Catalytic S_N2'- and Enantioselective Allylic Substitution with a Diborylmethane Reagent and Application in Synthesis

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SUPPORTING INFORMATION

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1 General

Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, λ_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) or Varian Unity INOVA 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constant (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). High-resolution mass spectrometry was performed on a JEOL AccuTOF DART (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by GC analysis (Alltech Associated Chiraldex B-DM (30 m x 0.25 mm), Chiraldex G-TA (30 m x 0.25 mm), and Betadex 120 column (30 m x 0.25 mm)), or HPLC analysis (Chiral Technologies Chiralpak AZ–H (4.6 x 250 mmin comparison with authentic racemic materials. Specific rotations were measured on an ATAGO® AP-300 Automatic Polarimeter or a Rudolph Research Analytical Autopol IV Polarimeter. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Solvents were purified under a positive pressure of dry argon by a modified Innovative Technologies purification system: toluene, benzene and hexanes were purified through a copper oxide and alumina column; CH_2Cl_2 and Et_2O were purged with Ar and purified by passage through two alumina columns. Tetrahydrofuran (Aldrich Chemical Co.) was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific, Inc.) in air.

2 Reagents

Allyl phosphate was purchased from Aldrich and used as received.

Benzoic acid (BzOH) was purchased from Aldrich and used as received.

[1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride) ($PdCl_2$(dppf)) was purchased from TCI chemicals and used as received.

Bis[(pinacolato)boryl]methane ($CH_2B_2(pin)_2$) was purchased from TCI chemicals and used as received.

1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride (SIMes) was purchased from Aldrich and used as received.

9-Borabicyclo[3.3.1]nonane dimer (9-BBN) was purchased from Aldrich and used as received.

(*E*)-4-[(*tert*-Butyldimethylsilyloxy)but-2en-1-yl] diethyl phosphate (2p)[1]

Copper (I) chloride (CuCl) was purchased from Strem and used as received.

(*E*)-Diethyl 3-(2-bromophenyl)prop-2-enyl phosphate (2d)[2]

(*E*)-Diethyl 3-(3-bromophenyl)prop-2-enyl phosphate (2e)[3]

(*E*)-Diethyl 3-(4-chlorophenyl)prop-2-enyl phosphate (2f)[3]

(*E*)-Diethyl 3-cyclohexylprop-2-enyl phosphate (2m)[3]

(*E*)-Diethyl 3-(2-fluorophenyl)prop-2-enyl phosphate (2c)[2]

(*E*)-Diethyl 3-(2-methoxyphenyl)prop-2-enyl phosphate (2b)[3]

(*E*)-Diethyl 3-(4-nitrophenyl)prop-2-enyl phosphate (2h)[4]

(*E*)-Diethyl 3-phenylprop-2-enyl phosphate (2a)[4]

(*E*)-Diethyl (3-(pyridin-3-yl)allyl) phosphate (2k)[5]

(*E*)-Diethyl (3-(thiophen-3-yl)allyl) phosphate (2l)[5]

(*E*)-Diethyl 3-(4-trifluoromethylphenyl)prop-2-enyl phosphate (2g)[2]

(*E*)-3-[Dimethyl(phenyl)silyl]prop-2-enyl diethyl phosphate (2o)[2]

Imidazolinium salts 8,9 were prepared according to previously reported procedures.[6]

(1*E*,5*E*)-1-Iodo-2,6,10-trimethylundeca-1,5,9-triene (**14**) was prepared according to previously reported procedures.[7]

Lithium methoxide (LiOMe) was purchased from Aldrich and used as received.

Methanol was purchased from Acros and purified by distillation from Na (Aldrich) prior to use.

Methyl (*E*)-4-(3-((diethoxyphosphoryl)oxy)prop-1-en-1-yl)benzoate (2j)[5]

NHC–Ag complex 11a and **11b** were prepared according to a previously reported procedure.[8]

Palladium (II) Acetate ($Pd(OAc)_2$) was purchased from Strem and used as received.

Potassium *t*-butoxide (KO*t*-Bu) was purchased from Strem and used as received.

Potassium methoxide (KOMe) was purchased from Aldrich and used as received.

Pyrrolidine was purchased from Aldrich and used as received.

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[1] L. B. Delvos, D. J. Vyas, M. Oestreich, *Angew. Chem. Int. Ed.* **2013**, *52*, 4650–4653.

[2] B. Jung, A. H. Hoveyda, *J. Am. Chem. Soc.* **2012**, *134*, 1490–1493.

[3] K. Akiyama, F. Gao, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2010**, *49*, 419–423.

[4] C. A. Luchaco-Cullis, H. Mizutani, K. E. Murphy, A. H. Hoveyda, *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 1456–1460.

[5] Y. Shi, B. Jung, S. Torker, A. H. Hoveyda, *J. Am. Chem. Soc.* **2015**, *127*, 6877–6882.

[6] a) J. J. Van Veldhuizen, J. E. Campbell, R. E. Guidici, A. H. Hoveyda, *J. Am. Chem. Soc.* **2005**, *127*, 6877–6882; b) K.-s. Lee, A. H. Hoveyda, *J. Org. Chem.* **2009**, *74*, 4455–4462.

[7] R. S. Sulake, H.–H. Lin, C.–Y. Hsu, C.–F. Weng, C. Chen, *J. Org. Chem.* **2015**, *80*, 6044–6051.

[8] T. L. May, M. K. Brown, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2008,** *47*, 7358–7362.

Ruthenium complex (17) was purchased from Aldrich and used as received.

Sodium perborate tetrahydrate ($NaBO_3•4H_2O$) was purchased from Aldrich and used as received.

Sodium methoxide (NaOMe) was purchased from Strem and used as received.

Silver (I) Acetate (AgOAc) was purchased from Aldrich and used as received.

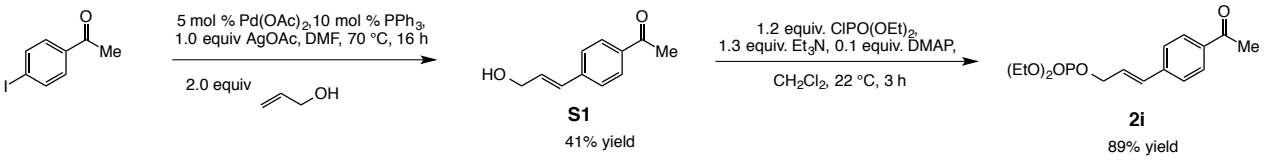
p-Toluenesulfonic acid (p-TsOH) was purchased from Aldrich and used as received.

Triethylamine (Et_3N) was purchased from Fisher Scientific, Inc. and distilled over CaH_2 prior to use.

Tripotassium phosphate (K_3PO_4) was purchased from Fisher Scientific, Inc. and distilled over CaH_2 prior to use.

3 Characterization Data for Allylic Phosphates Not Previously Reported

Scheme S1. Preparation of Allylic Phosphate **2i**



(*E*)-3-(4-Acetylphenyl)allyl diethyl phosphate (**2i**): **IR (neat):** 2985 (w), 2932 (w), 1681 (s), 1603 (m), 1563 (w), 1360 (w), 1266 (s), 1182 (w), 1166 (w), 1101 (w), 1028 (s), 975 (s), 853 (w), 801 (w), 594 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 600 MHz):** δ 7.90 (2H, d, J = 8.4 Hz), 7.45 (2H, d, J = 8.4 Hz), 6.70 (1H, d, J = 15.6 Hz), 6.40 (1H, dt, J = 15.6, 6.0 Hz), 4.70 (2H, t, J = 8.4 Hz), 4.15–4.10 (4H, m), 2.57 (3H, s), 1.33 (6H, t, J = 7.2 Hz; **^{13}C NMR ($CDCl_3$, 150 MHz):** δ 197.5, 140.7, 136.6, 132.3, 128.9, 126.8, 126.6 (d, J_{CP} = 6.9 Hz), 67.5 (d, J_{CP} = 4.7 Hz), 64.0 (d, J_{CP} = 5.7 Hz), 26.7, 16.2 (d, J_{CP} = 6.9 Hz). HRMS (ESI^+): Calcd for $C_{15}H_{22}O_5P_1$ $[M+H]^+$: 313.1205; Found: 313.1217.

4 Representative Procedure for NHC–Cu-Catalyzed Enantioselective Methylene-Boryl Addition to Disubstituted Allylic Phosphates

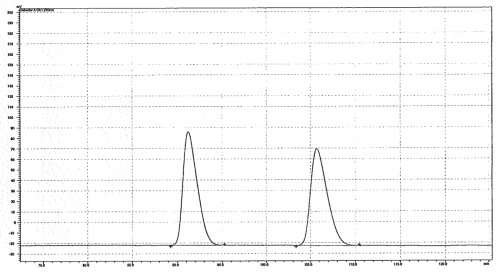
An oven-dried 1-dram vial equipped with a stir bar was charged with imidazolinium salt **10b** (4.8 mg, 5.5 μmol), NaOMe (6.5 mg, 150 μmol), and CuCl (0.5 mg, 5.0 μmol) in a nitrogen-filled glove box. The vial was sealed with a cap (phenolic open top cap with a red PFTE/white silicon septum) and electrical tape, and removed from the glove box. Tetrahydrofuran (thf; 0.50 mL) was added and the mixture was allowed to stir for 2 h under N_2 at 22 °C (the mixture became bright-yellow solution). The mixture of allylic phosphate **2a** (28 mg, 0.10 mmol) and bis[(pinacolato)boryl]methane **1** (40 mg, 0.15 mmol) in thf (0.5 mL) was added to the mixture slowly through a syringe. The resulting mixture was allowed to stir at 22 °C for 18 h. The mixture was passed through a short plug of silica gel (4 cm x 1 cm) and eluted with Et_2O. The organic layer was concentrated *in vacuo*, resulting in a yellow oily residue, which was diluted with thf

(0.5 ml) and water (0.5 ml), then $NaBO_3$•$4H_2O$ (78mg, 0.3 mmol) was added and the mixture was allowed to stir at 22 °C for 3 h. The mixture was washed with Et_2O (1.0 ml) three times and the combined organic layers was passed through a short plug of $MgSO_4$, concentrated and purified by silica gel chromatography (6:1 hexanes/Et_2O, R_f = 0.18) to afford 12.3 mg of the desired product **3a** as colorless oil (0.083 mmol, 83% yield).

5 Characterization Data for Alcohols with a *Tertiary* Carbon Stereogenic Center

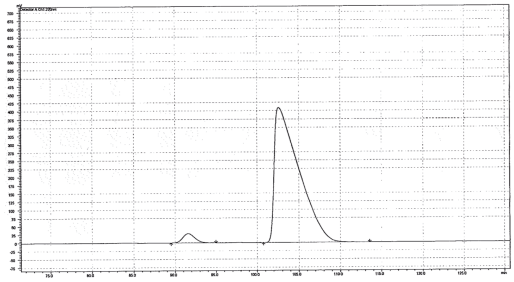
(*R*)-2-Phenylbut-3-en-1-ol (3a). IR (neat): 3353 (br, s), 2925 (w), 2873 (w), 1637 (w), 1601 (w), 1493 (w), 1452 (w), 1051 (m), 1027 (m), 916 (m), 755 (m), 698 (s), 679 (m), 593 (w), 537 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.35–7.31 (2H, m), 7.26–7.22 (3H, m), 6.00 (1H, ddd, *J* = 18.0, 10.4, 8.0 Hz), 5.22–5.15 (2H, m), 3.82 (1H, d, *J* = 6.8 Hz), 3.81 (1H, d, *J* = 6.8 Hz), 3.52 (1H, q, *J* = 7.2 Hz), 1.54 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 140.7, 138.3, 128.9, 128.1, 127.1, 117.3, 66.2, 52.7. **HRMS (ESI$^+$)**: Calcd for $C_{10}H_{11}$ $[M+H-H_2O]^+$: 131.0854; Found: 131.0861. Specific rotation: $[\alpha]_D^{20.0}$ −36.0 (*c* 0.25, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r. Based on reported optical rotation value ($[\alpha]_D^{26}$ +19 (*c* 0.81, $CHCl_3$) for 33:67 er) , the absolute stereochemistry of the major enantiomer is assigned to be *R*.[9]

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.5:0.5 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	91.224	11950190	108127	49.885	53.974
2	105.687	12005426	92203	50.115	46.026
Total		23955616	200331	100.000	100.000



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	91.569	2846041	28078	3.300	6.420
2	102.605	83400095	409263	96.700	93.580
Total		86246136	437341	100.000	100.000

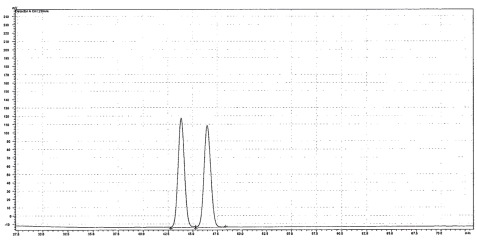
Retention Time	Area	Area%	Retention Time	Area	Area%
91.224	11050190	49.885	91.569	2846041	3.300
105.687	120005426	50.115	102.605	83400095	96.700

(*R*)-2-(2-Methoxyphenyl)but-3-en-1-ol (3b): **IR (neat)**: 3379 (br, s), 2937 (w), 2836 (w), 1636 (w), 1597 (w), 1585 (w), 1491 (s), 1462 (m), 1438 (m), 1288 (w), 1240 (w), 1187 (w), 1168 (w), 1109 (w), 1051 (s), 1026 (s), 996 (m), 915 (m), 751 (s), 670 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.26-7.21 (1H, m), 7.20 (1H, m), 6.94 (1H, t, *J* = 7.6 Hz), 6.89 (1H, d, *J* = 8.4 Hz), 6.12–6.03 (1H, m), 5.22–5.17 (2H, m), 3.87 (1H, q, *J* = 7.2 Hz), 3.86–3.80 (5H, m), 1.61 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 157.3, 138.0, 129.0, 128.5, 128.0, 120.9, 117.0, 111.0, 65.3, 55.6,

[9] K. B. Selim, K. Yamada, K. Tomioka, *Chem. Commun.* **2008**, 5140–5142.

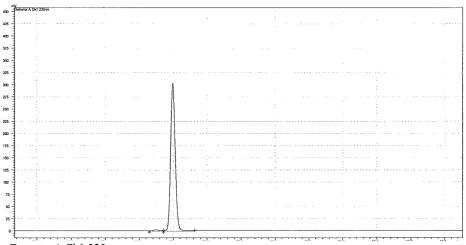
45.9. **HRMS (ESI$^+$)**: Calcd for $C_{11}H_{13}O_1$ $[M+H-H_2O]^+$: 161.0966; Found: 161.0968. Specific rotation: $[\alpha]_D^{20.0}$ –25.2 (*c* 0.85, $CHCl_3$) for an enantiomerically enriched sample of 99:1 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.824	5928380	131557	49.978	51.762
2	46.472	5933496	122599	50.022	48.238
Total		11861877	254156	100.000	100.000



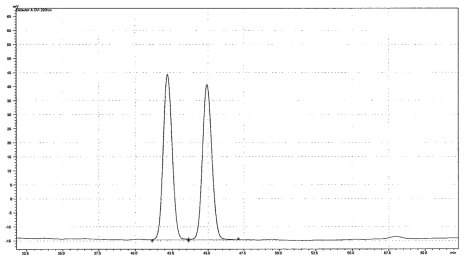
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.468	212733	3070	1.437	1.002
2	44.929	14593269	303369	98.563	98.998
Total		14806002	306439	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
43.824	5928380	49.978	42.468	212733	1.437
46.472	5933496	50.022	44.929	14593269	98.563

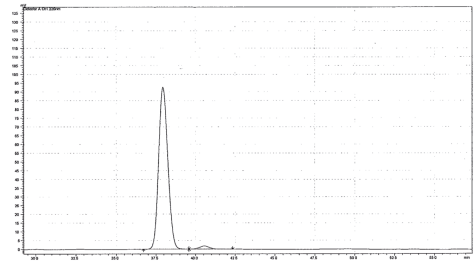
(*R*)-2-(2-Fluorophenyl)but-3-en-1-ol (**3c**): **IR (neat)**: 3358 (br, s), 2938 (w), 1638 (w), 1583 (w), 1490 (s), 1454 (m), 1418 (w), 1228 (s), 1175 (w), 1055 (s), 1036 (s), 993 (m), 919 (s), 824 (w), 806 (w), 665 (w), 602 (w), 479 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.27–7.20 (2H, m), 7.14–7.10 (1H, m), 7.07–7.03 (1H, m), 6.08–6.00 (1H, m), 5.23 (1H, d, J = 10.8 Hz), 5.13 (1H, J = 17.2 Hz), 3.86 (3H, app.s), 1.58 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 161.0 (d, J_{CF} = 244.4 Hz), 137.0, 129.3 (d, J_{CF} = 4.5 Hz), 128.5 (d, J_{CF} = 8.4 Hz), 127.7 (d, J_{CF} = 15.2 Hz), 124.4 (d, J_{CF} = 3.0 Hz), 117.8.0, 115.9 (d, J_{CF} = 22.0 Hz), 65.1, 46.2. **HRMS (ESI$^+$)**: Calcd for $C_{10}H_{10}F$ $[M+H-H_2O]^+$: 149.0767; Found: 149.0773. Specific rotation: $[\alpha]_D^{20.0}$ –34.2 (*c* 0.89, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.201	2521279	59044	49.764	51.605
2	44.920	2545157	55372	50.236	48.395
Total		5066436	114416	100.000	100.000



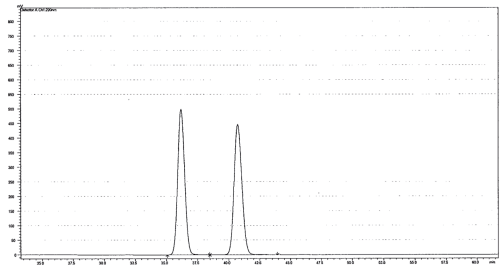
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.938	3737434	92579	98.073	98.142
2	40.564	73451	1753	1.927	1.858
Total		3810885	94331	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
42.201	2521279	49.764	37.938	3737434	98.073
44.920	2545157	50.236	40.564	73451	1.927

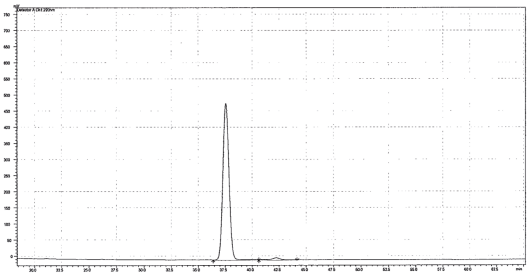
(*R*)-2-(2-Bromophenyl)but-3-en-1-ol (3d): **IR (neat)**: 3353 (br, s), 3080 (w), 2928 (w), 2874 (w), 1730 (w), 1637 (w), 1469 (m), 1437 (w), 1417 (w), 1373 (w), 1222 (w), 1021 (s), 992 (s), 918 (s), 832 (w), 750 (s), 724 (m), 646 (m), 600 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.59 (1H, *J* = 8.0 Hz), 7.32–7.28 (2H, m), 7.13–7.08 (1H, m), 5.99 (1H, ddd, *J* = 17.6, 10.0, 6.8 Hz), 5.27 (1H, dd, *J* = 10.4 Hz), 5.23 (1H, d, *J* = 17.6 Hz), 4.11 (1H, *J* = 6.8 Hz), 3.91–3.87 (2H, m), 1.56 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 139.8, 137.1, 133.4, 128.9, 128.5, 127.8, 125.3, 118.0, 65.1, 50.7. **HRMS (ESI$^+$)**: Calcd for $C_{10}H_{10}Br$ $[M+H-H_2O]^+$: 208.9966; Found: 208.9964. Specific rotation: $[\alpha]_D^{20.0}$ –11.9 (*c* 1.33, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.168	19585946	499227	49.867	52.770
2	40.717	19690233	446815	50.133	47.230
Total		39276178	946042	100.000	100.000



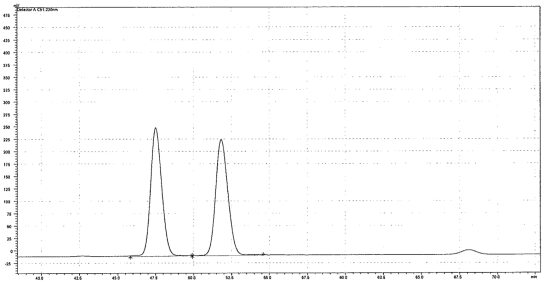
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.549	19349954	486593	97.161	98.520
2	42.225	565421	7309	2.839	1.480
Total		19915375	493902	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
36.168	19585946	49.867	37.549	19349954	97.161
40.717	19690233	50.133	42.225	565421	2.839

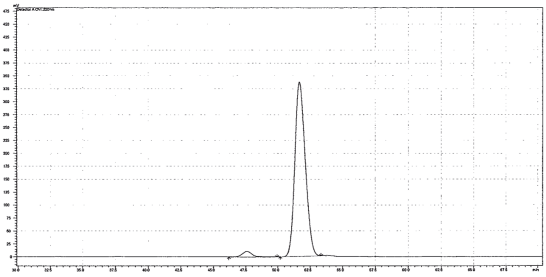
(*R*)-2-(3-Bromophenyl)but-3-en-1-ol (3e): **IR (neat)**: 3333 (br, s), 2925 (w), 2874 (w), 1638 (w), 1593 (m), 1566 (m), 1474 (m), 1426 (m), 1299 (w), 1187 (w), 1127 (w), 1071 (s), 1053 (s), 1027 (s), 996 (s), 919 (s), 878 (m), 836 (w), 804 (w), 779 (s), 693 (s), 656 (m), 435 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.39–7.37 (2H, m), 7.23–7.16 (2H, m), 5.96 (1H, ddd, *J* = 17.2, 9.6, 6.8 Hz), 5.24 (1H, d, *J* = 9.6 Hz), 5.19 (1H, d, *J* = 16.8 Hz), 3.82 (2H, app. d, *J* = 7.2 Hz), 3.50 (1H, app. q, *J* = 7.2 Hz), 1.56 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 143.2, 137.6, 131.2, 130.4, 130.2, 126.8, 122.9, 117.8, 66.0, 52.2. **HRMS (ESI$^+$)**: Calcd for $C_{10}H_{10}Br$ $[M+H–H_2O]^+$: 208.9966; Found: 208.9957. Specific rotation: $[\alpha]_D^{20.0}$ –39.5 (*c* 1.32, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.512	13339096	258887	49.983	52.487
2	51.825	13347987	234354	50.017	47.513
Total		26687084	493241	100.000	100.000



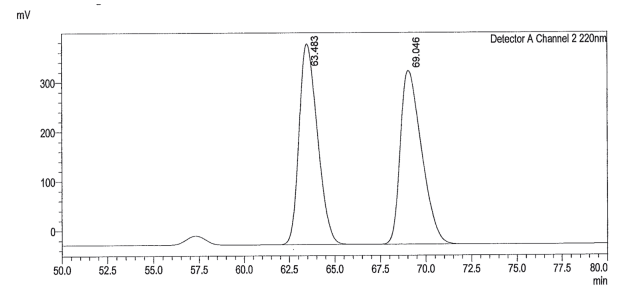
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.586	656466	11102	3.328	3.185
2	51.663	19067927	337503	96.672	96.815
Total		19724393	348605	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
47.512	13339096	49.983	47.586	656466	3.328
51.825	13347987	50.017	51.663	19067927	96.672

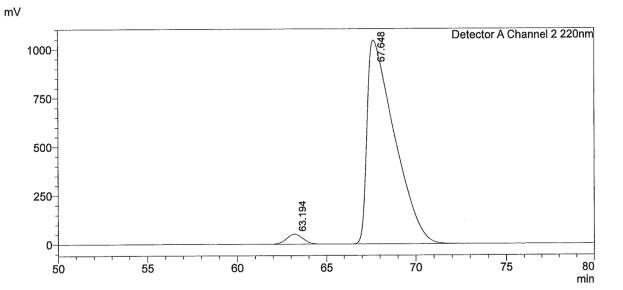
(*R*)-2-(4-Chlorophenyl)but-3-en-1-ol (**3f**): **IR (neat)**: 3345 (br, s), 2926 (w), 2876 (w), 1637 (w), 1490 (s), 1406 (m), 1297 (w), 1181 (w), 1091 (s), 1053 (s), 1030 (s), 1014 (s), 993 (s), 919 (s), 870 (w), 824 (w), 784 (m), 723 (m), 625 (m), 540 (s), 521 (s), 457 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.33–7.29 (2H, m), 7.19–7.16 (2H, m), 5.97 (1H, ddd, *J* = 17.6, 10.0, 7.2 Hz), 5.23 (1H, app. dt, *J* = 10.4, 1.2 Hz), 5.17 (1H, app. dt, *J* = 17.2, 1.2 Hz), 3.81 (2H, app. d, *J* = 7.2 Hz), 3.51 (1H, app. q, *J* = 7.2 Hz), 1.50 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 139.3, 137.8, 132.8, 129.5, 129.0, 117.6, 66.0, 51.9. HRMS (ESI^+): Calcd for $C_{10}H_{10}Cl$ $[M+H-H_2O]^+$: 165.0471; Found: 165.0470. Specific rotation: $[\alpha]_D^{20.0}$ –49.5 (*c* 0.58, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	63.483	28543632	405247	49.950	53.594
2	69.046	28600276	350898	50.050	46.406
Total		57143908	756145	100.000	100.000



Detector A Channel 2 220nm

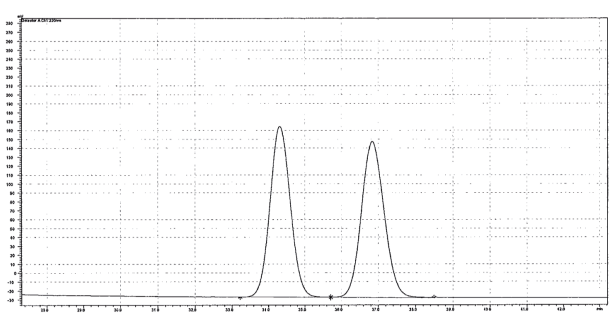
Peak#	Ret. Time	Area	Height	Area%	Height%
1	63.194	3312871	51181	2.896	4.667
2	67.648	111076701	1045436	97.104	95.333
Total		114389572	1096616	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
63.483	28543632	49.950	63.194	3312871	2.896
69.046	28600276	50.050	67.648	111076701	97.104

(*R*)-2-(4-(Trifluoromethyl)phenyl)but-3-en-1-ol (**3g**): **IR (neat)**: 3344 (br, s), 2923 (m), 2853 (w), 1731 (w), 1619 (w), 1554 (w), 14612 (w), 1377 (w), 1325 (s), 1261 (w), 1164 (m), 1124 (s), 1068 (s), 1018 (m), 922 (w), 839 (w), 738 (w), 605 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ

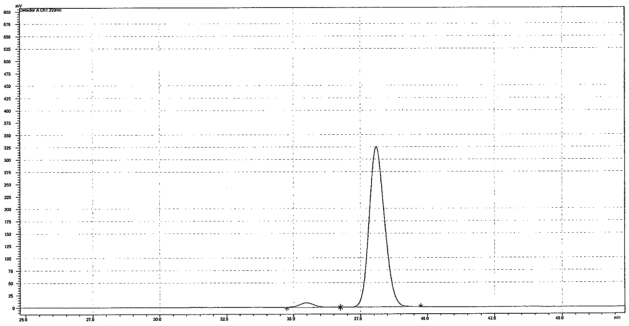
7.60 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz), 6.00 (1H, ddd, *J* = 17.6, 10.0, 7.2 Hz), 5.26 (1H, d, *J* = 10.0 Hz), 5.20 (1H, dd, *J* = 17.2, 0.8 Hz), 3.86 (2H, d, *J* = 7.2 Hz), 3.60 (1H, app. q, *J* = 7.2 Hz), 1.57 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: 145.0, 137.4, 129.4 (q, J_{CF} = 31.9 Hz), 128.5, 125.8 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 270.2 Hz), 118.0, 65.9, 52.4. **HRMS (ESI$^+$)**: Calcd for $C_{11}H_{10}F_3$ $[M+H-H_2O]^+$: 199.0735; Found: 199.0737. Specific rotation: $[\alpha]_D^{20.0}$ 11.7 (*c* 1.09, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.311	7407524	191387	49.802	52.231
2	36.835	7466527	175034	50.198	47.769
Total		14874051	366421	100.000	100.000



