Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary/Supporting Information

Visible-Light-Mediated, Nitrogen-Centered Radical Amination of Tertiary Alkyl Halides under Metal-Free Conditions to Form α-Tertiary Amines

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General Experimental.

^{1}H and ^{13}C NMR spectra were recorded on a Varian 400/100 (400 MHz) spectrometer or on a Varian 90 MHz (at Hanover College) in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide ($(CD_3)_2SO$) with the solvent residual peak as internal reference unless otherwise stated ($CDCl_3$: ^{1}H = 7.26 ppm, ^{13}C = 77.23 ppm; $(CD_3)_2SO$: ^{1}H = 2.50 ppm, ^{13}C = 39.52 ppm). Data are reported in the following order: chemical shifts are given (_); multiplicities are indicated as br (broadened), s (singlet), d (doublet), dd (doublet of doublets), t (triplet), dt (double of triplets), td (triplet of doublets), q (quartet), p (pentet), m (multiplet); coupling constants, *J*, are reported (Hz); integration is provided. The solvent impurity (H_2O – approx. 1.55 ppm) observed in several spectra was experimentally determined to originate from our $CDCl_3$ source, and was not presumed to be present in the respective products. Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrometer. Peaks are reported (cm^{-1}) with the following relative intensities: vs (very strong), s (strong), m (medium), w (weak), and br (broad). Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator. Visualization was accomplished by UV light (254 nm). Purification by chromatography was performed using Whatman 60Å 230-400 mesh SiO_2 with compressed air as a source of positive pressure. Solvents for chromatography and additional reactions ($CHCl_3$, benzene, EtOAc, heptane, acetone, Et_2O, THF) were reagent grade and used as received. Dichloromethane solvent for reactions was dried via GlassContour Solvent Dispensing System. Accurate mass spectrum was performed using a Thermo Scientific Exactive spectrometer operating in negative ion electrospray mode by Mrs. J. Holland and Dr. K. P. Roberts at the Department of Chemistry and Biochemistry, the University of Tulsa.

Starting Materials.

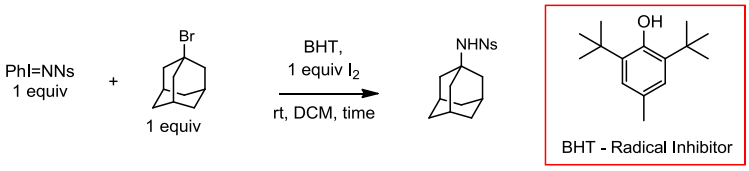
All tertiary alkyl halides, TEMPO, and BHT were purchased from commercial sources and used without further purification. I_2 was purchased from Alfa Aesar in 99.99+% purity (metals basis). PhI=NNs and PhI=NTs were prepared according to literature precedent[1,2] from $PhI(OAc)_2$, 4-$NO_2PhSO_2NH_2$ (or 4-$CH_3PhSO_2NH_2$), and KOH, and the purity of the PhI=NNs was verified by decomposition point (123 °C, followed immediately by a dark red coloration). The iminoiodinanes (PhI=NNs and PhI=NTs) were stored under an argon atmosphere at -4 °C (freezer). The *N,N*-diiodosulfonamide, 4-$NO_2PhSO_2NI_2$ (**15**), was prepared according to literature precedent and used immediately.[2]

General Procedure for aminosulfonation of 3° alkyl halides:

To an oven-dried flask was added alkyl halide (0.25 mmol), PhI=NNs (0.101 g, 0.25 mmol), I_2 (0.063 g, 0.25 mmol) and dry dichloromethane (2-4 mL). The mixture was stirred at room temperature under argon for 3-6 hours with the laboratory and fume hood lights left on. Upon completion of the reaction, solvent was evaporated via compressed air. The crude was purified directly via flash chromatography (typically using a minimal amount of DCM to help dissolve the solid, then using an eluant of 20% EtOAc/hexanes unless otherwise stated).

Investigation of the Effect of a Radical Inhibitor (BHT):

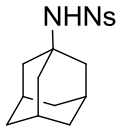
Following the general procedure for aminosulfonation of tertiary alkyl halides:



Entry	Time	Equiv. BHT	Isolated %Yield
1	3 hrs	0	81
2	3 hrs	0.25	41
3	3 hrs	1	trace
4	16 hrs	1	trace

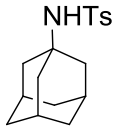
Compounds and Characterization:

***N*-Adamantan-1-yl-4-nitro-benzenesulfonamide[2] (2)**



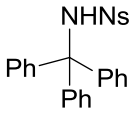
Prepared according to the general procedure from 1-bromoadamantane to give the product as a white solid (68 mg, 81%). R_f = 0.3, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 8.10 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 4.84 (br s, 1H), 2.03 (br s, 3H), 1.80 (d, *J* = 2.7 Hz, 6H), 1.59 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 128.1, 124.2, 55.9, 43.1, 35.7, 29.4; IR (neat, cm^{-1}): 3223(br), 3098(w), 2901(m), 2849(m), 1523(s), 1345(s); HRMS (ESI - neg) calculated for $C_{16}H_{20}O_4N_2S_1$ $[M-H]^-$ requires *m/z* 335.10656, found *m/z* 335.10664.

***N*-Adamantan-1-yl-4-methyl-benzenesulfonamide[2] (3)**



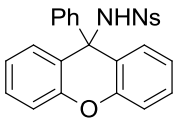
Prepared according to the general procedure (16 hour reaction) from 1-bromoadamantane to give the product as a white solid (33 mg, 43%). R_f = 0.3, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dt, *J* = 2.0 Hz, 8.2 Hz, 2H), 7.27 (dt, *J* = 2.0 Hz, 8.2 Hz, 2H), 4.40 (br s, 1H), 2.43 (s, 3H), 1.99 (br s, 3H), 1.77 (d, *J* = 2.7 Hz, 6H), 1.57 (m, 6H); GCMS (EI) 305 (M^+).

4-Nitro-*N*-tritylbenzenesulfonamide[3] (4)



Prepared according to a modification of the general procedure employing 5 equivalents (1.25 mmol) of triphenylmethyl bromide to give the product as an off-white solid (78 mg, 70%). R_f = 0.35, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 9.14 (br s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 6H), 7.23-7.13 (m, 9H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$): δ 148.9, 148.3, 143.8, 129.4, 128.0, 127.9, 127.2, 123.7, 72.2; IR (cm^{-1}): 3281(br), 3055(w), 2923(w), 1525(m), 1538(s), 1340(m), 1157(m); HRMS (ESI - neg) calculated for $C_{25}H_{20}O_4N_2S_1$ $[M-H]^-$ requires *m/z* 443.10656, found *m/z* 443.10603.

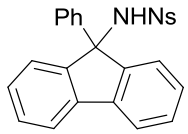
4-Nitro-*N*-(9-phenyl-9*H*-xanthen-9-yl)benzenesulfonamide (5)



Prepared according to a modification of the general procedure employing 5 equivalents (1.25 mmol) of 9-chloro-9-phenylxanthene and 40 ^{o}C (5 hr) to give the product as an off-white solid (79 mg, 71%). R_f = 0.15, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 7.52 (dt, *J* = 1.2 Hz, 7.8 Hz, 2H), 7.35-7.25 (m, 9H), 7.18 (dt, *J* = 0.8 Hz, 7.4

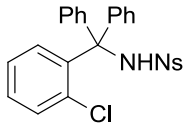
Hz, 2H), 7.10 (td, *J* = 1.0 Hz, 7.5 Hz, 2H), 5.92 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 149.3, 146.4, 144.7, 130.4, 129.7, 128.3, 127.9, 127.8, 127.7, 123.4, 123.3, 123.1, 116.3, 61.8; IR (neat, cm^{-1}): 3279(br), 3070(w), 1604(w), 1521(m), 1346(m), 1314(m), 1169(m), 752(s); HRMS (ESI - neg) calculated for $C_{25}H_{18}O_5N_2S_1$ $[M-H]^-$ requires *m/z* 457.08582, found *m/z* 457.08505.

