

Supporting Information

Formal Synthesis of Leustroducsin B via Reformatsky/Claisen Condensation of Silyl Glyoxylates

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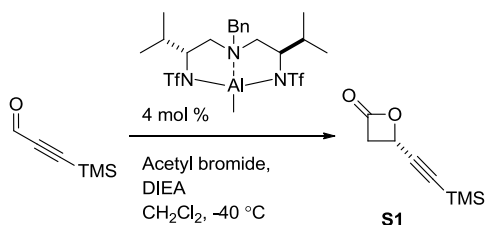
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Methods: General. Infrared (IR) spectra were obtained using a Jasco 460 Plus Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a Bruker model Avance 400 (^1H NMR at 400 MHz and ^{13}C at 100 MHz) or a Bruker model Avance 500 (^1H NMR at 500 MHz and ^{13}C NMR at 125 MHz) spectrometer with solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm). ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, br t = broad triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained using a Bruker BioTOF II spectrometer with electrospray ionization calibrated with CsOAc. All samples were prepared in methanol. Analytical thin layer chromatography (TLC) was performed on Sorbent Technologies 0.20 mm Silica G TLC plates. Visualization was accomplished with UV light and/or aqueous ceric ammonium nitrate solution followed by heating. Purification of the reaction products was carried out by flash chromatography using Siliaflash-P60 silica gel (40-63 μm) purchased from Silicycle. Purification via HPLC was performed on a Varian Prepstar SD-1 Solvent Delivery System equipped with a Cyano 60 Å 6 μm column from Berger Instruments. Specific parameters used in the separation of compounds are detailed under applicable entries. Unless otherwise noted, all reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware with magnetic stirring. Yield refers to isolated yield of analytically pure material unless otherwise noted. Yields are reported for a specific experiment and as a result may differ slightly from those found in the tables, which are averages of at least two experiments

Materials: General. Tetrahydrofuran, diethyl ether, dichloromethane, and toluene were dried by passage through a column of neutral alumina under nitrogen prior to use. Zinc metal was washed with 1 M HCl, water, acetone, and diethyl ether and then dried under vacuum at 60 °C for 16 h prior to storage in a nitrogen-filled glove box. Lithium chloride was dried and stored in a 100 °C oven. Diisopropylethylamine and triethylamine were freshly distilled from calcium hydride prior to use.

All other reagents were purchased from commercial sources and were used as received unless otherwise noted.

Preparation of S1:



(S)-4-((trimethylsilyl)ethynyl)oxetan-2-one (S1):

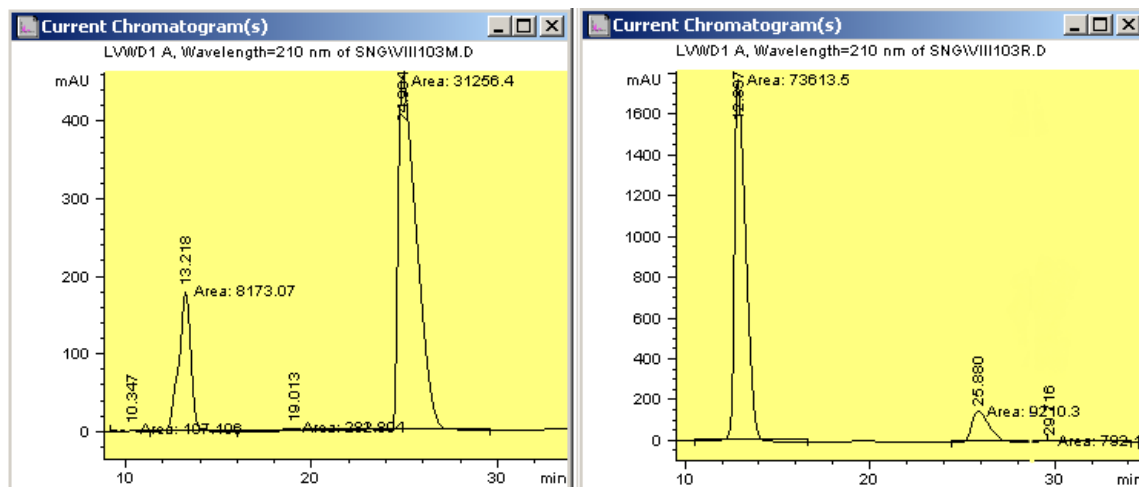
The title compound was prepared according to the procedure described by Nelson¹ with the following modifications:

1. Instead of purification via Kugelrohr distillation, the crude β -lactone was purified via flash chromatography (92.5:7.5 to 85:15 hexanes:ethyl acetate), affording the title compound (67% yield) as a light yellow oil whose spectral properties matched those reported in the literature.¹

2. The enantiomeric excess of the prepared lactone was assayed via supercritical fluid chromatographic (SFC) analysis of the corresponding β -hydroxyketone **1a** (*vide infra*). Enantiomeric excesses ranged from 78-83% using this method. CSP-SFC analysis of a sample of **1a** showed that the product was enriched to 78% ee (Chiralpak OD column, 3.0% MeOH, 1.0 mL/min, 150 psi, 24 °C, 210 nm, t_r -major enantiomer: 12.9 min, t_r -minor enantiomer: 25.9 min; CSP-SFC traces for a mixture of enantiomers and of the enantioenriched product are attached below:

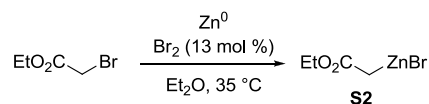
Enantiomeric Mixture:

Enantioenriched Sample:



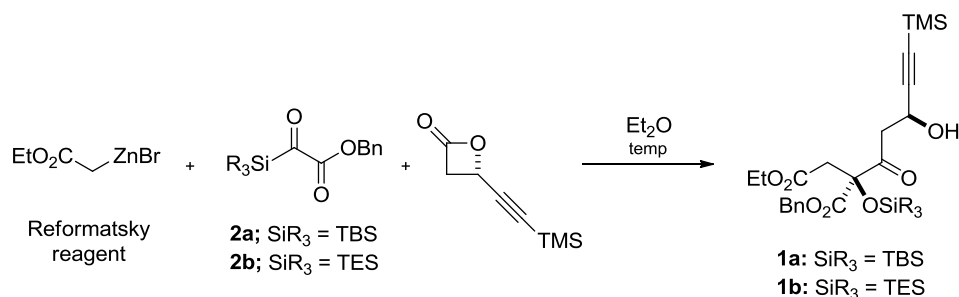
¹ Nelson, S. G., Peelen, T. J., Wan, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9742-9743.

Preparation of Reformatsky Reagent (S2):



An oven-dried 100-mL round-bottomed flask equipped with a magnetic stir bar was charged with zinc dust (1.41 g, 21.6 mmol, 2 equiv) and diethyl ether (25 mL). The flask was fitted with a condenser and purged with nitrogen. Br₂ (0.07 mL, 1.4 mmol, 0.13 equiv) was added dropwise over 5 min with stirring (exotherm observed). The suspension was heated to reflux, and ethyl bromoacetate (1.2 mL, 10.8 mmol, 1.0 equiv) was added dropwise over 15 min. The solution was stirred at this temperature for 4 h then cooled to RT. An aliquot was titrated with I₂, typically reflecting concentrations of active reagent of 0.35-0.43 M (81-100% yield). The solution was stored under nitrogen at 0 °C for up to one week and titrated immediately prior to each subsequent use.

Table S-1. Optimization of Reformatsky/Claisen Cascade:

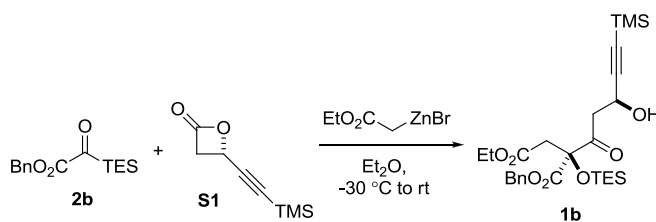


Entry	SiR ₃	activation method	equiv Reformatsky reagent	equiv lactone	temp (°C)	yield (%) ^{a,b,c}
1	TBS	5 mol % TMSCl	1.5	2.0	-20 to 0	43
2	TBS	5 mol % TMSCl	1.5	3.0	-20 to 0	51
3	TBS	5 mol % TMSCl + 2.0 equiv LiCl	1.5	3.0	-20 to rt	54
4	TBS	5 mol % TMSCl	1.5	2.5	-20 to rt	68
5	TBS	5 mol % TMSCl	1.5	1.5	-20 to rt	63
6	TBS	5 mol % TMSCl	2.3	1.5	-20 to rt	56
7	TES	5 mol % TMSCl	1.5	1.4	-30 to rt	50
8	TES	5 mol % TMSCl	1.8	1.6	-30 to rt	66
9	TES	5 mol % TMSCl	2.3	1.6	-30 to rt	62
10	TES	25 mol % Br ₂	2.3	1.6	-30 to rt	48
11	TES	25 mol % Br ₂	2.3	1.6	-30 to 0	61
12	TBS	25 mol % Br ₂	2.3	1.6	-30 to 0	57
13	TBS	25 mol % Br ₂	1.6	1.6	-30 to 0	56
14	TBS	25 mol % Br ₂	1.1	1.6	-30 to 0	23

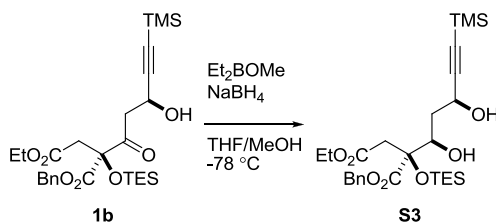
^a All reactions: yields determined by ¹H NMR analysis using an internal standard. ^b Diastereomeric ratios were all >20:1. ^c Relative stereochemistry was determined by NOESY analysis.²

² Greszler, S. N.; Malinowski, J. T.; Johnson, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 17393.

Experimental Procedures:

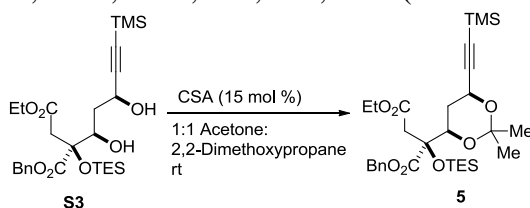


(S)-1-benzyl-4-ethyl-2-((S)-3-hydroxy-5-(trimethylsilyl)pent-4-ynoyl)-2-((triethylsilyl)oxy)succinate (1b): A solution of Reformatsky reagent (0.34 M, 150 mL) was prepared according to the standard procedure. The Reformatsky reagent solution (120 mL, 40.9 mmol, 2.3 equiv) was diluted with diethyl ether (150 mL), and the solution was cooled to -30 °C in an acetone/dry ice bath (bath temperature, monitored with a thermocouple probe). An oven-dried vial was charged with benzyl triethylsilyl glyoxylate **2b** (4.95 g, 17.8 mmol, 1.0 equiv) and (*S*)-4-((trimethylsilyl)ethynyl)oxetan-2-one (4.8 g, 28.5 mmol, 1.6 equiv) **S1**. The vial was purged with N₂, and a solution of the silyl glyoxylate and β-lactone in diethyl ether (20 mL) was added dropwise to the Reformatsky reagent solution over 5 min via cannula transfer. Additional diethyl ether (5 mL) was used to rinse the vial. The flask was allowed to warm slowly in the acetone bath (generally over 30 min from -30 °C to 0 °C). Consumption of the silyl glyoxylate was generally observed by TLC analysis between -15 °C and -10 °C. Once the reaction had reached 0 °C, it was then warmed to room temperature for 30 min. Once the reaction was complete as indicated by TLC analysis, it was quenched with saturated ammonium chloride (75 mL) and was stirred until clear layers were observed. The organic layer was removed, and the aqueous layer was extracted with diethyl ether (3 x 30 mL). The combined organic extracts were washed with brine, dried with magnesium sulfate, and concentrated in vacuo. The product was purified via flash chromatography (93.5:7.5 to 70:30 petroleum ether: diethyl ether) to give the desired product as a light yellow oil with > 25:1 diastereomeric ratio² (6.57 g, 69%). Analytical data: $[\alpha]_D^{25.3}$ -5.3 (*c* = 1.25, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.36-7.31 (m, 5H), 5.17 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.87 (dd, *J* = 6.5, 4.5 Hz, 1H), 4.09 (q, *J* = 7.5 Hz, 2H), 3.47 (d, *J* = 17 Hz, 1H), 3.36 (dd, *J* = 18.5, 2.5 Hz, 1H), 3.12 (dd, *J* = 18.5, 9.0 Hz, 1H), 2.91 (d, *J* = 17.0 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H), 0.56 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 208.8, 169.3, 168.5, 134.4, 128.7, 128.6, 128.5, 104.8, 89.3, 83.7, 68.1, 61.1, 58.8, 46.0, 42.5, 14.0, 6.7, 5.7, -0.2; HRMS (ESI⁺) Calcd. for C₂₇H₄₂O₇Si₂+Cs, 667.1524; Found, 667.1516; IR (thin film, cm⁻¹) 3515, 2958, 2911, 2878, 2176, 1738, 1456, 1373, 1343, 1250, 1181, 844, 699; TLC(80:20 Hex:EtOAc): R_f = 0.42.



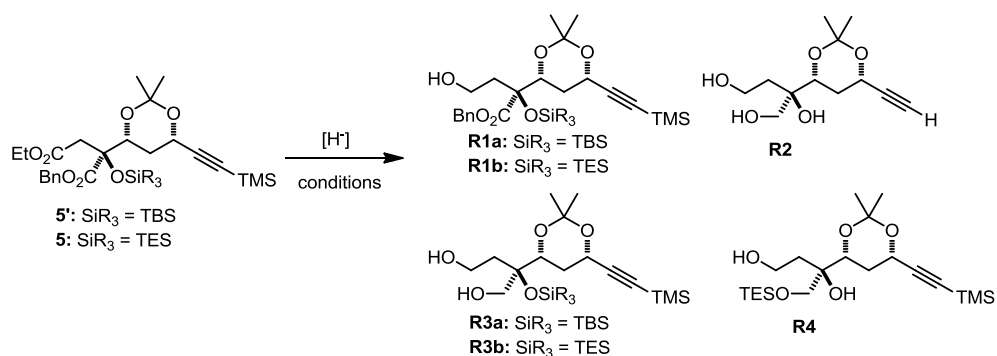
(S)-1-benzyl 4-ethyl 2-((1R,3S)-1,3-dihydroxy-5-(trimethylsilyl)pent-4-yn-1-yl)-2-((triethylsilyl)oxy)succinate (S3): A flame-dried and N₂-purged 500-mL round-bottomed flask

was charged with ketone **1b** (6.0 g, 11.2 mmol, 1.0 equiv). Tetrahydrofuran (200 mL) and methanol (50 mL) were added. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ (acetone/dry ice), and diethylmethoxyborane (1 M in tetrahydrofuran, 14.6 mL, 14.6 mmol) was added dropwise. After stirring for 45 minutes at $-78\text{ }^{\circ}\text{C}$, sodium borohydride (1.27 g, 33.7 mmol, 3.0 equiv) was added in one portion and the reaction was maintained at the same temperature. Once TLC analysis indicated complete consumption of the starting material (3.5 h), the reaction was quenched with acetic acid (9.0 mL). After warming to room temperature, the reaction was stirred for 1.5 h and was then concentrated *in vacuo*. Methanol (30 mL) was added, and the solution was again concentrated *in vacuo*; this procedure was repeated with four additional portions of methanol (30 mL). The residue was dissolved in ethyl acetate and saturated sodium bicarbonate, and the organic layer was washed with saturated sodium bicarbonate, water, and brine. The organic extracts were dried with magnesium sulfate and concentrated *in vacuo* to give a light yellow viscous oil (5.7 g, 95%) that was used without additional purification. Analytical data: $[\alpha]_{\text{D}}^{25.2} -1.7$ ($c = 1.25$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.36-7.33 (m, 5H), 5.20 (s, 2H), 4.60 (br. s., 1H), 4.10-3.99 (m, 3H), 3.05 (d, $J = 6.0$ Hz, 1H), 2.87 (d, $J = 4.0$ Hz, 1H), 2.83 (d, $J = 9.0$ Hz, 2H), 1.98 (dd, $J = 13.5, 5.5$ Hz, 1H), (dd, $J = 10.5, 2.5$ Hz, 1H), 1.21 (t, $J = 7.0$ Hz, 3H), 0.91 (t, $J = 8.0$ Hz, 9H), 0.67-0.62 (m, 6H), 0.15 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.1, 169.9, 135.0, 128.6, 128.5, 128.4, 105.6, 89.7, 80.6, 75.3, 67.6, 62.1, 60.9, 41.2, 38.7, 14.0, 7.1, 6.4, -0.2; **HRMS (ESI⁺)** Calcd. for $\text{C}_{27}\text{H}_{44}\text{O}_7\text{Si}_2 + \text{Cs}$, 669.1681; Found, 669.1710; **IR** (thin film, cm^{-1}) 3470, 2957, 2876, 2172, 1740, 1185, 1022, 844, 734; **TLC**(80:20 Hex:EtOAc): $R_f = 0.21$.

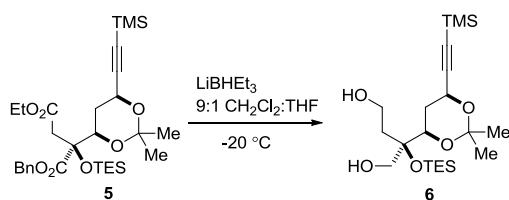


(S)-1-benzyl-4-ethyl-2-((4R,6S)-2,2-dimethyl-6-((trimethylsilyl)ethynyl)-1,3-dioxan-4-yl)-2-((triethylsilyloxy) succinate (5) A 500-mL round-bottomed flask was charged with diol **S3** (11.0 g, 20.6 mmol, 1.0 equiv), acetone (250 mL) and 2,2-dimethoxypropane (250 mL). CSA (0.716 g, 3.09 mmol, 0.15 equiv) was added, and the reaction was allowed to stir at room temperature for 16 h. The reaction was quenched by the addition of 0.5 mL of triethylamine and was concentrated *in vacuo*. The residue was purified via column chromatography (90:10 hexanes: ethyl acetate) to give the product as a white solid (8.6 g, 73%). Analytical data: $[\alpha]_{\text{D}}^{25.4} -14.0$ ($c = 1.5$, CHCl_3); mp $75\text{--}79\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.35-7.33 (m, 5H), 5.30 (d, $J = 12.5$ Hz, 1H), 5.05 (d, $J = 12.0$ Hz, 1H), 4.62 (dd, $J = 12.0, 2.5$ Hz, 1H), 4.12-4.06 (m, 3H), 2.74 (d, $J = 14.5$ Hz, 1H), 2.65 (d, $J = 14.0$ Hz, 1H), 1.88-1.60 (m, 2H), 1.33 (s, 3H), 1.23 (t, $J = 7.5$ Hz, 3H), 1.19 (s, 3H), 0.95 (t, $J = 16.0$ Hz, 9H), 0.74-0.65 (m, 6H), 0.17 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.6, 169.4, 135.6, 128.7, 128.4, 128.3, 103.7, 99.6, 89.4, 80.2, 72.9, 67.0, 60.7, 60.5, 41.9, 30.8, 29.5, 18.8, 14.0, 7.3, 6.7, -0.21; **HRMS (ESI⁺)** Calcd. for $\text{C}_{30}\text{H}_{48}\text{O}_7\text{Si}_2 + \text{Na}$, 599.2837; Found, 599.2809; **IR** (thin film, cm^{-1}) 2956, 2875, 2181, 1739, 1457, 1379, 1251, 1163, 844, 734; **TLC**(80:20 Hex:EtOAc): $R_f = 0.30$.

Table S-2. Screen of Hydride Sources for Reduction of **5'** and **5**

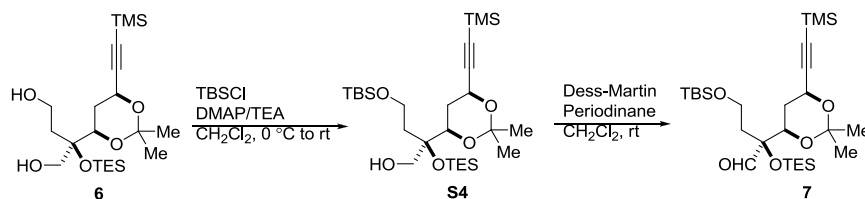


Entry	acetonide	reducing agent	Solvent	temp (°C)	Result
1	5'	LiAlH ₄ (4.0 equiv)	Et ₂ O	35	R2 , 73% yield
2	5'	DIBAL-H (5.0 equiv)	THF	-78 to rt	R1a , 89% yield
3	5'	DIBAL-H (5.0 equiv)	CH ₂ Cl ₂	-10 to rt	R1a
4	5'	LiBHEt ₃ (7.0 equiv)	THF	Rt	Mess
5	5'	LiBHEt ₃ (7.0 equiv)	THF	-10	R1a
6	5'	LiBHEt ₃ (7.0 equiv)	9:1 Et ₂ O:THF	-10	1:1 R1a : R3a
7	5'	LiBHEt ₃ (7.0 equiv)	15:1 Et ₂ O:THF	-10 to 0	R3a , 58% yield
8	5'	LiBHEt ₃ (7.0 equiv)	12:1 CH ₂ Cl ₂ :THF	-50 to rt	R3a , 75% yield
9	5	DIBAL-H (5.0 equiv)	CH ₂ Cl ₂	-10 to rt	R1b
10	5	LiBHEt ₃ (7.0 equiv)	THF	-30 to 0	R1b
11	5	LiBHEt ₃ (7.0 equiv)	10:1 toluene:THF	-30 to rt	1:1 R3b : R4
12	5	LiBHEt ₃ (7.0 equiv)	10:1 Et ₂ O:THF	-50 to rt	1:1 R3b : R4
13	5	LiBHEt ₃ (5.0 equiv)	10:1 Et ₂ O:THF	-30 to rt	1:1 R3b : R4
14	5	LiBHEt ₃ (7.0 equiv)	10:1 CH ₂ Cl ₂ :THF	-30 to 0	R3b , 73% (40 mg scale)
15	5	LiBHEt ₃ (7.0 equiv)	10:1 CH ₂ Cl ₂ :THF	-30 to -10	1:1 R3b : R4
16	5	LiBHEt ₃ (7.0 equiv)	10:1 CH ₂ Cl ₂ :THF	-30 to -20	R3b , 60%; R1b , 12% (1g scale)
17	5	LiBHEt ₃ (7.0 equiv)	12:1 CH ₂ Cl ₂ :THF	-20	R3b , 52% yield



(R)-2-((4R,6S)-2,2-dimethyl-6-((trimethylsilyl)ethynyl)-1,3-dioxan-4-yl)-2-((triethylsilyl)oxy)butane-1,4-diol (6**):** A flame-dried and cooled 1L round-bottomed flask was charged with acetonide **5** (5.0 g, 8.7 mmol, 1.0 equiv). The flask was purged with N₂, and CH₂Cl₂ (500 mL) was added. The solution was cooled to -30 °C, and lithium triethylborohydride (1M in THF, 57 mmol, 57 mL) was added dropwise over 15 min via syringe pump. The reaction temperature was maintained for 2 h, at which point the temperature was increased to -20 °C for 1 h. The reaction was quenched by the dropwise addition of HOAc (8 mL) and MeOH (30 mL). The resulting suspension was warmed to room temperature and concentrated *in vacuo*, keeping the bath temperature at or below 30 °C to avoid migration of the triethylsilyl group. The residue was redissolved in MeOH (30 mL) and concentrated *in vacuo* an additional four times. The residue

was partitioned between ethyl acetate and saturated aqueous sodium bicarbonate, and the organic extracts were washed successively with saturated sodium bicarbonate (x2), water, and brine. The combined organic extracts were dried with sodium sulfate and concentrated *in vacuo*. The resulting crude oil was purified via column chromatography, eluting with a gradient of 80:20 to 70:30 hexanes:ethyl acetate to give the desired diol as a white solid (2.1 g, 56%). Analytical data: $[\alpha]_D^{25.2}$ -2.8 ($c = 1.8$, CHCl_3); mp 93-95 °C; $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 4.67 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.93 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.86-3.73 (m, 3H), 3.50 (dd, $J = 11.0, 3.0$ Hz, 1H), 2.83 (s, 1H), 2.65 (s, 1H), 1.98-1.70 (m, 4H), 1.46 (s, 6H), 0.95 (t, $J = 3.5$ Hz, 9H), 0.74-0.65 (dq, $J = 16.0, 3.0$ Hz 6H), 0.17 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 103.7, 99.6, 89.6, 78.0, 73.2, 65.6, 60.9, 58.3, 37.7, 31.3, 29.9, 19.2, 7.1, 6.8, -0.2; **HRMS (ESI⁺)** Calcd. for $\text{C}_{21}\text{H}_{42}\text{O}_5\text{Si}_2+\text{Na}$, 453.2469; Found, 453.2464; **IR** (thin film, cm^{-1}) 3389, 2956, 2876, 2183, 1739, 1460, 1380, 1250, 1161, 1055, 844, 733; **TLC**(75:25 Hex:EtOAc): $R_f = 0.09$.



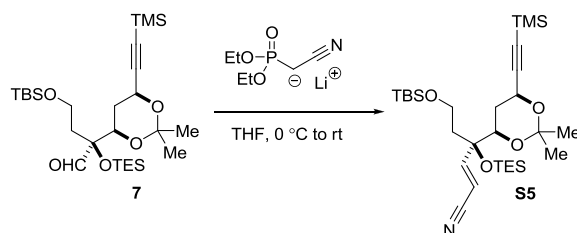
(S)-4-((tert-butyldimethylsilyloxy)-2-((4R,6S)-2,2-dimethyl-6-((trimethylsilyl)ethynyl)-1,3-dioxan-4-yl)-2-((triethylsilyloxy)butanal (7): A 100-mL oven-dried round bottomed flask was charged with diol **6** (0.840 g, 1.95 mmol, 1.0 equiv) and CH_2Cl_2 (60 mL). The solution was cooled to 0 °C, and triethylamine (0.540 mL, 3.9 mmol, 2.0 equiv), *tert*-butyldimethylsilyl chloride (0.339 g, 2.25 mmol, 1.15 equiv), and DMAP (0.071 g, 0.585 mmol, 0.3 equiv) were added successively. The reaction was allowed to warm slowly to room temperature over 1 h. Once TLC analysis indicated complete consumption of the starting material (5 h), the reaction was quenched by the addition of 5 mL of saturated aqueous sodium bicarbonate. The organic layer was washed with saturated NaHCO_3 , water, and brine and was then dried with sodium sulfate. After concentration *in vacuo*, the resulting oil was used without further purification:

The unpurified oil was dissolved in dry CH_2Cl_2 (30 mL) in an oven-dried 250-mL round-bottomed flask, and Dess-Martin Periodinane (1.32 g, 3.12 mmol, 1.6 equiv) was added in one portion at room temperature. The reaction was stirred at the same temperature under an N_2 atmosphere. Once TLC analysis indicated complete consumption of the monoalcohol (1.5 h), the reaction was diluted with diethyl ether (30 mL). Saturated aqueous sodium bicarbonate (20 mL) and saturated aqueous sodium thiosulfate (20 mL) were added, and biphasic mixture was stirred vigorously for 15 minutes. After partitioning the layers, the aqueous layer was extracted with diethyl ether (3x10 mL), and the combined organic extracts were washed with water and brine and dried with sodium sulfate. The combined extracts were concentrated *in vacuo* to give an oil that was purified via column chromatography (95:5 hexanes: ethyl acetate) to give the desired product **7** as a colorless oil (0.880 g, 83% over two steps).

