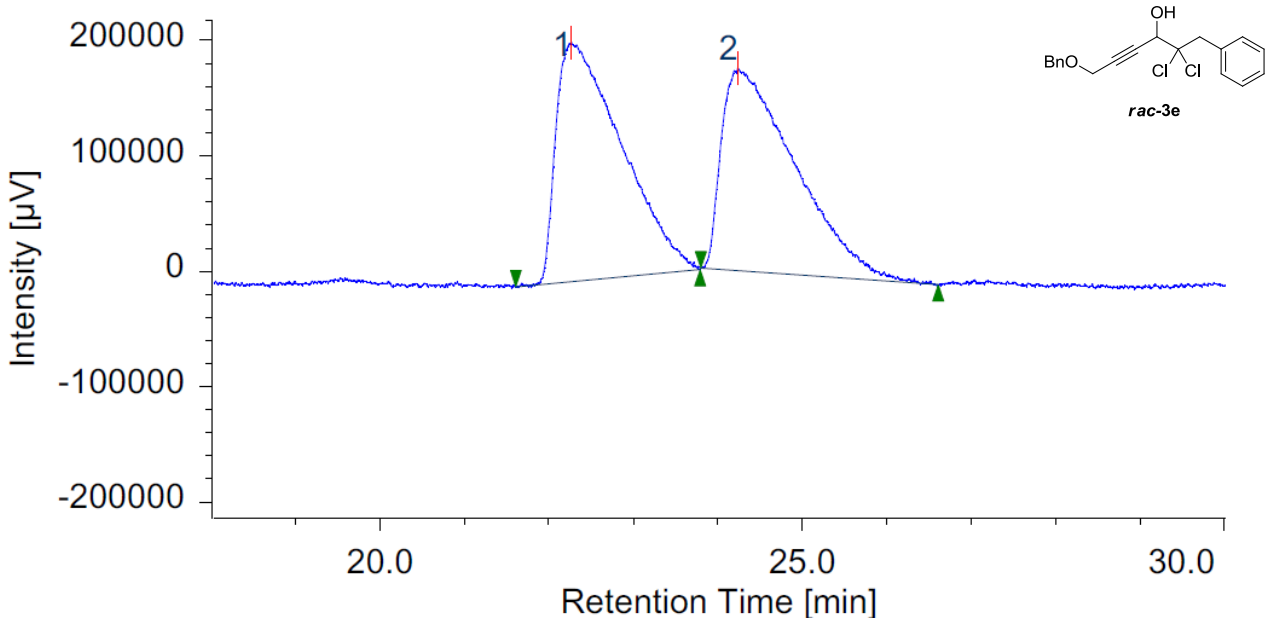
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	6.727	69088	7329	1.145	1.638
2	Unknown	9	7.947	5965827	440219	98.855	98.362



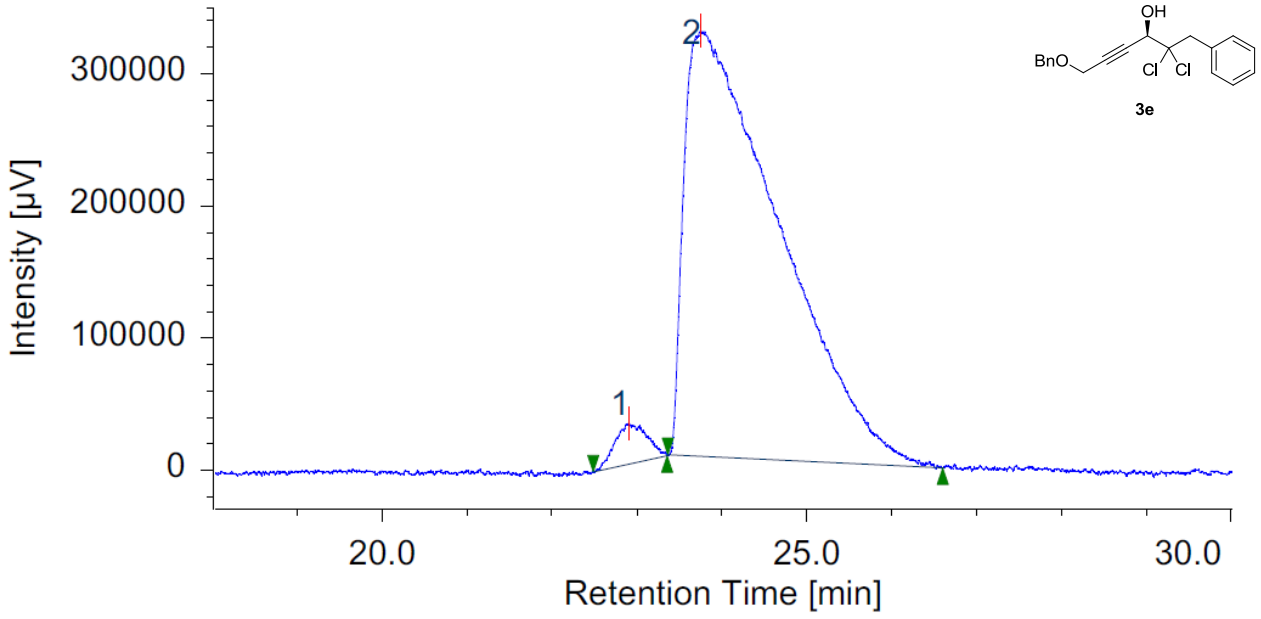
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	1	7.508	3724981	217918	48.702	56.326
2	Unknown	1	8.925	3923462	168968	51.298	43.674



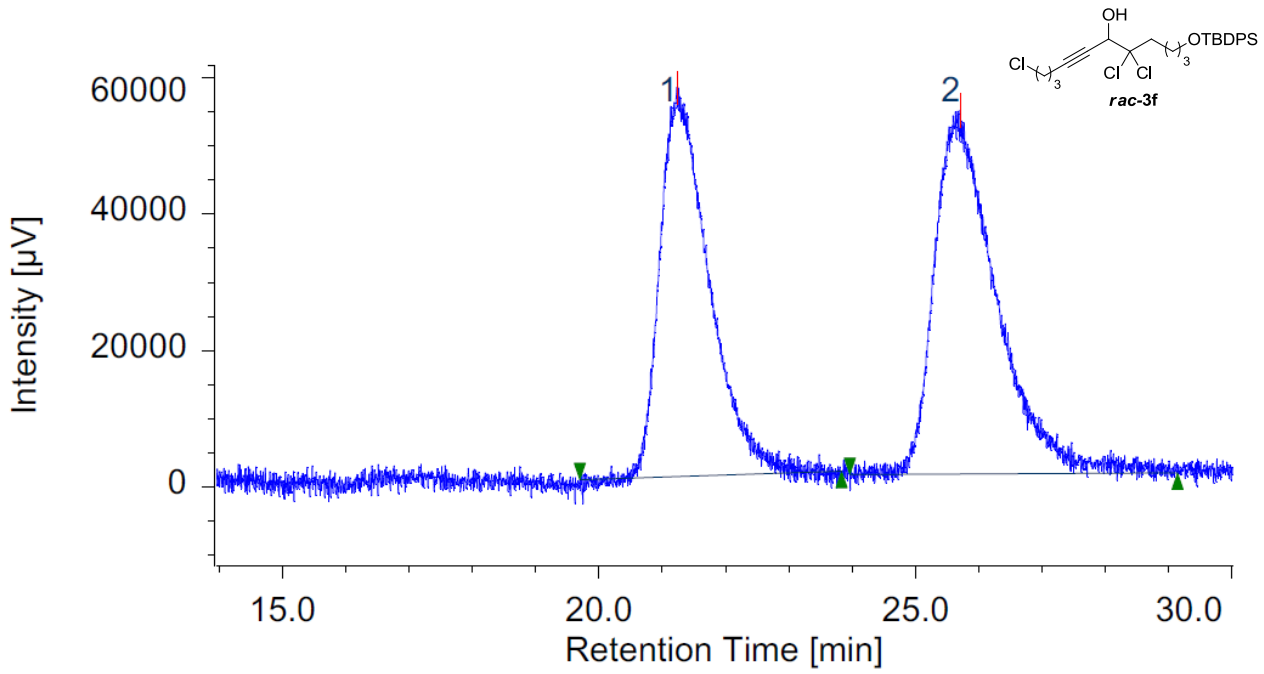
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	7.640	199014	12300	2.491	3.994
2	Unknown	9	8.740	7790081	295635	97.509	96.006



