Supporting Information

Gold(I)-Catalyzed Stereoselective Cyclization of 1,3-Enyne Aldehydes by 1,3-Acyloxy Migration/Nazarov/Aldol Cascade

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1. Materials and Methods

1.1. General Methods. All non-aqueous reactions were performed under an inert atmosphere of dry nitrogen or argon in flame dried glassware sealed with a rubber septum unless otherwise noted. The protecting gas was passed over a column of $CaCl_2$ and supplied through a glass manifold. Reactions were stirred magnetically and monitored by thin layer chromatography (TLC). Analytical thin layer chromatography was performed using MERCK SILICA GEL F254 TLC glass plates and visualized by ultraviolet light (UV). Additionally, TLC plates were stained with aqueous potassium permanganate ($KMnO_4$) [1.5 g $KMnO_4$, 200 mL H_2O, 10 g K_2CO_3, 2.5 mL 1 M NaOH aq.] or ethanolic p-anisaldehyde [3.7 mL p-anisaldehyde, 135 mL EtOH, 5 mL conc. H_2SO_4, 1.5 mL AcOH]. Concentration under reduced pressure (= *in vacuo*) was performed by rotator evaporation at 40 °C at the appropriate pressure. Chromatographic purification was performed as flash chromatography[1] on FLUKA silica gel 60 Å (230-400 mesh) at 0.3 – 0.5 bar over-pressure. Yields refer to the purified compound.

1.2. Chemicals. All chemicals and solvents were purchased from ABCR, ACROS, ALDRICH, COMBI-BLOCKS, FLUOROCHEM, J. T. BAKER, FLUKA, MERCK, FISHER-SCIENTIFIC, TCI, STREM or LANCASTER and were used as received from the commercial supplier without further purification unless mentioned otherwise. THF, Et_2O, CH_2Cl_2, MeCN and toluene were dried on a LC TECHNOLOGY SOLUTIONS *SP-1* solvent purification system under N_2. (H_2O content < 30 ppm, Karl–Fischer titration).[2] Deuterated solvents were obtained from ARMAR CHEMICALS, Döttingen, Switzerland. Diisopropylamine and pyridine were distilled from KOH, DMPU and NEt_3 were distilled from calcium hydride under an atmosphere of dry nitrogen or high vacuum. $BF_3{\cdot}OEt_2$ was purified by a quick, heat gun promoted "bulb-to-bulb" distillation under an atmosphere of nitrogen prior to use. Aqueous buffer solutions were prepared according to the Sørensen's phosphate buffer table from 0.067 M aqueous solutions of Na_2HPO_4 and KH_2PO_4.

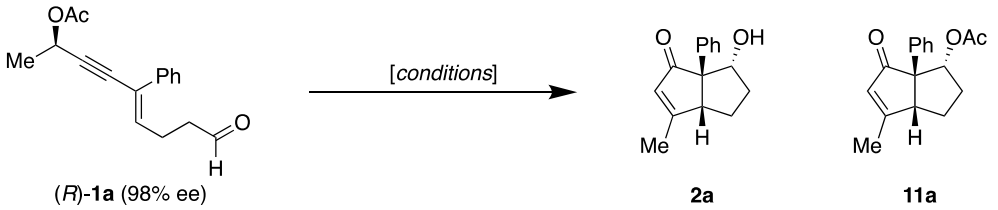
1.3. Analytics. Nuclear Magnetic Resonance (NMR) spectra were recorded on VARIAN MERCURY(300 MHz), BRUKER AV and DRX (400 MHz), BRUKER DRX and DRXII (500 MHz) or BRUKER AVIII (600 MHz with cryoprobe) spectrometers. Measurements were carried out at ambient temperature (ca. 22 °C). Chemical shifts (δ) are reported in ppm with the residual solvent signal as internal standard ($CHCl_3$ at 7.26 and 77.16 ppm for ^{1}H- and ^{13}C NMR spectroscopy, respectively; DMSO at 2.50 and 39.52 ppm), unless otherwise noted. The data is reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved,

[1] W. C. Still, M. Kahn, A. J. Mitra, *J. Org. Chem.* **1978**, *43*, 2923-2925.
[2] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520.

b = broad signal, app = apparent, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded with broadband ^{1}H-decoupling. Service measurements were performed by the NMR service team of the *Laboratorium für Organische Chemie at ETH Zürich* by Mr. *René Arnold*, Mr. *Rainer Frankenstein* and Mr. *Philipp Zumbrunnen* under direction of Dr. *Marc-Olivier Ebert*. Infrared (IR) spectra were recorded on a PERKIN ELMER TWO-FT-IR (UATR) as thin films. Absorptions are given in wavenumbers (cm^{-1}). Supercritical fluid chromatography (SFC) was performed on a JASCO 2080 PLUS system under the conditions given for each measurement. Optical rotations were measured with JASCO P-2000 POLARIMETER, 10 cm, 1.5 mL cell (c = 1.00 corresponds to 10.0 $mg \cdot mL^{-1}$). Mass spectrometry (MS) analyses were performed as high resolution EI measurements on a WATERS MICROMASS AUTOSPEC ULTIMA at 70 eV, as high resolution ESI measurements on a BRUKER DALTONICS MAXIS (UHR-TOF) instrument or as MALDI on a BRUKER SOLARIX – MALDI-FTICR-MS instrument by the mass spectrometry service of the *Laboratorium für Organische Chemie at ETH Zürich* by Mr. *Louis Bertschi*, Mr. *Oswald Greter* and Mr. *Rolf Häfliger* under direction of Dr. *Xiangyang Zhang*.

2. Optimization Studies

Selected Preliminary Results:



(*R*)-**1a** (98% ee) **2a** **11a**

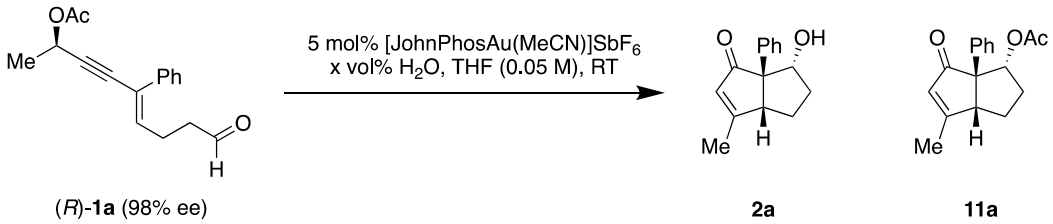
General Procedure for Optimization Studies

Aldehyde **1a** was dissolved in a solvent in an oven-dried 10 mL one-neck flask and water was added. The resulting solution was cooled to –10 °C and Au-catalyst was added in one portion. The resulting slightly yellow solution was stirred at –10 °C for 24 h. The reaction mixture was filtered through a short pad of silica gel with EtOAc, concentrated in vacuo, and purified by flash column chromatography. Diastereomeric ration was determined by ^{1}H NMR and enantiomeric excess was determined by SFC on a chiral stationary phase.

Effect of water amount

Standard Conditions: 5 mol% [JohnPhosAu(MeCN)]SbF_6, x vol% H_2O, THF (0.05M), RT

Table S1



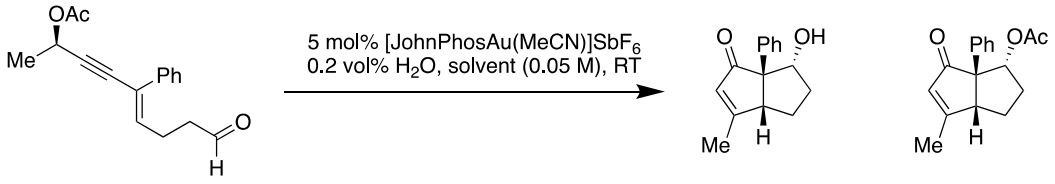
(*R*)-**1a** (98% ee) **2a** **11a**

Entry	H_2O	Yield (2a)	Yield (11a)	*dr (2a)*	*ee (2a)*	Ratio 2:11a
1	0.0%	33%	49%	67:33	92%	1.8:1
2	0.1%	59%	19%	81:19	91%	3.1:1
3	0.2%	71%	6%	85:15	91%	5.7:1
4	0.4%	76%	4%	85:15	85%	18.9:1

Solvent screening

Standard Conditions: 5 mol% [JohnPhosAu(MeCN)]SbF_6, 0.2 vol% H_2O, solvent (0.05 M), RT

Table S2



(*R*)-**1a** (98% ee) **2a** **11a**

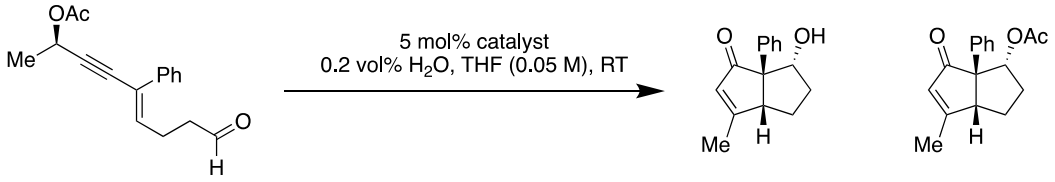
Entry	Solvent	Yield (2a)	Yield (11a)	*dr (2a)*	*ee (2a)*	Ratio 2:11a
1	Acetone	51%	23%	88:12	91%	2.2:1
2	THF	71%	6%	85:15	91%	5.7:1
3	Dioxane	50%	18%	60:40	91%	2.8:1
4	Et_2O	49%	23%	61:39	91%	2.2:1
5	MeCN	no rxn	-	-	-	-
6	CH_2Cl_2	36%	42%		92%	0.9:1
7[a]	CH_2Cl_2	19%	74%		-	1:3.9

[a] dry CH_2Cl_2 was used as solvent

Catalyst screening

Standard Conditions: 5 mol% catalyst, 0.2 vol% H_2O, THF (0.05 M), RT

Table S3



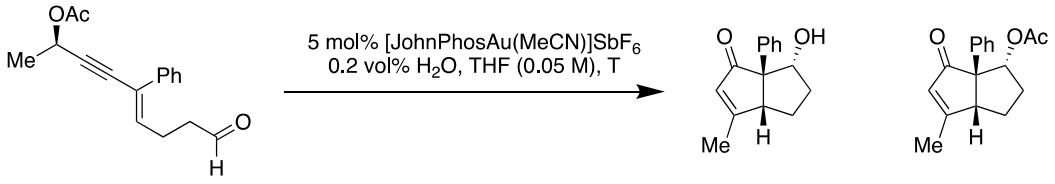
(*R*)-**1a** (98% ee) **2a** **11a**

Entry	Cat.	Yield (2a)	Yield (11a)	*dr (2)*	*ee (2)*	Ratio 2:11a
1	**$AuCl_3$**	42%	-		79%	-
2	**JohnPhos Au(MeCN)SbF6**	71%	6%	85:15	91%	5.7:1
3	**tBuXPhos Au(MeCN)SbF6**	51%	9%	65:35	96%	5.6:1
4	**Ipr AuCl + $AgSbF_6$**	61%	-	81:19	67%	-
5	**$AuCl(PPh_3)$ + $AgSbF_6$**	67%	-	81:19	44%	-

Effect of Temperature

Standard Conditions: 5 mol% [JohnPhosAu(MeCN)]SbF_6, 0.2 vol% H_2O, THF (0.05 M), Temperature

Table S4



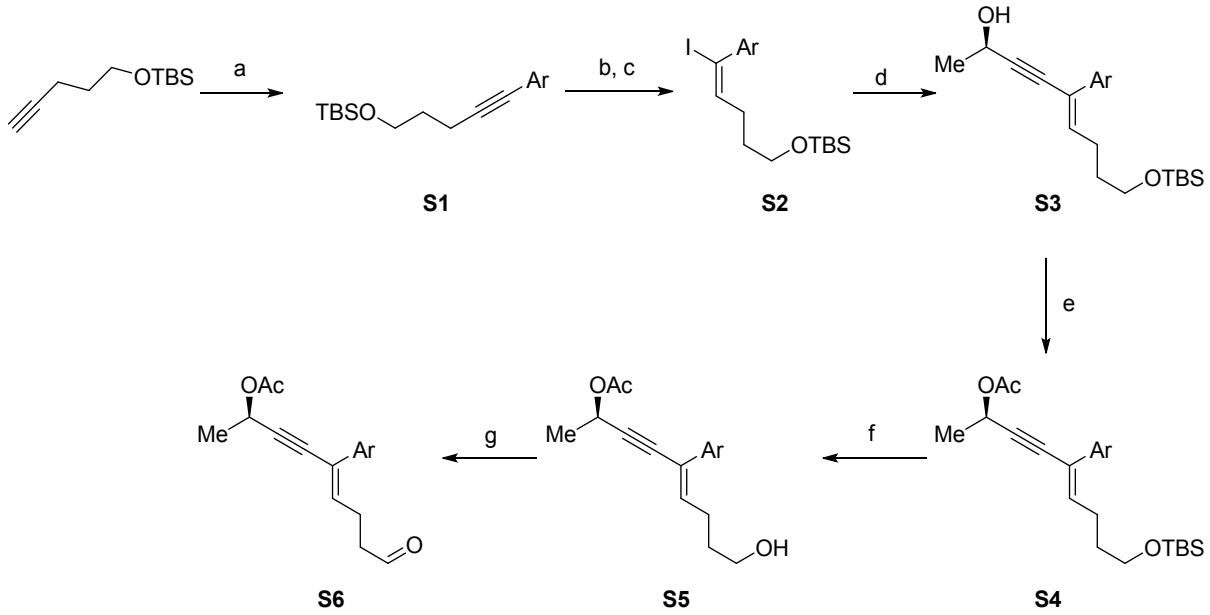
(*R*)-**1a** (98% ee) **2a** **11a**

Entry	T	rxn time	Yield (2a)	Yield (3a)	*dr (2a)*	*ee (2a)*	Ratio 2:11a
1	rt	15 min	71%	6%	85:15	91%	3.1:1
2	0 °C	60 min	73%	-	88:12	92%	-
3	–10 °C	24 h	76%	-	89:11	93%	-
4	–30 to 10°C	72 h	69%	-	92:8	93%	-

3. Synthesis and Characterization of Substrates

2.1 Synthesis of Aryl Substrates

General Procedures for Aryl-Substrate Synthesis



Reagents and conditions: a) Aryl iodide (1.3 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), Et_3N/THF (2:1), RT; b) $Pd(PPh_3)_4$ (5 mol%), nBu_3SnH (1.5 equiv), THF; c) I_2 (1.1 equiv), CH_2Cl_2, 0°C to RT; d) (R)-3-butyn-2-ol (1.3 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), Et_3N/THF (2:1); e) Ac_2O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH_2Cl_2; f) TBAF (8 equiv), THF; g) $(COCl)_2$ (1.2 equiv), DMSO (2.4 equiv), NEt_3 (5 equiv), –78 °C to –30 °C CH_2Cl_2.

Alkyne S1. To a degassed solution of 1-(*tert*-butyldimethylsilyloxy)-4-pentyne (1.0 equiv) and aryl iodide (1.0 equiv) in NEt_3/THF (2:1, 0.15 M) was added $PdCl_2(PPh_3)_2$ (0.05 equiv) and CuI (0.1 equiv) and the resulting mixture was stirred at RT for 18 h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated *in vacuo*. Purification by column chromatography afforded alkyne **S1**.

Vinyl iodide S2. To a degassed solution of alkyne **S1** (1.0 equiv) in THF (0.1 M) was added dropwise *n*Bu_3SnH (1.5 equiv) and $Pd(PPh_3)_4$ (0.1 equiv) at ambient temperature. After 60 min, the solution was partially concentrated under reduced pressure until a solid phase started to crush out and was then directly loaded onto a silica gel column. Purification by flash column chromatography afforded the corresponding vinyl stannane (hexane/EtOAc 40:1). To a solution of the vinyl stannane (1.0 equiv) in CH_2Cl_2 (0.1 M) was added I_2 (1.2 equiv) at 0 °C. After 30 min, the reaction was quenched with sat. aq. $Na_2S_2O_3$ solution and stirred vigorously for 5 min. The phases were separated and the aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography afforded vinyl iodide **S2**.

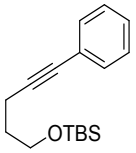
Propargyl alcohol S3. To a degassed solution of **S2** (1.0 equiv) and (*R*)-but-3-yn-2-ol (1.2 equiv) in NEt_3/THF (2:1, 0.15 M) was added $PdCl_2(PPh_3)_2$ (0.05 equiv) and CuI (0.1 equiv) and the resulting mixture was stirred at RT for 2h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated *in vacuo*. Purification by column chromatography afforded enyne **S3**.

Propargyl acetate S4. To a stirred solution of enyne **S3** (1.0 equiv) dissolved in CH_2Cl_2 (0.1 M) at ambient temperature was added pyridine (5.0 equiv), DMAP (0.2 equiv), and Ac_2O (1.5 equiv). The resulting solution was stirred for 1h before it was quenched with H_2O. The aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with sat. aq. $CuSO_4$ solution, H_2O (1x), and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided propargyl acetate **S4**.

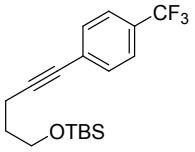
Primary alcohol S5. To a stirred solution of propargyl acetate **S4** (1.0 equiv) in dry THF (0.1 M) in at 0 °C was added TBAF (1.0 M in THF, 2 equiv). After the addition, the solution was allowed to warm to ambient temperature and stirred for another 90 min. The mixture was quenched by the addition of sat. aq. $NaHCO_3$ solution. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided primary alcohol **S5**.

Aldehyde 1. To a solution of oxalyl chloride (1.2 equiv) in CH_2Cl_2 (0.15 M) at –78 °C was added DMSO (2.4 equiv) dropwise and stirred for 15 min. Then a solution of alcohol **S5** in CH_2Cl_2 (0.05-0.1M) was added dropwise and stirred for 30min. After that time, NEt_3 (5 equiv) was added and stirred for another 30min at –78 °C and then slowly warmed to –30 °C over 30 min and then quenched by the addition of sat. aq. $NaHCO_3$ solution. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided aldehyde **1**.[3]

[3] Aldehyde **1** was found to decompose when stored in commercial CD_3Cl. Thus, filtration through basic Al_2O_3 or the use of CD_2Cl_2 is advised.

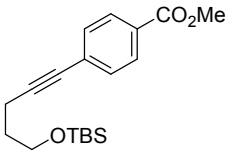


***tert*-Butyldimethyl((5-phenylpent-4-yn-1-yl)oxy)silane (S1a).** General procedure for **S1** was followed on a 3.64 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (1.86 g, 3.29 mmol, 90%). The characterization was consistant with reported values in the literature.[4]



***tert*-Butyldimethyl((5-(4-(trifluoromethyl)phenyl)pent-4-yn-1-yl)oxy)silane (S1b).** General procedure for **S1** was followed on a 1.83 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (585 mg, 1.71 mmol, 93%).

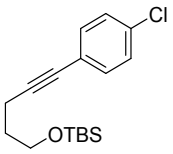
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 3.76 (t, *J* = 6.0 Hz, 4H), 2.52 (t, *J* = 7.0 Hz, 4H), 2.01 – 1.74 (m, 3H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.9, 125.2 (q, *J* = 3.7 Hz), 93.0, 79.8, 61.7, 31.7, 26.1, 18.5, 16.0, -5.2. **IR** (neat) 2954, 2931, 2897, 2858, 2233, 2105, 1921, 1616, 1571, 1516, 1472, 1464, 1431, 1406, 1389, 1361, 1322, 1255, 1166, 1128, 1104, 1067, 1018, 1007, 982, 953, 940, 835, 814, 775, 737, 699, 681, 663, 597, 563, 520, 497, 466 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{25}NaF_3OSi$ $[M+Na]^+$ 365.1519, found 365.1516.



Methyl 4-(5-((tert-butyldimethylsilyl)oxy)pent-1-yn-1-yl)benzoate (S1c). General procedure for **S1** was followed on a 3.02 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (988 mg, 2.97 mmol, 98%).

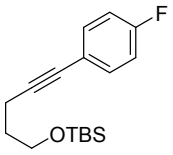
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.73 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.82, 137.87, 131.59, 129.55, 129.00, 93.61, 80.36, 61.69, 52.30, 31.73, 26.10, 18.52, 16.09, -5.16. **IR** (neat) 2952, 2929, 2897, 1857, 2229, 2080, 1930, 1724, 1607, 1588, 1560, 1508, 1472, 1463, 1435, 1406, 1390, 1361, 1307, 1272, 1257, 1192, 1175, 1104, 1070, 1019, 1009, 982, 956, 857, 834, 769, 756, 709, 697, 663, 566, 528, 456 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{19}H_{28}NaO_3Si$ $[M+Na]^+$ 355.1700, found 355.1700.

[4] F. Pape, N. O. Thiel, J. F. Teichert, *Chem. Eur. J.* **2015**, *21*, 15934-15938.



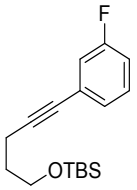
***tert*-Butyl((5-(4-chlorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1d).** General procedure for **S1** was followed on a 2.10 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (630 mg, 2.04 mmol, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 1.88 – 1.76 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.57, 132.89, 128.64, 122.67, 91.16, 79.79, 61.72, 31.79, 26.10, 18.52, 15.97, -5.16. **IR** (neat) 2953, 2929, 2896, 2857, 2230, 2048, 1899, 1646, 1594, 1490, 1472, 1464, 1430, 1389, 1361, 1350, 1326, 1287, 1255, 1189, 1104, 1093, 1071, 1015, 1007, 983, 951, 828, 775, 751, 719, 663, 582, 524, 498 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{25}OSi$ $[M-Cl]^+$ 273.1669, found 273.1672.



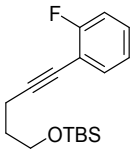
***tert*-Butyl((5-(4-fluorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1e).** General procedure for **S1** was followed on a 3.60 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (982 mg, 3.36 mmol, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 1H), 7.08 – 6.84 (m, 1H), 3.75 (t, *J* = 6.0 Hz, 1H), 2.48 (t, *J* = 7.0 Hz, 1H), 2.01 – 1.74 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 248.1 Hz), 133.4 (d, *J* = 8.2 Hz), 120.2 (d, *J* = 3.5 Hz), 115.5 (d, *J* = 21.9 Hz), 89.7 (d, *J* = 1.5 Hz), 79.8, 61.8, 31.9, 26.1, 18.5, 15.9, -5.2. **IR** (neat) 3050, 2953, 2930, 2897, 2858, 2232, 2037, 1888, 1645, 1603, 1507, 1472, 1464, 1444, 1431, 1388, 1361, 1350, 1328, 1294, 1256, 1231, 1189, 1155, 1104, 1070, 1007, 983, 952, 940, 833, 775, 721, 664, 634, 575, 527 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{25}FNaOSi$ $[M+Na]^+$ 315.1551, found 315.1551.



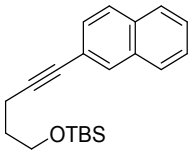
***tert*-Butyl((5-(3-fluorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1f).** General procedure for **S1** was followed on a 4.03 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (1.06 g, 3.61 mmol, 89%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 1H), 7.16 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.07 (ddd, *J* = 9.6, 2.6, 1.4 Hz, 1H), 7.02 – 6.92 (m, 1H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.72 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245.9 Hz), 129.8 (d, *J* = 8.8 Hz), 127.5 (d, *J* = 3.0 Hz), 126.1 (d, *J* = 9.6 Hz), 118.5 (d, *J* = 22.5 Hz), 115.0 (d, *J* = 21.2 Hz), 91.2, 79.8 (d, *J* = 3.3 Hz), 61.7, 31.8, 26.1, 18.5, 15.9, -5.2. **IR** (neat) 2953, 2929, 2896, 2857, 2231, 1571, 1482, 1472, 1462, 1361, 1326, 1258, 1217, 1189, 1103, 1070, 1032, 1002, 986, 955, 832, 816, 775, 753, 677, 661, 572 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{25}FNaOSi$ $[M+Na]^+$ 315.1551, found 315.1551.



***tert*-Butyl((5-(2-fluorophenyl)pent-4-yn-1-yl)oxy)dimethylsilane (S1g).** General procedure for **S1** was followed on a 4.59 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (976 mg, 3.34 mmol, 73%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

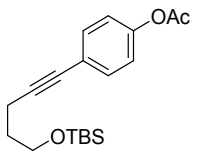
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (td, *J* = 7.6, 1.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.12 – 6.98 (m, 2H), 3.77 (t, *J* = 6.1 Hz, 2H), 2.54 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.77 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.2, 161.7, 133.6 (d, *J* = 1.6 Hz), 129.2 (d, *J* = 7.9 Hz), 123.9 (d, *J* = 3.7 Hz), 115.5 (d, *J* = 21.2 Hz), 95.5 (d, *J* = 3.3 Hz), 74.2 (d, *J* = 1.1 Hz), 61.7, 31.77, 26.1, 18.5, -5.2. **IR** (neat) 2953, 2929, 2896, 2857, 2235, 1574, 1493, 1472, 1463, 1454, 1389, 1361, 1326, 1255, 1217, 1189, 1103, 1070, 1032, 1006, 983, 954, 939, 833, 818, 775, 753, 677, 661, 577, 509 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{25}FNaOSi$ $[M+Na]^+$ 315.1551, found 315.1551.



***tert*-Butyldimethyl((5-(naphthalen-2-yl)pent-4-yn-1-yl)oxy)silane (S1h).** General procedure for **S1** was followed including heating at 70 °C for 7h on a 3.62 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (600 mg, 1.85 mmol, 51%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

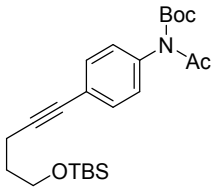
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 1H), 7.84 – 7.71 (m, 3H), 7.53 – 7.38 (m, 3H), 3.80 (t, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 1.93 – 1.80 (m, 2H), 0.93 (d, *J* = 0.5 Hz, 9H), 0.10 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.3, 132.7, 131.3, 129.0, 128.0, 127.9, 127.8, 126.6, 126.5, 121.6, 90.6, 81.3, 61,9., 32.1, 26.2, 16.2, -5.0. **IR** (neat) 3059, 2953, 2928, 2896, 2856, 1628, 1598, 1502, 1471, 1463, 1431, 1388, 1361, 1324,

1254, 1188, 1102, 1071, 1006, 990, 960, 939, 891, 833, 815, 775, 745, 721, 663, 610, 542, 474 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{28}NaOSi$ $[M+Na]^+$ 347.1802, found 347.1802.



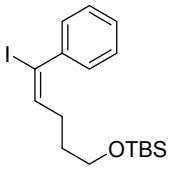
4-(5-((*tert*-Butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl acetate (S1i). General procedure for **S1** was followed on a 4.03 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, yellow oil (1.32 g, 3.97 mmol, 98%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 3.75 (t, *J* = 6.0 Hz, 1H), 2.48 (t, *J* = 7.0 Hz, 1H), 2.29 (s, 2H), 1.95 – 1.75 (m, 1H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.34, 150.03, 132.76, 121.90, 121.62, 90.14, 80.03, 61.74, 31.86, 26.11, 21.27, 18.52, 15.94, -5.15. **IR** (neat) 2953, 2929, 2896, 2857, 1768, 1602, 1505, 1472, 1431, 1369, 1255, 1191, 1164, 1102, 1070, 1009, 983, 951, 909, 834, 775, 719, 688, 663, 593, 532, 501 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{19}H_{28}NaO_3Si$ $[M+Na]^+$ 355.1700, found 355.1700.

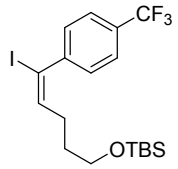


***tert*-Butylacetyl(4-(5-((tert-butyldimethylsilyl)oxy)pent-1-yn-1-yl)phenyl)carbamate (S1j).** General procedure for **S1** was followed on a 2.77 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, yellow oil (1.04 g, 2.41 mmol, 87%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.10 – 6.93 (m, 2H), 3.75 (t, *J* = 6.0 Hz, 2H), 2.56 (s, 3H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.37 (s, 9H), 0.91 (s, 9H), 0.08 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.99, 152.68, 138.16, 132.27, 128.21, 123.84, 90.81, 83.49, 80.28, 61.74, 31.84, 27.97, 26.59, 26.11, 18.51, 15.97, -5.16. **IR** (neat) 2954, 2931, 2858, 1740, 1712, 1510, 1473, 1462, 1429, 1394, 1370, 1304, 1282, 1255, 1156, 1098, 1028, 1016, 983, 947, 922, 836, 775, 727, 663, 612, 545, 486, cm^{-1}. **HRMS (ESI):** m/z calcd for $C_{24}H_{38}NFO_4Si$ $[M+H]^+$ 432.2565, found 432.2566.

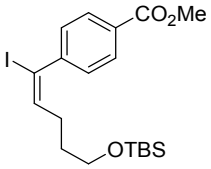


(*E*)-*tert*-Butyl((5-iodo-5-phenylpent-4-en-1-yl)oxy)dimethylsilane (S2a). General procedure for **S2** was followed on a 13.81 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (4.6 g, 11.43 mmol, 97%). The characterization was consistant with reported values in the literature.[5]



(*E*)-*tert*-Butyl((5-iodo-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl)oxy)dimethylsilane (S2b). General procedure for **S2** was followed on a 2.86 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (962 mg, 2.05 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.0, 2H), 6.57 (t, *J* = 7.8 Hz, 1H), 3.55 (t, *J* = 6.1 Hz, 2H), 2.15 – 1.98 (m, 2H), 1.66 – 1.51 (m, 2H), 0.82 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.7, 129.4, 125.5, 125.5 (q, *J* = 3.7 Hz), 125.4, 125.4, 92.4, 62.2, 32.3, 29.1, 26.1, 18.4, -5.1. **IR** (neat) 2954, 2930, 2896, 2858, 2087, 1923, 1613, 1576, 1472, 1464, 1405, 1388, 1361, 1322, 1256, 1167, 1129, 1107, 1066, 1019, 1007, 955, 939, 865, 834, 775, 742, 715, 681, 662, 604, 506, 486 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{26}F_3INaOSi$ $[M+Na]^+$ 493.0642, found 493.0638.

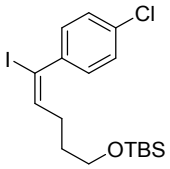


(*E*)-Methyl 4-(5-((tert-butyldimethylsilyl)oxy)-1-iodopent-1-en-1-yl)benzoate (S2c). General procedure for **S2** was followed on a 2.97 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (1.10 g, 2.39 mmol, 80%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.89 (m, 2H), 7.42 – 7.31 (m, 2H), 6.55 (t, *J* = 7.7 Hz, 1H), 3.92 (s, 3H), 3.54 (t, *J* = 6.2 Hz, 2H), 2.05 (q, *J* = 7.6 Hz, 2H), 1.66 – 1.50 (m, 2H), 0.83 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 146.3, 144.3, 129.6, 129.0, 93.1, 62.2, 52.3, 32.3, 29.0, 26.0, 18.4, -5.2. **IR** (neat)

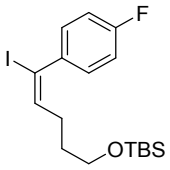
[5] K. Murai, A. Nakamura, T. Matsushita, M. Shimura, H. Fujioka, *Chem. Eur. J.* **2012**, *18*, 8448-8453.

2952, 2928, 2856, 1725, 1605, 1465, 1471, 1463, 1435, 1402, 1361, 1309, 1273, 1255, 1179, 1102, 1020, 1006, 966, 939, 834, 809, 771, 712, 682, 662, 560, 478 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{19}H_{29}INaO_3Si$ $[M+Na]^+$ 483.0823, found 483.0822.



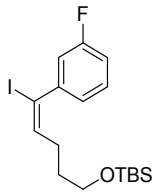
(*E*)-*tert*-Butyl((5-(4-chlorophenyl)-5-iodopent-4-en-1-yl)oxy)dimethylsilane (S2d). General procedure for **S2** was followed on a 1.94 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorlesjs oil (650 mg, 1.49 mmol, 77%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 6.54 (t, *J* = 7.7 Hz, 1H), 3.57 (t, *J* = 6.2 Hz, 2H), 2.08 (q, *J* = 7.6 Hz, 2H), 0.95 (t, *J* = 7.2 Hz, 2H), 0.87 (s, 9H), 0.03 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 140.3, 133.9, 130.2, 128.5, 93.2, 62.2, 32.3, 28.9, 26.0, 18.4, -5.2. **IR** (neat) 2954, 2928, 2856, 1590, 1486, 1471, 1463, 1394, 1361, 1255, 1193, 1092, 1015, 940, 834, 814, 774, 729, 662, 581, 557, 483 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{27}ClIOSi$ $[M+H]^+$ 437.0559, found 437.0558.



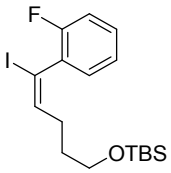
(*E*)-*tert*-Butyl((5-(4-fluorophenyl)-5-iodopent-4-en-1-yl)oxy)dimethylsilane (S2e). General procedure for **S2** was followed on a 3.21 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, light brown oil (750 mg, 1.78 mmol, 55%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.03 – 6.94 (m, 2H), 6.50 (t, *J* = 7.7 Hz, 1H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.05 (q, *J* = 7.6 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 2H), 0.84 (s, 9H), 0.00 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4, 160.9, 130.7 (d, *J* = 8.3 Hz), 115.3 (d, *J* = 21.7 Hz), 93.6 , 62.2 , 32.3 , 28.9 , 26.0 , 18.4 , -5.2 .**IR** (neat) 2954, 2928, 2856, 1770, 1598, 1505, 1471, 1463, 11387, 1361, 1253, 1232, 1174, 1157, 1099, 1006, 939, 834, 774, 719, 661, 623, 558, 511 cm^{-1}.**HRMS (MALDI):** m/z calcd for $C_{17}H_{26}FINaOSi$ $[M+Na]^+$ 443.0674, found 443.0673.



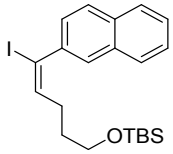
(*E*)-*tert*-Butyl((5-(3-fluorophenyl)-5-iodopent-4-en-1-yl)oxy)dimethylsilane (S2f). General procedure for **S2** was followed on a 3.56 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (1.04 g, 2.47 mmol, 63%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 1H), 7.06 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.03 – 6.89 (m, 2H), 6.51 (t, *J* = 7.7 Hz, 1H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.07 (q, *J* = 7.6 Hz, 2H), 1.63 – 1.51 (m, 2H), 0.84 (s, 9H), -0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.5, 161.1, 144.1, 129.8 (d, *J* = 8.4 Hz), 124.6 (d, *J* = 2.9 Hz), 116.0 (d, *J* = 22.1 Hz), 115.1 (d, *J* = 21.1 Hz), 92.7 (d, *J* = 2.3 Hz), 62.2, 32.3, 29.0, 26.0, 18.4, -5.2. **IR** (neat) 2953, 2928, 2895, 2856, 1608, 1582, 1472, 1463, 1431, 1388, 1361, 1286, 1254, 1232, 1191, 1134, 1101, 1028, 1006, 966, 939, 875, 834, 814, 774, 698, 681, 662, 572, 521 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{26}NaFIOSi$ $[M+H]^+$ 420.0776, found 420.0766.



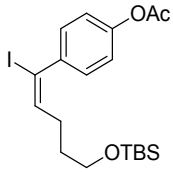
(*E*)-*tert*-Butyl((5-(2-fluorophenyl)-5-iodopent-4-en-1-yl)oxy)dimethylsilane (S2g). General procedure for **S2** was followed on a 3.16 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (1.20 g, 2.85 mmol, 90%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.15 – 7.07 (m, 1H), 7.05 – 6.97 (m, 1H), 6.61 (t, *J* = 7.7 Hz, 1H), 3.53 (t, *J* = 6.3 Hz, 2H), 1.95 (dd, *J* = 15.1, 7.7 Hz, 1H), 1.62 – 1.55 (m, 2H), 0.83 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 157.3, 146.1, 131.0 (d, *J* = 2.5 Hz), 130.1 (d, *J* = 8.2 Hz), 124.2 (d, *J* = 3.7 Hz), 116.0 (d, *J* = 21.8 Hz), 84.9, 62.3, 31.9, 29.3, 26.0, 18.4, -5.2. **IR** (neat) 2953, 2928, 2856, 166, 1577, 1486, 1472, 1463, 1450, 1388, 1361, 1255, 1226, 1193, 1100, 1031, 1006, 939, 83, 775, 754, 659, 590 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{26}NaFIOSi$ $[M+H]^+$ 420.0776, found 420.0765.



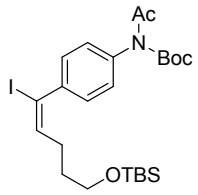
(*E*)-*tert*-Butyl((5-iodo-5-(naphthalen-2-yl)pent-4-en-1-yl)oxy)dimethylsilane (S2h). General procedure for **S2** was followed on a 1.85 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (670 mg, 1.48 mmol, 80%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.76 (m, 3H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.59 (t, *J* = 7.7 Hz, 1H), 3.54 (t, *J* = 6.3 Hz, 2H), 2.11 (q, *J* = 7.6 Hz, 2H), 1.64 – 1.57 (m, 2H), 0.80 (s, 9H), -0.02 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.5, 139.2, 133.0, 132.9, 128.3, 128.1, 127.8, 127.5, 127.0, 126.6, 126.5, 95.2, 62.4, 32.4, 29.0, 26.0, 18.4, -5.2. **IR** (neat) 3056, 2954, 2928, 2856, 1770, 1596, 1503, 1471, 1463, 1387, 1361, 1251, 1189, 1100, 1006, 961, 834, 816, 774, 754, 714, 663, 597, 563, 476 cm_{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{29}INaOSi$ $[M+Na]^+$ 475.0925, found 475.0924.



(*E*)-4-(5-((*tert*-Butyldimethylsilyl)oxy)-1-iodopent-1-en-1-yl)phenyl acetate (S2i). General procedure for **S2** was followed on a 3.61 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (826 mg, 1.79 mmol, 50%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

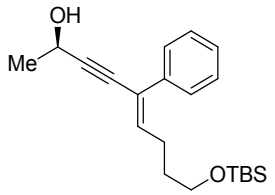
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.06 – 7.01 (m, 2H), 6.51 (t, *J* = 7.7 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.30 (s, 3H), 2.07 (q, *J* = 7.6 Hz, 2H), 1.66 – 1.51 (m, 2H), 0.85 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.3, 150.2, 143.8, 139.3, 130.1, 121.4, 93.8, 62.3, 32.4, 28.9, 26.1, 21.3, 18.4, -5.2. **IR** (neat) 2953, 2928, 2894, 2856, 2101, 1765, 1598, 1499, 1471, 1463, 1432, 1405, 1368, 1254, 1193, 1165, 1100, 1017, 1008, 940, 911, 834, 814, 774, 736, 714, 683, 663, 640, 605, 593, 521 cm^{-1}.



(*E*)-*tert*-Butyl-acetyl(4-(5-((tert-butyldimethylsilyl)oxy)-1-iodopent-1-en-1-yl)phenyl)-carbamate (S2j). General procedure for **S2** was followed on a 0.95 mmol scale. The crude product was purified by flash

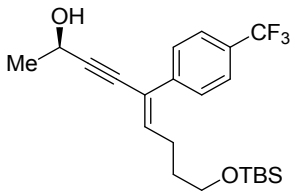
column chromatography on silica gel (hexane/EtOAc 20:1). The title compound was isolated as clear, colorless oil (450 mg, 0.80 mmol, 84%). Purification by standard column chromatography proofed difficult and lead to the isolation of the product containing minor impurities (purity >85%). The product was used in the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.08 – 6.95 (m, 2H), 6.52 (t, *J* = 7.6 Hz, 1H), 3.55 (t, *J* = 6.4 Hz, 2H), 2.57 (s, 3H), 2.18 – 1.98 (m, 2H), 1.66 – 1.53 (m, 2H), 1.38 (s, 9H), 0.87 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.9, 152.7, 143.8, 141.1, 138.7, 129.5, 128.0, 93.8, 83.5, 62.4, 32.3, 28.9, 27.9, 26.6, 26.1, 18.4, -5.2. **IR** (neat) 2929, 2857, 1739, 1711, 1601, 1504, 1472, 1393, 1370, 1338, 1300, 1272, 1254, 1156, 1097, 1028, 1016, 923, 836, 774, 748, 690, 662, 619 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{24}H_{39}NNaO_4Si$ $[M+Na]^+$ 582.1507, found 582.1498.



(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-phenylnon-5-en-3-yn-2-ol (S3a). General procedure for **S3** was followed on a 11.43 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (3.1 g, 9.00 mmol, 79%).

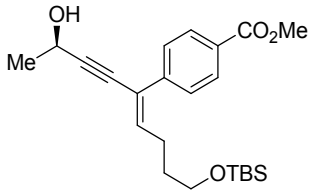
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 6.19 (t, *J* = 7.7 Hz, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 1.86 (s, 1H), 1.68 – 1.56 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 137.5, 128.8, 128.3, 127.6, 123.1, 88.9, 86.1, 62.5, 59.0, 32.7, 26.2, 26.0, 24.6, 18.4, -5.2. **IR** (neat) 3508, 3059, 3023, 2854, 2929, 2885, 2857, 2215, 1673, 1600, 1494, 1472, 1463, 1444, 1388, 1362, 1329, 1255, 1186, 1144, 1095, 1031, 1007, 964, 939, 920, 907, 891, 835, 813, 775, 662, 589, 527 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{32}NaO_2Si$ $[M+Na]^+$ 367.2064, found 367.2064. $[\alpha]_D^{26}$ = +11.3 (c = 1.0, $CHCl_3$).



(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-ol (S3b). General procedure for **S3** was followed on a 0.79 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (244 mg, 0.59 mmol, 75%).

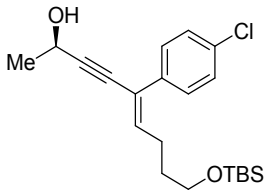
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.26 (t, *J* = 7.8 Hz, 1H), 4.65 (t, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 1.80 (s, 1H), 1.71 – 1.56 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 129.2, 125.3 (q, *J* = 3.8 Hz), 122.1, 89.6, 85.3, 62.3, 59.0, 32.6, 26.3, 26.0, 24.6, 18.4, -5.2. **IR** (neat) 3339, 2955, 2931, 2887, 2859, 1618, 1472,

1464, 1408, 1389, 1362, 1325, 1256, 1167, 1128, 1110, 1066, 1020, 940, 911, 36, 814, 776, 710, 662, 622, 493, 469 cm^{-1}. **HRMS (ESI):** m/z calcd for $C_{22}H_{31}F_3NaO_2Si$ $[M+Na]^+$ 435.1938, found 435.1934. $[\alpha]_D^{26}$ = +10.2 (c = 1.0, $CHCl_3$).



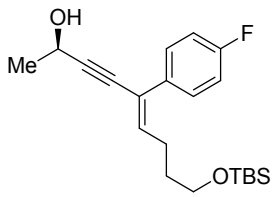
(*R*,*E*)-Methyl4-(9-((*tert*-butyldimethylsilyl)oxy)-2-hydroxynon-5-en-3-yn-5-yl)-benzoate (S3c). General procedure for **S3** was followed on a 1.13 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, yellow oil (330 mg, 0.82 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 7.86 (m, 2H), 7.68 – 7.37 (m, 2H), 6.25 (t, *J* = 7.8 Hz, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 3.92 (s, 3H), 3.57 (t, *J* = 6.2 Hz, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 1.88 (s, 1H), 1.71 – 1.56 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.84 (s, 9H), -0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 142.2, 141.7, 129.6, 129.2, 128.8, 122.4, 89.5, 85.3, 62.4, 59.0, 52.3, 32.6, 26.3, 26.0, 24.5, 18.4, -5.2. **IR** (neat) 3426, 2953, 2930, 2886, 2857, 1724, 1609, 1565, 1472, 1463, 1436, 1405, 1389, 1362, 1311, 1278, 1256, 1191, 1144, 1104, 1021, 966, 911, 892, 835, 775, 707, 663, 591, 498 cm^{-1}. $[\alpha]_D^{26}$ = +11.1 (c = 1.0, $CHCl_3$).



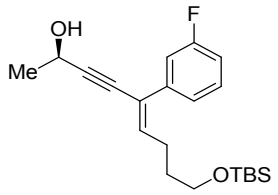
(R,E)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(4-chlorophenyl)non-5-en-3-yn-2-ol (S3d). General procedure for **S3** was followed on a 1.26 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (350 mg, 0.92 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 6.19 (t, *J* = 7.7 Hz, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.25 (q, *J* = 7.6 Hz, 2H), 1.81 (s, 1H), 1.69 – 1.55 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 135.9, 133.4, 130.2, 128.5, 122.1, 89.3, 85.6, 62.4, 59.0, 32.6, 26.3, 26.0, 24.6, 18.4, -5.2. **IR** (neat) 3347, 2954, 2930, 2886, 2858, 1594, 1491, 1472, 1396, 1362, 1329, 1256, 1144, 1094, 1016, 940, 910, 835, 776, 720, 663, 590, 511 cm^{-1}. $[\alpha]_D^{26}$ = +10.8 (c = 1.0, $CHCl_3$).



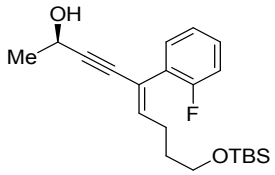
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(4-fluorophenyl)non-5-en-3-yn-2-ol (S3e). General procedure for **S3** was followed on a 1.31 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (330 mg, 0.91 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.09 – 6.93 (m, 2H), 6.18 (t, *J* = 7.7 Hz, 1H), 4.77 – 4.58 (m, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.26 (q, *J* = 7.6 Hz, 2H), 1.78 (s, 1H), 1.68 – 1.57 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.8 Hz), 140.5, 133.4 (d, *J* = 3.5 Hz), 130.5 (d, *J* = 8.1 Hz), 122.1, 115.2 (d, *J* = 21.5 Hz), 89.1 , 85.9, 62.4, 59.0, 32.7, 26.2, 26.0, 24.6, 18.4, -5.2. **IR** (neat) 3333, 2955, 2930, 2858, 1603, 1509, 1472, 1362, 1256, 1226, 1159, 1143, 1100, 1007, 940, 837, 776, 725, 662, 573, 526, 484, 464, 695, 613, 504, 487, 460 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{31}NaFO_2Si$ $[M+Na]^+$ 385.1970, found 385.1969. $[\alpha]_D^{26}$ = +11.8 (c = 1.0, $CHCl_3$).



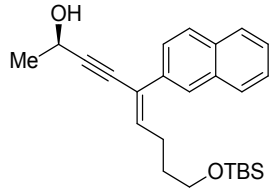
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(3-fluorophenyl)non-5-en-3-yn-2-ol (S3f). General procedure for **S3** was followed on a 0.95 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (265 mg, 0.73 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 1H), 7.16 – 7.09 (m, 1H), 7.06 (ddd, *J* = 9.9, 2.6, 1.6 Hz, 1H), 6.97 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.21 (t, *J* = 7.7 Hz, 1H), 4.78 – 4.58 (m, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 1.81 (s, 1H), 1.70 – 1.58 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **^{3}C NMR** (101 MHz, $CDCl_3$) δ 162.7 (d, *J* = 245.8 Hz), 141.2, 139.6 (d, *J* = 7.7 Hz), 129.7 (d, *J* = 8.3 Hz), 124.6 (d, *J* = 2.9 Hz), 122.1 (d, *J* = 2.3 Hz), 115.8 (d, *J* = 22.0 Hz), 114.5 (d, *J* = 21.1 Hz), 89.3, 85.5, 62.4, 59.0, 32.6, 26.3, 26.0, 24.6, 18.4, -5.2. **IR** (neat) 3343, 2954, 2930, 2886, 2858, 1611, 1581, 1486, 1472, 1463, 1438, 1388, 1362, 1329, 1256, 1209, 1158, 1095, 1007, 964, 924, 884, 835, 814, 776, 704, 662, 594, 520, 460 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{31}FNaO_2Si$ $[M+Na]^+$ 385.1970, found 385.1968. $[\alpha]_D^{26}$ = +11.8 (c = 1.0, $CHCl_3$).



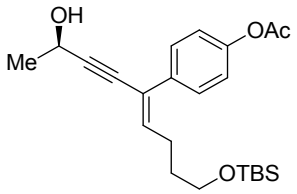
(*R*,*Z*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(2-fluorophenyl)non-5-en-3-yn-2-ol (S3g) General procedure for **S3** was followed on a 1.19 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (308 mg, 0.85 mmol, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.02 (m, 1H), 6.29 (t, *J* = 7.7 Hz, 1H), 4.63 (q, *J* = 6.6 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.63 – 1.53 (m, 2H), 1.46 (d, *J* = 6.6 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). **^{3}C NMR** (101 MHz, $CDCl_3$) δ 159.4 (d, *J* = 247.7 Hz), 143.1, 131.1 (d, *J* = 3.5 Hz), 129.6 (d, *J* = 8.1 Hz), 125.1 (d, *J* = 16.0 Hz), 124.1 (d, *J* = 3.6 Hz), 116.8, 115.9 (d, *J* = 22.3 Hz), 88.9, 85.0, 62.6, 59.0, 32.1, 26.6 (d, *J* = 2.2 Hz), 26.0, 24.5, 18.4, -5.2. **IR** (neat) 3354, 2954, 2930, 2886, 2857, 1611, 1579, 1491, 1472, 1463, 1450, 1388, 1361, 1329, 1255, 1220, 1143, 1100, 1032, 1007, 940, 911, 836, 776, 757, 662, 593, 521 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{31}FNaO_2Si$ $[M+Na]^+$ 385.1970, found 385.1970. $[\alpha]_D^{26}$ = +12.5 (c = 1.0, $CHCl_3$).



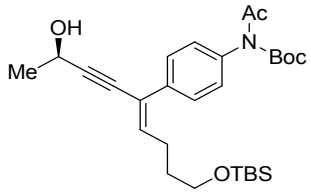
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(naphthalen-2-yl)non-5-en-3-yn-2-ol (S3h). General procedure for **S3** was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, yellow oil (131 mg, 0.33 mmol, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.87 – 7.79 (m, 3H), 7.79 – 7.76 (m, 1H), 7.54 – 7.43 (m, 3H), 6.28 (t, *J* = 7.7 Hz, 1H), 4.69 (q, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.3 Hz, 2H), 2.34 (q, *J* = 7.6 Hz, 2H), 1.84 (s, 1H), 1.72 – 1.60 (m, 2H), 1.50 (d, *J* = 6.6 Hz, 3H), 0.82 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 135.0, 133.2, 132.8, 128.2, 127.9, 127.8, 126.9, 126.3, 126.2, 123.1, 89.2, 86.0, 62.6, 59.1, 32.8, 26.4, 26.0, 24.6, 18.4, -5.2. **IR** (neat) 3346, 3057, 2953, 2929, 2885, 2857, 1599, 1504, 1471, 1463, 1435, 1388, 1361, 1329, 1255, 1185, 1141, 1096, 1007, 940, 899, 835, 776, 747, 662, 568, 524, 478 cm^{-1}. **HRMS (ESI):** m/z calcd for $C_{25}H_{34}NaO_2Si$ $[M+Na]^+$ 417.2220, found 417.2221. $[\alpha]_D^{26}$ = +10.9 (c = 1.0, $CHCl_3$).



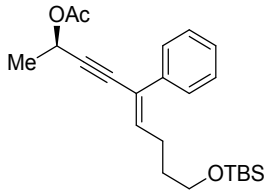
(*R*,*E*)-4-(9-((*tert*-Butyldimethylsilyl)oxy)-2-hydroxynon-5-en-3-yn-5-yl)phenyl acetate (S3i). General procedure for **S3** was followed on a 0.95 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, yellow oil (252 mg, 0.63 mmol, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.19 (t, *J* = 7.7 Hz, 1H), 4.91 – 4.53 (m, 1H), 3.59 (t, *J* = 6.2 Hz, 2H), 2.32 – 2.22 (m, 5H), 1.80 (s, 1H), 1.66 – 1.60 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 150.0, 140.6, 135.0, 129.9, 122.2, 121.4, 89.1, 85.9, 62.5, 59.0, 32.7, 26.3, 26.1, 24.6, 21.3, 18.4, -5.2. **IR** (neat) 3415, 2954, 2930, 2886, 2857, 1761, 1603, 1506, 1472, 1463, 1369, 1329. 1255, 1198, 1167, 1144, 1096, 1010, 940, 913, 836, 776, 712, 662, 629, 593, 530 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{23}H_{34}NaO_4Si$ $[M+Na]^+$ 425.2119, found 425.2119. $[\alpha]_D^{26}$ = +8.6 (c = 1.0, $CHCl_3$).



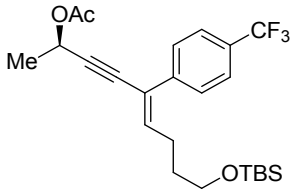
(*R*,*E*)-*tert*-Butylacetyl(4-(9-((tert-butyldimethylsilyl)oxy)-2-hydroxynon-5-en-3-yn-5-yl)phenyl)carbamate (S3j). General procedure for **S3** was followed on a 0.63 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, yellow oil (192 mg, 0.38 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.21 (t, *J* = 7.7 Hz, 1H), 4.84 – 4.45 (m, 1H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.57 (s, 6H), 2.28 (q, *J* = 7.6 Hz, 2H), 1.80 (d, *J* = 5.3 Hz, 1H), 1.68 – 1.58 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.39 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 152.8, 140.9, 138.1, 136.9, 129.5, 128.0, 122.4, 89.1, 85.8, 83.5, 62.6, 59.0, 32.7, 28.0, 26.7, 26.3, 26.1, 24.6, 18.5, -5.2. **IR** (neat) 3419, 2954, 2931, 2887, 2858, 1740, 1712, 1606, 1510, 1473, 1462, 1394, 1370, 1303, 1272, 1255, 1156, 1097, 1029, 1016, 947, 923, 837, 775, 739, 662, 629, 529, 489 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{28}H_{43}NNaO_5Si$ $[M+Na]^+$ 524.2803, found 524.2803. $[\alpha]_D^{26}$ = +8.0 (c = 1.0, $CHCl_3$).



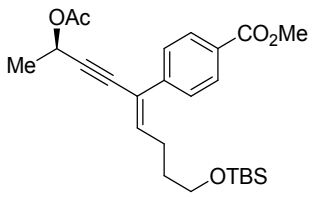
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-phenylnon-5-en-3-yn-2-yl acetate (S4a). General procedure for **S4** was followed on a 5.78 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (2.23 g, 5.77 mmol, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 6.22 (t, *J* = 7.7 Hz, 1H), 5.60 (q, *J* = 6.7 Hz, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.66 – 1.57 (m, 2H), 1.51 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 141.1, 137.2, 128.8, 128.3, 127.6, 122.9, 86.6, 85.3, 62.6, 61.1, 32.7, 26.3, 26.1, 21.7, 21.3, 18.4, -5.2. **IR** (neat) 2954, 2930, 2886, 2857, 2226, 1743, 1600, 1495, 1472, 1463, 1445, 1371, 1340, 1307, 1232, 1154, 1098, 1068, 1030, 948, 835, 814, 775, 699, 662, 610 , 567, 526 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{23}H_{34}NaO_3Si$ $[M+Na]^+$ 409.2169, found 409.2171. $[\alpha]_D^{26}$ = +73.0 (c = 1.0, $CHCl_3$).



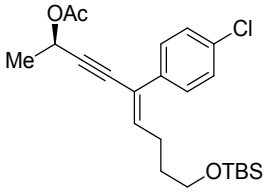
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-yl acetate (S4b). General procedure for **S4** was followed on a 0.58 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (259 mg, 0.57 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.51 (m, 2H), 7.46 (dt, *J* = 7.7, 0.9 Hz, 2H), 6.30 (t, *J* = 7.8 Hz, 1H), 5.58 (q, *J* = 6.7 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 2.28 (q, *J* = 7.7 Hz, 2H), 2.07 (s, 3H), 1.62 (m, 2H), 1.51 (d, *J* = 6.7 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 142.5, 140.9, 129.2, 125.3 (q, *J* = 3.8 Hz), 121.9, 86.1, 85.8, 62.3, 61.0, 32.5, 26.3, 26.0, 21.6, 21.3, 18.4, -5.2. **IR** (neat) 2954, 2932, 2887, 2858, 1745, 1618, 1473, 1408, 1371, 1325, 1234, 1167, 1127, 1109, 1066, 1019, 948, 836, 776, 711, 662, 622, 528, 495, 471 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{24}H_{33}F_3NaO_3Si$ $[M+Na]^+$ 477.2043, found 477.2043. $[\alpha]_D^{26}$ = +70.7 (c = 1.0, $CHCl_3$).



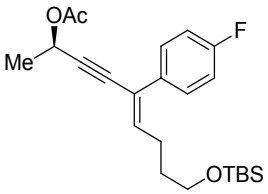
(*R*,*E*)-Methyl 4-(2-acetoxy-9-((*tert*-butyldimethylsilyl)oxy)non-5-en-3-yn-5-yl)benzoate (S4c). General procedure for **S4** was followed on a 0.82 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (337 mg, 0.76 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 2H), 7.47 – 7.34 (m, 2H), 6.29 (t, *J* = 7.8 Hz, 1H), 5.59 (q, *J* = 6.6 Hz, 1H), 3.92 (s, 3H), 3.57 (t, *J* = 6.2 Hz, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.70 – 1.55 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 167.0, 142.4, 141.9, 129.6, 128.9, 122.2, 85.93, 85.89, 62.4, 61.0, 52.3, 32.6, 26.4, 26.0, 21.6, 21.3, 18.4, -5.2. **IR** (neat) 2953, 2931, 2857, 1744, 1725, 1609, 1472, 1436, 1405, 1371, 1340, 1278, 1233, 1191, 1154, 1103, 1071, 1021, 948, 836, 776, 708, 662, 610, 502 cm^{-1}. $[\alpha]_D^{26}$ = +73.4 (c = 1.0, $CHCl_3$).



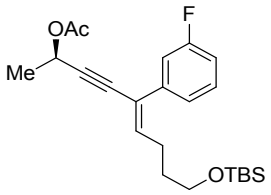
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(4-chlorophenyl)non-5-en-3-yn-2-yl acetate (S4d). General procedure for **S4** was followed on a 0.92 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (368 mg, 0.87 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 6.22 (t, *J* = 7.7 Hz, 1H), 5.58 (q, *J* = 6.7 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 2.26 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.65 – 1.55 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 141.5, 135.7, 133.4, 130.2, 128.5, 121.8, 86.1, 85.7, 62.4, 61.0, 32.6, 26.3, 26.0, 21.7, 21.3, 18.4, -5.2. **IR** (neat) 2954, 2930, 2886, 2857, 2226, 1744, 1594, 1491, 1472, 1463, 1370, 1340, 1307, 1233, 1153, 1095, 1071, 1016, 948, 835, 776, 721, 662, 607, 569, 506 cm^{-1}. $[\alpha]_D^{26}$ = +74.5 (c = 1.0, $CHCl_3$).



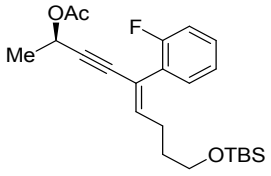
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(4-fluorophenyl)non-5-en-3-yn-2-yl acetate (S4e). General procedure for **S4** was followed on a 0.88 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil

(342 mg, 0.85 mmol, 96%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.06 – 6.98 (m, 2H), 6.20 (t, *J* = 7.7 Hz, 1H), 5.59 (q, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 2.26 (q, *J* = 7.6 Hz, 2H), 2.07 (d, *J* = 0.6 Hz, 3H), 1.66 – 1.57 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 162.2 (d, *J* = 246.7 Hz), 141.1, 133.2 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 8.1 Hz), 121.9, 115.2 (d, *J* = 21.5 Hz), 86.4, 85.5, 62.4, 61.0, 32.6, 26.3, 26.0, 21.7, 21.3, 18.4, -5.2. **IR** (neat) 2954, 2931, 2887, 2224, 1743, 1604, 1509, 1472, 1464, 1405, 1371, 1340, 1307, 1232, 1152, 1099, 1071, 1023, 948, 836, 776, 726, 661, 609, 582, 525 cm^{-1}. $[\alpha]_D^{26}$ = +78.5 (c = 1.0, $CHCl_3$).



(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(3-fluorophenyl)non-5-en-3-yn-2-yl acetate (S4f). General procedure for **S4** was followed on a 0.72 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (280 mg, 0.69 mmol, 97%).

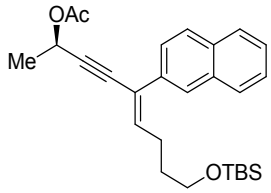
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, *J* = 8.0, 5.9 Hz, 1H), 7.12 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.09 – 7.03 (m, 1H), 6.97 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.24 (t, *J* = 7.7 Hz, 1H), 5.59 (q, *J* = 6.7 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.67 – 1.57 (m, 2H), 1.51 (d, *J* = 6.7 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 162.5 (d, *J* = 245.7 Hz), 141.8, 139.2 (d, *J* = 7.7 Hz), 129.6 (d, *J* = 8.4 Hz), 124.4 (d, *J* = 2.9 Hz), 121.7 (d, *J* = 2.2 Hz), 115.7 (d, *J* = 22.0 Hz), 114.4 (d, *J* = 21.1 Hz), 85.9, 85.6, 62.3, 60.9, 32.4, 26.2, 25.9, 21.5, 21.1, 18.3, -5.4. **IR** (neat) 2954, 2931, 2887, 2858, 1743, 1612, 1582, 1487, 1472, 1441, 1371, 1340, 1256, 1234, 1137, 1103, 1024, 949, 909, 879, 836, 813, 777, 704, 662, 609, 522, 488, 461 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{23}H_{33}FNaO_3Si$ $[M+Na]^+$ 427.2075, 427.2076. $[\alpha]_D^{26}$ = +79.6 (c = 1.0, $CHCl_3$).



(*R*,*Z*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(2-fluorophenyl)non-5-en-3-yn-2-yl acetate (S4g). General procedure for **S4** was followed on a 0.84 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (324 mg, 0.80 mmol, 95%).

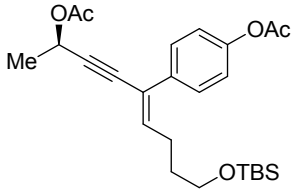
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.15 – 7.10 (m, 1H), 7.09 – 7.02 (m, 1H), 6.32 (t, *J* = 7.7 Hz, 1H), 5.58 (q, *J* = 6.6 Hz, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.13 – 2.03 (m, 5H), 1.62 – 1.55 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 0.83 (s, 9H), -0.01 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 159.4 (d, *J* = 247.8 Hz), 143.9, 131.1 (d, *J* = 3.4 Hz), 129.6 (d, *J* = 8.1 Hz), 124.9 (d, *J* = 16.0 Hz), 124.1 (d, *J* = 3.6 Hz), 116.6, 115.9 (d, *J* =

22.3 Hz), 85.6, 85.2, 62.6, 61.0, 32.1, 26.6 (d, *J* = 2.4 Hz), 26.0, 21.7, 21.3, 18.4, -5.2. **IR** (neat) 2931, 2857, 1743, 1492, 1450, 1371, 1233, 1100, 1030, 948, 836, 776, 759 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{23}H_{33}FNaO_3Si$ $[M+Na]^+$ 427.2075, 427.2075. $[\alpha]_D^{26}$ = +80.3 (c = 1.0, $CHCl_3$).



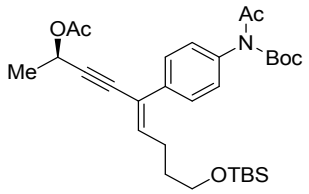
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-(naphthalen-2-yl)non-5-en-3-yn-2-yl acetate (S4h). General procedure for **S4** was followed on a 0.33 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (133 mg, 0.31 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 3H), 7.79 – 7.75 (m, 1H), 7.51 – 7.45 (m, 3H), 6.31 (t, *J* = 7.7 Hz, 1H), 5.63 (q, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.3 Hz, 2H), 2.35 (q, *J* = 7.6 Hz, 2H), 2.08 (s, 3H), 1.64 (m, 2H), 1.52 (d, *J* = 6.7 Hz, 3H), 0.82 (s, 9H), -0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 141.4, 134.7, 133.2, 132.8, 128.2, 127.86, 127.84, 127.7, 126.9, 126.26, 126.23, 86.6, 85.6, 62.6, 61.1, 32.7, 26.4, 26.0, 21.7, 21.3, 18.4, -5.2. **IR** (neat) 2954, 2931, 2858, 1743, 1603, 1506, 1472, 1370, 1234, 1198, 1167, 1153, 1101, 1071, 1018, 947, 912, 836, 76, 663, 609, 525 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{25}H_{36}FNaO_5Si$ $[M+Na]^+$ 467.2224, 467.2224. $[\alpha]_D^{26}$ = +66.3 (c = 1.0, $CHCl_3$).



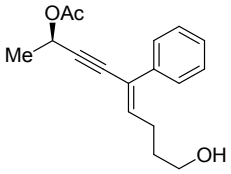
(*R*,*E*)-4-(2-Acetoxy-9-((*tert*-butyldimethylsilyl)oxy)non-5-en-3-yn-5-yl)phenyl acetate (S4i). General procedure for **S4** was followed on a 0.62 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (262 mg, 0.59 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.16 – 7.02 (m, 2H), 6.21 (t, *J* = 7.7 Hz, 1H), 5.59 (q, *J* = 6.6 Hz, 1H), 3.58 (t, *J* = 6.2 Hz, 2H), 2.33 – 2.25 (m, 5H), 2.07 (s, 3H), 1.70 – 1.56 (m, 2H), 1.50 (d, *J* = 6.6 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.9, 169.4, 149.8, 141.2, 134.7, 129.8, 121.9, 121.2, 86.3, 85.3, 62.4, 60.9, 32.5, 26.2, 25.9, 21.5, 21.2, 21.1, 18.3, -5.3. **IR** (neat) 2954, 2931, 2858, 1743, 1603, 1506, 1472, 1370, 1234, 1198, 1167, 1154, 1101, 1071, 1018, 947, 912, 836, 776, 663, 609, 525 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{25}H_{36}NaO_5Si$ $[M+Na]^+$ 467.2224, found 467.2224. $[\alpha]_D^{26}$ = +66.3 (c = 1.0, $CHCl_3$).



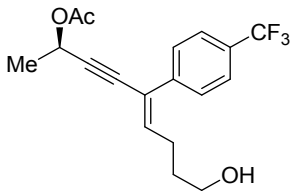
(*R*,*E*)-5-(4-(*N*-(*tert*-Butoxycarbonyl)acetamido)phenyl)-9-((tert-butyldimethylsilyl)oxy)non-5-en-3-yn-2-yl acetate (S4j). General procedure for **S4** was followed on a 0.49 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, colorless oil (253 mg, 0.47 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 2H), 7.08 – 7.00 (m, 2H), 6.23 (t, *J* = 7.7 Hz, 1H), 5.59 (q, *J* = 6.7 Hz, 1H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.57 (s, 3H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.67 – 1.59 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.39 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H). **^{3}C NMR** (101 MHz, $CDCl_3$) δ 173.0, 170.1, 152.8, 141.5, 138.1, 136.7, 129.5, 128.0, 122.2, 86.3, 85.5, 83.5, 62.6, 61.0, 32.7, 28.0, 26.7, 26.4, 26.1, 21.7, 21.3, 18.5, -5.2. **IR** (neat) 2932, 2857, 1739, 1712, 1607, 1510, 1473, 1462, 1370, 1337, 1302, 1271, 1254, 1234, 1155, 1096, 1072, 1017, 948, 923, 836, 775, 738, 662, 614, 529 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{30}H_{45}NNaO_6Si$ $[M+Na]^+$ 566.2908, found 566.2906. $[\alpha]_D^{26}$ = +57.1 (c = 1.0, $CHCl_3$).



(*R*,*E*)-9-Hydroxy-5-phenylnon-5-en-3-yn-2-yl acetate (S5a). General procedure for **S5** was followed on a 1.95 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (457 mg, 1.68 mmol, 86%).

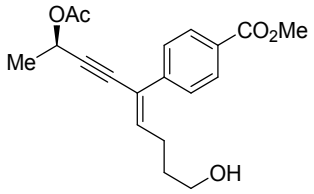
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.21 (t, *J* = 7.7 Hz, 1H), 5.60 (q, *J* = 6.6 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.31 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.75 – 1.58 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 140.4, 137.1, 128.8, 128.4, 127.7, 123.4, 86.4, 85.6, 62.3, 61.1, 32.5, 26.0, 21.7, 21.3. **IR** (neat) 2419, 2988, 2937, 2872, 2221, 1740, 1599, 1494, 1444, 1371, 1234, 1153, 1067, 1028, 947, 857, 768, 700, 611, 567, 526, 477 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{20}NaO_3$ $[M+Na]^+$ 295.1305, 295.1305. $[\alpha]_D^{26}$ = +112.6 (c = 1.0, $CHCl_3$).



(*R*,*E*)-9-Hydroxy-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-yl acetate (S5b). General procedure for **S5** was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography

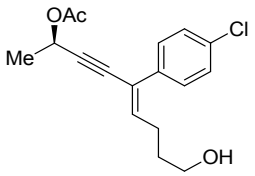
on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (96 mg, 0.28 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.56 (m, 2H), 7.52 – 7.37 (m, 2H), 6.28 (t, *J* = 7.7 Hz, 1H), 5.58 (q, *J* = 6.7 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.78 – 1.62 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 141.8, 140.8 (d, *J* = 1.4 Hz), 129.8 (d, *J* = 32.5 Hz), 129.2, 127.5, 125.4 (q, *J* = 3.8 Hz), 122.3, 86.3, 85.6, 62.2, 60.9, 32.3, 26.1, 21.6, 21.3. **IR** (neat) 3422, 2939, 1741, 1618, 1448, 1408, 1372, 1323, 1233, 116, 1018, 947, 848, 708, 621, 527, 496, 471 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{17}F_3NaO_3$ $[M+Na]^+$ 361.1022, found 361.1022. $[\alpha]_D^{26}$ = +86.7 (c = 1.0, $CHCl_3$).



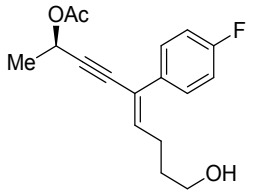
(*R*,*E*)-methyl 4-(2-acetoxy-9-hydroxynon-5-en-3-yn-5-yl)benzoate (S5c). General procedure for **S5** was followed on a 0.74 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (175 mg, 0.53 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 7.86 (m, 2H), 7.44 – 7.38 (m, 2H), 6.27 (t, *J* = 7.7 Hz, 1H), 5.58 (q, *J* = 6.6 Hz, 1H), 3.91 (s, 3H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.06 (s, 3H), 1.74 – 1.58 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 166.9, 141.8, 141.7, 129.7, 129.3, 128.8, 122.6, 86.2, 85.7, 62.2, 60.9, 52.3, 32.3, 26.1, 21.6, 21.2. **IR** (neat) 3443, 2990, 2939, 1721, 1609, 1565, 1436, 1405, 1372, 1338, 1279, 1233, 1192, 1153, 1105, 1070, 1020, 947, 869, 777, 708, 610, 498 cm^{-1}. $[\alpha]_D^{26}$ = +93.8 (c = 1.0, $CHCl_3$).



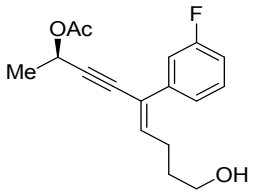
(*R*,*E*)-5-(4-Chlorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5d). General procedure for **S5** was followed on a 0.86 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (238 mg, 0.78 mmol, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.29 – 7.25 (m, 2H), 6.20 (t, *J* = 7.7 Hz, 1H), 5.57 (q, *J* = 6.7 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.28 (q, *J* = 7.6 Hz, 2H), 2.06 (s, 3H), 1.65 (m, 2H), 1.49 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 140.9, 135.6, 133.6, 130.2, 128.6, 122.3, 85.9, 62.2, 61.0, 32.4, 26.1, 21.6, 21.3. **IR** (neat) 3421, 2937, 22224, 1740, 1594, 1491, 1447, 1397, 1371, 1339, 1233, 1152, 1093, 1069, 1015, 948, 839, 721, 608, 507 cm^{-1}. $[\alpha]_D^{26}$ = +98.1 (c = 1.0, $CHCl_3$).



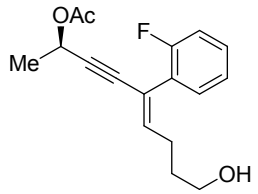
(*R*,*E*)-5-(4-Fluorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5e). General procedure for **S5** was followed on a 0.76 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (182 mg, 0.63 mmol, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.07 – 7.00 (m, 2H), 6.19 (t, *J* = 7.6 Hz, 1H), 5.58 (q, *J* = 6.7 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.28 (q, *J* = 7.5 Hz, 2H), 2.07 (s, 3H), 1.67 (dt, *J* = 8.4, 6.7 Hz, 2H), 1.50 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.01, 162.2 (d, *J* = 247.0 Hz), 140.4, 133.1 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 8.1 Hz), 122.3, 115.3 (d, *J* = 21.6 Hz), 86.2, 85.8, 62.3, 61.0, 32.4, 26.0, 21.6, 21.3. **IR** (neat) 3408, 2989, 2938, 2874, 2222, 1739, 1603, 1508, 1447, 1405, 1372, 1340, 1308, 1232, 1152, 1097, 1070, 1025, 948, 843, 726, 610, 580, 525 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{19}FNaO_3$ $[M+Na]^+$ 313.1210, found 313.1211. $[\alpha]_D^{26}$ = +110.0 (c = 1.0, $CHCl_3$).



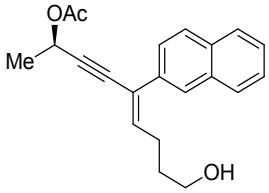
(*R*,*E*)-5-(3-Fluorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5f). General procedure for **S5** was followed on a 0.69 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (188 mg, 0.65 mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 8.0, 5.9 Hz, 1H), 7.11 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.05 (ddd, *J* = 9.9, 2.6, 1.6 Hz, 1H), 6.98 (tdd, *J* = 8.5, 2.7, 1.0 Hz, 1H), 6.22 (t, *J* = 7.7 Hz, 1H), 5.58 (q, *J* = 6.6 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.71 – 1.62 (m, 2H), 1.50 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 162.7 (d, *J* = 246.0 Hz), 141.2, 139.3 (d, *J* = 7.7 Hz), 129.8 (d, *J* = 8.4 Hz), 124.5 (d, *J* = 2.9 Hz), 122.3 (d, *J* = 2.2 Hz), 115.8 (d, *J* = 22.0 Hz), 114.6 (d, *J* = 21.1 Hz), 86.0, 85.8, 62.2, 61.0, 32.3, 26.1, 21.6, 21.2. **IR** (neat) 3416, 1989, 2937, 2874, 2223, 1739, 1611, 1581, 1486, 1440, 1371, 1339, 1308, 1233, 1207, 1160, 1135, 1064, 1024, 948, 908, 879, 848, 787, 703, 645, 610, 574, 521, 497, 465 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{24}FO_4$ $[M+H]^+$ 323.1653, found 323.1644. $[\alpha]_D^{26}$ = +107.3 (c = 1.0, $CHCl_3$).



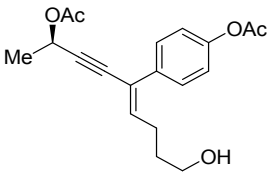
(*R*,*E*)-5-(2-Fluorophenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5g). General procedure for **S5** was followed on a 0.76 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (195 mg, 0.67 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.14 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.31 (t, *J* = 7.6 Hz, 1H), 5.57 (q, *J* = 6.6 Hz, 1H), 2.16 – 2.07 (m, 3H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.14 – 2.08 (m, 2H), 2.06 (s, 3H), 1.70 – 1.60 (m, 2H), 1.48 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 159.3 (d, *J* = 247.6 Hz), 143.2, 131.0 (d, *J* = 3.4 Hz), 129.7 (d, *J* = 8.1 Hz), 124.8 (d, *J* = 16.0 Hz), 124.2 (d, *J* = 3.6 Hz), 117.0, 116.0 (d, *J* = 22.2 Hz), 85.5, 85.4, 62.4, 61.0, 31.8, 26.4 (d, *J* = 2.4 Hz), 21.6, 21.3. **IR** (neat) 3419, 2989, 2938, 2873, 1739, 1579, 1491, 1450, 1372, 1340, 1233, 1159, 1148, 1095, 1069, 1026, 948, 893, 838, 809, 760, 612, 527, 480 cm^{-1}. $[\alpha]_D^{26}$ = +108.4 (c = 1.0, $CHCl_3$).



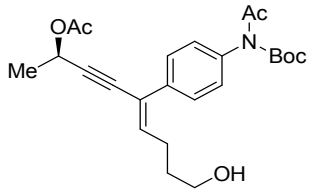
(*R*,*E*)-9-Hydroxy-5-(naphthalen-2-yl)non-5-en-3-yn-2-yl acetate (S5h). General procedure for **S5** was followed on a 0.30 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (66 mg, 0.20 mmol, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 3H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.45 (m, 3H), 6.29 (t, *J* = 7.7 Hz, 1H), 5.62 (q, *J* = 6.7 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.37 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.78 – 1.64 (m, 2H), 1.52 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 140.7, 134.6, 133.2, 132.8, 128.2, 128.0, 127.82, 127.76, 126.8, 126.4, 126.3, 123.4, 86.4, 85.9, 62.3, 61.1, 32.5, 26.1, 21.7, 21.3. **IR** (neat) 3410, 2936, 1738, 1504, 1445, 1371, 139, 1233, 1147, 1070, 1024, 952, 900, 862, 823, 750, 526, 478 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{22}NaO_3$ $[M+Na]^+$ 345.1461, found 345.1461. $[\alpha]_D^{26}$ = +95.0 (c = 1.0, $CHCl_3$).



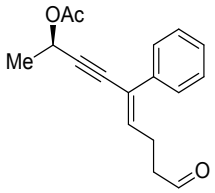
(*R*,*E*)-4-(2-Acetoxy-9-hydroxynon-5-en-3-yn-5-yl)phenyl acetate (S5i). General procedure for **S5** was followed on a 0.59 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (260 mg, 0.44 mmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.29 (m, 2H), 7.13 – 7.02 (m, 2H), 6.20 (t, *J* = 7.6 Hz, 1H), 5.58 (q, *J* = 6.6 Hz, 1H), 3.67 – 3.49 (m, 2H), 2.37 – 2.26 (m, 5H), 2.07 (s, 3H), 1.72 – 1.62 (m, 2H), 1.50 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 169.6, 150.1, 140.6, 134.7, 129.9, 122.5, 121.5, 86.2, 85.8, 62.3, 61.0, 32.4, 26.1, 21.6, 21.3. **IR** (neat) 3456, 2989, 2938, 2874, 2223, 1740, 1603, 1506, 1432, 1407, 1370, 1339, 1307, 1232, 1197, 1167, 1153, 1103, 1070, 1018, 947, 913, 852, 703, 609, 574, 526, 494 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{19}H_{22}NaO_5$ $[M+Na]^+$ 353.1359, found 353.1360. $[\alpha]_D^{26}$ = +83.6 (c = 1.0, $CHCl_3$).



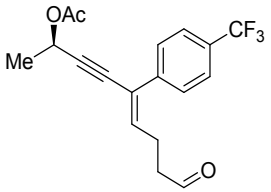
(*R*,*E*)-5-(4-(*N*-(*tert*-Butoxycarbonyl)acetamido)phenyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S5j). General procedure for **S5** was followed on a 0.46 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (80 mg, 0.19 mmol, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.08 – 7.04 (m, 2H), 6.22 (t, *J* = 7.7 Hz, 1H), 5.59 (q, *J* = 6.7 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.58 (s, 3H), 2.31 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.70 – 1.62 (m, 2H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 170.1, 152.8, 140.9, 138.2, 136.6, 129.5, 128.1, 122.7, 86.1, 85.8, 83.6, 62.3, 61.0, 32.4, 28.0, 26.7, 26.0, 21.6, 21.3. **IR** (neat) 3456, 2982, 2937, 1737, 1708, 1509, 1370, 1339, 1304, 1272, 1234, 1154, 1097, 1070, 1016, 948, 924, 848, 774, 737, 615, 530, 490, 474 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{24}H_{31}NNaO_6$ $[M+Na]^+$ 452.2044, 452.2043. $[\alpha]_D^{26}$ = +64.7 (c = 1.0, $CHCl_3$).



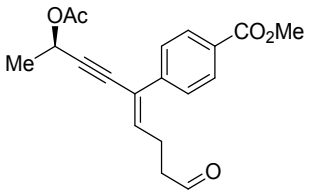
(*R*,*E*)-9-Oxo-5-phenylnon-5-en-3-yn-2-yl acetate (1a). General procedure for **1** was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (131 mg, 0.49 mmol, 88%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.90 – 9.53 (m, 1H), 7.45 – 7.22 (m, 5H), 6.26 – 6.04 (m, 1H), 5.55 (q, *J* = 6.7 Hz, 1H), 2.57 – 2.48 (m, 4H), 2.04 (s, 3H), 1.49 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.3, 170.1, 138.8, 137.2, 129.0, 128.7, 128.2, 124.3, 86.5, 86.1, 61.1, 43.6, 22.6, 21.7, 21.3. **IR** (neat) 3058, 3024, 2989, 2938, 2896, 2728, 2223, 2095, 2018, 1958, 1738, 1616, 1599, 1575, 1494, 1444, 1409, 1371, 1340, 1307, 1232, 1153, 1067, 1048, 1022, 946, 923, 856, 701, 657, 610, 589, 563, 525 cm^{-1}. **HRMS (MALDI):** m/z calculated for $C_{17}H_{19}O_3$ $[M+H]^+$ 271.1329, found 271.1327. $[\alpha]_D^{26}$ = +105.8 (c = 1.0, CH_2Cl_2).



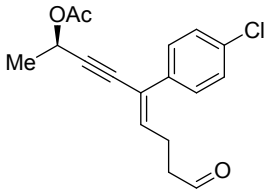
(*R*,*E*)-9-Oxo-5-(4-(trifluoromethyl)phenyl)non-5-en-3-yn-2-yl acetate (1b). General procedure for **1** was followed on a 0.15 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, slightly yellow oil (40 mg, 0.12 mmol, 80%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.71 (t, *J* = 1.1 Hz, 1H), 7.69 – 7.61 (m, 1H), 7.58 – 7.35 (m, 1H), 6.22 (t, *J* = 7.4 Hz, 1H), 5.53 (q, *J* = 6.7 Hz, 1H), 2.59 – 2.53 (m, 2H), 2.52 – 2.46 (m, 3H), 2.04 (s, 4H), 1.48 (d, *J* = 6.7 Hz, 4H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.0, 170.1, 141.1 (d, *J* = 1.5 Hz), 140.3, 129.5, 125.7 (q, *J* = 3.8 Hz), 123.2, 87.2, 85.3, 60.9, 43.4, 22.6, 21.6, 21.2. **IR** (neat) 2991, 2939, 2829, 2729, 2225, 1739, 1617, 1448, 1408, 1372, 1323, 1231, 1165, 1154, 1122, 1109, 1064, 1017, 946, 848, 777, 712, 645, 620, 527 cm cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{17}F_3NaO_3$ $[M+Na]^+$ 361.1022, found 361.1022. $[\alpha]_D^{26}$ = +94.0 (c = 1.0, CH_2Cl_2).



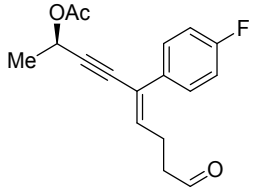
(*R*,*E*)-Methyl 4-(2-acetoxy-9-oxonon-5-en-3-yn-5-yl)benzoate (1c). General procedure for **1** was followed on a 0.26 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (72 mg, 0.22 mmol, 84%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.70 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.21 (t, *J* = 7.3 Hz, 1H), 5.54 (q, *J* = 6.7 Hz, 1H), 3.90 (s, 3H), 2.61 – 2.44 (m, 4H), 2.04 (s, 3H), 1.49 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.0, 170.1, 166.9, 141.8, 140.1, 129.9, 129.1, 123.5, 87.1, 85.4, 61.0, 52.4, 43.4, 22.6, 21.6, 21.2. **IR** (neat) 2991, 2953, 2842, 2728, 1721, 1609, 1565, 1507, 1436, 1406, 1372, 1339, 1309, 1279, 1233, 1192, 1181, 1153, 1113, 1070, 1019, 947, 869, 818, 776, 708, 658, 611, 529 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{19}H_{20}NaO_5$ $[M+Na]^+$ 351.1203, found 351.1200. $[\alpha]_D^{26}$ = +91.3 (c = 1.0, CH_2Cl_2)



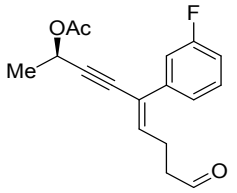
(*R*,*E*)-5-(4-Chlorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1d). General procedure for **1** was followed on a 0.35 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, slightly yellow oil (82 mg, 0.27 mmol, 76%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.70 (t, *J* = 1.1 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 6.14 (t, *J* = 7.4 Hz, 1H), 5.53 (q, *J* = 6.7 Hz, 1H), 2.67 – 2.42 (m, 4H), 2.04 (s, 3H), 1.48 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 200.7, 169.7, 138.9, 135.3, 133.5, 130.0, 128.4, 122.7, 86.4, 85.2, 60.6, 43.1, 22.1, 21.2, 20.8. **IR** (neat) 3453, 2989, 2938, 2895, 2827, 2727, 2225, 1738, 1593, 1491, 1446, 1397, 1371, 1339, 1307, 1231, 1152, 1092, 1070, 1015, 947, 839, 747, 722, 654, 608, 570, 507 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{17}NaO_3$ $[M+Na]^+$ 327.0758, found 327.0758. $[\alpha]_D^{26}$ = +99.8 (c = 1.0, CH_2Cl_2).



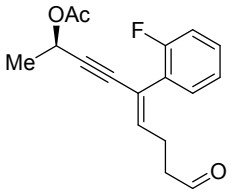
(*R*,*E*)-5-(4-Fluorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1e). General procedure for **1** was followed on a 0.23 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (60 mg, 0.21 mmol, 90%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.70 (t, *J* = 1.1 Hz, 1H), 7.44 – 7.24 (m, 2H), 7.19 – 6.98 (m, 2H), 6.13 (t, *J* = 7.1 Hz, 1H), 5.54 (q, *J* = 6.7 Hz, 1H), 2.59 – 2.41 (m, 4H), 2.04 (s, 3H), 1.48 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 203.2, 169.0 (d, *J* = 631.3 Hz), 163.4, 141.0, 135.3 (d, *J* = 3.3 Hz), 132.8 (d, *J* = 8.1 Hz), 125.2, 117.6 (d, *J* = 21.6 Hz), 88.7, 87.9, 63.0, 45.5, 24.5, 23.6, 23.2. **IR** (neat) 2990, 2938, 2829, 2728, 2225, 2086, 1736, 1603, 1508, 1447, 1407, 1371, 1340, 1307, 1230, 1152, 1098, 1070, 1048, 1023, 947, 843, 727, 654, 609, 568, 524 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{17}FNaO_3$ $[M+Na]^+$ 311.1054, found 311.1053. $[\alpha]_D^{26}$ = +103.4 (c = 1.0, CH_2Cl_2).



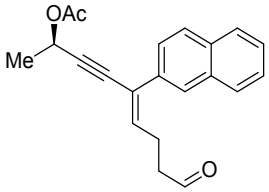
(*R*,*E*)-5-(3-Fluorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1f). General procedure for **1** was followed on a 0.22 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (58 mg, 0.20 mmol, 93%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.71 (d, *J* = 1.1 Hz, 1H), 7.36 (td, *J* = 8.0, 6.0 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.11 – 6.98 (m, 2H), 6.16 (t, *J* = 7.2 Hz, 1H), 5.54 (q, *J* = 6.7 Hz, 1H), 2.63 – 2.43 (m, 4H), 2.04 (s, 3H), 1.48 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.1, 170.1, 163.0 (d, *J* = 245.5 Hz), 139.7, 139.4 (d, *J* = 7.7 Hz), 130.3 (d, *J* = 8.4 Hz), 124.8 (d, *J* = 2.9 Hz), 123.2 (d, *J* = 2.2 Hz), 115.9 (d, *J* = 22.1 Hz), 115.0 (d, *J* = 21.1 Hz), 86.9, 85.5, 61.0, 43.5, 22.6, 21.6, 21.2. **IR** (neat) 2990, 2938, 2929, 2729, 2224, 2082, 1736, 1612, 1581, 1487, 1439, 1410, 1371, 1339, 1306, 1231, 1208, 1260, 1136, 1072, 1048, 1023, 948, 907, 880, 849, 788, 699, 645, 610 521 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{18}FO_3$ $[M+H]^+$ 289.1234, found 289.1236. $[\alpha]_D^{26}$ = +100.5 (c = 1.0, CH_2Cl_2).



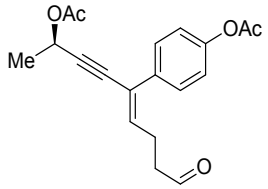
(*R*,*Z*)-5-(2-Fluorophenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1g). General procedure for **1** was followed on a 0.18 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (46 mg, 0.16 mmol, 89%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ δ 9.69 (t, *J* = 1.2 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.18 (td, *J* = 7.5, 1.2 Hz, 1H), 7.11 (ddd, *J* = 9.6, 8.2, 1.2 Hz, 1H), 6.26 (t, *J* = 7.6 Hz, 1H), 5.52 (q, *J* = 6.6 Hz, 1H), 2.58 – 2.46 (m, 2H), 2.36 – 2.26 (m, 2H), 2.03 (s, 3H), 1.47 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.2, 170.1, 159.5 (d, *J* = 246.9 Hz), 141.7, 131.2 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 8.1 Hz), 124.8, 124.7 (d, *J* = 3.6 Hz), 117.9, 116.2 (d, *J* = 22.1 Hz), 86.4, 85.0, 61.0, 22.9 (d, *J* = 2.6 Hz), 21.6, 21.2. **IR** (neat) 3444, 2989, 2939, 2730, 1738, 1610, 1580, 1491, 1451, 1372, 1340, 1307, 1232, 1149, 1095, 1069, 1045, 1024, 947, 907, 858, 838, 810, 761, 610, 529 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{17}FNaO_3$ $[M+Na]^+$ 311.1054, found 311.1052. $[\alpha]_D^{26}$ = +106.1 (c = 1.0, CH_2Cl_2).

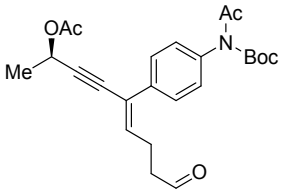


(*R*,*E*)-5-(Naphthalen-2-yl)-9-oxonon-5-en-3-yn-2-yl acetate (1h). General procedure for **1** was followed on a 0.24 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (71 mg, 0.22 mmol, 93%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.69 (t, *J* = 1.1 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.79 (s, 1H), 7.54 – 7.46 (m, 3H), 6.30 – 6.11 (m, 1H), 5.57 (q, *J* = 6.7 Hz, 1H), 2.69 – 2.47 (m, 4H), 2.04 (s, 3H), 1.50 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.2, 170.1, 139.2, 134.7, 133.5, 133.1, 128.4, 128.3, 128.00, 127.97, 126.9, 126.7, 124.3, 86.8, 86.1, 61.1, 43.6, 22.7, 21.7, 21.3. **IR** (neat) 3056, 2989, 2937, 2826, 2726, 2225, 1738, 1598, 1504, 1434, 1408, 1371, 1339, 1307, 1233, 1199, 1148, 1127, 1070, 1023, 951, 901, 863, 847, 823, 751, 705, 667, 611, 524 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{21}H_{20}NaO_3$ $[M+Na]^+$ 343.1305, found 343.1303. $[\alpha]_D^{26}$ = +93.6 (c = 1.0, CH_2Cl_2).



(*R*,*E*)-4-(2-Acetoxy-9-oxonon-5-en-3-yn-5-yl)phenyl acetate (1i). General procedure for **1** was followed on a 0.12 mmol scale. The crude product was purified by a quick flash column chromatography on silica gel (hexane/EtOAc 1:1). The title compound was isolated as clear, colorless oil (35 mg, 0.11 mmol, 90%). Aldehyde **1I** was found to be extremely instable when concentrated and even short term storage was not possible. Thus, the freshly isolated product was immediately used in the subsequent gold(I)-catalyzed cyclization.

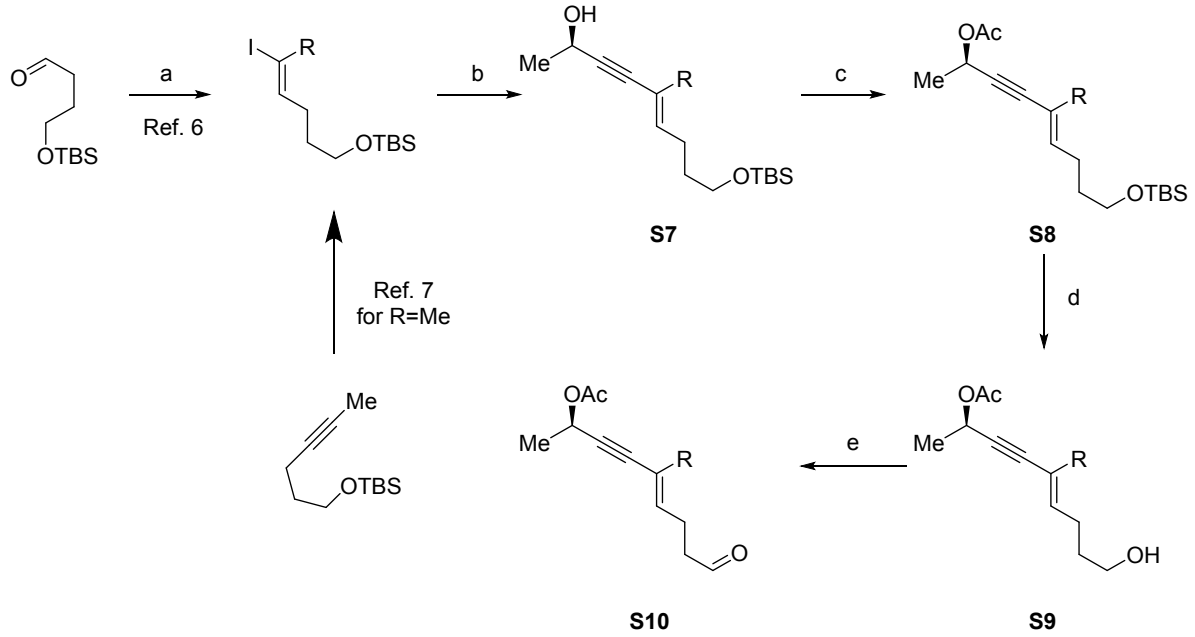


(*R*,*E*)-5-(4-(*N*-(*tert*-Butoxycarbonyl)acetamido)phenyl)-9-oxonon-5-en-3-yn-2-yl acetate (1j). General procedure for **1** was followed on a 0.15 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1). The title compound was isolated as clear, colorless oil (54 mg, 0.13 mmol, 85%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.70 (d, *J* = 0.9 Hz, 1H), 7.49 – 7.26 (m, 2H), 7.18 – 7.00 (m, 2H), 6.28 – 6.09 (m, 1H), 5.55 (q, *J* = 6.7 Hz, 1H), 2.56 (s, 3H), 2.55 – 2.50 (m, 4H), 2.04 (s, 3H), 1.49 (d, *J* = 6.7 Hz, 3H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 201.1, 173.2, 170.1, 152.9, 139.2, 139.0, 136.5, 129.5, 128.7, 123.6, 86.8, 85.8, 83.7, 61.0, 43.5, 27.9, 26.8, 22.6, 21.6, 21.3. **IR** (neat) 2982, 2938, 2729, 1736, 1708, 1605, 1511, 1478, 1456, 1414, 1394, 1370, 1340, 1303, 1271, 1253, 1233, 1154, 1097, 1070, 1028, 1016, 947, 924, 848, 774, 743, 610 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{24}H_{29}NaO_6$ $[M+Na]^+$ 450.1887, found 450.1887. $[\alpha]_D^{26}$ = +85.4 (c = 1.0, CH_2Cl_2).

2.2 Synthesis of Alkyl Substrates

General Procedures for Alkyl-Substrate Synthesis



Reagents and conditions: a) PhLi (1.0 equiv), LiBr (2.0 equiv), alkyltriphenylphosphonium bromide (1 equiv), –78°C; then PhLi, –78°C to RT; then I_2, –78°C to RT.; b) (R)-3-butyn-2-ol (1.3 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), Et_3N/THF (2:1); c) Ac_2O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH_2Cl_2; d) TBAF (2 equiv), THF; e) $(COCl)_2$ (1.2 equiv), DMSO (2.4 equiv), NEt_3 (5 equiv), –78 °C to –30 °C CH_2Cl_2.

Propargyl alcohol S7.[6,7] (*step 1*) To a solution of anhydrous LiBr (1.0 equiv) in dry THF (0.4 M) at ambient temperature was added alkyltriphenylphosphonium bromide (1.0 equiv) and stirred for 10 min. The resulting suspension was cooled to –78°C and PhLi (1.9 M in Bu_2O, 1.0 equiv) was added dropwise. The solution was allowed to warm to RT over 15 min and then stirred for another 30 min at that temperature. Then the solution was recooled to –78°C and a solution of 4-(*tert*-butyldimethylsilanyloxy)butanal (1.0 M in THF, 1.0 equiv) was added dropwise. After 10 min, PhLi (1.9M in Bu_2O, 1.1 equiv) was added dropwise and stirred for 30 min at –78°C, then allowed to warm to RT over 15 min. After 30 min at ambient temperature, the mixture was recooled to –78°C and transferred via cannula to a solution of I_2 (1.0 M in THF, 1.2 equiv) at –78°C and stirred for 30min. Then the solution was allowed to warm to RT and stirred for another hour. The resulting mixture was quenched by the addition of sat. aq. $Na_2S_2O_3$ solution and stirred vigorously for 5 min. The phases were separated and the aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography afforded the corresponding vinyl iodide.

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[6] D. M. Hodgson, T. Aric, *J. Am. Chem. Soc.* **2008**, *130*, 16500-16501.

[7] a) Z. Huang, E.-I. Negishi, *Org. Lett.* **2006**, *8*, 3675-3678; b) L. M. Kreis, E. M. Carreira, *Angew. Chem. Int. Ed.* **2012**, *51*, 3436-3439.

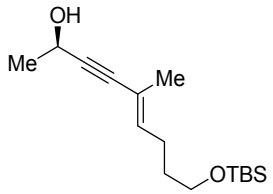
(*step 2*) To a degassed solution of the vinyl iodide (1.0 equiv) and (*R*)-but-3-yn-2-ol (1.2 equiv) in NEt_3/THF (2:1, 0.15 M) was added $PdCl_2(PPh_3)_2$ (0.05 equiv) and CuI (0.1 equiv) and the resulting mixture was stirred at RT for 2h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated *in vacuo*. Purification by column chromatography afforded enyne **S7**.

