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

Supporting Information

Metal-free Photocatalytic Thiol-ene/Thiol-yne Reactions

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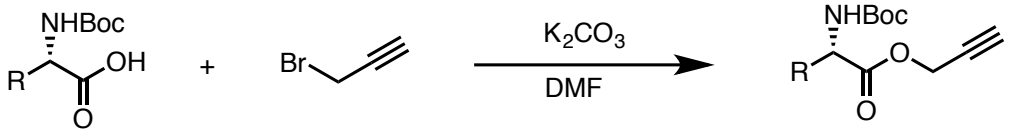
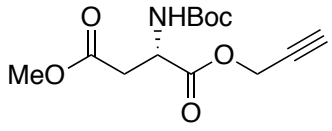
General Information

All commercially available chemicals were used without further purification unless otherwise noted. All reactions were carried out in well ventilated fume hoods. Reactions were monitored by TLC on silica gel 60 F254. Flash column chromatography was performed using SiliaFlash P60 silica gel (40-63 μm). Visualization of developed TLC was performed by irradiation with UV light or treatment with a solution of ninhydrin or ceric ammonium molybdate stain followed by heating. Yields refer to purified compound unless otherwise noted.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 MHz and 500 MHz spectrometers. Chemical shifts were reported as parts per million (ppm) relative to residual solvent $CDCl_3$ (^{1}H, 7.26 ppm, ^{13}C, 77.0 ppm). The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Infrared spectra were recorded on a PerkinElmer Spectrum Two IR spectrometer . Absorption bands are reported in wavenumbers (cm^{-1}) in the range of 4000-800 cm^{-1}. High-resolution mass spectral analysis (HRMS) data were obtained using Agilent Technologies 6530 Accurate mass Q-TOF LC/MS. Technologies 6530 Accurate Mass Q-TOF LC/MS. Irradiation of photochemical reactions was carried out using two 12W PAR38 blue LED flood lamps from ABi LED lighting. Yields refer to chromatographically and spectroscopically purified compounds.

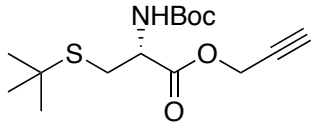


General procedure for preparation of starting material (A):
To a stirred solution of N-protected amino acid (1 equiv) in DMF (0.4 M) at -10°C was added anhydrous K_2CO_3 (1 equiv). The resulting solution was stirred for 30 min. Propargyl bromide (80% solution in toluene, 1 equiv) was added dropwise. The mixture was stirred at -10°C for 1 h before warmed to room temperature. The solvent was evaporated. Then ethyl acetate (50 mL) was added followed by saturated citric acid solution (50 mL). The aqueous layer was separated and extracted with ethyl acetate (2 X 25 mL). The combined organic layers were washed with saturated solution of sodium chloride (50 mL), dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was subjected to flash column chromatography to give desired product.



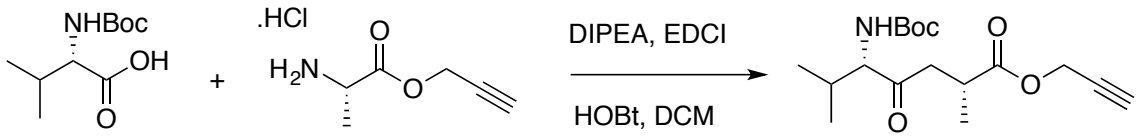
S1

4-methyl 1-(prop-2-yn-1-yl) (tert-butoxycarbonyl)-L-aspartate (S1):
The compound was prepared according to general procedure (A). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **S1** (465mg, 80% yield) as colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (d, J = 7.6 Hz, 1H), 4.74 (s, 2H), 4.62-4.60 (m, 1H), 3.69 (s, 3H), 3.05-3.00 (m, 1H), 2.86-2.81 (m, 1H), 2.48 (s, 1H), 1.44 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.1, 170.3, 155.2, 80.1, 75.4, 53.0, 52.0, 49.9, 36.5, 28.2. IR (neat): ν 3381, 2979, 1717, 1501, 1441, 1367, 1166, 1164, 1048 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{19}NNaO_6^+$ 308.1105; found: 308.1094.

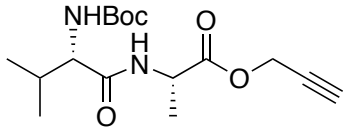


S2

prop-2-yn-1-yl N-(tert-butoxycarbonyl)-S-(tert-butyl)-L-cysteinate (S2):
The compound was prepared according to general procedure (A). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/2) to give **S2** (593 mg, 85% yield) as light yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (d, J = 8 Hz, 1H), 4.74 (s, 2H), 4.59 (br, 1H), 2.98 (s, 2H), 2.49 (s, 1H), 1.44 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 154.9, 79.8, 75.6, 53.2, 52.8, 42.4, 30.7, 30.4, 28.1. IR (neat): ν 3292, 2972, 1751, 1710, 1499, 1459, 1366, 1309, 1051, 1023, 941 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{26}NO_4S^+$ 316.1577; found: 316.157.



S_a **S_b** **S3**



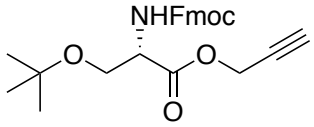
S3

prop-2-yn-1-yl (tert-butoxycarbonyl)-L-valylalaninate (**S3**)**:**

To a stirred solution of **S_a** (4.095 mmol) in DCM (40 mL) was added **S_b** (4.095 mmol) followed by N,N-Diisopropylethylamine (10.23 mmol), HOBt (0.409 mmol), EDCI (4.504 mmol). The reaction mixture was stirred at room temperature for 4 h. Then ethyl acetate (50 mL) was added followed by water (50 mL). The aqueous layer was separated and extracted with ethyl acetate (2 X 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was subjected to flash column chromatography (5% methanol in DCM) to give **S3** (1.2 g, 82% yield) as white solid;

mp 80°-85°C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (br, 1H), 5.07-5.05 (m, 1H), 4.78-4.59 (m, 3H), 3.92 (d, *J* = 7.2 Hz, 1H), 2.49 (s, 1H), 2.13-2.12 (m, 1H), 1.44 (s, 12H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9, 171.4, 155.9, 79.8, 75.3, 59.6, 52.7, 47.8, 31.0, 28.3, 19.1, 17.8. IR (neat): ν 3299, 2975, 1752, 1653, 1519, 1453, 1366, 1246, 1160, 1017, 991 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{26}N_2NaO_5^+$ 349.1734; found: 349.1724.



S4

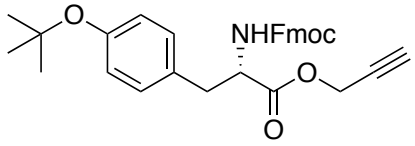
prop-2-yn-1-yl N-(((9H-fluoren-9-yl)methoxy)carbonyl)-O-(tert-butyl)-L-serinate (**S4**)**:**

The compound was prepared according to general procedure (A). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **S4** (712 mg, 87% yield) as light yellow solid;

mp 80°C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6 Hz, 2H), 7.66 (t, *J* = 6.4 Hz, 2H), 7.43 (t, *J* = 6 Hz, 2H), 7.35 (t, *J* = 6 Hz, 2H), 5.76 (d, *J* = 7.2 Hz, 1H), 4.80-4.78 (m, 2H), 4.60-4.58 (m, 1H), 4.49-4.46 (m, 1H), 4.42-4.39 (m, 1H), 4.29 (t, *J* = 6 Hz, 1H), 3.91 (dd, *J* = 2.4, 2.4 Hz, 1H), 3.65 (dd, *J* = 2.4, 2.4 Hz, 1H), 2.53-2.52 (m, 1H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 155.9, 143.8, 143.6, 141.1, 127.5, 126.9, 125.0, 124.9, 119.8, 76.7, 75.1, 73.3, 67.0, 61.8, 54.5, 52.5, 47.0, 27.1. IR

(neat): ν 3065, 2945, 1757, 1723, 1508, 1449, 1393, 1334, 1076, 1022 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{27}NNaO_5^+$ 444.1781; found: 444.1768.



S5

prop-2-yn-1-yl (S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(4-(tert-butoxy)phenyl)propanoate (**S5**)**:**

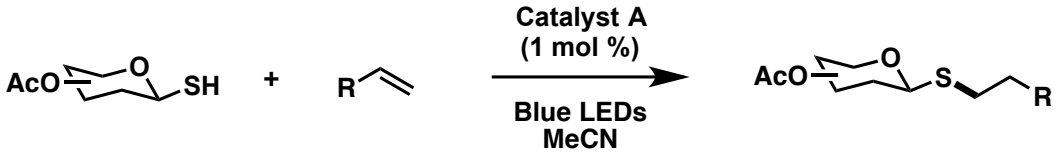
The compound was prepared according to general procedure (A). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/2) to give **S5** (463 mg, 85% yield) as light yellow oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6 Hz, 2H), 7.61 (t, *J* = 6 Hz, 2H), 7.43 (t, *J* = 6 Hz, 2H), 7.34 (t, *J* = 6 Hz, 2H), 7.07 (d, *J* = 8 Hz, 2H), 6.95 (d, *J* = 8 Hz, 2H), 5.44 (d, *J* = 6.4 Hz, 1H), 4.79-4.73 (m, 3H), 4.48-4.45 (m, 1H), 4.41-4.37 (m, 1H), 4.24 (t, *J* = 6 Hz, 1H), 3.18-3.08 (m, 2H), 2.54 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 155.6, 154.6, 143.9, 143.7, 141.3,130.2, 129.9, 127.7, 127.1, 125.2, 125.1, 124.2, 120.0, 78.4, 76.9, 75.7, 67.0, 54.8, 52.7, 47.2, 37.4, 28.8.

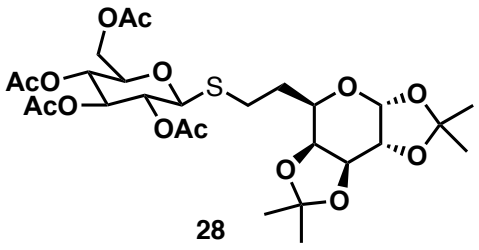
IR (neat): ν 3065, 2945, 1757, 1723, 1508, 1449, 1393, 1334, 1076, 1022 cm^{-1};

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{32}NO_5^+$ 498.2275; found: 498.2268.

Preparation of thiol-ene products:



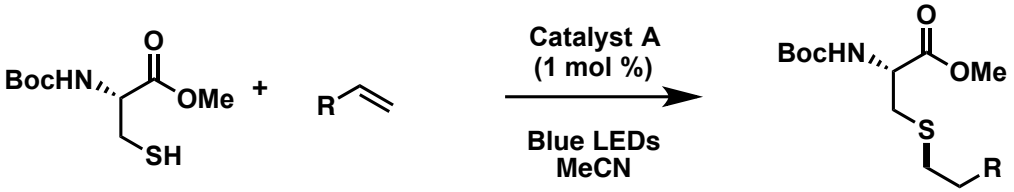
To an oven dried vial equipped with stirbar were added thiol (0.2 mmol), followed by olefin (0.24 mmol), Catalyst **A** (0.002 mmol)**,** and acetonitrile (1 mL). The vial was sealed with Teflon cap and stirred at room temperature under irradiation with Blue LEDs. Upon completion of reaction, the solvent was evaporated and the residue was purified with flash column chromatography to yield thiol-ene adduct.



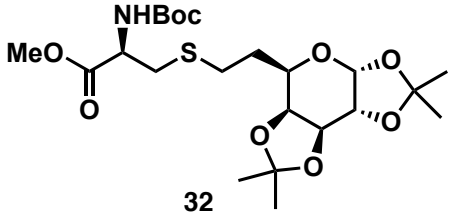
28

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((2-((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)ethyl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**28**):

The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/8) to give **28** (113 mg, 91% yield) as colorless oil;
HRMS (ESI) m/z: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (d, *J* = 4 Hz, 1H), 5.17-5.12 (m, 1H), 5.03-4.92 (m, 2H), 4.53-4.51 (m, 2H), 4.25-4.23 (m, 1H), 4.17-4.05 (m, 3H), 3.85 (d, *J* = 6.8 Hz, 1H), 3.65 (d, *J* = 6.8 Hz, 1H), 2.75 (t, *J* = 6.8 Hz, 2H), 2.02-1.94 (m, 13H), 1.84-1.73 (m, 1H), 1.50 (s, 3H), 1.38 (m, 3H), 1.27 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 169.9, 170.0, 169.2, 169.1, 108.8, 108.3, 96.3, 84.1, 75.5, 73.7, 72.5, 70.7, 70.3, 70.0, 68.2, 65.3, 62.0, 30.3, 27.1, 25.9, 25.8, 24.8, 24.2, 20.5, 20.5, 20.4. IR (neat): ν 2987, 1748, 1433, 1372, 1213, 1175, 1141, 1064, 1036, 999 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{41}O_{14}S^+$ 621.2212; found: 621.2207.

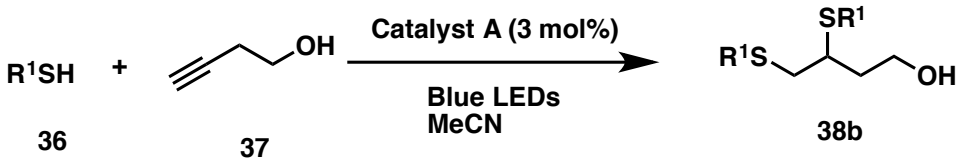


To an oven dried vial equipped with stirbar were added thiol (0.2 mmol), followed by olefin (0.24 mmol), Catalyst **A** (0.002 mmol)**,** and acetonitrile (1 mL). The vial was sealed with Teflon cap and stirred at room temperature under irradiation with Blue LEDs. Upon completion of reaction, the solvent was evaporated and the residue was purified with flash column chromatography to yield thiol-ene adduct.



32

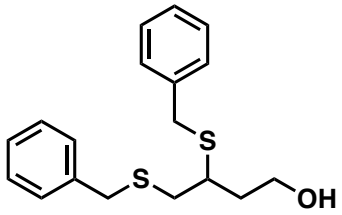
methyl N-(tert-butoxycarbonyl)-S-(2-((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)ethyl-L-cysteinate (**32**):
The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/5) to give **32** (87 mg, 89% yield) as colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (d, *J* = 4 Hz, 1H), 5.36 (d, *J* = 8 Hz, 1H), 4.55 (d, *J* = 8 Hz, 1H), 4.48 (br, 1H), 4.25 (d, *J* = 4 Hz, 1H), 4.08 (d, *J* = 8 Hz, 1H), 3.90-3.85 (m, 1H), 3.72 (s, 3H), 2.93 (d, *J* = 4 Hz, 2H), 2.67-2.63 (m, 1H), 2.60-2.55 (m, 1H), 1.99-1.90 (m, 1H), 1.69-1.66 (m, 1H), 1.51 (s, 3H), 1.41 (s, 12H), 1.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 155.0, 109.0, 108.4, 96.3, 79.9, 72.7, 70.8, 70.4, 65.6, 53.1, 52.3, 34.3, 29.9, 28.8, 28.2, 25.9, 25.9, 24.9, 24.3. IR (neat): ν 2981, 1715, 1499, 1369, 1166, 1212, 1000 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{37}NNaO_9S^+$ 514.2081; found: 514.2088.



36 37 38b

General procedures for synthesis of **38b:**

To an oven dried vial equipped with a stir bar were added **37** (0.5706 mmol), followed by Catalyst **A** (0.0171 mmol), **36** (2.282 mmol), and acetonitrile (1.14 mL). The reaction mixture was stirred at ambient temperature under Blue LEDs for 14 h. The solvent was evaporated and residue was purified by flash column chromatography to give the double hydrothiolation products.

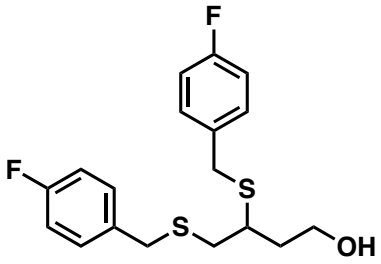


39

3,4-bis(benzylthio)butan-1-ol (**39**):

The compound was prepared according to the general procedure **38b.** The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/8) to give **39** (169 mg, 93% yield) as light yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 10H), 3.71-3.64 (m, 6H), 2.78-2.72 (m, 2H), 2.62-2.58 (m, 1H), 2.08-1.97 (m, 1H), 1.61-1.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 138.0, 128.8, 128.7, 128.5, 128.4, 127.0, 126.9, 60.2, 41.7, 37.5, 35.8, 35.4. IR (neat): ν 3378, 3060, 3026, 2914, 1601, 1493, 1452, 1420, 1238, 1198, 1069, 1028 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{22}NaOS_2^+$ 341.1004; found: 341.1018.



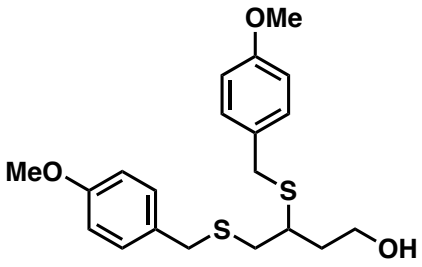
40

3,4-bis((4-fluorobenzyl)thio)butan-1-ol (**40**):

The compound was prepared according to the general procedure **38b**. The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/6) to give **40** (192 mg, 95% yield) as light yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.23 (m, 4H), 7.01-6.97 (m, 4H), 3.69-3.65 (m, 6H), 2.78-2.69 (m, 2H), 2.60-2.55 (m, 1H), 2.05-1.98 (m, 1H), 1.69-1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

162.9, 160.4, 133.7, 133.7, 133.6, 130.2, 130.1, 115.3, 115.2, 115.1, 115.0, 60.0, 41.8, 37.4, 36.0, 35.9, 34.6. IR (neat): ν 3368, 3039, 2920, 1891, 1599, 1505, 1423, 1293, 1219, 1155, 1088, 1038, 1015, 830 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}F_2OS_2^+$ 355.0996; found: 355.0989.

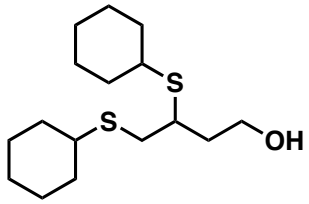


41

3,4-bis((4-methoxybenzyl)thio)butan-1-ol (**41**):

The compound was prepared according to the general procedure **38b**. The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/7) to give **41** (156 mg, 72% yield) as colorless oil;

^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.18 (m, 4H), 6.85-6.83 (m, 4H), 3.78 (s, 6H), 3.67-3.64 (m, 6H), 2.77-2.74 (m, 2H), 2.60-2.54 (m, 1H), 2.04-1.99 (m, 1H), 1.71 (s, 1H), 1.64-1.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 130.3, 130.0, 129.9, 113.9, 113.8, 60.5, 55.2, 41.9, 37.6, 36.2, 35.9, 34.9. IR (neat): ν 3417, 3000, 2952, 2907, 2833, 1608, 1583, 1509, 1463, 1440, 1316, 1300, 1238, 1031, 829 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}O_3S_2^+$ 379.1396; found: 379.1395.

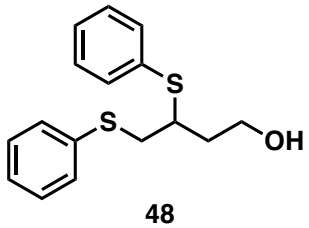


42

3,4-bis(cyclohexylthio)butan-1-ol (**42**):

The compound was prepared according to the general procedure **38b**. The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/8) to give **42** oil (152 mg, 88% yield) as colorless oil;

^1H NMR (400 MHz, $CDCl_3$) δ 3.80-3.78 (m, 2H), 2.95-2.91 (m, 2H), 2.88-2.61 (m, 3H), 2.21 (s, 1H), 2.12-2.09 (m, 1H), 1.94-1.91 (m, 4H), 1.74-1.60 (m, 7H), 1.29-1.24 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.4, 44.2, 43.3, 41.5, 37.1, 36.4, 34.1, 33.8, 33.6, 33.5, 26.0, 25.9, 25.8, 25.8, 25.6, 25.6. IR (neat): ν 3390, 2923, 2850, 1447, 1340, 1262, 1201, 1178, 1047, 998 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{30}NaOS_2^+$ 325.1630; found: 325.1626.

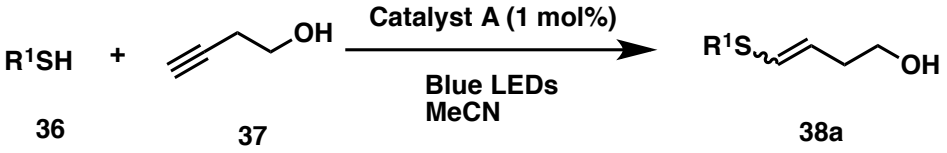


48

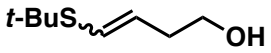
3,4-bis(phenylthiol)butan-1-ol (**48**):

The compound was prepared according to the general procedure **38b**. The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/8) to give **48** (159 mg, 96% yield) as light yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.33 (m, 3H), 7.28-7.27 (m, 3H), 7.22-7.20 (m, 4H), 3.89-3.86 (m, 2H), 3.31-3.28 (m, 2H), 2.96-2.89 (m, 1H), 2.32-2.24 (m, 1H), 1.82-1.73 (m, 1H), 1.70 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.4, 132.4, 129.6, 128.9, 128.8, 127.2, 126.1, 125.4, 61.5, 60.1, 45.1, 39.4, 36.1, 35.2, 32.4. IR (neat): ν 3343, 3055, 2923, 1755, 1582, 1478, 1437, 1302, 1218, 1156, 1088, 1040, 1024, 912 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}OS_2^+$ 291.0872; found: 291.0877.



36 37 38a

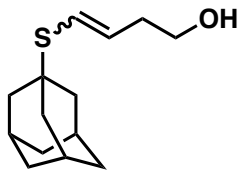


43

4-(tert-butylthio)but-3-en-1-ol (**43**):

To an oven dried vial equipped with a stir bar were added 3-butyn-1-ol (132.1 mg, 1.885 mmol), followed by Catalyst **A** (5.38 mg, 0.011 mmol), tert-Butylthiol (100 mg, 1.108 mmol), and acetonitrile (0.2 M). The reaction mixture was stirred at ambient temperature under Blue LEDs for 2 h. The solvent was evaporated and residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/8) to give desired product **43** (148 mg, 83% yield, *E:Z* 1:3.5) as colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1:3.5 mixture of *E/Z* isomers) δ 6.26 (d, *J* = 9.6 Hz, $1H_{major}$), 6.19 (d, *J* = 14.8 Hz, $1H_{minor}$), 5.85-5.78 (m, $1H_{minor}$), 5.71-5.65 (m, $1H_{major}$), 3.68-3.63 (m, 2H), 2.44-2.36 (m, 2H), 1.68 (br, 1H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 126.4, 124.1, 123.4, 61.8, 43.5, 36.6, 32.5, 30.8, 30.7. IR (neat): ν 3335, 2960, 2924, 2897, 1605, 1457, 1364, 1162, 1044, 949, 889, 855 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{17}OS^+$ 161.0995; found: 161.0998.

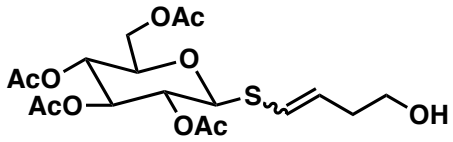


44

4-(((3s,5s,7s)-adamantan-1-yl)thio)but-3-en-1-ol (**44**):

To an oven dried vial equipped with a stir bar were added 3-butyn-1-ol (70.79 mg, 1.010 mmol), followed by Catalyst **A** (2.88 mg, 0.005 mmol), 1-Adamantanethiol (100 mg, 0.594 mmol), and acetonitrile (0.2 M). The reaction mixture was stirred at ambient temperature under Blue LEDs for 2 h. The solvent was evaporated and residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/7) to give **44** (70% yield, *E:Z* 1:1.7) as light yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1:1.7 mixture of *E/Z* isomers) δ 6.32 (d, *J* = 9.6 Hz, $1H_{major}$), 6.23 (d, *J* = 14.8 Hz, $1H_{minor}$), 5.82-5.74 (m, $1H_{minor}$), 5.70-5.65 (m, $1H_{major}$), 3.69-3.63 (m, 2H), 2.45-2.36 (m, 2H), 2.04 (s, 3H), 1.89-1.86 (m, 6H), 1.72-1.65 (m, 6H), 1.50 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 1:1.7 mixture of *E/Z* isomers) δ 130.9, 126.2, 122.1, 121.6, 61.9, 61.7, 45.7, 43.5, 43.4, 36.6, 36.1, 32.5, 29.7, 29.5. IR (neat): ν 3408, 2901, 2848, 1608, 1511, 1449, 1342, 1299, 1251, 1100, 976 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{22}NaOS^+$ 261.1284; found: 261.1270.

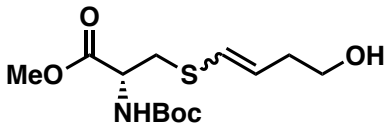


45

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((4-hydroxybut-1-en-1-yl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**45**):

To an oven dried vial equipped with a stir bar were added 3-butyn-1-ol (32.7 mg, 0.466 mmol), followed by Catalyst **A** (1.33 mg, 0.002 mmol), glucose thiol (100 mg, 0.2744 mmol), and acetonitrile (0.2 M). The reaction mixture was stirred at ambient temperature under Blue LEDs for 2 h. The solvent was evaporated and residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 2/1) to give **45** (85 mg, 71% yield, *E:Z* 1:4) as colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1:4 mixture of *E/Z* isomers) δ 6.22 (d, *J* = 8.8 Hz, $1H_{major}$), 6.13 (d, *J* = 15.2 Hz, $1H_{minor}$), 5.85-5.81 (m, 1H), 5.19 (t, *J* = 9.2 Hz, 1H), 5.07 (d, *J* = 9.2 Hz, 2H), 4.51 (d, *J* = 10 Hz, $1H_{major}$), 4.44 (d, *J* = 10 Hz, $1H_{minor}$), 4.24-4.20 (m, 1H), 4.12-4.09 (m, 1H), 3.73-3.71 (m, 1H), 3.67-3.64 (m, 2H), 2.36-2.34 (m, 2H), 2.36-1.97 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, 1:4 mixture of *E/Z* isomers) δ 170.5, 170.0, 169.3, 169.2, 135.8, 131.1, 120.5, 119.1, 82.8, 76.0, 73.7, 69.9, 69.5, 68.0, 61.9, 61.4, 61.2, 36.6, 32.5, 20.6, 20.5, 20.4. IR (neat): ν 3517, 2955, 1748, 1431, 1367, 1217, 1090, 1037, 957, 914 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{27}O_{10}S^+$ 435.1319; found: 435.1315.

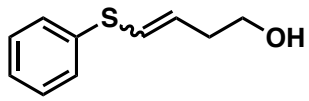


46

Methyl N-(tert-butoxycarbonyl)-S-(4-hydroxybut-1-en-1-yl)-L-cysteinate (**46**):

To an oven dried vial equipped with a stir bar were added 3-butyn-1-ol (50.63 mg, 0.722 mmol), followed by Catalyst **A** (2.06 mg, 0.004 mmol), methyl (tert-butoxycarbonyl)-L-cysteinate (100 mg, 0.424 mmol), and acetonitrile (0.2 M). The reaction mixture was stirred at ambient temperature under Blue LEDs for 2 h. The solvent was evaporated and residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **46** (104 mg, 80% yield, *E:Z* 1.2:1) as light yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1.2:1 mixture of *E/Z* isomers) δ 5.94 (d, *J* = 8.4 Hz, $1H_{minor}$), 5.93 (d, *J* = 13.6 Hz, $1H_{major}$), 5.73-5.59 (m, 1H), 5.47-5.37 (m, 1H), 4.51 (br, 1H), 3.70-3.69 (m, 3H), 3.64-3.58 (m, 2H), 3.09-2.92 (m, 2H), 2.37-2.26 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 1.2:1 mixture of *E/Z* isomers) δ 171.3, 171.0, 155.0, 129.9, 128.0, 126.4, 124.4, 80.2, 80.1, 61.4, 53.6, 52.9, 52.5, 52.4, 36.4, 35.3, 32.4, 28.2. IR (neat): ν 3373, 2977, 1743, 1693, 1502, 1436, 1391, 1366, 1309, 1247, 1214, 1159, 1049, 1017, 946, 859 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{23}NNaO_5S^+$ 328.1189; found: 328.1187.



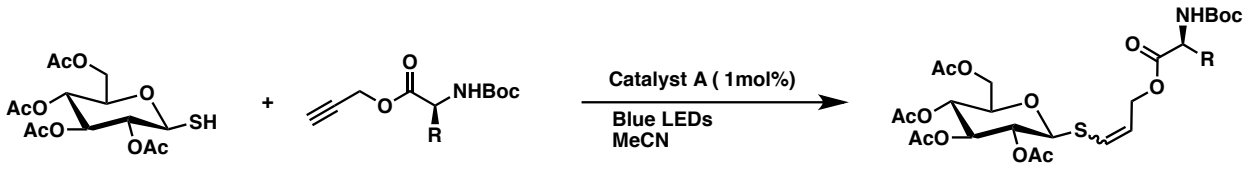
47

4-(phenylthiol)but-3-en-1-ol (**47**):

To an oven dried vial equipped with a stir bar were added 3-butyn-1-ol (108.14 mg, 1.542 mmol), followed by Catalyst **A** (4.40 mg, 0.009 mmol), benzenethiol (100 mg, 0.907 mmol), and acetonitrile (0.2 M). The reaction mixture was stirred at ambient temperature under Blue LEDs for 2 h. The solvent was evaporated and residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/4) to give **47** (103 mg, 63% yield, *E:Z* 1:2) as light yellow oil;

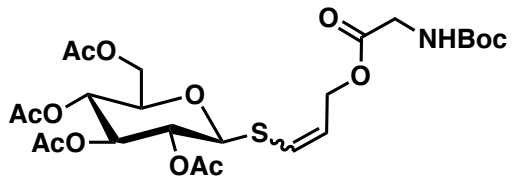
^{1}H NMR (400 MHz, $CDCl_3$, *E* isomers) δ 7.28-7.19 (m, $5H_{minor}$), 6.28 (d, *J* = 15 Hz, $1H_{minor}$), 5.95-5.88 (m, $1H_{minor}$), 3.70 (t, *J* = 8 Hz, $2H_{minor}$), 2.45-2.40 (m, $2H_{minor}$). ^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomers) δ 7.36-7.30 (m, $5H_{major}$), 6.36 (d, *J* = 9.6 Hz, $1H_{major}$), 5.87-5.82 (m, $1H_{major}$), 3.75 (t, *J* = 6.4 Hz, $2H_{major}$), 2.56-2.51 (m, $2H_{major}$). ^{13}C NMR (100 MHz, $CDCl_3$, 1:2 mixture of *E/Z* isomers) δ 135.8, 135.6, 131.2, 128.4, 126.4, 126.4, 125.9, 124.6, 61.8, 61.6, 36.3, 32.6.

