Supporting Information

Palladium-Catalyzed 1,4-Difunctionalization of Butadiene to Form Skipped Polyenes

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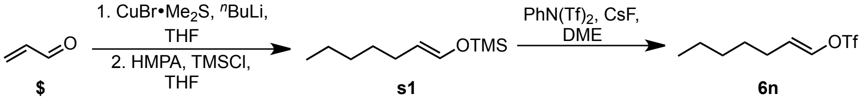
I. General Considerations:

Anhydrous dimethylacetamide (DMA) was purchased from Aldrich and stored over activated 3 Å molecular sieves (3 Å MS). $Pd_2(dba)_3$ was synthesized according to known procedure.[1] 1,3-butadiene was used as supplied by Aldrich (15 wt% in *n*-hexane). Vinyl triflates and nonaflates were synthesized according to previously reported procedures.[2-7] Unless otherwise noted all reagents and solvents were purchased from Aldrich, Acros, or TCI and used without further purification. ^{1}H-NMR spectra were obtained at 300, 400, or 500 MHz, chemical shifts are reported in ppm, and referenced to the $CHCl_3$ singlet at 7.26 ppm. The abbreviations s, d, t, q, quint, sext, dd, ddd, dt, and m stand for the resonance multiplicities singlet, doublet, triplet, quartet, quintet, sextet, doublet of doublets, doublet of doublets of doublets, doublet of triplets and multiplet, respectively. Isomeric product ratios were determined using ^{1}H NMR with a d_1 relaxation time of five seconds of the crude mixtures. ^{13}C NMR spectra were obtained at 75, 100, or 126MHz and referenced to the centerline of the $CDCl_3$ triplet at 77.23 ppm. Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). GC separations were performed with an HP6890 GC with a flame ionization detector equipped with a DB-5 column using a 50:1 split. IR spectra were recorded using a Thermo Nicolet FT-IR. HRMS data were obtained on a Waters LCP Premier XE instrument by ESI/TOF. LR GCMS data were obtained on an Agilent Technologies 5975C VL MSD instrument.

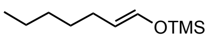
II. Synthesis of Starting Materials:

A. Preparation of Starting Material 6n

Scheme s1: Synthetic route to triflate **6n**

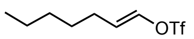


(*E*)-(hept-1-en-1-yloxy)trimethylsilane – s1



A previously reported procedure was used for the synthesis of **s1**.[8] To a stirred suspension of 2.47 g (12 mmol) of CuBr•Me$_2$S in 40 mL of THF at -70 °C was added dropwise 9.6 mL of *n*-butyllithium in hexane (2.5 M). The mixture was stirred at -40 °C for 30 minutes, and then cooled to -70 °C. 7.0 mL (40.0 mmol) of hexamethylphosphoramide was added, and following several minutes of stirring a mixture of 1.3 mL (20.0 mmol) of acrolein and 5.0 mL (40.0 mmol) of chlorotrimethylsilane in 12 mL of THF was added dropwise. After 2.5 hours of stirring at -70 °C, 5.6 mL (40.0 mmol) of triethylamine and pH 7 phosphate buffer (12 mL) was added. The mixture was diluted with hexanes (20 mL) and filtered through Celite. The filtrate was washed with H$_2$O (10 x 5 mL) and the aqueous layer was extracted one time with hexanes (10 mL). The combined organics were washed with brine (10 mL), dried over MgSO$_4$, and concentrated *in vacuo*. The crude product was purified by distillation to give product in 57% yield (2.135 g, 11.45 mmol) in an *E*/*Z* ratio of 95:5. Analytical data matched the literature.[8]

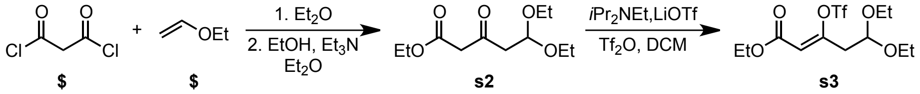
(*E*)-hept-1-en-1-yl trifluoromethanesulfonate – 6n



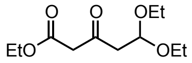
A previously reported procedure was used for the synthesis of **6n**.[9] To a dried round bottom flask 5.72 g (16.0 mmol) of N-Phenyl-bis(trifluoromethanesulfonimide) and 3.65 g (24.0 mmol) of vacuum dried (300 °C, 16 hours) cesium fluoride was added. A rubber septum was added and the vessel was flushed with N$_2$. 1.49 g (8.00 mmol) of **s1** in 23 mL of DME was added and the rubber septum was replaced with a teflon wrapped plastic cap. The exterior was wrapped with teflon tape and parafilm. After 5 hours of stirring the pressure inside the flask was carefully released and the reaction mixture was portioned between Et$_2$O (10 mL) and pH 7 phosphate buffer (10 mL). The aqueous phase was extracted with Et$_2$O (3 x 10 mL). The combined organics were dried over Na$_2$SO$_4$, and concentrated *in vacuo.* The crude product was purified by silica gel flash chromatography eluting with 2.5% ethyl acetate in hexanes to give product in 56% yield (477 mg, 2.05 mmol) in an *E*/*Z* ratio of 97:3. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.50 (d, *J*=11.7 Hz, 1H), 5.77 (dt, *J*=12, 4.2 Hz, 1H), 2.04 (q, *J*=7.5 Hz, 2H), 1.47-1.22 (m, 6H), 0.89 (t, *J*=6.9 Hz, 3H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (75 MHz, CDCl$_3$): δ 136.0, 123.1, 118.8 (q, ^1J=319 Hz), 31.2, 28.5, 26.7, 22.5, 14.1; IR (neat): 1666, 1421, 1202, 1052, 970, 851, 764 cm^{-1}; LR GCMS: calcd. 246.05, obsvd. 246.00.

B. Preparation of Starting Material s3

Scheme s2: Synthetic route to triflate **s3**

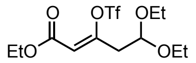


Ethyl-5,5-diethoxy-3-oxopentanoate – s2



A previously reported procedure was used for the synthesis of **s2**.[10] To a solution of 1.8 mL (18.5 mmol) of ethyl vinyl ether in 1.1 mL of diethyl ether was added a solution of 0.36 mL (3.70 mmol) of malonyl chloride in 1.1 mL of diethyl ether dropwise at 0 °C. This mixture was stirred for 1 hour at 0 °C after which time 1.9 mL of absolute ethanol and 1.0 mL (7.40 mmol) of triethyl amine in 1.1 mL of diethyl ether was added (caution: exothermic reaction). At completion, 50 mL of saturated solution of ammonium chloride was added and the mixture was allowed to warm to room temperature. Organics were washed with H_2O (2 x 30 mL) and brine (30 mL), then dried over sodium sulfate, and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography eluting with 25% ethyl acetate in hexanes to give product in 56% yield (477 mg, 2.05 mmol). Analytical data matched the literature.[10]

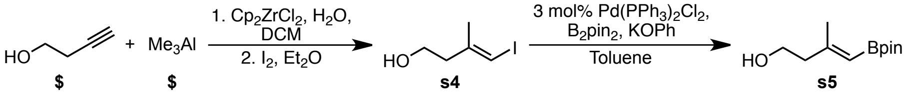
(*Z*)-ethyl 5,5-diethoxy-3-(((trifluoromethyl)sulfonyl)oxy)pent-2-enoate – s3



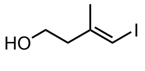
A previously reported procedure was used in the synthesis of **s3**.[11] To a solution of 430 mg (1.85 mmol) of **s2** and 577 mg (3.70 mmol) of lithium trifluoromethylsulfonate in 57 mL dichlormethane was added 0.35 mL (2.03 mmol) of diisopropyl ethyl amine at 0 °C. After twenty minutes of stirring at 0 °C, 0.34 mL (2.03 mmol) of trifluoromethanesulfonic anhydride was added and stirred at 0 °C for 25 minutes at which time TLC analysis showed no remaining starting material. At completion, the mixture was allowed to warm to room temperature followed by addition of 55 mL of saturated solution of ammonium chloride. The aqueous phase was extracted with dichlormethane (2 x 18 mL). The combined organic layers were dried over sodium sulfate, and concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography eluting with 25% ethyl acetate in hexanes with 1% triethyl amine to give product in 65% yield (440 mg, 1.2 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.89 (s, 1H), 4.71 (t, *J*=5.7 Hz, 1H), 4.25 (q, *J*=7.2 Hz, 2H), 3.66 (m, 2H), 3.52 (m, 2H), 2.67 (d, *J*=5.7 Hz, 2H), 1.30 (t, *J*=7.2 Hz, 3H), 1.21 (t, *J*=7.2 Hz, 6H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.5, 154.2, 118.5 (q, ^1J=319 Hz), 114.5, 99.3, 62.5, 61.4, 39.7, 15.2, 14.2; IR (neat): 2980, 2359, 1732, 1427, 1140, 926, 668 cm^{-1}; HRMS [M + Na]$^+$: calcd. 387.0701, obsvd. 387.0704.

C. Preparation of Starting Material s5

Scheme s3: Synthetic route to boronic pinacol ester **s5**

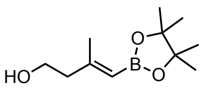


(*E*)-4-iodo-3-methylbut-3-en-1-ol – s4



A previously reported procedure was used for the synthesis of **s4** from but-3-yn-1-ol in one step. Analytical data matched the literature.[12]

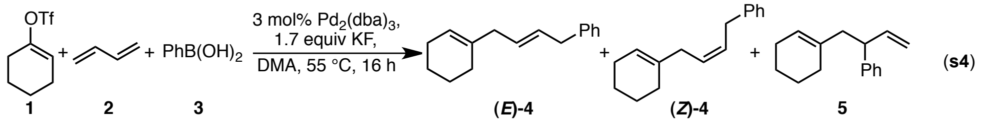
(*E*)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol – s5



To a mixture of 51 mg (0.072 mmol) of $Pd(PPh_3)_2Cl_2$, 1.22 g (4.80 mmol) of bis(pinacolato)diboron, and 952 mg (7.20 mmol) of potassium phenoxide was added a solution of 510 mg (2.40 mmol) of **s4** in 9.0 mL of toluene. The mixture was stirred at 50 °C for 6 h. The reaction mixture was cooled to room temperature, and diluted with 10 mL of diethyl ether. The organic layer was washed with 15 mL of H_2O, 15 mL of brine, dried using magnesium sulfate, and concentrated *in vacuo*. The resulting crude mixture was purified by silica gel flash chromatography eluting with 15% acetone in hexanes to give product in 72% yield (364 mg, 1.72 mmol), R_f = 0.25 (1:5 acetone:hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ 5.18 (s, 1H), 3.74 (q, *J*=6.0 Hz, 2H), 2.37 (t, *J*=6.4 Hz, 2H), 2.01 (s, 3H), 1.26 (s, 12H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, (vinylic carbon adjacent to boron did not resolve), 83.0, 60.5, 45.2, 25.0, 21.3; IR (neat): 3420, 2359, 1637, 1139, 969, 850 cm^{-1}; HRMS $[M + Na]^+$: calcd. 235.1481, obsvd. 235.1479.

III. Pd-Catalyzed Three-Component Coupling Reactions with 1,3-Butadiene

A. General Procedure for Reaction Optimization



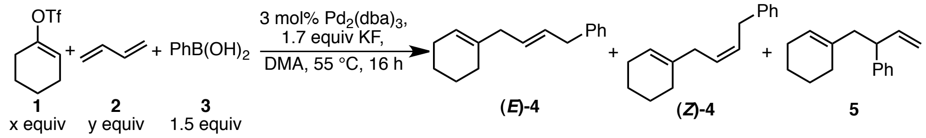
(**s4**)

In a nitrogen atmosphere glove box, to an oven dried 10 mL Schlenk tube were added 20 mg (0.34 mmol, 1.7 equiv.) of KF, 37 mg (0.30 mmol, 1.5 equiv.) of **3**, 6 mg (0.006 mmol, 0.03 equiv.) of $Pd_2(dba)_3$, and a solution of 46 mg (0.20 mmol, 1.0 equiv.) of **1** in 4.0 mL of DMA containing an internal standard (tetradecane). The Schlenk tube was transferred from the glove box and a balloon of **2** was installed via a three-way stopcock followed by evacuation and re-pressurization. This process was repeated three times using a three-way stopcock. The vessel was heated at 55 °C in a constant temperature oil bath with stirring for 16 hours. After 16 hours, a

~200 μL aliquot of the reaction mixture was removed via syringe and filtered through a silica plug, eluting with ethyl acetate. The mixture was analyzed by GC. Conversion of **1** was calculated using a response factor (^{1}H NMR was used to measure the response factor to account for varying detector response). Products were purified by silica gel flash chromatography.

B. Table Summarizing Reaction Optimization

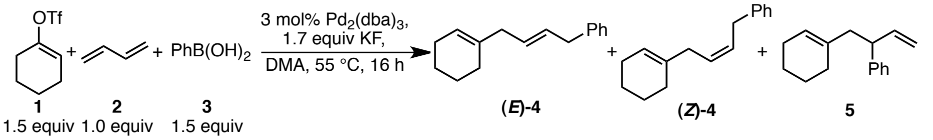
Table s1 Reaction Optimization



Entry	Concentration	x	y	% Conversion[a]	% Yield[b]	Ratio ***E*** : ***Z***[c]	Ratio **4** : **5**[c]
1	0.05 M	1.0	*balloon*	100	81	88:12	2.4
2	0.05 M	1.0	1.0[d]	100	50	91:9	12.6
3	0.025 M	1.0	1.0[d]	98	–	92:8	7.6
4	0.1 M	1.0	1.0[d]	97	–	92:8	9.2
5	0.2 M	1.0	1.0[d]	100	79	91:9	15.0
6	0.05 M	1.2	1.0[d]	–	–	90:10	12.3
7	0.05 M	1.5	1.0[d]	–	71	90:10	16.7
8	0.2 M	1.5	1.0[d]	–	84	92:8	>20
9[e]	0.2 M	1.5	1.0[d]	–	73	92:8	14.3

[a] Conversion of **1** measured by GC using an internal standard and response factor correction. [b] Isolated yield. [c] Ratio of isomers determined by ^{1}H NMR. [d] 15 wt% solution **2** used. [e] Nonaflate usd in place of triflate

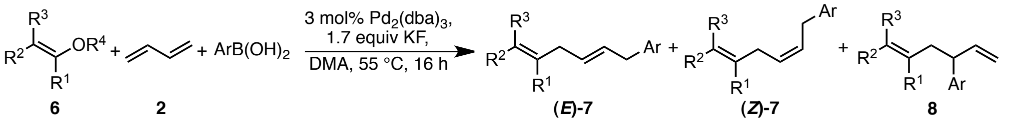
C. Optimized General Procedure



(**s5**)

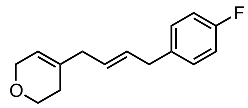
In a nitrogen atmosphere glove box, to an oven dried 10 mL Schlenk tube were added 49 mg (0.85 mmol, 1.7 equiv.) of KF, 91 mg (0.75 mmol, 1.5 equiv.) of **3**, 14 mg (0.015 mmol, 0.03 equiv.) of $Pd_2(dba)_3$, and a solution of 173 mg (0.75 mmol, 1.5 equiv.) of **1** in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and 0.36 mL (0.50 mmol, 1.0 equiv.) of **2** was added as a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.41 M). The vessel was heated at 55 °C in an oil bath with stirring for 16 hours. After completion, the mixture was cooled to ambient temperature and diluted with diethyl ether. The organics were washed with H_2O (3 x 10 mL) and brine (1 x 10 mL), then dried over sodium sulfate and concentrated *in vacuo*. ^{1}H NMR of the crude product mixture was used to determine ratios of stereo and regioisomers. Crude products were purified by silica gel flash chromatography as noted below. Yields represent a mixture of stereo and regioisomers.

D. Scope of the Vinylarylation Reaction



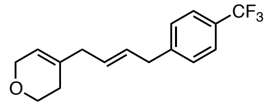
(s6)

(*E*)-4-(4-(4-fluorophenyl)but-2-en-1-yl)-3,6-dihydro-2*H*-pyran - 7a



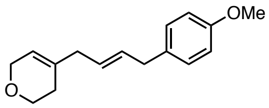
The general procedure was followed using 49 mg (0.85 mmol) of KF, 105 mg (0.75 mmol) of (4-fluorophenyl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 174 mg (0.75 mmol) of 3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7a** was isolated as a colorless oil in an average 55% yield (*E*/*Z* = 90:10, experiment 1: 61 mg, 52%, 16.1:1 regioselectivity; experiment 2: 67 mg, 58%, >20:1 regioselectivity). R_f = 0.42 (3:1 Hexanes : EtOAc). **(*E*)-7a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (m, 2H), 6.97 (m, 2H), 5.60 (app. dt, *J*=15.3, 6.6 Hz, 1H), 5.52-5.41 (m, 2H), 4.12 (m, 2H), 3.78 (t, *J*=5.7 Hz, 2H), 3.34 (d, *J*=6.6 Hz, 2H), 2.72 (d, *J*=6.6 Hz, 2H), 2.04 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5 (d, ^1J=244 Hz), 136.4, 134.7, 131.1, 129.9 (d, ^3J=8 Hz), 128.9, 120.5, 115.2 (d, ^2J=21 Hz), 65.7, 64.5, 40.3, 38.3, 28.7; The following signals can be assigned to **(*Z*)-7a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (d, *J*=7.2 Hz, 2H), 2.83 (d, *J*=7.2 Hz, 2H); IR (neat): 2893, 1507, 1218, 1125, 970, 821, 668 cm^{-1}; HRMS [M + H]$^+$: calcd. 233.1342, obsvd. 233.1345.

(*E*)-4-(4-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)-3,6-dihydro-2*H*-pyran – 7b



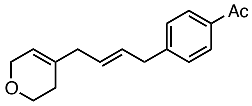
The general procedure was followed using 49 mg (0.85 mmol) of KF, 142 mg (0.75 mmol) of (4-(trifluoromethyl)phenyl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 287 mg (0.75 mmol) of 3,6-dihydro-2*H*-pyran-4-yl perfluorobutane-1-sulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7b** was isolated as a yellow oil in an average 59% yield (*E*/*Z* = 90:10, experiment 1: 75 mg, 54%, >20:1 regioselectivity; experiment 2: 90 mg, 64%, >20:1 regioselectivity). R_f = 0.43 (3:1 Hexanes : EtOAc). **(*E*)-7b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J*=7.9 Hz, 2H), 7.29 (d, *J*=8.5 Hz, 2H), 5.61 (app. dt, *J*=15.3, 6.6 Hz, 1H), 5.51 (app. dt, *J*=15.3, 6.6 Hz, 1H), 5.44 (m, 1H), 4.12 (m, 2H), 3.78 (t, *J*=5.4 Hz, 2H), 3.41 (d, *J*=6.0 Hz, 2H), 2.72 (d, *J*=6.3 Hz, 2H), 2.03 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.9, 134.6, 130.1, 129.7, 128.9, 128.6 (q, ^2J=32 Hz), 125.4 (q, ^3J=4 Hz), 124.5 (q, ^1J=272 Hz), 120.7, 65.7, 64.5, 40.3, 38.9, 28.7; The following signals can be assigned to **(*Z*)-7b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.47 (d, *J*=6.4 Hz, 2H), 2.84 (d, *J*=7.2 Hz, 2H); IR (neat): 2923, 2829, 1321, 1160, 1118, 1065, 970, 848, 668 cm^{-1}; HRMS [M + H]$^+$: calcd. 283.1310, obsvd. 283.1307.

(*E*)-4-(4-(4-methoxyphenyl)but-2-en-1-yl)-3,6-dihydro-2*H*-pyran – 7c



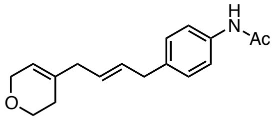
The general procedure was followed using 49 mg (0.85 mmol) of KF, 114 mg (0.75 mmol) of (4-methoxyphenyl)boronic acid, 14 mg (0.015 mmol) of Pd$_2$(dba)$_3$, and a solution of 174 mg (0.75 mmol) of 3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7c** was isolated as a colorless oil in an average 56% yield (*E*/*Z* = 91:9, experiment 1: 67 mg, 55%, 11.1:1 regioselectivity; experiment 2: 69 mg, 57%, 15:1 regioselectivity). R$_f$ = 0.4 (3:1 Hexanes : EtOAc). **(*E*)-7c**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.10 (d, *J*=8.9 Hz, 2H), 6.84 (d, *J*=8.8 Hz, 2H), 5.61 (app. dt, *J*=15, 6.6 Hz, 1H), 5.50-5.40 (m, 2H), 4.12 (m, 2H), 3.80-3.76 (m, 5H), 3.30 (d, *J*=6.6 Hz, 2H), 2.70 (d, *J*=6.9 Hz, 2H), 2.04 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 158.0, 134.8, 131.7, 129.5, 128.5, 128.3, 120.4, 114.0, 65.7, 64.6, 55.4, 40.4, 38.2, 28.6; The following signals can be assigned to **(*Z*)-7c**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.34 (d, *J*=7.5 Hz, 2H), 2.82 (d, *J*=7.2 Hz, 2H); IR (neat): 2896, 2832, 1609, 1242, 1125, 1033, 970, 817 cm^{-1}; HRMS [M + H]$^+$: calcd. 245.1542, obsvd. 245.1548.

(*E*)-1-(4-(4-(3,6-dihydro-2*H*-pyran-4-yl)but-2-en-1-yl)phenyl)ethanone – 7d



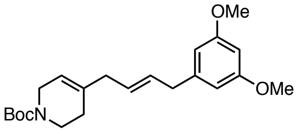
The general procedure was followed using 49 mg (0.85 mmol) of KF, 124 mg (0.75 mmol) of (4-acetylphenyl)boronic acid, 14 mg (0.015 mmol) of Pd$_2$(dba)$_3$, and a solution of 287 mg (0.75 mmol) of 3,6-dihydro-2*H*-pyran-4-yl perfluorobutane-1-sulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7d** was isolated as a yellow oil in an average 62% yield (*E*/*Z* = 90:10, experiment 1: 73 mg, 57%, >20:1 regioselectivity; experiment 2: 86 mg, 67%, >20:1 regioselectivity). R$_f$ = 0.36 (3:1 Hexanes : EtOAc). **(*E*)-7d**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.90 (d, *J*=8.4 Hz, 2H), 7.27 (d, *J*=7.9 Hz, 2H), 5.62 (app. dt, *J*=15, 6.6 Hz, 1H), 5.51 (app. dt, *J*=15.3, 6.6 Hz, 1H), 5.44 (m, 1H), 4.12 (m, 2H), 3.78 (t, *J*=5.7 Hz, 2H), 3.42 (d, *J*=6.5 Hz, 2H), 2.72 (d, *J*=6.5 Hz, 2H), 2.59 (s, 3H), 2.04 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 198.0, 146.6, 135.4, 134.6, 130.1, 129.6, 128.8, 128.7, 120.7, 65.7, 64.5, 40.3, 39.1, 28.7, 26.7; IR (neat): 2921, 2828, 1680, 1357, 1267, 1125, 970, 848, 668 cm^{-1}; HRMS [M + Na]$^+$: calcd. 279.1361, obsvd. 279.1362.

(*E*)-*N*-(4-(4-(3,6-dihydro-2*H*-pyran-4-yl)but-2-en-1-yl)phenyl)acetamide – 7e



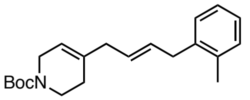
The general procedure was followed using 49 mg (0.85 mmol) of KF, 134 mg (0.75 mmol) of (4-acetamidophenyl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 287 mg (0.75 mmol) of 3,6-dihydro-2*H*-pyran-4-yl perfluorobutane-1-sulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 6:4:1:1 ethyl acetate : dichloromethane : acetone : hexanes eluent. The product **7e** was isolated as a colorless oil in an average 59% yield (*E*/*Z* = 91:9, experiment 1: 74 mg, 55%, >20:1 regioselectivity; experiment 2: 87 mg, 64%, >20:1 regioselectivity). R_f = 0.35 (6:4:1:1 EtOAc:DCM:acetone:hexanes). **(*E*)-7e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 2H), 7.24-7.08 (m, 2H), 6.93 (d, *J*=7.7 Hz, 1H), 5.61 (app. dt, *J*=15.3, 6.6 Hz, 1H), 5.54-5.42 (m, 2H) 4.12 (m, 2H), 3.38 (t, *J*=5.7 Hz, 2H), 3.34 (d, *J*=6.3 Hz, 2H), 2.70 (d, *J*=6.6 Hz, 2H), 2.17 (s, 3H), 2.04 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3, 141.9, 138.1, 134.8, 130.9, 129.1, 128.9, 124.6, 120.5, 120.0, 117.7, 65.7, 64.6, 40.3, 39.0, 28.6, 24.8; The following signals can be assigned to **(*Z*)-7e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.40 (d, *J*=7.2 Hz, 2H), 2.85 (d, *J*=7.3 Hz, 2H); IR (neat): 3303, 2922, 2829, 1664, 1549, 1436, 1317, 1125, 969 cm^{-1}; HRMS [M + Na]$^+$: calcd. 294.1470, obsvd. 294.1462.

(*E*)-*tert*-butyl 4-(4-(3,5-dimethoxyphenyl)but-2-en-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate – 7f



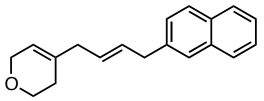
The general procedure was followed using 49 mg (0.85 mmol) of KF, 136 mg (0.75 mmol) of (3,5-dimethoxyphenyl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 249 mg (0.75 mmol) of *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-5,6-dihydropyridine-1(2*H*)-carboxylate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7f** was isolated as a yellow oil in an average 66% yield (*E*/*Z* = 93:7, experiment 1: 121 mg, 65%, >20:1 regioselectivity; experiment 2: 125 mg, 67%, >20:1 regioselectivity). R_f = 0.38 (3:1 Hexanes : EtOAc). **(*E*)-7f**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.34 (d, *J*=2.3 Hz, 2H), 6.30 (t, *J*=2.2 Hz, 1H), 5.59 (app. dt, *J*=15.1, 7 Hz, 1H), 5.48 (app. dt, *J*=15.1, 7 Hz, 1H), 5.38 (s, 1H), 3.85 (m, 2H), 3.77 (s, 6H), 3.47 (t, *J*=6.0 Hz, 2H), 3.28 (d, *J*=6.5 Hz, 2H), 2.70 (d, *J*=7.0 Hz, 2H), 2.03 (m, 2H) 1.46 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.9, 155.1, 143.2, 135.7, 130.9, 128.9, 118.7, 106.6, 98.1, 79.5, 55.4, 43.4, 40.4, 39.3, 34.9, 28.6, 28.5; The following signals can be assigned to **(*Z*)-7f**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.31 (d, *J*=7.5 Hz, 2H), 2.80 (d, *J*=7.5 Hz, 2H); IR (neat): 2972, 2836, 1693, 1417, 1238, 1143, 1058, 828 cm^{-1}; HRMS [M + Na]$^+$: calcd. 396.2151, obsvd. 396.2153.

(*E*)-*tert*-butyl 4-(4-(*o*-tolyl)but-2-en-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate – 7g



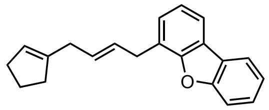
The general procedure was followed using 49 mg (0.85 mmol) of KF, 102 mg (0.75 mmol) of *o*-tolylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 249 mg (0.75 mmol) of *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-5,6-dihydropyridine-1(2*H*)-carboxylate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^1H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7g** was isolated as a colorless oil in an average 57% yield (*E*/*Z* = 90:10, experiment 1: 96 mg, 58%, 16.4:1 regioselectivity; experiment 2: 92 mg, 56%, >20:1 regioselectivity). R_f = 0.5 (3:1 Hexanes : EtOAc). **(*E*)-7g** ^1H NMR (500 MHz, $CDCl_3$): δ 7.13 (m, 4H), 5.59 (app. dt, *J*=15.5, 6.5 Hz, 1H), 5.38 (app. dt, *J*=15, 6.5 Hz, 1H), 5.35 (m, 1H), 3.85 (m, 2H), 3.47 (t, *J*=6.0 Hz, 2H), 3.34 (d, *J*=6.5 Hz, 2H), 2.70 (d, *J*=7.0 Hz, 2H), 2.29 (s, 3H), 2.02 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.1, 138.8, 136.4, 130.5, 130.3, 129.1, 128.5, 126.3, 126.2, 118.6, 79.5, 43.4, 40.5, 36.6, 35.1, 28.6, 28.5, 19.5; The following signals can be assigned to **(*Z*)-7g**: ^1H NMR (500 MHz, $CDCl_3$): δ 3.37 (d, *J*=7.5 Hz, 2H), 2.80 (d, *J*=7.0 Hz, 2H); IR (neat): 2973, 1693, 1415, 1363, 1237, 1167, 970 cm^{-1}; HRMS HRMS $[M + Na]^+$: calcd. 350.2096, obsvd. 350.2072.

(*E*)-4-(4-(naphthalen-2-yl)but-2-en-1-yl)-3,6-dihydro-2*H*-pyran – 7h



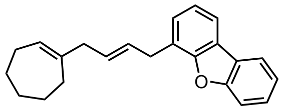
The general procedure was followed using 49 mg (0.85 mmol) of KF, 129 mg (0.75 mmol) of naphthalen-2-ylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 174 mg (0.75 mmol) of 3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^1H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **7h** was isolated as a colorless oil in an average 54% yield (*E*/*Z* = 93:7, experiment 1: 67 mg, 50%, >20:1 regioselectivity; experiment 2: 77 mg, 58%, >20:1 regioselectivity). R_f = 0.44 (3:1 Hexanes : EtOAc). **(*E*)-7h** ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (dd, *J*=8.0, 6.5 Hz, 3H), 7.62 (s, 1H), 7.44 (quint, *J*=7.5 Hz, 2H), 7.33 (d, *J*=8.5 Hz, 1H) 5.71 (app. dt, *J*=15, 7.5 Hz, 1H), 5.54 (app. dt, *J*=15, 7.0 Hz, 1H), 5.46 (m, 1H), 4.12 (m, 2H), 3.79 (t, *J*=5.5 Hz, 2H), 3.53 (d, *J*=6.5 Hz, 2H), 2.74 (d, *J*=7.0 Hz, 2H), 2.06 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.3, 134.8, 133.8, 132.2, 131.2, 128.9, 128.1, 127.8, 127.6, 127.5, 126.6, 126.0, 125.4, 120.5, 65.7, 64.6, 40.4, 39.3, 28.7; The following signals can be assigned to **(*Z*)-7h**: ^1H NMR (500 MHz, $CDCl_3$): δ 3.58 (d, *J*=7.5 Hz, 2H), 2.90 (d, *J*=7.5 Hz, 2H); IR (neat): 2890, 1507, 1425, 1233, 1124, 970, 815, 745 cm^{-1}; HRMS $[M + H]^+$: calcd. 265.1592, obsvd. 265.1584.