Propargyl Acetate S8. To a stirred solution of enyne **S7** (1.0 equiv) dissolved in CH_2Cl_2 (0.1 M) at ambient temperature was added pyridine (5.0 equiv), DMAP (0.2 equiv), and Ac_2O (1.5 equiv). The resultinh solution was stirred for 1h before it was quenched with H_2O. The aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with sat. aq. $CuSO_4$ solution, H_2O (1x), and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided propargyl acetate **S8**.

Primary alcohol S9. To a stirred solution of propargyl acetate **S8** (1.0 equiv) in dry THF (0.1 M) at 0 °C was added TBAF (1.0 M in THF, 2 equiv). After the addition, the solution was allowed to warm to ambient temperature and stirred for another 90 min. The mixture was quenched by the addition of sat. aq. $NaHCO_3$ solution. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided primary alcohol **S9**.

Aldehyde 1. To a solution of oxalyl chloride (1.2 equiv) in CH_2Cl_2 (0.15 M) at –78 °C was added DMSO (2.4 equiv) dropwise and stirred for 15 min. Then a solution of alcohol **S9** in CH_2Cl_2 (0.05-0.1 M) was added dropwise and stirred for 30min. After that time, NEt_3 (5 equiv) was added and stirred for another 30 min at –78 °C and then slowly warmed to –30 °C over 30 min and then quenched by the addition of sat. aq. $NaHCO_3$ solution. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided aldehyde **1**.[8]

(*R*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-5-methylnon-5-en-3-yn-2-ol

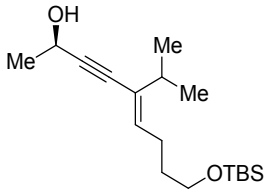


(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-methylnon-5-en-3-yn-2-ol (S7k). The general procedure for **S7** (part b) was followed on a 1.76 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, orange oil (312 mg, 1.10 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 – 5.75 (m, 1H), 4.70 – 4.49 (m, 1H), 3.60 (t, *J* = 6.2 Hz, 2H), 2.20 – 2.09 (m, 2H), 1.80 (d, *J* = 4.6 Hz, 1H), 1.77 (dd, *J* = 1.6, 0.9 Hz, 3H), 1.62 – 1.54 (m, 2H), 1.46 (d, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.3, 117.5, 87.5, 87.2, 62.5, 59.0, 32.2, 26.1, 25.0,

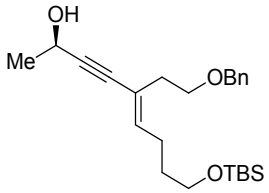
[8] Aldehyde **10** were found to decompose when stored in commercial CD_3Cl. Thus, filtration through basic Al_2O_3 or the use of CD_2Cl_2 is advised.

24.7, 18.5, 17.2, -5.2. **IR** (neat) 3342, 2954, 2930, 2886, 2858, 2217, 1633, 1472, 1463, 1446, 1387, 1361, 1329, 1288, 1254, 1180, 1101, 1006, 859, 839, 916, 887, 835, 814, 775, 720, 680, 662, 573, 542, 494 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{16}H_{30}KO_2Si$ $[M+K]^+$ 321.1647, found 321.1647. $[\alpha]_D^{26}$ = +14.9 (c = 1.0, $CHCl_3$).



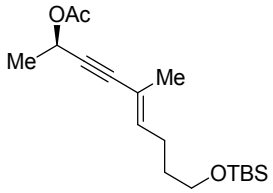
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-isopropylnon-5-en-3-yn-2-ol (S7l). General procedure for **S7** was followed on a 4.94 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 6:1). The title compound was isolated as clear, orange oil (513 mg, 1.65 mmol, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (t, *J* = 7.6 Hz, 1H), 4.82 – 4.55 (m, 1H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.88 – 2.62 (m, 1H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.76 (s, 1H), 1.62 – 1.53 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H), 1.03 (dd, *J* = 6.8, 0.9 Hz, 6H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.4, 129.6, 89.9, 83.9, 62.5, 59.1, 32.7, 28.0, 26.1, 24.8, 24.4, 21.6, 18.5, -5.1. **IR** (neat) 3342, 2958, 2930, 2887, 2858, 2214, 2087, 1472, 1385, 1362, 1328, 1288, 1255, 1186, 1162, 1104, 1007, 960, 939, 922, 887, 835, 813, 775, 716, 662, 639, 573, 521 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{34}FO_2Si$ $[M+Na]^+$ 333.2220, found 333.2221. $[\alpha]_D^{26}$ = +11.2 (c = 1.0, $CHCl_3$).



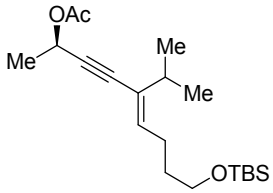
(*R*,*E*)-5-(2-(Benzyloxy)ethyl)-9-((*tert*-butyldimethylsilyl)oxy)non-5-en-3-yn-2-ol (S7m). General procedure for **S7** was followed on a 5.88 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 5:1). The title compound was isolated as clear, orange oil (555 mg, 1.38 mmol, 24%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 5H), 7.32 – 7.27 (m, 1H), 5.95 (t, *J* = 7.6 Hz, 1H), 4.61 (t, *J* = 6.5 Hz, 1H), 4.53 (d, *J* = 1.9 Hz, 2H), 3.60 (q, *J* = 6.7 Hz, 4H), 2.54 – 2.42 (m, 2H), 2.19 (q, *J* = 7.6 Hz, 2H), 1.66 – 1.54 (m, 3H), 1.43 (d, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 138.6, 128.5, 127.8, 127.7, 119.2, 88.6, 85.7, 73.0, 68.7, 62.6, 59.0, 32.5, 31.3, 26.1, 25.0, 24.6, 18.5, -5.1. **IR** (neat) 2954, 2929, 2885, 2857, 1472, 1463, 1455, 1388, 1362, 1328, 1255, 1099, 1029, 1006, 964, 939, 912, 890, 835, 814, 776, 735, 697, 662, 498 cm^{-1}. **HRMS (MALDI):** m/z m/z calcd for $C_{24}H_{39}O_3Si$ $[M+H]^+$ 403.2663, found 403.2657. $[\alpha]_D^{26}$ = +9.8 (c = 1.0, $CHCl_3$).



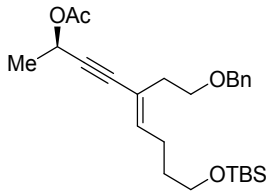
(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-methylnon-5-en-3-yn-2-yl acetate (S8k). General procedure for **S8** was followed on a 1.1 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, yellow oil (331 mg, 1.02 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (td, *J* = 7.5, 1.6 Hz, 1H), 5.57 (q, *J* = 6.6 Hz, 1H), 3.59 (t, *J* = 6.2 Hz, 2H), 2.18 – 2.09 (m, 2H), 2.07 (s, 3H), 1.78 – 1.74 (m, 3H), 1.62 – 1.53 (m, 2H), 1.49 (d, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 139.1, 117.3, 87.8, 83.9, 62.5, 61.1, 32.2, 26.1, 25.0, 21.8, 21.3, 18.4, 17.1, -5.2. **IR** (neat) 2989, 2954, 2930, 2887, 2858, 2219, 1745, 1472, 1463, 1446, 1371, 1341, 1308, 1231, 1099, 1040, 1008, 944, 889, 835, 814, 75, 721, 680, 662, 609, 543 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{32}KO_3Si$ $[M+K]^+$ 363.1752, found 363.1750. $[\alpha]_D^{26}$ = +96.8 (c = 1.0, $CHCl_3$).



(*R*,*E*)-9-((*tert*-Butyldimethylsilyl)oxy)-5-isopropylnon-5-en-3-yn-2-yl acetate (S8l). General procedure for **S8** was followed on a 1.65 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 10:1). The title compound was isolated as clear, yellow oil (519 mg, 1.47 mmol, 89%).

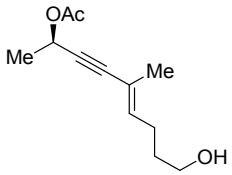
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (t, *J* = 7.6 Hz, 1H), 5.58 (q, *J* = 6.7 Hz, 1H), 3.60 (t, *J* = 6.3 Hz, 2H), 2.84 – 2.60 (m, 1H), 2.17 (q, *J* = 7.6 Hz, 2H), 2.07 (s, 3H), 1.57 (dt, *J* = 8.3, 6.5 Hz, 2H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.02 (dd, *J* = 6.8, 2.9 Hz, 6H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 136.8, 129.2, 86.1, 84.4, 62.3, 61.0, 32.5, 27.9, 25.9, 24.3, 21.7, 21.4, 21.2, 18.3, -5.3. **IR** (neat) 2958, 2930, 2896, 2858, 2219, 1744, 1472, 1464, 1371, 1339, 1308, 1231, 1164, 1099, 1056, 1018, 947, 889, 834, 814, 775, 718, 679, 662, 638, 609, 523, 469 cm^{-1}. $[\alpha]_D^{26}$ = +87.3 (c = 1.0, $CHCl_3$).



(*R*,*E*)-5-(2-(Benzyloxy)ethyl)-9-((*tert*-butyldimethylsilyl)oxy)non-5-en-3-yn-2-yl acetate (S8m). General procedure for **S8** was followed on a 1.19 mmol scale. The crude product was purified by flash column

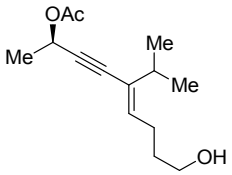
chromatography on silica gel (hexane/EtOAc 8:1). The title compound was isolated as clear, yellow oil (485 mg, 1.09 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.4 Hz, 5H), 7.32 – 7.25 (m, 1H), 5.98 (t, *J* = 7.7 Hz, 1H), 5.55 (q, *J* = 6.7 Hz, 1H), 4.53 (s, 2H), 3.60 (q, *J* = 6.7 Hz, 4H), 2.46 (td, *J* = 7.1, 1.1 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 2.06 (d, *J* = 1.2 Hz, 3H), 1.63 – 1.53 (m, 2H), 1.47 (d, *J* = 6.7 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 140.8, 138.7, 128.5, 127.7, 127.6, 118.9, 86.3, 85.0, 73.06, 68.7, 62.6, 61.1, 32.4, 31.2, 26.1, 25.0, 21.8, 21.3, 18.5, -5.1. **IR** (neat) 2953, 2930, 2885, 2857, 1742, 1472, 1463, 1454, 1370, 1339, 1308, 1232, 1180, 1099, 1056, 1029, 946, 891, 836, 814, 776, 735, 698, 662, 608 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{26}H_{40}NaO_4Si$ $[M+Na]^+$ 467.2588, found 467.2588. $[\alpha]_D^{26}$ = +70.6 (c = 1.0, $CHCl_3$).



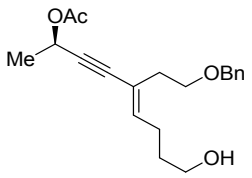
(*R*,*E*)-9-Hydroxy-5-methylnon-5-en-3-yn-2-yl acetate (S9k). General procedure for **S9** was followed on a 1.02 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (184 mg, 0.88 mmol, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.83 (m, 1H), 5.56 (q, *J* = 6.6 Hz, 1H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.21 – 2.13 (m, 2H), 2.07 (d, *J* = 1.4 Hz, 3H), 1.80 – 1.75 (m, 3H), 1.70 – 1.58 (m, 2H), 1.49 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 138.5, 117.7, 87.6, 84.1, 62.4, 61.1, 32.0, 24.9, 21.8, 21.3, 17.2. **IR** (neat) 3419, 2989, 2938, 2872, 2219, 1741, 1446, 1372, 1340, 1309, 1232, 1127, 1087, 1041, 948, 888, 844, 610, 542, 498 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{12}H_{18}NaO_3$ $[M+Na]^+$ 233.1148, found 233.1148. $[\alpha]_D^{26}$ = +131.2 (c = 1.0, $CHCl_3$).



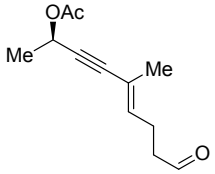
(*R*,*E*)-9-Hydroxy-5-isopropylnon-5-en-3-yn-2-yl acetate (S9l). General procedure for **S9** was followed on a 0.85 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The title compound was isolated as clear, colorless oil (169 mg, 0.71 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (t, *J* = 7.6 Hz, 1H), 5.57 (q, *J* = 6.6 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.81 – 2.64 (m, 1H), 2.20 (q, *J* = 7.5 Hz, 2H), 2.06 (s, 2H), 1.69 – 1.57 (m, 2H), 1.50 (dd, *J* = 6.6, 0.6 Hz, 3H), 1.03 (dd, *J* = 6.7, 2.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 136.4, 129.7, 86.5, 84.4, 62.4, 61.1, 32.4, 28.1, 24.4, 21.9, 21.6, 21.3. **IR** (neat) 3425, 2964, 2936, 2871, 2218, 1740, 1448, 1371, 1339, 1309, 1232, 1161, 1131, 1095, 1055, 1019, 948, 888, 856, 638, 610, 523, 469 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{14}H_{22}NaO_3$ $[M+Na]^+$ 261.1461, found 261.1462. $[\alpha]_D^{26}$ = +123.2 (c = 1.0, $CHCl_3$).



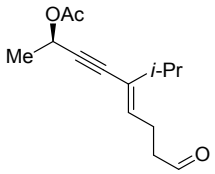
(*R*,*E*)-5-(2-(Benzyloxy)ethyl)-9-hydroxynon-5-en-3-yn-2-yl acetate (S9m). General procedure for **S9** was followed on a 1.06 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1). The title compound was isolated as clear, colorless oil (250 mg, 0.76 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 5H), 7.30 – 7.26 (m, 1H), 6.02 – 5.92 (m, 1H), 5.53 (q, *J* = 6.6 Hz, 1H), 4.53 (s, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 3.56 (t, *J* = 6.0 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 2.25 (q, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.67 – 1.57 (m, 2H), 1.45 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 140.4, 138.3, 128.6, 128.0, 127.9, 119.8, 86.1, 85.3, 73.3, 68.2, 61.4, 61.1, 31.7, 31.3, 24.6, 21.8, 21.4. **IR** (neat) 3425, 2987, 2936, 2865, 1740, 1496, 1454, 1371, 1339, 1309, 1233, 1175, 1100, 1088, 1055, 1029, 947, 888, 844, 738, 699, 608, 524, 493, 459 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{20}H_{26}NaO_4$ $[M+Na]^+$ 353.1723, found 353.1723. $[\alpha]_D^{26}$ = +93.6 (c = 1.0, $CHCl_3$).



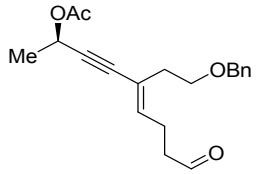
(*R*,*E*)-5-Methyl-9-oxonon-5-en-3-yn-2-yl acetate (1k). General procedure for **1** was followed on a 0.57 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (99 mg, 0.48 mmol, 83%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.74 (t, *J* = 1.3 Hz, 1H), 5.83 – 5.73 (m, 1H), 5.50 (q, *J* = 6.7 Hz, 1H), 2.57 – 2.48 (m, 3H), 2.43 – 2.33 (m, 3H), 2.03 (s, 4H), 1.83 – 1.75 (m, 4H), 1.45 (d, *J* = 6.7 Hz, 4H). **^{13}C NMR** (101 MHz, CD_2Cl_3) δ 201.5, 170.1, 137.0, 118.7, 87.3, 85.0, 61.0, 43.3, 21.8, 21.5, 21.3, 17.2. **IR** (neat) 3457, 2989, 2938, 2729, 2222, 1737, 1634, 1446, 1411, 1371, 1340, 1308, 1229, 1124, 1088, 1040, 1016, 948, 889, 844, 654, 609, 543, 526, 502 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 209.1172, found 209.1171. $[\alpha]_D^{26}$ = +130.8 (c = 1.0, CH_2Cl_2).



(*R*,*E*)-5-Isopropyl-9-oxonon-5-en-3-yn-2-yl acetate (1l). General procedure for **1** was followed on a 0.35 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (70 mg, 0.30 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 5.72 (t, *J* = 7.4 Hz, 1H), 5.56 (q, *J* = 6.5 Hz, 1H), 2.75 (p, *J* = 6.7 Hz, 1H), 2.52 (m, 2H), 2.49 – 2.39 (m, 2H), 2.07 (s, 3H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.04 (dd, *J* = 6.7, 2.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 201.4, 170.1, 134.3, 133.1, 130.7, 87.0, 84.0, 61.1, 43.5, 28.3, 21.8, 21.5, 21.3, 20.7. **IR** (neat) 3474, 2966, 2937, 2872, 2726, 2216, 2082, 2005, 1740, 1449, 1410, 1372, 1339, 1308, 1234, 1163, 1132, 1096, 1056, 1019, 948, 854, 640, 609, 576, 523, 498, 470 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{12}H_{17}O_3$ $[M+H]^+$ 259.1305, found 259.1304. $[\alpha]_D^{26}$ = +87.7 (c = 1.0, $CHCl_3$).



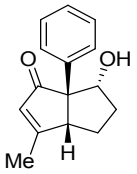
(*R*,*E*)-5-(2-(Benzyloxy)ethyl)-9-oxonon-5-en-3-yn-2-yl acetate (1m). General procedure for **1** was followed on a 0.55 mmol scale. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1). The title compound was isolated as clear, colorless oil (140 mg, 0.43 mmol, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (t, *J* = 1.2 Hz, 1H), 7.35 – 7.31 (m, 5H), 7.30 – 7.25 (m, 1H), 5.91 (t, *J* = 7.3 Hz, 1H), 5.50 (q, *J* = 6.6 Hz, 1H), 4.50 (s, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.54 – 2.38 (m, 6H), 2.02 (s, 3H), 1.45 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.0, 171.6, 140.6, 140.1, 130.1, 129.4, 129.3, 122.3, 87.5, 87.4, 74.8, 70.2, 62.5, 45.0, 33.1, 23.2, 22.9, 22.8. **IR** (neat) 3064, 3030, 2988, 2935, 2858, 2726, 2222, 1737, 1496, 1454, 1409, 1370, 1339, 1308, 1230, 1179, 1101, 1055, 1028, 946, 910, 842, 738, 699, 653, 608, 525 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{20}H_{24}NaO_4$ $[M+Na]^+$ 351.1567, found 351.1566. $[\alpha]_D^{26}$ = +96.5 (c = 1.0, CH_2Cl_2).

4. Synthesis and Characterization of Products[9]

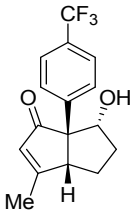
General Procedure for Au-Catalyzed Enantiospecific tandem Nazarov-Aldol Cyclization:

Aldehyde **1** (1.0 equiv) was dissolved in dry THF (0.05 M) and water (0.2 vol%) was added. The resulting clear solution was cooled to –10 °C and **3** (5 mol%) was added in one portion. The resulting faintly yellow solution was stirred at –10 °C for 16 hours and, if necessary, allowed to warm to ambient temperature to achieve full conversion. The reaction mixture was filtered through a short pad of silica gel washing with EtOAc, concentrated *in vacuo*, and subsequently subjected to silica gel flash chromatogroaphy to afford the product.



(3a*R*,6a*R*)-6-Hydroxy-3-methyl-6a-phenyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2a). General procedure was followed on a 0.107 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (18.5 mg, 0.081 mmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.26 – 7.22 (m, 1H), 6.08 (t, *J* = 1.3 Hz, 1H), 4.50 – 4.35 (m, 1H), 4.06 (d, *J* = 7.6 Hz, 1H), 3.27 (d, *J* = 10.5 Hz, 0H), 2.24 (dd, *J* = 1.3, 0.8 Hz, 3H), 2.11 – 2.05 (m, 1H), 1.92 – 1.86 (m, 1H), 1.76 – 1.69 (m, 1H), 1.52 – 1.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.36, 182.53, 140.47, 131.25, 128.85, 127.20, 126.56, 79.30, 63.37, 57.99, 32.35, 24.16, 18.08. **IR** (neat) 3459, 3060, 3026, 2958, 2873, 1679, 1618, 1581, 1497, 1433, 1378, 1296, 1250, 1188, 1104, 1091, 1050, 1018, 953, 932, 906, 856, 765, 738, 719, 699, 598, 572, 533, 497 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{15}H_{17}O_2$ $[M+H]^+$ 229.1223, found 229.1223. $[\alpha]_D^{26}$ = –176.8 (c = 0.5, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 93% *ee* (t_R (1, major enantiomer, major diastereomer) = 9.83 min, t_R (2, minor enantiomer, major diastereomer) = 12.19 min, t_R (3, minor enantiomer, minor diastereomer) = 15.96 min, t_R (4, major enantiomer, major diastereomer) = 17.38 min).

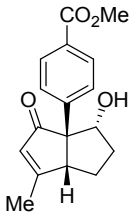


(3a*R*,6a*R*)-6-Hydroxy-3-methyl-6a-(4-(trifluoromethyl)phenyl)-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2b). General procedure was followed on a 0.092 mmol scale. The solution was stirred at -10 °C for

[9] For the synthesis and characterizatino of substrate 2n, see: M. Brandstätter, M. Freis, N. Huwyler, E. M. Carreira, *Angew. Chem. Int. Ed.* Accepted Article, DOI: 10.1002/ange.201813090.

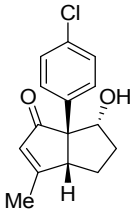
24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (19 mg, 0.064 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.45 (m, 4H), 6.09 (p, *J* = 1.3 Hz, 1H), 4.48 – 4.32 (m, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.36 – 3.20 (m, 1H), 2.26 (t, *J* = 1.1 Hz, 3H), 2.09 (dddd, *J* = 11.9, 5.8, 5.0, 1.4 Hz, 1H), 1.90 (ddd, *J* = 13.2, 9.6, 5.9 Hz, 1H), 1.76 (ddt, *J* = 13.4, 6.5, 1.5 Hz, 1H), 1.48 (tdd, *J* = 12.6, 11.1, 6.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.3, 182.7, 144.4 (d, *J* = 1.5 Hz), 131.2, 128.3, 127.1, 125.7 (q, *J* = 3.7 Hz), 79.4, 63.3, 57.7, 54.0, 32.2, 24.2, 18.1. **IR** (neat) 3465, 2961, 1684, 1618, 1518, 1435, 1411, 1379, 1326, 1300, 1285, 1248, 1165, 1120, 1070, 1018, 953, 926, 859, 835, 776, 752, 738, 715, 688, 622, 610, 521 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{16}H_{16}F_3O_2$ $[M+H]^+$ 297.1097, found 297.1097. $[\alpha]_D^{26}$ = –134.2 (c = 1.0, $CHCl_3$). **SFC** (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 96% *ee* (t_R (1, major enantiomer, major diastereomer) = 8.13 min, t_R (2, minor enantiomer, major diastereomer) = 9.13 min)



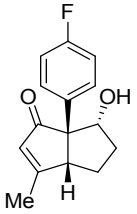
Methyl 4-((3*R*,3a*R*,6a*R*)-3-hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropentalen-3a-yl)benzoate (2c). General procedure was followed on a 0.167 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (33 mg, 0.115 mmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.52 – 7.47 (m, 2H), 6.08 (s, 1H), 4.50 – 4.37 (m, 1H), 3.98 (d, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 3.28 (d, *J* = 9.5 Hz, 5H), 2.25 (s, 3H), 2.13 – 2.04 (m, 1H), 1.97 – 1.85 (m, 1H), 1.79 – 1.69 (m, 1H), 1.53 – 1.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.4, 182.6, 166.9, 145.6, 131.2, 130.1, 129.0, 126.7, 79.3, 63.6, 57.7, 52.2, 32.3, 24.2, 18.1. **IR** (neat) 3472, 2954, 2875, 2071, 1719, 1699, 1683, 1611, 1569, 1510, 1435, 1409, 1378, 1318, 1280, 1190, 1111, 1055, 1020, 964, 926, 861, 825, 774, 741, 727, 703, 617, 607, 574, 536 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{19}O_4$ $[M+H]^+$ 287.1278, found 287.1278. $[\alpha]_D^{26}$ = –163.8 (c = 1.0, $CHCl_3$). **SFC** (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 15% MeOH, 2.0 mL/min., 25 °C, 95% *ee* (t_R (1, minor enantiomer, major diastereomer) = 11.65 min, t_R (2, minor enantiomer, minor diastereomer) = 23.59 min, t_R (3, major enantiomer, major diastereomer) = 23.59 min, t_R (4, major enantiomer, minor diastereomer) = 28.47 min).



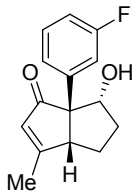
(3a*R*,6*R*,6a*R*)-6a-(4-Chlorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2d). General procedure was followed on a 0.174 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (32 mg, 0.122 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 4H), 6.06 (s, 1H), 4.43 – 4.31 (m, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.23 (d, *J* = 9.2 Hz, 7H), 2.24 (dd, *J* = 1.3, 0.8 Hz, 3H), 2.14 – 2.01 (m, 1H), 1.97 – 1.82 (m, 1H), 1.79 – 1.67 (m, 1H), 1.53 – 1.34 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 182.4, 138.8, 131.1, 128.8, 128.5, 127.9, 79.3, 62.7, 57.6, 32.1, 24.0, 18.0. **IR** (neat) 3462, 3070, 2959, 2873, 1679, 1618, 1593, 1493, 1451, 1433, 1401, 1378, 1296, 1250, 1185, 1093, 1054, 1014, 953, 858, 823, 742, 719, 705, 618, 608, 573, 536, 524, 507 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{15}H_{16}ClO_2$ $[M+H]^+$ 263.0833, found 263.0834. $[\alpha]_D^{26}$ = –142.1 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 95% *ee* (t_R (1, major enantiomer, major diastereomer) = 11.69 min, t_R (2, minor enantiomer, major diastereomer) = 13.09 min).



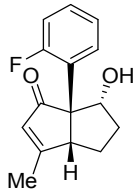
(3a*R*,6a*R*)-6a-(4-Fluorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2e). General procedure was followed on a 0.191 mmol scale. The solution was stirred at -10 °C for 16h, and then allowed to warm to RT and stirred for another 8h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (35 mg, 0.142 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.35 (m, 2H), 7.17 – 6.95 (m, 2H), 6.09 (s, 1H), 4.47 – 4.33 (m, 1H), 4.02 (d, *J* = 7.9 Hz, 1H), 3.26 (d, *J* = 9.7 Hz, 1H), 2.27 (s, 3H), 2.17 – 2.04 (m, 1H), 2.00 – 1.84 (m, 1H), 1.75 (dd, *J* = 13.4, 6.5 Hz, 1H), 1.57 – 1.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.1, 182.5, 162.0 (d, *J* = 246.0 Hz), 131.2, 129.5 (d, *J* = 7.9 Hz), 128.2 (d, *J* = 7.9 Hz), 115.6 (d, *J* = 21.3 Hz), 79.5, 62.7, 57.9, 32.3, 24.1, 18.1. **IR** (neat) 3460, 3072, 2959, 2875, 1679, 1618, 1606, 1509, 1451, 1434, 1409, 1378, 1297, 1225, 1189, 1164, 1134, 1100, 1089, 1054, 1015, 996, 953, 922, 859, 832, 812, 775, 743, 706, 647, 613, 576, 563, 526, 456 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{15}H_{16}FO_2$ $[M+H]^+$ 247.1129, found 247.1129. $[\alpha]_D^{26}$ = –180.5 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 93% ee (t_R (1, major enantiomer, major diastereomer) = 6.89 min, t_R (2, minor enantiomer, major diastereomer) = 7.63 min, t_R (3, minor enantiomer, minor diastereomer) = 11.61 min, t_R (4, major enantiomer, minor diastereomer) = 13.61 min).



(3a*R*,6a*R*)-6a-(3-Fluorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2f). General procedure was followed on a 0.146 mmol scale. The solution was stirred at -10 °C for 16h, and then allowed to warm to RT and stirred for another 8h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (26 mg, 0.106 mmol, 73%).

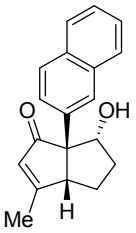
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 1H), 7.23 – 7.13 (m, 2H), 6.97 – 6.91 (m, 1H), 6.07 (p, *J* = 1.3 Hz, 1H), 4.40 (ddd, *J* = 11.1, 7.9, 5.7 Hz, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.31 – 3.16 (m, 1H), 2.24 (t, *J* = 1.1 Hz, 3H), 2.16 – 2.01 (m, 1H), 2.01 – 1.80 (m, 1H), 1.80 – 1.66 (m, 1H), 1.55 – 1.37 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 182.6, 163.1 (d, *J* = 245.9 Hz), 143.0 (d, *J* = 7.3 Hz), 131.2, 130.2 (d, *J* = 8.4 Hz), 122.2 (d, *J* = 2.9 Hz), 114.2 (d, *J* = 21.1 Hz), 113.9 (d, *J* = 22.4 Hz), 79.3, 63.1 (d, *J* = 1.9 Hz), 57.8, 32.3, 24.1, 18.1. **IR** (neat) 3461, 3072, 2959, 2874, 1680, 1614, 1586, 1488, 1436, 1379, 1296, 1262, 1189, 1166, 1128, 1105, 1090, 1059, 1018, 998, 953, 929, 892, 860, 826, 785, 741, 724, 693, 672, 625, 583, 558, 524, 511, 454 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{15}H_{16}NaFO_2$ $[M+Na]^+$ 269.0948, found 269.0948. $[\alpha]_D^{26}$ = –180.2 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 1% MeOH, 2.0 mL/min., 25 °C, 94% *ee* (t_R (1, major enantiomer, major diastereomer) = 10.55 min, t_R (2, minor enantiomer, major diastereomer) = 11.62 min, t_R (3, minor enantiomer, minor diastereomer) = 17.65 min, t_R (4, minor enantiomer, major diastereomer) = 23.47 min).



(3a*R*,6*R*,6a*R*)-6a-(2-Fluorophenyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2g). General procedure was followed on a 0.187 mmol scale. The solution was stirred at -10 °C for 16h, and then allowed to warm to RT and stirred for another 8h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (31 mg, 0.126 mmol, 67%).

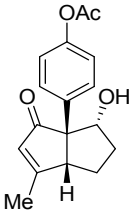
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (td, *J* = 8.0, 1.8 Hz, 1H), 7.35 – 7.20 (m, 1H), 7.15 (td, *J* = 7.6, 1.4 Hz, 1H), 7.03 (ddd, *J* = 12.2, 8.1, 1.4 Hz, 1H), 4.80 – 4.53 (m, 1H), 3.92 (d, *J* = 7.8 Hz, 1H), 3.40 (d, *J* = 9.3 Hz, 1H), 2.21 (t, *J* = 1.0 Hz, 3H), 2.13 – 2.05 (m, 1H), 2.04 – 1.94 (m, 1H), 1.75 (dd, *J* = 13.1, 6.4 Hz, 1H), 1.52 – 1.38 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.0, 182.5 (d, *J* = 1.4 Hz), 161.5 (d, *J* = 246.7 Hz), 131.1 (d, *J* = 1.6 Hz), 129.5 (d, *J* = 4.3 Hz), 129.0 (d, *J* = 8.8 Hz), 127.7 (d, *J* = 11.8 Hz), 124.4 (d, *J* = 3.3 Hz), 116.3 (d, *J* = 22.8 Hz), 78.2 (d, *J* = 1.8 Hz), 60.8 (d, *J* = 2.8 Hz), 56.9 (d, *J* = 4.7 Hz), 31.5, 24.0 (d, *J* = 1.0 Hz), 18.0. **IR** (neat) 3463, 2958, 1678, 1621, 1490, 1450, 1377, 1298, 1277, 1227, 1203, 1109, 1059, 1038, 923, 858, 807, 759,

663, 599, 543, 464 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{15}H_{15}FNaO_2$ $[M+Na]^+$ 269.0948, found 269.0948. $[\alpha]_D^{26}$ = -53.7 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 86% *ee* (t_R (1, major enantiomer, major diastereomer) = 5.72 min, t_R (2, minor enantiomer, major diastereomer) = 6.35 min).



(3a*R*,6*R*,6a*R*)-6-Hydroxy-3-methyl-6a-(naphthalen-2-yl)-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2h). General procedure was followed on a 0.109 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (26 mg, 0.094 mmol, 86%).

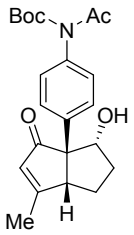
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.8 Hz, 1H), 7.84 – 7.80 (m, 3H), 7.51 – 7.40 (m, 3H), 6.14 (t, *J* = 1.4 Hz, 1H), 4.58 (ddd, *J* = 11.0, 7.4, 5.7 Hz, 1H), 4.12 (d, *J* = 7.6 Hz, 1H), 3.37 (d, *J* = 9.6 Hz, 1H), 2.27 (s, 3H), 2.13 (dtd, *J* = 11.9, 5.7, 1.4 Hz, 1H), 2.01 – 1.88 (m, 1H), 1.77 (ddt, *J* = 13.4, 6.5, 1.5 Hz, 1H), 1.53 (tdd, *J* = 12.7, 11.2, 6.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.3, 182.5, 137.7, 133.5, 132.5, 131.5, 128.6, 128.2, 127.6, 126.4, 126.1, 125.5, 124.6, 79.3, 63.6, 58.0, 32.4, 24.2, 18.1. **IR** (neat) 3459, 3055, 2956, 2927, 2871, 1677, 1599, 1506, 1450, 1432, 1377, 1329, 1293, 1247, 1215, 1187, 1137, 1102, 1087, 1059, 1018, 997, 952, 926, 886, 856, 816, 749, 666, 638, 576, 558, 528, 504, 477 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{19}H_{19}O_2$ $[M+H]^+$ 279.1380, found 279.1380. $[\alpha]_D^{26}$ = –206.6 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 10% MeOH, 2.0 mL/min., 25 °C, 91% *ee* (t_R (1, major enantiomer, major diastereomer) = 12.49 min, t_R (2, minor enantiomer, major diastereomer) = 14.41 min).



4-((3*R*,3a*R*,6a*R*)-3-Hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropentalen-3a-yl)phenyl acetate (2i). General procedure was followed on a 0.107 mmol scale. The solution was stirred at -10 °C for 16h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (22 mg, 0.077 mmol, 72% over two steps (see **250i**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.34 (m, 2H), 7.12 – 6.96 (m, 2H), 6.06 (s, 1H), 4.45 – 4.34 (m, 1H), 4.02 (d, *J* = 7.9 Hz, 1H), 3.25 (d, *J* = 9.2 Hz, 6H), 2.28 (s, 3H), 2.12 – 2.01 (m, 8H), 1.99 – 1.81 (m, 1H), 1.76 – 1.69 (m, 1H), 1.52 – 1.39 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.1, 182.5, 169.7, 149.7, 138.0, 131.2, 127.7, 121.9, 79.4, 62.9, 57.9, 32.3, 24.1, 21.3, 18.1. **IR** (neat) 3465, 2958, 2874, 1754, 1679, 1618, 1508, 1434, 1411, 1371, 1297, 1200, 1171, 1135, 1118, 1102, 1089, 1054, 1019, 951, 926, 911, 846, 799, 745, 716,

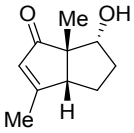
684, 619, 610, 595, 575, 528 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{17}H_{19}O_4$ $[M+H]^+$ 287.1278, found 287.1278. $[\alpha]_D^{26}$ = –135.7 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 2% MeOH, 2.0 mL/min., 25 °C, 92% *ee* (t_R (1, major enantiomer, major diastereomer) = 17.08 min, t_R (2, minor enantiomer, major diastereomer) = 20.53 min).



***tert*-Butyl acetyl(4-((3a*R*,6a*R*)-3-hydroxy-6-methyl-4-oxo-1,2,3,3a,4,6a-hexahydropenta-len-3a-yl)phenyl) carbamate (2j).** General procedure was followed on a 0.105 mmol scale. The solution was stirred at -10 °C for 16h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 4:1 to 2:1). The title compound was isolated as clear, colorless oil (30 mg, 0.078 mmol, 74%).

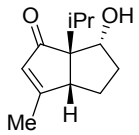
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.09 – 7.04 (m, 2H), 6.09 (s, 1H), 4.45 (m, 1H), 4.06 (d, *J* = 7.8 Hz, 1H), 3.30 (d, *J* = 9.5 Hz, 1H), 2.58 (s, 3H), 2.26 (s, 3H), 2.15 – 2.06 (m, 1H), 1.99 – 1.85 (m, 1H), 1.75 (ddt, *J* = 13.3, 6.5, 1.5 Hz, 1H), 1.57 – 1.44 (m, 1H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.9, 182.5, 173.1, 152.9, 140.1, 137.8, 131.3, 128.5, 127.3, 83.6, 79.4, 63.1, 57.9, 32.3, 28.0, 26.7, 24.2, 18.1. **IR** (neat) 3472, 2976, 1737, 1704, 1619, 1513, 1414. 1395, 1371, 1340, 1275, 1255, 1157, 1098, 1055, 1016, 923. 849, 774, 743, 612, 544 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{22}H_{28}NO_5$ $[M+H]^+$ 386.1962, found 386.1963. $[\alpha]_D^{26}$ = –101.1 (c = 1.0, $CHCl_3$). **SFC** (of the corresponding 4-bromophenyl-carbamate) Daicel Chiralcel OJ-H, 1% MeOH, 2.0 mL/min., 25 °C, 93% *ee* (t_R (1, major enantiomer, major diastereomer) = 11.68 min, t_R (2, minor enantiomer, major diastereomer) = 12.83 min).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.54 (m, 1H), 7.25 – 7.19 (m, 1H), 7.17 (td, *J* = 7.3, 1.5 Hz, 1H), 7.14 – 7.09 (m, 1H), 4.71 (dt, *J* = 11.5, 6.0 Hz, 1H), 3.77 (d, *J* = 6.9 Hz, 1H), 3.37 (d, *J* = 8.9 Hz, 1H), 2.43 – 2.29 (m, 1H), 2.23 (s, 3H), 2.20 (t, *J* = 1.0 Hz, 3H), 2.13 – 2.00 (m, 1H), 1.98 – 1.80 (m, 1H), 1.75 (ddt, *J* = 13.3, 6.3, 1.3 Hz, 1H), 1.45 (dddd, *J* = 13.1, 12.1, 11.2, 6.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.2, 181.2, 138.1, 136.4, 132.6, 132.5, 128.6, 127.2, 126.4, 77.3, 64.2, 56.3, 30.8, 24.0, 21.3, 17.7.



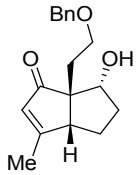
(3a*R*,6*R*,6a*S*)-6-Hydroxy-3,6a-dimethyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2k). General procedure was followed on a 0.125 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (13 mg, 0.078 mmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) Major Diastereomer: δ 5.91 (s, 1H), 3.90 – 3.73 (m, 1H), 3.33 (s, 1H), 2.71 – 2.66 (m, 1H), 2.12 (t, *J* = 1.1 Hz, 3H), 1.96 – 1.89 (m, 1H), 1.74 – 1.67 (m, 1H), 1.53 – 1.44 (m, 1H), 1.42 – 1.30 (m, 1H), 1.25 (s, 3H). Minor Diastereomer: 5.81 (s, 1H), 4.13 – 3.96 (m, 1H), 2.75 (d, *J* = 10.5 Hz, 1H), 2.22 – 2.13 (m, 1H), 2.10 (t, *J* = 1.1 Hz, 3H), 1.85 – 1.75 (m, 1H), 1.66 – 1.59 (m, 1H), 1.57 – 1.52 (m, 1H), 1.18 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) Major diastereomer: δ 214.1, 181.2, 130.2, 79.6, 56.5, 42.9, 32.8, 32.7, 20.9, 17.9. Minor diastereomer: δ 212.9, 179.6, 128.6, 75.6, 61.4, 56.6, 32.8, 18.0, 17.9, 16.7. **IR** (neat) 3443, 2828, 2856, 1740, 1620, 1448, 1373, 1237, 1066, 967, 859, 604, 534, 496 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{10}H_{14}NaO_2$ $[M+Na]^+$ 189.0886, found 189.0887. $[\alpha]_D^{26}$ = +4.7 (c = 0.33, $CHCl_3$) **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 90% *ee* (t_R (1, major enantiomer, minor diastereomer) = 1.38 min, t_R (2, minor enantiomer, minor diastereomer) = 1.53 min, t_R (3, major enantiomer, major diastereomer) = 1.78 min, t_R (4, minor enantiomer, major diastereomer) = 2.25 min).



(3a*R*,6*R*,6a*S*)-6-Hydroxy-6a-isopropyl-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2l). General procedure was followed on a 0.118 mmol scale. The solution was stirred at -10 °C for 16h, then warmed to RT and stirred for 8h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient from 6:1 to 3:1). The title compound was isolated as clear, colorless oil (13 mg, 0.067 mmol, 57%).

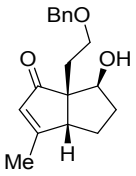
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (t, *J* = 1.4 Hz, 1H), 4.14 – 3.99 (m, 1H), 3.58 (d, *J* = 6.5 Hz, 1H), 2.87 – 2.69 (m, 1H), 2.15 – 2.07 (m, 4H), 1.96 – 1.87 (m, 1H), 1.73 – 1.60 (m, 2H), 1.38 – 1.26 (m, 1H), 1.21 – 1.09 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.9, 182.2, 132.4, 75.9, 63.8, 51.6, 32.5, 31.4, 24.3, 18.7, 18.2, 17.8. **IR** (neat) 3472, 2962, 2874, 1984, 1744, 1677, 1620, 1464, 1436, 1372, 1299, 1240, 1208, 1085, 921, 893, 852, 744, 520, 464 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{12}H_{18}NaO_2$ $[M+Na]^+$ 217.1199, found 217.1199. $[\alpha]_D^{26}$ = –2.6 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 3% MeOH, 2.0 mL/min., 25 °C, 88% *ee* (t_R (1, minor enantiomer, minor diastereomer) = 2.87 min, t_R (2, major enantiomer, minor diastereomer) = 3.13 min, t_R (3, major enantiomer, major diastereomer) = 3.57 min, t_R (4, minor enantiomer, major diastereomer) = 3.97 min).



(3a*R*,6*R*,6a*S*)-6a-(2-(Benzyloxy)ethyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (251m). General procedure was followed on a 0.305 mmol scale. The solution was stirred at -10 °C for 24h. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc gradient

from 6:1 to 4:1). The two diastereomers of the title compound could be separated and isolated to give **2m** (51 mg, 0.178 mmol, 59%) and **2m'** (12 mg, 0.042 mmol, 14%).

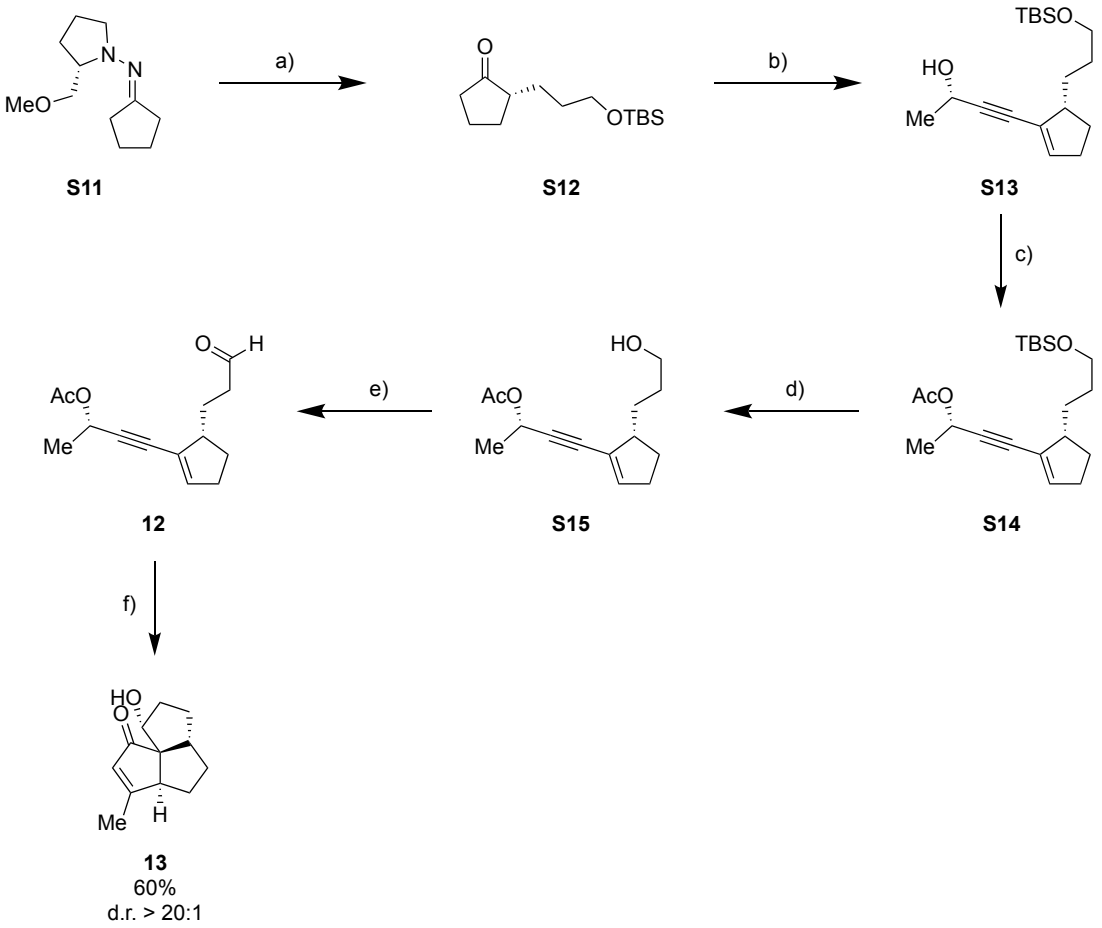
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 5.90 (t, *J* = 1.4 Hz, 1H), 4.39 (d, *J* = 1.9 Hz, 2H), 3.84 (dd, *J* = 10.5, 5.6 Hz, 1H), 3.62 – 3.46 (m, 1H), 3.46 – 3.34 (m, 1H), 3.00 (d, *J* = 9.2 Hz, 0H), 2.19 (ddd, *J* = 14.2, 6.9, 5.8 Hz, 1H), 2.06 (t, *J* = 1.1 Hz, 3H), 1.89 – 1.79 (m, 2H), 1.78 – 1.65 (m, 1H), 1.60 (ddt, *J* = 13.2, 6.6, 2.0 Hz, 1H), 1.37 – 1.14 (m, 1H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 213.7, 182.5, 138.9, 131.5, 128.6, 128.0, 127.9, 79.0, 73.4, 67.7, 59.1, 54.5, 35.0, 32.1, 24.3, 17.9. **IR** (neat) 3461, 3063, 3031, 2937, 2909, 2868, 1956, 1677, 1617, 1497, 1454, 1433, 1377, 1366, 1302, 1256, 1199, 1091, 1028, 1003, 948, 916, 882, 858, 796, 738, 699, 666, 607, 581, 532 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{22}NaO_3$ $[M+Na]^+$ 309.1461, found 309.1461. $[\alpha]_D^{26}$ = –36.3 (c=1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 2% MeOH, 2.0 mL/min., 25 °C, 95% *ee* (t_R (1, major enantiomer, major diastereomer) = 17.77 min, t_R (2, minor enantiomer, major diastereomer) = 25.69 min,).



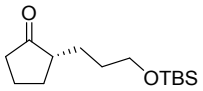
(3a*R*,6*S*,6a*S*)-6a-(2-(Benzyloxy)ethyl)-6-hydroxy-3-methyl-4,5,6,6a-tetrahydropentalen-1(3a*H*)-one (2m').

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 5.77 (t, *J* = 1.3 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 11.6 Hz, 1H), 4.20 (t, *J* = 2.9 Hz, 1H), 4.06 (ddd, *J* = 10.6, 9.5, 2.1 Hz, 1H), 3.81 (t, *J* = 2.3 Hz, 1H), 3.48 (ddd, *J* = 9.4, 4.6, 3.2 Hz, 1H), 2.73 (d, *J* = 9.8 Hz, 1H), 2.22 (dddd, *J* = 14.4, 9.4, 7.6, 3.4 Hz, 2H), 2.13 – 2.05 (m, 3H), 1.75 (dd, *J* = 13.4, 6.2 Hz, 1H), 1.65 (ddd, *J* = 15.2, 4.7, 2.1 Hz, 1H), 1.54 (dd, *J* = 12.7, 7.0 Hz, 1H), 1.47 – 1.33 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.9, 179.4, 137.7, 129.2, 128.6, 128.0, 127.9, 74.6, 73.7, 66.2, 64.8, 56.9, 32.1, 31.6, 25.3, 18.2. **IR** (neat) 3438, 3064, 3031, 2942, 2866, 1688, 1618, 1497, 1454, 1435, 1376, 1365, 1330, 1305, 1250, 1186, 1165, 1089, 1073, 1029, 989, 959, 943, 921, 860, 826, 738, 698, 637, 609, 566 cm^{-1}. $[\alpha]_D^{26}$ = -11.7 (c = 1.0, $CHCl_3$).

5. Synthesis of Triquinane 12



Reagents and Conditions: a) (i) n-BuLi (1.05 equiv), 0 °C, THF, 60 min; then tert-butyl(3-iodopropoxy)dimethylsilane (1.05 equiv), –78 °C to RT, 20h (ii) O_3, CH_2Cl_2, –78 °C, 10min, then PPh_3 (1.3 equiv), RT, 18h, 70% over two steps; b) (i) LDA (1.1 equiv), –78 °C, 30 min; then TMSCl (1.1 equiv), –78 °C to –40 °C; (ii) MeLi (1.00 equiv), 0 °C, 30min; then Comin's Reagent (1.3 equiv), –78 °C to RT, 2h, 80% over two steps; (iii) (S)-3-butyn-2-ol (1.3 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), Et_3N/THF (2:1), 71%; c) Ac_2O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH_2Cl_2, 93%; d) TBAF (2 equiv), THF, 94%; e) DMP (2.0 equiv), t-BuOH (2.0 equiv), CH_2Cl_2, 84%; f) Au(MeCN)(JohnPhos)SbF_6 (5 mol%), THF, 0.2% H_2O, –10 °C, 24h, 60%.

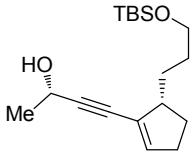


(*S*)-2-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)cyclopentanone (S12). To a solution of **S11**[10] (2.00 g, 10.2 mmol, 1.0 equiv) in THF (51 ml) at 0 °C was added *n*-BuLi (1.6 M in hexanes, 6.69 ml, 10.7 mmol, 1.05 equiv) and stirred for 60 min. The solution was then cooled to –78 °C and a solution of *tert*-butyl(3-iodopropoxyl)dimethylsilane (3.21 g, 10.7 mmol, 1.05 equiv) in THF (10 ml) was added dropwise and then slowly warmed to RT. The reaction mixture was quenched by the addition of sat. aq. NH_4Cl. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided the alkylated hydrazone (3.70 g, 10.0 mmol, 98%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 – 3.55 (m, 2H), 3.46 (d, *J* = 5.2 Hz, 1H), 3.34 (s, 3H), 3.30 – 3.16 (m, 3H), 2.40 (q, *J* = 9.0 Hz, 3H), 2.23 – 2.08 (m, 1H), 1.95 (ddd, *J* = 11.9, 7.6, 5.2 Hz, 2H), 1.88 – 1.74 (m, 3H), 1.73 – 1.47 (m, 6H), 1.44 – 1.20 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

The alkylated hydrazone (3.70 g, 10.0 mmol, 1 equiv) was dissolved in CH_2Cl_2 (100 ml) and cooled to –78 °C. At that temperature, ozone was bubbled through the reaction mixture until the yellow reaction mixture turned green (TLC control). After bubbling through O_2 for 5 min, PPh_3 (7.90 g, 30.1 mmol, 3 equiv) was added and the mixture was allowed to warm to RT and stirred overnight. The reaction mixture was reduced to about 15ml and then pentane (100 ml) was added. The formed suspension was filtered through celite and concentrated *in vacuo*. Flash column chromatography (pentane to pentane–Et_2O 25:1) furnished cyclopentone **S12** (1.83 g, 7.14 mmol, 71%) as a colorless oil.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.61 (td, *J* = 6.4, 1.2 Hz, 2H), 2.31 – 2.15 (m, 2H), 2.13 – 1.92 (m, 3H), 1.84 – 1.67 (m, 2H), 1.60 – 1.44 (m, 3H), 1.35 – 1.20 (m, 1H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 221.1, 63.5, 49.2, 38.5, 31.2, 30.1, 26.6, 26.1, 21.1, 18.6, -5.2. **IR** (neat) 2954, 2929, 2884, 2857, 1739, 1472, 1463, 1407, 1388, 1361, 1333, 1305, 1253, 1215, 1200, 1154, 1096, 1038, 1006, 955, 938, 887, 834, 813, 774, 72, 680, 662, 572, 544, 515 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{32}NaO_3Si$ $[M+Na]^+$ 279.1751, found 279.1748. $[\alpha]_D^{26}$ = –61.9 (c = 1.0, CH_2Cl_2).



(*S*)-4-((*S*)-5-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)cyclopent-1-en-1-yl)but-3-yn-2-ol (S13). To a freshly prepared solution of LDA (0.2 M, 230 mg, 2.1 5mmol, 1.1 equiv) was added a solution of **S12** (500 mg, 2.15 mmol, 1.0 equiv) and stirred for 30 min. After that time, TMSCl (0.272 ml, 2.15 mmol, 1.1 equiv) was added dropwise and slowly warmed to –40 °C over 30 min. The reaction was quenched with Sorensen Buffer (pH = 7.0). Et_2O was added to the mixture and the phases separated. The aqueous phase was

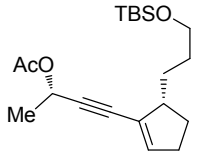
[10] a) B. Bockstiegel, D. Enders, *Synthesis*, **1989**, *7*, 493-496; b) A. B. III Smith, Z. Liu, V. Simov, *Synlett*, **2009**, *19*, 3131-3134.

extracted with Et_2O (3x). The combined organic phases were dried over K_2CO_3, filtered, and concentrated *in vacuo*.

The crude mixture was dissolved in THF and at 0 °C MeLi (1.6 M in hexanes, 1.27 ml, 2.04 mmol, 1.1 equiv) was added dropwise and stirred for 30 min. The solution as then cooled to –78 °C. At that temperature, Comin's reagent (948 mg, 2.41 mmol, 1.3 equiv) was added in one portion and the cooling bath was removed. After 60min, the reaction was quenched with sat. aq. $NaHCO_3$. Et_2O was added to the mixture and the phases separated. The aqueous phase was extracted with Et_2O (3x). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (hexane/EtOAc 10:1) furnished the vinyl triflate as colorless oil (600 mg, 1.54 mmol, 80%).

To a degassed solution of the crude vinyl triflate (240 mg,0.62 mmol, 1.0 equiv) and (*R*)-but-3-yn-2-ol (0.06 ml, 0.74 mmol, 1.2 equiv) in NEt_3/THF (1:1, 0.15 M) was added $PdCl_2(PPh_3)_2$ (21.7 mg, 0.03 mmol, 0.05 equiv) and CuI (11.8 mg, 0.06 mmol, 0.1 equiv) and the resulting mixture was stirred at RT for 2 h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated *in vacuo*. Purification by column chromatography (hexane/EtOAc 5:1) afforded enyne **S13** (135 mg, 0.44 mmol, 71%).

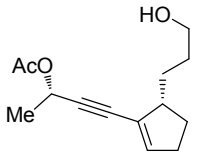
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (q, *J* = 2.4 Hz, 1H), 4.66 (q, *J* = 6.6 Hz, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.74 – 2.59 (m, 1H), 2.45 – 2.28 (m, 2H), 2.15 – 2.02 (m, 1H), 1.82 – 1.69 (m, 1H), 1.66 – 1.49 (m, 3H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.31 – 1.17 (m, 1H), 0.90 (s, 9H), 0.06 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9, 128.5, 93.2, 81.1, 63.6, 59.0, 47.8, 32.1, 30.7, 30.5, 29.8, 26.1, 24.6, 18.5, -5.1. **IR** (neat) 3357, 2953, 2930, 2893, 2857, 1472, 1388, 1361, 1327, 1255, 1102, 1039, 1006, 940, 910, 835, 775, 663 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{32}NaO_3Si$ $[M+Na]^+$ 331.2064, found 331.2064. $[\alpha]_D^{26}$ = –7.3 (c = 1.0, $CHCl_3$).



(*S*)-4-((*S*)-5-(3-((*tert*-Butyldimethylsilyl)oxy)propyl)cyclopent-1-en-1-yl)but-3-yn-2-yl acetate (S14). To a stirred solution of enyne **S13** (135 mg, 0.44 mmol, 1.0 equiv) dissolved in CH_2Cl_2 (4.5 ml) at ambient temperature was added pyridine (0.177 ml, 2.19 mmol, 5.0 equiv), DMAP (10.7 mg, 0.09 mmol, 0.2 equiv), and Ac_2O (0.062 ml, 0.66 mmol, 1.5 equiv). The resulting solution was stirred for 1h before it was quenched with H_2O. The aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with sat. aq. $CuSO_4$ solution, H_2O (1x), and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided propargyl acetate **S14** (142 mg, 0.41 mmol, 93%) as a colorless oil.

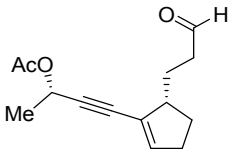
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (q, *J* = 2.5 Hz, 1H), 5.60 (q, *J* = 6.7 Hz, 1H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.73 – 2.60 (m, 0H), 2.41 – 2.31 (m, 2H), 2.14 – 2.03 (m, 4H), 1.76 (dddd, *J* = 12.9, 10.2, 6.1, 4.1 Hz, 1H), 1.62 – 1.44 (m, 6H), 1.31 – 1.17 (m, 1H), 0.90 (s, 9H), 0.05 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 138.8, 128.3, 89.5, 81.7, 63.5, 61.1, 47.8, 32.1, 30.7, 30.5, 29.7, 26.1, 21.8, 21.3, 18.5, -5.1. **IR** (neat) 2952, 2930, 2857, 2227, 1746, 1472, 1463, 1371, 1340, 1308, 1230, 1097, 1033, 1009, 953, 939, 835, 813, 775, 713,

662, 610, 510, 470 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{20}H_{34}NaO_3Si$ $[M+Na]^+$ 373.2169, found 373.2170. $[\alpha]_D^{26}$ = –85.5 (c = 1.0, $CHCl_3$).



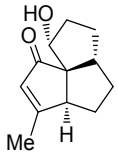
(*S*)-4-((*S*)-5-(3-Hydroxypropyl)cyclopent-1-en-1-yl)but-3-yn-2-yl acetate (S15). To a stirred solution of propargyl acetate **S14** (140 mg, 0.40 mmol, 1.0 equiv) in dry THF (3.3 ml) in 0 °C was added TBAF (1.0 M in THF, 0.799 ml, 0.80 mmol, 2.0 equiv). After the addition, the solution was allowed to warm to ambient temperature and stirred for another 90 min. The mixture was quenched by the addition of sat. aq. $NaHCO_3$ solution. EtOAc was added to the mixture and the phases separated. The aqueous phase was extracted with EtOAc (3x). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided primary alcohol **S15** (89 mg, 0.38 mmol, 94%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (q, *J* = 2.6 Hz, 1H), 5.56 (q, *J* = 6.7 Hz, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.83 – 2.63 (m, 0H), 2.43 – 2.31 (m, 2H), 2.16 – 2.04 (m, 4H), 1.80 – 1.69 (m, 1H), 1.67 – 1.58 (m, 2H), 1.51 (d, *J* = 6.7 Hz, 4H), 1.40 – 1.27 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 139.0, 128.0, 89.7, 81.7, 63.3, 61.2, 47.6, 32.1, 30.6, 30.3, 29.8, 21.6, 21.3. **IR** (neat) 3420, 3054, 2989, 2937, 2855, 2226, 2095, 1770, 1743, 1619, 1450, 1372, 1339, 1309, 1232, 1076, 1057, 1032, 956, 844, 810, 612, 533, 483 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{14}H_{20}NaO_3$ $[M+Na]^+$ 259.1305, found 259.1305. $[\alpha]_D^{26}$ = –134.77 (c = 1.0, $CHCl_3$).



(*S*)-4-((*S*)-5-(3-Oxopropyl)cyclopent-1-en-1-yl)but-3-yn-2-yl acetate (12). To a solution of **S15** (85 mg, 0.36 mmol, 1.0 equiv) in CH_2Cl_2 (3.6 ml) at RT was added *t*-BuOH (68 µl, 0.72 mmol, 2.0 equiv) and DMP (305 mg, 0.72 mmol, 2.0 equiv). The mixture was stirred for 15 min and then quenched by the addition of sat. aq. $Na_2S_2O_3$. The mixture was poured on sat. aq. $NaHCO_3$ solution and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography provided aldehyde **12** (71 mg, 0.30 mmol, 84%) as a colorless oil.

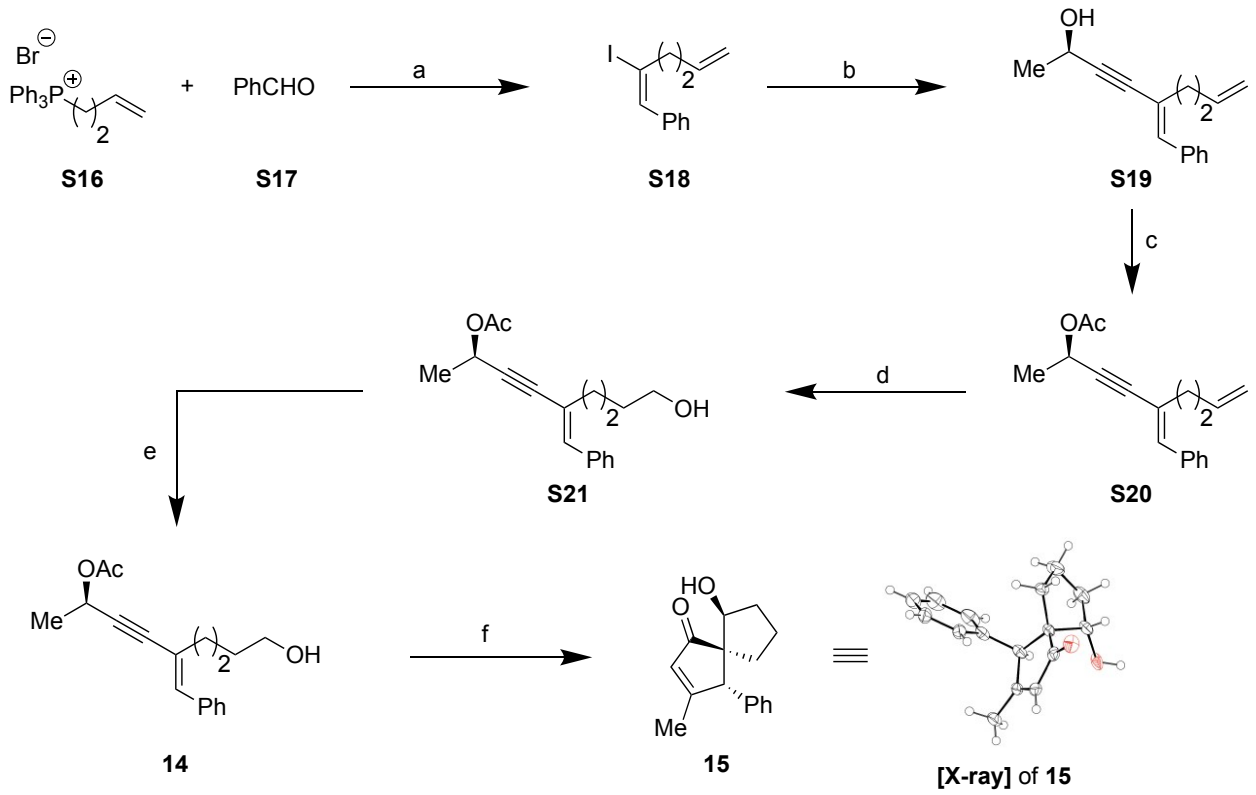
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (t, *J* = 1.8 Hz, 1H), 6.10 (q, *J* = 2.5 Hz, 1H), 5.57 (q, *J* = 6.7 Hz, 1H), 2.78 – 2.67 (m, 1H), 2.49 (td, *J* = 7.8, 1.8 Hz, 2H), 2.42 – 2.33 (m, 2H), 2.16 – 2.05 (m, 4H), 2.04 – 1.94 (m, 1H), 1.70 – 1.61 (m, 1H), 1.50 (d, *J* = 6.7 Hz, 3H), 1.48 – 1.43 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.7, 170.1, 139.6, 127.6, 90.1, 81.3, 61.0, 47.1, 41.7, 32.1, 29.6, 26.4, 21.7, 21.3. **IR** (neat) 2989, 2937, 2947, 2723, 2226, 2099, 1740, 1724, 1448, 1412, 1371, 1339, 1307, 1229, 1150, 1088, 1076, 1031, 954, 887, 843, 656, 611, 532, 497, 480 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{14}H_{19}O_3$ $[M+H]^+$ 235.1329, found 235.1328. $[\alpha]_D^{26}$ = –117.6 (c = 1.0, $CHCl_3$).



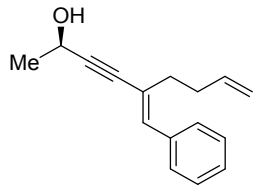
(3a*S*,8*S*,8a*S*)-8-Hydroxy-3-methyl-4,5,5a,6,7,8-hexahydrocyclopenta[c]pentalen-1(3a*H*)-one (13). Enyne **12** (53 mg, 0.23 mmol, 1.0 equiv) was dissolved in THF (4.5 ml) and H_2O (9.0 µl) was added at ambient temperature. **3** (8.73 mg, 0.011 mmol, 0.05 equiv) was added in one portion and stirred for 16h. Then the reaction mixture was filtered through a short pad of silica gel washing with EtOAc, concentrated in vacuo, and subsequently subjected to silica gel flash chromatogroaphy to afford triquinine **13** (26 mg, 0.135 mmol, 60%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 – 5.75 (m, 0H), 4.70 – 4.38 (m, 1H), 3.33 (d, *J* = 8.9 Hz, 0H), 2.48 – 2.32 (m, 1H), 2.13 – 2.08 (m, 3H), 2.06 – 1.99 (m, 1H), 1.96 – 1.90 (m, 1H), 1.88 – 1.80 (m, 1H), 1.75 (ddt, *J* = 13.1, 6.6, 2.1 Hz, 1H), 1.68 – 1.54 (m, 3H), 1.50 (ddt, *J* = 12.9, 6.8, 2.1 Hz, 1H), 1.39 – 1.31 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 212.8, 180.4, 130.8, 76.9, 71.7, 51.2, 46.6, 35.3, 32.1, 28.2, 27.2, 17.8. **IR** (neat) 3405, 3067, 2946, 2867, 1678, 1615, 1470, 1435, 1377, 1305, 1285, 1237, 1197, 1169, 1099, 1084, 1051, 1038, 1021, 979, 960, 925, 911, 854, 810, 762, 650, 626, 603, 586, 571, 512 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{12}H_{16}NaO_2$ $[M+Na]^+$ 215.1043, found 215.1042. $[\alpha]_D^{26}$ = +32.2 (c = 1.0. $CHCl_3$).

6. Synthesis of spiro[4.4]nonane 14



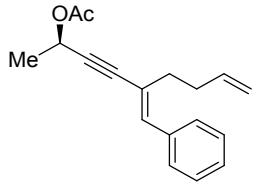
Reagents and Conditions: a) PhLi (1.0 equiv), LiBr (2.0 equiv), ***S16*** *(1.0 equiv), –78°C; then PhLi (1.1 equiv), then* ***S17*** *(1.0 equiv), 10 min, then PhLi (1.1 equiv), then –78°C to RT; then 1,2-diiodoethane (1.2 equiv), –78°C to RT; 47%, E/Z = 6:1; b) (R)-3-butyn-2-ol (1.3 equiv), $PdCl_2(PPh_3)_2$ (5 mol%), CuI (10 mol%), Et_3N/THF (2:1), 63%, E/Z = 6:1; c) Ac_2O (1.1 equiv), DMAP (0.1 equiv), pyridine (1.5 equiv), CH_2Cl_2, 82%, E/Z = 6:1; d) 9-BBN (1.8 equiv), THF, 0 °C to RT, then H_2O, $NaBO_3 \cdot 4H_2O$ (30.0 equiv), RT, 87%, E/Z = 6:1; e) DMP (2.0 equiv), t-BuOH (2.0 equiv), CH_2Cl_2, 89%, E/Z = 6:1.*



(*R*,*E*)-5-Benzylidenenon-8-en-3-yn-2-ol (S19). To a solution of anhydrous LiBr (3.42 g, 39.4 mmol, 2.0 equiv) in dry THF (90 ml) at ambient temperature was added **S16**[11] (8.10 g, 19.7 mmol, 1.0 equiv) and stirred for 10 min. The resulting suspension was cooled to –78°C and PhLi (1.9 M in Bu_2O, 10.37 ml, 19.7 mmol, 1.0 equiv) was added dropwise. The solution was allowed to warm to RT over 15 min and then stirred for another 30 min at that temperature. Then the solution was recooled to –78°C and benzaldehyde (2.0 ml, 19.7 mmol, 1.0 equiv) in THF (5 ml) was added dropwise. After 10 min, PhLi (1.9 M in Bu_2O, 11.40 ml, 21.7 mmol 1.1 equiv) was added dropwise and stirred for 30 min at –78°C, then allowed to warm to RT over 15 min. After 30 min at ambient temperature, the mixture was cooled to –78°C and transferred via cannula to a solution of 1,2-diiodoethane (1.0 M in THF, 1.2 equiv) at –78°C and stirred for 30 min. Then the solution was allowed to warm to RT and stirred for another hour. The resulting mixture was quenched by the addition of sat. aq. $Na_2S_2O_3$ solution and stirred vigorously for 5 min. The phases were separated and the aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (hexane/EtOAc 40:1) afforded the corresponding vinyl iodide **S18** (2.60 g, 9.2 mmol, 47%) as a mixture of diastereomers (*E*/*Z* = 6:1) and a yellow oil, which contained impurities unseparable by silica gel chromatography and was used in the following step directly.
To a degassed solution of the vinyl iodide (584 mg, 2.06 mmol) and (*R*)-but-3-yn-2-ol (0.18 ml, 1.1 equiv) in NEt_3/THF (2:1, 0.15 M) was added $PdCl_2(PPh_3)_2$ (72 mg, 0.10 mmol, 0.05 equiv) and CuI (39 mg, 0.21 mmol, 0.1 equiv) and the resulting mixture was stirred at RT for 2 h before it was filtered through a short plug of silica gel eluting with EtOAc and concentrated *in vacuo*. Purification by column chromatography (hexane/EtOAc 8:1) afforded enyne **S19** (310 mg, 1.37 mmol, 67%, *E*/*Z* = 6:1) as an orange oil.

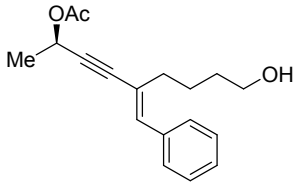
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.28 – 7.22 (m, 3H), 6.87 (s, 1H), 5.93 – 5.73 (m, 1H), 5.09 – 5.02 (m, 1H), 5.01 – 4.94 (m, 1H), 2.51 – 2.44 (m, 2H), 2.41 – 2.36 (m, 2H), 1.53 (d, *J* = 6.6 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 136.7, 136.6, 128.9, 128.5, 127.5, 124.1, 115.2, 91.3, 86.2, 59.1, 32.6, 30.8, 24.7. **IR** (neat) 3342, 3079, 2980, 2929, 1641, 1598, 1493, 1446, 1370, 1328, 1182, 1117, 1076, 1032, 997, 943, 916, 871, 755, 696, 634, 542, 508, 414 cm^{-1}. **HRMS (ESI):** m/z calcd for $C_{16}H_{18}NaO$ $[M+Na]^+$ 249.1250, found 249.1250. $[\alpha]_D^{26}$ = +23.0 (c = 0.5, $CHCl_3$).

[11] Q. Yang, C. Draghici, J. T. Njardarson, F. Li, B. R. Smith, P. Das, *Org. Biomol. Chem.,* **2014**, *12*, 330-344.



(*R*,*E*)-5-Benzylidenenon-8-en-3-yn-2-yl acetate (S20). To a stirred solution of propargyl alcohol **S19** (250 mg, 1.11 mmol) dissolved in CH_2Cl_2 (10 ml) at ambient temperature was added pyridine (0.45 ml, 5.52 mmol, 5.0 equiv), DMAP (27.0 mg, 0.22 mmol, 0.2 equiv), and Ac_2O (0.16 ml, 1.66 mmol, 1.5 equiv). The resulting solution was stirred for 1 h before it was quenched with H_2O. The aqueous phase was extracted with Et_2O (3x). The combined organic phases were washed with sat. aq. $CuSO_4$ solution, H_2O (1x), and brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (hexane/EtOAc 20:1) provided propargyl acetate **S20** (260 mg, 0.97 mmol, 88%, *E*/*Z* = 6:1) as a colorless oil.

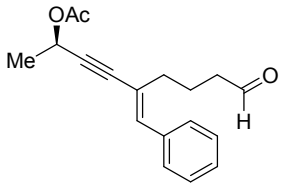
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.26 – 7.21 (m, 3H), 6.88 (s, 1H), 5.60 (q, *J* = 6.6 Hz, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.40 (td, *J* = 7.4, 1.2 Hz, 2H), 2.10 (d, *J* = 1.4 Hz, 3H), 1.74 – 1.63 (m, 2H), 1.63 – 1.56 (m, 2H), 1.55 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 137.2, 136.5, 135.6, 128.9, 128.5, 127.5, 124.4, 87.6, 86.8, 62.8, 61.1, 32.3, 30.9, 24.6, 21.6, 21.3. **IR** (neat) 2928, 2855, 1742, 1641, 1493, 1446, 1371, 1339, 1262, 1075, 134, 954, 918, 845, 756, 697, 607, 497, 414 cm^{-1}. **HRMS (ESI):** m/z calcd for $C_{18}H_{20}NaO_2$ $[M+Na]^+$ 291.1356, found 291.1360. $[\alpha]_D^{26}$ = +97.1 (c = 0.5, $CHCl_3$).



(*R*,*E*)-5-Benzylidene-9-hydroxynon-3-yn-2-yl acetate (S21). To a solution of 9-BBN (0.5 M in THF, 2.68 ml, 1.34 mmol, 1.8 equiv) was added THF (5.4 ml) and cooled to 0 °C. A solution of **S20** (200 mg, 0.75 mmol, 1.0 equiv) in THF (0.9 ml) was added dropwise. The resulting mixture was stirred at RT for 2 h. The mixture was then cooled to 0 °C and diluted with H_2O (7 ml), THF (2 ml) and sodium perborate tetrahydrate (3.44 g, 22.4 mmol, 30.0 equiv) was added. The mixture was allowed to warm up to RT and was stirred at the same temperature for 2 h. The phases were separated and the aqueous phase was extracted with EtOAc (3x). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash chromatography (hexane/EtOAc 15:1 to 2:1) provided the desired product **S21** (186 mg, 0.65 mmol, 87%, *E*/*Z* = 6:1) as a faint yellow oil.

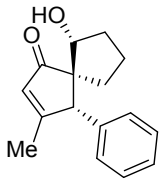
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.21 (m, 3H), 6.88 (s, 1H), 5.60 (q, *J* = 6.7 Hz, 1H), 3.63 (t, *J* = 6.3 Hz, 2H), 2.40 (t, *J* = 7.9 Hz, 2H), 2.10 (s, 3H), 1.74 – 1.63 (m, 2H), 1.63 – 1.56 (m, 2H), 1.55 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.1, 137.0, 136.4, 135.4, 128.8, 128.3, 127.4, 124.2, 87.5, 86.7, 62.7, 61.0, 32.2, 30.8, 24.5, 21.5, 21.2. **IR** (neat) 3424, 2988, 2936, 2865, 2217, 1739, 1597, 1492, 1446, 1371, 1338, 1308, 1230, 1197, 1157, 1061, 1030, 954, 922, 874, 845, 757, 697, 611, 510, 415

cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{22}NaO_3$ $[M+Na]^+$ 309.1461, found 309.1461. $[\alpha]_D^{26}$ = +138.0 (c = 1.0, $CHCl_3$).



(*R*,*E*)-5-Benzylidene-9-oxonon-3-yn-2-yl acetate (14). To a solution of **S21** (60 mg, 0.21 mmol, 1.0 equiv) in CH_2Cl_2 (2.1 ml) at RT was added *t*-BuOH (30 µl, 0.31 mmol, 2.0 equiv) and DMP (68 mg, 0.31 mmol, 2.0 equiv). The mixture was stirred for 30 min and then quenched by the addition of sat. aq. $Na_2S_2O_3$. The mixture was poured on sat. aq. $NaHCO_3$ solution and CH_2Cl_2 was added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (hexane/EtOAc 4:1) provided aldehyde **13** (50 mg, 0.18 mmol, 84%, *E*/*Z* = 6:1) as a colorless oil.

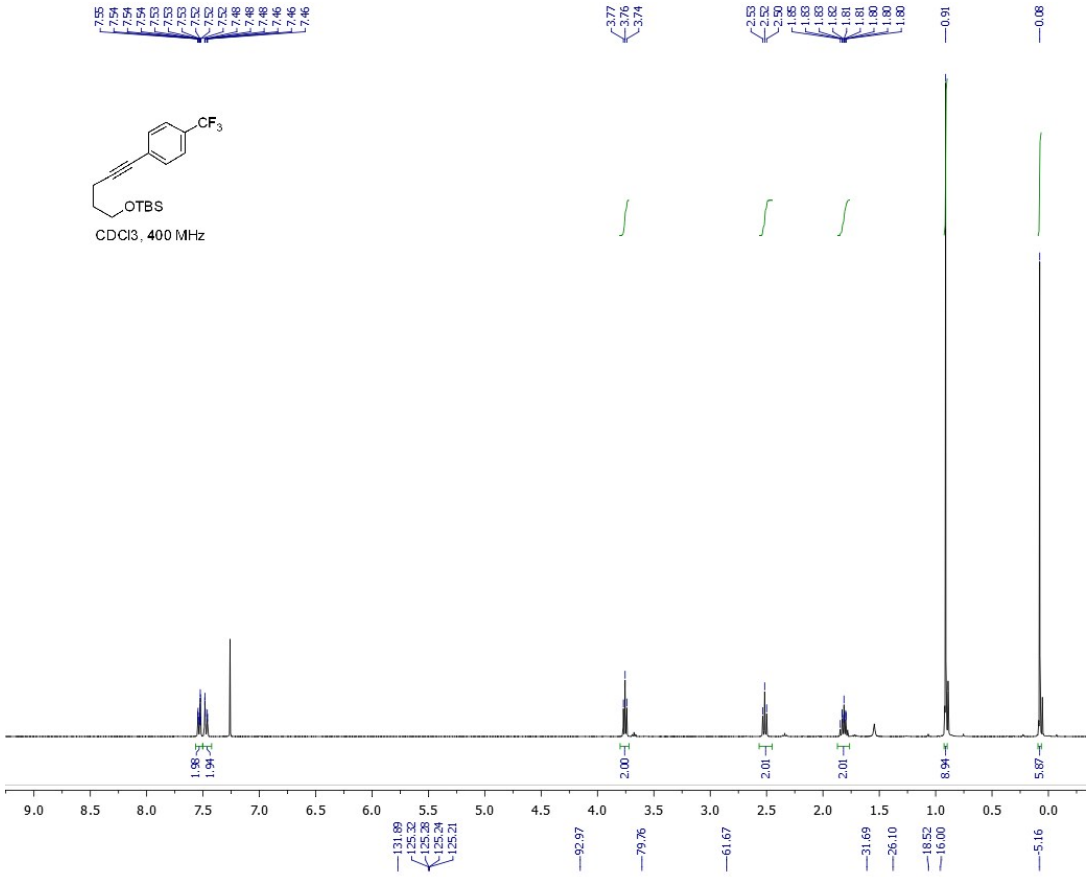
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 1.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.28 – 7.20 (m, 3H), 6.91 (s, 1H), 5.61 (q, *J* = 6.7 Hz, 1H), 2.52 – 2.37 (m, 4H), 2.10 (s, 3H), 1.98 – 1.86 (m, 2H), 1.55 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.2, 170.0, 137.7, 136.1, 128.7, 128.4, 127.5, 123.2, 87.8, 86.2, 60.9, 43.1, 30.3, 21.5, 21.2, 20.7. **IR** (neat) 2989, 2937, 2724, 1739, 1492, 1446, 1371, 1339, 1307, 1232, 1092, 1063, 1033, 955, 923, 845, 758, 698, 608, 510, 417 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{18}H_{20}NaO_3$ $[M+Na]^+$ 307.1305, found 307.1307. $[\alpha]_D^{26}$ = +107.4 (c = 1.0, $CHCl_3$).

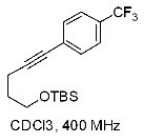


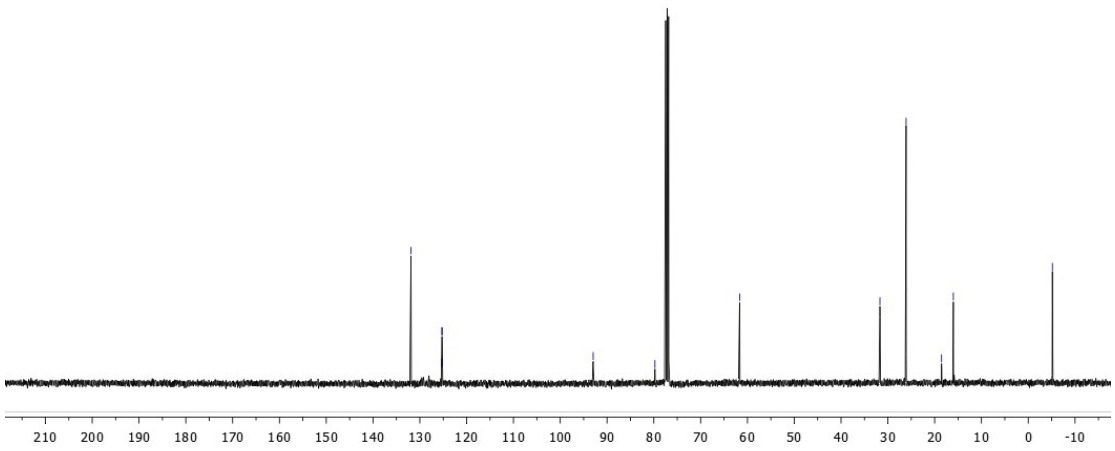
(4*S*,5*R*,6*R*)-6-Hydroxy-3-methyl-4-phenylspiro[4.4]non-2-en-1-one (15). Enyne **14** (37 mg, 0.13 mmol, 1.0 equiv) was dissolved in THF (2.6 ml) and H_2O (5.2 µl) was added at ambient temperature. **3** (5.0 mg, 0.0065 mmol, 0.05 equiv) was added in one portion and stirred for 2 h. Then the reaction mixture was filtered through a short pad of silica gel washing with EtOAc, concentrated in vacuo, and subsequently subjected to silica gel flash chromatogroaphy (hexane/EtOAc 2:1) to afford triquinine **15** as a single diastereomer (24 mg, 0.10 mmol, 76%) as a whit solid.

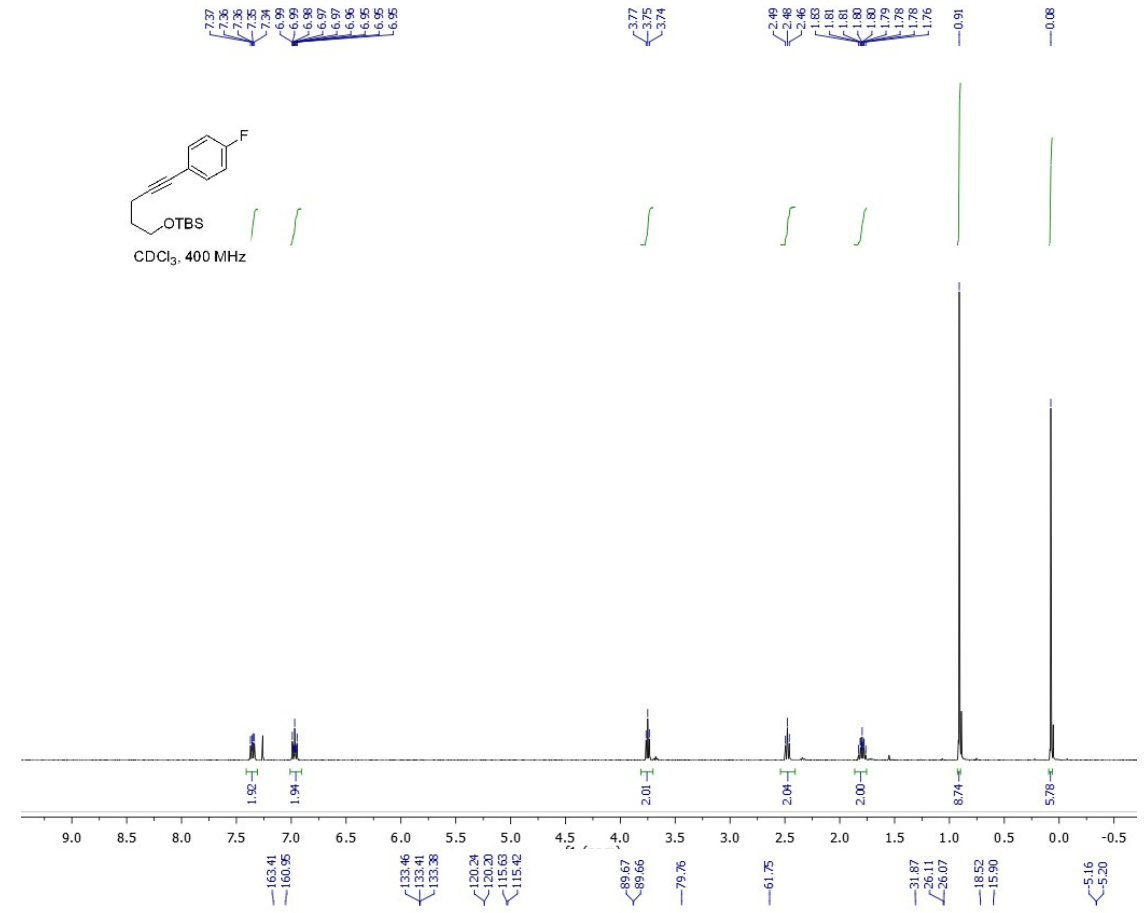
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 4H), 6.28 – 6.02 (m, 1H), 4.25 – 4.19 (m, 2H), 2.18 – 2.07 (m, 1H), 1.99 (s, 3H), 1.79 – 1.60 (m, 2H), 1.59 – 1.46 (m, 1H), 1.28 – 1.17 (m, 1H), 1.17 – 1.08 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.0, 180.4, 139.0, 131.0, 128.8, 127.3, 80.0, 65.2, 55.6, 32.9, 29.3, 19.3, 18.6. **IR** (neat) 3396, 3061, 3027, 2956, 2875, 1681, 1623, 1601, 1493, 1454, 1435, 1375, 1309, 1208, 1079, 1017, 880, 851, 741, 703, 627, 556, 493, 458, 417 cm^{-1}. **HRMS (MALDI):** m/z calcd for $C_{16}H_{18}NaO_2$ $[M+Na]^+$ 265.1199, found 265.1198. $[\alpha]_D^{26}$ = –124.6 (c = 1.0, $CHCl_3$). **SFC** Daicel Chiralcel OJ-H, 10% MeOH, 2.0 mL/min., 25 °C, 78% *ee* (t_R (1, major enantiomer) = 3.35 min, t_R (2, minor enantiomer) = 3.91 min).