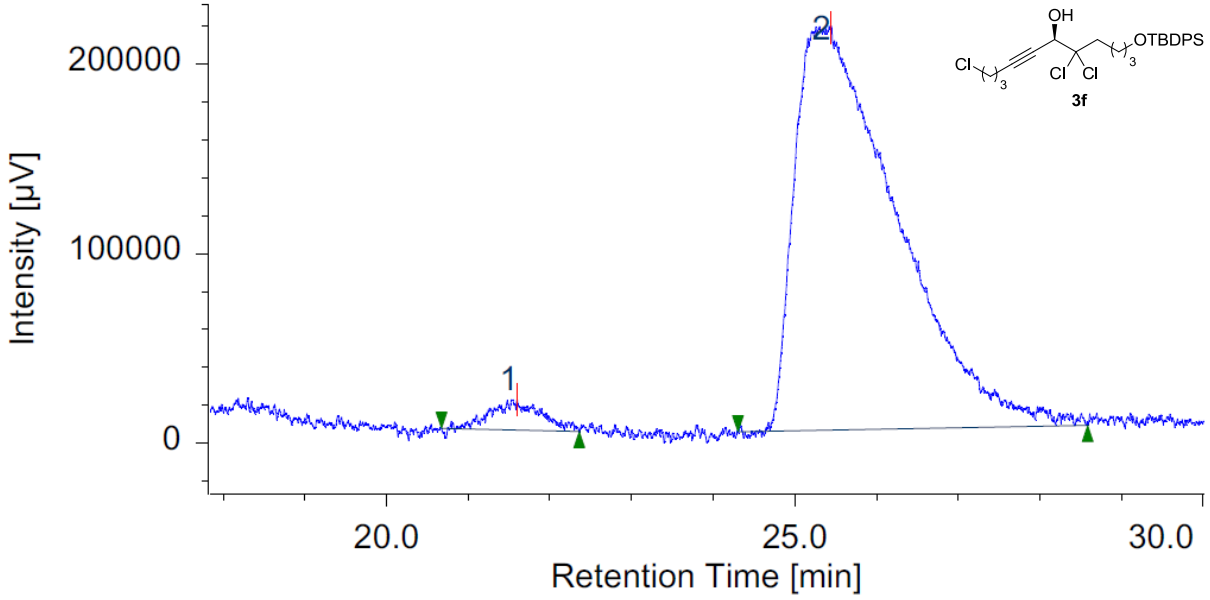
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	9	22.267	9271796	177190	51.340	54.453
2	Unknown	9	24.200	8787664	148208	48.660	45.547



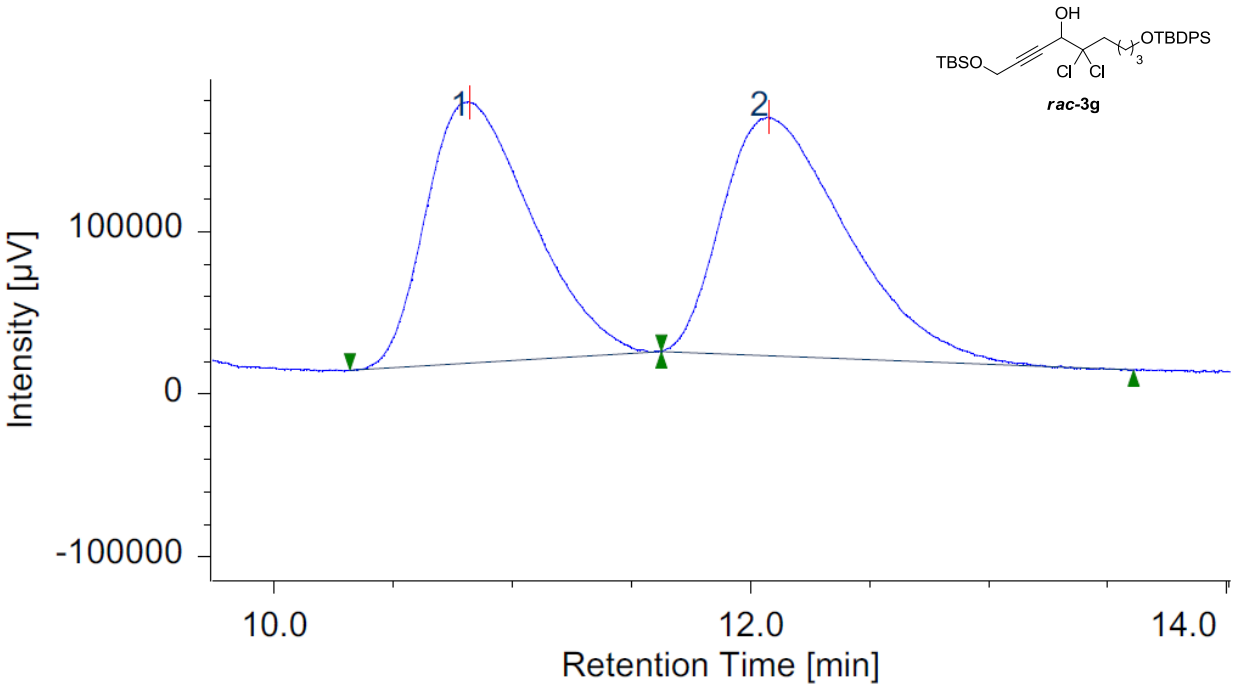
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	1	22.908	814784	30989	3.158	8.783
2	Unknown	1	23.750	24989673	321854	96.842	91.217