(*E*)-4-(4-(cyclopent-1-en-1-yl)but-2-en-1-yl)dibenzo[*b,d*]furan – 7i



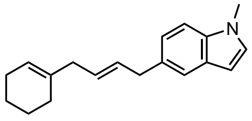
The general procedure was followed using 49 mg (0.85 mmol) of KF, 159 mg (0.75 mmol) of dibenzo[*b,d*]furan-4-ylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 275 mg (0.75 mmol) of cyclopent-1-en-1-yl perfluorobutane-1-sulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^1H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 1% ethyl acetate to hexanes eluent. The product **7i** was isolated as a colorless oil in an average 57% yield (*E*/*Z* = 91:9 experiment 1: 75 mg, 52%, >20:1 regioselectivity; experiment 2: 88 mg, 62%, >20:1 regioselectivity). R_f = 0.53 (20:1 Hexanes : EtOAc). **(*E*)-7i** ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (dt, *J*=7.7 Hz, 1H), 7.81 (t, *J*=4.5 Hz, 1H), 7.58 (d, *J*=8.5 Hz, 1H), 7.45 (td, *J*=7.8, 1.5 Hz, 1H), 7.33 (td, *J*=7.7, 1.0 Hz, 1H), 7.28 (d, *J*=5.0 Hz, 2H), 5.76 (app. dt, *J*=15, 6.5 Hz, 1H), 5.66 (app. dt, *J*=15, 7 Hz, 1H), 5.36 (m, 1H), 3.72 (d, *J*=6.5 Hz, 2H), 2.80 (d, *J*=6.6 Hz, 2H), 2.30 (m, 2H), 2.23 (t, *J*=6.6 Hz, 2H), 1.85 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.2, 137.0, 130.0, 128.5, 127.3, 127.1, 125.1, 124.7, 124.2, 124.0, 122.9, 122.7, 120.8, 118.5, 111.9, 111.8, 35.3, 34.7, 32.9, 32.6, 23.6; The following signals can be assigned to **(*Z*)-7i**: ^1H NMR (500 MHz, $CDCl_3$): δ 3.77 (d, *J*=7.5 Hz, 2H), 3.02 (d, *J*=7.5 Hz, 2H); IR (neat): 2842, 1450, 1184, 969, 844, 749 cm^{-1}; HRMS $[M + H]^+$: calcd. 289.1592, obsvd. 289.1595.

(*E*)-4-(4-(cyclohept-1-en-1-yl)but-2-en-1-yl)dibenzo[*b,d*]furan– 7j



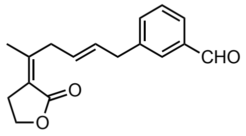
The general procedure was followed using 49 mg (0.85 mmol) of KF, 159 mg (0.75 mmol) of dibenzo[*b,d*]furan-4-ylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 183 mg (0.75 mmol) of cyclohept-1-en-1-yl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.41 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^1H NMR - 1.22 M). Crude product was purified using silica gel flash chromatography with a 1% diethyl ether to hexanes eluent. The product **7j** was isolated as a colorless oil in an average 51% yield (*E*/*Z* = 92:8, experiment 1: 82 mg, 51%, 20:1 regioselectivity; experiment 2: 81 mg, 51%, >20:1 regioselectivity). R_f = 0.54 (99:1 Hexanes : Et_2O). **(*E*)-7j** ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (dt, *J*=8.0 Hz, 1H), 7.81 (t, *J*=4.5 Hz, 1H), 7.59 (d, *J*=8.0 Hz, 1H), 7.46 (td, *J*=7.4, 1.0 Hz, 1H), 7.33 (td, *J*=8.0, 1.0 Hz, 1H), 7.29 (d, *J*=5 Hz, 2H), 5.76 (app. dt, *J*=15.5, 7.0 Hz, 1H), 5.58 (m, 2H), 3.73 (d, *J*=6.5 Hz, 2H), 2.72 (d, *J*=6.5 Hz, 2H), 2.08 (m, 4H), 1.71 (quint, *J*=5.5 Hz, 2H), 1.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 154.7, 143.5, 130.8, 128.6, 127.3, 127.0, 126.7, 125.2, 124.7, 124.0, 122.9, 122.7, 120.8, 118.5, 111.8, 43.4, 32.9, 32.8, 32.7, 28.5, 27.5, 26.8; The following signals can be assigned to **(*Z*)-7j**: ^1H NMR (500 MHz, $CDCl_3$): δ 3.79 (d, *J*=7.0 Hz, 2H), 2.95 (d, *J*=7.5 Hz, 2H); IR (neat): 2916, 2360, 1449, 968, 748 cm^{-1}; HRMS $[M + H]^+$: calcd. 317.1905, obsvd. 317.1914.

(*E*)-5-(4-(cyclohex-1-en-1-yl)but-2-en-1-yl)-1-methyl-1*H*-indole – 7k



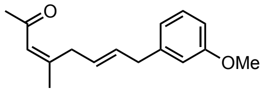
The general procedure was followed using 49 mg (0.85 mmol) of KF, 131 mg (0.75 mmol) of (1-methyl-1*H*-indol-5-yl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 173 mg (0.75 mmol) of cyclohex-1-en-1-yl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.41 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.22 M). Crude product was purified using silica gel flash chromatography with a 5% acetone to hexanes eluent. The product **7k** was isolated as a colorless oil in an average 85% yield (*E*/*Z* = 94:6, experiment 1: 114 mg, 86%, >20:1 regioselectivity; experiment 2: 112 mg, 84%, >20:1 regioselectivity). R_f = 0.42 (19:1 Hexanes : Acetone). **(*E*)-7k** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.24 (m, 1H), 7.06 (d, *J*=8.6 Hz, 1H), 7.02 (d, *J*=3.0 Hz, 1H), 6.42 (d, *J*=3.0 Hz, 1H), 5.65 (app. dt, *J*=15.3, 7.5 Hz, 1H), 5.48 (m, 2H), 3.77 (s, 3H), 3.44 (d, *J*=6.6 Hz, 2H), 2.65 (d, *J*=6.3 Hz, 2H), 2.03-1.88 (m, 4H), 1.70-1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.4, 131.7, 131.4, 128.9, 128.7, 125.4, 122.6, 121.4, 120.1, 109.0, 100.6, 41.3, 39.1, 32.8, 28.4, 25.3, 23.0 22.6; The following signals can be assigned to **(*Z*)-7k**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.51 (d, *J*=7.1 Hz, 2H), 2.83 (d, *J*=7.4 Hz, 2H); IR (neat): 2920, 1512, 1338, 1243, 968, 791 cm^{-1}; HRMS [M + H]$^+$: calcd. 266.1909, obsvd. 266.1906.

3-((2*E*,5*Z*)-5-(2-oxodihydrofuran-3(2*H*)-ylidene)hex-2-en-1-yl)benzaldehyde – 7l



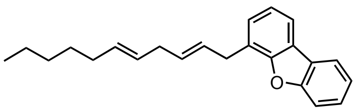
The general procedure was followed using 49 mg (0.85 mmol) of KF, 113 mg (0.75 mmol) of (3-formylphenyl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 195 mg (0.75 mmol) of (*Z*)-1-(2-oxodihydrofuran-3(2*H*)-ylidene)ethyl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.30 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.66 M). Crude product was purified using silica gel flash chromatography with a 50% ethyl acetate to hexanes eluent. The product **7l** was isolated as a colorless oil in an average 60% yield (*E*/*Z* = 89:11, experiment 1: 74 mg, 55%, >20:1 regioselectivity; experiment 2: 88 mg, 65%, >20:1 regioselectivity). R_f = 0.38 (1:1 Hexanes : EtOAc). **(*E*)-7l** ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.70 (m, 2H), 7.44 (m, 2H), 5.69 (app. dt, *J*=15, 7.0 Hz, 1H), 5.51 (app. dt, *J*=15.5, 7.0 Hz, 1H), 4.30 (t, *J*=7.5 Hz, 2H), 3.52 (d, *J*=7.0 Hz, 2H), 3.41 (d, *J*=6.5 Hz, 2H), 2.88 (m, 2H), 1.86 (t, *J*=1.5 Hz, 3H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (126 MHz, $CDCl_3$): δ 192.7, 151.7, 141.9, 136.8, 134.9, 130.6, 129.6, 129.2, 128.9, 128.0, 127.4, 119.1, 64.4, 38.7, 35.9, 27.9, 22.2; The following signals can be assigned to **(*Z*)-7l**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.72 (d, *J*=6.5 Hz, 2H), 3.60 (d, *J*=7.5 Hz, 2H); IR (neat): 2913, 2841, 1736, 1374, 1215, 1035, 969 cm^{-1}; HRMS [M + Na]$^+$: calcd. 293.1154, obsvd. 293.1150.

(3*Z*,6*E*)-8-(3-methoxyphenyl)-4-methylocta-3,6-dien-2-one – 7m



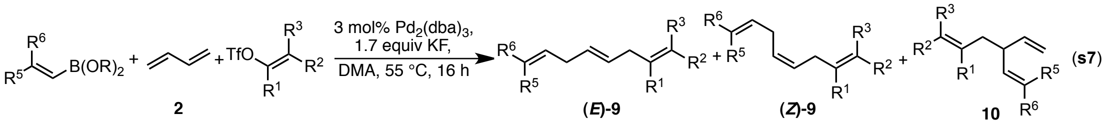
The general procedure was followed using 49 mg (0.85 mmol) of KF, 114 mg (0.75 mmol) of (3-methoxyphenyl)boronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 174 mg (0.75 mmol) of (*Z*)-4-oxopent-2-en-2-yl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.41 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR - 1.22 M). Crude product was purified using silica gel flash chromatography with a 10% acetone to hexanes eluent. The product **7m** was isolated as a colorless oil in an average 44% yield (*E*/*Z* = 91:9, experiment 1: 57 mg, 46%, >20:1 regioselectivity; experiment 2: 52 mg, 43%, >20:1 regioselectivity). R_f = 0.36 (9:1 Hexanes : Acetone). **(*E*)-7m** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (t, *J*=7.6 Hz, 1H), 6.76 (m, 3H), 6.08 (s, 1H), 5.67 (app. dt, *J*=15.3, 6.9 Hz, 1H), 5.48 (app. dt, *J*=15.0, 6.6 Hz, 1H), 3.90 (s, 3H), 3.35 (d, *J*=6.9 Hz, 2H), 2.83 (d, *J*=7.2 Hz, 2H), 2.18 (s, 3H), 2.12 (s, 3H; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 159.7, 157.2, 142.0, 132.4, 129.4, 127.2, 124.0, 120.8, 114.3, 111.3, 55.1, 44.0, 38.9, 31.7, 19.3; The following signals can be assigned to **(*Z*)-7m**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41 (d, *J*=6.4 Hz, 2H), 2.97 (d, *J*=7.1 Hz, 2H); IR (neat): 1772, 1684, 1506, 1259, 668, 655 cm^{-1}; HRMS [M + Na]$^+$: calcd. 267.1361, obsvd. 267.1361.

4-((2*E*,5*E*)-undeca-2,5-dien-1-yl)dibenzo[*b*,*d*]furan – 7n

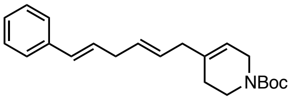


The general procedure was followed using 49 mg (0.85 mmol) of KF, 159 mg (0.75 mmol) of dibenzo[*b*,*d*]furan-4-ylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 185 mg (0.75 mmol) of (*E*)-hept-1-en-1-yl trifluoromethanesulfonate **6n** in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.54 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR – 0.92 M). Crude product was purified using silica gel flash chromatography with a 2.5% ethyl acetate to hexanes eluent. The product **7n** was isolated as a colorless oil in an average 60% yield (*E*/*Z* = 93:7, experiment 1: 96 mg, 60%, 15.2:1 regioselectivity; experiment 2: 94 mg, 59%, 18.1:1 regioselectivity). R_f = 0.45 (39:1 Hexanes : Ethyl acetate). **(*E*)-7n** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, *J*=8.0 Hz, 1H), 7.82 (t, *J*=4.4 Hz, 1H), 7.60 (d, *J*=8.2 Hz, 1H), 7.46 (t, *J*=8.0 Hz, 1H), 7.34 (t, *J*=7.6 Hz, 1H), 7.29 (m, 2H), 5.75 (app. dt, *J*=15.8, 7.7 Hz, 1H), 5.63 (app. dt, *J*=15.8, 8.2 Hz, 1H), 5.44 (m, 2H), 3.73 (d, *J*=6.6 Hz, 2H), 2.75 (t, *J*=6.0 Hz, 2H), 1.99 (q, *J*=6.9 Hz, 2H), 1.38-1.23 (m, 6H), 0.88 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 154.8, 131.7, 131.1, 128.3, 127.9, 127.4, 127.1, 125.2, 124.8, 124.1, 123.0, 122.8, 120.9, 118.6, 111.9, 35.8, 32.9, 32.8, 31.7, 29.4, 22.8, 14.3; The following signals can be assigned to **(*Z*)-7n**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (d, *J*=7.8 Hz, 2H), 2.98 (t, *J*=6.8 Hz, 2H); IR (neat): 2922, 1472, 1183, 966, 844, 747 cm^{-1}; HRMS [M + H]$^+$: calcd. 319.2062, obsvd. 319.2070.

E. Scope of the Vinylvinylation Reaction

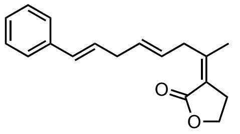


tert-butyl 4-((2*E*,5*E*)-6-phenylhexa-2,5-dien-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate – 9a



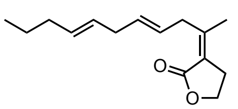
The general procedure was followed using 49 mg (0.85 mmol) of KF, 111 mg (0.75 mmol) of (*E*)-styrylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 249 mg (0.75 mmol) of *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-5,6-dihydropyridine-1(2*H*)-carboxylate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.38 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR – 1.30 M). Crude product was purified using silica gel flash chromatography with a 10% ethyl acetate to hexanes eluent. The product **9a** was isolated as a colorless oil in an average 43% yield (*E*/*Z* = 93:7, experiment 1: 72 mg, 43%, 4.6:1 regioselectivity; experiment 2: 73 mg, 43%, 8.3:1 regioselectivity). R_f = 0.26 (10:1 Hexanes : EtOAc). Major product: **(*E*)-9a** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (m, 2H), 7.29 (t, *J*=7.7 Hz, 2H), 7.20 (t, *J*=7.2 Hz, 1H), 6.37 (t, *J*=16 Hz, 1H), 6.21 (app. dt, *J*=16.4, 6.5 Hz, 1H), 5.54 (app. dt, *J*=15.4, 6.5 Hz, 1H), 5.48 (app. dt, *J*=16.3, 6.5 Hz, 1H), 5.38 (s, 1H), 3.86 (m, 2H), 3.48 (m, 2H), 2.93 (t, *J*=6.0 Hz, 2H), 2.71 (d, *J*=6.0 Hz, 2H), 2.05 (m, 2H), 1.47 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.1, 137.8, 132.5, 130.6, 130.1, 129.0, 128.6, 127.1, 126.2, 126.1, 114.9, 79.5, 42.9, 40.5, 36.0, 30.5, 28.6, 28.5; The following signals can be assigned to **(*Z*)-9a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.79 (d, *J*=6.5 Hz, 2H); IR (neat): 2973, 2899, 1675, 1418, 1364, 1171, 668 cm^{-1}; HRMS $[M + Na]^+$: calcd. 362.2096, obsvd. 362.2097.

(*Z*)-3-((4*E*,7*E*)-8-phenylocta-4,7-dien-2-ylidene)dihydrofuran-2(3*H*)-one – 9b



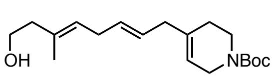
The general procedure was followed using 49 mg (0.85 mmol) of KF, 111 mg (0.75 mmol) of (*E*)-styrylboronic acid, 14 mg (0.015 mmol) of $Pd_2(dba)_3$, and a solution of 195 mg (0.75 mmol) of (*Z*)-1-(2-oxodihydrofuran-3(2*H*)-ylidene)ethyl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.41 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR – 1.22 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **9b** was isolated as a colorless oil in an average 67% yield (*E*/*Z* = 93:7, experiment 1: 84 mg, 62%, 10.1:1 regioselectivity; experiment 2: 95 mg, 71%, 7.8:1 regioselectivity). R_f = 0.29 (3:1 Hexanes : EtOAc). **(*E*)-9b** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J*=7.2 Hz, 2H), 7.29 (t, *J*=7.6 Hz, 2H), 7.20 (t, *J*=7.2 Hz, 1H), 6.38 (d, *J*=16 Hz, 1H), 6.20 (app. dt, *J*=16, 6.8 Hz, 1H), 5.62 (app. dt, *J*=15.2, 6.4 Hz, 1H), 5.48 (app. dt, *J*=15.2, 6.8 Hz, 1H), 4.30 (t, *J*=8.0 Hz, 2H), 3.51 (d, *J*=6.8 Hz, 2H), 2.89 (m, 4H), 1.87 (s, 3H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.2, 152.0, 137.8, 130.6, 130.5, 128.9, 128.6, 127.7, 127.1, 126.1, 118.9, 64.4, 36.0, 35.9, 27.9, 22.2; The following signals can be assigned to **(*Z*)-9b**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.63 (t, *J*=7.6 Hz, 2H), 3.64 (d, *J*=7.6 Hz, 2H); IR (neat): 2911, 1493, 1373, 1213, 1035, 966 cm^{-1}; HRMS [M + Na]$^+$: calcd. 291.1361, obsvd. 291.1361.

(*Z*)-3-((4*E*,7*E*)-undeca-4,7-dien-2-ylidene)dihydrofuran-2(3*H*)-one – 9c



The general procedure was followed using 49 mg (0.85 mmol) of KF, 86 mg (0.75 mmol) of (*E*)-pent-1-en-1-ylboronic acid, 14 mg (0.015 mmol) of Pd$_2$(dba)$_3$, and a solution of 195 mg (0.75 mmol) of (*Z*)-1-(2-oxodihydrofuran-3(2*H*)-ylidene)ethyl trifluoromethanesulfonate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.41 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR – 1.22 M). Crude product was purified using silica gel flash chromatography with a 25% ethyl acetate to hexanes eluent. The product **9c** was isolated as a yellow oil in an average 70% yield (*E*/*Z* = 92:8, experiment 1: 82 mg, 70%, 6.6:1 regioselectivity; experiment 2: 83 mg, 70%, 5.8:1 regioselectivity). R$_f$ = 0.37 (3:1 Hexanes : EtOAc). **(*E*)-9c** ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.53 (app. dt, *J*=15, 8.5 Hz, 1H), 5.39 (m, 3H), 4.23 (t, *J*=7.5 Hz, 2H), 3.47 (d, *J*=7.0 Hz, 2H), 2.87 (t, *J*=6.0 Hz, 2H), 2.68 (t, *J*=5.5 Hz, 2H), 1.95 (m, 2H), 1.85 (m, 3H), 1.36 (sext, *J*=6.0 Hz, 2H), 0.88 (t, *J*=6.0 Hz, 3H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.3, 152.4, 131.7, 131.4, 128.4, 126.8, 118.7, 64.4, 36.0, 35.7, 34.8, 28.0, 22.8, 22.2, 13.8; The following signals can be assigned to **(*Z*)-9c**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 3.58 (d, *J*=7.5 Hz, 2H); IR (neat): 2957, 2359, 1740, 1373, 1036, 967 cm^{-1}; HRMS [M + Na]$^+$: calcd. 257.1517, obsvd. 257.1519.

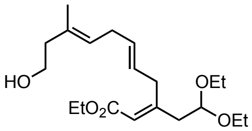
tert-butyl 4-((2*E*,5*E*)-8-hydroxy-6-methylocta-2,5-dien-1-yl)-5,6-dihydropyridine-1(2*H*)-carboxylate – 9d



The general procedure was followed using 49 mg (0.85 mmol) of KF, 159 mg (0.75 mmol) of (*E*)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol **s5**, 28 mg (0.03 mmol) of Pd$_2$(dba)$_3$, and a solution of 249 mg (0.75 mmol) of *tert*-butyl 4-(((trifluoromethyl)sulfonyl)oxy)-5,6-dihydropyridine-1(2*H*)-carboxylate in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.36 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR – 1.41 M). Crude product was purified using silica gel flash chromatography with a 50% ethyl acetate to hexanes eluent. The product **9d** was isolated as a colorless oil in an average 49% yield (*E*/*Z* = 92:8, experiment 1: 83 mg, 52%, 3.0:1 regioselectivity; experiment 2: 75 mg, 46%, 2.8:1 regioselectivity). R$_f$ = 0.43 (1:1 Hexanes : EtOAc). **(*E*)-9d** ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.42 (app. dt, *J*=16.5, 8.5 Hz, 1H), 5.40-5.31 (m, 2H), 5.26 (t, *J*=10 Hz, 1H), 3.85 (m, 2H), 3.68 (t, *J*=8.4 Hz, 2H), 3.47 (t, *J*=8.4 Hz, 2H), 2.75 (t, *J*=7.2 Hz, 2H), 2.67 (m, 2H), 2.27 (t, *J*=8.4

Hz, 2H), 2.01 (m, 2H), 1.64 (s, 3H), 1.46 (s, 9H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (126 MHz, CDCl$_3$): δ 155.2, 132.4, 130.8, 127.5, 126.4, 125.8, 115.7, 79.6, 60.4, 43.7, 42.9, 40.5, 35.1, 31.4, 28.7, 28.5, 15.9; The following signals can be assigned to **(*Z*)-9d**: ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.85 (t, *J*=7.8 Hz, 2H);IR (neat): 3392, 2359, 1713, 1436, 1218, 1140, 1042, 968, 858 cm^{-1}; HRMS [M + Na]$^+$: calcd. 275.1623, obsvd. 275.1623.

(2*E*,5*E*,8*E*)-ethyl 3-(2,2-diethoxyethyl)-11-hydroxy-9-methylundeca-2,5,8-trienoate – 9e



The general procedure was followed using 49 mg (0.85 mmol) of KF, 159 mg (0.75 mmol) of (*E*)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-ol **s5**, 28 mg (0.03 mmol) of Pd$_2$(dba)$_3$, and a solution of 268 mg (0.75 mmol) of (*Z*)-ethyl 5,5-diethoxy-3-(((trifluoromethyl)sulfonyl)oxy)pent-2-enoate **s3** in 2.5 mL of DMA. The Schlenk tube was transferred from the glove box and added was 0.36 mL (0.50 mmol) of **2** in a 15 wt% solution of *n*-hexane (concentration determined by ^{1}H NMR – 1.41 M). Crude product was purified using silica gel flash chromatography with a 33% ethyl acetate to hexanes eluent. The product **9e** was isolated as a colorless oil in an average 71% yield (*E*/*Z* = 91:9, experiment 1: 127 mg, 72%, 2.0:1 regioselectivity; experiment 2: 125 mg, 70%, 6.7:1 regioselectivity). R$_f$ = 0.27 (2:1 Hexanes : EtOAc). **(*E*)-9e** ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.75 (s, 1H), 5.50 (app. dt, *J*=15.8, 6.0 Hz, 1H), 5.41 (app. dt, *J*=15.5, 6.3 Hz, 1H), 5.24 (t, *J*=7.2 Hz, 1H), 4.62 (t, *J*=6.0 Hz, 1H), 4.15 (q, *J*=7.2 Hz, 2H), 3.65 (m, 4H), 3.48 (m, 2H), 3.38 (d, *J*=6.3 Hz, 2H), 2.73 (t, *J*=6.3 Hz, 2H), 2.43 (d, *J*=5.7 Hz, 2H), 2.25 (t, *J*=6.3 Hz, 2H), 1.62 (m, 3H), 1.27 (dt, *J*=7.2, 1.2 Hz, 3H), 1.19 (dt, *J*=6.9, 1.0 Hz, 6H); (The stereochemistry was confirmed by NOESY1D NMR spectroscopy); ^{13}C NMR (100 MHz, CDCl$_3$): δ 166.4, 156.6, 132.4, 131.0, 126.7, 125.6, 118.3, 101.7, 61.9, 60.3, 59.8, 42.8, 42.0, 35.8, 31.4, 15.9, 15.4, 14.4; IR (neat): 3420, 2359, 1698, 1419, 1170, 969, 770 cm^{-1}; HRMS [M + Na]$^+$: calcd. 377.2304, obsvd. 377.2312.