7. NMR Spectra





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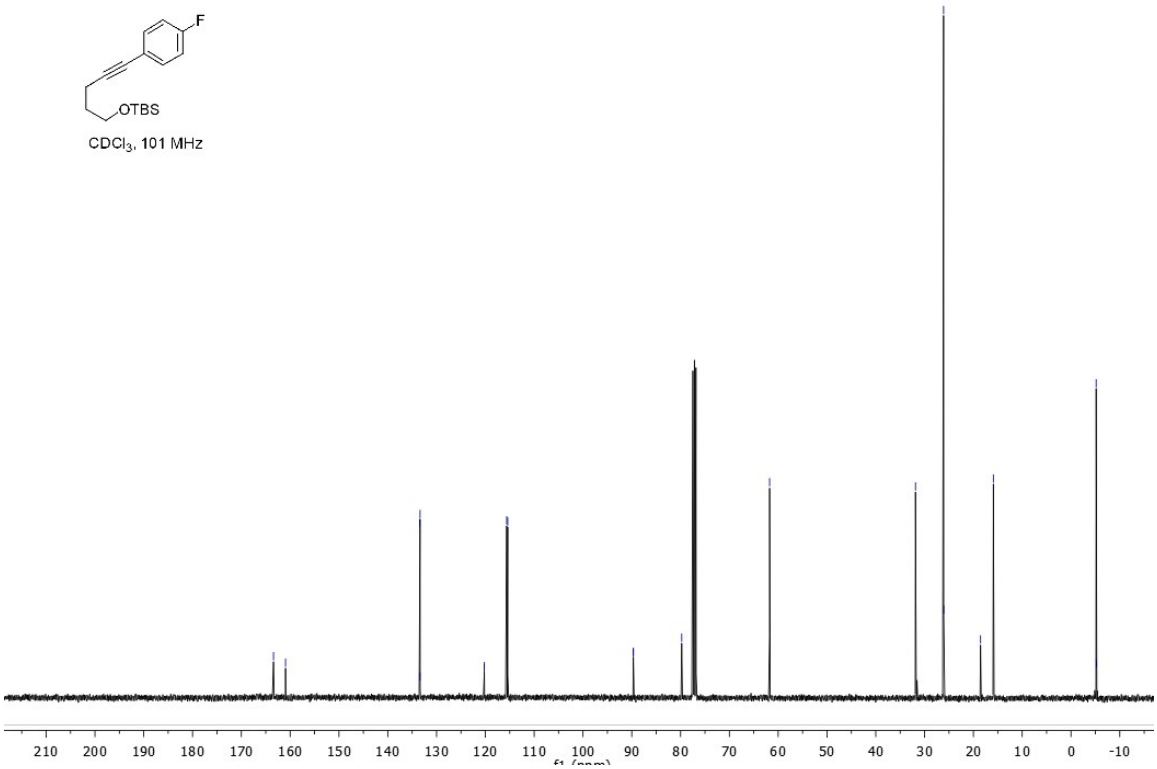
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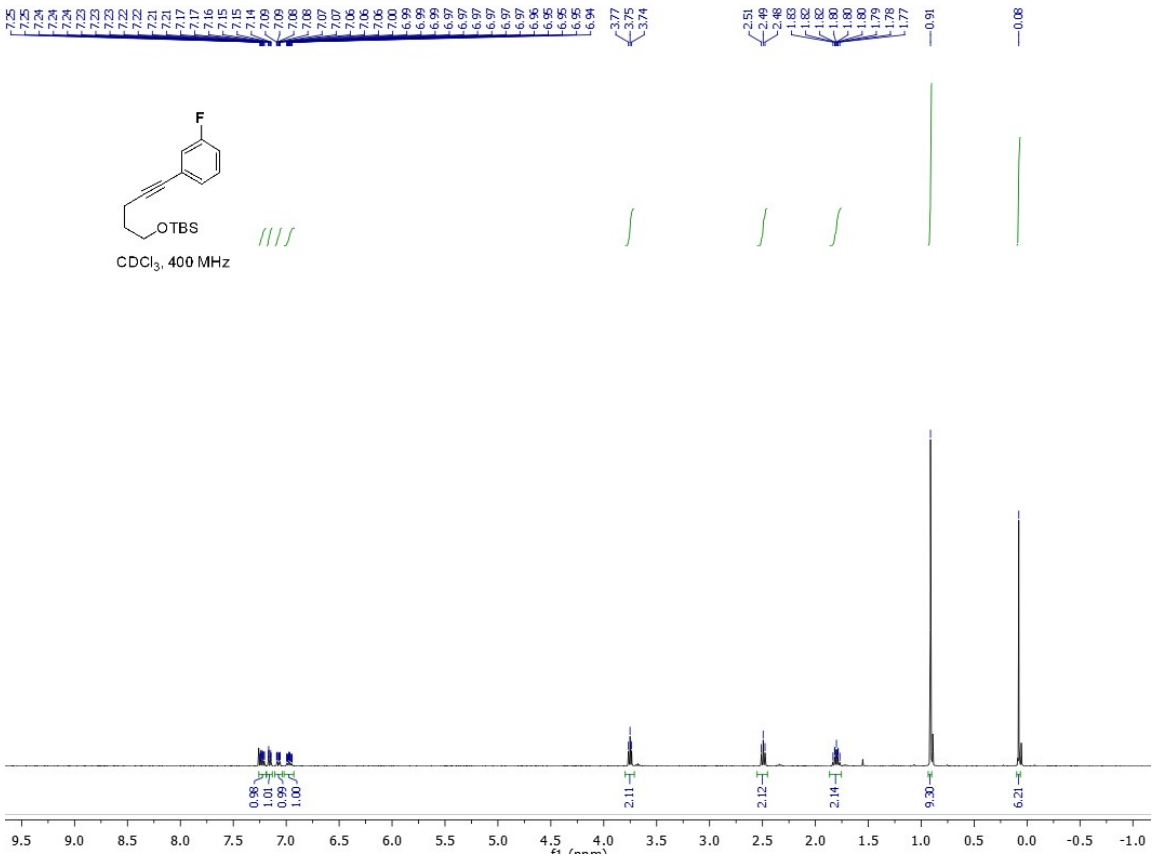
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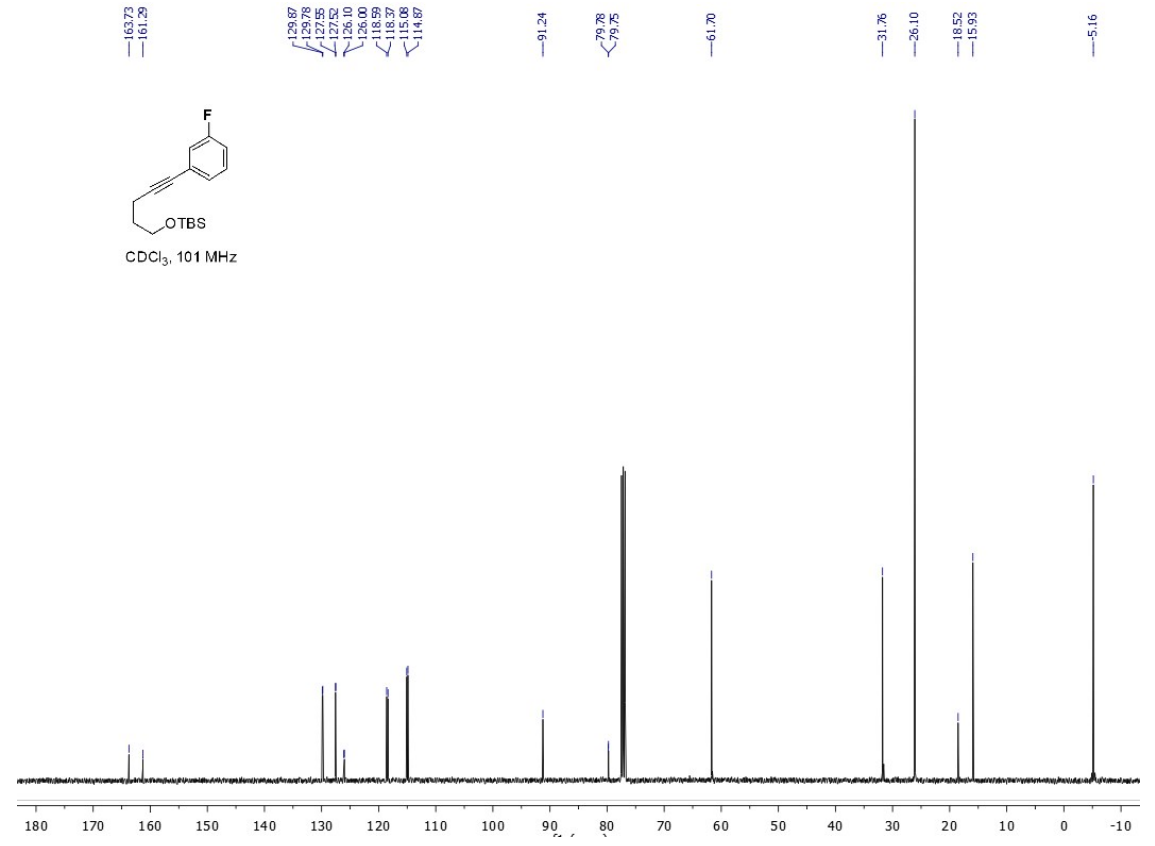
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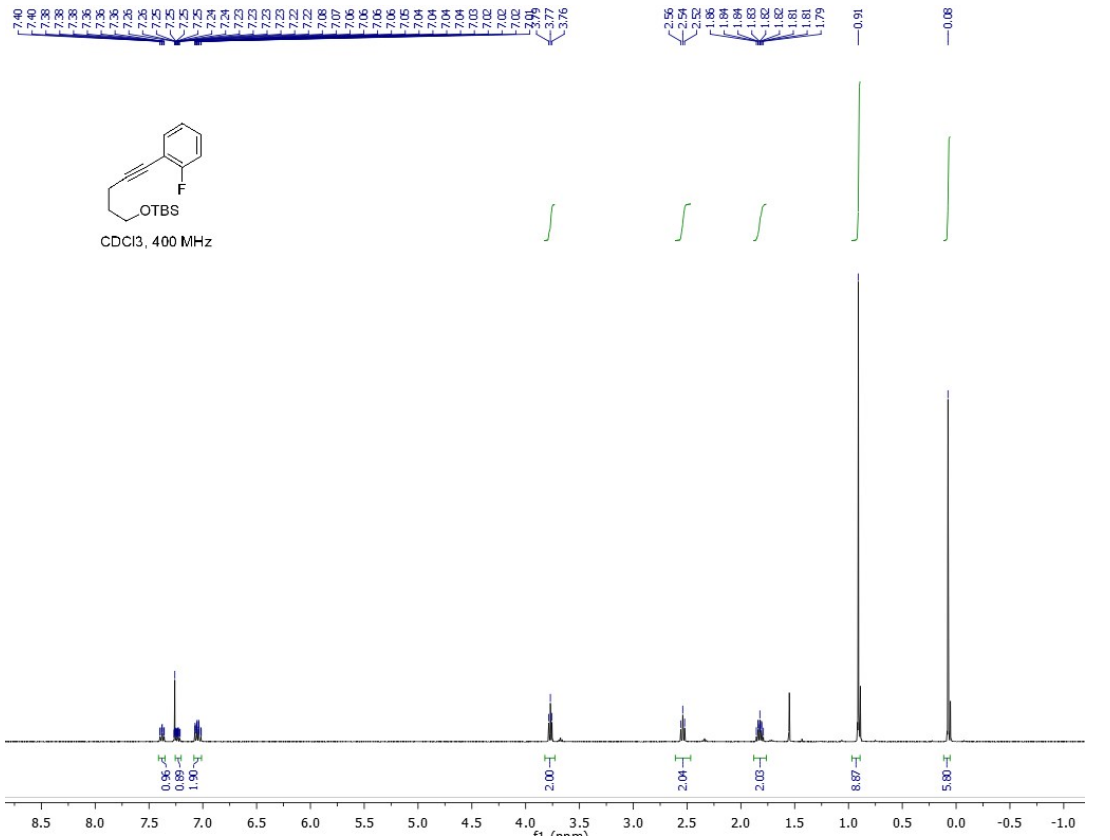
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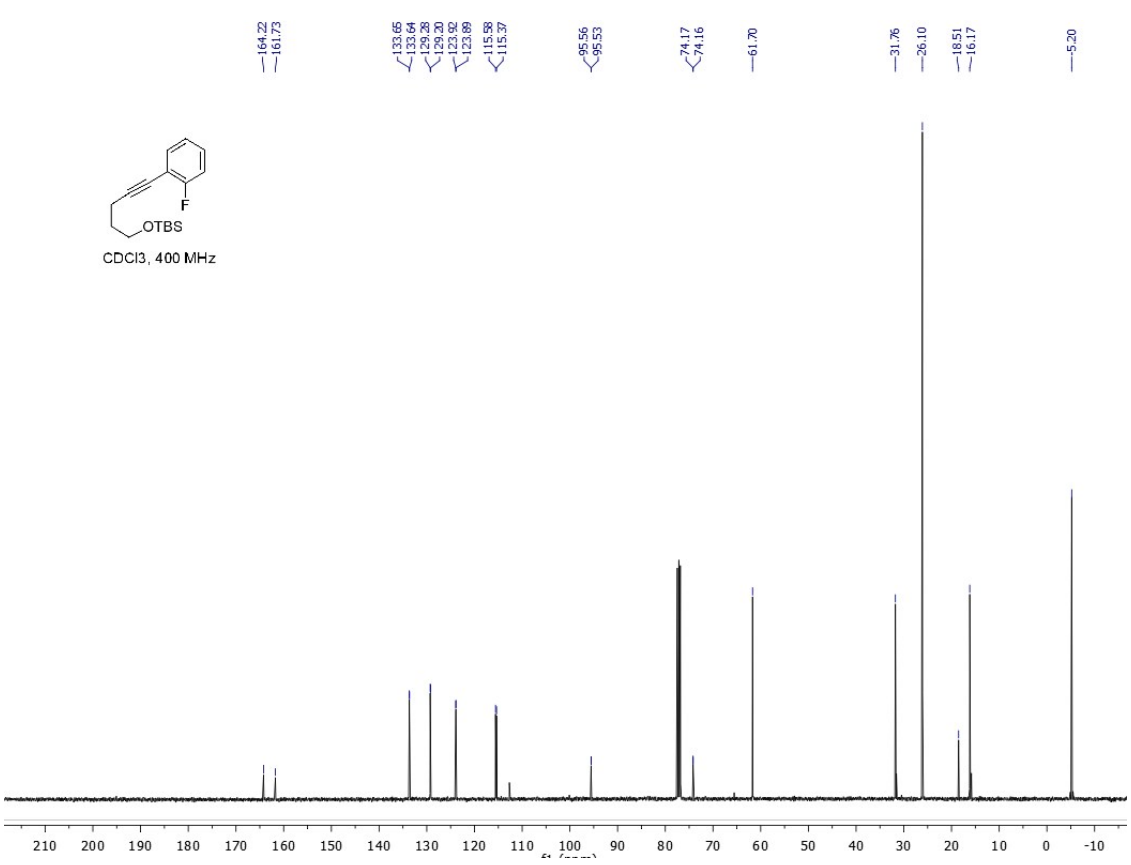
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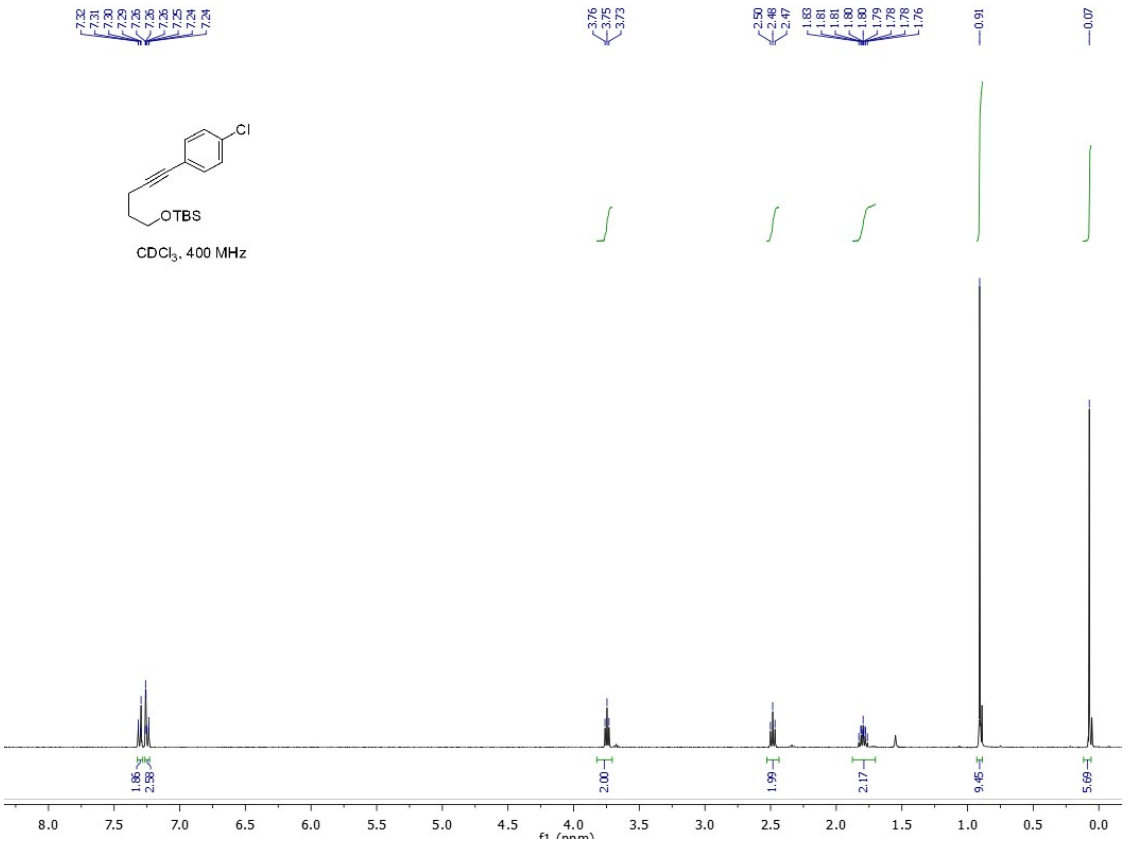
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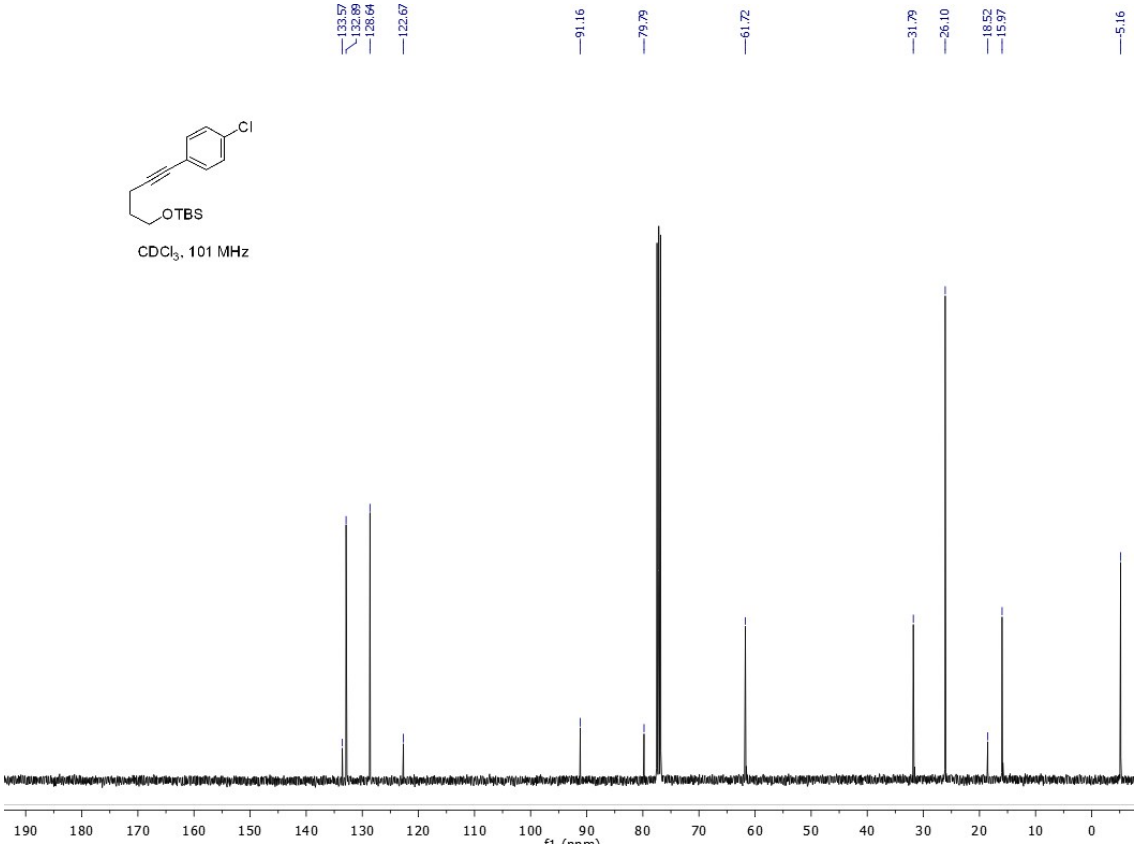
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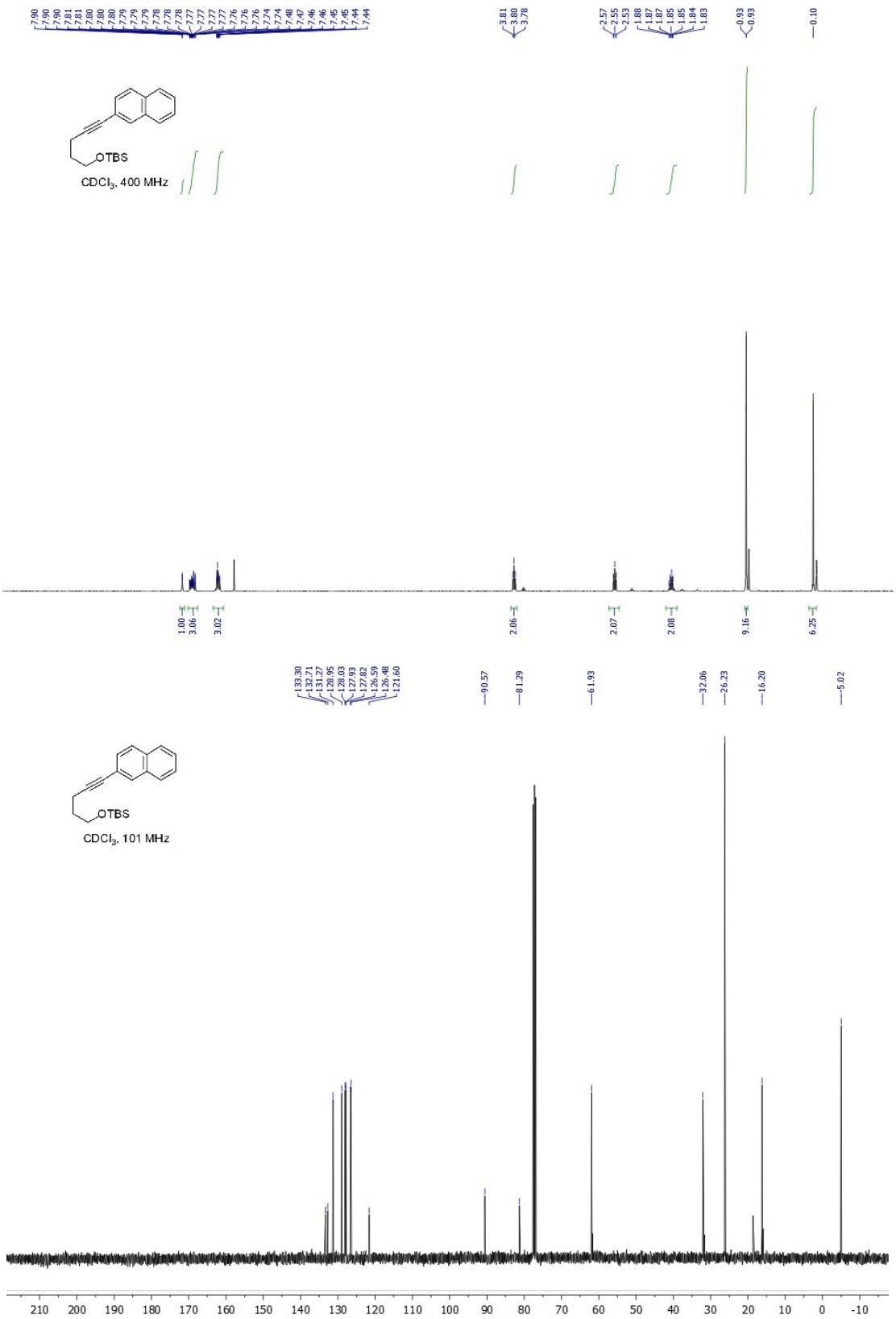
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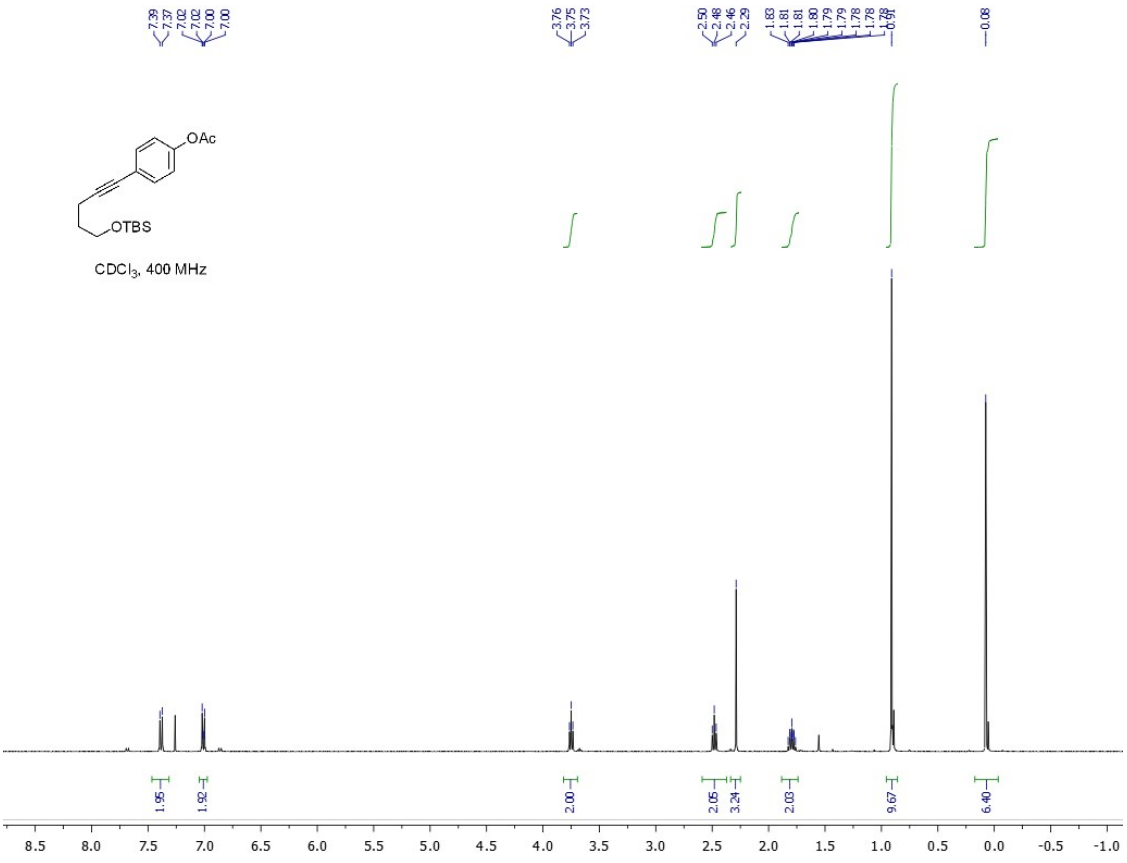
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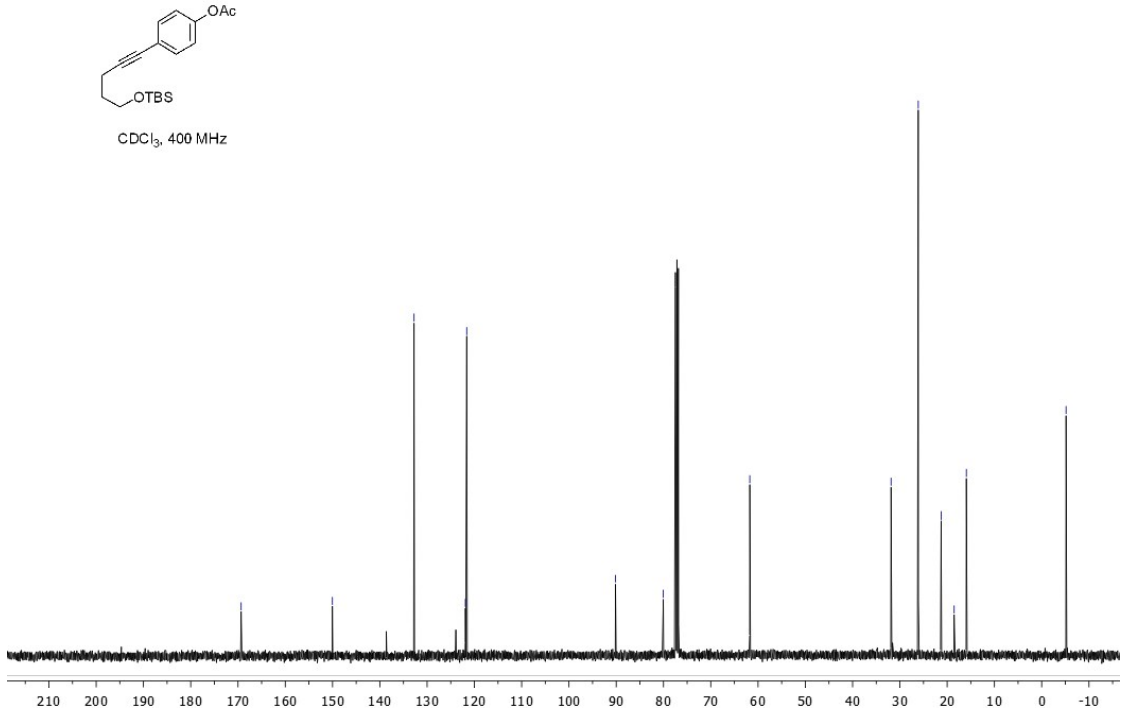
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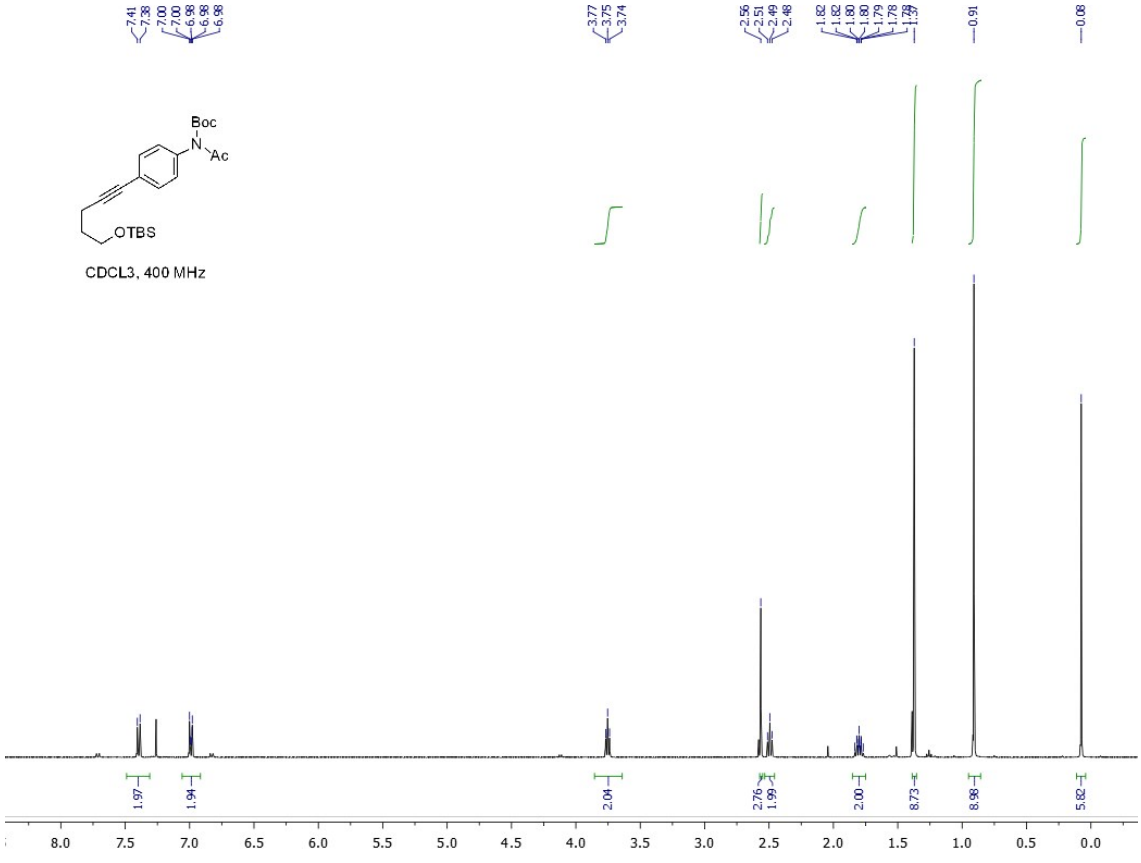
Boc
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Ac
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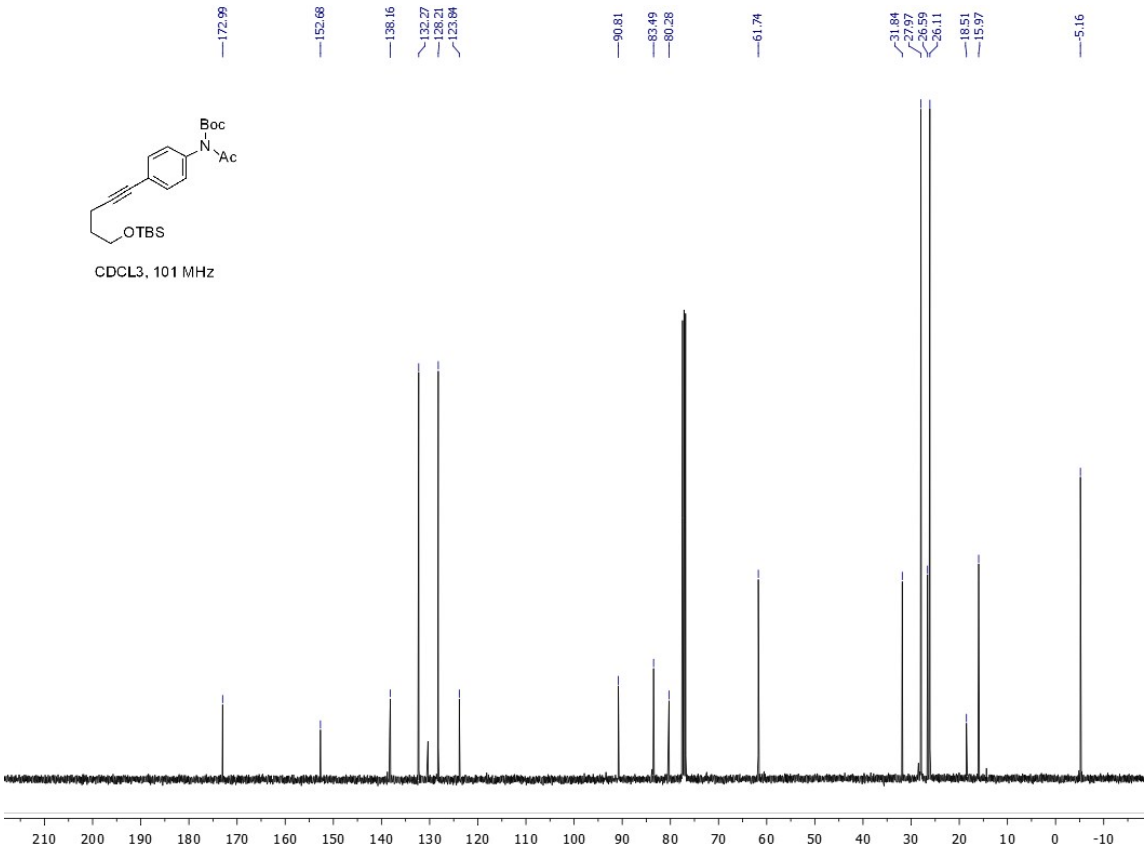
CDCL3, 400 MHz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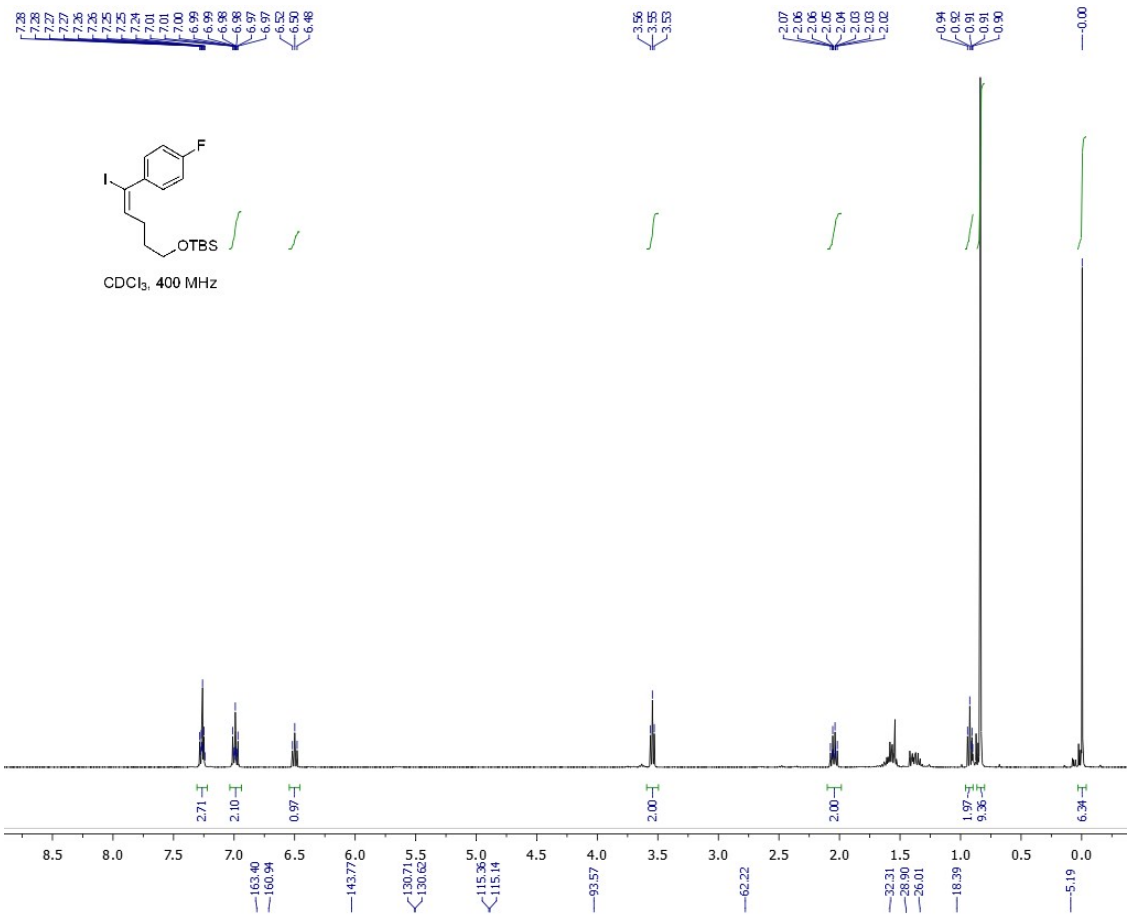
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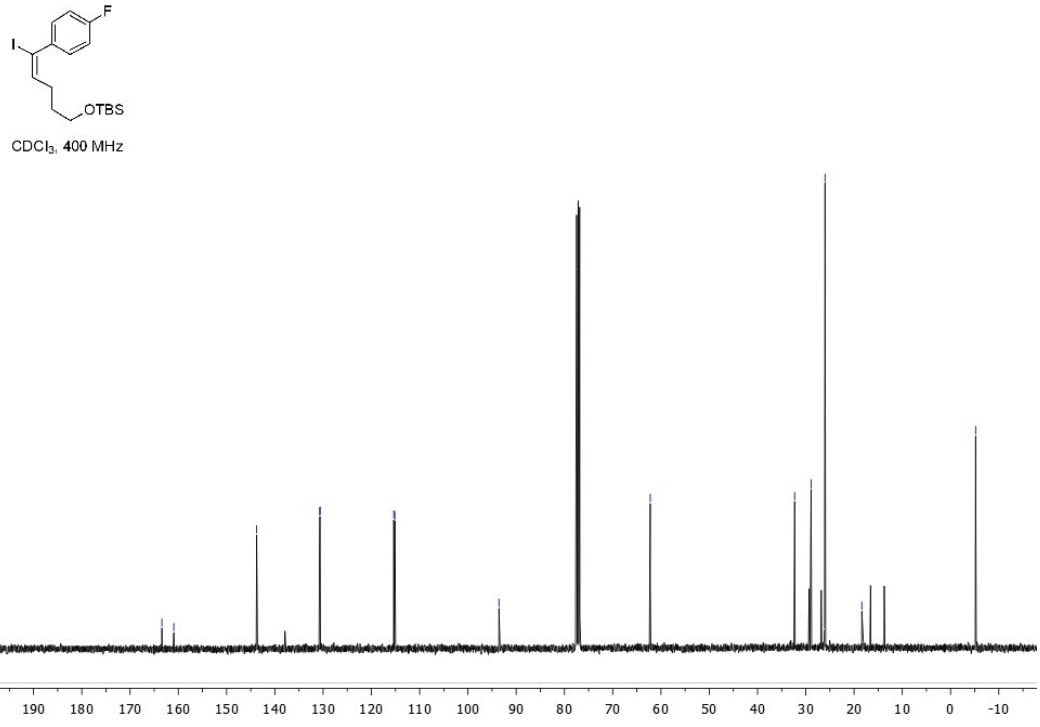
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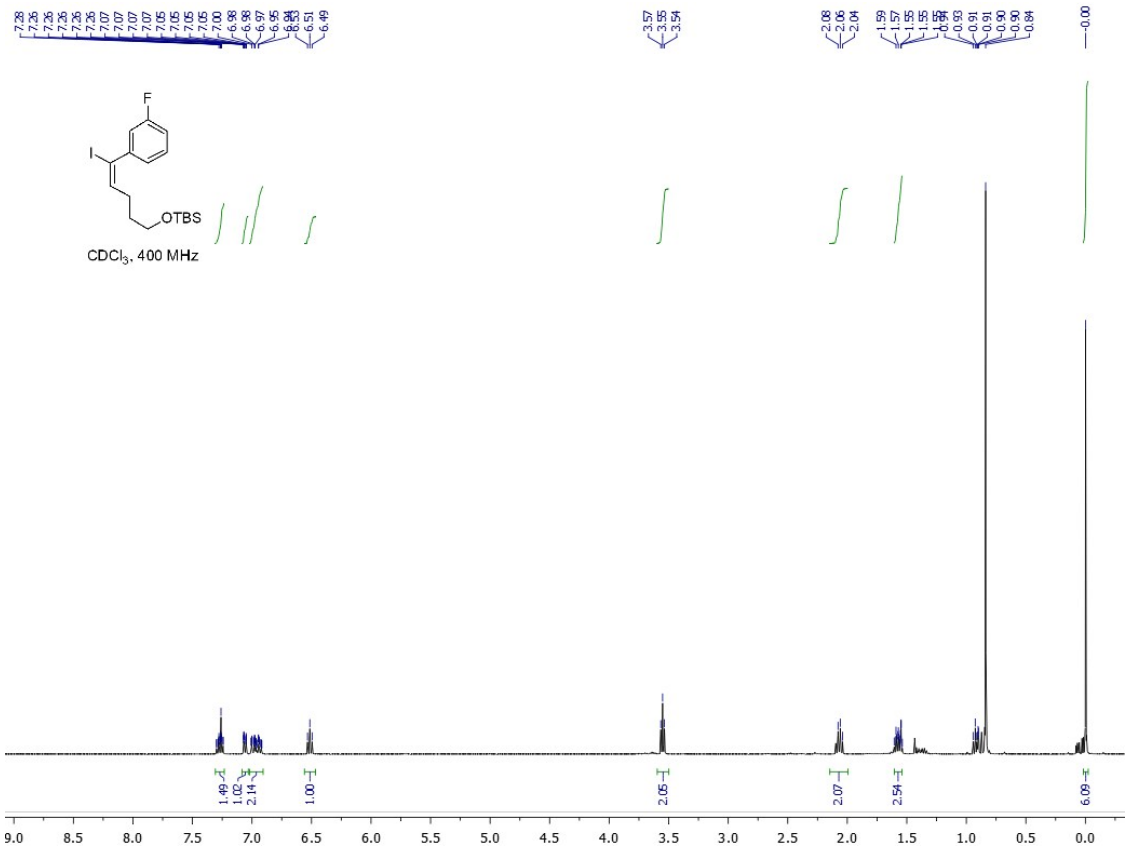
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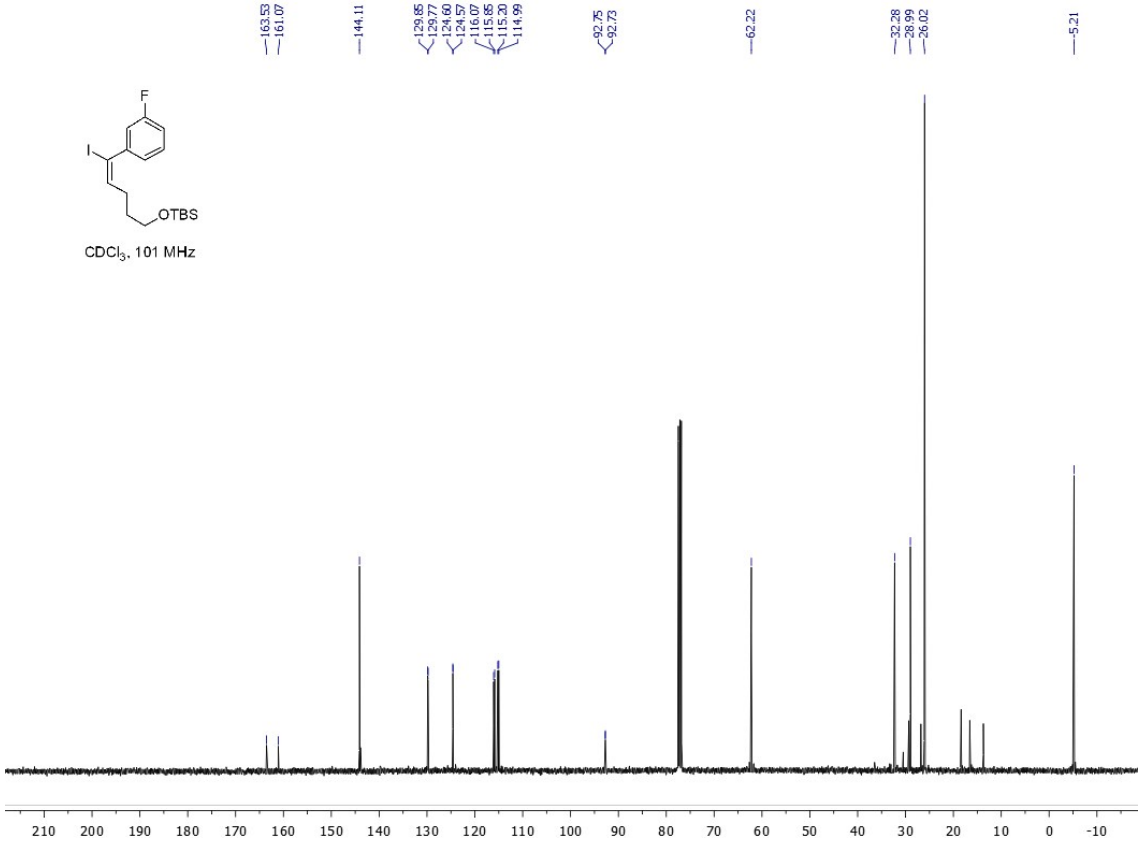
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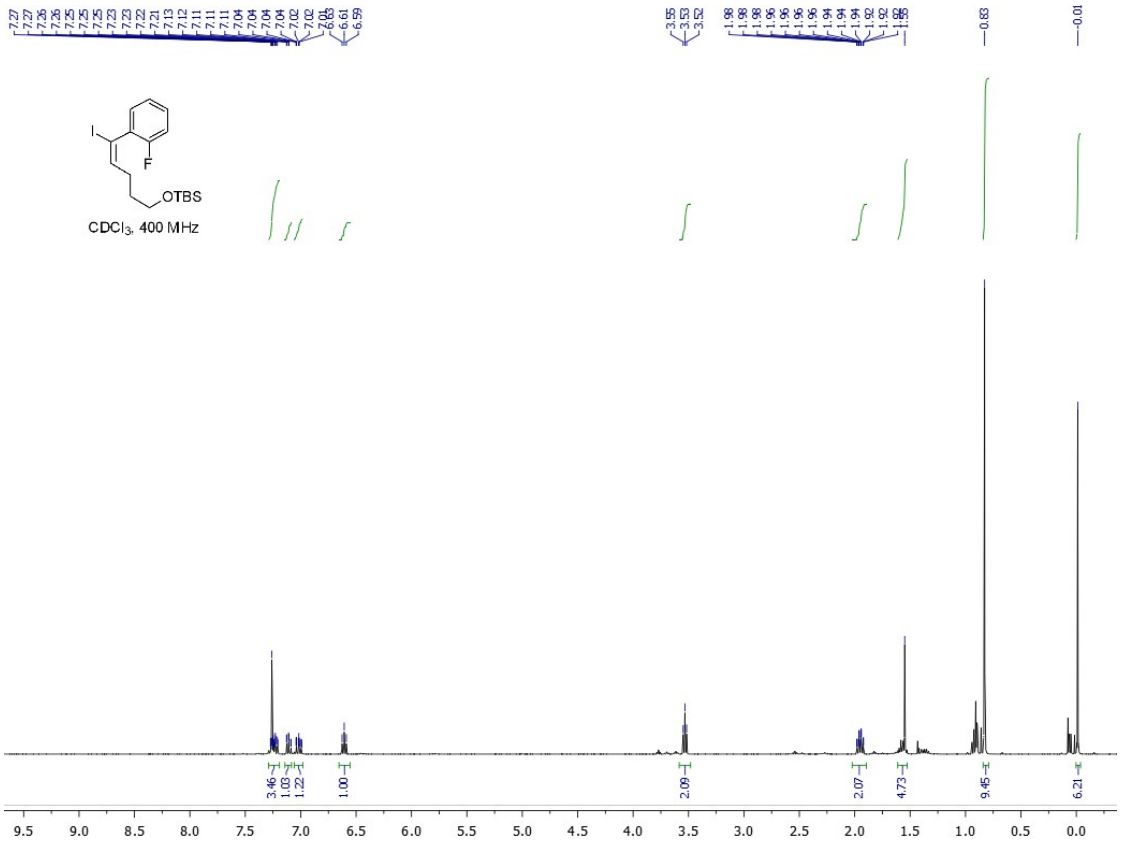
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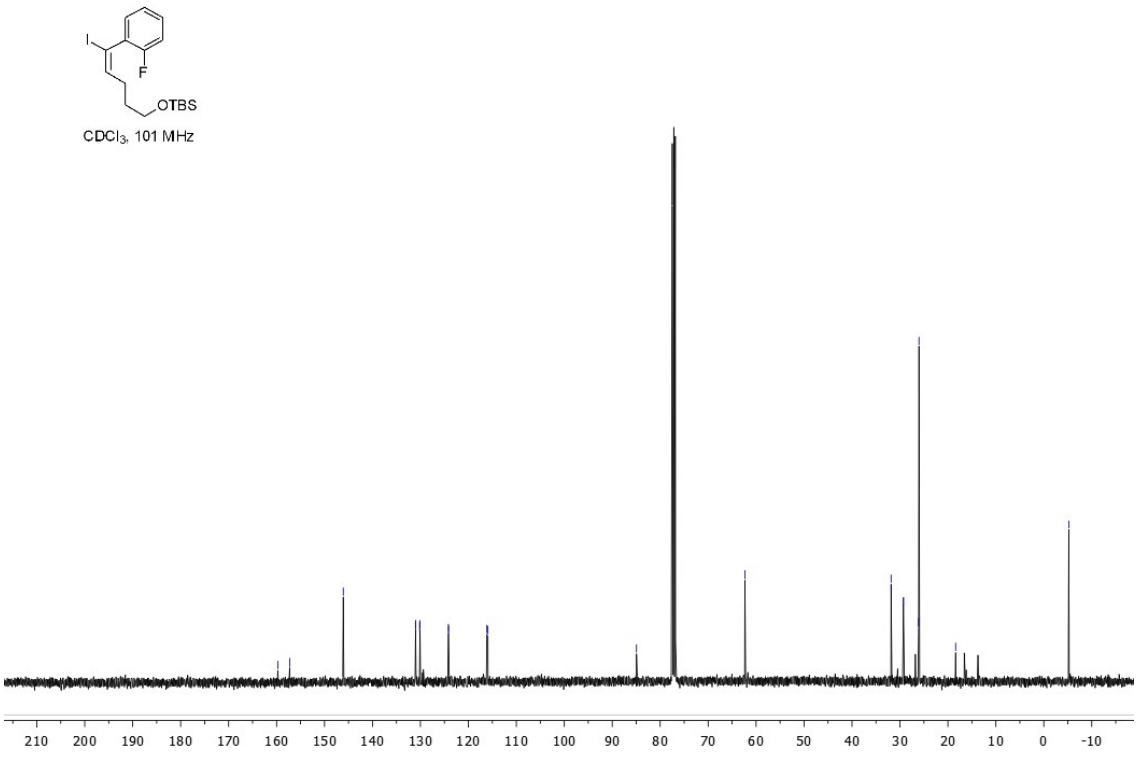
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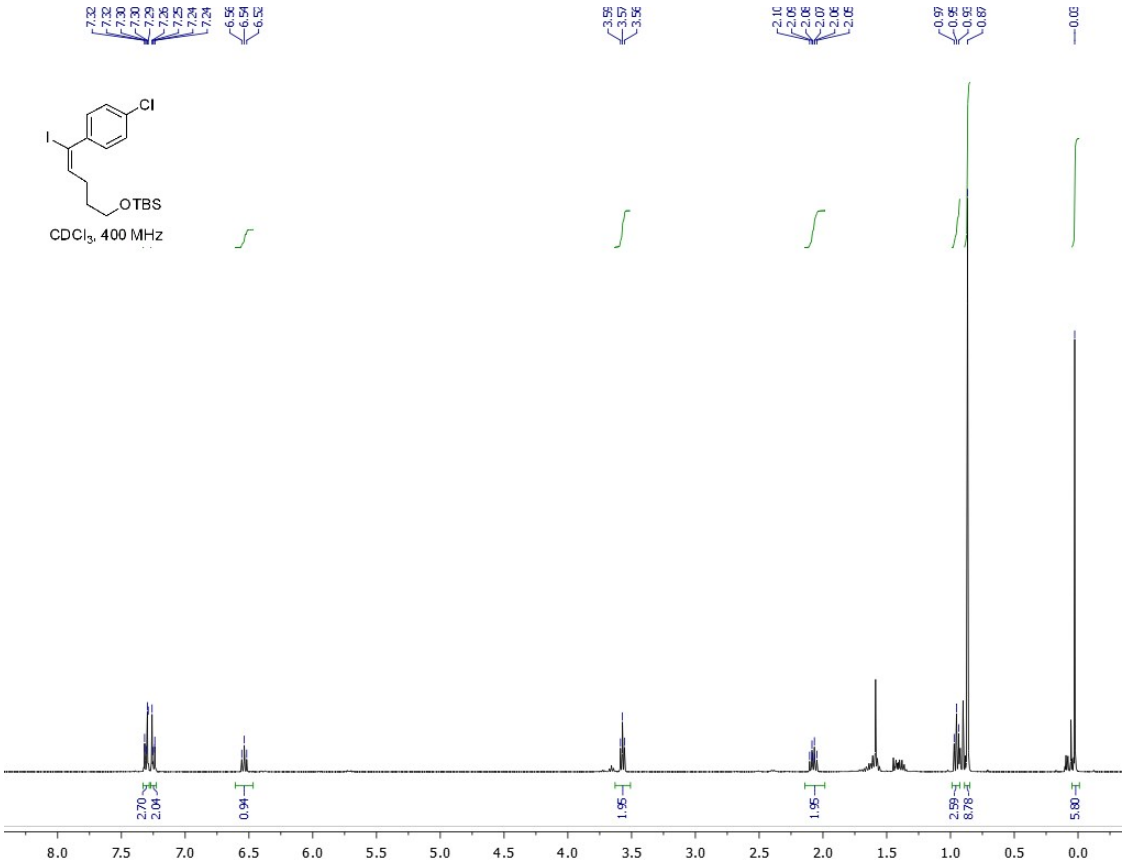
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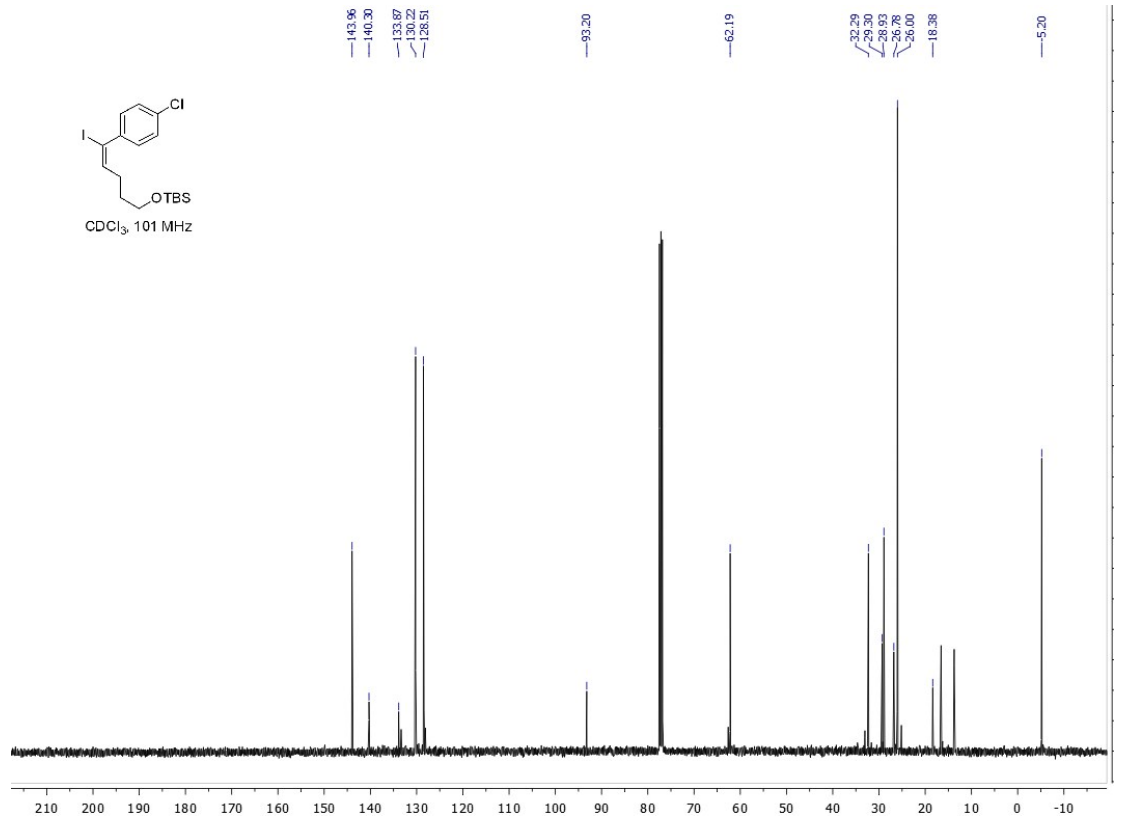
Cl
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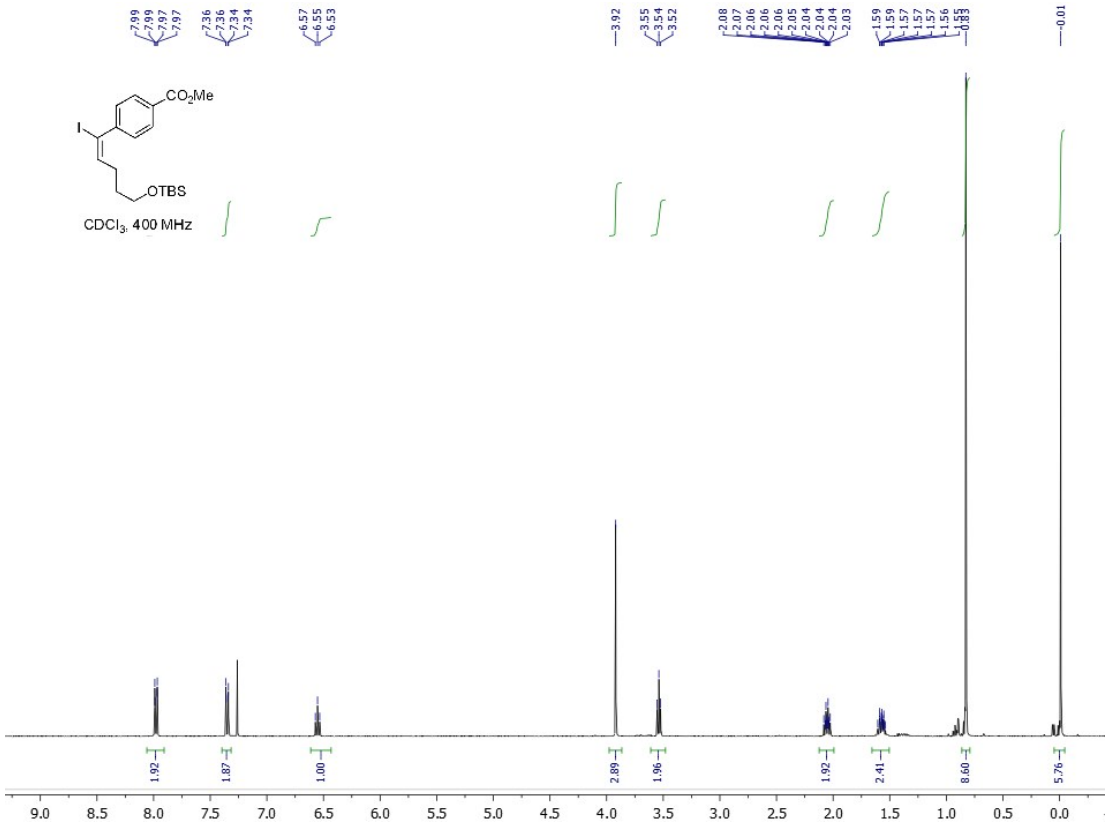
CO2Me
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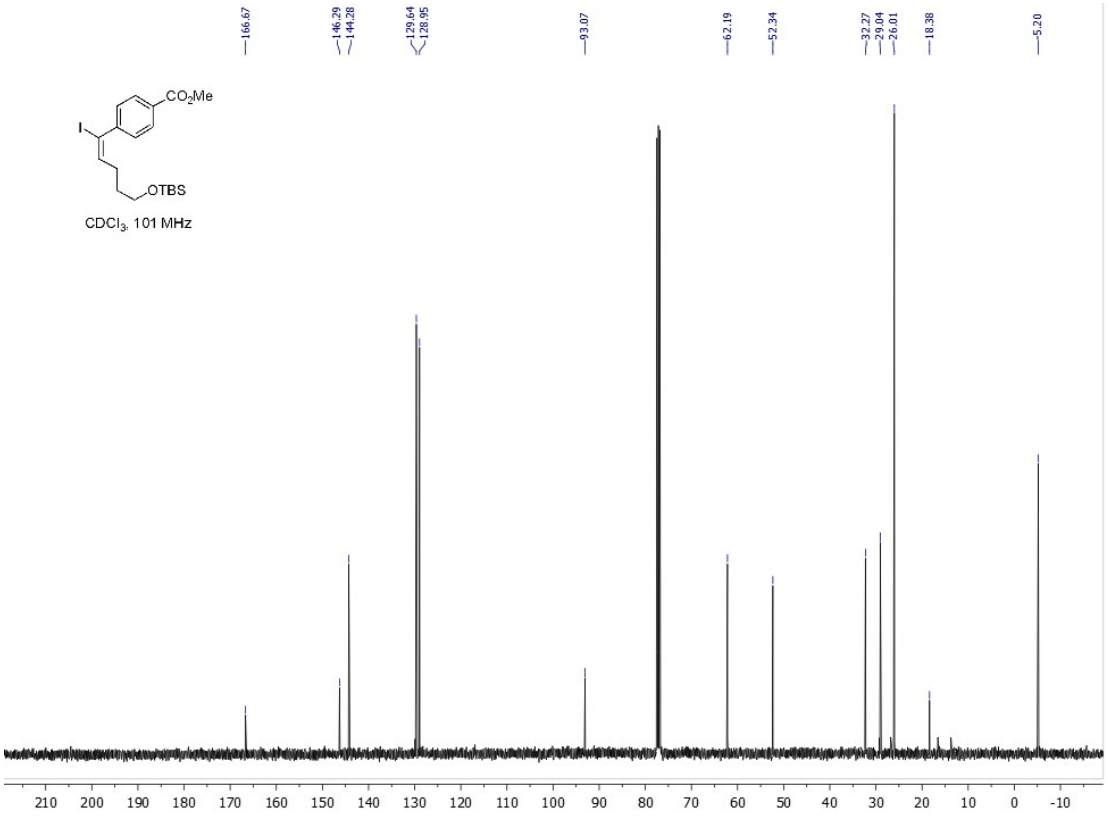
CO2Me
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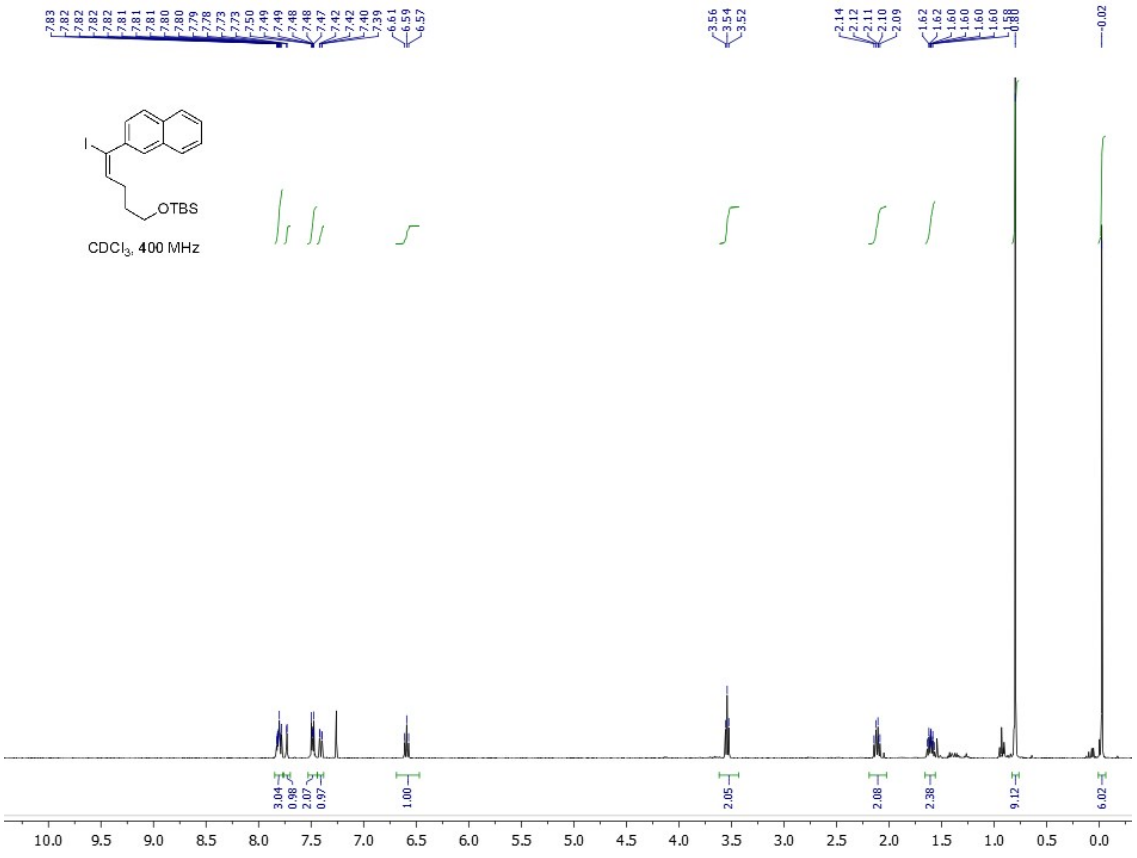
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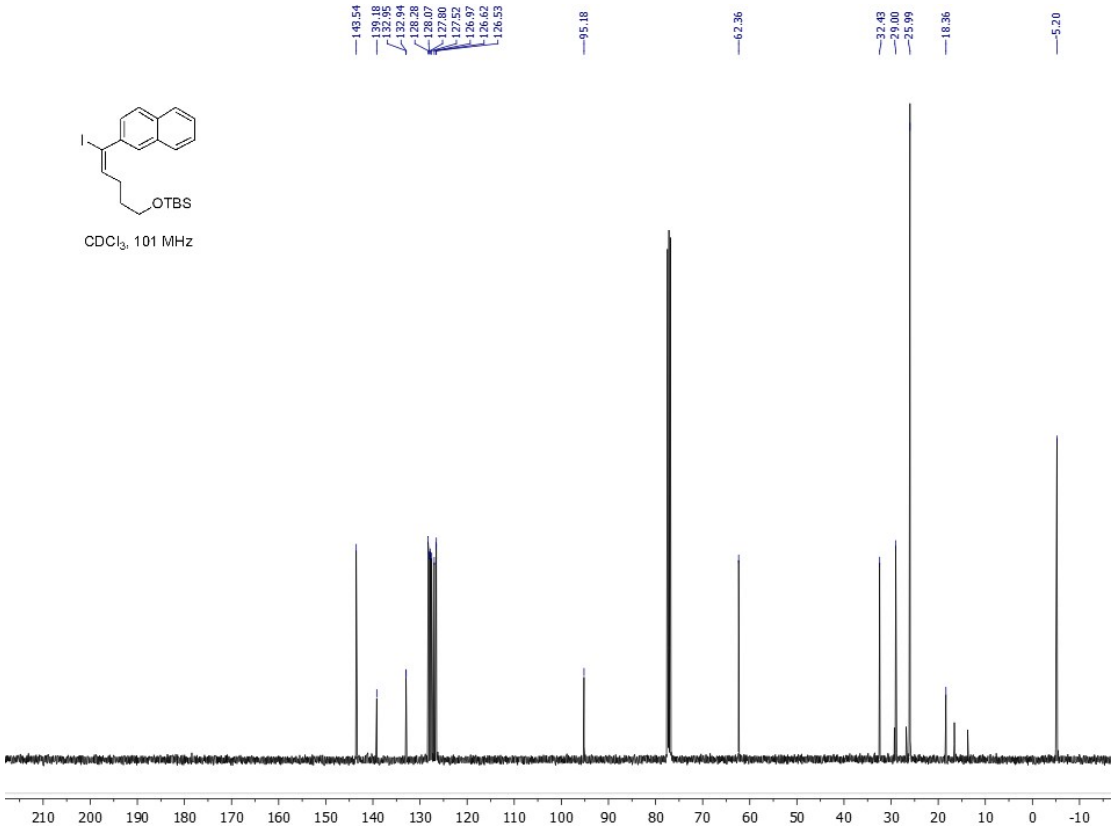
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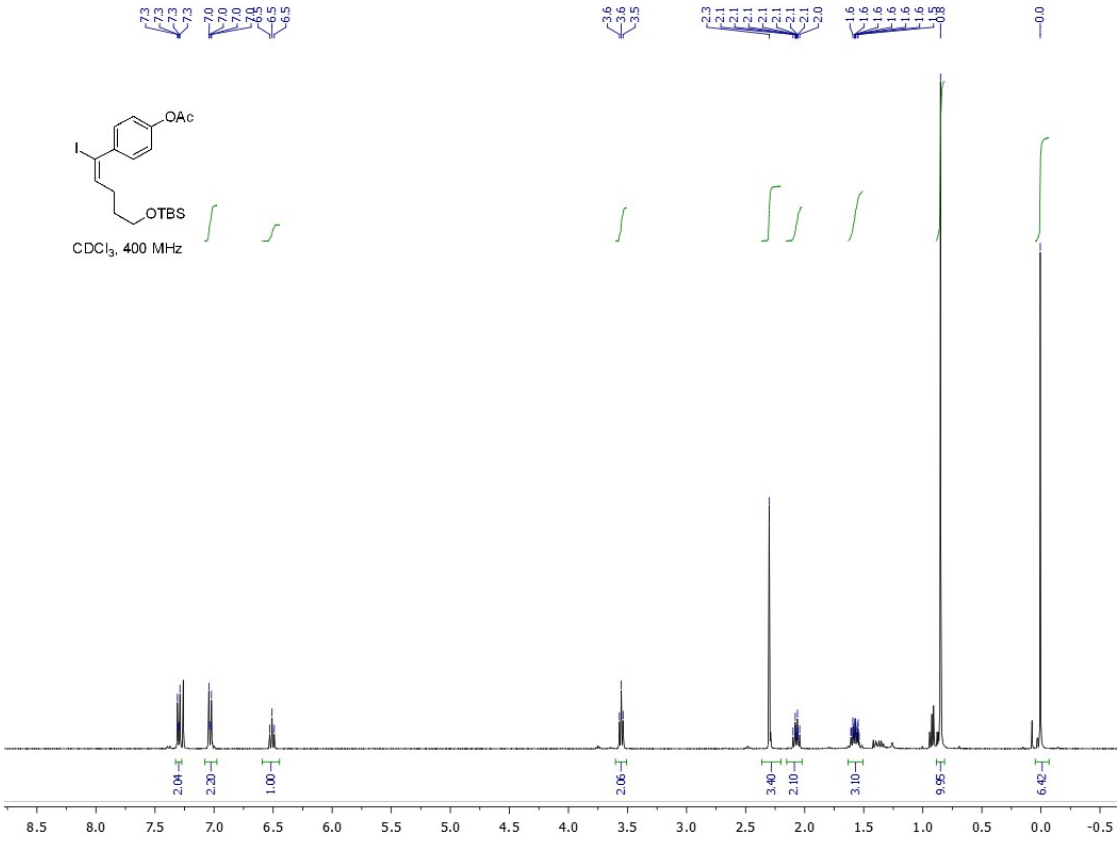
OAc
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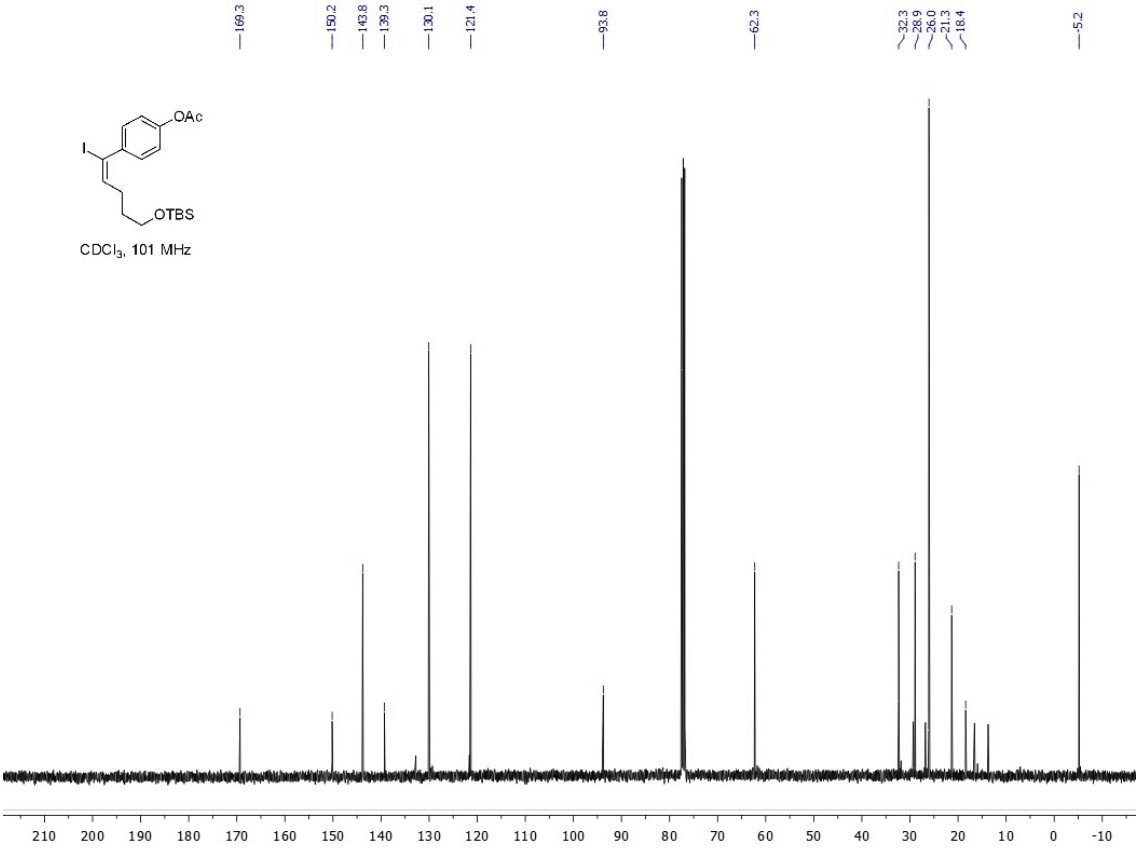
OTBS
CDCl3, 400 MHz


OAc
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OTBS
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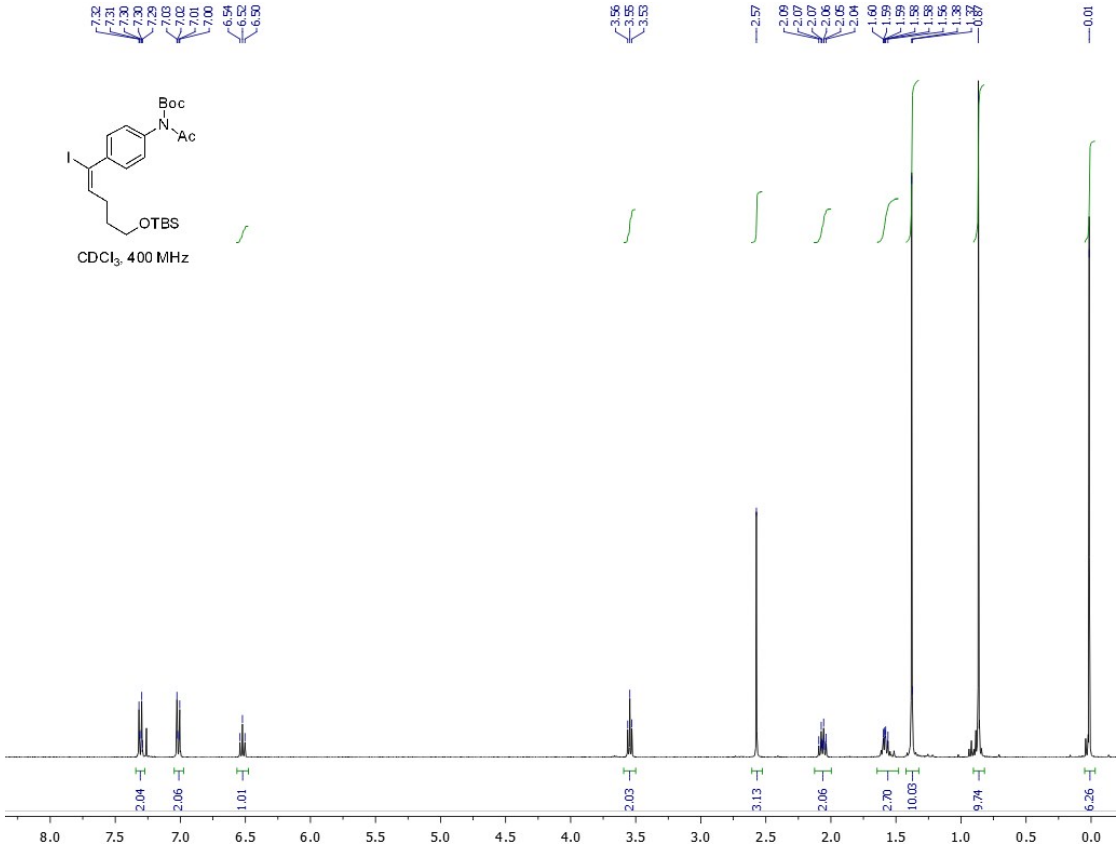
Boc
N
Ac
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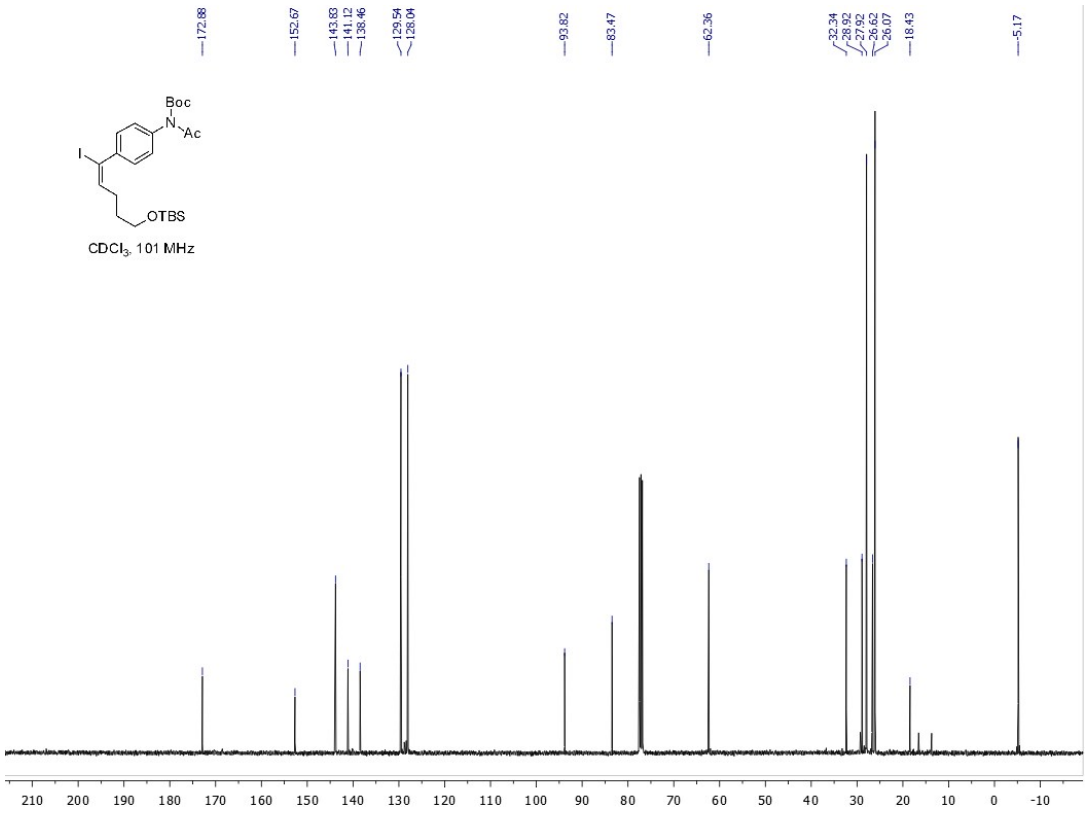
OTBS
CDCl3, 400 MHz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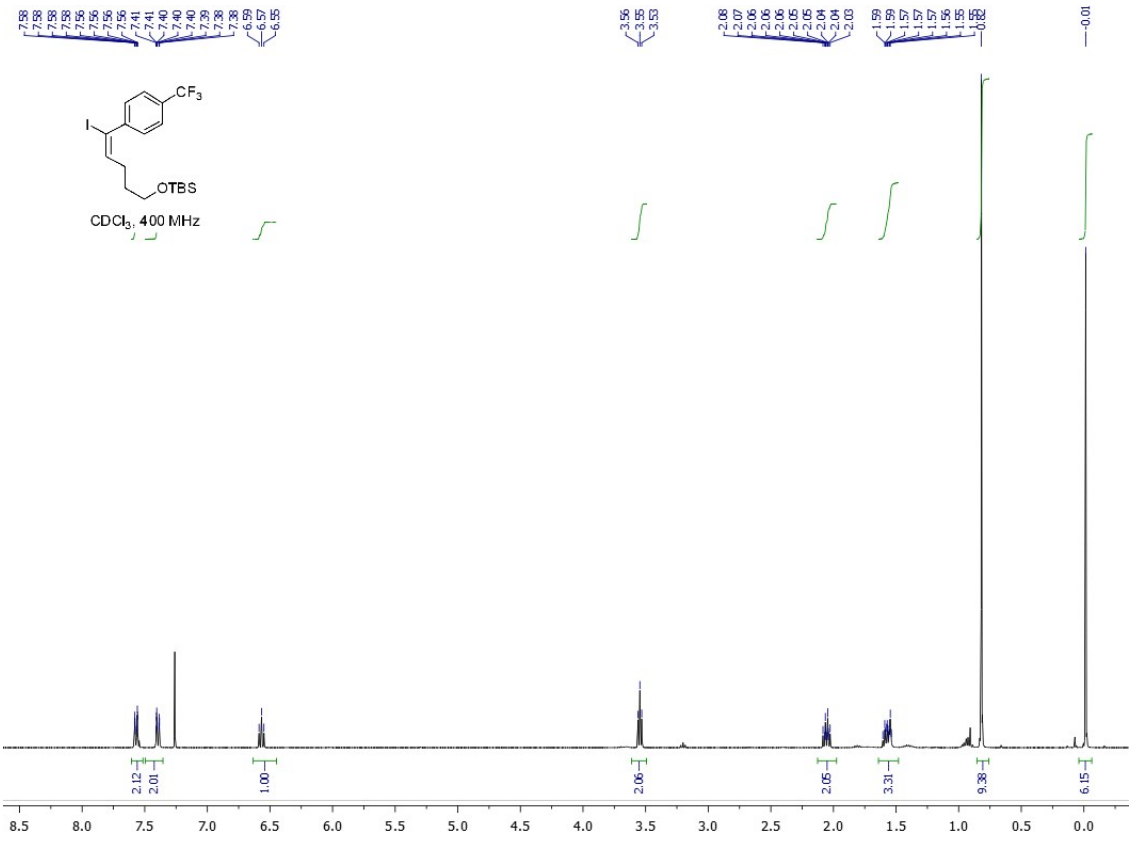
CF3
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OTBS
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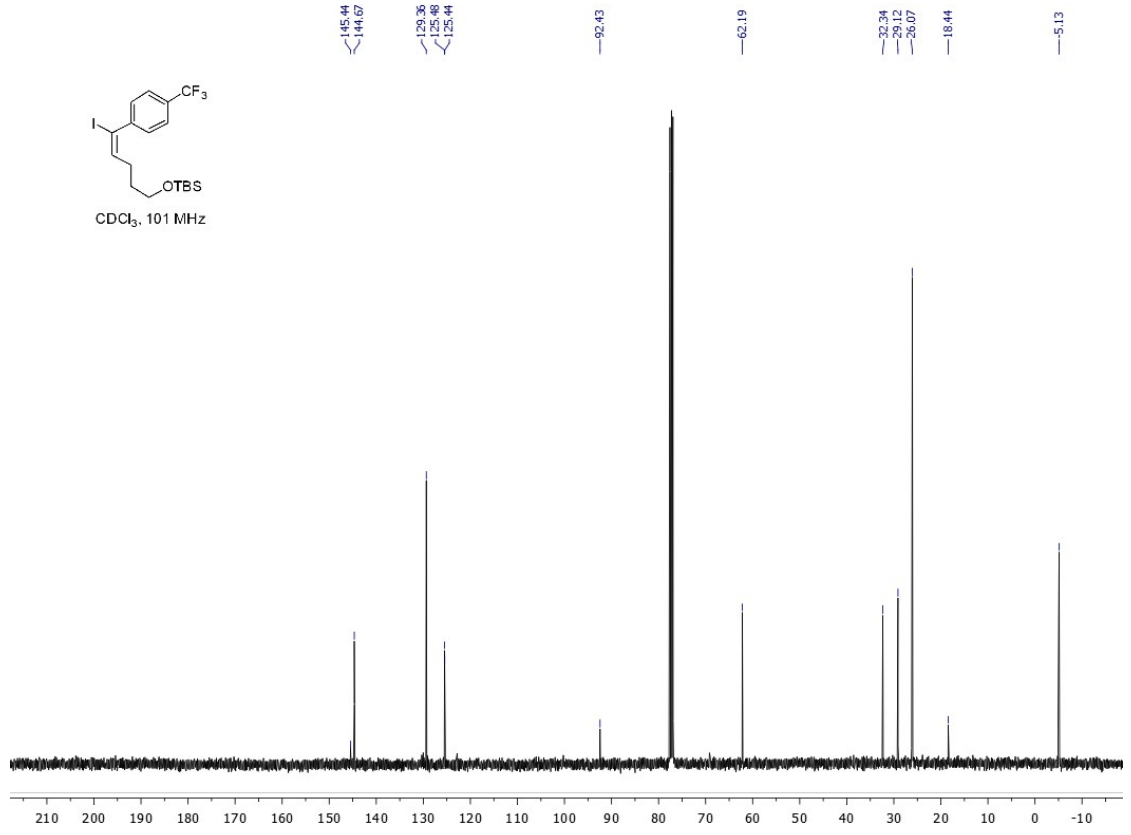
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OTBS
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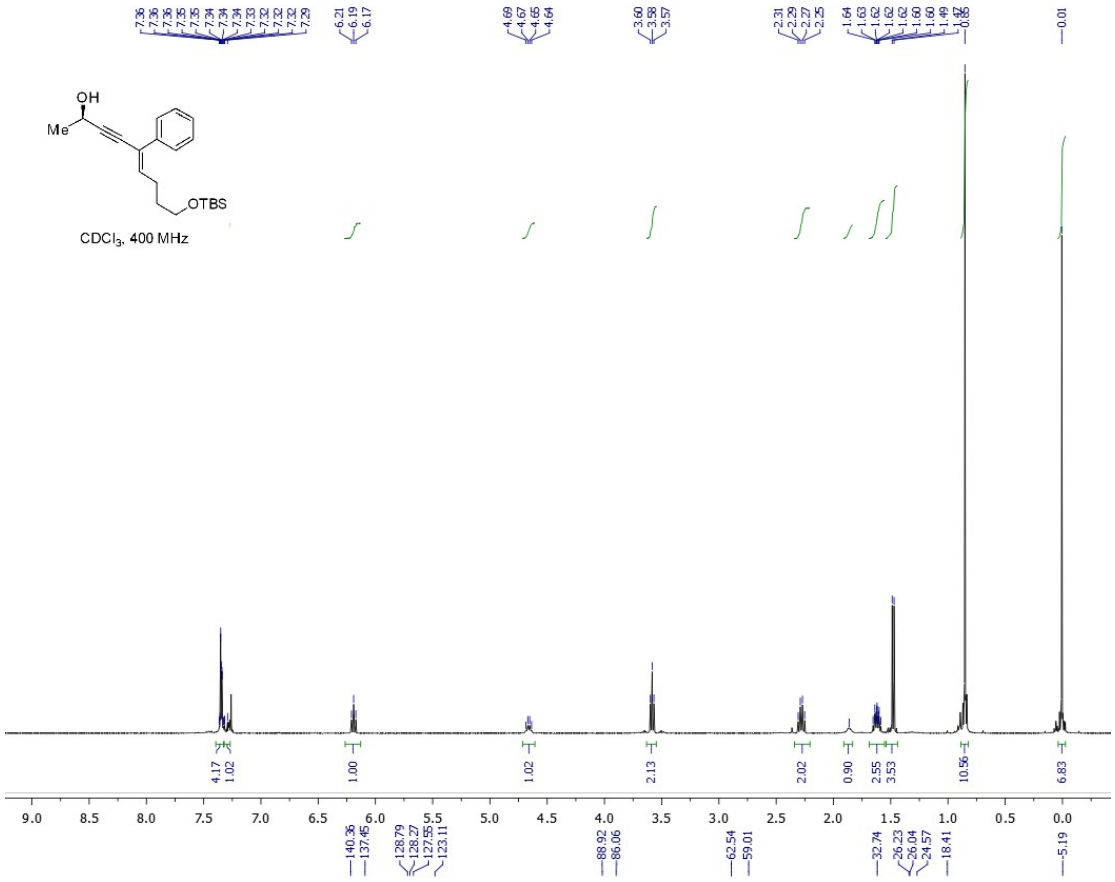
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OTBS
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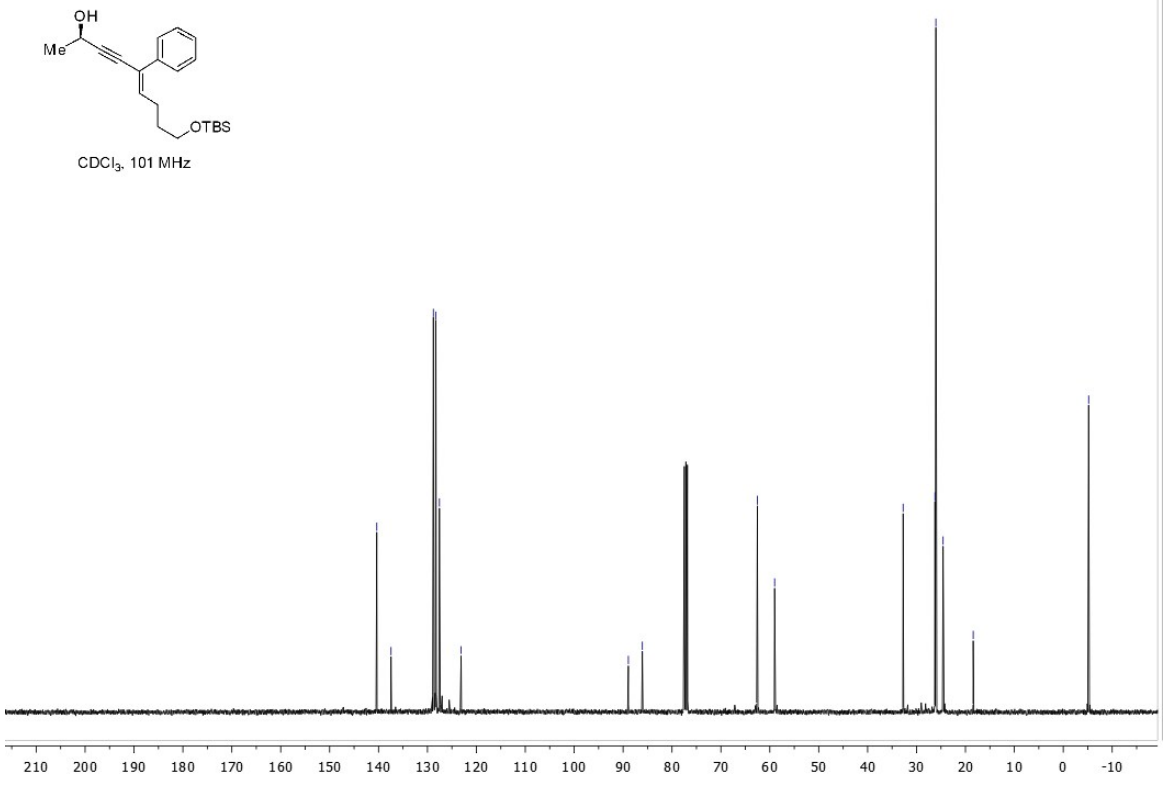
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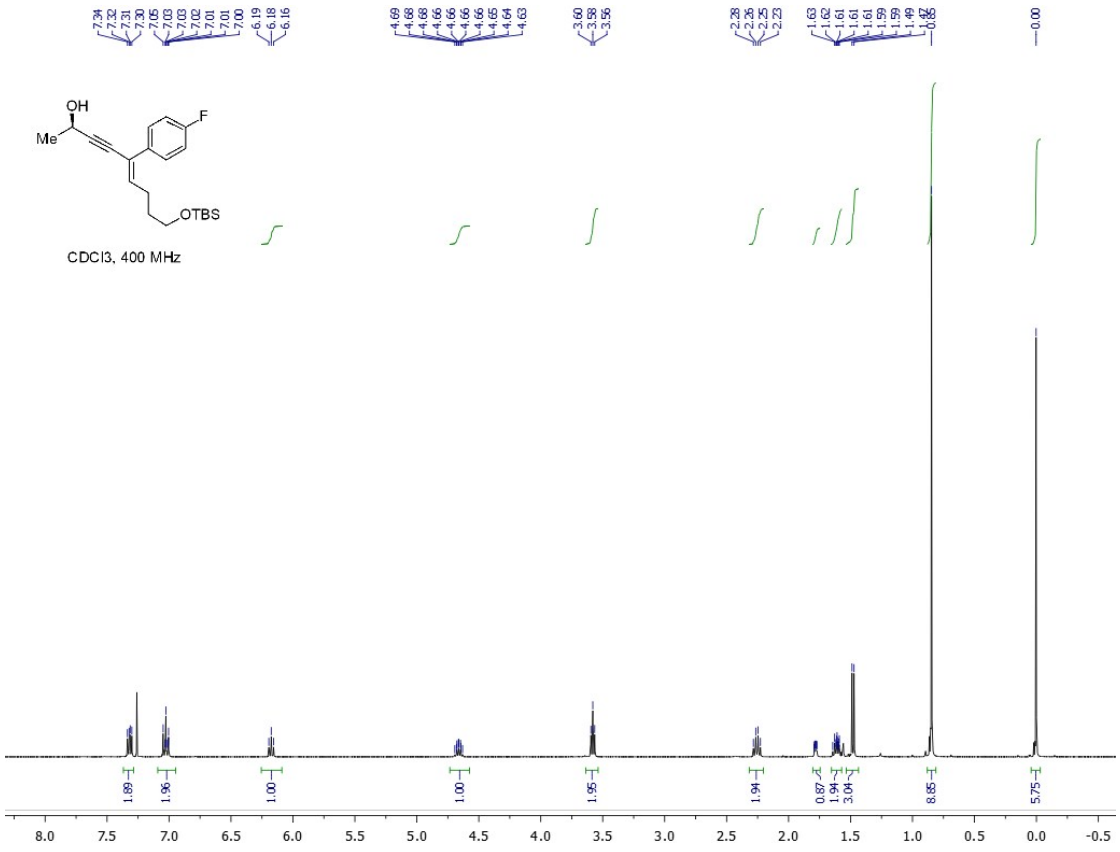
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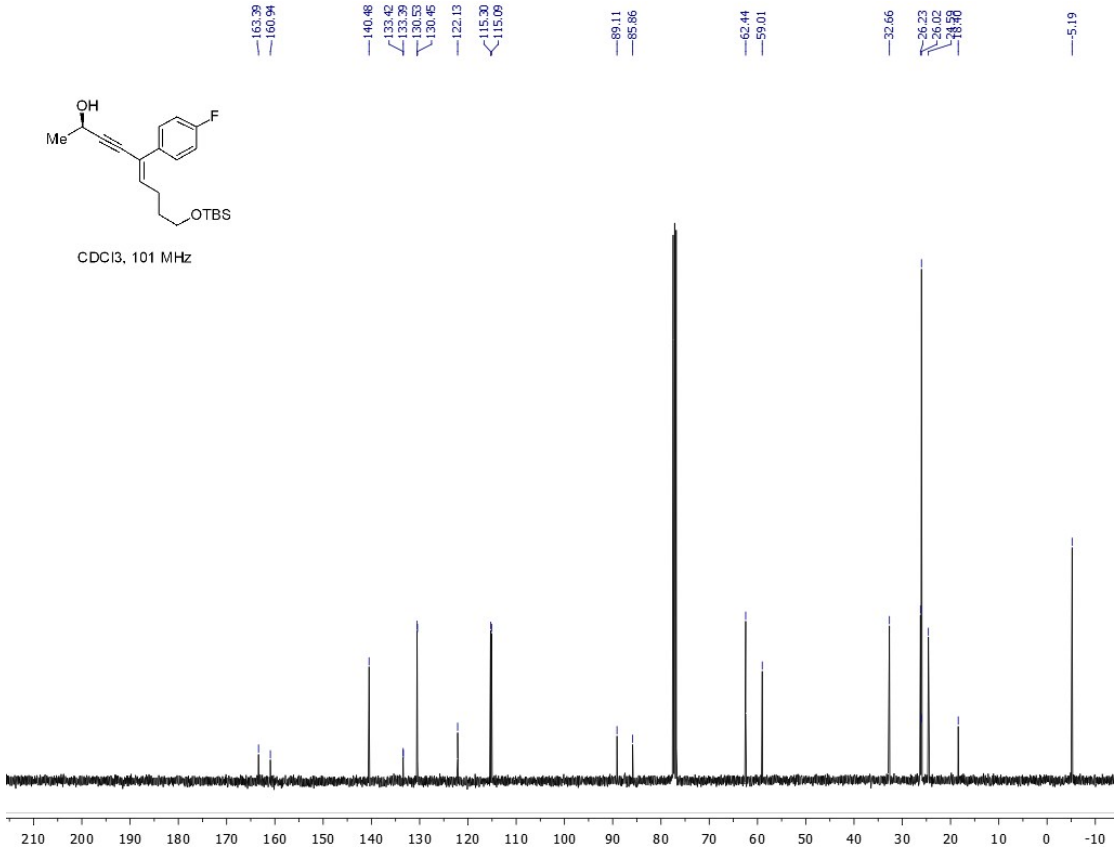
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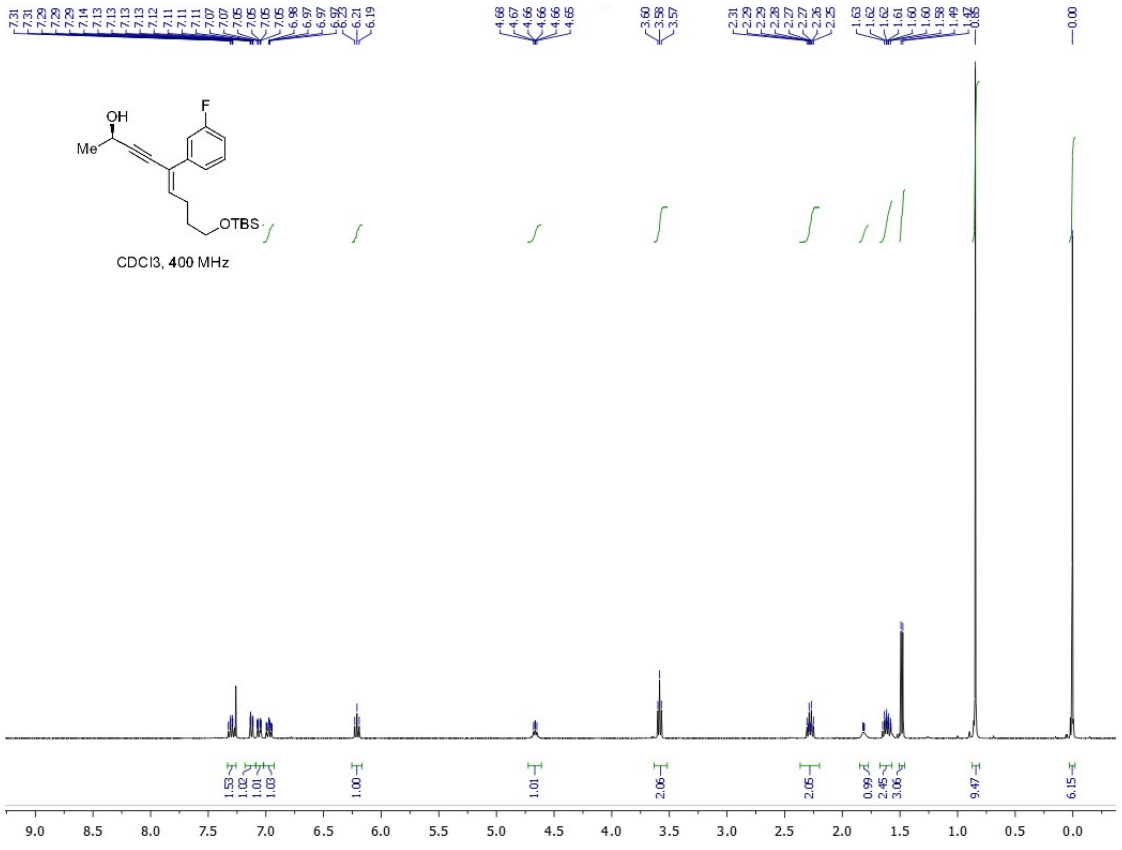
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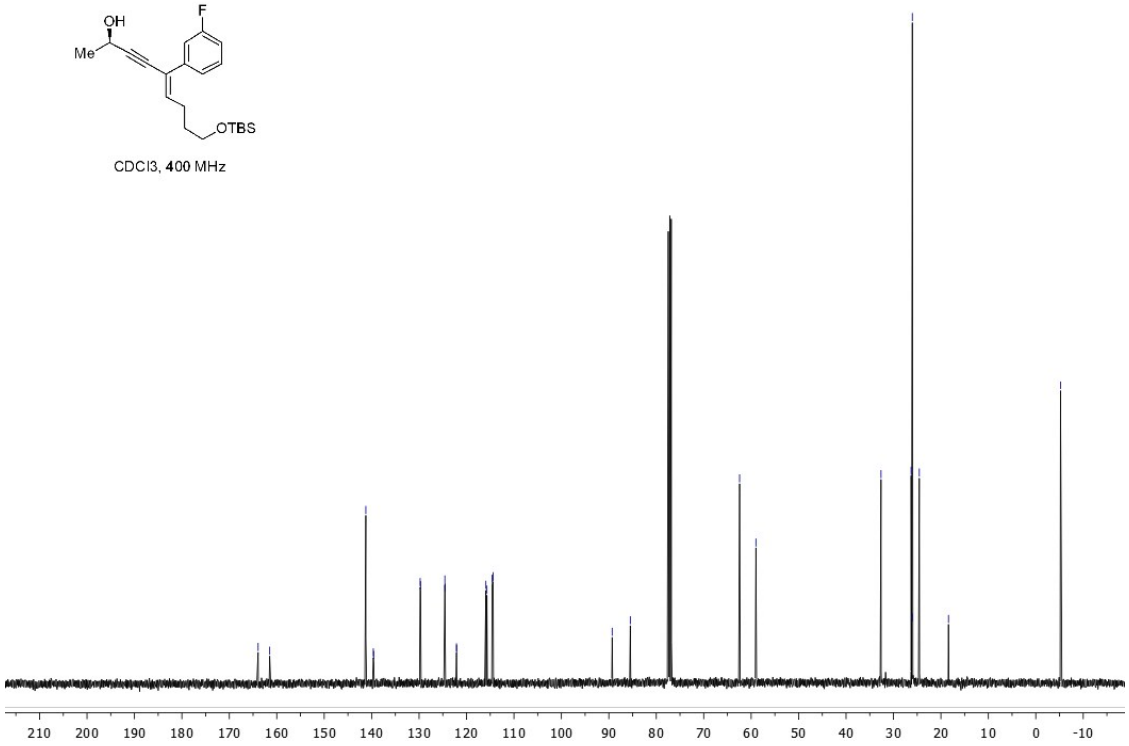
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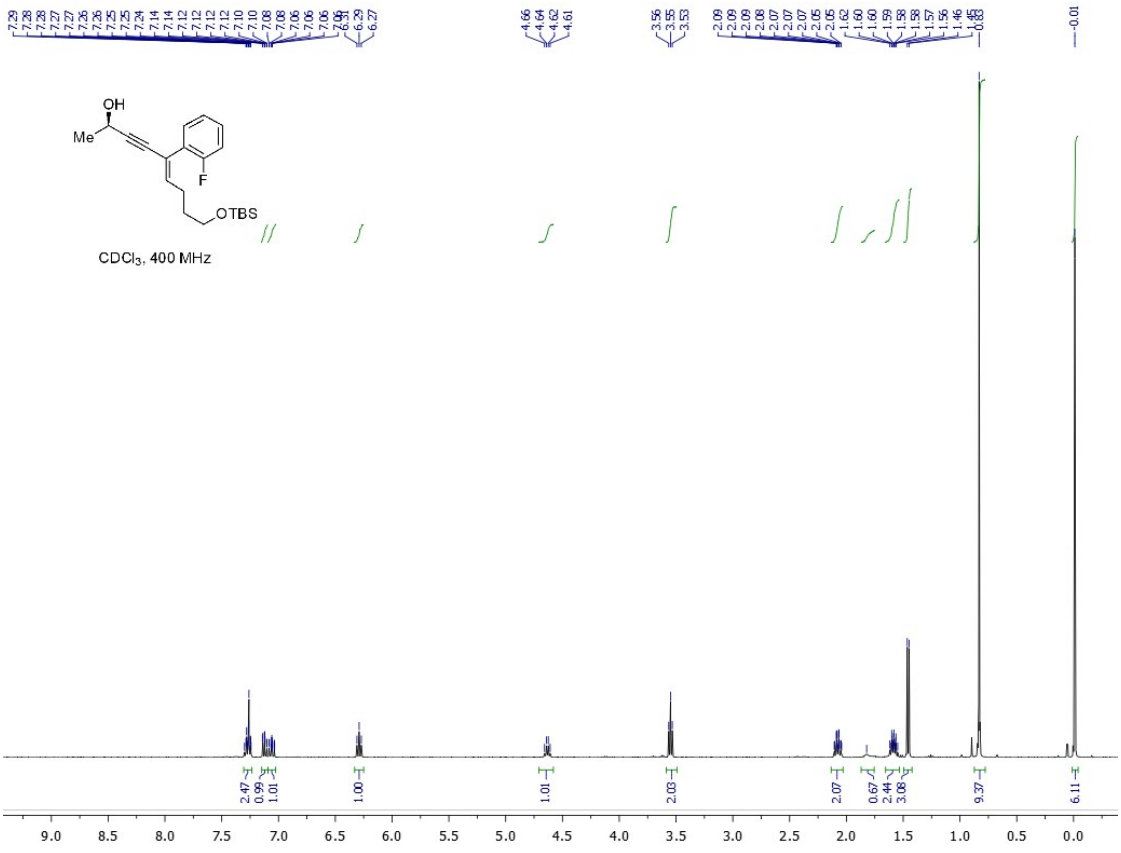
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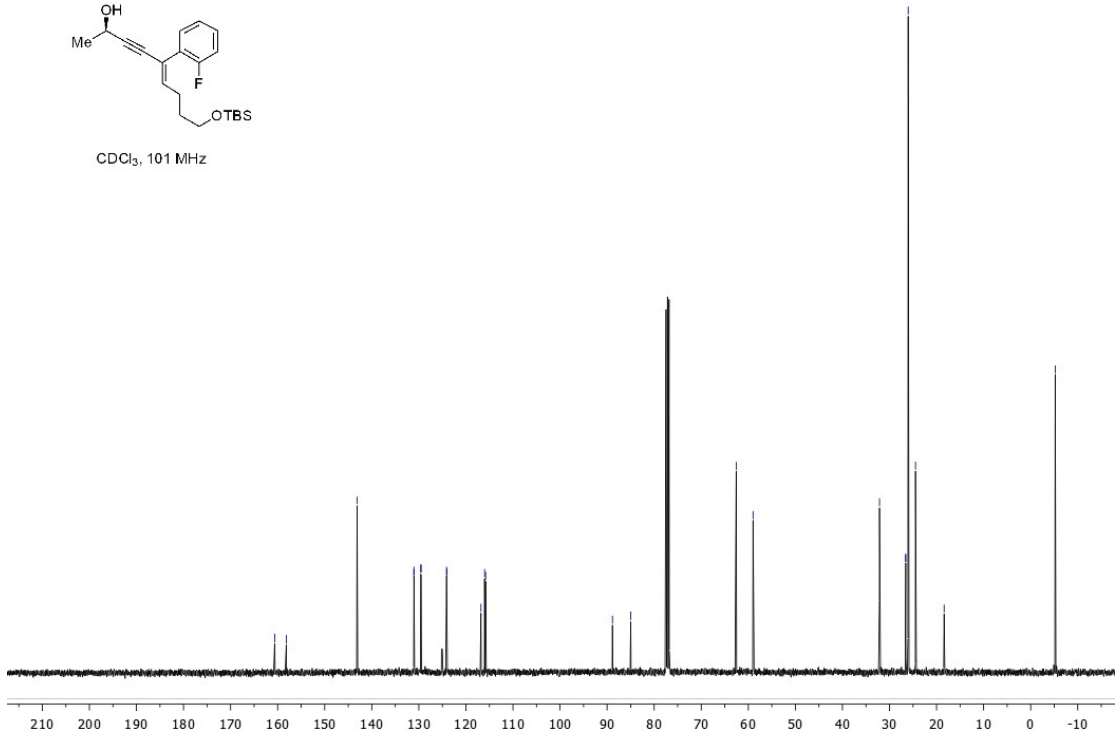
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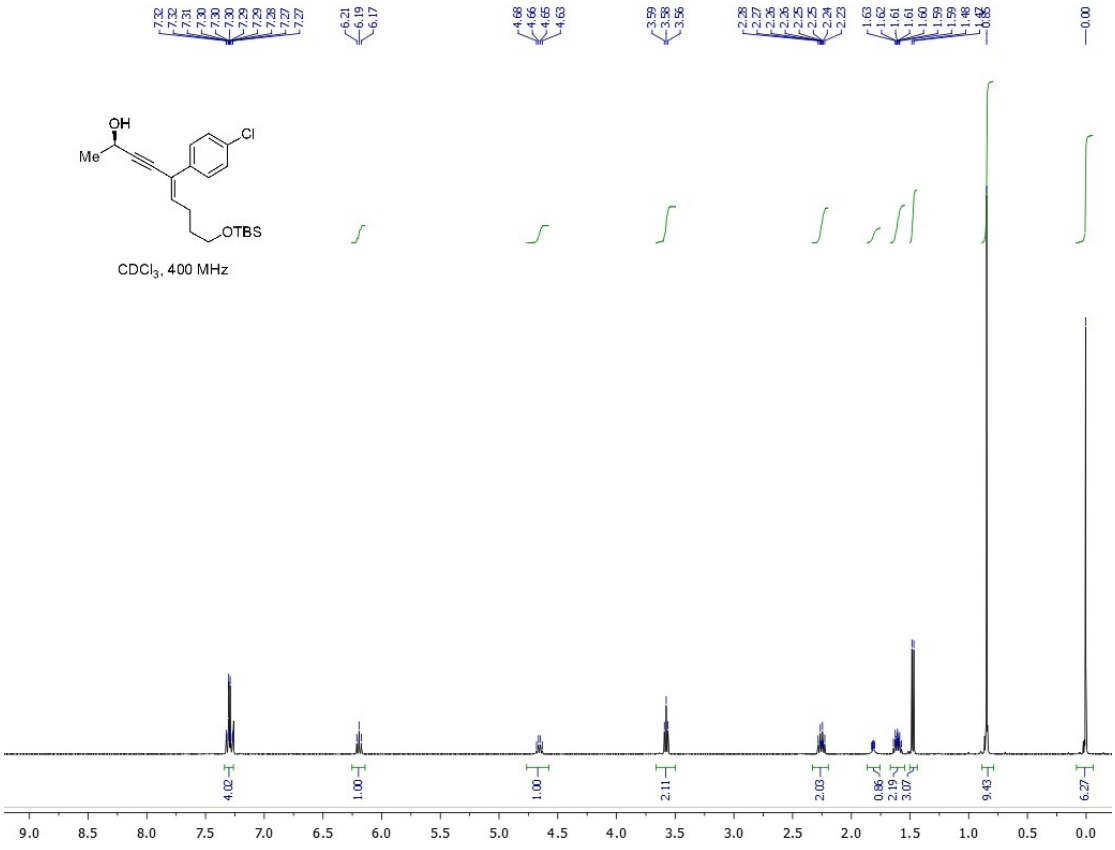
OH
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Cl
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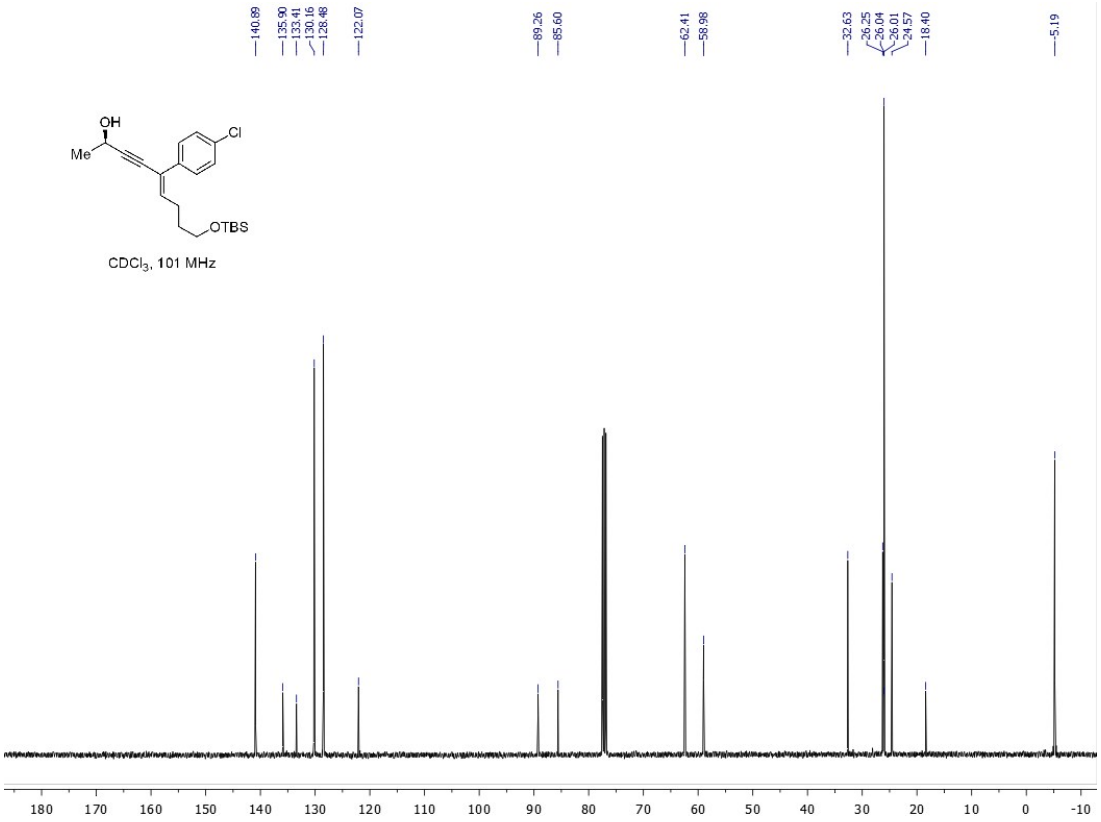
CDCl3, 400 MHz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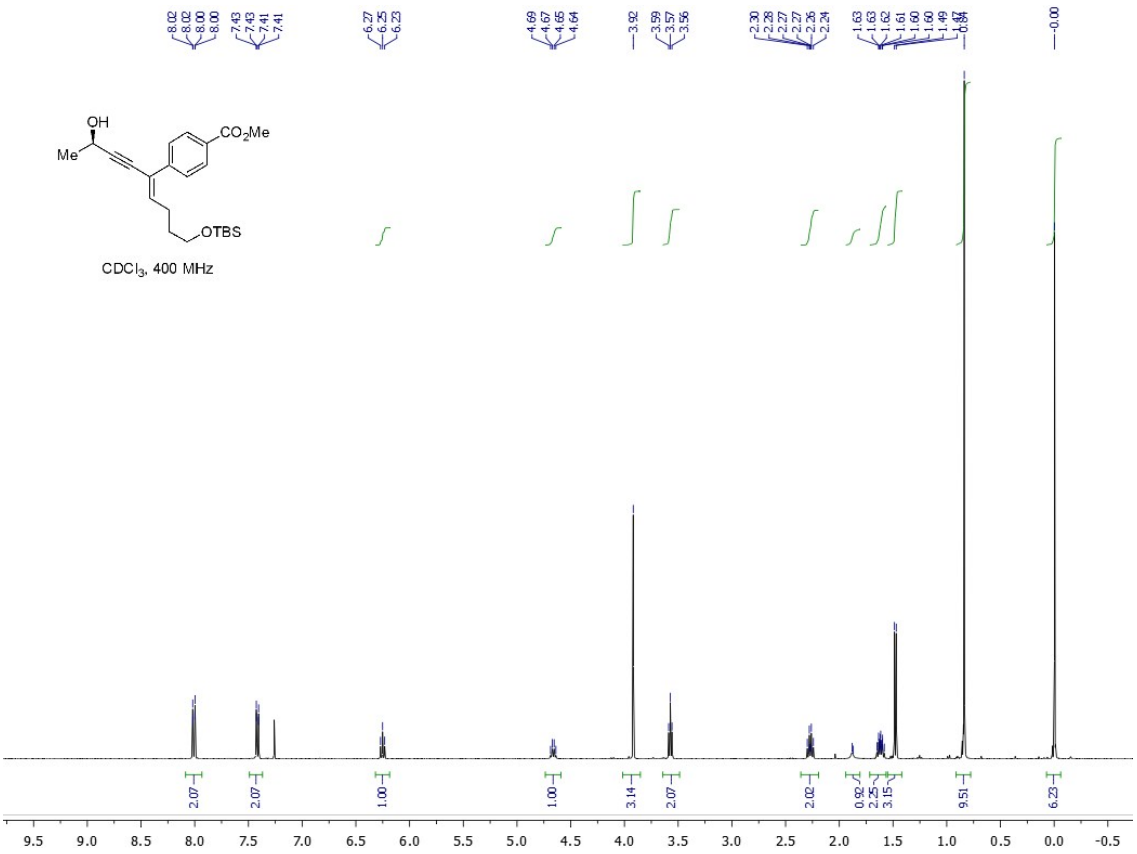
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CO2Me
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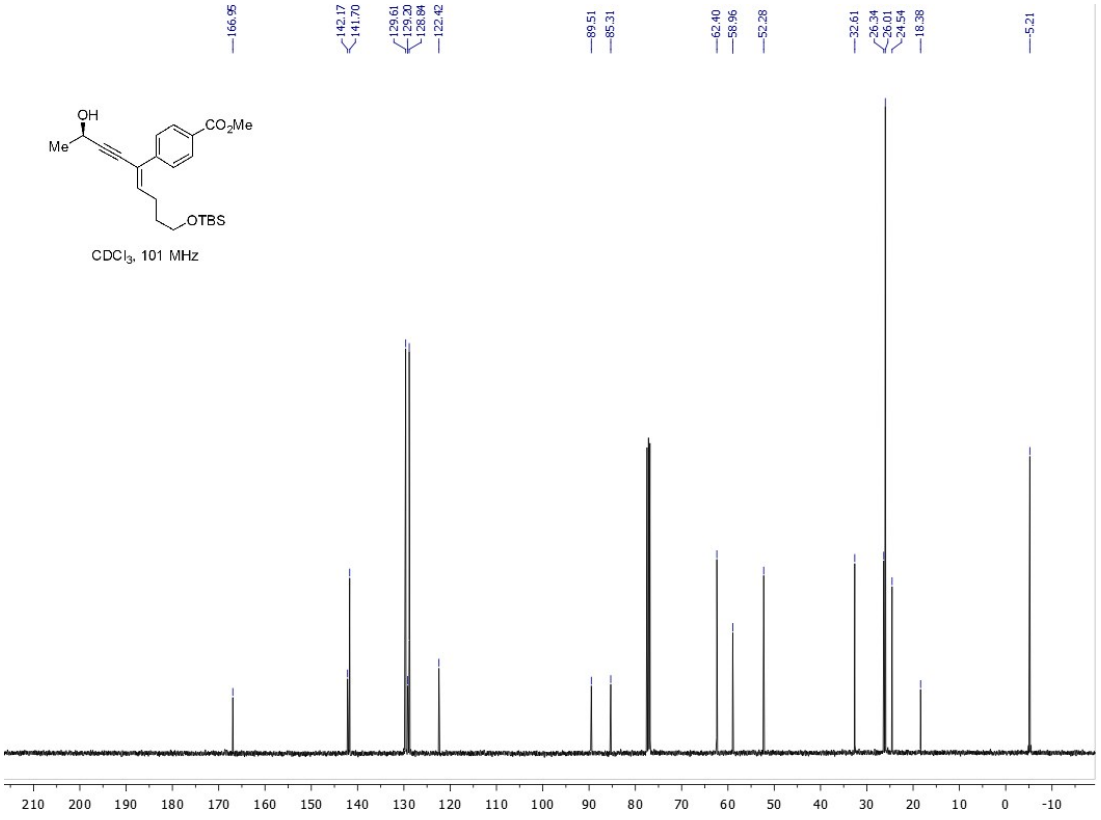
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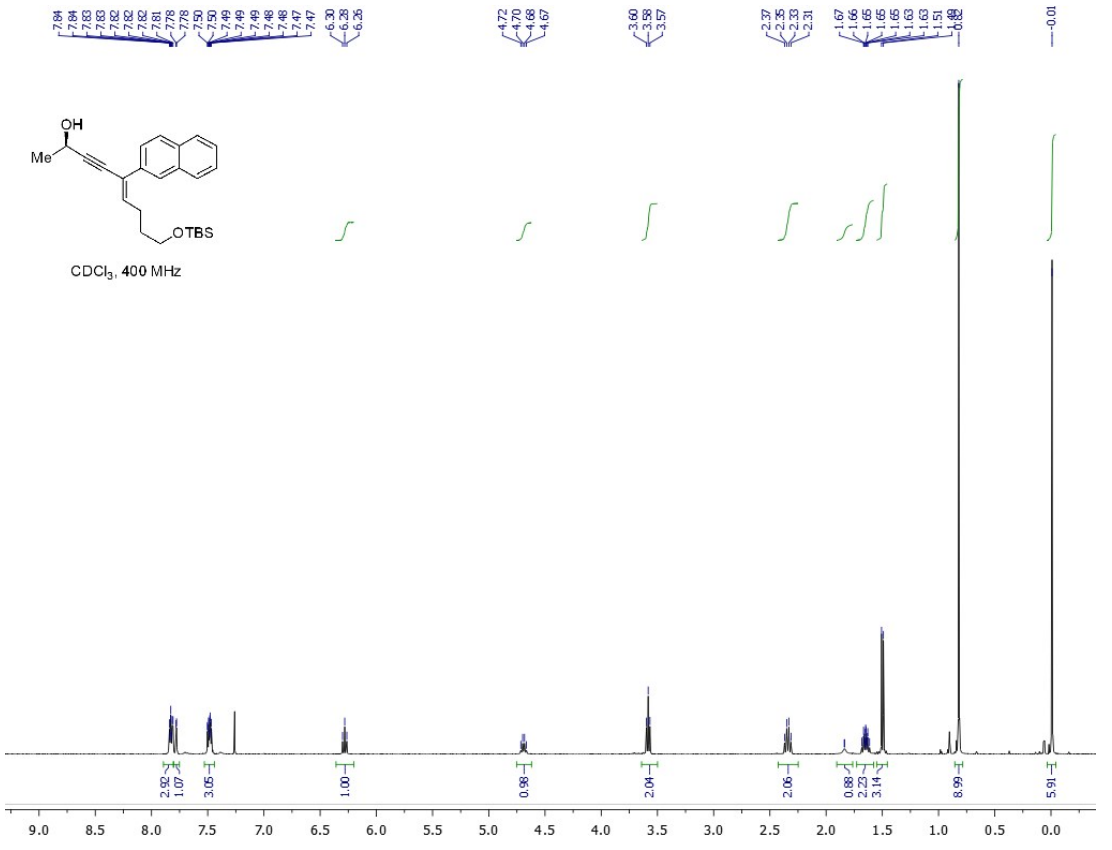
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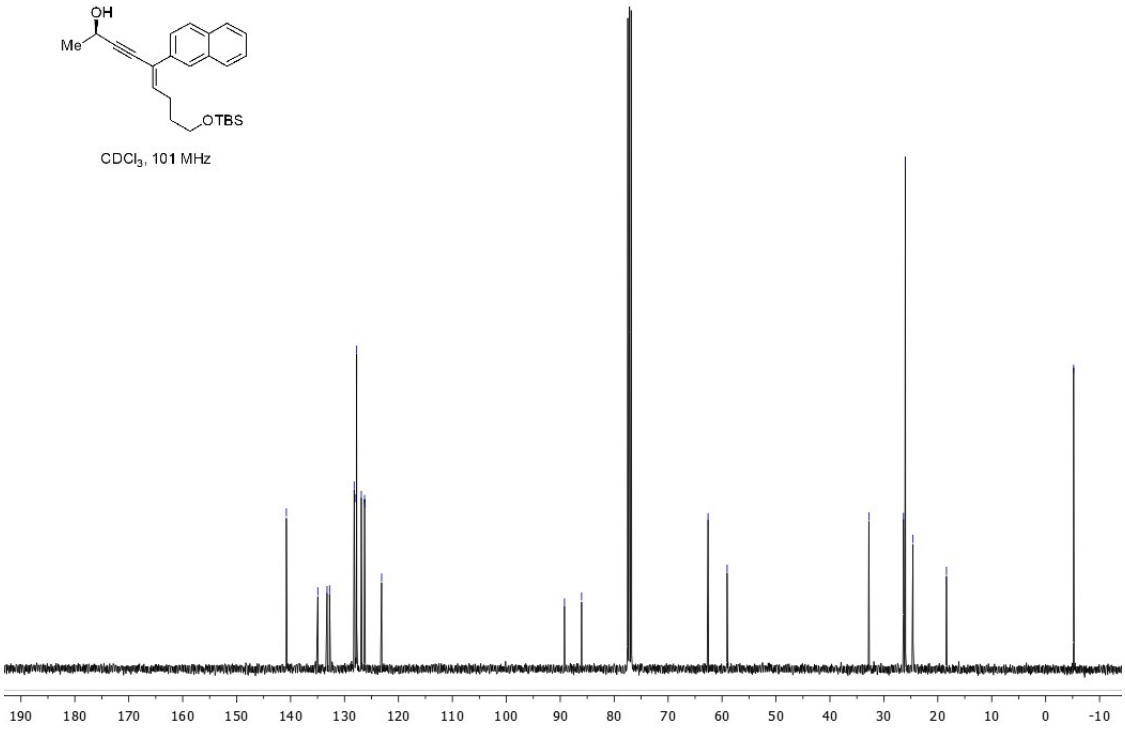
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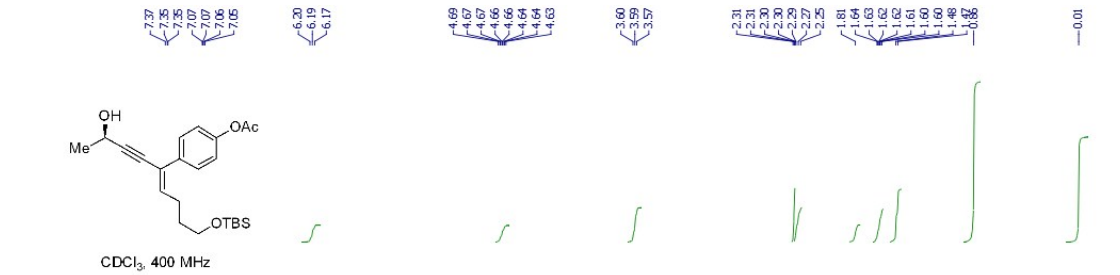
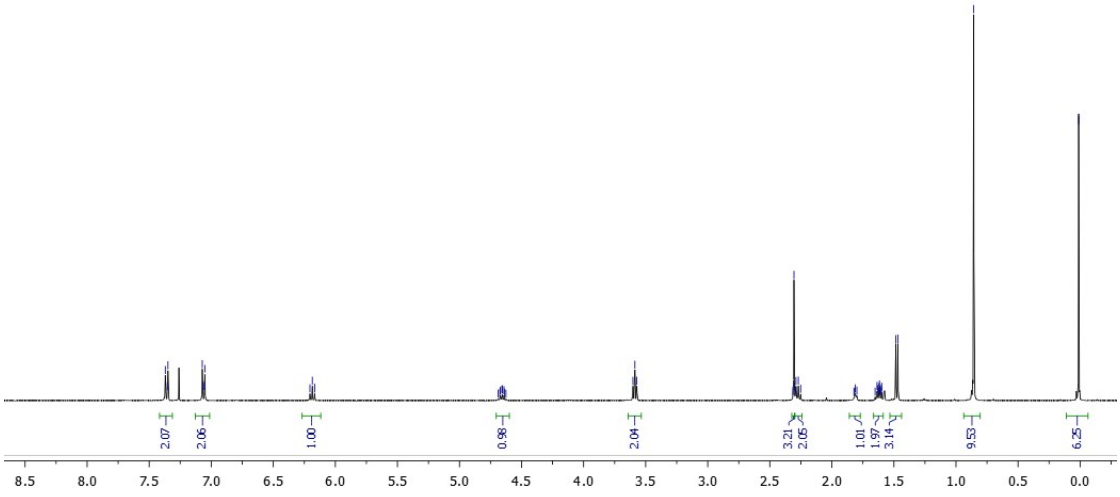
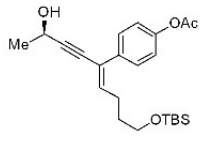
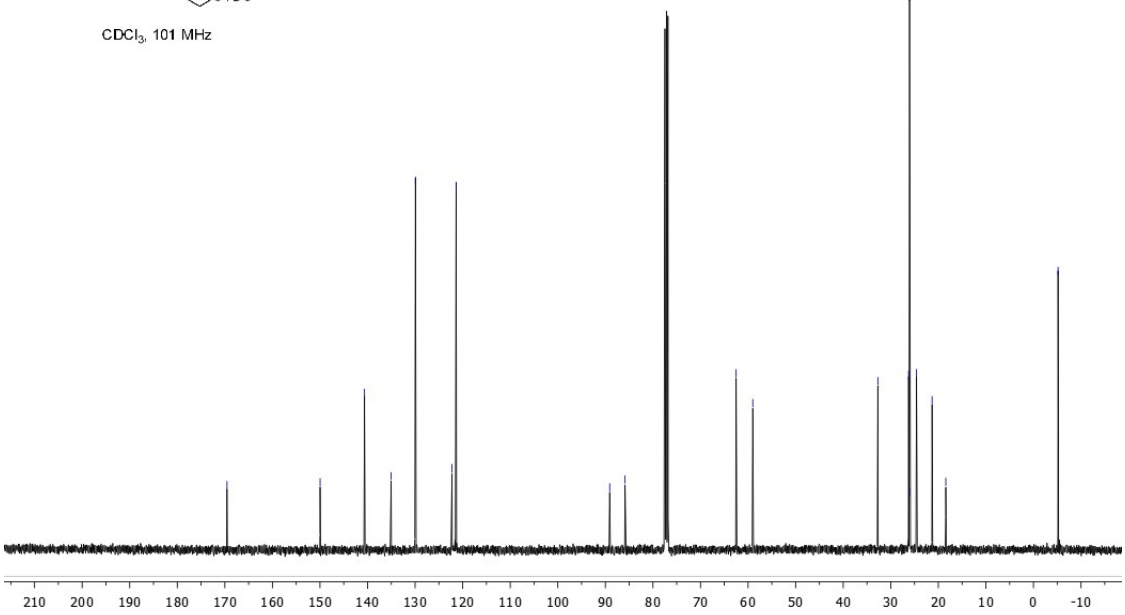