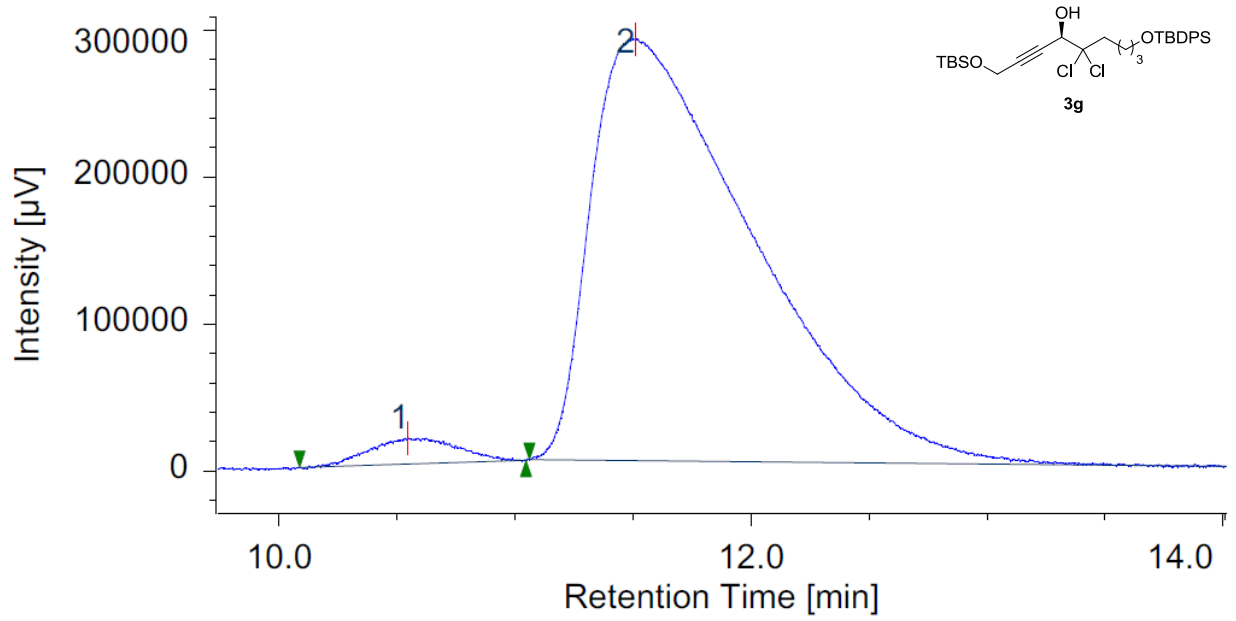
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	21.233	3070621	57113	47.231	51.900
2	Unknown	9	25.700	3430683	52931	52.769	48.100



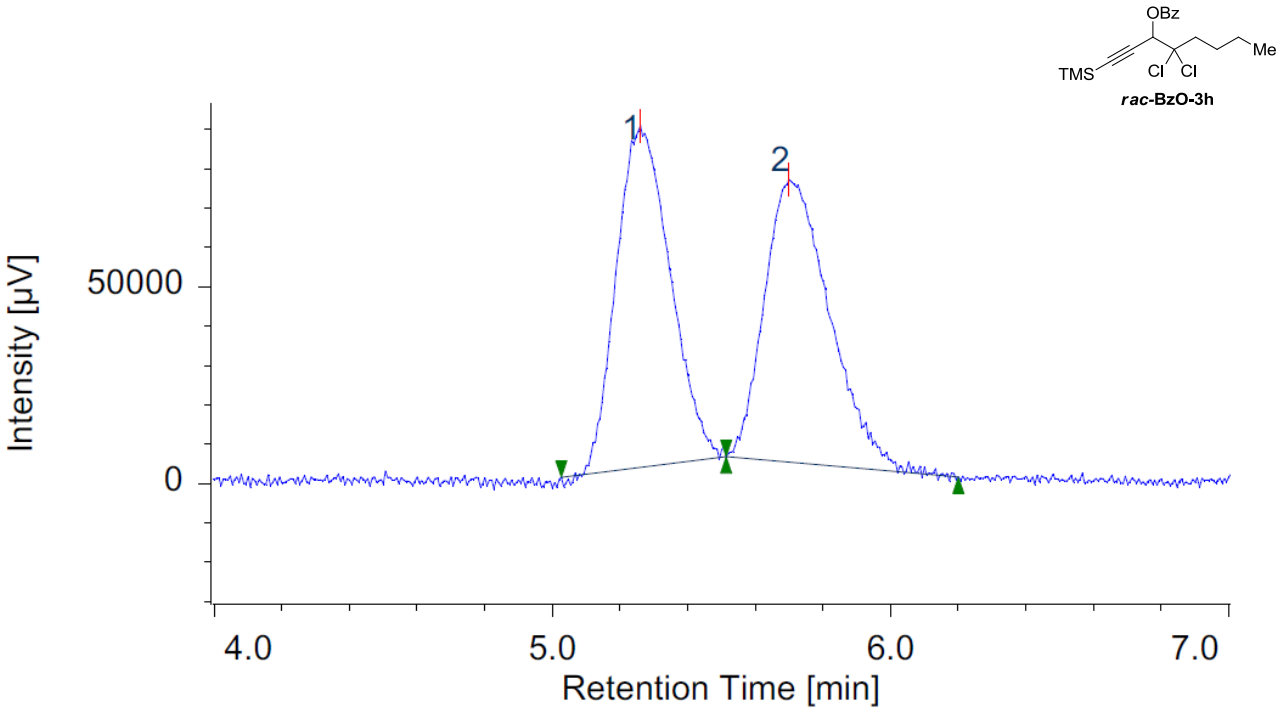
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	21.573	182764	5570	3.090	6.093
2	Unknown	9	25.447	5732855	85850	96.910	93.907



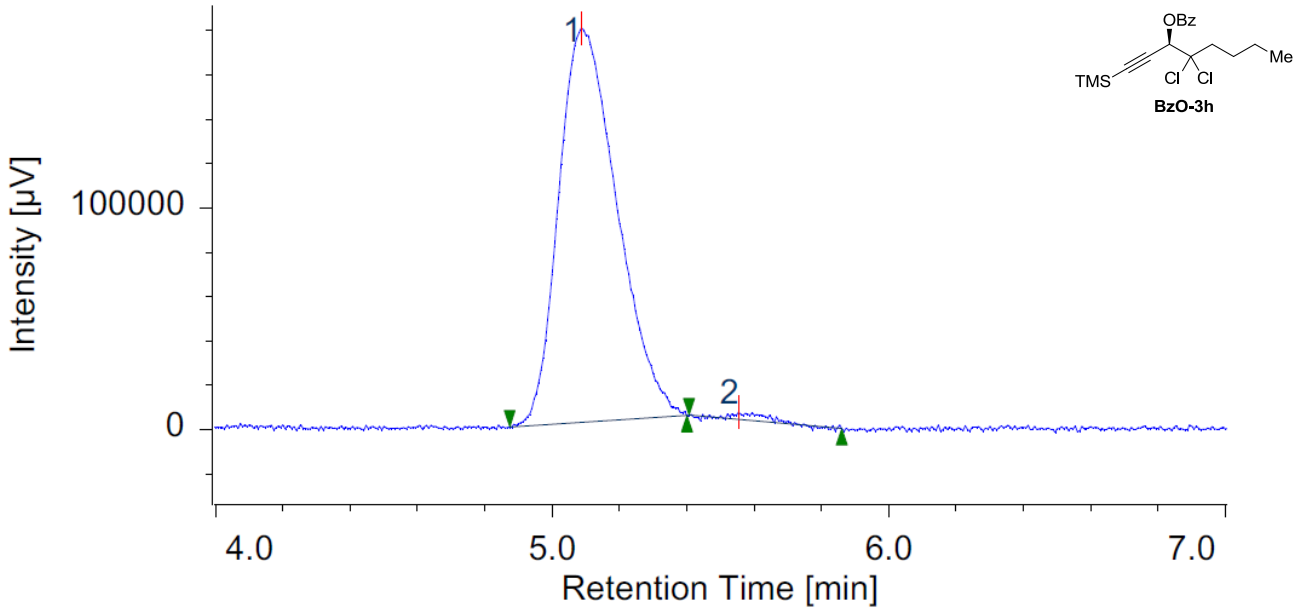
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	1	10.817	4942337	160147	48.051	52.234
2	Unknown	1	12.075	5343197	146449	51.949	47.766