V. References:

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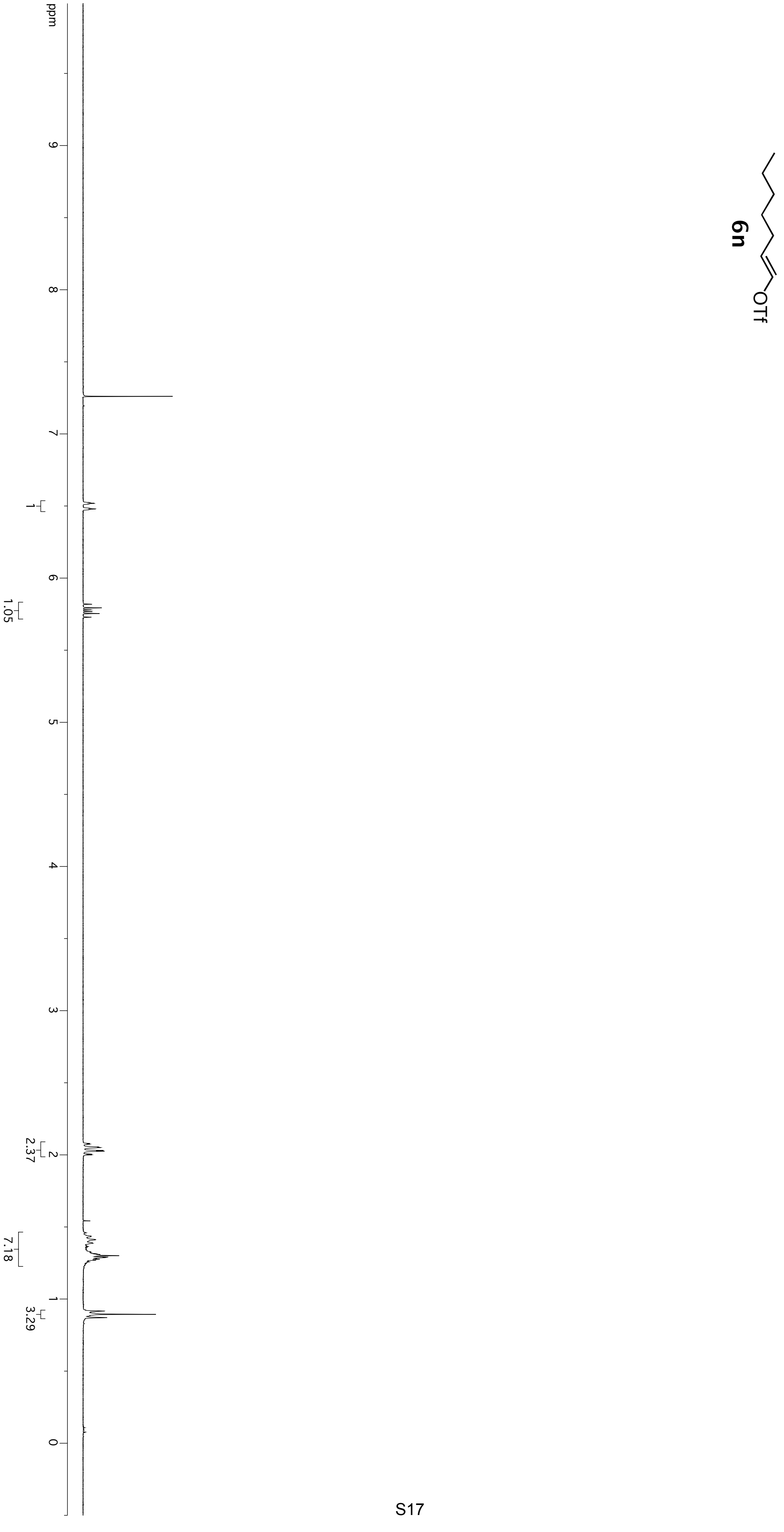
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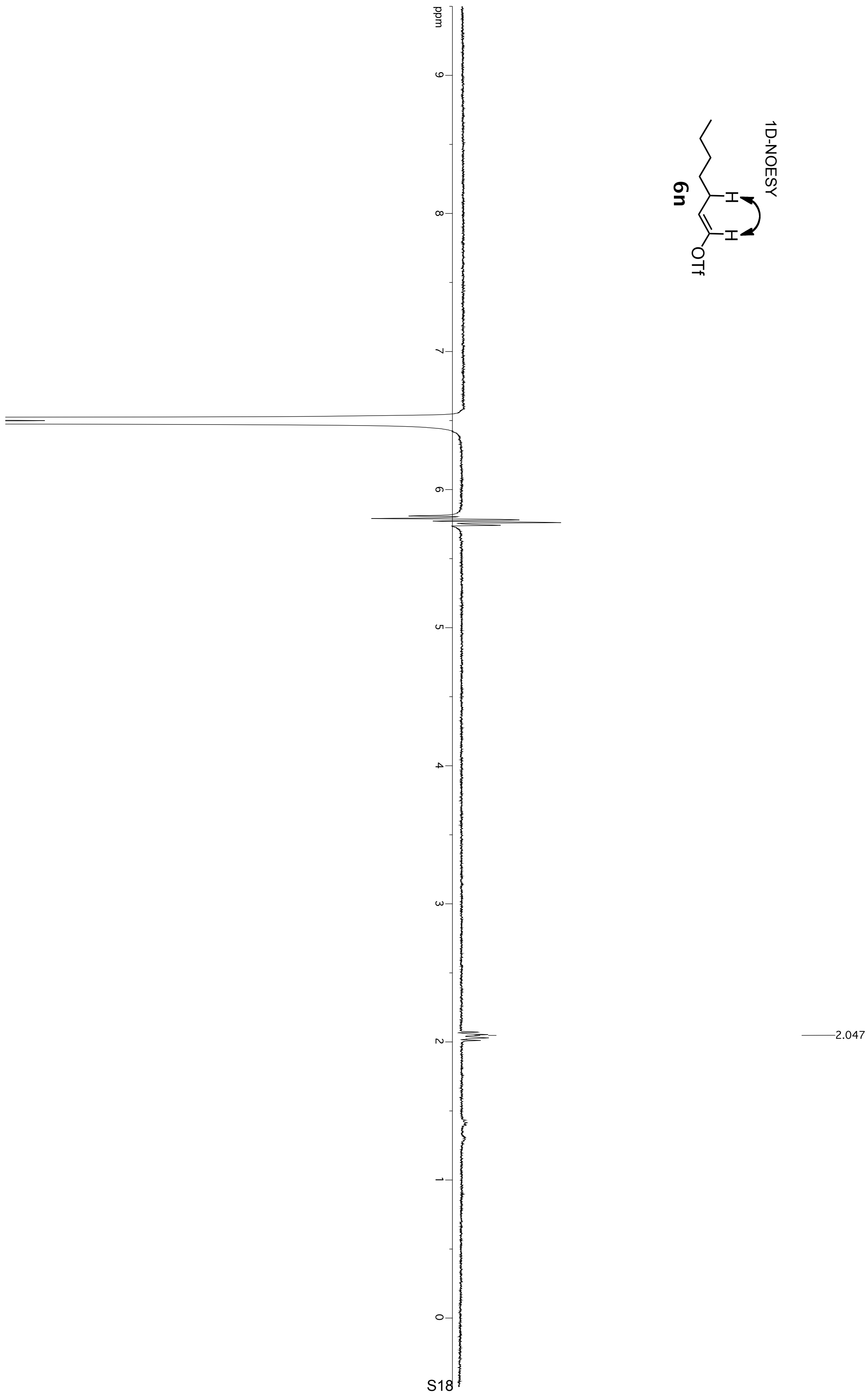
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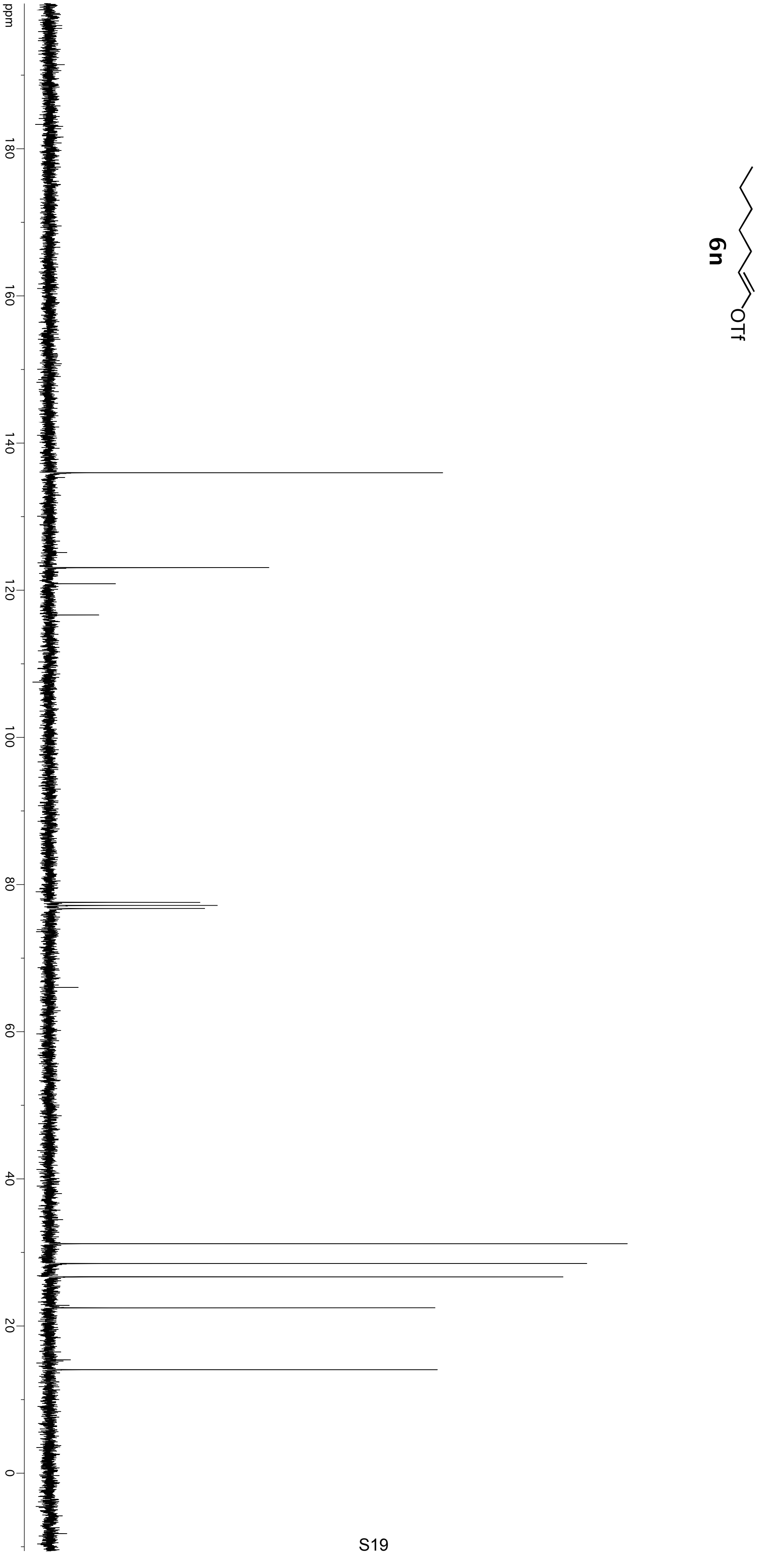

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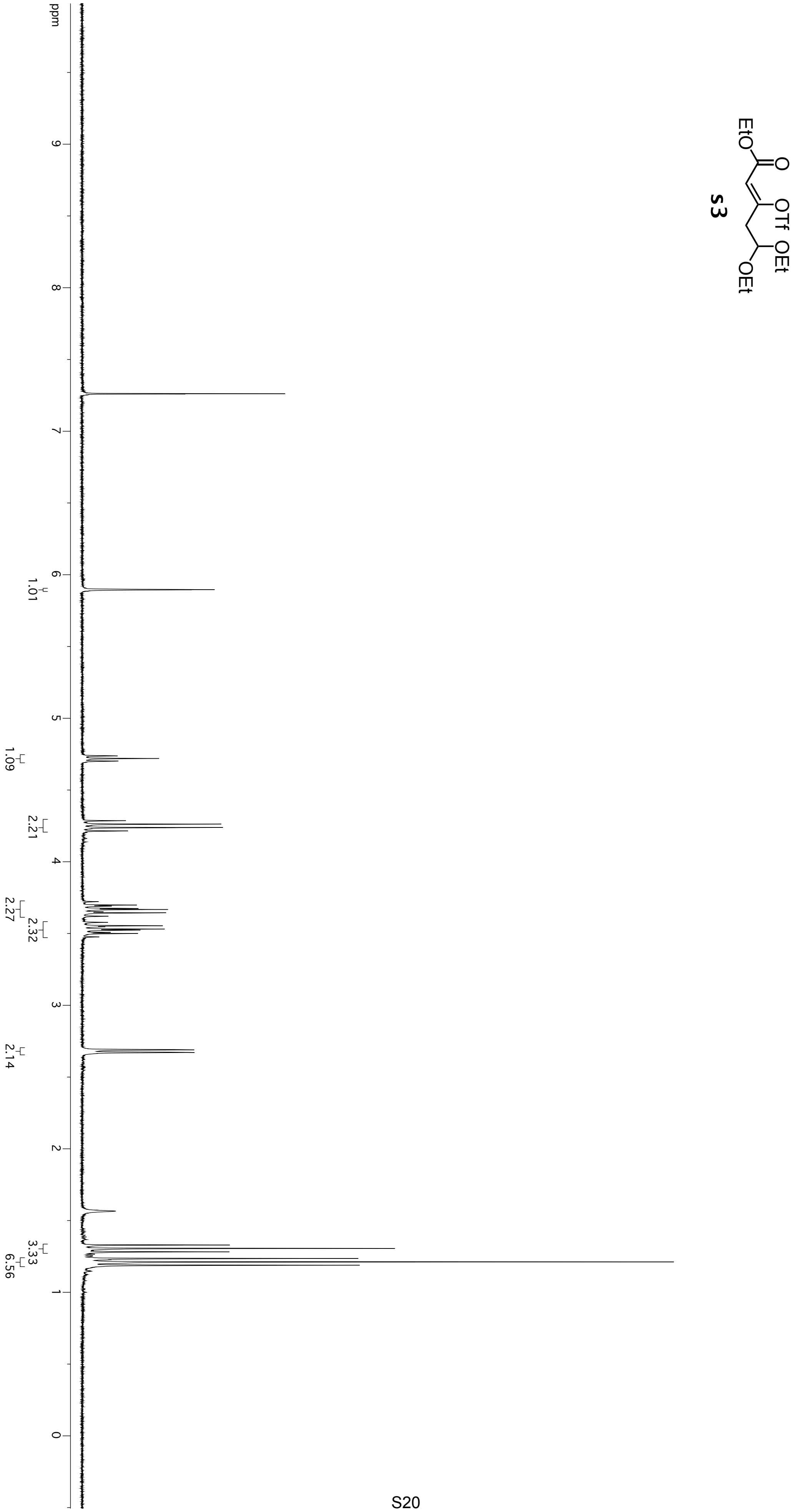

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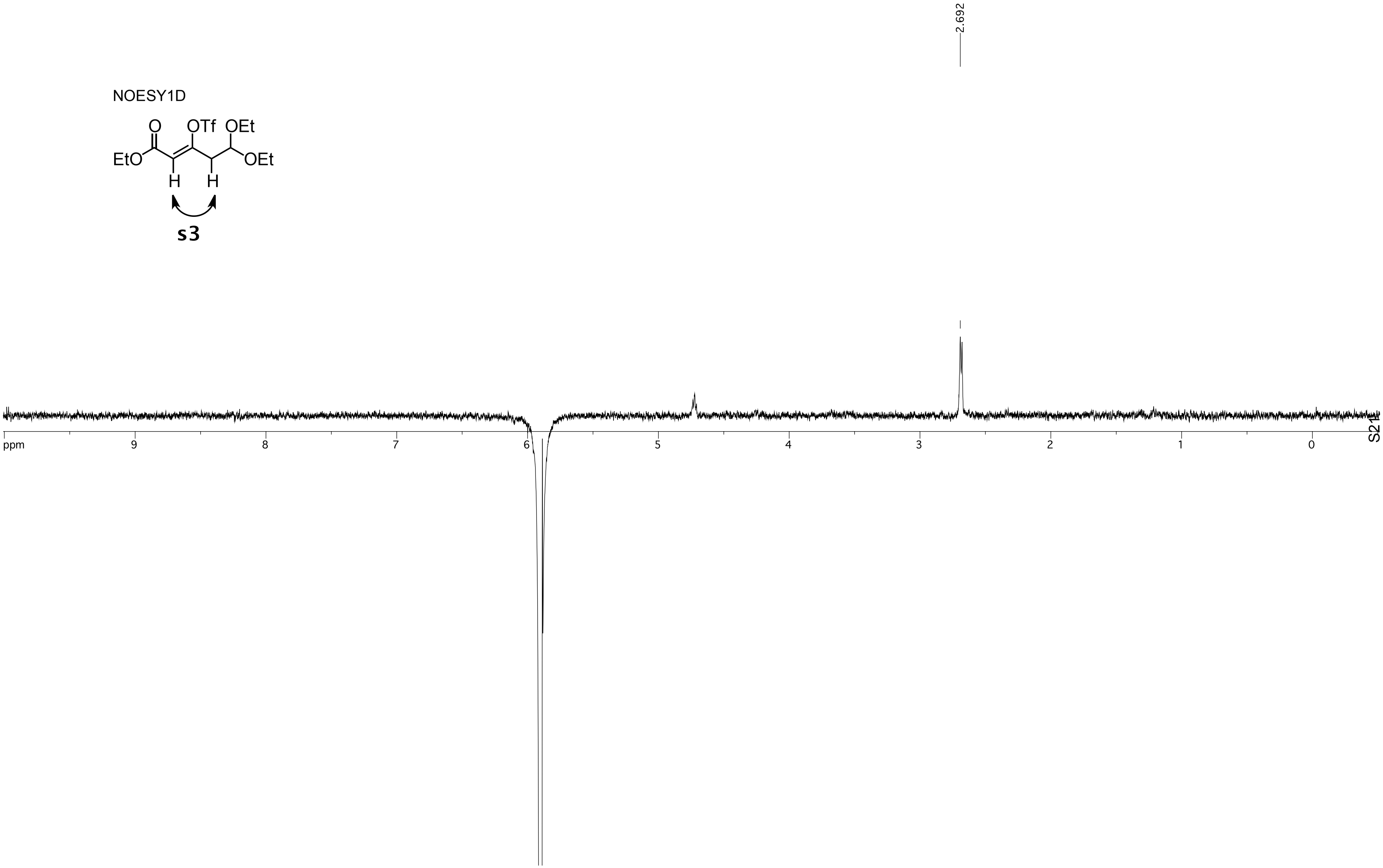

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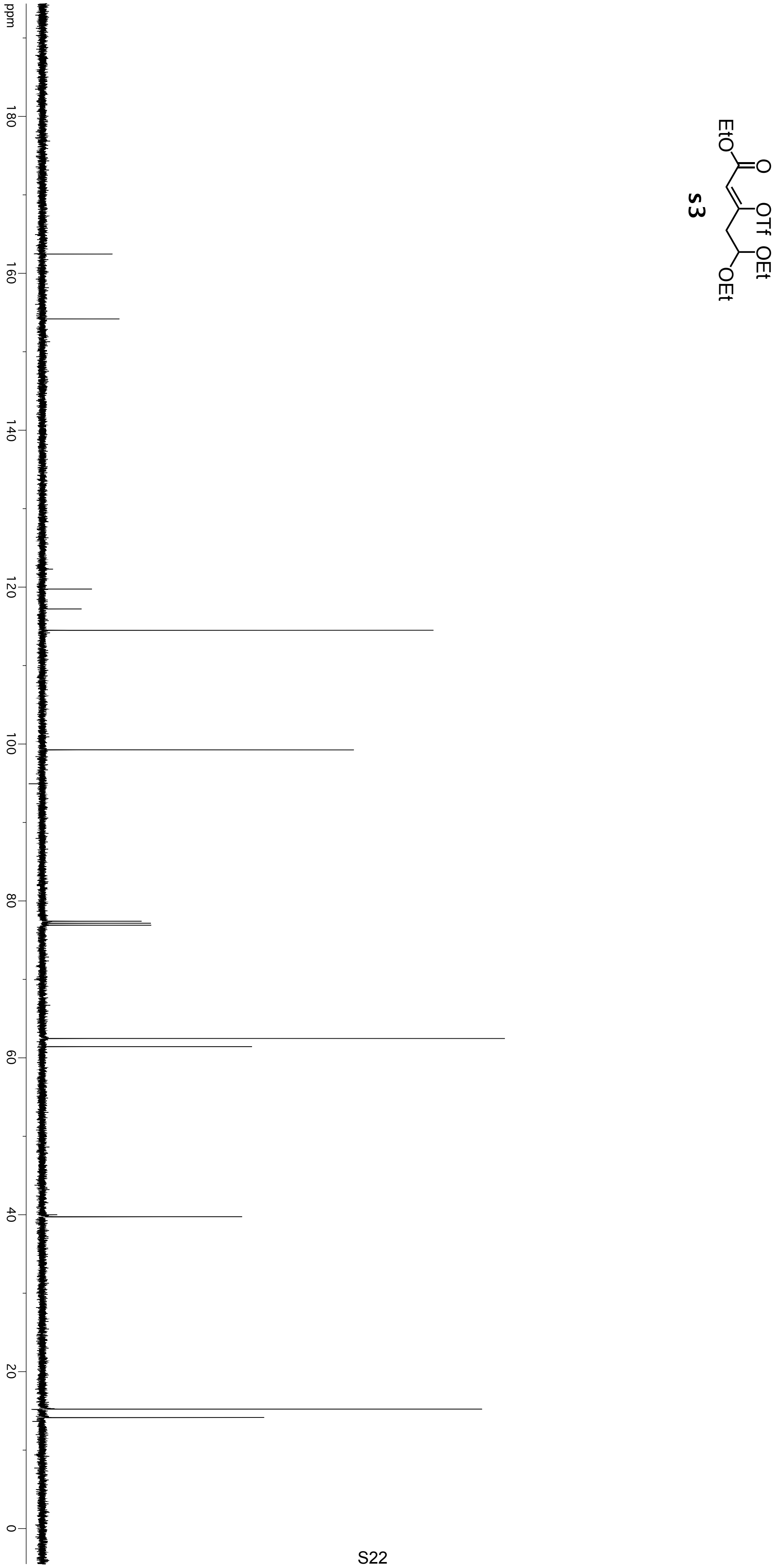

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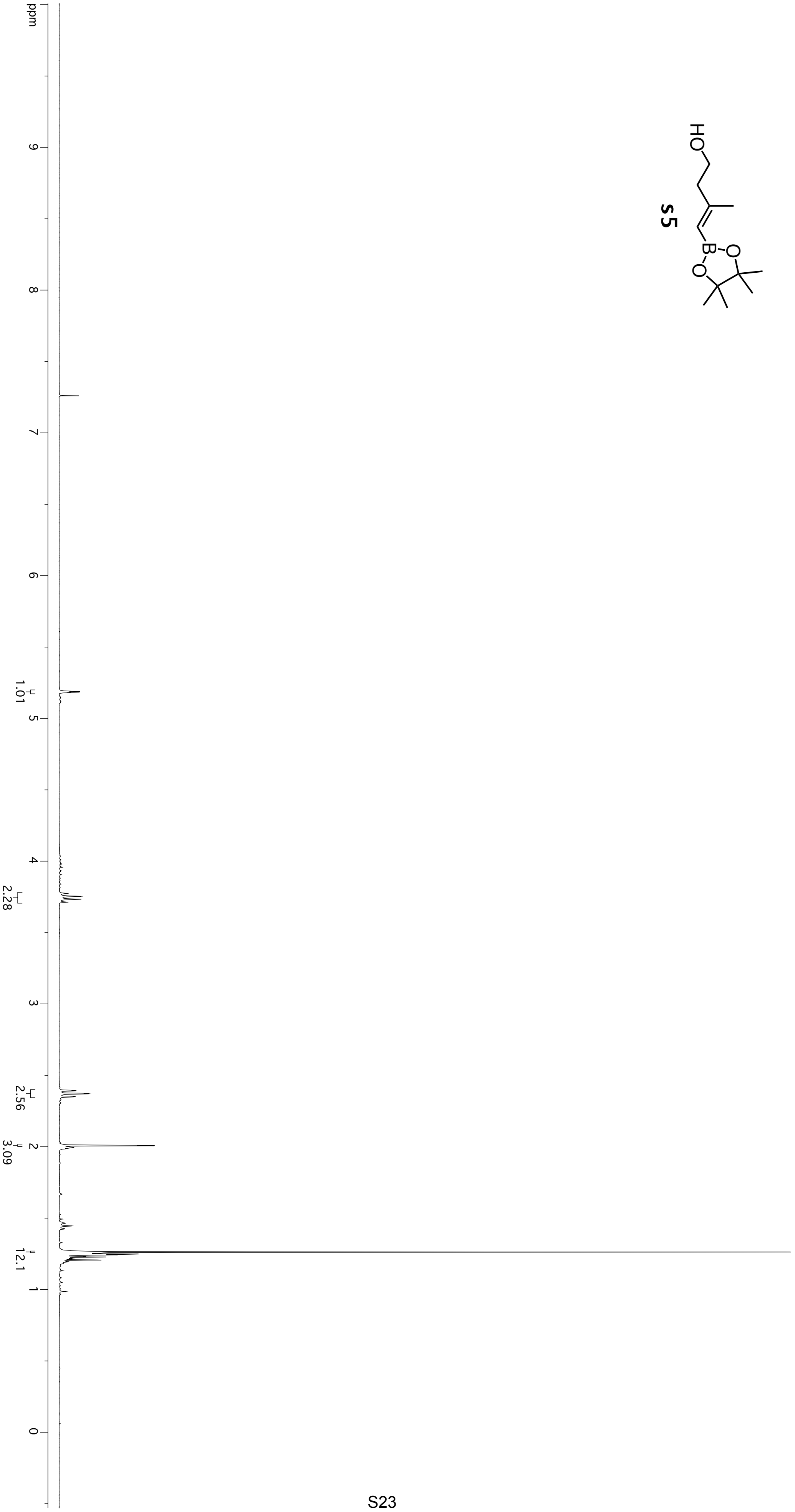HO
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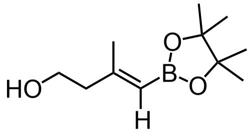

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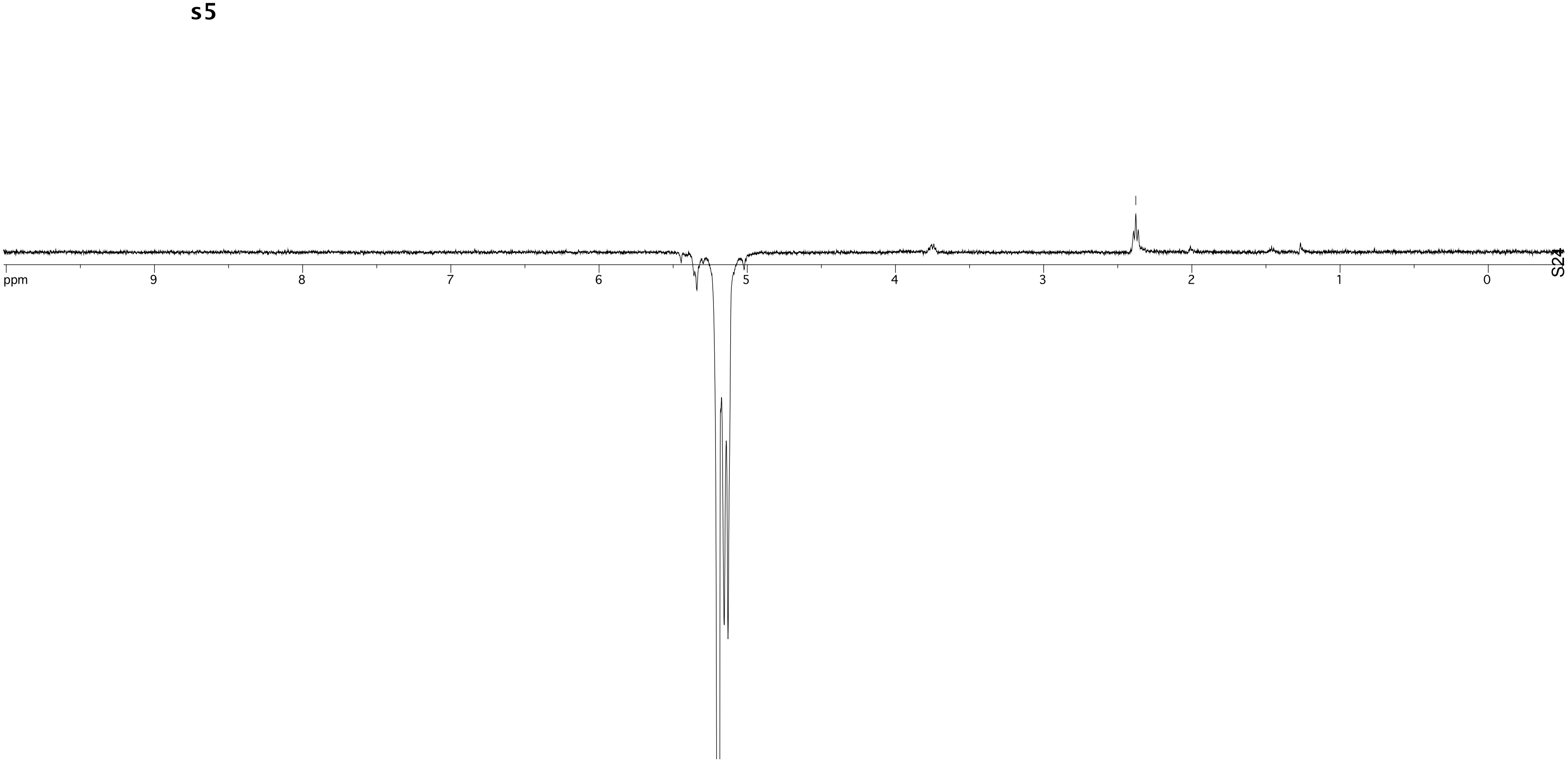

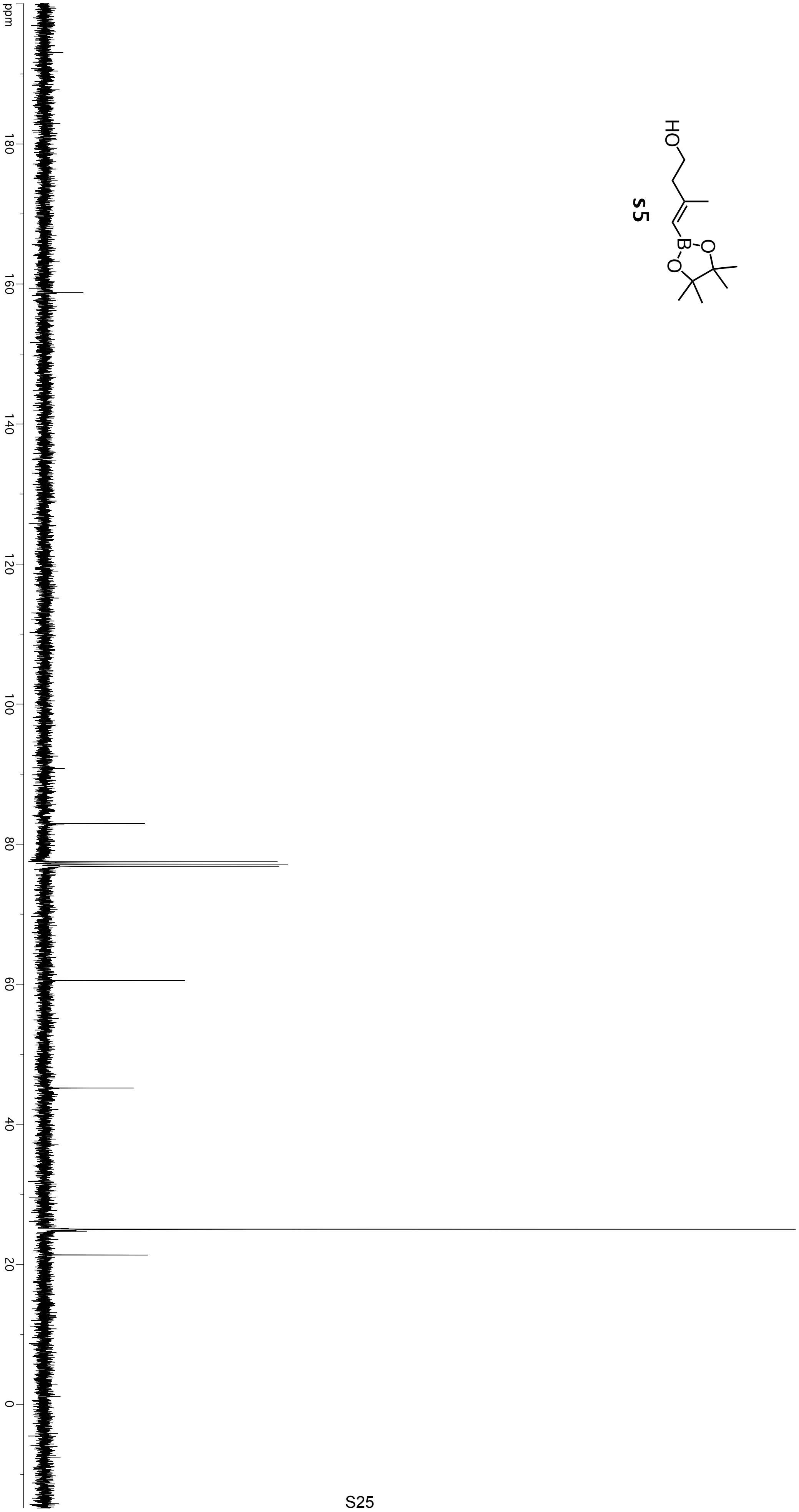
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80
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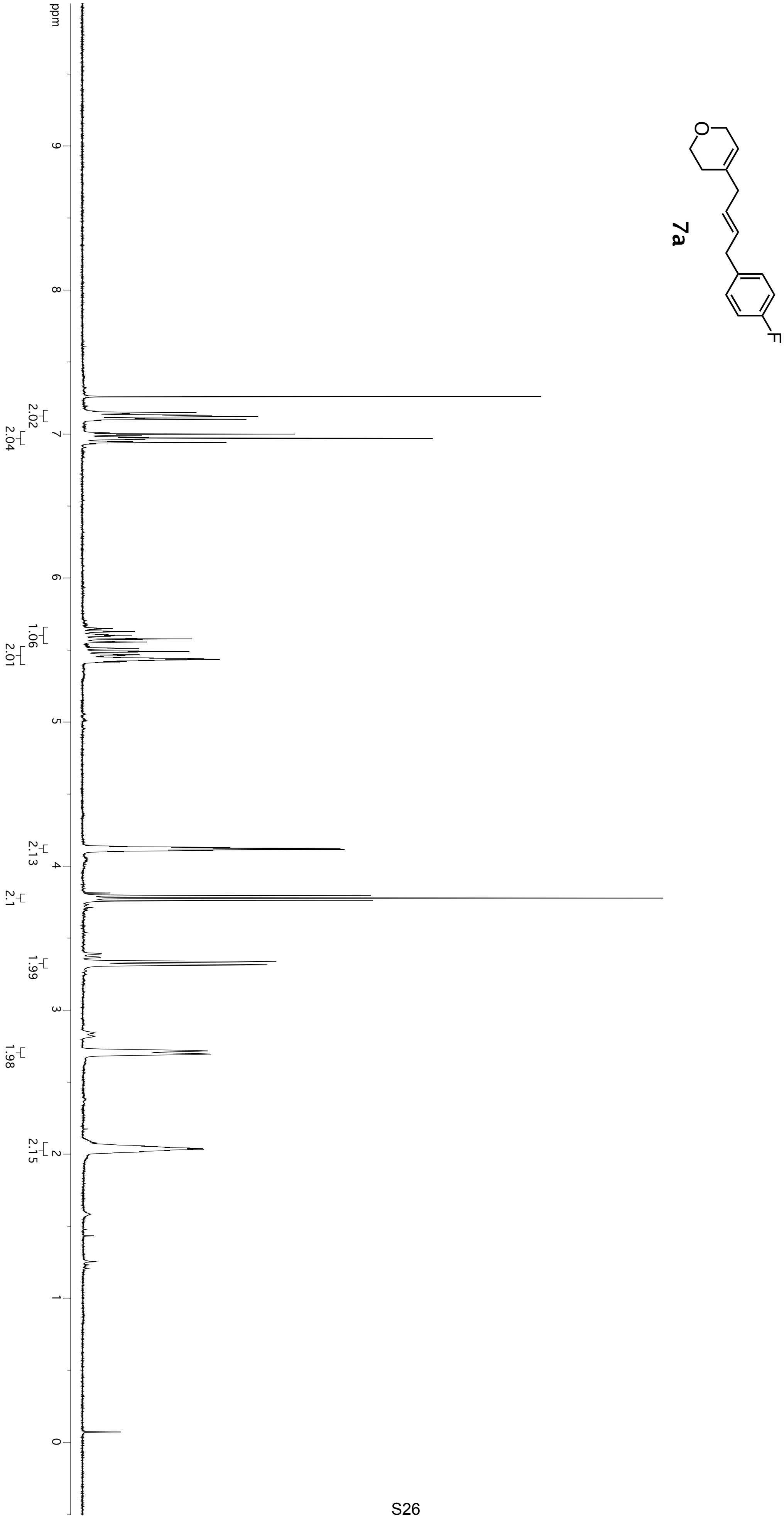
40
20
0
HO
B
O
O
S5