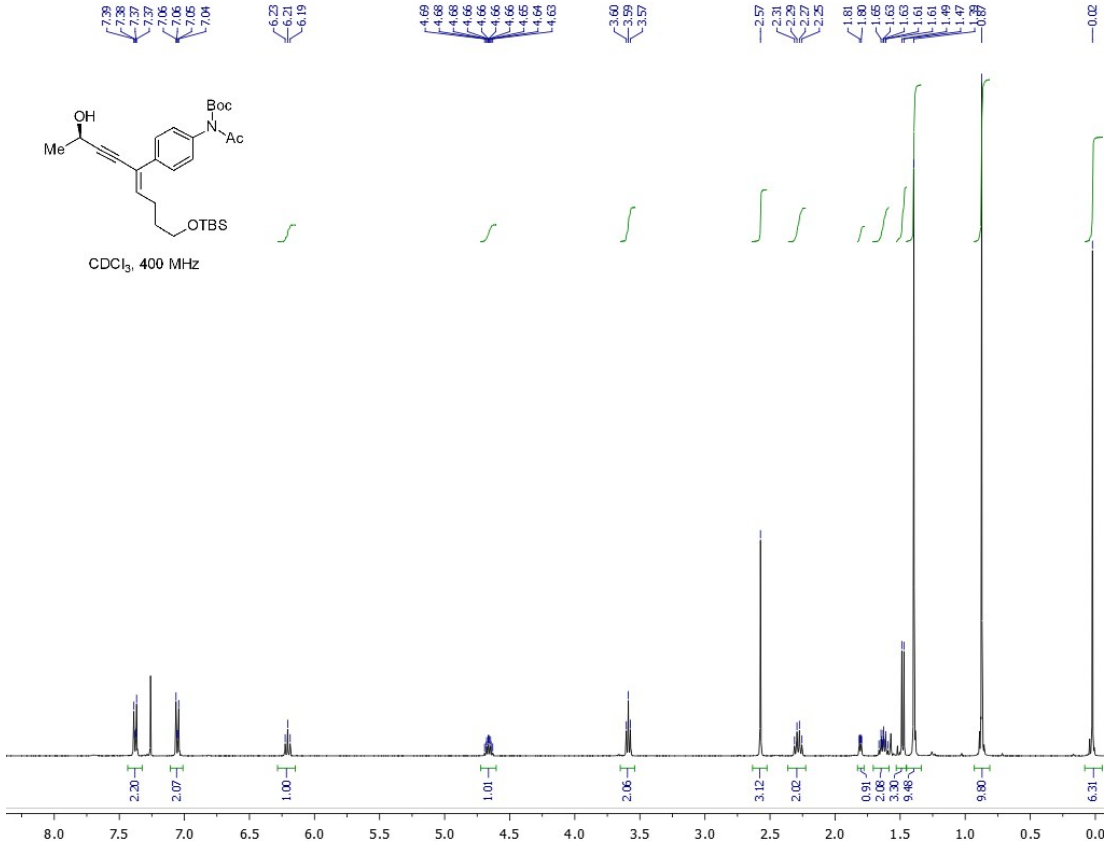
$CDCl_3$, 400 MHz

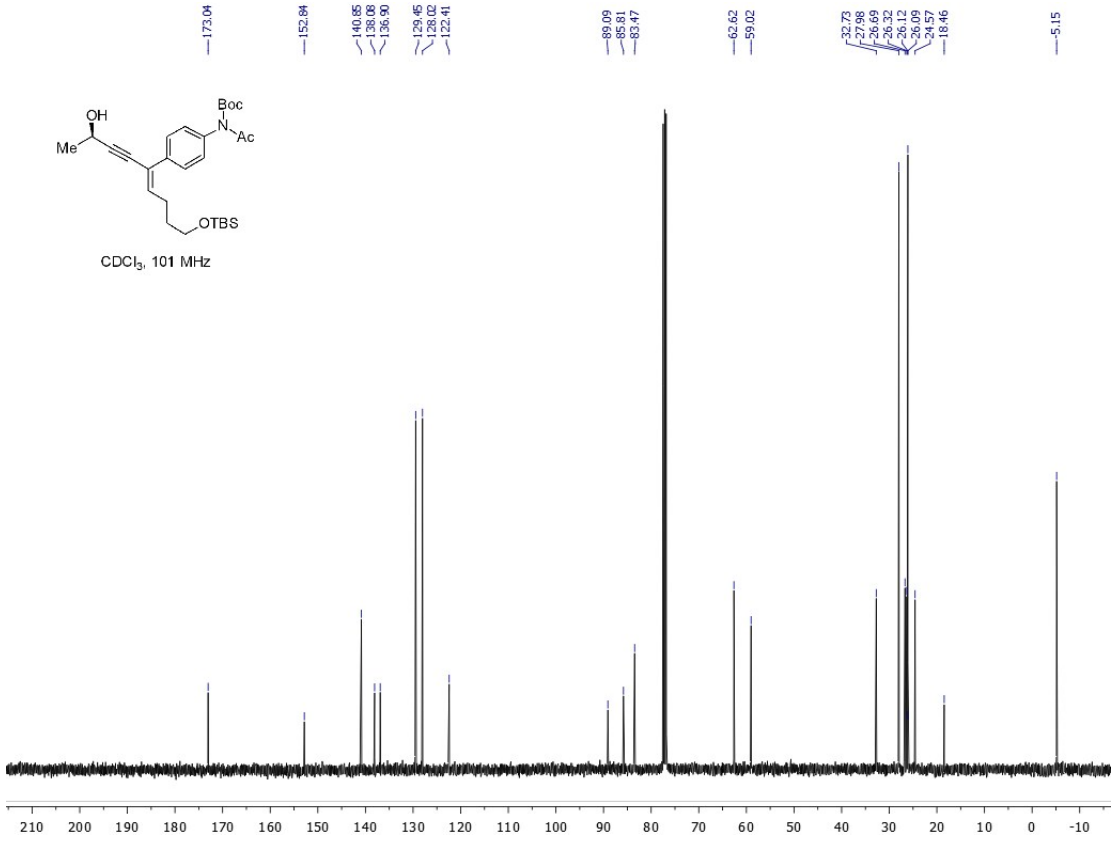




$CDCl_3$, 101 MHz




OH
Me
Boc
N
Ac
OTBS
CDCl3, 400 MHz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Boc
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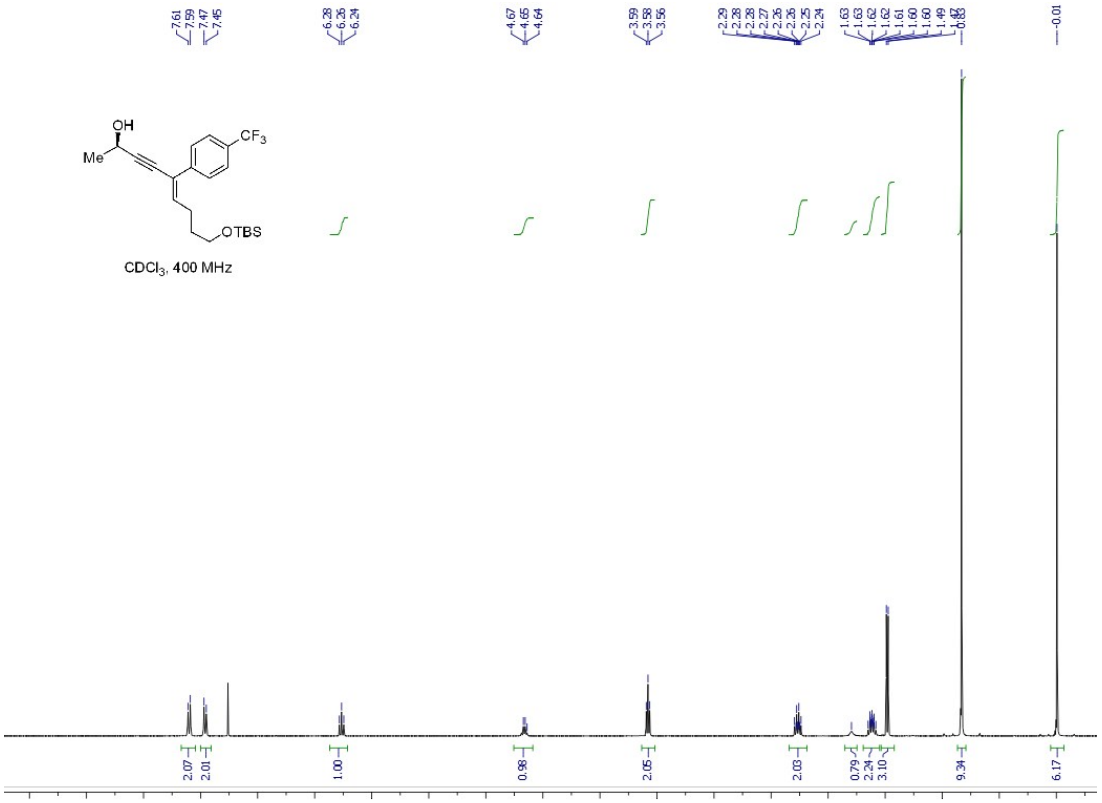
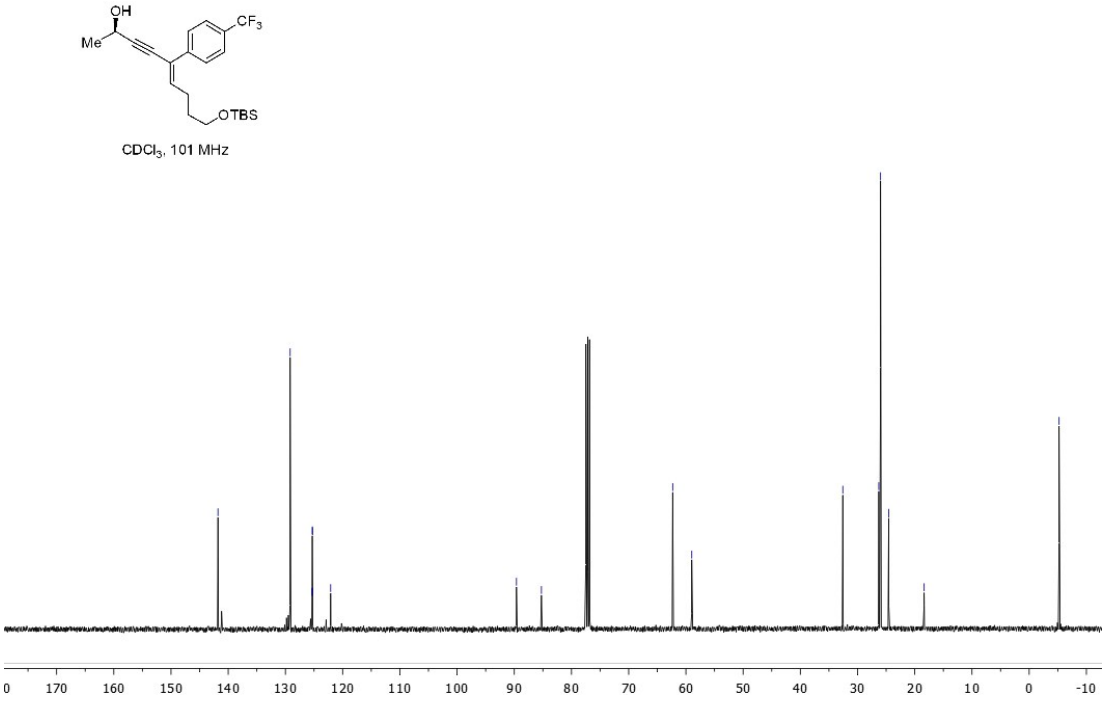
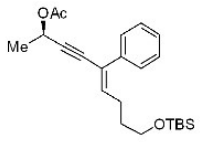
OTBS
CDCl3, 101 MHz

