Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Materials

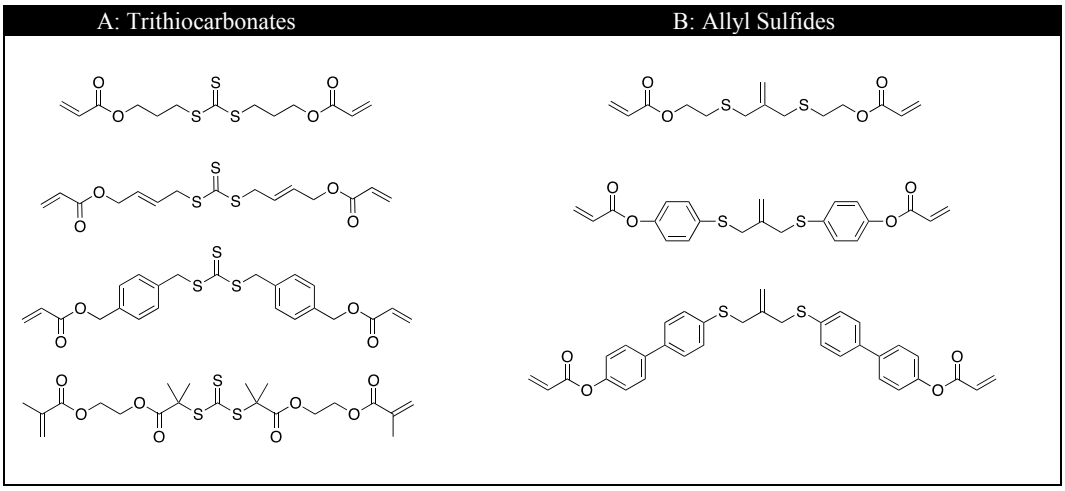


Figure1: CRAFT monomers synthesized in this study

Compound 1: To a solution of dry DMF (100 mL = 1M solution concentration) under N_2 and degassed for 30 minutes was added potassium carbonate (14.5 g, 105 mmol) and carbon disulfide (8.37 g, 110 mmol). The reaction was stirred vigorously for 15 minutes. The solution turned a deep blood-red color. To the solution was added 3-(tert-butyl) dimethyl silyl-1-bromopropane (26.5 g, 105 mmol), and the reaction turned an immediate yellow color. The reaction was heated to 40 C for 24 hours. The reaction showed 40% conversion by NMR analysis. To the reaction was added another 0.5 eq of carbon disulfide. The reaction was monitored by NMR, and over time small portions of CS_2 and K_2CO_3 were added until the reaction was complete by NMR. A total of 2.5 eq of carbon disulfide and 1.5 eq of potassium carbonate were added to the reaction. The reaction was quenched with 250 mL of water and taken up in ethyl acetate (500 mL). The organic layer was washed with water (250 mL x 3) and brine (250 mL). The organic layer was dried over sodium sulfate, filtered, and reduced in vacuo to yield crude yellow oil. The oil was purified by flash chromatography in a gradient fashion 100% hexanes to 99:1 hexanes/ethyl acetate to yield 22.18 g of pure product. Yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.69 (t, J = 8 Hz, 4H), 3.45 (t, J = 8 Hz, 4H), 1.91 (p, J = 8 Hz, 4H), 0.90 (s, 18H), 0.06 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 224.63 (C=S), 61.62 (C4), 33.62 (C2), 31.23 (C3), 26.08 (C7), 18.45 (C6), 5.19 (C5); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{19}H_{42}O_2S_3Si_2$, 477.2; found, 477.2.

Compound 2: To a solution of the silyl-protected alkyl trithiocarbonate (22.18 g, 48.75 mmol) in THF (487 mL = 0.1M) at 0 C under N_2 was added AcOH (6.44 g, 2.2 eq) and TBAF (107 mL, 107 mmol). The reaction was allowed to warm up to RT overnight. After 24 hrs, the reaction was reduced in vacuo, and the organic layer was taken up in 500 mL of ethyl acetate. The organic layer was washed with water (250 mL x 3) and brine (250 mL). The organic layer was dried over sodium sulfate, filtered, and reduced in vacuo to yield a crude yellow oil. The oil was purified by flash chromatography in a gradient fashion 40%:60% ethyl acetate/hexanes to 60:40 ethyl acetate/hexanes to afford 7.12 g of a pure yellow oil. Yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.70 (t, J = 8 Hz, 4H), 3.48 (t, J = 8 Hz, 4H), 2.28 (s, OH, 2H), 1.94 (p, J = 8 Hz, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 225.25 (C=S), 61.04 (C4), 33.43 (C2), 31.19 (C3); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_7H_{14}O_2S_3$, 249.0; found, 249.0.

Compound 3: To a solution of Compound 2 (5.0 g, 22.1 mmol) in THF (220 mL) was added triphenylphosphine (20.27 g, 77.3 mmol) and acrylic acid (5.3 mL, 3.5 eq). The solution was cooled to 0 C and placed under N_2. To the reaction was added 40% DEAD (35.21 mL, 3.5 eq) dropwise. After 1 hour, the reaction was warmed to 25 C and allowed to stir 16 hours. The reaction was diluted with hexanes and cooled to 0 C to precipitate the triphenylphosphine oxide bi-product. The reaction was filtered and reduced in vacuo to a crude yellow oil. The oil was purified by flash chromatography in a gradient fashion using 100% hexanes to 85:15 hexanes/ethyl acetate to afford 6.52 g of the product. Yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.42 (dd, 2H), 6.13 (dd, 2H), 5.85 (dd, 2H), 4.24 (t, J = 8 Hz, 4H; CH_2), 3.46 (t, J = 8 Hz, 4H; CH_2), 2.09 (p, J = 8 Hz, 4H, CH_2); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 223.47 (C=S), 166.15 (C5), 131.18 (C7), 128.36 (C6), 63.04 (C4), 33.33 (C2), 27.66 (C3); UV-vis (methanol): λ_{max} (ε) = 430nm (27000); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{13}H_{18}O_4S_3$, 357.0; found, 357.0.

Compound 4: The following molecule was synthesized from either 4-bromocrotonoate or methyl trans-4-bromo-2-butenoate. To 4-bromocrotonoate (25 g, 139.66 mmol) in a solution of diethyl ether (500 mL) at -78 C under N_2 was added 1M DIBAL-H in hexanes (350 mL, 2.5 eq). The DIBAL-H was added through an addition funnel dropwise over 3-4 hrs. The reaction was warmed to 0 C, and the reaction was stirred for an additional hour before being quenched with 40 mL of AcOH. The reaction was warmed to RT and filtered over celite. The product was reduced in vacuo, and the crude yellow oil (appr. 22 g) was carried forward immediately to be TBDMS protected due to the instability of the intermediate.

To a solution of the 4-bromo-2-butenol (22 g, 145.69 mmol) and imidazole (19.84 g, 291.39 mmol) in DCM (730 mL) at 0^0C under N_2 was added TBDMSCl (32.93 g, 1.5 eq) in 3 portions over 30 minutes. The reaction was allowed to warm up to room temperature overnight. After 12 hours, the reaction was complete by TLC. The reaction was filtered, washed with 1N HCl (1 x 100 mL), water (2 x 100 mL), brine (1 x 200 mL), and dried over sodium sulfate. The organic layer was filtered and reduced in vacuo to yield 32.4 g of a crude material. The crude was purified by FC using 100% hexanes to yield 23 g of the desired product. Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.89 (m, 2H), 4.21 (m, 2H), 3.98 (dt, 2H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 134.63 (C3), 125.78 (C2), 62.57 (C4), 32.36 (C1), 25.91 (C7), 18.36 (C6), 5.26 (C5); MS (ESI, m/z): $[M + H]^+$ calcd for $C_{10}H_{21}BrO_2Si$, 265.1; found, 265.1.

Compound 5: To a solution of silyl-protected bromo-alkene (26.84 g, 101.2 mmol) in N,N-dimethylacetamide (200 mL) was added carbon disulfide (15.42 g, 202.4 eq) and potassium carbonate (27.96 g, 202.4 mmol). The reaction was placed under inert atmosphere and heated to 40 C for 24 hours. The reaction was cooled to 25 C and quenched with water. The aqueous layer was extracted with methylene chloride. The organic layer was washed with water, brine, and dried over sodium sulfate. The organic layer was reduced in vacuo to a crude yellow oil. The oil was purified by flash chromatography 95:5 hexanes/ethyl acetate to yield 8.12g of the silyl protected alkene trithiocarbonate. Yield 34%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.79 (m, 4H), 4.15 (m, 4H), 4.03 (m, 4H), 0.90 (s, 18H), 0.06 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 222.87 (C=S), 135.09 (C4), 122.57 (C3), 63.17 (C5), 38.88 (C2), 26.08 (C8), 18.54 (C7), 5.07 (C6); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{21}H_{42}O_2S_3Si_2$, 501.2; found, 501.2.

Compound 6: To a solution of the compound 5 (8.12 g, 16.98 mmol) in THF (200 mL) at 0 C under N_2 was added AcOH (3.0 mL, 50.94 mmol) and TBAF (43 mL, 42.5 mmol). The reaction was allowed to warm up to RT overnight. After 16 hrs, the reaction was reduced in vacuo to yield a crude yellow oil. The oil was purified by flash chromatography in a gradient fashion 40% : 60% ethyl acetate/hexanes to 60:40 ethyl acetate/hexanes to afford 3.8 g of a pure yellow oil. Yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.93 (m, 2H), 5.77 (m, 2H), 4.14 (m, 4H), 4.05 (dq, 4H), 1.39 (d, OH, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 222.38 (C=S), 134.55 (C4), 124.39 (C3), 63.0 (C5), 38.59 (C2); MS (ESI, m/z): $[M + Li]^+$ calcd for $C_9H_{14}O_2S_3$, 257.0; found, 257.0.

Compound 7: To a solution of compound 6 (5.0 g, 19.96 mmol) in THF (220 mL) degassed under N_2 at 0 C was added triphenylphosphine (18.33 g, 70 eq) and acrylic acid (5.03 g, 70 mmol). To the reaction was added DEAD 40% in toluene (32 mL, 70 mmol) dropwise over 30 minutes. The reaction was allowed to warm to RT and stir overnight. The triphenylphosphine oxide salts were precipitated out with hexanes. The oil was purified by flash chromatography using 10:90 ethyl acetate/hexanes to yield 2.25 g of the trans-trans isomer. Yield 33%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.42 (dd, 2H), 6.12 (dd, 2H), 5.86 (m, 6H), 4.63 (m, 4H, CH_2), 4.05 (dt, 4H, CH_2); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 221.94 (C=S), 165.88 (C6), 131.26 (C8), 129.26 (C7), 128.31 (C4), 127.51 (C3), 64.15 (C5), 38.43 (C2); UV-vis (methanol): λ_{max} (ε) = 420nm (34000); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{15}H_{18}O_4S_3$, 381.0; found, 381.0.

Compound 8: The following molecule was synthesized from 4-(chloromethyl) benzyl alcohol (15 g, 96 mmol) in a solution of DCM (500 mL), where as the concentration of the solution was 0.19M, at O C under N_2 was added imidazole (16.31g, 239 mmol). The reaction was allowed to stir for 15 minutes. To the reaction was added TBDMSCl (18.76 g, 125 mmol). The solution was allowed to warm to room temperature overnight. After 16 hours, the reaction was filtered. The organic layer was washed with 1N HCL (100 mL), DI Water (100 mL x 3), and brine (100 mL). The organic layer was dried over sodium sulfate and filtered. The product was reduced in vacuo, and the crude clear oil was purified by flash chromatography using 100% hexanes to yield 23.12 g of pure product. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.34 (m, 4H), 4.75 (s, 2H), 4.59 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 141.99 (Ar-C5), 136.20 (Ar-C2), 128.66 (Ar-C3), 126.46 (Ar-C4) 64.75 (C6), 46.34 (C1), 26.10 (C9), 18.57 (C8), 5.11 (C7); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{14}H_{23}ClOSi$, 293.1; found, 293.1.

Compound 9: To a solution of dry Acetonitrile (100 mL = 1M solution concentration) under N_2 and degassed for 30 minutes was added potassium carbonate (11.8 g, 85.3 mmol) and carbon disulfide (6.82 g, 89.6 mmol). The reaction was stirred vigorously for 15 minutes. To the solution was added (23.12 g, 85.3 mmol), and the reaction turned an immediate yellow color. The reaction was heated to 40 C and allowed to react for 48 hours. The reaction showed complete conversion by NMR analysis. The reaction was reduced in vacuo to yield a pure yellow solid. The yield of the reaction was quantitative in yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.30 (m, 8H, Ar-H), 4.73 (s, 4H), 4.62 (s, 4H), 0.96 (s, 18H), 0.11 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 222.95 (C=S), 141.26 (Ar-C6), 133.49 (Ar-C3), 129.27 (Ar-C4), 126.46 (Ar-C5), 64.73 (C7), 41.49 (C2), 26.08 (C10), 18.53 (C9), 5.13 (C8); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{29}H_{46}O_2S_3Si$, 601.2; found, 601.2.

Compound 10: To a solution of the benzyl trithiocarbonate (22.1 g, 38.2 mmol) in DCM (550 mL) at 0 C under N_2 was added AcOH (8.03 g, 3.5 eq) and TBAF (114 mL, 114 mmol). The reaction was allowed to warm up to RT overnight. After 24 hrs, the reaction was ceased. The organic layer was washed with water (250 mL x 2), 1N HCL, and brine (250 mL). The organic layer was dried over sodium sulfate, filtered, and reduced in vacuo to yield a crude yellow solid. The solid was purified by flash chromatography in a gradient fashion 30%:70% ethyl acetate/hexanes to 100% ethyl acetate to afford 9.65 g of a pure yellow solid. Yield 72%. ^{1}H NMR (400 MHz, DMSO-d6, δ): 7.30 (m, 8H, Ar-H), 5.18 (t, OH, 2H), 4.65 (s, 4H), 4.47 (d, 4H); ^{13}C NMR (400 MHz, DMSO-d6, δ): 222.55 (C=S), 142.14 (C6), 133.27 (C3), 129.01 (C4), 126.769 (C5), 62.59 (C7), 40.40 (C2); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{17}H_{18}O_2S_3$, 373.1; found, 373.1.

Compound 11: To a solution of CRF-2-15 (5.0 g, 14.3 mmol) in THF (160 mL) degassed under N_2 was added triphenylphosphine (13.1 g, 49.9 mmol) and acrylic acid (3.6 g, 49.9 mmol). The reaction was cooled to 0 C and DEAD 40% in toluene (22.73 mL, 49.9 mmol) was added dropwise. After an hour the reaction was warmed to room temperature and stirred for 24 hours. The reaction was diluted with hexanes to precipitate the triphenylphosphine oxide by-product and was filtered. The crude solid was purified by flash chromatography using 80:20 ethyl acetate/hexanes to yield 6.51 g of a yellow waxy solid. Yield 99%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.32 (m, 8H, Ar-H), 6.44 (dd, 2H), 6.15 (dd, 2H), 5.84 (dd, 2H), 5.17 (s, 4H), 4.60 (s, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 222.28 (C=S), 165.96 (C=O), 135.52 (C3), 135.16 (C6), 131.27(C10), 129.50 (C4), 128.59 (C5), 128.22 (C9), 65.90 (C7), 41.11(C2); UV-vis (methanol): λ_{max} (ε) = 430nm (45401); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{23}H_{22}O_4S_3$, 481.1; found, 481.1.

Comopund 12: Synthesis of 4-methoxy-4'-methylthiobiphenyl

The intermediate was synthesized by Kumada coupling of 4-bromothioanisole and 4-iodoanisole. A Grignard solution was prepared by adding Mg turnings (2.87 g, 118.2 mmol) and catalytic I_2 to 4-Bromothioanisole (20.0 g, 98.5 mmol) under N_2. The solution was gently refluxed in 200 mL of THF until only trace Mg metal was present in the reaction mixture. The solution was cooled and placed into an addition funnel under N_2.

To a solution of 4-iodoanisole (23.05 g, 98.5 mmol) and palladium triphenylphosphine tetrakis (1.14 g, 0.98 mmol) in 200 mL of refluxing THF under N_2 was added the above Grignard solution dropwise. After one hour the addition was complete and Mg salts began to crash out of the reaction solution. The solution was refluxed for an additional hour and then cooled to RT. The reaction was poured into a solution of ice and 1N HCL. The solution immediately became cloudy and a precipitate formed. The precipitate was filtered, washed with water, and dried in vacuo. The crude material was recrystallized from 1:1 Hexane/IPA to yield 16.52 g of pure compounds. Yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.51 (m, 4H, Ar-H), 7.33 (m, 2H, Ar-H), 6.99 (m, 2H, Ar-H), 3.86 (s, 3H, OCH_3), 2.53 (s, 3H, SCH_3); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 159.21 (C2), 137.82 (C6), 136.82 (C5), 133.14 (C9), 127.93 (C8), 127.21 (C4), 127.15 (C7), 114.35 (C3), 55.43 (C1), 16.141 (C10); MS (ESI, m/z): $[M + Li]^+$ calcd for $C_{14}H_{14}OS$, 231.1; found, 231.1.

Compound 13: Synthesis of 4-hydroxy-4'-mercaptobiphenyl

To a solution of 4-methoxy-4'methylthiobiphenyl (16.0 g, 69.5 mmol) in 275 mL DMF under N_2 was added sodium thiosulfate (14.6 g, 2.5eq). The solution was heated to a gentle reflux overnight. The solution was quenched with a solution of ice water with 50 mL of 1N HCl. The crude solid was filtered, dried, and recrystallized from 1:1: hexanes/IPA to yield 11.52g of product. 81.9% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 (m, 4H, Ar-CH), 7.32 (m, 2H, Ar-CH), 6.88 (m, 2H, Ar-CH), 2.50 (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 157.6 (C1), 138.9 (C5), 138.4 (C4), 133.7 (C8), 130.3 (C7), 128.7 (C3), 127.7 (C6), 114.3 (C2), 55.4 (C9), 16.1 (C10); MS (ESI, m/z): $[M-H]^-$ calcd for $C_{12}H_{10}OS$, 201.0; found, 201.0.

Compound 14: Synthesis of the Biphenyl Allyl Sulfide

To a solution of MeOH at 0 C under N_2 was added Na metal (1.03 g, 45 mmol). The reaction was slowly allowed to warm to room temperature. 4-hydroxy-4'mercaptobiphenyl (8.0 g, 40 mmol) was added to the reaction, and the reaction was heated to reflux. 3-chloro-2-chloromethyl propene (2.25 g, 18 mmol) was added dropwise over an hour, and the reaction was allowed to reflux overnight. The solution was reduced in vacuo and purified by flash chromatography 20:80 acetone/hexanes to yield 3.92 g of the pure allyl sulfide. Yield 47.7%. ^{1}H NMR (400 MHz, DMSO-d6, δ): 9.56 (s, 2H, Ar-OH), 7.46 (m, 8H, Ar-H), 7.33 (m, 4H, Ar-H), 6.82 (m, 4H, Ar-H), 5.06 (s, 2H, C=CH_2), 3.8 (s, 4H); ^{13}C NMR (400 MHz, DMSO-d6, δ): 157.13 (C1), 139.57 (C10), 137.92 (C5), 133.15 (C8), 129.97 (C4), 129.52 (C7), 127.43 (C3), 126.24 (C6), 116.55 (C11), 115.71 (C2) 36.89 (C9); MS (ESI, m/z): $[M-H]^-$ calcd for $C_{28}H_{24}O_2S_2$, 455.1; found, 455.1.

Compound 15: Synthesis of the Biphenyl Allyl Sulfide Diacrylate

To a solution of the Biphenyl Allyl Sulphide (3.5 g, 7.67 mmol) in 77 mL of THF at 0 C under N_2 was added triethylamine (2.67 mL, 2.5 eq). The solution was stirred for 5 minutes and then acryloyl chloride (1.55 mL, 2.5 eq) was added dropwise. The solution was allowed to warm to room temperature and stir overnight. The solution was filtered and reduced in vacuo to a crude solid. The solid was purified by flash chromatography to yield 1.82 g. Yield 42%. ^{1}H NMR (400 MHz, Acetone d-6, δ): 7.66 (m, 4H, Ar-H), 7.58 (m, 2H, Ar-H), 7.43 (m, 2H, Ar-H), 7.24 (m, 2H, Ar-H), 6.57 (dd, 2H), 6.39 (dd, 2H), 6.10 (dd, 2H), 5.12 (s, 2H), 3.88 (s, 4H); ^{13}C NMR (400 MHz, Acetone d-6, δ): 165.05 (C3), 151.47 (C4), 141.16 (C13), 138.91 (C8), 138.80 (C7), 136.49 (C11), 133.29 (C1), 130.91 (C10), 129.04 (C2), 128.65 (C6), 128.28 (C9), 123.20 (C5), 117.39 (C14), 38.48 (C12); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{34}H_{28}O_4S_2$, 587.10; found, 587.10.

Compound 16: Synthesis of MBH

The allyl sulfides were synthesized following a modified procedure from literature **[9]**. To a 1L flask at 0 C was added 600 mL of methanol. The solution was kept under 30 C as Na metal (19 g, 0.83 mol) was added in small portions. After all the sodium had reacted, 2-mercaptoethanol (57.8 g, 2.2 eq) was added to the solution of sodium methoxide. The solution was heated to reflux and 3-chloro-2-chloromethyl-1-propene (42 g, 1 eq) was added dropwise over 1 hour. The solution was allowed to reflux overnight. The solution was cooled to 25 C, filtered, and reduced in vacuo to remove the methanol. The crude material was taken up in 500 mL's of water and extracted with ether (4 x 150 mL). The ether layer was washed with brine and dried over sodium sulfate. The organic layer was reduced in vacuo. The crude light-yellow oil was purified by vacuum distillation to yield 65 g of the MBH. Yield 92.3%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.00 (s, 2H), 3.68 (t, 4H), 3.29 (s, 4H), 2.67 (s, OH, 2H), 2.61 (t, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 140.31 (C=CH_2), 116.14 (C5), 60.31 (C1), 34.85 (C3), 33.55 (C2).

Compound 17: Synthesis of MBTMA

To MBH (50 g, 1 eq) under N_2 at 0 C was added freshly distilled methylene chloride and triethylamine (53.42 g, 2.2 eq). After 30 minutes of degassing with N_2, acryloyl chloride (40 mL, 47.78 g, 2.2 eq) was added dropwise over 3 hours. The reaction was warmed to 25 C and allowed to stir overnight. The organic layer was washed with water, brine, and dried over magnesium sulfate. The organic layer was filtered and reduced in vacuo to a brownish-yellow crude oil. The oil was purified by flash chromatography 70:30 hexanes/ethyl acetate to yield an off-colored oil 46 g. Yield 60.5%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.40 (dd, 2H), 6.10 (dd, 2H), 5.83 (dd, 2H), 5.04 (s, 2H), 4.26 (t, 4H), 3.32 (s, 4H), 2.67 (t, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 166.03 (C=O), 140.40 (C7), 131.39 (C1), 128.35 (C2), 116.85 (C8), 63.33 (C4), 35.47 (C6), 29.41 (C7).

Compound 18: Synthesis of Phenyl Allyl Sulfide

To a 1L flask at 0 C was added 160 mL of methanol. The solution was kept under 30 C as Na metal (5.10 g, 221.24 mmol) was added in small portions. After all the sodium had reacted, 4-hydroxythiophenol (25.0 g, 2.2 eq) was added to the solution of sodium methoxide. The solution was heated to reflux and 3-chloro-2-chloromethyl-1-propene (11.26 g, 1 eq) was added dropwise over 1 hour. The solution was allowed to reflux overnight. The solution was cooled to 25C, filtered, and reduced in vacuo to remove the methanol. The crude material was taken up in 500 mL of water and extracted with ether (4 x 150 mL). The ether layer was washed with 1N HCl, water, brine, and dried over sodium sulfate. The organic layer was reduced in vacuo to a crude orange oil. The oil was purified by flash chromatography 90:10 hexanes/ethyl acetate to yield 23.52 g of a colorless oil. Yield 85.8%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.23 (m, 4H, Ar-H), 6.74 (m, 4H, Ar-H), 5.84 (s, 2H, Ar-OH), 4.70 (s, 2H, C=CH_2), 3.57 (s, 4H, CH_2); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 155.3 (C1), 140.45 (C10), 138.6 (C5),

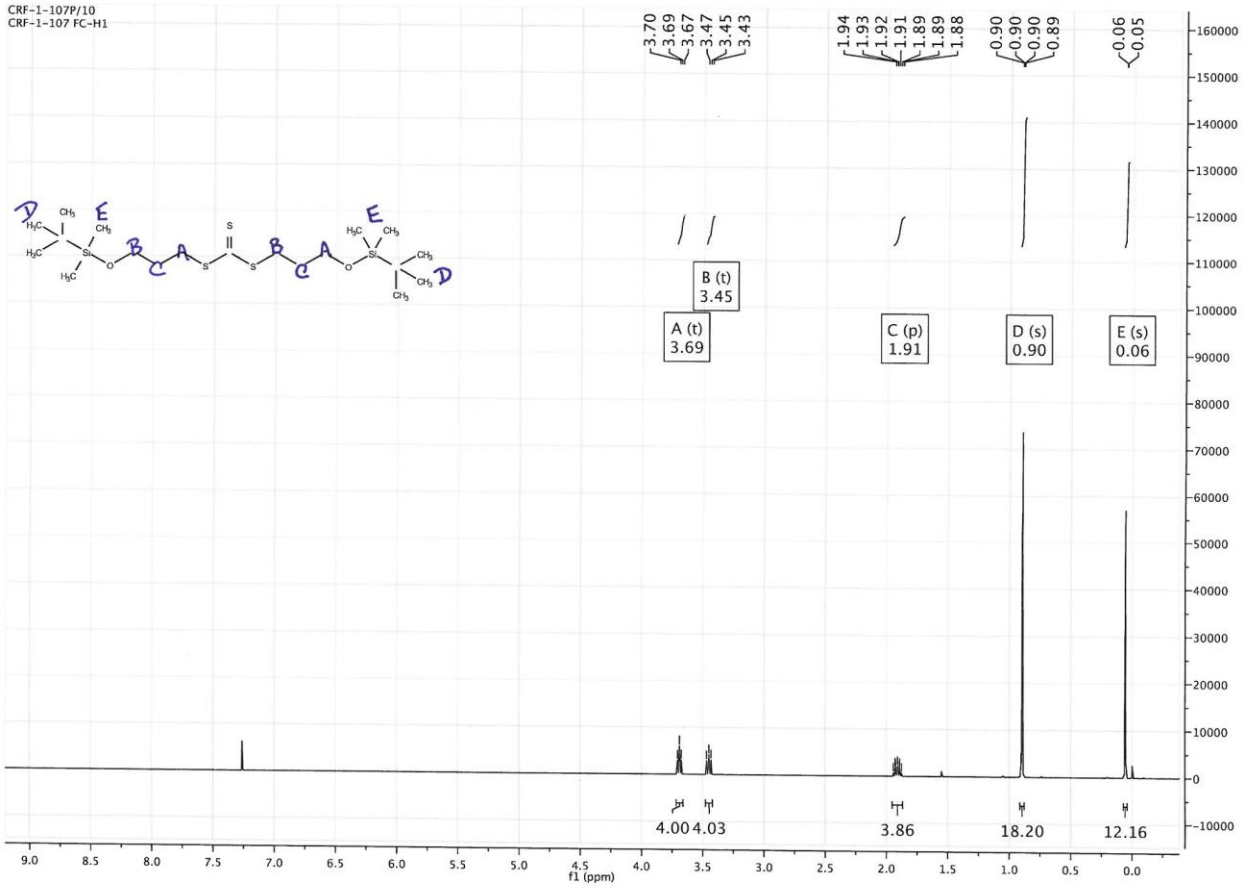
134.3 (C8), 132.7 (C4), 126.0 (C7), 116.5 (C3), 116.0 (C6), 40.63 (C11); MS (ESI, m/z): $[M + Li]^+$ calcd for $C_{16}H_{16}O_2S_2$, 344.3; found, 344.3.

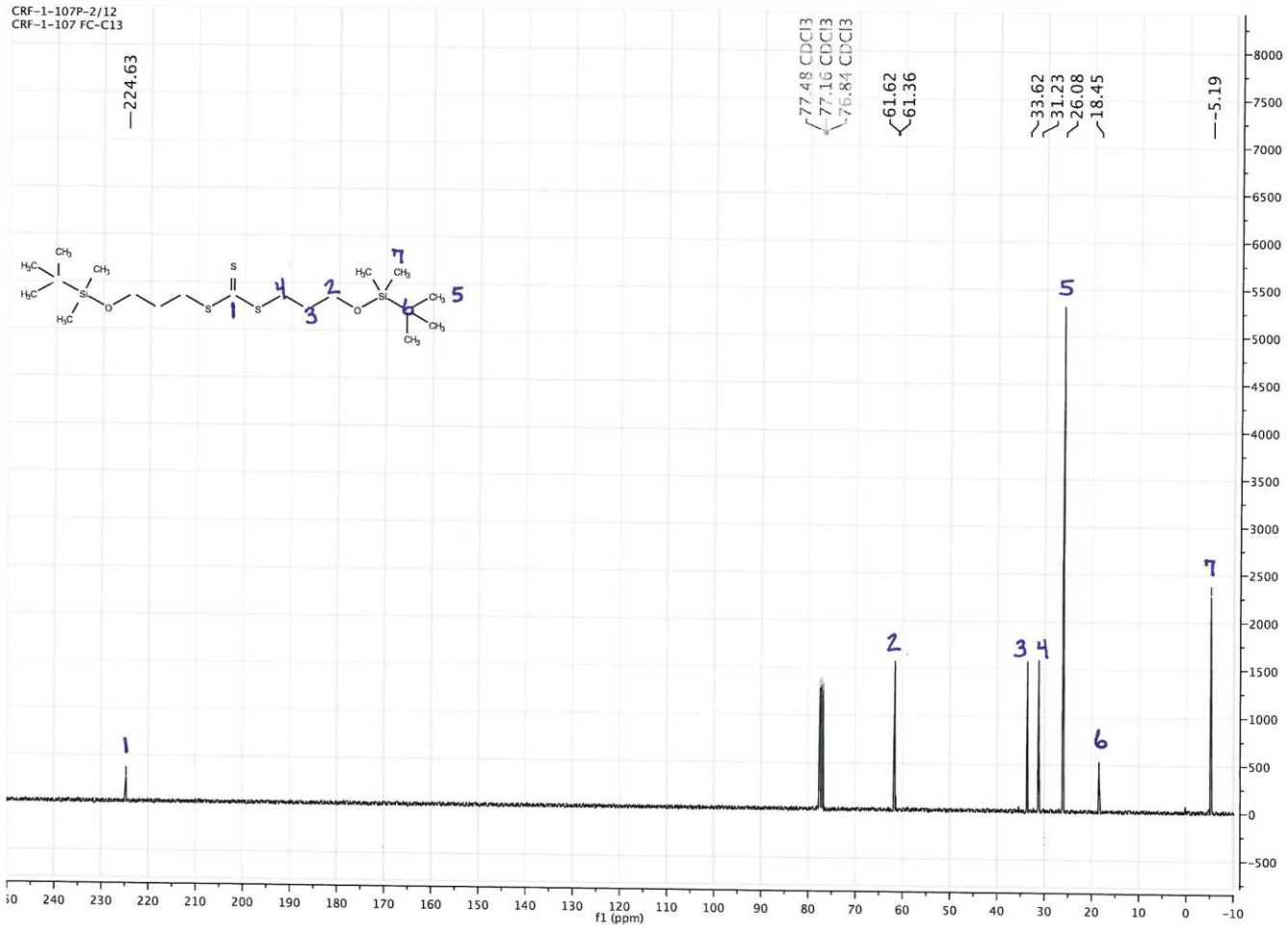
Compound 19: Phenyl Allyl Sulfide Diacrylate

To compound 18 (23.52 g, 1 eq) under N_2 at 0 C was added freshly distilled methylene chloride and triethylamine (17.2 g, 2.2 eq). After 30 minutes of degassing with N_2, acryloyl chloride (15.38 g, 2.2 eq) was added dropwise over 1 hours. The reaction was warmed to 25 C and allowed to stir overnight. The organic layer was washed with 1N HCl, sodium bicarbonate, water, brine, and dried over magnesium sulfate. The organic layer was filtered and reduced in vacuo to an orange oil. The oil was purified by flash chromatography 95:5 hexanes/ethyl acetate going to 90:10 hexanes/ethyl acetate to yield an off-colored oil 12.82 g. Yield 40.2%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.35 (m, 4H, Ar-H), 7.06 (m, 4H, Ar-H), 6.59 (dd, 2H), 6.30 (dd, 2H), 6.00 (dd, 2H), 4.91 (s, 2H), 3.69 (s, 4H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 164.29 (C=O), 149.44 (C4), 139.65 (C9), 133.02 (C1), 132.72 (C6), 131.75 (C2), 127.82 (C5), 122.01 (C10), 39.17 (C9); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{22}H_{20}O_4S_2$, 435.04; found, 435.04.