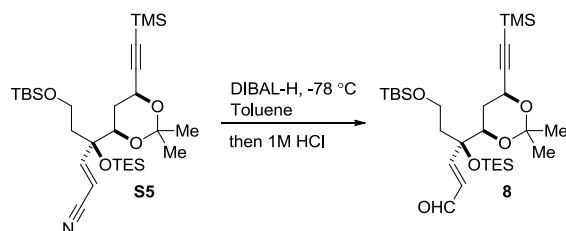
Mono alcohol S4: Analytical data: $[\alpha]_D^{25.6}$ -7.1 ($c = 2.15$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 4.66 (dd, $J = 12.0, 3.0$ Hz, 1H), 3.90 (dd, $J = 12.0, 2.5$ Hz, 1H), 3.88-3.80 (m, 1H), 3.75-3.65 (m, 2H), 3.48-3.39 (m, 2H), 1.87-1.64 (m, 4H), 1.45 (s, 6H), 0.94 (t, $J = 8.0$ Hz, 9H), 0.90 (s, 9H), 0.71-0.56 (m, 6H), 0.17 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 104.1, 99.4, 89.1, 78.3, 72.1, 64.7, 60.9, 58.7, 37.4, 31.0, 29.9, 25.8, 19.3, 18.1, 7.2,

6.8, -0.2, -5.6; **HRMS (ESI⁺)** Calcd. for C₂₇H₅₆O₅Si₃+Cs, 677.2491; Found, 677.2477; **IR** (thin film, cm⁻¹) 3492, 2955, 2877, 2360, 2183, 1463, 1414, 1251, 1107, 841, 736; **TLC**(85:15 Hex:EtOAc): R_f = 0.54.

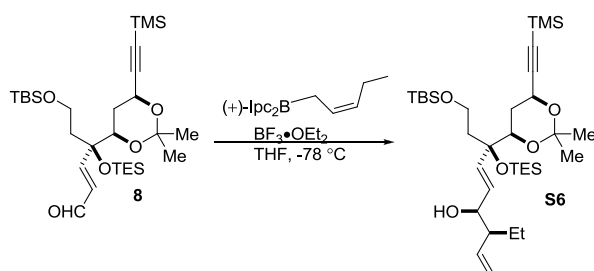
Aldehyde 7: Analytical data: [α]_D^{25.2} -15.0 (*c* = 1.25, CHCl₃); **¹H NMR** (400 MHz, CDCl₃): δ 9.56 (s, 1H), 4.68 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.13 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.74 (ddd, *J* = 12.0, 4.0, 2.8 Hz, 1H), 3.62 (ddd, *J* = 12.0, 4.0, 2.8 Hz, 1H), 1.90-1.65 (m, 4H), 1.40 (s, 3H), 1.39 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.86 (s, 9H), 0.81-0.66 (m, 6H), 0.17 (s, 9H), 0.02 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 203.2, 103.9, 99.5, 89.4, 83.7, 72.3, 60.7, 57.8, 38.7, 30.9, 29.6, 25.8, 19.1, 18.1, 7.2, 6.9, -0.2, -5.5, -5.6; **HRMS (ESI⁺)** Calcd. for C₂₇H₅₄O₅Si₃+Cs, 675.2352; Found, 675.2354; **IR** (thin film, cm⁻¹) 2955, 2876, 2360, 2342, 1736, 1462, 1415, 1380, 1251, 1110, 842, 738; **TLC**(85:15 Hex:EtOAc): R_f = 0.67.



(*R,E*)-6-((tert-butyldimethylsilyl)oxy)-4-((4*R*,6*S*)-2,2-dimethyl-6-((trimethylsilyl)ethynyl)-1,3-dioxan-4-yl)-4-((triethylsilyl)oxy)hex-2-enenitrile (5S): A flame-dried 25-mL round-bottomed flask was charged with the Horner-Wadsworth-Emmons reagent (0.320 g, 1.81 mmol, 1.05 equiv). THF (11.0 mL) was added and the solution was cooled to 0 °C. *n*-Butyllithium (1.2 mL, 1.5 M in hexanes, 1.05 equiv) was added dropwise, and the resulting orange solution was stirred for 1 h at the same temperature. A second flame-dried 100-mL round-bottomed flask was charged with the aldehyde (0.917 g, 1.69 mmol, 1.0 equiv) and THF (25 mL). The aldehyde solution was cooled to 0 °C, and the solution of the metalated Horner-Wadsworth-Emmons reagent was added via cannula. After the addition was complete, the reaction was warmed to room temperature for 30 minutes, at which point the starting material had been completely consumed as indicated by TLC analysis. The reaction was quenched by the addition of saturated ammonium chloride (0.3 mL), and the resulting suspension was concentrated to approximately 3 mL *in vacuo*. The remaining suspension was loaded directly onto a short silica plug and eluted with 95:5 hexanes: ethyl acetate to give the desired nitrile (0.920 g, 96%) with greater than 25:1 diastereoselectivity for the (*E*)-isomer. Analytical data: [α]_D^{25.7} +2.9 (*c* = 0.50, CHCl₃); **¹H NMR** (400 MHz, CDCl₃): δ 6.81 (d, *J* = 16.0 Hz, 1H), 5.61 (d, *J* = 16.0 Hz, 1H), 4.60 (dd, *J* = 11.6, 2.0 Hz, 1H), 3.70 (dd, *J* = 10.8, 2 Hz, 1H), 2.14 (ddd, *J* = 21.2, 14.4, 7.2 Hz, 1H), 1.81 (ddd, *J* = 19.6, 13.6, 6.8 Hz, 1H), 1.70 (d, *J* = 12.8 Hz, 1H), 1.55-1.46 (m, 1H), 1.44 (s, 3H), 1.43 (s, 3H), 0.98 (t, *J* = 7.6 Hz, 9H), 0.89 (s, 9H), 0.65 (q, *J* = 8.0 Hz, 6H), 0.18 (s, 9H), 0.04 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 156.8, 117.6, 103.2, 99.5, 99.2, 89.8, 79.1, 74.2, 60.6, 58.3, 40.3, 32.0, 29.8, 25.9, 19.1, 18.2, 7.1, 6.7, -0.2, -5.3, -5.4; **HRMS (ESI⁺)** Calcd. for C₂₉H₅₅NO₄Si₃+Cs, 698.2494; Found, 698.2470; **IR** (thin film, cm⁻¹) 2956, 2878, 2224, 1461, 1379, 1251, 1106, 840, 740; **TLC**(90:10 Hex:EtOAc): R_f = 0.46.



(*R,E*)-6-((*tert*-butyldimethylsilyl)oxy)-4-((4*R*,6*S*)-2,2-dimethyl-6-((trimethylsilyl)ethynyl)-1,3-dioxan-4-yl)-4-((triethylsilyl)oxy)hex-2-enal (8**):** A 50-mL oven dried and cooled round-bottomed flask was charged with the nitrile **S5** (0.920 g, 1.63 mmol, 1.0 equiv), and the flask was purged with N₂. Dry toluene (20 mL) was added, and the resulting solution was cooled to -78 °C in an acetone/dry ice bath. A solution of DIBAL-H (0.56 M in toluene, 4.9 mL, 1.7 equiv) was added dropwise, and the reaction was stirred at the same temperature for 1.5 h. Methanol (2.5 mL) was added at -78 °C, and the solution was warmed to 0 °C. Ice cold 1M HCl (20 mL) was added, and the biphasic mixture was stirred vigorously for 10 min at room temperature. Diethyl ether (20 mL) was added and the layers were separated. The aqueous layer was extracted with additional ether (3x5 mL), and the combined organic extracts were washed with saturated sodium bicarbonate, water, and brine and dried with magnesium sulfate. The dried extracts were concentrated *in vacuo* to give a light yellow oil, which was purified via column chromatography (93.5:7.5 hexanes: ethyl acetate) to give enal **8** as a colorless oil (0.745 g, 81%). Analytical data: $[\alpha]_D^{25.4} +6.2$ ($c = 0.45$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 9.60 (d, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 15.6$ Hz, 1H), 6.30 (dd, $J = 15.6, 8.0$ Hz, 1H), 4.62 (dd, $J = 11.6, 1.6$ Hz, 1H), 3.77 (dd, $J = 11.6, 1.6$ Hz, 1H), 3.76-3.52 (m, 2H), 2.20-2.13 (m, 1H), 1.92-1.85 (m, 1H), 1.76 (d, $J = 13.2$ Hz, 1H), 1.53 (dd, $J = 24.4, 12.0$ Hz, 1H), 1.44 (s, 6H), 0.97 (t, $J = 8.0$ Hz, 9H), 0.86 (s, 9H), 0.65 (q, $J = 8.0$ Hz, 6H), 0.16 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 193.6, 159.5, 131.7, 103.5, 99.5, 89.7, 79.0, 60.8, 58.6, 40.7, 32.1, 29.9, 25.9, 19.2, 18.2, 7.1, 6.9, -0.2, -5.3, -5.4; **HRMS (ESI⁺)** Calcd. for C₂₉H₅₆O₅Si₃+Na, 591.3334; Found, 591.3333; **IR** (thin film, cm⁻¹) 2956, 2878, 1694, 1462, 1379, 1251, 1105, 842; **TLC**(90:10 Hex:EtOAc): R_f = 0.33.



(3*S*,4*S*,7*R*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-7-((4*R*,6*S*)-2,2-dimethyl-6-((trimethylsilyl)ethynyl)-1,3-dioxan-4-yl)-3-ethyl-7-((triethylsilyl)oxy)nona-1,5-dien-4-ol (S6**):**

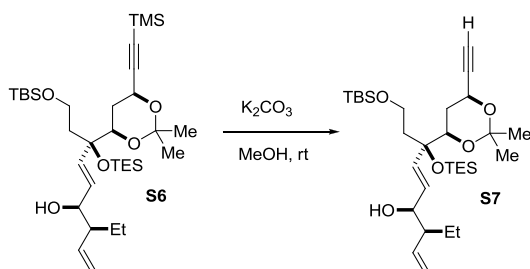
Preparation of (+)-Ipc₂BH:

A flame-dried and cooled 200-mL round-bottomed flask equipped with a magnetic stir bar was charged with (–)- α -pinene (5 mL, 4.28 g, 31.4 mmol, 2.4 equiv) and THF (4 mL). The flask was purged with N₂ and was placed into a room temperature water bath. Borane•DMS (2M

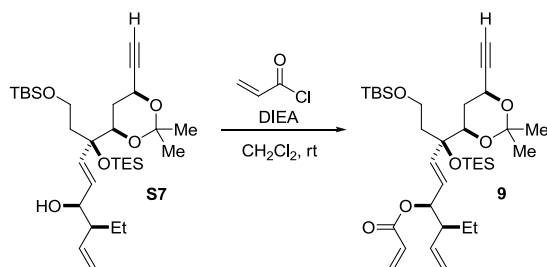
in THF, 6.5 mL, 0.981 g, 13.08 mmol, 1.0 equiv) was added dropwise with vigorous stirring over 2 min. Stirring of the reaction was ceased, and the stir bar was removed. The flask was again purged with N₂, and the resulting solution was allowed to sit at room temperature for 16 h. Crystals were observed on the side of the flask after 1 h at room temperature. The solvent was removed from the flask via cannula, and the remaining solid was washed with dry hexanes (2x20 mL), which was removed via cannula transfer. The flask was evacuated to remove residual solvent, and the resulting white solid was removed to a dry box freezer. The reagent was able to be stored without degradation for months when prepared and stored in this manner (2.7 g, 73%).

(+)-Ipc₂BOMe was prepared *in situ* according to the following:

An oven-dried and cooled 50-mL round-bottomed flask was charged with Ipc₂BH (2.95 g, 10.32 mmol, 2.5 equiv) under a nitrogen atmosphere and dry THF (30 mL). Dry MeOH (0.417 mL, 10.32 mmol, 2.5 equiv) was added dropwise, and the resulting solution was stirred at room temperature for 4 h. A second 250-mL oven-dried round-bottomed flask was charged with potassium *tert*-butoxide (0.926 g, 8.26 mmol, 2.0 equiv) under a nitrogen atmosphere. Dry THF (45 mL) and *cis*-2-pentene (2.68 mL, 24.8 mmol, 6.0 equiv) were added, and the solution was cooled to -50 °C in an acetone/dry ice bath. ⁿButyllithium (1.5 M, 5.5 mL, 2.0 equiv) was added dropwise, and the resulting orange solution was stirred at the same temperature for 5 minutes before cooling to -78 °C. The solution of (+)-Ipc₂BOMe was added dropwise via cannula transfer, and the resulting colorless solution was stirred at -78°C for 20 minutes. BF₃•OEt₂ (1.02 mL, 8.26 mmol, 2.0 equiv) was added, followed by a solution of the aldehyde (**8**) (2.35 g, 4.13 mmol, 1.0 equiv) in dry THF (10 mL + 5 mL rinse). The bath temperature was maintained at -78 °C until complete consumption of the starting material was indicated by TLC analysis (2 h). The reaction was quenched by the dropwise addition of 3M NaOH (6.0 mL) and 30% H₂O₂ (3.2 mL). After warming to room temperature, the suspension was refluxed for 1 h. The cooled biphasic mixture was partitioned between ether and water, and the combined ethereal extracts were washed with water and brine and dried with magnesium sulfate. The organic extracts were concentrated *in vacuo* to give a crude oil, which was purified via flash chromatography (93.5:7.5 to 90:10 petroleum ether: ether) to give the desired product as a viscous colorless oil (2.23 g, 85%). The title compound was obtained as a diastereomeric mixture whose ratio was dependent on the initial enantiomeric ratio of the β-lactone used in the initial 3-component coupling. This diastereomeric mixture was progressed without separation until the final compound (**16**), at which point separation of the isomers via HPLC afforded diastereomerically pure material. Analytical data: $[\alpha]_D^{25.2} -1.8$ (*c* = 0.50, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 5.73 (dd, *J* = 16.0, 5.5 Hz, 1H), 5.66 (dd, *J* = 15.5, 10.5 Hz, 1H), 5.55 (ddd, *J* = 17.5, 9.5, 6.0 Hz, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 5.11 (d, *J* = 17.0 Hz, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.13 (t, *J* = 6.0 Hz, 1H), 3.66-3.61 (m, 3H), 1.94-1.91 (m, 2H), 1.59-1.42 (m, 2H), 1.42 (s, 3H), 1.41 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 9H), 0.89 (s, 9H), 0.63 (q, *J* = 7.5 Hz, 6H), 0.17 (s, 9H), 0.04 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 138.3, 132.8, 130.6, 118.0, 104.1, 99.1, 89.1, 78.2, 74.1, 74.0, 60.9, 59.4, 52.7, 40.0, 31.9, 29.9, 26.0, 23.3, 19.2, 18.3, 11.9, 7.2, 6.9, -0.2, -5.2, -5.3; HRMS (ESI⁺) Calcd. for C₃₄H₆₆O₅Si₃+Na, 661.4116; Found, 661.4091; IR (thin film, cm⁻¹) 3465, 2956, 2877, 2183, 1461, 1378, 1251, 1090, 842; TLC(90:10 Hex:EtOAc): R_f = 0.30.

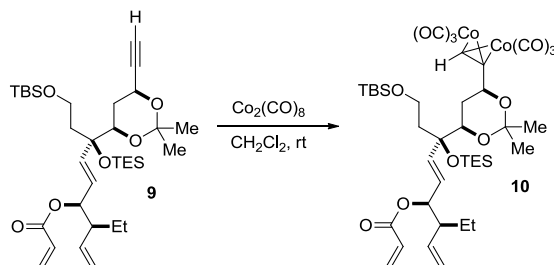


(3*S*,4*S*,7*R*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-3-ethyl-7-((4*R*,6*S*)-6-ethynyl-2,2-dimethyl-1,3-dioxan-4-yl)-7-((triethylsilyl)oxy)nona-1,5-dien-4-ol (S5**):** Silyl alkyne **S6** (2.2 g, 3.46 mmol, 1.0 equiv) was dissolved in methanol (20 mL), and potassium carbonate (0.2 g, 1.45 mmol, 0.42 equiv) was added at room temperature. Once the starting material was completely consumed as indicated by TLC analysis ($R_f = 0.30$, 90:10 Hex:EtOAc; 1 h), the suspension was loaded directly onto a short silica plug and eluted with 80:20 hexanes:ethyl acetate to give the crude alkyne. Analytical data: $[\alpha]_D^{25.3} +6.2$ ($c = 1.70$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 5.72 (dd, $J = 16.0, 5.5$ Hz, 1H), 5.65 (d, $J = 14.0$ Hz, 1H), 5.55 (dd, $J = 9.5, 7.5$ Hz, 1H), 5.17 (d, $J = 15.0$ Hz, 1H), 5.11 (d, $J = 17.0$ Hz, 1H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.13 (br. s., 1H), 3.68-3.63 (m, 3H), 2.46 (s, 1H), 2.14-2.12 (m, 1H), 1.94-1.91 (m, 6H), 1.43 (s, 3H), 1.41 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 9H), 0.89 (s, 9H), 0.63 (q, $J = 7.5$ Hz, 6H), 0.04 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 138.3, 132.7, 130.7, 118.1, 99.2, 82.7, 78.1, 73.9, 73.8, 72.7, 60.3, 59.4, 52.7, 40.1, 31.6, 29.9, 26.0, 23.3, 19.2, 18.3, 11.9, 7.2, 6.8, -5.2, -5.3; **HRMS (ESI⁺)** Calcd. for $\text{C}_{31}\text{H}_{58}\text{O}_5\text{Si}_2 + \text{Cs}$, 825.3379; Found, 825.3399; **IR** (thin film, cm^{-1}) 3433, 3032, 2958, 2359, 2253, 1637, 908, 725, 650, 452; **TLC**(75:25 Hex:EtOAc): $R_f = 0.39$.

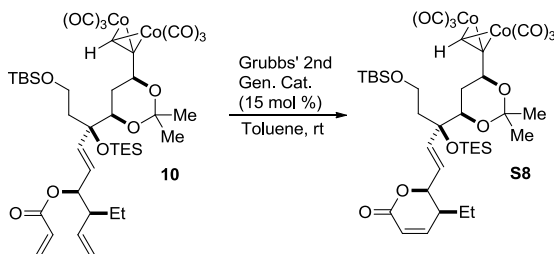


(3*S*,4*S*,7*R*,*E*)-9-((*tert*-butyldimethylsilyl)oxy)-3-ethyl-7-((4*R*,6*S*)-6-ethynyl-2,2-dimethyl-1,3-dioxan-4-yl)-7-((triethylsilyl)oxy)nona-1,5-dien-4-yl acrylate (9**):** A flame-dried and cooled 100-mL round-bottomed flask equipped with a magnetic stir bar was charged with the crude allylic alcohol (**S7**) (1.95 g, 3.46 mmol, 1.0 equiv) and dry CH_2Cl_2 (40 mL), and the solution was cooled to 0 °C. Hünig's base (1.82 mL, 10.73 mmol, 3.1 equiv) and acryloyl chloride (0.846 mL, 10.37 mmol, 3.0 equiv) were added dropwise. After maintaining the solution at 0 °C for 1.5, TLC analysis indicated complete consumption of the starting material ($R_f = 0.39$, 75:25 Hex:EtOAc). The reaction was quenched by the addition of saturated sodium bicarbonate (10.0 mL), and the organic layer was washed with additional saturated sodium bicarbonate (3x 10.0 mL), water, and brine and was dried with magnesium sulfate. Concentration *in vacuo* yielded a colorless oil (2.14 g) that was used without additional purification. Analytical data: $[\alpha]_D^{25.0} +24.9$ ($c = 0.21$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 6.40 (d, $J = 17.6$ Hz, 1H), 6.12 (dd, $J = 17.2, 10.4$ Hz, 1H), 5.81 (d, $J = 13.0$ Hz, 1H), 5.70-5.52 (m, 3H), 5.32 (t, $J = 7.5$ Hz, 1H), 5.14 (d, $J = 12.5$ Hz, 1H), 5.05 (d, $J = 16.8$ Hz, 1H), 4.58 (d, $J = 12.0$ Hz, 1H), 3.66-3.59 (m, 3H),

2.45 (s, 1H), 2.32-2.19 (m, 1H), 1.99-1.80 (m, 2H), 1.77-1.61 (m, 2H), 1.41 (s, 3H), 1.39 (s, 3H), 1.35-1.15 (m, 2H), 0.94 (t, $J = 9.5$ Hz, 9H), 0.88 (s, 9H), 0.60 (q, $J = 7.6$ Hz, 6H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.2, 137.4, 135.2, 130.5, 128.7, 126.7, 117.6, 99.2, 82.7, 778.0, 76.2, 73.8, 72.6, 60.3, 59.3, 49.8, 40.0, 31.2, 29.9, 26.0, 23.2, 19.2, 18.3, 11.5, 7.2, 6., -5.2, -5.3; **HRMS** (ESI^+) Calcd. for $\text{C}_{34}\text{H}_{60}\text{O}_6\text{Si}_2+\text{Cs}$, 753.2983; Found, 753.3014; **IR** (thin film, cm^{-1}) 3426, 2956, 2877, 2359, 1798, 1725, 1634, 1402, 1097, 981, 836, 630; **TLC**(80:20 Hex:EtOAc): $R_f = 0.63$.

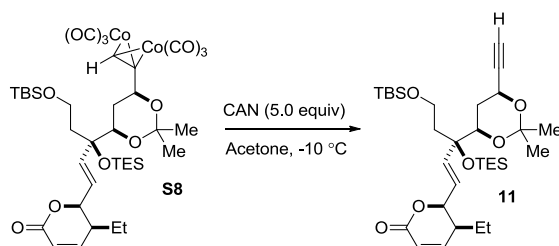


Protected Alkyne 10: The crude acrylate **9** (2.14 g, 3.46 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (40 mL) under an atmosphere of nitrogen, and dicobalt octacarbonyl (1.18 g, 3.46 mmol, 1.0 equiv) was added. The reaction was stirred at room temperature for 1.5 h, at which point TLC analysis indicated complete consumption of the starting material ($R_f = 0.63$, 80:20 Hex:EtOAc). The reaction was concentrated *in vacuo*, and the crude material was purified via flash chromatography (95:5 petroleum ether: ether) to give the desired product as a dark red oil (2.7 g, 89% over 3 steps). Analytical data: $[\alpha]_D^{24.2} -153.9$ ($c = 0.46$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 6.38 (d, $J = 17.2$ Hz, 1H), 6.10 (dd, $J = 28.0, 10.4$ Hz, 1H), 5.96 (s, 1H), 5.80 (d, $J = 10.4$ Hz, 1H), 5.74-5.54 (m, 3H), 5.36 (t, $J = 5.2$ Hz, 1H), 5.10 (d, $J = 10.4$ Hz, 1H), 5.04 (d, $J = 17.2$ Hz, 1H), 4.85 (d, $J = 10.8$ Hz, 1H), 3.78 (dd, $J = 10.8, 7.2$ Hz, 1H), 3.68-3.63 (m, 2H), 2.27-2.20 (m, 1H), 1.95-1.90 (m, 2H), 1.82 (d, $J = 12.4$ Hz, 1H), 1.49-1.32 (m, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.89 (s, 9H), 0.63-0.56 (m, 6H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.7, 165.1, 137.5, 134.6, 130.5, 128.7, 126.3, 117.3, 99.2, 77.9, 75.9, 74.0, 70.4, 69.6, 59.4, 49.8, 40.1, 34.0, 29.5, 26.0, 22.9, 19.8, 18.4, 11.6, 7.2, 6.8, 6.7, -5.2, -5.3; **HRMS** (ESI^+) Calcd. for $\text{C}_{40}\text{H}_{60}\text{Co}_2\text{O}_{12}\text{Si}_2+\text{Cs}$, 1039.1342; Found, 1039.1344; **IR** (thin film, cm^{-1}) 2956, 2929, 2877, 2857, 2095, 2054, 2030, 1726, 1462, 1404, 1190, 1098, 836; **TLC**(80:20 Hex:EtOAc): $R_f = 0.71$.

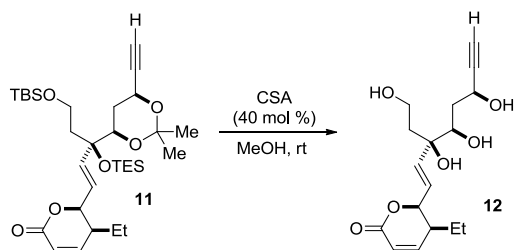


Dihydropyrone 88: A 250-mL flame-dried and cooled round-bottomed flask was charged with acrylate **10** (0.530 g, 0.543 mmol, 1.0 equiv). Under a nitrogen atmosphere, dry toluene (125 mL) and Grubbs' 2nd generation catalyst (0.092 g, 0.122 mmol, 0.15 equiv) were added, and the reaction was stirred under nitrogen for 16 h at room temperature. The solvent was removed *in vacuo*, and the resulting crude oil was purified via column chromatography (90:10 to 80:20

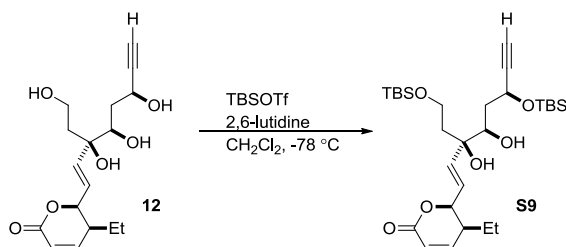
hexanes:ethyl acetate) to give the dihydropyrone as a dark red oil (0.340 g, 66%). Analytical data: $[\alpha]_D^{24.7}$ -29.5 ($c = 2.55$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.93 (dd, $J = 9.5, 5.0$ Hz, 1H), 6.04 (d, $J = 9.5$ Hz, 1H), 5.98 (s, 1H), 5.93 (d, $J = 16.0$ Hz, 1H), 5.74 (dd, $J = 15.5, 5.5$ Hz, 1H), 4.99 (t, $J = 4.5$ Hz, 1H), 4.87 (d, $J = 11.5$ Hz, 1H), 3.82 (d, $J = 11.0$ Hz, 1H), 3.66 (t, $J = 8.0$ Hz, 2H), 2.43-2.34 (m, 1H), 2.07-1.82 (m, 3H), 1.68-1.56 (m, 1H), 1.47 (s, 3H), 1.37 (s, 3H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.95 (t, $J = 7.0$ Hz, 9H), 0.89 (s, 9H), 0.63 (q, $J = 7.5$ Hz, 6H), 0.04 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 199, 6, 164.0, 149.8, 135.7, 124.6, 120.9, 99.4, 97.0, 80.1, 78.1, 74.4, 40.6, 69.6, 59.3, 40.5, 39.4, 34.0, 29.5, 25.9, 21.6, 19.7, 18.3, 11.0, 7.2, 6.8, -5.2, -5.3; **HRMS (ESI⁺)** Calcd. for $\text{C}_{38}\text{H}_{56}\text{Co}_2\text{O}_{12}\text{Si}_2+\text{Cs}$, 1011.1029; Found, 1011.1057; **IR** (thin film, cm^{-1}) 2928, 2856, 2360, 2095, 2054, 2029, 1732, 1462, 1379, 1254, 1099, 835, 776; **TLC**(80:20 Hex:EtOAc): $R_f = 0.48$.