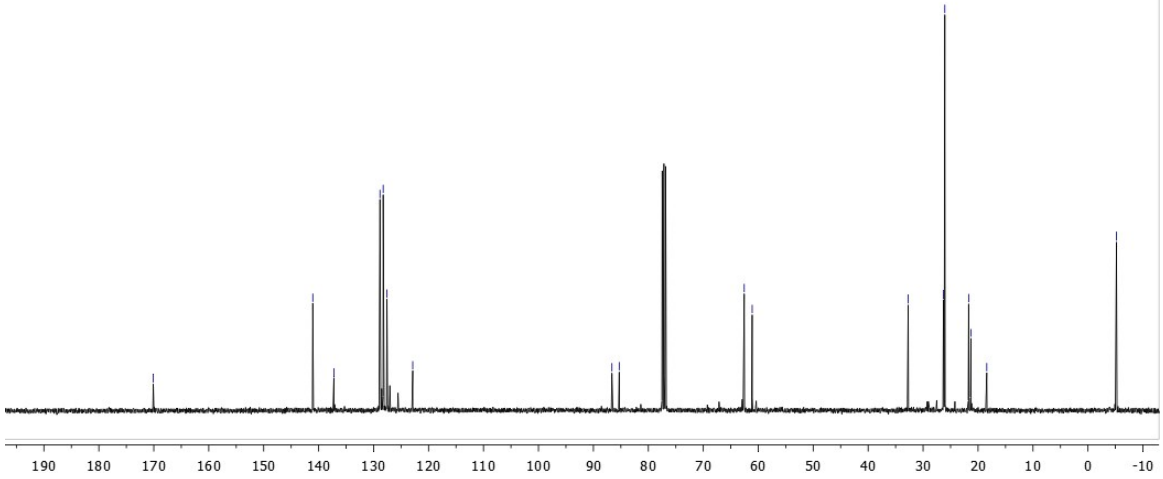

OH
Me
CF3
OTBS
CDCl3, 400 MHz

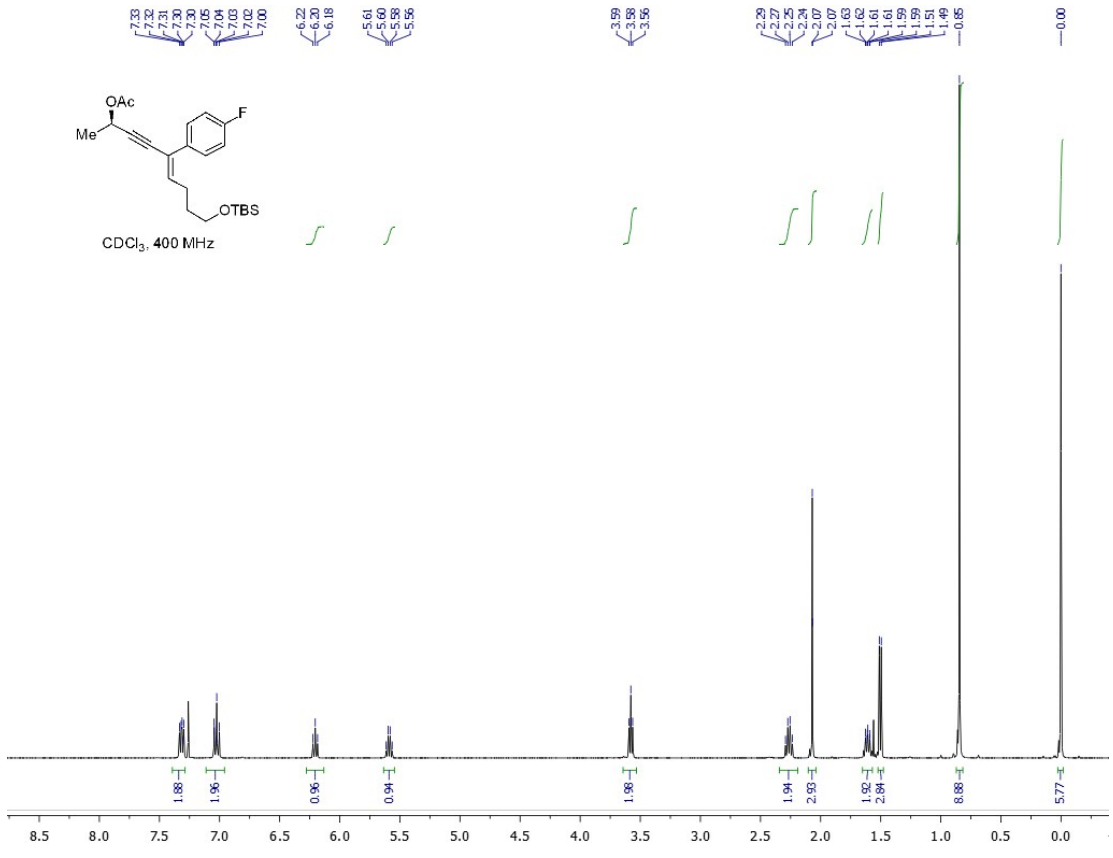

OH
Me
CF3
OTBS
CDCl3, 101 MHz

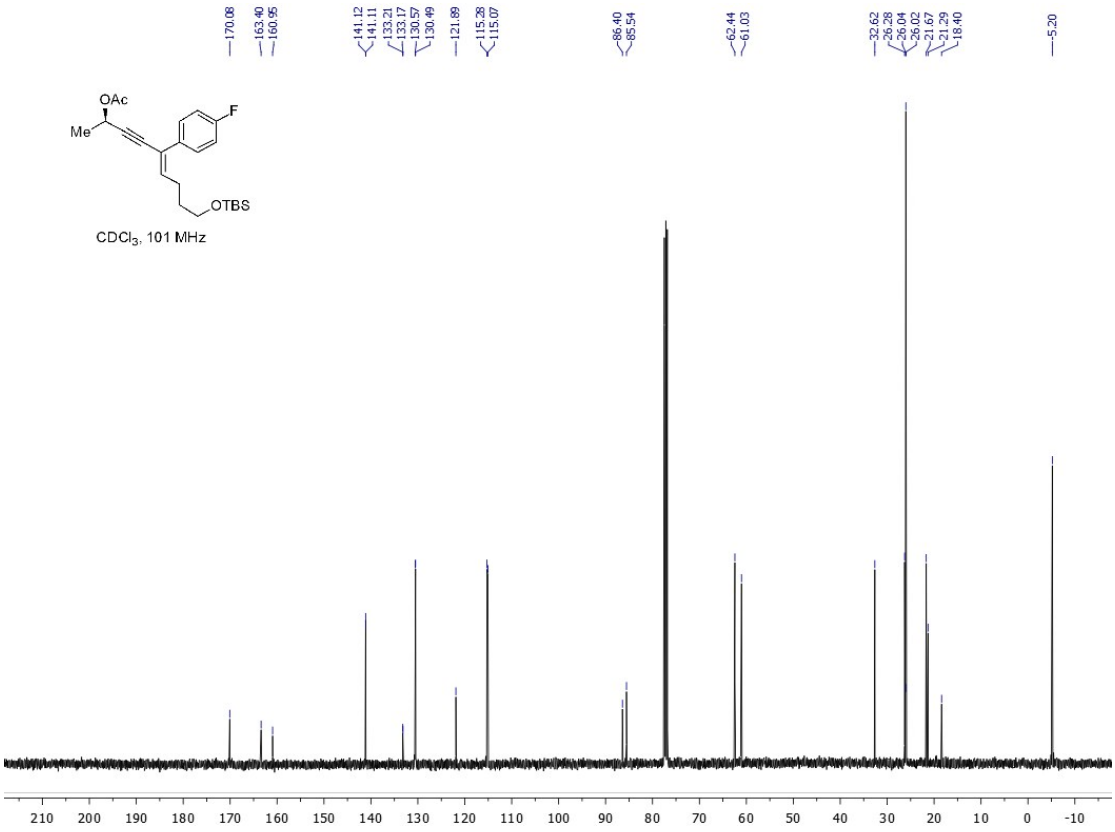
$CDCl_3$, 400 MHz

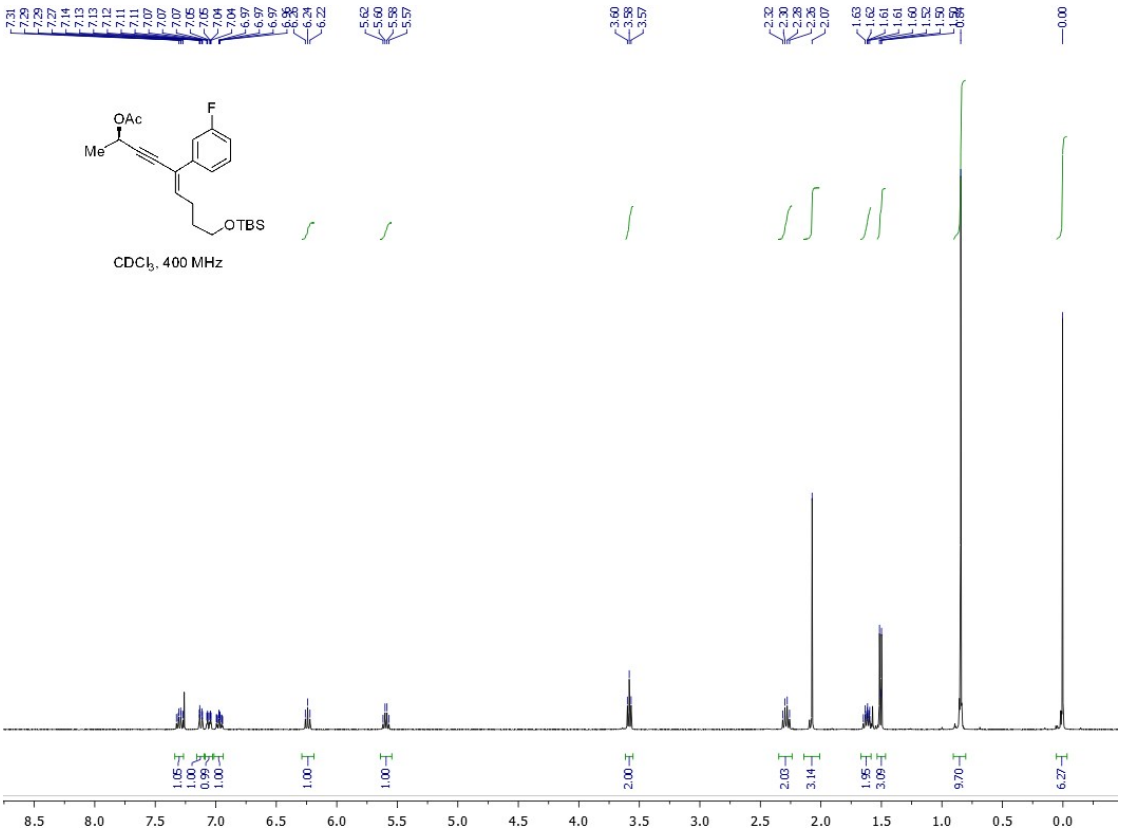


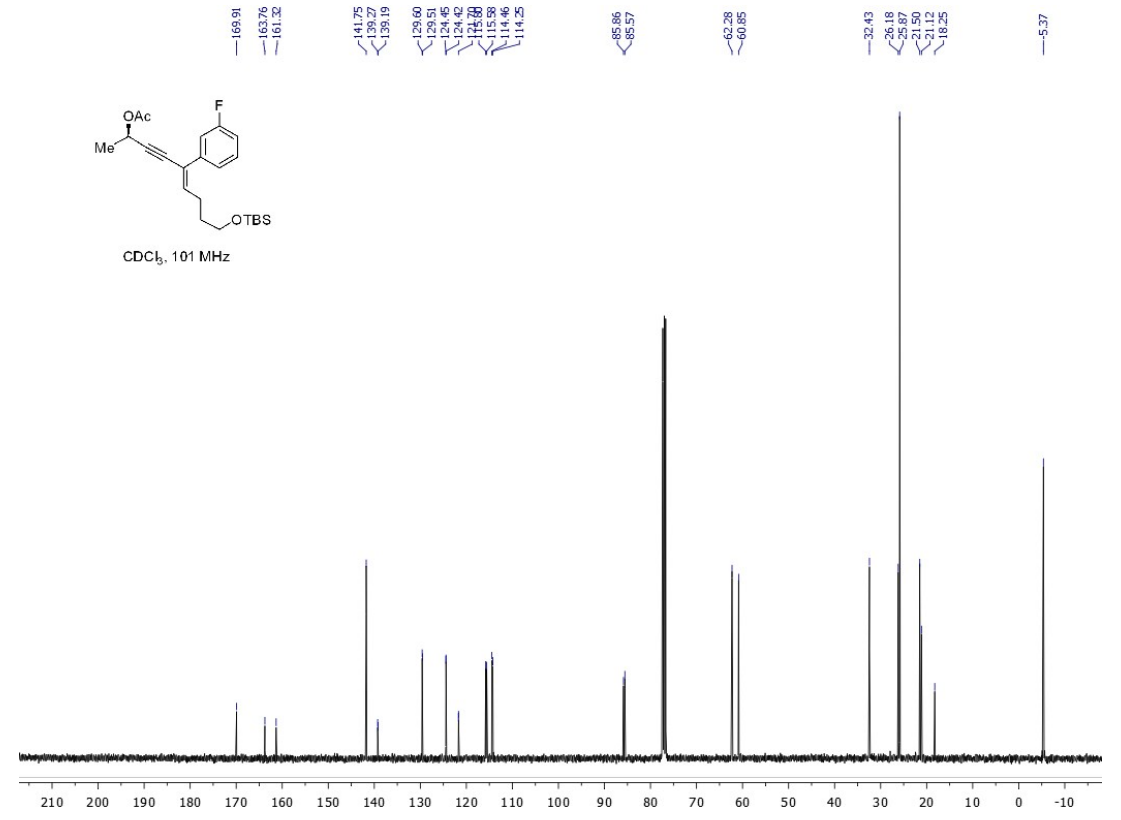
$CDCl_3$, 101 MHz

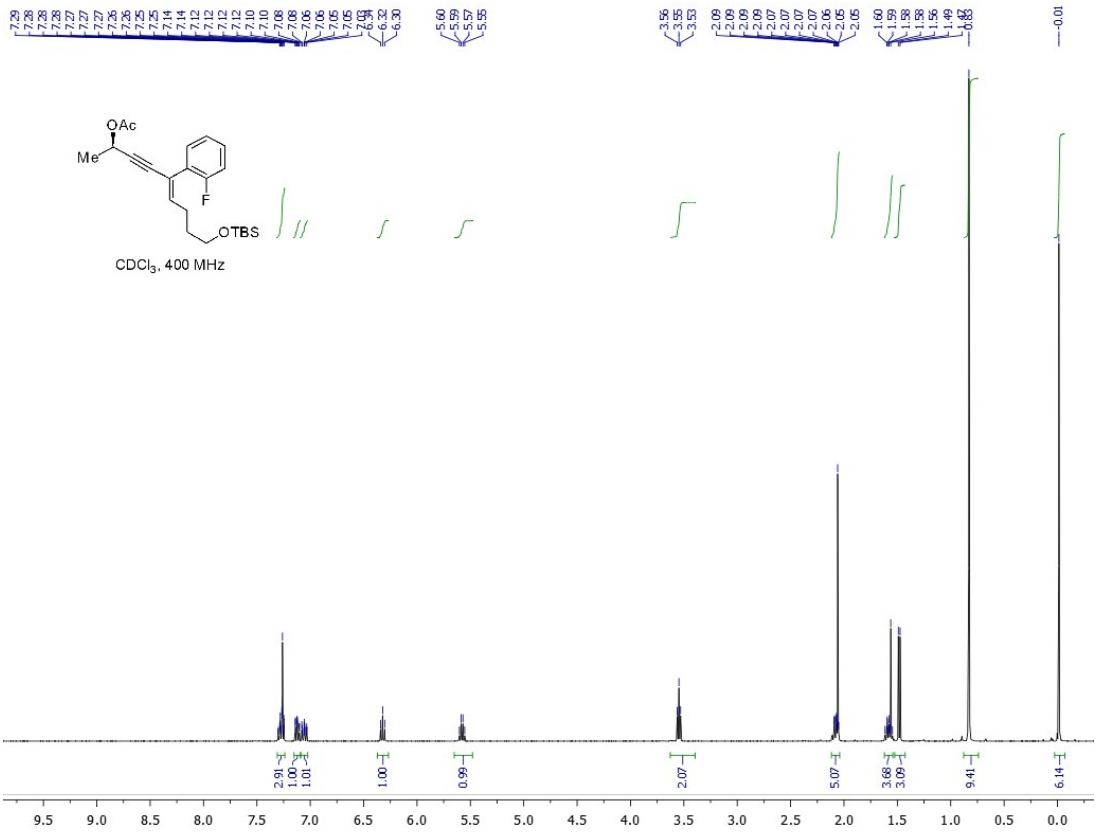


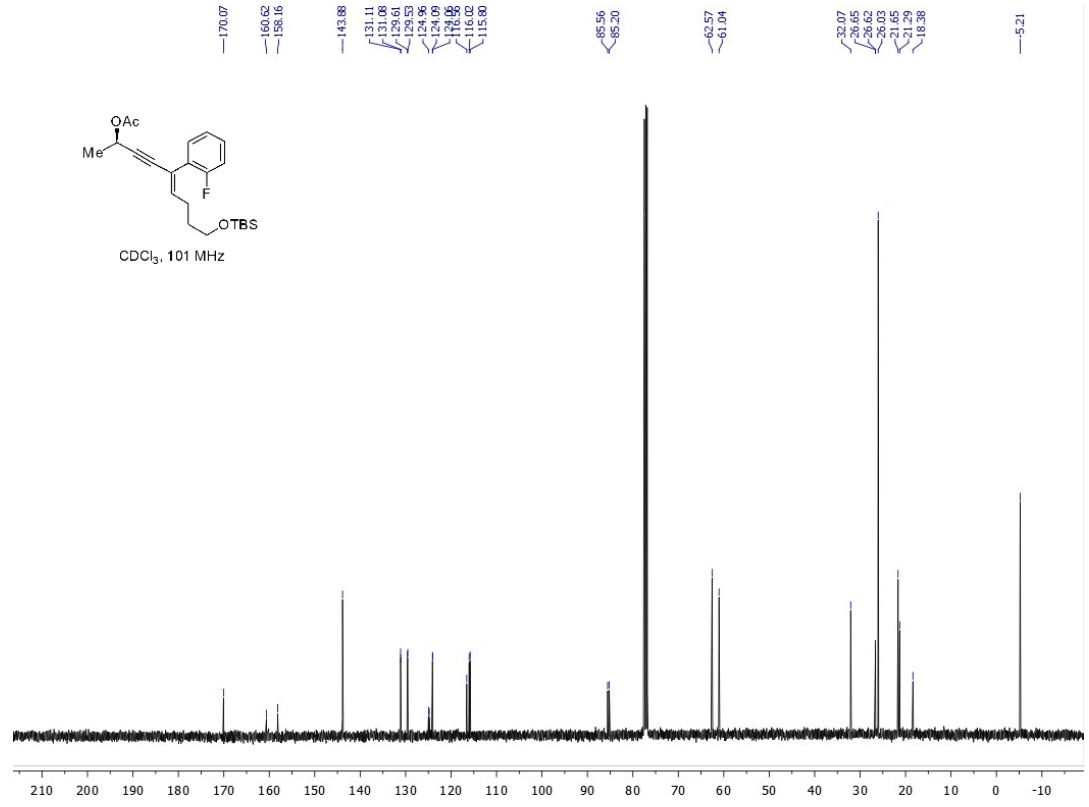

OAc
Me
F
OTBS
CDCl3, 400 MHz

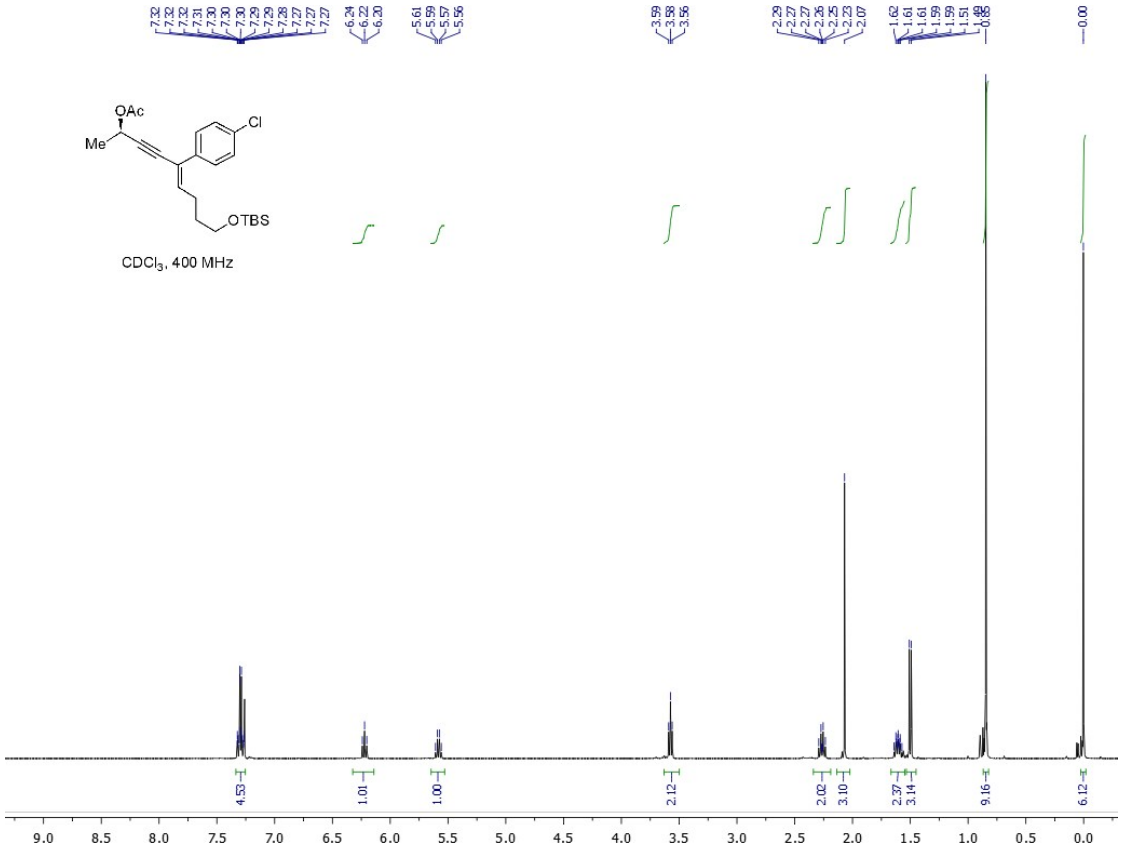

OAc
Me
F
OTBS
CDCl3, 101 MHz

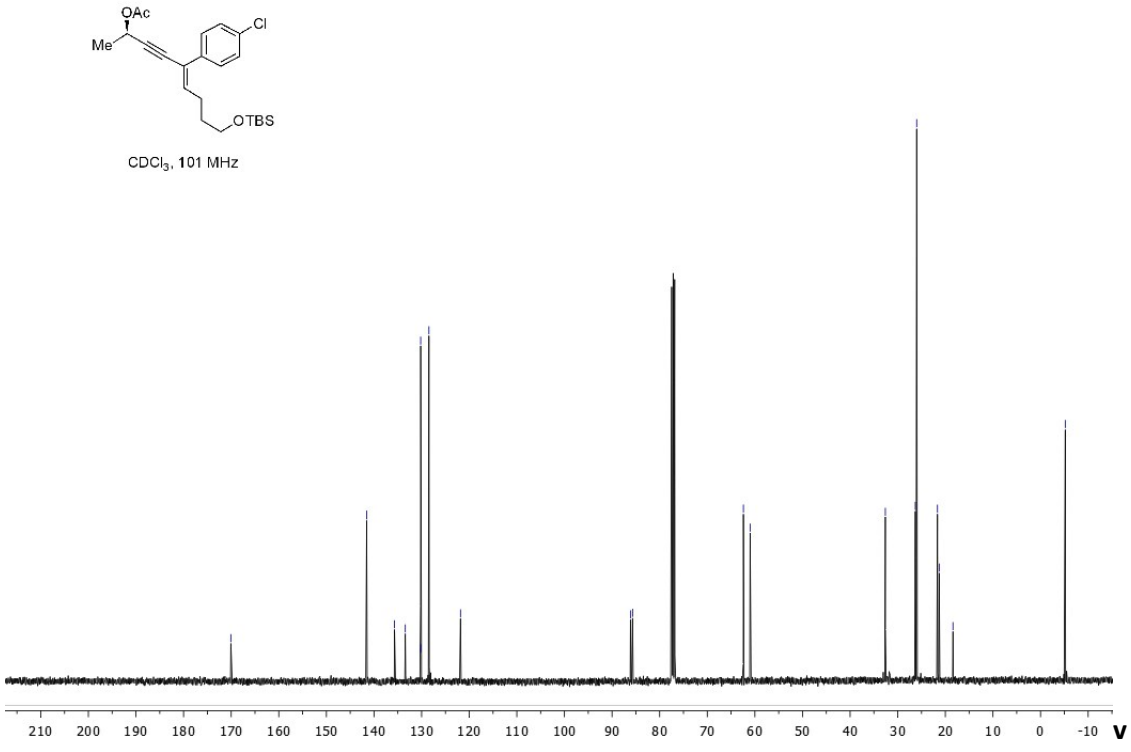

OAc
Me
F
OTBS
CDCl3, 400 MHz

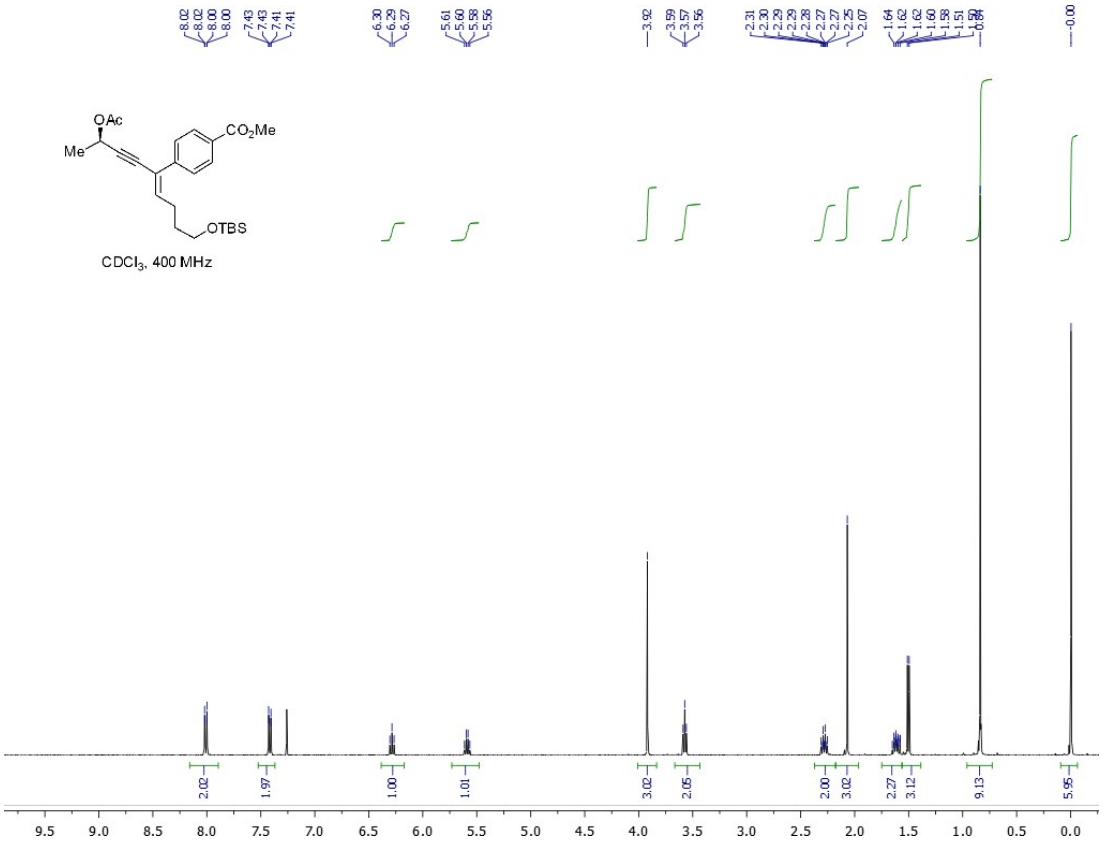

OAc
Me
F
OTBS
CDCl3, 101 MHz

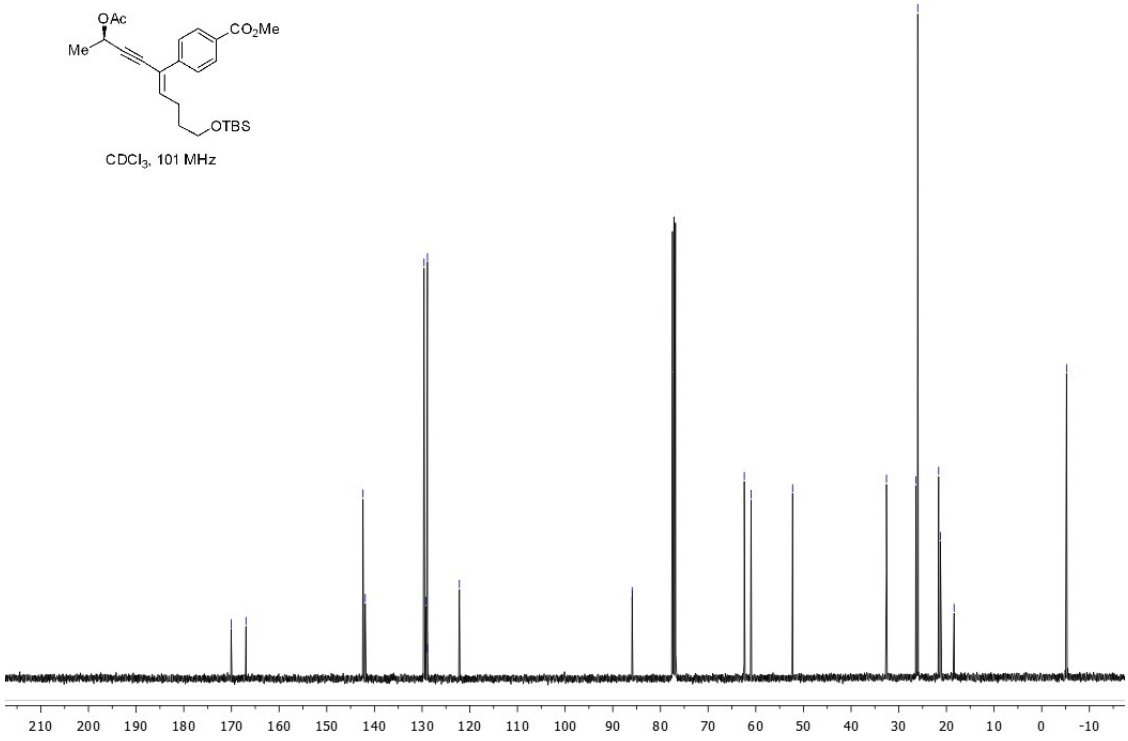

OAc
Me
F
OTBS
CDCl3, 400 MHz

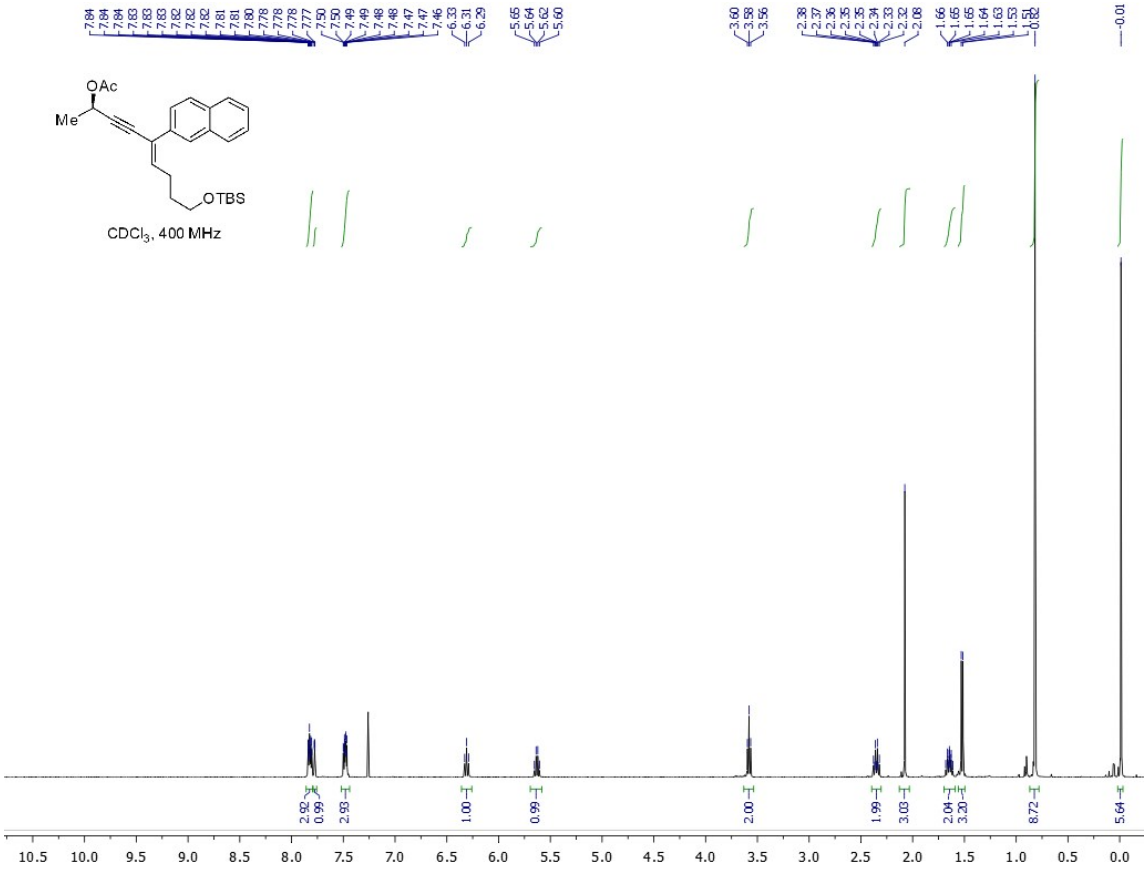

OAc
Me
F
OTBS
CDCl3, 101 MHz

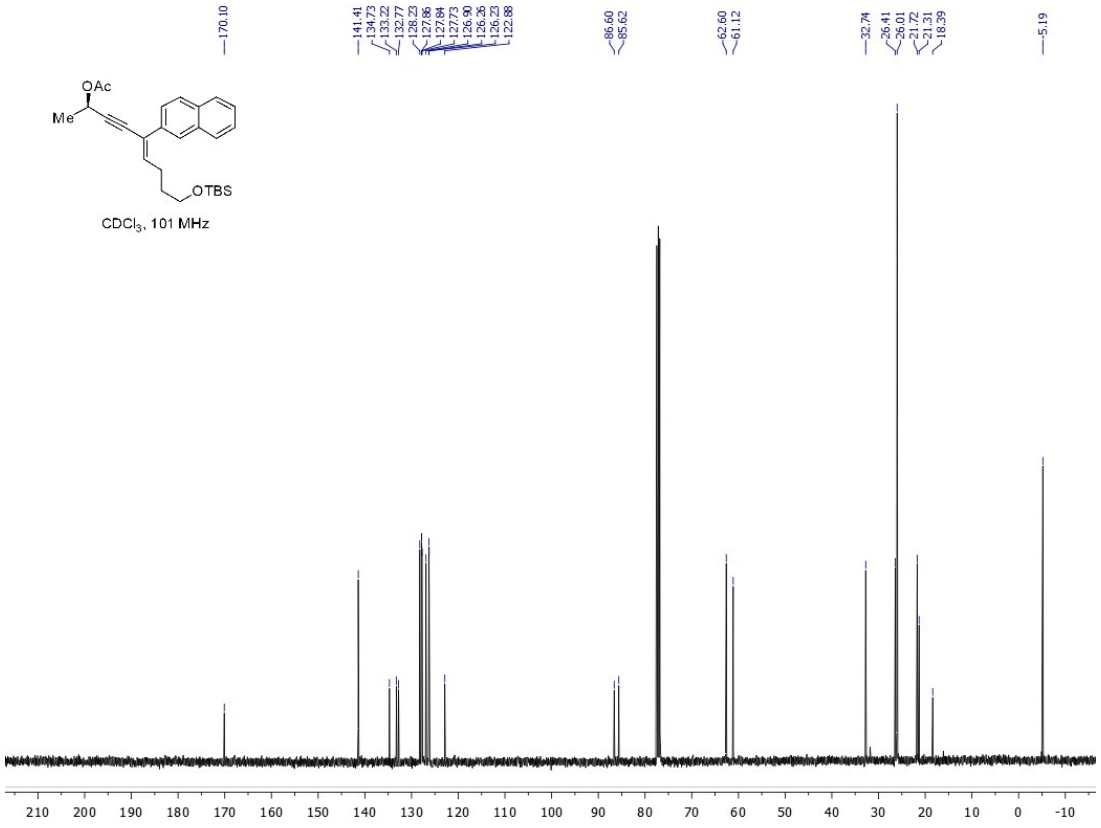

OAc
Me
Cl
OTBS
CDCl3, 400 MHz

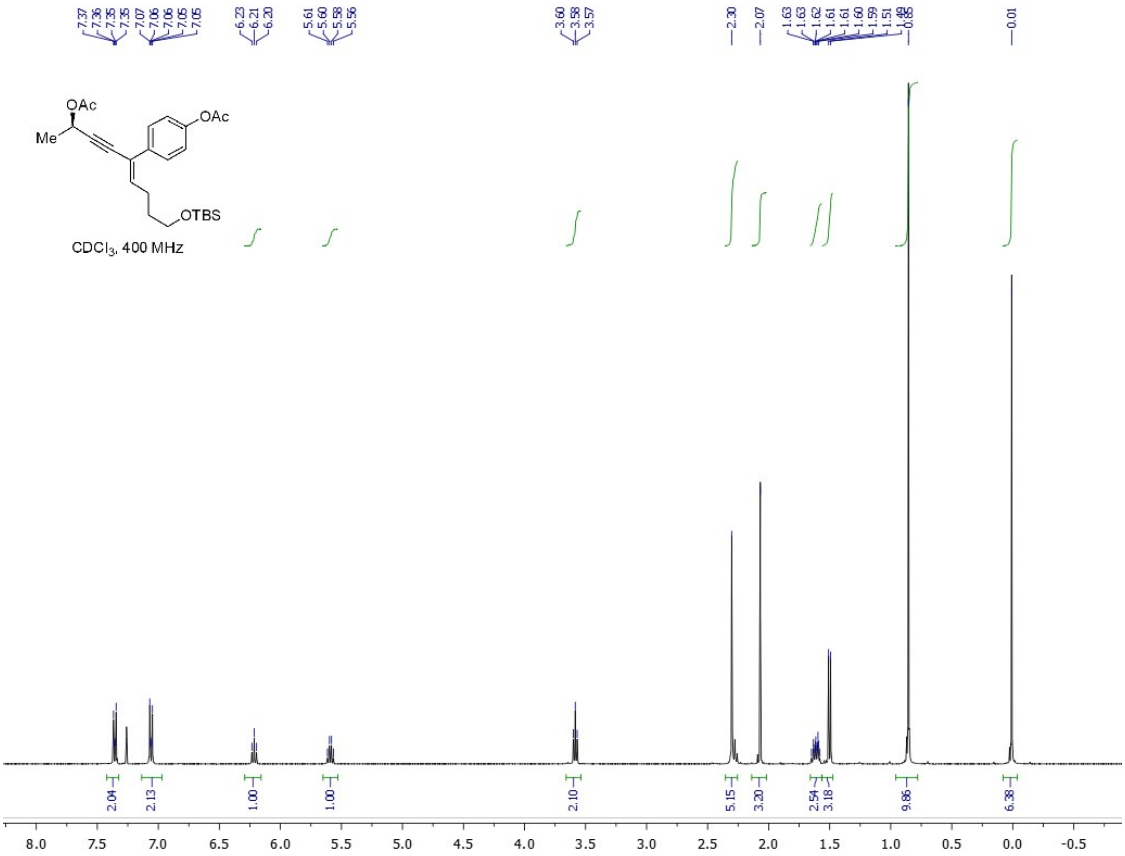

OAc
Me
Cl
OTBS
CDCl3, 101 MHz

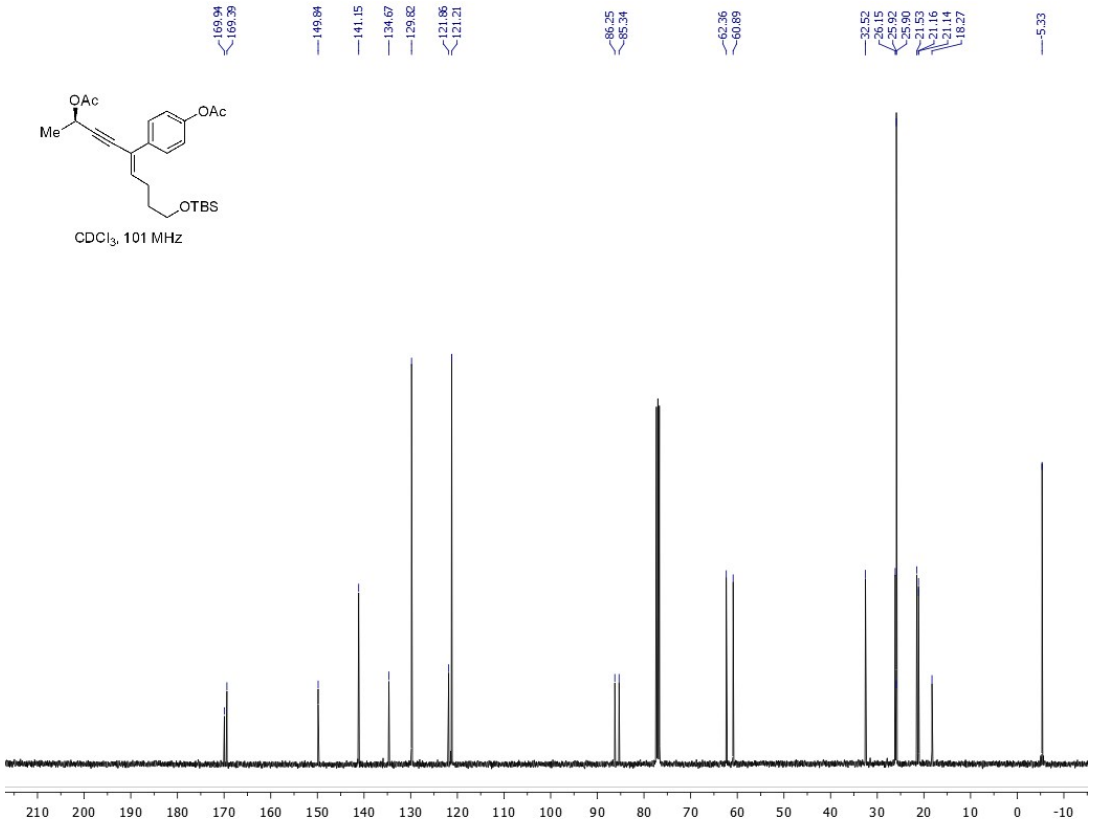

OAc
Me
CO2Me
OTBS
CDCl3, 400 MHz

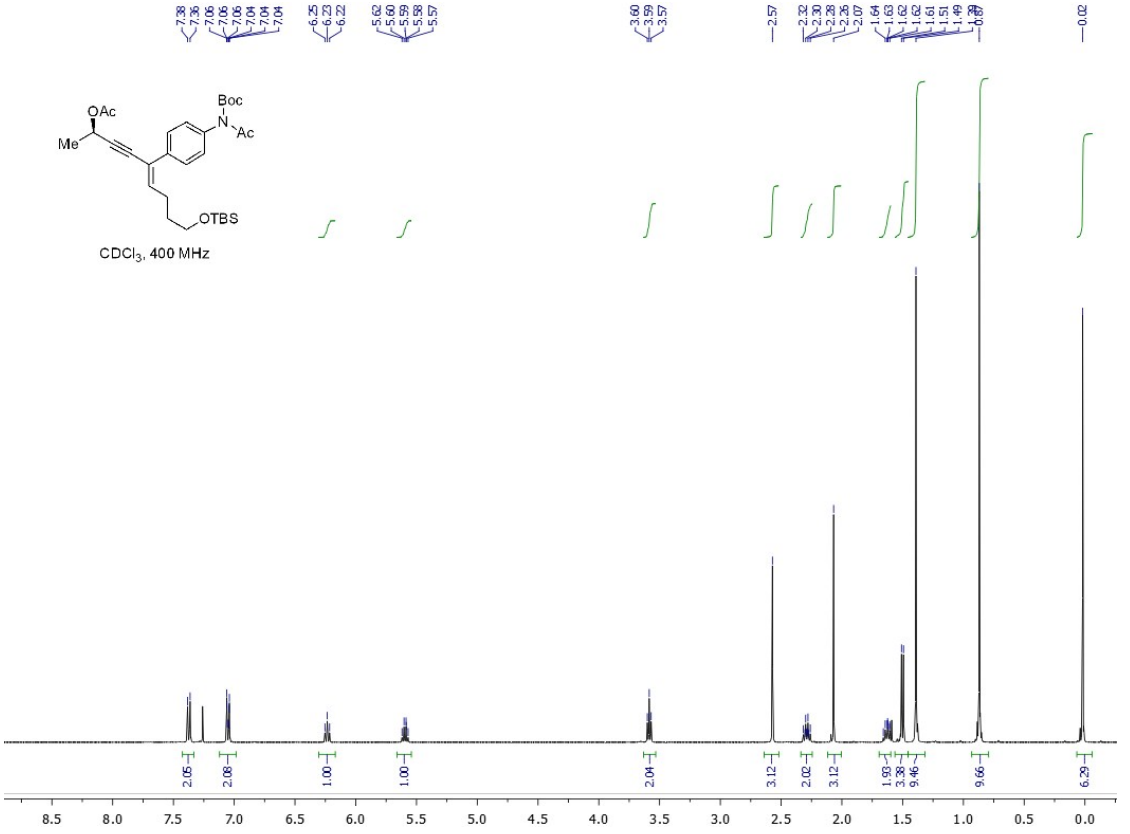

OAc
Me
CO2Me
OTBS
CDCl3, 101 MHz

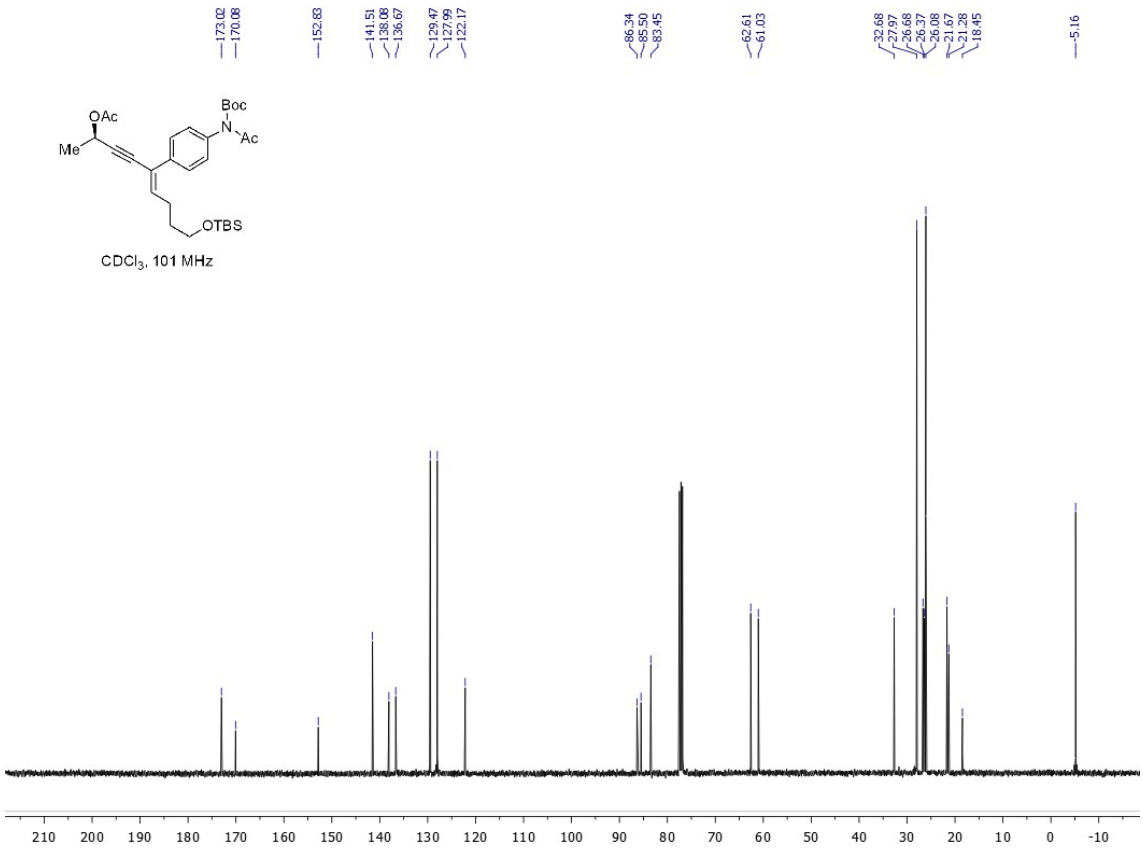

OAc
Me
OTBS
CDCl3, 400 MHz

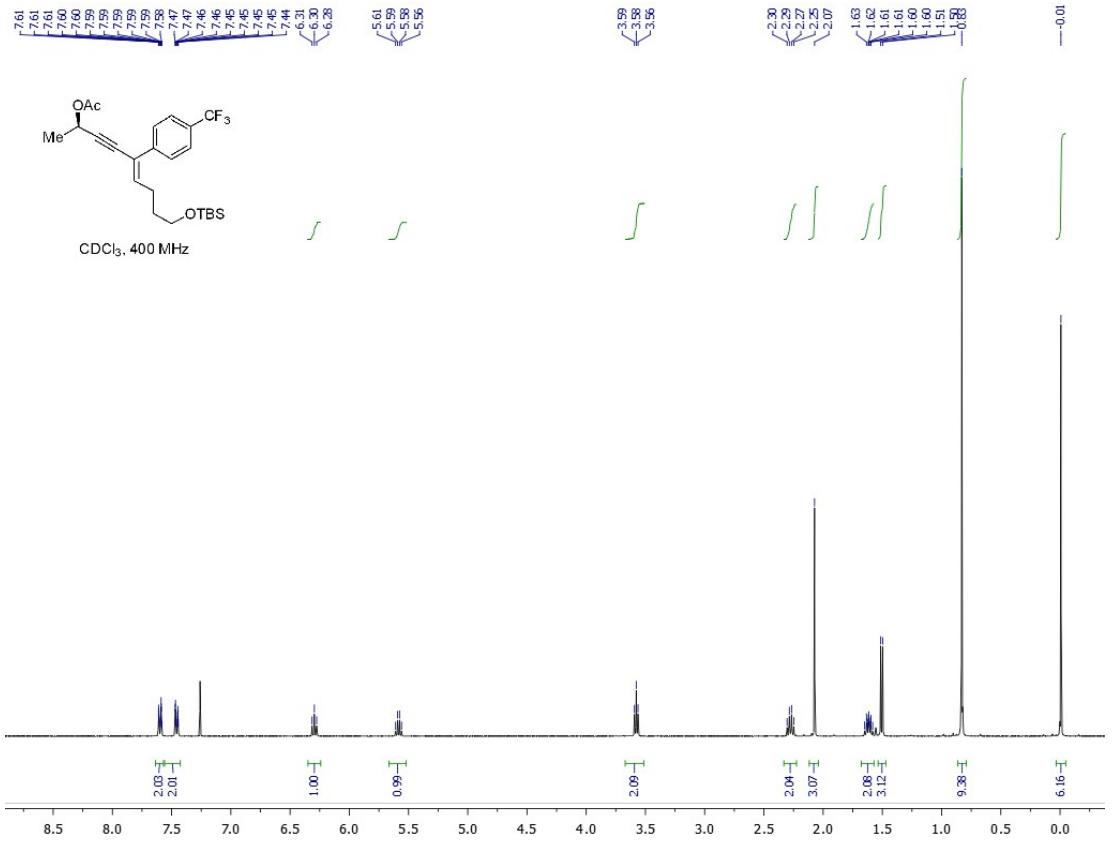

OAc
Me
OTBS
CDCl3, 101 MHz

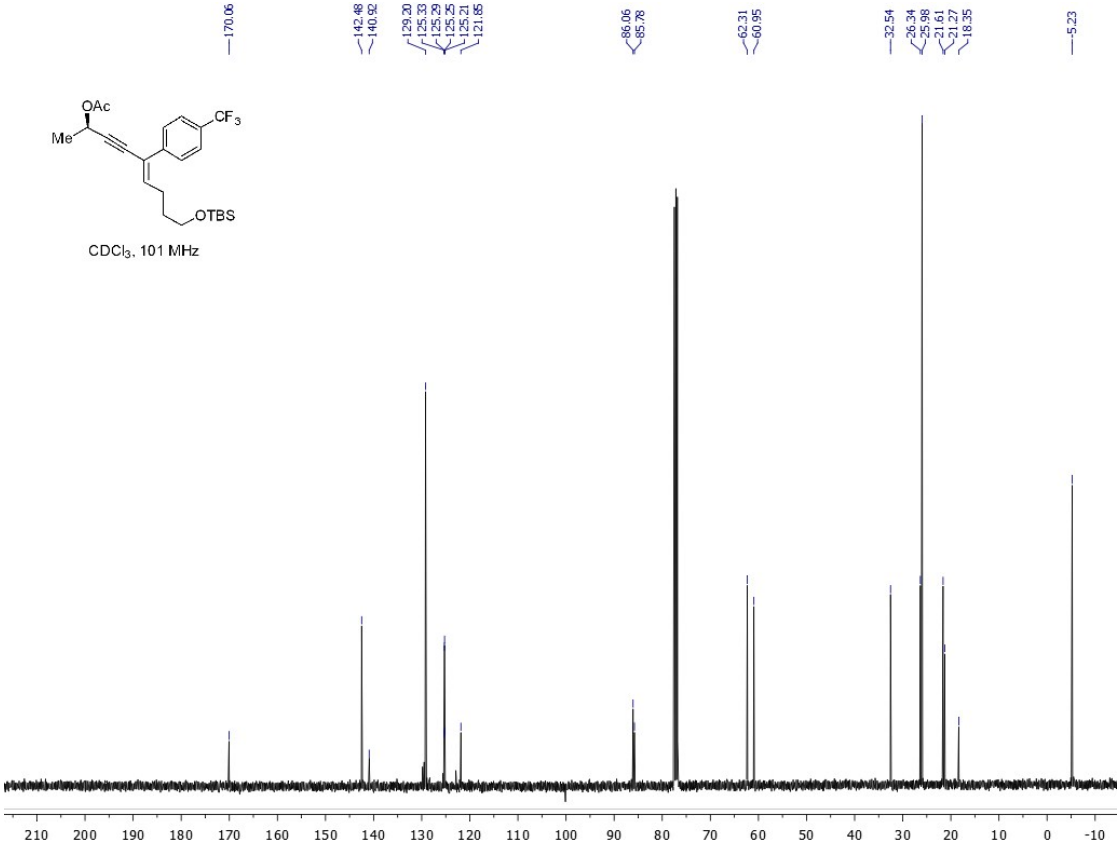

OAc
Me
OAc
OTBS
CDCl3, 400 MHz

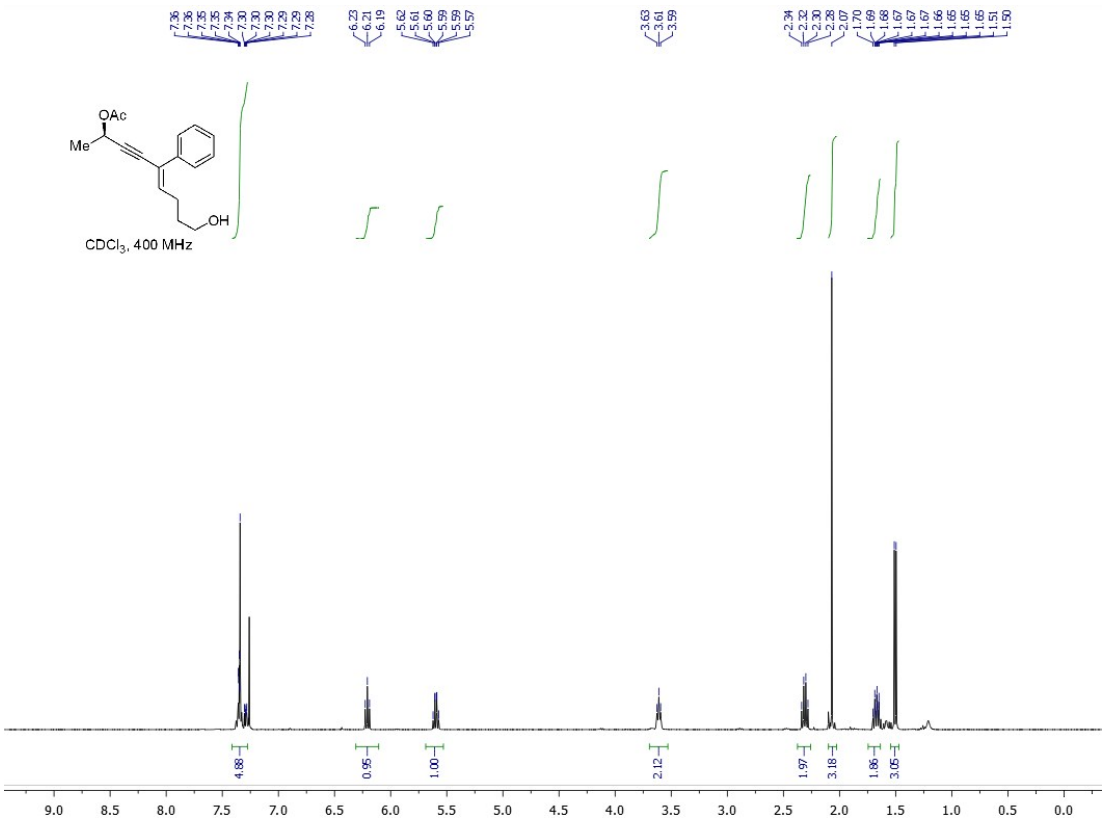

OAc
Me
OAc
OTBS
CDCl3, 101 MHz

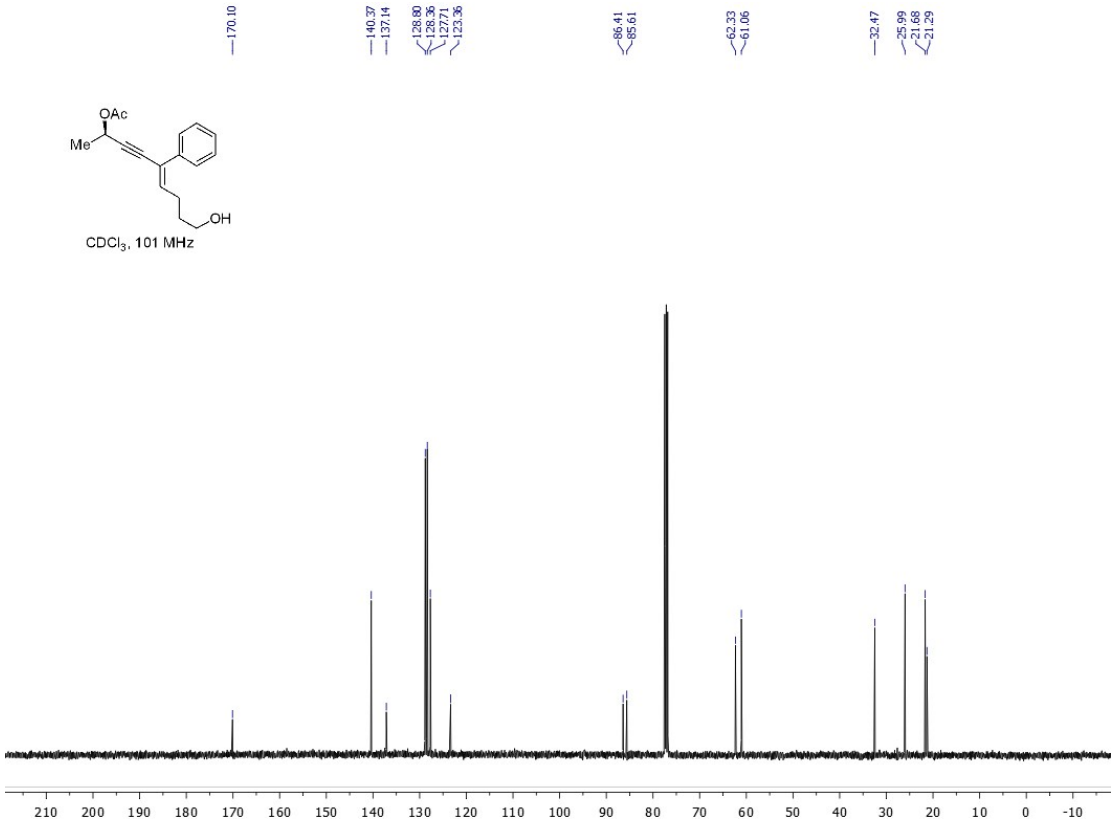

OAc
Me
Boc
N
Ac
OTBS
CDCl3, 400 MHz

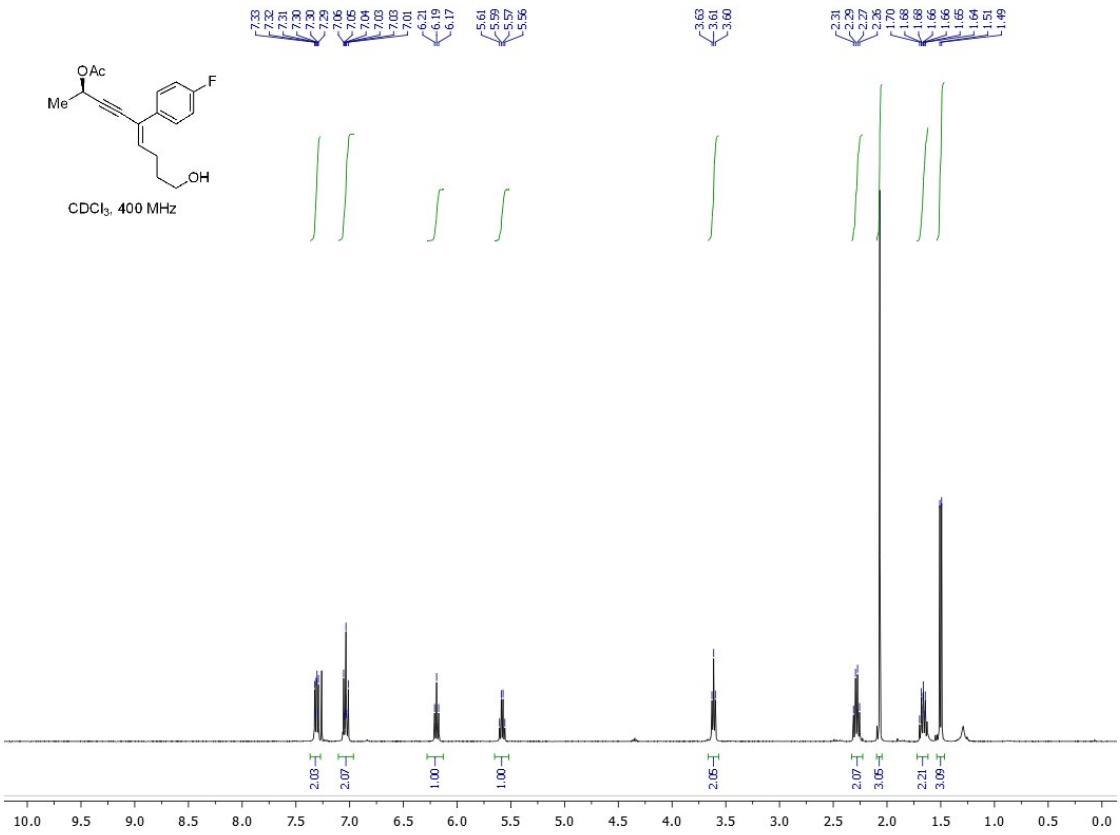

OAc
Me
Boc
N
Ac
OTBS
CDCl3, 101 MHz

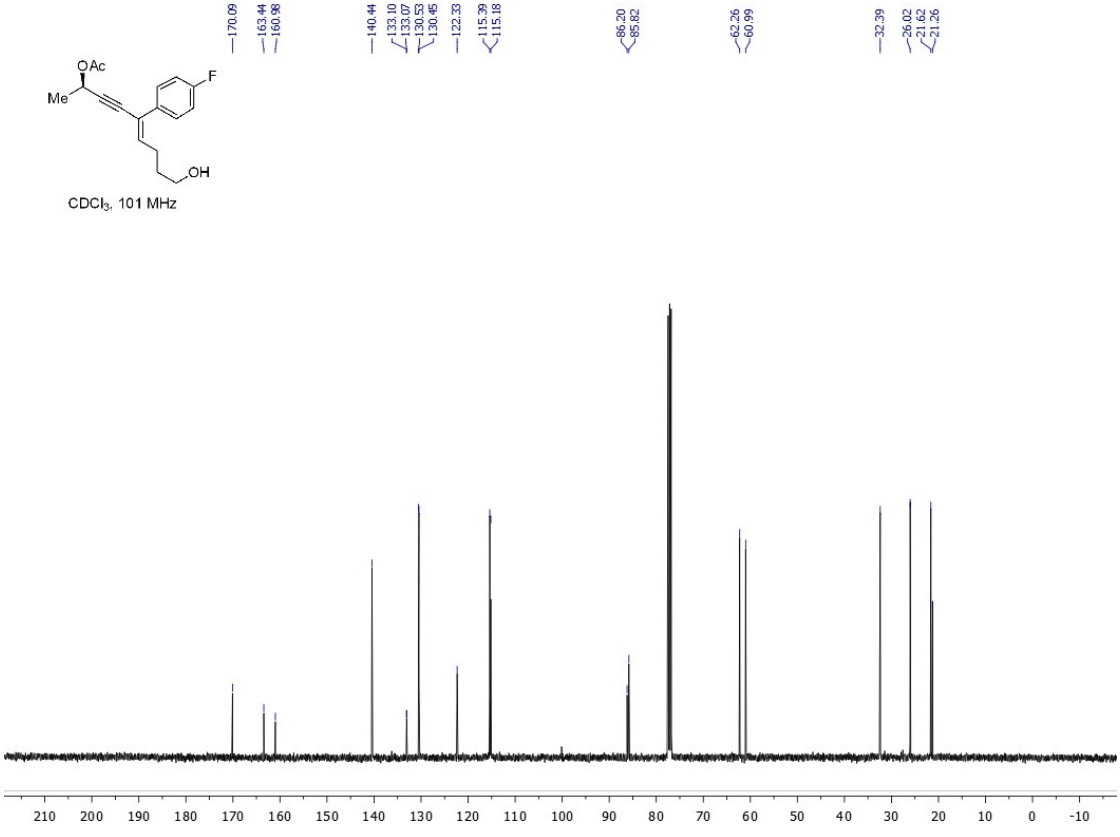

OAc
Me
CF3
OTBS
CDCl3, 400 MHz

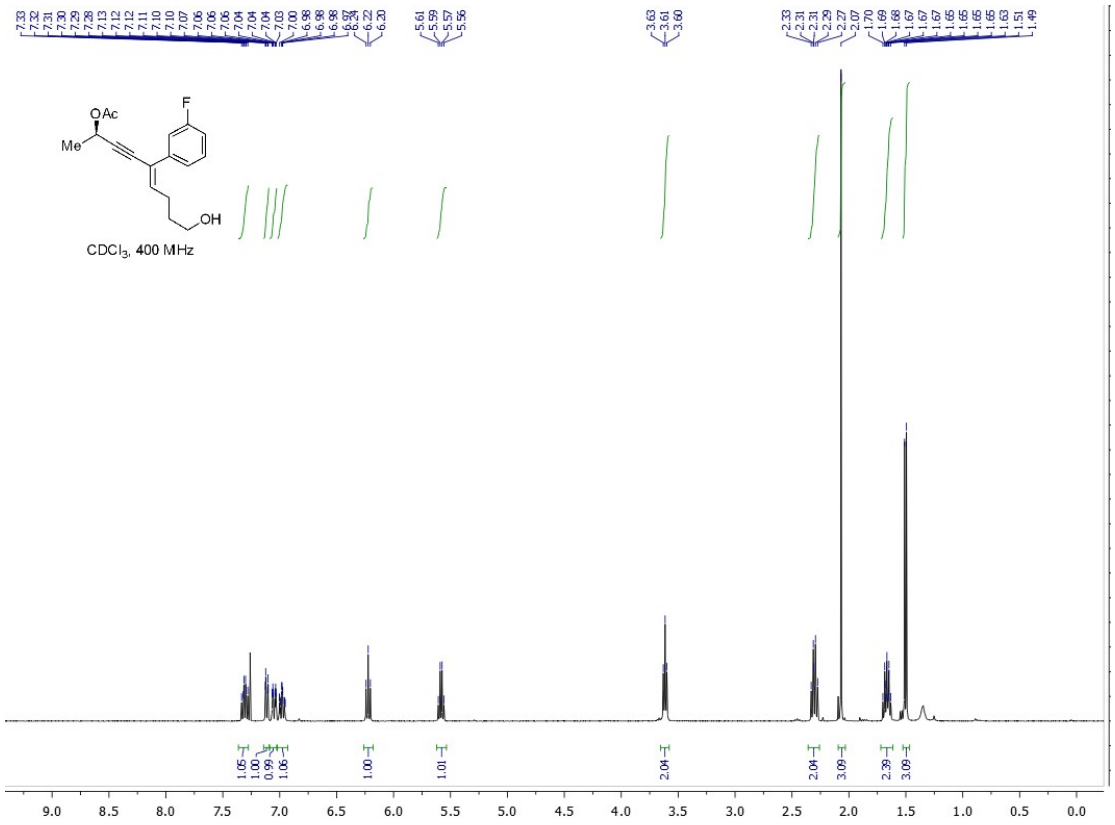

OAc
Me
CF3
OTBS
CDCl3, 101 MHz

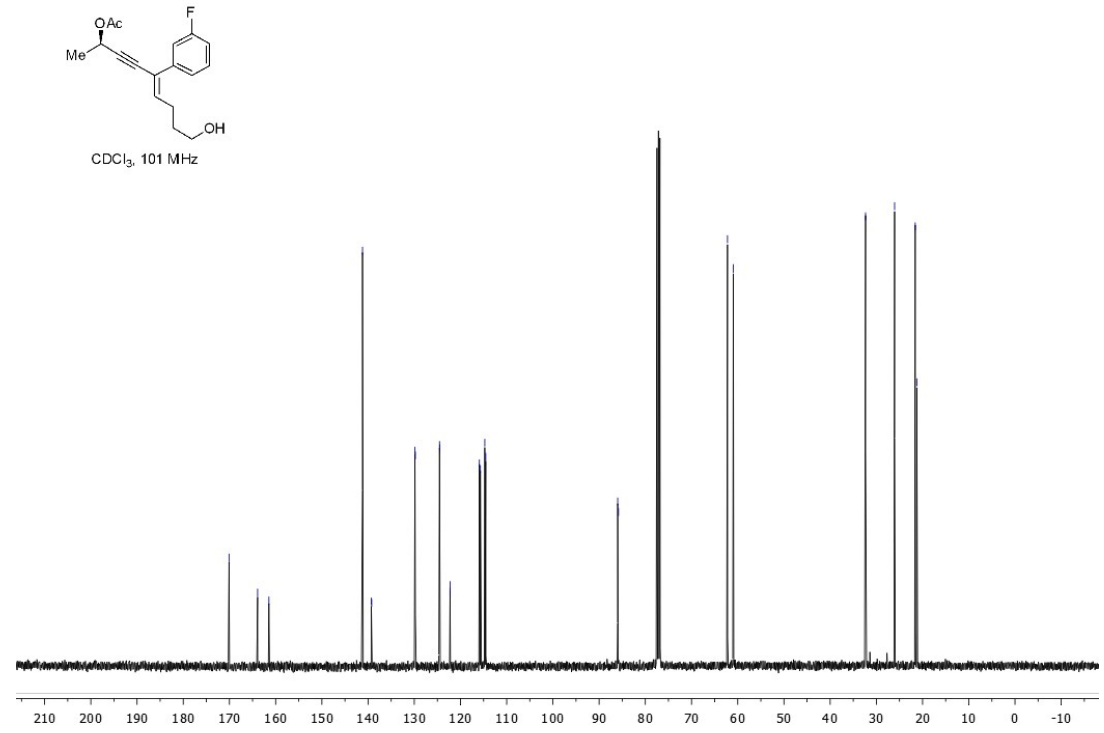

OAc
Me
OH
CDCl3, 400 MHz

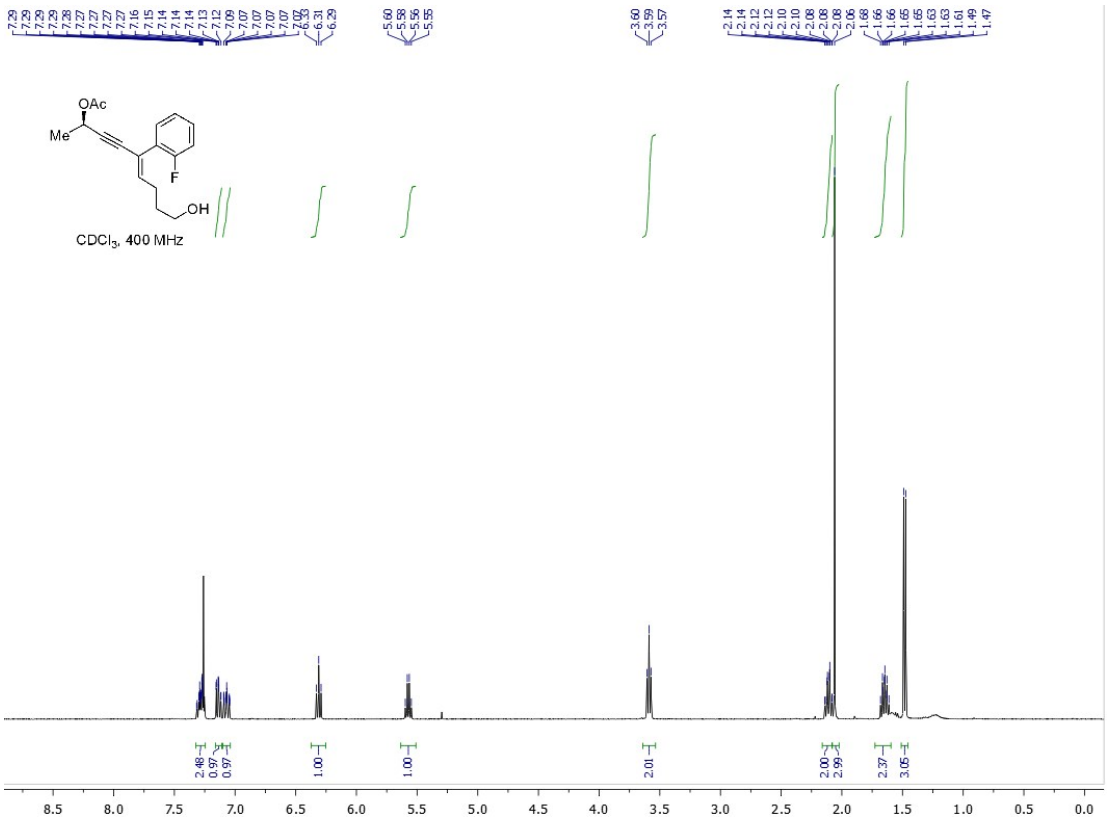

OAc
Me
OH
CDCl3, 101 MHz

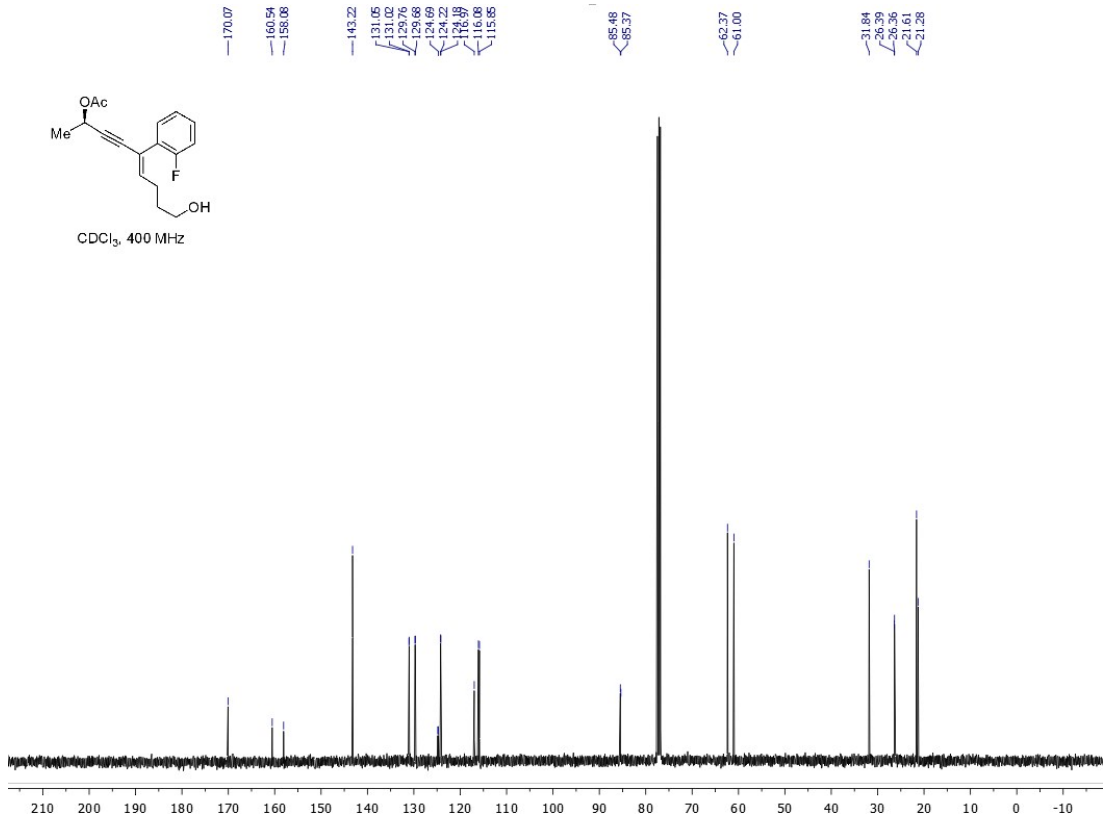

OAc
Me
F
OH
CDCl3, 400 MHz

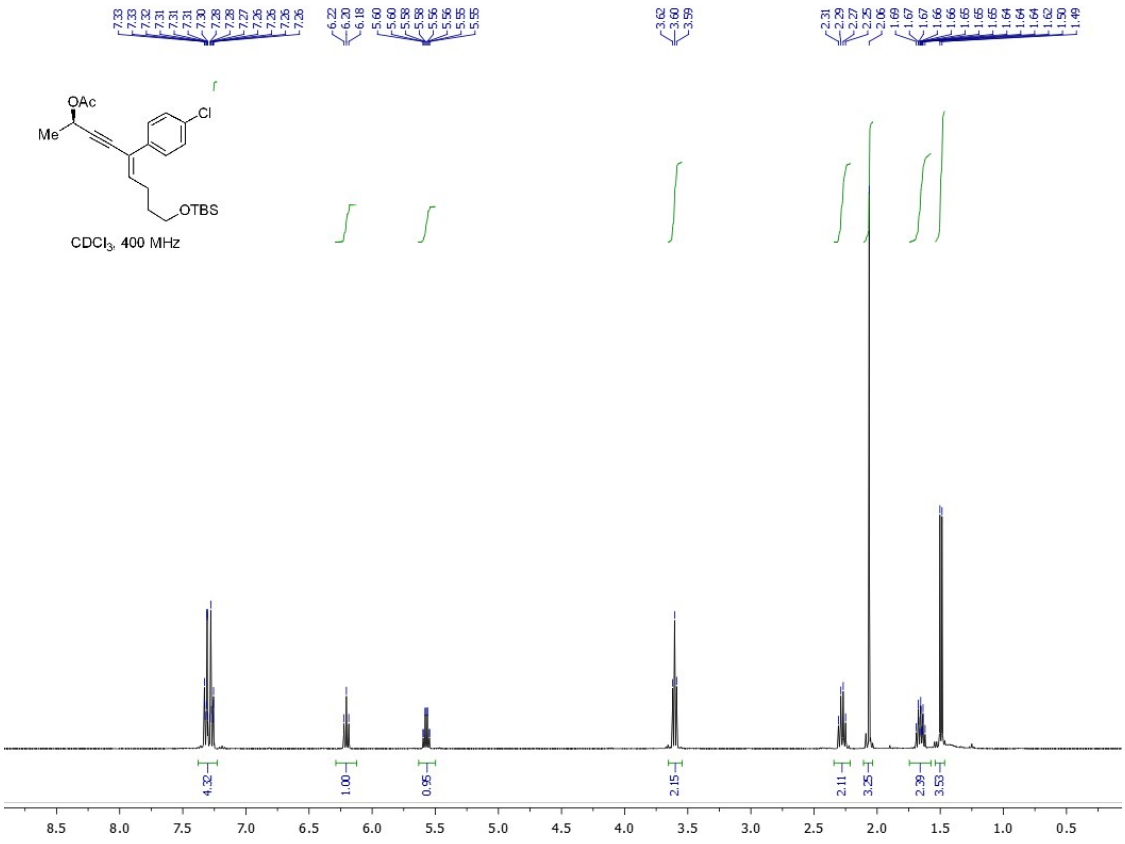

OAc
Me
F
OH
CDCl3, 101 MHz

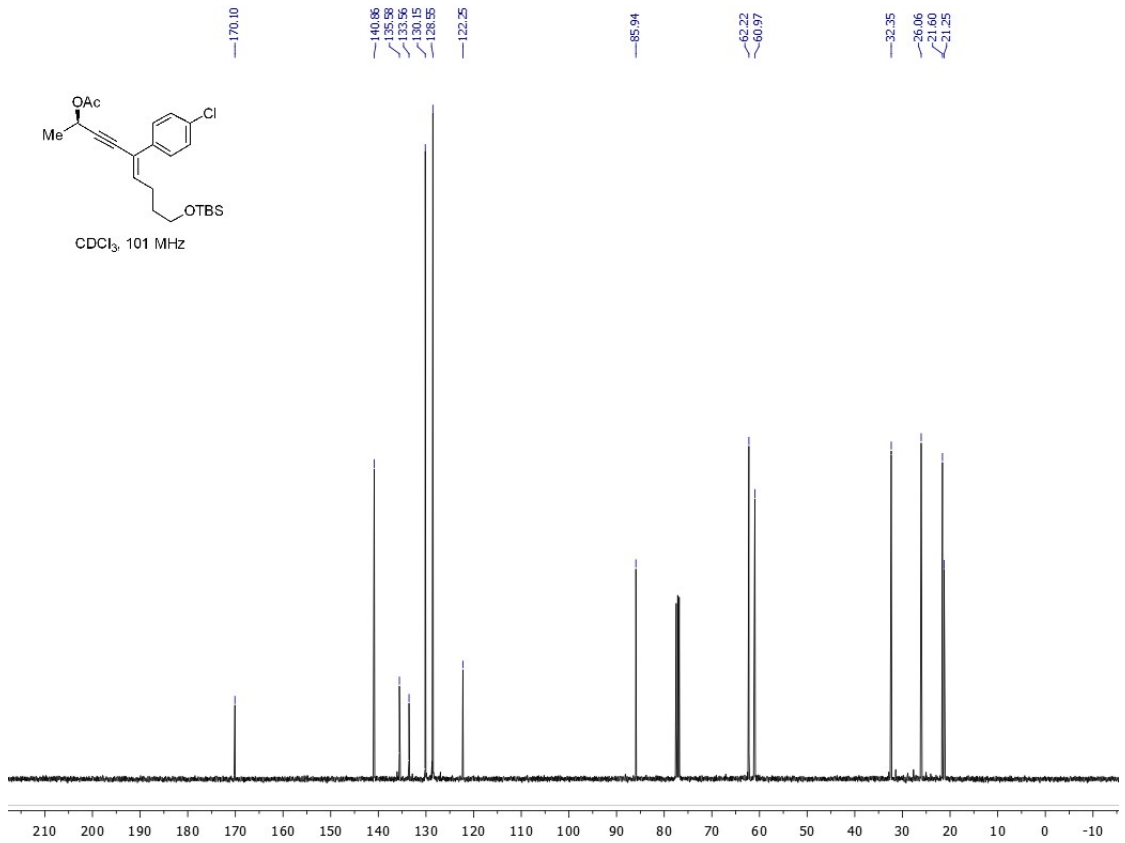

OAc
Me
F
OH
CDCl3, 400 MHz

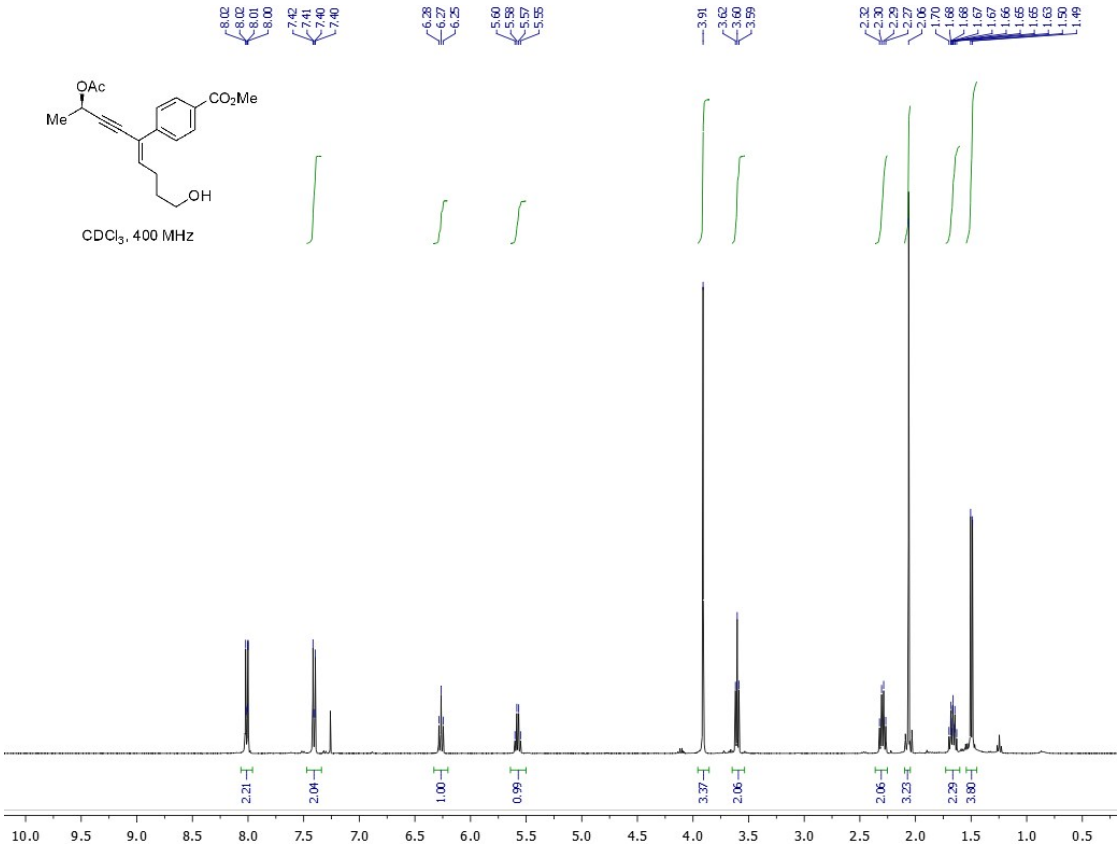

OAc
Me
F
OH
CDCl3, 101 MHz

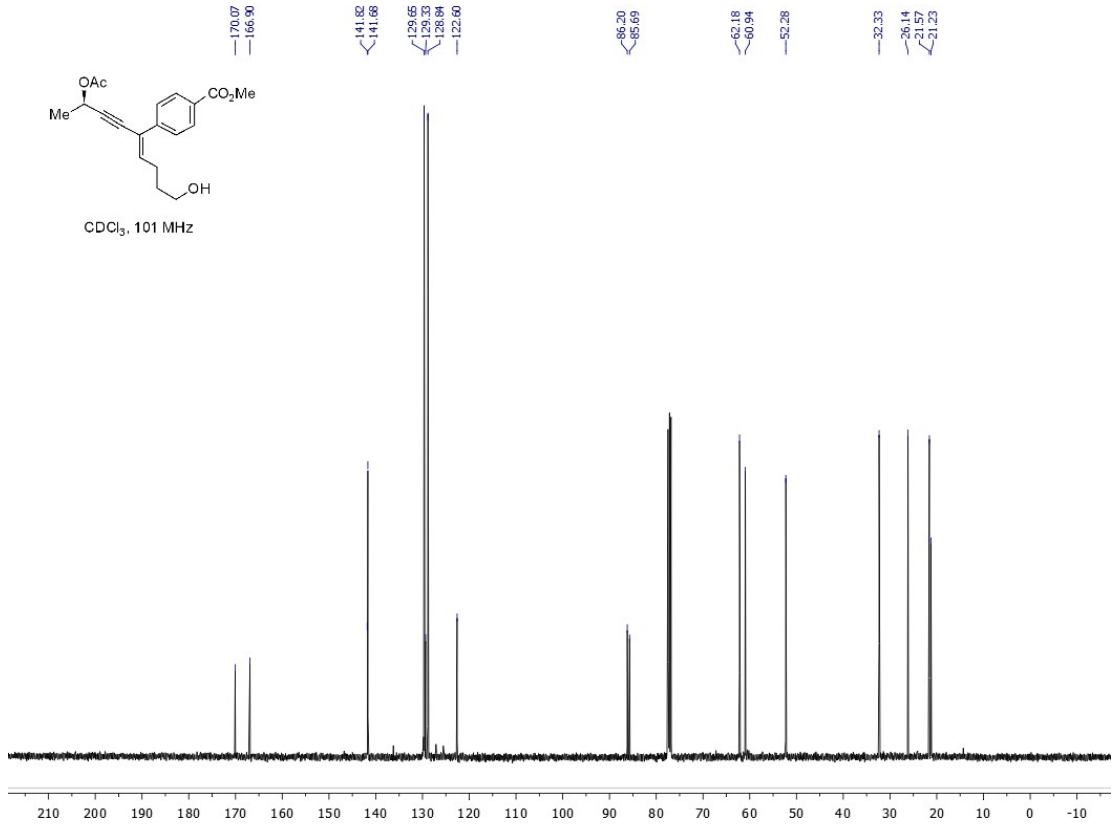

OAc
Me
F
OH
CDCl3, 400 MHz

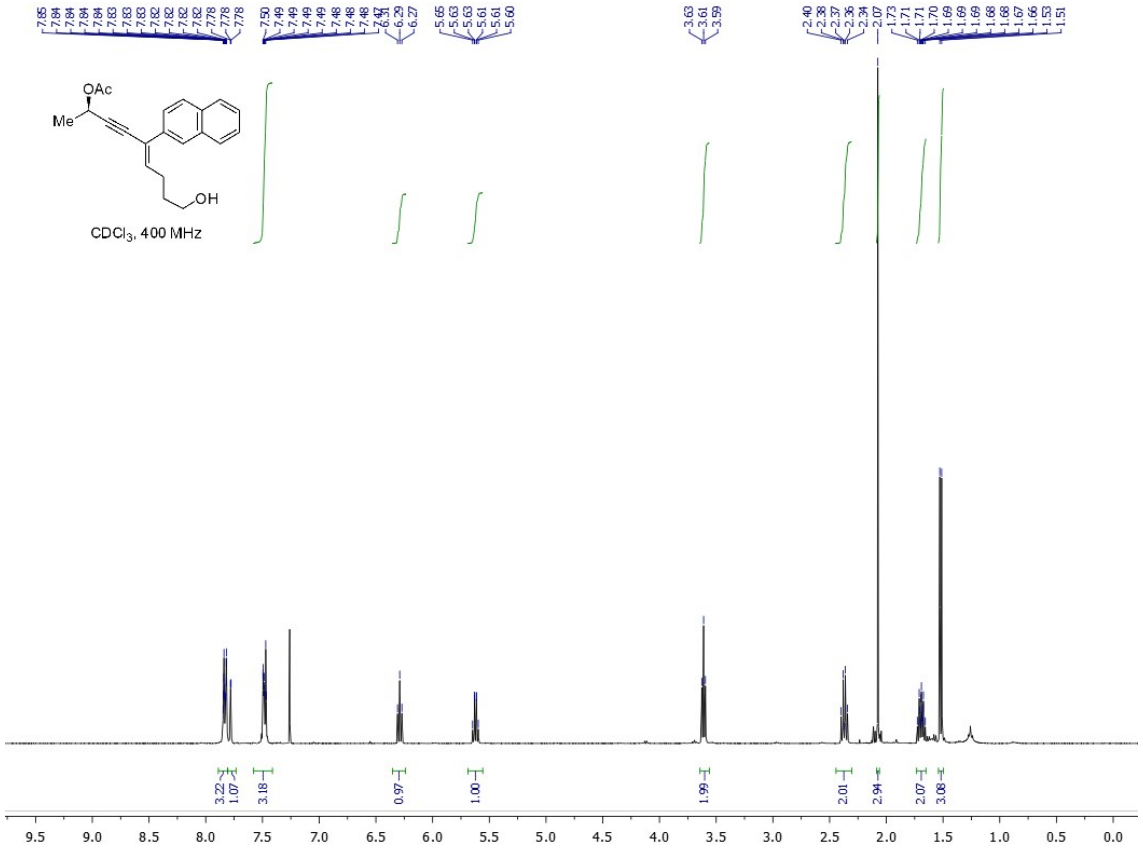

OAc
Me
F
OH
CDCl3, 400 MHz

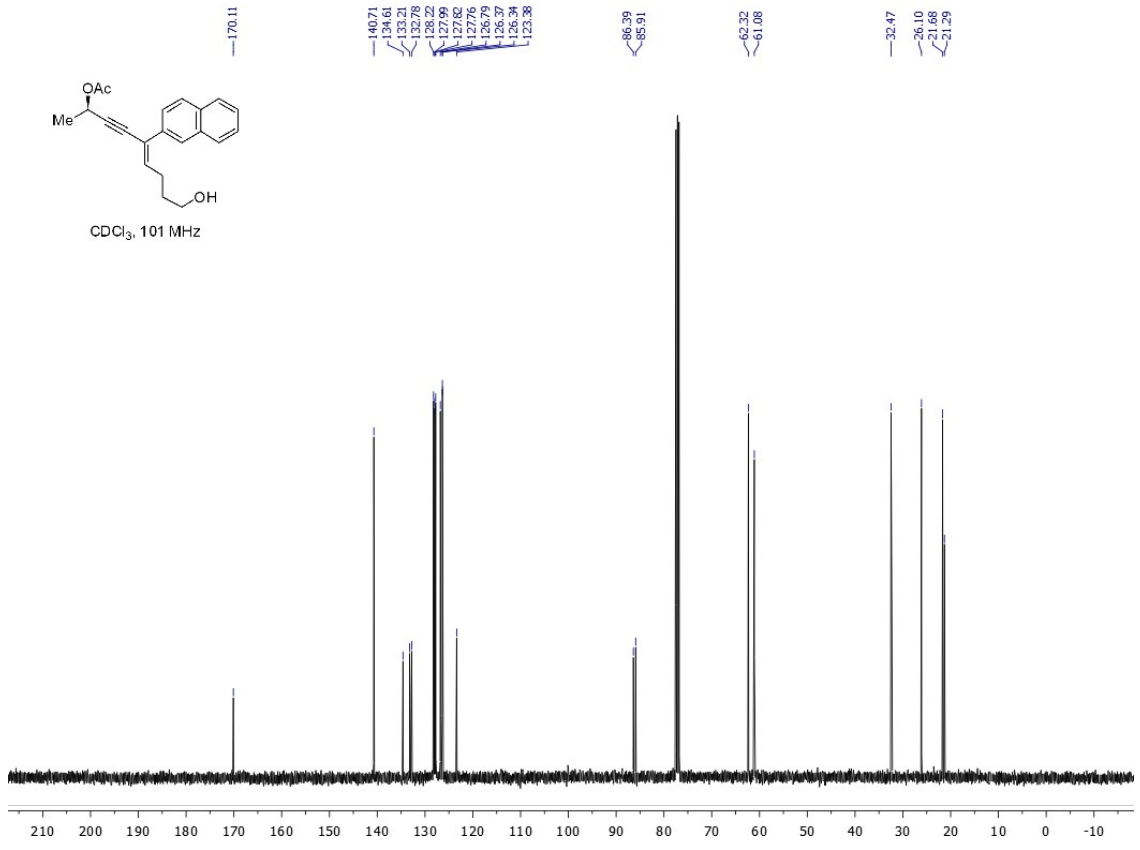

OAc
Me
Cl
OTBS
CDCl3, 400 MHz

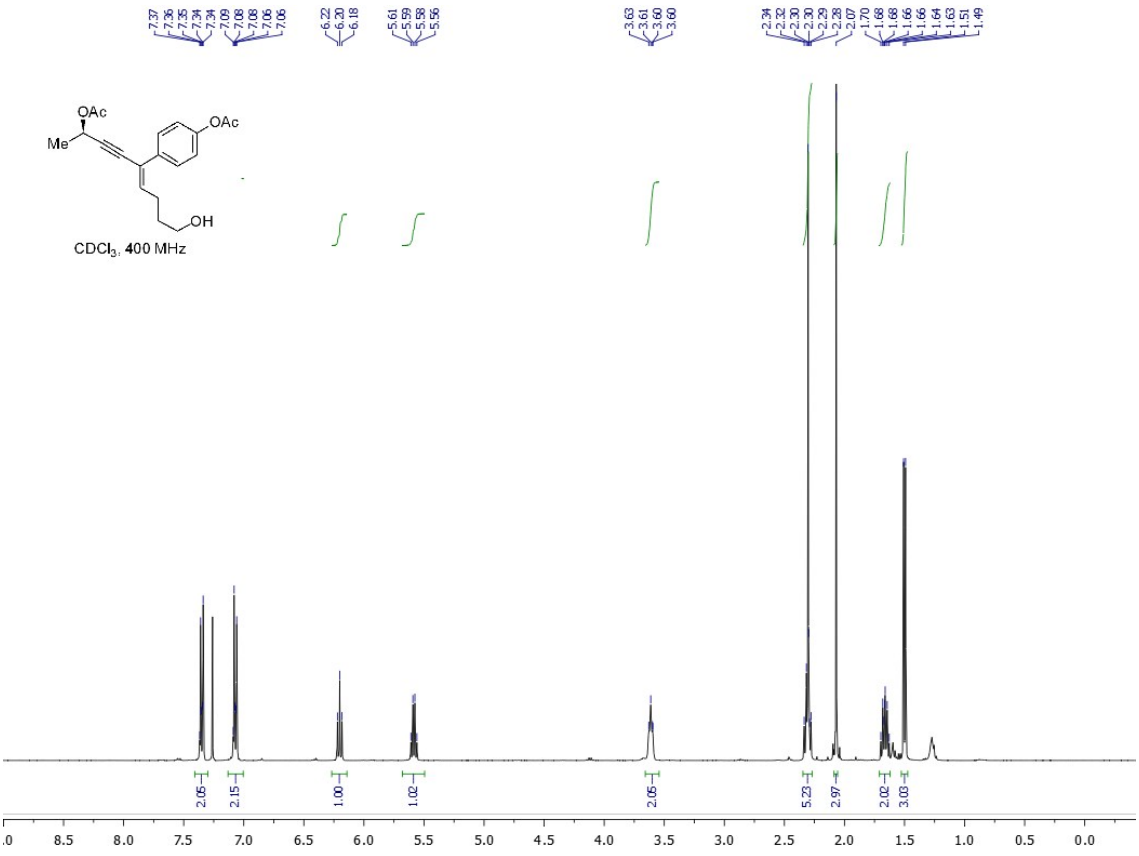

OAc
Me
Cl
OTBS
CDCl3, 101 MHz

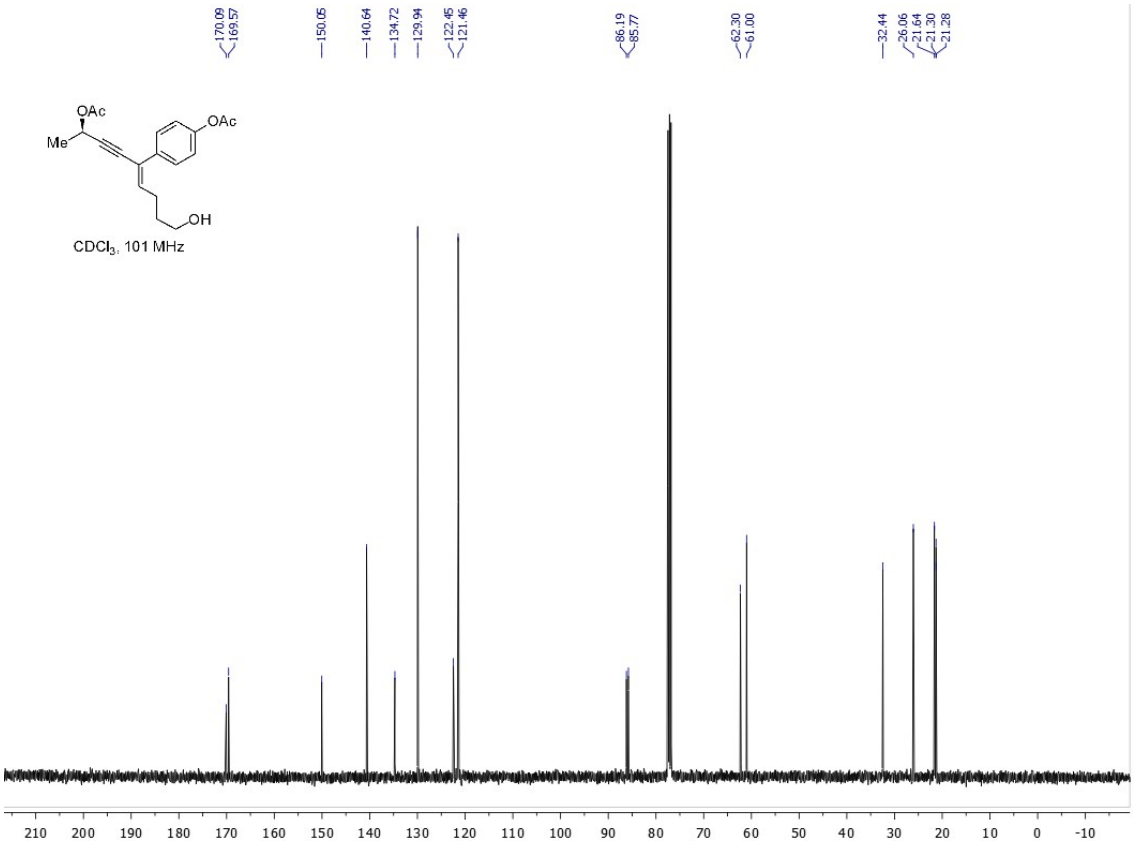

OAc
Me
CO2Me
OH
CDCl3, 400 MHz

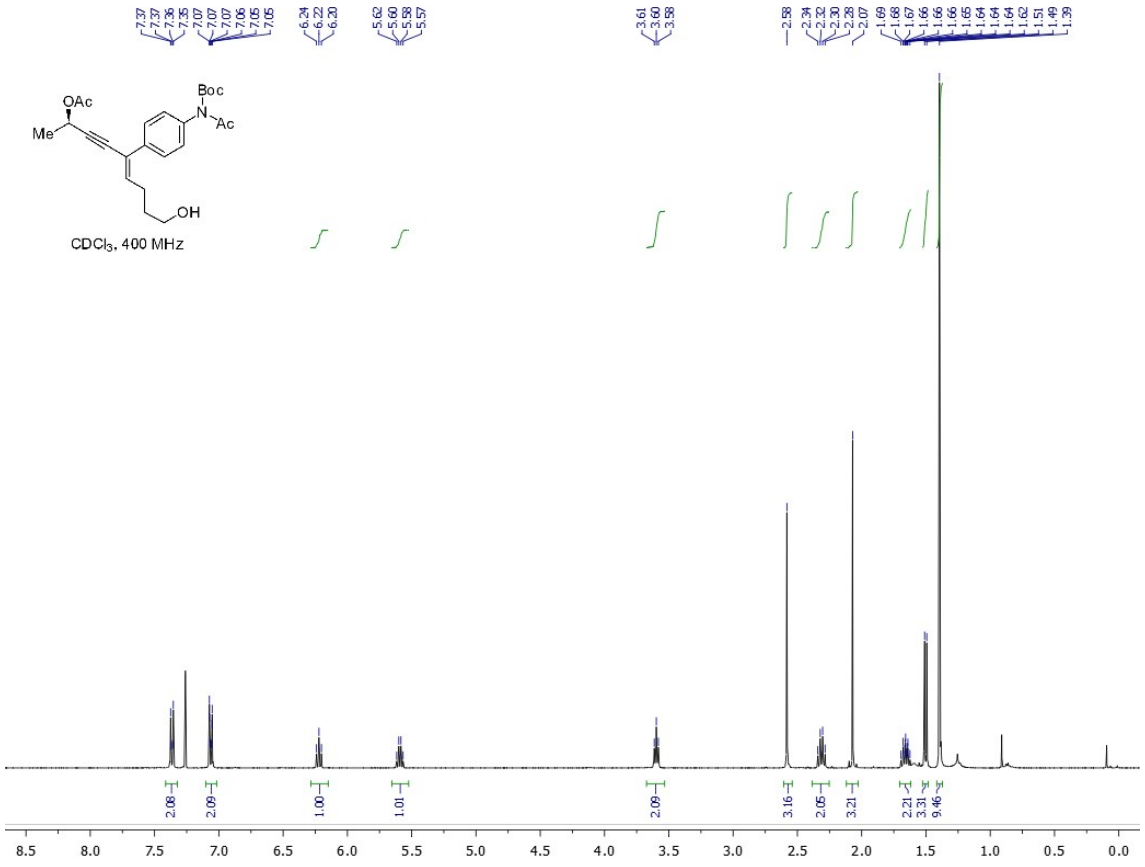

OAc
Me
CO2Me
OH
CDCl3, 101 MHz

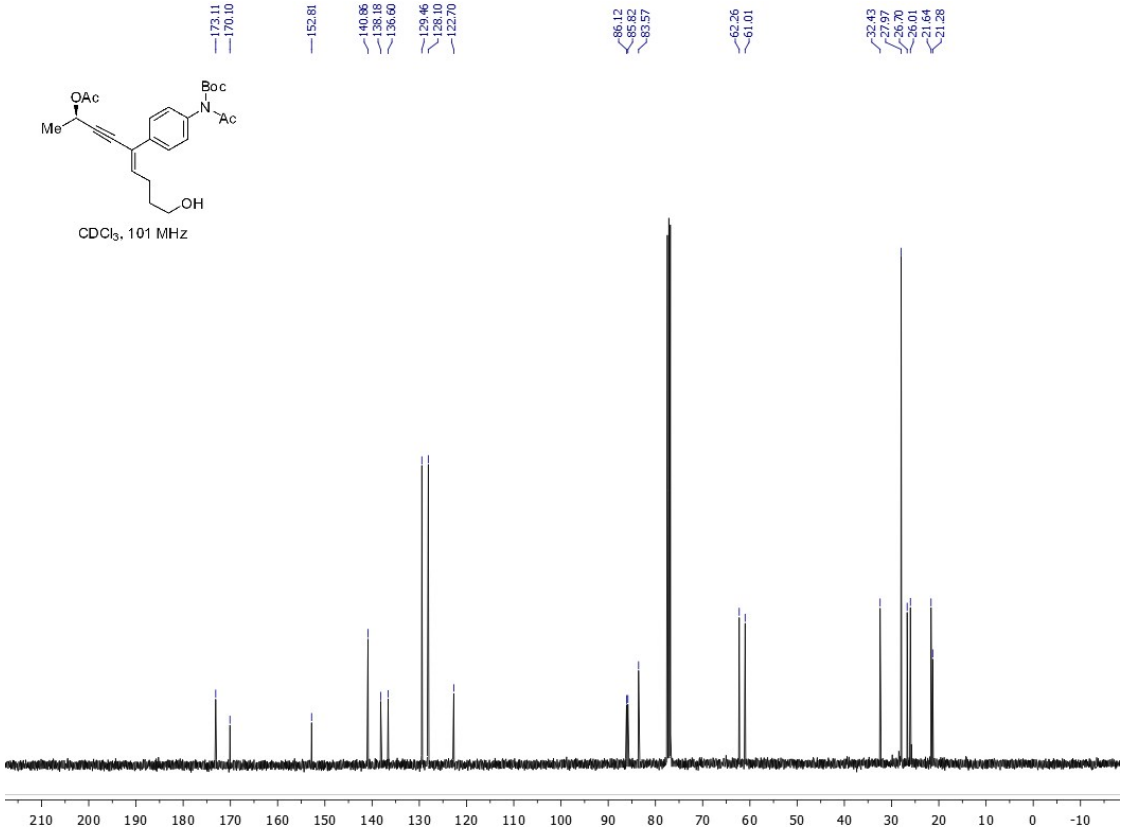

OAc
Me
OH
CDCl3, 400 MHz

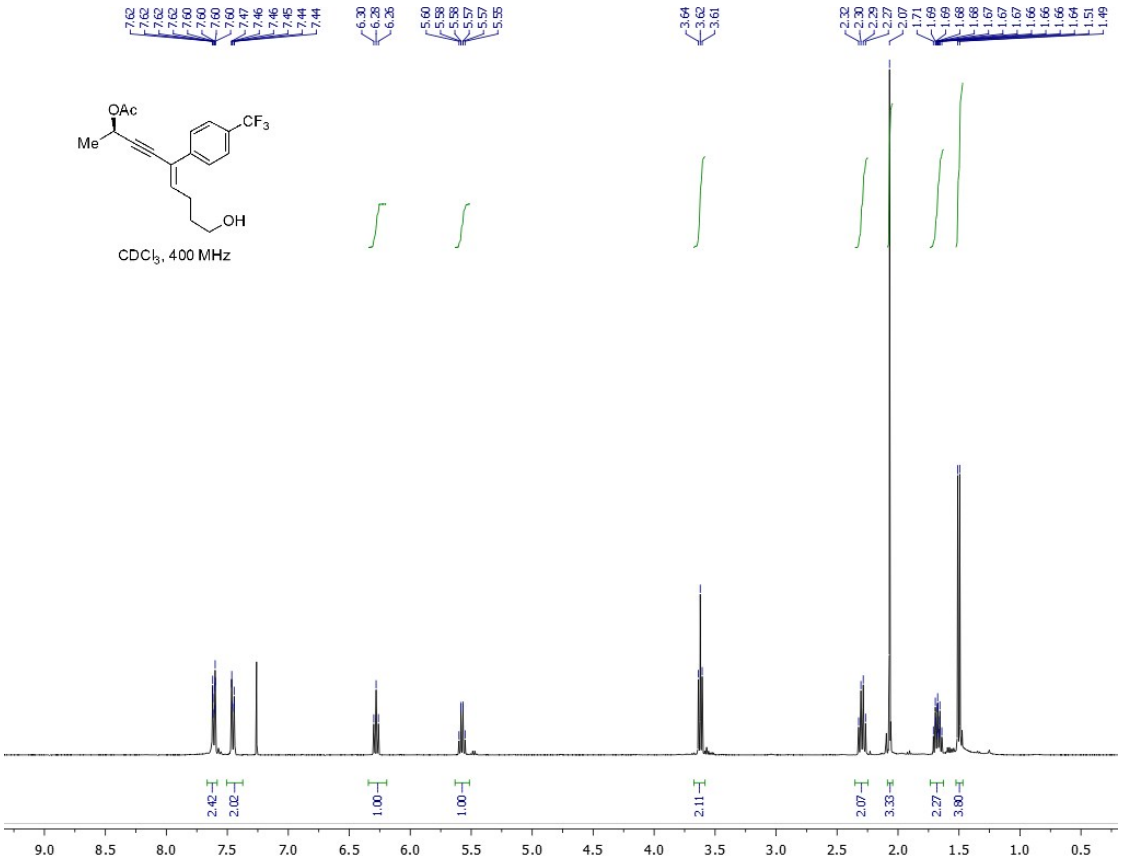

OAc
Me
OH
CDCl3, 101 MHz

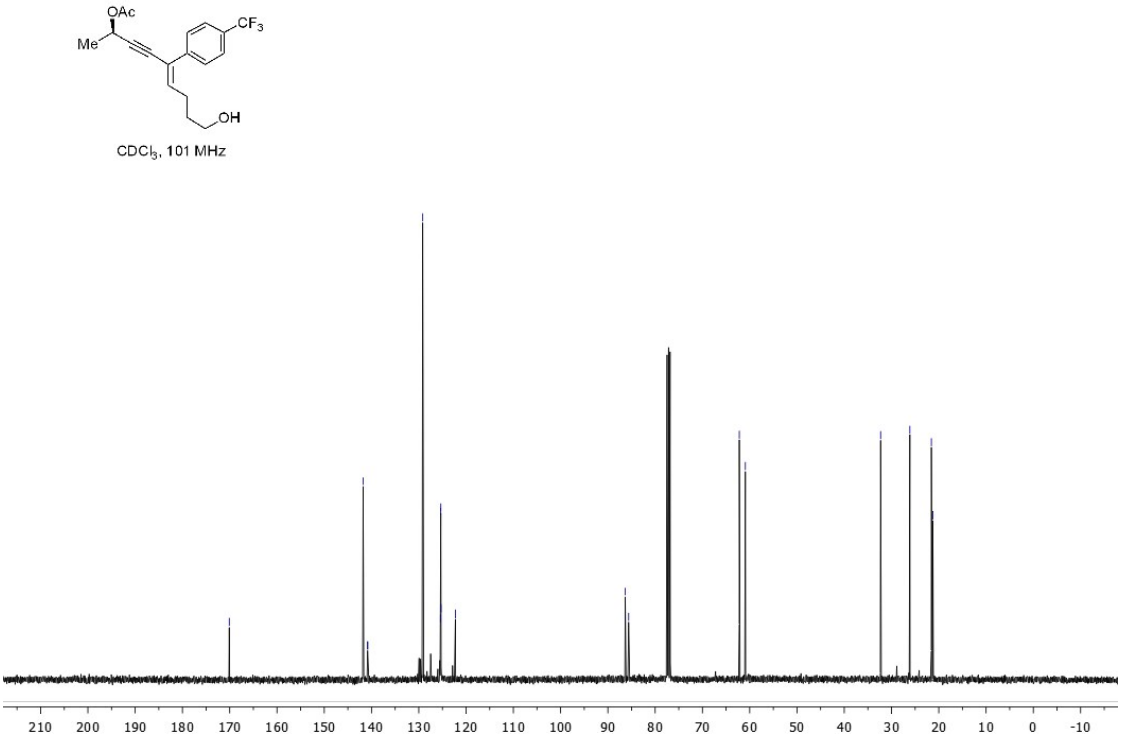

OAc
Me
OAc
OH
CDCl3, 400 MHz

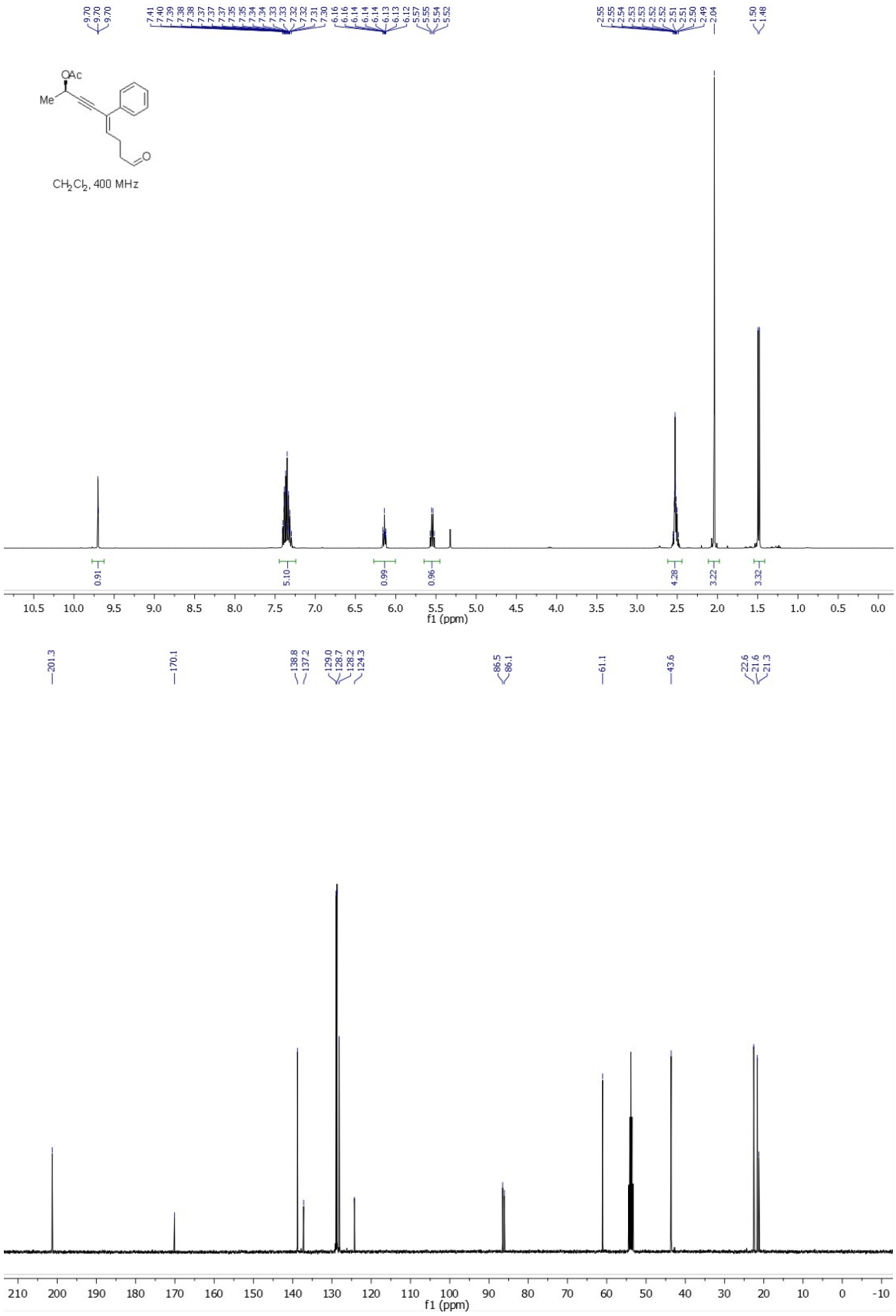

OAc
Me
OAc
OH
CDCl3, 101 MHz

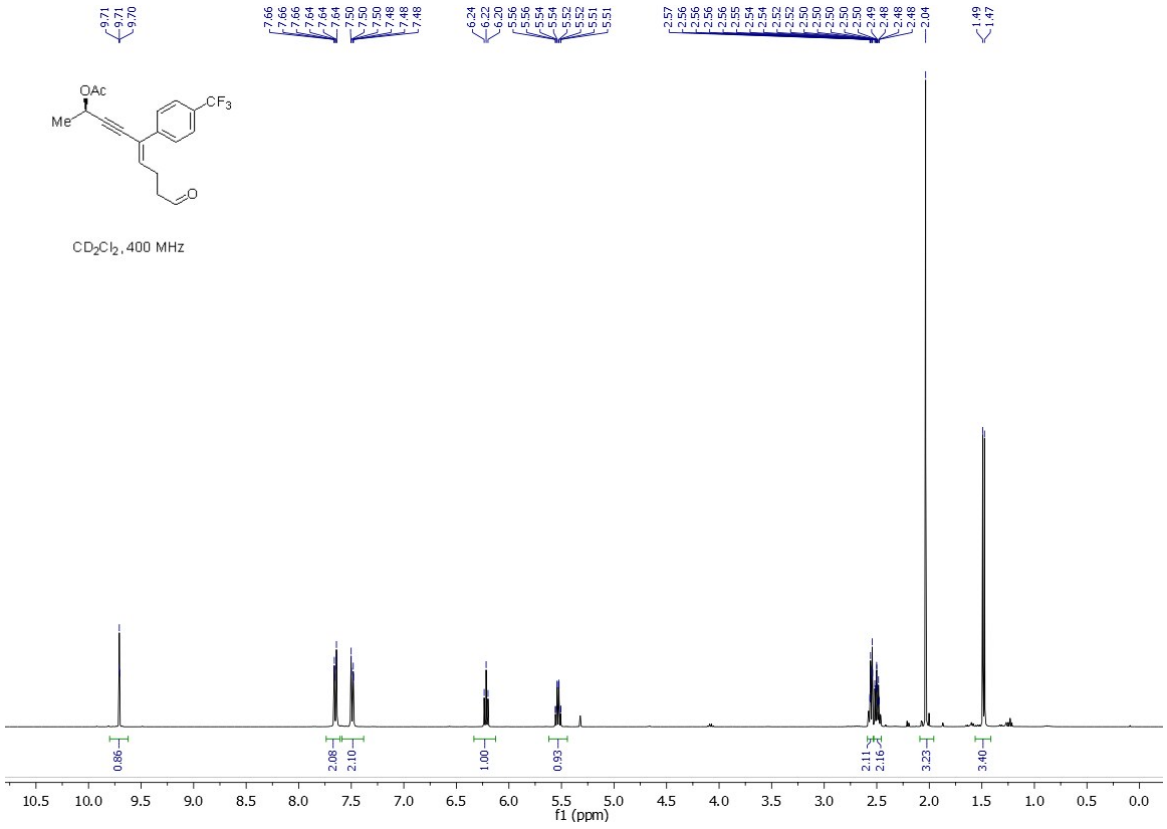

OAc
Me
Boc
N
Ac
OH
CDCl3, 400 MHz

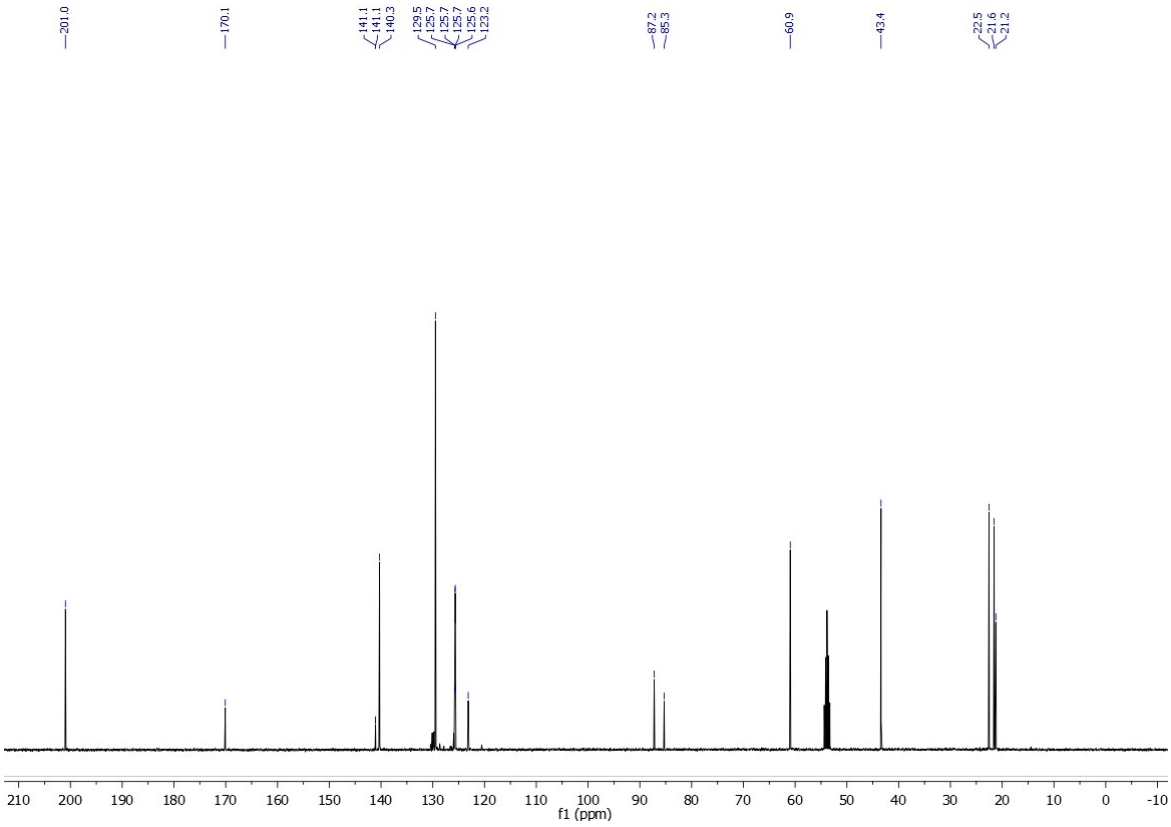

OAc
Me
Boc
N
Ac
OH
CDCl3, 101 MHz

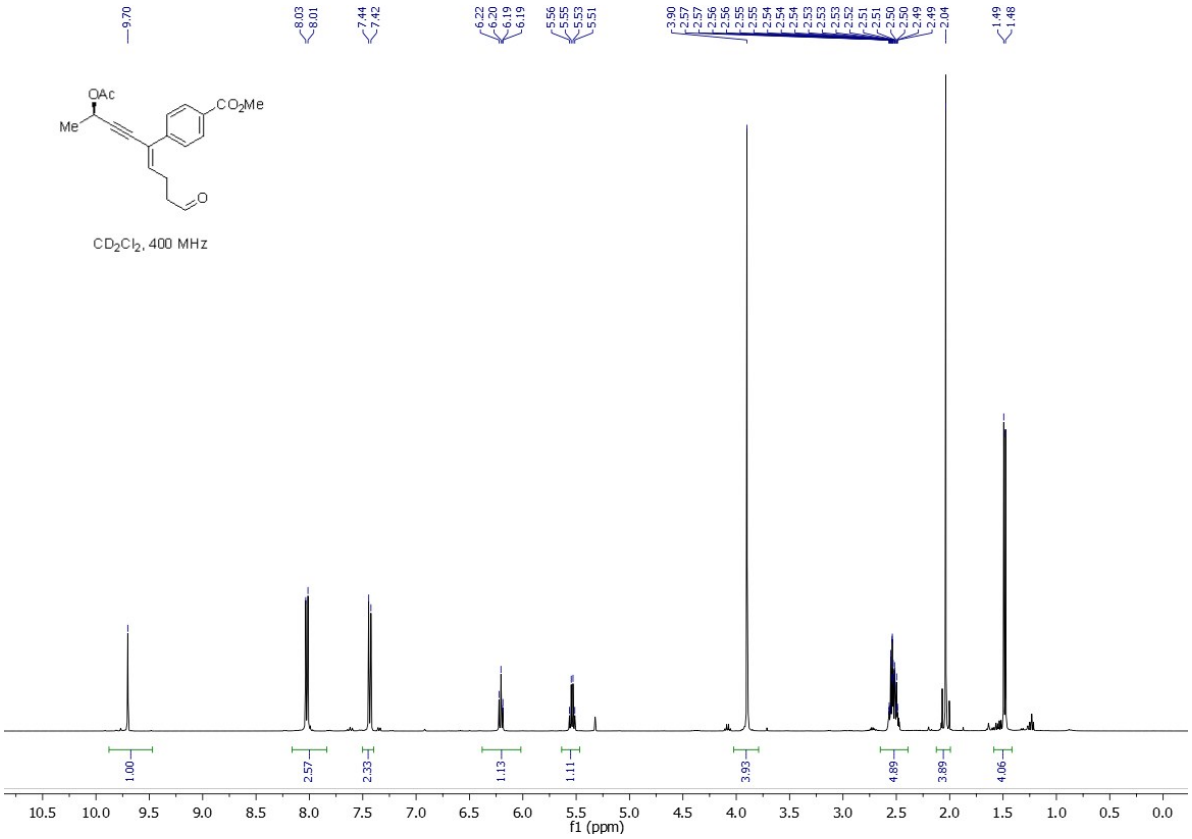

OAc
Me
CF3
OH
CDCl3, 400 MHz

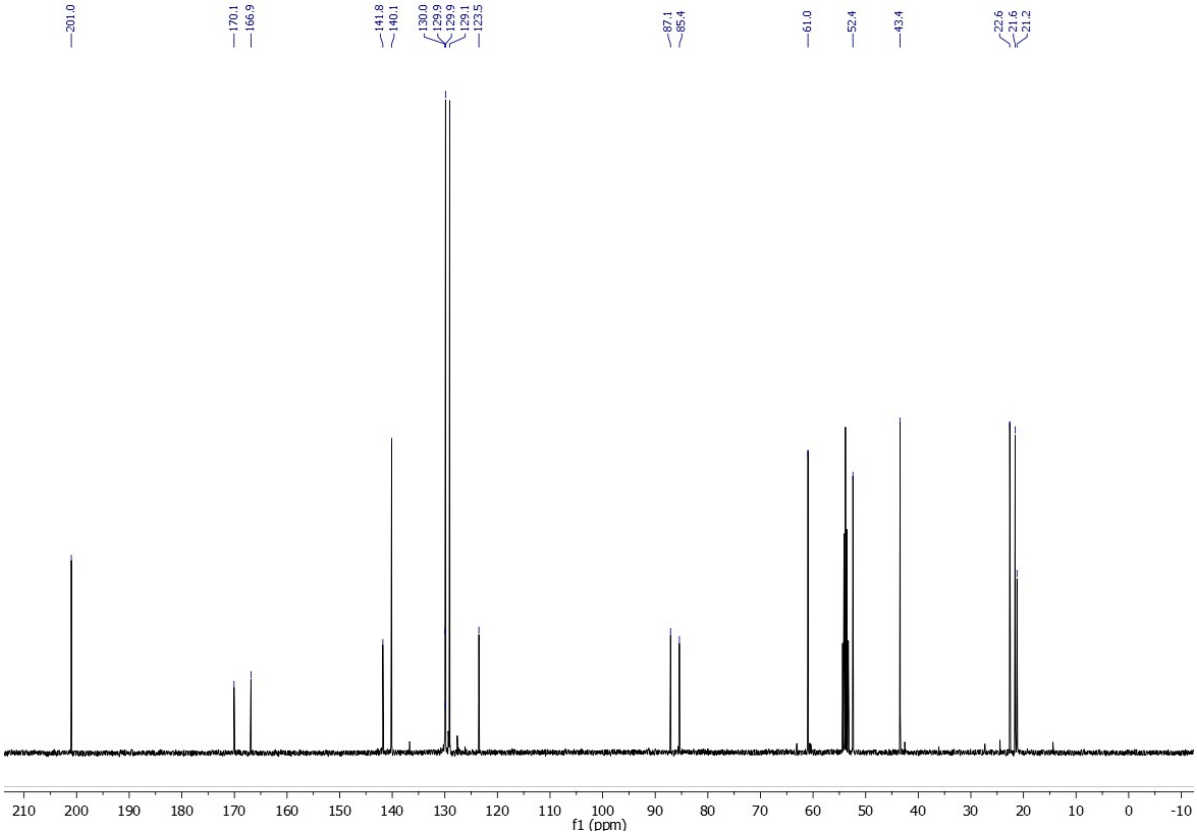

OAc
Me
CF3
OH
CDCl3, 101 MHz

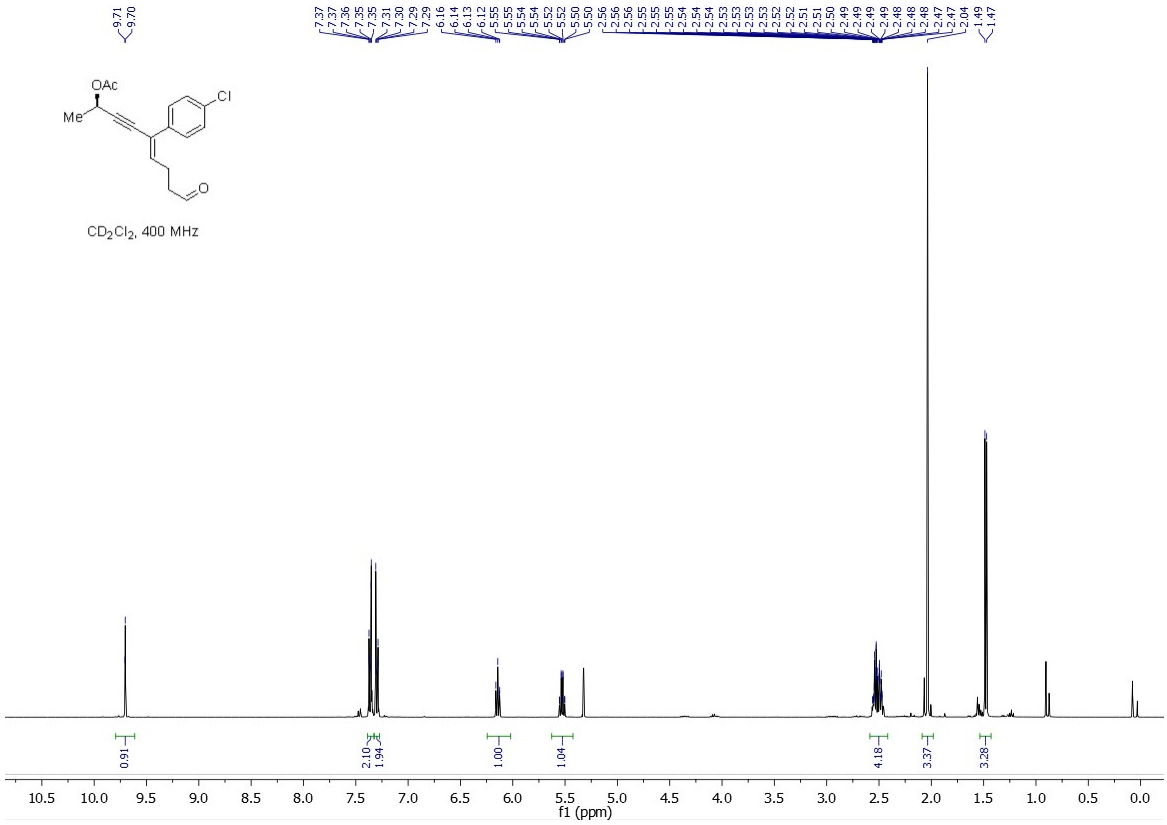

OAc
Me
O
CH2Cl2, 400 MHz
f1 (ppm)
f1 (ppm)

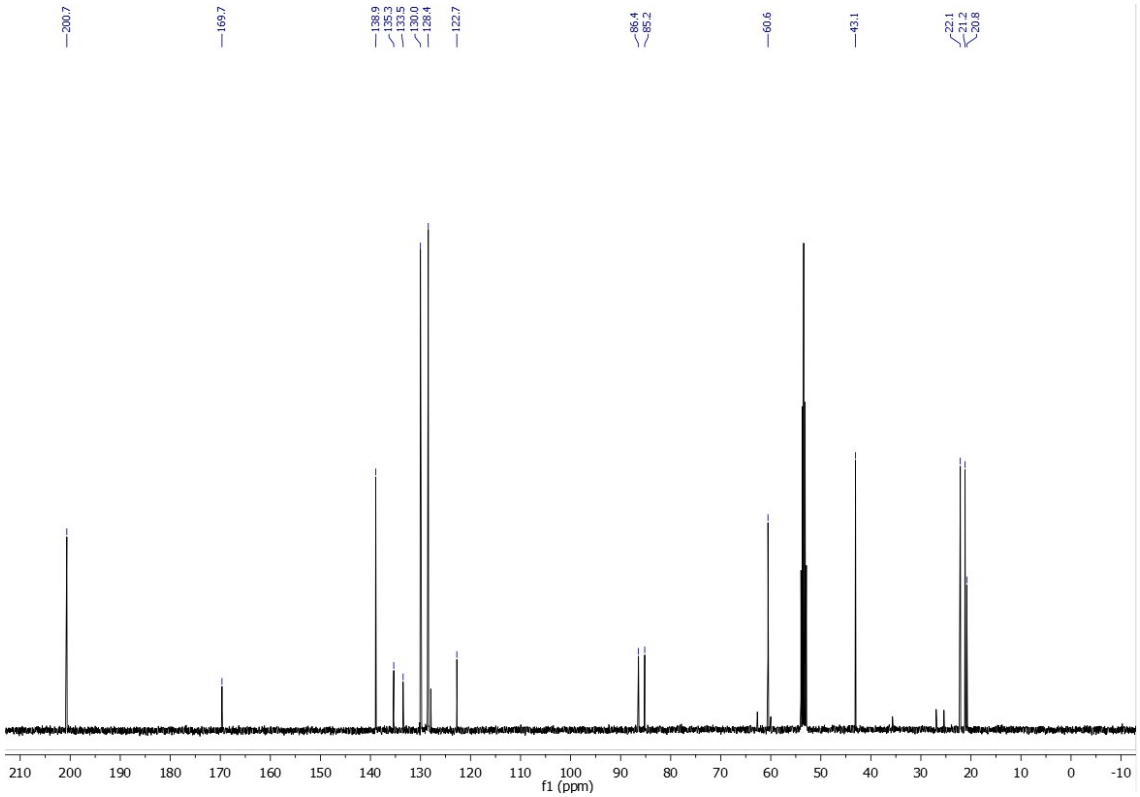

9.71
9.71
9.70
7.66
7.66
7.66
7.64
7.64
7.64
7.50
7.50
7.50
7.48
7.48
7.48
6.24
6.22
6.20
5.56
5.56
5.54
5.54
5.52
5.52
5.51
5.51
2.57
2.56
2.56
2.56
2.56
2.55
2.54
2.54
2.52
2.52
2.50
2.50
2.50
2.50
2.50
2.49
2.48
2.48
2.48
2.04
1.49
1.47
OAc
Me
CF3
O
CD2Cl2, 400 MHz
0.86
2.08
2.10
1.00
0.93
2.11
2.16
3.23
3.40
f1 (ppm)

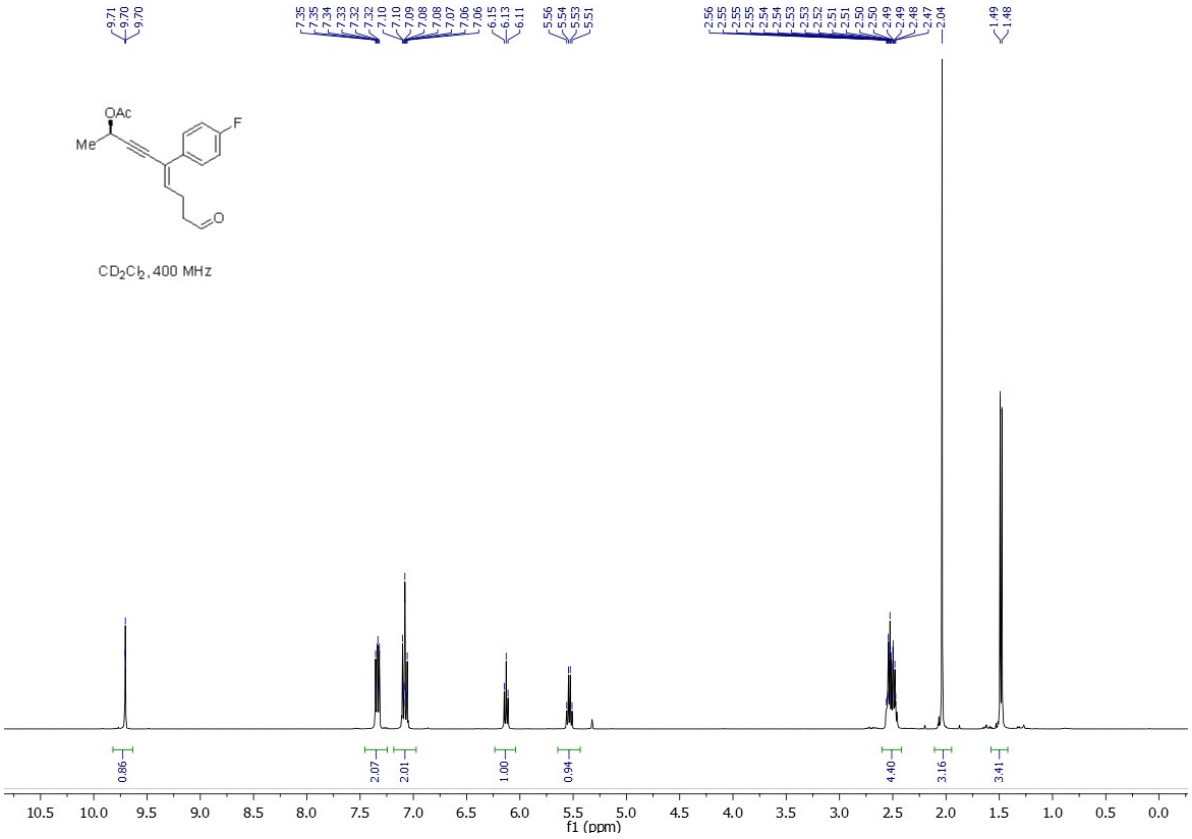

201.0
170.1
141.1
141.1
140.3
129.5
125.7
125.7
125.7
125.6
123.2
87.2
85.3
60.9
43.4
22.5
21.6
21.2
f1 (ppm)

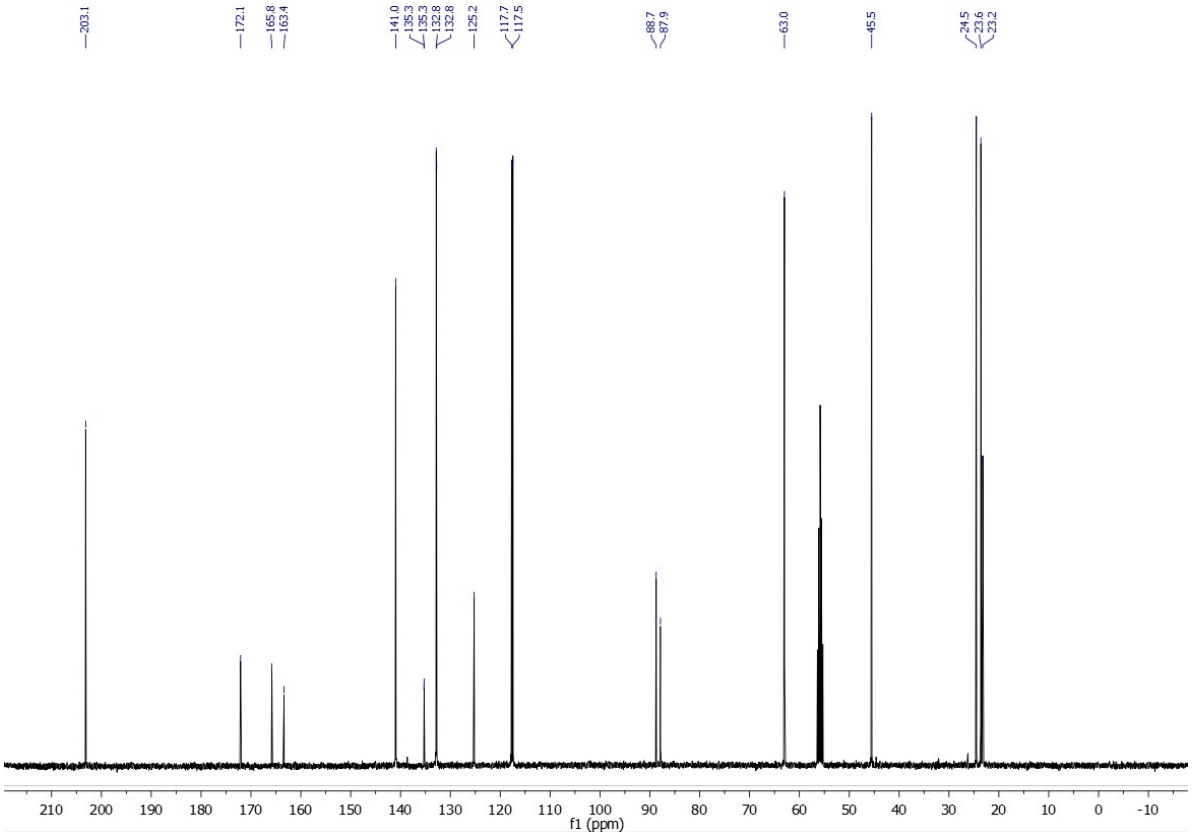

9.70
8.03
8.01
7.44
7.42
6.22
6.20
6.19
6.19
5.56
5.55
5.53
5.51
3.90
2.57
2.57
2.56
2.56
2.55
2.55
2.54
2.54
2.54
2.53
2.53
2.53
2.52
2.52
2.51
2.51
2.50
2.50
2.49
2.49
2.04
1.49
1.48
OAc
Me
CO2Me
O
CD2Cl2, 400 MHz
1.00
2.57
2.33
1.13
1.11
3.93
4.89
3.89
4.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

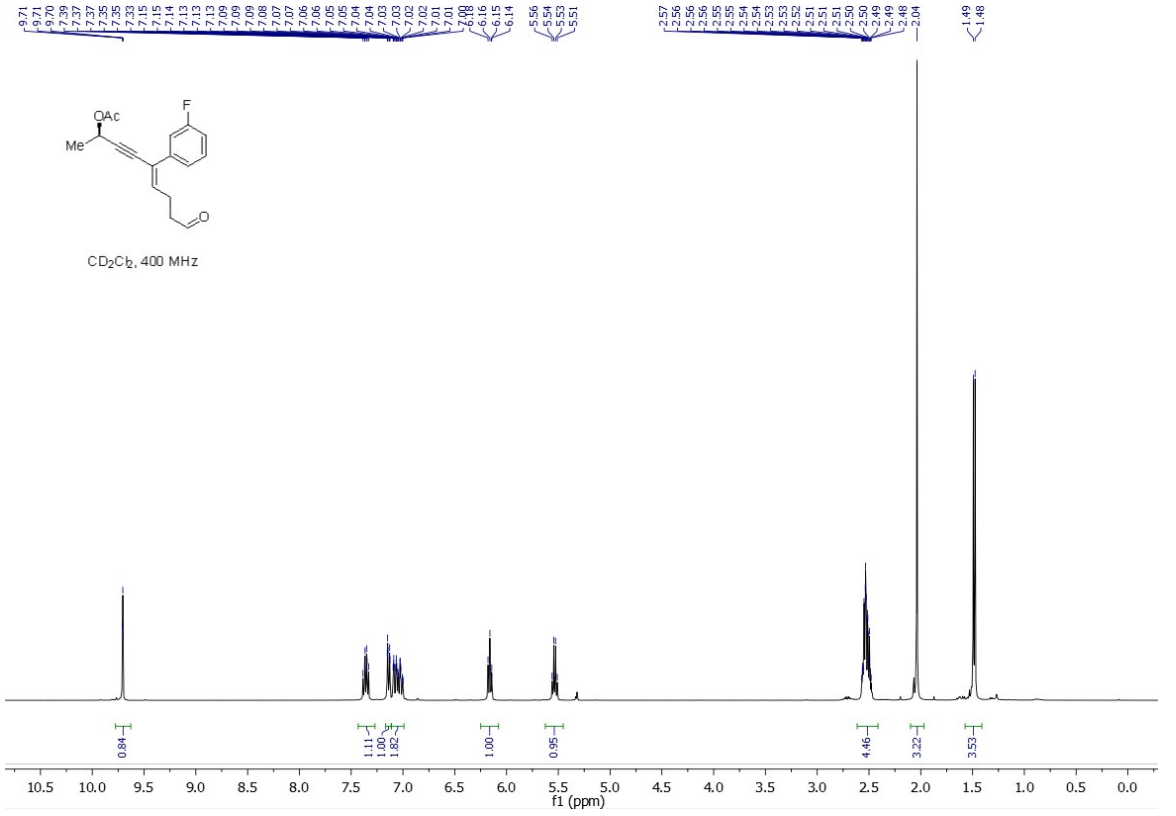

201.0
170.1
166.9
141.8
140.1
130.0
129.9
129.9
129.1
123.5
87.1
85.4
61.0
52.4
43.4
22.6
21.6
21.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

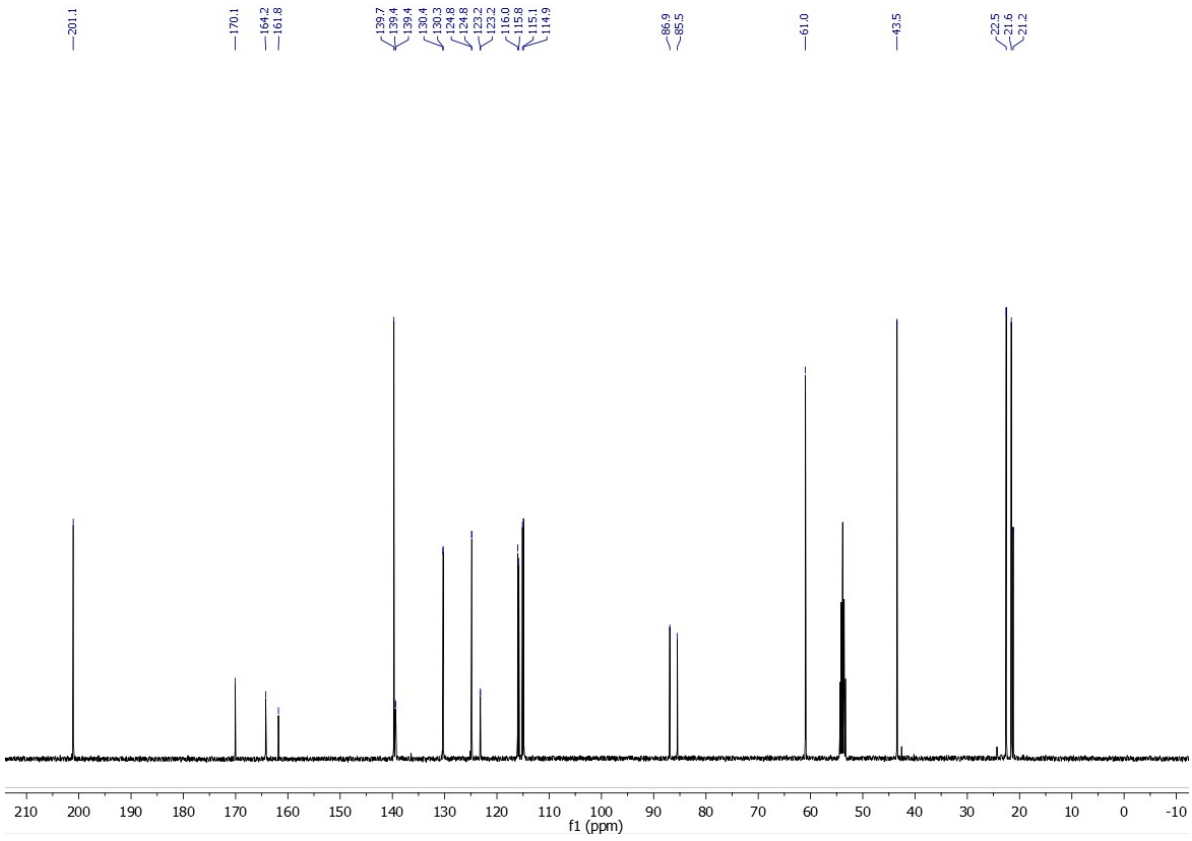

OAc
Me
Cl
O
CD2Cl2, 400 MHz
f1 (ppm)

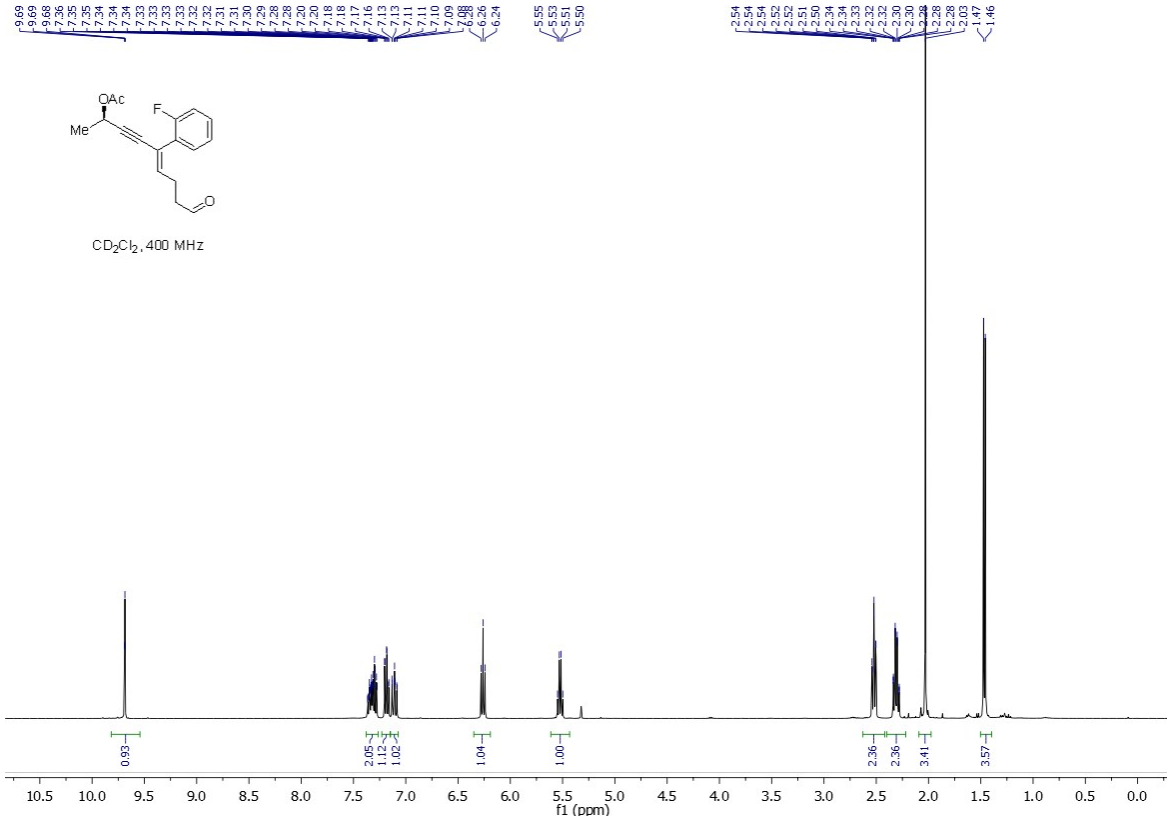

f1 (ppm)

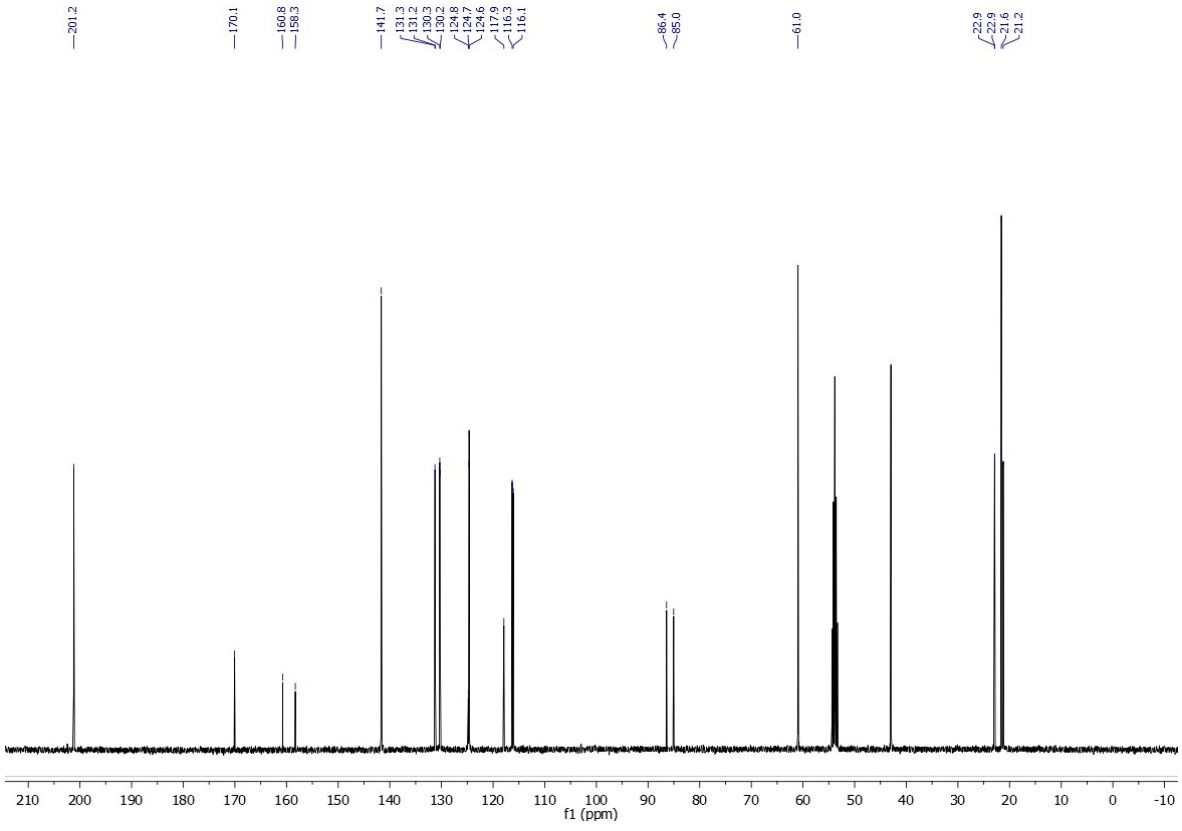

9.71
9.70
9.70
7.35
7.35
7.34
7.33
7.32
7.32
7.10
7.09
7.08
7.08
7.07
7.06
7.06
6.15
6.13
6.11
5.56
5.54
5.53
5.51
2.56
2.55
2.55
2.55
2.54
2.54
2.53
2.53
2.52
2.51
2.51
2.50
2.50
2.49
2.49
2.48
2.47
2.04
1.49
1.48
OAc
Me
F
O
CD2Cl2, 400 MHz
0.86
2.07
2.01
1.00
0.94
4.40
3.16
3.41
f1 (ppm)

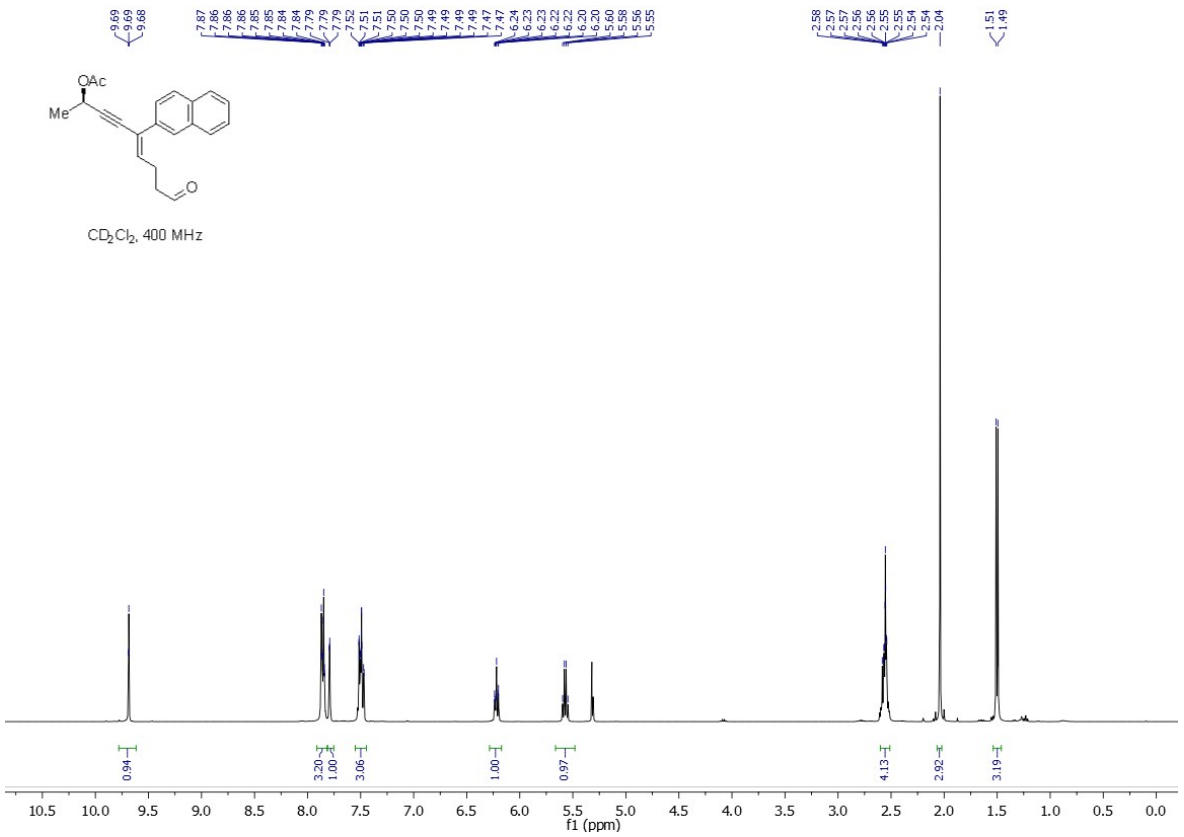

203.1
172.1
165.8
163.4
141.0
135.3
135.3
132.8
132.8
125.2
117.7
117.5
88.7
87.9
63.0
45.5
24.5
23.6
23.2
f1 (ppm)