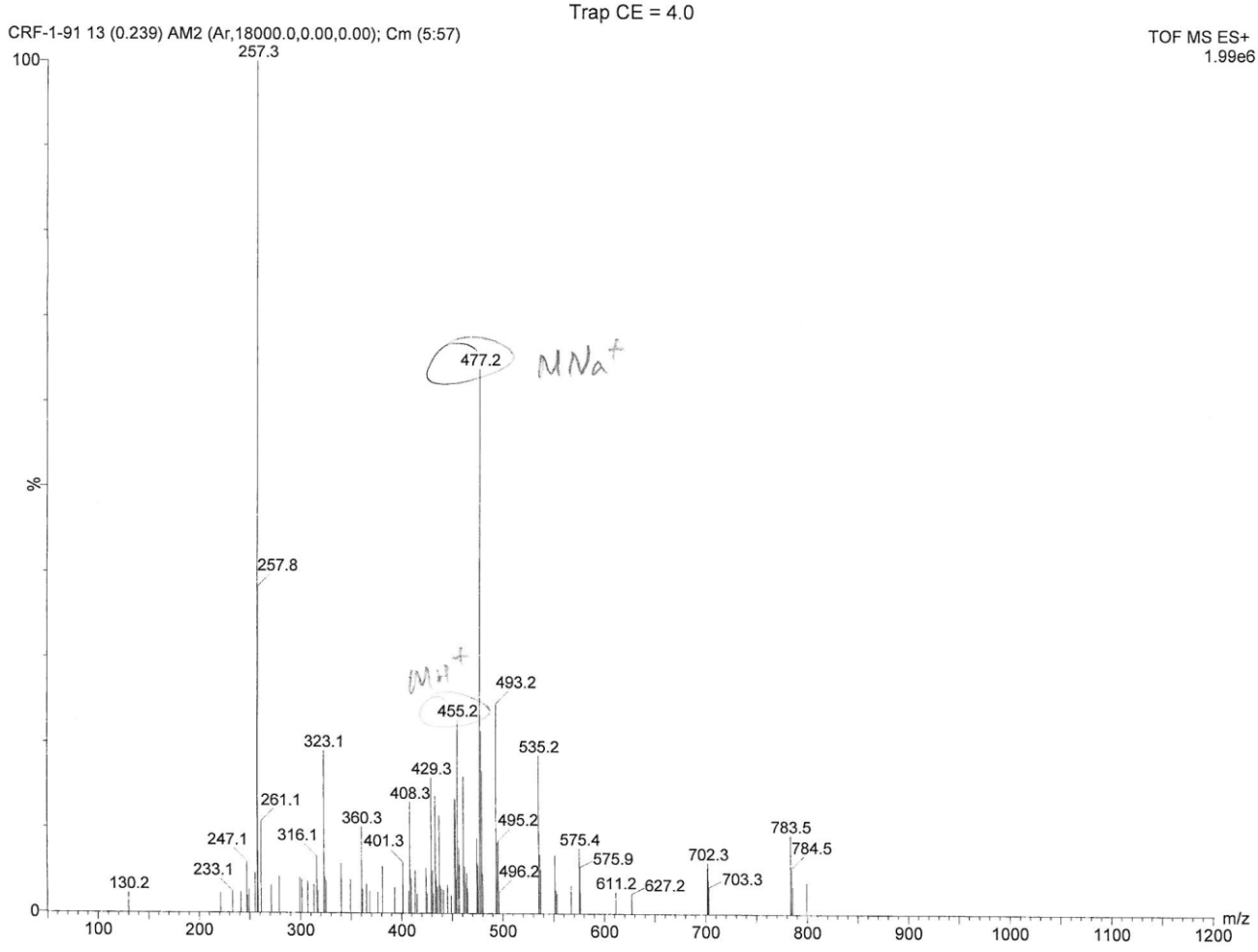
Compound 20: S,S′-bis(□,□'-dimethyl-□''-acetic acid) Trithiocarbonate Dimethacrylate

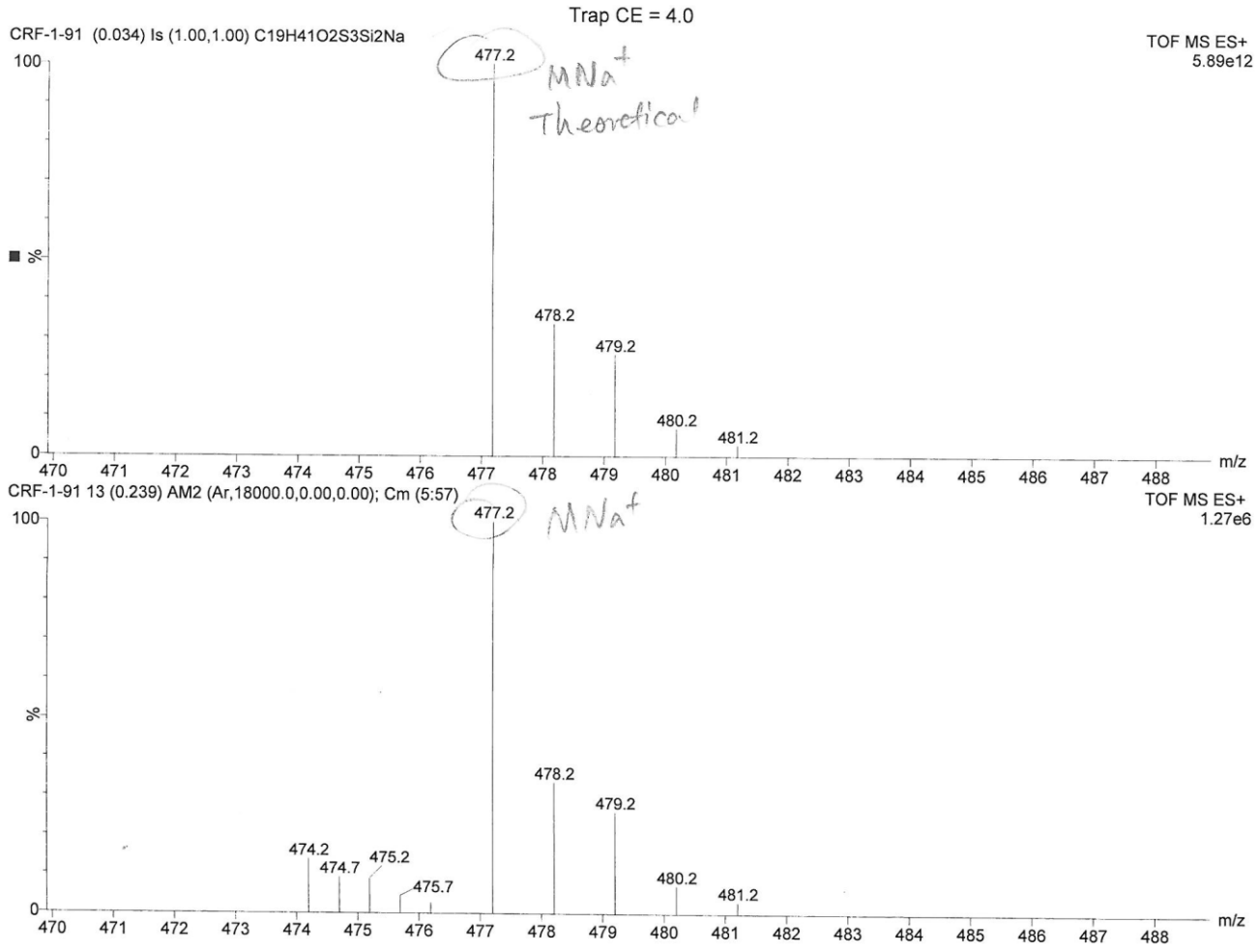
The compound was synthesized from a literature procedure [8]. The flask was charged with S,S′-bis(□,□'-dimethyl-□''-acetic acid)-trithiocarbonate (2.78 g, 9.8 mmol) and triphenylphosphine (9.03 g, 34.5 mmol) and subsequently deoxygenated by purging with nitrogen for 30 min. 2-Hydroxyethyl methacrylate (4.48 g, 34.5 mmol) and anhydrous tetrahydrofuran (110 mL) were added. The flask was immersed in an ice bath, and cooled to 0 C. A solution of diethyl azodicarboxylate (15.7 mL, 34.5 mmol) was added dropwise. The reaction was warmed to RT and stirred for 16 hours. The reaction was diluted with hexanes and the triphenylphosphine oxide salts were filtered off. The filtrate was reduced in vacuo to a crude red oil. The oil was purified by flash chromatography 90:10 hexanes/ethyl acetate to yield 2.8 g of the trithiocarbonate. Yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.11 (dd, 2H), 5.57 (dd, 2H), 4.33 (s, 8H), 1.93 (s, 6H), 1.63 (s, 12H); ^{13}C NMR (400 MHz, $CDCl_3$, δ): 218.45 (C=S), 172.41 (C7), 166.97 (C4), 135.90 (C2), 126.03 (C1), 63.49 (C6), 62.06 (C5), 56.05 (C8), 25.05 (C9), 18.25 (C3); MS (ESI, m/z): $[M + Na]^+$ calcd for $C_{21}H_{30}O_8S_3$, 529.1; found, 529.1.

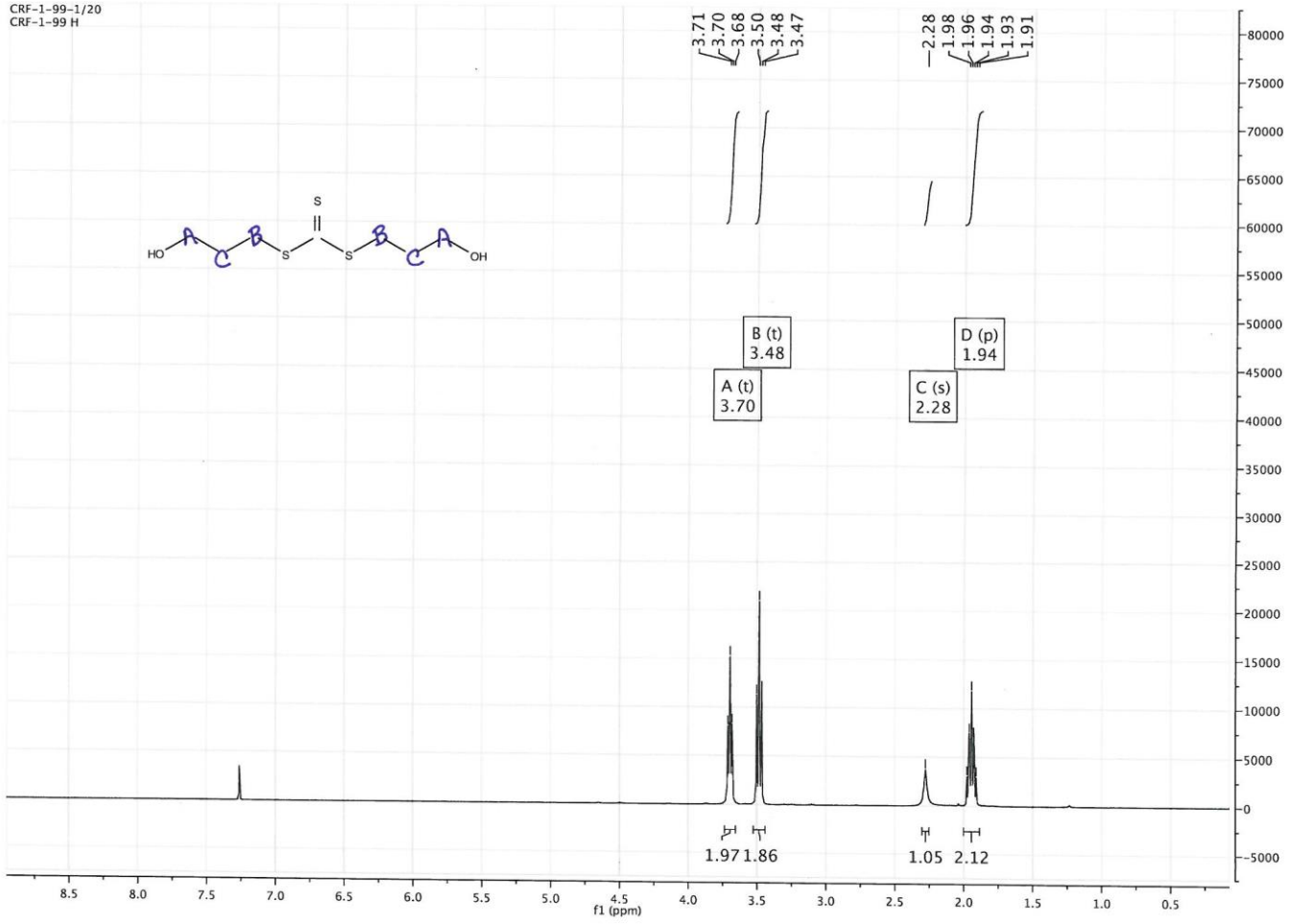

CRF-1-107P/10
CRF-1-107 FC-H1
3.70
3.69
3.67
3.47
3.45
3.43
1.94
1.93
1.92
1.91
1.89
1.89
1.88
0.90
0.90
0.90
0.89
0.06
0.05
B (t)
3.45
A (t)
3.69
C (p)
1.91
D (s)
0.90
E (s)
0.06
4.00
4.03
3.86
18.20
12.16
f1 (ppm)

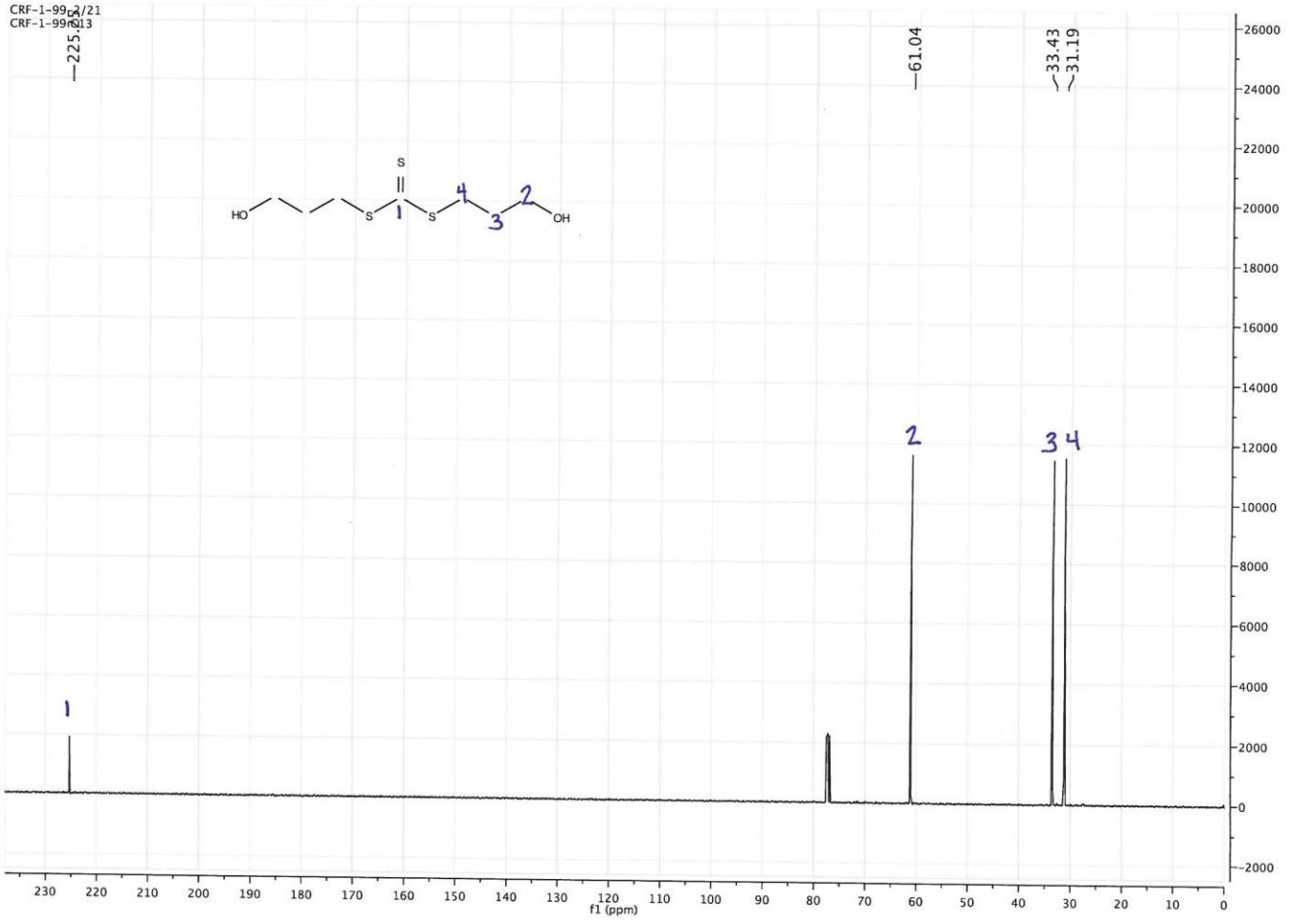

CRF-1-107P-2/12
CRF-1-107 FC-C13
224.63
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.62
61.36
33.62
31.23
26.08
18.45
5.19
1
2
3
4
5
6
7
f1 (ppm)

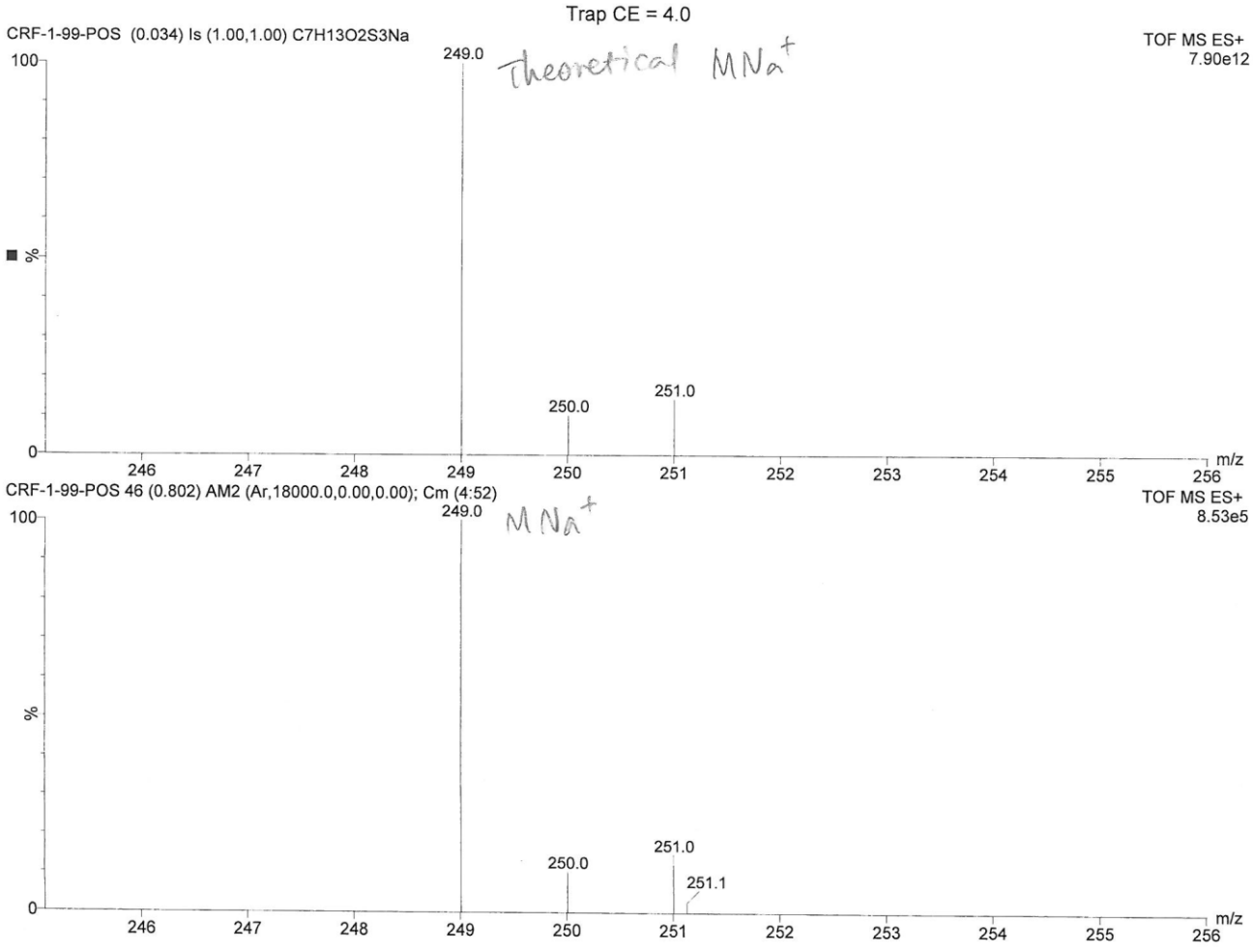
Trap CE = 4.0

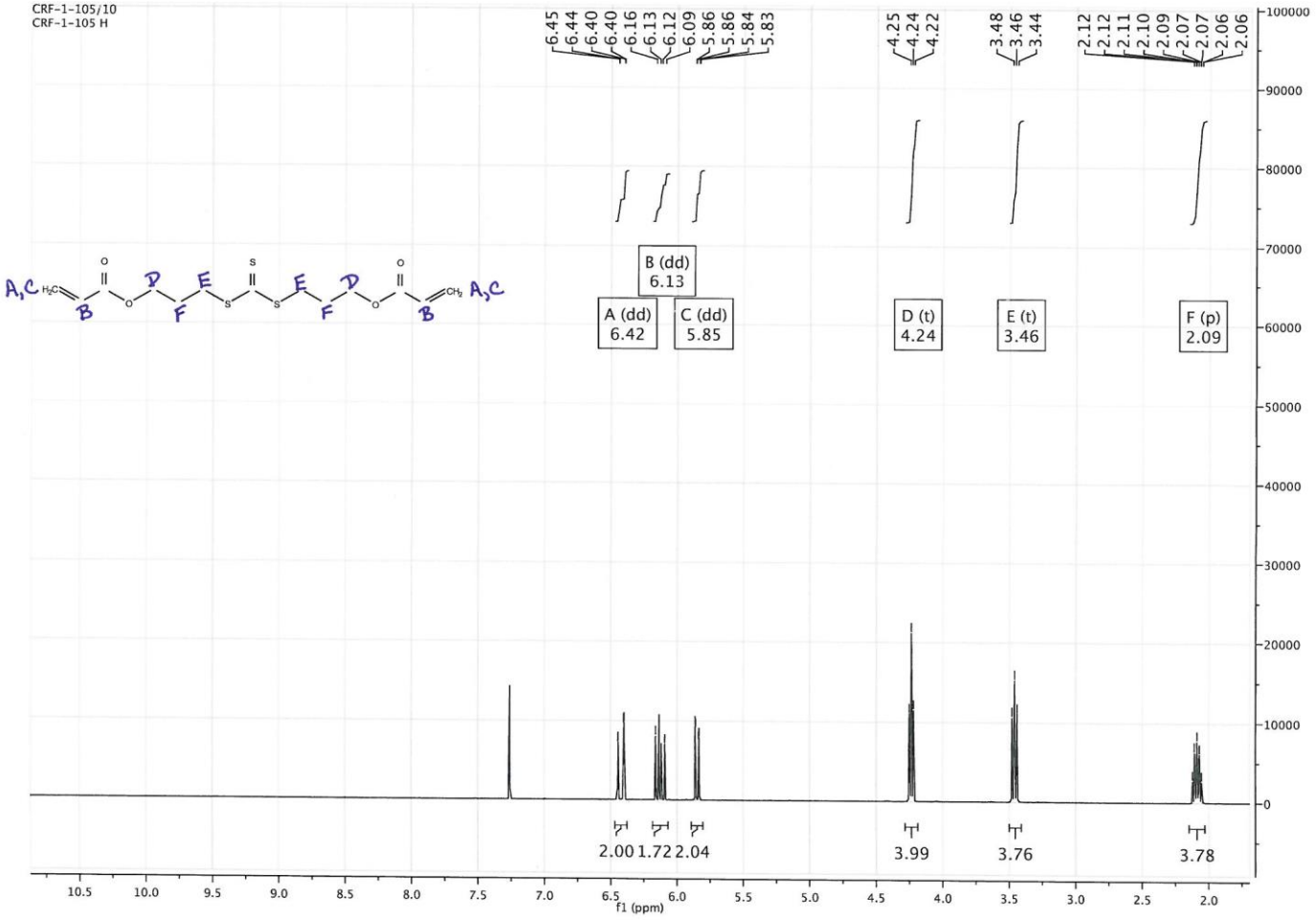

CRF-1-91 13 (0.239) AM2 (Ar,18000.0,0.00,0.00); Cm (5:57)
TOF MS ES+
1.99e6
100
%
0
257.3
477.2
MNa+
257.8
MH+
493.2
455.2
323.1
535.2
429.3
408.3
261.1
360.3
495.2
247.1
316.1
401.3
575.4
783.5
784.5
575.9
702.3
233.1
496.2
703.3
130.2
611.2
627.2
100
200
300
400
500
600
700
800
900
1000
1100
1200
m/z

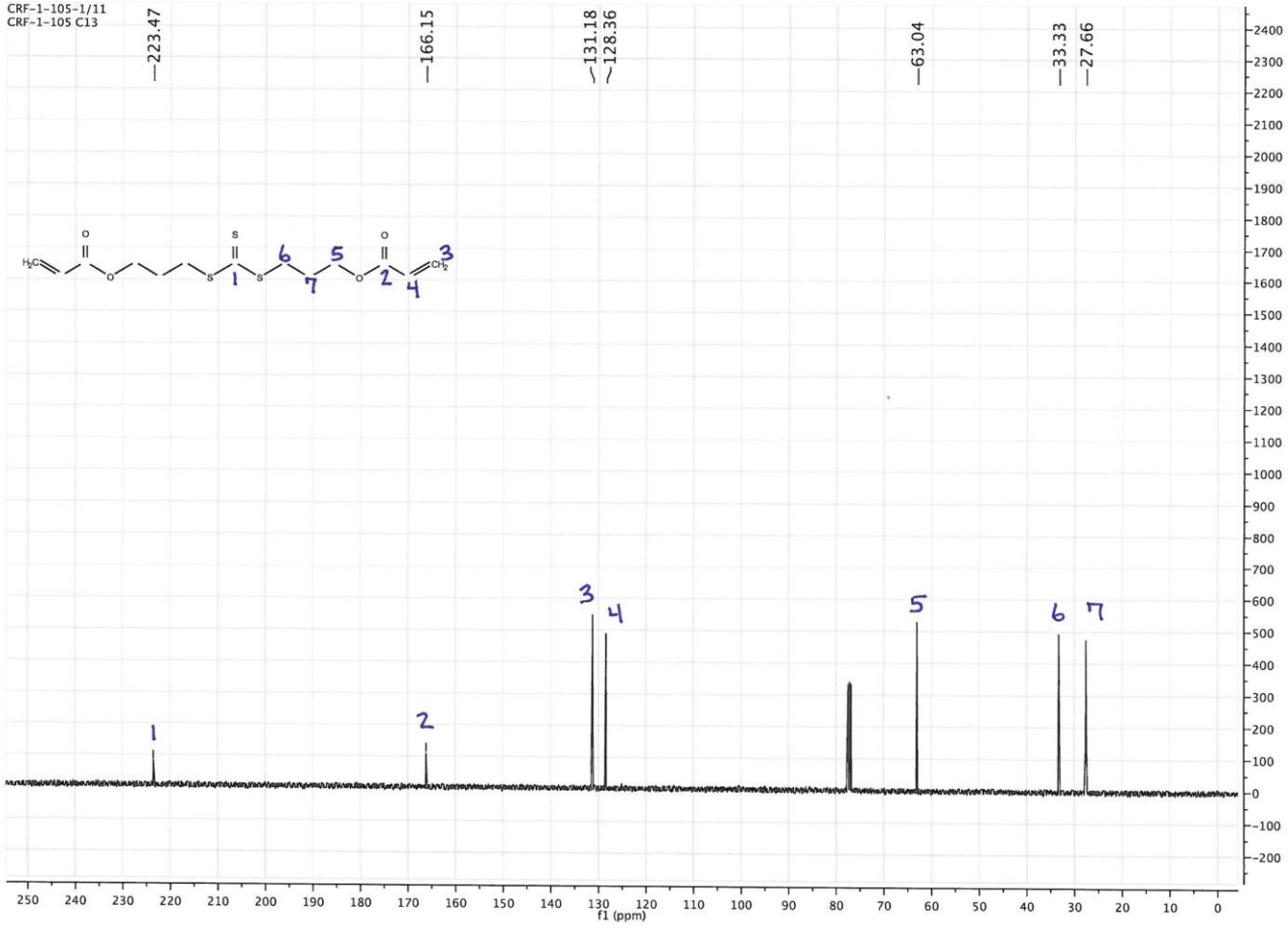

Trap CE = 4.0
CRF-1-91 (0.034) Is (1.00,1.00) C19H41O2S3Si2Na
TOF MS ES+
5.89e12
100
%
0
477.2
MNa+
Theoretical
478.2
479.2
480.2
481.2
470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488
m/z
CRF-1-91 13 (0.239) AM2 (Ar,18000.0,0.00,0.00); Cm (5:57)
TOF MS ES+
1.27e6
100
%
0
477.2
MNa+
478.2
479.2
474.2
474.7
475.2
475.7
480.2
481.2
470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488
m/z

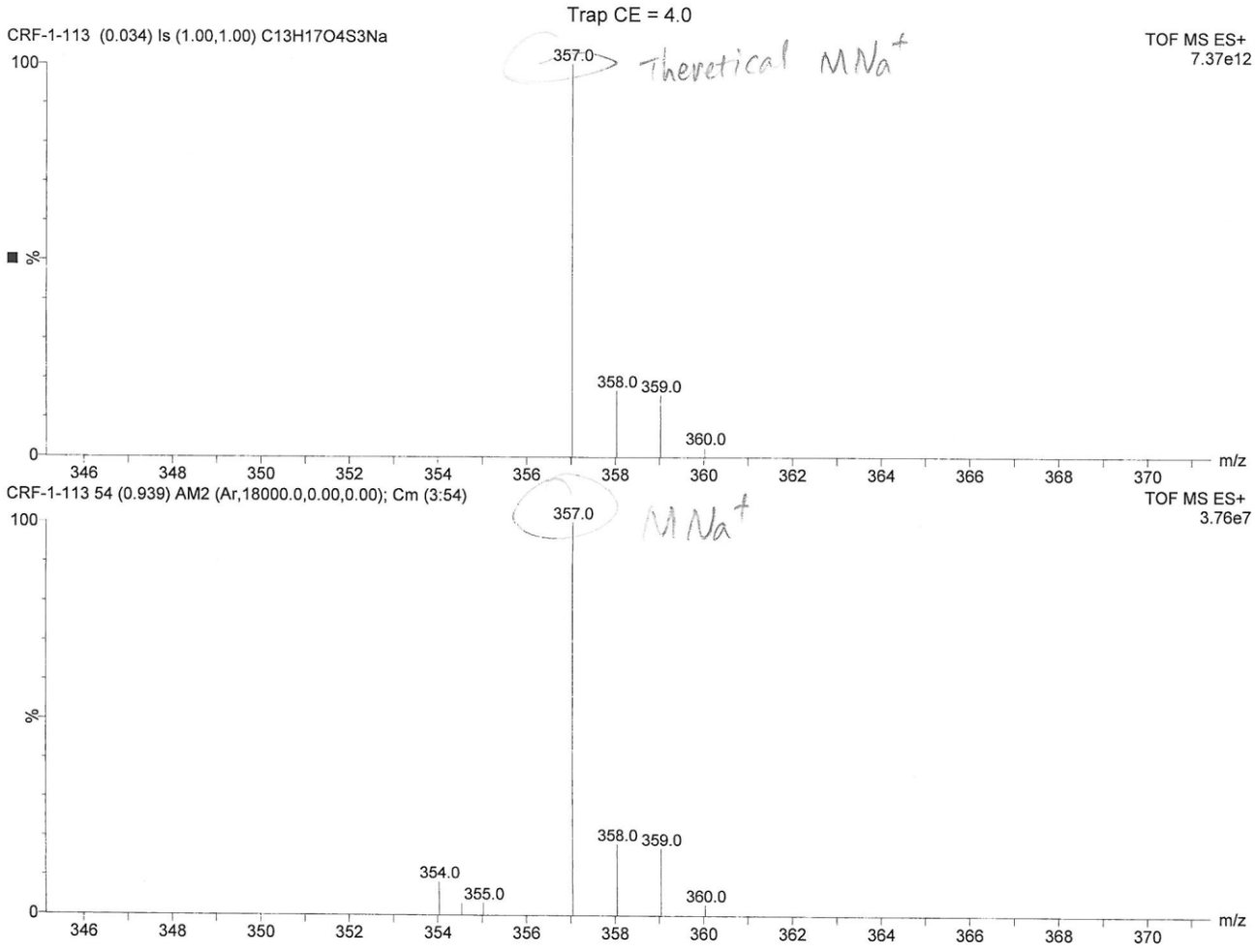

CRF-1-99-1/20
CRF-1-99 H
3.71
3.70
3.68
3.50
3.48
3.47
2.28
1.98
1.96
1.94
1.93
1.91
HO
OH
S
B (t)
3.48
A (t)
3.70
D (p)
1.94
C (s)
2.28
1.97
1.86
1.05
2.12
f1 (ppm)


CRF-1-99-2/21
CRF-1-99-C13
225.51
61.04
33.43
31.19
HO
S
S
S
OH
1
2
3
4
1
2
3 4
f1 (ppm)


Trap CE = 4.0
CRF-1-99-POS (0.034) Is (1.00,1.00) C7H13O2S3Na
TOF MS ES+
7.90e12
100
%
0
249.0
Theoretical MNa+
250.0
251.0
246
247
248
249
250
251
252
253
254
255
256
m/z
CRF-1-99-POS 46 (0.802) AM2 (Ar,18000.0,0.00,0.00); Cm (4:52)
TOF MS ES+
8.53e5
100
%
0
249.0
MNa+
250.0
251.0
251.1
246
247
248
249
250
251
252
253
254
255
256
m/z


CRF-1-105/10
CRF-1-105 H
6.45
6.44
6.40
6.40
6.16
6.13
6.12
6.09
5.86
5.86
5.84
5.83
4.25
4.24
4.22
3.48
3.46
3.44
2.12
2.12
2.11
2.10
2.09
2.07
2.07
2.06
2.06
B (dd)
6.13
A (dd)
6.42
C (dd)
5.85
D (t)
4.24
E (t)
3.46
F (p)
2.09
A,C
B
D
F
E
S
S
F
D
O
B
A,C
2.00
1.72
2.04
3.99
3.76
3.78
f1 (ppm)