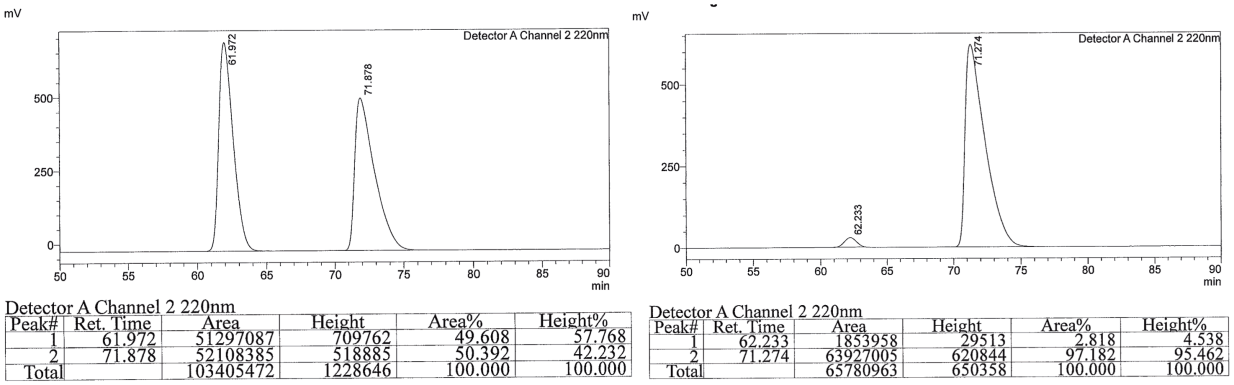
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.486	390190	9594	2.883	2.867
2	38.085	13143231	325010	97.117	97.133
Total		13533421	334604	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
34.311	7407524	49.802	35.486	390190	2.883
36.835	7466527	50.198	38.085	13143231	97.117

(R)-2-(4-Nitrophenyl)but-3-en-1-ol (3h): **IR (neat)**: 3374 (br, s), 2927 (w), 2877 (w), 1638 (w), 1597 (m), 1514 (s), 1411 (w), 1342 (s), 1182 (w), 1109 (w), 1052 (m), 1014 (m), 994 (m), 923 (m), 850 (s), 827 (m), 779 (w), 751 (m), 702 (s), 535 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 8.18 (2H, d, *J* = 8.8 Hz), 7.42 (2H, d, *J* = 8.8 Hz), 5.99 (1H, ddd, *J* = 17.6, 10.0, 7.2 Hz), 5.28 (1H, d, *J* = 10.4 Hz), 5.20 (1H, d, *J* = 17.2 Hz), 3.88 (2H, d, *J* = 7.6 Hz), 3.65 (1H, app. q, *J* = 7.2 Hz), 1.86 (1H, br); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 148.7, 147.1, 136.8, 129.1, 124.0, 118.5, 65.7, 52.3. **HRMS (ESI$^+$)**: Calcd for $C_{10}H_{12}O_3N$ $[M+H]^+$: 194.0817; Found: 194.0811. Specific rotation: $[\alpha]_D^{20.0}$ –62.8 (*c* 0.78, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 96.0:4.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	61.972	51297087	709762	49.608	57.768
2	71.878	52108385	518885	50.392	42.232
Total		103405472	1228646	100.000	100.000

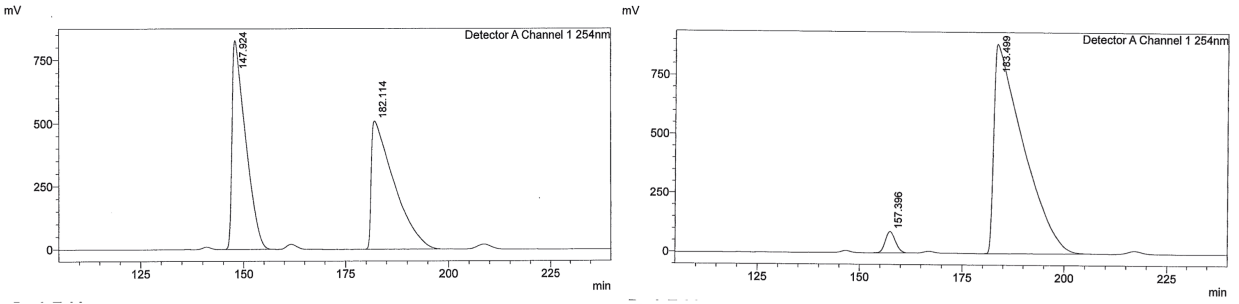
Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	62.233	1853958	29513	2.818	4.538
2	71.274	63927005	620844	97.182	95.462
Total		65780963	650358	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
61.972	51297087	49.608	62.233	1853958	2.818
71.878	52108385	50.392	71.274	63927005	97.182

(*R*)-1-(4-(1-Hydroxybut-3-en-2-yl)phenyl)ethan-1-one (**3i**): **IR (neat)**: 3423 (br, s), 2924 (m), 2827 (w), 1679 (s), 1605 (s), 1459 (w), 1411 (m), 1359 (m), 1307 (w), 1270 (s), 1184 (w), 1115 (w), 1056 (m), 1017 (m), 996 (w), 959 (w), 835 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.94–7.91 (2H, m), 7.35–7.33 (2H, m), 6.00 (1H, ddd, *J* = 17.6, 10.0, 7.2 Hz), 5.25 (1H, d, *J* = 10.4 Hz), 5.20 (1H, d, *J* = 17.6 Hz), 3.86 (2H, d, *J* = 5.2 Hz), 3.61 (1H, q, *J* = 7.2 Hz), 2.59 (3H, s), 1.59 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 197.9, 146.5, 137.5, 136.0, 128.9, 128.4, 118.0, 65.9, 52.6, 26.7. **HRMS (ESI$^+$)**: Calcd for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072; Found: 191.1073. Specific rotation: $[\alpha]_D^{20.0}$ –55.6 (*c* 0.73, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 96.0:4.0 hexanes/*i*PrOH, 0.5 mL/min, 254 nm.



Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	147.924	191706307	828230	49.424	61.877
2	182.114	196173222	510289	50.576	38.123
Total		387879528	1338520	100.000	100.000

Detector A Channel 1 254nm

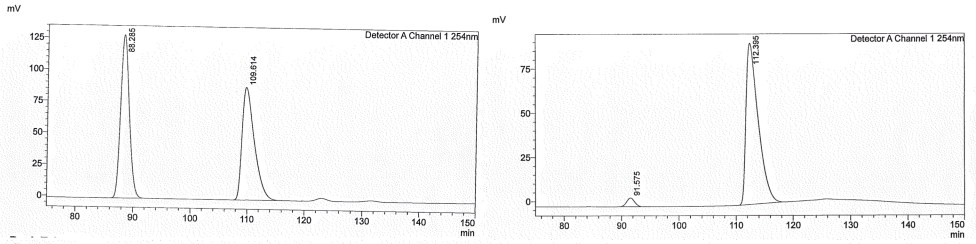
Peak#	Ret. Time	Area	Height	Area%	Height%
1	157.396	15715158	90111	3.438	9.213
2	183.499	441445152	887994	96.562	90.787
Total		457160310	978106	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
147.924	191706307	49.424	157.396	15715158	3.438
182.114	196173222	50.576	183.499	441445152	96.562

Methyl (*R*)-4-(1-hydroxybut-3-en-2-yl)benzoate (**3j**): **IR (neat)**: 3419 (br, s), 2951 (w), 2878 (w), 1718 (s), 1637 (w), 1609 (m), 1574 (w), 1436 (m), 1413 (w), 1312 (m), 1277 (s), 1181 (m), 1110 (s), 1054 (m), 1019 (m), 996 (w), 966 (w), 920 (w), 769 (m), 709 (m) cm^{-1}; **^{1}H NMR**

($CDCl_3$, 600 MHz): δ 8.01 (2H, *J* = 8.4 Hz), 7.32 (2H, *J* = 8.4 Hz), 6.00 (1H, ddd, *J* = 17.4, 9.6, 7.2 Hz), 5.25 (1H, app. d, *J* = 10.2 Hz), 5.20 (1H, app. d, *J* = 18.0 Hz), 3.91 (3H, s), 3.85 (2H, d, *J* = 6.6 Hz), 3.60 (1H, q, *J* = 7.2 Hz)), 1.52 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 167.1, 146.2, 137.6, 130.2, 129.0, 128.2, 117.9, 66.0, 52.6, 52.2. **HRMS (ESI$^+$)**: Calcd for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.1021; Found: 207.1025. Specific rotation: $[\alpha]_D^{20.0}$ –51.7 (*c* 1.05, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 96.0:4.0 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm.



Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	88.285	13394628	129208	50.006	59.154
2	109.614	13391298	89217	49.994	40.846
Total		26785926	218425	100.000	100.000

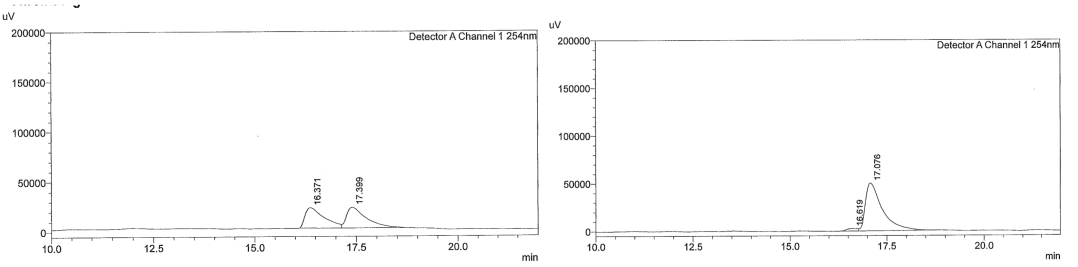
Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	91.575	489606	4999	3.478	5.191
2	112.395	13586141	91316	96.522	94.809
Total		14075746	96315	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
88.285	13394628	50.006	91.575	489606	3.478
109.614	13391298	49.994	112.395	13586141	96.522

(*R*)-2-(Pyridin-3-yl)but-3-en-1-ol (3k): **IR (neat)**: 3222 (br, s), 3081 (w), 2922 (w), 2868 (w), 1638 (w), 1592 (w), 1479 (m), 1425 (m), 1369 (w), 1060 (s), 1028 (s), 994 (m), 918 (s), 810 (m), 785 (m), 713 (s), 633 (m), 400 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 600 MHz)**: δ 8.49–8.47 (2H, m), 7.57 (1H, dt, *J* = 7.8, 1.8 Hz), 7.27–7.25 (1H, m), 6.00 (1H, ddd, *J* = 18.0, 10.2, 7.2 Hz), 5.26 (1H, td, *J* = 10.2, 1.2 Hz), 5.19 (1H, td, *J* = 17.4, 1.2 Hz), 3.87–3.86 (1H, m), 3.56 (1H, q, *J* = 7.2 Hz), 1.95 (1H, s)**; ^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 149.8, 148.2, 137.3, 136.7, 135.6, 123.7, 118.0, 65.8, 50.0. **HRMS (ESI$^+$)**: Calcd for $C_9H_{12}NO$ $[M+H]^+$: 150.0919; Found: 150.0921. Specific rotation: $[\alpha]_D^{20.0}$ –20.6 (*c* 0.67, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material before oxidation; Chiralpak AZ–H column, 98.0:2.0 hexanes/ *i*PrOH, 1.0 mL/min, 254 nm.



Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.371	676373	20497	49.119	49.670
2	17.399	700622	20769	50.881	50.330
Total		1376995	41266	100.000	100.000

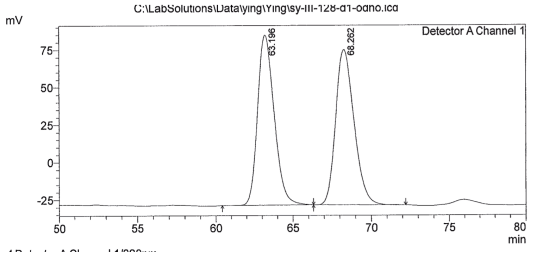
Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.619	51849	2658	3.283	5.042
2	17.076	1527232	50058	96.717	94.958
Total		1579080	52716	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
16.371	676373	49.119	16.619	51849	3.283
17.399	700622	50.881	17.076	1527232	96.717

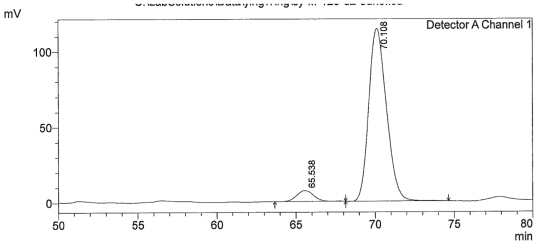
(*R*)-2-(Thiophen-3-yl)but-3-en-1-ol (3l): IR (neat): 3392 (br, s), 2923 (s), 2853 (m), 1733 (w), 1639 (w), 1461 (m), 1414 (m), 1382 (m), 1259 (m), 1156 (m), 1079 (s), 1030 (s), 993 (s), 965 (m), 921 (s), 840 (m), 783 (s), 714 (m), 632 (m), 482 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 500 MHz)**: δ 7.32 (1H, dd, *J* = 5.2, 3.2 Hz), 7.08–7.07 (1H, m), 7.00 (1H, dd, *J* = 5.2, 1.2 Hz), 5.97 (1H, ddd, *J* = 17.2, 10.0, 7.2 Hz), 5.24–5.17 (2H, m), 3.86–3.76 (2H, m), 3.65 (1H, q, *J* = 7.2 Hz), 1.57 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 141.2, 138.0, 127.2, 126.1, 121.3, 117.4, 65.9, 48.2. **HRMS (ESI$^+$)**: Calcd for C_8H_9S $[M+H-H_2O]^+$: 137.0425; Found: 137.0420. Specific rotation: $[\alpha]_D^{20.0}$ –13.6 (*c* 0.87, $CHCl_3$) for an enantiomerically enriched sample of 94:6 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material before oxidation; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	63.196	8529375	113441	50.223	52.292
2	68.262	8453654	103495	49.777	47.708
Total		16983029	216936	100.000	100.000



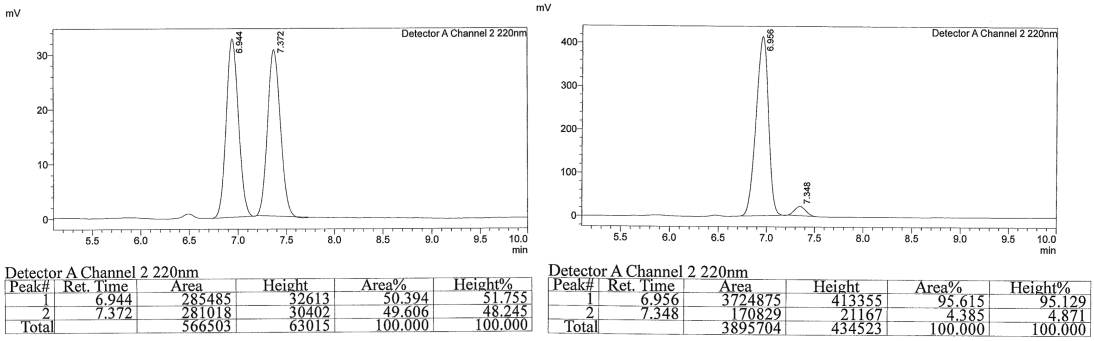
Detector A Channel 1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	65.538	552387	7290	5.850	5.998
2	70.108	8890482	114250	94.150	94.002
Total		9442868	121539	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
63.196	8529375	50.223	65.538	552387	5.850
68.262	8453654	49.777	70.108	8890482	94.150

(*R*)-2-Cyclohexylbut-3-en-1-ol (3m): **IR (neat)**: 3358 (br, s), 2923 (s), 2852 (m), 1449 (w), 1055 (w), 1016 (w), 997 (w), 913 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 5.63 (1H, dt, *J* = 16.8, 10.0 Hz), 5.19 (1H, dd, *J* = 10.4, 2.0 Hz), 5.11 (1H, dd, *J* = 17.2, 2.0 Hz), 3.70 (1H, dd, *J* = 10.4, 4.8 Hz), 3.44 (1H, dd, *J* = 10.4, 9.2 Hz), 2.07–2.00 (1H, m), 1.73–1.62 (5H, m), 1.43 (1H, s), 1.37–1.31 (1H, m), 1.27–1.10 (3H, m), 1.07–0.93 (2H, m); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 138.9, 118.3, 63.6, 53.2, 38.7, 31.3, 30.4, 26.7, 26.6, 26.5. **HRMS (ESI$^+$):** Calcd for $C_{10}H_{19}O$ $[M+H]^+$: 155.1426; Found: 155.1432. Specific rotation: $[\alpha]_D^{20.0}$ –10.8 (*c* 0.65, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material after benzoylation; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 1.0 mL/min, 220 nm.



Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.944	285485	32613	50.394	51.755
2	7.372	281018	30402	49.606	48.245
Total		566503	63015	100.000	100.000

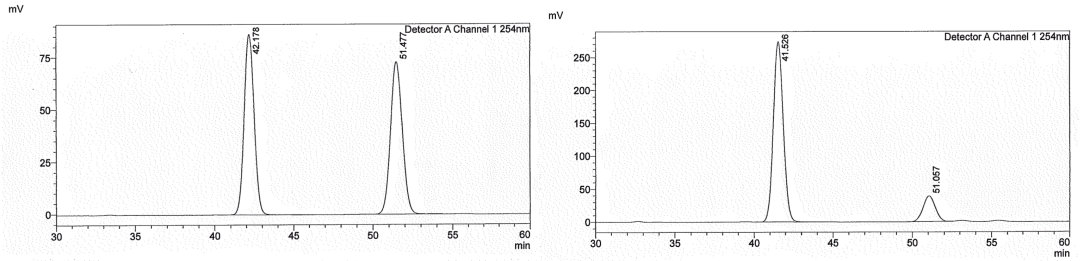
Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	6.956	3724875	413355	95.615	95.129
2	7.348	170829	21167	4.385	4.871
Total		3895704	434523	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
6.944	285485	50.394	6.956	3724875	95.615
7.372	282018	49.606	7.348	170829	4.385

(*R*,*E*)-4-Phenyl-2-vinylbut-3-en-1-ol (3n): **IR (neat)**: 3349 (br, s), 3080 (w), 3059 (w), 3025 (w), 2926 (w), 2872 (w), 1637 (w), 1598 (w), 1493 (w), 1448 (w), 1415 (w), 1028 (m), 990 (m), 965 (s), 915 (s), 862 (w), 842 (w), 746 (s), 691 (s), 601 (w), 508 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.38 (2H, d, *J* = 7.2 Hz), 7.31 (2H, app. t, *J* = 7.2 Hz), 7.25–7.21 (1H, m), 6.51 (1H, d, *J* = 16.0 Hz), 6.14 (1H, dd, *J* = 16.0, 8.0 Hz), 5.89–5.80 (1H, m), 5.25– 5.21(2H, m), 3.66 (2H, d, *J* = 6.8 Hz), 3.18–3.11 (1H, m), 1.59 (1H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 137.5, 137.1, 132.4, 128.70, 128.68, 128.63, 126.4, 117.4, 65.4, 50.2. HRMS (ESI^+): Calcd for $C_{12}H_{13}$ $[M+H-H_2O]^+$: 157.1017; Found: 157.1014; specific rotation: $[\alpha]_D^{20.0}$ –43.8 (*c* 0.84, $CHCl_3$) for an enantiomerically enriched sample of 85:15 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 254 nm.



Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	42.178	3766154	86250	49.949	54.156
2	51.477	3773786	73011	50.051	45.844
Total		7539940	159261	100.000	100.000

Detector A Channel 1 254nm

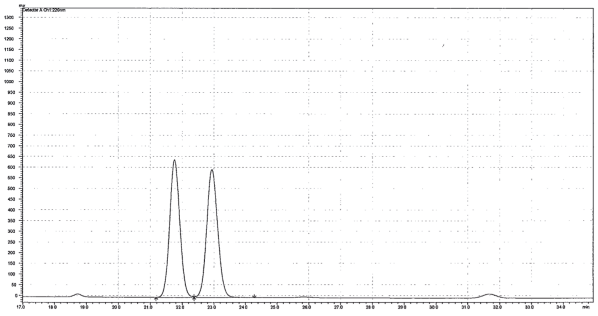
Peak#	Ret. Time	Area	Height	Area%	Height%
1	41.526	12122695	274137	85.254	87.506
2	51.057	2096846	39143	14.746	12.494
Total		14219541	313280	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
42.178	3766154	49.949	41.526	12122695	85.254
51.477	3773786	50.051	51.057	2096846	14.746

(*S*)-2-(Dimethyl(phenyl)silyl)but-3-en-1-ol (3o): **IR (neat)**: 3347(br, s), 2956 (w), 2868 (w), 1627 (w), 1427 (w), 1412 (w), 1301 (w), 1248 (m), 1111(m), 1049 (m), 993 (m), 896 (m), 832 (s), 812 (s), 793 (s), 775 (m), 759 (m), 729 (s), 698 (s), 653 (s), 594 (w), 469 (m), 417 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 500 MHz)**: δ 7.50–7.48 (2H, m), 7.39–7.33 (3H, m), 5.69 (1H, dt, *J* = 17.6, 10.4

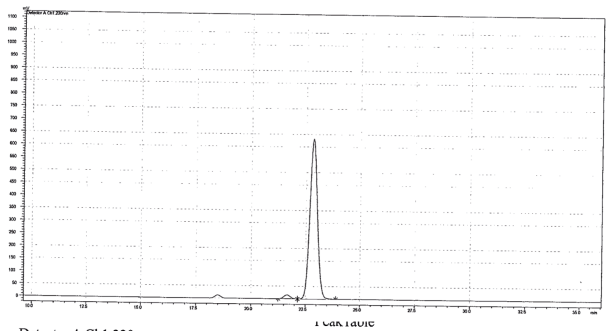
Hz), 5.08 (1H, d, *J* = 10.4 Hz), 5.02 (2H, 1H, d, *J* = 10.4 Hz), 3.74–3.65 (2H, m), 2.15 (1H, td, *J* = 10.0, 4.8 Hz), 1.47 (1H, s), 0.32 (6H, s); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 136.84, 136.75, 134.4, 129.4, 128.0, 115.6, 62.4, 39.7, –4.13, –4.81. **HRMS (ESI$^+$)**: Calcd for $C_{12}H_{17}Si$ $[M+H-H_2O]^+$: 189.1100; Found: 189.1106. Specific rotation: $[\alpha]_D^{20.0}$ –4.22 (*c* 1.47, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material; Chiralpak AZ–H column, 99.0:1.0 hexanes/*i*PrOH, 0.5 mL/min, 220 nm.



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.752	14471832	644648	49.743	51.839
2	22.934	14621157	598921	50.257	48.161
Total		29092989	1243569	100.000	100.000



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.655	297603	14657	1.900	2.272
2	22.836	15364427	630434	98.100	97.728
Total		15662030	645091	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
21.752	14471832	49.743	21.655	297603	1.900
22.934	14621157	50.257	22.836	15364427	98.100

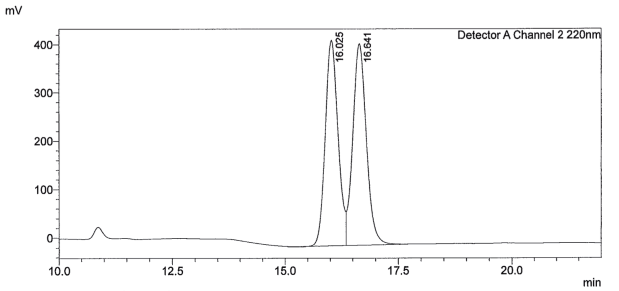
6 Formal Synthesis of Rhopaloic Acid A

6.1 NHC–Cu-Catalyzed EAS with Allylic Phosphate 2p

A 100-mL oven-dried flask equipped with a stir bar was charged with imidazolinium salt **11b** (35 mg, 55 μmol), NaOMe (65 mg, 1.20 mmol), and CuCl (5.0 mg, 50 μmol) in an N_2-filled glove box. The vial was sealed with a septum and electrical tape, and removed from the glove box. Tetrahydrofuran (5.0 mL) was added and the mixture was allowed to stir for 2 h under N_2 at 22 °C. The solution became bright yellow. Bis[(pinacolato)boryl]methane **1** (400 mg, 1.5 mmol) and allylic phosphate **2p** (338 mg, 1.0 mmol) dissolved in thf (5.0 mL) was added through a syringe and the resulting solution was allowed to stir at 22 °C for 6 h. The solution was then passed through a short plug of silica gel and eluted with Et_2O. The organic layer was concentrated *in vacuo*, resulting in yellow oil that was purified by silica gel chromatography (20:1 hexanes/Et_2O, R_f 0.19) to afford 290 mg of **12p** (>98:2 S_N2'/S_N2) as pale yellow oil (0.89 mmol, 89% yield). **(*R*)-*tert*-Butyldimethyl((2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-en-1-yl)oxy)silane** (**12p**): **IR (neat)**: 2978 (w), 2956 (w), 2929 (w), 2888 (w), 2857(w), 1471 (w), 1407 (w), 1368 (s), 1317 (s), 1253 (s), 1213 (w), 1145 (s), 1095 (s), 1004 (w), 969 (w), 888 (w), 834 (s), 774 (s), 667 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 5.78 (1H, ddd, *J* = 18.0, 10.4, 7.6 Hz), 5.03 (1H, app. d, *J* = 17.2 Hz), 4.97 (1H, app. d, *J* = 10.8 Hz), 3.49 (2H, d, *J* = 6.4 Hz), 2.50–

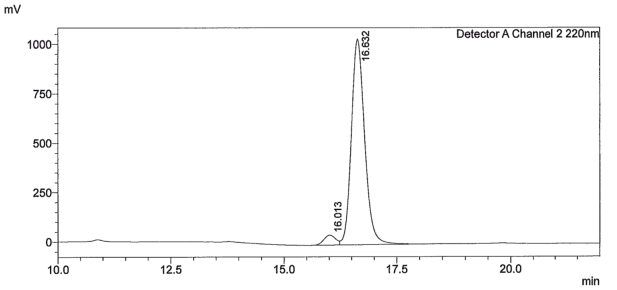
2.41 (1H, m), 1.23 (12H, d, *J* = 2.4 Hz), 0.96 (1H, dd, *J* = 15.6, 10.0 Hz), 0.88 (9H, s), 0.79 (1H, dd, *J* = 16.0, 9.2 Hz), 0.03 (6H, s); **^{13}C NMR ($CDCl_3$, 150 MHz)**: δ 141.7, 114.2, 83.3, 68.2, 42.1, 26.1, 25.1, 24.9, –5.1, –5.2. **HRMS (ESI$^+$)**: Calcd for $C_{17}H_{36}BO_3Si$ $[M+H]^+$: 327.2527; Found: 327.2527. Specific rotation: $[\alpha]_D^{20.0}$ 7.89 (*c* 0.84, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material after desilylation and benzoylation of the resulting alcohol; Chiralpak AZ–H column, 97.0:3.0 hexanes/*i*PrOH, 0.3 mL/min, 220 nm.



Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.025	8362169	425138	49.258	50.497
2	16.641	8614075	416767	50.742	49.503
Total		16976243	841905	100.000	100.000



Detector A Channel 2 220nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.013	943644	50972	4.216	4.671
2	16.632	21438366	1040246	95.784	95.329
Total		22382009	1091218	100.000	100.000

Retention Time	Area	Area%	Retention Time	Area	Area%
16.025	8362169	49.258	16.013	50972	4.216
16.641	8614075	50.742	16.632	1040246	95.784

6.2 Phosphine–Palladium Catalyzed Suzuki Cross-Coupling[10] with Alkenyl Iodide

A 4-dram vial with a stir bar was charged with alkyl–B(pin) **12p** (290 mg, 0.89 mmol) and a solution of 9-BBN dimer (119 mg, 0.97 mmol) in thf (0.5 ml). After 12 h, the mixture was transferred to a 25 mL flask under nitrogen atmosphere containing $PdCl_2(dppf)_2$ (36 mg, 0.045 mmol), K_3PO_4 (378 mg, 1.78 mmol), alkenyl iodide **14** (308 mg, 0.97 mmol) and 3 mL dmf. Then 150 μL deionized water (sparged with nitrogen) was transferred to the flask and the mixture was allowed to stir at 50 °C for 24 h. At this time, the reaction was quenched by addition of a saturated solution of NH_4Cl and the inorganic layer was washed with Et_2O (5.0 mL, three times). The combined organic layer was concentrated *in vacuo* and purified by silica gel chromatography (20:1 hexanes/Et_2O, R_f = 0.25) to afford **15** as colorless oil (402 mg, 87% yield). ***tert*-Butyldimethyl(((*R*,5*E*,9*E*)-6,10,14-trimethyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pentadeca-5,9,13-trien-1-yl)oxy)silane** (**15**): **IR (neat)**: 2956 (s), 2927 (s), 2855 (s), 1447 (m), 1372 (s), 1317 (m), 1252 (m), 1146 (s), 1093 (s), 969 (w), 8356 (s), 813 (w), 774 (s) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 5.14–5.07 (3H, m), 3.50 (1H, dd, *J* = 10.0, 5.6 Hz), 3.44 (1H, dd, *J* = 9.6, 6.4 Hz), 2.10–2.03 (4H, m), 1.99–1.95 (6H, m), 1.77–1.71 (1H, m), 1.67 (3H, s), 1.59 (9H, s), 1.53–1.43 (2H, m), 1.23 (12H, s), 0.88 (9H, s), 0.82–0.76 (2H, m), 0.03 (6H, s); **^{13}C**

[10] S. R. Chemler, D. Trauner, S. J. Danishefsky, *Angew. Chem. Int. Ed.* **2001**, *40*, 4544–4568.

