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Electronic Supporting Information

A Pd-Mediated ω-alkynone cycloisomerization approach for central tetrahydropyran and synthesis of C(31)–C(48) fragment of Aflastatin A

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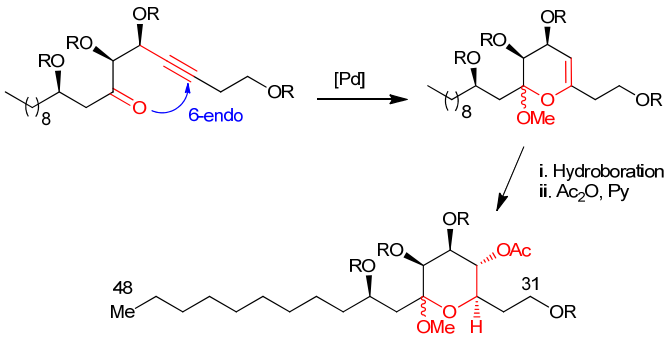

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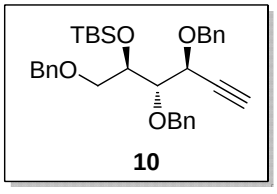
Experimental Section

1. General

Air and/or moisture sensitive reactions were carried out in anhydrous solvents under an atmosphere of argon in oven-dried glassware. All anhydrous solvents were distilled prior to use: dichloromethane and DMF from CaH_2; methanol from Mg cake; THF on Na/benzophenone; triethylamine and pyridine over KOH; acetic anhydride from sodium acetate. Commercial reagents were used without purification. Column chromatography was carried out by using spectrochem silica gel (230–400 mesh). Optical rotations were determined on a Jasco DIP-370 digital polarimeter. Specific optical rotations $[\alpha]_D$ are given in 10^{-1} x deg x cm^2 x g^{-1}. ^1H and ^{13}C NMR spectroscopy measurements were carried out on Bruker AC 200 MHz or Bruker DRX 400 MHz spectrometers, and TMS was used as an internal standard. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from Chloroform-d (δ = 7.25) or TMS and coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. The Multiplicity of ^{13}C NMR signals was assigned with the help of DEPT spectra and the abbreviations used: s = singlet d = doublet t = triplet q = quartet, represent C (quaternary), CH, CH_2 and CH_3 respectively. Mass spectroscopy was carried out on PI QStar Pulsar (Hybrid Quadrupole-TOF LC/MS/MS) and 4800 plus MALDI TOF/TOF Applied Biosystem spectrometer. Elemental analysis data were obtained on a Thermo Finnigan Flash EA 1112 Series CHNS Analyzer.

2. Synthesis of alkyne 10:

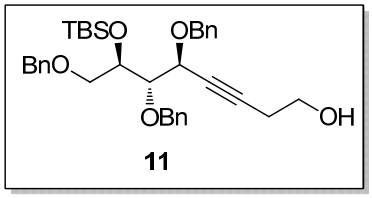


10

To an ice-cooled solution of alcohol **9** (200 mg, 0.48 mmol) and imidazole (186 mg, 2.9 mmol) in anhydrous DMF (2 mL) was added TBSCl (216 mg, 1.44 mmol) and stirred at room temperature for 4 h. Then reaction mixture was diluted with ethyl acetate (20 mL) and washed with water (3 × 5 mL), brine (5 mL), dried over sodium sulphate and evaporated under reduced pressure. The crude was

purified by column chromatography (5:95 ethyl acetate/petroleum ether) to afford compound **10** (210 mg, 82% yield) as a colorless oil. $[\alpha]_D^{25}$ +21.1 (*c* 0.8, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3297, 2917, 2838, 2137, 1642, 1453, 1071, 756, 652 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ –0.08 (s, 6H), 0.71 (s, 9H), 2.42 (d, *J* = 2.2 Hz, 1H), 3.43 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.50 (dd, *J* = 10.0, 2.2 Hz, 1H), 3.74 (dd, *J* = 7.1, 3.7 Hz, 1H), 3.86–3.93 (m, 1H), 4.33 (s, 2H), 4.41 (dd, *J* = 3.7, 2.1 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 7.14–7.28 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ –5.1 (q), –4.3 (q), 18.0 (s), 25.84 (q, 3C), 70.8 (d), 70.9 (t), 71.8 (t), 72.1 (d), 73.2 (t), 74.4 (t), 75.6 (d), 80.3 (s), 81.0 (d), 127.39 (d, 2C), 127.6 (d), 127.70 (d, 2C), 127.95 (d, 2C), 128.01 (d, 2C), 128.14 (d, 2C), 128.23 (d, 2C), 128.31 (d, 2C), 137.6 (s), 138.3 (s), 138.6 (s) ppm; ESI-MS (*m/z*): 530.57 (68% $[M]^+$), 532.63 (100%), 553.59 (45%, $[M+Na]^+$), 569.54 (25% $[M+K]^+$); Anal. Calcd for $C_{33}H_{42}O_4Si$: C, 74.68; H, 7.98; Found: C, 74.63; H, 8.05.

3. Synthesis of alcohol 11:

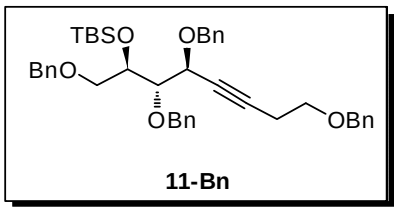


11

At –78 °C, a solution of alkyne **10** (1.3 g, 2.45 mmol) in anhydrous THF (10 mL) was treated with *n*-BuLi (1.84 mL, 1.6 M in hexane, 2.94 mmol) and stirred for 20 minutes and then introduced a solution of $BF_3.Et_2O$ (417 mg, 2.94 mmol) and stirred at –78 °C for 20 minutes. To this, a solution of ethylene oxide (6.2 M) in anhydrous THF (3 mL) was added slowly at –78 °C and the contents stirred for 1 h at the same temperature. Reaction mixture was quenched by adding saturated sodium bicarbonate (1 mL) and partitioned between ethyl acetate (80 mL) and water (20 mL). The organic layer was washed with brine (20 mL), dried over sodium sulphate and evaporated under reduced pressure. The crude was purified by column chromatography (silica 230–400 mesh, 1:4 ethyl acetate/petroleum ether) to afford compound **11** (1.18 g, 84% yield) as a colorless oil. $[\alpha]_D^{25}$ +62.6 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3436, 3017, 2929, 2858, 2112, 1455, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ –0.02 (s, 6H), 0.77 (s, 9H), 1.99 (bs, 1H), 2.46 (dt, *J* = 1.6, 6.2 Hz, 2H), 3.47 (dd, *J* = 4.9, 10.0

Hz, 1H), 3.53 (dd, J = 2.8, 10.0 Hz, 1H), 3.62 (t, J = 6.2, 1H), 3.79 (dd, J = 3.7, 7.0 Hz, 1H), 3.8–83.95 (m, 1H), 4.40 (bs, 2H), 4.44–4.50 (m, 2H), 4.64 (d, J = 11.4 Hz, 1H), 4.81 (d, J = 11.9 Hz, 1H), 4.89 (d, J = 11.4 Hz, 1H), 7.20–7.29 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ –5.1 (q), –4.3 (q), 18.0 (s), 23.2 (t), 25.81 (q, 3C), 60.9 (t), 70.8 (t), 71.2 (d), 71.8 (t), 72.1 (d), 73.2 (t), 74.4 (t), 78.8 (s), 81.3 (d), 84.7 (s), 127.4 (d), 127.5 (d), 127.6 (d), 127.73 (d, 2C), 127.91 (d, 2C), 128.08 (d, 2C), 128.19 (d, 4C), 128.31 (d, 2C), 137.8 (s), 138.3 (s), 138.5 (s) ppm; MALDI TOF: 575.65 (100% $[M+1]^+$), 597.30 (14% $[M+Na]^+$); HRMS: 613.2752 ($[M+K]^+$) calculated, 613.2789 ($[M+K]^+$) observed; Anal. Calcd for $C_{35}H_{46}O_5Si$: C, 73.13; H, 8.07; Found: C, 73.35; H, 7.98.

4. Synthesis of benzyl ether 11-Bn:

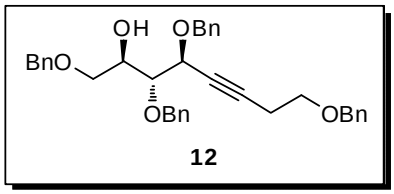


11-Bn

To a solution of alcohol **11** (540 mg, 0.94 mmol) in anhydrous DMF (5 mL), sodium hydride (60% oil suspension, 75 mg, 1.88 mmol) was added at 0 °C and allowed to stir for 10 minutes. To this cold reaction mixture benzyl bromide (192 mg, 1.13 mmol) was added slowly and stirred at room temperature for 2 h. The reaction mixture was partitioned between ethyl acetate (50 mL) and water (10 mL). Organic layer was washed with water (3 × 10 mL), brine, dried over sodium sulphate and evaporated under reduced pressure. The crude was purified by column chromatography (silica 230–400 mesh, 15:85 ethyl acetate/petroleum ether) to afford compound **11-Bn** (560 mg, 89% yield) as pale yellow oil. $[\alpha]_D^{25}$ +30.1 (c 1.7, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3017, 2928, 2858, 2136, 1455, 1101 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ –0.01 (s, 6H), 0.82 (s, 9H), 2.57–2.65 (m, 2H), 3.52 (dd, J = 5.2, 10.0 Hz, 1H), 3.57–3.67 (m, 3H), 3.76–3.79 (m, 1H), 4.00–4.02 (m, 1H), 4.43–4.47 (m, 2H), 4.48 – 4.52 (m, 2H), 4.53–4.58 (m, 2H), 4.67 (d, J = 11.5 Hz, 1H), 4.84 (d, J = 12.1 Hz, 1H), 4.91 (d, J = 11.5 Hz, 1H), 7.27–7.40 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ –5.1 (q), –4.3 (q), 18.0 (s), 20.3 (t), 25.85 (q, 3C), 68.6 (t), 70.7 (t), 71.0 (d), 71.9 (t), 72.2 (d), 72.9 (t), 73.2 (t), 74.3 (t), 77.5 (s), 81.5 (d), 84.6 (s), 127.36 (d, 2C), 127.5 (d), 127.63 (d, 2C), 127.71 (d, 2C), 127.89 (d, 2C), 128.09 (d, 3C), 128.25 (d,

2C), 128.31 (d, 2C), 128.38 (d, 2C), 128.78 (d), 129.0 (d), 138.0 (s), 138.1 (s), 138.4 (s), 138.8 (s) ppm; LCMS (*m/z*): 595.21 (35%), 687.39 (100% $[M+Na]^+$); HRMS: 703.3221 ($[M+K]^+$) calculated, 703.3202 ($[M+K]^+$) observed; Anal. Calcd for $C_{42}H_{52}O_5Si$: C, 75.86; H, 7.88; Found: C, 75.63; H, 7.98.

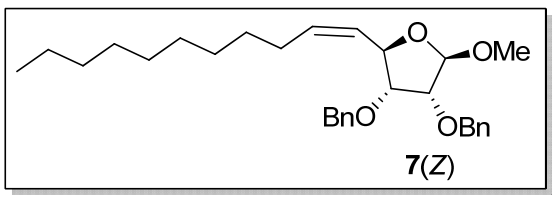
5. Synthesis of alcohol 12:



12

To a ice cooled solution of TBS ether **11-Bn** (560 mg, 0.84 mmol) in anhydrous THF (5 mL), was added a solution of TBAF (290 mg, 1.1 mmol) in anhydrous THF (1 mL) under argon atmosphere and allowed to stir at room temperature for 4 h. Reaction mixture was concentrated and residue was purified by column chromatography (silica 230–400 mesh, 2:8 ethyl acetate/petroleum ether) to afford compound **12** (392 mg, 84% yield) as a colorless oil. $[\alpha]_D^{25}$ +65.5 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3445, 3030, 2864, 2111, 1496, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.57 (dt, *J* = 1.7, 7.0 Hz, 2H), 2.67 (bs, 1H), 3.53–3.63 (m, 4H), 3.74 (dd, *J* = 3.5, 7.0 Hz, 1H), 3.93 (bs, 1H), 4.42–4.46 (m, 2H), 4.48–4.50 (m, 4H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.87 (d, *J* = 11.4 Hz, 1H), 7.20–7.32 (m, 20H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.3 (t), 68.4 (t), 70.80 (t, 2C), 70.81 (d), 71.3 (d), 72.9 (t), 73.3 (t), 74.0 (t), 77.1 (s), 80.4 (d), 85.1 (s), 127.5 (d), 127.60 (d, 3C), 127.68 (d, 2C), 127.82 (d, 2C), 127.87 (d, 2C), 128.13 (d, 2C), 128.18 (d, 2C), 128.35 (d, 2C), 128.38 (d, 4C), 137.8 (s), 137.9 (s), 138.0 (s), 138.4 (s) ppm; MALDI TOF: 573.16 (100% $[M+Na]^+$); HRMS: 589.2356 ($[M+K]^+$) calculated, 589.2347 ($[M+K]^+$) observed; Anal. Calcd for $C_{36}H_{38}O_5$: C, 78.52; H, 6.96; Found: C, 78.33; H, 6.91.

6. Synthesis of olefin 7(*Z*):



7(*Z*)

At –78 °C, a solution of DMSO (11.34 g, 145.2 mmol) in CH_2Cl_2 (55 mL) was treated with oxallyl chloride (11.06 g, 87.1 mmol) and stirred for 15 min. To this were added a solution of alcohol **8** (10 g, 29 mmol) in CH_2Cl_2 (25 mL)

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and Et_3N (29.38 g, 290.4 mmol) after 15 min. The contents were stirred at –78 °C for another 15 minutes, and diluted with saturated NH_4Cl solution (50 mL). Two layers were separated and the aqueous layer was extracted with DCM (3 × 150 mL), dried over Na_2SO_4, volatiles were removed and the crude was directly used for next reaction without purification.

n-BuLi (72.6 mL, 116.1 mmol) was added to an ice cooled solution of decyl triphenylphophonium bromide (70.2 g, 145.1 mmol) in anhydrous THF (350 mL) and stirred at rt for 1 h. This ylide was transfered to a stirred solution of aldehyde (9.94 g, 29 mmol) in THF (100 mL) at 0 °C and stirred at room temperature for 2 h. The reaction mixture was quenched with sat NH_4Cl solution (20 mL); THF was removed and the aqueous layer was extracted with ethyl acetate (3 × 70 mL), combined organic layers were dried over Na_2SO_4, volatiles were removed and the crude was purified by column chromatography (silica 230–400 mesh, 5:95 ethyl acetate/petroleum ether) to provide the olefin **7**(*Z*) (10.43 g, 77% yield) as a pale yellow oil. $[\alpha]_D^{25}$ –10.9 (*c* 1.6, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3064, 2954, 2854, 1715, 1606, 1465, 1455, 1145, 1046, 734, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J = 6.6 Hz, 3H), 1.24 (bs, 14H), 2.00–2.21 (m, 2H), 3.32 (s, 3H), 3.82–3.91 (m, 2H), 4.51 (d, J = 12.2 Hz, 1H), 4.58 (d, J = 12.2 Hz, 1H), 4.66 (d, J = 12.3 Hz, 1H), 4.74 (d, J = 12.3 Hz, 1H), 4.87 (s, 1H), 4.94 (ddd, J = 0.8, 7.1, 9.1 Hz, 1H), 5.35 (dt, J = 10.8, 9.3 Hz, 1H), 5.69 (ddd, J = 10.8, 6.4, 7.3Hz, 1H), 7.30–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.6 (t), 27.7 (t), 29.30 (t, 2C), 29.54 (t, 2C), 29.8 (t), 31.9 (t), 54.9 (q), 72.3 (t), 72.4 (t), 76.9 (d), 80.0 (d), 82.7 (d), 106.1 (d), 127.52 (d,2C), 127.6 (d), 127.8 (d), 128.02 (d, 2C), 128.26 (d, 2C), 128.37 (d, 2C), 129.5 (d), 135.0 (d), 137.8 (s), 137.9 (s), ppm; MALDI-TOF: 489.21 (68% $[M+Na]^+$), 505.18 (100% $[M+K]^+$); Anal. Calcd for $C_{30}H_{42}O_4$: C, 77.21; H, 9.07; Found: C, 77.49; H, 9.32.

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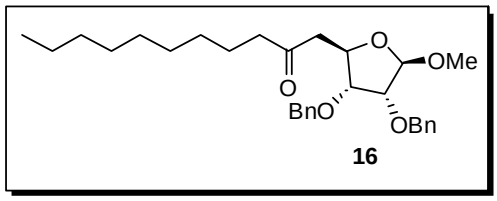
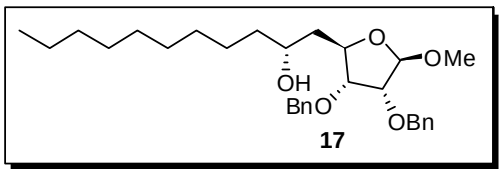
7. Synthesis of ketone 16:



16

A solution of $PdCl_2$ (5 mg, 0.03 mmol) in N,N dimethyl acetamide (20 mL) and water (3 mL) was stirred at room temperature for 1 h under O_2 atmosphere (12 bar). Then to this, a solution of olefin **7** (1 g, 2.1 mmol) in N,N dimethyl acetamide (10 mL) was added and stirring was continued for 12 h at 90 °C under O_2 atmosphere (4 bar). Reaction mixture was cooled and partitioned between diethyl ether (2 × 50 mL) and water (30 mL). Combined organic phase was washed with brine (20 mL), dried and concentrated under reduced pressure. Crude compound was purified by column chromatography (silica 230–400 mesh, 2:8 ethyl acetate/petroleum ether) to procure compound **16** [720 mg, 76% yield based on **7** recovered (78 mg)] as a colorless oil. $[\alpha]_D^{25}$ +14.5 (*c* 0.7 in $CHCl_3$); IR (neat) $\tilde{\nu}$ 2926, 2855, 1714, 1455, 1046, 736, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, J = 6.5 Hz, 3H), 1.24 (bs, 12H), 1.51–1.58 (m, 2H), 2.44 (t, J = 7.4 Hz, 2H), 2.62 (d, J = 6.7 Hz, 2H), 3.30 (s, 3H), 3.79–3.88 (m, 2H), 4.46 (d, J = 11.8 Hz, 1H), 4.53–4.59 (m, 3H), 4.68 (d, J = 12.1 Hz, 1H), 4.88 (s, 1H), 7.30–7.36 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (q), 22.6 (t), 23.5 (t), 29.1 (t), 29.2 (t), 29.37 (t, 2C), 31.8 (t), 43.1 (t), 48.3 (t), 55.1 (q), 72.2 (t), 72.4 (t), 77.2 (d), 79.3 (d), 81.3 (d), 106.4 (d), 127.82 (d, 2C), 127.91 (d, 2C), 128.97 (d, 2C), 128.38 (d, 4C), 137.59 (s, 2C), 208.7 (s); MALDI-TOF: 505.20 (17% $[M+Na]^+$), 521.17 (10% $[M+K]^+$); HRMS: 521.2669 ($[M+K]^+$) calculated, 521.2703 ($[M+K]^+$) observed; Anal. calcd for $C_{30}H_{42}O_5$; C, 74.65, H, 8.77; Found C, 74.59, H, 8.83.

8. Synthesis of alcohol 17:

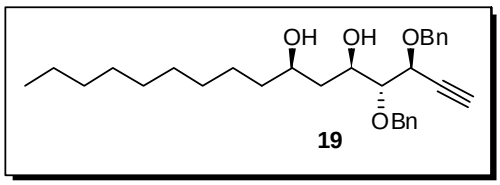


17

LiI (2.77 g, 20.7 mmol) was added to a solution of ketone **16** (1g, 2.1 mmol) in diethyl ether (40 mL) at –40 °C and stirred for 10 min. Then reaction mixture was cooled to –100 °C and LAH (785 mg, 20.7 mmol) was introduced in three portions. Stirring was continued for next 45 min at the same temperature. Reaction mixture was quenched by 10% sodium potassium tartarate (5 mL) at –

100 °C and allowed to warm to room temperature. Organic phase was separated and aqueous layer was extracted with diethyl ether (2 × 10 mL). Combined organic phase was washed with brine (25 mL), dried and concentrated under reduced pressure. The resulting crude compound (9:1 dr) was purified by column chromatography (silica 100–200 mesh, 2:8 ethyl acetate/petroleum ether) to procure compound **17** (898 mg, 89% yield) as a colorless oil. $[\alpha]_D^{25}$ +26.5 (*c* 1.2 in $CHCl_3$); IR (neat) $\tilde{\nu}$ 3479, 3016, 2928, 2856, 1455, 1216, 1045, 756, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, J = 6.5 Hz, 3H), 1.20 (bs, 14H), 1.33–1.36 (m, 2H), 1.45–1.53 (m, 1H), 1.67–1.77 (m, 1H), 3.26 (s, 3H), 3.71–3.73 (m, 1H), 3.76–3.78 (m, 1H), 3.79–3.82 (m, 1H), 4.20–4.26 (m, 1H), 4.37 (d, J = 11.7 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.84 (s, 1H), 7.19–7.32 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 14.1 (q), 22.6 (t), 25.5 (t), 29.3 (t), 29.51 (t), 29.58 (t), 29.63 (t), 31.9 (t), 37.3 (t), 41.9 (t), 55.2 (q), 71.2 (d), 72.3 (t), 72.6 (t), 78.7 (d), 80.9 (d), 82.2 (d), 106.3 (d), 127.95 (d, 4C), 128.02 (d, 2C), 128.43 (d, 4C), 137.4 (s), 137.5 (s) ppm; MALDI-TOF: 507.23 (33% $[M+Na]^+$), 523.20 (100% $[M+K]^+$); HRMS: 507.3086 ($[M+Na]^+$) calculated, 507.3083 ($[M+K]^+$) observed; Anal. calcd for $C_{30}H_{44}O_5$; C, 74.34, H, 9.15; Found C, 74.45, H, 9.21.

9. Synthesis of diol 19:

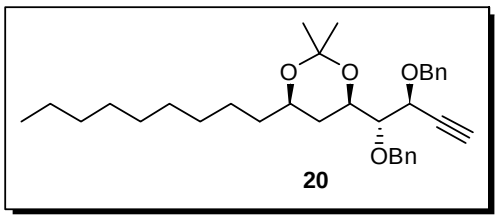


19

To a solution of alcohol **17** (100 mg, 0.21 mmol) in dioxane (5 mL) and water (2 mL) was added conc. H_2SO_4 (100 µL) at room temperature and stirred at reflux in water bath for 6 h. After complete consumption of starting material as indicated by TLC, the reaction mixture was cooled in ice bath and neutralized with triethyl amine. Dioxane was removed under vacuum and residual material was extracted with ethyl acetate (3 × 5 mL). The combined organic layer was washed with water (5 mL), brine (5 mL), dried over sodium sulphate and concentrated under reduced pressure. The crude product (92 mg, 0.19 mmol) was dissolved in anhydrous methanol (4 mL) and treated with K_2CO_3 (80 mg, 0.58 mmol) followed by a solution of dimethyl 1-diazo-2-oxopropyl phosphonate (110 mg, 0.58

mmol) in methanol (1 mL). After stirring for 7 h, the reaction mixture was filtered through celite bed and filtrate was concentrated. The residue was extracted with ethyl acetate (20 mL) and water (5 mL). Organic layer washed with brine (5 mL), dried over sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (silica 230–400 mesh, 15:85 ethyl acetate/petroleum ether) to procure compound **19** (55 mg, 58% yield over two steps) as colorless oil. $[\alpha]_D^{25}$ +48.2 (*c* 0.4 in $CHCl_3$); IR (neat) $\tilde{\nu}$ 3431, 3016, 2927, 2856,2114, 1629, 1455, 1216, 1085, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.5 Hz, 3H), 1.25 (bs, 14H), 1.34–1.43 (m, 3H), 1.80–1.83 (m, 1H), 2.59 (d, *J* = 2.1 Hz, 1H), 3.57 (dd, *J* = 4.7, 6.6 Hz, 1H), 3.78–3.82 (m, 1H), 3.98–4.02 (m, 1H), 4.43 (dd, *J* = 2.1, 4.7 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.92 (d, *J* = 11.2 Hz, 1H), 7.28–7.35 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) 14.1 (q), 22.7 (t), 25.3 (t), 29.3 (t), 29.5 (t), 29.59 (t, 2C), 31.9 (t), 38.2 (t), 38.4 (t), 70.4 (d), 71.0 (t), 73.0 (d), 73.3 (d), 74.4 (t), 75.8 (d), 80.3 (s), 82.8 (d), 127.8 (d), 127.9 (d), 128.08 (d, 2C), 128.34 (d, 2C), 128.42 (d, 2C), 128.48 (d, 2C), 137.2 (s), 137.9 (s); MALDI-TOF: 489.21 (17% $[M+Na]^+$), 505.18 (100% $[M+K]^+$), 997.43 (20%); HRMS: 505.2720 ($[M+K]^+$) calculated, 505.2705 ($[M+K]^+$) observed; Anal. calcd for $C_{30}H_{42}O_4$; C, 77.21, H, 9.07; Found C, 76.93, H, 9.18.

10. Synthesis of acetonide 20:

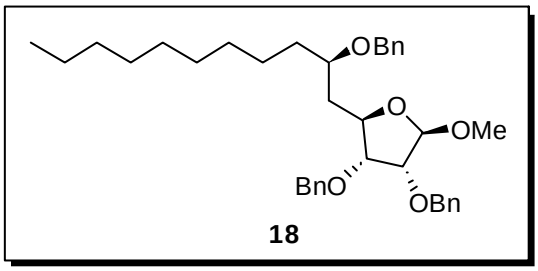


20

At 0 °C, to a solution of diol **19** (32 mg, 0.06 mmol) in 2,2 dimethoxy propane (1 mL) was added *p*-TSA (2 mg) and stirred at 0 °C for 20 min. The reaction mixture was warmed to room temperature and stirring was continued for next 2 h. The reaction mixture was neutralized with triethyl amine and concentrated. Residual material was purified by column chromatography (silica 230–400 mesh, 1:9 ethyl acetate/petroleum ether) to procure compound **20** (30 mg, 88% yield) as a colorless oil. $[\alpha]_D^{25}$ +50.9 (*c* 0.5 in $CHCl_3$); IR ($CHCl_3$) $\tilde{\nu}$ 3306, 3018, 2928, 2857, 2131, 1216, 1110, 758, 621 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz,

3H), 1.26 (bs, 12H), 1.28–1.32 (m, 4H), 1.34 (s, 3H), 1.39 (s, 3H), 1.44–1.47 (m, 1H), 1.65 (dt, J = 2.4, 12.9 Hz, 1H), 2.52 (d, J = 2.1 Hz, 1H), 3.63 (dd, J = 3.4, 7.3 Hz, 1H), 3.70–3.75 (m, 1H), 4.01 (ddd, J = 2.4, 7.4, 11.6 Hz, 1H). 4.47–4.49 (m, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.71 (d, J = 11.5 Hz, 1H), 4.90 (d, J = 11.7 Hz, 1H), 4.94 (d, J = 11.4 Hz, 1H), 7.26–7.37 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1 (q), 19.6 (q), 22.7 (t), 24.8 (t), 29.3 (t), 29.54 (t, 3C), 30.1 (q), 31.9 (t), 33.0 (t), 36.4 (t), 68.8 (d), 68.9 (d), 70.8 (d), 71.1 (t), 74.5 (t), 75.3 (d), 79.9 (s), 82.1 (d), 98.5 (s), 127.5 (d), 127.6 (d), 127.79 (d, 2C), 128.18 (d, 2C), 128.31 (d, 2C), 128.49 (d, 2C), 137.8 (s), 138.4 (s) ppm; MALDI-TOF: 529.24 (18% $[M+Na]^+$), 545.21 (100% $[M+K]^+$); HRMS: 529.3294 ($[M+Na]^+$) calculated, 529.3257 ($[M+Na]^+$) observed; Anal. calcd for $C_{33}H_{46}O_4$; C, 78.22, H, 9.15; Found C, 78.31, H, 9.22.

11. Synthesis of benzyl ether 18:

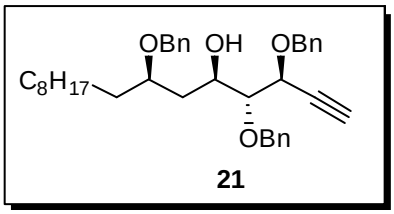


18

To an ice cooled solution of alcohol **17** (1.4 g, 2.89 mmol) in DMF (15 mL) was added NaH (0,084 g, 3.47 mmol) followed by benzyl bromide (0.3 mL, 3.18 mmol). The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was partitioned between water (50 mL) and ethyl acetate (3 × 50 mL). Organic layer washed with water (3 × 30 mL), brine (25 mL), dried over Na_2SO_4, concentrated and the crude was purified by column chromatography (silica 230–400 mesh, 1:9 ethyl acetate/petroleum ether) to afford compound **18** (1.58 g, 96% yield) as a colorless syrup. $[\alpha]_D^{25}$ +21.3 (*c* 1.6, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3019, 2927, 1653, 1454, 1215, 1045, 750, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J = 6.82 Hz, 3H), 1.25 (bs, 16H), 1.59 (m, 2H), 3.33 (s, 3H), 3.47(m, 1H), 3.84 (dd, J = 0.73, 4.54 Hz 1H), 4.03 (dd, J = 7.6, 4.5 Hz, 1H), 4.21(dd, J = 4.5, 7.6 Hz, 1H), 4.32 (d, J = 11.7 Hz, 1H), 4.50 (d, J = 11.7 Hz, 1H), 4.49–4.62 (m, 3H), 4.70 (d, J = 11.7 Hz, 1H), 4.93 (s, 1H), 7.26–7.38 (m, 15H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.7 (t), 25.5 (t), 29.3 (t), 29.62 (t, 3C), 29.8 (t), 30.6 (t), 31.9 (t), 54.9 (q), 72.2 (t), 72.27 (t), 72.3 (t), 77.9 (d), 79.3 (d), 79.7 (d), 82.7 (d), 105.5

(d), 127.3 (d), 127.65 (d, 2C), 127.8 (d), 127.84 (d), 128.07 (d, 2C), 128.11 (d, 2C), 128.23 (d, 2C), 128.31 (d, 2C), 128.40 (d, 2C), 137.6 (s), 137.7 (s), 139.0 (s) ppm; MALDI-TOF: 597.49 (27% $[M+Na]^+$), 613.47 (100% $[M+K]^+$); HRMS: 597.3556 ($[M+Na]^+$) calculated, 597.3557 ($[M+Na]^+$) observed; Anal. Calcd for $C_{37}H_{50}O_5$: C, 77.31; H, 8.77; Found: C, 77.38; H, 8. 96.

12. Synthesis of alkyne 21:



21

A solution of benzyl ether **18** (2.0 g, 3.5 mmol) in 4:1 mixture of dioxane/water (20 mL) was treated with H_2SO_4 (2 mL) and stirred at reflux in water bath for 6 h. Reaction mixture was neutralized with triethyl amine, dioxane removed under reduced pressure and residue was extracted with ethyl acetate (3 × 40 mL). Combined organic layer dried over sodium sulphate, concentrated under reduced pressure. The crude was treated with K_2CO_3 (1.4 g, 10.2 mmol) and Ohira-Bestmann reagent (1.0 g, 5.1 mmol) at room temperature for 14 h. Reaction mixture was filtered through celite and concentrated under reduced pressure. The residue obtained was purified by column chromatography (silica 230–400 mesh, 0.5:9.5 ethyl acetate/petroleum ether) to afford **21** (1.03 g, 53% yield) as colorless oil. $[\alpha]_D^{25}$ +94.3 (*c* 1.6, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3548, 3306, 3031, 2926, 2855, 2138, 1496, 1454, 1216, 1067, 757, 697, 614 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, J = 6.7 Hz, 3H), 1.25 (bs, 16H), 1.59–1.70 (m, 2H), 2.58 (d, J = 2.2 Hz, 1H), 3.57 (dt, J = 1.1, 9.3 Hz, 1H), 3.69 (dt, J = 1.1, 6.7 Hz, 1H), 3.79 (dd, J = 2.2, 8.9 Hz, 1H), 4.20 (d, J = 11.4 Hz, 1H), 4.46–4.55 (m, 3H), 4.73 (t, J = 2.2 Hz, 1H), 4.94 (d, J = 11.7 Hz, 1H), 5.00 (d, J = 11.7 Hz, 1H), 7.20–7.40 (m, 15H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 22.7 (t), 25.5 (t), 29.3 (t), 29.5 (t), 29.58 (t, 2C), 29.8 (t), 30.8 (t), 31.9 (t), 71.2 (t), 71.9 (t), 72.1 (d), 72.2 (d), 73.5 (t), 76.2 (d), 76.7 (d), 79.6 (s), 80.2 (d), 127.6 (d), 127.65 (d, 2C), 127.72 (d, 2C), 127.79 (d, 2C), 128.24 (d, 2C), 128.32 (d, 6C), 137.8 (s), 138.4 (s), 138.4 (s) ppm; ESI–MS (*m/z*): 579.43 (100% $[M+Na]^+$); Anal. Calcd for $C_{37}H_{48}O_4$: C, 79.82; H, 8.69; Found: C, 79.60 H, 8.83.

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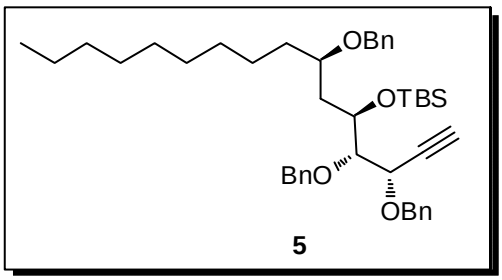
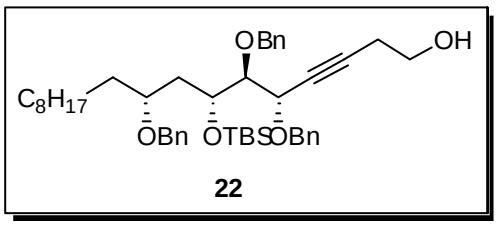
13. Synthesis of TBS ether 5:



5

To an ice cooled solution of alkynol **21** (117 mg, 0.2 mmol) and Et_3N (42 µL) in CH_2Cl_2 (5 mL) was added TBSOTf (60 µL, 0.2 mmol) and stirred at room temperature for 2 h. Usual workup followed by purification (silica 230–400 mesh, 5:95 ethyl acetate/petroleum ether) gave the TBS ether **5** (0.132 g, 96% yield) as colorless thick oil. $[\alpha]_D^{25}$ +52.6 (*c* 1.0 in $CHCl_3$); IR (neat) $\tilde{\nu}$ 3307, 2927, 2855, 2143, 1651, 1455, 1215, 1067, 757, 668, 618 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.03 (s, 3H), 0.82 (s, 9H), 0.87 (t, *J* = 6.6 Hz, 3H), 1.20–1.23 (m, 16H), 1.41–1.51 (m, 2H), 2.51 (d, *J* = 2.2 Hz, 1H), 3.49–3.67 (m, 1H), 3.83 (dd, *J* = 4.4, 5.4 Hz, 1H), 3.94 (dd, *J* = 4.4, 5.4 Hz, 1H), 4.32–4.39 (m, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.53–4.56 (m, 1H), 4.66 (d, *J* = 11.4 Hz, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 7.23–7.39 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ –4.3 (q), –4.2 (q), 14.1 (q), 18.2 (s), 22.7 (t), 25.9 (t), 26.04 (q, 3C), 29.3 (t), 29.5 (t), 29.60 (t, 2C), 29.7 (t), 30.4 (t), 31.9 (t), 70.8 (t), 71.0 (d), 71.8 (t), 73.7 (d), 73.8 (t), 75.6 (d), 80.0 (d), 80.8 (s), 81.2 (d), 127.1 (d), 127.3 (d), 127.44 (d, 2C), 127.6 (d), 127.93 (d, 2C), 128.06 (d, 6C), 128.31 (d, 2C), 137.7 (s), 138.7 (s), 139.2 (s) ppm; MALDI-TOF: 693.60 (85% $[M+Na]^+$), 709.57 (100% $[M+K]^+$); HRMS: 709.4054 ($[M+K]^+$) calculated, 709.3989 ($[M+K]^+$) observed; Anal. calcd for $C_{43}H_{62}O_4Si$; C, 76.96, H, 9.31; Found C, 77.03, H, 9.42.

14. Synthesis of alcohol 22:

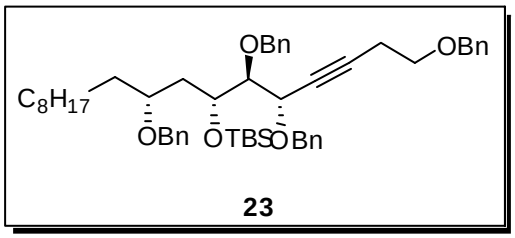


22

At –78 °C, a solution of alkyne **10** (0.5 g, 0.74 mmol) in anhydrous THF (5 mL) was treated with *n*-BuLi (0.56 mL, 1.6 M in hexane, 0.89 mmol) and stirred for 20 minutes and then introduced a solution of $BF_3.Et_2O$ (106 mg, 0.74 mmol) and stirred at –78 °C for 20 minutes. To this, a solution of ethylene oxide (6.2 M) in anhydrous THF (2.5 mL) was added slowly at –78 °C and the contents stirred for 1 h at the same temperature. Reaction mixture was quenched by adding saturated

sodium bicarbonate (1 mL) and partitioned between ethyl acetate (50 mL) and water (10 mL). The organic layer was washed with brine (10 mL), dried over sodium sulphate and evaporated under reduced pressure. The crude was purified by column chromatography (silica 230–400 mesh, 1:4 ethyl acetate/petroleum ether) to afford compound **22** (462 mg, 87% yield) as a pale yellow oil. $[\alpha]_D^{25}$ +31.8 (*c* 0.9, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3434, 2927, 2856, 2126, 1454, 1216, 1095, 758, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ –0.01 (s, 3H), 0.02 (s, 3H), 0.82 (s, 9H), 0.86 (t, *J* = 6.3 Hz, 3H), 1.22 (bs, 16H), 1.44–1.52 (m, 2H), 1.90 (bs, 1H), 2.49 (dt, *J* = 1.7, 6.1 Hz, 2H), 3.42–3.55 (m, 2H), 3.63 (t, *J* = 6.1 Hz, 2H), 3.83 (dd, *J* = 4.0, 5.6 Hz, 1H), 3.91 (dd, *J* = 4.2, 5.6 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.48 (d, *J* = 11.7 Hz, 1H), 4.51–4.57 (m, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.84 (d, *J* = 12.1 Hz, 1H), 4.90 (d, *J* = 11.7 Hz, 1H), 7.24–7.37 (m, 15H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ –4.4 (q), –4.2 (q), 14.1 (q), 18.2 (s), 22.7 (t), 23.4 (t), 26.00 (q, 3C), 26.1 (t), 29.3 (t), 29.60 (t, 3C), 29.7 (t), 30.4 (t), 31.9 (t), 60.9 (t), 70.8 (t), 71.5 (d), 71.8 (t), 73.4 (d), 73.8 (t), 79.6 (s), 80.2 (d), 81.7 (d), 84.6 (s), 127.1 (d), 127.3 (d), 127.50 (d, 2C), 127.6 (d), 127.84 (d, 2C), 127.91 (d, 2C), 128.10 (d, 4C), 128.30 (d, 2C), 138.0 (s), 138.7 (s), 139.2 (s) ppm; ESI–MS (*m/z*): 715.69 (20% $[M+1]^+$), 737.85 (100% $[M+Na]^+$), 753.68 (50%, $[M+K]^+$); HRMS: 753.4317 ($[M+K]^+$) calculated, 753.4371 ($[M+K]^+$) observed; Anal. Calcd for $C_{45}H_{66}O_5Si$: C, 75.58; H, 9.30; Found: C, 75.64; H, 9.48.

15. Synthesis of benzyl ether 23:

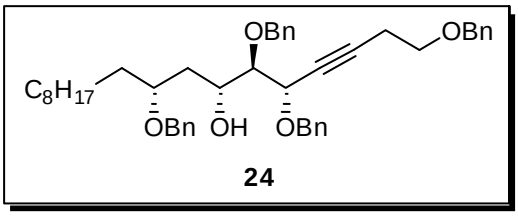


23

To a solution of alcohol **22** (100 mg, 0.14 mmol) in anhydrous DMF (3 mL) sodium hydride (60% oil suspension, 11 mg, 0.28 mmol) was added at 0 °C and allowed to stir for 10 minutes and treated with benzyl bromide (31 mg, 0.18 mmol) slowly. The contents were stirred at room temperature for 2 h. The reaction mixture was partitioned between ethyl acetate (30 mL) and water (50 mL). Organic layer was washed with water (3 × 5 mL), brine (5 mL), dried over sodium sulphate and evaporated under reduced pressure. The crude was purified by column

chromatography (silica 230–400 mesh, 15:85 ethyl acetate/petroleum ether) to afford compound **23** (96 mg, 86% yield) as colorless oil. $[\alpha]_D^{25}$ +41.7 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3019, 2925, 2856, 2210, 1464, 1215, 1095, 757, 669 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.00 (s, 3H), 0.04 (s, 3H), 0.84 (s, 9H), 0.88 (t, *J* = 6.2 Hz, 3H), 1.20–1.24 (m, 16H), 1.42–1.53 (m, 2H), 2.59 (dt, *J* = 1.8, 7.3 Hz, 2H), 3.46–3.58 (m, 1H), 3.59 (t, *J* = 7.3 Hz, 2H), 3.78 (t, *J* = 4.9 Hz, 1H), 3.94 (t, *J* = 4.9 Hz, 1H), 4.45 (dd, *J* = 4.1, 11.8 Hz, 2H), 4.51–4.58 (m, 4H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.86 (d, *J* = 12.0, 1H), 4.92 (d, *J* = 12.0, 1H), 7.23–7.39 (m, 20H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ –4.3 (q), –4.2 (q), 14.1 (q), 18.2 (s), 20.4 (t), 22.7 (t), 25.9 (t), 26.05 (q, 3C), 29.3 (t), 29.60 (t, 3C), 29.7 (t), 30.6 (t), 31.9 (t), 68.6 (t), 70.6 (t), 71.1 (d), 71.9 (t), 72.9 (t), 73.7 (t), 74.0 (d), 78.3 (s), 80.1 (d), 81.6 (d), 84.3 (s), 127.1 (d), 127.2 (d), 127.44 (d, 3C), 127.60 (d, 3C), 127.84 (d, 2C), 127.92 (d, 2C), 128.0 (d), 128.04 (d, 3C), 128.22 (d, 2C), 128.30 (d, 2C), 138. 10 (s, 2C), 139.0 (s), 139.3 (s) ppm; ESI–MS (*m/z*): 319.32 (100%), 827.80 (10% $[M+Na]^+$), 843.94 (10% $[M+K]^+$); HRMS: 843.4786 ($[M+K]^+$) calculated, 843.4781 ($[M+K]^+$) observed; Anal. Calcd for $C_{52}H_{72}O_5Si$: C, 77.56; H, 9.01; Found: C, 77.65; H, 9.09.

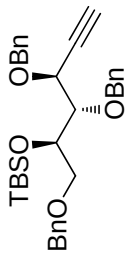
16. Synthesis of alcohol 24:



24

To an ice cooled solution of TBS ether **23** (100 mg, 0.12 mmol) in anhydrous THF (3 mL), was added a solution of TBAF (65 mg, 0.24 mmol) in anhydrous THF (0.5 mL) under Argon atmosphere and allowed to stir at room temperature for 4 h. Reaction mixture was concentrated and residue was purified by column chromatography (silica 230–400 mesh, 2:8 ethyl acetate/petroleum ether) to afford compound **24** (70 mg, 82% yield) as a colorless oil. $[\alpha]_D^{25}$ +39.6 (*c* 1.2, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}$ 3475, 3018, 2925, 2132, 1454, 1215, 1095, 759, 667 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.25 (bs, 16H), 1.57–1.70 (m, 2H), 2.43 (bs, 1H), 2.61 (dt, *J* = 1.8, 7.2 Hz, 2H), 3.54–3.59 (m, 1H), 3.62 (t, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 2.5, 8.7 Hz, 1H), 3.82–3.88 (m, 1H), 4.21 (d, *J* = 11.3 Hz, 1H), 4.46–4.54 (m, 5H), 4.67–4.70 (m, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.98 (d, *J* = 11.7

Hz, 1H), 7.21–7.34 (m, 20H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1 (q), 20.4 (t), 22.67 (t, 2C), 24.5 (t), 29.3 (t), 29.56 (t, 2C), 29.8 (t), 31.89 (t, 2C), 68.5 (t), 70.4(t), 70.8 (t), 71.1 (d), 71.9 (d), 73.0 (t), 74.3 (t), 76.8 (s), 80.2 (d), 83.2 (d), 84.7 (s), 127.5 (d), 127.54 (d, 2C), 127.65 (d), 127.74 (d), 127.81 (d, 2C), 128.19 (d, 2C), 128.3 (d), 128.35 (d, 3C), 128.40 (d, 4C), 128.52 (d, 3C), 137.9 (s), 138.02 (s), 138.05 (s), 138.5 (s) ppm; ESI–MS (*m/z*): 691.33 (9% $[M+1]^+$), 713.47 (100% $[M+Na]^+$); HRMS: 729.3921 ($[M+K]^+$) calculated, 729.3822 ($[M+K]^+$) observed; Anal. Calcd for $C_{46}H_{58}O_5$: C, 79.96; H, 8.46; Found: C, 79.84; H, 8.48.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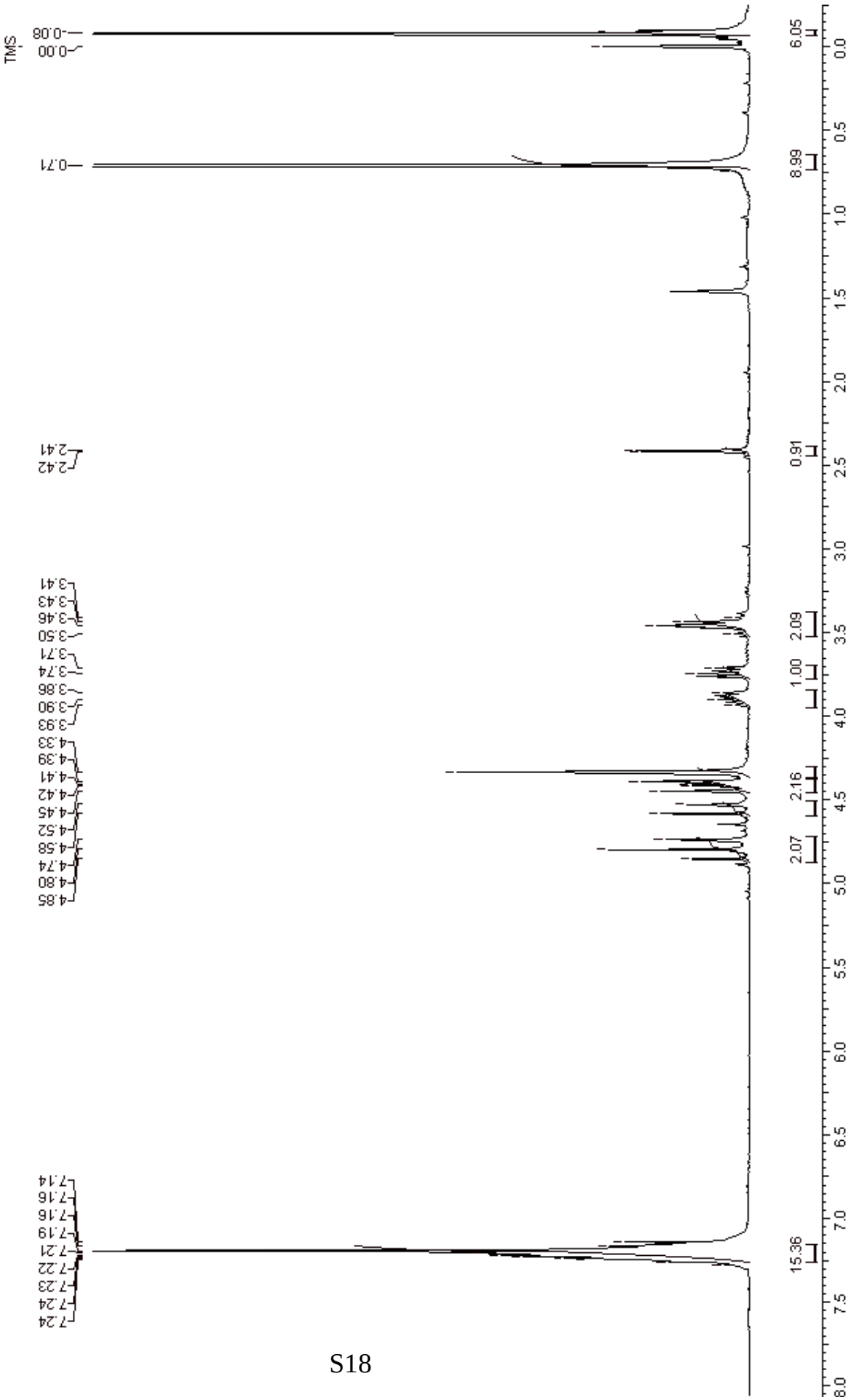
10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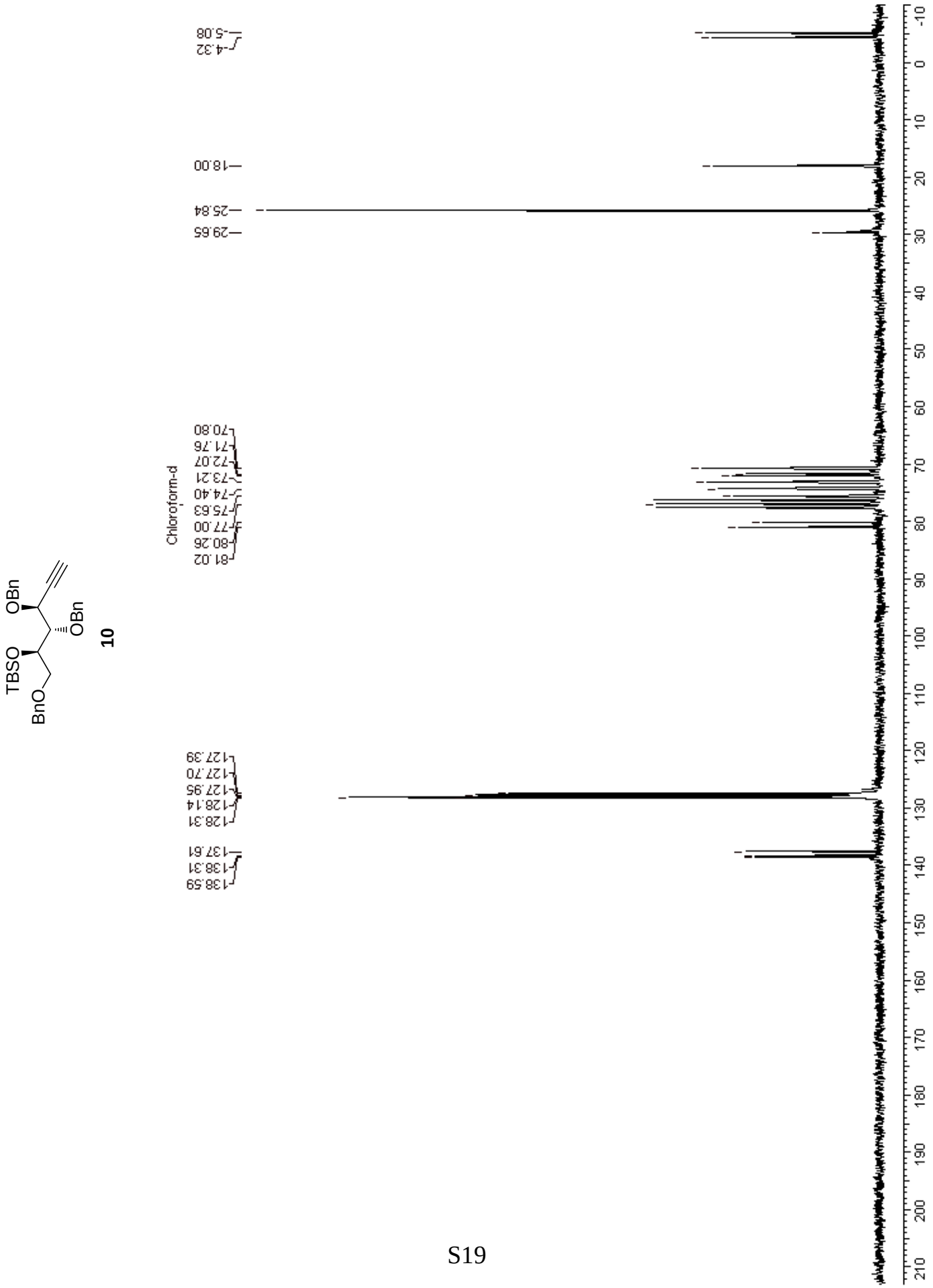
8.99
0.91
2.09
1.00
2.16
2.07
15.36


-5.08
-4.32
18.00
25.84
29.65
70.80
71.76
72.07
73.21
74.40
75.63
77.00
80.26
81.02
Chloroform-d
127.39
127.70
127.95
128.14
128.31
137.61
138.31
138.59
OBn
OBn
TBSO
BnO
10

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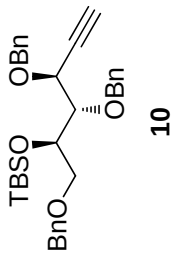

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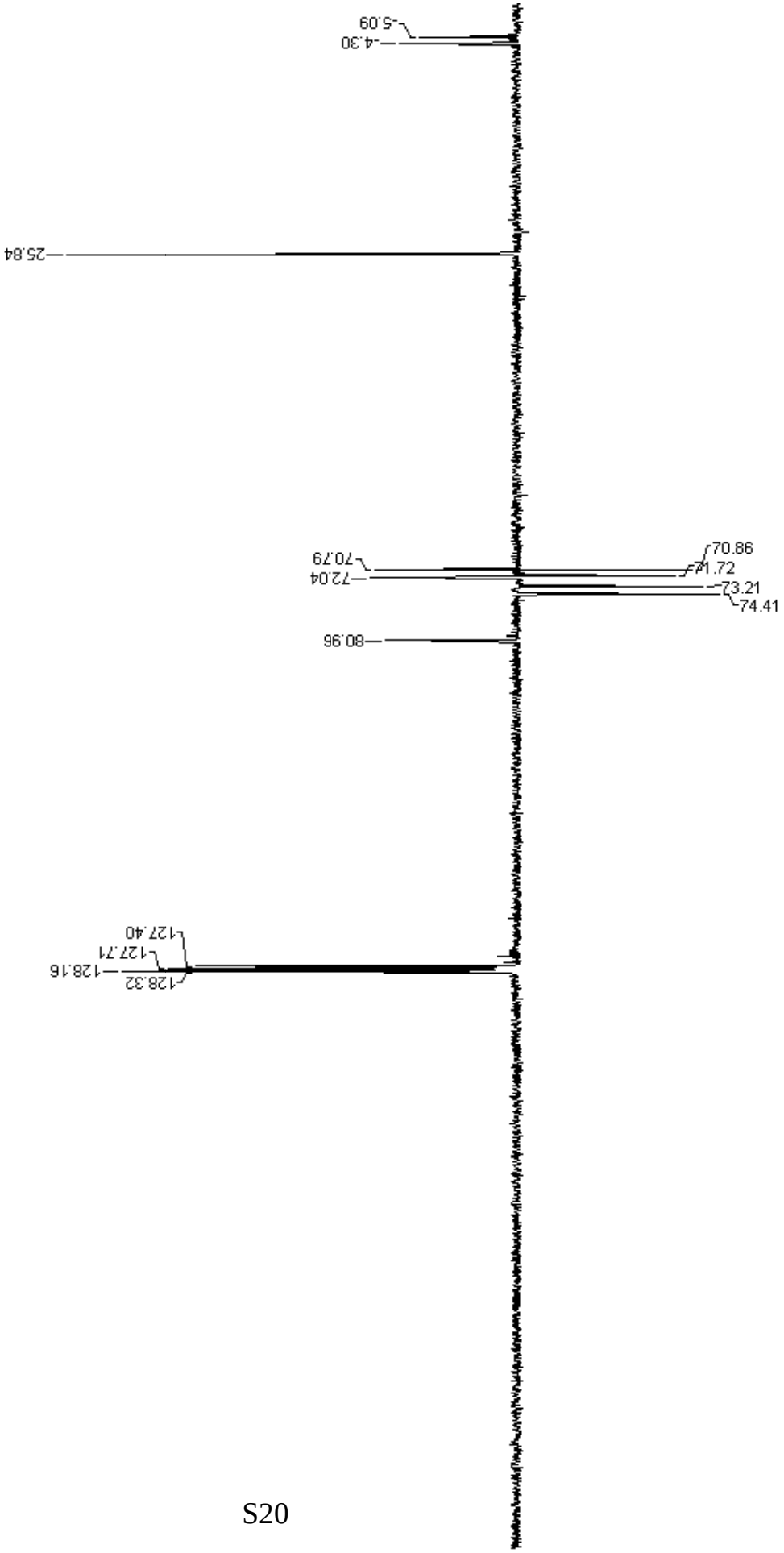
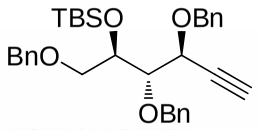
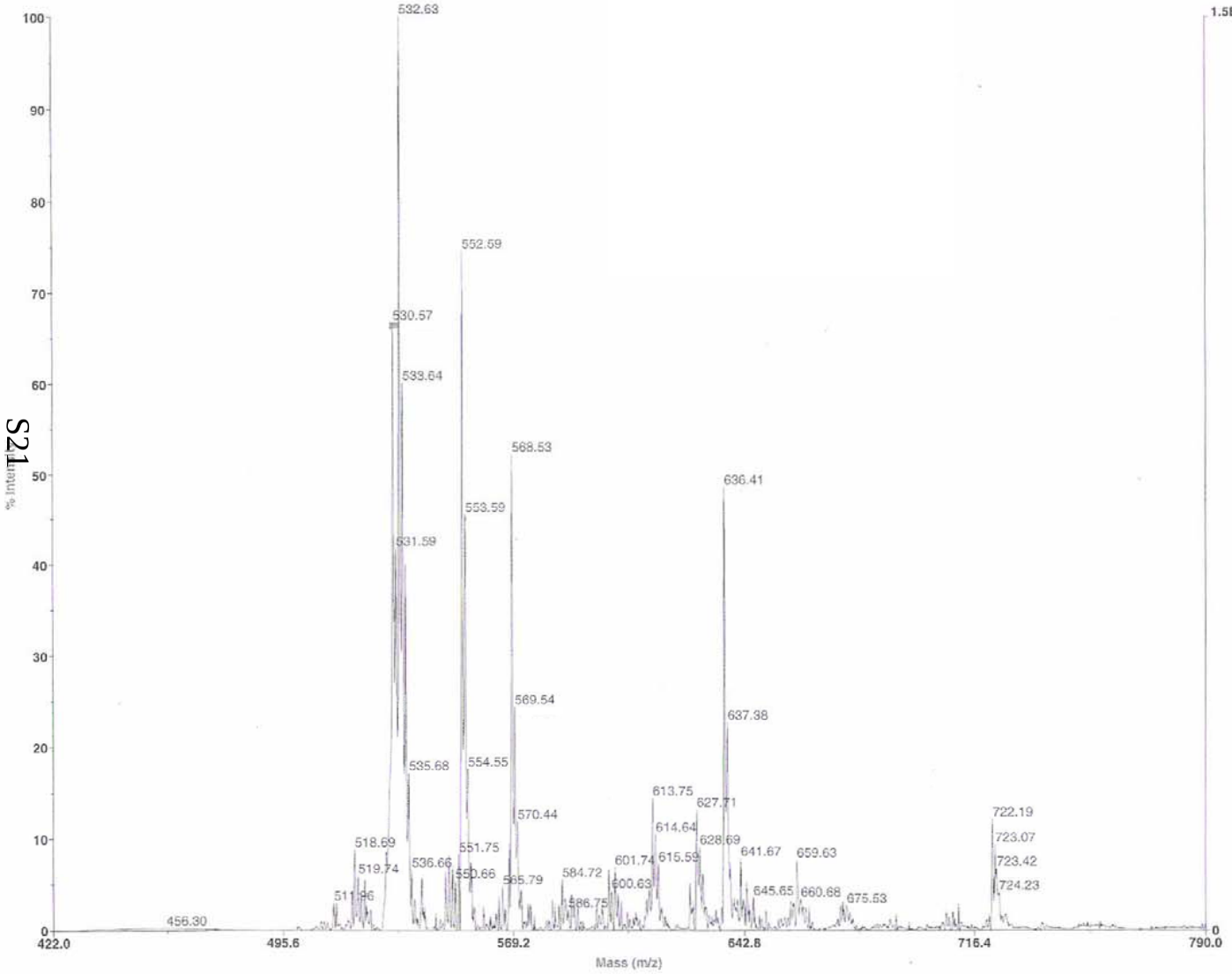




10

Applied Biosystems Voyager System 4383

Voyager Spec #1=>AdvBC(32,0.5,0.1)=>NR(2.00)[BP = 532.6, 15375]



Mode of operation:	Linear
Extraction mode:	Delayed
Polarity:	Positive
Acquisition control:	Manual
Accelerating voltage:	20000 V
Grid voltage:	94%
Guide wire 0:	0.05%
Extraction delay time:	100 nsec
Acquisition mass range:	100 -- 3000 Da
Number of laser shots:	100/spectrum
Laser intensity:	2402
Laser Rep Rate:	20.0 Hz
Calibration type:	Default
Calibration matrix:	2,5-Dihydroxybenzoic acid
Low mass gate:	500 Da
Digitizer start time:	10.042
Bin size:	2 nsec
Number of data points:	22235
Vertical scale:	500 mV
Vertical offset:	0%
Input bandwidth:	500 MHz
Sample well:	12
Plate ID:	100 WELL NUMBER PLATE
Serial number:	4383
Instrument name:	Voyager-DE STR
Plate type filename:	C:\VOYAGER\100 well plate.plt
Lab name:	PE Biosystems
Absolute x-position:	6365.62
Absolute y-position:	42272.1
Relative x-position:	-301.883
Relative y-posititon:	44.5895
Shots in spectrum:	100
Source pressure:	1.961e-007
Mirror pressure:	4.312e-008
TC2 pressure:	0.001
TIS gate width:	8
TIS flight length:	1189

