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Palladium-Catalyzed C–H Activation of N-Allyl Imines: Regioselective Allylic Alkylations to Deliver Substituted Aza-1,3-Dienes**

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Contents:

Experimentals: page

General ..…….3

General Method for Synthesis of Cyanoester Nucleophiles: ..……3

General Method for Synthesis of Imines: ..……5

General Method for Synthesis of β-Amino Ester via Oxidative C-H Activation: ..……11

Test of Diastereoselectivity for Imine addition by Lewis Acid Activation: ..……...21

General Method for Synthesis of 2-Aza Diene via Oxidative C-H Activation: ..……21

General Method for Synthesis of Pyridine Derivatives: ……...24

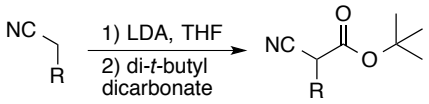
References: …….26

^{1}H and ^{13}C NMR Spectra:

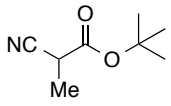
Compound #	Page #	Compound #	Page #	Compound #	Page #
2	27	S17	65	15	103
S1	29	S18	67	16	105
S2	31	S19	69	17	107
S3	33	S20	71	18	109
25	35	S21	73	19	111
S4	37	S22	75	20	113
1	39	S23	77	21	115
S5	41	3	79	22	117
S6	43	4	81	23	119
S7	45	5	83	24	121
S8	47	6	85	26	123
S9	49	7	87	27	125
S10	51	8	89	28	127
S11	53	9	91	29	129
S12	55	10	93	30	131
S13	57	11	95	31	133
S14	59	12	97	33	135
S15	61	13	99	34	137
S16	63	14	101		

General: All reactions were performed in flame- or oven-dried glassware with magnetic stirring under nitrogen or argon atmosphere using freshly distilled solvents. THF was distilled over sodium and CH_2Cl_2 was obtained from a solvent purification system. All commercial reagents were used without purification unless otherwise noted. Air and moisture sensitive liquids and solutions were transferred via stainless steel syringe or cannula and introduced into the reaction vessel through rubber septa. Thin-layer chromatography was performed on EMD silica gel 60 F_{254} plates (0.25 mm); visualization of the developed chromatogram was performed by fluorescence quenching and staining with aqueous ceric ammonium molybdate, *p*-anisaldehyde, or potassium permanganate. Organic solutions were concentrated by rotary evaporation below 40 ºC at *ca.* 25 mm Hg. Chromatographic purification of products was accomplished using forced-flow chromatography on Silicycle silica gel (particle size 0.040-0.063 μm). All isolated and characterized compounds were >95% pure as judged by ^{1}H NMR spectroscopic analysis. Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectroscopy were performed on a Varian Mercury NMR operating at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to the residual protiated solvent (CDCl3: δ_H = 7.26 ppm, δ_C = 77.16 ppm); all ^{13}C NMR spectra are proton decoupled. Data for ^{1}H are reported in terms of chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constant, and integration; data for ^{13}C are reported in terms of chemical shift. Infrared spectroscopic data was recorded as thin films on sodium chloride plates on a Thermo Scientific Nicolet IR100 FT-IR spectrometer. High-resolution mass spectrometry (HRMS) was measured on a Bruker micrOTOF-Q II electronspray ionization (ESI) mass spectrometer by the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University. Mass peaks are reported in *m*/*z* units.

General Method for Synthesis of Cyanoester Nucleophiles:

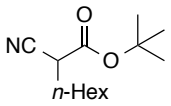


To a stirred solution of nitrile (10.0 mmol, 1.0 equiv.) in THF (30.0 mL) at -78 ºC was cannulated a solution of LDA (25.0 mL, 25.0 mmol, 1M in THF, 2.5 equiv.). After 30 min, the reaction was warmed to rt. After another 30 min, the reaction was cooled back down to -78 ºC. A solution of di-*t*-butyl dicarbonate (2.30 g, 10.5 mmol, 1.05 equiv.) in THF (20 mL) was added dropwise. After 3 h, the reaction mixture was quenched with satd. aq. NH_4Cl (25 mL) and aqueous layer was extracted with Et_2O (2 X 40 mL). The combined organic extract was washed with 10% aq. HCl (2 X 30 mL) and brine (30 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and was purified by flash chromatography over silica gel, eluting with 5-10% EtOAC / hexanes to give desired cyanoesters (**2**, **S1**-**S3**, **25**) as colorless oils.



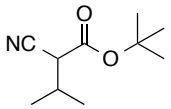
2

***t*-Butyl 2-cyanopropanoate (2):** Obtained as colorless oil (1.35 g, 8.70 mmol, 87%). Previously reported compound:[1] ^{1}H NMR (400 MHz; CDCl3): δ 3.44 (q, *J* = 7.4 Hz, 1H), 1.53 (d, *J* = 7.4 Hz, 3H), 1.49 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 117.9, 84.0, 32.6, 27.9, 15.4 ppm.



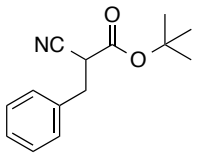
S1

***t*-Butyl 2-cyanooctanoate (S1):** Obtained as colorless oil (2.06 g, 9.14 mmol, 91%). Previously reported compound:[1] ^{1}H NMR (400 MHz; CDCl3): δ 3.38 (t, *J* = 7.0 Hz, 1H), 1.89 (q, *J* = 7.6 Hz, 2H), 1.44-1.49 (m, 11H), 1.29-1.37 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 117.1, 84.0, 38.7, 31.5, 30.0, 28.6, 27.9, 26.8, 22.6, 14.1 ppm.



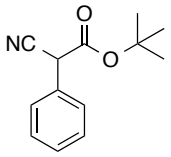
S2

***t*-Butyl-2-cyano-3-methylbutanoate (S2):** Obtained as colorless oil (1.70 g, 9.28 mmol, 93%). Previously reported compound:[2] ^{1}H NMR (400 MHz; CDCl3): δ 3.29 (d, *J* = 5.4 Hz, 1H), 2.33-2.41 (m, 1H), 1.50 (s, 9H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 115.9, 83.9, 46.5, 30.1, 27.9, 20.8, 18.9 ppm.



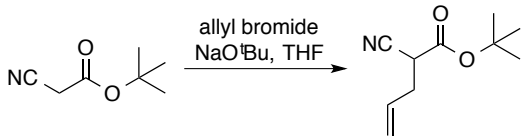
S3

***t*-Butyl 2-cyano-3-phenylpropanoate (S3):** Obtained as colorless oil (2.27 g, 9.81 mmol, 98%). Previously reported compound:[1] ^{1}H NMR (400 MHz; CDCl3): δ 7.27-7.36 (m, 5H), 3.63 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.24 (dd, *J* = 13.9, 6.0 Hz, 1H), 3.16 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 135.6, 129.2, 128.9, 127.8, 116.7, 84.4, 40.6, 35.9, 27.9 ppm.



25

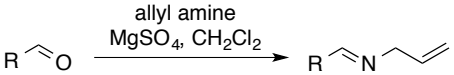
***t*-Butyl 2-cyano-2-phenylacetate (25):** Obtained as colorless oil (2.07 g, 9.53 mmol, 95%). Previously reported compound:[1] ^{1}H NMR (400 MHz; CDCl3): δ 7.38-7.46 (m, 5H), 4.61 (s, 1H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 130.5, 129.3, 129.1, 127.8, 116.1, 84.6, 44.9, 27.7 ppm.



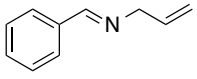
S4

***t*-Butyl-2-cyanopent-4-enoate (S4):** To a stirred suspension of NaO^{t}Bu (961 mg, 10.0 mmol, 1.0 equiv.) in THF (40 mL) at 0 ºC was added *t*-butyl 2-cyanoacetate (1.41 g, 10.0 mmol, 1 equiv.) slowly. After 30 min, allyl bromide (1.21 g, 10.0 mmol, 1.0 equiv.) was added dropwise. After 3 h, the reaction was quenched with H_2O (25 mL) and aqueous layer was extracted with Et_2O (2 X 30 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and was purified by flash chromatography over silica gel, eluting with 2-5% EtOAC / hexanes to give cyanoester **S4** (783 mg, 4.32 mmol, 43%) as colorless oil. Previously reported compound:[2] ^{1}H NMR (400 MHz; CDCl3): δ 5.81 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.21-5.28 (m, 2H), 3.46 (dd, *J* = 7.2, 6.3 Hz, 1H), 2.62-2.67 (m, 2H), 1.49 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 131.7, 119.9, 116.6, 84.3, 38.5, 34.1, 27.9 ppm.

General Method for Synthesis of Imines:

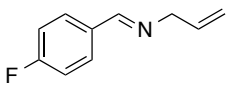


To a stirred solution of aldehyde (10.0 mmol, 1.0 equiv.) in CH_2Cl_2 (12 mL) was added MgSO4 (1.0 g) followed by allyl amine (0.82 mL, 628 mg, 11.0 mmol, 1.1 equiv.). After 24 h, the reaction was filtered through a sintered glass funnel. Solvent was removed *in vacuo* and kept under high vacuum for 3 h. The crude was sufficiently clean (>95% purity by NMR) and was directly used for oxidative C-H activation.



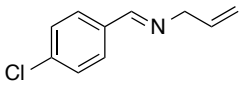
1

(*E*)-*N*-Allyl-1-phenylmethanimine (1): Obtained as colorless oil (1.45 g, quant.). Previously reported compound:[3] ^{1}H NMR (400 MHz; CDCl3): δ 8.30 (t, *J* = 1.3 Hz, 1H), 7.75-7.78 (m, 2H), 7.40-7.44 (m, 3H), 6.08 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.17 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.27 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 136.2, 135.9, 130.8, 128.6, 128.2, 116.1, 63.6 ppm.



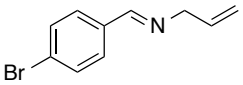
S5

(*E*)-*N*-Allyl-1-(4-fluorophenyl)methanimine (S5): Obtained as colorless oil (1.63 g, quant.). Previously reported compound:[4] ^{1}H NMR (400 MHz; CDCl3): δ 8.25 (t, *J* = 1.2 Hz, 1H), 7.72-7.76 (m, 2H), 7.06-7.12 (m, 2H), 6.06 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.24 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, *J* = 249.5 Hz), 160.6, 135.9, 132.5 (d, *J* = 2.9 Hz), 130.1 (d, *J* = 9.0 Hz), 116.1 (d, *J* = 35.9 Hz), 115.7, 63.5 ppm.



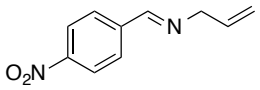
S6

(*E*)-*N*-Allyl-1-(4-chlorophenyl)methanimine (S6): Obtained as colorless oil (1.79 g, quant.). Previously reported compound:[5] ^{1}H NMR (400 MHz; CDCl3): δ 8.23 (t, *J* = 1.3 Hz, 1H), 7.66-7.69 (m, 2H), 7.35-7.39 (m, 2H), 6.05 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.24 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 136.7, 135.7, 134.7, 129.4, 128.9, 116.3, 63.5 ppm.



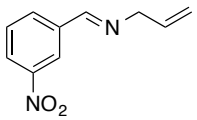
S7

(*E*)-*N*-Allyl-1-(4-bromophenyl)methanimine (S7):): Obtained as light yellow oil (2.25 g, quant.). Previously reported compound:[5] ^{1}H NMR (400 MHz; CDCl3): δ 8.23 (s, 1H), 7.60-7.63 (m, 2H), 7.52-7.55 (m, 2H), 6.05 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.24 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 135.7, 135.1, 131.9, 129.6, 125.2, 116.4, 63.6 ppm.



S8

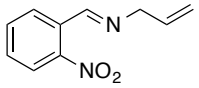
(*E*)-*N*-Allyl-1-(4-nitrophenyl)methanimine (S8): Obtained as pale yellow solid (1.89 g, quant.). Previously reported compound:[6] ^{1}H NMR (400 MHz; CDCl3): δ 8.37 (t, *J* = 1.4 Hz, 1H), 8.23-8.26 (m, 2H), 7.89-7.92 (m, 2H), 6.06 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.18 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.31 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 149.1, 141.7, 135.2, 128.9, 123.9, 116.8, 63.7 ppm.



S9

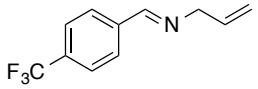
(*E*)-*N*-Allyl-1-(3-nitrophenyl)methanimine (S9): Obtained as pale yellow oil (1.90 g, quant.). IR: (neat) 3041, 2970, 2940, 2835, 1626, 1508, 1420, 1332, 980, 907 cm^{-1}; ^{1}H

NMR (400 MHz; CDCl3): δ 8.56 (t, *J* = 1.9 Hz, 1H), 8.36 (s, 1H), 8.24 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.08 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 6.06 (d dt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.17 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.30 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 148.6, 137.9, 135.3, 133.6, 129.7, 125.1, 122.9, 116.7, 63.5 ppm; HRMS (ESI+) calcd. for $C_{10}H_{11}N_2O_2$ (M+H) 191.0815, found 191.0810.



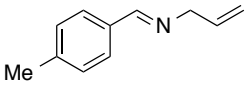
S10

(*E*)-*N*-Allyl-1-(2-nitrophenyl)methanimine (S10): Obtained as pale yellow oil (1.89 g, quant.). Previously reported compound:[7] ^{1}H NMR (400 MHz; CDCl3): δ 8.69 (s, 1H), 8.06 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.97 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.61-7.66 (m, 1H), 7.53 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 1H), 6.05 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.30 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 157.7, 148.9, 135.2, 133.5, 131.1, 130.7, 129.7, 124.3, 116.7, 63.5 ppm.



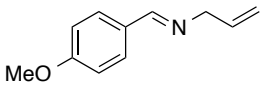
S11

(*E*)-*N*-Allyl-1-(4-(trifluoromethyl)phenyl)methanimine (S11): Obtained as colorless oil (2.13 g, quant.). Previously reported compound:[8] ^{1}H NMR (400 MHz; CDCl3): δ 8.33 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 6.07 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.18 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.29 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 139.4, 135.5, 132.3 (q, *J* = 32.3 Hz), 128.4, 125.7 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 270.5 Hz), 116.5, 63.7 ppm.



S12

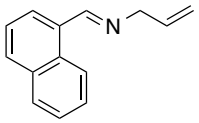
(*E*)-*N*-Allyl-1-(*p*-tolyl)methanimine (S12): Obtained as colorless oil (1.59 g, quant.). Previously reported compound:[4] ^{1}H NMR (400 MHz; CDCl3): δ 8.26 (s, 1H), 7.64-7.67 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.08 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.25 (dq, *J* = 5.7, 1.5 Hz, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 141.0, 136.1, 133.6, 129.4, 128.2, 116.0, 63.6, 21.6 ppm.



S13

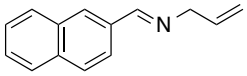
(*E*)-*N*-Allyl-1-(4-methoxyphenyl)methanimine (S13): Obtained as colorless oil (1.75 g, quant.). Previously reported compound:[8] ^{1}H NMR (400 MHz; CDCl3): δ 8.22 (s, 1H), 7.68-7.71 (m, 2H), 6.90-6.94 (m, 2H), 6.06 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.14 (dq, *J* = 10.2, 1.6 Hz, 1H), 4.22 (dq, *J* = 5.7, 1.5 Hz, 2H), 3.83 (s,

3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.4, 136.3, 129.8, 129.2, 116.0, 114.1, 63.6, 55.4 ppm.



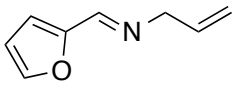
S14

(*E*)-*N*-Allyl-1-(naphthalen-1-yl)methanimine (S14): Obtained as light yellow oil (1.96 g, quant.). Previously reported compound:[9] ^{1}H NMR (400 MHz; CDCl3): δ 8.97 (d, *J* = 8.5 Hz, 1H), 8.96 (s, 1H), 7.90-7.96 (m, 3H), 7.62 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.52-7.57 (m, 2H), 6.22 (ddt, *J* = 17.2, 10.3, 5.6 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.25 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.42 (dq, *J* = 5.6, 1.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 136.2, 133.8, 131.6, 131.3, 131.1, 128.8, 128.6, 127.2, 126.1, 125.3, 124.3, 116.0, 64.5 ppm.



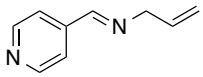
S15

(*E*)-*N*-Allyl-1-(naphthalen-2-yl)methanimine (S15): Obtained as white solid (1.95 g, quant.). Previously reported compound:[9] ^{1}H NMR (400 MHz; CDCl3): δ 8.45 (s, 1H), 8.06 (s, 1H), 8.03 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.85-7.91 (m, 3H), 7.49-7.55 (m, 2H), 6.13 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.29 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.20 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.33 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 136.0, 134.8, 133.9, 133.2, 130.1, 128.7, 128.6, 128.0, 127.2, 126.6, 123.9, 116.3, 63.7 ppm.



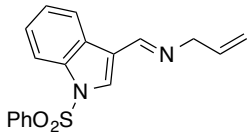
S16

(*E*)-*N*-Allyl-1-(furan-2-yl)methanimine (S16): Obtained as light yellow oil (1.34 g, quant.) Previously reported compound:[10] ^{1}H NMR (400 MHz; CDCl3): δ 8.08 (s, 1H), 7.49 (d, *J* = 1.6 Hz, 1H), 6.74 (d, *J* = 3.4 Hz, 1H), 6.46 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.99-6.09 (m, 1H), 5.20 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.13 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.21 (dq, *J* = 5.9, 1.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 150.4, 144.8, 135.6, 116.5, 114.0, 111.7, 63.7 ppm.



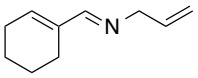
S17

(*E*)-*N*-Allyl-1-(pyridin-4-yl)methanimine (S17): Obtained as colorless oil (1.47 g, quant.). Previously reported compound:[11] ^{1}H NMR (400 MHz; CDCl3): δ 8.69 (dd, *J* = 6.0, 2.8 Hz, 2H), 8.26 (s, 1H), 7.60 (dd, *J* = 6.0, 2.8 Hz, 2H), 6.06 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.24 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.18 (dq, *J* = 10.3, 1.5 Hz, 1H), 4.29 (dq, *J* = 5.7, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 150.3, 142.7, 134.9, 121.7, 116.5, 63.4 ppm.



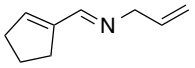
S18

(*E*)-*N*-Allyl-1-(1-(phenylsulfonyl)-1*H*-indol-3-yl)methanimine (S18): Obtained as pale yellow solid (3.24 g, quant.). IR: (neat) 3075, 2788, 1621, 1456, 1428, 1354, 1229, 1163, 1108, 1081 cm^{-1}; ^1H NMR (400 MHz; CDCl3): δ 8.45 (t, *J* = 1.3 Hz, 1H), 8.37 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 1H), 7.99 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.90-7.93 (m, 2H), 7.85 (s, 1H), 7.52-7.57 (m, 1H), 7.42-7.47 (m, 2H), 7.38 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.31 (td, *J* = 7.5, 1.1 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.3, 5.5 Hz, 1H), 5.26 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.7 Hz, 1H), 4.26 (dq, *J* = 5.5, 1.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 138.0, 136.2, 135.6, 134.3, 129.6, 129.5, 128.1, 127.0, 125.8, 124.4, 123.2, 120.9, 115.9, 113.3, 64.3 ppm; HRMS (ESI+) calcd. for $C_{18}H_{17}N_2O_2S$ (M+H) 325.1005, found 325.1010.



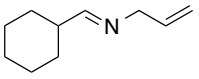
S19

(*E*)-*N*-Allyl-1-(cyclohex-1-en-1-yl)methanimine (S19): Obtained as colorless oil (1.49 g, quant.). IR: (neat) 2889, 2818, 2792, 1625, 1605, 1413, 1281, 1174, 1006, 978 cm^{-1}; ^1H NMR (400 MHz; CDCl3): δ 7.77 (s, 1H), 6.13 (tt, *J* = 3.8, 1.8 Hz, 1H), 5.97 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.13 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.06 (dq, *J* = 10.2, 1.6 Hz, 1H), 4.06 (dd, *J* = 5.6, 0.9 Hz, 2H), 2.27-2.30 (m, 2H), 2.18-2.21 (m, 2H), 1.59-1.67 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 139.0, 138.1, 136.4, 115.6, 63.4, 26.1, 23.8, 22.5, 22.1 ppm; HRMS (ESI+) calcd. for $C_{10}H_{16}N$ (M+H) 150.1277, found 150.1273.



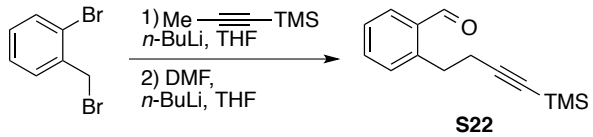
S20

(*E*)-*N*-Allyl-1-(cyclopent-1-en-1-yl)methanimine (S20): Obtained as colorless oil (1.35 g, quant.). Previously reported compound.[12] ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 6.17 (quintet, *J* = 2.2 Hz, 1H), 5.97 (ddt, *J* = 17.2, 10.3, 5.8 Hz, 1H), 5.12 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.07 (dq, *J* = 10.2, 1.6 Hz, 1H), 4.08 (d, *J* = 5.6 Hz, 2H), 2.55-2.60 (m, 2H), 2.44-2.49 (m, 2H), 1.92 (quintet, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 144.5, 140.7, 136.1, 115.8, 63.7, 33.3, 30.6, 23.1 ppm.



S21

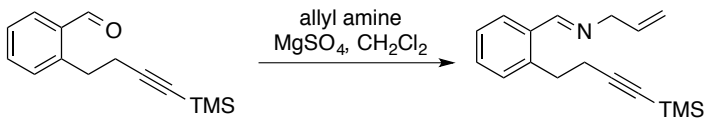
(*E*)-*N*-Allyl-1-cyclohexylmethanimine (S21): Obtained as colorless oil (1.52 g, quant.). Previously reported compound.[13] ^1H NMR (400 MHz; CDCl3): δ 7.50 (dt, *J* = 4.9, 1.2 Hz, 1H), 5.94 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H), 5.11 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.06 (dq, *J* = 10.3, 1.6 Hz, 1H), 3.96 (dq, *J* = 5.7, 1.5 Hz, 2H), 2.12-2.21 (m, 1H), 1.62-1.82 (m, 5H), 1.15-1.33 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 136.3, 115.6, 63.5, 43.6, 29.8, 26.1, 25.6 ppm.



S22

2-(4-(Trimethylsilyl)but-3-yn-1-yl)benzaldehyde (S22): To a stirred solution of 1-(trimethylsilyl)propyne (1.25 g, 11.1 mmol, 1.05 equiv.) in THF (35.0 mL) at -78 ºC was added *n*-BuLi (4.4 mL, 11.1 mmol, 2.51 M in hexanes, 1.05 equiv.) dropwise. After 2 h, a solution of 2-bromobenzylbromide (2.65 g, 10.6 mmol, 1.0 equiv.) in THF (4.0 mL) was cannulated over 15 min. The reaction was allowed to warm to rt. After 15 h, the solvent was removed *in vacuo* and the residue was purified by flash chromatography over silica gel, eluting with 2-5% EtOAc / hexanes to give known intermediate aryl bromide[14] (2.65 g, 9.42 mmol, 89%) as colorless oil.

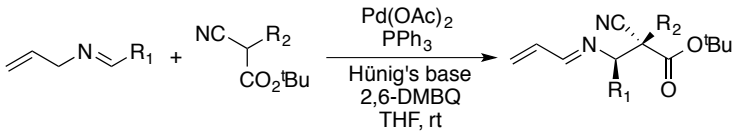
To a stirred solution of intermediate aryl bromide (2.60 g, 9.24 mmol, 1.0 equiv.) in THF (10 mL) at -78 ºC was added *n*-BuLi (5.5 mL, 13.8 mmol, 2.51 M in hexanes, 1.5 equiv.) dropwise. After 30 min, DMF (1.69 g, 23.1 mmol, 2.5 equiv.) was added dropwise and the reaction was warmed to rt. After 16 h, the reaction was poured into a mixture of satd. aq. NH4Cl and Et2O (50 mL, 1:1) and the aqueous layer was extracted with Et_2O (2 X 30 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and was purified by flash chromatography over silica gel, eluting with 5-10% EtOAC / hexanes to give aldehyde **S22** (1.72 g, 7.47 mmol, 81 %) as colorless oil. IR: (neat) 2917, 2859, 2143, 1673, 1578, 1552, 1232, 1175, 1025, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.84 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.53 (td, *J* = 7.5, 1.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 (dt, *J* = 7.6, 1.2 Hz, 1H), 3.24 (t, *J* = 7.1 Hz, 2H), 2.56 (t, *J* = 7.1 Hz, 2H), 0.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 142.9, 134.0, 133.7, 132.6, 131.8, 127.2, 105.9, 86.4, 31.4, 22.1, 0.11 ppm; HRMS (ESI+) calcd. for $C_{14}H_{19}OSi$ (M+H) 231.1200, found 231.1193.



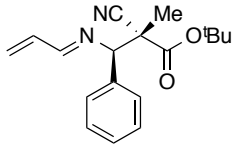
S22 **S23**

(*E*)-*N*-Allyl-1-(2-(4-(trimethylsilyl)but-3-yn-1-yl)phenyl)methanimine (S23): To a stirred solution of aldehyde **S22** (1.18 g, 5.12 mmol, 1.0 equiv.) in CH_2Cl_2 (6.0 mL) was added MgSO4 (500 mg) followed by allyl amine (0.42 mL, 322 mg, 5.63 mmol, 1.1 equiv.). After 24 h, the reaction was filtered through a sintered glass funnel. Solvent was removed *in vacuo* and kept under high vacuum for 3 h to give imine **S23** (1.38 g, 5.12 mmol, quant.) as colorless oil. The crude was sufficiently clean (>95% purity by NMR) and was directly used for oxidative C-H activation. IR: (neat) 2916, 2858, 2144, 1618, 1425, 1232, 1026, 979, 905, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.89 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.21-7.36 (m, 4H), 6.09 (ddt, *J* = 17.2, 10.3, 5.6 Hz, 1H), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.16 (dq, *J* = 10.3, 1.6 Hz, 1H), 4.28 (dq, *J* = 5.6, 1.5 Hz, 2H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 0.13 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 140.2, 136.1, 134.0, 130.6, 130.3, 128.3, 127.0, 116.0, 106.3, 85.8, 64.2, 31.8, 22.3, 0.21 ppm; HRMS (ESI+) calcd. for $C_{17}H_{24}NSi$ (M+H) 270.1673, found 270.1664.

General Method for Synthesis of β-Amino Ester via Oxidative C-H Activation:

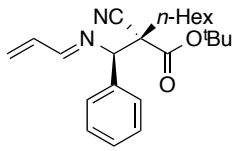


An oven dried Pyrex microwave vial was charged with $Pd(OAc)_2$ (0.03 equiv.), PPh_3 (0.06 equiv.), 2,6-dimethylbenzoquinone (1.1 equiv.) and was sealed with a rubber septa. The vial was evacuated and filled with nitrogen three times in an interval of 10 min. In a separate sealed nitrogen flushed vial, cyanoester (1.0 equiv.) and *N*-allyl imine (1.1 equiv.) were taken in freshly distilled THF. The solution was cannulated to the microwave vial with palladium catalyst. *N,N*-diisopropylethylamine (1.1 equiv.) was added to the resulting turbid solution and was allowed to stir at rt for 10-60 h depending on the substrates. Upon completion (monitored by crude NMR), the reaction was passed through a plug of silica gel (pre-neutralized with 2% Et_3N in Hexanes). Solvent was removed *in vacuo* and the residue was purified by flash chromatography over silica gel (pre-neutralized with 1% Et_3N in Hexanes), eluting with EtOAc / hexanes, to give β-amino-α-cyanoesters **3**-**24**.



3

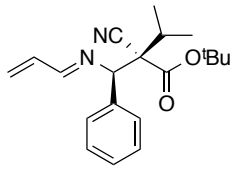
***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-phenylpropanoate (3):** The reaction was performed with *N*-allyl imine **1** (160 mg, 1.10 mmol), cyanoester **2** (155 mg, 1.00 mmol), $Pd(OAc)_2$ (6.7 mg, 0.030 mmol), PPh_3 (15.7 mg, 0.060 mmol) 2,6-dimethylbenzoquinone (150 mg, 1.10 mmol) and *N,N*-diisopropylethylamine (142 mg, 0.19 mL, 1.10 mmol) in THF (5.0 mL) for 12 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **3** (278 mg, 0.932 mmol, 93%) as white solid. Mp. 108-110 ºC; IR: (neat) 2940, 1710, 1622, 1435, 1351, 1261, 1240, 1140, 1108, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 1H), 7.49-7.52 (m, 2H), 7.31-7.39 (m, 3H), 6.58 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.81 (d, *J* = 10.2 Hz, 1H), 5.69 (dd, *J* = 17.4, 1.0 Hz, 1H), 4.47 (s, 1H), 1.47 (s, 9H), 1.41 (s, 3H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 167.9, 165.4, 137.3, 136.9, 128.9, 128.8, 128.7, 128.6, 119.0, 84.2, 78.6, 51.7, 27.9, 21.2 ppm; HRMS (ESI+) calcd. for $C_{18}H_{23}N_2O_2$ (M+H) 299.1754, found 299.1750.



4

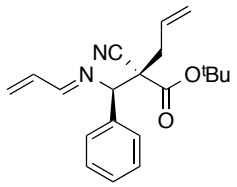
***t*-Butyl-2-(((*E*)-allylidene)amino)(phenyl)methyl)-2-cyanooctanoate (4):** The reaction was performed with *N*-allyl imine **1** (89.2 mg, 0.660 mmol), cyanoester **S1** (135 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 14 h. Purification by flash chromatography (5-

15% EtOAC / hexanes) gave product **4** (168 mg, 0.456 mmol, 76%) as colorless oil. IR: (neat) 2915, 2888, 2819, 1709, 1622, 1582, 1435, 1350, 1236, 1140, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.9, 0.3 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.39-7.31 (m, 3H), 6.57 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.79 (dt, *J* = 10.3, 0.9 Hz, 1H), 5.69-5.65 (m, 1H), 4.44 (s, 1H), 1.83 (td, *J* = 12.4, 3.3 Hz, 1H), 1.49-1.55 (m, 1H), 1.47 (s, 9H), 1.38 (td, *J* = 12.3, 4.1 Hz, 1H), 1.26-1.18 (m, 7H), 0.84 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.2, 137.5, 136.9, 129.0, 128.8, 128.7, 128.6, 118.4, 84.3, 79.2, 57.5, 35.2, 31.6, 29.1, 28.0, 27.9, 25.2, 22.5, 14.1 ppm; HRMS (ESI+) calcd. for $C_{23}H_{33}N_2O_2$ (M+H) 369.2537, found 369.2527.



5

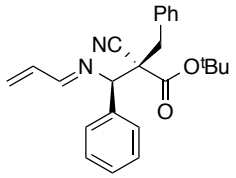
***t*-Butyl-2-(((*E*)-allylidene)amino)(phenyl)methyl)-2-cyano-3-methylbutanoate (5):** The reaction was performed with *N*-allyl imine **1** (95.9 mg, 0.660 mmol), cyanoester **S2** (110 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 18 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **5** (165 mg, 0.505 mmol, 84%) as colorless oil. IR: (neat) 2936, 2895, 1708, 1621, 1582, 1435, 1374, 1350, 1232, 1139, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.9, 0.5 Hz, 1H), 7.57-7.59 (m, 2H), 7.32-7.38 (m, 3H), 6.56 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.78 (dt, *J* = 10.3, 0.9 Hz, 1H), 5.66 (dd, *J* = 17.4, 1.1 Hz, 1H), 4.70 (s, 1H), 1.99 (quintet, *J* = 6.8 Hz, 1H), 1.45 (s, 9H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.3, 137.9, 137.0, 128.9, 128.7, 128.5, 118.6, 84.1, 75.9, 61.3, 32.5, 28.0, 19.3, 18.3 ppm; HRMS (ESI+) calcd. for $C_{20}H_{27}N_2O_2$ (M+H) 327.2067, found 327.2067.



6

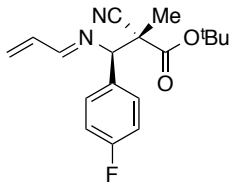
***t*-Butyl-2-(((*E*)-allylidene)amino)(phenyl)methyl)-2-cyanopent-4-enoate (6):** The reaction was performed with *N*-allyl imine **1** (95.9 mg, 0.660 mmol), cyanoester **S4** (109 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 14 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **6** (177 mg, 0.545 mmol, 91%) as colorless oil. IR: (neat) 2939, 1711, 1621, 1581, 1350, 1293, 1241, 1218, 1132, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.9, 0.4 Hz, 1H), 7.52-7.54 (m, 2H), 7.34-7.40 (m, 3H), 6.58 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.80 (dt, *J* = 10.3, 0.8 Hz, 1H), 5.70-5.80 (m, 1H), 5.66-5.70 (m, 1H), 5.16-5.18 (m, 1H), 5.13 (dq, *J* = 4.0, 1.2 Hz, 1H), 4.48 (s, 1H), 2.56 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.18 (ddt, *J* = 13.6, 6.2, 1.3 Hz, 1H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.4, 137.3, 137.0, 130.7, 129.1, 129.03, 128.99, 128.8,

120.7, 118.0, 84.6, 78.8, 57.1, 39.6, 28.1 ppm; HRMS (ESI+) calcd. for $C_{20}H_{25}N_2O_2$ (M+H) 325.1911, found 325.1901.



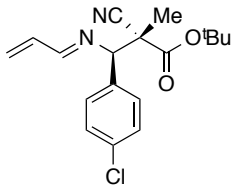
7

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-benzyl-2-cyano-3-phenylpropanoate (7):** The reaction was performed with *N*-allyl imine **1** (47.9 mg, 0.330 mmol), cyanoester **S3** (109 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.009 mmol), PPh_3 (4.7 mg, 0.018 mmol) 2,6-dimethylbenzoquinone (44.9 mg, 0.330 mmol) and *N,N*-diisopropylethylamine (42.7 mg, 58.0 μL, 0.660 mmol) in THF (1.5 mL) for 12 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **7** (103 mg, 0.275 mmol, 92%) as colorless oil. IR: (neat) 2990, 2938, 2892, 1703, 1621, 1581, 1434, 1349, 1242, 1138, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.9, 0.5 Hz, 1H), 7.61-7.65 (m, 2H), 7.38-7.45 (m, 3H), 7.21-7.24 (m, 5H), 6.58 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.80 (ddd, *J* = 10.2, 1.1, 0.7 Hz, 1H), 5.68 (ddd, *J* = 17.4, 1.2, 0.4 Hz, 1H), 4.63 (s, 1H), 3.11 (d, *J* = 13.3 Hz, 1H), 2.65 (d, *J* = 13.3 Hz, 1H), 1.22 (s, 9H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.8, 165.4, 137.3, 136.9, 134.0, 130.3, 129.1, 128.9, 128.7, 128.4, 127.7, 118.2, 84.3, 79.5, 58.6, 40.9, 27.7 ppm; HRMS (ESI+) calcd. for $C_{24}H_{26}N_2O_2Na$ (M+Na) 397.1886, found 397.1875.



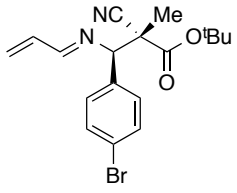
8

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-3-(4-fluorophenyl)-2-methylpropanoate (8):** The reaction was performed with *N*-allyl imine **S5** (108 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 12 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **8** (162 mg, 0.512 mmol, 85%) as white solid. Mp. 85-86 ºC; IR: (neat) 2941, 1711, 1621, 1582, 1488, 1352, 1263, 1239, 1142, 1108 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.85 (d, *J* = 8.9 Hz, 1H), 7.47-7.52 (m, 2H), 7.03-7.09 (m, 2H), 6.56 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.82 (dt, *J* = 10.2, 0.8 Hz, 1H), 5.68-5.72 (m, 1H), 4.45 (s, 1H), 1.46 (s, 9H), 1.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 165.5, 163.0 (d, *J* = 247.9 Hz), 136.8, 133.1 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 7.9 Hz), 129.1, 118.9, 115.5 (d, *J* = 21.3 Hz), 84.4, 77.8, 51.7 (d, *J* = 1.3 Hz), 27.9, 21.2 ppm; HRMS (ESI+) calcd. for $C_{18}H_{22}FN_2O_2$ (M+H) 317.1660, found 317.1651.



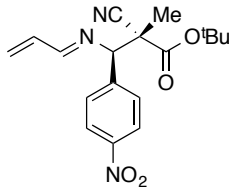
9

***t*-Butyl-3-(((*E*)-allylidene)amino)-3-(4-chlorophenyl)-2-cyano-2-methylpropanoate (9):** The reaction was performed with *N*-allyl imine **S6** (119 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 10 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **9** (186 mg, 0.558 mmol, 93%) as white solid. Mp. 86-88 ºC; IR: (neat) 2940, 2896, 1711, 1622, 1470, 1351, 1260, 1142, 1108, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.9, 0.3 Hz, 1H), 7.43-7.47 (m, 2H), 7.31-7.34 (m, 2H), 6.55 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.82 (dt, *J* = 10.3, 0.8 Hz, 1H), 5.70 (ddd, *J* = 17.4, 1.0, 0.4 Hz, 1H), 4.43 (s, 1H), 1.45 (s, 9H), 1.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 165.6, 136.6, 135.8, 134.6, 130.2, 129.2, 128.7, 118.7, 84.4, 77.7, 51.5, 27.8, 21.1 ppm; HRMS (ESI+) calcd. for $C_{18}H_{22}ClN_2O_2$ (M+H) 333.1364, found 333.1363.



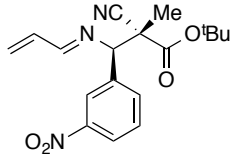
10

***t*-Butyl-3-(((*E*)-allylidene)amino)-3-(4-bromophenyl)-2-cyano-2-methylpropanoate (10):** The reaction was performed with *N*-allyl imine **S7** (148 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 12 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **10** (170 mg, 0.451 mmol, 75%) as colorless oil. IR: (neat) 2939, 1711, 1622, 1581, 1465, 1351, 1259, 1142, 1108, 996 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.48-7.51 (m, 2H), 7.38-7.41 (m, 2H), 6.55 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.82 (d, *J* = 10 Hz, 1H), 5.70 (dd, *J* = 17.4, 1.1 Hz, 1H), 4.42 (s, 1H), 1.46 (s, 9H), 1.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 165.6, 136.7, 136.3, 131.7, 130.5, 129.3, 122.9, 118.7, 84.4, 77.8, 51.5, 27.9, 21.2 ppm; HRMS (ESI+) calcd. for $C_{18}H_{21}BrN_2O_2Na$ (M+Na) 399.0679, found 399.0672.



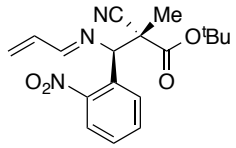
11

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(4-nitrophenyl)propanoate (11):** The reaction was performed with *N*-allyl imine **S8** (126 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 10 h. Purification by flash chromatography (10-25% EtOAC / hexanes) gave product **11** (178 mg, 0.518 mmol, 86%) as white solid. Mp. 122-125 ºC; IR: (neat) 2940, 1711, 1622, 1581, 1502, 1330, 1263, 1143, 1109, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21-8.24 (m, 2H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.70-7.74 (m, 2H), 6.57 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.87 (dt, *J* = 10.2, 0.8 Hz, 1H), 5.75 (ddd, *J* = 17.4, 1.0, 0.4 Hz, 1H), 4.56 (s, 1H), 1.47 (s, 9H), 1.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.3, 148.2, 144.4, 136.5, 130.0, 129.9, 123.7, 118.3, 84.9, 77.7, 51.4, 27.9, 21.2 ppm; HRMS (ESI+) calcd. for $C_{18}H_{21}N_3O_4Na$ (M+Na) 366.1424, found 366.1413.



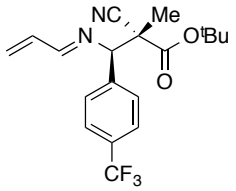
12

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(3-nitrophenyl)propanoate (12):** The reaction was performed with *N*-allyl imine **S9** (126 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 12 h. Purification by flash chromatography (10-25% EtOAC / hexanes) gave product **12** (171 mg, 0.498 mmol, 83%) as white solid. Mp. 111-113 ºC; IR: (neat) 3048, 2941, 2832, 1710, 1622, 1509, 1331, 1263, 1141, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 2.2, 1.8 Hz, 1H), 8.20 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.96-7.99 (m, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.58 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.87 (dt, *J* = 10.3, 0.8 Hz, 1H), 5.73-5.78 (m, 1H), 4.57 (s, 1H), 1.47 (s, 9H), 1.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.4, 148.0, 139.4, 136.5, 135.0, 130.0, 129.7, 123.9, 123.7, 118.4, 84.8, 77.6, 51.5, 27.9, 21.0 ppm; HRMS (ESI+) calcd. for $C_{18}H_{22}N_3O_4$ (M+H) 344.1605, found 344.1601.



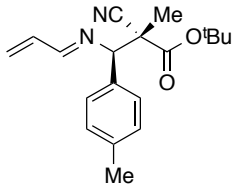
13

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(2-nitrophenyl)propanoate (13):** The reaction was performed with *N*-allyl imine **S10** (126 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 12 h. Purification by flash chromatography (10-25% EtOAC / hexanes) gave product **13** (194 mg, 0.564 mmol, 94%) as white solid. Mp. 84-86 ºC; IR: (neat) 2940, 1713, 1620, 1509, 1434, 1349, 1260, 1143, 1108, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.68 (td, *J* = 7.7, 1.4 Hz, 1H), 7.48 (ddd, *J* = 8.1, 7.4, 1.4 Hz, 1H), 6.55 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.87 (dt, *J* = 10.3, 0.8 Hz, 1H), 5.77 (dd, *J* = 17.4, 0.6 Hz, 1H), 5.40 (s, 1H), 1.46 (s, 9H), 1.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.03, 167.00, 150.0, 136.6, 133.2, 131.4, 131.3, 130.0, 129.3, 124.1, 118.8, 84.7, 70.0, 52.3, 20.9 ppm; HRMS (ESI+) calcd. for $C_{18}H_{22}N_3O_4$ (M+H) 344.1605, found 344.1596.



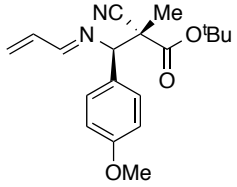
14

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(4-(trifluoromethyl)phenyl)-propanoate (14):** The reaction was performed with *N*-allyl imine **S11** (141 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 18 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **14** (174 mg, 0.474 mmol, 79%) as colorless oil. IR: (neat) 2940, 1710, 1618, 1505, 1440, 1348, 1262, 1145, 1110, 827 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.9, 0.4 Hz, 1H), 7.62-7.67 (m, 4H), 6.57 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.85 (dt, *J* = 10.3, 0.9 Hz, 1H), 5.72 (ddd, *J* = 17.4, 1.0, 0.4 Hz, 1H), 4.52 (s, 1H), 1.47 (s, 9H), 1.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166.0, 141.3, 136.6, 130.9 (q, *J* = 32.2 Hz), 129.5, 129.4, 125.5 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 271 Hz), 118.6, 84.6, 78.0, 51.5, 27.9, 21.2 ppm.



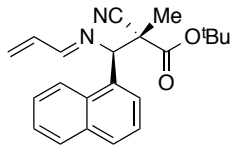
15

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(*p*-tolyl)propanoate (15):** The reaction was performed with *N*-allyl imine **S12** (105 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 14 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **15** (178 mg, 0.570 mmol, 95%) as white solid. Mp. 102-104 ºC; IR: (neat) 2939, 2897, 1711, 1621, 1435, 1351, 1262, 1142, 1108, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.9, 0.5 Hz, 1H), 7.38-7.41 (m, 2H), 7.16-7.18 (m, 2H), 6.57 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.79 (dt, *J* = 10.2, 0.9 Hz, 1H), 5.67 (ddd, *J* = 17.4, 1.1, 0.4 Hz, 1H), 4.43 (s, 1H), 2.34 (s, 3H), 1.47 (s, 9H), 1.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 165.2, 138.6, 137.0, 134.3, 129.3, 128.8, 128.7, 119.1, 84.2, 78.4, 51.7, 27.9, 21.3, 21.2 ppm; HRMS (ESI+) calcd. for $C_{19}H_{25}N_2O_2$ (M+H) 313.1911, found 313.1906.



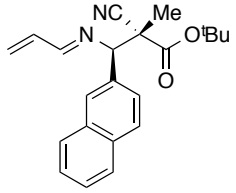
16

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-3-(4-methoxyphenyl)-2-methylpropanoate (16):** The reaction was performed with *N*-allyl imine **S13** (116 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 16 h. Purification by flash chromatography (10-20% EtOAC / hexanes) gave product **16** (176 mg, 0.536 mmol, 89%) as white solid. Mp. 73-75 ºC; IR: (neat) 2939, 2896, 1710, 1584, 1491, 1351, 1235, 1144, 1108, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.41-7.45 (m, 2H), 6.88-6.91 (m, 2H), 6.57 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.79 (dt, *J* = 10.3, 0.8 Hz, 1H), 5.65-5.70 (m, 1H), 4.42 (s, 1H), 3.80 (s, 3H), 1.47 (s, 9H), 1.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 165.1, 159.9, 136.9, 130.0, 129.4, 128.7, 119.2, 113.9, 84.1, 78.1, 55.4, 51.8, 27.9, 21.2 ppm; HRMS (ESI+) calcd. for $C_{19}H_{24}N_2O_3Na$ (M+Na) 351.1679, found 351.1675.



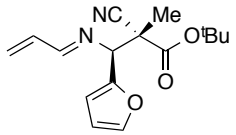
17

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(naphthalen-1-yl)propanoate (17):** The reaction was performed with *N*-allyl imine **S14** (129 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 16 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **17** (189 mg, 0.542 mmol, 90%) as white solid. Mp. 114-116 ºC; IR: (neat) 3012, 2939, 1709, 1621, 1580, 1434, 1351, 1258, 1144, 1108 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 19.8, 7.9 Hz, 2H), 7.93 (dd, *J* = 8.9, 0.4 Hz, 1H), 7.84-7.89 (m, 2H), 7.50-7.59 (m, 3H), 6.60 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.80 ((dt, *J* = 10.2, 0.8 Hz, 1H)), 5.64-5.68 (m, 1H), 5.57 (s, 1H), 1.51 (s, 9H), 1.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 165.3, 137.0, 133.8, 133.5, 132.1, 129.5, 129.0, 128.9, 127.9, 126.6, 126.0, 125.7, 122.7, 119.3, 84.5, 71.3, 53.3, 28.0, 21.8 ppm; HRMS (ESI+) calcd. for $C_{22}H_{25}N_2O_2$ (M+H) 349.1911, found 349.1903.



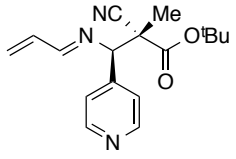
18

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(naphthalen-2-yl)propanoate (18):** The reaction was performed with *N*-allyl imine **S15** (129 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 14 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **18** (171 mg, 0.491 mmol, 82%) as white solid. Mp. 96-98 ºC; IR: (neat) 3014, 2939, 2896, 1710, 1620, 1582, 1351, 1241, 1142, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.92 (d, *J* = 11.2 Hz, 1H), 7.82-7.89 (m, 3H), 7.70 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.47-7.51 (m, 2H), 6.62 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.82 (d, *J* = 10.2 Hz, 1H), 5.70 (dd, *J* = 17.4, 0.9 Hz, 1H), 4.66 (s, 1H), 1.50 (s, 9H), 1.46 (s, 3H) ppm; ^{13}C NMR (176 MHz, $CDCl_3$) δ 168.0, 165.6, 136.9, 134.8, 133.5, 133.1, 129.0, 128.35, 128.34, 128.28, 127.8, 126.5, 126.4, 126.3, 119.1, 84.3, 78.7, 51.7, 27.9, 21.3 ppm; HRMS (ESI+) calcd. for $C_{22}H_{25}N_2O_2$ (M+H) 349.1911, found 349.1908.



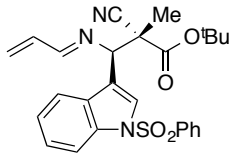
19

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-3-(furan-2-yl)-2-methylpropanoate (19):** The reaction was performed with *N*-allyl imine **S16** (89.2 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 18 h. Purification by flash chromatography (10-20% EtOAC / hexanes) gave product **19** (151 mg, 0.524 mmol, 87%) as colorless oil. IR: (neat) 2940, 1711, 1624, 1583, 1352, 1259, 1142, 1107, 992, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.9, 0.6 Hz, 1H), 7.42 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.56 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 6.49 (dt, *J* = 3.3, 0.7 Hz, 1H), 6.38-6.39 (m, 1H), 5.84 (dt, *J* = 10.2, 0.9 Hz, 1H), 5.73 (ddd, *J* = 17.4, 1.1, 0.4 Hz, 1H), 4.75 (s, 1H), 1.51 (s, 3H), 1.47 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.4, 150.3, 142.8, 136.7, 129.5, 119.0, 110.8, 109.7, 84.4, 71.8, 50.9, 27.9, 20.4 ppm; HRMS (ESI+) calcd. for $C_{16}H_{21}N_2O_3$ (M+H) 289.1547, found 289.1546.



20

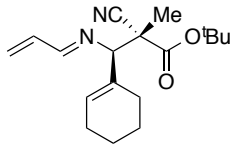
***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(pyridin-4-yl)propanoate (20):** The reaction was performed with *N*-allyl imine **S17** (96.5 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 16 h. Purification by flash chromatography (40-80% EtOAC / hexanes) gave product **20** (154 mg, 0.514 mmol, 86%) as white solid. Mp. 133-135 ºC; IR: (neat) 2940, 1711, 1621, 1578, 1393, 1351, 1243, 1143, 1109, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.43 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.56 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.86 (dt, *J* = 10.3, 0.8 Hz, 1H), 5.73 (dd, *J* = 17.4, 1.0 Hz, 1H), 4.42 (s, 1H), 1.46 (s, 9H), 1.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.3, 150.1, 145.8, 136.5, 129.8, 123.8, 118.3, 84.8, 77.4, 51.2, 27.9, 21.1 ppm; HRMS (ESI+) calcd. for $C_{17}H_{22}N_3O_2$ (M+H) 300.1707, found 300.1708.



21

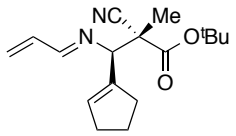
***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-2-methyl-3-(1-(phenylsulfonyl)-1*H*-indol-3-yl)propanoate (21):** The reaction was performed with *N*-allyl imine **S18** (214 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-

diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 15 h. Purification by flash chromatography (20-40% EtOAC / hexanes) gave product **21** (232 mg, 0.486 mmol, 81%) as white gum. IR: (neat) 2940, 1711, 1622, 1581, 1427, 1352, 1262, 1162, 1104, 828 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.91-7.94 (m, 2H), 7.89 (s, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.66 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.50-7.54 (m, 1H), 7.41-7.45 (m, 2H), 7.33 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.23-7.27 (m, 1H), 6.58 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.83 (d, *J* = 10.3 Hz, 1H), 5.68 (dd, *J* = 17.4, 0.7 Hz, 1H), 4.84 (s, 1H), 1.47 (s, 9H), 1.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 165.5, 137.8, 136.6, 134.7, 134.0, 130.0 129.4, 129.3, 127.1, 126.1, 125.2, 123.6, 120.2, 119.3, 119.2, 114.0, 84.4, 70.7, 52.6, 27.9, 21.4 ppm; HRMS (ESI+) calcd. for $C_{26}H_{27}N_3O_4SNa$ (M+Na) 500.1614, found 500.1606.