NMR ($CDCl_3$, 100 MHz): δ 135.0, 134.7, 131.3, 125.1, 124.6, 124.5, 82.9, 62.6, 39.90, 39.87, 36.9, 33.6, 27.0, 26.9, 26.8, 26.1, 25.8, 25.6, 25.0, 24.9, 18.5, 17.8, 16.13, 16.10, –5.2. **HRMS (ESI$^+$)**: Calcd for $C_{31}H_{60}BO_3Si$ $[M+H]^+$: 519.4405; Found: 519.4422. Specific rotation: $[\alpha]_D^{20.0}$ 2.61 (*c* 1.15, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

6.3 Deprotection/NHC–Cu-catalyzed Allylic Substitition to Obtain 18

To a solution of alkyl-B(pin) **15** (402 mg, 0.77 mmol) in anhydrous methanol (1.0 ml) was added *p*-TsOH (6.6 mg, 0.039 mmol) at 22 °C and the mixture was allowed to stir for 2 h. The resulting solution was concentrated *in vacuo* to remove methanol. A 4-dram vial was charged with CuCl(19 mg, 0.19 mmol), imidazolinium salt (26 mg, 0.076 mmol), KO*t*Bu (129 mg, 1.2 mmol) and thf (5.0 ml) was allowed to stir at 22 °C for 2 h. Then the crude of desilylation and allyl phosphate (224 mg, 1.2mol) in thf (2.0 ml) was transferred to the vial and the reaction mixture was allowed to stir at 70 °C for 24 h. The reaction was then quenched by passing the solution through a short plug of silica gel, after which it was washed with Et_2O (20 ml), concentrated *in vacuo* to afford a pale yellow oily residue, which was purified by silica gel chromatography (6:1 hexanes/Et_2O, R_f = 0.30) to deliver alcohol **16** as colorless oil (165 mg, 0.51 mmol, 67% yield). **(*R*,5*E*,9*E*)-2-(But-3-en-1-yl)-6,10,14-trimethylpentadeca-5,9,13-trien-1-ol (16)**: **IR (neat)**: 3323 (s), 2966 (m), 2917 (s), 2855 (s), 1641 (w), 1449 (m), 1379 (m), 1202 (w), 1107 (w), 1032 (s), 993 (s), 908 (s), 833 (m), 743 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 5.87 (1H, m), 5.14–5.08 (1H, m), 5.05–4.99 (1H, m), 4.95 (1H, dt, *J* = 10.0, 0.8 Hz), 3.57 (2H, d, *J* = 4.8 Hz),), 2.12–2.05 (6H, m), 2.03–1.95 (6H, m), 1.68 (3H, s), 1.60 (9H, s), 1.54–1.33 (5H, m); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 139.1, 135.4, 135.1, 131.4, 124.6, 124.5, 124.3, 114.6, 65.5, 39.9, 39.7, 31.6, 31.3, 31.1, 30.3, 26.9, 26.8, 25.5, 25.3, 17.8, 16.18, 16.16. **HRMS (ESI$^+$)**: Calcd for $C_{22}H_{39}O$ $[M+H]^+$: 319.3001; Found: 319.3008. Specific rotation: $[\alpha]_D^{20.0}$ –3.74 (*c* 0.80, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

6.4 Catalytic Cross-Metathesis with Acrolein[11]

In a 1-dram vial with a stir bar was charged with alkene **16** (16 mg, 0.051 mmol) and acrolein (67 μl, 1.02 mmol). A solution of Ru complex **17** (0.01 M in CH_2Cl_2, 0.5 mL, 0.005 mmol, 1.0 mol %) was introduced and the mixture was allowed to stir at 22 °C for 0.5 h under nitrogen atomsphere. Then the mixture was flushed through a short plug of silica gel with Et_2O and concentrated *in vacuo* and purified by silica gel chromatography (6:1 hexanes/Et_2O, R_f = 0.35 to 1:1 hexanes/Et_2O) to afford α,β-unsaturated aldehyde **18** (>98:2 E/Z) as colorless oil (13.5 mg, 71% yield). **(*R*,2*E*,9*E*,13*E*)-6-(Hydroxymethyl)-10,14,18-trimethylnonadeca-2,9,13,17-tetraenal (18)**: **IR (neat)**: 2962 (m), 2917 (s), 2870 (m), 2851 (m), 2184 (w), 2138 (w), 2033 (w), 1691 (s), 1636 (w), 1449 (w), 1379 (w), 1131 (w), 1102 (w), 1035 (w), 1023 (w) cm^{-1}; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 9.51 (1H, d, *J* = 8.0 Hz), 6.86 (1H, dt, *J* = 15.6, 6.4 Hz), 6.14 (1H, ddt, *J* = 16.0, 8.0, 1.6 Hz), 5.13–5.07 (3H, m), 3.63 (1H, *J* = 10.4, 4.0 Hz), 2.37 (2H, *J* = 6.0 Hz), 2.10–1.95 (10H, m), 1.68 (3H, d, *J* = 1.2 Hz), 1.60 (9H, s), 1.58–1.34 (5H, m); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 194.2, 158.8, 135.7, 135.2, 133.1, 131.5, 124.5, 124.25, 124.20, 65.2, 39.9, 39.8, 39.7,

(11) J. C. Killen, J. Leonard, V. K. Aggarwal, *Synlett.* **2010**, *4*, 579–582.

31.0, 30.3, 29.4, 26.9, 26.7, 25.9, 25.3, 17.8, 16.22, 16.17. **HRMS (ESI$^+$)**: Calcd for $C_{23}H_{39}O_2$ $[M+H]^+$: 374.2950; Found: 374.2957. Specific rotation: $[\alpha]_D^{20.0}$ –3.17 (*c* 0.80, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

6.5 Catalytic Oxa-Michael Addition[12]

To a solution of aldehyde **18** (32.3 mg, 0.078 mmol) in CH_2Cl_2 (3.0 mL, 0.026 M) was added dropwise a 1:1 mixture of pyrrolidine/BzOH (0.28 mL, 0.054 M in CH_2Cl_2) at 22 ºC. After the solution was allowed to stir for 1 h at 22 ºC, it was diluted with hexanes (30.0 mL), filtered through a short pad of silica gel (hexanes/EtOAc, 3/1), and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (5:1 hexanes/Et_2O, R_f 0.36) to afford aldehyde **19** (31.6 mg, diastereoisomer ratio 8:1) as colorless oil. **2-((2*R*,5*S*)-5-((3*E*,7*E*)-4,8,12-Trimethyltrideca-3,7,11-trien-1-yl)tetrahydro-2*H*-pyran-2-yl)acetaldehyde** (**19**): **IR (neat)**: 3070 (w), 2958 (w), 2899 (w), 2173 (w), 1626 (w), 1487 (w), 1427 (w), 1411 (w), 1317 (w), 1248 (m), 1112 (m), 1040 (w), 998 (w), 942 (w), 899 (w), 836 (s), 813 (s), 778 (m), 758 (s), 723 (s), 697 (s), 642 (m), 548 (w), 469 (m) cm^{-1}; **^{1}H NMR ($CDCl_3$, 600 MHz)**: δ 9.79 (1H, t, *J* = 2.4 Hz), 5.11–5.07 (3H, m), 3.94–3.91 (1H, m), 3.78–3.73 (1H, m), 3.06 (1H, t, *J* = 10.8 Hz), 2.58 (1H, ddd, *J* = 16.8, 7.8, 3.0 Hz), 2.47 (1H, ddd, *J* = 16.2, 4.8, 1.8 Hz), 2.09–2.04 (4H, m), 2.00–1.96 (6H, m), 1.68–1.67 (4H, m), 1.60 (9H, d), 1.57–1.54 (1H, m), 1.37 (1H, qd, *J* = 10.8, 3.0 Hz), 1.21–1.11 (2H, m); **^{13}C NMR ($CDCl_3$, 150 MHz)**: δ 201.6, 135.5, 135.1, 131.4, 124.5, 124.29, 124.25, 73.8, 73.2, 50.1, 39.9, 39.8, 35.2, 32.7, 31.9, 30.3, 26.9, 26.1, 25.8, 25.1, 17.8, 16.2, 16.1. **HRMS (ESI$^+$)**: Calcd for $C_{17}H_{27}Si_2$ $[M+H]^+$: 287.1651; Found: 287.1654. Specific rotation: $[\alpha]_D^{20.0}$ – 1.97 (*c* 0.65, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

7 ^{1}H NMR and ^{13}C NMR Spectra

[12] K. Lee, H. Kim, J. Hong, *Org Lett*. **2011**, *13*, 2722–2725.

XCF-II-110-2

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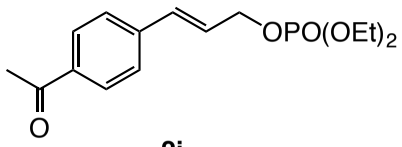

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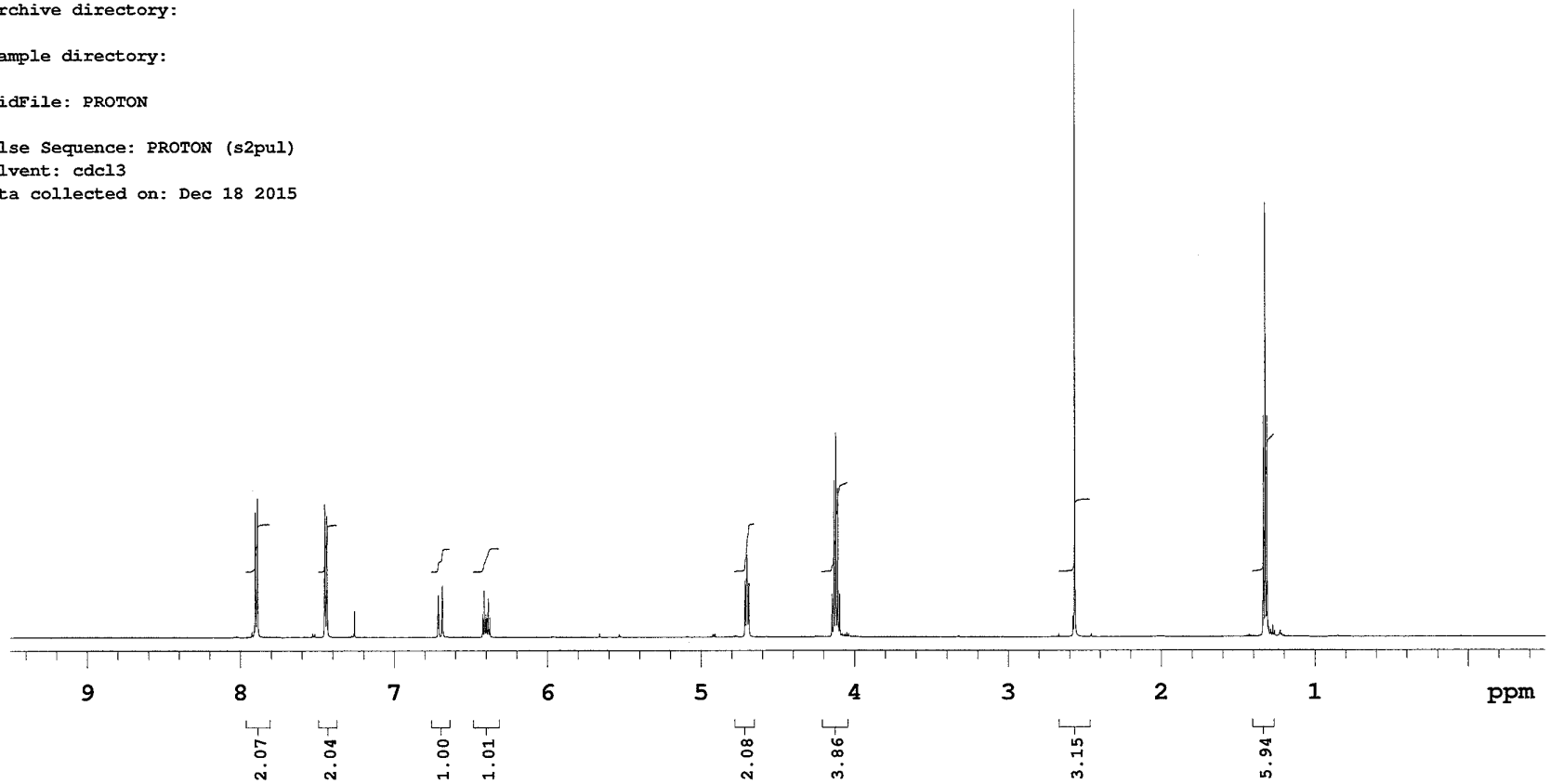

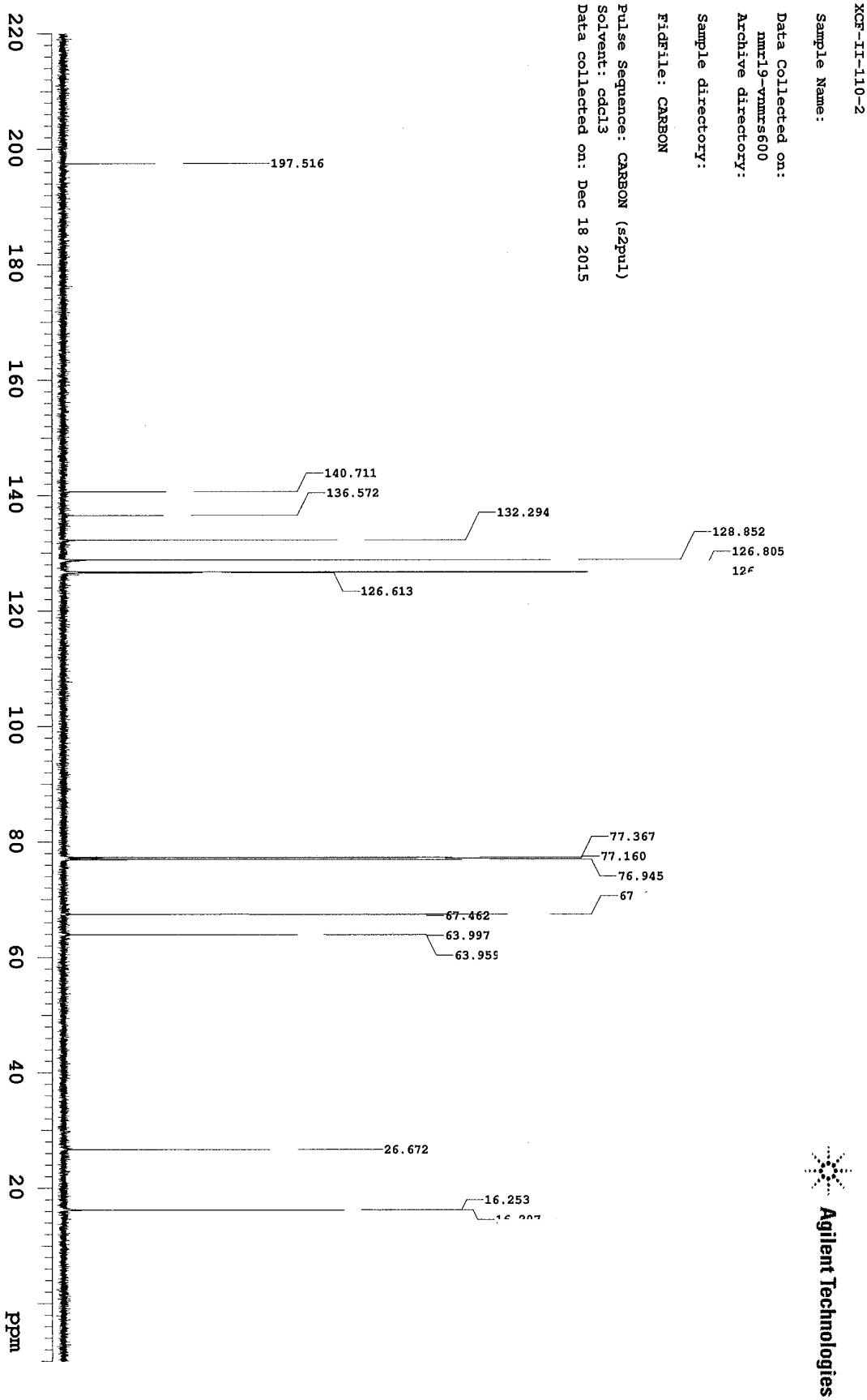
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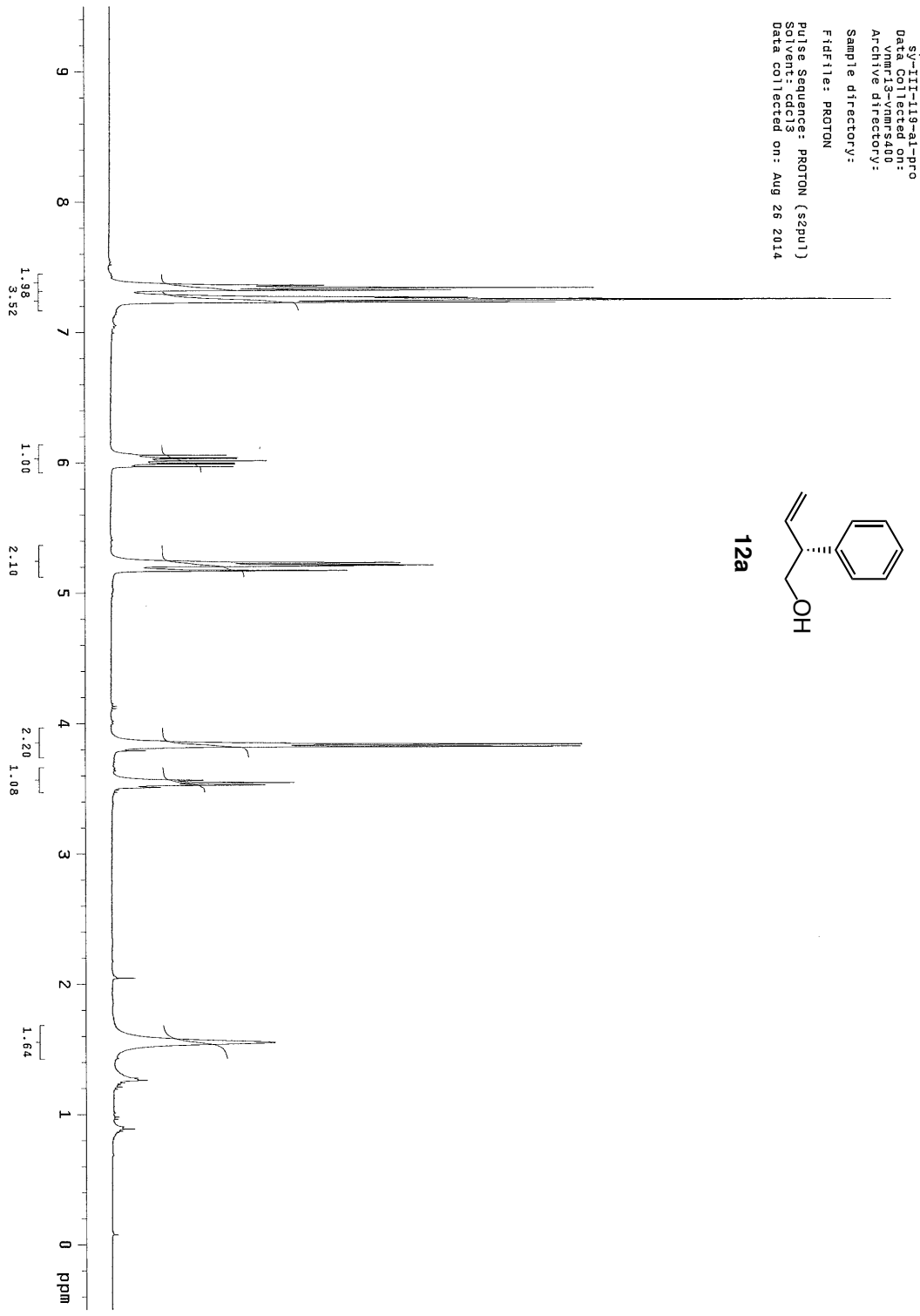
Agilent Technologies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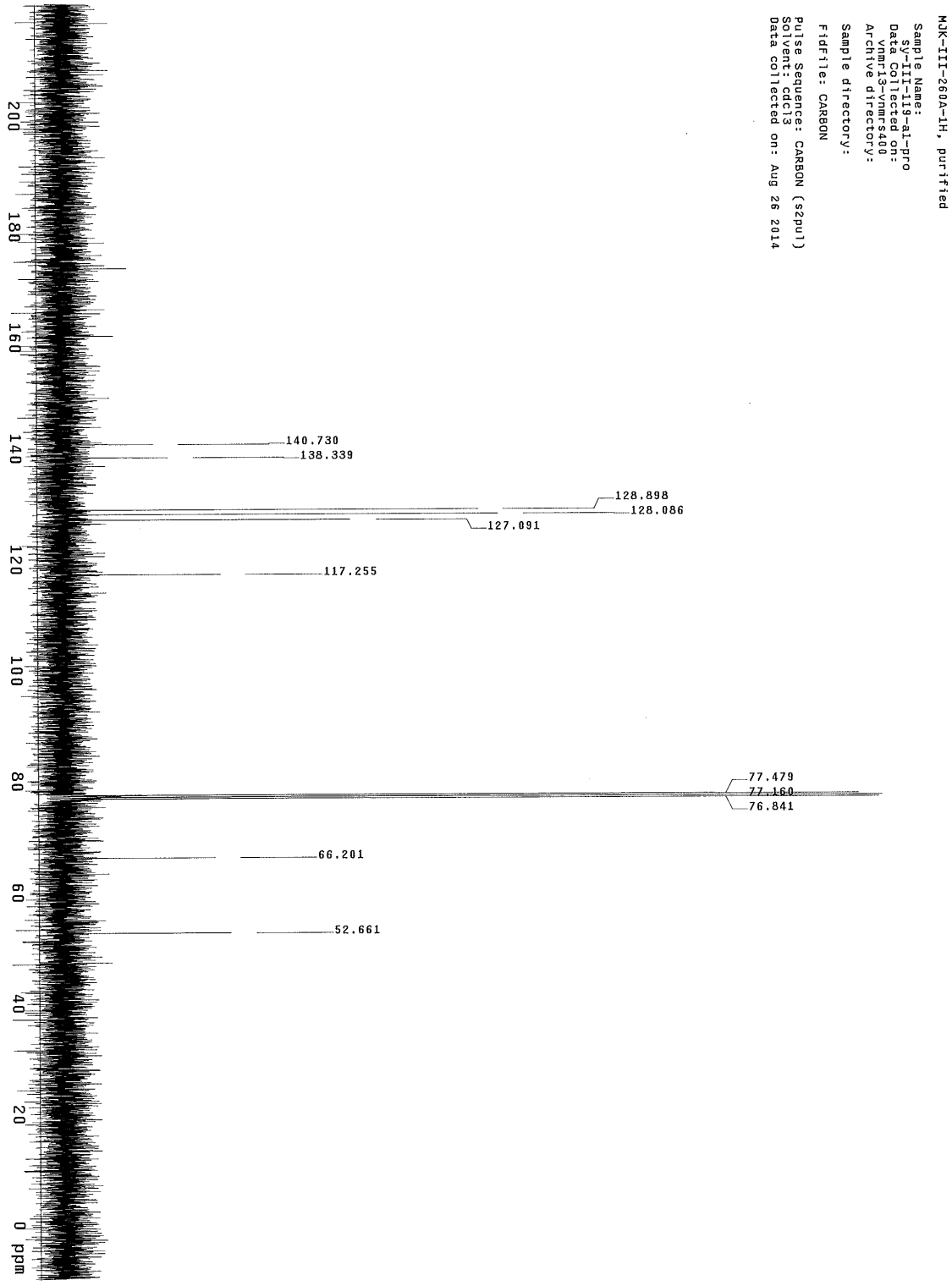
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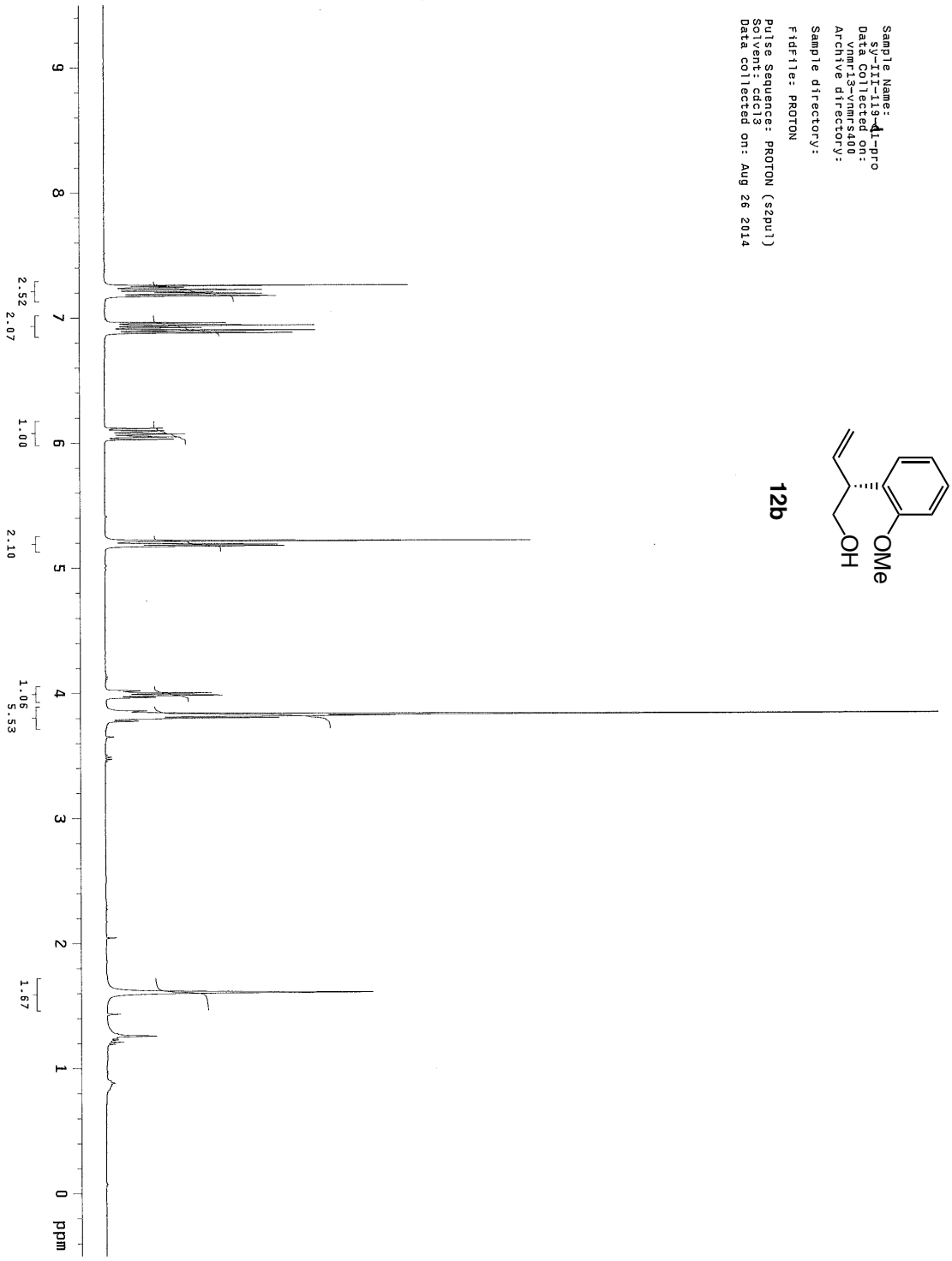
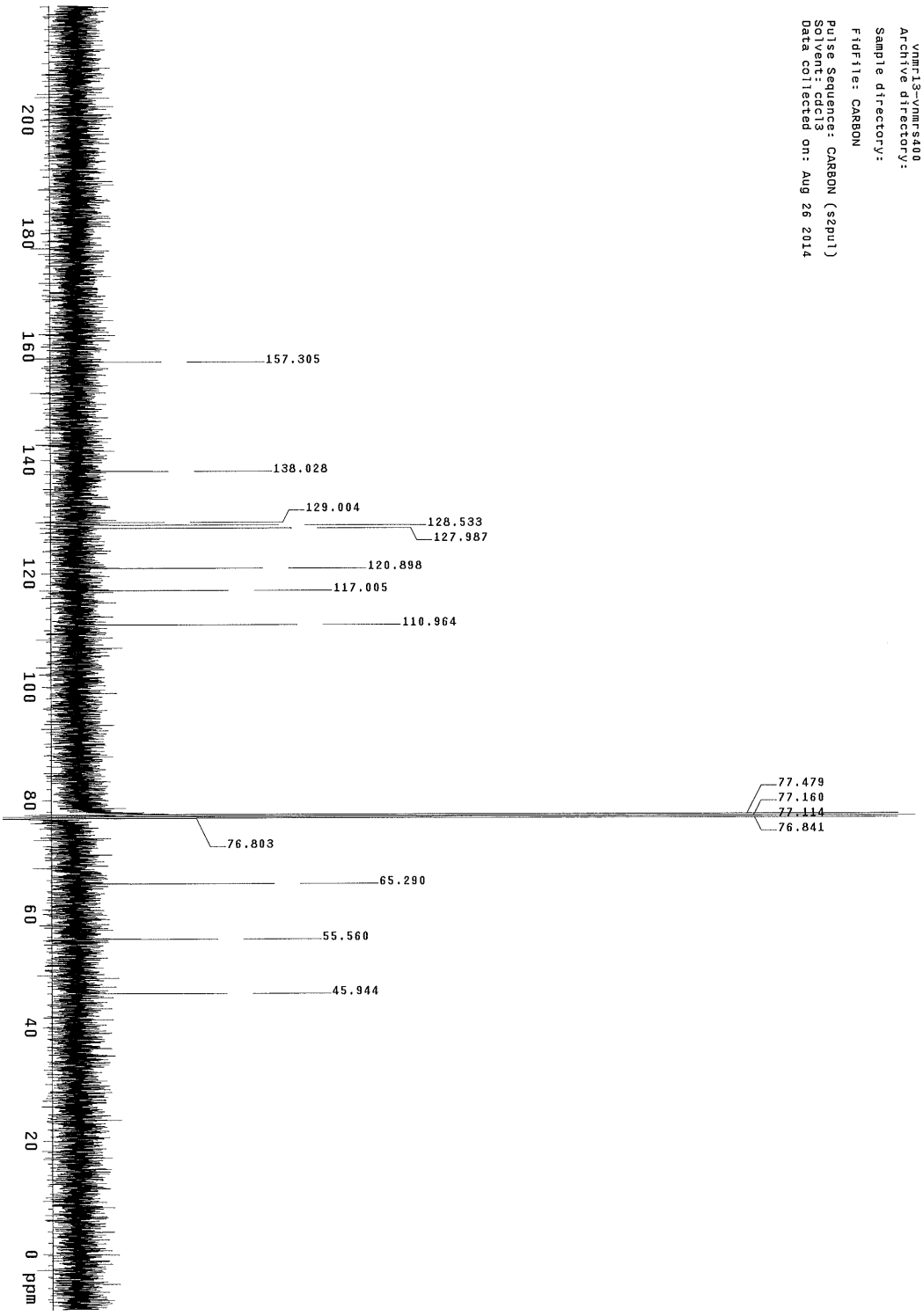
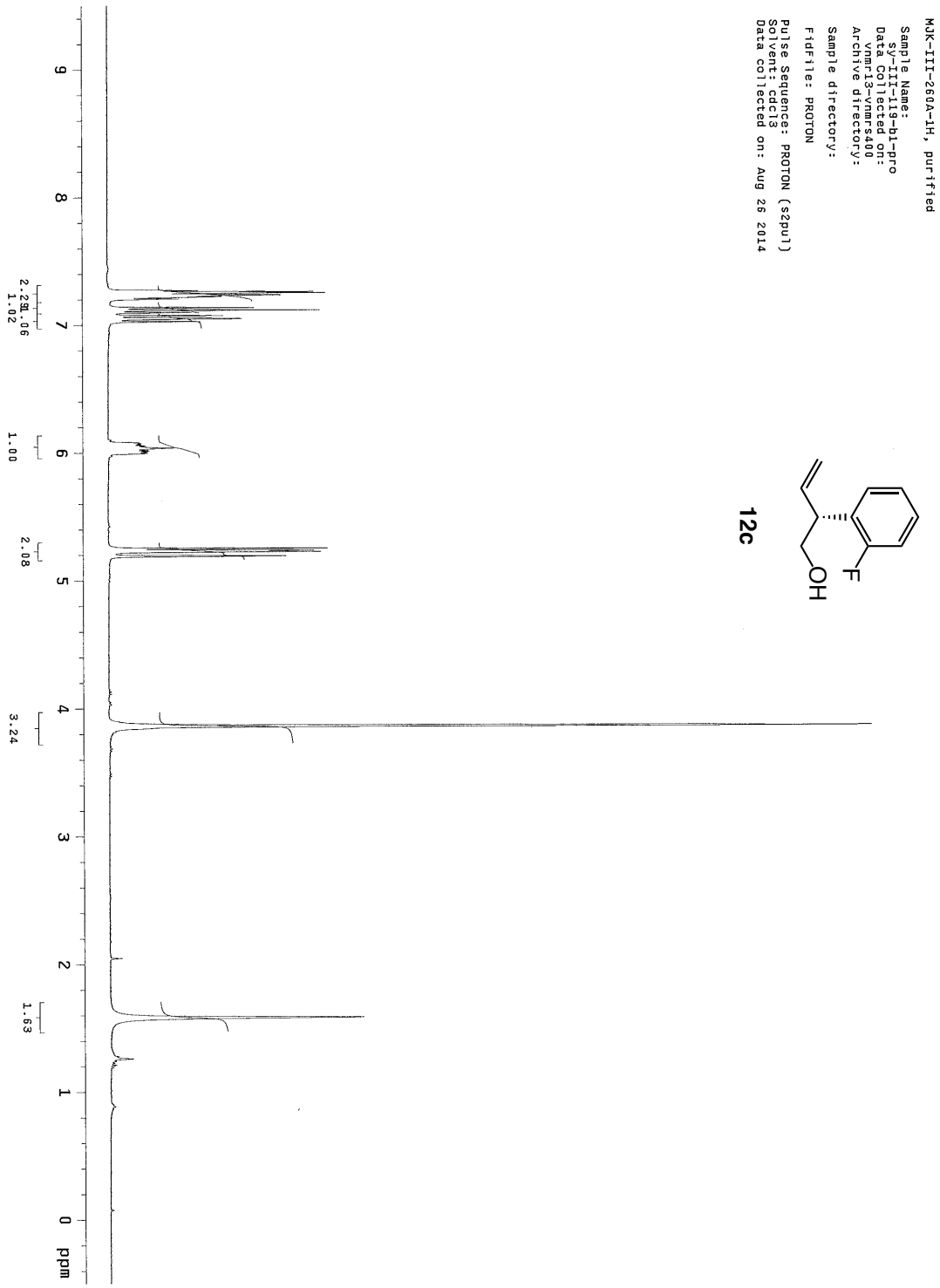
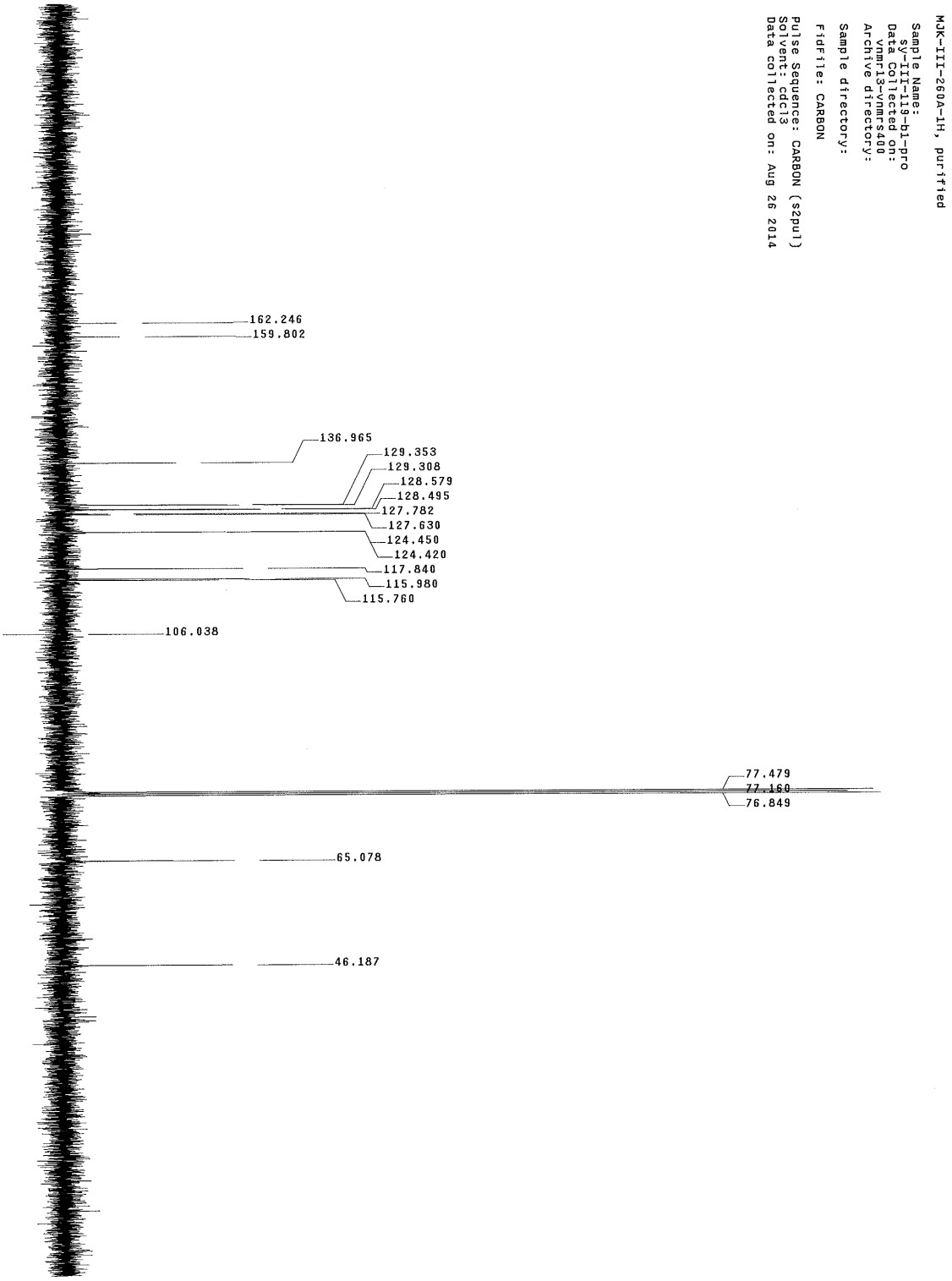
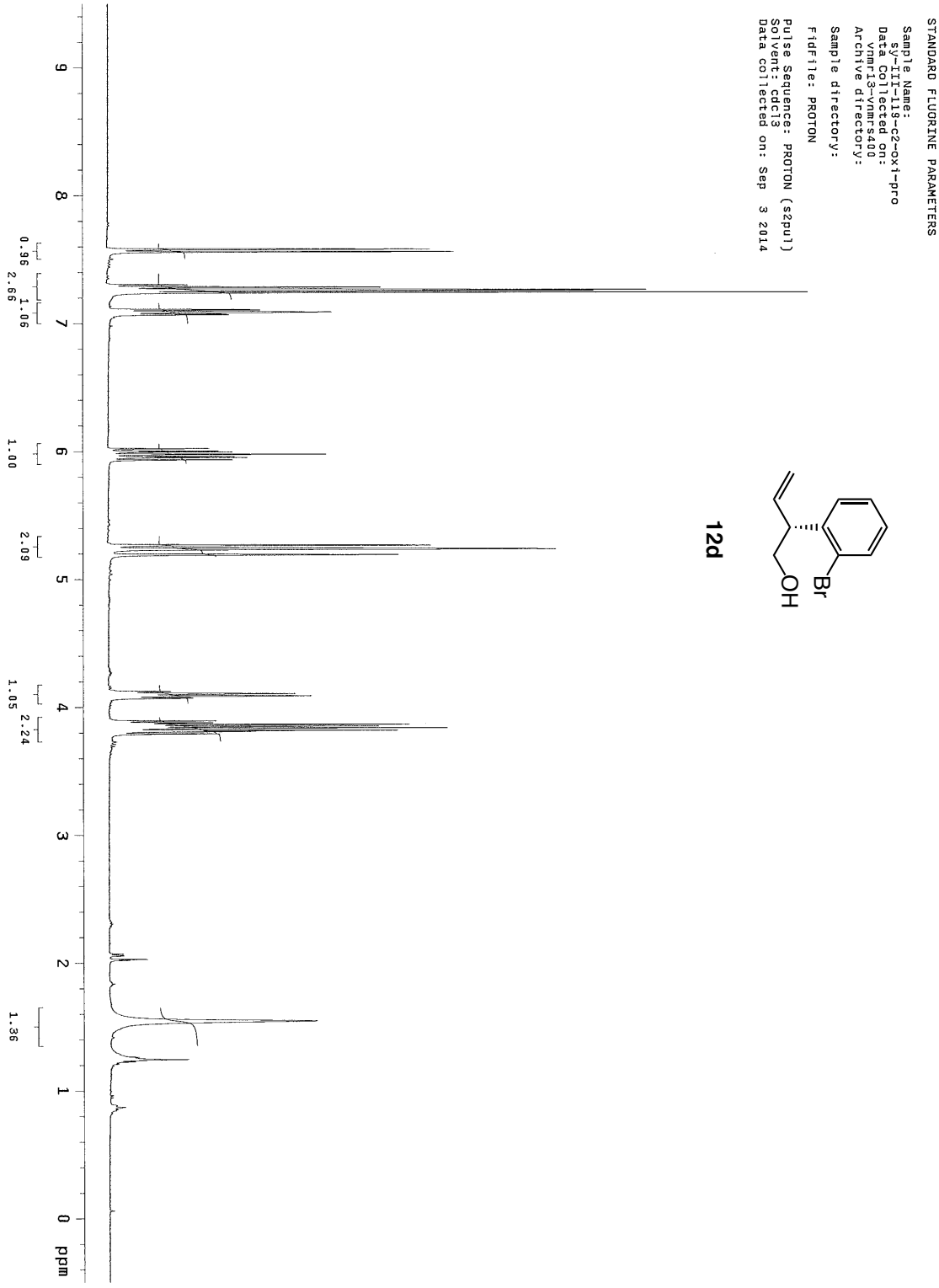
20
0 ppm

