Stereospecific Access to α-Haloalkyl Esters via Enol Ester Epoxides and Synthesis of a C3–C21 Fragment of Bastimolide A

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Supporting Information

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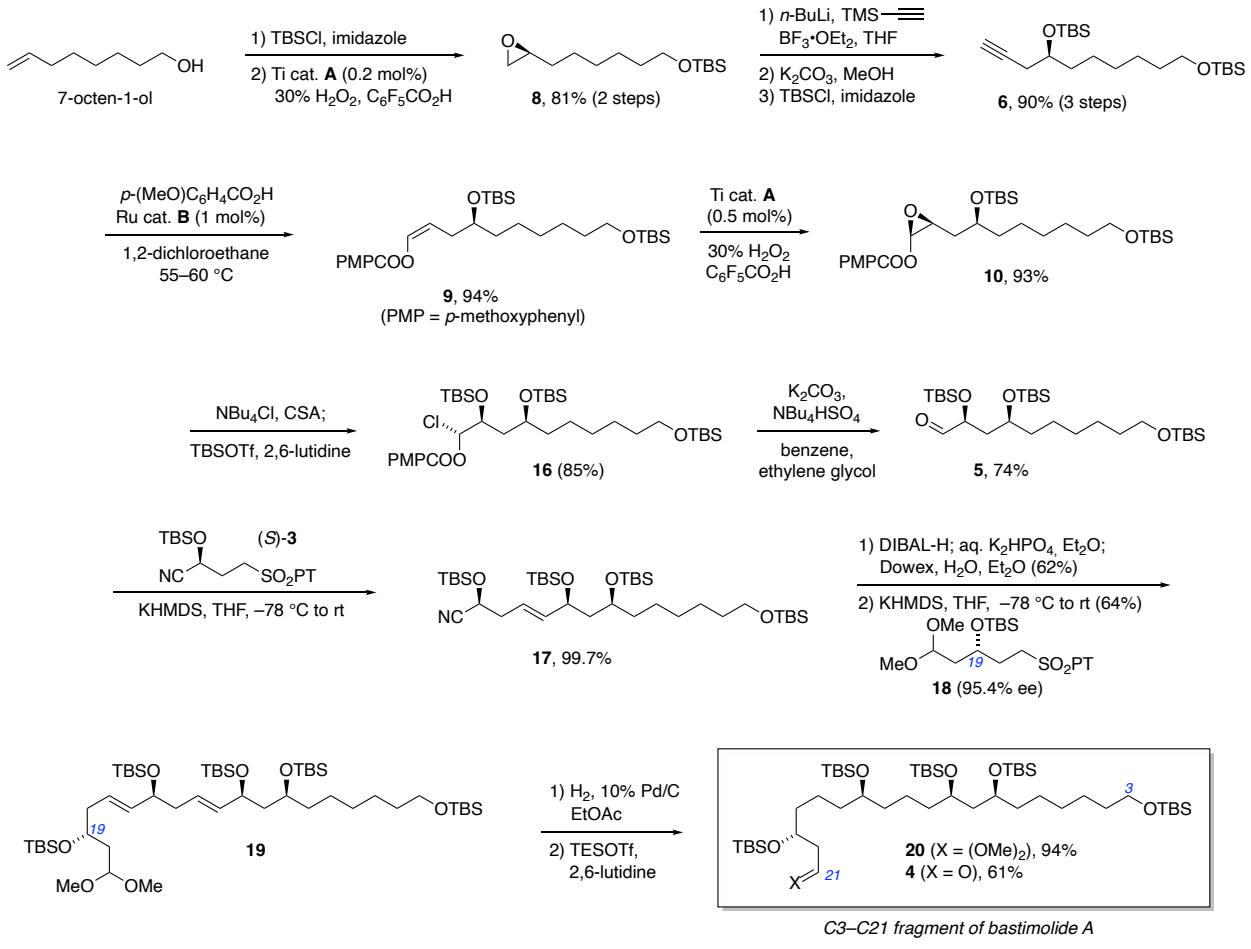
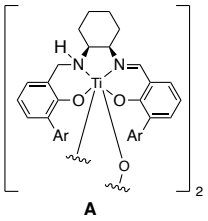
Materials and Methods

Reactions employed oven- or flame-dried glassware under nitrogen or argon unless otherwise noted. THF, diethyl ether, CH_2Cl_2, benzene and toluene were purchased inhibitor-free, sparged with argon, and passed through columns of activated alumina prior to use (dropwise addition of blue benzophenone ketyl solution revealed the THF purified in this manner sustained the blue color more readily than the control sample purified by distillation). Nitrogen was passed successively through columns of anhydrous $CaSO_4$ and R3-11 catalyst for removal of water and oxygen, respectively. All other materials were used as received from commercial sources unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator. Flash chromatography columns were packed with 230–400 mesh silica gel as a slurry in the initial elution solvent. Gradient flash chromatography was conducted by adsorption of product mixtures on silica gel, packing over a short pad of clean silica gel as a slurry in hexane, and eluting with a continuous gradient from hexane to the indicated solvent. Radial chromatography refers to centrifugally accelerated thin-layer chromatography performed with a Chromatotron using commercially supplied rotors. Melting points are uncorrected. Nuclear magnetic resonance (NMR) data were obtained at operating frequencies of 600, 500, 400, or 300 MHz for ^{1}H and 150, 125, 100 or 75 MHz for ^{13}C, respectively. Optical rotations were determined using a digital polarimeter operating at ambient temperature. Low- and high-resolution mass spectra were obtained using sample introduction by dip, liquid chromatography or gas chromatography. Chromatographic stereoisomer ratio analyses employed HPLC with Whelk O1, Chiralcel OD-H, Chiralcel AD-H, or Chiralcel OJ-3 columns using 2-propanol/hexane as mobile phase with UV photodiode array detection.

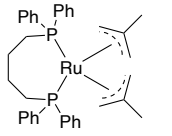
Summary of the Synthetic Route to C3–C21 Fragment of the Bastimolides



C3–C21 fragment of bastimolide A



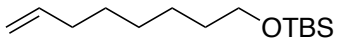
A



Ru(dppb)(methallyl)$_2$

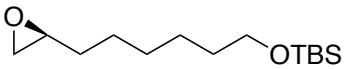
B

Preparative Procedures and Characterization Data for New Compounds



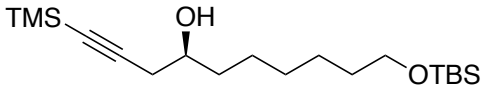
7

1-(*tert*-Butyldimethylsilyloxy)-oct-7-ene (7). To a mixture of 7-octen-1-ol (5.04 g, 39.3 mmol) and imidazole (5.36 g, 78.7 mmol, 2.0 equiv) in reagent-grade CH_2Cl_2 (196.0 mL) at room temperature was added *tert*-butyldimethylsilyl chloride (8.89 g, 59.0 mmol, 1.5 equiv). After 21 h, the mixture was partitioned between H_2O (150 mL) and CH_2Cl_2 (3 x 50 mL). The organic phase was washed with brine (100 mL) and dried over Na_2SO_4. Vacuum short-path distillation (ca. 1 mmHg/100 °C oil bath temp) afforded silyl ether **7** (7.73 g, 81%) as a colorless liquid. Characterization data matched prior reports.[1]



8

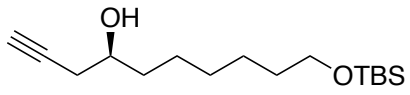
1-(*tert*-Butyldimethylsilyloxy)-7-epoxyoctane (8). To a solution of silyl ether **7** (6.46 g, 26.7 mmol, 1.0 equiv) in 1,2-dichloroethane (4.5 mL), was added (1*R*,2*S*)-Berkessel catalyst (**A**, 0.158 g, 0.11 mmol, 0.4 mol %), followed by aqueous H_2O_2 (30%, no stabilizers, 5.45 mL, 53.7 mmol, 2.0 eq). After stirring for 91 h, the mixture was partitioned between H_2O (5 mL) and CH_2Cl_2 (3 x 15 mL). The organic phase was washed with brine (25 mL), dried over Na_2SO_4, and concentrated. Flash chromatography (10% Et_2O in hexanes) afforded **8** (6.90 g, 100%) as a pale yellow liquid. $[\alpha]_D^{22}$ –4.8 (*c* = 1.3, $CHCl_3$). Further characterization data matched prior reports.[1]



S1

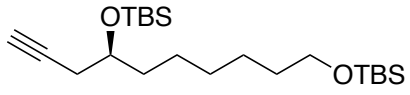
(*S*)-10-((*tert*-butyldimethylsilyl)oxy)-1-(trimethylsilyl)dec-1-yn-4-ol (S1). To a solution of trimethylsilylacetylene (3.12 mL, 21.9 mmol, 2.0 equiv) in THF (47.4 mL) at –78 °C was added *n*-BuLi (2.5 M, 8.76 mL, 2.0 equiv) via syringe over 15 min. The reaction was warmed to 0 °C, and stirred for 30 min. The mixture was recooled to –78 °C, and freshly distilled BF_3•OEt_2 (2.70 mL, 21.9 mmol, 2.0 equiv) was added via syringe over 5 minutes. The mixture was stirred for 30 minutes at –78 °C, and then epoxide **8** (2.83 g, 10.9 mmol, 1.0 equiv), in THF (10.9 mL) was added via cannula over 10 minutes. The reaction mixture was allowed to warm to rt and stir for an additional 5 h. The mixture was partitioned between H_2O (50 mL) and CH_2Cl_2 (3 x 50 mL). The organic phase was washed with brine (100 mL), dried over Na_2SO_4, and concentrated to afford crude **S1** as a light brown-orange oil which was carried forward to the next step without purification. A sample for characterization was obtained from a smaller scale reaction; gradient flash chromatography (5 to 30% Et_2O in hexanes) afforded **S1** as a colorless oil. $[\alpha]_D^{23}$ +2.8 (*c* = 0.12, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 3.74–3.68 (m, 1H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.46–2.42 (dd, *J* = 16.9 Hz, 4.7 Hz, 1H), 2.35–2.31 (dd, *J* = 17.1 Hz, 7.0 Hz 1H), 1.97 (m, 1H), 1.52–1.32 (m, 10H), 0.88 (s, 9H), 0.15 (s, 9H), 0.03 (s, 6H); ^{13}C NMR {1H} (125 MHz, $CDCl_3$): δ 103.5, 87.7, 70.0, 63.4, 33.0, 29.5, 29.1, 26.2, 25.9, 25.8, 18.5, 0.2, –5.1 (2C). HRMS (FTMS +

pESI): *m/z* calc'd for $C_{19}H_{41}O_2Si_2$ $[M+H]^+$: 357.2640; found 357.2638. The benzoate derivative was found to have er 97.7:2.3 (95.4% ee); HPLC (Chiralcel OD-H, 0.1% IPA/hexanes, 1 mL/min): t_R 9.9 min (major), t_R 15.1 min (minor).



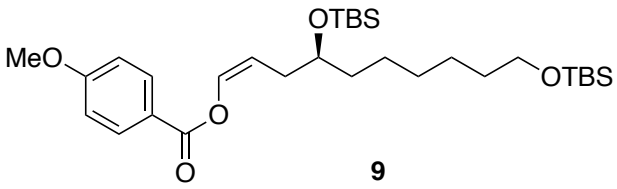
S2

(*S*)-10-((*tert*-butyldimethylsilyl)oxy)dec-1-yn-4-ol (S2). To a solution of crude alcohol **S1** (assume 10.9 mmol, 1.0 equiv) in MeOH (27.2 mL), at rt and open to air, was added K_2CO_3 (3.01 g, 21.9 mmol, 2.0 equiv) in portions. The reaction vessel was capped and left to stir. After 14h, the mixture was partitioned between aqueous NH_4Cl (20 mL) and CH_2Cl_2 (3 x 30 mL). The organic phase was washed with brine (50 mL), dried over Na_2SO_4, and concentrated to afford **S2**, which was carried forward to the next step without purification. A sample for characterization was obtained from a smaller scale reaction; gradient flash chromatography (5 to 30% Et_2O in hexanes) afforded homopropargyl alcohol **S2** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 3.70 (m, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.39–2.34 (ddd, *J* = 16.7 Hz, *J* = 4.9 Hz, 2.6 Hz, 1H), 2.29–2.24 (ddd, *J* = 16.7 Hz, 6.6 Hz, 2.6 Hz, 1H), 2.23 (m, 1H), 2.00 (t, *J* = 2.8 Hz, 1H), 1.51–1.28 (m, 10H), 0.85 (s, 9H), 0.00 (s, 6H); ^{13}C NMR {1H} (125 MHz, $CDCl_3$): δ 81.1, 70.8, 69.9, 63.3, 36.2, 32.9, 29.4, 27.4, 26.1, 25.8, 25.7, 18.4, -5.2 (2C); HRMS (FTMS + pESI): *m/z* calc'd for $C_{16}H_{33}O_2Si$ $[M+H]^+$: 285.2244; found 285.2243.



6

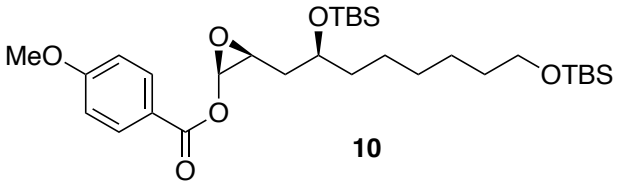
(*S*)-2,2,3,3,13,13,14,14-octamethyl-5-(prop-2-yn-1-yl)-4,12-dioxa-3,13-disilapentadecane (6). To a mixture of **S2** (assume 10.9 mmol) and imidazole (1.86 g, 27.3 mmol, 2.5 eq) in CH_2Cl_2 (54.5 mL) at rt under Ar was added *tert*-butyldimethylsilyl chloride (3.29 g, 21.8 mmol, 2.0 equiv). After ca. 21 h, the mixture was partitioned between H_2O (50 mL) and CH_2Cl_2 (3 x 50 mL). The organic phase was washed with brine (100 mL) and dried over Na_2SO_4. Gradient flash chromatography (1 to 3% Et_2O in hexanes) afforded silyl ether **6** (3.10 g, 90% over 3 steps) as a pale yellow oil. $[\alpha]_D^{24}$ –13.8 (*c* = 2.79, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 3.79 (m, 1H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.36–2.27 (m, *2*H), 1.96 (t, *J* = 2.8 Hz, 1H), 1.64–1.26 (m, 10H), 0.89 (s, 9H), 0.89 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (s, 6H); ^{13}C NMR {^1H} (125 MHz, $CDCl_3$): δ 82.0, 71.1, 69.9, 63.5, 36.8, 33.0, 30.0, 27.6, 26.2, 26.0 (2C), 25.3, 18.6, 18.3, –4.3, –4.5, –5.1. Attempted HRMS analysis led to decomposition.



9

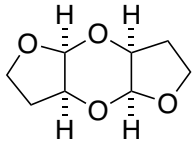
(*S,Z*)-4,10-bis((*tert*-butyldimethylsilyl)oxy)dec-1-en-1-yl-4-methoxybenzoate (9). To a Schlenk flask equipped with a rubber septum was added alkyne **6** (117.5 mg, 0.295 mmol), *p*-anisic acid (45.5 mg, 0.299 mmol, 1.0 equiv), and toluene (0.15 mL), followed by

Ru(dppb)(methallyl)$_2$ (**B**, 2 mg, 0.003 mmol, 1 mol%). The resulting suspension was heated to 75–80 °C and the rubber septum was replaced by a greased ground-glass stopper. After stirring for 22 h, the mixture was dark orange and mostly homogeneous. The mixture was partitioned between saturated aqueous $NaHCO_3$ (1 mL) and EtOAc (2 x 3 mL). The organic phase was dried over Na_2SO_4 and concentrated. Gradient flash chromatography (50:1 to 10:1 hexanes/EtOAc) afforded **9** (153 mg, 94%) as a pale yellow oil. $[\alpha]_D^{24}$ –2.5 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06–8.04 (d, *J* = 9.0 Hz, 2H), 7.31–7.29 (dt, *J* = 6.4 Hz, *J* = 1.4 Hz, 1H), 6.96–6.93 (d, *J* = 9.0 Hz, 2H), 5.06–5.00 (apparent q, 1H), 3.88 (s, 3H), 3.78–3.73 (quintet, 1H), 3.59–3.55 (t, *J* = 6.6 Hz, 2H), 2.49–2.39 (m, 2H), 1.52–1.26 (m, 10H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.03 (s, 6H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 163.9, 163.4 135.4, 132.1, 121.8, 113.9, 110.5, 71.8, 63.4, 55.6, 36.9, 32.9, 32.7, 29.7, 26.1, 26.0, 25.9, 25.5, 18.5, 18.2, –4.2, –4.3, –5.1; HRMS (FTMS + pESI): *m/z* calc'd for $C_{30}H_{55}O_5Si_2$ $[M+H]^+$: 551.3583; found 551.3579.



10

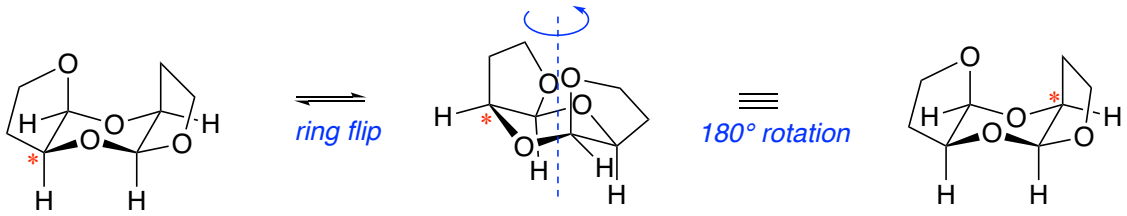
(2*R*,3*S*)-3-((*S*)-2,8-bis((*tert*-butyldimethylsilyl)oxy)octyl)oxiran-2-yl 4-methoxybenzoate (10). To a solution of enol ester **9** (0.807 g, 1.47 mmol, free of Ru contaminants[2]), 1,2-dichloroethane (0.25 mL) was added (1*R*,2*S*)-Berkessel catalyst (**A**, 10.7 mg, 0.00716 mmol, 0.5 mol %), followed by aqueous H_2O_2 (30%, no stabilizers, 0.6 mL, 5.8 mmol, 4.0 equiv). After 3 d, the mixture was partitioned between H_2O (5 mL) and CH_2Cl_2 (3 x 10 mL). The organic phase was dried over Na_2SO_4 and concentrated. Gradient flash chromatography (20:1 to 3:1 hexanes/EtOAc, then EtOAc) afforded **10** (0.772 g, 93%) as a viscous light yellow oil. $[\alpha]_D^{24}$ 13.7 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98–7.96 (d, *J* = 9.0 Hz, 2H), 6.93–6.91 (d, *J* = 9.0 Hz, 2H), 5.76 (d, *J* = 2.6 Hz, 1H), 3.91 (quintet, 1H), 3.78–3.73 (quintet, 1H), 3.89 (s, 3H), 3.58 (t, *J* = 6.6 Hz, 2H), 3.26–3.23 (td, *J* = 5.9 Hz, *J* = 3.2 Hz, 1H), 1.93 (t, *J* = 5.69 Hz, 1H),1.58–1.25 (m, 10H), 0.89 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H), 0.03 (s, 6H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 165.9, 164.2, 132.1, 121.6, 114.0, 76.0, 70.3, 63.4, 55.6, 54.1, 37.4, 34.8, 33.0, 29.7, 26.2, 26.0 (2C), 25.7, 18.5, 18.2, -4.3, -4.4, -5.1. HRMS (FTMS + pESI): *m/z* calc'd for $C_{30}H_{55}O_6Si_2$ $[M+H]^+$: 567.3532; found 567.3526.



13

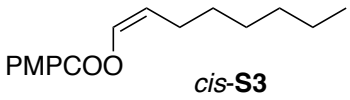
(3a*R*,4a*S*,7a*R*,8a*S*)-Octahydrodifuro[2,3-b:2',3'-e][1,4]dioxine (13). To a solution of enol ester epoxide **11a** (98.5 mg, 0.279 mmol) in CH_2Cl_2 (1 mL) were added 2,6-lutidine (0.065 mL, 0.56 mmol, 2.0 equiv) and freshly distilled triethylsilyl triflate (0.069 mL, 0.31 mmol, 1.1 equiv). After 15 min, the reaction mixture was quenched with aqueous saturated ammonium chloride solution and extracted with CH_2Cl_2 (15 mL). Concentration and flash chromatography (10:1 hexanes/EtOAc) yielded **13** (8.5 mg, 18%) as a colorless waxy solid that evaporated readily under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.03 (d, *J* = 3.7 Hz, 2H), 4.16-4.10 (m, 2H), 4.02-4.00 (m, 2H), 3.97-3.93 (m, 2H), 2.15-2.11 (m, 4H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 98.7,

73.1, 67.3, 32.8; HRMS (FTMS + p ESI) Calculated for $C_{18}H_{28}O_5NaSi$ ([M+H]$^+$): 173.0808, Found: 173.0809.



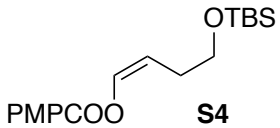
Chair–chair interconversion produces apparent C2-symmetry

General Procedure A: Ru-Catalyzed Addition of Carboxylic Acids to Alkynes. This modification of the procedure reported by Goossen provided selective access to (*Z*)-1,2-disubstituted enol esters.[3] A mixture of 1,2-dichloroethane (1,2-DCE) and 3Å molecular sieves was deoxygenated by sonication under vacuum for 30 s, then releasing the vacuum to argon (repeated six times). To a mixture of [(*p*-cymene)$RuCl_2$]$_2$ (0.05 equiv), $P(C_6H_4Cl)_3$ (0.15 equiv), and DMAP (0.20 equiv) was added deoxygenated 1,2-dichloroethane (0.0036 M with respect to [(*p*-cymene)$RuCl_2$]$_2$) and the mixture was stirred for 45 min at 75°C. While hot, this mixture was added via cannula into a suspension of *p*-anisic acid (1.0 equiv) and alkyne (1.4 equiv) in deoxygenated 1,2-DCE (0.167 M with respect to *p*-anisic acid) and the mixture was stirred at 75°C[4] for 12 h. The cooled reaction mixture was filtered through silica gel, eluting with CH_2Cl_2. Flash chromatography (50:1 hexanes/EtOAc) the (*Z*)-enol ester with traces of Ru byproducts, as judged by color (orange, red or black), that interfere with subsequent epoxidation reactions. The semipure product was dissolved in EtOAc at 70 °C and Ru scavenger Snatch-Cat[5] was added in 20-mg aliquots every 20 min until there was no color change. Then the sample was filtered through silica gel, eluting with EtOAc to afford the pure (*Z*)-enol ester.



cis-**S3**

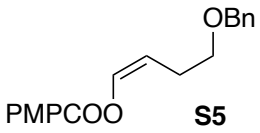
(*Z*)-Oct-1-en-1-yl 4-methoxybenzoate (*cis*-S3). From oct-1-yne (0.1094 g, 0.150 mL, 1.4 equiv) and *p*-anisic acid (0.1079 g, 0.709 mmol) via General Procedure A was obtained known compound *cis*-**S3**[6] (0.1459 g, 78%, *Z/E* >98:2) as a colorless oil.



S4

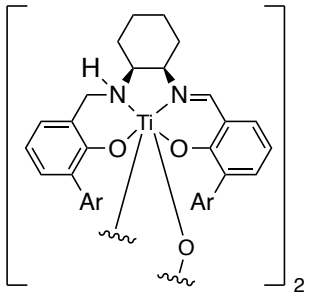
(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)but-1-en-1-yl 4-methoxybenzoate (S4). From (but-3-yn-1-yloxy)(*tert*-butyl)dimethylsilane[7] (1.808 g, 9.807 mmol, 1.4 equiv) and *p*-anisic acid (1.079 g, 7.09 mmol) via General Procedure A was obtained enol ester **S4** (1.779 g, 76%, *Z/E*>98:2) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, 2H, *J* = 9.2 Hz), 7.30 (d, 1H, *J* = 6.4 Hz), 6.95 (d, *J* = 9.2 Hz, 2H), 5.03 (dt, apparent q, *J* = 6.4 Hz, 1H), 3.88 (s, 3H), 3.70 (t, *J* = 6.8 Hz, 2H), 2.53-2.49 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 163.9,

163.3, 135.4, 132.1, 121.7, 113.9, 110.5, 62.5, 55.5, 28.7, 26.0, 18.4, -5.1; HRMS (FTMS + p ESI) Calculated for $C_{18}H_{28}O_4SiNa$ ([M+Na]$^+$): 359.1636, Found: 359.1642.

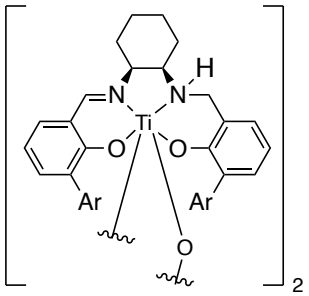


S5

(*Z*)-4-(Benzyloxy)but-1-en-1-yl 4-methoxybenzoate (S5). From ((but-3-yn-1-yloxy)methyl)benzene[8] (1.5000 g, 9.36 mmol, 1.4 equiv) and *p*-anisic acid (1.017 g, 6.68 mmol) via General Procedure A was obtained enol ester **S5** (1.3429 g, 64%, *Z/E* >98:2) as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.41-7.26 (m, 6H), 6.95 (d, *J* = 9.0 Hz, 2H), 5.07 (dt, appt. q, *J* = 7.0 Hz, 1H), 4.57 (s, 2H), 3.86 (s, 3H), 3.60 (t, *J* = 6.9 Hz, 2H), 2.69-2.63 (m, 2H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 163.8, 163.0, 138.3, 135.4, 132.0, 128.3, 127.6, 127.5, 121.4, 113.8, 110.1, 72.9, 69.3, 55.4, 25.5; HRMS (FTMS + p ESI) Calculated for $C_{19}H_{20}O_4Na$ ([M+Na]$^+$): 335.1254, Found: 335.1247.

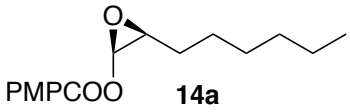


A



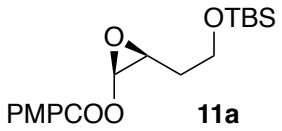
ent-**A**

General Procedure B: Berkessel–Katsuki Epoxidation. To screw cap vial equipped with micro stir bar was added enol ester (1.0 equiv), Berkessel epoxidation catalyst **A** or *ent*-**A** (0.002 eq), 1,2-dichloroethane (6 M with respect to enol ester), and aqueous H_2O_2 (30%, 2.5 equiv). This mixture was vigorously stirred for 48 hours at room temperature, then diluted with CH_2Cl_2 and tested for peroxides with a water-wetted test strip, if positive, then the reaction was quenched with saturated aqueous thiosulfate solution. The resultant biphasic mixture was extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated in vacuo. Flash column chromatography (10:1 hexanes/EtOAc) furnished the pure enol ester epoxide.



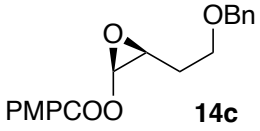
14a

(2*R*,3*S*)-3-Hexyloxiran-2-yl 4-methoxybenzoate (14a). From enol ester *cis*-**S3** (0.1118 g, 0.4261 mmol) and catalyst **A** (3.5 mg, 0.002 equiv) via General Procedure B, was obtained known compound **14a**[9] (74.9 mg, 63%, 97.8% ee) as a colorless waxy solid. Spectroscopic data matched the literature data. $[\alpha]_D^{23}$ +27.1 (*c* 5.39, $CHCl_3$); HPLC: Major isomer: 9.7 min, minor isomer: 9.4 min (Chiralcel OD-H, 0.5 mL per min, 0.3%-40% IPA in hexanes over 40 min, UV detection at 254 nm).



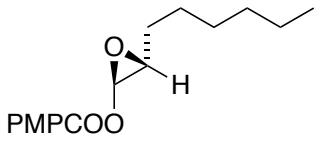
11a

(2*R*,3*S*)-3-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)oxiran-2-yl 4-methoxybenzoate (11a). From enol ester **S4** (0.3463 g, 1.03 mmol) and **A** (3 mg, 0.2 mol%) via General Procedure B was obtained **11a** (0.2552 g, 70%, 98.3% ee) as a pale yellow oil. $[\alpha]_D^{23}$ +18.8 (*c* 9.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.80 (d, *J* = 2.6 Hz, 1H), 3.87 (s, 3H), 3.87-3.84 (m, 2H), 3.28 (ddd, *J* = 7.3, 5.0, 2.6 Hz, 1H), 2.07-1.90 (m, 2H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR {^1H} (125 MHz, $CDCl_3$): δ 165.7, 164.0, 131.9, 121.4, 113.8, 76.2, 60.0, 55.4, 54.0, 30.6, 25.9, 18.3, –5.3 (2C); HRMS (FTMS + p ESI) Calculated for $C_{16}H_{28}O_5SiNa$ ([M+Na]$^+$): 375.1598, Found: 375.1592. HPLC: Major isomer: 8.3 min, minor isomer: 7.6 min (Chiralcel OD-H, 0.5 mL per min, 0.3%-40% IPA in hexanes over 40 min, UV detection at 254 nm).



14c

(2*R*,3*S*)-3-(2-(Benzyloxy)ethyl)oxiran-2-yl 4-methoxybenzoate (14c). From enol ester **S5** (0.750 g, 2.40 mmol) and catalyst **A** (6.5 mg, 0.2 mol%) via General Procedure B was obtained **3.26e** (0.5070 g, 68%, 98.2% ee) as a pale yellow semisolid. $[\alpha]_D^{21}$ +24.3 (*c* 12.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 9.0 Hz, 2H), 7.37-7.26 (m, 5H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.82 (d, *J* = 2.6 Hz, 1H), 4.57 (s, 2H), 3.84 (s, 3H), 3.75-3.71 (m, 2H), 3.30 (ddd, *J* = 7.2 Hz, 5.0, 2.6 Hz, 1H), 2.20-2.03 (m, 2H); ^{13}C NMR {^1H} (125 MHz, $CDCl_3$): δ 165.6, 163.9, 138.1, 131.9, 128.3, 127.6, 127.5, 121.2, 113.7, 75.9, 73.0, 66.9, 55.4, 54.3, 27.9; HRMS (FTMS + p ESI) Calculated for $C_{19}H_{20}O_5$ ([M+Na]$^+$): 351.1203, Found: 351.1200. HPLC: Major isomer: 31.9 min, minor isomer: 30.8 min (Chiralcel OD-H, 0.5 mL per min, 0.3%-40% IPA in hexanes over 40 min, hold at 40% to 60 min, UV detection at 254 nm).

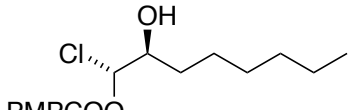


trans-**14a** (racemic)

(2*S*,3*S*)-3-Hexyloxiran-2-yl 4-methoxybenzoate and (2*R*,3*R*)-3-hexyloxiran-2-yl 4-methoxybenzoate (*trans*-14a, racemic). Using General Procedure A, except substituting Na_2CO_3 in place of DMAP to promote Markovnikov addition of *p*-anisic acid to 1-octyne,[10] a mixture of *cis*- and *trans*-enol esters was obtained as the minor components along with the major 1,1-disubstituted product. These were separated by treatment with a catalytic amount of triflic acid in dichloromethane,[11] followed by flash chromatography (10:1 hexanes/EtOAc). To a solution of the *cis*- and *trans*-enol esters (0.151 g, 0.51 mmol, 46:54 *Z/E*) in acetone (6.5 mL) was added a solution of $NaHCO_3$ (2.86 g) and oxone (3.56 g) in water (4.3 mL). After 3 h, the reaction mixture was partitioned between water and ethyl acetate. The organic phase was dried over Na_2SO_4 and concentrated to afford a mixture of cis and trans epoxides. Flash chromatography (100:1 hexanes/EtOAc) afforded *trans*-**14a** as a colorless oil (27.6 mg, 17%)

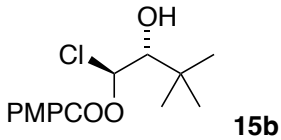
followed by known *cis*-**14a** (33.7 mg, 21%). Data for *trans*-**14a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.54 (d, *J* = 0.6 Hz, 1H), 3.86 (s, 3H), 3.24 (t, *J* = 5.7 Hz, 1H), 1.71-1.22 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 166.1, 164.1, 132.1, 121.5, 113.9, 77.3, 57.9, 55.61, 31.8, 29.8, 29.1, 25.0, 22.7, 14.2; HRMS (FTMS + p ESI) Calculated for $C_{16}H_{23}O_4$ ([M+H]$^+$): 279.1591, Found: 279.1588.

General Procedure C: Ring-Opening of Enol Ester Epoxides to 1-Haloalkyl Esters. To a solution of enol ester epoxide in THF (0.1 M) was added oven-dried LiX (X = Cl or Br, 3 equiv) followed by *p*-toluenesulfonic acid monohydrate (1.1 equiv) at room temperature. After 5 min, or when the reactant was consumed (TLC), the mixture was partitioned between saturated aqueous sodium bicarbonate and CH_2Cl_2, and the organic phase was washed with brine, dried (Na_2SO_4) and concentrated. Flash chromatography (hexanes/EtOAc) afforded the 1-haloalkyl ester.



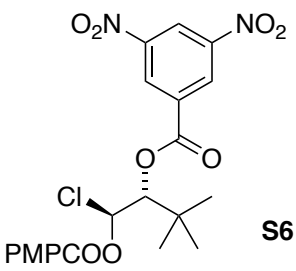
15a

(1*R*,2*S*)-1-Chloro-2-hydroxyoctyl 4-methoxybenzoate (15a). From enol ester epoxide **14a** (25.1 mg, 0.089 mmol), LiCl (21 mg, 0.116 mmol, 3 equiv), and *p*-toluenesulfonic acid monohydrate (18.7 mg, 0.098 mmol, 1.1 equiv) via General Procedure C was obtained **15a** (25.5 mg, 89%, dr >95:5) as a colorless oil. $[\alpha]_D^{23}$ –63.3 (*c* 1.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.58 (d, *J* = 4.5 Hz, 1H), 3.98-3.95 (m, 1H), 3.87 (s, 3H), 2.16 (broad d, *J* = 5.4 Hz, 1H), 1.76-1.23 (m, 10H), 0.88 (broad t, *J* = 6.7 Hz, 3H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 164.4, 163.8, 132.4, 120.9, 114.0, 87.3, 74.0, 55.6, 32.3, 31.8, 29.2, 25.4, 22.7, 14.1; HRMS (FTMS + p ESI) Calculated for $C_{16}H_{24}ClO_4$ ([M+H]$^+$): 315.1358, Found: 315.1354. Configuration of **15a** was assigned via analogy with **15b**.

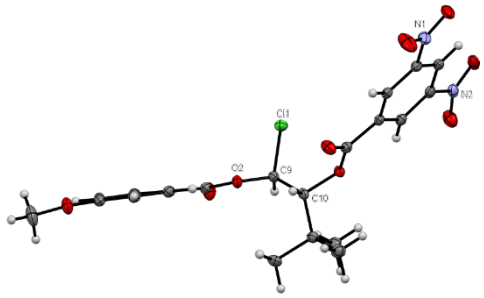


15b

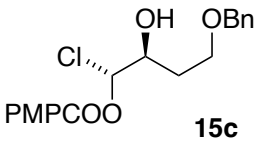
(1*S*,2*R*)-1-Chloro-2-hydroxy-3,3-dimethylbutyl 4-methoxybenzoate (15b). From enol ester epoxide *ent*-**14b**[12] (0.100 g, 0.400 mmol), LiCl (41 mg, 1.04 mmol, 2.6 equiv), and *p*-toluenesulfonic acid monohydrate (0.105 g, 0.098 mmol, 1.4 equiv) via General Procedure C, was obtained **15b** (90.5 mg, 79%, dr >95:5) as a colorless oil. $[\alpha]_D^{21}$ +57.2 (*c* 1.61, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 5.6 Hz, 1H), 3.87 (s, 3H), 3.69 (t, *J* = 5.4 Hz, 1H), 2.37 (d, *J* = 5.2 Hz, 1H), 1.03 (s, 9H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 164.4, 163.4, 132.5, 120.9, 114.1, 87.2, 79.9, 55.6, 34.9, 26.6; HRMS (FTMS + p ESI) Calculated for $C_{14}H_{20}ClO_4$ ([M+H]$^+$): 287.1045, Found: 287.1044. Configurations of **15b** were assigned via x-ray crystallography of the 3,5-dintrobenzoate derivative **S6** prepared as described below.



S6

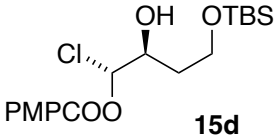


(1*R*,2*R*)-1-Chloro-1-((4-methoxybenzoyl)oxy)-3,3-dimethylbutan-2-yl 3,5-dinitrobenzoate (S6). To a solution of α-chloroalkyl ester *ent*-**14b** (90.5 mg, 0.315 mmol) in DCM (1 mL) was added *N*,*N*-dimethylaminopyridine (57 mg, 0.47 mmol, 1.5 equiv) and 3,5-dinitrobenzoyl chloride (0.109 g, 0.47 mmol, 1.5 equiv). After 1 h at room temperature, the mixture was partitioned between saturated aqueous NH_4Cl and CH_2Cl_2. The organic phase was dried (Na_2SO_4) and concentrated. Flash chromatography (10:1 hexanes/EtOAc) gave 3,5-dinitrobenzoate **S6** (0.118 g, 77%). Recrystallization from petroleum ether and ethyl acetate via slow evaporation in a screw-capped vial gave colorless flat plates suitable for x-ray crystallography. $[\alpha]_D^{24}$ –6.7 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (t, *J* = 2.1 Hz, 1H), 9.24 (d, *J* = 2.1 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 5.3 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 5.52 (d, *J* = 5.3 Hz, 1H), 3.87 (s, 3H), 1.15 (s, 9H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 164.6, 163.2, 162.0, 149.0, 133.6, 132.5, 129.79, 122.9, 120.4, 114.2, 83.0, 81.8, 55.7, 35.1, 26.8; HRMS (FTMS + p ESI) Calculated for $C_{21}H_{21}O_9N_2ClNa$ ([M+Na]$^+$): 503.0828, Found: 503.0832.



15c

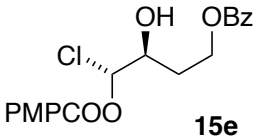
(1*R*,2*S*)-4-(Benzyloxy)-1-chloro-2-hydroxybutyl 4-methoxybenzoate (**15c**). From enol ester epoxide **14c** (21.8 mg, 0.061 mmol), LiCl (7 mg, 0.18 mmol, 3 equiv), and *p*-toluenesulfonic acid monohydrate (12.7 mg, 0.067 mmol, 1.1 equiv) via General Procedure C was obtained **15c** (17.4 mg, 72%, dr >95:5) as a colorless oil. $[\alpha]_D^{23}$ –39.1 (*c* 0.81, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 9.0 Hz, 2H), 7.37-7.28 (m, 5H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 4.3 Hz, 1H), 4.55 (s, 2H), 4.24-4.21 (m, 1H), 3.87 (s, 3H), 3.82-3.78 (m, 1H), 3.74-3.69 (m, 1H), 3.14 (d, *J* = 3.8 Hz, 1H), 2.14-2.07 (m, 1H), 2.02-1.93 (m, 1H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$): δ 164.3, 163.8, 137.9, 132.4, 128.6, 128.0, 127.9, 121.0, 114.0, 86.3, 73.5, 73.1, 67.8, 55.7, 31.6; HRMS (FTMS + p ESI) Calculated for $C_{19}H_{21}O_5ClNa$ ([M+Na]$^+$): 387.0970, Found: 387.0965.



15d

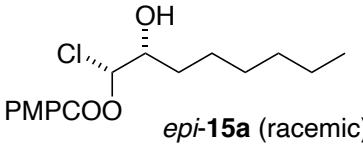
(1*R*,2*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-1-chloro-2-hydroxybutyl 4-methoxybenzoate (15d). From enol ester epoxide **11a** (0.1586 g, 0.449 mmol), LiCl (43.6 mg, 0.585 mmol, 2.3 equiv), and *p*-toluenesulfonic acid monohydrate (89 mg, 0.472 mmol, 1.05 equiv) via General Procedure C was obtained **15d** (0.10 g, 57%, dr >95:5) as a colorless oil that gradually

decomposed on storage. $[\alpha]_D^{21}$ –34.9 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 4.3 Hz, 1H), 4.26-4.22 (m, 1H), 4.01-3.96 (m, 1H), 3.92-3.90 (m, 1H), 3.88 (s, 3H), 3.61 (br s,1H), 2.06-1.99 (m, 1H), 1.96-1.85 (m, 1H), 0.92 (s, 9H), 0.11 (s, 6H); ^{13}C NMR {^1H} (100 MHz, $CDCl_3$): δ 164.3, 163.9, 132.4, 121.1, 114.0, 86.1, 73.6, 61.3, 55.6, 33.6, 25.9, 18.3, –5.41, –5.42. HRMS (FTMS + p ESI) Calculated for $C_{18}H_{30}O_5ClSi$ ($[M+H]^+$): 389.1546, Found: 389.1540.



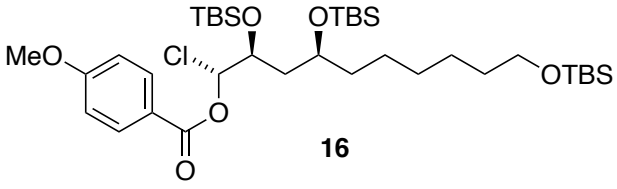
15e

(1*R*,2*S*)-4-(Benzoyloxy)-1-chloro-2-hydroxybutyl 4-methoxybenzoate (15e). From enol ester epoxide **11b**[12] (18.2 mg, 0.058 mmol), LiCl (7.4 mg, 0.175 mmol, 3 equiv), and *p*-toluenesulfonic acid monohydrate (12.2 mg, 0.0642 mmol, 1.1 equiv) via General Procedure C, was obtained **15e** (15.4 mg, 77%, dr >95:5) as a colorless oil. $[\alpha]_D^{22}$ –43.1 (*c* 0.47, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06-7.99 (m, 4H), 7.60-7.54 (m, 1H), 7.47-7.42 (m, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 4.5 Hz, 1H), 4.63-4.53 (m, 2H), 4.24-4.19 (m, 1H), 3.87 (s, 3H), 2.56 (br s,1H), 2.31-2.24 (m, 1H), 2.11-2.01 (m, 1H); ^{13}C NMR {^1H} (100 MHz, $CDCl_3$): δ 166.8, 164.5, 163.7, 133.3, 132.5, 130.1, 129.8, 128.6, 120.8, 114.1, 86.6, 71.2, 61.4, 55.7, 31.6, 22.8; HRMS (FTMS + p ESI) Calculated for $C_{19}H_{20}O_6Cl$ ($[M+H]^+$): 379.0943, Found: 379.0933.



epi-**15a** (racemic)

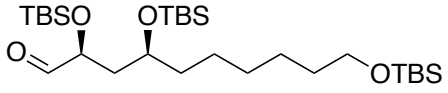
(1*R*,2*R*)-1-Chloro-2-hydroxyoctyl 4-methoxybenzoate and **(1*S*,2*S*)-1-chloro-2-hydroxyoctyl 4-methoxybenzoate** (***epi*-15a**, **racemic).** From enol ester epoxide *trans*-**14a** (20.4 mg, 0.073 mmol), LiCl (16.3 mg, 0.219 mmol, 3 equiv), and *p*-toluenesulfonic acid monohydrate (15 mg, 0.080 mmol, 1.1 equiv) via General Procedure C was obtained *epi*-**15a** (23.8 mg, quantitative, dr >95:5) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 4.1 Hz, 1H), 3.98-3.88 (m, 1H), 3.86 (s, 3H), 1.77-1.71 (m, 1H), 1.68-1.61 (m, 1H), 1.43-1.19 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR {^1H} (100 MHz, $CDCl_3$): δ 164.4, 163.9, 132.4, 120.9, 114.1, 86.3, 74.14, 55.68, 32.1, 31.8, 29.3, 25.4, 22.7, 14.2; HRMS (FTMS + p ESI) Calculated for $C_{16}H_{24}O_4Cl$ ($[M+H]^+$): 315.1358, Found: 315.1357.



16

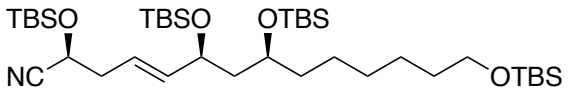
(1*R*,2*S*,4*S*)-2,4,10-tris((*tert*-butyldimethylsilyl)oxy)-1-chlorodecyl 4-methoxybenzoate (16). A solution of enol ester **10** (0.500 g, 0.882 mmol) was azeotropically dried by concentration in vacuo from a solution in benzene (1 mL). To the residue was added tetrabutylammonium chloride (0.98 g, 3.53 mmol, 4.0 equiv) and CH_2Cl_2 (8.8 mL), followed by (*R*)-camphorsulfonic acid (0.22 g, 0.95 mmol, 1.1 equiv). After 20 minutes, the mixture was poured into saturated aqueous $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The organic phase was

washed with aqueous 0.1 M HCl, dried oer Na_2SO_4, and concentrated. Filtration through a 2 cm plug of silica gel, eluting with 1:1 hexanes/EtOAc and concentration gave a pale yellow viscous oil. This was taken up in CH_2Cl_2 (8.8 mL), and then 2,6-lutidine (0.46 mL, 3.97 mmol, 4.5 equiv) and TBSOTf (0.61 mL, 2.65 mmol, 3.0 equiv) were added sequentially. After stirring 3 h, the mixture was partitioned between aqueous 0.1 M HCl and CH_2Cl_2 (3 x 15 mL) and the organic phase was dried over Na_2SO_4 and concentrated. Flash column chromatography (20:1 to 10:1 hexanes/EtOAc) afforded *O*-TBS-chlorohydrin **16** (0.535 g, 85%) as a colorless viscous oil. Relative configuration was assigned by analogy with **15b**. $[\alpha]_D^{23}$ –30.0 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–8.01 (d, *J* = 9.0 Hz, 2H), 6.94–6.93 (d, *J* = 9.0 Hz, 2H), 6.64–6.63 (d, *J* = 2.6 Hz, 1H),4.11–4.08 (m, 1H), 3.90–3.87 (m, 1H), 3.88 (s, 3H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.07–2.02 (m, 1H), 1.93–1.88 (m, 1H), 1.53–1.26 (m, 10H), 0.90 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.04 (s, 6H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 164.3, 164.2, 132.4, 121.5, 114.0, 85.4, 72.2, 69.3, 63.4, 55.7, 40.0, 36.9, 33.0, 29.8, 26.2, 26.1, 26.0, 25.9, 25.3, 18.6, 18.3, 18.1, –4.2 (2C), –4.26, –4.28, –5.1 (2C); HRMS (FTMS + pESI): *m/z* calc'd for $C_{36}H_{70}ClO_6Si_3$ [M+H]+: 717.4163; found 717.4163.