22

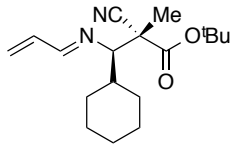
***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-3-(cyclohex-1-en-1-yl)-2-methylpropanoate (22):** The reaction was performed with *N*-allyl imine **S19** (98.5 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 18 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **22** (137 mg, 0.453 mmol, 75%) as white solid. Mp. 93-95 ºC; IR: (neat) 2939, 2892, 1711, 1620, 1433, 1352, 1240, 1144, 1102, 828 cm^{-1}; ^1H-NMR (400 MHz; $CDCl_3$): δ 7.79 (dd, *J* = 8.9, 0.5 Hz, 1H), 6.55 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.80 (dt, *J* = 10.2, 0.9 Hz, 1H), 5.75-5.77 (m, 1H), 5.67-5.71 (m, 1H), 3.79 (s, 1H), 2.14-2.33 (m, 2H), 2.04-2.07 (m, 2H), 1.52-1.73 (m, 4H), 1.50 (s, 3H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 164.5, 137.1, 135.1, 129.1, 128.3, 120.2, 83.9, 81.4, 49.1, 27.9, 25.7, 25.5, 22.7, 22.4, 21.3 ppm; HRMS (ESI+) calcd. for $C_{18}H_{26}N_2O_2Na$ (M+Na) 325.1886, found 325.1885.



23

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-3-(cyclopent-1-en-1-yl)-2-methylpropanoate (23):** The reaction was performed with *N*-allyl imine **S20** (89.3 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 17 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **23** (152 mg, 0.527 mmol, 88%) as colorless oil. IR: (neat) 2938, 1711, 1622, 1582, 1434, 1351, 1257, 1144, 1103, 929 cm^{-1}; ^1H-NMR (400 MHz; $CDCl_3$): δ 7.79 (dd, *J* = 8.9, 0.6 Hz, 1H), 6.55 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.78-5.81 (m, 2H), 5.69 (ddd, *J* = 17.4, 0.8, 0.4 Hz, 1H), 4.16 (s, 1H), 2.54-2.63 (m, 1H), 2.36-2.44 (m, *J* = 9.3 Hz, 1H), 2.30-2.36 (m, 2H), 1.78-1.96 (m, 2H), 1.51 (s, 3H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

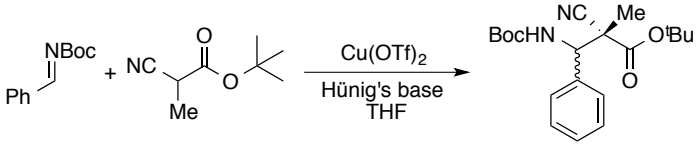
168.0, 164.8, 140.4, 137.0, 131.9, 128.5, 120.0, 84.0, 75.6, 49.3, 32.4, 31.9, 27.9, 23.5, 21.0 ppm; HRMS (ESI+) calcd. for $C_{17}H_{25}N_2O_2$ (M+H) 289.1911, found 289.1909.



24

***t*-Butyl-3-(((*E*)-allylidene)amino)-2-cyano-3-cyclohexyl-2-methylpropanoate (24):** The reaction was performed with *N*-allyl imine **S21** (99.8 mg, 0.660 mmol), cyanoester **2** (93.2 mg, 0.600 mmol), $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol) 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 60 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **24** (102 mg, 0.335 mmol, 56%) as white solid. Mp. 93-95 ºC; IR: (neat) 2886, 2813, 1705, 1623, 1581, 1429, 1350, 1240, 1142, 942 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 1H), 6.54 (ddd, *J* = 17.4, 10.2, 8.9 Hz, 1H), 5.81 (ddd, *J* = 10.2, 1.0, 0.8 Hz, 1H), 5.69-5.73 (m, 1H), 3.10 (d, *J* = 4.1 Hz, 1H), 2.00-2.04 (m, 1H), 1.70-1.81 (m, 3H), 1.59 (s, 3H), 1.49-1.53 (m, 1H), 1.43 (s, 9H), 1.14-1.33 (m, 2H), 0.95-1.12 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 165.0, 136.7, 128.5, 120.1, 83.9, 79.6, 49.0, 39.2, 32.1, 28.2, 27.8, 26.5, 26.3, 26.1, 20.3 ppm; HRMS (ESI+) calcd. for $C_{18}H_{29}N_2O_2$ (M+H) 305.2224, found 305.2222.

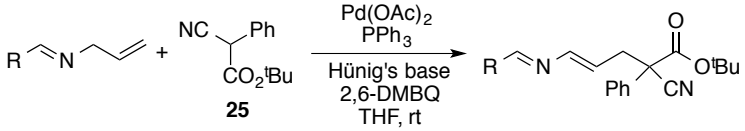
Test of Diastereoselectivity for Imine addition by Lewis Acid Activation:



2 **S24**

***t*-Butyl 3-((*t*-butoxycarbonyl)amino)-2-cyano-2-methyl-3-phenylpropanoate (S24):** To a stirred solution of *N*-boc phenyl imine (67.8 mg, 0.330 mmol, 1.1 equiv.) and cyanoester **2** (46.6 mg, 0.300 mmol, 1.0 equiv.) in THF (1.5 mL) was added $Cu(OTf)_2$ (10.9 mg,0.030 mmol, 0.10 equiv.) followed by *N,N*-diisopropylethylamine (58 μL, 42.6 mg, 0.330 mmol, 1.1 equiv.). After 2.5 h, the reaction was quenched with satd. aq. $NaHCO_3$ (5 mL) and the aqueous layer was extracted with Et_2O (2 X 10 mL). The dried extract ($MgSO_4$) was concentrated *in vacuo* and was purified by flash chromatography over silica gel, eluting with 10-20% EtOAC / hexanes to give coupled adduct **S24** (72.1 mg, 0.200 mmol, 67%) as colorless oil in 1:1 dr.

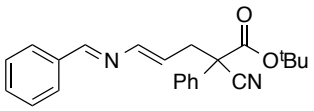
General Method for Synthesis of 2-Aza Diene via Oxidative C-H Activation:



25

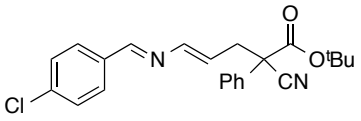
An oven dried Pyrex microwave vial was charged with $Pd(OAc)_2$ (0.05 equiv.), PPh_3 (0.10 equiv.), 2,6-dimethylbenzoquinone (1.1 equiv.) and was sealed with a rubber

septa. The vial was evacuated and filled with nitrogen three times in an interval of 10 min. In a separate sealed nitrogen flushed vial, cyanoester **25** (1.0 equiv.) and *N*-allyl imine (1.1 equiv.) were taken in freshly distilled THF. The solution was cannulated to the microwave vial with palladium catalyst. *N,N*-diisopropylethylamine (1.1 equiv.) was added to the resulting turbid solution and was allowed to stir at rt for 48-65 h depending on the substrates. Upon completion (monitored by crude NMR), the reaction was passed through a plug of silica gel (pre-neutralized with 2% Et_3N in Hexanes). Solvent was removed *in vacuo* and the residue was purified by flash chromatography over silica gel (pre-neutralized with 1% Et_3N in Hexanes), eluting with EtOAc / hexanes, to give 2-aza-dienes **26**-**31**.



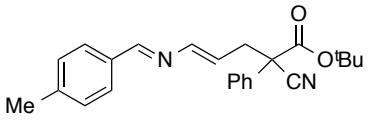
26

***t*-Butyl-(*E*)-5-(((*E*)-benzylidene)amino)-2-cyano-2-phenylpent-4-enoate (26):** The reaction was performed with *N*-allyl imine **1** (145 mg, 1.10 mmol), cyanoester **25** (217 mg, 1.00 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), PPh_3 (26.2 mg, 0.100 mmol), 2,6-dimethylbenzoquinone (150 mg, 1.10 mmol) and *N,N*-diisopropylethylamine (142 mg, 0.19 mL, 1.10 mmol) in THF (5.0 mL) for 52 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **26** (175 mg, 0.485 mmol, 81%) as colorless oil. IR: (neat) 2937, 2892, 1712, 1578, 1550, 1429, 1351, 1236, 1136, 826 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.21 (s, 1H), 7.76-7.78 (m, 2H), 7.56-7.58 (m, 2H), 7.35-7.44 (m, 6H), 6.97 (d, *J* = 12.9 Hz, 1H), 6.04 (dt, *J* = 12.9, 7.8 Hz, 1H), 3.20 (ddd, *J* = 14.1, 8.2, 1.0 Hz, 1H), 2.94 (ddd, *J* = 14.1, 7.5, 1.1 Hz, 1H), 1.43 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.0, 147.4, 135.9, 134.6, 131.4, 129.2, 128.9, 128.81, 128.79, 126.2, 123.8, 118.4, 84.7, 55.3, 39.2, 27.7 ppm; HRMS (ESI+) calcd. for $C_{23}H_{25}N_2O_2$ (M+H) 361.1911, found 361.1906.



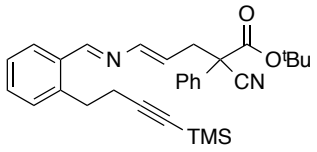
27

***t*-Butyl-(*E*)-5-(((*E*)-4-chlorobenzylidene)amino)-2-cyano-2-phenylpent-4-enoate (27):** The reaction was performed with *N*-allyl imine **S6** (119 mg, 0.660 mmol), cyanoester **25** (130 mg, 0.600 mmol), $Pd(OAc)_2$ (6.7 mg, 0.030 mmol), PPh_3 (15.7 mg, 0.060 mmol), 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N,N*-diisopropylethylamine (85.3 mg, 115 μL, 0.660 mmol) in THF (3.0 mL) for 48 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **27** (199 mg, 0.504 mmol, 84%) as colorless oil. IR: (neat) 2939, 2893, 1713, 1568, 1469, 1351, 1237, 1136, 1073, 825 cm^{-1}; 1H-NMR (400 MHz; CDCl3): δ 8.15 (s, 1H), 7.68-7.72 (m, 2H), 7.55-7.57 (m, 2H), 7.35-7.44 (m, 5H), 6.95 (d, *J* = 12.9 Hz, 1H), 6.04 (dt, *J* = 12.9, 7.8 Hz, 1H), 3.20 (ddd, *J* = 14.1, 8.1, 1.0 Hz, 1H), 2.93 (ddd, *J* = 14.1, 7.6, 1.1 Hz, 1H), 1.43 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 160.4, 147.1, 137.3, 134.5, 134.4, 129.9, 129.2, 129.1, 128.9, 126.1, 124.5, 118.4, 84.7, 55.2, 39.1, 27.7 ppm; HRMS (ESI+) calcd. for $C_{23}H_{24}ClN_2O_2$ (M+H) 395.1521, found 395.1515.



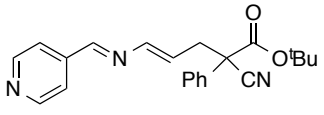
28

***t*-Butyl-(*E*)-2-cyano-5-(((*E*)-4-methylbenzylidene)amino)-2-phenylpent-4-enoate (28):** The reaction was performed with *N*-allyl imine **S12** (105 mg, 0.660 mmol), cyanoester **25** (130 mg, 0.600 mmol), $Pd(OAc)_2$ (6.7 mg, 0.030 mmol), PPh_3 (15.7 mg, 0.060 mmol), 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 μL, 0.660 mmol) in THF (3.0 mL) for 55 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **28** (201 mg, 0.537 mmol, 89%) as colorless oil. IR: (neat) 2938, 2890, 1712, 1573, 1543, 1351, 1236, 1136, 825 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$): δ 8.17 (s, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.56-7.58 (m, 2H), 7.35-7.44 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 13.0 Hz, 1H), 6.01 (dt, *J* = 13.0, 7.8 Hz, 1H), 3.20 (ddd, *J* = 14.1, 8.2, 0.9 Hz, 1H), 2.93 (ddd, *J* = 14.1, 7.5, 1.1 Hz, 1H), 2.38 (s, 3H), 1.43 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.0, 147.6, 141.9, 134.6, 133.3, 129.6, 129.2, 128.9, 128.8, 126.2, 123.1, 118.5, 84.6, 55.3, 39.2, 27.7, 21.7 ppm; HRMS (ESI+) calcd. for $C_{24}H_{27}N_2O_2$ (M+H) 375.2067, found 375.2062.



29

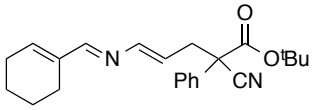
***t*-Butyl-(*E*)-2-cyano-2-phenyl-5-(((*E*)-2-(4-(trimethylsilyl)but-3-yn-1-yl)benzylidene)amino)pent-4-enoate (29):** The reaction was performed with *N*-allyl imine **S23** (178 mg, 0.660 mmol), cyanoester **25** (130 mg, 0.600 mmol), $Pd(OAc)_2$ (6.7 mg, 0.030 mmol), PPh_3 (15.7 mg, 0.060 mmol), 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 mL, 0.660 mmol) in THF (3.0 mL) for 60 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **29** (219 mg, 0.452 mmol, 75%) as colorless oil. IR: (neat) 2918, 2861, 2143, 1713, 1564, 1429, 1351, 1234, 1136, 829 cm^{-1}; ^1H-NMR (400 MHz; $CDCl_3$): δ 8.51 (s, 1H), 7.96 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.56-7.58 (m, 2H), 7.36-7.45 (m, 3H), 7.34 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.22-7.29 (m, 2H), 6.99 (d, *J* = 12.9 Hz, 1H), 6.04 (dt, *J* = 12.9, 7.8 Hz, 1H), 3.20 (ddd, *J* = 14.1, 8.1, 0.9 Hz, 1H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.94 (ddd, *J* = 14.1, 7.6, 1.1 Hz, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 1.44 (s, 9H), 0.12 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.0, 147.9, 141.0, 134.6, 133.6, 131.0, 130.7, 129.2, 128.9, 128.4, 127.0, 126.2, 123.9, 118.5, 106.0, 86.0, 84.7, 55.3, 39.3, 31.8, 27.8, 22.4, 0.19 ppm; HRMS (ESI+) calcd. for $C_{30}H_{37}N_2O_2Si$ (M+H) 485.2619, found 485.2604.



30

***t*-Butyl-(*E*)-2-cyano-2-phenyl-5-(((*E*)-pyridin-4-ylmethylene)amino)pent-4-enoate (30):** The reaction was performed with *N*-allyl imine **S17** (96.5 mg, 0.660 mmol),

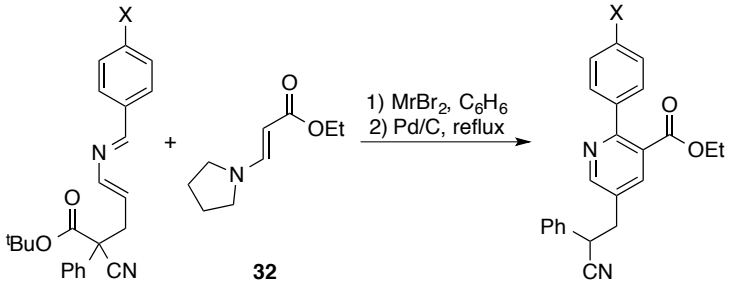
cyanoester **25** (130 mg, 0.600 mmol), $Pd(OAc)_2$ (6.7 mg, 0.030 mmol), PPh_3 (15.8 mg, 0.060 mmol), 2,6-dimethylbenzoquinone (89.8 mg, 0.660 mmol) and *N*,*N*-diisopropylethylamine (85.4 mg, 116 mL, 0.660 mmol) in THF (3.0 mL) for 54 h. Purification by flash chromatography (40-80% EtOAC / hexanes) gave product **30** (155 mg, 0.429 mmol, 71%) as colorless oil. IR: (neat) 2938, 2893, 1713, 1576, 1430, 1393, 1351, 1237, 1136, 964 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.68 (dd, *J* = 6.4, 2.8 Hz, 2H), 8.15 (s, 1H), 7.61 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.54-7.56 (m, 2H), 7.35-7.44 (m, 3H), 6.99 (d, *J* = 12.8 Hz, 1H), 6.15 (dt, *J* = 12.9, 7.7 Hz, 1H), 3.21 (ddd, *J* = 14.1, 8.1, 1.0 Hz, 1H), 2.95 (ddd, *J* = 14.1, 7.6, 1.1 Hz, 1H), 1.42 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 159.4, 150.6, 146.7, 142.7, 134.4, 129.3, 129.0, 127.2, 126.1, 122.2, 118.3, 84.8, 55.1, 39.1, 27.7 ppm; HRMS (ESI+) calcd. for $C_{22}H_{24}N_3O_2$ (M+H) 362.1863, found 362.1865.



31

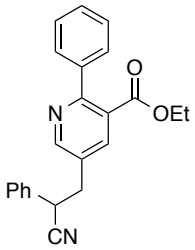
***t*-Butyl-(*E*)-2-cyano-5-(((*E*)-cyclohex-1-en-1-ylmethylene)amino)-2-phenylpent-4-enoate (31):** The reaction was performed with *N*-allyl imine **S19** (164 mg, 1.10 mmol), cyanoester **25** (217 mg, 1.00 mmol), $Pd(OAc)_2$ (11.3 mg, 0.050 mmol), PPh_3 (26.3 mg, 0.100 mmol), 2,6-dimethylbenzoquinone (150 mg, 1.10 mmol) and *N*,*N*-diisopropylethylamine (142 mg, 0.19 mL, 1.10 mmol) in THF (5.0 mL) for 65 h. Purification by flash chromatography (5-15% EtOAC / hexanes) gave product **31** (283 mg, 0.776 mmol, 78%) as colorless oil. IR: (neat) 2937, 2890, 2819, 1713, 1562, 1429, 1351, 1236, 1136, 827 cm^{-1}; ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.73 (s, 1H), 7.53-7.55 (m, 2H), 7.33-7.42 (m, 3H), 6.78 (d, *J* = 13.0 Hz, 1H), 6.25-6.27 (m, 1H), 5.86 (dt, *J* = 13.0, 7.8 Hz, 1H), 3.13 (ddd, *J* = 14.1, 8.1, 0.9 Hz, 1H), 2.88 (ddd, *J* = 14.1, 7.5, 1.0 Hz, 1H), 2.28-2.30 (m, 2H), 2.22-2.24 (m, 2H), 1.64 (dt, *J* = 6.2, 3.0 Hz, 4H), 1.41 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.7, 148.0, 142.0, 138.3, 134.6, 129.1, 128.8, 126.2, 121.7, 118.5, 84.5, 55.3, 39.2, 27.7, 26.6, 23.7, 22.4, 22.0 ppm; HRMS (ESI+) calcd. for $C_{23}H_{29}N_2O_2$ (M+H) 365.2224, found 365.2220.

General Method for Synthesis of Pyridine Derivatives:



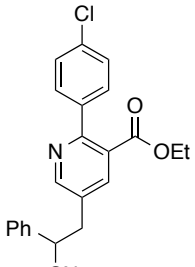
An oven dried round bottom flask was charged with 2-aza-diene (1.0 equiv.), enamine ester **32**[15] (2.0 equiv.), $MgBr_2$ (1.2 equiv.), and 4 Å mol. sieves. The flask was evacuated and filled with argon (X 3). Toluene was added to the mixture and warmed to 60 ºC. After 24 h, Pd/C (5 wt. %) was added and heated to reflux. After 10 h, the reaction was cooled down to rt. The reaction mixture was directly loaded onto column and purified by flash

chromatography over silica gel, eluting with 20-40% EtOAc / hexanes, to give hetero biaryl systems **33** and **34**.



33

Ethyl 5-(2-cyano-2-phenylethyl)-2-phenylnicotinate (33): The first step was performed with 2-aza-diene **26** (32.7 mg, 0.091 mmol, 1.0 equiv.), enamine ester **32** (30.7 mg, 0.181 mmol, 2.0 equiv.), $MgBr_2$ (40.1 mg, 0.219 mmol, 2.4 equiv.), and 4 Å mol. Sieves (50 mg) in toluene (1.0 mL). The second step was performed in the same pot by the addition of Pd/C (40 mg, 5 wt. %). Purification by flash chromatography (20-40% EtOAC / hexanes) gave product **33** (19.3 mg, 0.054 mmol, 59%) as colorless oil. IR: (neat) 3017, 2988, 2940, 1698, 1578, 1428, 1269, 1202, 1082, 1004 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$): δ 8.46 (d, *J* = 2.3 Hz, 1H), 7.85 (d, *J* = 2.3 Hz, 1H), 7.50-7.53 (m, 2H), 7.36-7.43 (m, 6H), 7.28-7.31 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 1H), 3.22-3.32 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 158.1, 151.8, 139.8, 138.6, 134.2, 129.8, 129.5, 128.8, 128.7, 128.3, 127.6, 127.1, 119.7, 61.8, 39.2, 38.7, 13.8 ppm; HRMS (ESI+) calcd. for $C_{23}H_{21}N_2O_2$ (M+H) 357.1598, found 357.1601.



34

Ethyl 2-(4-chlorophenyl)-5-(2-cyano-2-phenylethyl)nicotinate (34): The first step was performed with 2-aza-diene **27** (62.5 mg, 0.158 mmol, 1.0 equiv.), enamine ester **32** (53.6 mg, 0.316 mmol, 2.0 equiv.), $MgBr_2$ (70.0 mg, 0.380 mmol, 2.4 equiv.), and 4 Å mol. Sieves (100 mg) in toluene (1.7 mL). The second step was performed in the same pot by the addition of Pd/C (69.5 mg, 5 wt. %). Purification by flash chromatography (20-40% EtOAC / hexanes) gave product **34** (31.5 mg, 0.081 mmol, 51%) as colorless oil. IR: (neat) 2940, 2894, 1699, 1576, 1473, 1428, 1268, 1202, 1080, 998 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$): δ 8.45 (d, *J* = 2.3 Hz, 1H), 7.87 (d, *J* = 2.3 Hz, 1H), 7.44-7.47 (m, 2H), 7.36-7.42 (m, 5H), 7.28-7.30 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.10 (t, *J* = 7.2 Hz, 1H), 3.22-3.32 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 157.0, 152.0, 138.9, 138.2, 135.1, 134.1, 130.2, 130.1, 129.5, 128.9, 128.4, 127.6, 127.3, 126.9, 119.6, 61.9, 39.1, 38.7, 13.9 ppm; HRMS (ESI+) calcd. for $C_{23}H_{20}N_2O_2Cl$ (M+H) 391.1208, found 391.1200.

References:

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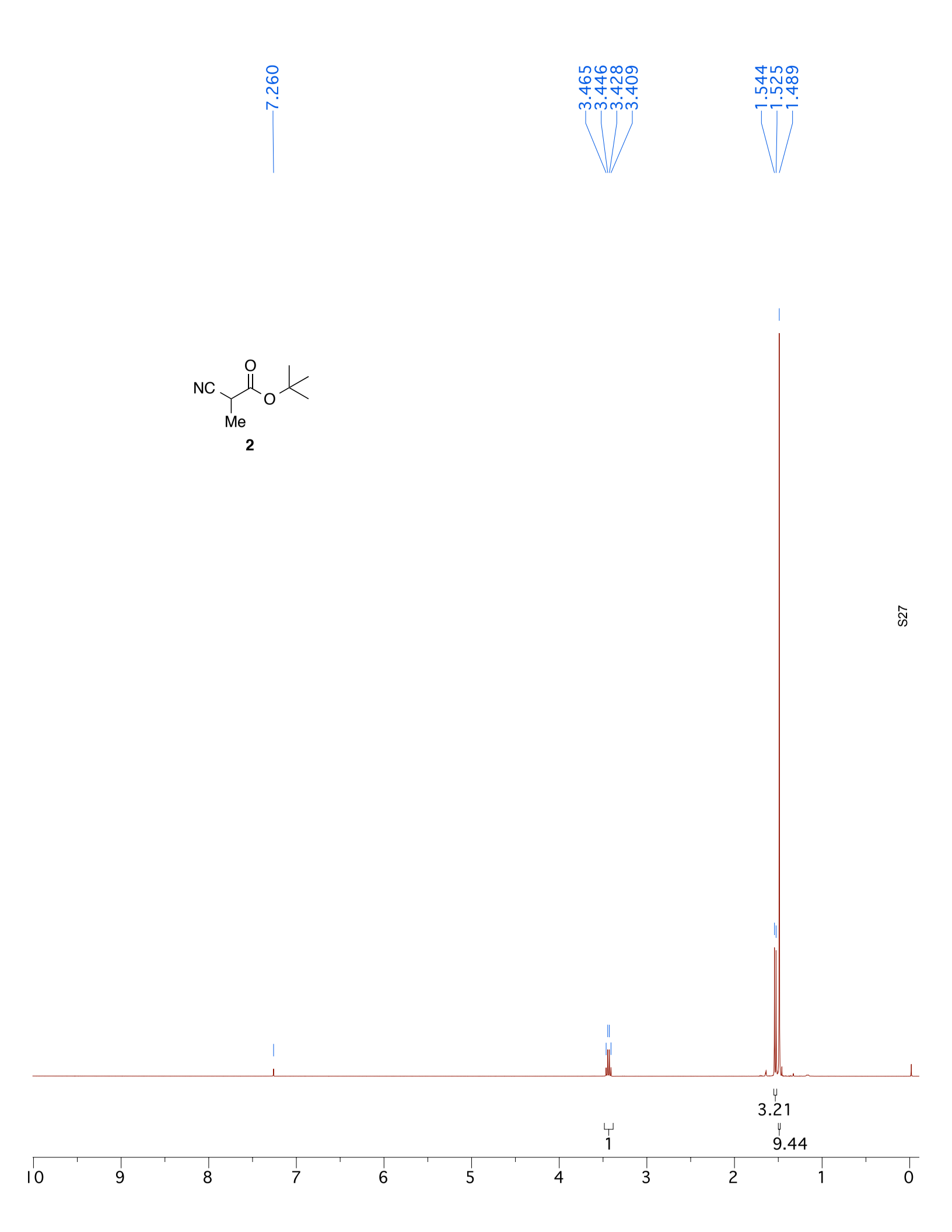
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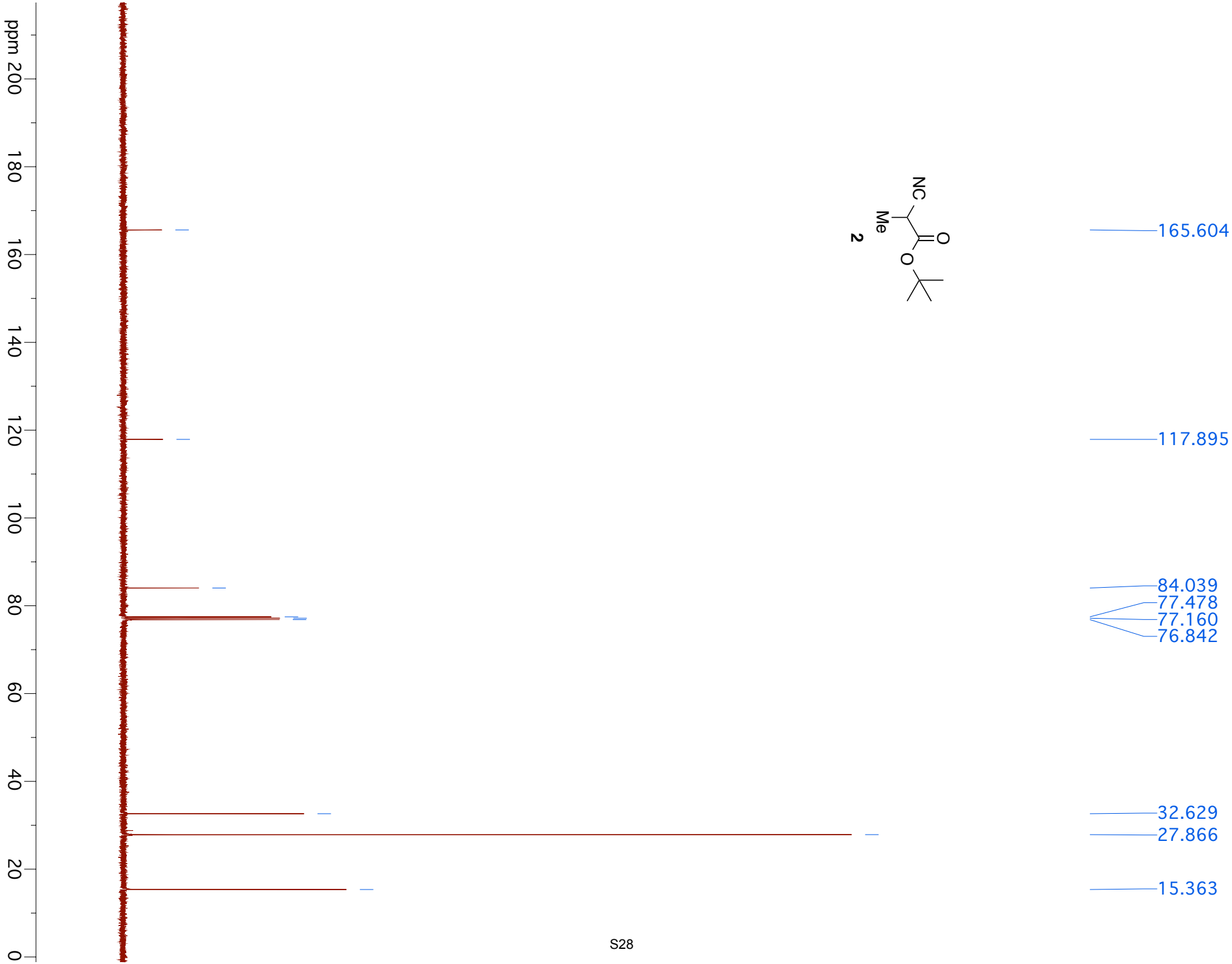
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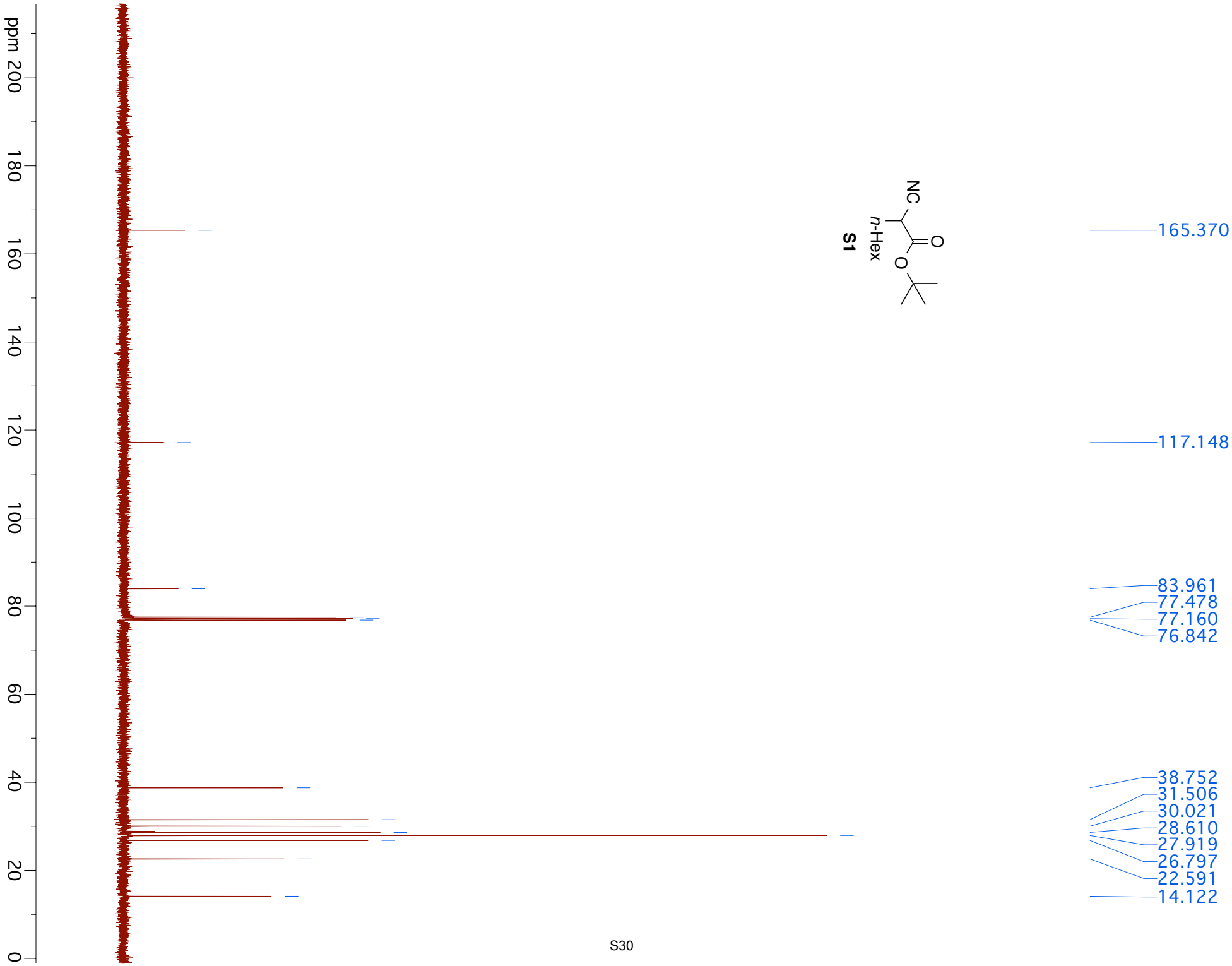
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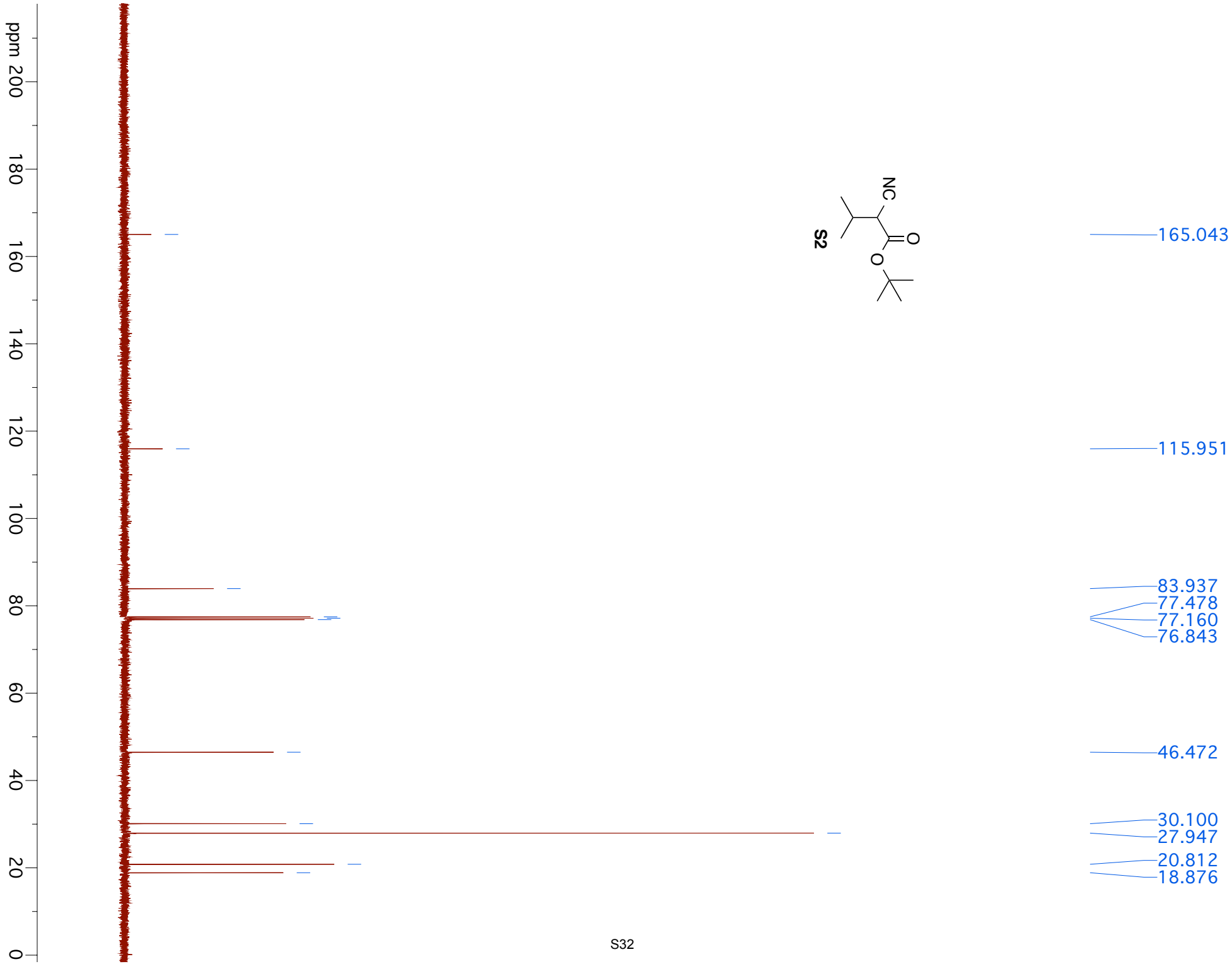
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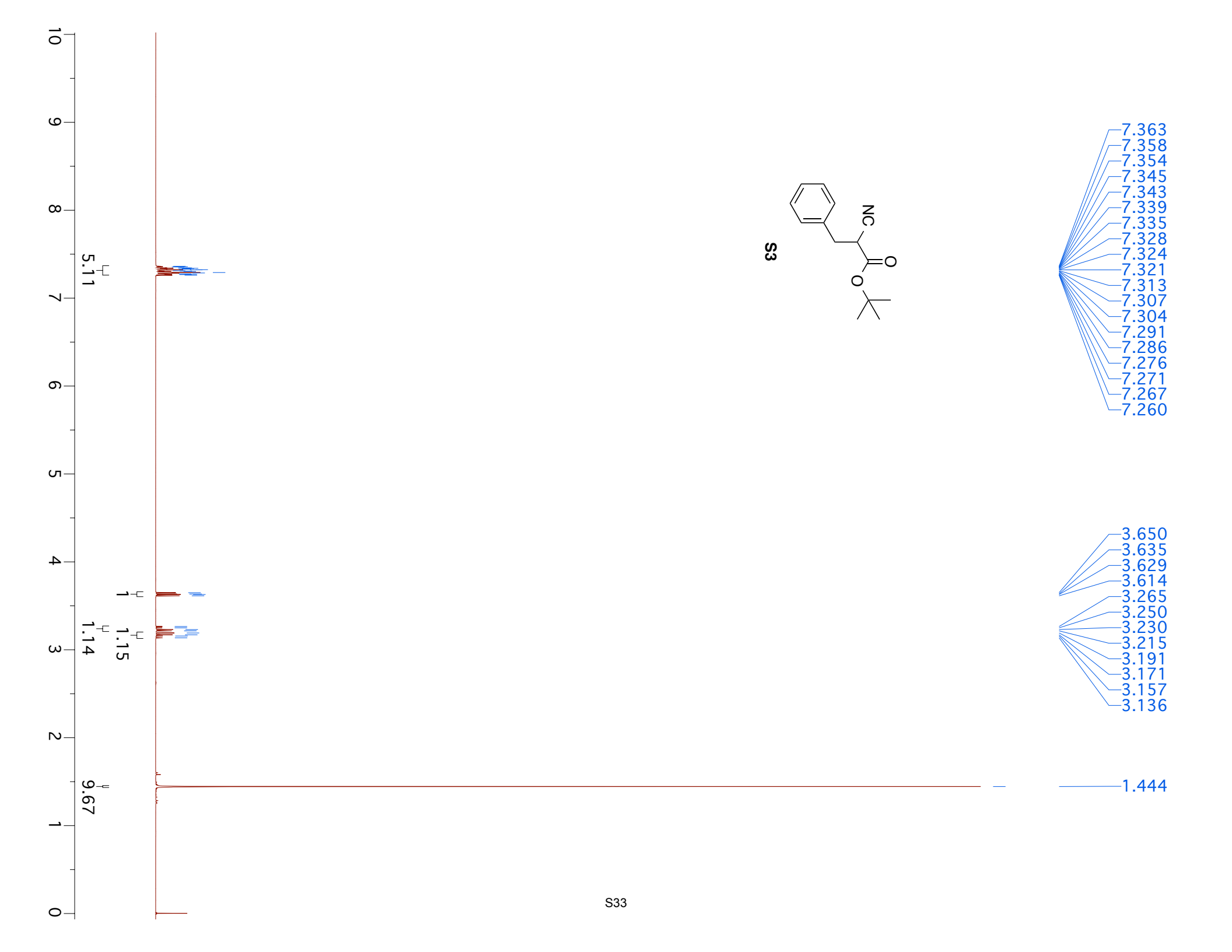
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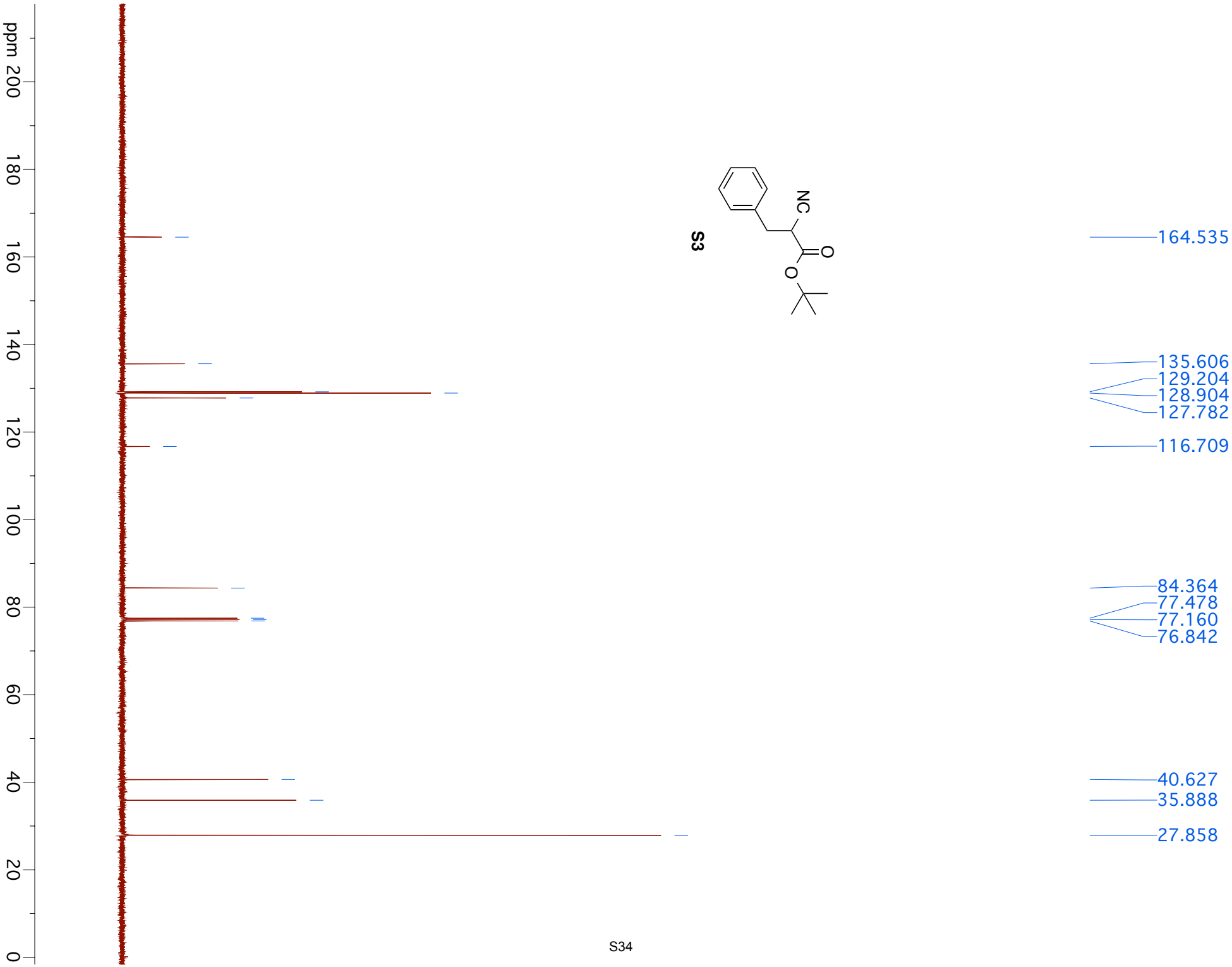
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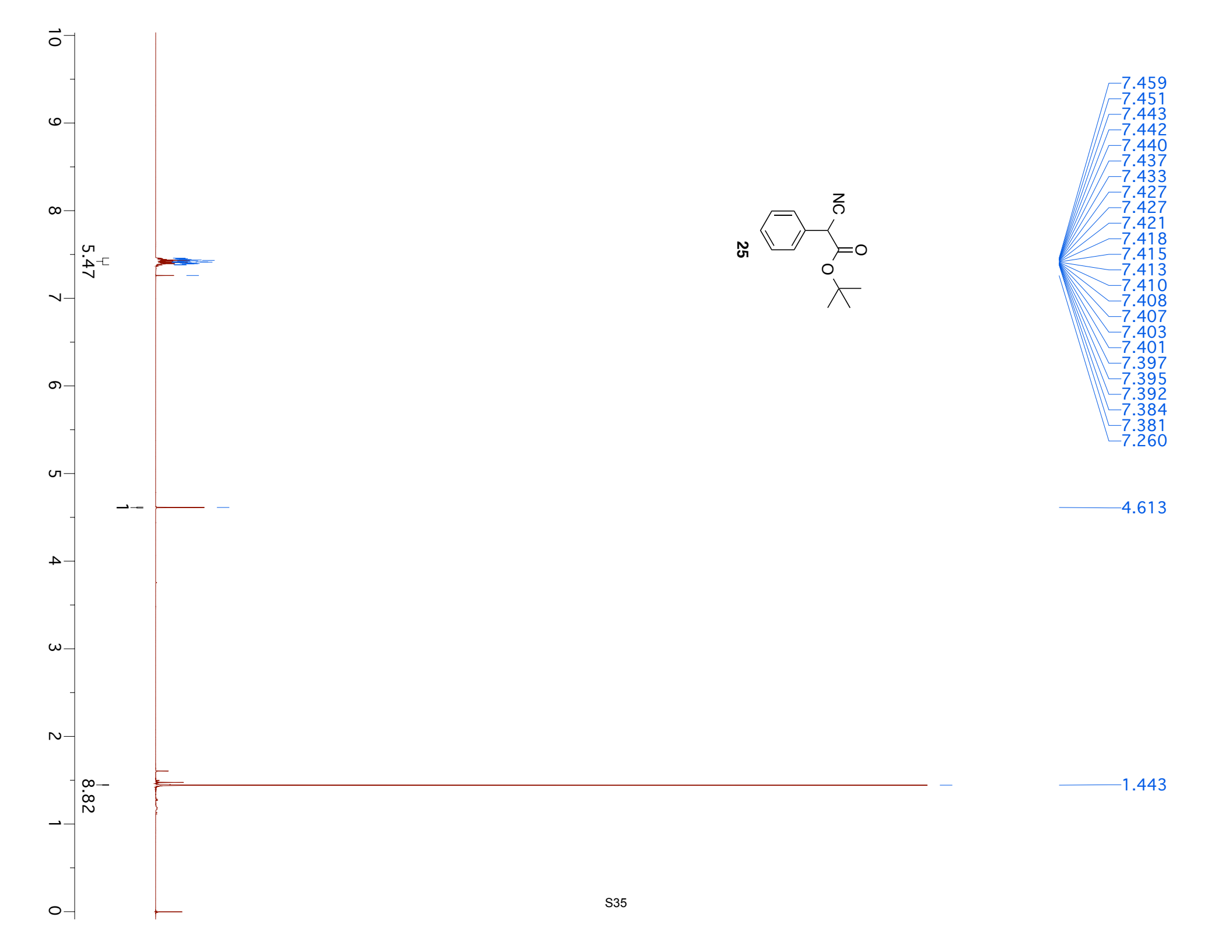
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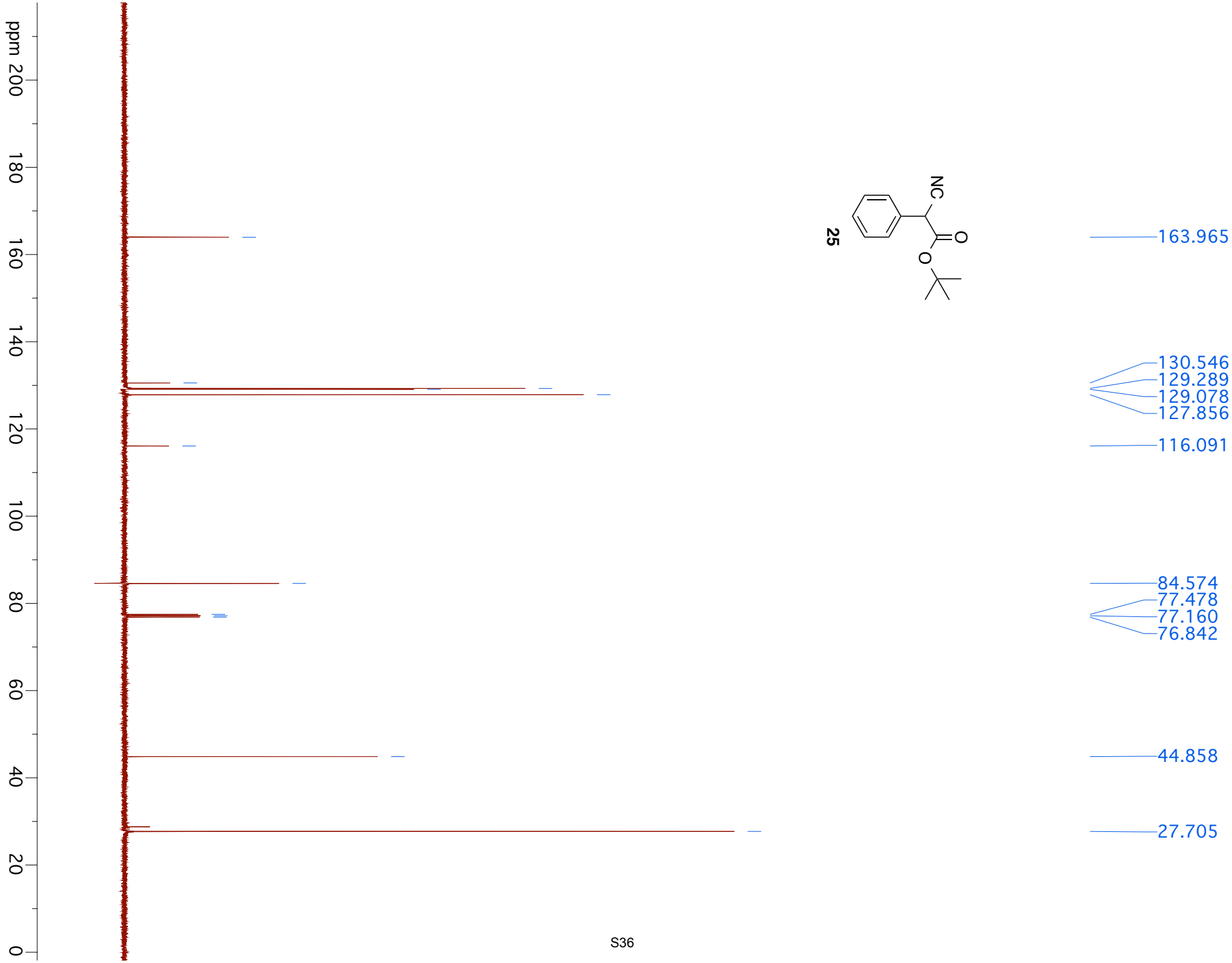
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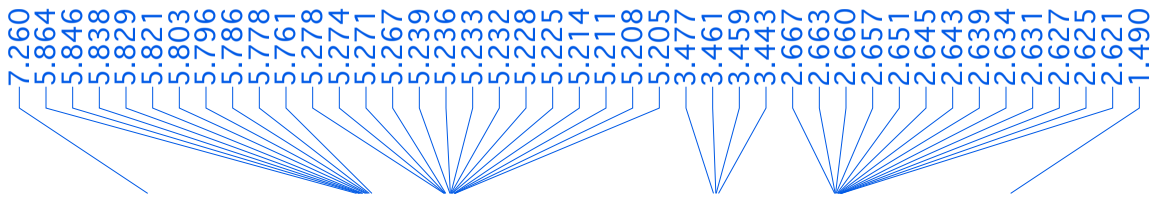
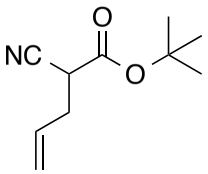
27.705