4-Nitro-*N*-(9-phenyl-9*H*-fluoren-9-yl)benzenesulfonamide (6)



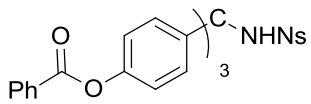
Prepared according to the general procedure from 9-bromo-9-phenylfluorene to give the product as an off-white solid (44 mg, 40%). R_f = 0.30, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 2.3 Hz, 9.0 Hz, 2H), 7.51 (dt, *J* = 0.8 Hz, 7.4 Hz, 2H), 7.35-7.25 (m, 9H), 7.18 (dt, *J* = 0.8 Hz, 7.4 Hz, 2H), 7.10 (td, *J* = 1.2 Hz, 7.0 Hz, 2H), 5.86 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 146.0, 145.5, 141.8, 140.0, 129.2, 128.9, 128.30, 128.29, 127.9, 125.9, 125.5, 123.2, 120.0, 71.5; IR (neat, cm^{-1}): 3201(br), 3108(w), 2921(w), 2850(w), 1526(m), 1350(m), 1166(m), 730(s); HRMS (ESI - neg) calculated for $C_{25}H_{18}O_4N_2S_1$ $[M-H]^-$ requires *m/z* 441.09091, found *m/z* 441.09051.

4-Nitro-*N*-[(2-chlorophenyl)diphenylmethyl]benzenesulfonamide (7)



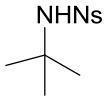
Prepared according to a modification of the general procedure employing 5 equivalents (1.25 mmol) of 2-chlorotrityl chloride and 40 °C (5 hr) to give the product as an off-white solid (79 mg, 62%). Note – The room temperature reaction results in an easier isolation/purification, albeit lower yield. Isolation consists of a 20% EtOAc/hexanes column followed by a 75% DCM/hexanes column. R_f = 0.45, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 7.76 (dd, *J* = 1.6 Hz, 7.8 Hz, 1H), 7.36-7.32 (m, 7H), 7.26-7.16 (m, 7H), 6.91 (dd, *J* = 1.6 Hz, 7.8 Hz, 1H), 6.37 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 146.3, 142.6, 138.2, 134.7, 133.6, 131.7, 129.8, 128.12, 128.10, 127.6, 127.2, 126.3, 123.2, 72.7; IR (neat, cm^{-1}): 3281(br), 3061(w), 2921(w), 1525(m), 1338(m), 1157(m); HRMS (ESI - neg) calculated for $C_{25}H_{19}O_4N_2S_1Cl_1$ $[M-H]^-$ requires *m/z* 477.06758, found *m/z* 477.06696.

4-Nitro-*N*-[[tris[4-benzoyloxy)phenyl]methyl]]benzenesulfonamide (8)



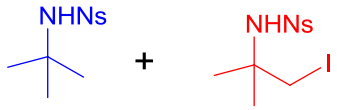
Prepared according to the general procedure (17 hr reaction time) to give the product as a white solid (113 mg, 56%). R_f = 0.45, 20% EtOAc/hexanes. Note – The product appears to decompose in solvent, so all analysis and utilization of the compound is relatively time-sensitive. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, 6H), 7.94 (d, 2H), 7.64 (t, 3H), 7.51 (t, 6H), 7.38 (d, 2H), 7.23-7.17 (m, 12H), 5.65 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 149.5, 141.1, 133.6, 131.7, 130.5, 130.3, 130.2, 129.5, 128.7, 128.6, 121.8, 121.7, 55.1; IR (neat, cm^{-1}): 3451(br), 1727(s), 1503(m), 1262(s), 1198(s), 1058(s), 705(s).

***N*-(*tert*-butyl)-4-nitrobenzenesulfonamide[4] (9)**



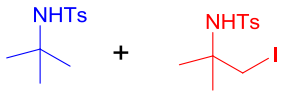
To an oven-dried flask was added 2-bromo-2-methylpropane (0.342 g, 2.50 mmol), $PhI(OAc)_2$ (0.320 g, 1.0 mmol), I_2 (0.126 g, 0.50 mmol), $4\text{-}NO_2PhSO_2NH_2$ (0.100 g, 0.5 mmol) and dry dichloromethane (4 mL). The mixture was stirred at room temperature under argon for 72 hours with the laboratory and fume hood lights left on. Upon completion of the reaction, solvent was evaporated via compressed air. The crude was purified directly via flash chromatography to give the product as a white solid (10 mg, 15%). R_f = 0.30, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dt, *J* = 2.3 Hz, 9.0 Hz, 2H), 8.08 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 4.75 (br s, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 129.7, 128.2, 124.2, 55.5, 30.2; IR (neat, cm^{-1}): 3268(br), 3123(w), 2969(w), 1528(s), 1348(m), 1332(m), 1152(s); HRMS (ESI - neg) calculated for $C_{10}H_{14}O_4N_2S_1$ $[M\text{-}H]^-$ requires *m/z* 257.05961, found *m/z* 257.05975.

***N*-(1-iodo-2-methylpropan-2-yl)-4-nitrobenzenesulfonamide (10)**



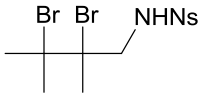
Compound **10** was prepared as major product in an inseparable mixture with product **9** according to the general procedure from 2-bromo-2-methylpropane (1.25 mmol; 5 equiv) to give the products as a yellowish-white solid (59 mg total, 72% - approximately a 4:5 ratio of **9**/**10** according to ^{1}H NMR integration). R_f = 0.30, 20% EtOAc/hexanes.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 8.35 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 8.11 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 8.09 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 5.02 (br s, 1H), 4.79 (br s, 1H), 3.41 (s, 2H), 1.80 (s, 6H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 149.1, 148.3, 128.3, 128.2, 124.3, 124.2, 56.0, 55.5, 30.2, 27.2, 20.8; IR (neat, cm^{-1}): 3276(br), 3108(w), 2980(w), 1529(s), 1331(m), 1154(s), 613(s); HRMS (ESI - neg) calculated for $C_{10}H_{14}O_4N_2S_1$ $[M\text{-}H]^-$ requires *m/z* 257.05961, found *m/z* 126.90397 and 257.05974.

***N*-(4-Methylphenylsulfonyl)-*N*-(*tert*-butyl)amine[5] (11)**



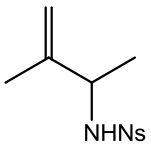
Compound **11** was prepared as major product in an inseparable mixture with product **12** according to the general procedure (using 0.25 mmol, 0.093 g; PhI=NTs) from 2-bromo-2-methylpropane (1.25 mmol; 5 equiv) to give the products as a yellowish-white solid (56 mg total, 70% - approximately a 3:1 ratio of **11**/**12** according to ^{1}H NMR integration). R_f = 0.30, 20% EtOAc/hexanes.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2H), 7.77 (d, 2H), 7.30 (d, 2H), 7.28 (d, 2H), 4.72 (br s, 1H), 4.41 (br s, 1H), 3.38 (s, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 1.36 (s, 6H), 1.23 (s, 9H).

***N*-(2,3-dibromo-2,3-dimethylbutyl)-4-nitrobenzenesulfonamide (13)**



Prepared according to the general procedure from 2,3-dibromo-2,3-dimethylbutane to give the product as a white solid (26 mg, 24%). R_f = 0.33, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (dt, *J* = 2.0 Hz, 8.6 Hz, 2H), 8.09 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 5.18 (dd, *J* = 9.6 Hz, 3.7 Hz, 1H), 3.81 (dd, *J* = 13.7 Hz, 9.8 Hz, 1H), 3.58 (dd, *J* = 13.7 Hz, 3.5 Hz, 1H), 2.00 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 145.9, 128.2, 124.6, 70.0, 52.3, 31.9, 31.8, 25.8; IR (neat, cm^{-1}): 3272(br), 3116(w), 2932(w), 1607(w), 1525(m), 1342(m), 1167(m), 1067(m); HRMS (ESI - neg) calculated for $C_{12}H_{16}O_4N_2S_1Br_2$ $[M-H]^-$ requires *m/z* 440.91193, 442.90988, 444.90784 (1:2:1 ratio); found *m/z* 440.91144, 442.90932, 444.90714 (1:2:1 ratio).