CRF-1-105-1/11
CRF-1-105 C13
223.47
166.15
131.18
128.36
63.04
33.33
27.66
1
2
3
4
5
6
7
f1 (ppm)


Trap CE = 4.0
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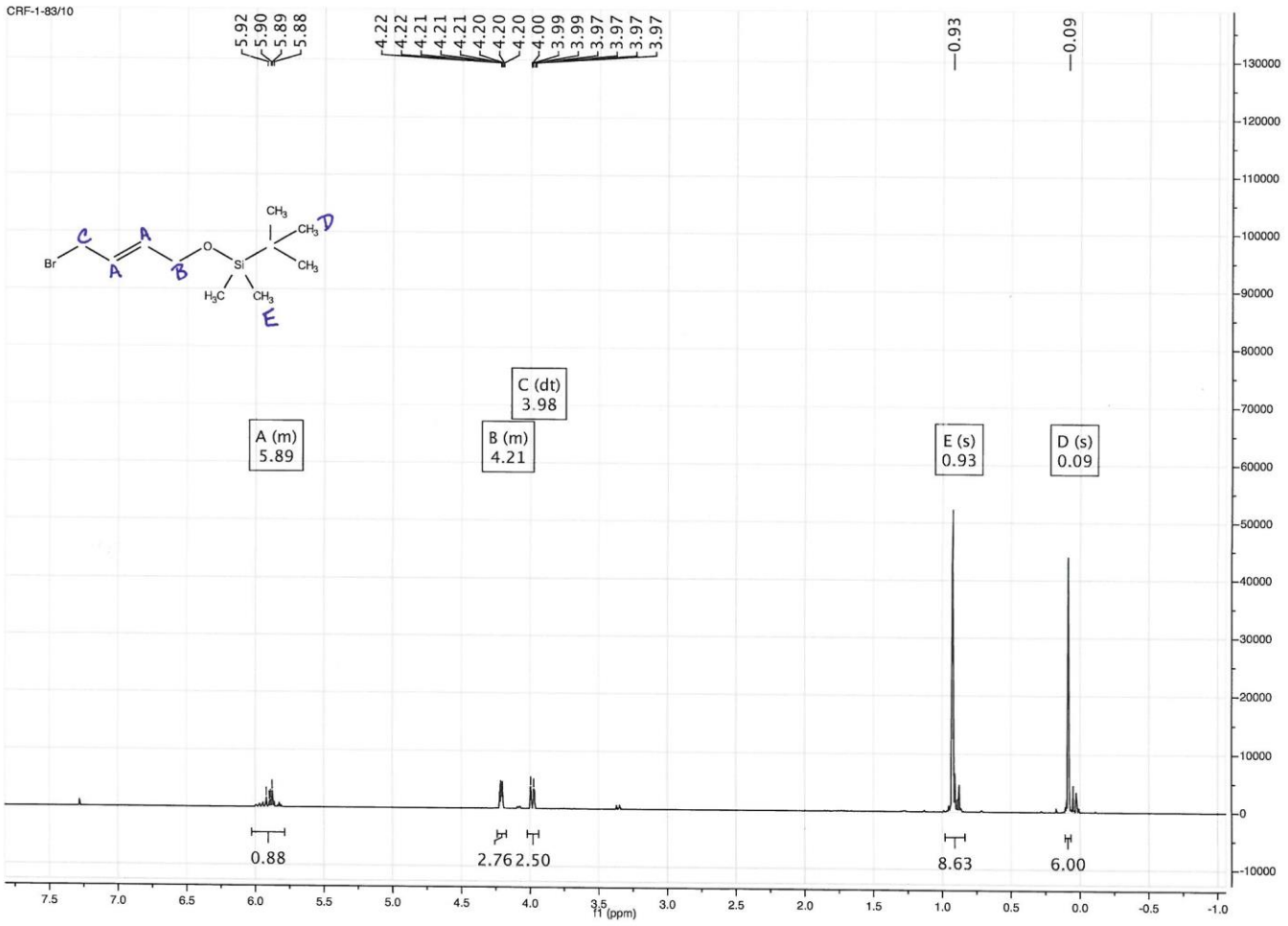
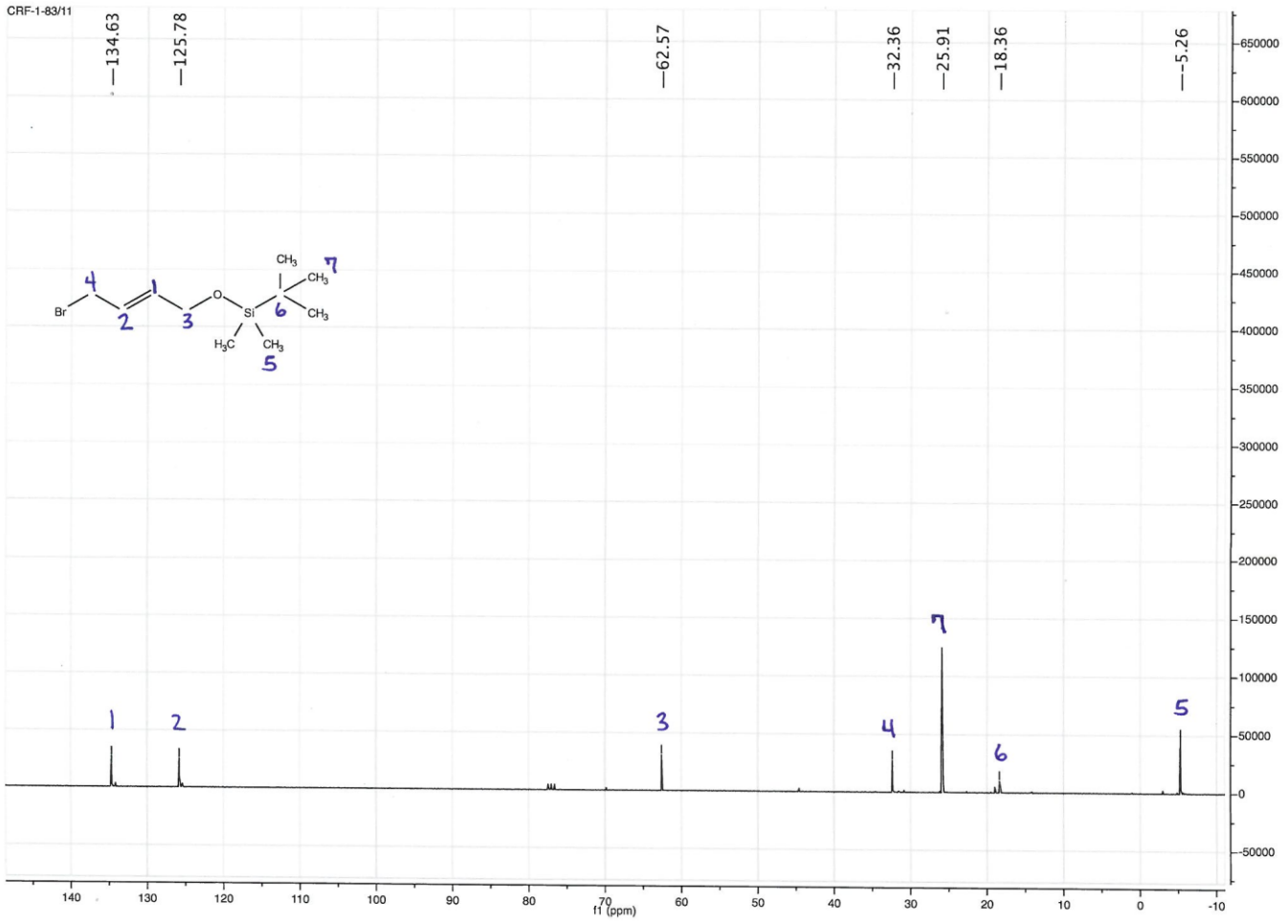
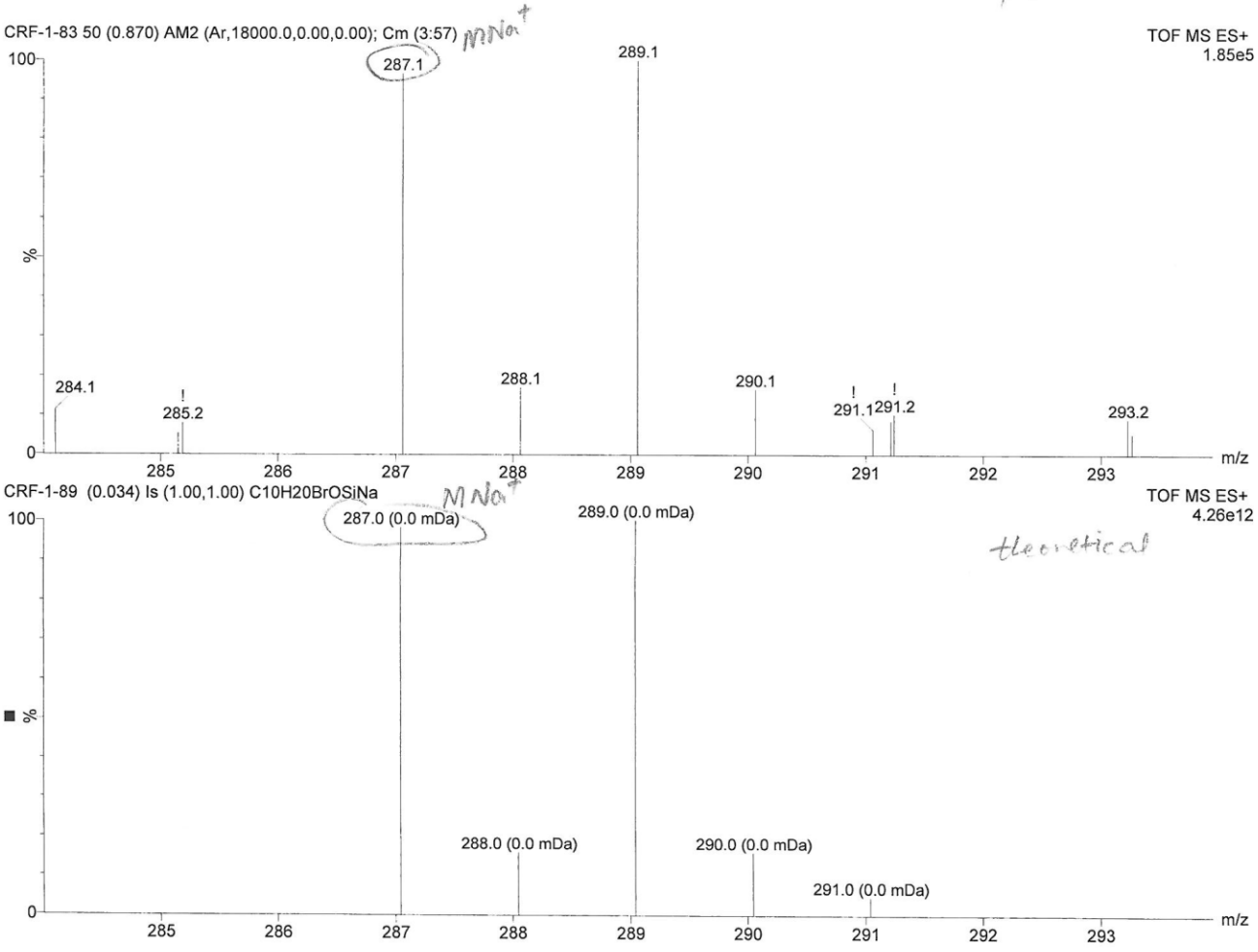
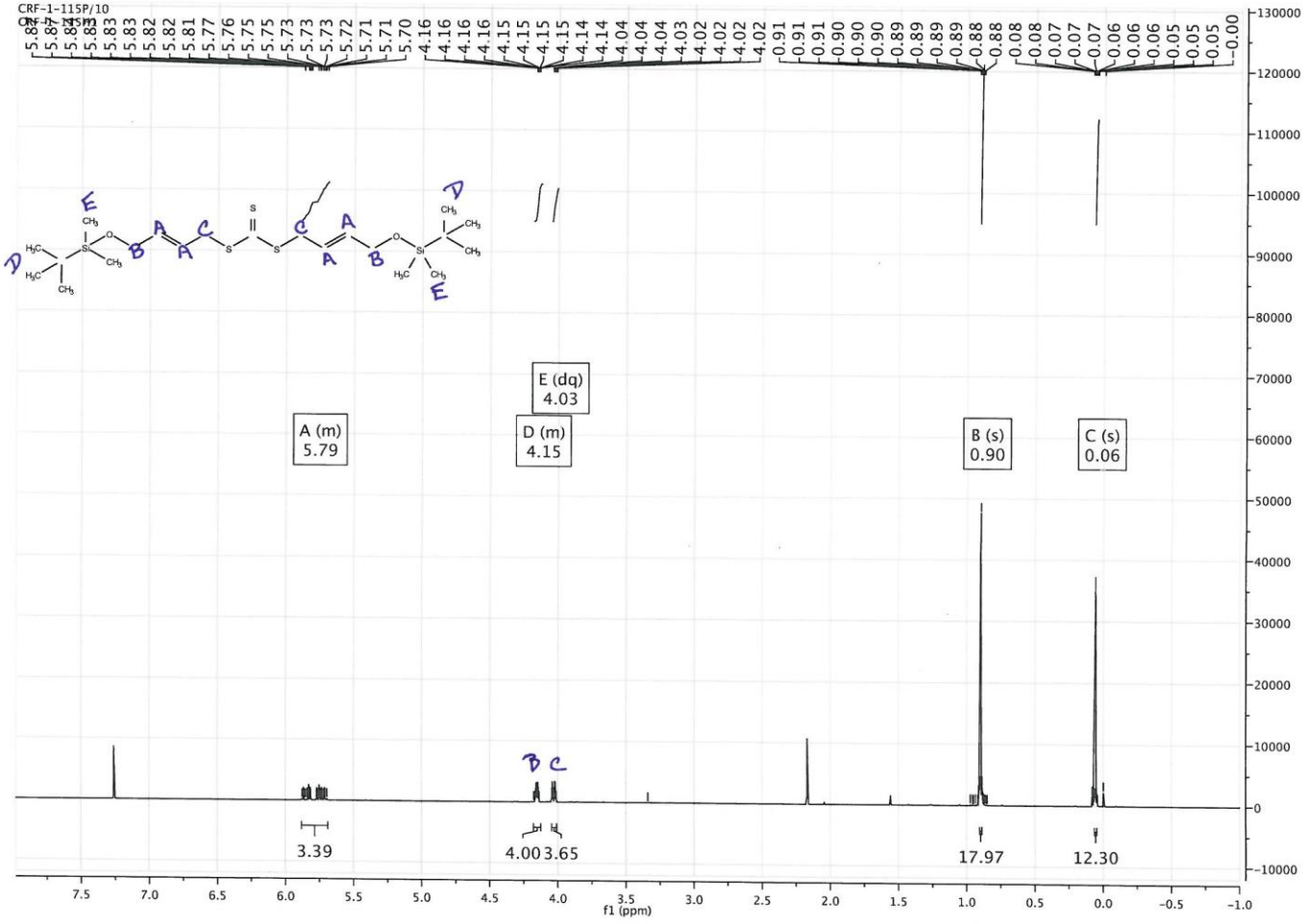
TOF MS ES+
7.37e12
357.0
Theretical MNa+
100
%
0
358.0
359.0
360.0
346
348
350
352
354
356
358
360
362
364
366
368
370
m/z
CRF-1-113 54 (0.939) AM2 (Ar,18000.0,0.00,0.00); Cm (3:54)
TOF MS ES+
3.76e7
357.0
MNa+
100
%
0
354.0
355.0
358.0
359.0
360.0
346
348
350
352
354
356
358
360
362
364
366
368
370
m/z

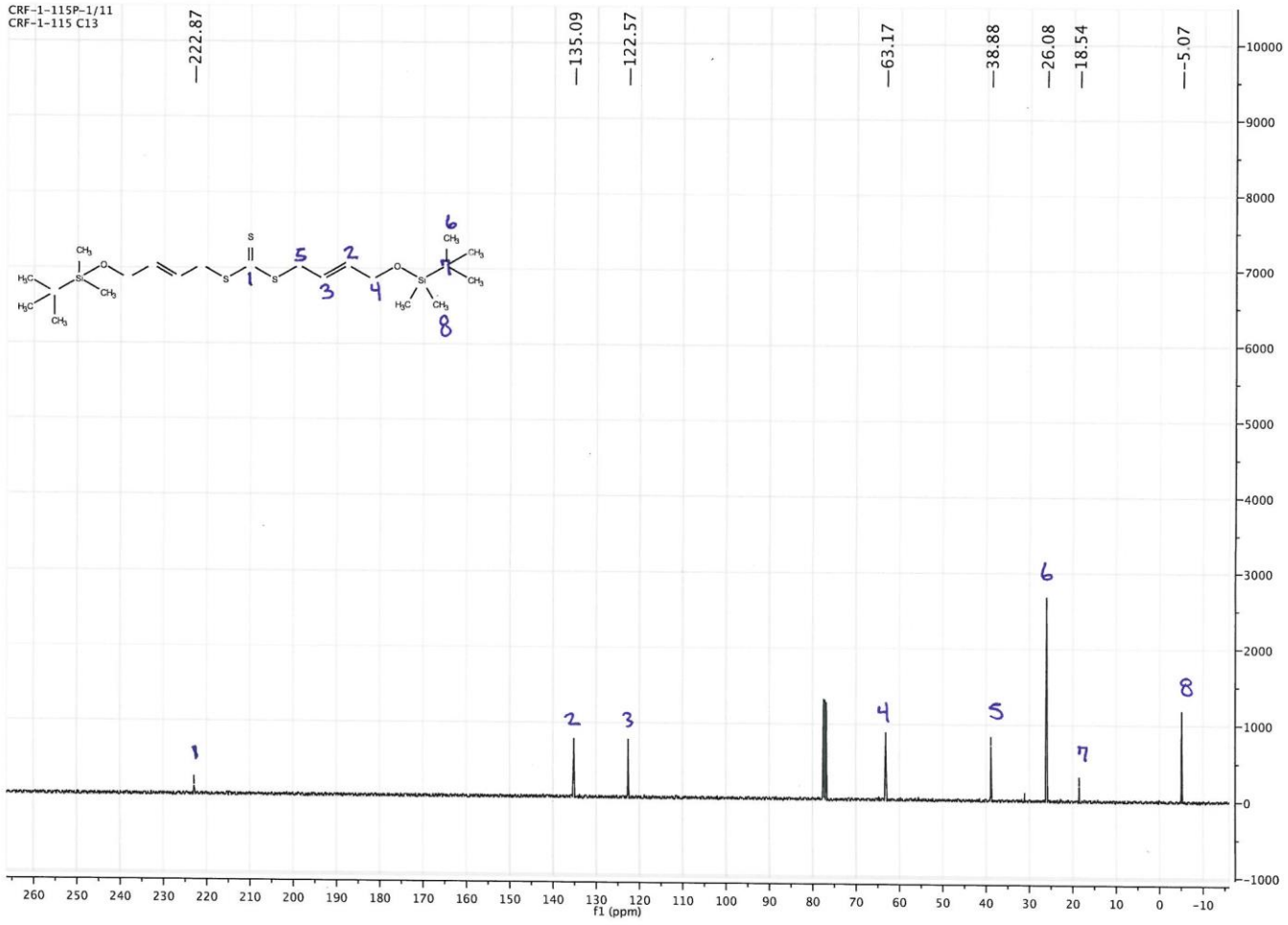

CRF-1-83/10
5.92
5.90
5.89
5.88
4.22
4.22
4.21
4.21
4.21
4.20
4.20
4.20
4.00
3.99
3.99
3.97
3.97
3.97
3.97
0.93
0.09
Br
O
Si
C
A
A
B
D
E
A (m)
5.89
C (dt)
3.98
B (m)
4.21
E (s)
0.93
D (s)
0.09
0.88
2.76
2.50
8.63
6.00
f1 (ppm)

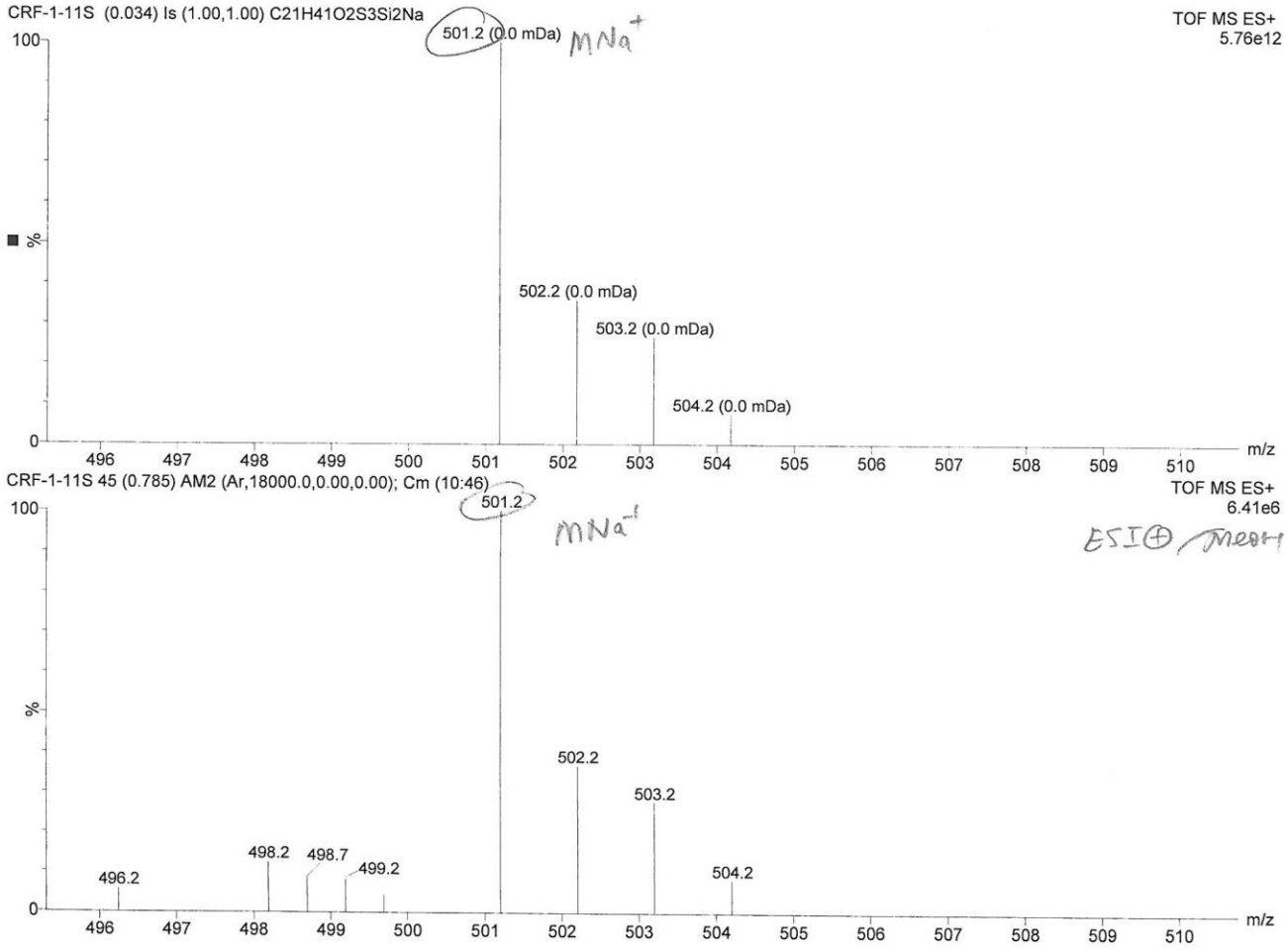

CRF-1-83/11
134.63
125.78
62.57
32.36
25.91
18.36
-5.26
Br
O
Si
CH3
H3C
1
2
3
4
5
6
7
f1 (ppm)

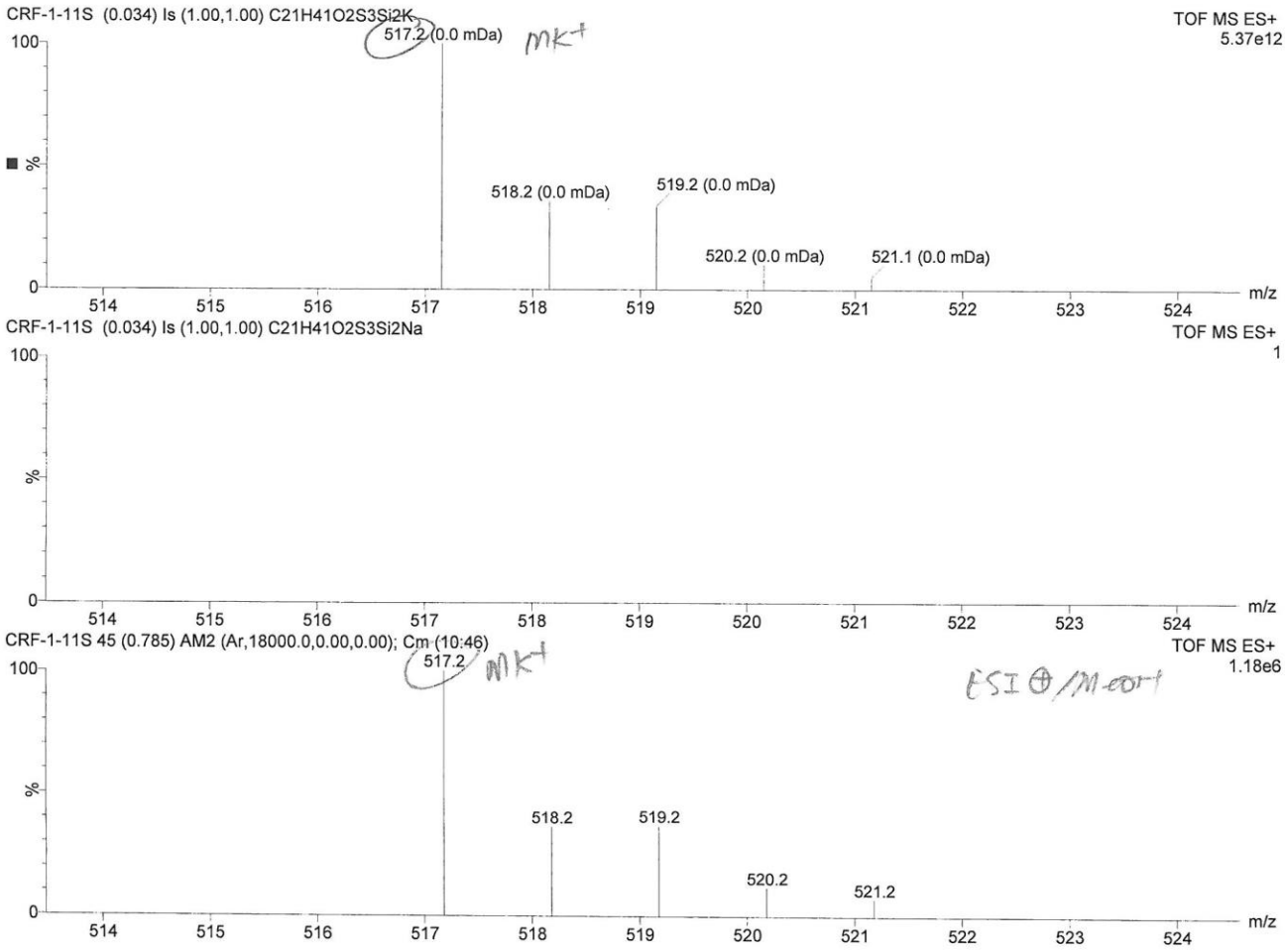
ESI⊕/MeOH

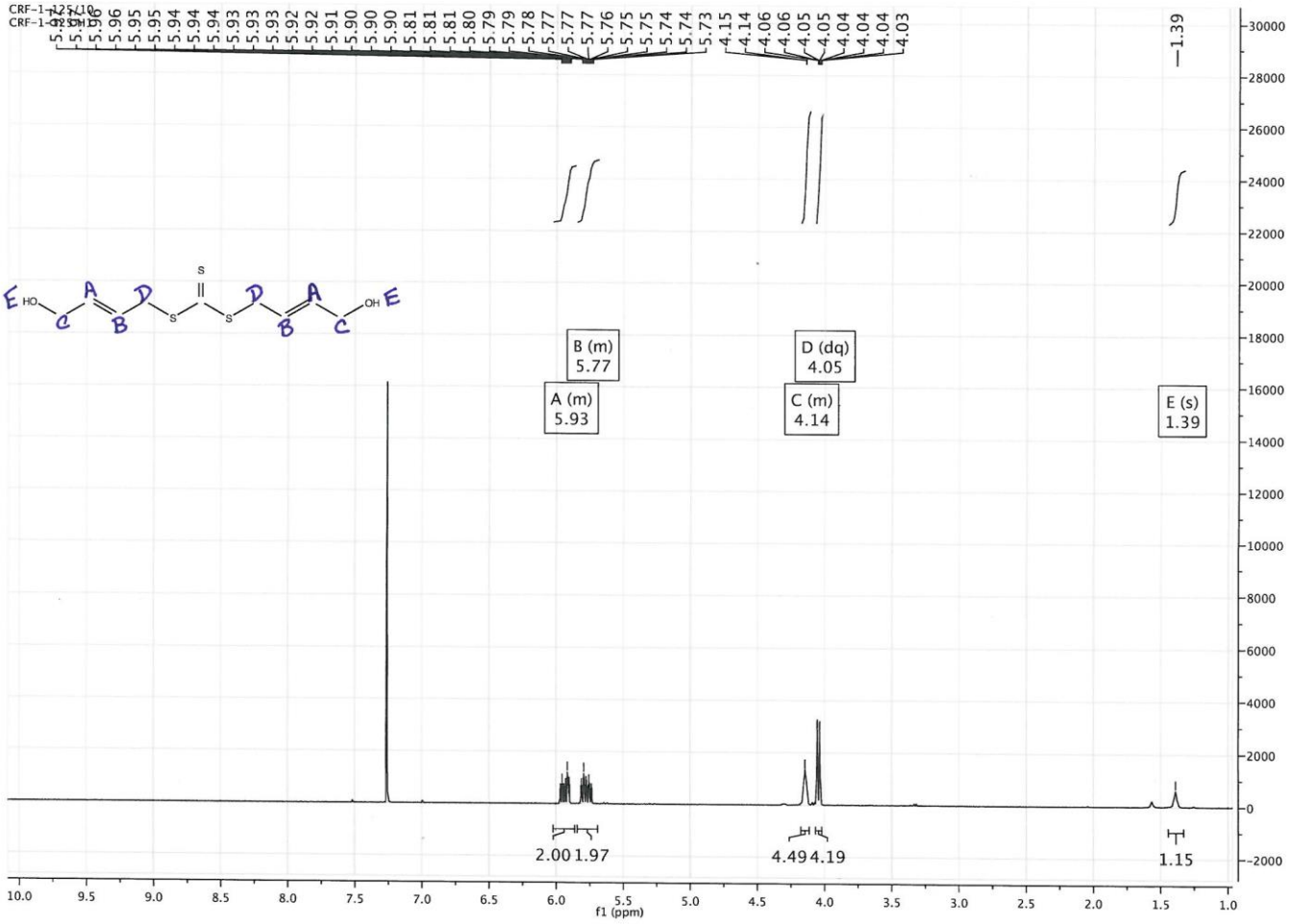

CRF-1-83 50 (0.870) AM2 (Ar,18000.0,0.00,0.00); Cm (3:57)
MNa+
TOF MS ES+
1.85e5
100
%
0
287.1
289.1
284.1
285.2
288.1
290.1
291.1
291.2
293.2
285
286
287
288
289
290
291
292
293
m/z
CRF-1-89 (0.034) Is (1.00,1.00) C10H20BrOSiNa
MNa+
TOF MS ES+
4.26e12
theoretical
100
%
0
287.0 (0.0 mDa)
289.0 (0.0 mDa)
288.0 (0.0 mDa)
290.0 (0.0 mDa)
291.0 (0.0 mDa)
285
286
287
288
289
290
291
292
293
m/z