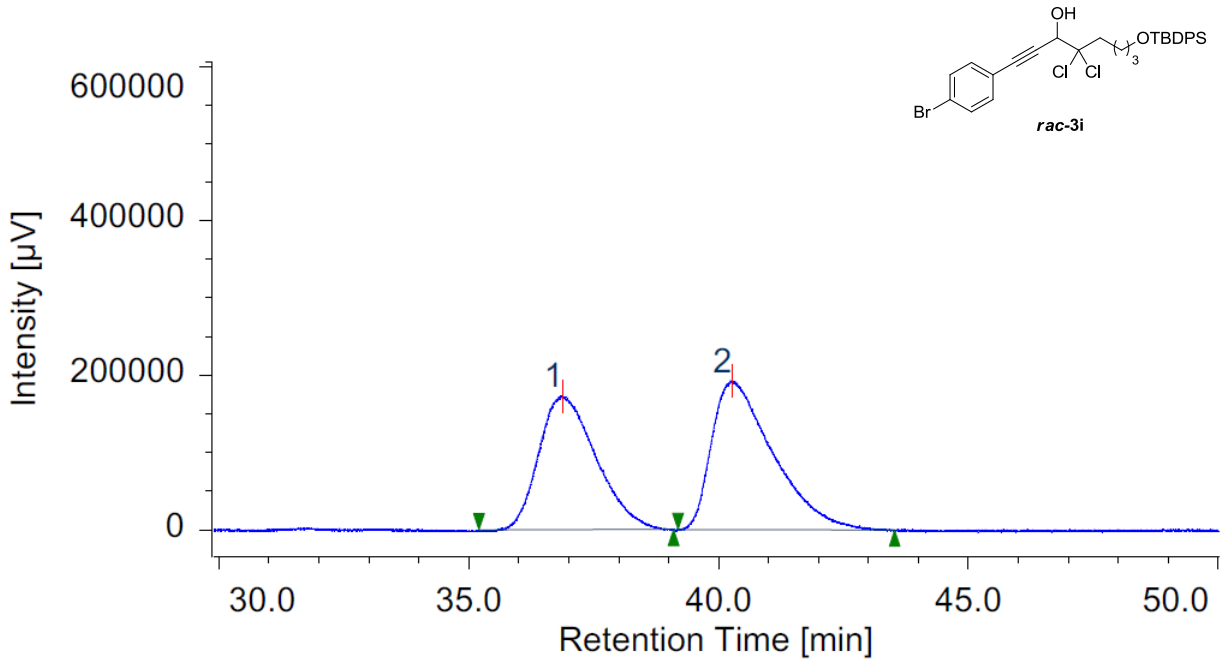
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%
1	Unknown	9	10.547	454618	17755	3.197	5.844
2	Unknown	9	11.507	13764958	286069	96.803	94.156



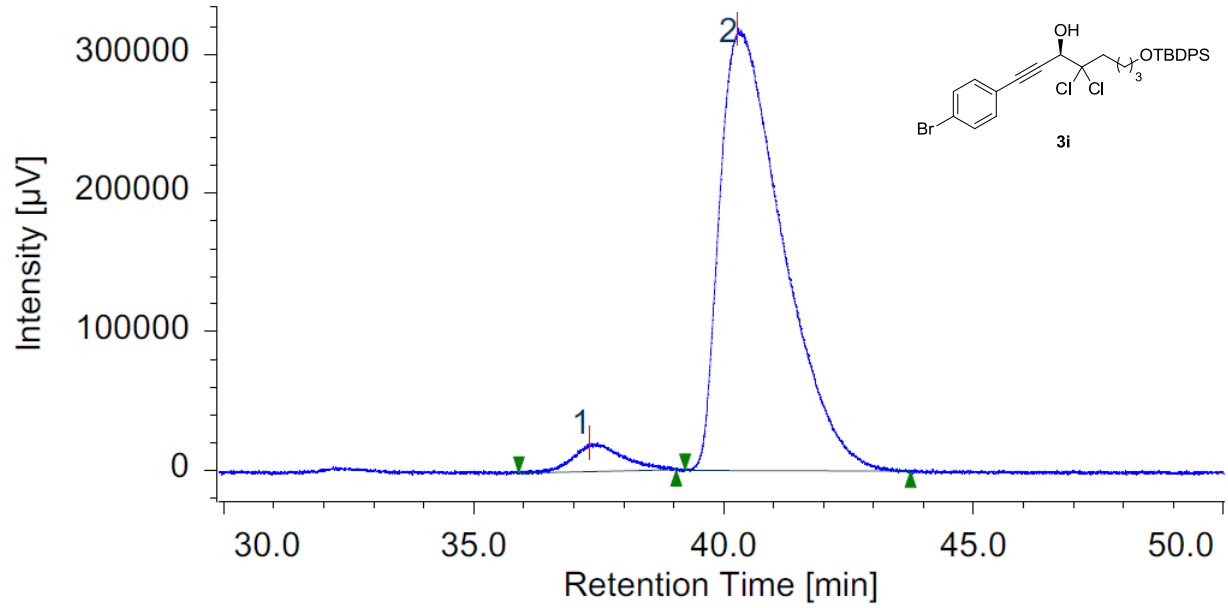
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	5.260	1089948	96691	49.813	54.849
2	Unknown	9	5.700	1098133	79595	50.187	45.151