***N*-(3-methylbut-3-en-2-yl))-4-nitrobenzenesulfonamide[6] (14)**

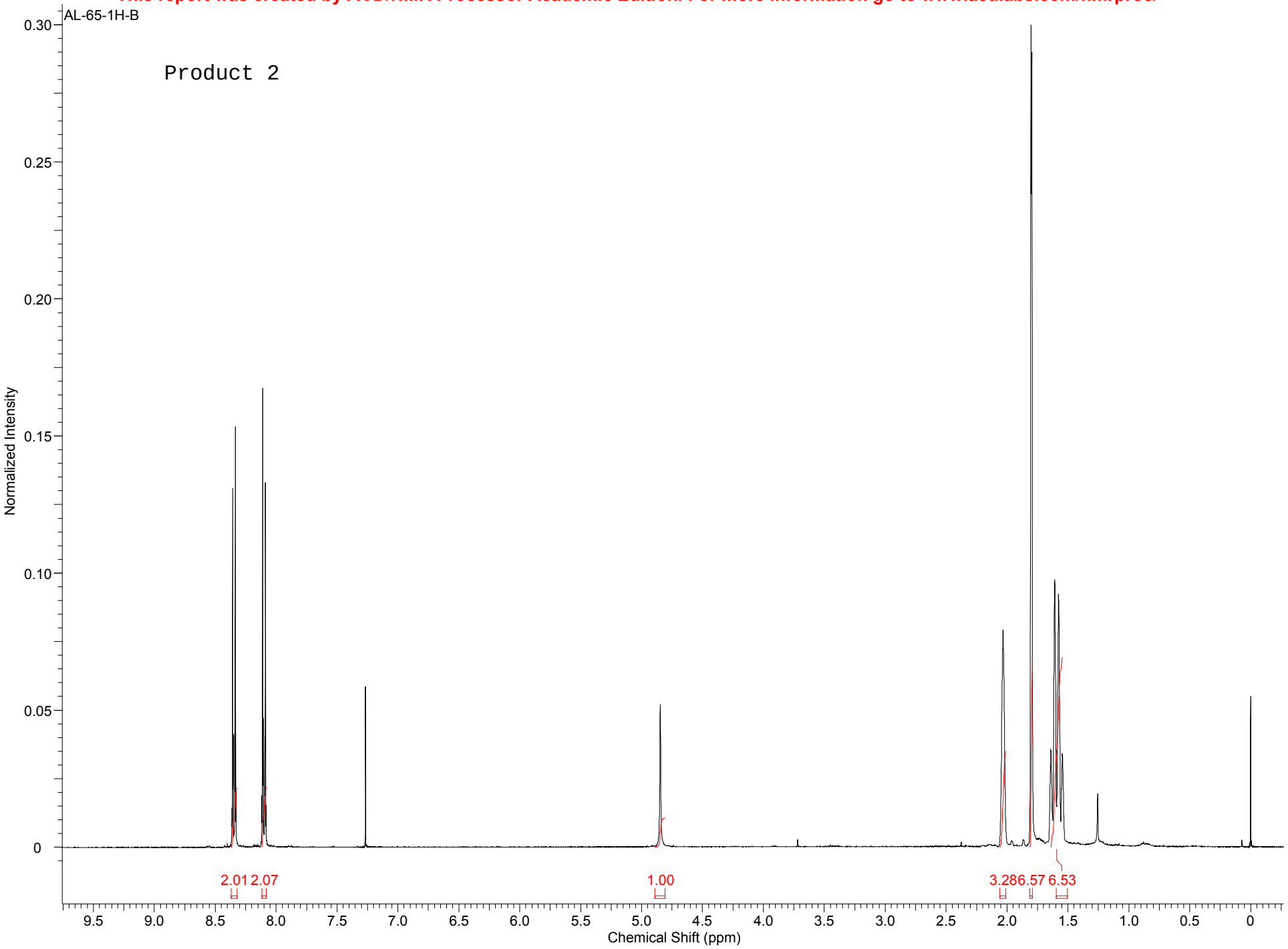


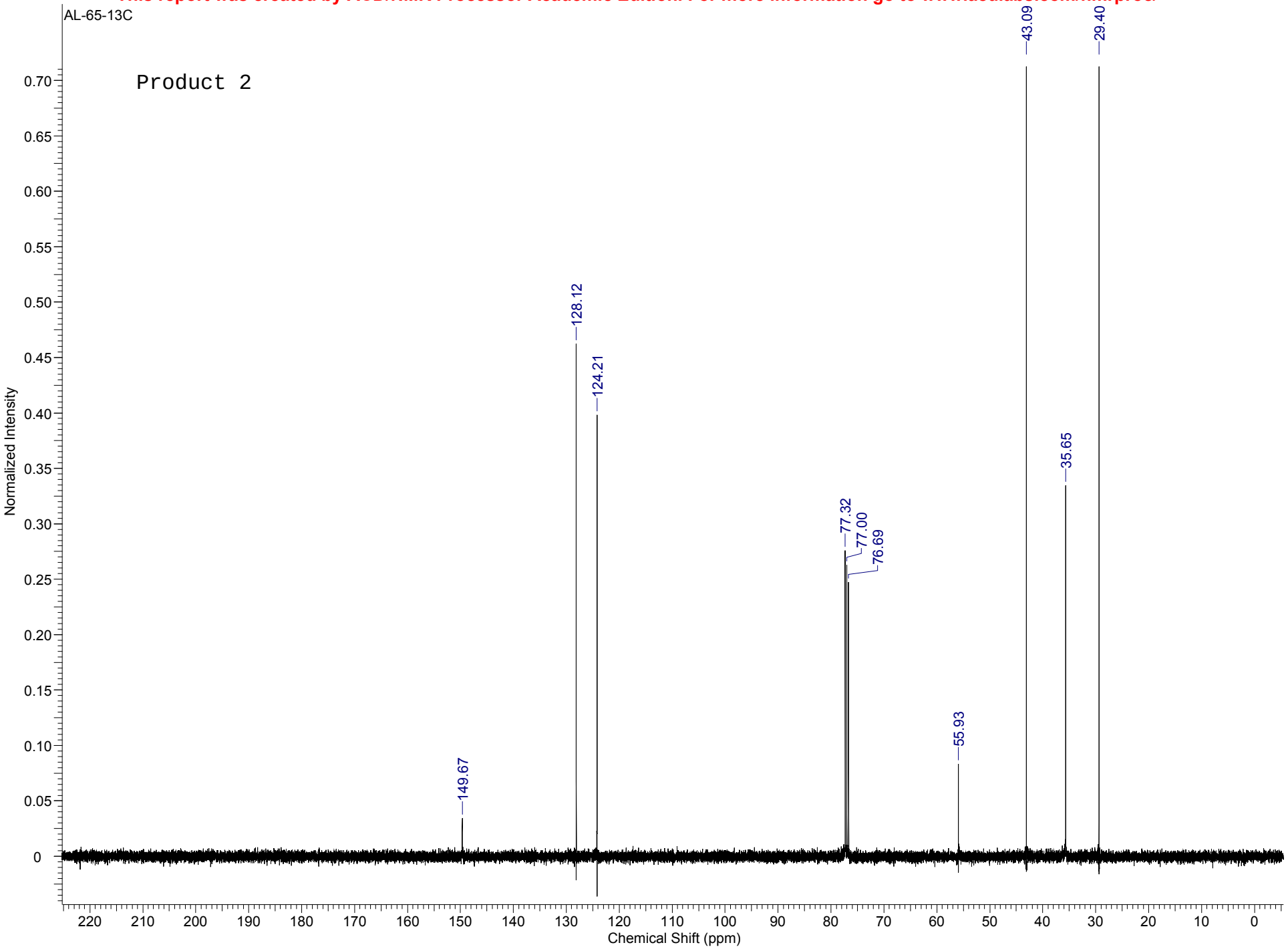
Prepared according to the general procedure from 2-bromo-2-methylbutane (0.25 mmol; 1 equiv) to give the product (with inseperable minor isomers) as a white solid (14 mg, 21%). The yield was obtained by ^{1}H NMR integration using 1,4-dimethoxybenzene as an internal standard. R_f = 0.30, 20% EtOAc/hexanes. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (dt, *J* = 2.0 Hz, 9.0 Hz, 2H), 8.04 (dt, *J* = 2.3 Hz, 9.0 Hz, 2H), 4.81 (m, 1H), 4.73 (br t, *J* = 1.4(x2) Hz 1H), 4.67 (br d, 1H), 3.99 (p, 1H), 1.53 (s, 3H), 1.24 (d, 3H); IR (neat, cm^{-1}): 3314(br), 3065(w), 1639(vs), 1541(s), 1490(m), 1311(m), 695(vs); HRMS (ESI - neg) calculated for $C_{11}H_{14}O_4N_2S_1$ $[M-H]^-$ requires *m/z* 269.05961, found *m/z* 269.05981.