(5*S*,6*S*)-6-((*R,E*)-5-((tert-butyl dimethylsilyloxy)-3-((4*R*,6*S*)-6-ethynyl-2,2-dimethyl-1,3-dioxan-4-yl)-3-((triethylsilyloxy)pent-1-en-1-yl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (11): A 50-mL round-bottomed flask was charged with **S8** (0.340 g, 0.400 mmol, 1.0 equiv) and acetone (20 mL). The flask was cooled to $-10\text{ }^\circ\text{C}$ (acetone-ice), and ceric ammonium nitrate (0.988 g, 1.8 mmol, 4.5 equiv) was added in small portions. The reaction was stirred at $-10\text{ }^\circ\text{C}$ for 45 minutes, at which time TLC analysis indicated complete consumption of the starting material. The reaction was poured into saturated aqueous sodium bicarbonate (20 mL) and was extracted with diethyl ether (3x 20 mL). The combined organic extracts were washed with saturated bicarbonate, water, and brine and were dried with magnesium sulfate. Removal of the solvent *in vacuo* afforded a light yellow oil (220 mg, 93%) that was used without further purification. Analytical data: $[\alpha]_D^{25.3}$ -57.6 ($c = 0.49$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.96 (dd, $J = 10.0, 5.5$ Hz, 1H), 6.06 (d, $J = 10.0$ Hz, 1H), 5.90 (d, $J = 15.5$ Hz, 1H), 5.76 (dd, $J = 15.5, 5.5$ Hz, 1H), 5.03 (t, $J = 5.0$ Hz, 1H), 4.59 (d, $J = 12.0$ Hz, 1H), 3.69 (d, $J = 11.5$ Hz, 1H), 3.63 (t, $J = 8.0$ Hz, 2H), 2.46 (s, 1H), 2.42-2.41 (m, 1H), 1.76 (d, $J = 13.0$ Hz, 1H), 1.60-1.41 (m, 3H), 0.96 (t, $J = 8.0$ Hz, 9H), 0.96 (t, $J = 8.0$ Hz, 3H); 2 coincident resonances, 0.95 (t, $J = 7.0$ Hz, 9H), 0.88 (s, 9H), 0.64 (dq, $J = 8.0, 4.0$ Hz, 6H), 0.04 (s, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 164.0, 149.9, 135.2, 124.8, 120.8, 103.8, 99.2, 89.2, 80.0, 78.2, 74.2, 60.7, 59.2, 39.7, 39.6, 32.0, 29.9, 25.9, 21.5, 19.2, 18.2, 11.0, 7.2, 6.8, -0.2, -5.3, -5.4; **HRMS (ESI⁺)** Calcd. for $\text{C}_{32}\text{H}_{56}\text{O}_6\text{Si}_2+\text{Na}$, 615.3513; Found, 615.3515; **IR** (thin film, cm^{-1}) 3420, 3029, 2874, 2359, 1645, 1384, 1112, 821, 581; **TLC**(75:25 Hex:EtOAc): $R_f = 0.32$.

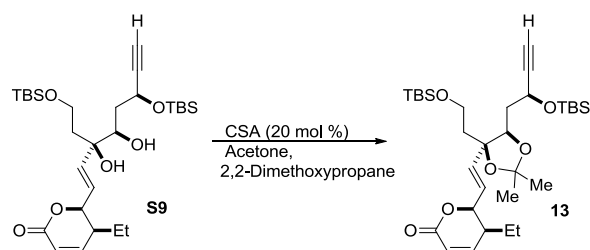


(5*S*,6*S*)-5-ethyl-6-((3*R*,4*R*,6*S*,*E*)-3,4,6-trihydroxy-3-(2-hydroxyethyl)oct-1-en-7-yn-1-yl)-5,6-dihydro-2*H*-pyran-2-one (12): A 20-mL scintillation vial was charged with alkyne **11** (150 mg, 0.253 mmol, 1.0 equiv) and methanol (5 mL). CSA (24 mg, 0.101 mmol, 0.4 equiv) was added, and the reaction was allowed to stir at room temperature for 1 h. The reaction was quenched with triethylamine (0.050 mL) and was concentrated *in vacuo*. The crude material was pushed through a short silica plug (95:5 to 92.5:7.5 CH₂Cl₂: MeOH, SiO₂ deactivated with TEA) to give the crude tetraol as a yellow oil that was used without further purification. Analytical data: $[\alpha]_D^{25.4} +78.3$ ($c = 0.5$, CHCl₃); **¹H NMR** (400 MHz, CDCl₃): δ 6.99 (dd, $J = 5.5, 10.0$ Hz, 1H), 6.06 (d, $J = 10.0$ Hz, 1H), 6.00 (dd, $J = 5.0, 15.5$ Hz, 1H), 5.95 (d, $J = 16.0$ Hz, 1H), 5.09 (t, $J = 4.5$ Hz, 1H), 4.62 (br. s., 1H), 4.34 (br. s., 1H), 3.87 (br. s., 2H), 3.75 (d, $J = 9.5$ Hz, 1H), 3.65 (br. s., 1H), 3.00 (br. s., 1H), 2.50 (d, $J = 1.5$ Hz, 1H), 2.50-2.46 (m, 1H), 2.12-1.42 (m, 6H), 0.97 (t, $J = 7.5$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 164.4, 150.4, 135.4, 126.0, 120.6, 84.1, 80.3, 77.9, 76.3, 73.2, 61.8, 59.7, 39.2, 38.2, 35.9, 29.7, 21.5, 11.0; **HRMS (ESI⁺)** Calcd. for C₁₇H₂₄O₆+Na, 347.1485; Found, 347.1471; **IR** (thin film, cm⁻¹) 3433, 3019, 2400, 1645, 1521, 1215, 928, 768, 669; **TLC**(90:10 CH₂Cl₂:MeOH): R_f = 0.37.

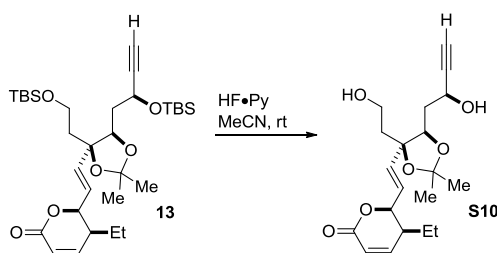


(5*S*,6*S*)-6-((3*R*,4*R*,6*S*,*E*)-6-((tert-butyldimethylsilyl)oxy)-3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3,4-dihydroxyoct-1-en-7-yn-1-yl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (9): An oven-dried 20-mL scintillation vial was charged with crude tetraol **12** (82 mg, 0.218 mmol, 1.0 equiv) and CH₂Cl₂ (6.0 mL). The solution was cooled to -78 °C in an acetone-dry ice bath, and 2,6-lutidine (0.060 mL, 54 mg, 0.501 mmol, 2.3 equiv) and TBSOTf (0.105 mL, 121 mg, 0.458 mmol, 2.1 equiv) were added successively. The reaction was maintained at -78 °C for 10 min, at which point TLC indicated complete consumption of the starting material and clean formation of the desired diol. The reaction was quenched by the addition of MeOH (0.100 mL) and was warmed to room temperature. After diluting with diethyl ether (20 mL), the solution was washed with 1 M HCl (3x5 mL), saturated aqueous NaHCO₃ (5 mL), water (5 mL), and brine (5 mL) and was dried with sodium sulfate. Concentration *in vacuo* gave a light yellow oil (110 mg) that was used without additional purification. Analytical data: $[\alpha]_D^{25.6} +41.2$ ($c = 0.3$, CHCl₃); **¹H NMR** (400 MHz, CDCl₃): δ 6.89 (dd, $J = 10.0, 4.8$ Hz, 1H), 6.04-5.88 (m, 3H), 5.03 (t, $J = 4.4$ Hz, 1H), 4.55 (dd, $J = 13.6, 1.6$ Hz, 1H), 4.53 (br. s. 1H), 3.83 (t, $J = 3.6$ Hz, 2H), 3.66 (d, $J = 9.2$ Hz, 1H), 2.48-2.42 (m, 1H), 2.40 (d, $J = 2.0$ Hz, 1H), 2.01-1.36 (m, 6H), 0.94 (t, $J = 7.6$ Hz, 3H), 0.88 (s, 9H), 0.86 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H); **¹³C NMR** (100

MHz, CDCl_3): δ 163.8, 149.5, 136.3, 125.4, 120.9, 84.6, 80.6, 80.0, 77.4, 75.8, 73.0, 62.9, 60.8, 39.4, 36.5, 25.7, 25.7 (2 coincident resonances), 21.6, 18.0, 17.9, 11.0, -4.5, -5.2, -5.7, -5.8; **HRMS (ESI⁺)** Calcd. for $\text{C}_{29}\text{H}_{52}\text{O}_6\text{Si}_2+\text{Cs}$, 685.2357; Found, 685.2366; **IR** (thin film, cm^{-1}): 3433, 3019, 2930, 2359, 1646, 1472, 1212, 983, 769, 668; **TLC**(90:10 CH_2Cl_2 :MeOH): $R_f = 0.79$.

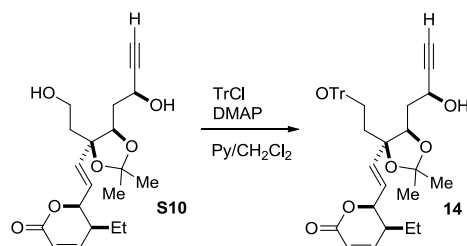


(5*S*,6*S*)-6-((*E*)-2-((4*R*,5*S*)-5-((*S*)-2-((tert-butyl dimethylsilyloxy)but-3-yn-1-yl)-4-(2-((tert-butyl dimethylsilyloxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (13): A 20-mL scintillation vial was charged with crude diol **S9** (110 mg, 0.200 mmol, 1.0 equiv). Dry acetone (6.0 mL) and 2,2-dimethoxypropane (6.0 mL) were added, followed by CSA (10.0 mg, 0.040 mmol, 0.22 equiv). The reaction was allowed to stir at room temperature for 1.5 h, at which point TLC analysis indicated complete consumption of the diol ($R_f = 0.45$, 60:40 hexanes:EtOAc). The reaction was quenched with triethylamine (4 drops) and was concentrated *in vacuo*. The resulting crude oil was purified via flash chromatography, eluting with 80:20 hexanes: ethyl acetate to give the desired product in 73% yield over 3 steps (109 mg) as a colorless oil. Analytical data: $[\alpha]_D^{24.3} +43.9$ ($c = 0.3$, CHCl_3); **¹H NMR** (400 MHz, CDCl_3): δ 6.94 (dd, $J = 9.6, 5.6$ Hz, 1H), 6.03 (d, $J = 10.0$ Hz, 1H), 5.90-5.72 (br. s., 2H), 4.98 (t, $J = 3.6$ Hz, 1H), 4.50 (dd, $J = 8.0, 5.6$ Hz, 1H), 3.87 (d, $J = 8.8$ Hz, 1H), 3.75-3.56 (m, 2H), 2.44-2.23 (m, 1H), 2.44 (s, 1H), 2.00-1.31 (m, 6H), 0.92 (t, $J = 7.6$ Hz, 3H), 0.88 (s, 9H), 0.86 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H), 0.01 (s, 6H); **¹³C NMR** (100 MHz, CDCl_3): δ 163.6, 149.5, 134.3, 124.5, 121.0, 108.1, 108.0, 84.4, 82.8, 80.4, 79.6, 73.2, 61.3, 59.4, 39.3, 37.5, 37.2, 28.3, 26.3, 25.9, 25.7, 21.6, 18.3, 18.1, 10.9, -4.6, -5.0, -5.3; **HRMS (ESI⁺)** Calcd. for $\text{C}_{32}\text{H}_{56}\text{O}_6\text{Si}_2+\text{Na}$, 615.3513; Found, 615.3554; **IR** (thin film, cm^{-1}): 3019, 1521, 1215, 930, 758, 669, 521, 509; **TLC**(97.5:2.5 CH_2Cl_2 :MeOH): $R_f = 0.72$.



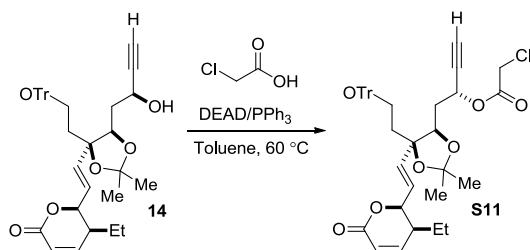
(5*S*,6*S*)-5-ethyl-6-((*E*)-2-((4*R*,5*S*)-5-((*S*)-2-hydroxybut-3-yn-1-yl)-4-(2-hydroxyethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-5,6-dihydro-2*H*-pyran-2-one (S10): A plastic scintillation vial equipped with a magnetic stir bar was charged with **13** (97 mg, 0.163 mmol, 1.0 equiv) and acetonitrile (4 mL). The resulting solution was cooled to 0°C, and HF•pyridine (70% HF, 0.25 mL) was added dropwise. The solution was allowed to warm to room temperature and was stirred for 90 min. The reaction was quenched by the addition of saturated aqueous NaHCO_3 (5.0 mL). The resulting suspension was diluted with EtOAc, and the layers were separated. The

aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with 1M HCl, NaHCO₃, and brine and dried with MgSO₄. The solvent was removed *in vacuo* to afford a crude white solid that was used without additional purification (65 mg). Analytical data: $[\alpha]_D^{25.6} +99.4$ ($c = 0.45$, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 6.98(dd, $J = 9.5, 5.5$ Hz, 1H), 6.07(d, $J = 9.5$ Hz, 1H), 6.00-5.87 (m, 2H), 5.06 (t, $J = 3.5$ Hz, 1H), 4.57 (br. s, 1H), 3.96 (d, $J = 10.5$ Hz, 1H), 3.81 (dt, $J = 10.5, 4.0$ Hz, 1H), 3.79-3.71 (m, 1H), 3.79-3.71 (m, 1H), 2.69 (br. s, 1H), 2.55 (br s, 1H), 2.49 (d, $J = 1.5$ Hz, 1H), 2.46-2.43 (m, 1H), 2.17-1.53 (m, 4H), 1.53 (s, 3H), 1.38 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.8, 150.0, 132.6, 125.4, 120.8, 109.0, 85.3, 83.5, 81.4, 79.3, 73.6, 61.1, 59.5, 39.1, 36.4, 35.4, 28.1, 26.3, 21.6, 11.0; **HRMS (ESI⁺)** Calcd. for C₂₀H₂₈O₆+Na, 387.1784; Found, 387.1773; **IR** (thin film, cm⁻¹) 3433, 2389, 2095, 1900, 1690, 1641, 1549, 1501, 1217; **TLC**(75:25 Hex:EtOAc): R_f = 0.17.

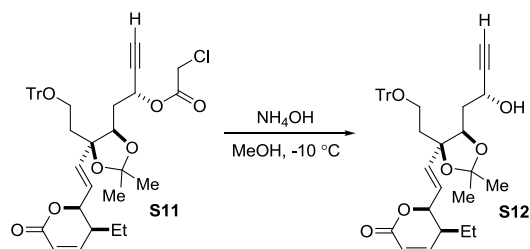


(5*S*,6*S*)-5-ethyl-6-((*E*)-2-((4*R*,5*S*)-5-((*S*)-2-hydroxybut-3-yn-1-yl)-2,2-dimethyl-4-(2-(trityloxy)ethyl)-1,3-dioxolan-4-yl)vinyl)-5,6-dihydro-2H-pyran-2-one (14):

An oven-dried and cooled 20-mL scintillation vial equipped with a magnetic stir bar was charged with diol **S10** (35 mg, 0.097 mmol, 1.0 equiv), TrCl (81 mg, 0.290 mmol, 3.0 equiv), and DMAP (cat.). CH₂Cl₂ (2.0 mL) and pyridine (0.2 mL) were added, and the resulting solution was allowed to stir at rt for 16 h. The reaction was quenched by the addition of saturated aqueous NaHCO₃ and was diluted with Et₂O. The resulting suspension was washed with aqueous NaHCO₃ and brine and dried with MgSO₄. After concentration *in vacuo*, the crude product was purified via flash chromatography, eluting with a gradient of 80:20 to 60:40 hexanes:EtOAc, to yield the title compound as a colorless oil (44.5 mg, 76% from **13**). Analytical data: $[\alpha]_D^{24.4} +48.0$ ($c = 0.70$, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.41-7.19 (m, 15H), 6.87 (dd, $J = 9.5, 5.5$ Hz, 1H), 5.97 (d, $J = 10.0$ Hz, 1H), 5.73 (d, $J = 22.5$ Hz, 1H), 5.67 (dd, $J = 19.5, 4.0$ Hz, 1H), 4.91 (t, $J = 3.5$ Hz, 1H), 4.55 (t, $J = 3.0$ Hz, 1H), 3.82 (dd, $J = 10.5, 2.0$ Hz, 1H), 3.32-3.31 (m, 1H), 3.07-3.05 (m, 1H), 2.68 (d, $J = 3.0$ Hz, 1H), 2.49 (d, $J = 1.5$ Hz, 1H), 2.30-1.62 (m, 5H), 1.36-1.30 (m, 2H), 1.36 (s, 3H), 1.30 (s, 3H), 0.76 (t, $J = 7.5$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.9, 149.9, 144.2, 144.2, 132.9, 128.6, 128.6, 127.7, 127.7, 126.9, 124.6, 120.7, 108.7, 86.8, 83.6, 83.1, 81.9, 79.2, 73.3, 61.4, 59.8, 38.9, 36.4, 34.2, 28.2, 26.5, 21.4, 10.9; **HRMS (ESI⁺)** Calcd. for C₃₉H₄₂O₆+Na, 629.2879; Found, 629.2871; **IR** (thin film, cm⁻¹) 3434, 3019, 2849, 2399, 2083, 1900, 1724, 1612, 1482, 1216, 1045, 755; **TLC**(75:25 Hex:EtOAc): R_f = 0.77.

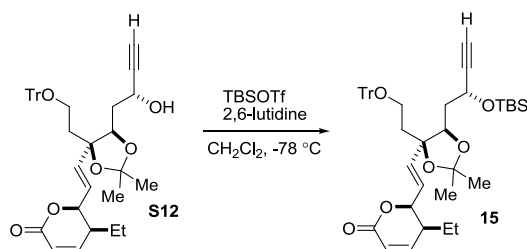


(R)-1-((4S,5R)-5-((E)-2-((2S,3S)-3-ethyl-6-oxo-3,6-dihydro-2H-pyran-2-yl)vinyl)-2,2-dimethyl-5-(2-(trityloxy)ethyl)-1,3-dioxolan-4-yl)but-3-yn-2-yl 2-chloroacetate (S11): An oven-dried and cooled 20-mL scintillation vial equipped with magnetic stir bar was charged with alcohol **14** (85 mg, 0.141 mmol, 1.0 equiv), chloroacetic acid (53 mg, 0.566 mmol, 4.0 equiv), and PPh₃ (78 mg, 0.296 mmol, 2.1 equiv). The vial was purged with N₂, and toluene (2.0 mL) was added. DEAD (43 μL, 49 mg, 0.282 mmol, 2.0 equiv) was added dropwise. The reaction was allowed to stir at 60 °C for 30 min and was quenched by the addition of a saturated aqueous solution of ammonium chloride (3 drops). The resulting suspension was loaded directly onto a silica gel column and was purified via flash chromatography, eluting with 100:0 to 95:5 CH₂Cl₂:Et₂O, to afford the title compound as a colorless oil (74 mg, 77%). Analytical data: $[\alpha]_D^{25.7} +56.7$ (*c* = 0.16, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.47-7.24 (m, 15H), 6.91 (dd, *J* = 9.6, 5.6 Hz, 1H), 6.02(d, *J* = 10.0 Hz, 1H), 5.77 (d, *J* = 16.4 Hz, 1H), 5.70 (dd, *J* = 15.2, 3.6 Hz, 1H), 5.58 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.96 (t, *J* = 3.2 Hz, 1H), 4.12 (s, 2H), 3.78 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.37 (ddd, *J* = 14.4, 9.6, 4.8 Hz, 1H), 3.12 (ddd, *J* = 15.2, 9.6, 4.8 Hz, 1H), 2.61 (d, *J* = 2.0 Hz, 1H), 2.35-2.01 (m, 4H), 1.80-1.56 (m, 1H), 1.39 (s, 3H), 1.30 (s, 3H), 1.20-1.05 (m, 1H), 0.81 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.1, 163.6, 149.7, 144.2, 133.0, 128.6, 128.6, 127.7, 126.8, 124.7, 120.7, 108.3, 86.8, 82.5, 79.9, 79.2, 78.7, 74.7, 62.9, 59.8, 40.6, 39.0, 34.1, 34.0, 28.1, 26.3, 21.3, 10.8; **HRMS (ESI⁺)** Calcd. for C₄₁H₄₃ClO₇+Cs, 815.1752; Found, 815.1796; **IR** (thin film, cm⁻¹) 3434, 3019, 2849, 1737, 1658, 1442, 1331, 1215, 755, 668; **TLC**(50:50Hex:EtOAc): R_f = 0.63.

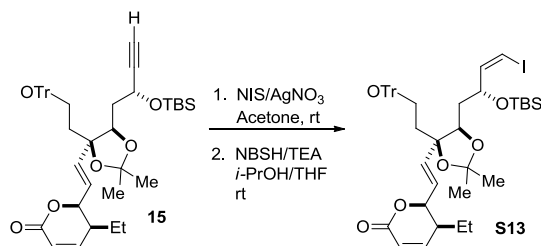


(5S,6S)-5-ethyl-6-((E)-2-((4R,5S)-5-((R)-2-hydroxybut-3-yn-1-yl)-2,2-dimethyl-4-(2-(trityloxy)ethyl)-1,3-dioxolan-4-yl)vinyl)-5,6-dihydro-2H-pyran-2-one (S12): A 20-mL scintillation vial equipped with magnetic stir bar was charged with chloroacetate **S11** (69 mg, 0.102 mmol, 1.0 equiv). MeOH (2 mL) was added, and the resulting solution was cooled to -10 °C in an acetone-ice bath. Saturated NH₄OH (4 drops) was added, and the solution was allowed to stir at the same temperature for 10 min. The solution was diluted with Et₂O and brine, and the layers were separated. The organic layer was washed successively with saturated aqueous NaHCO₃ and brine and dried with MgSO₄. Concentration *in vacuo* yielded a colorless oil that was used without additional purification (59 mg, 96%). Analytical data: $[\alpha]_D^{24.6} +53.3$ (*c* = 0.24,

CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.57-7.12 (m, 15H), 6.89 (dd, *J* = 8.8, 5.2 Hz, 1H), 6.00 (d, *J* = 9.6 Hz, 1H), 5.77 (d, *J* = 17.6 Hz, 1H), 5.70 (d, *J* = 16.4 Hz, 1H), 4.95 (s, 1H), 4.64 (br. s, 1H), 4.14 (d, *J* = 10.8), 3.37 (br. s, 1H), 3.12-2.94 (m, 2H), 2.52 (s, 1H), 2.31-2.11 (m, 1H), 2.07-1.72 (m, 4H), 1.40-1.36 (m, 1H), 1.40 (s, 3H), 1.36 (s, 3H), 1.17-1.05 (m, 1H), 0.80 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.7, 149.7, 144.3, 133.1, 128.6, 127.6, 126.8, 124.6, 120.7, 108.5, 86.8, 83.9, 82.9, 79.9, 79.2, 73.2, 60.1, 59.9, 39.0, 35.3, 34.3, 28.1, 26.4, 21.3, 10.8; **HRMS (ESI⁺)** Calcd. for C₃₉H₄₂O₆+Na, 629.2879; Found, 629.2990; **IR** (thin film, cm⁻¹) 3435, 2390, 1936, 1786, 1723, 1630, 1426, 1212, 521; **TLC**(50:50Hex:EtOAc): R_f = 0.48.

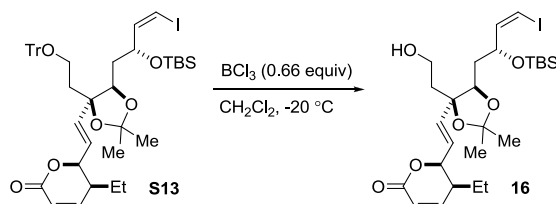


(5*S*,6*S*)-6-((*E*)-2-((4*R*,5*S*)-5-((*R*)-2-((tert-butyldimethylsilyloxy)but-3-yn-1-yl)-2,2-dimethyl-4-(2-(trityloxy)ethyl)-1,3-dioxolan-4-yl)vinyl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (15): An oven-dried and cooled 20-mL scintillation vial equipped with magnetic stir bar was charged with alcohol **S12** (59 mg, 0.098 mmol, 1.0 equiv). CH₂Cl₂ (1.0 mL) was added, and the resulting solution was cooled to -78 °C in an acetone-dry ice bath. 2,6-lutidine (23 μL, 21 mg, 0.196 mmol, 2.0 equiv) was added, followed by a dropwise addition of TBSOTf (27 μL, 31 mg, 0.118 mmol, 1.2 equiv). The reaction was allowed to stir at the same temperature for 2 h, at which point it was quenched by the addition of MeOH (0.25 mL) and warmed to rt. After dilution with Et₂O and 1M HCl, the layers were separated and the organic layer was washed with saturated aqueous NaHCO₃, water, and brine and dried with MgSO₄. The solvent was removed *in vacuo*, and the resulting crude oil was purified via flash chromatography, eluting with 100:0 to 80:20 hexanes:EtOAc, to afford the title compound as a colorless oil (59 mg, 84%). Analytical data: [α]_D^{25.1} +41.2 (*c* = 0.20, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.22 (m, 15H), 6.88 (dd, *J* = 9.6, 5.6 Hz, 1H), 6.00 (d, *J* = 9.6 Hz, 1H), 5.77-5.67 (m, 2H), 4.90 (t, *J* = 4.0 Hz, 1H), 4.54 (d, *J* = 10.0 Hz, 1H), 3.89 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.39-3.31 (m, 1H), 3.15-3.09 (m, 1H), 2.45 (d, *J* = 2.0 Hz, 1H), 2.31-2.26 (m, 1H), 2.10-1.61 (m, 4H), 1.37 (s, 3H), 1.30 (s, 3H), 1.30-1.10 (m, 2H), 0.91 (s, 9H), 0.82 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 3H), 0.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.6, 149.5, 144.4, 133.9, 128.6, 127.7, 126.8, 124.4, 120.9, 108.0, 86.8, 85.4, 82.6, 79.5, 79.0, 72.1, 60.0, 59.5, 39.3, 37.8, 34.4, 28.2, 26.5, 25.7, 21.3, 18.1, 10.9, -4.6, -5.3; **HRMS (ESI⁺)** Calcd. for C₄₅H₅₆O₆Si+Cs, 853.2901; Found, 853.2925; **IR** (thin film, cm⁻¹) 3435, 2917, 2848, 2393, 2002, 1725, 1611, 1530, 1381, 1218, 1060, 707; **TLC**(50:50Hex:EtOAc): R_f = 0.83.