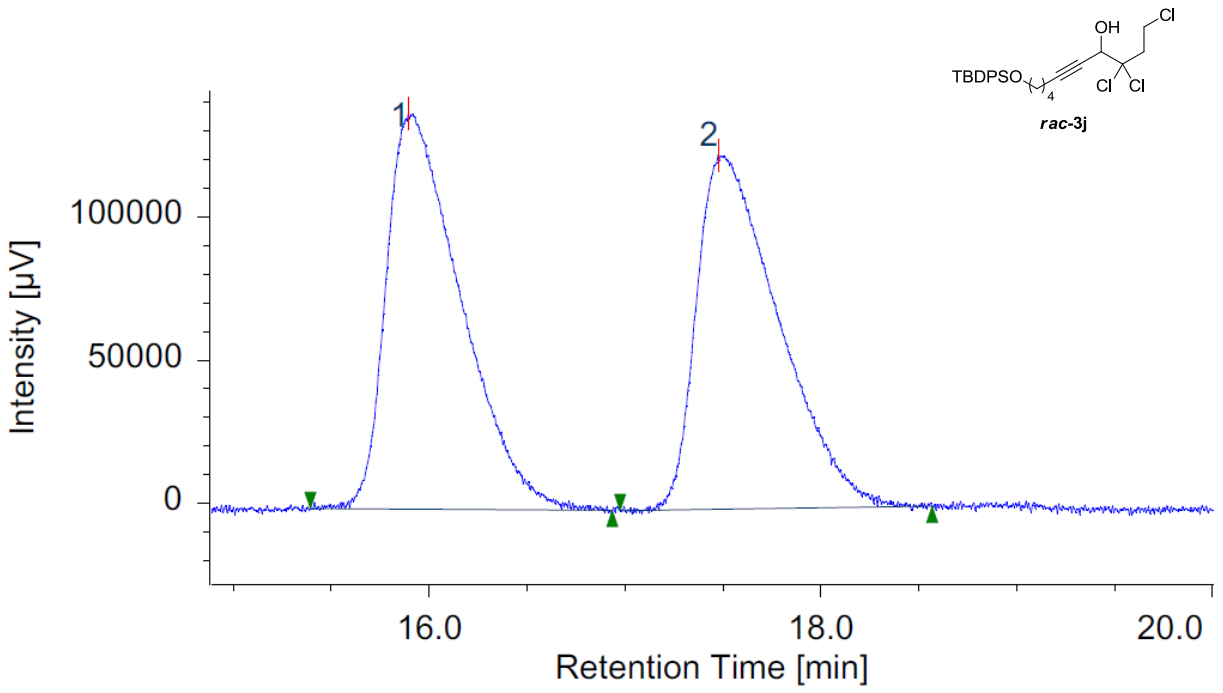
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	5.087	2375228	196516	98.842	98.464
2	Unknown	9	5.553	27832	3065	1.158	1.536



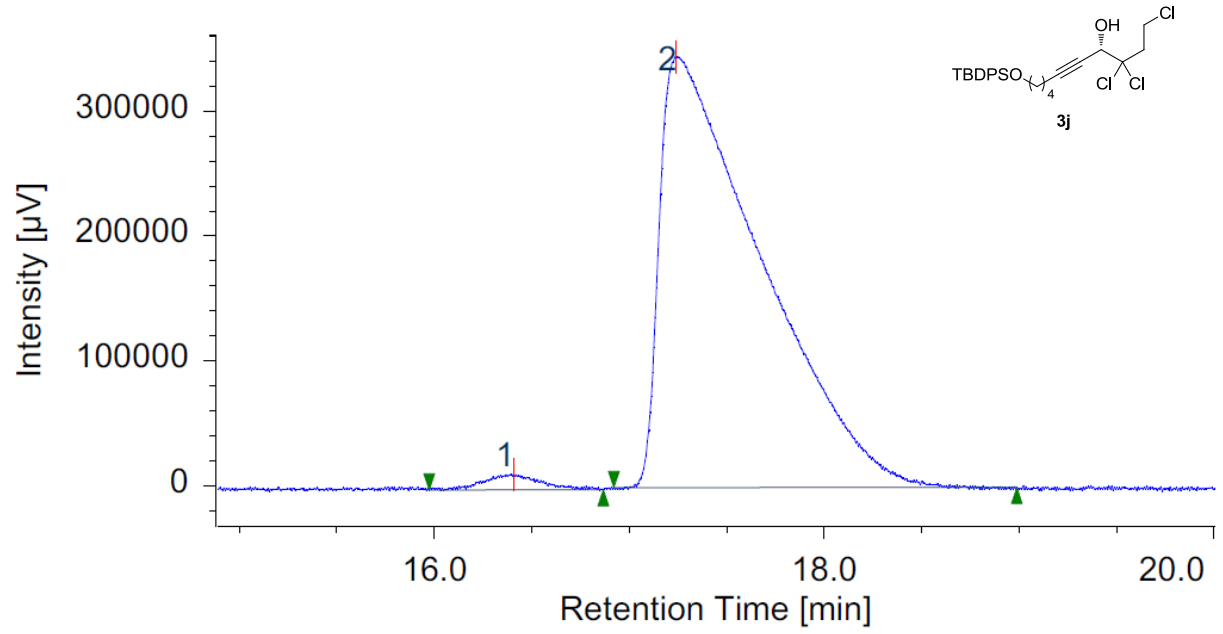
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	36.873	13702824	172515	45.658	47.290
2	Unknown	9	40.253	16308975	192286	54.342	52.710



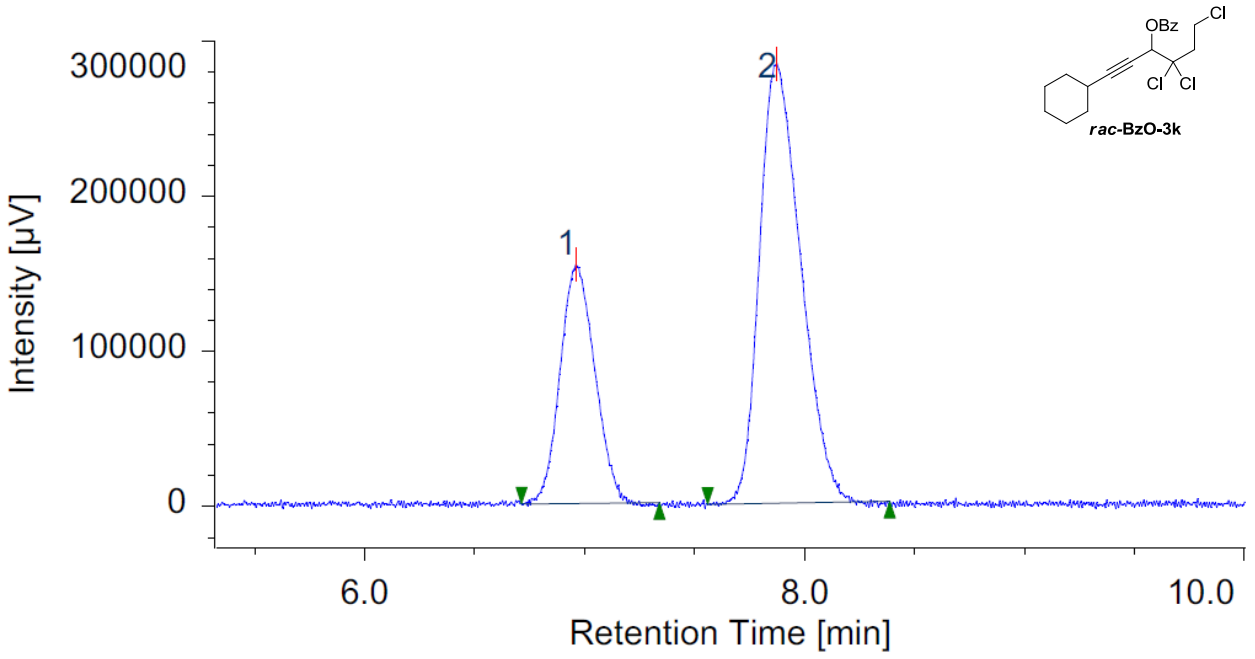
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	37.320	1387445	20804	4.762	6.125
2	Unknown	9	40.267	27751010	318845	95.238	93.875