5

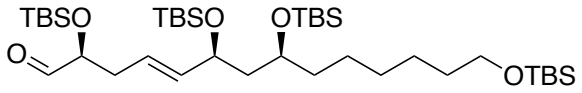
(2*S*,4*S*)-2,4,10-tris((*tert*-butyldimethylsilyl)oxy)decanal (5). To a solution of the *O*-silylchlorohydrin **16** (351 mg, 0.489 mmol) in benzene (10 mL) was added tetrabutylammonium bisulfate (165 mg, 0.48 mmol, 1 equiv) and potassium carbonate (407 mg, 2.9 mmol, 6 equiv). Ethylene glycol (2 mL) was added and the reaction was heated in a 75–80 °C oilbath under a coldfinger condenser with vigorous stirring. After 6.5 h, the mixture was partitioned between water (30 mL) and Et_2O (2 x 30 mL). The organic phase was washed with aqueous 0.1 M HCl (30 mL) and brine (30 mL) dried over Na_2SO_4, and concentrated. Flash chromatography (10% Et_2O in hexanes) afforded α-silyloxyaldehyde **5** (133 mg) as a colorless oil, and mixed fractions (120 mg) containing unreacted **16** (54 mg, 0.075 mmol) and **5** (66 mg). The total yield of **5** was 199 mg (74%, or 88% based on conversion of **16**). Longer reaction times resulted in partial decomposition of **5**. Pale yellow oil; $[\alpha]_D^{23}$ +2.5 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.60 (d, *J* = 1.4 Hz, 1H), 4.10–4.07 (td, *J* = 5.7, 1.4 Hz, 1H), 3.93–3.88 (apparent quint., 1H), 3.60 (apparent t, *J* = 6.6 Hz, 2H), 1.82–1.80 (apparent t, *J* = 6.1 Hz, 2H), 1.53–1.44 (m, 4H), 1.33–1.26 (m, 6H), 0.92 (s, 9H), 0.89 (s, 9H), 0.87 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 (m, 12H), ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 203.9, 75.2, 68.2, 63.4, 40.6, 37.2, 33.0, 29.8, 26.2, 26.1, 26.0, 25.9, 25.2, 18.6, 18.3, 18.2, –4.2 (2C), –4.26, –4.28, –5.1 (2C); HRMS (FTMS + pESI): *m/z* calc'd for $C_{28}H_{63}O_4Si_3$ [M+H]$^+$: 547.4029; found 547.4027.



17

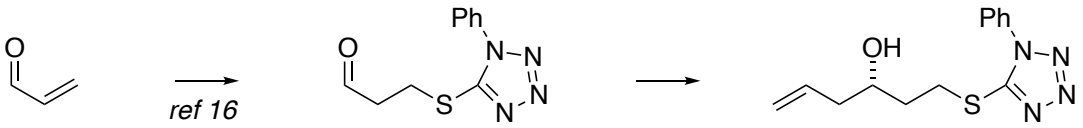
(2*S*,6*S*,8*S*,*E*)-2,6,8,14-tetrakis((*tert*-butyldimethylsilyl)oxy)tetradec-4-enenitrile (16). To a solution of (*S*)-**3** (0.701 g, 1.72 mmol, 3.0 equiv) in THF (10 mL) at –78 °C was added KHMDS (0.5 M in toluene, 3.2 mL, 1.6 mmol, 2.8 equiv) dropwise via syringe. After 30 min, a solution of **5** (314.2 mg, 0.5743 mmol) in THF (2 mL) was added via cannula, with additional THF (2 x 0.5

mL) to rinse the source flask. The reaction was stirred at –78 °C for 3 h, warmed to 0 °C over 2 h, then quenched by addition of brine (1 mL). The reaction was partitioned between brine (40 mL) and EtOAc (3 x 40 mL). The organic phase was dried over Na_2SO_4 and concentrated. Gradient flash chromatography (20:1 to 1:1 hexanes/EtOAc) afforded TBS-cyanohydrin **17** (417 mg, 99.7%) as a colorless oil; $[\alpha]_D^{24}$ –10.0 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.37–5.55 (m, 2H), 4.43 (t, *J* = 6.2 Hz, 1H), 4.22–4.19 (m, 1H), 3.76–3.72 (m, 1H), 3.60 (apparent t, *J* = 6.6 Hz, 2H), 2.54–2.45 (m, 2H), 1.74–1.69 (m, 2H), 1.55–1.46 (m, 4H), 1.40–1.25 (m, 6H), 0.91 (s, 9H), 0.89 (18H), 0.88 (s, 9H), 0.18 (s, 3H), 0.14 (s, 3H), 0.05 (s, 6H), 0.04 (s, 6H), 0.03 (s, 6H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 139.3, 121.9, 119.4, 70.4, 69.3, 63.3, 62.0, 46.0, 39.2, 37.1, 32.8, 29.7, 26.0, 25.91, 25.89, 25.8, 25.5, 25.0, 18.3, 18.1, 18.0 (2C), -4.1, -4.2, -4.3, -4.8, -5.2, -5.27 (2C), -5.33; HRMS (FTMS + pESI) *m/z* calc'd for $C_{38}H_{82}NO_4Si_4$ $[M+H]^+$: 728.5338; found 728.5324.



S7

(2*R*,4*E*,6*S*,8*E*,10*S*,12*S*)-2,6,10,12,18-pentakis((*tert*-butyldimethylsilyl)oxy)octadeca-4,8-dienal (S7). To a solution of nitrile **17** (117.7 mg, 0.1616 mmol) in toluene (0.24 mL) at –40 °C (acetonitrile/dry ice bath) was added DIBAL-H (1.0 M in toluene, 0.24 mL) dropwise via syringe. After stirring for 3.5 h at –40 °C, the reaction was quenched while cold by addition of MeOH (0.24 mL) dropwise. To this solution was added Et_2O (3.3 mL) and saturated aqueous K_2HPO_4 (1.1 mL). After stirring vigorously for 1 h, there were two clearly separated phases. The organic phase was withdrawn by pipet. Additional portions of Et_2O (2 x 3 mL) were added, stirred vigorously, and withdrawn by pipet. The organic phase was filtered through Na_2SO_4. To this solution was added activated[13] Dowex 50wx acidic ion exchange resin (0.16 g) and water (1 mL). The mixture was stirred for 1 d, then the organic phase was withdrawn by pipet. Additional portions of Et_2O (2 x 3 mL) were added, stirred vigorously, and withdrawn by pipet. The organic phase was dried over Na_2SO_4 and concentrated, furnished **S7** (87.1 mg, 58% w/w as a mixture with unreacted **17**, 62% based on conversion).[14] Chromatographic enrichment of the ratio **S7**/**17** was accompanied by material losses; mixtures were carried forward without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.59 (d, *J* = 1.6 Hz, 1H), 5.61-5.45 (m, 2H), 4.18-4.10 (m, apparent q, *J* = 5.6 Hz, 1H), 4.01 (td, *J* = 5.8, 1.6 Hz, 1H), 3.77-3.67 (m, apparent quintet, *J* = 5.8 Hz, 1H), 3.59 (m, apparent t, *J* = 6.6 Hz, 2H), 2.43-2.37 (m, 2H), 1.74-1.64 (m, 1H), 1.56-1.42 (m, 4H), 1.42-1.21 (m, 7H), 0.92 (s, 9H), 0.89 (s, 9H), 0.879 (s, 9H), 0.876 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.04 (s, 6H), 0.03 (s, 6H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$): δ 203.8, 137.4, 123.7, 77.3, 70.6, 69.3, 63.3, 46.1, 37.1, 36.1, 32.9, 29.7, 26.0, 25.93, 25.89, 25.8, 25.5, 25.0, 18.4, 18.2, 18.14, 18.07, –4.1, –4.2, –4.4, –4.7, –4.79, –4.80, –5.24 (2C); HRMS (FTMS + pESI) *m/z* calc'd for $C_{38}H_{82}O_5Si_4Na$ $[M+Na]^+$: 753.5125; found 753.5132.

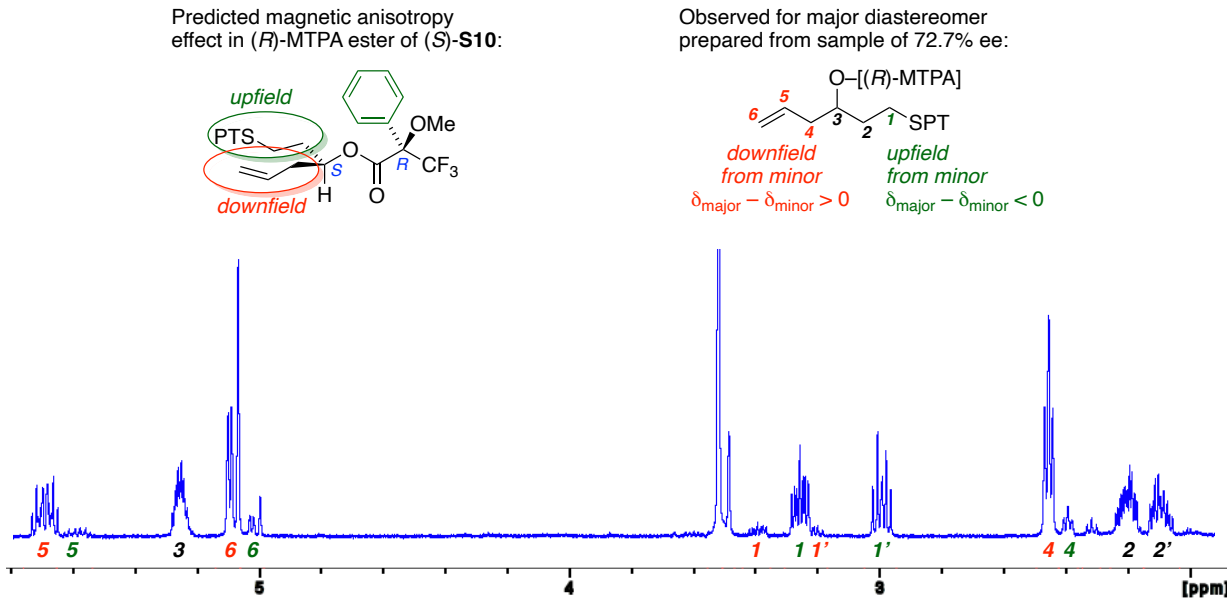


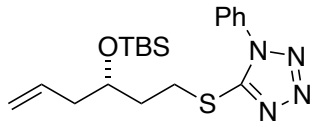
S8 **S9** **S10**

5-((3-Hydroxyhex-5-en-1-yl)sulfanyl)-1-phenyl-1H-tetrazole (S10). Compound **S9** was prepared from acrolein (**S8**) according to the previously reported procedure.[16] Using a

modification of Keck's procedure,[15] to a mixture of (*S*)-BINOL (32 mg, 0.11 mmol) and 4A molecular sieves (powdered, 0.35 g) in CH_2Cl_2 (4 mL) at ambient temperature was added titanium isopropoxide (0.027 mL, 0.10 mmol). The reddish-brown mixture was heated with an oilbath at 35–38 °C with stirring for 1.5 h. After cooling to ambient temperature, a solution of aldehyde **S9**[16] (237 mg, 1.01 mmol) in CH_2Cl_2 (1 mL + 0.2 mL rinse) was added via cannula. The mixture was cooled to –78 °C and allyltributylstannane (0.47 mL, 1.5 mmol) was added. After stirring for 1 h at –78 °C the reaction flask was placed in a –20 °C freezer with occasional manual swirling. After 2 d, the cold reaction mixture was rapidly filtered into a stirred mixture of CH_2Cl_2 (5 mL) and saturated aq. $NaHCO_3$ (5 mL), rinsing the flask and filter cake with CH_2Cl_2 (2 x 5 mL). After stirring the filtrate for 30 min, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). Combined organic phases were dried (Na_2SO_4) and concentrated. The residual oil was further partitioned between hexanes (10 mL) and acetonitrile (3 x 10 mL); the acetonitrile phase was concentrated to an orange oil. Gradient flash chromatography (3:1 hexanes/ethyl acetate to ethyl acetate) furnished a colorless oil with trace amounts of tin impurities, which were removed by a second pass of gradient flash chromatography to give **S10** (221.8 mg, 79%) as a colorless oil. $[\alpha]_D^{24}$ +12.3 (c 0.84, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.62-7.50 (m, 5H), 5.90-5.75 (m, 1 H), 5.17-5.13 (m, 1H), 5.12-5.09 (m, 1H), 3.86-3.77 (m, 1H), 3.63-3.45 (m, 2H), 2.84-2.76 (br s, 1H), 2.37-2.19 (m, 2H), 2.10-1.86 (m, 2H); ^{13}C NMR {^1H} (75 MHz, $CDCl_3$): δ 154.8, 134.3, 133.6, 130.2, 129.8, 123.8, 118.3, 68.4, 41.8, 36.6, 29.9; HRMS (FTMS + p ESI) Calculated for $C_{13}H_{17}N_4OS$ ($[M+H]^+$): 277.1115, Found: 277.1118. HPLC: Major isomer: 34.1 min; minor isomer: 35.6 min, 95.4% ee (Whelk O1, 0.5 mL/min 20% IPA in hexanes, UV detection at 254 nm). A sample of **S10** produced by Brown allylation[17] using (–)-chlorodiisopinocampheylborane and allylmagnesium bromide also gave the (+)-enantiomer (72.7% ee) as the major product, $[\alpha]_D^{20}$ +10.2 (c 0.635, $CHCl_3$); the (*R*)-Mosher ester from this sample ((*S*)-MTPA-Cl, pyridine) showed major and minor diastereomer peaks that correlated the major (+)-**S10** enantiomer with (*S*)-configuration.

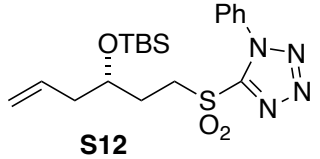
Figure S1. Assignment of configuration of **S10** via the Mosher ester.





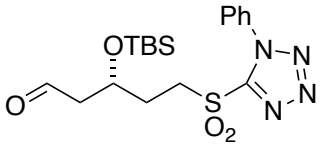
S11

5-((3-*tert*-Butyldimethylsilyloxyhex-5-en-1-yl)sulfanyl)-1-phenyl-1H-tetrazole (S11). To a solution of homoallylic alcohol **S10** (95.4% ee, 222 mg, 0.803 mmol) in CH_2Cl_2 (4 mL) at 20 °C was added 2,6-lutidine (0.19 mL, 1.6 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 0.28 mL, 1.2 mmol). After 2 h, the reaction mixture was partitioned between 0.1 M aq. HCl (30 mL) and Et_2O (3 x 10 mL. The organic phase was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Flash chromatography (20:1 to 10:1 hexanes/ethyl acetate) afforded **S11** (291.6 mg, 93%) as a colorless oil. $[\alpha]_D^{24}$ +21.7 (c 1.96, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61-7.51 (m, 5H), 5.85-5.70 (m, 1H), 5.10-5.05 (m, 1 H), 5.04-5.02 (m, 1H), 3.92-3.83 (m, 1H), 3.52-3.34 (m, 2H), 2.30-2.24 (m, 2H), 2.06-1.85 (m, 2H), 0.88 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$): δ 154.4, 134.1, 133.7, 130.0, 129.7, 123.8, 117.6, 70.4, 41.7, 35.8, 29.6, 25.8, 18.0, –4.3, –4.6; HRMS (FTMS + p ESI) Calculated for $C_{19}H_{31}N_4OSSi$ ($[M+H]^+$): 391.1982, Found: 391.1983.



S12

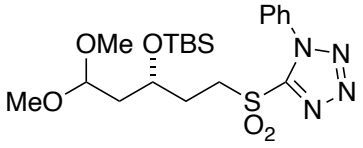
5-((3-*tert*-Butyldimethylsilyloxyhex-5-en-1-yl)sulfonyl)-1-phenyl-1H-tetrazole (S12). To a solution of sulfide **S11** (racemic, 457 mg, 1.17 mmol) in 95% ethanol at 20 °C were added ammonium molybdate tetrahydrate (29 mg, 0.023 mmol) and 30% aq. hydrogen peroxide (1.2 mL, 12 mmol). After 1 d, additional aliquots of 30% aq. hydrogen peroxide (1.2 mL, 12 mmol) and ammonium molybdate tetrahydrate (10 mg, 0.01 mmol) were added. After a total of 2 d, the reaction mixture was concentrated to remove most of the ethanol, then partitioned between water (60 mL) and diethyl ether (3 x 20 mL). The organic phase was washed with brine (30 mL) and dried over Na_2SO_4. Concentration and flash chromatography furnished racemic **S12** (471 mg, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74-7.66 (m, 2H), 7.65-7.55 (m, 3H), 5.83-5.69 (m, 1H), 5.14-5.04 (m, 2H), 3.94 (m, apparent quintet, J = 6.2 Hz, 1H), 3.91-3.71 (m, 2H), 2.36-2.19 (m, 2H), 2.19-1.97 (m, 2H), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR {^{1}H} (75 MHz, $CDCl_3$): δ 153.4, 133.5, 133.0, 131.4, 129.7, 125.0, 118.2, 69.5, 52.5, 41.5, 28.5, 25.8, 18.0, –4.3, –4.7; HRMS (FTMS + p ESI) Calculated for $C_{19}H_{31}N_4O_3SSi$ ($[M+H]^+$): 422.1881, Found: 422.1880. Using the same procedure, a sample of enantiomerically enriched sulfide **S11** (95.4% ee) was oxidized to afford the corresponding sulfone **S12**, $[\alpha]_D^{24}$ +14.5 (c 2.07, $CHCl_3$).



S13

5-((3-*tert*-Butyldimethylsilyloxy-5-oxo-1-hexyl)sulfonyl)-1-phenyl-1H-tetrazole (S13). To a solution of alkene **S12** (95.4% ee, 253 mg, 0.599 mmol) in 1,4-dioxane (6 mL) and water (2 mL)

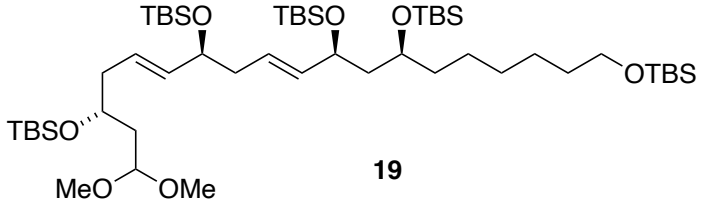
at 20 °C was added 2,6-lutidine (0.14 mL, 1.2 mmol), potassium osmate (11 mg, 0.030 mmol), and sodium periodate (0.645 g, 3.0 mmol). The mixture was stirred overnight, leading to a thick colorless solid/liquid suspension which was partitioned between water (50 mL) and ethyl acetate (3 x 20 mL). The organic phase was washed with 0.1 M aq. HCl (30 mL) and brine (30 mL), then dried over Na_2SO_4. Concentration afforded the crude aldehyde as a yellow oil which could be carried forward without purification. An analytical sample was obtained by gradient flash chromatography (5:1 hexanes/ethyl acetate to 100% ethyl acetate), affording the aldehyde **S13** (214.4 mg, 84%) as a colorless oil. $[\alpha]_D^{24}$ +0.24 (c 10.72, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 9.78 (m, apparent q, *J* = 1.7 Hz, 1 H), 7.71-7.55 (m, 5H), 4.46 (m, apparent quintet, *J* = 5.5 Hz, 1H), 3.92-3.72 (m, 2H), 2.73-2.57 (m, 2H), 2.32-2.06 (m, 2H), 0.88 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H); ^{13}C NMR {^1H} (75 MHz, $CDCl_3$): δ 199.9, 153.3, 133.0, 131.5, 129.7, 125.0, 77.4, 77.0, 76.6, 65.3, 52.1, 50.4, 29.6, 25.7, 17.9, –4.68, –4.73; HRMS (FTMS + p ESI) Calculated for $C_{18}H_{28}N_4O_4SSiNa$ ([M+Na]$^+$): 447.1493, Found: 447.1494.



18

5-((3-*tert*-Butyldimethylsilyloxy-5,5-dimethoxy-1-hexyl)sulfonyl)-1-phenyl-1H-tetrazole (18). To a solution of the aldehyde **S13** (95.4% ee, 214.4 mg, 0.5049 mmol) in trimethyl orthoformate (4 mL) at 20 °C was added toluenesulfonic acid monohydrate (12 mg, 0.06 mmol). TLC showed the reaction was complete within 1 min. After 5 min, the reaction was partitioned between saturated aq. $NaHCO_3$ (20 mL) and ethyl acetate (3 x 20 mL). The organic phase was dried (Na_2SO_4) and concentrated. Filtration through silica gel (2 cm in a pasteur pipet, eluting with 20:1 hexanes/ethyl acetate) afforded acetal **18** (227.9 mg, 96%) as a colorless oil. $[\alpha]_D^{24}$ –6.0 (c 1.87, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.71-7.55 (m, 5 H), 4.47 (dd, *J* = 6.2, 4.9 Hz, 1H), 4.06 (m, apparent quintet, *J* = 5.7 Hz, 1H), 3.90-3.71 (m, 2H), 3.31 (s, 3H), 3.30 (s, 3H), 2.26-2.00 (m, 2H), 1.86-1.69 (m, 2H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR {^1H} (75 MHz, $CDCl_3$): δ 153.4, 133.0, 131.4, 129.7, 125.0, 101.6, 66.5, 53.2, 52.6, 51.2, 39.5, 29.2, 25.7, 17.9, –4.6, –4.8; HRMS (FTMS + p ESI) Calculated for $C_{20}H_{34}N_4O_5SSiNa$ ([M+Na]$^+$): 493.1911, Found: 493.1912.

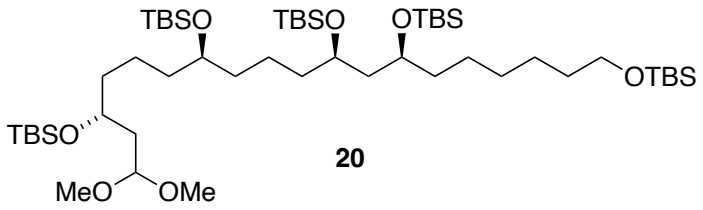
Telescoping the same procedures outlined above, oxidative cleavage of alkene **S12** (0.732 g, 1.73 mmol) afforded crude aldehyde **S13**, which was used without purification. Following conversion to the dimethyl acetal, flash chromatography (5:1 to 1:1 hexanes/EtOAc) afforded **18** (0.7018 g, 86% over 2 steps) as a colorless oil.



19

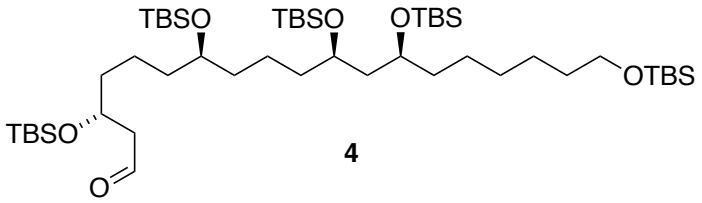
Diene 19. To a solution of the sulfone **18** (117 mg, 0.249 mmol) in tetrahydrofuran (1.5 mL) at –78 °C was added potassium bis(trimethylsilyl)amide (KHMDS, 0.5 M in toluene, 0.46 mL, 0.23

mmol). A yellow color developed immediately. After 30 min, a solution of aldehyde **S7** (87.1 mg, 58% w/w purity, 0.0691 mmol) in tetrahydrofuran (0.3 mL plus 2 x 0.2 mL rinses) was added via cannula to the reaction mixture at –78 °C. After stirring at –78 °C for 5 h, the reaction was allowed to warm to ambient temperature over 18 h, then partitioned between brine (20 mL) and ethyl acetate (3 x 10 mL). The organic phase was dried (Na_2SO_4) and concentrated. Gradient flash chromatography (5% to 10% Et_2O in hexanes) afforded diene **19** (84.2 mg, E,*E*/*Z*,*E* 80:20, 51% w/w purity, 64%) as a mixture with small amounts of nitrile **17** (44% w/w) and aldehyde **S7** (5% w/w). A sample of pure (*E,E*)-**19** for characterization was obtained by radial chromatography (5% to 10% Et_2O in hexanes). Colorless oil; $[\alpha]_D^{23}$ –12.9 (c 1.08, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 5.60-5.38 (m, 4H), 4.51 (dd, *J* = 7.6, 3.9 Hz, 1H), 4.15-4.08 (m, 2H), 3.86-3.80 (m, 1H), 3.74 (m, apparent quintet, *J* = 5.5 Hz, 1H), 3.60 (m, apparent t, *J* = 6.6 Hz, 2H), 3.30 (s, 3H), 3.28 (s, 3H), 2.27-2.13 (m, 4H), 1.76-1.60 (m, 3H), 1.54-1.45 (m, 4H), 1.40-1.22 (m, 7H), 0.894 (s, 9H), 0.891 (s, 9H), 0.882 (s, 18H), 0.880 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 6H), 0.04 (s, 3H), 0.034 (s, 6H), 0.028 (s, 3H), 0.025 (s, 3H), 0.01 (s, 3H); ^{13}C NMR {^1H} (125 MHz, $CDCl_3$): δ 135.9, 135.7, 126.3, 125.6, 102. 0, 73.1, 71.1, 69.4, 68.6, 63.3, 52.7, 52.2, 46.2, 41.5, 40.8, 39.4, 37.0, 32.9, 29.7, 26.0, 25.94, 25.91 (2C), 25.86, 25.8, 25.1, 18.4, 18.2, 18.15, 18.07, 18.0, –4.0, –4.26, –4.27, –4.31, –4.33, –4.73, –4.77, –4.81, –5.3 (2C); HRMS (FTMS + p ESI) Calculated for $C_{51}H_{110}O_7Si_5Na$ ($[M+Na]^+$): 997.6990, Found: 997.6989.



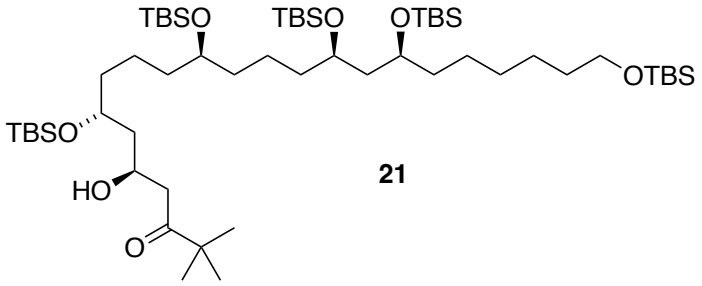
20

Acetal 20. To a solution of the diene **19** (10.7 mg, 0.0110 mmol) in ethyl acetate (0.5 mL) was added 10% palladium on carbon (5 mg). While vigorously stirring the mixture, the reaction flask was evacuated and refilled with H_2 from a balloon five times. The mixture was stirred at ambient temperature under H_2 for 18 h, then filtered through a cotton plug and concentrated in vacuo. Filtration through silica gel (1 cm plug in a pasteur pipet, eluting with 10% Et_2O in hexanes) afforded acetal **20** (10.1 mg, 94%) as a colorless oil. $[\alpha]_D^{23}$ –5.6 (c 0.50, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 4.51 (dd, *J* = 7.0, 4.4 Hz, 1H), 3.81-3.76 (m, 1H), 3.76-3.70 (m, 2H), 3.63-3.58 (m, 1H), 3.60 (m, apparent t, *J* = 6.6 Hz, 2H), 3.31 (s, 3H), 3.30 (s, 3H), 1.76-1.65 (m, 2H), 1.65-1.58 (m, 1H), 1.54-1.23 (m, 23H) 0.894 (s, 9H), 0.887 (s, 9H), 0.883 (s, 9H), 0.882 (s, 9H), 0.879 (s, 9H), 0.052 (s, 6H), 0.046 (s, 6H), 0.04-0.03 (m, 18H); ^{13}C NMR {^1H} (125 MHz, $CDCl_3$): δ 102.2, 72.4, 69.7 (2C), 68.9, 63.3, 52.8, 52.4, 44.9, 39.8, 38.1, 37.7, 37.47, 37.45, 37.2, 32.9, 29.7, 26.0, 25.94, 25.92 (2C), 25.90, 25.8, 25.1, 20.9, 20.6, 18.4, 18.10, 18.05 (2C), 18.03, –4.23, –4.26, –4.31, –4.37, –4.39, –4.41, –4.42, –4.7, –5.3 (2C); HRMS (FTMS + p ESI) Calculated for $C_{51}H_{114}O_7Si_5Na$ ($[M+Na]^+$): 1001.7303, Found: 1001.7313.



4

Aldehyde 4. To a solution of acetal **20** (10.0 mg, 0.0102 mmol) in CH_2Cl_2 (0.2 mL) was added 2,6-lutidine (10 mL, 0.08 mmol). The solution was cooled to 0 °C and triethylsilyl trifluoromethanesulfonate (11 mL, 0.05 mmol) was added. After stirring for 1 h at 0 °C, water (0.5 mL) was added and stirring was continued for 1 h. The mixture was partitioned between water (5 mL) and CH_2Cl_2 (2 x 5 mL). The organic phase was washed with 0.1 M aq. HCl, dried (Na_2SO_4) and concentrated. Flash chromatography (pipet column, 10% Et_2O in hexanes) furnished aldehyde **4** (5.9 mg, 61%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (t, *J* = 2.1 Hz, 1H), 4.18 (m, apparent quintet, *J* = 5.9 Hz, 1H), 3.76-3.69 (m, 2H), 3.65-3.60 (m, 1H), 3.60 (m, apparent t, *J* = 6.7 Hz, 2H), 2.52-2.49 (m, 1H), 1.66-1.59 (m, 1H), 1.57-1.22 (m, 24H), 0.89 (s, 9H), 0.88 (s, 27H), 0.87 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 6H), 0.04 (s, 18H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 202.3, 72.2, 69.6, 68.3, 63.3, 50.8, 44.9, 38.2, 37.7, 37.5, 37.2, 37.1, 32.9, 29.7, 26.0, 25.9 (3C), 25.83, 25.77, 25.1, 20.9, 20.8, 18.4, 18.1, 18.04, 17.97, –4.26, –4.30, –4.35, –4.38, –4.39, –4.42 (2C), –4.7, –5.3 (2C); HRMS (FTMS + p ESI) Calculated for $C_{49}H_{109}O_6Si_5$ ([M+H]$^+$): 933.7065, Found: 933.7083. Calculated for $C_{49}H_{108}O_6Si_5Na$ ([M+Na]$^+$): 955.6884, Found: 955.6893.



21

Mukaiyama Aldol Adduct 21. To a solution of aldehyde **20** (5.8 mg, 0.0062 mmol) and 2-trimethylsilyloxy-3,3-dimethyl-1-butene (0.007 mL, 0.031 mmol, 5 equiv) in CH_2Cl_2 (0.12 mL) at –78 °C was added BF_3•OEt_2 (0.002 mL, 0.012 mmol, 2 equiv). After 2 h at –78 °C, saturated aqueous $NaHCO_3$ (0.1 mL) was added and the mixture was partitioned between water and CH_2Cl_2. The organic phase was dried over Na_2SO_4 and concentrated to afford the crude product (*anti*/*syn* 88:12 by ^{1}H NMR integration). Flash chromatography (10% Et_2O in hexanes) gave **21** (3.6 mg, 56%), with early fractions slightly enriched in the major diastereomer (dr 92:8), as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.32-4.25 (m, 1H) 4.01-3.95 (m, 1H), 3.76-3.69 (m, 2H), 3.65-3.59 (m, 1H), 3.60 (m, apparent t, *J* = 6.6 Hz, 2H), 3.53 (br d, J = 1.8 Hz, 1H), 2.65 (dd, *J* = 17.7, 7.6 Hz, 1H), 2.59 (dd, *J* = 17.7, 4.3 Hz, 1H), 1.66-1.22 (m, 26H), 1.14 (s, 9H), 0.89 (s, 9H), 0.89-0.87 (m, 36H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 (s, 6H), 0.04-0.03 (s, 18H); ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 216.6, 72.3, 70.1, 69.7, 64.5, 63.3, 44.9, 44.3, 44.0, 42.3, 37.8, 37.6, 37.4, 37.2, 32.9, 29.7, 26.3, 25.98, 25.95, 25.93 (2C), 25.90, 25.8, 25.1, 20.9, 18.4, 18.11, 18.05, -4.2, -4.3, -4.38 (3C), -4.42(2C), -4.7, -5.3 (2C); HRMS (FTMS + p ESI) Calculated for $C_{55}H_{121}O_7Si_5$ ([M+H]$^+$): 1033.7953, Found: 1033.7950. Calculated for $C_{55}H_{120}O_7Si_5Na$ ([M+Na]$^+$): 1055.7773, Found: 1055.7765.

Stereochemical analysis of **21**: Diagnostic peaks for measuring the aldol diastereomer ratio were observed in the ^{1}H NMR spectrum at 4.28 ppm (*anti*) and 4.16 ppm (*syn*) for the C21 methine (bastimolide numbering, Figure S2). For several closely related aldol products of general structure **C** (Figure S3), we previously observed that the beta-methine peak of the *anti* diastereomer reliably appears 0.09–0.19 ppm downfield from the *syn* diastereomer; these were rigorously assigned via 1,3-diol acetonide derivatives.[18]

Figure S2. Measurement of diastereomer ratio of **21** by ^{1}H NMR integration.

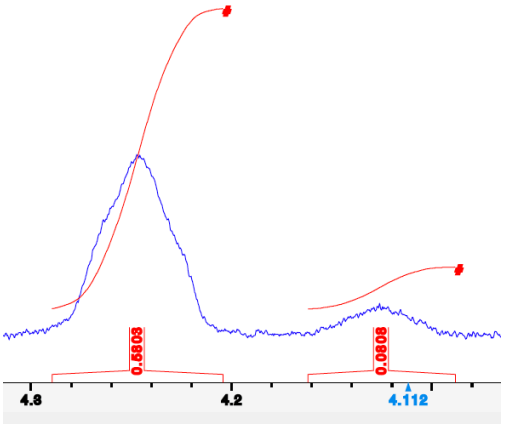
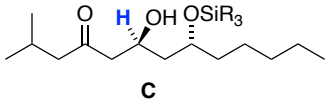
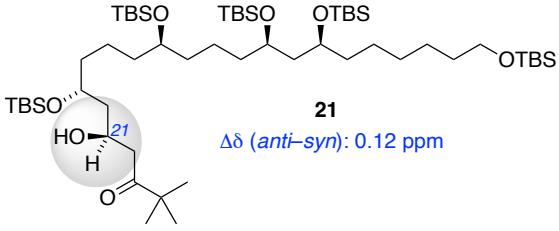


Figure S3. Diagnostic downfield shifts for *anti* configuration at C21–H (ref 17).



C

SiR_3	Δδ (*anti–syn*)
TMS	0.10 ppm
TES	0.14 ppm
TBS	0.14 ppm
TBDPS	0.09 ppm
TIPS	0.19 ppm



21

Δδ (*anti–syn*): 0.12 ppm

References

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[2] (a) Catalysis by Ru(dppb)(methallyl)$_2$ typically did not result in products contaminated with Ru byproducts. Doucet, H.; Martin-Vaca, B.; Bruneau, C.; Dixneuf, P. H. General Synthesis of (Z)-Alk-1-en-1-yl Esters via Ruthenium-Catalyzed anti-Markovnikov trans-Addition of Carboxylic Acids to Terminal Alkynes. *J. Org. Chem.* **1995**, *60*, 7247-7255. (b) Other catalyst systems, such as [Ru(*p*-cymene)Cl$_2$]$_2$ and triarylphosphine, sometimes left traces of Ru catalyst byproducts that persist after chromatography, and interfere with the epoxidation, presumably by decomposing the hydrogen peroxide. A wash with H_2O_2 during workup leads to Ru components that are more easily removed by flash chromatography.

[3] More recently we have generally adopted the Dixneuf procedure (ref 2a), as exemplified by the preparation of compound **9**, which is operationally simpler, higher yielding, and avoids product contamination with Ru byproducts.

[4] Lower temperatures in the Goossen conditions gave diminished yields. Data for 1-octyne at 50 °C (25%), 60 °C (55%), 70 °C (78%).

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[11] This treatment presumably decomposed the 1,1-disubstituted enol ester, leaving behind the 1,2-disubstituted enol ester mixture.

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[13] Dowex 50wx acidic ion exchange resin was activated by stirring for a few minutes with 0.5 M aqueous H_2SO_4, then dried by washing successively with water, MeOH, and Et_2O.

[14] In various runs using higher temperature and/or longer reaction times, **S7**/**17** ratios from 73:24 to 96:4 were observed. Increased proportions of aldehyde could be achieved with longer reaction times and/or higher temperature (–20 °C) during exposure to DIBAL-H. However, this also led to lower mass balance, with byproducts suggestive of overreduction to a primary amine.

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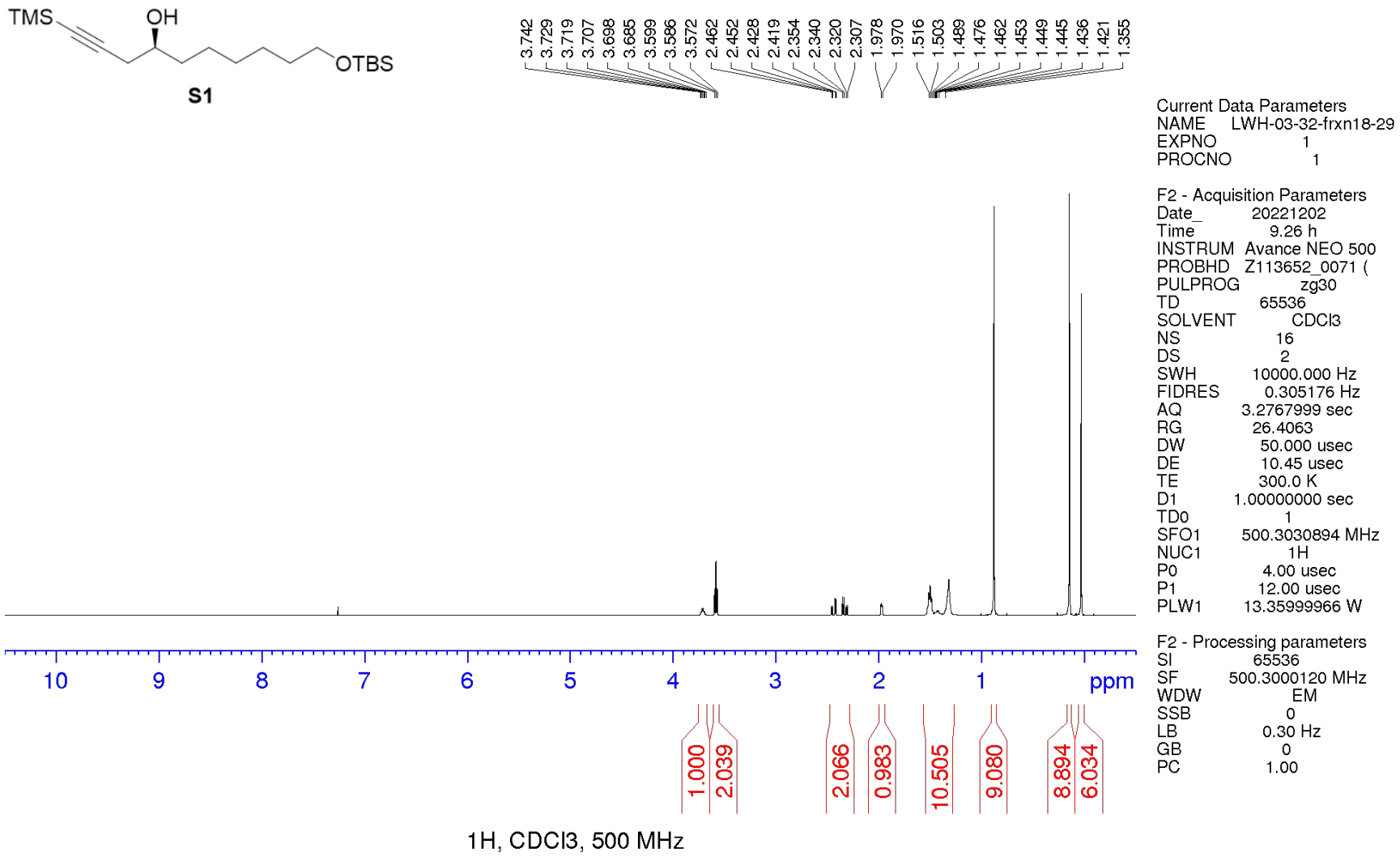
Characterization Data for New Compounds, Graphic Format



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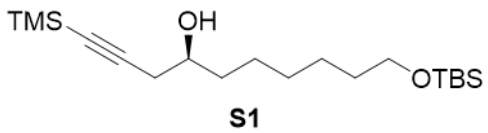

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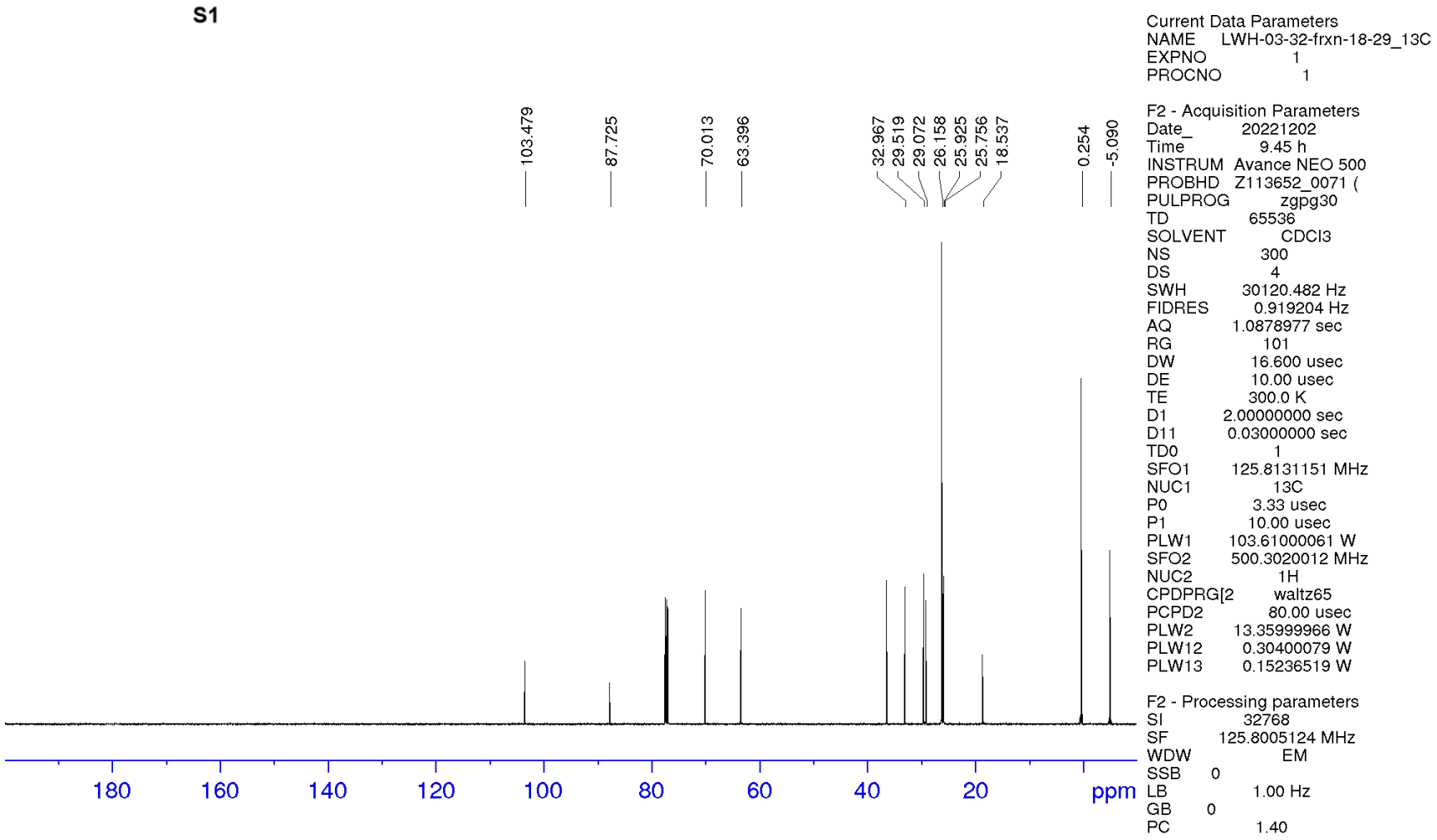

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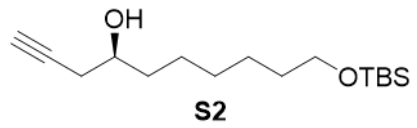

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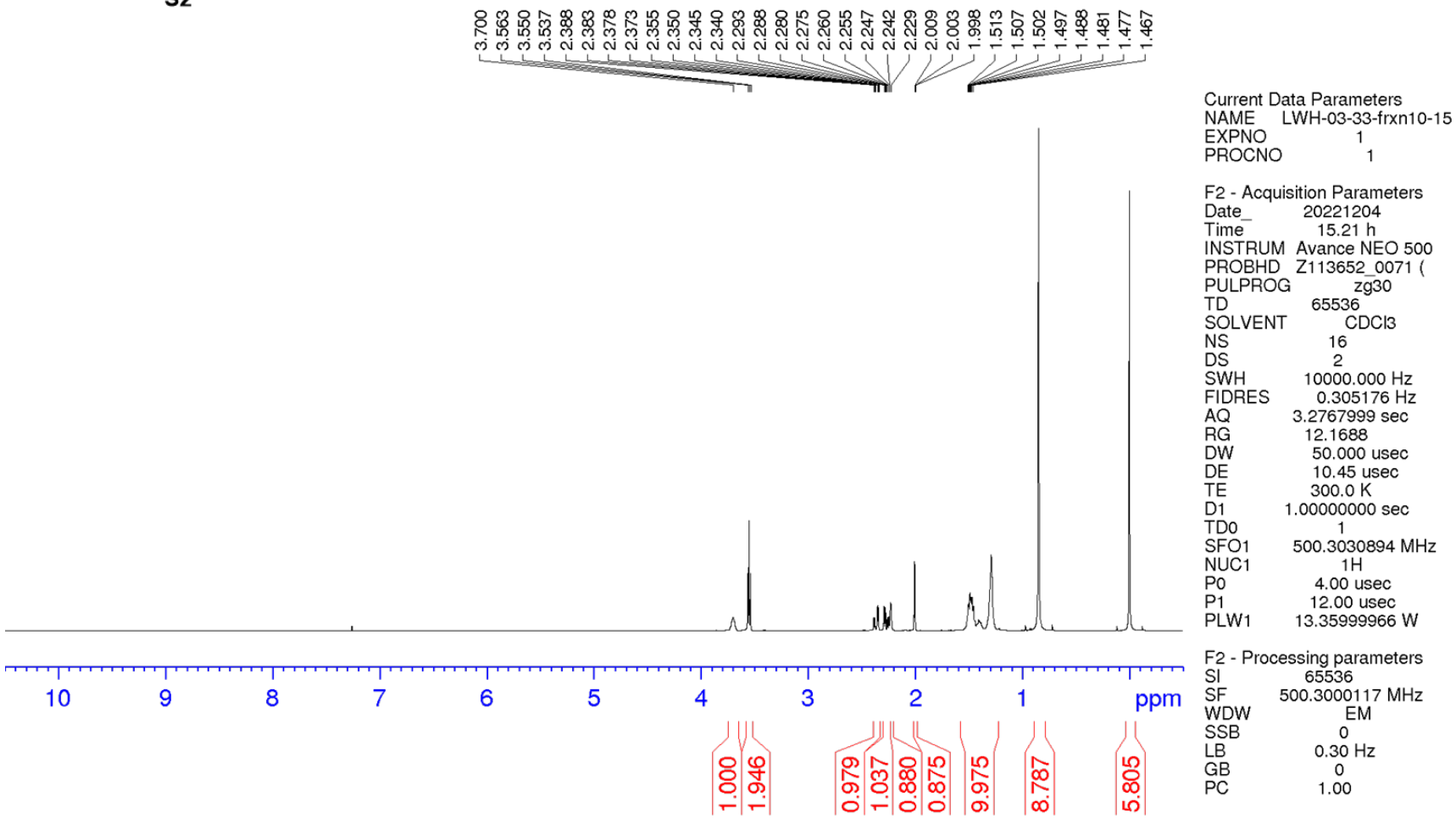