S4

S37

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2.16

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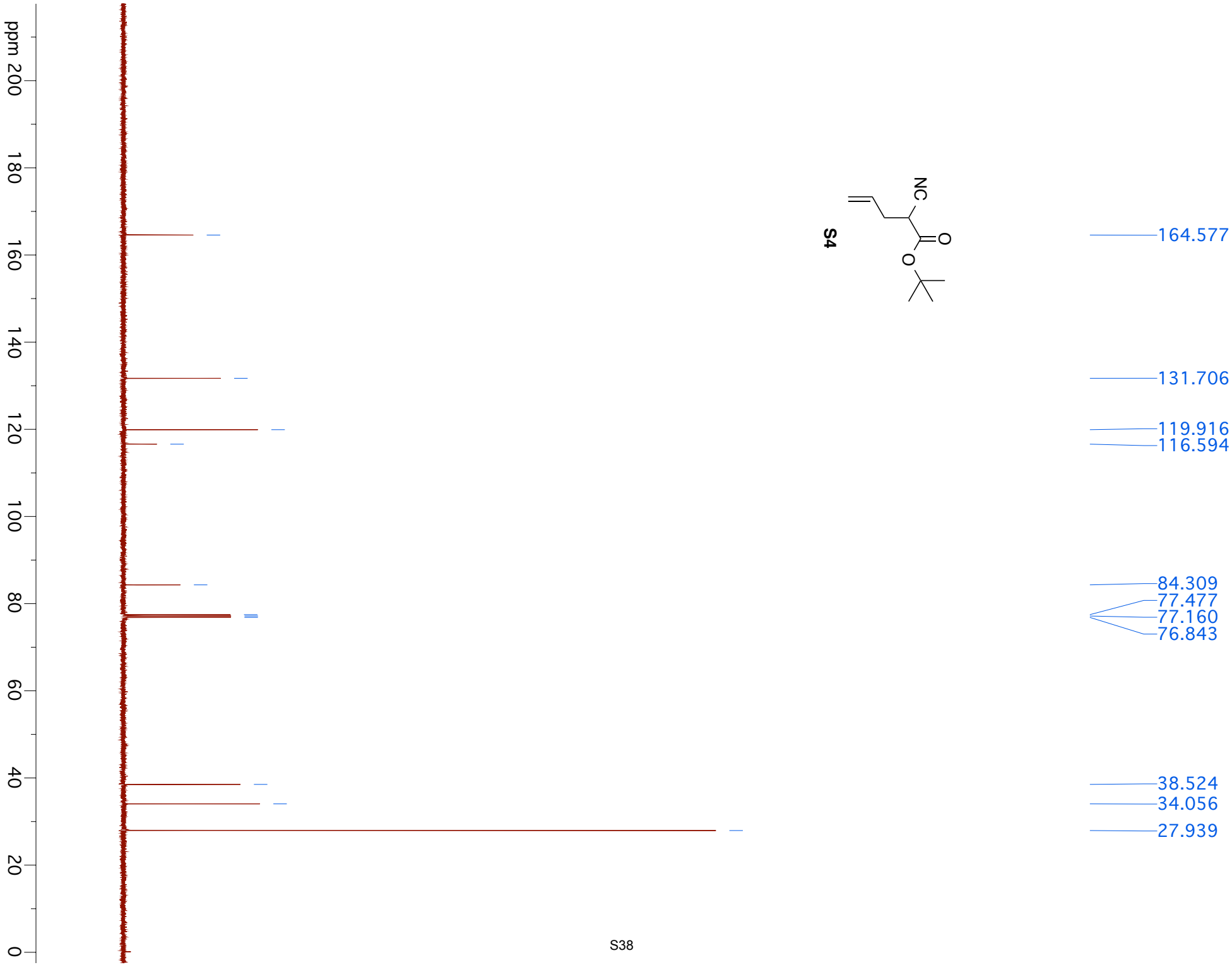
0.938

9.33

10 9 8 7 6 5 4 3 2 1 0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O
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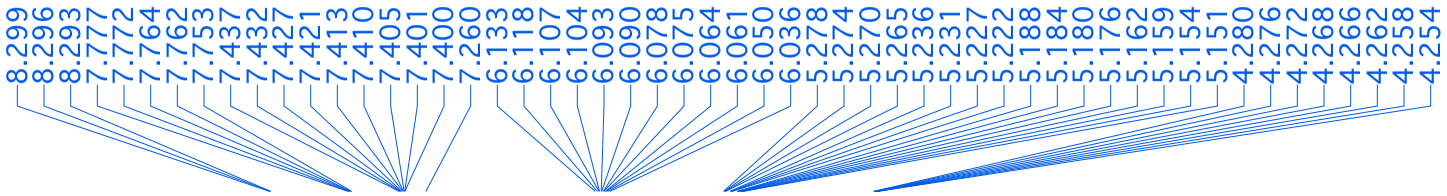
27.939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7.410
7.405
7.401
7.400
7.260
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6.093
6.090
6.078
6.075
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5.176
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4.272
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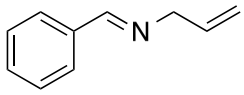
4.262
4.258
4.254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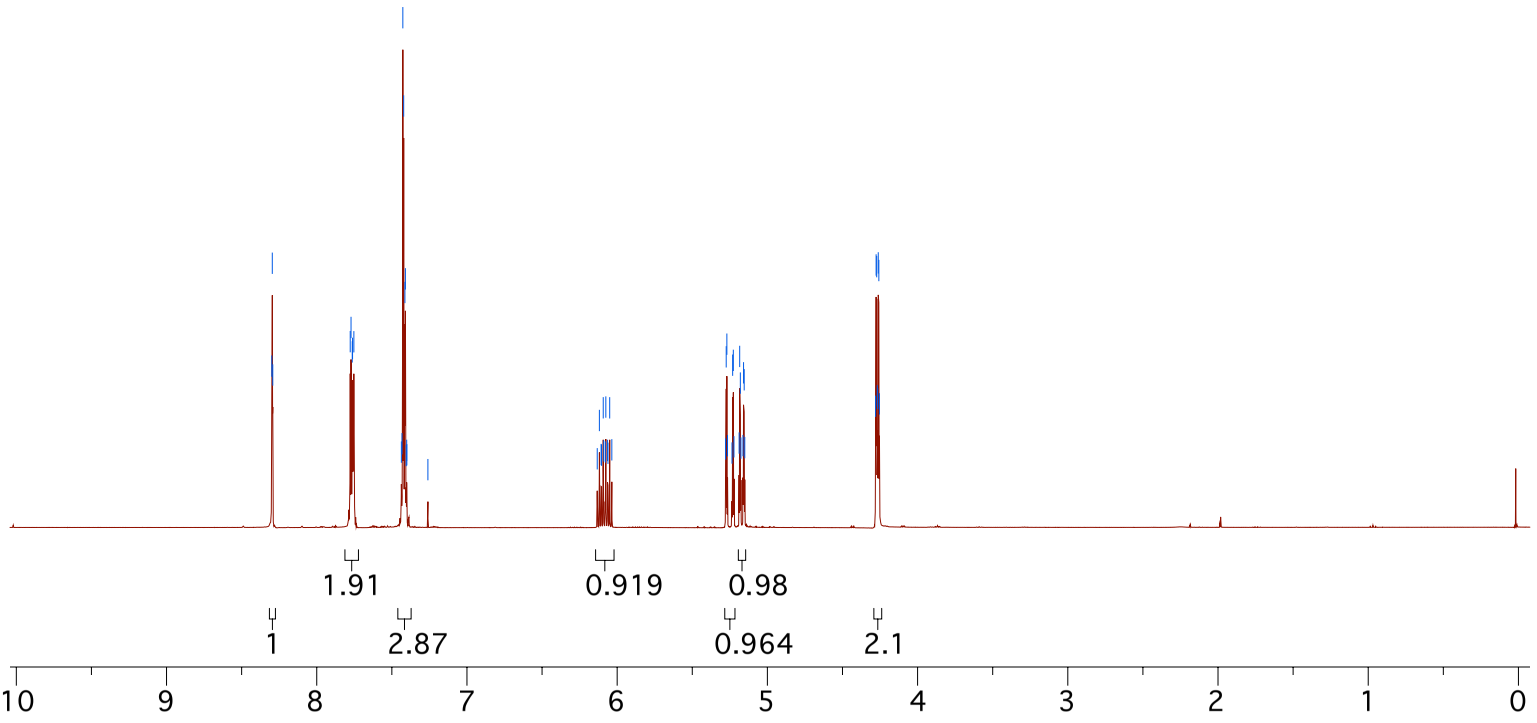
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8
7
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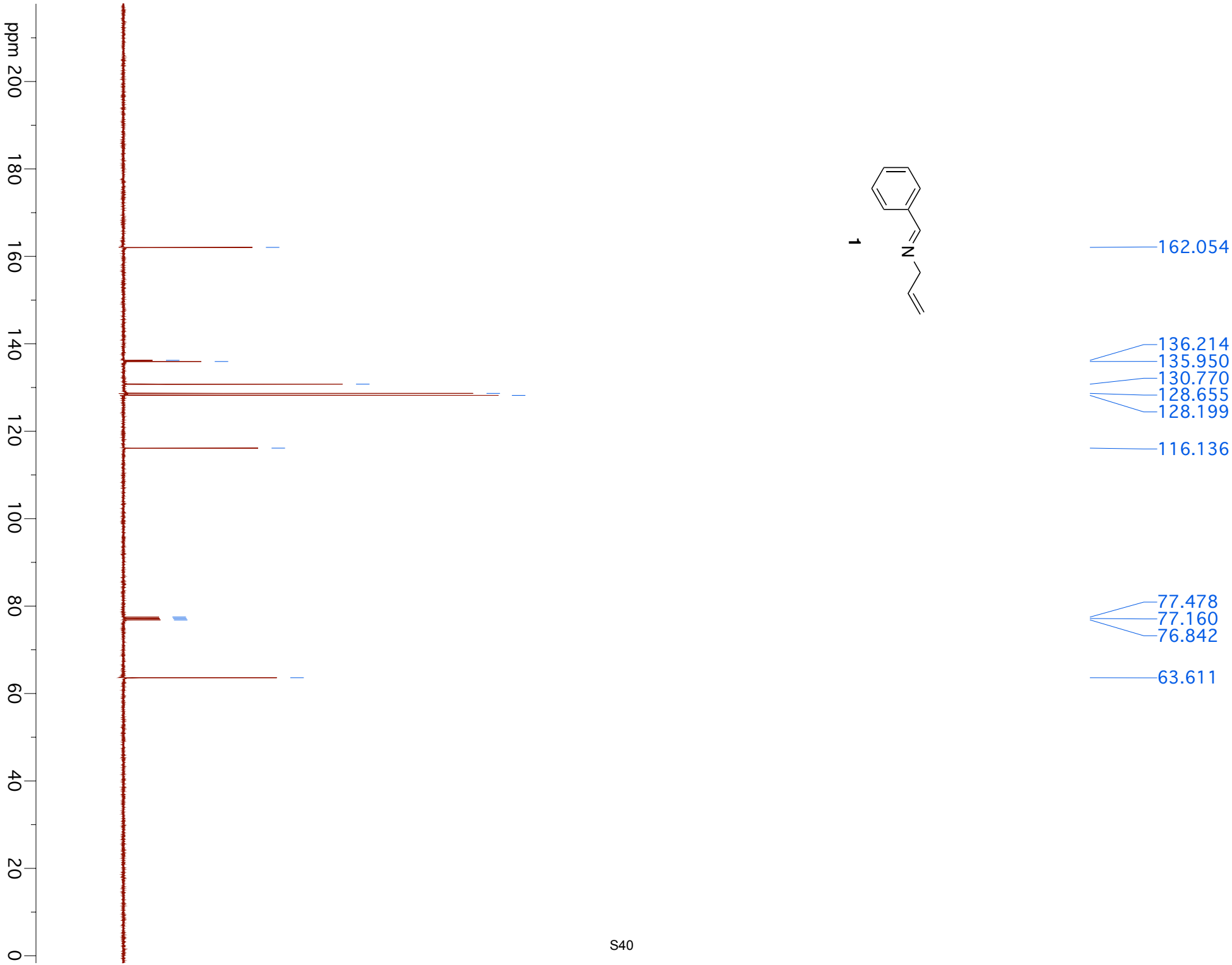
3
2
1
0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180
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120
100
80
60
40
20
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135.950
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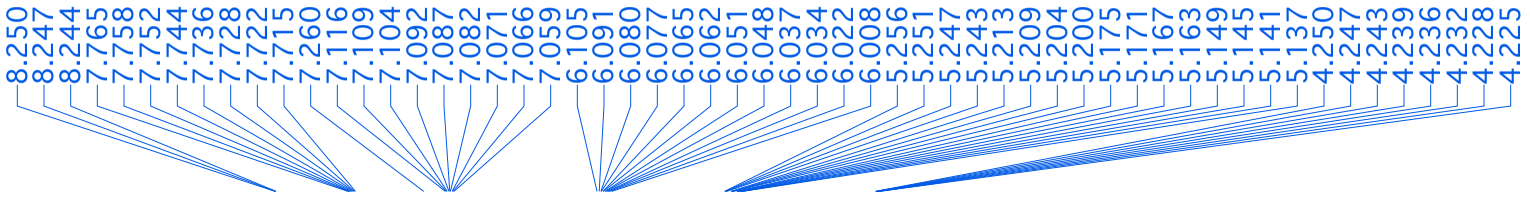
128.199
116.136
77.478
77.160
76.842
63.611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8.244
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7.758
7.752
7.744
7.736
7.728
7.722
7.715
7.260
7.116
7.109
7.104
7.092
7.087
7.082
7.071
7.066
7.059
6.105
6.091
6.080
6.077
6.065
6.062
6.051
6.048
6.037
6.034
6.022
6.008
5.256
5.251
5.247
5.243
5.213
5.209
5.204
5.200
5.175
5.171
5.167
5.163
5.149
5.145
5.141
5.137
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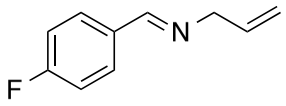
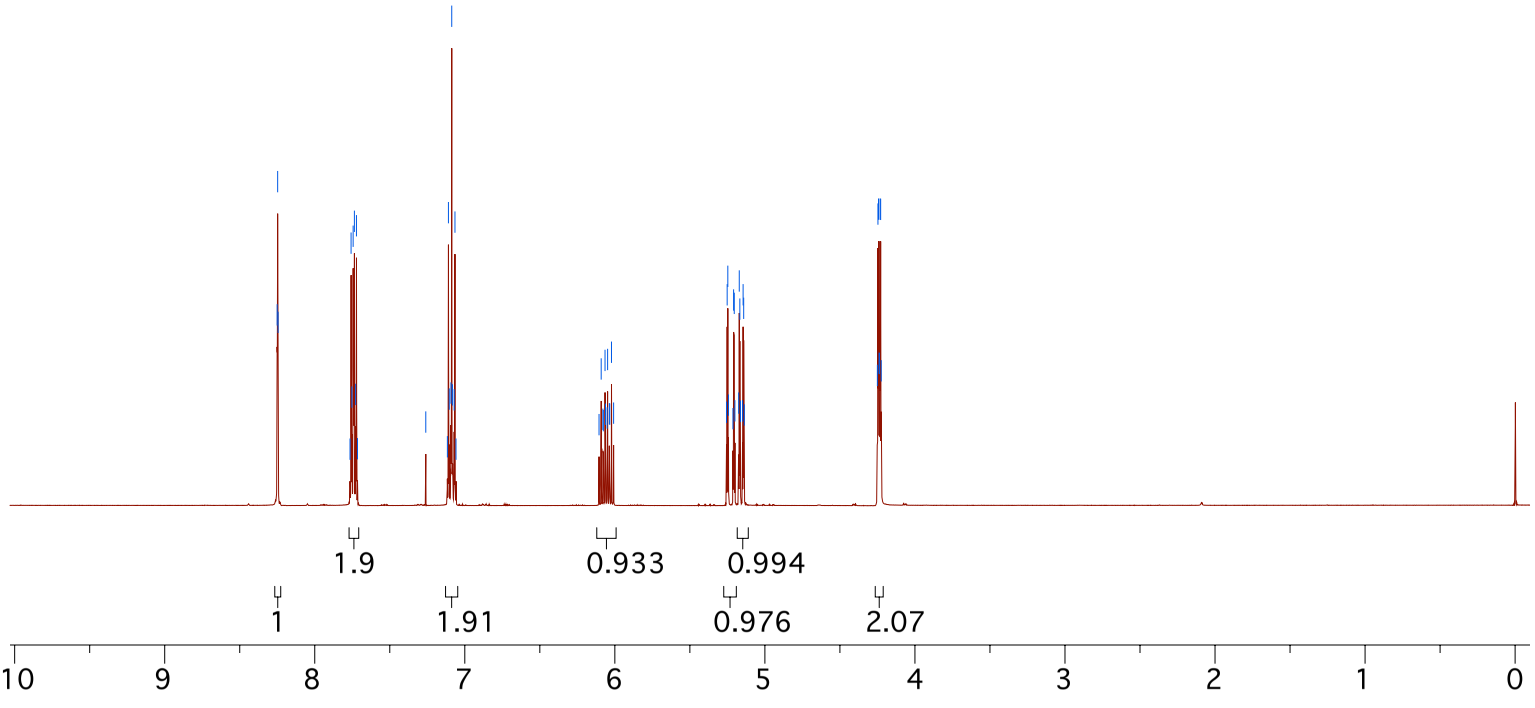
4.247
4.243
4.239
4.236
4.232
4.228
4.225


N
F

S5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0.976
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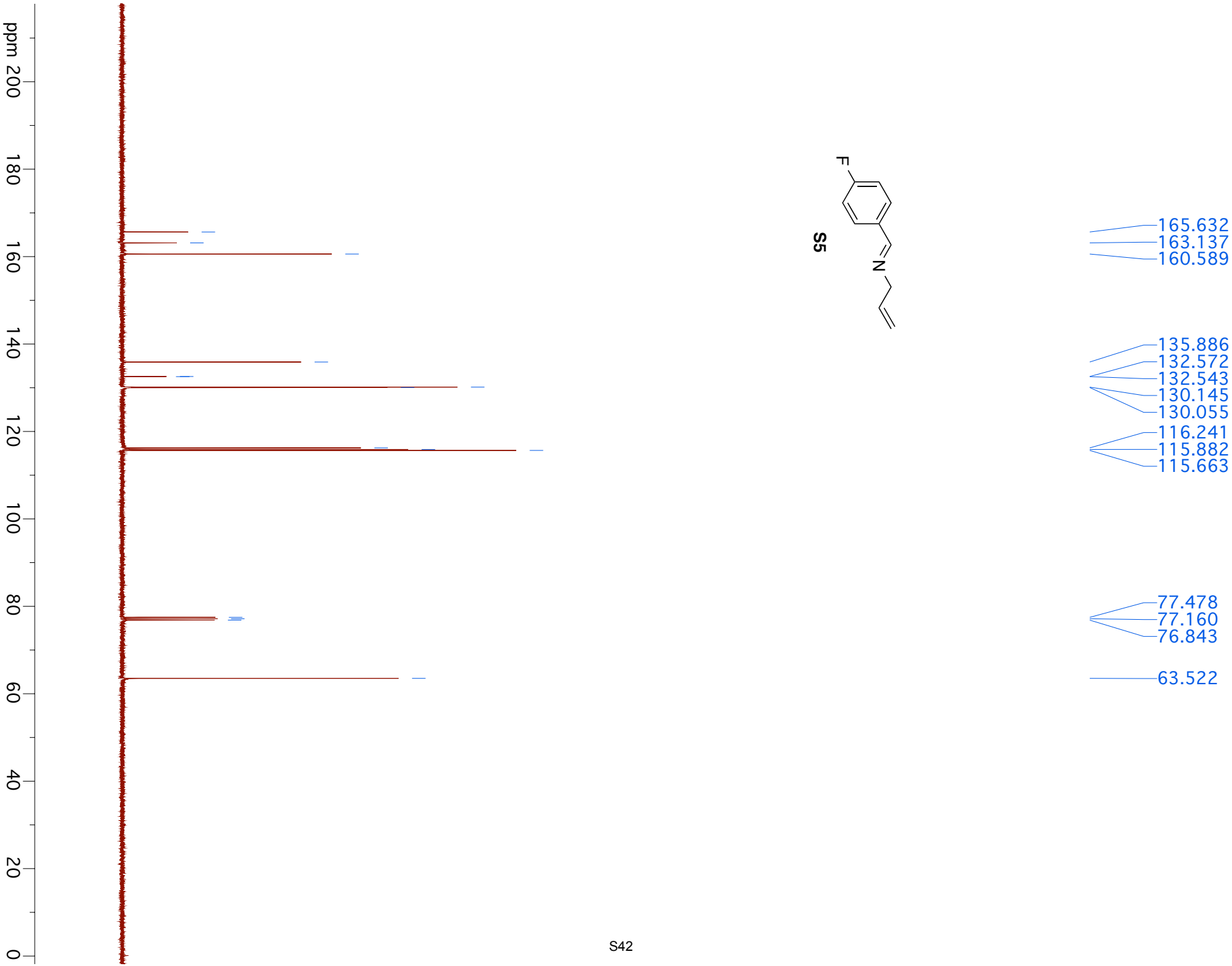
10
9
8
7
6
5
4
3
2
1
0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200
180
160
140
120
100
80
60
40
20
0
F
N
S5
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163.137
160.589
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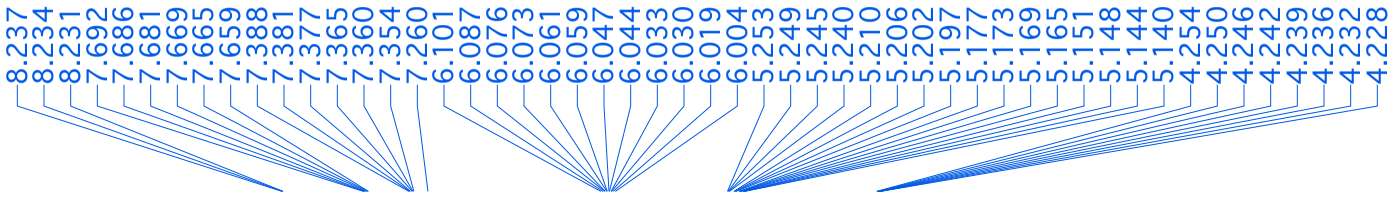
132.572
132.543
130.145
130.055
116.241
115.882
115.663
77.478
77.160
76.843
63.522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8.234
8.231
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7.686
7.681
7.669
7.665
7.659
7.388
7.381
7.377
7.365
7.360
7.354
7.260
6.101
6.087
6.076
6.073
6.061
6.059
6.047
6.044
6.033
6.030
6.019
6.004
5.253
5.249
5.245
5.240
5.210
5.206
5.202
5.197
5.177
5.173
5.169
5.165
5.151
5.148
5.144
5.140
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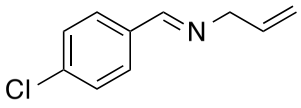
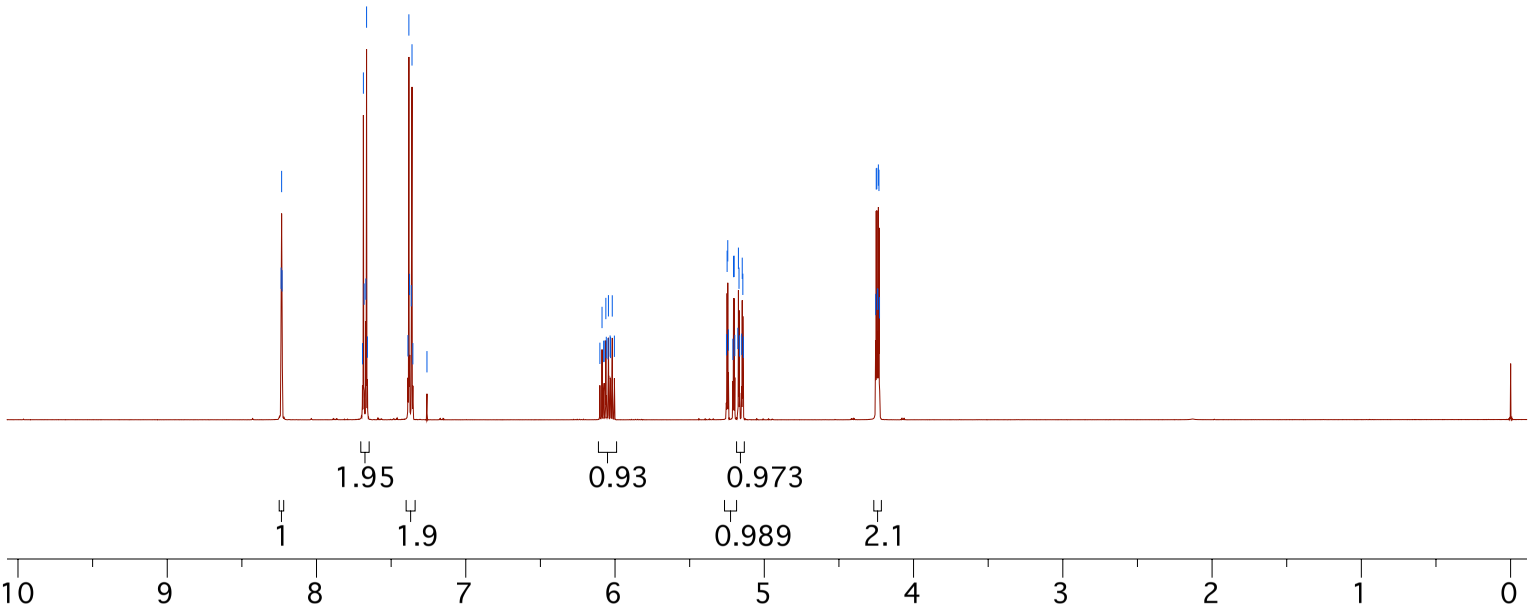
4.250
4.246
4.242
4.239
4.236
4.232
4.228


N
Cl

S6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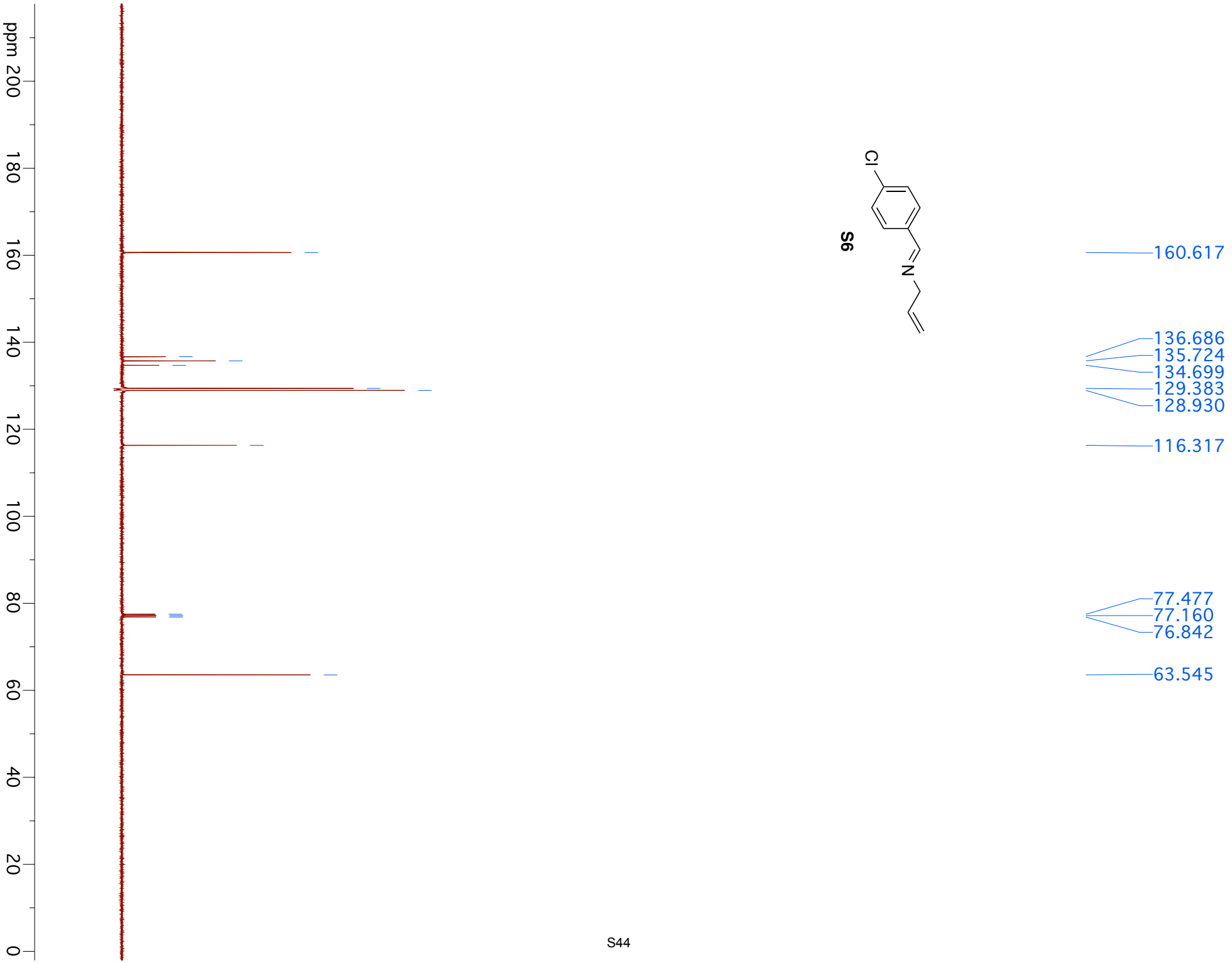
0.989
2.1
10
9
8
7
6
5
4
3
2
1
0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180
160
140
120
100
80
60
40
20
0
Cl
N
S6
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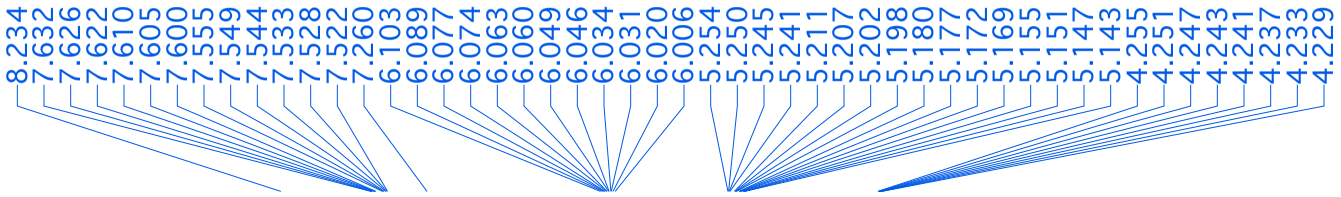
135.724
134.699
129.383
128.930
116.317
77.477
77.160
76.842
63.545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7.622
7.610
7.605
7.600
7.555
7.549
7.544
7.533
7.528
7.522
7.260
6.103
6.089
6.077
6.074
6.063
6.060
6.049
6.046
6.034
6.031
6.020
6.006
5.254
5.250
5.245
5.241
5.211
5.207
5.202
5.198
5.180
5.177
5.172
5.169
5.155
5.151
5.147
5.143
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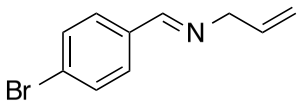
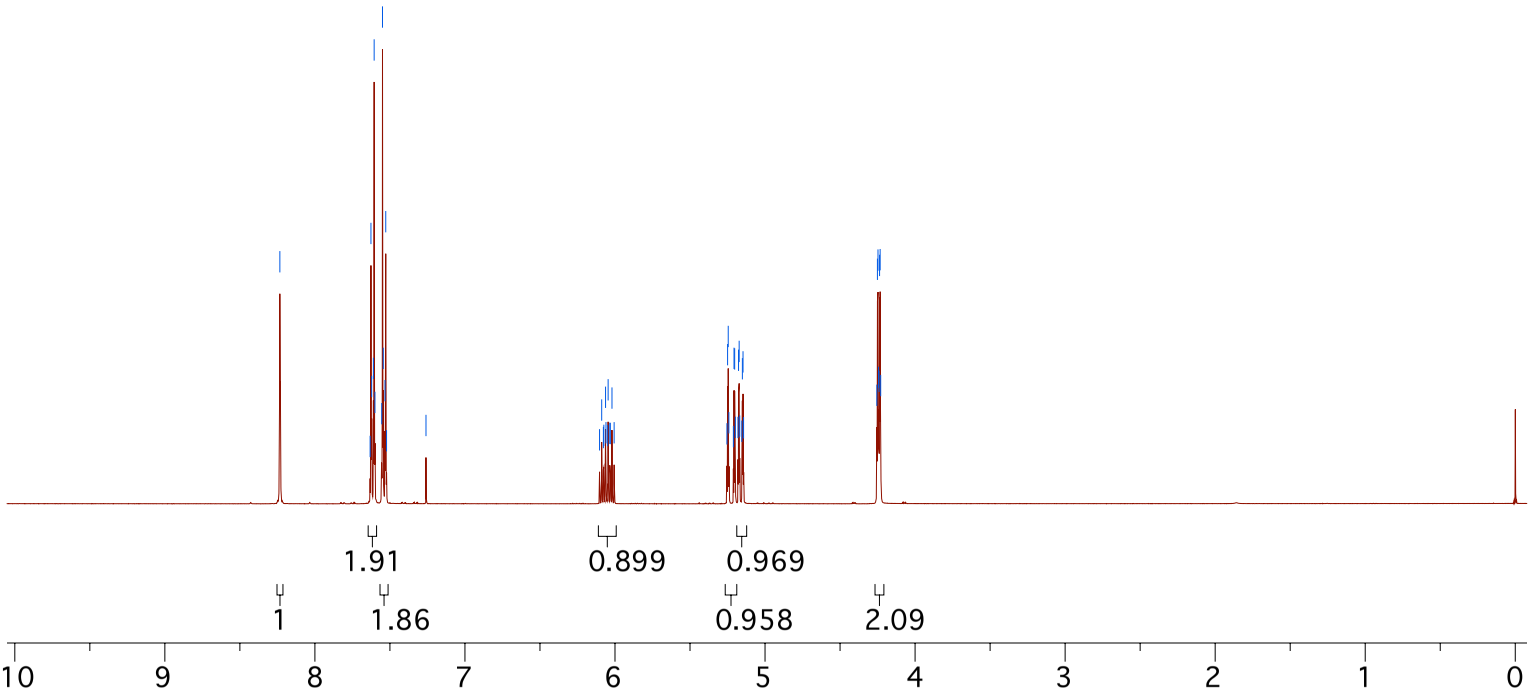
4.247
4.243
4.241
4.237
4.233
4.229


N
Br

S7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0.958
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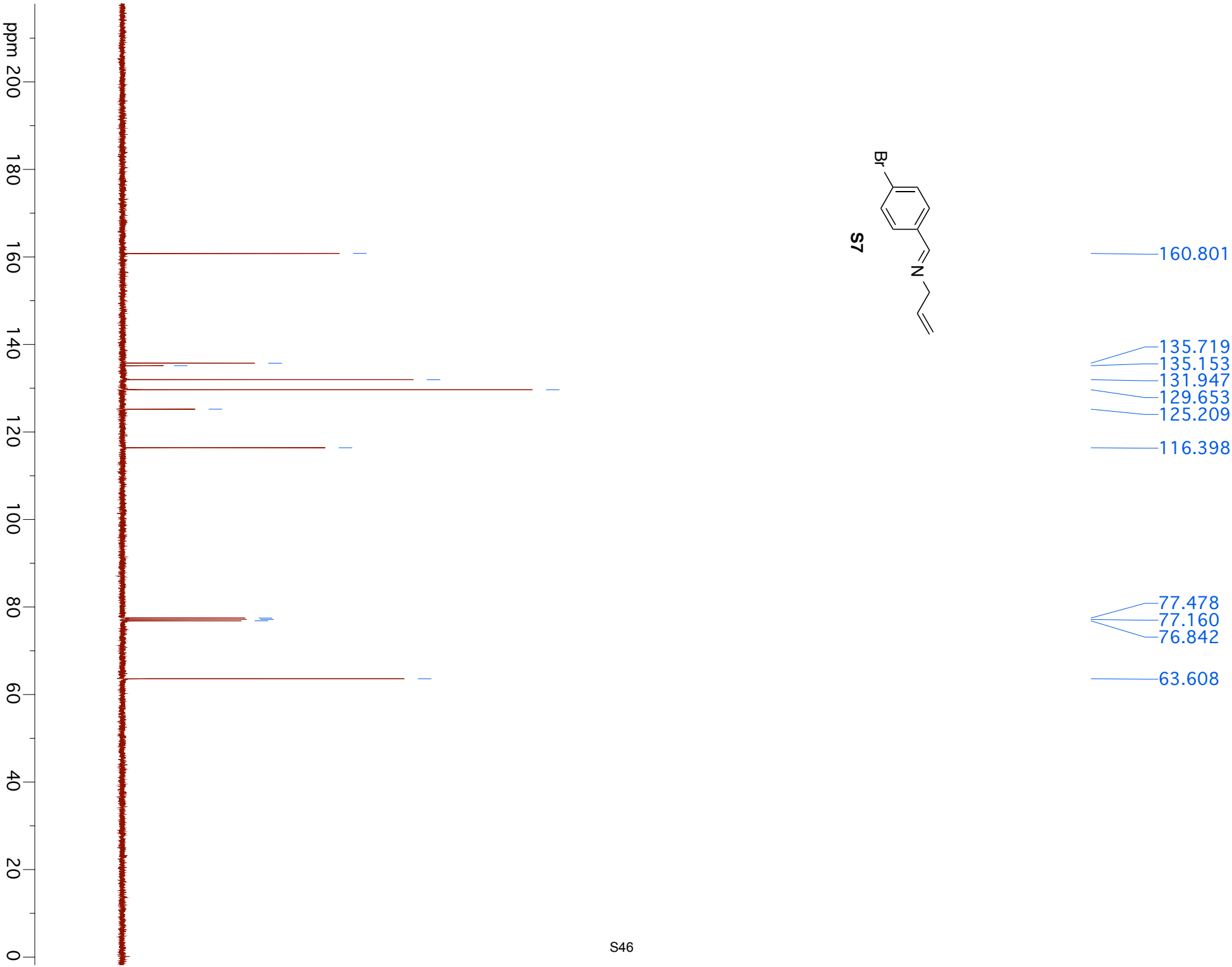
9
8
7
6
5
4
3
2
1
0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140
120
100
80
60
40
20
0
Br
N
S7
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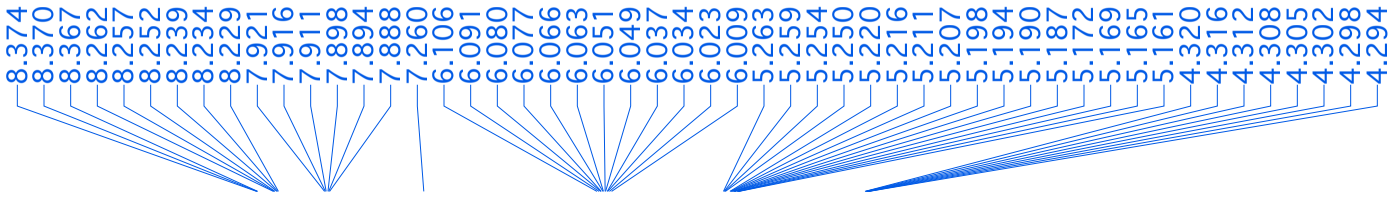
129.653
125.209
116.398
77.478
77.160
76.842
63.608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8.252
8.239
8.234
8.229
7.921
7.916
7.911
7.898
7.894
7.888
7.260
6.106
6.091
6.080
6.077
6.066
6.063
6.051
6.049
6.037
6.034
6.023
6.009
5.263
5.259
5.254
5.250
5.220
5.216
5.211
5.207
5.198
5.194
5.190
5.187
5.172
5.169
5.165
5.161
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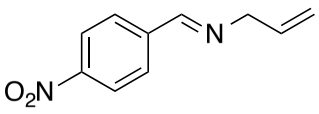
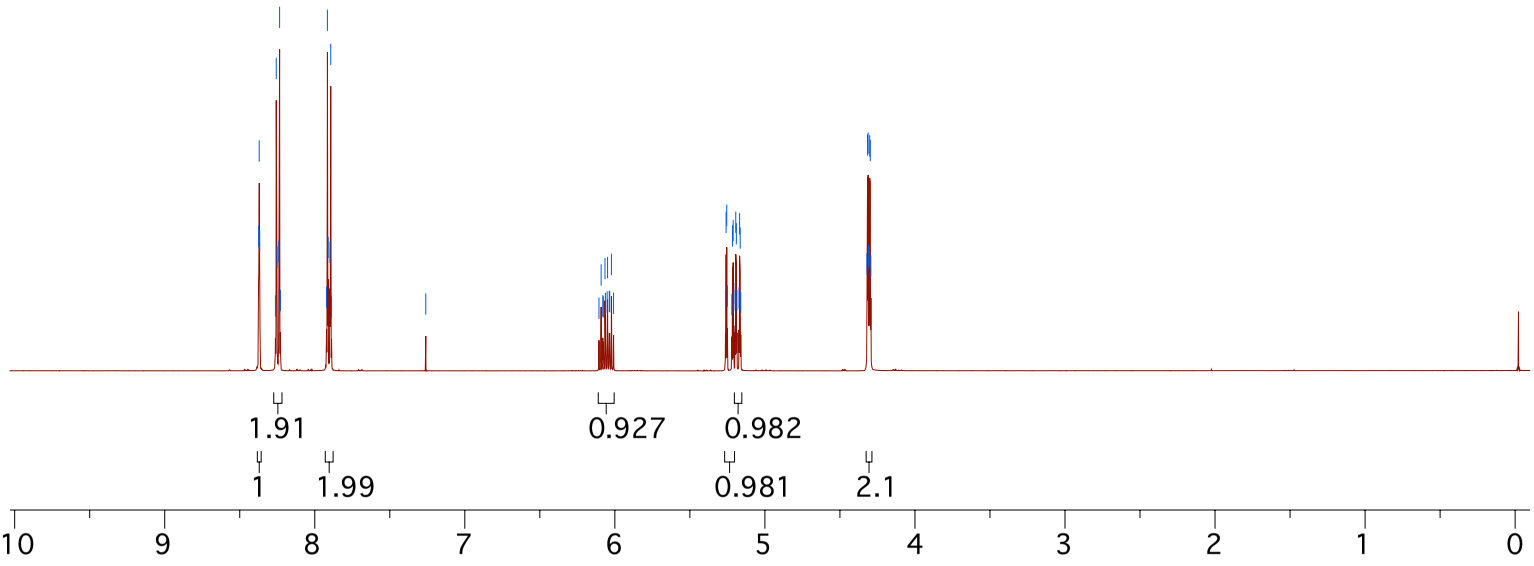
4.316
4.312
4.308
4.305
4.302
4.298
4.294


N
O2N

S8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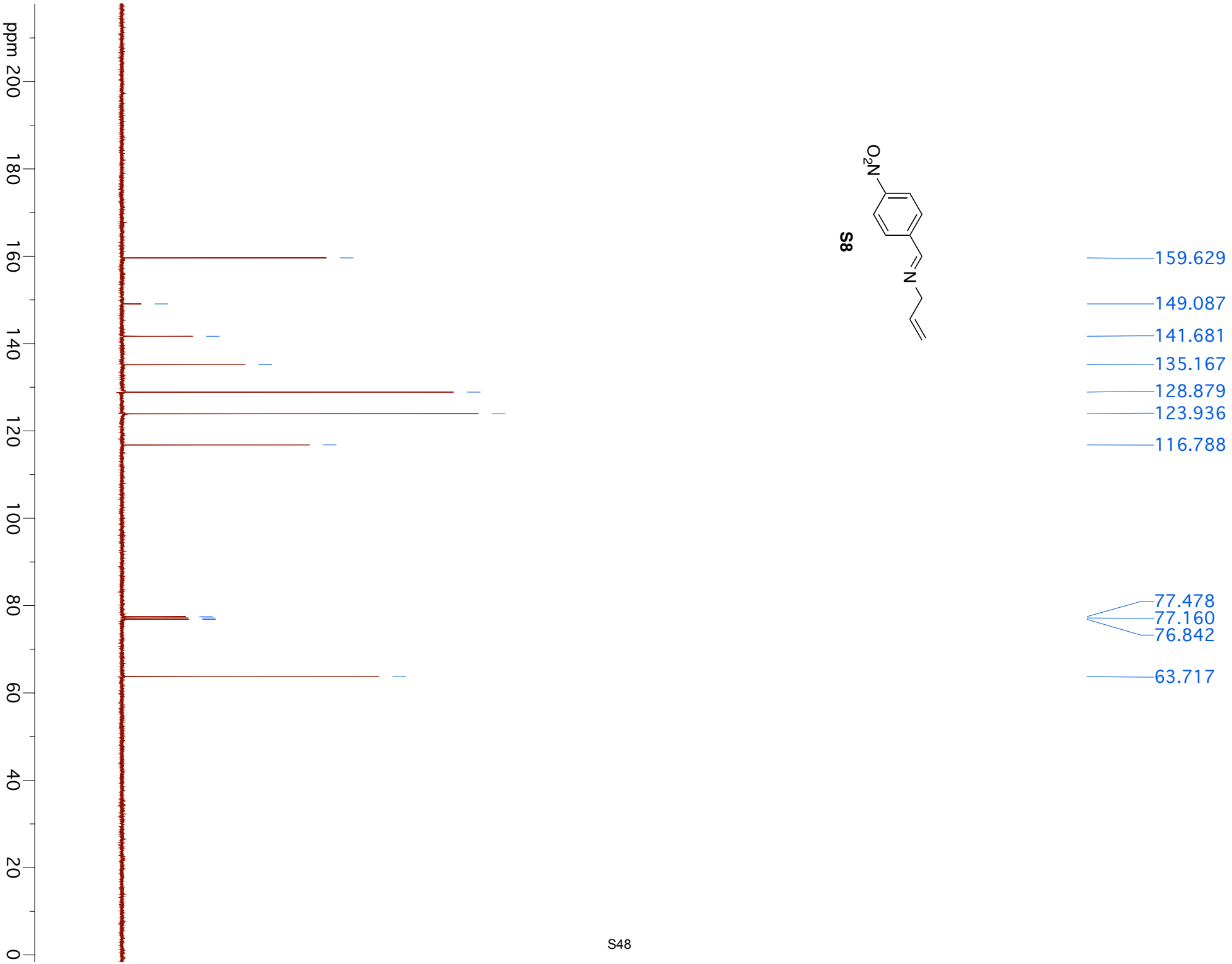
0.981
2.1
10
9
8
7
6
5
4
3
2
1
0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140
120
100
80
60
40
20
0
S8
O2N
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116.788
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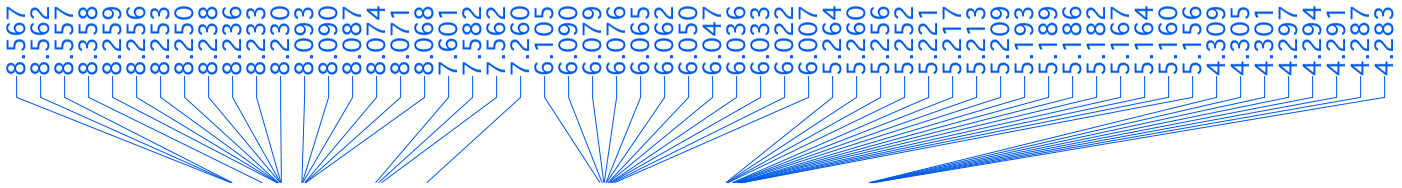
77.160
76.842
63.717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8.256
8.253
8.250
8.238
8.236
8.233
8.230
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8.090
8.087
8.074
8.071
8.068
7.601
7.582
7.562
7.260
6.105
6.090
6.079
6.076
6.065
6.062
6.050
6.047
6.036
6.033
6.022
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5.260
5.256
5.252
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5.193
5.189
5.186
5.182
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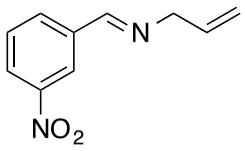
4.291
4.287
4.283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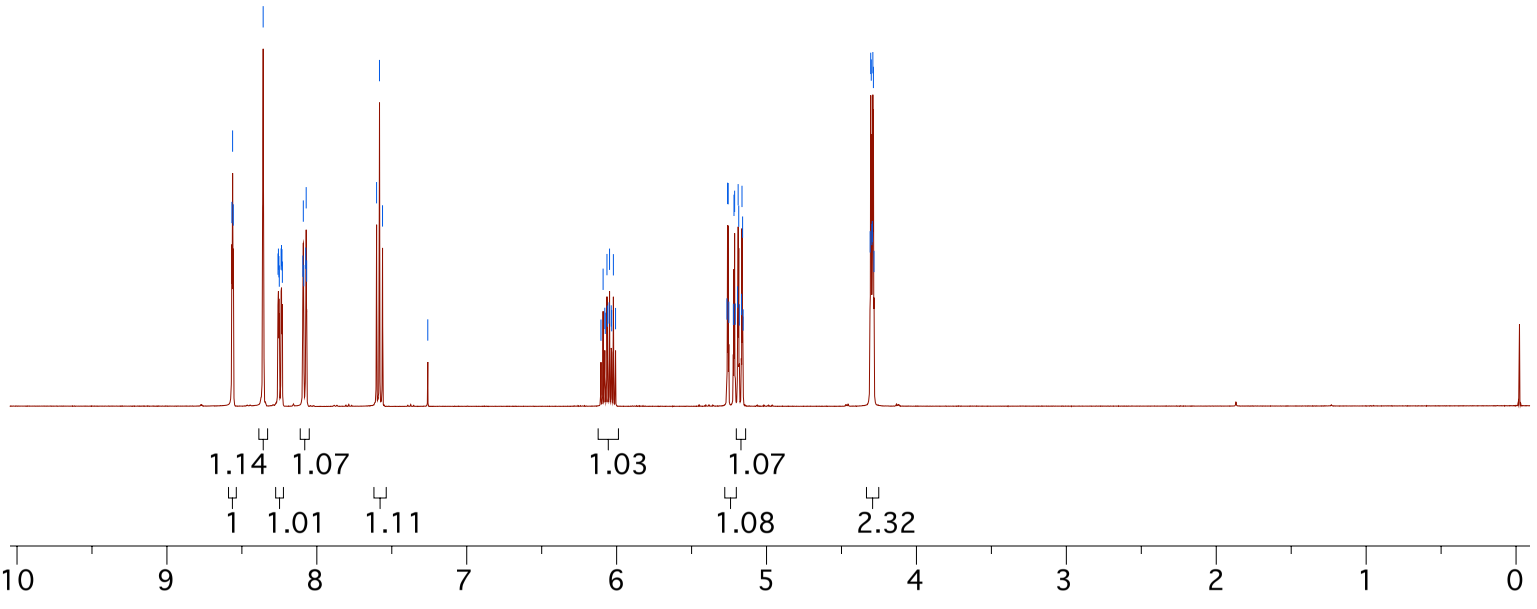
NO2