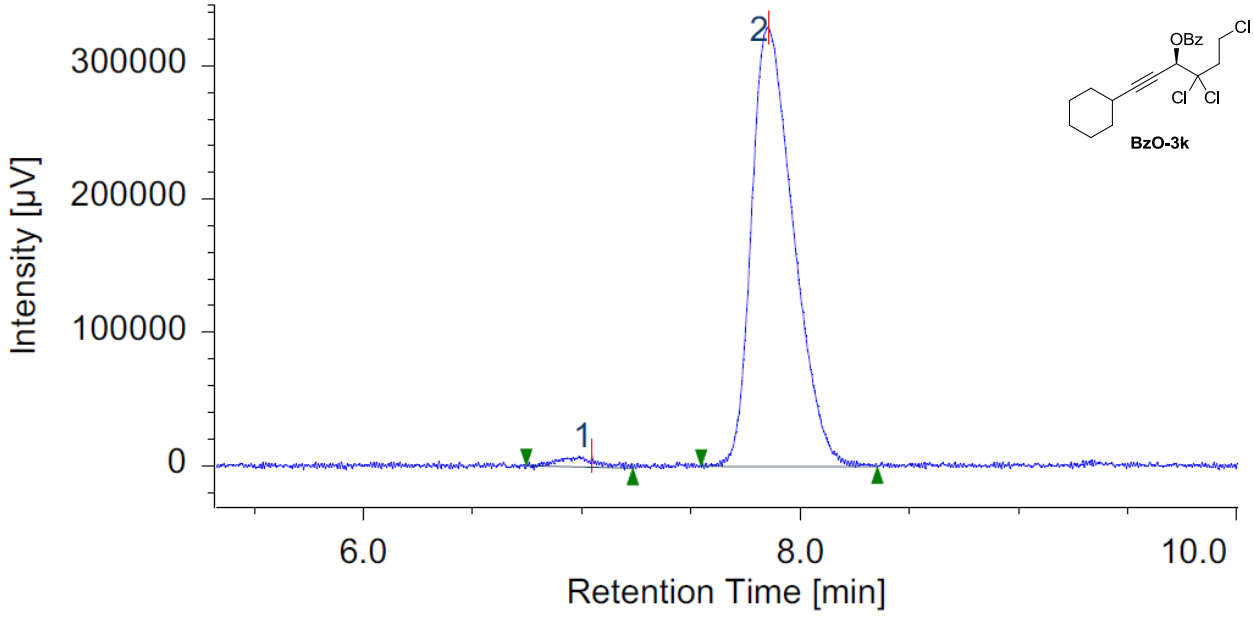
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	15.893	3660888	138220	50.479	52.807
2	Unknown	9	17.473	3591465	123527	49.521	47.193



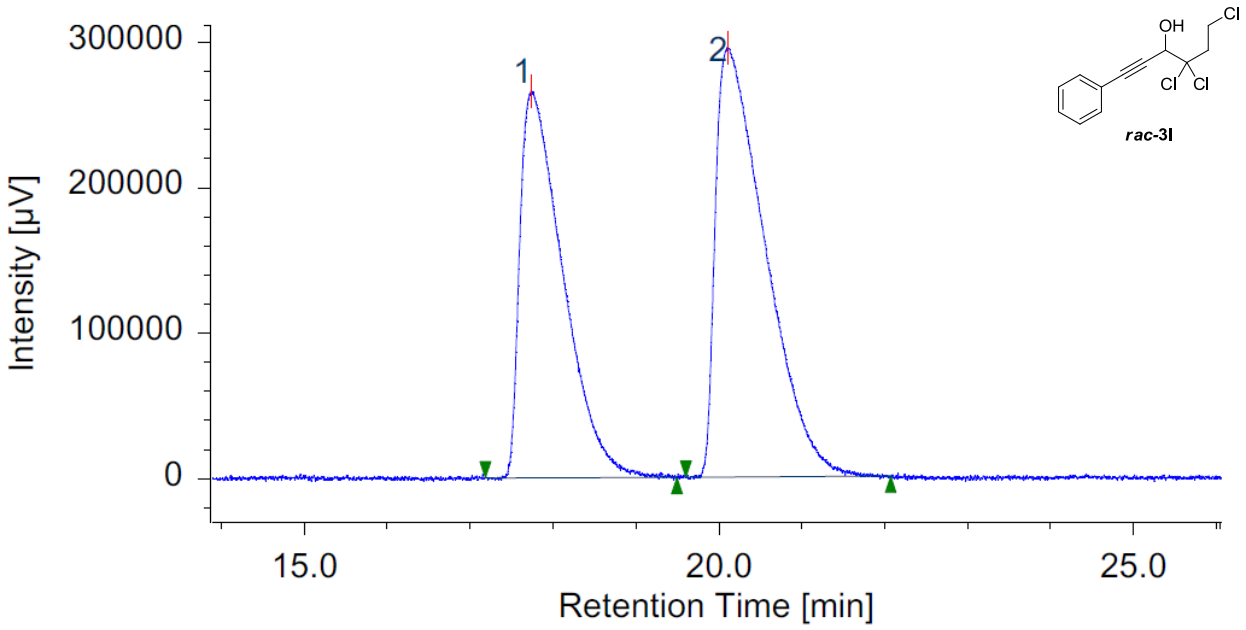
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	16.407	260728	12459	2.051	3.485
2	Unknown	9	17.240	12450944	345028	97.949	96.515



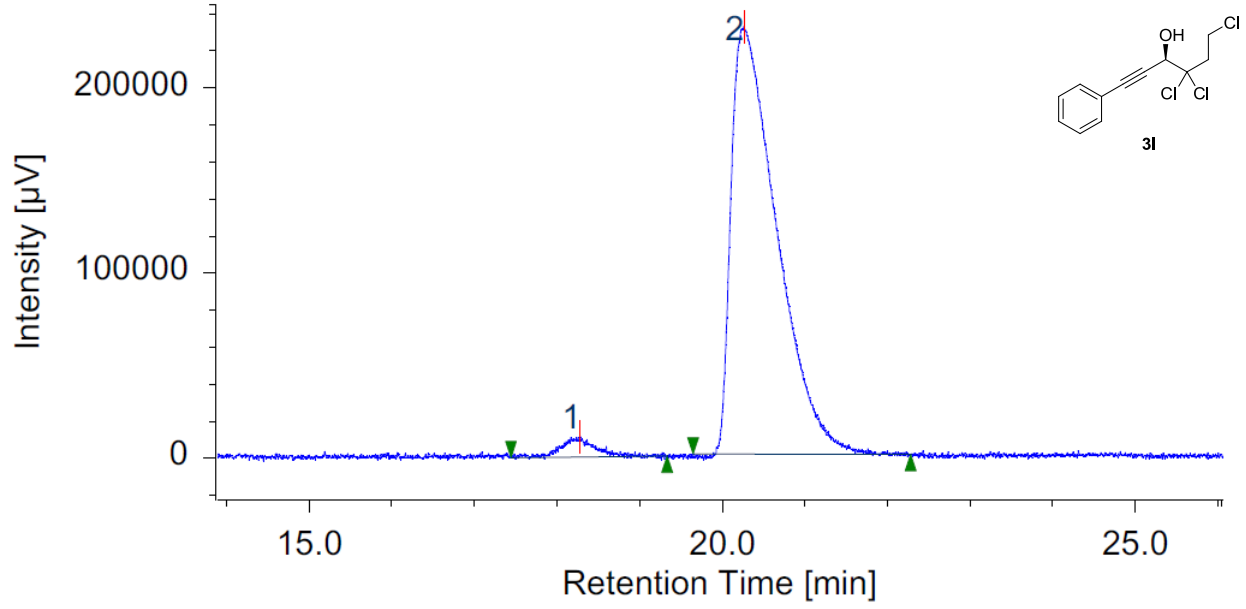
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	6.960	1685047	154296	31.245	35.258
2	Unknown	9	7.873	3708050	283319	68.755	64.742