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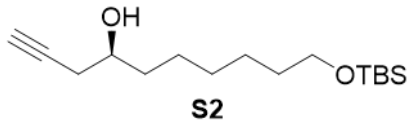

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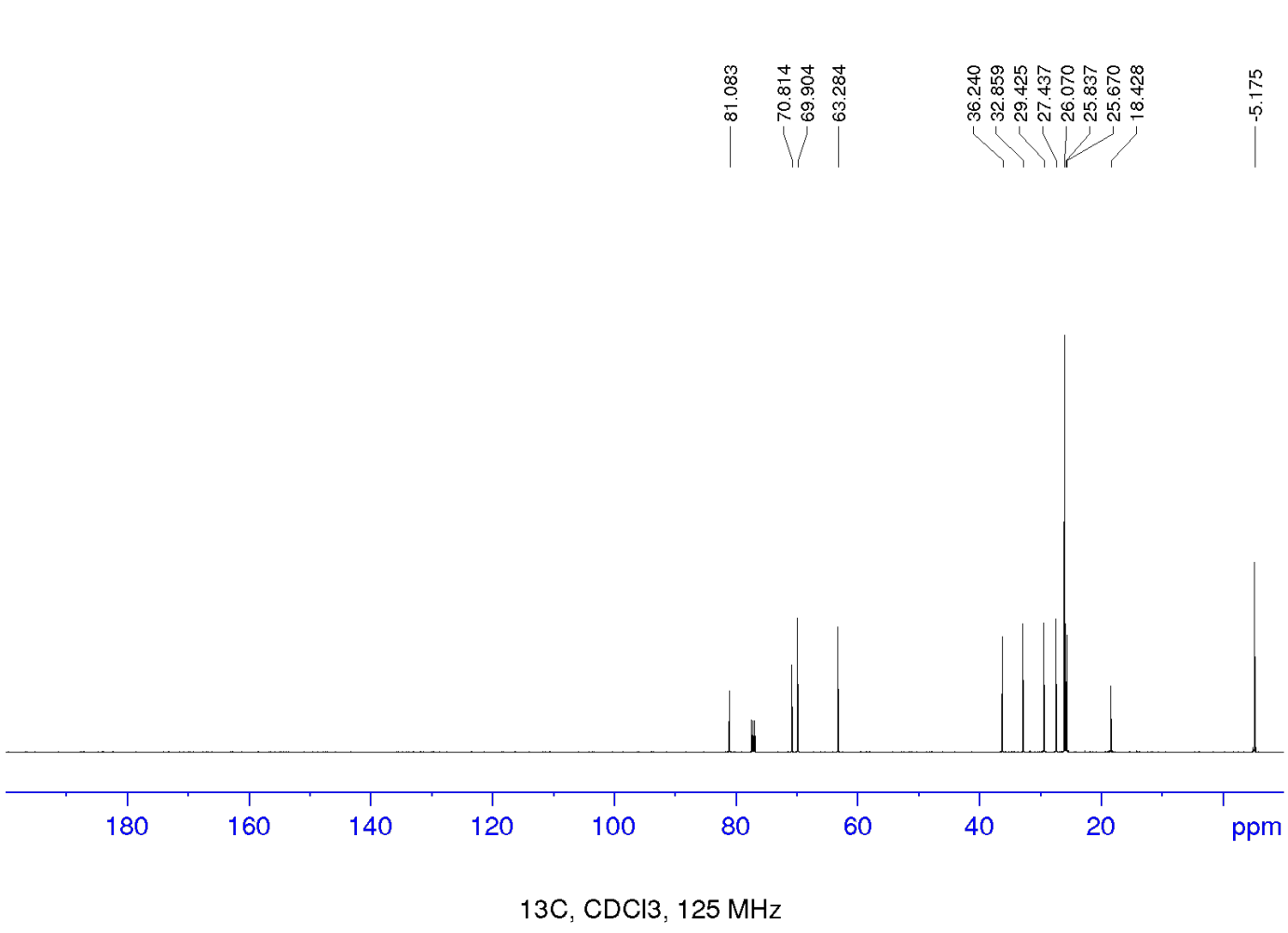

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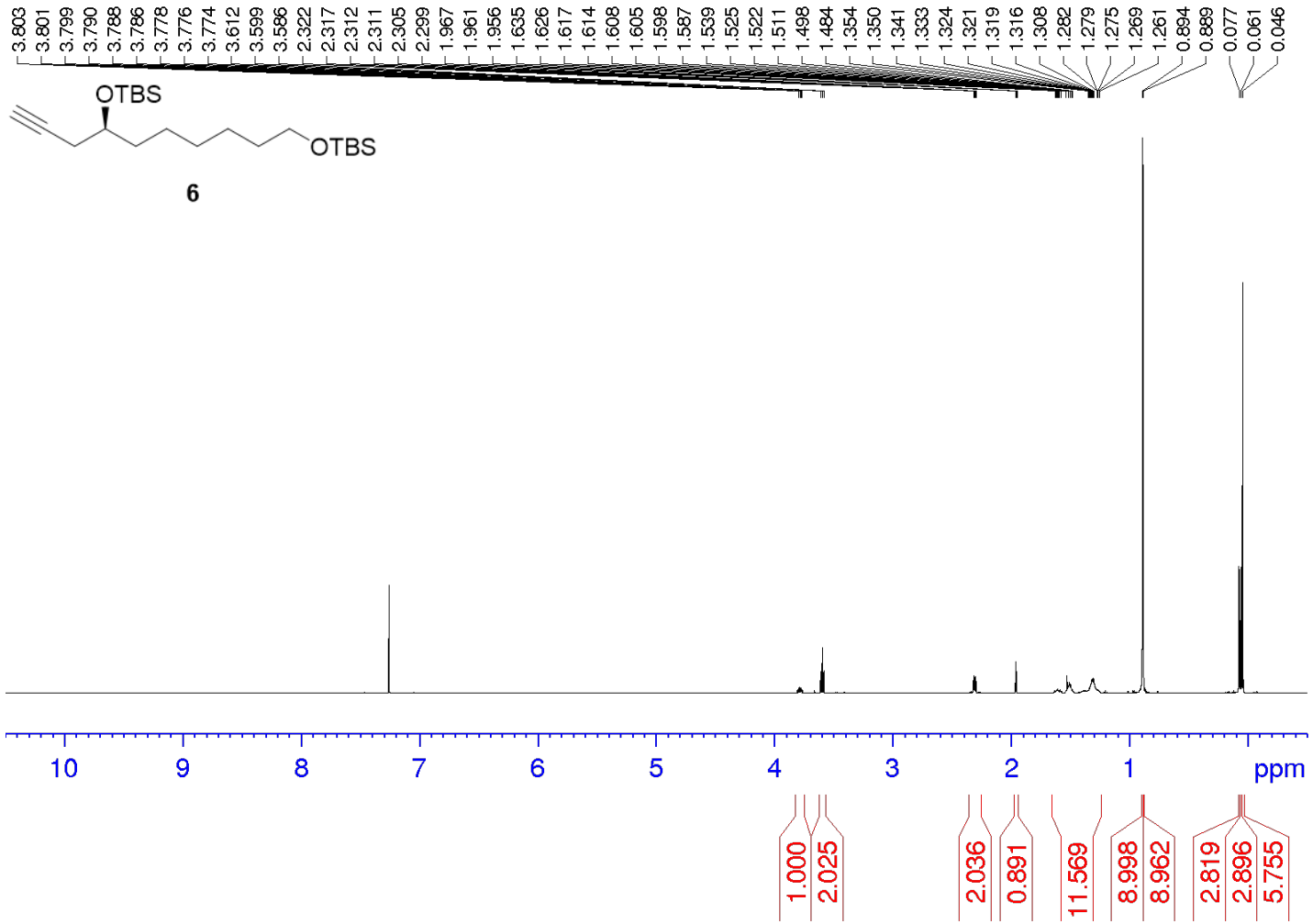

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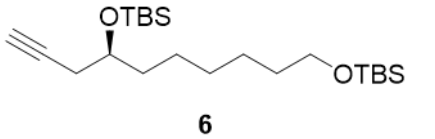

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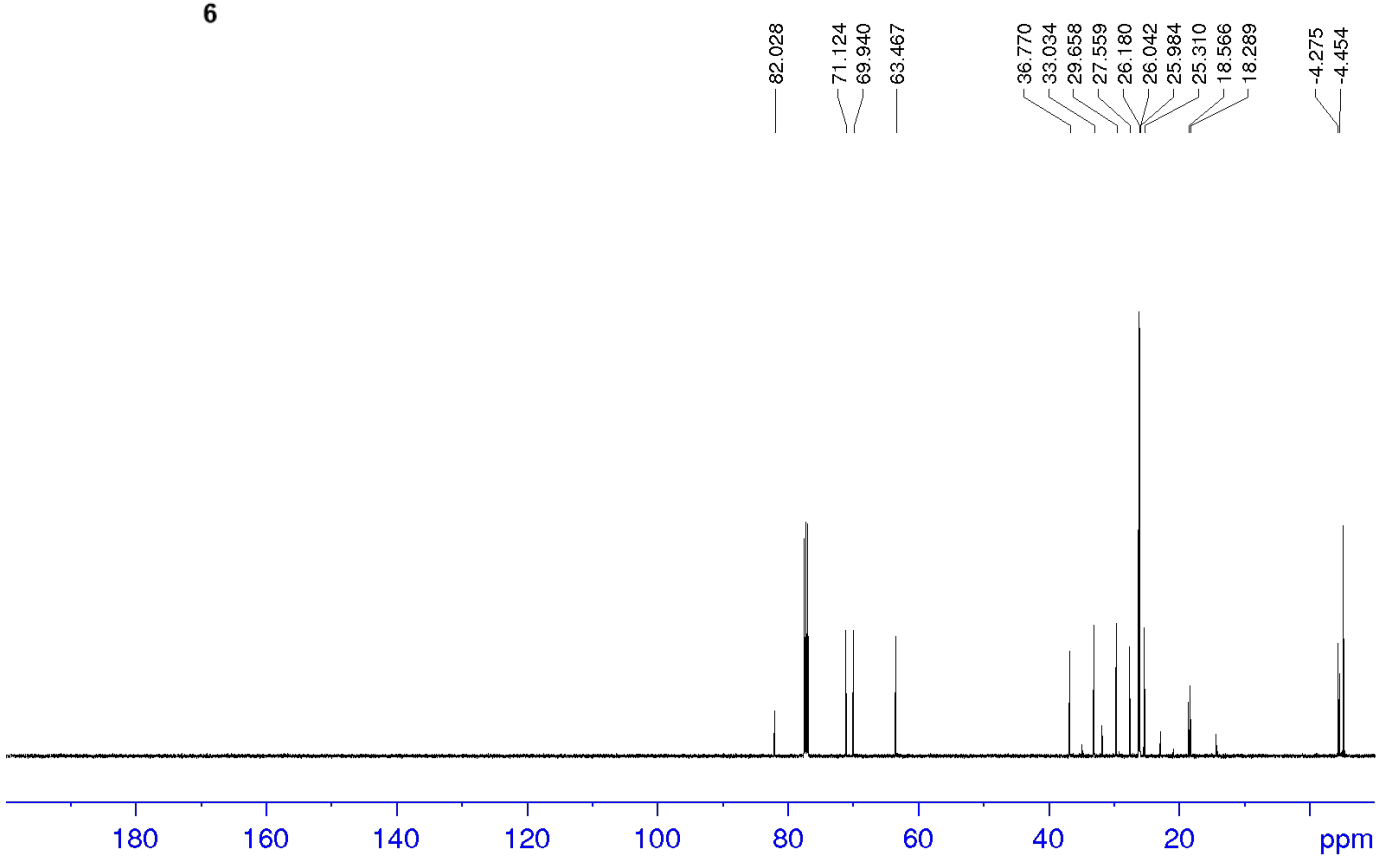

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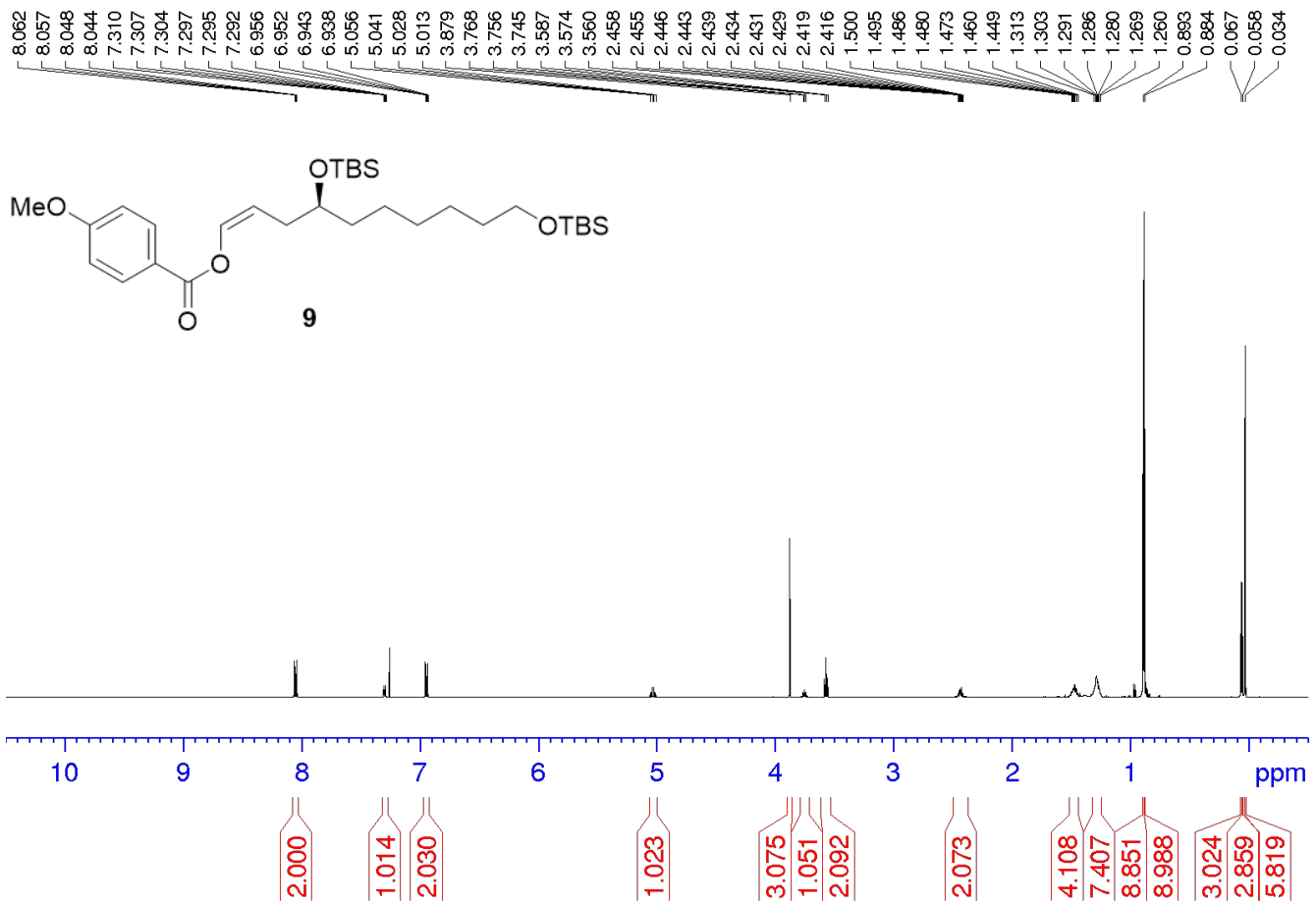
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 103.61000061 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 13.35999966 W
PLW12 0.30400079 W
PLW13 0.15236519 W

F2 - Processing parameters
SI 32768
SF 125.8005106 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

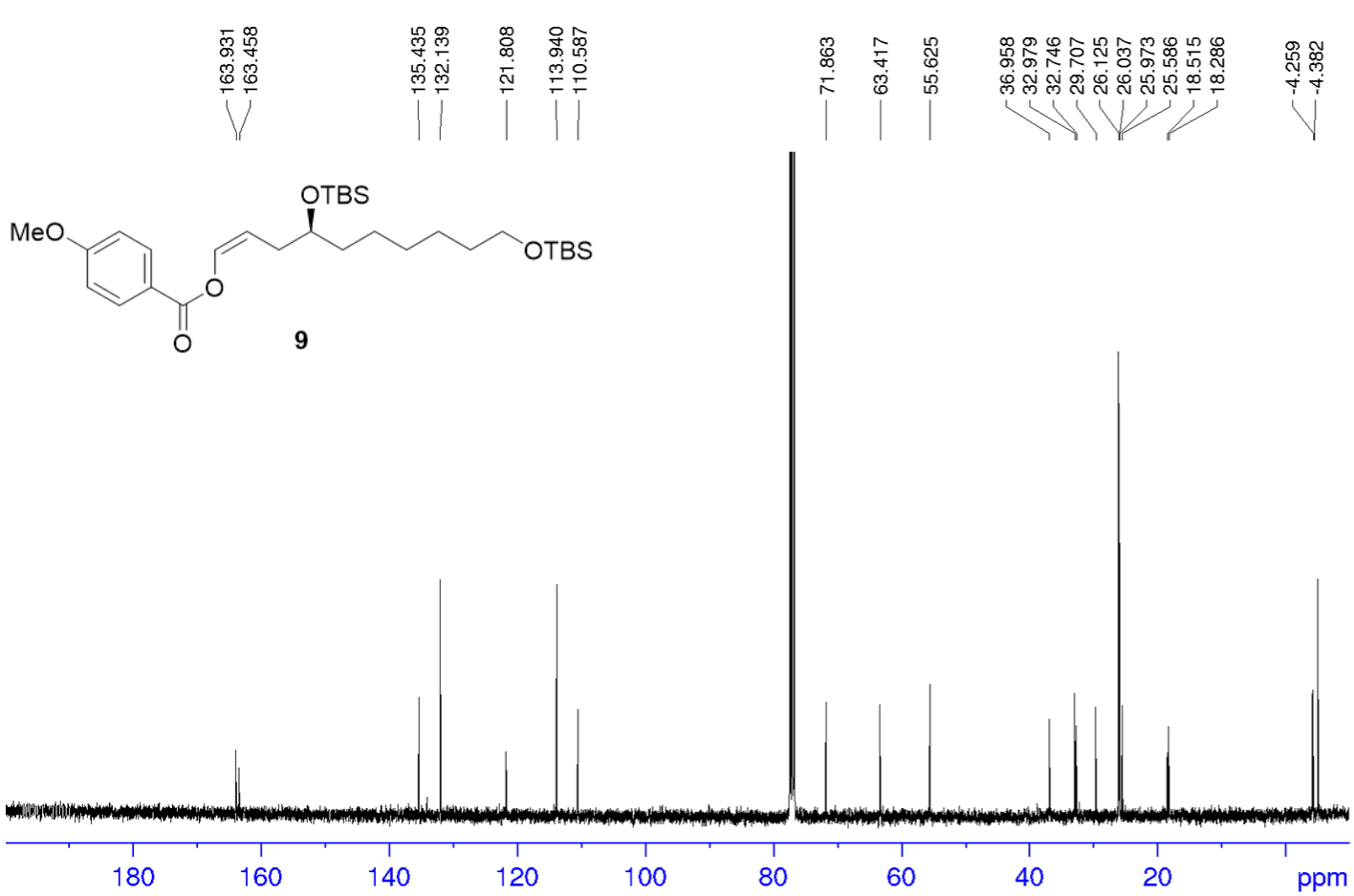


1H, CDCl3, 500 MHz

Current Data Parameters
NAME LWH-03-28-frxn21-end-column2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221128
Time 15.00 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 101
DW 50.000 usec
DE 10.45 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030894 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 13.35999966 W

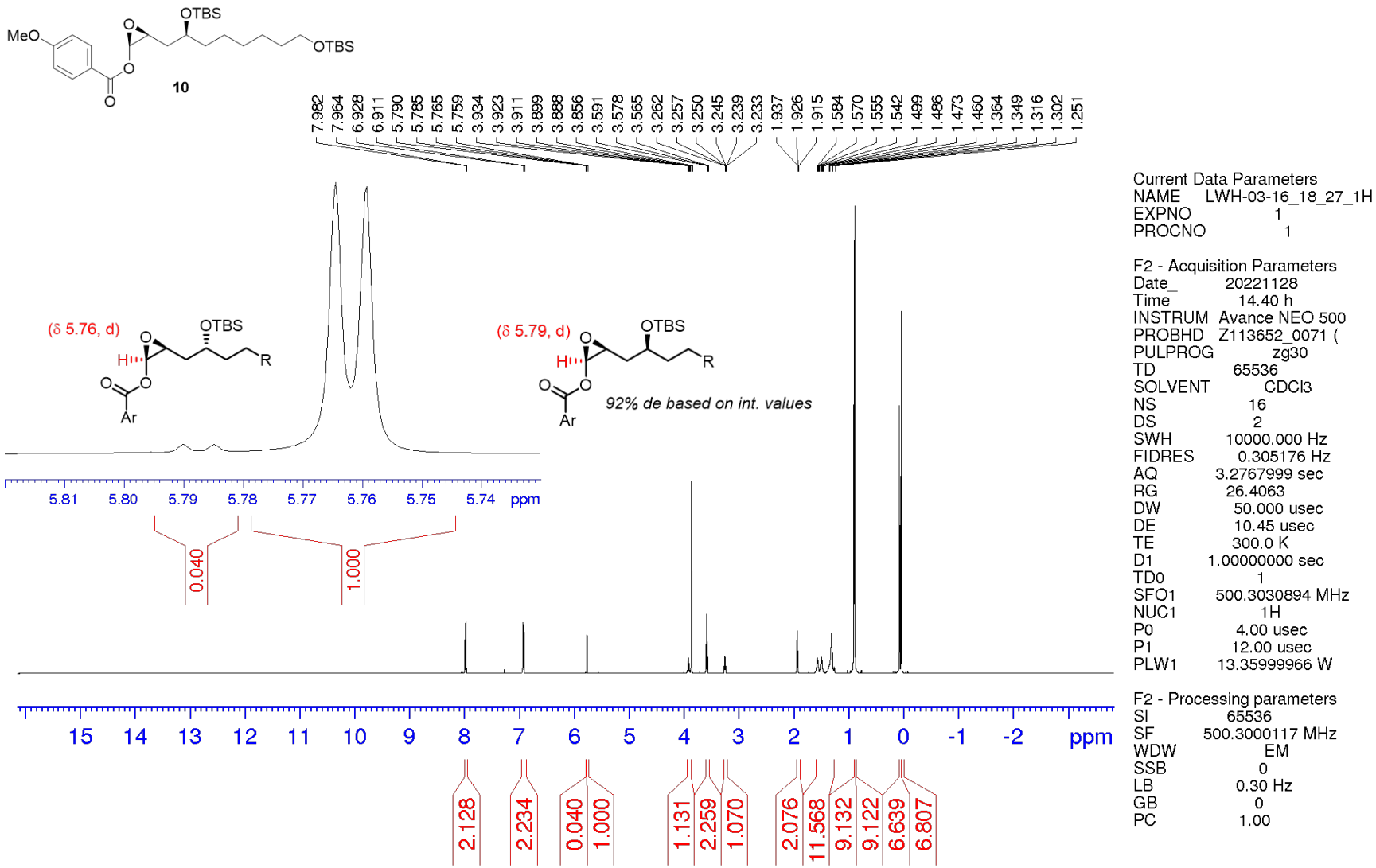
F2 - Processing parameters
SI 65536
SF 500.3000121 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



Current Data Parameters
NAME JNH_03_126 13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20220713
Time 21.16 h
INSTRUM spect
PROBHD Z104450_0192 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1645
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P0 3.28 usec
P1 9.85 usec
PLW1 28.63999939 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 90.00 usec
PLW2 8.47000027 W
PLW12 0.23528001 W
PLW13 0.11834000 W

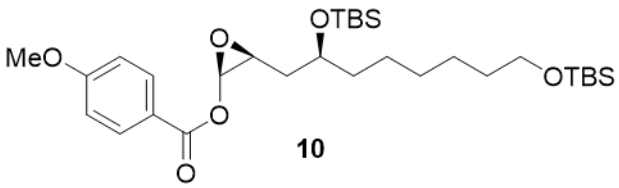
F2 - Processing parameters
SI 32768
SF 100.6127550 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME LWH-03-16_18_27_1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221128
Time 14.40 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 26.4063
DW 50.000 usec
DE 10.45 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030894 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 13.35999966 W

F2 - Processing parameters
SI 65536
SF 500.3000117 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



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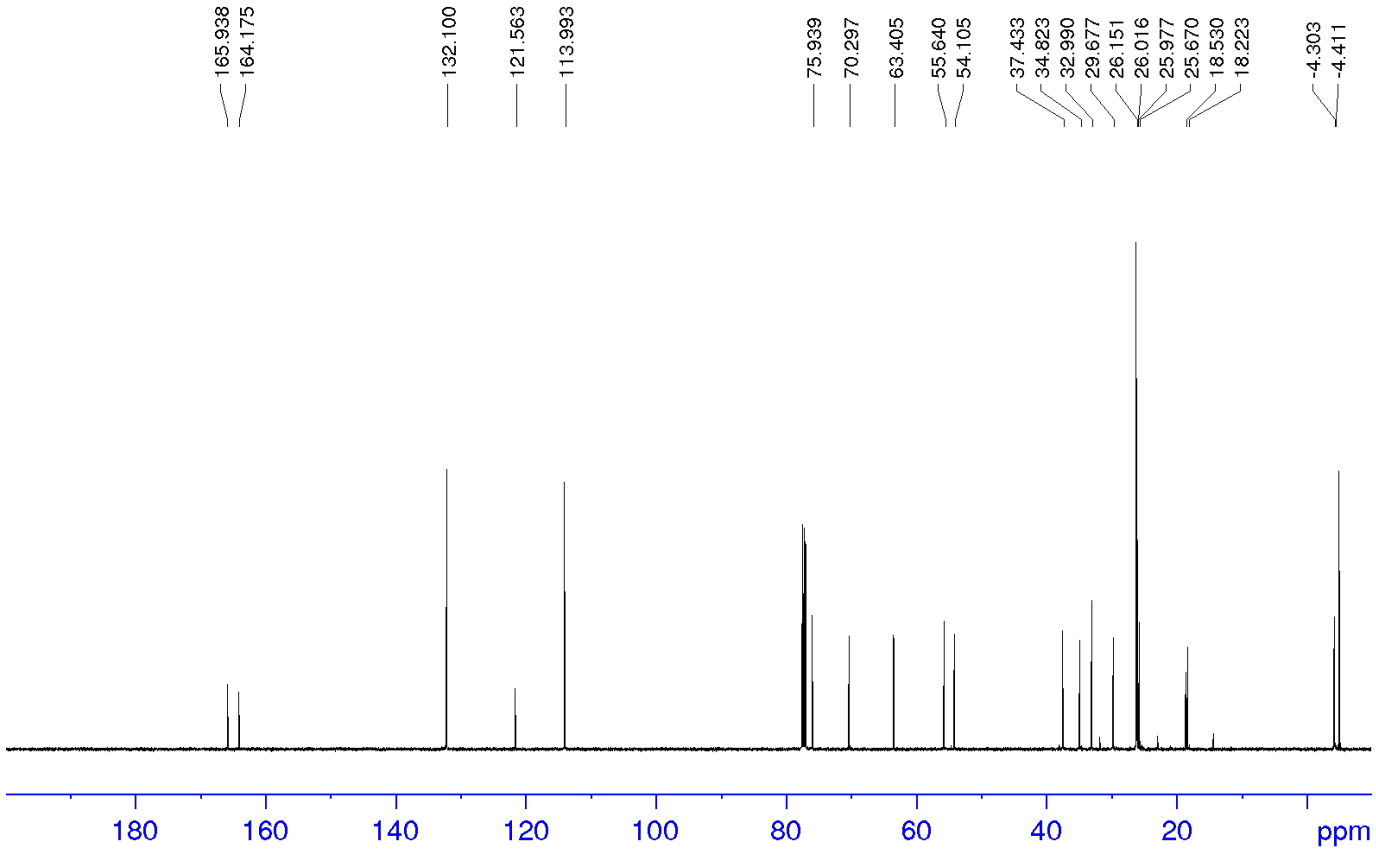
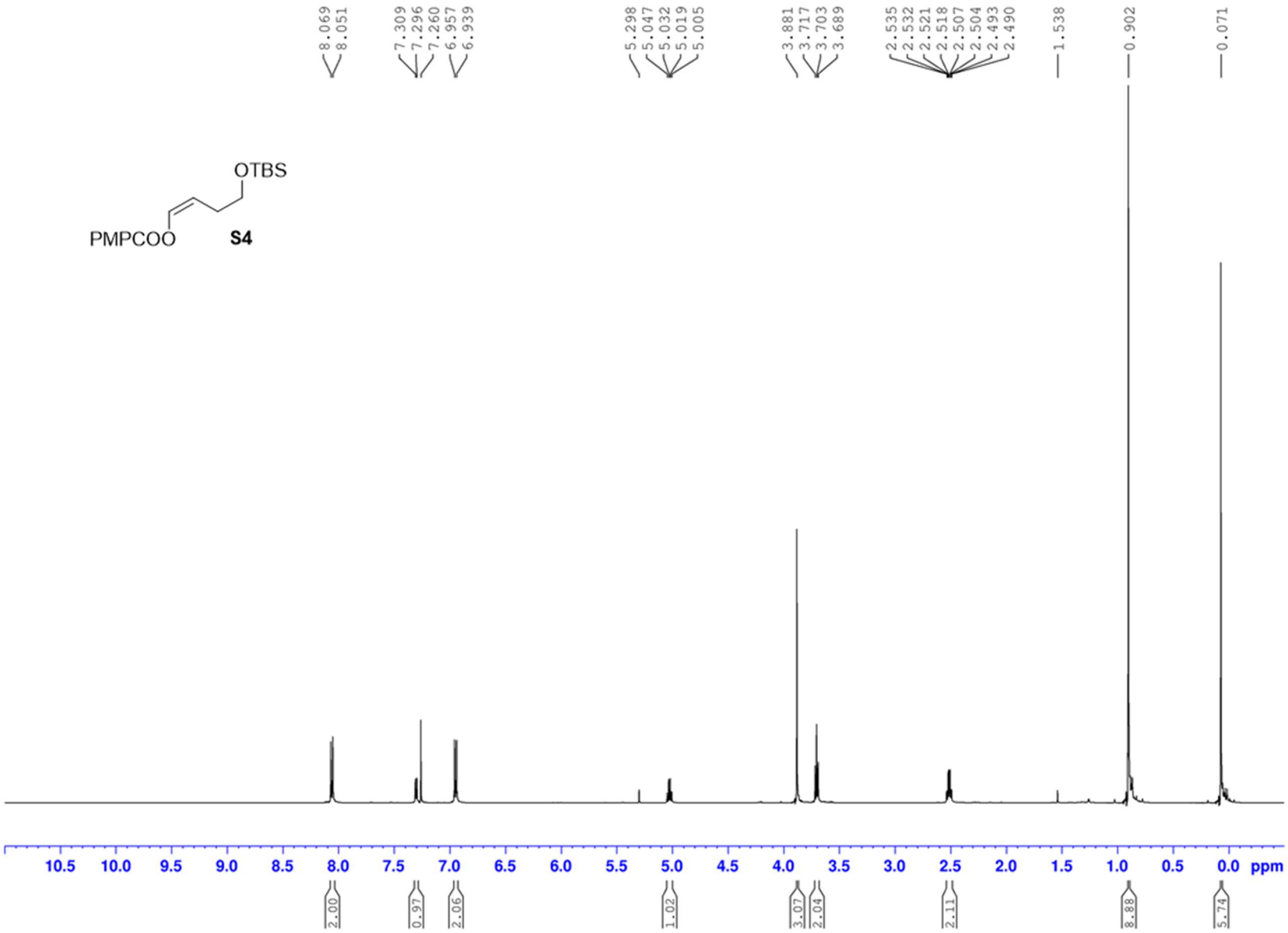


13C, CDCl3, 125 MHz

Current Data Parameters
NAME LWH-03-31-frxn11-31_13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20221202
Time 10.06 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 250
DS 4
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 1.0878977 sec
RG 101
DW 16.600 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 103.61000061 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 13.35999966 W
PLW12 0.30400079 W
PLW13 0.15236519 W

F2 - Processing parameters
SI 32768
SF 125.8005133 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



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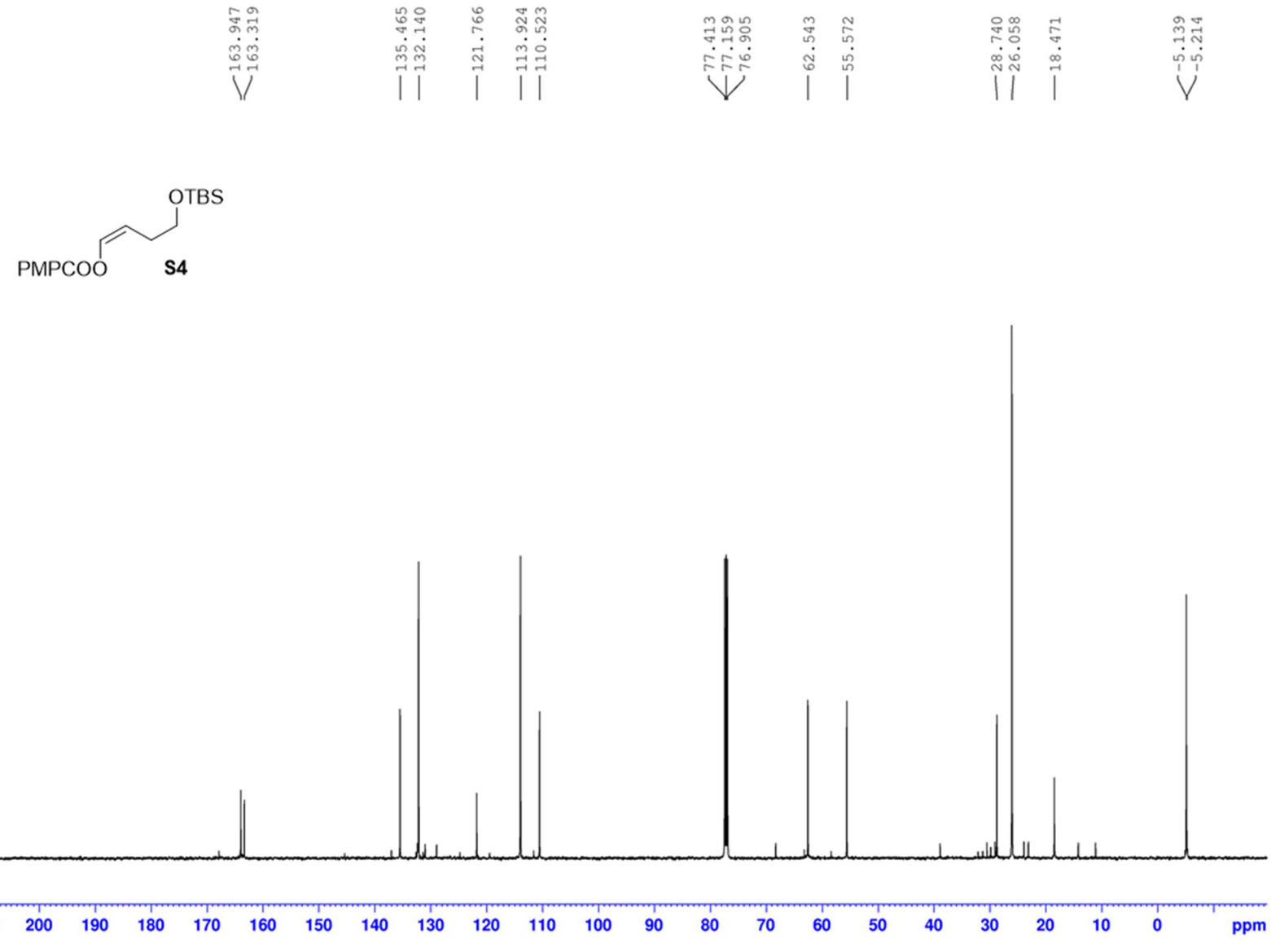
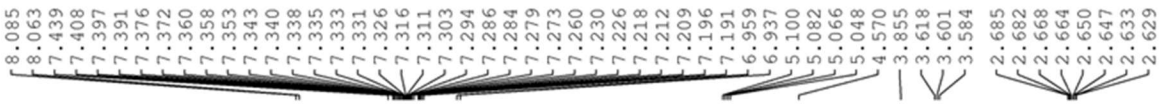
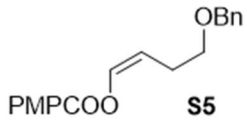
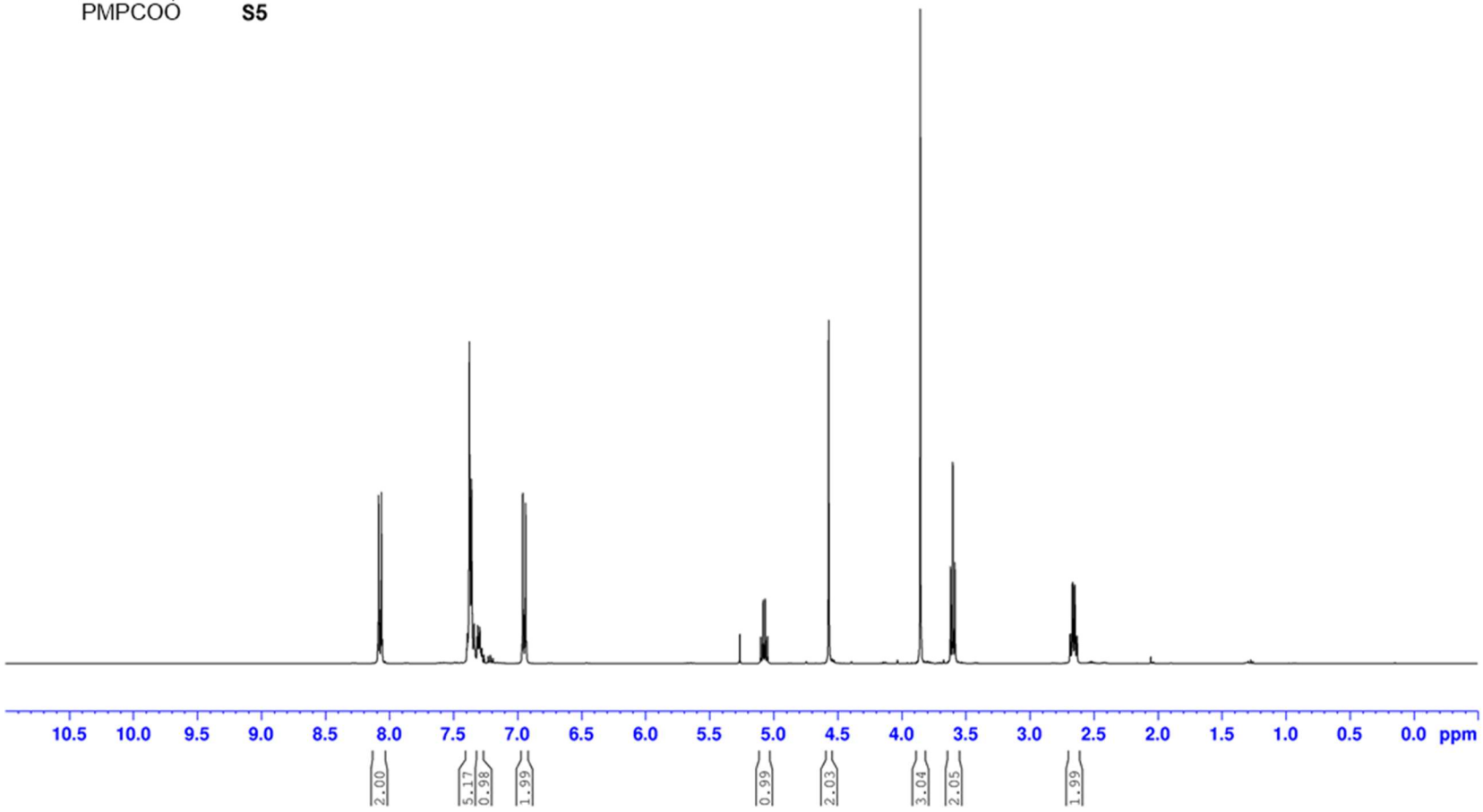
```
Current Data Parameters
NAME          JNH_02_170
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201013
Time               12.19
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     4
SWH            10000.000 Hz
FIDRES             0.152588 Hz
AQ             3.2767999 sec
RG                 161.3
DW                50.000 usec
DE                 6.50 usec
TE                 300.2 K
D1            0.01000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                12.00 usec
PL1               -1.10 dB
PL1W         19.41561890 W
SFO1         500.3020014 MHz

F2 - Processing parameters
SI                 65536
SF           500.3000129 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 1.00
```



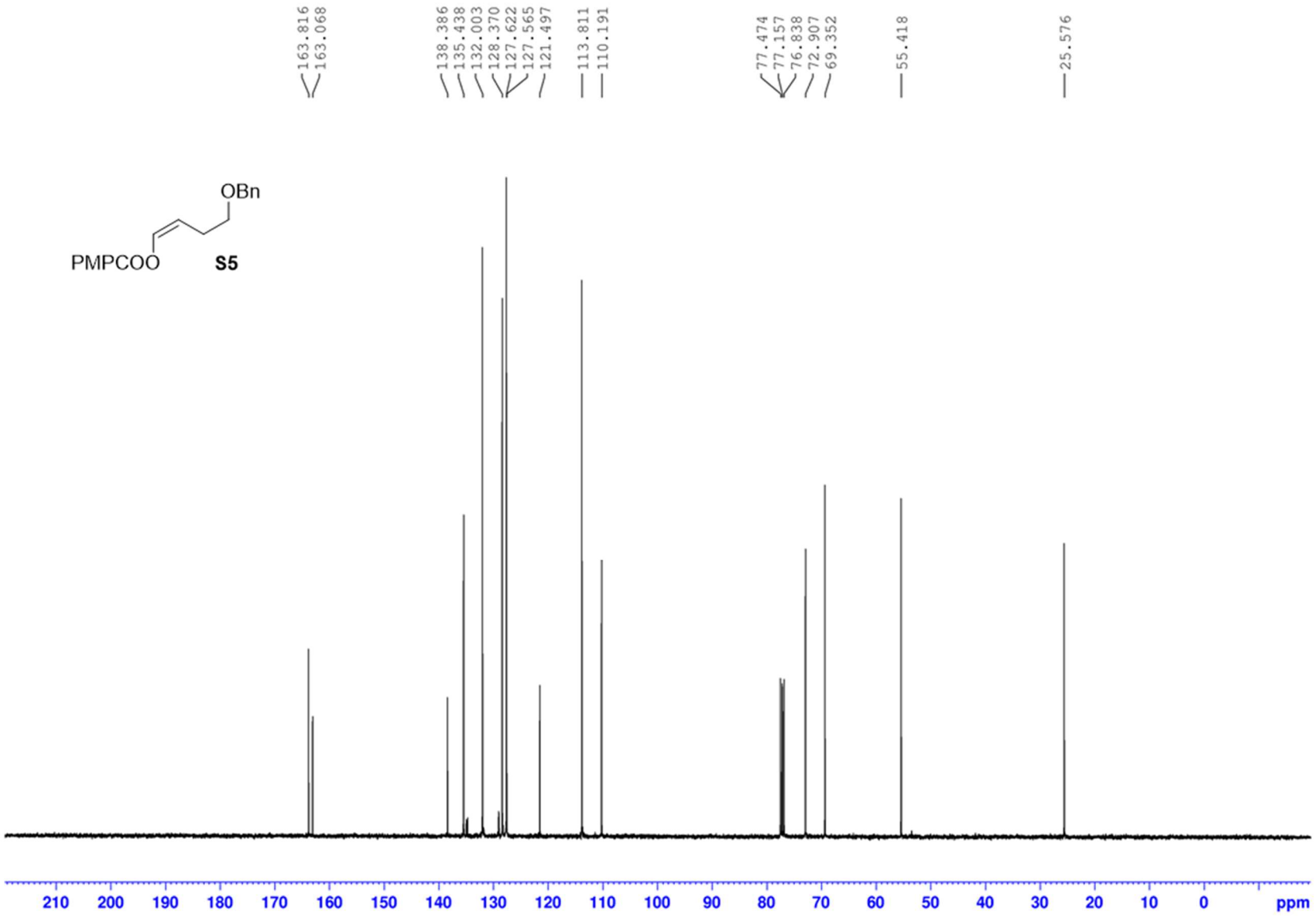

```
Current Data Parameters
NAME                  JNH_02_176
EXPNO                          3
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20201113
Time                       13.52
INSTRUM                    spect
PROBHD   5 mm PABBO BB-
PULPROG                   zgpg30
TD                        131072
SOLVENT                     CDCl3
NS                            256
DS                              8
SWH                   31446.541 Hz
FIDRES                 0.239918 Hz
AQ                     2.0840447 sec
RG                       18390.4
DW                        15.900 usec
DE                         6.50 usec
TE                        300.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                        10.00 usec
PL1                       -1.70 dB
PL1W               148.61408997 W
SFO1                125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       -1.10 dB
PL12                      15.40 dB
PL13                      17.40 dB
PL2W               19.41561890 W
PL12W               0.43466163 W
PL13W               0.27425295 W
SFO2                500.3025017 MHz

F2 - Processing parameters
SI                         131072
SF                  125.8005205 MHz
WDW                            EM
SSB                             0
LB                         3.00 Hz
GB                              0
PC                         1.40
```