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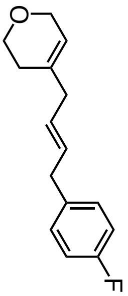

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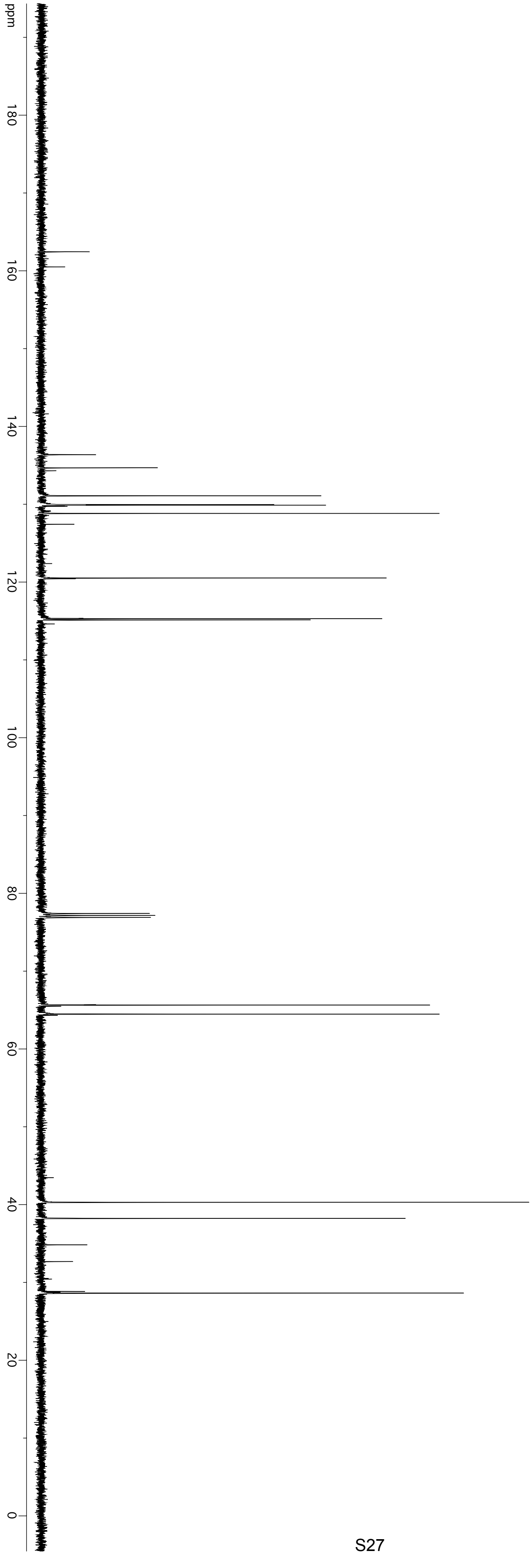

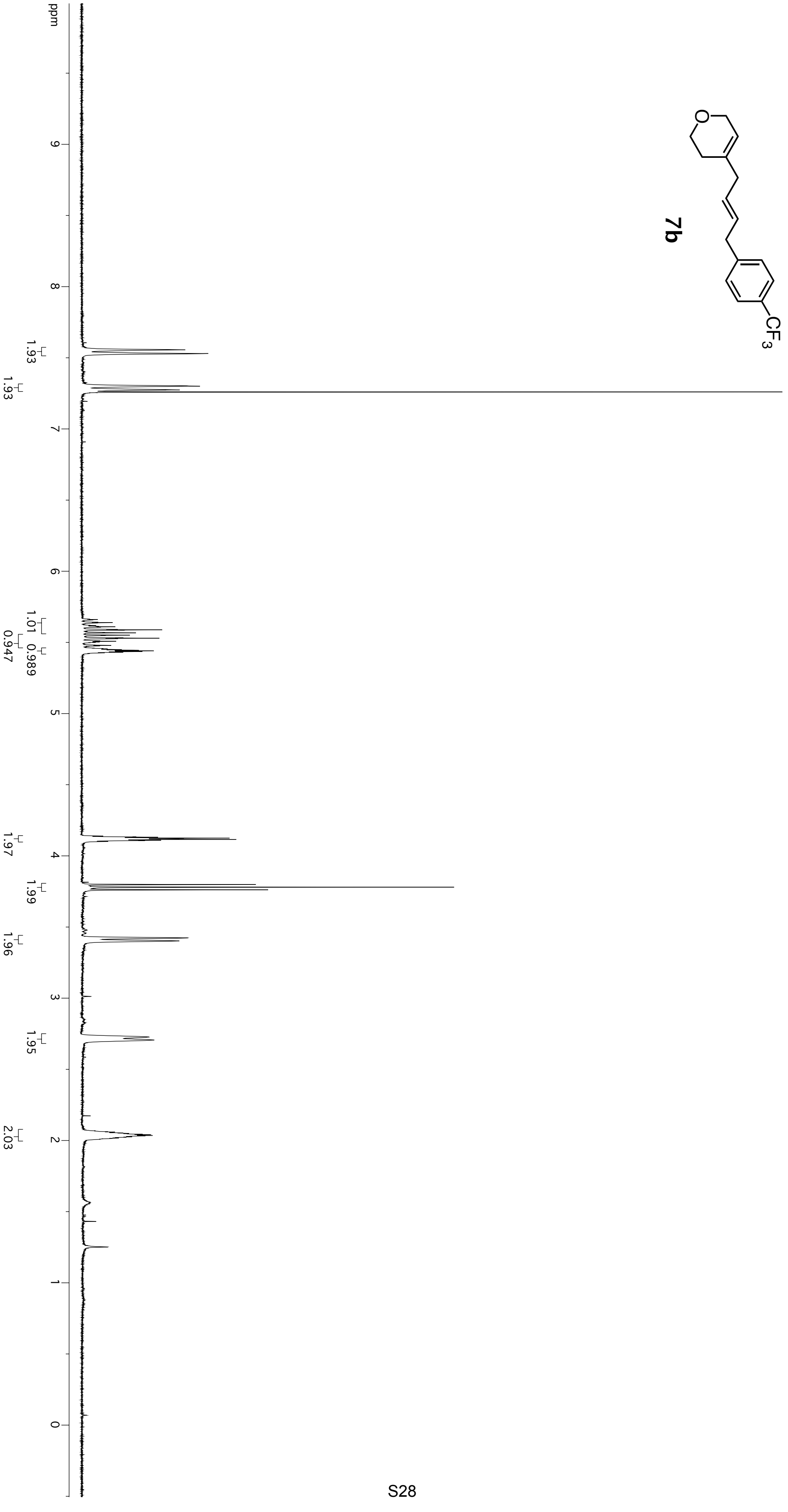

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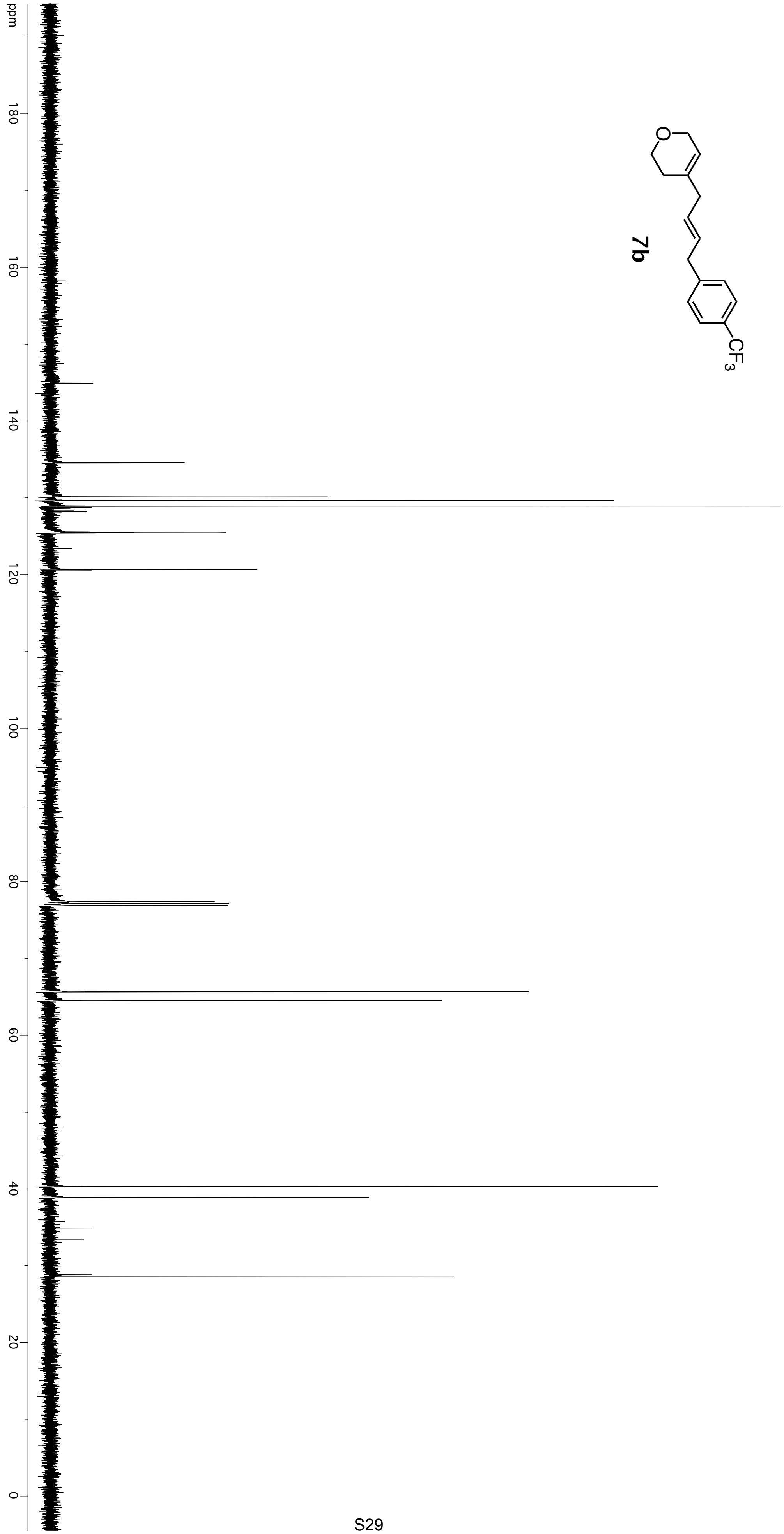

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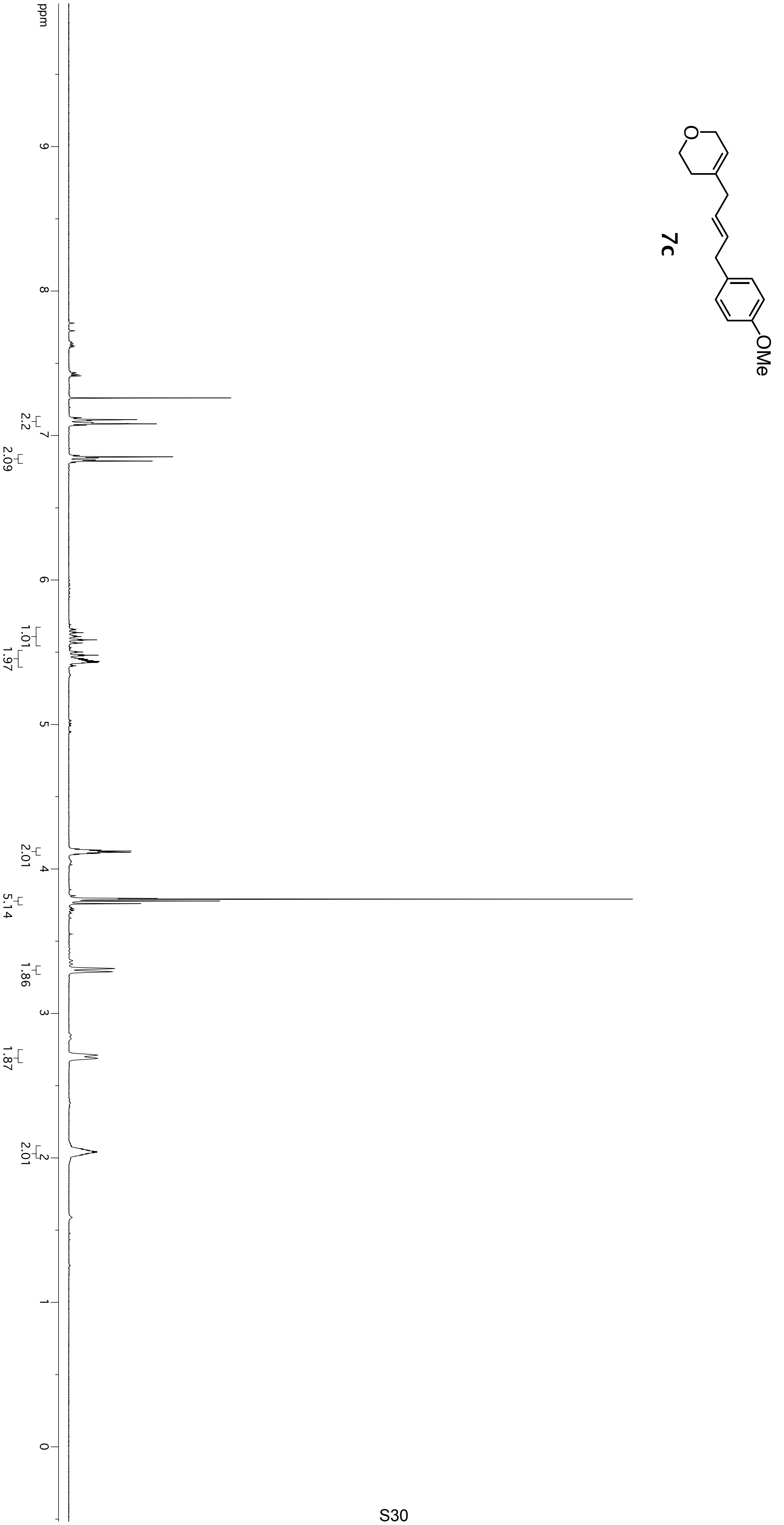
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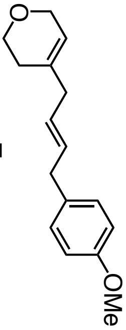
2.01



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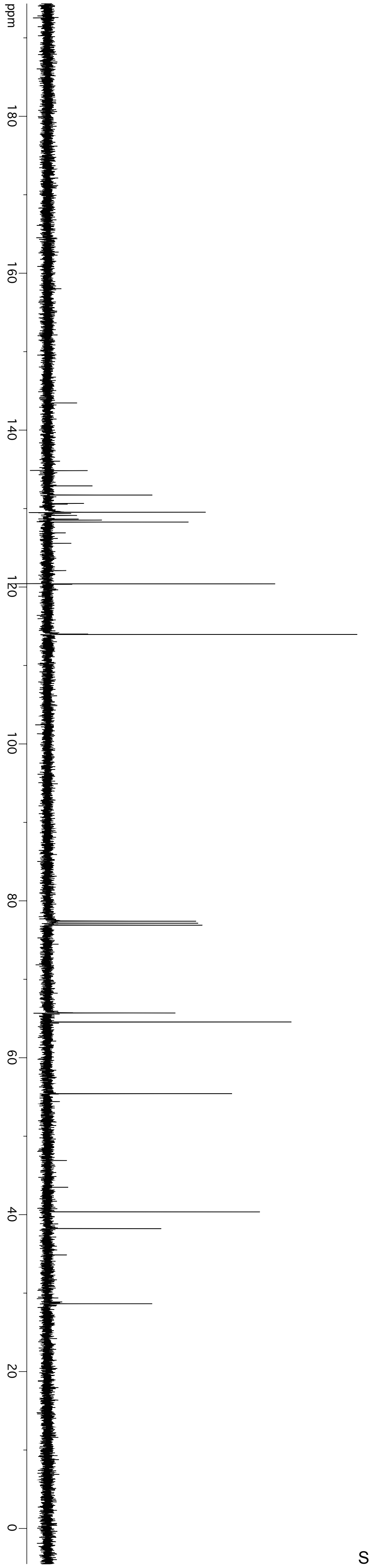

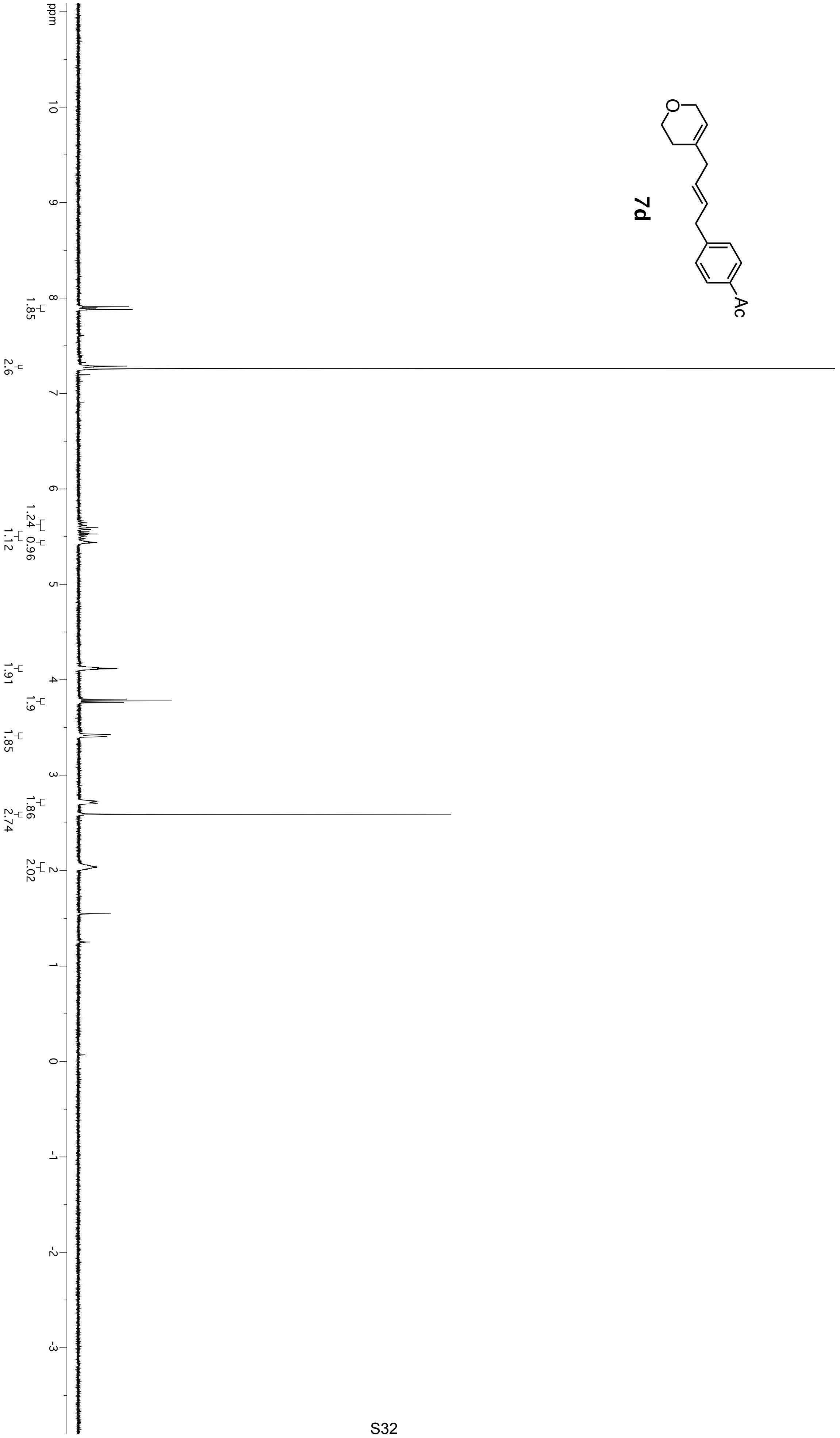
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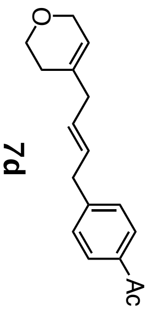
2.02

7d



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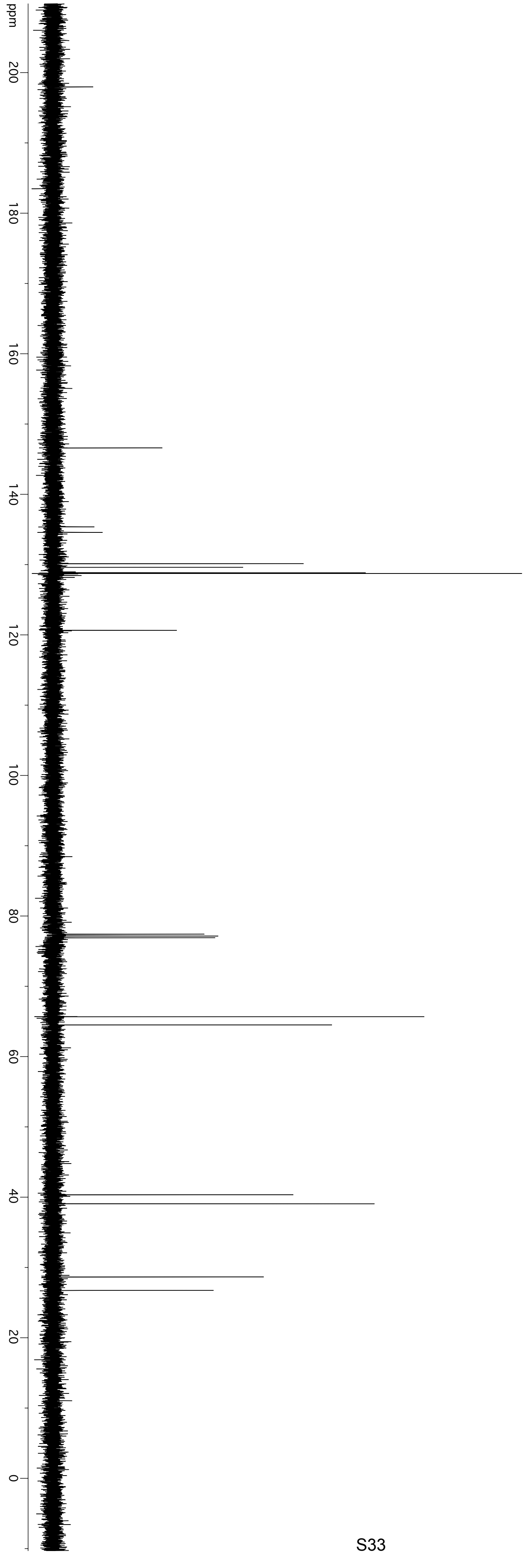

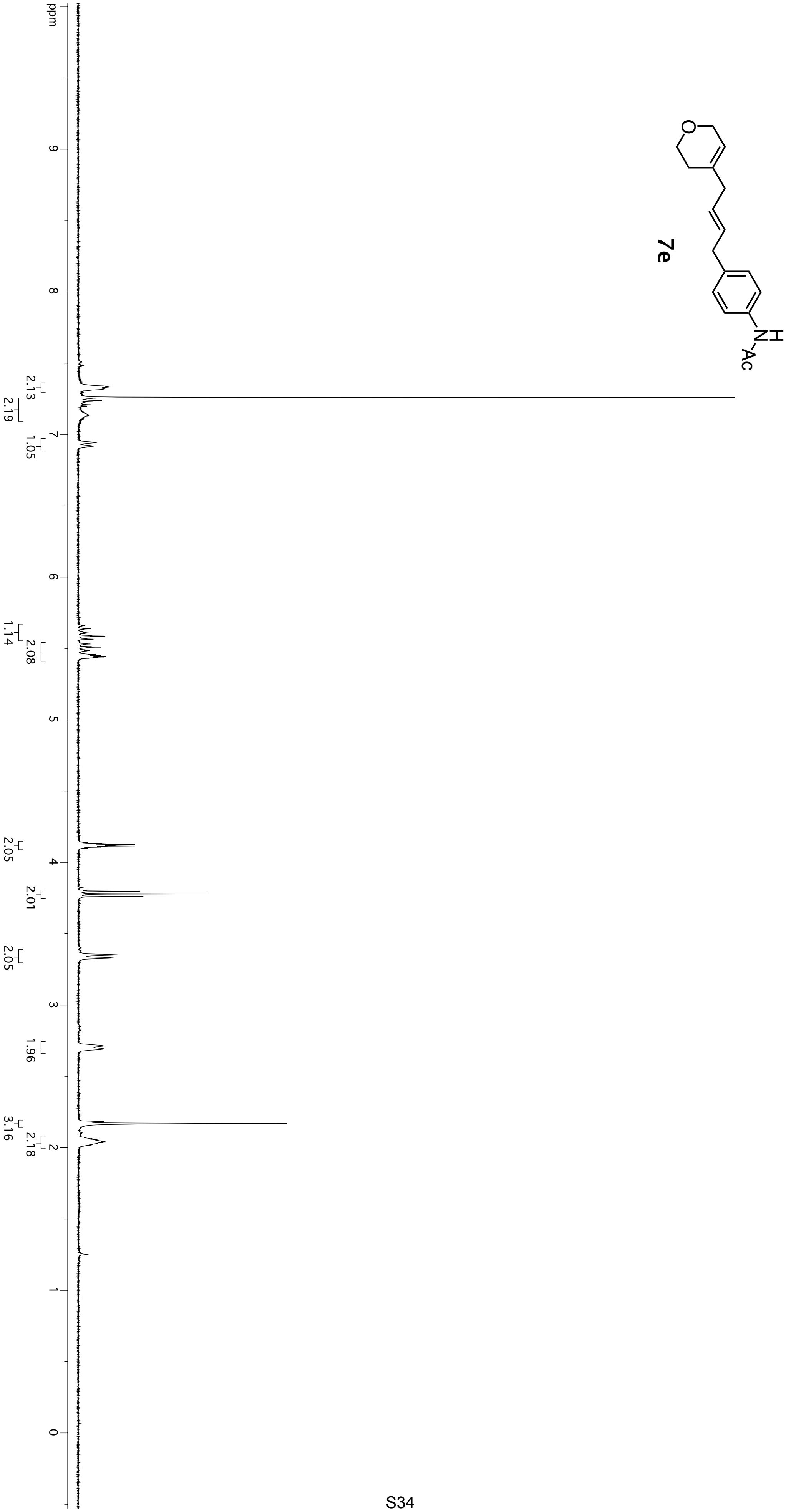

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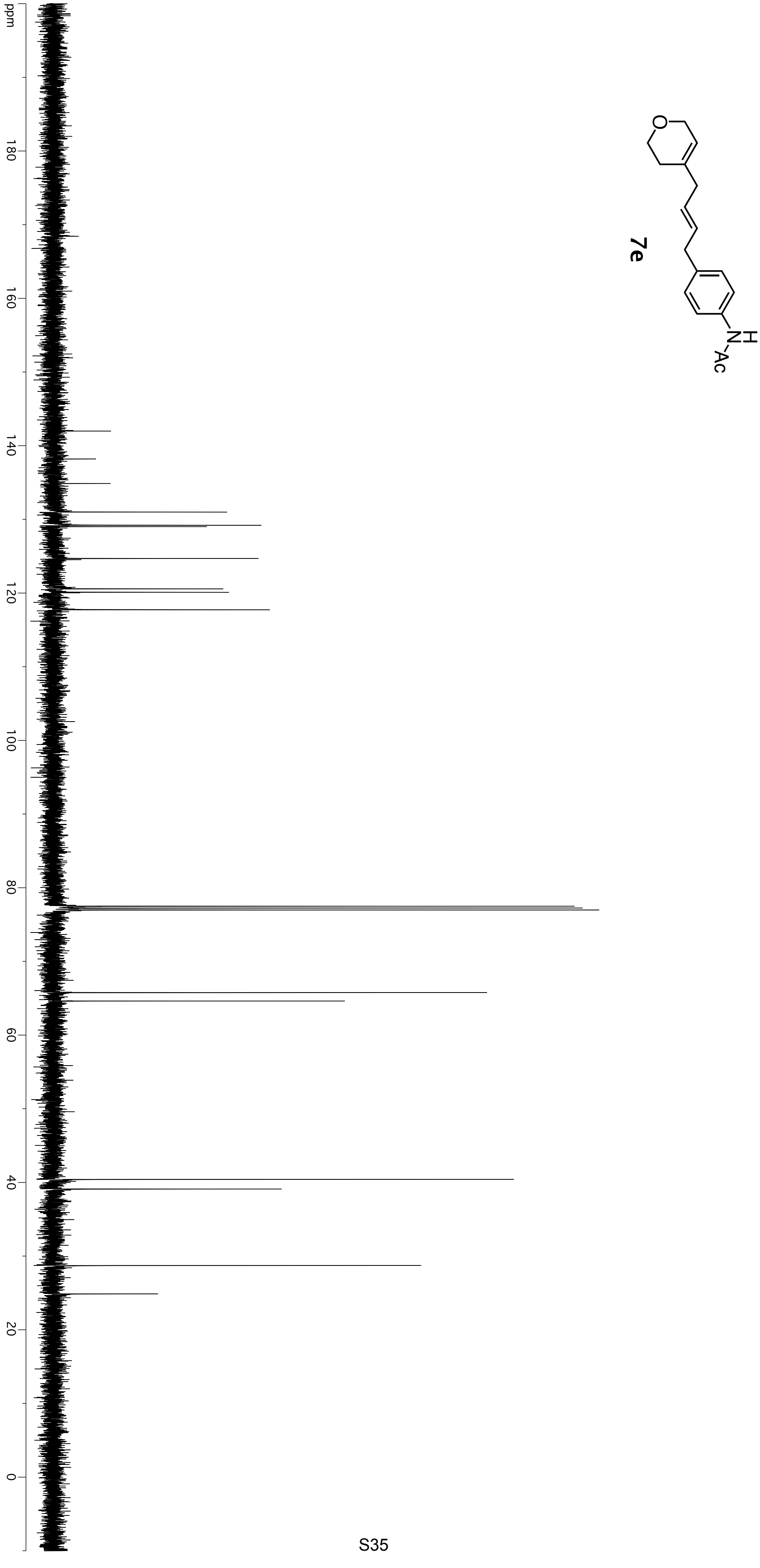
2.18
O
H
N
Ac