IR (neat): ν 3370, 3058, 2922, 2851, 1722, 1583, 1479, 1439, 1180, 1089, 1024, 918 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}OS^+$ 181.0682; found: 181.0690.



General procedure for synthesis of S-linked glycoconjugates (B):

To an oven dried vial equipped with a stir bar were added glucose thiol (0.2744 mmol), followed by Catalyst **A** (0.0027 mmol), alkyne containing amino acid derivative (0.4665 mmol), and acetonitrile (1.37 mL). The reaction mixture was stirred at ambient temperature under Blue LEDs for 2 h. The solvent was evaporated and residue was purified by flash column chromatography to give the desired products.

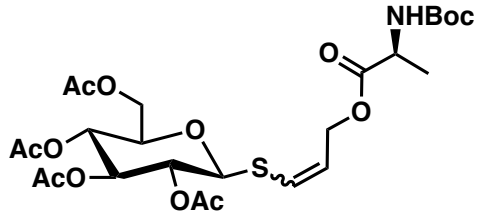


49

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3-(((tert-butoxycarbonyl)glycyl)oxy)prop-1-en-1-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**49**):

The compound was prepared according to the general procedure (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **49** (101 mg, 64% yield, *E:Z* 1.2:1) as colorless oil;

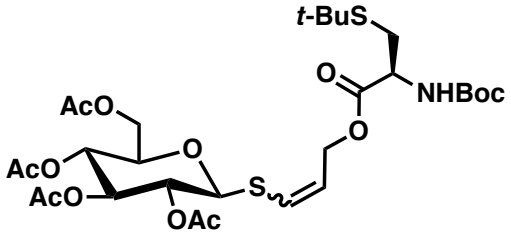
^{1}H NMR (400 MHz, $CDCl_3$, 1.2:1 mixture of *E/Z* isomers) δ 6.40 (d, J = 16 Hz, $1H_{major}$), 6.37 (d, J = 12 Hz, $1H_{minor}$), 5.90-5.83 (m, 1H), 5.22-5.17 (m, 1H), 5.10-5.01 (m, 3H), 4.70-4.67 (m, 1H), 4.62-4.53 (m, 2H), 4.25-4.21 (m, 1H), 4.13-4.11 (m, 1H), 3.90-3.88 (m, 2H), 3.76-3.72 (m, 1H), 2.06-1.97 (m, 12H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 1.2:1 mixture of *E/Z* isomers) δ 170.4, 169.9, 169.2, 169.0, 155.6, 126.7, 125.3, 123.8, 83.1, 82.9, 79.9, 76.1, 73.7, 73.6, 69.9, 69.7, 68.0, 64.7, 61.9, 61.6, 42.3, 28.2. IR (neat): ν 2980, 1751, 1367, 1263, 1225, 1511, 1162, 1052, 955 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{35}NNaO_{13}S^+$ 600.1721; found: 600.1728.



50

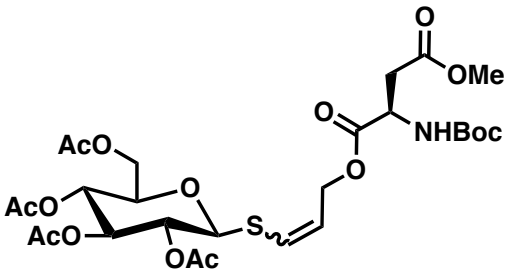
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3-(((tert-butoxycarbonyl)-L-alanyl)oxy)prop-1-en-1-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**50**):

The compound was prepared according to the general procedure (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **50** (106 mg, 65% yield, *E:Z* 1:1) as colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$, 1:1 mixture of *E/Z* isomers) δ 6.39 (d, *J* = 15.6 Hz, 1H), 6.36 (d, *J* = 10.3 Hz, 1H), 5.90-5.82 (m, 1H), 5.21-5.17 (m, 1H), 5.09-4.99 (m, 3H), 4.66-4.64 (m, 1H), 4.60-4.53 (m, 2H), 4.27-4.20 (m, 2H), 4.11-4.08 (m, 1H), 3.74-3.71 (m, 1H), 2.05-1.96 (m, 12H), 1.40 (s, 9H), 1.36-1.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture of *E/Z* isomers) δ 172.8, 170.4, 169.9, 169.2, 169.0, 154.9, 126.9, 126.8, 125.1, 123.9, 83.1, 82.9, 79.7, 76.1, 76.0, 73.7, 73.6, 69.9, 69.7, 68.0, 64.7, 61.9, 61.6, 49.1, 28.2, 20.4, 18.4. IR (neat): ν 3392, 2986, 1753, 1375, 1225, 1168, 1052 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{37}NNaO_{13}S^+$ 614.1878; found: 614.1887.



51

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-((3-((N-(tert-butoxycarbonyl)-S-(tert-butyl)-D-cysteinyl)oxy)prop-1-en-1-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**51**):
The compound was prepared according to the general procedure (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **51** (127 mg, 68% yield, *E:Z* 1.1:1) as colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$, 1.1:1mixture of *E/Z* isomers) δ 6.42 (d, *J* = 15.2 Hz, $1H_{major}$), 6.36 (d, *J* = 9.6 Hz, $1H_{minor}$), 5.92-5.83 (m, 1H), 5.32-5.28 (m, 1H), 5.23-5.17 (m, 1H), 5.10-5.01 (m, 2H), 4.67-4.52 (m, 4H), 4.26-4.22 (m, 1H), 4.13-4.09 (m, 1H), 3.76-3.71 (m, 1H), 2.95-2.94 (m, 2H), 2.06-1.97 (m, 12H), 1.41 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 1.1:1 mixture of *E/Z* isomers) δ 170.5, 170.4, 170.0, 169.2, 169.0, 155.0, 126.9, 126.5, 125.5, 123.7, 120.5, 118.7, 118.3, 117.0, 116.1, 115.7, 83.3, 83.0, 79.9, 76.1, 76.0, 73.7, 73.6, 69.9, 69.7, 65.1, 61.9, 61.8, 53.1, 42.6, 42.5, 30.7, 30.6, 28.2, 20.6, 20.4. IR (neat): ν 2988, 2945, 1737, 1501, 1446, 1366, 1214, 1162, 1040, 937, 913, 847 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{45}NNaO_{13}S_2^+$ 702.2225; found: 702.2224.

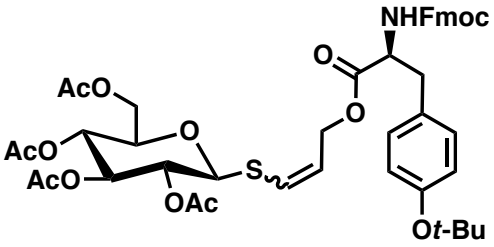


52

4-methyl 1-(3-(((2S,3R,4S,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)thio)allyl) (tert-butoxycarbonyl)-D-aspartate (**52**):

The compound was prepared according to the general procedures (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/1) to give **52** (109 mg, 61% yield, *E:Z* 1:1) as colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1:1 mixture of *E/Z* isomers) δ 6.39 (d, *J* = 15.6 Hz, 1H), 6.35 (d, *J* = 10 Hz, 1H), 5.87-5.81 (m, 1H), 5.45 (br, 1H), 5.22-5.16 (m, 1H), 5.08-5.00 (m, 2H), 4.68 (m, 4H), 4.24-4.21 (m, 1H), 4.12-4.05 (m, 1H), 3.74-3.71 (m, 1H), 3.65 (s, 3H), 2.98-2.93 (m, 1H), 2.82-2.77 (m, 1H), 2.05-1.96 (m, 12H), 1.41 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 1:1 mixture of *E/Z* isomers) δ 171.2, 170.5, 170.4, 169.9, 169.2, 169.0, 155.2, 126.7, 126.4, 125.3, 123.7, 83.2, 82.9, 80.0, 76.1, 76.0, 73.7, 73.6, 69.9, 67.9, 65.1, 62.0, 61.8, 60.2, 51.9, 51.8, 49.9, 36.5, 28.2, 20.6, 20.4. IR (neat): ν 2923, 2853, 1752, 1368, 1227, 1043 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{39}NNaO_{15}S^+$ 672.1933; found: 672.1944.



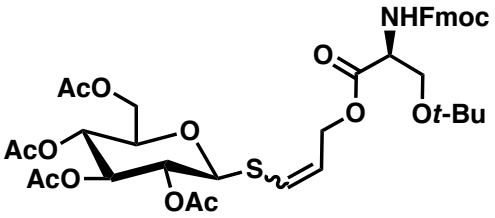
53

(2S,3R,4S,5R,6R)-2-((3-(((S)-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-(4-(tert-butoxy)phenyl)propanoyl)oxy)prop-1-en-1-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**53**):

The compound was prepared according to the general procedure (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/3) to give **53** (161 mg, 68% yield, *E:Z* 1:1.1) as colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1:1.1 mixture of *E/Z* isomers) δ 7.77 (d, *J* = 8 Hz, 2H), 7.58-7.56 (m, 2H), 7.40 (t, *J* = 8 Hz, 2H), 7.31 (t, *J* = 8 Hz, 2H), 7.00 (d, *J* = 8 Hz, 2H), 6.91-6.89 (m, 2H), 6.42 (d, *J* = 10.8 Hz, $1H_{minor}$), 6.39 (d, *J* = 5.2 Hz, $1H_{major}$), 5.87-5.82 (m, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 5.25-5.20 (m, 1H), 5.12-5.08 (m, 2H), 4.69-4.54 (m, 4H), 4.45-4.32 (m, 2H), 4.28-4.19 (m, 2H), 4.14-

4.11 (m, 1H), 3.76-3.74 (m, 1H), 3.12-3.01 (m, 2H), 2.08-1.99 (m, 12H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 1:1.1 mixture of *E/Z* isomers) δ 171.1, 171.0, 170.5, 170.0, 169.2, 169.1, 155.4, 154.5, 143.8, 143.7, 141.2, 130.3, 129.7, 127.6, 127.0, 126.5, 126.3, 125.7, 125.0, 124.1, 124.0, 119.9, 83.1, 82.9, 78.4, 78.3, 76.2, 76.0, 73.7, 73.6, 69.9, 69.7, 68.0, 66.9, 64.9, 61.8, 60.3, 54.8, 47.1, 37.5, 28.8, 20.6, 20.4, 14.1. IR (neat): ν 3054, 2947, 1744, 1608, 1505, 1447, 1390, 1332, 1213, 1035, 912, 895 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{45}H_{51}NNaO_{14}S^+$ 884.2922; found: 884.2929.

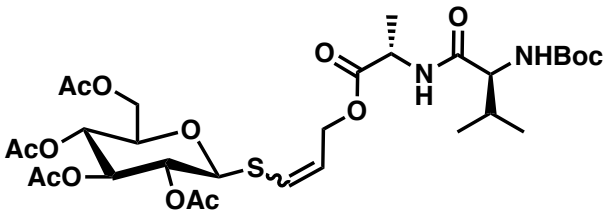


54

(**2S,3R,4S,5R,6R)-2-((3-((N-(((9H-fluoren-9-yl)methoxy)carbonyl)-O-(tert-butyl)-L-seryl)oxy)prop-1-en-1-yl)thio)-6-(acetoxymethyl)tetrahydro-2H-pyran-3,4,5-triyl triacetate** (**54**):

The compound was prepared according to the general procedure (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 1/2) to give **54** (134 mg, 62% yield, *E:Z* 1:1.1) as colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1:1.1 mixture of *E/Z* isomers) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 8 Hz, 2H), 7.39 (t, *J* = 8 Hz, 2H), 7.31 (t, *J* = 8 Hz, 2H), 6.43 (d, *J* = 15.2 Hz, $1H_{minor}$), 6.38 (d, *J* = 9.6 Hz, $1H_{major}$), 5.93-5.87 (m, 1H), 5.69 (d, *J* = 8 Hz, 1H), 5.21 (t, *J* = 9.2 Hz, 1H), 5.12-5.03 (m, 2H), 4.73 (d, *J* = 6 Hz, 1H), 4.66 (d, *J* = 6 Hz, 1H), 4.59-4.32 (m, 4H), 4.27-4.23 (m, 2H), 4.13-4.10 (m, 1H) 3.84 (d, *J* = 8 Hz, 1H), 3.73 (d, *J* = 8 Hz, 1H), 3.60 (d, *J* = 8 Hz, 1H), 2.07-1.99 (m, 12H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 1:1.1 mixture of *E/Z* isomers) δ 170.4, 170.2, 170.1, 170.0, 169.2, 169.0, 156.0, 143.9, 143.7, 141.2, 127.6, 127.0, 125.1, 123.7, 119.9, 83.2, 83.0, 79.4, 79.0, 78.7, 78.3, 77.9, 77.6, 77.3, 77.0, 76.6, 76.1, 76.0, 73.7, 73.6, 73.5, 73.4, 69.9, 69.7, 68.0, 67.1, 64.9, 62.0, 61.8, 60.2, 54.6, 47.1, 27.2, 20.9, 20.6, 20.4, 14.1. IR (neat): ν 3374, 2929, 1745, 1704, 1503, 1437, 1392, 1366, 1250, 1214, 1162, 1051 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{39}H_{48}NO_{14}S^+$ 786.2790; found: 786.2796.

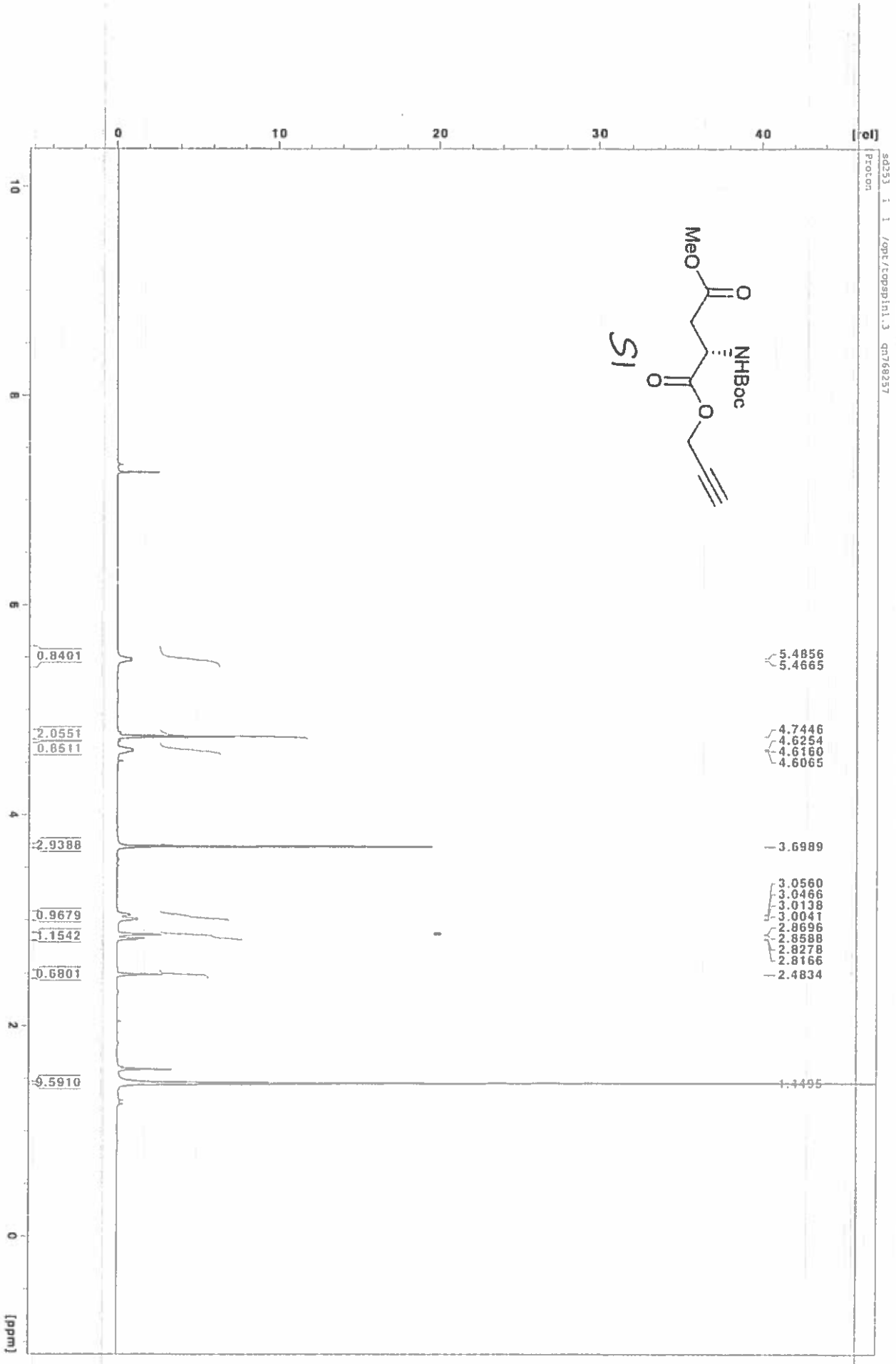


55

(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(((6S,9S)-6-isopropyl-2,2,9-trimethyl-4,7,10-trioxo-3,11-dioxa-5,8-diazatetradec-13-en-14-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate (**55**):

The compound was prepared according to the general procedure (B). The residue was purified by flash column chromatography (Ethyl acetate/Hexanes = 2/1) to give **55** (124 mg, 65% yield, *E:Z* 1.25:1) as light yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$, 1.25:1 mixture of *E/Z* isomers) δ 6.59-6.54 (m, 1H), 6.41 (d, *J* = 15.6 Hz, $1H_{major}$), 6.38 (d, *J* = 10.4 Hz, $1H_{minor}$), 5.92-5.85 (m, 1H), 5.23-5.02 (m, 4H), 4.67-4.54 (m, 4H), 4.26-4.21 (m, 1H), 4.14-4.06 (m, 1H), 3.93 (br, 1H), 3.75-3.73 (m, 1H), 2.06-1.98 (m, 12H), 1.41 (m, 12H), 1.23 (t, *J* = 6.8 Hz, 1H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 1.25:1 mixture of *E/Z* isomers) δ 172.1, 171.1, 171.0, 170.4, 169.9, 169.3, 169.2, 169.0, 155.7, 127.1, 126.7, 125.1, 124.0, 83.0, 82.8, 79.7, 76.1, 76.0, 73.7, 73.6, 70.0, 69.6, 68.0, 64.8, 61.9, 61.7, 59.6, 47.9, 30.9, 29.5, 28.2, 20.5, 20.4, 19.1, 18.1, 18.0, 17.6. IR (neat): ν 2975, 1749, 1661, 1520, 1367, 1223, 1163, 1041 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{47}N_2O_{14}S^+$ 691.2743; found: 691.2748.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O
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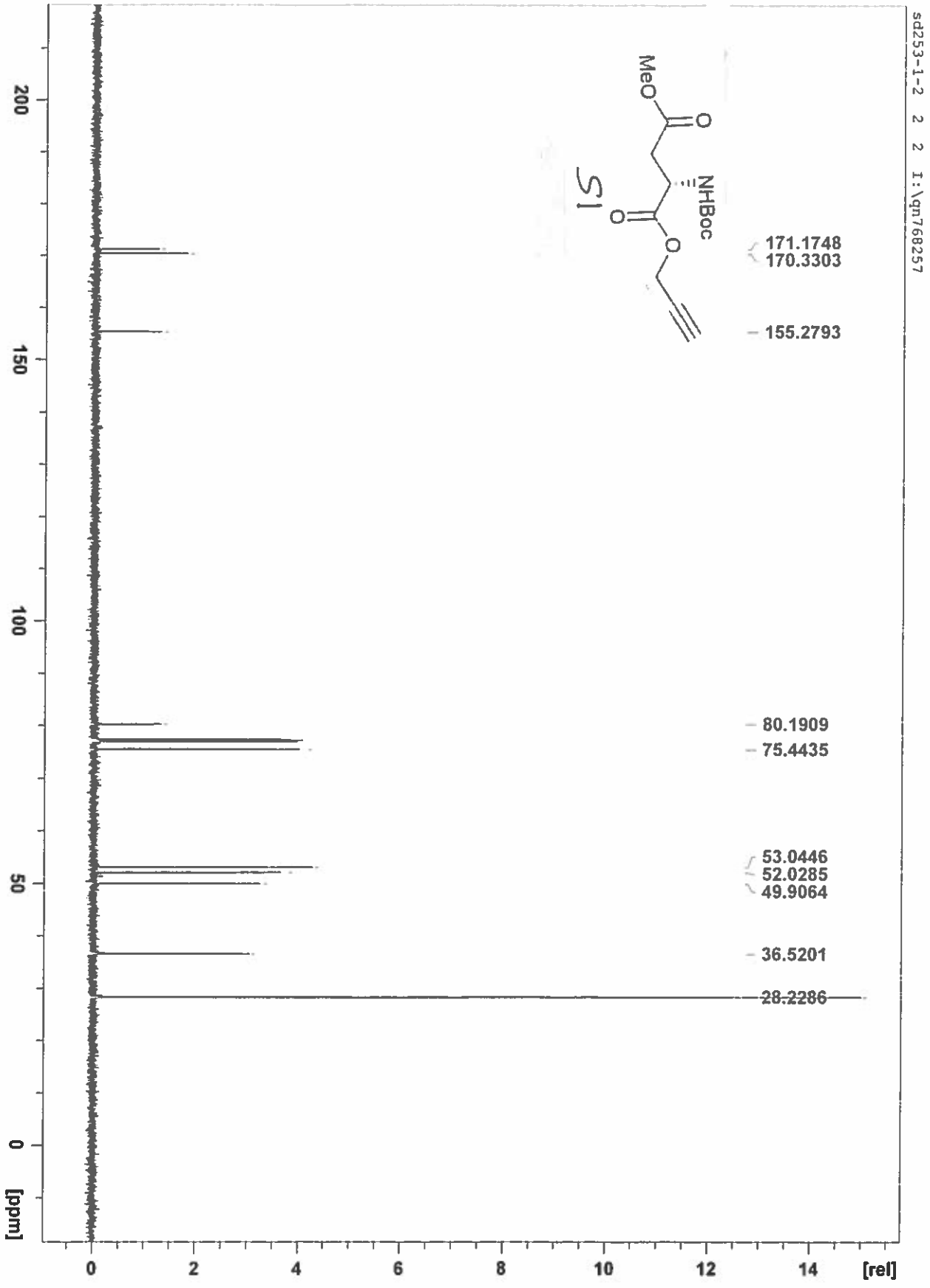
0.9679
1.1542
0.6801
9.5910
5.4856
5.4665
4.7446
4.6254
4.6160
4.6065
3.6989
3.0560
3.0466
3.0138
3.0041
2.8696
2.8588
2.8278
2.8166
2.4834
1.1495
[ppm]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O
NHBoc
O
O
S1
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155.2793
80.1909
75.4435
53.0446
52.0285
49.9064
36.5201
28.2286
200
150
100
50
0
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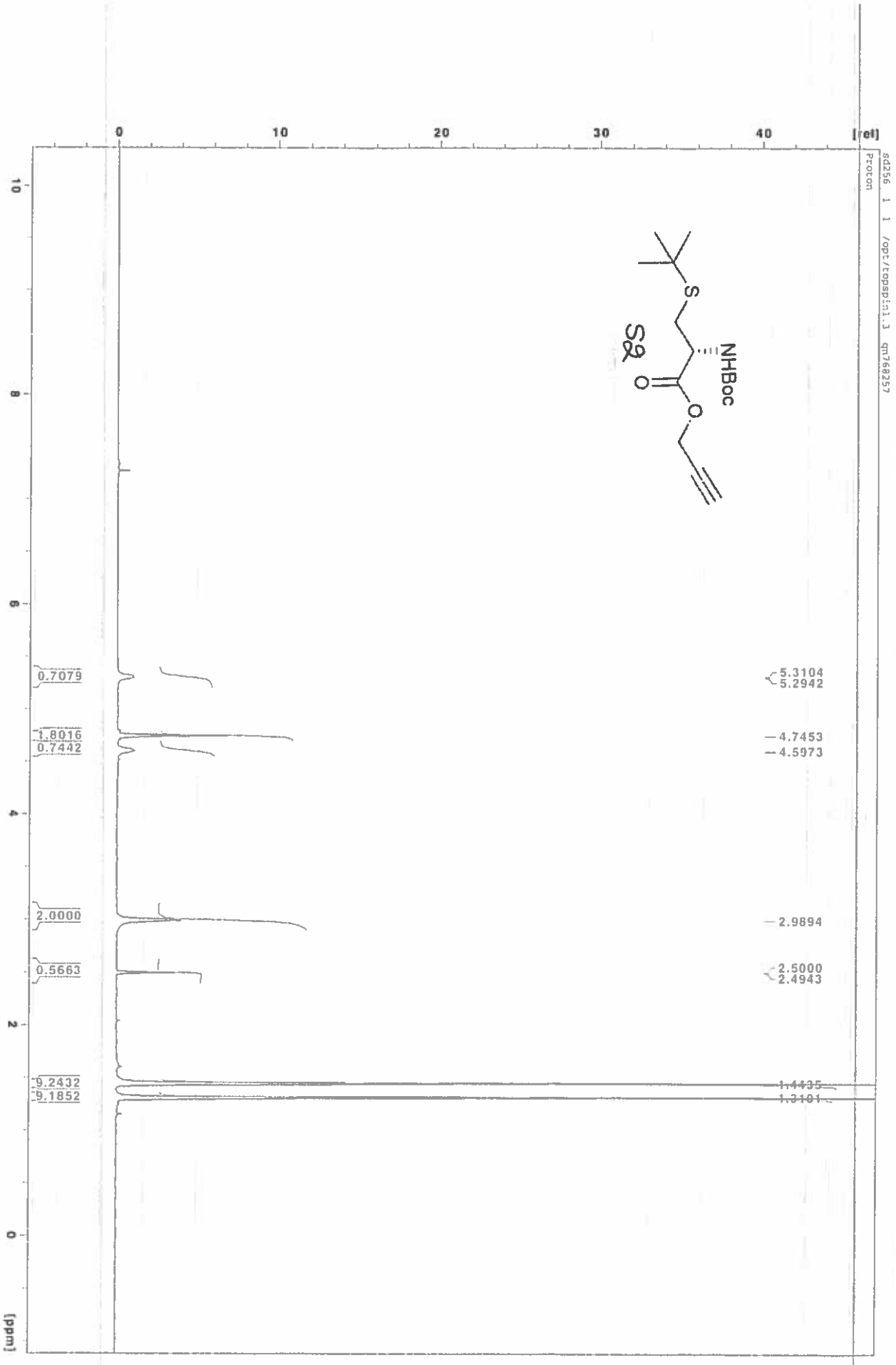
0
2
4
6
8
10
12
14
[rel]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8
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4
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0.5663
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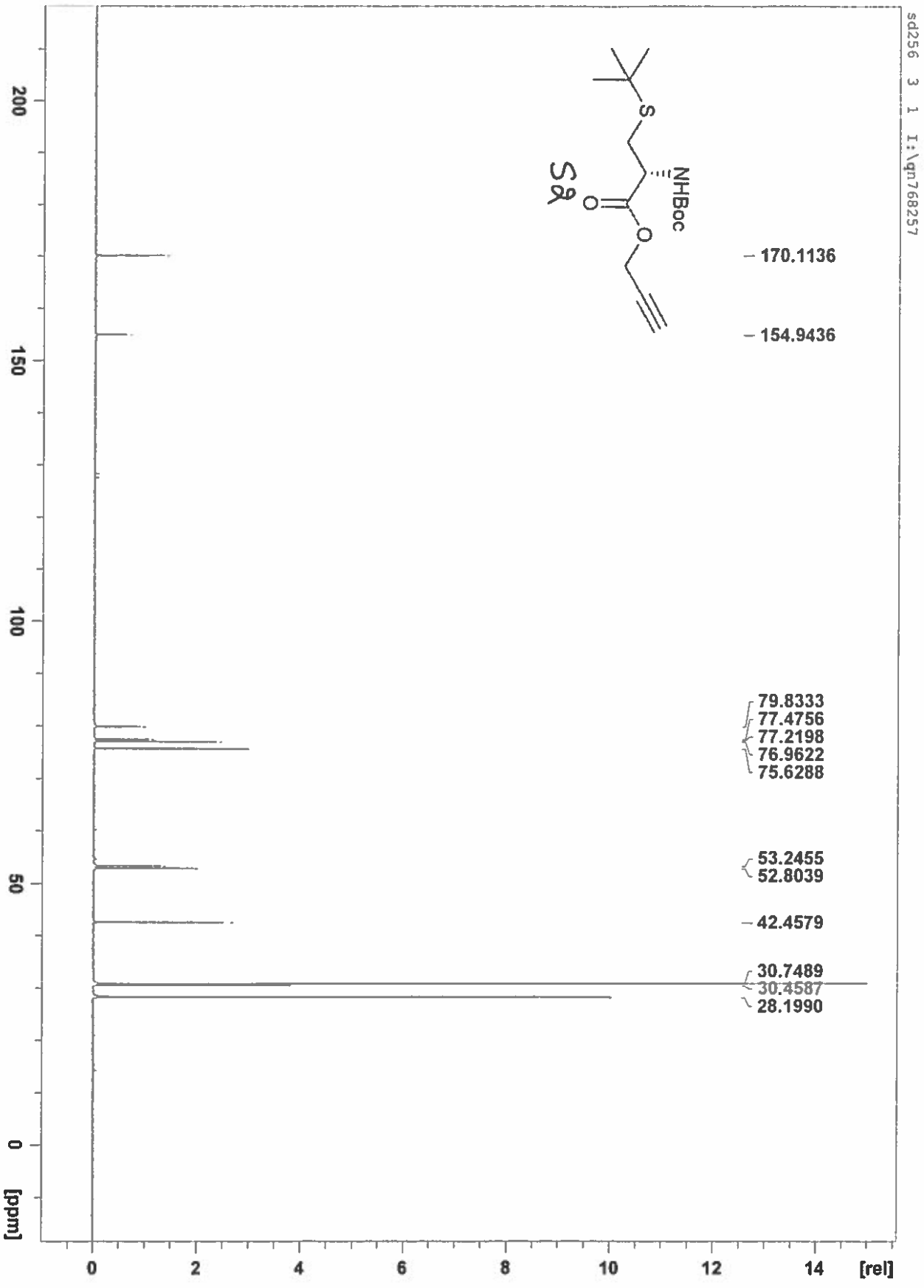
9.1852
5.3104
5.2942
4.7453
4.5973
2.9894
2.5000
2.4943
1.4435
1.3101
NHBoc
S
O
O
O
sd256 1 1 /opt/topspin1.3 qm768257
Procon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154.9436
79.8333
77.4756
77.2198
76.9622
75.6288
53.2455
52.8039
42.4579
30.7489
30.4587
28.1990
200
150
100
50
0
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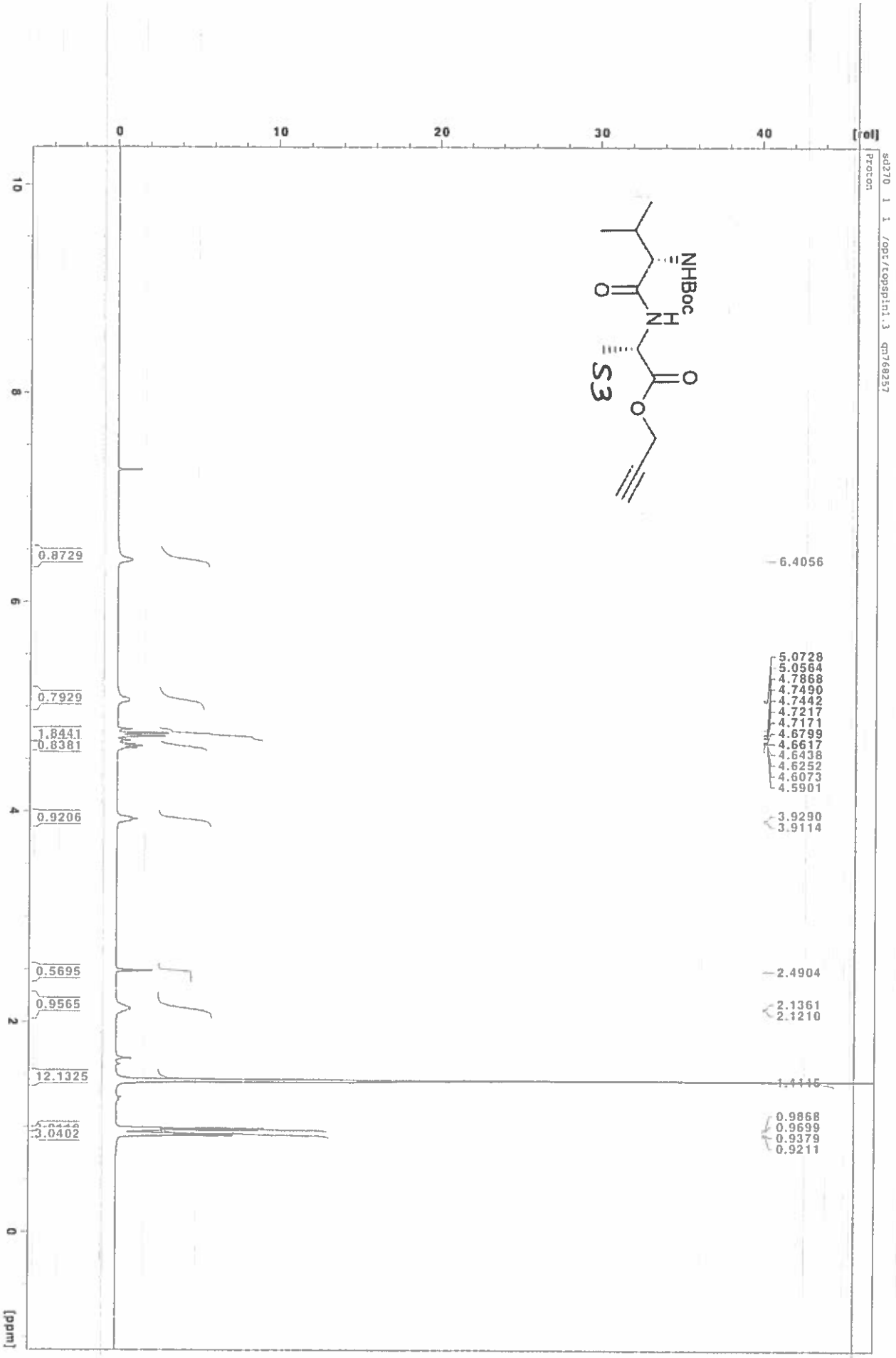
2
4
6
8
10
12
14
[rel]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NHBoc
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0.7929
1.8441
0.8381
0.9206
0.5695
0.9565
12.1325
3.0402
6.4056
5.0728
5.0564
4.7868
4.7490
4.7442
4.7217
4.7171
4.6799
4.6617
4.6438
4.6252
4.6073
4.5901
3.9290
3.9114
2.4904
2.1361
2.1210
1.4115
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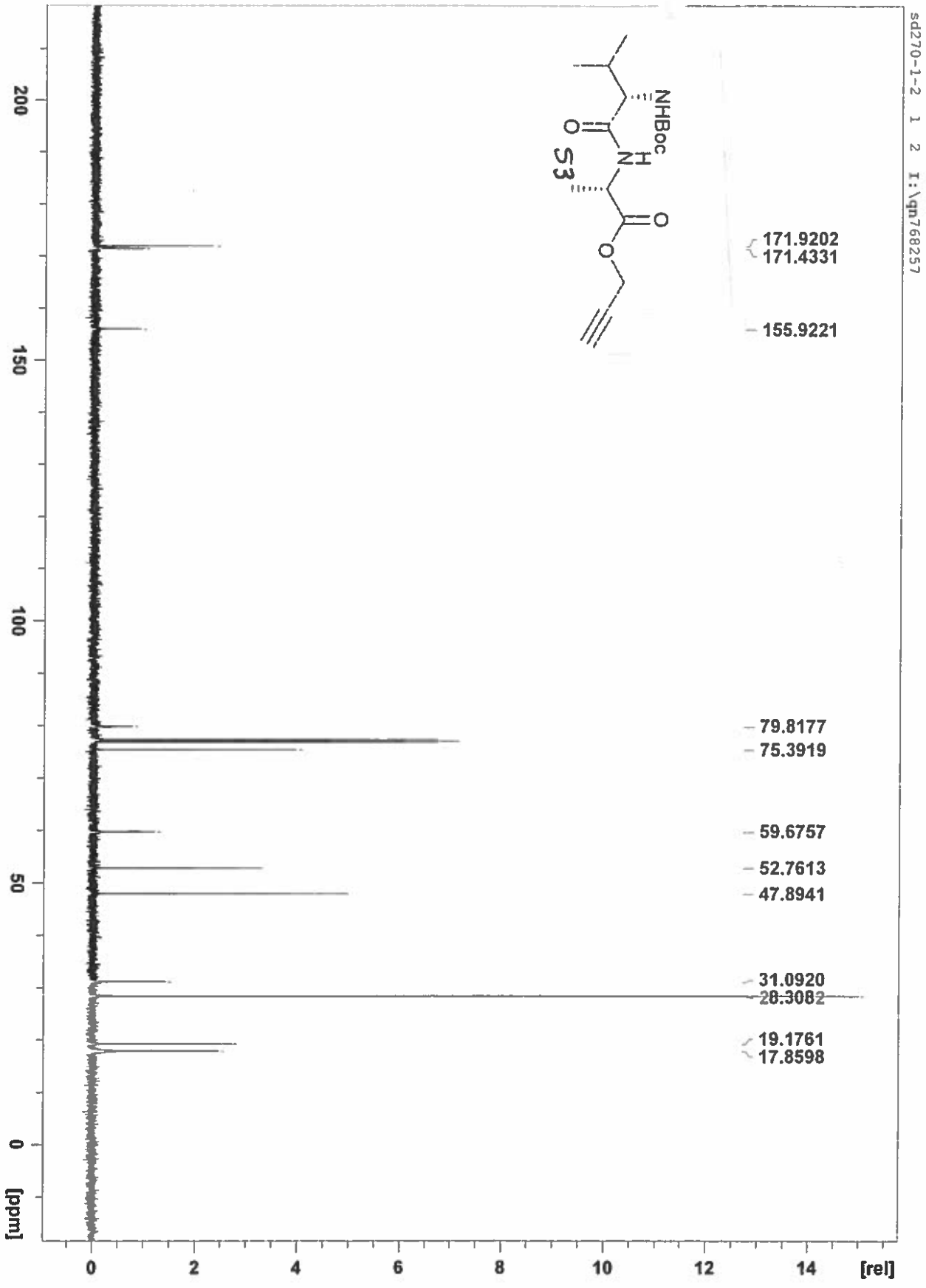
0.9699
0.9379
0.9211
[ppm]