Acquired: 16:23:00, June 12, 2009

Printed: 18:22, June 12, 2009

C:\VOYAGER\User_Data\2009\Narute\SN_67a_0002.dat

Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry
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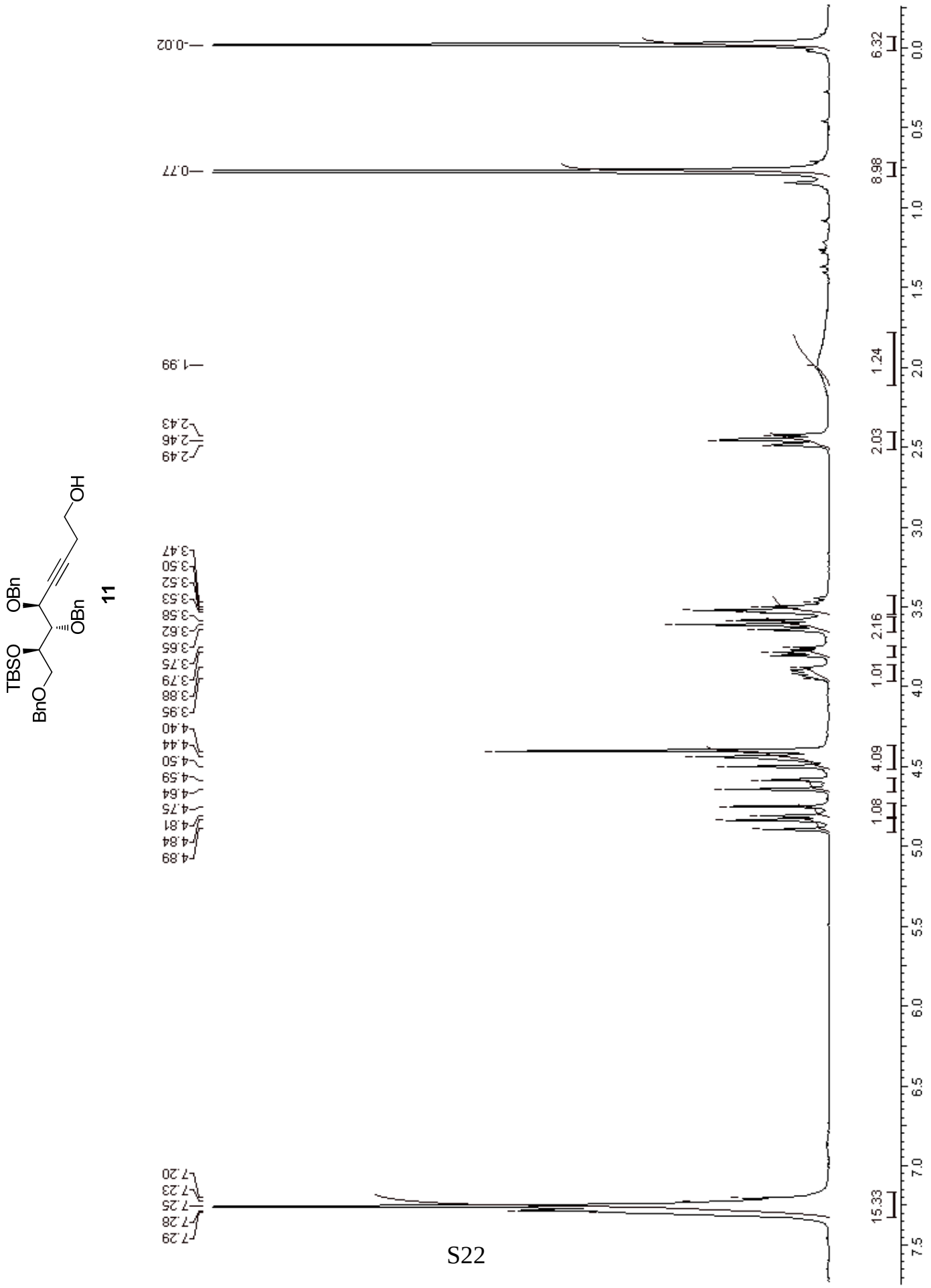

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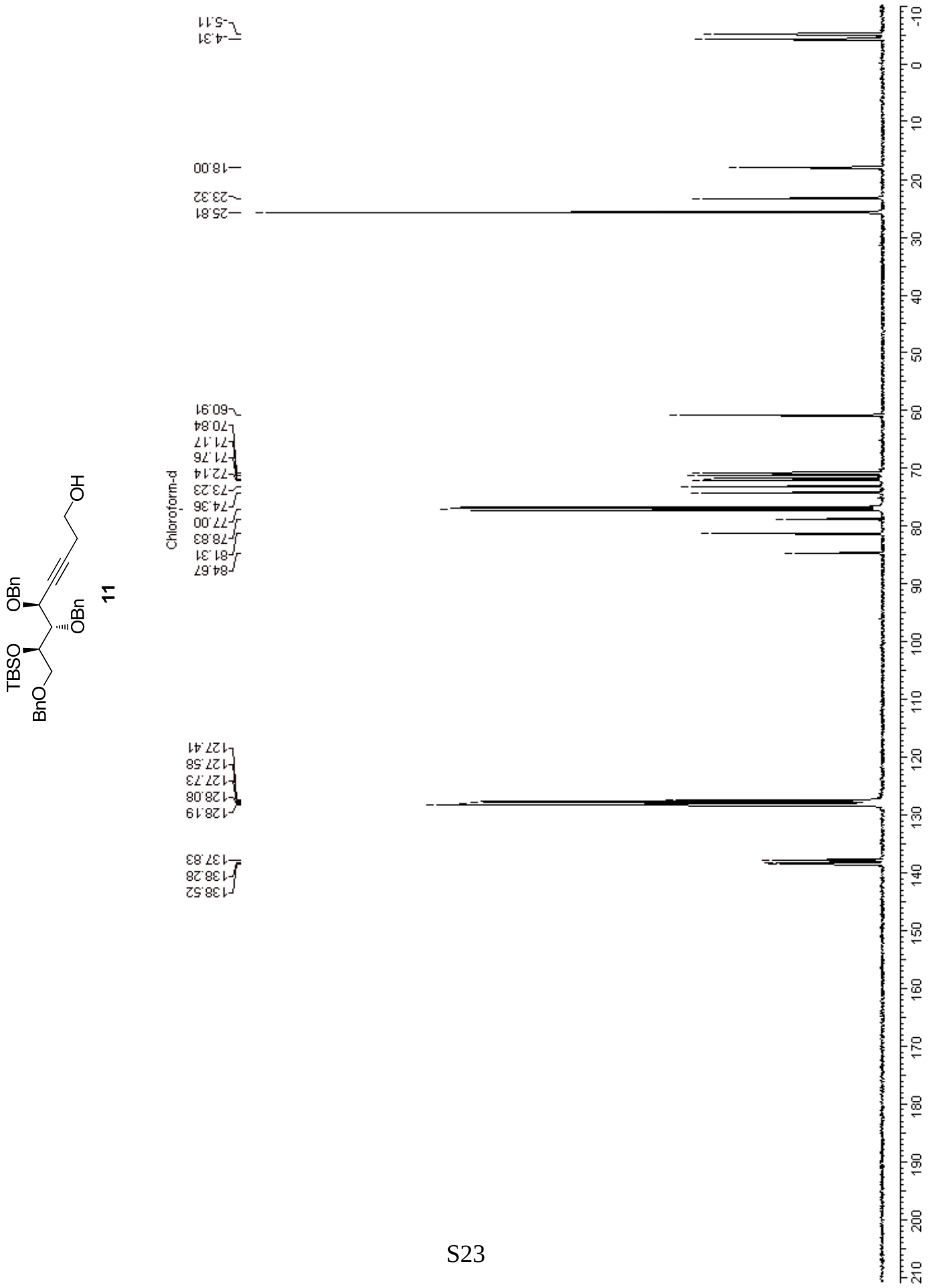

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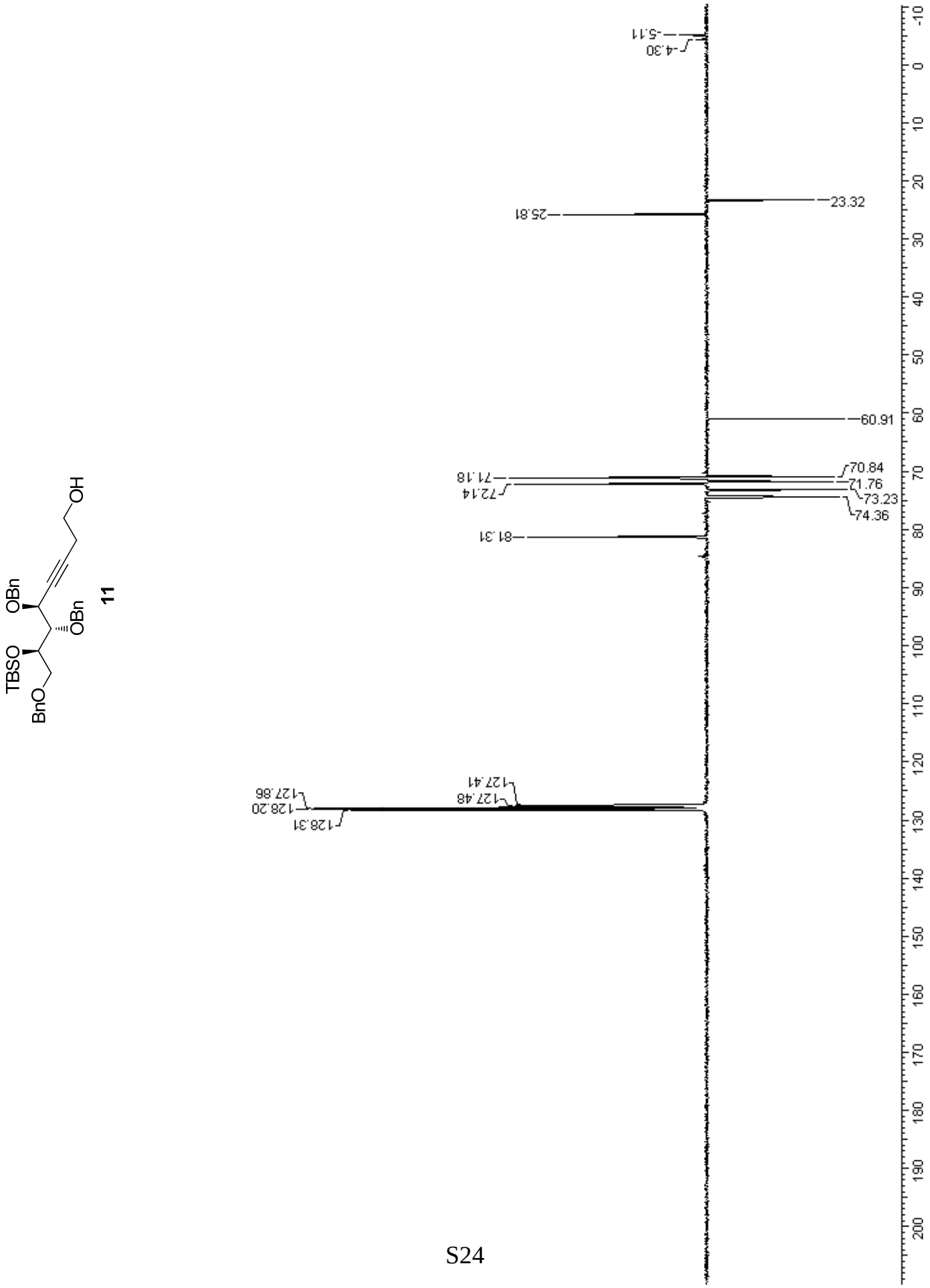

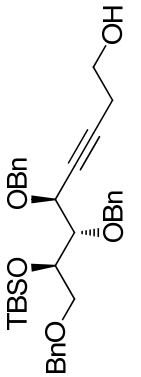

11

SN-469/10

*LCMSMS - Q STAR PULSAR

+TOF MS: 0.033 to 1.917 min from SN_469.wiff
a=3.29449504724565420e-004, t0=-3.49418683411422530e+001 R;

Max. 0.7 counts.

575.6525

597.3029

Intensity, counts

m/z, amu

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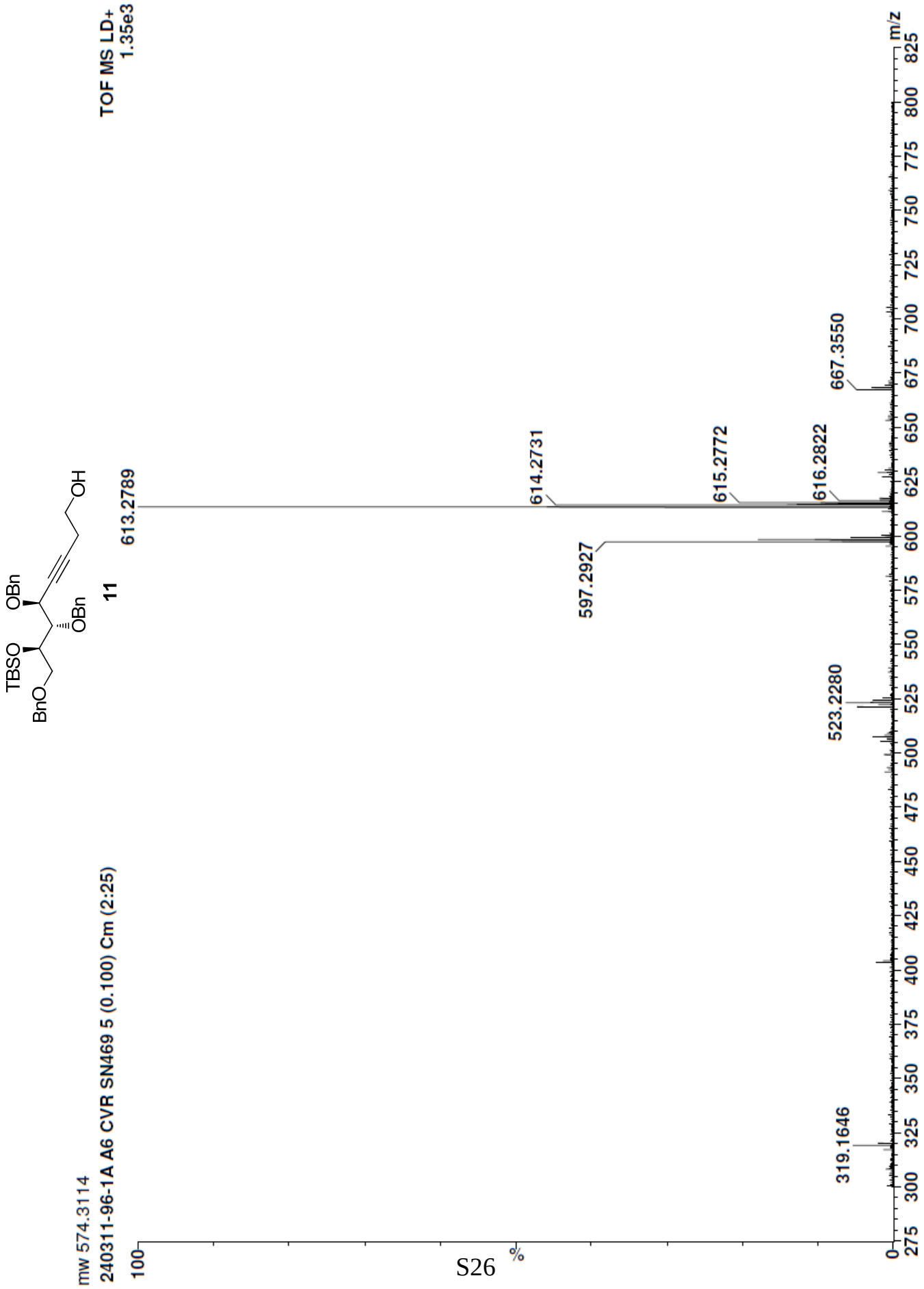

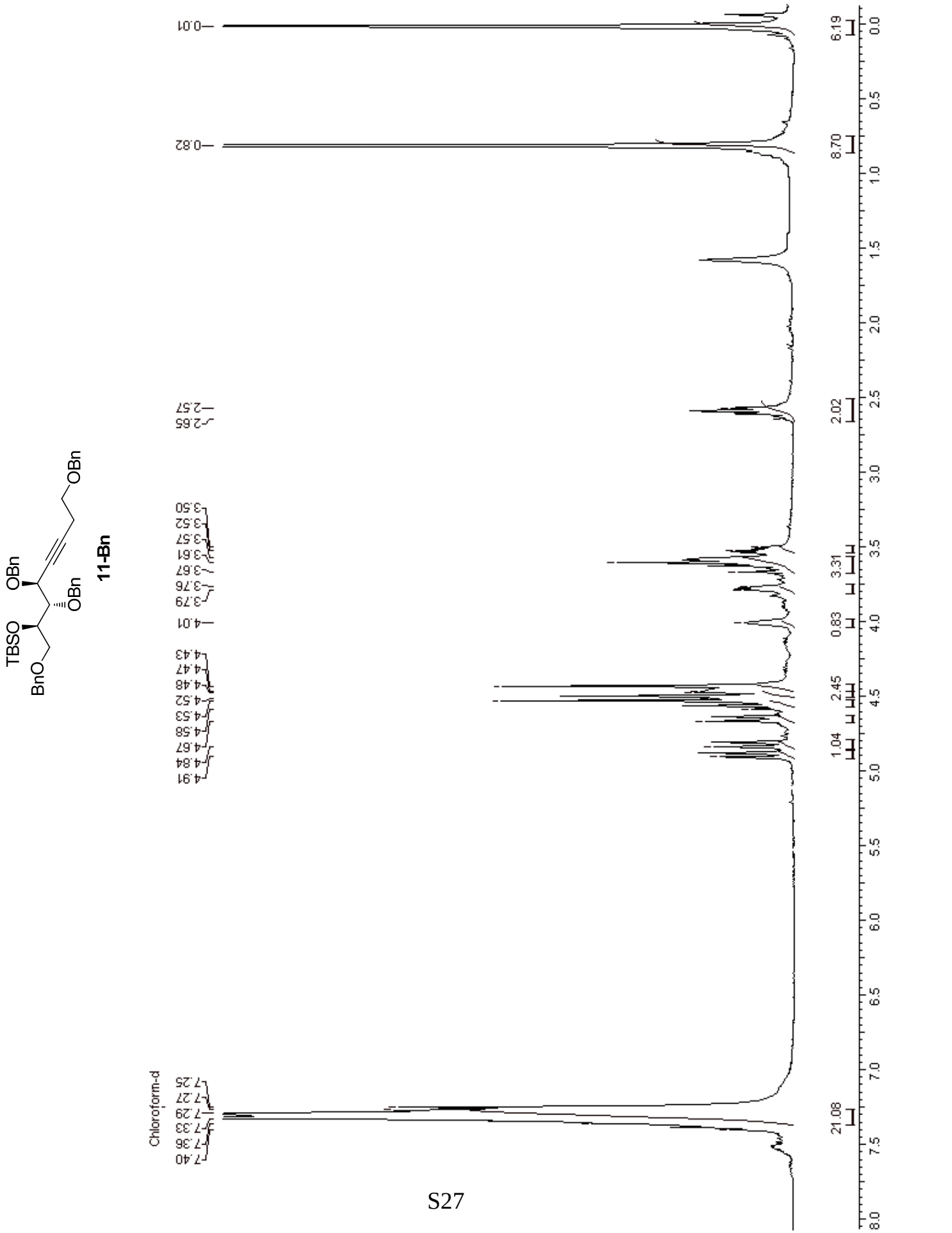
TBSO
OBn
BnO
OBn
OBn
11-Bn
0.01
0.82
2.57
2.65
3.50
3.52
3.57
3.61
3.67
3.76
3.79
4.01
4.43
4.47
4.48
4.52
4.53
4.58
4.67
4.84
4.91
Chloroform-d
7.25
7.27
7.29
7.33
7.36
7.40
6.19
8.70
2.02
3.31
0.83
2.45
1.04
21.08

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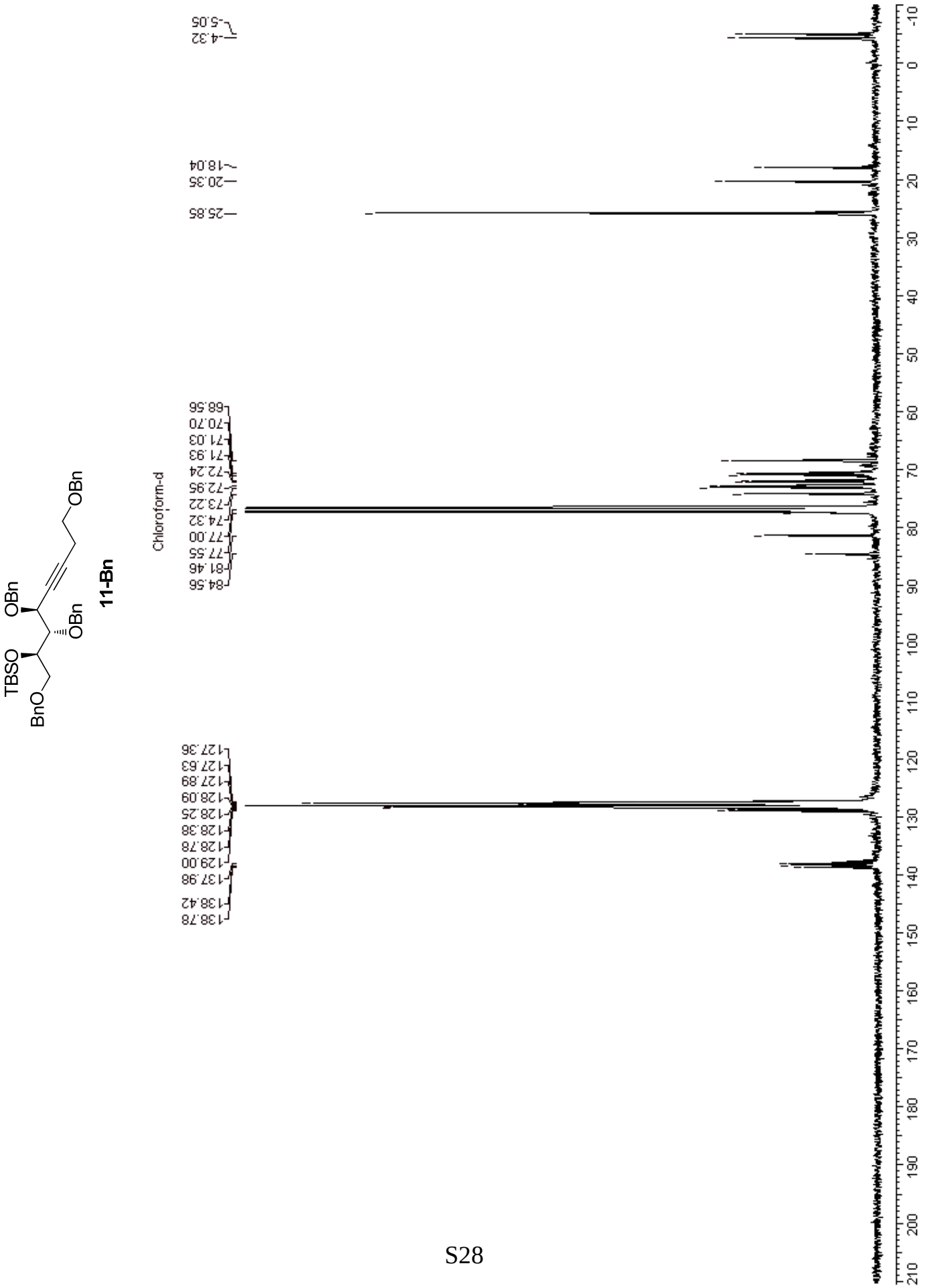

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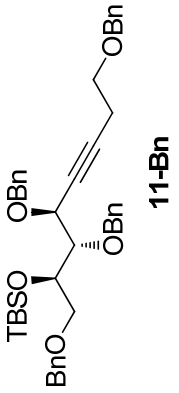
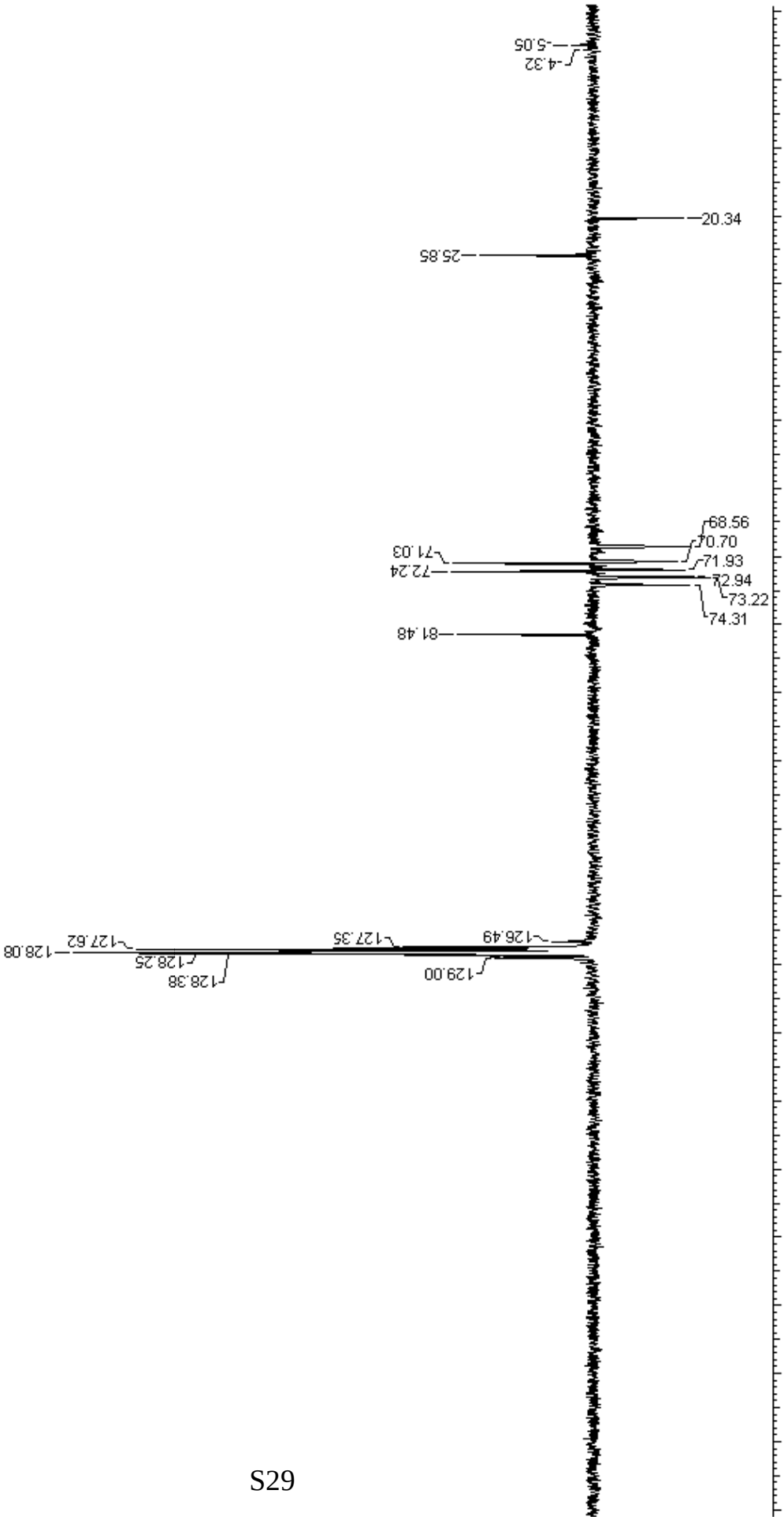
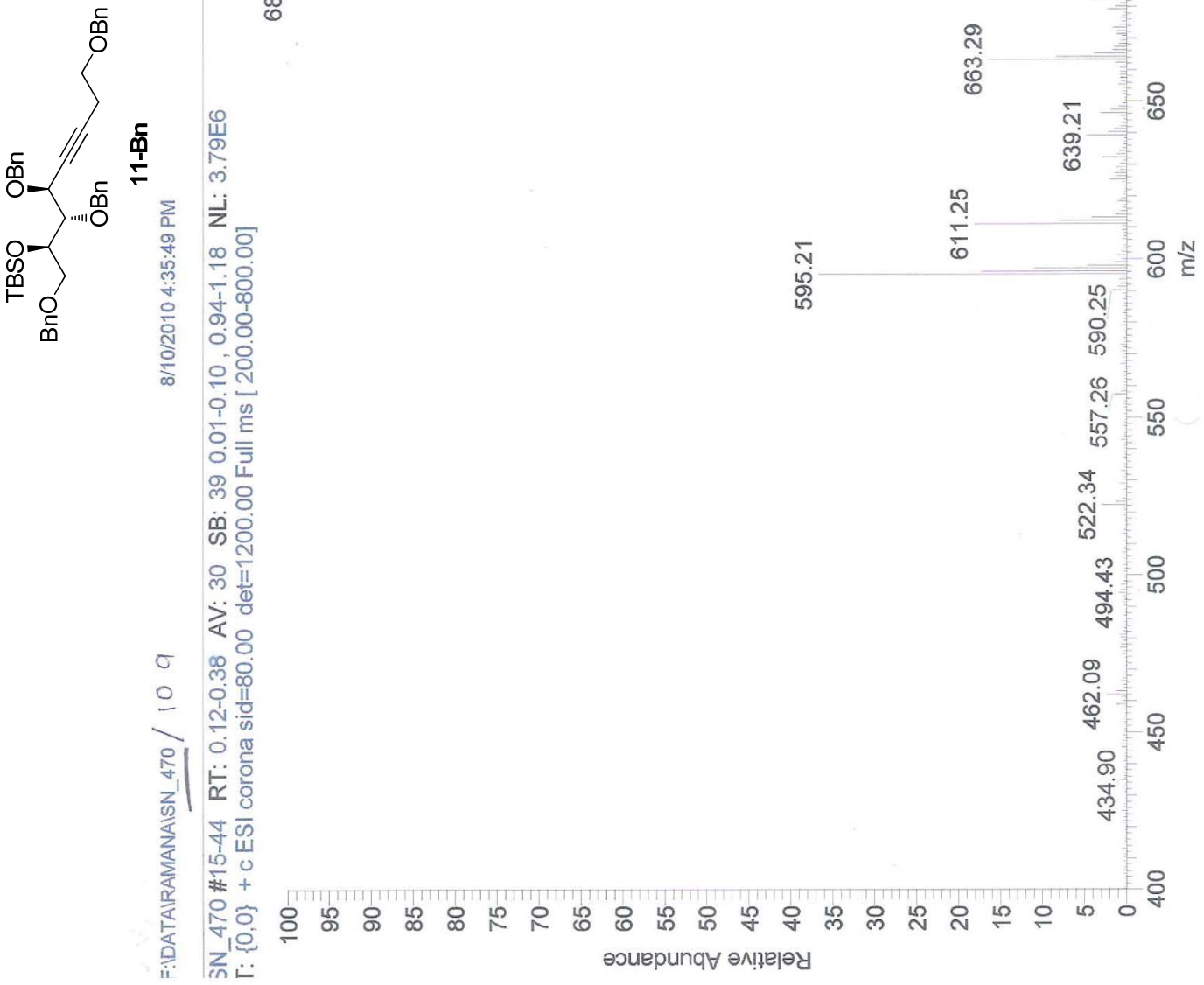


11-Bn




TBSO
OBn
BnO
OBn
OBn
11-Bn
8/10/2010 4:35:49 PM
F:\DATA\RAMANA\SN_470 / 10 9
SN_470 #15-44 RT: 0.12-0.38 AV: 30 SB: 39 0.01-0.10 , 0.94-1.18 NL: 3.79E6
T: {0,0} + c ESI corona sid=80.00 det=1200.00 Full ms [200.00-800.00]
687.39 (M+Na)
731.39
703.40
747.33
663.29
768.47
639.21
793.30
611.25
595.21
434.90
462.09
494.43
522.34
557.26
590.25
Relative Abundance
m/z

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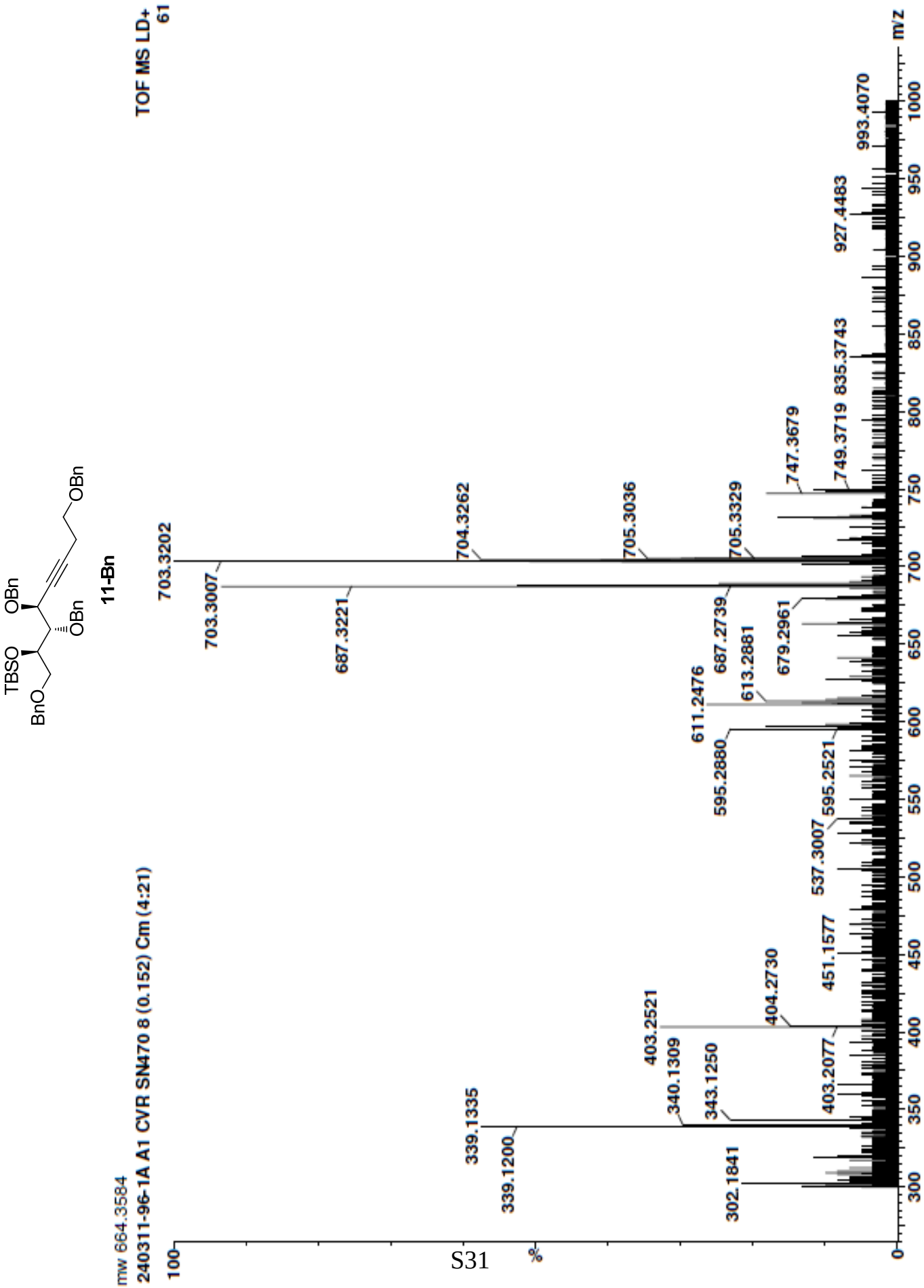
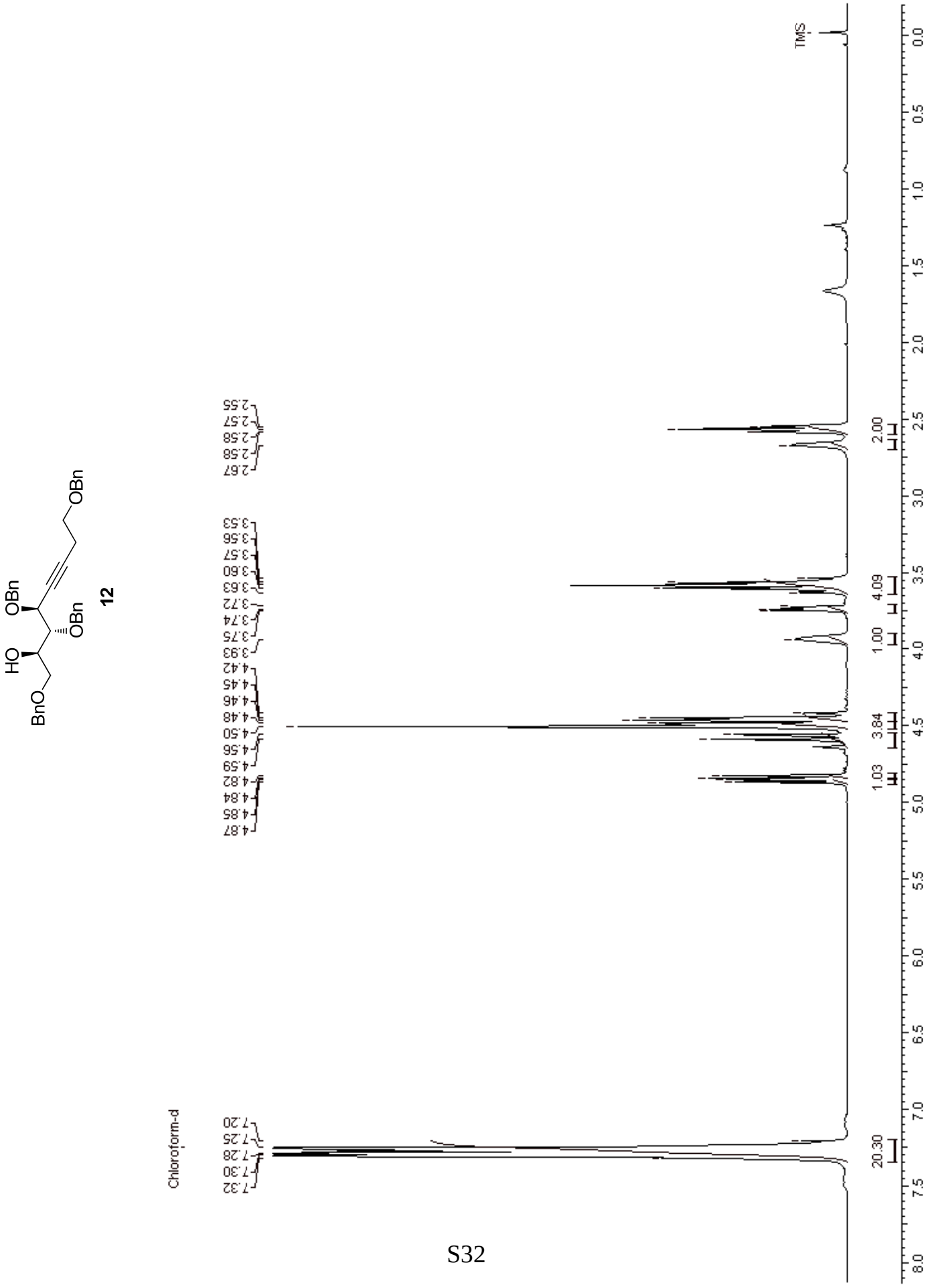
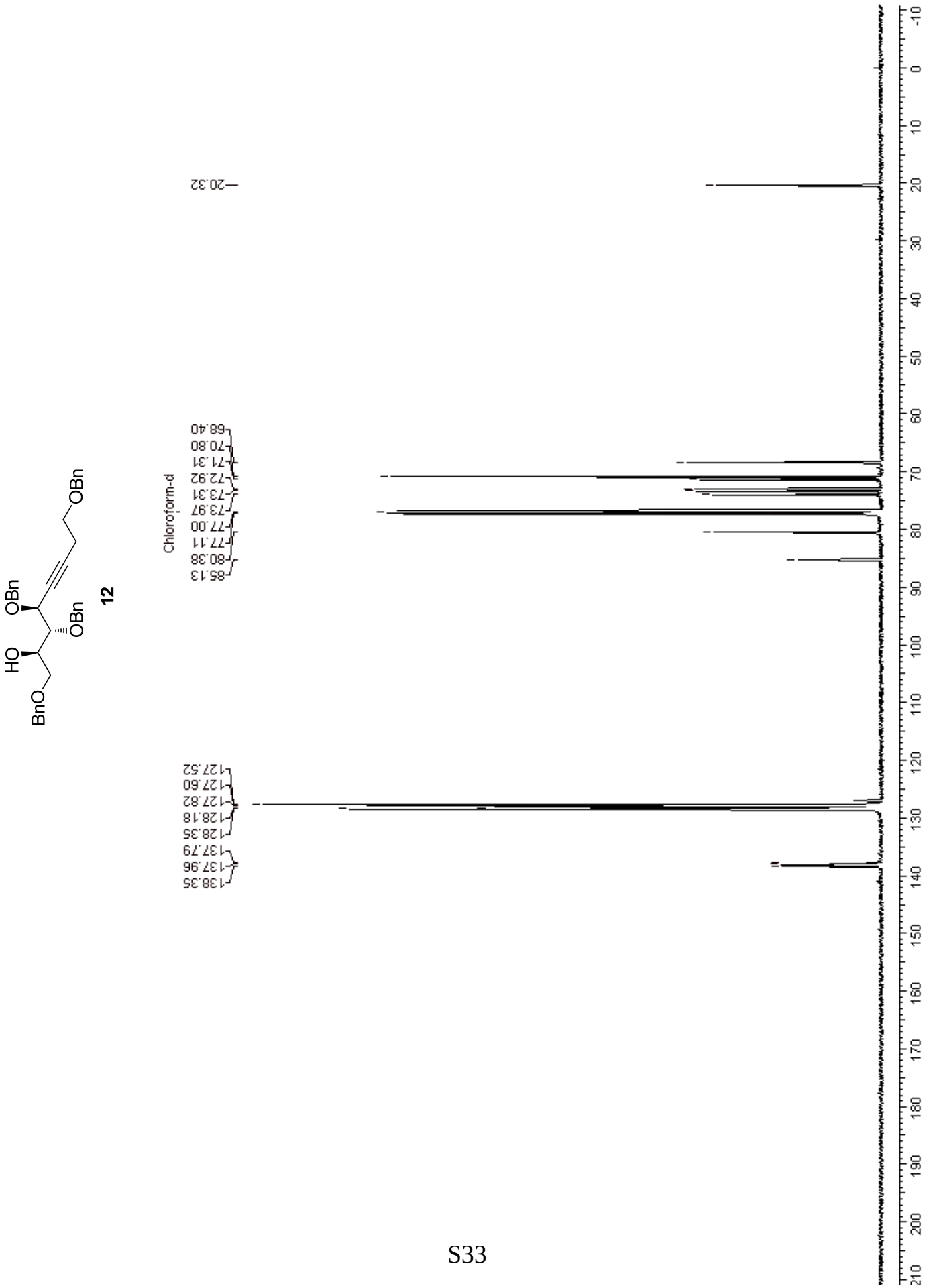



HO
OBn
OBn
OBn
BnO
12
TMS
Chloroform-d
2.55
2.57
2.58
2.58
2.67
3.53
3.56
3.57
3.60
3.63
3.72
3.74
3.75
3.93
4.42
4.45
4.46
4.48
4.50
4.56
4.59
4.82
4.84
4.85
4.87
7.20
7.25
7.28
7.30
7.32
2.00
4.09
1.00
3.84
1.03
20.30
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0


OBn
OBn
HO
BnO
12
Chloroform-d
20.32
68.40
70.80
71.31
72.92
73.31
73.97
77.00
77.11
80.38
85.13
127.52
127.60
127.82
128.18
128.35
137.79
137.96
138.35

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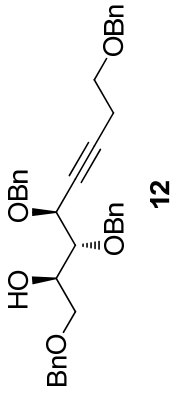
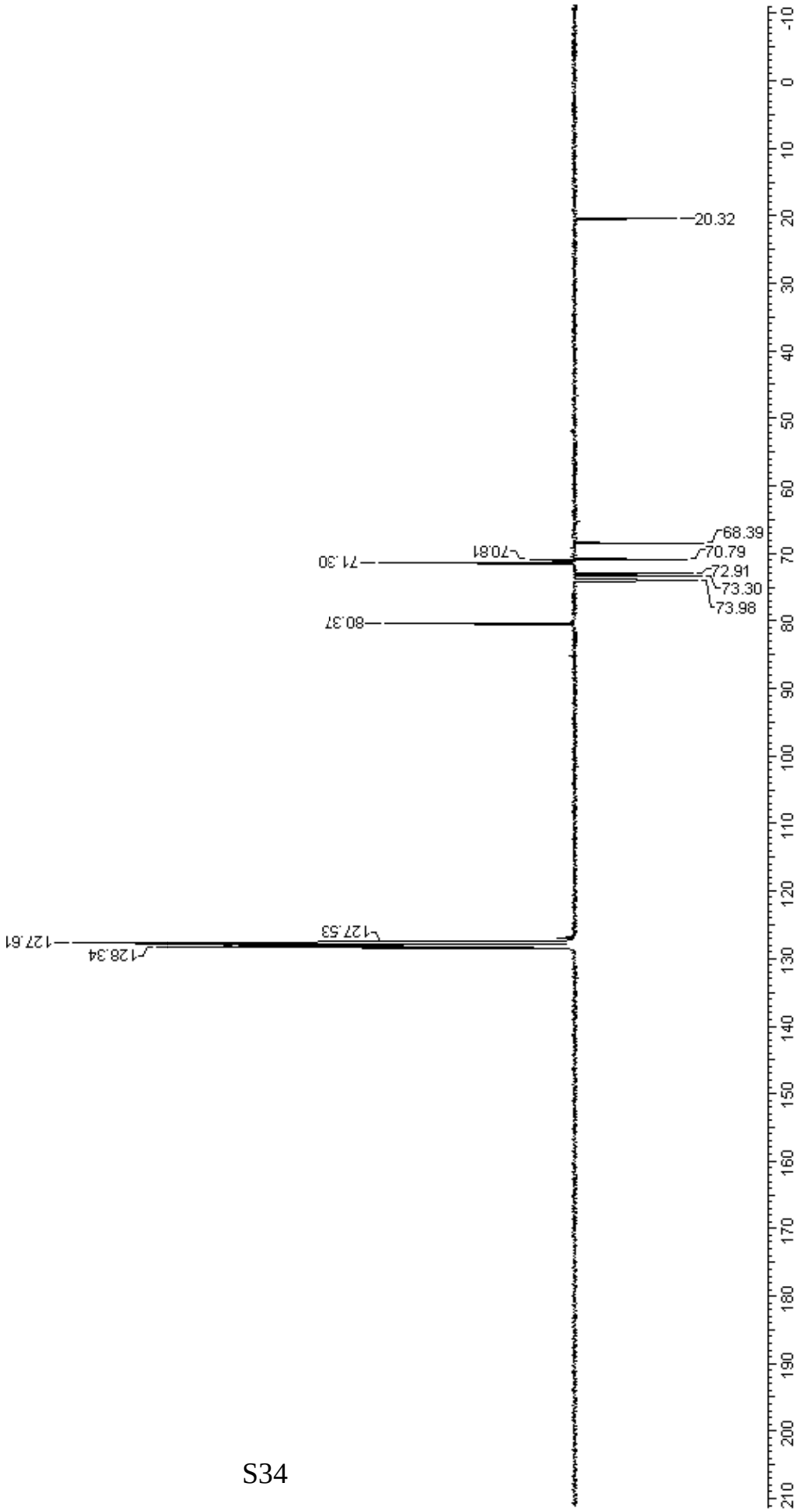
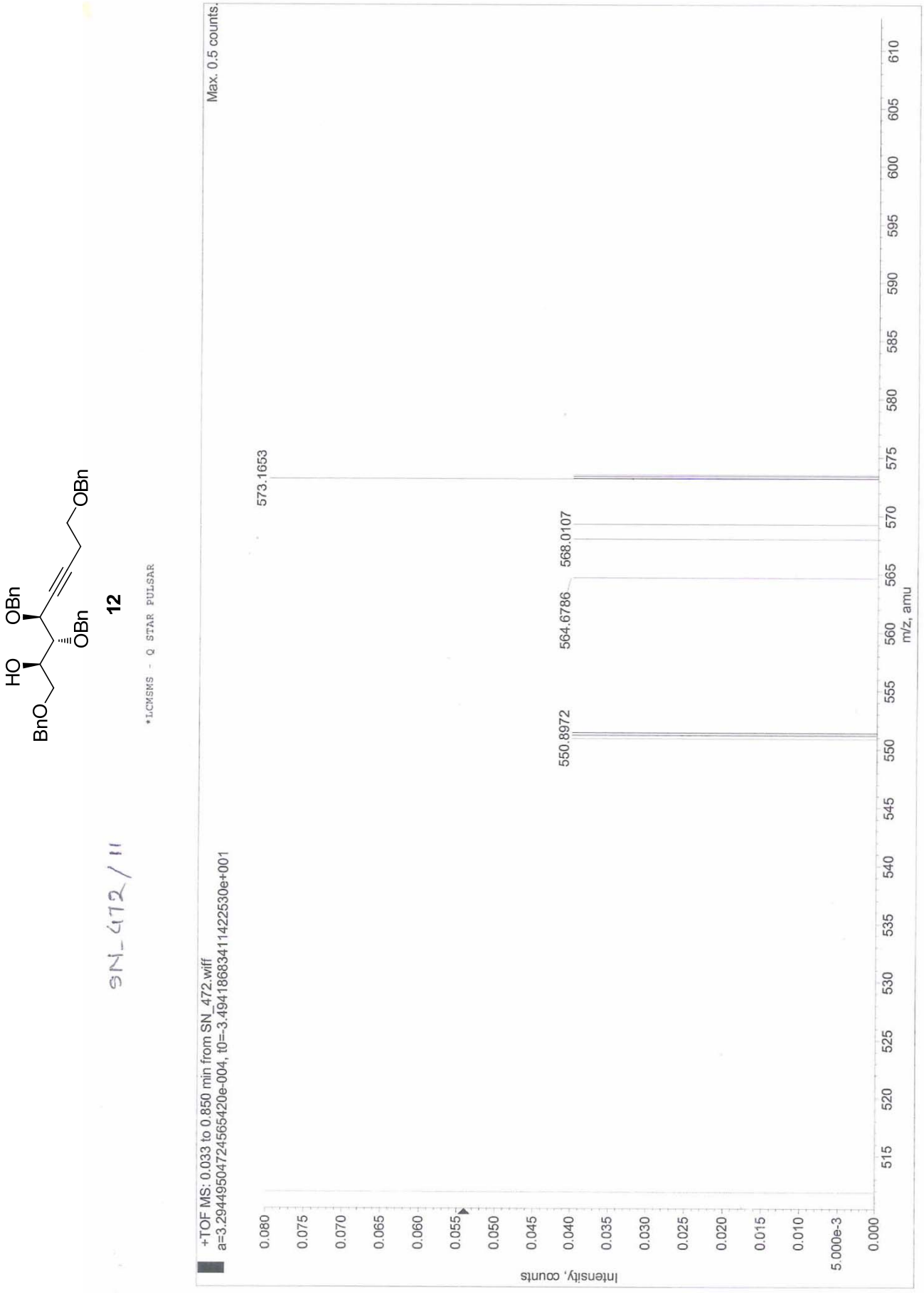
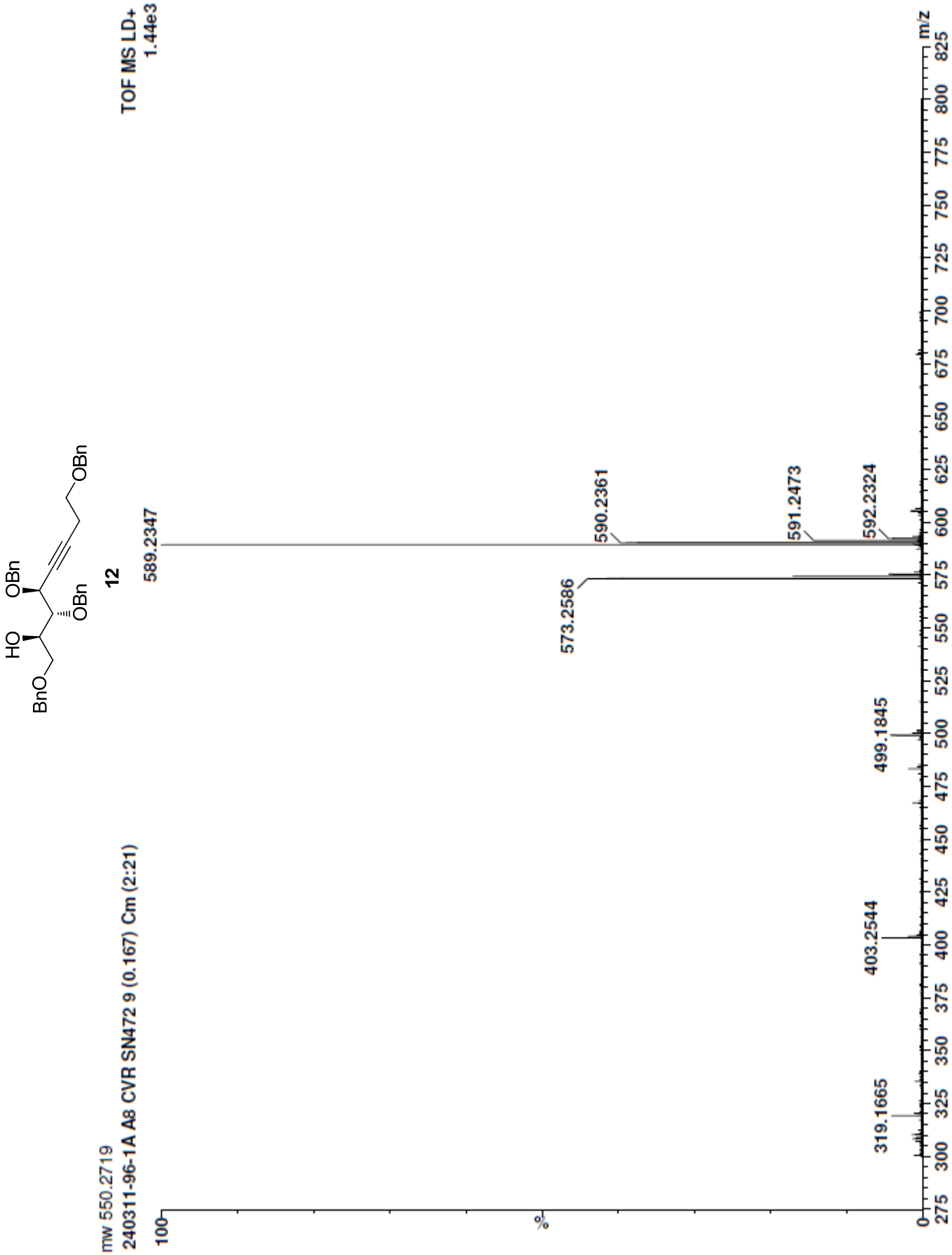


12




HO
OBn
OBn
OBn
BnO
12
*LCMSMS - Q STAR PULSAR
SN_472 / 11
+TOF MS: 0.033 to 0.850 min from SN_472.wiff
a=3.29449504724565420e-004, t0=-3.49418683411422530e+001
Max. 0.5 counts.
573.1653
568.0107
564.6786
550.8972
Intensity, counts
m/z, amu


TOF MS LD+
1.44e3
240311-96-1A A8 CVR SN472 9 (0.167) Cm (2:21)
mw 550.2719
12
HO
BnO
OBn
OBn
OBn
589.2347
590.2361
591.2473
592.2324
573.2586
499.1845
403.2544
319.1665
100
%
0
m/z
275
300
325
350
375
400
425
450
475
500
525
550
575
600
625
650
675
700
725
750
775
800
825

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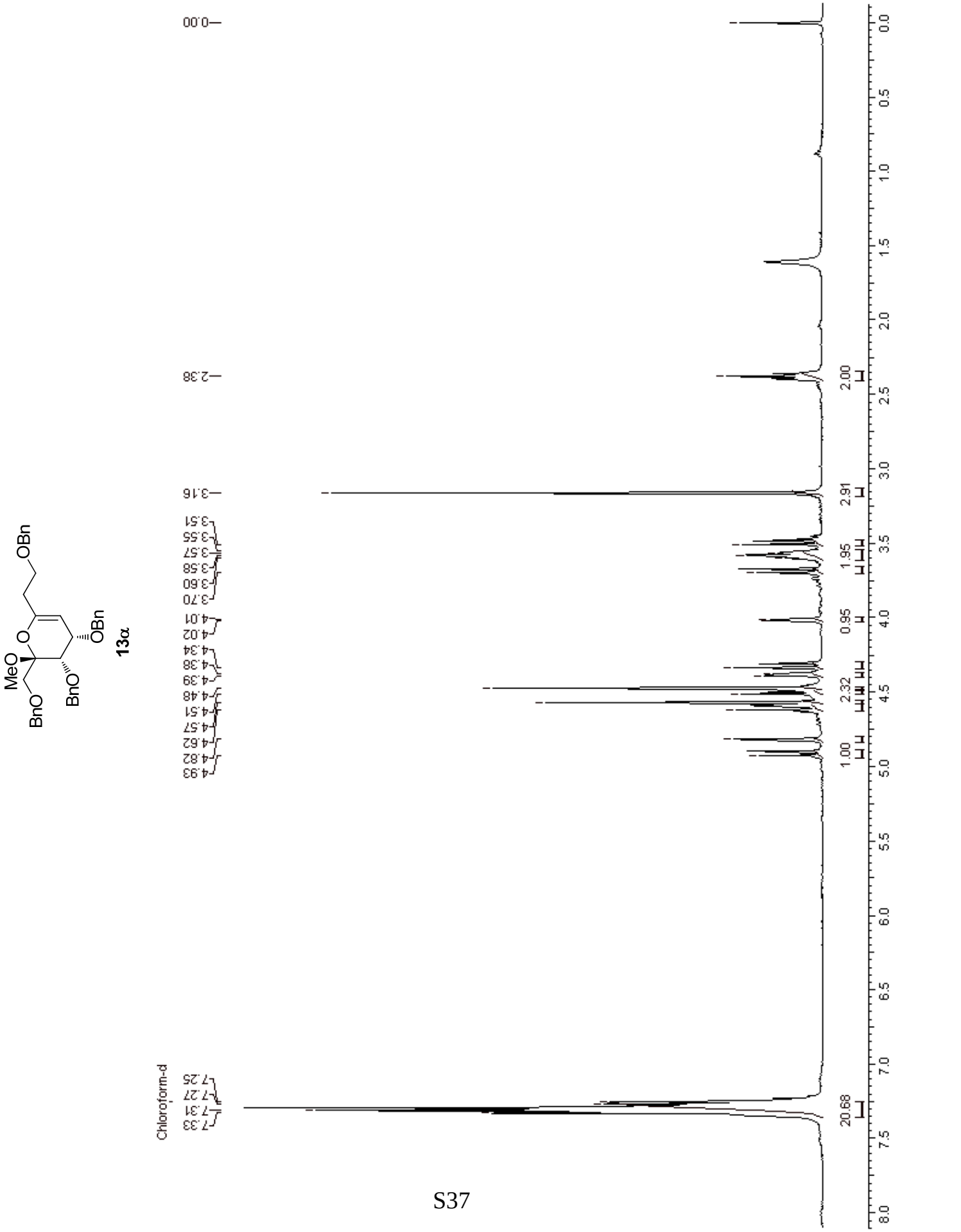

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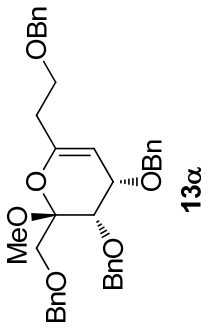
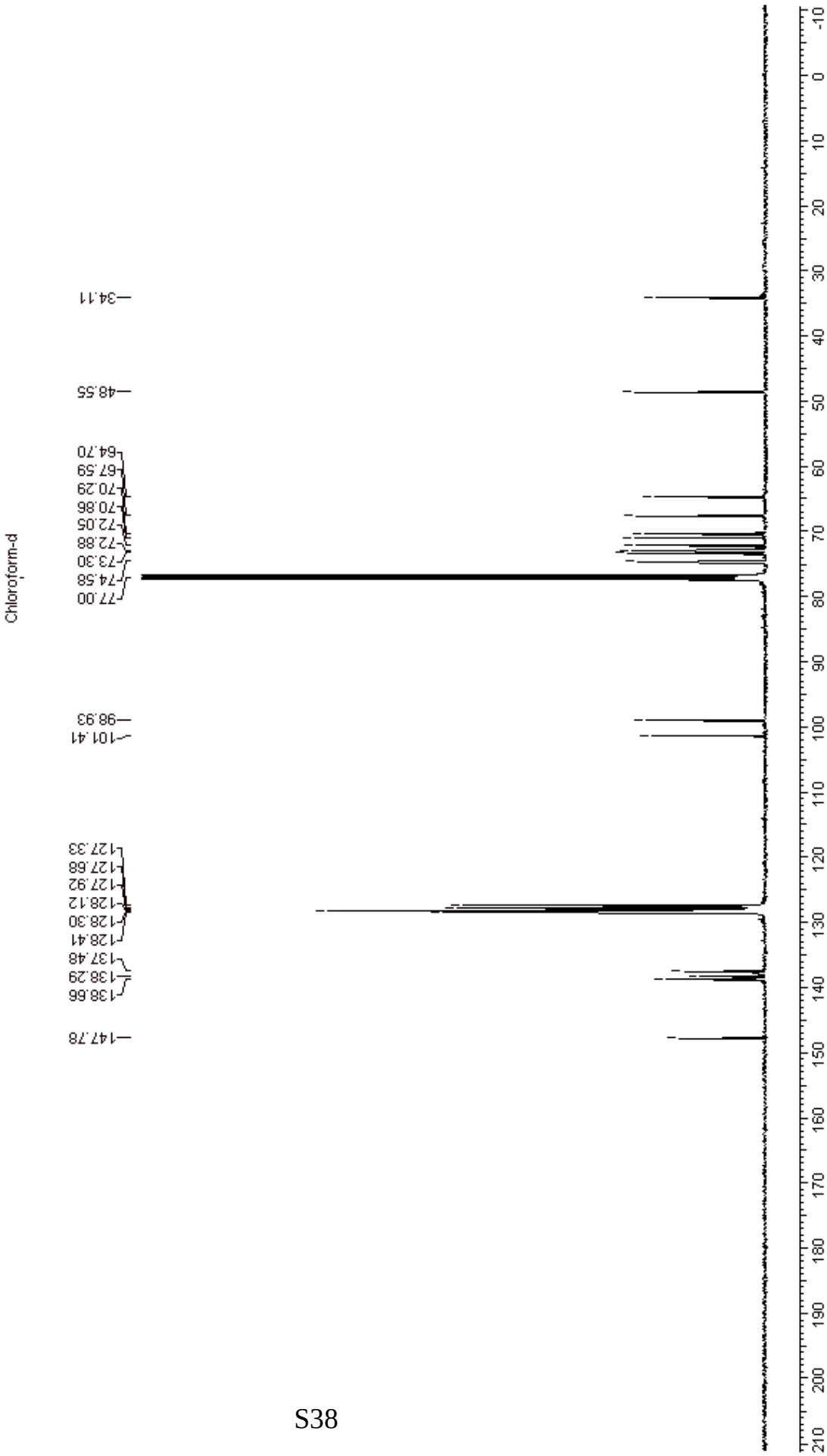
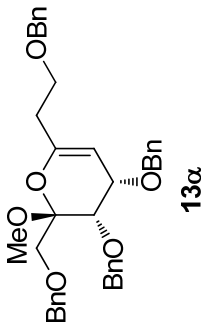
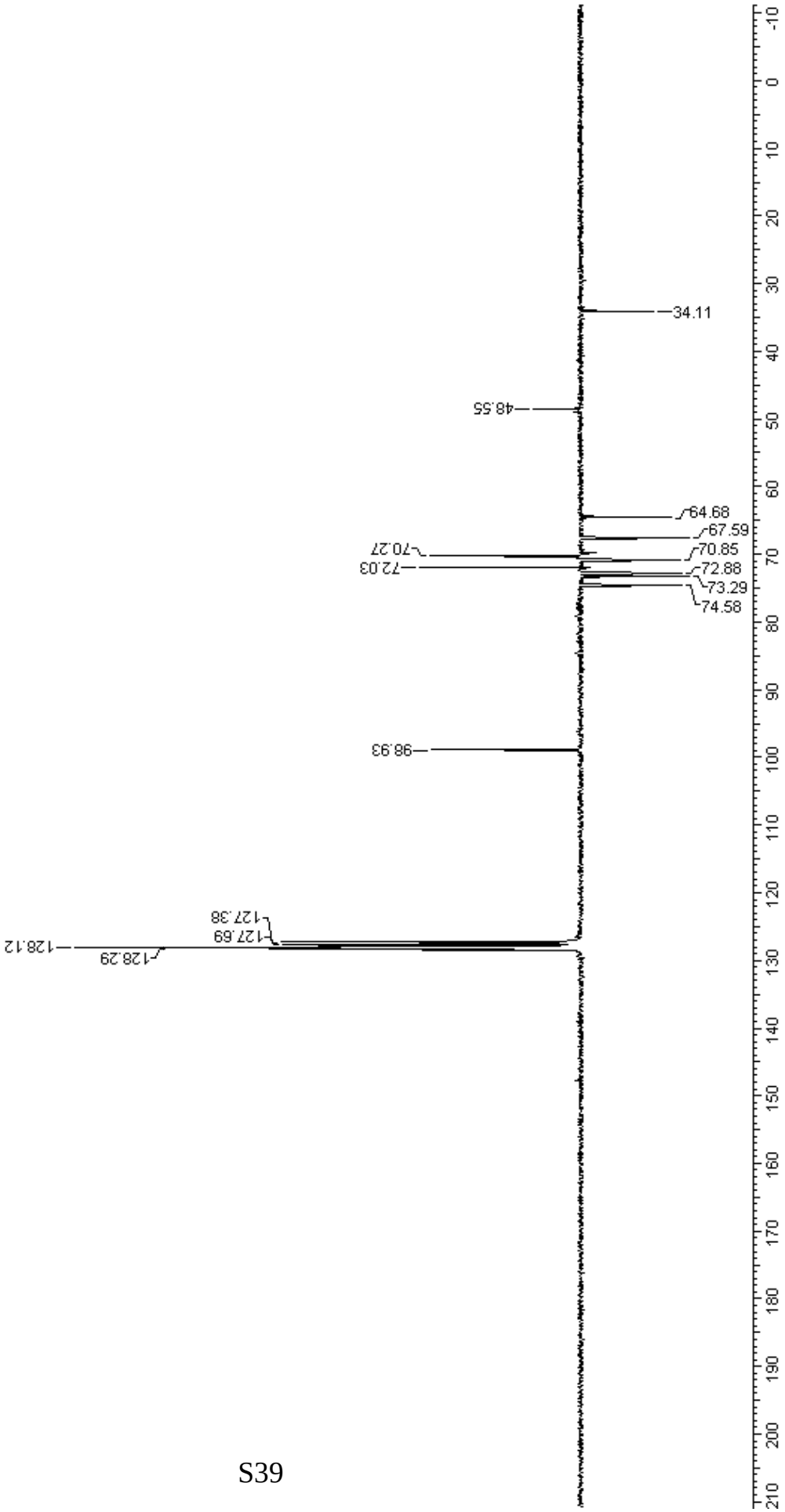