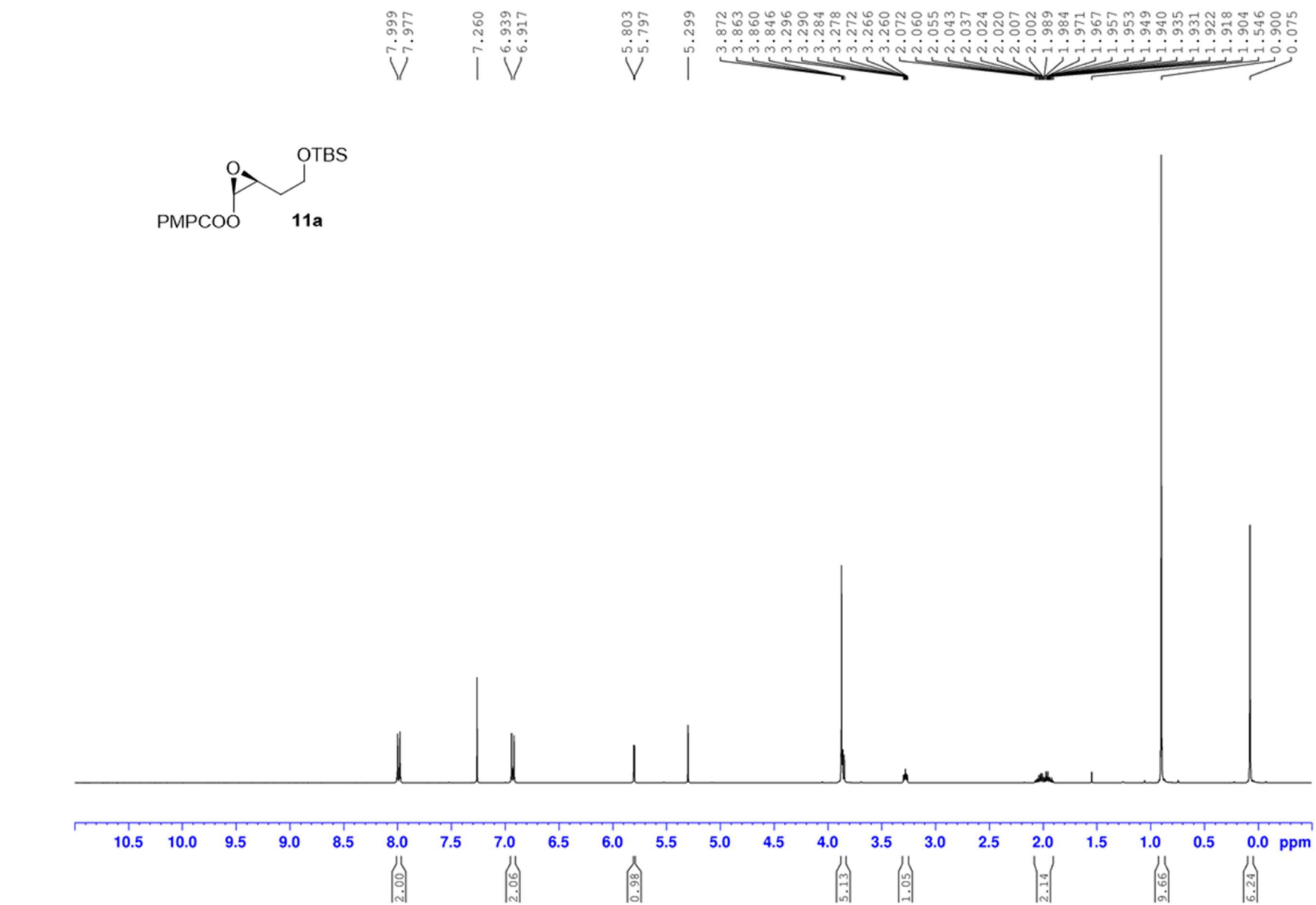




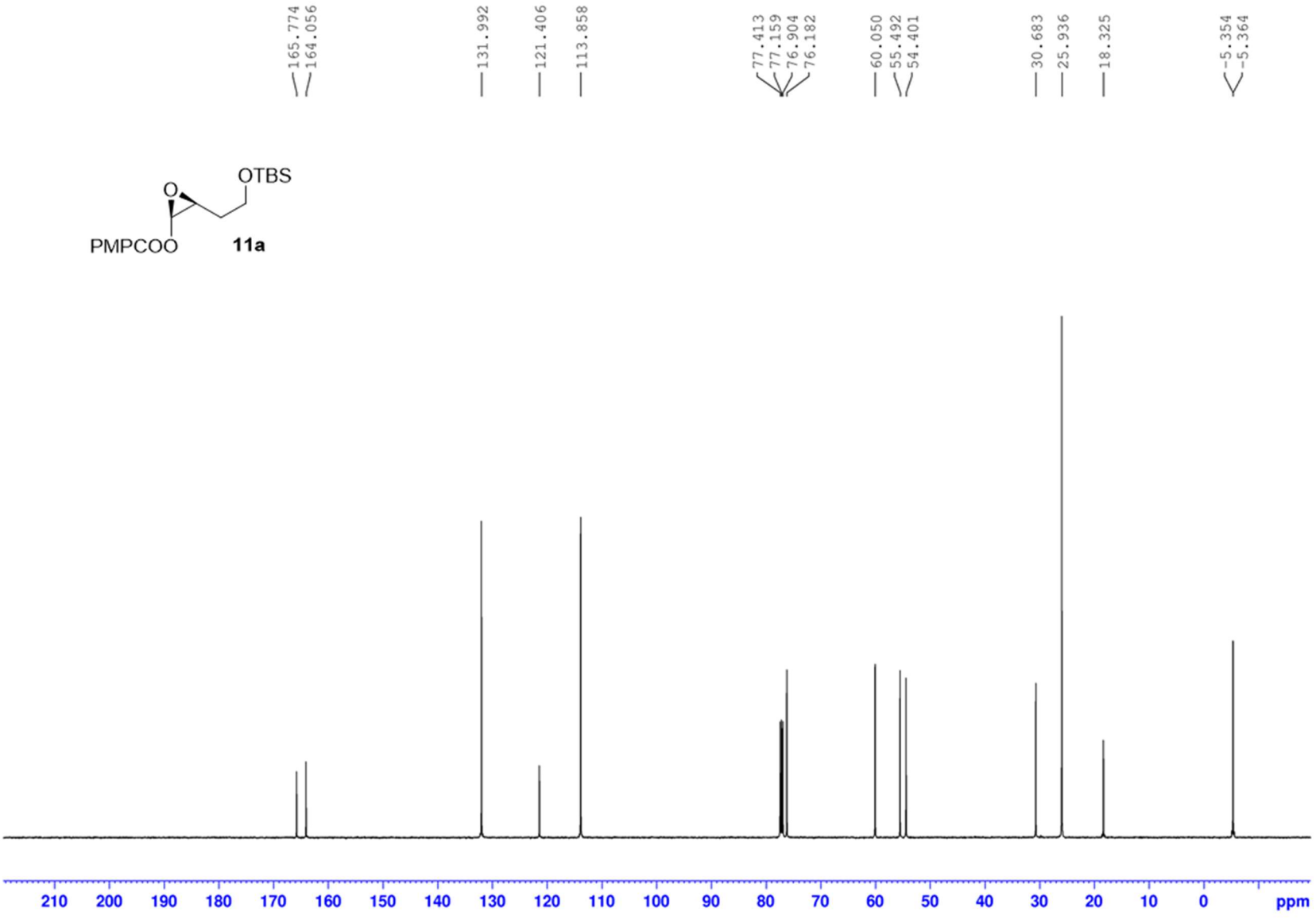

```
Current Data Parameters
NAME                  JNH_03_22
EXPNO                         3
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20211123
Time                      14.01 h
INSTRUM                   spect
PROBHD    Z104450_0192 (
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                     4.0894465 sec
RG                          32
DW                        62.400 usec
DE                        16.92 usec
TE                        296.3 K
D1                  1.00000000 sec
TD0                          1
SFO1                400.1324708 MHz
NUC1                        1H
P0                         5.00 usec
P1                        15.00 usec
PLW1                8.47000027 W

F2 - Processing parameters
SI                       65536
SF                  400.1300089 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



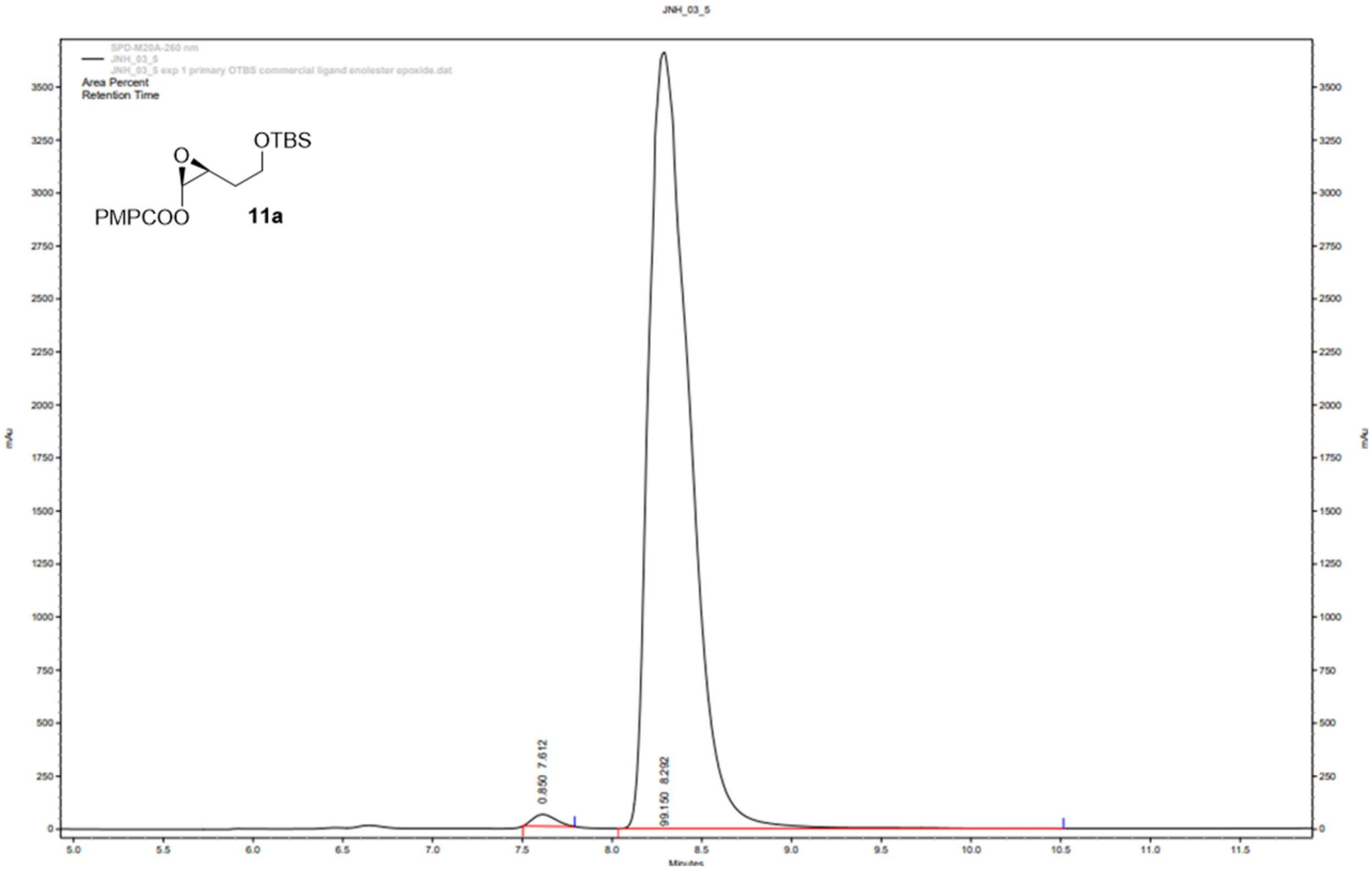

```
Current Data Parameters
NAME       JNH_03_22 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20211123
Time              14.15 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  100
DS                    2
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE               296.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                3.28 usec
P1                9.85 usec
PLW1         28.63999939 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2          8.47000027 W
PLW12         0.23528001 W
PLW13         0.11834000 W

F2 - Processing parameters
SI                32768
SF           100.6127752 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```

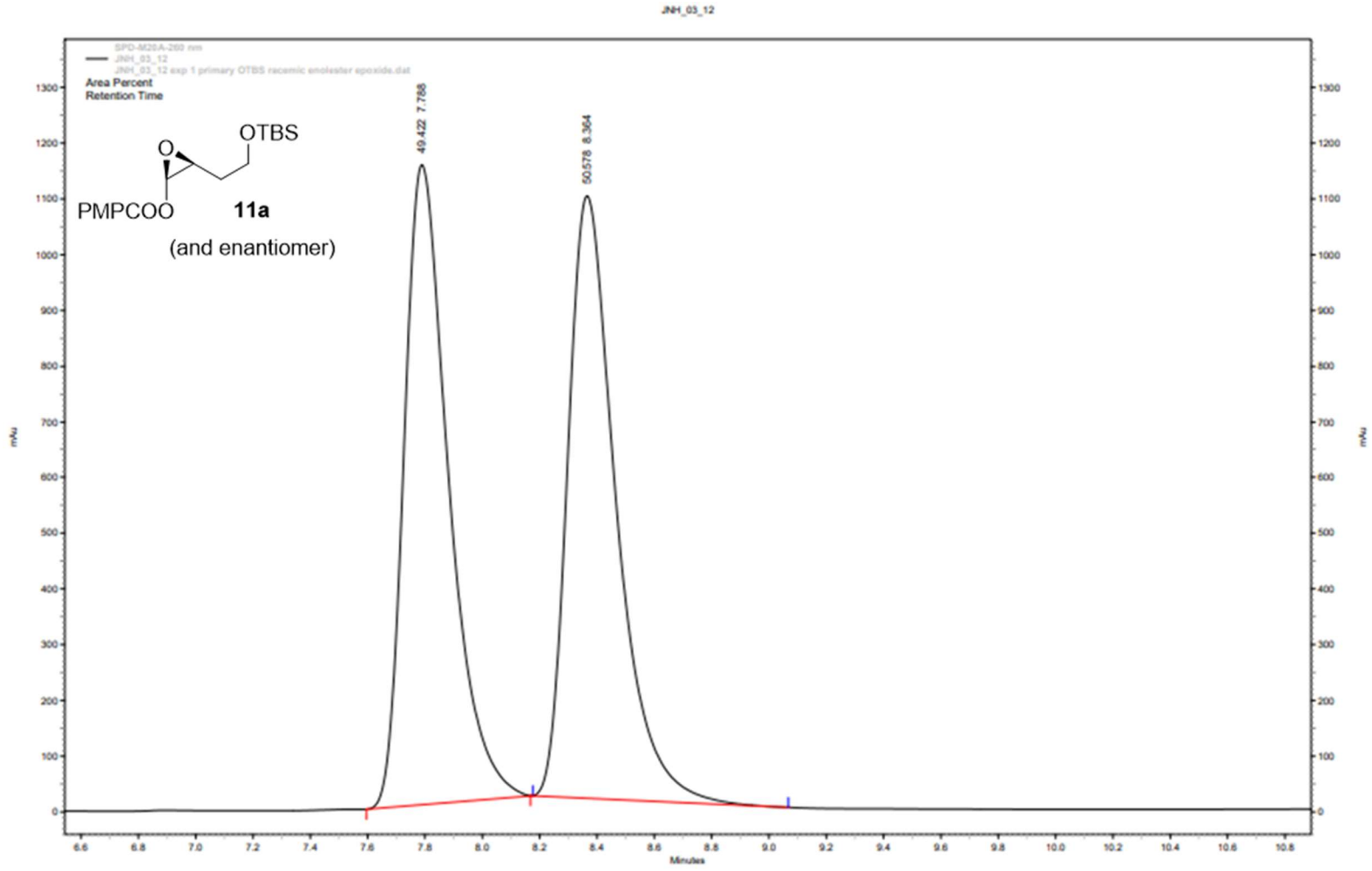


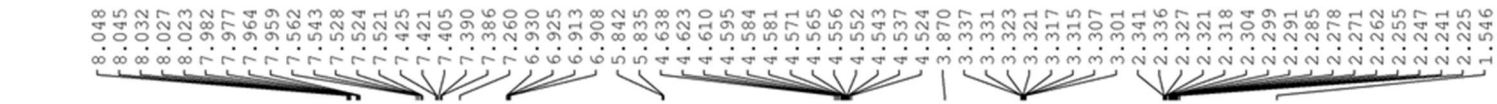

```
Current Data Parameters
NAME          JNH_02_176
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201020
Time               17.54 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                   456
DW                62.400 usec
DE                16.92 usec
TE                296.5 K
D1             1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P0                 5.00 usec
P1                15.00 usec
PLW1           8.47000027 W

F2 - Processing parameters
SI                 65536
SF           400.1300098 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

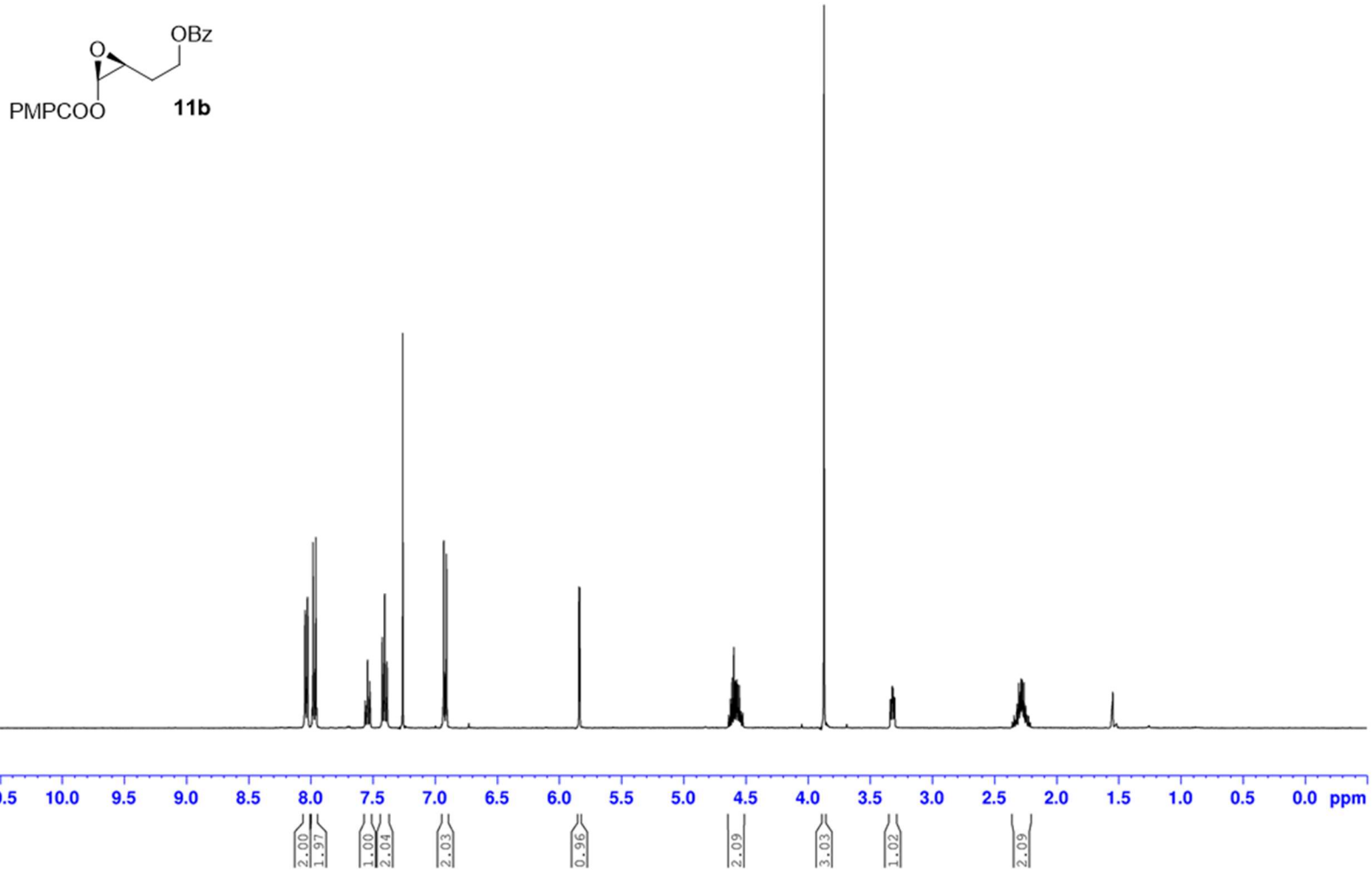



```
Current Data Parameters
NAME                  JNH_02_176
EXPNO                          5
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20201117
Time                        8.32
INSTRUM                    spect
PROBHD    5 mm PABBO BB-
PULPROG                   zgpg30
TD                        131072
SOLVENT                     CDC13
NS                            256
DS                              8
SWH                   31446.541 Hz
FIDRES                 0.239918 Hz
AQ                    2.0840447 sec
RG                      18390.4
DW                       15.900 usec
DE                        6.50 usec
TE                       300.2 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                         10.00 usec
PL1                        -1.70 dB
PL1W               148.61408997 W
SFO1                125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG[2                waltz16
NUC2                         1H
PCPD2                      80.00 usec
PL2                        -1.10 dB
PL12                       15.40 dB
PL13                       17.40 dB
PL2W               19.41561890 W
PL12W               0.43466163 W
PL13W               0.27425295 W
SFO2               500.3025017 MHz

F2 - Processing parameters
SI                        131072
SF                 125.8005277 MHz
WDW                           EM
SSB                            0
LB                          3.00 Hz
GB                             0
PC                          1.40
```

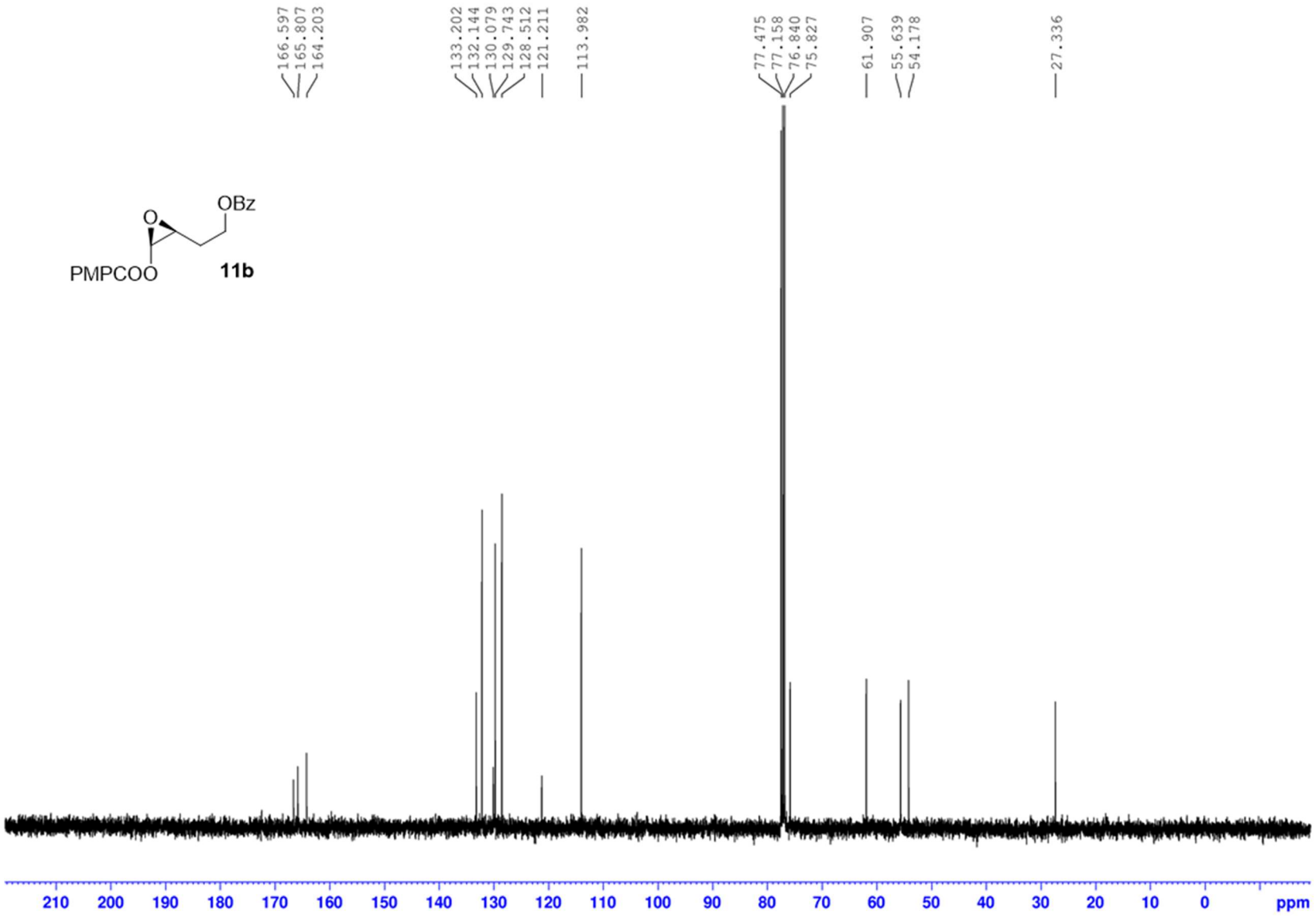

JNH_03_5
SPD-M20A-260 nm
JNH_03_5
JNH_03_5 exp 1 primary OTBS commercial ligand enolester epoxide.dat
Area Percent
Retention Time
OTBS
O
PMPCOO
11a
mAu
Minutes
0.850 7.612
99.150 8.292


JNH_03_12
SPD-M20A-280 nm
JNH_03_12
JNH_03_12 exp 1 primary OTBS racemic enolester epoxide.dat
Area Percent
Retention Time
OTBS
O
PMPCOO
11a
(and enantiomer)
49.422 7.788
50.578 8.364
mAu
Minutes






```
Current Data Parameters
NAME          JNH_02_211
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20210206
Time               17.36 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                   724
DW                62.400 usec
DE                16.92 usec
TE                297.2 K
D1           1.00000000 sec
TD0                    1
SFO1        400.1324708 MHz
NUC1                  1H
P0                 5.00 usec
P1                15.00 usec
PLW1          8.47000027 W

F2 - Processing parameters
SI                 65536
SF          400.1300097 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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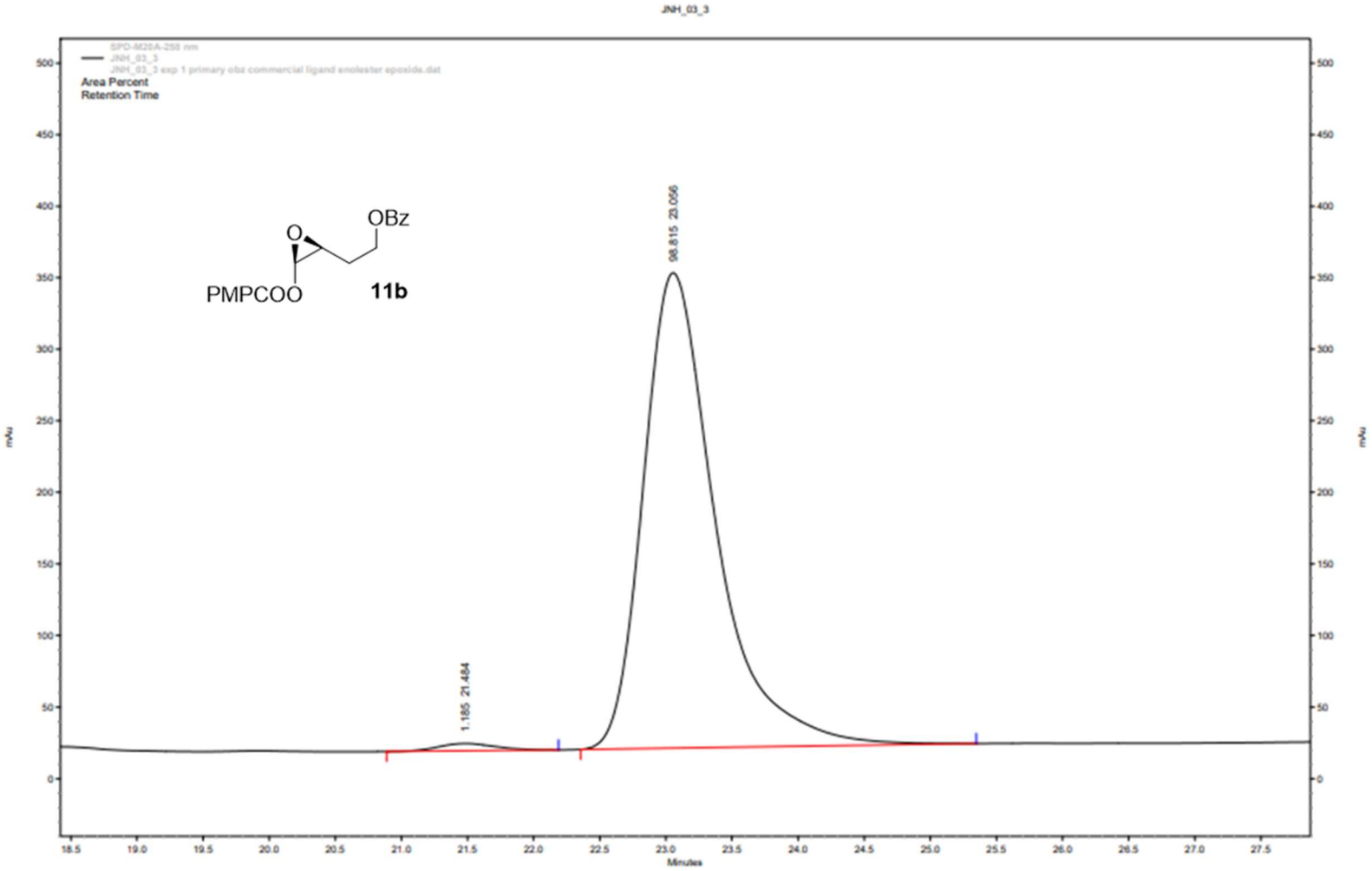
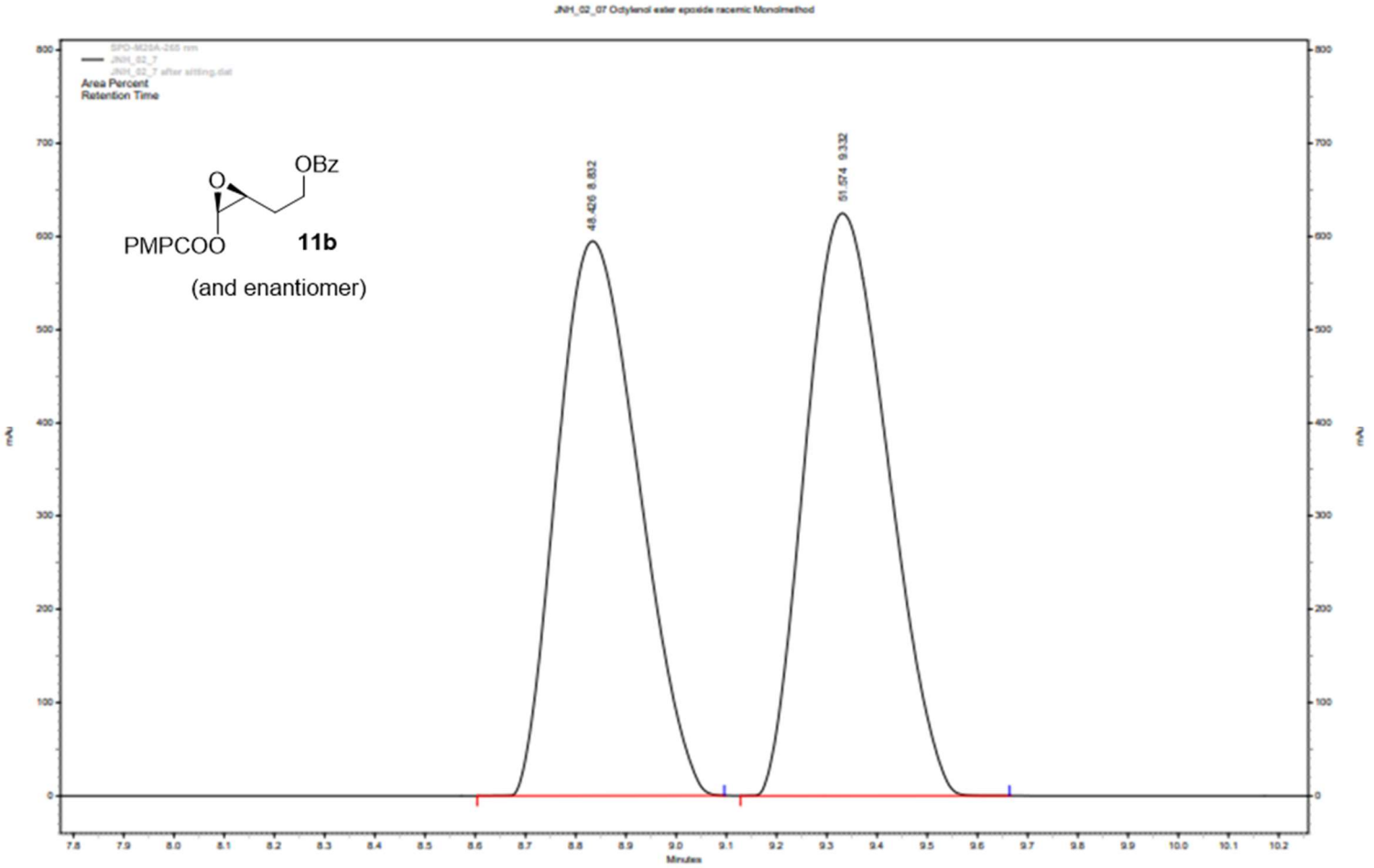
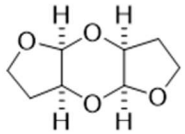
```
Current Data Parameters
NAME        JNH_03_3 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20220527
Time              19.58 h
INSTRUM           spect
PROBHD   Z104450_0192 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 101
DS                   2
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            1.3631488 sec
RG                 203
DW              20.800 usec
DE               6.50 usec
TE              298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1
SFO1        100.6228298 MHz
NUC1               13C
P0                3.28 usec
P1                9.85 usec
PLW1        28.63999939 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2       waltz65
PCPD2            90.00 usec
PLW2         8.47000027 W
PLW12        0.23528001 W
PLW13        0.11834000 W

F2 - Processing parameters
SI                32768
SF          100.6127561 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```


JNH_03_3
SPO-M20A-258 nm
JNH_03_3
JNH_03_3 exp 1 primary obz commercial ligand enolester epoxide.dat
Area Percent
Retention Time
OBz
O
PMPCOO
11b
98.815 23.056
1.185 21.484
mAu
Minutes


JNH_02_07 Octylenol ester epoxide racemic Monolmethod
SPD-M20A-265 nm
JNH_02_7
JNH_02_7 after sitting.dat
Area Percent
Retention Time
OBz
O
PMPCOO
11b
(and enantiomer)
48.426 8.832
51.574 9.332
mAU
Minutes



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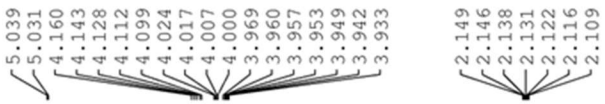
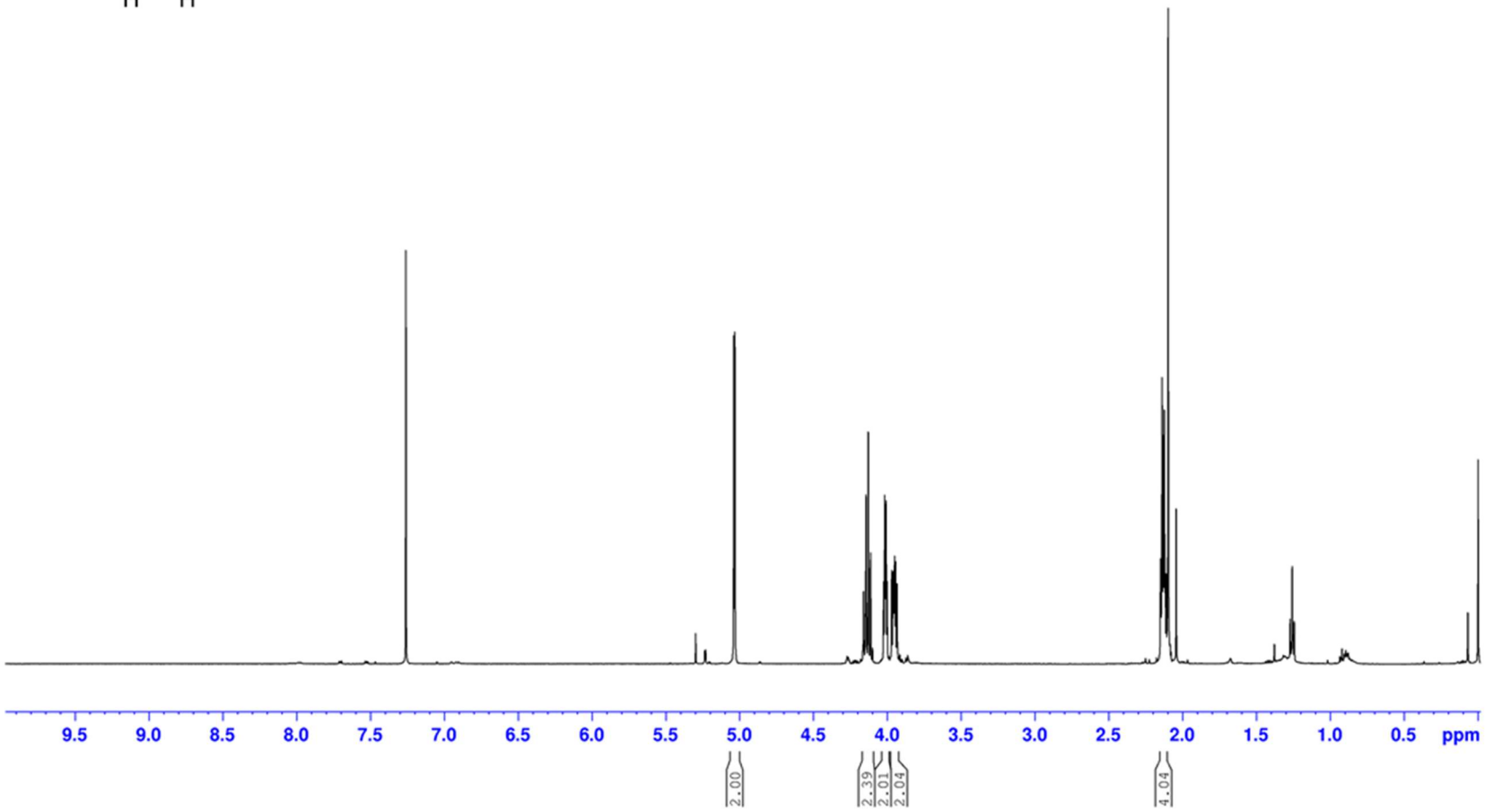
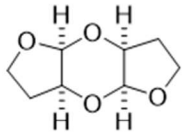


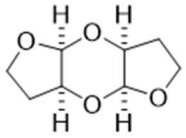



```
Current Data Parameters
NAME                  JNH_03_54
EXPNO                         9
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20220225
Time                      15.13 h
INSTRUM          Avance NEO 500
PROBHD           Z113652_0071 (
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                            8
DS                            2
SWH                    5000.000 Hz
FIDRES                 0.152588 Hz
AQ                     6.5535998 sec
RG                          101
DW                     100.000 usec
DE                      10.45 usec
TE                        300.0 K
D1                   5.00000000 sec
TD0                           1
SFO1                500.3025015 MHz
NUC1                        1H
P0                      4.00 usec
P1                     12.00 usec
PLW1                13.35999966 W

F2 - Processing parameters
SI                        65536
SF                  500.3000121 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