sd270-1-2 1 2 I:\qn768257
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S3
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155.9221
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59.6757
52.7613
47.8941
31.0920
28.3082
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150
100
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0
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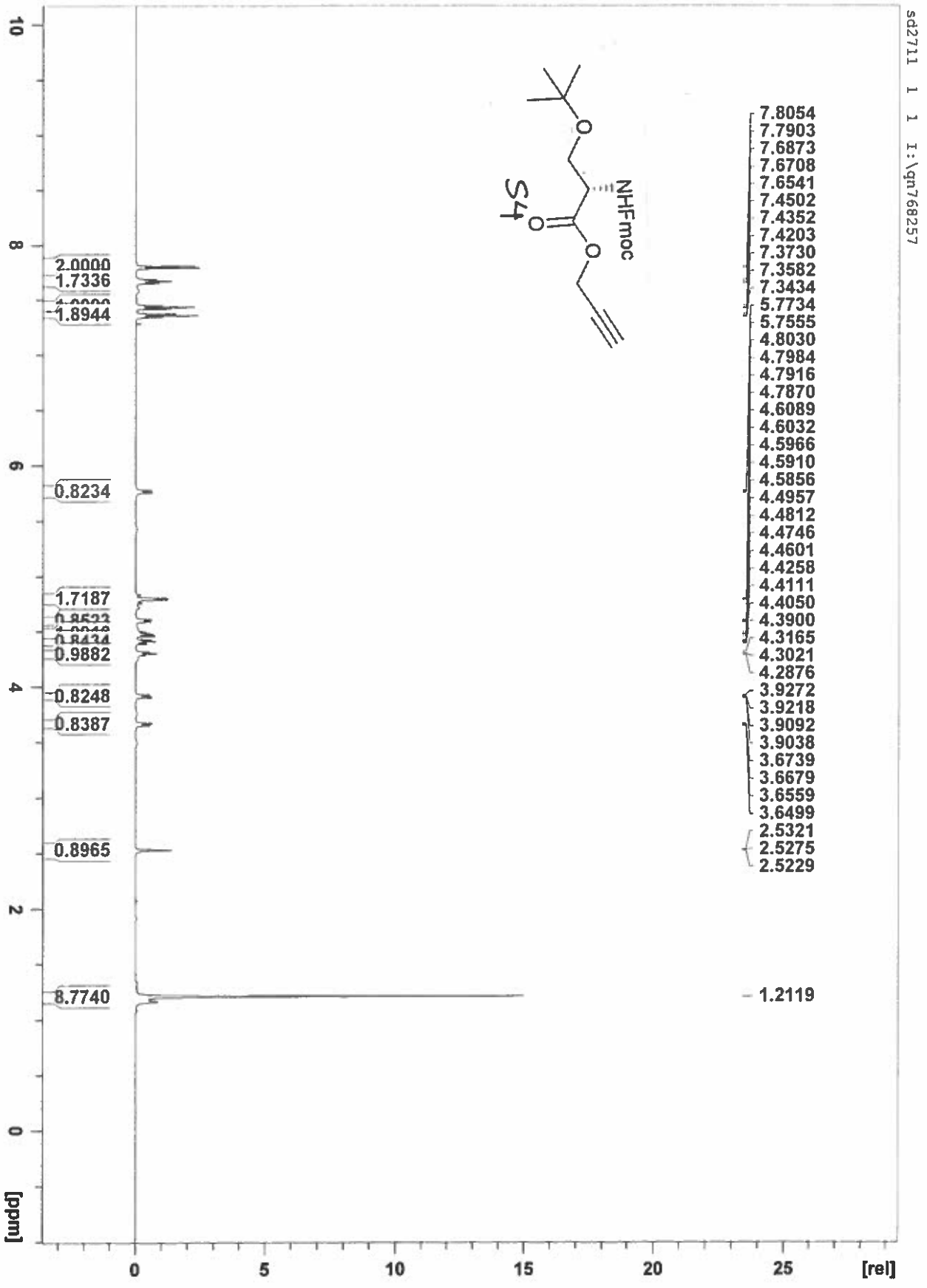
2
4
6
8
10
12
14
[rel]


sd2711 1 1 I:\qn768257
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S4
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7.6873
7.6708
7.6541
7.4502
7.4352
7.4203
7.3730
7.3582
7.3434
5.7734
5.7555
4.8030
4.7984
4.7916
4.7870
4.6089
4.6032
4.5966
4.5910
4.5856
4.4957
4.4812
4.4746
4.4601
4.4258
4.4111
4.4050
4.3900
4.3165
4.3021
4.2876
3.9272
3.9218
3.9092
3.9038
3.6739
3.6679
3.6559
3.6499
2.5321
2.5275
2.5229
1.2119
2.0000
1.7336
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0.8965
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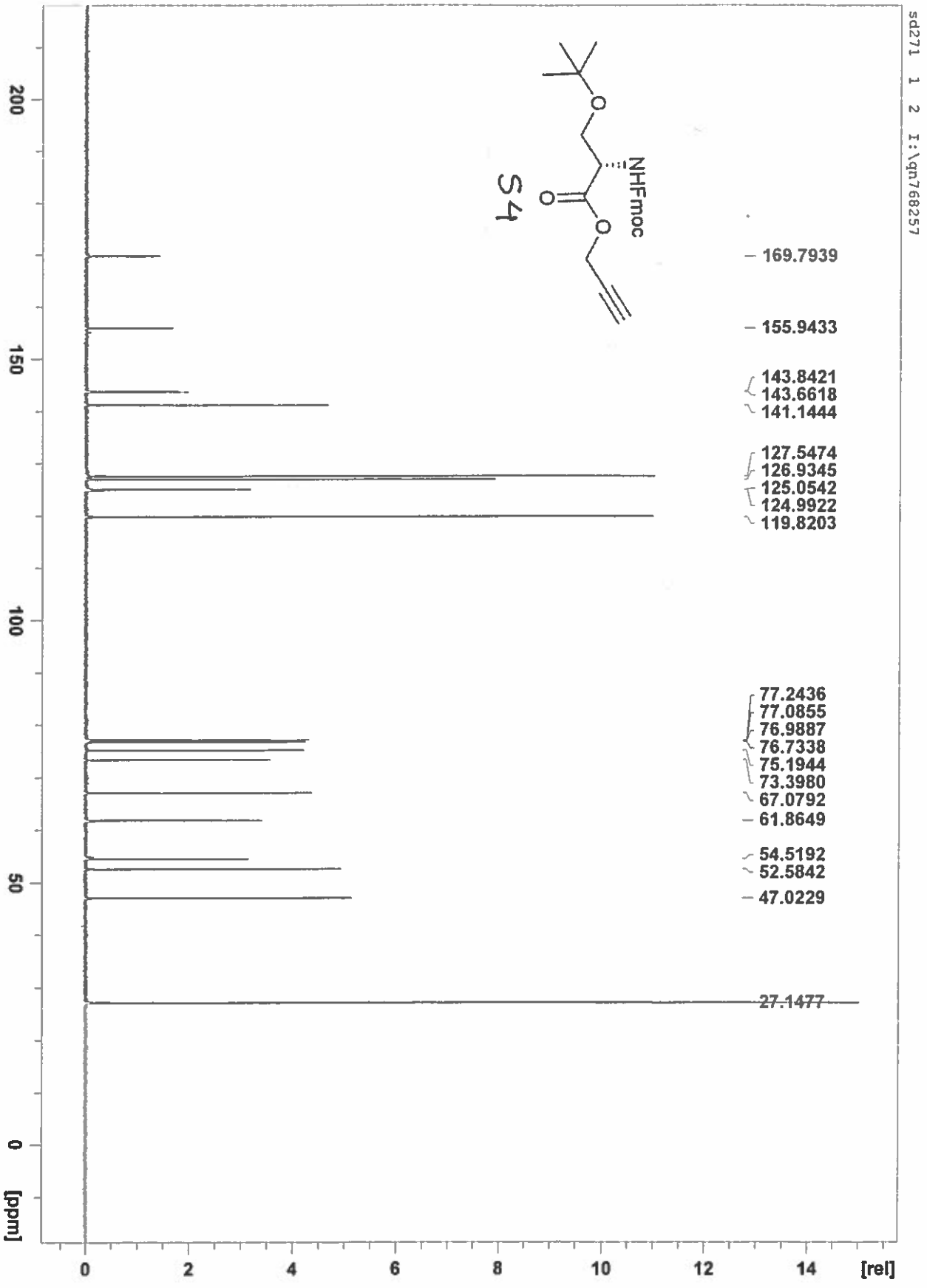
[rel]