S9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1.07
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1.11
1.08
2.32
10
9
8
7
6
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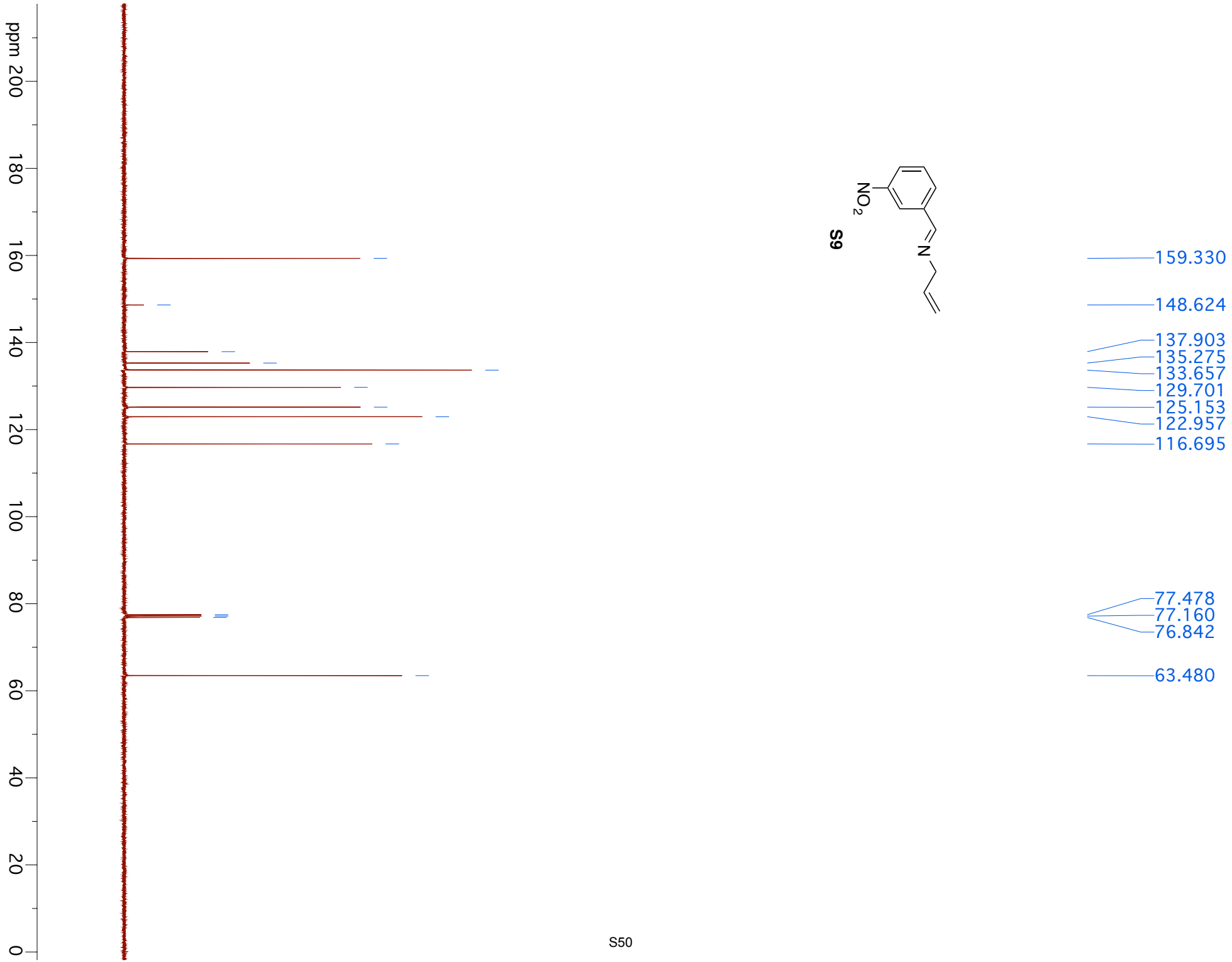
3
2
1
0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140
120
100
80
60
40
20
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159.330
148.624
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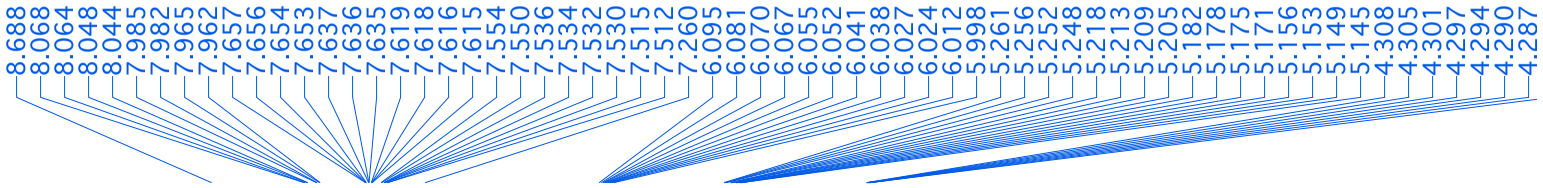
133.657
129.701
125.153
122.957
116.695
77.478
77.160
76.842
63.480

S9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7.962
7.657
7.656
7.654
7.653
7.637
7.636
7.635
7.619
7.618
7.616
7.615
7.554
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7.530
7.515
7.512
7.260
6.095
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6.070
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6.055
6.052
6.041
6.038
6.027
6.024
6.012
5.998
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5.256
5.252
5.248
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5.213
5.209
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5.182
5.178
5.175
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5.153
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4.297
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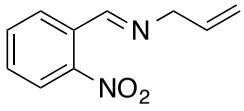
4.290
4.287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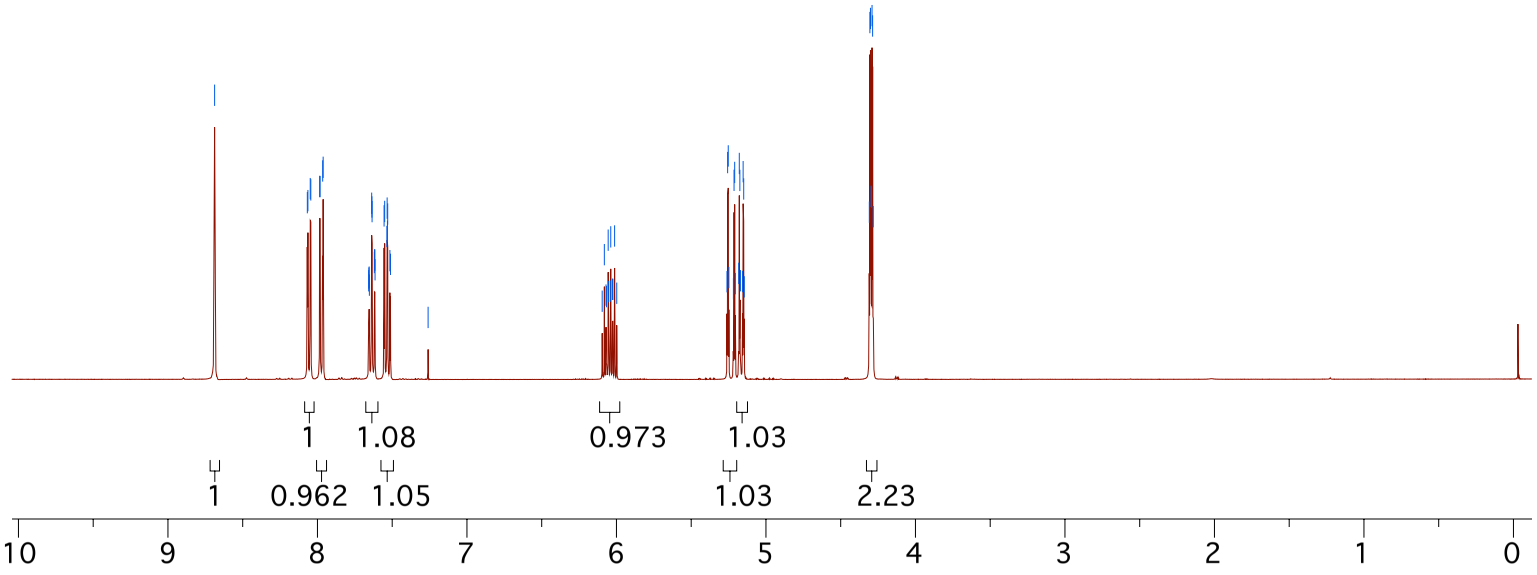
NO2

S10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1.03
1
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1.03
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10
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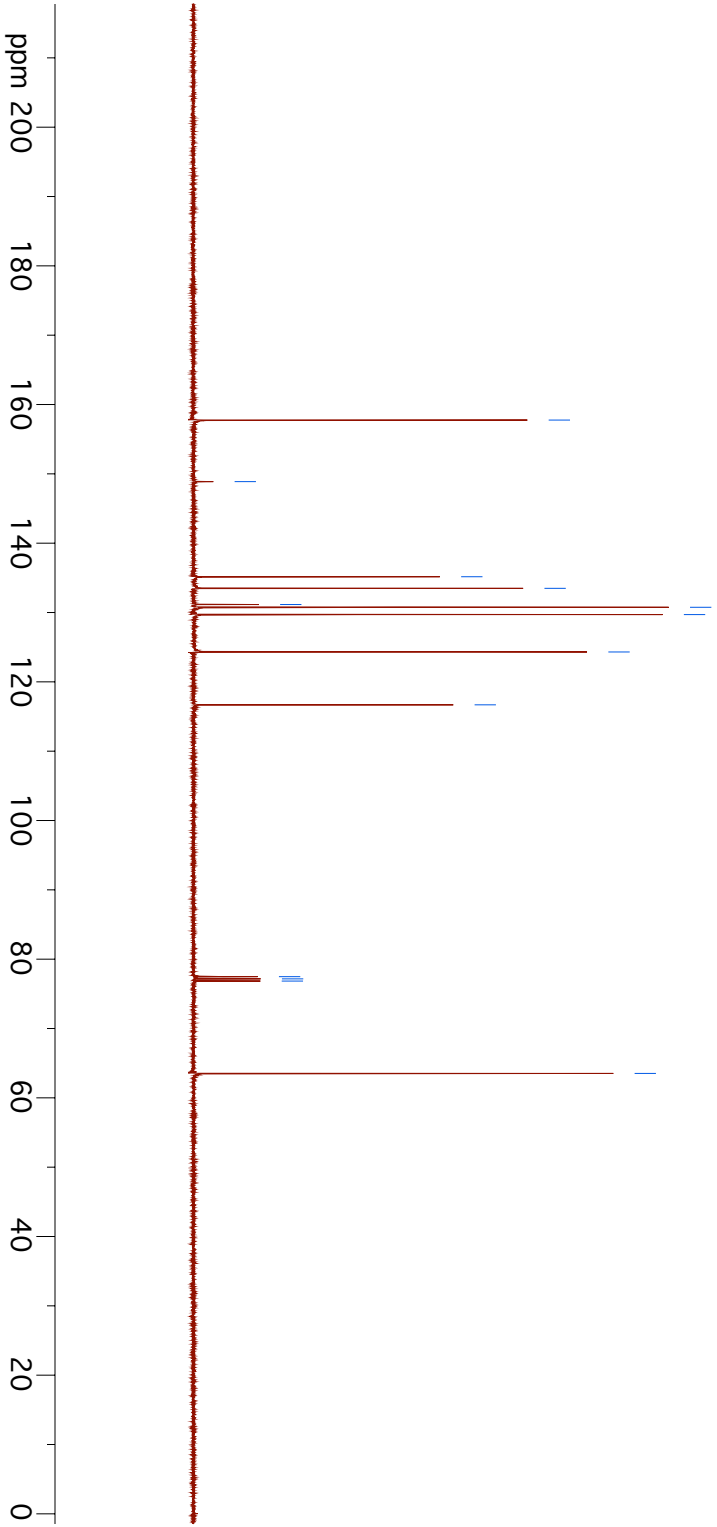
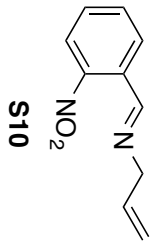
7
6
5
4
3
2
1
0





S10

157.757
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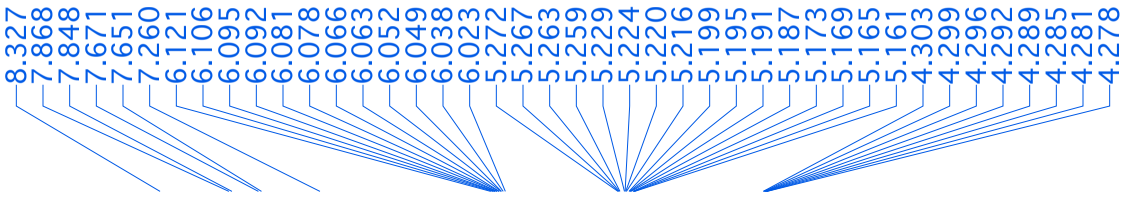
133.488
131.152
130.755
129.701
124.309
116.685

77.478
77.160
76.842

63.521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7.848
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7.260
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6.106
6.095
6.092
6.081
6.078
6.066
6.063
6.052
6.049
6.038
6.023
5.272
5.267
5.263
5.259
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5.224
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5.199
5.195
5.191
5.187
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4.292
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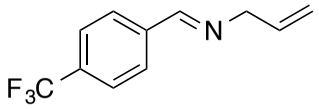
4.278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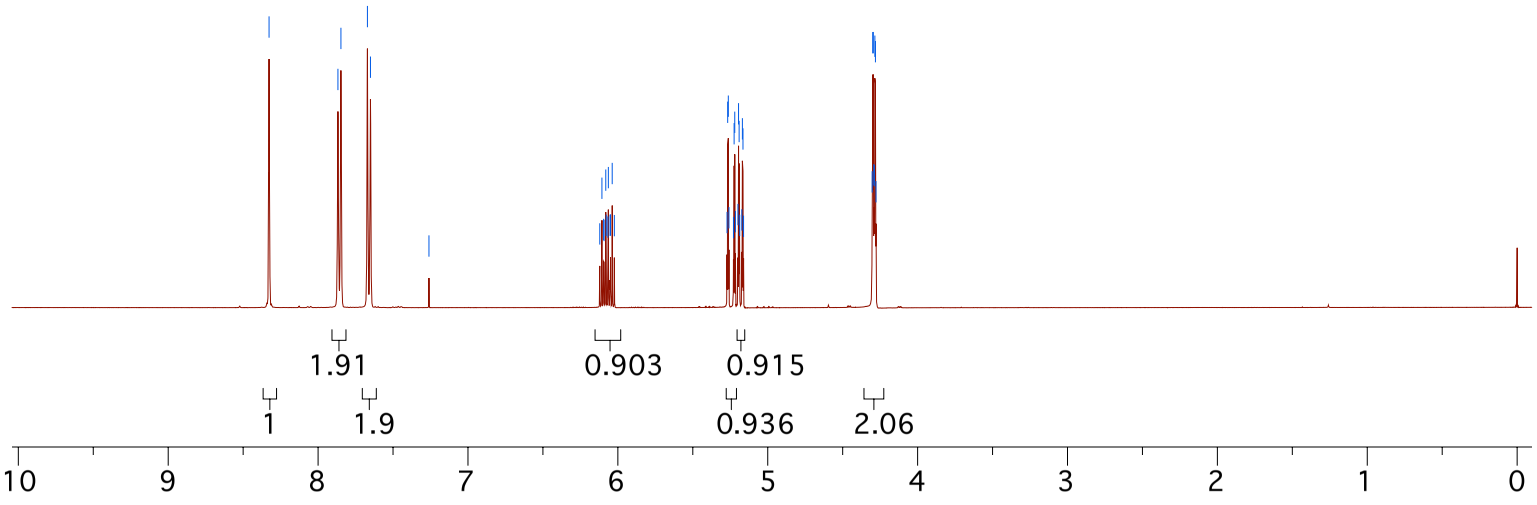
F3C

S11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0.936
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10
9
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1
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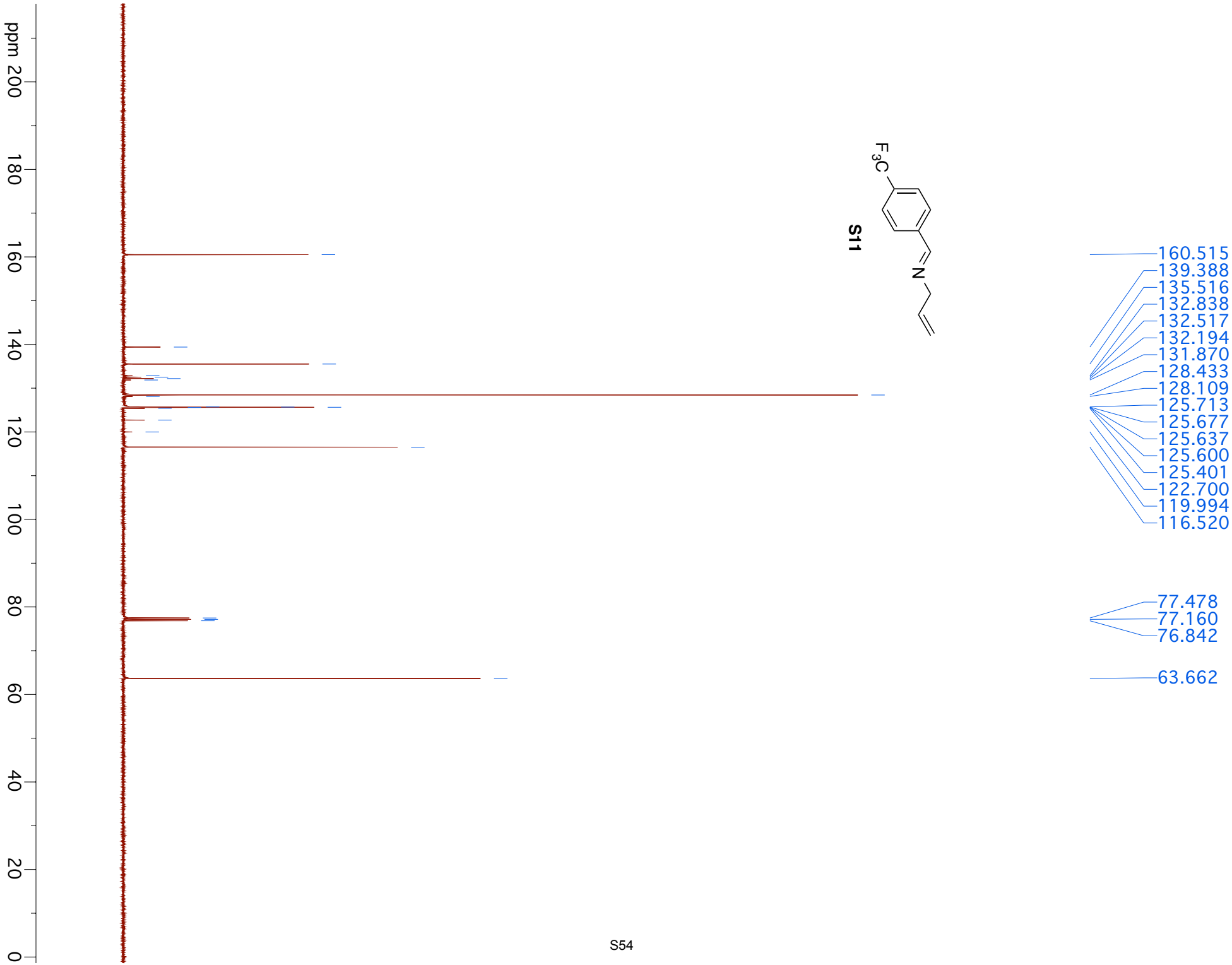
ppm 200
180
160
140
120
100
80
60
40
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F3C
N
S11
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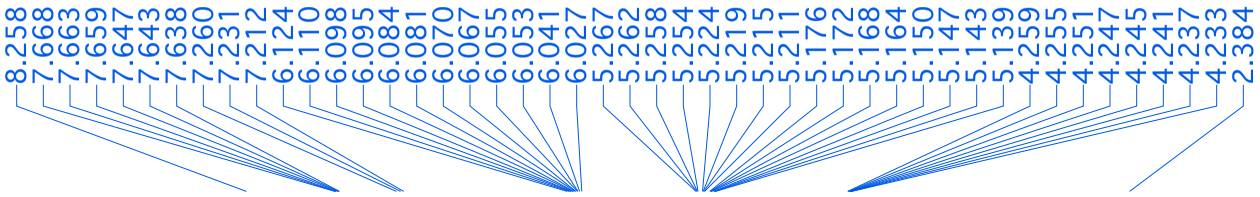
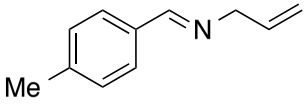
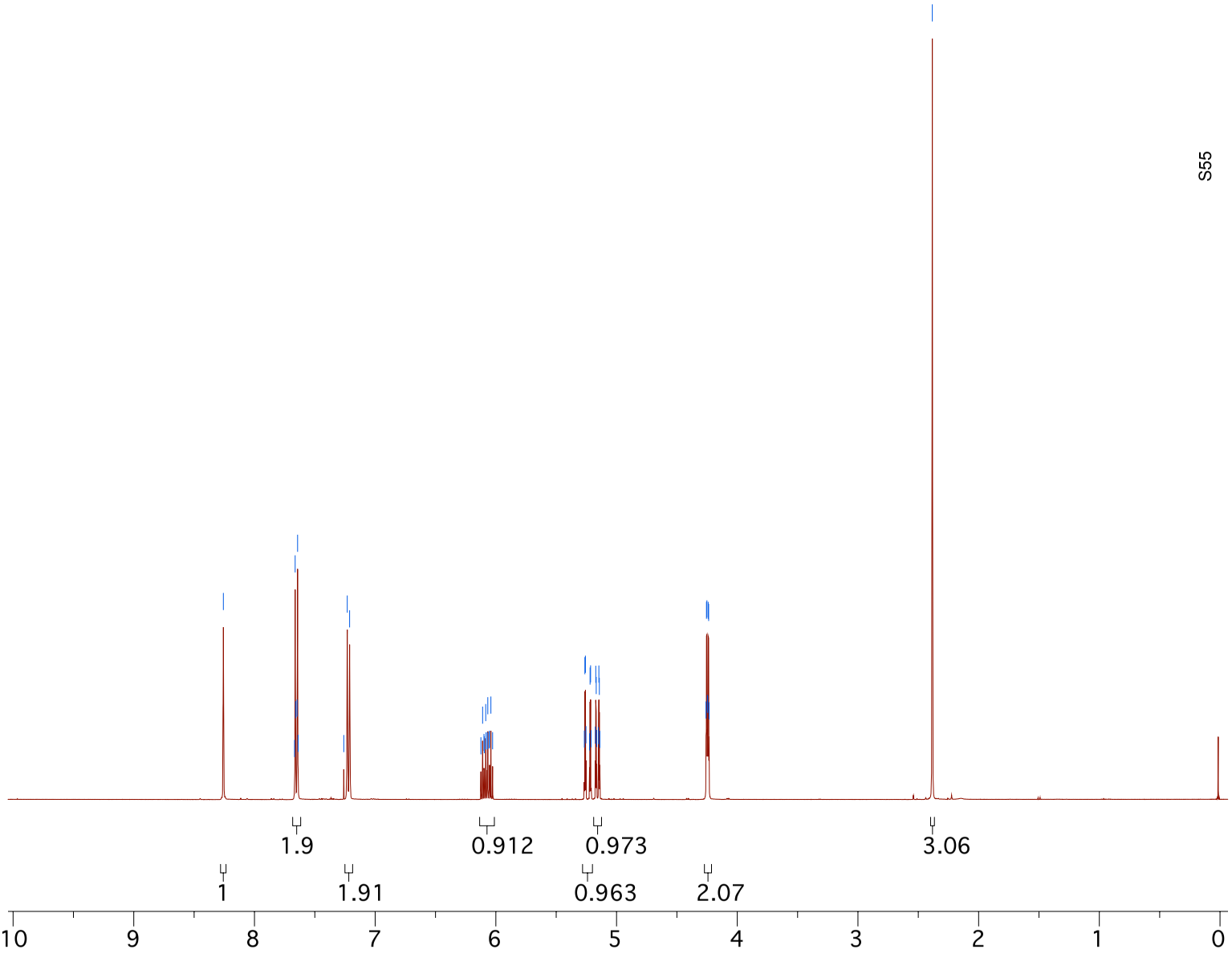
135.516
132.838
132.517
132.194
131.870
128.433
128.109
125.713
125.677
125.637
125.600
125.401
122.700
119.994
116.520
77.478
77.160
76.842
63.662


8.258
7.668
7.663
7.659
7.647
7.643
7.638
7.260
7.231
7.212
6.124
6.110
6.098
6.095
6.084
6.081
6.070
6.067
6.055
6.053
6.041
6.027
5.267
5.262
5.258
5.254
5.224
5.219
5.215
5.211
5.176
5.172
5.168
5.164
5.150
5.147
5.143
5.139
4.259
4.255
4.251
4.247
4.245
4.241
4.237
4.233
2.384


N
Me

S12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1.9
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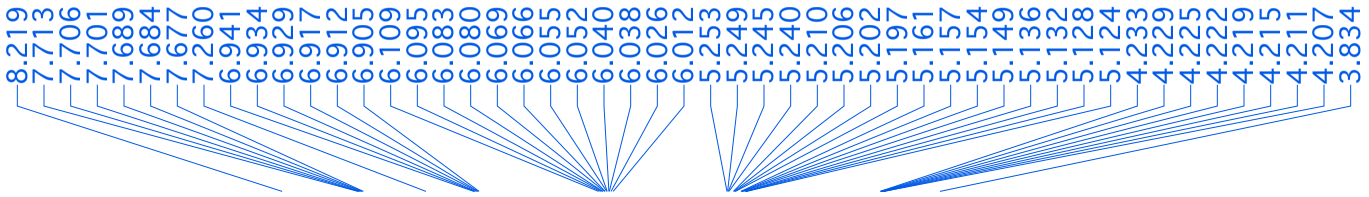
0.973
3.06
1
1.91
0.963
2.07
10
9
8
7
6
5
4
3
2
1
0

ppm
200
180
160
140
120
100
80
60
40
20
0
Me
N
S12
162.015
141.043
136.115
133.649
129.397
128.194
116.051
77.478
77.160
76.842
63.618
21.594


8.219
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7.689
7.684
7.677
7.260
6.941
6.934
6.929
6.917
6.912
6.905
6.109
6.095
6.083
6.080
6.069
6.066
6.055
6.052
6.040
6.038
6.026
6.012
5.253
5.249
5.245
5.240
5.210
5.206
5.202
5.197
5.161
5.157
5.154
5.149
5.136
5.132
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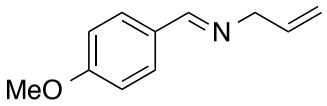
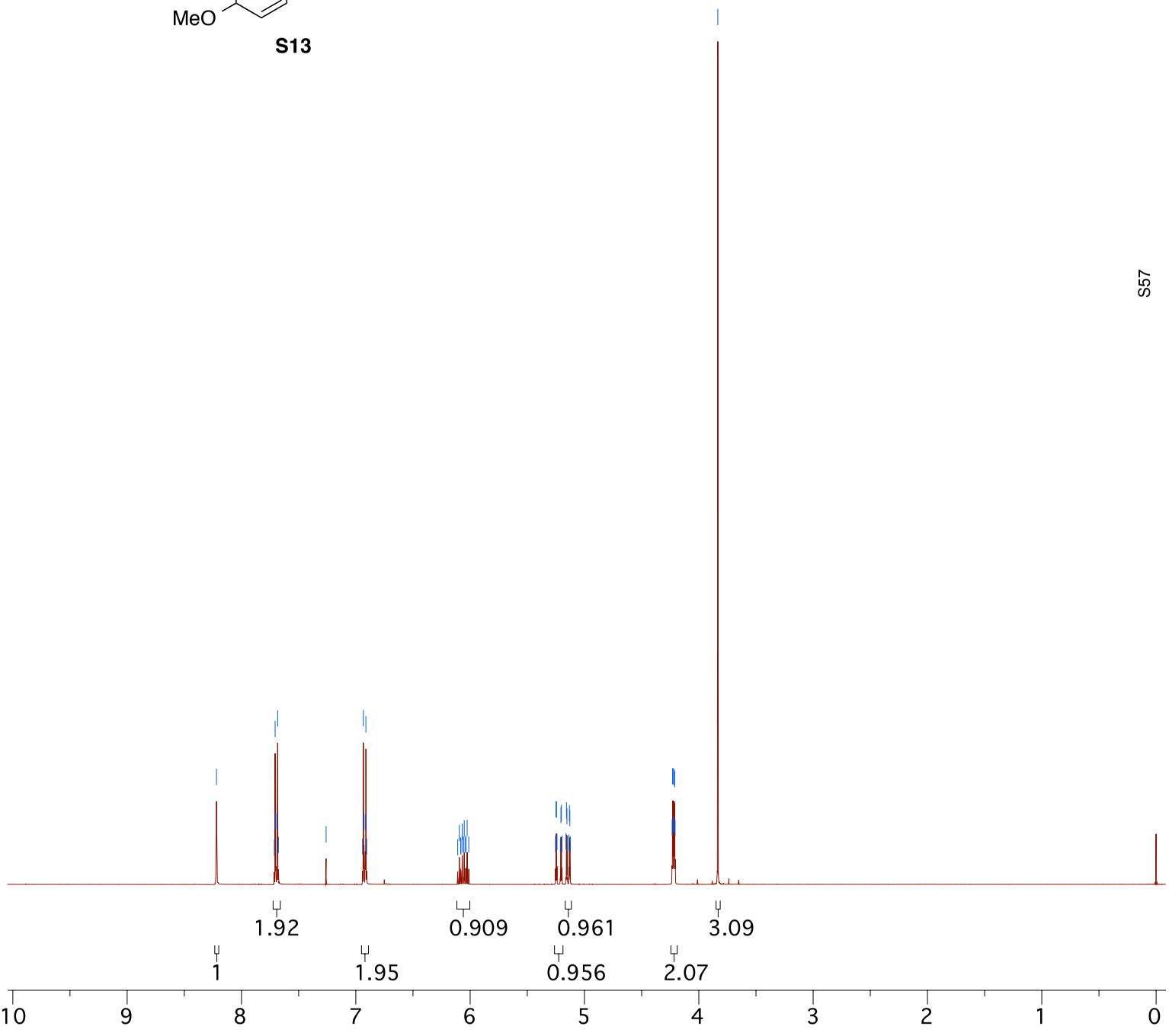
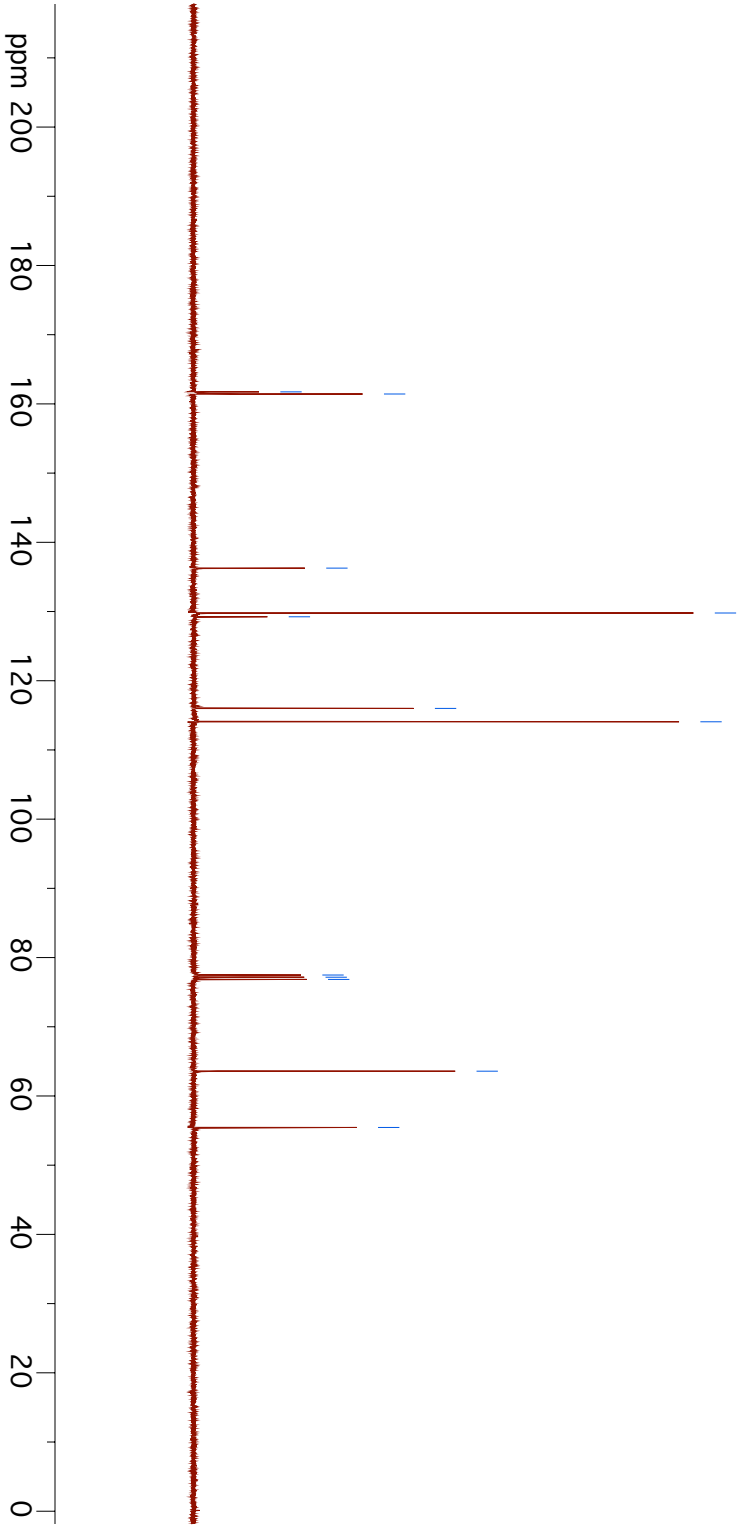
4.219
4.215
4.211
4.207
3.834

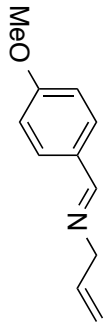

N
MeO

S13


1.92
0.909
0.961
3.09
1
1.95
0.956
2.07
10
9
8
7
6
5
4
3
2
1
0



S13



161.739
161.430

136.271

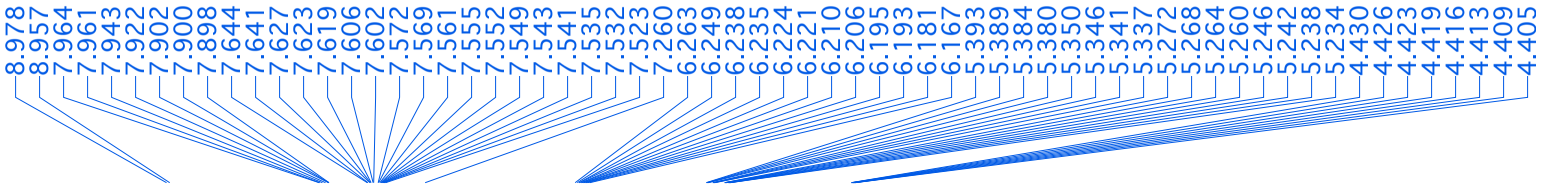
129.786
129.240

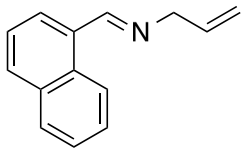
116.001
114.068

77.477
77.160
76.842

63.582

55.451


8.978
8.957
7.964
7.961
7.943
7.922
7.902
7.900
7.898
7.644
7.641
7.627
7.623
7.619
7.606
7.602
7.572
7.569
7.561
7.555
7.552
7.549
7.543
7.541
7.535
7.532
7.523
7.260
6.263
6.249
6.238
6.235
6.224
6.221
6.210
6.206
6.195
6.193
6.181
6.167
5.393
5.389
5.384
5.380
5.350
5.346
5.341
5.337
5.272
5.268
5.264
5.260
5.246
5.242
5.238
5.234
4.430
4.426
4.423
4.419
4.416
4.413
4.409
4.405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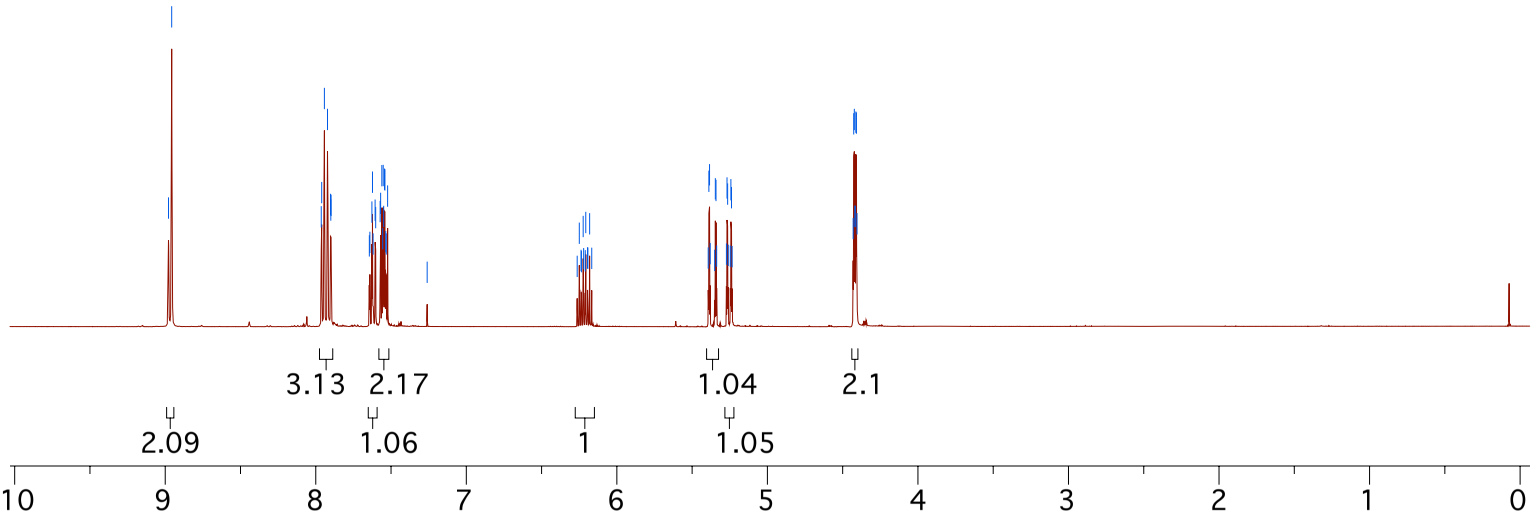
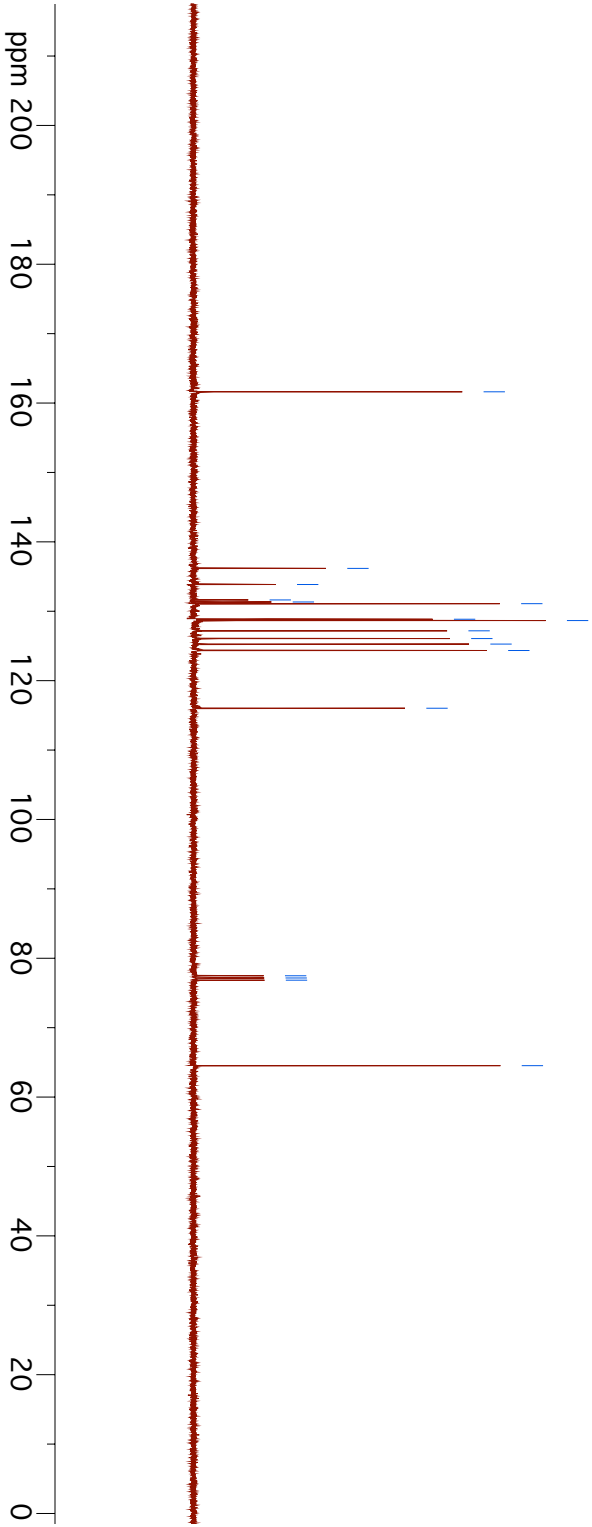
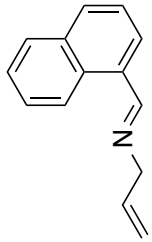
S14


3.13
2.17
1.04
2.1
2.09
1.06
1
1.05
10
9
8
7
6
5
4
3
2
1
0



S14



161.620

136.175
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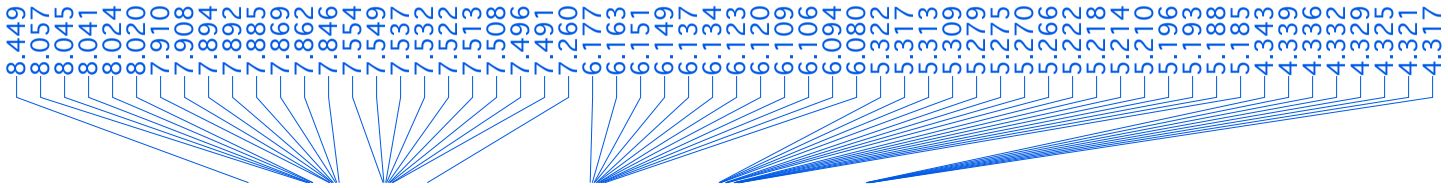
131.631
131.336
131.093
128.850
128.659
127.181
126.066
125.270
124.345
116.026

77.478
77.160
76.842

64.526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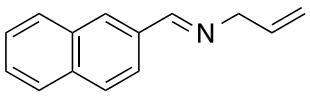
8.057
8.045
8.041
8.024
8.020
7.910
7.908
7.894
7.892
7.885
7.869
7.862
7.846
7.554
7.549
7.537
7.532
7.522
7.513
7.508
7.496
7.491
7.260
6.177
6.163
6.151
6.149
6.137
6.134
6.123
6.120
6.109
6.106
6.094
6.080
5.322
5.317
5.313
5.309
5.279
5.275
5.270
5.266
5.222
5.218
5.214
5.210
5.196
5.193
5.188
5.185
4.343
4.339
4.336
4.332
4.329
4.325
4.321
4.317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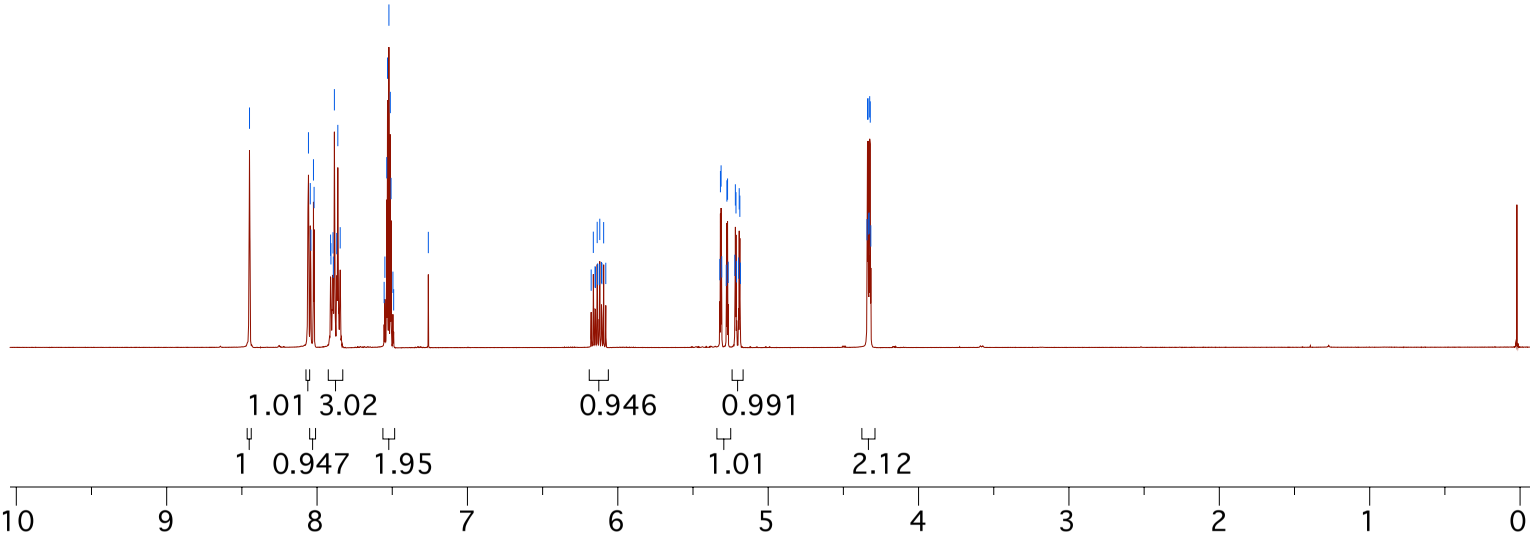
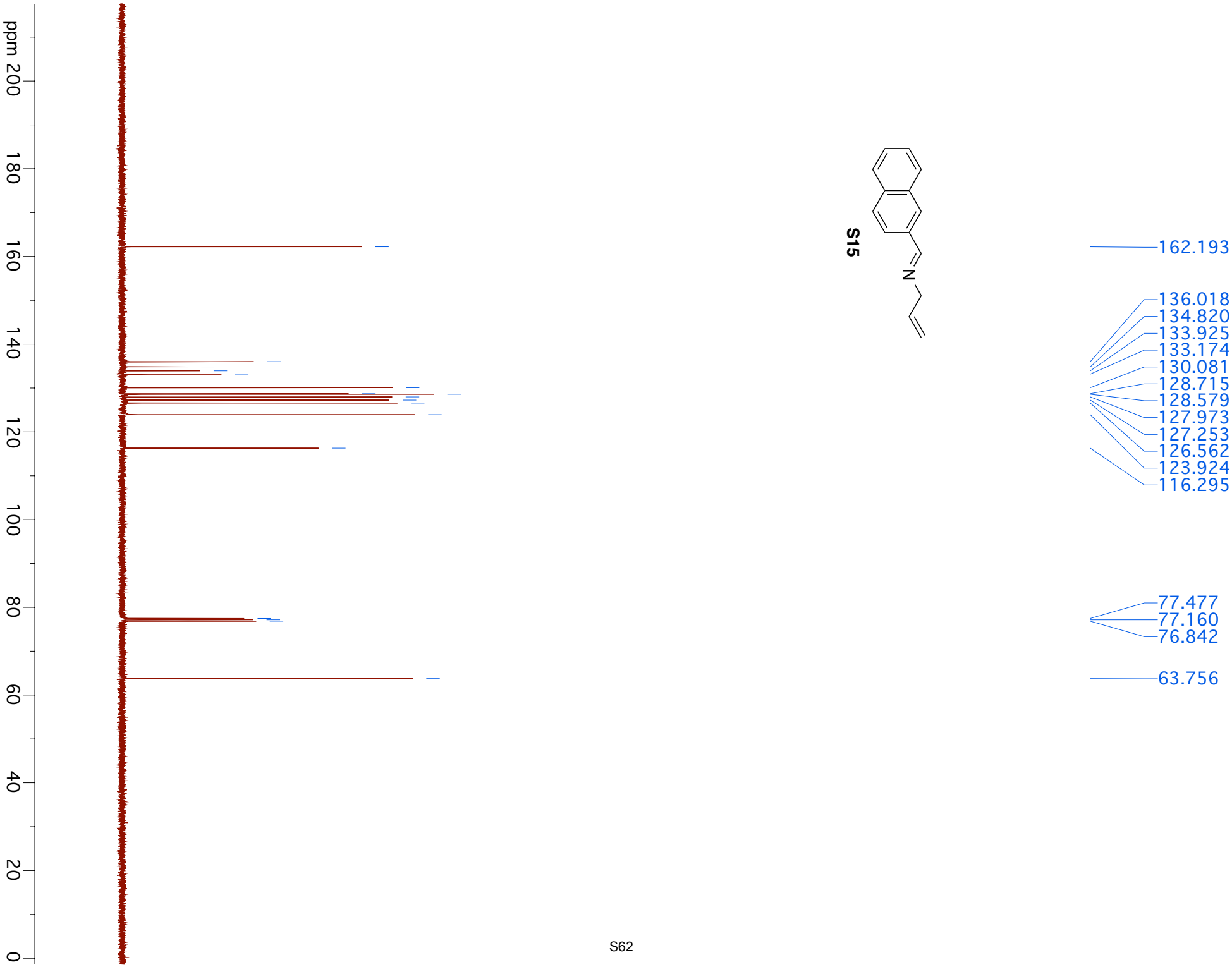
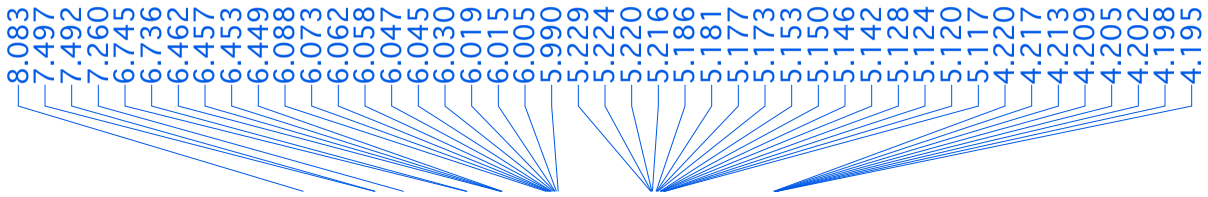
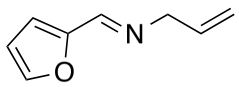
S15