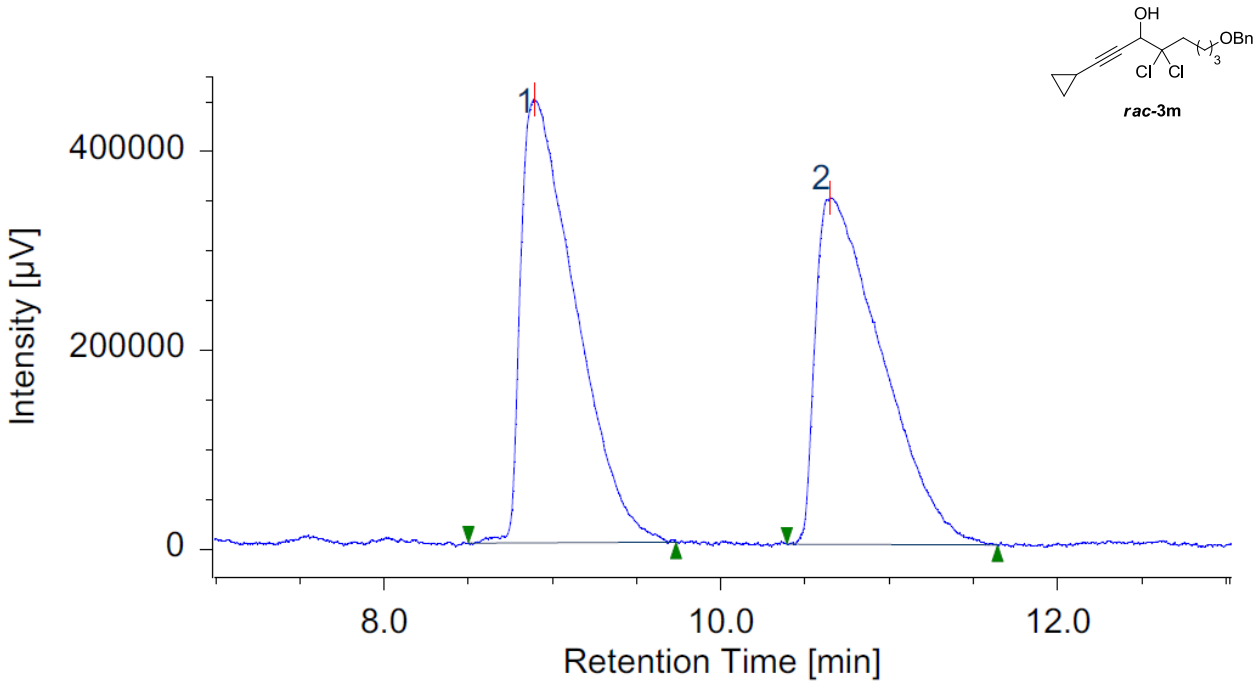
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	7.047	95352	8634	2.111	2.554
2	Unknown	9	7.853	4421229	329428	97.889	97.446



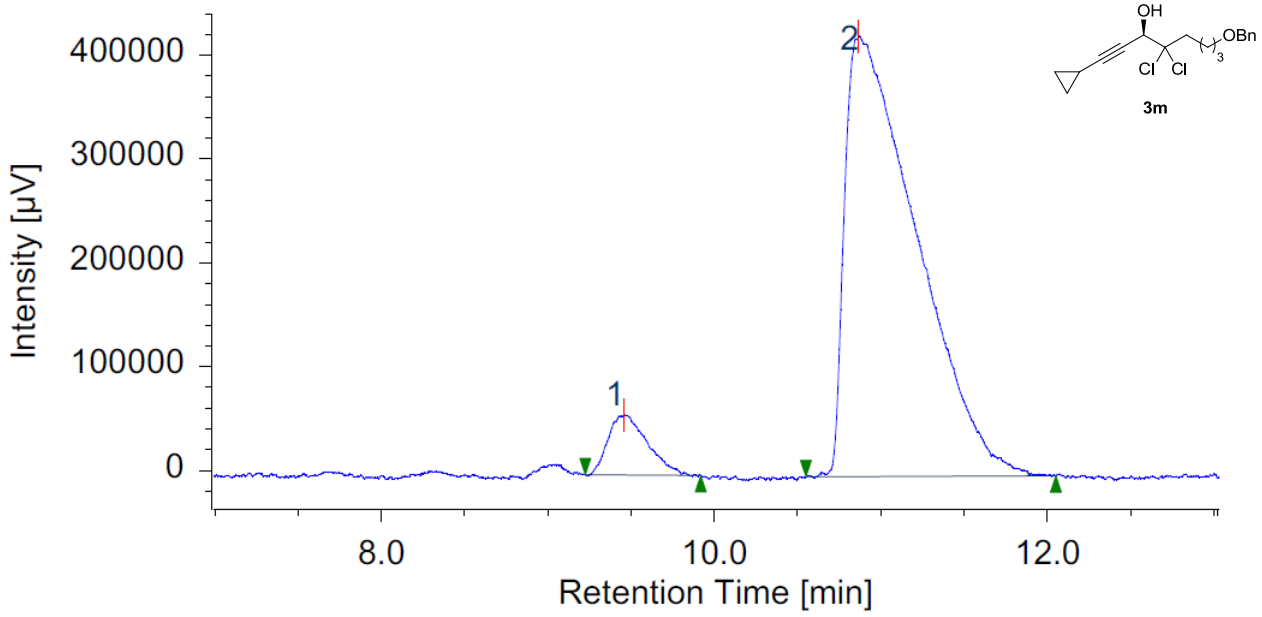
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	17.733	9545652	265476	43.685	47.354
2	Unknown	9	20.100	12305618	295143	56.315	52.646