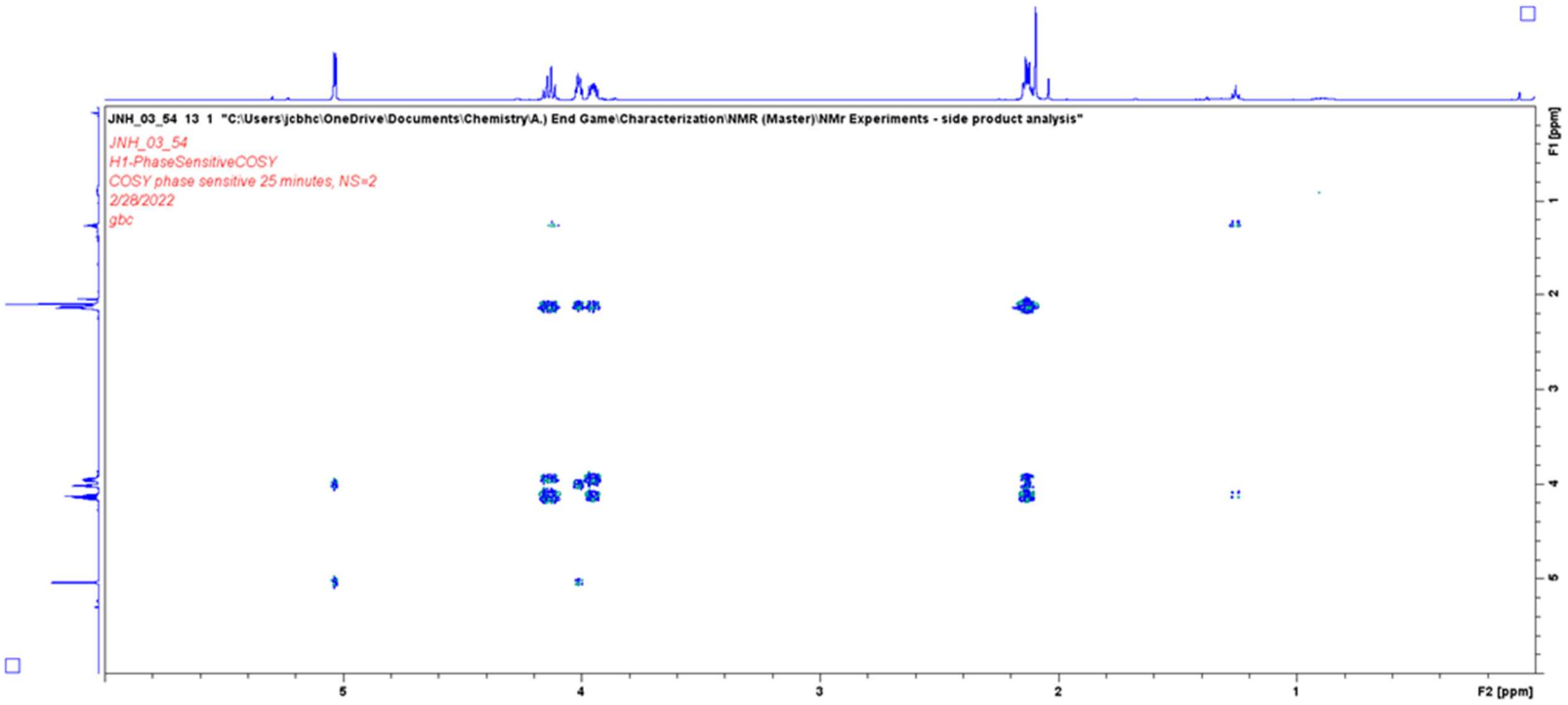


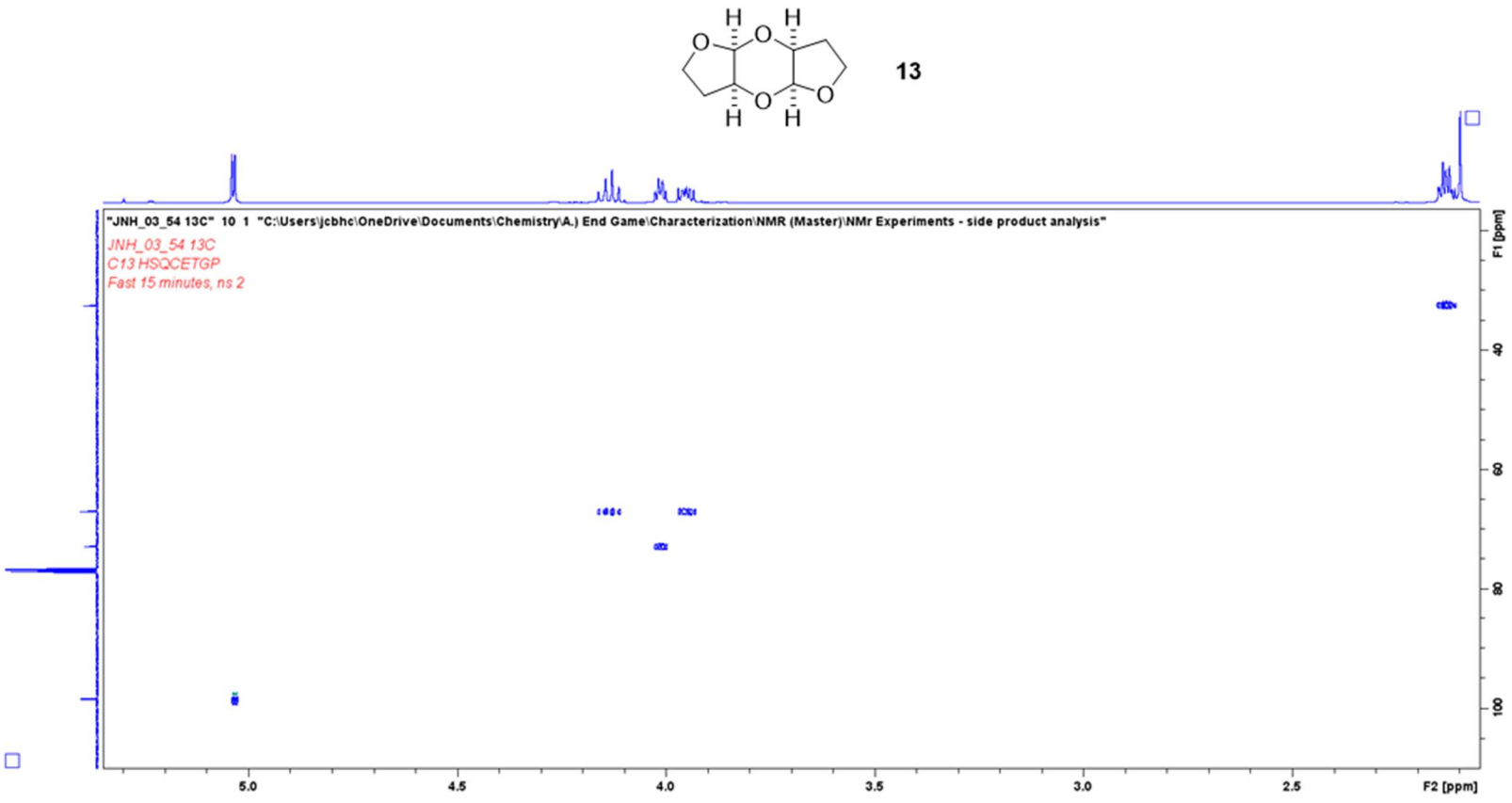
13

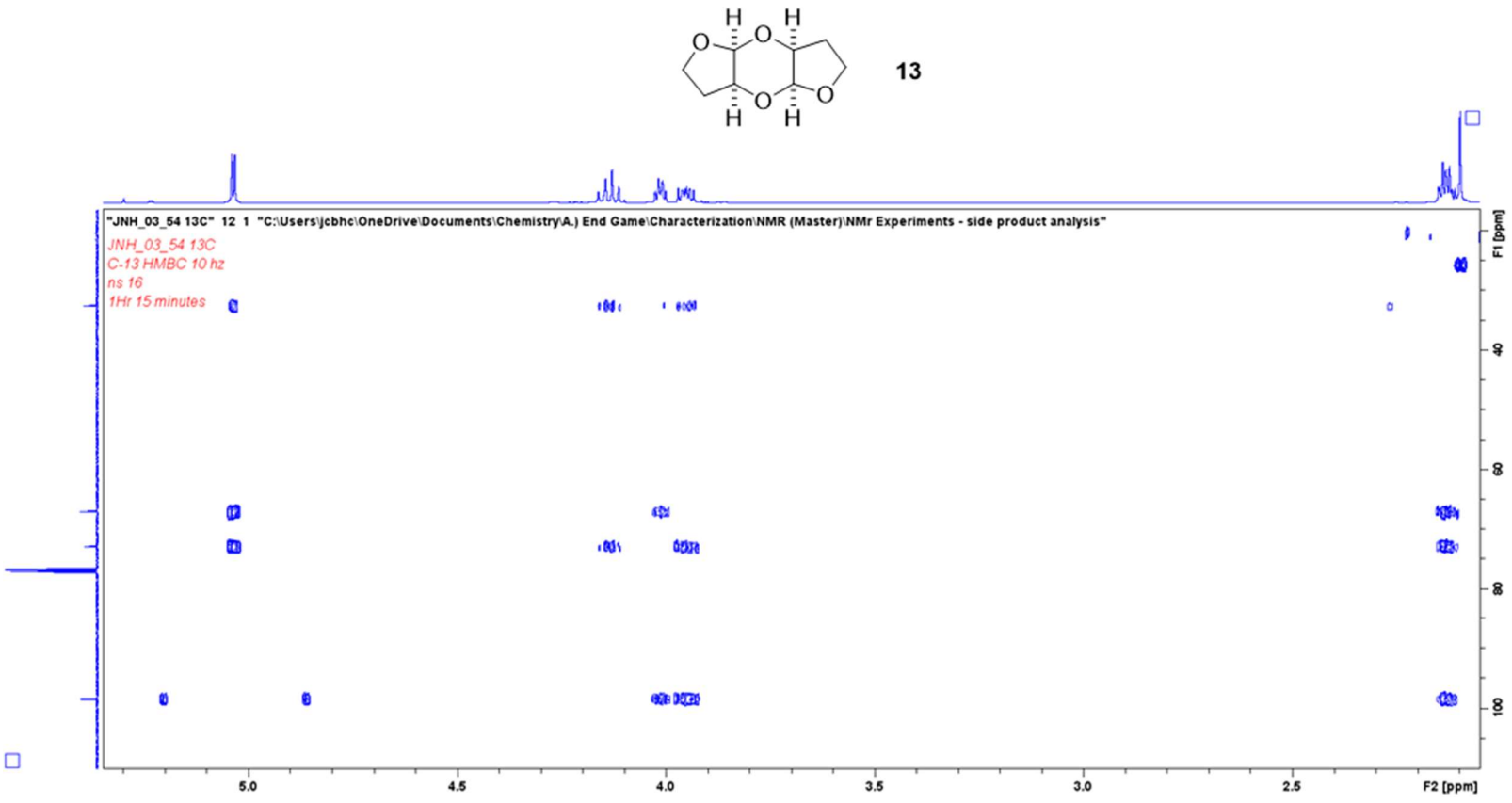

```
Current Data Parameters
NAME       JNH_03_54 13C
EXPNO                 8
PROCNO                1

F2 - Acquisition Parameters
Date_          20220225
Time              14.06 h
INSTRUM  Avance NEO 500
PROBHD   Z113652_0071 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  105
DS                    4
SWH           30120.482 Hz
FIDRES         0.919204 Hz
AQ             1.0878977 sec
RG                  101
DW               16.600 usec
DE               10.00 usec
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        125.8131151 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1       103.61000061 W
SFO2        500.3020012 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2            80.00 usec
PLW2        13.35999966 W
PLW12        0.30400079 W
PLW13        0.15236519 W

F2 - Processing parameters
SI                32768
SF          125.8005174 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

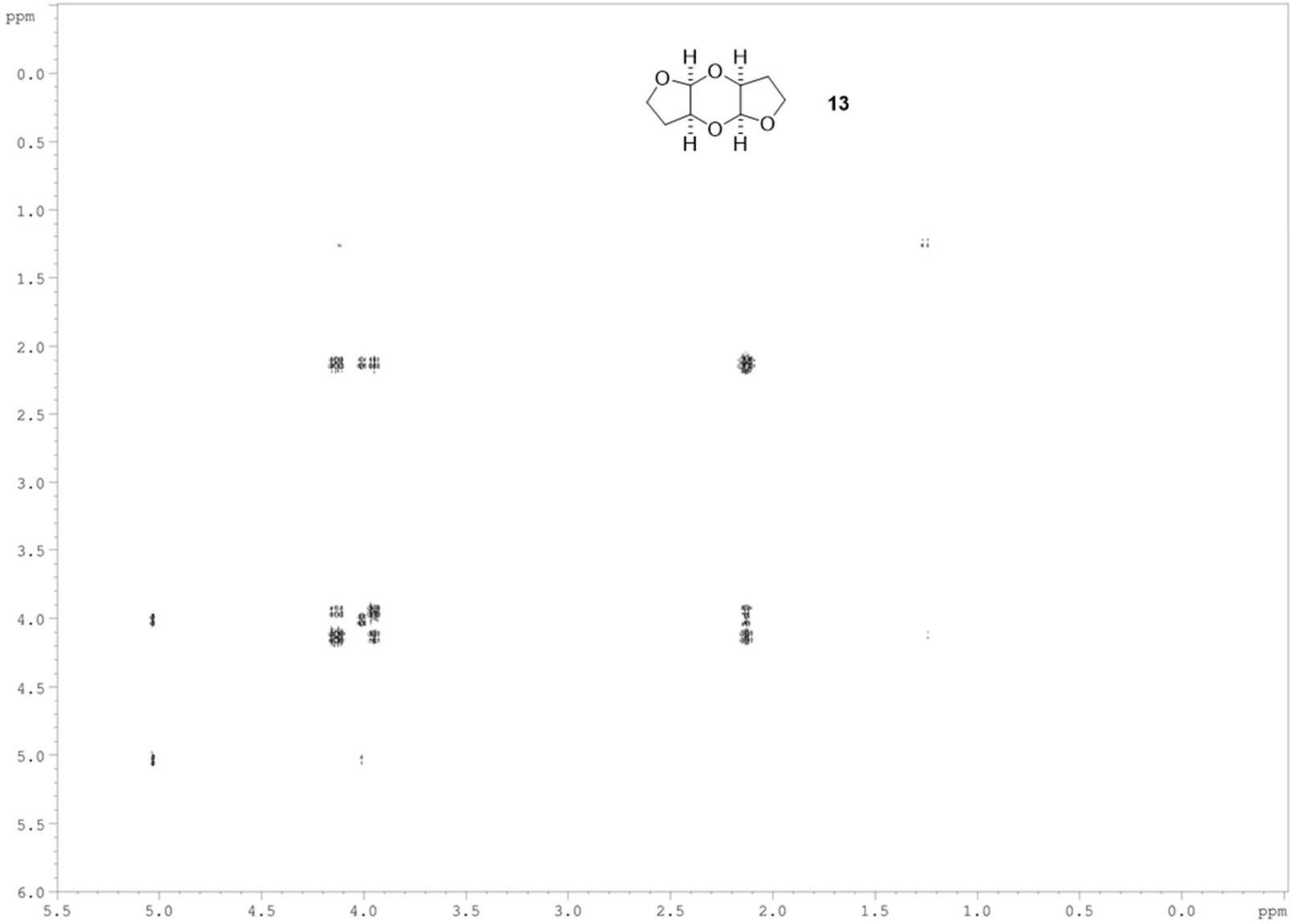


13


JNH_03_54 13 1 "C:\Users\jcbhc\OneDrive\Documents\Chemistry\A.) End Game\Characterization\NMR (Master)\NMr Experiments - side product analysis"
JNH_03_54
H1-PhaseSensitiveCOSY
COSY phase sensitive 25 minutes, NS=2
2/28/2022
gbc
F1 [ppm]
F2 [ppm]
5
4
3
2
1

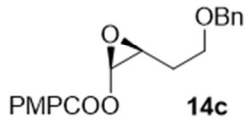

13
"JNH_03_54 13C" 10 1 "C:\Users\jcbhc\OneDrive\Documents\Chemistry\A.) End Game\Characterization\NMR (Master)\NMr Experiments - side product analysis"
JNH_03_54 13C
C13 HSQCETGP
Fast 15 minutes, ns 2
F1 [ppm]
F2 [ppm]
5.0
4.5
4.0
3.5
3.0
2.5
40
60
80
100


13
"JNH_03_54 13C" 12 1 "C:\Users\jcbhc\OneDrive\Documents\Chemistry\A.) End Game\Characterization\NMR (Master)\NMr Experiments - side product analysis"
JNH_03_54 13C
C-13 HMBC 10 hz
ns 16
1Hr 15 minutes
F1 [ppm]
F2 [ppm]
5.0
4.5
4.0
3.5
3.0
2.5
40
60
80
100

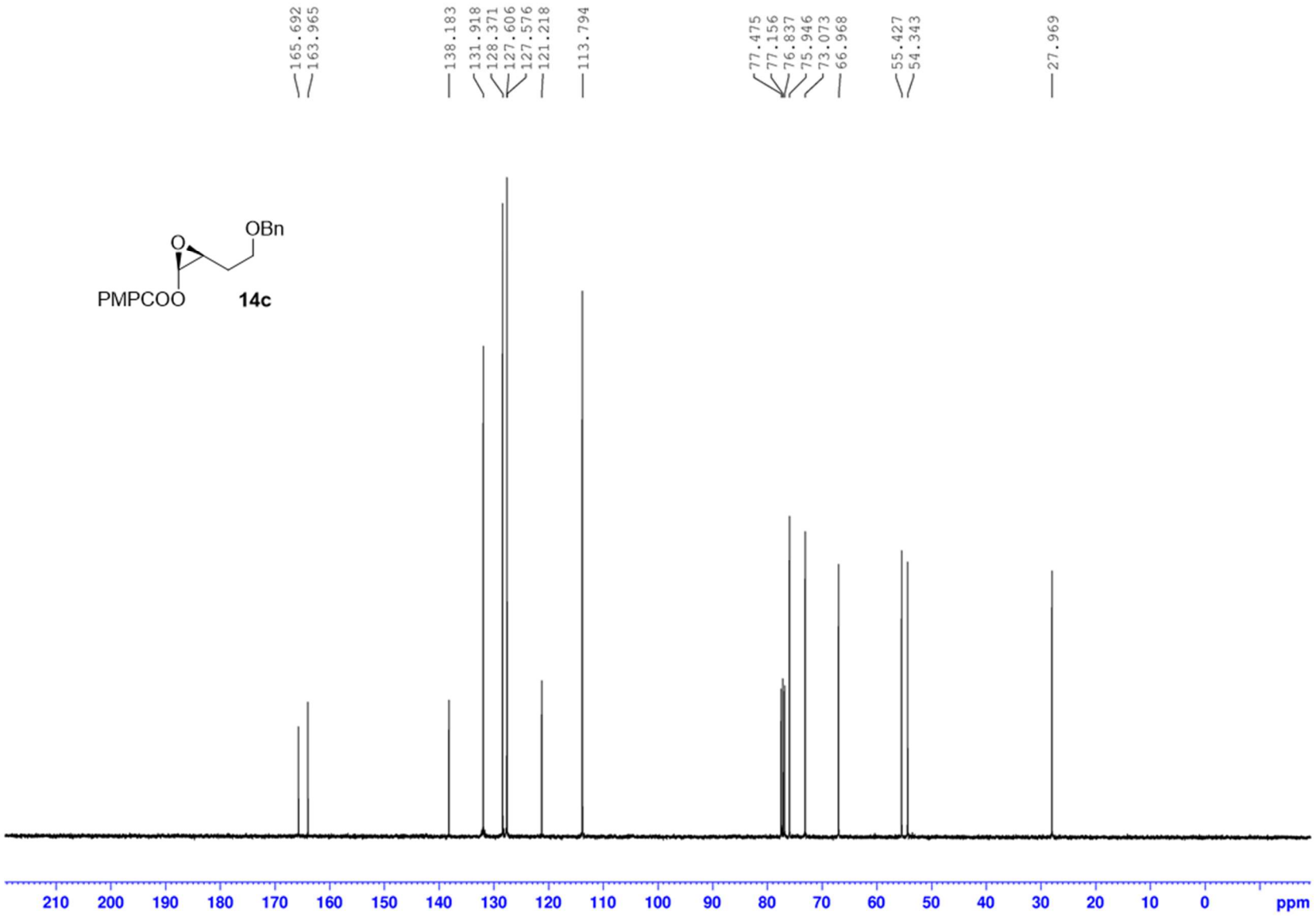


13

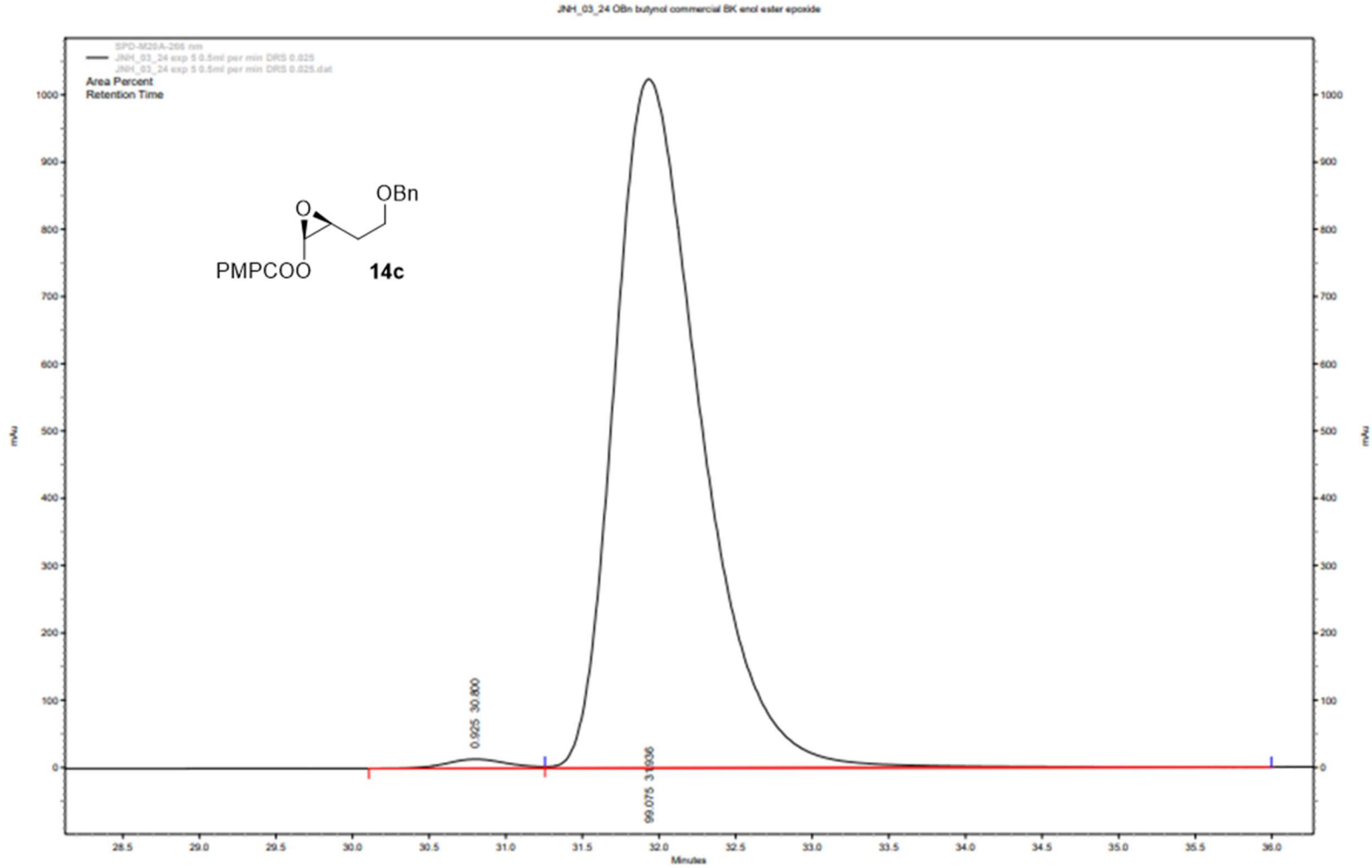

```
Current Data Parameters
NAME                  JNH_03_54
EXPNO                        13
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20220228
Time                       9.46 h
INSTRUM  Avance NEO 500
PROBHD   Z113652_0071 (
PULPROG     cosygpmfphpp
TD                         8192
SOLVENT                  CDCl3
NS                            2
DS                           16
SWH                  5000.000 Hz
FIDRES               1.220703 Hz
AQ                   0.8192000 sec
RG                           64
DW                    100.000 usec
DE                      6.50 usec
TE                     300.0 K
D0                   0.00008466 sec
D1                   2.00000000 sec
D11                  0.03000000 sec
D12                  0.00002000 sec
D16                  0.00020000 sec
IN0                  0.00019987 sec
TDav                          1
SFO1                500.3022514 MHz
NUC1                        1H
P1                       12.00 usec
P2                       24.00 usec
P17                    2500.00 usec
PLW1                13.35999966 W
PLW10                2.13750005 W
GPNAM[1]            SMSQ10.100
GPZ1                    10.00 %
GPNAM[2]            SMSQ10.100
GPZ2                    20.00 %
P16                    1000.00 usec

======== F1 INDIRECT DIMENSION ========
td1             256
sw_F1           10.000000

F1 - Acquisition parameters
TD                           256
SFO1                500.3023 MHz
FIDRES               39.086929 Hz
SW                      10.000 ppm
FnMODE           States-TPPI

F2 - Processing parameters
SI                         16384
SF                  500.3000121 MHz
WDW                        QSINE
SSB                            2
LB                             0 Hz
GB                             0
PC                          1.00

F1 - Processing parameters
SI                          1024
MC2              States-TPPI
SF                  500.3000121 MHz
WDW                        QSINE
SSB                            2
LB                             0 Hz
GB                             0
```

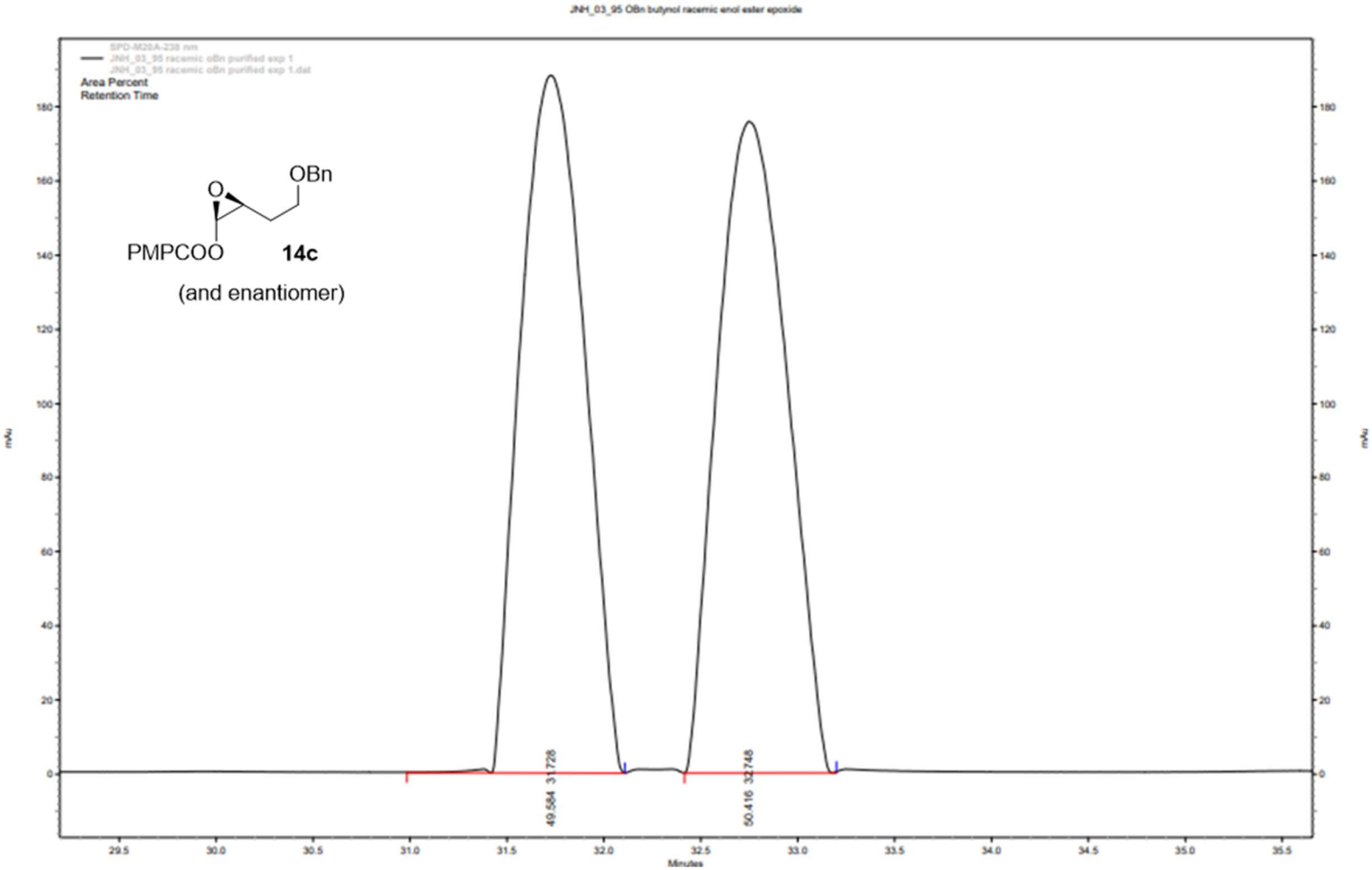


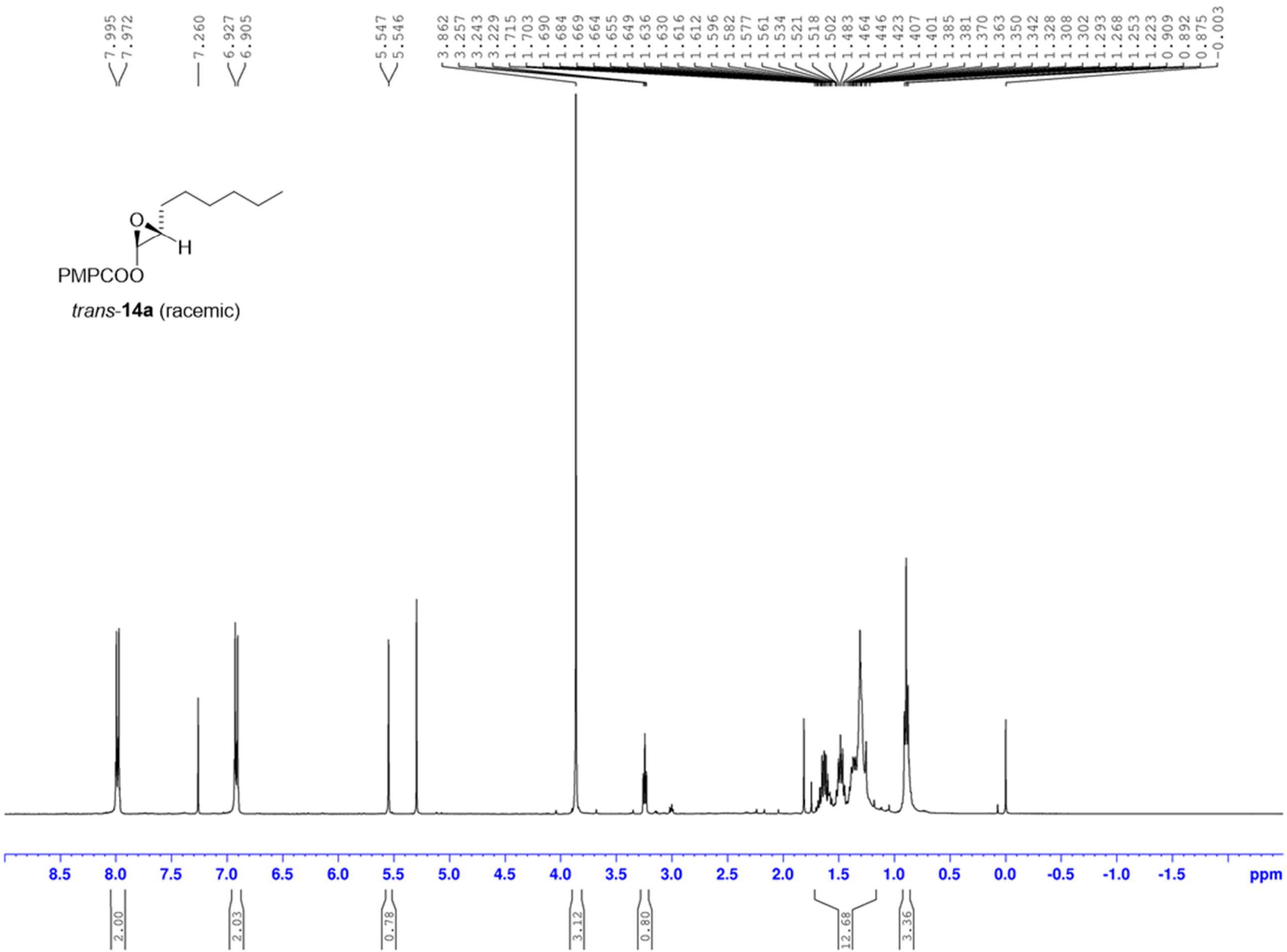

```
Current Data Parameters
NAME                  JNH_03_24
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20211123
Time                      14.24 h
INSTRUM                    spect
PROBHD    Z104450_0192 (
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                     4.0894465 sec
RG                           32
DW                        62.400 usec
DE                        16.92 usec
TE                        296.3 K
D1                  1.00000000 sec
TD0                           1
SFO1                400.1324708 MHz
NUC1                        1H
P0                         5.00 usec
P1                        15.00 usec
PLW1                 8.47000027 W

F2 - Processing parameters
SI                        65536
SF                  400.1300060 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```



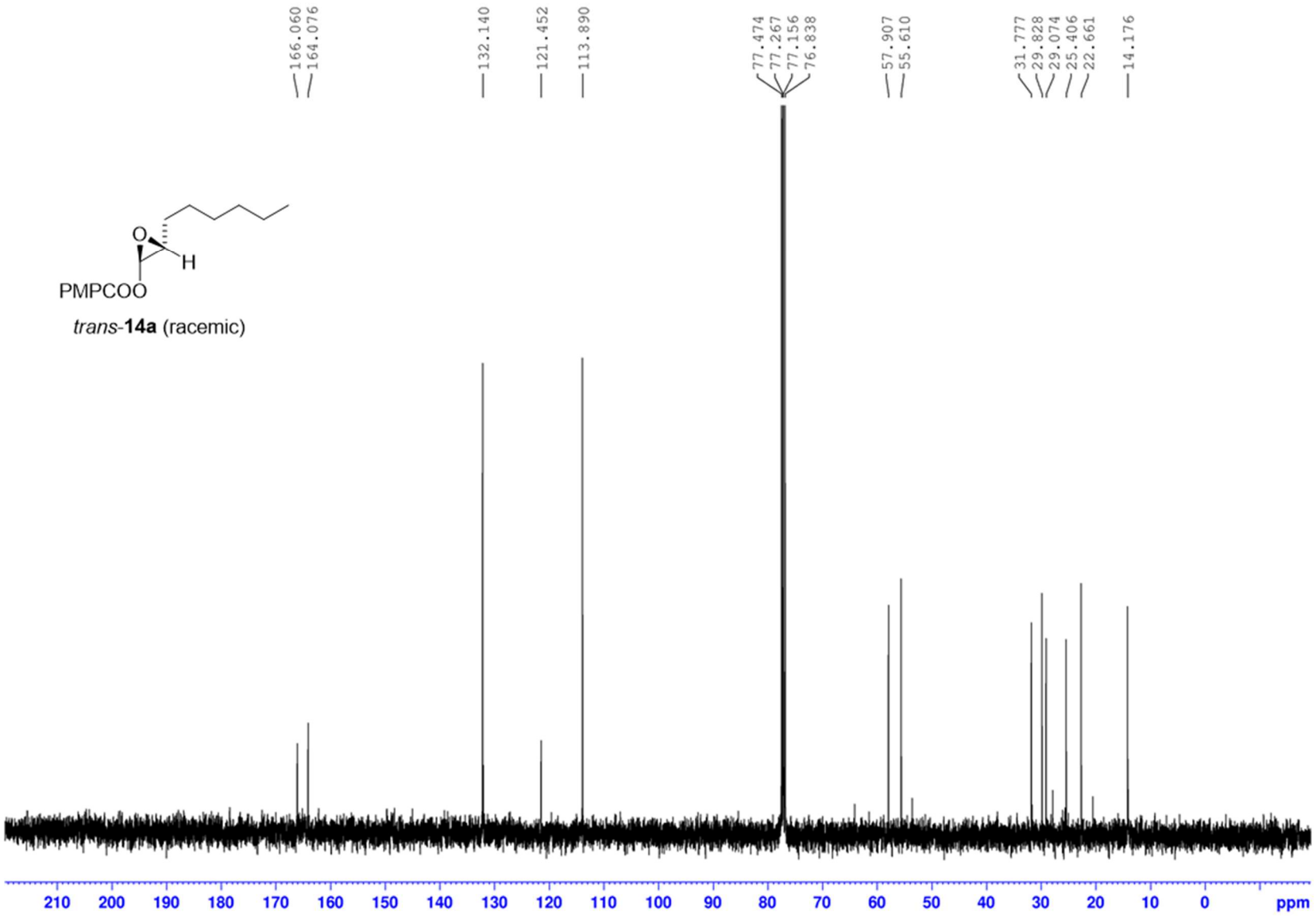

```
Current Data Parameters
NAME       JNH_03_24 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20211123
Time              14.36 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 100
DS                   2
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            1.3631488 sec
RG                 203
DW              20.800 usec
DE               6.50 usec
TE              296.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1
SFO1        100.6228298 MHz
NUC1               13C
P0                3.28 usec
P1                9.85 usec
PLW1        28.63999939 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2       waltz65
PCPD2            90.00 usec
PLW2         8.47000027 W
PLW12        0.23528001 W
PLW13        0.11834000 W

F2 - Processing parameters
SI                32768
SF          100.6127762 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```


JNH_03_24 OBn butynol commercial BK enol ester epoxide
SPD-M20A-295 nm
JNH_03_24 exp 5 0.5ml per min DRS 0.025
JNH_03_24 exp 5 0.5ml per min DRS 0.025.dat
Area Percent
Retention Time
OBn
O
PMPCOO
14c
mAu
0.925 30.800
99.075 31.936
Minutes

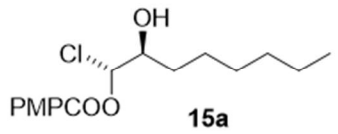

JNH_03_95 OBn butynol racemic enol ester epoxide
SPD-M20A-230.nm
JNH_03_95 racemic oBn purified exp 1
JNH_03_95 racemic oBn purified exp 1.dat
Area Percent
Retention Time
OBn
O
PMPCOO
14c
(and enantiomer)
mAu
49.584 31.728
50.416 32.748
Minutes



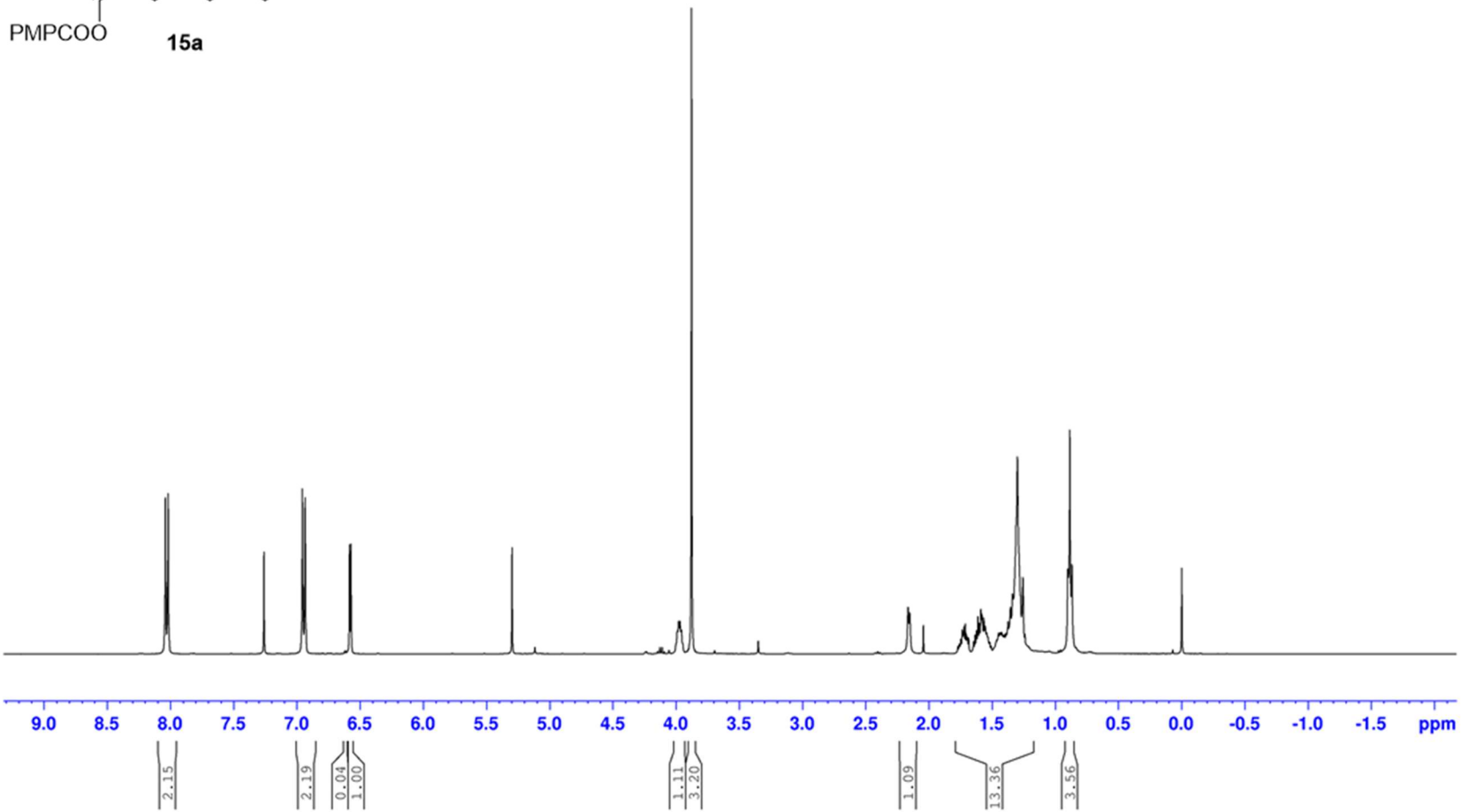

```
Current Data Parameters
NAME                  JNH_03_75
EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20220413
Time                      15.48 h
INSTRUM                   spect
PROBHD    Z104450_0192 (
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                     4.0894465 sec
RG                         144
DW                        62.400 usec
DE                        16.92 usec
TE                        297.3 K
D1                  1.00000000 sec
TD0                          1
SFO1                400.1324708 MHz
NUC1                        1H
P0                         5.00 usec
P1                        15.00 usec
PLW1                8.47000027 W

F2 - Processing parameters
SI                       65536
SF                  400.1300096 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



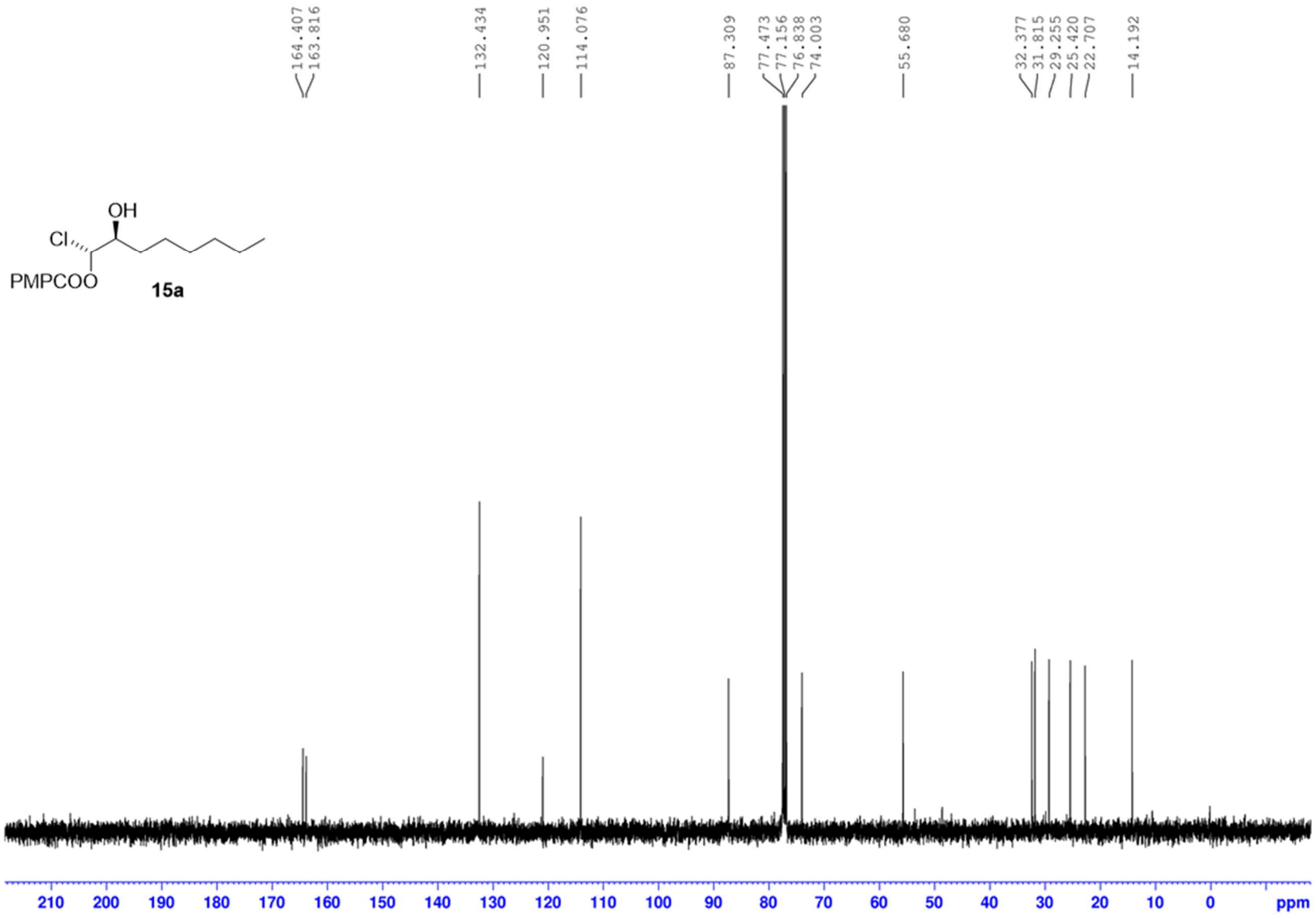

```
Current Data Parameters
NAME       JNH_03_75 13C
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20220413
Time              16.01 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  100
DS                    2
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG                  181
DW               20.800 usec
DE                6.50 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1                13C
P0                 3.28 usec
P1                 9.85 usec
PLW1        28.63999939 W
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz65
PCPD2             90.00 usec
PLW2         8.47000027 W
PLW12        0.23528001 W
PLW13        0.11834000 W

F2 - Processing parameters
SI                32768
SF        100.6127557 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



15a

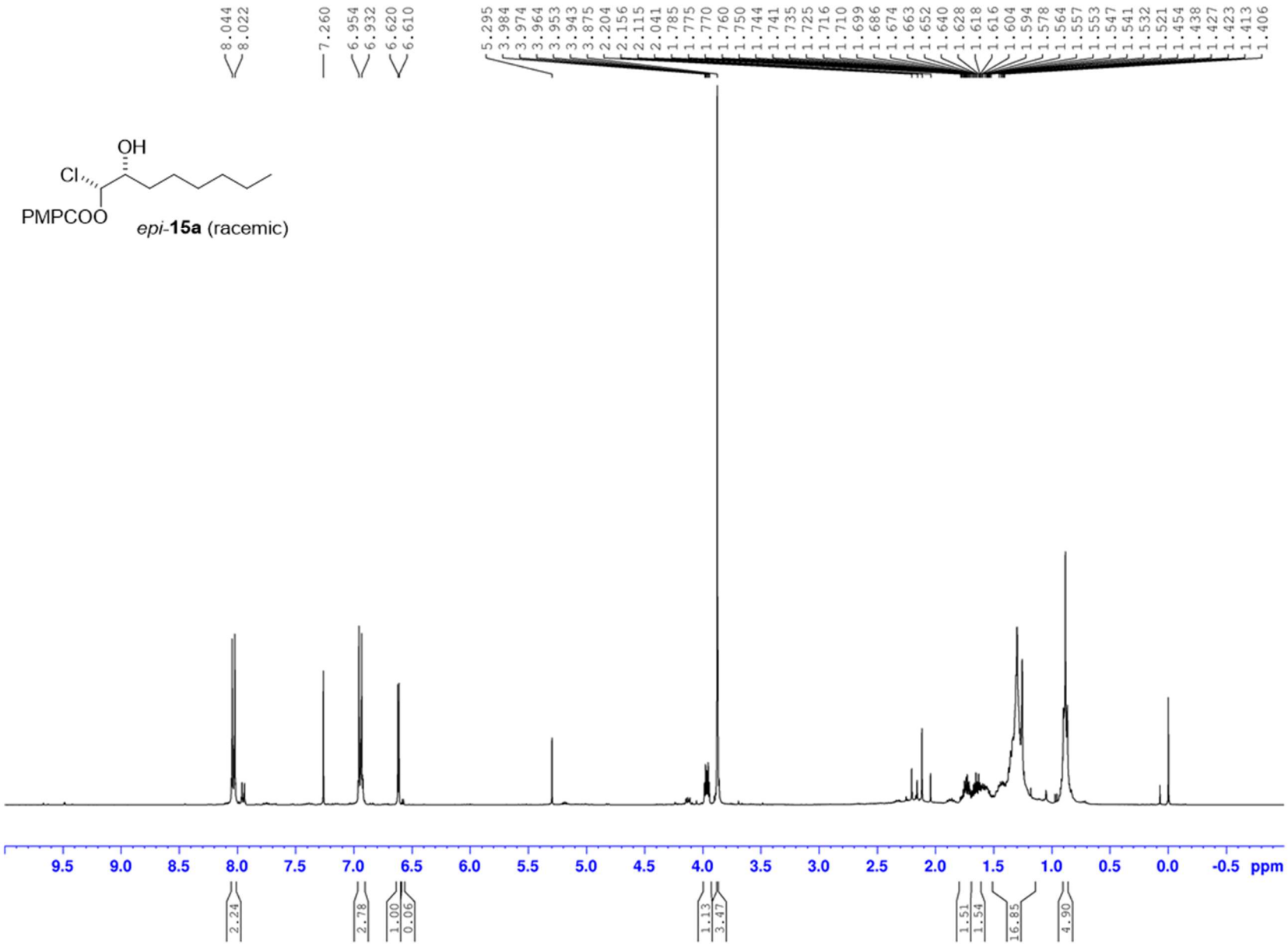



```
Current Data Parameters
NAME            JNH_03_76
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220418
Time                10.44 h
INSTRUM             spect
PROBHD    Z104450_0192 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                   161
DW                62.400 usec
DE                16.92 usec
TE                297.3 K
D1            1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P0                 5.00 usec
P1                15.00 usec
PLW1          8.47000027 W

F2 - Processing parameters
SI                 65536
SF           400.1300094 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

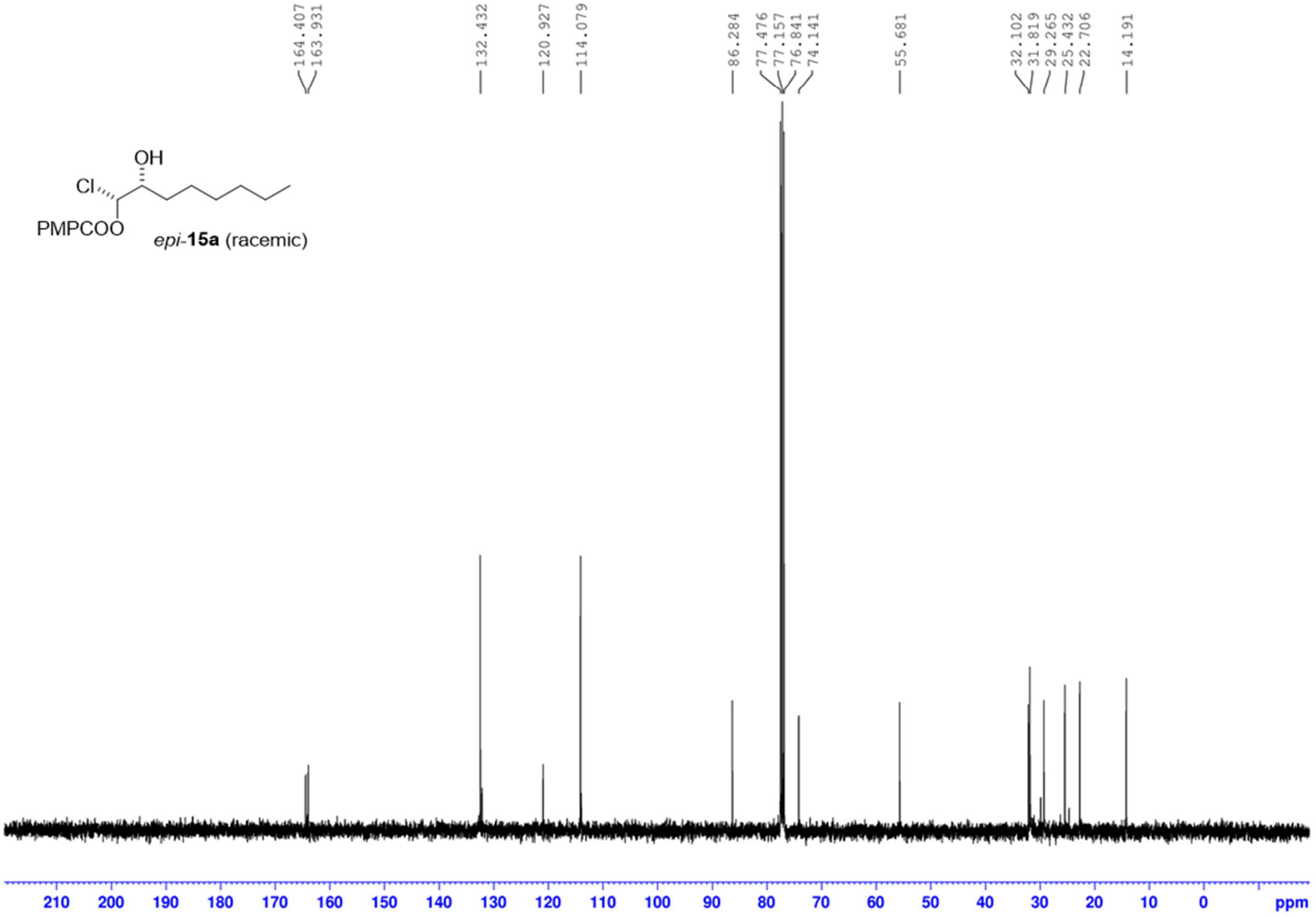


BRUKER

```
Current Data Parameters
NAME       JNH_03_76 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20220418
Time              10.58 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 112
DS                   2
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            1.3631488 sec
RG                 203
DW              20.800 usec
DE               6.50 usec
TE              297.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                  1
SFO1        100.6228298 MHz
NUC1               13C
P0                3.28 usec
P1                9.85 usec
PLW1        28.63999939 W
SFO2        400.1316005 MHz
NUC2               1H
CPDPRG[2        waltz65
PCPD2            90.00 usec
PLW2         8.47000027 W
PLW12        0.23528001 W
PLW13        0.11834000 W

F2 - Processing parameters
SI                32768
SF          100.6127554 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC                1.40
```