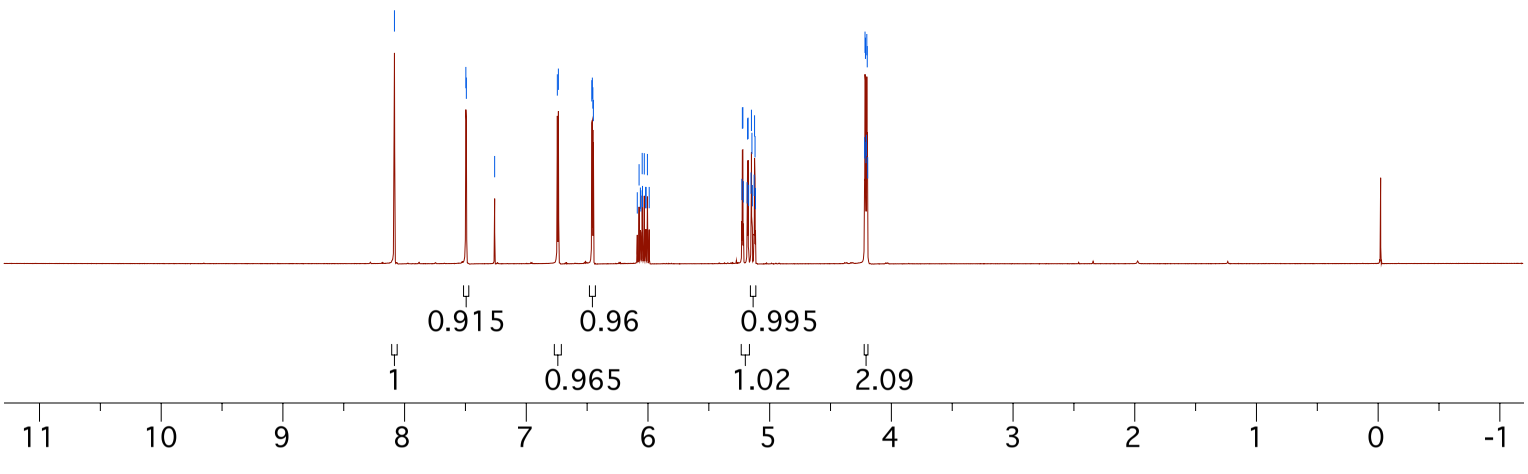

1.01
3.02
0.946
0.991
1
0.947
1.95
1.01
2.12
10
9
8
7
6
5
4
3
2
1
0

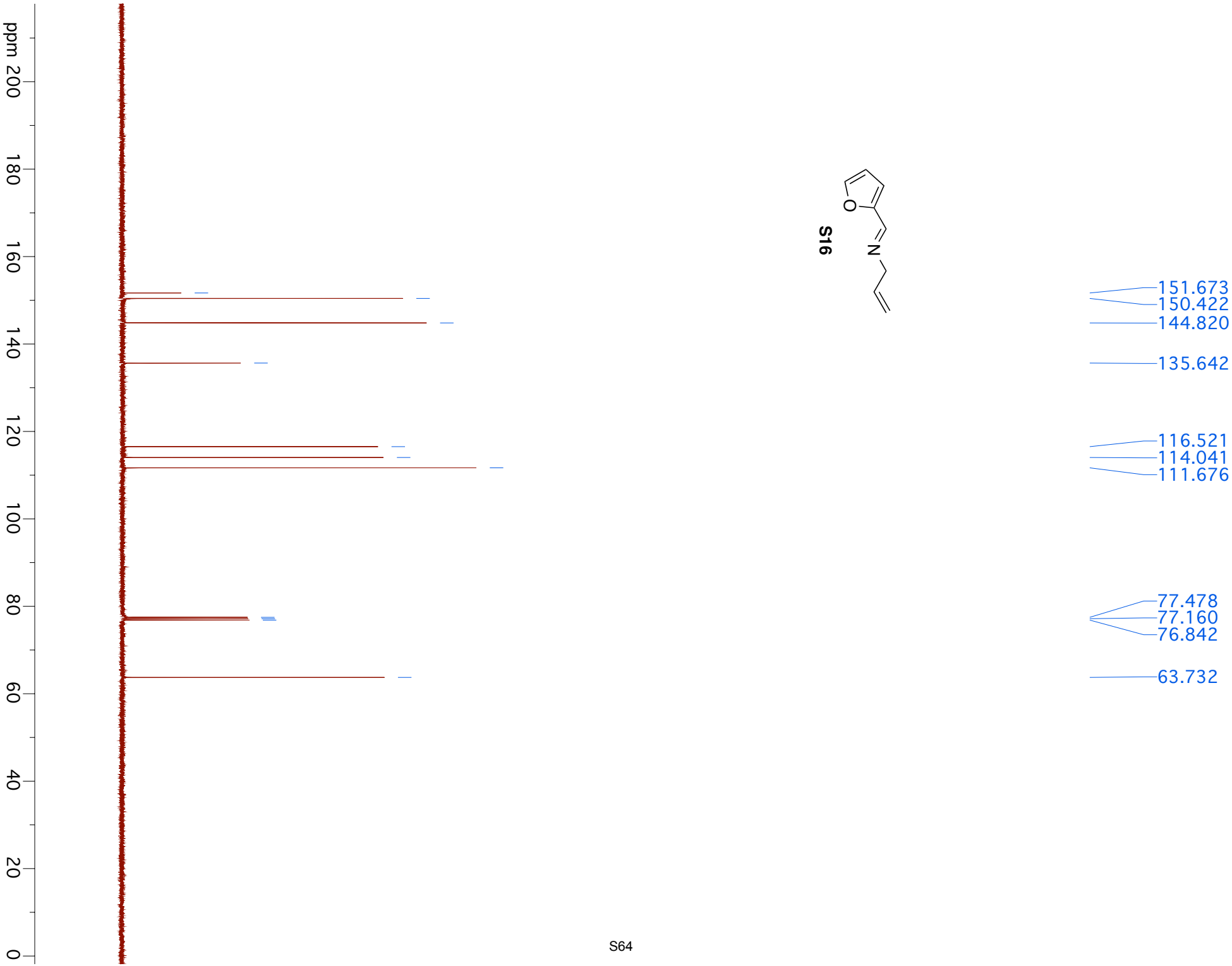

ppm
200
180
160
140
120
100
80
60
40
20
0
S15
N
162.193
136.018
134.820
133.925
133.174
130.081
128.715
128.579
127.973
127.253
126.562
123.924
116.295
77.477
77.160
76.842
63.756

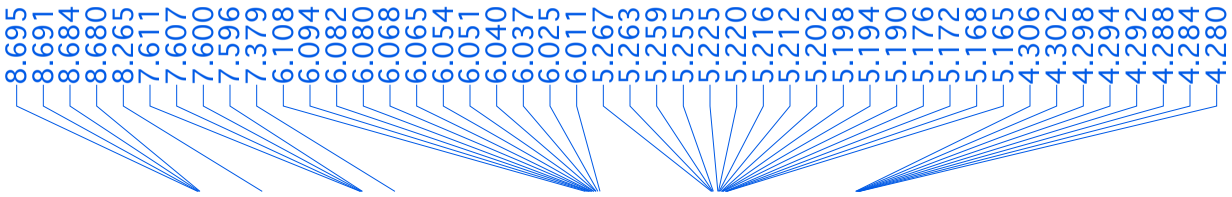

8.083
7.497
7.492
7.260
6.745
6.736
6.462
6.457
6.453
6.449
6.088
6.073
6.062
6.058
6.047
6.045
6.030
6.019
6.015
6.005
5.990
5.229
5.224
5.220
5.216
5.186
5.181
5.177
5.173
5.153
5.150
5.146
5.142
5.128
5.124
5.120
5.117
4.220
4.217
4.213
4.209
4.205
4.202
4.198
4.195

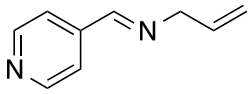

N
O

S16

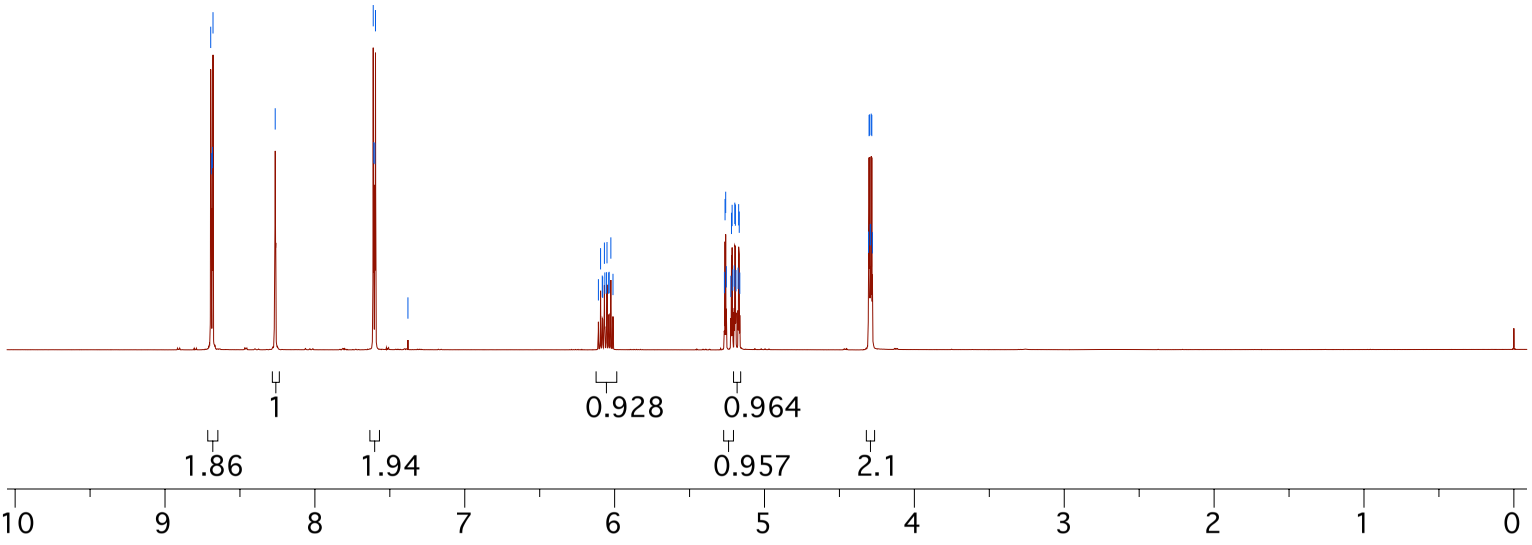

0.915
0.96
0.995
1
0.965
1.02
2.09
11
10
9
8
7
6
5
4
3
2
1
0
-1

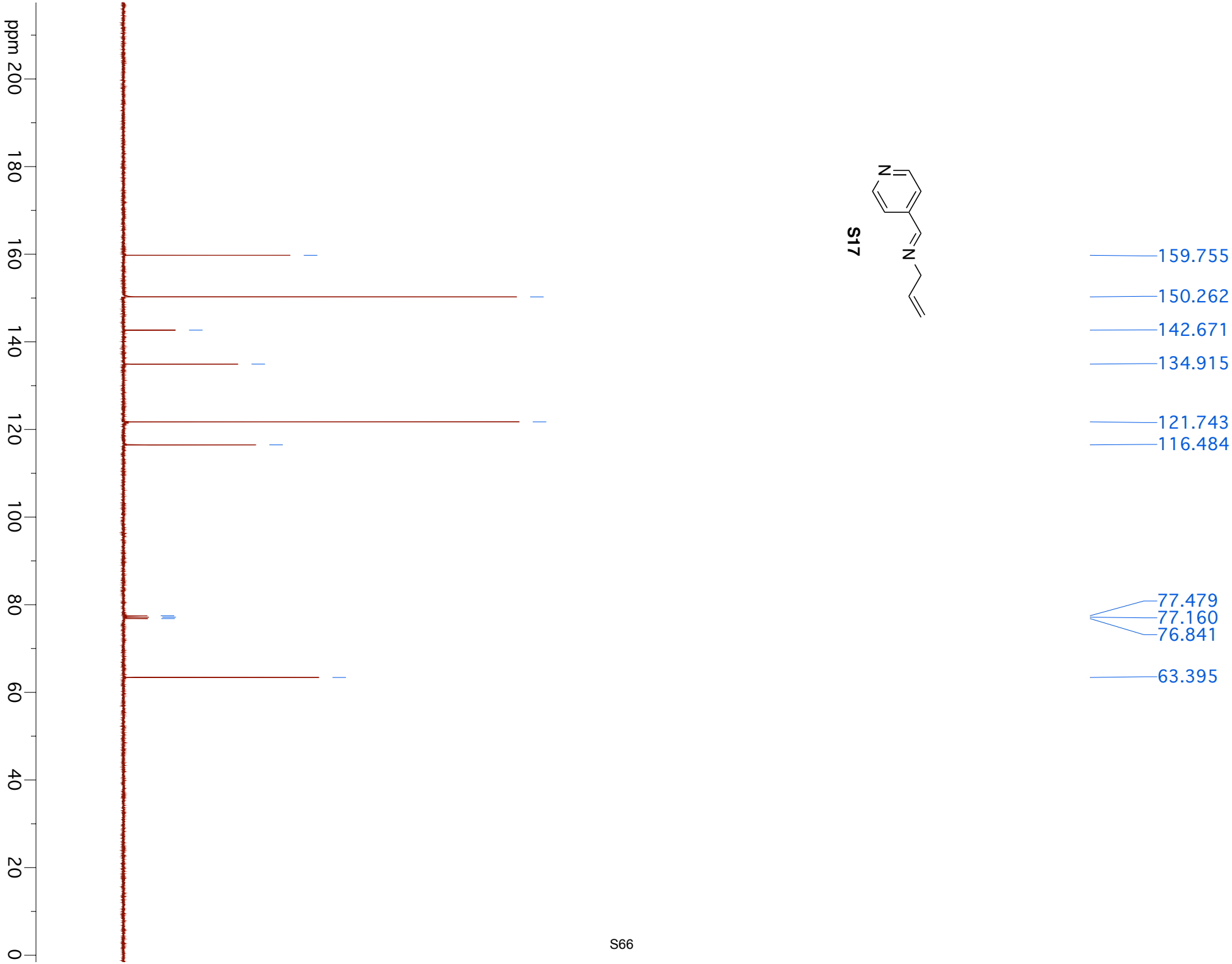

ppm
200
180
160
140
120
100
80
60
40
20
0
S16
151.673
150.422
144.820
135.642
116.521
114.041
111.676
77.478
77.160
76.842
63.732


8.695
8.691
8.684
8.680
8.265
7.611
7.607
7.600
7.596
7.379
6.108
6.094
6.082
6.080
6.068
6.065
6.054
6.051
6.040
6.037
6.025
6.011
5.267
5.263
5.259
5.255
5.225
5.220
5.216
5.212
5.202
5.198
5.194
5.190
5.176
5.172
5.168
5.165
4.306
4.302
4.298
4.294
4.292
4.288
4.284
4.280


N
N

S17


1
0.928
0.964
1.86
1.94
0.957
2.1
10
9
8
7
6
5
4
3
2
1
0


ppm
200
180
160
140
120
100
80
60
40
20
0
S17
N
N
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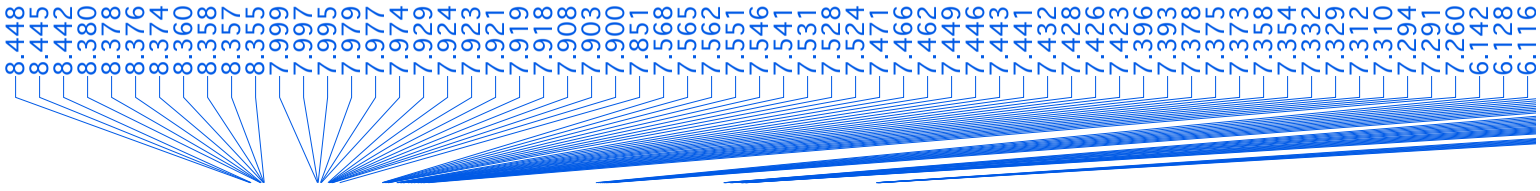
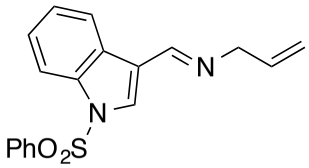
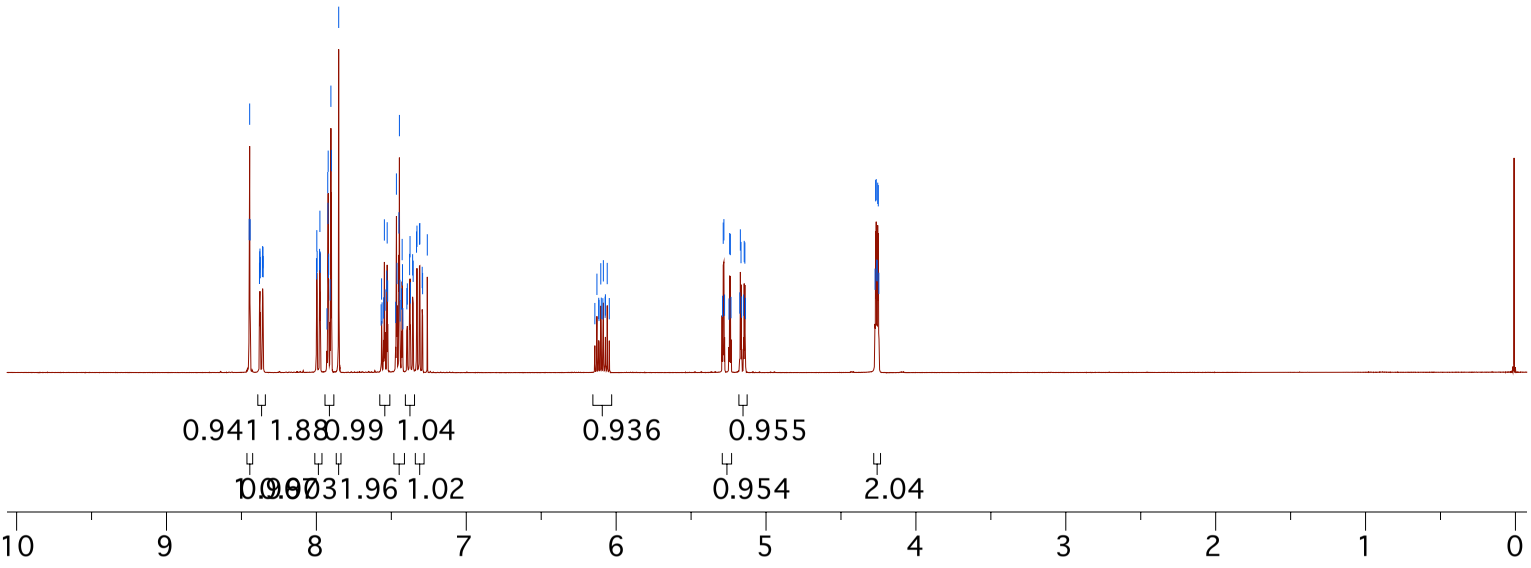
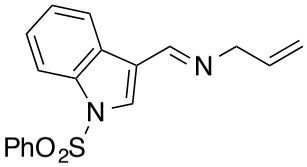
150.262
142.671
134.915
121.743
116.484
77.479
77.160
76.841
63.395


8.448
8.445
8.442
8.380
8.378
8.376
8.374
8.360
8.358
8.357
8.355
7.999
7.997
7.995
7.979
7.977
7.974
7.929
7.924
7.923
7.921
7.919
7.918
7.908
7.903
7.900
7.851
7.568
7.565
7.562
7.551
7.546
7.541
7.531
7.528
7.524
7.471
7.466
7.462
7.449
7.446
7.443
7.441
7.432
7.428
7.426
7.423
7.396
7.393
7.378
7.375
7.373
7.358
7.354
7.332
7.329
7.312
7.310
7.294
7.291
7.260
6.142
6.128
6.116

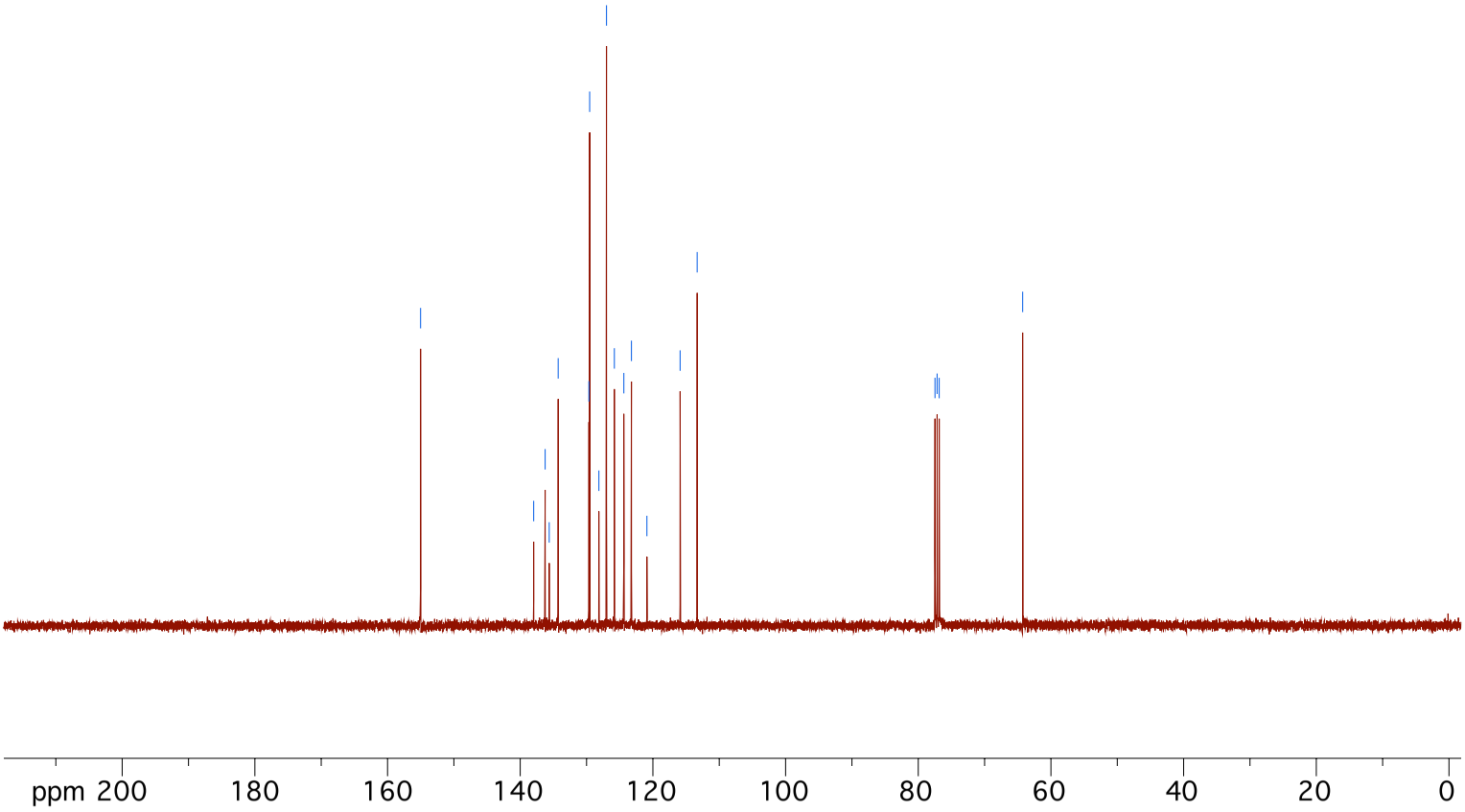

N
N
PhO2S

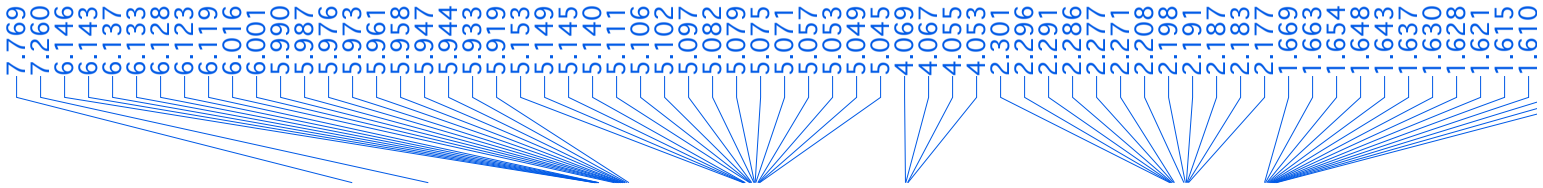
S18

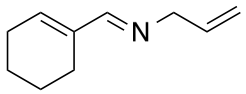

0.941
1.88
0.99
1.04
0.936
0.955
1.02
1.96
0.954
2.04
10
9
8
7
6
5
4
3
2
1
0


N
N
PhO2S

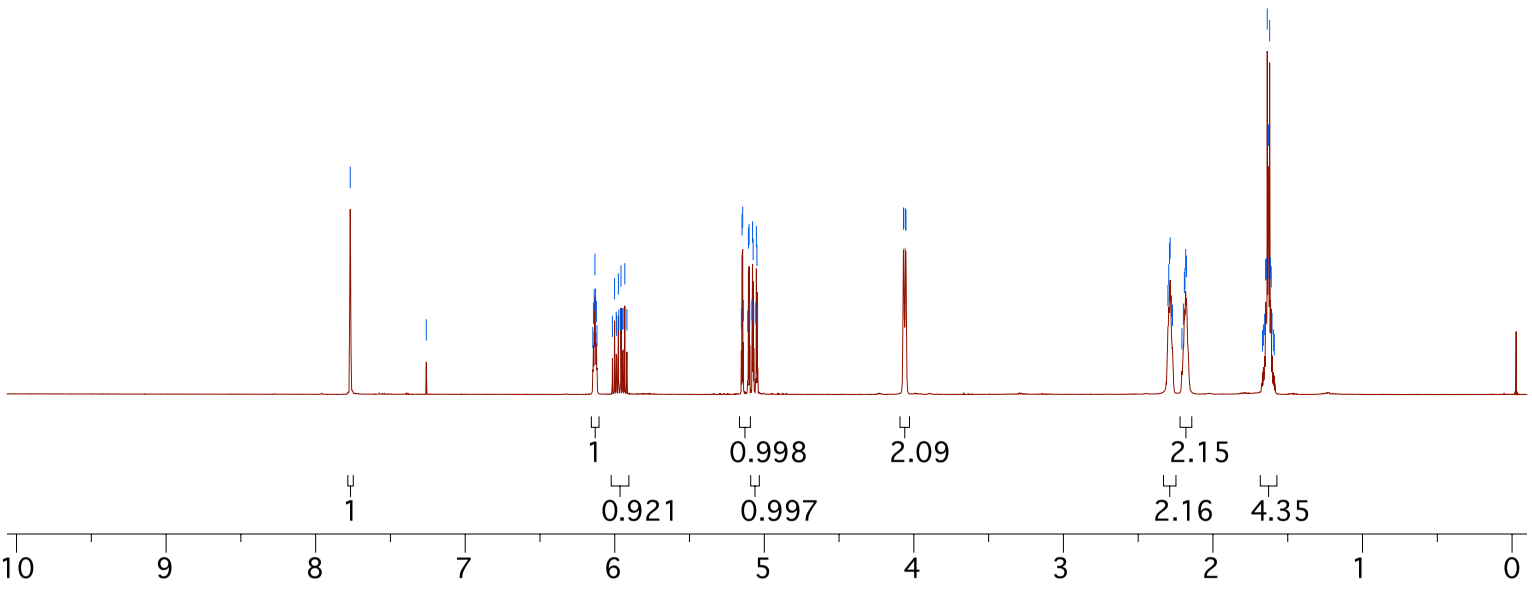
S18


155.017
137.971
136.241
135.630
134.278
129.648
129.532
128.143
126.992
125.808
124.381
123.232
120.905
115.898
113.328
77.478
77.160
76.842
64.261
ppm 200
180
160
140
120
100
80
60
40
20
0


7.769
7.260
6.146
6.143
6.137
6.133
6.128
6.123
6.119
6.016
6.001
5.990
5.987
5.976
5.973
5.961
5.958
5.947
5.944
5.933
5.919
5.153
5.149
5.145
5.140
5.111
5.106
5.102
5.097
5.082
5.079
5.075
5.071
5.057
5.053
5.049
5.045
4.069
4.067
4.055
4.053
2.301
2.296
2.291
2.286
2.277
2.271
2.208
2.198
2.191
2.187
2.183
2.177
1.669
1.663
1.654
1.648
1.643
1.637
1.630
1.628
1.621
1.615
1.610


N

S19


1
0.998
2.09
2.15
1
0.921
0.997
2.16
4.35
10
9
8
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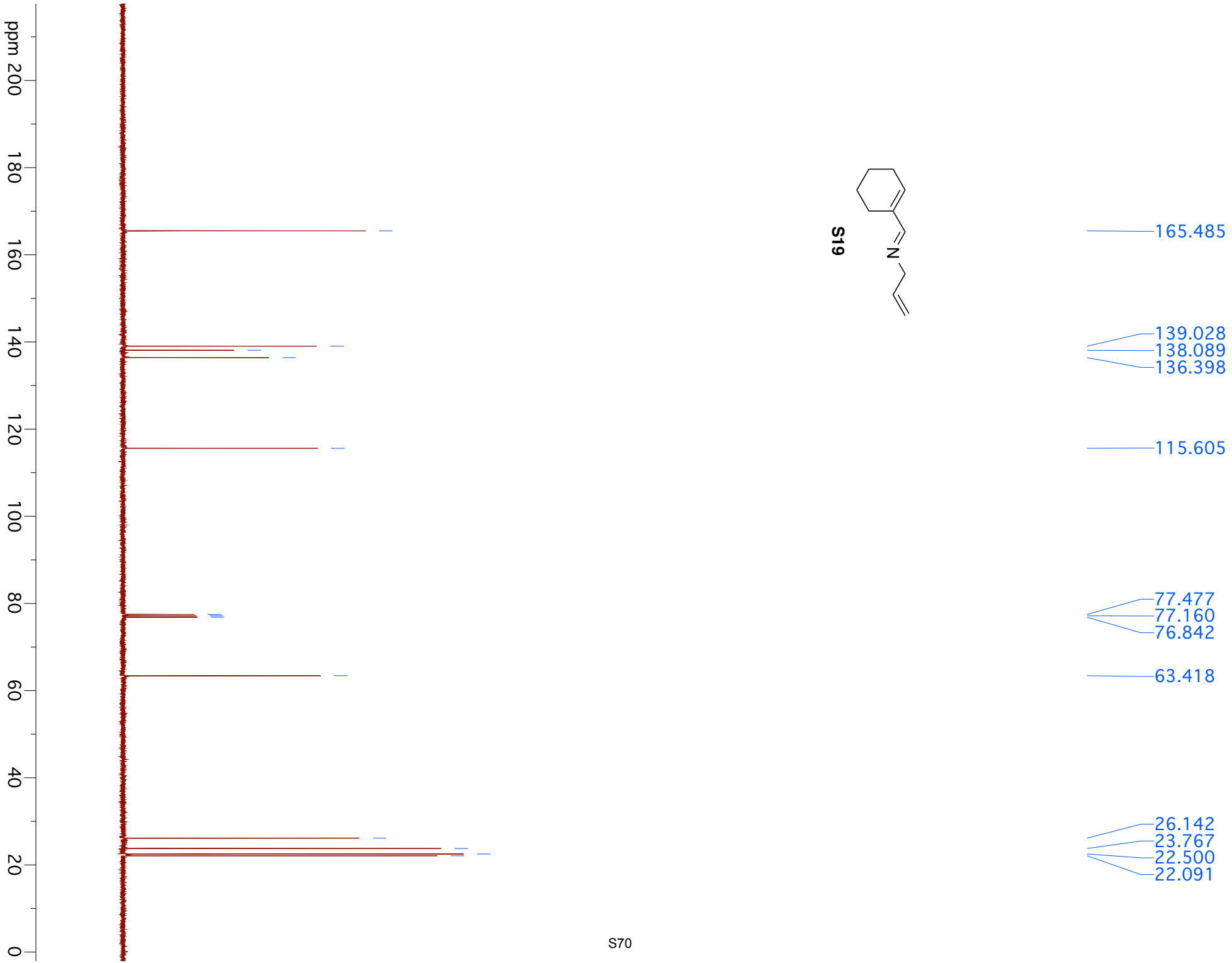
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63.418
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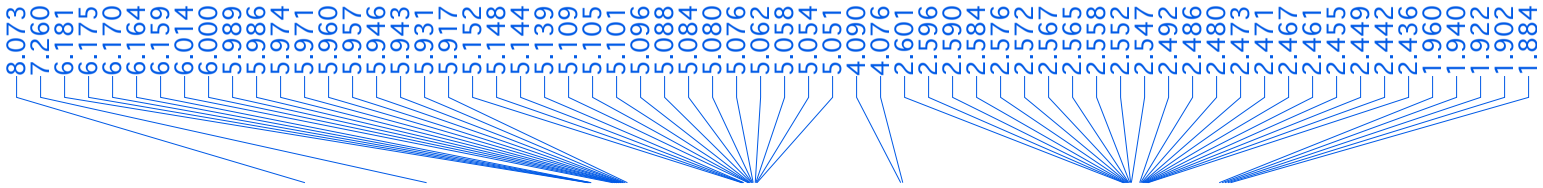
22.091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5.144
5.139
5.109
5.105
5.101
5.096
5.088
5.084
5.080
5.076
5.062
5.058
5.054
5.051
4.090
4.076
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2.596
2.590
2.584
2.576
2.572
2.567
2.565
2.558
2.552
2.547
2.492
2.486
2.480
2.473
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2.442
2.436
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1.940
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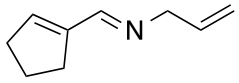
1.902
1.884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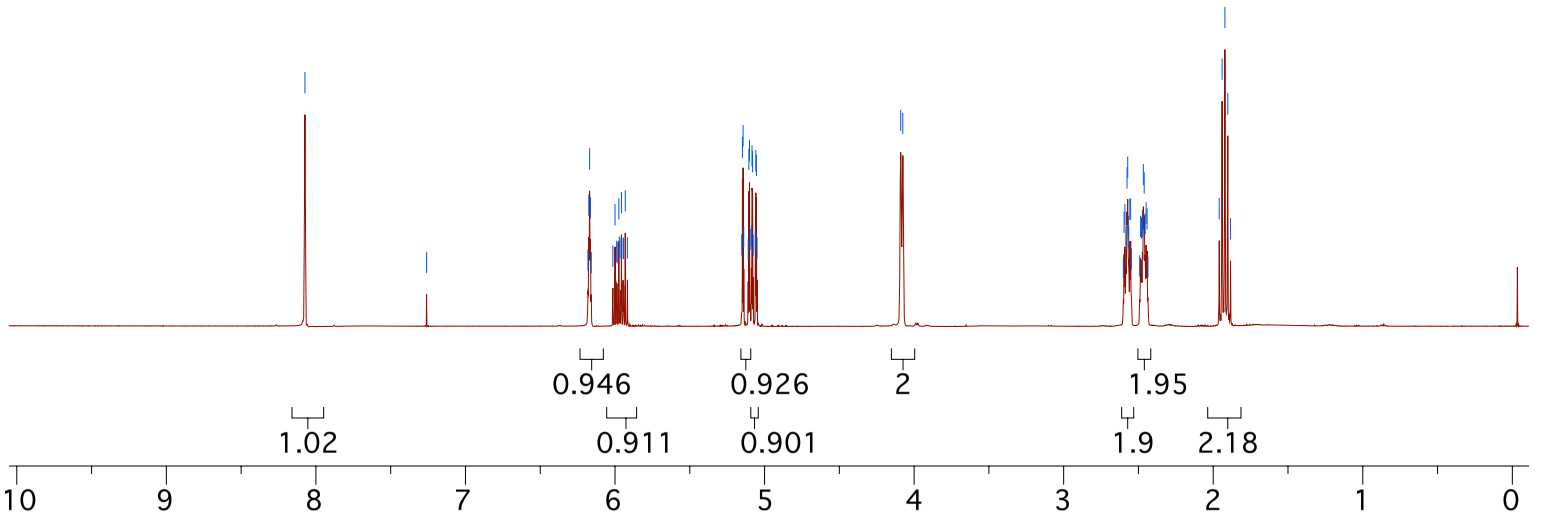
S20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0.901
1.9
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9
8
7
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5
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3
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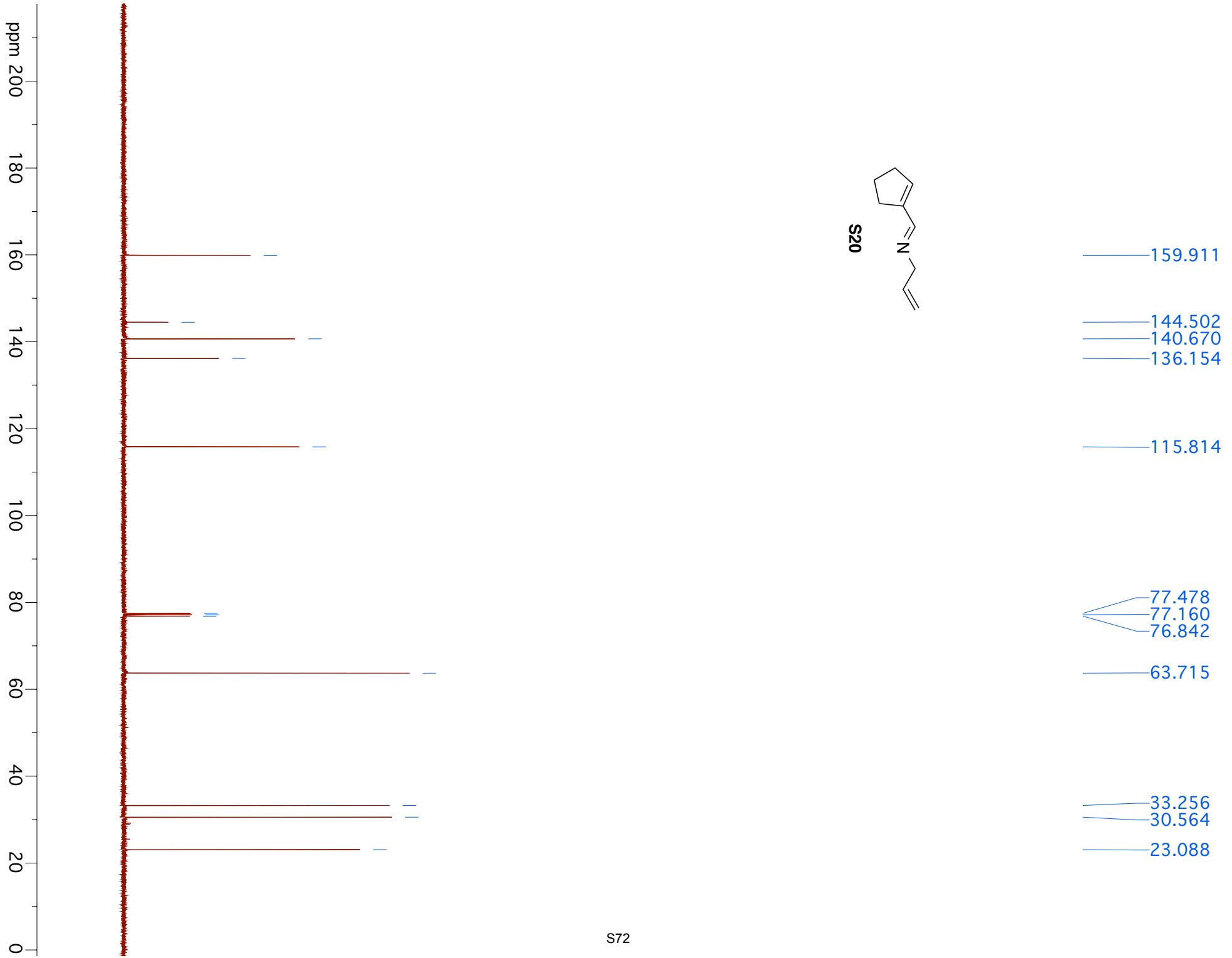
1
0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60
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S20
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77.160
76.842
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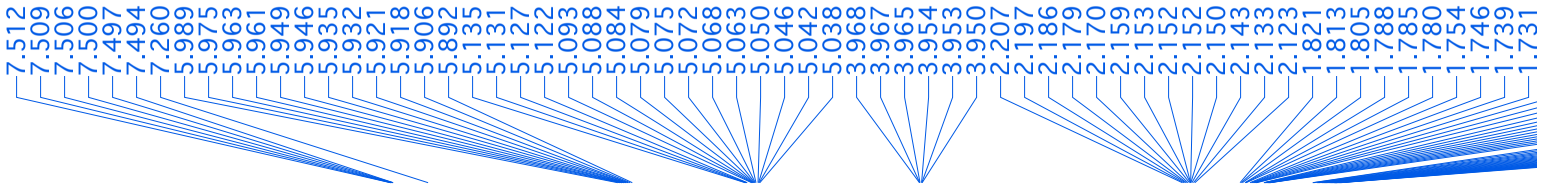
33.256
30.564
23.088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5.961
5.949
5.946
5.935
5.932
5.921
5.918
5.906
5.892
5.135
5.131
5.127
5.122
5.093
5.088
5.084
5.079
5.075
5.072
5.068
5.063
5.050
5.046
5.042
5.038
3.968
3.967
3.965
3.954
3.953
3.950
2.207
2.197
2.186
2.179
2.170
2.159
2.153
2.152
2.150
2.143
2.133
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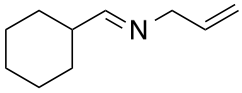
1.805
1.788
1.785
1.780
1.754
1.746
1.739
1.731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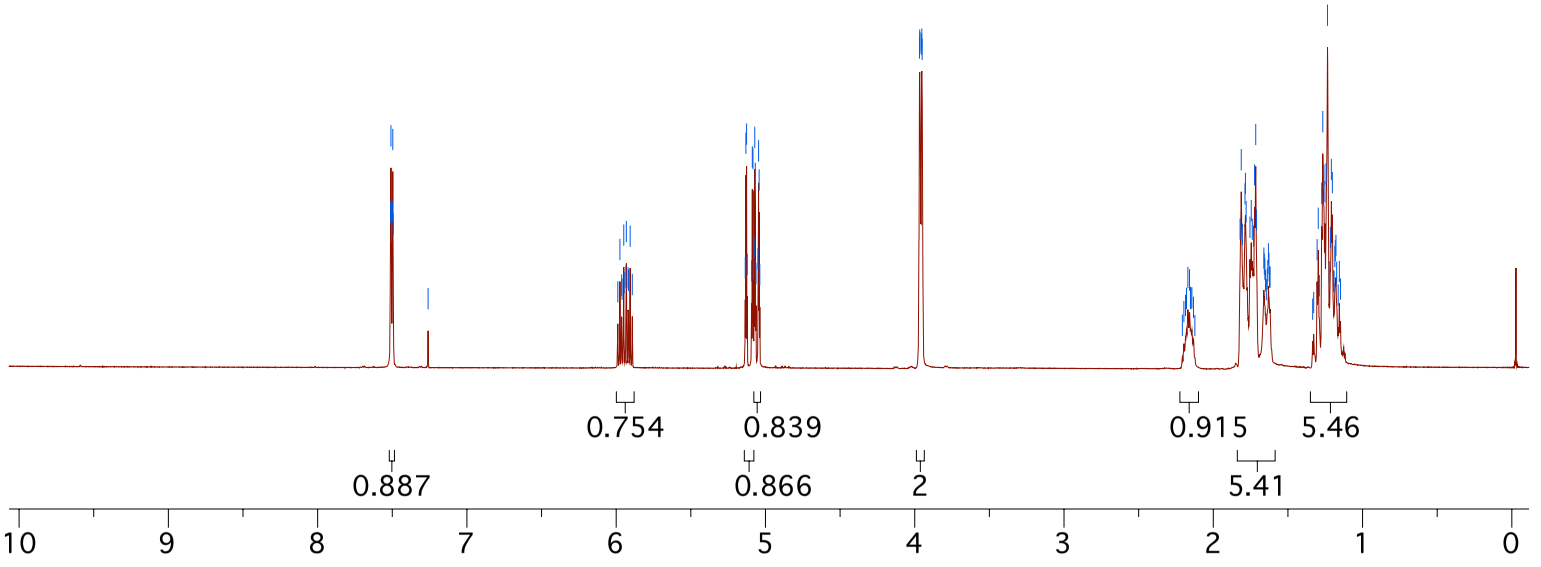
S21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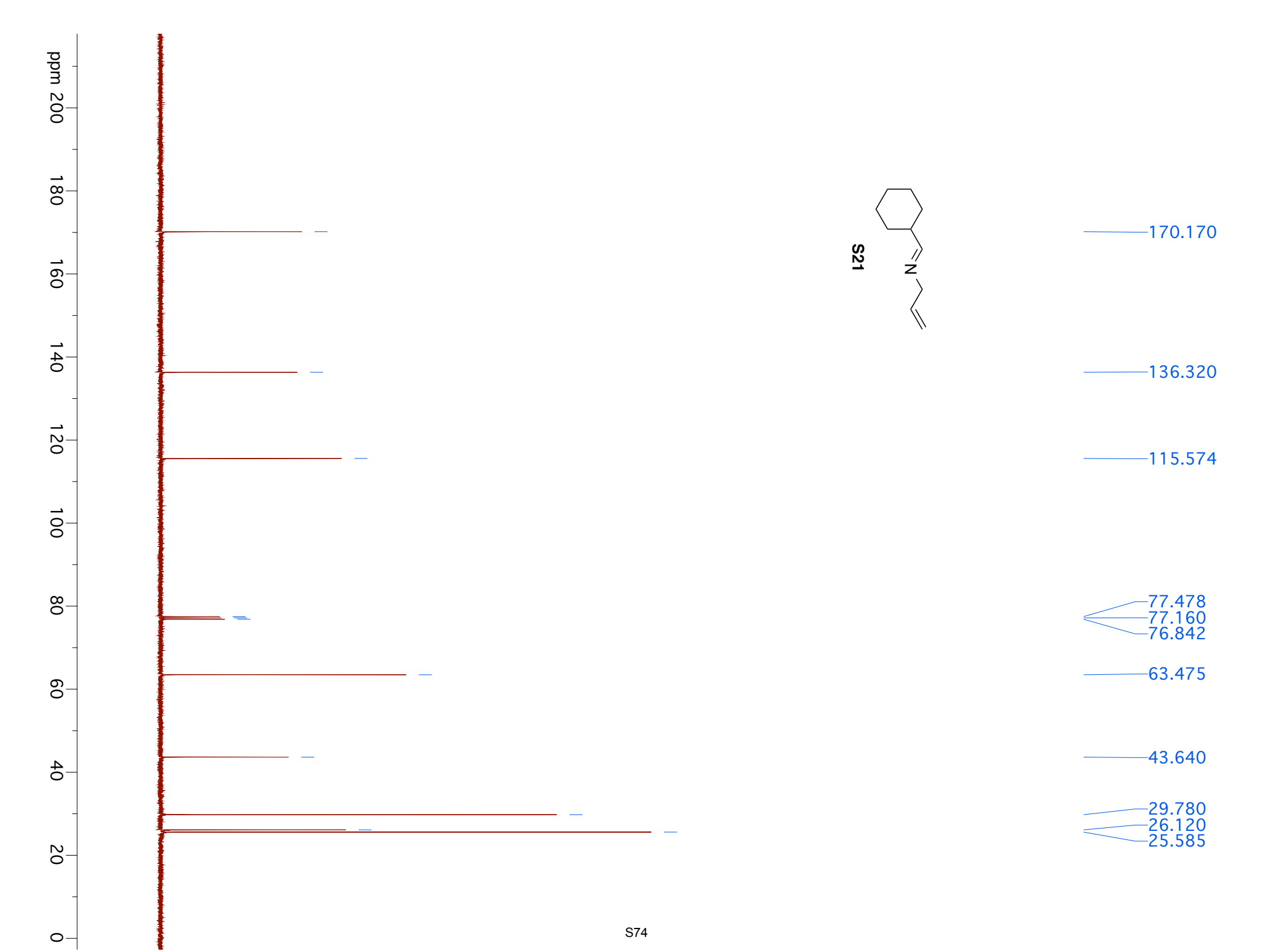
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60
40
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77.478
77.160
76.842
63.475
43.640
29.780
26.120
25.585

ppm
10
9
8
7
6
5
4
3
2
1
0
0.898
1.03
1.04
1.98
2.17
8.41
10.257
7.854
7.850
7.834
7.831
7.547
7.543
7.528
7.524
7.510
7.506
7.438
7.435
7.420
7.416
7.401
7.398
7.342
7.339
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2.546
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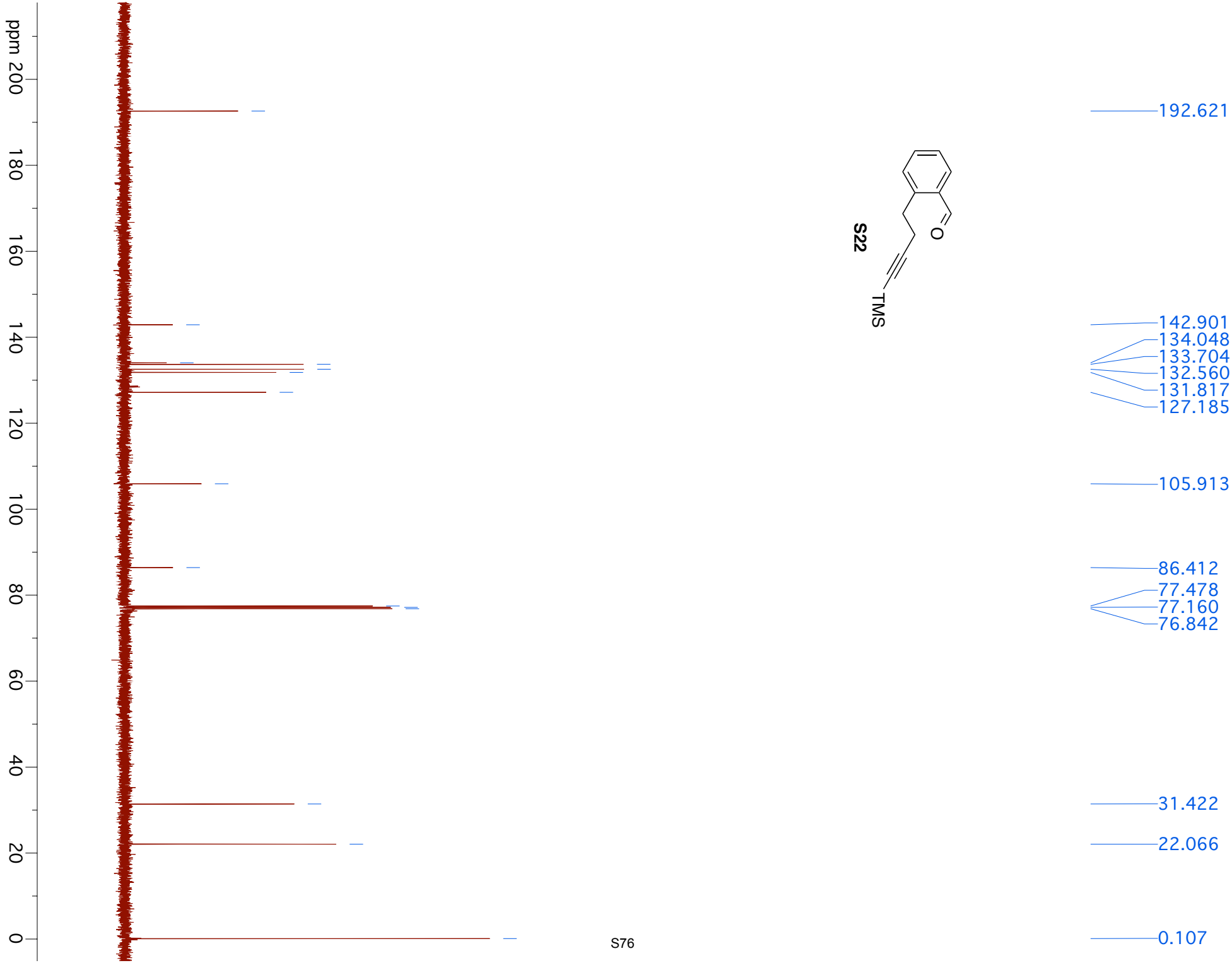
S22
O
TMS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160
140
120
100
80
60
40
20
0
S22
O
TMS
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127.185
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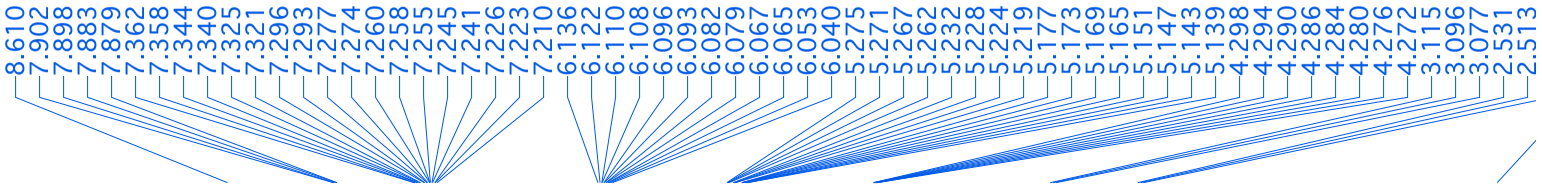
77.160
76.842
31.422
22.066
0.107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7.321
7.296
7.293
7.277
7.274
7.260
7.258
7.255
7.245
7.241
7.226
7.223
7.210
6.136
6.122
6.110
6.108
6.096
6.093
6.082
6.079
6.067
6.065
6.053
6.040
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5.271
5.267
5.262
5.232
5.228
5.224
5.219
5.177
5.173
5.169
5.165
5.151
5.147
5.143
5.139
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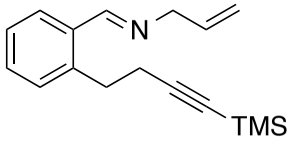
N
TMS