(5*S*,6*S*)-6-((*E*)-2-((4*R*,5*S*)-5-((*R*,*Z*)-2-((tert-butyl)dimethylsilyloxy)-4-iodobut-3-en-1-yl)-2,2-dimethyl-4-(2-(trityloxy)ethyl)-1,3-dioxolan-4-yl)vinyl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (S13): An oven-dried and cooled 20-mL scintillation vial equipped with magnetic stir bar was charged with alkyne **15** (54 mg, 0.076 mmol, 1.0 equiv), NIS (20 mg, 0.091 mmol, 1.2 equiv), and THF (2.0 mL). AgNO₃ (powdered, cat.) was added, and the resulting suspension was stirred vigorously in the dark at rt for 12 h. The suspension was filtered through a short SiO₂ plug, eluting with 100:0 to 75:25 hexanes:EtOAc, to afford the crude alkynyl iodide as a light yellow oil (57 mg, 90% crude yield) that was used without additional purification.

An oven-dried and cooled 20-mL scintillation vial equipped with magnetic stir bar was charged with the crude iodide (57 mg, 0.068 mmol, 1.0equiv), *i*PrOH (2.0 mL), and THF (2.0 mL). The vial was purged with N₂, and TEA (29 μ L, 21 mg, 0.204 mmol, 3.0 equiv) and NBSH (25 mg, 0.116 mmol, 1.7equiv) were added successively. The vial was sealed with a Teflon-lined cap and covered with foil, and the reaction was allowed to stir at rt for 16 h. ¹H NMR analysis of an aliquot revealed complete consumption of the starting material, and the reaction was concentrated *in vacuo*. The resulting crude yellow oil was purified via column chromatography, eluting with 100:0 to 70:30 petroleum ether:Et₂O, to afford the title compound as a colorless oil (54 mg, 85% over two steps). Analytical data: $[\alpha]_D^{23.8} +33.6$ ($c = 0.23$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 7.54-7.06 (m, 15H), 6.87 (dd, $J = 9.6, 5.2$ Hz, 1H), 6.27-6.21 (m, 2H), 5.98 (d, $J = 10.0$ Hz, 1H), 5.74-5.63 (m, 2H), 4.90 (t, $J = 4.0$ Hz, 1H), 4.53 (m, 1H), 3.89 (d, $J = 10.0$ Hz, 1H), 3.35-3.31 (m, 1H), 3.09-3.06 (m, 1H), 2.27 (dd, $J = 9.6, 4.8$ Hz, 1H), 2.04 (ddd, $J = 4.4, 4.0, 4.0$ Hz, 1H), 1.71-1.49 (m, 4H), 1.38-1.05 (m, 2H), 1.37 (s, 3H), 1.30 (s, 3H), 0.86 (s, 9H), 0.78 (t, $J = 7.6$ Hz, 3H), 0.09 (s, 3H), 0.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 163.7, 149.6, 144.4, 133.9, 128.6, 127.6, 126.8, 124.1, 120.8, 107.9, 86.8, 82.7, 79.8, 79.5, 79.0, 72.8, 60.1, 39.2, 35.3, 34.2, 28.3, 26.6, 25.7, 25.7, 21.3, 18.0, 10.9, -4.3, -4.9; HRMS (ESI⁺) Calcd. for C₄₅H₅₇IO₆Si+Cs, 981.2024; Found, 981.2055; IR (thin film, cm⁻¹) 3435, 2956, 2928, 2855, 1726, 1675, 1612, 1379, 1251, 1063, 835, 705; TLC(50:50 Et₂O:Petroleum Ether): R_f = 0.63.



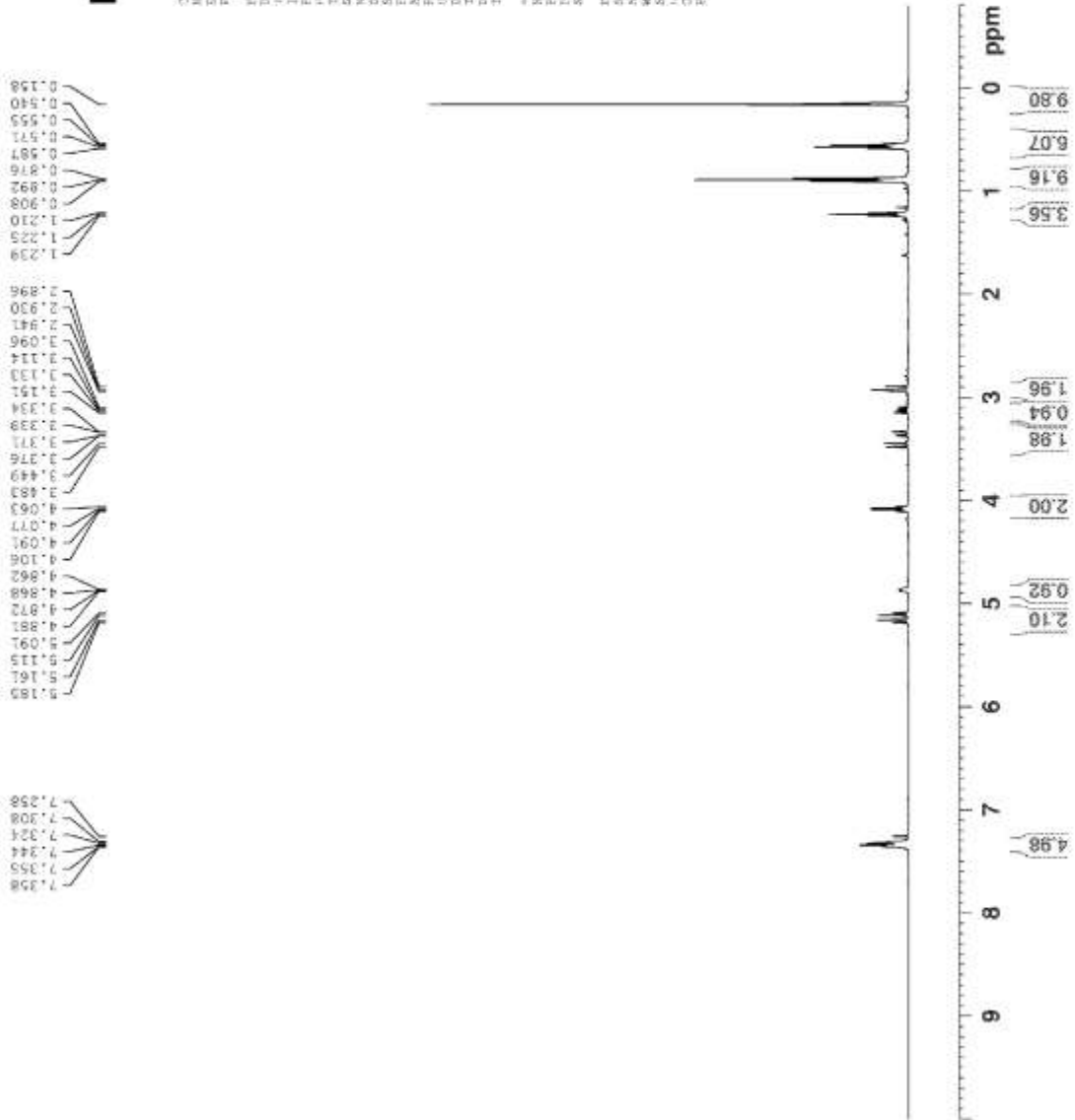
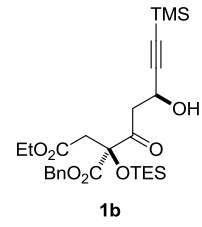
(5*S*,6*S*)-6-((*E*)-2-((4*R*,5*S*)-5-((*R*,*Z*)-2-((tert-butyl)dimethylsilyloxy)-4-iodobut-3-en-1-yl)-4-(2-hydroxyethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (16): An oven-dried and cooled 20-mL scintillation vial was charged with vinyl iodide **S13** (40 mg, 0.048 mmol, 1.0 equiv) and CH₂Cl₂ (8.0 mL). The resulting solution was cooled to -20 °C

in an acetone-dry ice bath, and BCl_3 (0.123 M in CH_2Cl_2 , 2.6 mL, 0.031 mmol, 0.66 equiv) was added dropwise. A bright yellow color was initially observed but disappeared during the course of the reaction. The reaction was allowed to stir at the same temperature for 30 min and was quenched by the addition of saturated aqueous NaHCO_3 (1.0 mL). The resulting suspension was warmed to rt, and the layers were separated. The organic layer was dried with Na_2SO_4 and concentrated *in vacuo* to afford a colorless oil that was purified via column chromatography, eluting with 70:30 to 50:50 petroleum ether: Et_2O , to afford the title compound (16 mg, 56%) as a 5:1 mixture of diastereomers. The diastereomers were separated via HPLC to afford diastereomerically pure material, whose spectral data were consistent with those reported in the literature for the title compound.³ Analytical data: $[\alpha]_{\text{D}}^{25.3} +64.5$ ($c = 0.14$, CHCl_3), lit:³ $[\alpha]_{\text{D}}^{22.0} +68.6$ ($c = 1.60$, CHCl_3); **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 6.99 (dd, $J = 9.6, 5.2$ Hz, 1H), 6.25-6.19 (m, 2H), 6.07 (d, $J = 10.0$ Hz, 1H), 5.95 (dd, $J = 15.2, 4.4$ Hz, 1H), 5.87 (d, $J = 15.6$ Hz, 1H), 5.05 (t, $J = 4.0$ Hz, 1H), 4.54 (ddd, $J = 16.8, 9.6, 2.8$ Hz, 1H), 4.01 (d, $J = 10.0$ Hz, 1H), 3.83 (dt, $J = 11.2, 3.6$ Hz, 1H), 3.70 (m, 1H), 2.66 (br s, 1H), 2.43 (dd, $J = 9.2, 4.8$ Hz, 1H), 2.02 (ddd, $J = 14.4, 9.6, 5.6$ Hz, 1H), 1.71-1.42(m, 6H), 1.54 (s, 3H), 1.37 (s, 3H), 0.96 (t, $J = 7.6$ Hz, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 163.9, 150.0, 144.3, 133.2, 125.0, 120.9, 108.4, 85.1, 80.1, 79.5, 78.8, 72.7, 59.7, 39.2, 35.3, 35.2, 28.2, 26.4, 25.8, 21.5, 18.0, 11.0, -4.2, -4.9; **HRMS (ESI⁺)** Calcd. for $\text{C}_{26}\text{H}_{43}\text{IO}_6\text{Si}+\text{Na}$, 629.1772; Found, 629.1771; **IR** (thin film, cm^{-1}) 3434, 2390, 2083, 1936, 1785, 1709, 1641, 1427, 1250, 1081, 780, 507; **TLC**(50:50Hex:EtOAc): $R_f = 0.32$.

³ (a) Miyashita, K.; Tsunemi, T.; Hosokawa, T.; Ikejiri, M.; Imanishi, T. *Tetrahedron Lett.* **2007**, 48, 3829. (b) Miyashita, K.; Tsunemi, T.; Hosokawa, T.; Ikejiri, M.; Imanishi, T. *J. Org. Chem.* **2008**, 73, 5360.

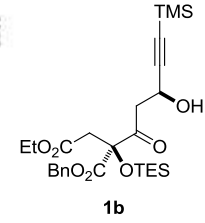
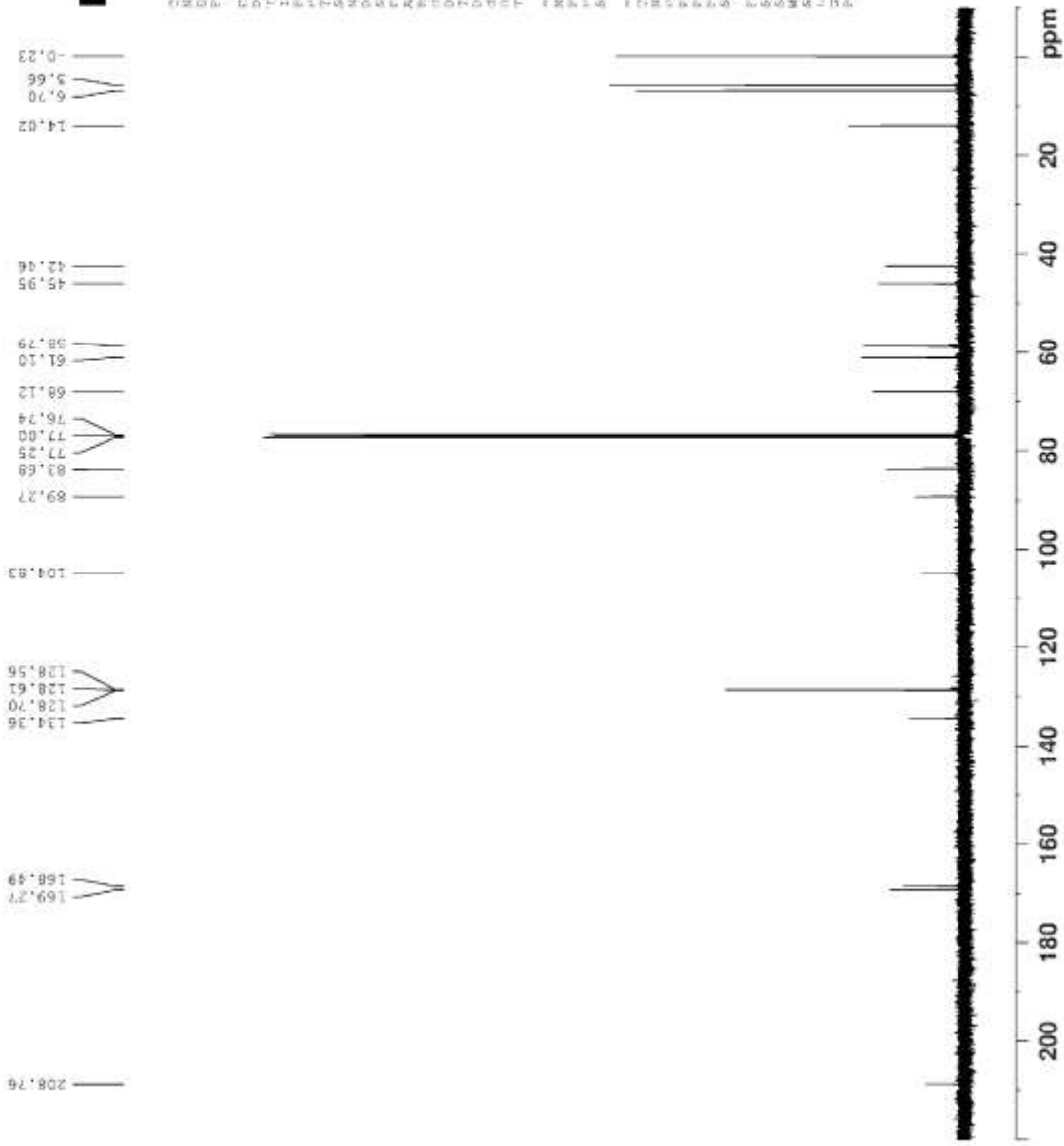


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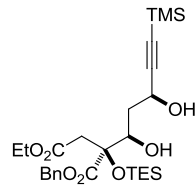
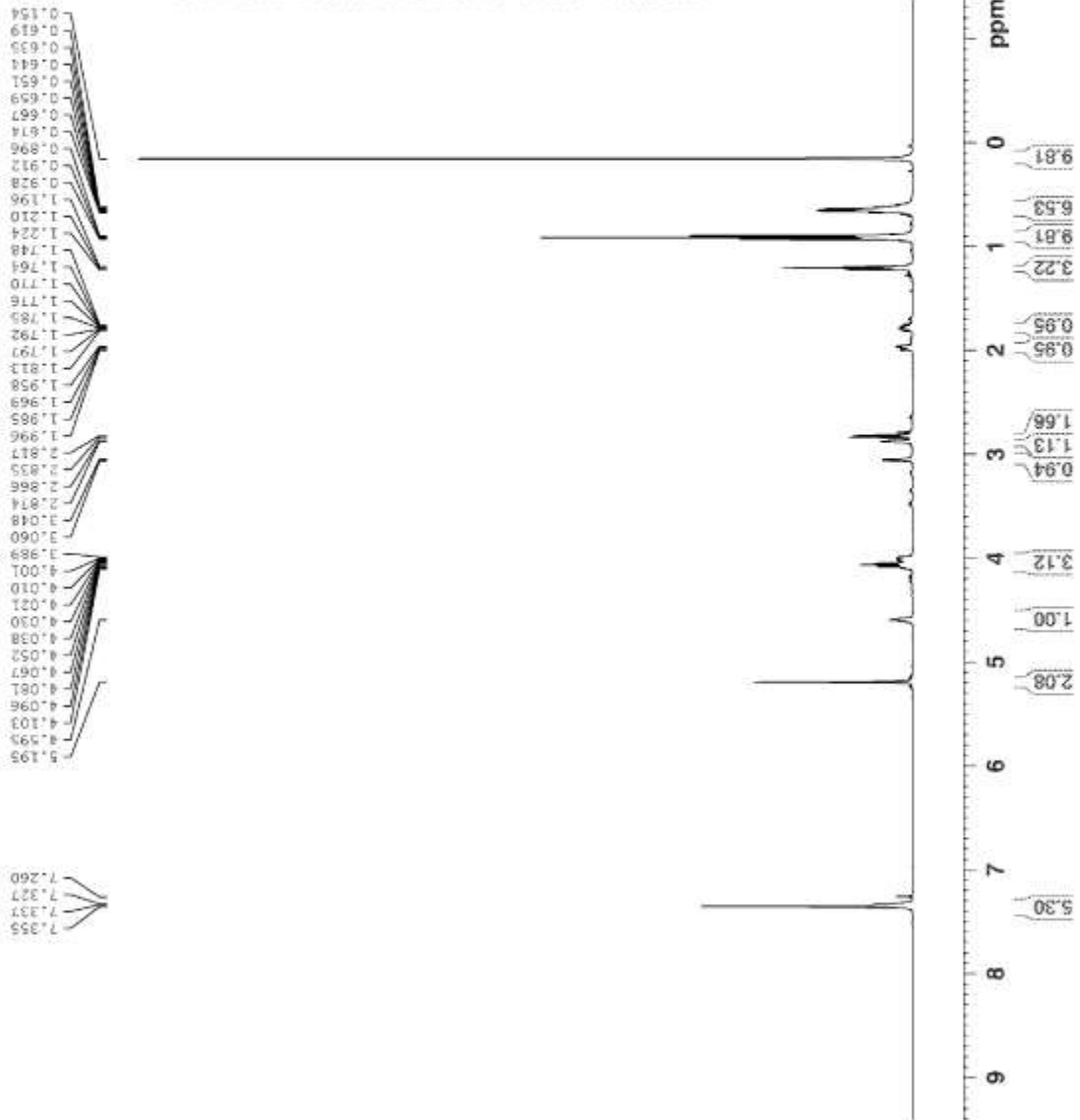


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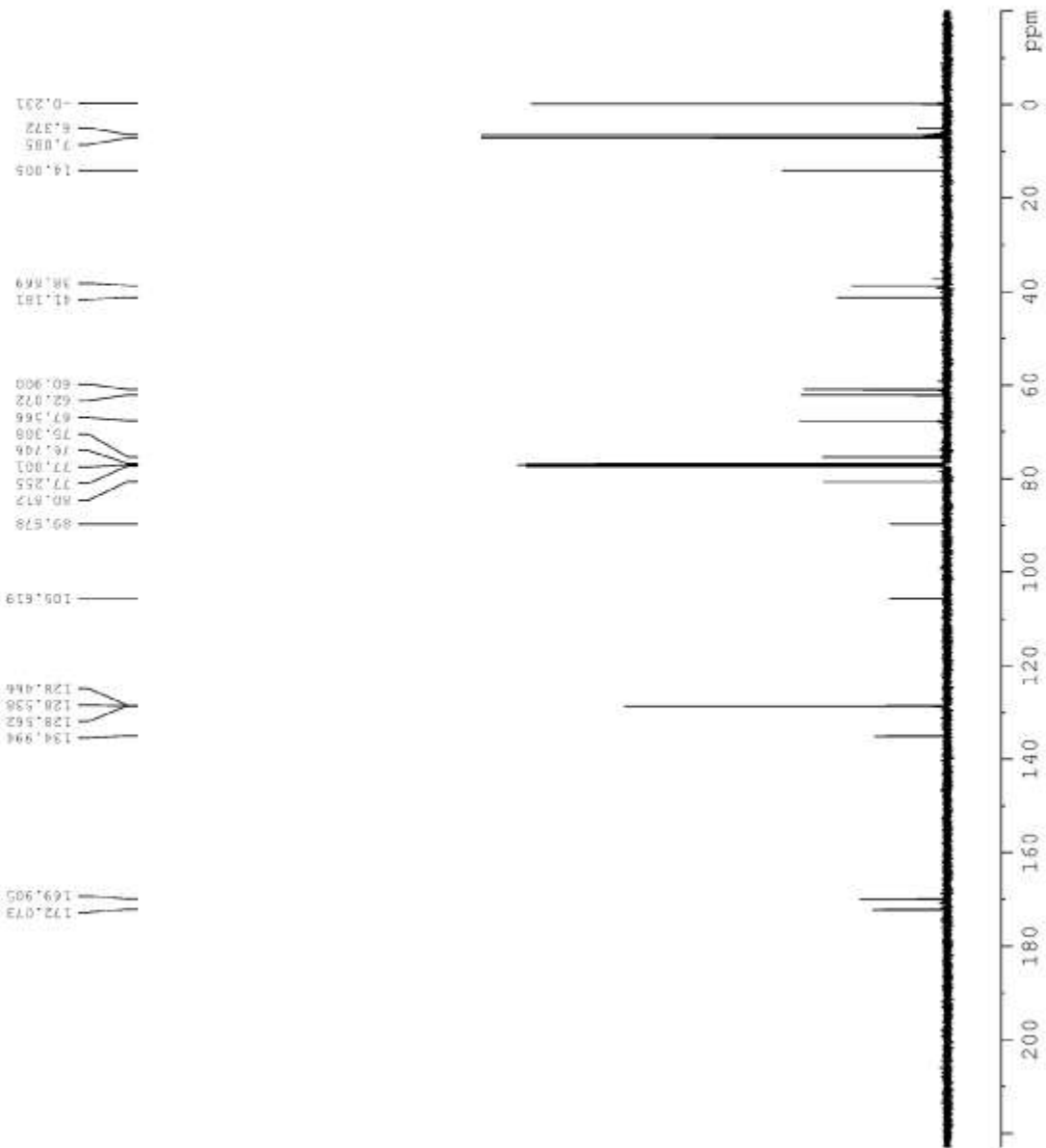
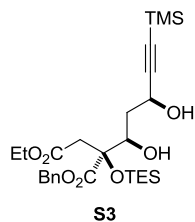
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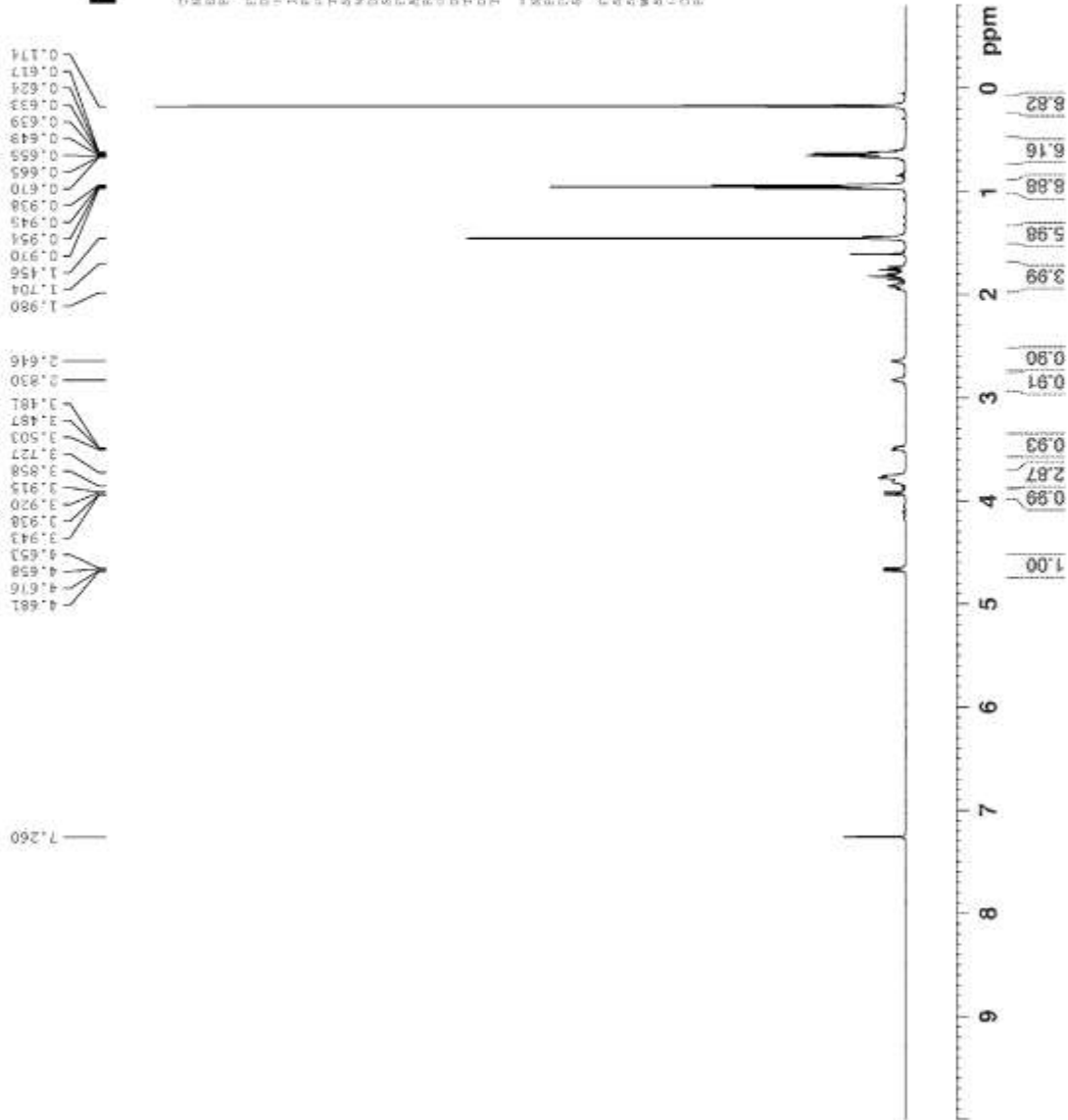
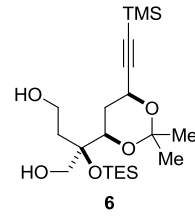
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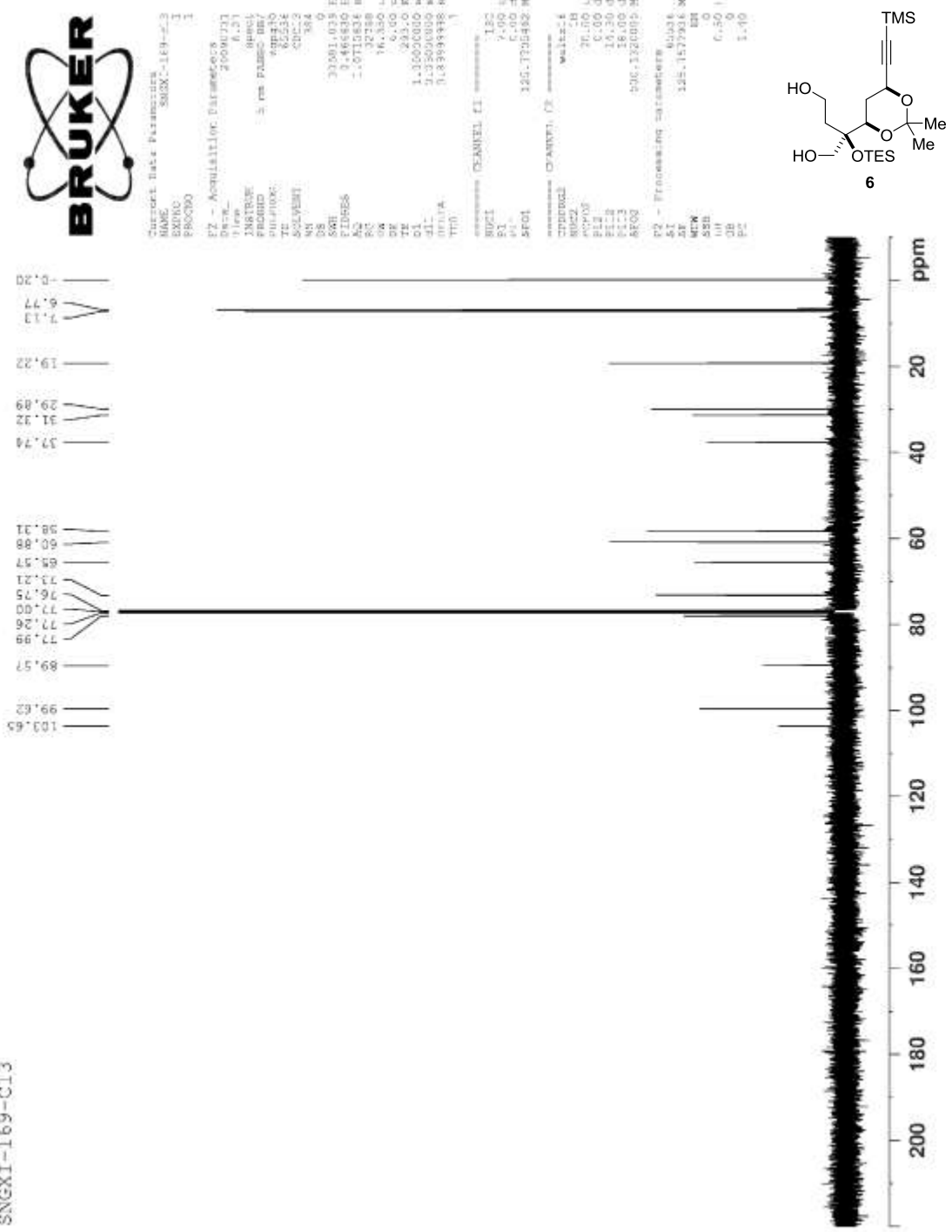