13α




OBn
OBn
MeO
BnO
BnO

13α


34.11
48.55
64.68
67.59
70.27
70.85
72.03
72.88
73.29
74.58
98.93
127.38
127.69
128.12
128.29

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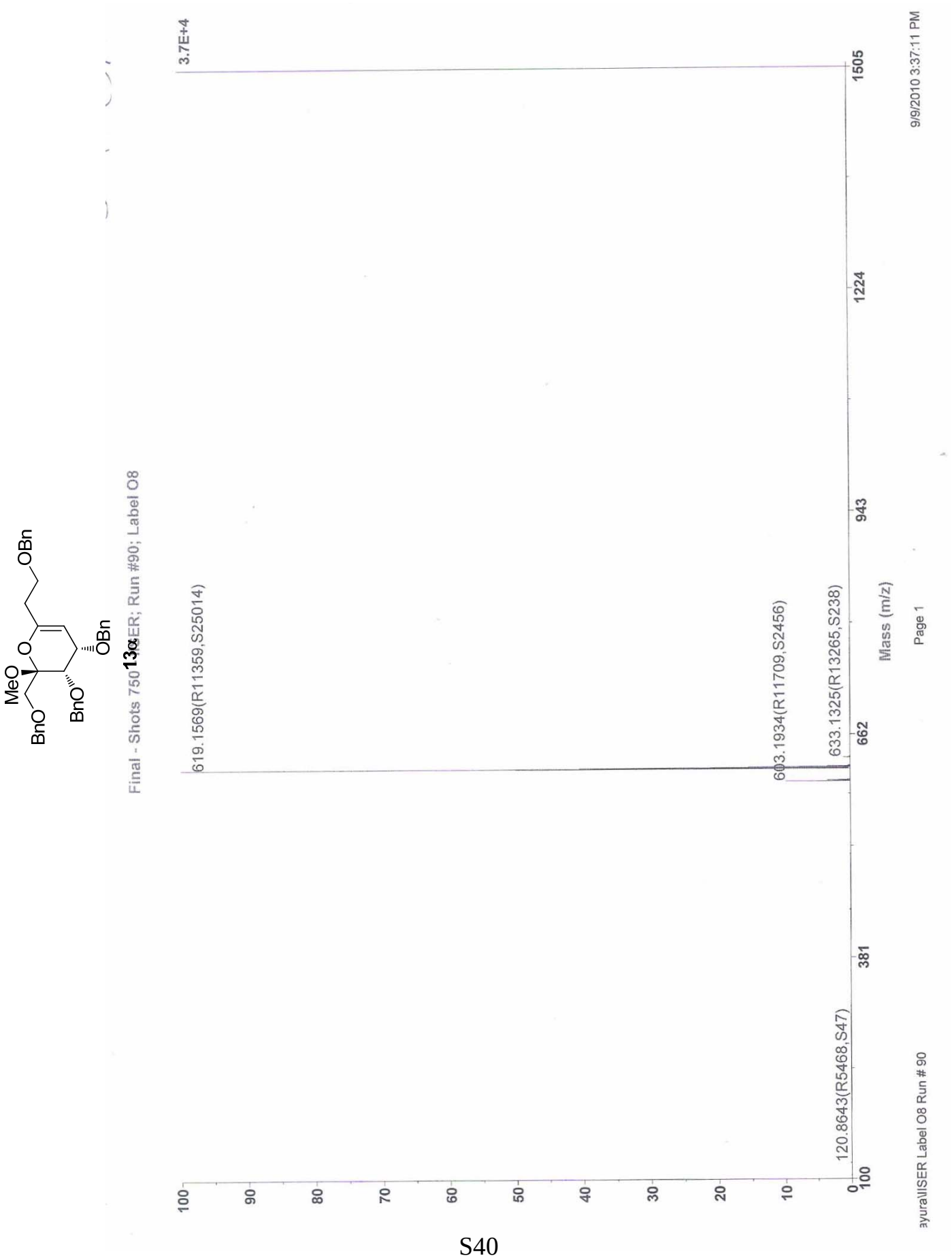

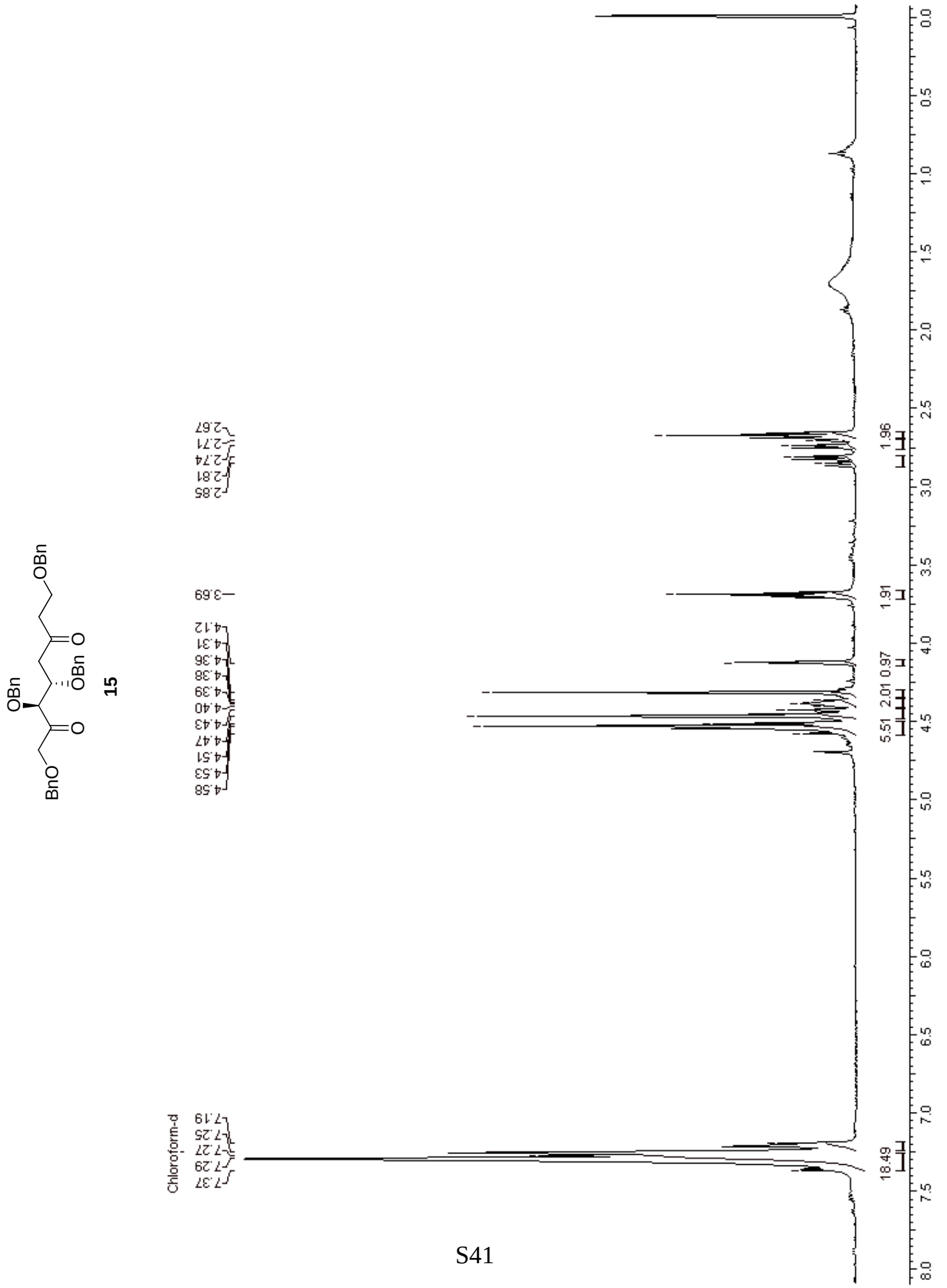
OBn
OBn
OBn
O
O
O
BnO
15
2.67
2.71
2.74
2.81
2.85
3.69
4.12
4.31
4.36
4.38
4.39
4.40
4.43
4.47
4.51
4.53
4.58
Chloroform-d
7.19
7.25
7.27
7.29
7.37
1.96
1.91
0.97
2.01
5.51
18.49

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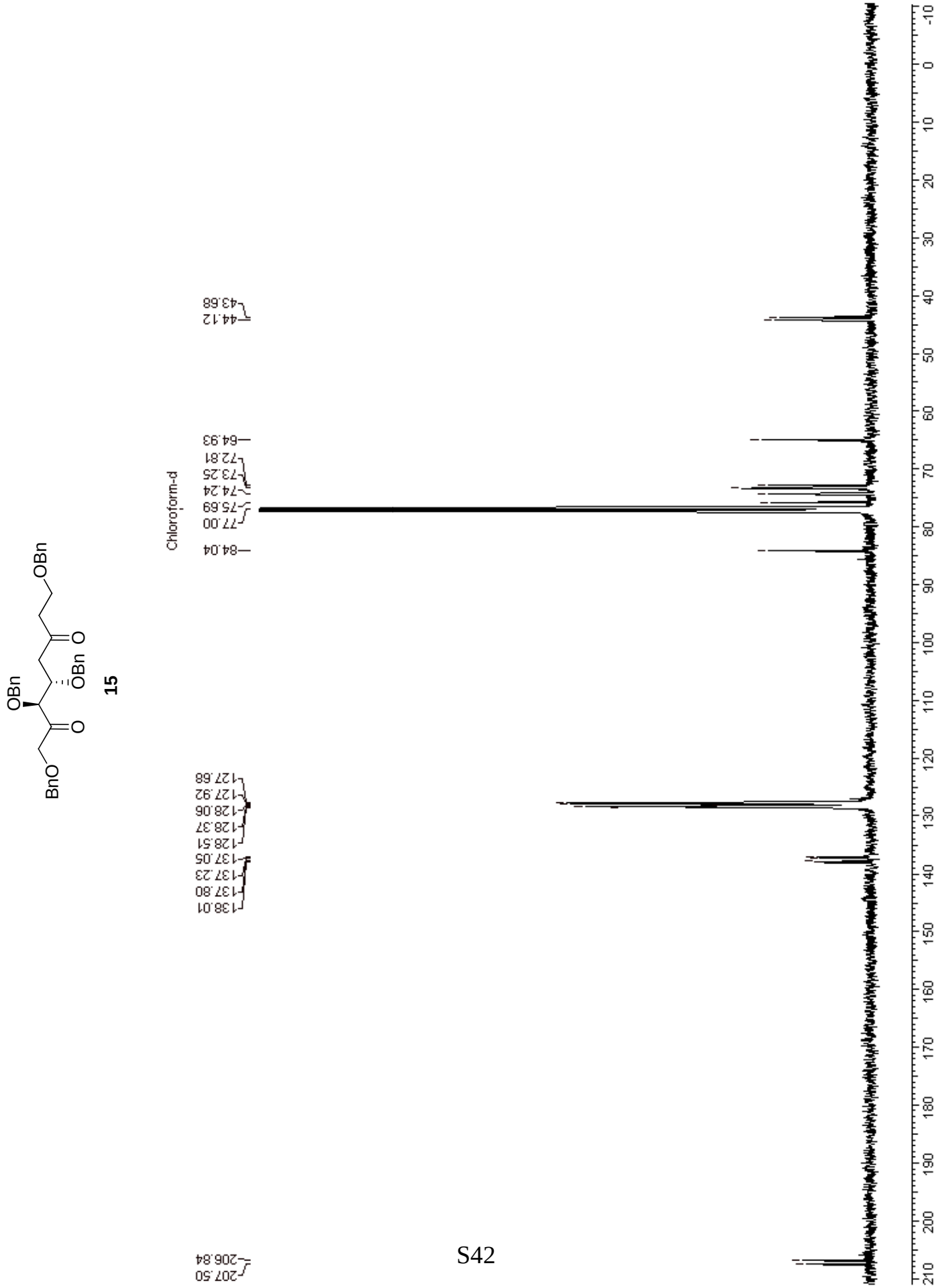
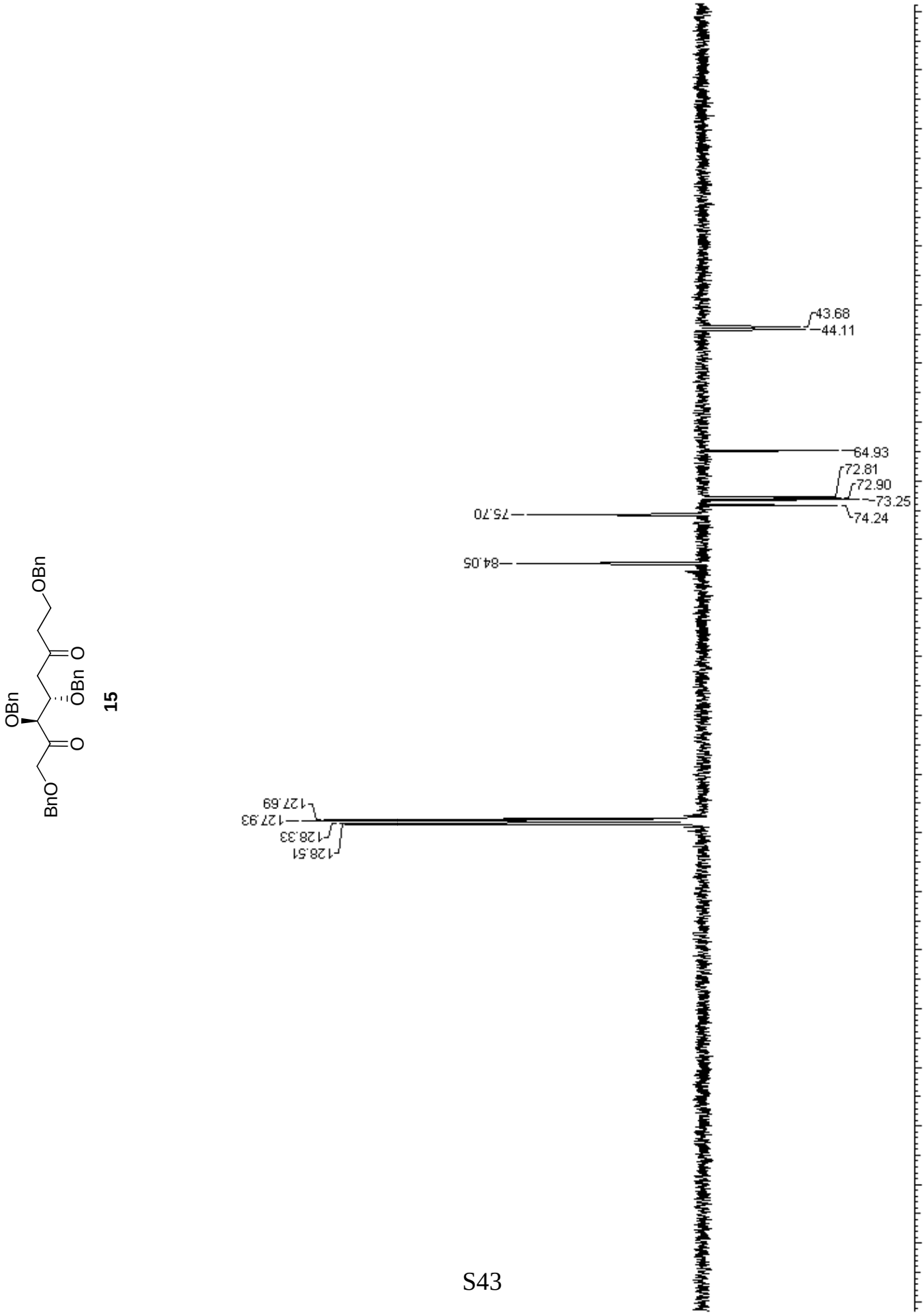
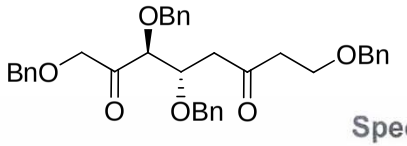



OBn
OBn
O
OBn
O
BnO
15
43.68
44.11
64.93
72.81
72.90
73.25
74.24
75.70
84.05
127.69
127.93
128.33
128.51

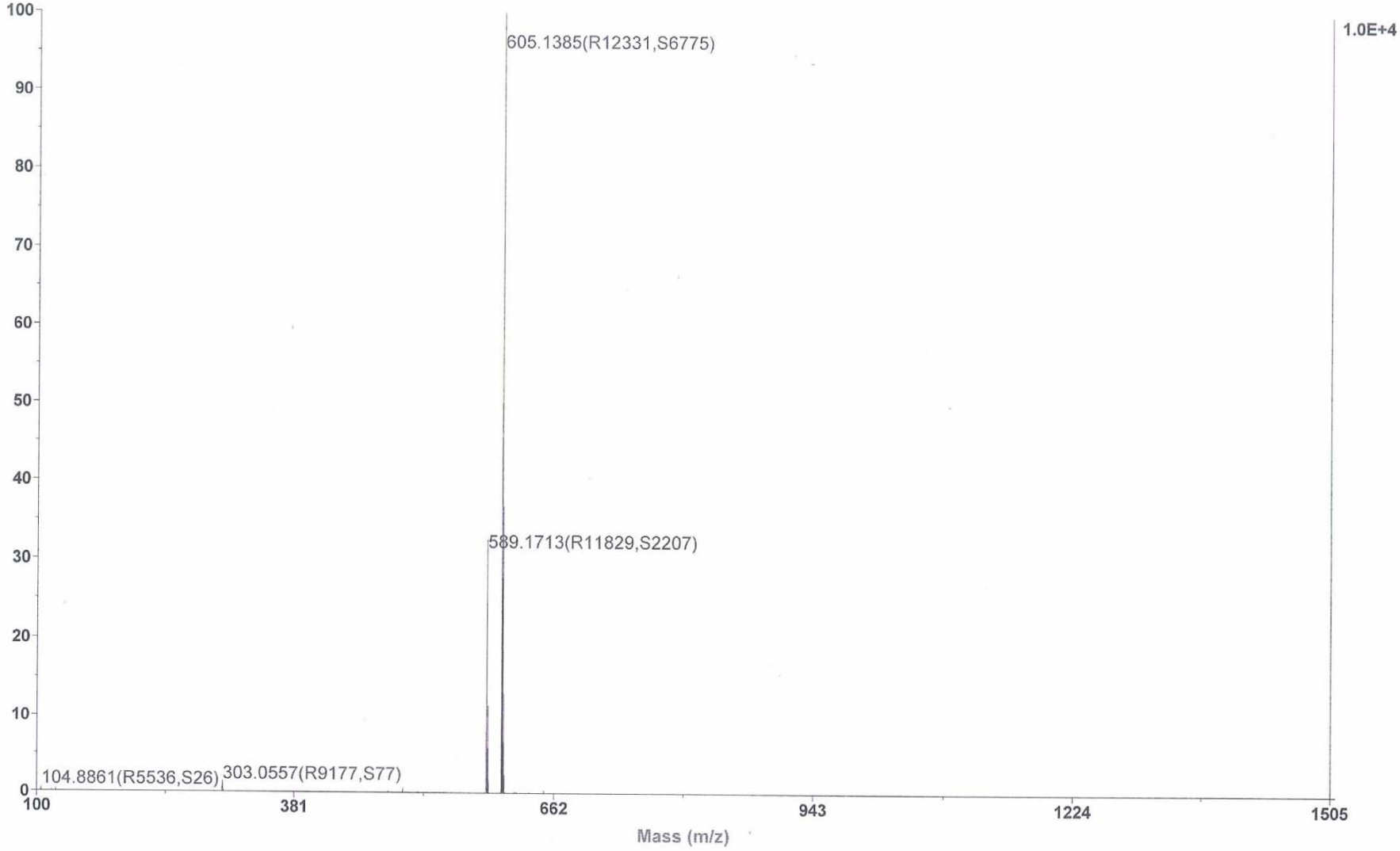


15

Spectrum Report

SN-476(A) / Rearranged

Final - Shots 750 - IISER; Run #90; Label O7



mayura\IISER Label O7 Run # 90

Page 1

9/9/2010 3:37:07 PM

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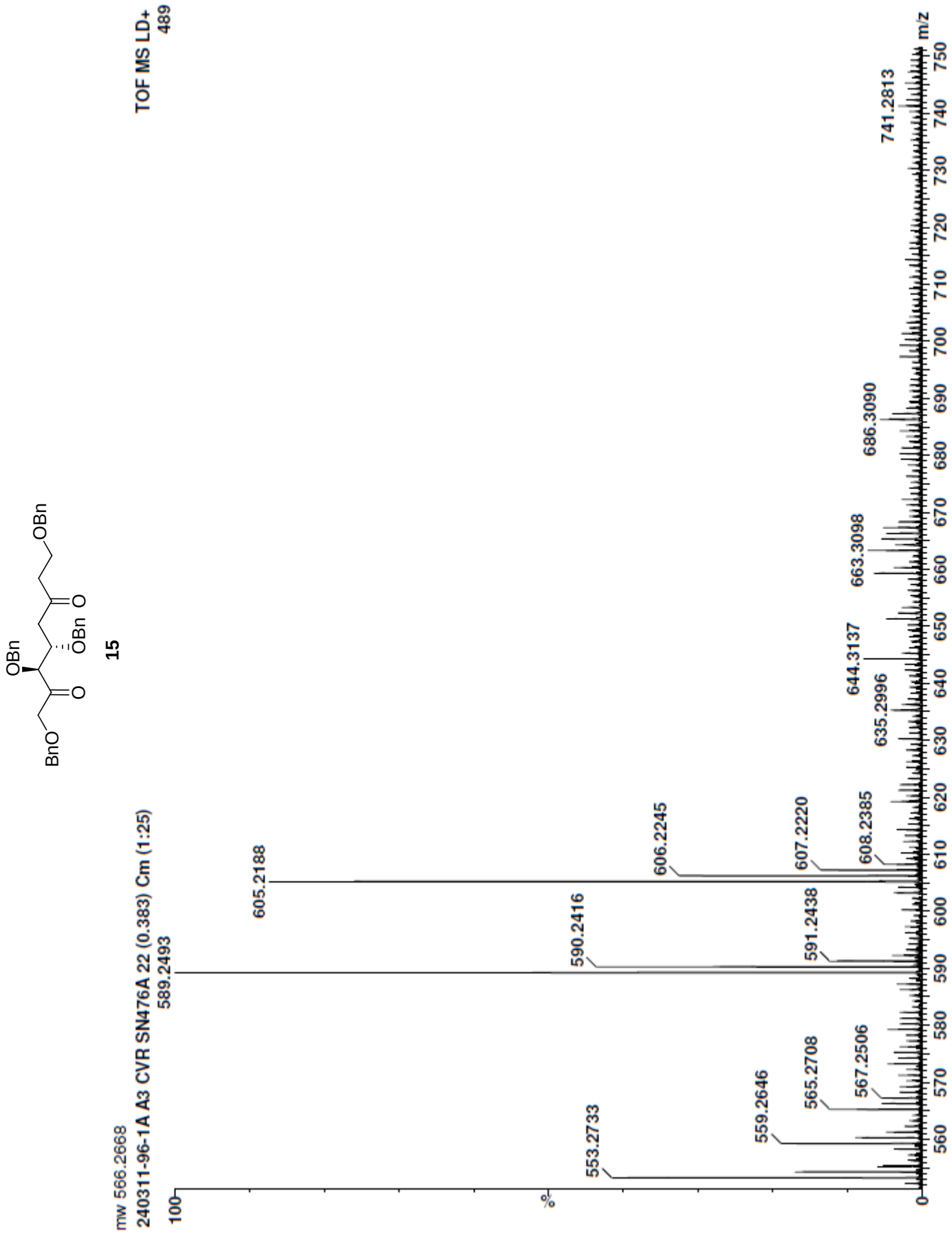
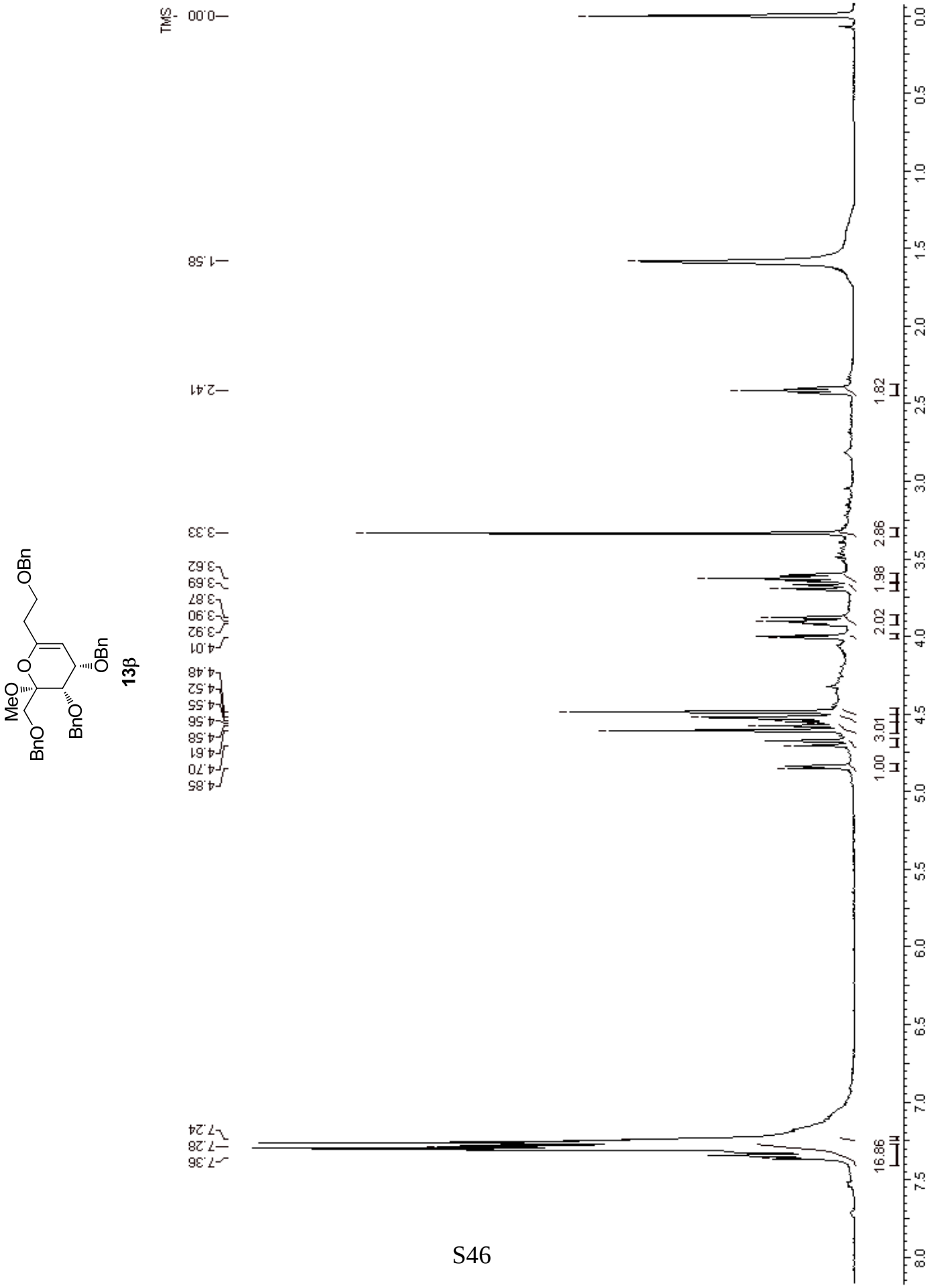

OBn
OBn
O
OBn
O
O
BnO
15
TOF MS LD+
489
mw 566.2668
240311-96-1A A3 CVR SN476A 22 (0.383) Cm (1:25)
100
%
0
m/z
553.2733
559.2646
565.2708
567.2506
589.2493
590.2416
591.2438
605.2188
606.2245
607.2220
608.2385
635.2996
644.3137
663.3098
686.3090
741.2813


OBn
MeO
BnO
BnO
13β
TMS
0.00
1.58
2.41
3.33
3.62
3.69
3.87
3.90
3.92
4.01
4.48
4.52
4.55
4.56
4.58
4.61
4.70
4.85
7.24
7.28
7.36
1.82
2.86
1.98
2.02
3.01
1.00
16.86

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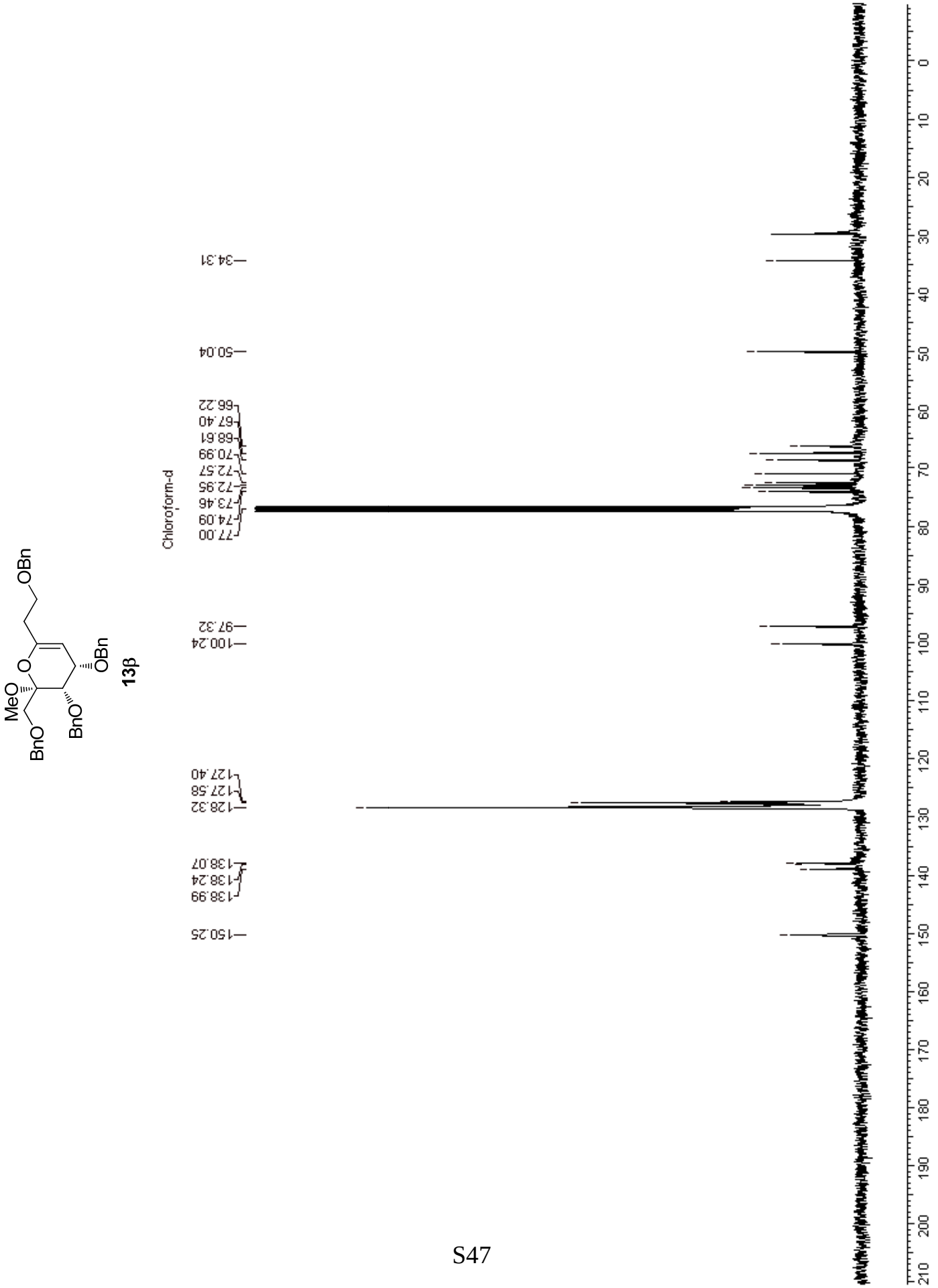

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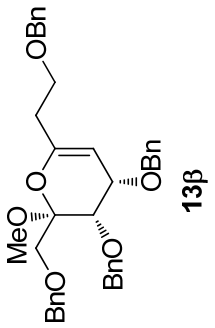
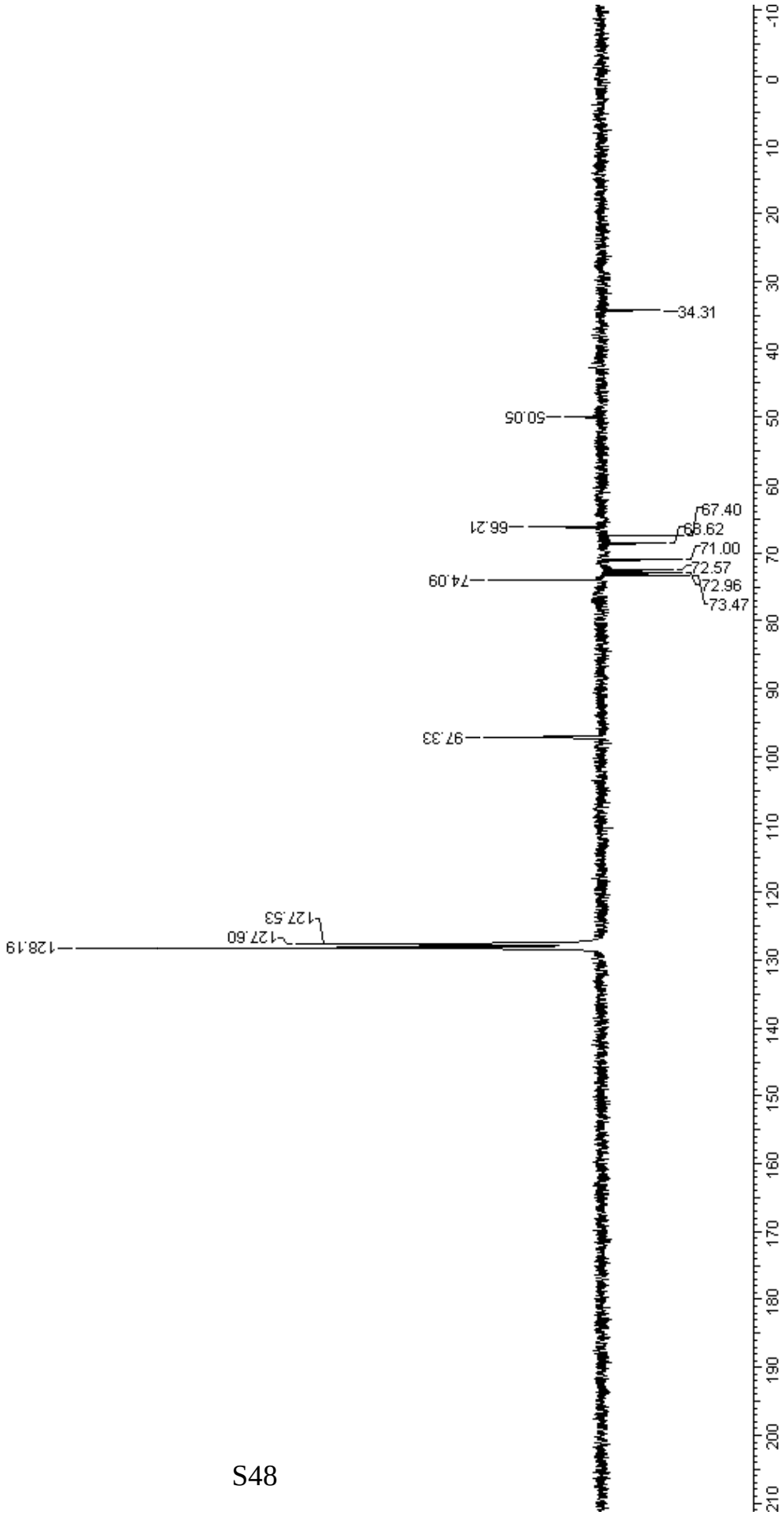
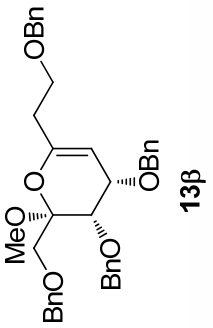


13β





13β

SN_476(B)/12 β

*LCMSNS - Q STAR PULSAR

+TOF MS: 0.033 to 0.833 min from SN_476(B).wiff
a=3.29449504724565420e-004, t0=-3.49418683411422530e+001

Max. 1.4 counts.

603.1040
473.1624
282.0688
148.9634

Intensity, counts

m/z, amu

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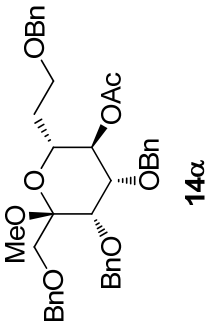
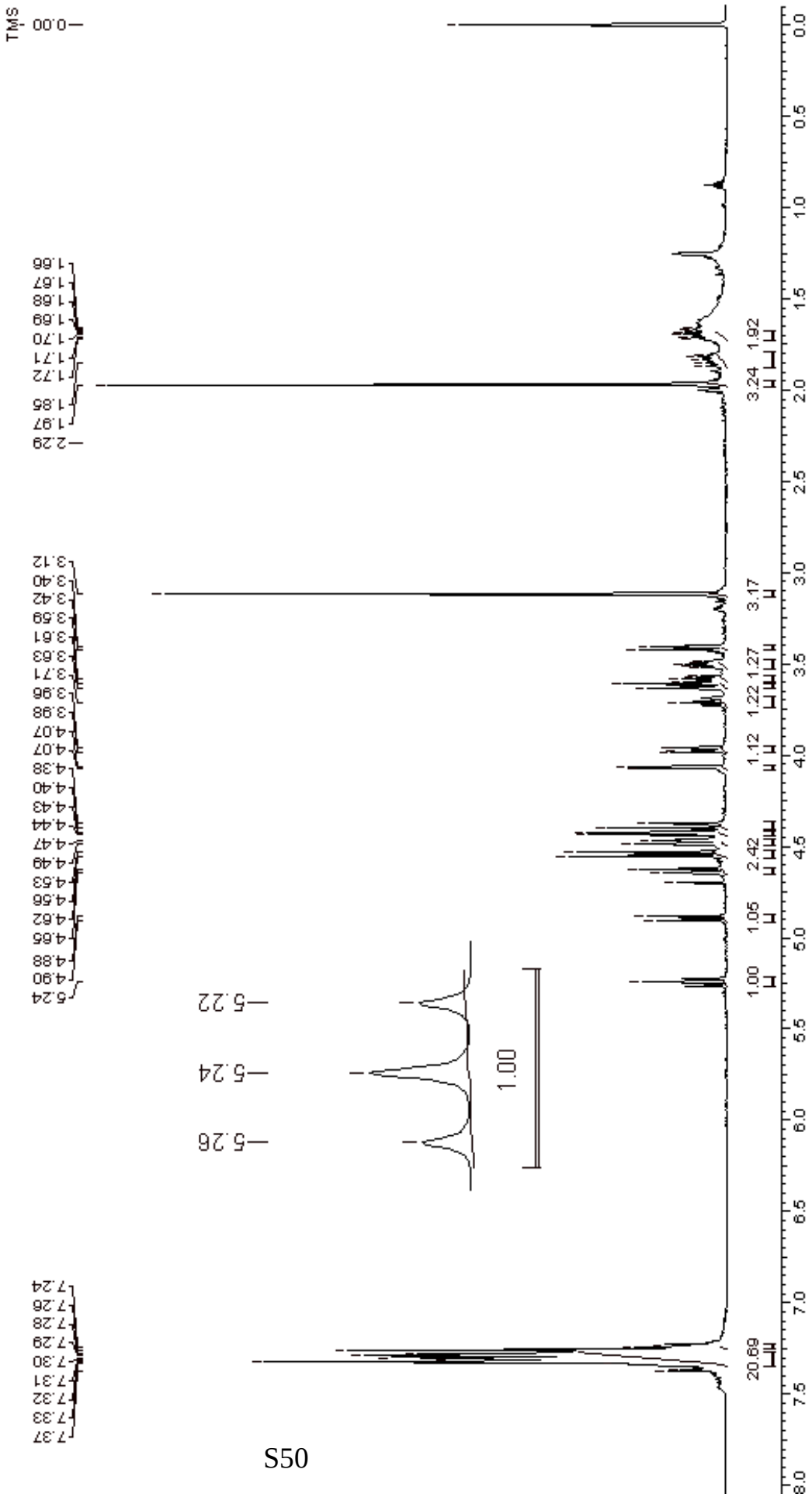
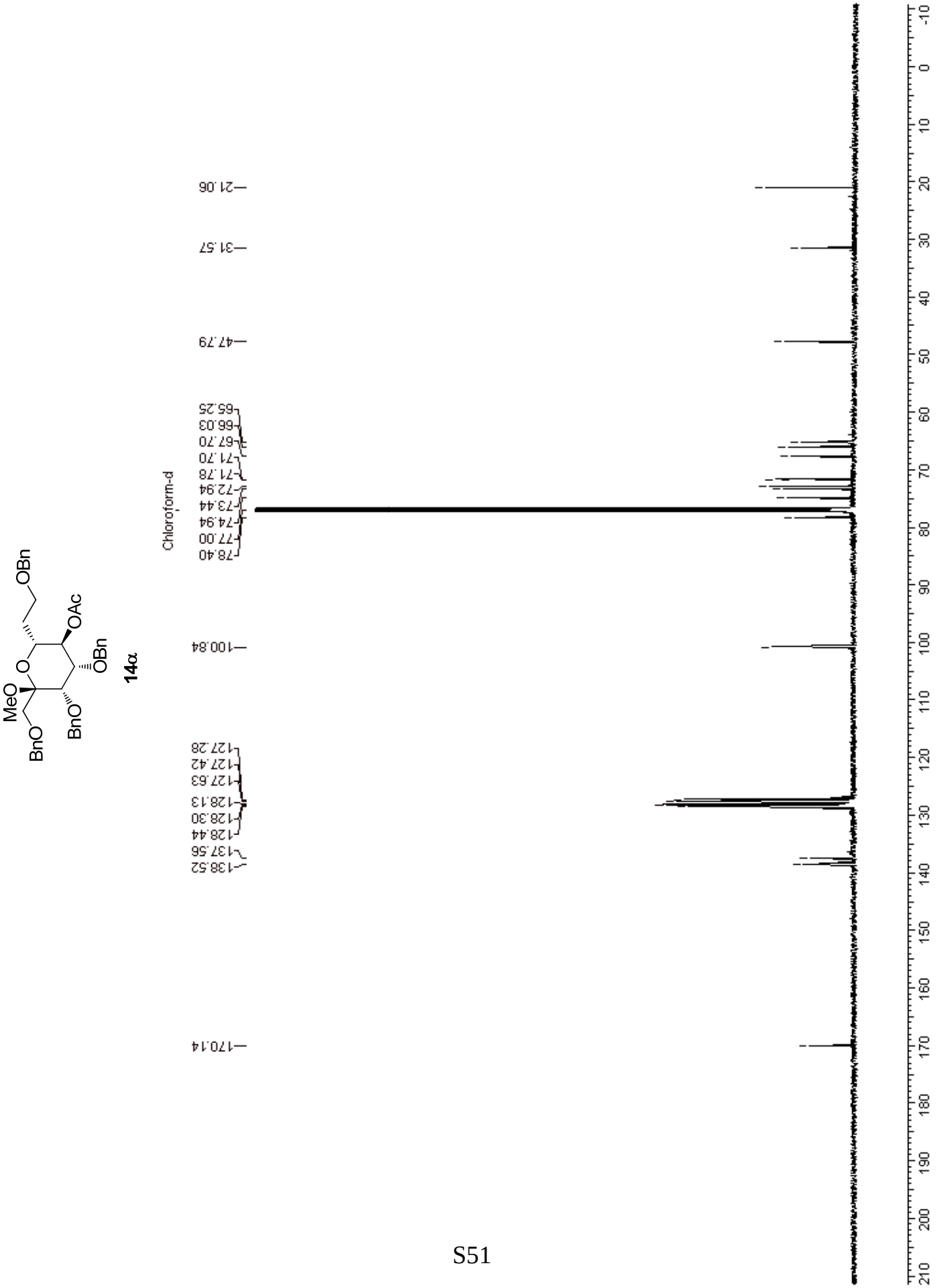


14α

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OAc
OBn
MeO
O
BnO
BnO
14α
Chloroform-d
21.06
31.57
47.79
65.25
66.03
67.70
71.70
71.78
72.94
73.44
74.94
77.00
78.40
100.84
127.28
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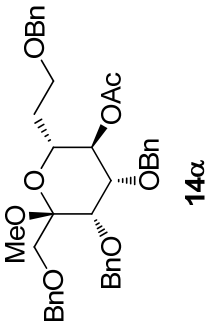
128.13
128.30
128.44
137.56
138.52
170.14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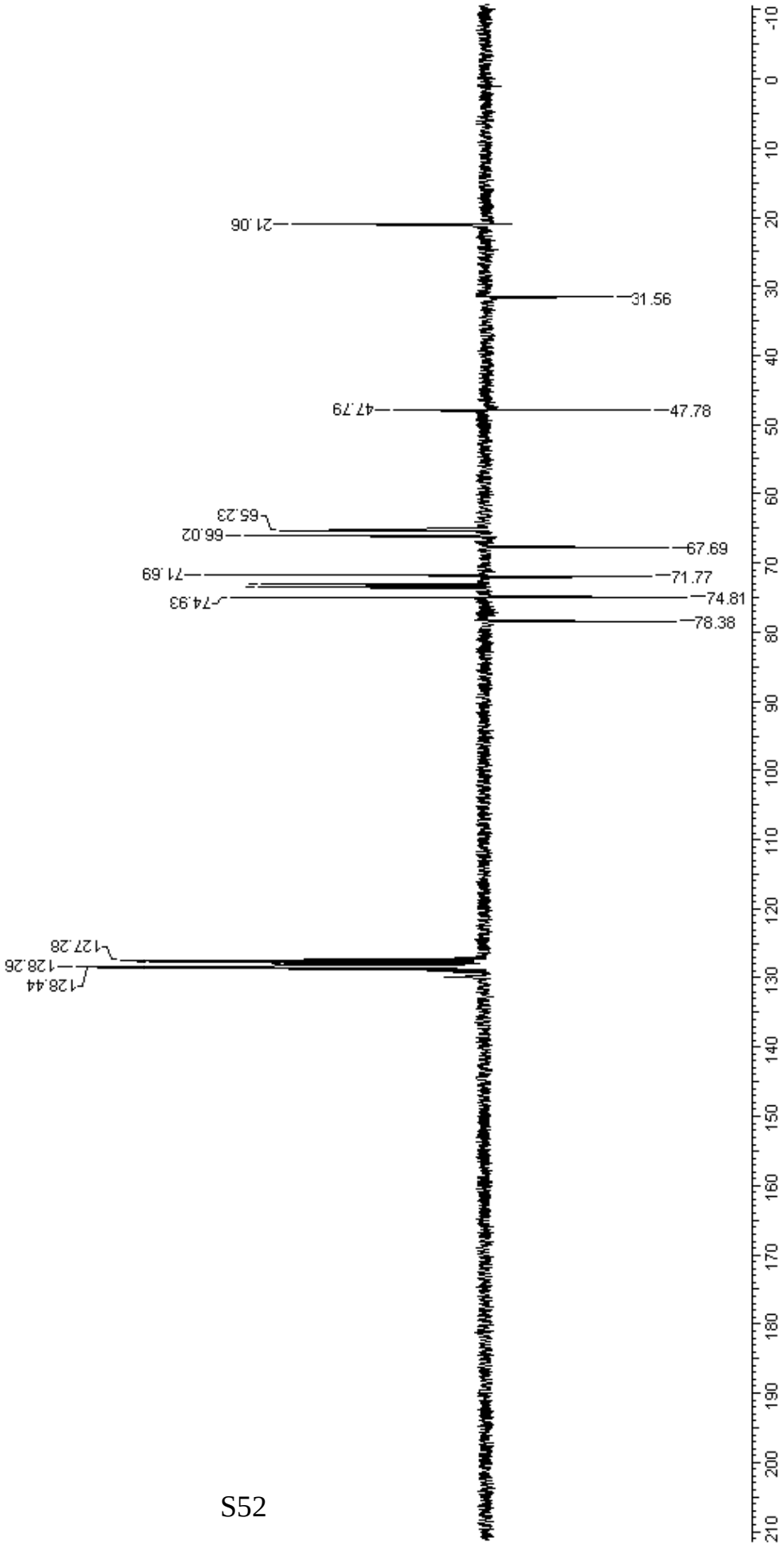
OAc
OBn
MeO
O
BnO
BnO

14α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31.56
47.79
47.78
65.23
66.02
67.69
71.69
71.77
74.93
74.81
78.38
127.28
128.26
128.44

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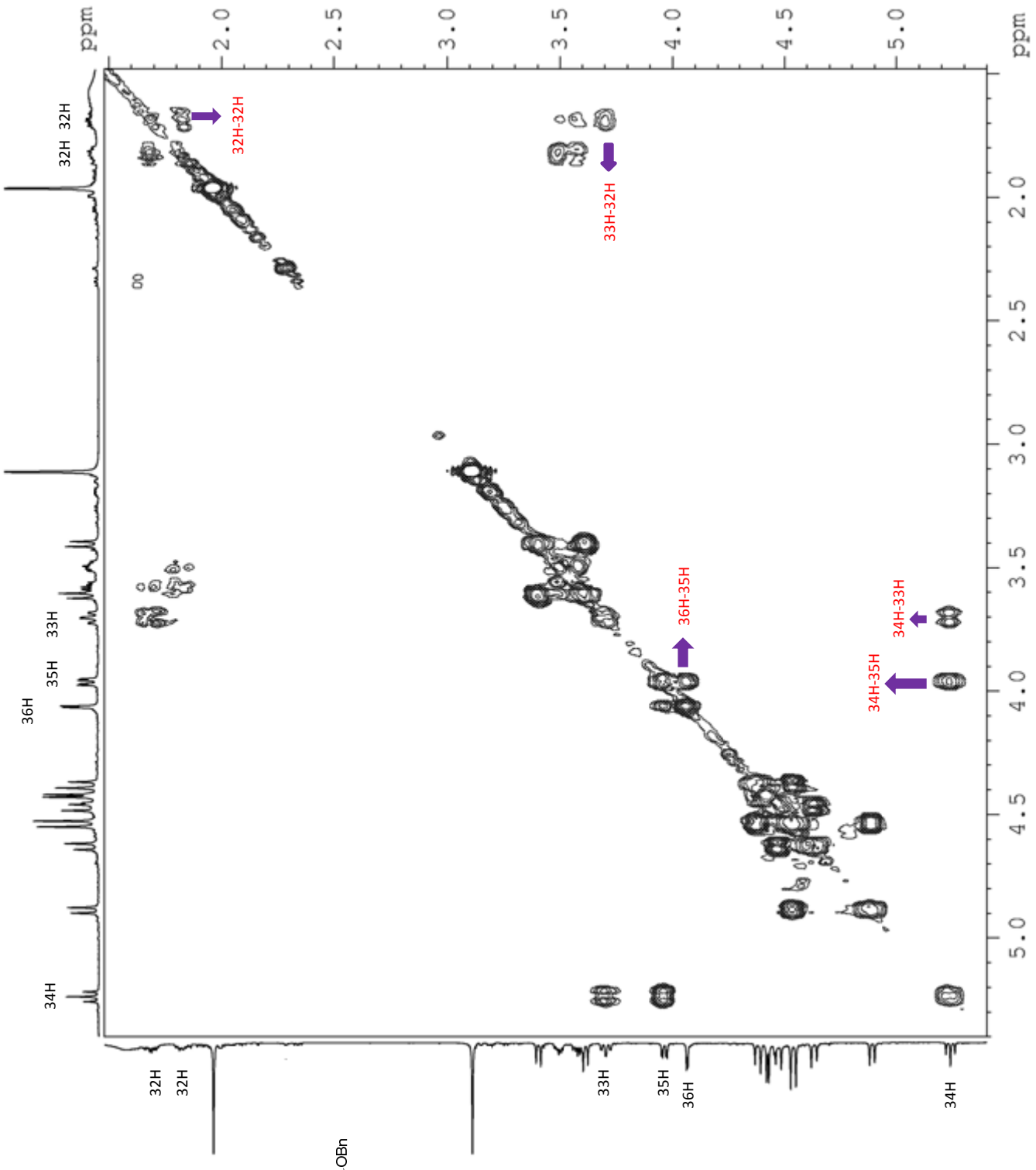
COSY-14α



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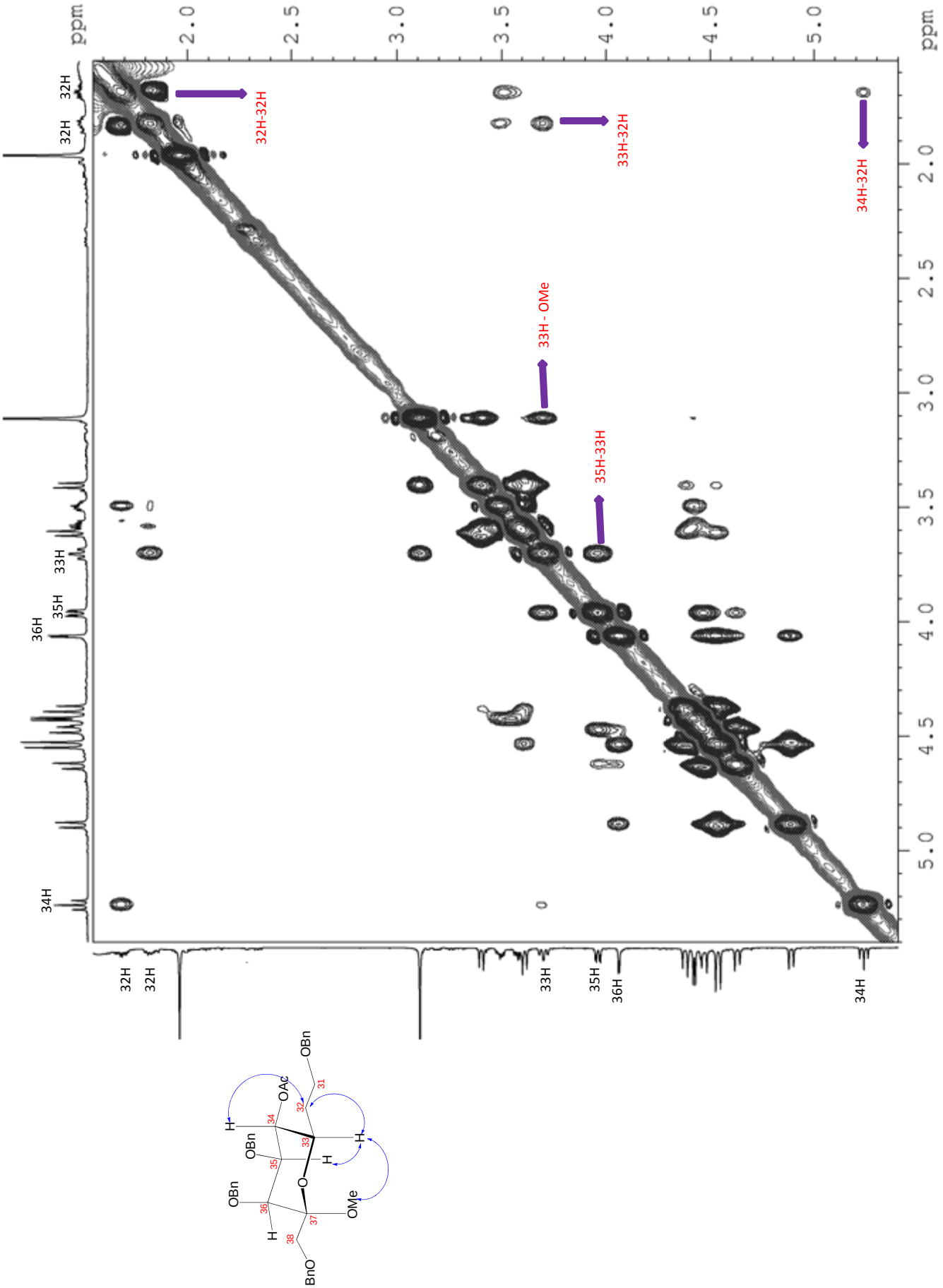
NOESY-14α



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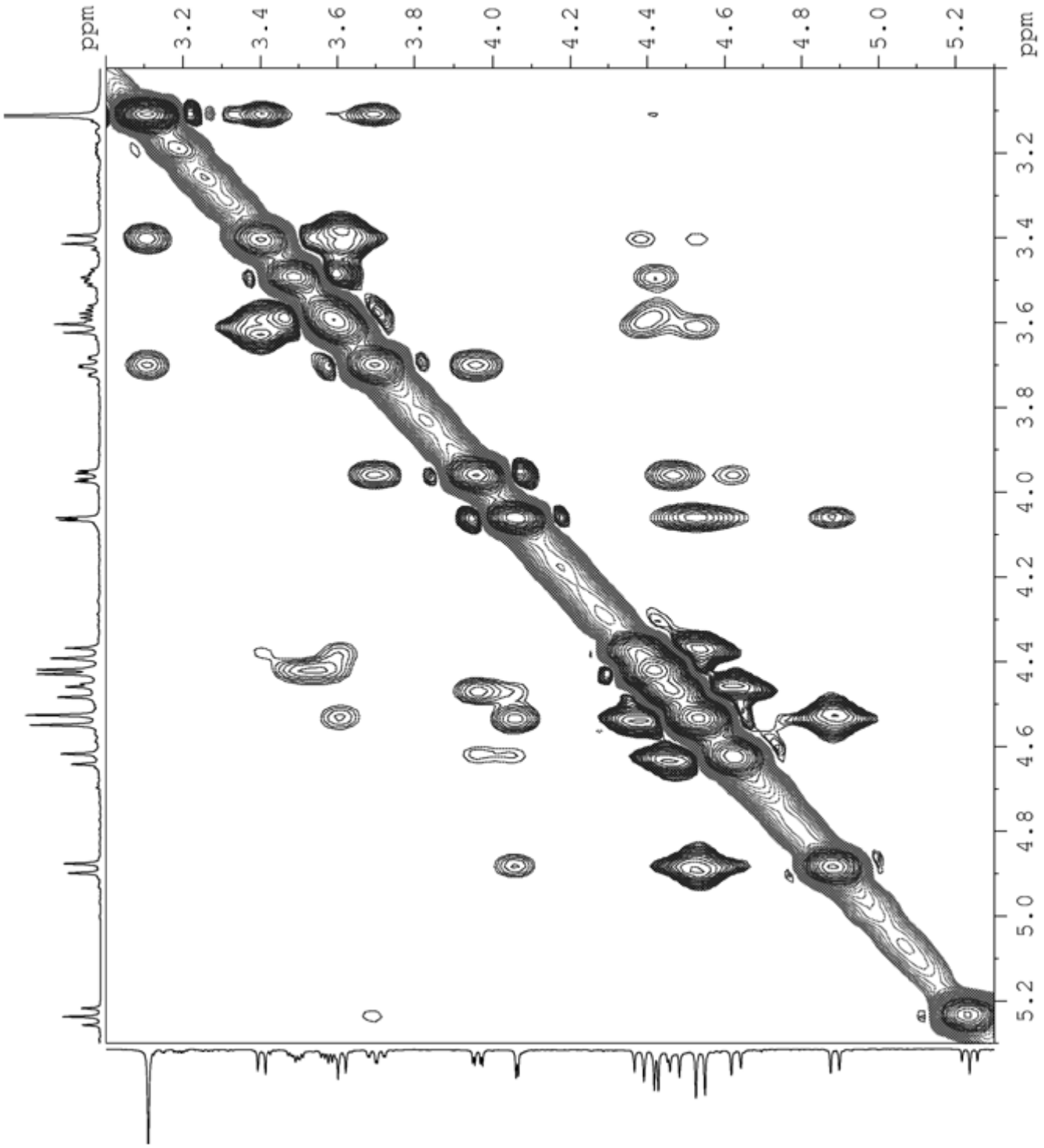
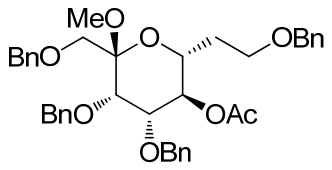
NOESY-14α (Expansion)