S4
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O
O
O
sd271 1 2 I:\qn768257
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143.6618
141.1444
127.5474
126.9345
125.0542
124.9922
119.8203
77.2436
77.0855
76.9887
76.7338
75.1944
73.3980
67.0792
61.8649
54.5192
52.5842
47.0229
27.1477
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150
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2
4
6
8
10
12
14
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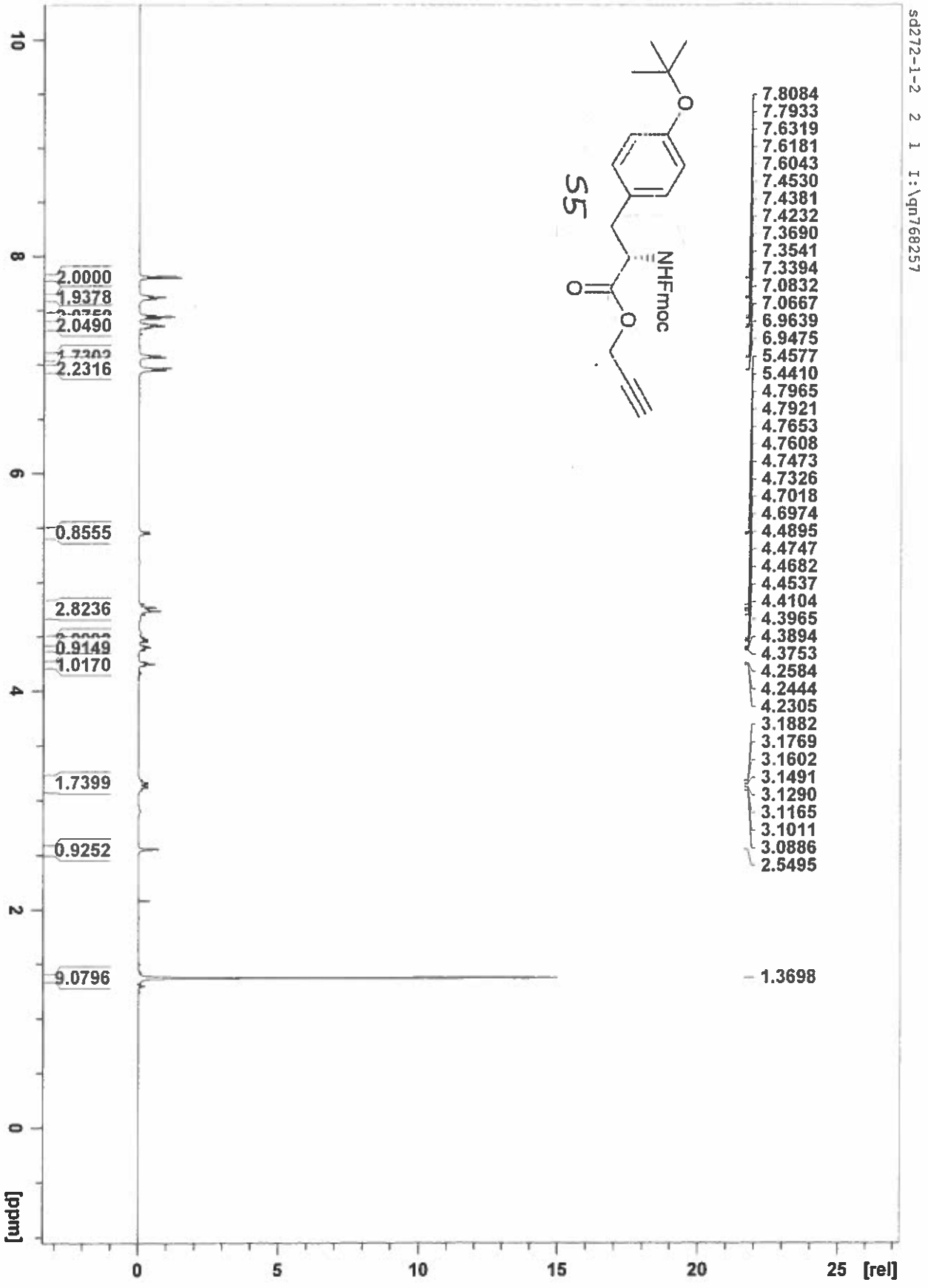
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O
O
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7.6319
7.6181
7.6043
7.4530
7.4381
7.4232
7.3690
7.3541
7.3394
7.0832
7.0667
6.9639
6.9475
5.4577
5.4410
4.7965
4.7921
4.7653
4.7608
4.7473
4.7326
4.7018
4.6974
4.4895
4.4747
4.4682
4.4537
4.4104
4.3965
4.3894
4.3753
4.2584
4.2444
4.2305
3.1882
3.1769
3.1602
3.1491
3.1290
3.1165
3.1011
3.0886
2.5495
1.3698
2.0000
1.9378
2.0490
2.2316
0.8555
2.8236
0.9149
1.0170
1.7399
0.9252
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6
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10
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20
25
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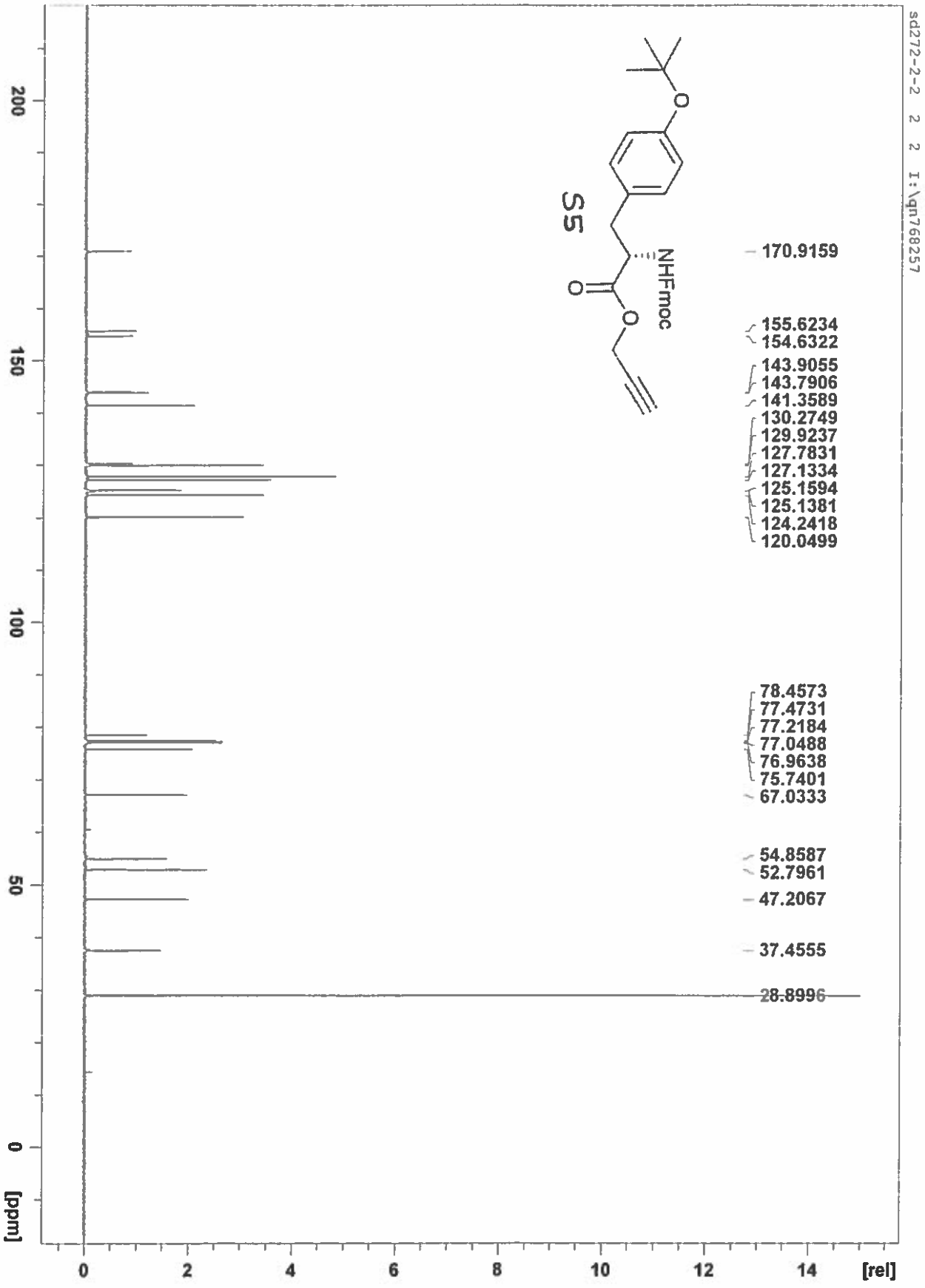
sd272-2-2 2 2 2 I:\qn768257
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O
O
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154.6322
143.9055
143.7906
141.3589
130.2749
129.9237
127.7831
127.1334
125.1594
125.1381
124.2418
120.0499
78.4573
77.4731
77.2184
77.0488
76.9638
75.7401
67.0333
54.8587
52.7961
47.2067
37.4555
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12
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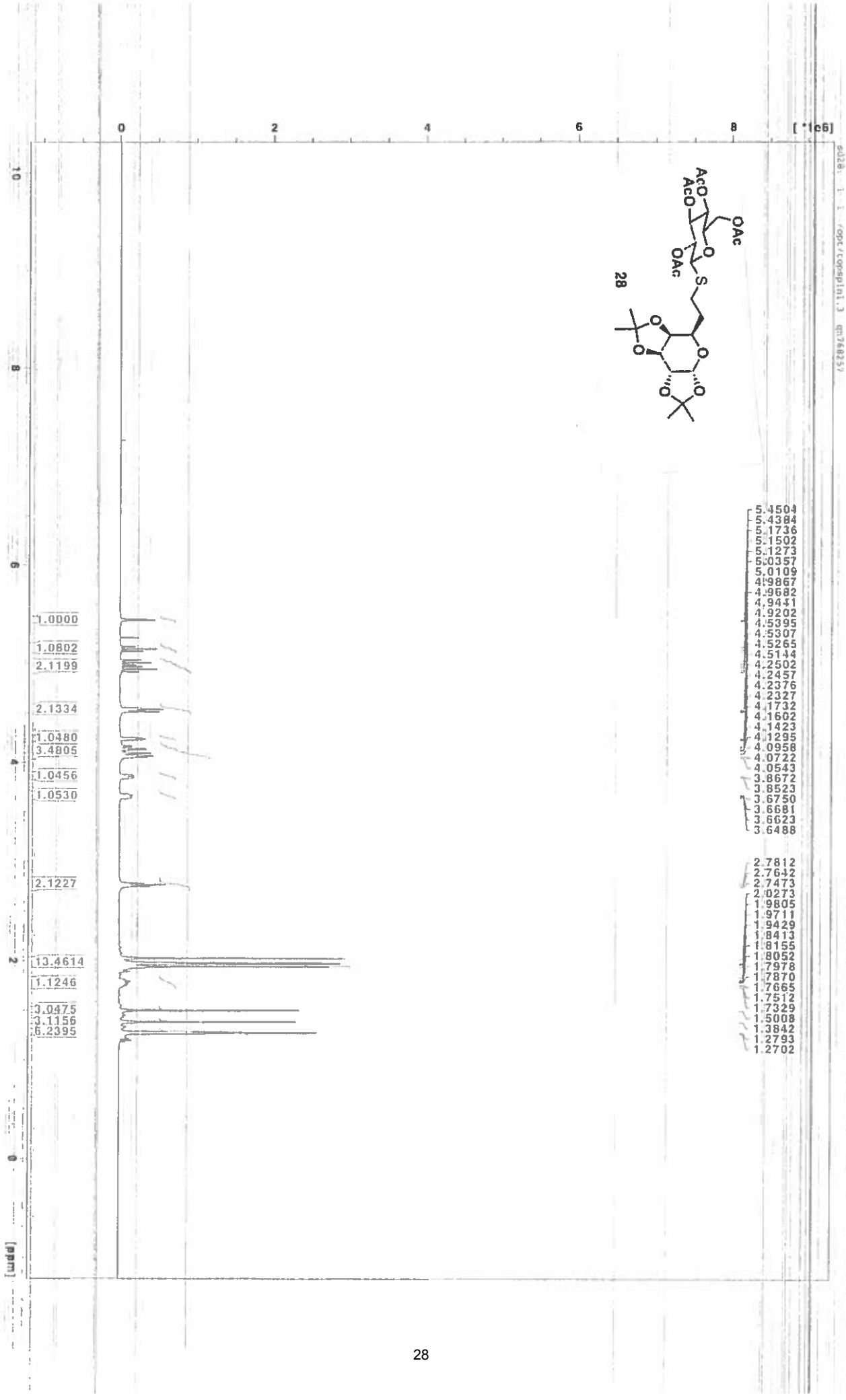
28
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AcO
OAc
OAc
O
S
O
O
O
O
O
O
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5.4384
5.1736
5.1502
5.1273
5.0357
5.0109
4.9867
4.9682
4.9411
4.9202
4.5395
4.5307
4.5265
4.5144
4.2502
4.2457
4.2376
4.2327
4.1732
4.1602
4.1423
4.1295
4.0958
4.0722
4.0543
3.8672
3.8523
3.6750
3.6681
3.6623
3.6488
2.7812
2.7642
2.7473
2.0273
1.9805
1.9711
1.9429
1.8413
1.8155
1.8052
1.7978
1.7870
1.7665
1.7512
1.7329
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1.3842
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1.0802
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1.0480
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1.0530
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6.2395
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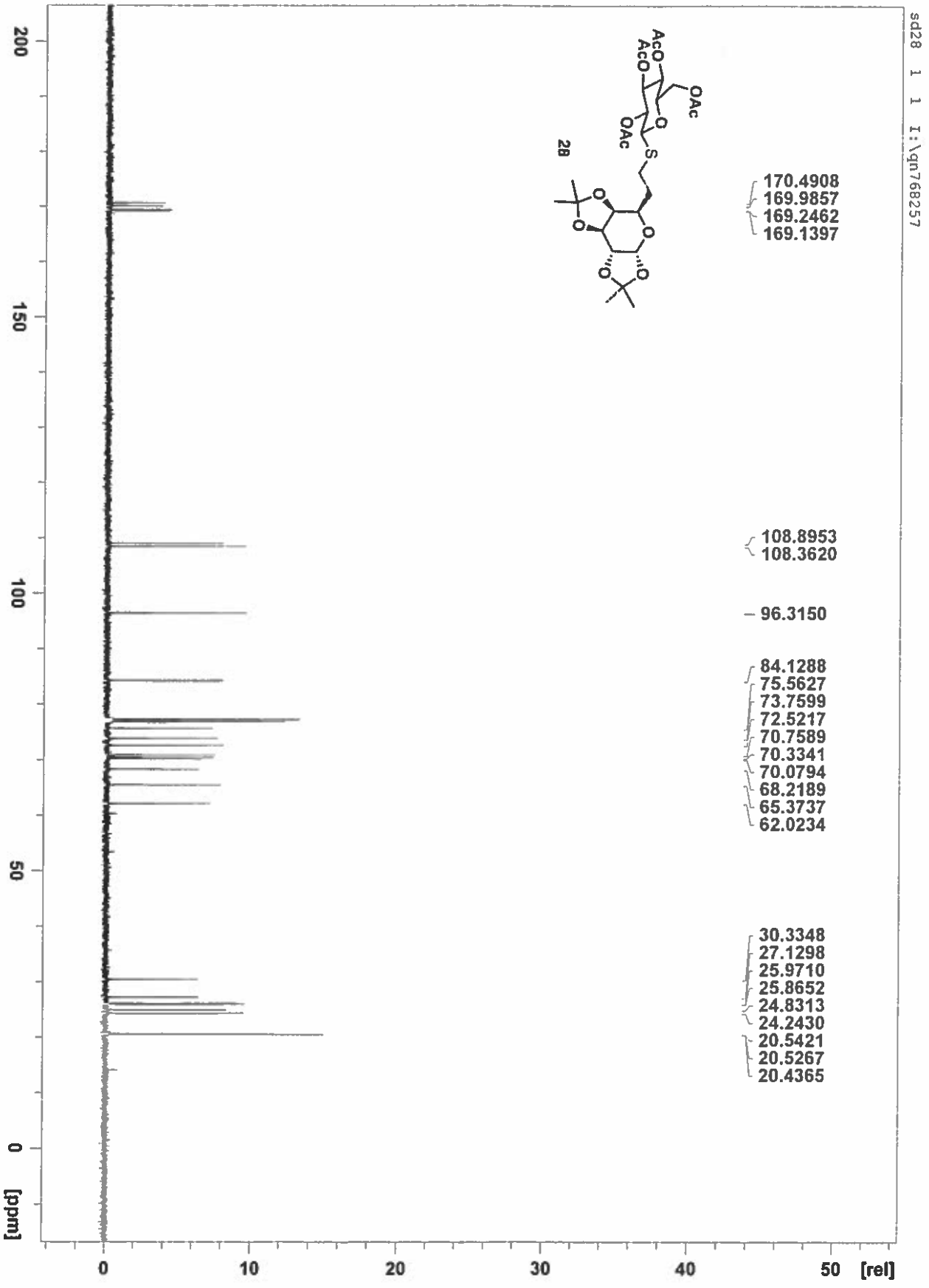
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108.3620
96.3150
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75.5627
73.7599
72.5217
70.7589
70.3341
70.0794
68.2189
65.3737
62.0234
30.3348
27.1298
25.9710
25.8652
24.8313
24.2430
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0
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30
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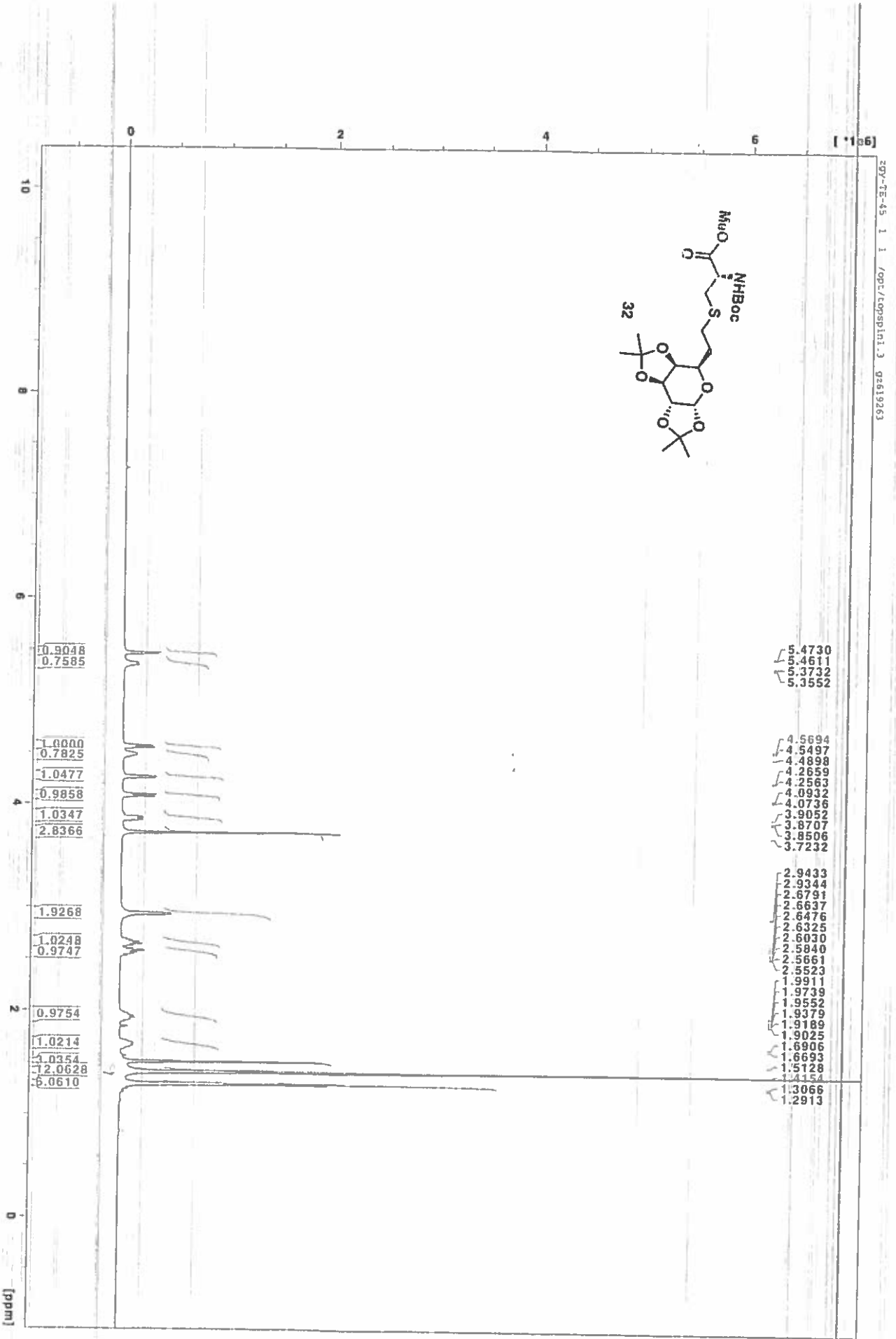
50
[rel]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1.0347
2.8366
1.9268
1.0248
0.9747
0.9754
1.0214
1.0354
12.0628
6.0610
5.4730
5.4611
5.3732
5.3552
4.5694
4.5497
4.4898
4.2659
4.2563
4.0932
4.0736
3.9052
3.8707
3.8506
3.7232
2.9433
2.9344
2.6791
2.6637
2.6476
2.6325
2.6030
2.5840
2.5661
2.5523
1.9911
1.9739
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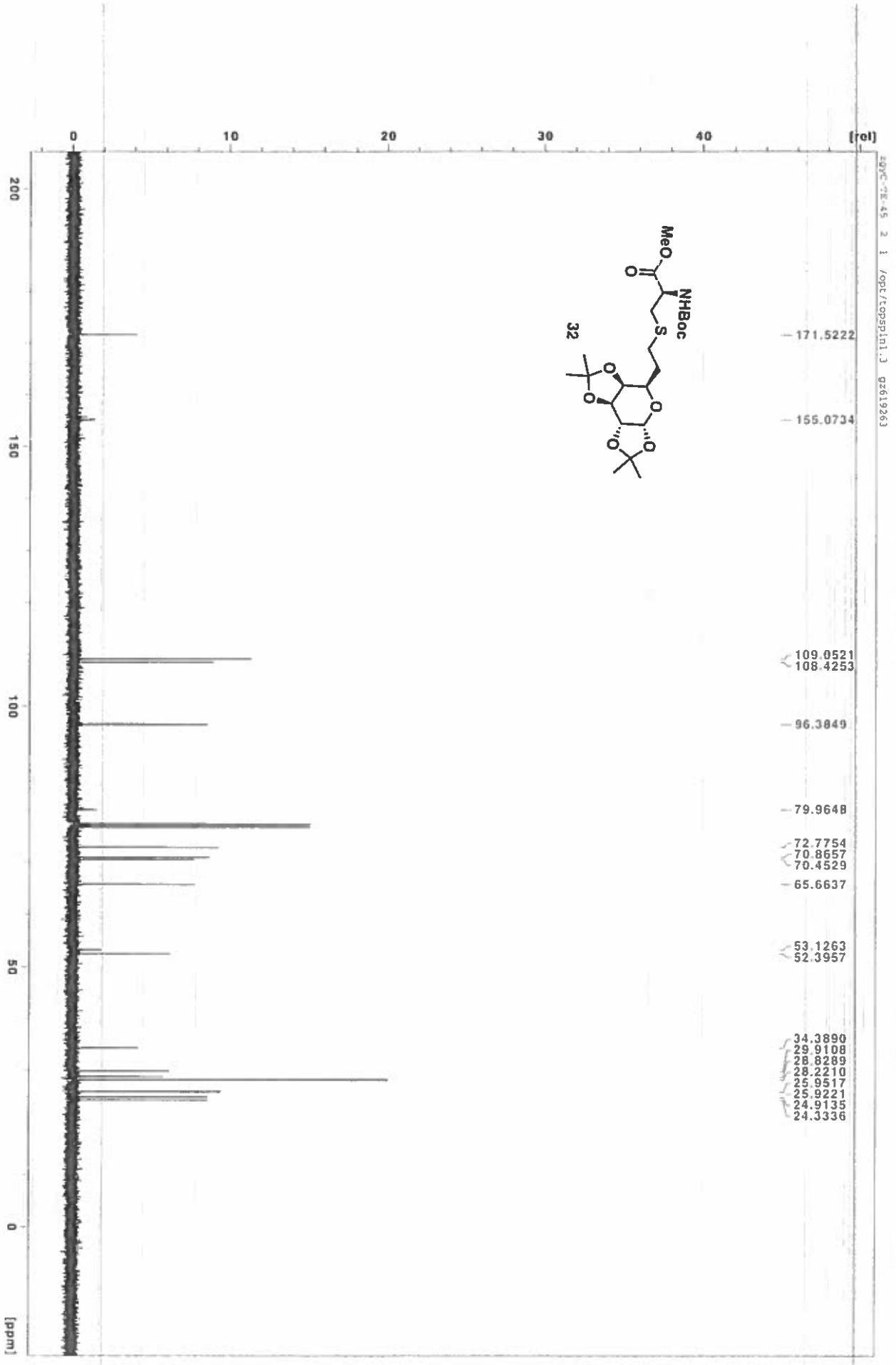
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10
20
30
40
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50
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70.8657
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28.2210
25.9517
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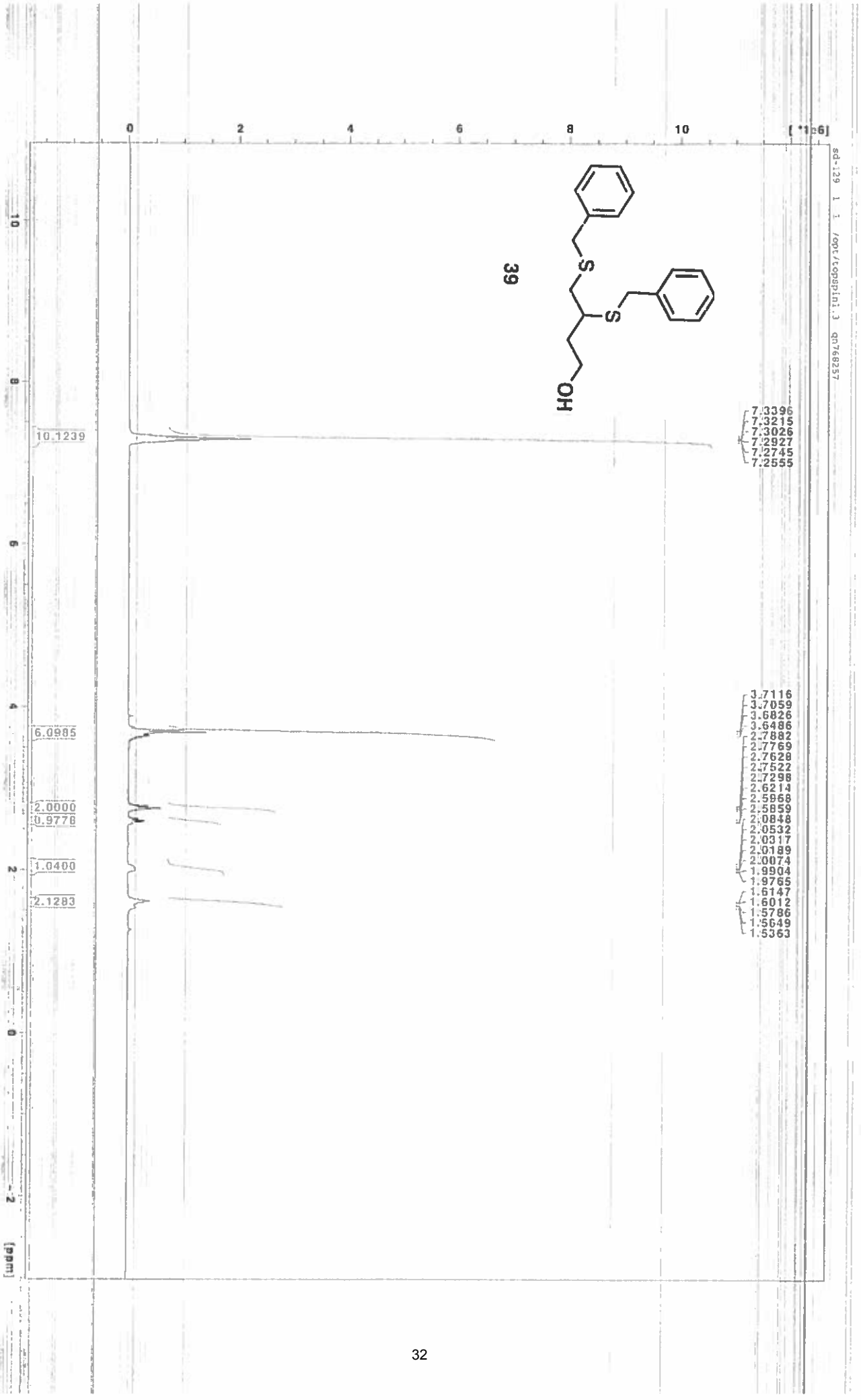
24.9135
24.3336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7.3396
7.3215
7.3026
7.2927
7.2745
7.2555
3.7116
3.7059
3.6826
3.6486
2.7882
2.7769
2.7628
2.7522
2.7298
2.6214
2.5968
2.5859
2.0848
2.0532
2.0317
2.0189
2.0074
1.9904
1.9765
1.6147
1.6012
1.5786
1.5649
1.5363
[ppm]


39
HO
S
S
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128.7797
128.7627
128.4458
128.4024
127.0383
126.9762
77.3242
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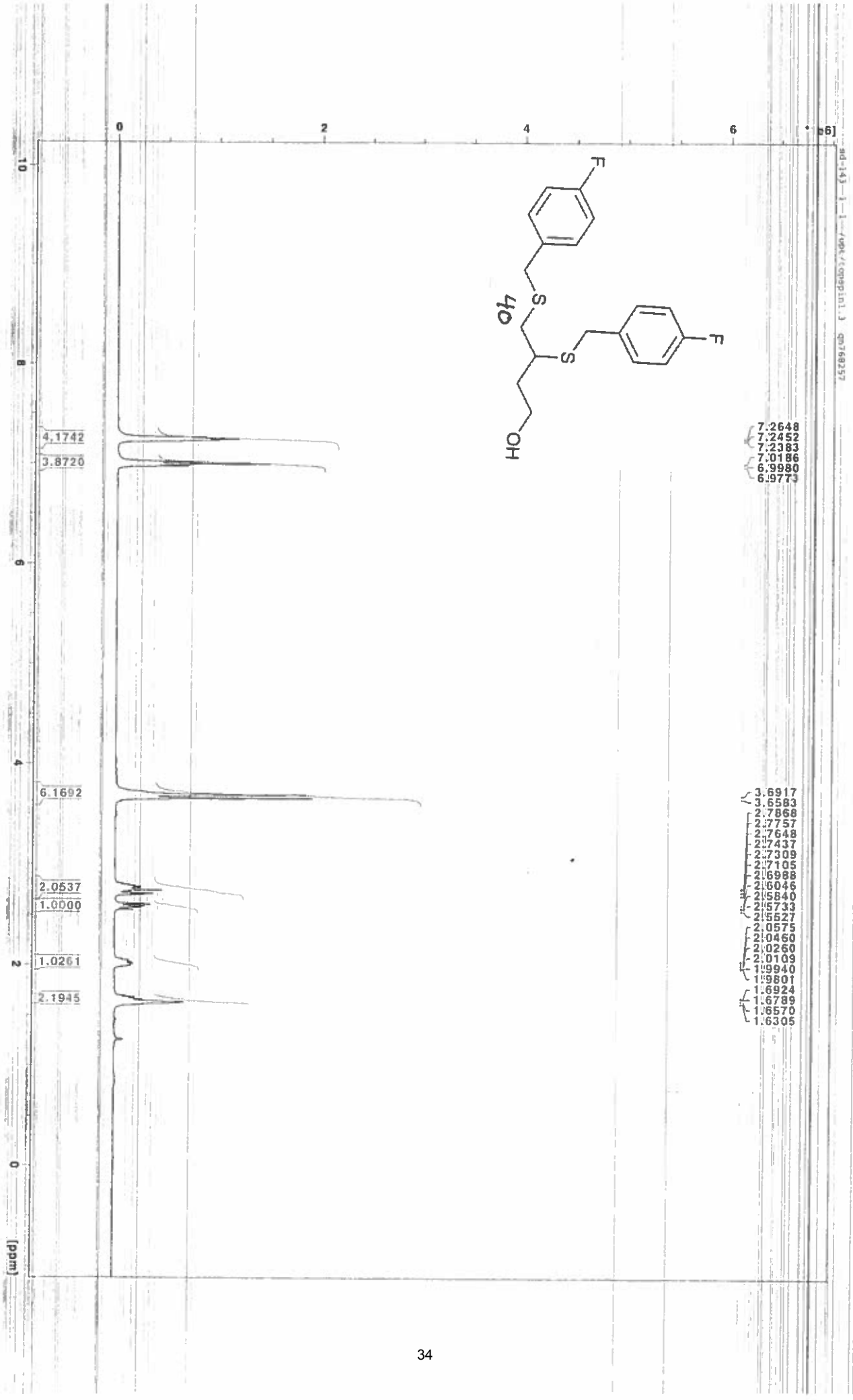
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S
F
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2.7757
2.7648
2.7437
2.7309
2.7105
2.6988
2.6046
2.5840
2.5733
2.5527
2.0575
2.0460
2.0260
2.0109
1.9940
1.9801
1.6924
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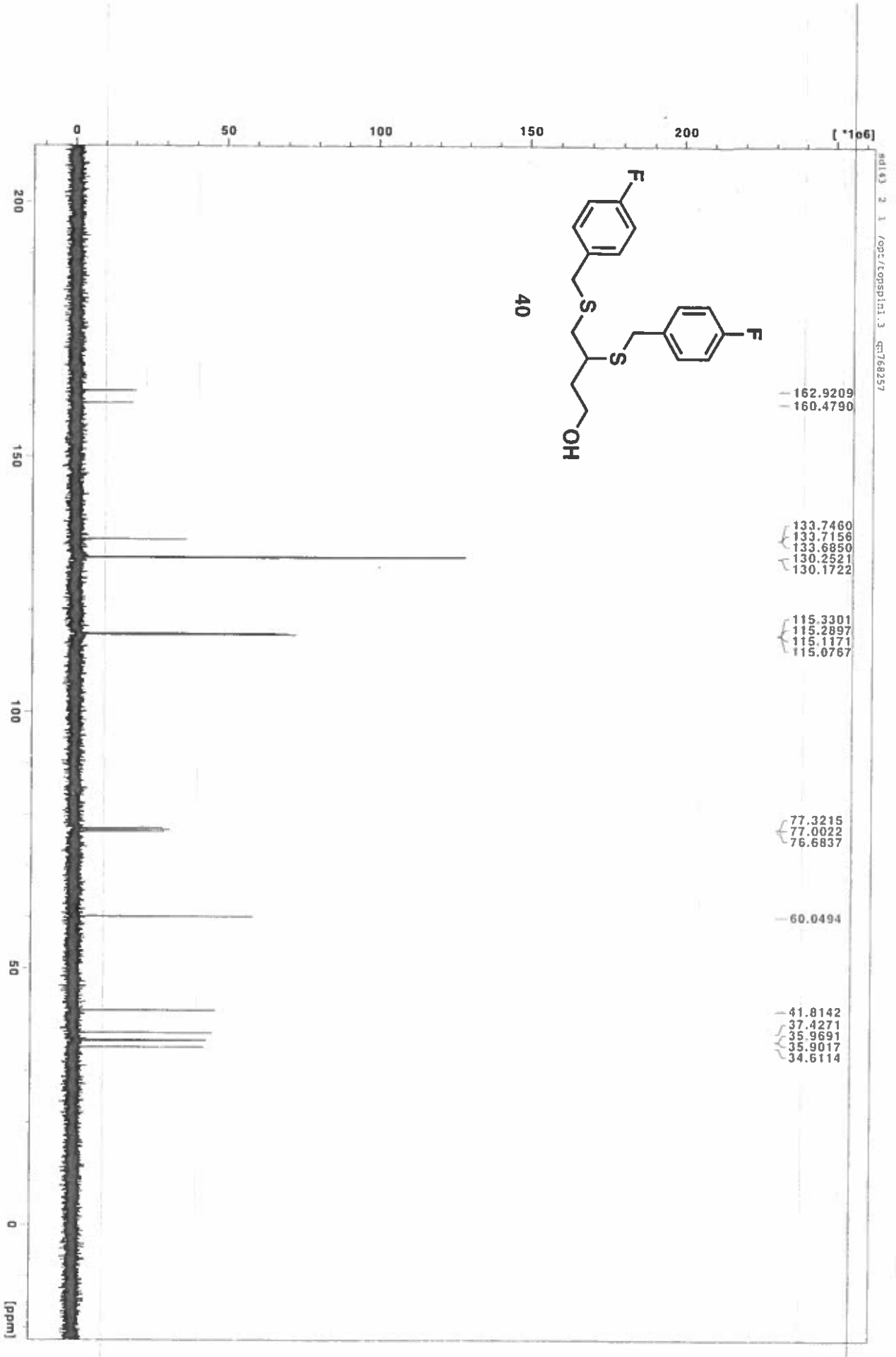
[ppm]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50
100
150
200
[*1e6]
200
150
100
50
0
[ppm]
F
S
S
F
OH
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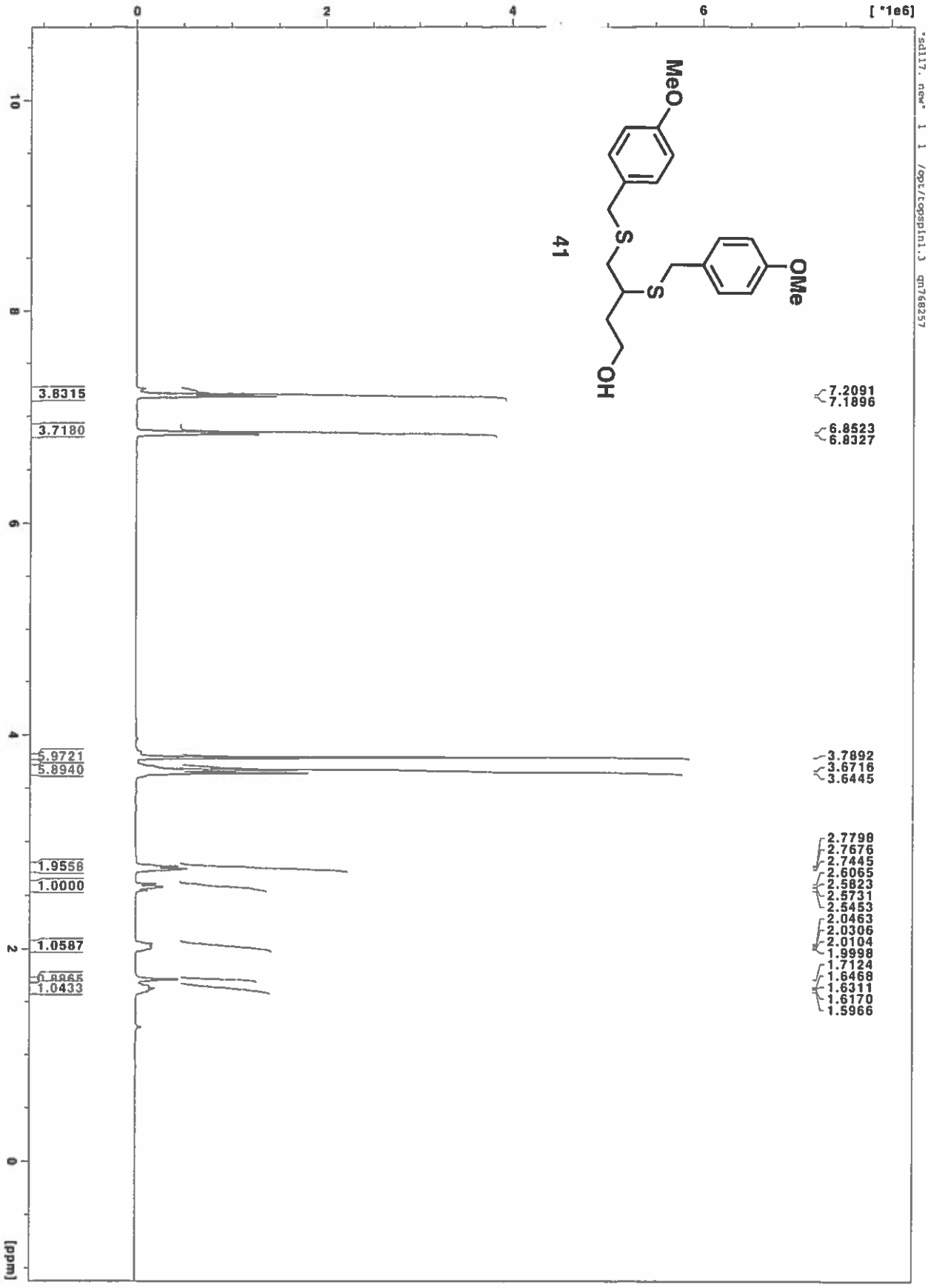
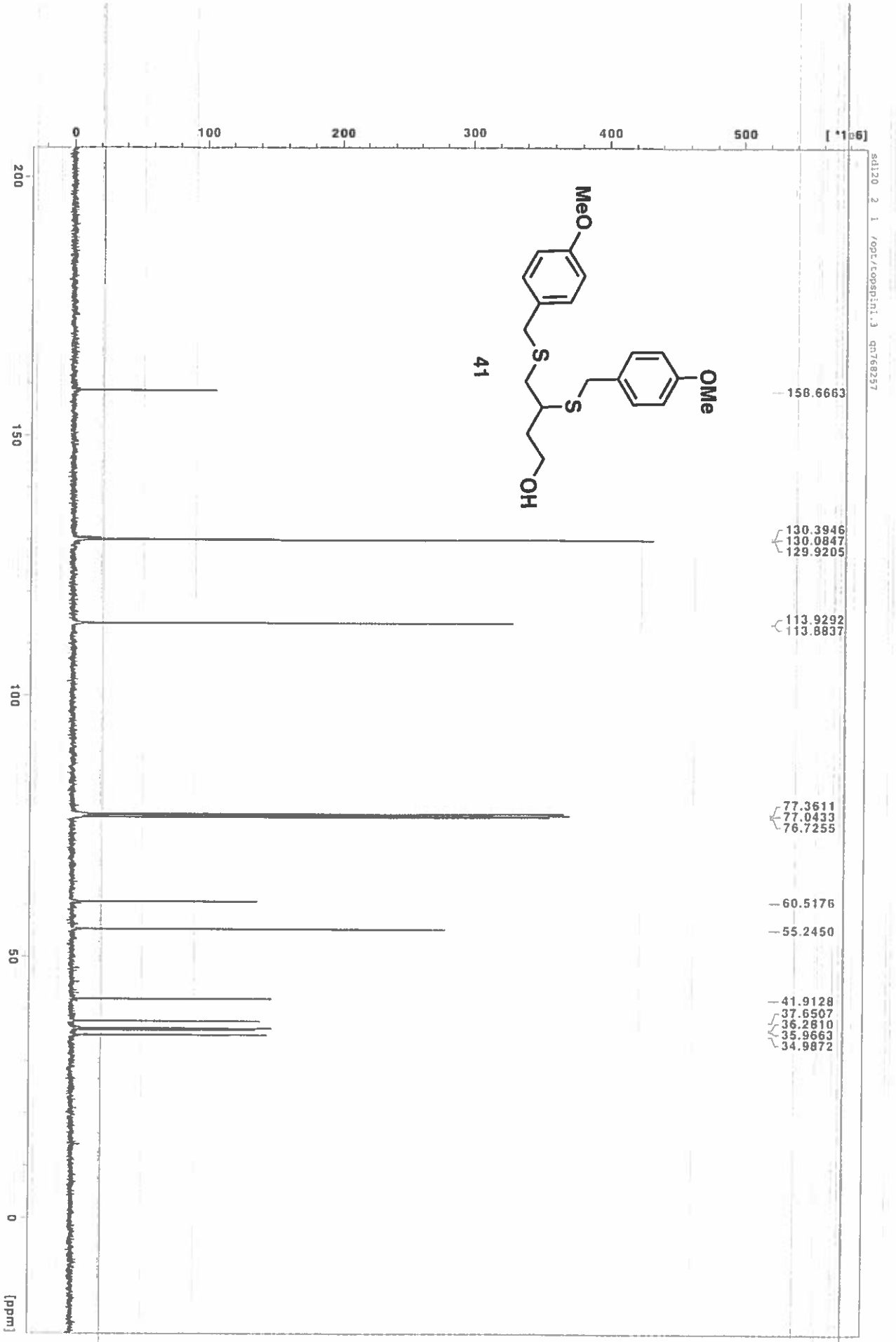
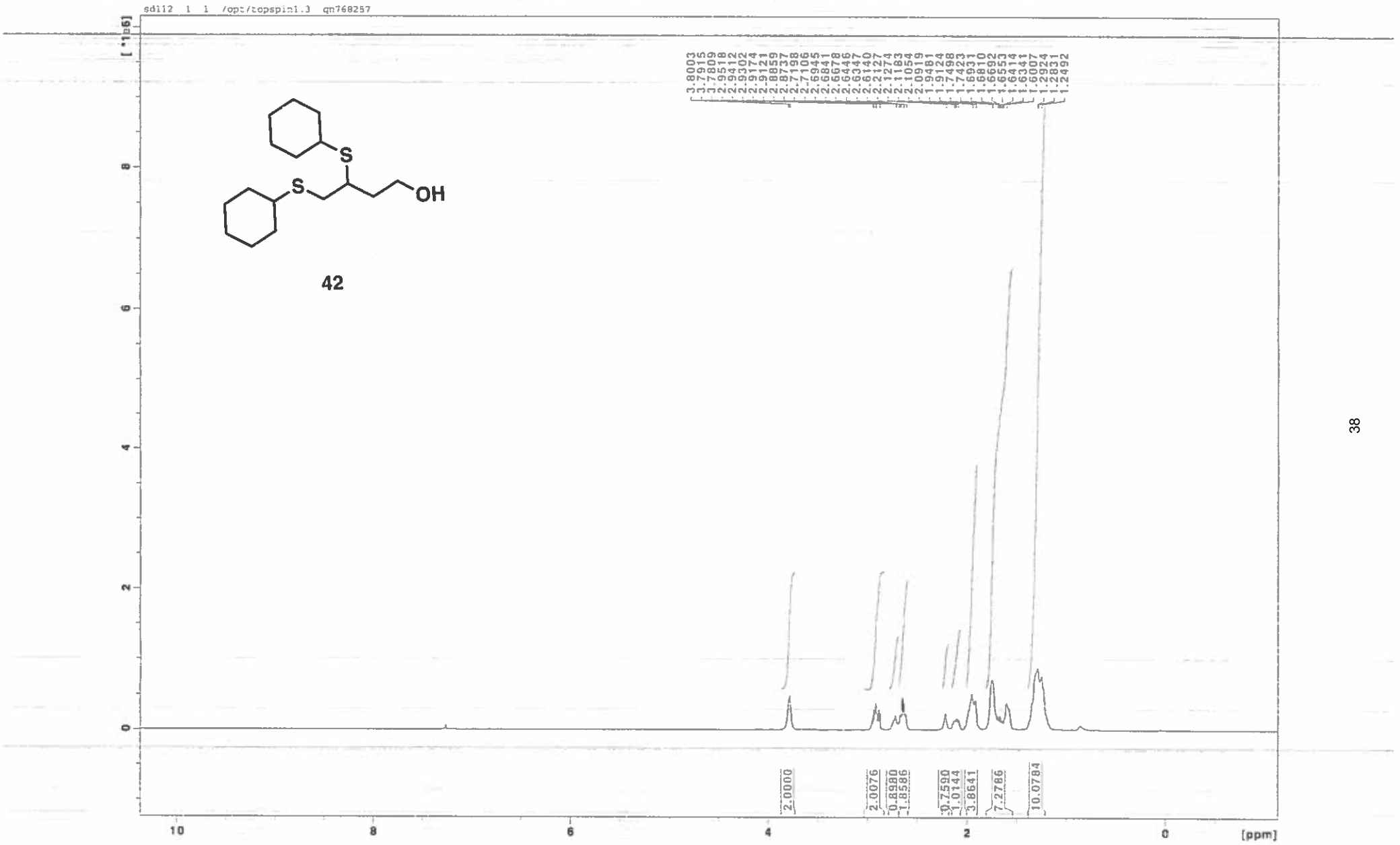
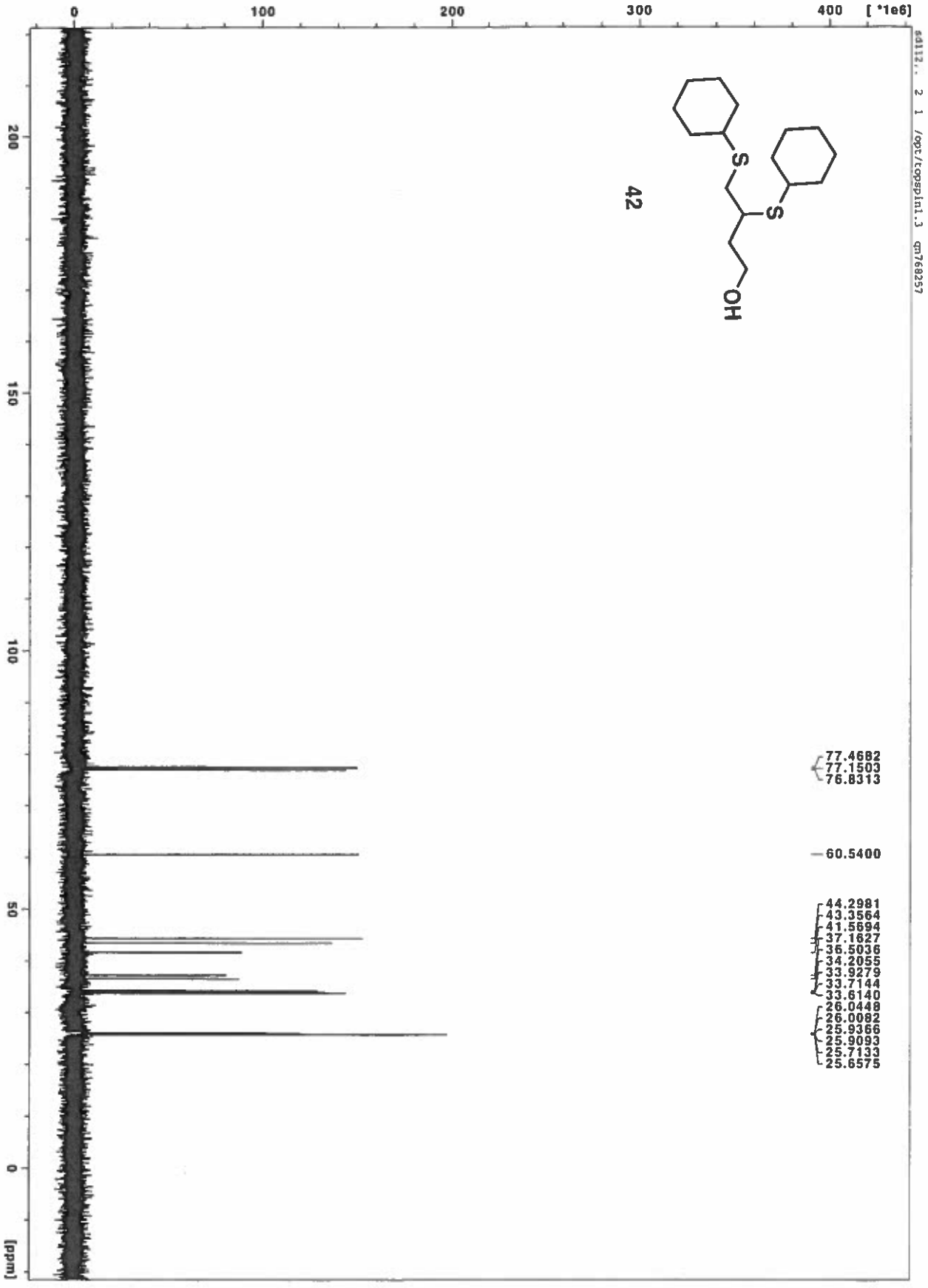
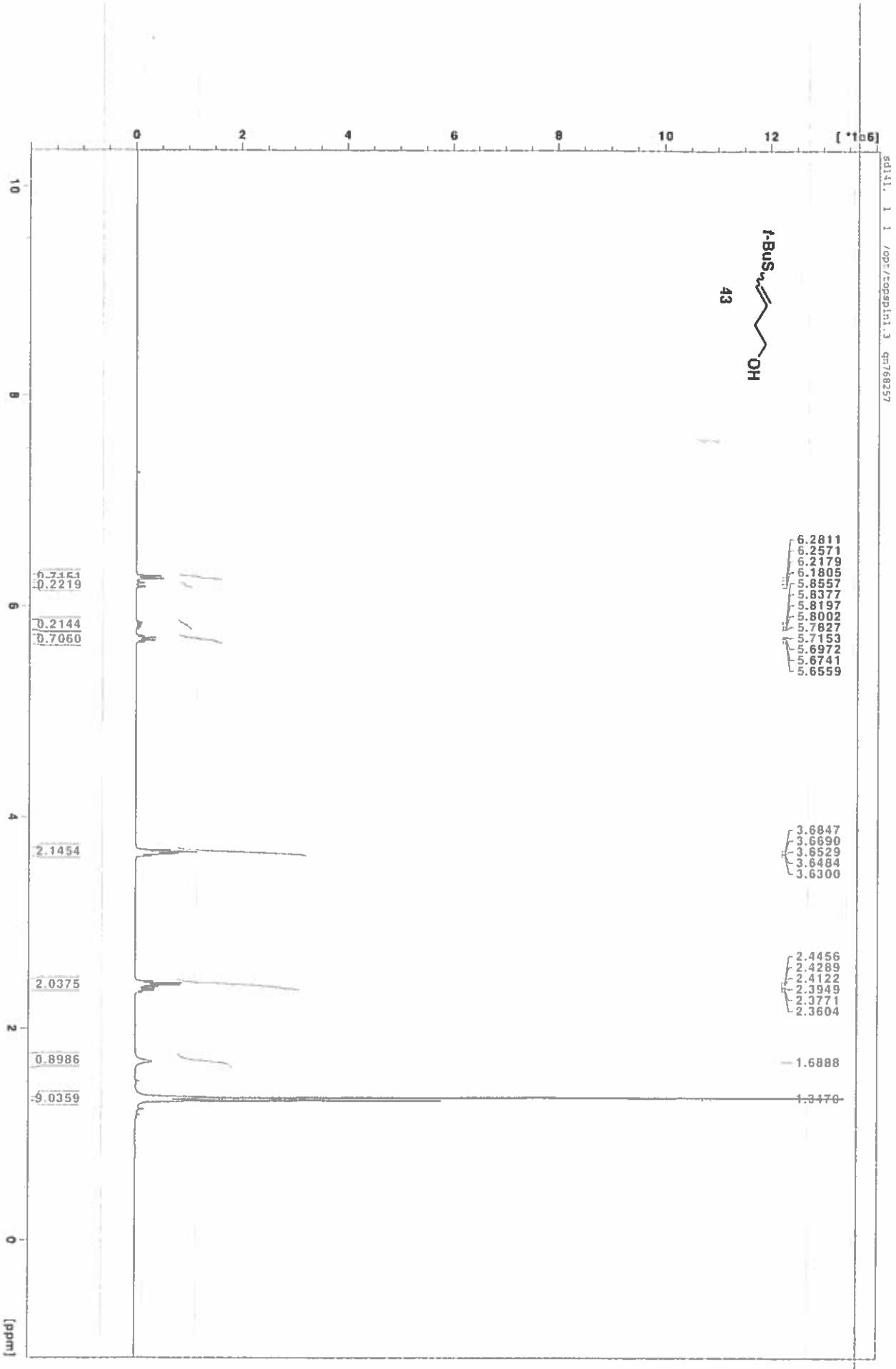
160.4790
133.7460
133.7156
133.6850
130.2521
130.1722
115.3301
115.2897
115.1171
115.0767
77.3215
77.0022
76.6837
60.0494
41.8142
37.4271
35.9691
35.9017
34.6114