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SNGXI-169-C13





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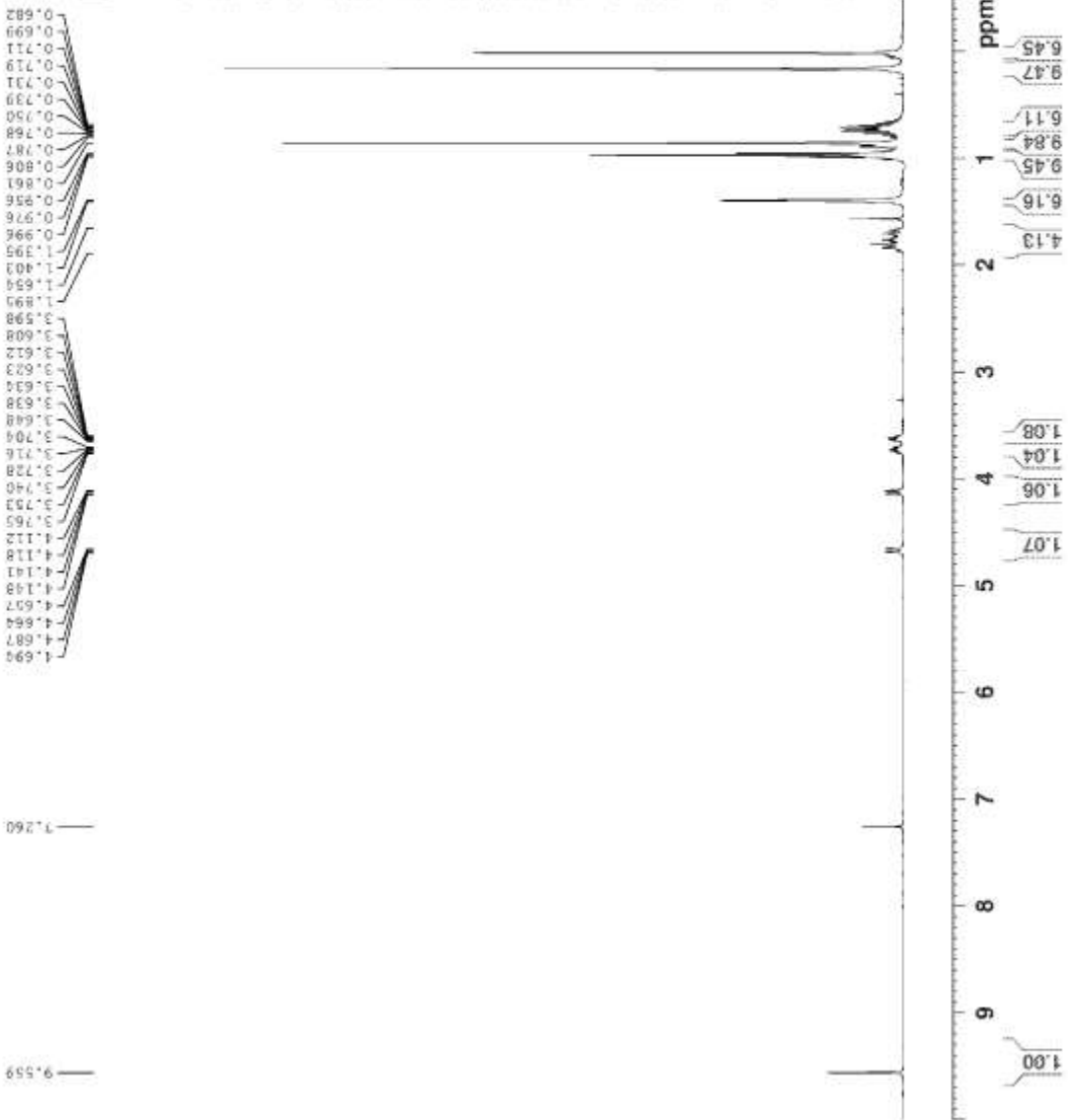
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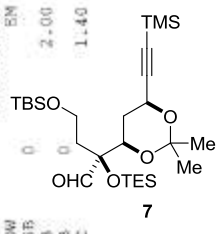
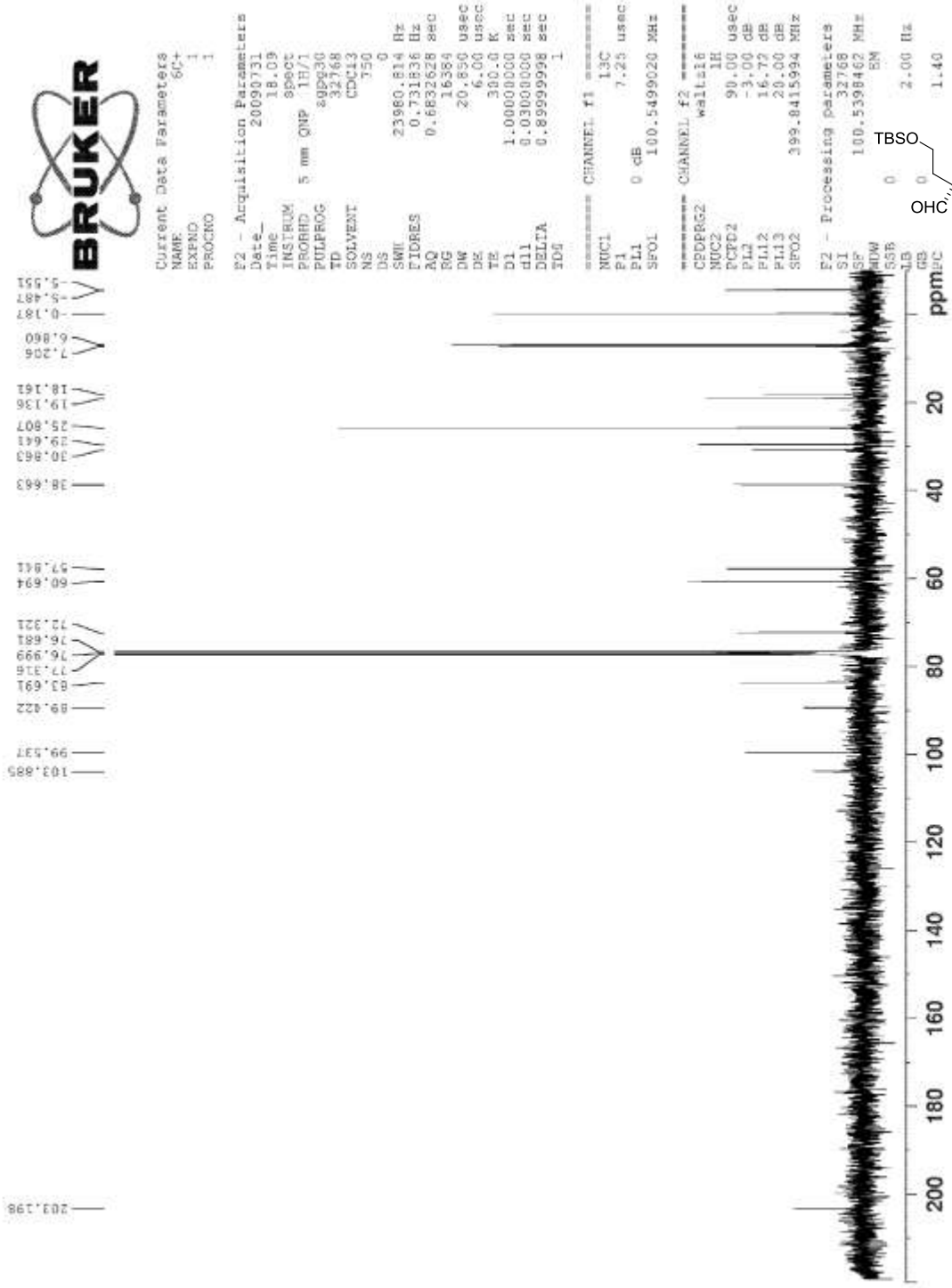
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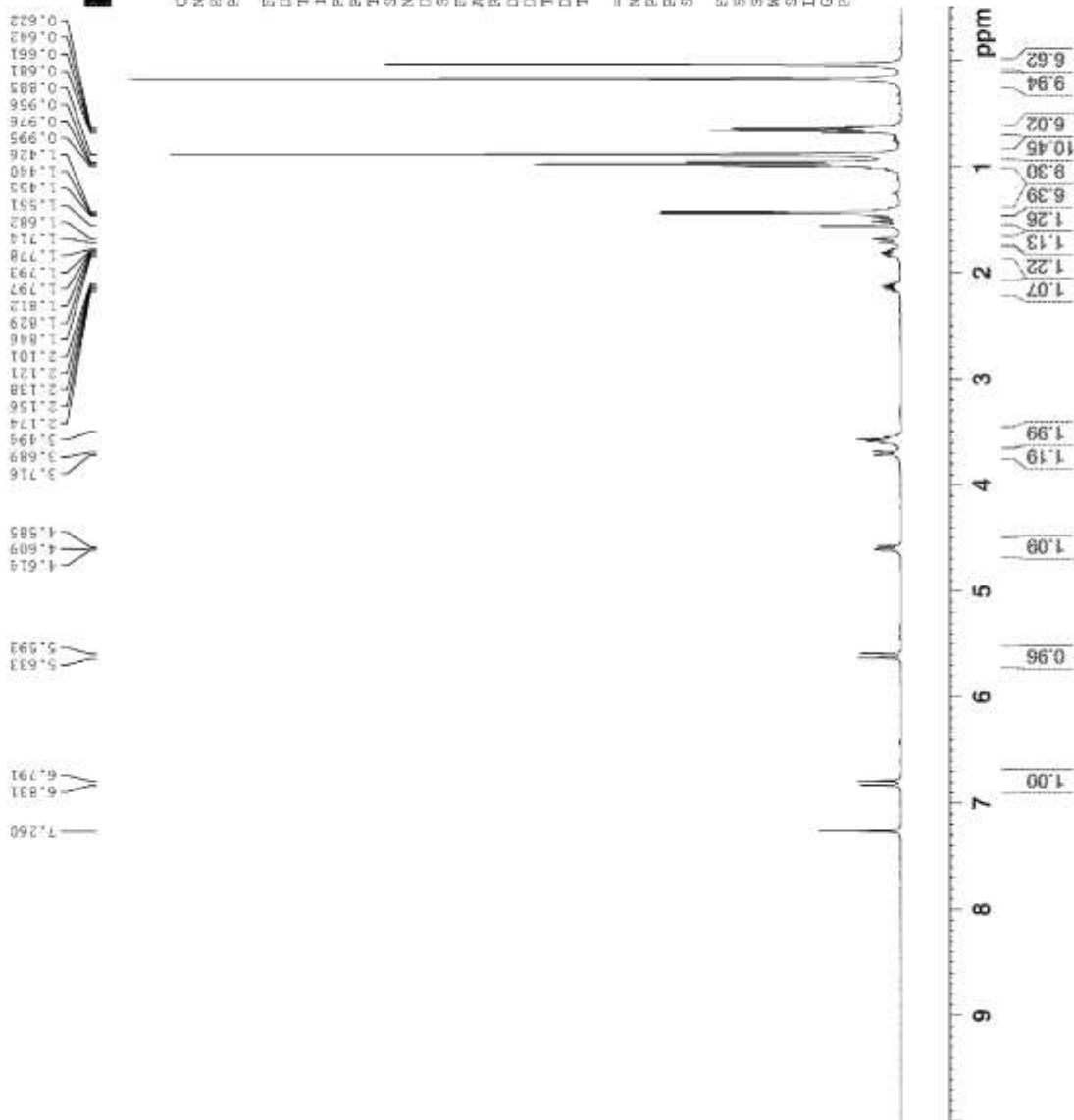
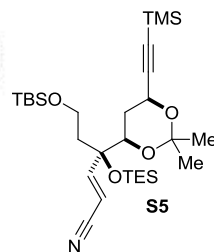


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PROCNO 1

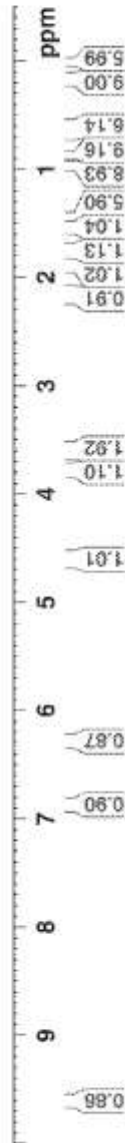
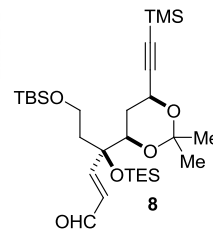
F2 - Acquisition Parameters

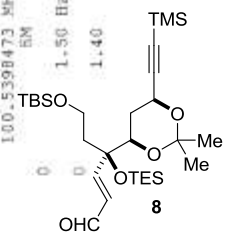
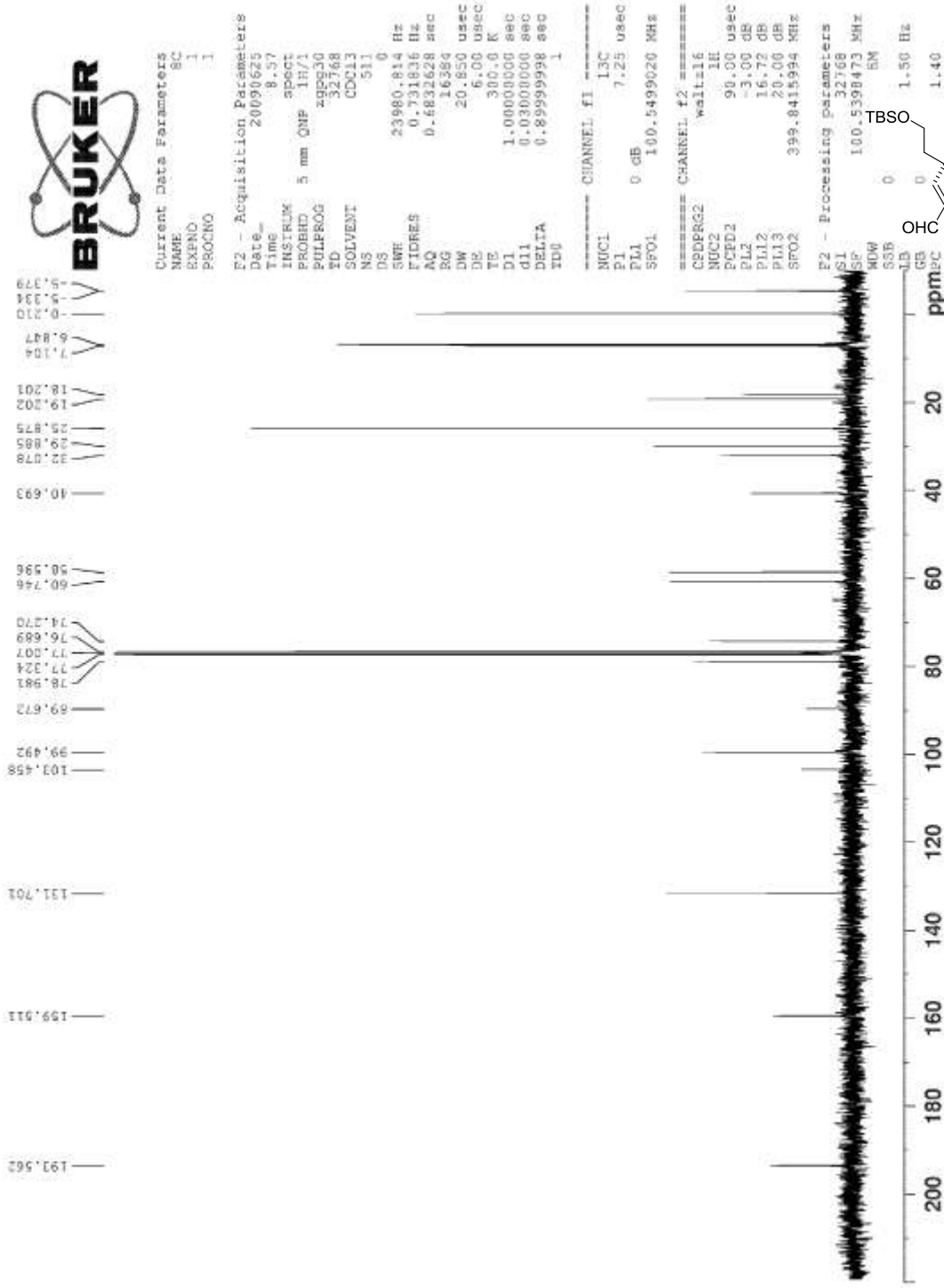
Date_ 20090625
Time 8.48
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 57
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
PI 9.30 usec
PL1 -3.00 dB
SFO1 399.8424924 MHz

F2 - Processing parameters
SI 32768
SF 399.840077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

0.642
0.661
0.681
0.682
0.693
0.912
0.992
1.442
1.481
1.513
1.545
1.574
1.740
1.773
1.849
1.851
1.870
1.884
1.884
1.898
1.904
1.918
2.127
2.147
2.169
2.183
2.200
3.533
3.533
3.759
3.785
3.788
4.598
4.598
4.603
4.628
4.632
5.415
5.445
6.266
6.286
6.305
6.325
6.860
6.899
7.260
9.589
9.609







Current Data Parameters
NAME 9H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

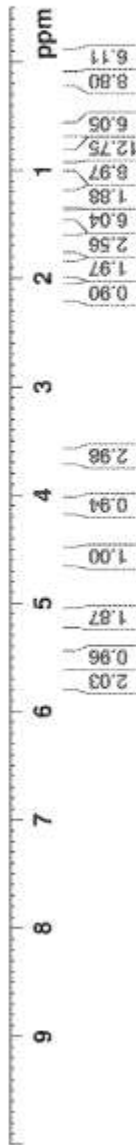
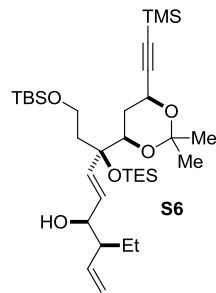
Date_ 20090803
Time 8.51
INSTRUM spect
PROBHD 5 mm PABBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 7507.507 Hz
FIDRES 0.114555 Hz
AQ 4.3647475 sec
RG 161.3
DM 66.600 usec
DE 6.00 usec
TE 292.5 K
D1 1.00000000 sec
TDC 1

===== CHANNEL f1 =====

NUC1 1H
P1 17.50 usec
PL1 -3.00 dB
SFO1 500.1330008 MHz

F2 - Processing parameters

SF 500.1300135 MHz
WDW EM
SSB 0
LB 0.25 Hz
GB 0
PC 1.00





5.1258
5.1238
0.171
6.854
7.222
11.888
18.343
19.227
23.260
25.968
29.948
31.946
29.990
52.721
59.426
60.888
73.995
74.062
76.747
77.001
77.255
78.203
89.112
99.156
104.065
118.017
130.640
132.791
138.318

Current Data Parameters
NAME 9C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090803
Time 8.55

INSTRUM spect
PROBHD 5 mm F4BBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2193
DS 0

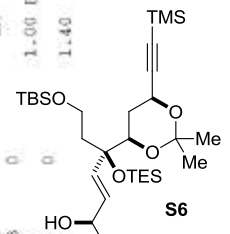
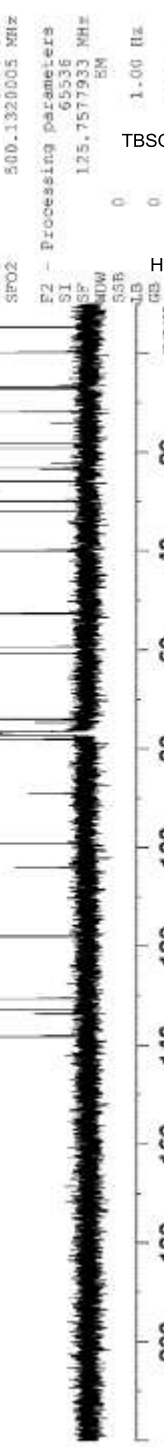
SWH 30581.039 Hz
FIDRES 0.466630 Hz
AQ 1.0715638 sec
RG 32768
DM 16.350 usec
DE 6.00 usec
TE 292.8 K

D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.00 usec
PL1 0 dB
SFO1 125.7705462 MHz

===== CHANNEL f2 =====
CDEPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0 dB
PL12 14.30 dB
PL13 18.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 65536
SF 125.7577933 MHz
WDW EN
SSB 0
GB 0
PC 1.00 Hz
MC 1.40





Current Data Parameters
NAME 10H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

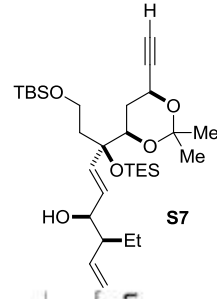
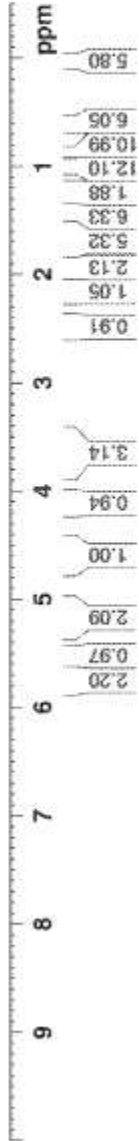
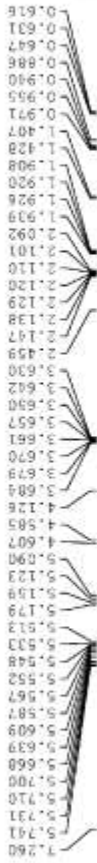
Date_ 20100522
Time 12.21
INSTRUM spect
PROBHD 5 mm F4BBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.114555 Hz
AQ 4.3647475 sec
RG 90.5
DM 66.600 usec
DE 6.00 usec
TE 292.3 K
D1 1.00000000 sec
TDC 1