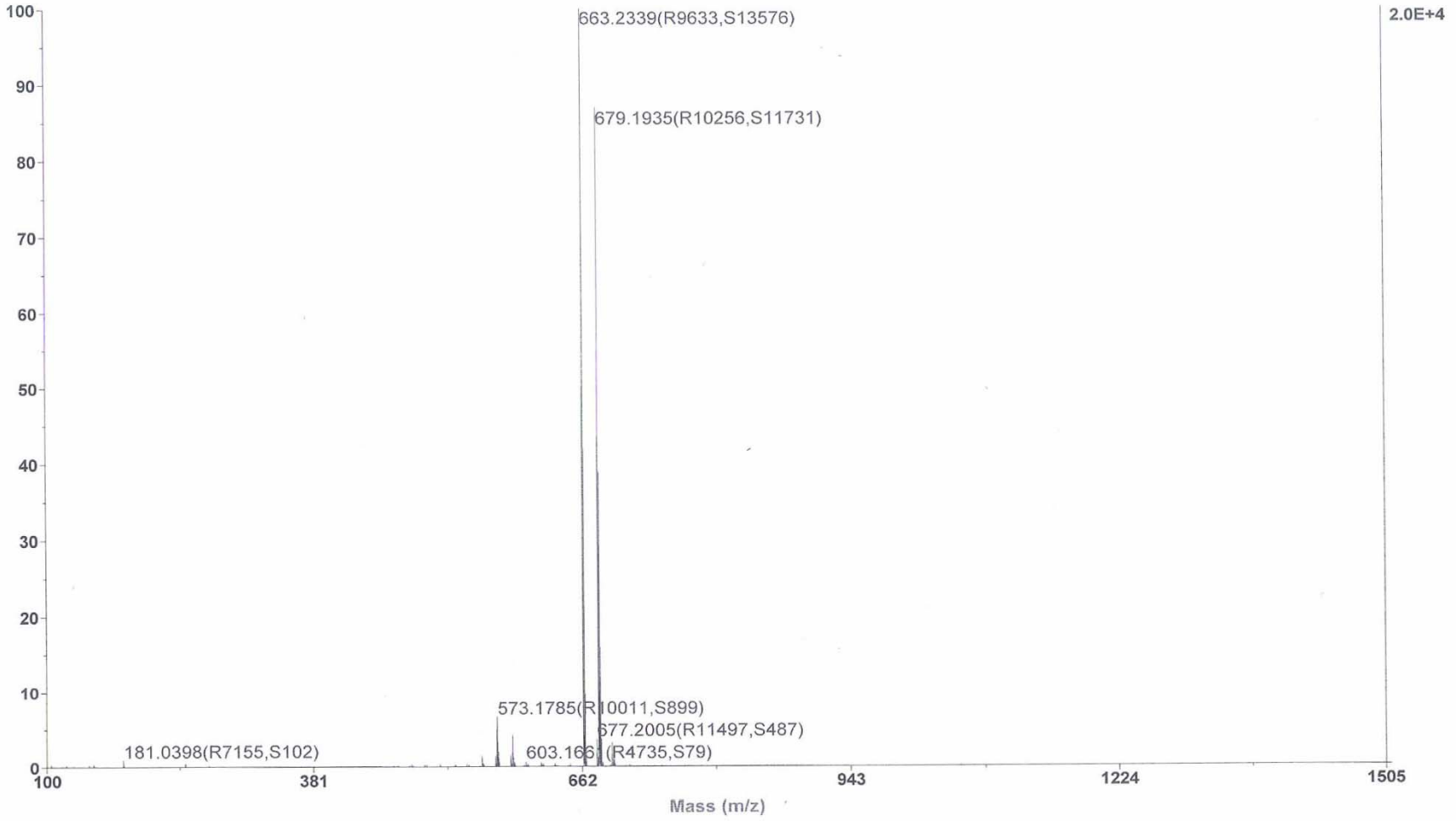


14α

Spectrum Report

SN-496(major)/13d

Final - Shots 750 - IISER; Run #90; Label O5



mayura\IISER Label O5 Run # 90

Page 1

9/9/2010 3:37:01 PM

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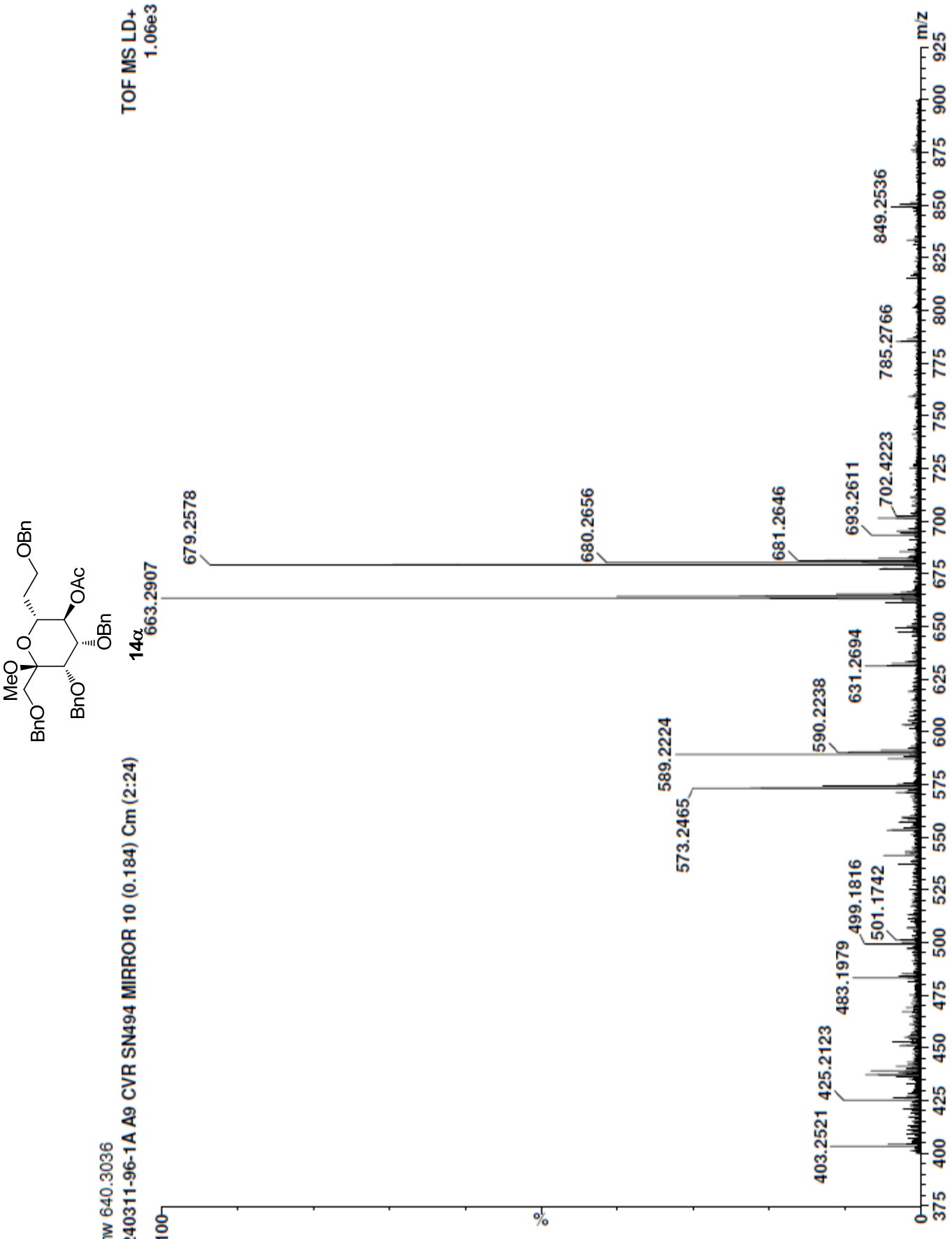

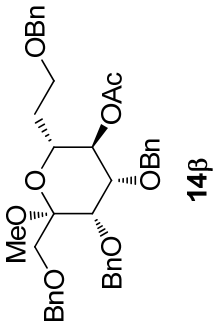
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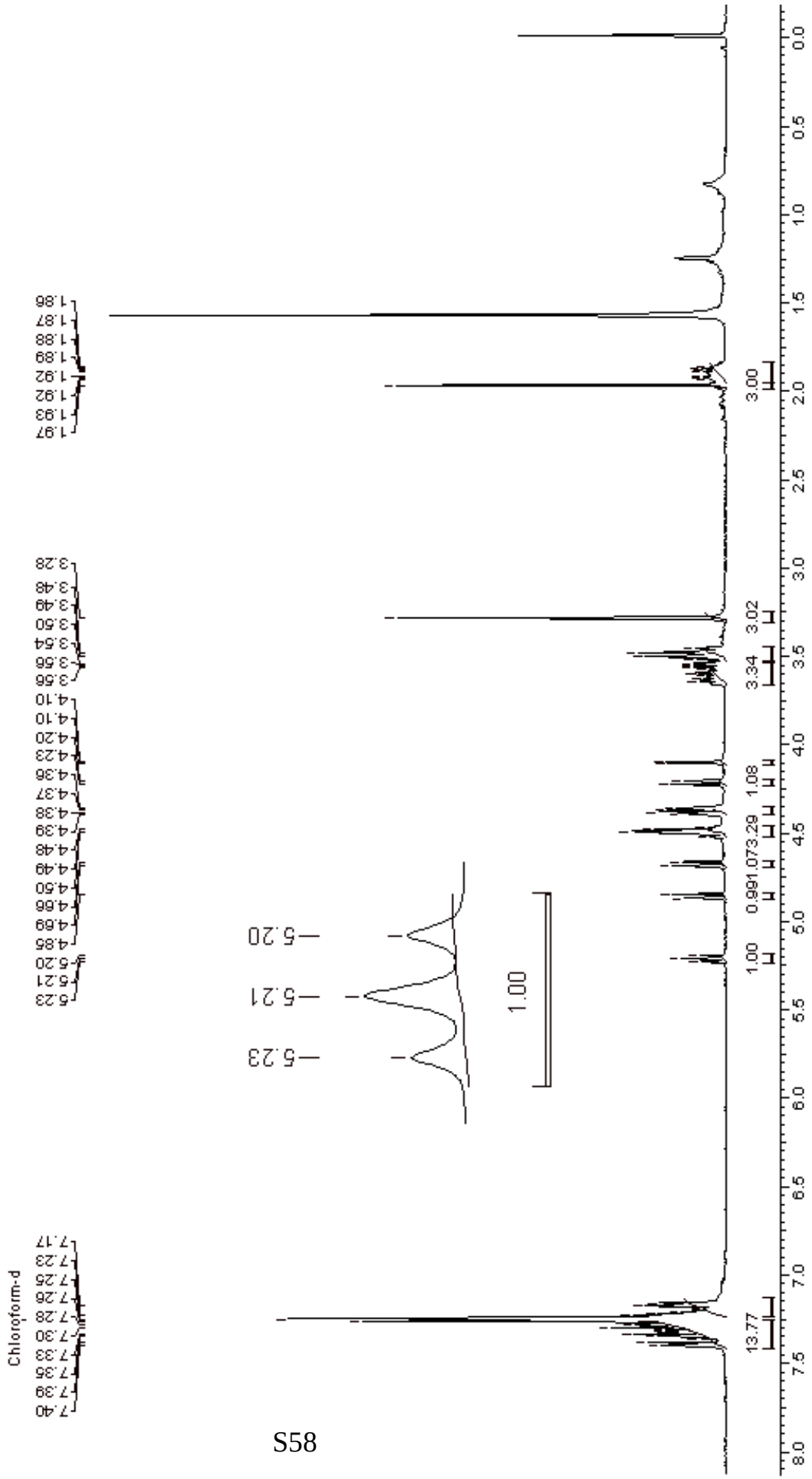
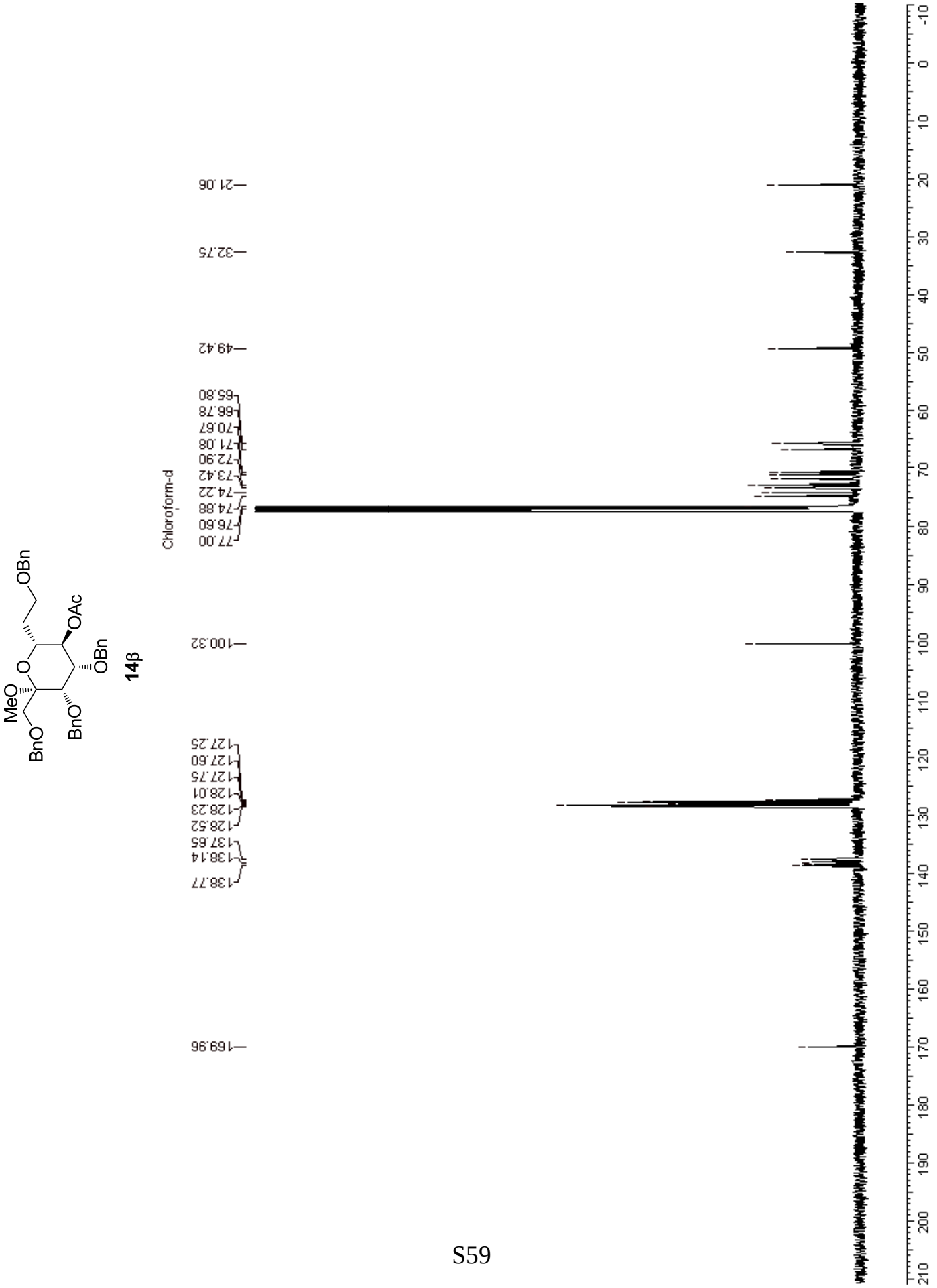
OAc
OBn
MeO
BnO
BnO

14β


Chloroform-d
5.23
5.21
5.20
1.00
13.77
1.00
0.99
1.07
3.29
1.08
3.34
3.02
3.00


OBn
OAc
OBn
MeO
BnO
BnO
14β
Chloroform-d
21.06
32.75
49.42
65.80
66.78
70.67
71.08
72.90
73.42
74.22
74.88
76.60
77.00
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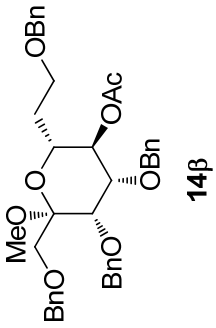
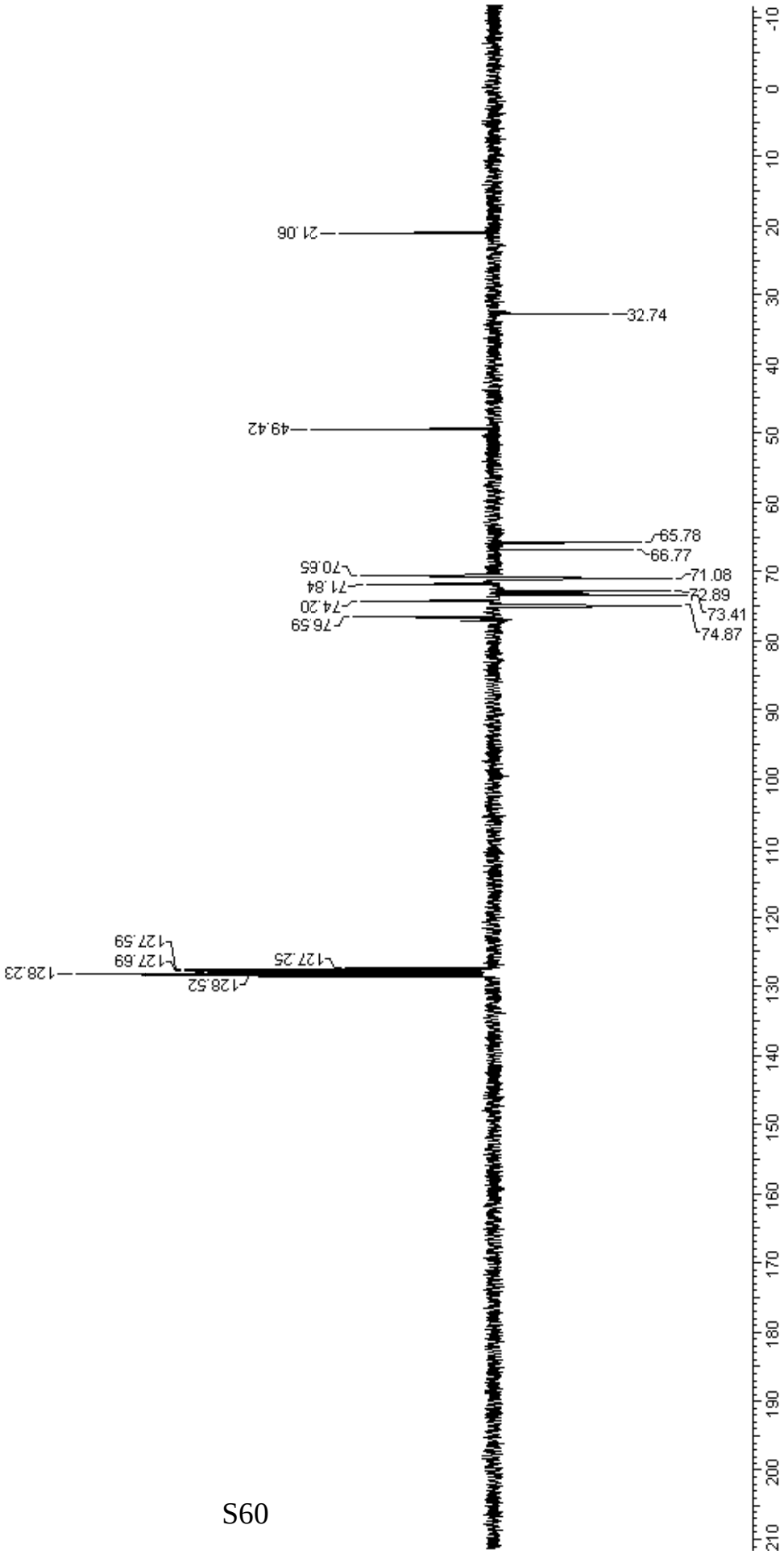
127.25
127.60
127.75
128.01
128.23
128.52
137.65
138.14
138.77
169.96


OBn
OAc
OBn
MeO
BnO
BnO

14β


21.06
32.74
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65.78
66.77
70.65
71.08
71.84
72.89
74.20
73.41
74.87
76.59
127.25
127.59
127.69
128.23
128.52

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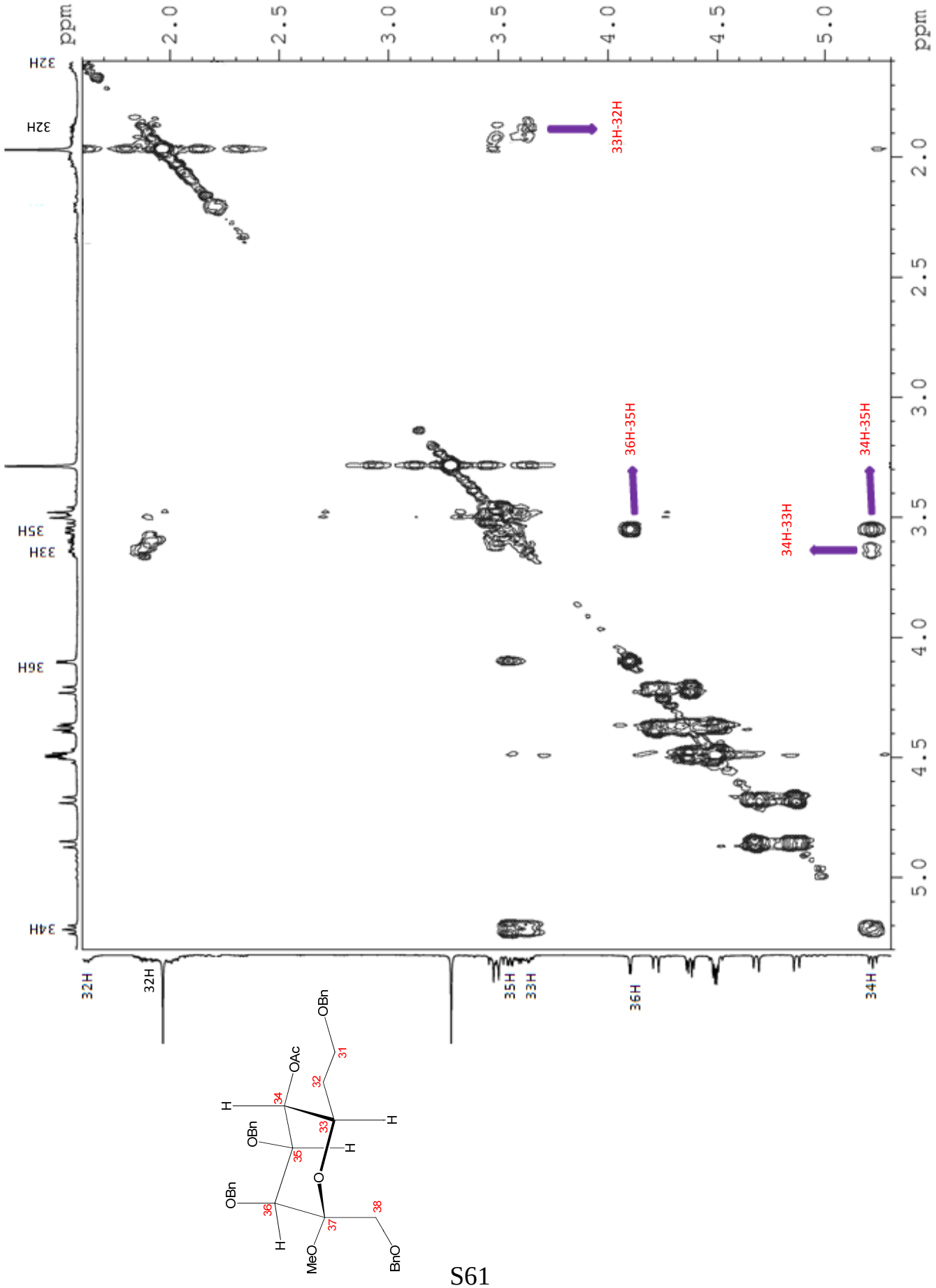
COSY-14β



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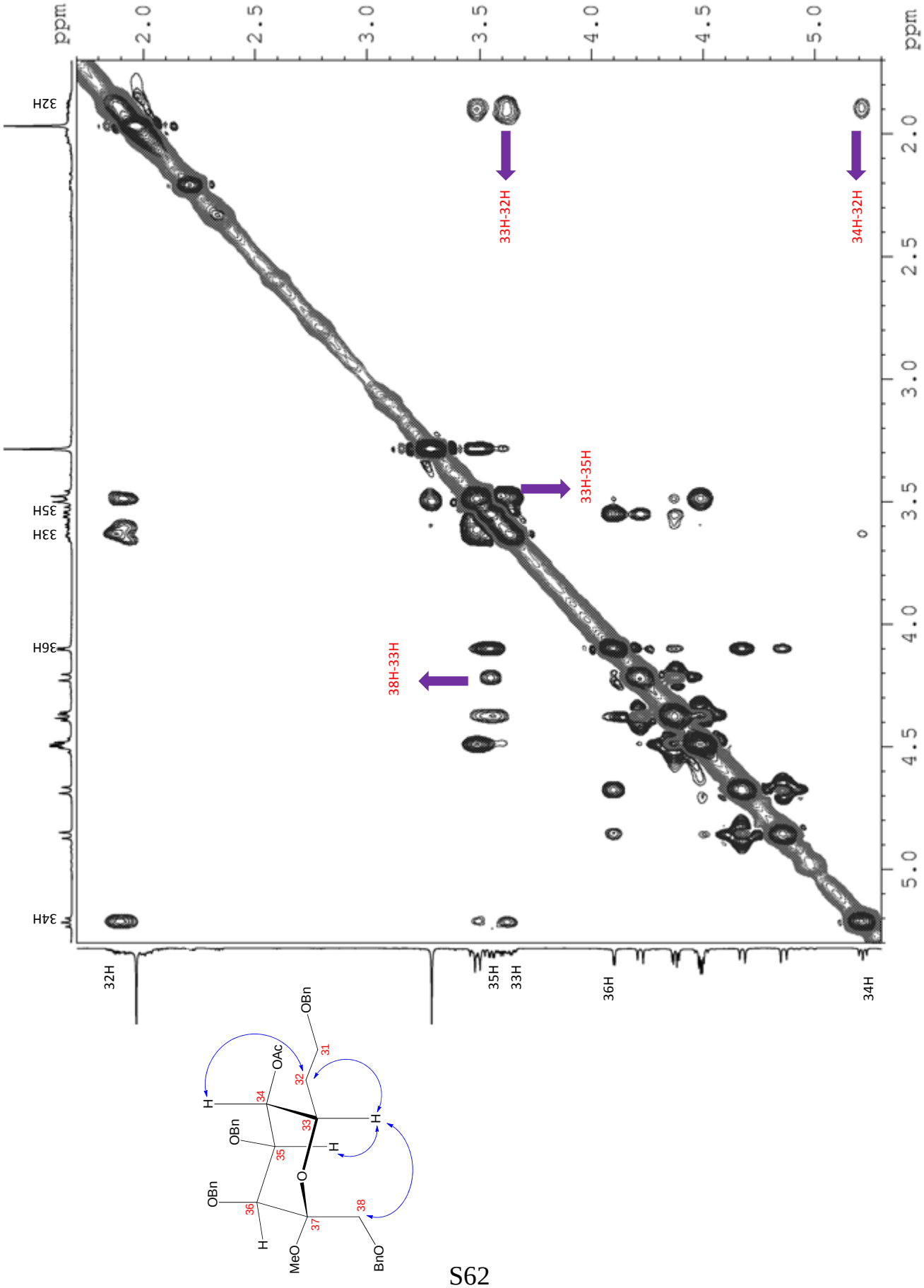
NOESY-14β



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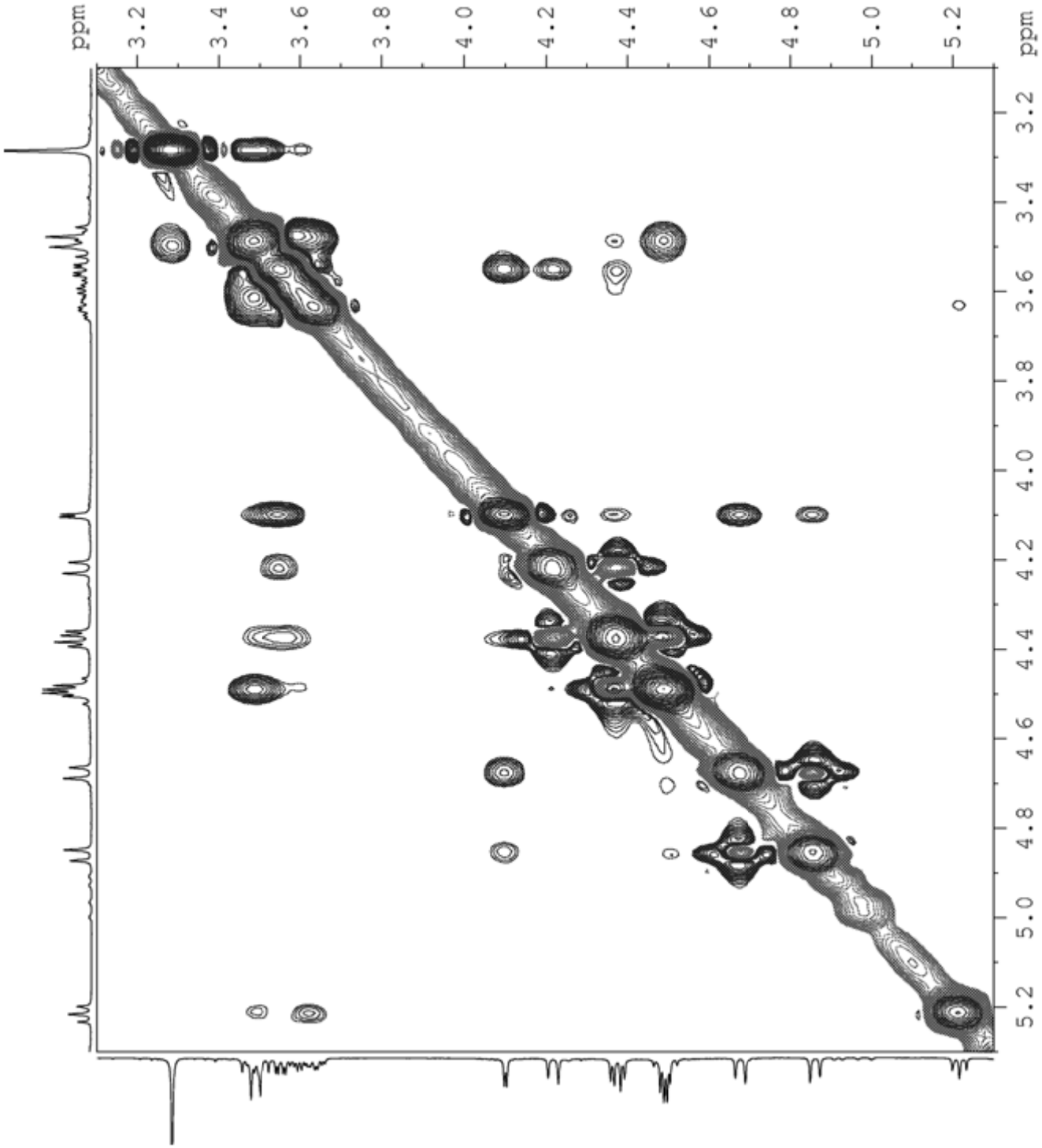
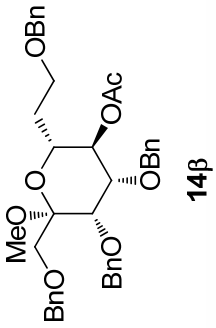
NOESY-14β (Expansion)

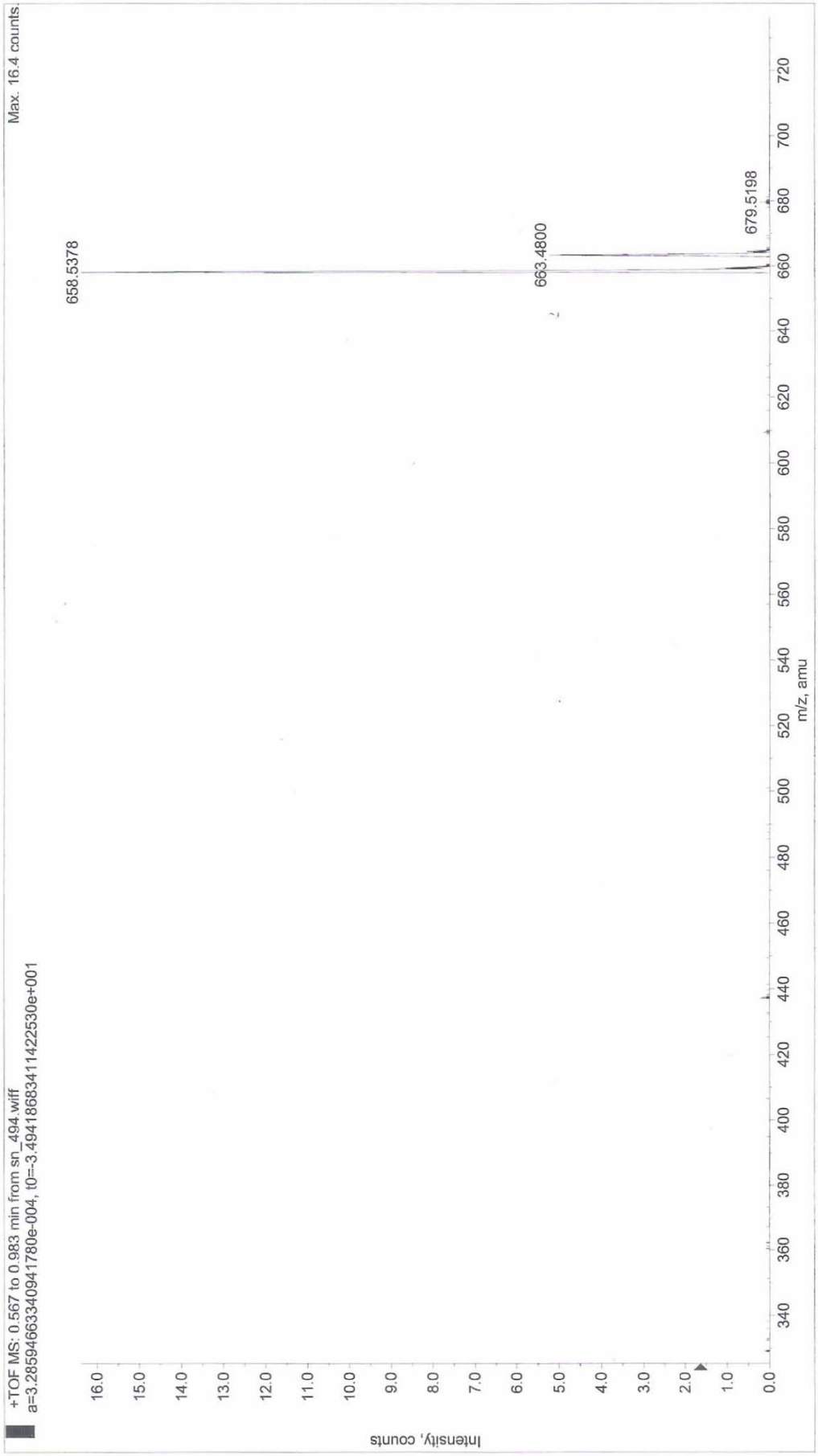




14β

SN-494 / 13 β

*LCMSMS - Q STAR PULSAR



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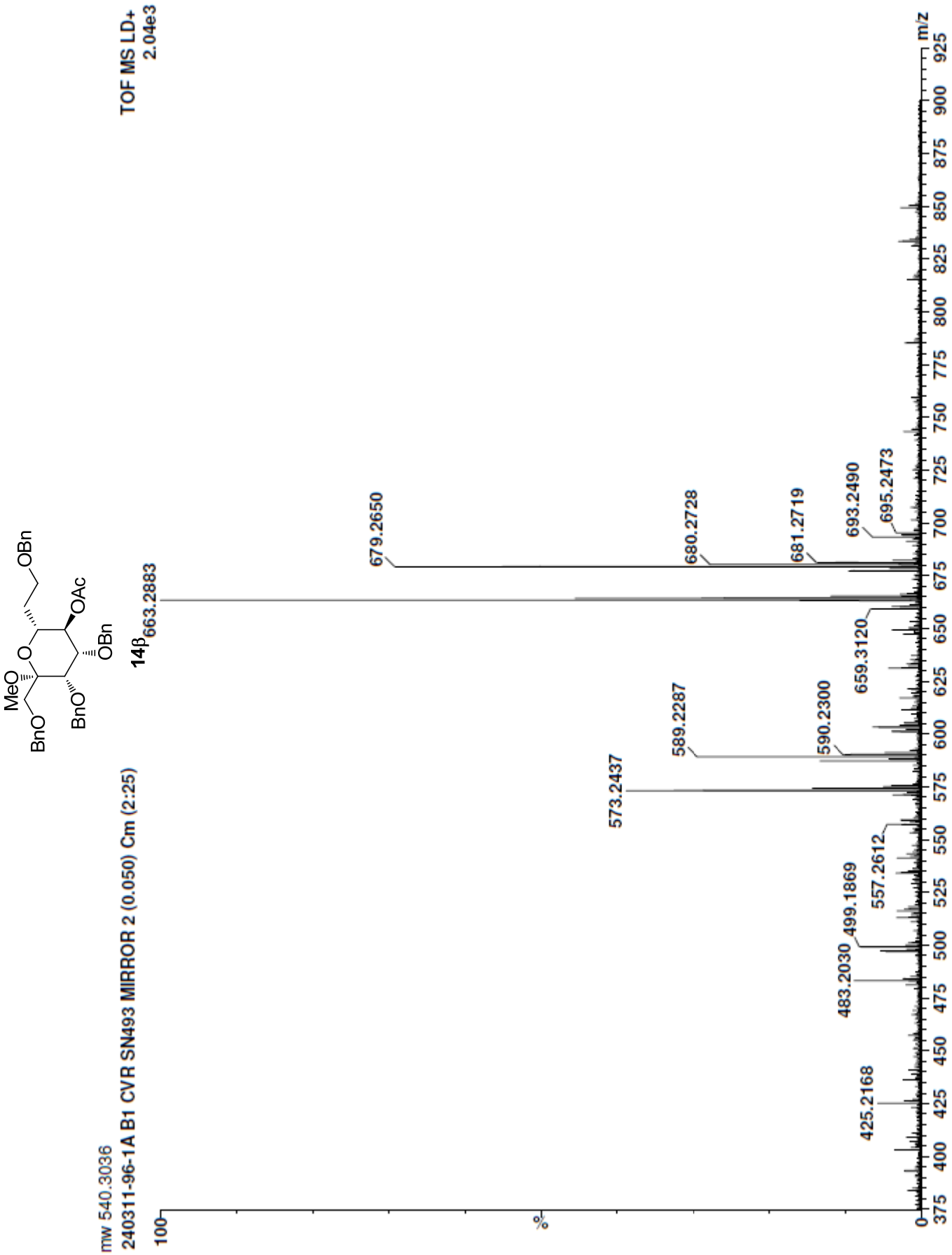

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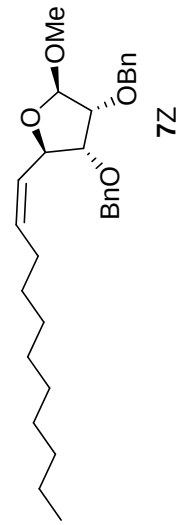
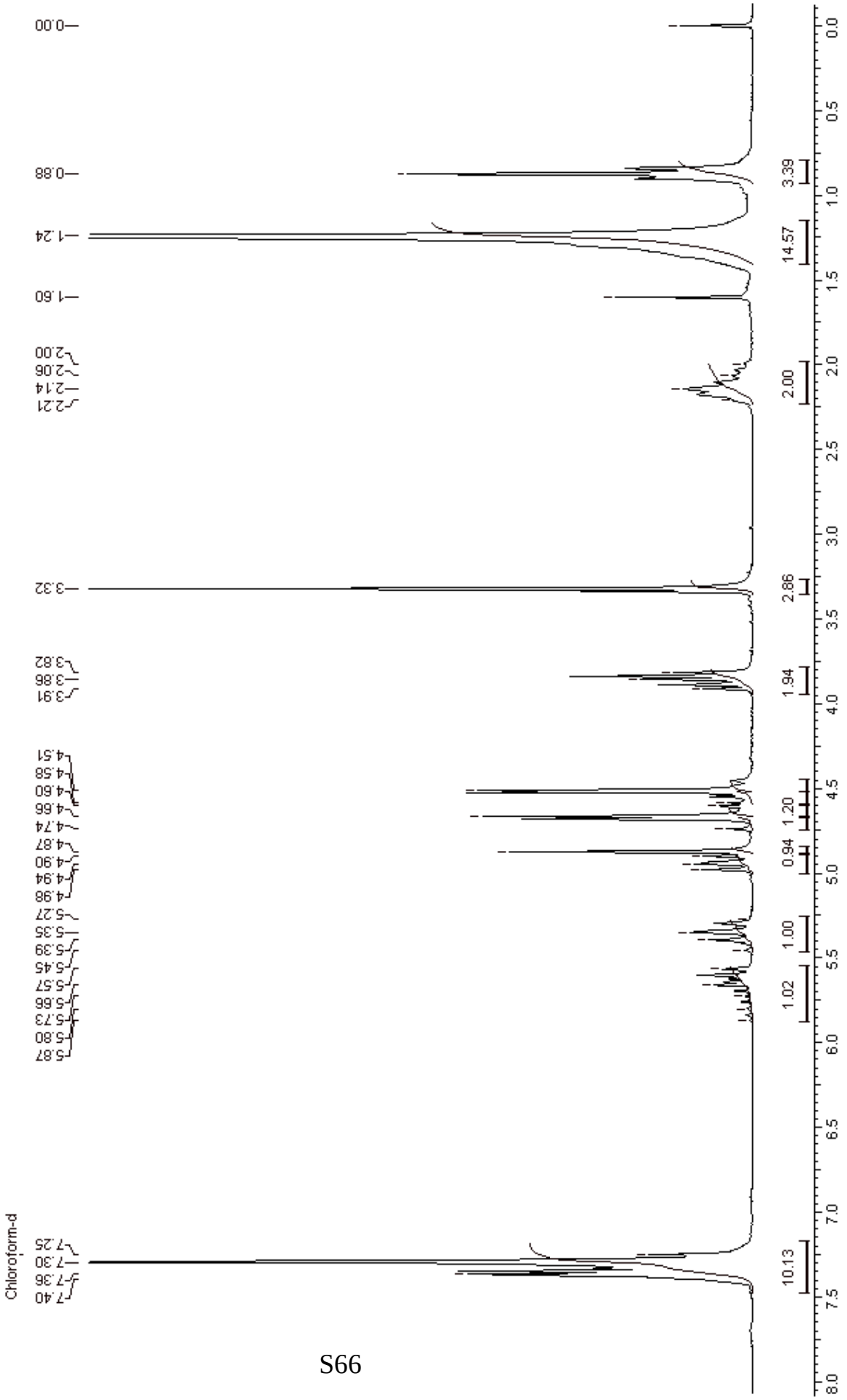


7Z



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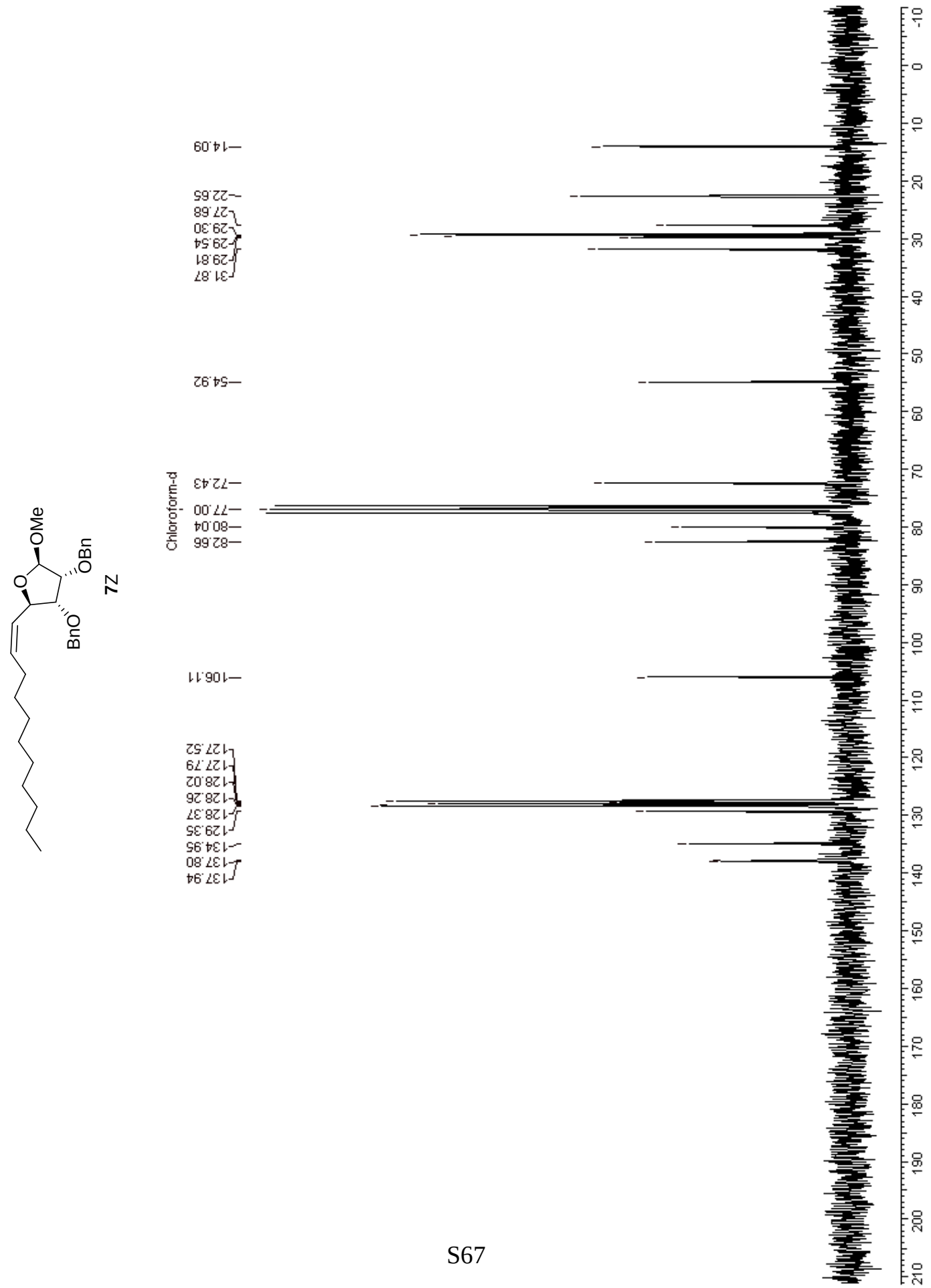

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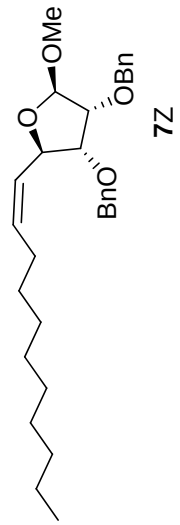

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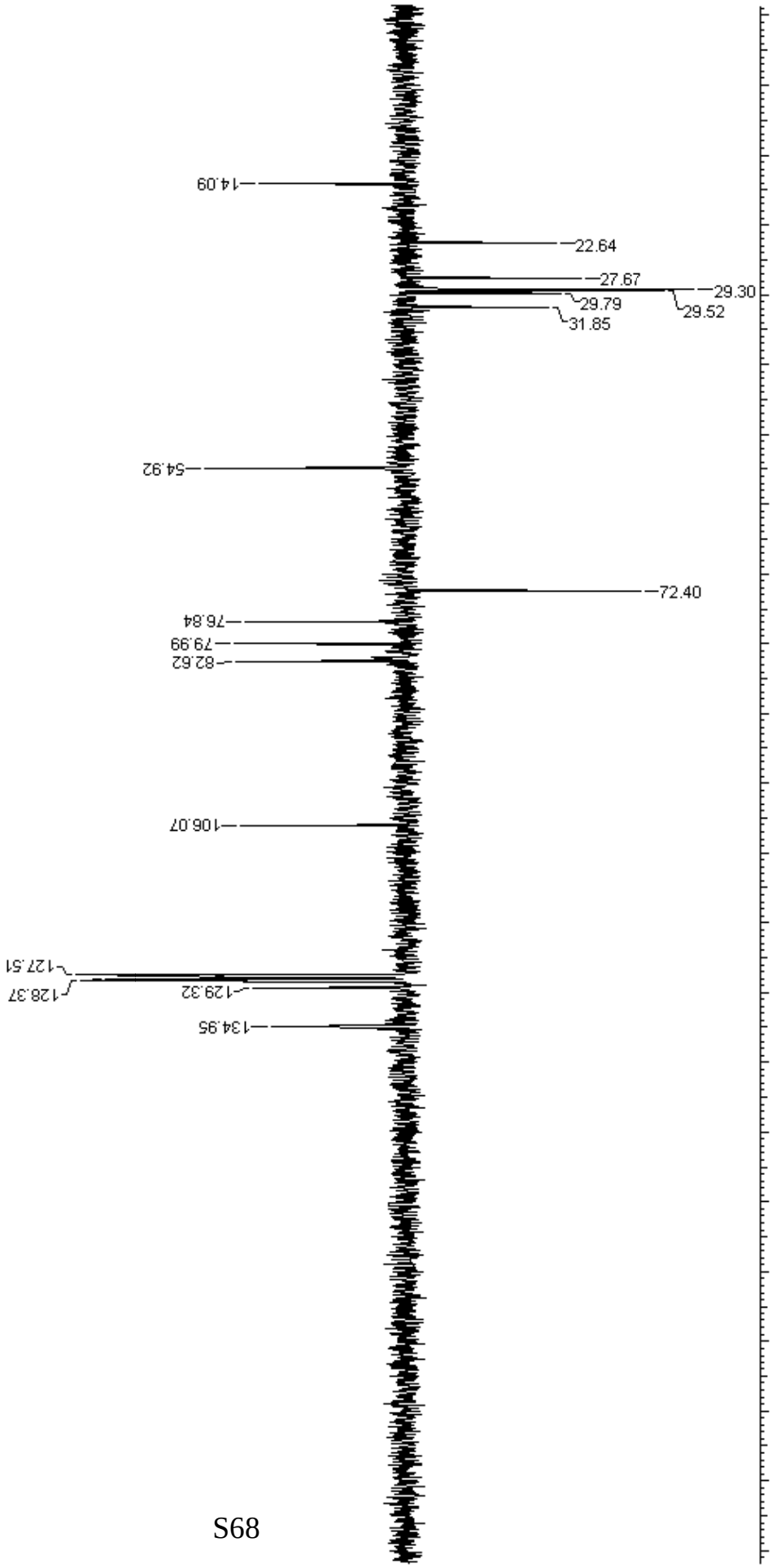

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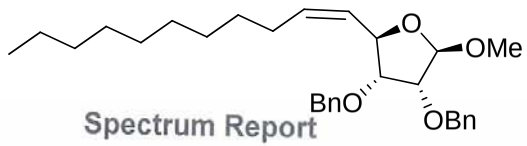

Spectrum Report

7Z

SN-406/7

Final - Shots 750 - IISER; Run #90; Label O4

505.1869(R10087,S3831)

5719.7

489.2175(R10329,S2533)

104.8978(R3243,S56)

100
90
80
70
60
50
40
30
20
10
0

100
381
662
943
1224
1505

Mass (m/z)

nayura\IISER Label O4 Run # 90

Page 1

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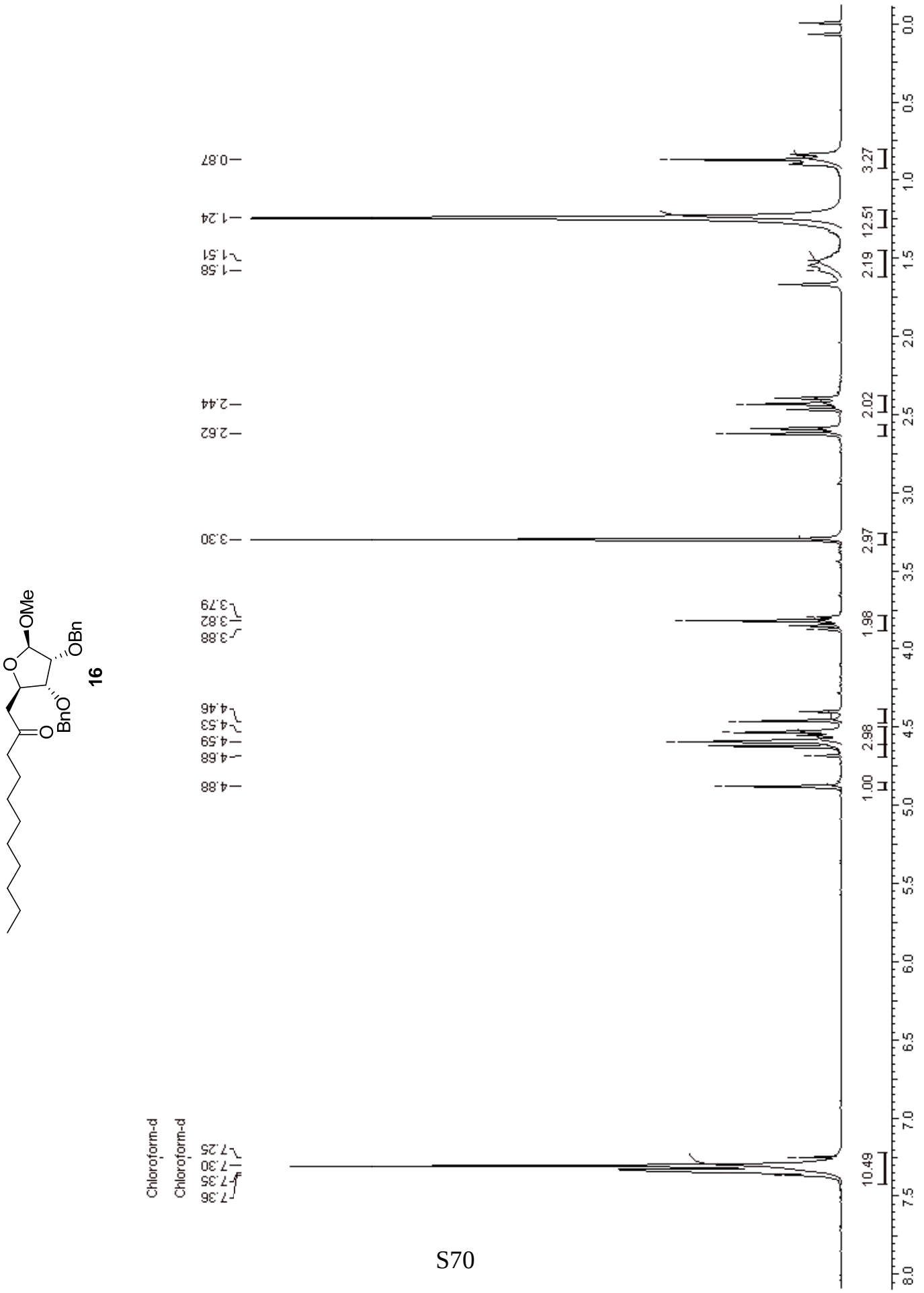
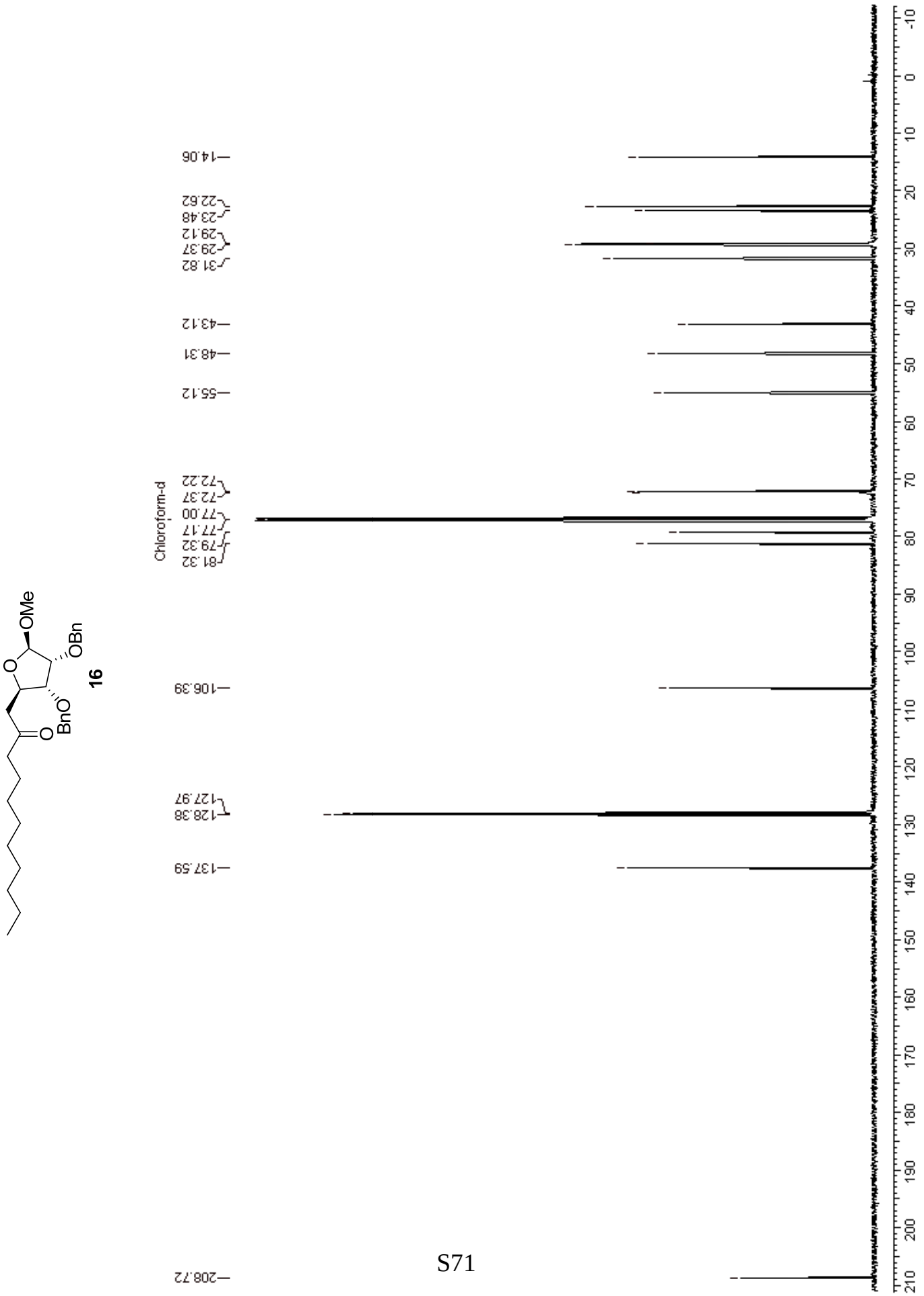
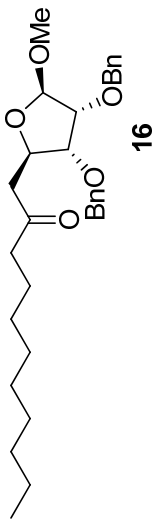
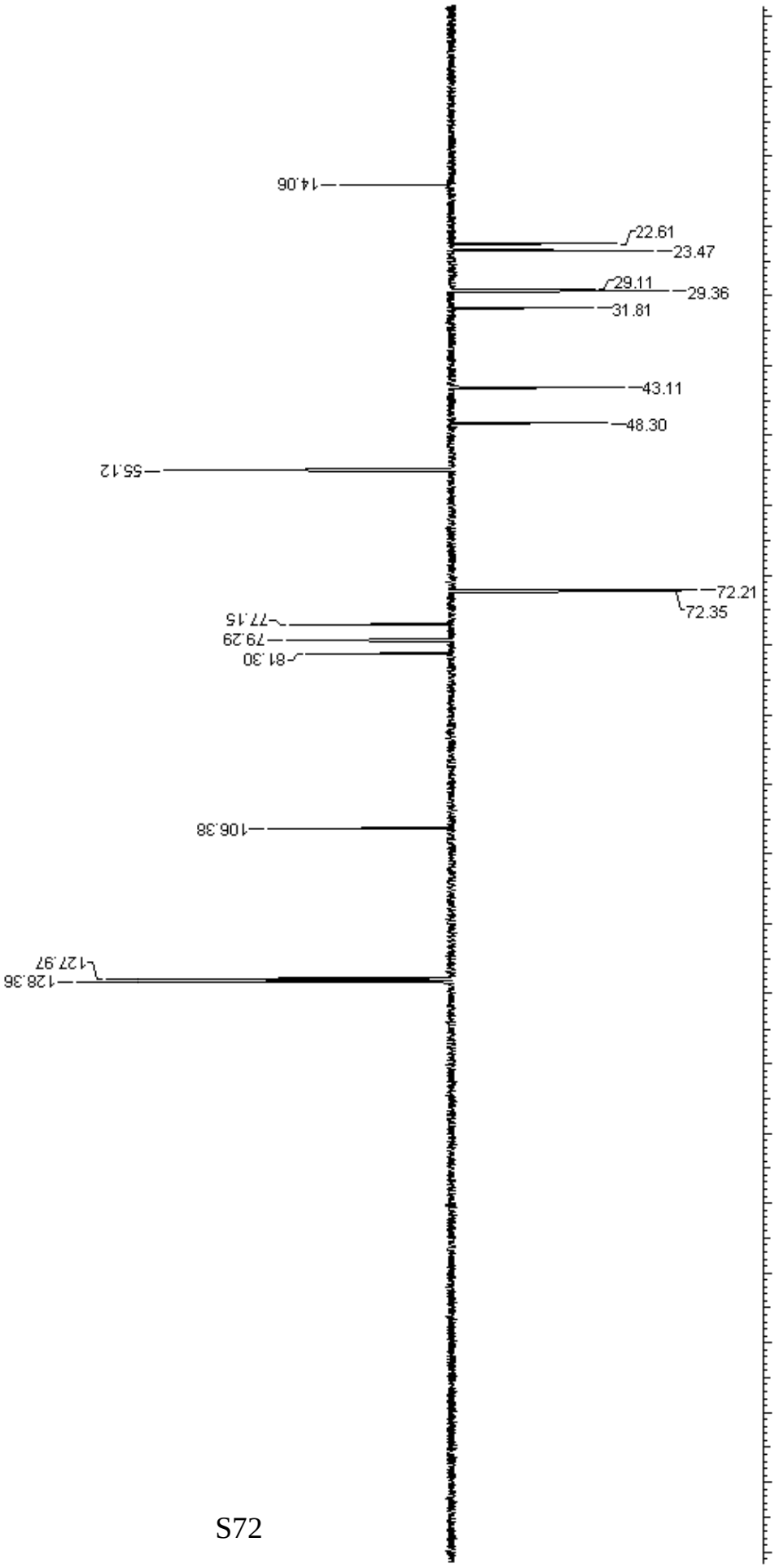