7e



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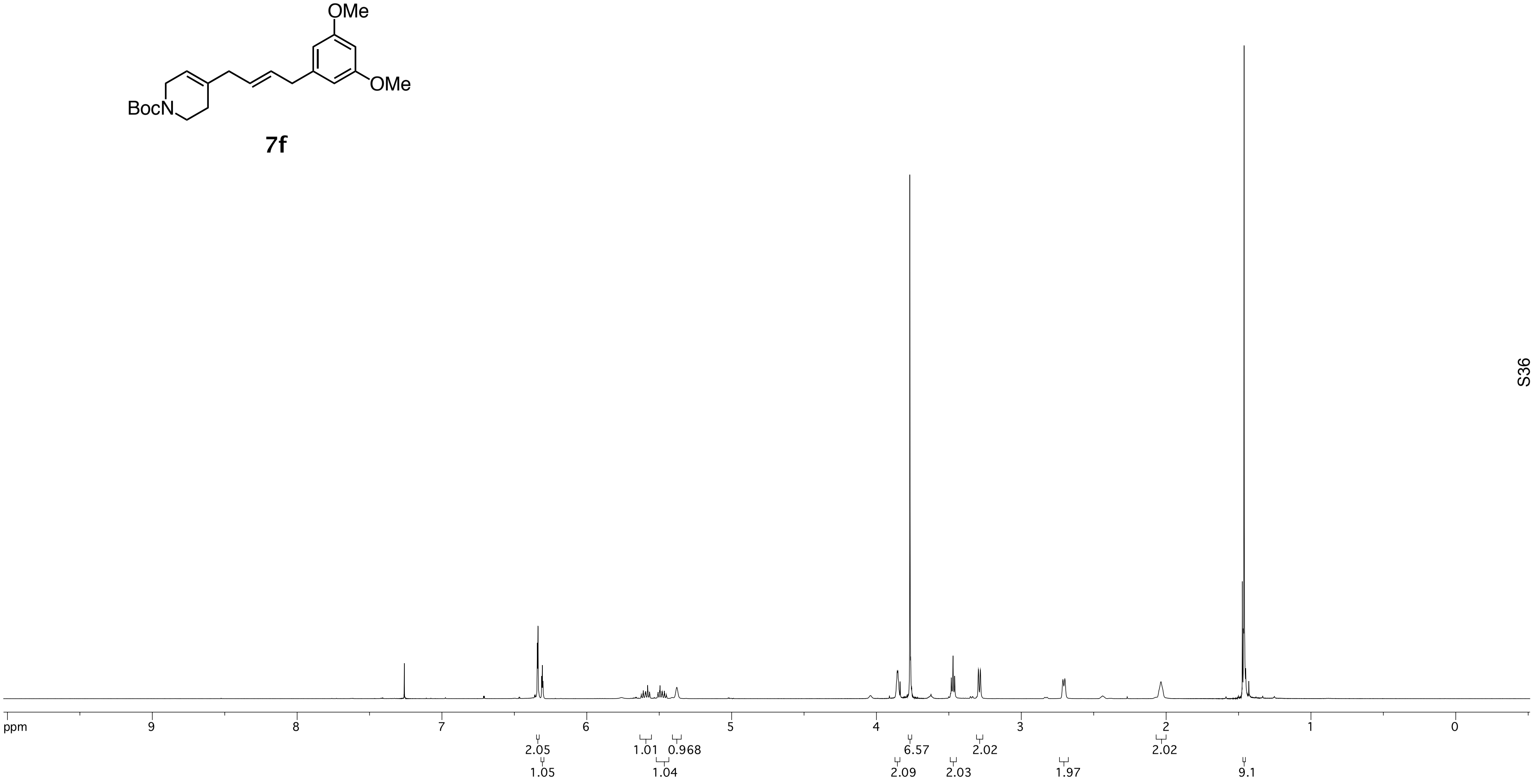
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OMe
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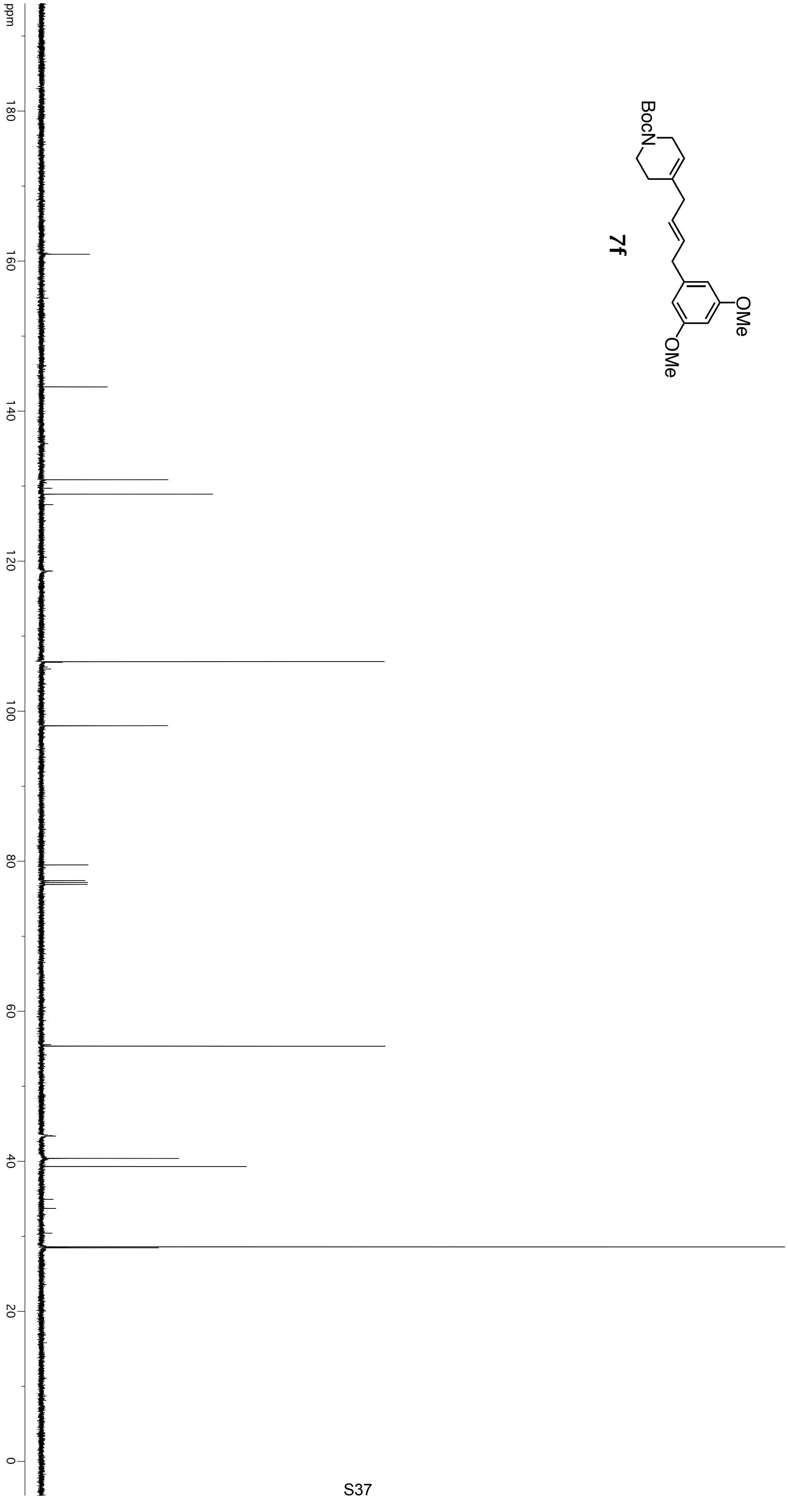
2.02
9.1

7f



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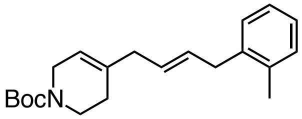
BocN

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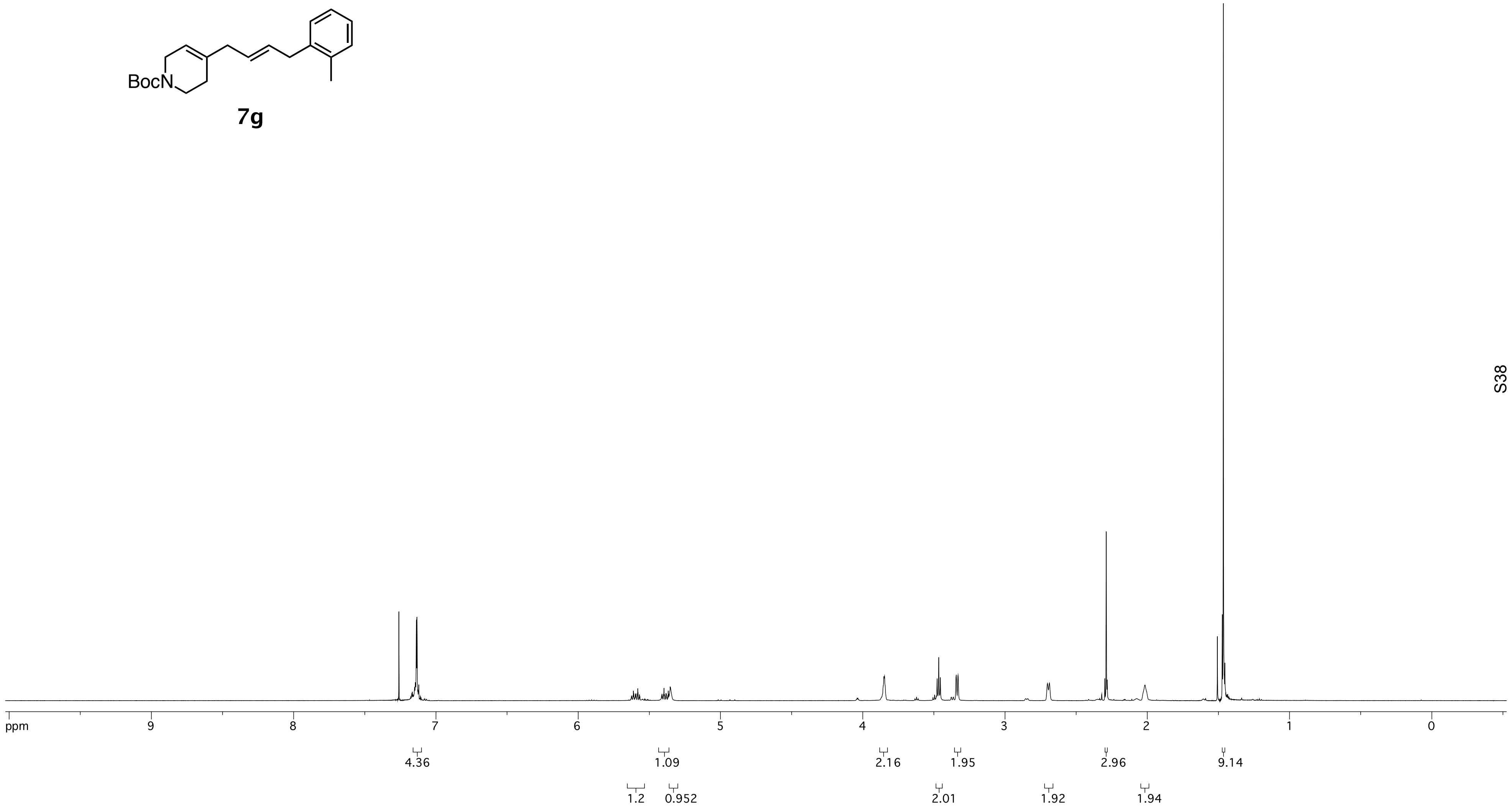
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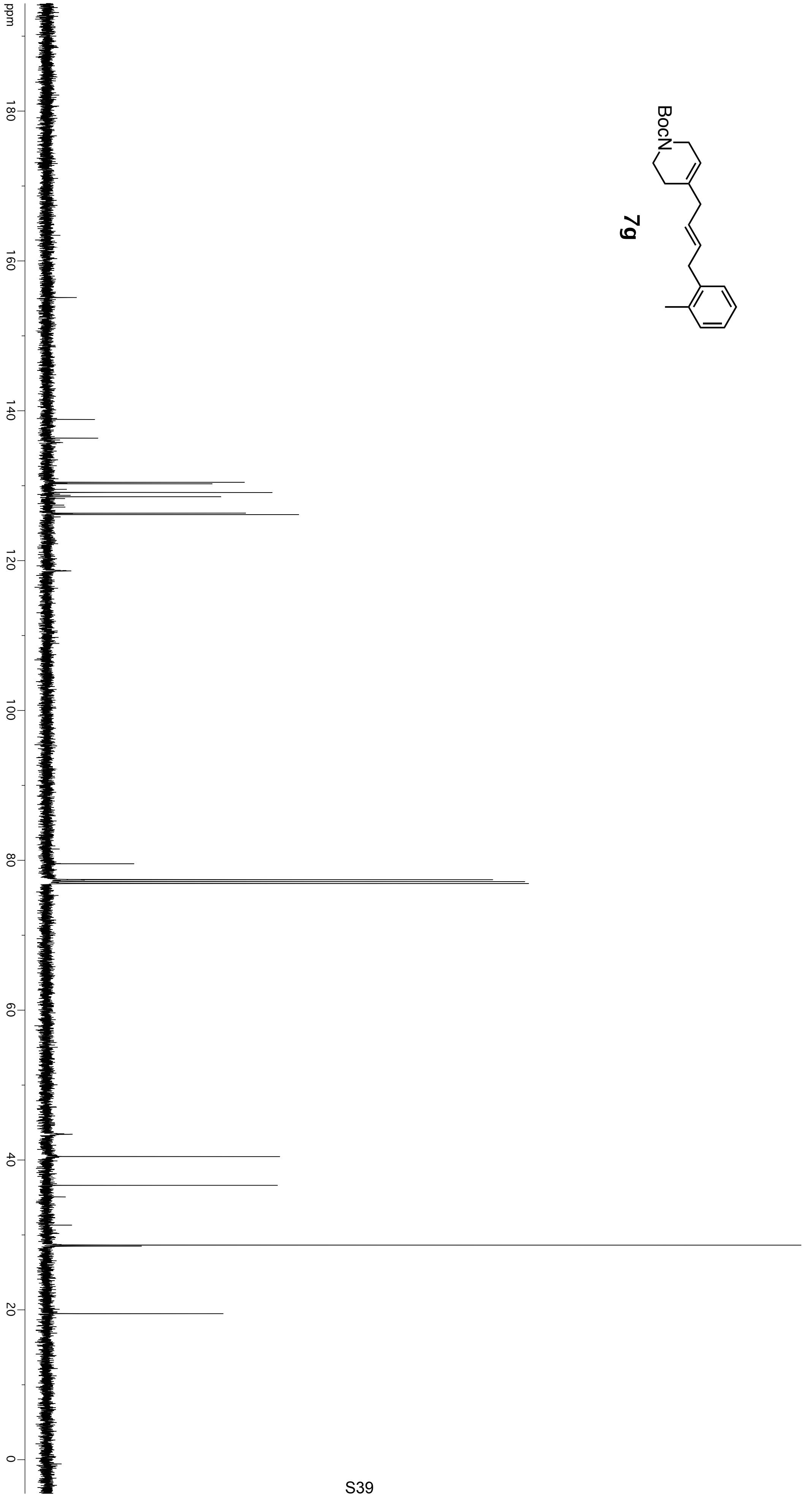
1.94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7g
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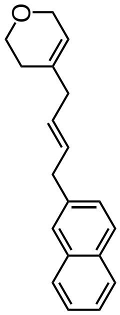

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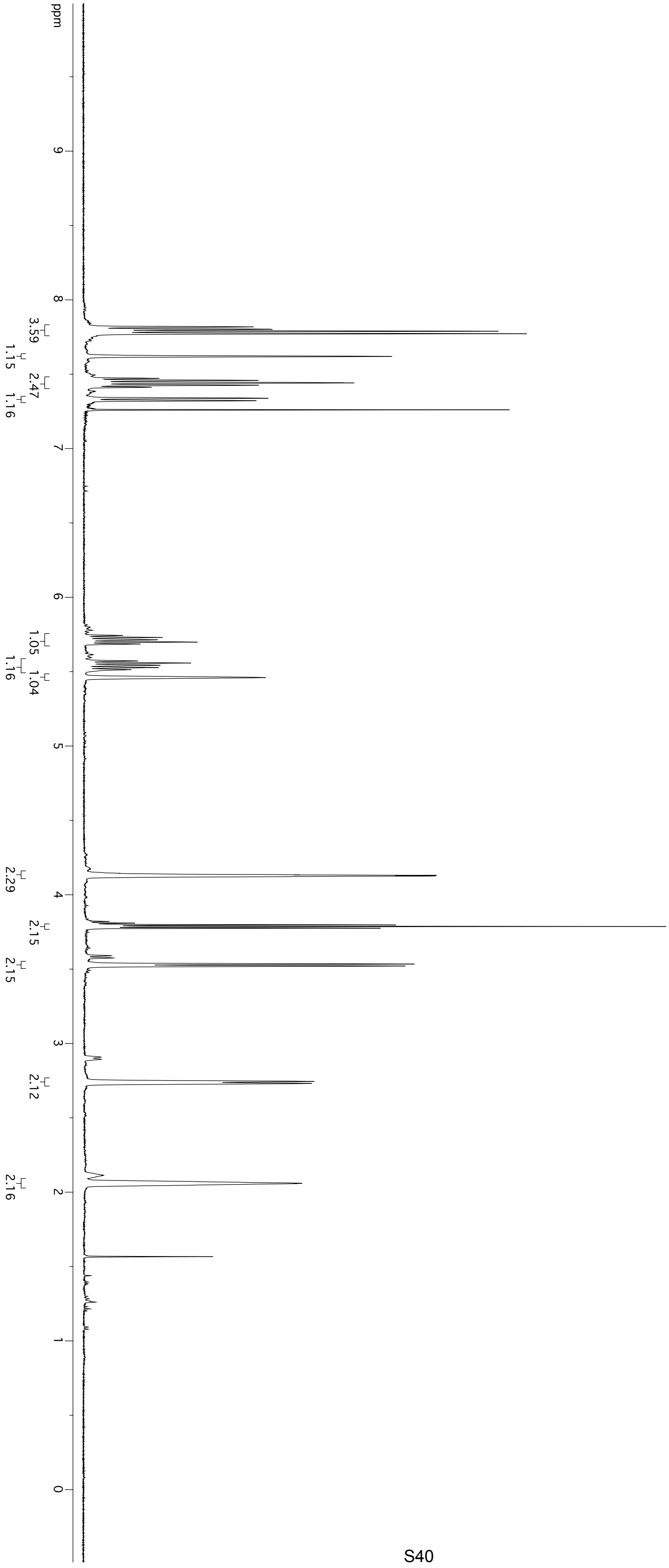


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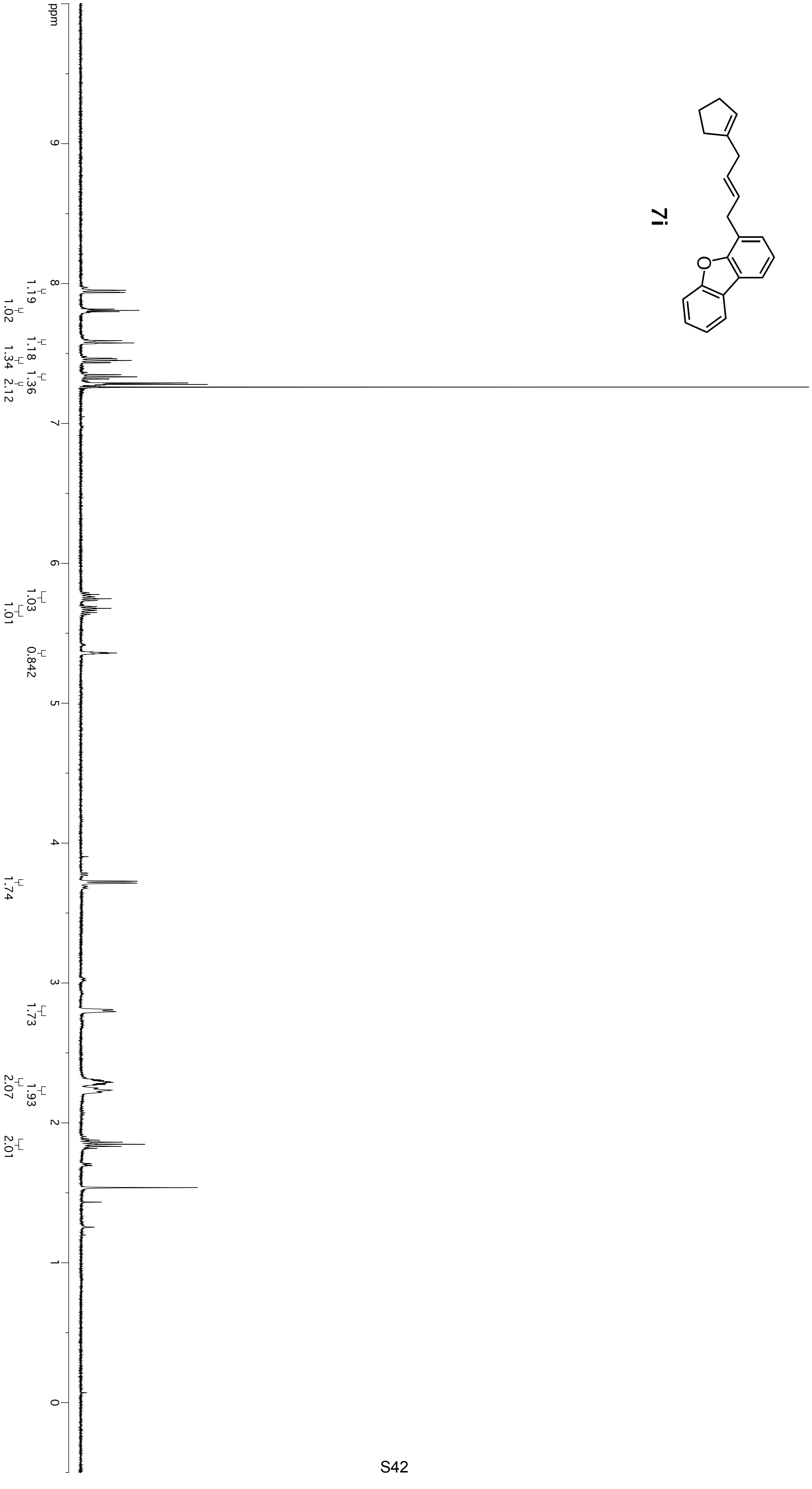

7i

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1.01
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1.73
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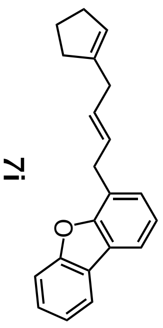
2.07
2.01
O



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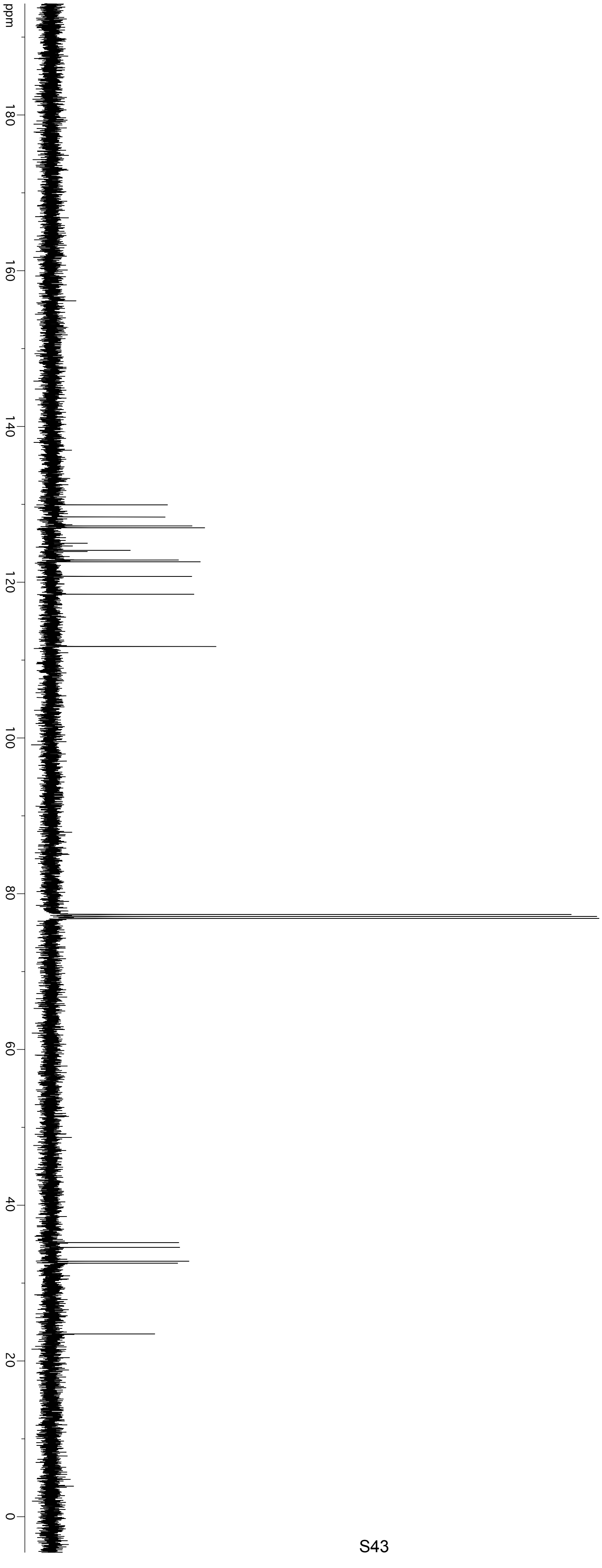

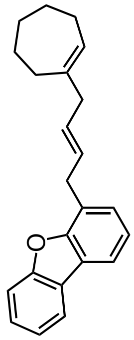

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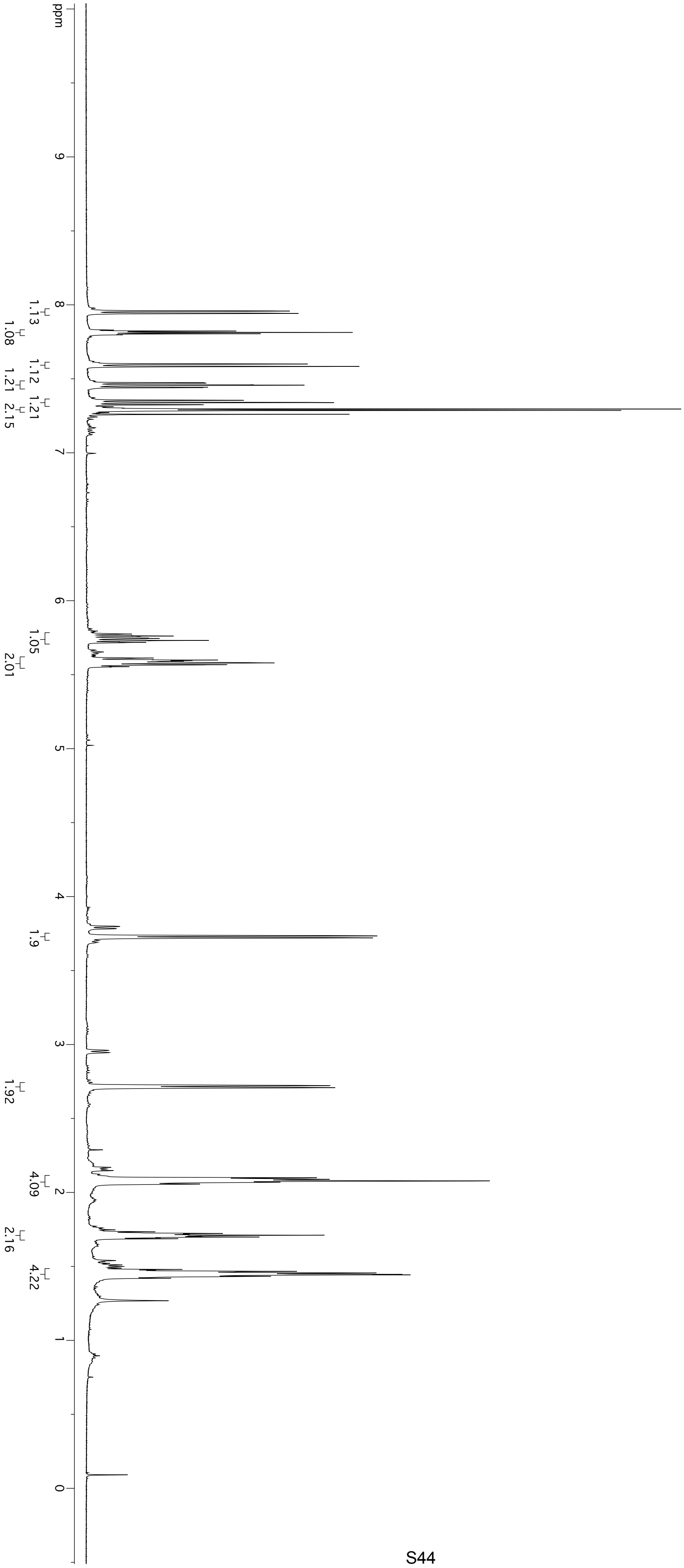