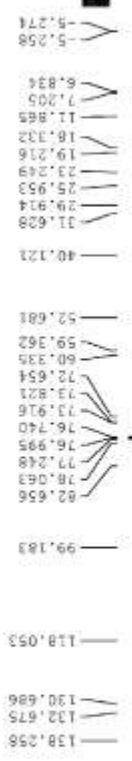
CHANNEL f1

NUC1 1H
P1 13.50 usec
PL1 0 dB
SFO1 500.1330008 MHz

F2 - Processing parameters

SF 500.1300127 MHz
WDW EM
SSB 0
LB 0.25 Hz
GB 0
PC 1.00





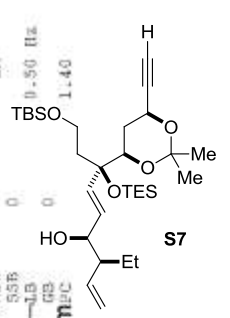
Current Data Parameters
NAME IDC
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100522
Time 12.29
INSTRUM spect
PROBHD 5 mm F4BBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 301
DS 0
SWH 30581.039 Hz
FIDRES 0.466630 Hz
AQ 1.0715638 sec
RG 32768
DM 16.350 usec
DE 6.00 usec
TE 293.4 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.00 usec
PL1 0 dB
SFO1 125.7705462 MHz

===== CHANNEL f2 =====
CDEPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0 dB
PL12 14.30 dB
PL13 18.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 65536
SF 125.7577946 MHz
WDW EM
SSB 0
LB 0.50 Hz
GB 0
PC 1.40





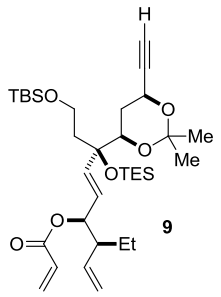
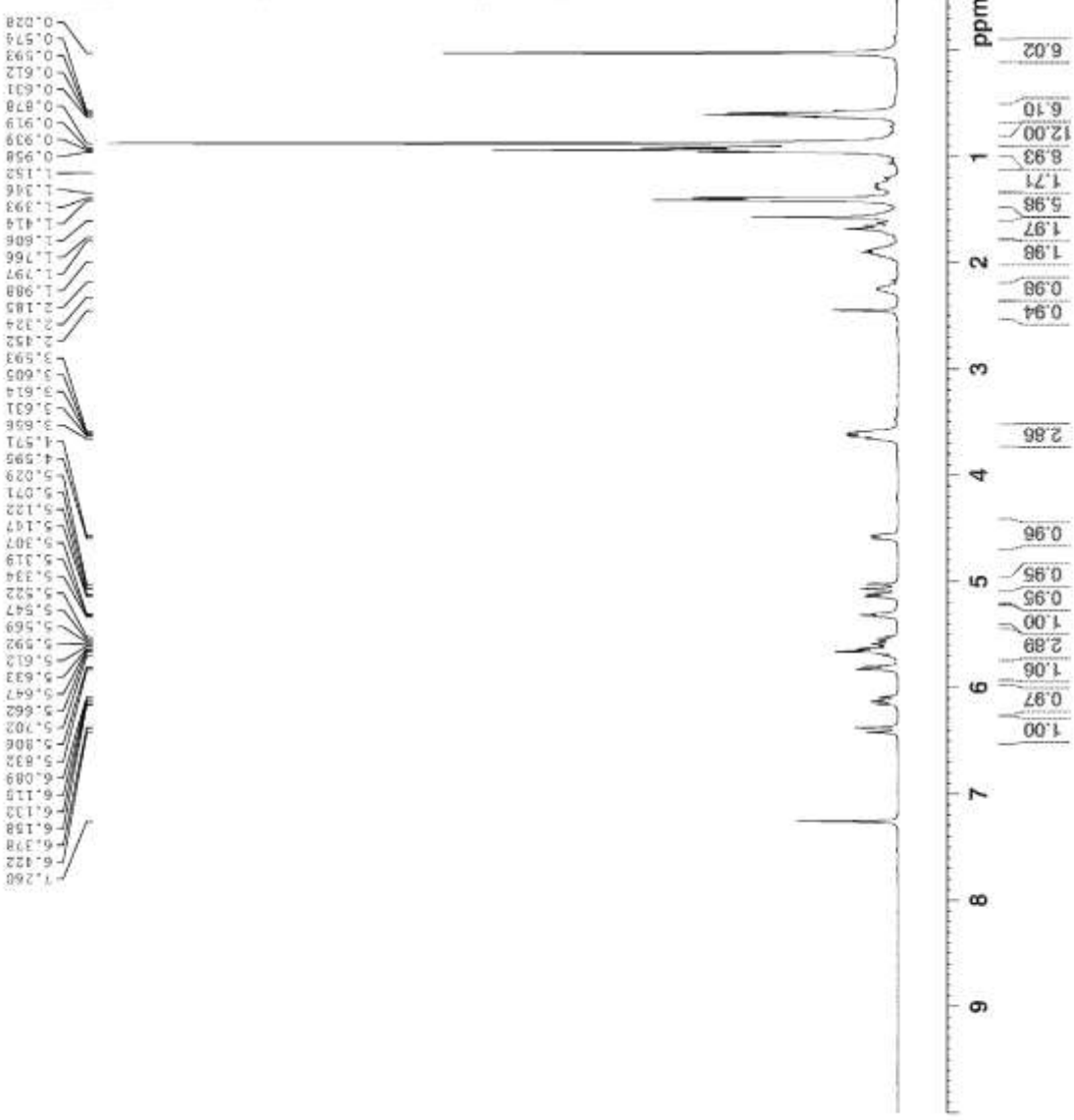
Current Data Parameters
NAME iih
EXPNO 1
PROCNO 1

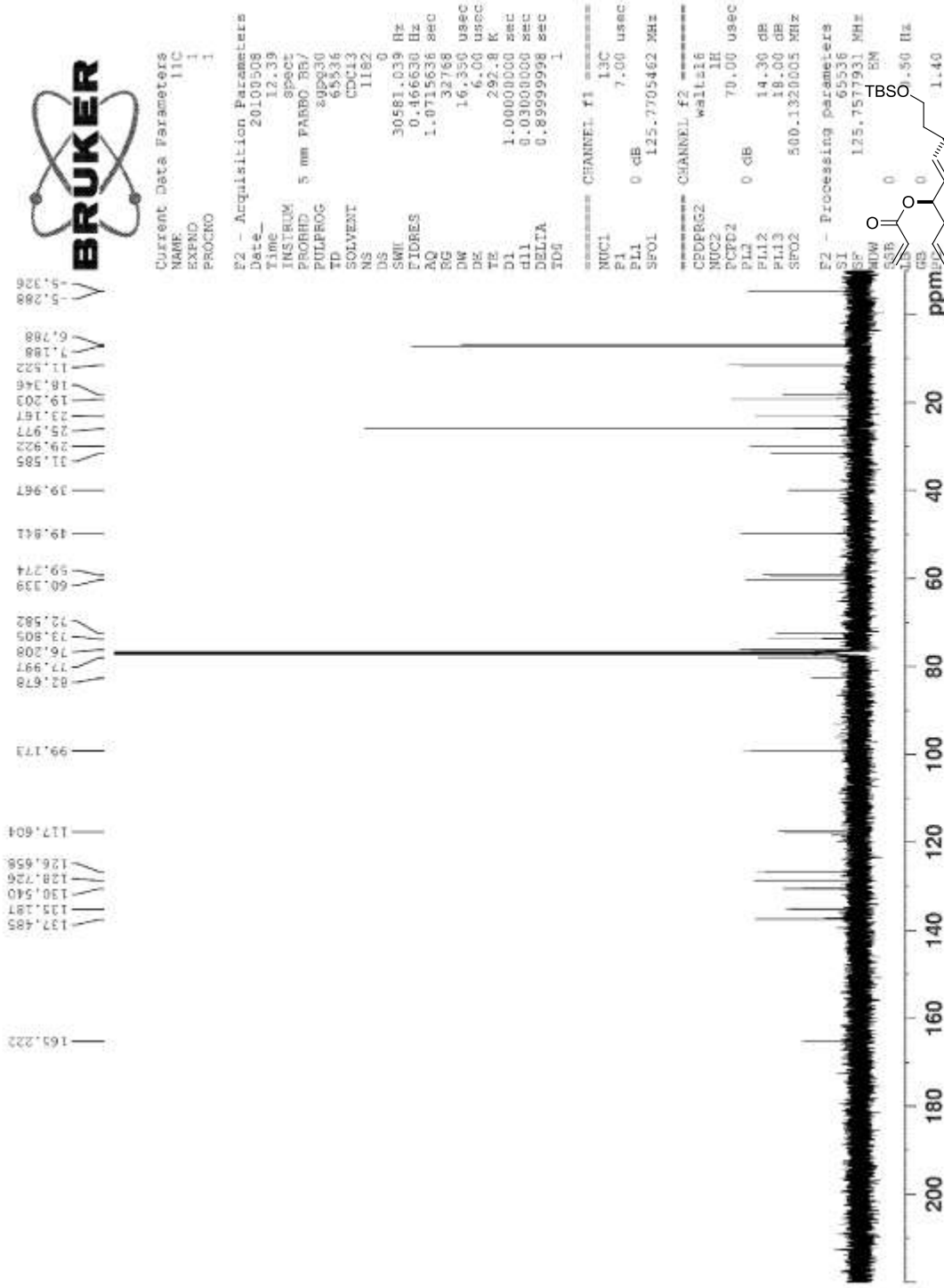
F2 - Acquisition Parameters
Date_ 20100506
Time 11:35

INSTRUM spect
PROBHD 5 mm TXI 13C Z
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5341.880 Hz
FIDRES 0.163021 Hz
AQ 3.0671349 sec
RG 90.3
DW 93.600 usec
DE 6.00 usec
TE 293.7 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.50 usec
PL1 0 dB
SFO1 400.0923618 MHz

F2 - Processing parameters
SI 32768
SF 400.0900027 MHz
WDW EM
SSB 0
LB 0.25 Hz
GB 0
PC 1.00





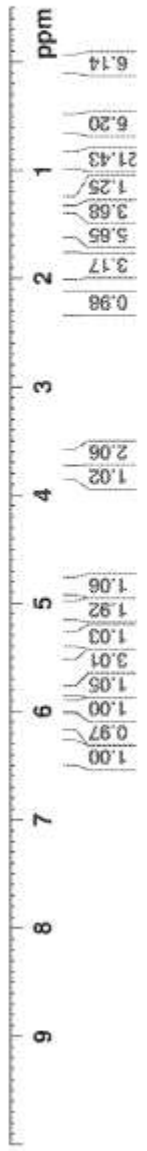
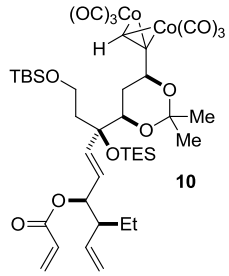


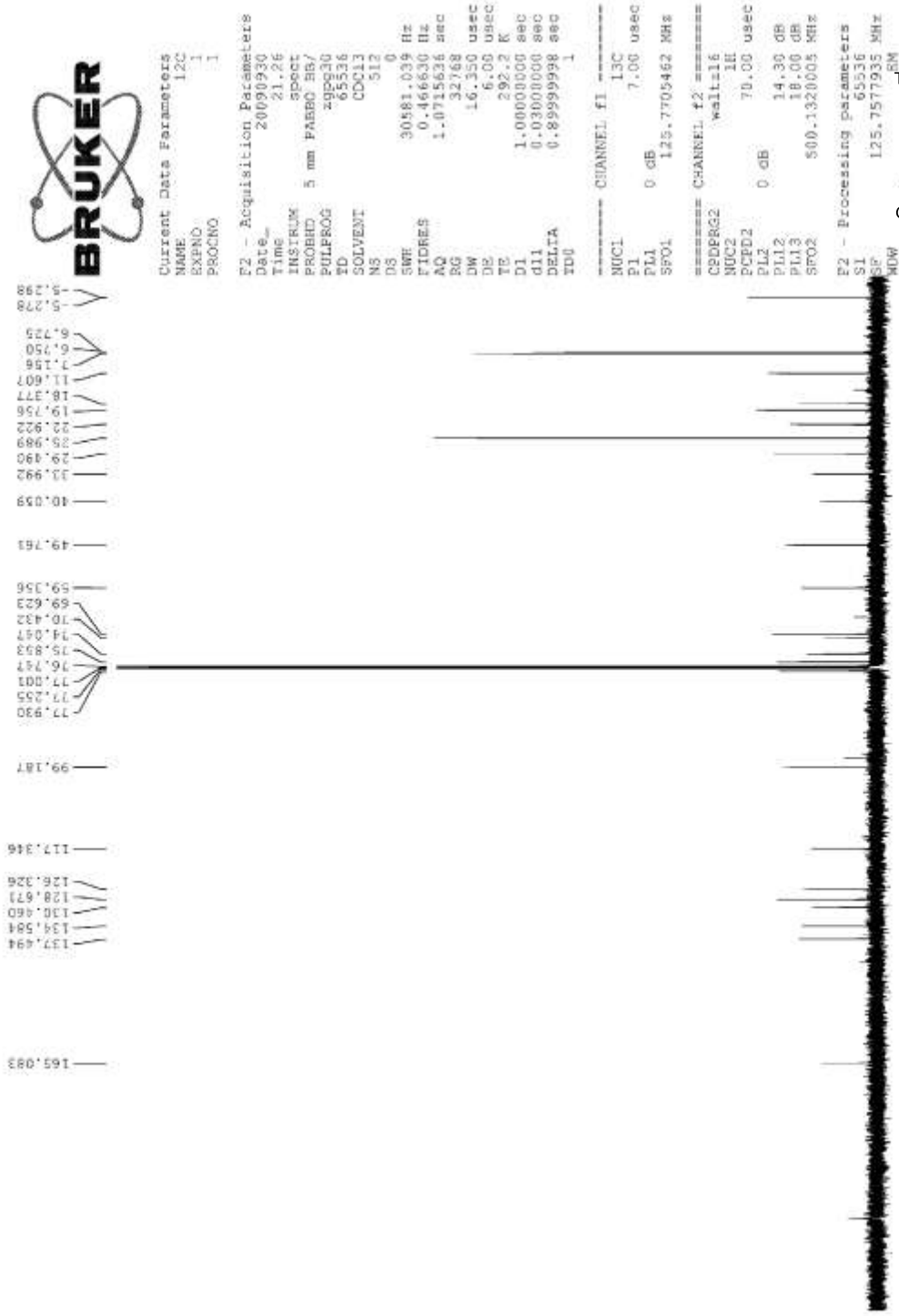
Current Data Parameters
 NAME 12H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090930
 Time_ 17.07
 INSTRUM spect
 PROBRD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 6218.905 Hz
 FIDRES 0.189786 Hz
 AQ 2.6345973 sec
 RG 161.3
 DW 80.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDC 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.30 usec
 PL1 -3.00 dB
 SFO1 399.8424924 MHz

F2 - Processing parameters
 SI 32768
 SF 399.840093 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





```

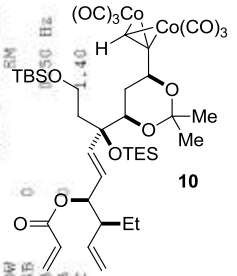
Current Data Parameters
NAME      I2C
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20090930
Time     21.26
INSTRUM  spect
PROBHD   5 mm PABBO HS/
PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       512
DS       0
SWH      30481.039 Hz
FIDRES   0.466630 Hz
AQ       1.0715628 sec
RG       32768
DW       16.350 usec
DE       6.00 usec
TE       292.2 K
d11      1.00000000 sec
d12      0.03000000 sec
DELTA    0.89999998 sec
TD0      1

===== CHANNEL f1 =====
NUC1      13C
P1        7.00 usec
PL1       0 dB
SFO1      125.7705462 MHz

===== CHANNEL f2 =====
CDEPRG2   waltz16
NUC2      1H
P2        70.00 usec
PL2       0 dB
PL12      14.30 dB
PL13      18.00 dB
SFO2      500.1320005 MHz

F2 - Processing parameters
SI        65536
SF        125.7577935 MHz
WDW       EM
SSB       0
GB        0
PC
  
```



SNCXI-187-H1

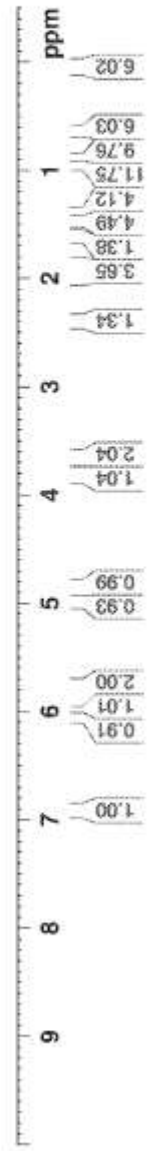
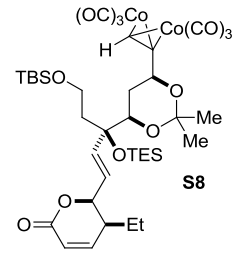


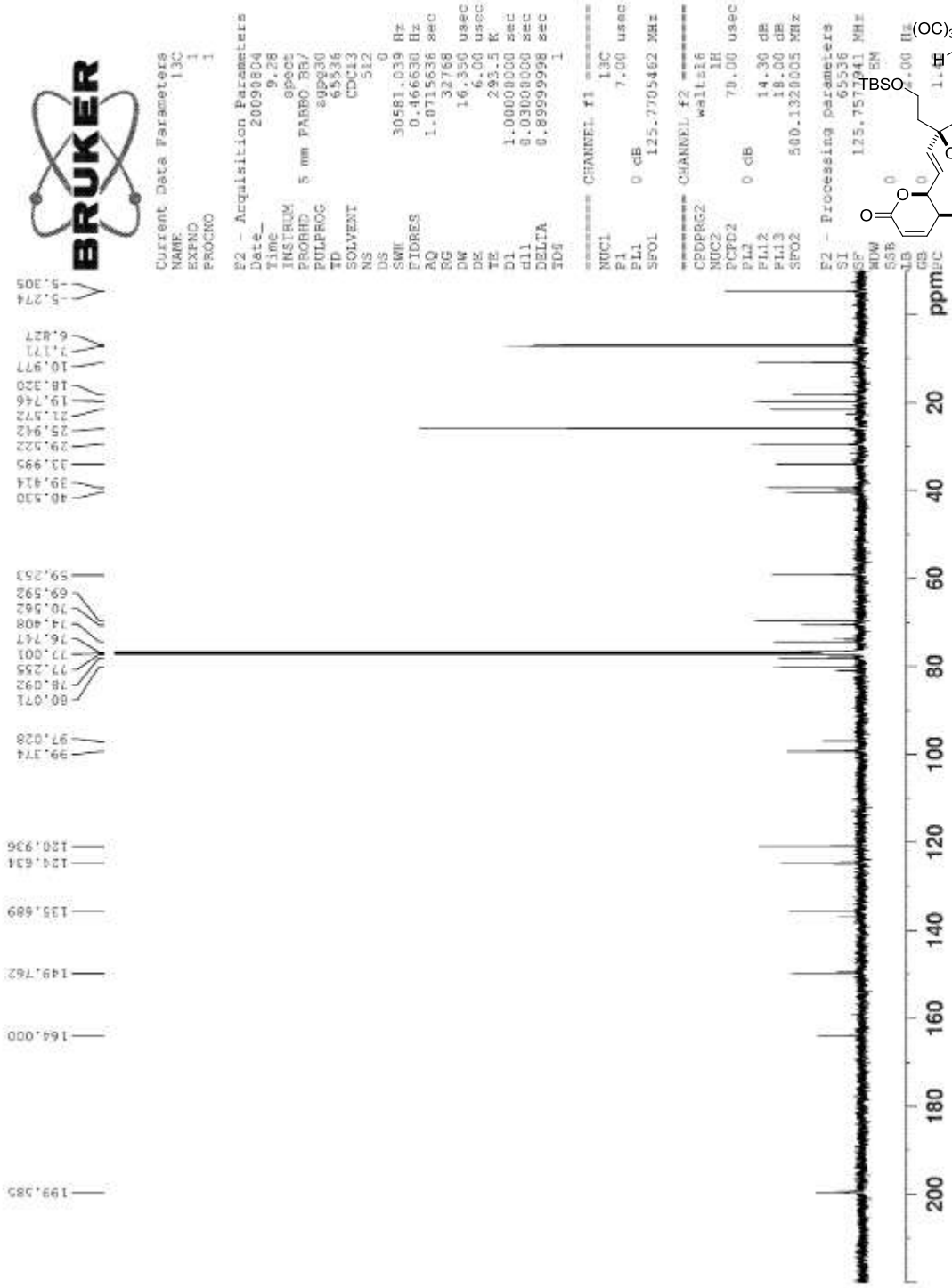
Current Data Parameters
NAME LH
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090804
Time 9.20
INSTRUM spect
PROBHD 5 mm PABBO HS/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 7507.507 Hz
FIDRES 0.114958 Hz
AQ 4.364743 sec
RG 57
DW 66.600 usec
DE 6.00 usec
TE 292.5 K
D1 1.00000000 sec
TD6 1

===== CHANNEL f1 =====
NUC1 1H
P1 17.50 usec
PL1 -3.00 dB
SFO1 500.1330008 MHz

F2 - Processing parameters
SI 32768
SF 500.1300142 MHz
WDW EM
SSB 0
LB 0.25 Hz
GB 0
PC 1.00





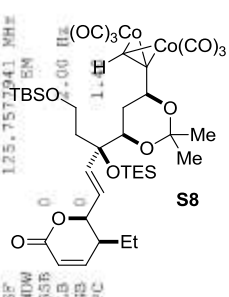
Current Data Parameters
NAME 13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090804
Time 9.28
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 0
SWH 30581.039 Hz
FIDRES 0.466630 Hz
AQ 1.0715638 sec
RG 32768
DW 16.350 usec
DE 6.00 usec
TE 293.5 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.00 usec
PL1 0 dB
SFO1 125.7705462 MHz

===== CHANNEL f2 =====
CDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0 dB
PL12 14.30 dB
PL13 18.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 65536
SF 125.7572411 MHz
WDW EN
SSB 0
LB 0.00 Hz
GB 0
PC 0



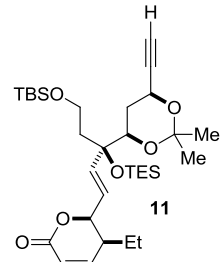
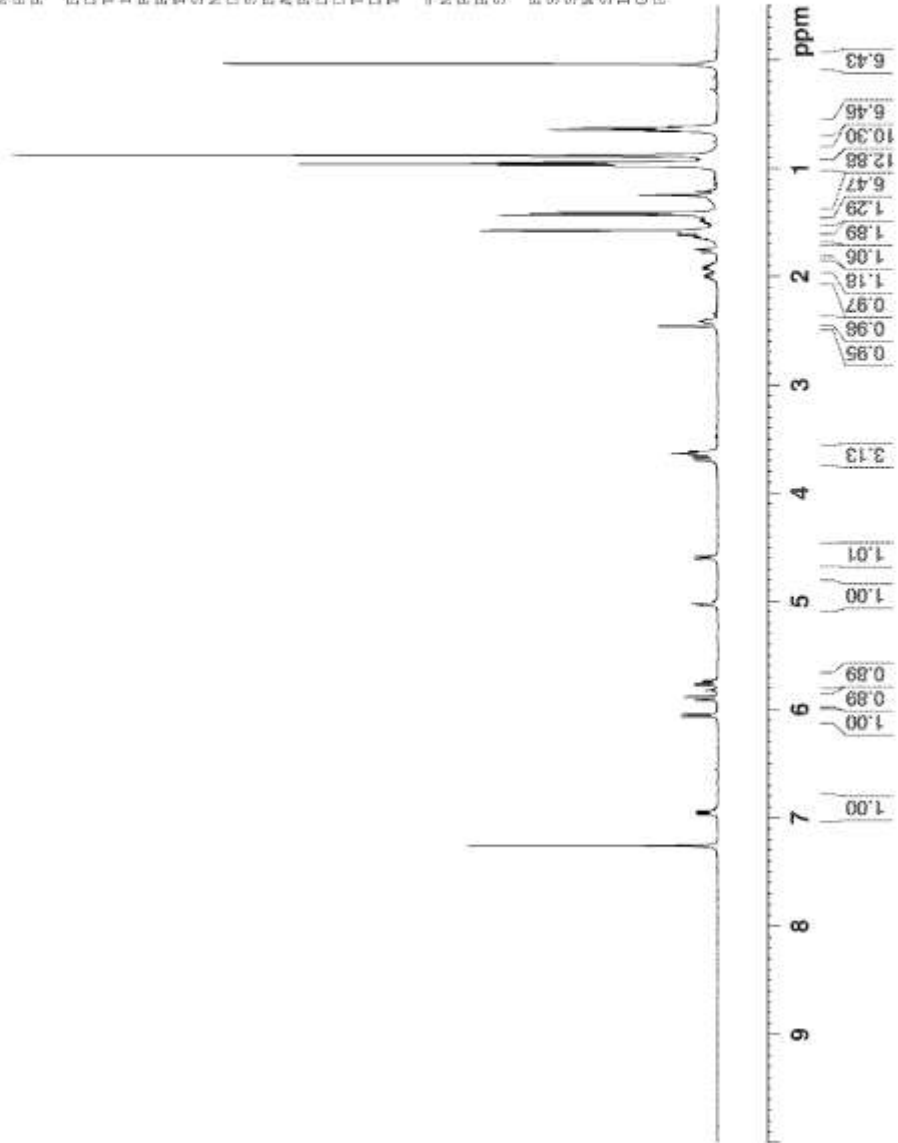


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1.455
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1.603
1.679
1.750
1.776
1.878
1.894
1.907
1.917
1.920
1.936
1.970
1.987
1.993
2.001
2.006
2.018
2.034
2.039
2.048
2.108
2.148
2.187
2.191
2.199
2.400
2.417
2.461
2.618
3.630
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3.699
4.585
4.609
5.022
5.030
5.040
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5.745
5.765
5.776
5.889
5.915
6.048
6.060
6.940
6.950
6.959
6.970
7.259

Current Data Parameters
NAME 14H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090717
Time 19.09
INSTRUM spect
PROBHD 5 mm PABBO HB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 7507.507 Hz
FIDRES 0.114958 Hz
AQ 4.3647475 sec
RG 322.3
DW 66.600 usec
DE 6.00 usec
TE 292.7 K
D1 1.00000000 sec
TD6 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 0 dB
SFO1 500.1330008 MHz
F2 - Processing parameters
SI 32768
SF 500.1300130 MHz
WDW EM
SSB 0
LB 0.25 Hz
GB 0
PC 1.00