OMe
OBn
BnO
O
O
16
Chloroform-d
14.06
22.62
23.48
29.12
29.37
31.82
43.12
48.31
55.12
72.22
72.37
77.00
77.17
79.32
81.32
106.39
127.97
128.38
137.59
208.72


OMe
OBn
BnO
O
O

16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22.61
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29.11
29.36
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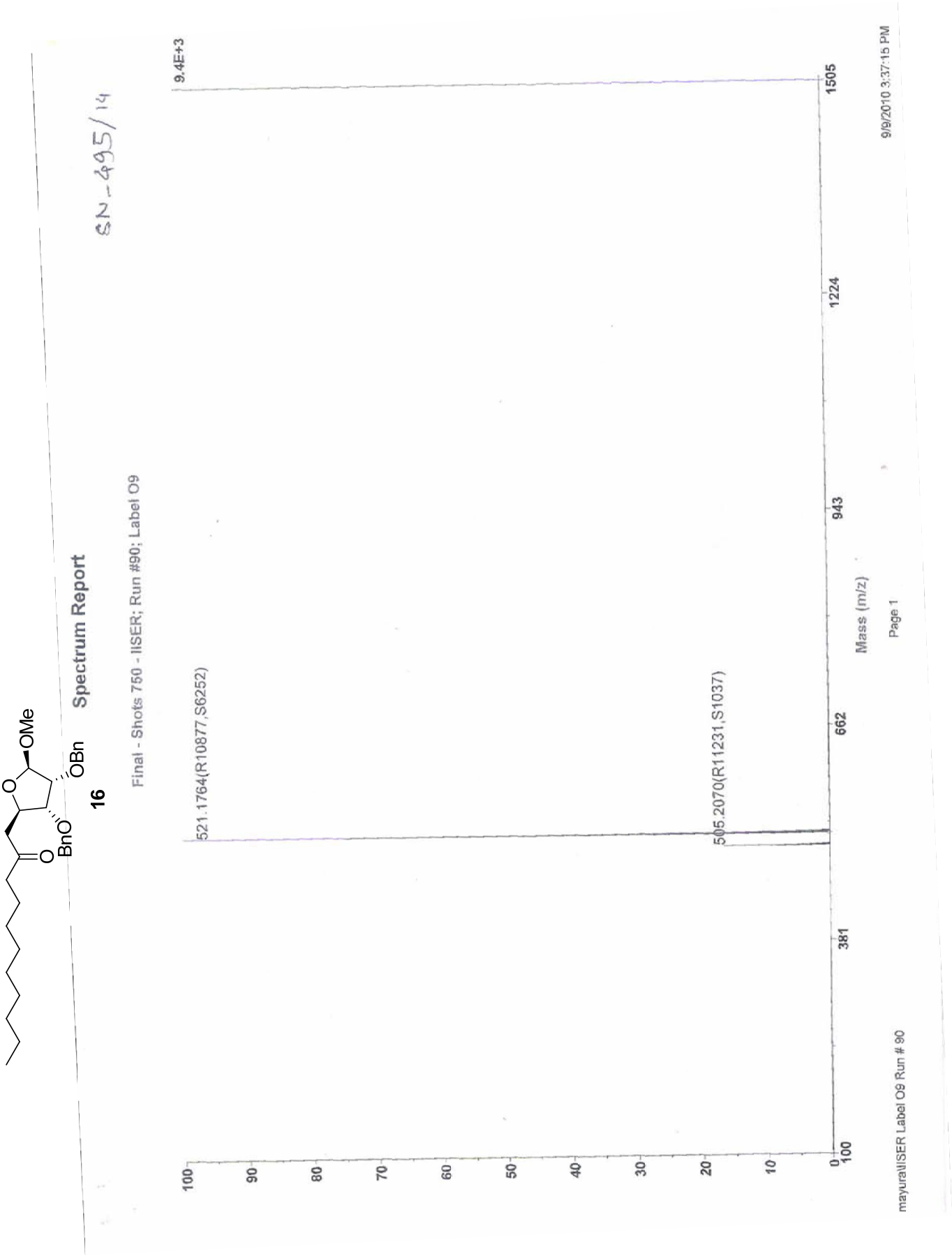
55.12
72.21
72.35
77.15
79.29
81.30
106.38
127.97
128.36


OMe
OBn
BnO
O
O
16
Spectrum Report
SN-495/14
Final - Shots 750 - IISER; Run #90; Label O9
521.1764(R10877,S6252)
505.2070(R11231,S1037)
9.4E+3
100
90
80
70
60
50
40
30
20
10
0
100
381
662
943
1224
1505
Mass (m/z)
Page 1
9/9/2010 3:37:15 PM
mayuraIISER Label O9 Run # 90

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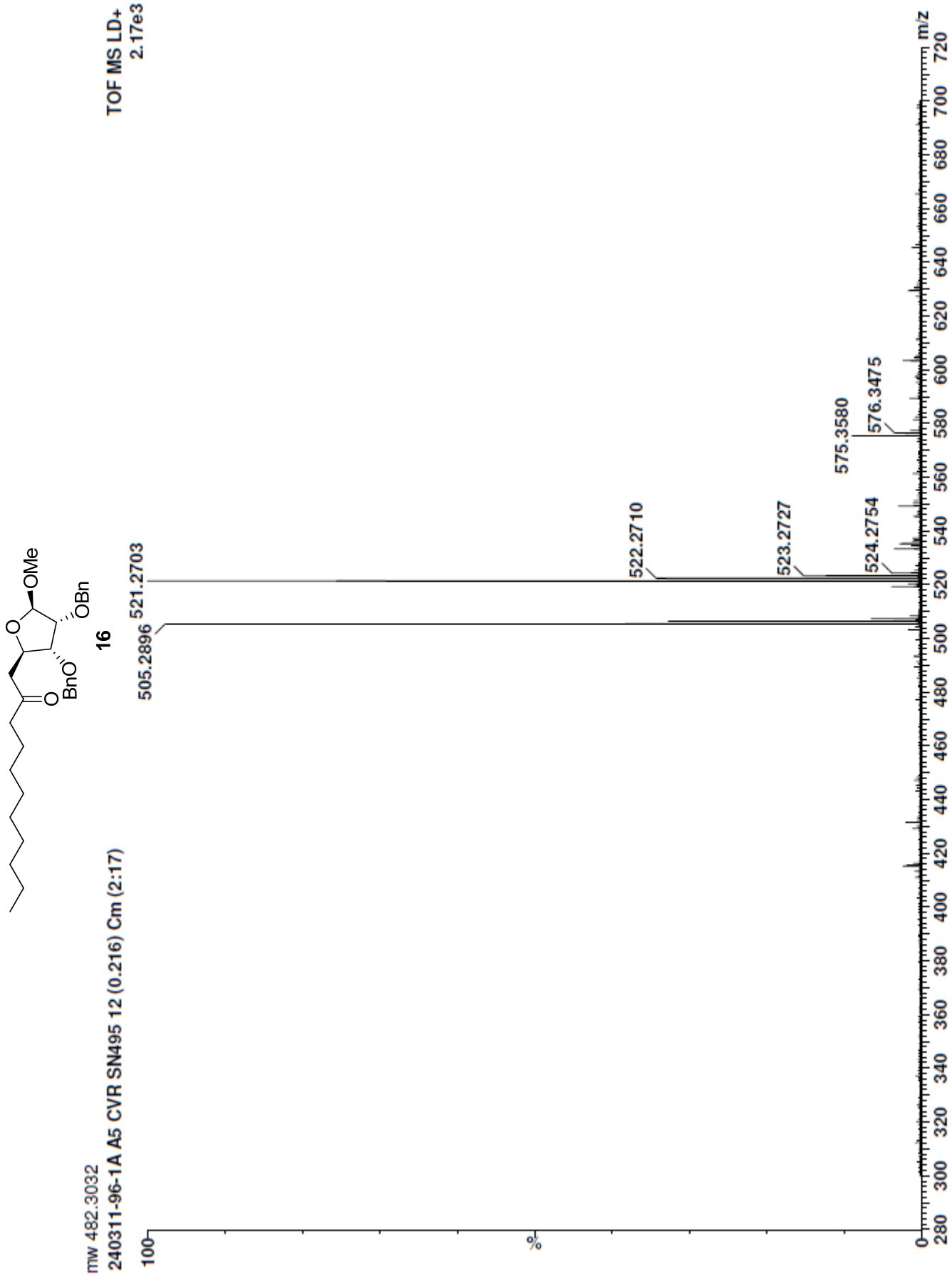

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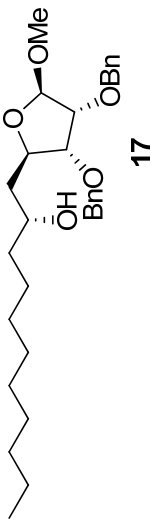
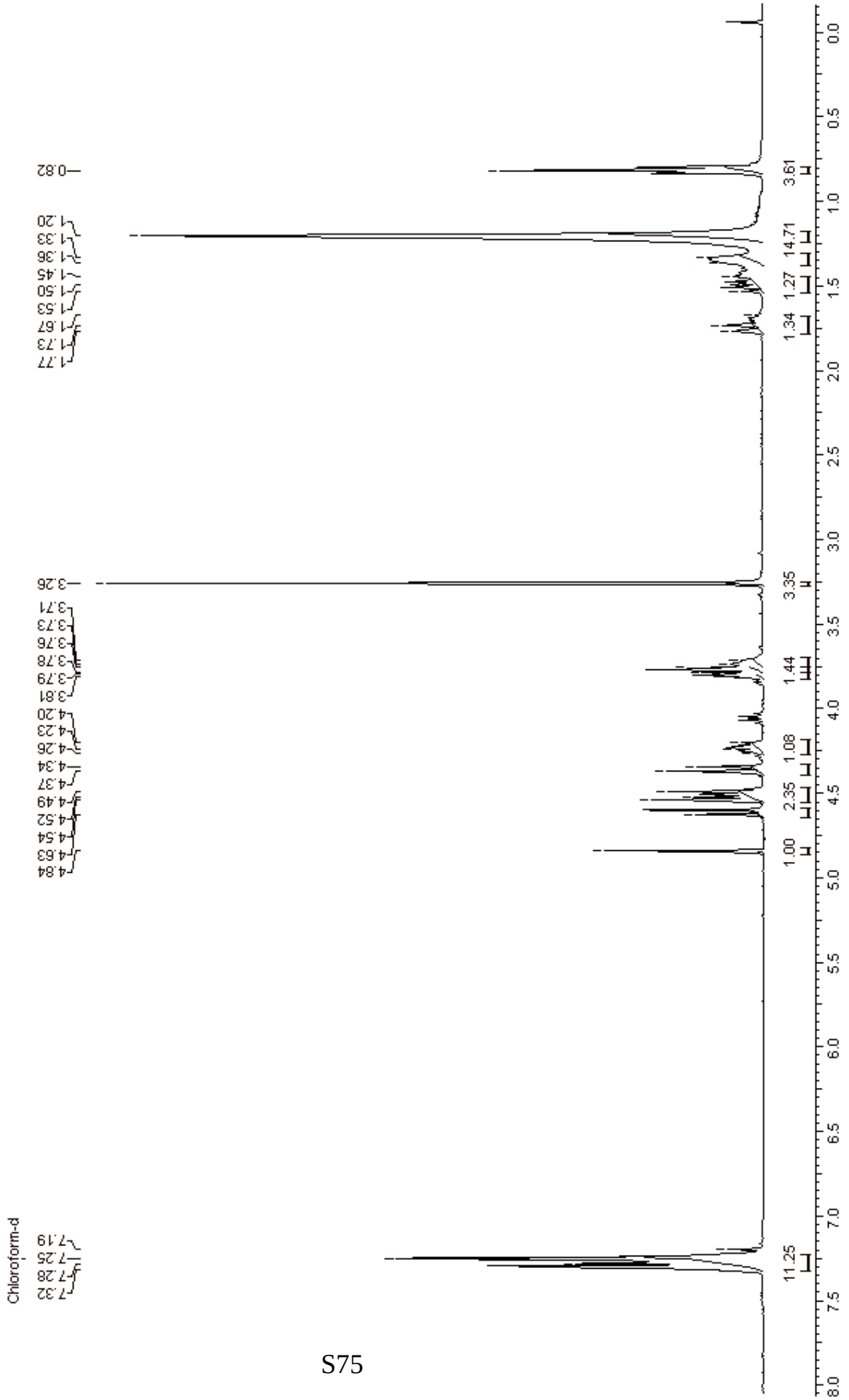
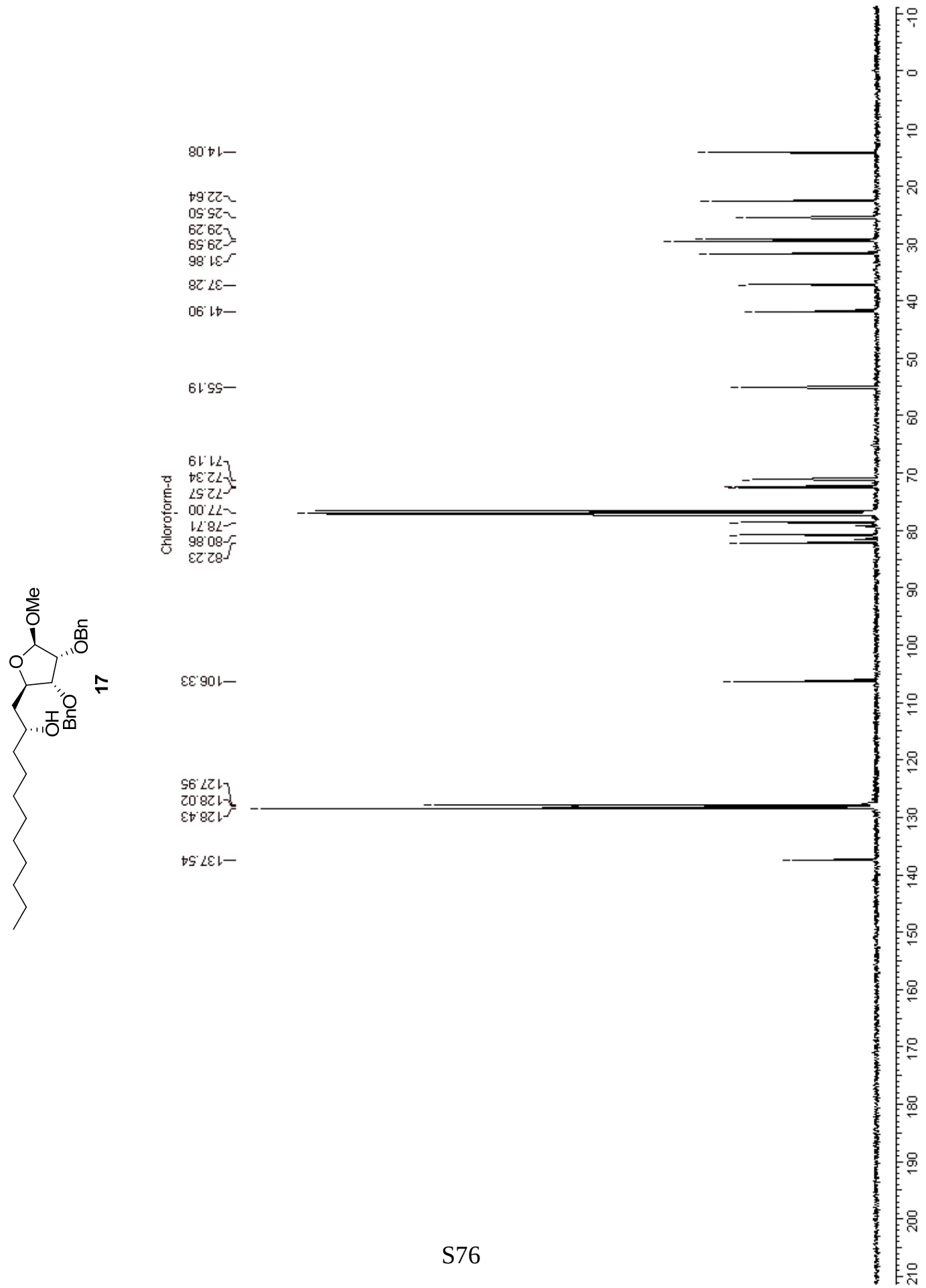


17




14.08
22.64
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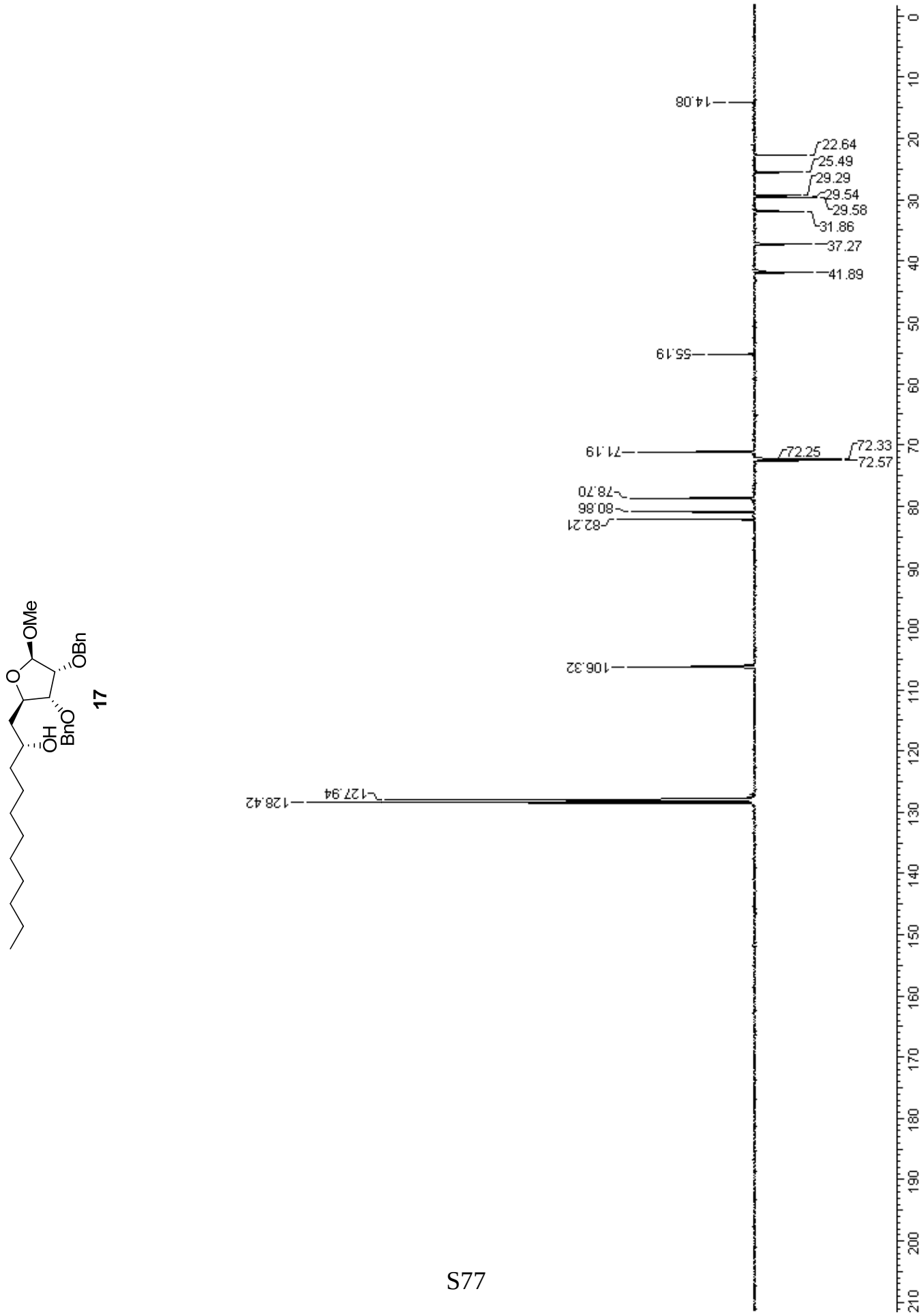
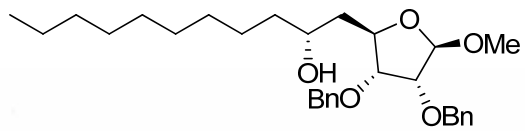
29.29
29.59
31.86
37.28
41.90
55.19
71.19
72.34
72.57
77.00
78.71
80.86
82.23
Chloroform-d
106.33
127.95
128.02
128.43
137.54
OMe
OBn
BnO
OH
17


14.08
22.64
25.49
29.29
29.54
29.58
31.86
37.27
41.89
55.19
71.19
72.25
72.33
72.57
78.70
80.86
82.21
106.32
127.94
128.42
OMe
OBn
OH
BnO
17

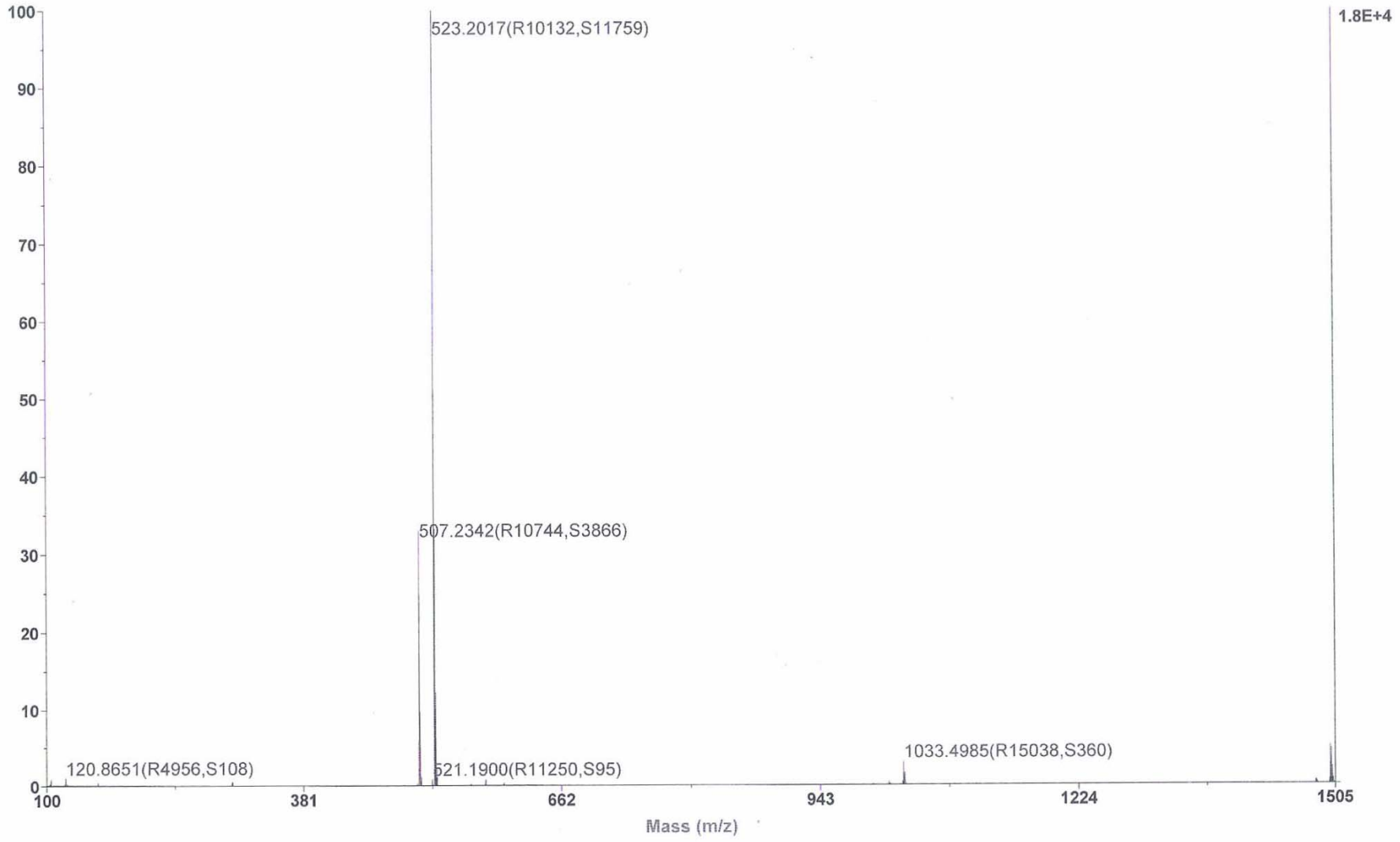


17

Spectrum Report

SN-497/15

Final - Shots 750 - IISER; Run #90; Label O6



mayura\IISER Label O6 Run # 90

Page 1

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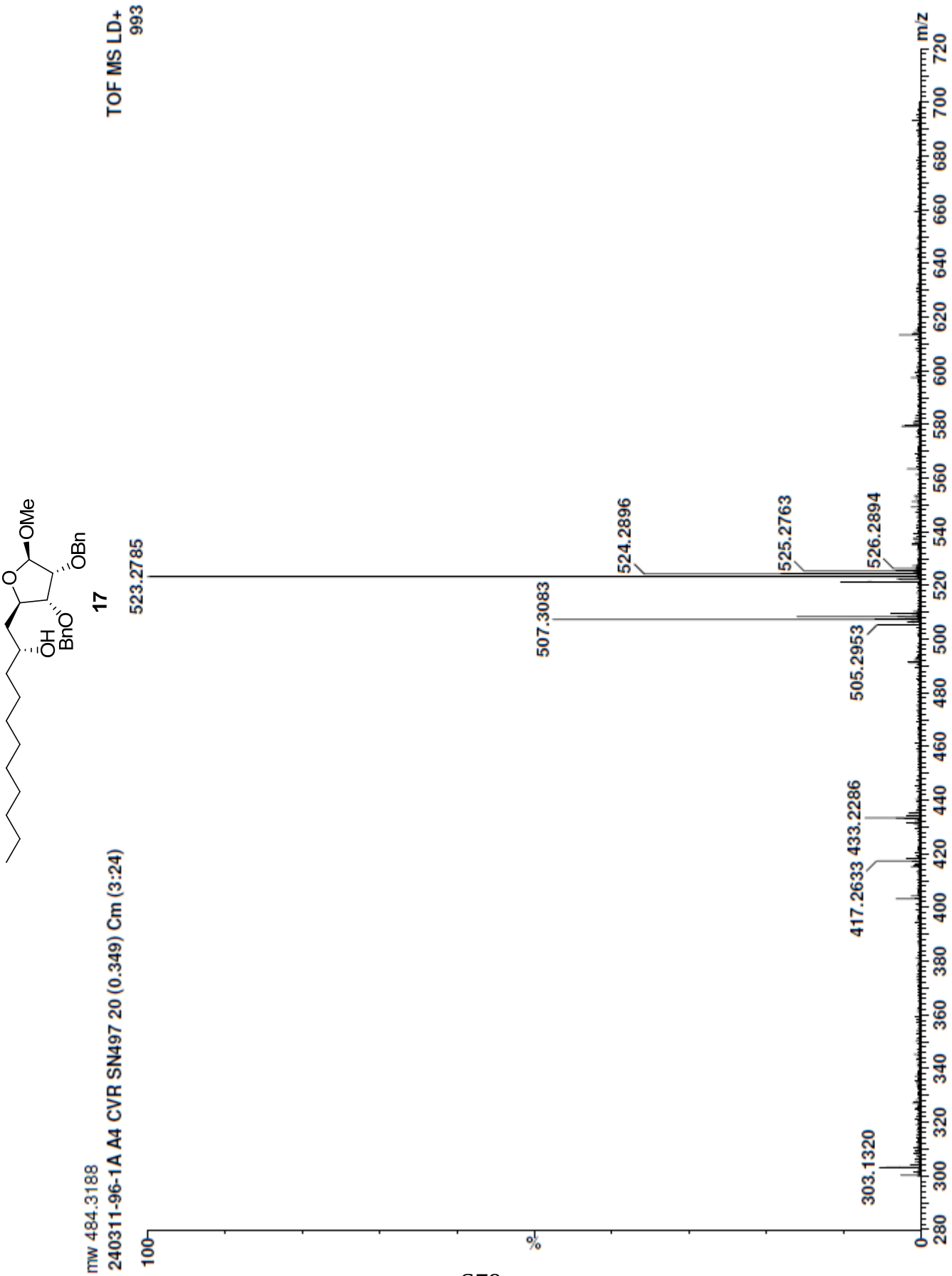

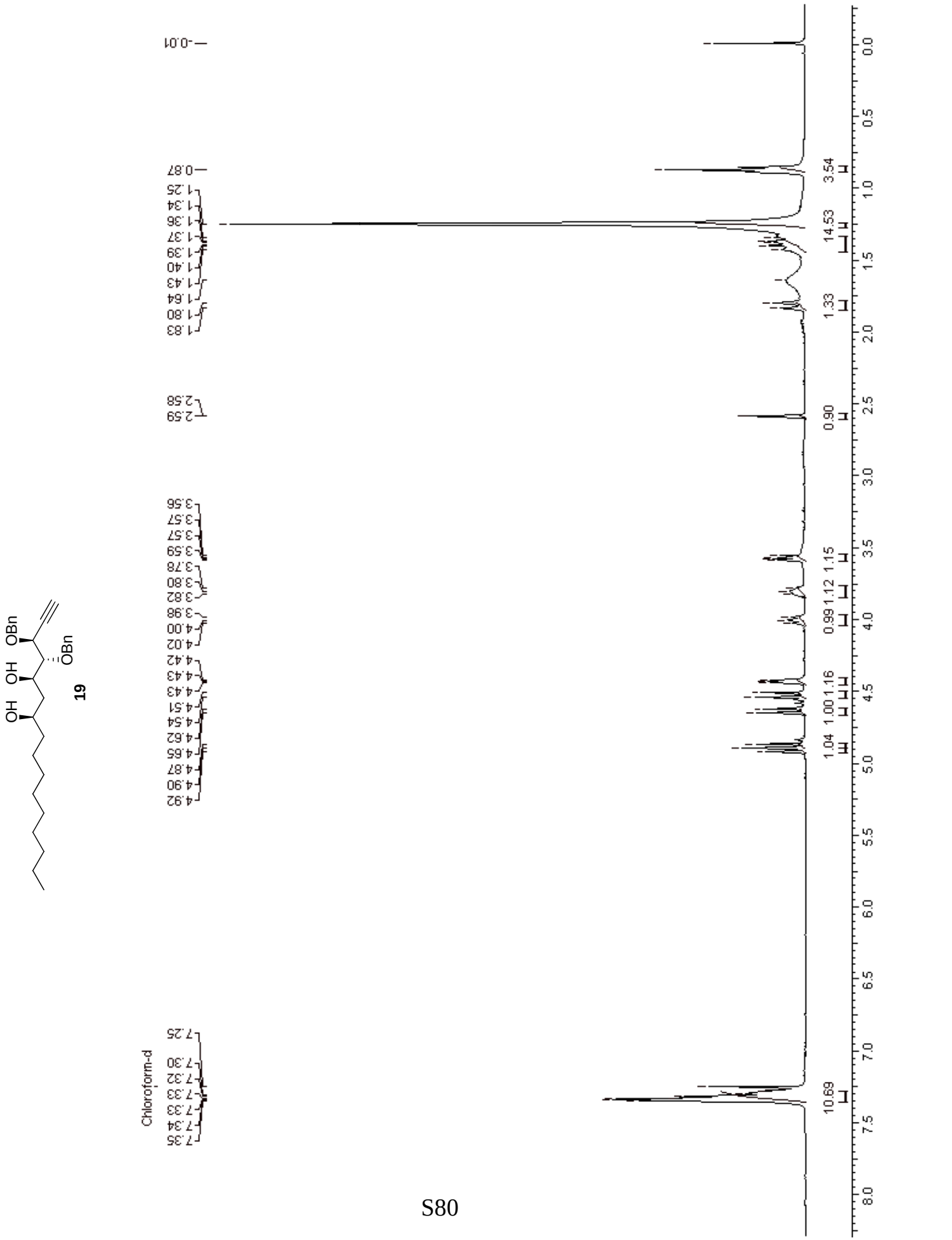
OBn
OH
OH
OBn
19
Chloroform-d
7.25
7.30
7.32
7.33
7.33
7.34
7.35
4.92
4.90
4.87
4.65
4.62
4.54
4.51
4.43
4.42
4.02
4.00
3.98
3.82
3.80
3.78
3.59
3.57
3.57
3.56
2.59
2.58
1.83
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1.43
1.40
1.39
1.37
1.36
1.34
1.25
0.87
0.01
10.69
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1.00
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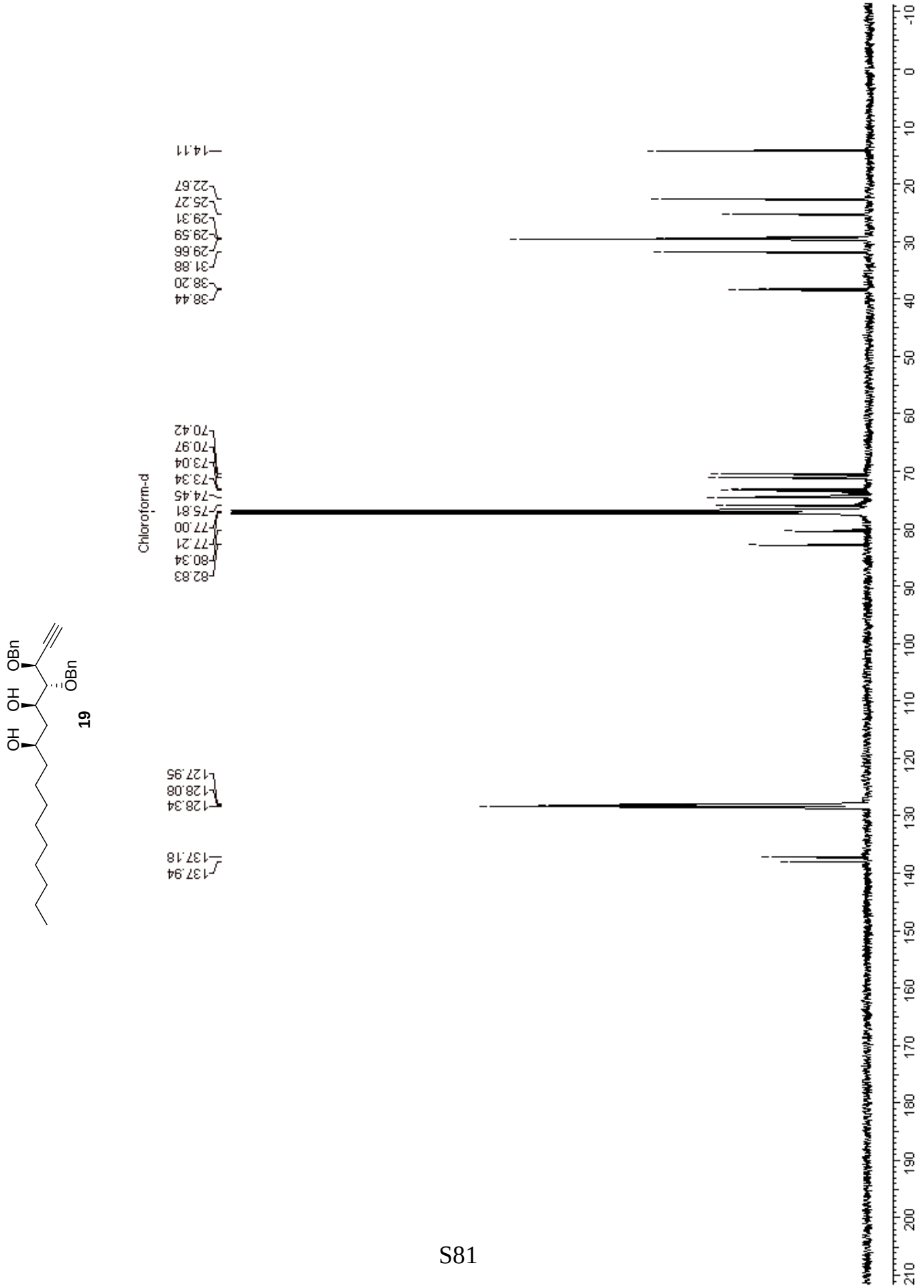
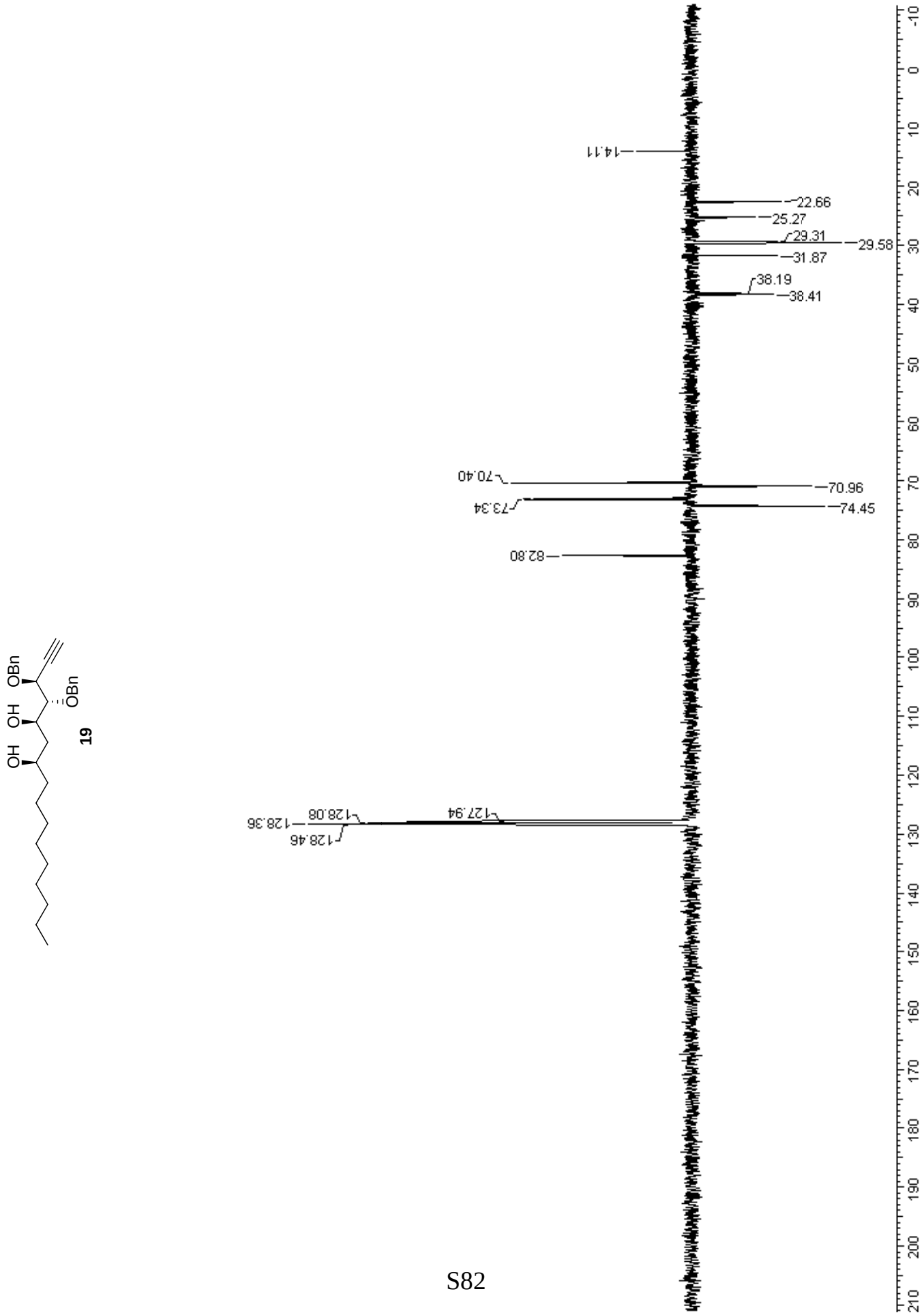
0.99
1.12
1.15
0.90
14.53
1.33
3.54


OBn
OH
OH
OBn
19
Chloroform-d
14.11
22.67
25.27
29.31
29.59
29.66
31.88
38.20
38.44
70.42
70.97
73.04
73.34
74.45
75.81
77.00
77.21
80.34
82.83
127.95
128.08
128.34
137.18
137.94


OBn
OH
OBn
OH
19
14.11
22.66
25.27
29.31
29.58
31.87
38.19
38.41
70.40
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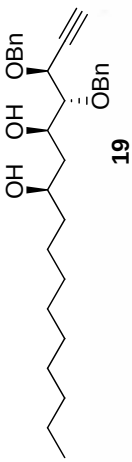
73.34
74.45
82.80
127.94
128.08
128.36
128.46



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Spectrum Report

SN-499 / 16

Final - Shots 750 - IISER; Run #90; Label O11

505.1806(R10638,S6378)
489.2126(R10838,S992)
397.1303(R9196,S602)
561.2391(R12476,S108)
871.3876(R14718,S581)
979.4376(R14575,S1417)
963.4712(R16206,S155)
242.2109(R8659,S140)

9.5E+3

100 90 80 70 60 50 40 30 20 10 0

100 381 662 943 1224 1505

Mass (m/z)

9/9/2010 3:37:42 PM

mayuraIISER Label O11 Run # 90

Page 1

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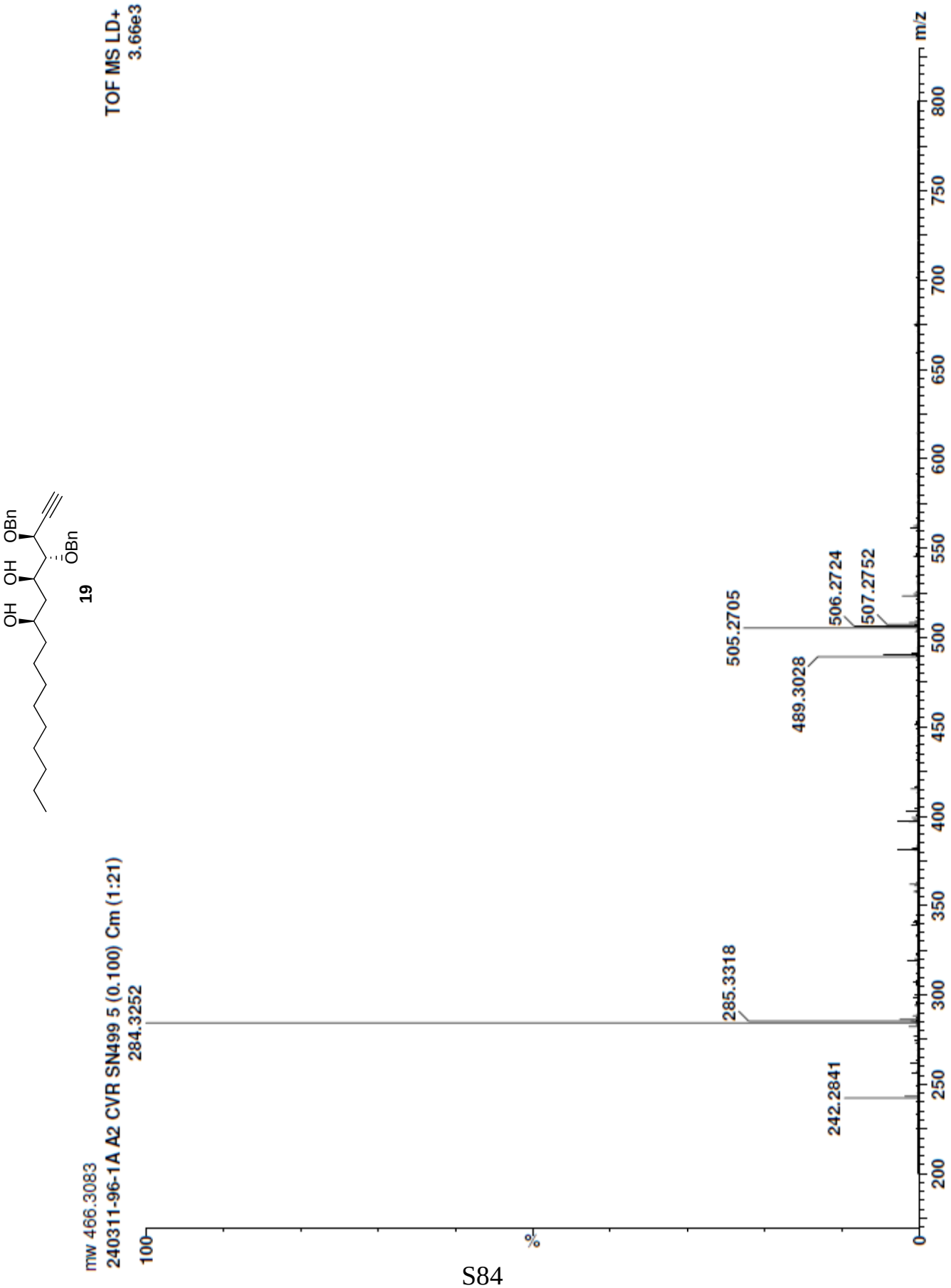

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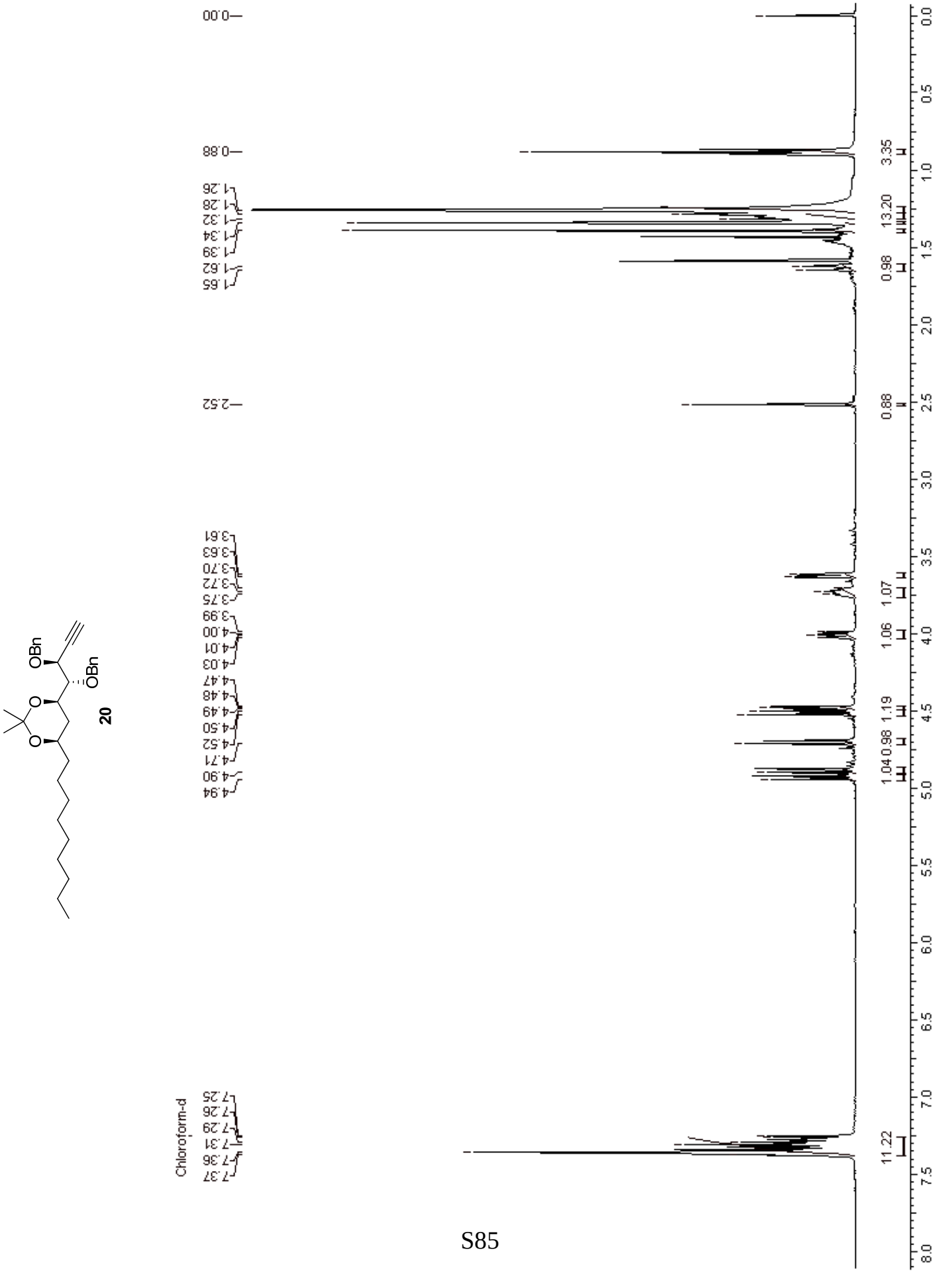

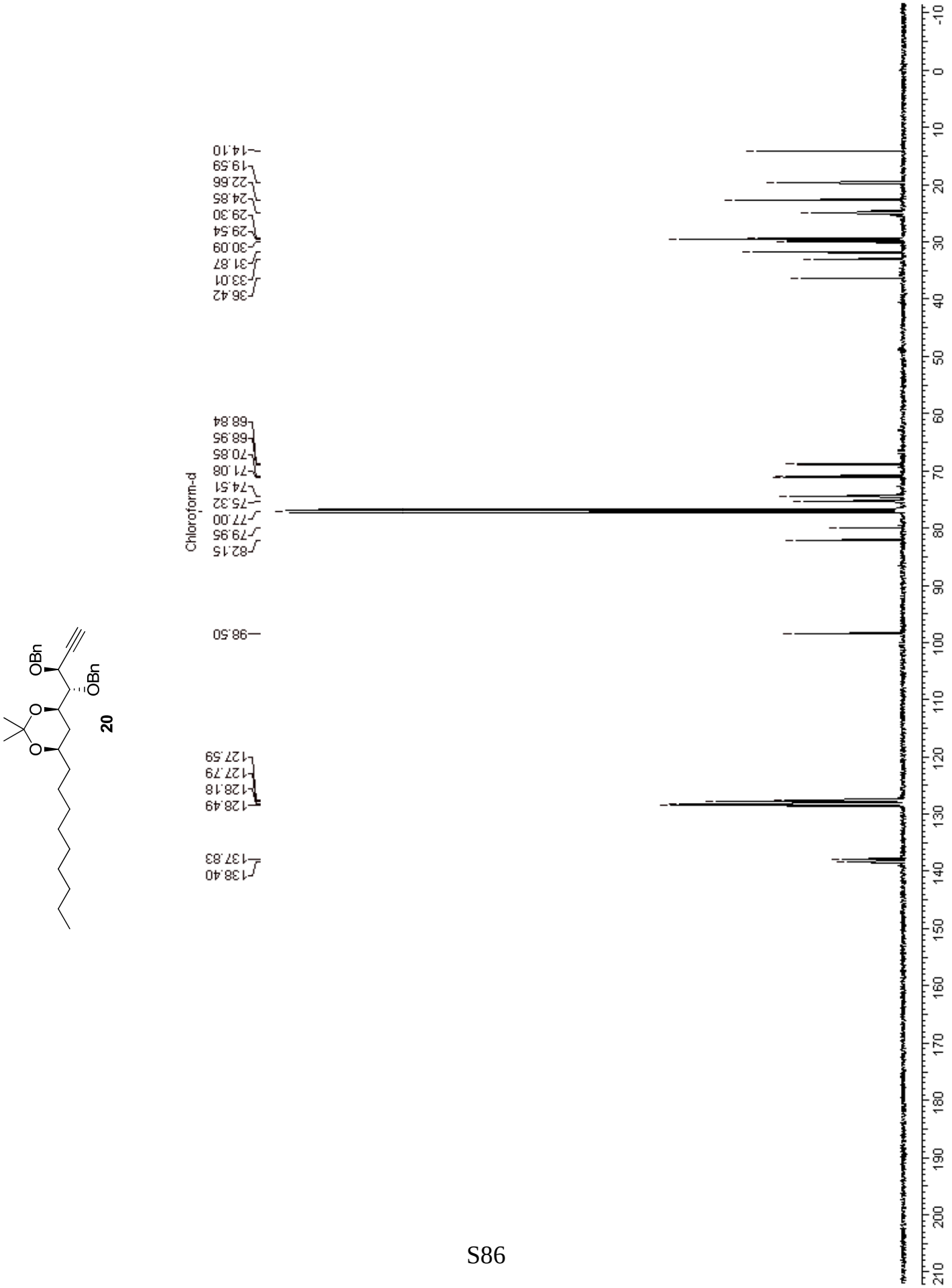
OBn
OBn
O
O
20
Chloroform-d
14.10
19.59
22.66
24.85
29.30
29.54
30.09
31.87
33.01
36.42
68.84
68.95
70.85
71.08
74.51
75.32
77.00
79.95
82.15
98.50
127.59
127.79
128.18
128.49
137.83
138.40

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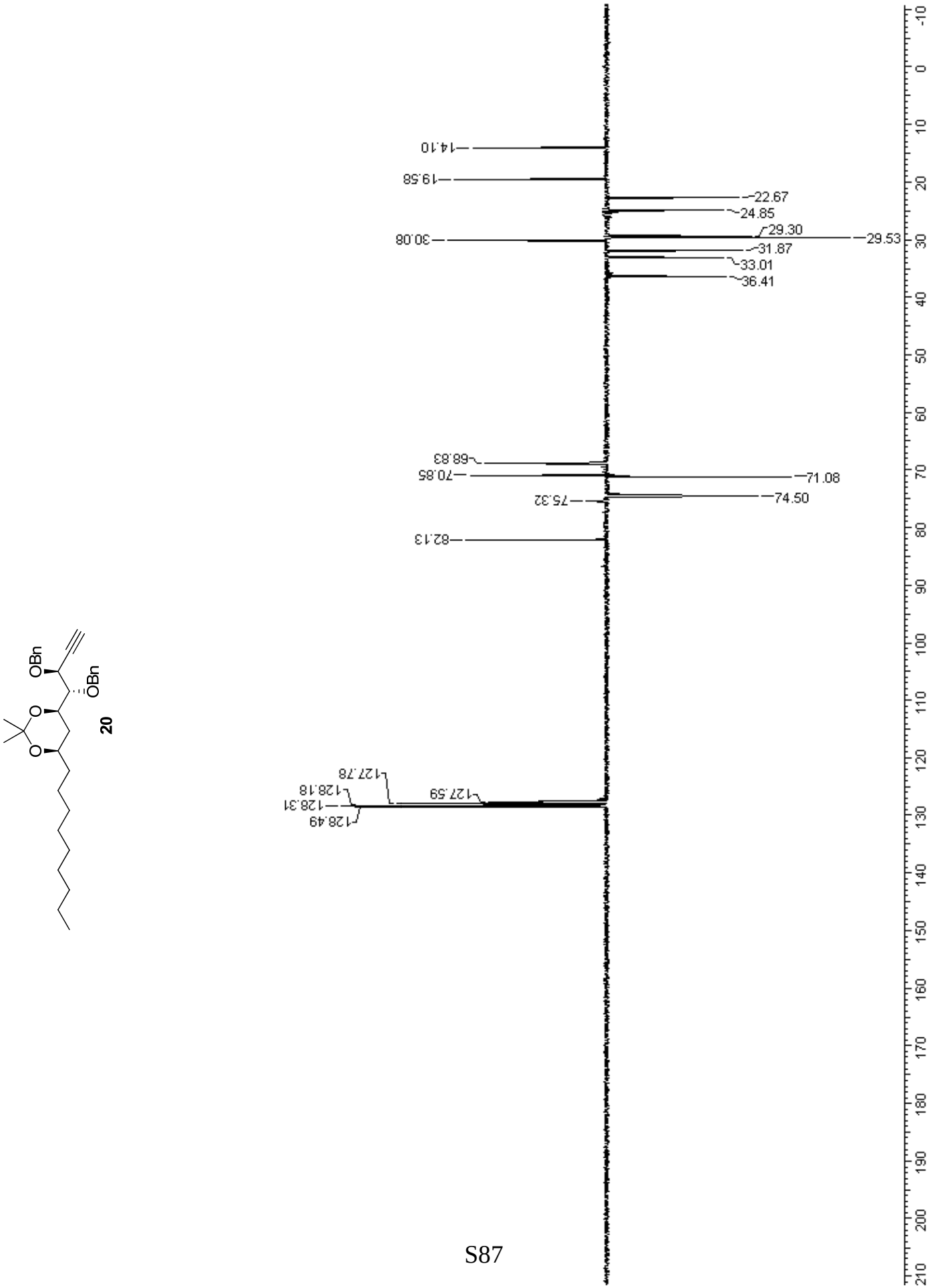
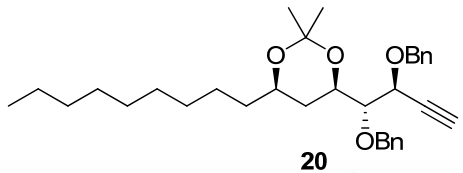


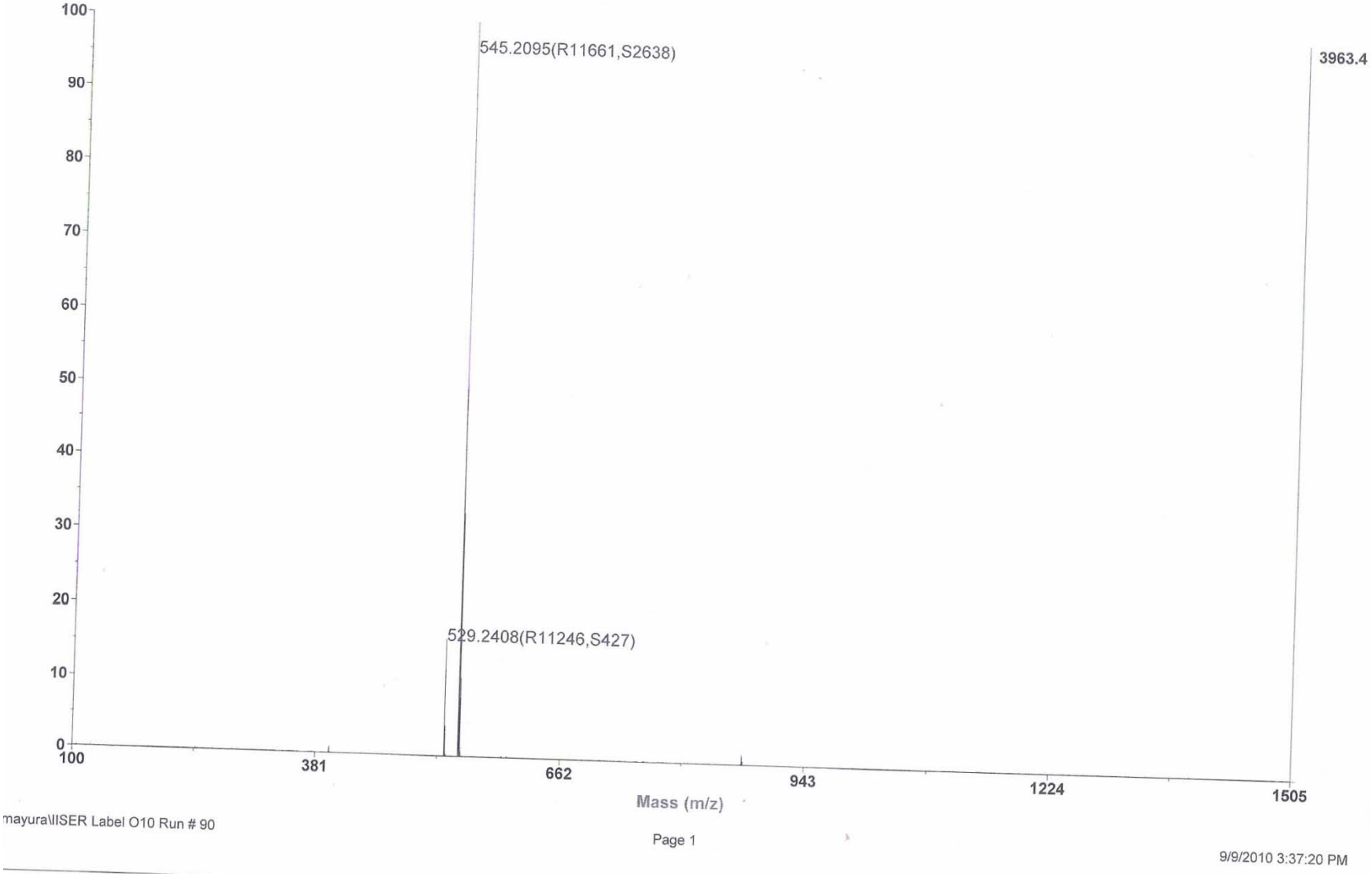


20

Spectrum Report

SN - 502 / 17

Final - Shots 750 - IISER; Run #90; Label O10



mayura\IISER Label O10 Run # 90

Page 1

9/9/2010 3:37:20 PM

Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry
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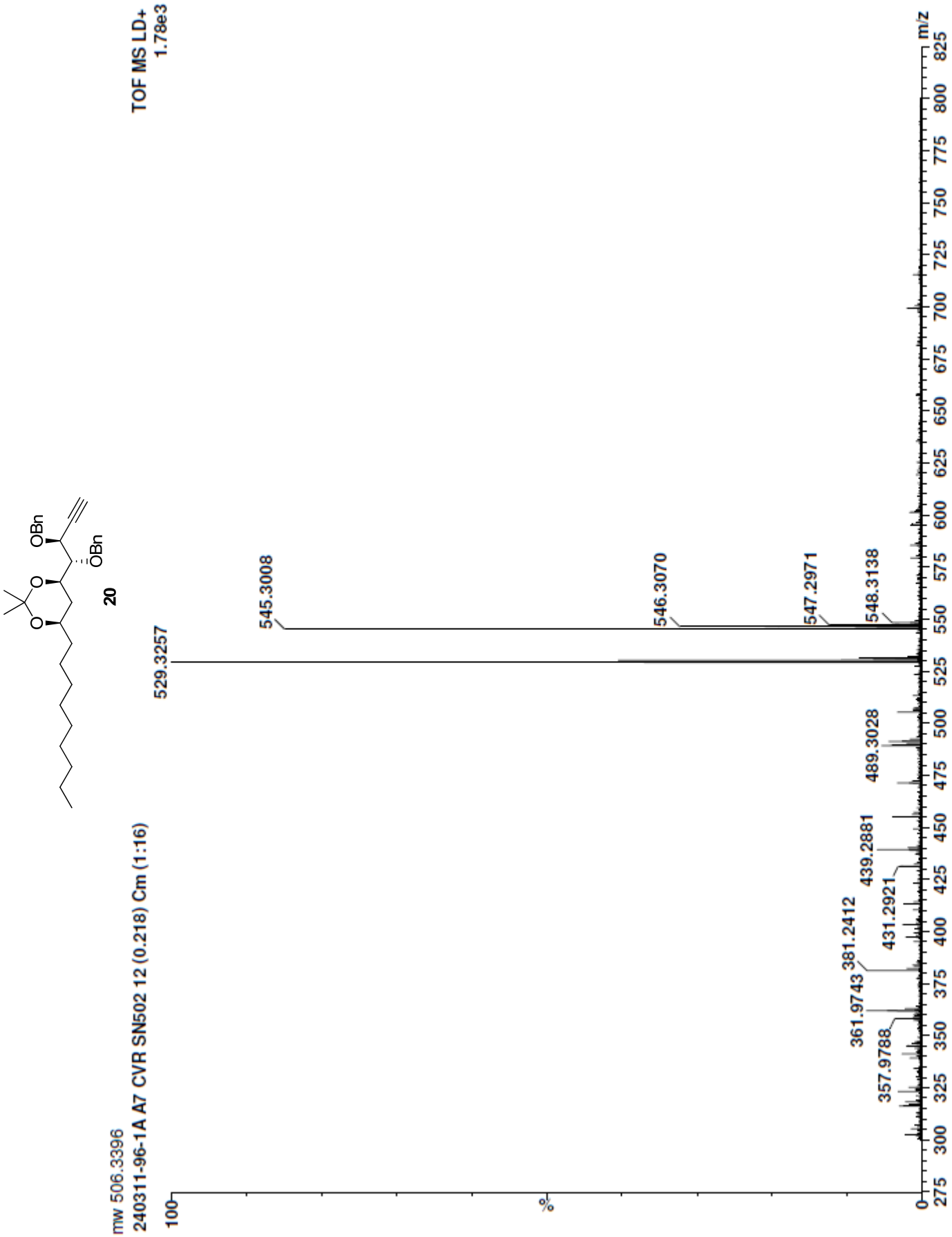