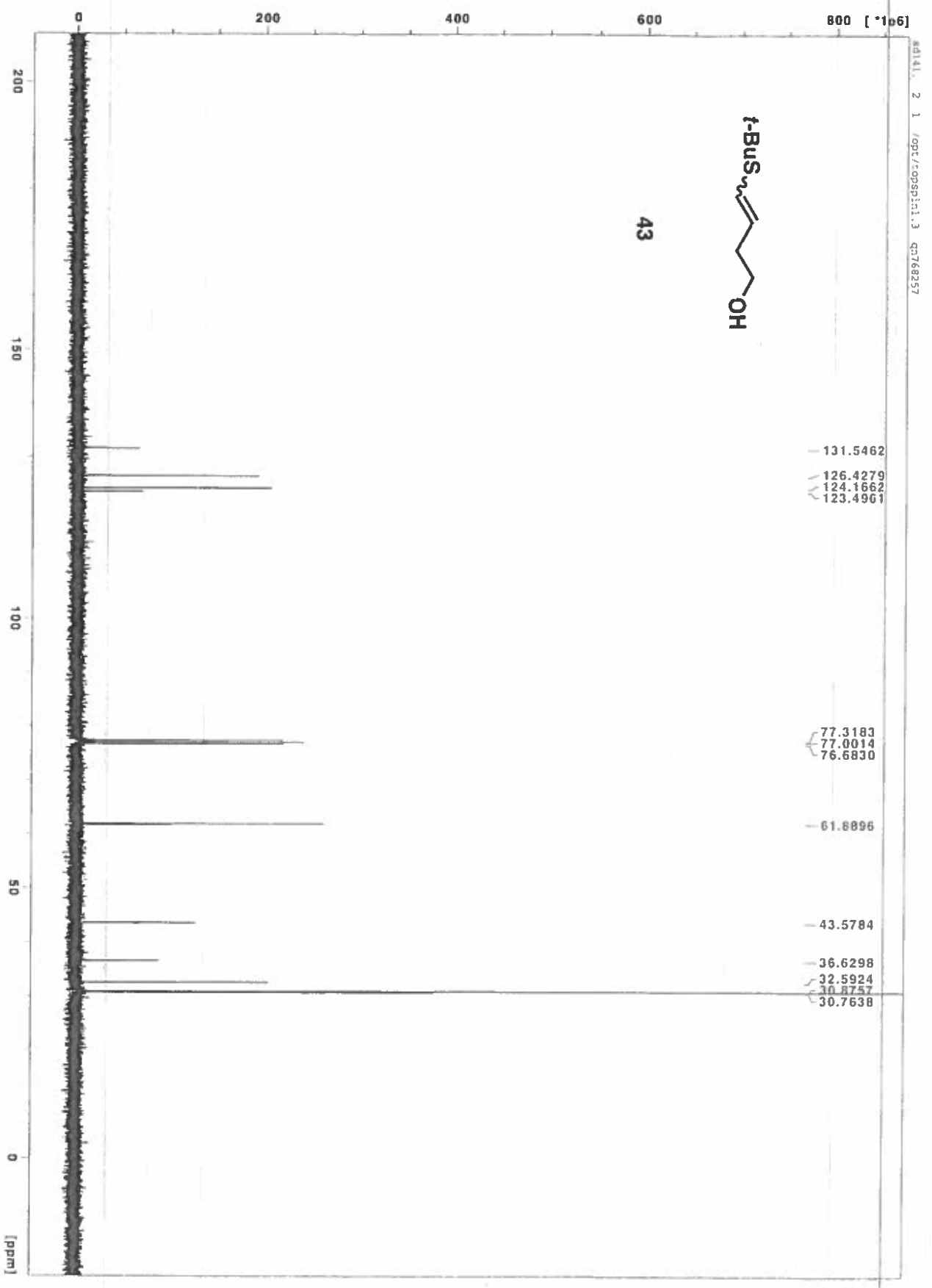

41
MeO
OMe
S
S
OH
3.8315
3.7180
5.9721
5.8940
1.9556
1.0000
1.0587
1.0433
7.2091
7.1896
6.8523
6.8327
3.7892
3.6716
3.6445
2.7798
2.7676
2.7445
2.6065
2.5823
2.5731
2.5453
2.0463
2.0306
2.0104
1.9998
1.7124
1.6468
1.6311
1.6170
1.5966
[ppm]
[*1e6]

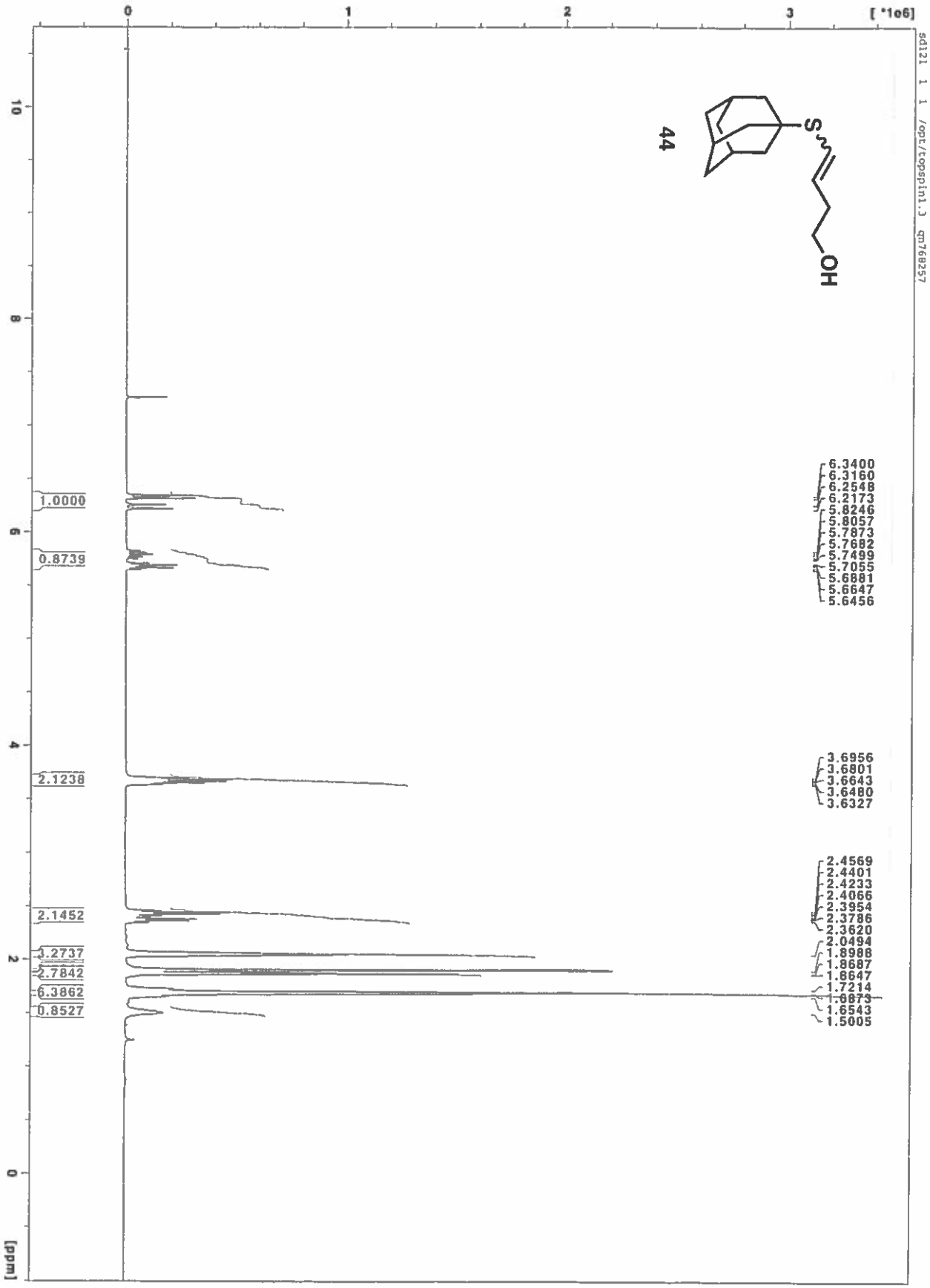

MeO
S
S
OMe
OH
41
158.6663
130.3946
130.0847
129.9205
113.9292
113.8837
77.3611
77.0433
76.7255
60.5176
55.2450
41.9128
37.6507
36.2810
35.9663
34.9872
0
100
200
300
400
500
[ppm]

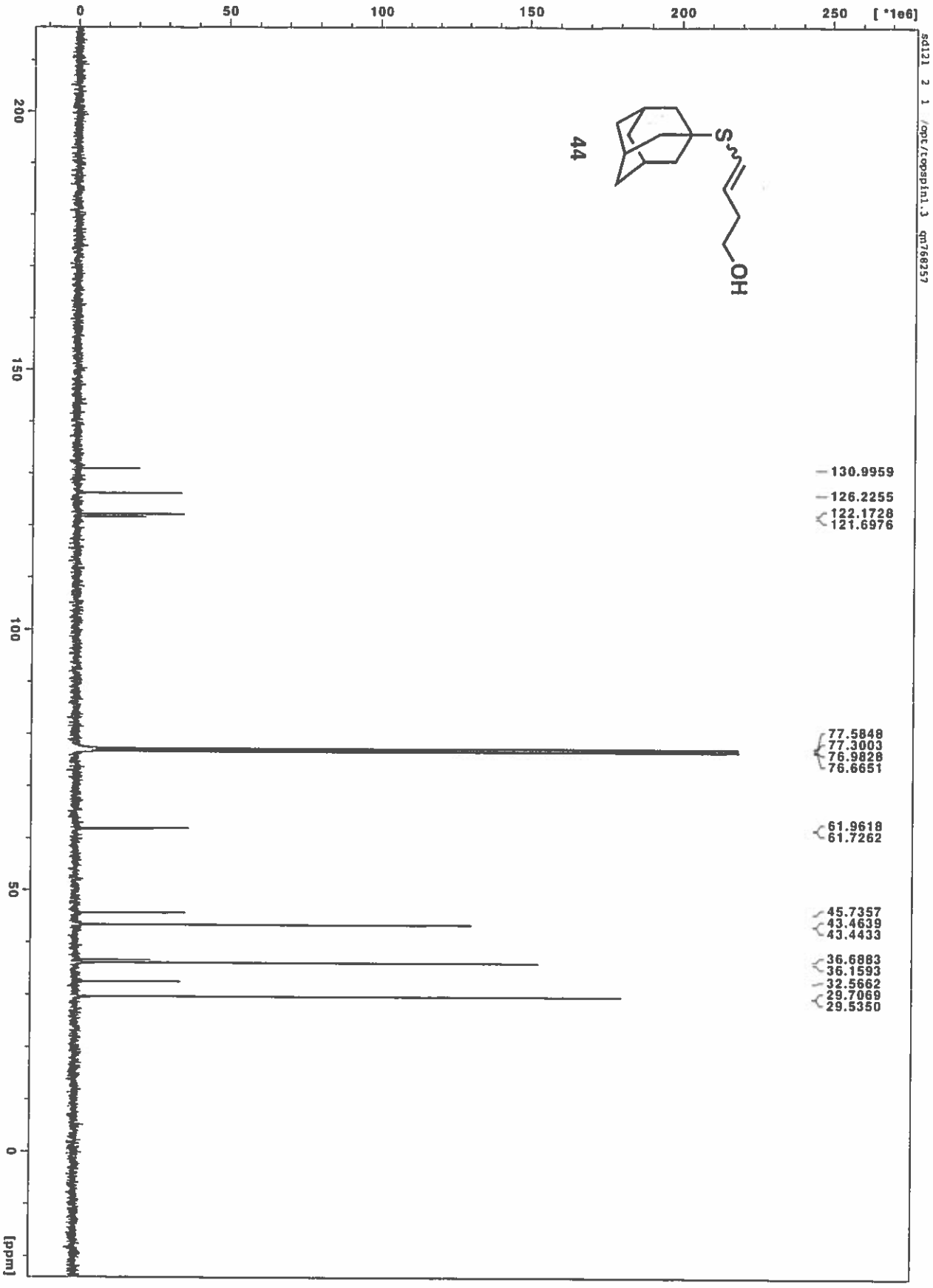

sdi12 1 1 /opt/topspin1.3 qn768257
[*1e6]
3.8003
3.7915
3.7809
2.9518
2.9412
2.9302
2.9174
2.9121
2.8859
2.8737
2.7198
2.7106
2.6945
2.6841
2.6678
2.6646
2.6547
2.6140
2.2127
2.2074
2.1183
2.1054
2.0919
1.9481
1.9124
1.7468
1.7423
1.6931
1.6810
1.6692
1.6553
1.6414
1.6341
1.6007
1.2924
1.2831
1.2492
S
S
OH
42
2.0000
2.0076
0.8980
1.8586
9.7590
1.0144
3.8641
7.2766
10.0784
10
8
6
4
2
0
[ppm]

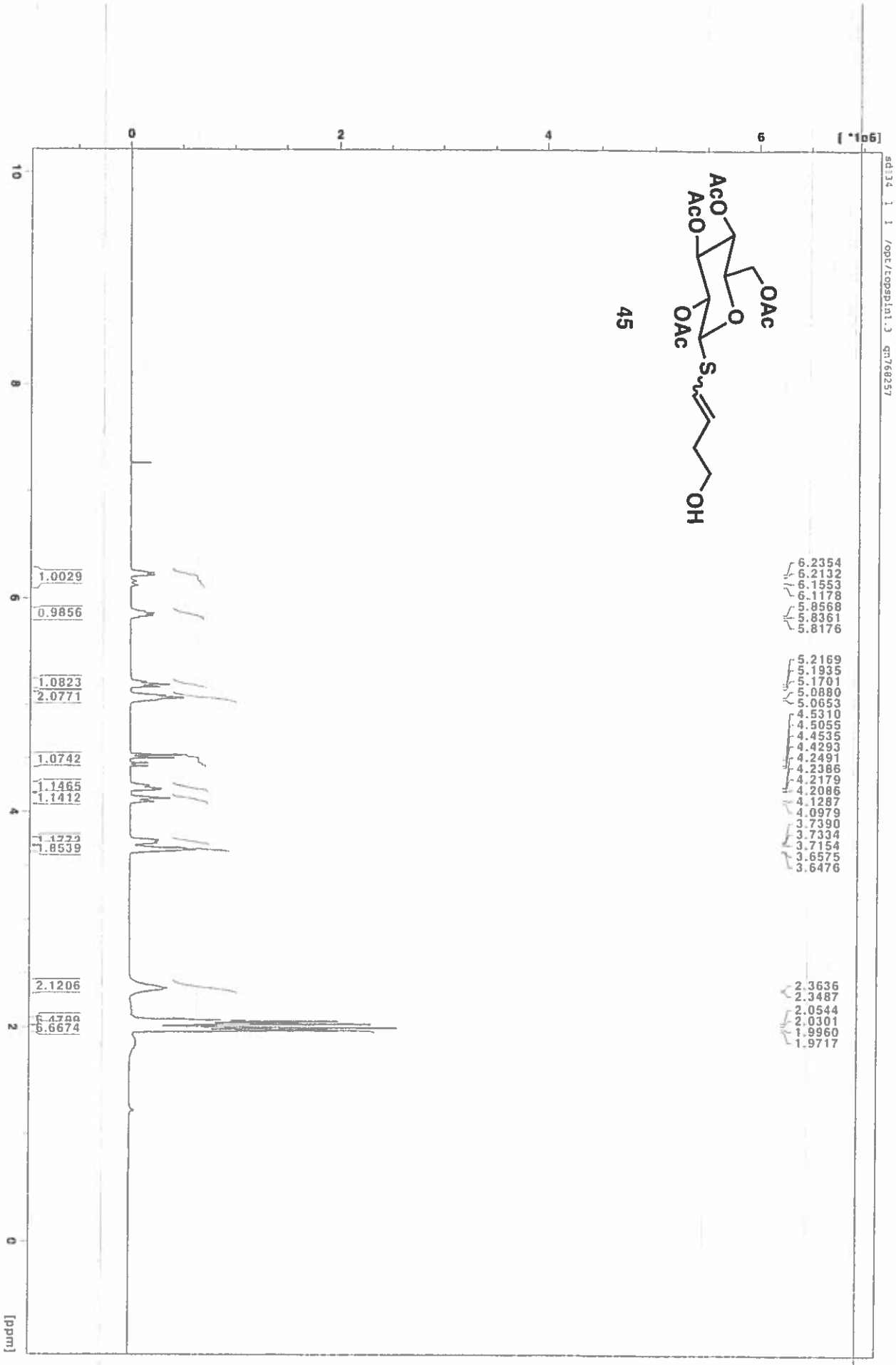

0
100
200
300
400
[*1e6]
200
150
100
50
0
[ppm]
edii2,, 2 1 /opt/topspin1.3 qm768257
42
S
S
OH
77.4682
77.1503
76.8313
60.5400
44.2981
43.3564
41.5694
37.1627
36.5036
34.2055
33.9279
33.7144
33.6140
26.0448
26.0082
25.9366
25.9093
25.7133
25.6575

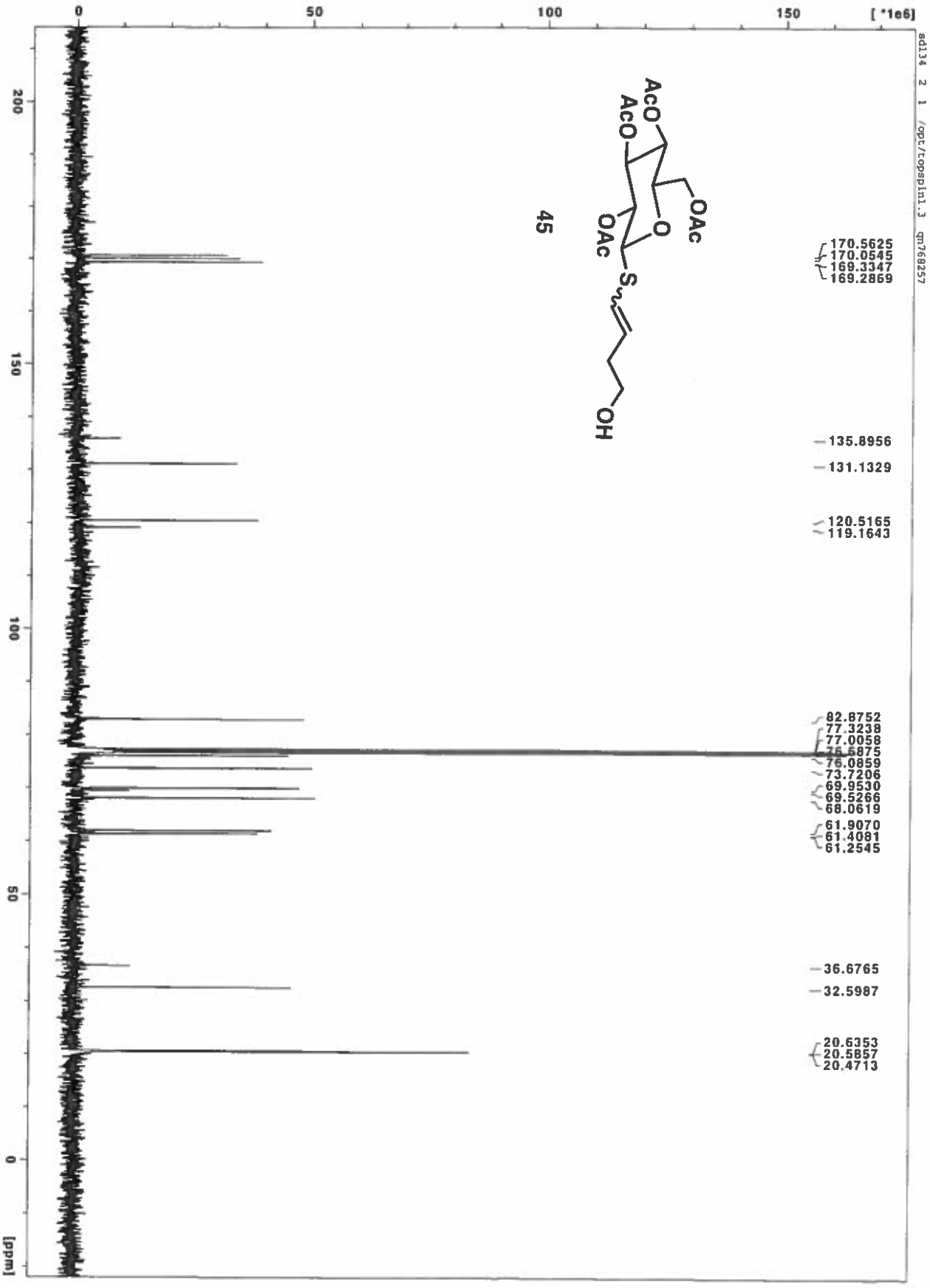

t-BuS
OH
43
6.2811
6.2571
6.2179
6.1805
5.8557
5.8377
5.8197
5.8002
5.7827
5.7153
5.6972
5.6741
5.6559
3.6847
3.6690
3.6529
3.6484
3.6300
2.4456
2.4289
2.4122
2.3949
2.3771
2.3604
1.6888
1.3170
0.2219
0.2144
0.7060
2.1454
2.0375
0.8986
9.0359
[ppm]