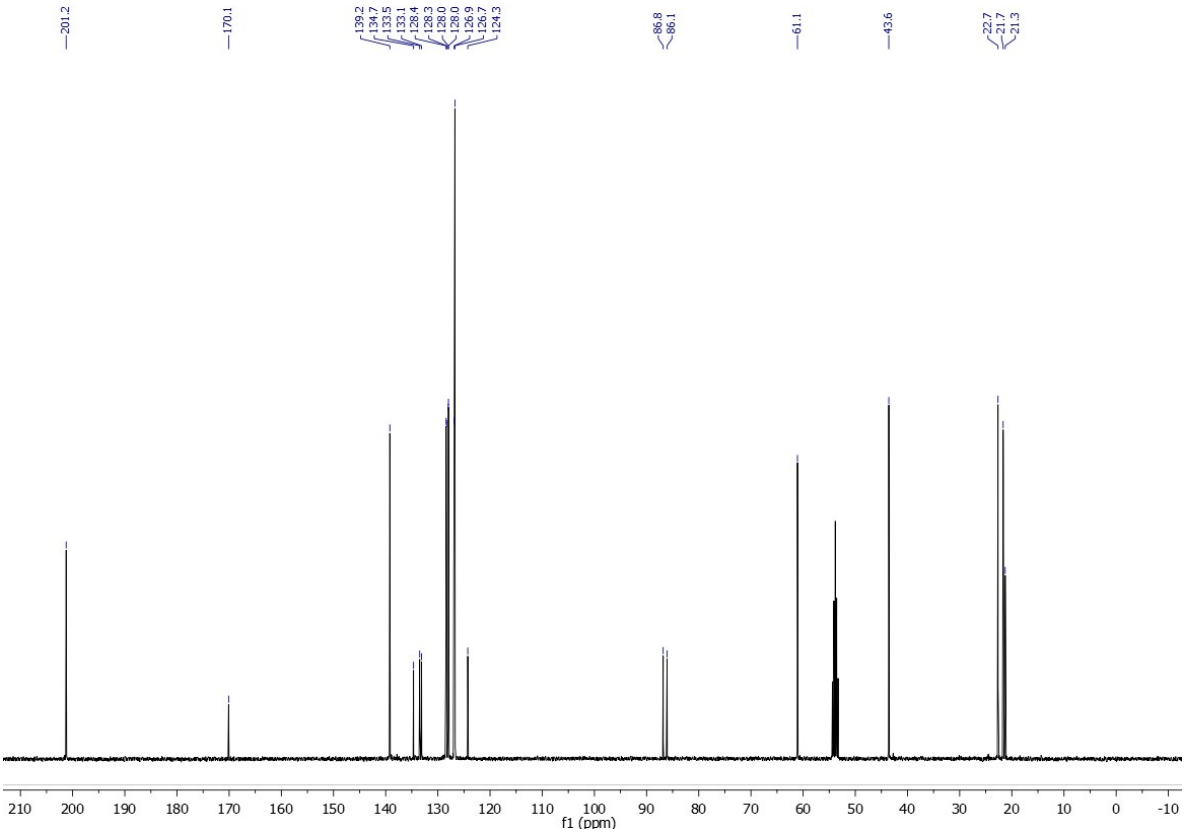

OAc
Me
F
O
CD2Cl2, 400 MHz
f1 (ppm)

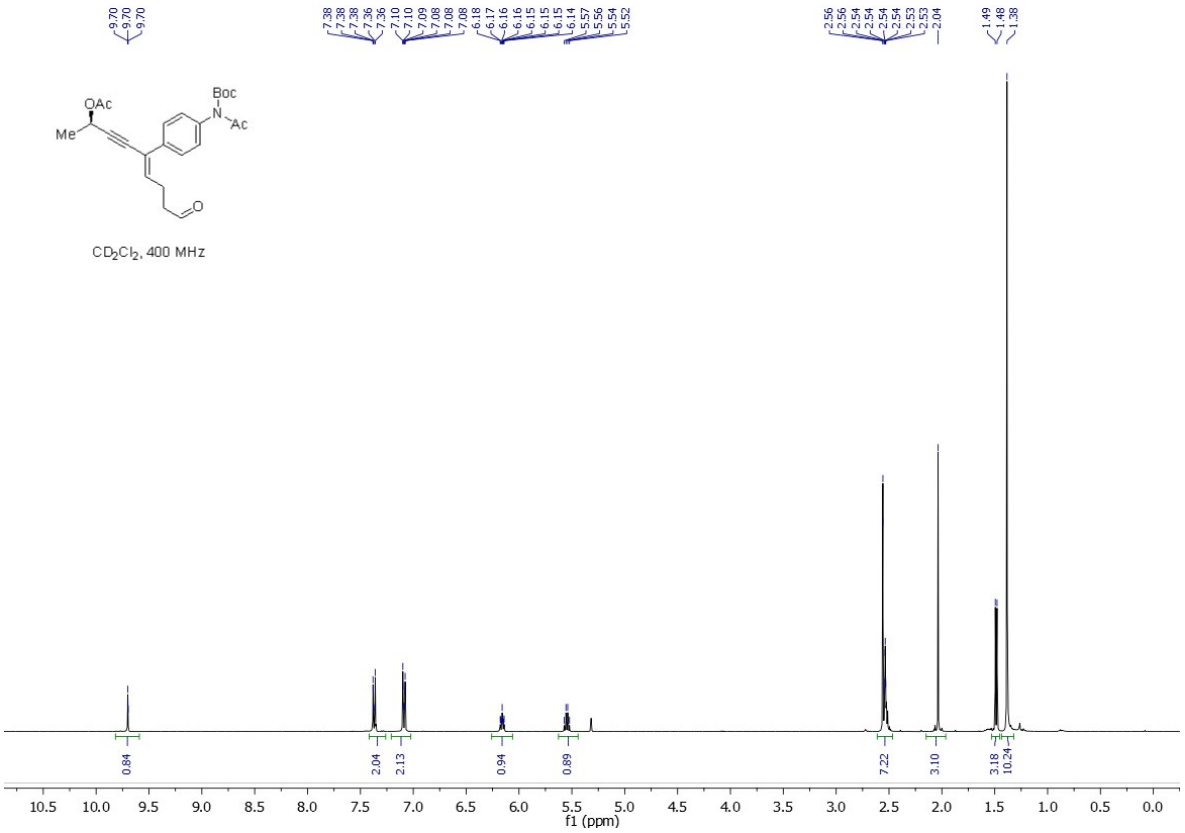

f1 (ppm)

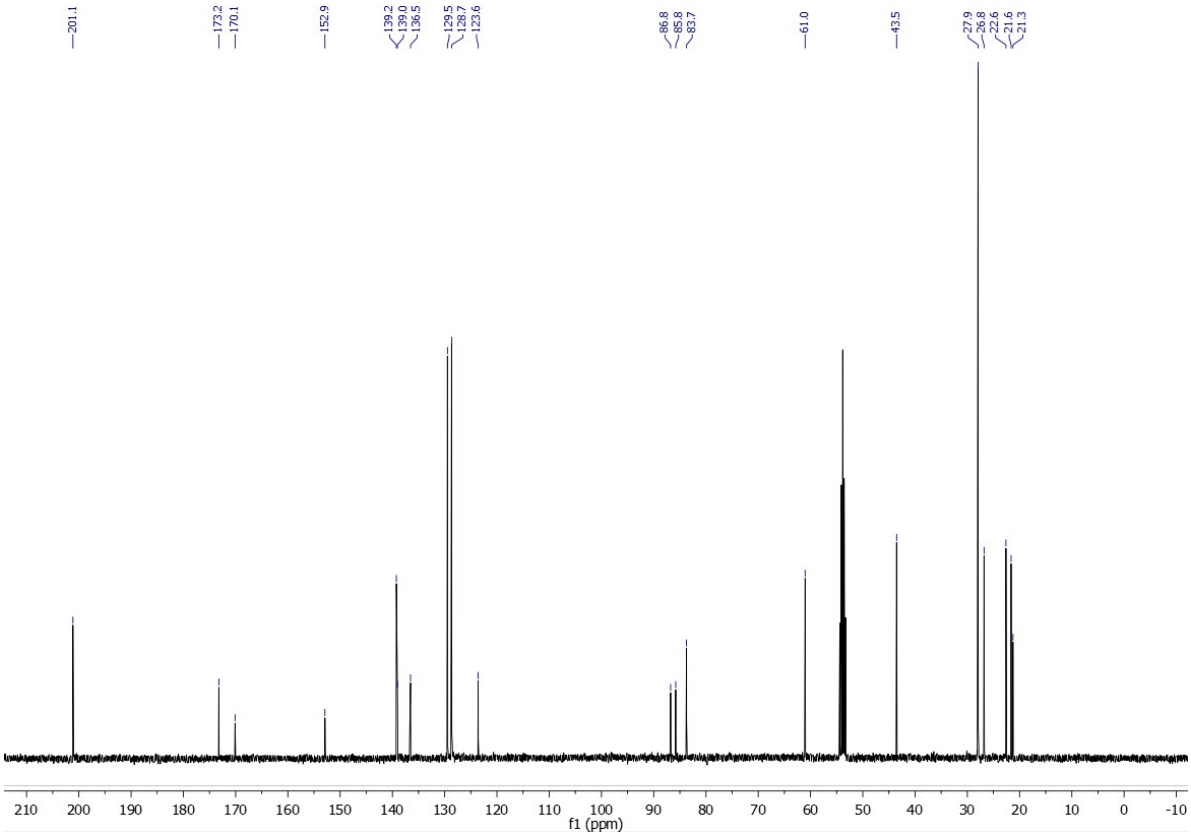

OAc
Me
F
O
CD_2Cl_2, 400 MHz
f1 (ppm)

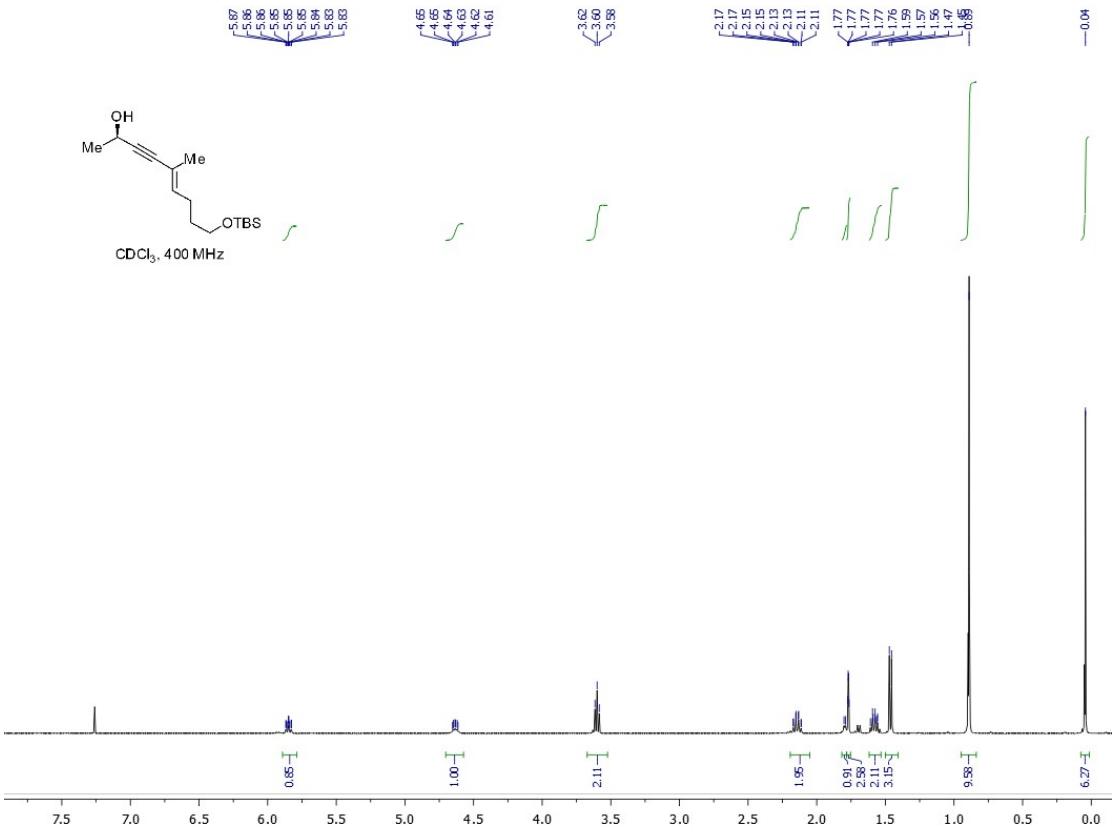

f1 (ppm)

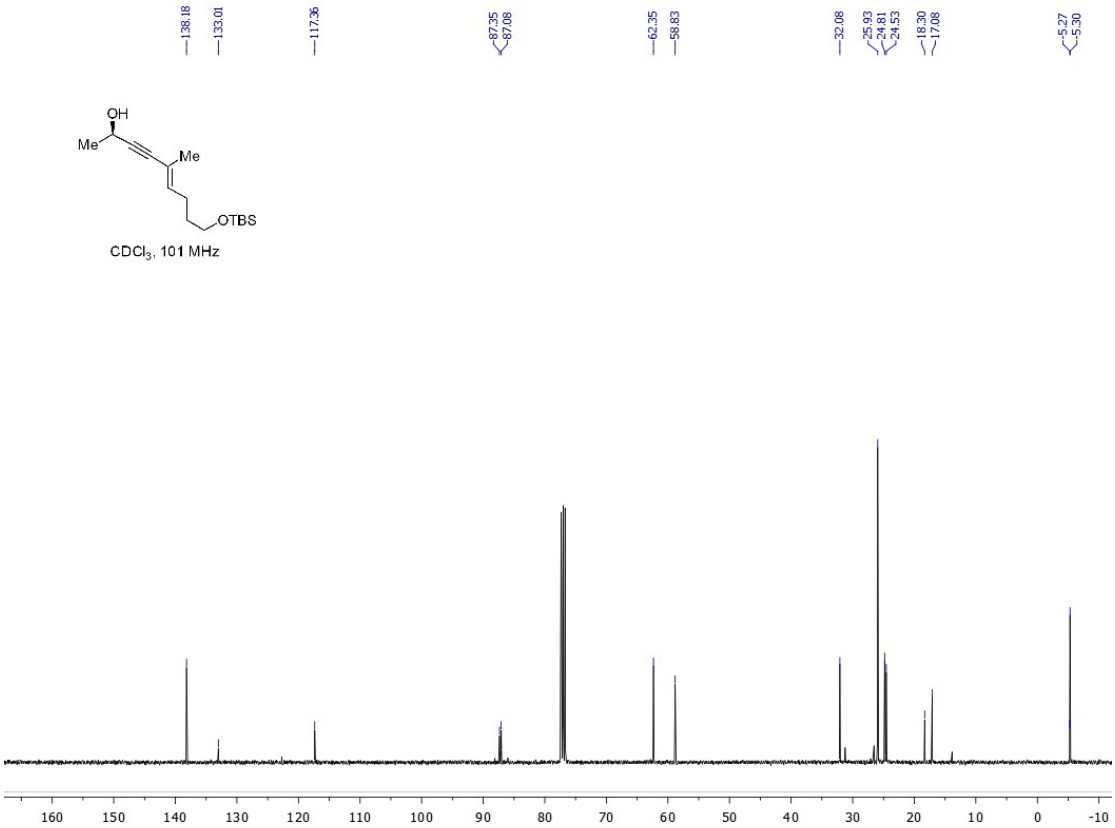

OAc
Me
O
CD2Cl2, 400 MHz
f1 (ppm)

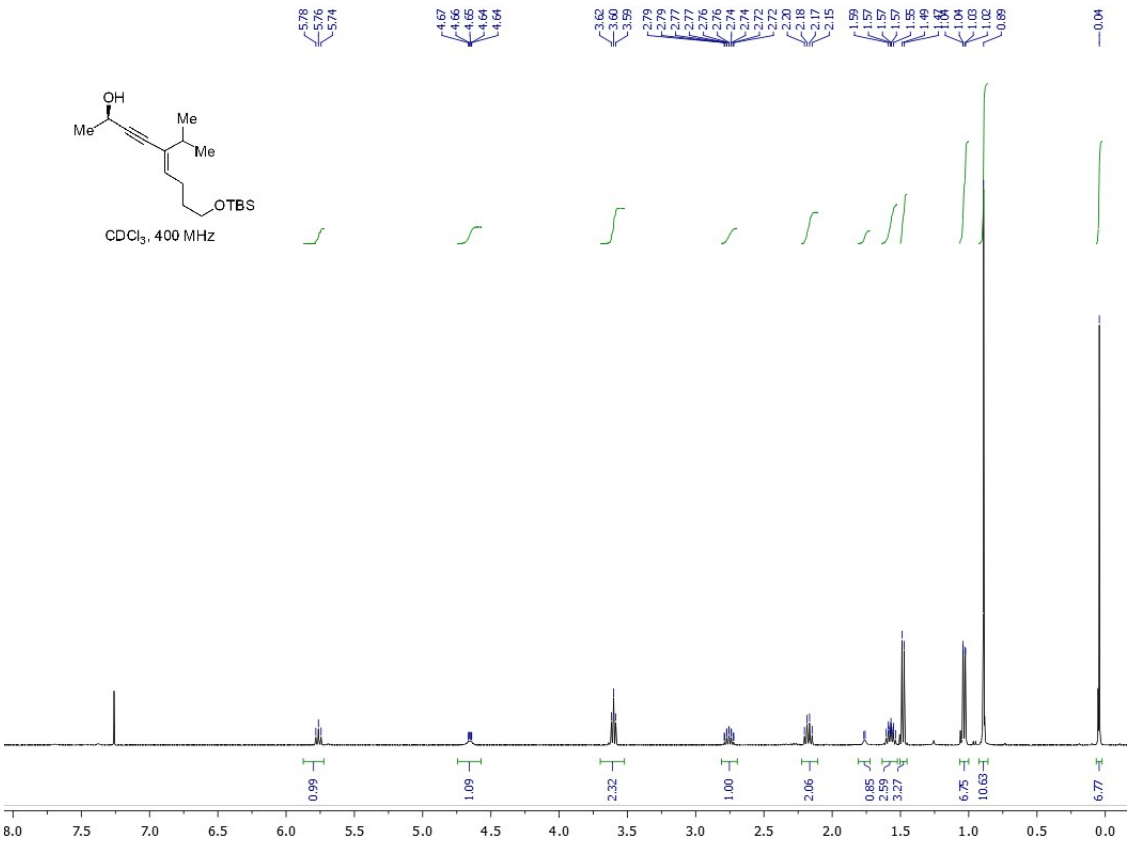

f1 (ppm)

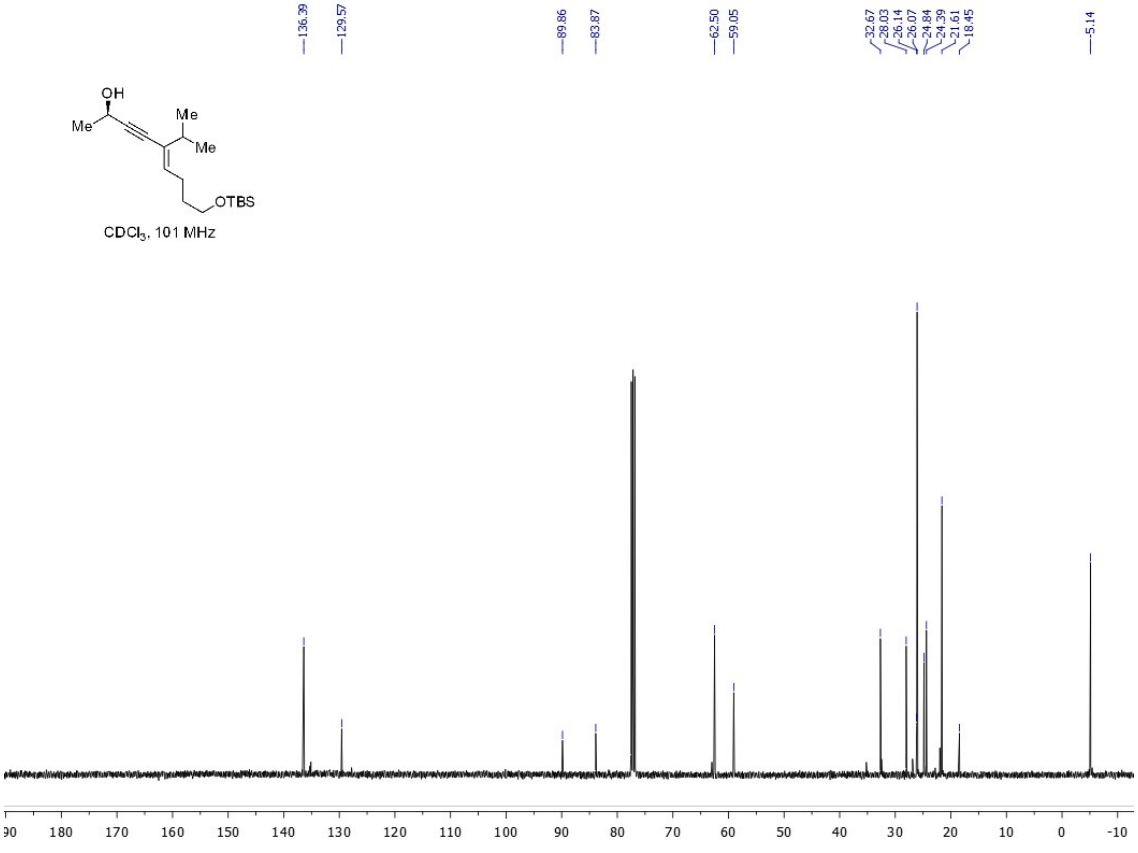

OAc
Me
Boc
N
Ac
O
CD2Cl2, 400 MHz
f1 (ppm)

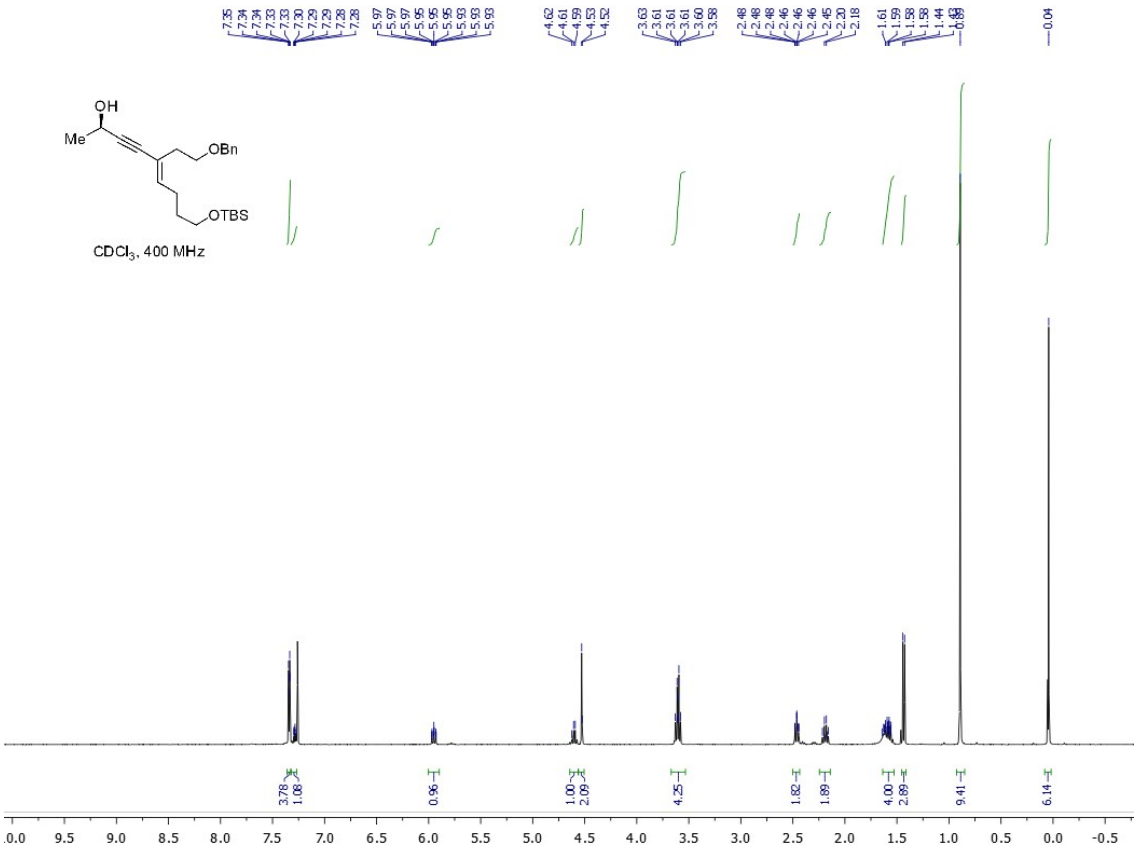

f1 (ppm)

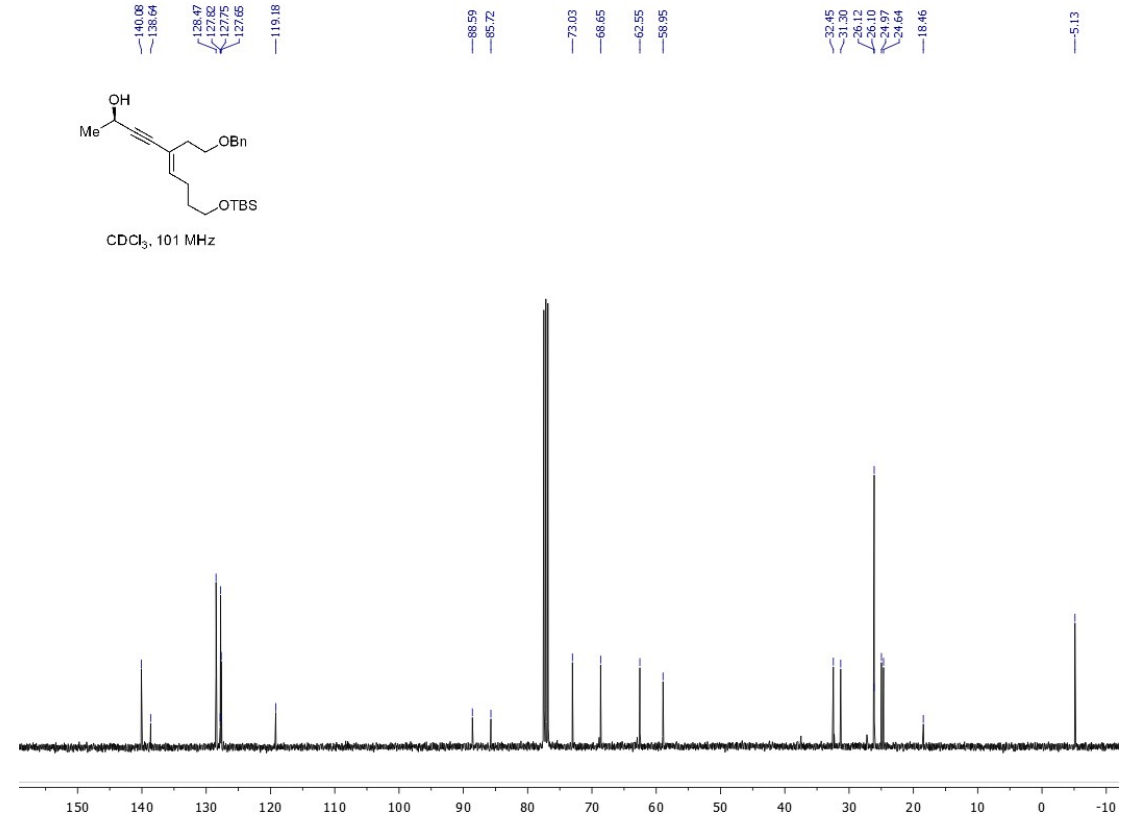

OH
Me
Me
OTBS
CDCl3, 400 MHz

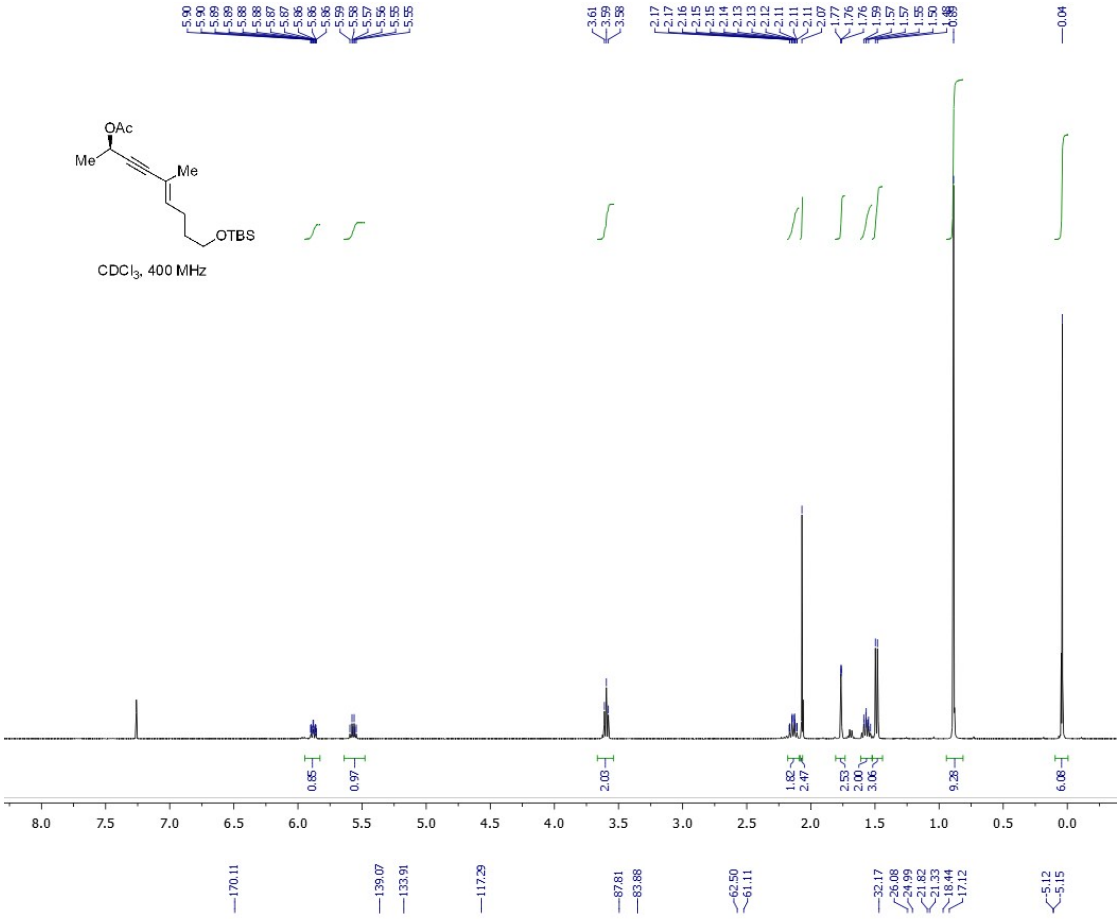

OH
Me
Me
OTBS
CDCl3, 101 MHz

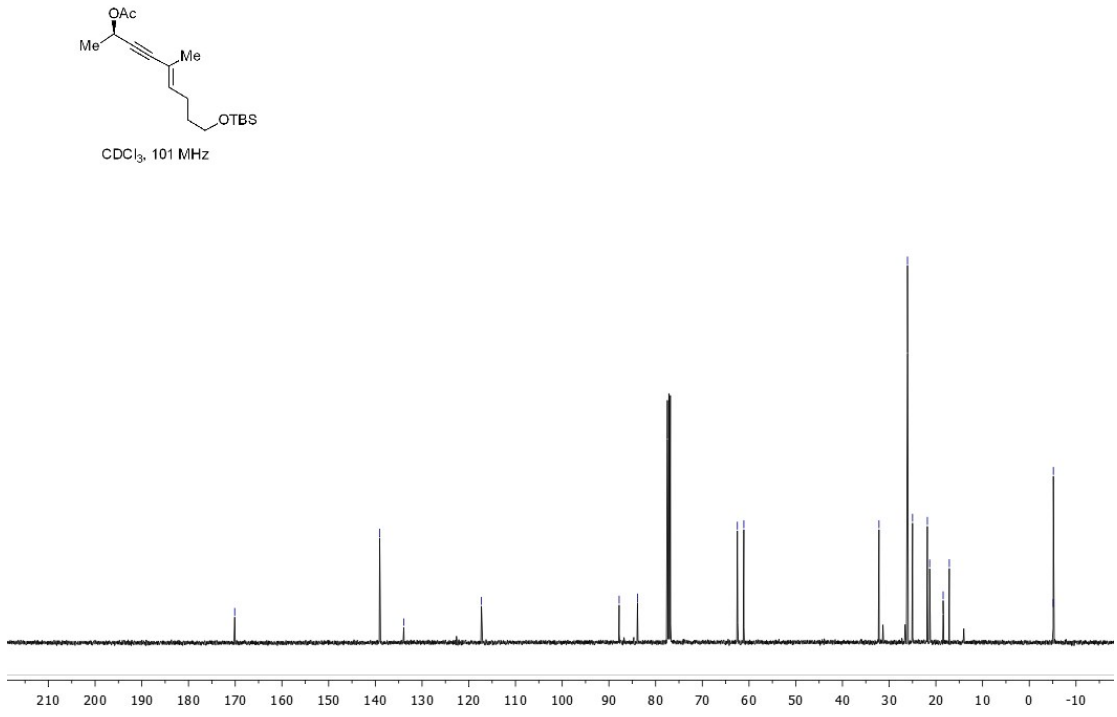

OH
Me
Me
Me
OTBS
CDCl3, 400 MHz

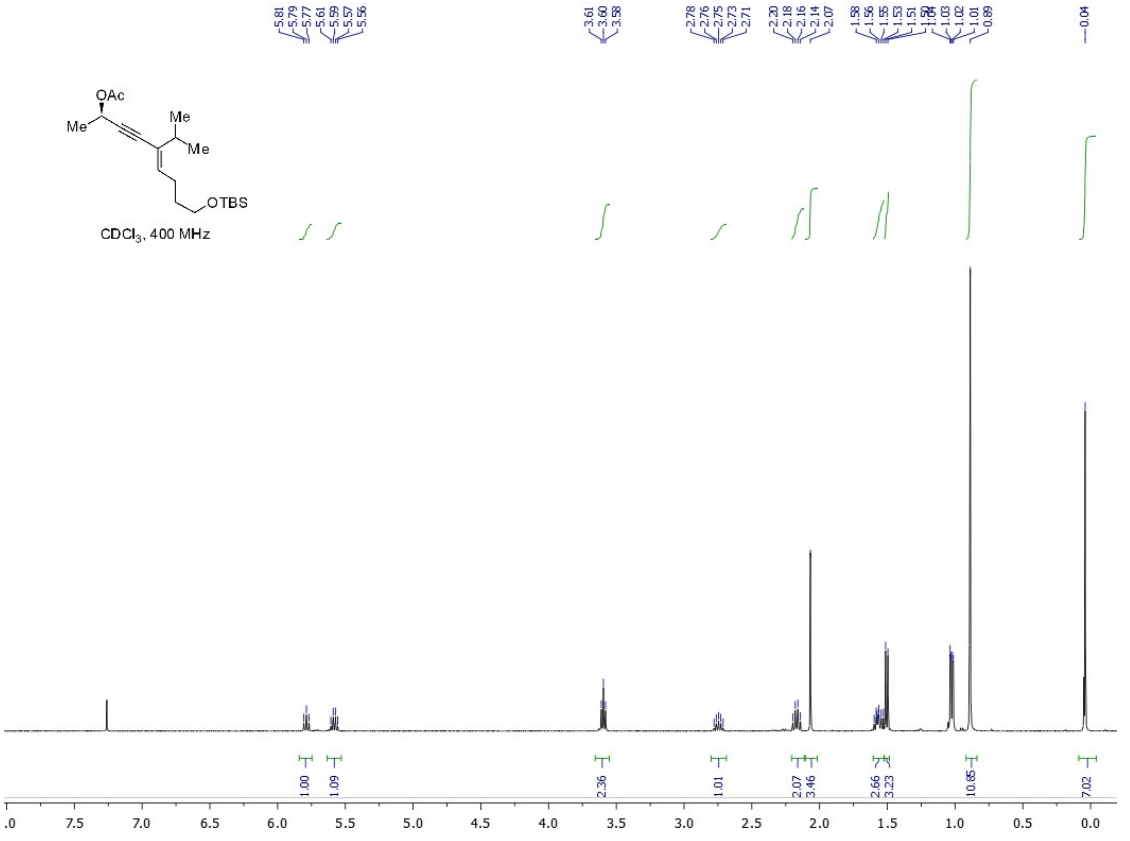

OH
Me
Me
Me
OTBS
CDCl3, 101 MHz

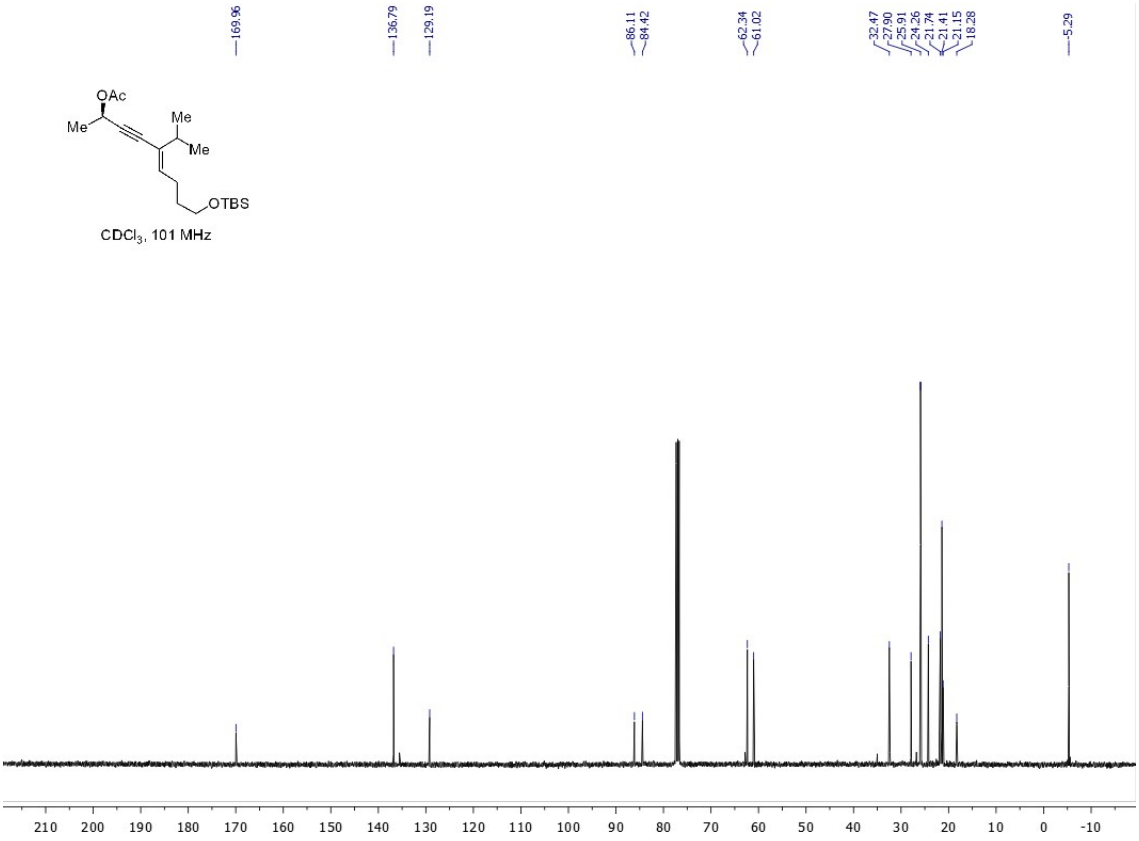

OH
Me
OBn
OTBS
CDCl3, 400 MHz

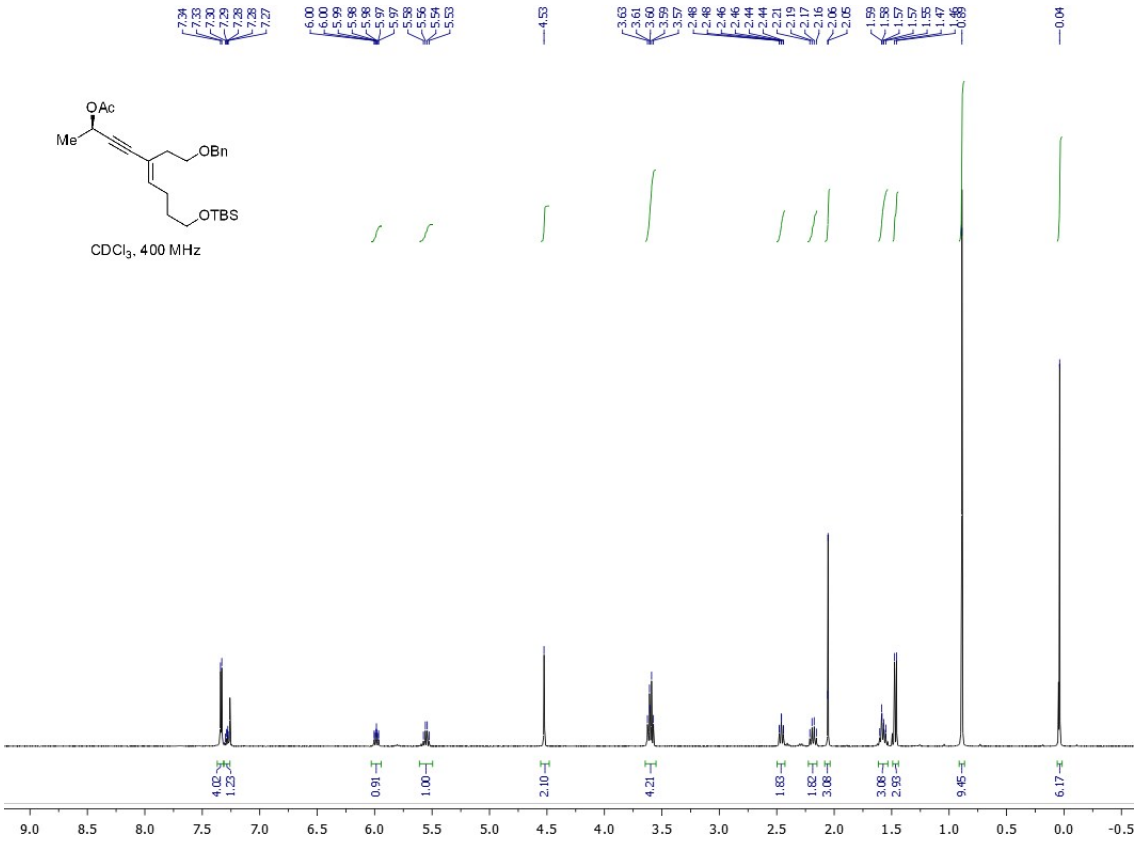

OH
Me
OBn
OTBS
CDCl3, 101 MHz

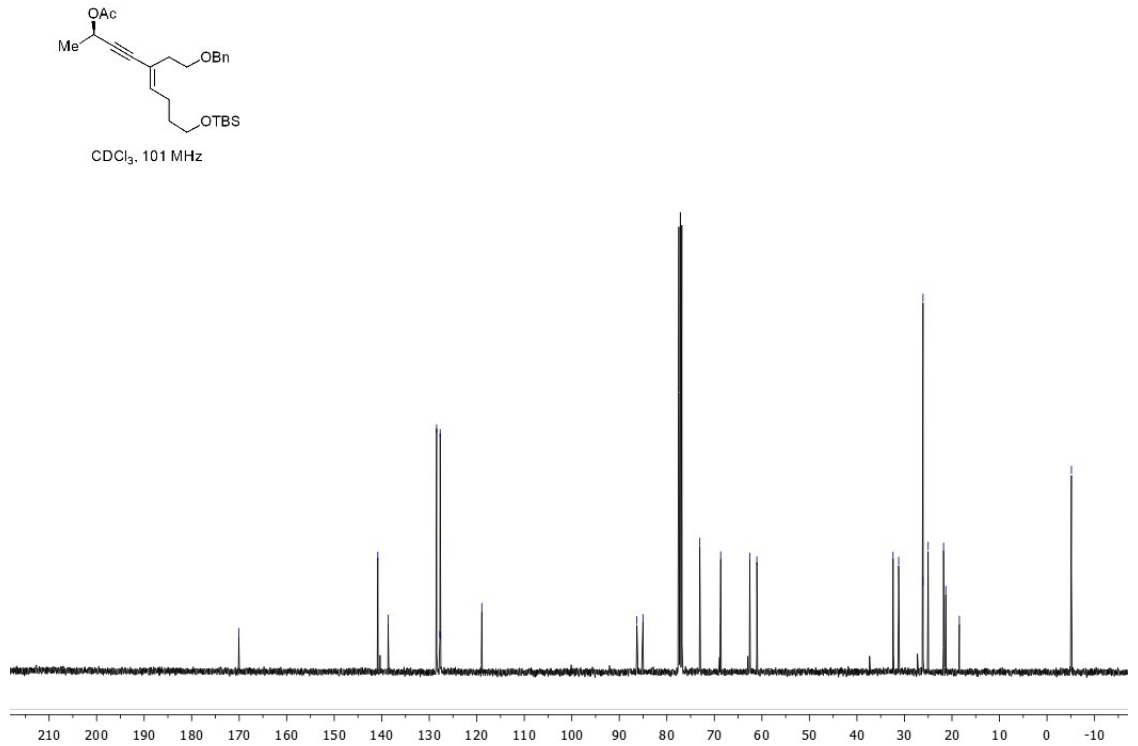

OAc
Me
Me
OTBS
CDCl3, 400 MHz

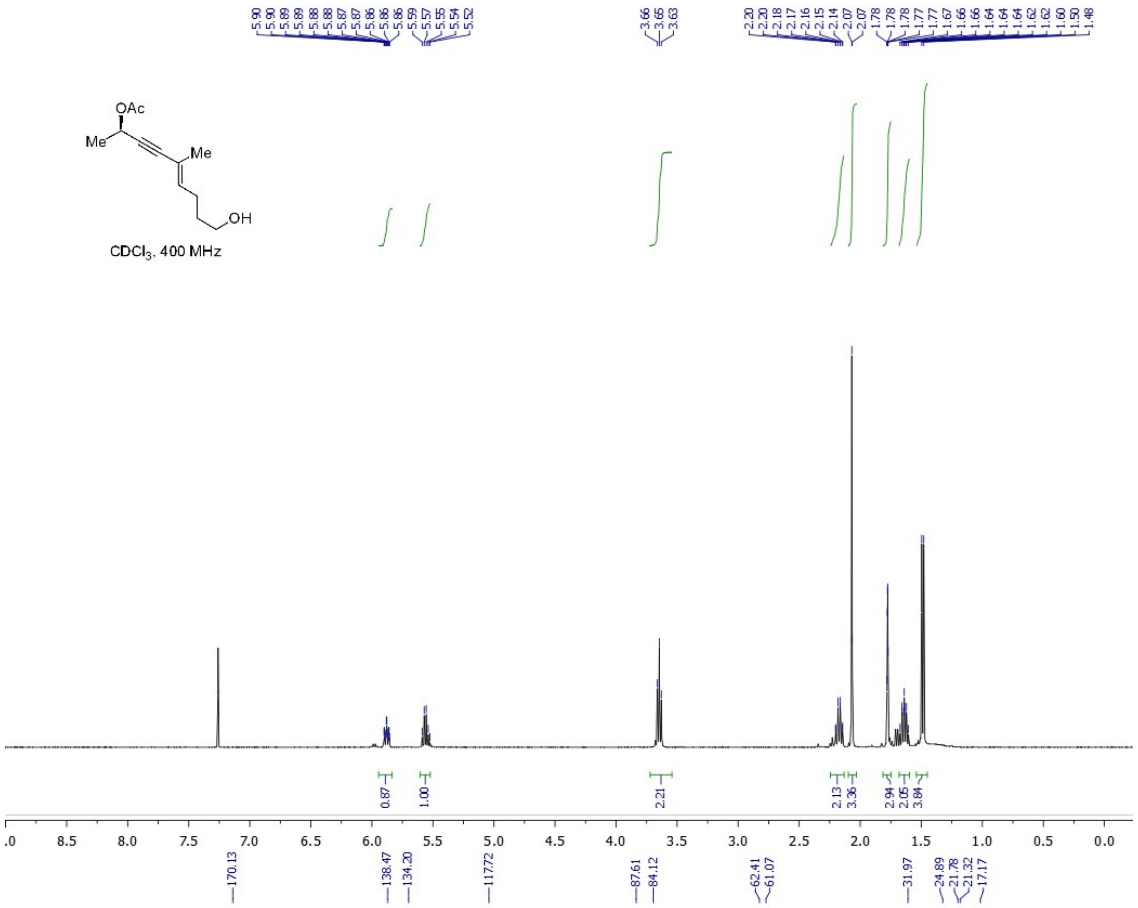

OAc
Me
Me
OTBS
CDCl3, 101 MHz

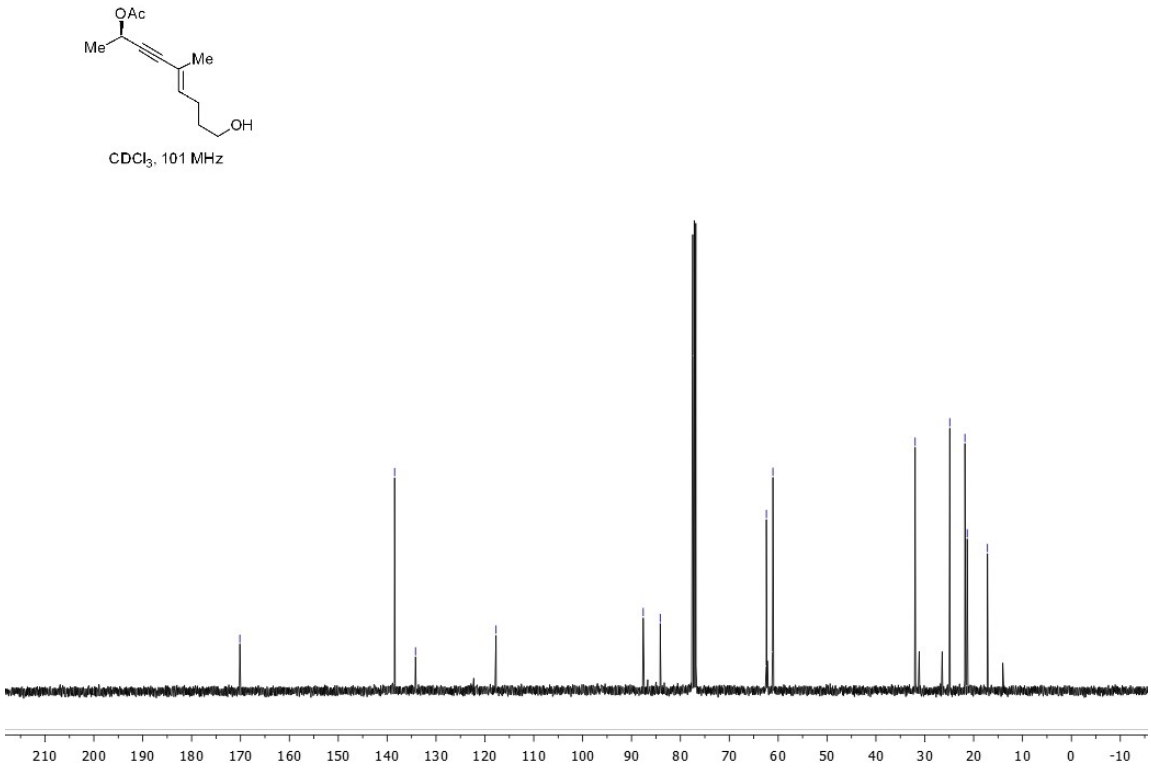

OAc
Me
Me
Me
OTBS
CDCl3, 400 MHz

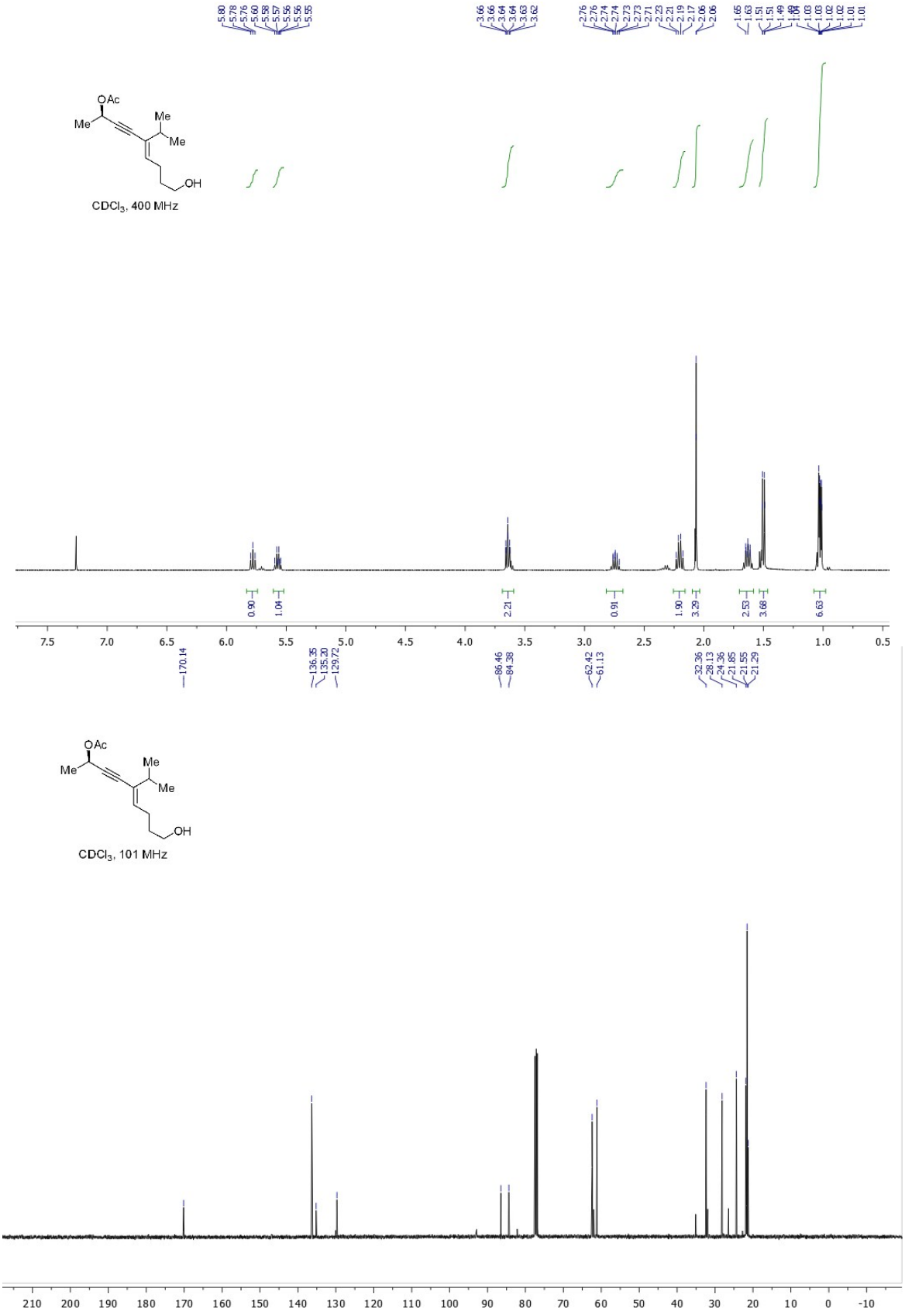

OAc
Me
Me
Me
OTBS
CDCl3, 101 MHz

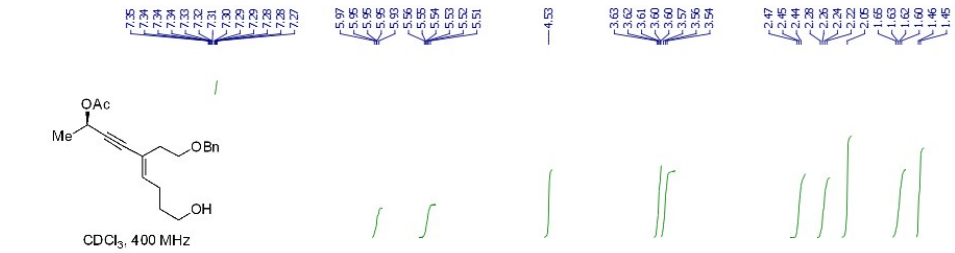

OAc
Me
OBn
OTBS
CDCl3, 400 MHz


OAc
Me
OBn
OTBS
CDCl3, 101 MHz

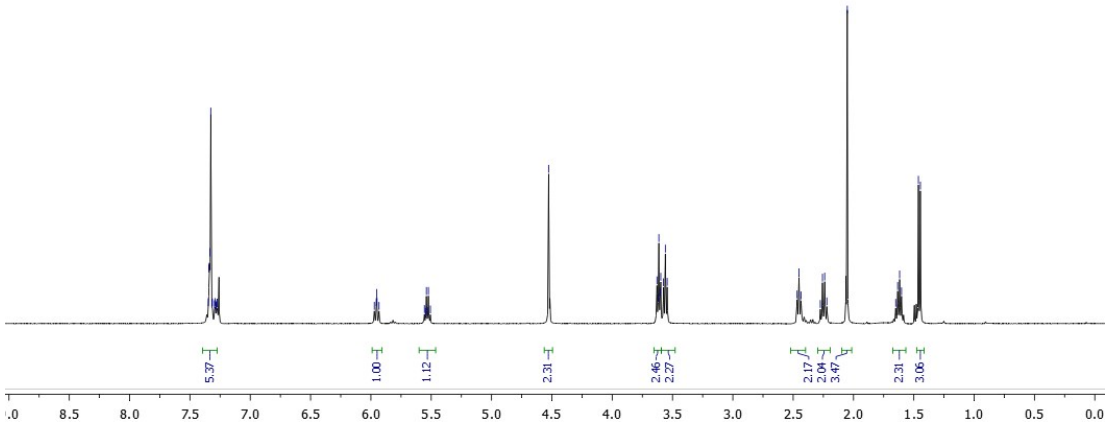

OAc
Me
Me
OH
CDCl3, 400 MHz

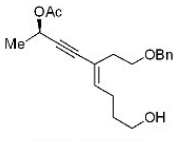

OAc
Me
Me
OH
CDCl3, 101 MHz


OAc
Me
Me
Me
OH
CDCl3, 400 MHz
OAc
Me
Me
Me
OH
CDCl3, 101 MHz

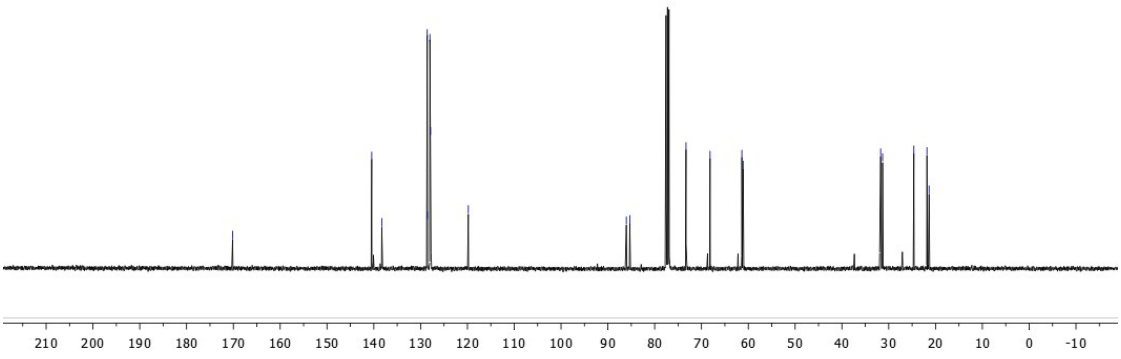


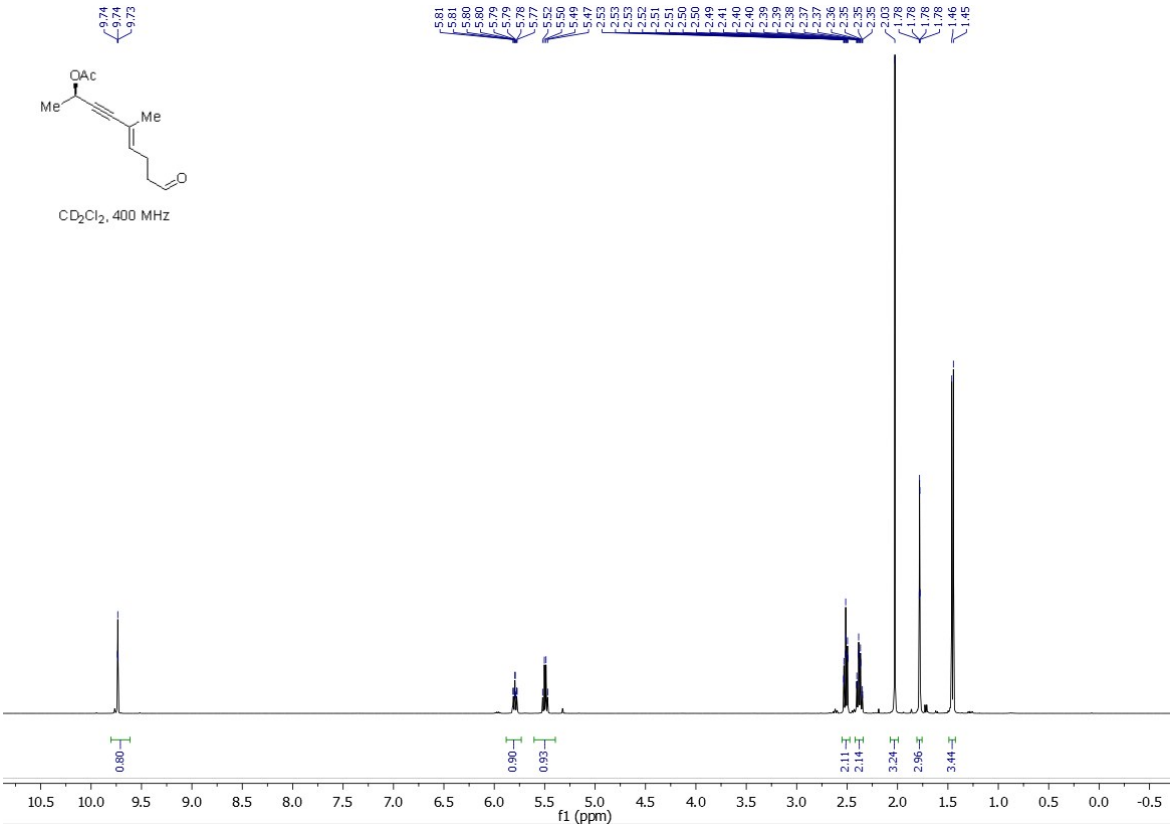
$CDCl_3$, 400 MHz

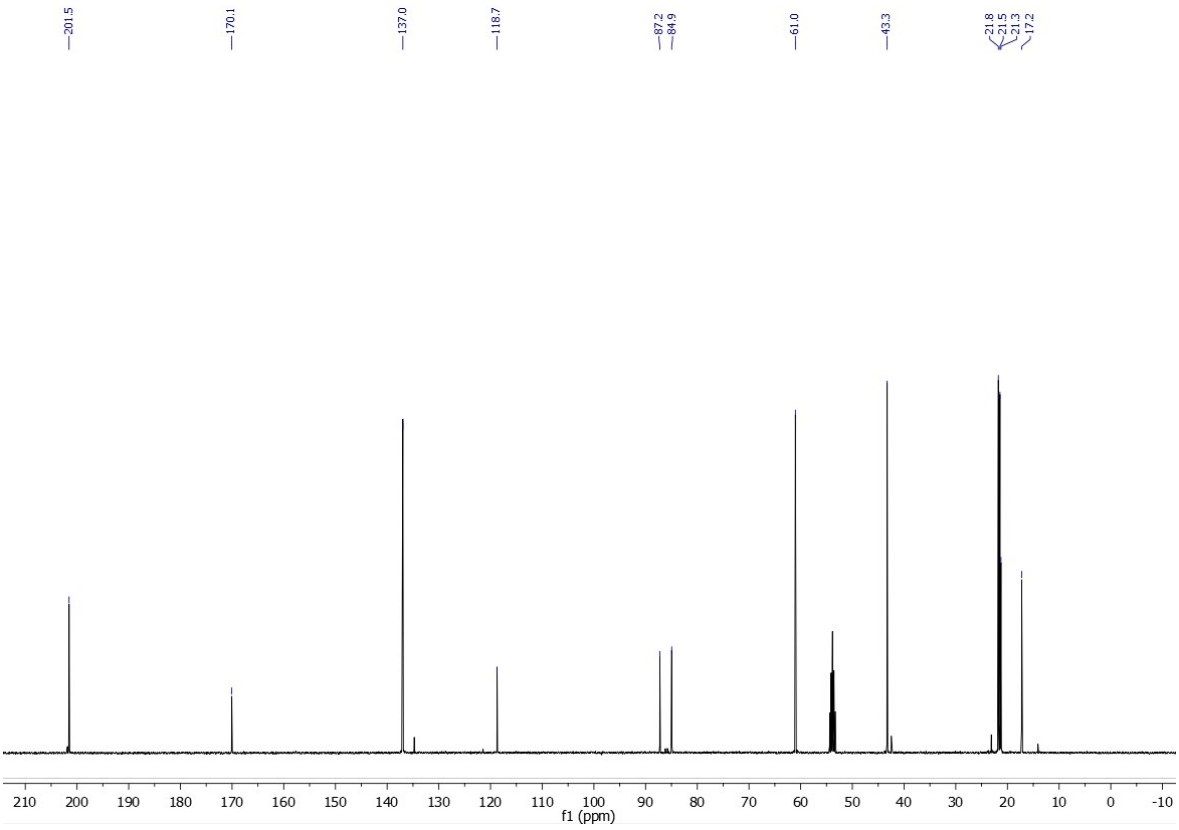


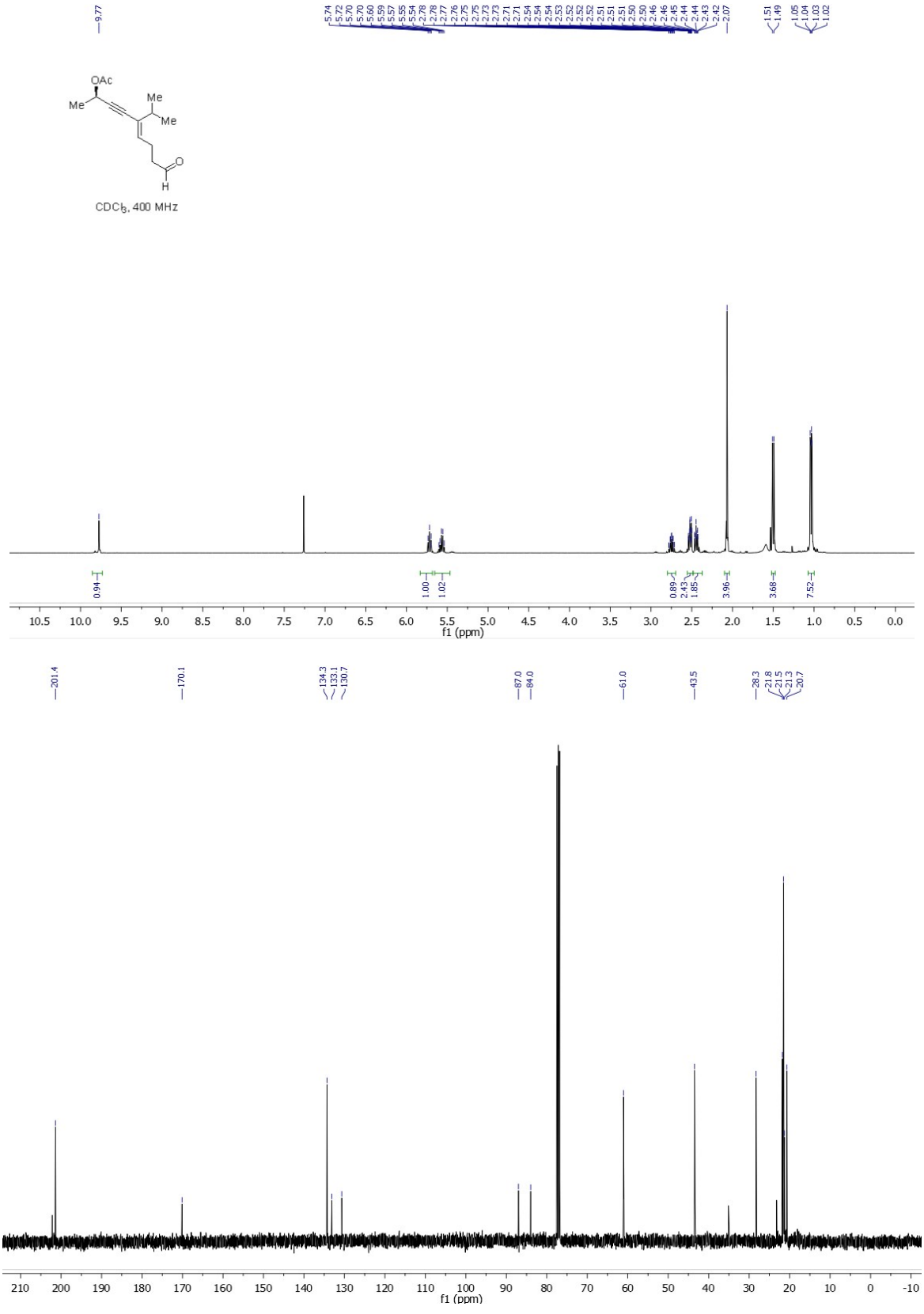


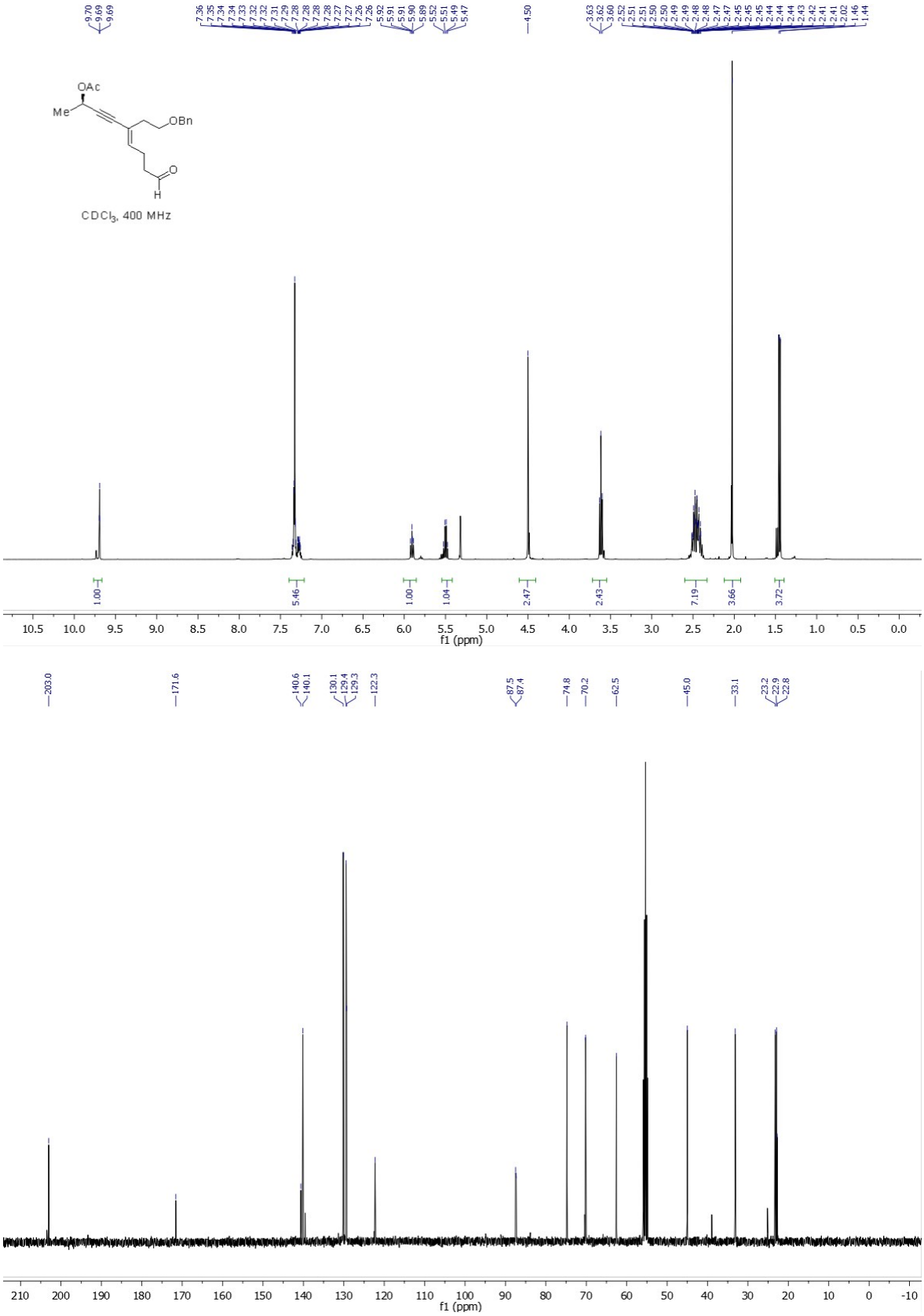
$CDCl_3$, 101 MHz

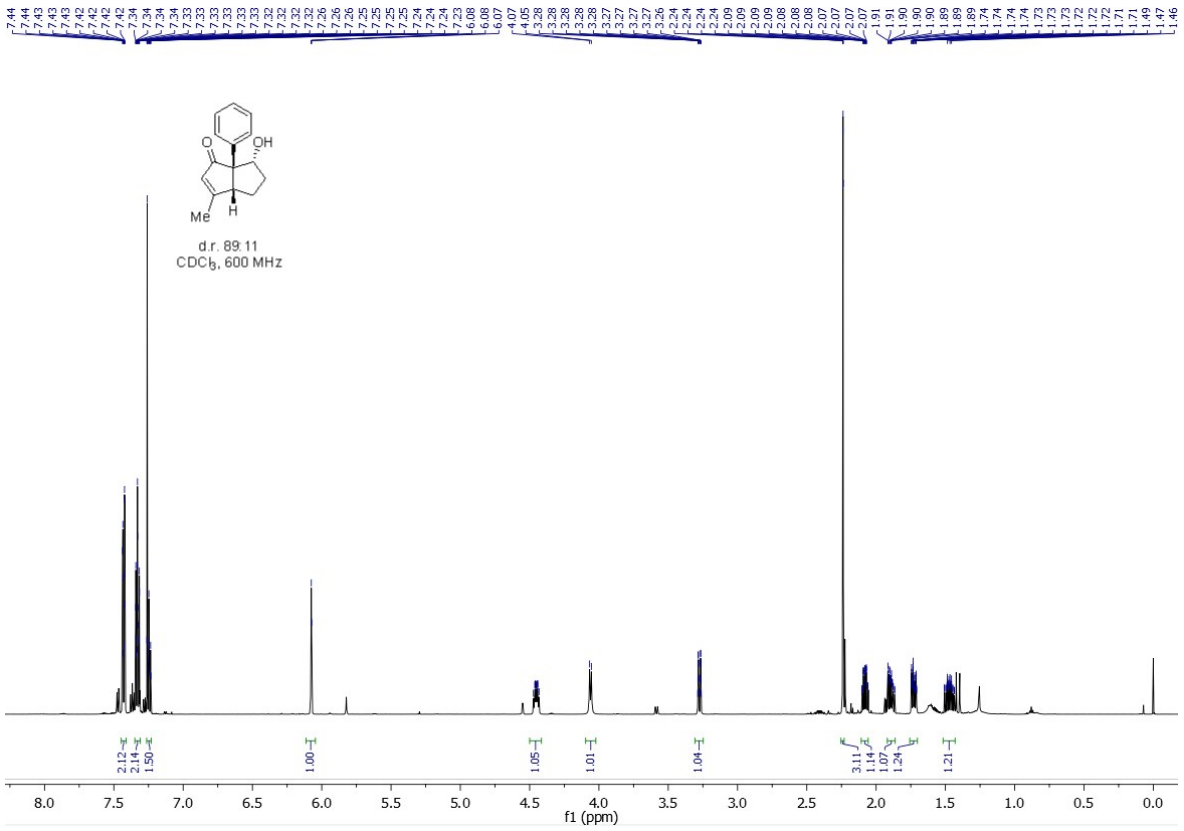


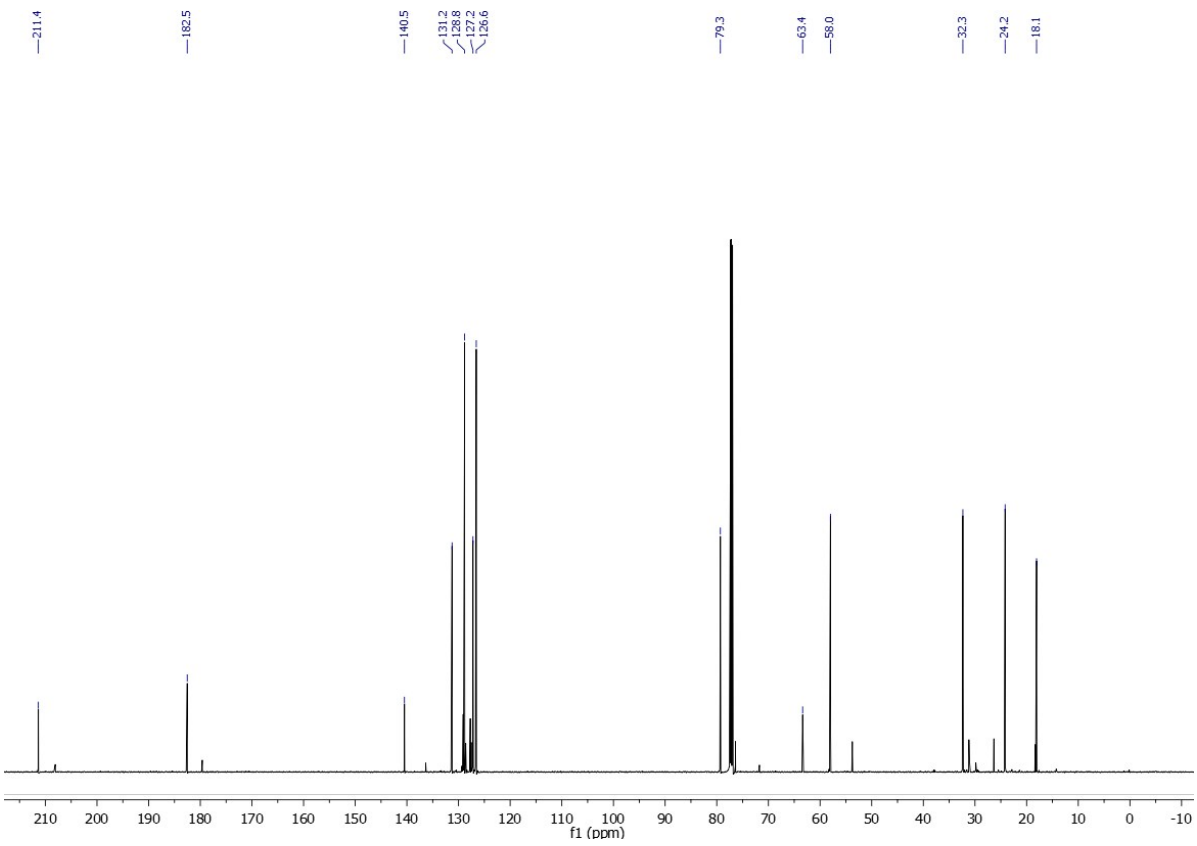

9.74
9.74
9.73
OAc
Me
Me
O
CD2Cl2, 400 MHz
5.81
5.81
5.80
5.80
5.79
5.79
5.78
5.77
5.52
5.50
5.49
5.47
2.53
2.53
2.53
2.52
2.51
2.51
2.50
2.50
2.49
2.41
2.40
2.40
2.39
2.39
2.38
2.37
2.37
2.36
2.35
2.35
2.03
1.78
1.78
1.78
1.78
1.46
1.45
0.80
0.90
0.93
2.11
2.14
3.24
2.96
3.44
f1 (ppm)

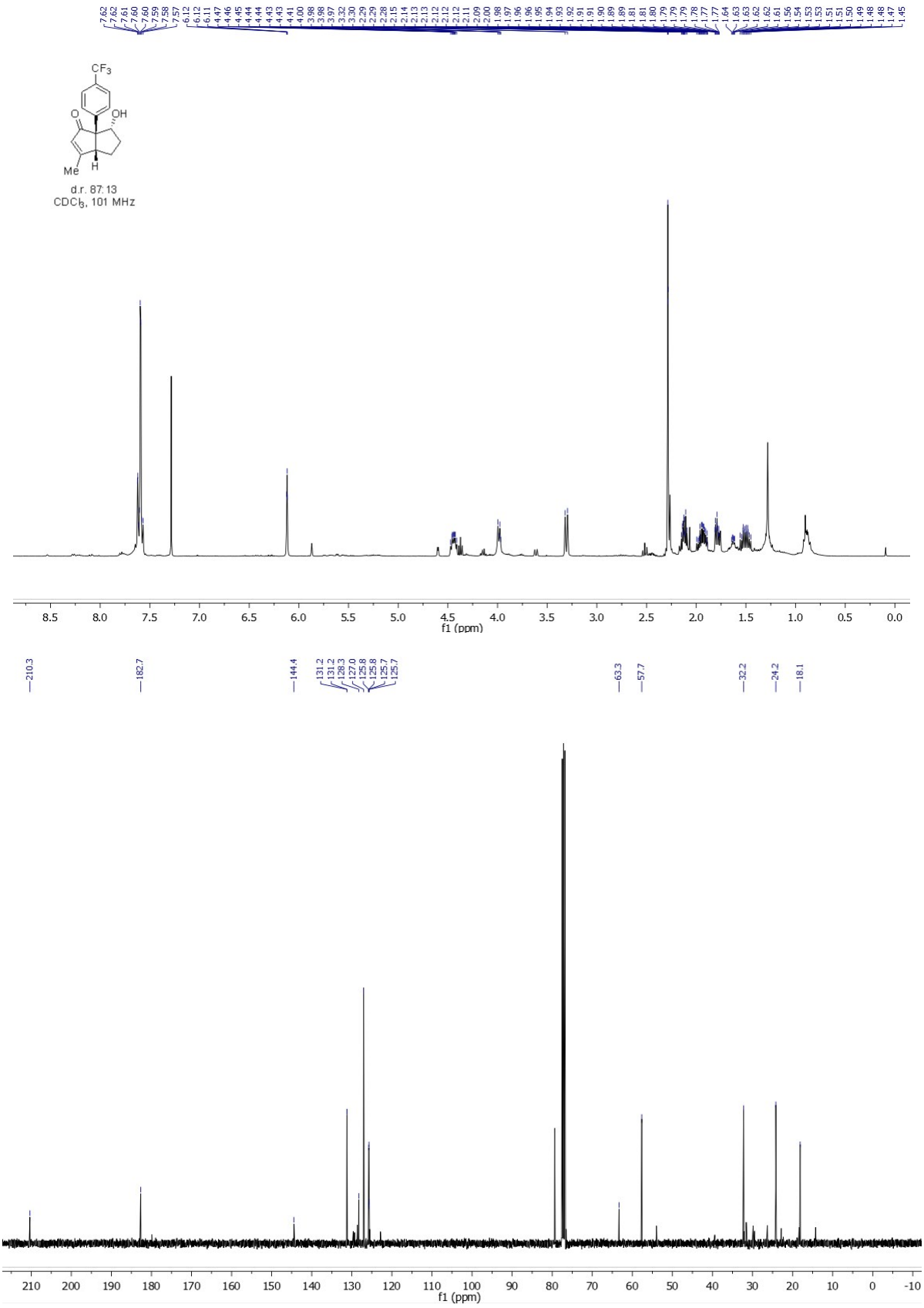

201.5
170.1
137.0
118.7
87.2
84.9
61.0
43.3
21.8
21.5
21.3
17.2
f1 (ppm)

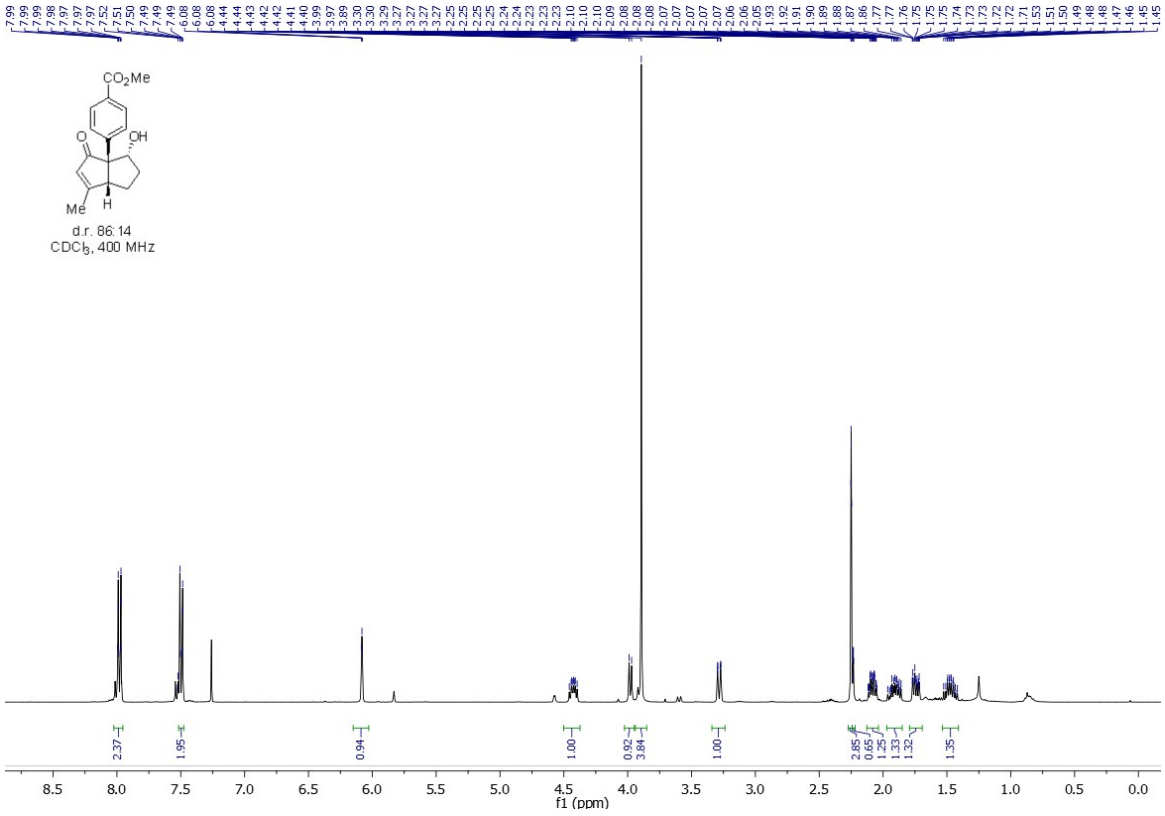

9.77
5.74
5.72
5.70
5.70
5.60
5.59
5.57
5.55
5.54
2.78
2.77
2.77
2.76
2.75
2.73
2.73
2.71
2.71
2.54
2.54
2.54
2.53
2.52
2.52
2.52
2.51
2.51
2.51
2.50
2.50
2.46
2.45
2.44
2.44
2.43
2.42
2.07
1.51
1.49
1.05
1.04
1.03
1.02
OAc
Me
Me
Me
O
H
CDCl3, 400 MHz
0.94
1.00
1.02
0.89
2.43
1.85
3.96
3.68
7.52
f1 (ppm)
201.4
170.1
134.3
133.1
130.7
87.0
84.0
61.0
43.5
28.3
21.8
21.5
21.3
20.7
f1 (ppm)

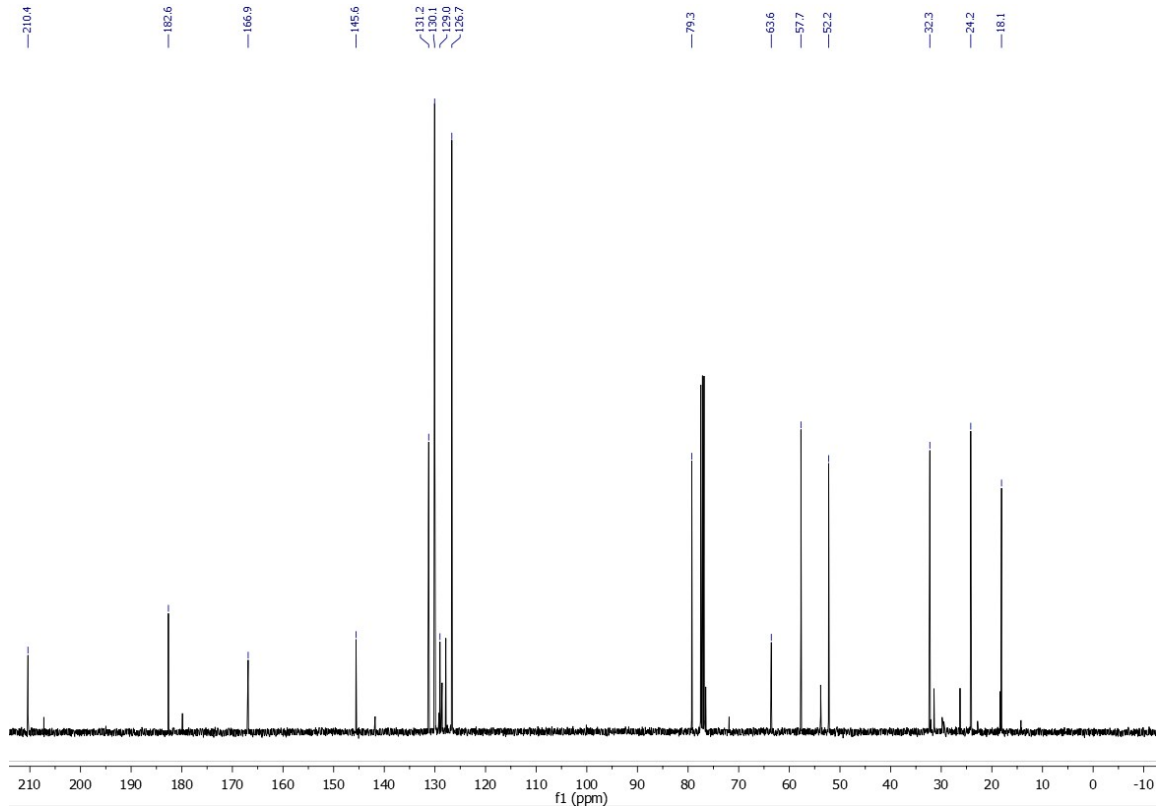

OAc
Me
OBn
O
H
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

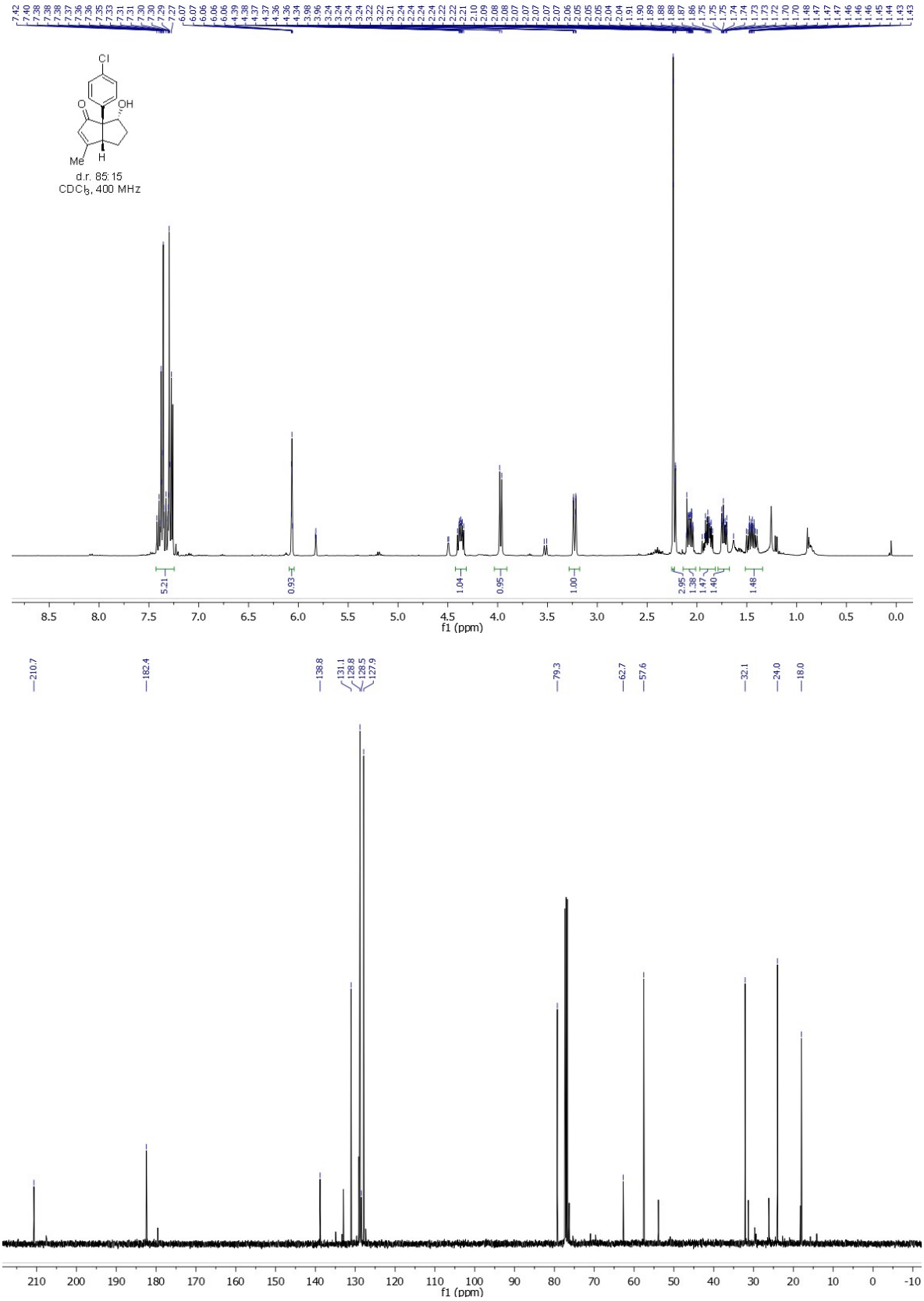

O
OH
Me
H
d.r. 89:11
CDCl3, 600 MHz
f1 (ppm)

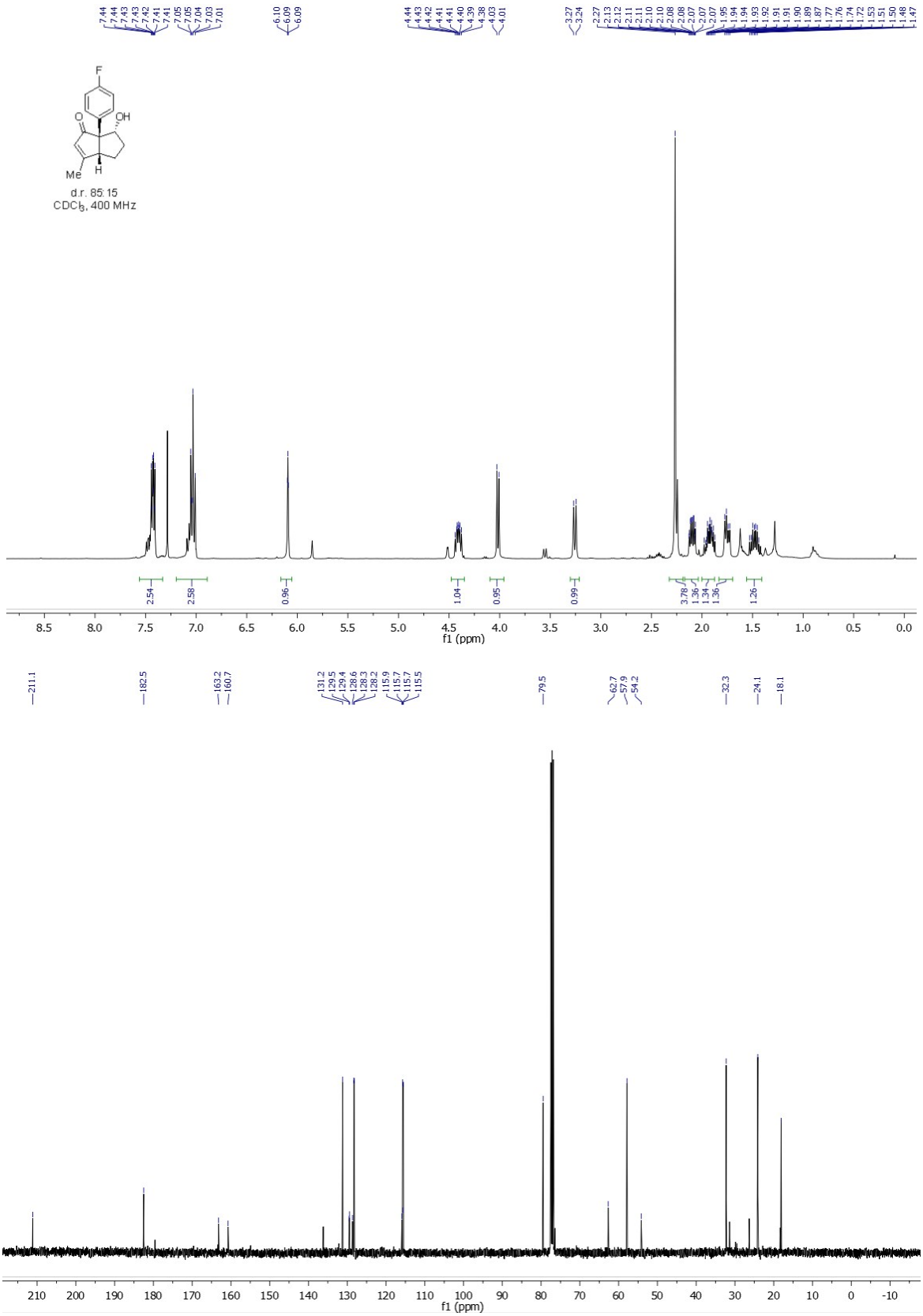

211.4
182.5
140.5
131.2
128.8
127.2
126.6
79.3
63.4
58.0
32.3
24.2
18.1
f1 (ppm)