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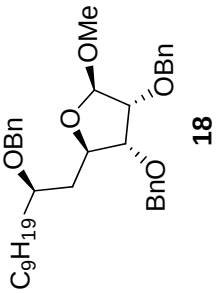

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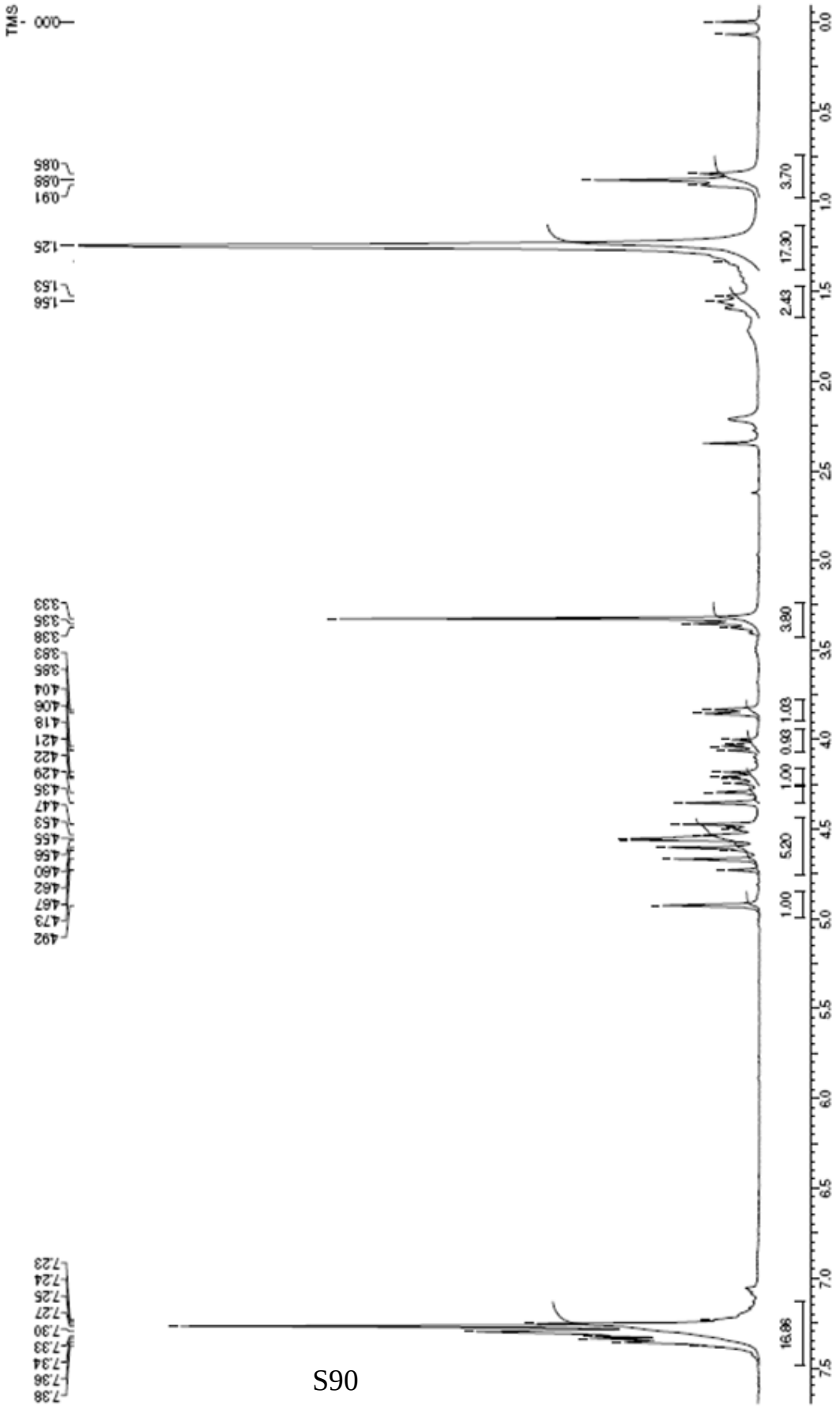
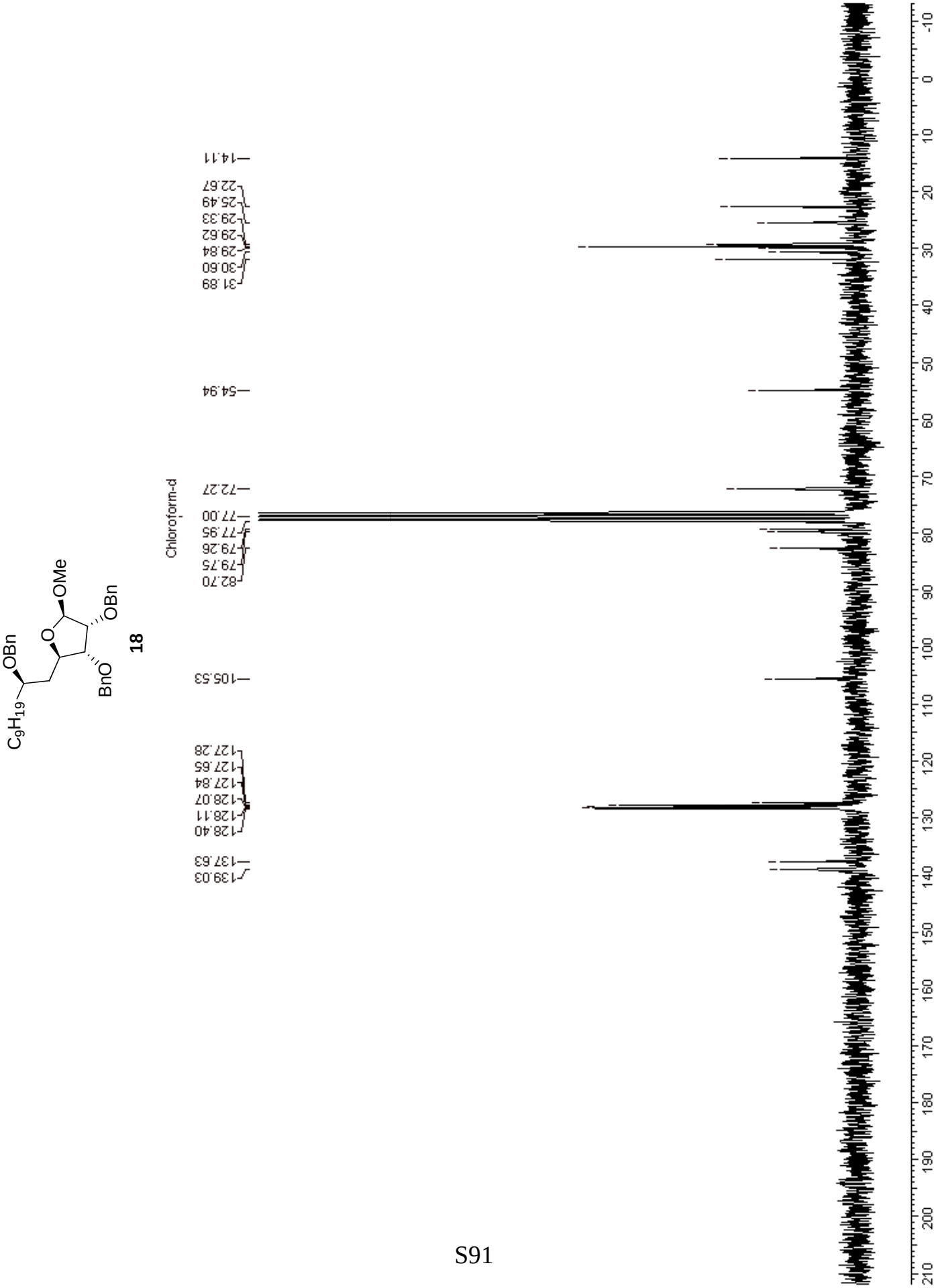
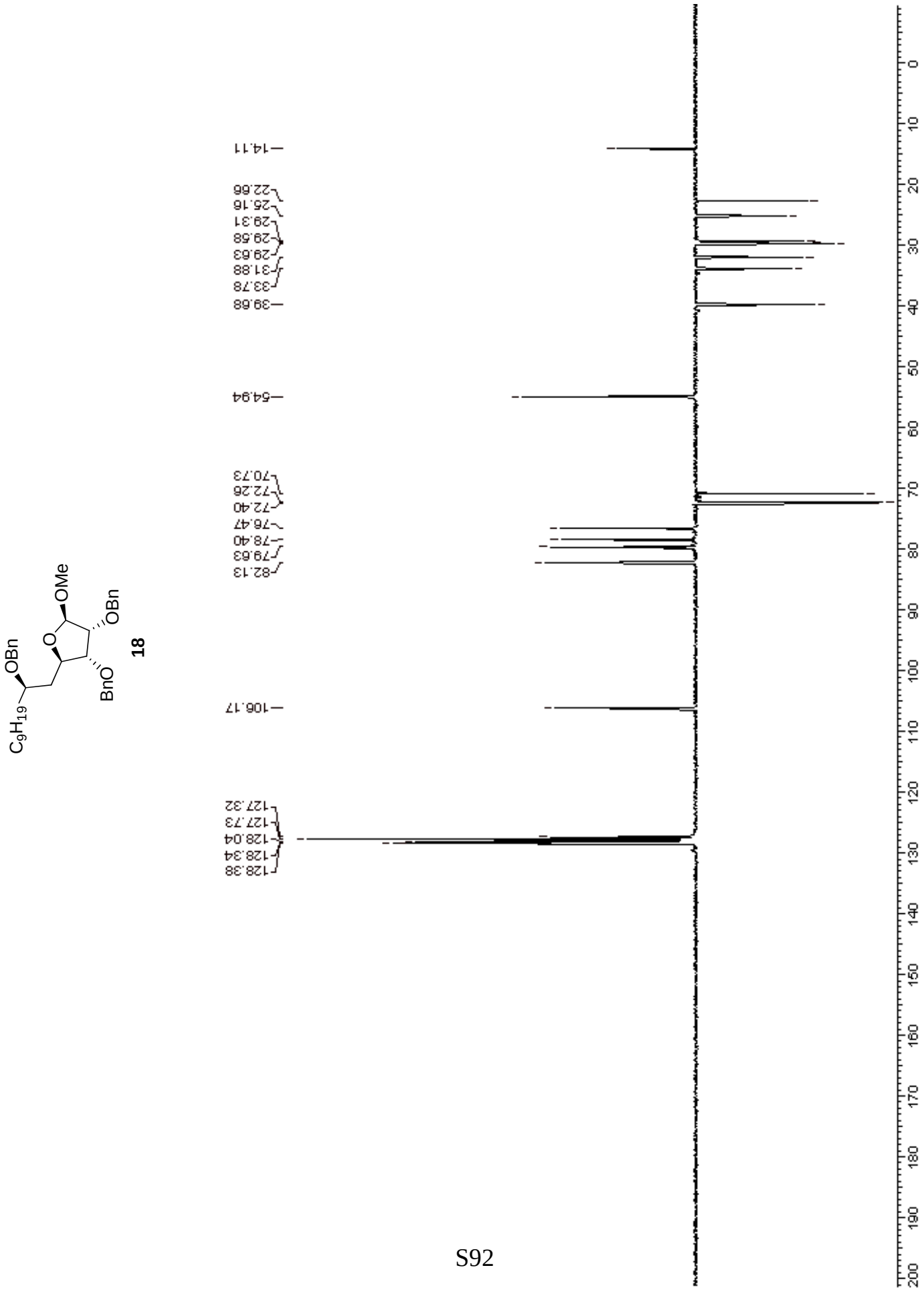
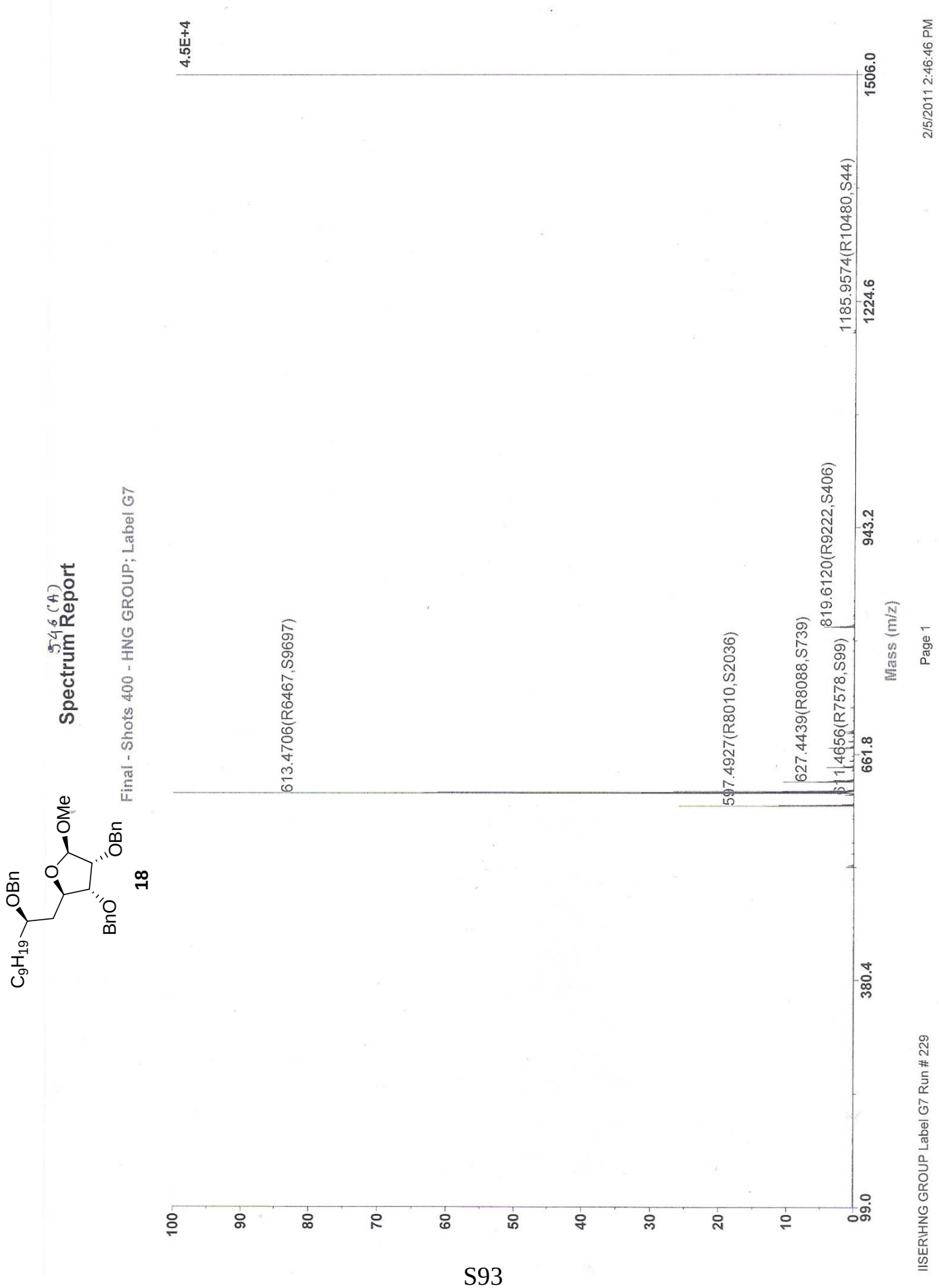



OMe
OBn
BnO
OBn
C_9H_{19}
18
Chloroform-d
14.11
22.67
25.49
29.33
29.62
29.84
30.60
31.89
54.94
72.27
77.00
77.95
79.26
79.75
82.70
105.53
127.28
127.65
127.84
128.07
128.11
128.40
137.63
139.03


14.11
22.66
26.16
29.31
29.58
29.63
31.88
33.78
39.68
64.94
70.73
72.26
72.40
76.47
78.40
79.63
82.13
106.17
127.32
127.73
128.04
128.34
128.38
OMe
OBn
O
OBn
BnO
C_9H_{19}
18


Spectrum Report
Final - Shots 400 - HNG GROUP; Label G7
18
OBn
OMe
OBn
BnO
C_9H_{19}
4.5E+4
613.4706(R6467,S9697)
597.4927(R8010,S2036)
627.4439(R8088,S739)
611.4656(R7578,S99)
819.6120(R9222,S406)
1185.9574(R10480,S44)
100
90
80
70
60
50
40
30
20
10
0
99.0
380.4
661.8
943.2
1224.6
1506.0
Mass (m/z)
Page 1
2/5/2011 2:46:46 PM
IISER\HNG GROUP Label G7 Run # 229

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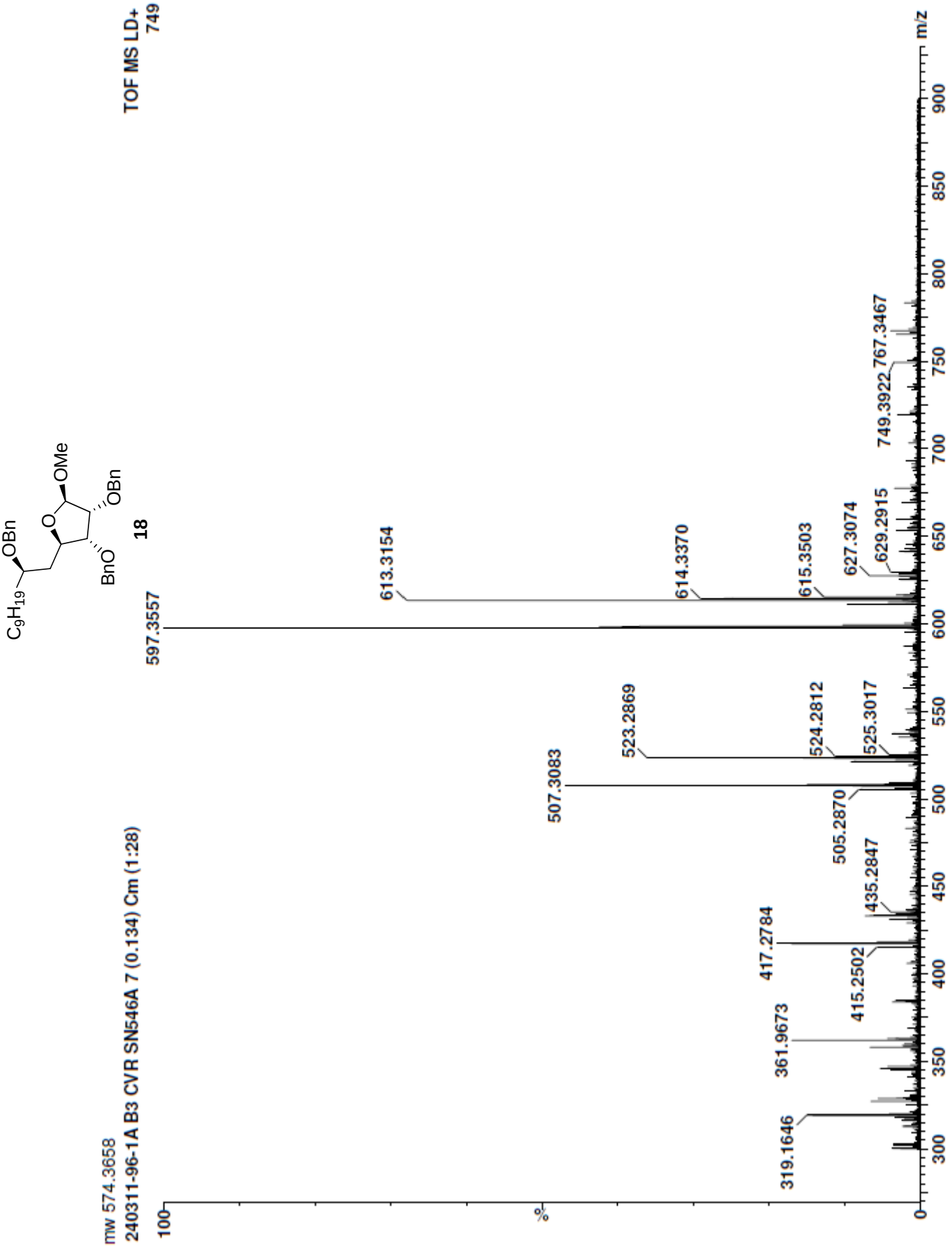

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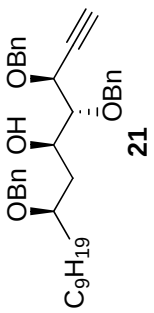

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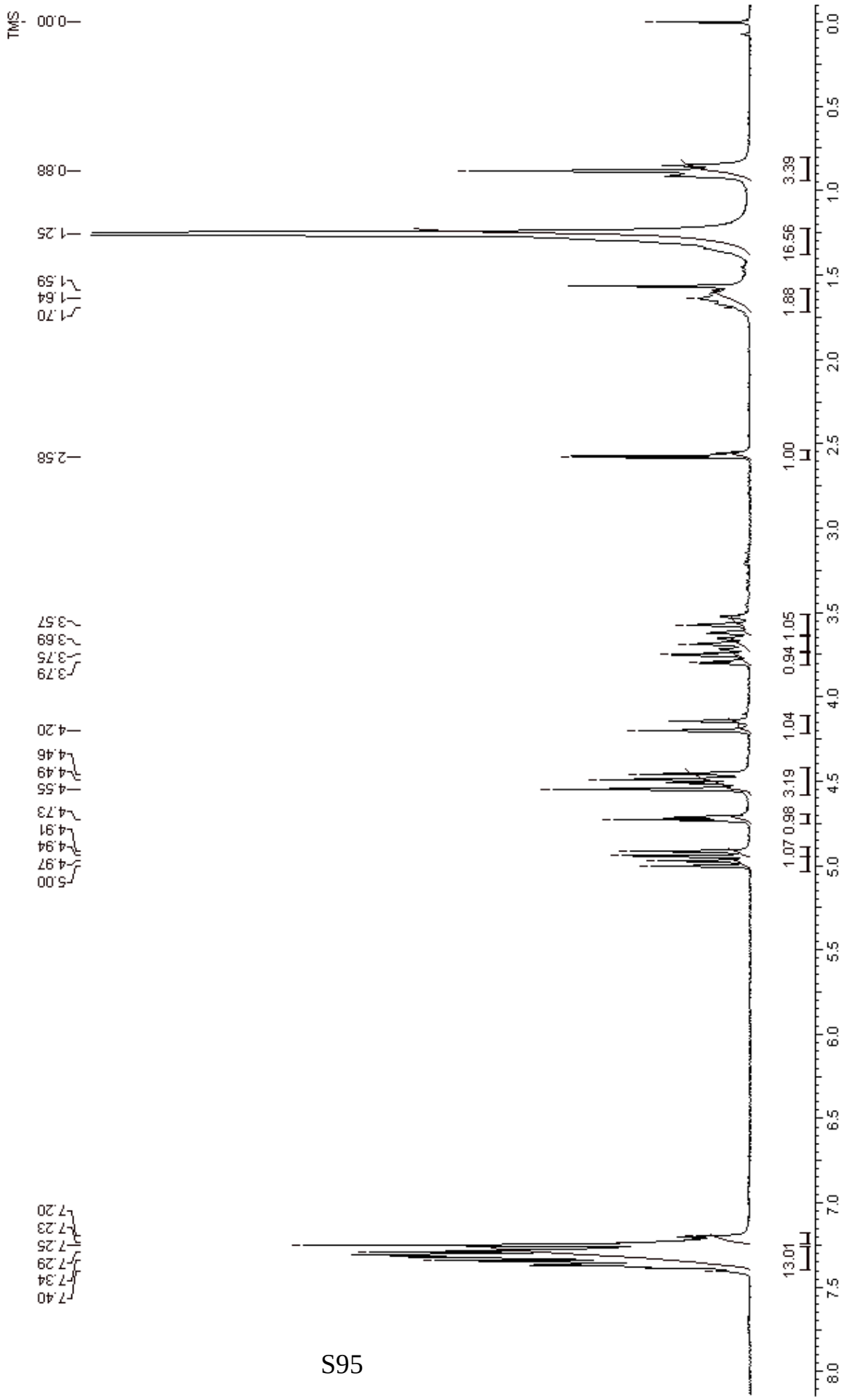

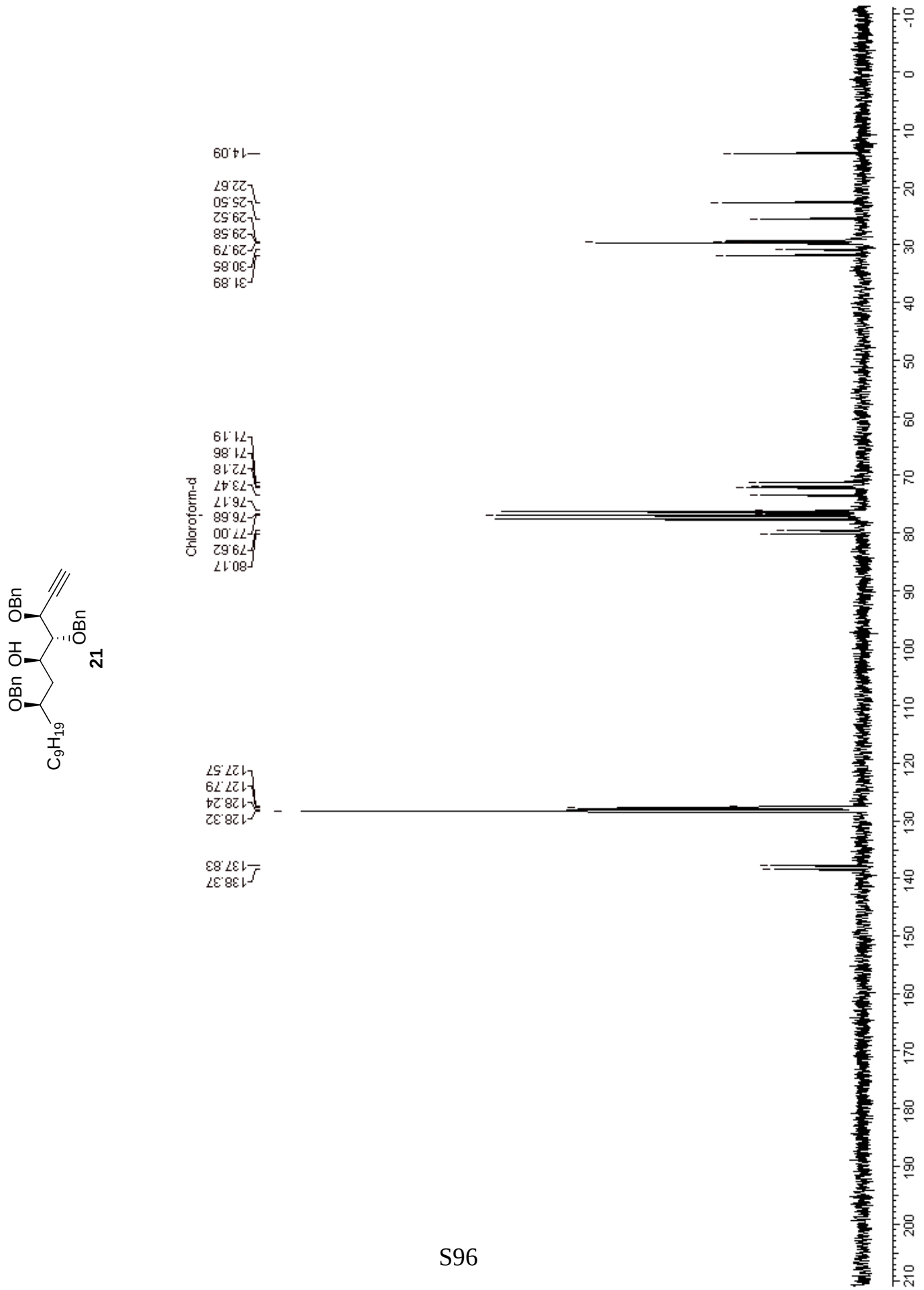
OBn
OH
OBn
OBn
C_9H_{19}
21
Chloroform-d
14.09
22.67
25.50
29.52
29.58
29.79
30.85
31.89
71.19
71.86
72.18
73.47
76.17
76.68
77.00
79.62
80.17
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127.79
128.24
128.32
137.83
138.37

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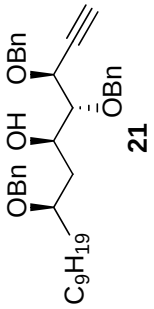

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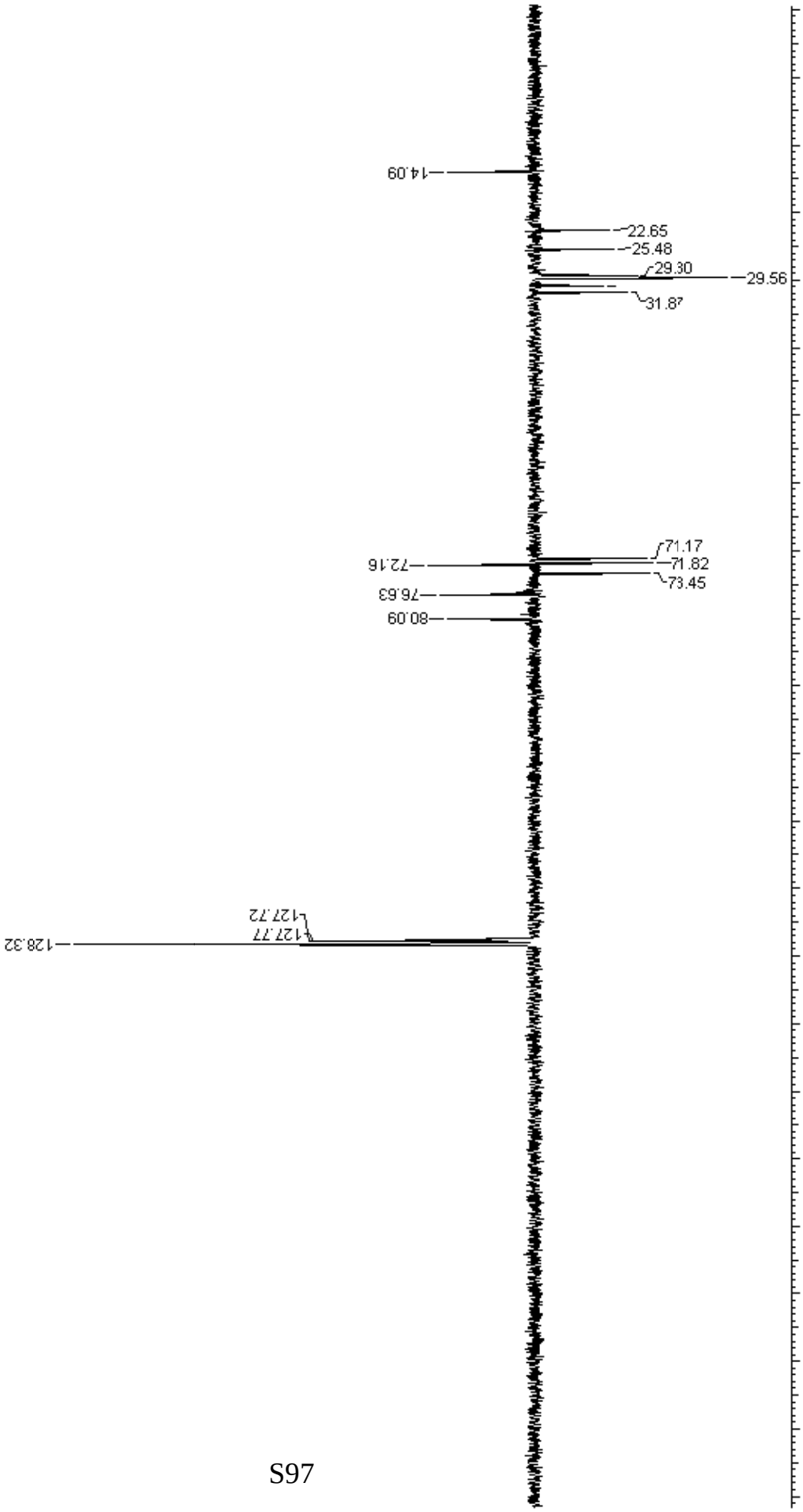

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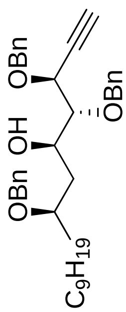

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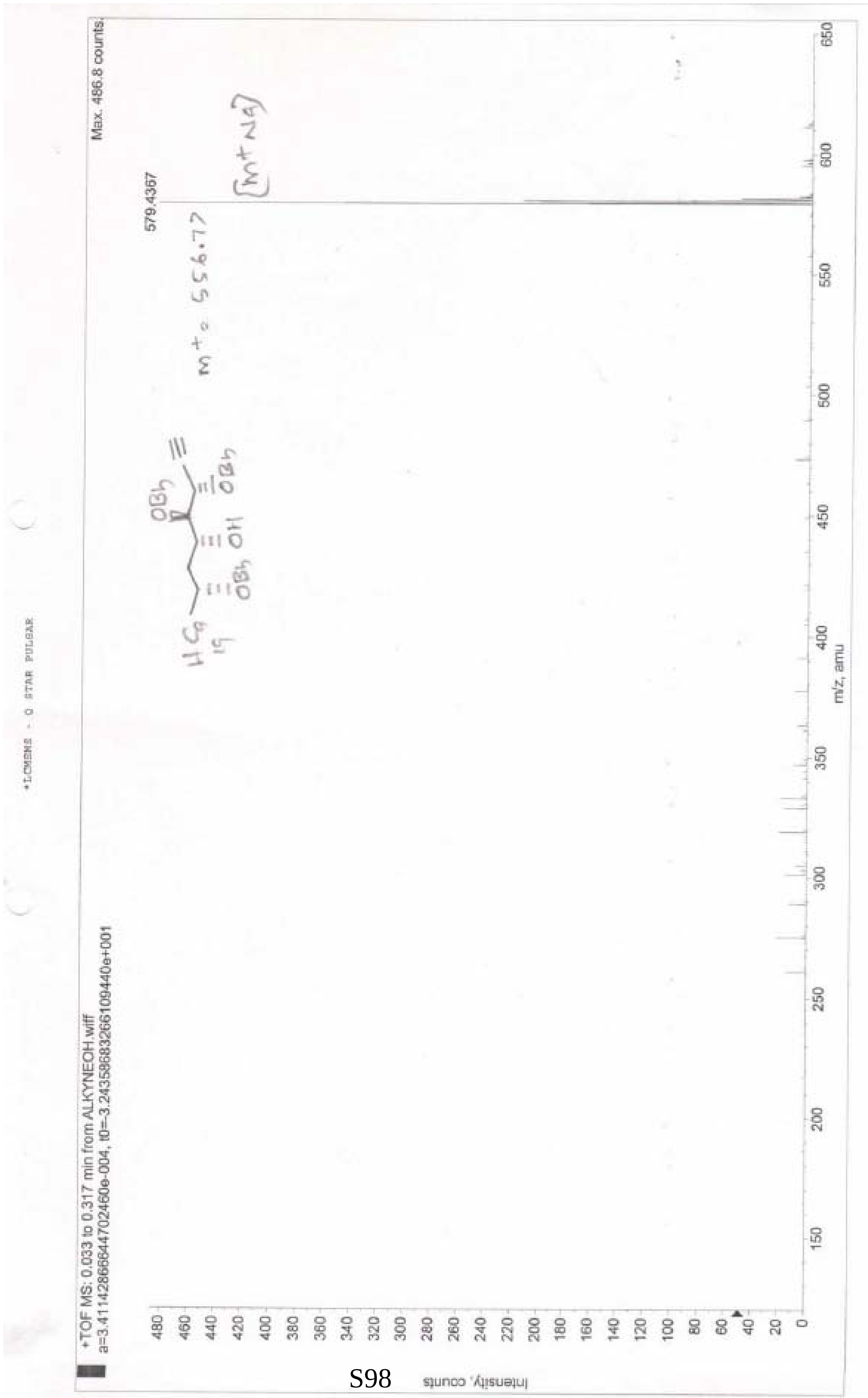
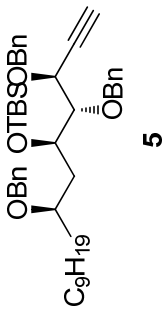
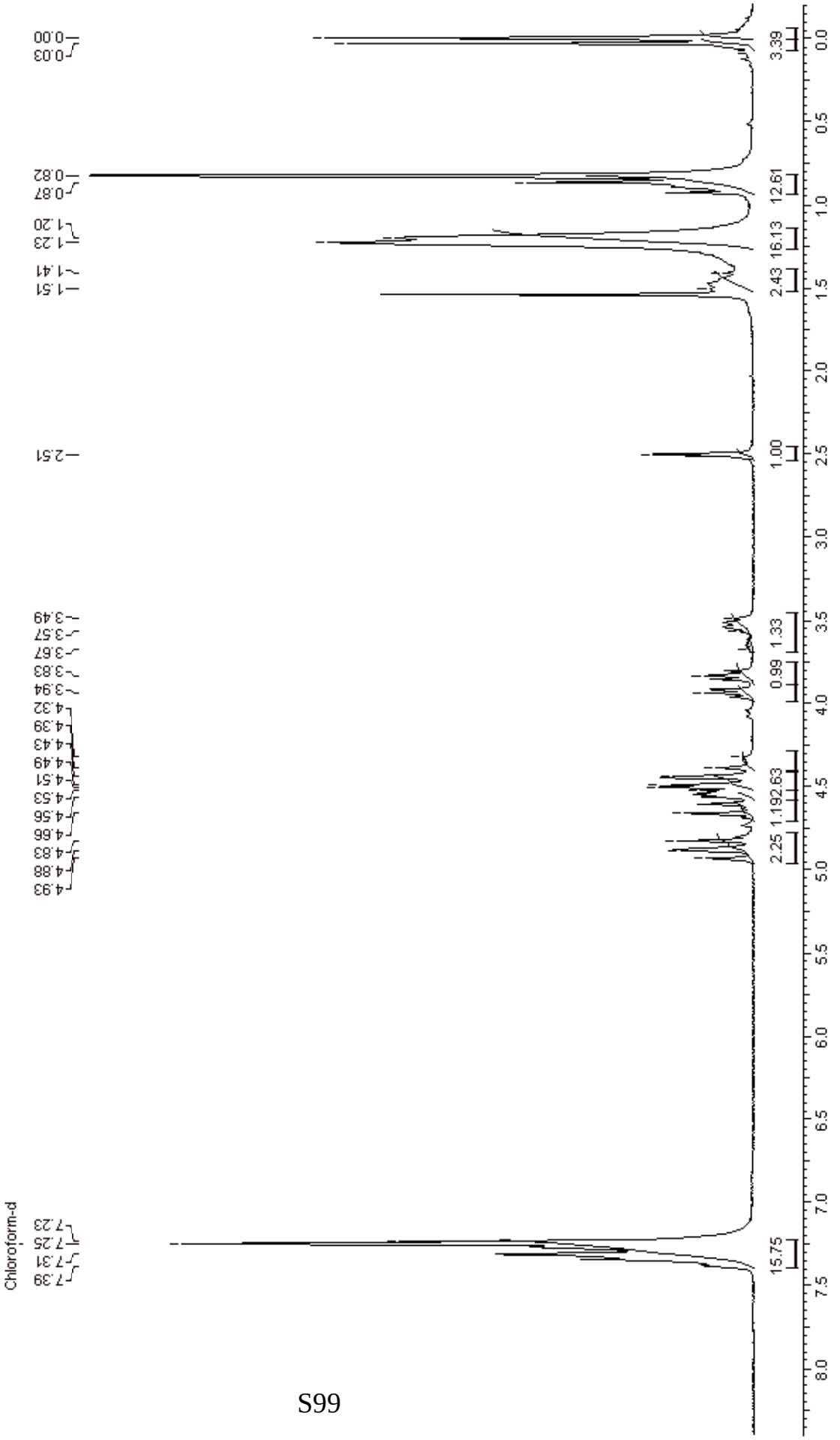
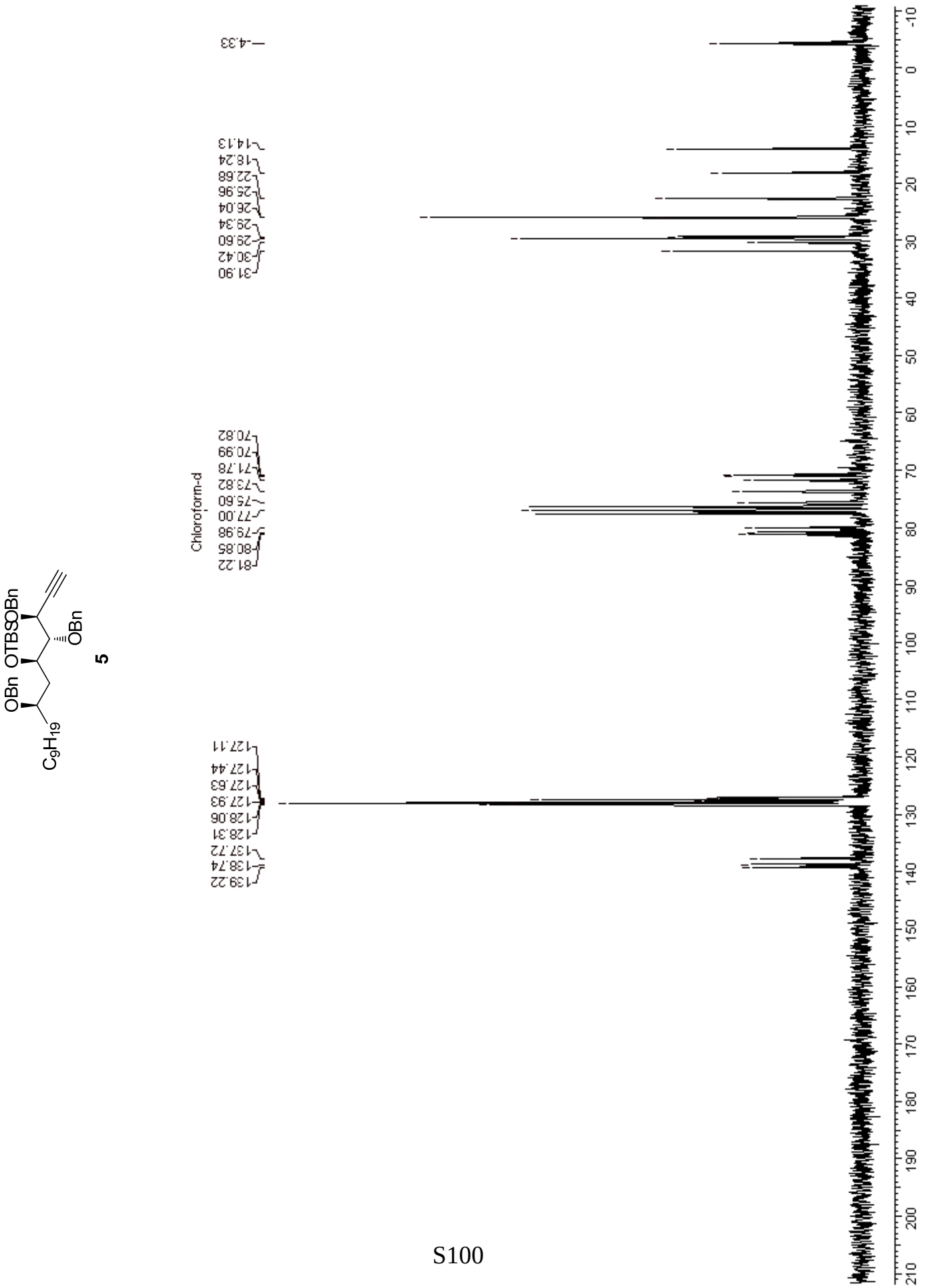
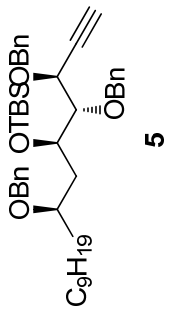



OBn
OTBS
OBn
OBn
C_9H_{19}

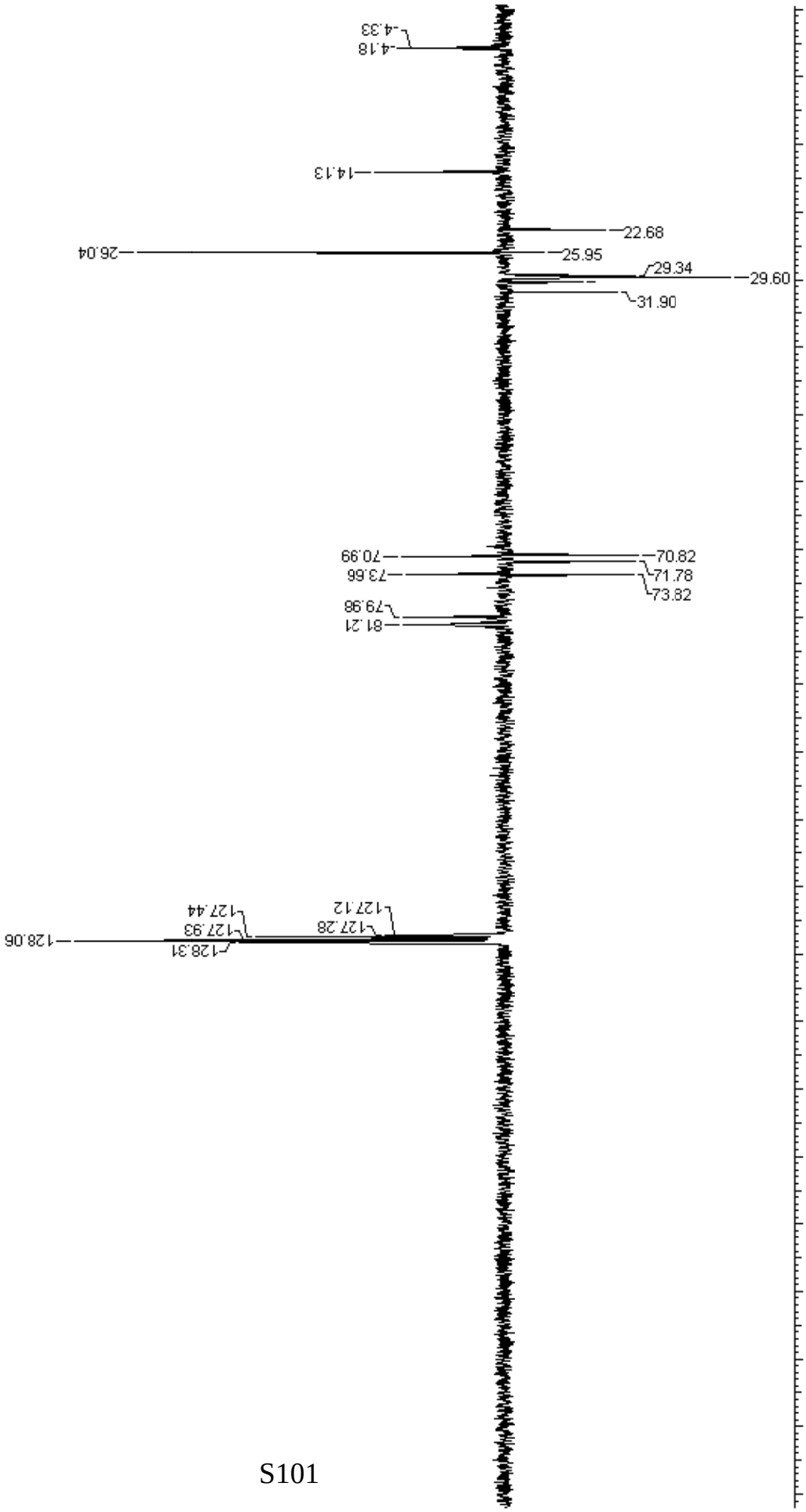
5


0.00
0.03
0.82
0.87
1.20
1.23
1.41
1.51
2.51
3.49
3.57
3.67
3.83
3.94
4.32
4.39
4.43
4.49
4.51
4.53
4.56
4.66
4.83
4.88
4.93
Chloroform-d
7.23
7.25
7.31
7.39
3.39
12.61
16.13
2.43
1.00
1.33
0.99
1.19
2.63
2.25
15.75


OBn
OTBSOBn
OBn
C_9H_{19}
5
Chloroform-d
-4.33
14.13
18.24
22.68
25.96
26.04
29.34
29.60
30.42
31.90
70.82
70.99
71.78
73.82
75.60
77.00
79.98
80.85
81.22
127.11
127.44
127.63
127.93
128.06
128.31
137.72
138.74
139.22


OBn
OTBSOBn
OBn
C_9H_{19}

5


-4.33
-4.18
14.13
22.68
26.04
25.95
29.34
29.60
31.90
70.99
73.66
79.98
81.21
70.82
71.78
73.82
128.06
128.31
127.93
127.44
127.28
127.12

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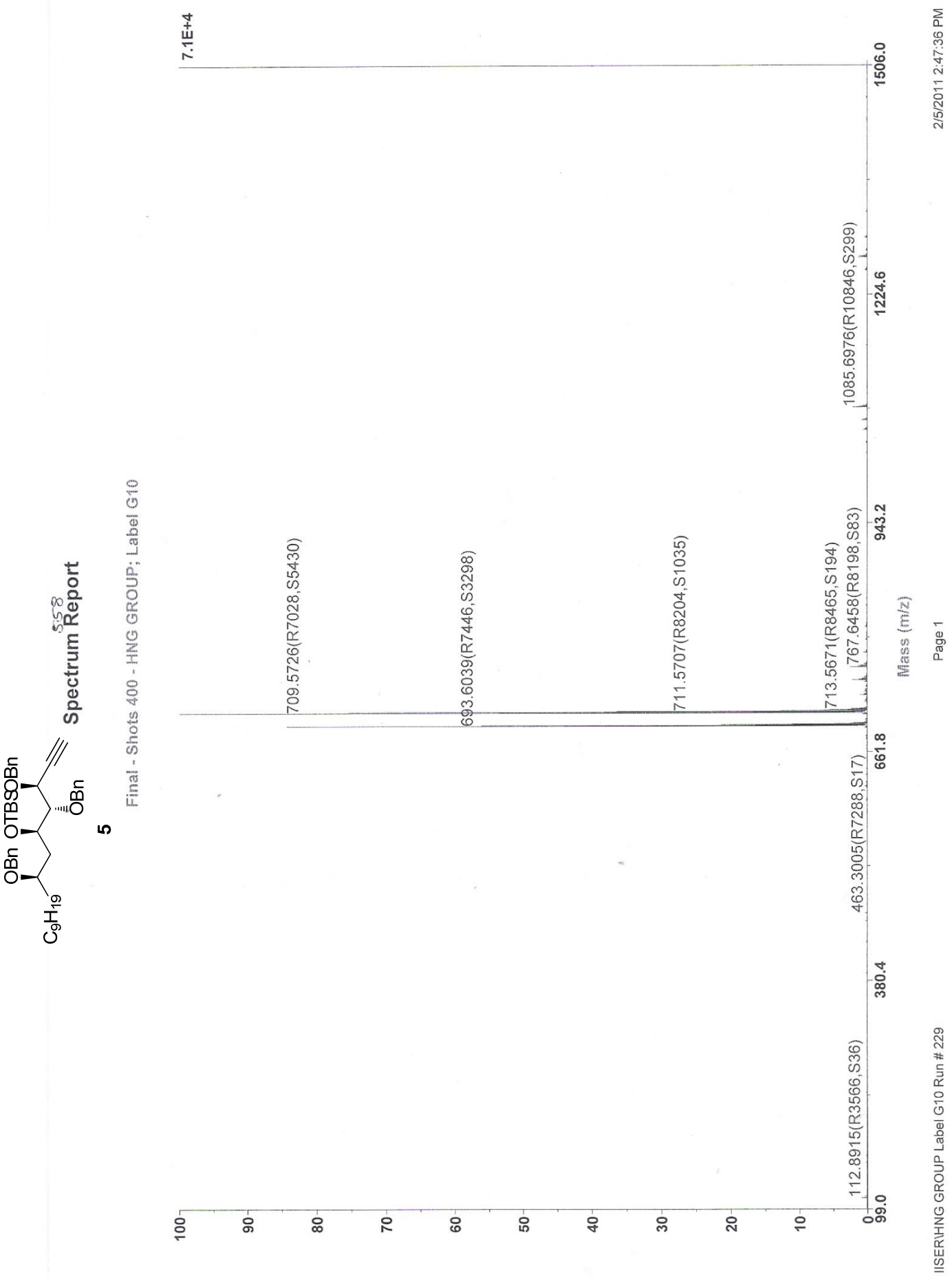

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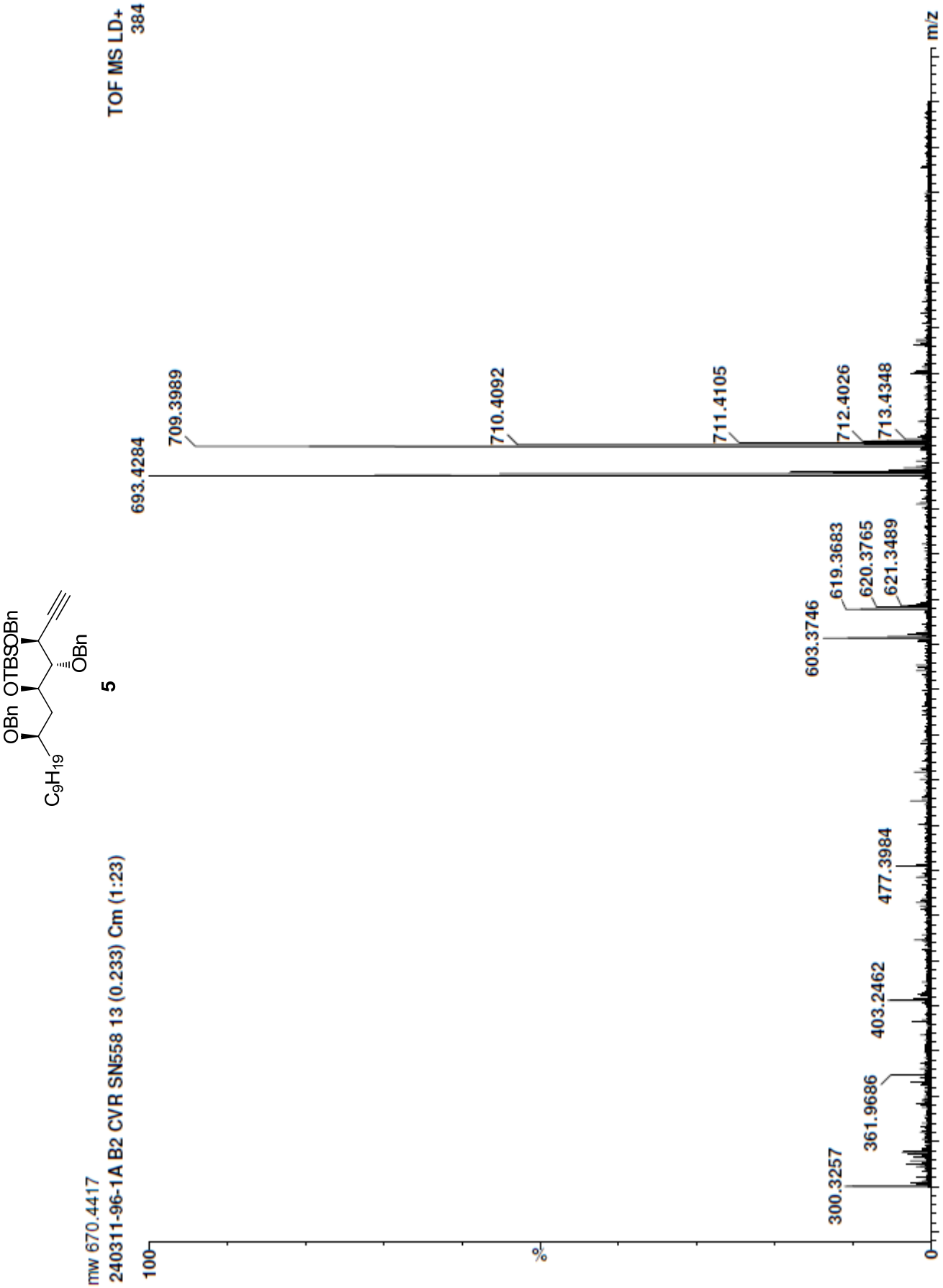

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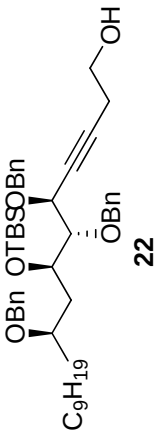
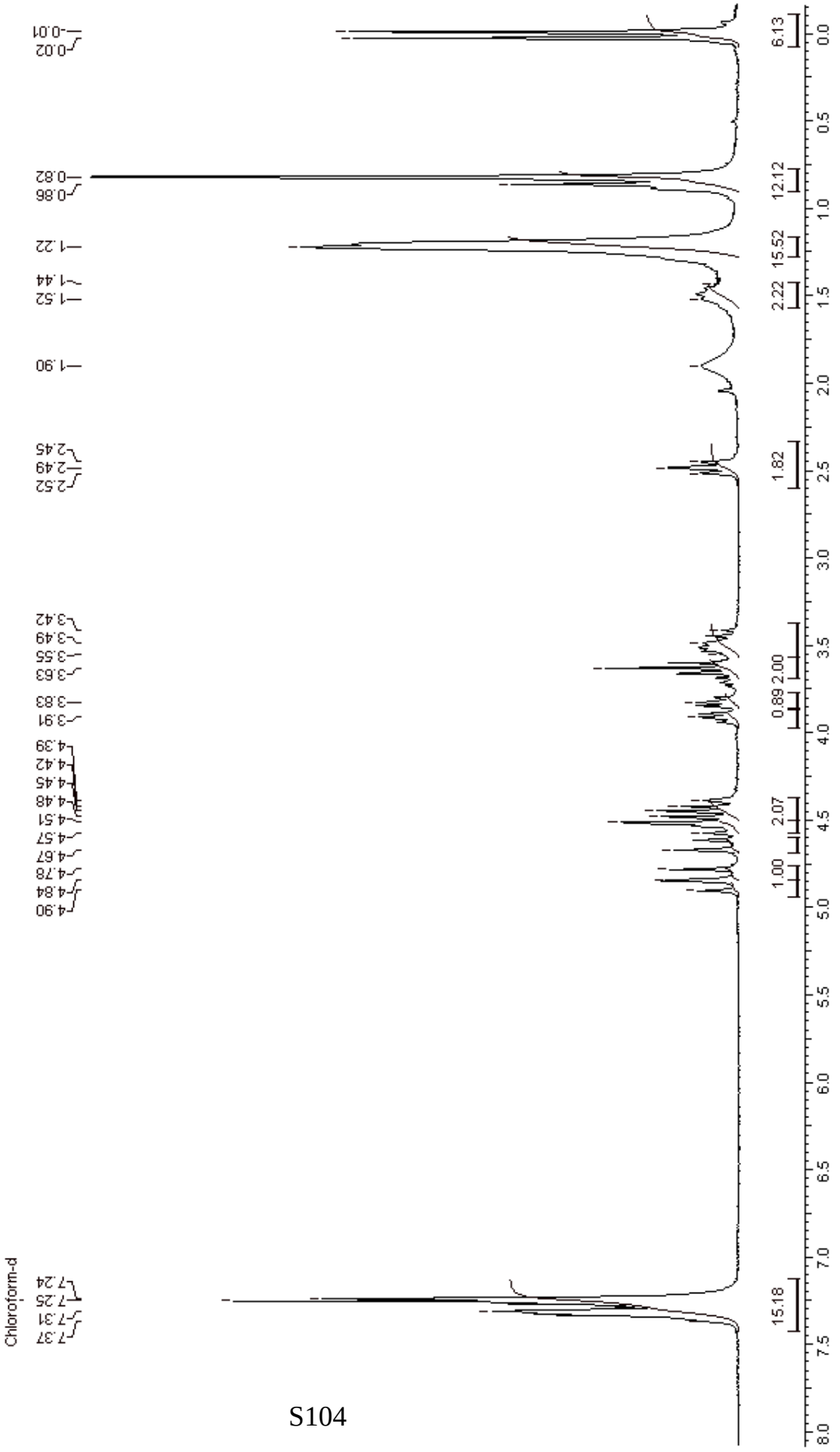
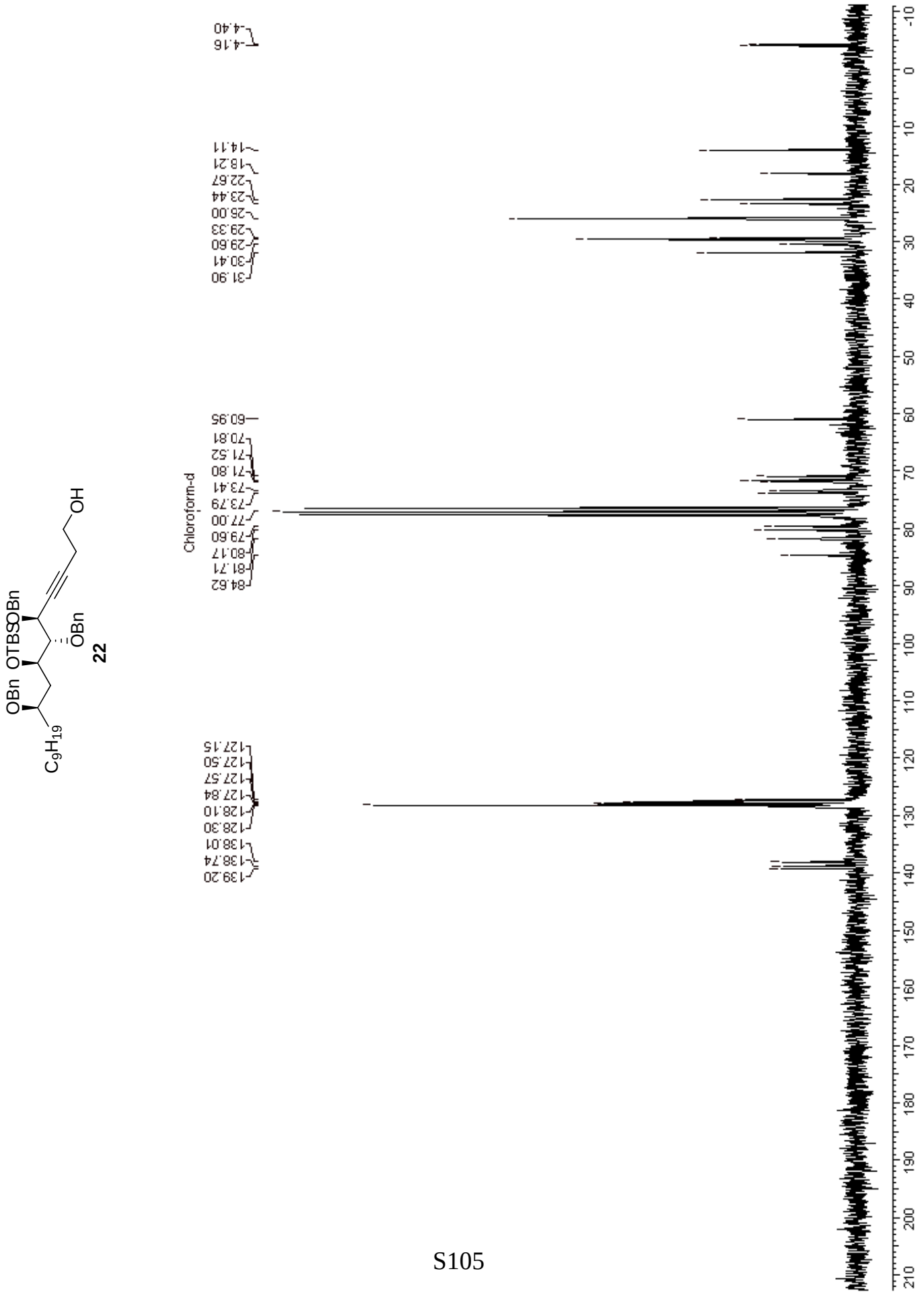