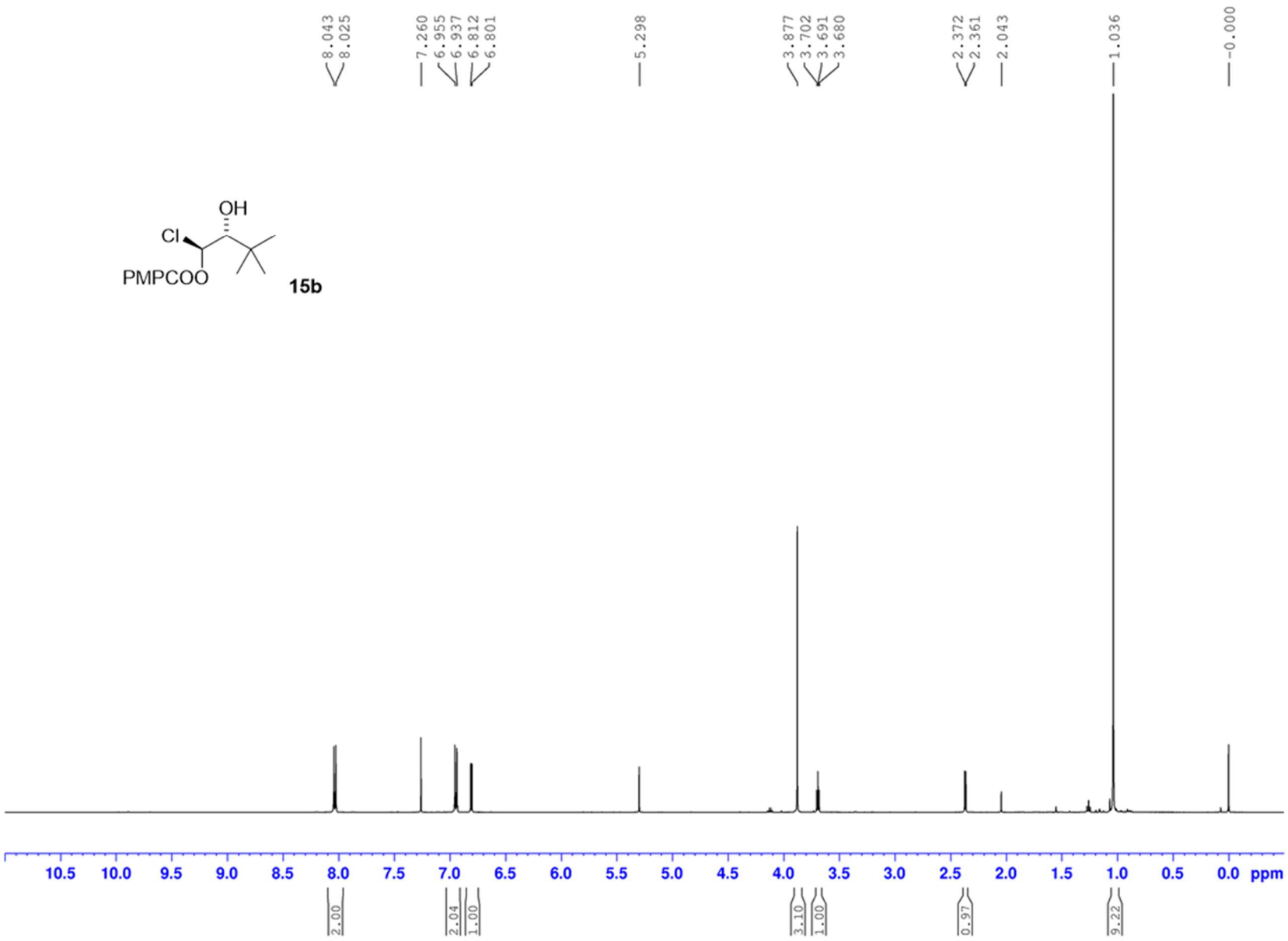



```
Current Data Parameters
NAME                  JNH_03_77
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20220420
Time                      12.43 h
INSTRUM                   spect
PROBHD    Z104450_0192 (
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                    8012.820 Hz
FIDRES                 0.244532 Hz
AQ                     4.0894465 sec
RG                         128
DW                      62.400 usec
DE                      16.92 usec
TE                      296.9 K
D1                  1.00000000 sec
TD0                          1
SFO1                400.1324708 MHz
NUC1                        1H
P0                       5.00 usec
P1                      15.00 usec
PLW1                 8.47000027 W

F2 - Processing parameters
SI                       65536
SF                  400.1300095 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



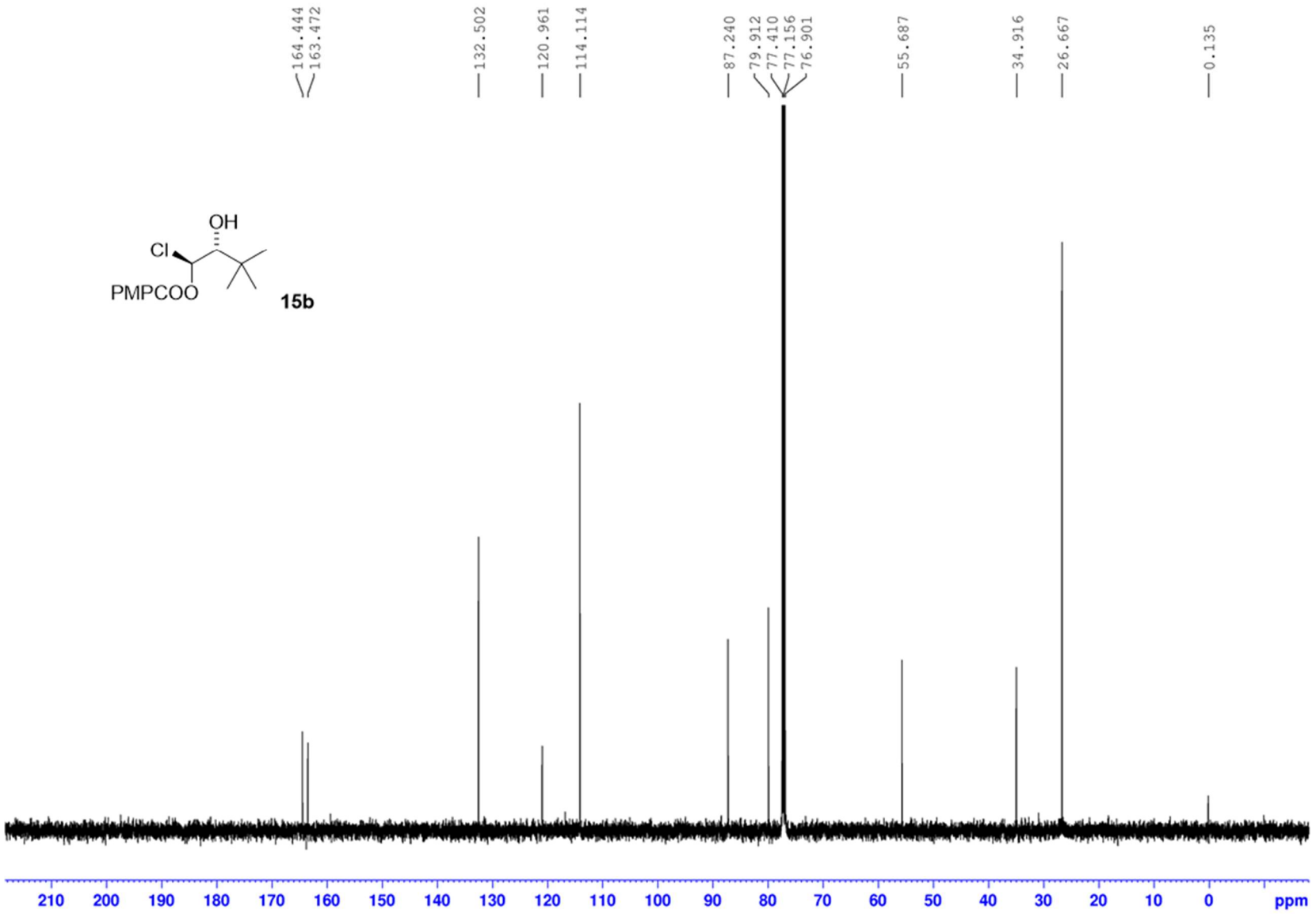
BRUKER

```
Current Data Parameters
NAME        JNH_03_77 13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220420
Time              13.01 h
INSTRUM             spect
PROBHD   Z104450_0192 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                  138
DS                    2
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ             1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE              297.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1                13C
P0                 3.28 usec
P1                 9.85 usec
PLW1        28.63999939 W
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2         8.47000027 W
PLW12        0.23528001 W
PLW13        0.11934000 W

F2 - Processing parameters
SI                32768
SF          100.6127557 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



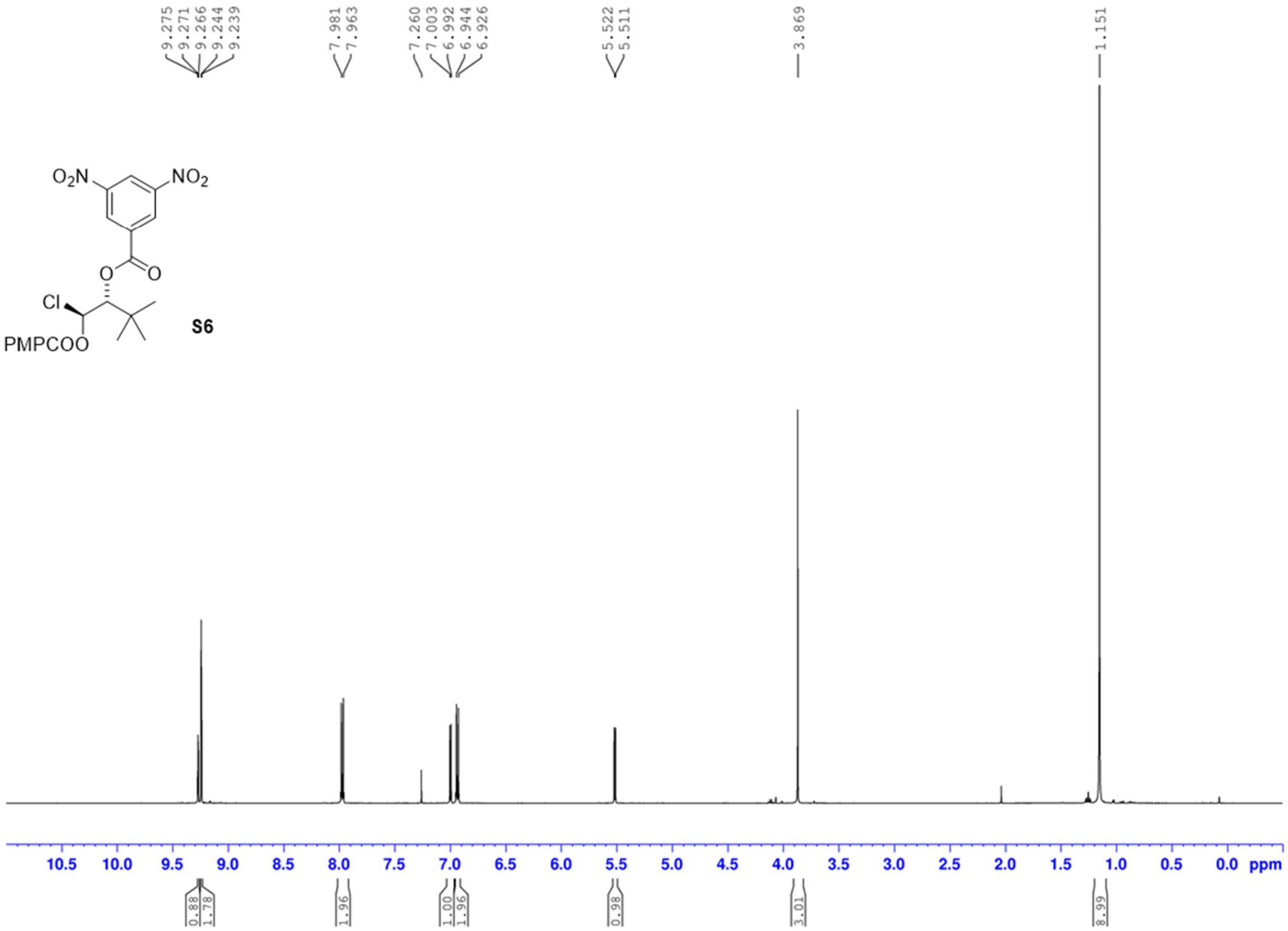
BRUKER

```
Current Data Parameters
NAME                  JNH_03_59
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20220310
Time                      15.49 h
INSTRUM          Avance NEO 500
PROBHD           Z113652_0071 (
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  10000.000 Hz
FIDRES                0.305176 Hz
AQ                    3.2767999 sec
RG                          101
DW                       50.000 usec
DE                       10.45 usec
TE                       300.0 K
D1                    1.00000000 sec
TD0                           1
SFO1                500.3030894 MHz
NUC1                        1H
P0                        4.00 usec
P1                       12.00 usec
PLW1                13.35999966 W

F2 - Processing parameters
SI                       65536
SF                  500.3000118 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



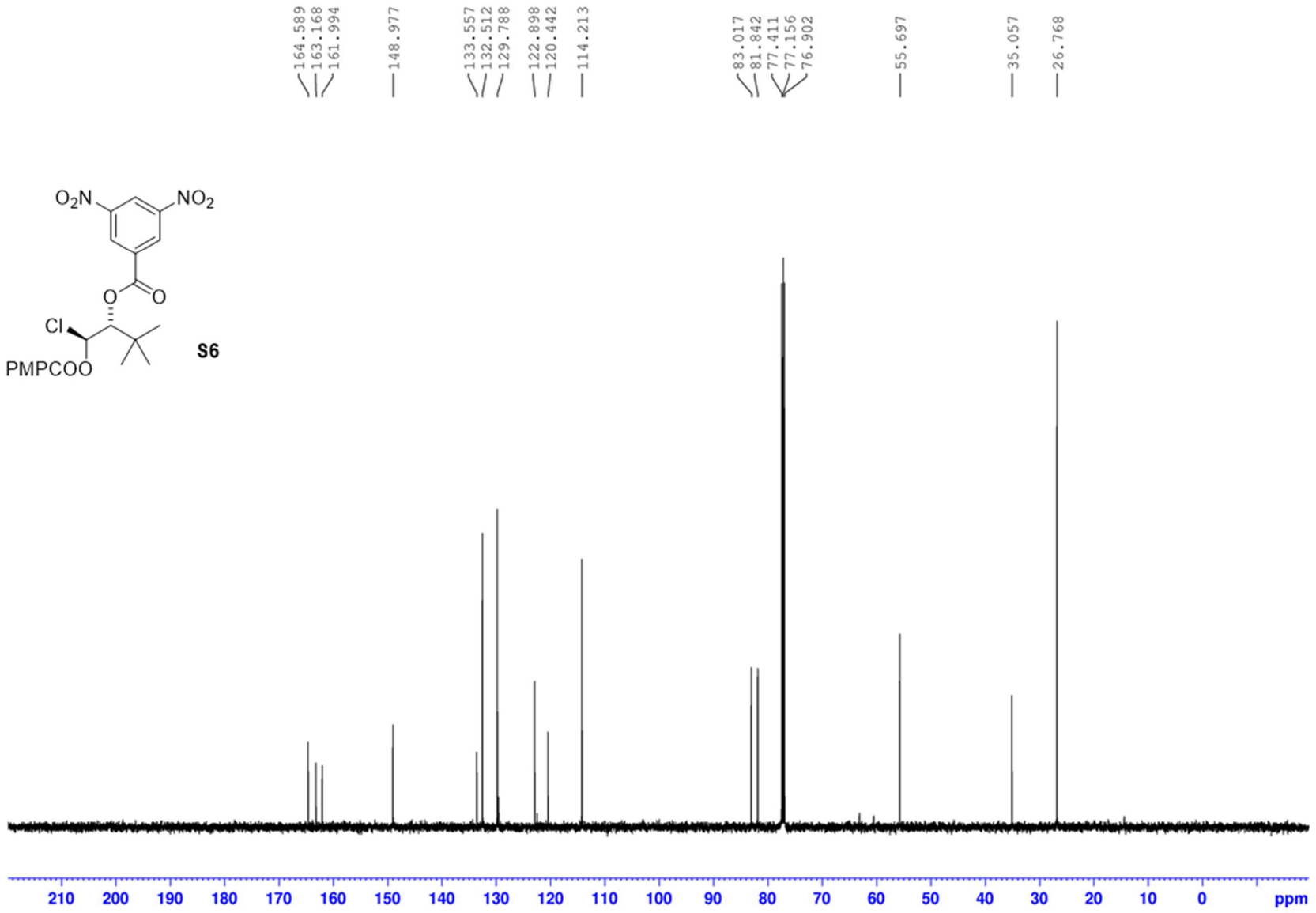
BRUKER

```
Current Data Parameters
NAME       JNH_03_59 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20220310
Time              16.03 h
INSTRUM  Avance NEO 500
PROBHD   Z113652_0071 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  167
DS                    4
SWH           30120.482 Hz
FIDRES         0.919204 Hz
AQ            1.0878977 sec
RG                  101
DW               16.600 usec
DE               10.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.8131151 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1       103.61000061 W
SFO2        500.3020012 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2            80.00 usec
PLW2        13.35999966 W
PLW12        0.30400079 W
PLW13        0.15236519 W

F2 - Processing parameters
SI                32768
SF          125.8005174 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

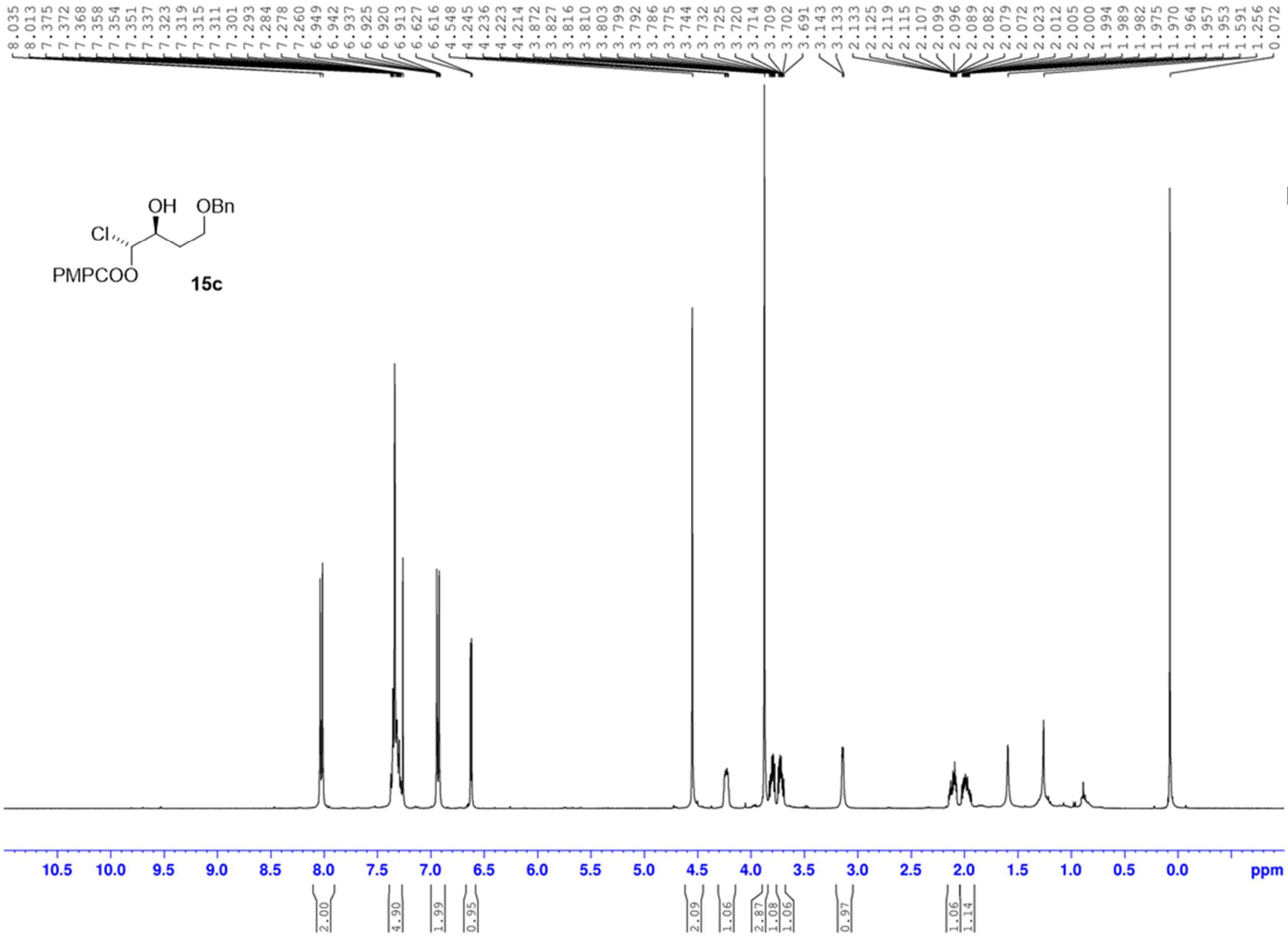


BRUKER

```
Current Data Parameters
NAME          JNH_03_109
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20220627
Time               16.54 h
INSTRUM  Avance NEO 500
PROBHD   Z113652_0071 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                   101
DW                50.000 usec
DE                10.45 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1
SFO1         500.3030894 MHz
NUC1                  1H
P0                 4.00 usec
P1                12.00 usec
PLW1         13.35999966 W

F2 - Processing parameters
SI                 65536
SF           500.3000121 MHz
WDW                   no
SSB                    0
LB                     0 Hz
GB                     0
PC                  1.00
```

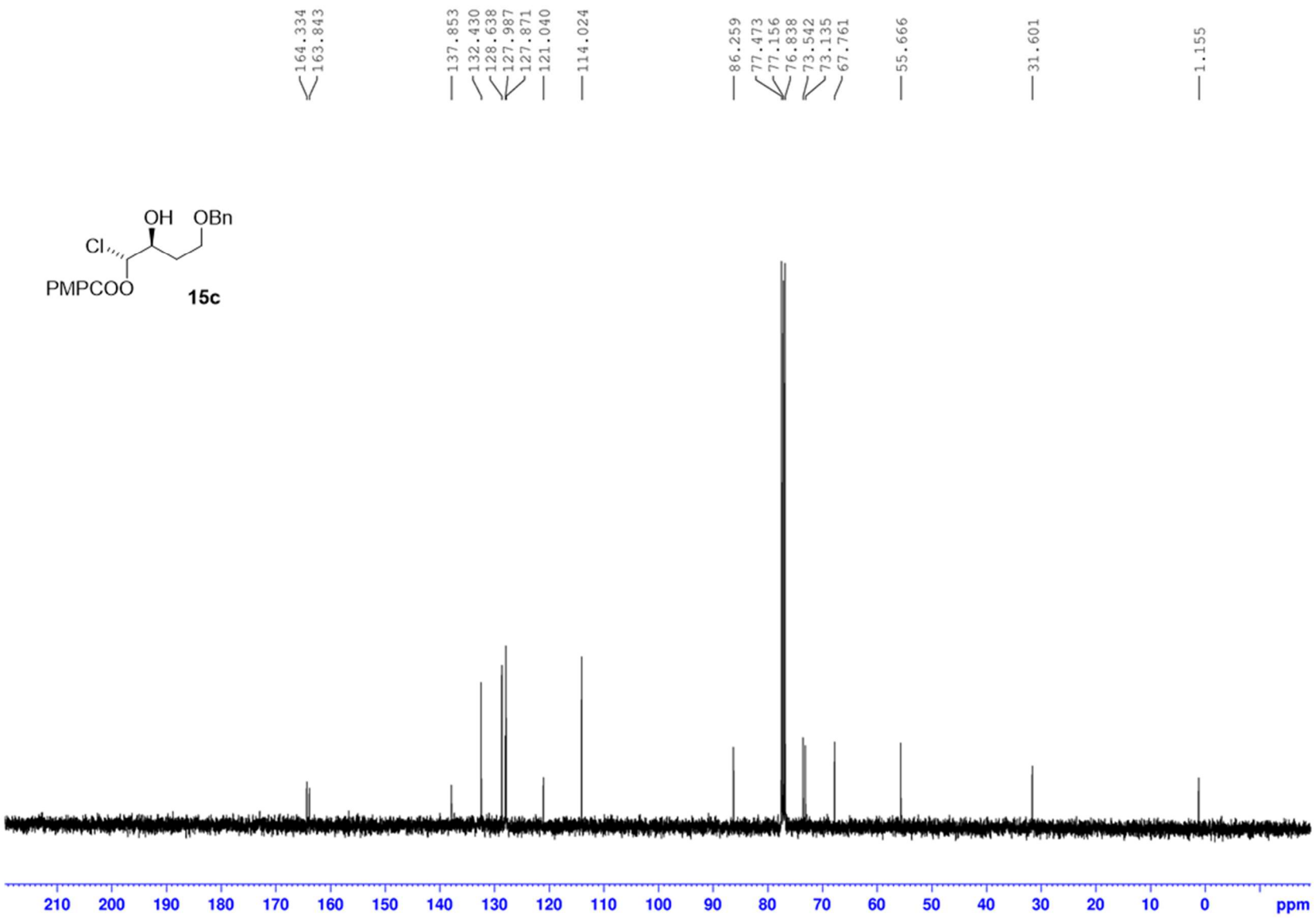



```
Current Data Parameters
NAME      JNH_03_109 13C
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20220627
Time               17.06 h
INSTRUM  Avance NEO 500
PROBHD   Z113652_0071 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   72
DS                    4
SWH           30120.482 Hz
FIDRES         0.919204 Hz
AQ             1.0878977 sec
RG                  101
DW               16.600 usec
DE               10.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1        125.8131151 MHz
NUC1                13C
P0                3.33 usec
P1               10.00 usec
PLW1       103.61000061 W
SFO2        500.3020012 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2            80.00 usec
PLW2        13.35999966 W
PLW12        0.30400079 W
PLW13        0.15236519 W

F2 - Processing parameters
SI                32768
SF          125.8005202 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

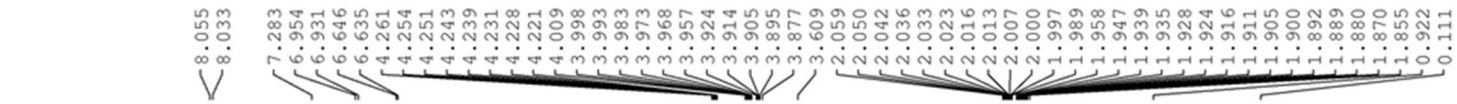


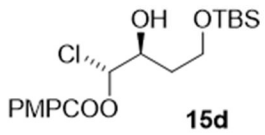
BRUKER

```
Current Data Parameters
NAME        JSA-01-30 1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20230103
Time              13.13 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.244532 Hz
AQ              4.0894465 sec
RG                   203
DW                62.400 usec
DE                16.92 usec
TE                296.8 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P0                 5.00 usec
P1                15.00 usec
PLW1           8.47000027 W

F2 - Processing parameters
SI                 65536
SF            400.1300096 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



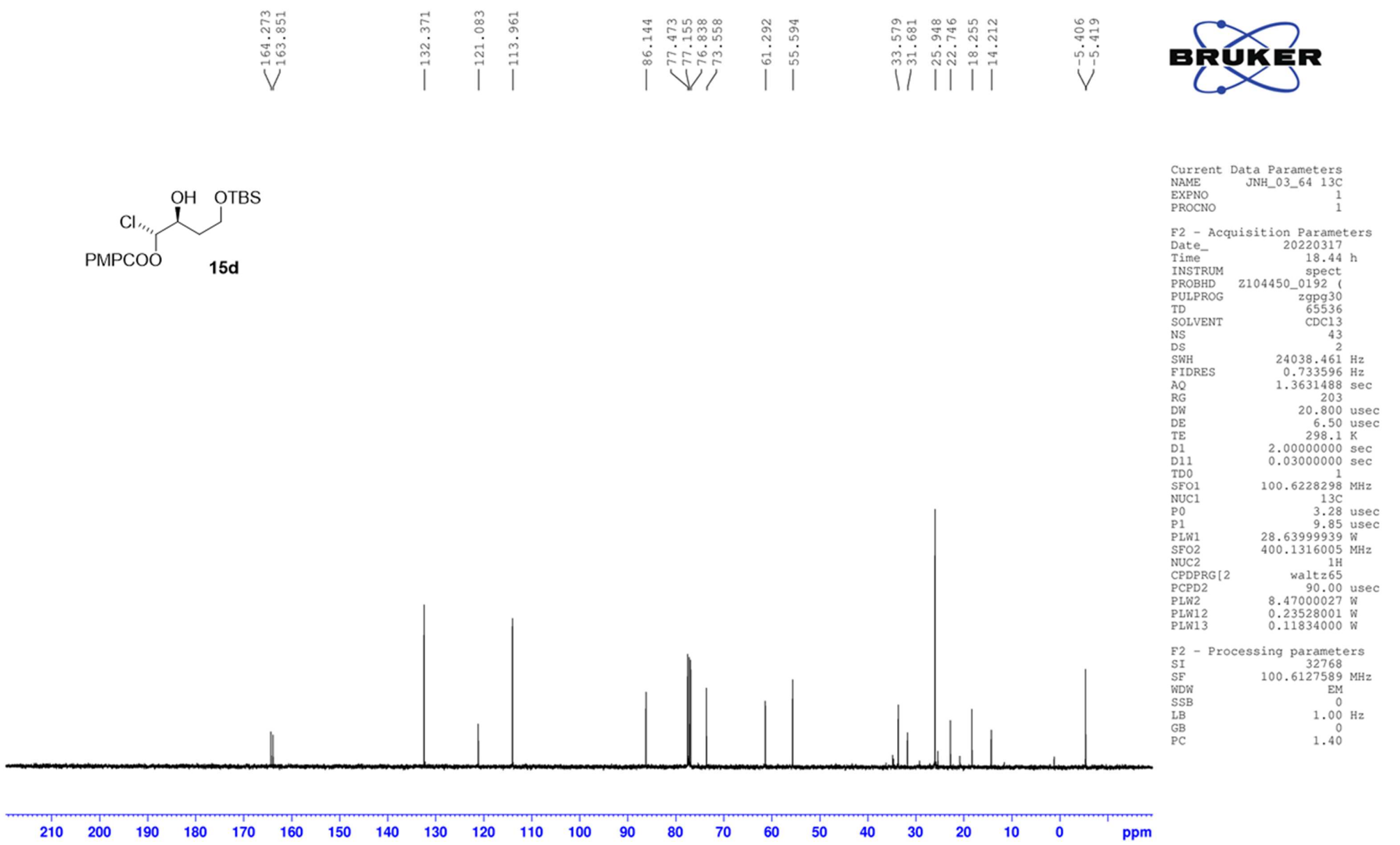

```
Current Data Parameters
NAME       JSA-01-30 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20230103
Time               13.36 h
INSTRUM            spect
PROBHD   Z104450_0192 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  113
DS                    2
SWH            24038.461 Hz
FIDRES         0.733596 Hz
AQ             1.3631488 sec
RG                  203
DW                20.800 usec
DE                 6.50 usec
TE                297.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1         100.6228298 MHz
NUC1                13C
P0                 3.28 usec
P1                 9.85 usec
PLW1         28.63999939 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             90.00 usec
PLW2          8.47000027 W
PLW12         0.23528001 W
PLW13         0.11834000 W

F2 - Processing parameters
SI                 32768
SF           100.6127561 MHz
WDW                   EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



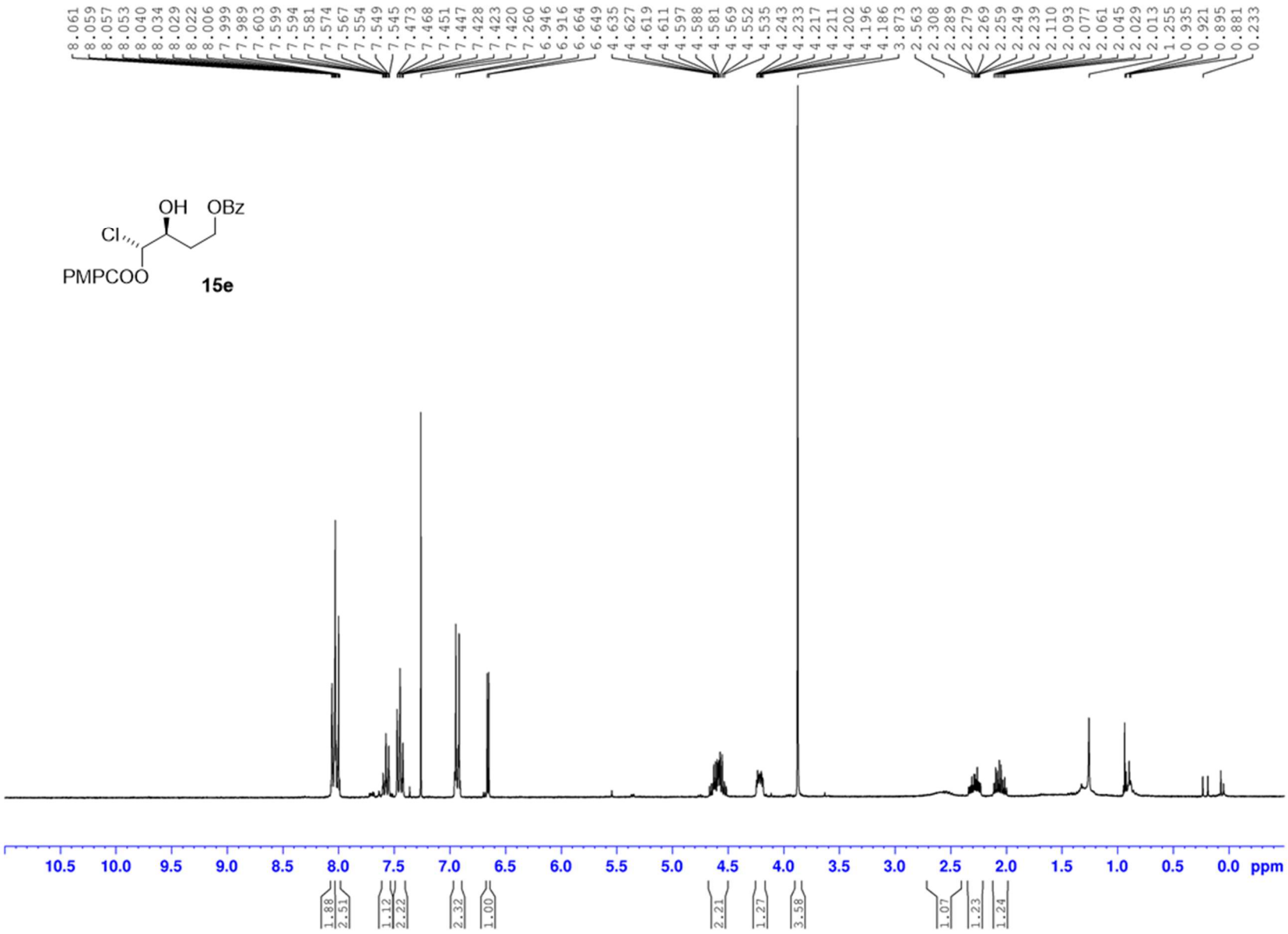


15d

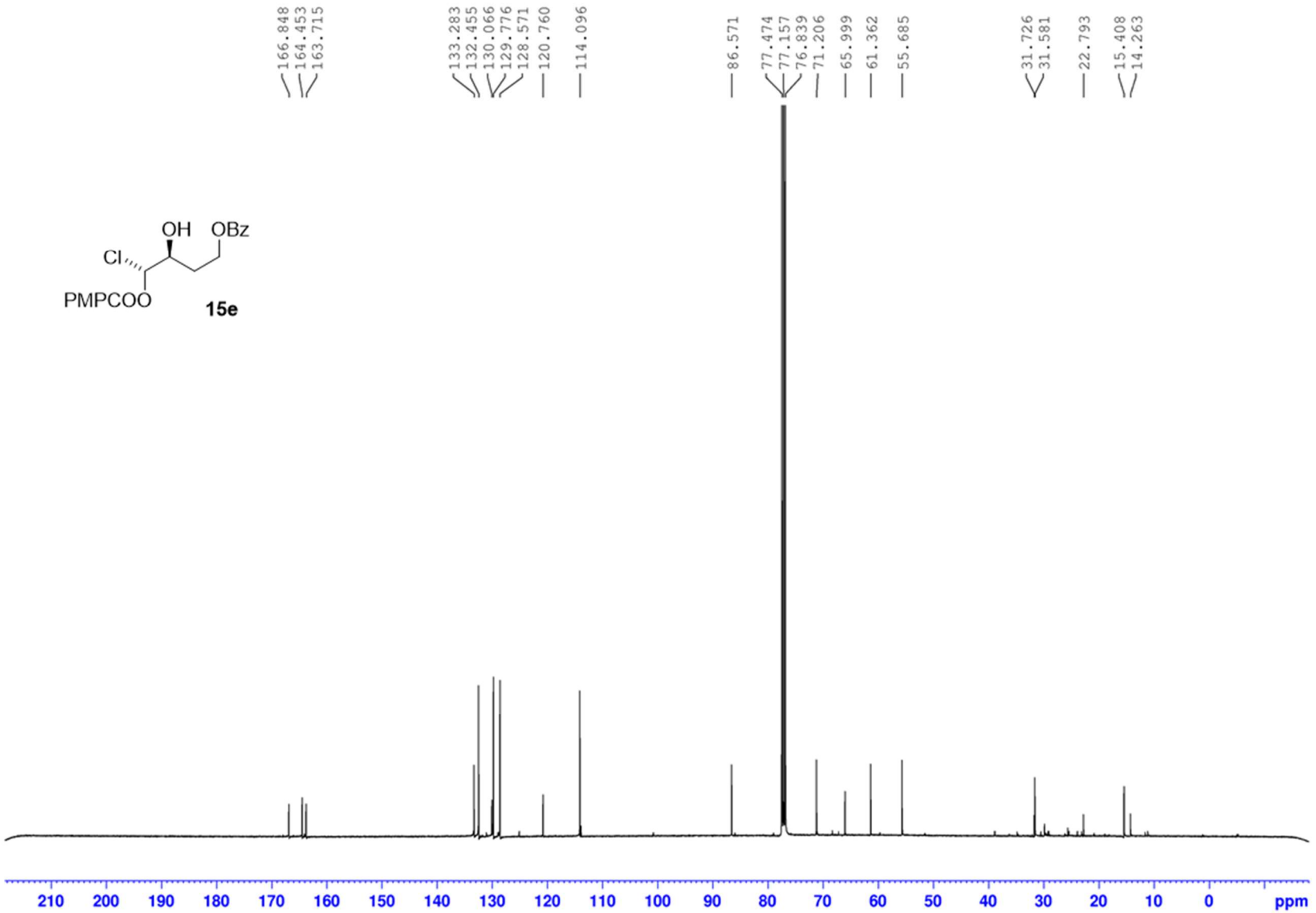

```
Current Data Parameters
NAME            JNH_03_64
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20220317
Time                18.33 h
INSTRUM             spect
PROBHD    Z104450_0192 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ               4.0894465 sec
RG                     32
DW                62.400 usec
DE                16.92 usec
TE                297.6 K
D1            1.00000000 sec
TD0                     1
SFO1         400.1324708 MHz
NUC1                   1H
P0                 5.00 usec
P1                15.00 usec
PLW1          8.47000027 W

F2 - Processing parameters
SI                  65536
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```




```
Current Data Parameters
NAME       JNH_03_64 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20220317
Time              18.44 h
INSTRUM             spect
PROBHD   Z104450_0192 (
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                   43
DS                    2
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG                  203
DW               20.800 usec
DE                6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228298 MHz
NUC1                13C
P0                 3.28 usec
P1                 9.85 usec
PLW1        28.63999939 W
SFO2        400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz65
PCPD2             90.00 usec
PLW2         8.47000027 W
PLW12        0.23528001 W
PLW13        0.11834000 W

F2 - Processing parameters
SI                32768
SF          100.6127589 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```




```
Current Data Parameters
NAME        JSA-01-37 1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20230307
Time              15.52 h
INSTRUM  Avance NEO nanobay
PROBHD   Z104275_0486 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5882.353 Hz
FIDRES          0.359030 Hz
AQ              2.7852800 sec
RG                   101
DW                85.000 usec
DE                 6.50 usec
TE                299.5 K
D1           1.00000000 sec
TD0                    1
SFO1        300.1362005 MHz
NUC1                  1H
P0                 4.67 usec
P1                14.00 usec
PLW1         6.14340019 W

F2 - Processing parameters
SI                 65536
SF          300.1350074 MHz
WDW                   no
SSB                    0
LB                     0 Hz
GB                     0
PC                  1.00
```



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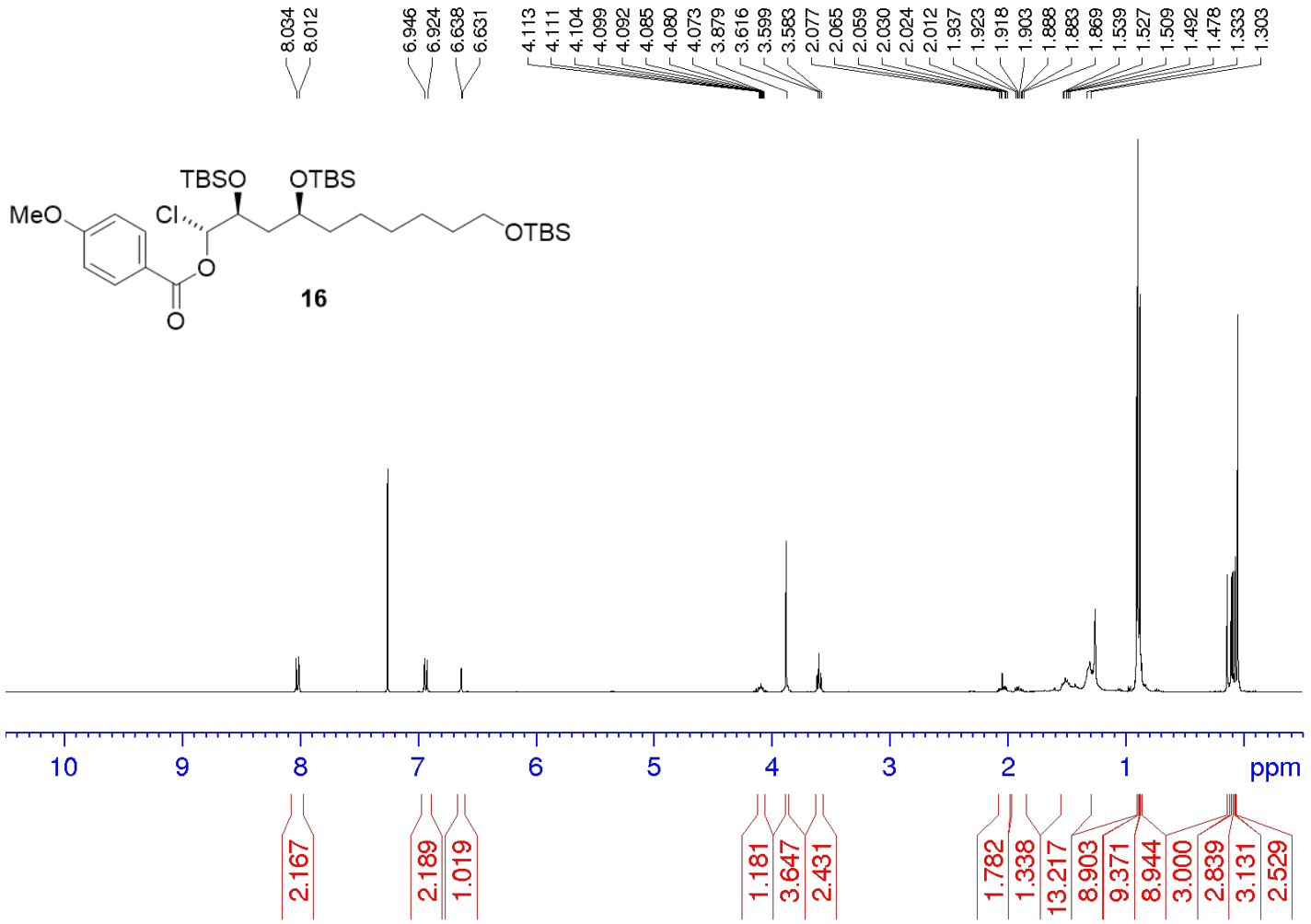
```
Current Data Parameters
NAME       JSA-01-37 13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20230307
Time              21.24 h
INSTRUM           Avance
PROBHD   Z167430_0032 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 5120
DS                    4
SWH           23809.523 Hz
FIDRES         0.726609 Hz
AQ             1.3762560 sec
RG                 3.25
DW               21.000 usec
DE               19.29 usec
TE               298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1         100.6655806 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1         39.31399918 W
SFO2         400.3016012 MHz
NUC2                1H
CPDPRG[2         waltz64
PCPD2             80.00 usec
PLW2          8.80000019 W
PLW12         0.20176961 W
PLW13         0.10112690 W

F2 - Processing parameters
SI                65536
SF           100.6555027 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

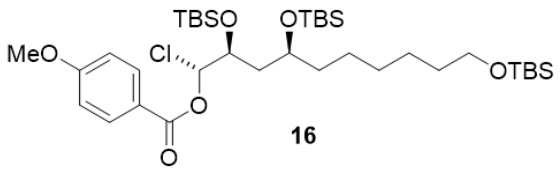


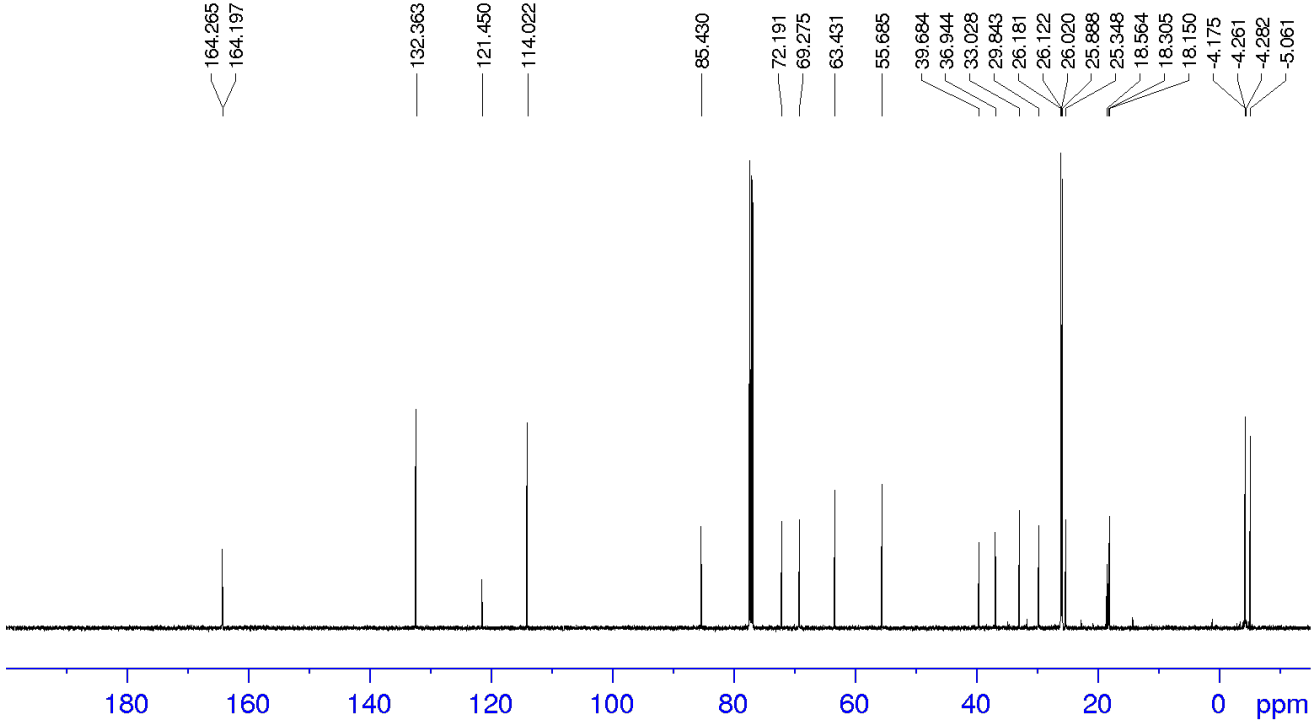
1H, CDCl3, 400 MHz

Current Data Parameters
NAME LWH-03-69-frxn5-12
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230119
Time 18.01 h
INSTRUM spect
PROBHD Z104450_0192 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 406
DW 62.400 usec
DE 16.92 usec
TE 297.9 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P0 5.00 usec
P1 15.00 usec
PLW1 8.47000027 W