S23

S77
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7
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3
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1
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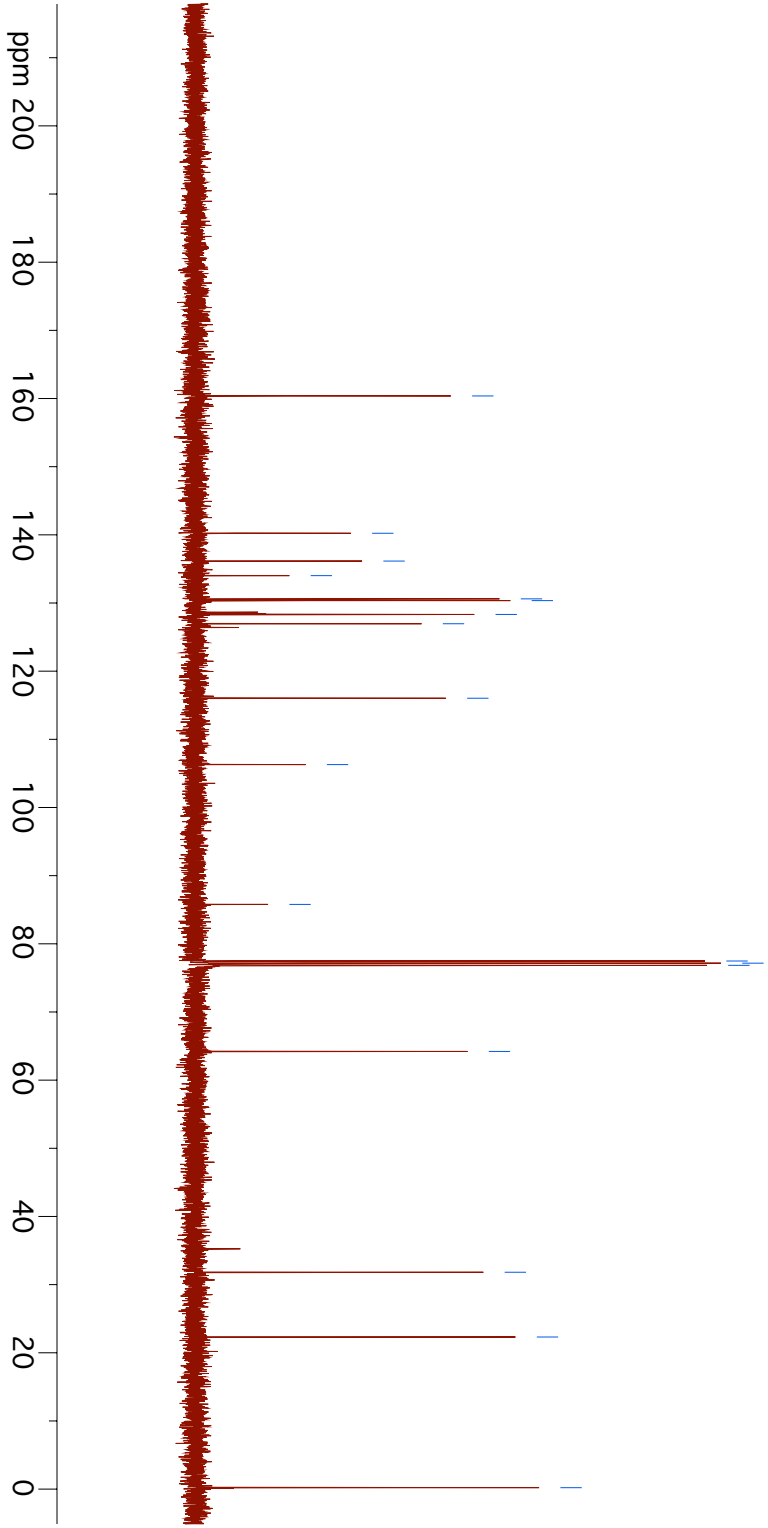
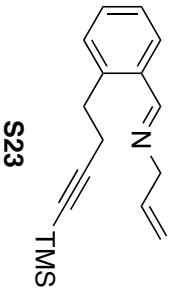


S23



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116.029

106.292

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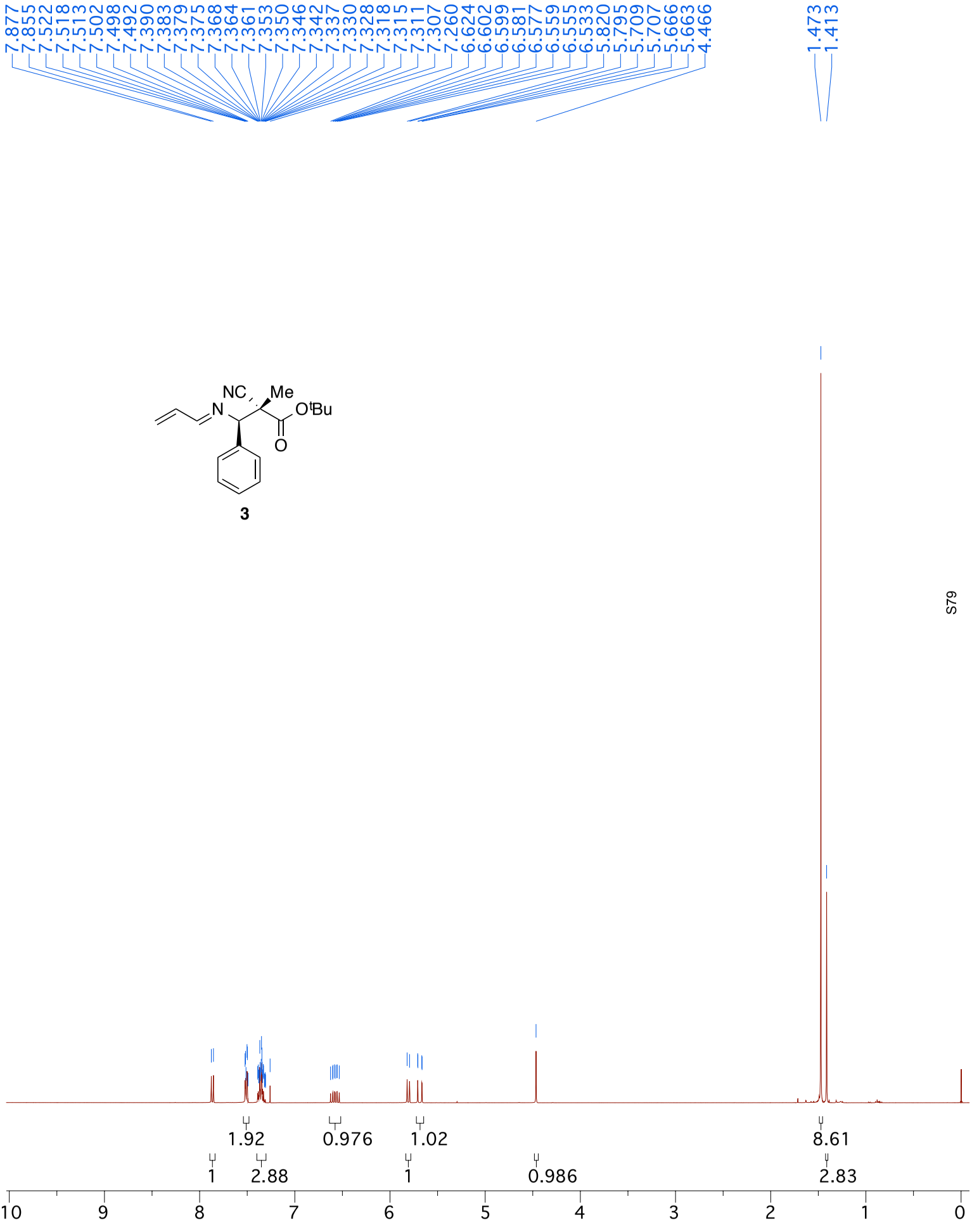
77.160
76.842

64.210

31.817

22.315

0.209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7.364
7.361
7.353
7.350
7.346
7.342
7.337
7.330
7.328
7.318
7.315
7.311
7.307
7.260
6.624
6.602
6.599
6.581
6.577
6.559
6.555
6.533
5.820
5.795
5.709
5.707
5.666
5.663
4.466
1.473
1.413
NC
Me
N
O
O
tBu
3
S79
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1.02
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6
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2
1
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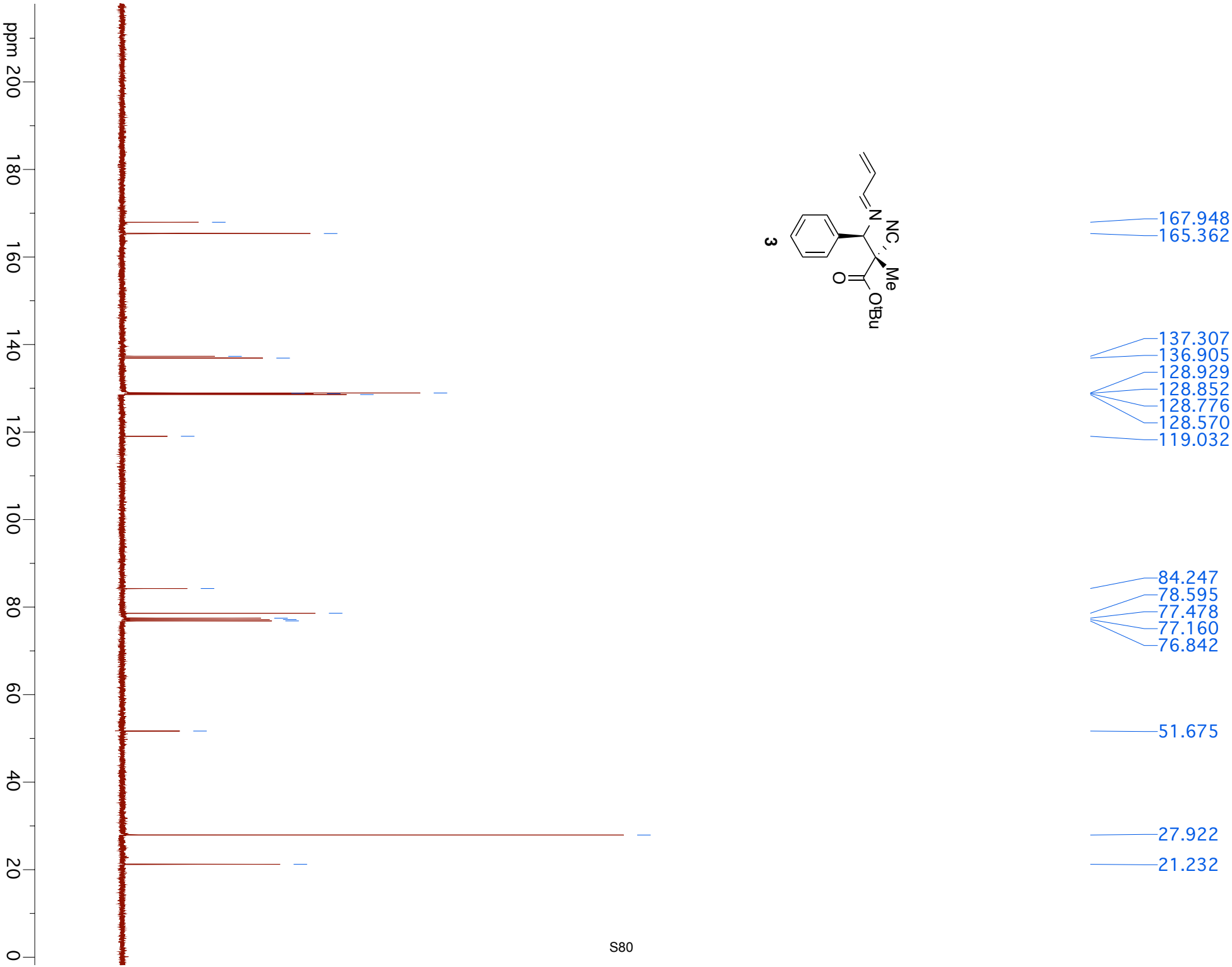
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60
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20
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3
N
NC
Me
O
O
tBu
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165.362
137.307
136.905
128.929
128.852
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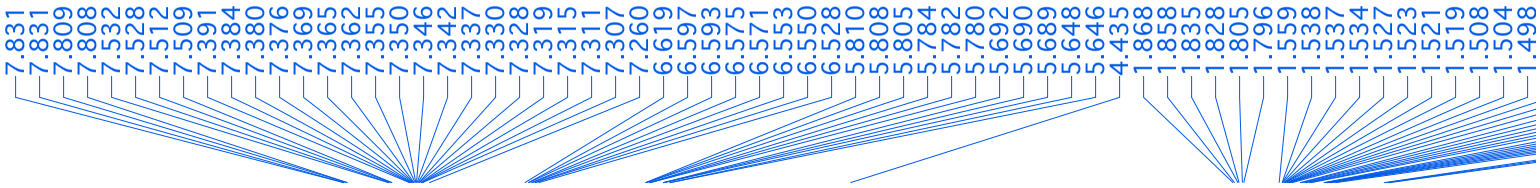
128.570
119.032
84.247
78.595
77.478
77.160
76.842
51.675
27.922
21.232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7.369
7.365
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7.350
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7.342
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7.319
7.315
7.311
7.307
7.260
6.619
6.597
6.593
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6.571
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6.550
6.528
5.810
5.808
5.805
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1.858
1.835
1.828
1.805
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1.523
1.521
1.519
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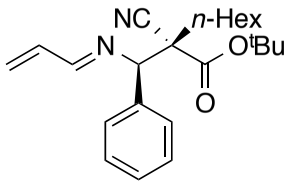
1.504
1.498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n-Hex
N
OtBu
O

4

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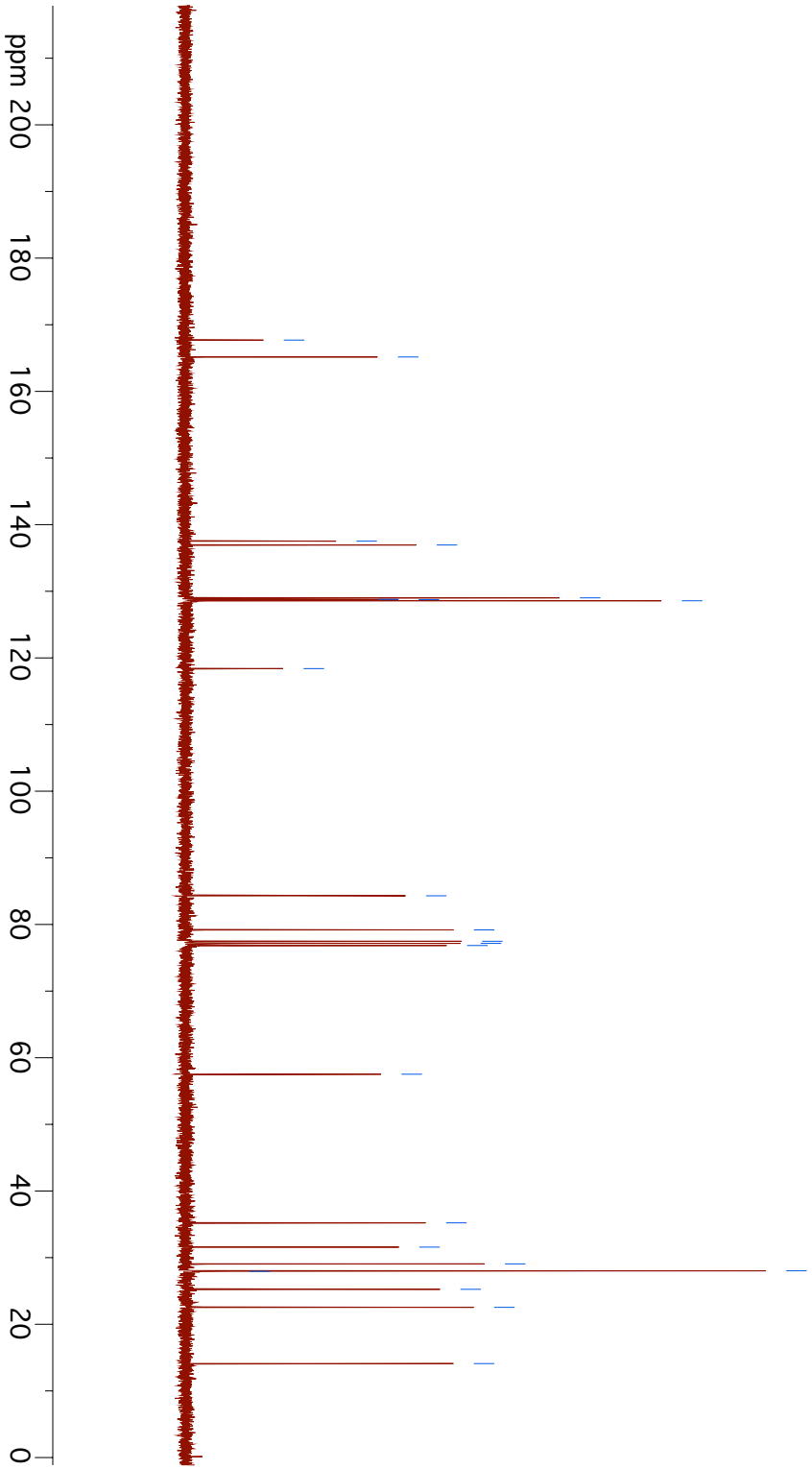

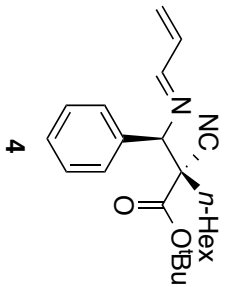

4

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136.946
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128.756
128.575
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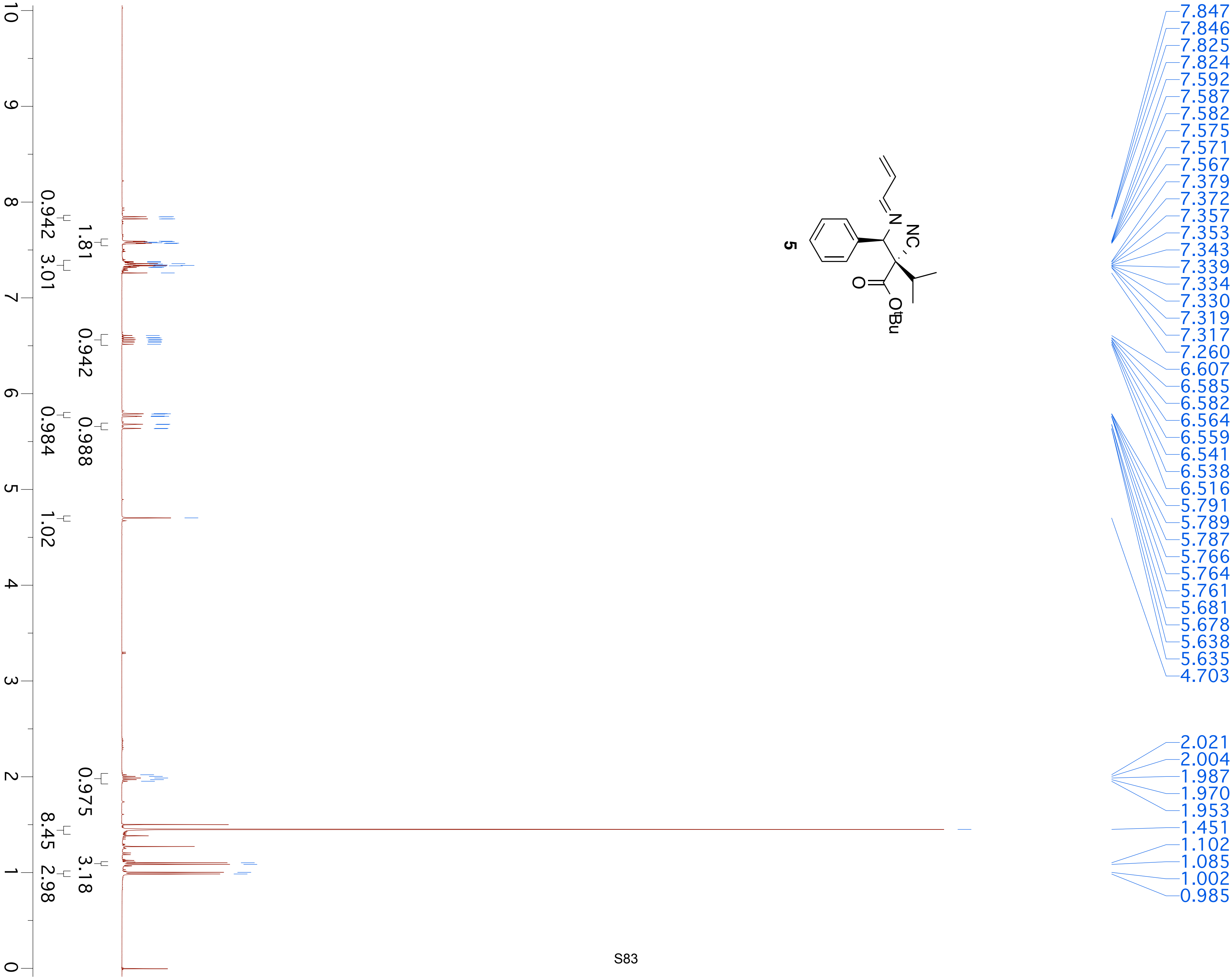
77.477
77.160
76.843
57.526
35.218
31.580
29.061
28.025
27.940
25.248
22.541
14.101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7.334
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6.564
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5.635
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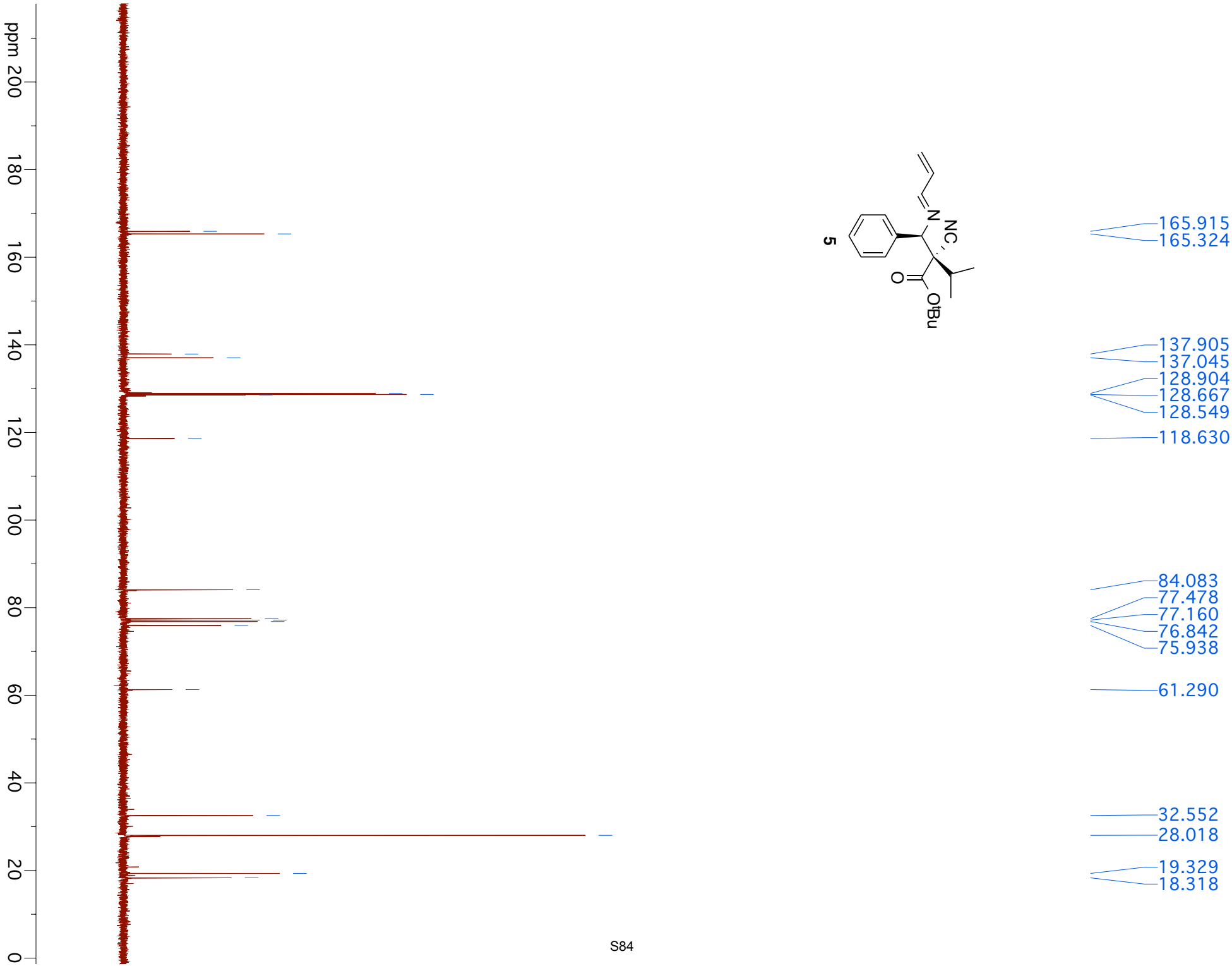
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O
OtBu
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128.904
128.667
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19.329
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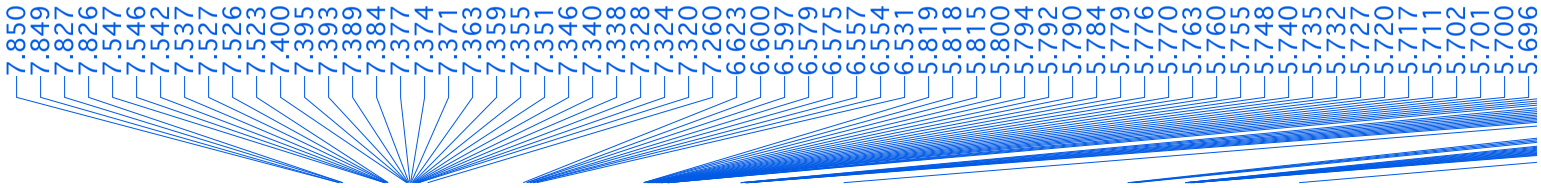
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6.554
6.531
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5.779
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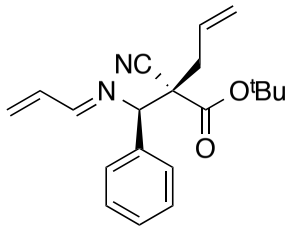
5.700
5.696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N
O
O
tBu

6

S85

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1.08
8.73
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7
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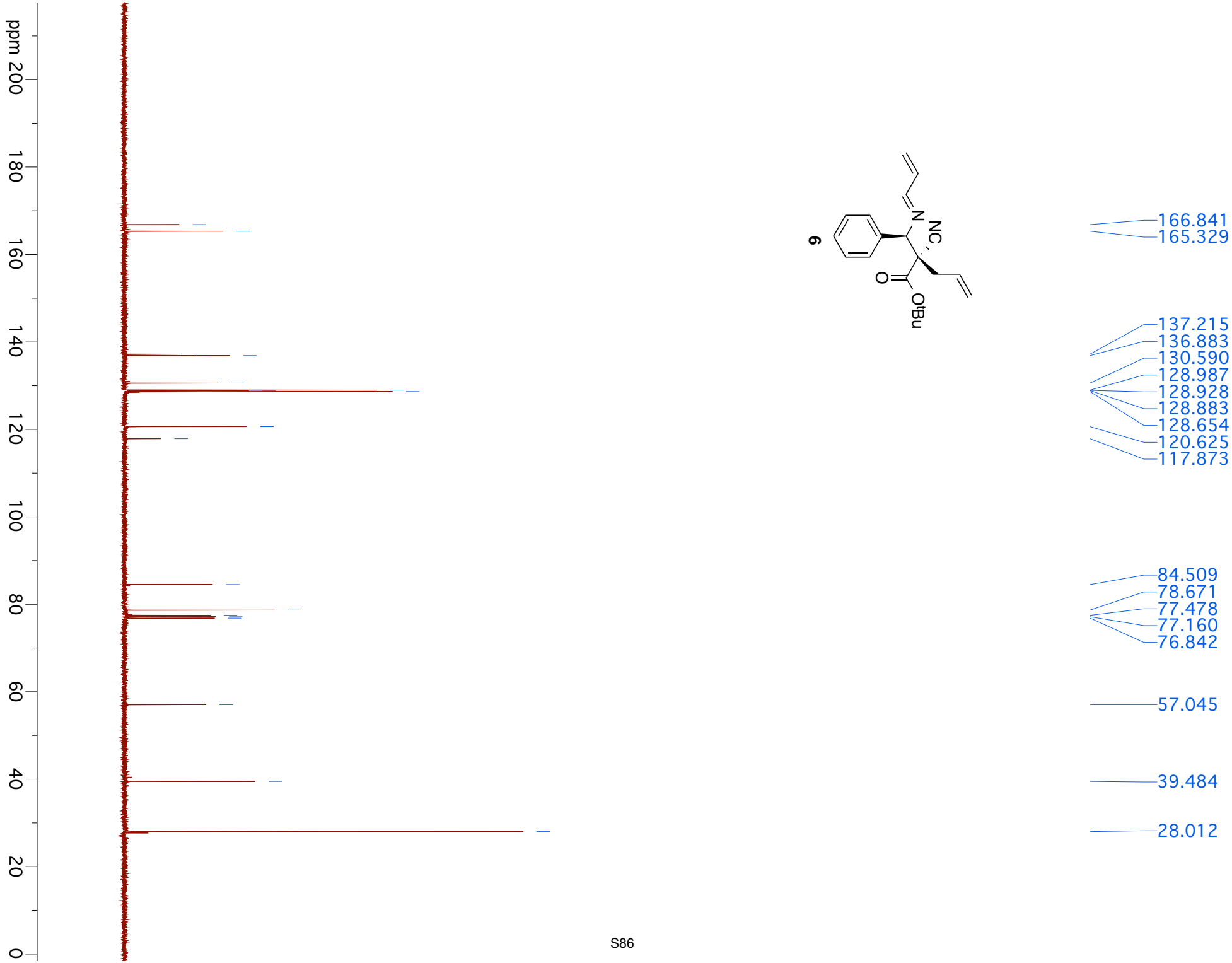
1
0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N
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OtBu
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137.215
136.883
130.590
128.987
128.928
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117.873
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76.842
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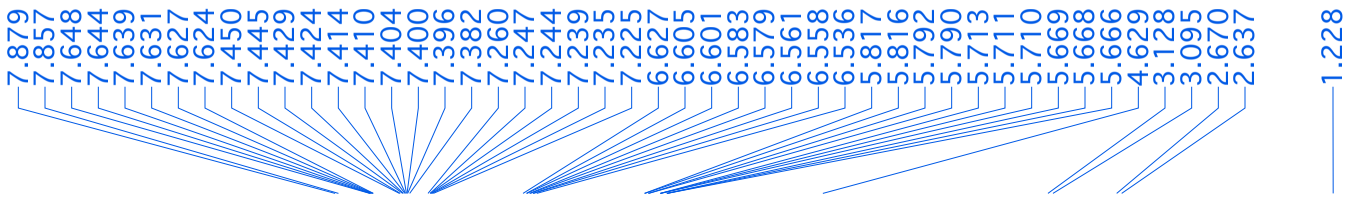
39.484
28.012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5.816
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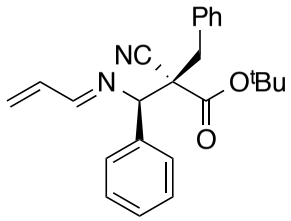
Ph
NC
N
O^{t}Bu
O

7

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1.05
1.03
9.26
10
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7
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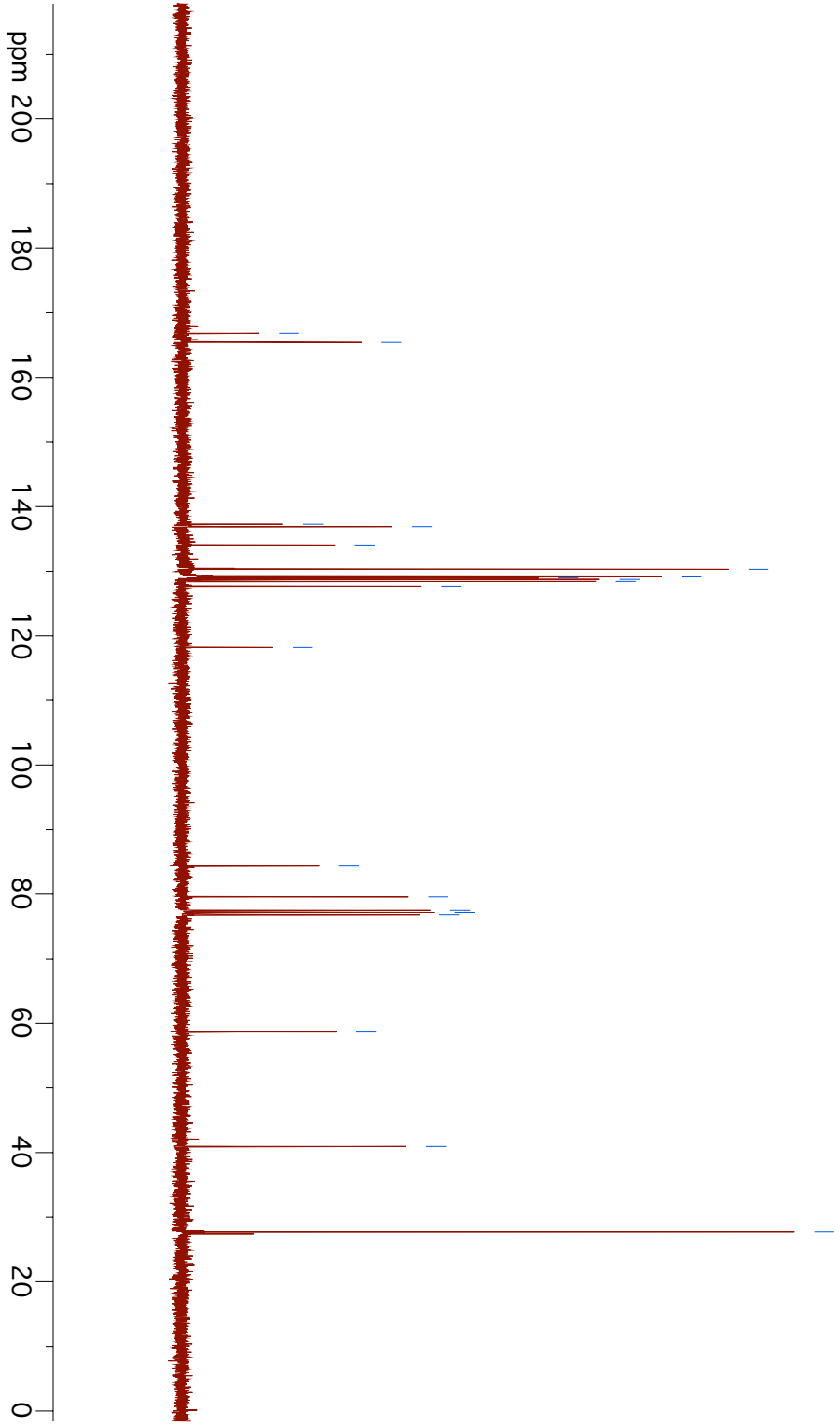
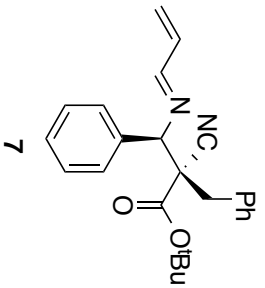
3
2
1
0





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118.181
84.353
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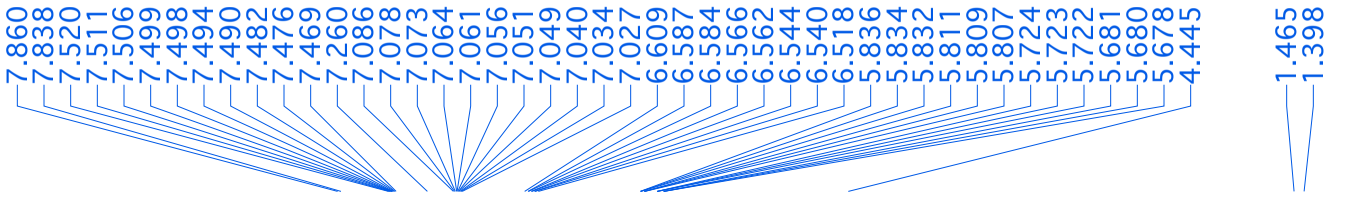
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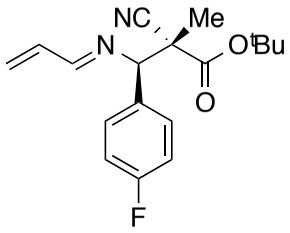
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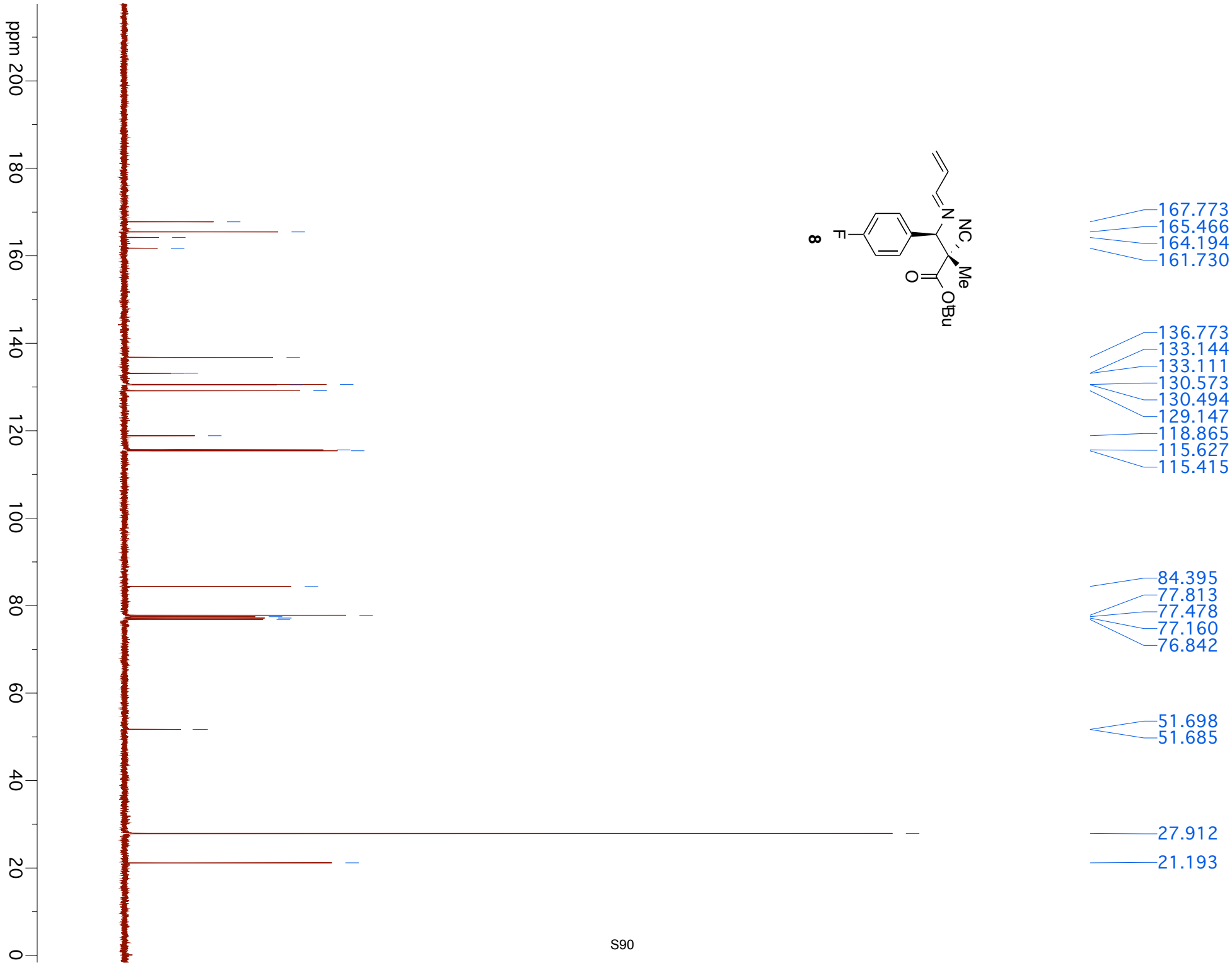
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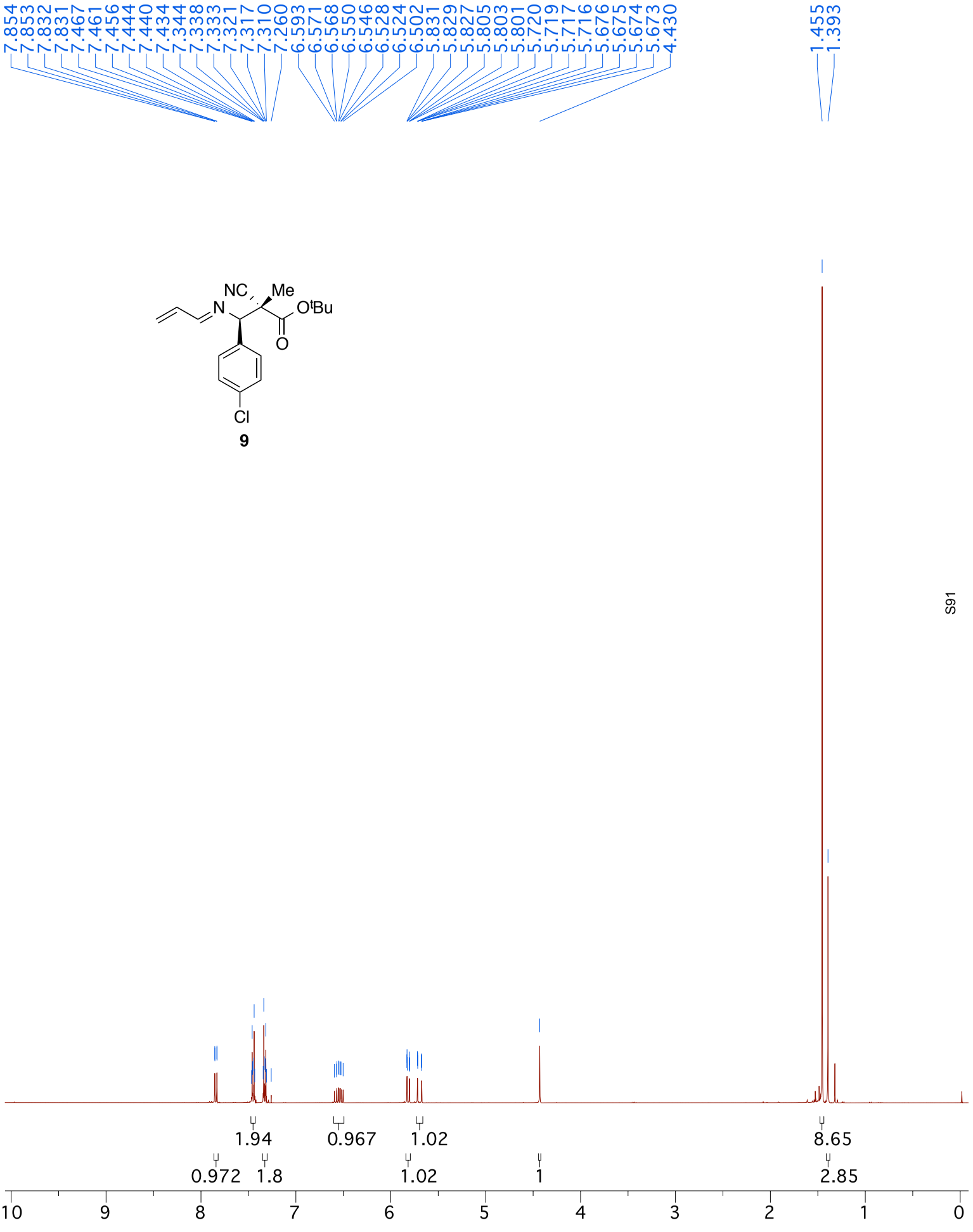
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6.524
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OtBu
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Cl
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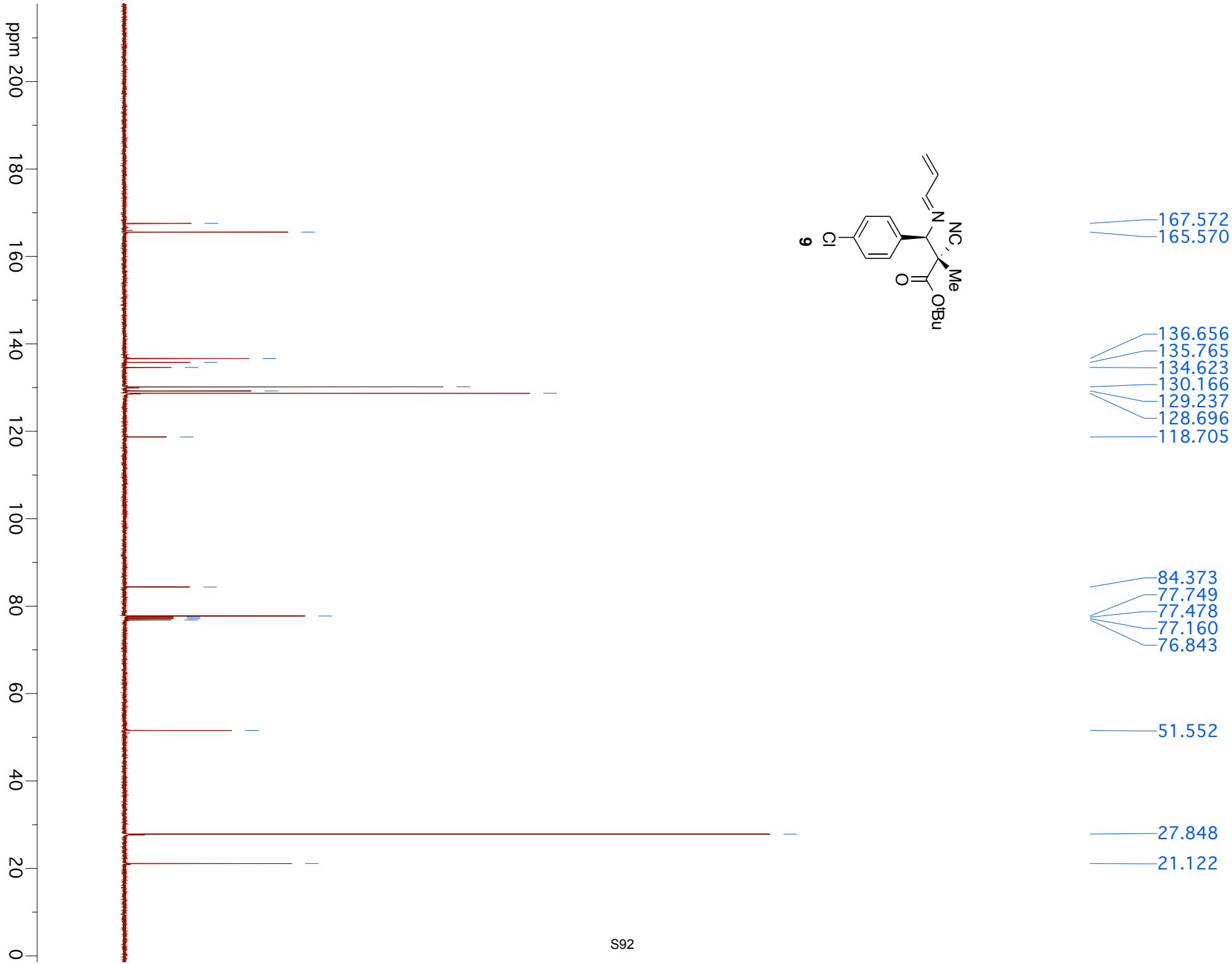
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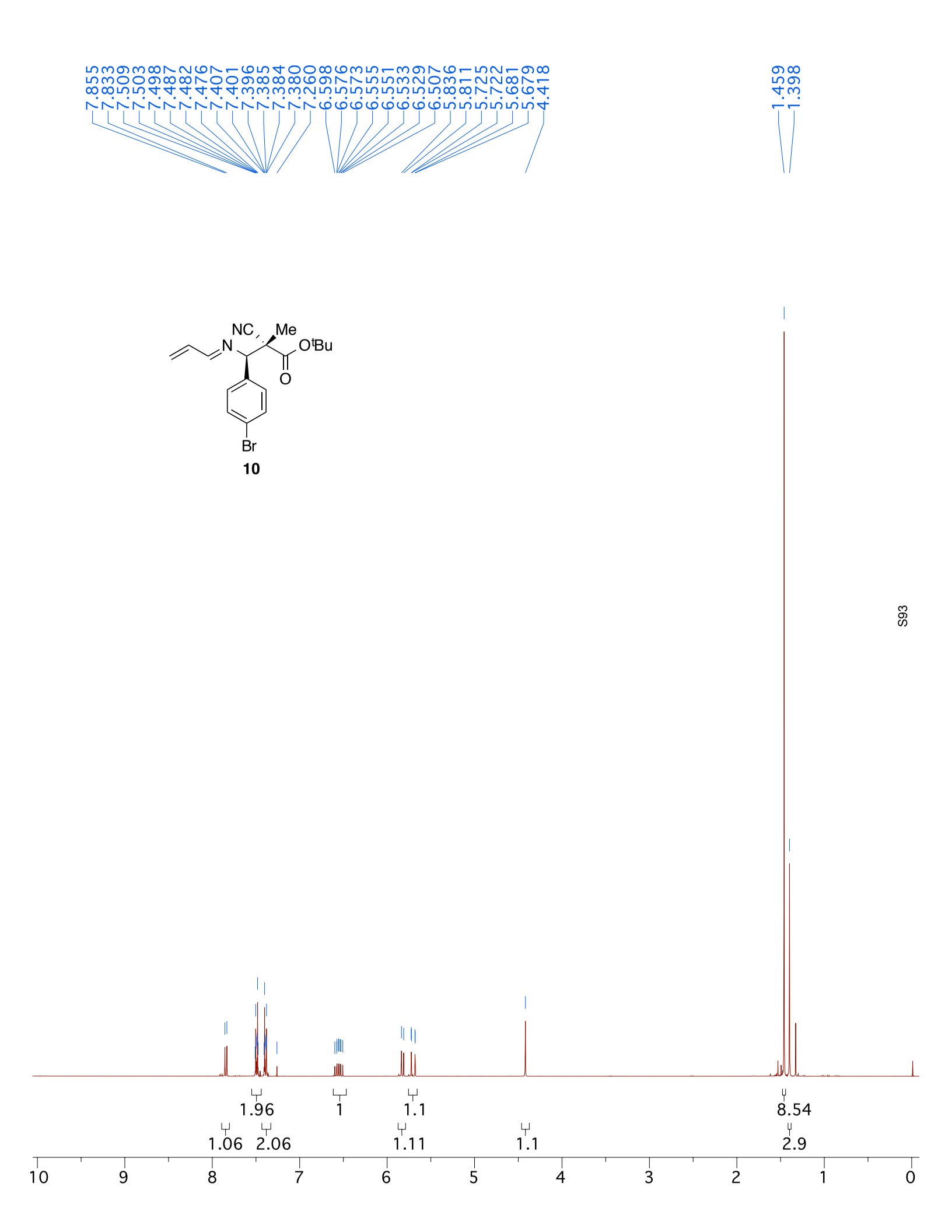
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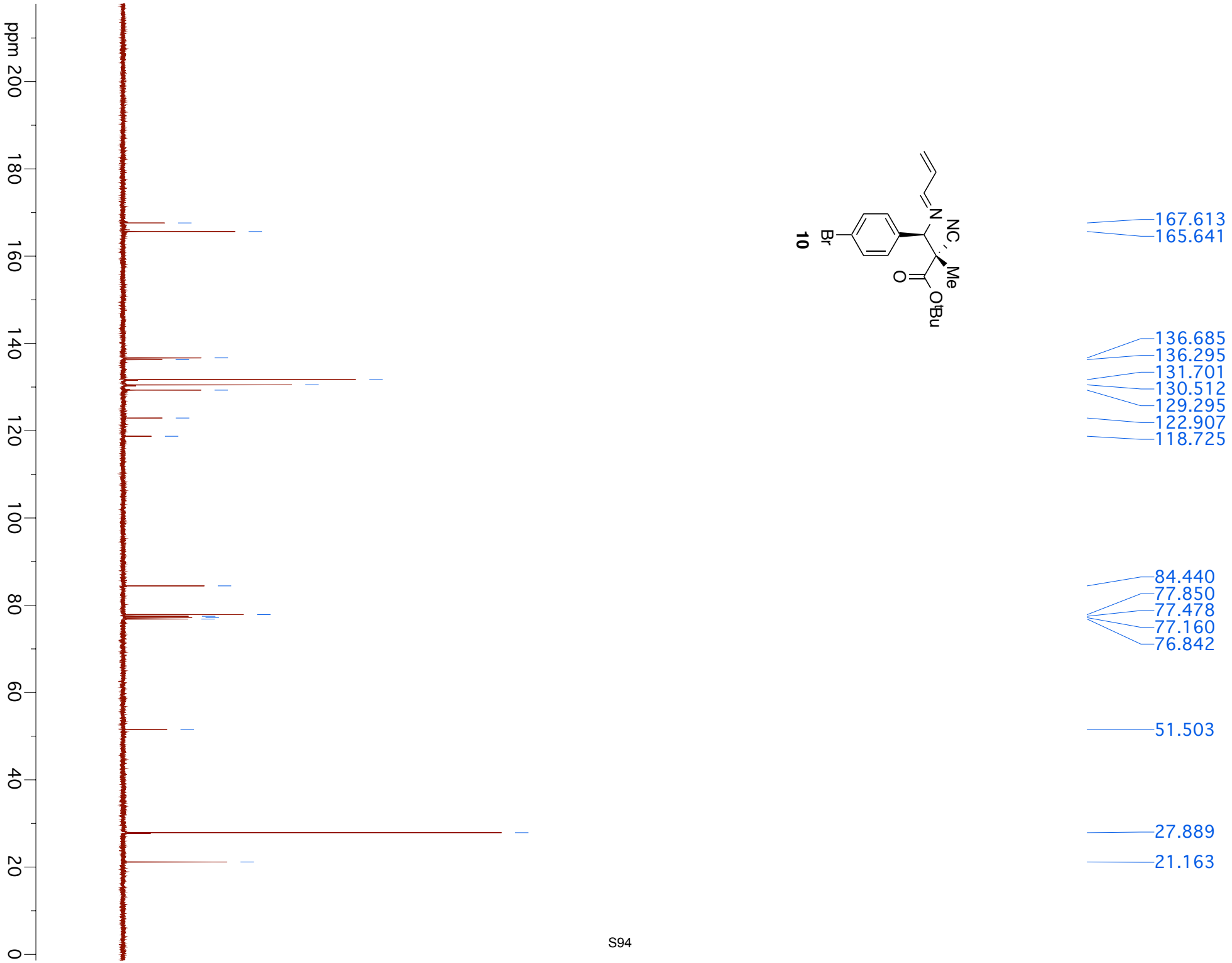
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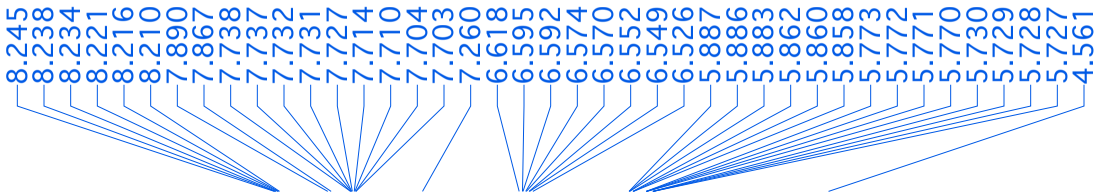
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7.704
7.703
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6.574
6.570
6.552
6.549
6.526
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5.883
5.862
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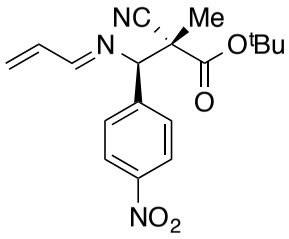
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tBu
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NO2