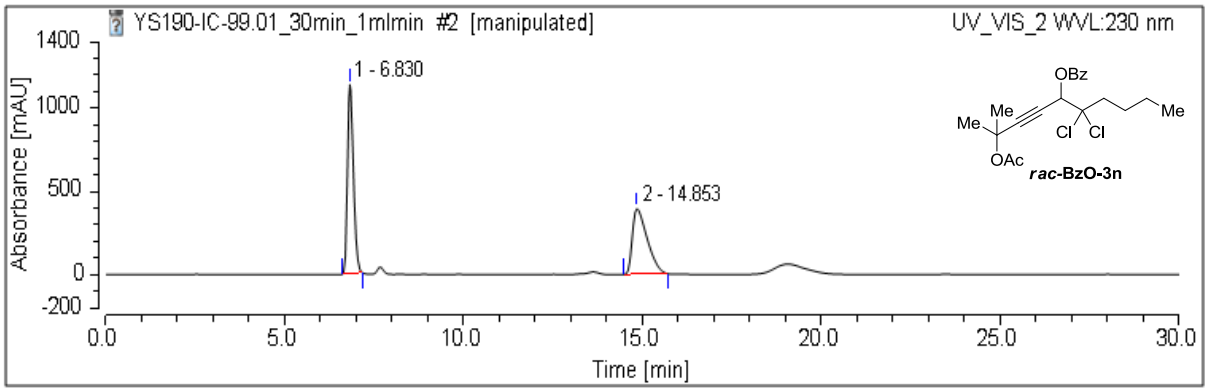
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	9	18.280	320268	10808	3.484	4.469
2	Unknown	9	20.260	8872436	231020	96.516	95.531



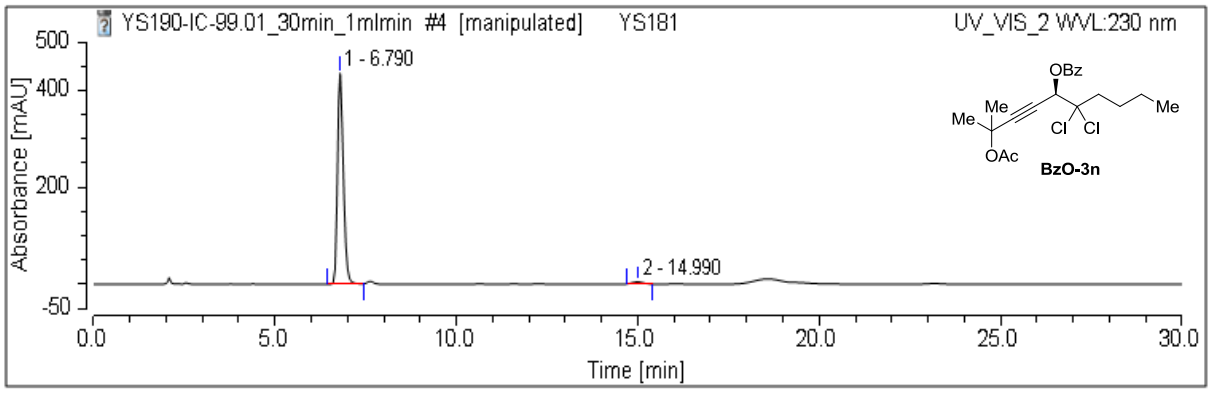
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	1	8.892	10037507	446183	51.298	56.159
2	Unknown	1	10.650	9529441	348318	48.702	43.841



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%
1	Unknown	1	9.458	951254	58006	6.977	12.037
2	Unknown	1	10.867	12682945	423872	93.023	87.963

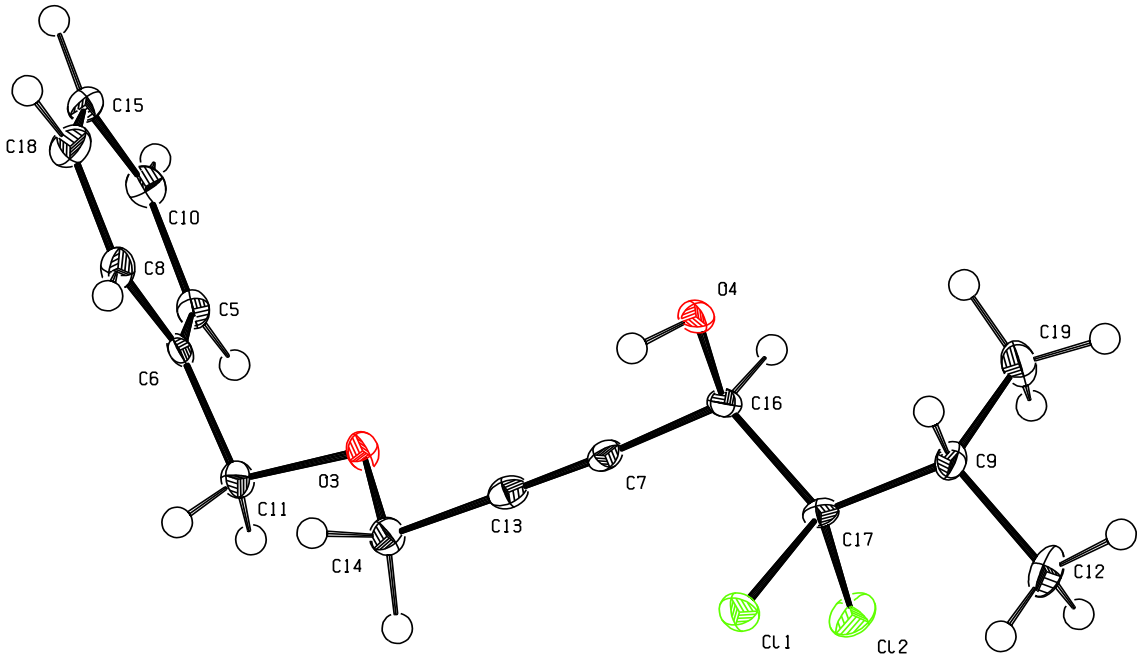


No.	Peakname	Ret.Time	Area	Height	Rel.Area
		min	mAU*min	mAU	%
1		6.830	216.8071	1136.408	53.45
2		14.853	188.8184	394.860	46.55



No.	Peakname	Ret.Time	Area	Height	Rel.Area
		min	mAU*min	mAU	%
1		6.790	81.1596	435.548	98.06
2		14.990	1.6036	4.432	1.94

VI. X-Ray Crystallographic Data for 3c



Identification code	ca111015_1_1_01
Empirical formula	$C_{15}H_{18}Cl_2O_2$
Formula weight	301.19
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.9062(3)
b/Å	9.1377(4)
c/Å	13.7532(6)
α/°	90
β/°	90.423(2)
γ/°	90
Volume/Å^3	742.23(6)
Z	2
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.432
F(000)	316.0
Crystal size/mm^3	0.22 × 0.17 × 0.035
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.352 to 54.972
Index ranges	$-7 \le h \le 7$, $-8 \le k \le 11$, $-17 \le l \le 17$

Reflections collected	6284
Independent reflections	3051 [R_{int} = 0.0750, R_{sigma} = 0.0792]
Data/restraints/parameters	3051/2/177
Goodness-of-fit on F^2	0.975
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0668
Final R indexes [all data]	R_1 = 0.0423, wR_2 = 0.0689
Largest diff. peak/hole / e $Å^{-3}$	0.41/-0.30
Flack parameter	-0.04(5)