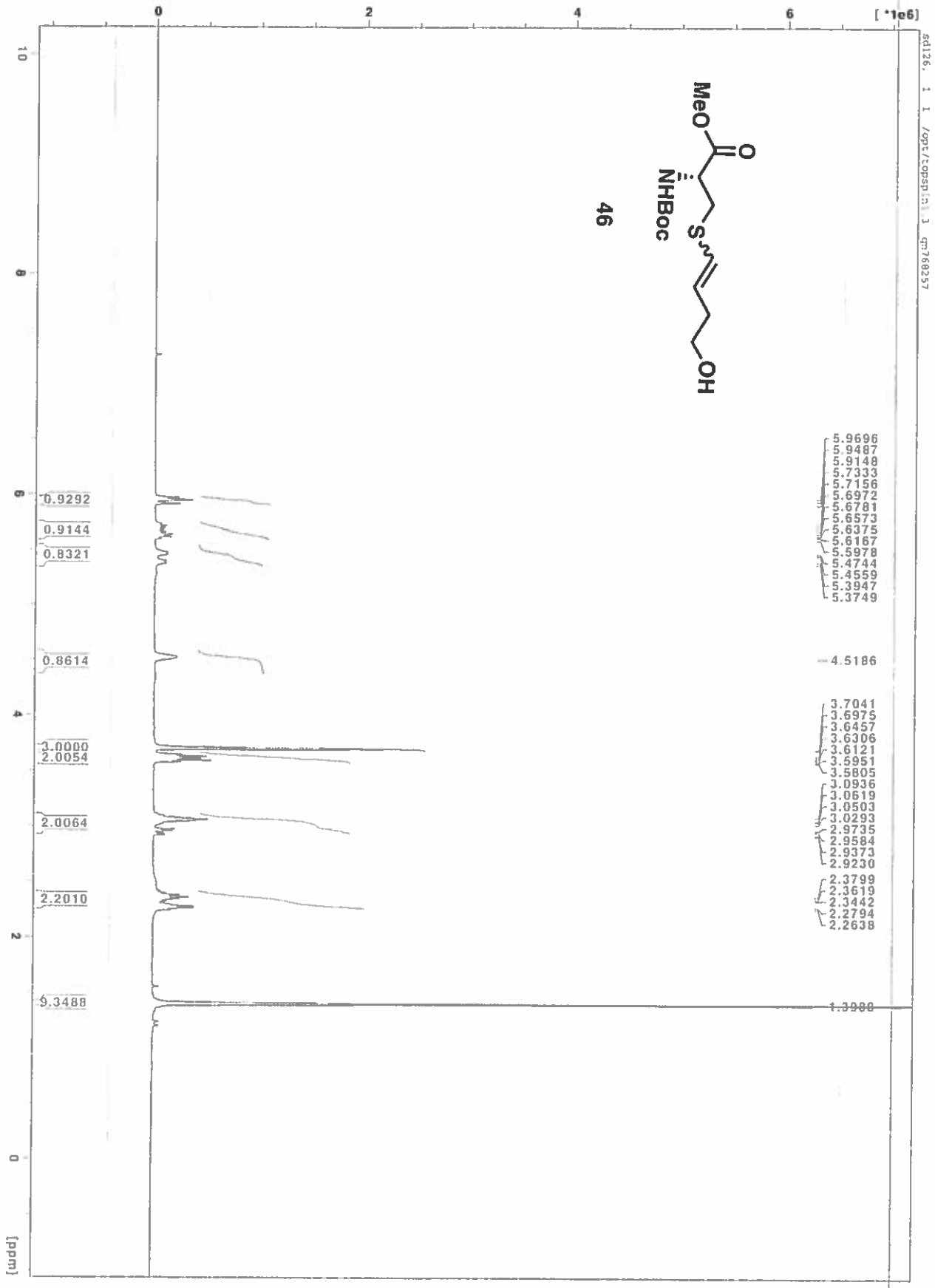

0
200
400
600
800 [*1e6]
200
150
100
50
0
[ppm]
43
HO
t-Bu
131.5462
126.4279
124.1662
123.4961
77.3183
77.0014
76.6830
61.8896
43.5784
36.6298
32.5924
30.8757
30.7638

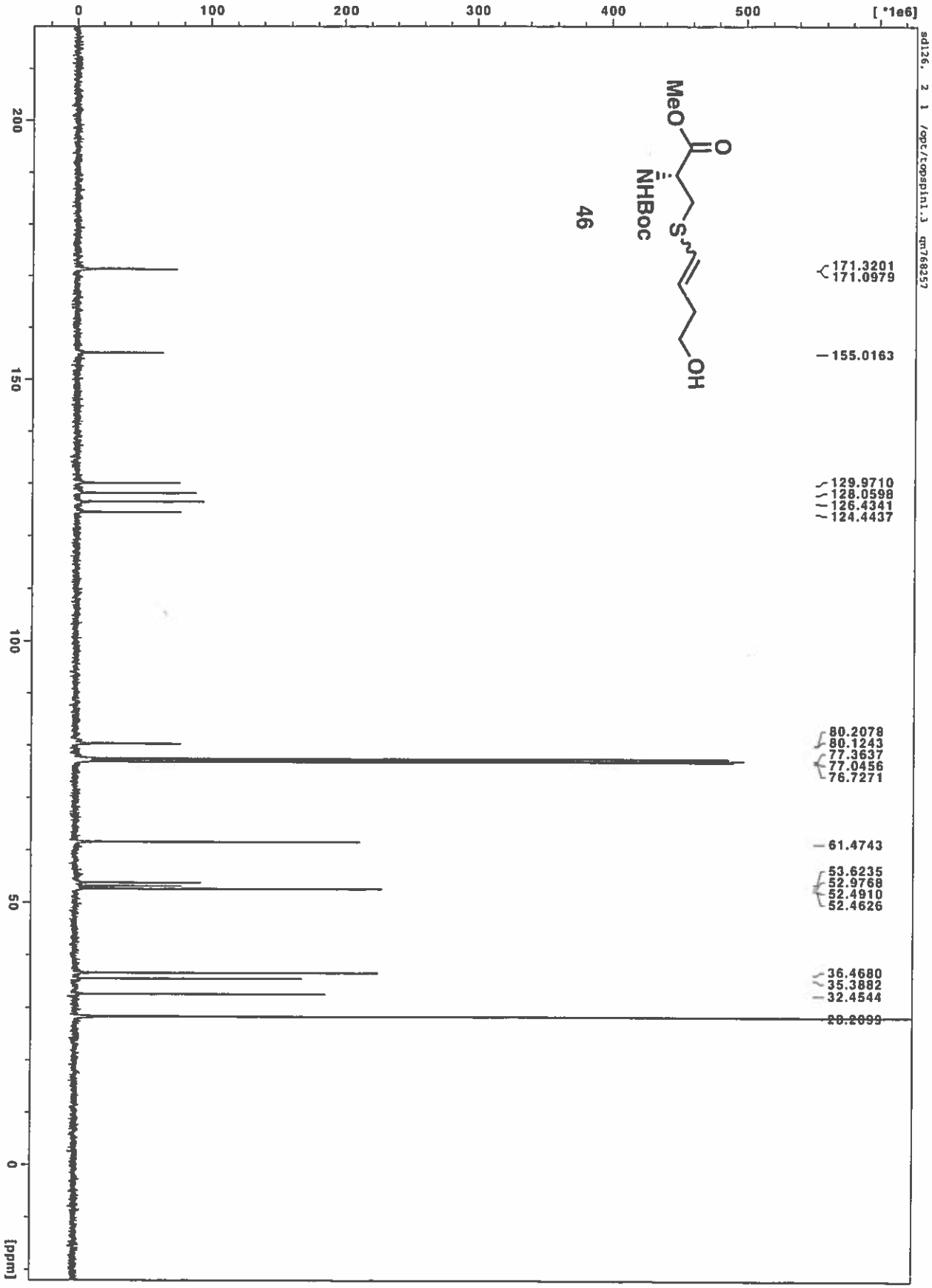

44
S
OH
6.3400
6.3160
6.2548
6.2173
5.8246
5.8057
5.7873
5.7682
5.7499
5.7055
5.6881
5.6647
5.6456
3.6956
3.6801
3.6643
3.6480
3.6327
2.4569
2.4401
2.4233
2.4066
2.3954
2.3786
2.3620
2.0494
1.8988
1.8687
1.8647
1.7214
1.6543
1.5005
1.0000
0.8739
2.1238
2.1452
3.2737
2.7842
6.3862
0.8527
[ppm]
[*1e6]
sd121 1 1 /opt/topspin1.3 qm768257

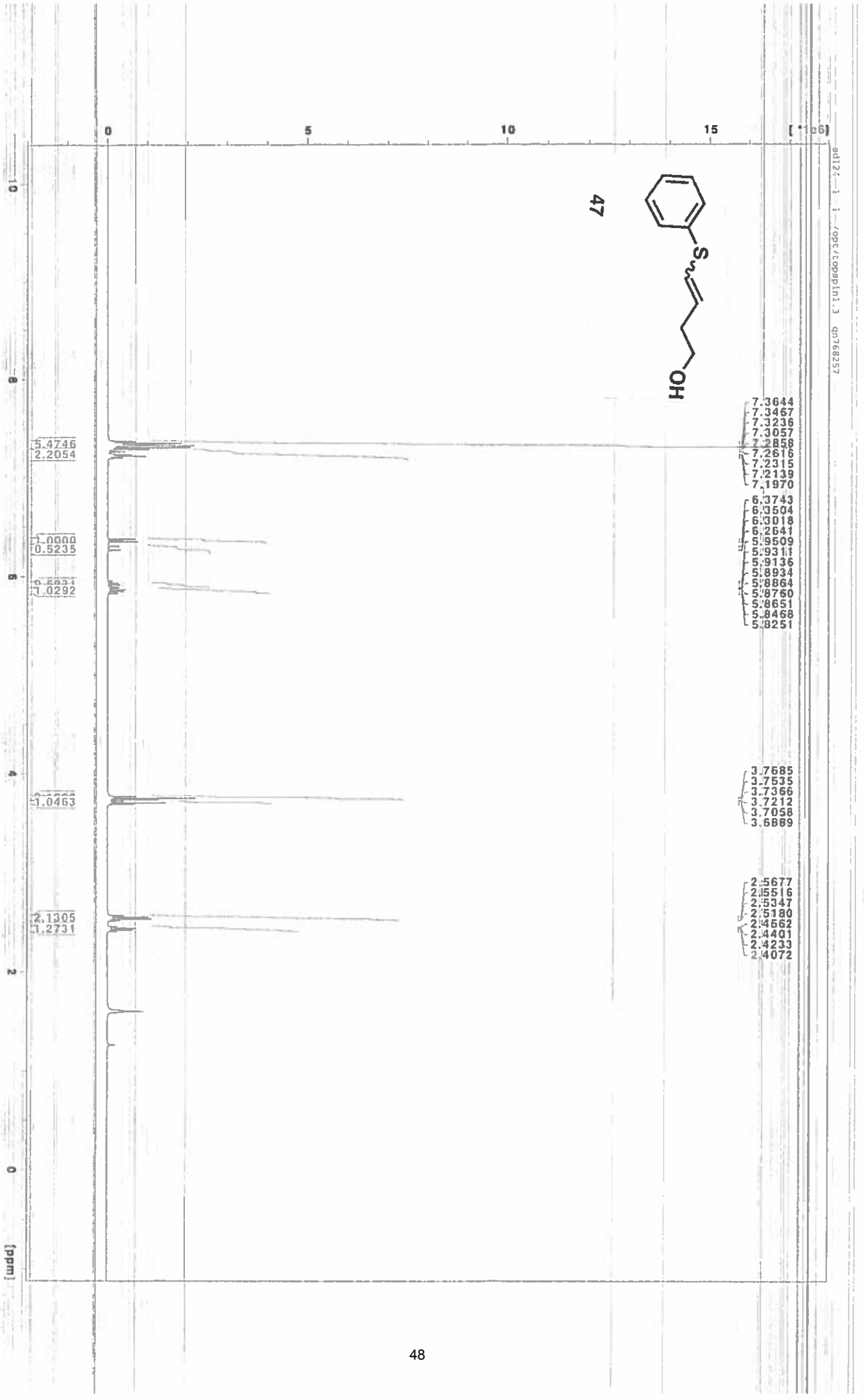

0
50
100
150
200
250
[*1e6]
200
150
100
50
0
[ppm]
sd121 2 1 /opt/topspin1.3 qm766257
44
S
OH
130.9959
126.2255
122.1728
121.6976
77.5848
77.3003
76.9828
76.6651
61.9618
61.7262
45.7357
43.4639
43.4433
36.6883
36.1593
32.5662
29.7069
29.5350

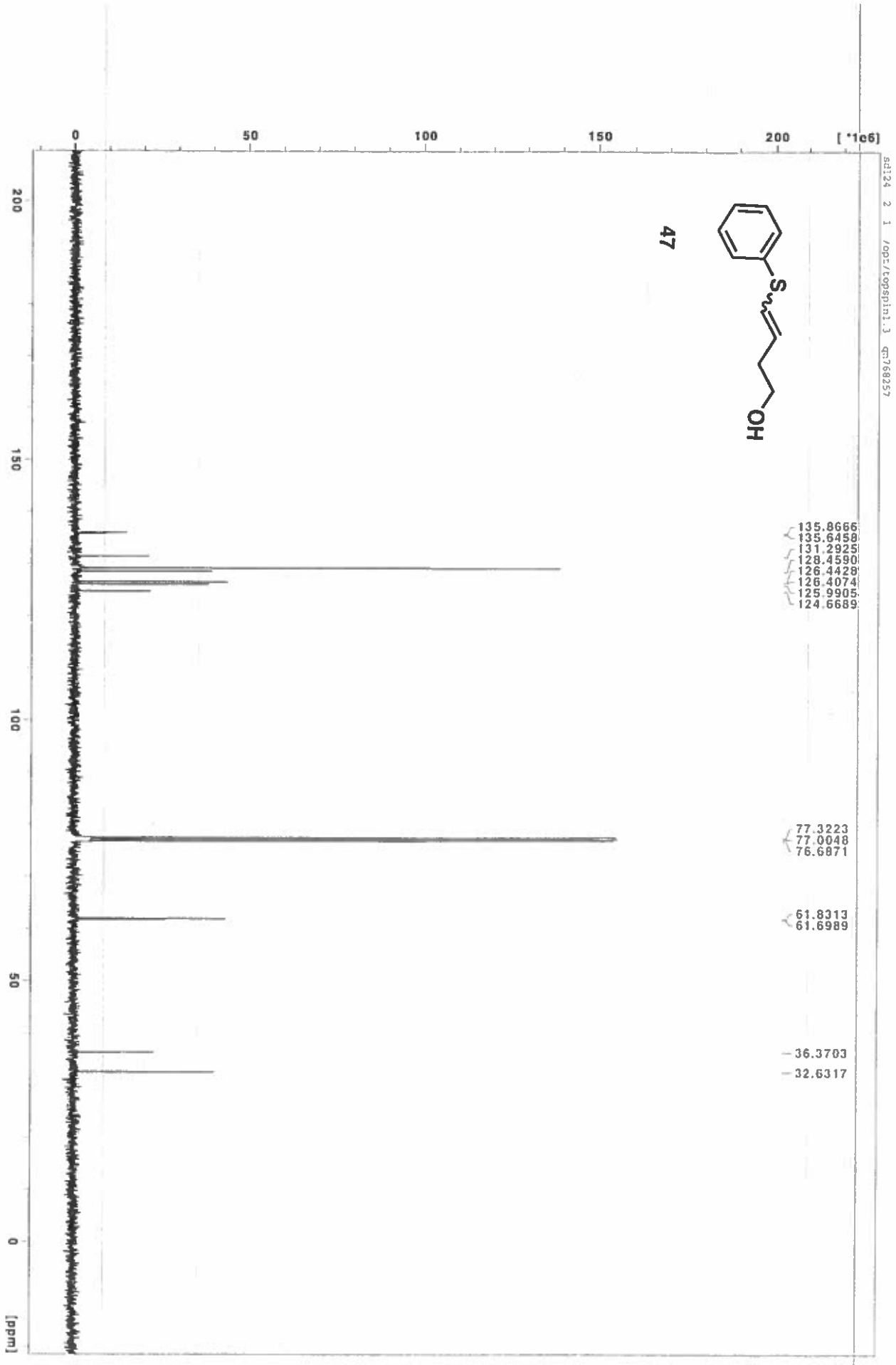

45
AcO
AcO
OAc
OAc
O
S
OH
[*1e6]
[ppm]
sdi34 1 1 /opt/topspin1.3 qn768257
1.0029
0.9856
1.0823
2.0771
1.0742
1.1465
1.1412
1.8539
2.1206
6.6674
6.2354
6.2132
6.1553
6.1178
5.8568
5.8361
5.8176
5.2169
5.1935
5.1701
5.0880
5.0653
4.5310
4.5055
4.4535
4.4293
4.2491
4.2366
4.2179
4.2086
4.1287
4.0979
3.7390
3.7334
3.7154
3.6575
3.6476
2.3636
2.3487
2.0544
2.0301
1.9960
1.9717

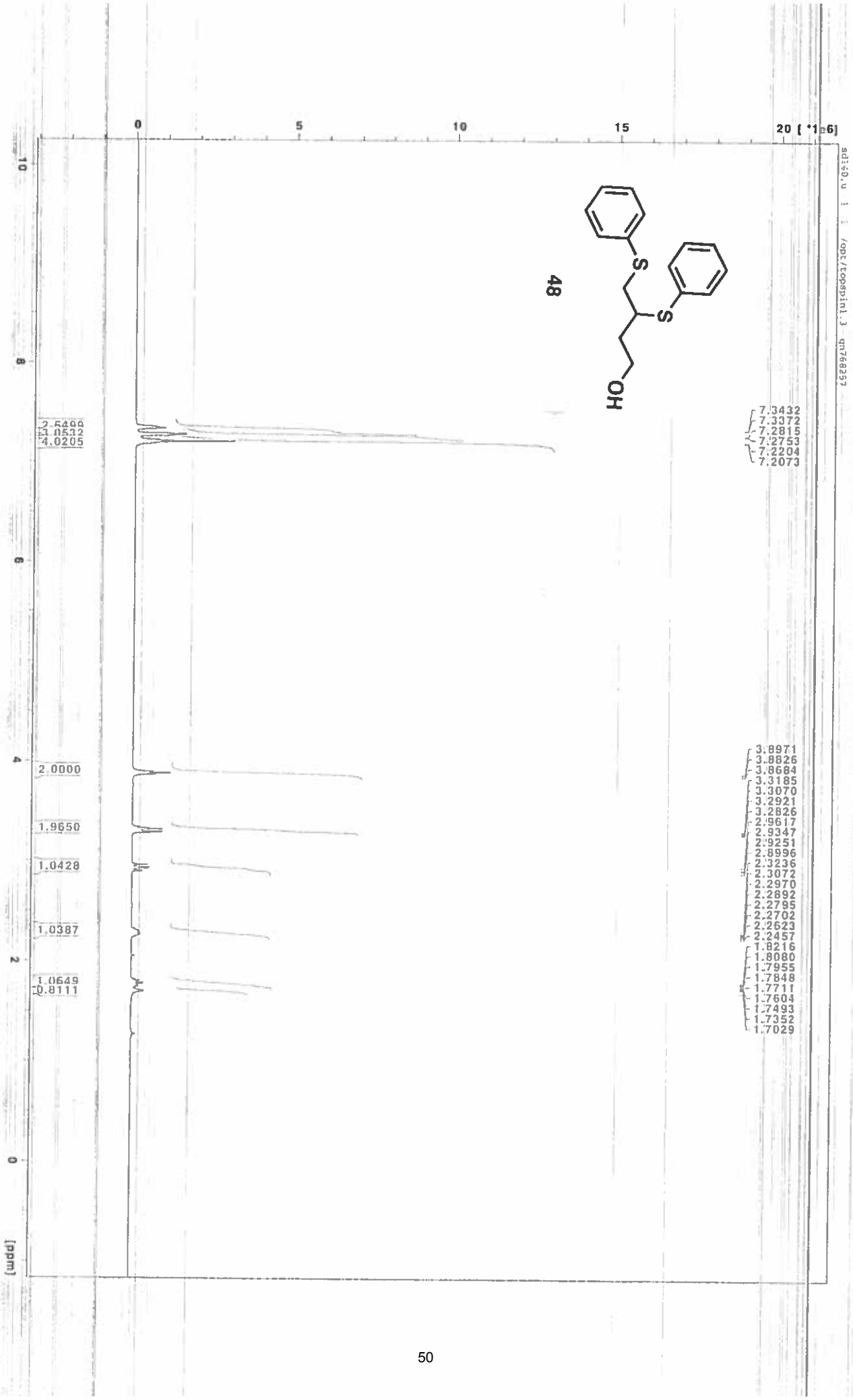

0
50
100
150
[*1e6]
200
150
100
50
0
[ppm]
AcO
AcO
OAc
O
OAc
S
OH
45
170.5625
170.0545
169.3347
169.2869
135.8956
131.1329
120.5165
119.1643
82.8752
77.3238
77.0058
76.5875
76.0859
73.7206
69.9530
69.5266
68.0619
61.9070
61.4081
61.2545
36.6765
32.5987
20.6353
20.5857
20.4713
sd134 2 1 /opt/topspin1.3 qm768257

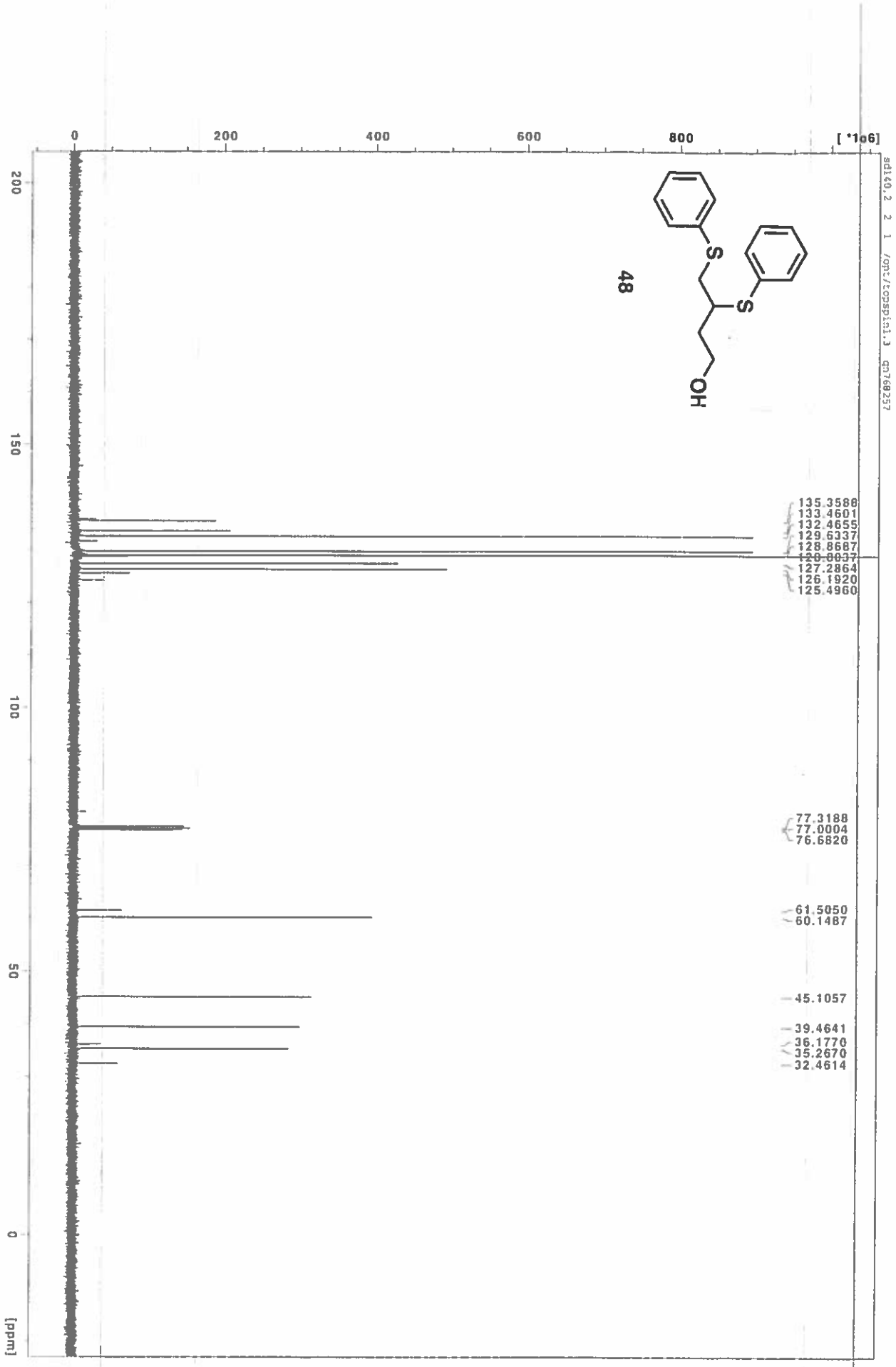

MeO
O
NHBoc
S
OH
46
0.9292
0.9144
0.8321
0.8614
3.0000
2.0054
2.0064
2.2010
9.3488
1.3988
5.9696
5.9487
5.9148
5.7333
5.7156
5.6972
5.6781
5.6573
5.6375
5.6167
5.5978
5.4744
5.4559
5.3947
5.3749
4.5186
3.7041
3.6975
3.6457
3.6306
3.6121
3.5951
3.5805
3.0936
3.0619
3.0503
3.0293
2.9735
2.9584
2.9373
2.9230
2.3799
2.3619
2.3442
2.2794
2.2638
[ppm]
[*1e6]

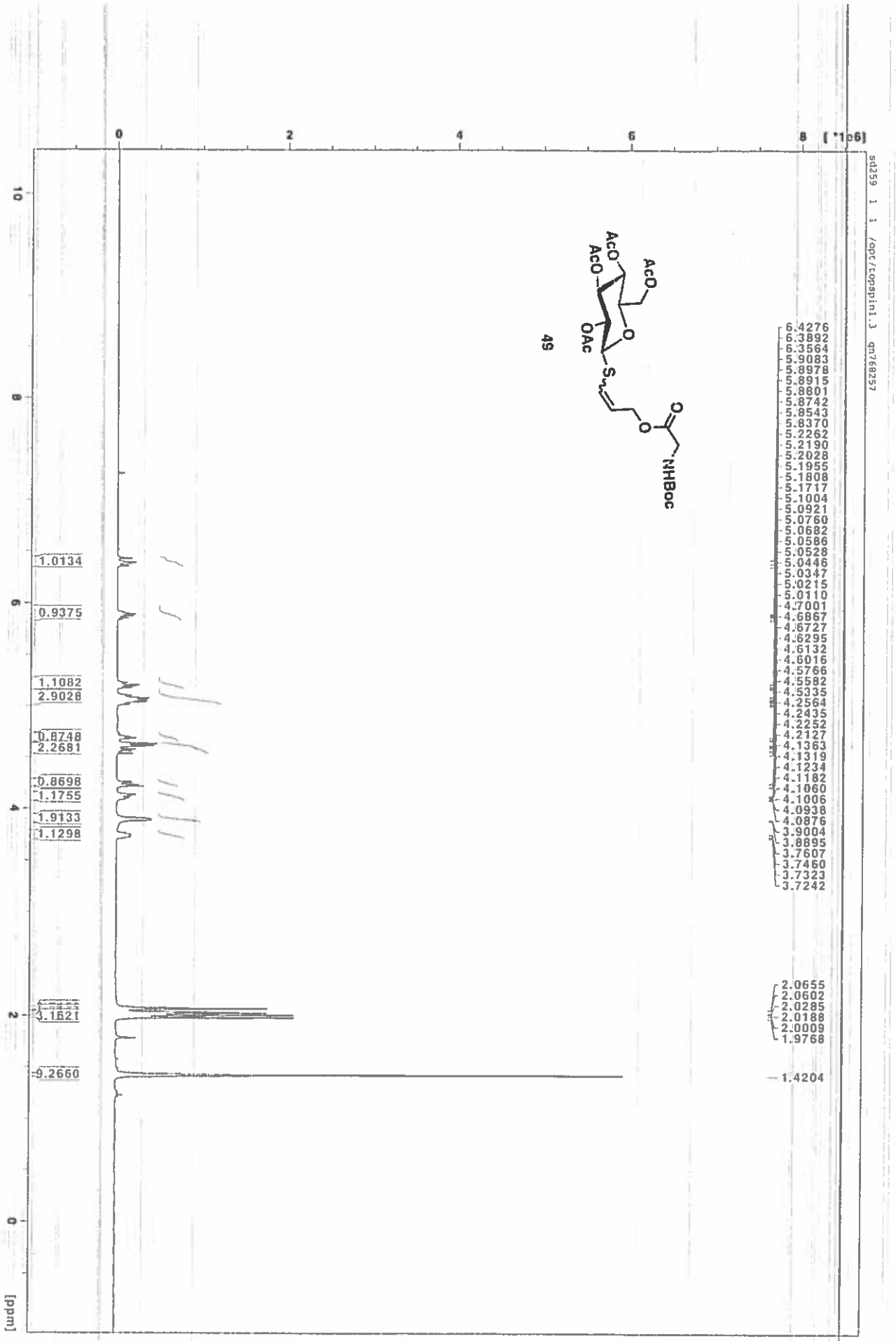

0
100
200
300
400
500
[*1e6]
200
150
100
50
0
[ppm]
MeO
O
NHBoc
S
OH
46
171.3201
171.0979
155.0163
129.9710
128.0598
126.4341
124.4437
80.2078
80.1243
77.3637
77.0456
76.7271
61.4743
53.6235
52.9768
52.4910
52.4626
36.4680
35.3882
32.4544
28.2699