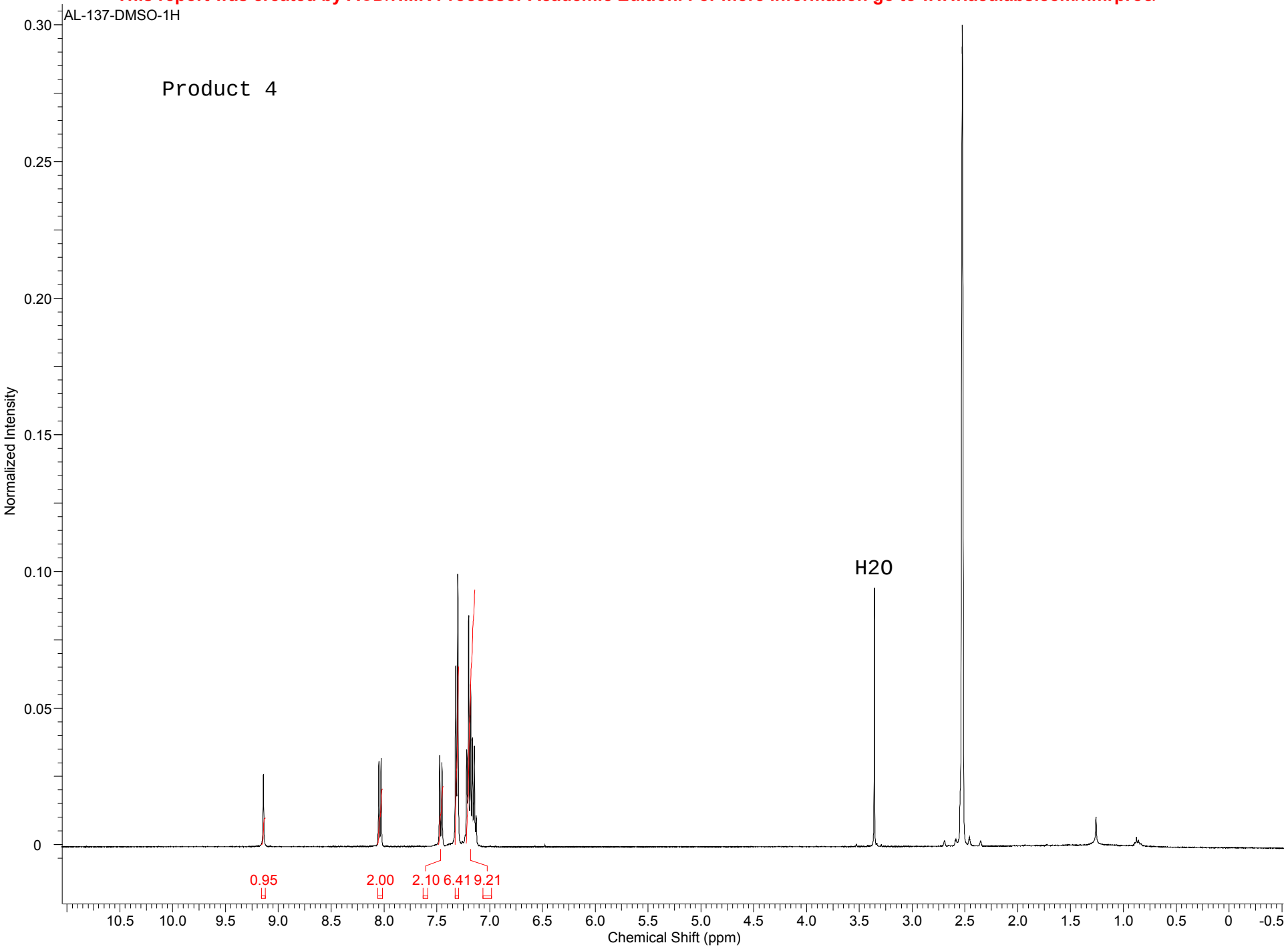
References:

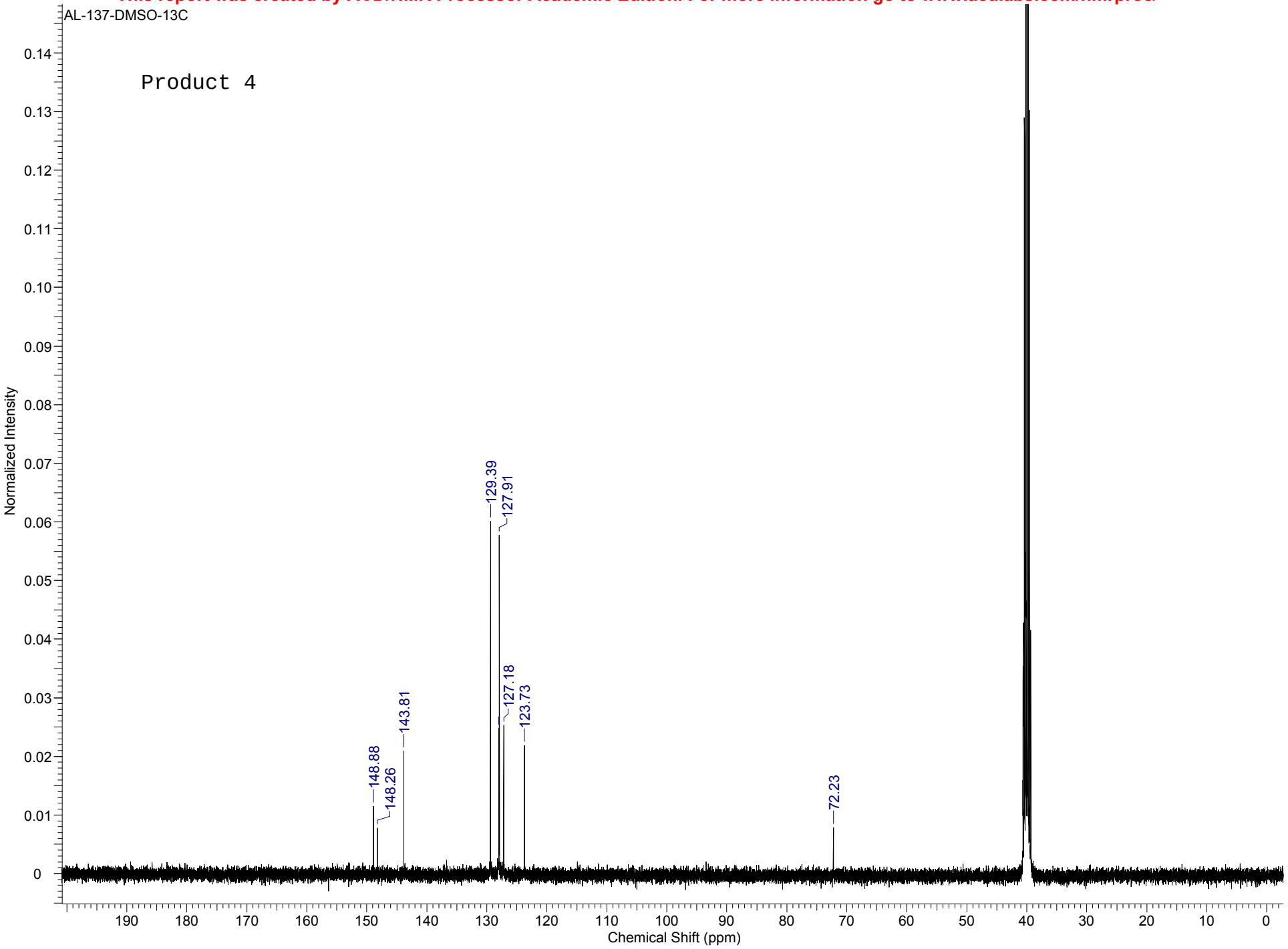
1) Nakanishi, M.; Minard, C.; Retailleau, P.; Cariou, K.; Dodd, R. H. *Org. Lett.* **2011**, *13,* 5792.
2) A. A. Lamar and K. M. Nicholas *J. Org. Chem.* **2010**, *75*, 7644.
3) Zhang, Y.; Feng, B.; Zhu, C. *Org. Biomol. Chem.* **2012**, *10*, 9137.
4) Tom J. Maricich, et. al. *Synthesis* **2013**, *45 (24)*, 3361.
5) Taniguchi, N. *Eur. J. Org. Chem.* **2010**, *14*, 2670.
6) A comparable compound (the R-NHTs instead of R-NHNs) has been reported and was used in the determination of the ^{1}H NMR of the inseparable mixture: Zhang, W. X.; Hu, W. G.; Su, L.; Liu, L. Q. *Chinese Chem. Lett.* **2012**, *23*, 285.