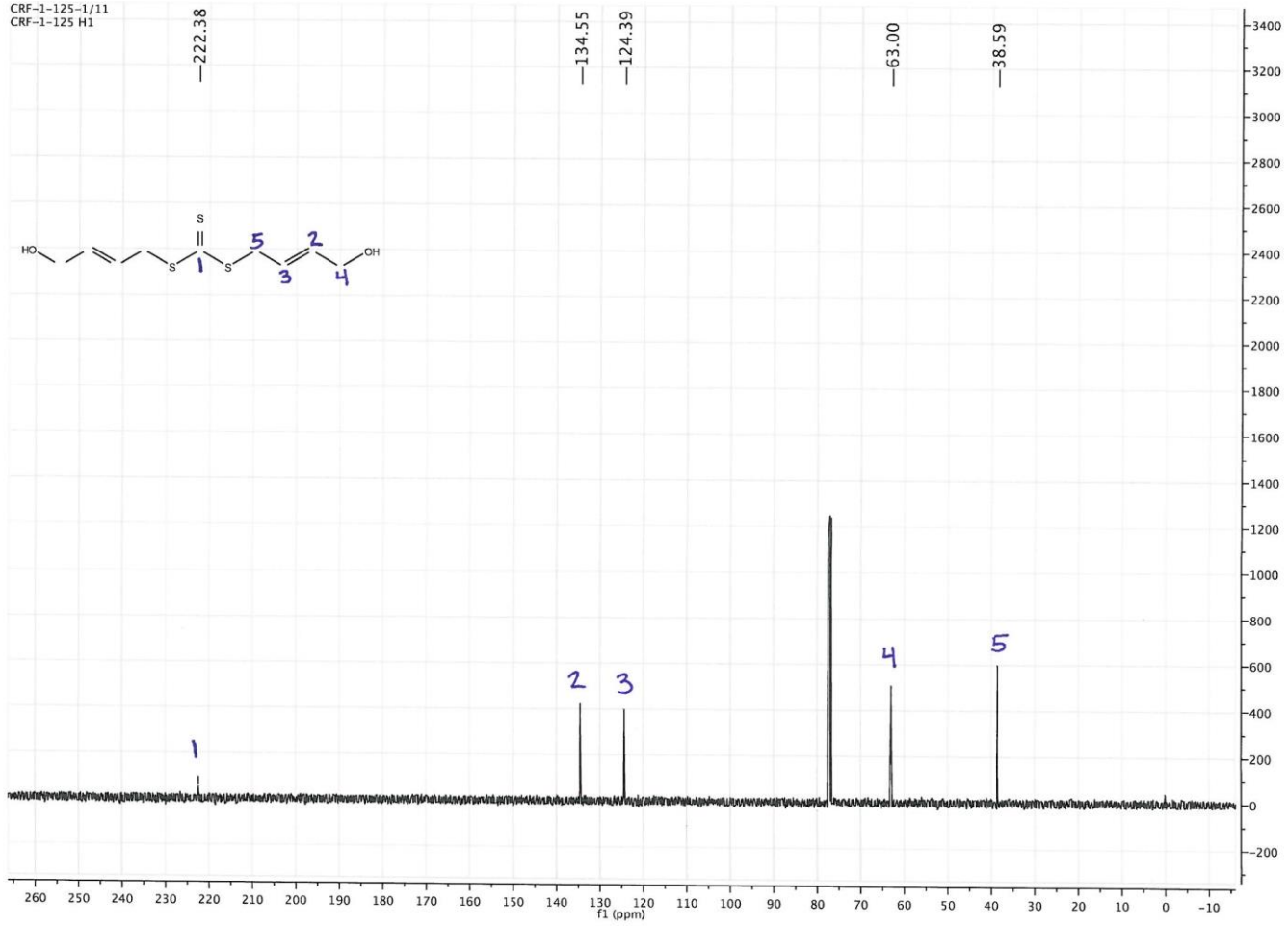

CRF-1-115P/10
A (m)
5.79
E (dq)
4.03
D (m)
4.15
B (s)
0.90
C (s)
0.06
3.39
4.00
3.65
17.97
12.30
f1 (ppm)

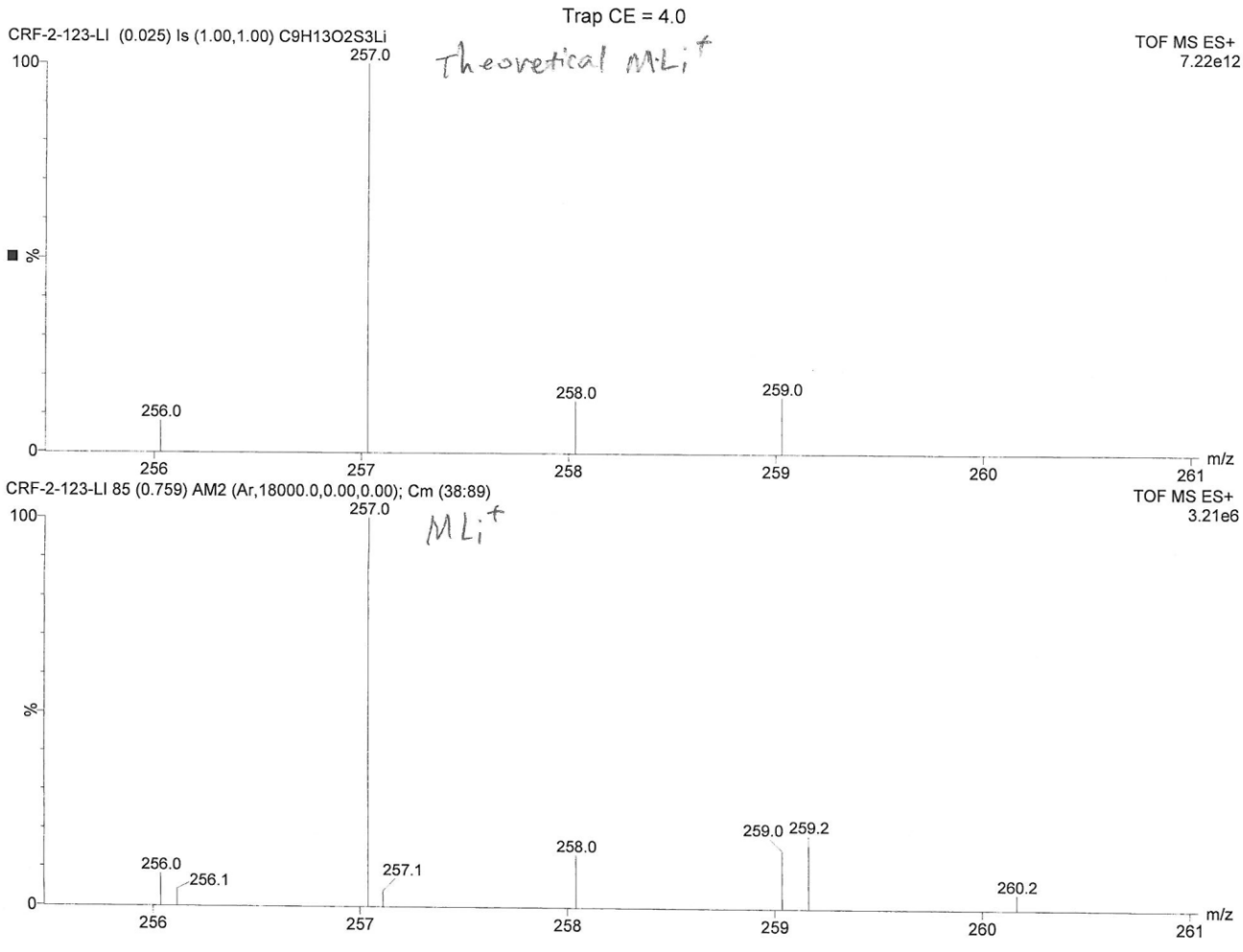

CRF-1-115P-1/11
CRF-1-115 C13
222.87
135.09
122.57
63.17
38.88
26.08
18.54
-5.07
1
2
3
4
5
6
7
8
f1 (ppm)

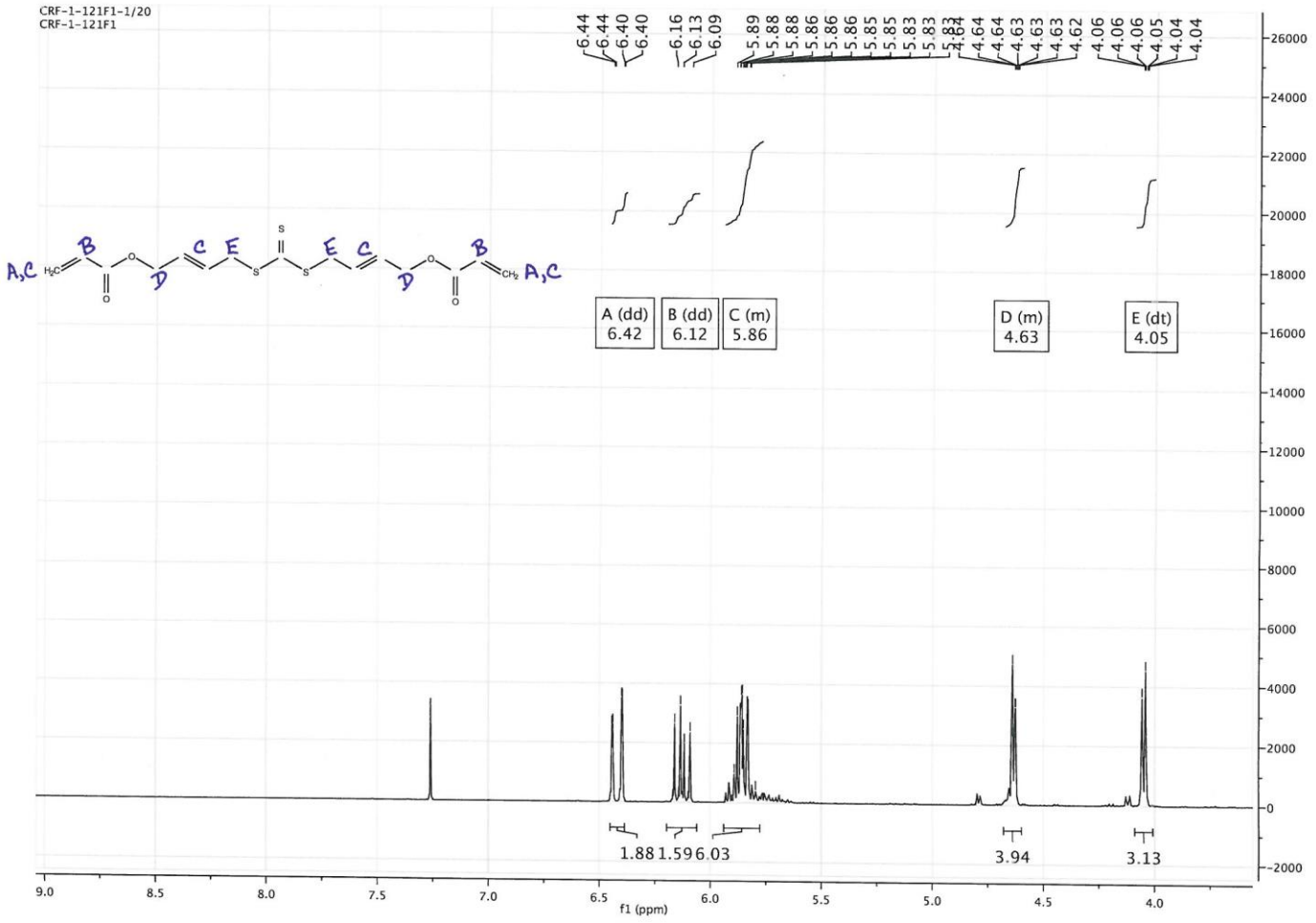

CRF-1-11S (0.034) Is (1.00,1.00) C21H41O2S3Si2Na
501.2 (0.0 mDa)
MNa+
TOF MS ES+
5.76e12
100
%
0
502.2 (0.0 mDa)
503.2 (0.0 mDa)
504.2 (0.0 mDa)
496 497 498 499 500 501 502 503 504 505 506 507 508 509 510
m/z
CRF-1-11S 45 (0.785) AM2 (Ar,18000.0,0.00,0.00); Cm (10:46)
501.2
MNa+
TOF MS ES+
6.41e6
ESI⊕ MeOH
100
%
0
502.2
503.2
496.2
498.2
498.7
499.2
504.2
496 497 498 499 500 501 502 503 504 505 506 507 508 509 510
m/z

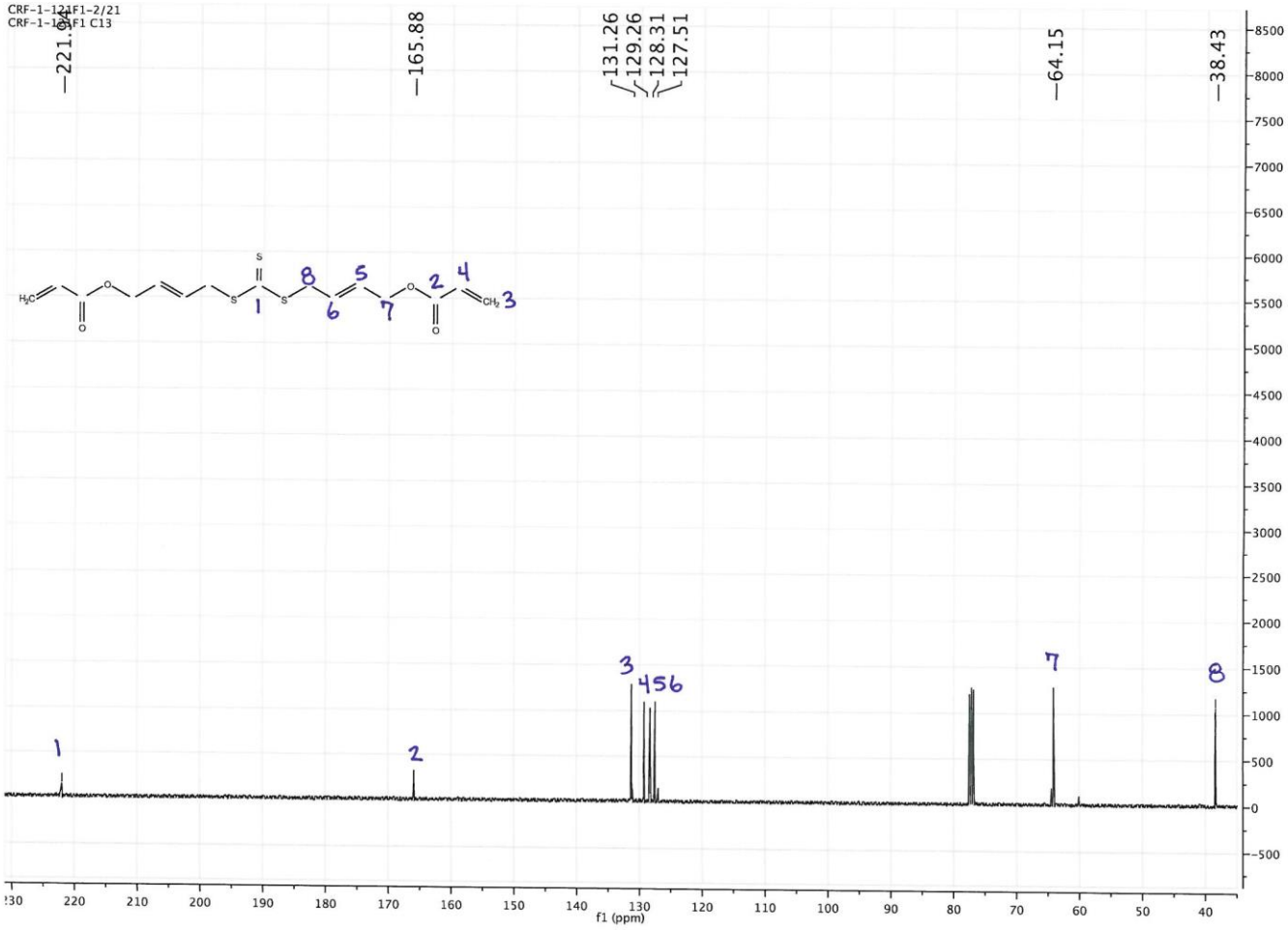

CRF-1-11S (0.034) Is (1.00,1.00) C21H41O2S3Si2K
TOF MS ES+
5.37e12
517.2 (0.0 mDa)
MK+
518.2 (0.0 mDa)
519.2 (0.0 mDa)
520.2 (0.0 mDa)
521.1 (0.0 mDa)
100
%
0
514 515 516 517 518 519 520 521 522 523 524
m/z
CRF-1-11S (0.034) Is (1.00,1.00) C21H41O2S3Si2Na
TOF MS ES+
1
100
%
0
514 515 516 517 518 519 520 521 522 523 524
m/z
CRF-1-11S 45 (0.785) AM2 (Ar,18000.0,0.00,0.00); Cm (10:46)
TOF MS ES+
1.18e6
517.2
MK+
ESI⊕/M-COOH
518.2
519.2
520.2
521.2
100
%
0
514 515 516 517 518 519 520 521 522 523 524
m/z


CRF-1-125/10
CRF-1-125/10
5.97 5.97 5.96 5.96 5.95 5.95 5.94 5.94 5.94 5.93 5.93 5.93 5.92 5.92 5.91 5.90 5.90 5.90 5.81 5.81 5.81 5.80 5.79 5.79 5.78 5.77 5.77 5.77 5.76 5.75 5.75 5.74 5.74 5.73 4.15 4.14 4.06 4.06 4.05 4.05 4.04 4.04 4.04 4.03
1.39
HO
OH
E
A
D
S
S
S
D
A
B
C
B
C
B (m)
5.77
A (m)
5.93
D (dq)
4.05
C (m)
4.14
E (s)
1.39
2.00 1.97
4.49 4.19
1.15
f1 (ppm)

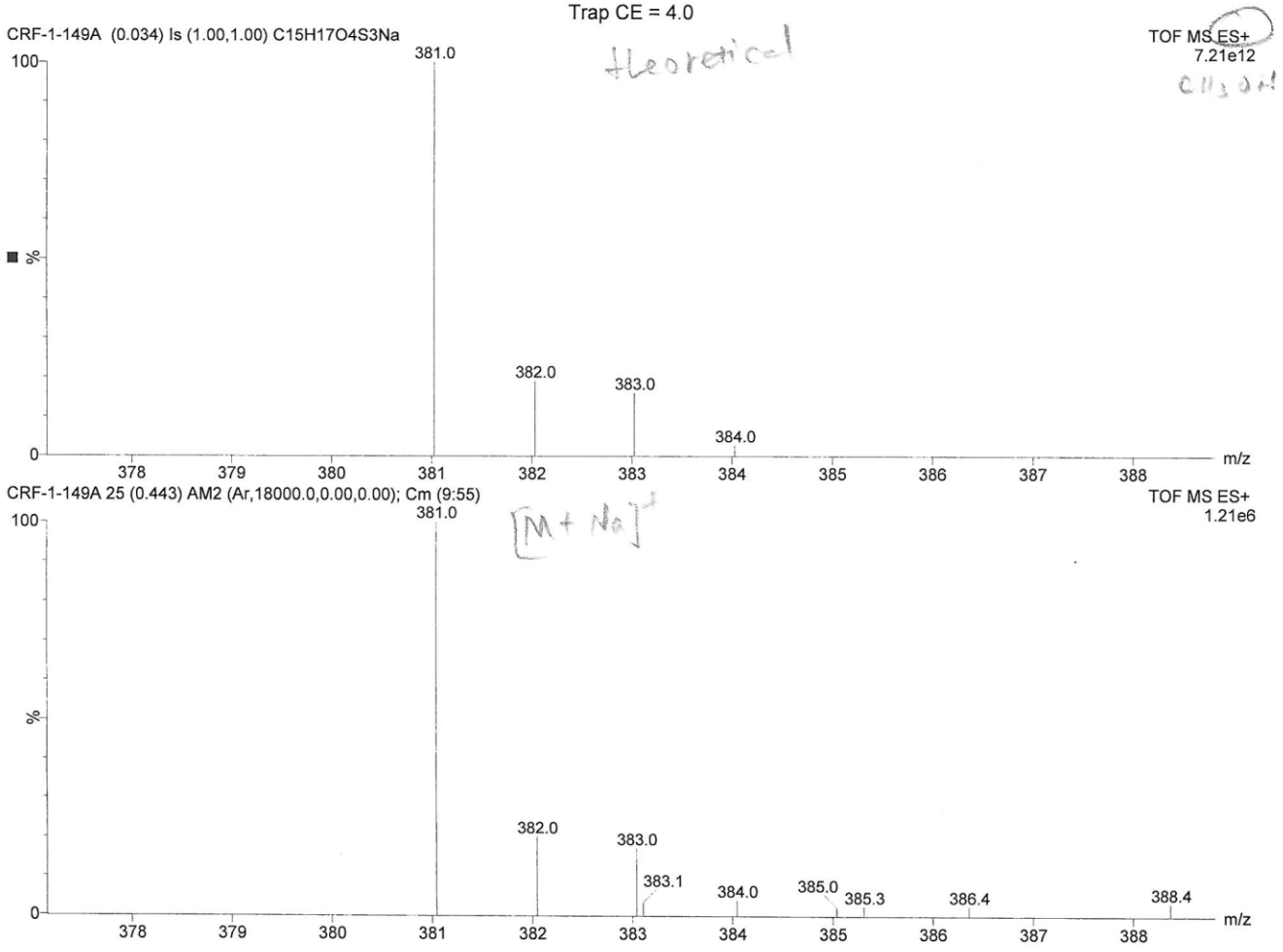

CRF-1-125-1/11
CRF-1-125 H1
222.38
134.55
124.39
63.00
38.59
HO
OH
S
1
2
3
4
5
f1 (ppm)

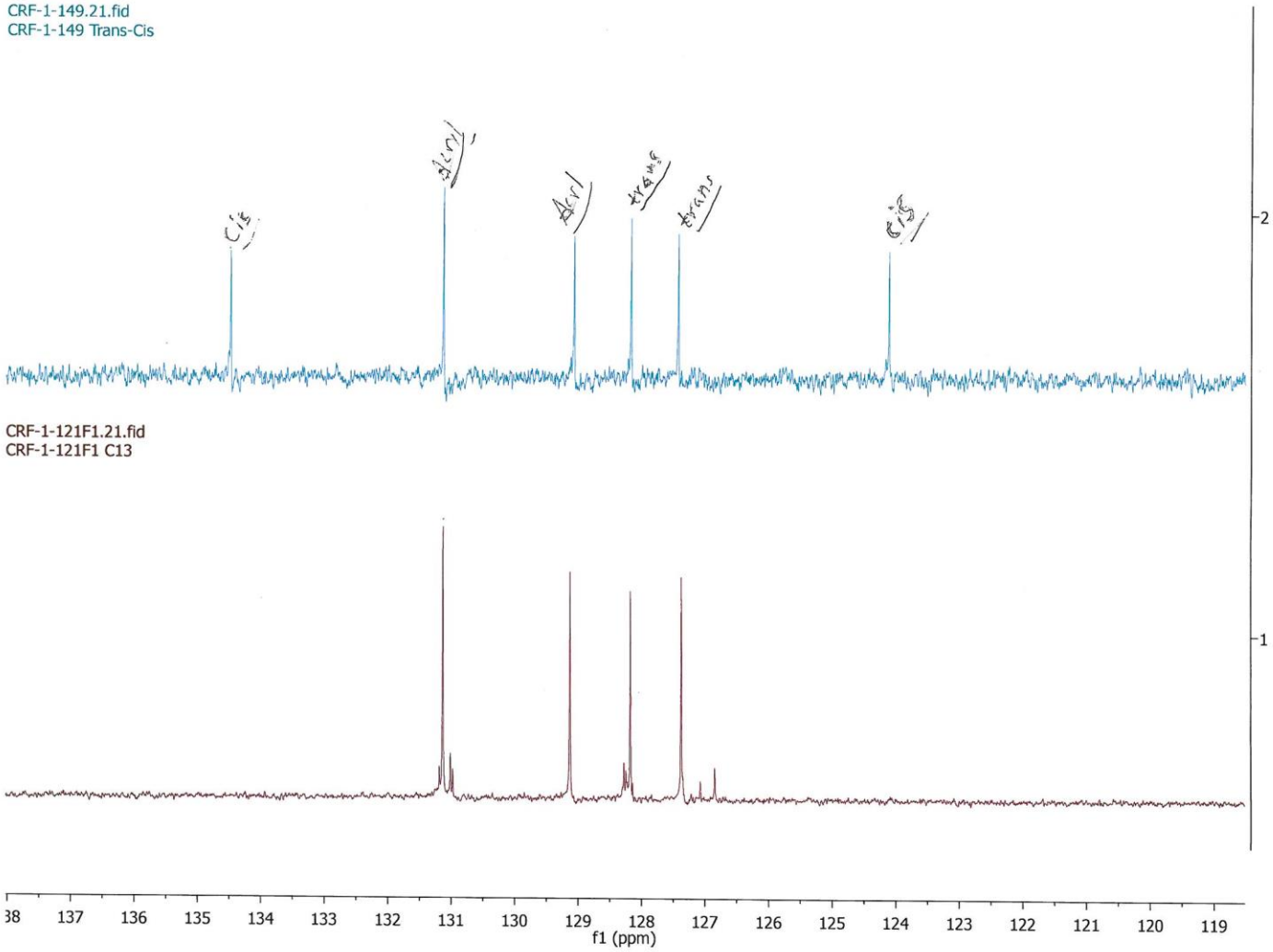

Trap CE = 4.0
CRF-2-123-LI (0.025) Is (1.00,1.00) C9H13O2S3Li
Theoretical M·Li+
TOF MS ES+
7.22e12
100
%
0
257.0
256.0
258.0
259.0
256
257
258
259
260
261
m/z
CRF-2-123-LI 85 (0.759) AM2 (Ar,18000.0,0.00,0.00); Cm (38:89)
M·Li+
TOF MS ES+
3.21e6
100
%
0
257.0
256.0
256.1
257.1
258.0
259.0
259.2
260.2
256
257
258
259
260
261
m/z

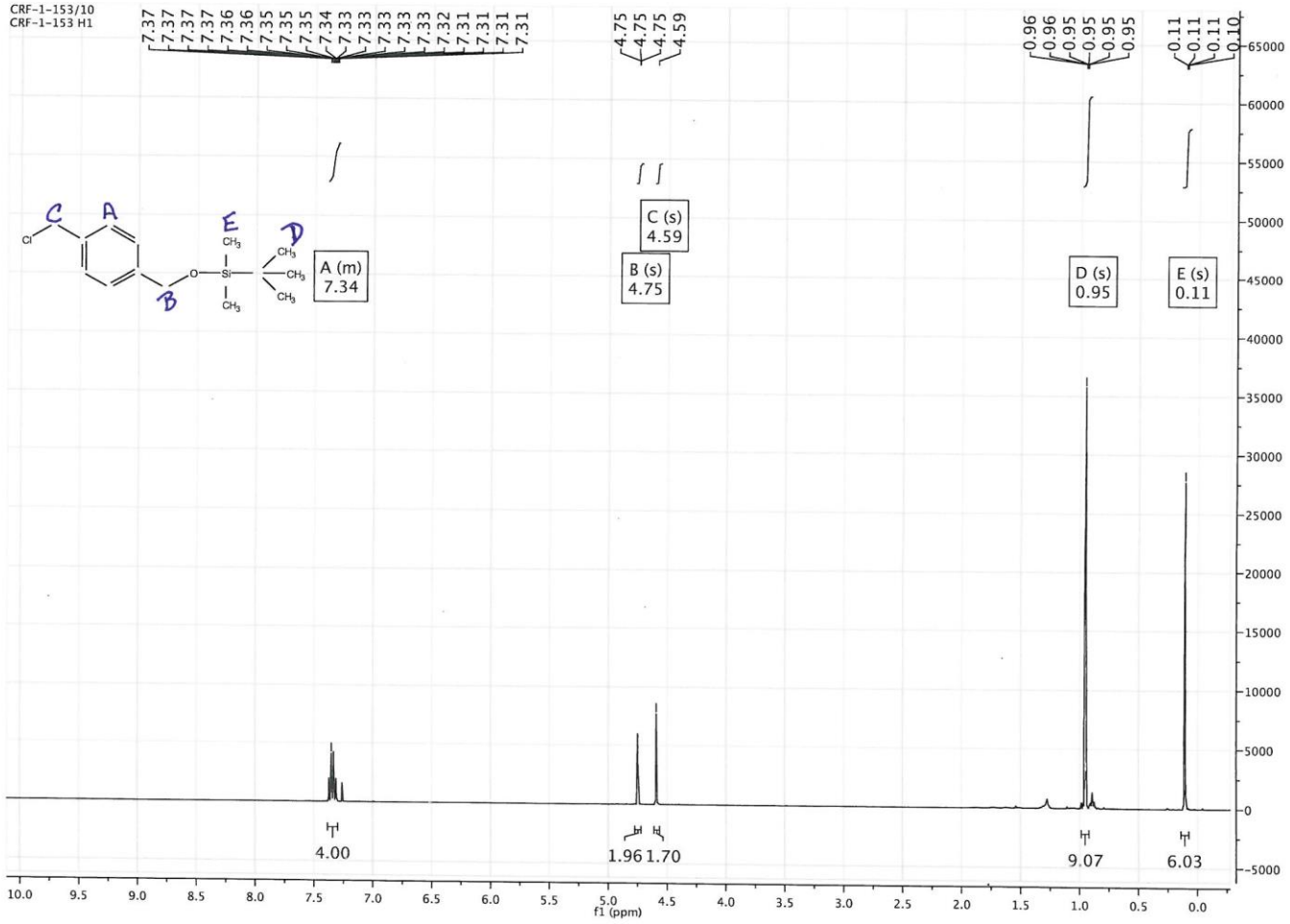

CRF-1-121F1-1/20
CRF-1-121F1
A,C
B
D
C
E
S
A (dd)
6.42
B (dd)
6.12
C (m)
5.86
D (m)
4.63
E (dt)
4.05
1.88
1.59
6.03
3.94
3.13
f1 (ppm)

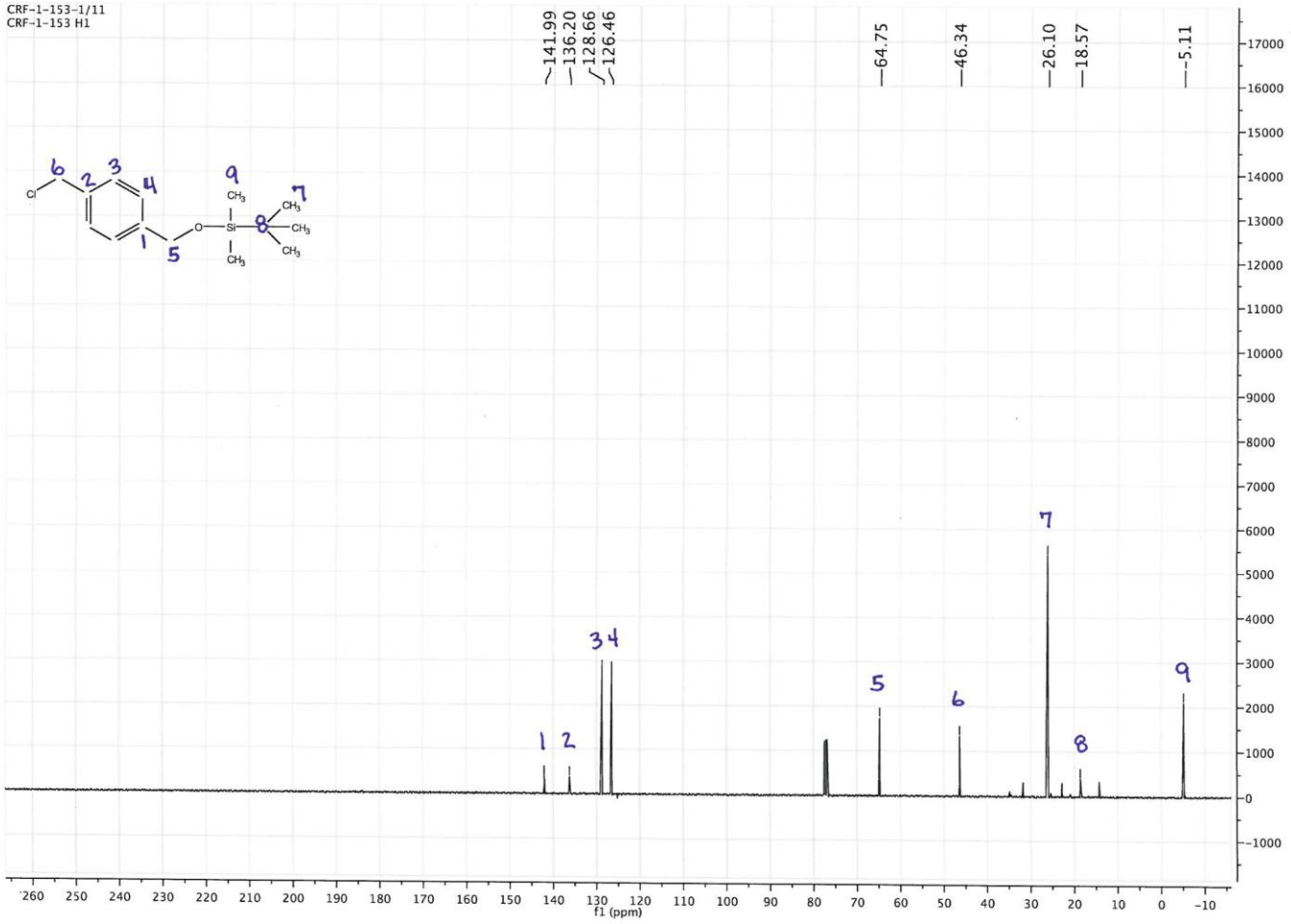

CRF-1-121F1-2/21
CRF-1-121F1 C13
221.64
165.88
131.26
129.26
128.31
127.51
64.15
38.43
1
2
3
456
7
8
f1 (ppm)