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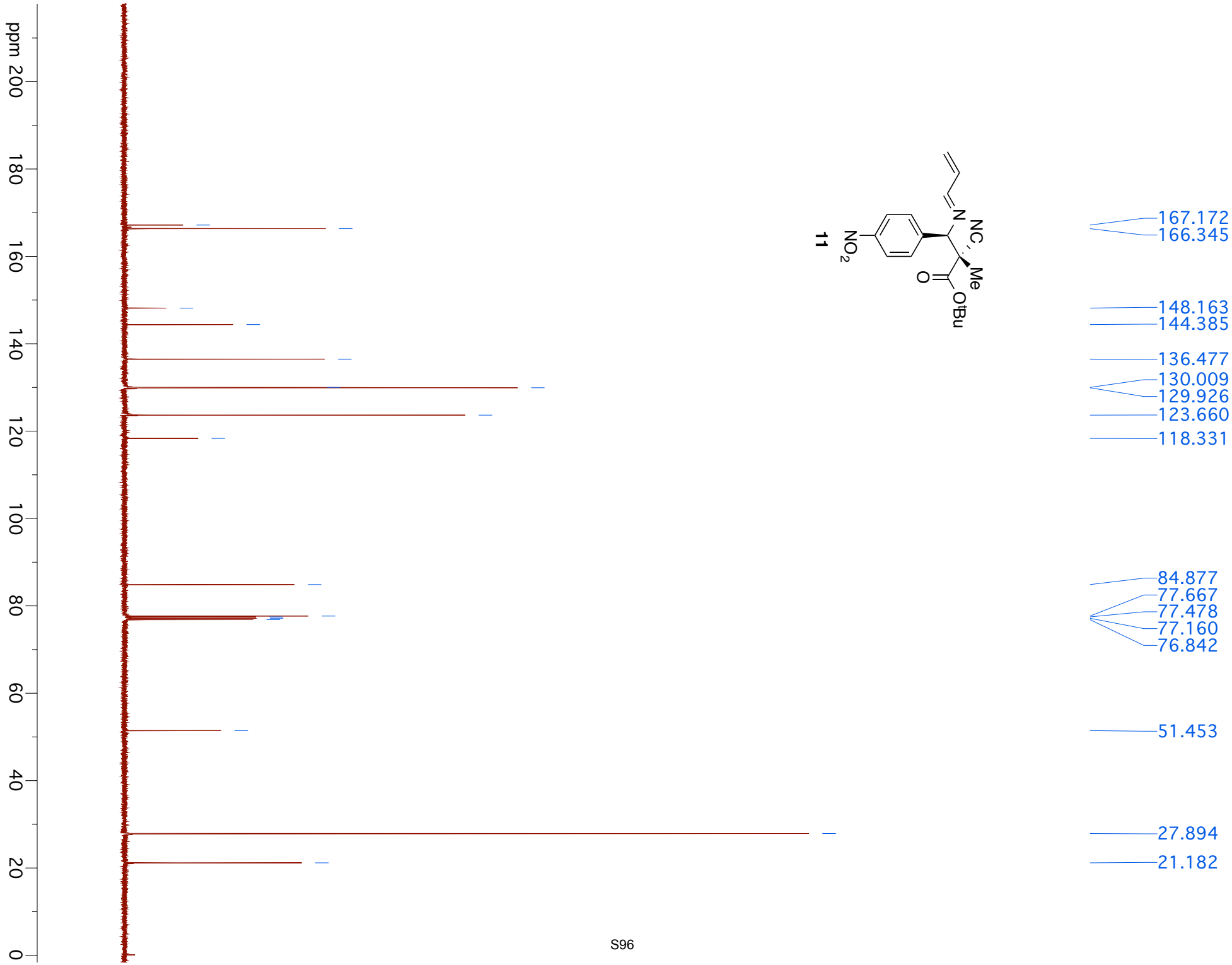
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NC
Me
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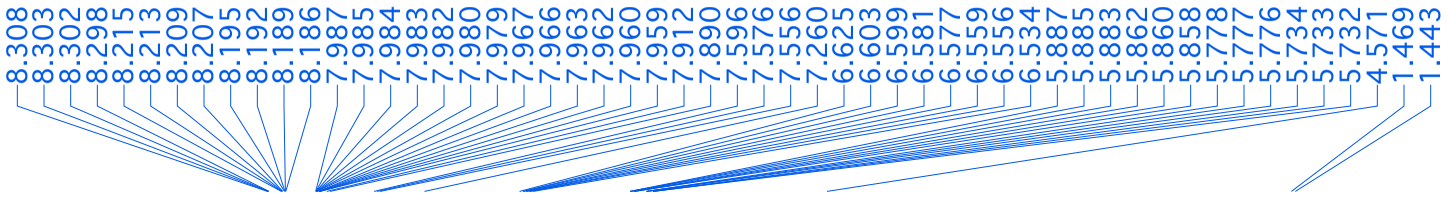
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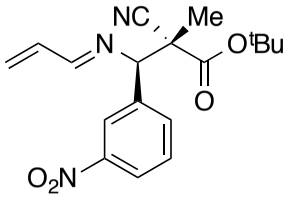
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O_2N

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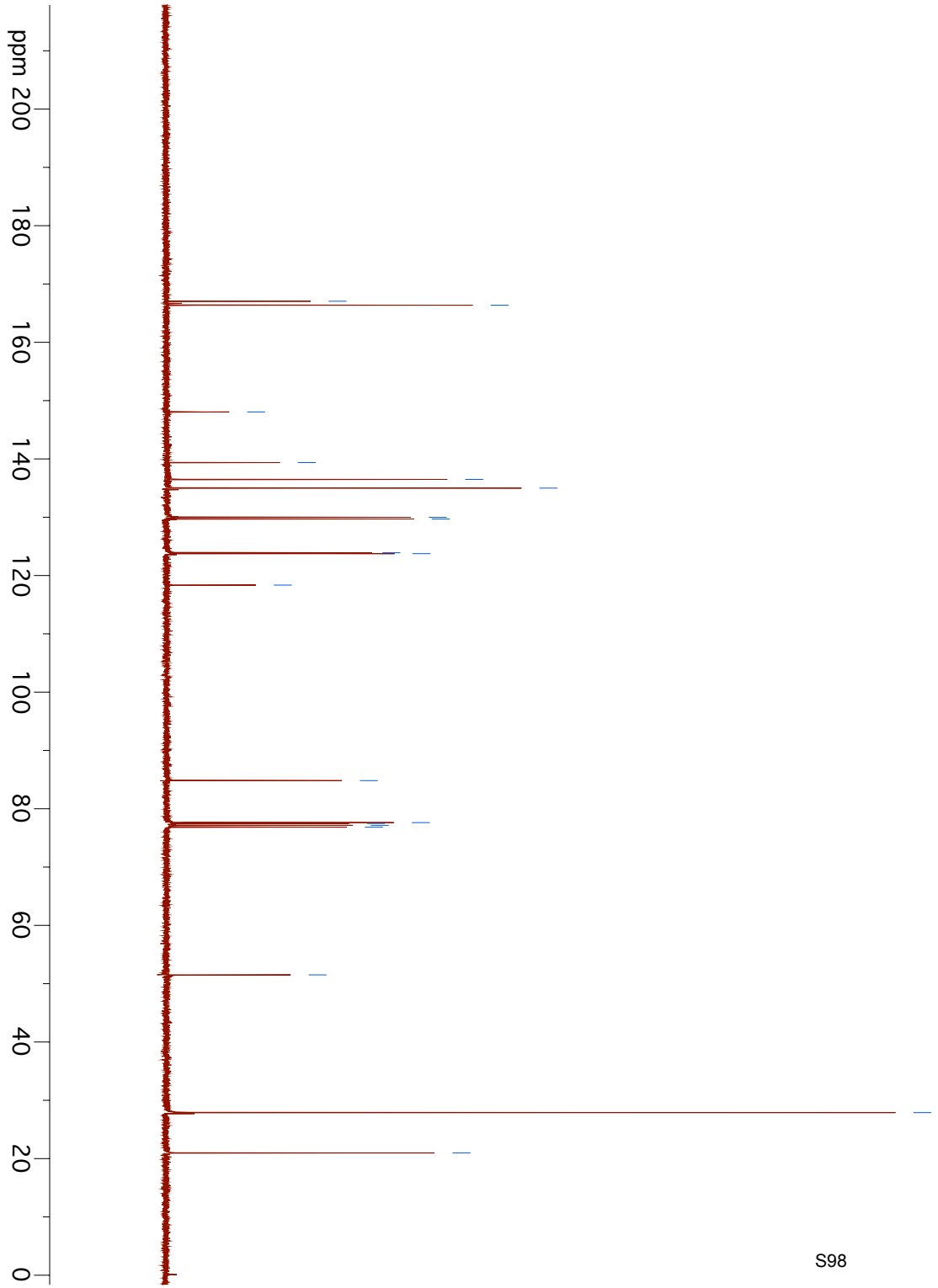

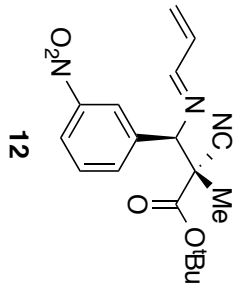

12

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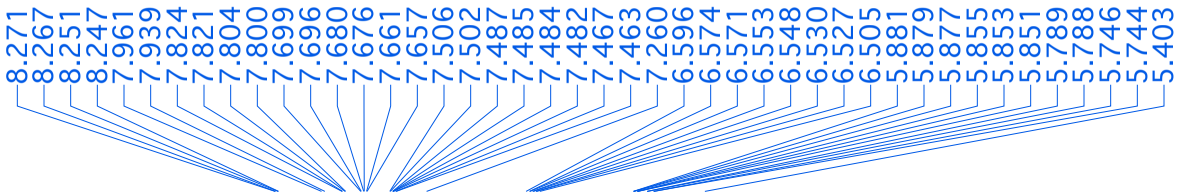
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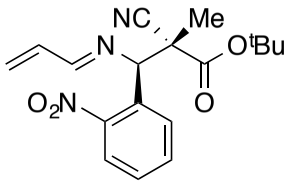
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O^{t}Bu
O_2N
O

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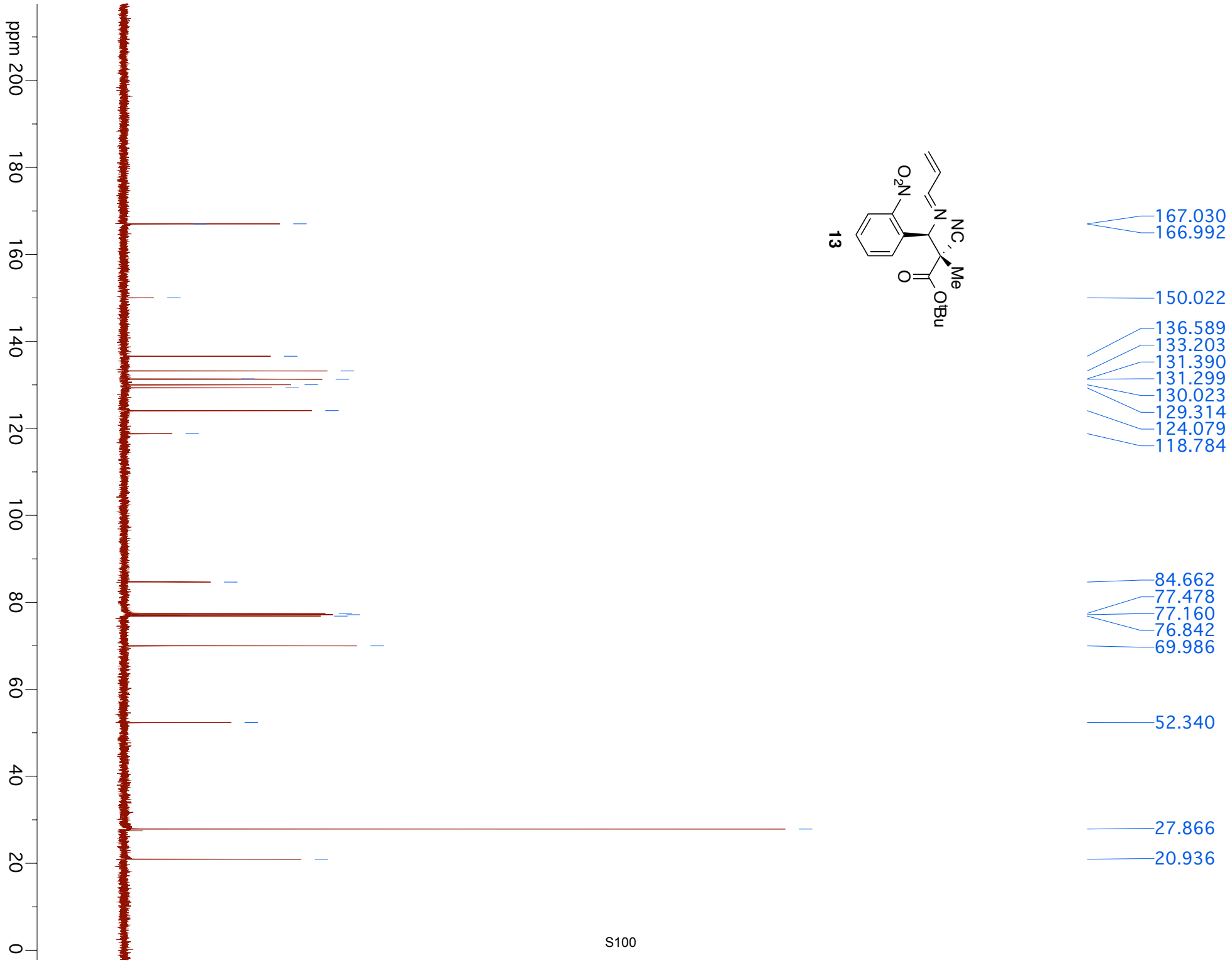
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N
NC
Me
O
O^{t}Bu
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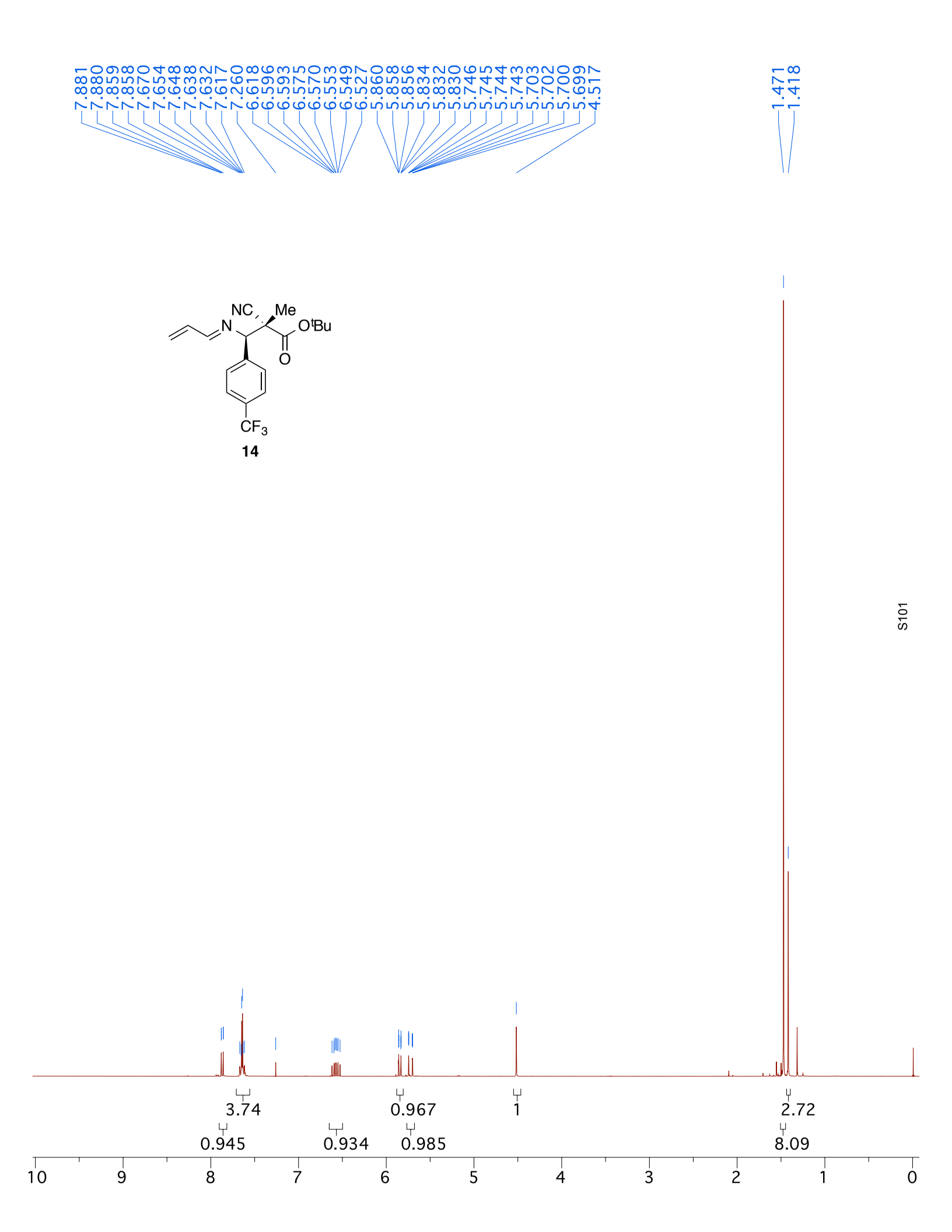
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1.418
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N
O^{t}Bu
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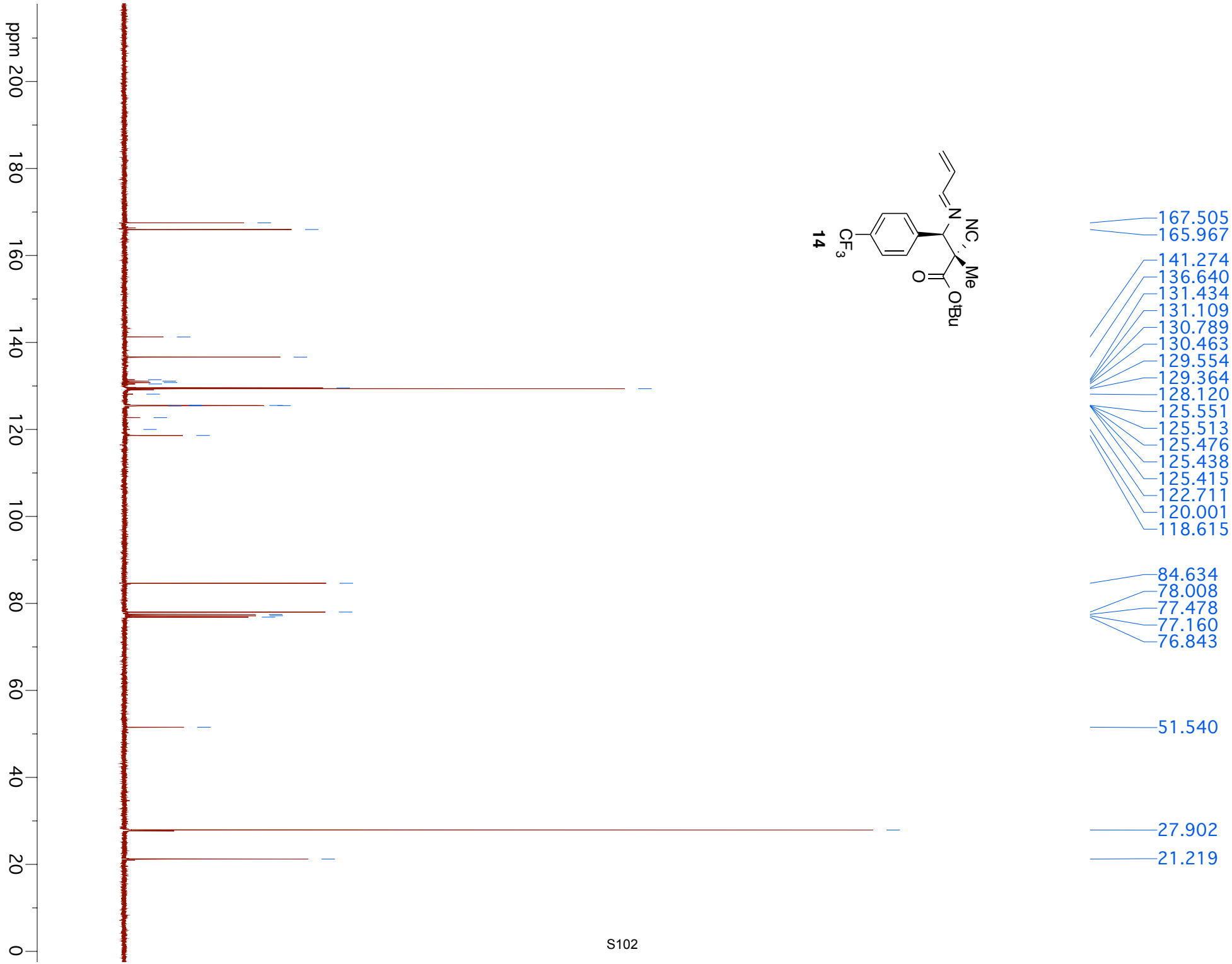
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CF3
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NC
Me
O
OtBu
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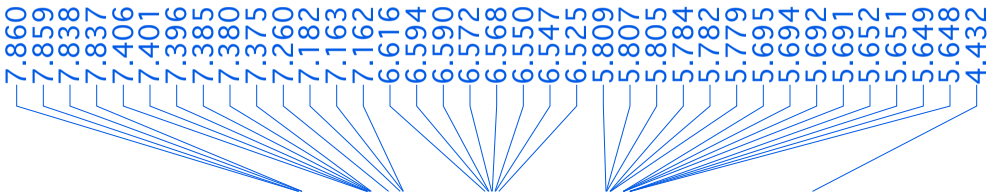
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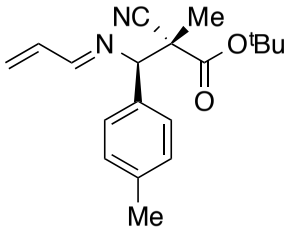
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O
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Me

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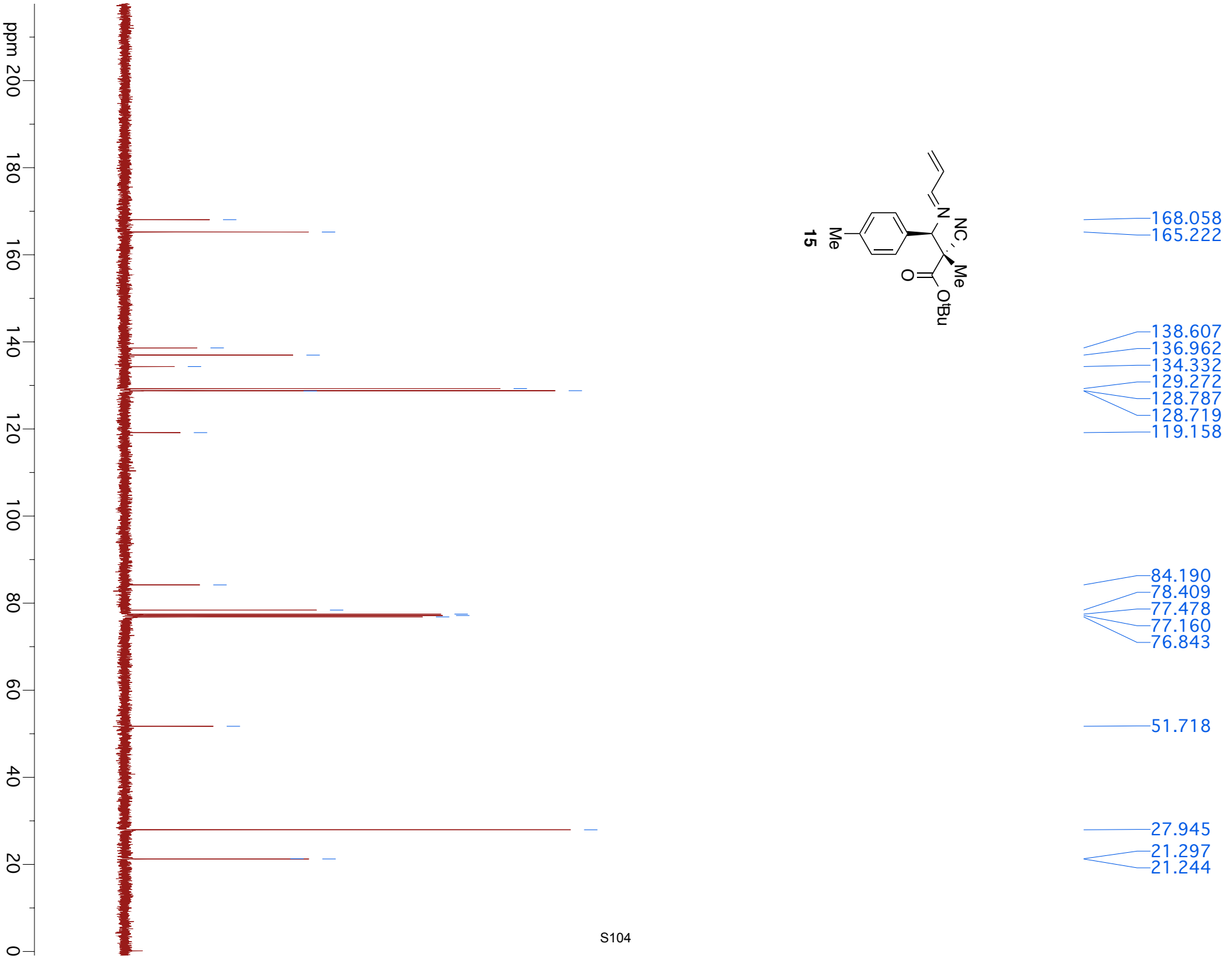
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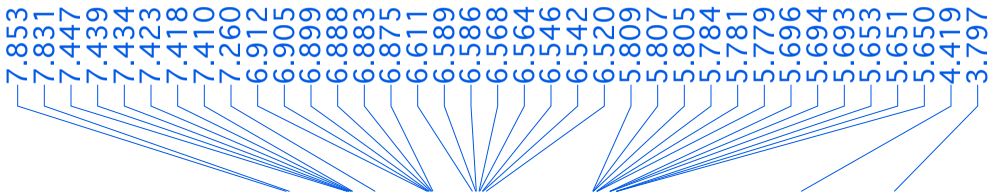
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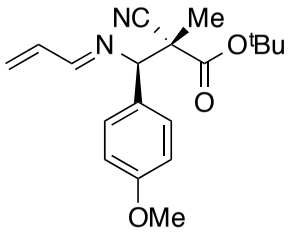
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O^{t}Bu
O
OMe

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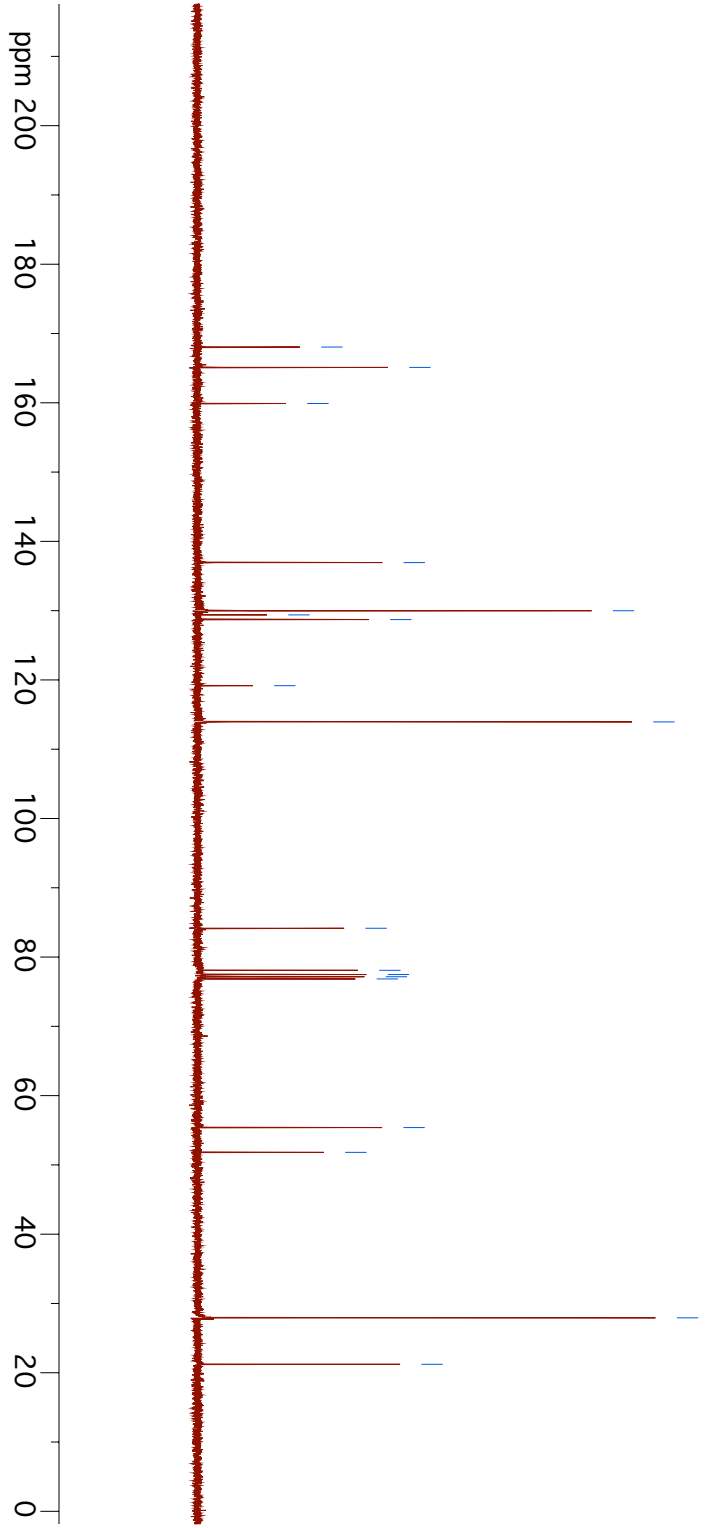

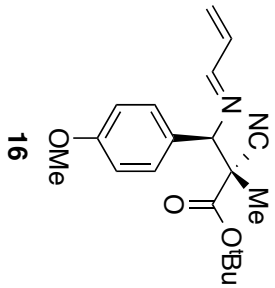

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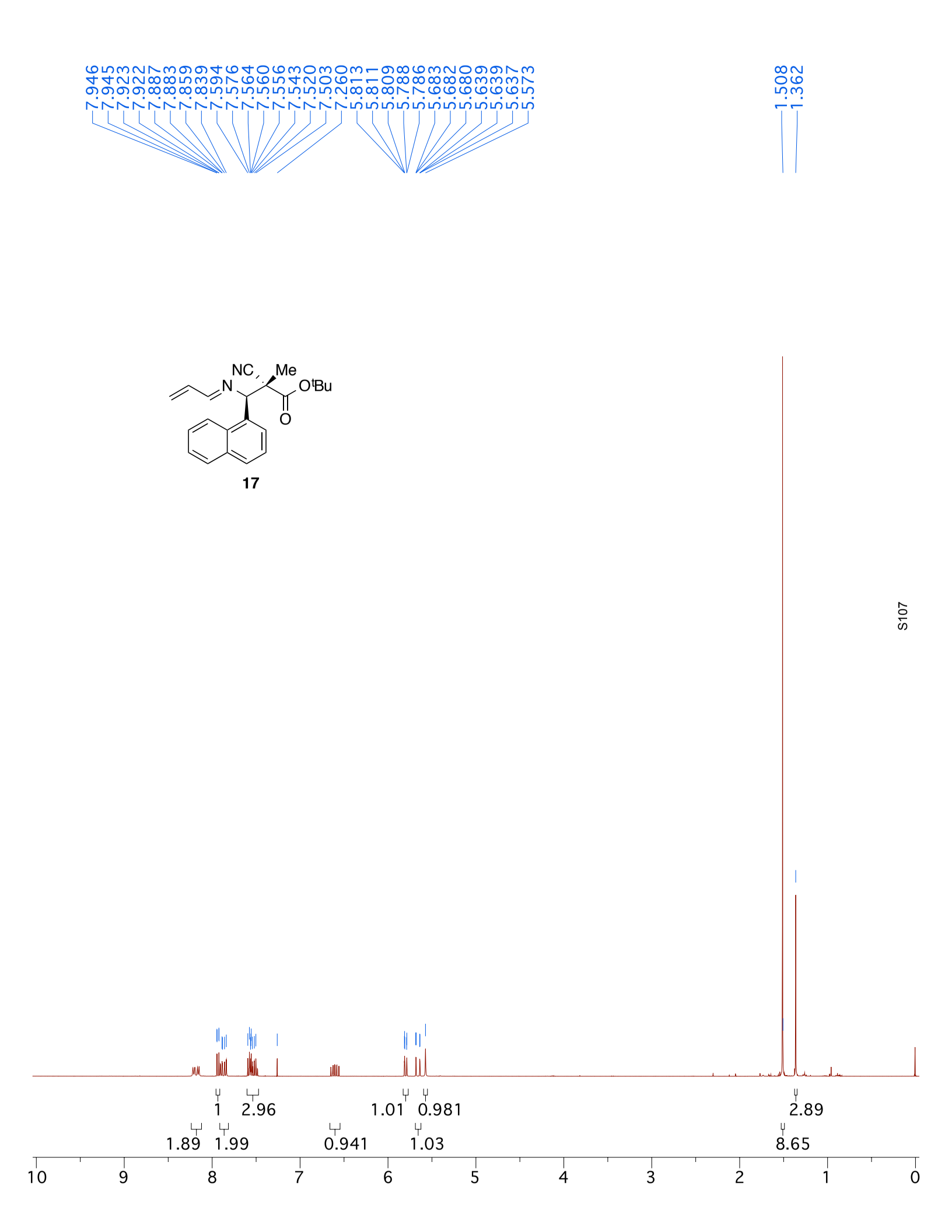
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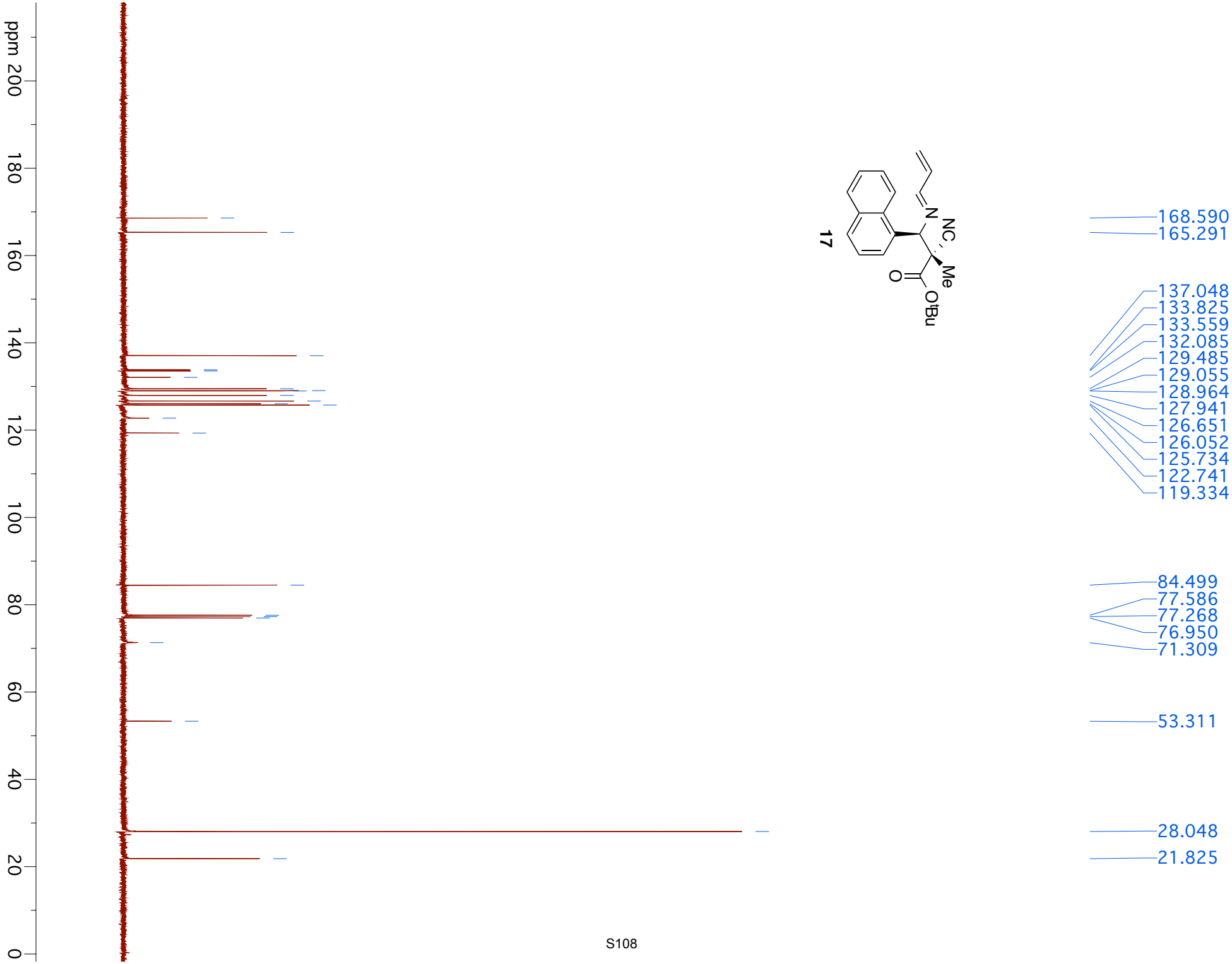
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NC
Me
O
O
tBu
168.590
165.291
137.048
133.825
133.559
132.085
129.485
129.055
128.964
127.941
126.651
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77.268
76.950
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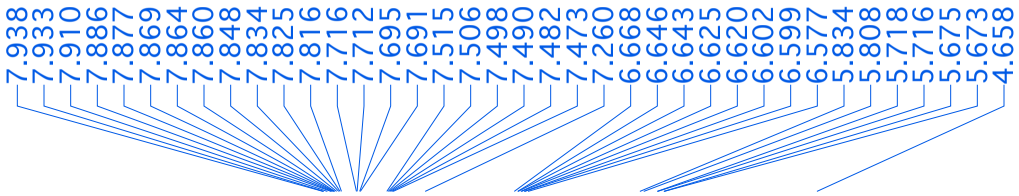
53.311
28.048
21.825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7.910
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7.877
7.869
7.864
7.860
7.848
7.834
7.825
7.816
7.716
7.712
7.695
7.691
7.515
7.506
7.498
7.490
7.482
7.473
7.260
6.668
6.646
6.643
6.625
6.620
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5.718
5.716
5.675
5.673
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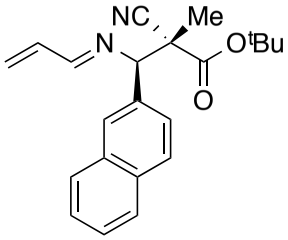
1.497
1.460


NC
Me
N
OtBu
O

18

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1.03
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1.05
8.65
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1
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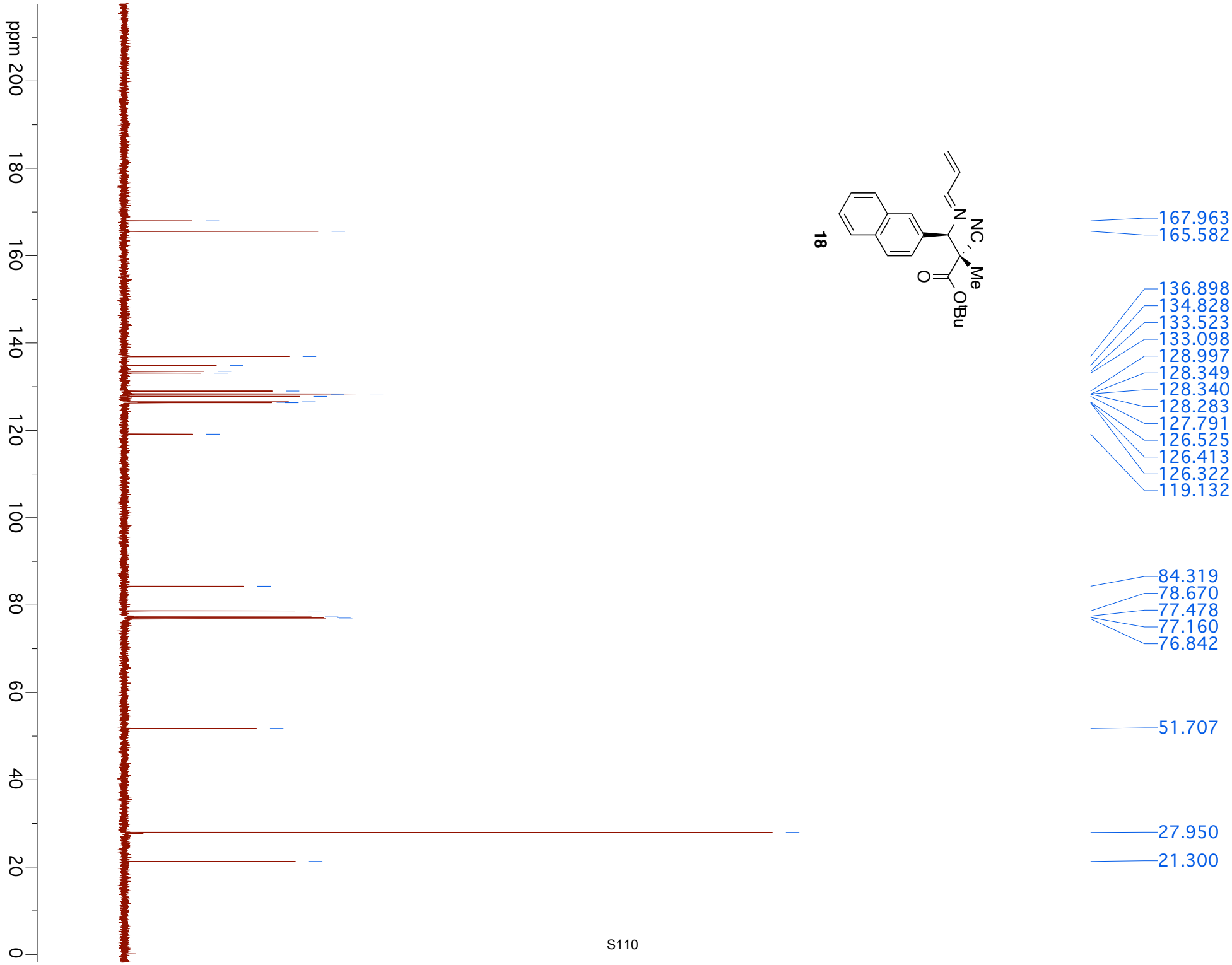
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18
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O
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N
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136.898
134.828
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133.098
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128.349
128.340
128.283
127.791
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77.160
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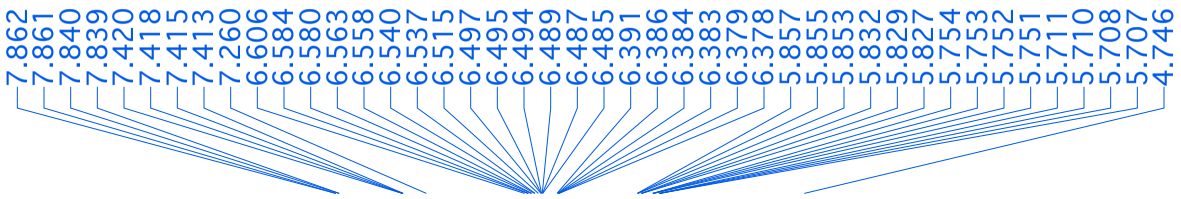
21.300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7.415
7.413
7.260
6.606
6.584
6.580
6.563
6.558
6.540
6.537
6.515
6.497
6.495
6.494
6.489
6.487
6.485
6.391
6.386
6.384
6.383
6.379
6.378
5.857
5.855
5.853
5.832
5.829
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5.708
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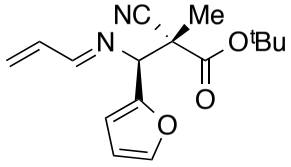
1.473