F2 - Processing parameters
SI 65536
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



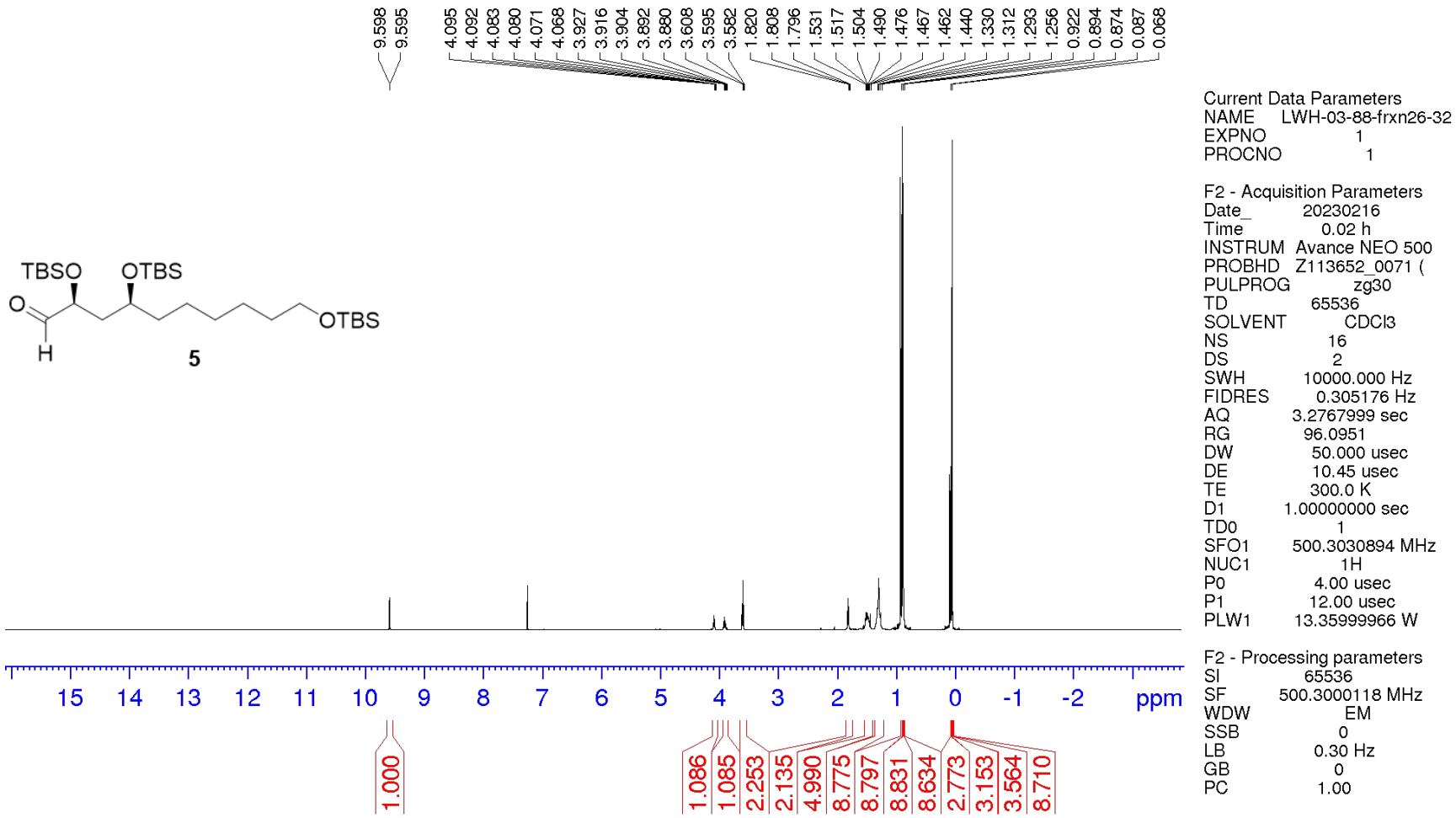


13C, CDCl3, 125 MHz

Current Data Parameters
NAME LWH-03-85-frxn25-37-13C_copy
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230212
Time 12.34 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 1.0878977 sec
RG 101
DW 16.600 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 103.61000061 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 13.35999966 W
PLW12 0.30400079 W
PLW13 0.15236519 W

F2 - Processing parameters
SI 32768
SF 125.8005115 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

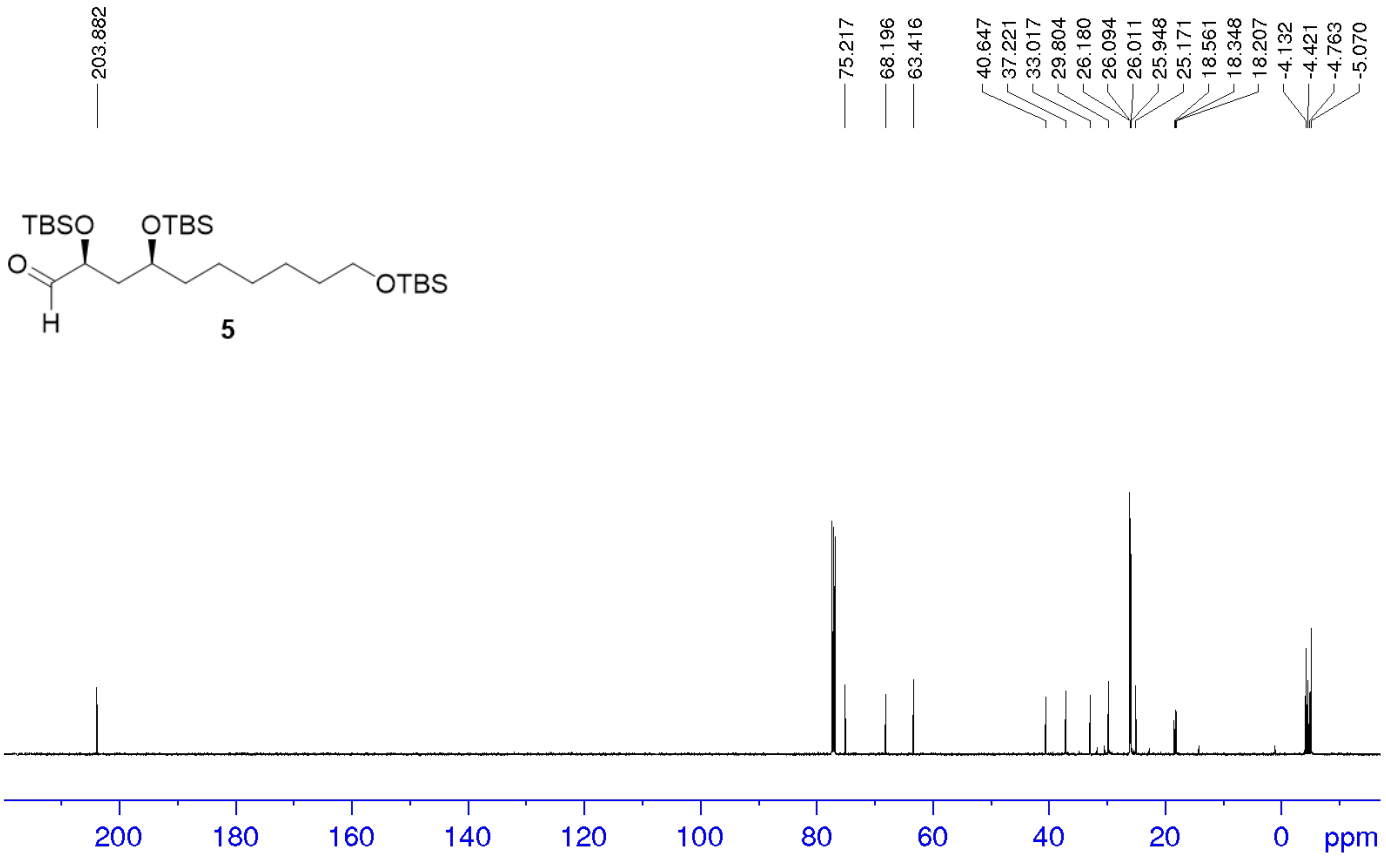


Current Data Parameters
NAME LWH-03-88-frxn26-32
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230216
Time 0.02 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 96.0951
DW 50.000 usec
DE 10.45 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030894 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 13.35999966 W

F2 - Processing parameters
SI 65536
SF 500.3000118 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1H, CDCl3, 500 MHz

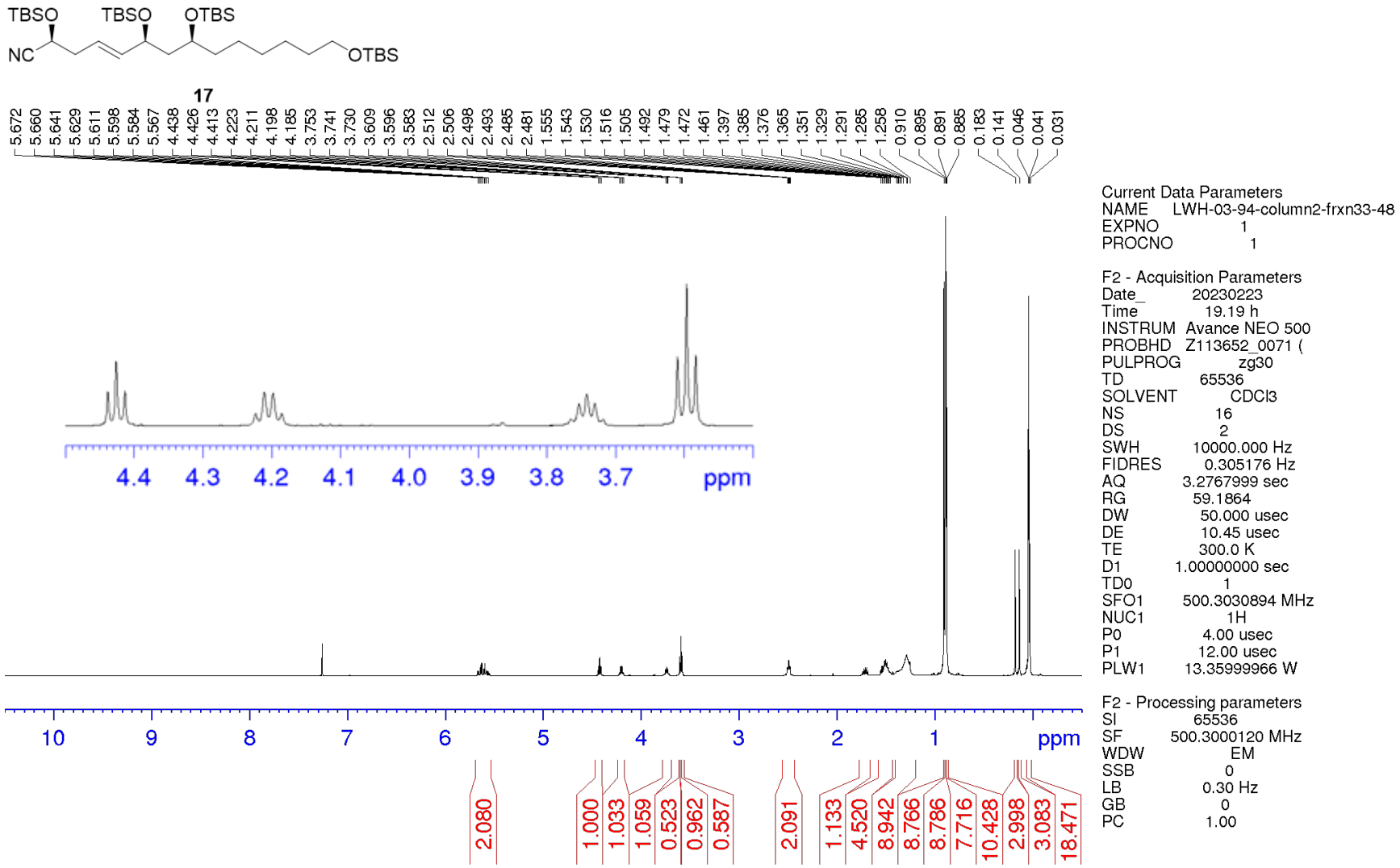


13C, CDCl3, 125 MHz

Current Data Parameters
NAME LWH-03-90-frxn33-41-13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230218
Time 16.16 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 4
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 1.0878977 sec
RG 101
DW 16.600 usec
DE 10.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 103.61000061 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz65
PCPD2 80.00 usec
PLW2 13.35999966 W
PLW12 0.30400079 W
PLW13 0.15236519 W

F2 - Processing parameters
SI 32768
SF 125.8005106 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

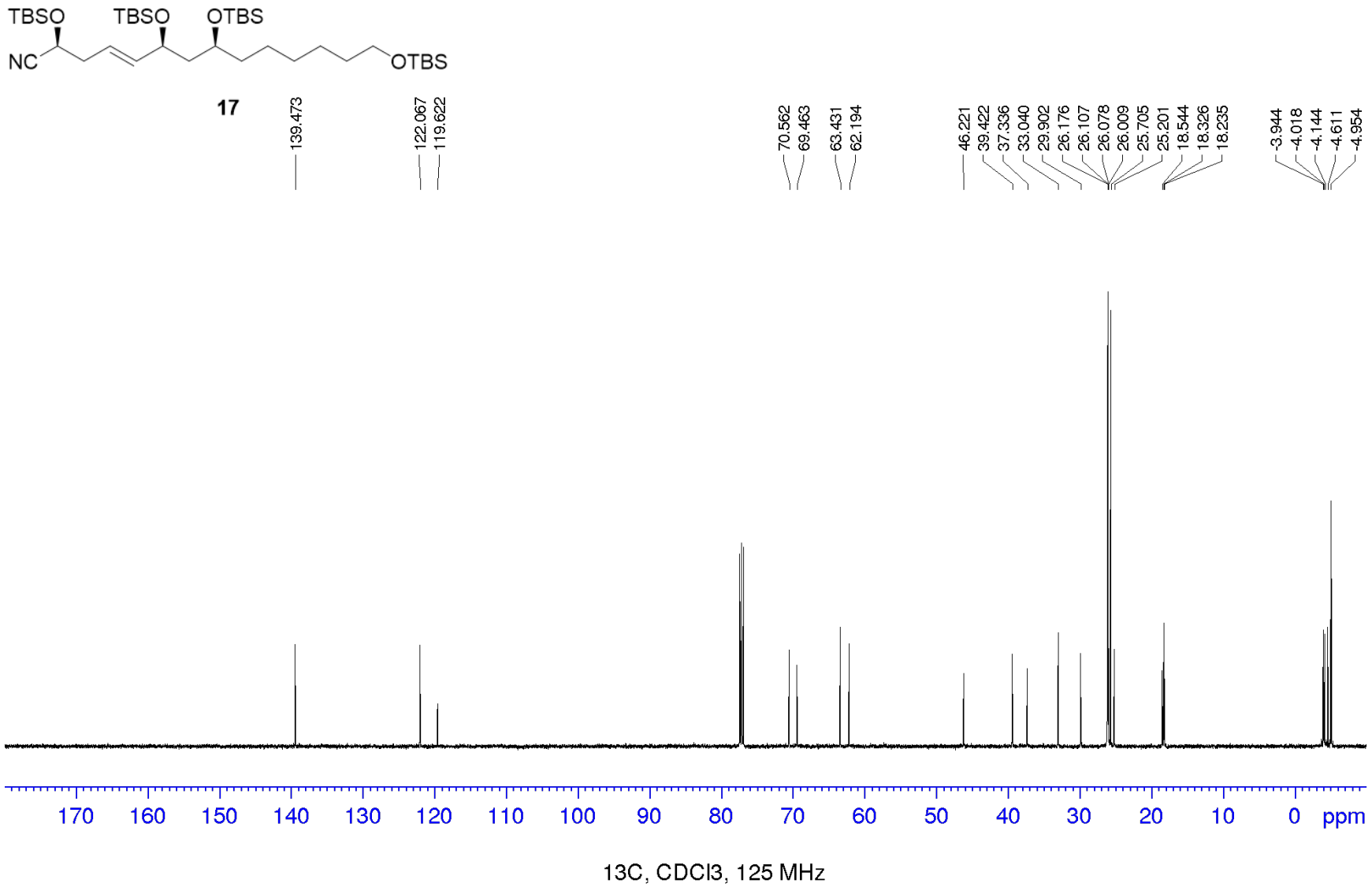


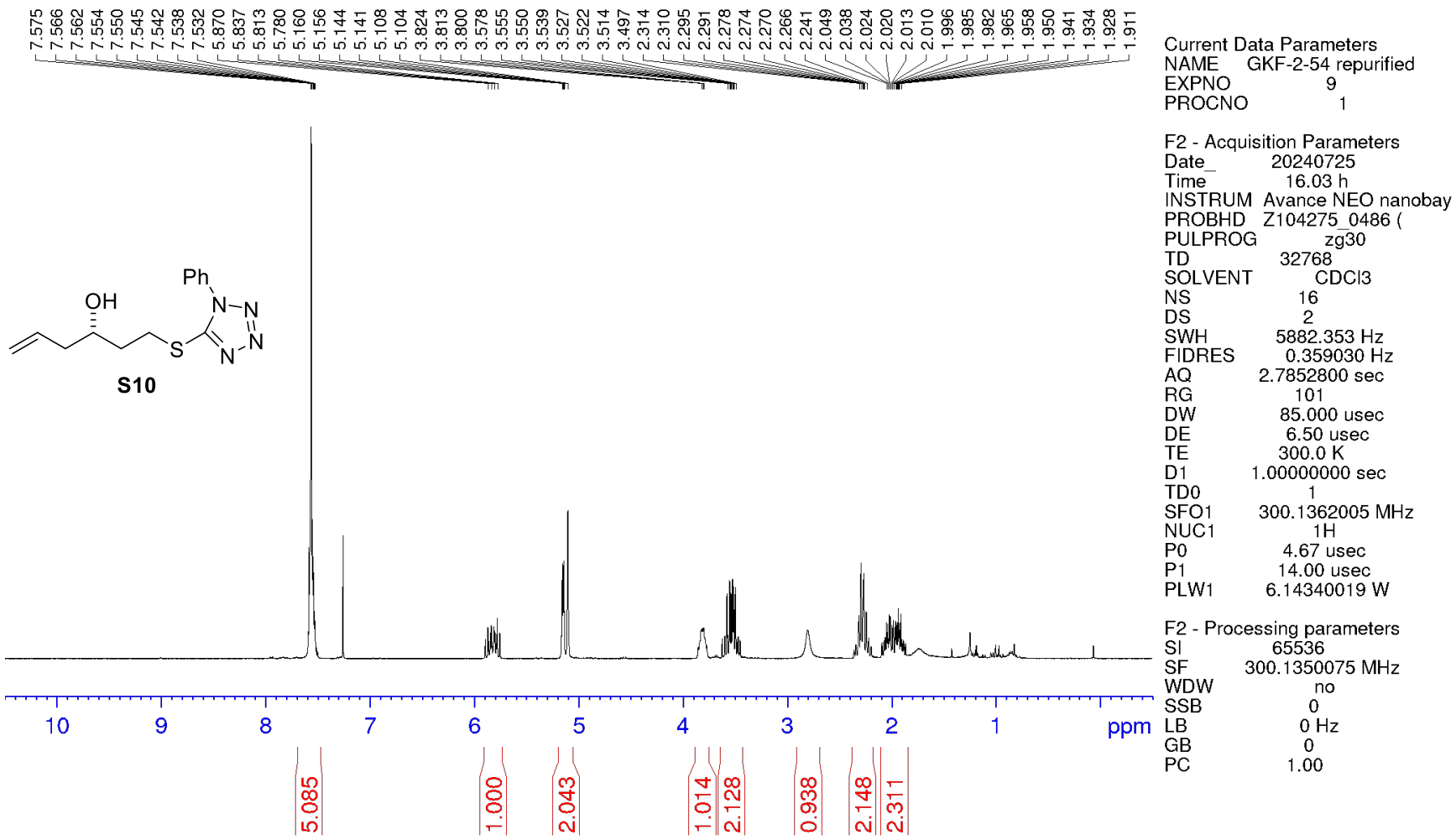
1H, CDCl3, 500 MHz

Current Data Parameters
NAME LWH-03-94-column2-frxn33-48
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20230223
Time 19.19 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 59.1864
DW 50.000 usec
DE 10.45 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3030894 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 13.35999966 W

F2 - Processing parameters
SI 65536
SF 500.3000120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


TBSO
TBSO
OTBS
NC
OTBS
17
139.473
122.067
119.622
70.562
69.463
63.431
62.194
46.221
39.422
37.336
33.040
29.902
26.176
26.107
26.078
26.009
25.705
25.201
18.544
18.326
18.235
-3.944
-4.018
-4.144
-4.611
-4.954
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
13C, CDCl3, 125 MHz

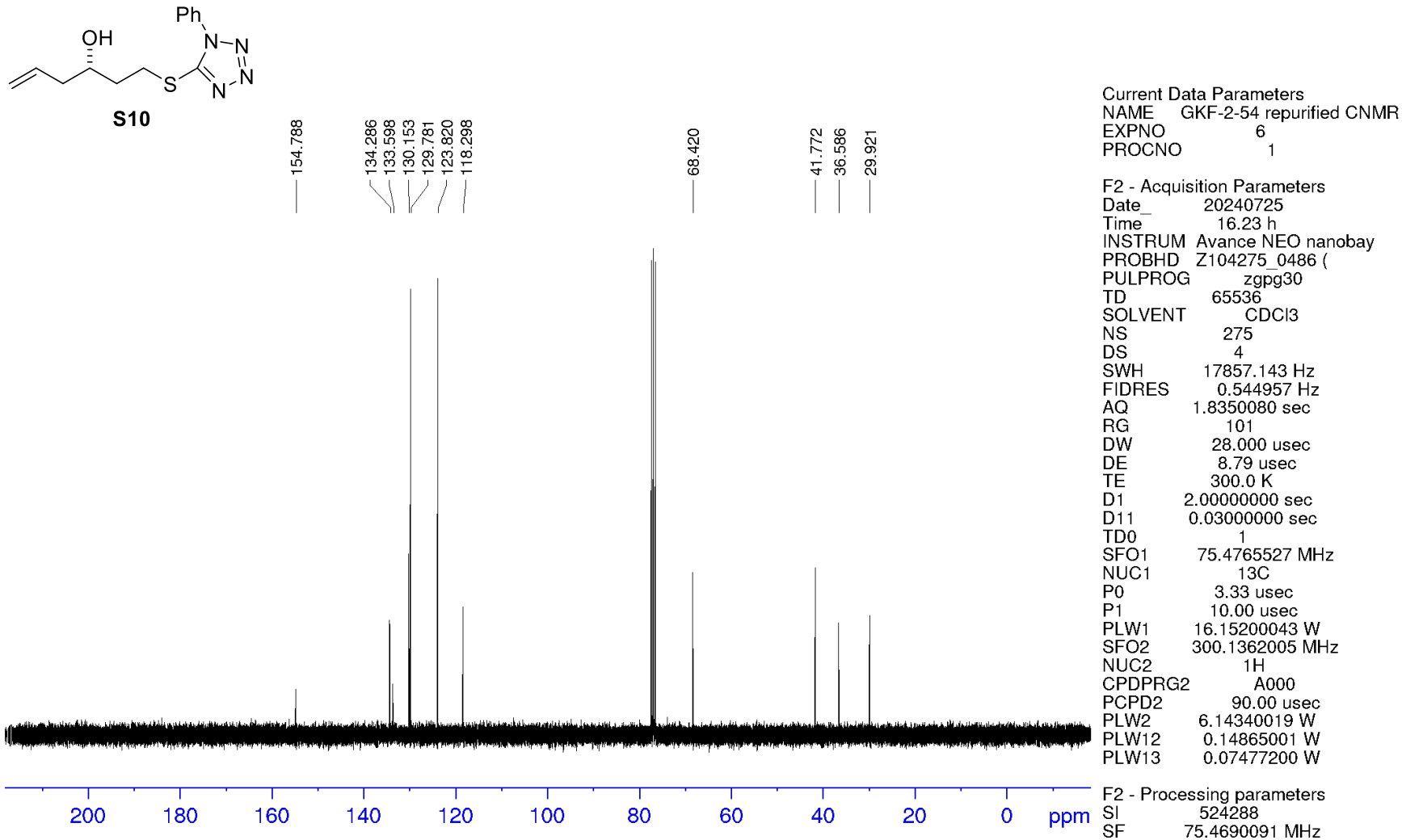


1H, CDCl3, 300 MHz

Current Data Parameters
NAME GKF-2-54 repurified
EXPNO 9
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240725
Time 16.03 h
INSTRUM Avance NEO nanobay
PROBHD Z104275_0486 (
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 5882.353 Hz
FIDRES 0.359030 Hz
AQ 2.7852800 sec
RG 101
DW 85.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 300.1362005 MHz
NUC1 1H
P0 4.67 usec
P1 14.00 usec
PLW1 6.14340019 W

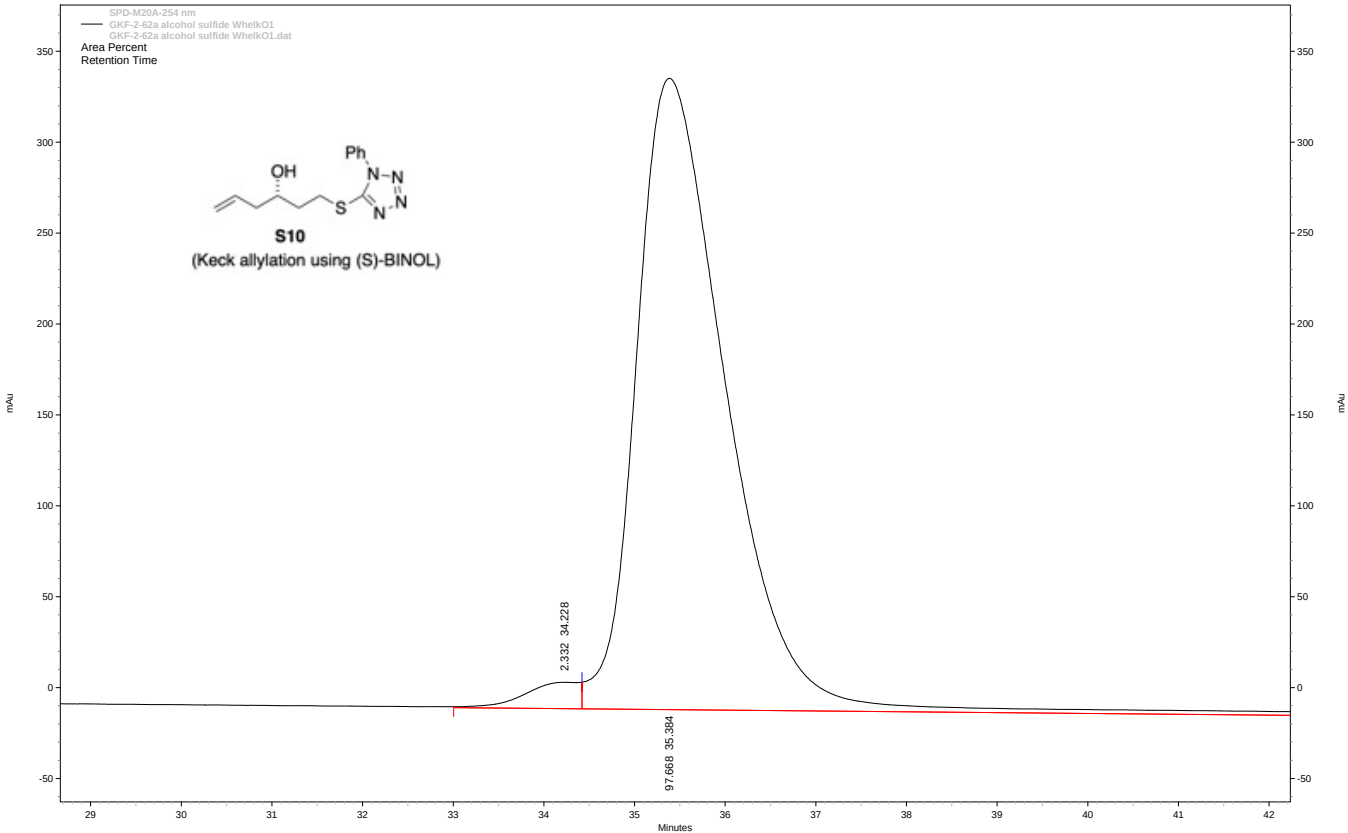
F2 - Processing parameters
SI 65536
SF 300.1350075 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



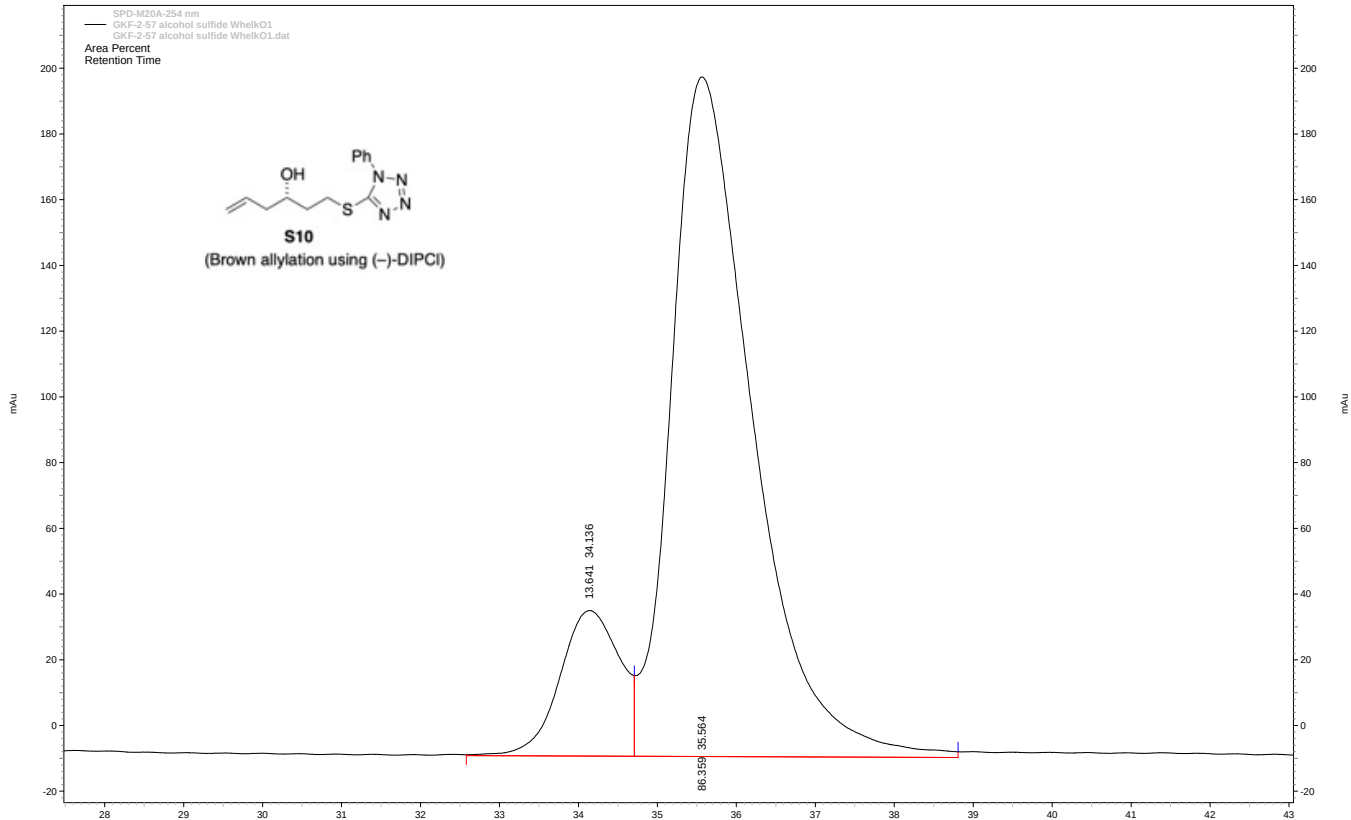
Current Data Parameters
NAME GKF-2-54 repurified CNMR
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240725
Time 16.23 h
INSTRUM Avance NEO nanobay
PROBHD Z104275_0486 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 275
DS 4
SWH 17857.143 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 28.000 usec
DE 8.79 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 75.4765527 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 16.15200043 W
SFO2 300.1362005 MHz
NUC2 1H
CPDPRG2 A000
PCPD2 90.00 usec
PLW2 6.14340019 W
PLW12 0.14865001 W
PLW13 0.07477200 W

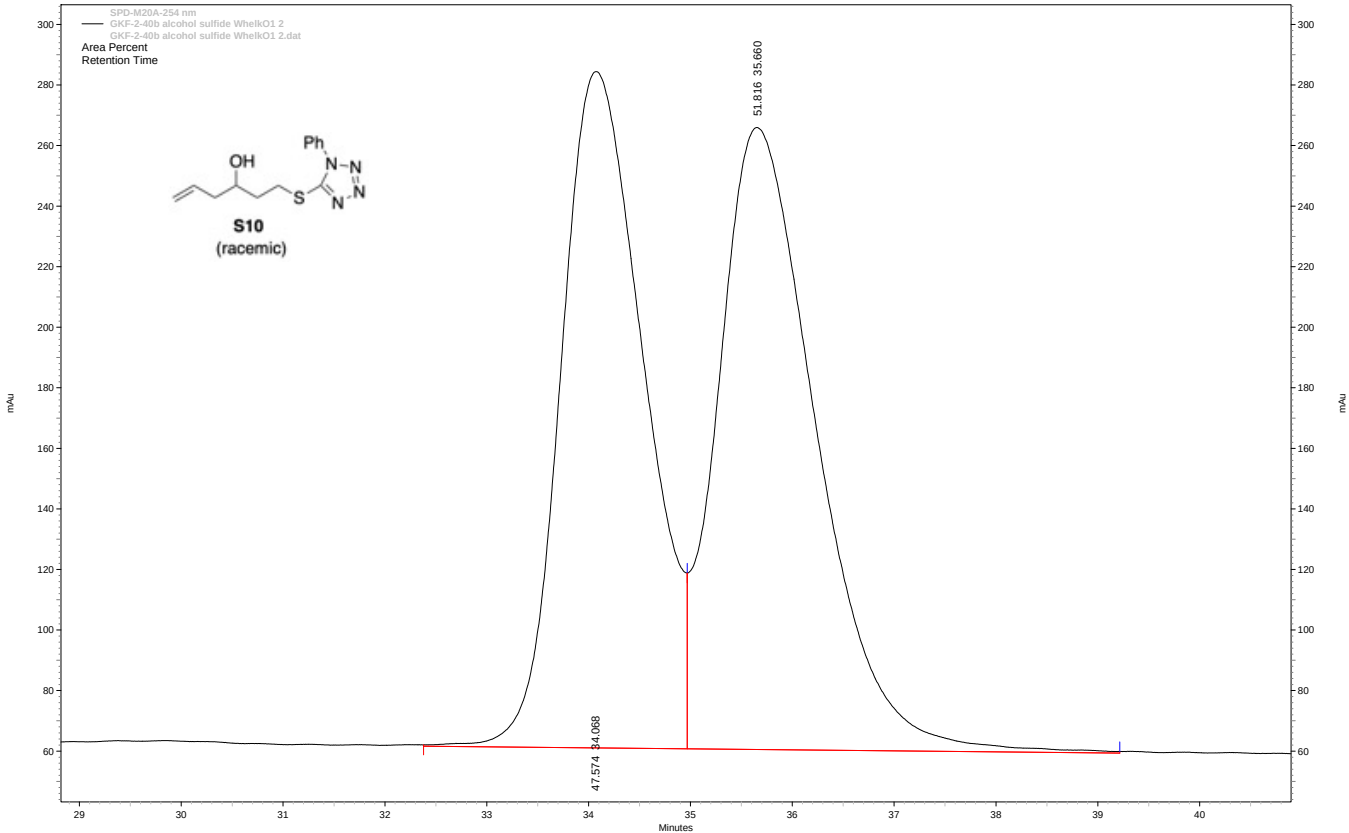
F2 - Processing parameters
SI 524288
SF 75.4690091 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40



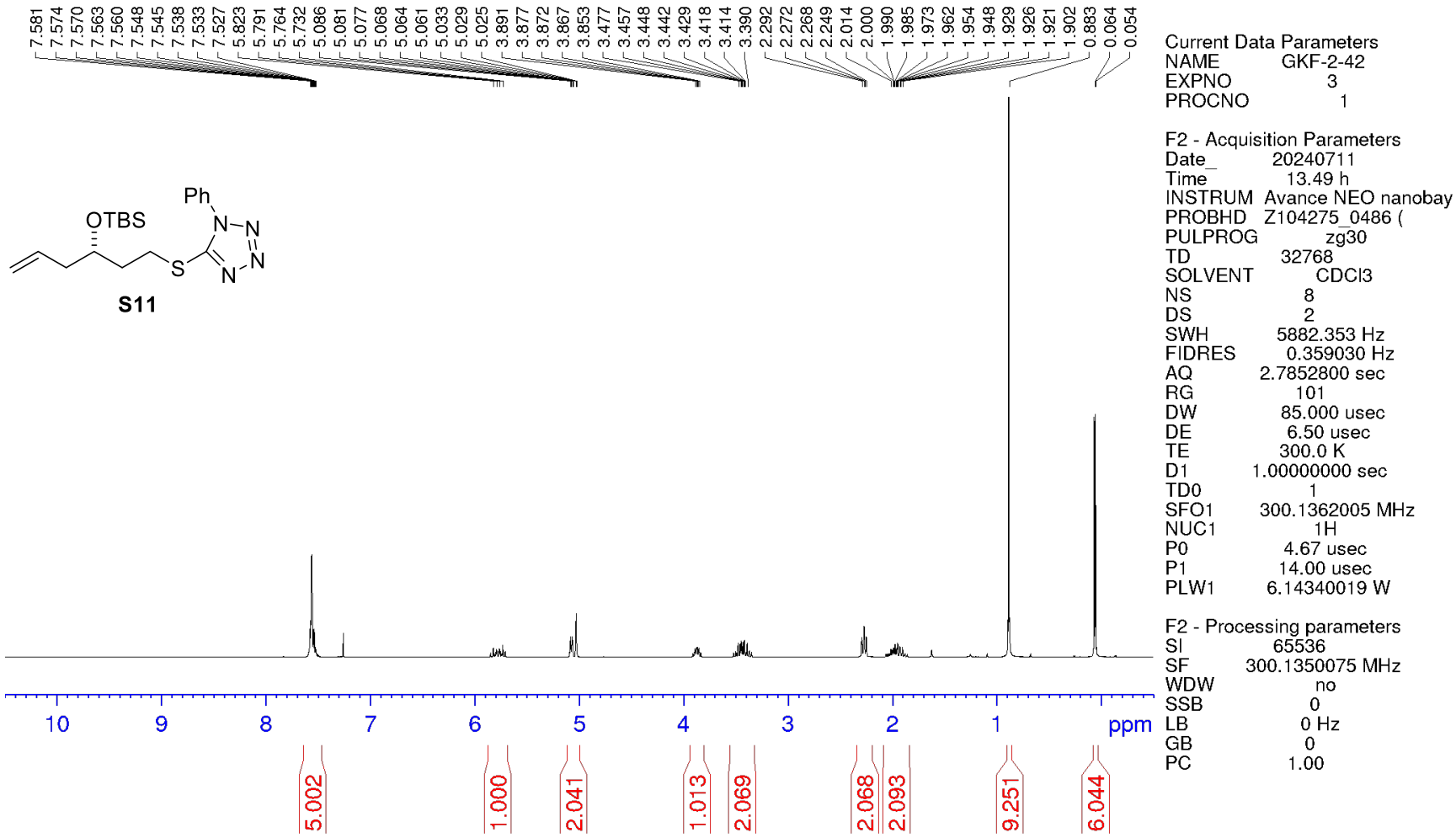
C:\EZStart\Projects\Default\Data\GKF data\GKF-2-62a alcohol sulfide WhelkO1.dat, SPD-M20A-254 nm



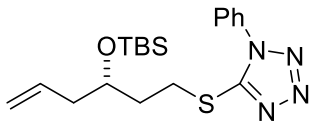
C:\EZStart\Projects\Default\Data\GKF data\GKF-2-57 alcohol sulfide WhelkO1.dat, SPD-M20A-254 nm



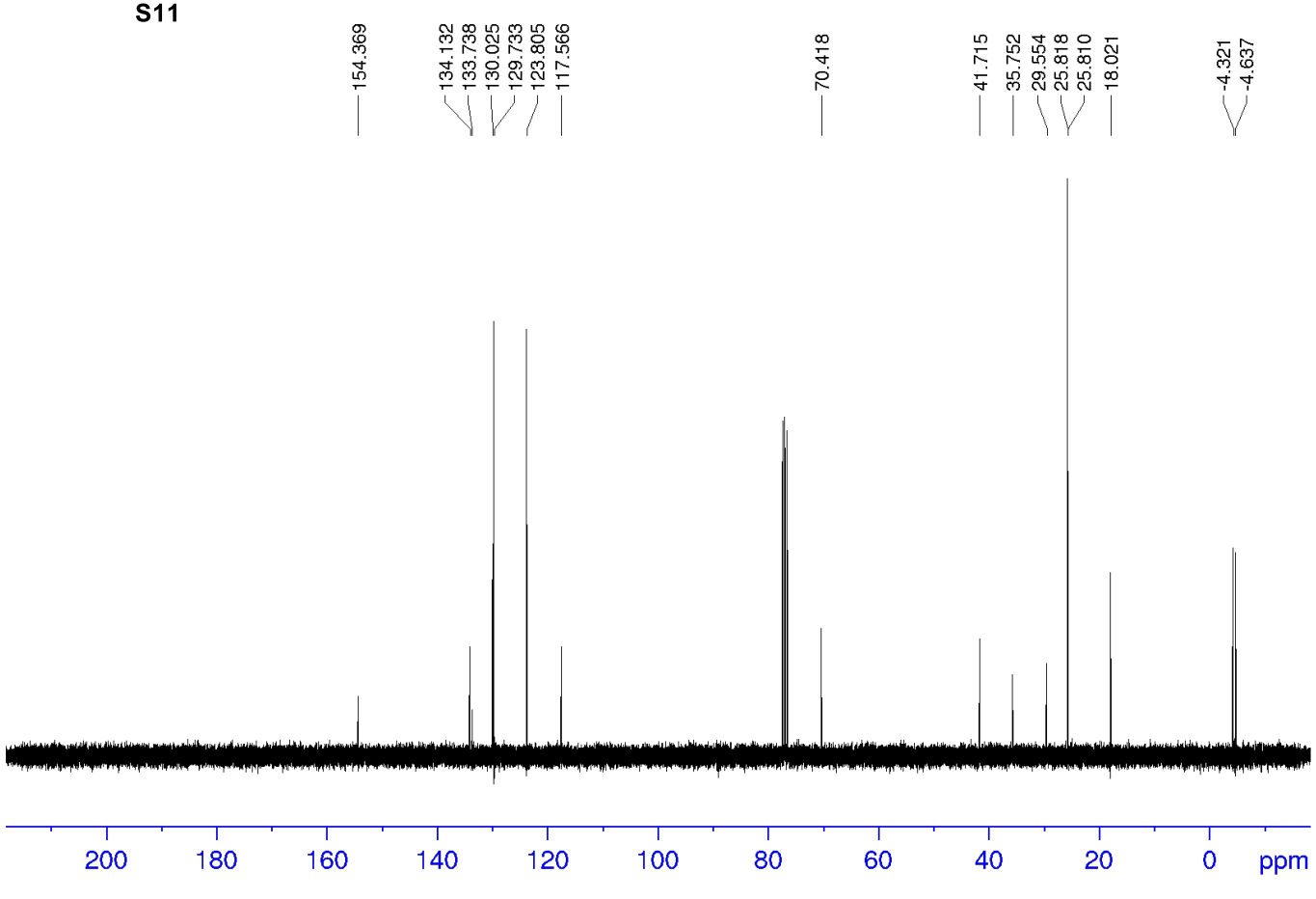
C:\EZStart\Projects\Default\Data\GKF data\GKF-2-40b alcohol sulfide WhelkO1 2.dat, SPD-M20A-254 nm