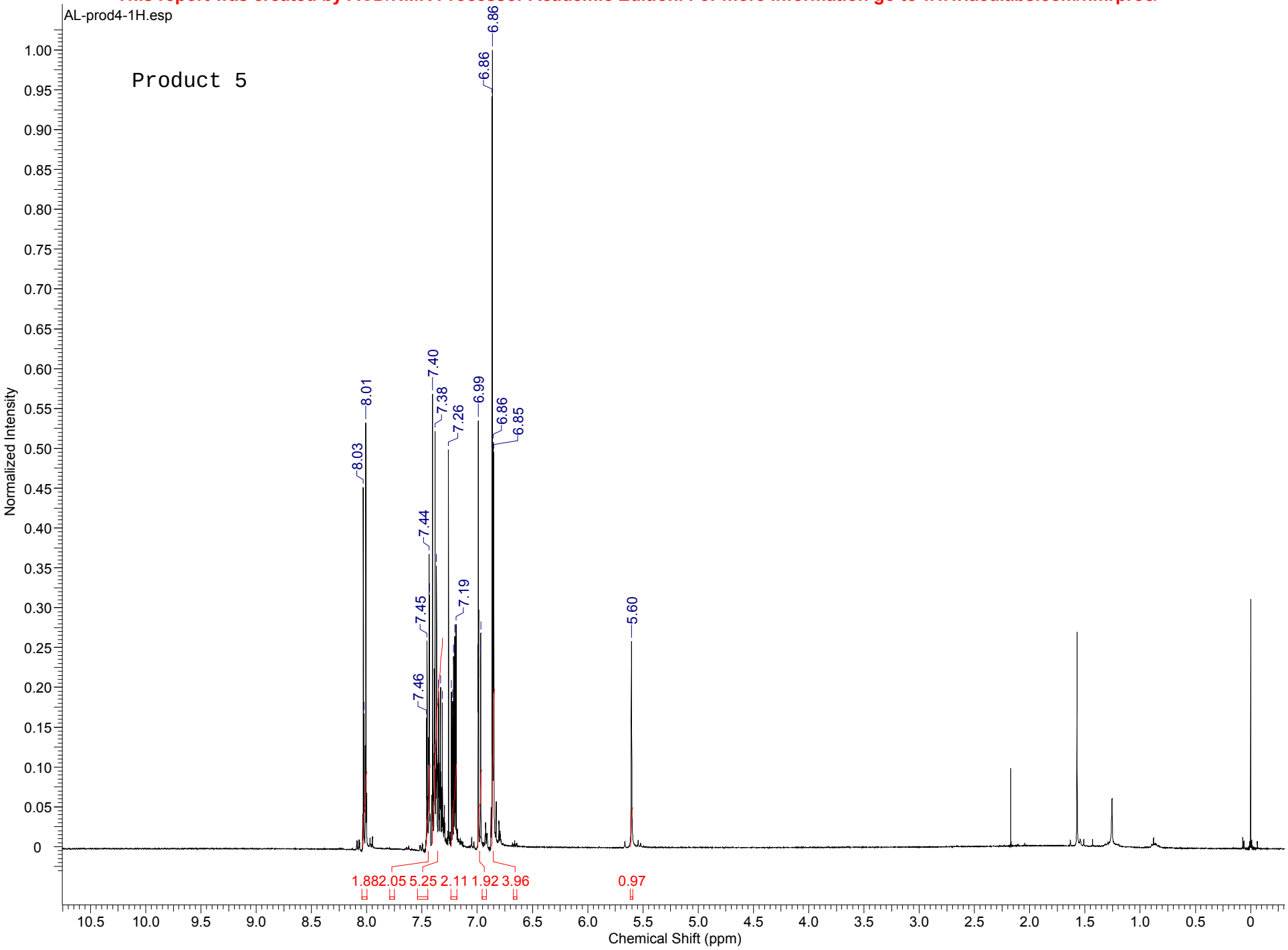
Spectra:

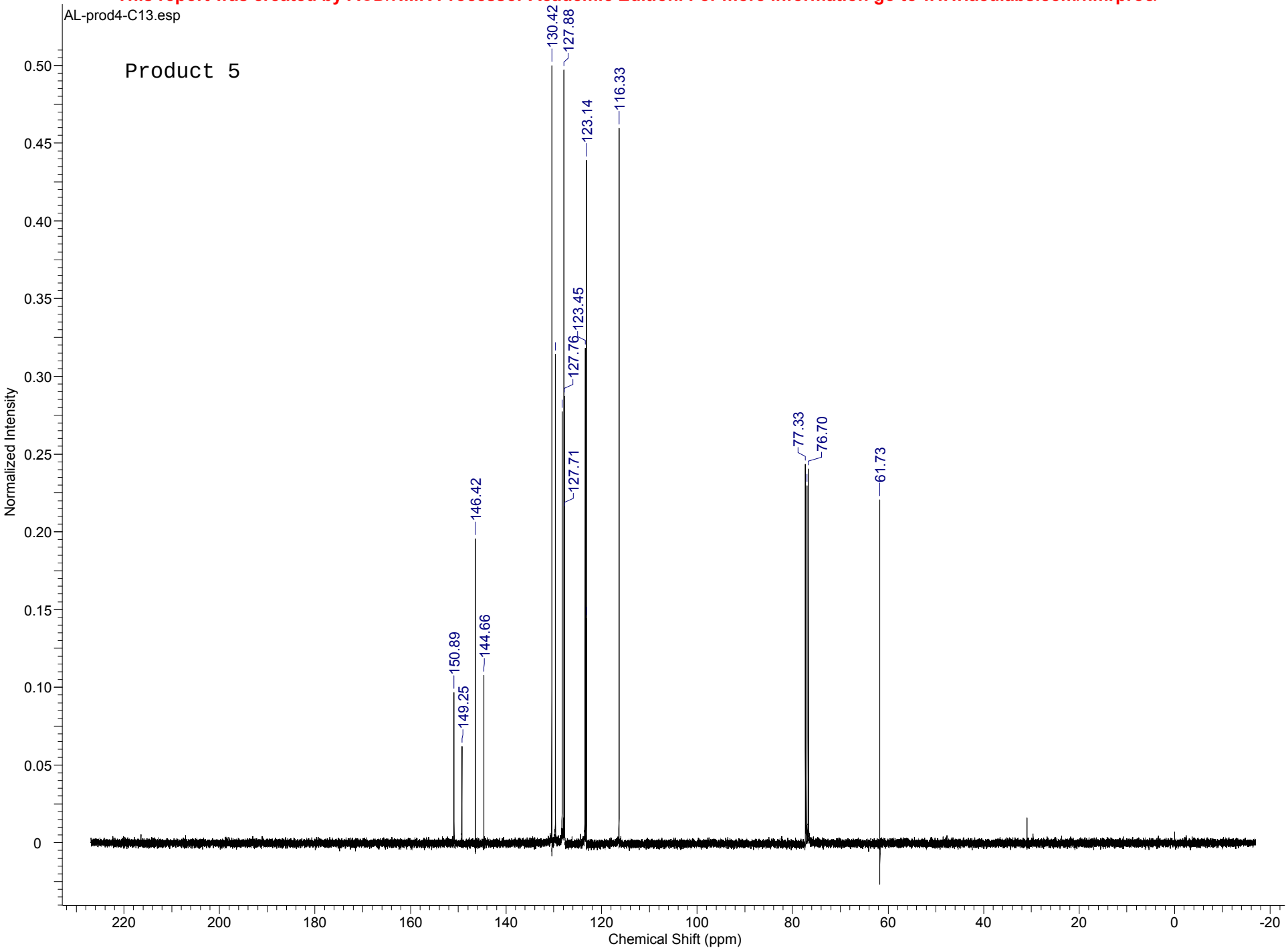


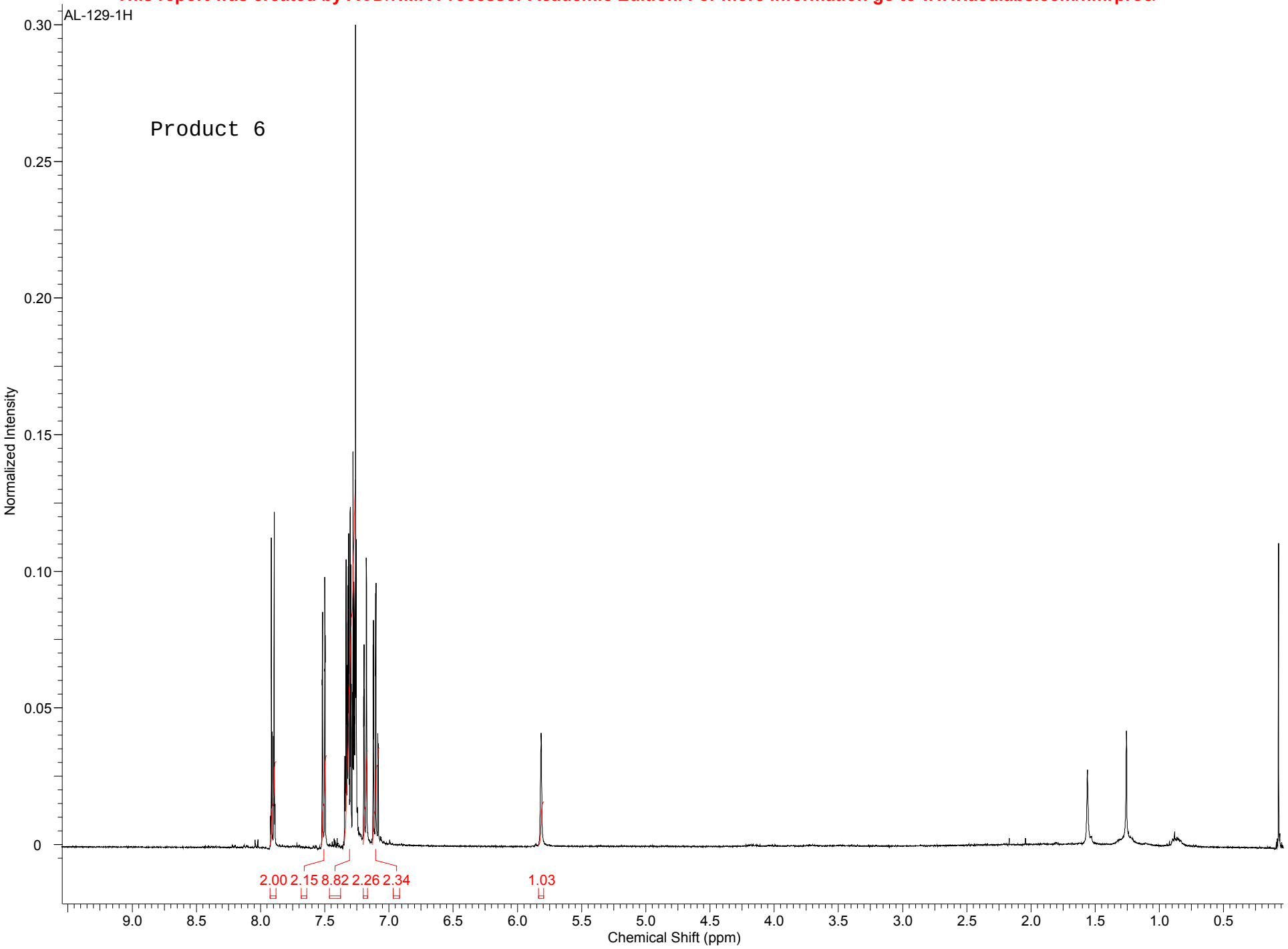


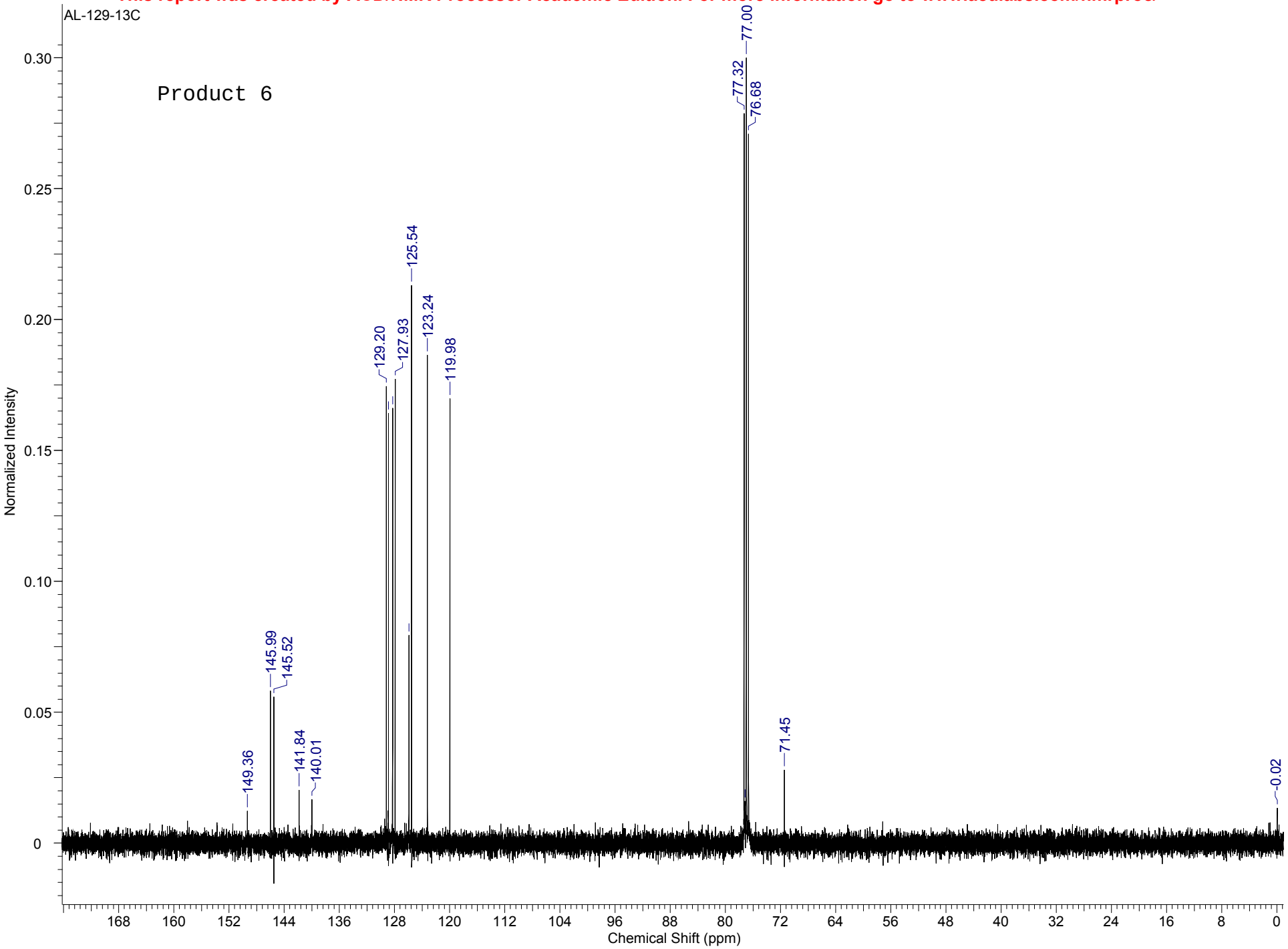