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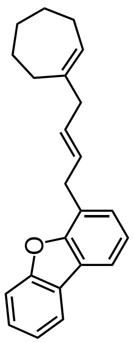
4.22



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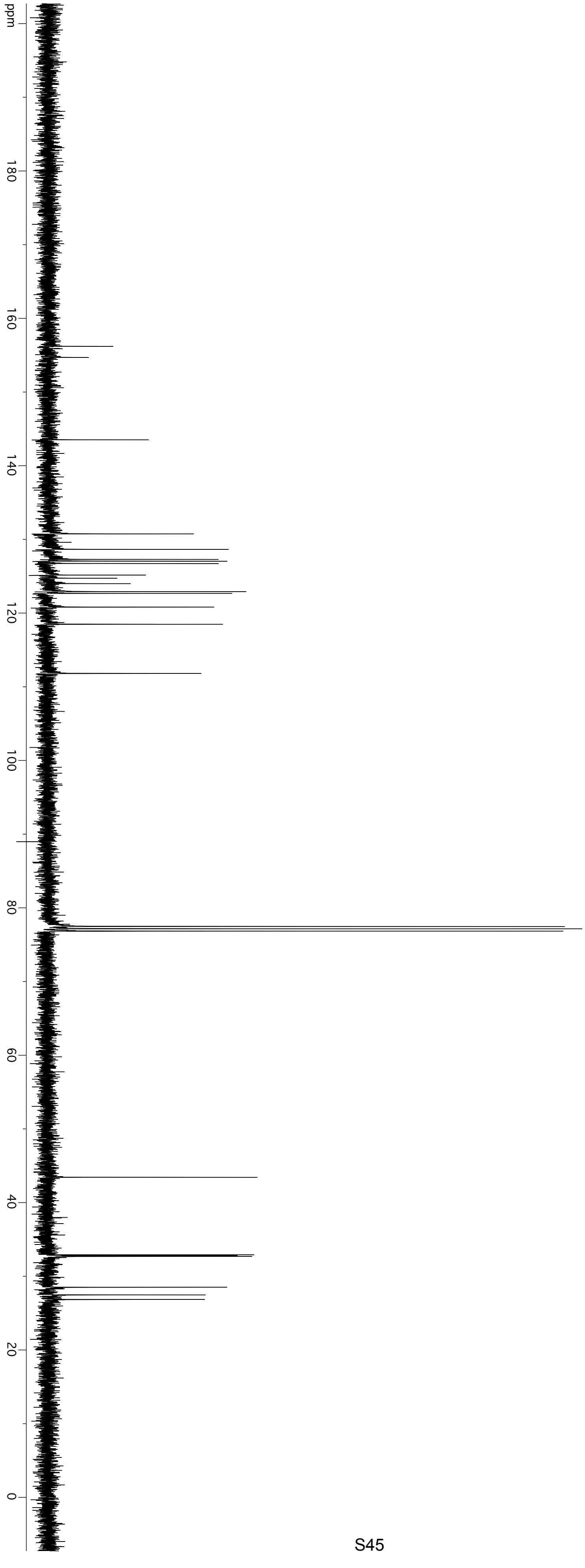
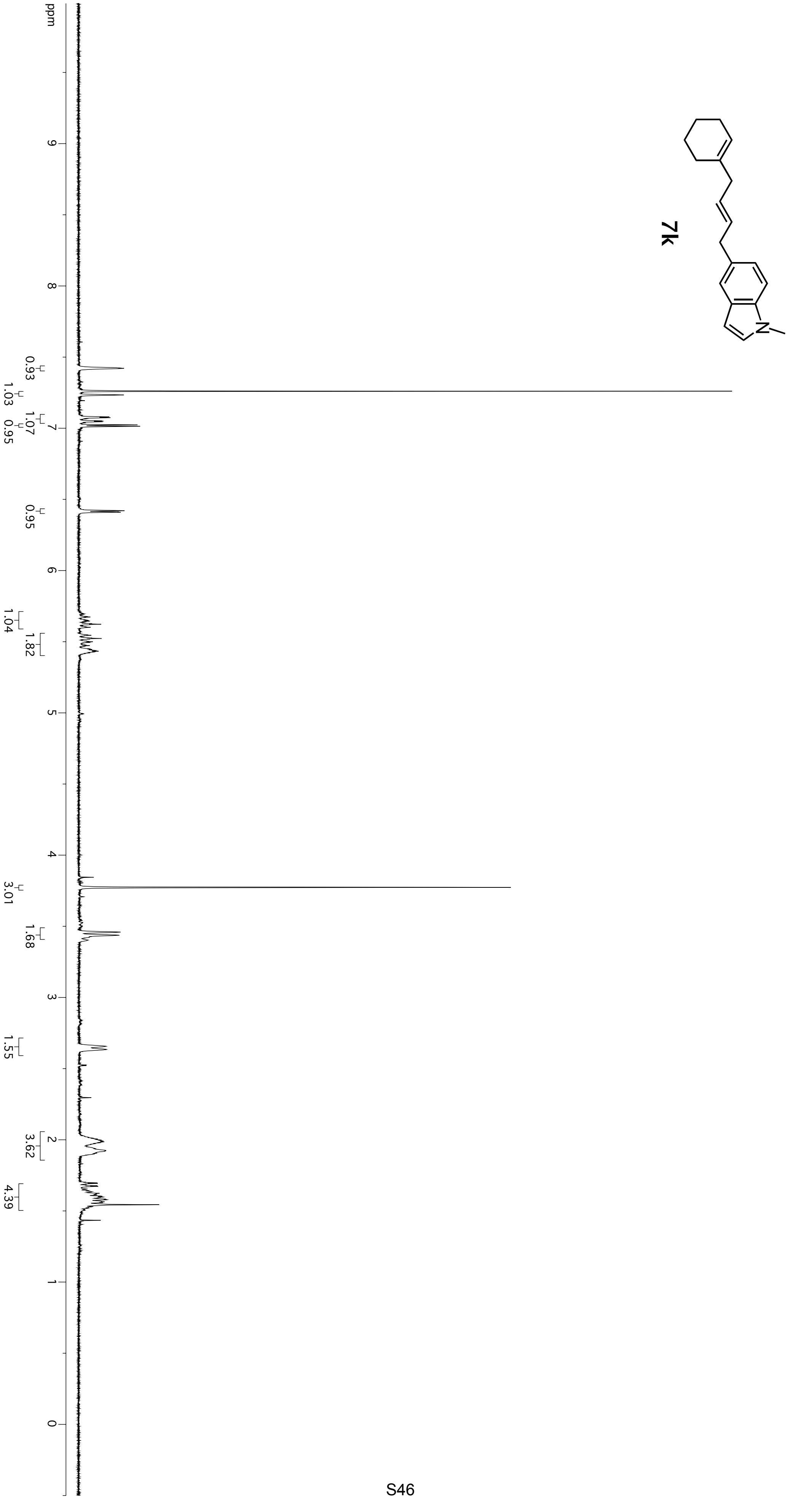
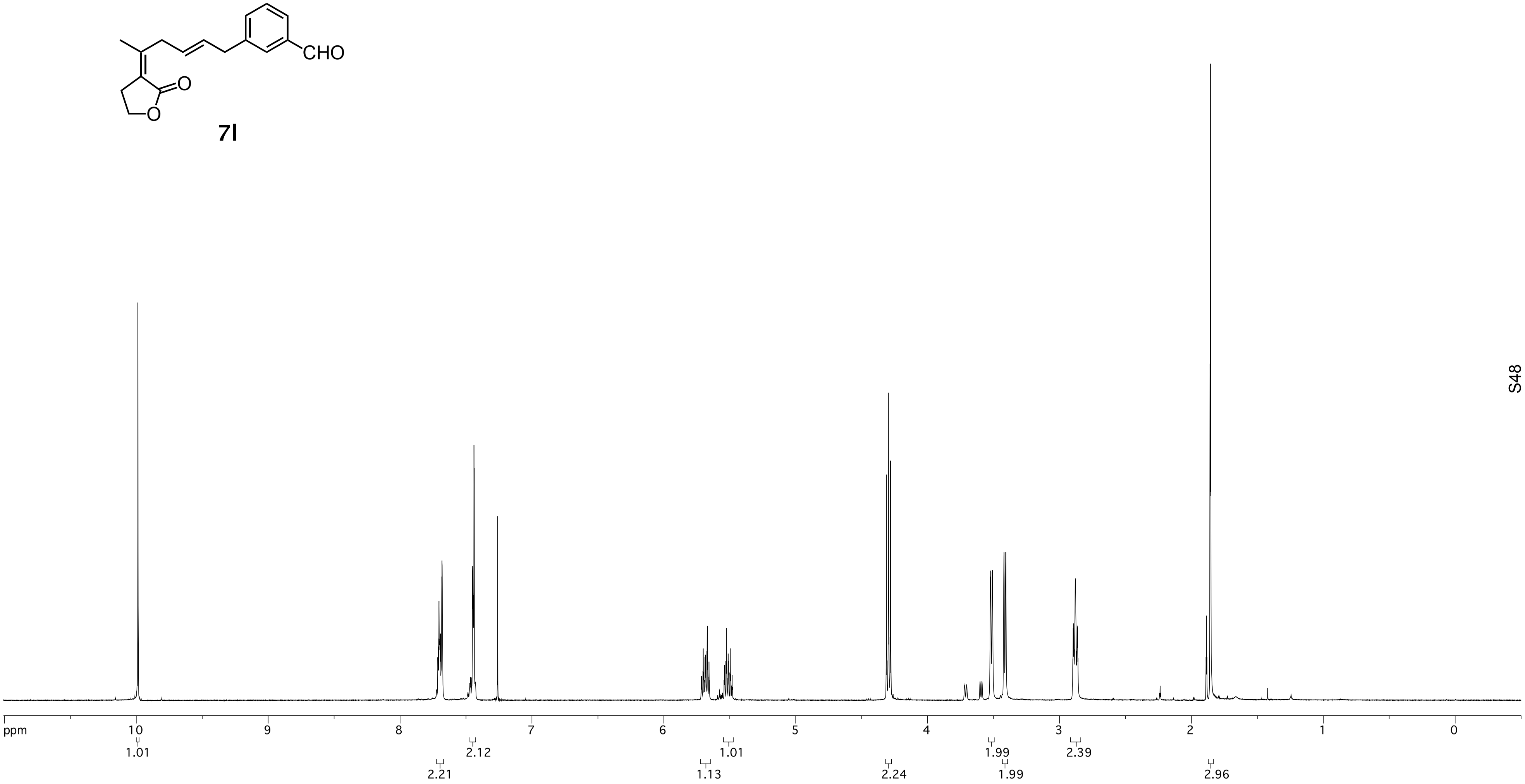




7k


7k



7l

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O
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3
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1.13
1.01
2.24
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1.99
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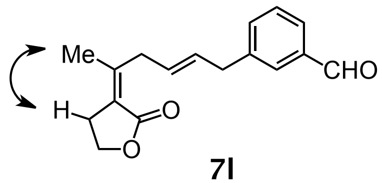
2.96

NOESY1D



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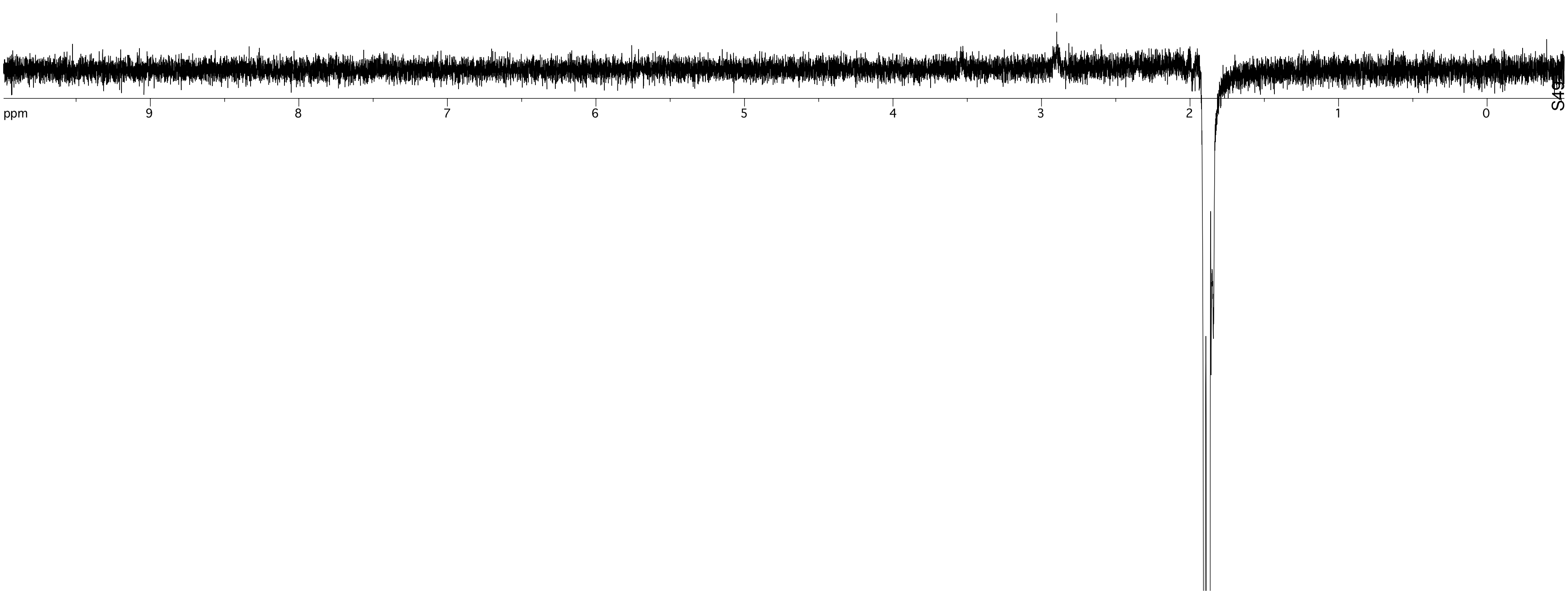

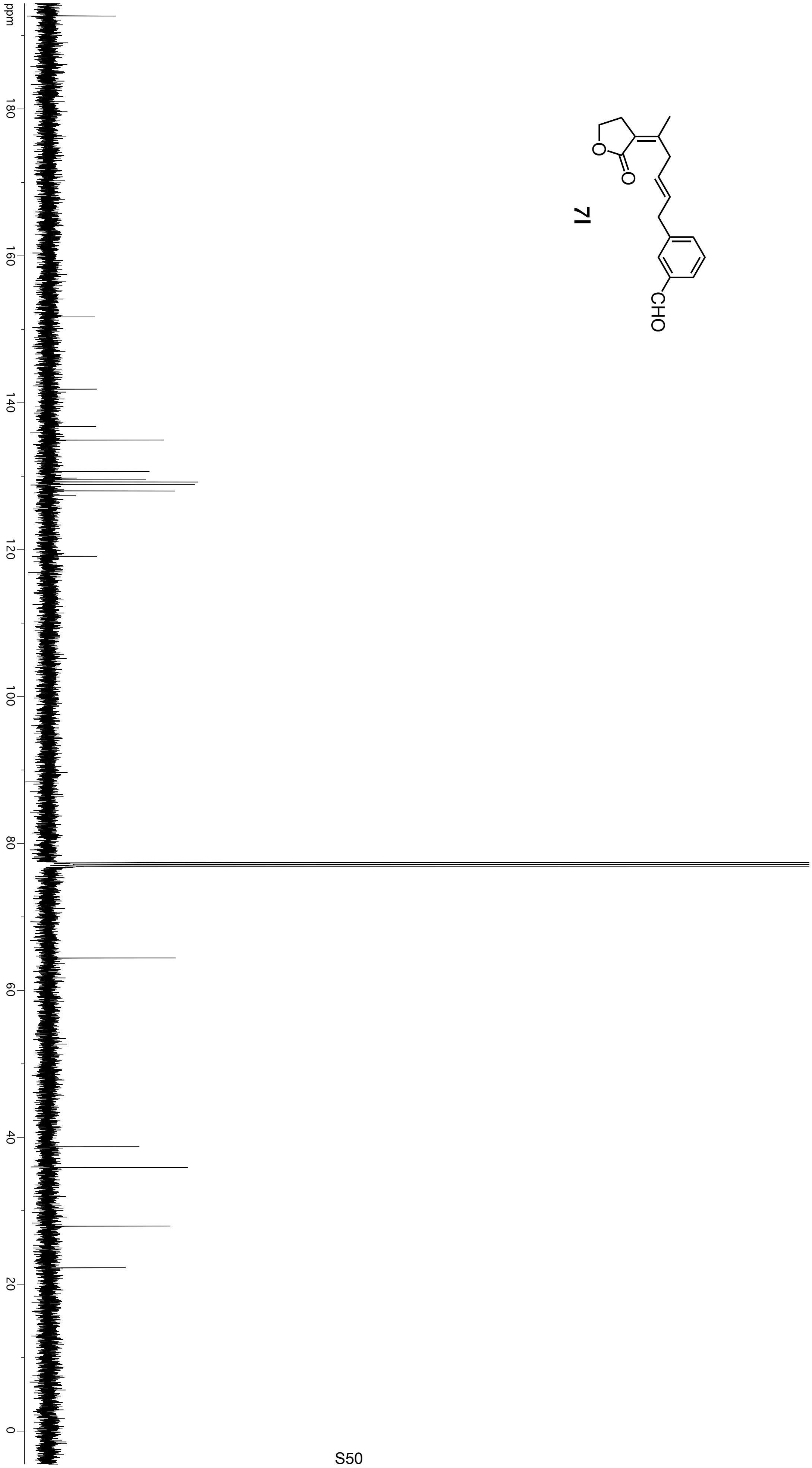

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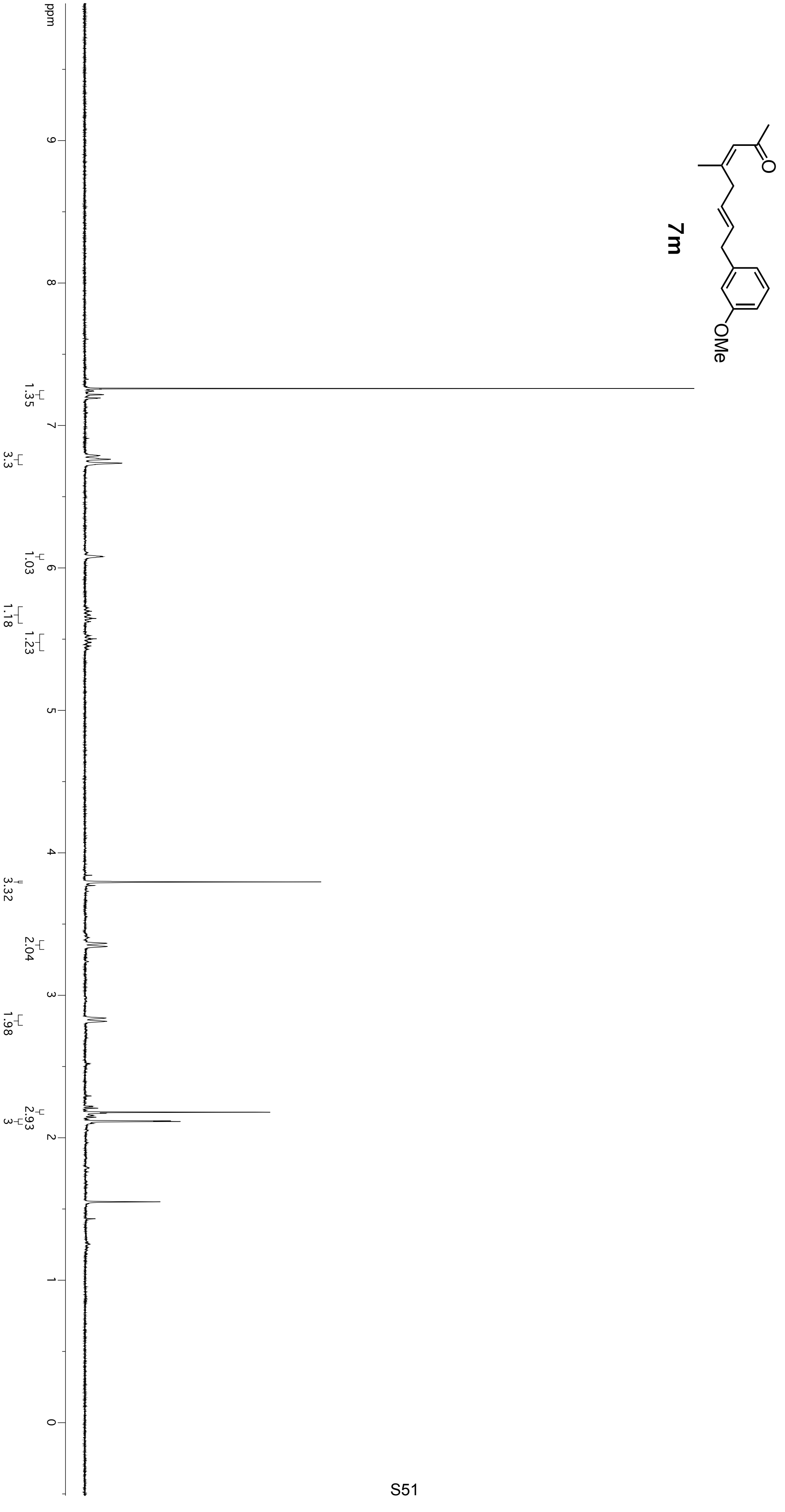
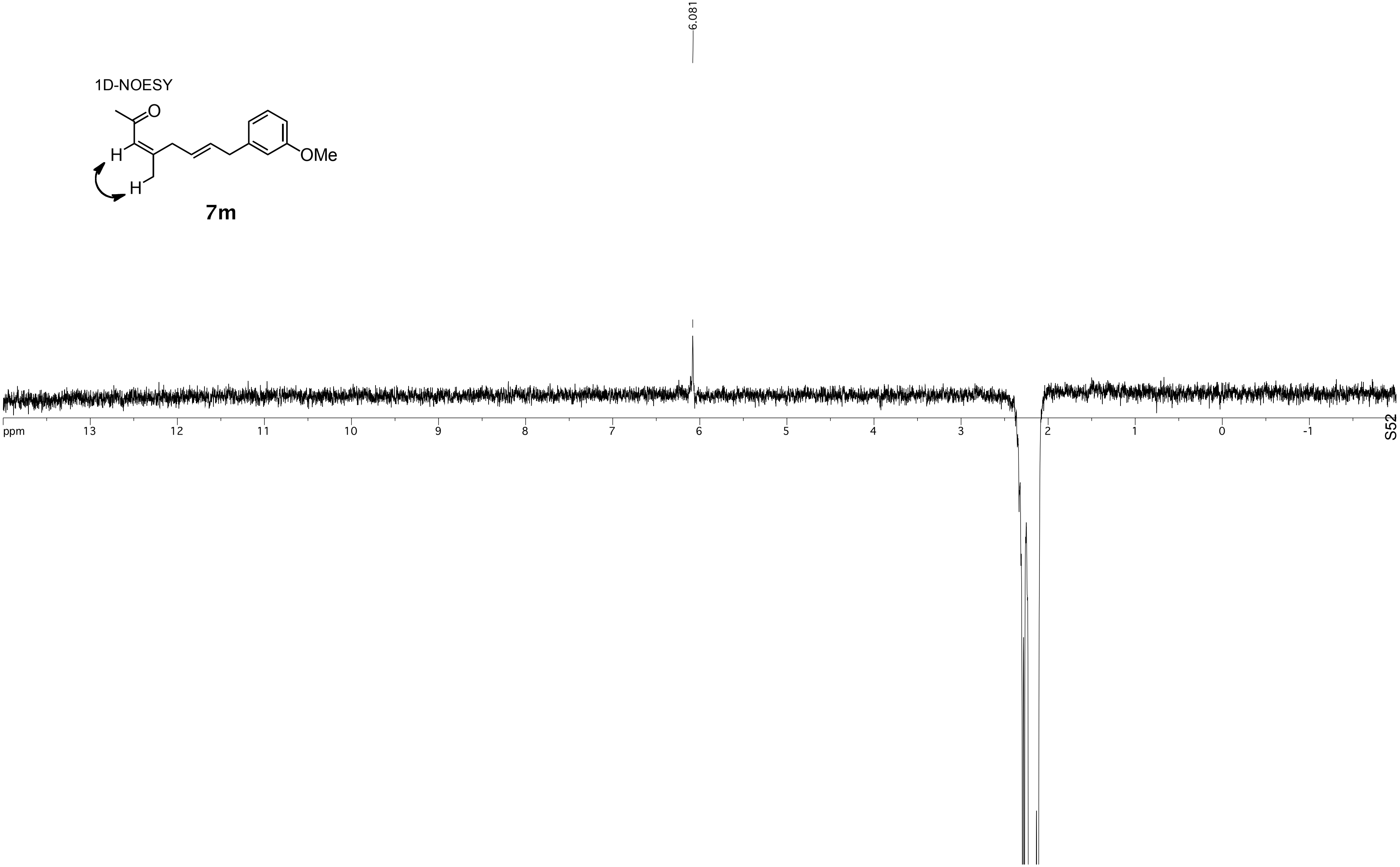


7m

1D-NOESY



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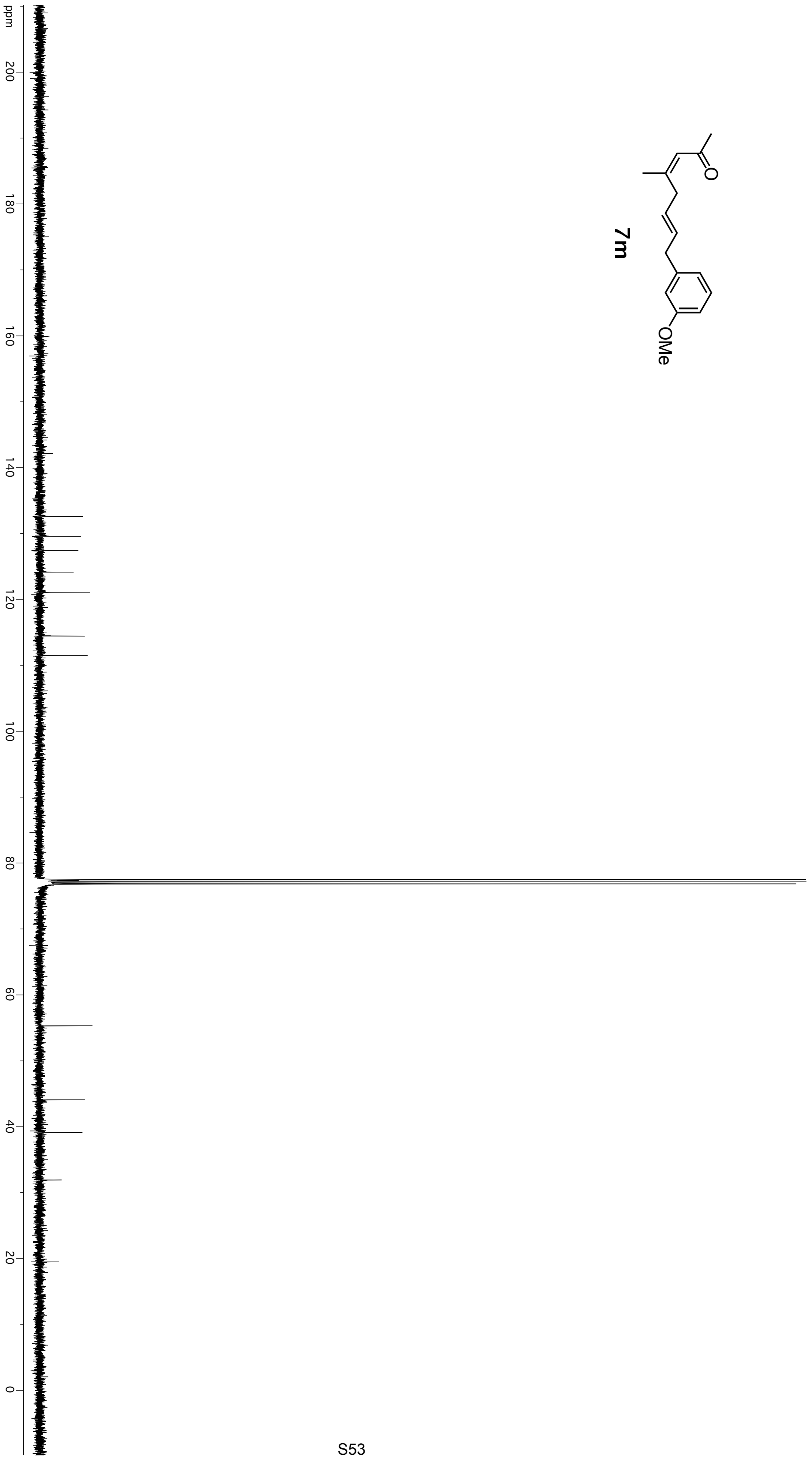