1H, CDCl3, 300 MHz



S11

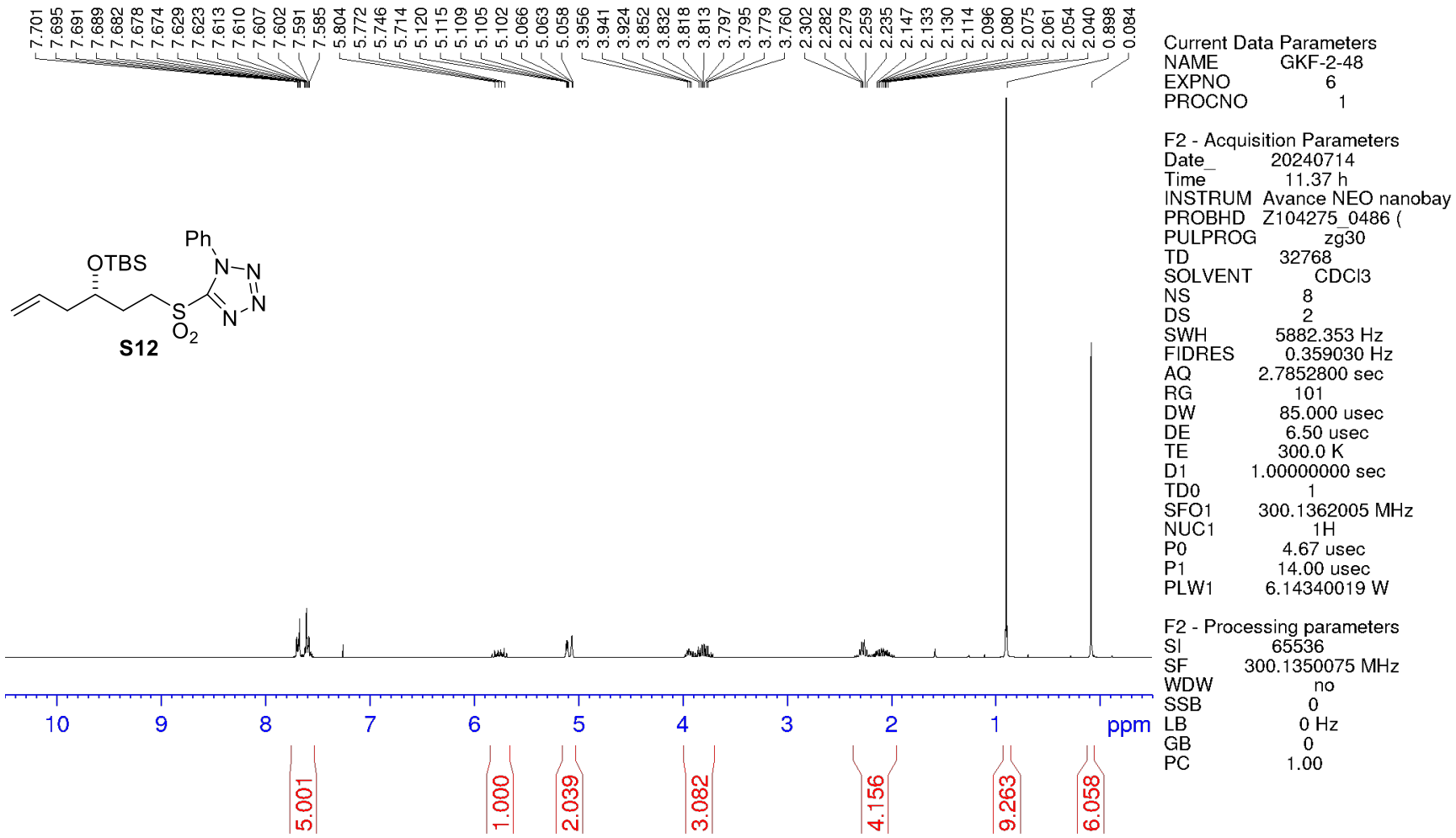


13C, CDCl3, 75 MHz

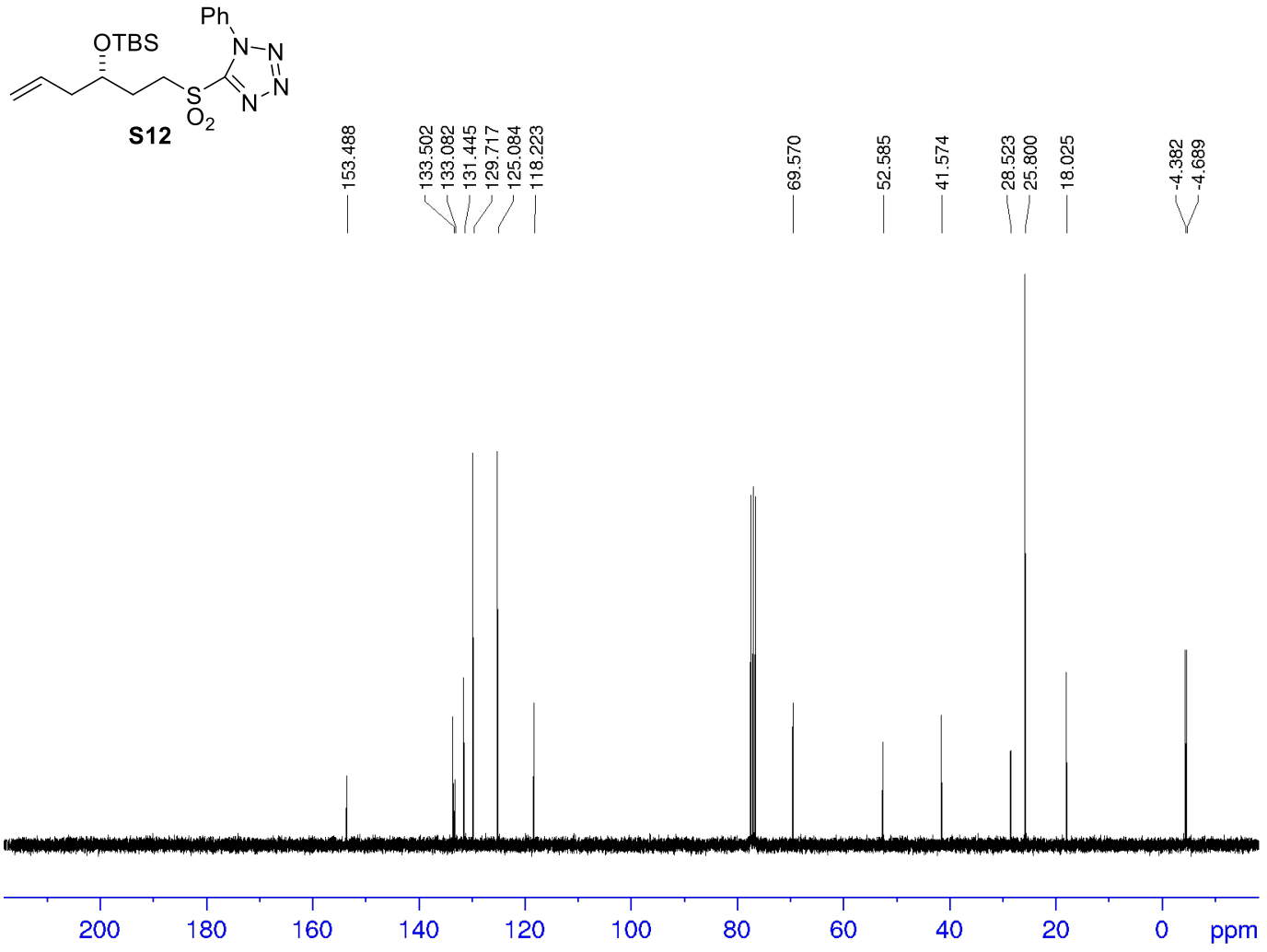
Current Data Parameters
NAME GKF-2-42 CNMR
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240711
Time 14.00 h
INSTRUM Avance NEO nanobay
PROBHD Z104275_0486 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 125
DS 4
SWH 17857.143 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 28.000 usec
DE 8.79 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 75.4765527 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 16.15200043 W
SFO2 300.1362005 MHz
NUC2 1H
CPDPRG2 A000
PCPD2 90.00 usec
PLW2 6.14340019 W
PLW12 0.14865001 W
PLW13 0.07477200 W

F2 - Processing parameters
SI 524288
SF 75.4690086 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40



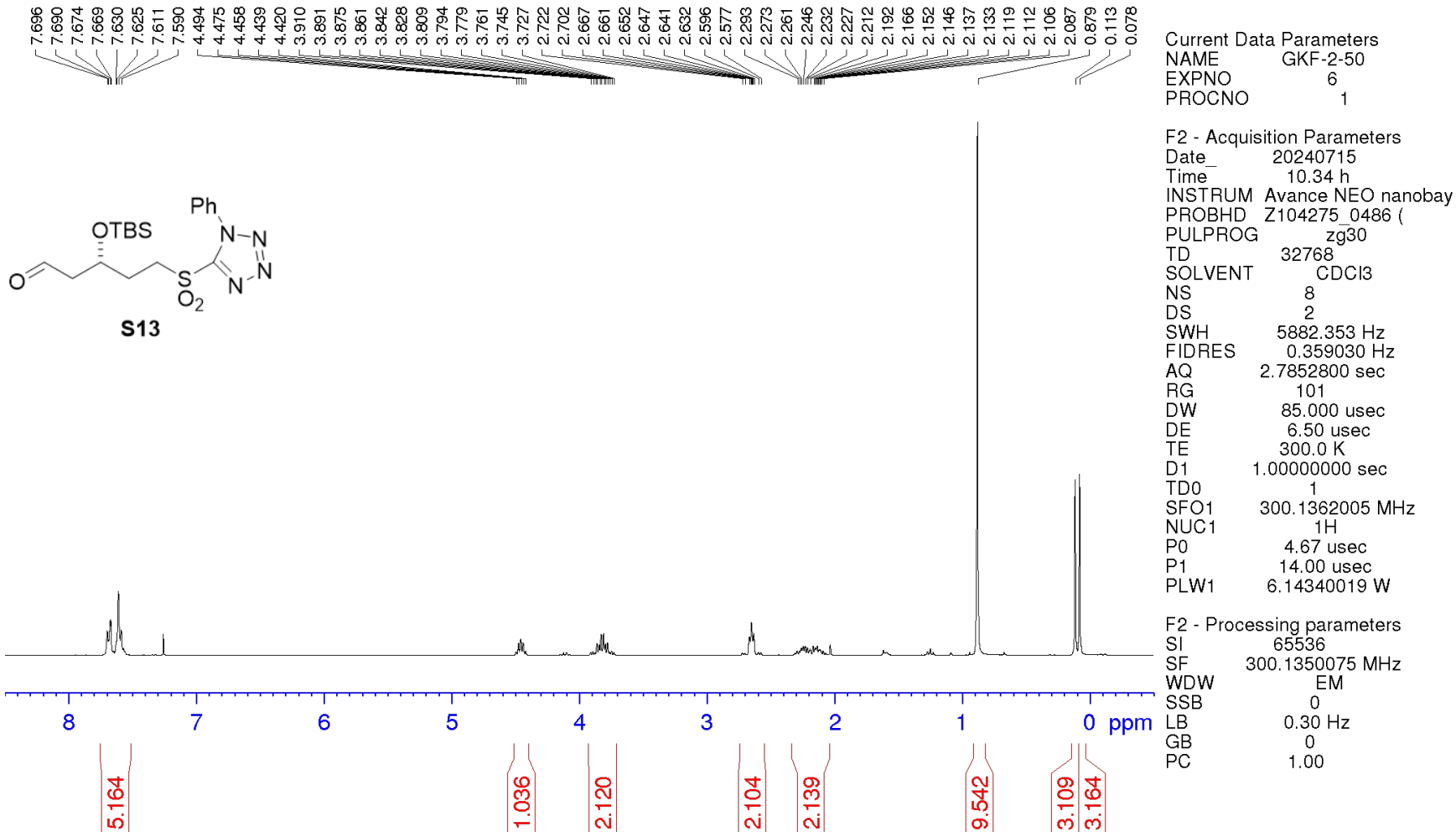
1H, CDCl3, 300 MHz



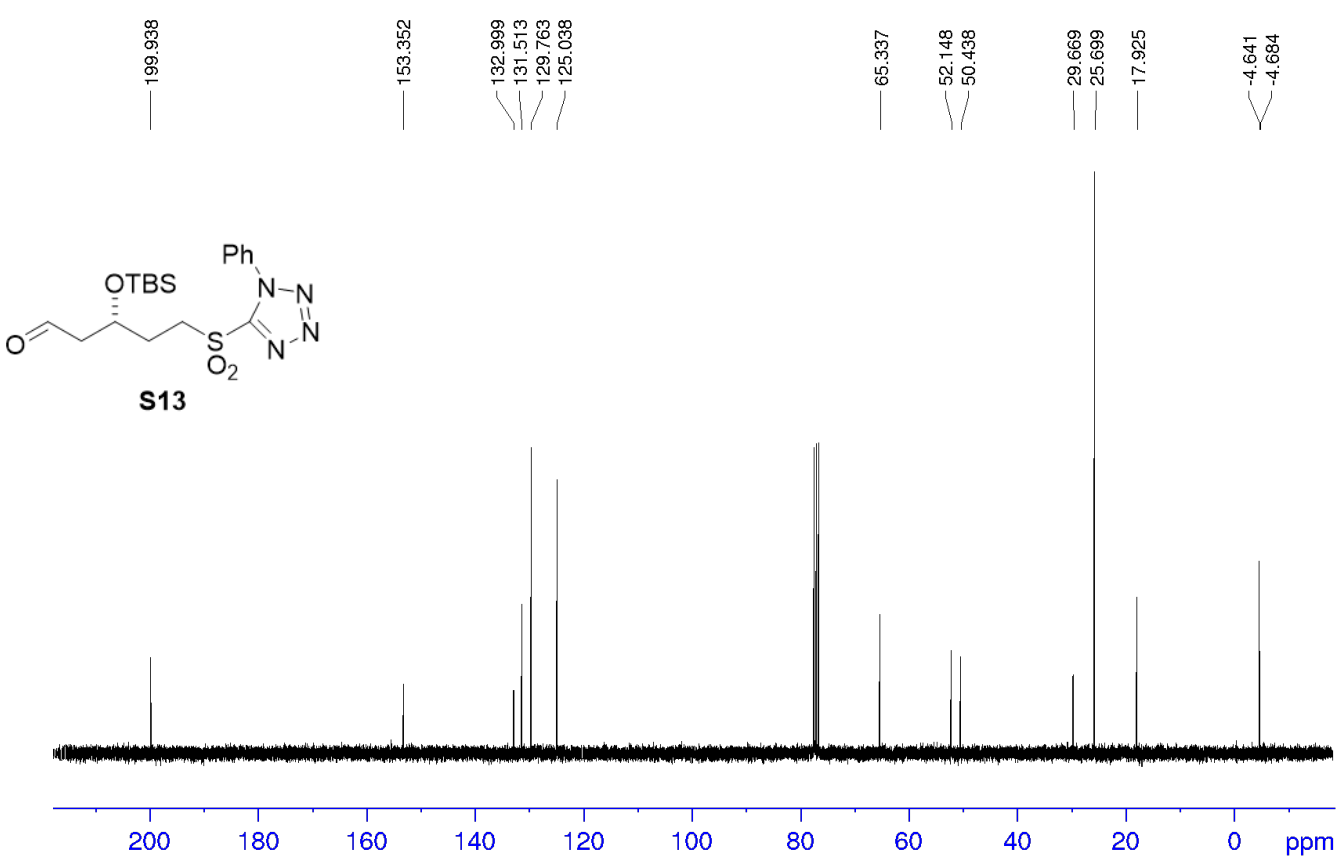
Current Data Parameters
NAME GKF-2-48 CNMR
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240714
Time 11.45 h
INSTRUM Avance NEO nanobay
PROBHD Z104275_0486 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 103
DS 4
SWH 17857.143 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 28.000 usec
DE 8.79 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 75.4765527 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 16.15200043 W
SFO2 300.1362005 MHz
NUC2 1H
CPDPRG2 A000
PCPD2 90.00 usec
PLW2 6.14340019 W
PLW12 0.14865001 W
PLW13 0.07477200 W

F2 - Processing parameters
SI 524288
SF 75.4690058 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40



1H, CDCl3, 300 MHz

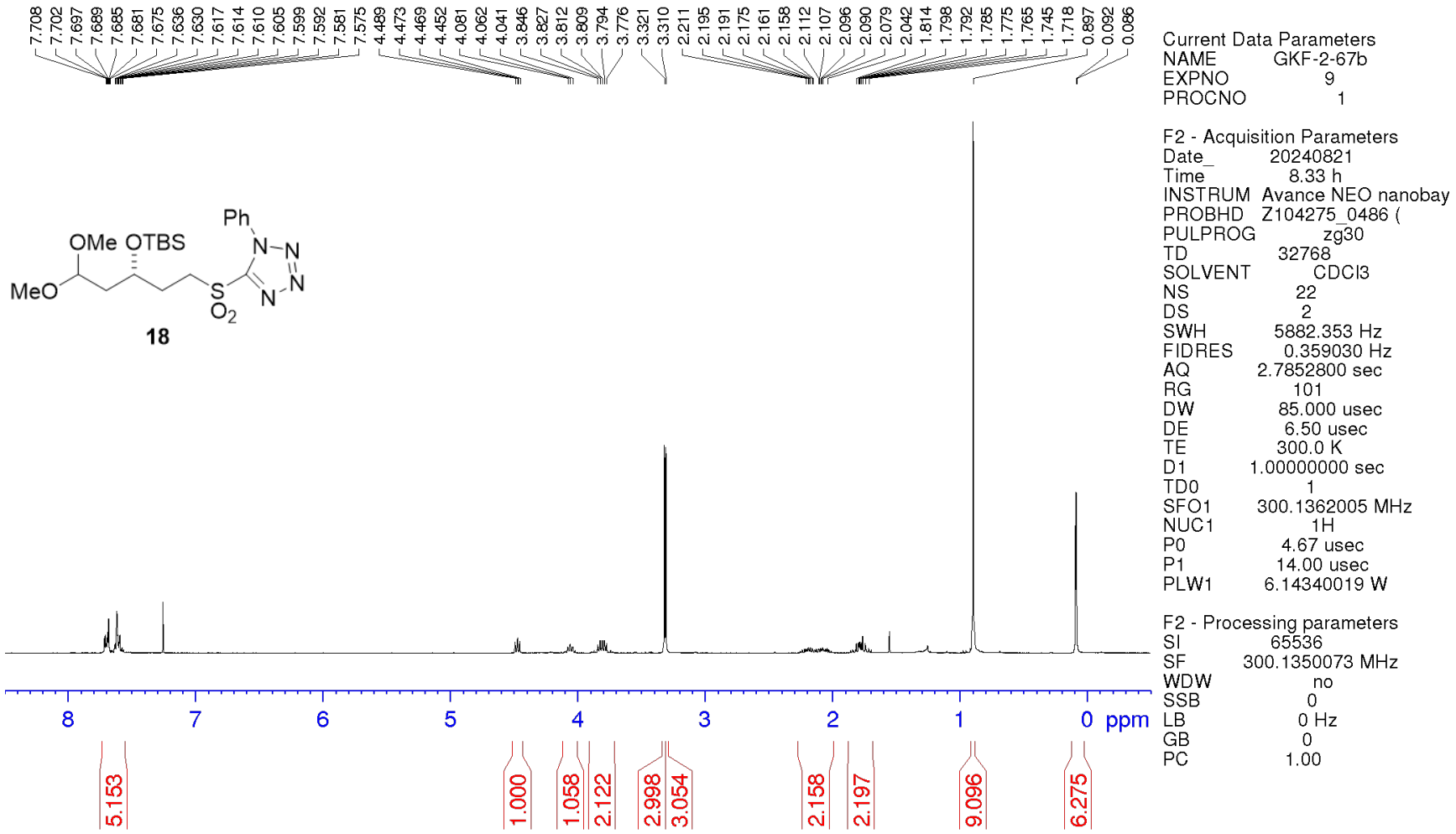


13C, CDCl3, 75 MHz

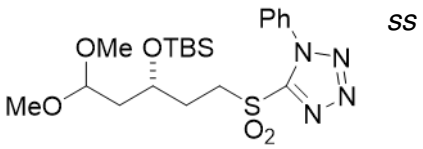
Current Data Parameters
NAME GKF-2-50 CNMR
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240715
Time 10.50 h
INSTRUM Avance NEO nanobay
PROBHD Z104275_0486 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 192
DS 4
SWH 17857.143 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 28.000 usec
DE 8.79 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 75.4765527 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 16.15200043 W
SFO2 300.1362005 MHz
NUC2 1H
CPDPRG2 A000
PCPD2 90.00 usec
PLW2 6.14340019 W
PLW12 0.14865001 W
PLW13 0.07477200 W

F2 - Processing parameters
SI 524288
SF 75.4690058 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

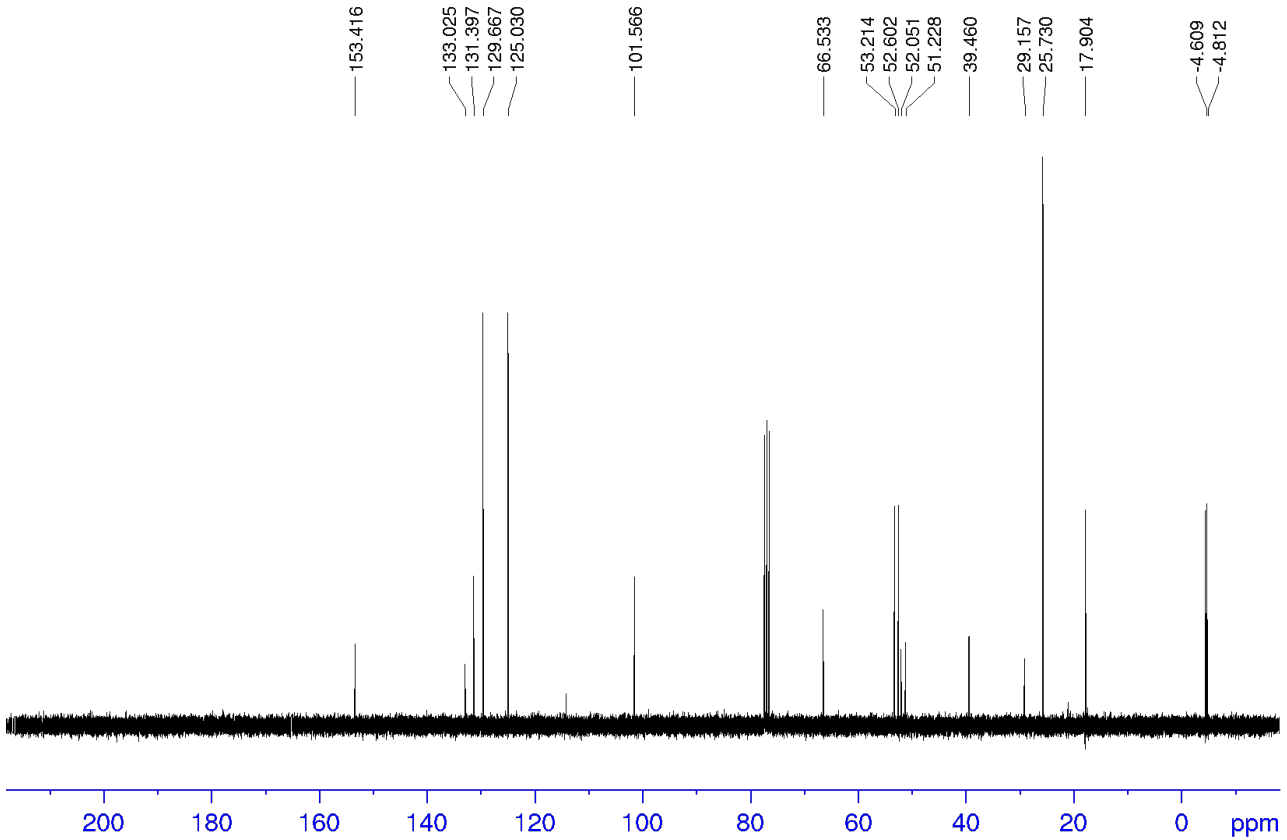


1H, CDCl3, 300 MHz



18

ss

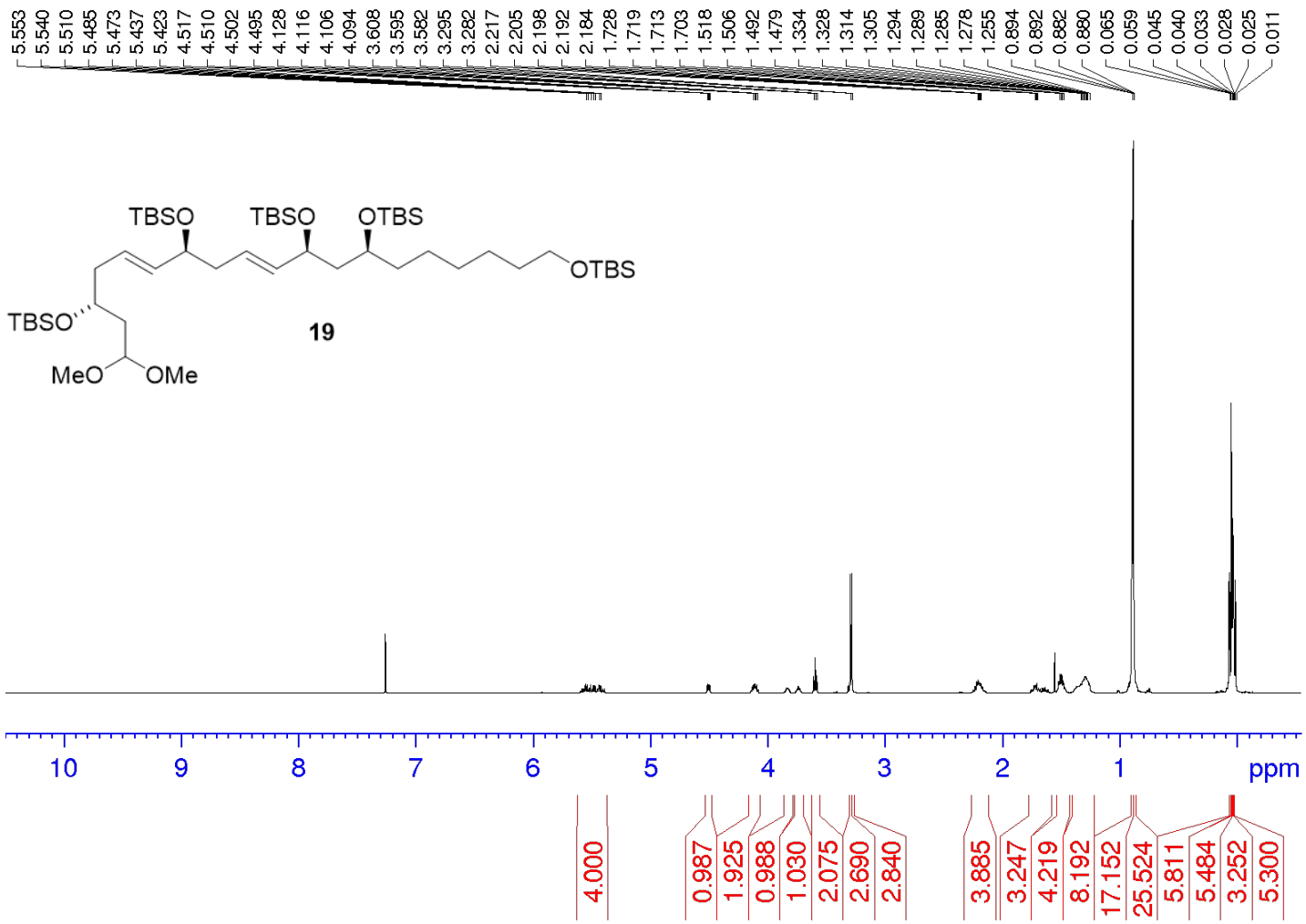


13C, CDCl3, 75 MHz

Current Data Parameters
NAME GKF-2-52 CNMR
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240715
Time 14.06 h
INSTRUM Avance NEO nanobay
PROBHD Z104275_0486 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 117
DS 4
SWH 17857.143 Hz
FIDRES 0.544957 Hz
AQ 1.8350080 sec
RG 101
DW 28.000 usec
DE 8.79 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 75.4765527 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 16.15200043 W
SFO2 300.1362005 MHz
NUC2 1H
CPDPRG2 A000
PCPD2 90.00 usec
PLW2 6.14340019 W
PLW12 0.14865001 W
PLW13 0.07477200 W

F2 - Processing parameters
SI 524288
SF 75.4690095 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

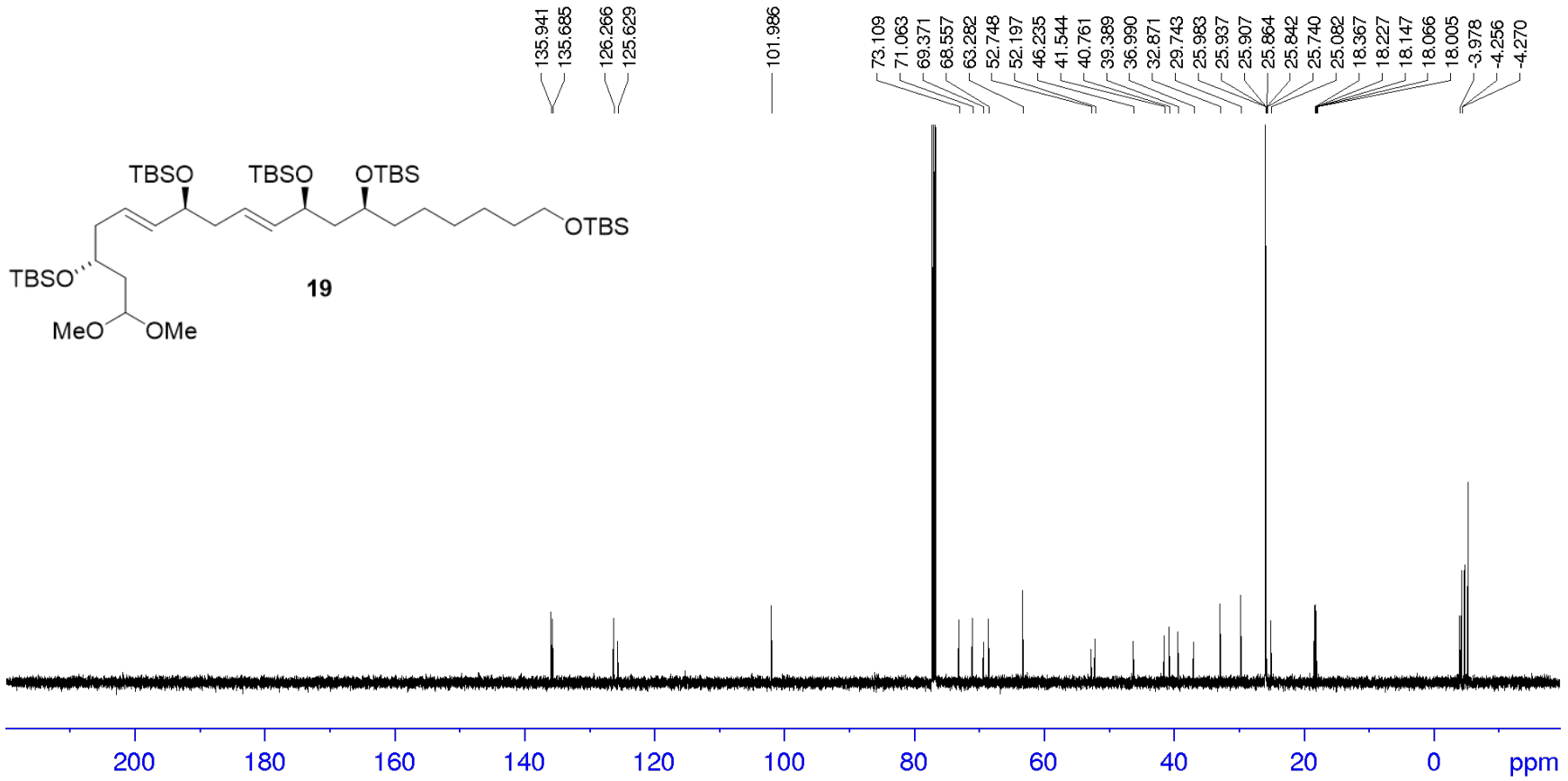


1H, CDCl3, 500 MHz

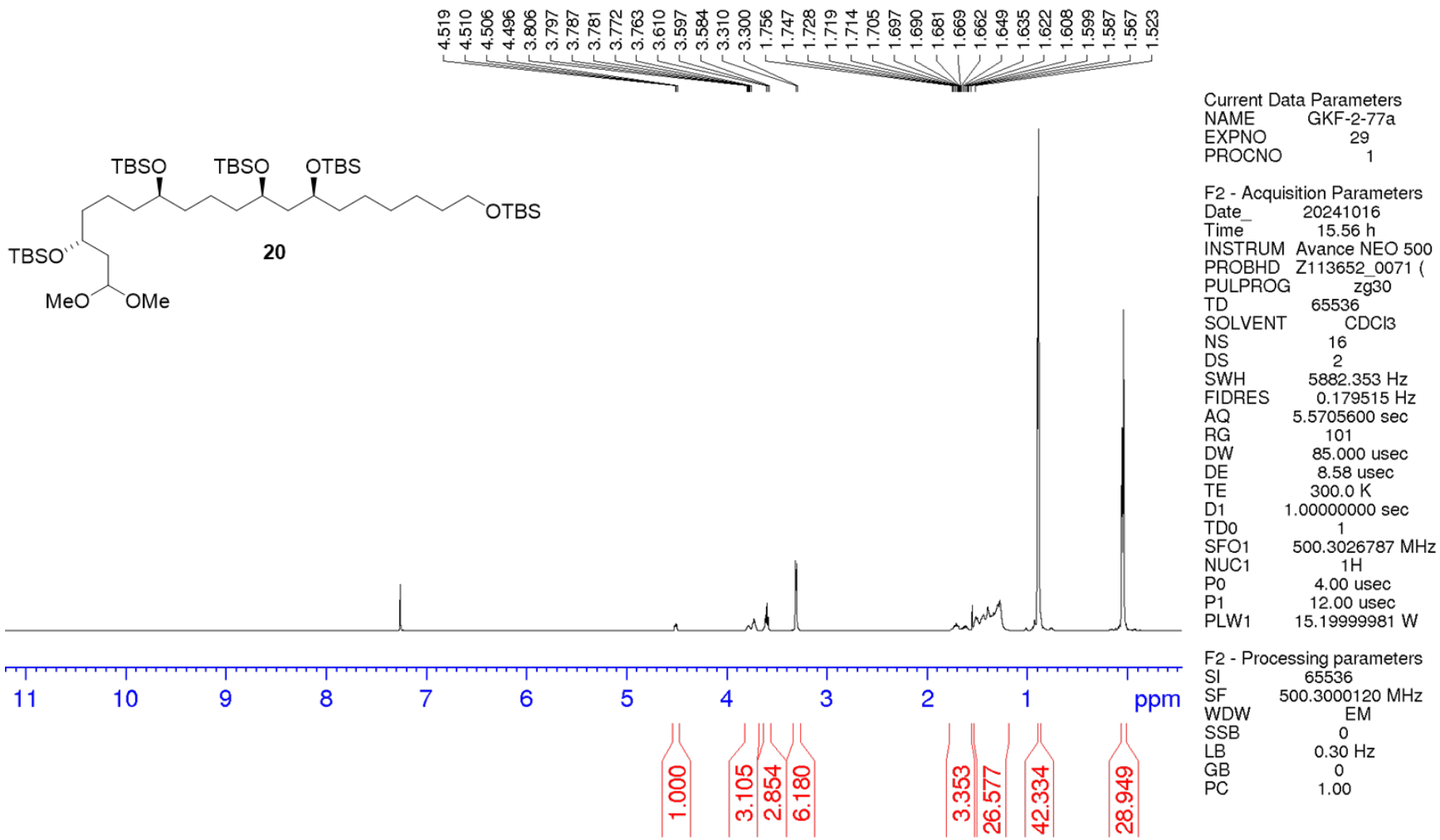
Current Data Parameters
NAME GKF-2-75-2b
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240905
Time 7.46 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 2
SWH 5882.353 Hz
FIDRES 0.179515 Hz
AQ 5.5705600 sec
RG 101
DW 85.000 usec
DE 8.58 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3026787 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 15.19999981 W

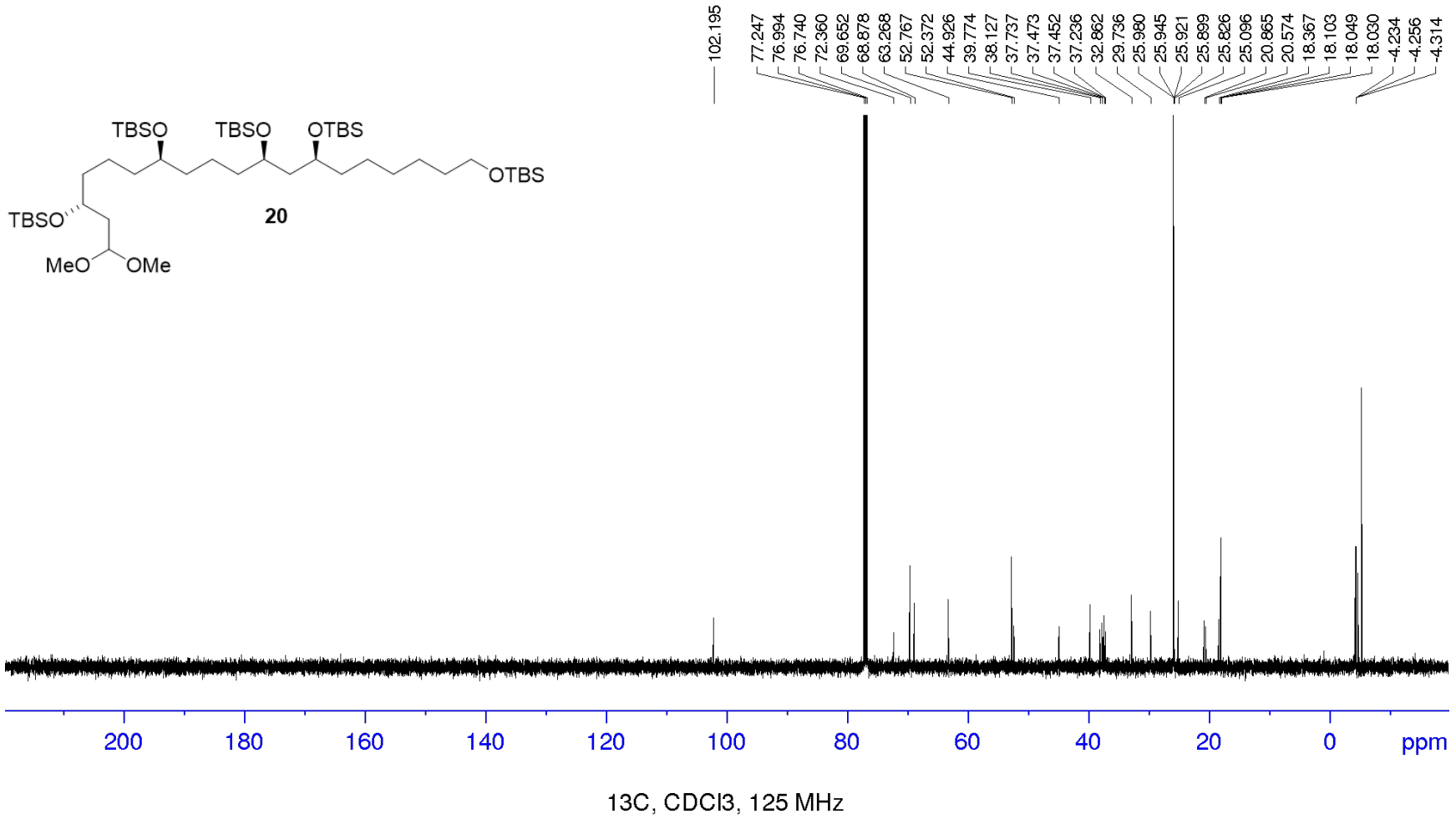
F2 - Processing parameters
SI 65536
SF 500.3000123 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



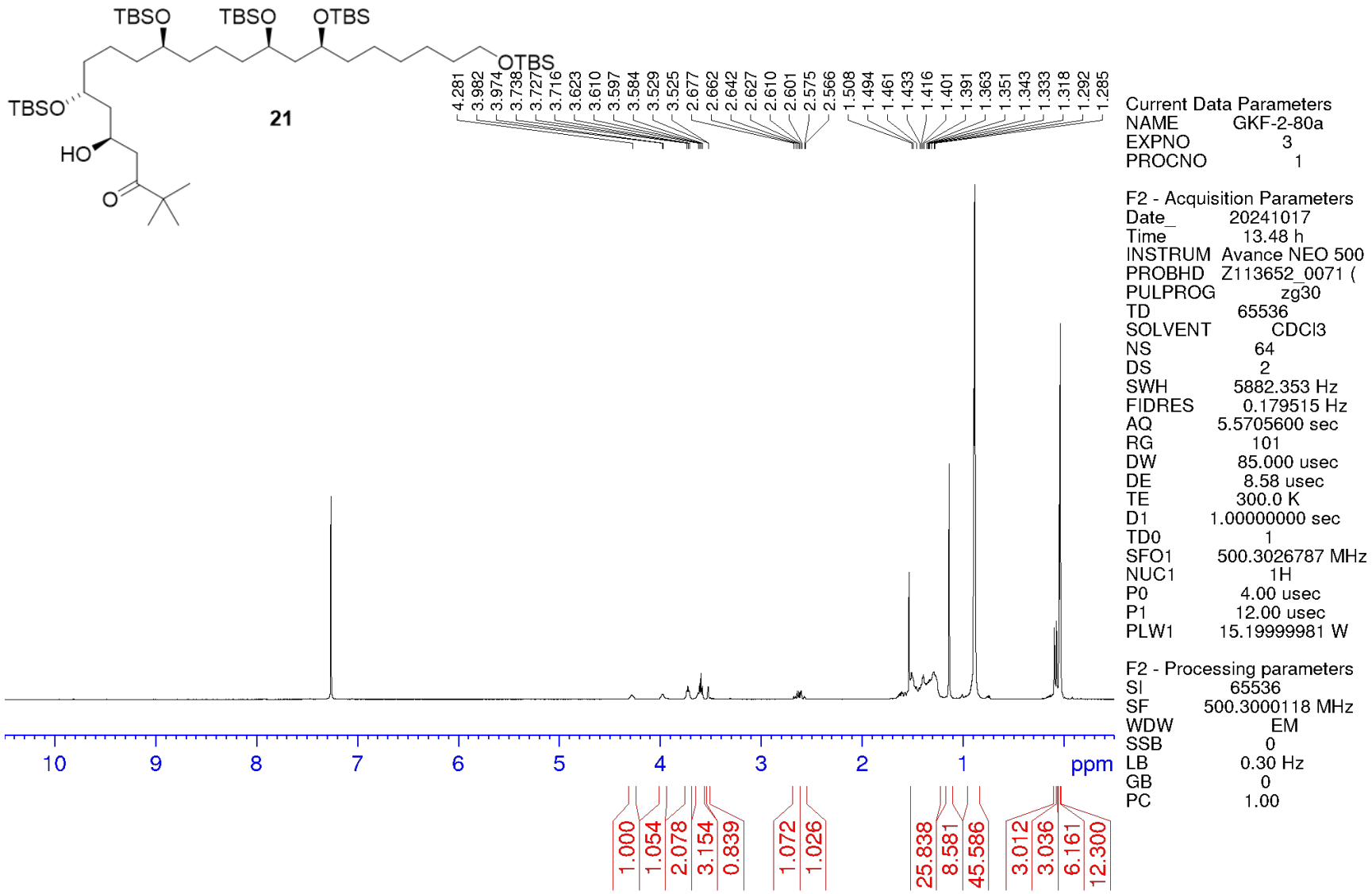
13C, CDCl3, 125 MHz



1H, CDCl3, 500 MHz



13C, CDCl3, 125 MHz

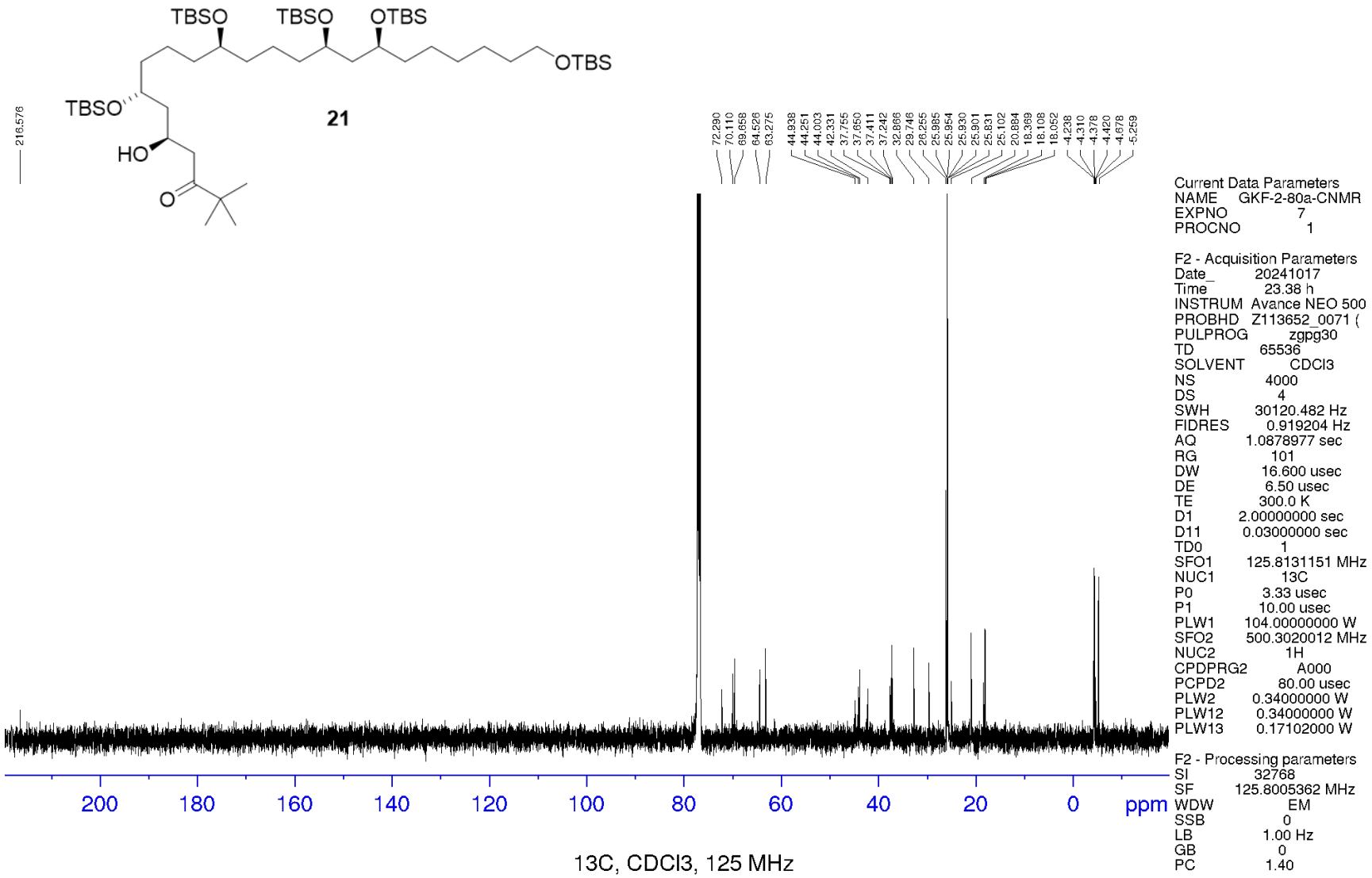


Current Data Parameters
NAME GKF-2-80a
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20241017
Time 13.48 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 5882.353 Hz
FIDRES 0.179515 Hz
AQ 5.5705600 sec
RG 101
DW 85.000 usec
DE 8.58 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.3026787 MHz
NUC1 1H
P0 4.00 usec
P1 12.00 usec
PLW1 15.19999981 W

F2 - Processing parameters
SI 65536
SF 500.3000118 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1H, CDCl3, 500 MHz


TBSO
TBSO
OTBS
OTBS
TBSO
HO
O
21
216.576
72.290
70.110
69.658
64.526
63.275
44.938
44.251
44.003
42.331
37.755
37.650
37.411
37.242
32.866
29.746
26.255
25.985
25.954
25.930
25.901
25.831
25.102
20.884
18.369
18.108
18.052
-4.238
-4.310
-4.378
-4.420
-4.678
-5.259
200
180
160
140
120
100
80
60
40
20
0
ppm
13C, CDCl3, 125 MHz
Current Data Parameters
NAME GKF-2-80a-CNMR
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20241017
Time 23.38 h
INSTRUM Avance NEO 500
PROBHD Z113652_0071 (
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4000
DS 4
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 1.0878977 sec
RG 101
DW 16.600 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8131151 MHz
NUC1 13C
P0 3.33 usec
P1 10.00 usec
PLW1 104.00000000 W
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG2 A000
PCPD2 80.00 usec
PLW2 0.34000000 W
PLW12 0.34000000 W
PLW13 0.17102000 W
F2 - Processing parameters
SI 32768
SF 125.8005362 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40