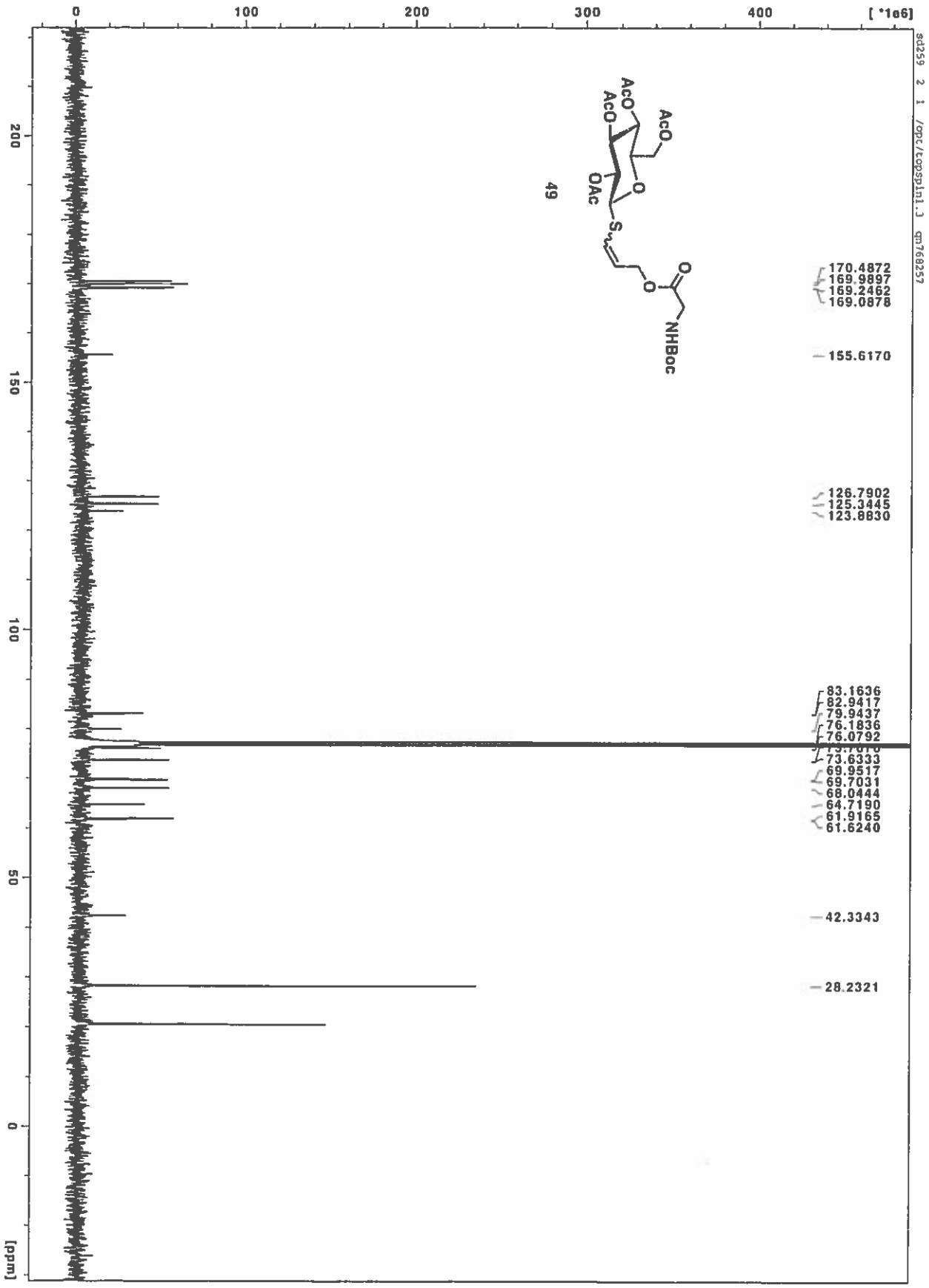

47
OH
S
7.3644
7.3467
7.3236
7.3057
7.2858
7.2616
7.2315
7.2139
7.1970
6.3743
6.3504
6.3018
6.2641
5.9509
5.9311
5.9136
5.8934
5.8864
5.8760
5.8651
5.8468
5.8251
3.7685
3.7535
3.7366
3.7212
3.7058
3.6889
2.5677
2.5516
2.5347
2.5180
2.4662
2.4401
2.4233
2.4072
5.4746
2.2054
1.0000
0.5235
1.0292
1.0463
2.1305
1.2731
[ppm]

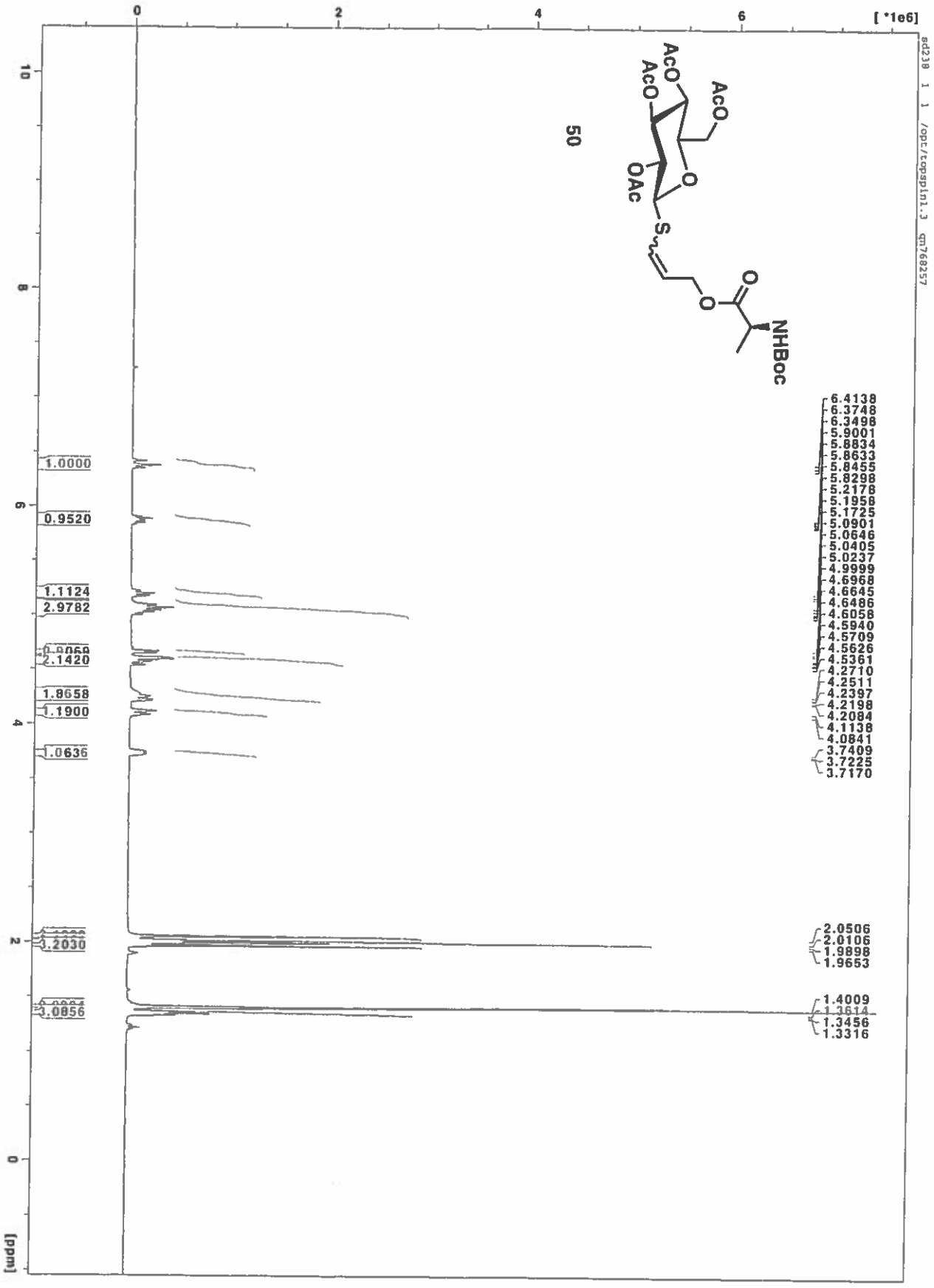

0
50
100
150
200
[*1e6]
200
150
100
50
0
[ppm]
47
OH
S
135.8666
135.6458
131.2925
128.4590
126.4428
126.4074
125.9905
124.6689
77.3223
77.0048
76.6871
61.8313
61.6989
36.3703
32.6317
sdi24 2 1 /opt/topspin1.3 qn:768257

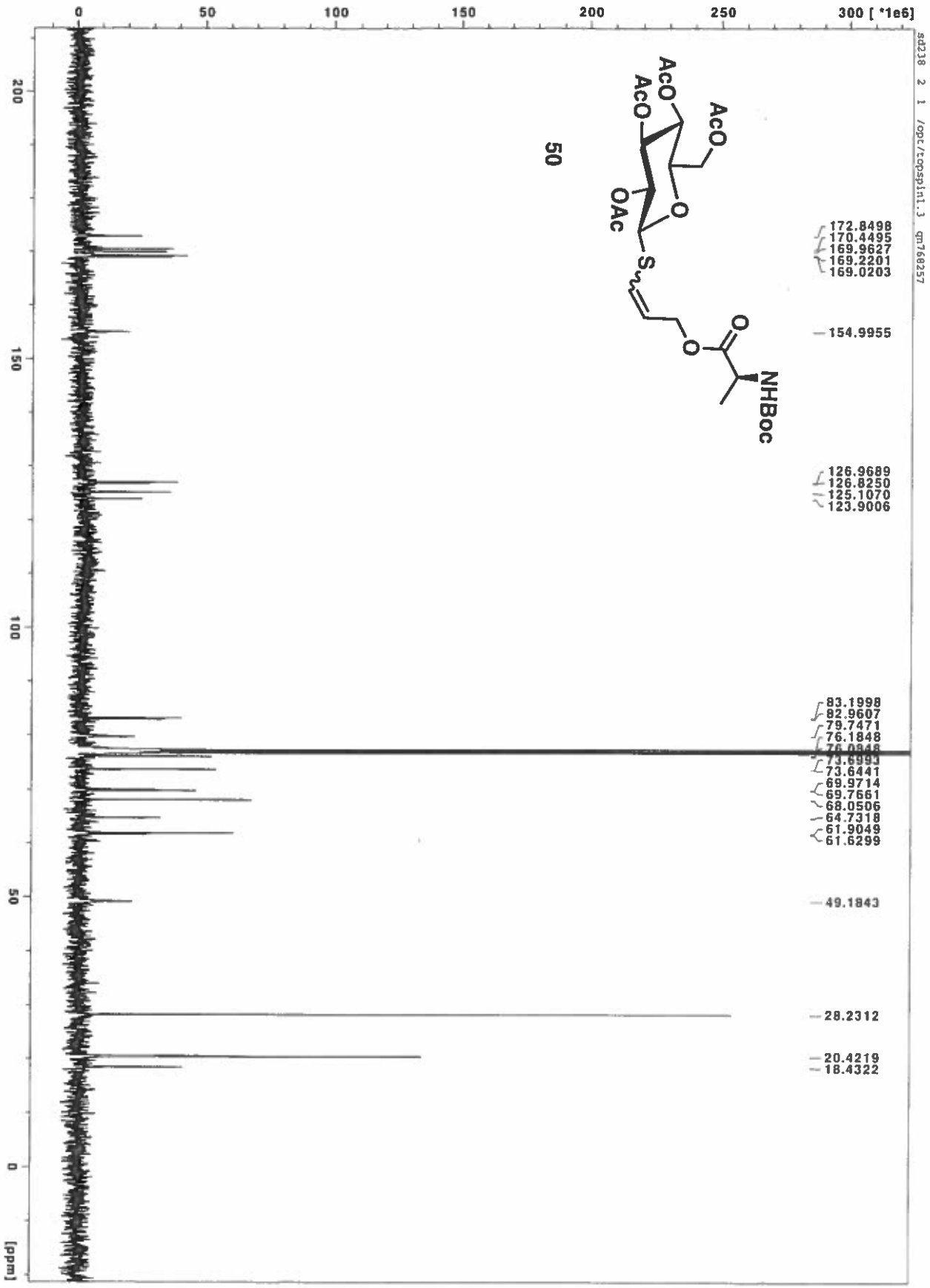

48
OH
S
S
7.3432
7.3372
7.2815
7.2753
7.2204
7.2073
3.8971
3.8826
3.8684
3.3185
3.3070
3.2921
3.2826
2.9617
2.9347
2.9251
2.8996
2.3236
2.3072
2.2970
2.2892
2.2795
2.2702
2.2623
2.2457
1.8216
1.8080
1.7955
1.7848
1.7711
1.7604
1.7493
1.7352
1.7029
2.0000
1.9650
1.0428
1.0387
1.0649
0.8111
[ppm]

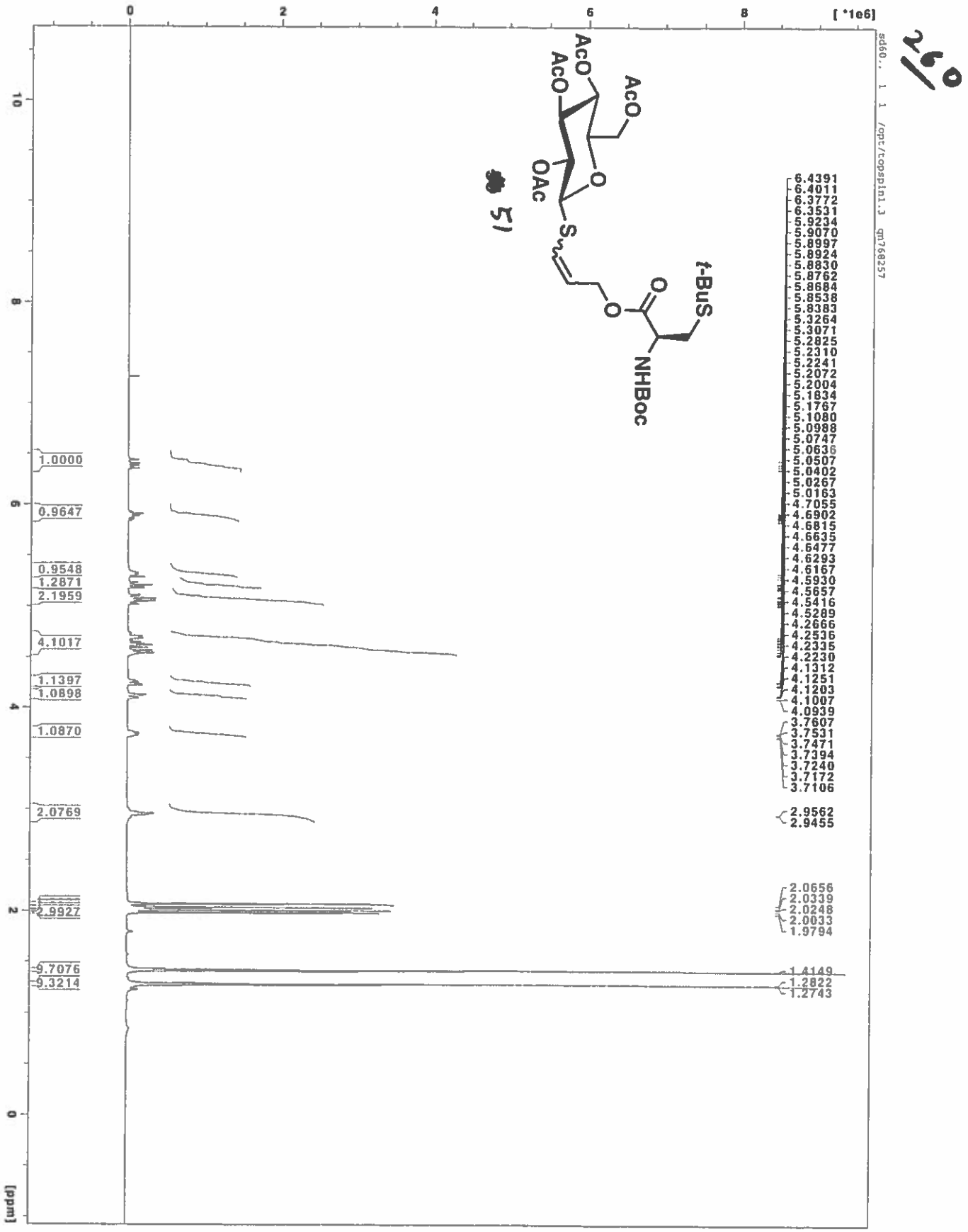

0
200
400
600
800
[*1e6]
200
150
100
50
0
[ppm]
48
S
S
OH
135.3588
133.4601
132.4655
129.6337
128.8687
127.2864
126.1920
125.4960
77.3188
77.0004
76.6820
61.5050
60.1487
45.1057
39.4641
36.1770
35.2670
32.4614
sd140,2 2 1 /opt/topspin1.3 qn760257

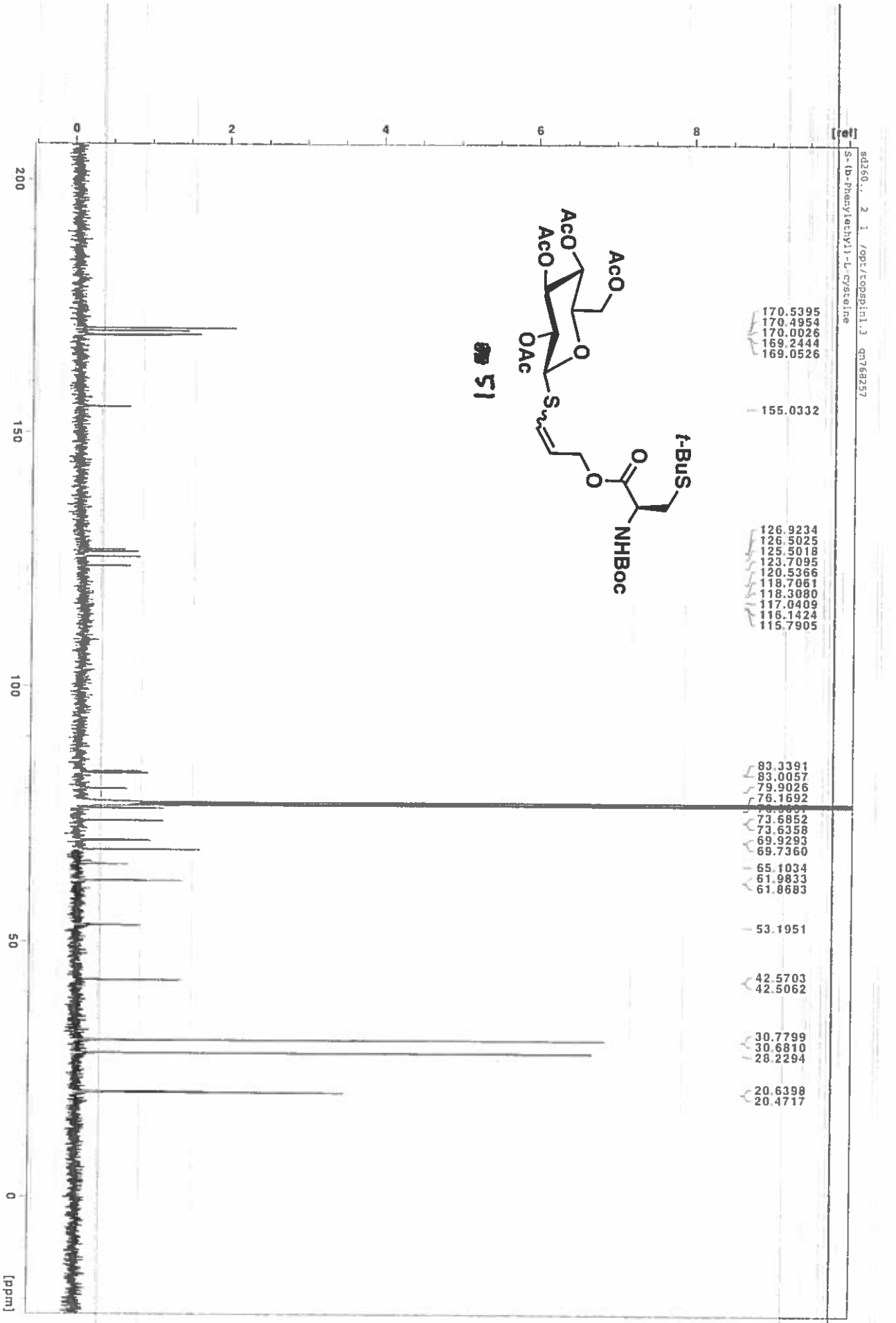

49
AcO
AcO
AcO
OAc
O
S
O
O
NHBoc
6.4276
6.3892
6.3564
5.9083
5.8978
5.8915
5.8801
5.8742
5.8543
5.8370
5.2262
5.2190
5.2028
5.1955
5.1808
5.1717
5.1004
5.0921
5.0760
5.0682
5.0586
5.0528
5.0446
5.0347
5.0215
5.0110
4.7001
4.6867
4.6727
4.6295
4.6132
4.6016
4.5766
4.5582
4.5335
4.2564
4.2435
4.2252
4.2127
4.1363
4.1319
4.1234
4.1182
4.1060
4.1006
4.0938
4.0876
3.9004
3.8895
3.7607
3.7460
3.7323
3.7242
2.0655
2.0602
2.0285
2.0188
2.0009
1.9768
1.4204
1.0134
0.9375
1.1082
2.9028
0.8748
2.2681
0.8698
1.1755
1.9133
1.1298
1.1621
9.2660
[ppm]


0
100
200
300
400
[*1e6]
200
150
100
50
0
[ppm]
sd259 2 1 /opc/topspin1.3 qm768257
AcO
AcO
AcO
OAc
O
Sn
O
O
NHBoc
49
170.4872
169.9897
169.2462
169.0878
155.6170
126.7902
125.3445
123.8830
83.1636
82.9417
79.9437
76.1836
76.0792
73.6333
69.9517
69.7031
68.0444
64.7190
61.9165
61.6240
42.3343
28.2321


50
AcO
AcO
AcO
OAc
O
S
O
O
NHBoc
6.4138
6.3748
6.3498
5.9001
5.8834
5.8633
5.8455
5.8298
5.2178
5.1958
5.1725
5.0901
5.0646
5.0405
5.0237
4.9999
4.6968
4.6645
4.6486
4.6058
4.5940
4.5709
4.5626
4.5361
4.2710
4.2511
4.2397
4.2198
4.2084
4.1138
4.0841
3.7409
3.7225
3.7170
2.0506
2.0106
1.9898
1.9653
1.4009
1.3614
1.3456
1.3316
1.0000
0.9520
1.1124
2.9782
2.1420
1.8658
1.1900
1.0636
3.2030
3.0856
[ppm]
[*1e6]


50
AcO
AcO
AcO
OAc
O
S
O
O
NHBoc
sd238 2 1 /opt/topspin1.3 qm768257
172.8498
170.4495
169.9627
169.2201
169.0203
154.9955
126.9689
126.8250
125.1070
123.9006
83.1998
82.9607
79.7471
76.1848
73.6441
69.9714
69.7661
68.0506
64.7318
61.9049
61.6299
49.1843
28.2312
20.4219
18.4322
0
50
100
150
200
[ppm]


AcO
AcO
AcO
OAc
O
S
O
O
NHBoc
t-Bu
51
[*1e6]
[ppm]
1.0000
0.9647
0.9548
1.2871
2.1959
4.1017
1.1397
1.0898
1.0870
2.0769
2.9927
9.7076
9.3214
6.4391
6.4011
6.3772
6.3531
5.9234
5.9070
5.8997
5.8924
5.8830
5.8762
5.8684
5.8538
5.8383
5.3264
5.3071
5.2825
5.2310
5.2241
5.2072
5.2004
5.1834
5.1767
5.1080
5.0988
5.0747
5.0636
5.0507
5.0402
5.0267
5.0163
4.7055
4.6902
4.6815
4.6635
4.6477
4.6293
4.6167
4.5930
4.5657
4.5416
4.5289
4.2666
4.2536
4.2335
4.2230
4.1312
4.1251
4.1203
4.1007
4.0939
3.7607
3.7531
3.7471
3.7394
3.7240
3.7172
3.7106
2.9562
2.9455
2.0656
2.0339
2.0248
2.0033
1.9794
1.4149
1.2822
1.2743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S-(b-Phenylethyl)-L cysteine
[rel]
[ppm]
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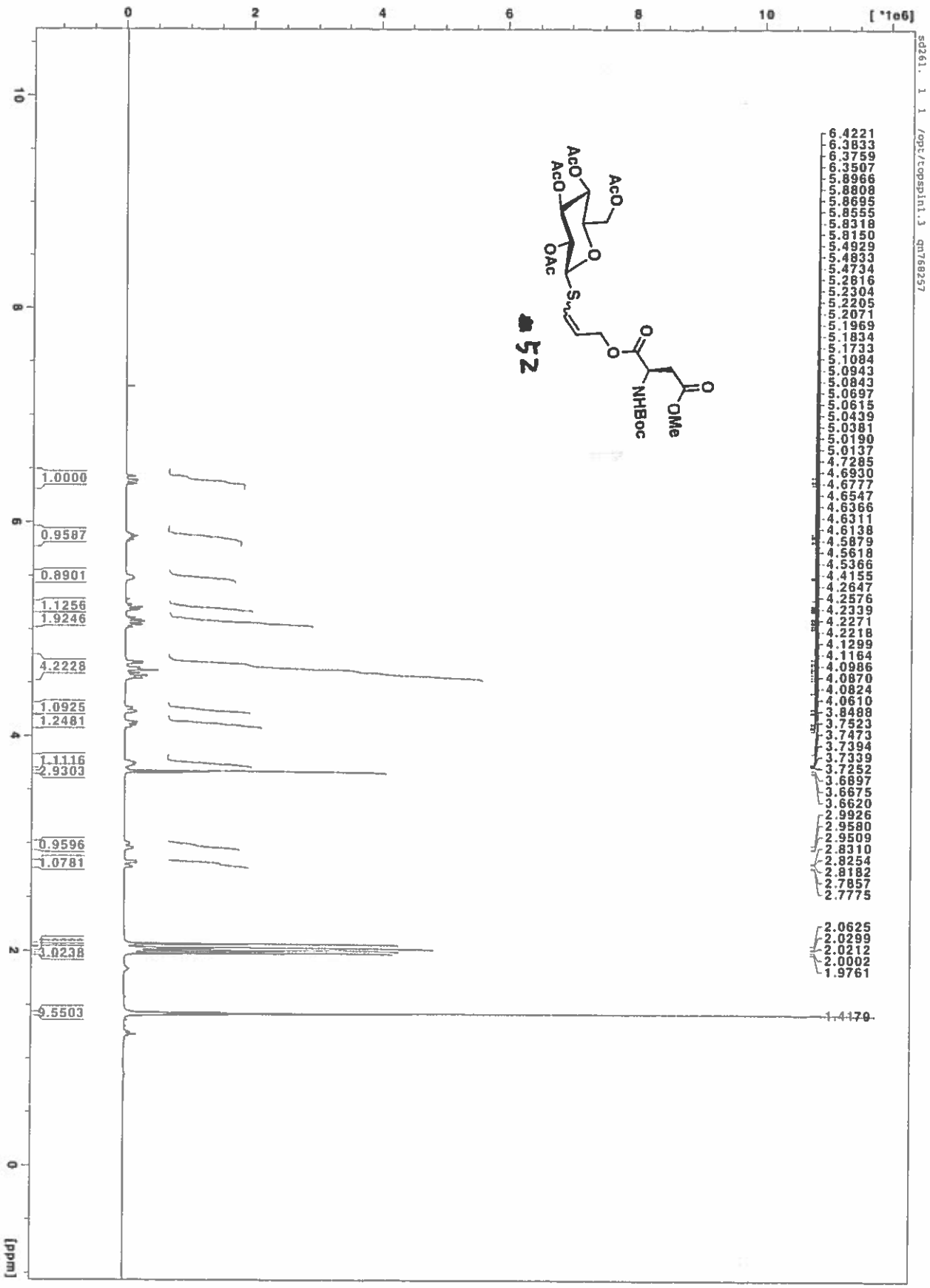
170.4954
170.0026
169.2444
169.0526
155.0332
126.9234
126.5025
125.5018
123.7095
120.5366
118.7061
118.3080
117.0409
116.1424
115.7905
83.3391
83.0057
79.9026
76.1692
73.6852
73.6358
69.9293
69.7360
65.1034
61.9833
61.8683
53.1951
42.5703
42.5062
30.7799
30.6810
28.2294
20.6398
20.4717
AcO
AcO
AcO
OAc
O
S
O
O
NHBoc
t-BuS
51