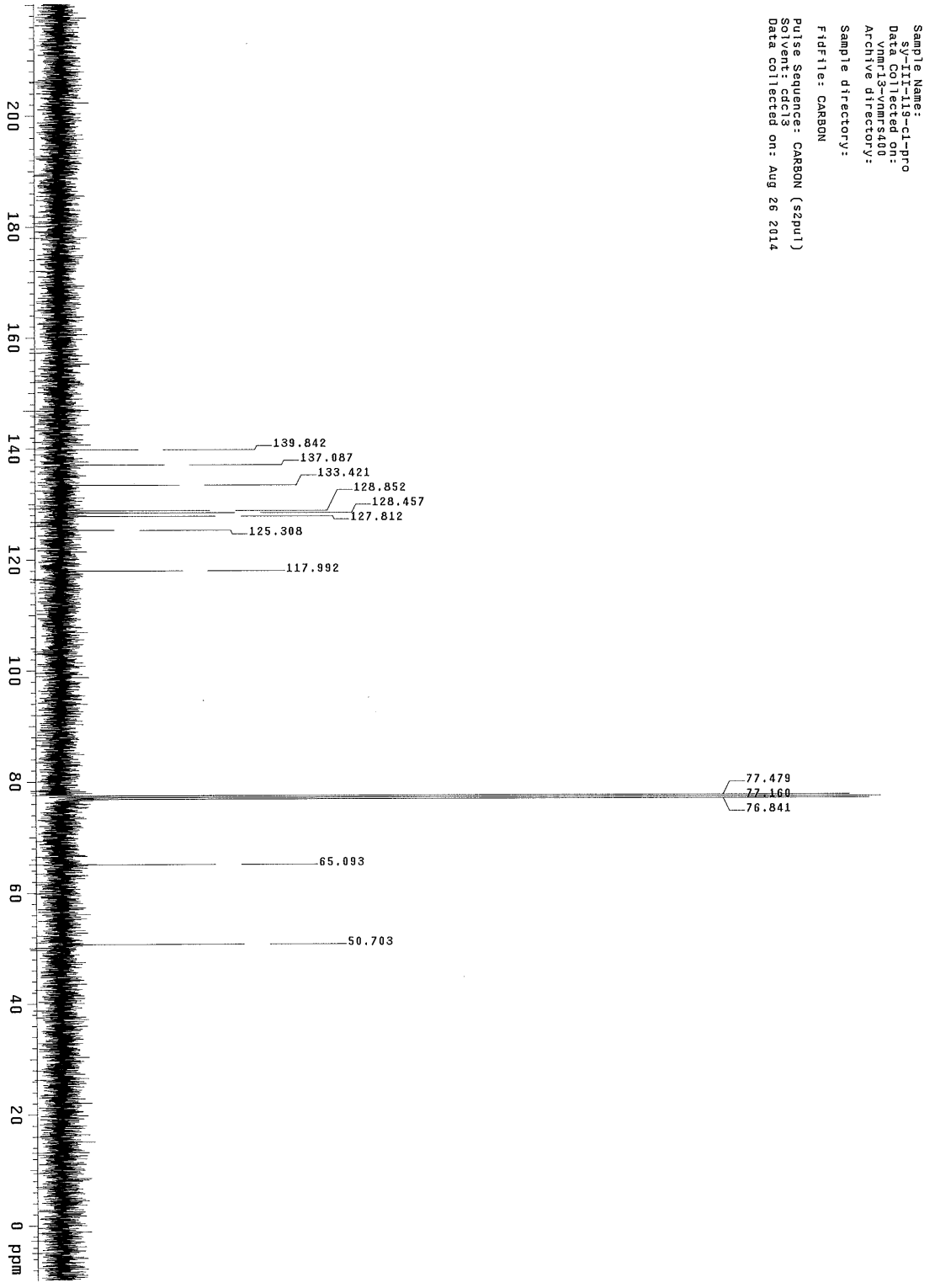

Sample Name: sy-III-119-4-pro
Data Collected on: vnmr13-vnmrs400
Archive directory:
Sample directory:
Fidfile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 26 2014
OMe
OH
12b
2.52
2.07
1.00
2.10
1.06
5.53
1.67
9
8
7
6
5
4
3
2
1
0
ppm

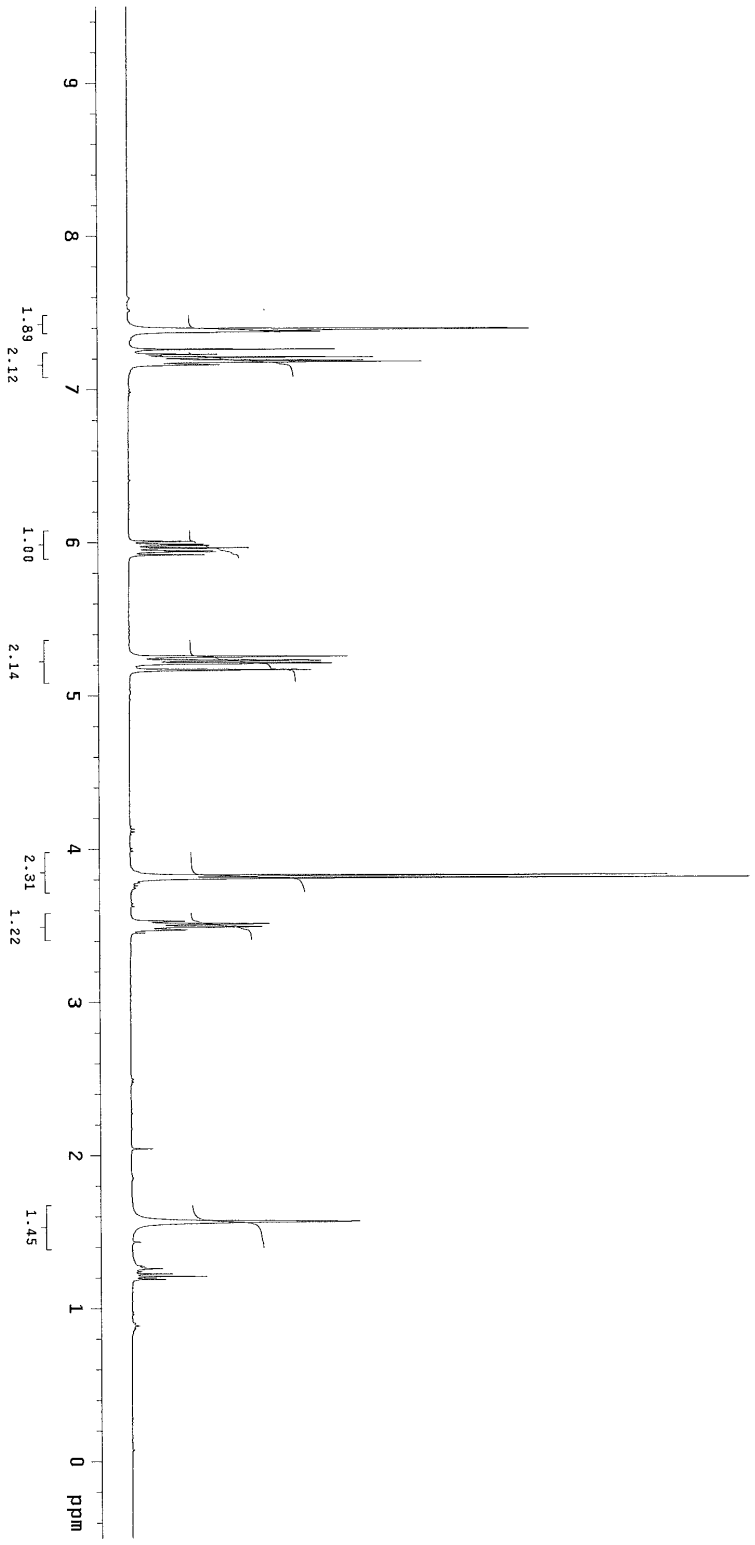

Sample Name:
sy-III-119-d1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 26 2014
157.305
138.028
129.004
128.533
127.987
120.898
117.005
110.964
77.479
77.160
77.114
76.841
76.803
65.290
55.560
45.944
200
180
160
140
120
100
80
60
40
20
0 ppm

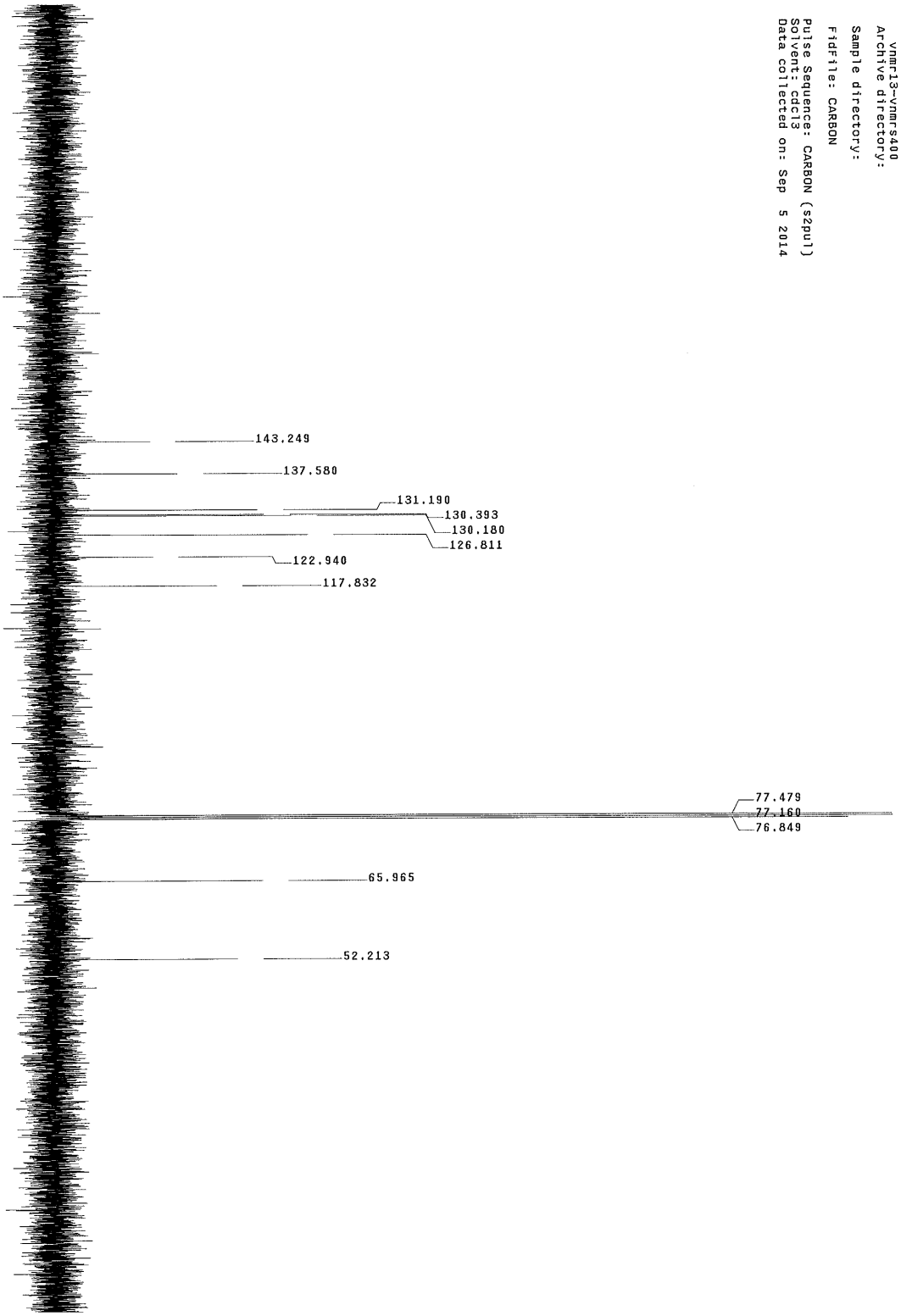

MJK-III-260A-1H, purified
Sample Name:
sy-III-119-b1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 26 2014
12c
F
OH
2.29
1.06
1.02
1.00
2.08
3.24
1.63
9
8
7
6
5
4
3
2
1
0
ppm

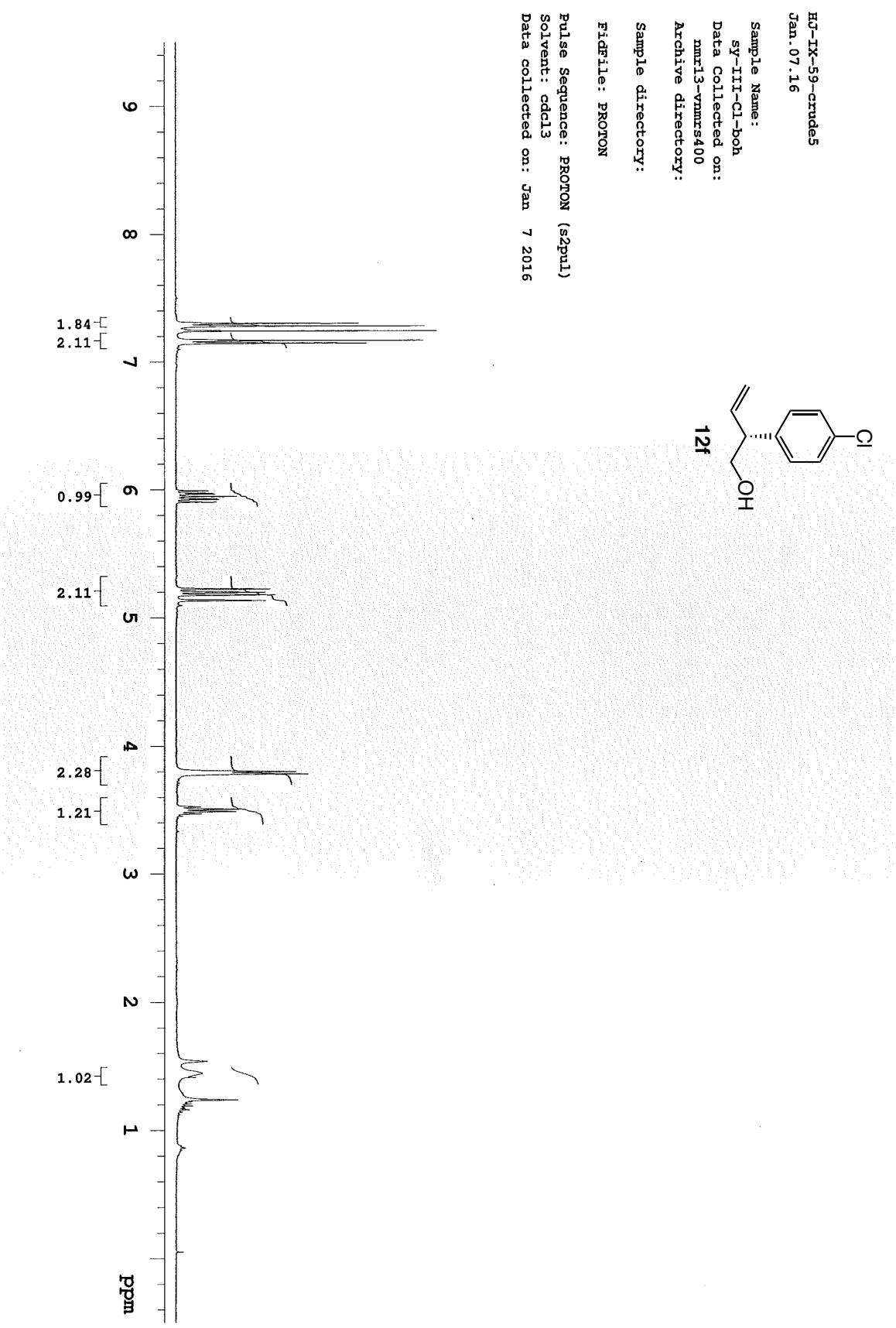

MJK-III-260A-1H, purified
Sample Name:
sy-III-119-b1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 26 2014
162.246
159.802
136.965
129.353
129.308
128.579
128.495
127.782
127.630
124.450
124.420
117.840
115.980
115.760
106.038
77.479
77.160
76.849
65.078
46.187