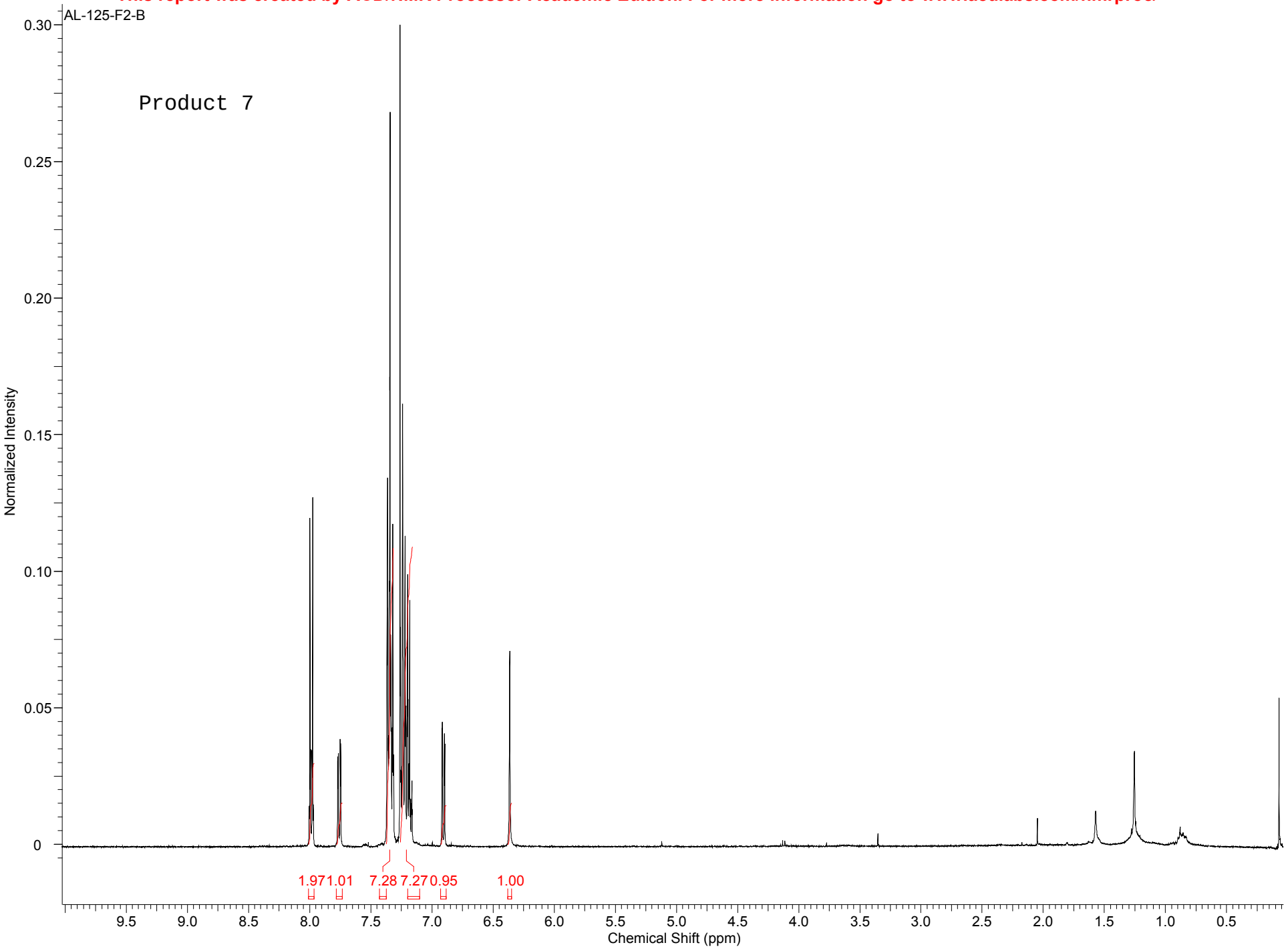


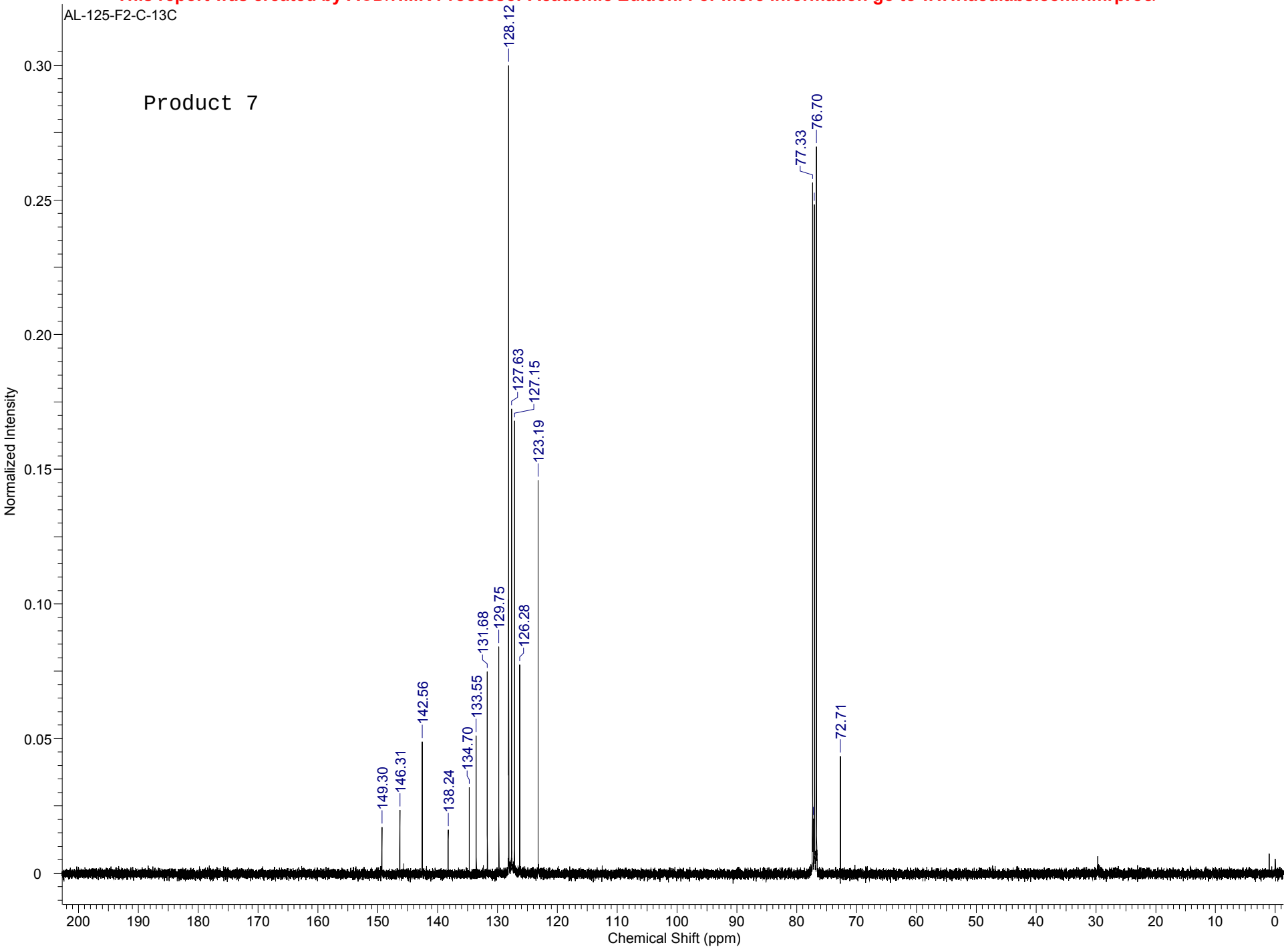


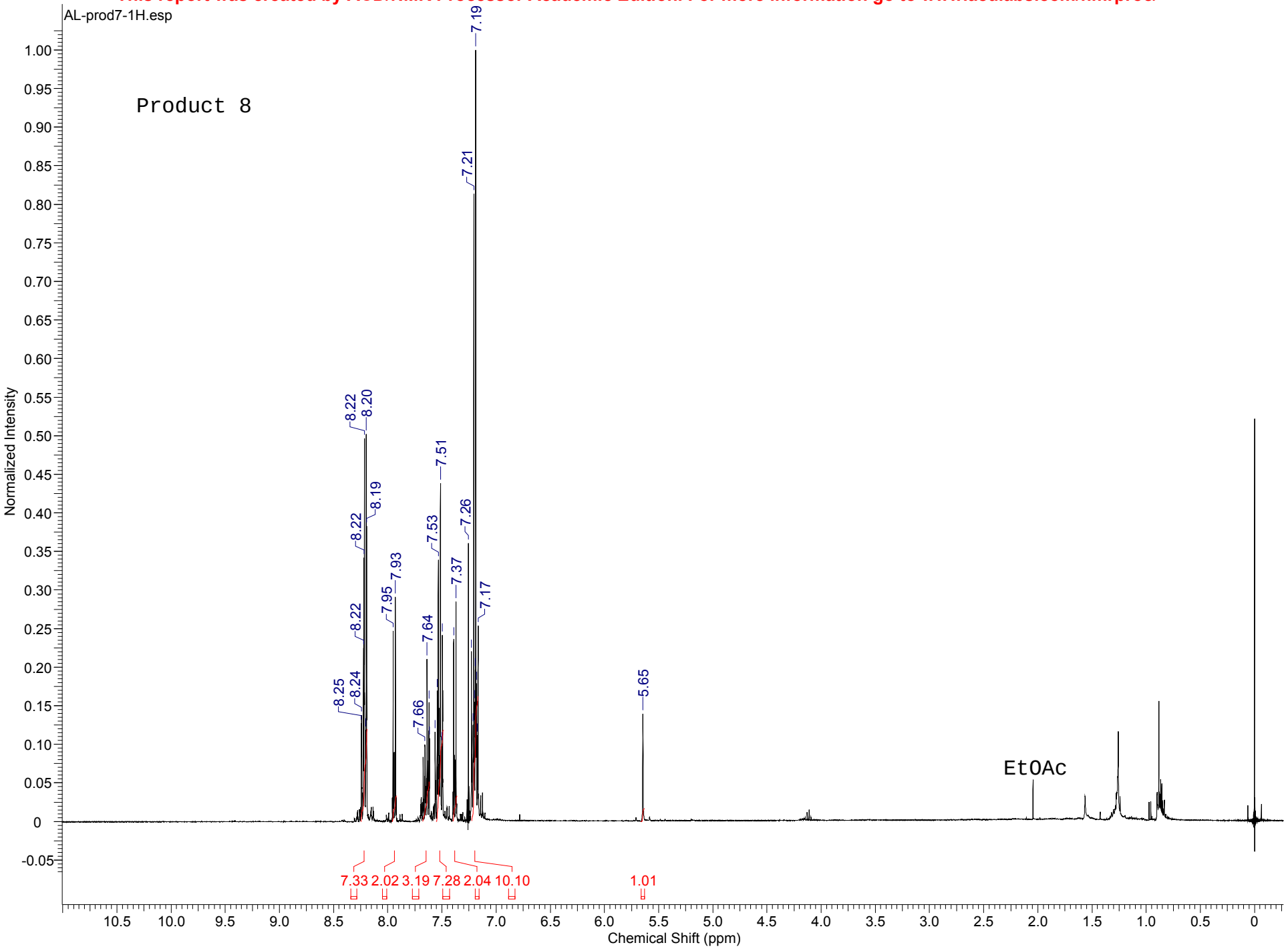