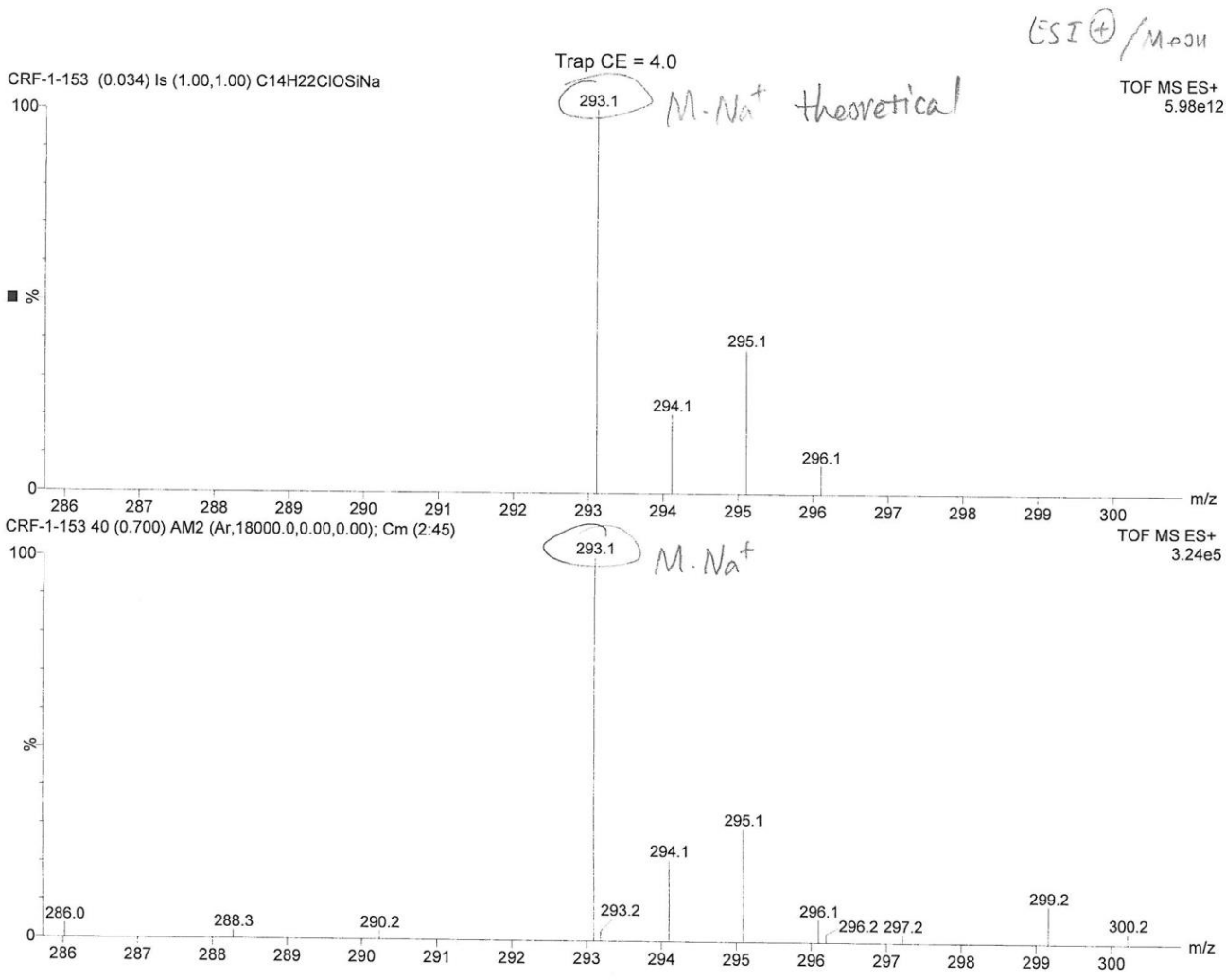
Trap CE = 4.0

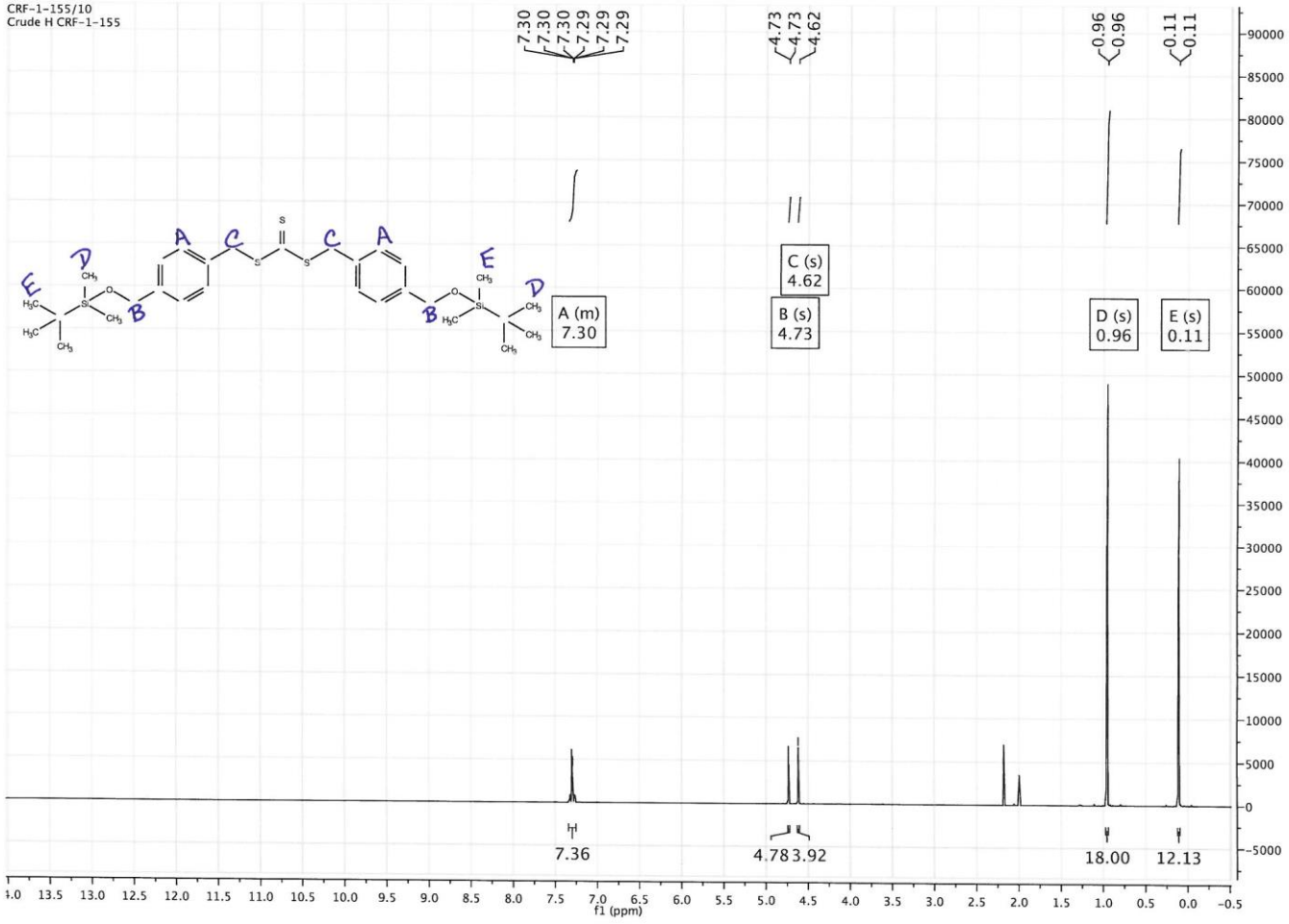

CRF-1-149A (0.034) Is (1.00,1.00) C15H17O4S3Na
TOF MS ES+
7.21e12
Theoretical
100
%
0
381.0
382.0
383.0
384.0
m/z
378
379
380
381
382
383
384
385
386
387
388
CRF-1-149A 25 (0.443) AM2 (Ar,18000.0,0.00,0.00); Cm (9:55)
TOF MS ES+
1.21e6
[M + Na]+
100
%
0
381.0
382.0
383.0
383.1
384.0
385.0
385.3
386.4
388.4
m/z
378
379
380
381
382
383
384
385
386
387
388

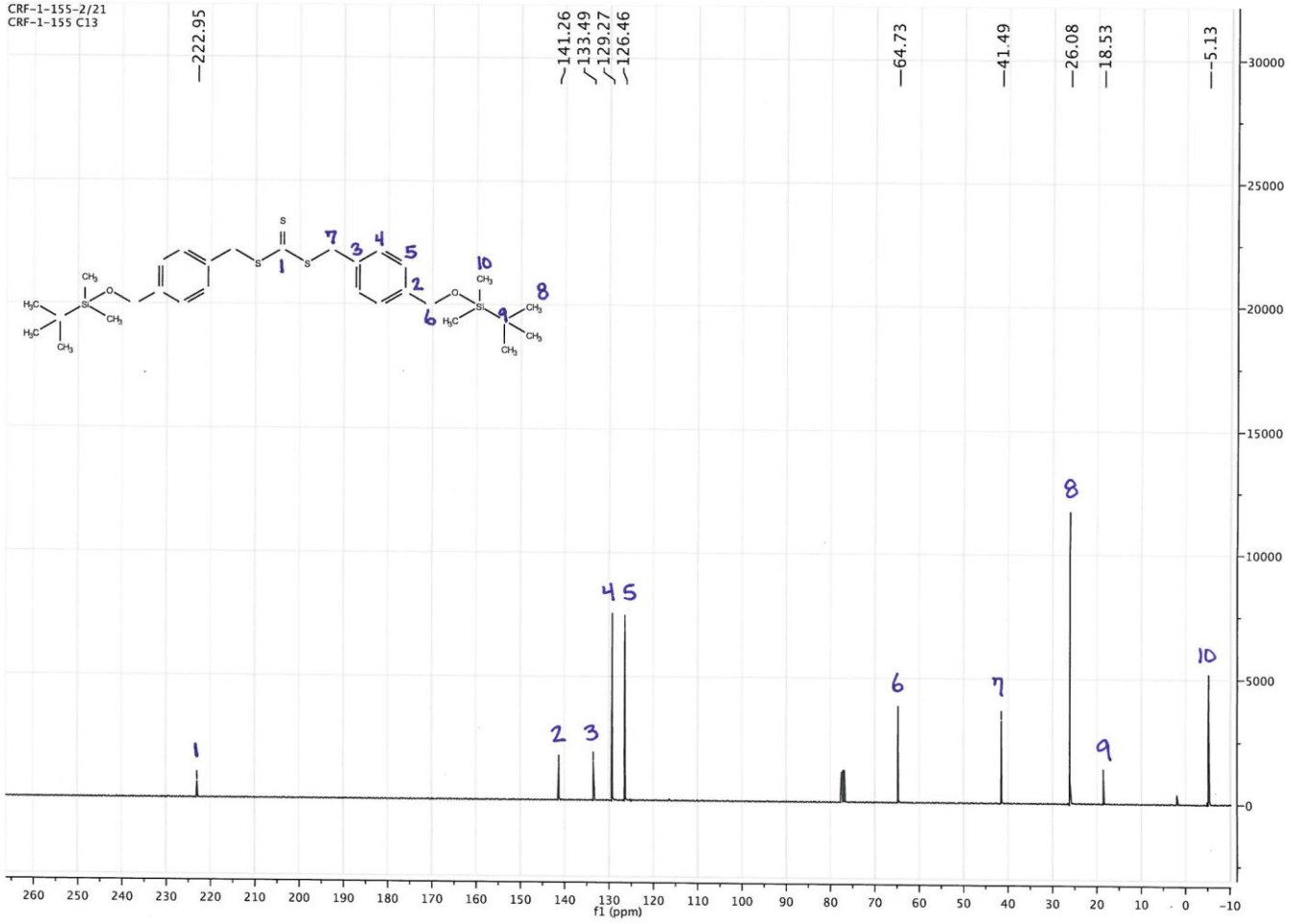

CRF-1-149.21.fid
CRF-1-149 Trans-Cis
CRF-1-121F1.21.fid
CRF-1-121F1 C13
2
1
38 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)


CRF-1-153/10
CRF-1-153 H1
7.37 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.33 7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.31
4.75 4.75 4.75 4.59
0.96 0.96 0.95 0.95 0.95 0.95
0.11 0.11 0.11 0.10
C A E D B
A (m) 7.34
C (s) 4.59
B (s) 4.75
D (s) 0.95
E (s) 0.11
4.00
1.96 1.70
9.07
6.03
f1 (ppm)

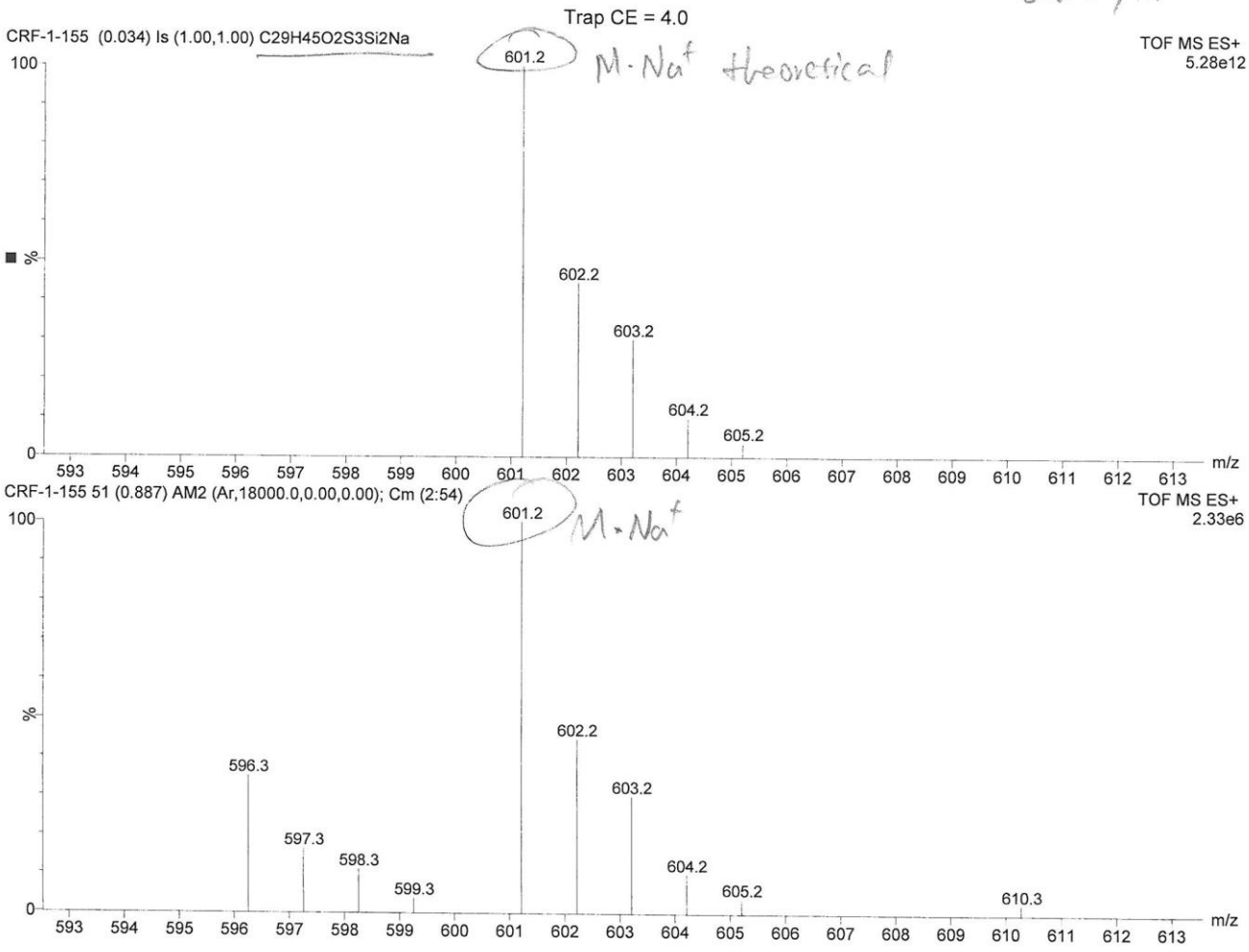

CRF-1-153-1/11
CRF-1-153 H1
141.99
136.20
128.66
126.46
64.75
46.34
26.10
18.57
-5.11
f1 (ppm)

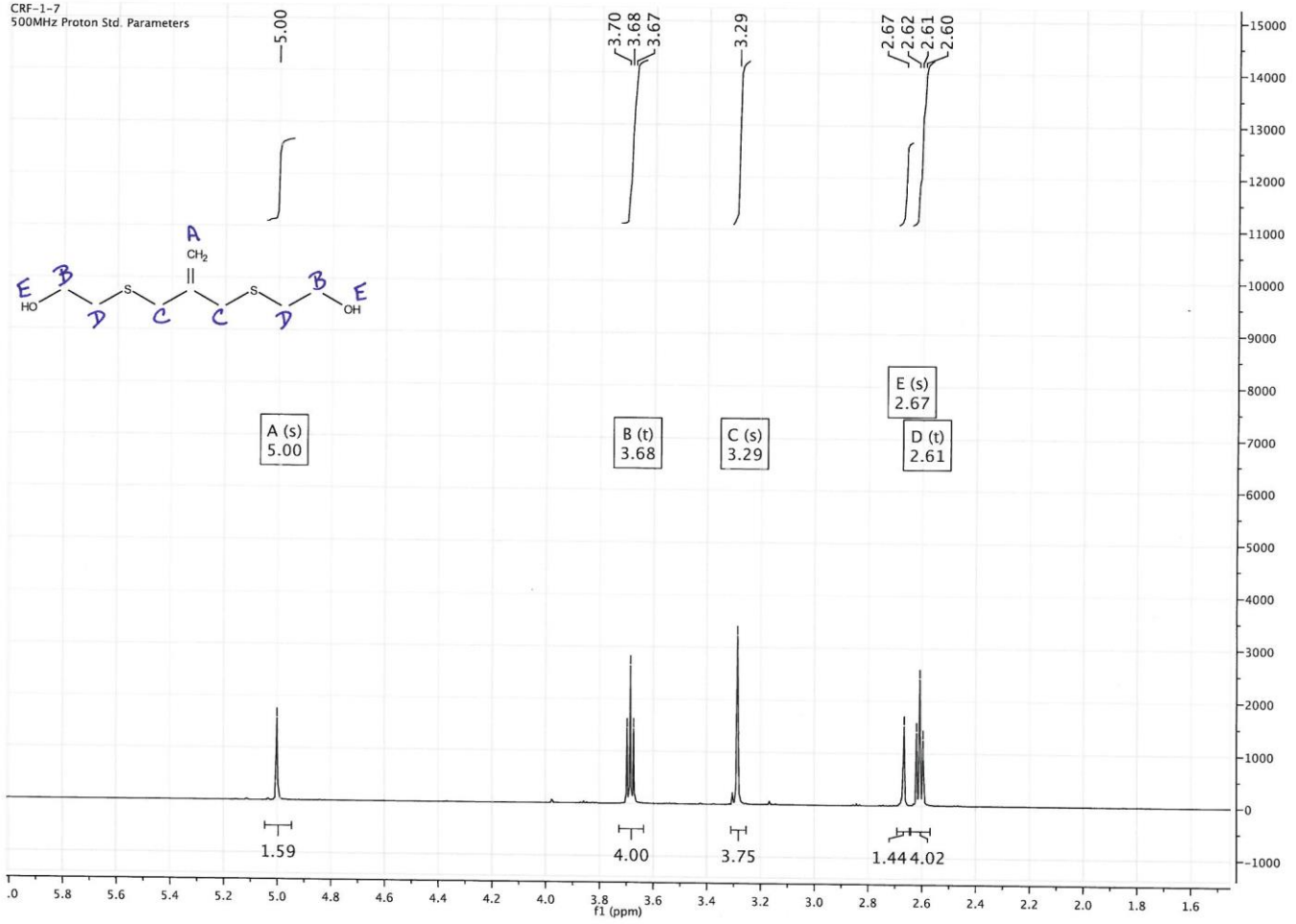

ESI⊕/MeOH
Trap CE = 4.0
CRF-1-153 (0.034) Is (1.00,1.00) C14H22ClOSiNa
293.1
M·Na+ theoretical
TOF MS ES+
5.98e12
100
%
0
295.1
294.1
296.1
286 287 288 289 290 291 292 293 294 295 296 297 298 299 300
m/z
CRF-1-153 40 (0.700) AM2 (Ar,18000.0,0.00,0.00); Cm (2:45)
293.1
M·Na+
TOF MS ES+
3.24e5
100
%
0
295.1
294.1
299.2
286.0
288.3
290.2
293.2
296.1
296.2 297.2
300.2
286 287 288 289 290 291 292 293 294 295 296 297 298 299 300
m/z

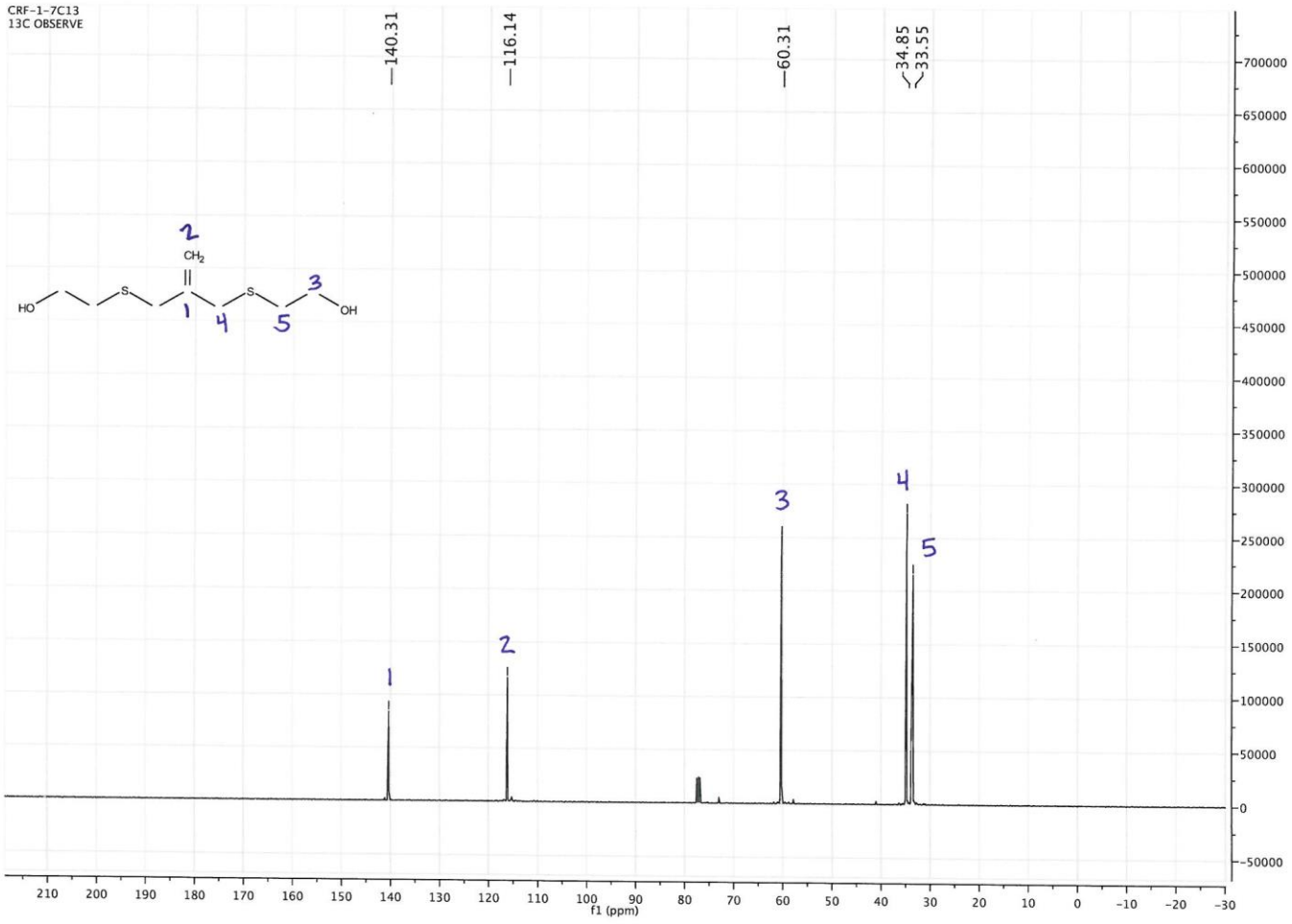

CRF-1-155/10
Crude H CRF-1-155
7.30
7.30
7.30
7.29
7.29
7.29
4.73
4.73
4.62
0.96
0.96
0.11
0.11
A
C
S
S
C
A
D
E
B
B
D
E
A (m)
7.30
C (s)
4.62
B (s)
4.73
D (s)
0.96
E (s)
0.11
7.36
4.78
3.92
18.00
12.13
f1 (ppm)

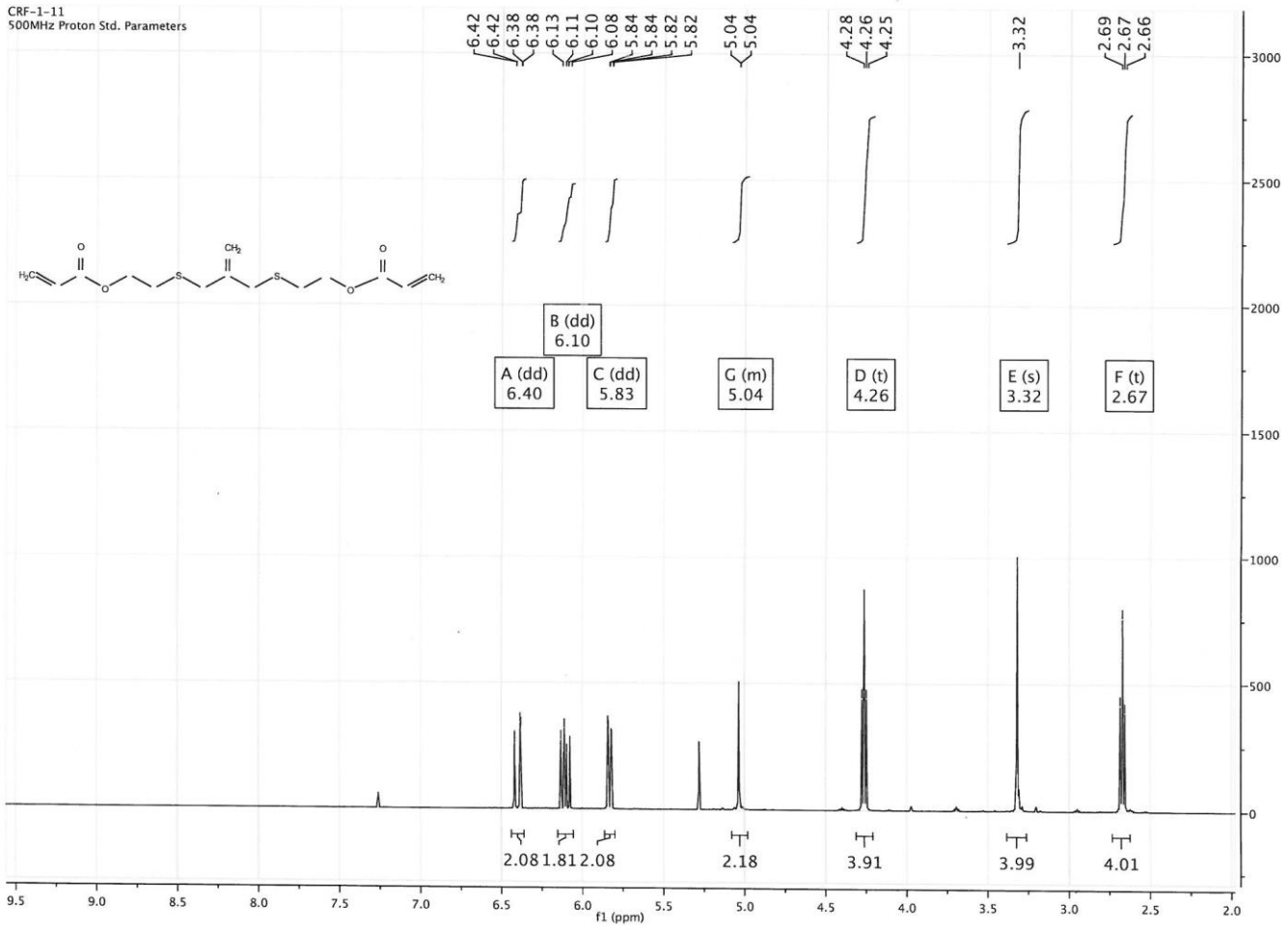

CRF-1-155-2/21
CRF-1-155 C13
222.95
141.26
133.49
129.27
126.46
64.73
41.49
26.08
18.53
5.13
1
2
3
4
5
6
7
8
9
10
f1 (ppm)

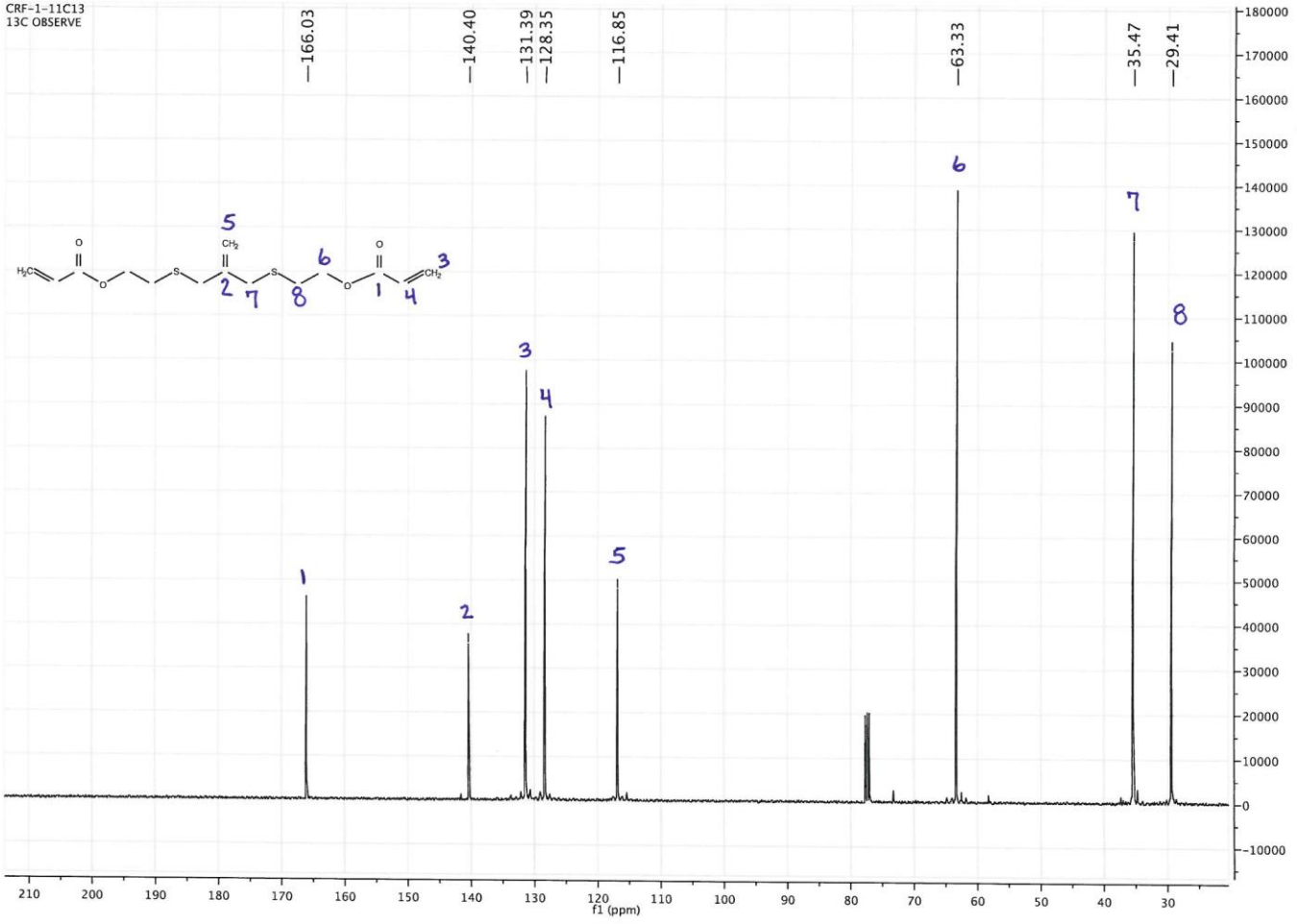
ESI⊕ / MeOH

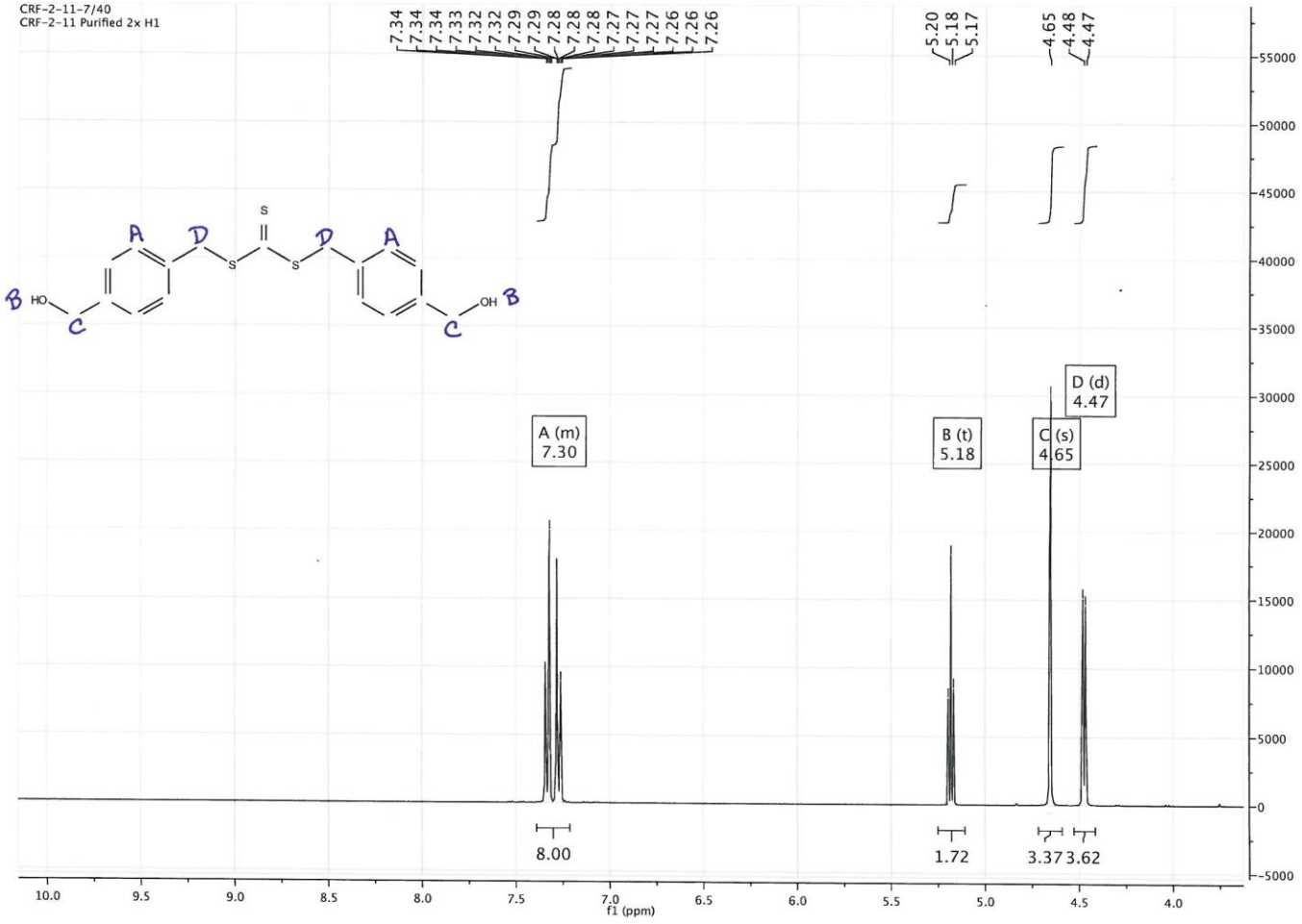

Trap CE = 4.0
CRF-1-155 (0.034) Is (1.00,1.00) C29H45O2S3Si2Na
601.2
M·Na+ theoretical
TOF MS ES+
5.28e12
100
%
0
602.2
603.2
604.2
605.2
593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613
m/z
CRF-1-155 51 (0.887) AM2 (Ar,18000.0,0.00,0.00); Cm (2:54)
601.2
M·Na+
TOF MS ES+
2.33e6
100
%
0
596.3
597.3
598.3
599.3
602.2
603.2
604.2
605.2
610.3
593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613
m/z