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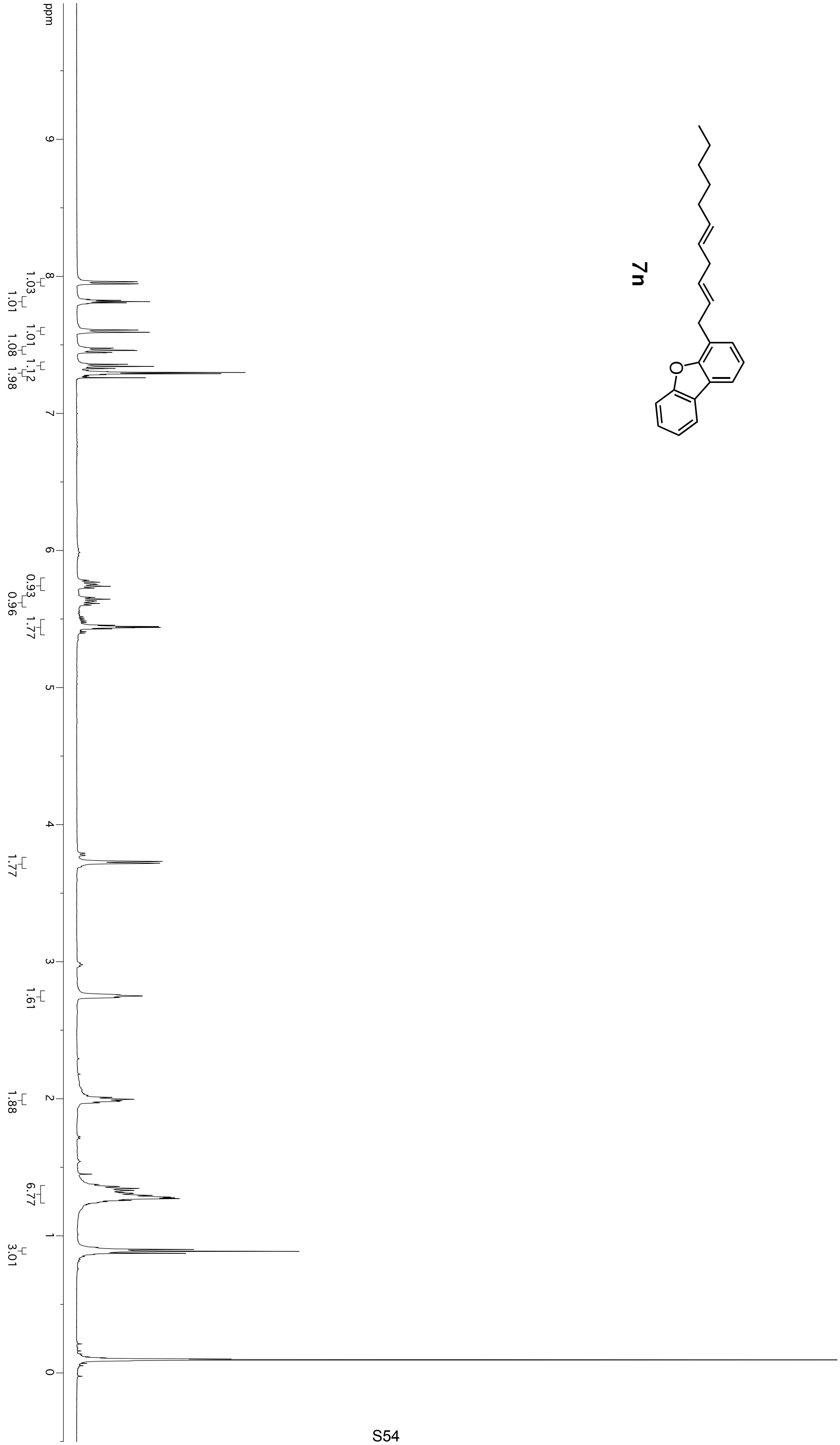
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1.01
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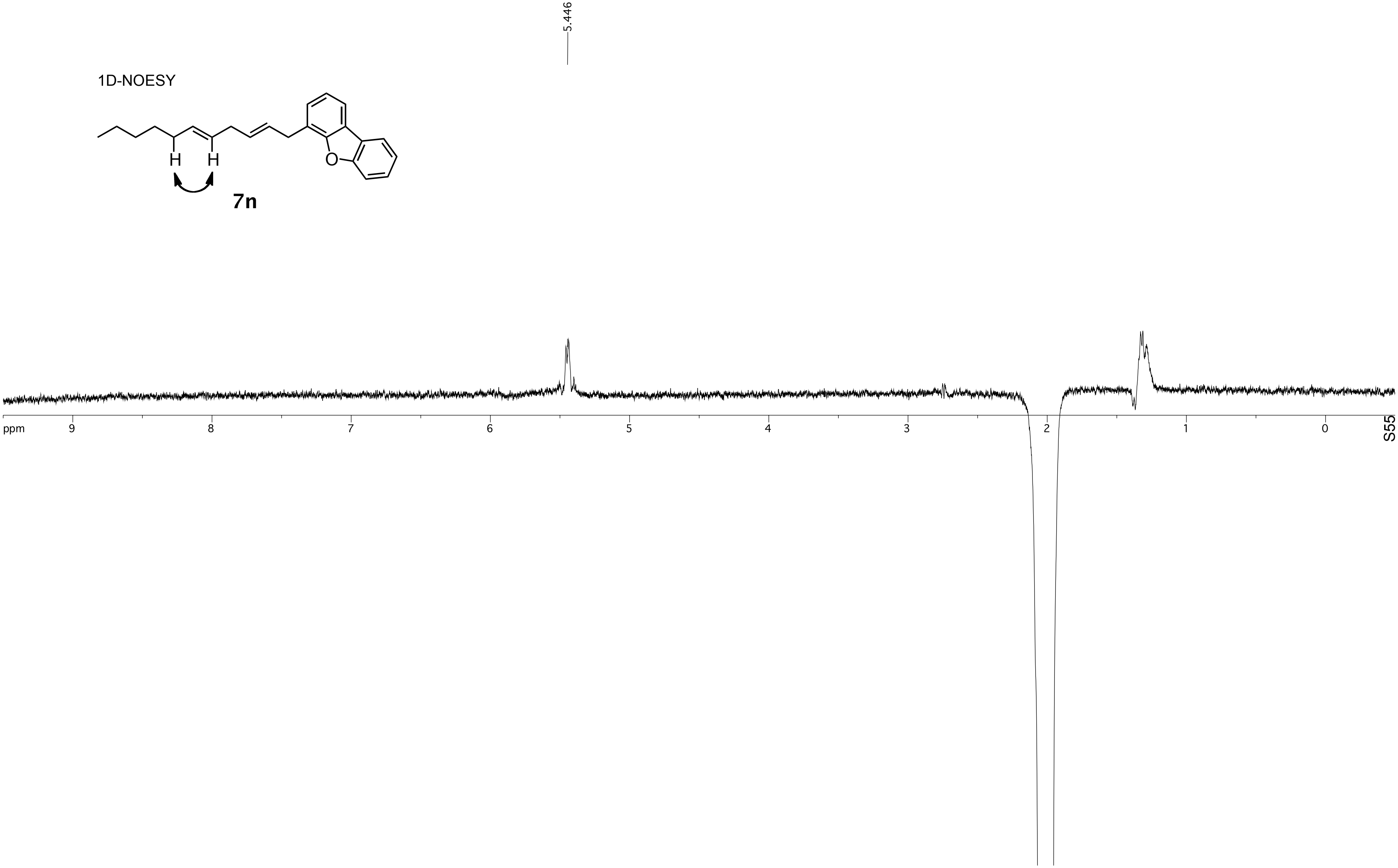
1.88
6.77
3.01

1D-NOESY



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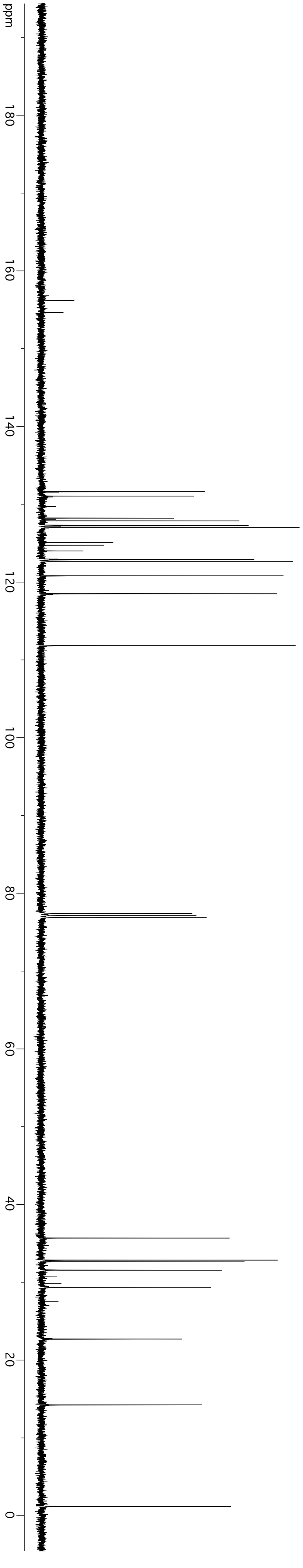

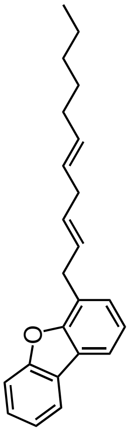

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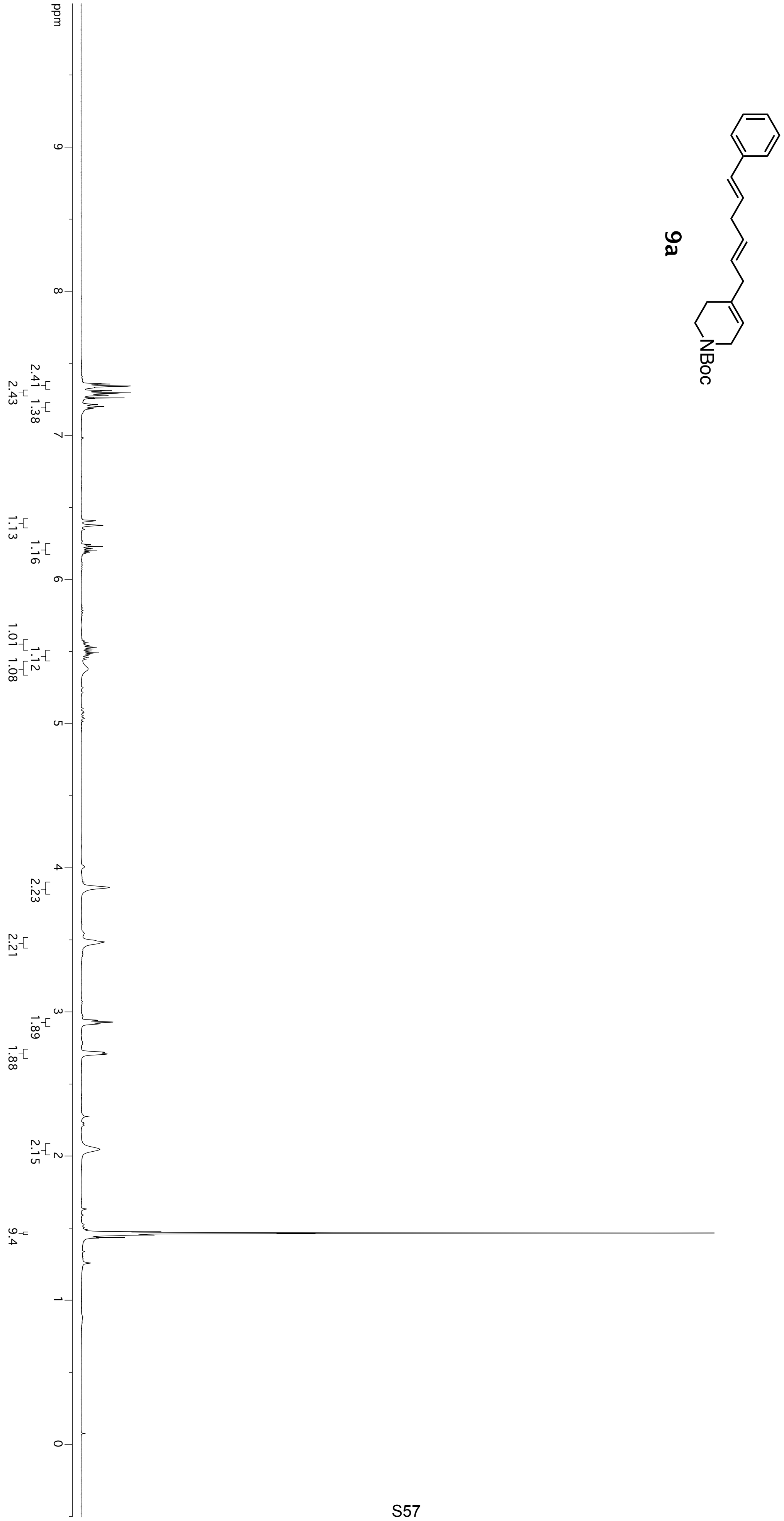
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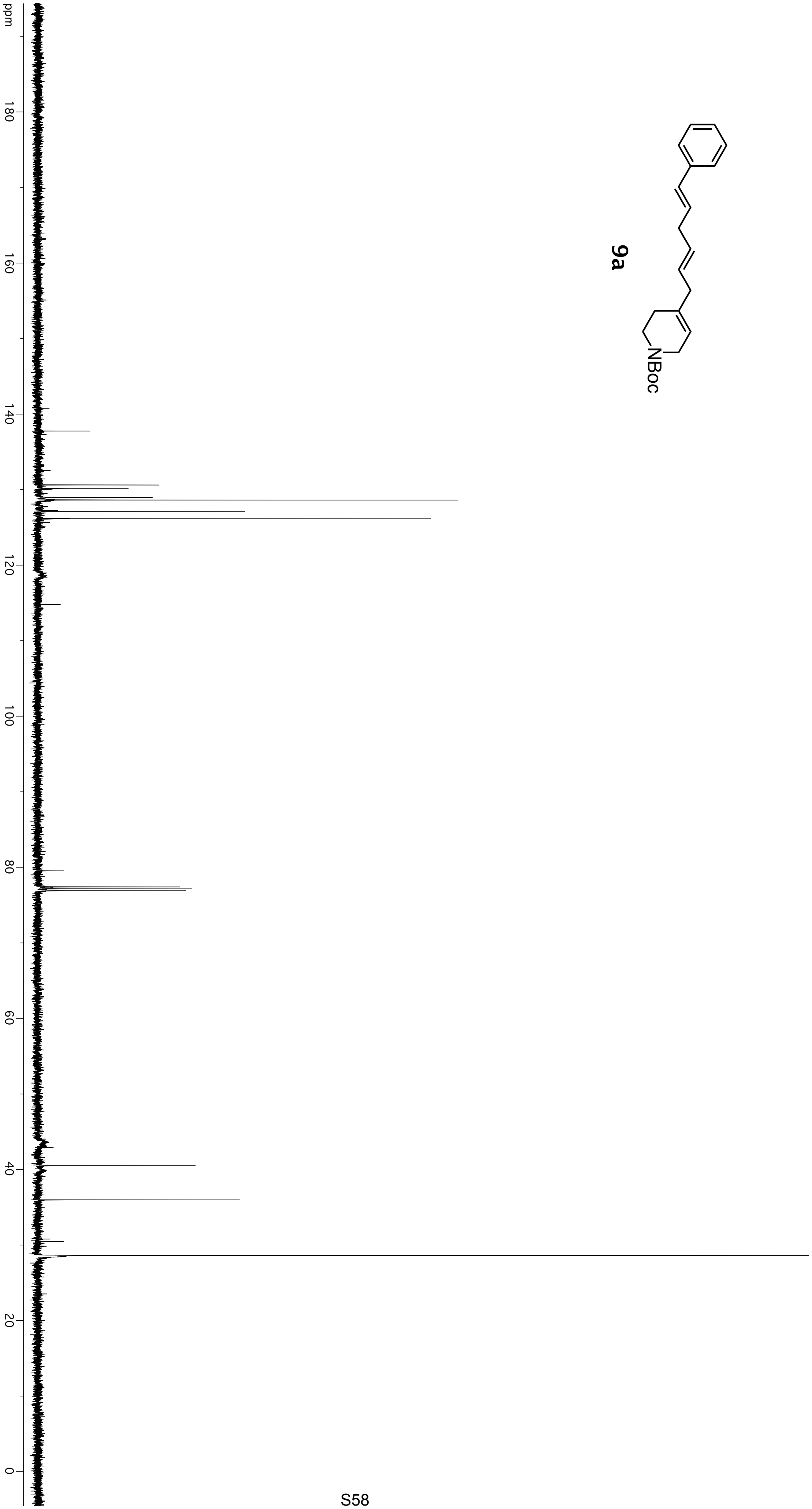
9a



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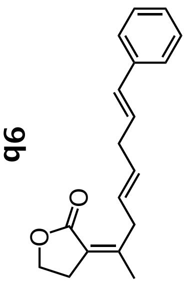

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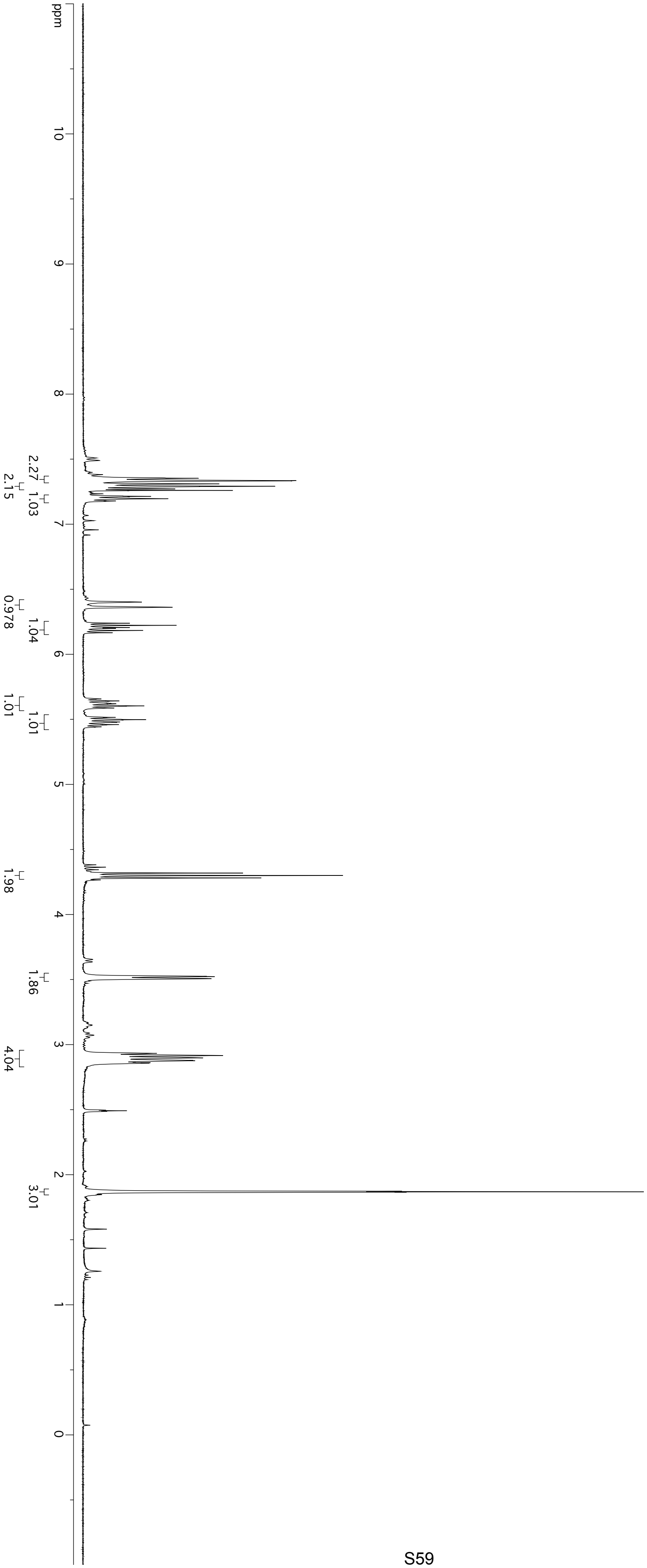
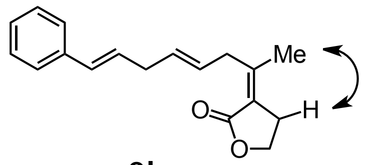


NOESY1D



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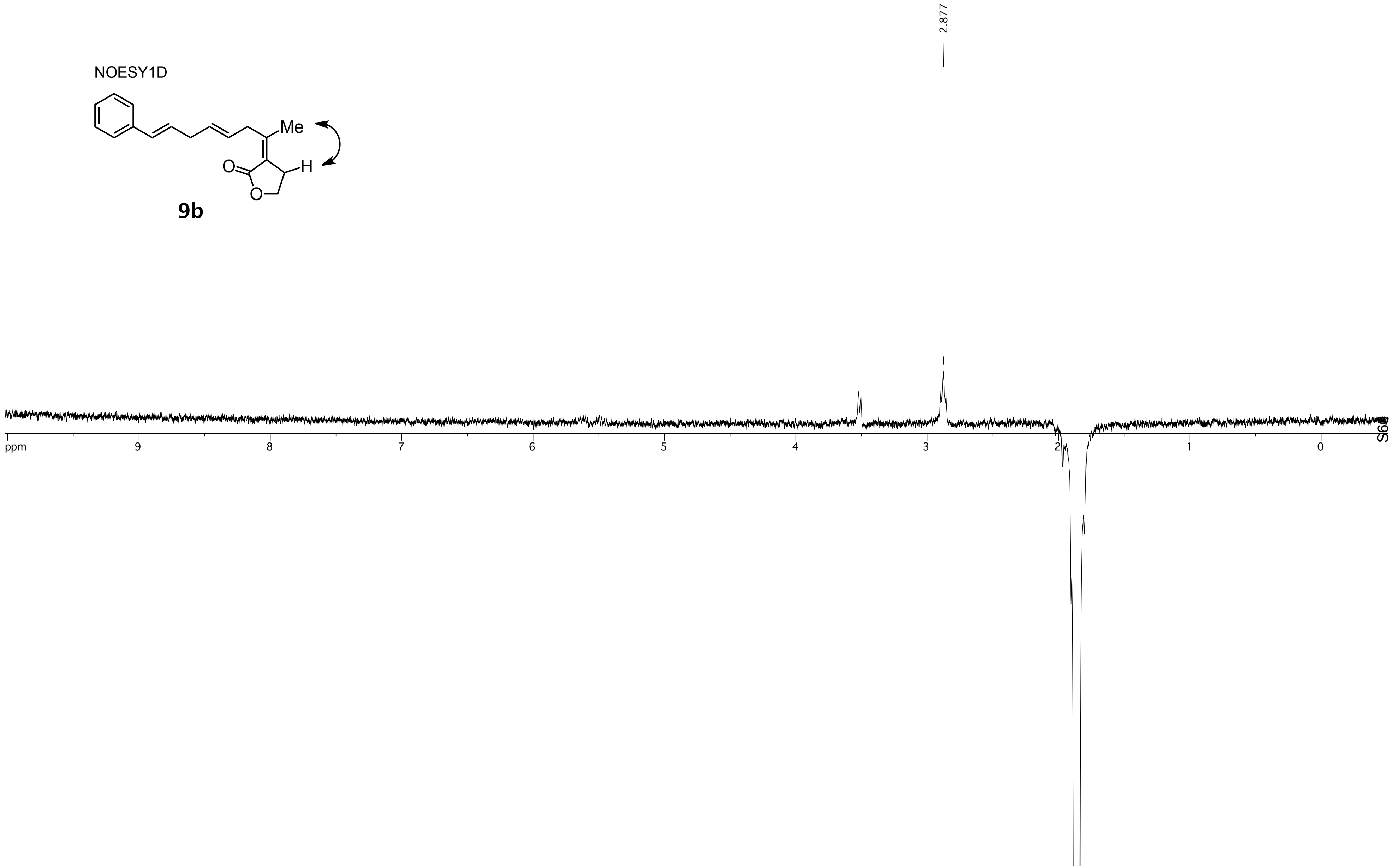

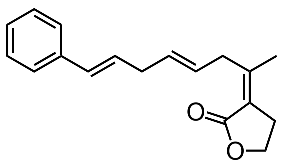

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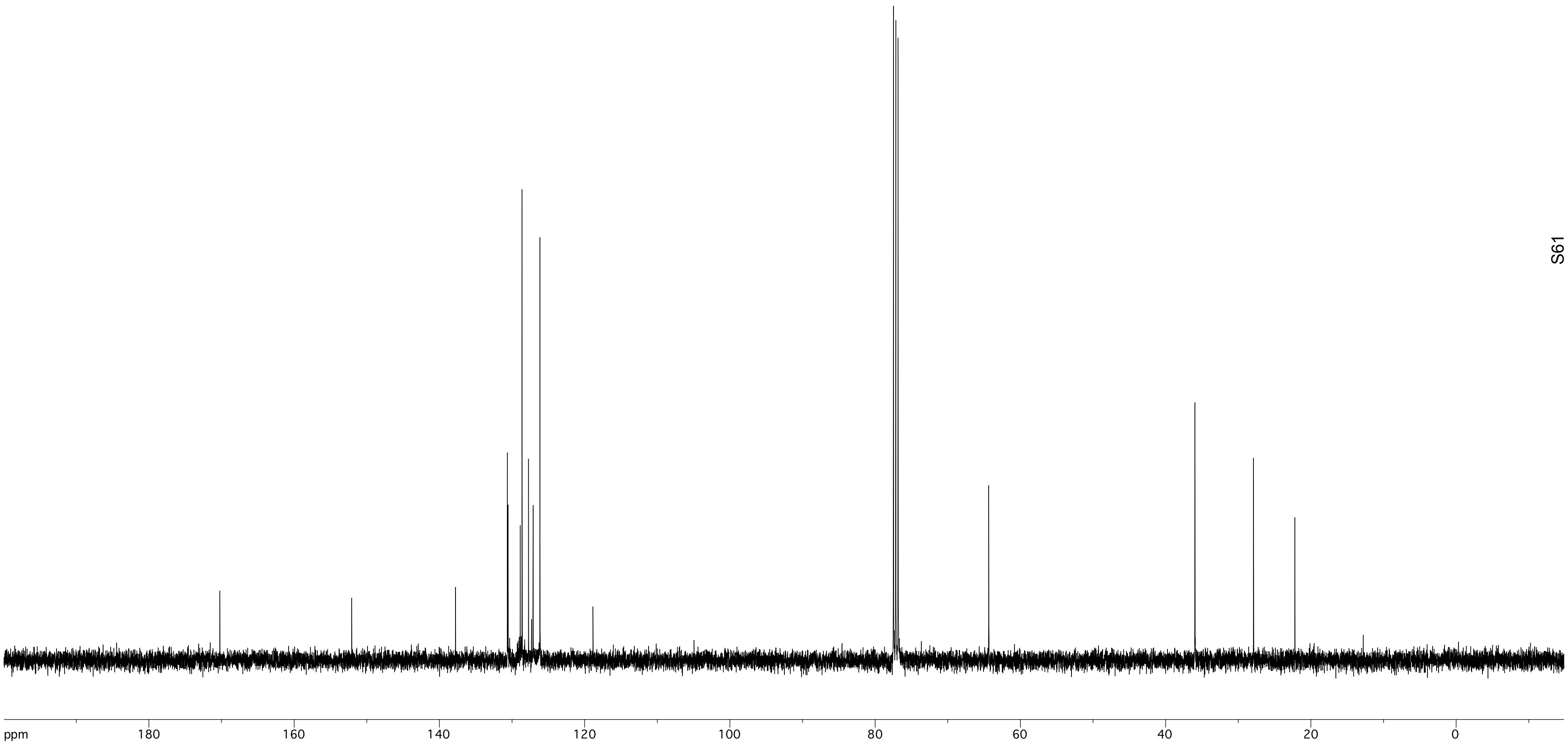

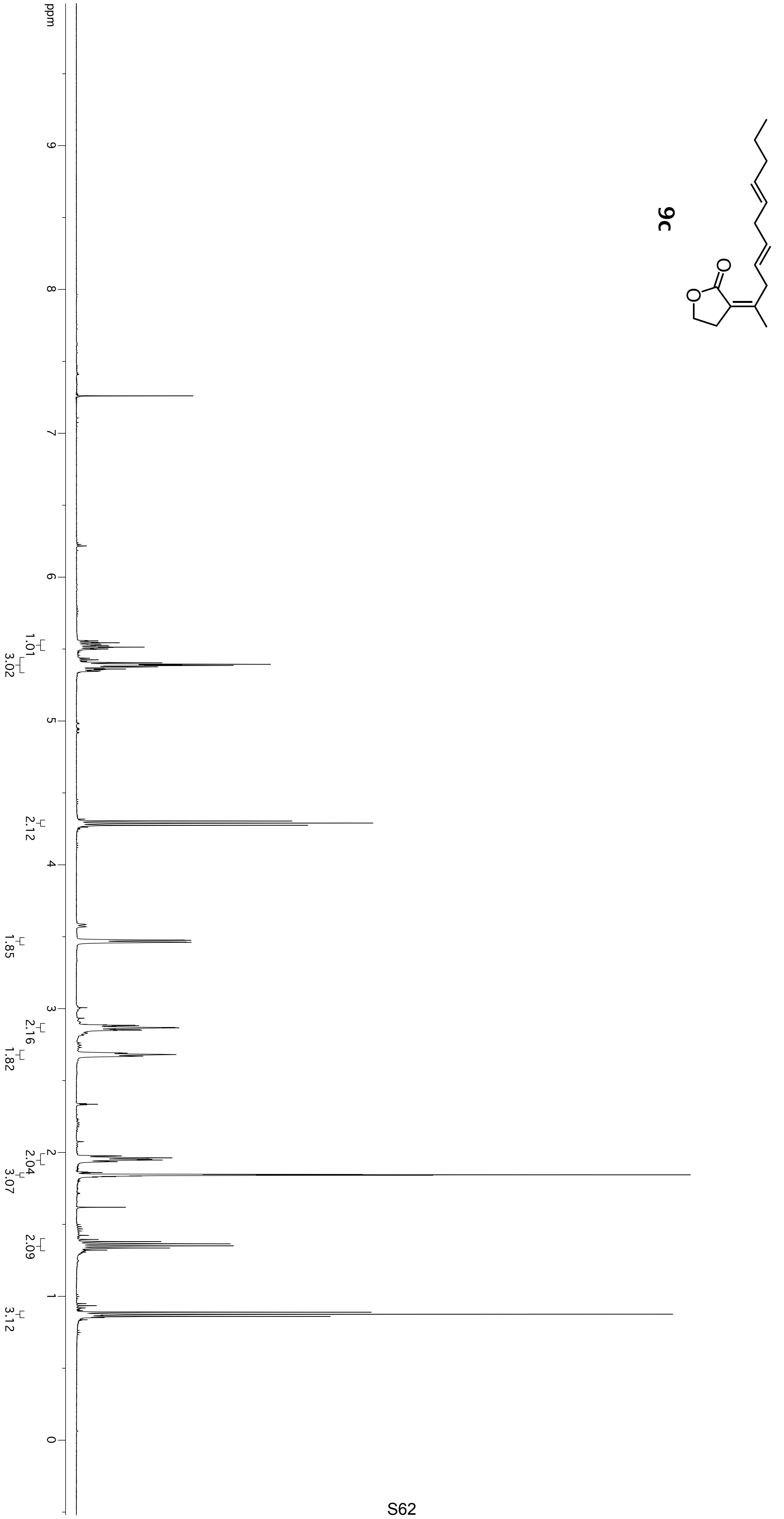
9c
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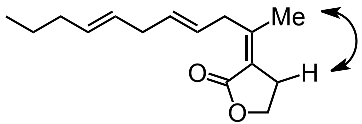
NOESY1D