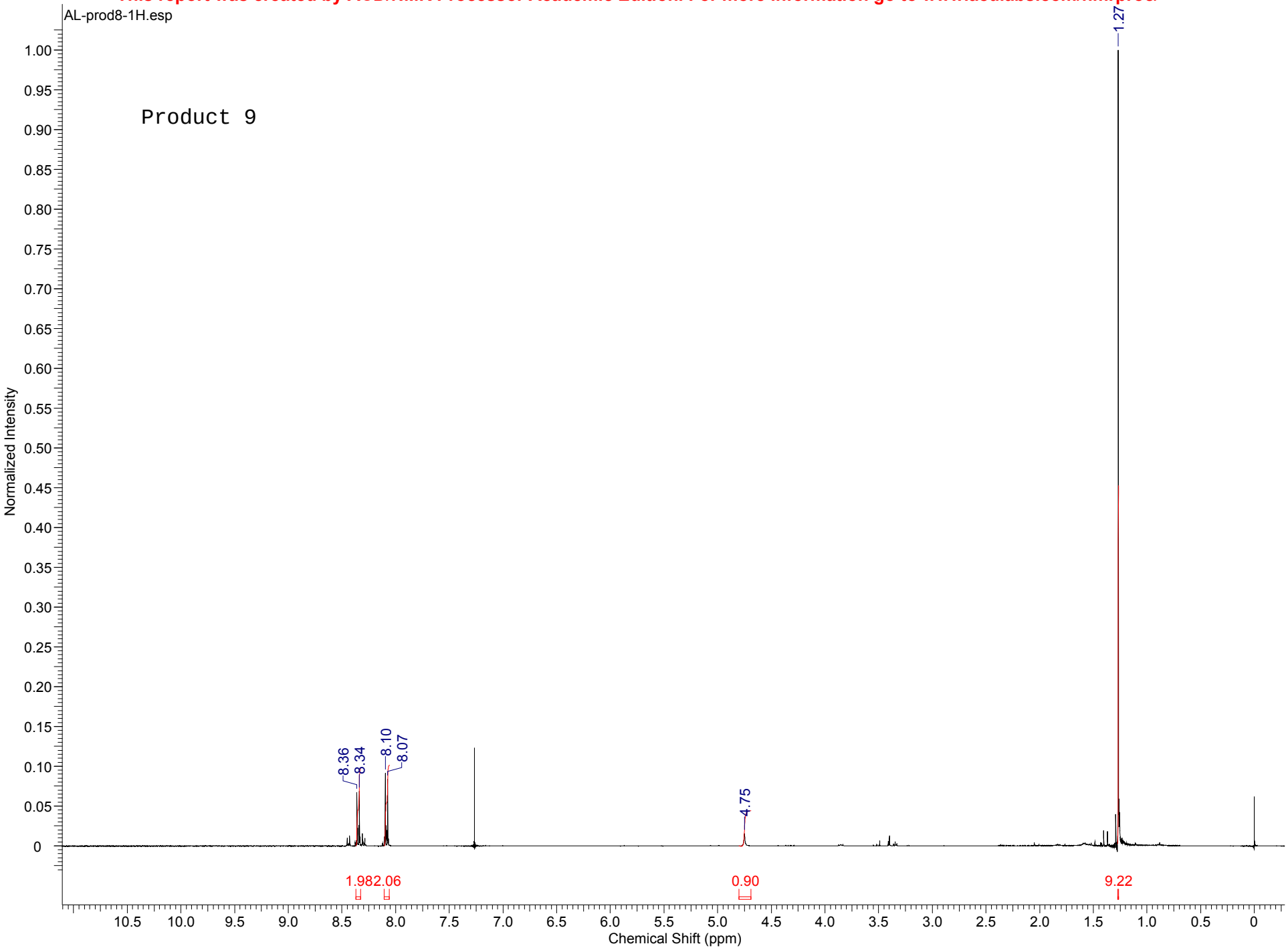


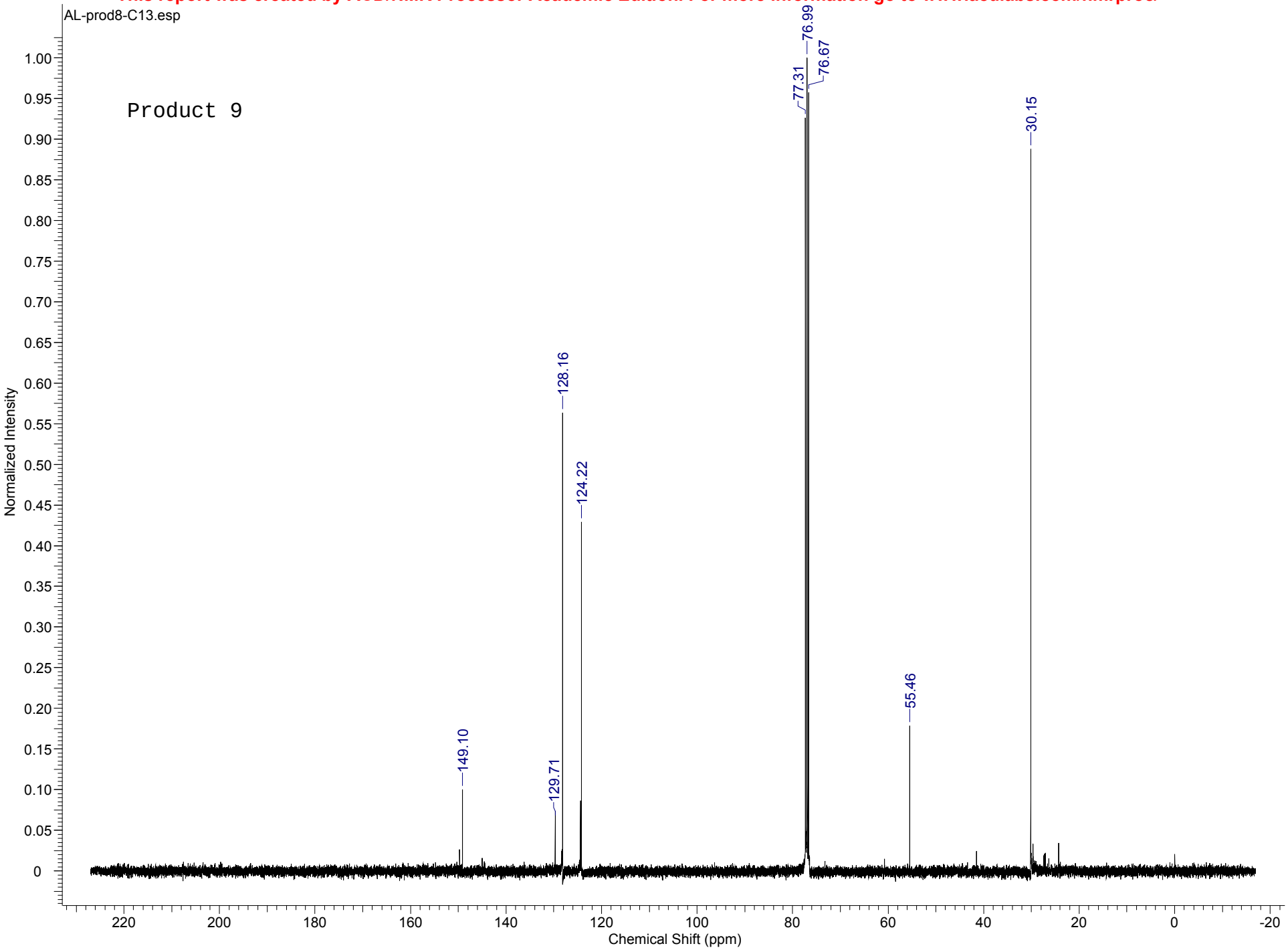












Product 9 and 10 mixture