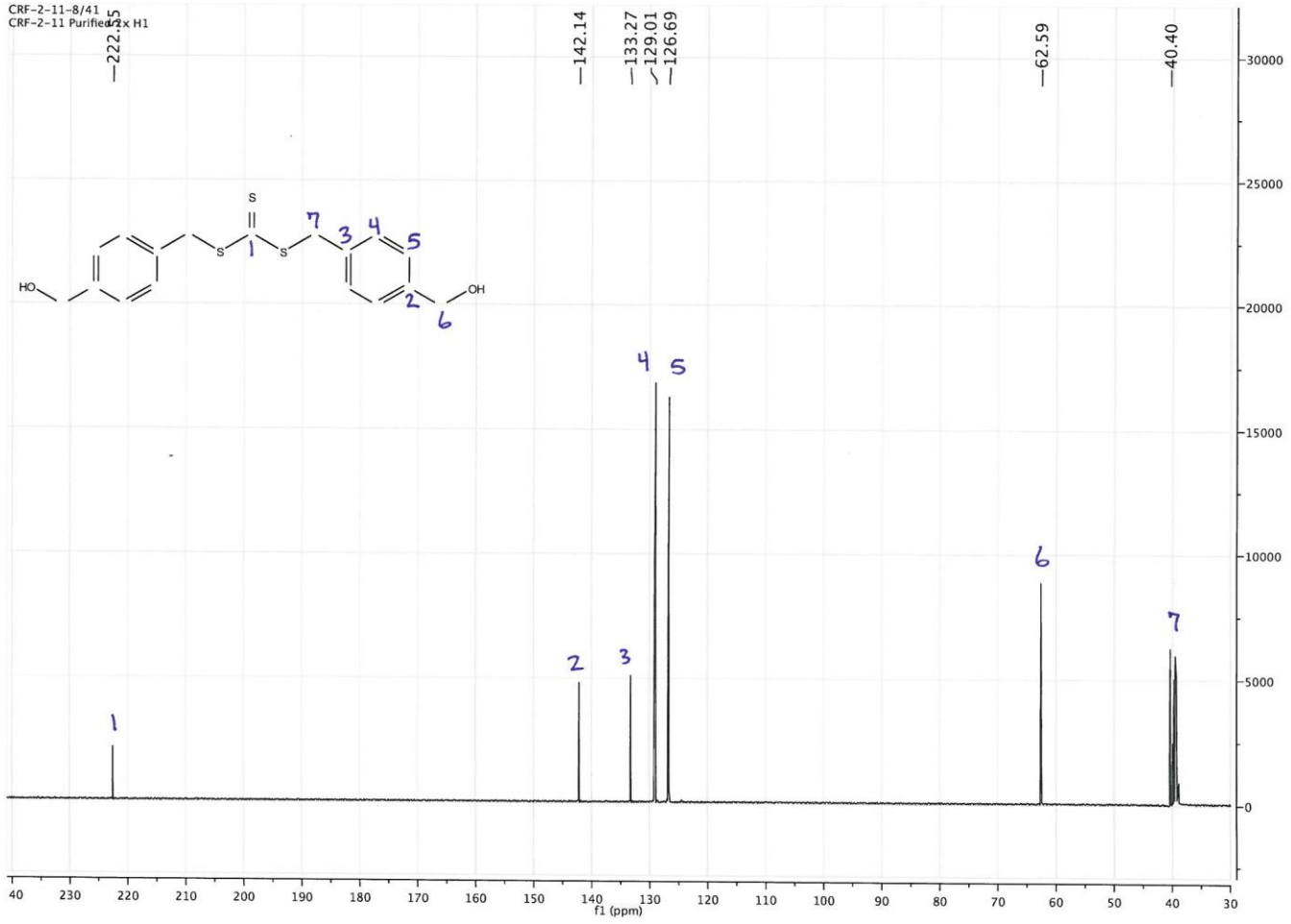

CRF-1-7
500MHz Proton Std. Parameters
5.00
3.70
3.68
3.67
3.29
2.67
2.62
2.61
2.60
A
CH2
E
B
HO
D
S
C
C
S
D
B
OH
E
A (s)
5.00
B (t)
3.68
C (s)
3.29
E (s)
2.67
D (t)
2.61
1.59
4.00
3.75
1.44
4.02
f1 (ppm)

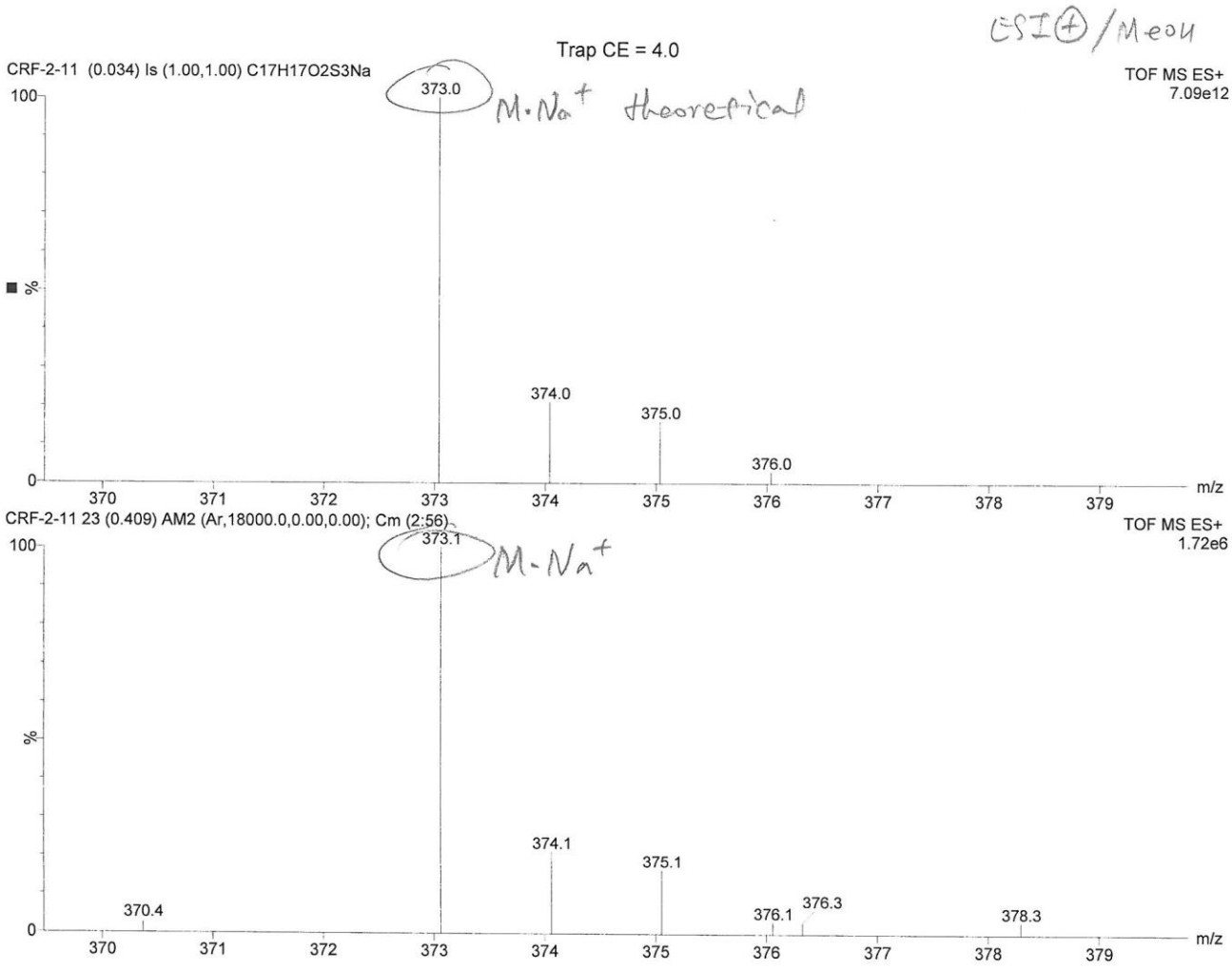

CRF-1-7C13
13C OBSERVE
140.31
116.14
60.31
34.85
33.55
HO
OH
S
S
CH2
1
2
3
4
5
f1 (ppm)

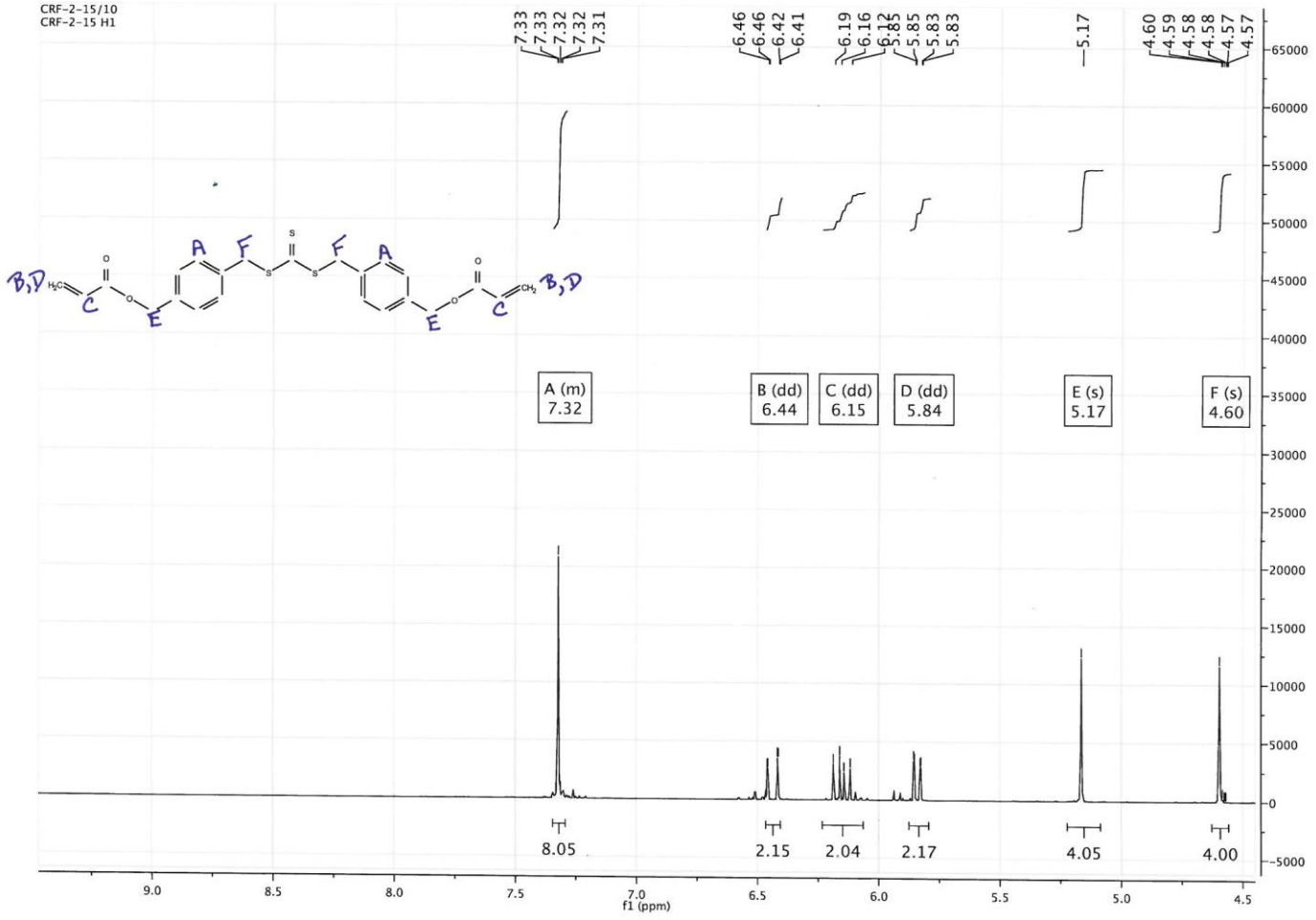

CRF-1-11
500MHz Proton Std. Parameters
6.42
6.42
6.38
6.38
6.13
6.11
6.10
6.08
5.84
5.84
5.82
5.82
5.04
5.04
4.28
4.26
4.25
3.32
2.69
2.67
2.66
B (dd)
6.10
A (dd)
6.40
C (dd)
5.83
G (m)
5.04
D (t)
4.26
E (s)
3.32
F (t)
2.67
2.08
1.81
2.08
2.18
3.91
3.99
4.01
f1 (ppm)

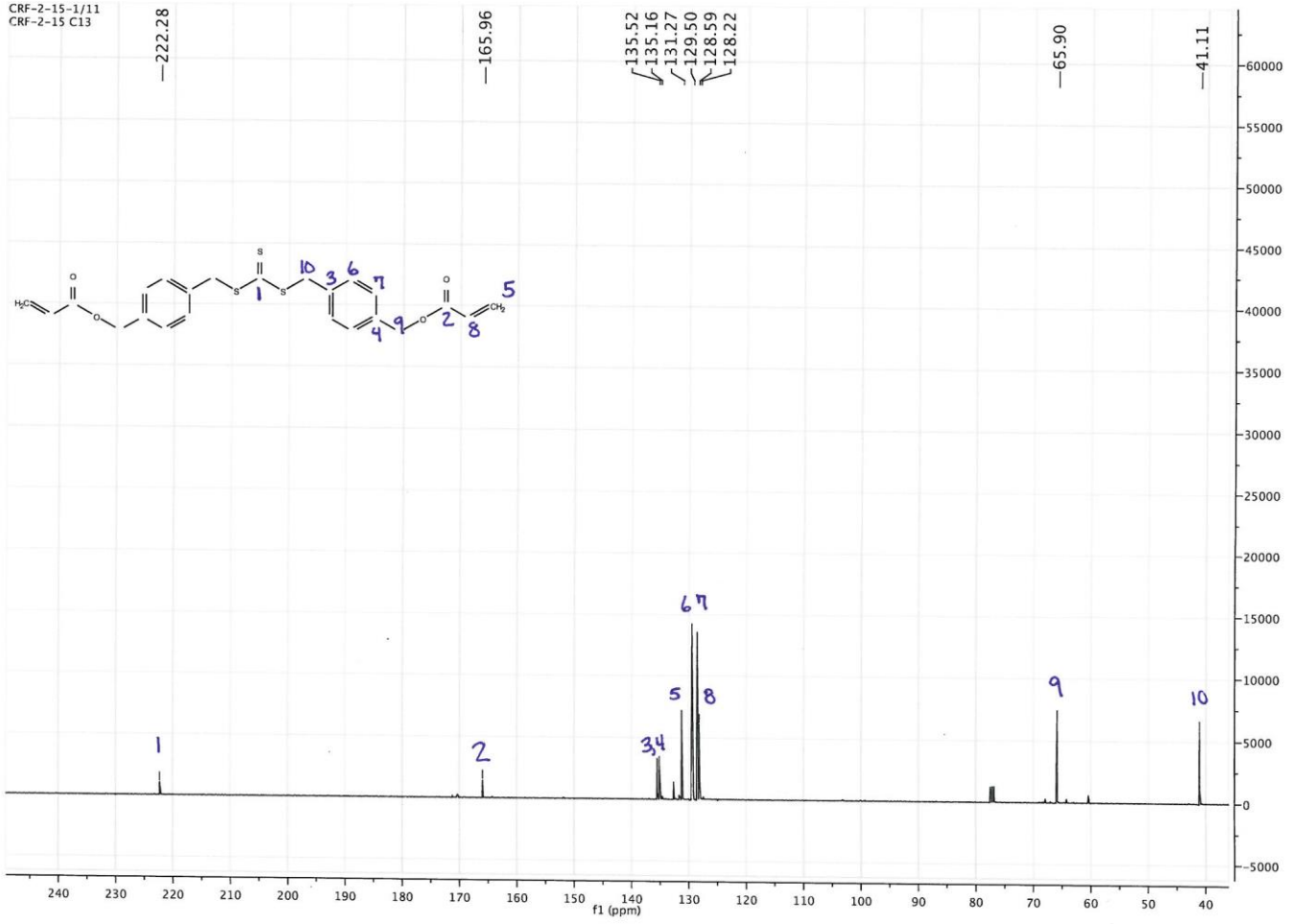

CRF-1-11C13
13C OBSERVE
166.03
140.40
131.39
128.35
116.85
63.33
35.47
29.41
f1 (ppm)


CRF-2-11-7/40
CRF-2-11 Purified 2x H1
7.34
7.34
7.34
7.33
7.32
7.32
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.26
5.20
5.18
5.17
4.65
4.48
4.47
A
D
S
S
S
D
A
B HO
C
OH B
C
A (m)
7.30
B (t)
5.18
C (s)
4.65
D (d)
4.47
8.00
1.72
3.37
3.62
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

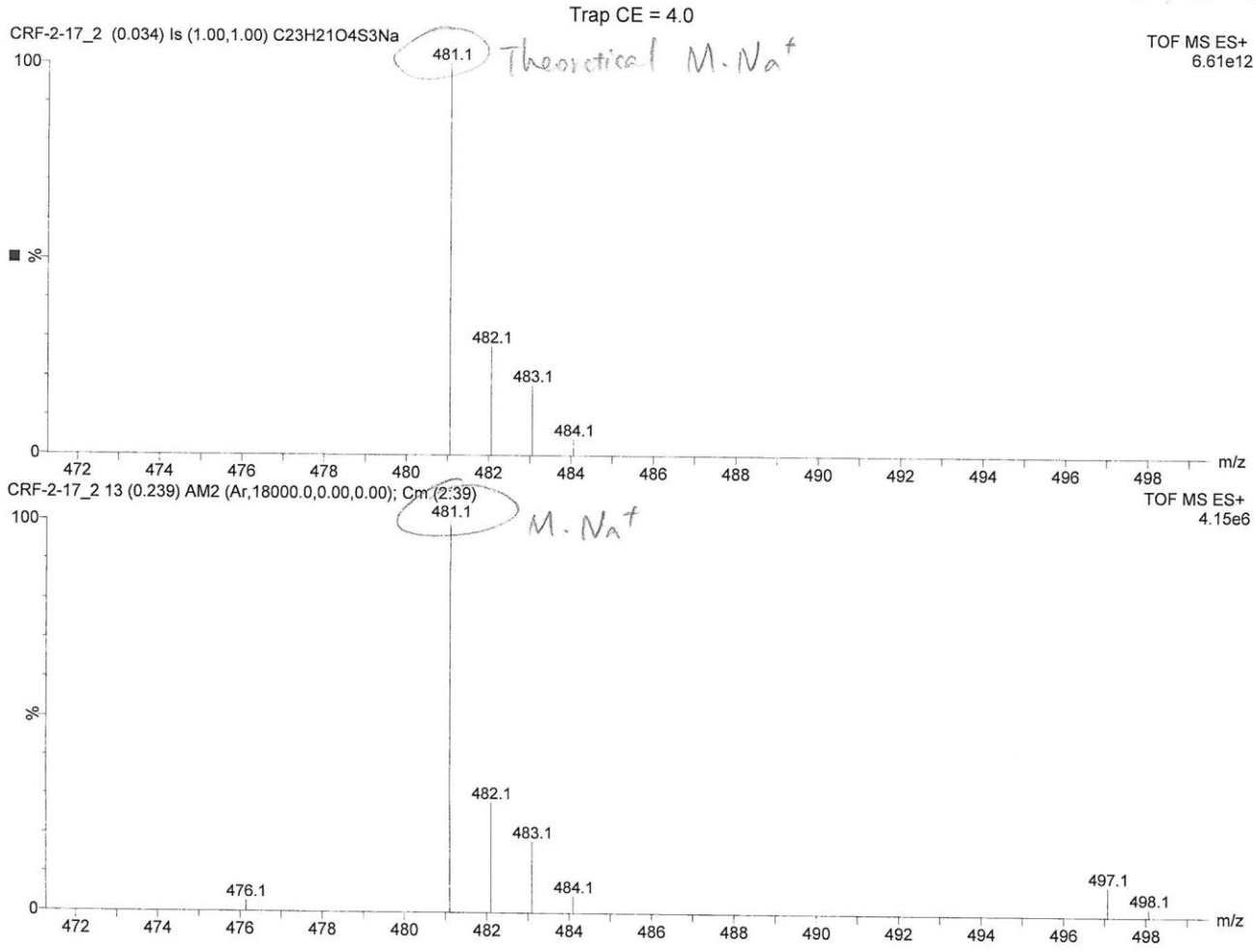

CRF-2-11-8/41
CRF-2-11 Purified 1x H1
222.35
142.14
133.27
129.01
126.69
62.59
40.40
HO
OH
S
1
2
3
4
5
6
7
f1 (ppm)

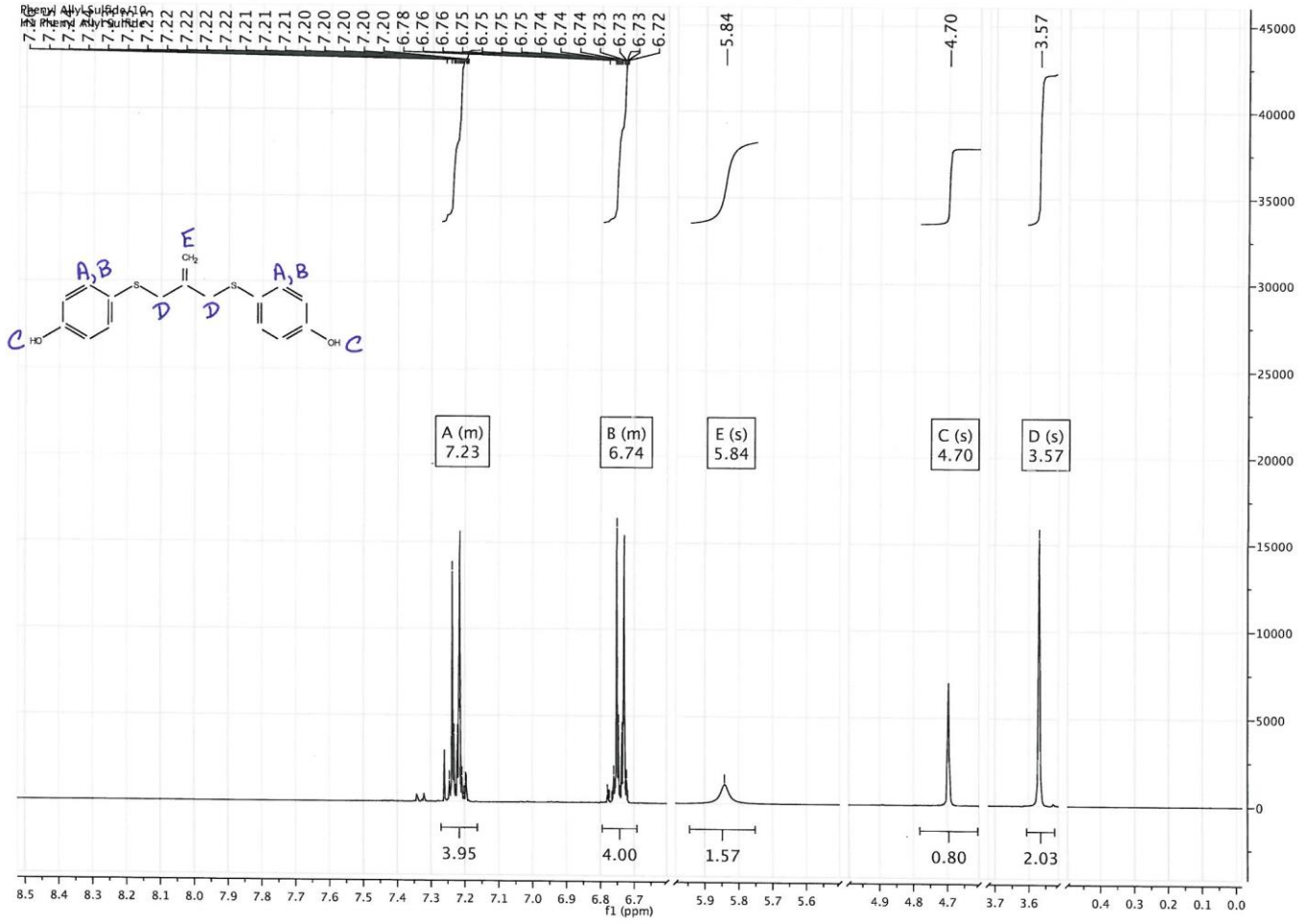

ESI⊕/MeOH
Trap CE = 4.0
CRF-2-11 (0.034) Is (1.00,1.00) C17H17O2S3Na
TOF MS ES+
7.09e12
373.0
M·Na+ theoretical
100
%
374.0
375.0
376.0
0
370
371
372
373
374
375
376
377
378
379
m/z
CRF-2-11 23 (0.409) AM2 (Ar,18000.0,0.00,0.00); Cm (2:56)
TOF MS ES+
1.72e6
373.1
M·Na+
100
%
374.1
375.1
370.4
376.1
376.3
378.3
0
370
371
372
373
374
375
376
377
378
379
m/z

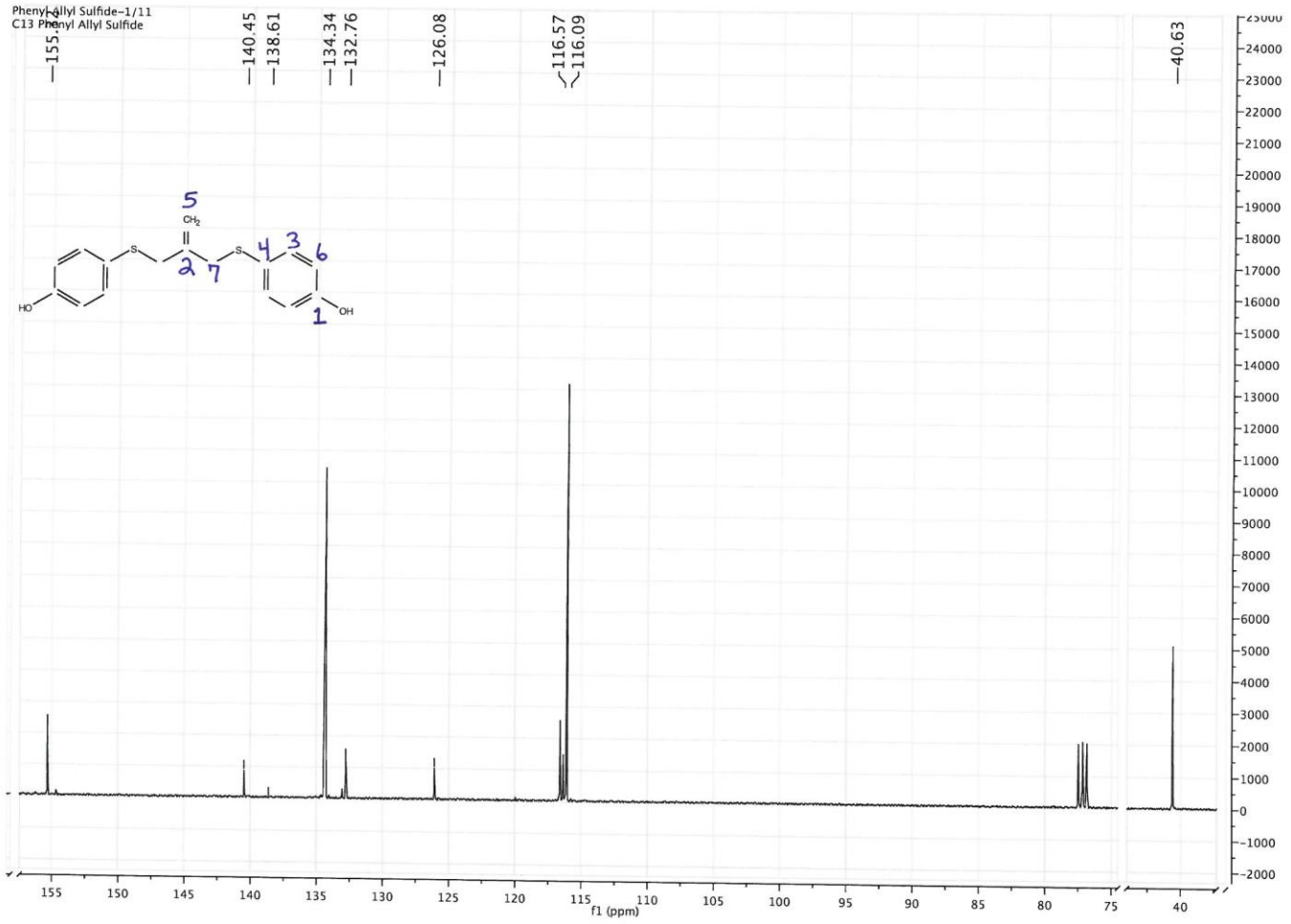

CRF-2-15/10
CRF-2-15 H1
7.33
7.33
7.32
7.32
7.31
6.46
6.46
6.42
6.41
6.19
6.16
5.85
5.85
5.83
5.83
5.17
4.60
4.59
4.58
4.58
4.57
4.57
A (m) 7.32
B (dd) 6.44
C (dd) 6.15
D (dd) 5.84
E (s) 5.17
F (s) 4.60
8.05
2.15
2.04
2.17
4.05
4.00
f1 (ppm)


CRF-2-15-1/11
CRF-2-15 C13
222.28
165.96
135.52
135.16
131.27
129.50
128.59
128.22
65.90
41.11
f1 (ppm)

ESI (+) /MeOH


Trap CE = 4.0
CRF-2-17_2 (0.034) Is (1.00,1.00) C23H21O4S3Na
481.1
Theoretical M.Na+
TOF MS ES+
6.61e12
100
%
0
482.1
483.1
484.1
472 474 476 478 480 482 484 486 488 490 492 494 496 498
m/z
CRF-2-17_2 13 (0.239) AM2 (Ar,18000.0,0.00,0.00); Cm (2:39)
481.1
M.Na+
TOF MS ES+
4.15e6
100
%
0
482.1
483.1
476.1
484.1
497.1
498.1
472 474 476 478 480 482 484 486 488 490 492 494 496 498
m/z


A (m)
7.23
B (m)
6.74
E (s)
5.84
C (s)
4.70
D (s)
3.57
3.95
4.00
1.57
0.80
2.03
f1 (ppm)