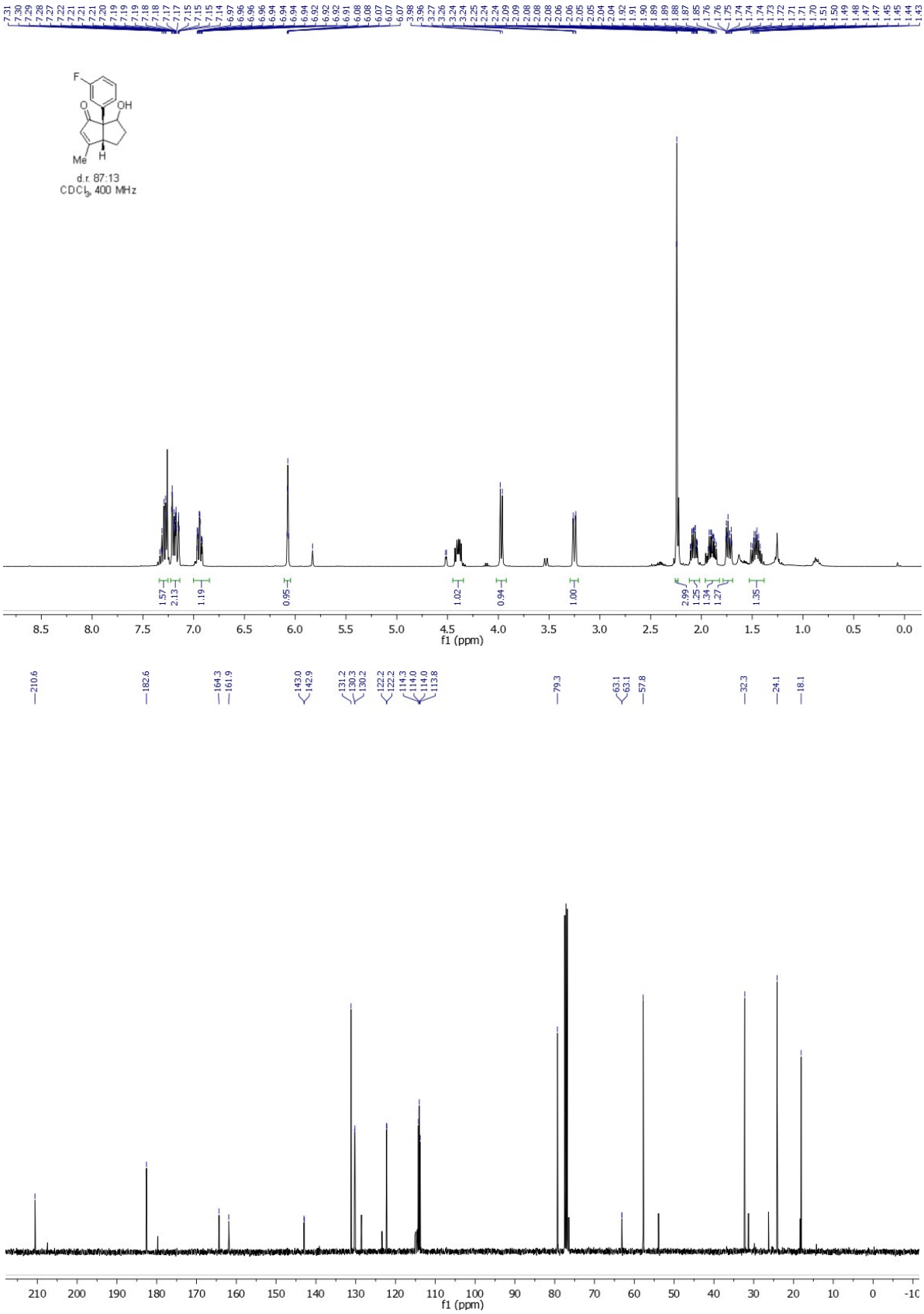

CF3
O
OH
Me
H
d.r. 87:13
CDCl3, 101 MHz
f1 (ppm)
f1 (ppm)

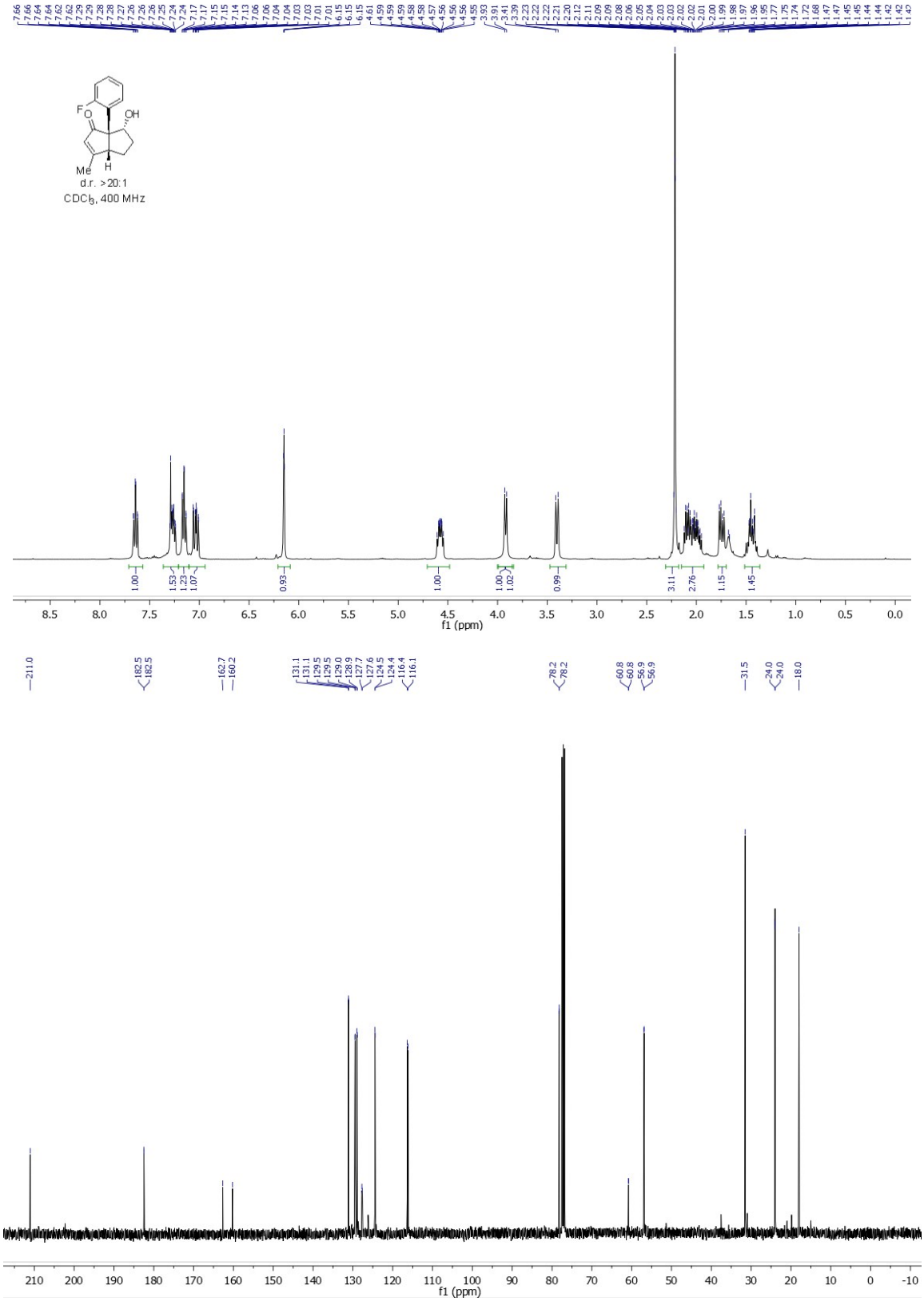

CO2Me
O
OH
Me
H
d.r. 86:14
CDCl3, 400 MHz
f1 (ppm)

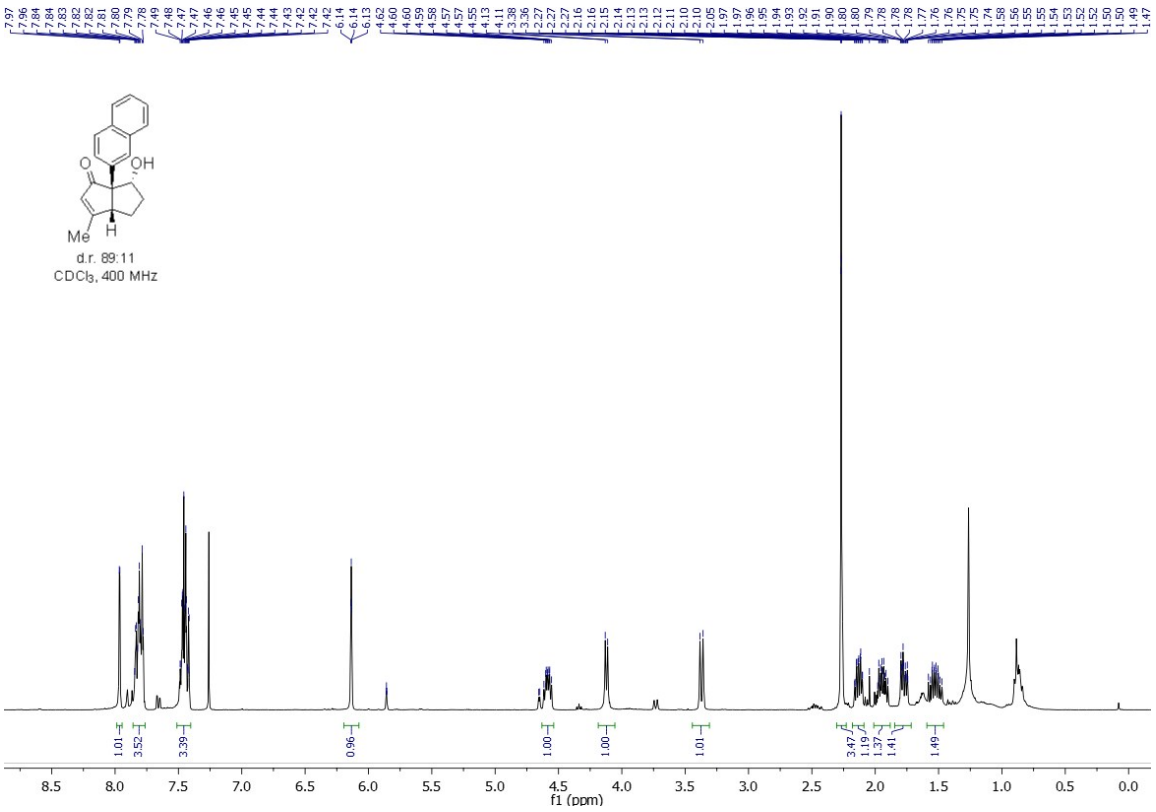

210.4
182.6
166.9
145.6
131.2
130.1
129.0
126.7
79.3
63.6
57.7
52.2
32.3
24.2
18.1
f1 (ppm)

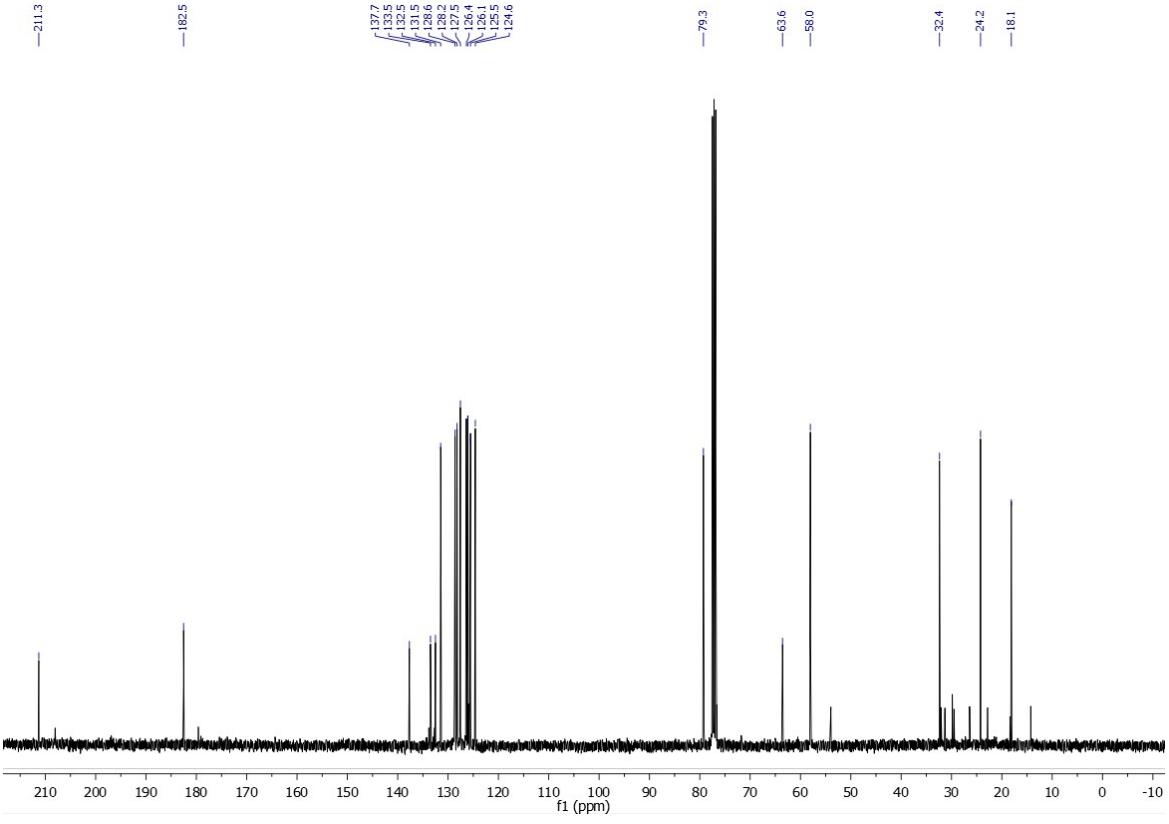

Cl
O
OH
Me
H
d.r. 85:15
CDCl3, 400 MHz
f1 (ppm)
210.7
182.4
138.8
131.1
128.8
128.5
127.9
79.3
62.7
57.6
32.1
24.0
18.0
f1 (ppm)

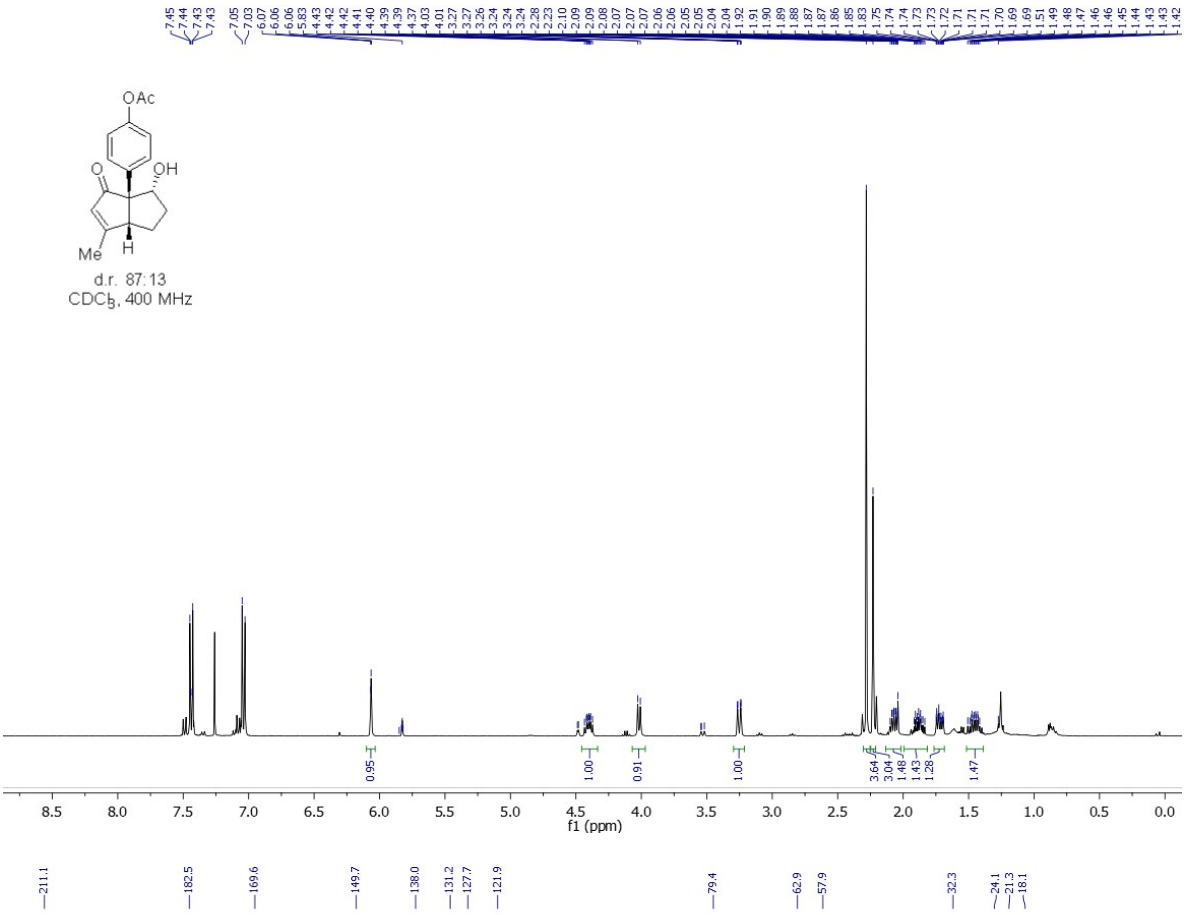

d.r. 85:15
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

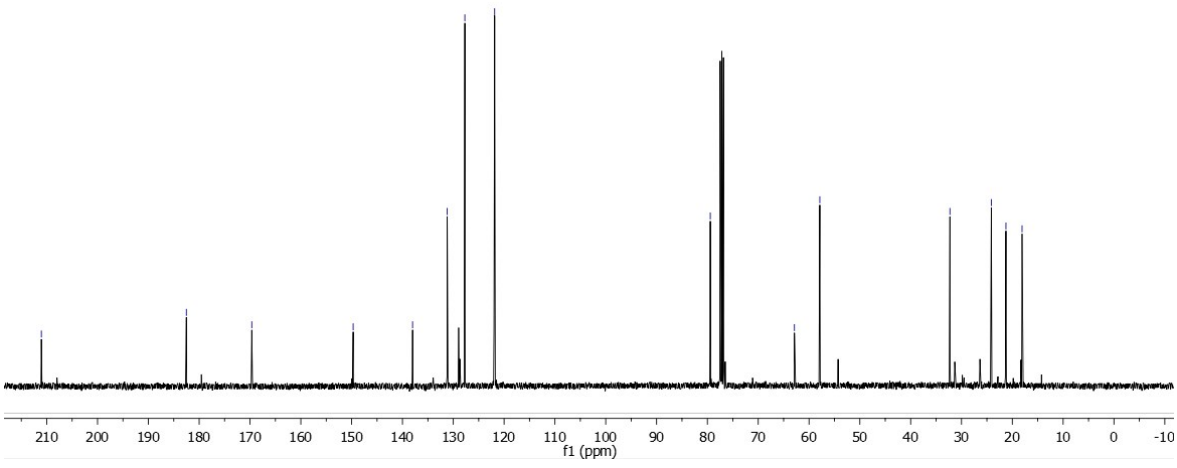

F
O
OH
Me
H
d.r. 87:13
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

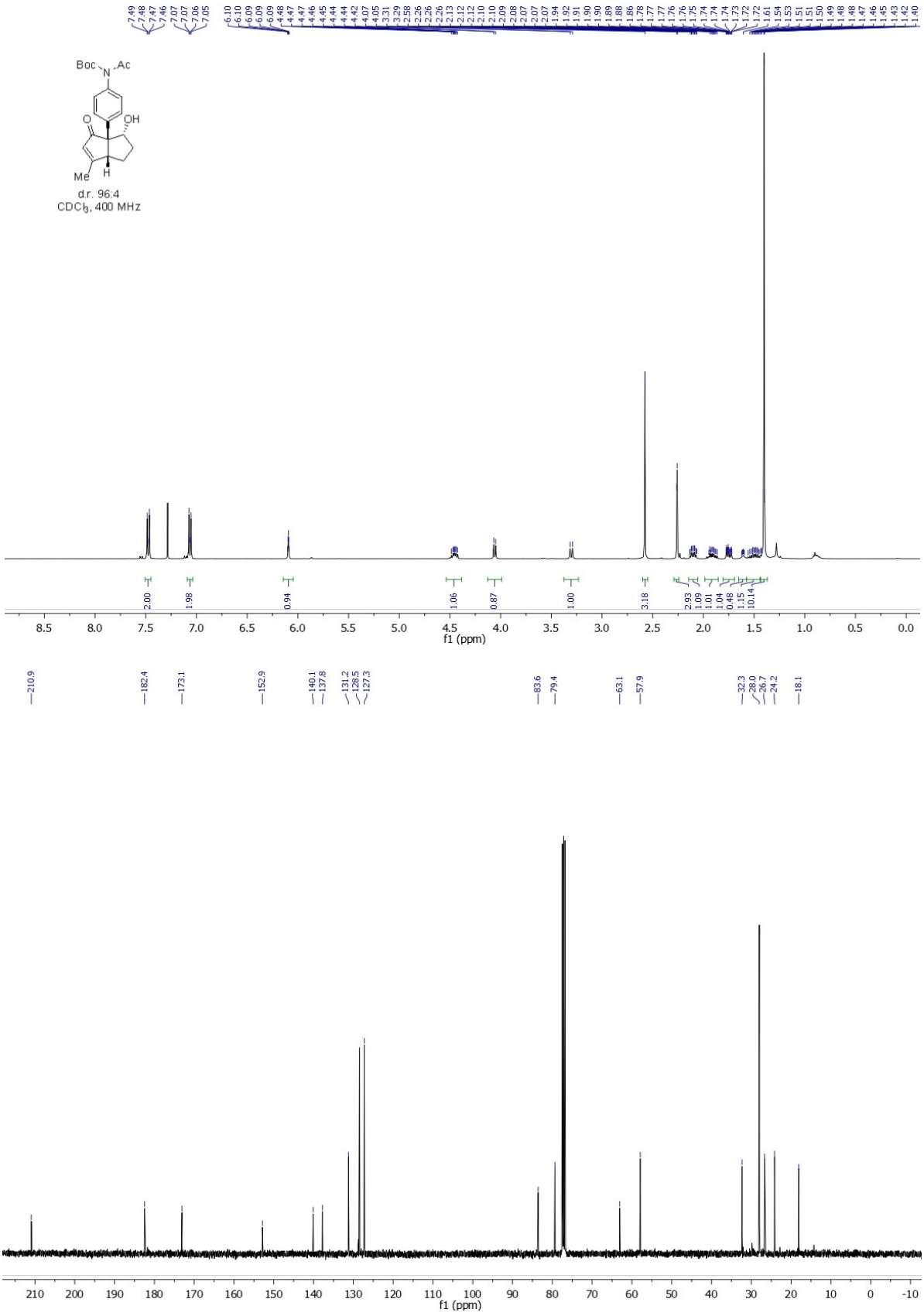

F
O
OH
Me
H
d.r. >20:1
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

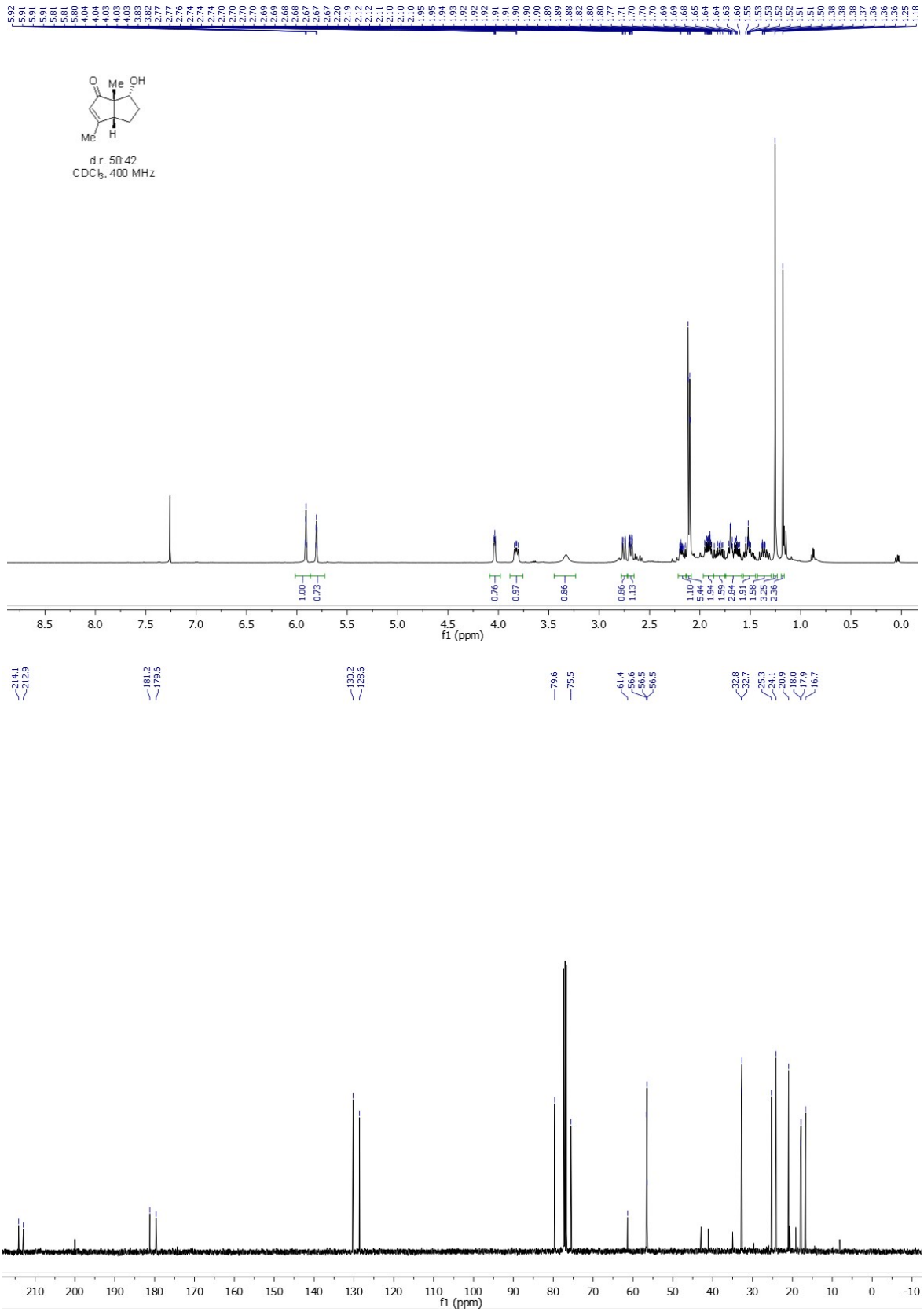

d.r. 89:11
CDCl3, 400 MHz
f1 (ppm)

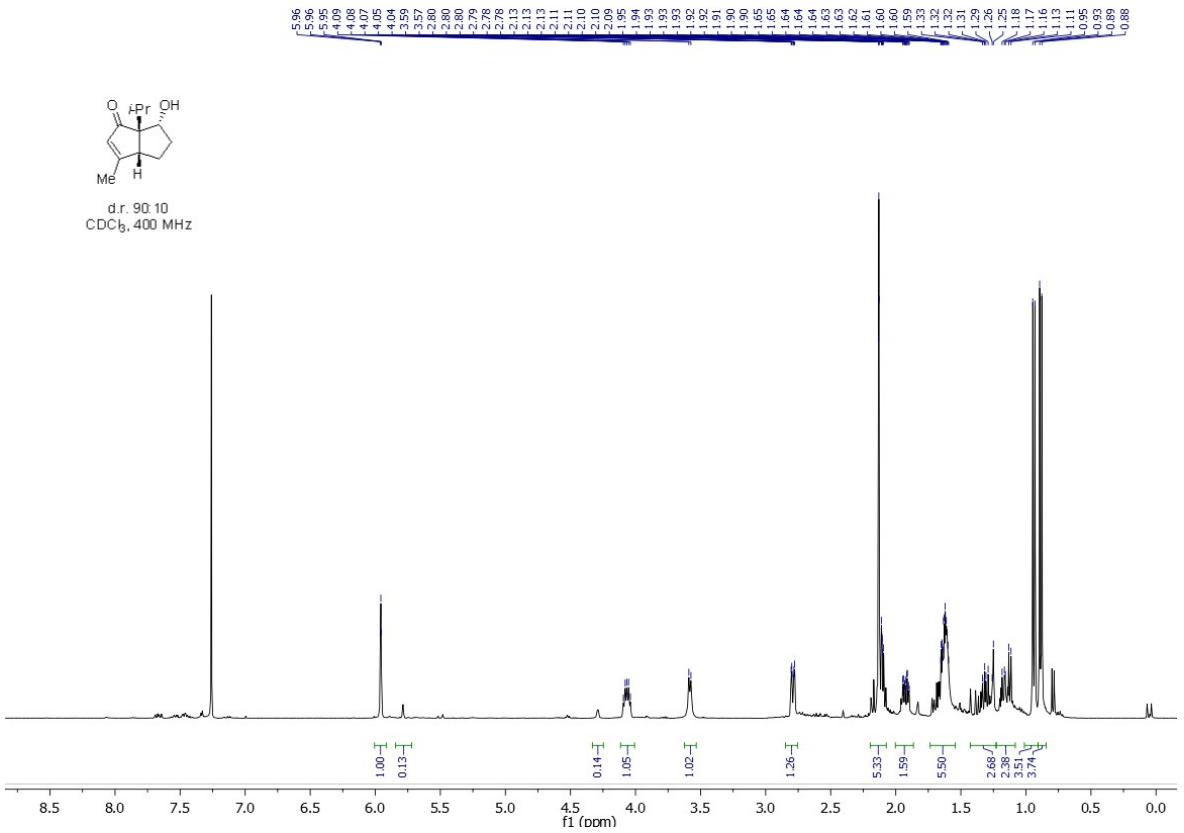

f1 (ppm)

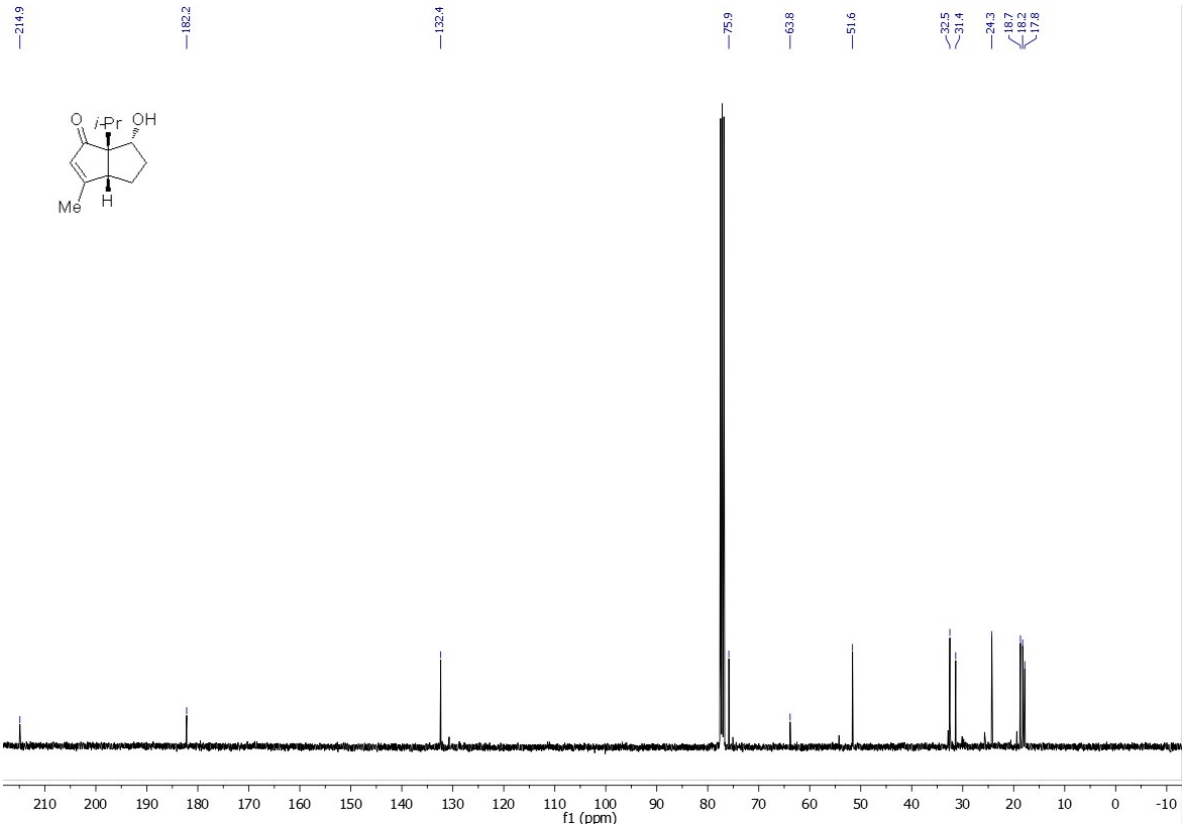

OAc
O
OH
Me
H
d.r. 87:13
CDCl3, 400 MHz
f1 (ppm)

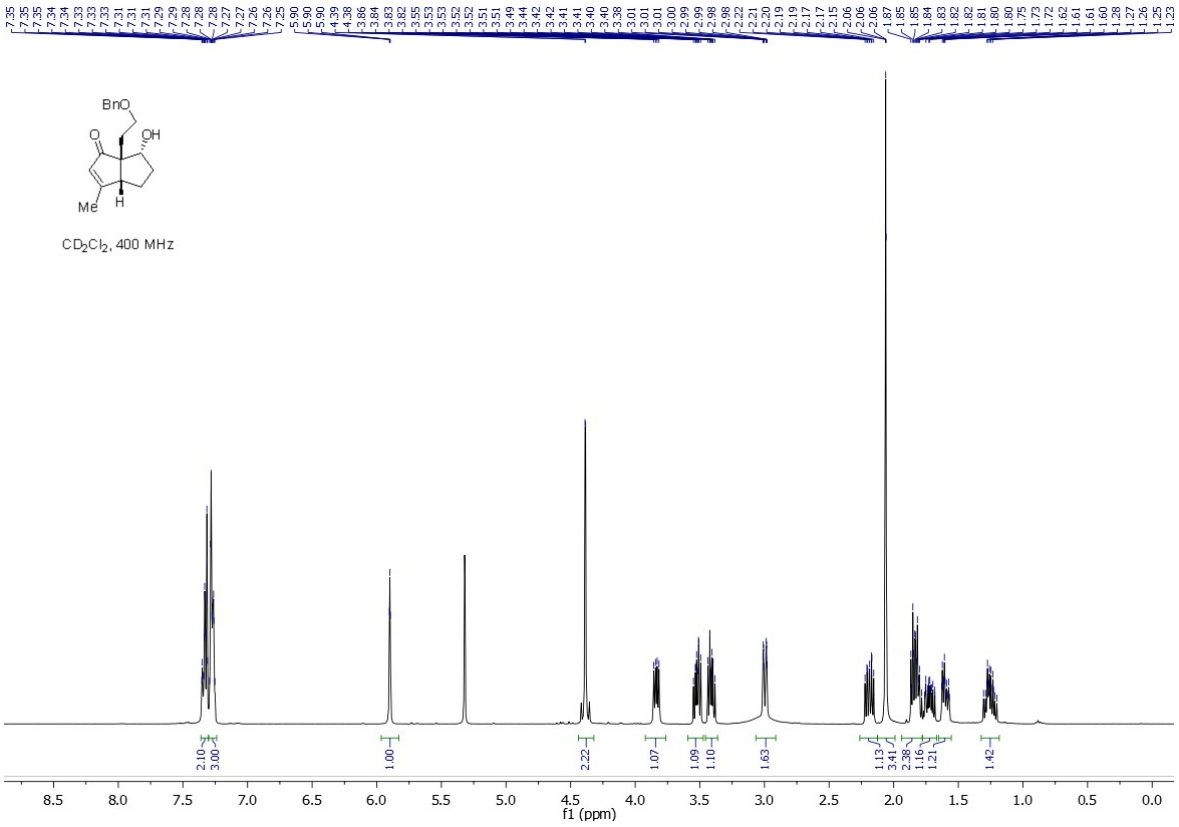

f1 (ppm)

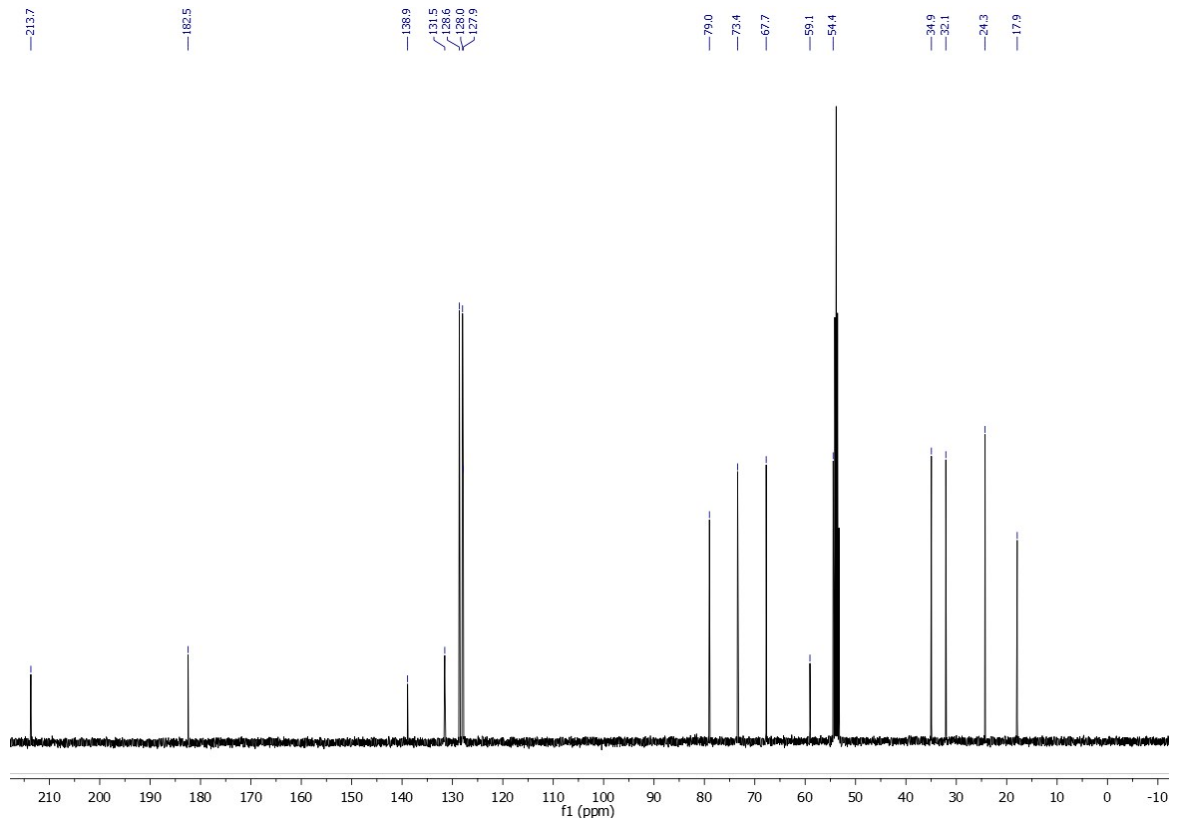

Boc
N
Ac
O
OH
Me
H
d.r. 96:4
CDCl3, 400 MHz
f1 (ppm)
210.9
182.4
173.1
152.9
140.1
137.8
131.2
128.5
127.3
83.6
79.4
63.1
57.9
32.3
28.0
26.7
24.2
18.1

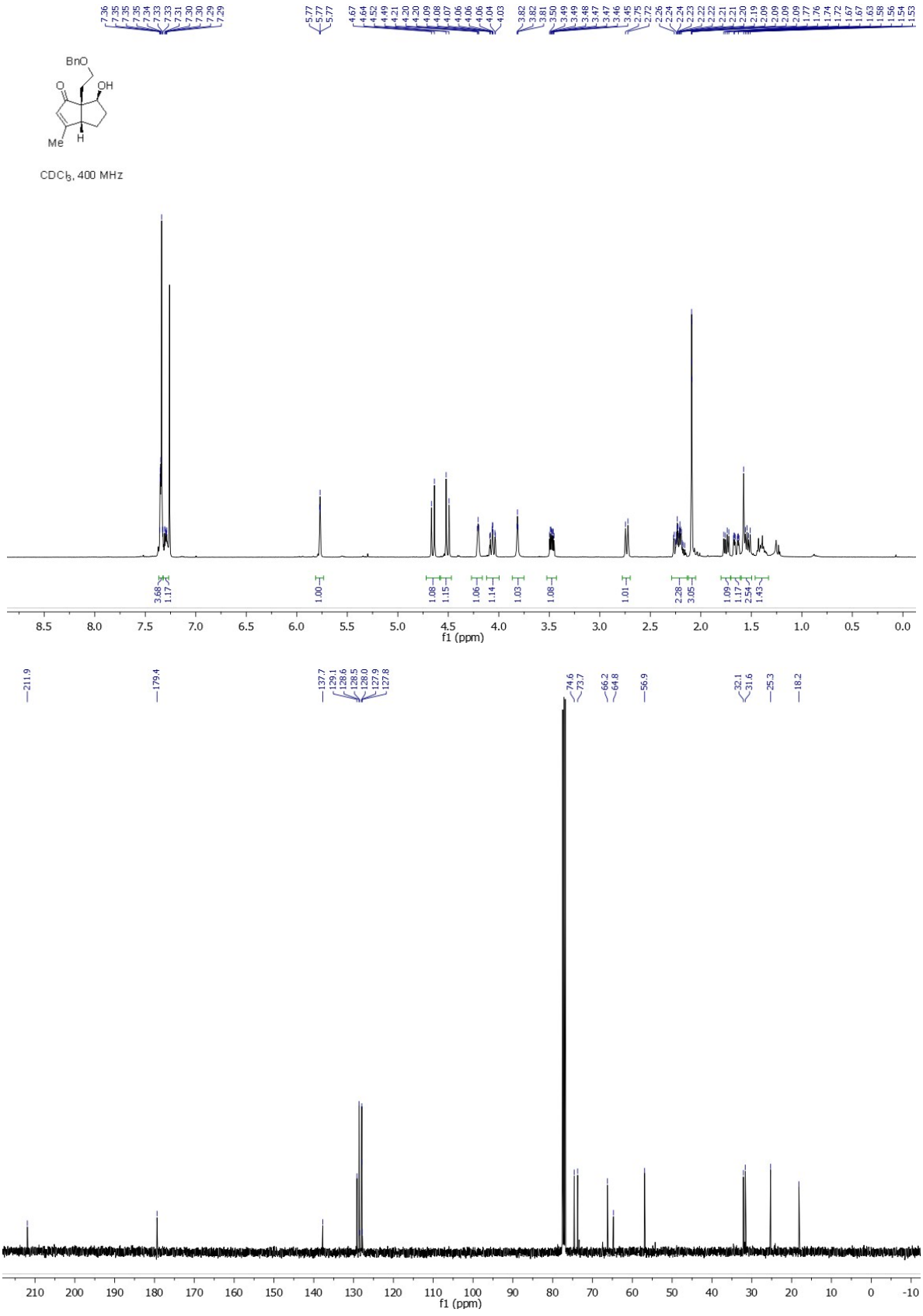

d.r. 58:42
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)


d.r. 90:10
CDCl3, 400 MHz
f1 (ppm)

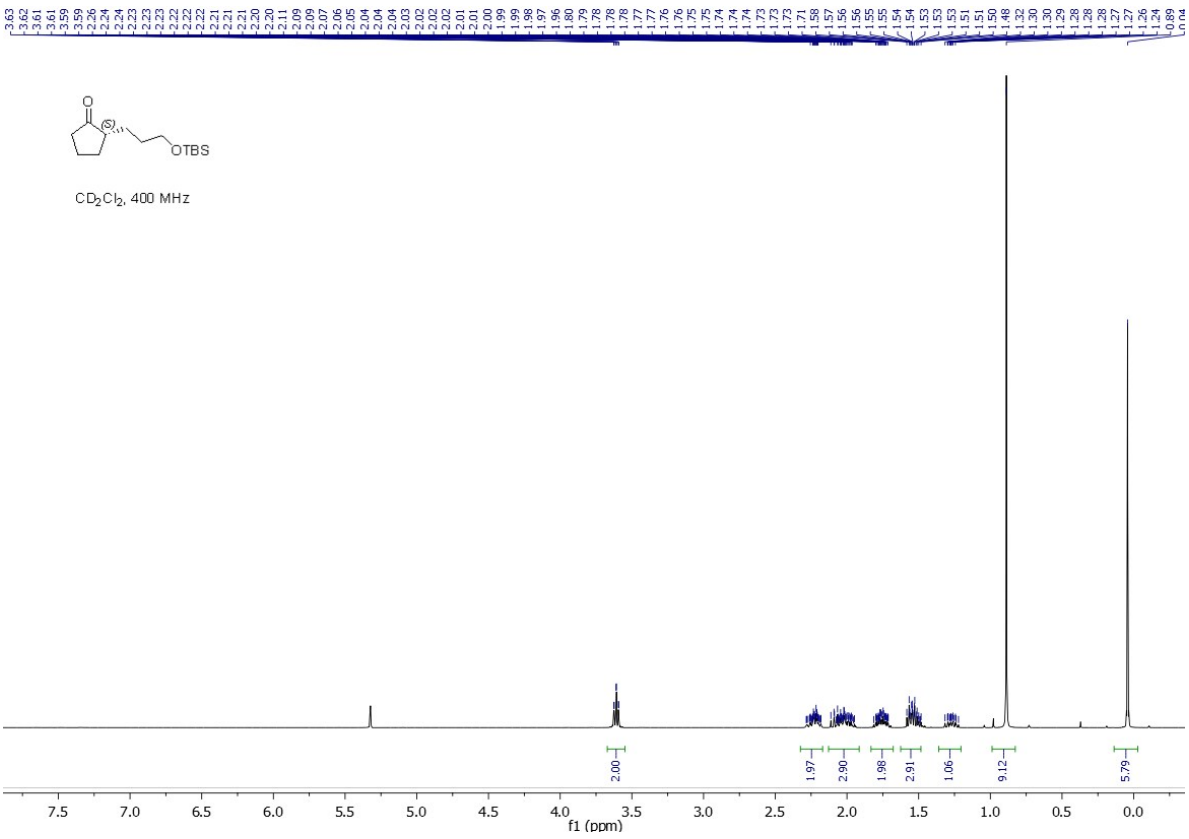

f1 (ppm)

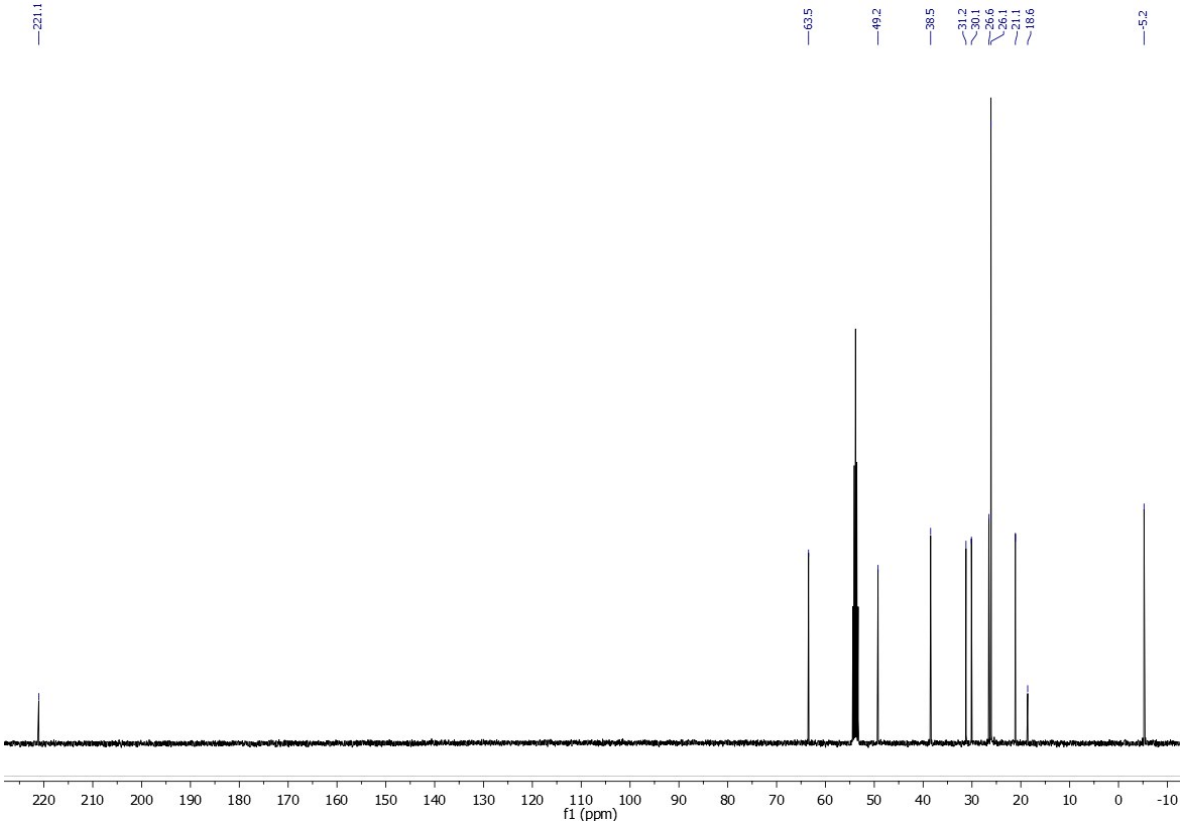

BnO
O
OH
Me
H
CD2Cl2, 400 MHz
f1 (ppm)

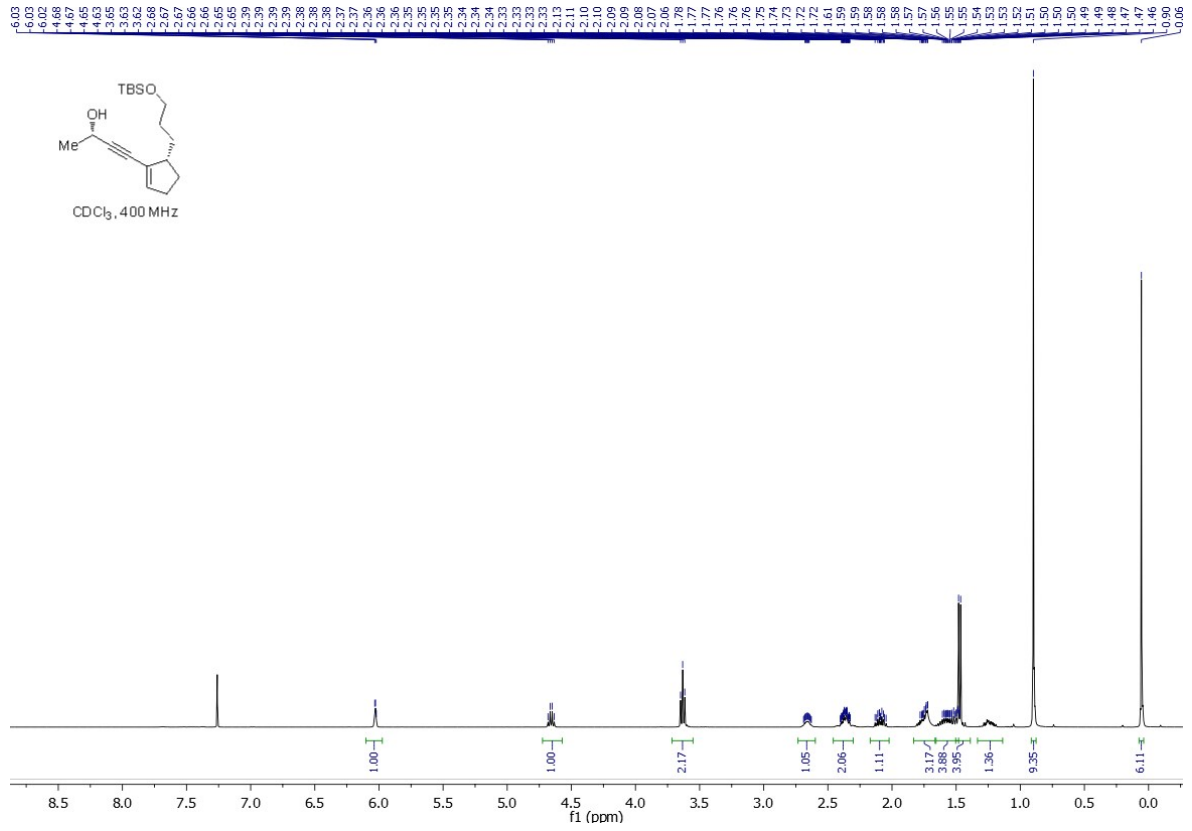

213.7
182.5
138.9
131.5
128.6
128.0
127.9
79.0
73.4
67.7
59.1
54.4
34.9
32.1
24.3
17.9
f1 (ppm)

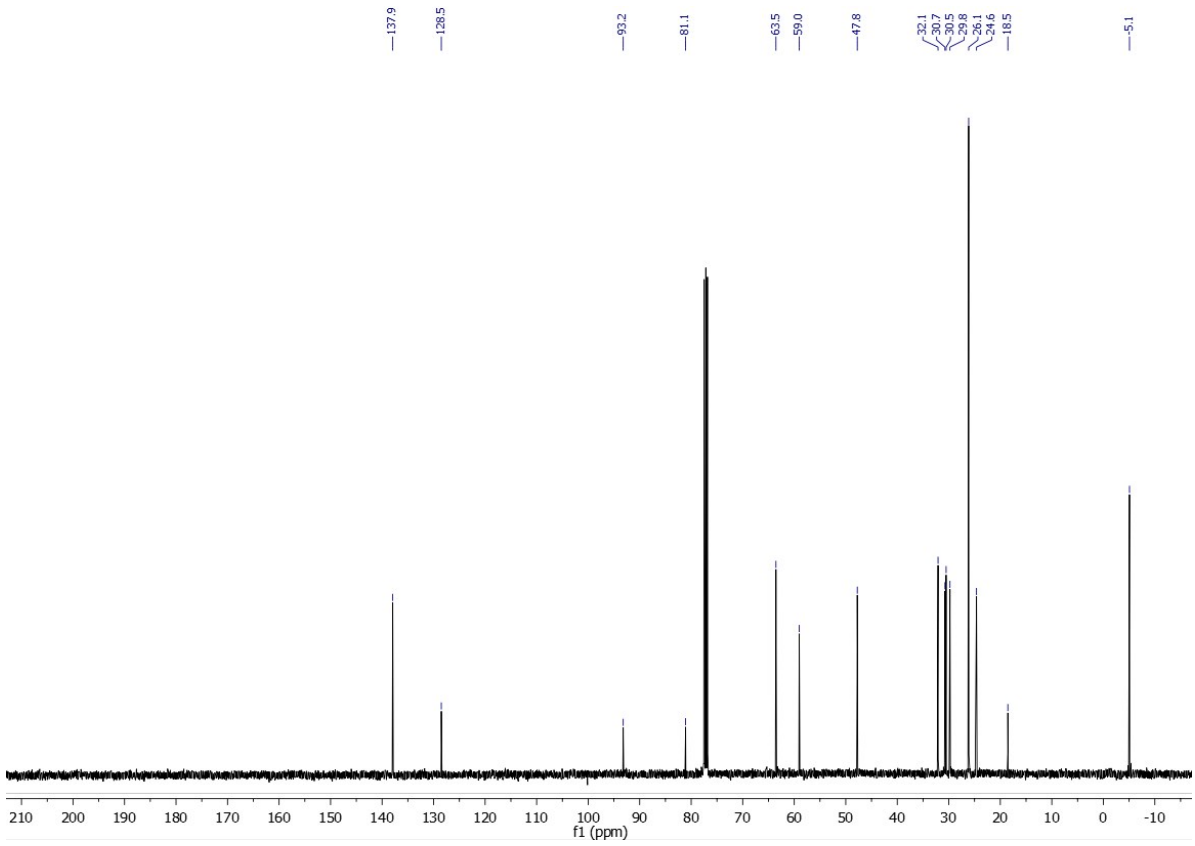

BnO
O
OH
Me
H
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

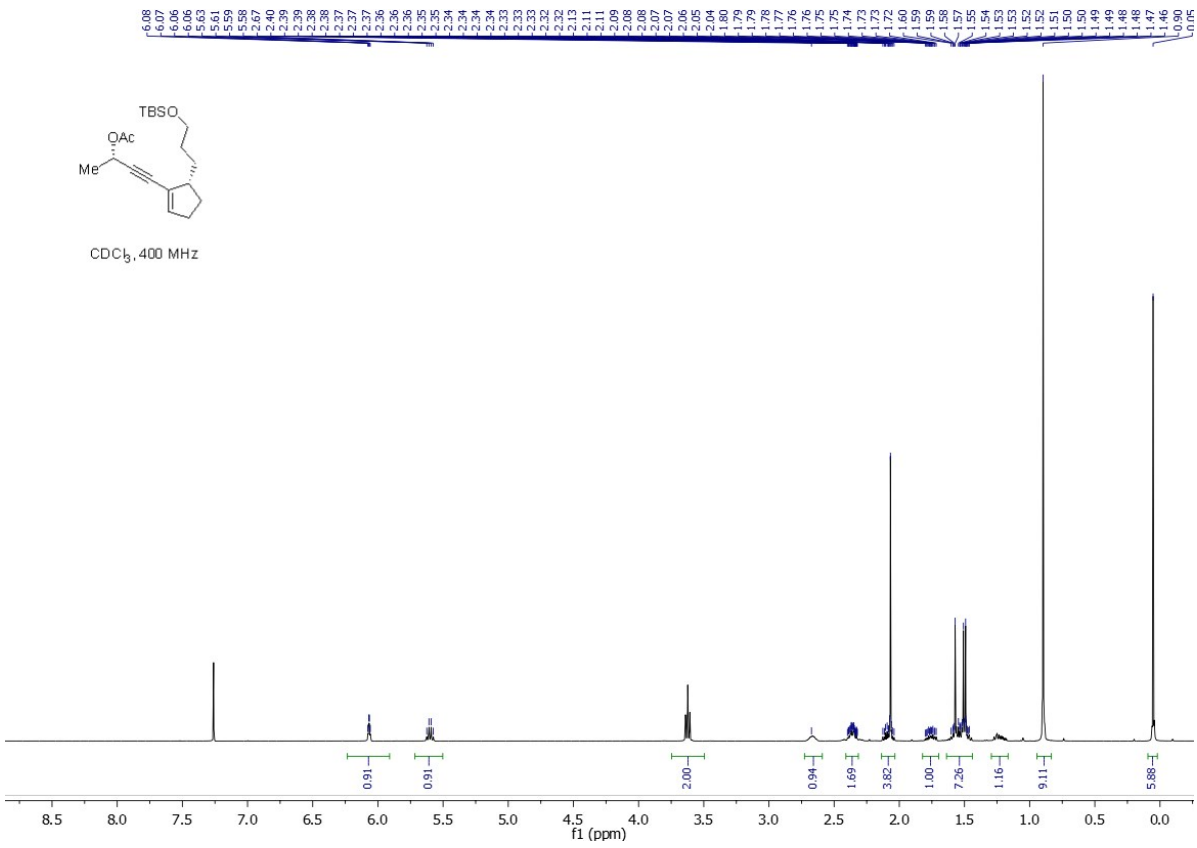
Synthesis of Triquinane 7

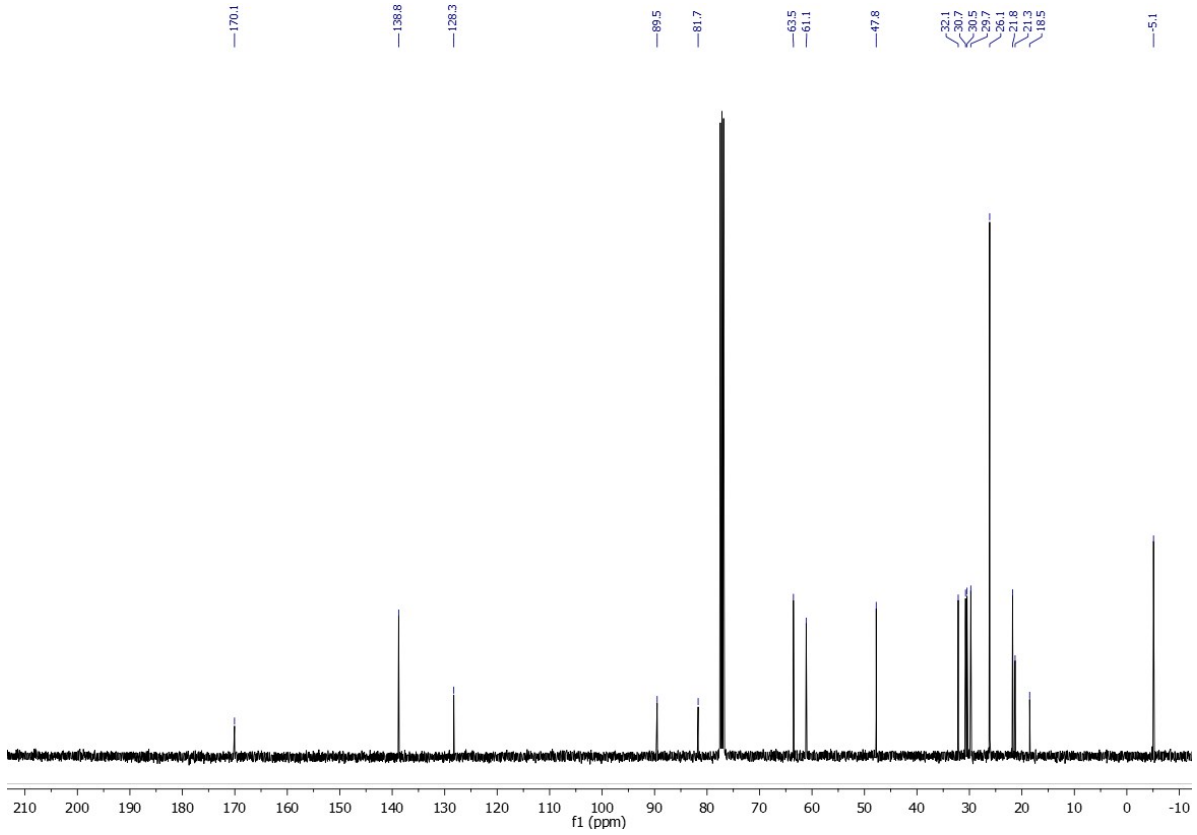


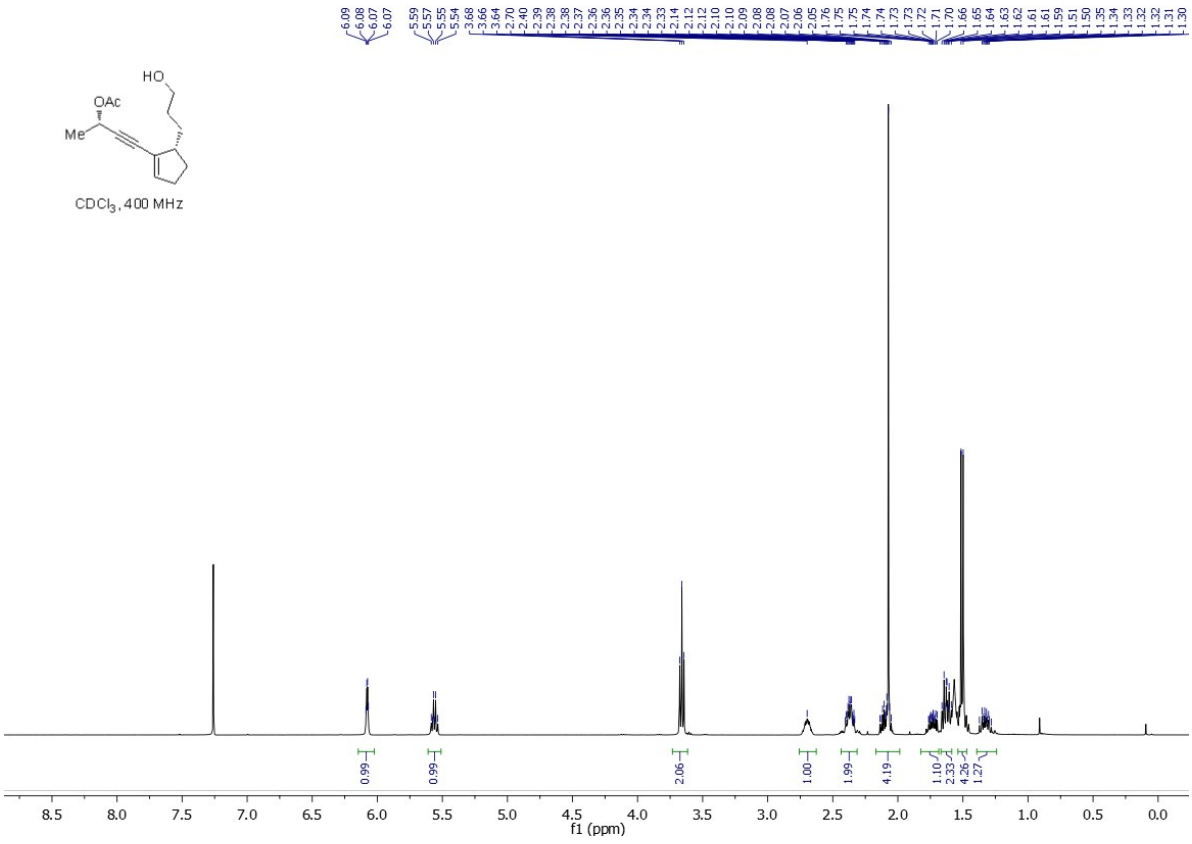


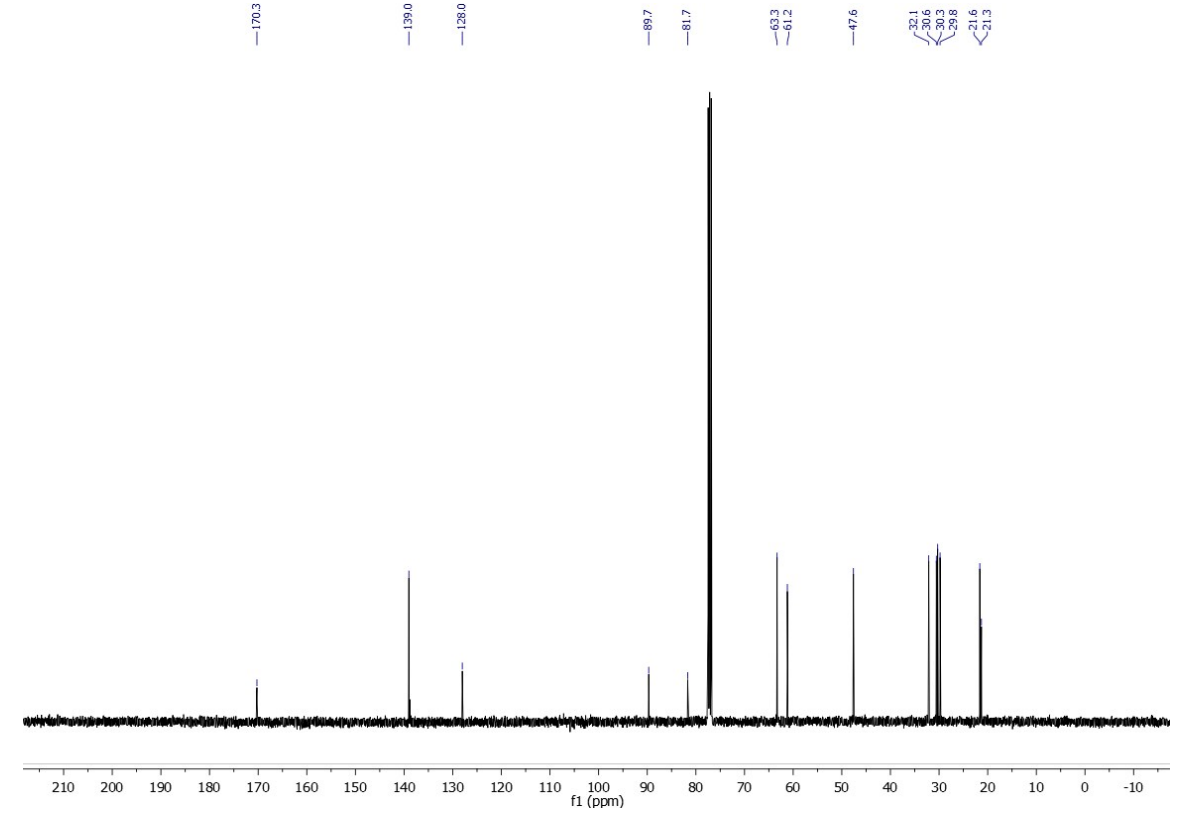

TBSO
OH
Me
CDCl3, 400 MHz
f1 (ppm)

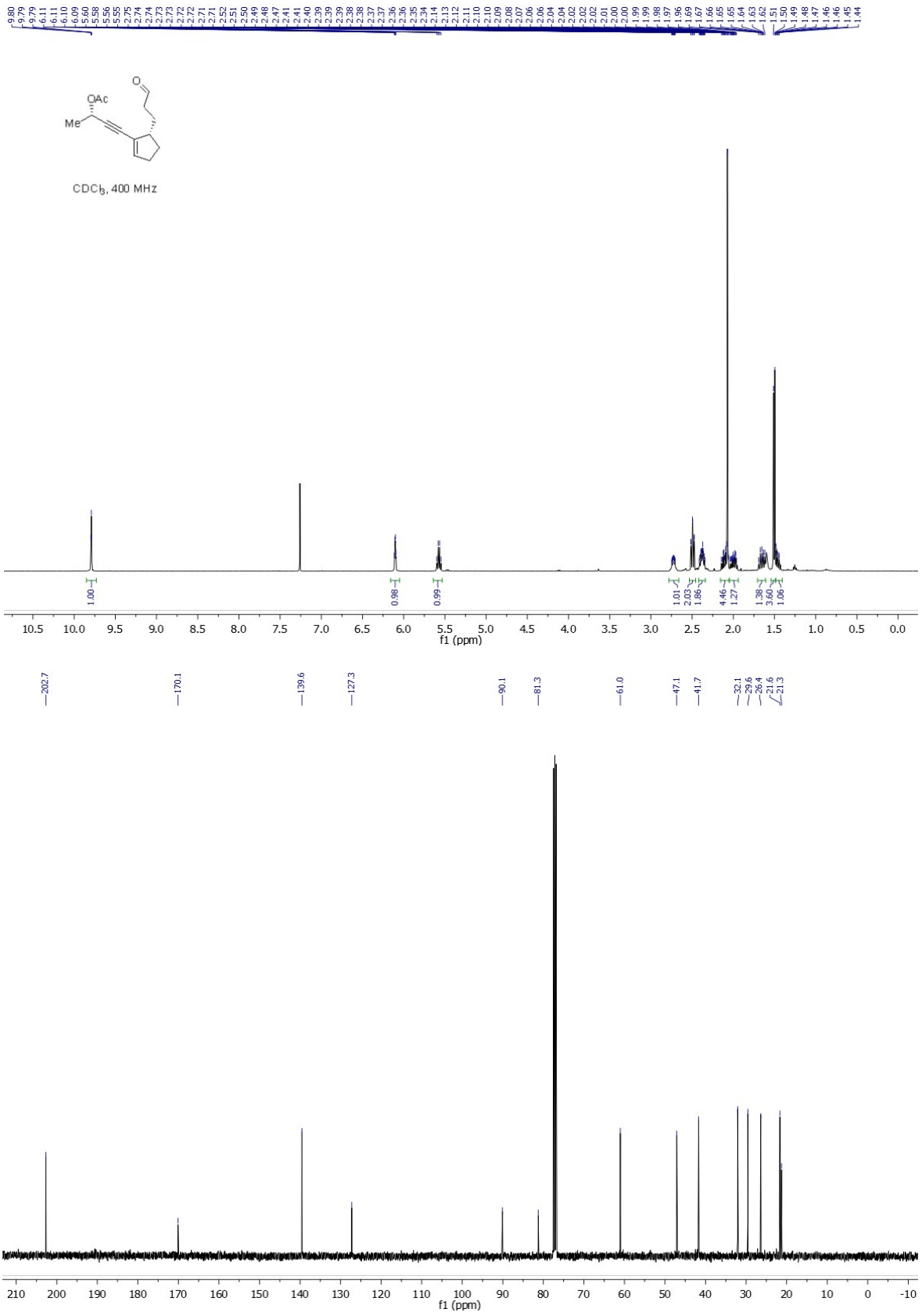

137.9
128.5
93.2
81.1
63.5
59.0
47.8
32.1
30.7
30.5
29.8
26.1
24.6
18.5
-5.1
f1 (ppm)

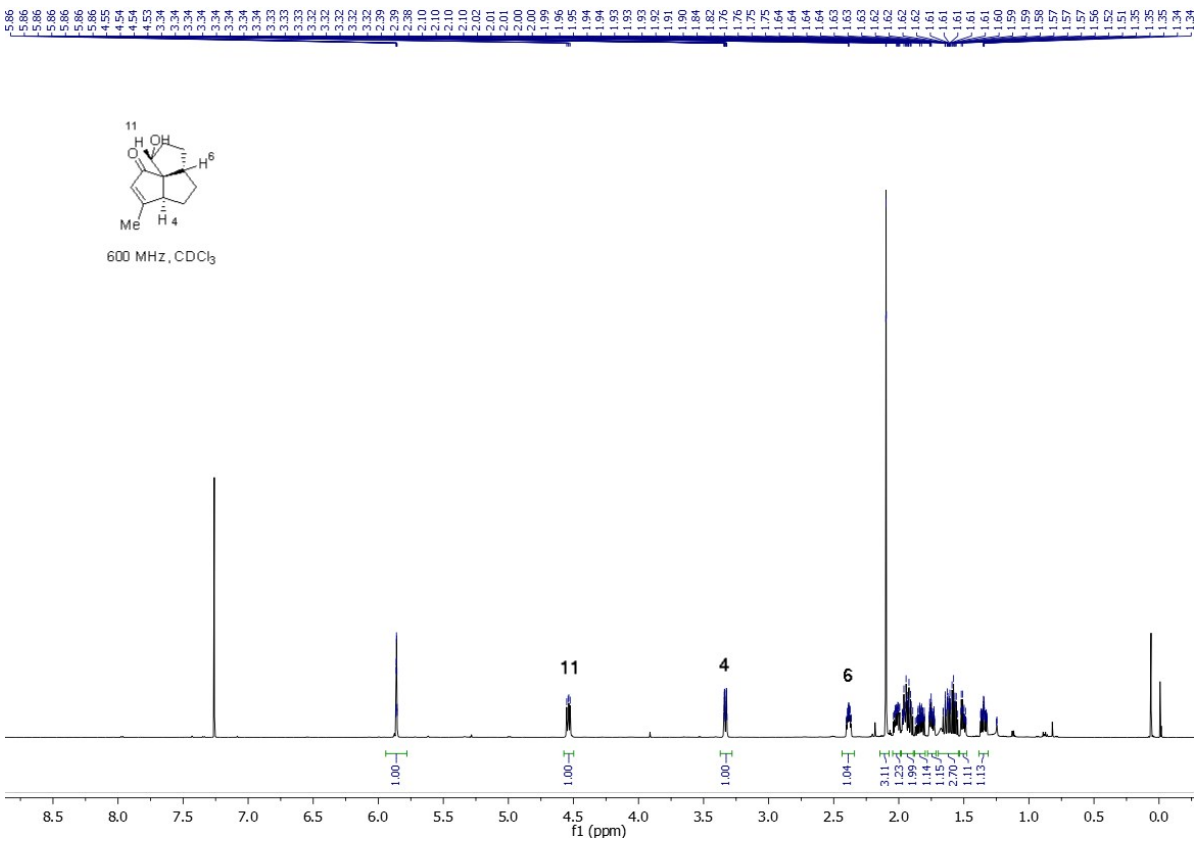

TBSO
OAc
Me
CDCl3, 400 MHz
f1 (ppm)

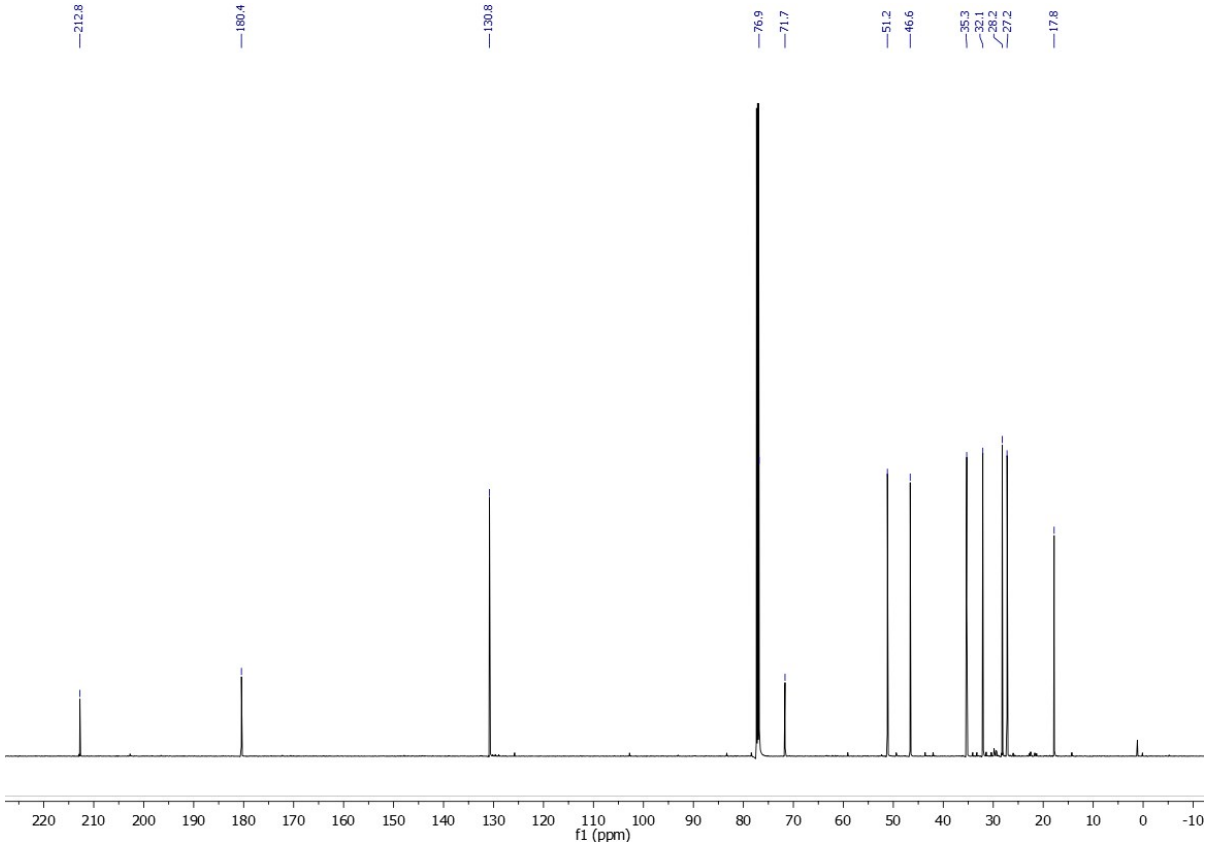

f1 (ppm)

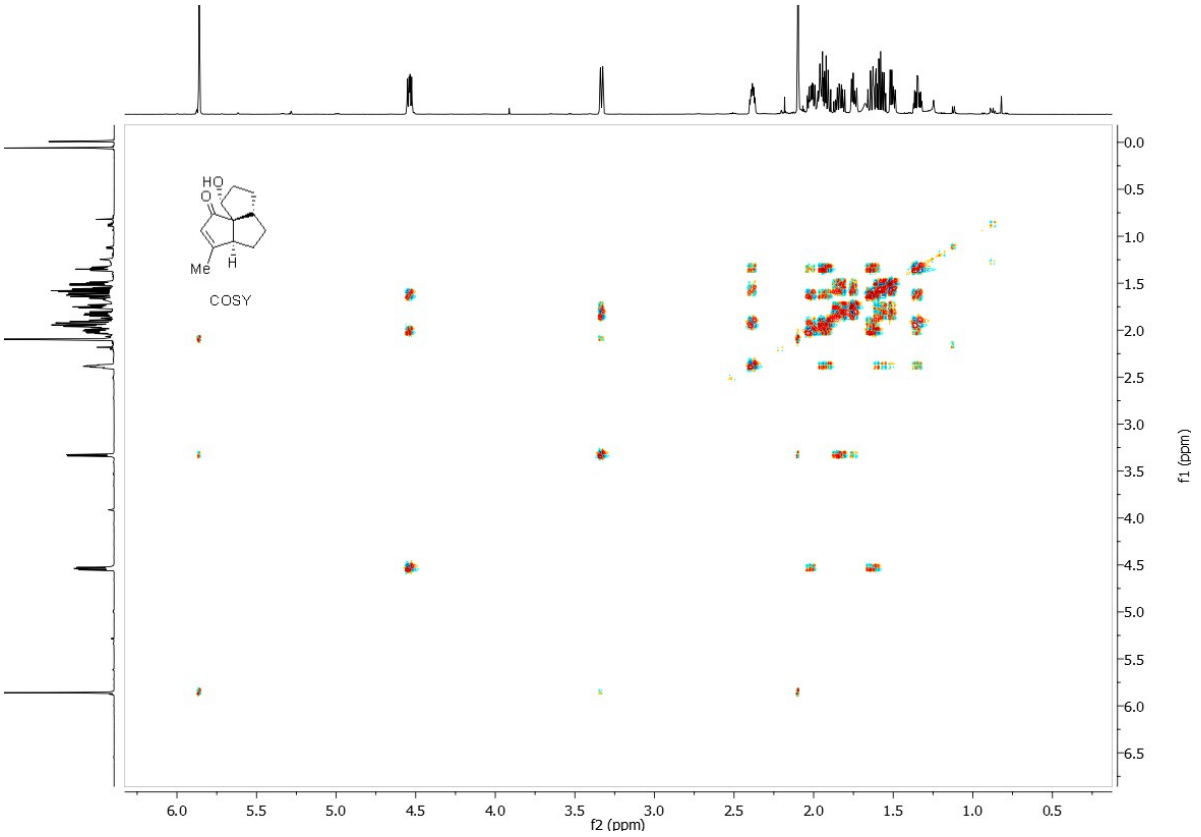

HO
OAc
Me
CDCl3, 400 MHz
f1 (ppm)

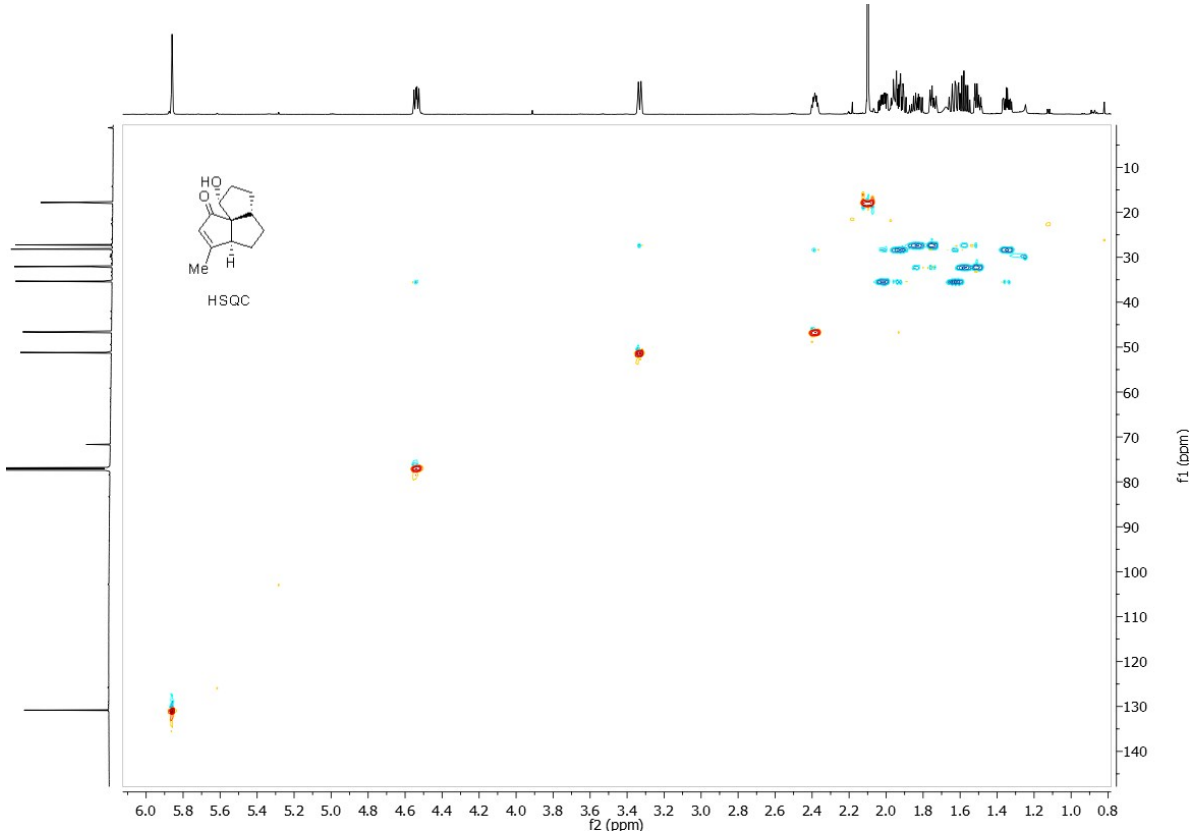

f1 (ppm)

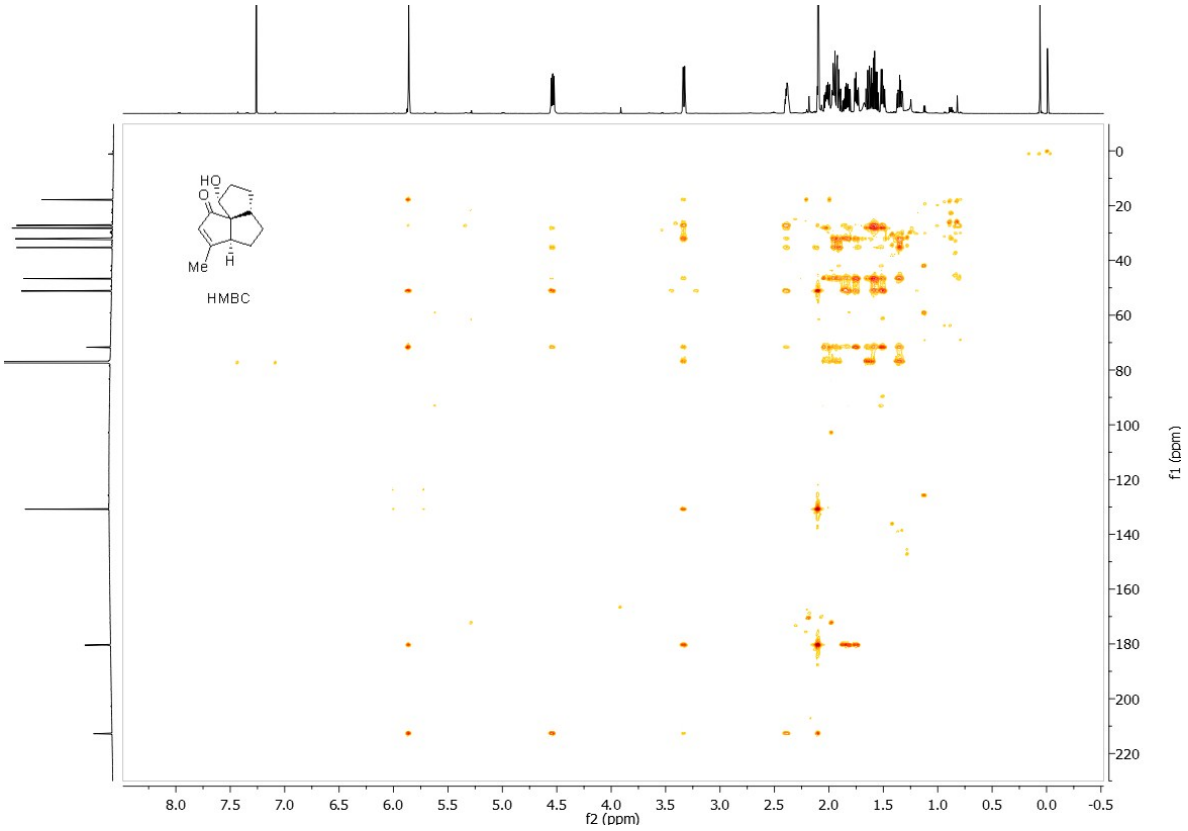

OAc
Me
O
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)

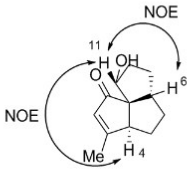

11
H OH
O
H6
Me
H 4
600 MHz, CDCl3
11
4
6
f1 (ppm)


212.8
180.4
130.8
76.9
71.7
51.2
46.6
35.3
32.1
28.2
27.2
17.8
f1 (ppm)

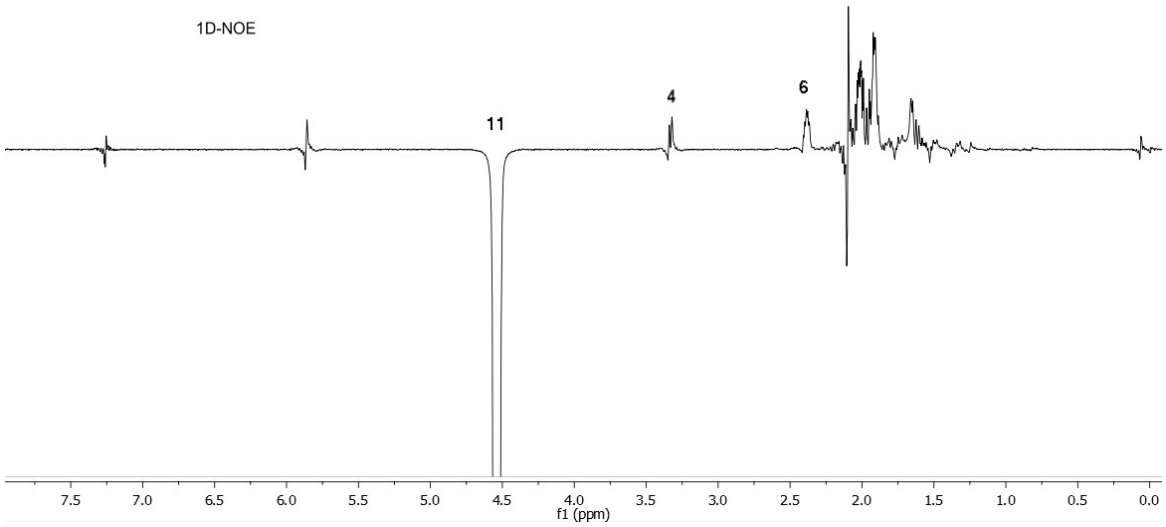

HO
O
Me
H
COSY
f2 (ppm)
f1 (ppm)

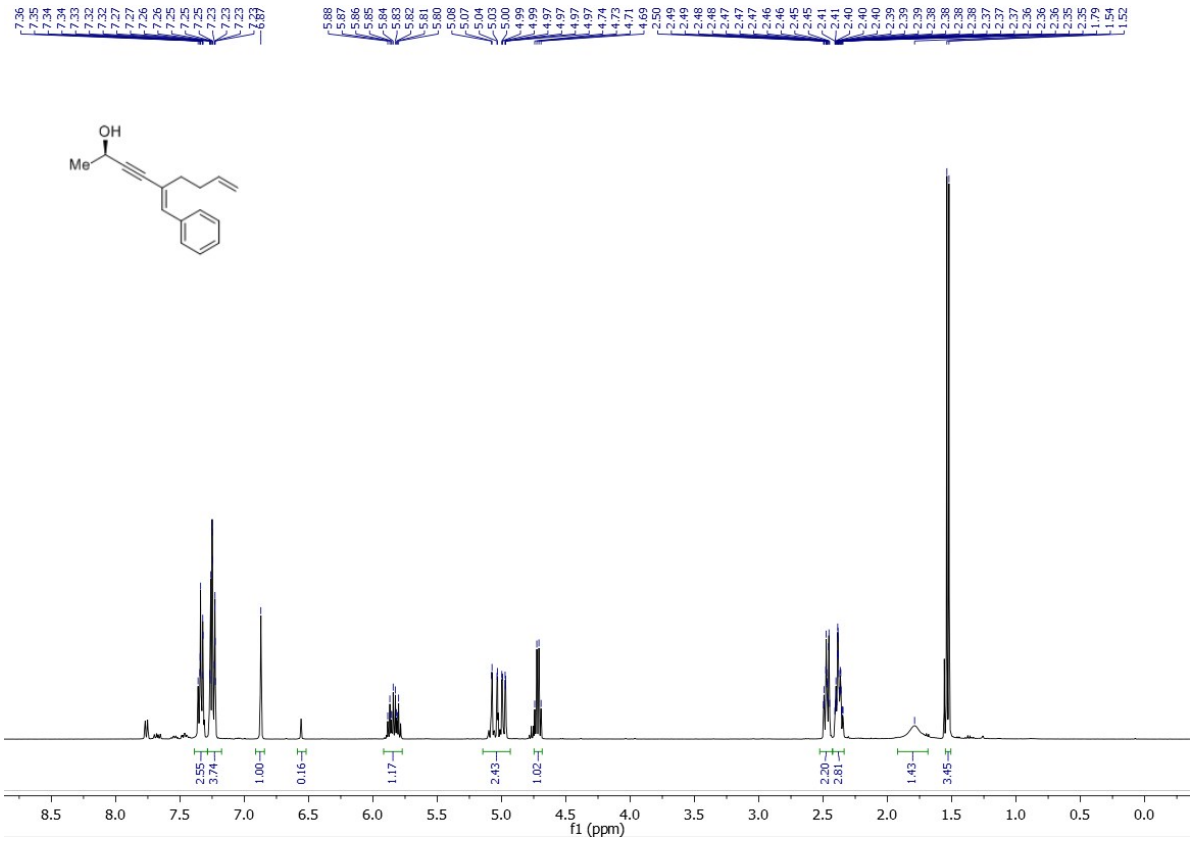

HO
O
Me
H
HSQC
f2 (ppm)
f1 (ppm)