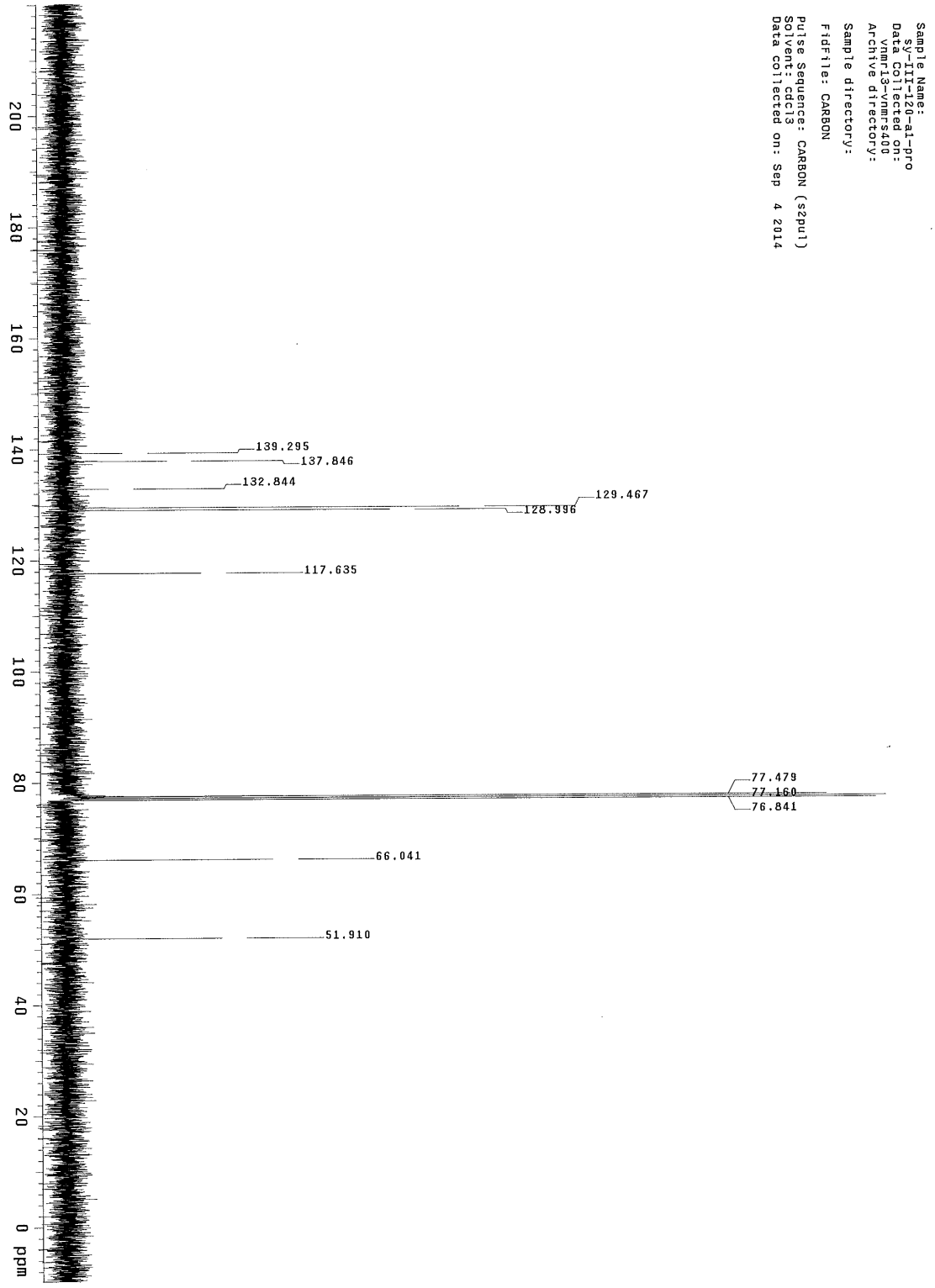

STANDARD FLUORINE PARAMETERS
Sample Name:
sy-III-119-c2-oxi-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 3 2014
12d
Br
OH
0.96
2.66
1.06
1.00
2.09
1.05
2.24
1.36
9
8
7
6
5
4
3
2
1
0
ppm

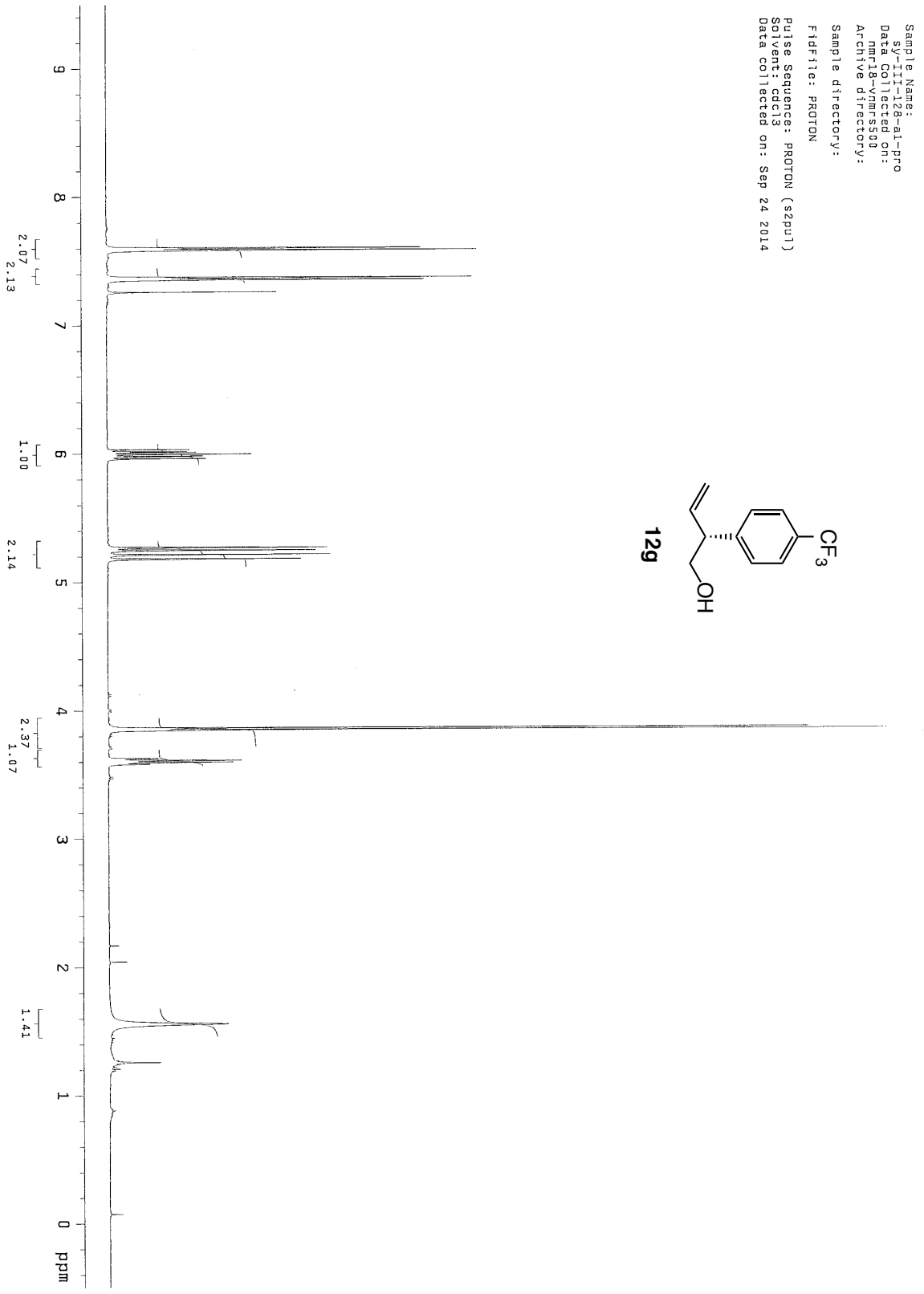

Sample Name:
sy-III-119-c1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 26 2014
139.842
137.087
133.421
128.852
128.457
127.812
125.308
117.992
77.479
77.160
76.841
65.093
50.703
200
180
160
140
120
100
80
60
40
20
0 ppm

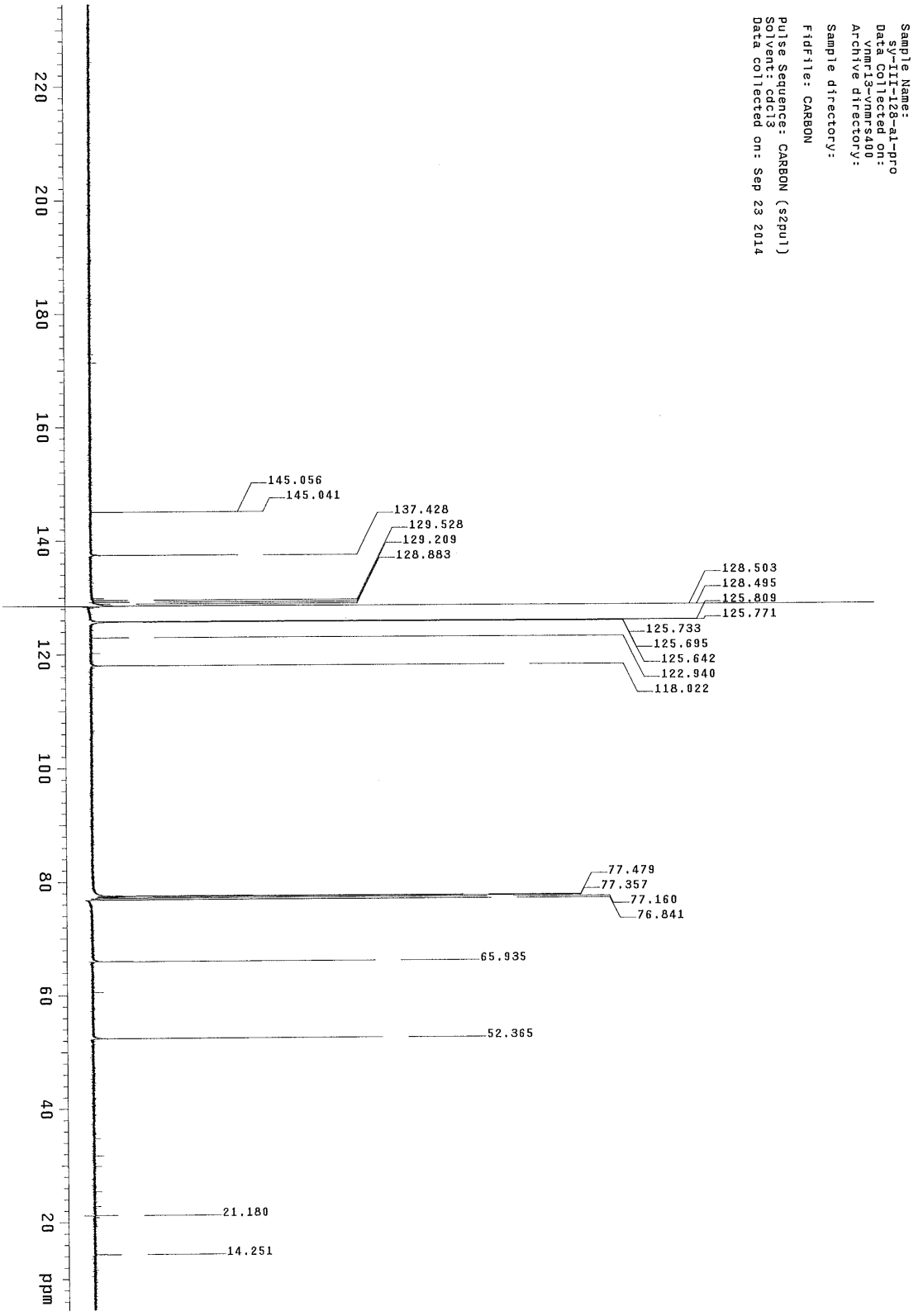

Sample Name:
sy-III-122-c1-pro
Data Collected on:
vnmr13-vnmr$40:
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 5 2014
12e
Br
OH
9
8
7
6
5
4
3
2
1
0
ppm
1.89
2.12
1.00
2.14
2.31
1.22
1.45

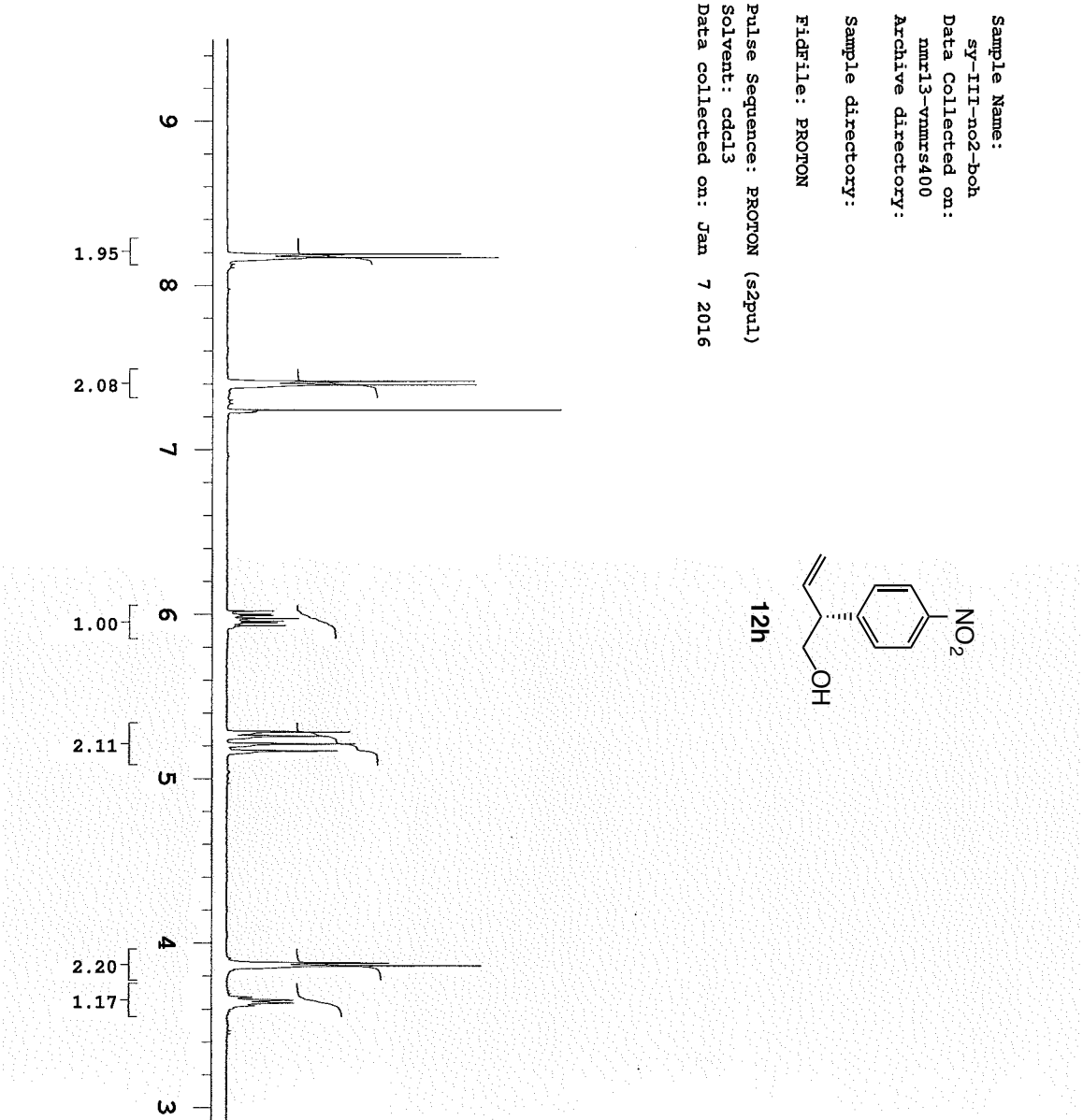

Sample Name:
sy-III-122-c1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
Fidfile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 5 2014
143.249
137.580
131.190
130.393
130.180
126.811
122.940
117.832
77.479
77.160
76.849
65.965
52.213

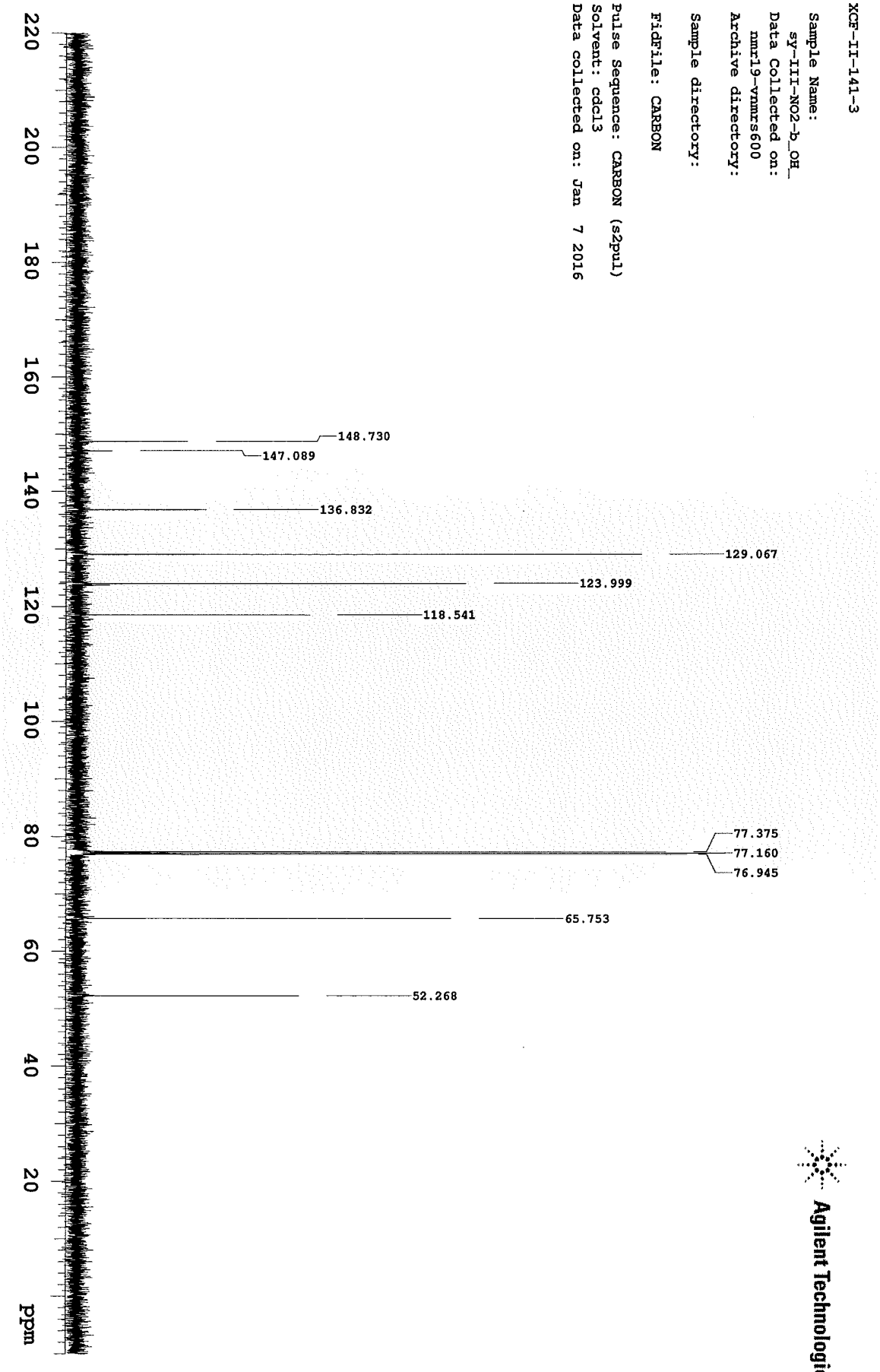

HJ-IX-59-crude5
Jan.07.16
Sample Name:
sy-III-Cl-boh
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 7 2016
12f
Cl
OH
1.84
2.11
0.99
2.11
2.28
1.21
1.02
9
8
7
6
5
4
3
2
1
ppm

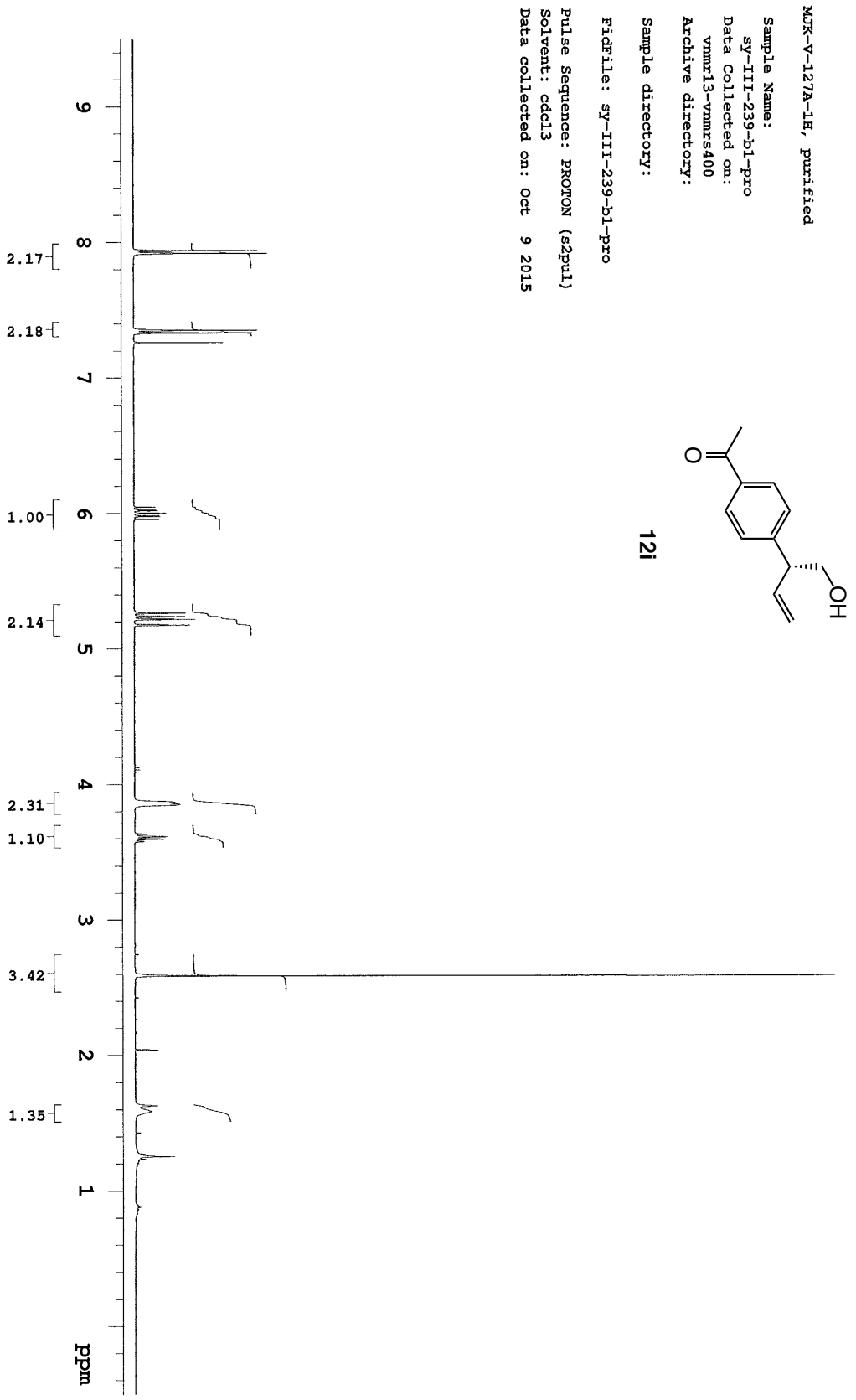

Sample Name:
sy-III-120-al-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 4 2014
139.295
137.846
132.844
129.467
128.996
117.635
77.479
77.160
76.841
66.041
51.910
200
180
160
140
120
100
80
60
40
20
0 ppm

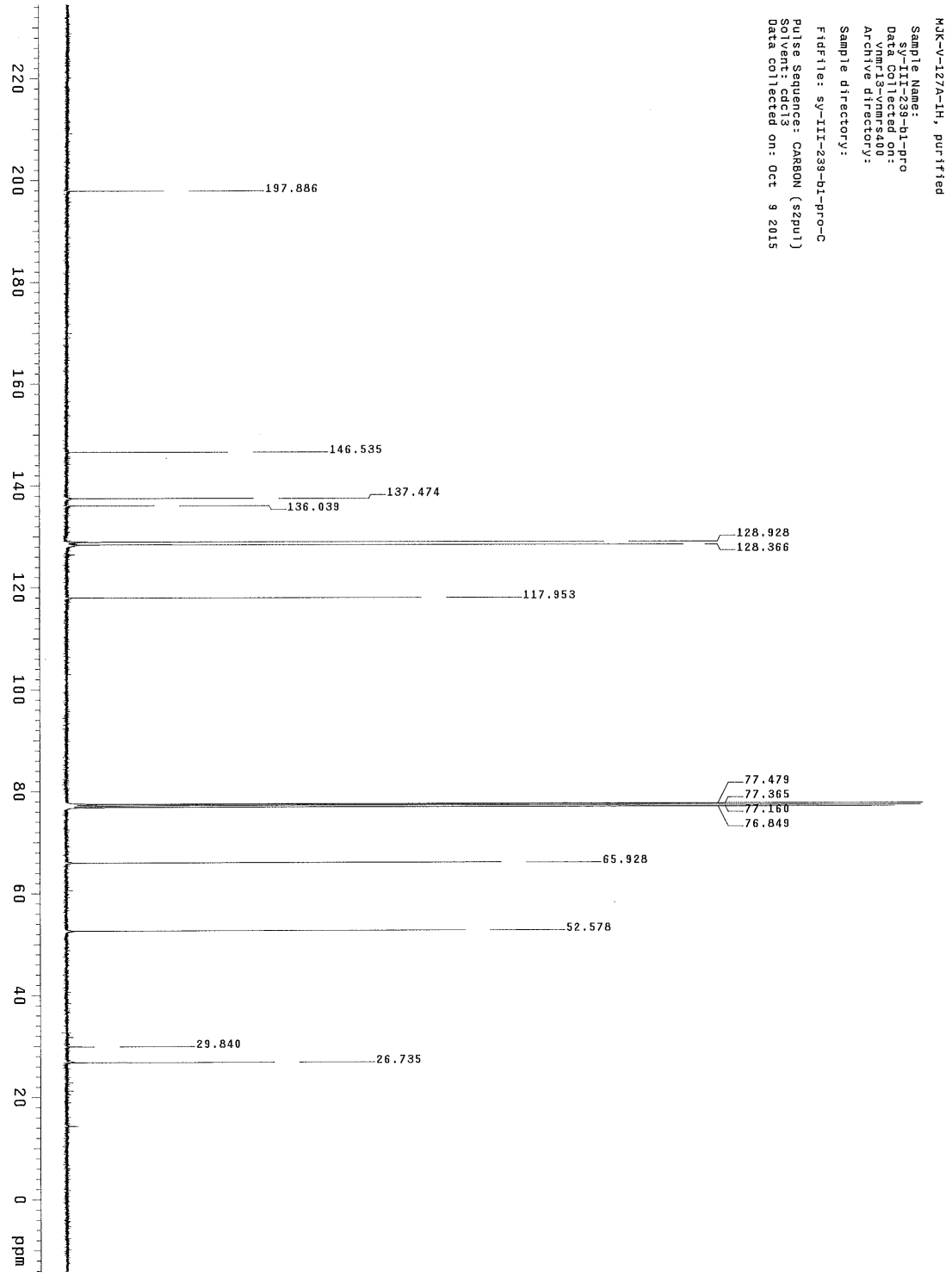

Sample Name:
sy-III-128-al-pro
Data Collected on:
nmr18-vnmrs500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 24 2014
CF3
OH
12g
9
8
7
6
5
4
3
2
1
0
ppm
2.07
2.13
1.00
2.14
2.37
1.07
1.41