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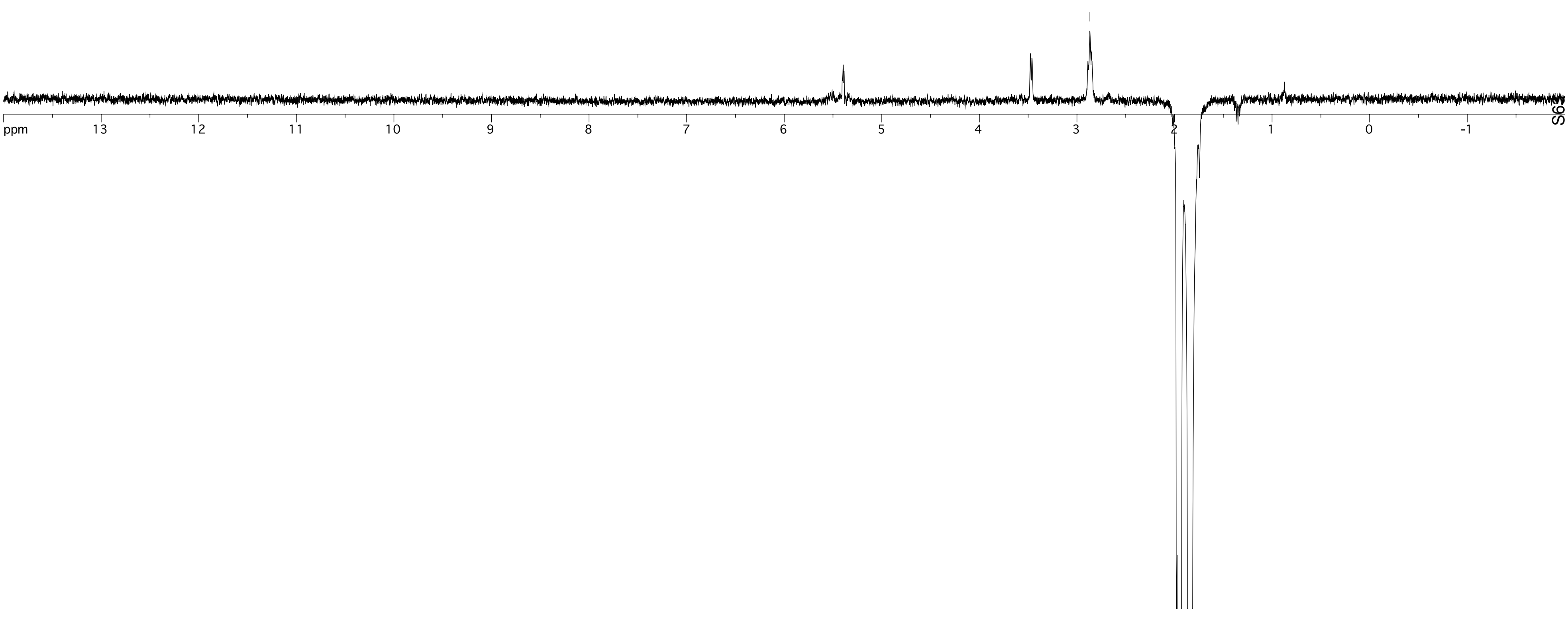

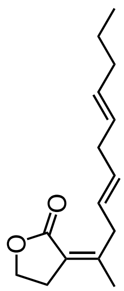

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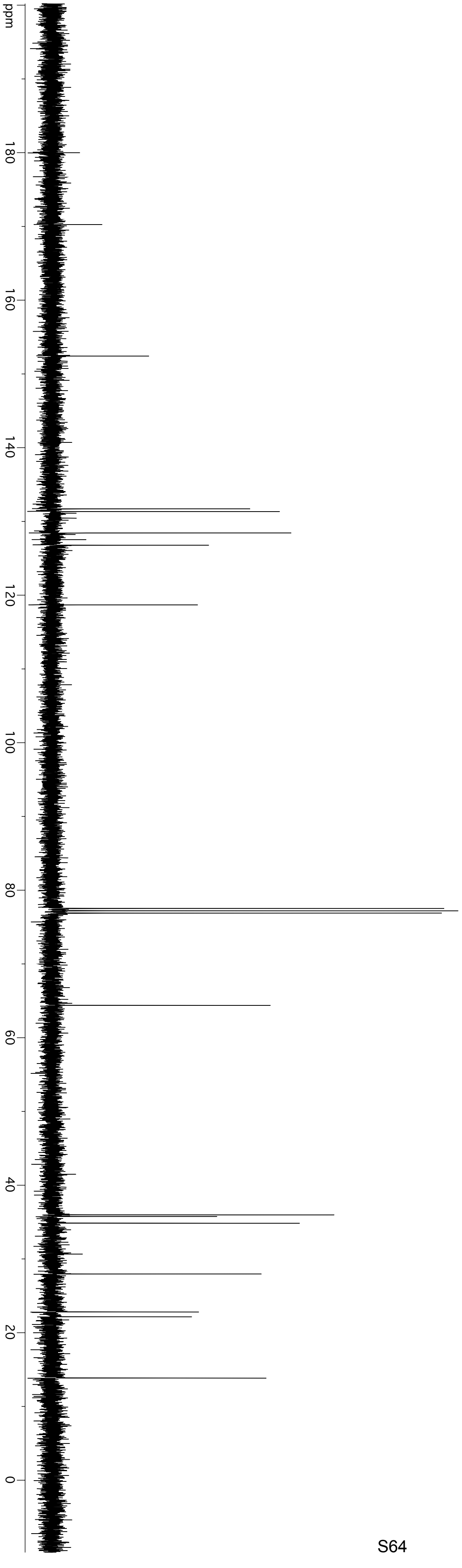

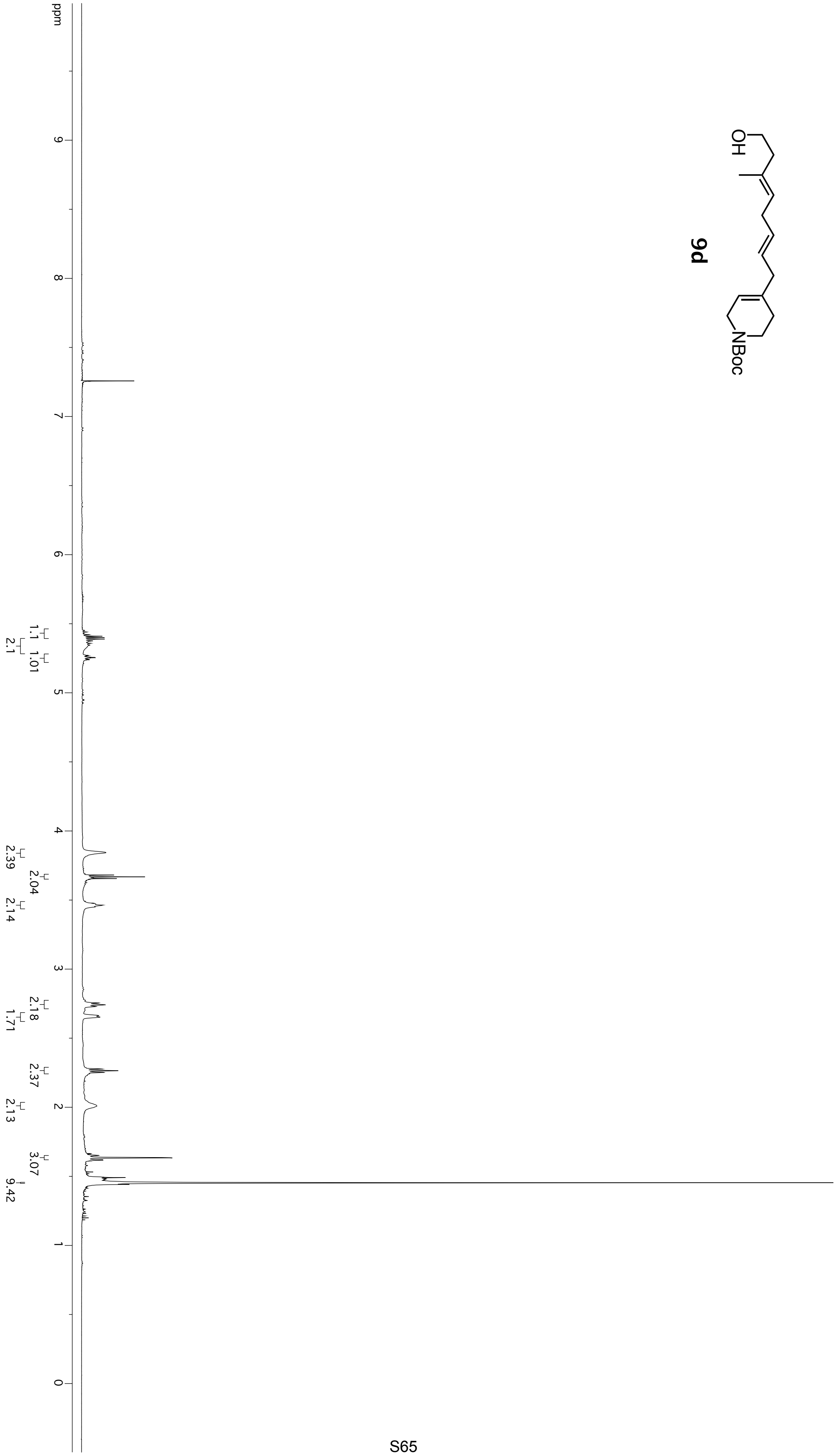
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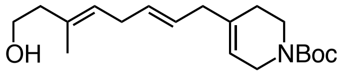
9d

NOESY1D



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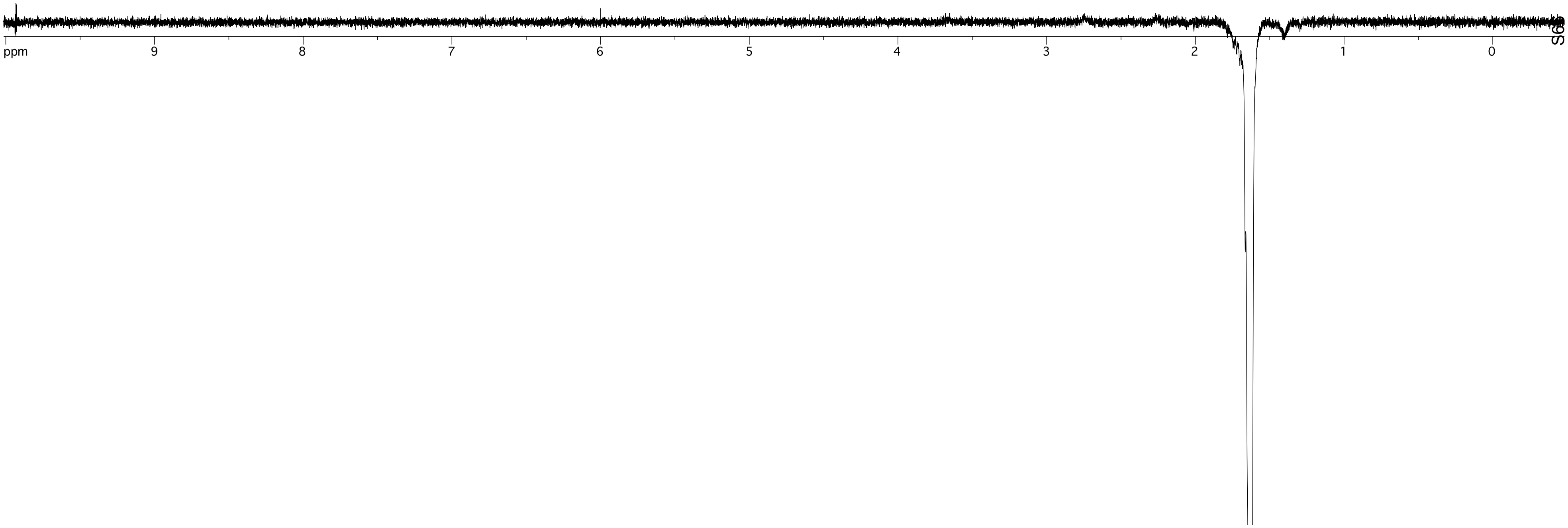

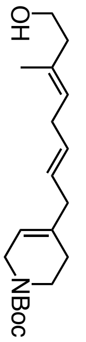

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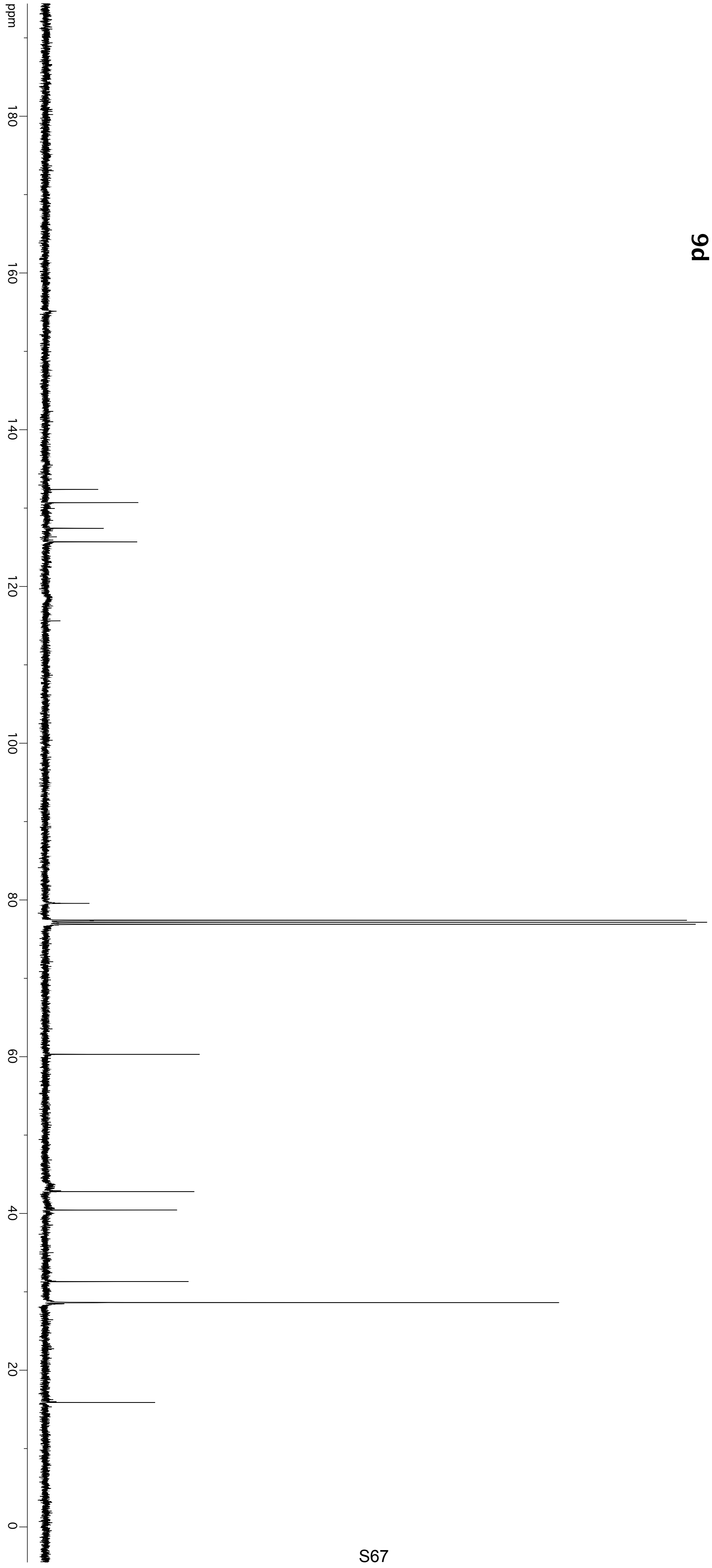

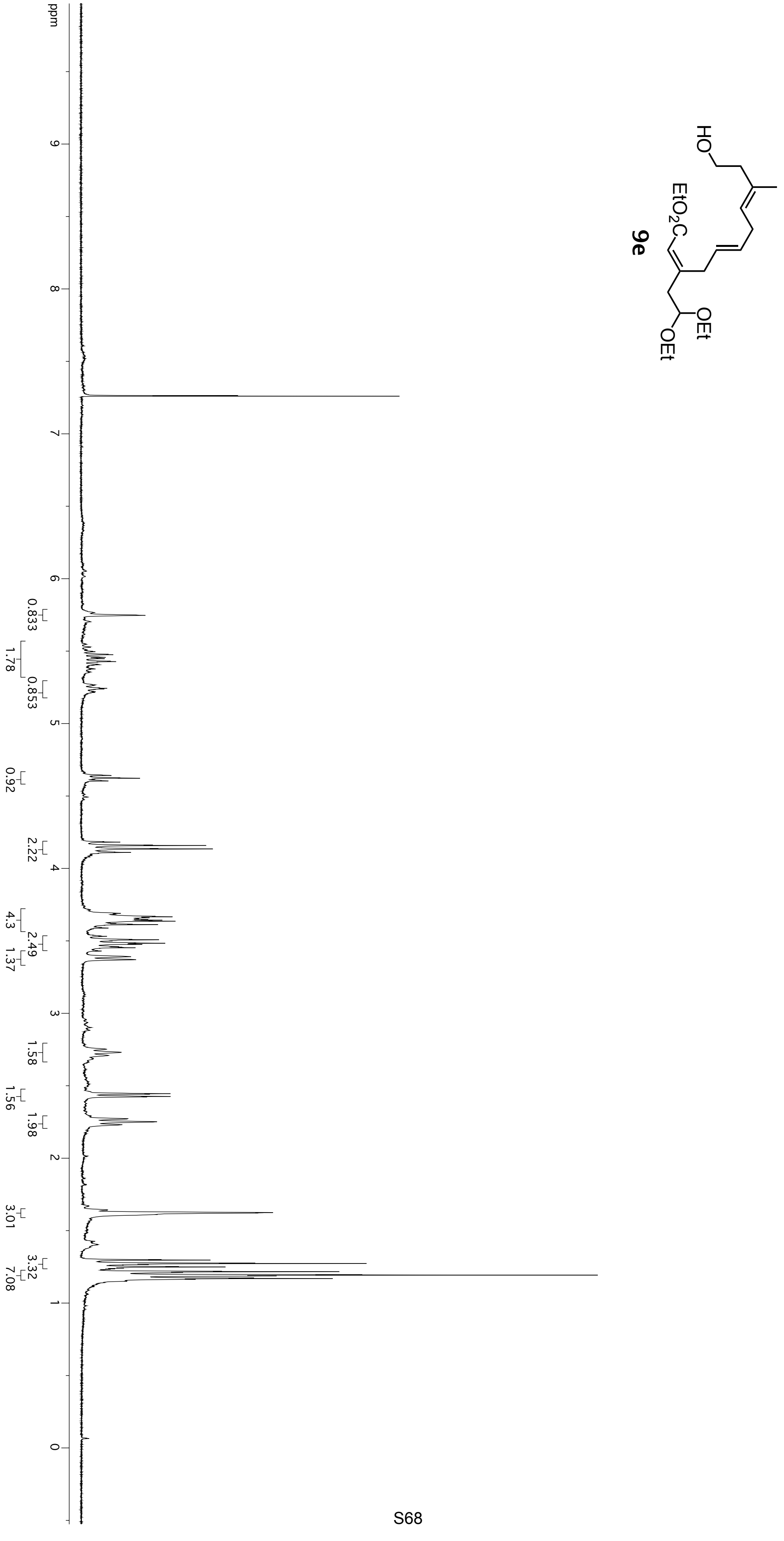

9e

HO
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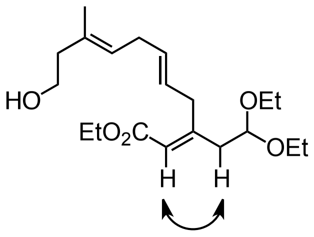
NOESY1D



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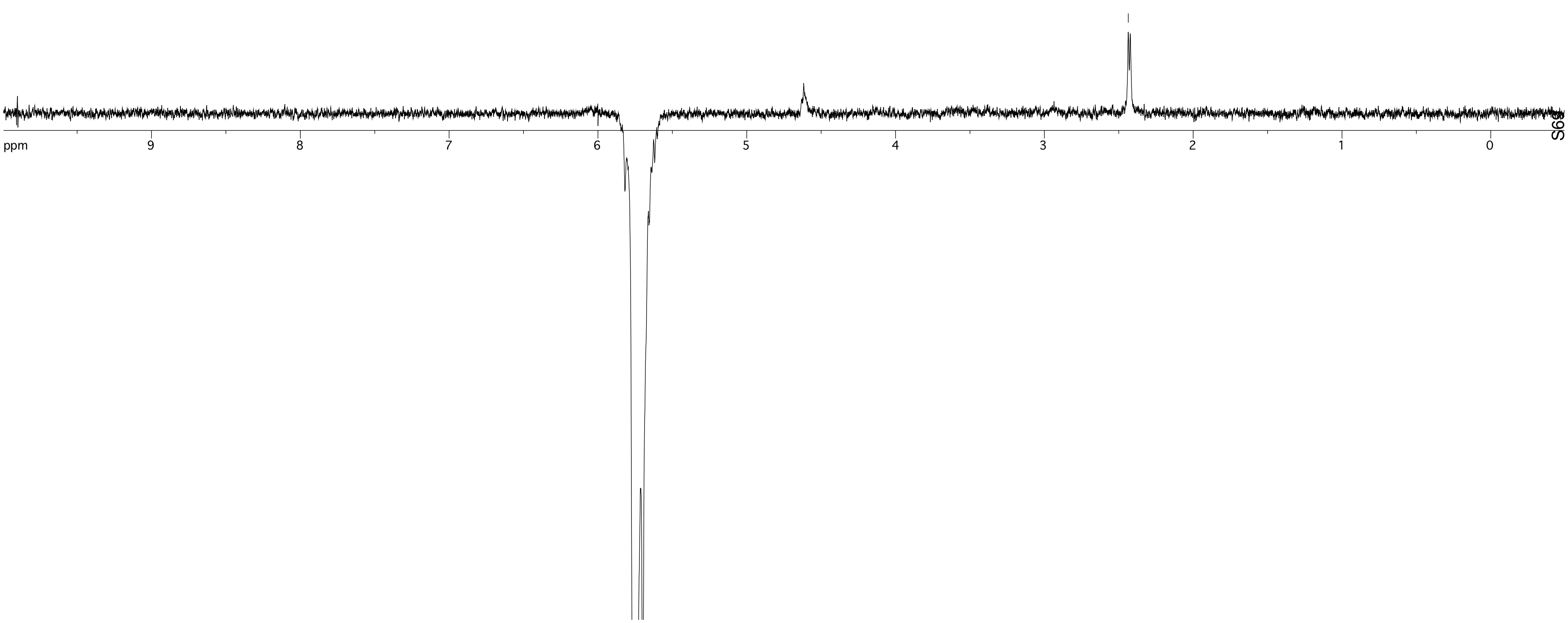

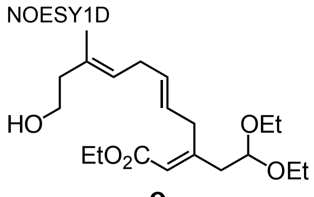

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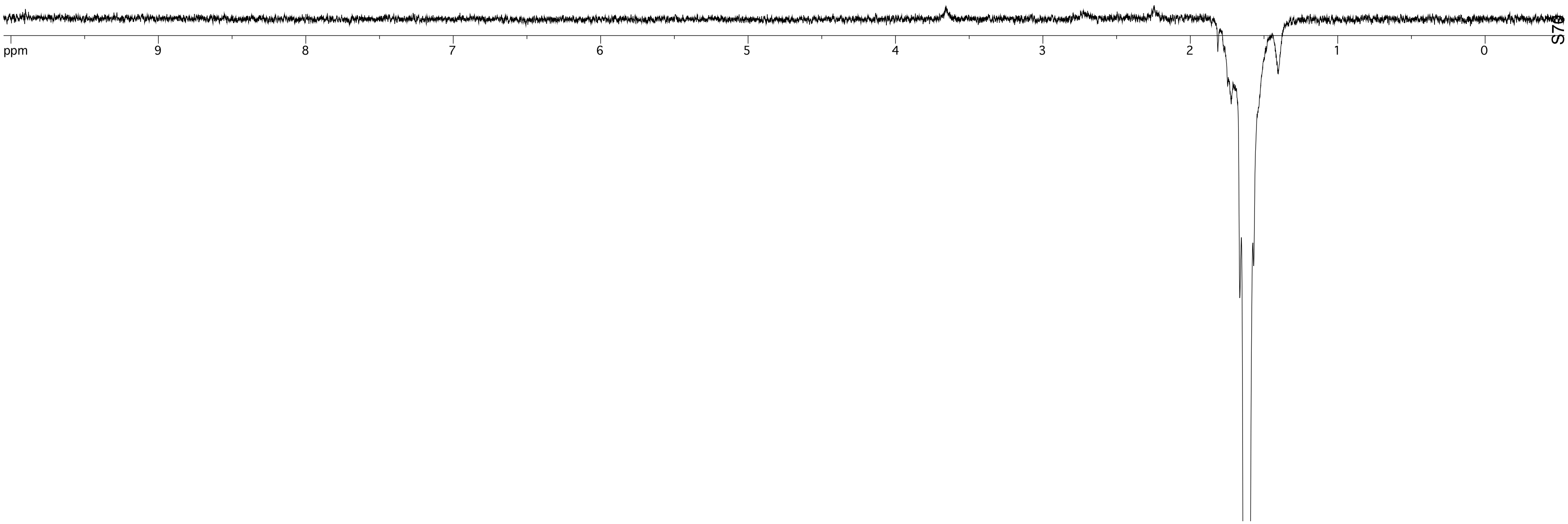

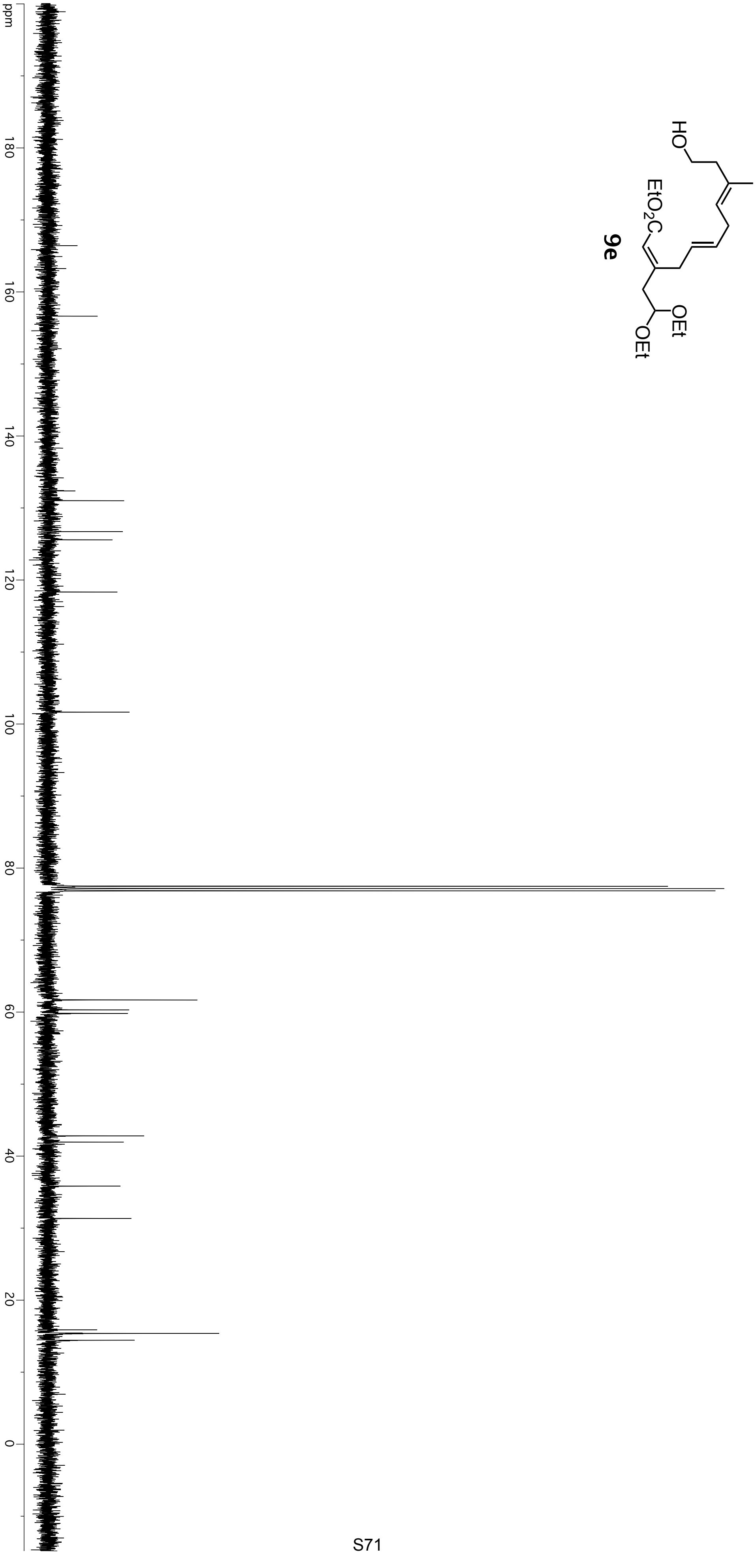

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