Current Data Parameters
NAME JTM-14C C13
EXPNO 1
PROCNO 1

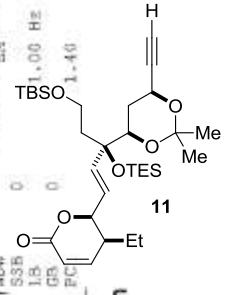
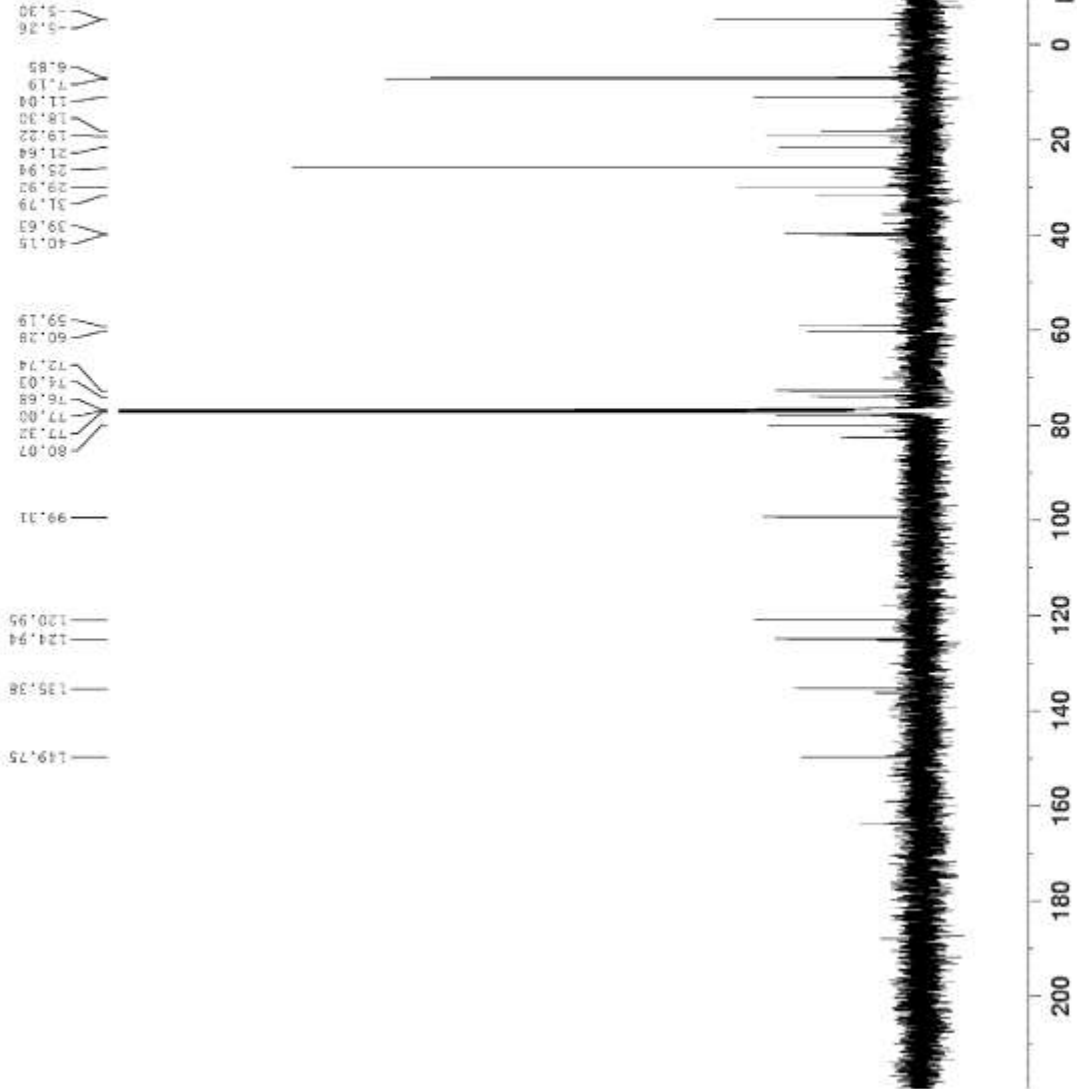
F2 - Acquisition Parameters

Date_ 20110319
Time 9.19
INSTRUM spect
PROBHD 5 mm F4BBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 928
DS 0
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 200.09
DM 20.800 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 7.50 usec
PLW1 51.20000076 W
SFO1 100.6127703 MHz

===== CHANNEL f2 =====
CSPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 11.19999981 W
PLW3 0.28820999 W
SFO2 400.0916004 MHz

F2 - Processing parameters
SI 32768
SF 100.6027125 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
FC 1.40





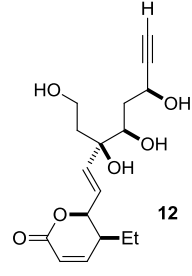
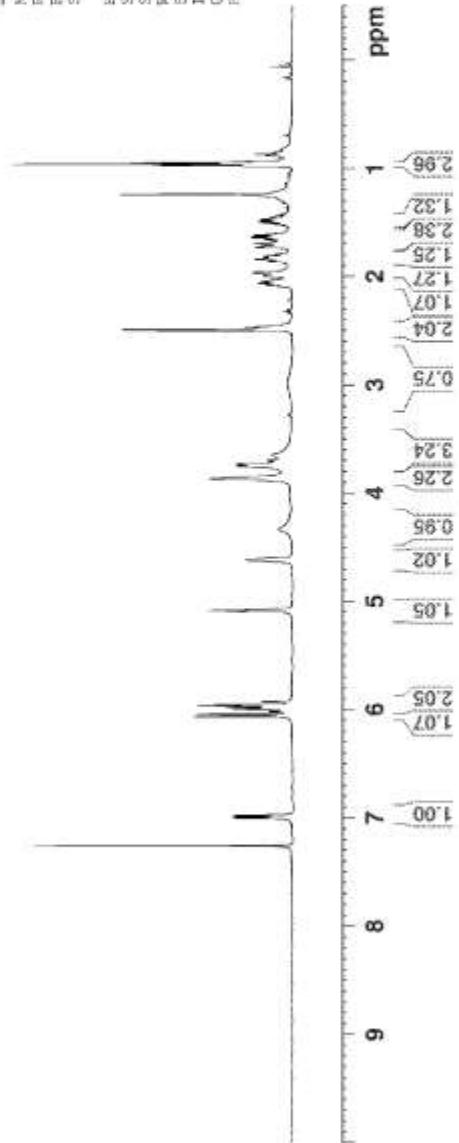
Current Data Parameters
 NAME 15H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20100409
 Time 14.49
 INSTRUM spect
 PROBRD 5 mm PABBO BB/
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 7507.507 Hz
 FIDRES 0.114555 Hz
 AQ 4.3647475 sec
 RG 228.1
 DW 66.600 usec
 DE 6.00 usec
 TE 291.5 K
 D1 1.00000000 sec
 TDC 1

CHANNEL f1

NUC1 1H
 P1 13.50 usec
 PL1 0 dB
 SFO1 500.1330008 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.1300133 MHz
 WDW EM
 SSB 0
 LB 0.25 Hz
 GB 0
 PC 1.00





Current Data Parameters
NAME 15C
EXPNO 1
PROCNO 1

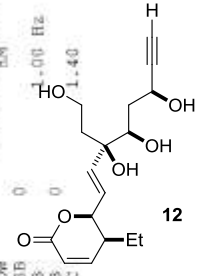
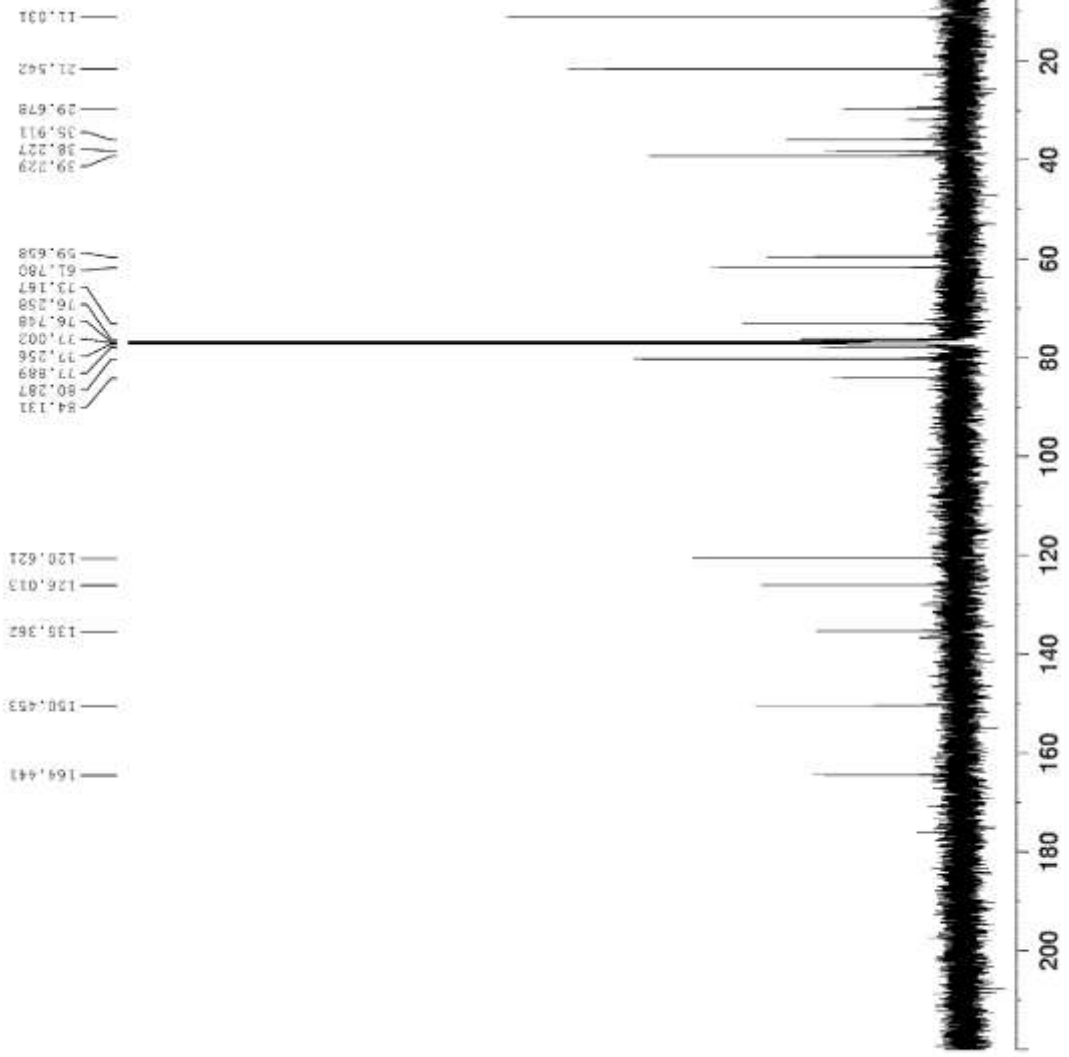
F2 - Acquisition Parameters

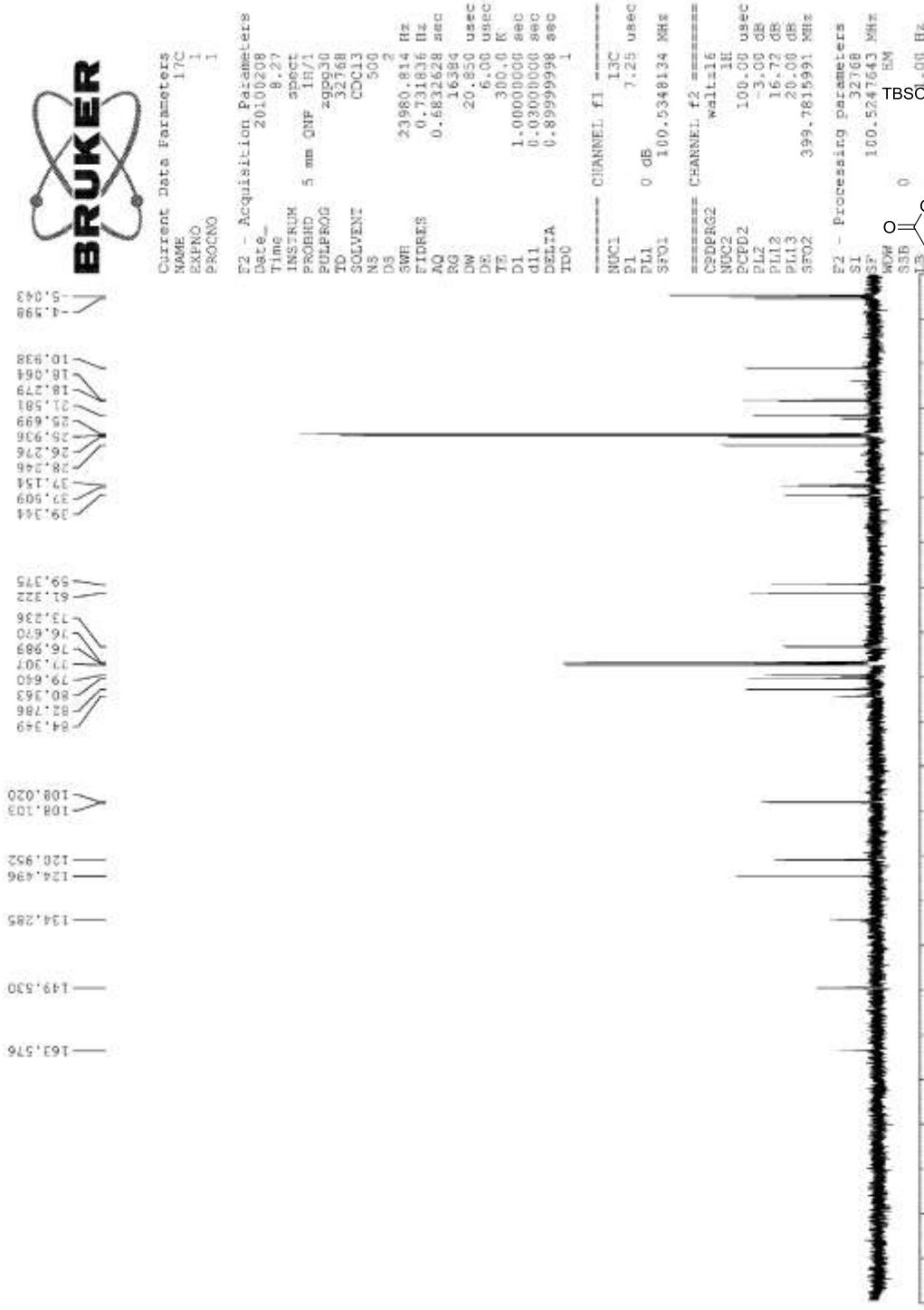
Date_ 20100409
Time 14.56
INSTRUM spect
PROBHD 5 mm PABBO HS/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1207
DS 0
SWH 30581.039 Hz
FIDRES 0.466630 Hz
AQ 1.0715636 sec
RG 32788
DW 16.350 usec
DE 6.00 usec
TE 292.1 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 6.80 usec
PL1 0 dB
SFO1 125.7705462 MHz

===== CHANNEL f2 =====
CSDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 14.00 dB
PL13 14.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 65536
SF 125.7577945 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.40







Current Data Parameters
NAME 1BFC
EXPNO 1
PROCNO 1

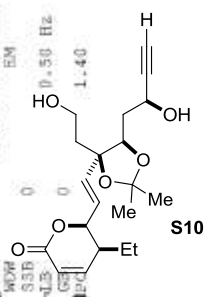
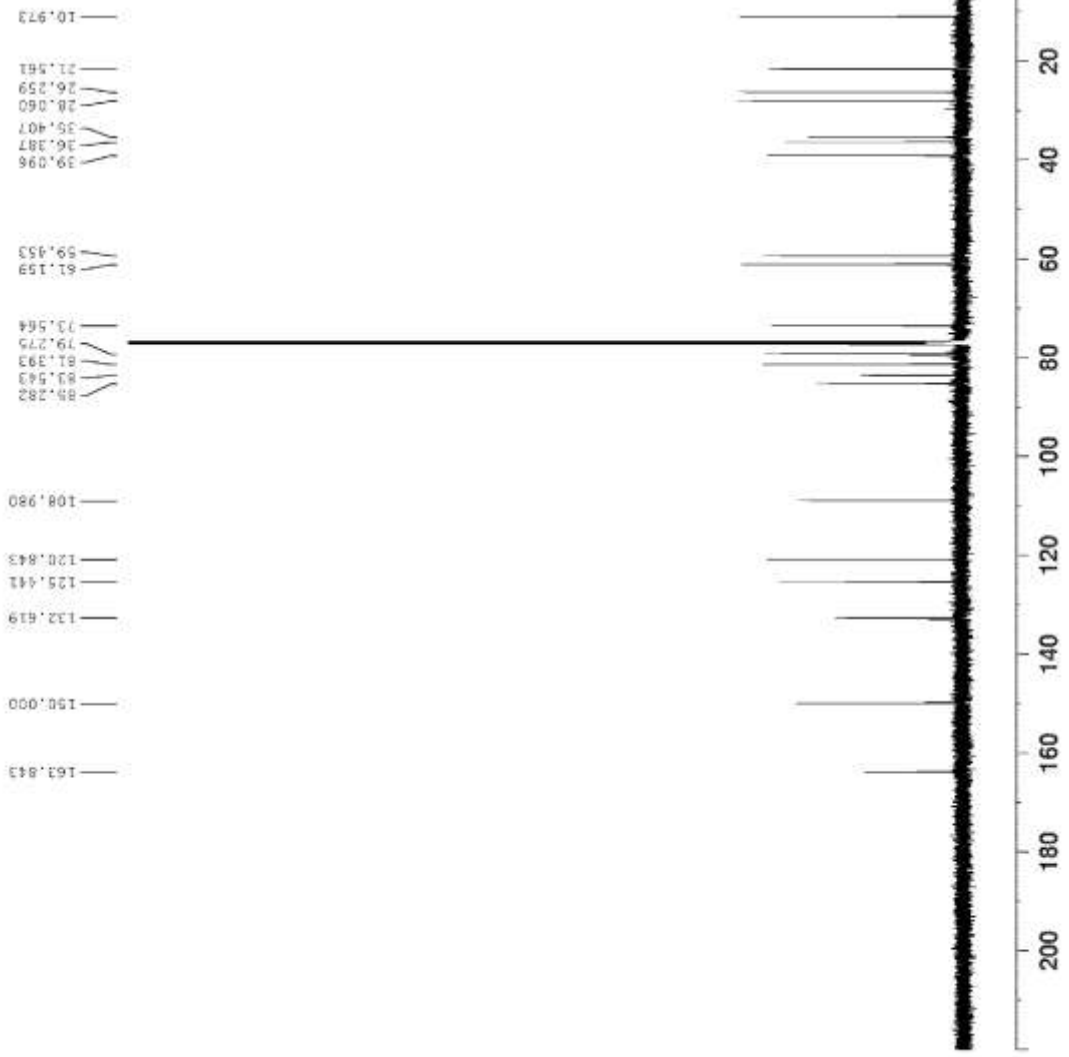
F2 - Acquisition Parameters

Date_ 20100621
Time 15.17
INSTRUM spect
PROBHD 5 mm PABBO HS/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2761
DS 0
SWH 30581.039 Hz
FIDRES 0.466630 Hz
AQ 1.0715636 sec
RG 32788
DW 16.350 usec
DE 6.00 usec
TE 298.3 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

CHANNEL f1
NUC1 13C
P1 7.00 usec
PL1 0 dB
SFO1 125.7705462 MHz

CHANNEL f2
CSDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0 dB
PL12 14.30 dB
PL13 18.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 65536
SF 125.7577917 MHz
RG 65536
EM



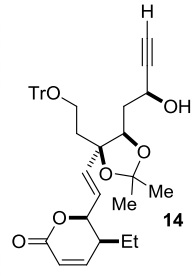


Current Data Parameters
NAME 19f2h
EXPNO 1
PROCNO 1

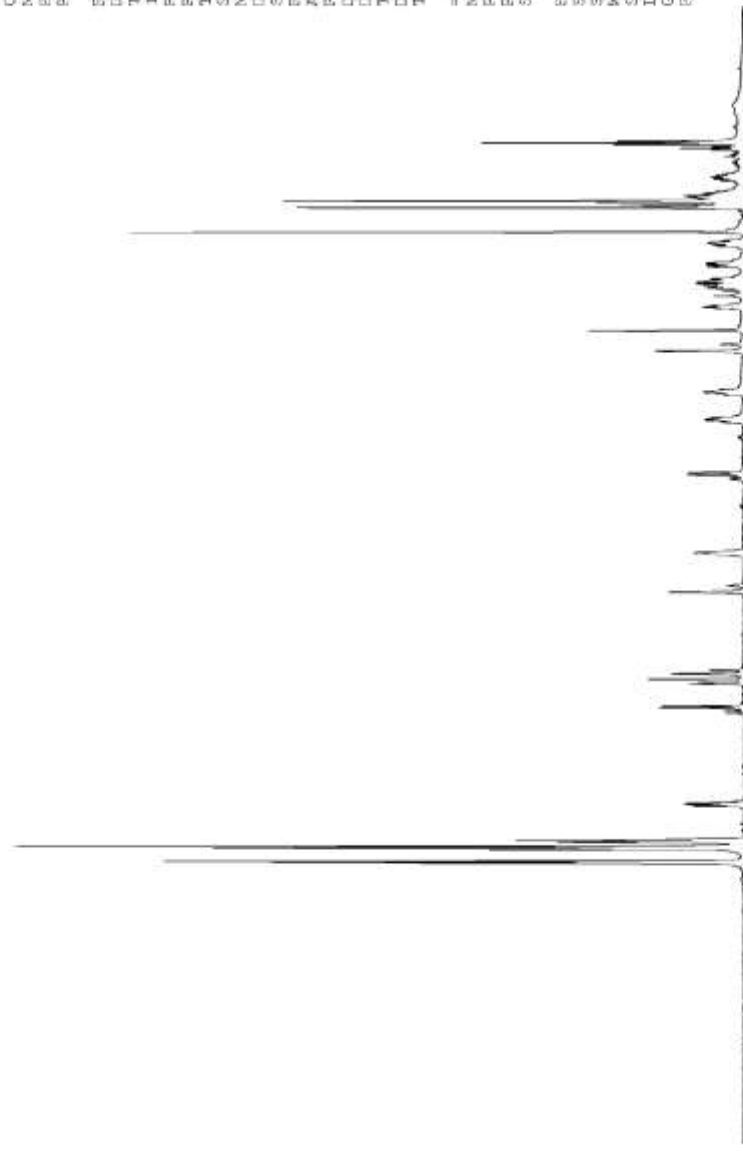
F2 - Acquisition Parameters
Date_ 20100709
Time 10.44
INSTRUM spect
PROBHD 5 mm PABBO HS/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 7507.507 Hz
FIDRES 0.114558 Hz
AQ 4.368773 sec
RG 287.4
DW 66.600 usec
DE 6.00 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 0 dB
SFO1 500.1330008 MHz

F2 - Processing parameters
SI 32768
SF 500.1300136 MHz
WDW EM
SSB 0
LB 0.25 Hz
GB 0
PC 1.00



7.410
7.395
7.287
7.273
7.260
7.250
7.220
7.210
7.206
7.192
7.188
6.876
6.868
6.857
5.983
5.963
5.757
5.712
5.669
5.661
5.638
5.630
4.915
4.908
4.903
4.559
4.553
4.547
3.823
3.808
3.800
3.445
3.335
3.324
3.315
3.305
3.295
3.087
3.078
3.066
3.059
3.048
3.038
2.686
2.680
2.494
2.191
2.177
2.142
1.632
1.357
1.316
1.296
1.019
0.772
0.757
0.743



8.53
8.24
3.13
0.98
1.00
1.21
0.91
0.83
0.17
1.07
1.09
4.17
4.13
3.18
3.15
1.16
1.37
2.49
1.01
1.19
1.18
1.13
1.17
3.29
1.31
1.97



Current Data Parameters
NAME 19f2c
EXPNO 1
PROCNO 1

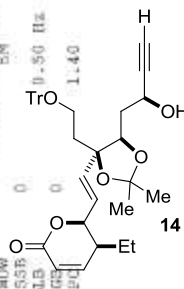
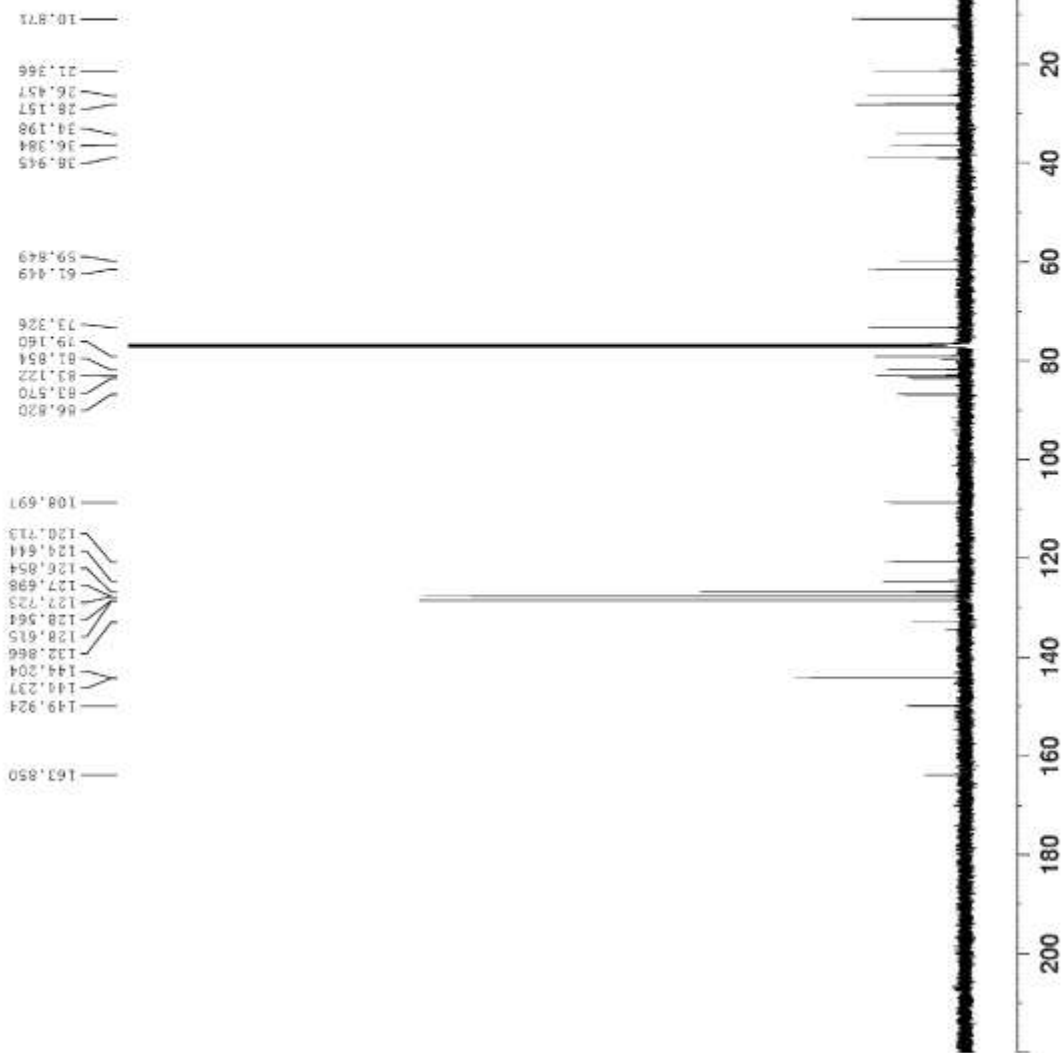
F2 - Acquisition Parameters