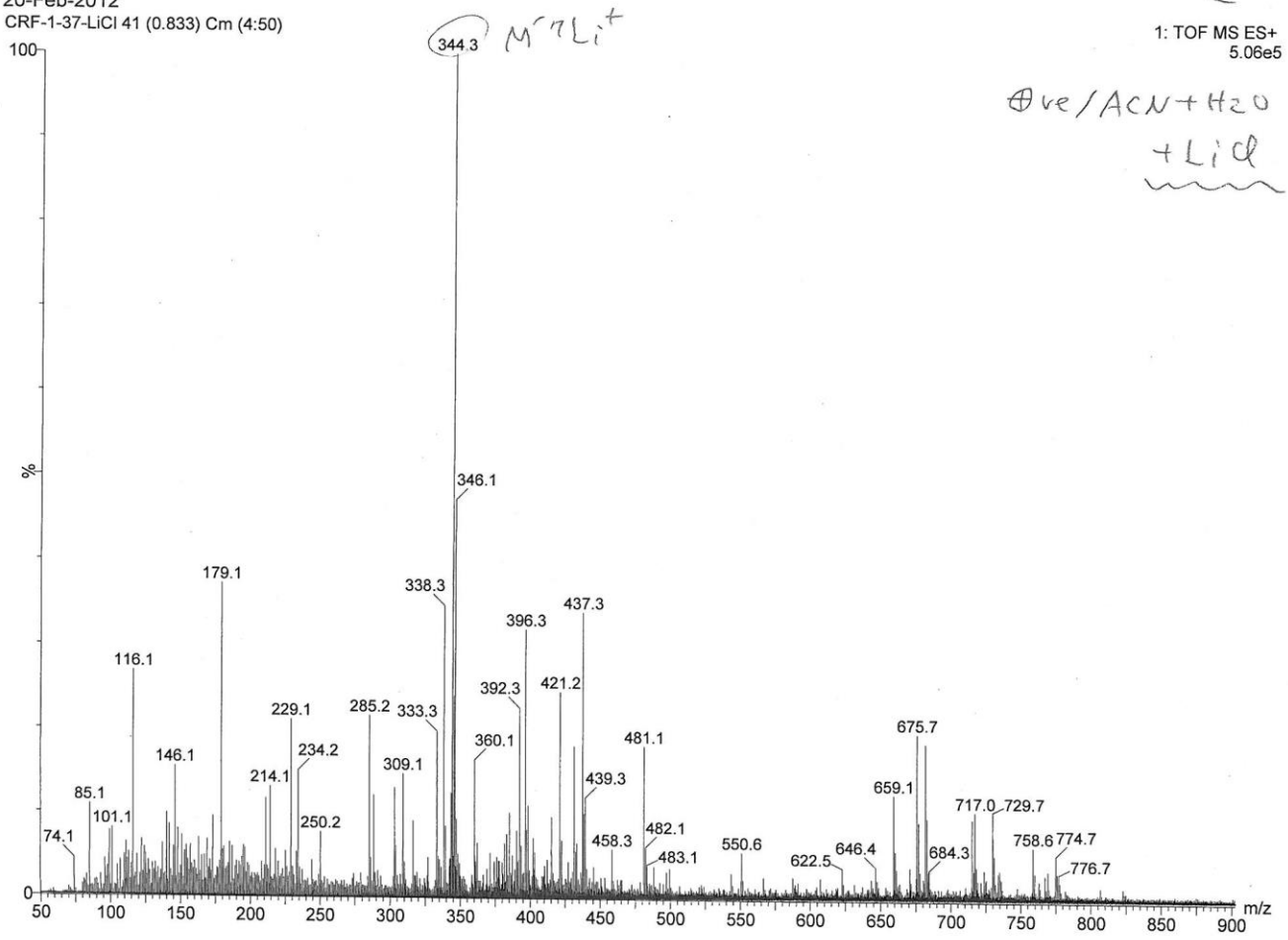

Phenyl Allyl Sulfide-1/11
C13 Phenyl Allyl Sulfide
155.33
140.45
138.61
134.34
132.76
126.08
116.57
116.09
40.63
HO
OH
S
S
CH2
1
2
3
4
5
6
7
f1 (ppm)

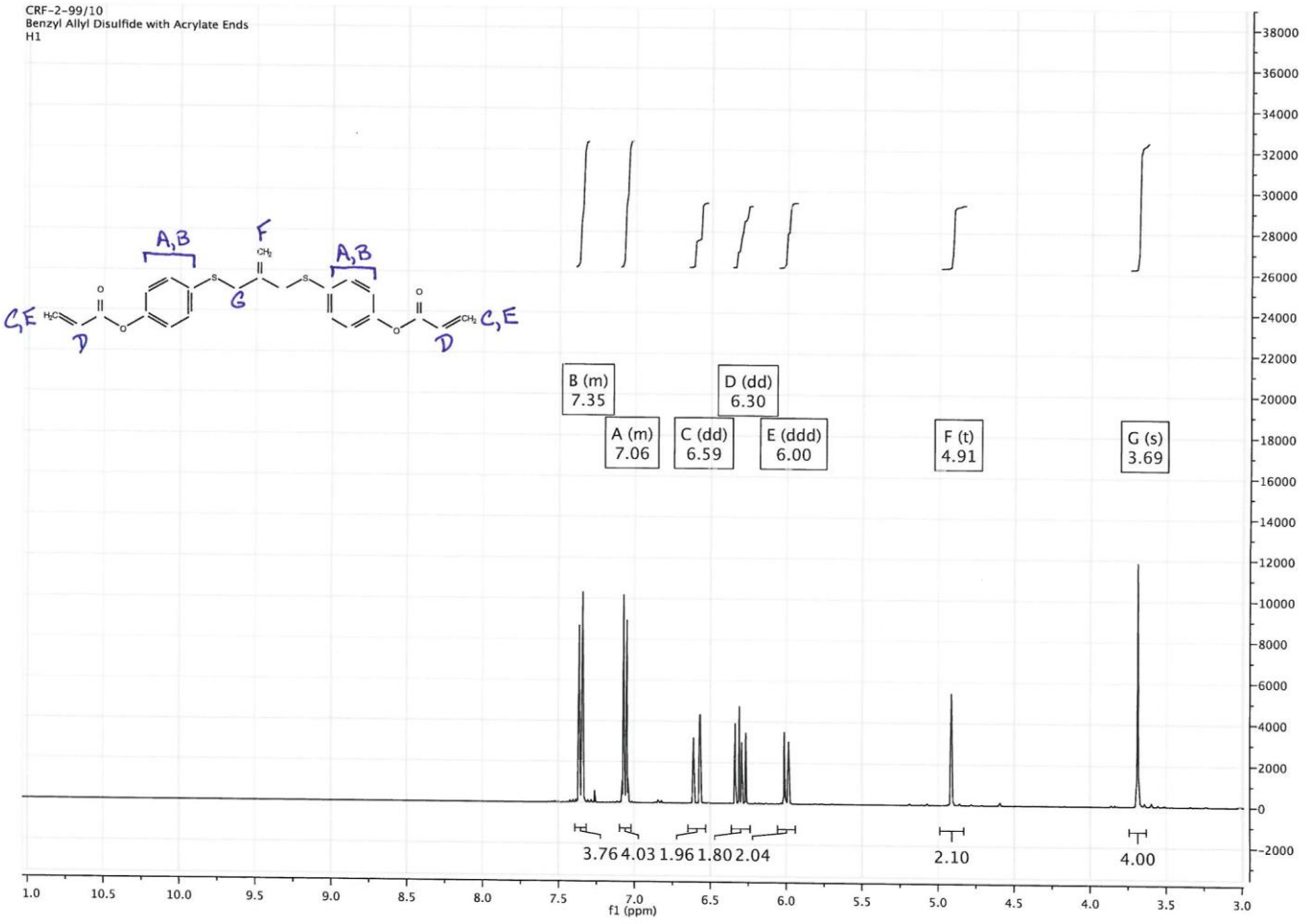
Fenoli :sample cone 20V
20-Feb-2012
CRF-1-37-LiCl 41 (0.833) Cm (4:50)

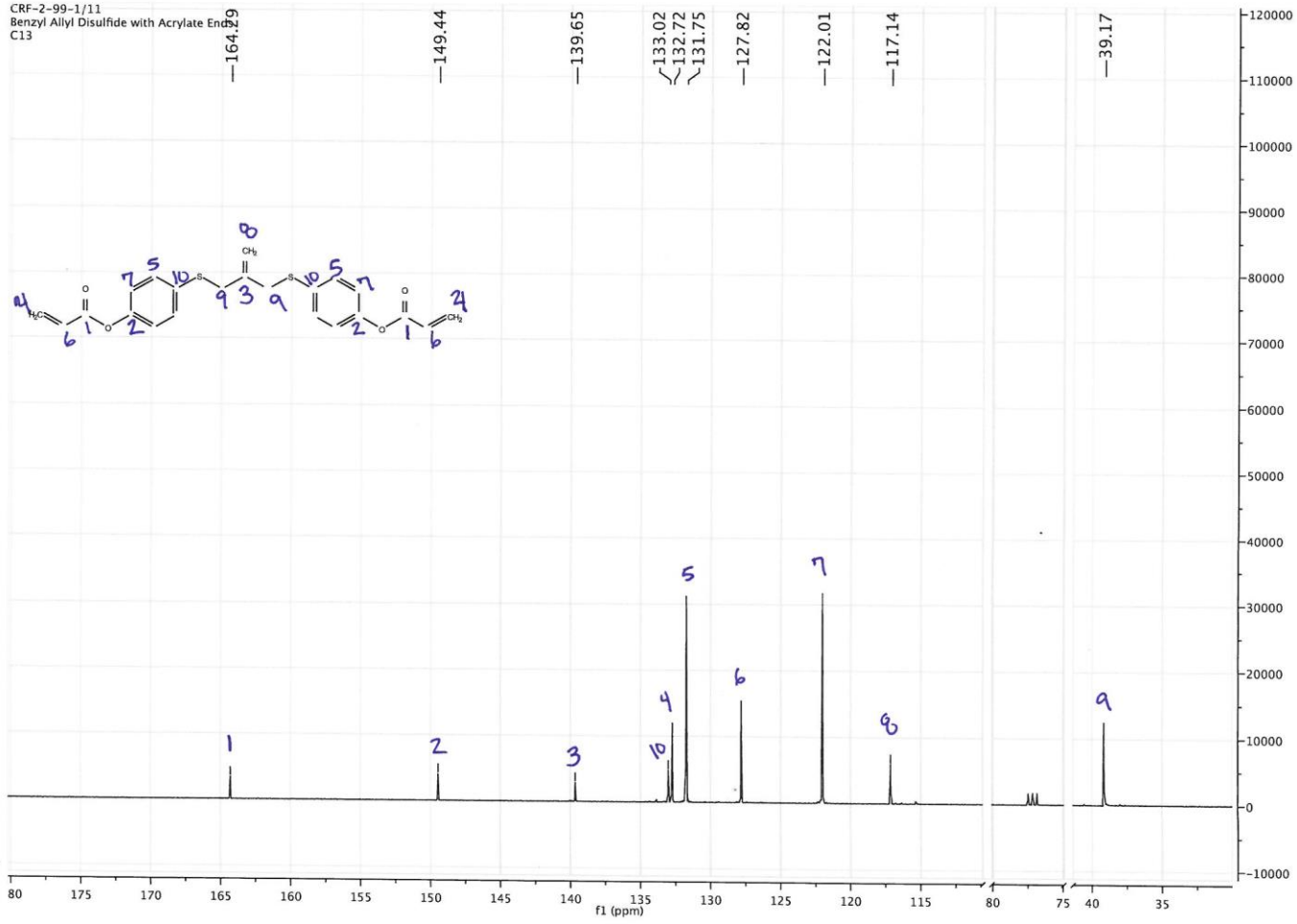
2

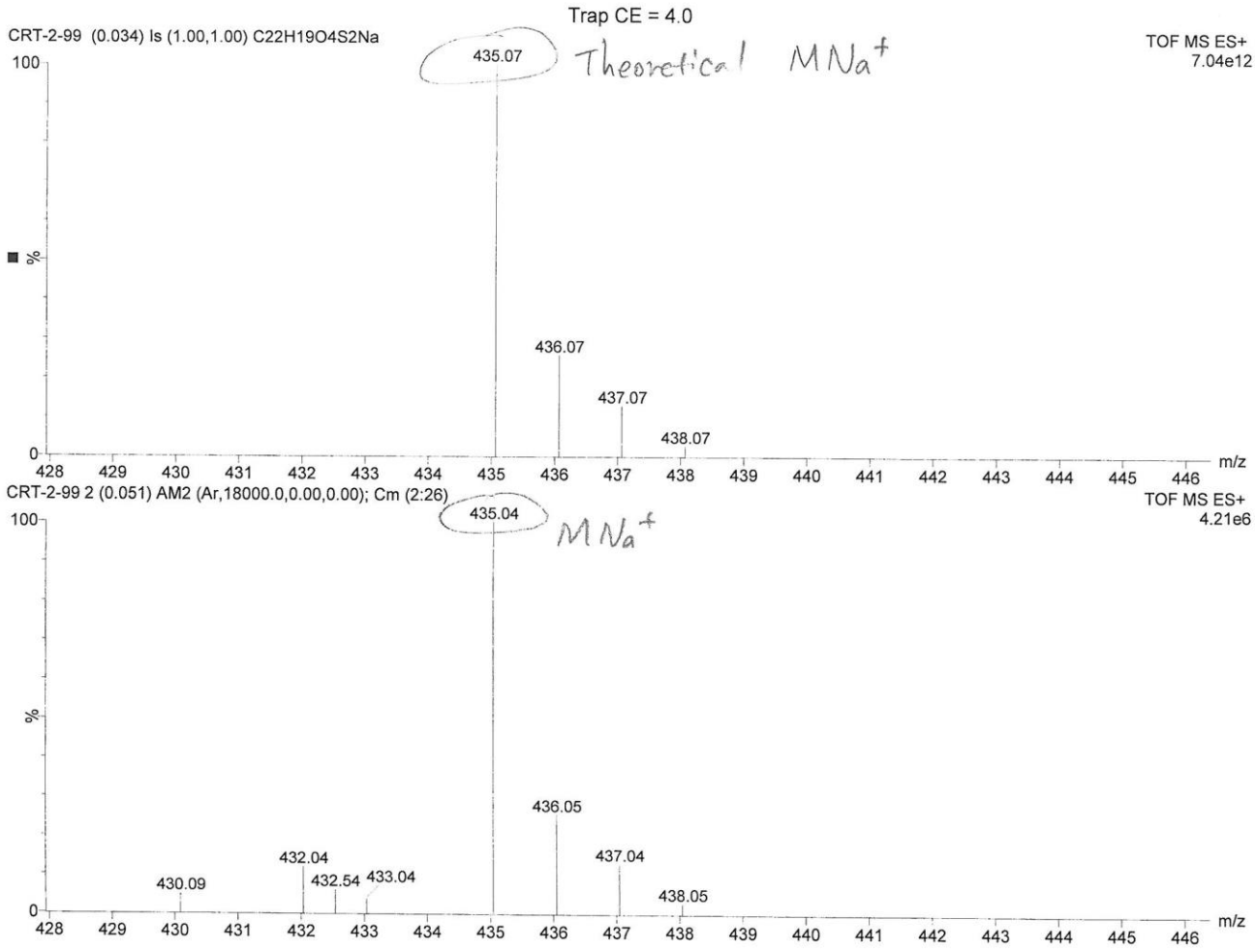
1: TOF MS ES+
5.06e5

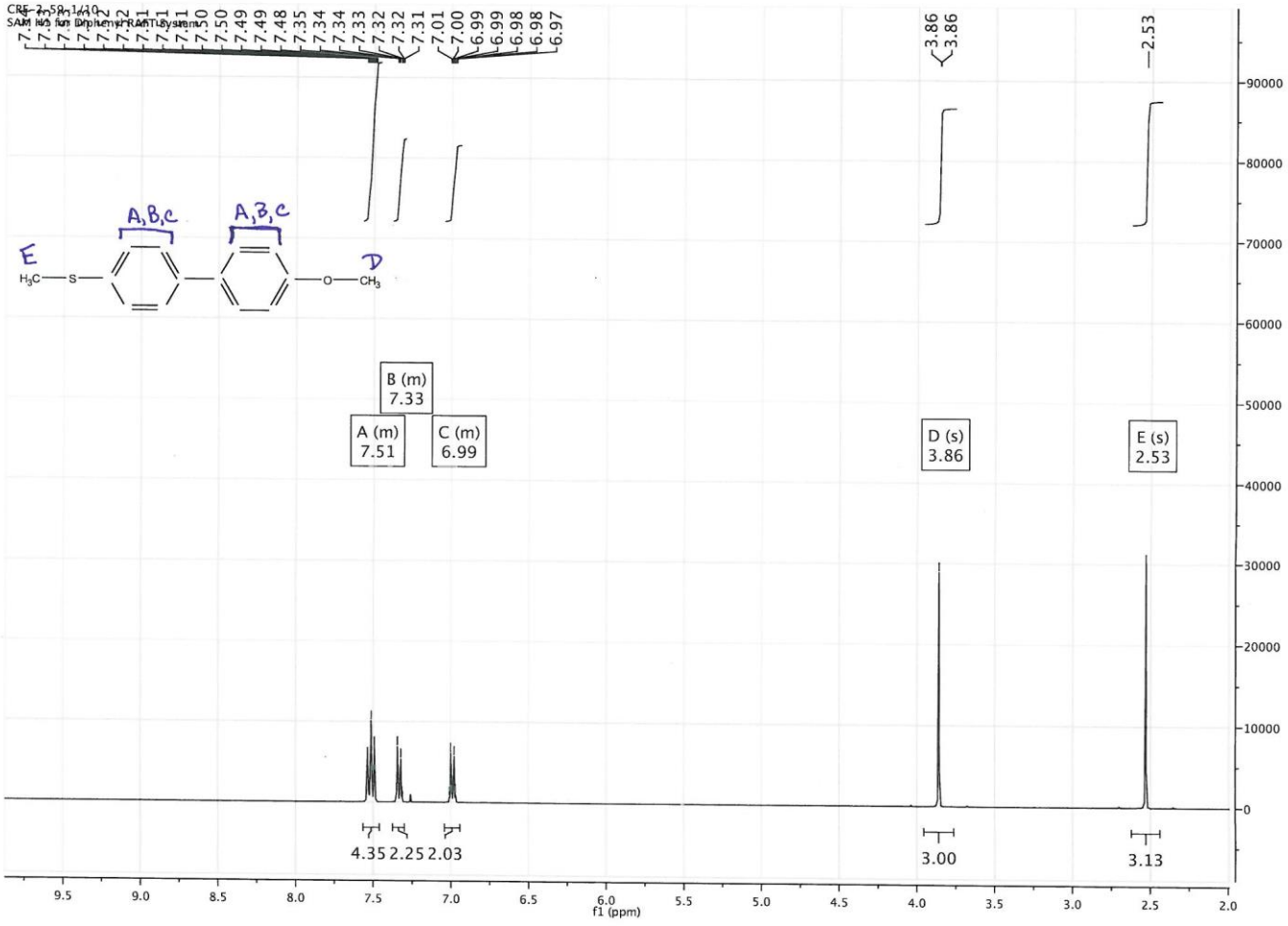
⊕ve/ACN+H2O
+LiCl

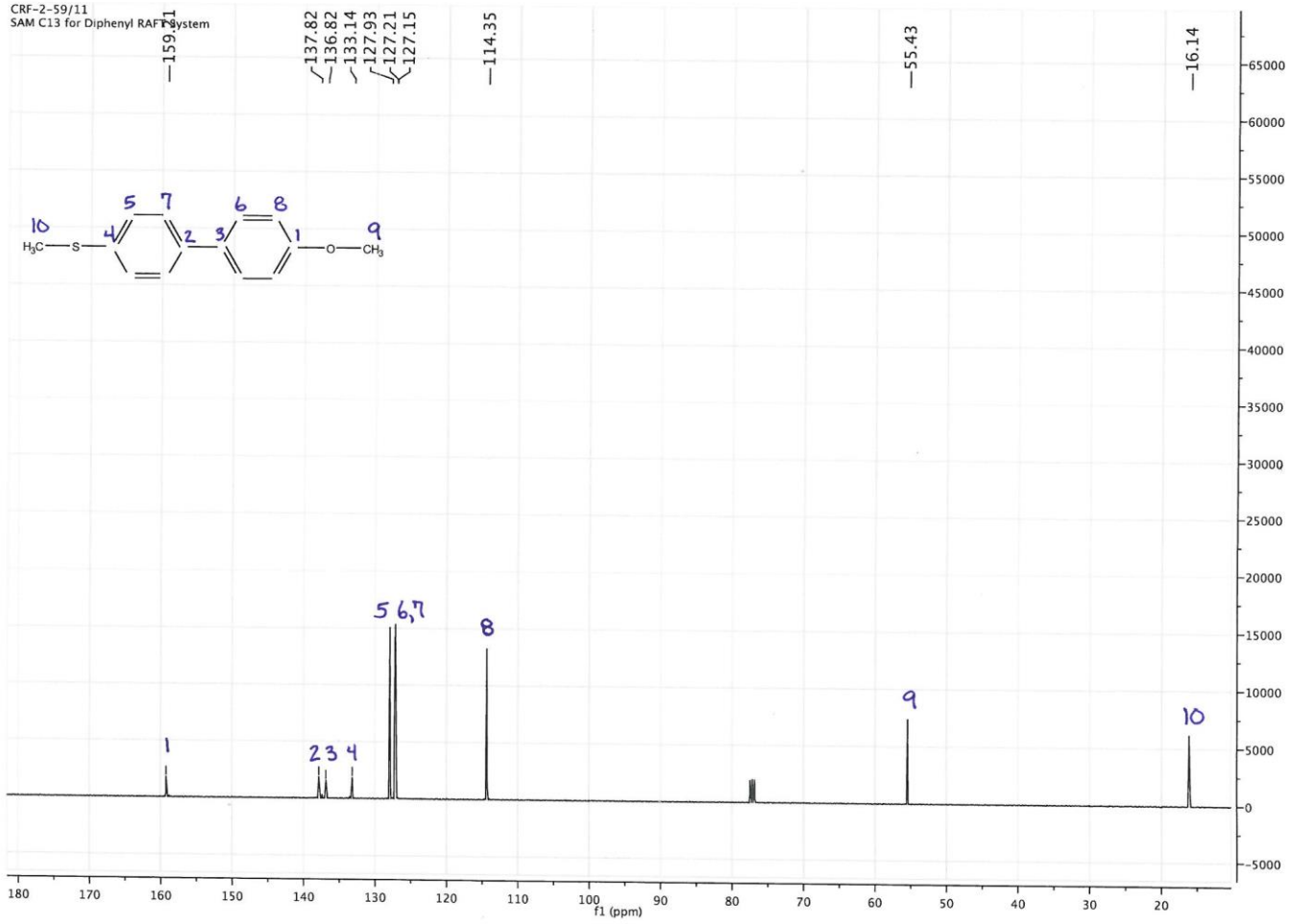


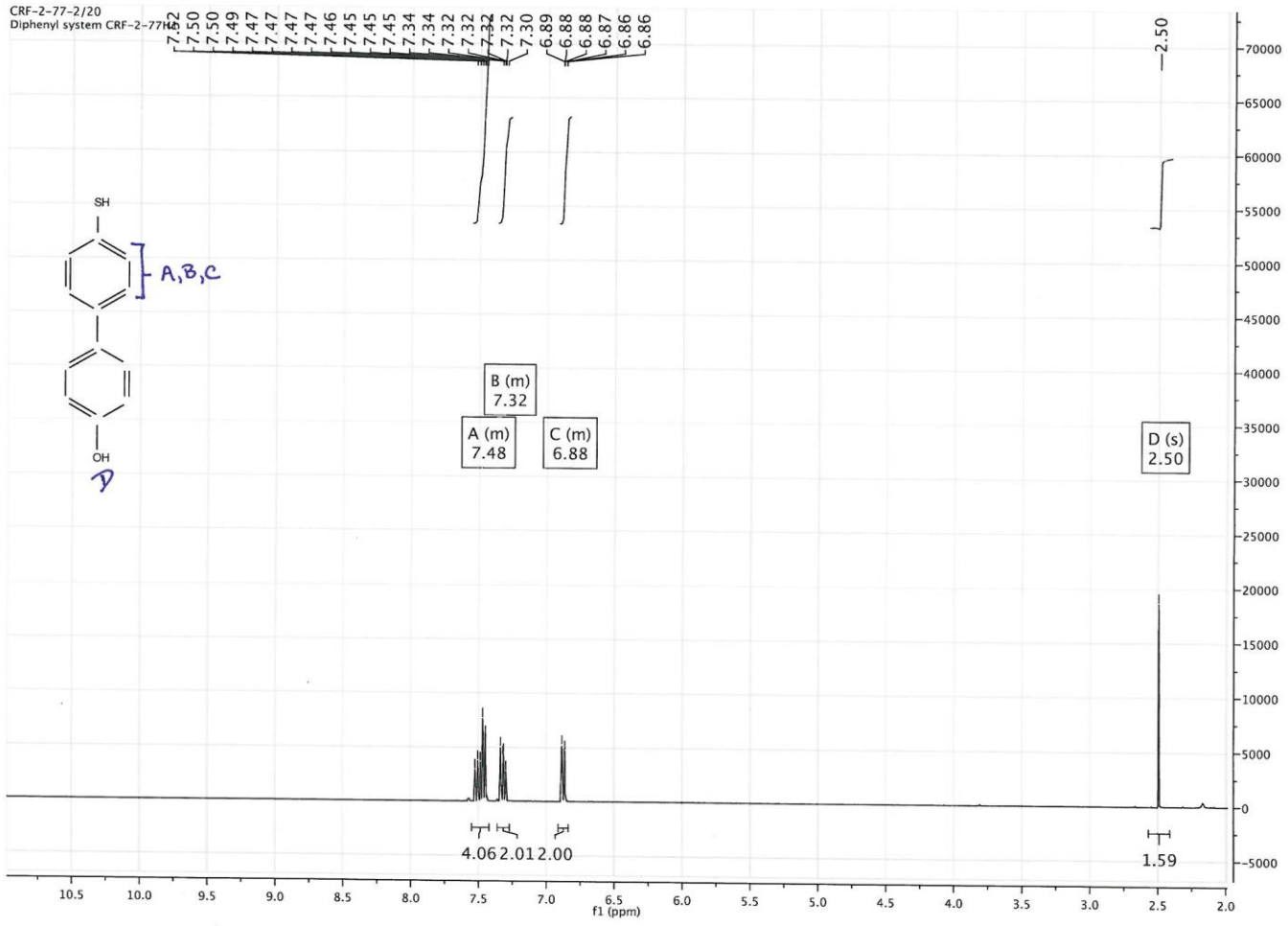

CRF-2-99/10
Benzyl Allyl Disulfide with Acrylate Ends
H1
A,B
F
A,B
C,E
G
D
D
C,E
B (m)
7.35
A (m)
7.06
C (dd)
6.59
D (dd)
6.30
E (ddd)
6.00
F (t)
4.91
G (s)
3.69
3.76 4.03 1.96 1.80 2.04
2.10
4.00
f1 (ppm)

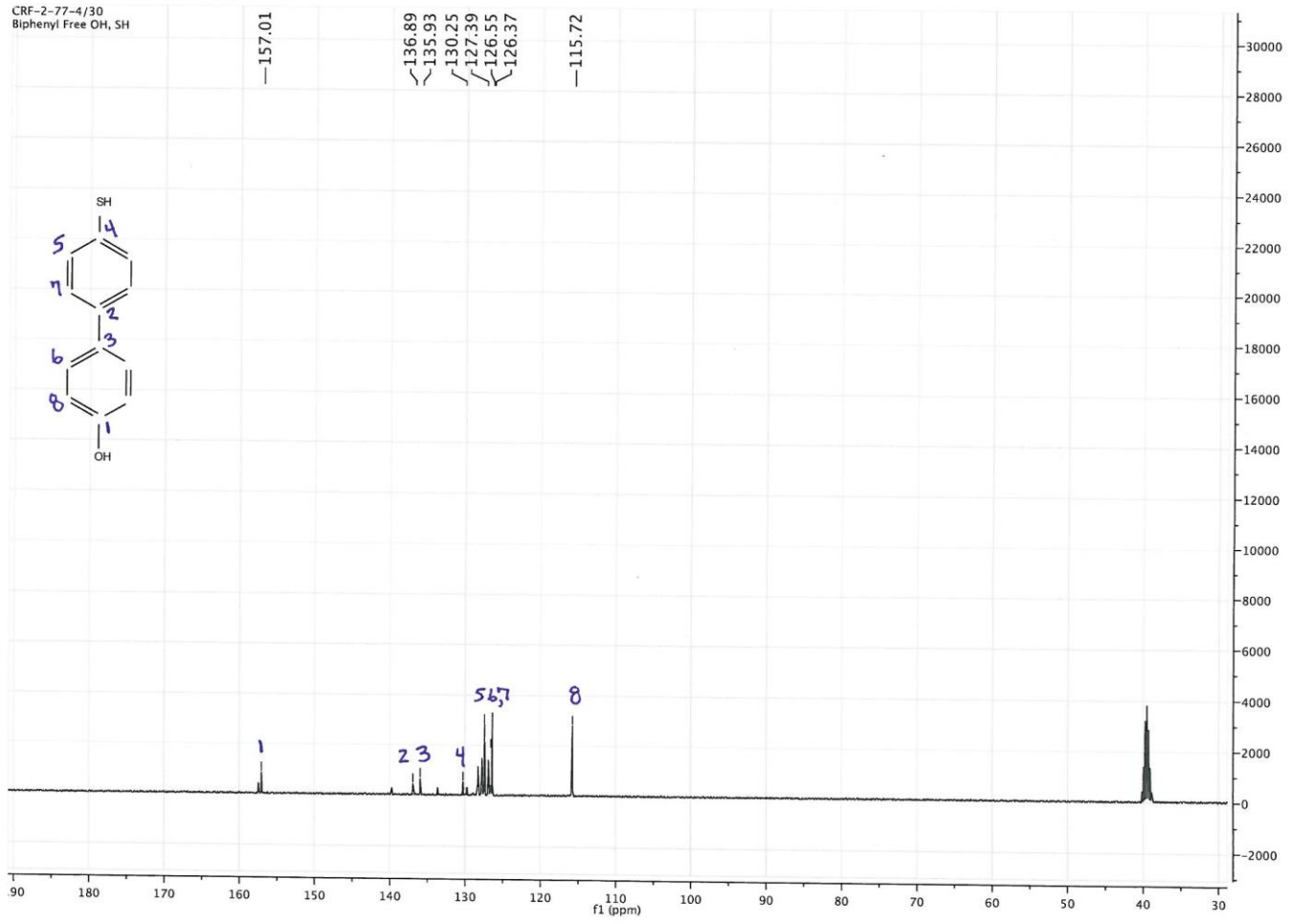

CRF-2-99-1/11
Benzyl Allyl Disulfide with Acrylate End
C13
164.29
149.44
139.65
133.02
132.72
131.75
127.82
122.01
117.14
39.17
f1 (ppm)


Trap CE = 4.0
CRT-2-99 (0.034) Is (1.00,1.00) C22H19O4S2Na
435.07
Theoretical MNa+
TOF MS ES+
7.04e12
100
%
436.07
437.07
438.07
0
428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446
m/z
CRT-2-99 2 (0.051) AM2 (Ar,18000.0,0.00,0.00); Cm (2:26)
435.04
MNa+
TOF MS ES+
4.21e6
100
%
436.05
432.04
437.04
430.09
432.54
433.04
438.05
0
428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446
m/z


A,B,C
A,B,C
E
D
B (m)
7.33
A (m)
7.51
C (m)
6.99
D (s)
3.86
E (s)
2.53
4.35
2.25
2.03
3.00
3.13
f1 (ppm)

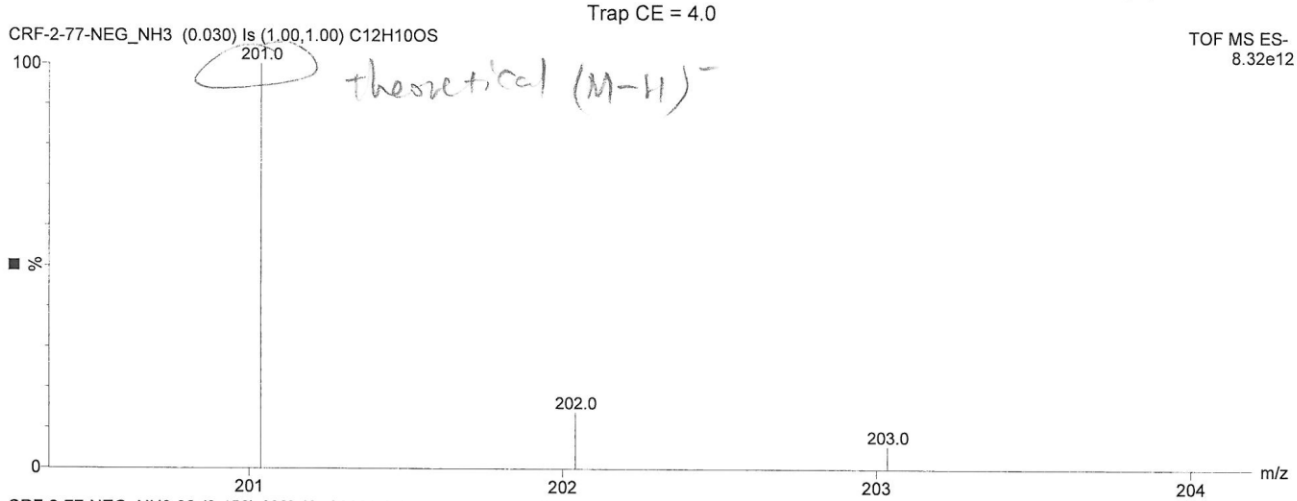

CRF-2-59/11
SAM C13 for Diphenyl RAFT system
159.71
137.82
136.82
133.14
127.93
127.21
127.15
114.35
55.43
16.14
10
5
7
6
8
4
2
3
1
9
H3C
S
O
CH3
1
2 3 4
5 6,7
8
9
10
f1 (ppm)

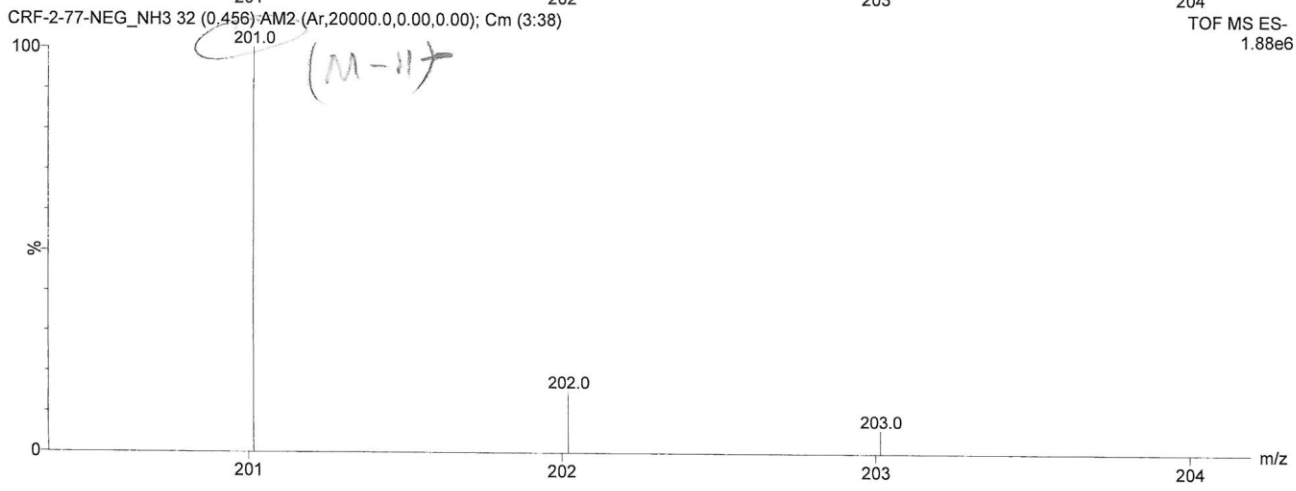

CRF-2-77-2/20
Diphenyl system CRF-2-77-H2
7.52
7.50
7.50
7.49
7.47
7.47
7.47
7.47
7.46
7.45
7.45
7.45
7.34
7.34
7.32
7.32
7.32
7.32
7.30
6.89
6.88
6.88
6.87
6.86
6.86
2.50
SH
A,B,C
OH
D
B (m)
7.32
A (m)
7.48
C (m)
6.88
D (s)
2.50
4.06
2.01
2.00
1.59
f1 (ppm)