22




OH
OBn
OTBS
OBn
OBn
C_9H_{19}
22
Chloroform-d
-4.40
-4.16
14.11
18.21
22.67
23.44
26.00
29.33
29.60
30.41
31.90
60.95
70.81
71.52
71.80
73.41
73.79
77.00
79.60
80.17
81.71
84.62
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127.57
127.84
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128.30
138.01
138.74
139.20

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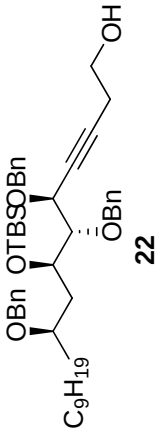

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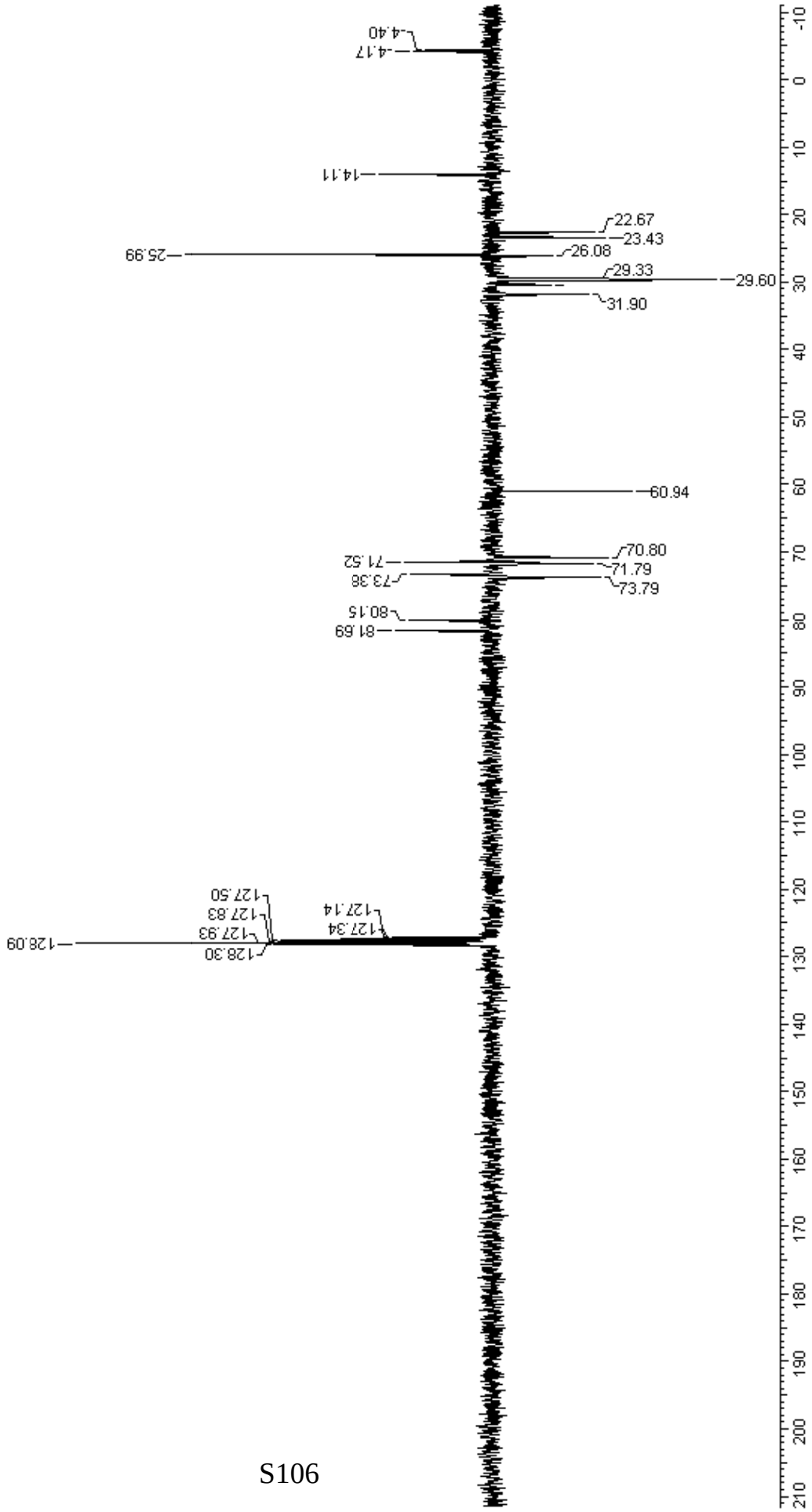
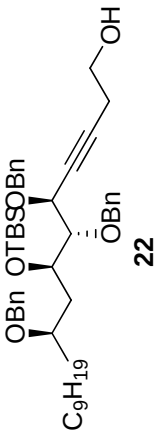
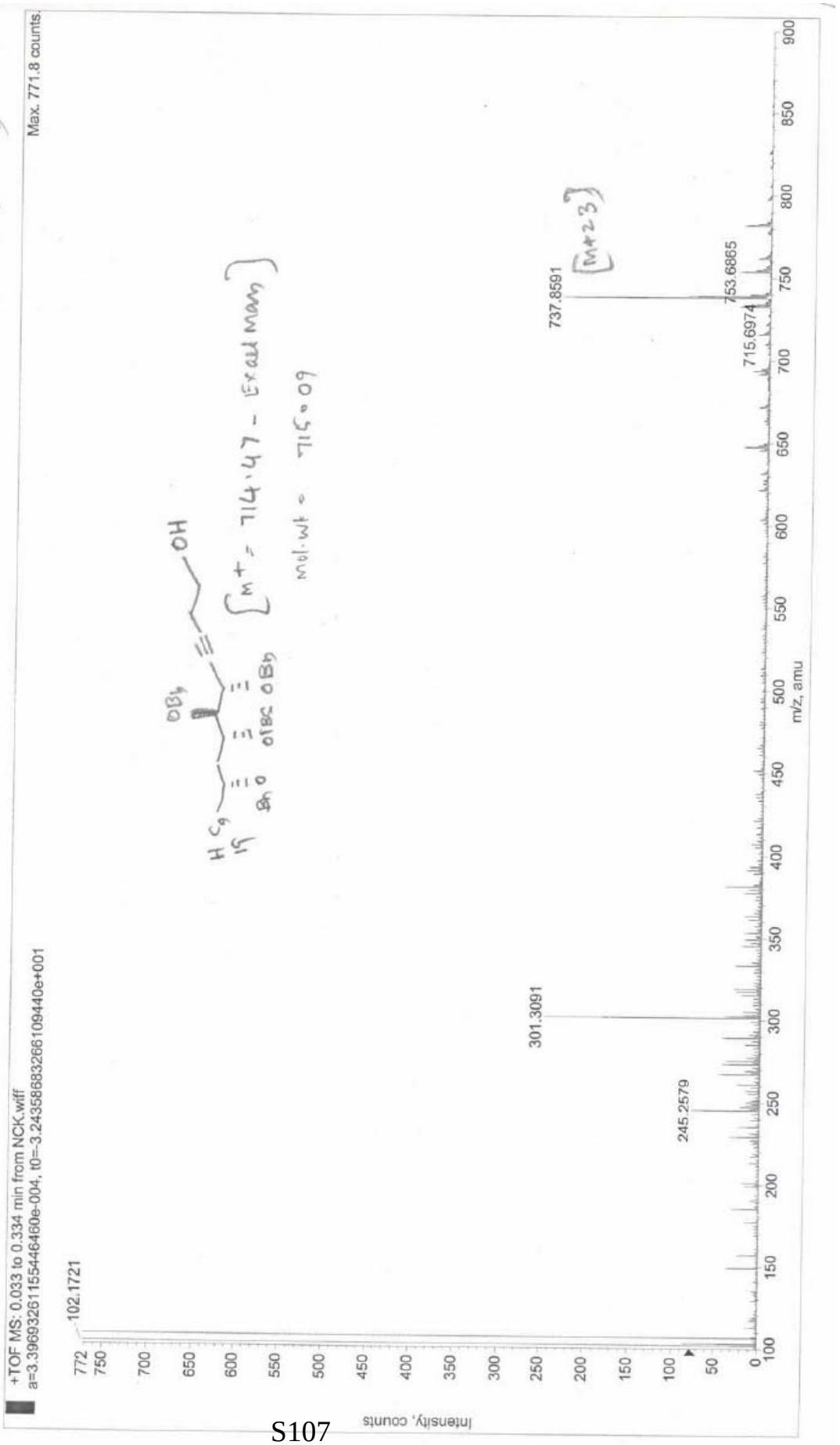



OBn
OTBSOBn
OBn
OH
C_9H_{19}

22


Actual
$[\alpha]_D^{20}$ = +31.84
c = (0.9, in CHCl3)
•LCMSMS - Q STAR PULSAR
OH
OBn
OBn
OTBS OBn
$H_{19}C_9$
[M+ = 714.47 - Exact Mass]
Mol.wt = 715.09
+TOF MS: 0.033 to 0.334 min from NCK.wiff
a=3.396932611554464 60e-004, t0=-3.243586832661094 40e+001
Max. 771.8 counts.
102.1721
245.2579
301.3091
737.8591
[M+23]
753.6865
715.6974
Intensity, counts
m/z, amu

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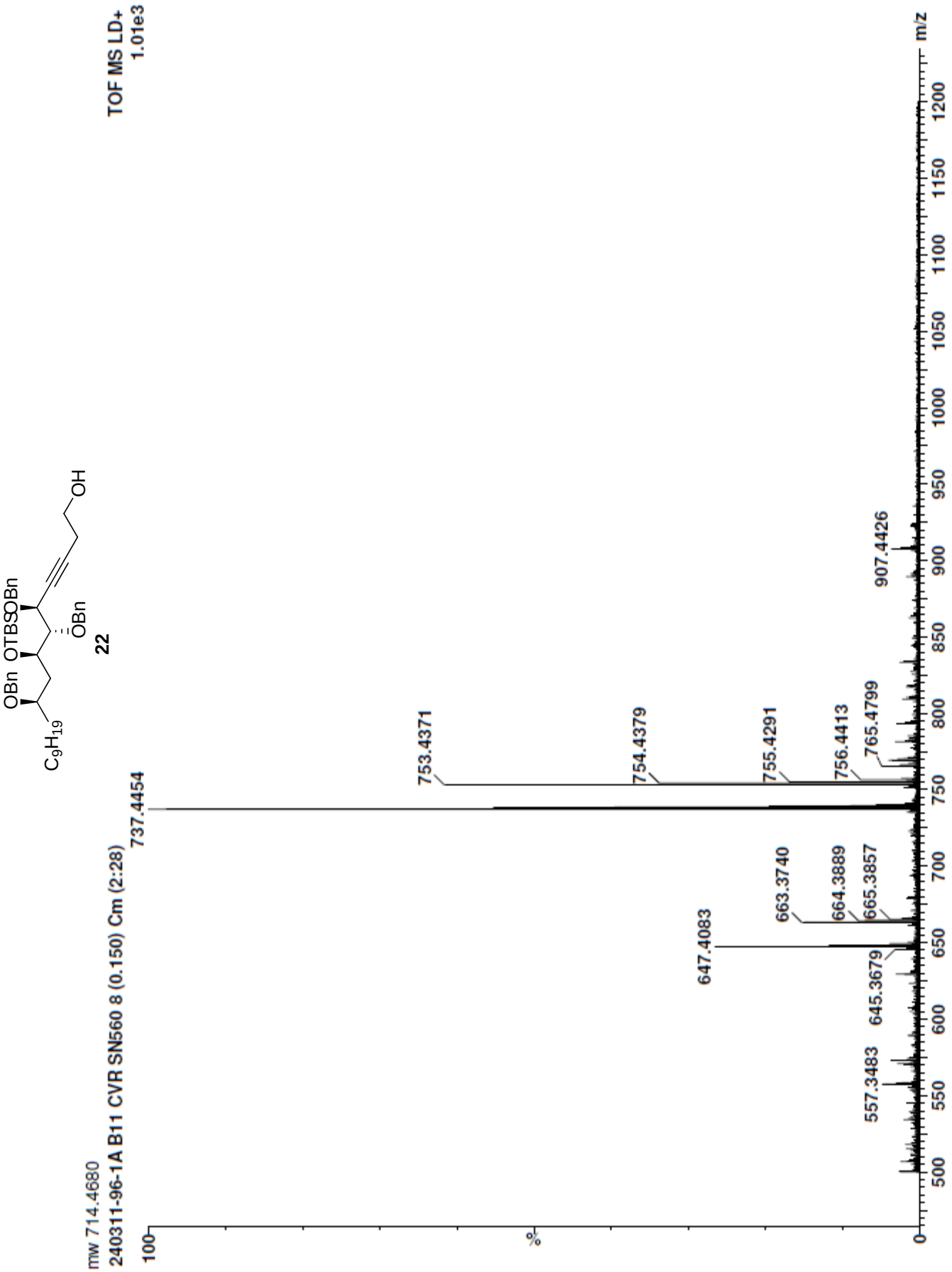

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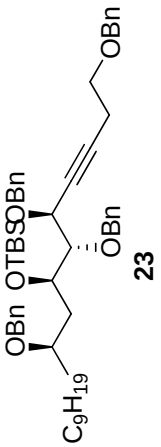
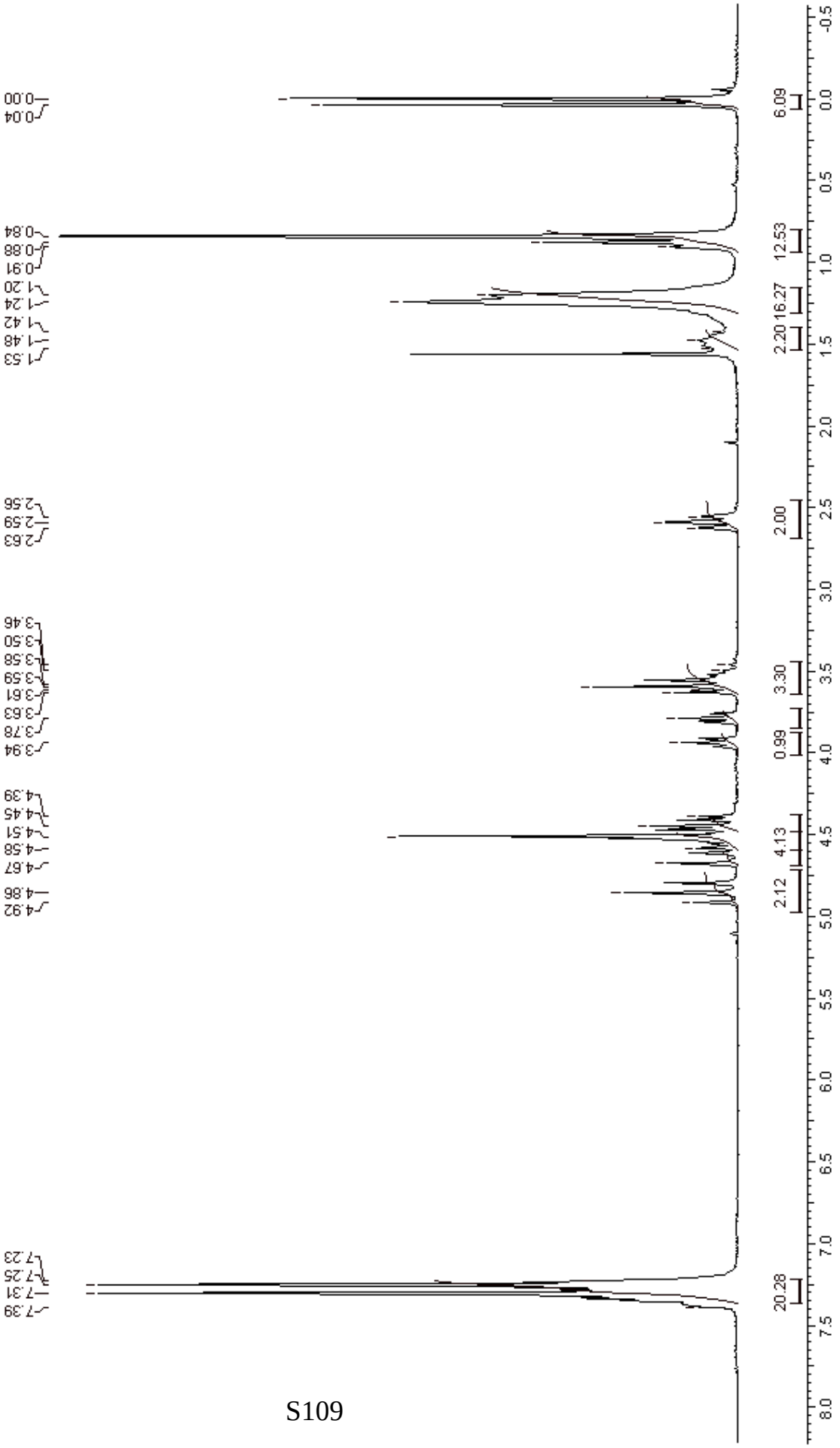


23



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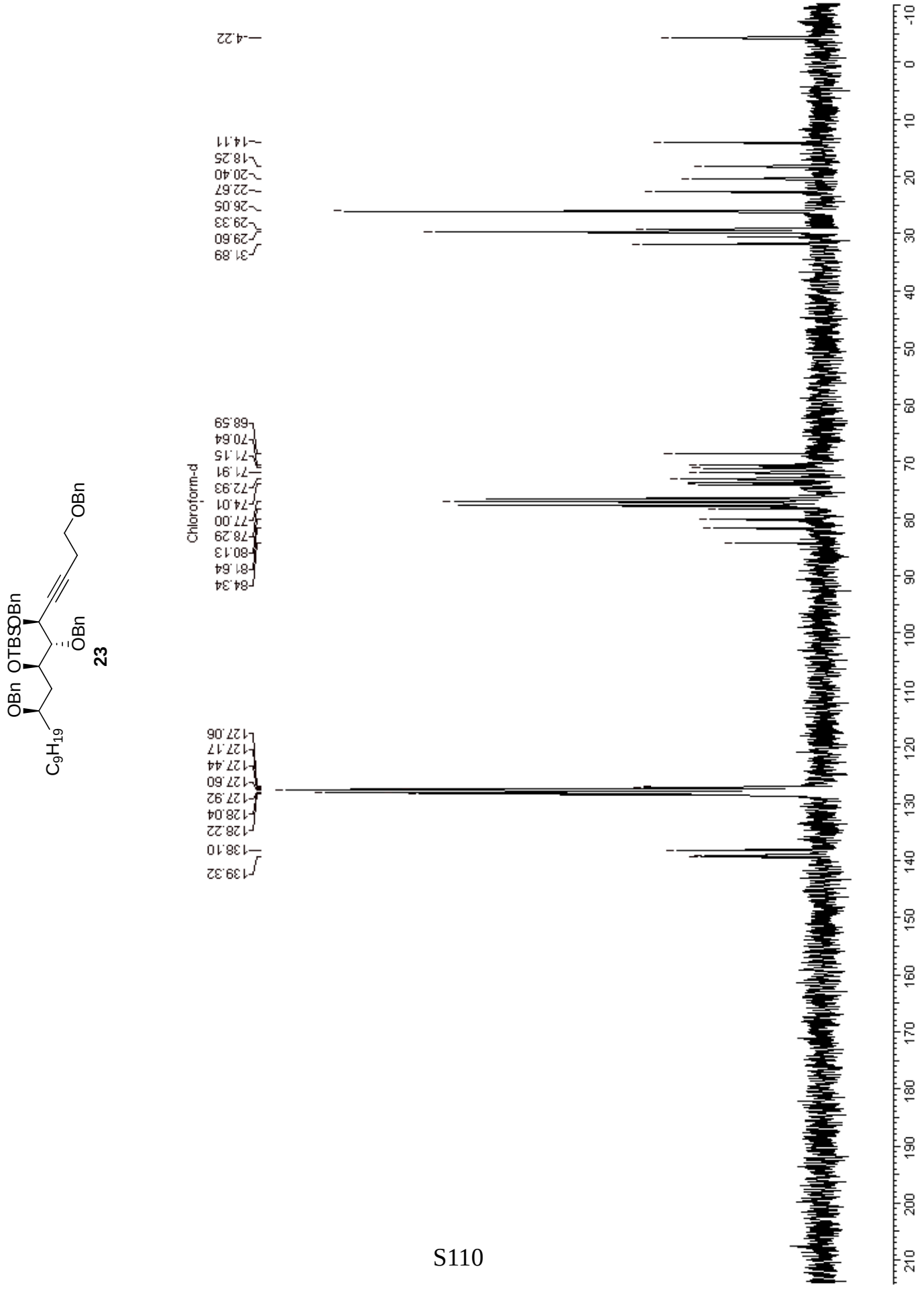

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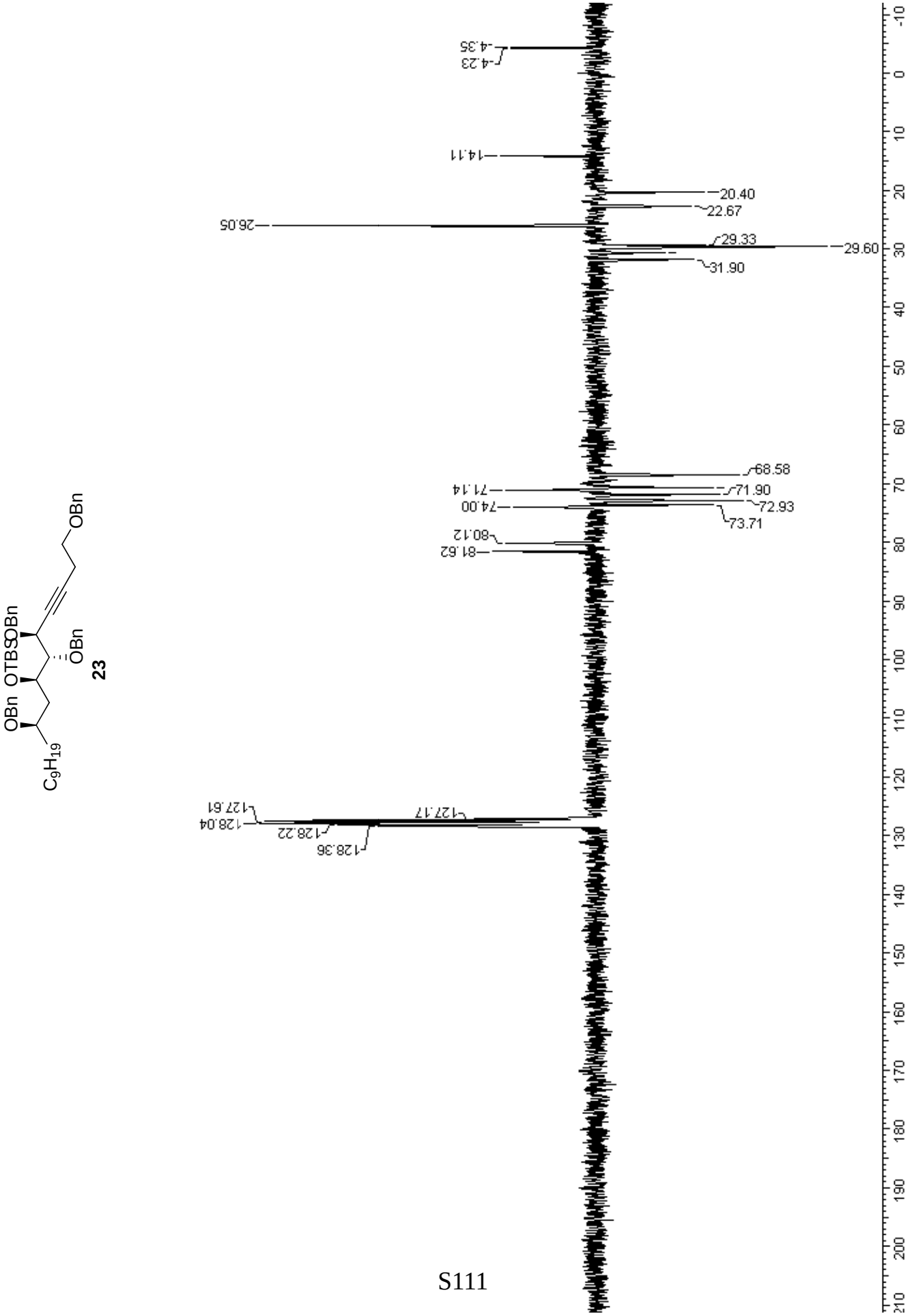
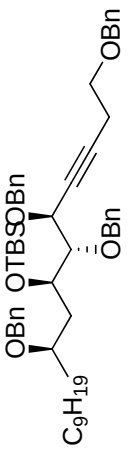
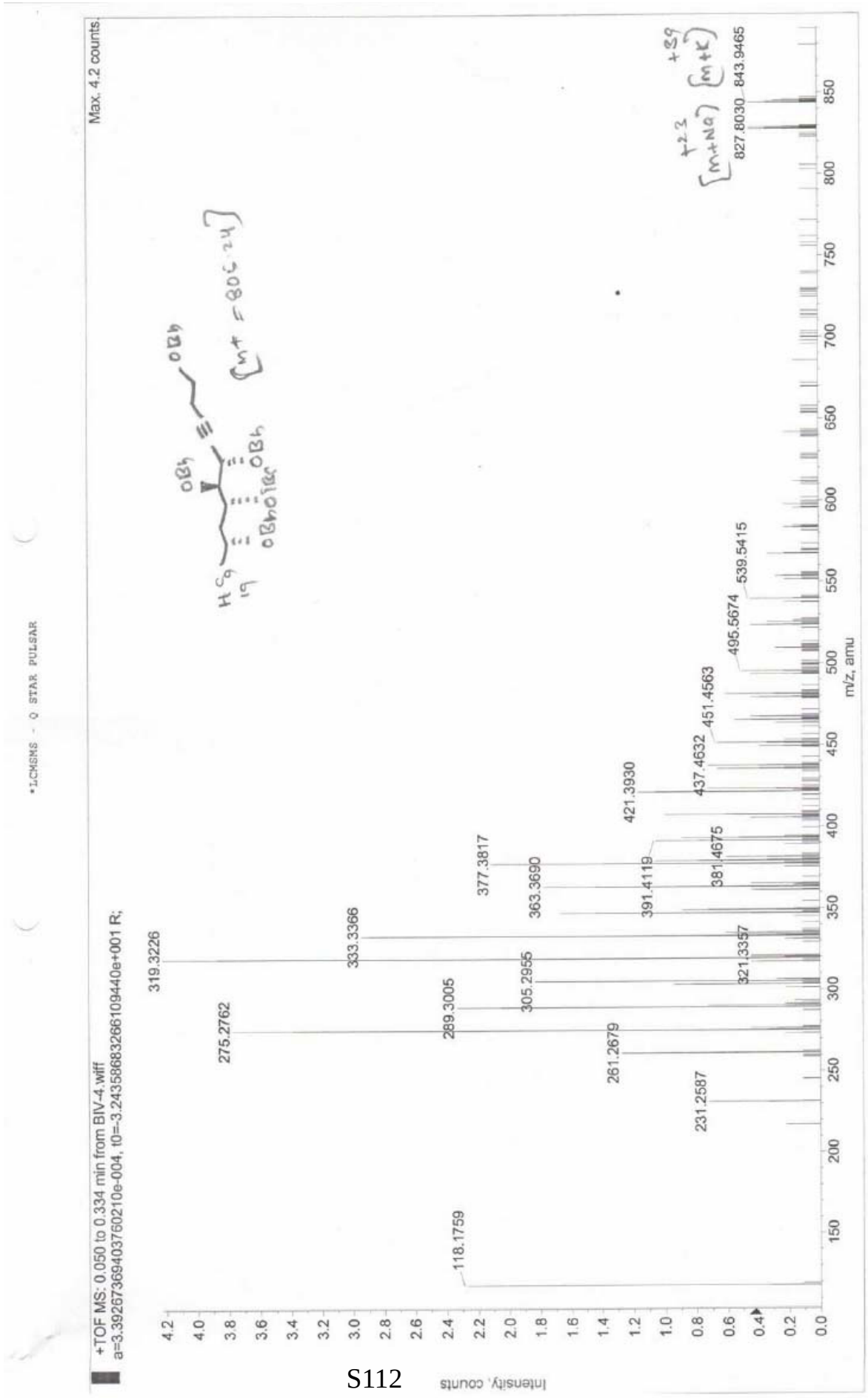
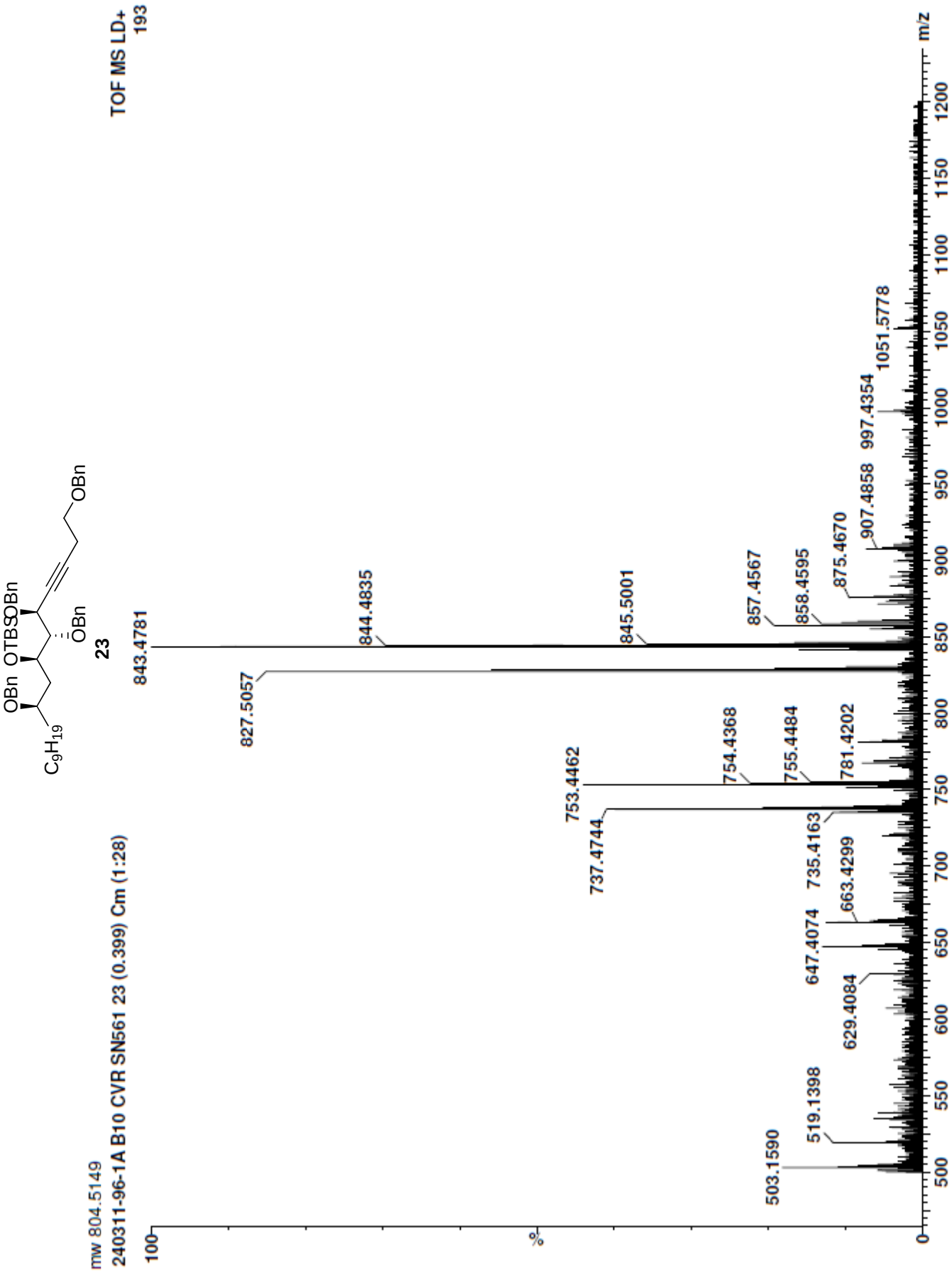



OBn
OTBS
OBn
OBn
C_9H_{19}

23


+TOF MS: 0.050 to 0.334 min from BIV-4.wiff
a=3.39267369403760210e-004, t0=-3.24358683266109440e+001 R;
Max. 4.2 counts.
*LCMSMS - Q STAR PULSAR
Intensity, counts
m/z, amu
319.3226
275.2762
333.3366
289.3005
305.2955
377.3817
363.3690
421.3930
391.4119
381.4675
437.4632
451.4563
321.3357
495.5674
539.5415
261.2679
231.2587
118.1759
827.8030
843.9465


TOF MS LD+
193
OBn
OBn
OTBS
OBn
C_9H_{19}
23
mw 804.5149
240311-96-1A B10 CVR SN561 23 (0.399) Cm (1:28)
100
%
0
m/z
503.1590
519.1398
629.4084
647.4074
663.4299
735.4163
737.4744
753.4462
754.4368
755.4484
781.4202
827.5057
843.4781
844.4835
845.5001
857.4567
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907.4858
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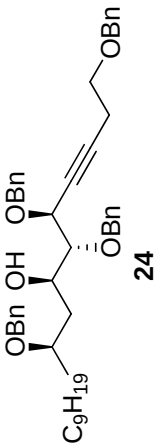
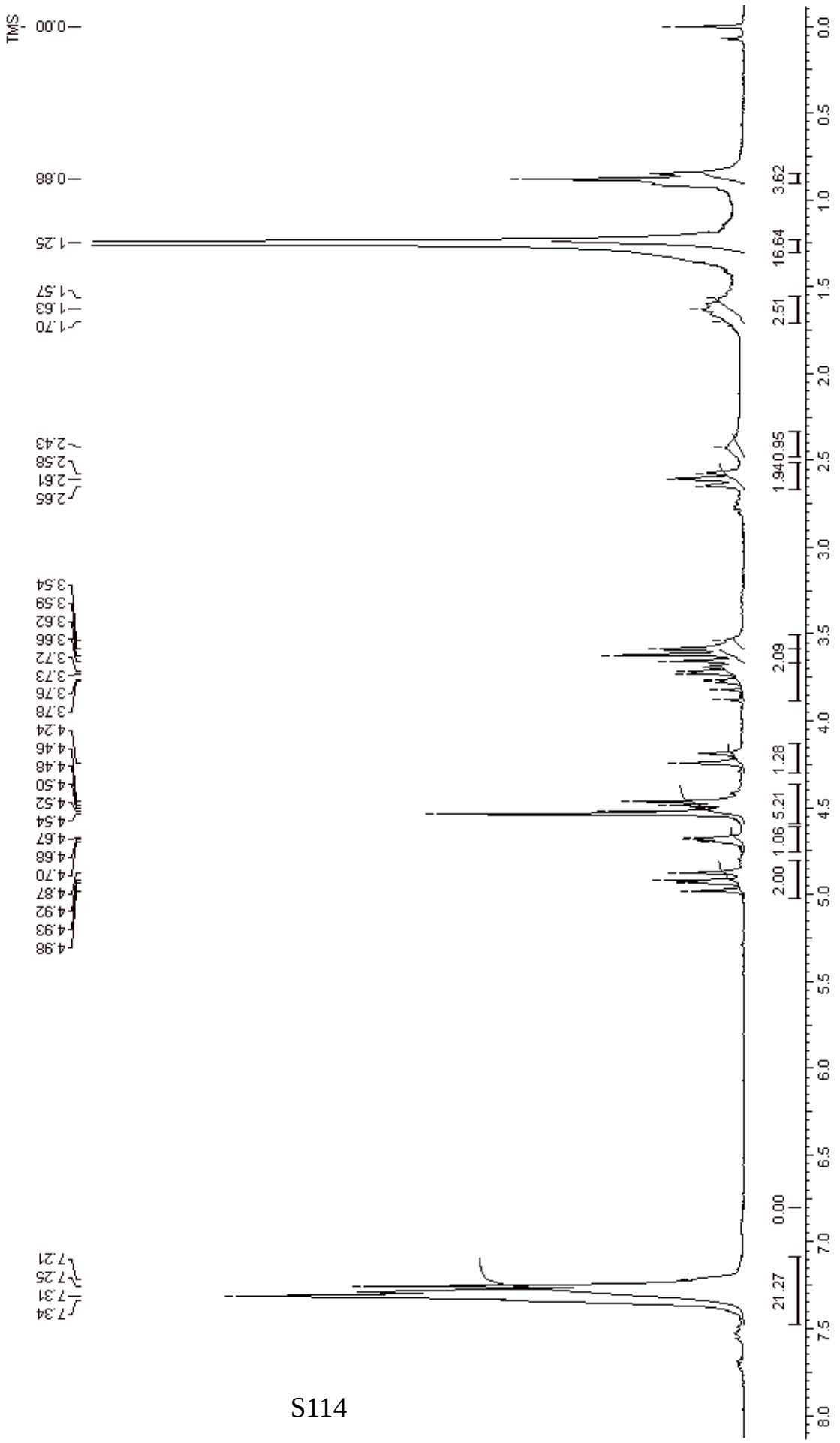
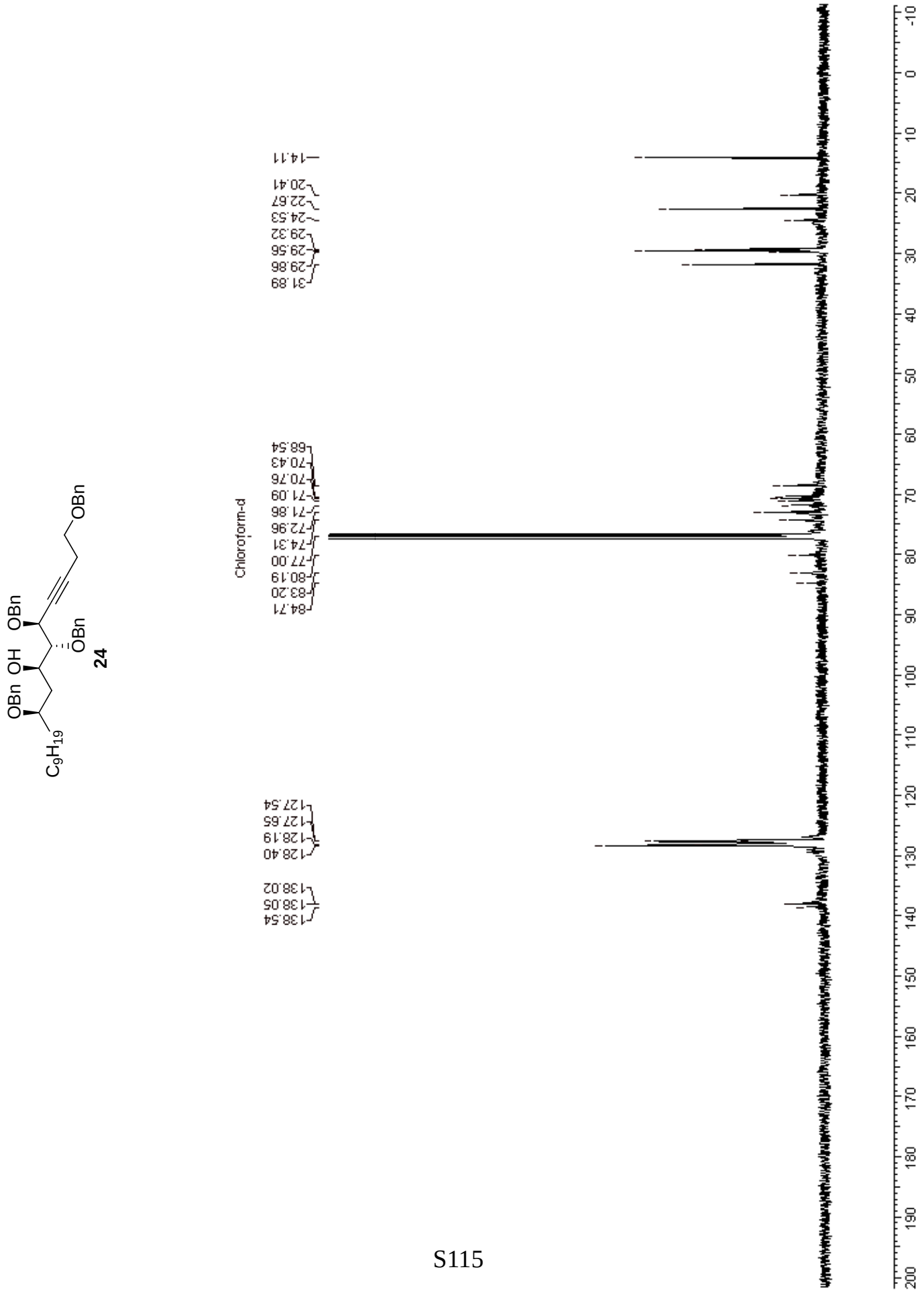
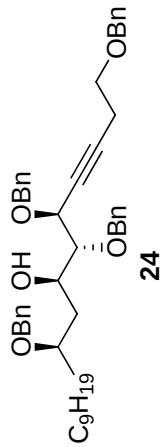


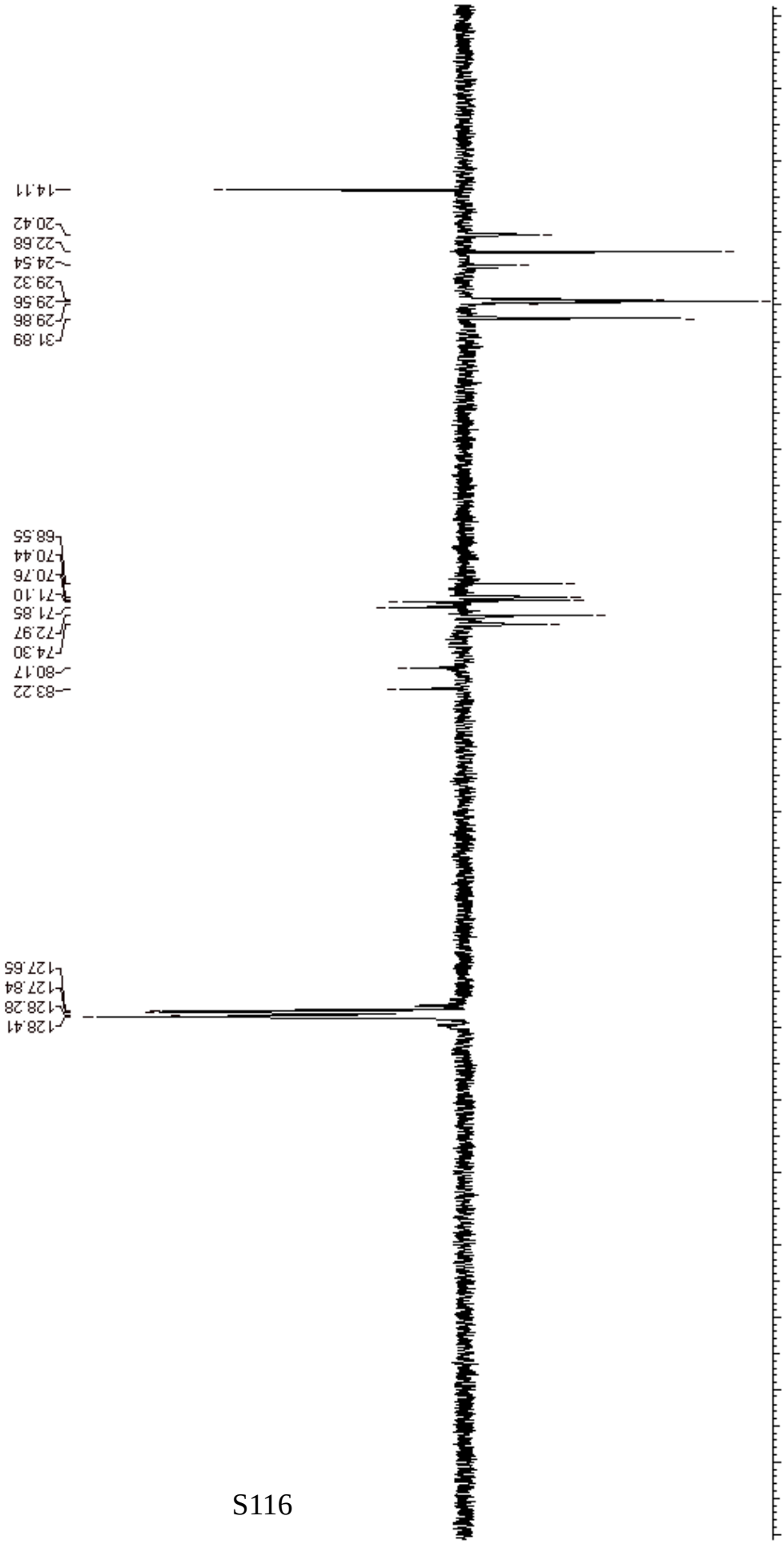
24




OBn
OBn
OH
OBn
C_9H_{19}
24
Chloroform-d
14.11
20.41
22.67
24.53
29.32
29.56
29.86
31.89
68.54
70.43
70.76
71.09
71.86
72.96
74.31
77.00
80.19
83.20
84.71
127.54
127.65
128.19
128.40
138.02
138.05
138.54


OBn
OBn
OBn
OH
OBn
C_9H_{19}

24


14.11
20.42
22.68
24.54
29.32
29.56
29.86
31.89
68.55
70.44
70.76
71.10
71.85
72.97
74.30
80.17
83.22
127.65
127.84
128.28
128.41

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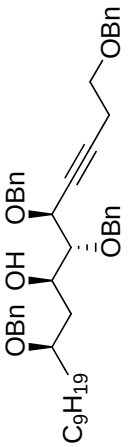

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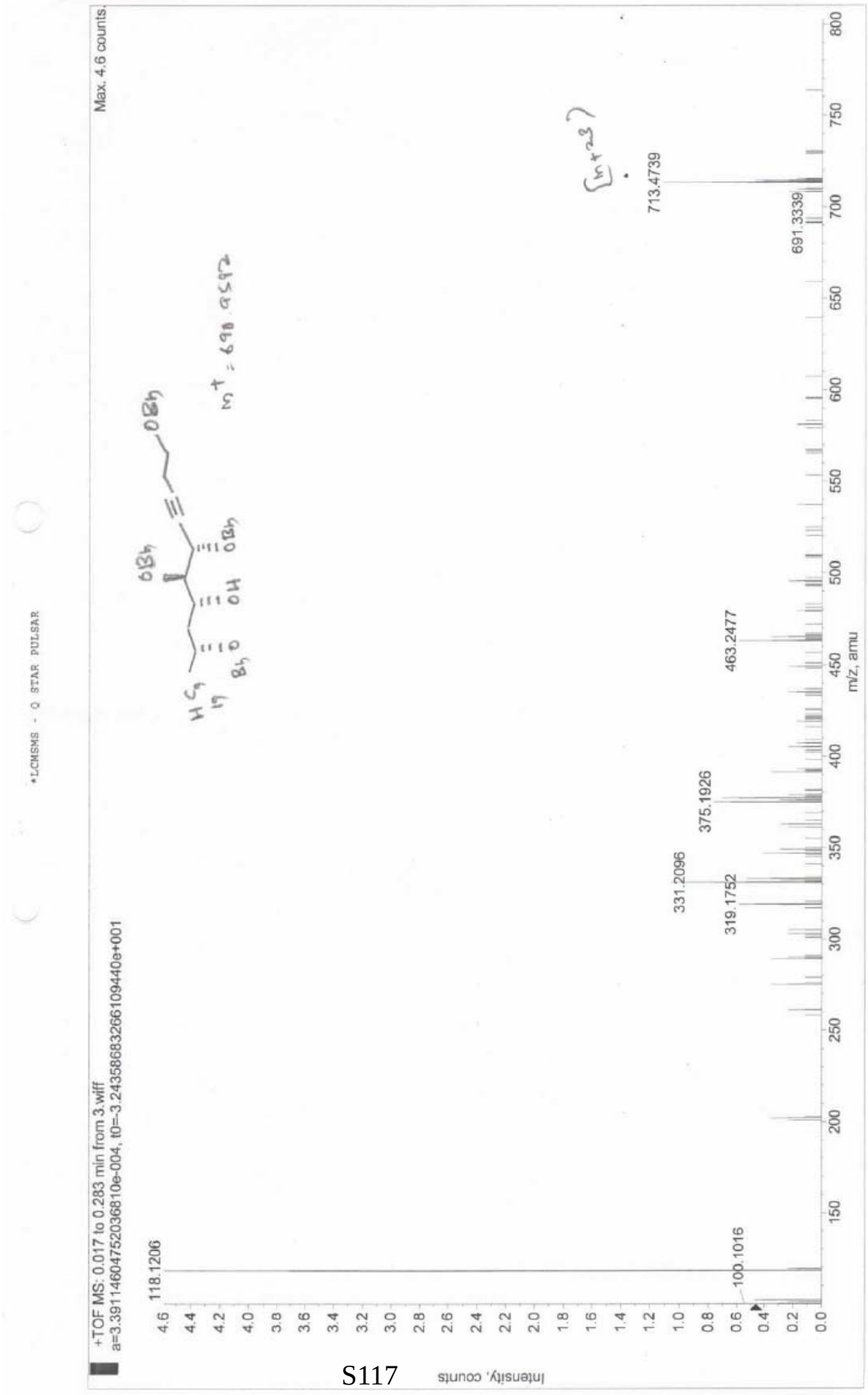

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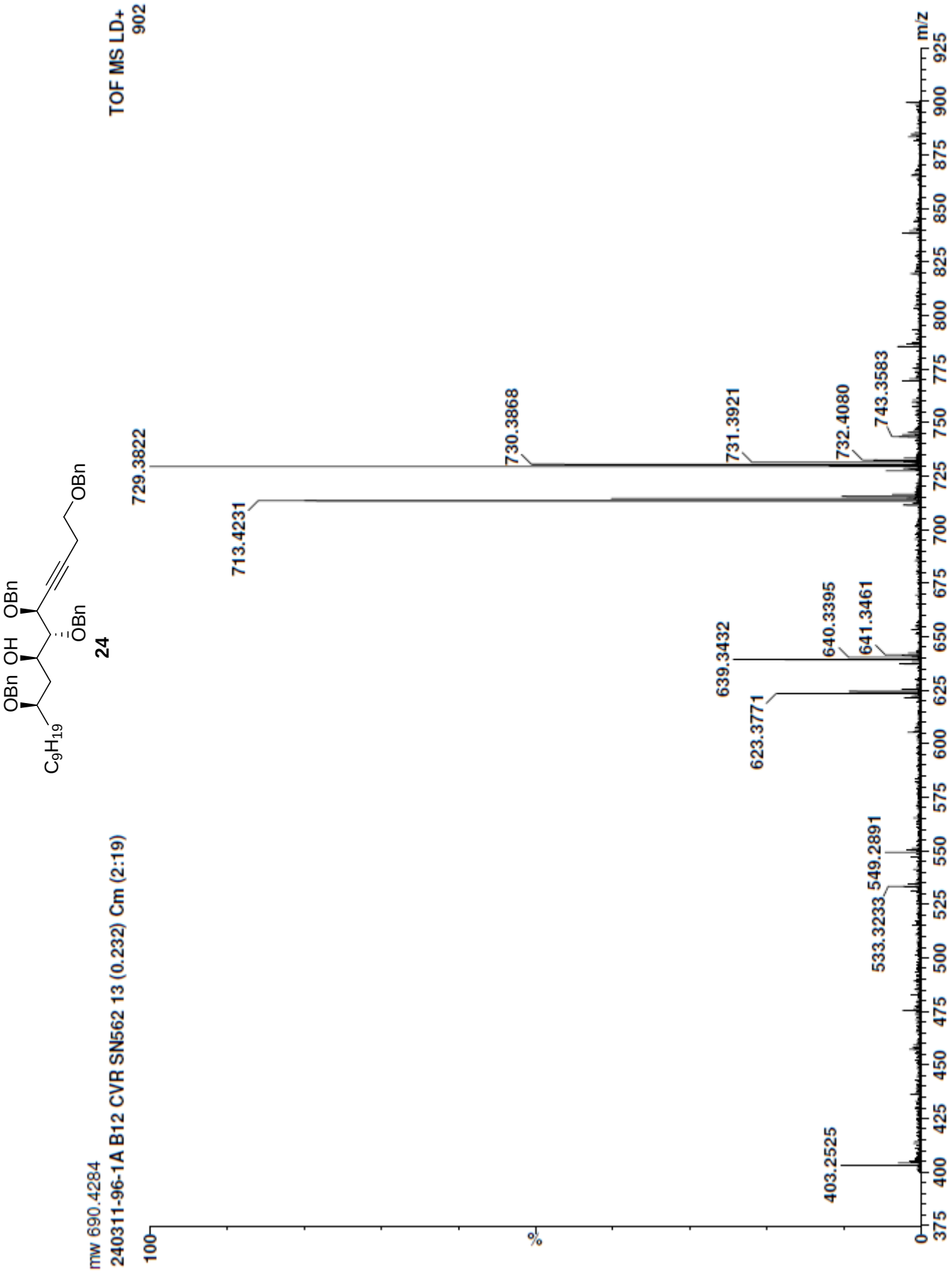
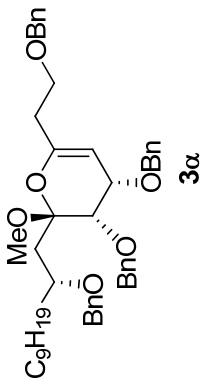
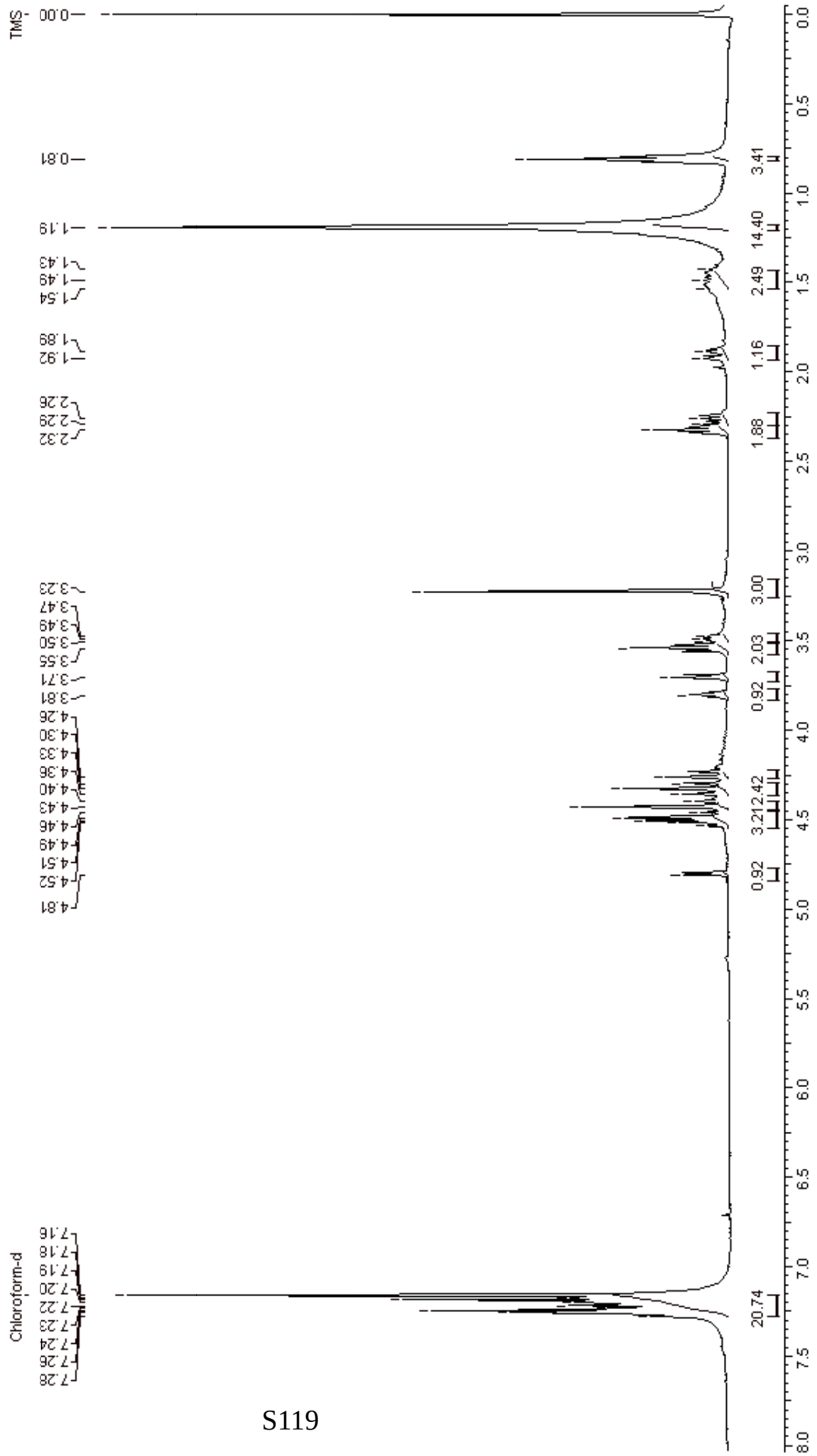
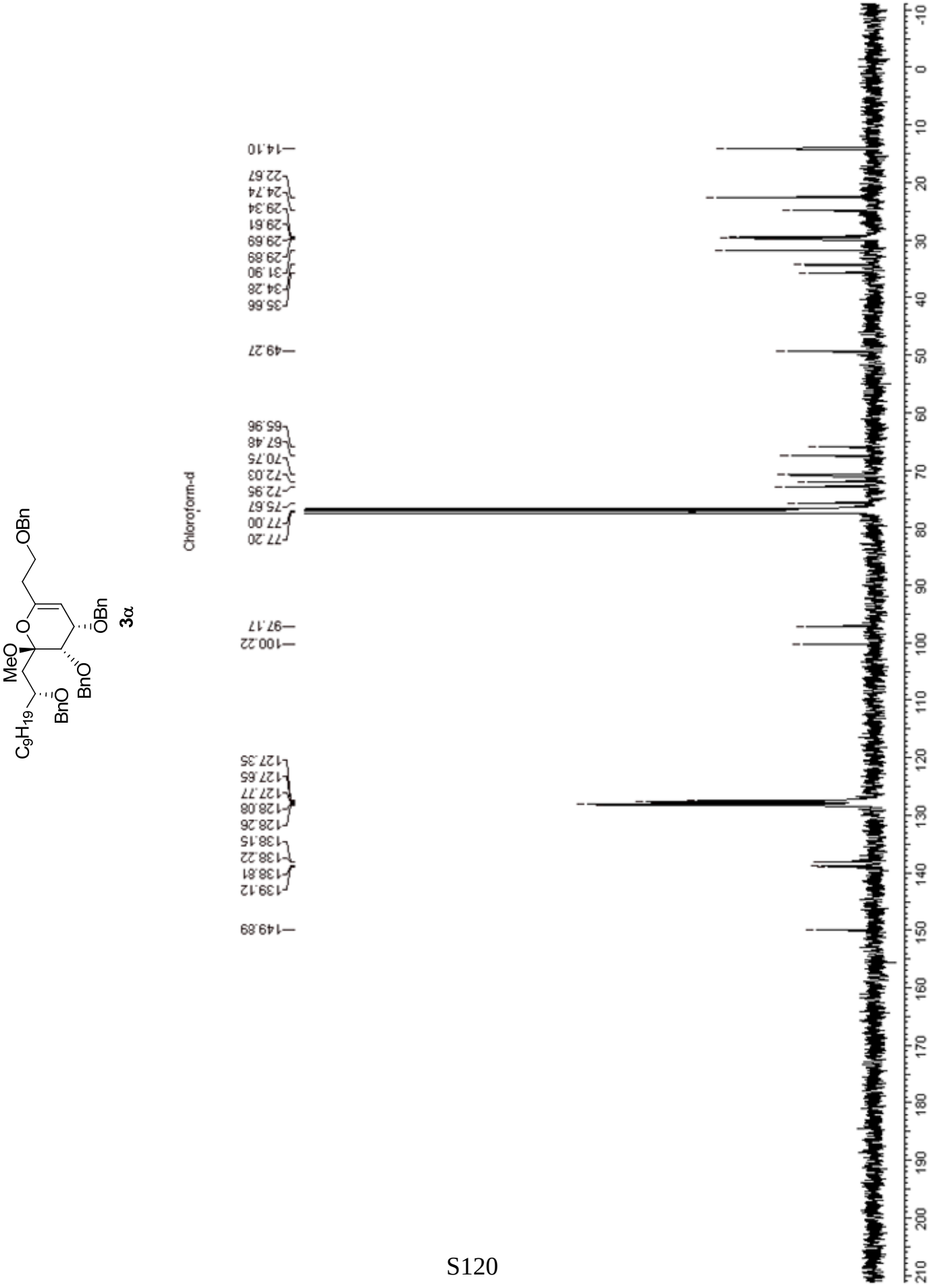
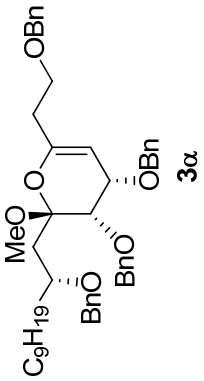