Date_ 20100709
Time 10.53
INSTRUM spect
PROBHD 5 mm F4BBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3131
DS 0
SWH 30581.039 Hz
FIDRES 0.466630 Hz
AQ 1.0715638 sec
RG 32768
DM 16.350 usec
DE 6.00 usec
TE 292.9 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TDF 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.00 usec
PL1 0 dB
SFO1 125.7705462 MHz

===== CHANNEL f2 =====
CDEPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0 dB
PL12 14.30 dB
PL13 18.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 65536
SF 125.7577940 MHz
WDW EN
SSB 0
LB 0.50 Hz
GB 0
PC 0





Current Data Parameters
 NAME 20F3H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

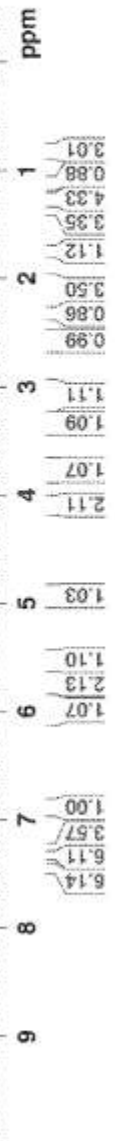
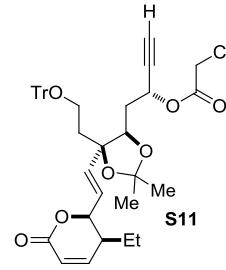
Date_ 20100610
 Time_ 9.38
 INSTRUM spect
 PROBRD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT Acetone
 NS 16
 DS 0
 SWH 6218.905 Hz
 FIDRES 0.189786 Hz
 AQ 2.6345973 sec
 RG 57
 DW 80.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDC 1

CHANNEL f1

NUC1 1H
 P1 9.30 usec
 PL1 -3.00 dB
 SFO1 399.7824920 MHz

F2 - Processing parameters

SF 399.7799909 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





Current Data Parameters
 NAME 21F4H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20100610
 Time 12.53
 INSTRUM spect
 PROBRD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT Acetone
 NS 16
 DS 0
 SWH 6218.905 Hz
 FIDRES 0.189786 Hz
 AQ 2.6345973 sec
 RG 57
 DW 80.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDC 1

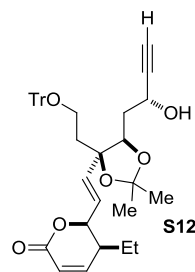
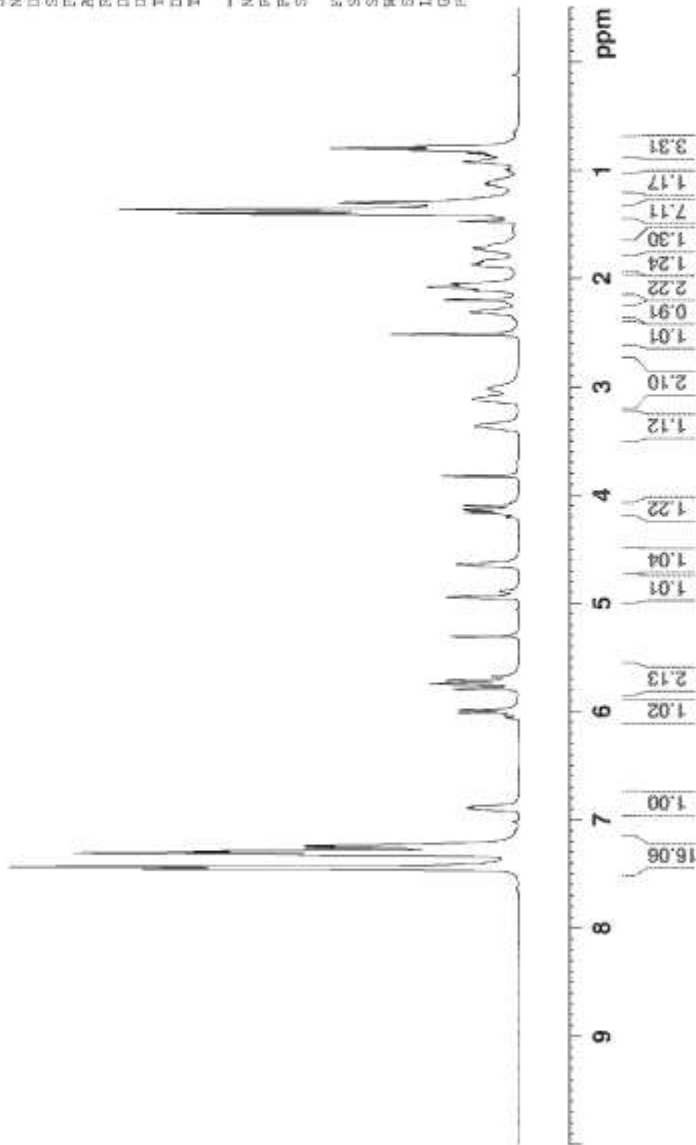
CHANNEL f1

NUC1 1H
 P1 9.30 usec
 PL1 -3.00 dB
 SFO1 399.7824920 MHz

F2 - Processing parameters

SF 399.7799950 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

7.567
 7.119
 6.911
 6.898
 6.889
 6.878
 6.013
 5.989
 5.793
 5.749
 5.719
 5.678
 4.946
 4.649
 4.163
 4.136
 4.101
 3.566
 3.119
 3.112
 3.077
 2.519
 2.311
 2.109
 2.079
 2.051
 1.884
 1.871
 1.854
 1.836
 1.740
 1.721
 1.695
 1.429
 1.402
 1.364
 1.278
 1.166
 1.054
 0.816
 0.797
 0.780





Current Data Parameters
NAME 21F4C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

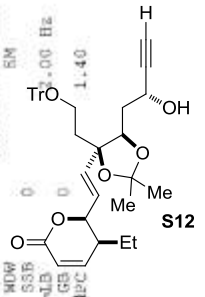
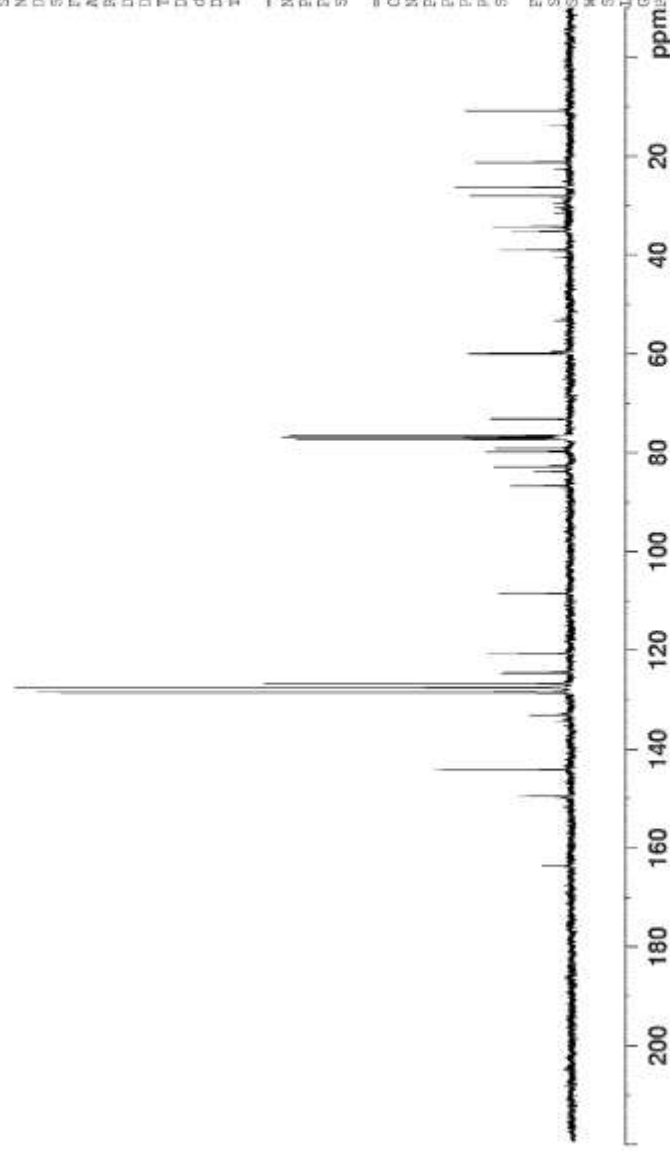
Date_ 20100610
Time 12.52
INSTRUM spect
PROBRD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 800
DS 0
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.6833628 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.25 usec
PL1 0 dB
SFO1 100.5348134 MHz

===== CHANNEL f2 =====
CSPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.7815991 MHz

F2 - Processing parameters
SI 32768
SF 100.5247703 MHz
WDW EM
SSB 0
LB 0
GB 0

10.796
21.301
26.389
28.106
34.271
35.274
39.029
59.875
60.051
73.213
76.651
76.970
77.288
79.927
83.943
86.822
108.450
120.687
124.618
127.622
128.547
133.151
144.255
149.630
163.667

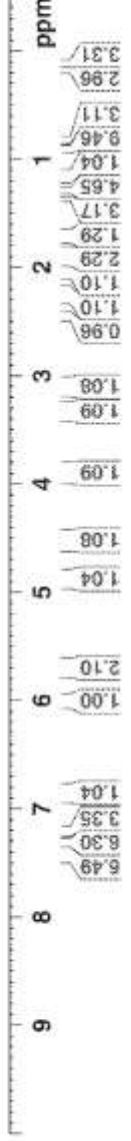
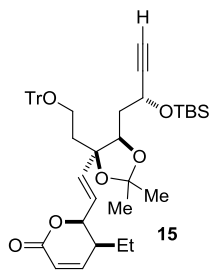
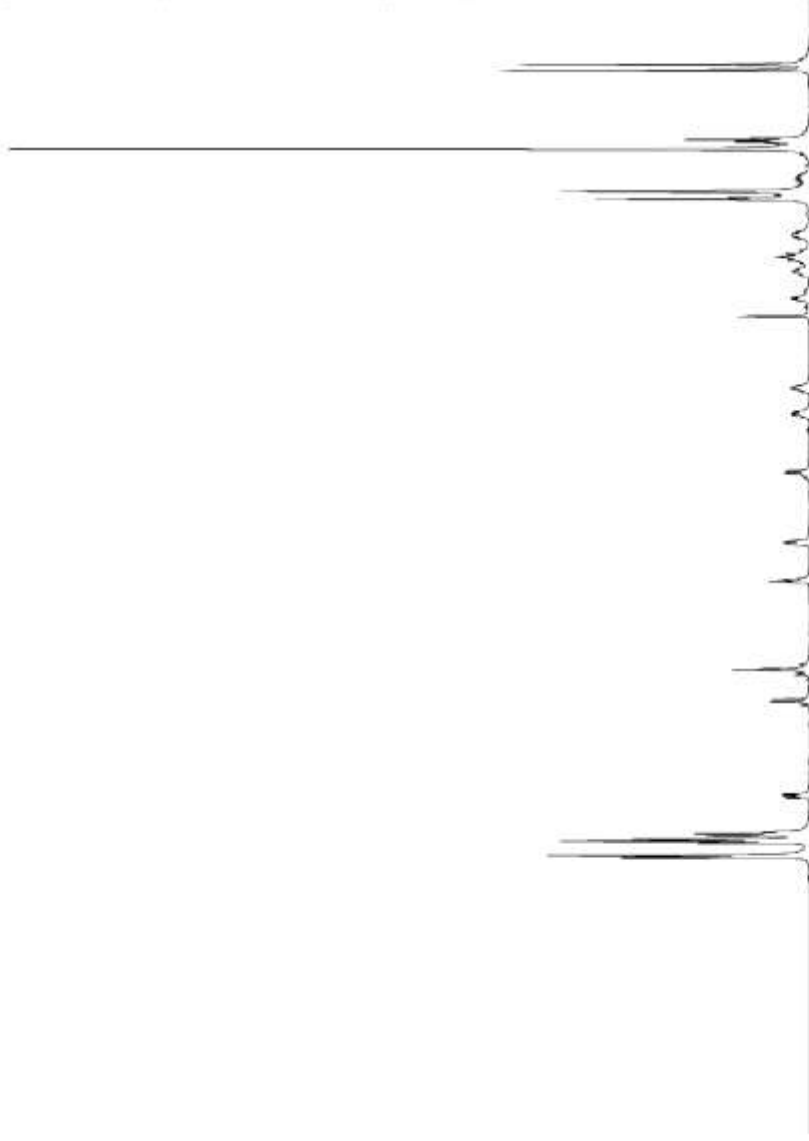




Current Data Parameters
 NAME 22F5H
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20100610
 Time 17.33
 INSTRUM spect
 PROBRD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 6218.905 Hz
 FIDRES 0.189786 Hz
 AQ 2.6345973 sec
 RG 57
 DW 80.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.30 usec
 PL1 -3.00 dB
 SFO1 399.7824920 MHz
 F2 - Processing parameters
 SI 32768
 SF 399.7800000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





Current Data Parameters
 NAME 22F5C
 EXPNO 1
 PROCNO 1

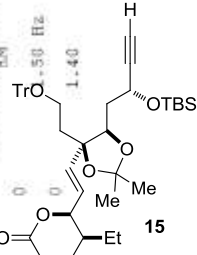
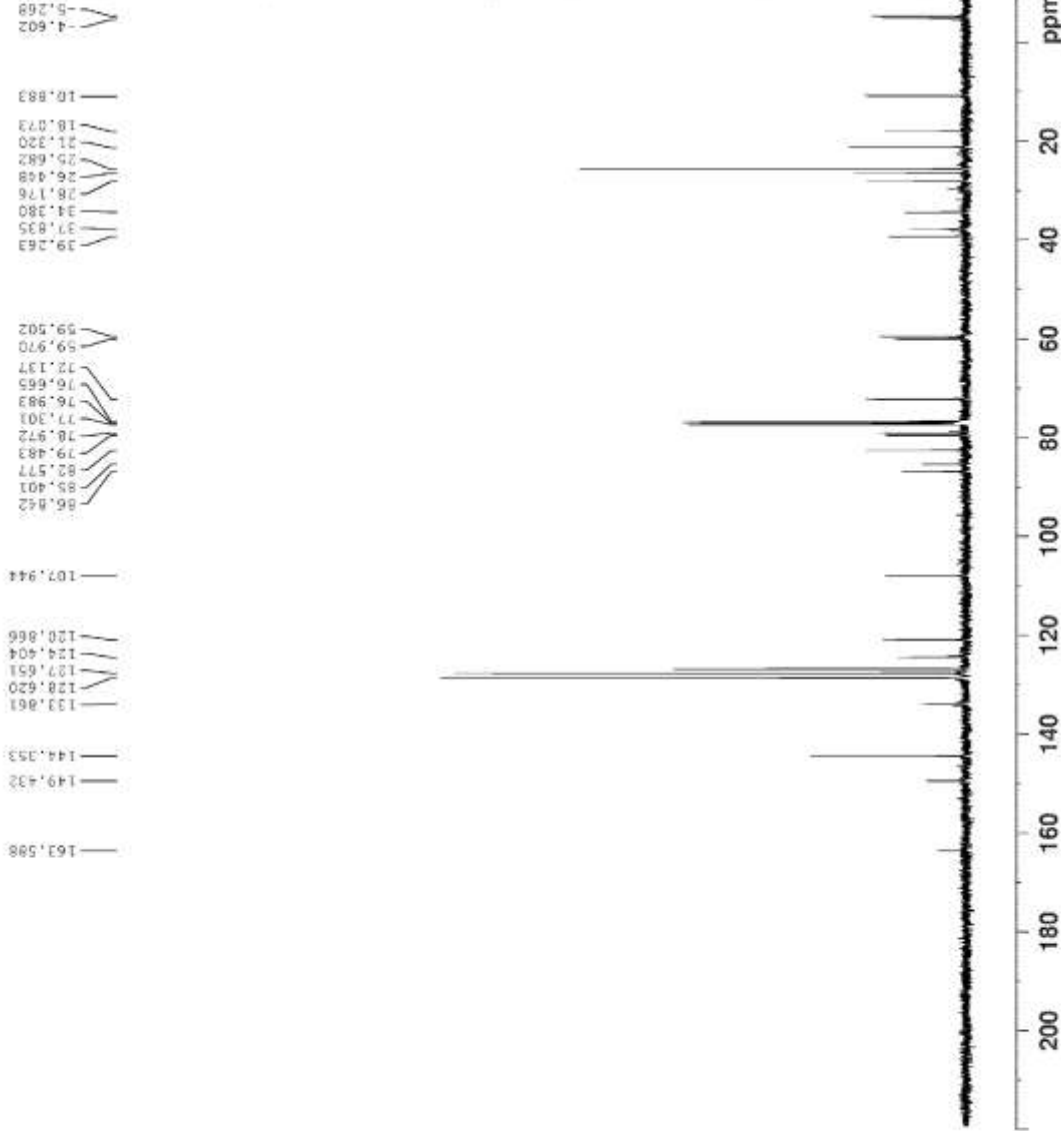
F2 - Acquisition Parameters

Date_ 20100610
 Time 17.39
 INSTRUM spect
 PROBRD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 620
 DS 0
 SWH 23980.814 Hz
 FIDRES 0.731836 Hz
 AQ 0.6832628 sec
 RG 16384
 DW 20.850 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 DELTA 0.89999998 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 7.25 usec
 PL1 0 dB
 SFO1 100.5348134 MHz

===== CHANNEL f2 =====
 CSDEPRG2 waltz16
 NUC2 1H
 EPCPD2 90.00 usec
 PL2 -3.00 dB
 PL12 16.72 dB
 PL13 20.00 dB
 SFO2 399.7815991 MHz

F2 - Processing parameters
 SI 32768
 SF 100.5247659 MHz
 NQW EM

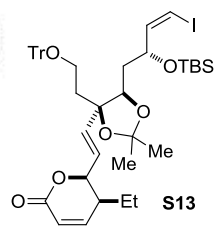
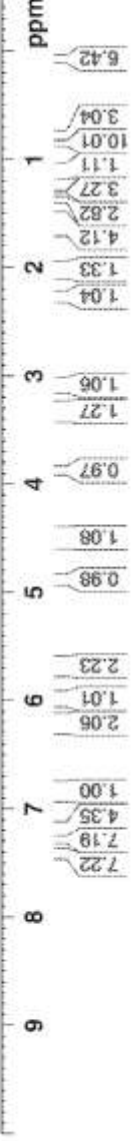
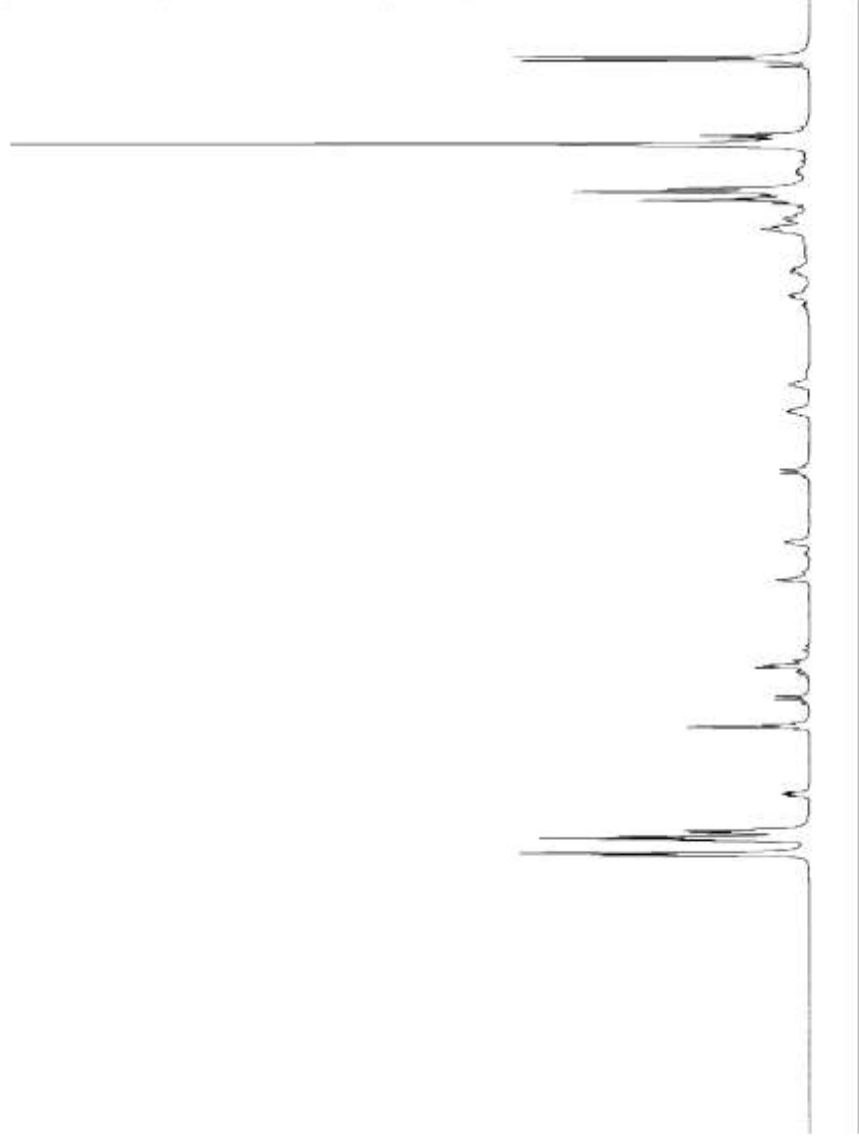




Current Data Parameters
NAME 23F6H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100615
Time 11:34
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 57
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
TD0 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.7824920 MHz
F2 - Processing parameters
SI 32768
SF 399.7800080 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





Current Data Parameters
NAME 23f6C
EXPRD 1
PROCNO 1

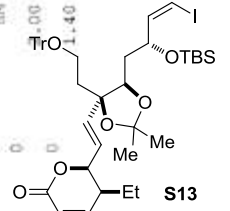
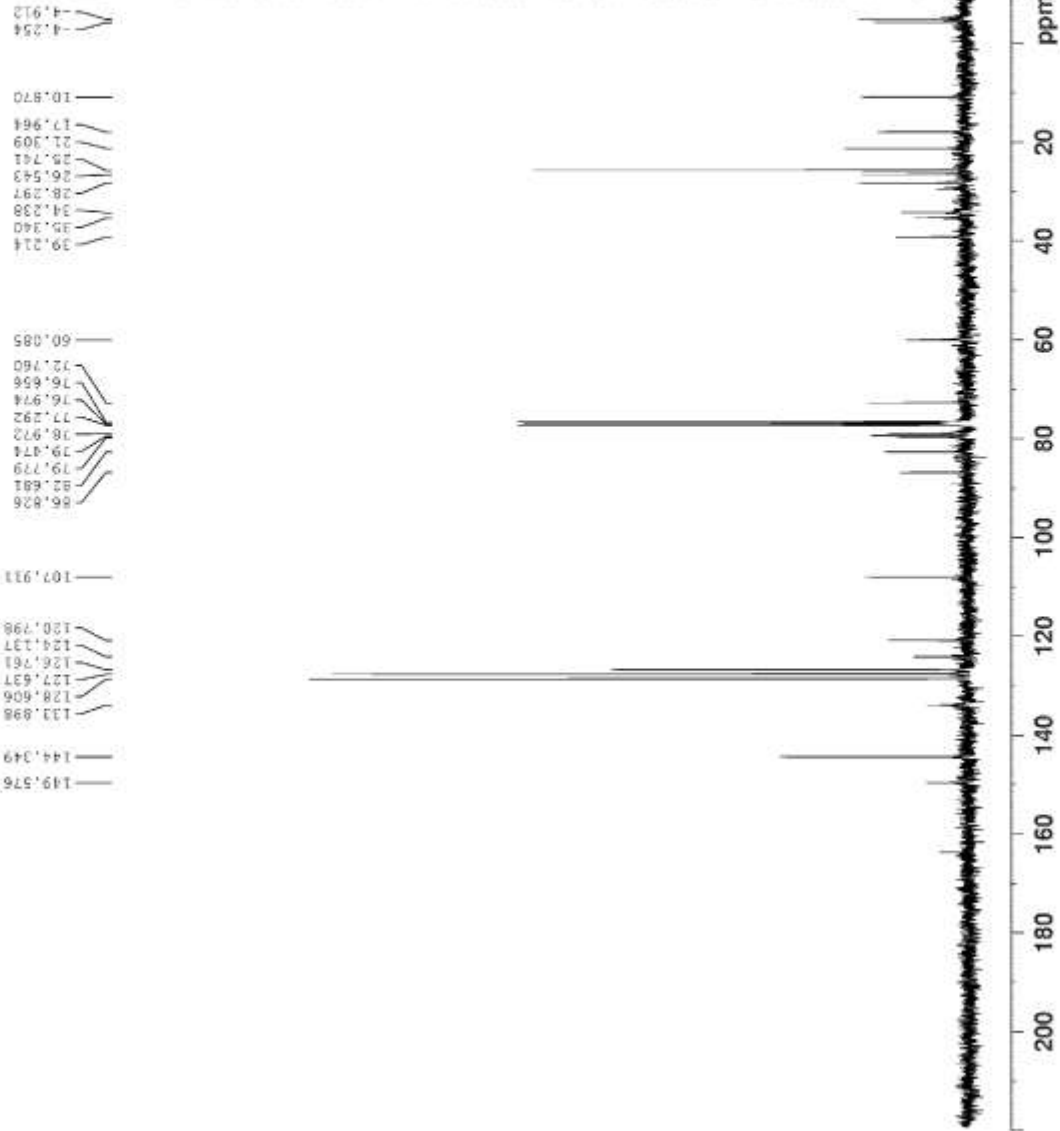
F2 - Acquisition Parameters

Date 20100615
Time 11:39
INSTRUM spect
PROBRD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 512
DS 0
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.6833628 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 7.25 usec
PL1 0 dB
SFO1 100.5348134 MHz

===== CHANNEL f2 =====
CSPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.7815991 MHz

F2 - Processing parameters
SI 32768
SF 100.5247673 MHz
WDW EM





Current Data Parameters
NAME SNGXIV-Imanishi
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 20100708
Time 15.42
INSTRUM spect
PROBHD 5 mm TWD 13C/3
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 4237.288 Hz
FIDRES 0.129312 Hz
AQ 3.8666733 sec
RG 4036
DW 116.000 usec
DE 168.57 usec
TE 293.0 K
HL1 1 dB
D1 1.0000000 sec
P1 11.25 usec
SFO1 300.1319000 MHz
NUCLEUS 1H

F2 - Processing parameters
SI 16384
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