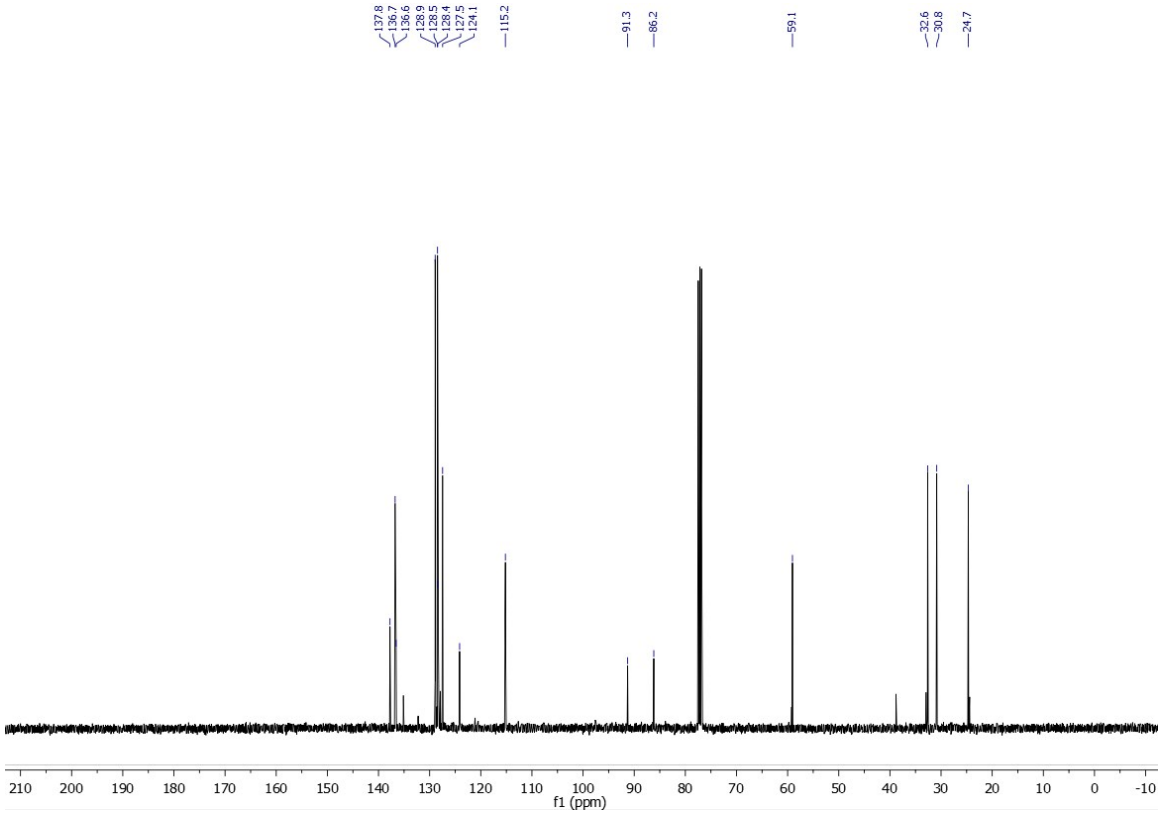


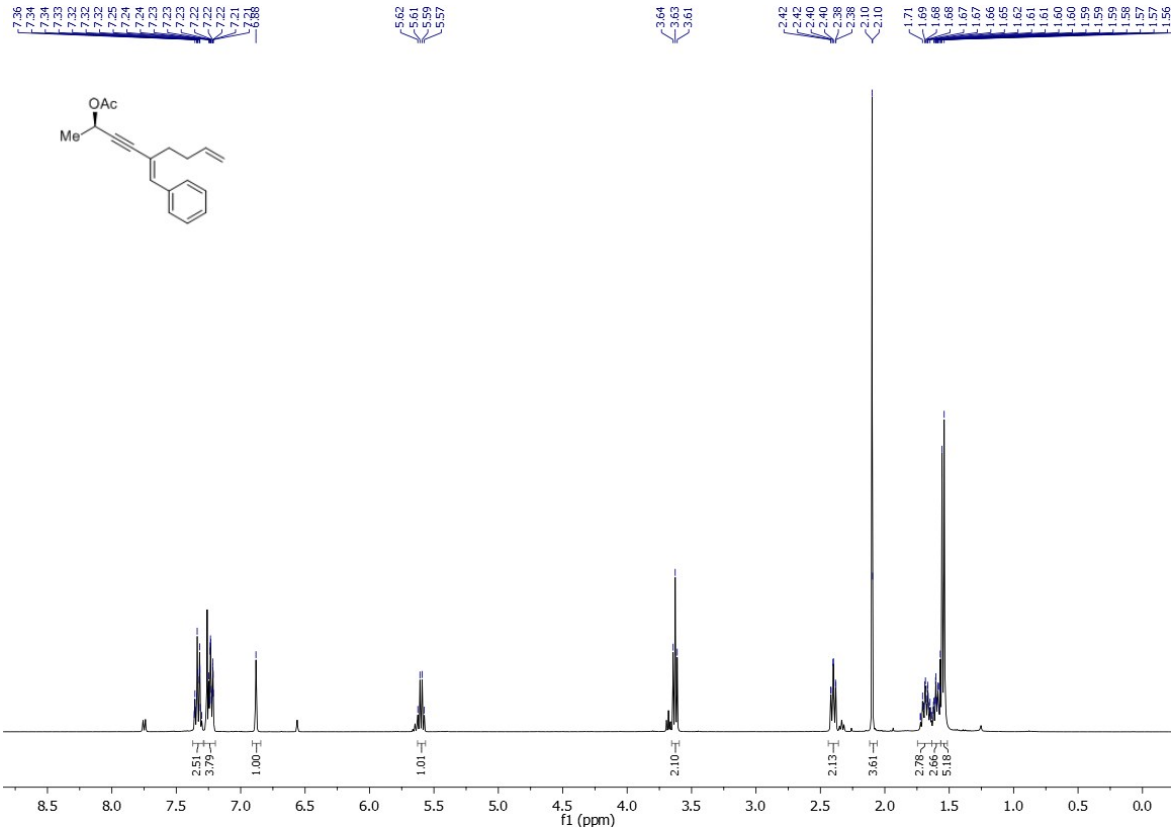


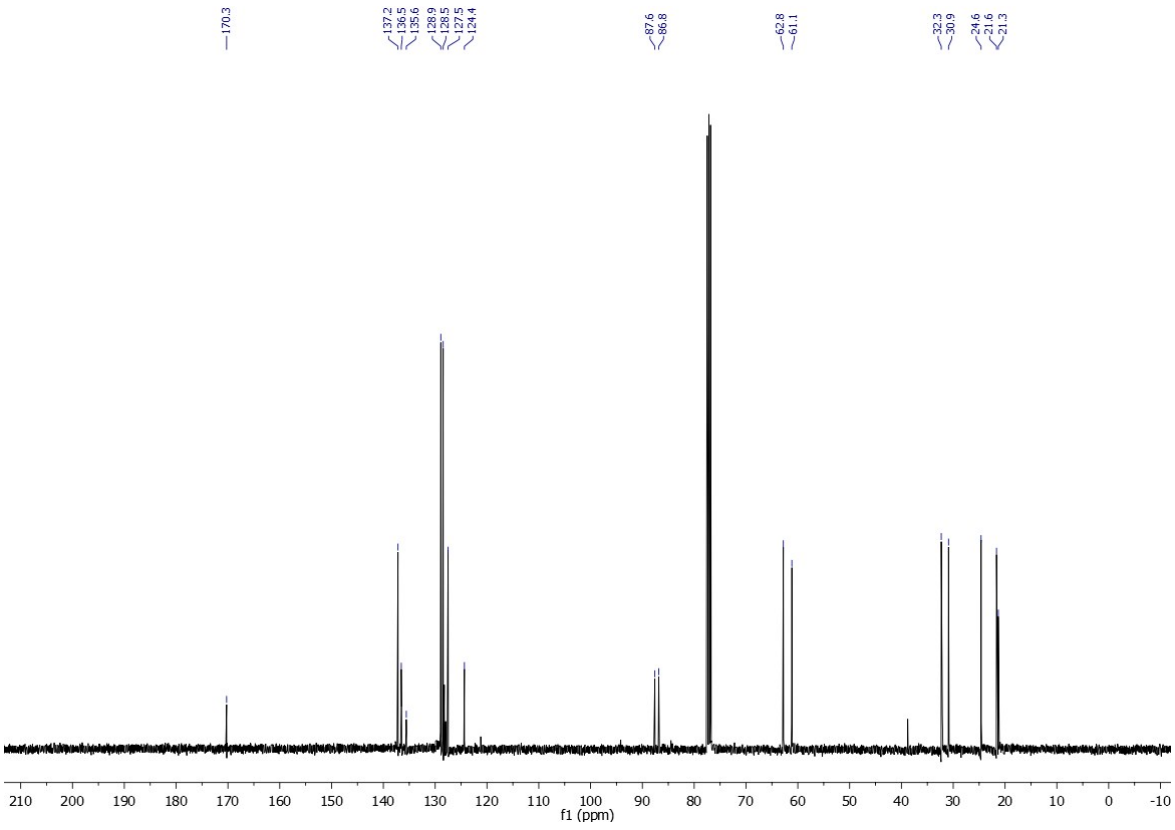
1D-NOE

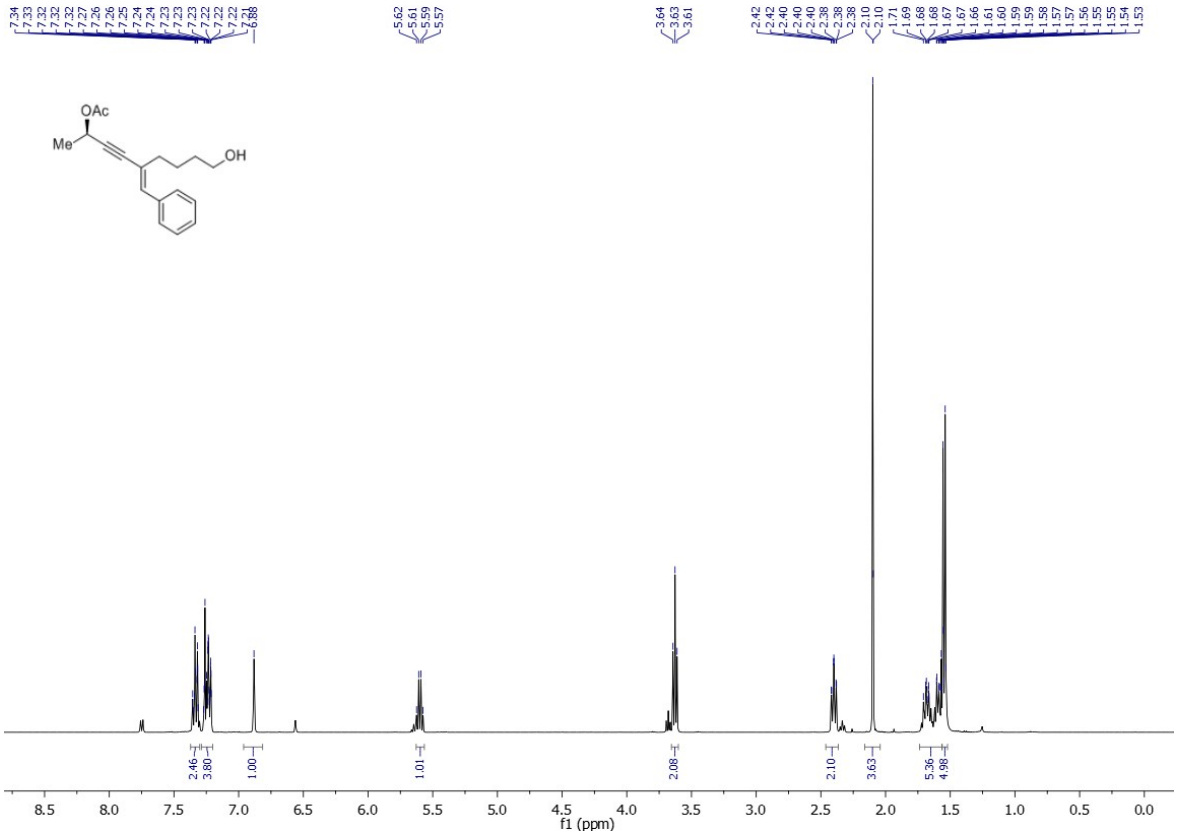


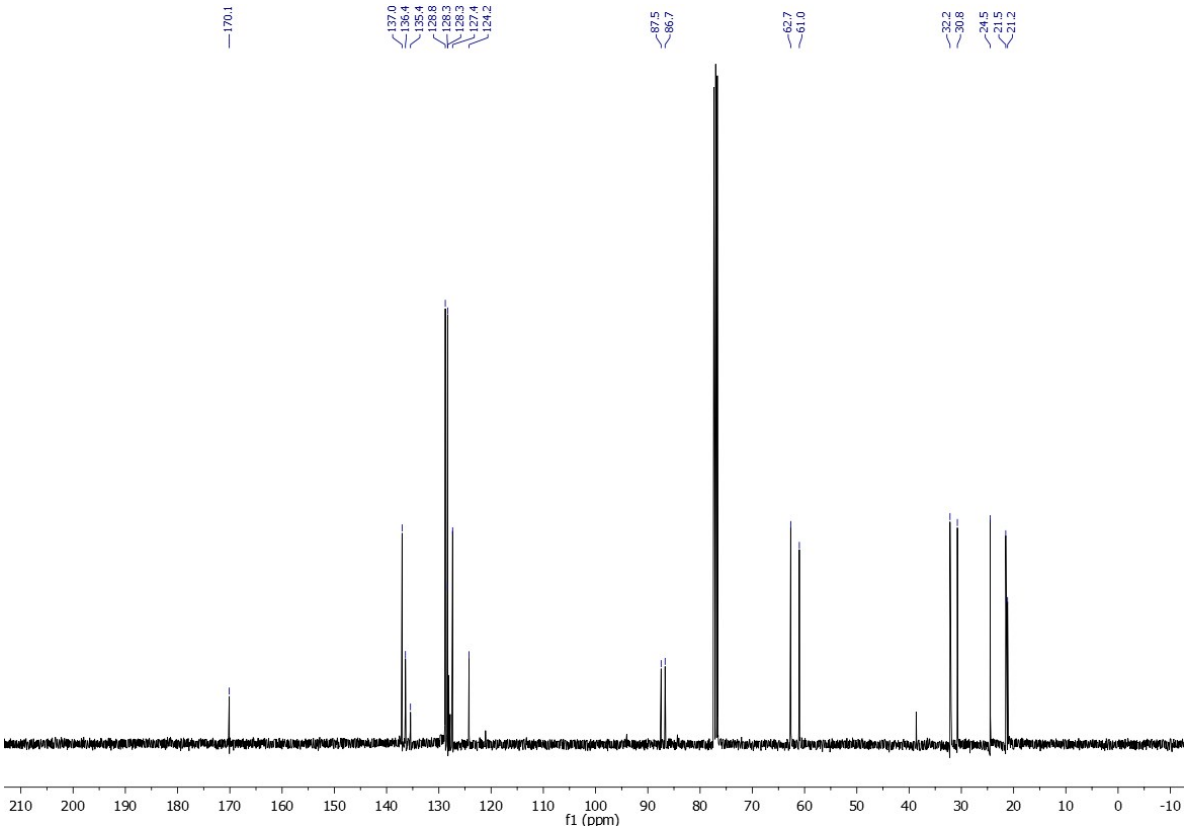

OH
Me
f1 (ppm)

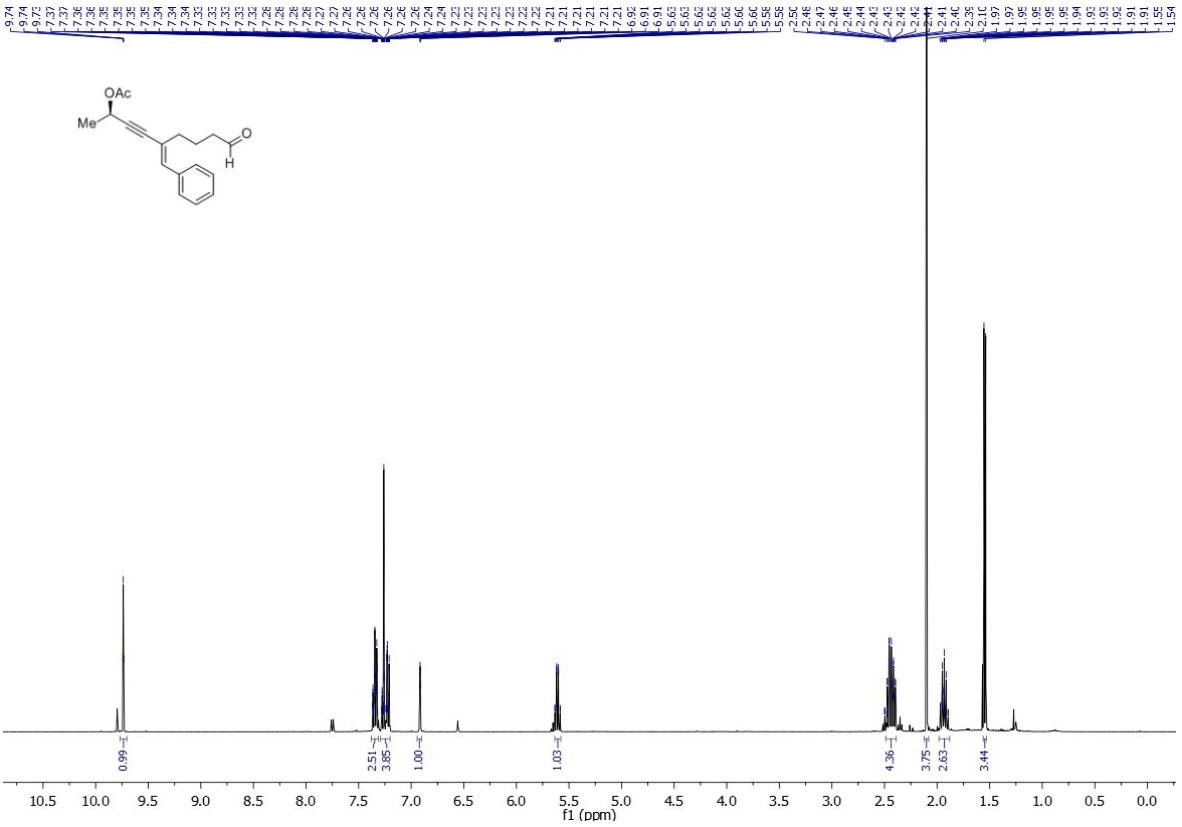

f1 (ppm)


OAc
Me
f1 (ppm)

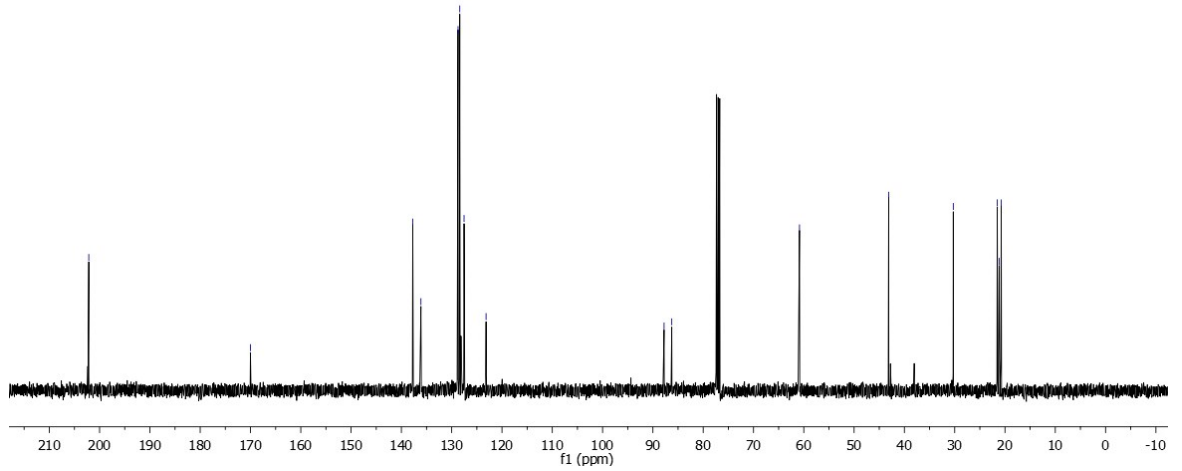

f1 (ppm)

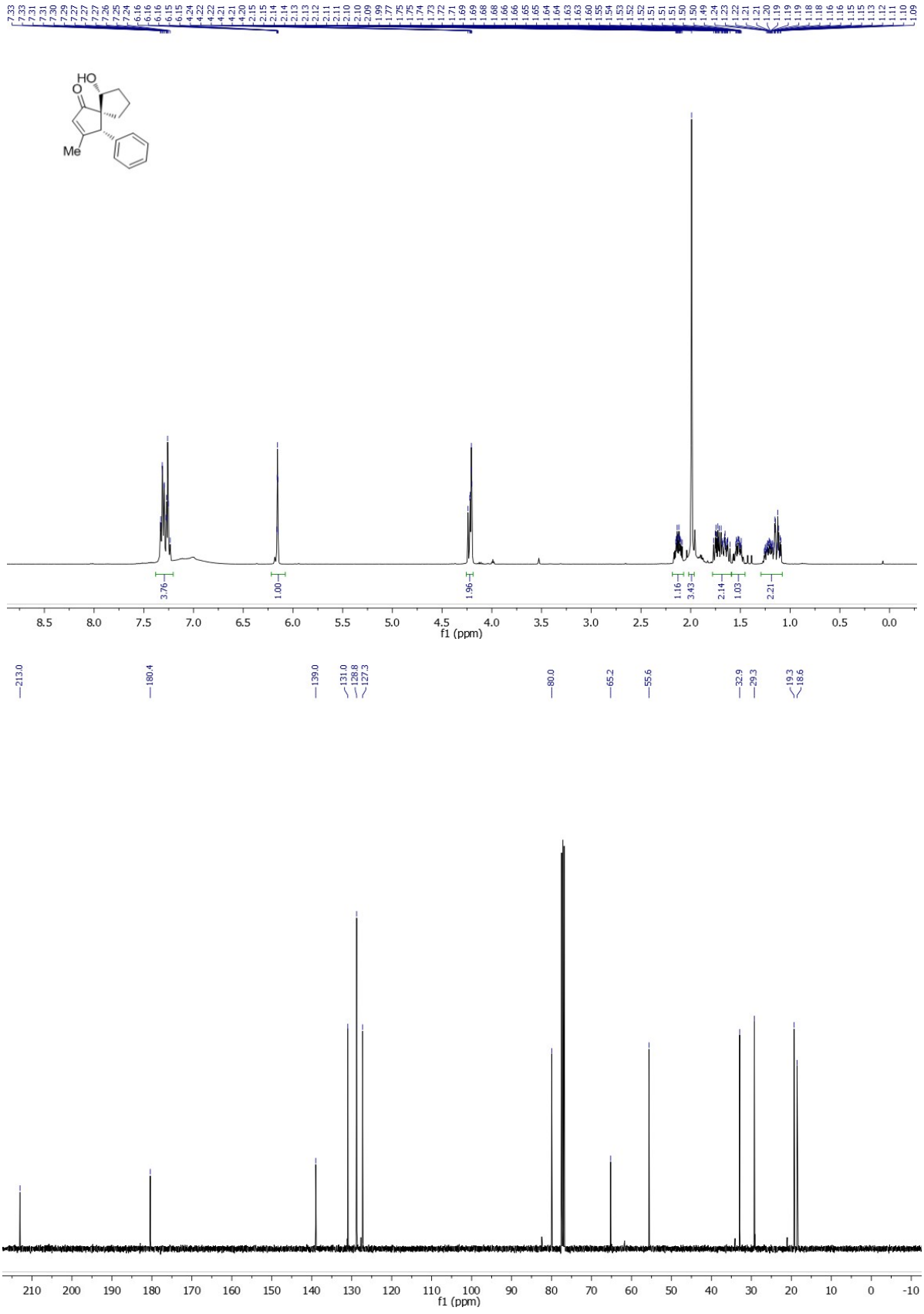

OAc
Me
OH
f1 (ppm)


f1 (ppm)

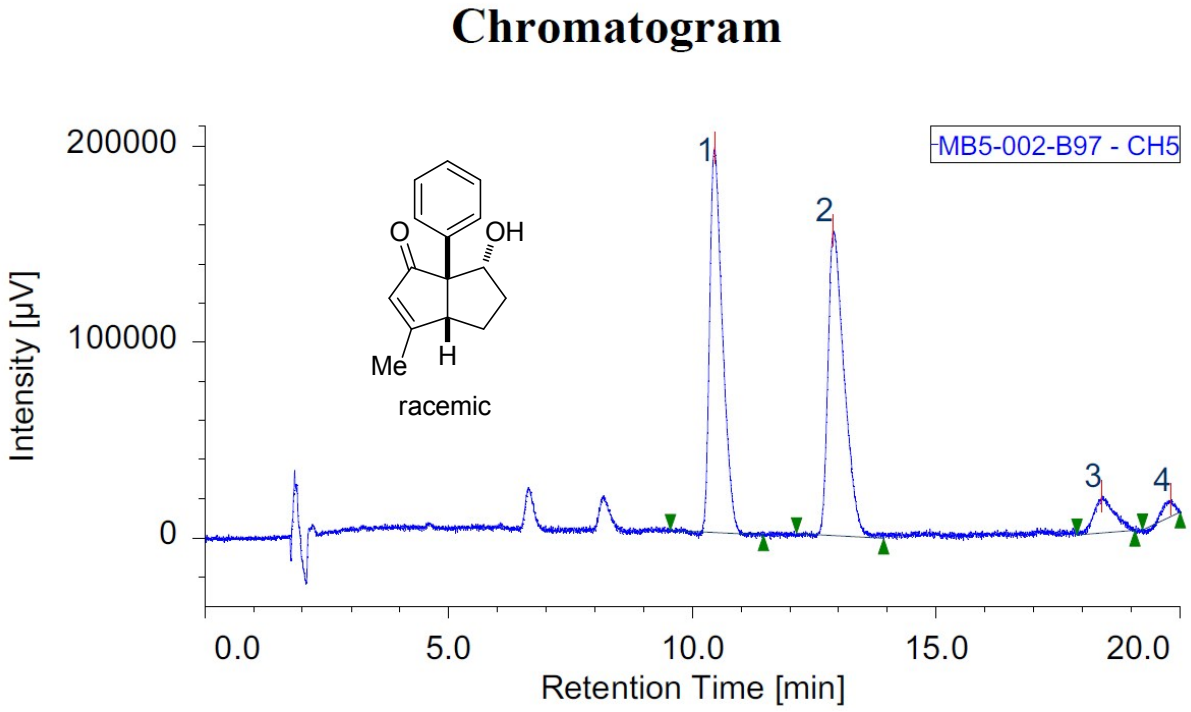

OAc
Me
O
H
0.99
2.51
3.85
1.00
1.03
4.36
3.75
2.63
3.44
f1 (ppm)


202.2
170.0
137.7
136.1
128.7
128.4
127.5
123.2
87.8
86.2
60.9
43.1
30.3
21.5
21.2
20.7

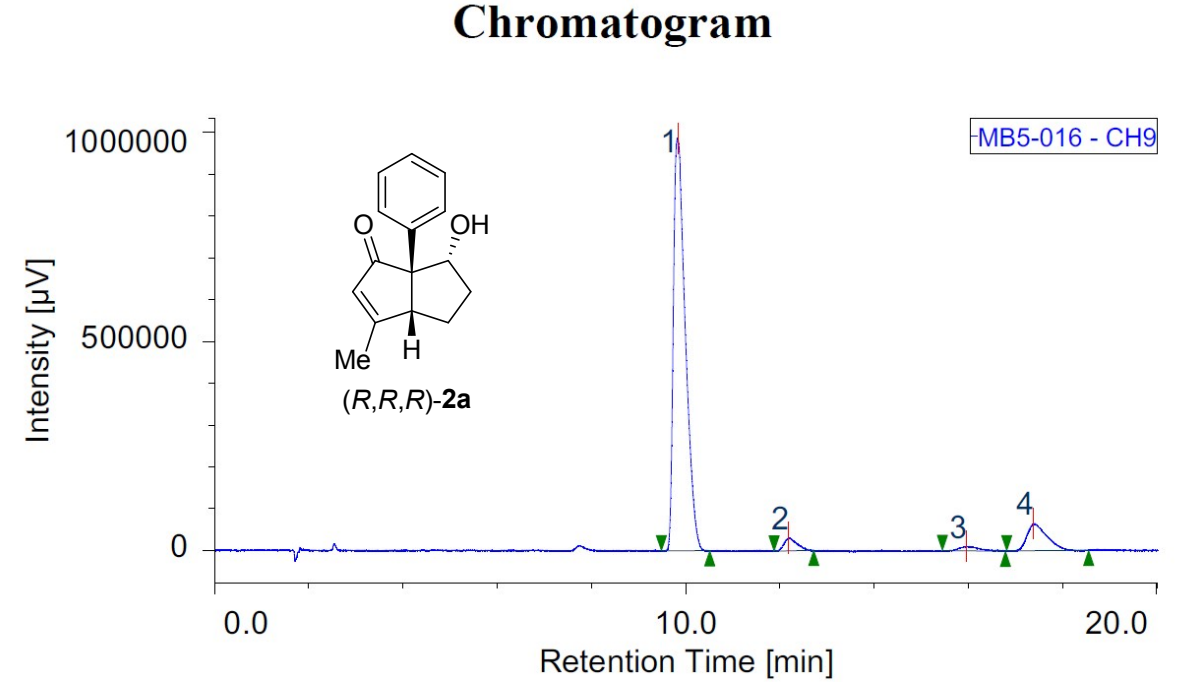

f1 (ppm)


HO
O
Me
3.76
1.00
1.96
1.16
3.43
2.14
1.03
2.21
f1 (ppm)
213.0
180.4
139.0
131.0
128.8
127.3
80.0
65.2
55.6
32.9
29.3
19.3
18.6
f1 (ppm)

8. SFC Traces

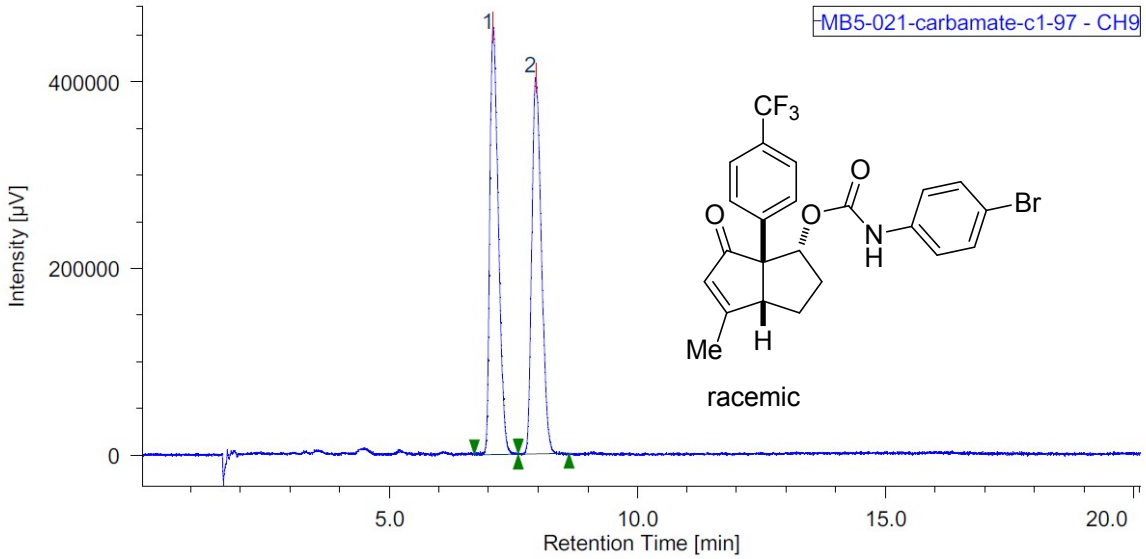


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	5	10.453	3546651	196673	45.063	51.718	N/A	7842	4.520	1.489
2	Unknown	5	12.880	3624120	156017	46.047	41.027	N/A	7267	7.761	1.694
3	Unknown	5	18.393	546574	18979	6.945	4.991	N/A	8047	2.044	1.144
4	Unknown	5	19.813	153167	8613	1.946	2.265	N/A	19130	N/A	0.785



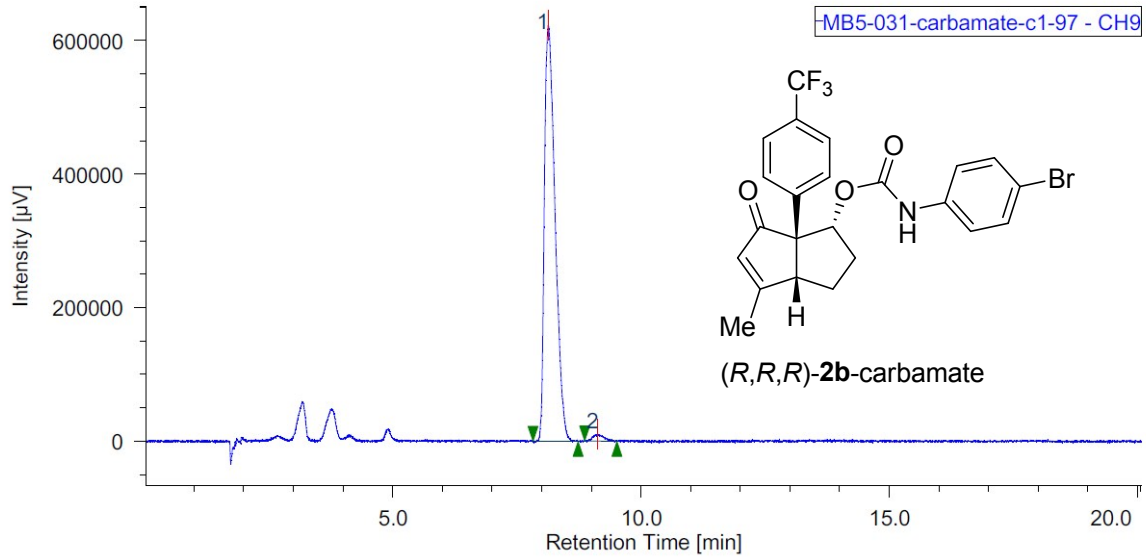
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	9.827	17366878	985771	86.238	90.230	N/A	7120	4.756	1.675
2	Unknown	9	12.187	589464	31195	2.927	2.855	N/A	8480	5.549	1.227
3	Unknown	9	15.960	303546	10781	1.507	0.987	N/A	5855	1.776	1.641
4	Unknown	9	17.380	1878522	64766	9.328	5.928	N/A	8175	N/A	1.602

Chromatogram



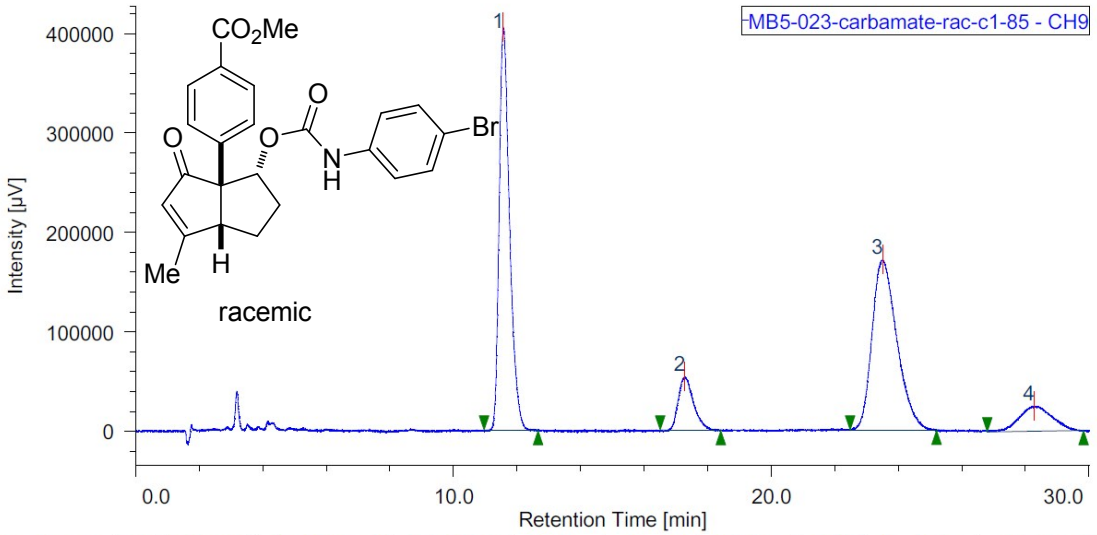
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	7.093	5463505	457463	50.303	53.210	N/A	8001	2.558	1.452
2	Unknown	9	7.953	5397626	402274	49.697	46.790	N/A	7937	N/A	1.281

Chromatogram



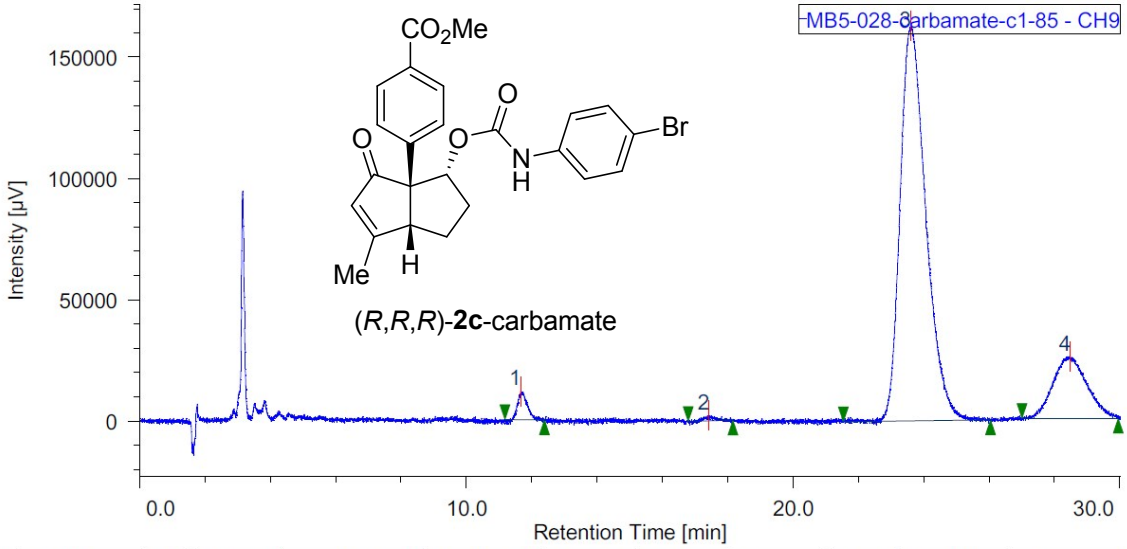
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	8.127	9286833	622648	98.344	98.381	N/A	6616	2.342	1.580
2	Unknown	9	9.127	156418	10246	1.656	1.619	N/A	6391	N/A	1.237

Chromatogram



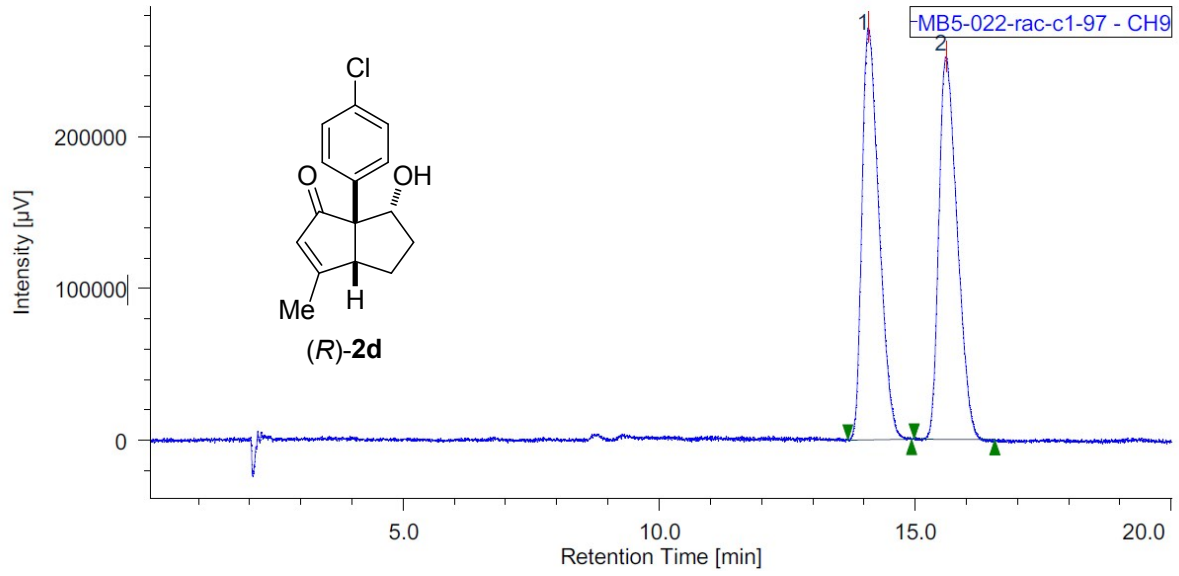
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	11.567	9212826	405614	41.566	61.741	N/A	6342	7.964	1.418
2	Unknown	9	17.267	1791783	54302	8.084	8.266	N/A	6537	5.486	1.424
3	Unknown	9	23.493	9322488	171667	42.061	26.130	N/A	4368	2.836	1.317
4	Unknown	9	28.260	1837089	25382	8.289	3.863	N/A	3365	N/A	0.950

Chromatogram



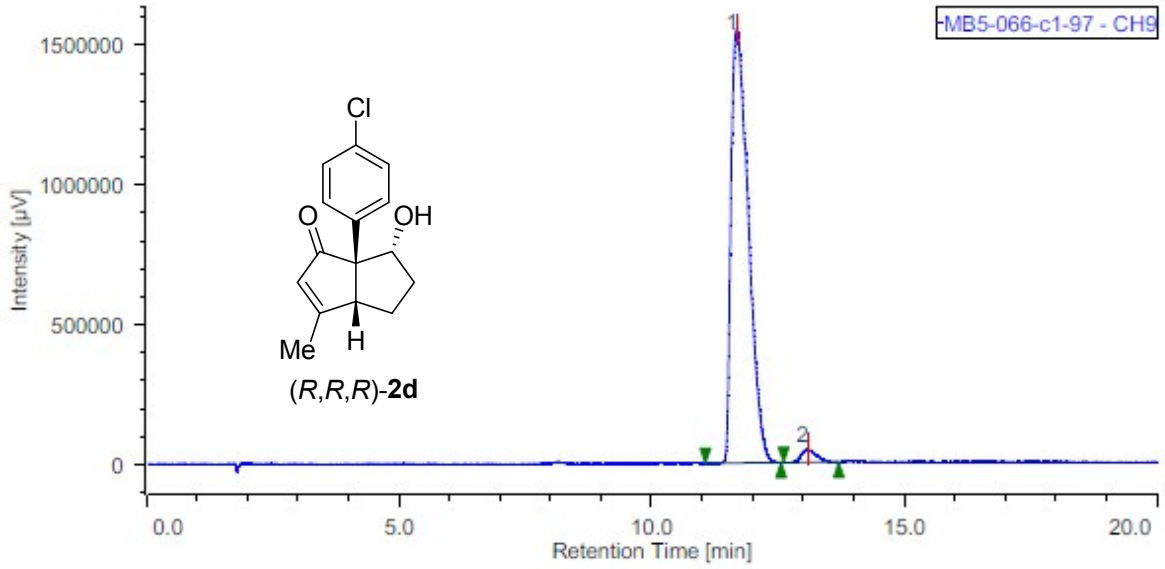
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	11.653	237316	11805	2.147	5.834	N/A	7136	6.833	1.575
3	Unknown	9	17.407	45600	2175	0.413	1.075	N/A	3753	4.852	1.119
2	Unknown	9	23.587	8932991	162873	80.811	80.494	N/A	4429	2.920	1.376
4	Unknown	9	28.467	1838215	25489	16.629	12.597	N/A	3469	N/A	1.123

Chromatogram



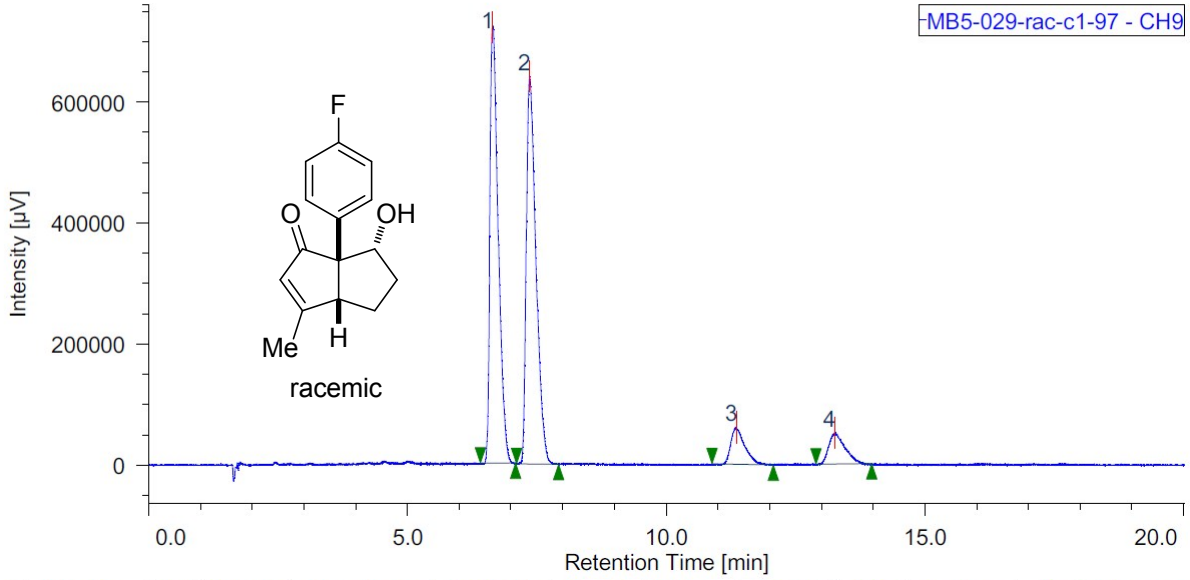
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	14.087	6261641	271810	49.964	51.903	N/A	8481	2.373	1.422
2	Unknown	9	15.600	6270766	251878	50.036	48.097	N/A	8747	N/A	1.351

Chromatogram



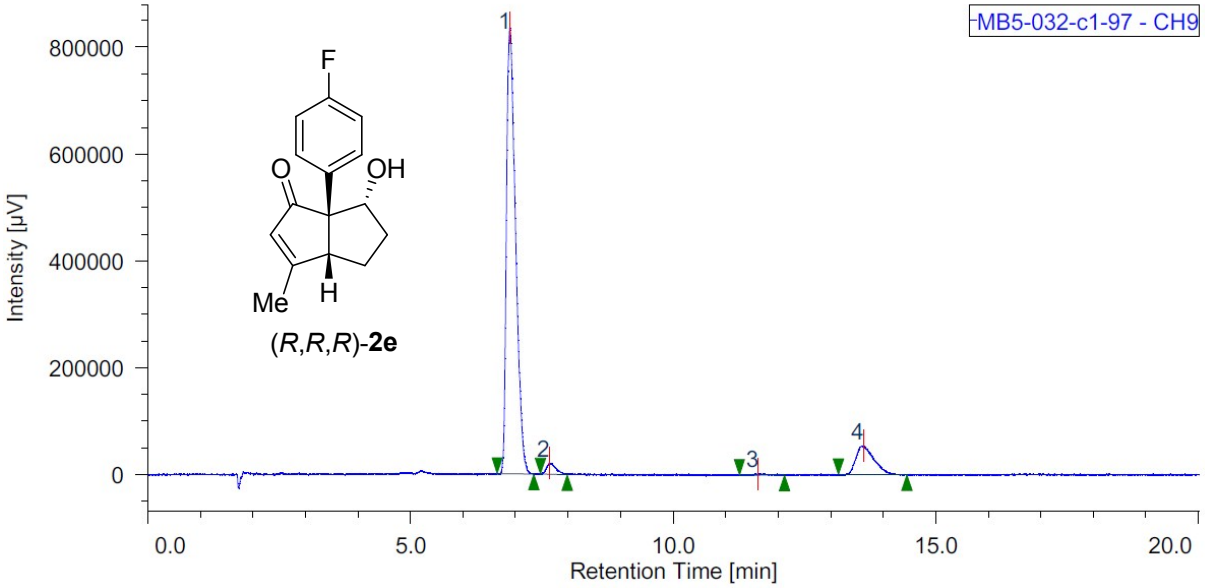
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	11.687	36775497	1552928	97.467	97.099	N/A	5141	2.303	1.822
2	Unknown	9	13.087	955908	46401	2.533	2.901	N/A	8522	N/A	1.322

Chromatogram



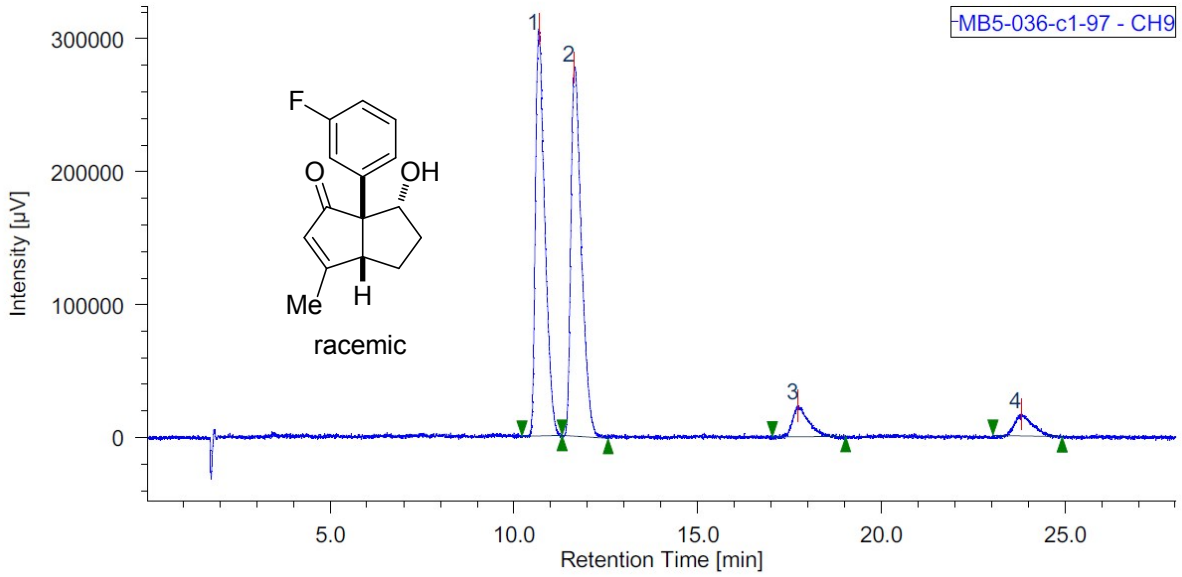
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	6.647	8179219	719969	43.841	48.898	N/A	7984	2.255	1.670
2	Unknown	9	7.360	8244457	640244	44.191	43.483	N/A	7641	9.835	1.655
3	Unknown	9	11.360	1124904	60446	6.030	4.105	N/A	9005	3.611	1.518
4	Unknown	9	13.260	1108012	51732	5.939	3.513	N/A	8467	N/A	1.457

Chromatogram



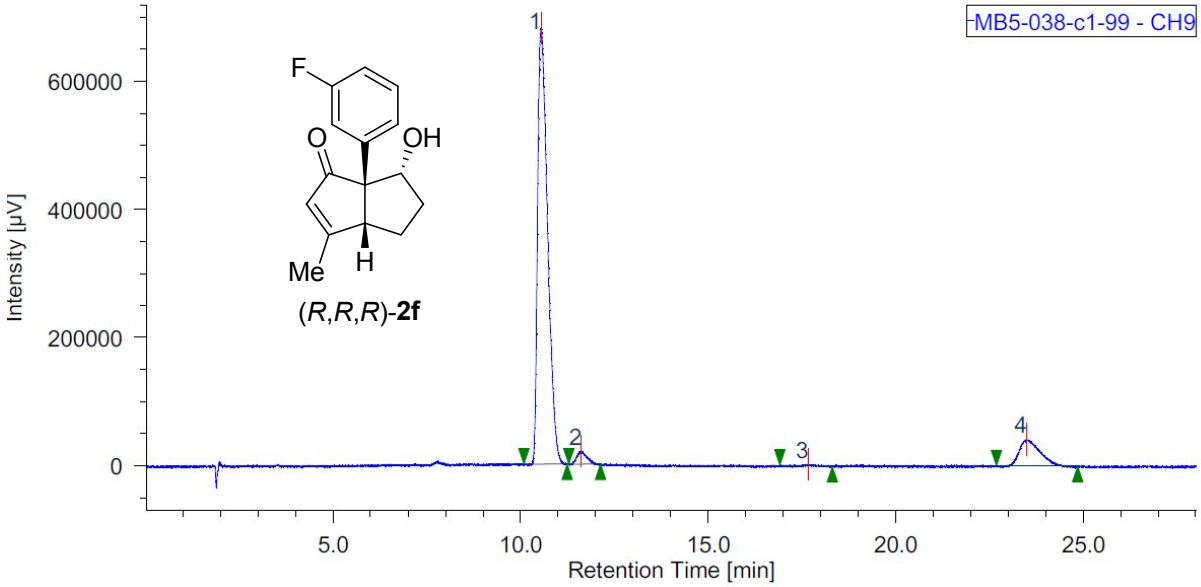
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	6.893	9972790	834716	86.220	91.479	N/A	7580	2.267	1.531
2	Unknown	9	7.633	257668	20508	2.228	2.248	N/A	8167	7.097	1.799
4	Unknown	9	11.613	38677	2605	0.334	0.286	N/A	3486	2.832	1.180
3	Unknown	9	13.613	1297580	54633	11.218	5.987	N/A	7482	N/A	1.433

Chromatogram



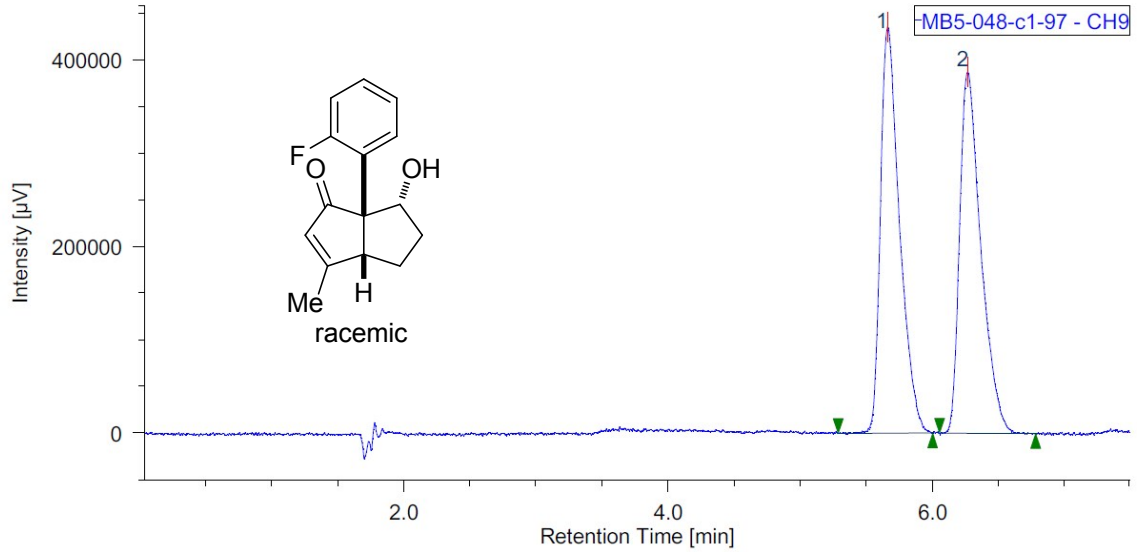
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	10.673	5364799	306007	44.392	49.145	N/A	8725	2.022	1.642
2	Unknown	9	11.647	5462269	276833	45.199	44.460	N/A	8402	9.196	1.660
3	Unknown	9	17.733	698454	23473	5.780	3.770	N/A	7502	7.017	1.468
4	Unknown	9	23.800	559504	16347	4.630	2.625	N/A	10829	N/A	1.723

Chromatogram



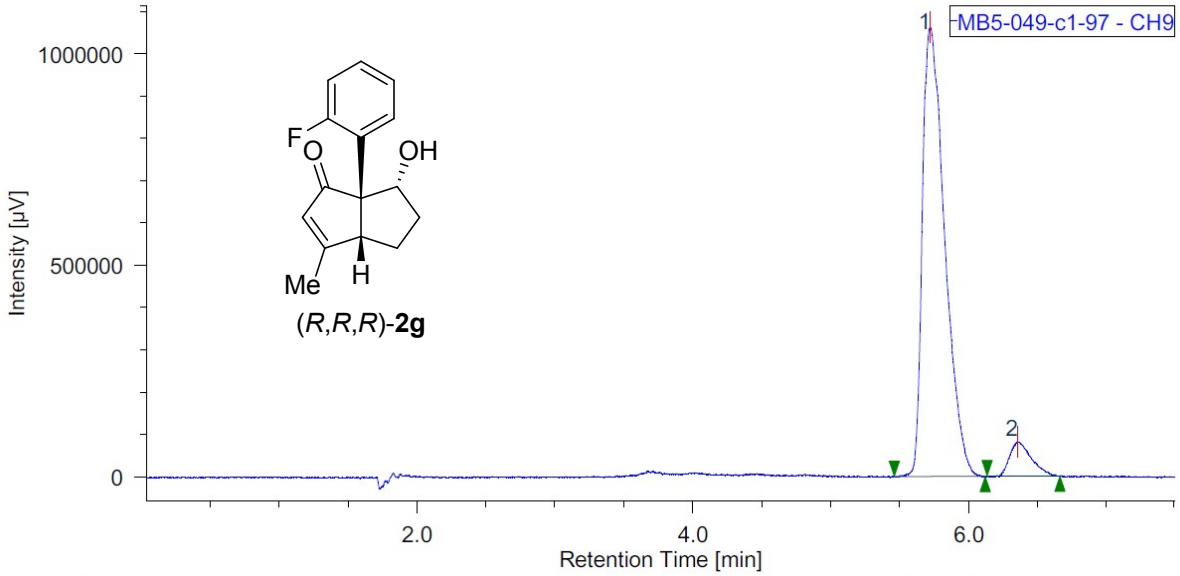
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	10.547	12409365	679915	86.418	91.380	N/A	7546	2.147	1.654
2	Unknown	9	11.620	364495	20476	2.538	2.752	N/A	8089	6.924	1.086
4	Unknown	9	17.653	36597	2353	0.255	0.316	N/A	3293	5.150	0.940
3	Unknown	9	23.473	1549311	41311	10.789	5.552	N/A	8218	N/A	1.501

Chromatogram



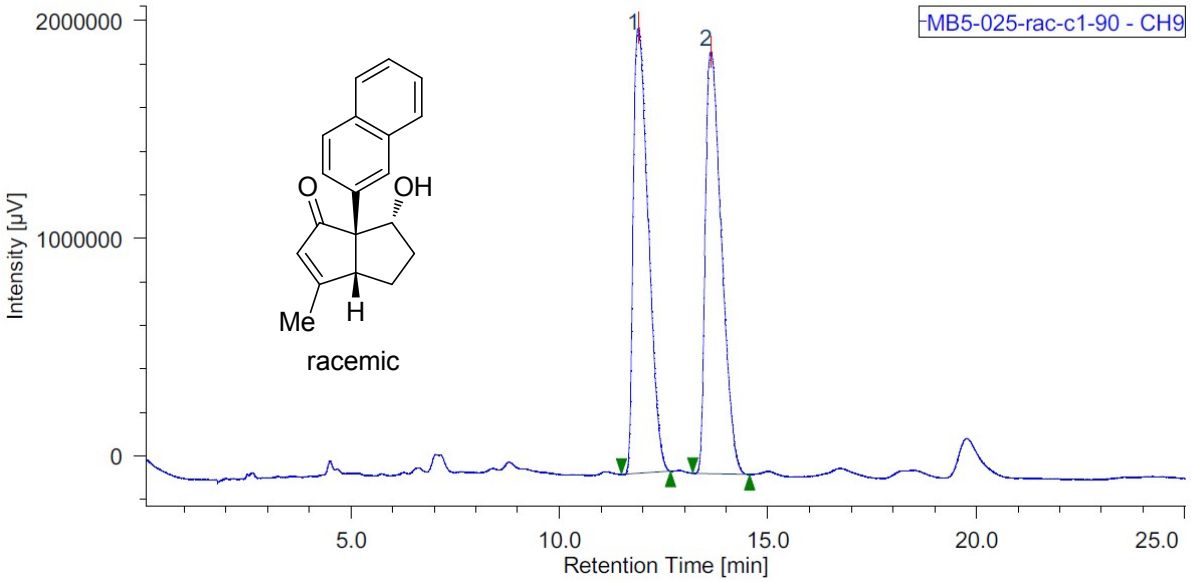
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	5.660	4358747	435148	50.240	52.927	N/A	7826	2.249	1.530
2	Unknown	9	6.267	4317159	387014	49.760	47.073	N/A	7736	N/A	1.519

Chromatogram



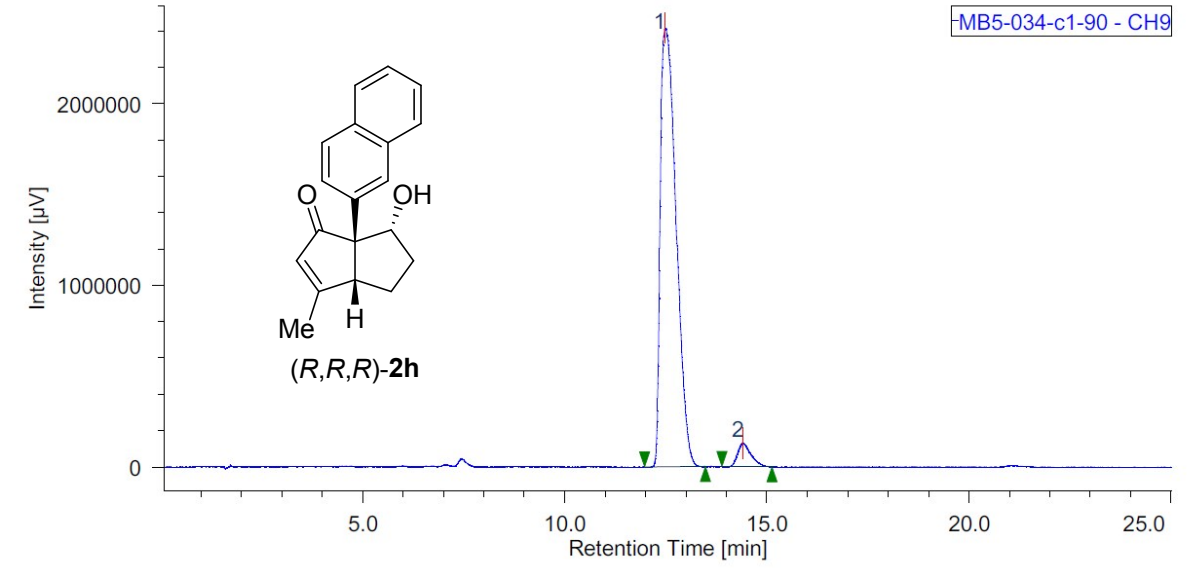
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	5.720	11878840	1061537	93.127	92.944	N/A	6110	2.198	1.673
2	Unknown	9	6.353	876745	80587	6.873	7.056	N/A	7952	N/A	1.517

Chromatogram



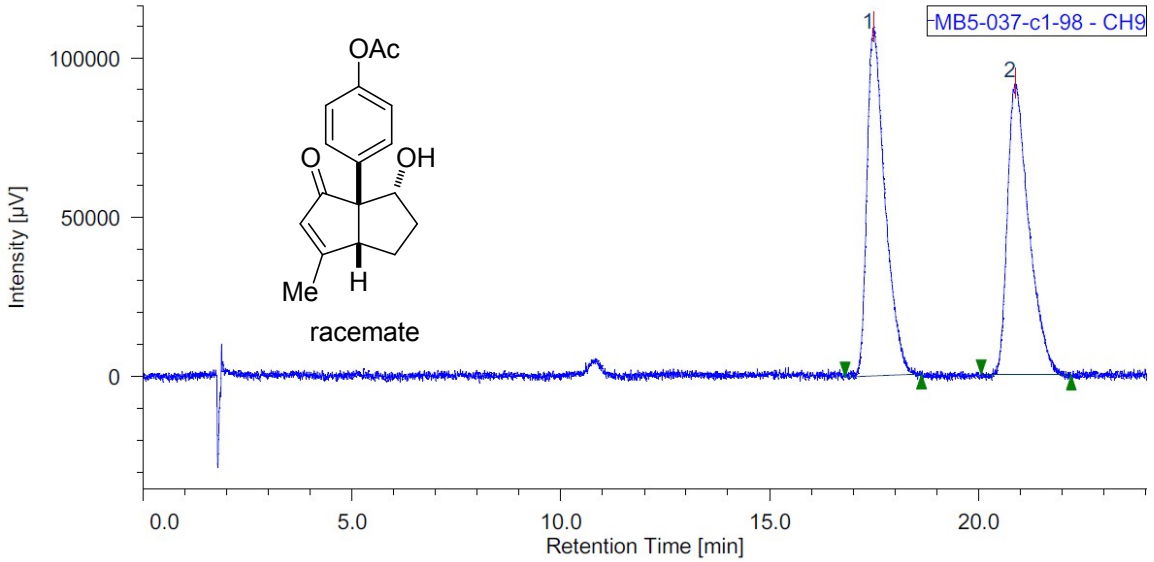
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	11.907	51275100	2045782	49.489	51.368	N/A	4730	2.433	1.635
2	Unknown	9	13.640	52333604	1936846	50.511	48.632	N/A	5495	N/A	1.630

Chromatogram



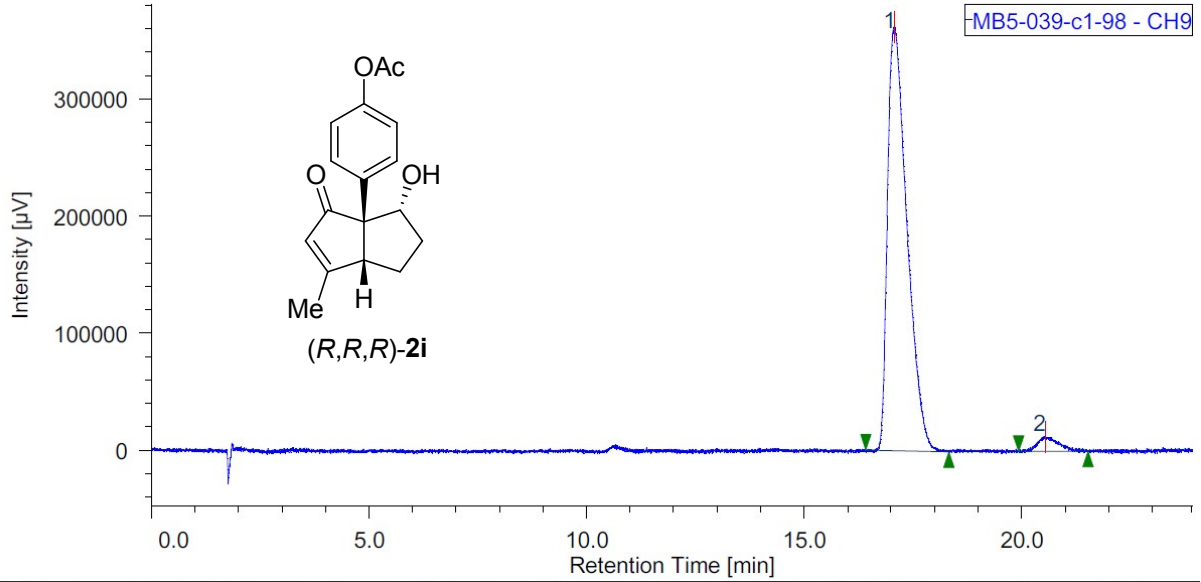
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	12.487	65118787	2416157	95.630	94.926	N/A	4534	2.895	1.825
2	Unknown	9	14.413	2976049	129136	4.370	5.074	N/A	9458	N/A	1.374

Chromatogram



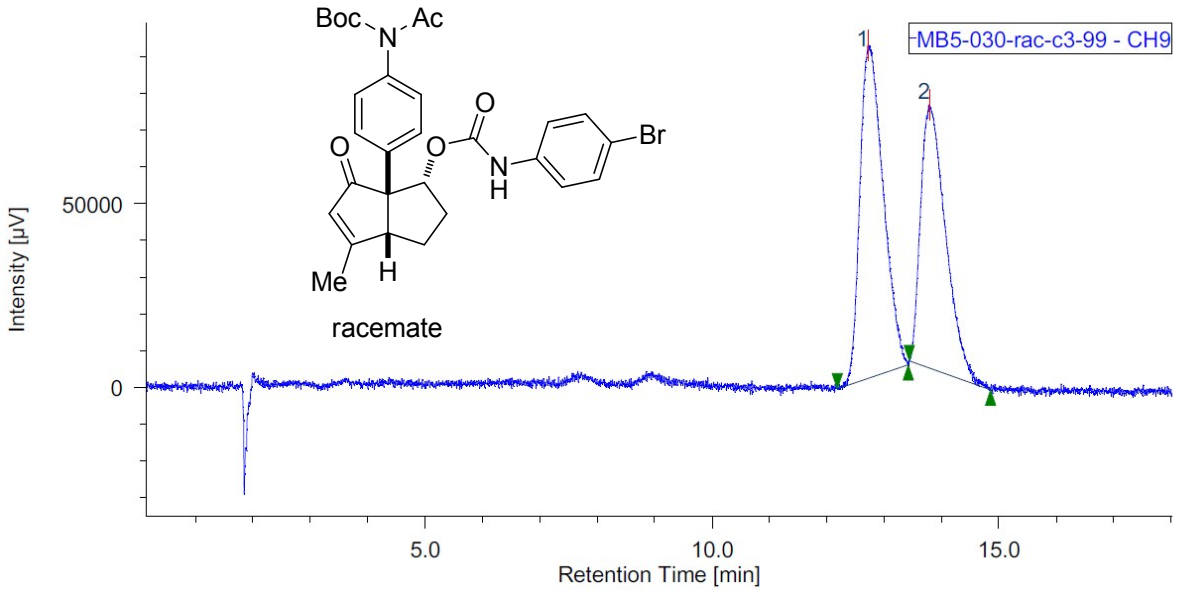
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	17.493	3276333	109514	50.097	54.493	N/A	8389	4.033	1.566
2	Unknown	9	20.880	3263671	91455	49.903	45.507	N/A	8242	N/A	1.622

Chromatogram



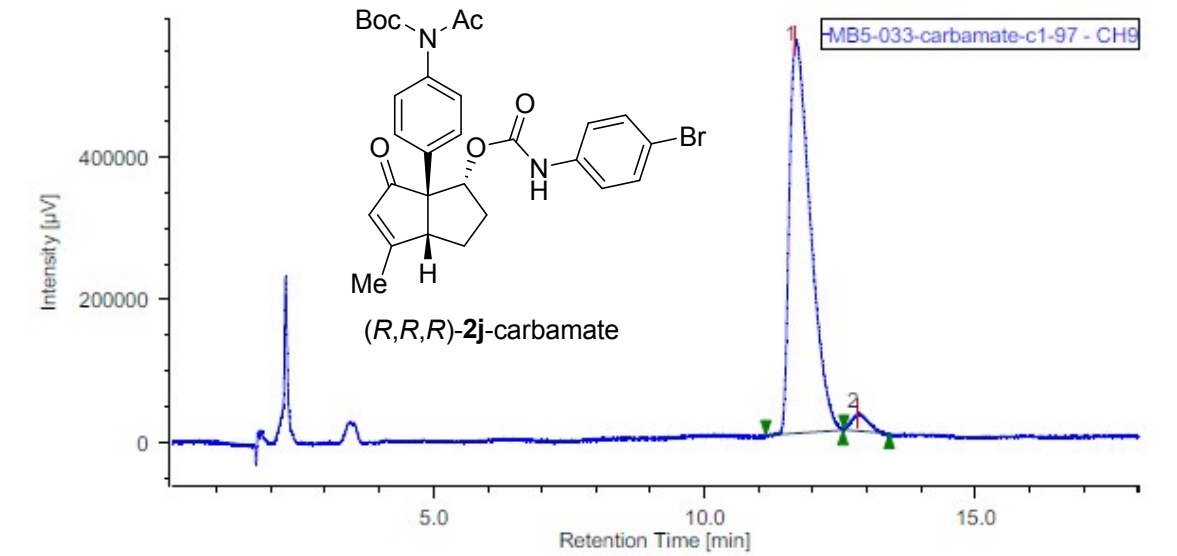
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	17.080	11191975	361873	96.263	96.624	N/A	6966	3.901	1.661
2	Unknown	9	20.533	434456	12643	3.737	3.376	N/A	7370	N/A	1.295

Chromatogram

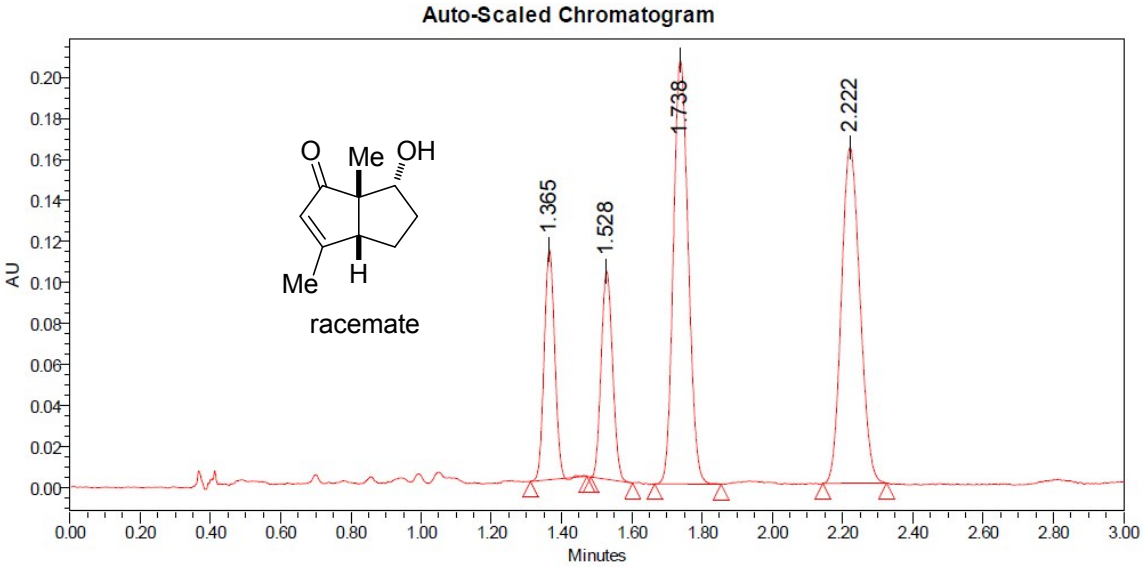


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	12.720	2548260	90621	53.971	55.857	N/A	4476	1.363	1.460
2	Unknown	9	13.787	2173283	71616	46.029	44.143	N/A	4648	N/A	1.715

Chromatogram

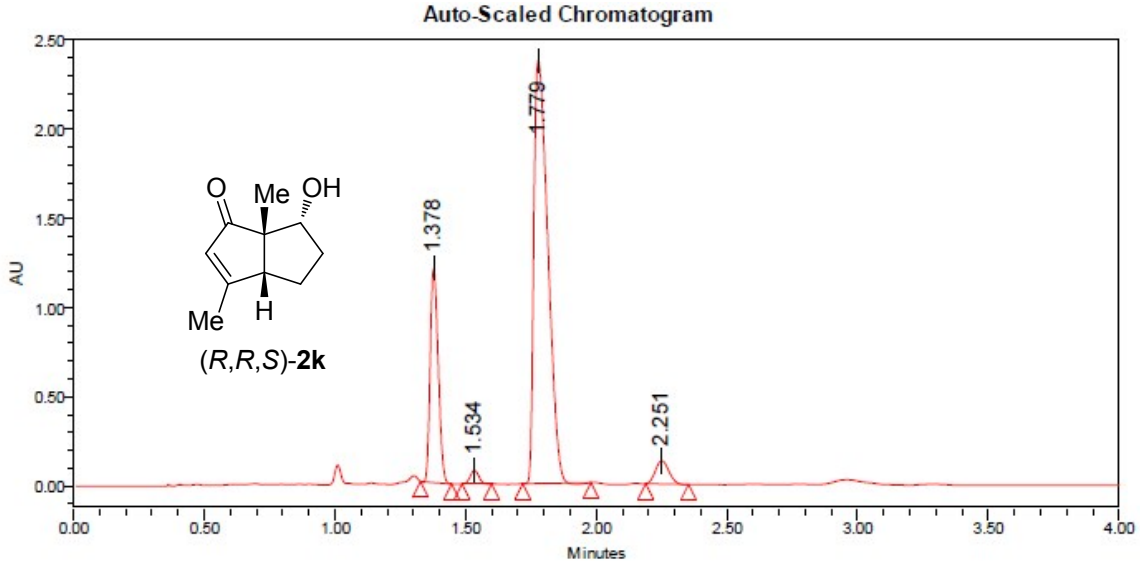


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	11.680	14837809	551516	96.681	95.625	N/A	4234	1.773	1.968
2	Unknown	9	12.833	509439	25233	3.319	4.375	N/A	7657	N/A	1.425



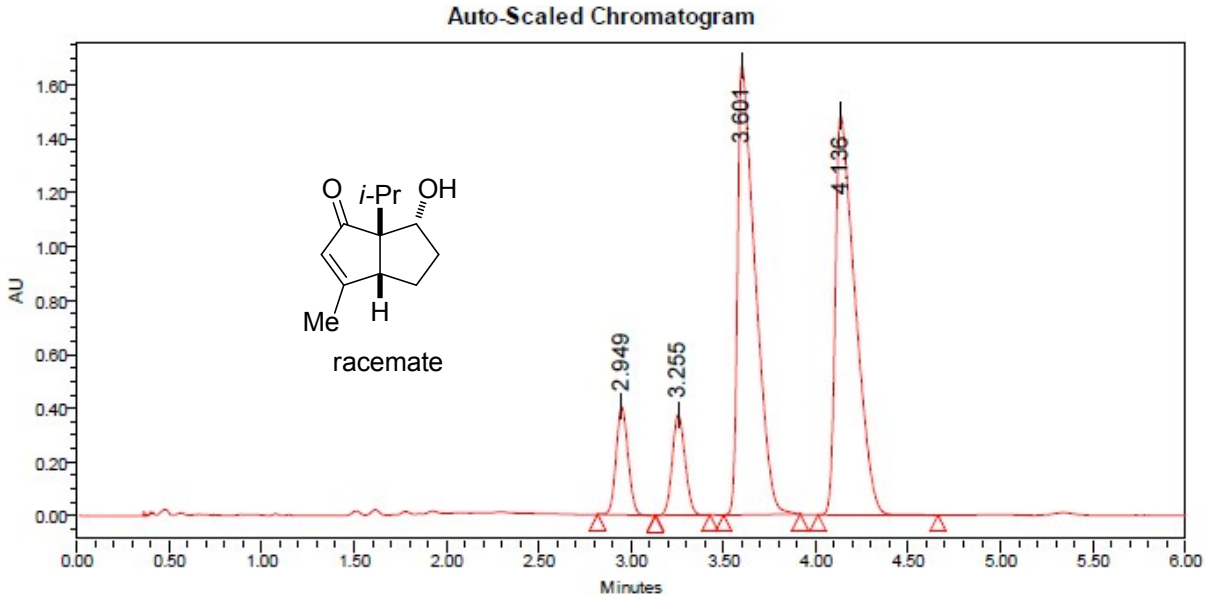
Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.365	234647	14.04	112140
2	PDA Ch2 214nm@1.2nm	1.528	228931	13.69	101497
3	PDA Ch2 214nm@1.2nm	1.738	607220	36.32	206533
4	PDA Ch2 214nm@1.2nm	2.222	600924	35.95	163695



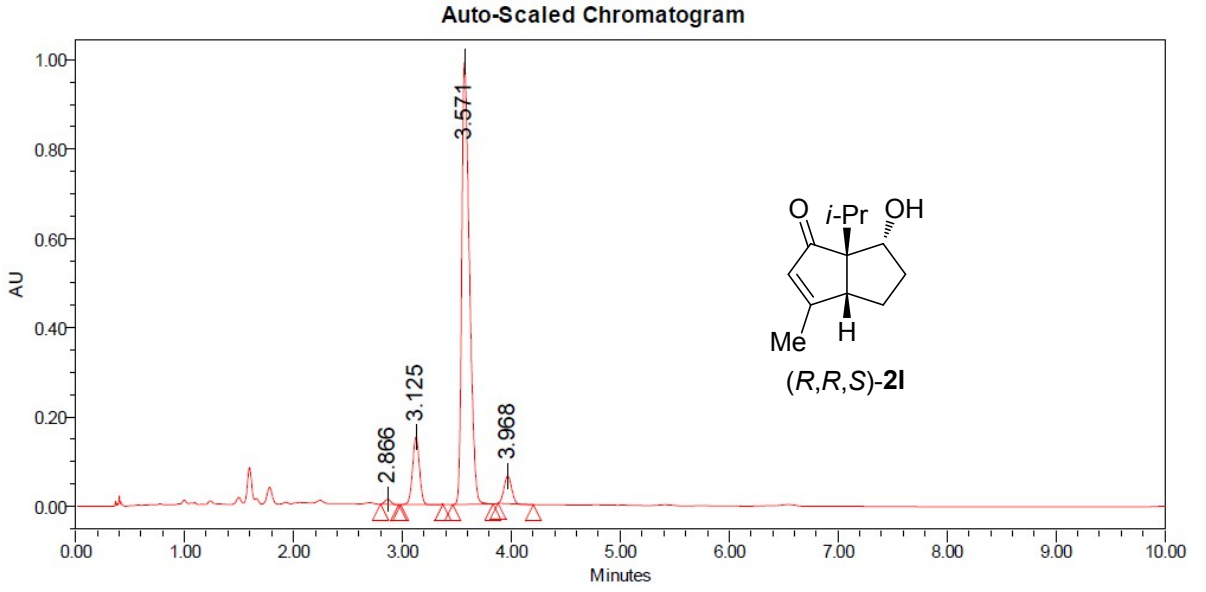
Processed Channel: PDA Ch2 214nm@1.2nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	1.378	2563036	21.32	1199676
2	PDA Ch2 214nm@1.2nm	1.534	173323	1.44	76593
3	PDA Ch2 214nm@1.2nm	1.779	8823315	73.38	2368879
4	PDA Ch2 214nm@1.2nm	2.251	464284	3.86	129725



Processed Channel: PDA Ch2 214nm@1.2nm

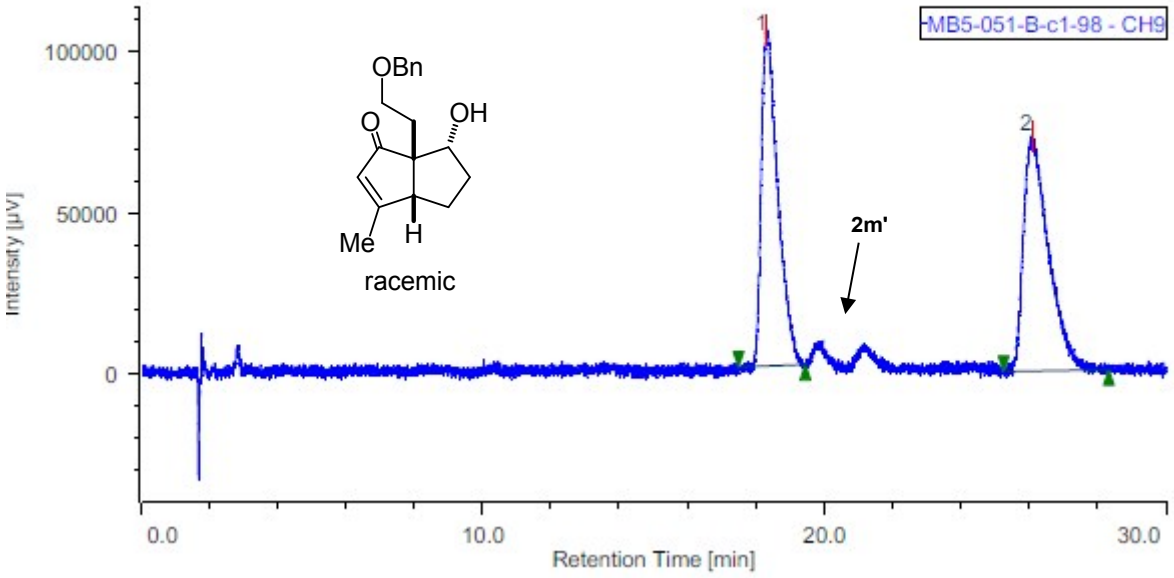
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	2.949	1797538	6.99	400967
2	PDA Ch2 214nm@1.2nm	3.255	1795074	6.98	372444
3	PDA Ch2 214nm@1.2nm	3.601	11070054	43.05	1669990
4	PDA Ch2 214nm@1.2nm	4.136	11051684	42.98	1483420



Processed Channel: PDA Ch2 214nm@1.2nm

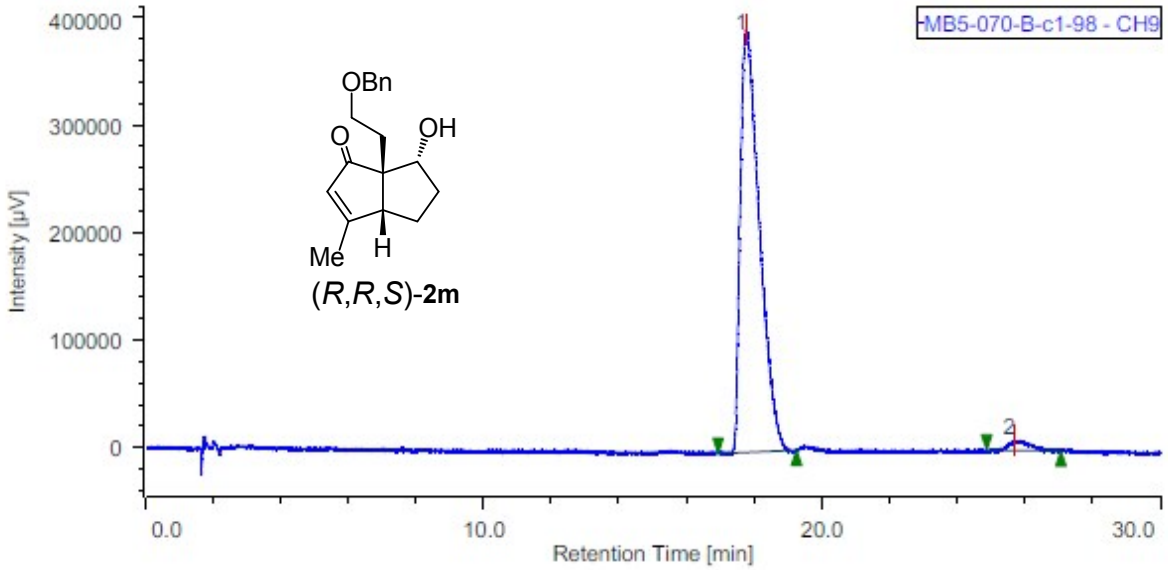
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA Ch2 214nm@1.2nm	2.866	44287	0.76	1145
2	PDA Ch2 214nm@1.2nm	3.125	664729	11.37	151009
3	PDA Ch2 214nm@1.2nm	3.571	4836731	82.72	990670
4	PDA Ch2 214nm@1.2nm	3.968	301670	5.16	62114

Chromatogram



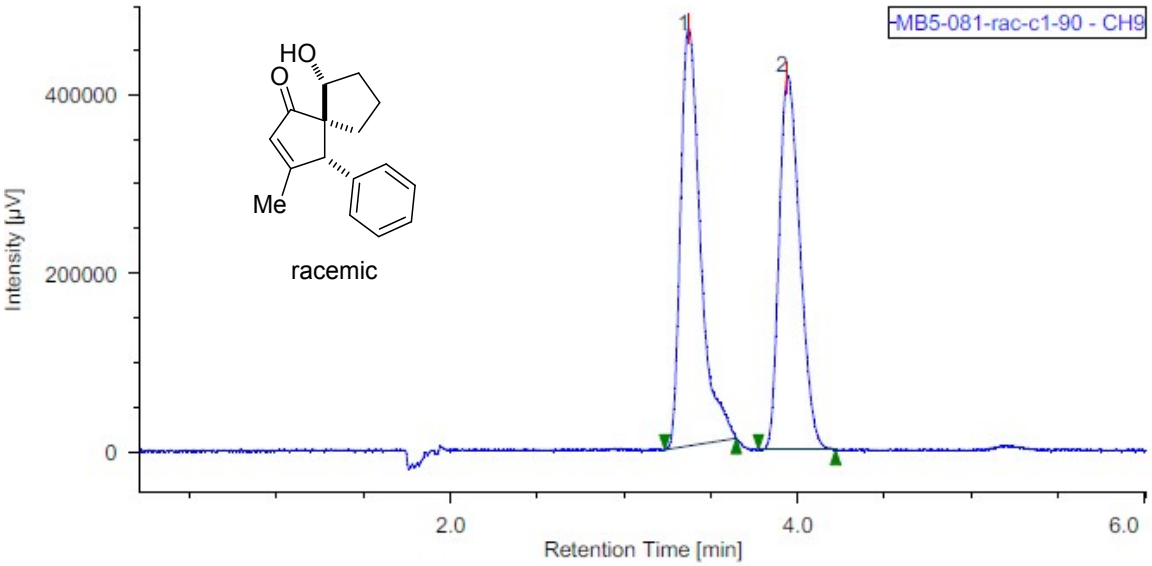
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	18.327	3512980	104617	48.464	58.847	N/A	7224	7.086	1.758
2	Unknown	9	26.060	3735665	73159	51.536	41.153	N/A	6179	N/A	1.809

Chromatogram



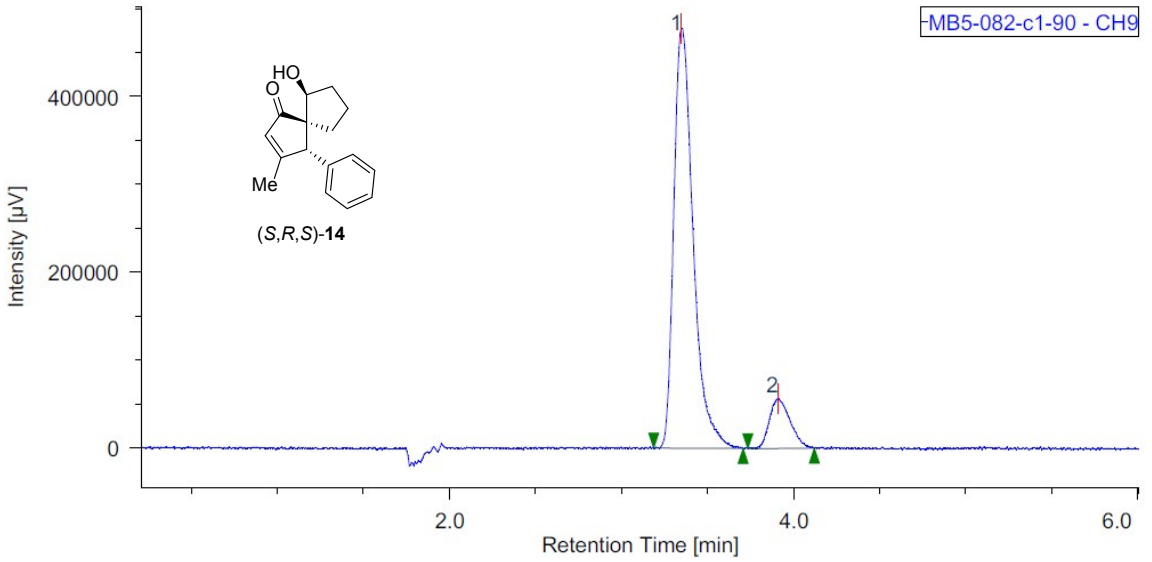
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	17.767	15286487	393088	97.531	97.610	N/A	4680	6.968	1.964
2	Unknown	9	25.687	386924	9623	2.469	2.390	N/A	6860	N/A	1.436

Chromatogram



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	3.373	3719175	467146	51.768	52.850	N/A	4659	2.702	1.668
2	Unknown	9	3.940	3465079	416757	48.232	47.150	N/A	5003	N/A	1.341

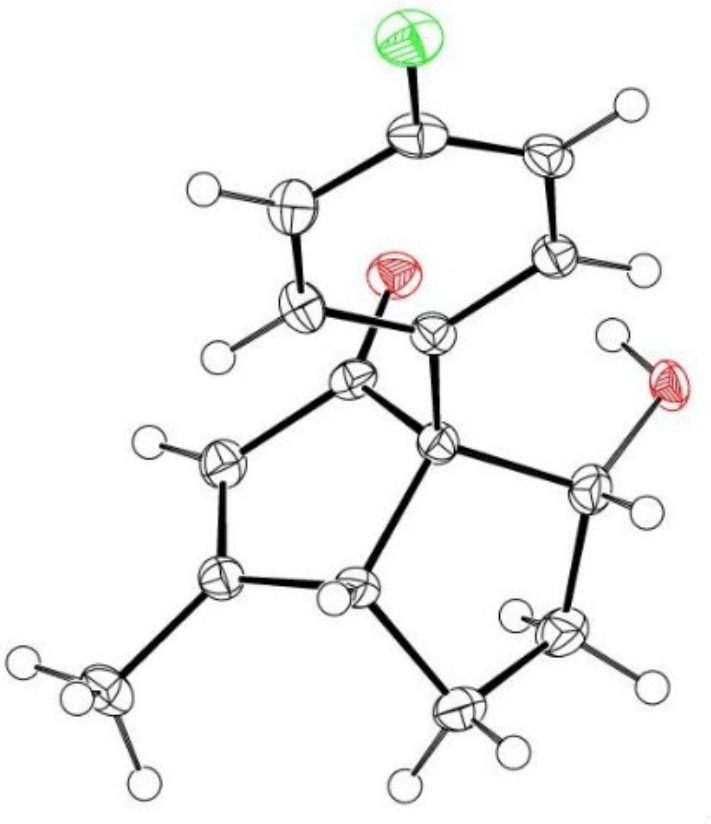
Chromatogram



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor
1	Unknown	9	3.347	3727002	477828	88.627	89.409	N/A	4563	2.660	1.551
2	Unknown	9	3.907	478269	56602	11.373	10.591	N/A	4866	N/A	1.298

9. X-Ray Crystallographic Data

9.1 X-Ray Cystallographic Data of **2e**

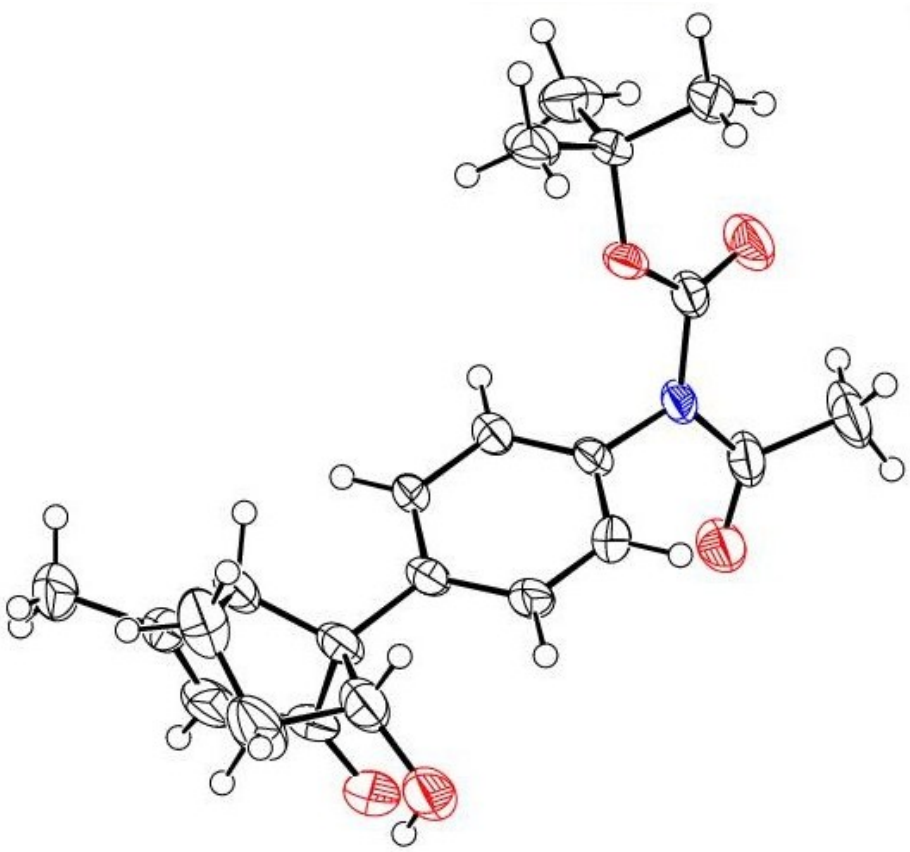


Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1517155)

CCDC Deposit Number	CCDC 1517155
Empirical formula	$C_{15}H_{15}FO_2$
Formula weight	246.27
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.4982(2)
b/Å	8.0473(2)
c/Å	20.6908(6)
α/°	90
β/°	99.071(2)
γ/°	90
Volume/Å³	1232.87(6)
Z	4
ρ_{calc}g/cm³	1.327
μ/mm⁻¹	0.800
F(000)	520.0
Crystal size/mm³	0.2 × 0.15 × 0.03
Radiation	CuKα (λ = 1.54178)

2Θ range for data collection/°	4.324 to 133.278
Index ranges	$-7 \le h \le 8$, $-9 \le k \le 9$, $-24 \le l \le 24$
Reflections collected	25303
Independent reflections	4301 [R_{int} = 0.0290, R_{sigma} = 0.0172]
Data/restraints/parameters	4301/17/350
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0773
Final R indexes [all data]	R_1 = 0.0302, wR_2 = 0.0774
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.25
Flack parameter	0.07(5)

9.2 X-Ray Crystallographic Data of **2j**

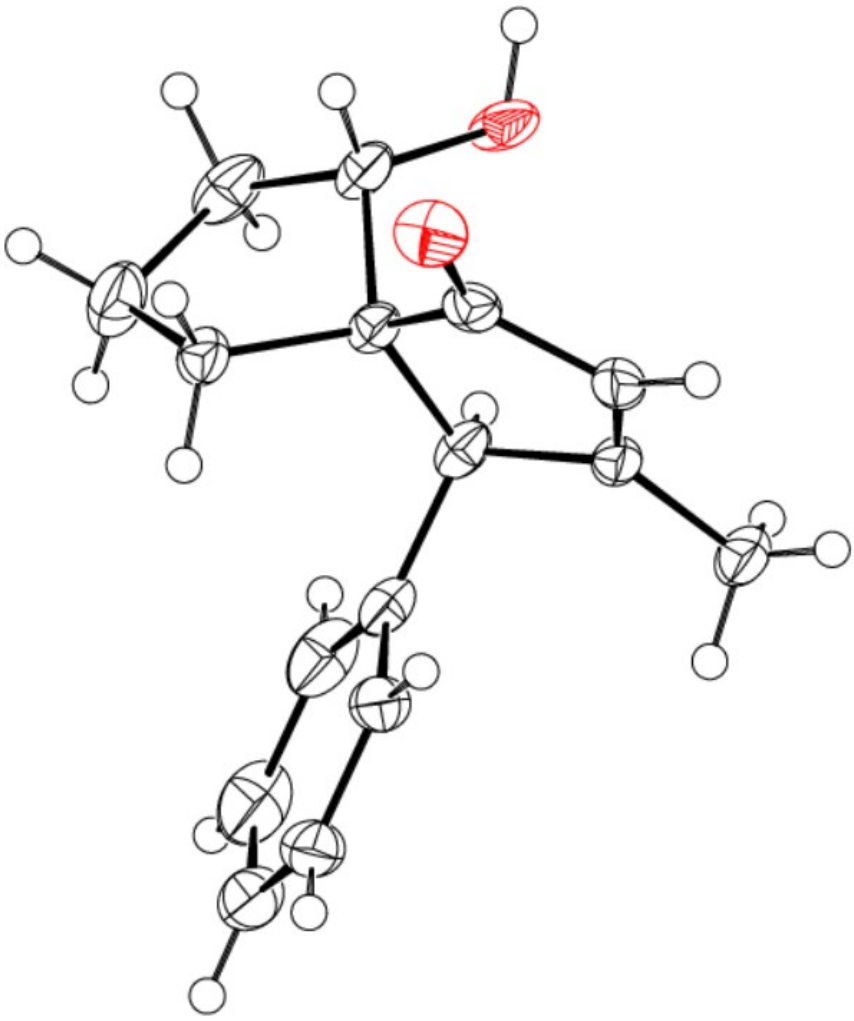


Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1517154)

CCDC Deposit Number	CCDC 1517154
Empirical formula	$C_{22}H_{27}NO_5$
Formula weight	385.44
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.6297(2)
b/Å	11.1898(2)
c/Å	14.5794(3)
α/°	90
β/°	96.0660(10)
γ/°	90
Volume/Å³	2048.88(6)
Z	4
ρ_{calc}g/cm³	1.250
μ/mm⁻¹	0.720
F(000)	824.0
Crystal size/mm³	0.25 × 0.17 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.096 to 134.282

Index ranges	$-15 \leq h \leq 15, -13 \leq k \leq 13, -17 \leq l \leq 14$
Reflections collected	31920
Independent reflections	7145 [R_{int} = 0.0324, R_{sigma} = 0.0281]
Data/restraints/parameters	7145/499/643
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0970, wR_2 = 0.2559
Final R indexes [all data]	R_1 = 0.1005, wR_2 = 0.2603
Largest diff. peak/hole / e $Å^{-3}$	0.84/-0.62
Flack parameter	0.03(8)

9.3 X-Ray Crystallographic Data of **14**



Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1913669)

Empirical formula	$C_{16}H_{18}O_2$
Formula weight	242.30
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	C2
a/Å	14.76169(11)
b/Å	6.20905(4)
c/Å	14.27446(9)
α/°	90
β/°	95.4272(6)
γ/°	90
Volume/Å³	1302.475(16)
Z	4
ρ_{calc}g/cm³	1.236
μ/mm⁻¹	0.632
F(000)	520.0

Crystal size/mm³	0.234 × 0.214 × 0.139
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.22 to 158.98
Index ranges	-18 ≤ h ≤ 18, -7 ≤ k ≤ 7, -18 ≤ l ≤ 18
Reflections collected	25439
Independent reflections	2793 [R_{int} = 0.0297, R_{sigma} = 0.0126]
Data/restraints/parameters	2793/4/170
Goodness-of-fit on F^2	1.075
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0773
Final R indexes [all data]	R_1 = 0.0308, wR_2 = 0.0775
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.17
Flack parameter	0.00(5)