OBn
MeO
O
OBn
BnO
BnO
C_9H_{19}

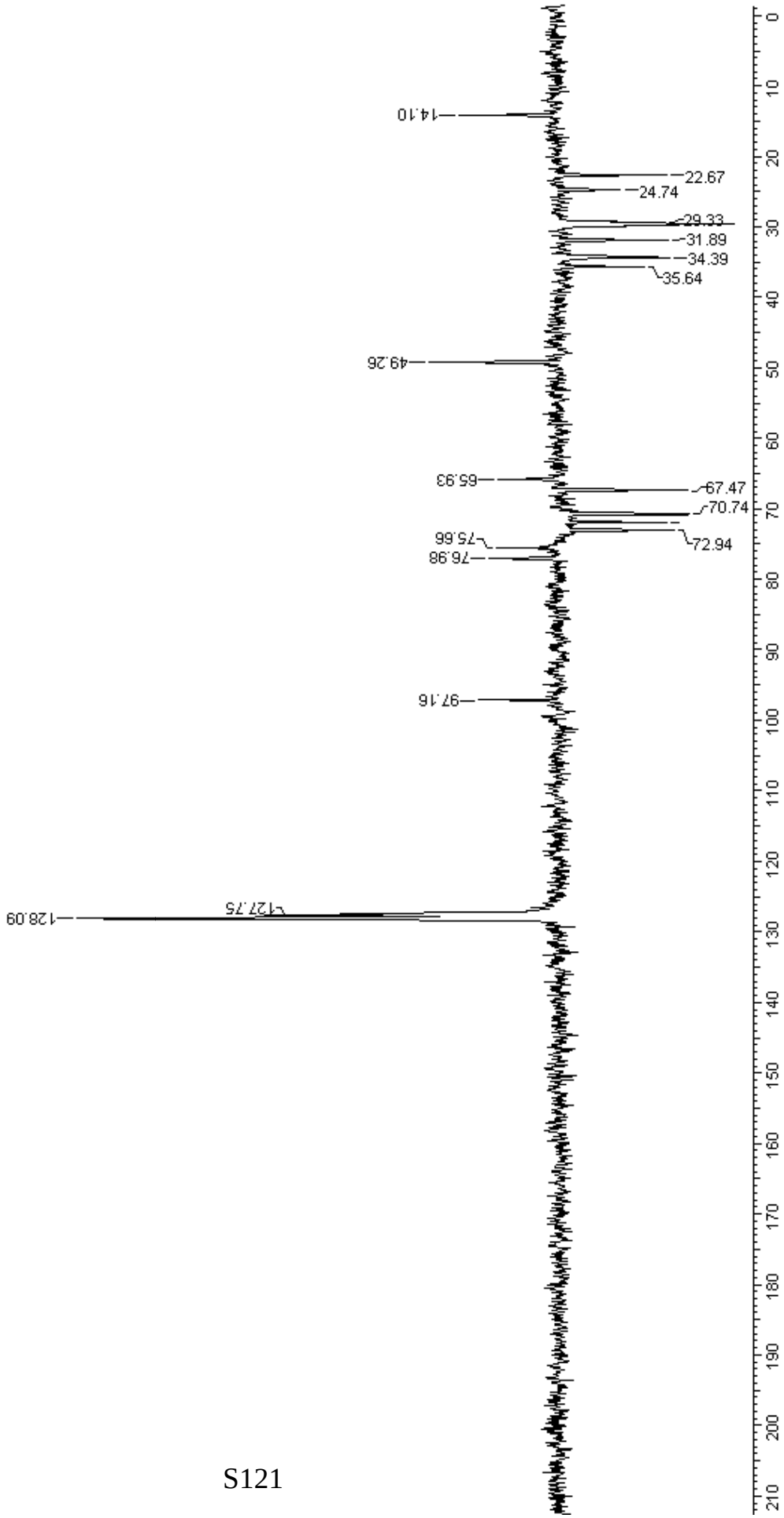
3α

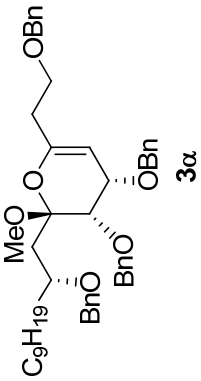

TMS
0.00
0.81
1.19
1.43
1.49
1.54
1.89
1.92
2.26
2.29
2.32
3.23
3.47
3.49
3.50
3.55
3.71
3.81
4.26
4.30
4.33
4.36
4.40
4.43
4.46
4.49
4.51
4.52
4.81
7.16
7.18
7.19
7.20
7.22
7.23
7.24
7.26
7.28
Chloroform-d
3.41
14.40
2.49
1.16
1.88
3.00
2.03
0.92
3.21
2.42
0.92
20.74


OBn
MeO
O
OBn
BnO
BnO
C_9H_{19}
3α
Chloroform-d
14.10
22.67
24.74
29.34
29.61
29.69
29.89
31.90
34.28
35.66
49.27
65.96
67.48
70.75
72.03
72.95
75.67
77.00
77.20
97.17
100.22
127.35
127.65
127.77
128.08
128.26
138.15
138.22
138.81
139.12
149.89

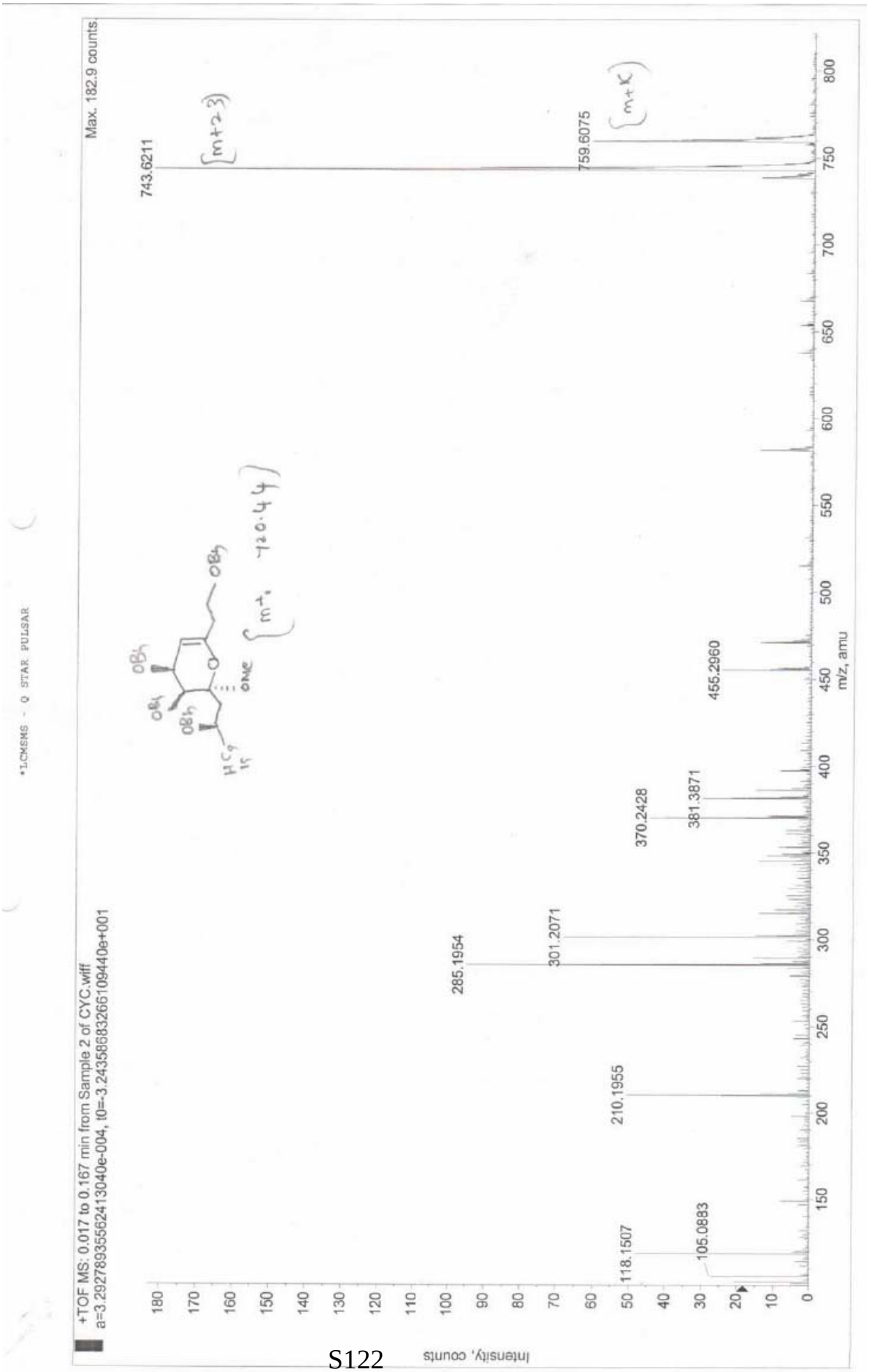

OBn
O
OBn
MeO
BnO
BnO
C_9H_{19}

3α


14.10
22.67
24.74
29.33
31.89
34.39
35.64
49.26
65.93
67.47
70.74
72.94
75.66
76.98
97.16
127.75
128.09


OBn
MeO
O
OBn
BnO
BnO
C_9H_{19}

3α


*LCMSMS - Q STAR PULSAR
+TOF MS: 0.017 to 0.167 min from Sample 2 of CYC.wiff
a=3.29278935562413040e-004, t0=-3.24358683266109440e+001
Max. 182.9 counts.
743.6211
759.6075
455.2960
381.3871
370.2428
301.2071
285.1954
210.1955
118.1507
105.0883
Intensity, counts
m/z, amu

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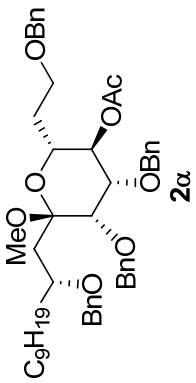
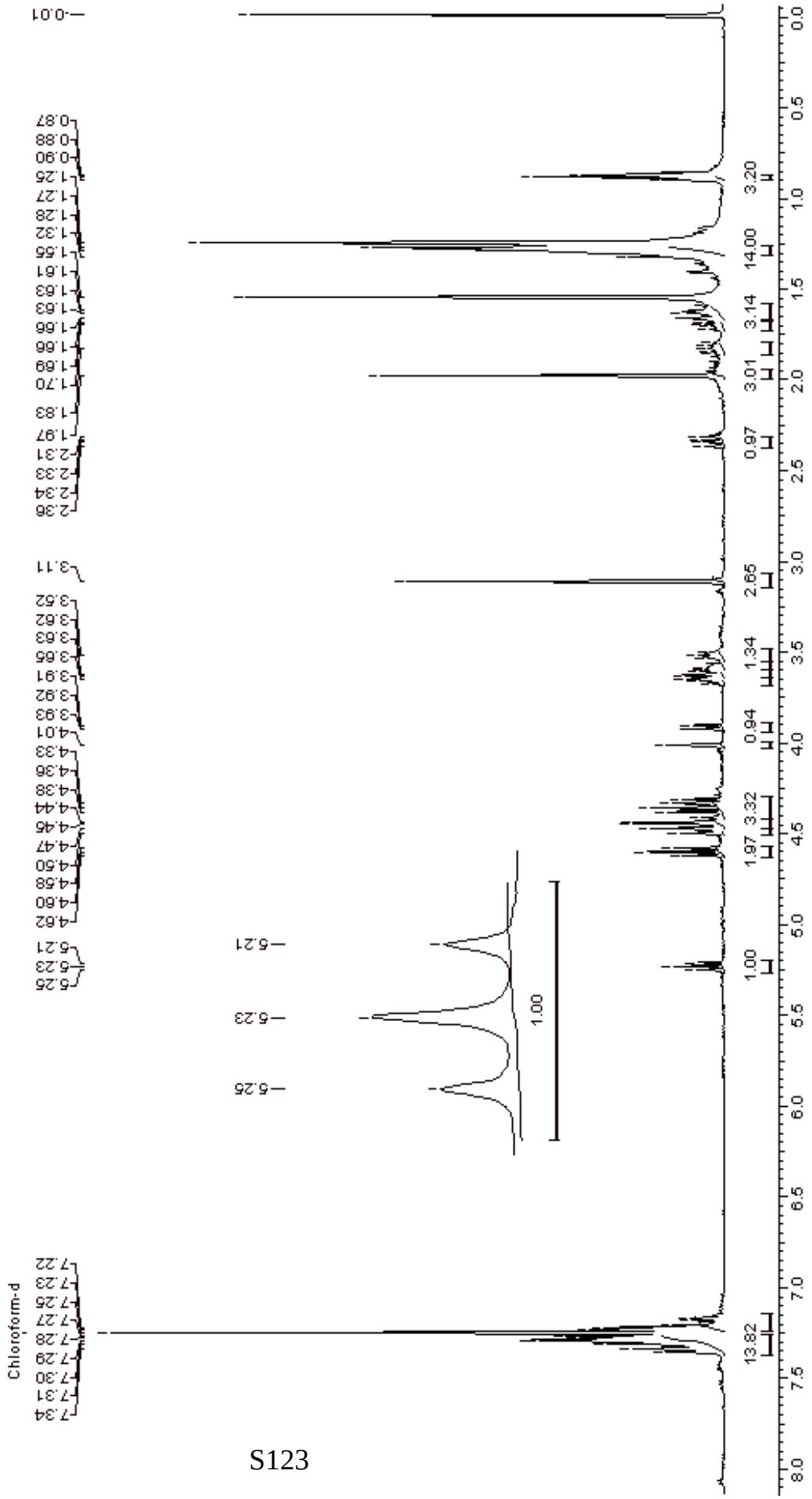
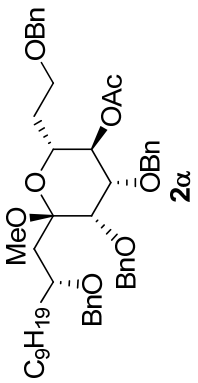
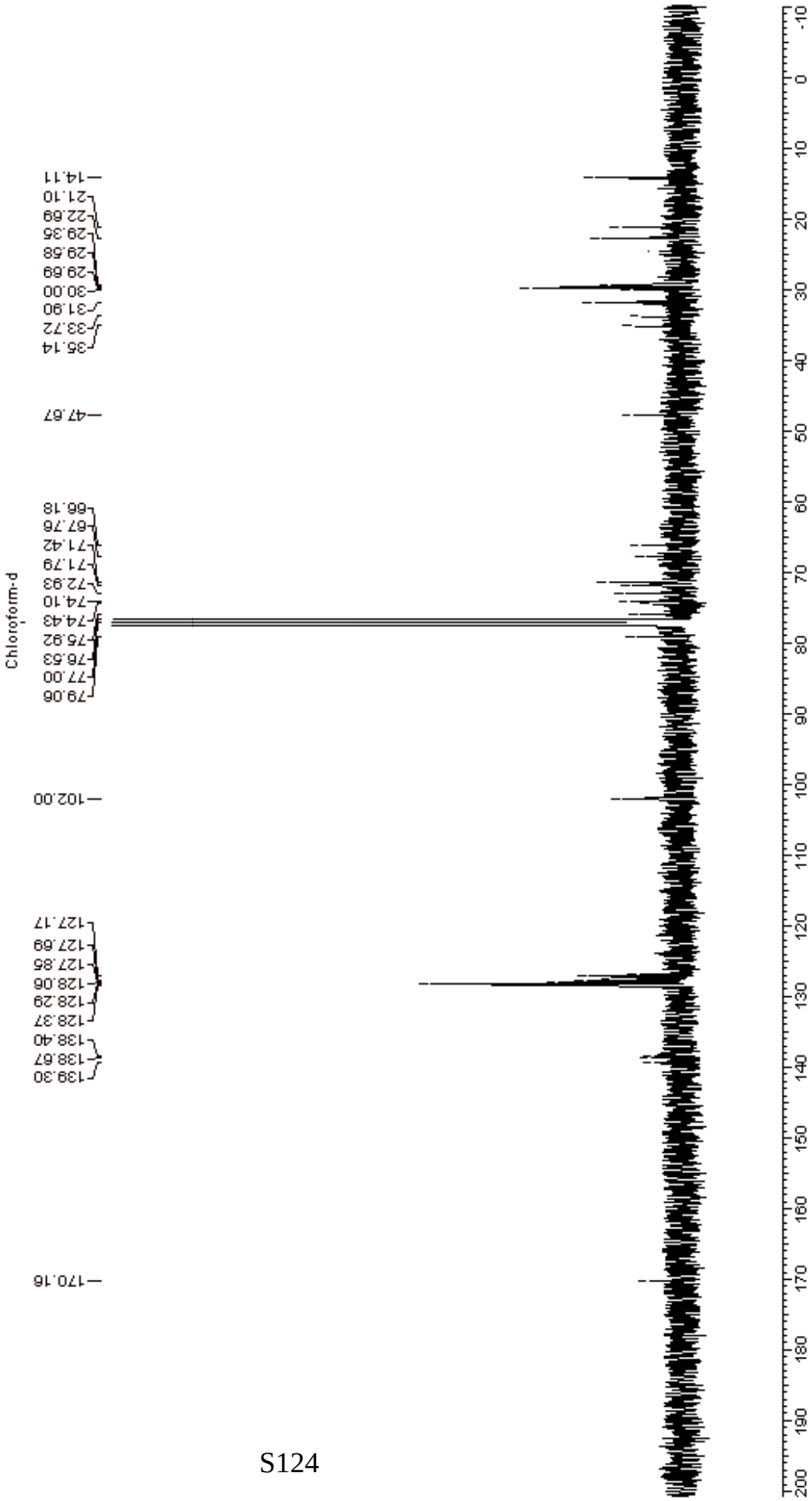





OBn
OAc
OBn
MeO
O
BnO
BnO
C_9H_{19}
2α


Chloroform-d
14.11
21.10
22.69
29.35
29.58
29.69
30.00
31.90
33.72
35.14
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66.18
67.76
71.42
71.79
72.93
74.10
74.43
75.92
76.53
77.00
79.06
102.00
127.17
127.69
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128.06
128.29
128.37
138.40
138.67
139.30
170.16

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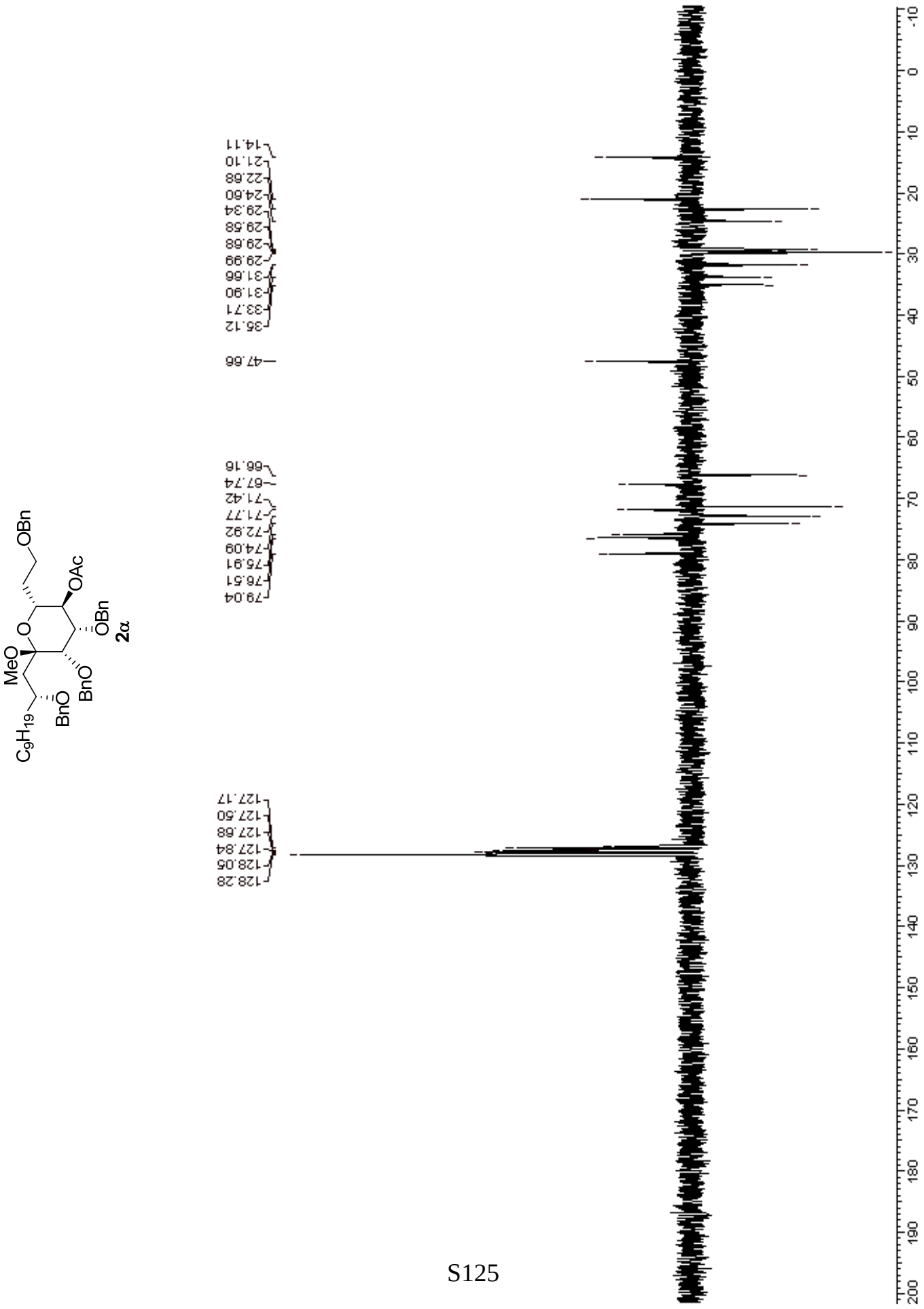

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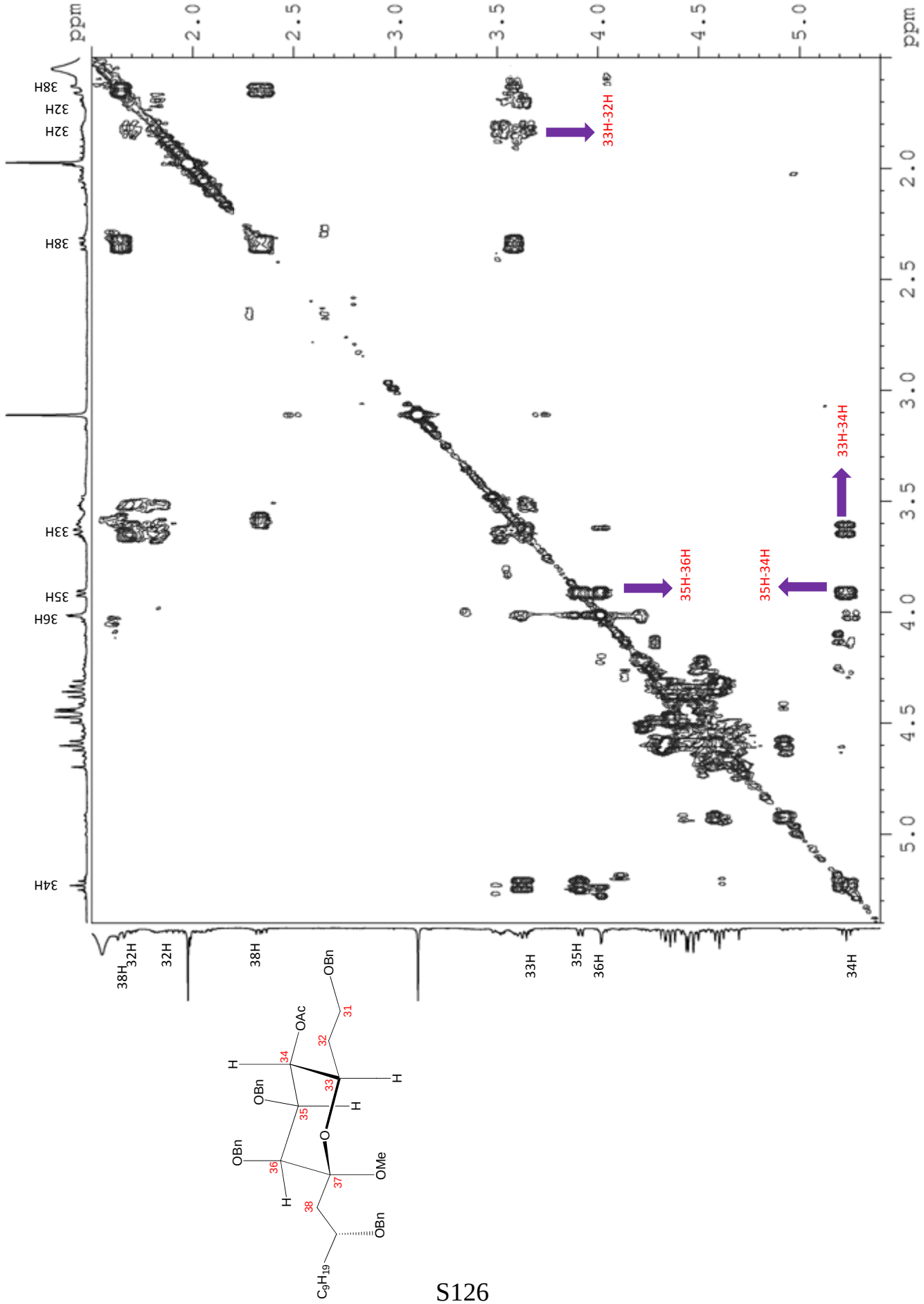
COSY-2α



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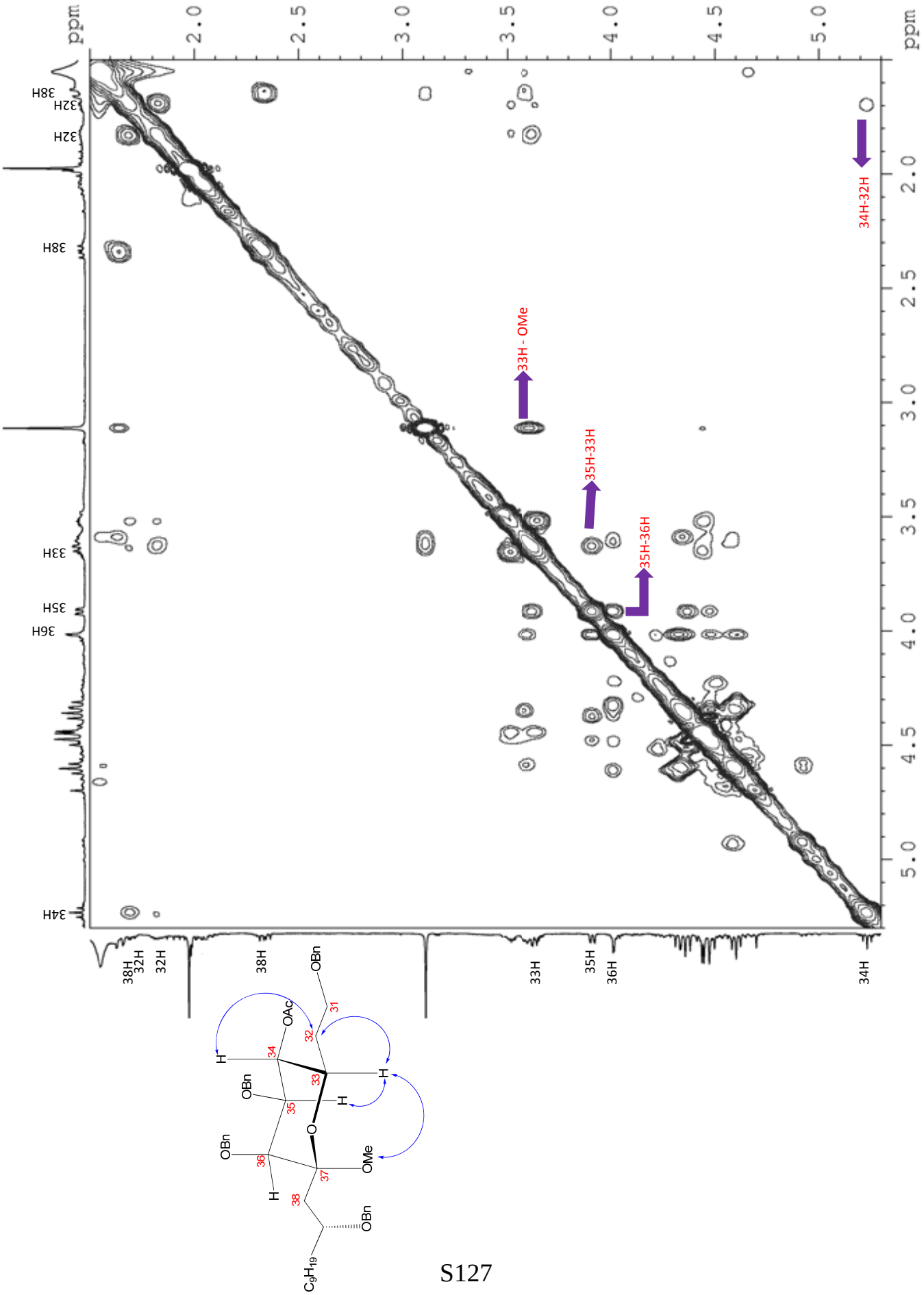
NOESY-2α



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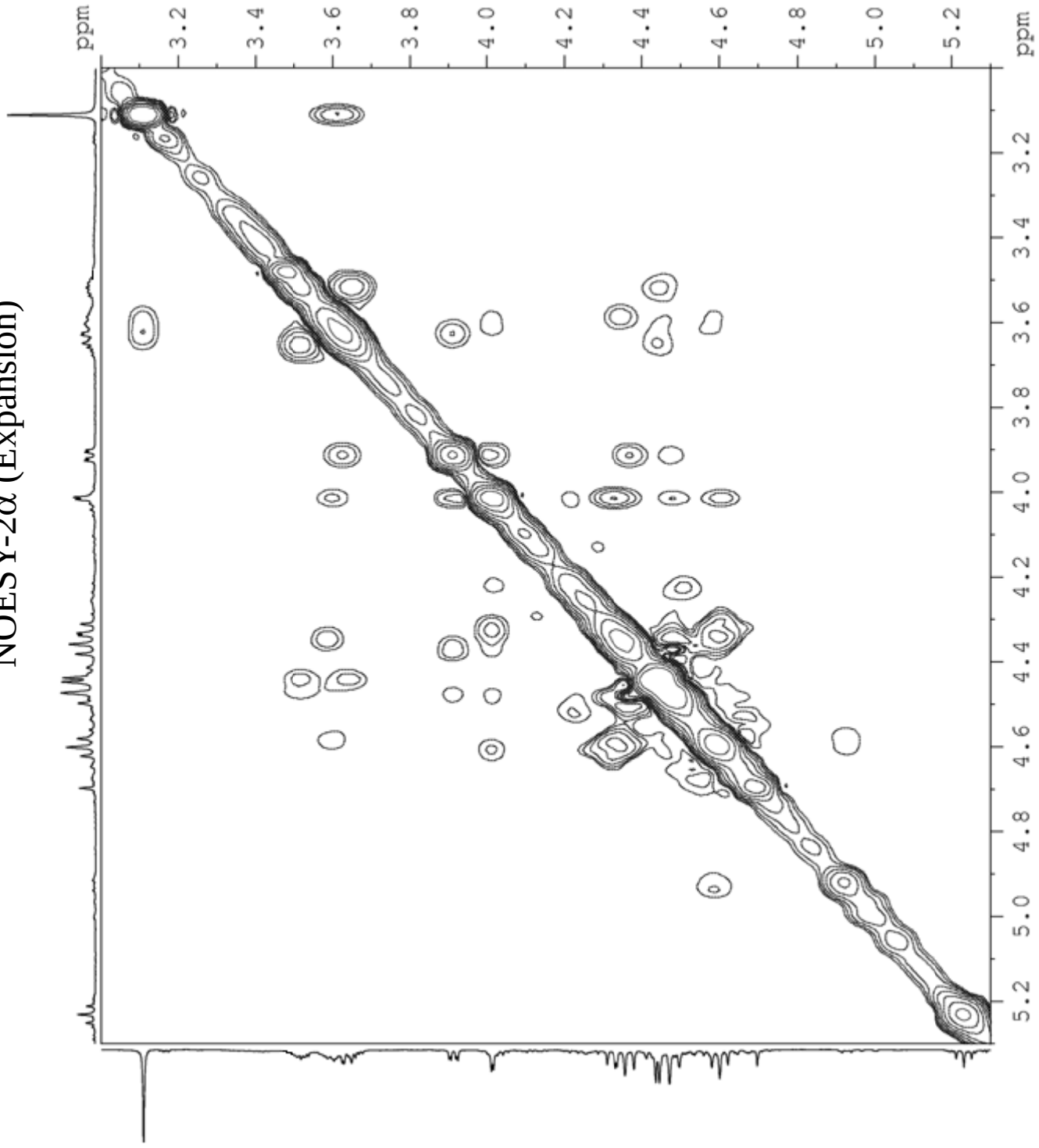
NOESY-2α (Expansion)



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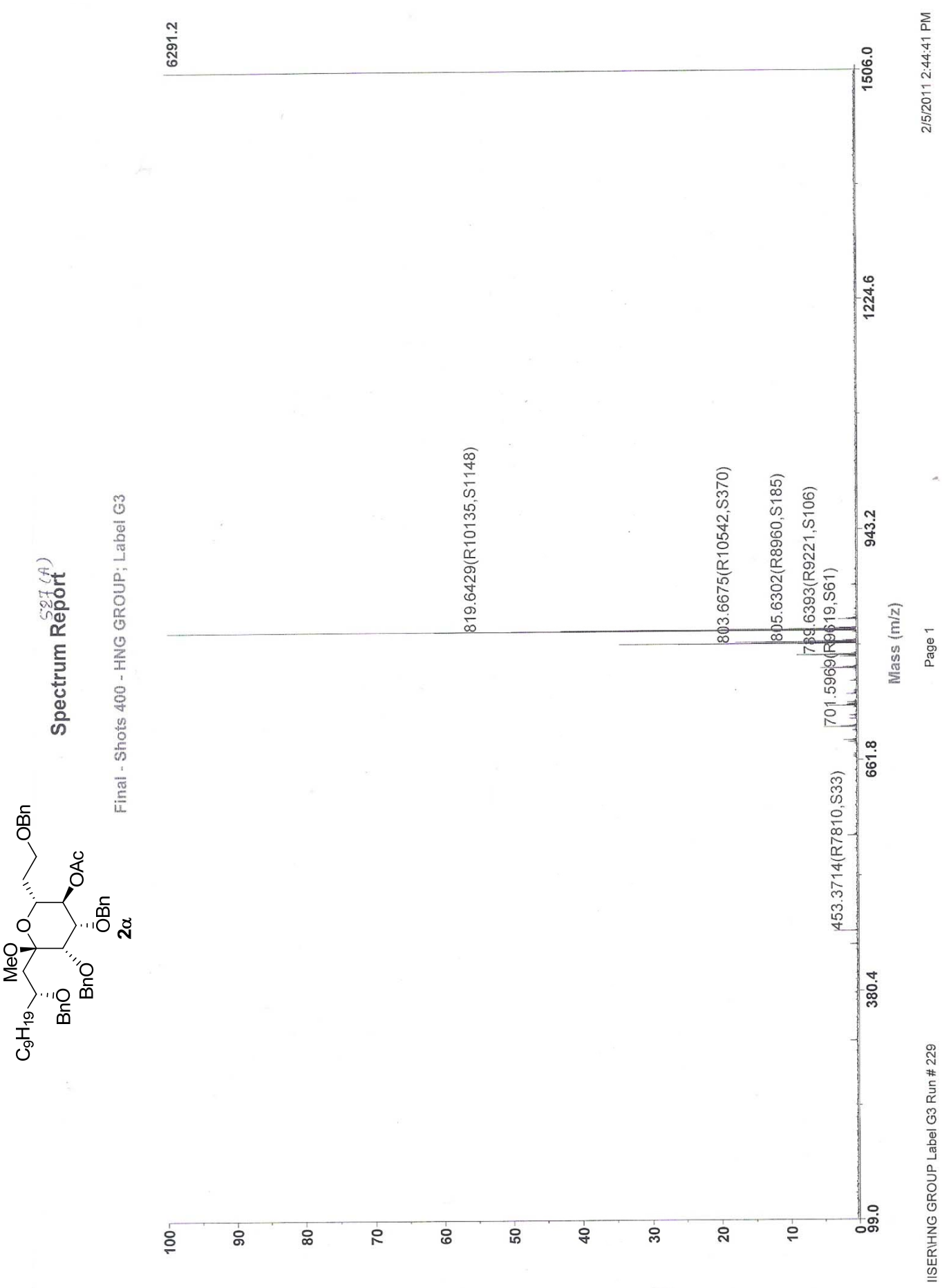

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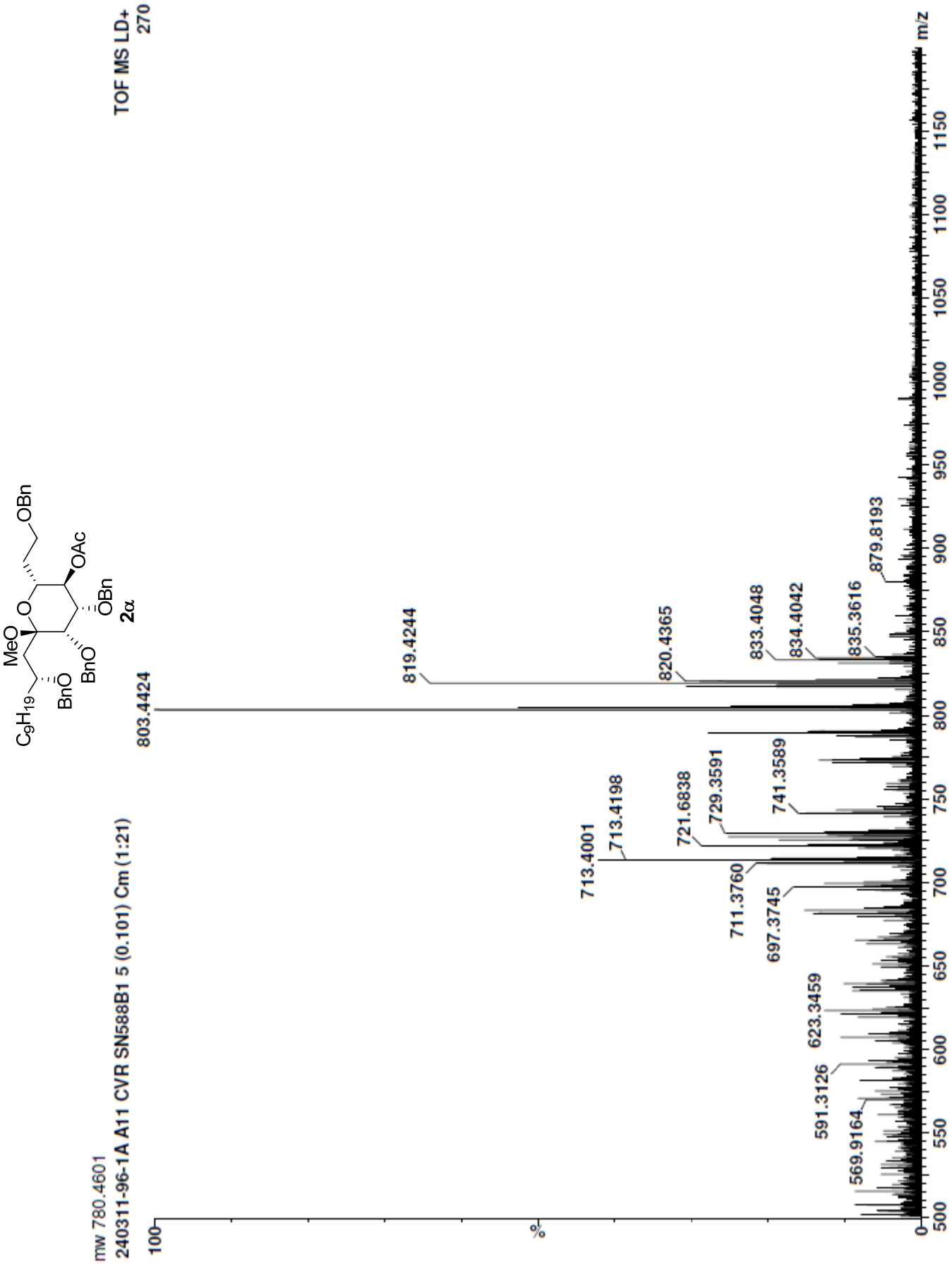

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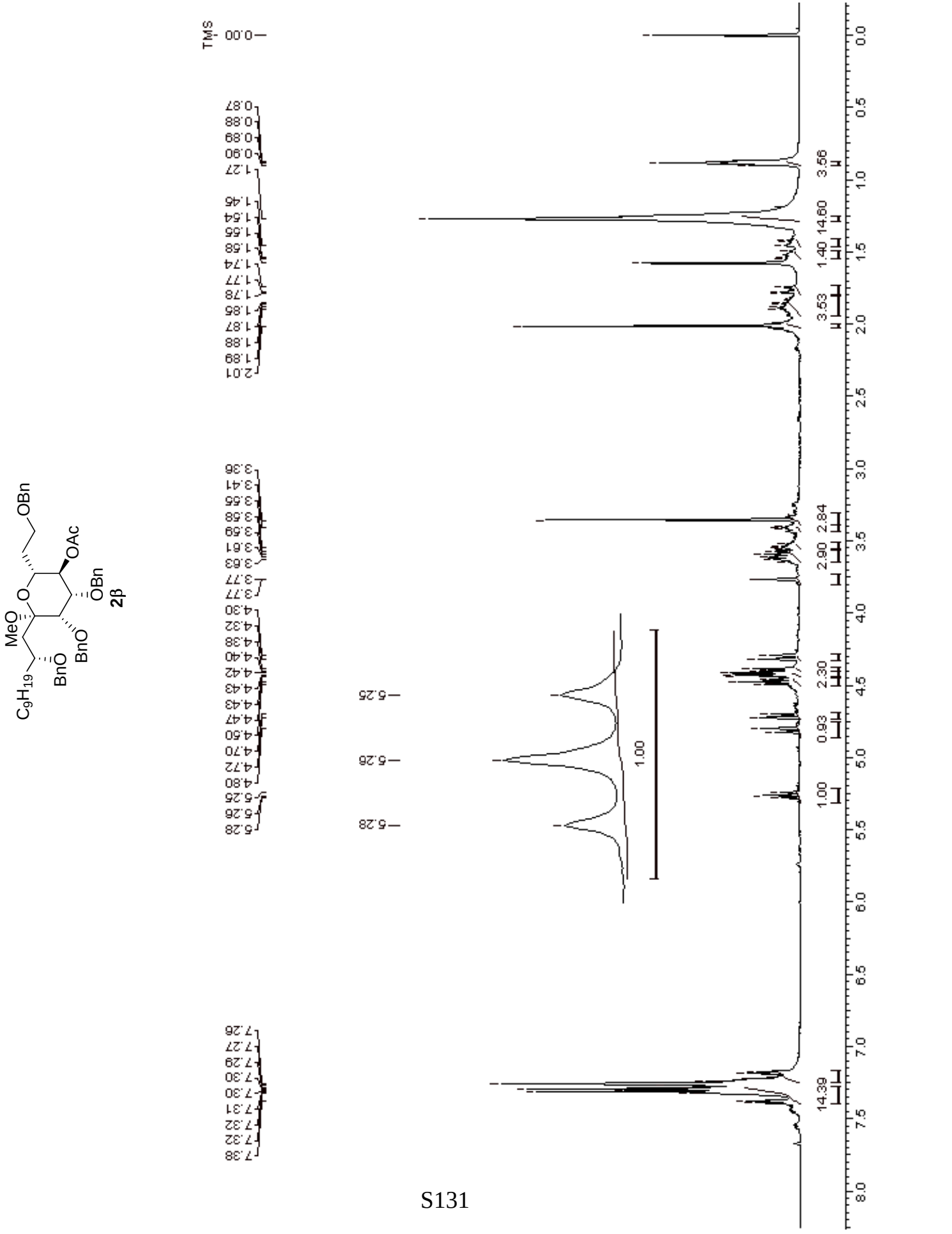

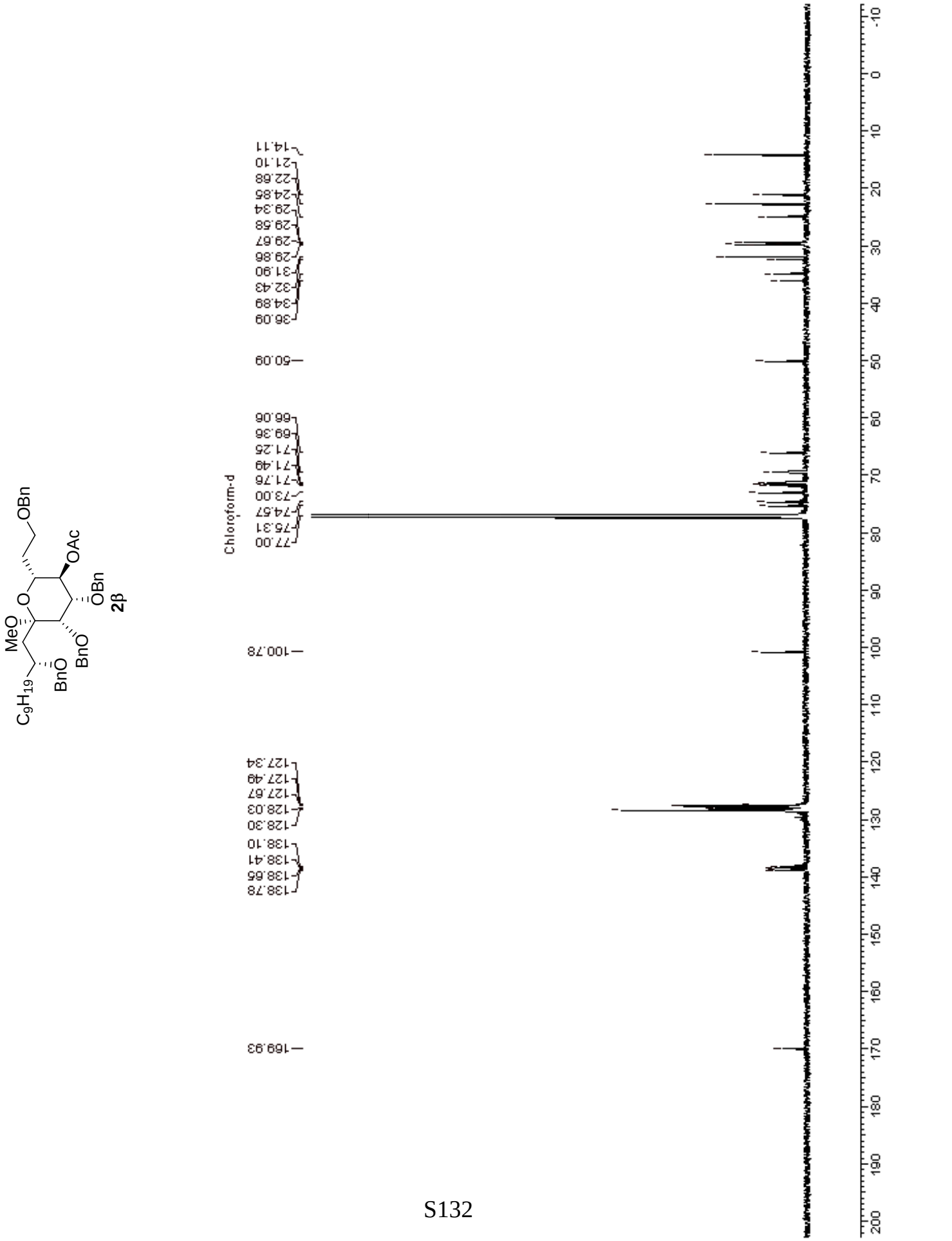
OBn
OAc
OBn
2β
MeO
O
BnO
BnO
C_9H_{19}
Chloroform-d
14.11
21.10
22.68
24.85
29.34
29.58
29.67
29.86
31.90
32.43
34.89
36.09
50.09
66.06
69.36
71.25
71.49
71.76
73.00
74.57
75.31
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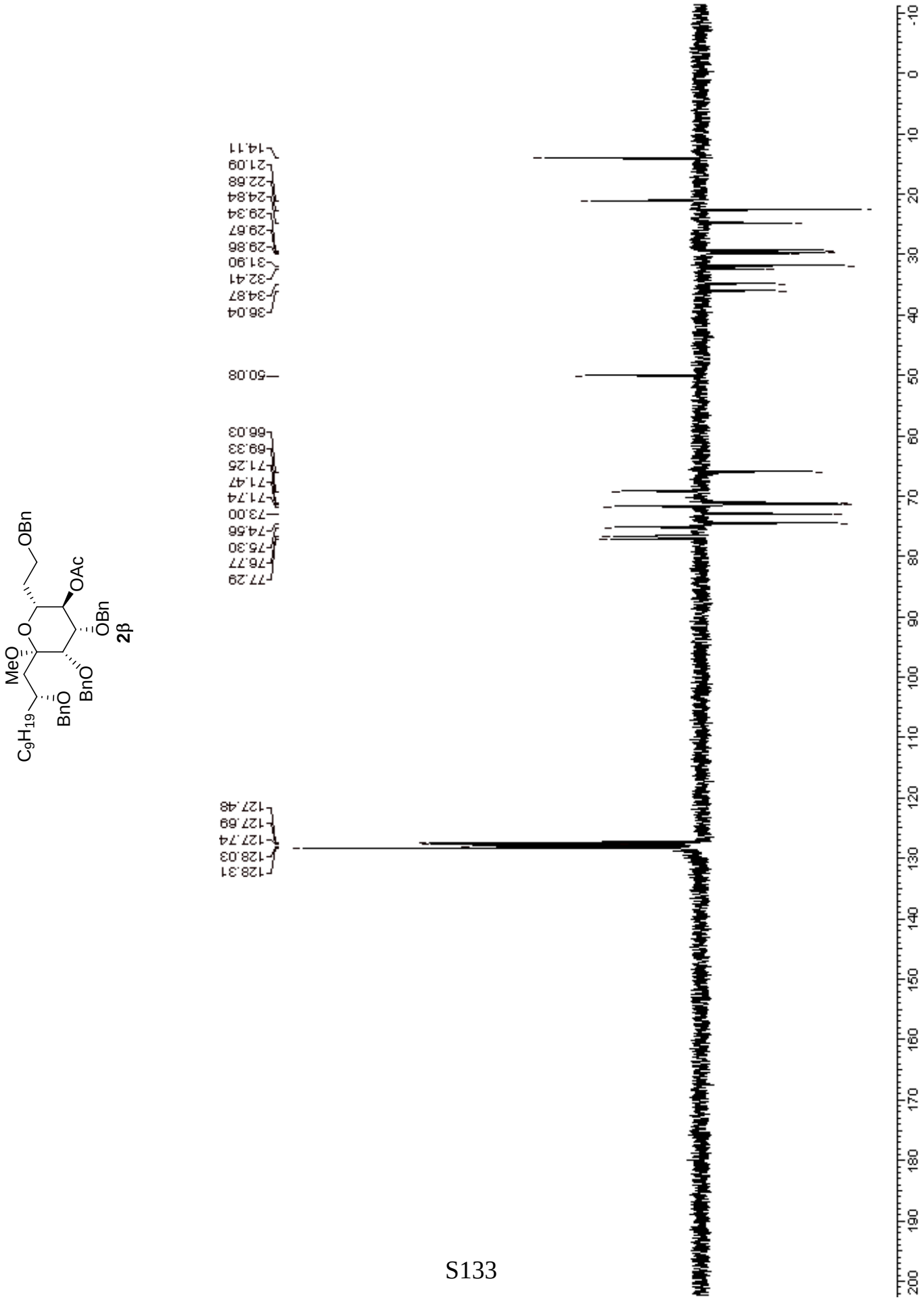
OBn
OAc
OBn
MeO
O
BnO
BnO
C_9H_{19}
2β
14.11
21.09
22.68
24.84
29.34
29.67
29.86
31.90
32.41
34.87
36.04
50.08
66.03
69.33
71.25
71.47
71.74
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127.48
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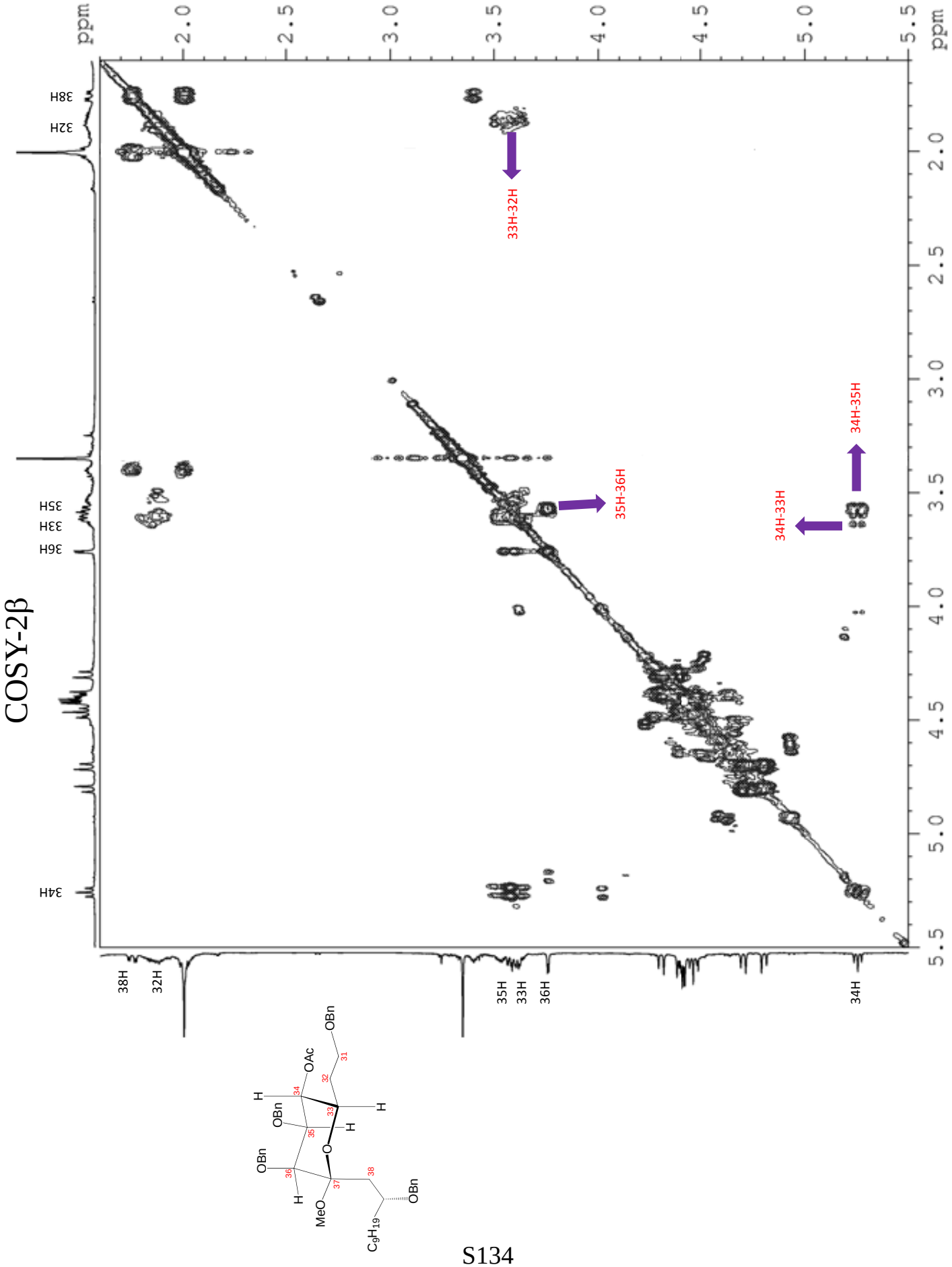

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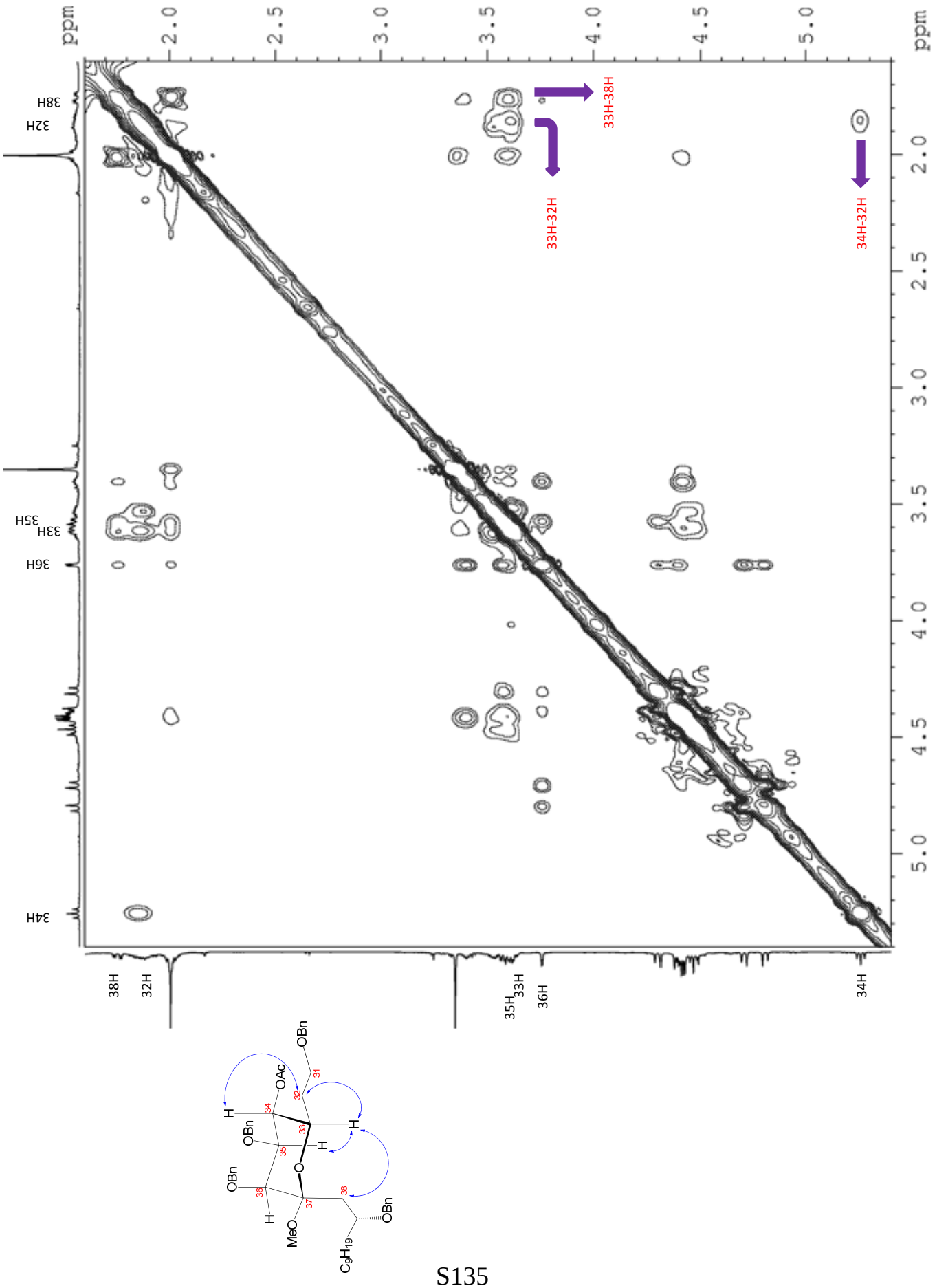
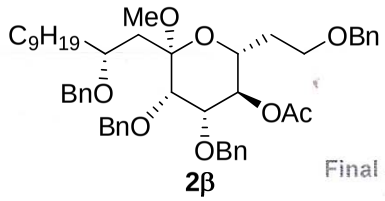
NOESY-2β



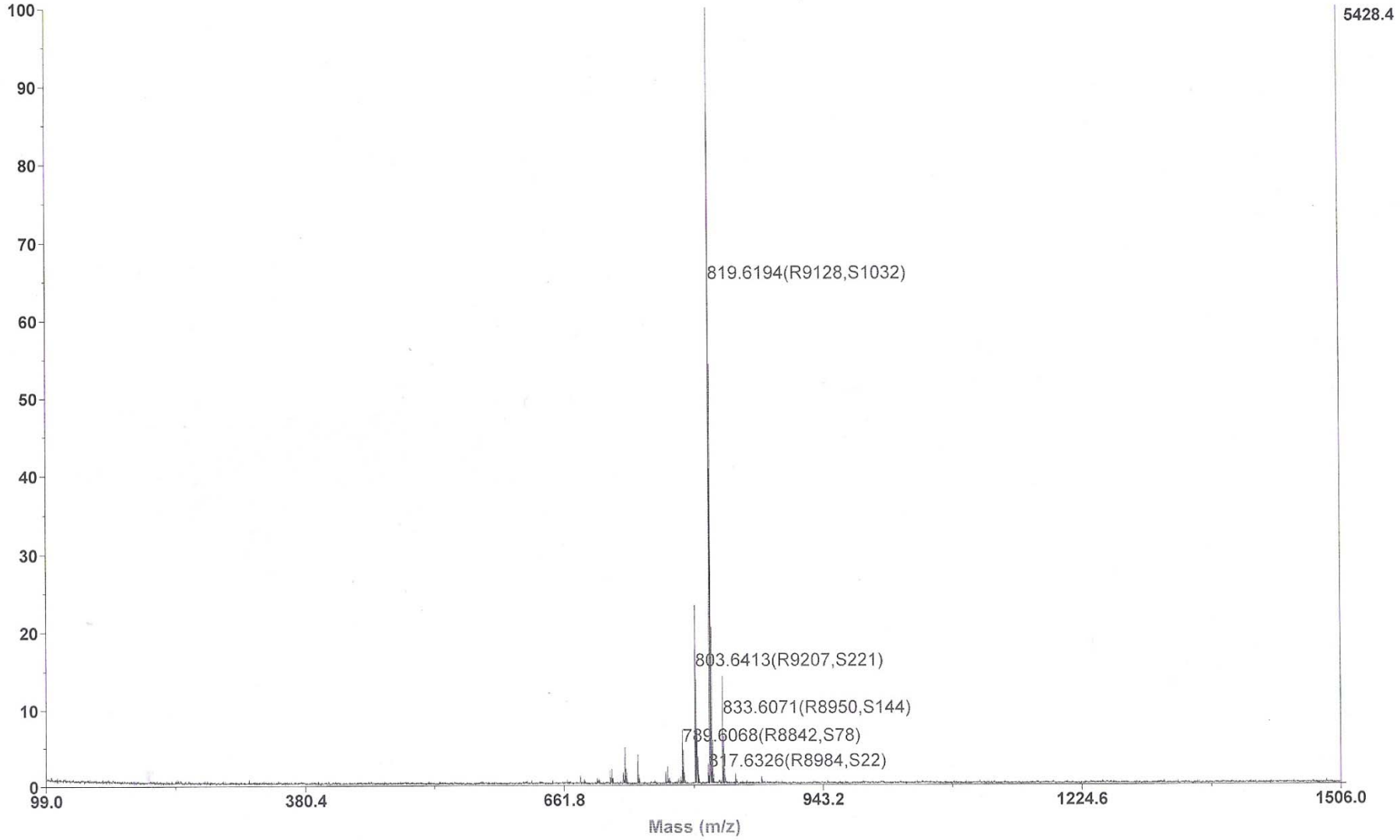


2β

588(8-1)

Spectrum Report

Final - Shots 400 - HNG GROUP; Label G4



IISER\HNG GROUP Label G4 Run # 229

Page 1

2/5/2011 2:45:32 PM

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