[*1e6]
[ppm]
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AcO
OAc
O
Sn
O
O
NHBoc
O
OMe
52
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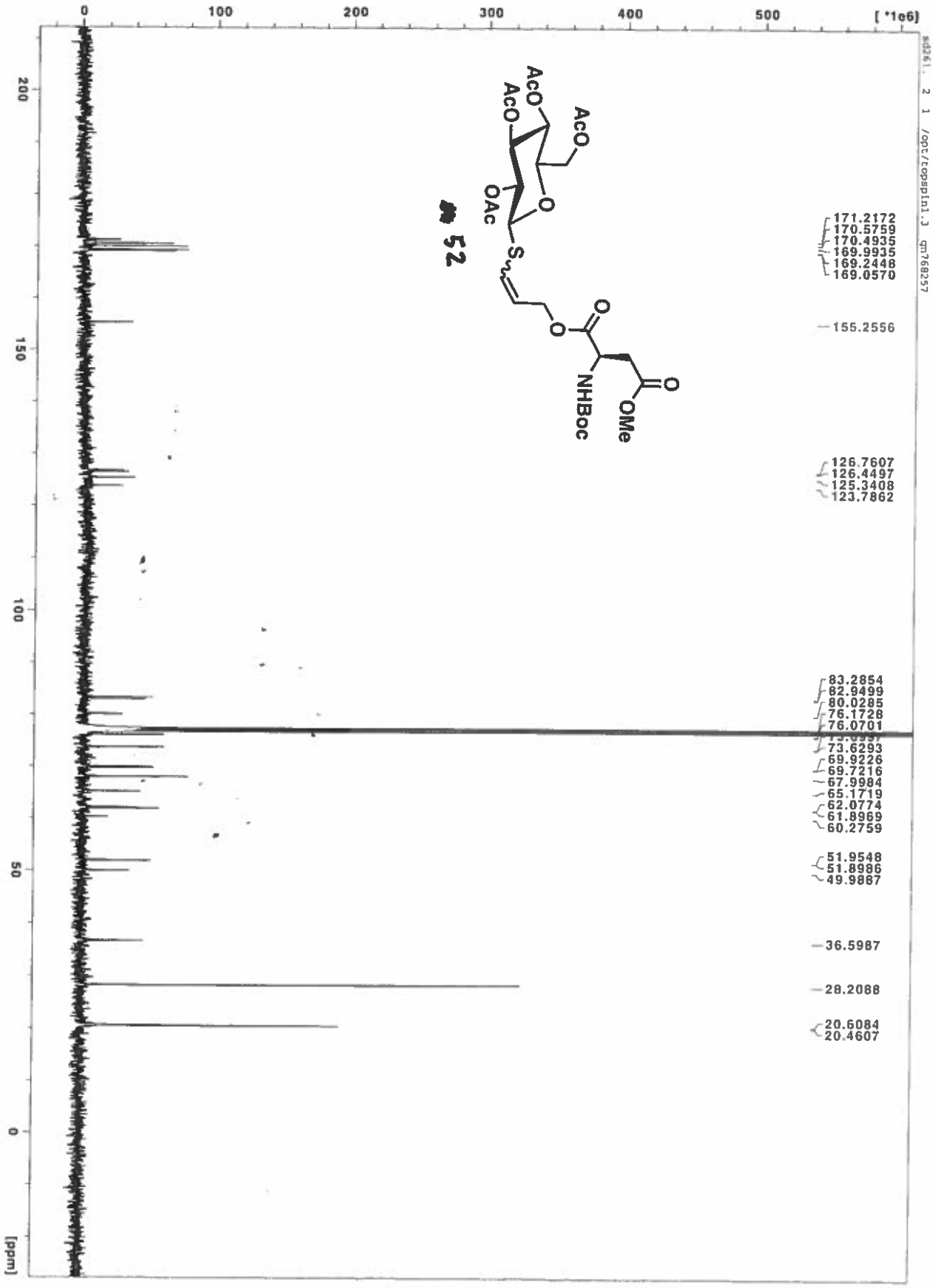
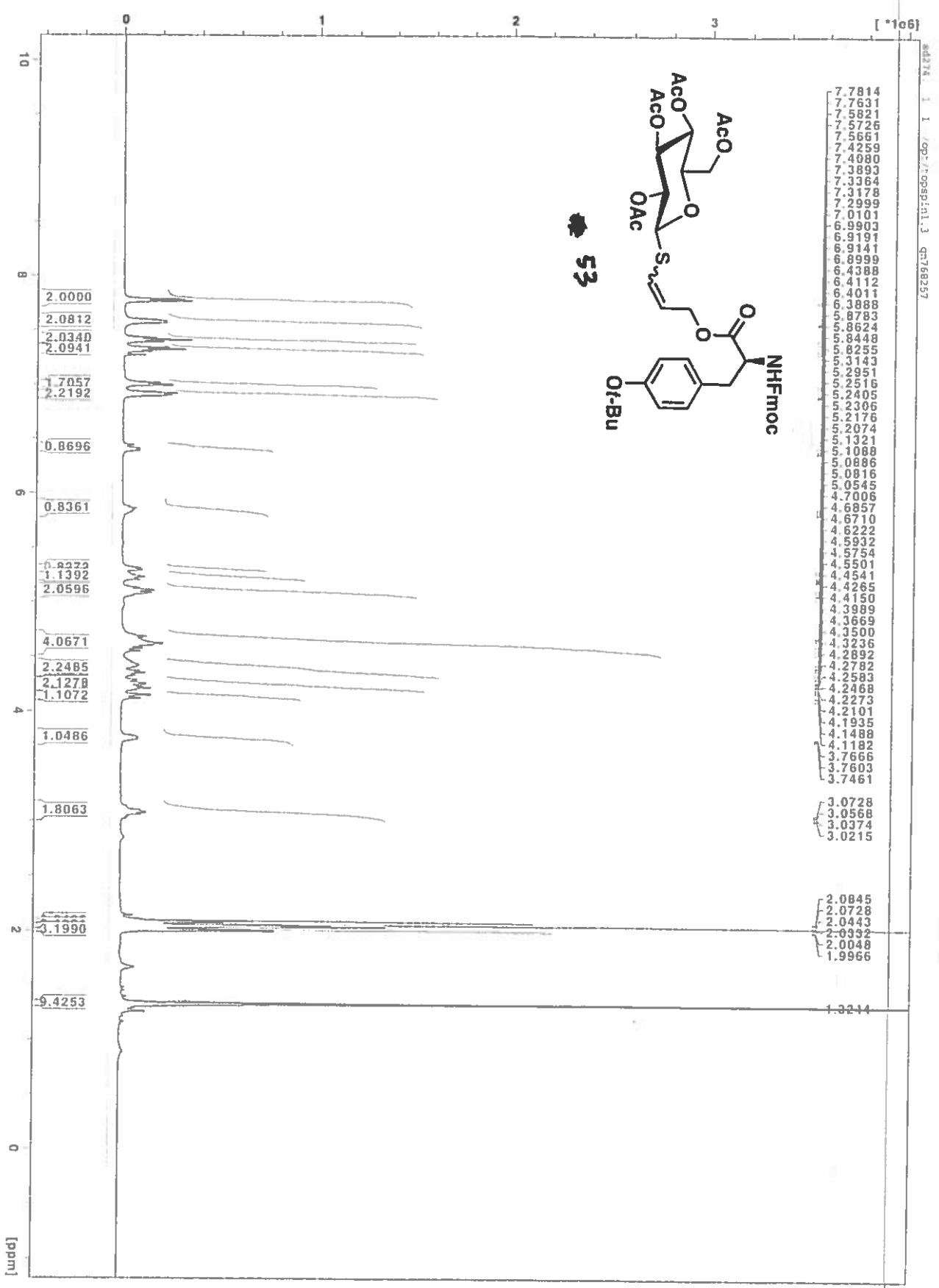
0.9587
0.8901
1.1256
1.9246
4.2228
1.0925
1.2481
1.1116
2.9303
0.9596
1.0781
3.0238
9.5503
6.4221
6.3833
6.3759
6.3507
5.8966
5.8808
5.8695
5.8555
5.8318
5.8150
5.4929
5.4833
5.4734
5.2816
5.2304
5.2205
5.2071
5.1969
5.1834
5.1733
5.1084
5.0943
5.0843
5.0697
5.0615
5.0439
5.0381
5.0190
5.0137
4.7285
4.6930
4.6777
4.6547
4.6366
4.6311
4.6138
4.5879
4.5618
4.5366
4.4155
4.2647
4.2576
4.2339
4.2271
4.2218
4.1299
4.1164
4.0986
4.0870
4.0824
4.0610
3.8488
3.7523
3.7473
3.7394
3.7339
3.7252
3.6897
3.6675
3.6620
2.9926
2.9580
2.9509
2.8310
2.8254
2.8182
2.7857
2.7775
2.0625
2.0299
2.0212
2.0002
1.9761
1.4179



Synthetic 123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AcO
AcO
OAc
O
S
O
O
NHFmoc
Ot-Bu
53
[*1e6]
[ppm]
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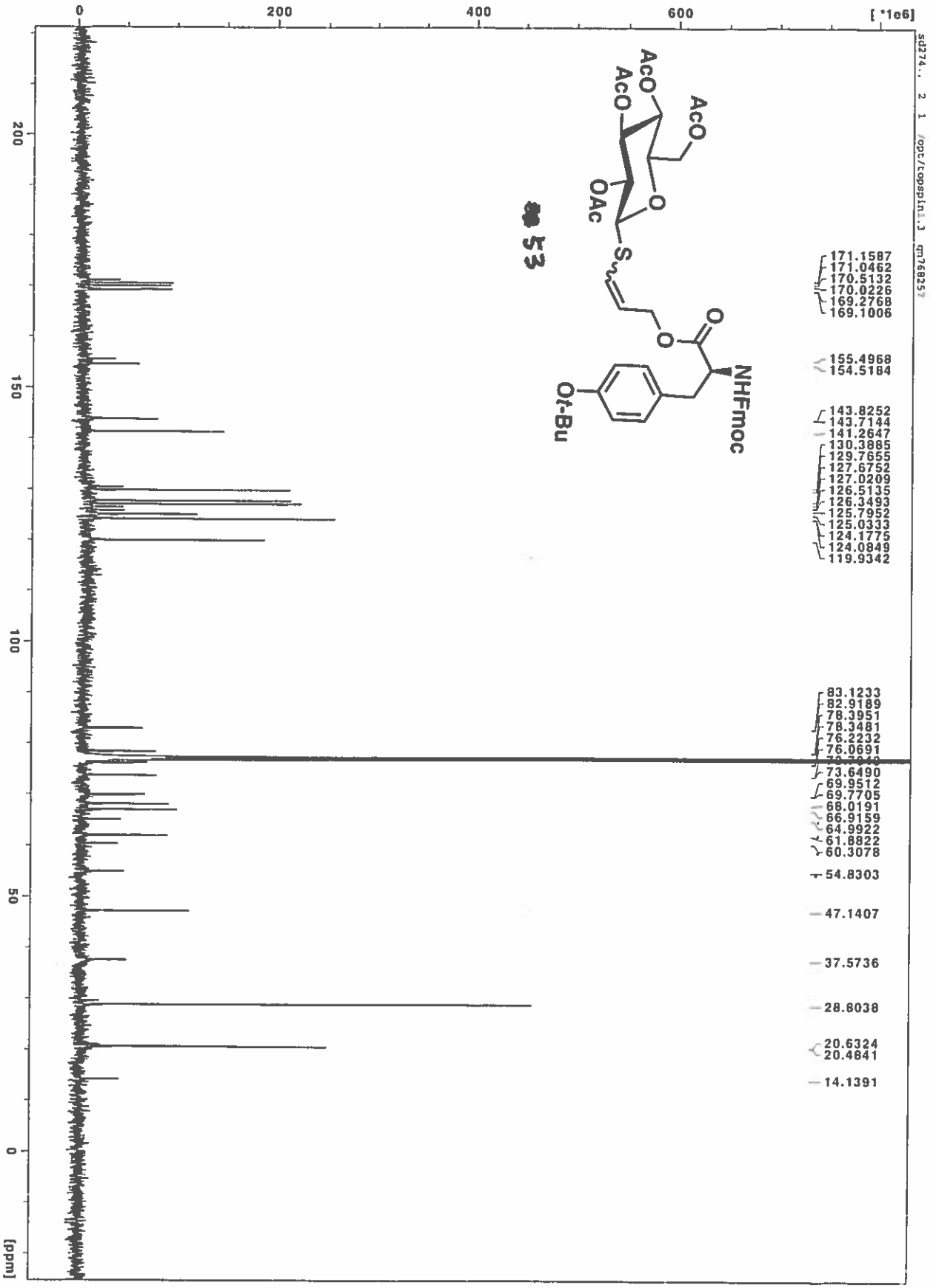
7.7631
7.5821
7.5726
7.5661
7.4259
7.4080
7.3893
7.3364
7.3178
7.2999
7.0101
6.9903
6.9191
6.9141
6.8999
6.4388
6.4112
6.4011
6.3888
5.8783
5.8624
5.8448
5.8255
5.3143
5.2951
5.2516
5.2405
5.2306
5.2176
5.2074
5.1321
5.1088
5.0886
5.0816
5.0545
4.7006
4.6857
4.6710
4.6222
4.5932
4.5754
4.5501
4.4541
4.4265
4.4150
4.3989
4.3669
4.3500
4.3236
4.2892
4.2782
4.2583
4.2468
4.2273
4.2101
4.1935
4.1488
4.1182
3.7666
3.7603
3.7461
3.0728
3.0568
3.0374
3.0215
2.0845
2.0728
2.0443
2.0332
2.0048
1.9966
1.3214
2.0000
2.0812
2.0340
2.0941
1.7057
2.2192
0.8696
0.8361
1.1392
2.0596
4.0671
2.2485
2.1278
1.1072
1.0486
1.8063
3.1990
9.4253


0
200
400
600
[*1e6]
200
150
100
50
0
[ppm]
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AcO
AcO
OAc
O
S
O
O
NHFmoc
Ot-Bu
#53
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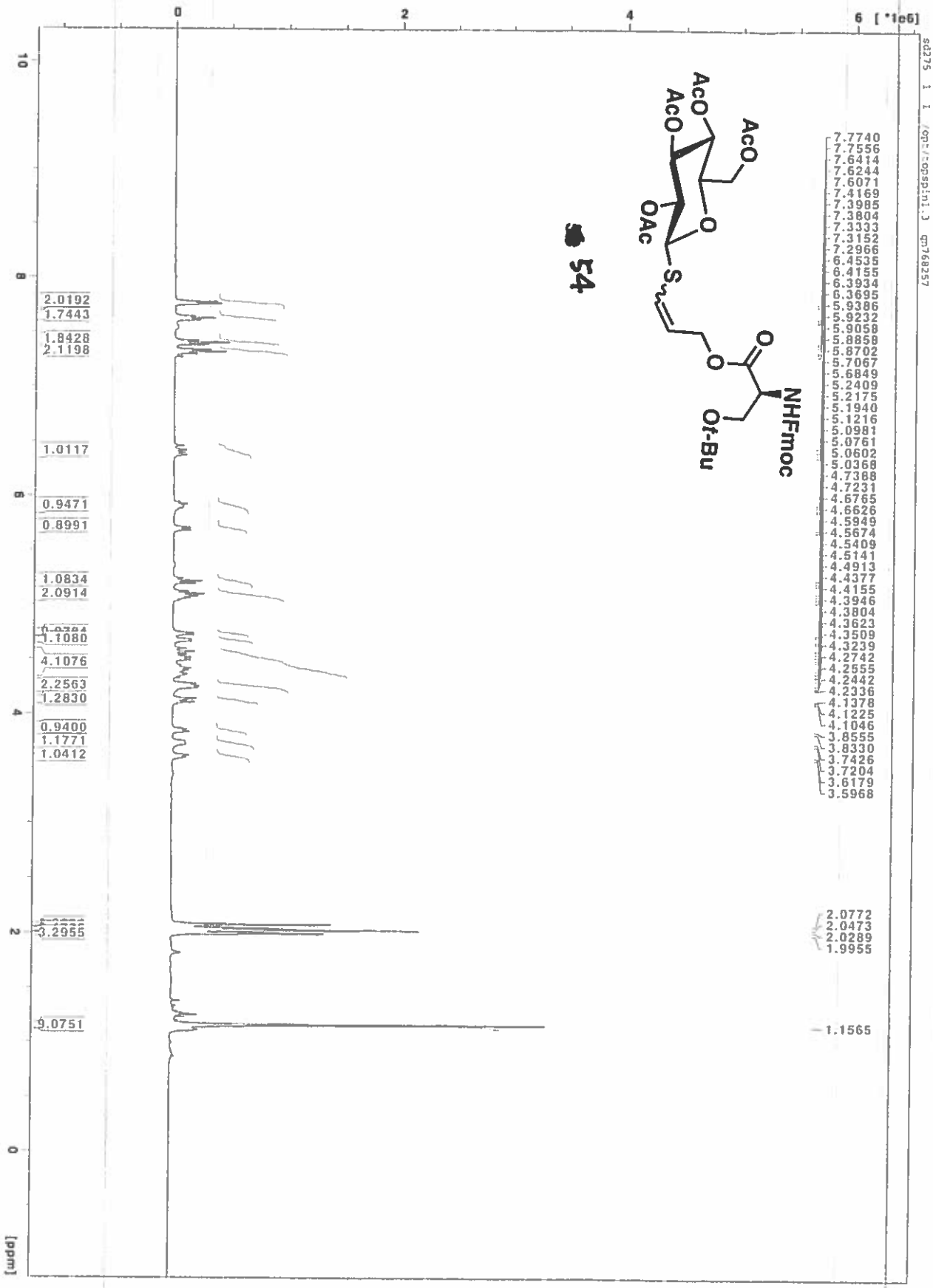
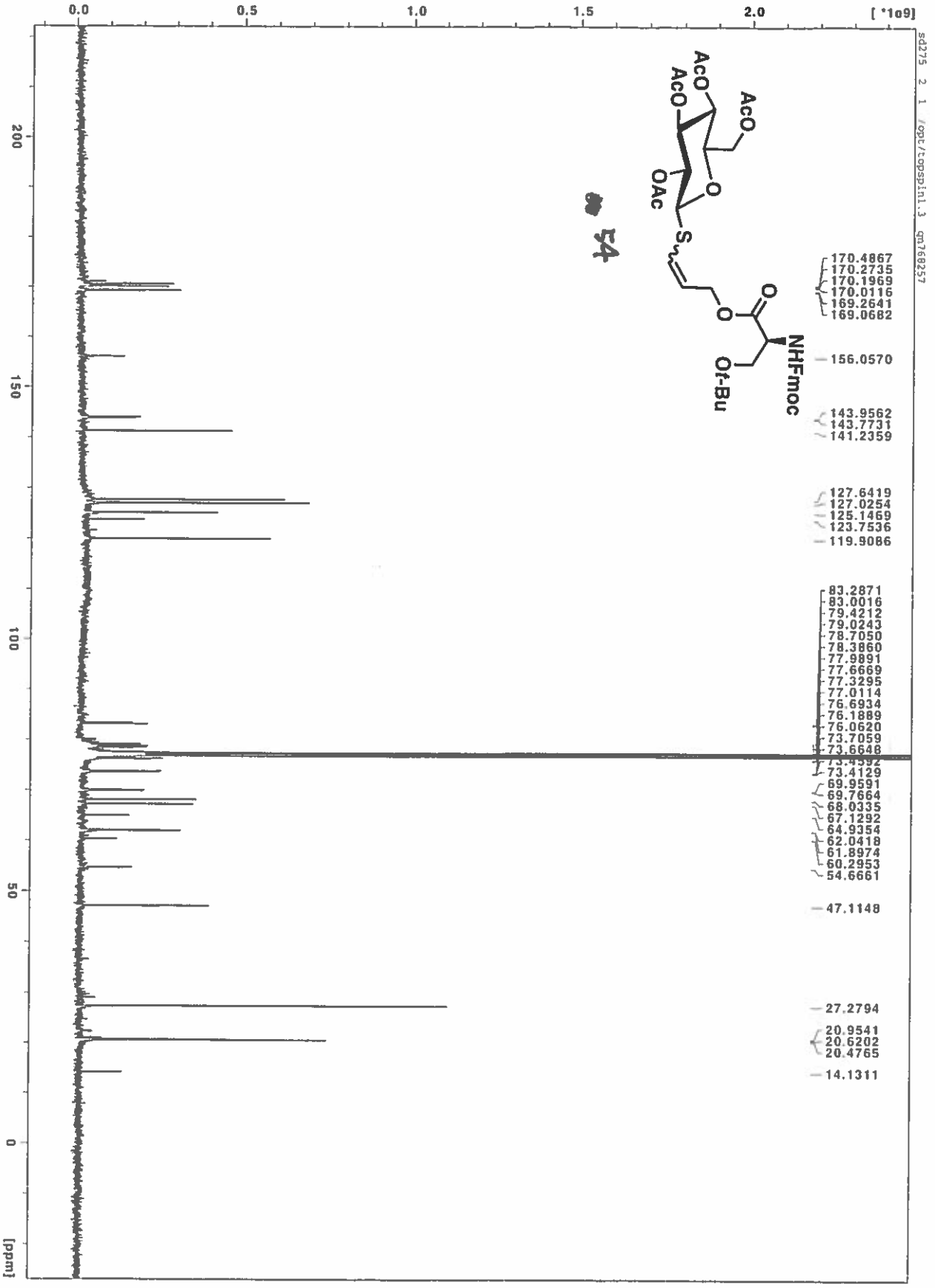
171.0462
170.5132
170.0226
169.2768
169.1006
155.4968
154.5184
143.8252
143.7144
141.2647
130.3885
129.7655
127.6752
127.0209
126.5135
126.3493
125.7952
125.0333
124.1775
124.0849
119.9342
83.1233
82.9189
78.3951
78.3481
76.2232
76.0691
73.6490
69.9512
69.7705
68.0191
66.9159
64.9922
61.8822
60.3078
54.8303
47.1407
37.5736
28.8038
20.6324
20.4841
14.1391


AcO
AcO
AcO
OAc
O
S
O
O
NHFmoc
Ot-Bu
54
7.7740
7.7556
7.6414
7.6244
7.6071
7.4169
7.3985
7.3804
7.3333
7.3152
7.2966
6.4535
6.4155
6.3934
6.3695
5.9386
5.9232
5.9058
5.8858
5.8702
5.7067
5.6849
5.2409
5.2175
5.1940
5.1216
5.0981
5.0761
5.0602
5.0368
4.7368
4.7231
4.6765
4.6626
4.5949
4.5674
4.5409
4.5141
4.4913
4.4377
4.4155
4.3946
4.3804
4.3623
4.3509
4.3239
4.2742
4.2555
4.2442
4.2336
4.1378
4.1225
4.1046
3.8555
3.8330
3.7426
3.7204
3.6179
3.5968
2.0772
2.0473
2.0289
1.9955
1.1565
2.0192
1.7443
1.8428
2.1198
1.0117
0.9471
0.8991
1.0834
2.0914
1.1080
4.1076
2.2563
1.2830
0.9400
1.1771
1.0412
3.2955
9.0751
[ppm]
[*1e6]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1.0
1.5
2.0
[*1e9]
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100
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0
[ppm]
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AcO
AcO
OAc
O
S
O
O
NHFmoc
Of-Bu
54
sd275 2 1 /opt/topspin1.3 qm76257
170.4867
170.2735
170.1969
170.0116
169.2641
169.0682
156.0570
143.9562
143.7731
141.2359
127.6419
127.0254
125.1469
123.7536
119.9086
83.2871
83.0016
79.4212
79.0243
78.7050
78.3860
77.9891
77.6669
77.3295
77.0114
76.6934
76.1889
76.0620
73.7059
73.6648
73.4129
69.9591
69.7664
68.0335
67.1292
64.9354
62.0418
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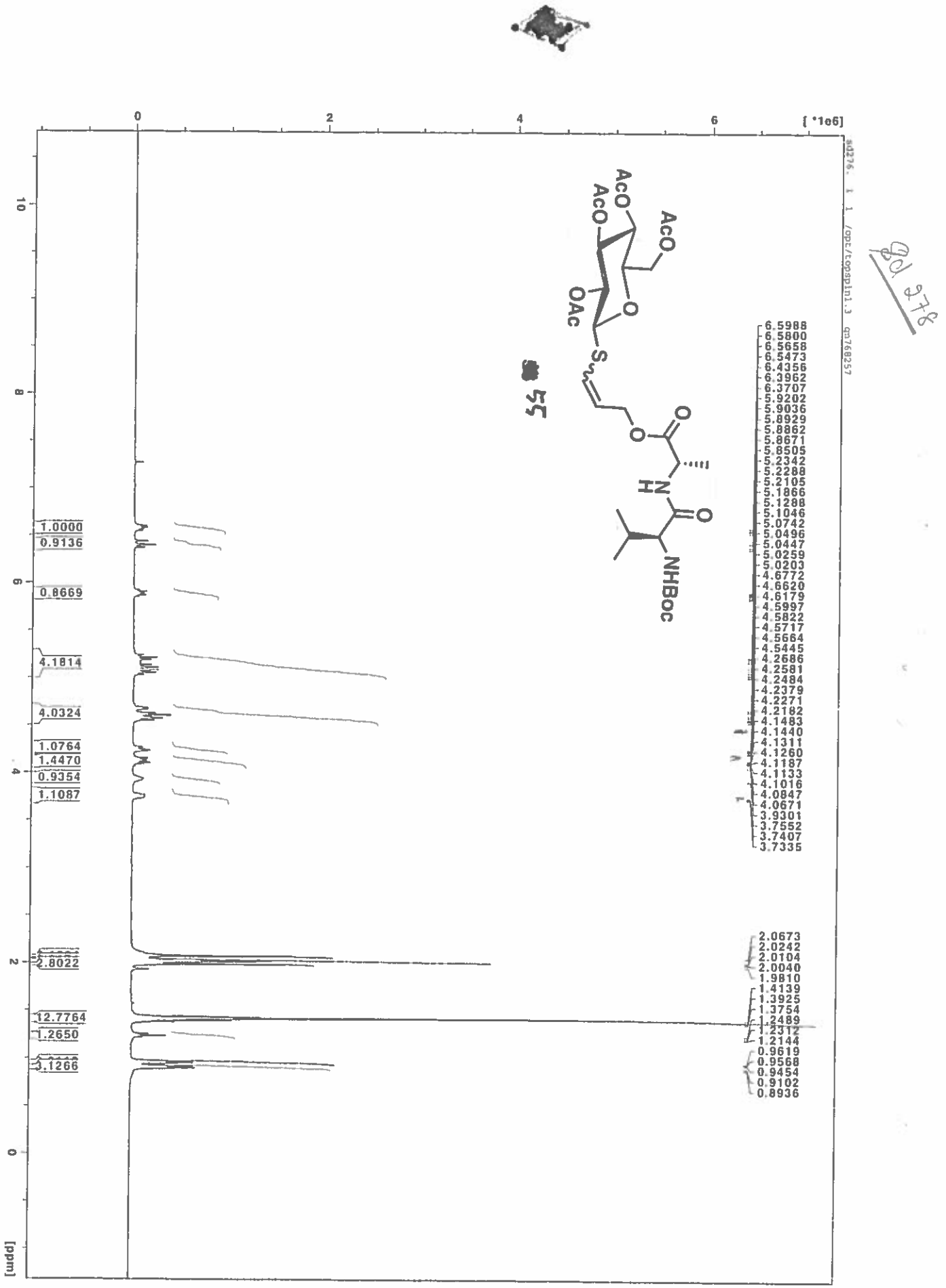
60.2953
54.6661
47.1148
27.2794
20.9541
20.6202
20.4765
14.1311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AcO
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O
S
O
O
H
N
O
NHBoc
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6.5473
6.4356
6.3962
6.3707
5.9202
5.9036
5.8929
5.8862
5.8671
5.8505
5.2342
5.2288
5.2105
5.1866
5.1288
5.1046
5.0742
5.0496
5.0447
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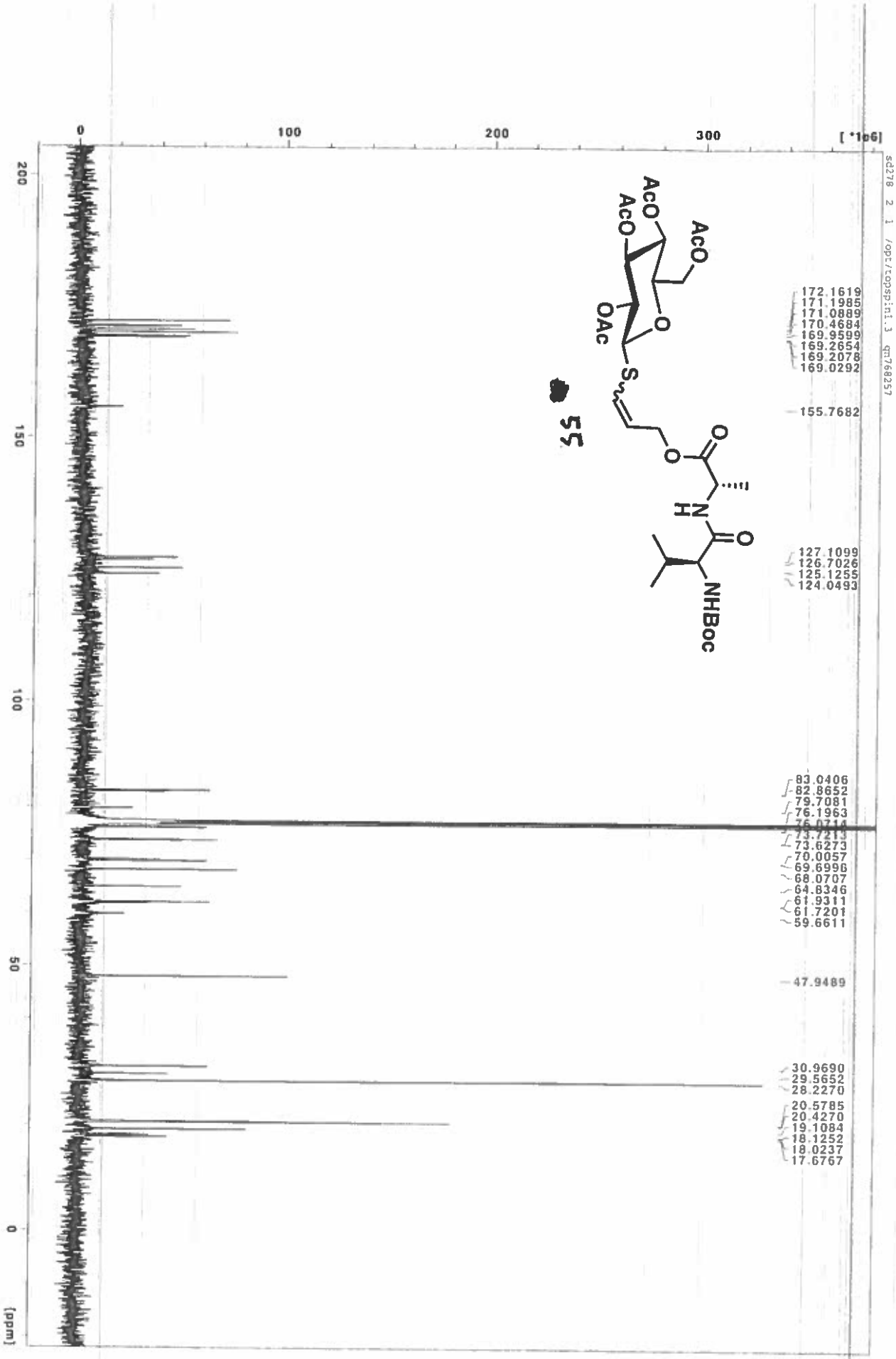
5.0203
4.6772
4.6620
4.6179
4.5997
4.5822
4.5717
4.5664
4.5445
4.2686
4.2581
4.2484
4.2379
4.2271
4.2182
4.1483
4.1440
4.1311
4.1260
4.1187
4.1133
4.1016
4.0847
4.0671
3.9301
3.7552
3.7407
3.7335
2.0673
2.0242
2.0104
2.0040
1.9810
1.4139
1.3925
1.3754
1.2489
1.2312
1.2144
0.9619
0.9568
0.9454
0.9102
0.8936
1.0000
0.9136
0.8669
4.1814
4.0324
1.0764
1.4470
0.9354
1.1087
2.8022
12.7764
1.2650
3.1266
[ppm]
[*1e6]

Bd 278


0
100
200
300
[*1e6]
200
150
100
50
0
[ppm]
sd278 2 1 /opt/topspin1.3 qm768257
AcO
AcO
AcO
OAc
O
S
O
O
N
H
O
NHBoc
55
172.1619
171.1985
171.0889
170.4684
169.9599
169.2654
169.2078
169.0292
155.7682
127.1099
126.7026
125.1255
124.0493
83.0406
82.8652
79.7081
76.1963
73.6273
70.0057
69.6996
68.0707
64.8346
61.9311
61.7201
59.6611
47.9489
30.9690
29.5652
28.2270
20.5785
20.4270
19.1084
18.1252
18.0237
17.6767