Sample Name:
sy-III-128-a1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 23 2014
145.056
145.041
137.428
129.528
129.209
128.883
128.503
128.495
125.809
125.771
125.733
125.695
125.642
122.940
118.022
77.479
77.357
77.160
76.841
65.935
52.365
21.180
14.251
220
200
180
160
140
120
100
80
60
40
20
ppm


Sample Name:
sy-III-no2-boh
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 7 2016
12h
NO2
OH
1.95
2.08
1.00
2.11
2.20
1.17
1.77
9
8
7
6
5
4
3
2
1
ppm


XCF-II-141-3
Sample Name:
sy-III-NO2-b_OH_
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 7 2016
148.730
147.089
136.832
129.067
123.999
118.541
77.375
77.160
76.945
65.753
52.268
220
200
180
160
140
120
100
80
60
40
20
ppm
Agilent Technologies


MJK-V-127A-1H, purified
Sample Name:
sy-III-239-b1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: sy-III-239-b1-pro
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 9 2015
12i
OH
O
2.17
2.18
1.00
2.14
2.31
1.10
3.42
1.35
9
8
7
6
5
4
3
2
1
ppm


MJK-V-127A-1H, purified
Sample Name:
sy-III-239-b1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: sy-III-239-b1-pro-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 9 2015
197.886
146.535
137.474
136.039
128.928
128.366
117.953
77.479
77.365
77.160
76.849
65.928
52.578
29.840
26.735
220
200
180
160
140
120
100
80
60
40
20
0
ppm

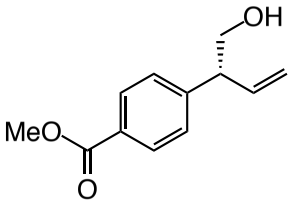
FV-I-264-13C
H-Cinn Imine
12/16/15

Sample Name:
sy-~~FV-45-5mol-1h~~ III-239-91-pro
Data Collected on:
nmr19-vnmrs600
Archive directory:

Sample directory:

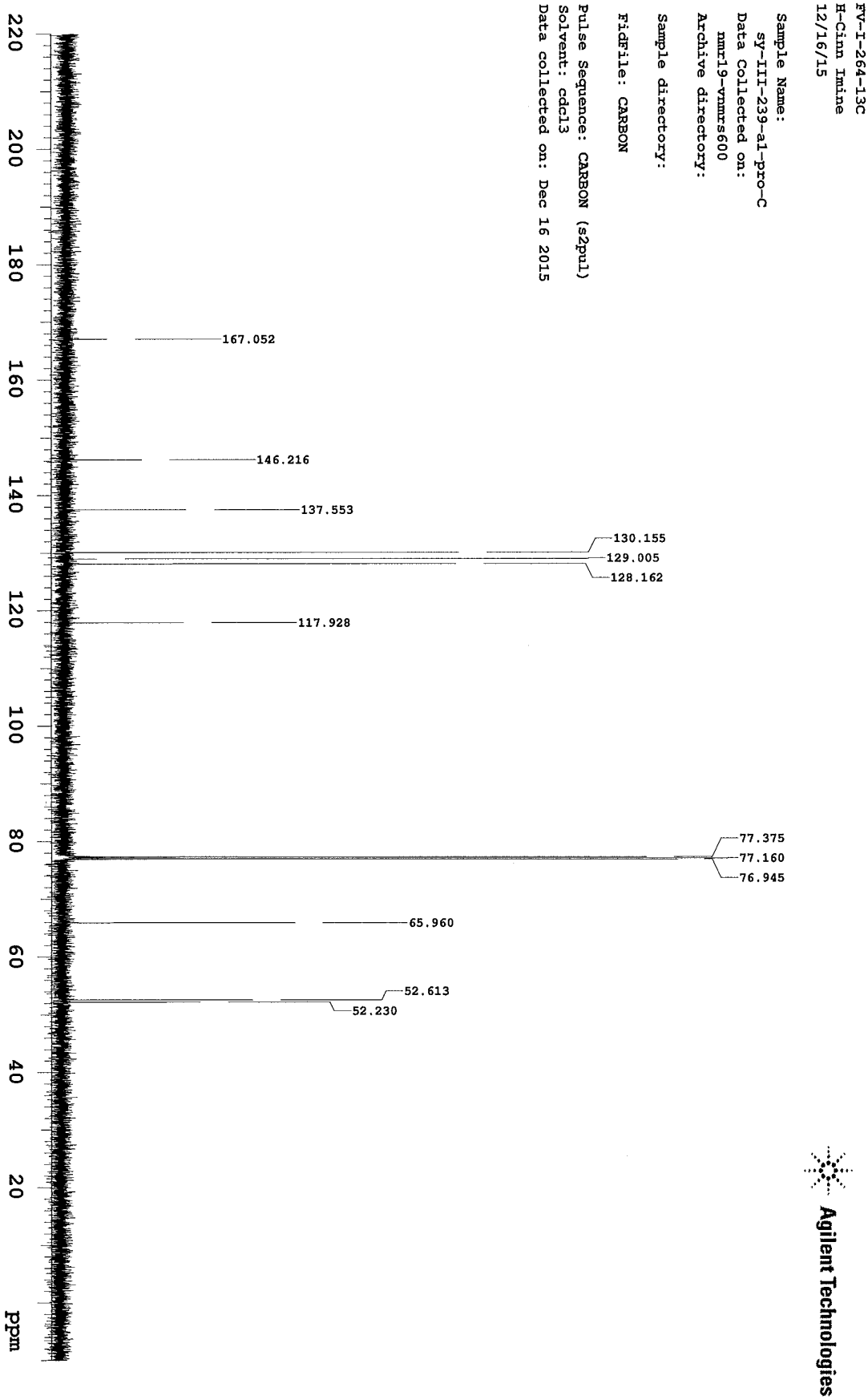
FidFile: PROTON

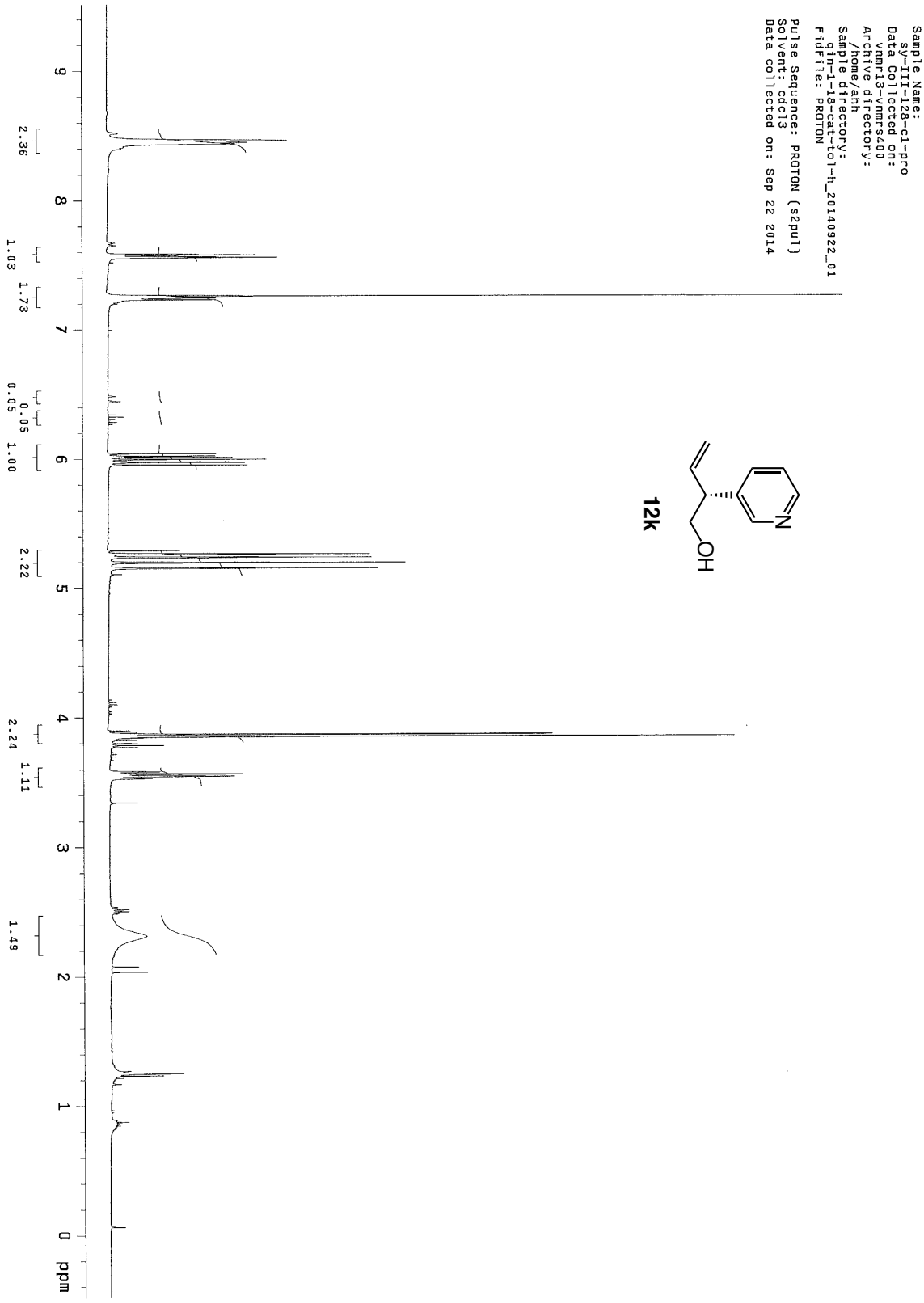
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 16 2015

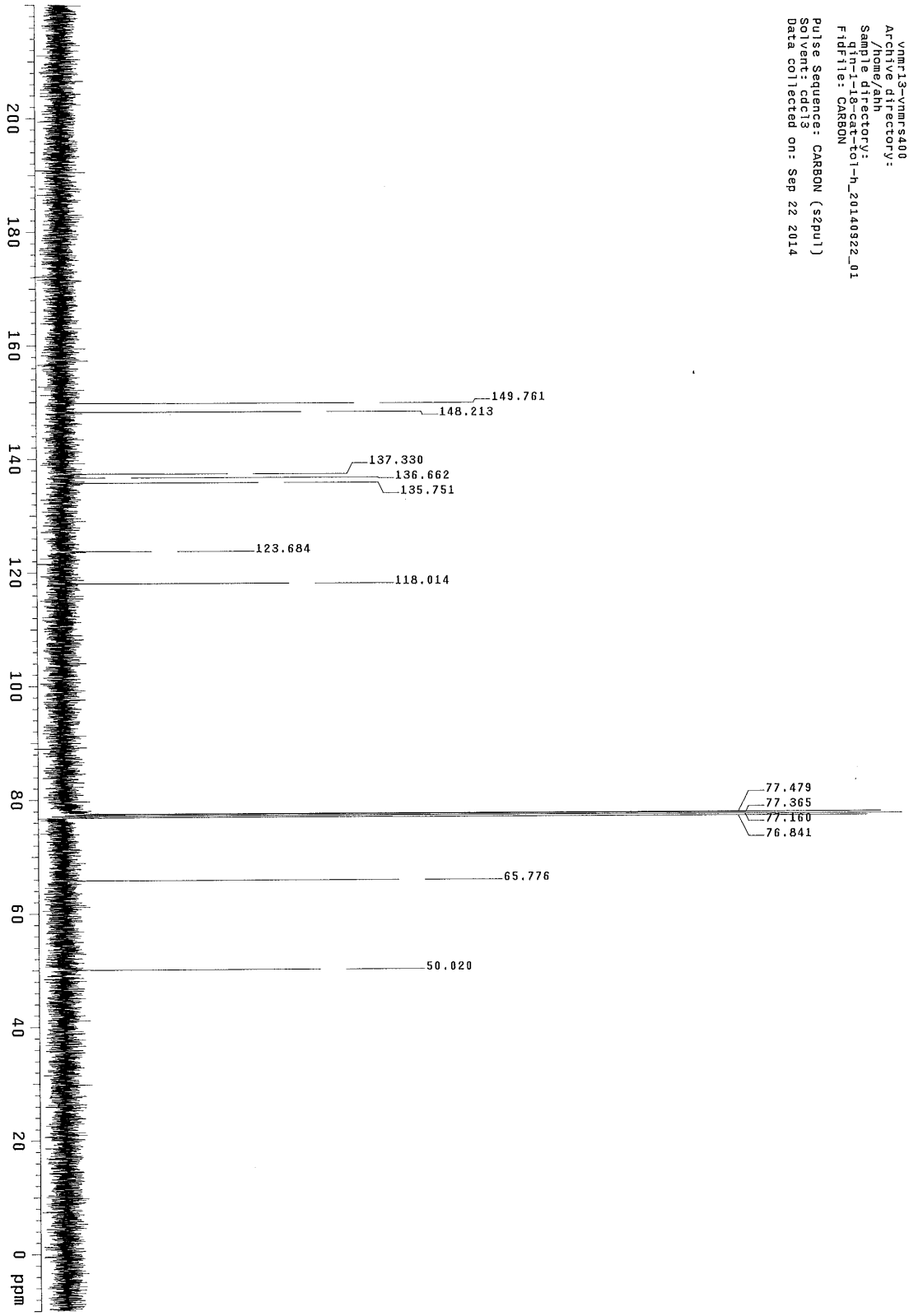


12j

Agilent Technologies


FV-I-264-13C
H-Cinn Imine
12/16/15
Sample Name:
sy-III-239-a1-pro-C
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 16 2015
167.052
146.216
137.553
130.155
129.005
128.162
117.928
77.375
77.160
76.945
65.960
52.613
52.230
220
200
180
160
140
120
100
80
60
40
20
ppm
Agilent Technologies


Sample Name:
sy-III-128-cl-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
/home/ahh
Sample directory:
qln-1-18-cat-tol-h_20140922_01
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 22 2014
12k
OH
N
2.36
1.03
1.73
0.05
1.00
2.22
2.24
1.11
1.49
9
8
7
6
5
4
3
2
1
0
ppm

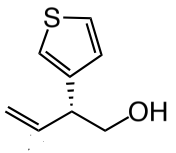

sy-III-128-c1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
/home/ahh
Sample directory:
qin-1-18-cat-tol-h_20140922_01
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 22 2014
149.761
148.213
137.330
136.662
135.751
123.684
118.014
77.479
77.365
77.160
76.841
65.776
50.020
200
180
160
140
120
100
80
60
40
20
0 ppm

Sample Name:
sy-III-128-d2-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:

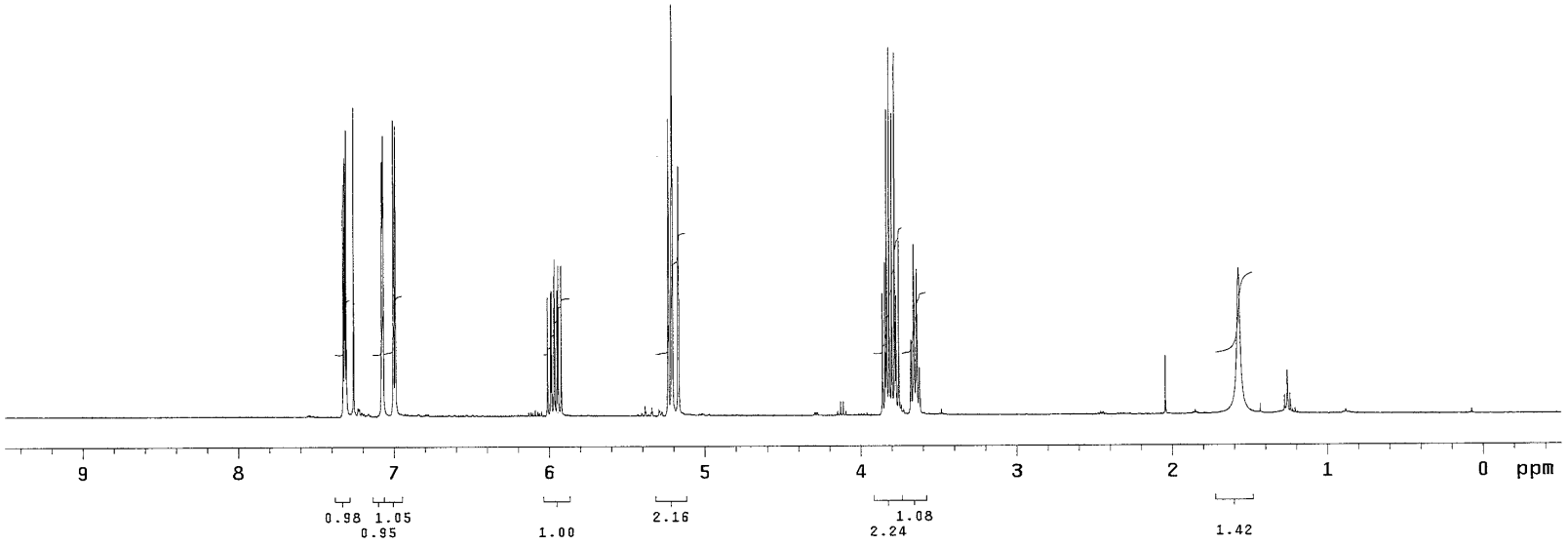
Sample directory:

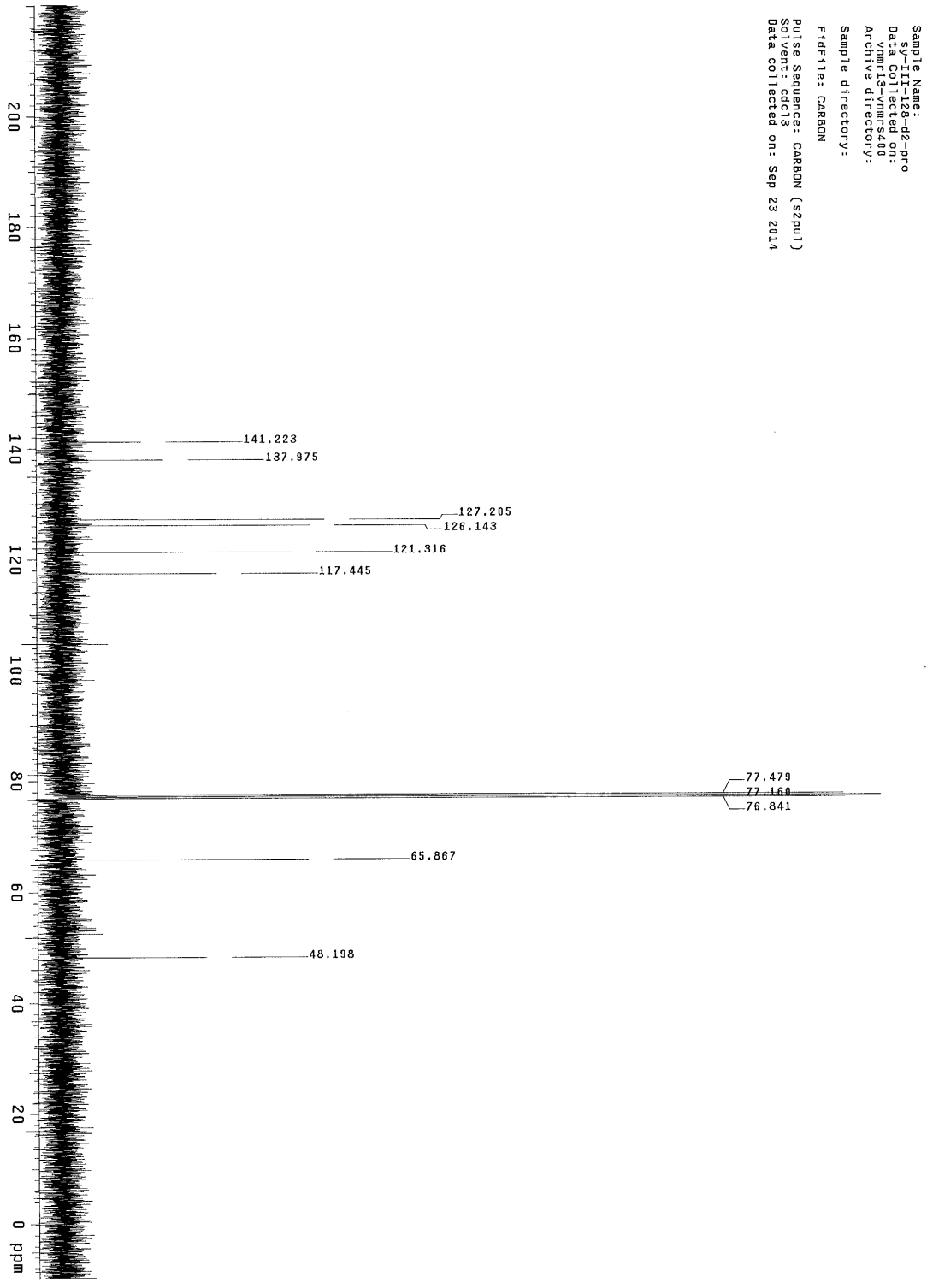
FidFile: sy-III-128-d2-pro

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 23 2014



12l




Sample Name:
sy-III-128-d2-pro
Data Collected on:
vnmrj3-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 23 2014
141.223
137.975
127.205
126.143
121.316
117.445
77.479
77.160
76.841
65.867
48.198
200
180
160
140
120
100
80
60
40
20
0 ppm

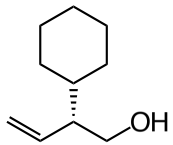
STANDARD FLUORINE PARAMETERS

Sample Name:
sy-III-120-c2-oxi-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:

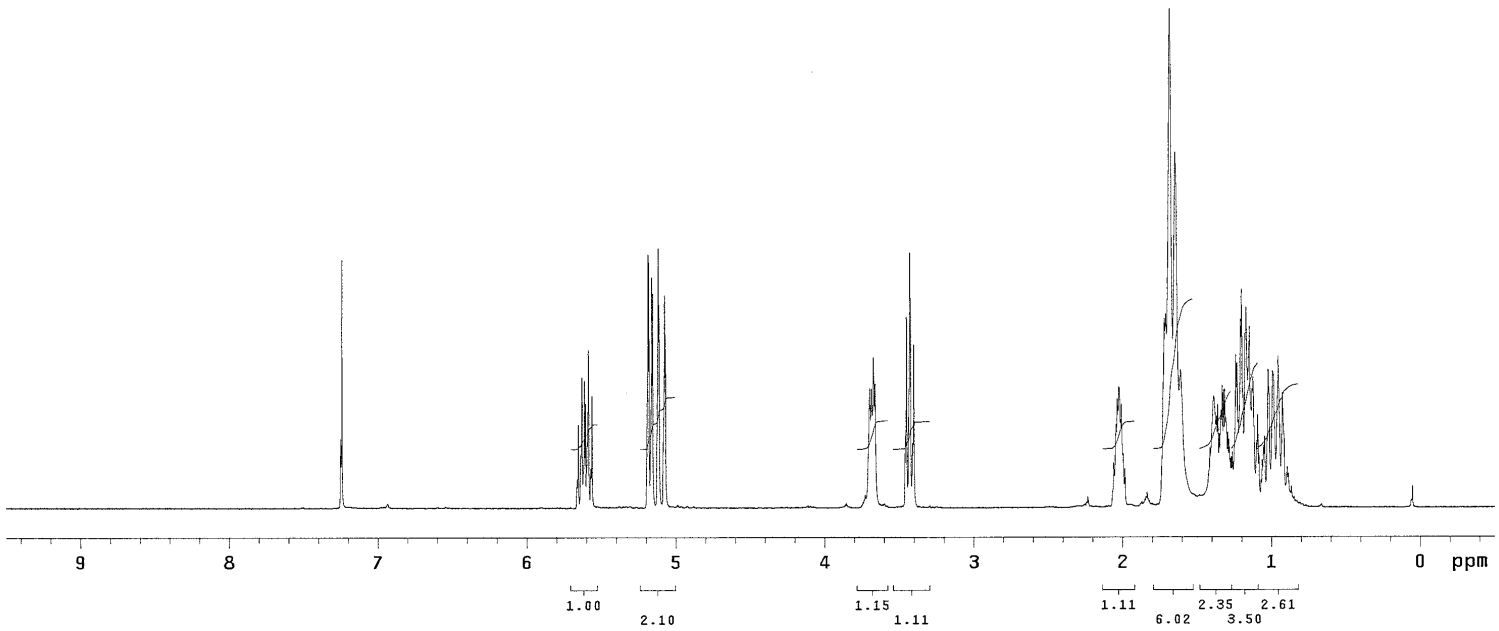
Sample directory:

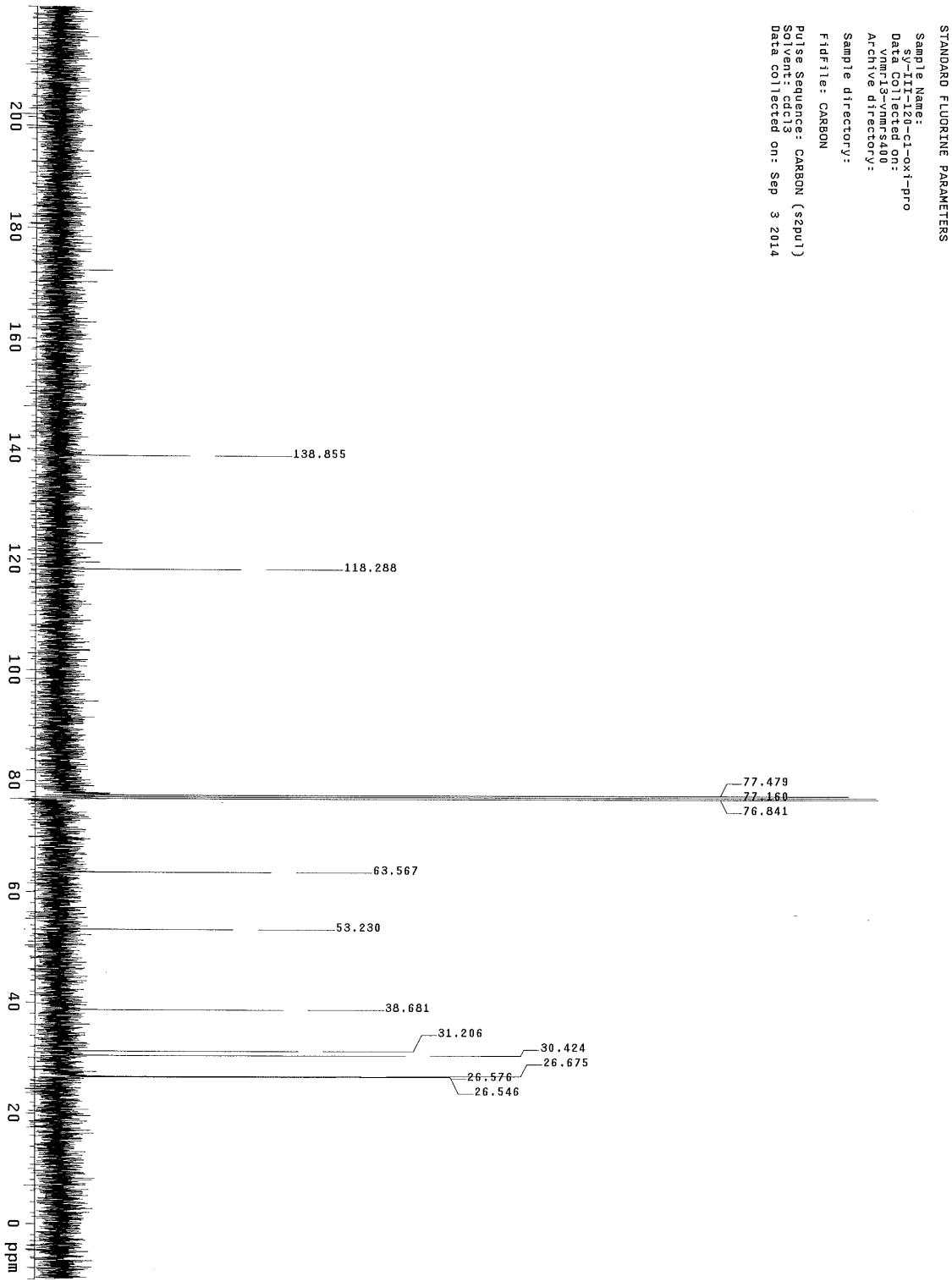
FidFile: PROTON

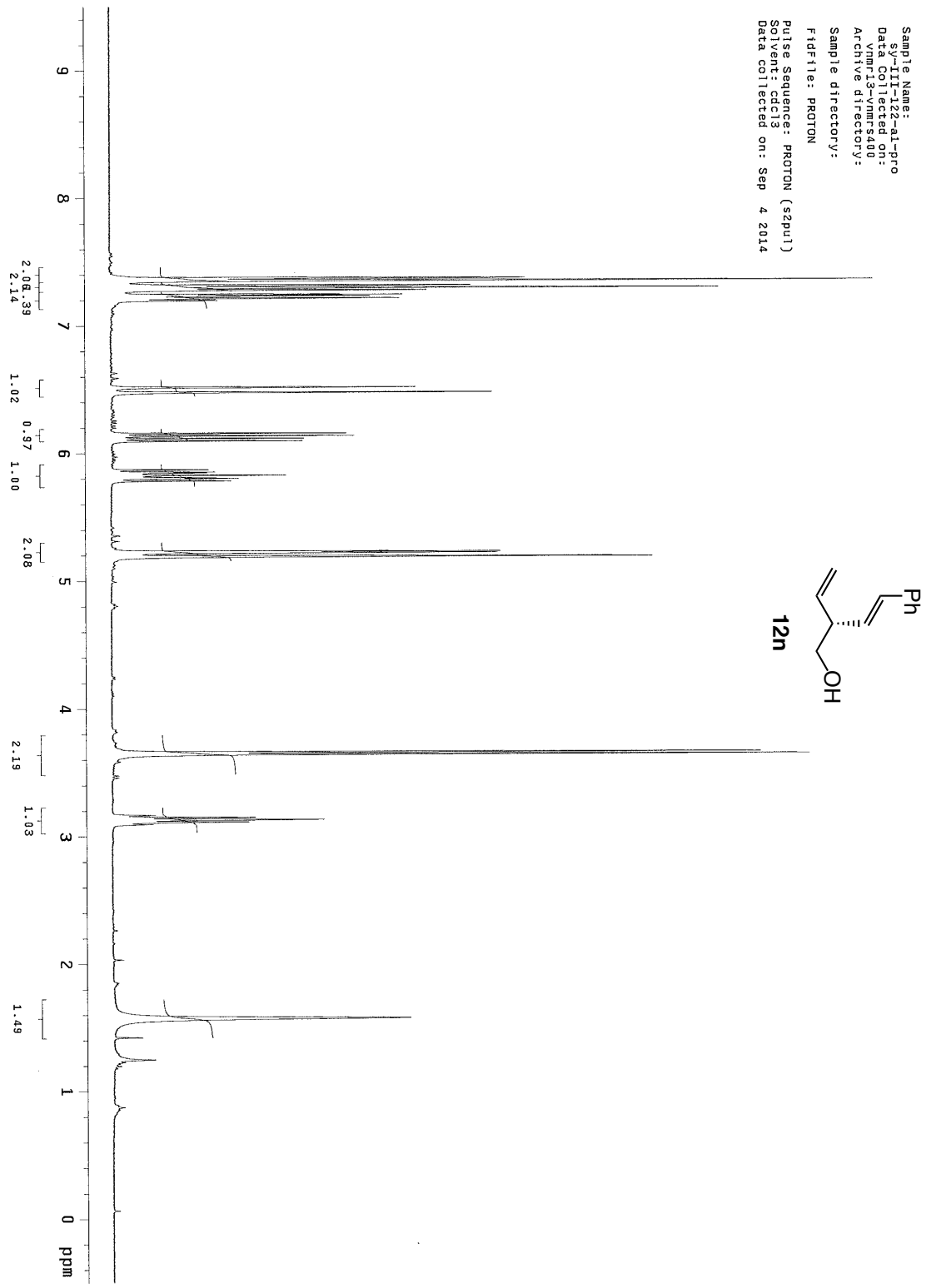
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 3 2014

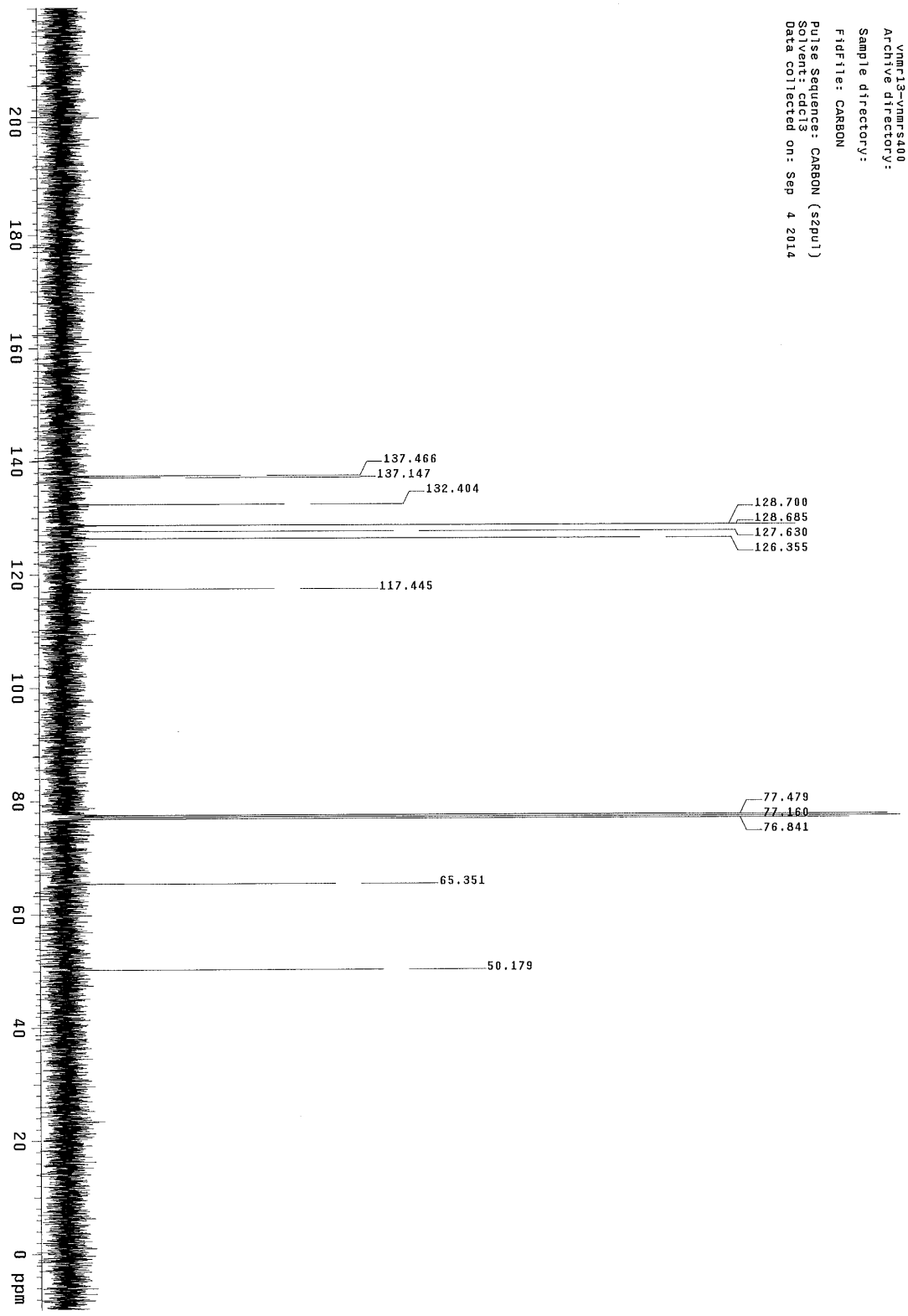


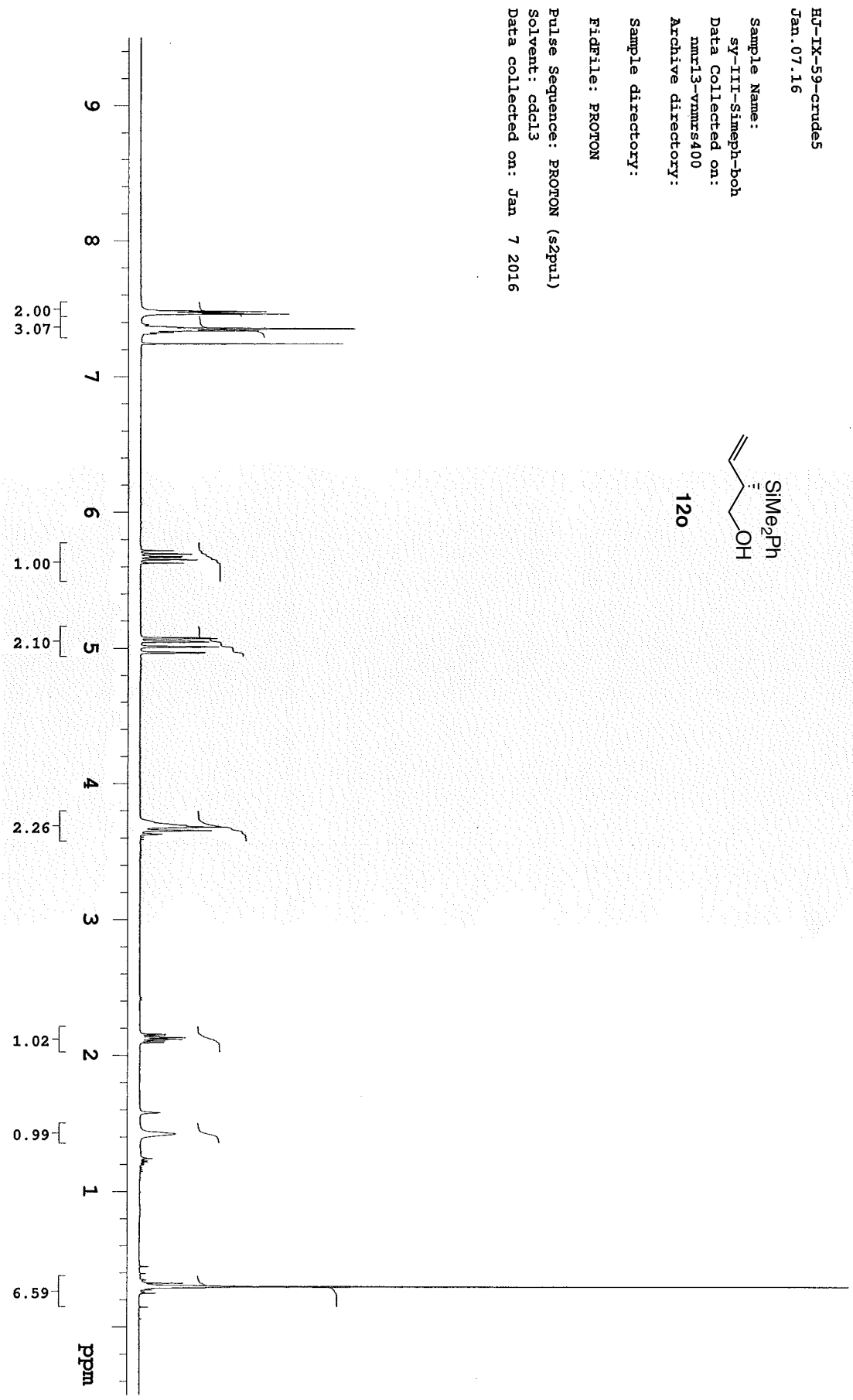
12m

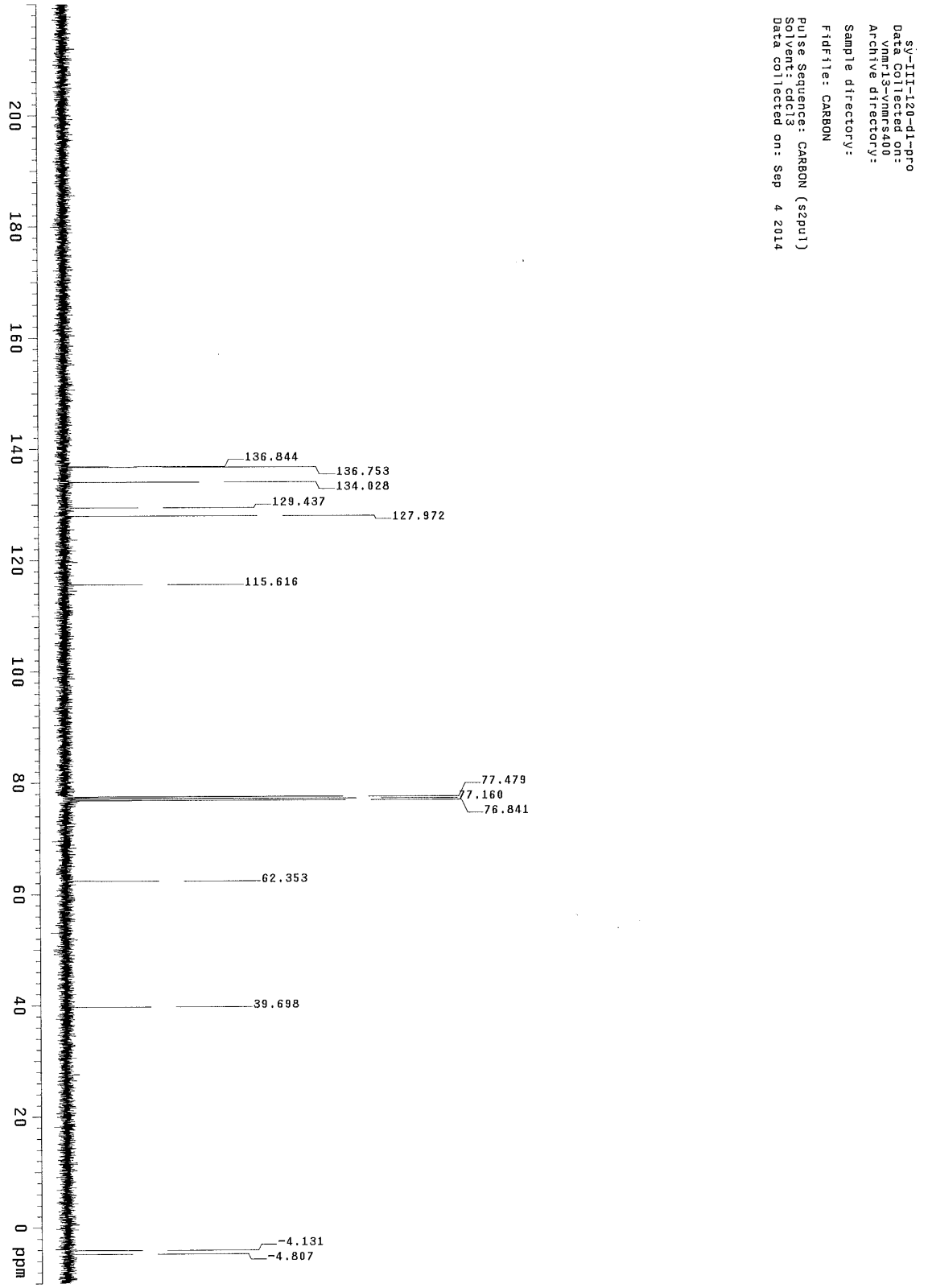


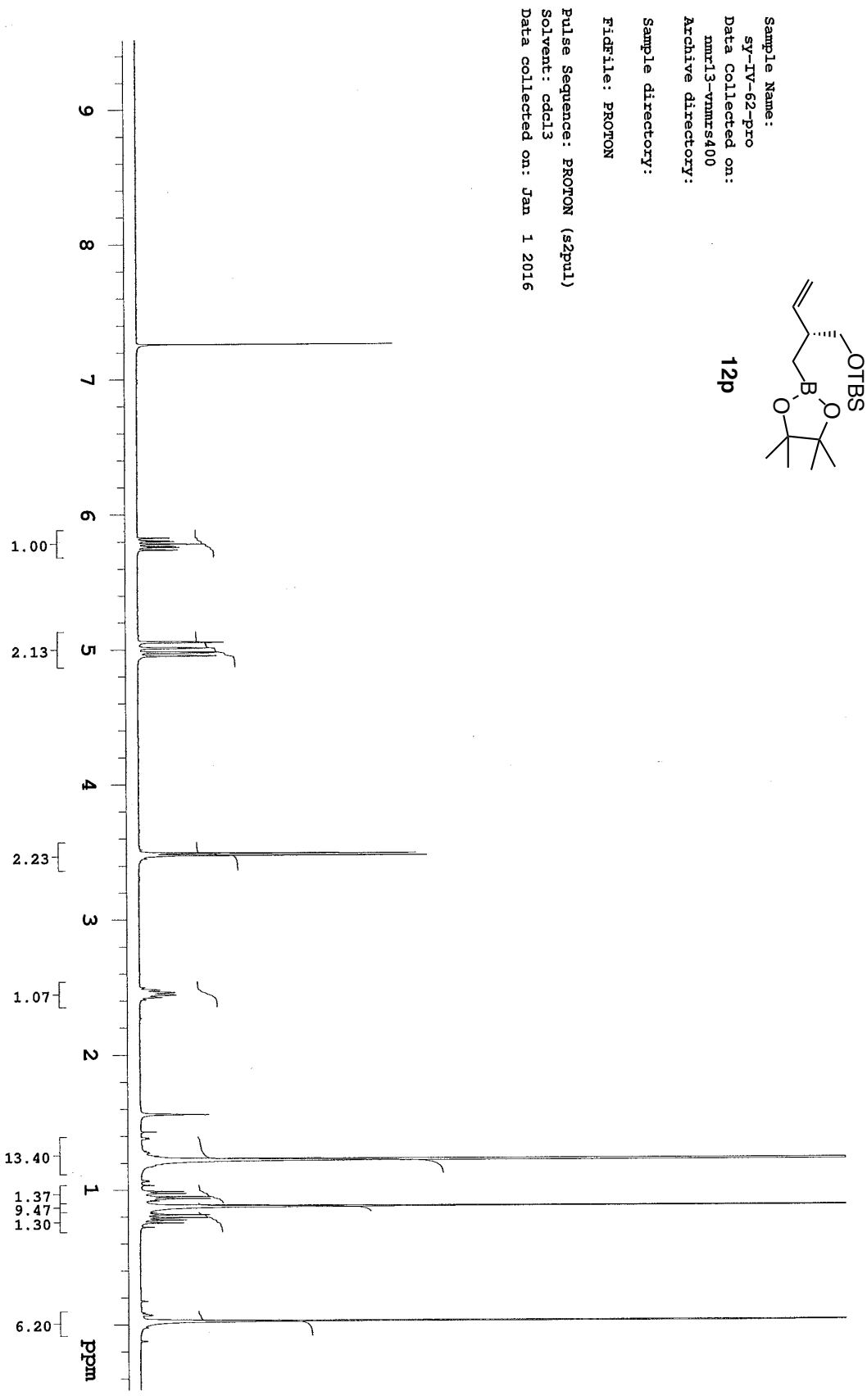

STANDARD FLUORINE PARAMETERS
Sample Name:
sy-III-120-ci-oxi-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 3 2014
138.855
118.288
77.479
77.160
76.841
63.567
53.230
38.681
31.206
30.424
26.675
26.576
26.546
200
180
160
140
120
100
80
60
40
20
0 ppm

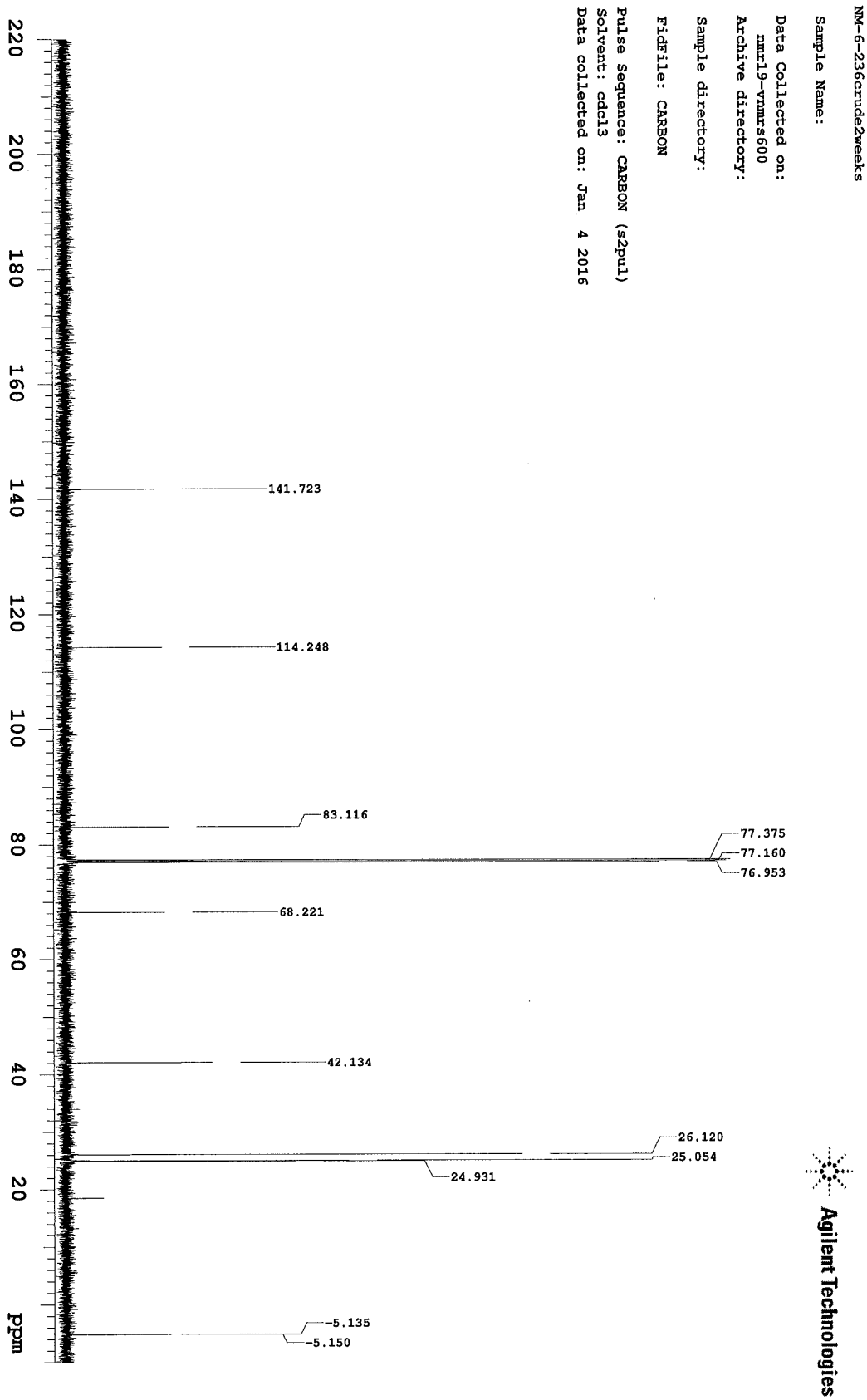

Sample Name:
sy-III-122-al-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 4 2014
Ph
OH
12n
2.08
2.39
2.14
1.02
0.97
1.00
2.08
2.19
1.03
1.49
9
8
7
6
5
4
3
2
1
0
ppm

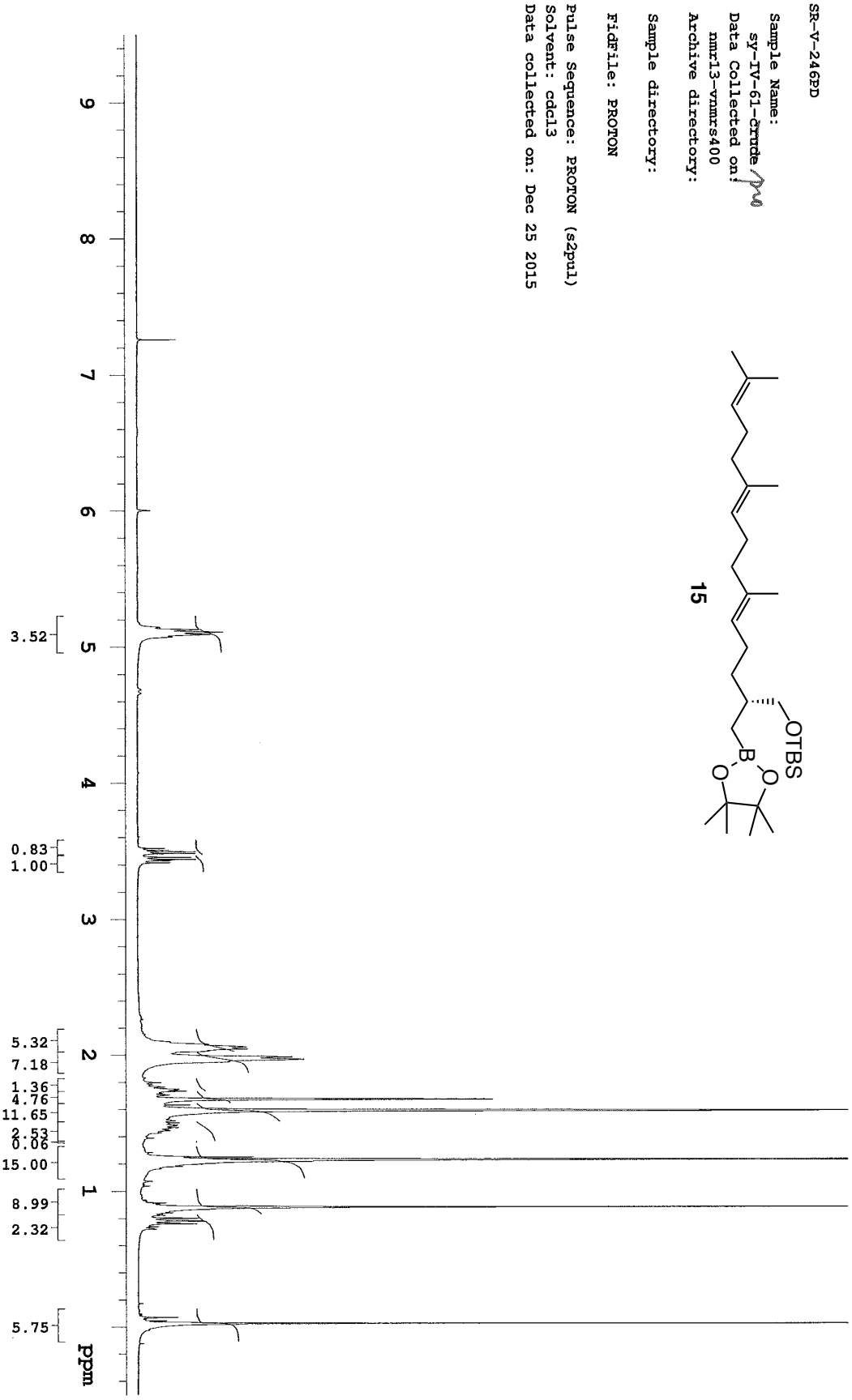

Sample Name:
sy-III-122-al-prro
Data Collected on:
vnmrs13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 4 2014
137.466
137.147
132.404
128.700
128.685
127.630
126.355
117.445
77.479
77.160
76.841
65.351
50.179
200
180
160
140
120
100
80
60
40
20
0 ppm