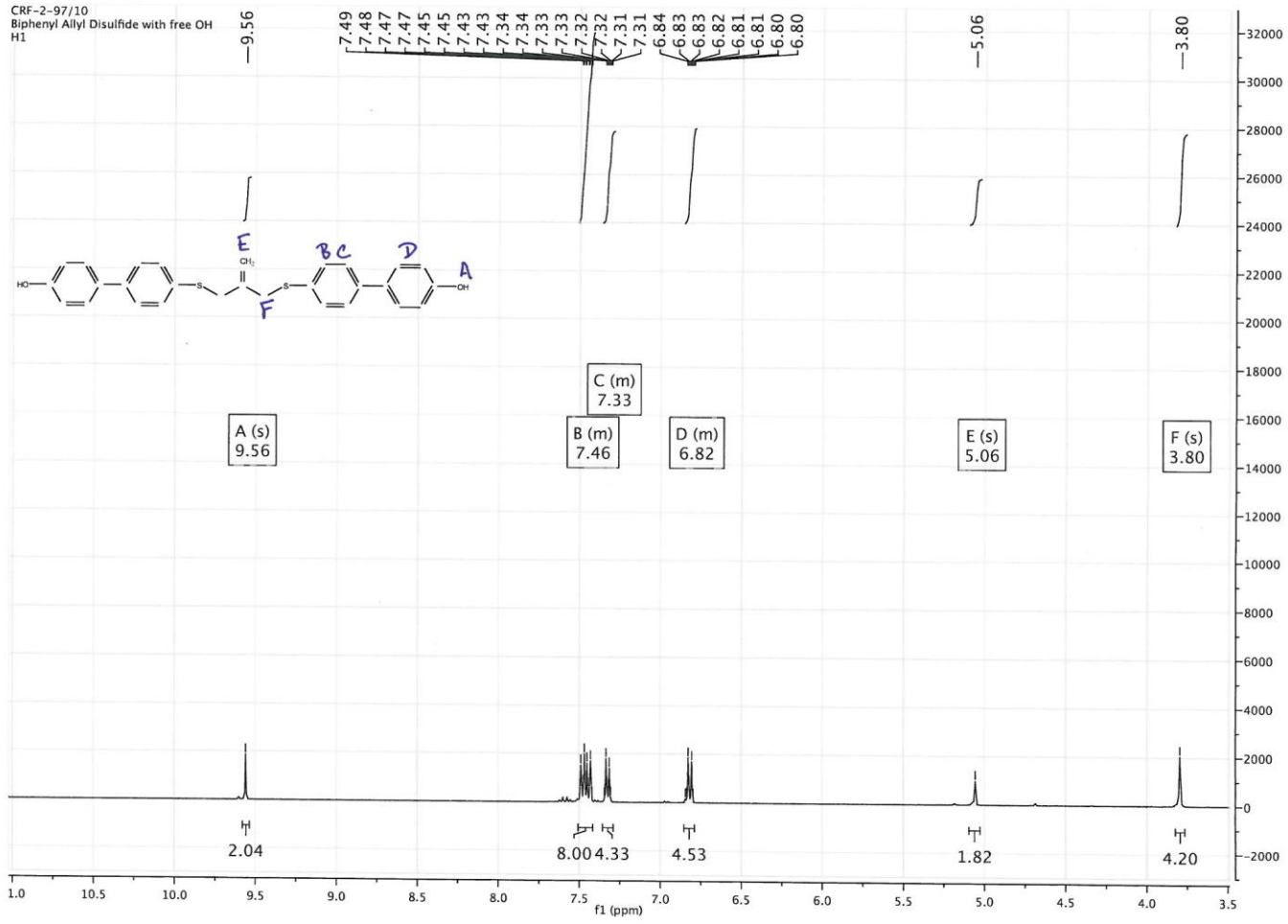

CRF-2-77-4/30
Biphenyl Free OH, SH
157.01
136.89
135.93
130.25
127.39
126.55
126.37
115.72
SH
OH
1
2 3
4
5,6,7
8
f1 (ppm)

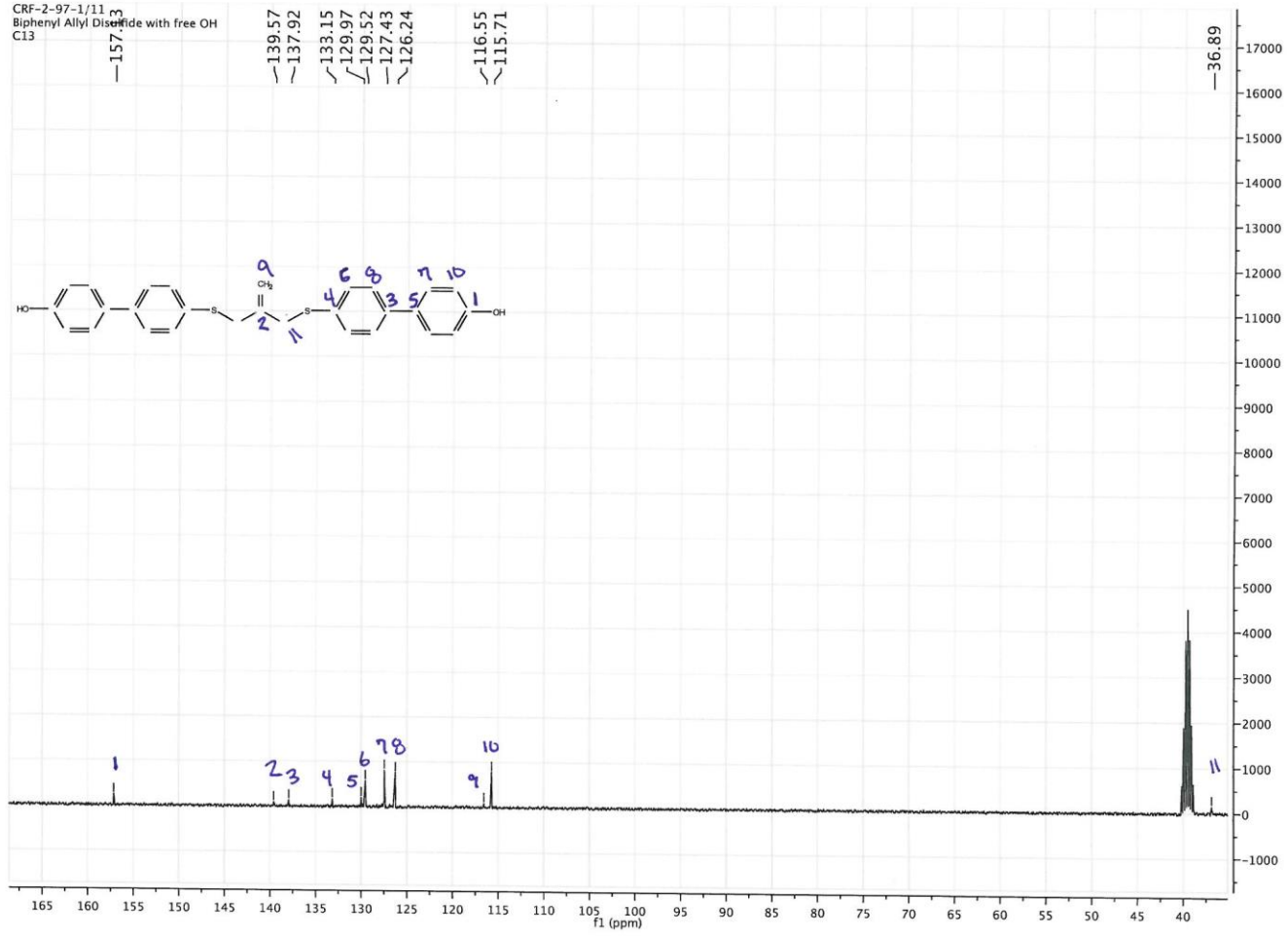
ESI (-)

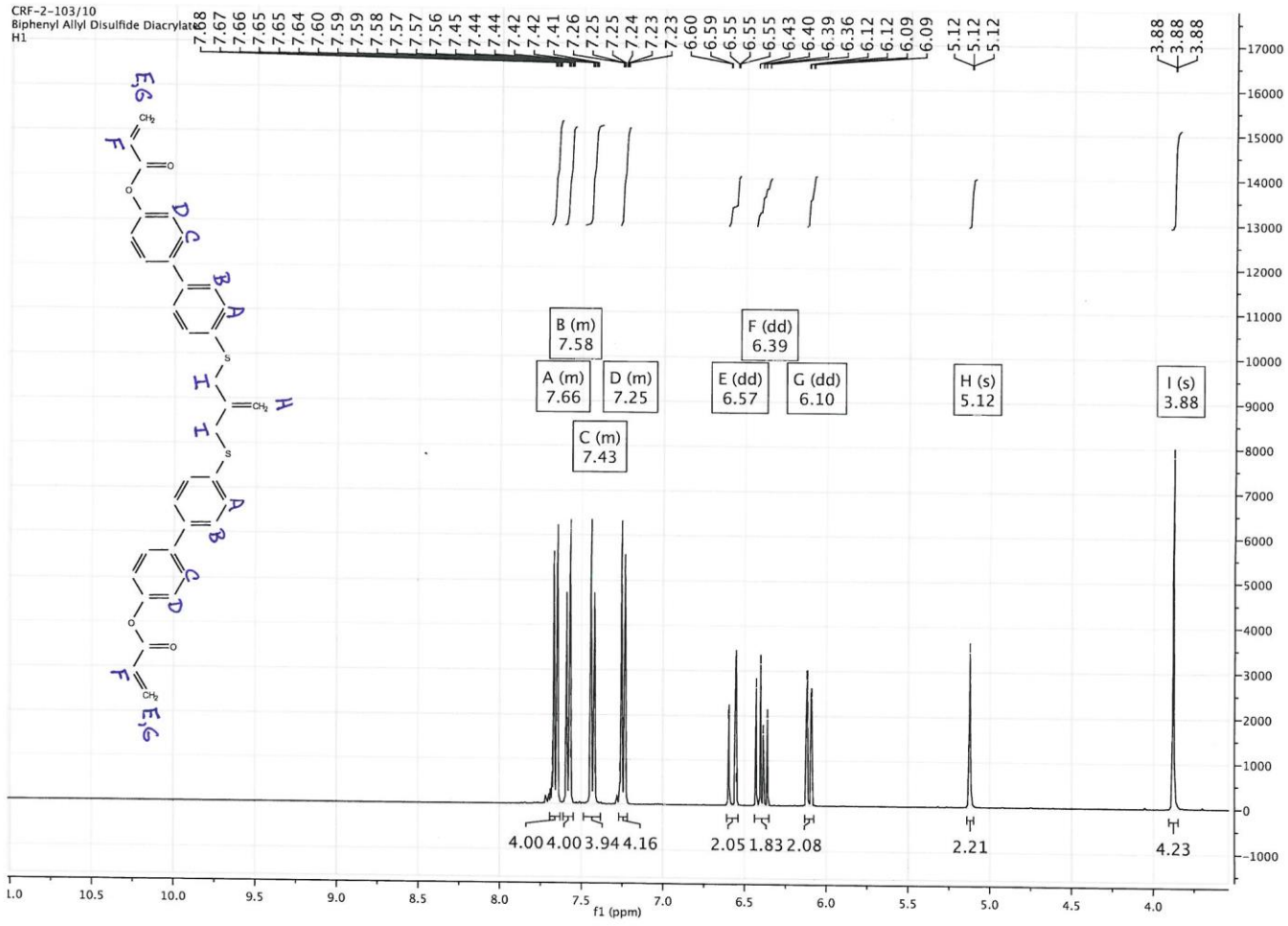
Trap CE = 4.0

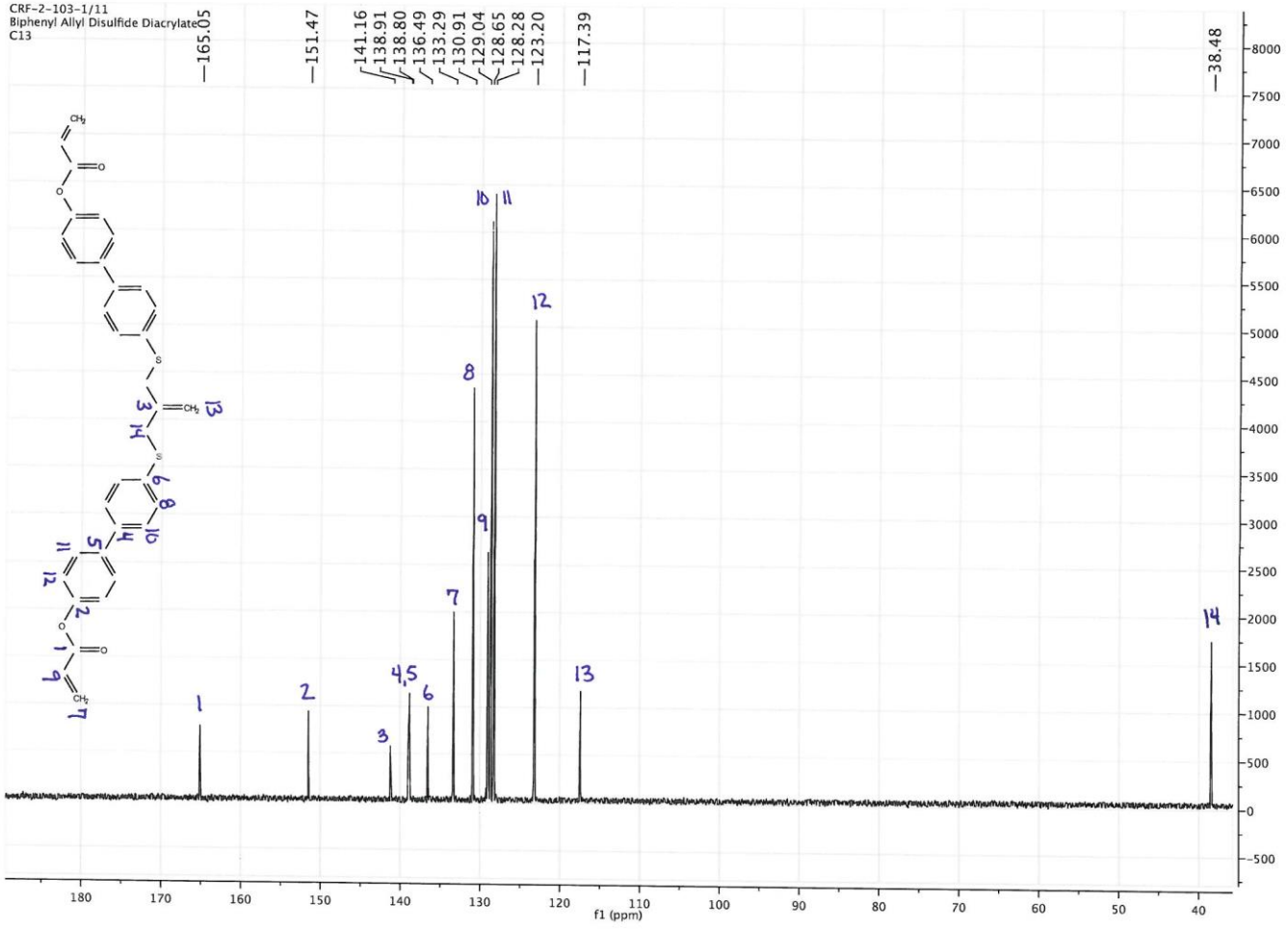


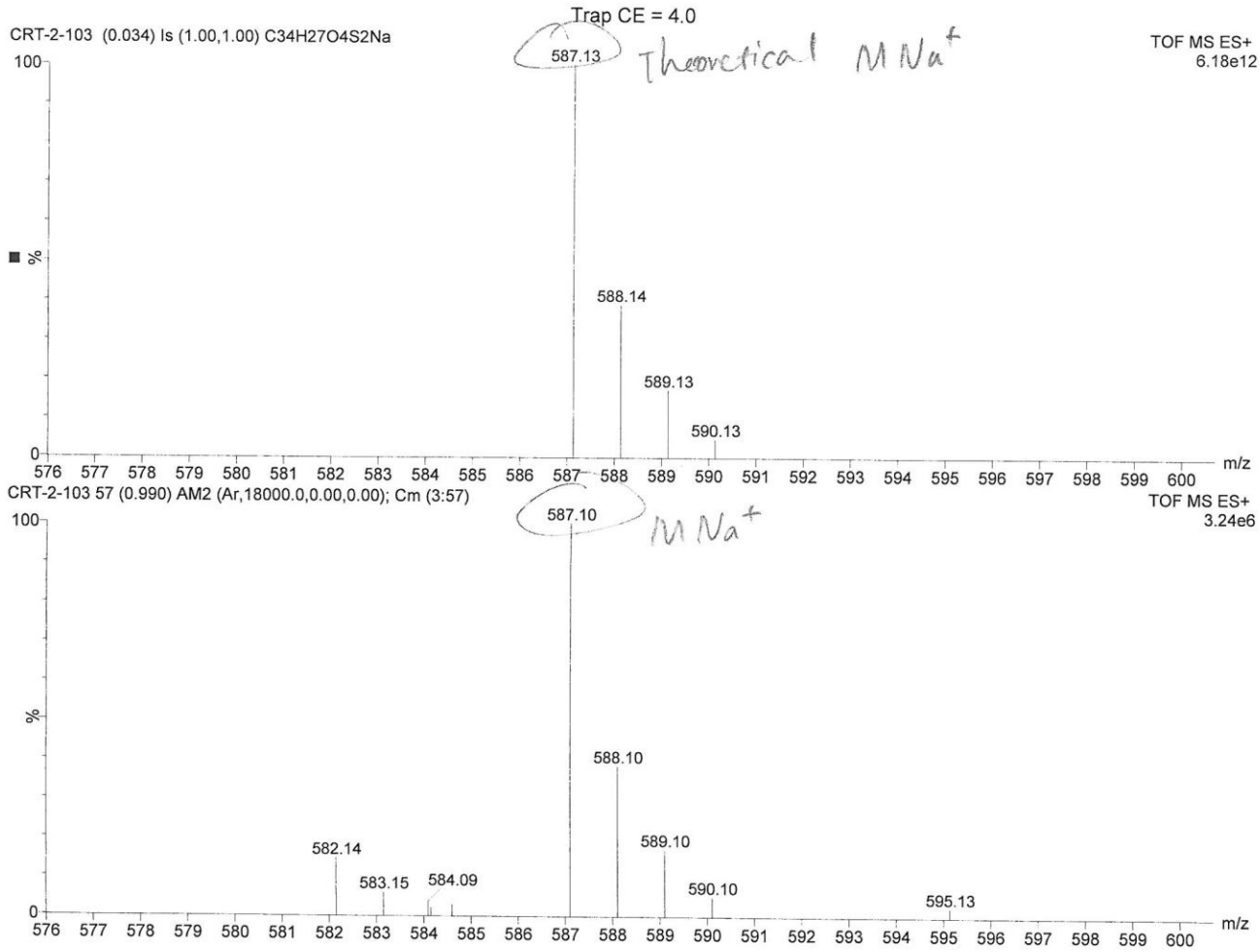


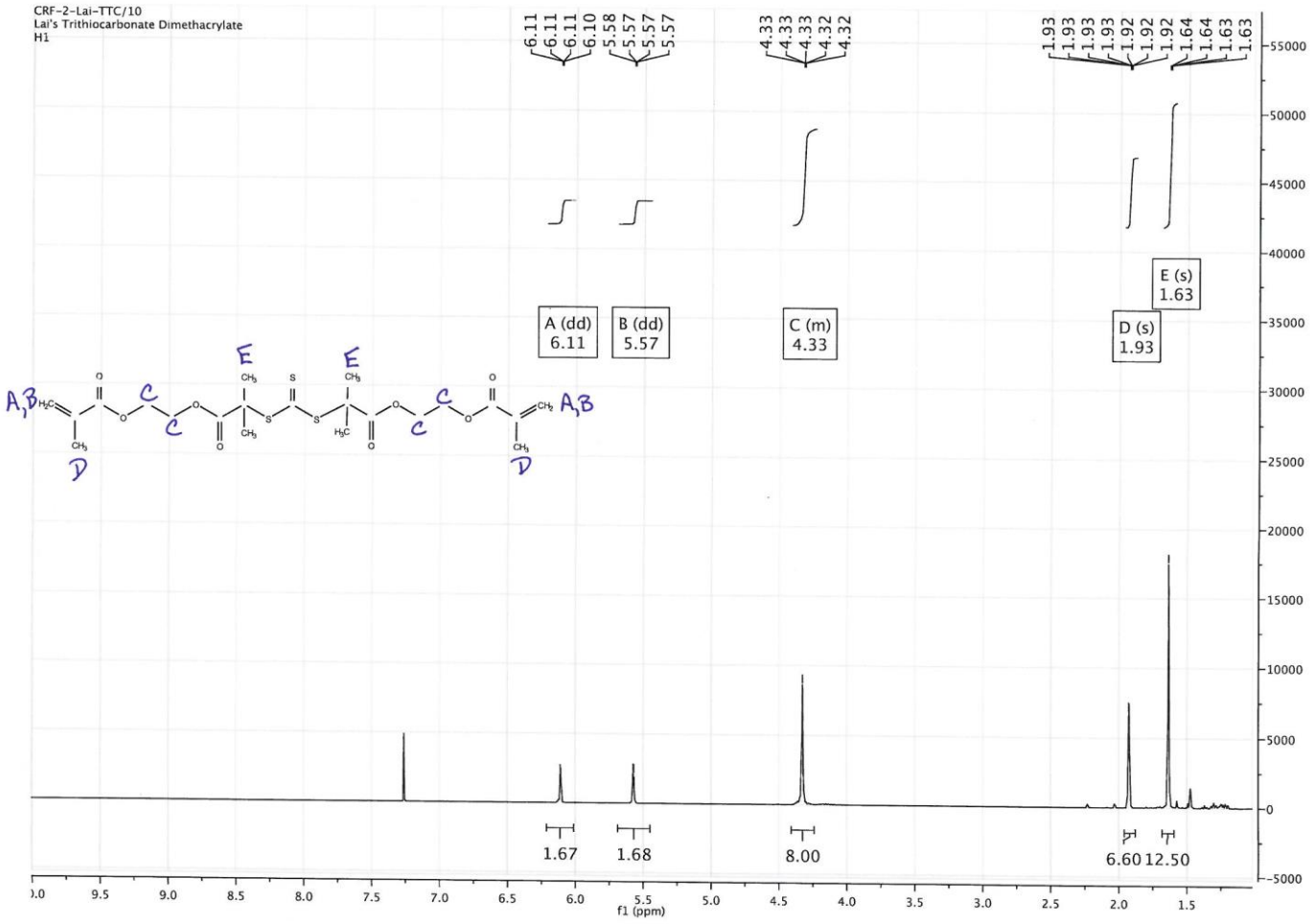

CRF-2-97/10
Biphenyl Allyl Disulfide with free OH
H1
9.56
7.49
7.48
7.47
7.47
7.45
7.45
7.43
7.43
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
6.84
6.83
6.83
6.82
6.81
6.81
6.80
6.80
5.06
3.80
E
BC
D
A
F
A (s)
9.56
C (m)
7.33
B (m)
7.46
D (m)
6.82
E (s)
5.06
F (s)
3.80
2.04
8.00
4.33
4.53
1.82
4.20
f1 (ppm)

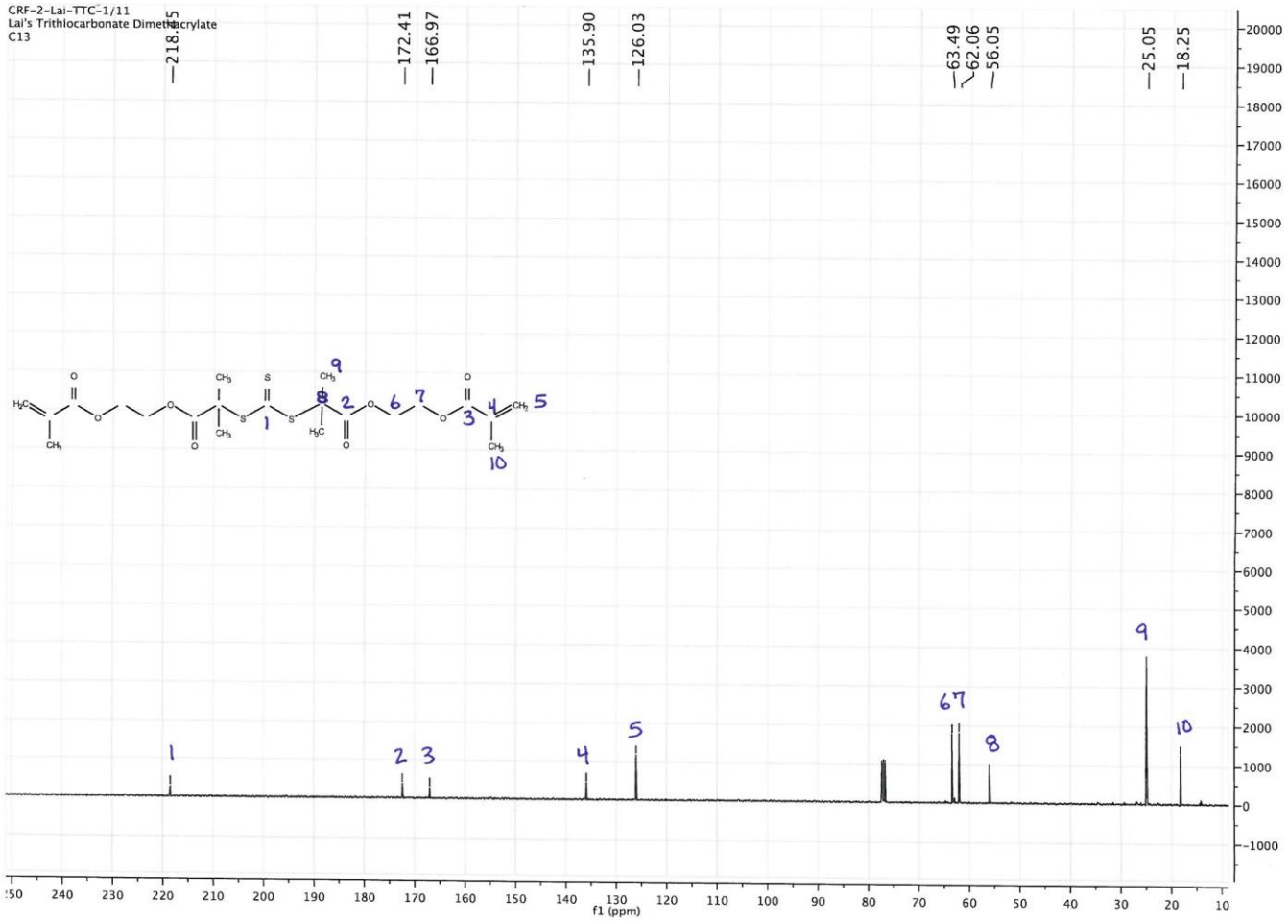

CRF-2-97-1/11
Biphenyl Allyl Disulfide with free OH
C13
157.33
139.57
137.92
133.15
129.97
129.52
127.43
126.24
116.55
115.71
36.89
f1 (ppm)

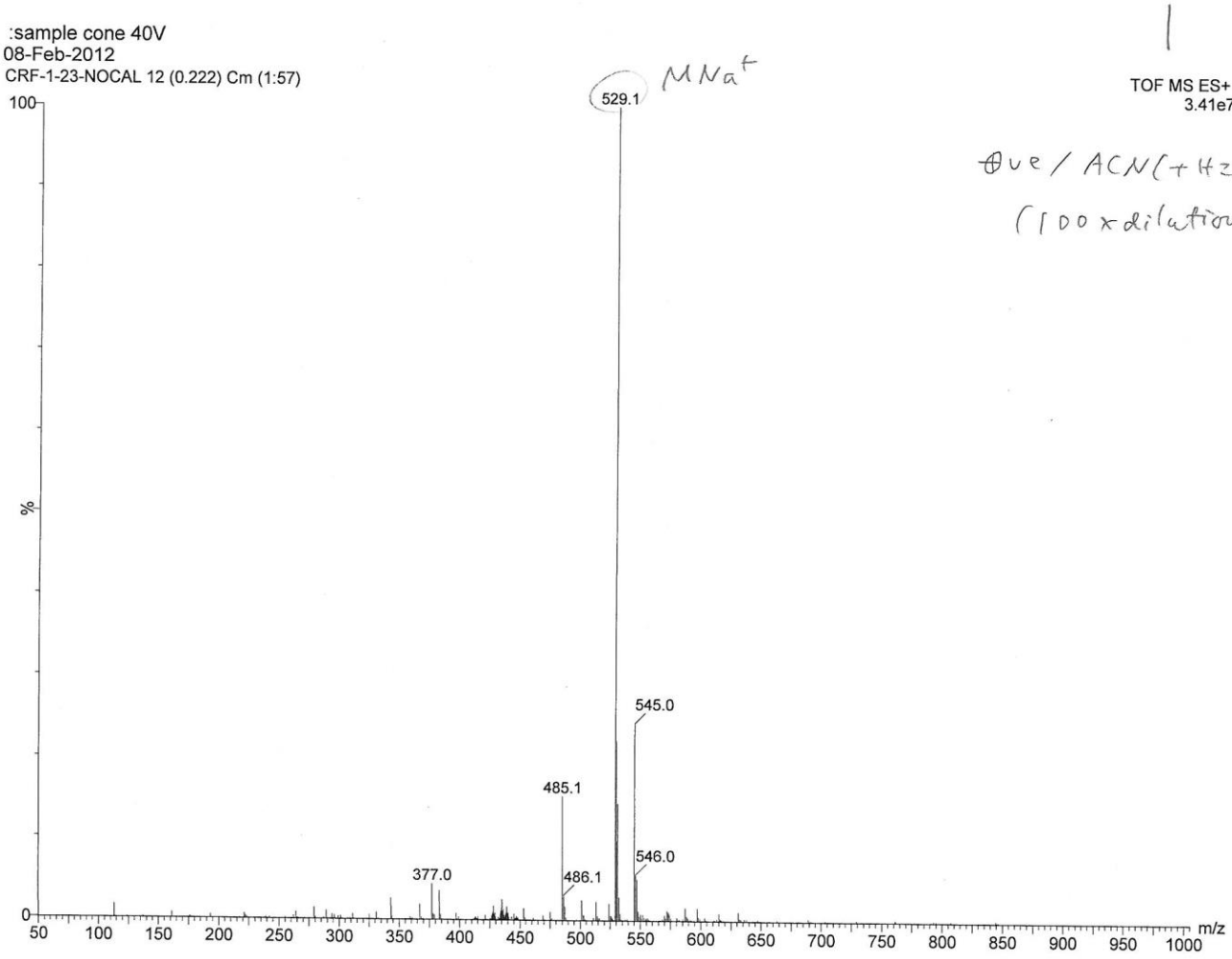

CRF-2-103/10
Biphenyl Allyl Disulfide Diacrylate
H1
B (m)
7.58
A (m)
7.66
D (m)
7.25
C (m)
7.43
F (dd)
6.39
E (dd)
6.57
G (dd)
6.10
H (s)
5.12
I (s)
3.88
4.00 4.00 3.94 4.16
2.05 1.83 2.08
2.21
4.23
f1 (ppm)


CRF-2-103-1/11
Biphenyl Allyl Disulfide Diacrylate
C13
165.05
151.47
141.16
138.91
138.80
136.49
133.29
130.91
129.04
128.65
128.28
123.20
117.39
38.48
f1 (ppm)


Trap CE = 4.0
CRT-2-103 (0.034) Is (1.00,1.00) C34H27O4S2Na
587.13
Theoretical MNa+
TOF MS ES+
6.18e12
100
%
588.14
589.13
590.13
0
576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600
m/z
CRT-2-103 57 (0.990) AM2 (Ar,18000.0,0.00,0.00); Cm (3:57)
587.10
MNa+
TOF MS ES+
3.24e6
100
%
588.10
582.14
589.10
583.15
584.09
590.10
595.13
0
576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600
m/z


CRF-2-Lai-TTC/10
Lai's Trithiocarbonate Dimethacrylate
H1
6.11
6.11
6.11
6.10
5.58
5.57
5.57
5.57
4.33
4.33
4.33
4.32
4.32
1.93
1.93
1.93
1.93
1.92
1.92
1.92
1.64
1.64
1.63
1.63
A (dd)
6.11
B (dd)
5.57
C (m)
4.33
D (s)
1.93
E (s)
1.63
A,B
A,B
C
C
C
C
E
E
D
D
1.67
1.68
8.00
6.60
12.50
f1 (ppm)


CRF-2-Lai-TTC-1/11
Lai's Trithlocarbonate Dimethacrylate
C13
218.45
172.41
166.97
135.90
126.03
63.49
62.06
56.05
25.05
18.25
1
2 3
4
5
67
8
9
10
f1 (ppm)



1

Ave / ACN (+H2O)

(100 x dilution)