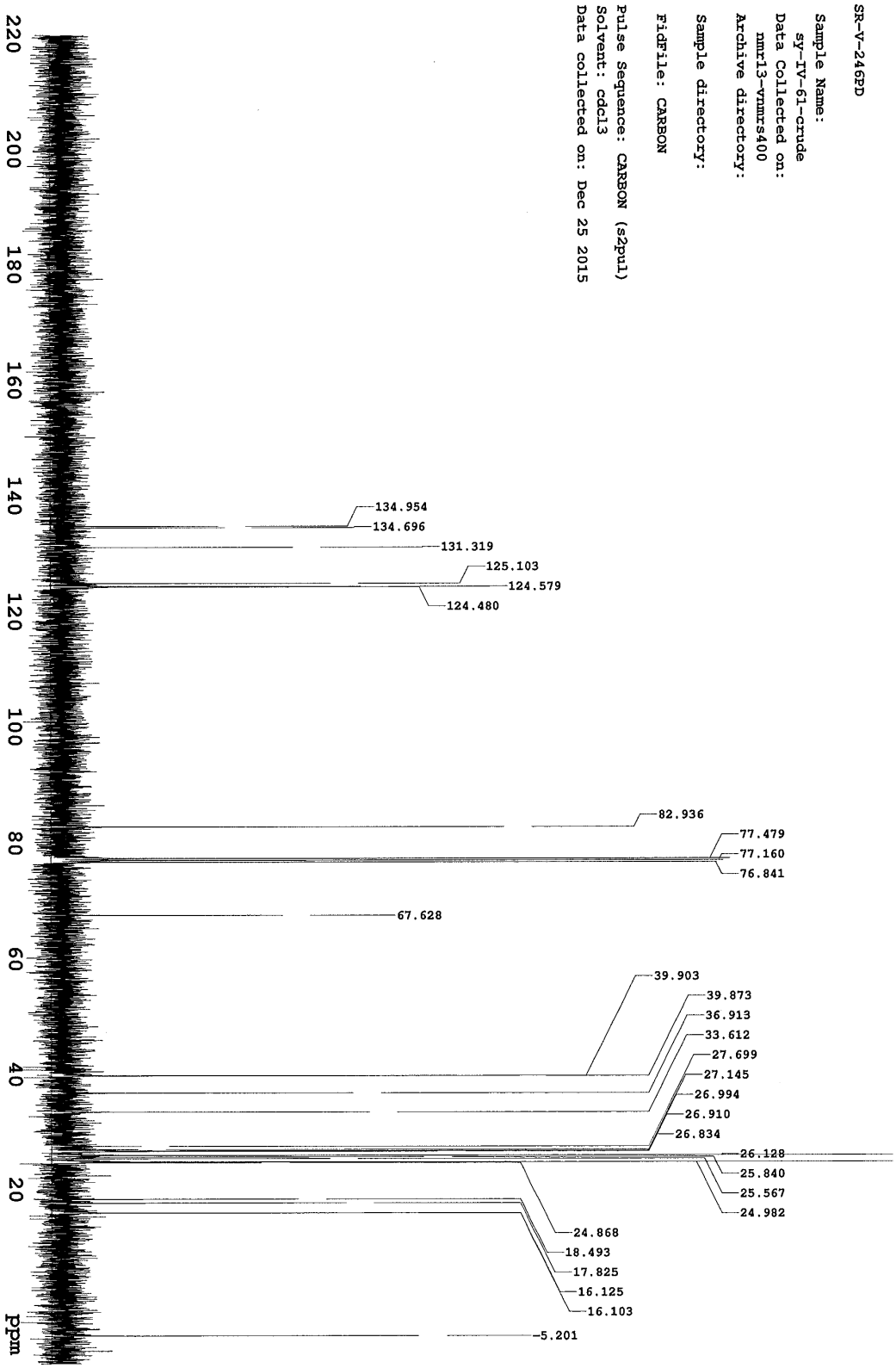

EJ-TX-59-crude5
Jan.07.16
Sample Name:
sy-III-Simeph-boh
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 7 2016
SiMe2Ph
OH
12o
2.00
3.07
1.00
2.10
2.26
1.02
0.99
6.59
ppm

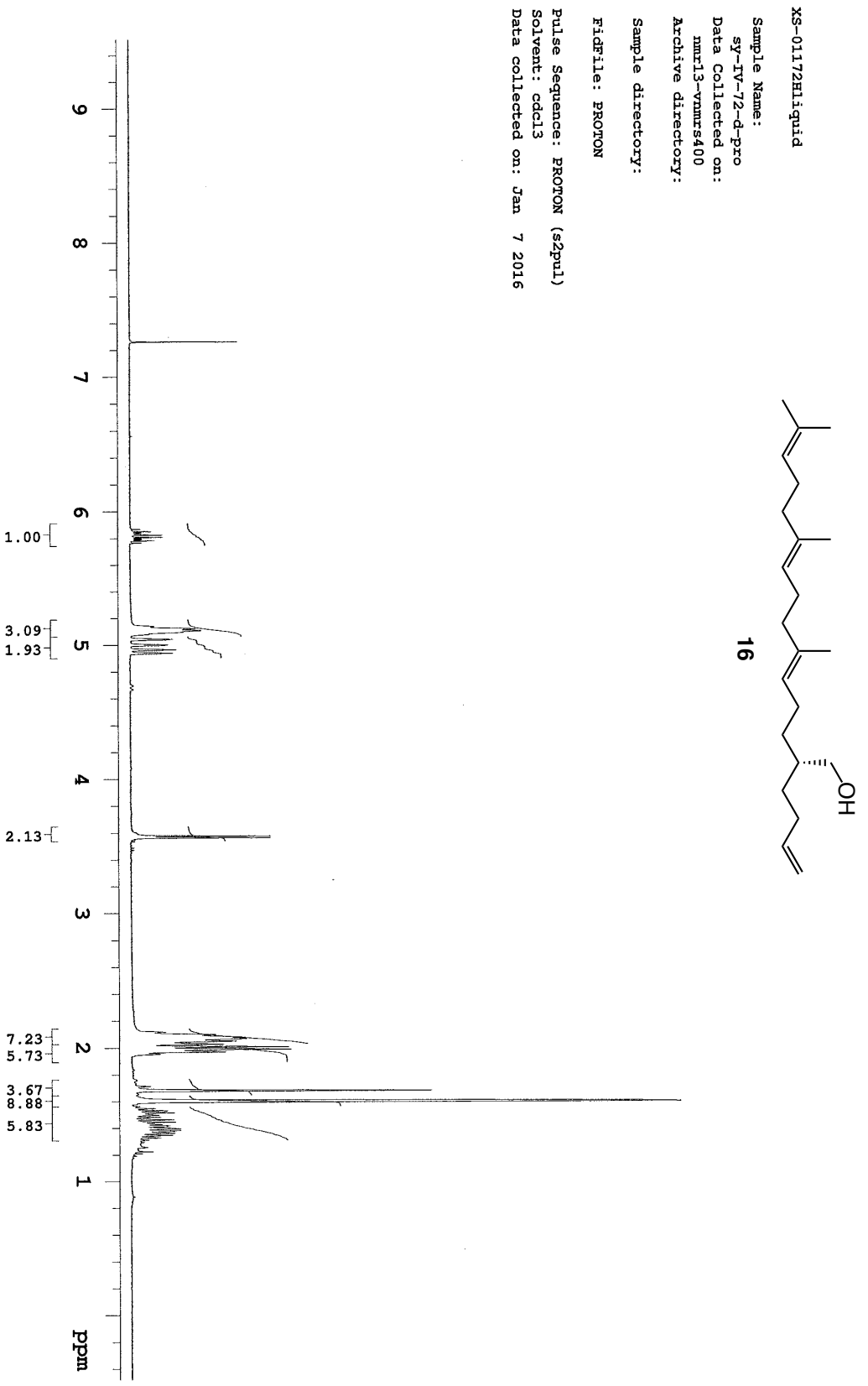

sy-III-120-d1-pro
Data Collected on:
vnmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 4 2014
136.844
136.753
134.028
129.437
127.972
115.616
77.479
77.160
76.841
62.353
39.698
-4.131
-4.807
200
180
160
140
120
100
80
60
40
20
0
ppm

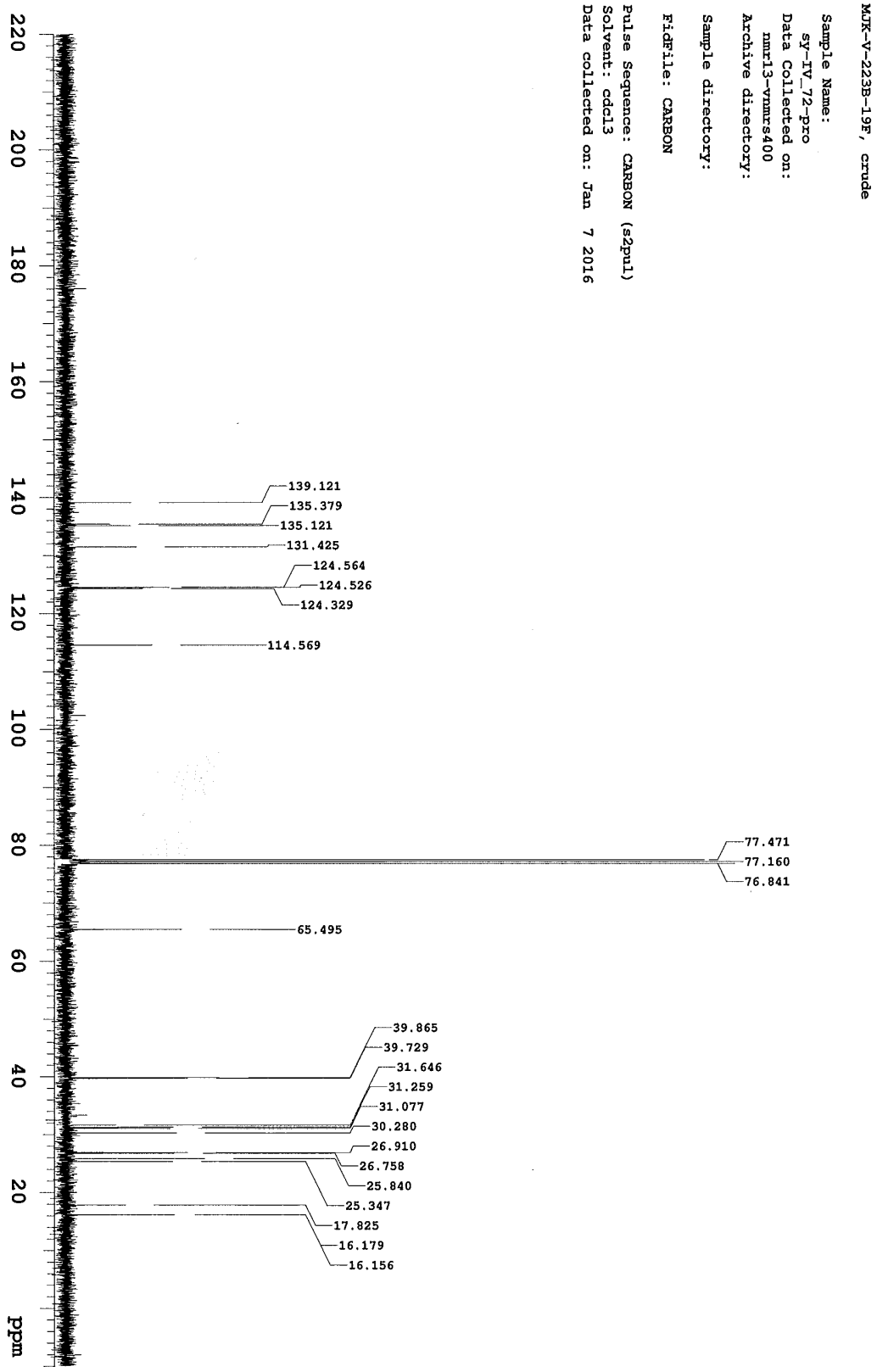

Sample Name:
sy-IV-62-pro
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 1 2016
OTBS
B
O
O
12p
1.00
2.13
2.23
1.07
13.40
1.37
9.47
1.30
6.20
9
8
7
6
5
4
3
2
1
ppm

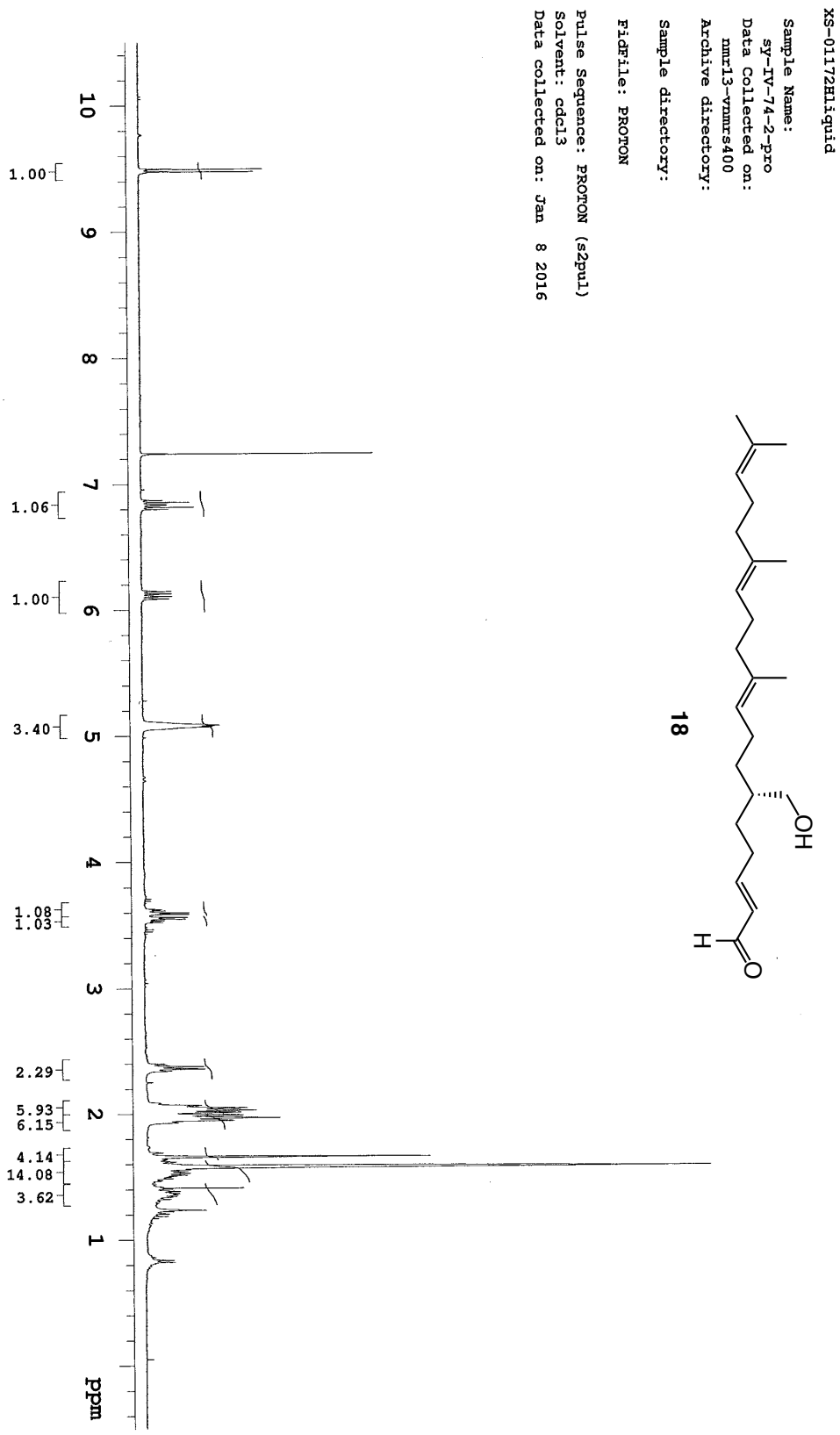

NM-6-236crude2weeks
Sample Name:
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 4 2016
220
200
180
160
140
120
100
80
60
40
20
ppm
141.723
114.248
83.116
77.375
77.160
76.953
68.221
42.134
26.120
25.054
24.931
-5.135
-5.150
Agilent Technologies

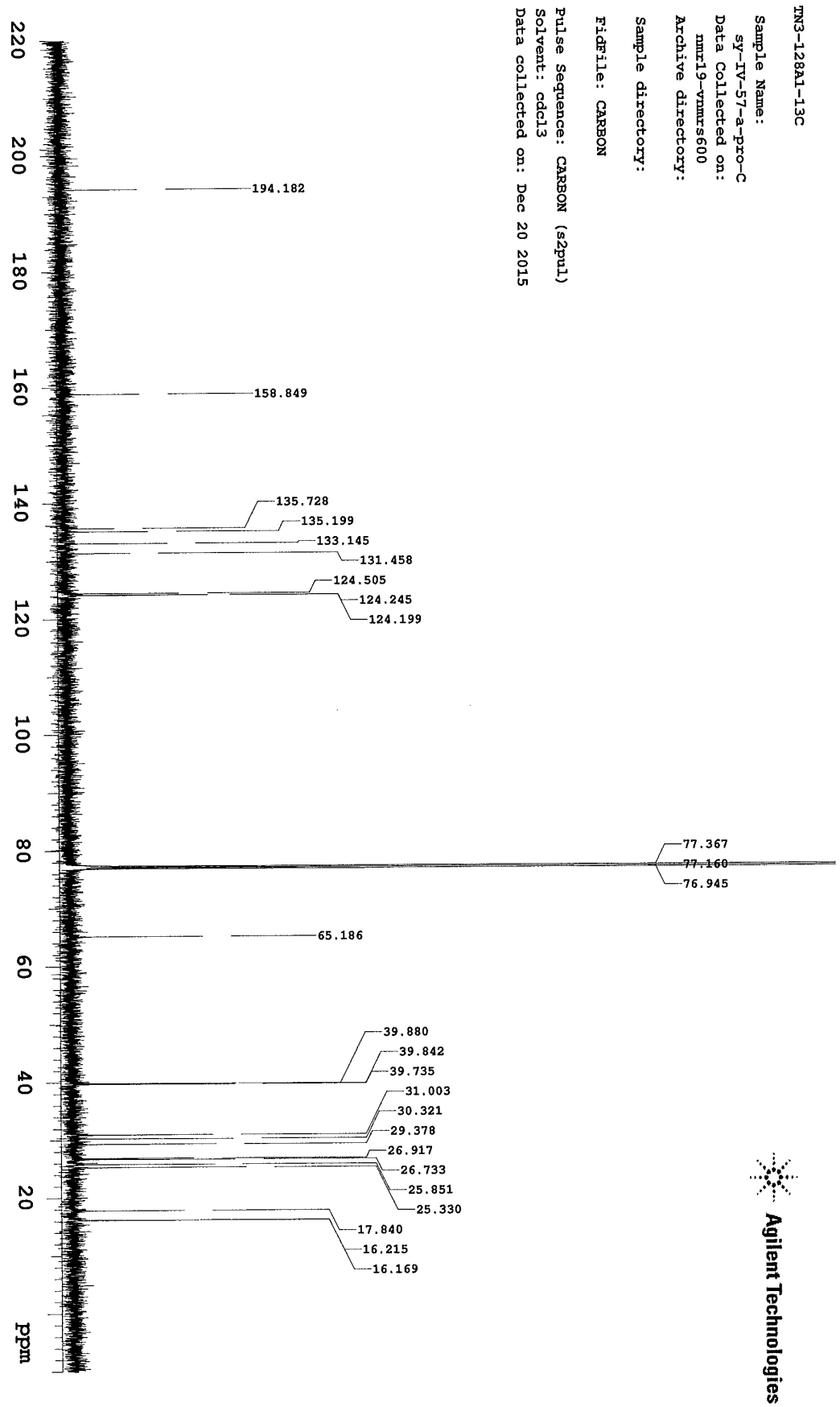

SR-V-246PD
Sample Name:
sy-IV-61-crude
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 25 2015
15
OTBS
B
O
O
3.52
0.83
1.00
5.32
7.18
1.36
4.76
11.65
2.53
0.06
15.00
8.99
2.32
5.75
9
8
7
6
5
4
3
2
1
ppm

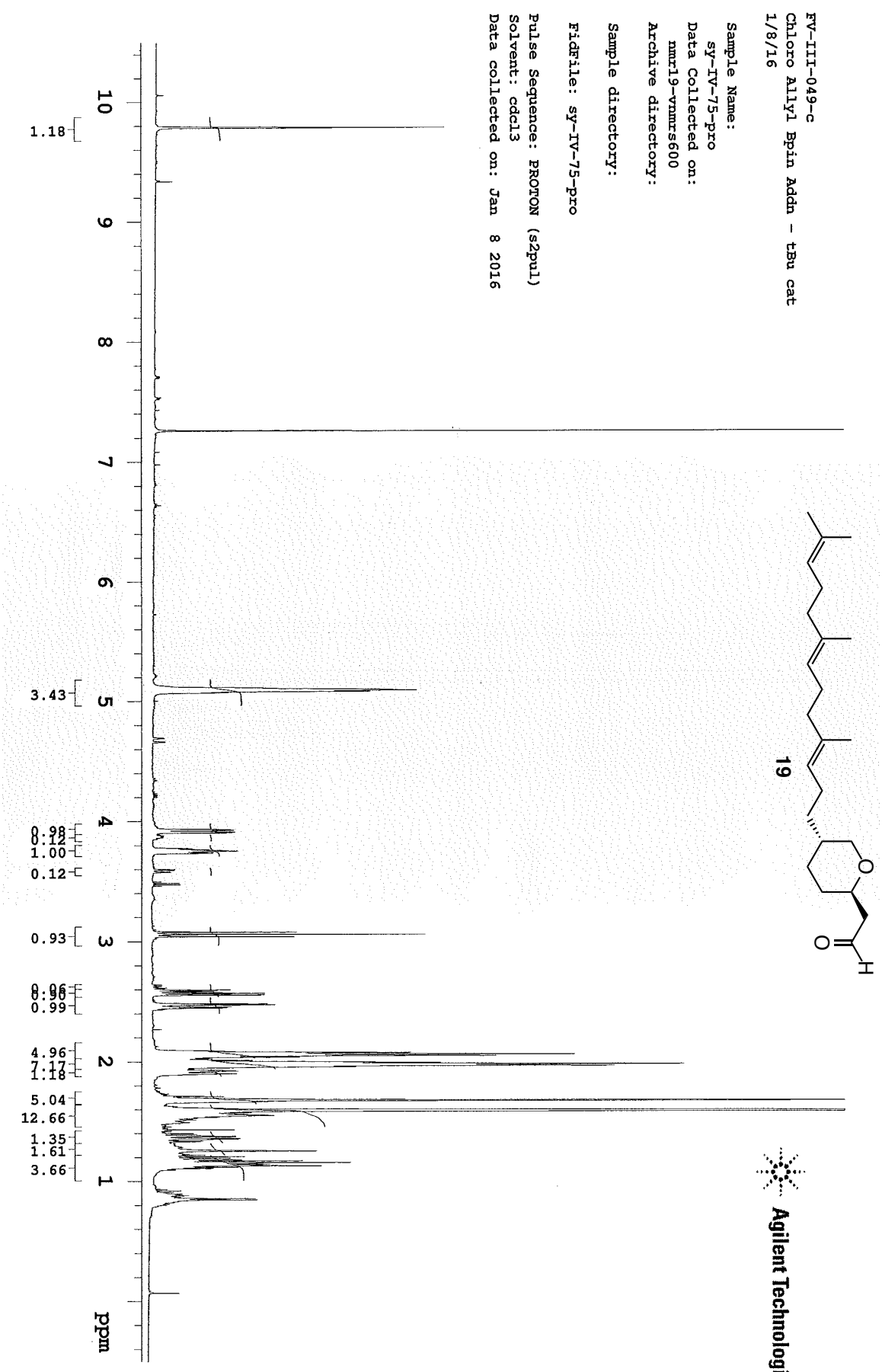

SR-V-246PD
Sample Name:
sy-IV-61-crude
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 25 2015
220
200
180
160
140
120
100
80
60
40
20
ppm
134.954
134.696
131.319
125.103
124.579
124.480
82.936
77.479
77.160
76.841
67.628
39.903
39.873
36.913
33.612
27.699
27.145
26.994
26.910
26.834
26.128
25.840
25.567
24.982
24.868
18.493
17.825
16.125
16.103
-5.201

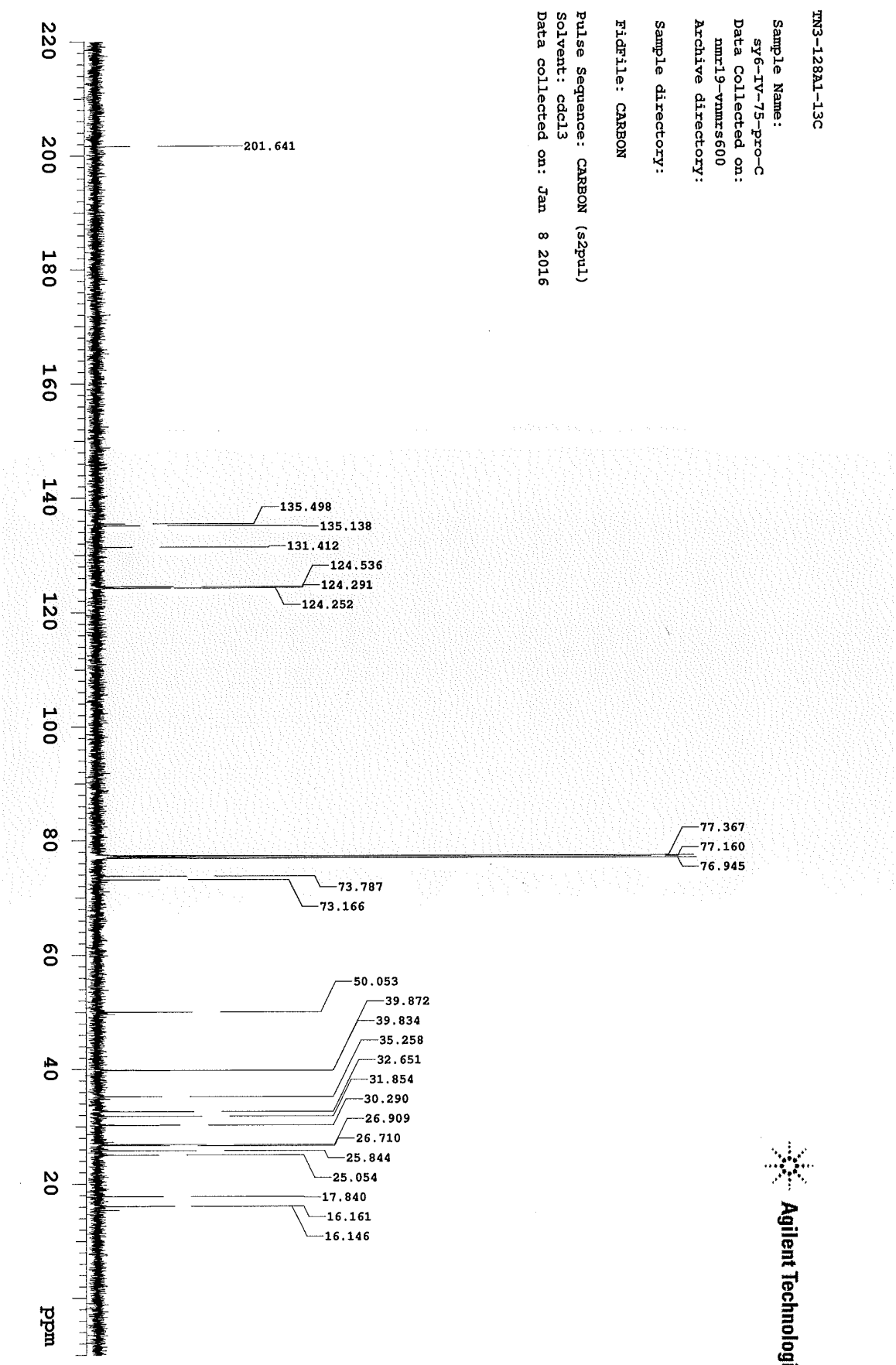

XS-01172Hliquid
Sample Name:
sy-IV-72-d-pro
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 7 2016
OH
16
1.00
3.09
1.93
2.13
7.23
5.73
3.67
8.88
5.83
9
8
7
6
5
4
3
2
1
ppm


MJK-V-223B-19F, crude
Sample Name:
sy-IV_72-pro
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 7 2016
220
200
180
160
140
120
100
80
60
40
20
ppm
139.121
135.379
135.121
131.425
124.564
124.526
124.329
114.569
77.471
77.160
76.841
65.495
39.865
39.729
31.646
31.259
31.077
30.280
26.910
26.758
25.840
25.347
17.825
16.179
16.156


XS-01172Hliquid
Sample Name:
sy-IV-74-2-pro
Data Collected on:
nmr13-vnmrs400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 8 2016
18
OH
H
O
1.00
1.06
1.00
3.40
1.08
1.03
2.29
5.93
6.15
4.14
14.08
3.62
10
9
8
7
6
5
4
3
2
1
ppm


TN3-128A1-13C
Sample Name:
sy-IV-57-a-pro-C
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Dec 20 2015
194.182
158.849
135.728
135.199
133.145
131.458
124.505
124.245
124.199
77.367
77.160
76.945
65.186
39.880
39.842
39.735
31.003
30.321
29.378
26.917
26.733
25.851
25.330
17.840
16.215
16.169
220
200
180
160
140
120
100
80
60
40
20
ppm
Agilent Technologies


FV-III-049-c
Chloro Allyl Bpin Addn - tBu cat
1/8/16
Sample Name:
sy-IV-75-pro
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: sy-IV-75-pro
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 8 2016
19
Agilent Technologies
1.18
3.43
0.98
0.12
1.00
0.12
0.93
0.96
0.90
0.99
4.96
7.17
1.18
5.04
12.66
1.35
1.61
3.66
10
9
8
7
6
5
4
3
2
1
ppm


TN3-128A1-13C
Sample Name:
sy6-IV-75-pro-C
Data Collected on:
nmr19-vnmrs600
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 8 2016
201.641
135.498
135.138
131.412
124.536
124.291
124.252
77.367
77.160
76.945
73.787
73.166
50.053
39.872
39.834
35.258
32.651
31.854
30.290
26.909
26.710
25.844
25.054
17.840
16.161
16.146
220
200
180
160
140
120
100
80
60
40
20
ppm
Agilent Technologies