NC
Me
N
O
O
O
tBu

19

S111

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0.845
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2.83
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7
6
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4
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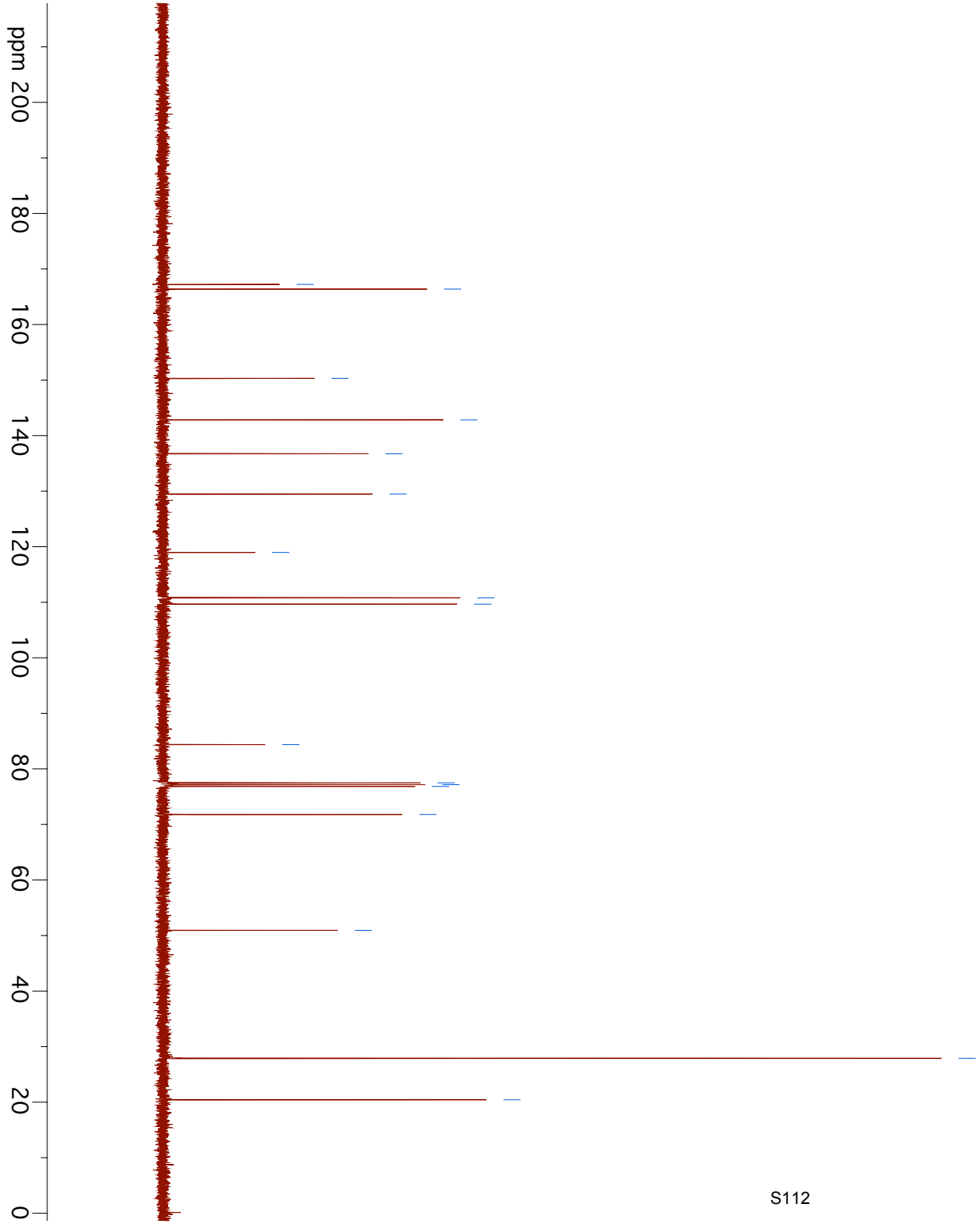
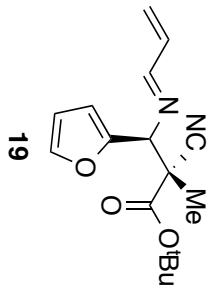
1
0





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110.796
109.659
84.362
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76.842
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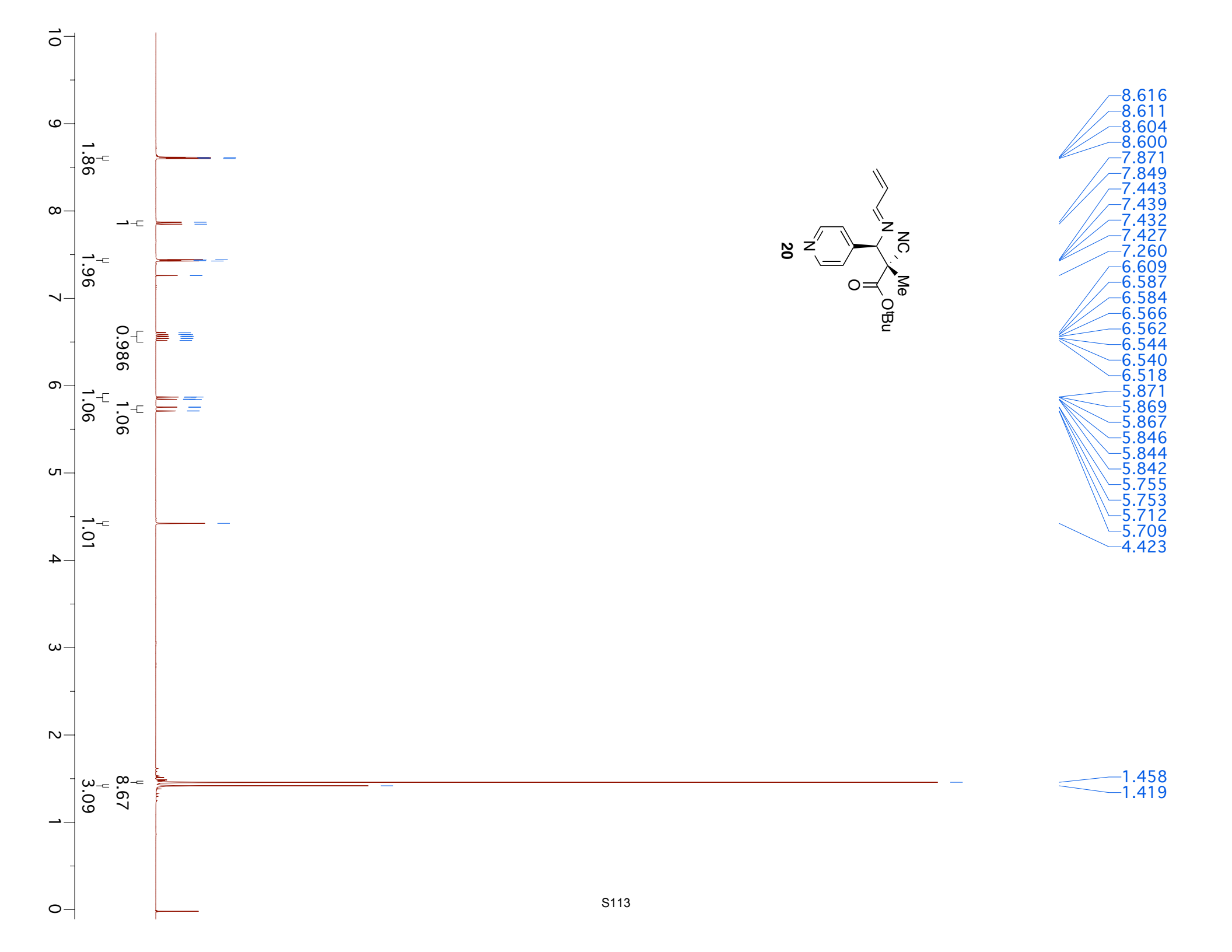
50.932
27.879
20.442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7
6
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4
3
2
1
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1
1.96
0.986
1.06
1.06
1.01
8.67
3.09
20
N
N
NC
Me
O
O
tBu
8.616
8.611
8.604
8.600
7.871
7.849
7.443
7.439
7.432
7.427
7.260
6.609
6.587
6.584
6.566
6.562
6.544
6.540
6.518
5.871
5.869
5.867
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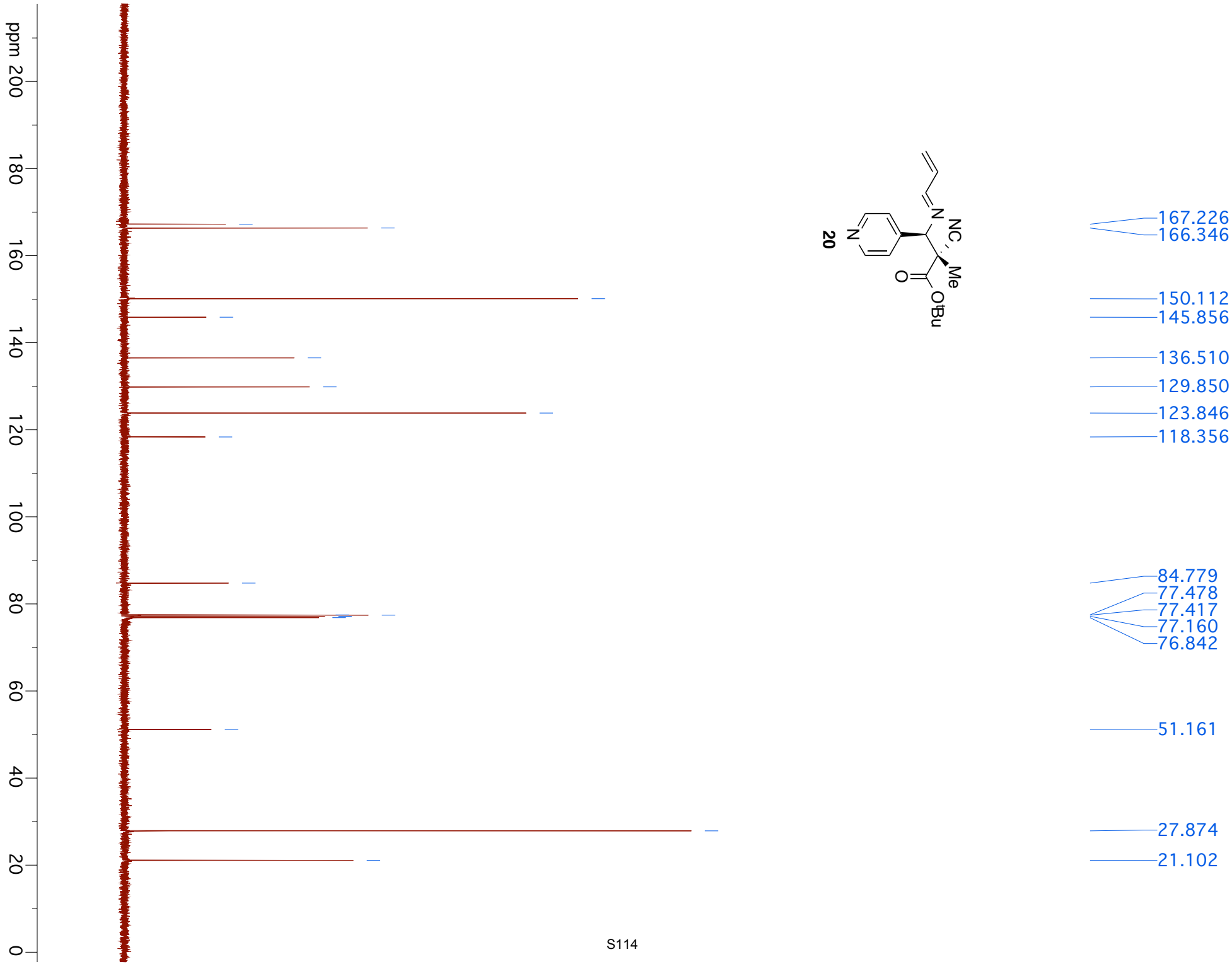
5.753
5.712
5.709
4.423
1.458
1.419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60
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N
N
NC
Me
O
O
tBu
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166.346
150.112
145.856
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118.356
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77.417
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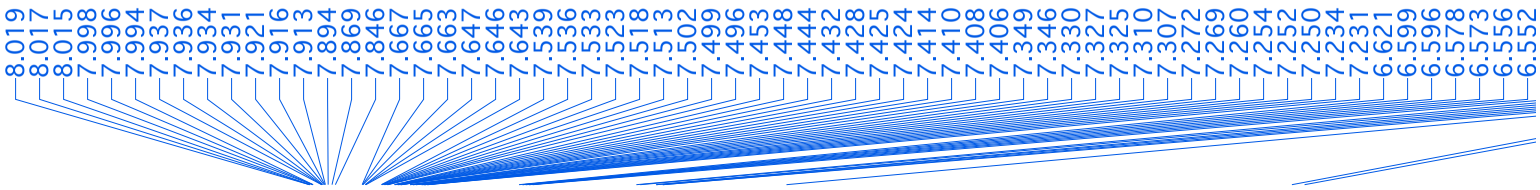
76.842
51.161
27.874
21.102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8.015
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7.936
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7.931
7.921
7.916
7.913
7.894
7.869
7.846
7.667
7.665
7.663
7.647
7.646
7.643
7.539
7.536
7.533
7.523
7.518
7.513
7.502
7.499
7.496
7.453
7.448
7.444
7.432
7.428
7.425
7.424
7.414
7.410
7.408
7.406
7.349
7.346
7.330
7.327
7.325
7.310
7.307
7.272
7.269
7.260
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6.596
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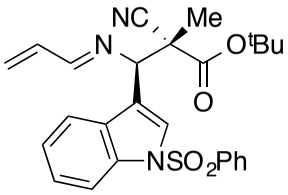
6.573
6.556
6.552


NC
Me
N
O^{t}Bu
O
NSO$_2$Ph

21

S115

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1.02
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1.02
1
2.72
10
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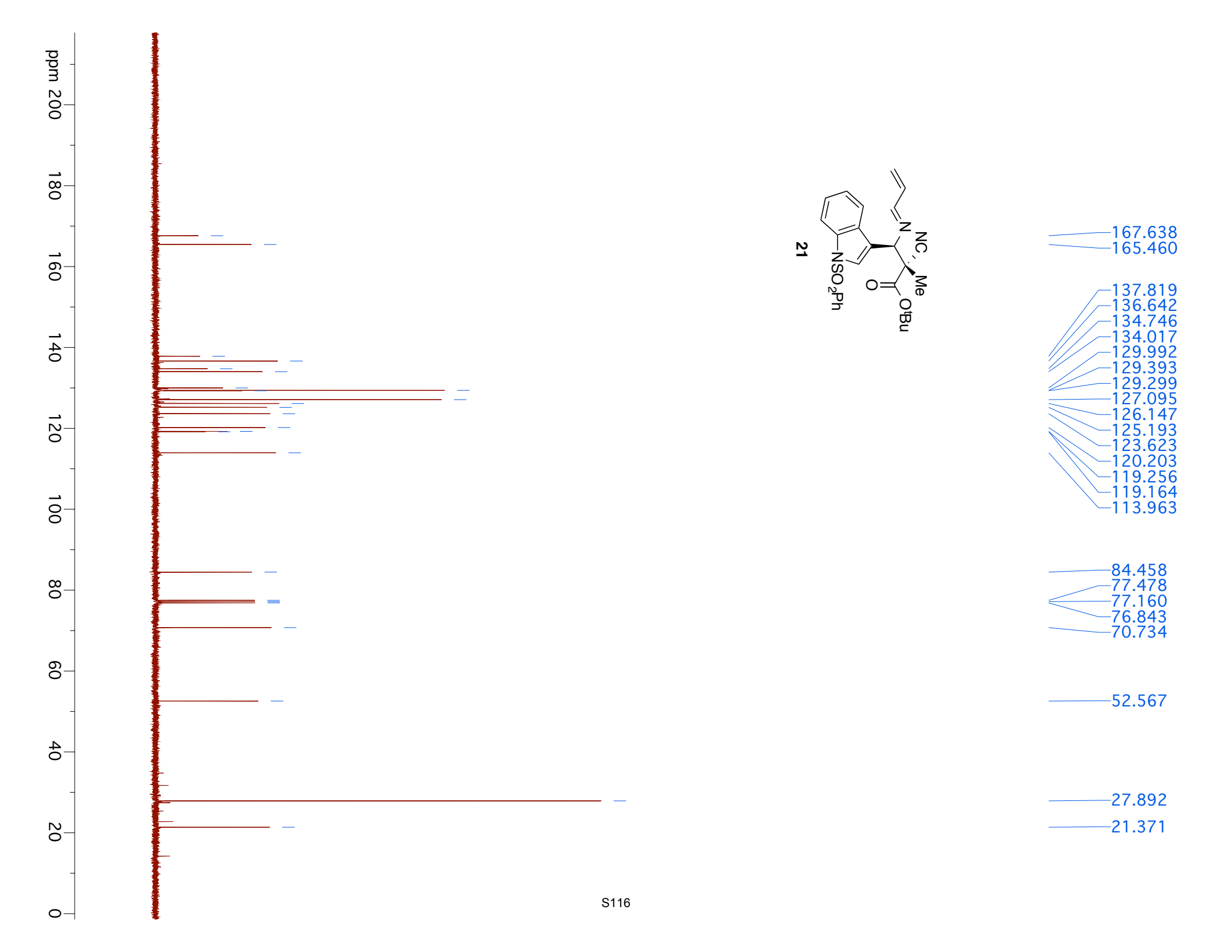
3
2
1
0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140
120
100
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60
40
20
0
21
NSO2Ph
N
NC
Me
O
OtBu
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165.460
137.819
136.642
134.746
134.017
129.992
129.393
129.299
127.095
126.147
125.193
123.623
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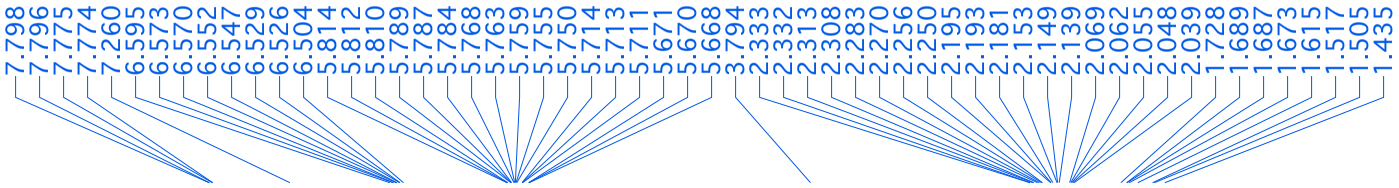
119.256
119.164
113.963
84.458
77.478
77.160
76.843
70.734
52.567
27.892
21.371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6.570
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6.547
6.529
6.526
6.504
5.814
5.812
5.810
5.789
5.787
5.784
5.768
5.763
5.759
5.755
5.750
5.714
5.713
5.711
5.671
5.670
5.668
3.794
2.333
2.332
2.313
2.308
2.283
2.270
2.256
2.250
2.195
2.193
2.181
2.153
2.149
2.139
2.069
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2.055
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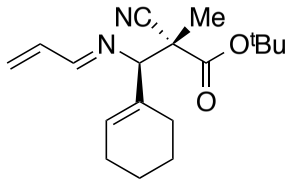
1.673
1.615
1.517
1.505
1.435


NC
Me
N
O^{t}Bu
O

22

S117

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1.01
1.02
2.11
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1.04
2.27
7.47
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9
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7
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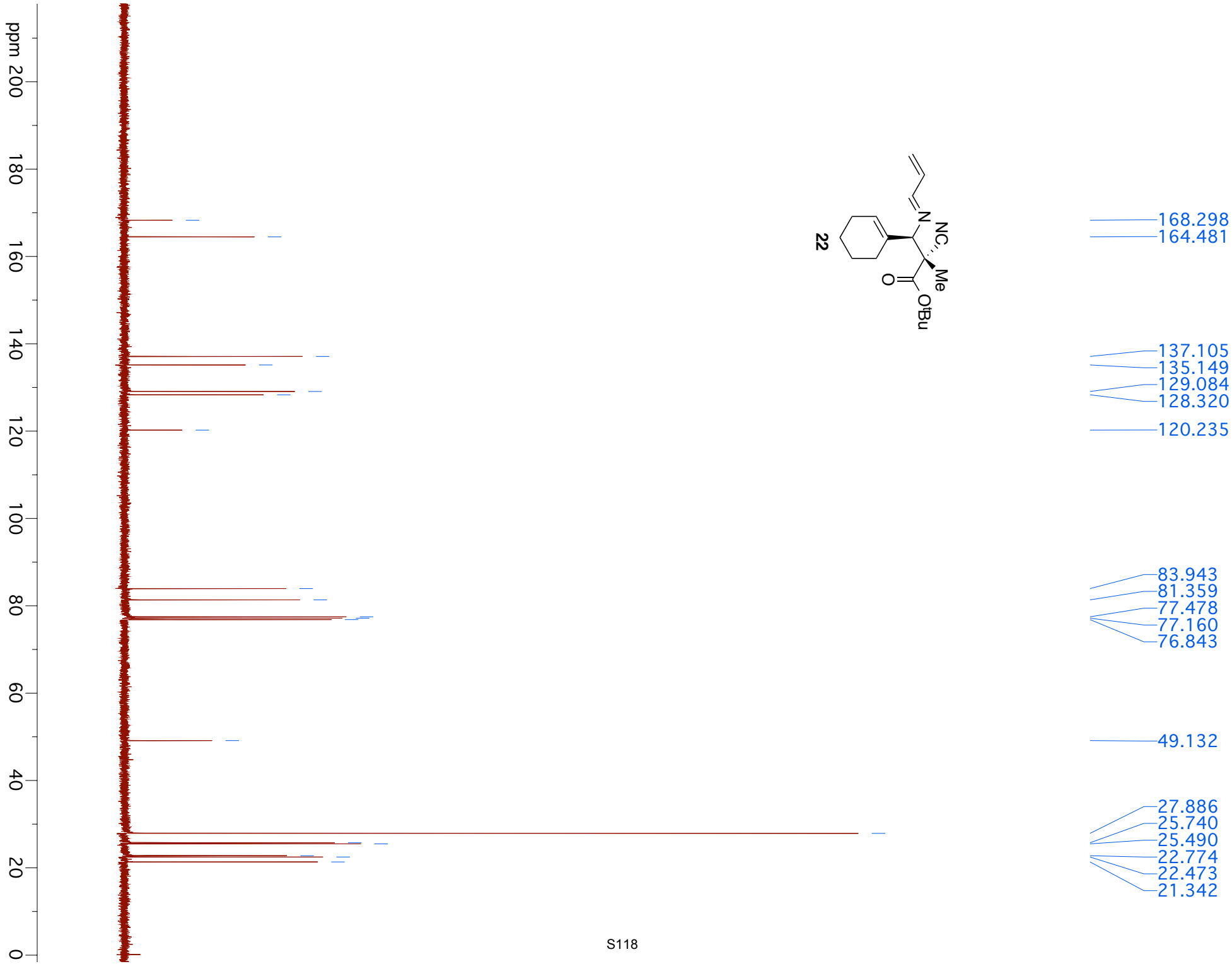
5
4
3
2
1
0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100
80
60
40
20
0
22
N
NC
Me
O
OtBu
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164.481
137.105
135.149
129.084
128.320
120.235
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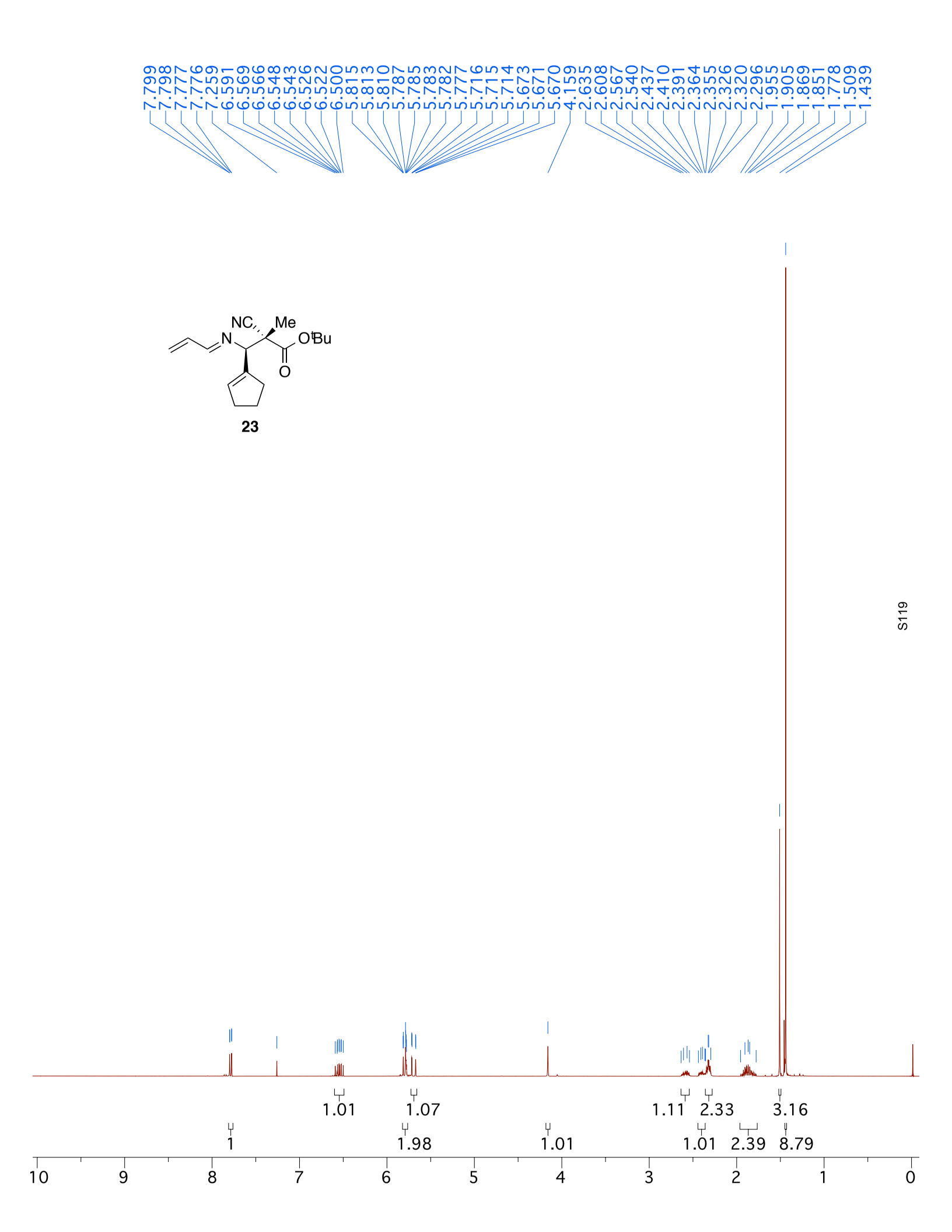
77.478
77.160
76.843
49.132
27.886
25.740
25.490
22.774
22.473
21.342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6.566
6.548
6.543
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6.522
6.500
5.815
5.813
5.810
5.787
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5.777
5.716
5.715
5.714
5.673
5.671
5.670
4.159
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2.608
2.567
2.540
2.437
2.410
2.391
2.364
2.355
2.326
2.320
2.296
1.955
1.905
1.869
1.851
1.778
1.509
1.439
NC
Me
N
OtBu
O
23
S119
1.01
1.07
1.11
2.33
3.16
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1.01
1.01
2.39
8.79
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7
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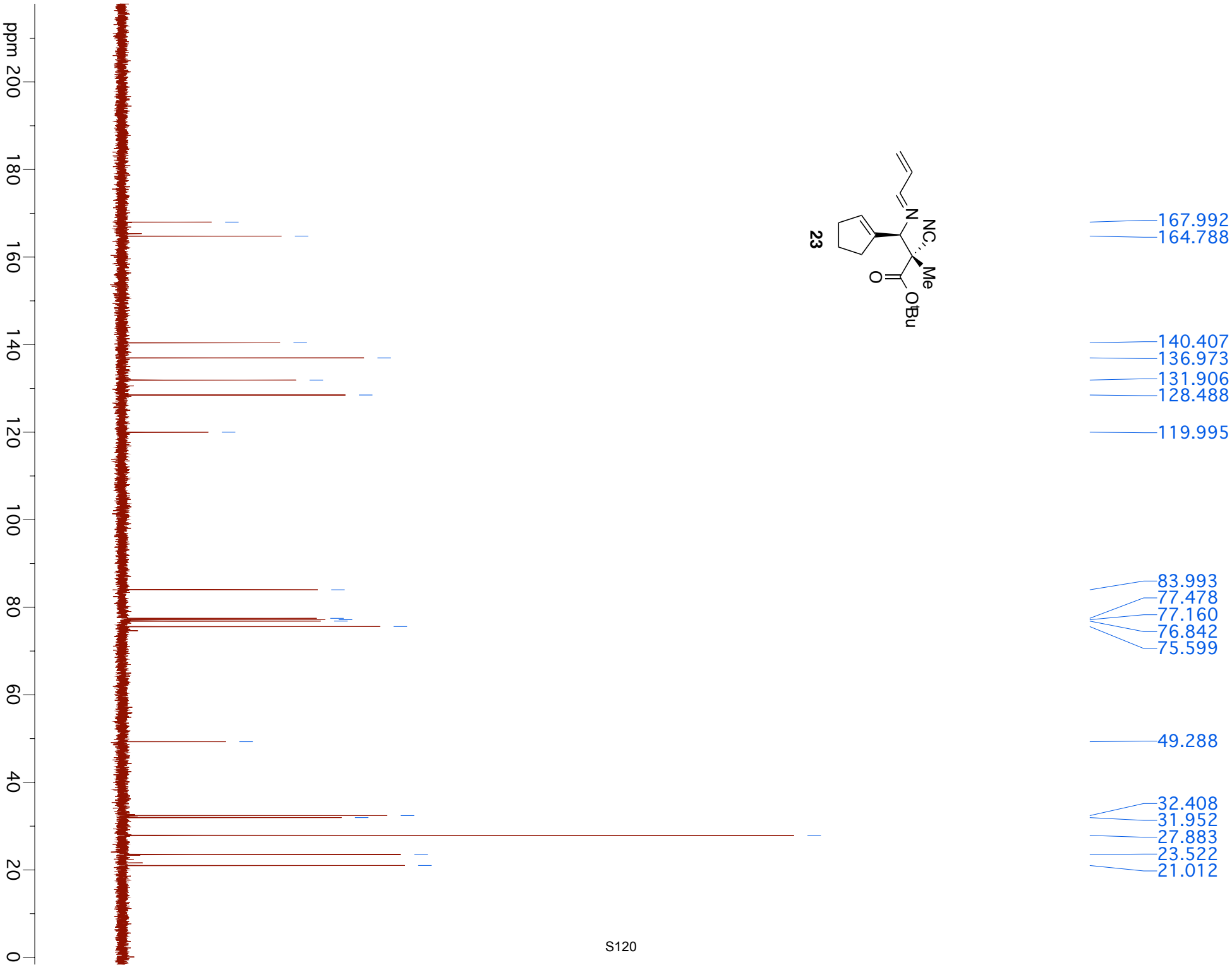
2
1
0


ppm 200
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120
100
80
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40
20
0
23
N
NC
Me
O
O
tBu
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164.788
140.407
136.973
131.906
128.488
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32.408
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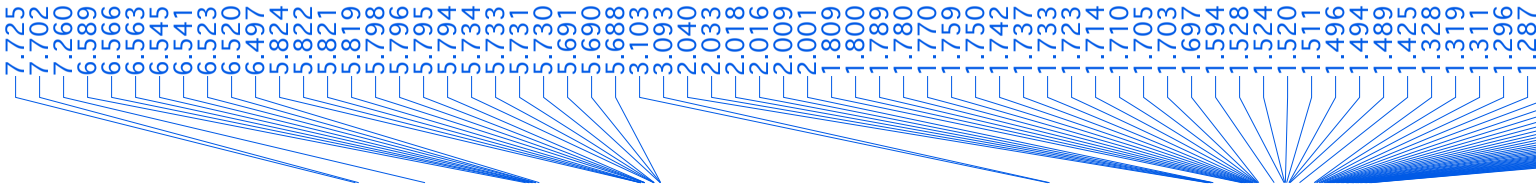
23.522
21.012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6.520
6.497
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5.822
5.821
5.819
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5.731
5.730
5.691
5.690
5.688
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3.093
3.040
2.033
2.018
2.016
2.009
2.001
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1.800
1.789
1.780
1.770
1.759
1.750
1.742
1.737
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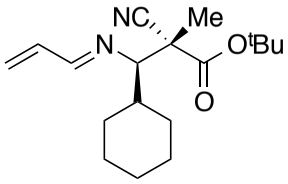
1.287


NC
Me
N
O^{t}Bu
O

24

S121
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1.02
1.06
3.8
4.52
2.86
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3.01
3.46
2.2
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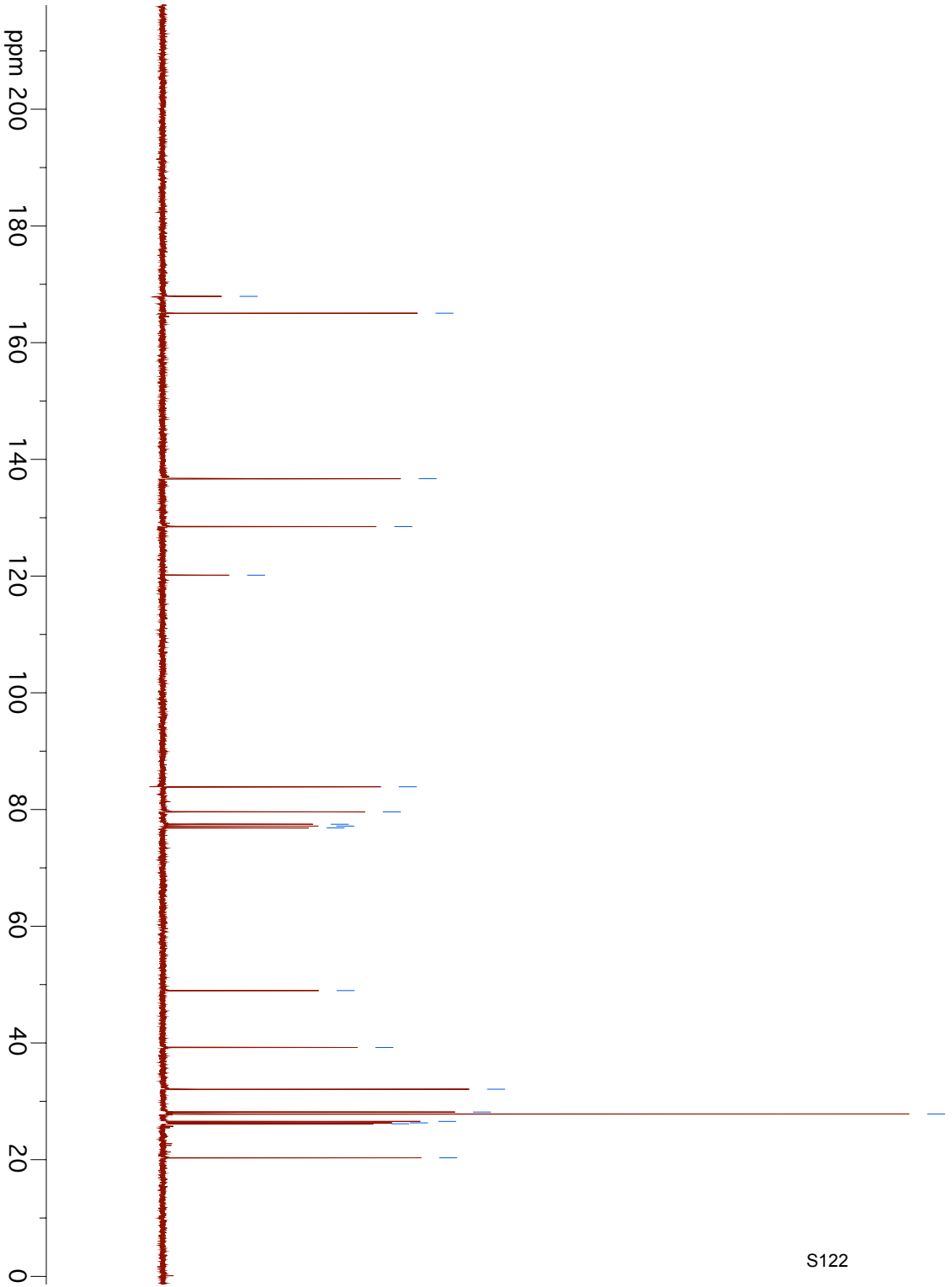
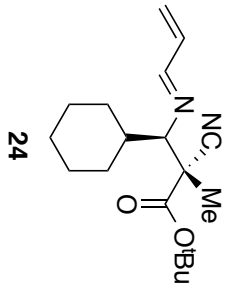
9
8
7
6
5
4
3
2
1
0





167.934
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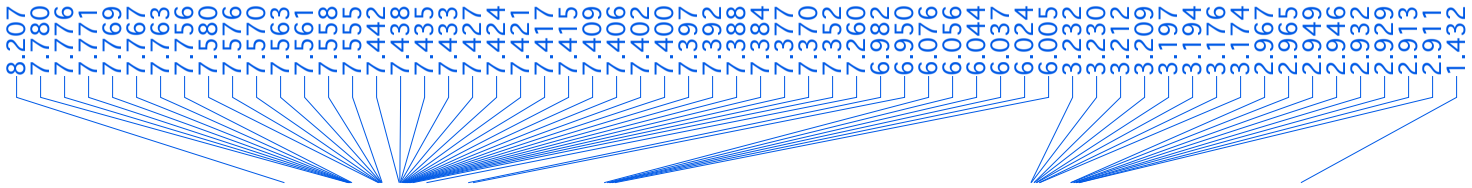
128.487
120.154
83.899
79.588
77.478
77.160
76.842
48.975
39.218
32.073
28.160
27.833
26.552
26.305
26.149
20.320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7.561
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7.415
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7.406
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2.911
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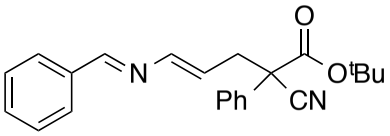
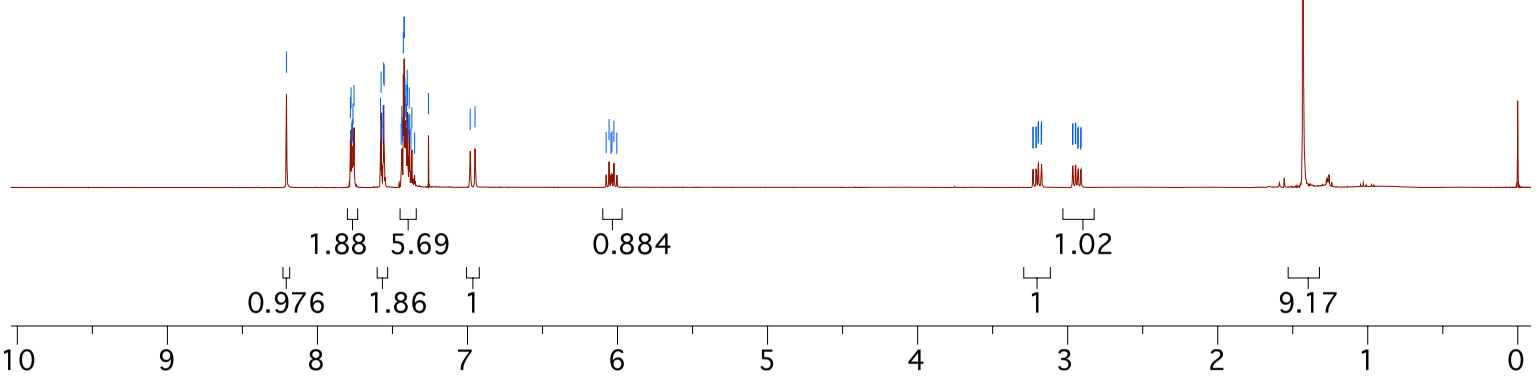

O
N
O
tBu
Ph
CN

26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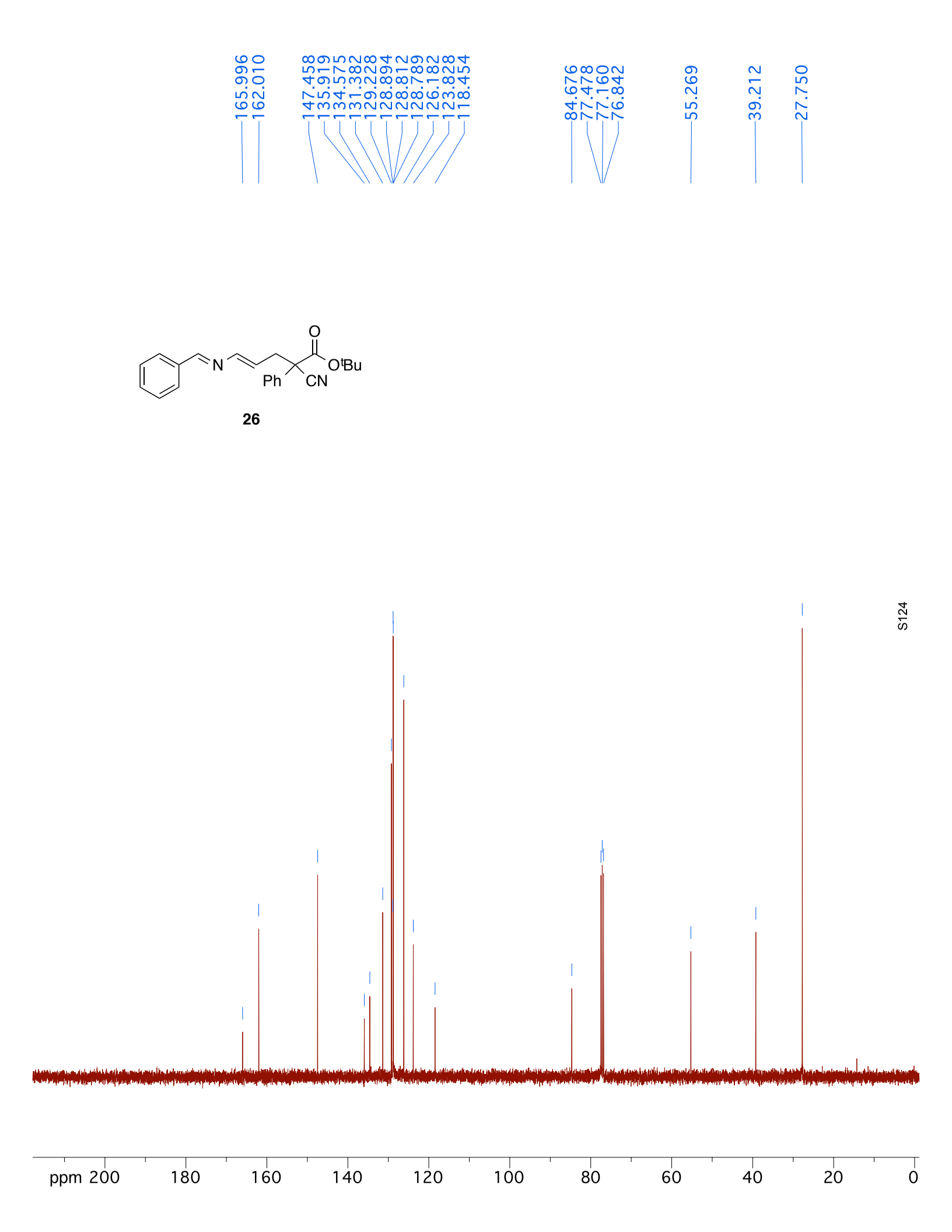
1
0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131.382
129.228
128.894
128.812
128.789
126.182
123.828
118.454
84.676
77.478
77.160
76.842
55.269
39.212
27.750
O
N
O
tBu
Ph
CN
26
S124
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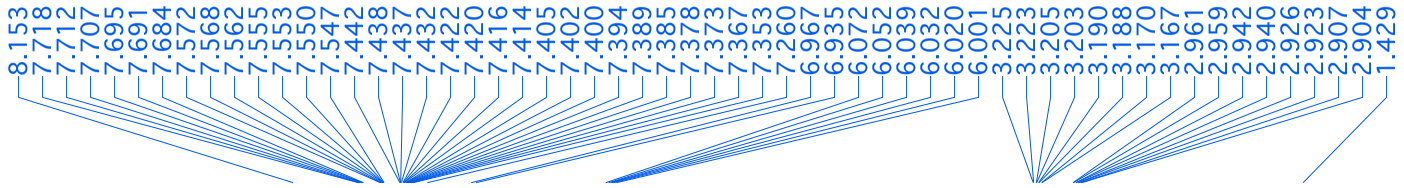
80
60
40
20
0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7.562
7.555
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7.405
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7.385
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7.373
7.367
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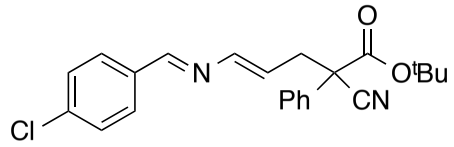
O
N
O^{t}Bu
Ph
CN
Cl

27

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1.06
8.95
10
9
8
7
6
5
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3
2
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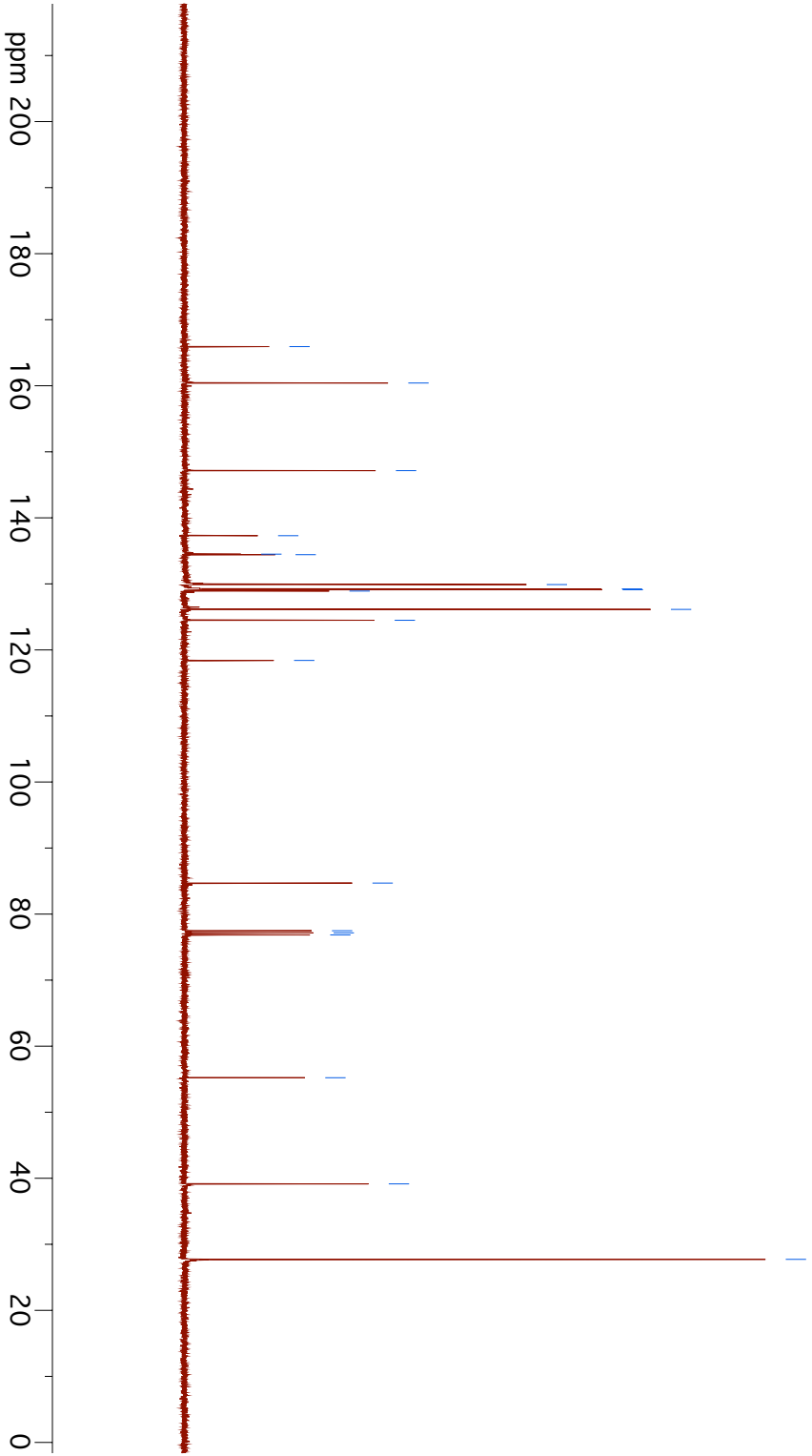
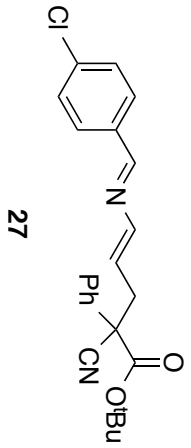
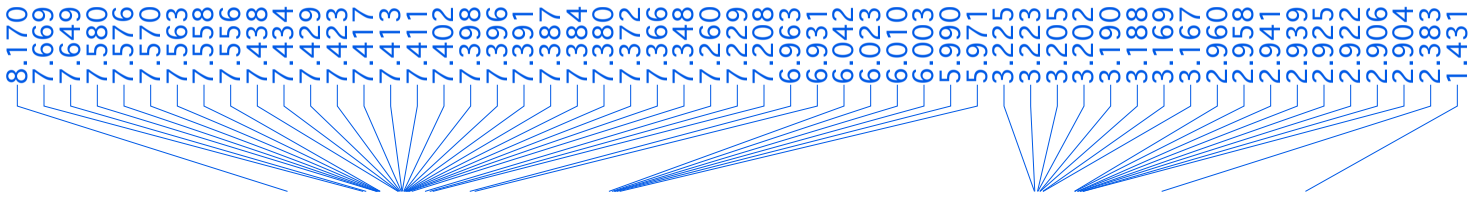




27

165.927
160.415
147.146
137.297
134.501
134.421
129.894
129.235
129.108
128.913
126.135
124.488
118.407
84.695
77.478
77.160
76.842
55.223
39.147
27.722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7.434
7.429
7.423
7.417
7.413
7.411
7.402
7.398
7.396
7.391
7.387
7.384
7.380
7.372
7.366
7.348
7.260
7.229
7.208
6.963
6.931
6.042
6.023
6.010
6.003
5.990
5.971
3.225
3.223
3.205
3.202
3.190
3.188
3.169
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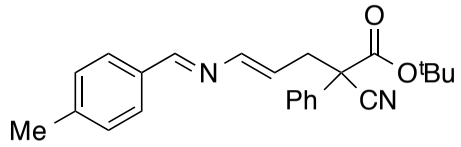
2.958
2.941
2.939
2.925
2.922
2.906
2.904
2.383
1.431


O
N
O^{t}Bu
Ph
CN
Me

28

1.91
2.95
1.07
1.08
2.9
1
1.9
1.95
0.963
1.08
8.96
10
9
8
7
6
5
4
3
2
1
0

28

166.005
162.032
147.632
141.885
134.613
133.318
129.571
129.201
128.861
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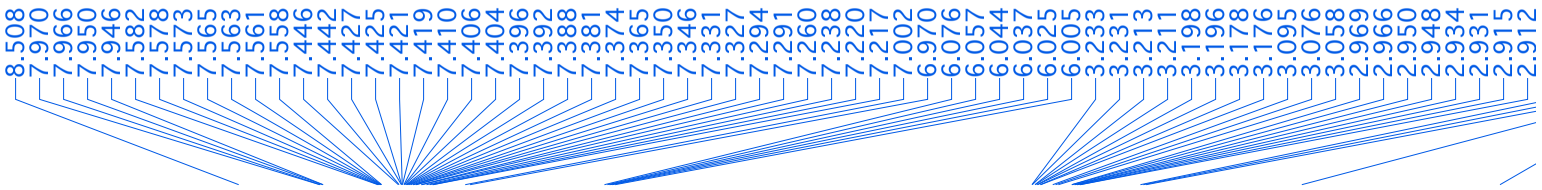
123.089
118.463
84.622
77.478
77.160
76.842
55.308
39.226
27.742
21.740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7.966
7.950
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7.582
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7.573
7.565
7.563
7.561
7.558
7.446
7.442
7.427
7.425
7.421
7.419
7.410
7.406
7.404
7.396
7.392
7.388
7.381
7.374
7.365
7.350
7.346
7.331
7.327
7.294
7.291
7.260
7.238
7.220
7.217
7.002
6.970
6.076
6.057
6.044
6.037
6.025
6.005
3.233
3.231
3.213
3.211
3.198
3.196
3.178
3.176
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3.058
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2.966
2.950
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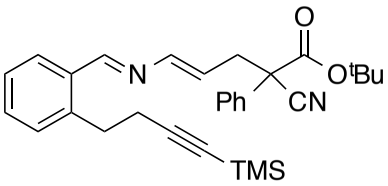
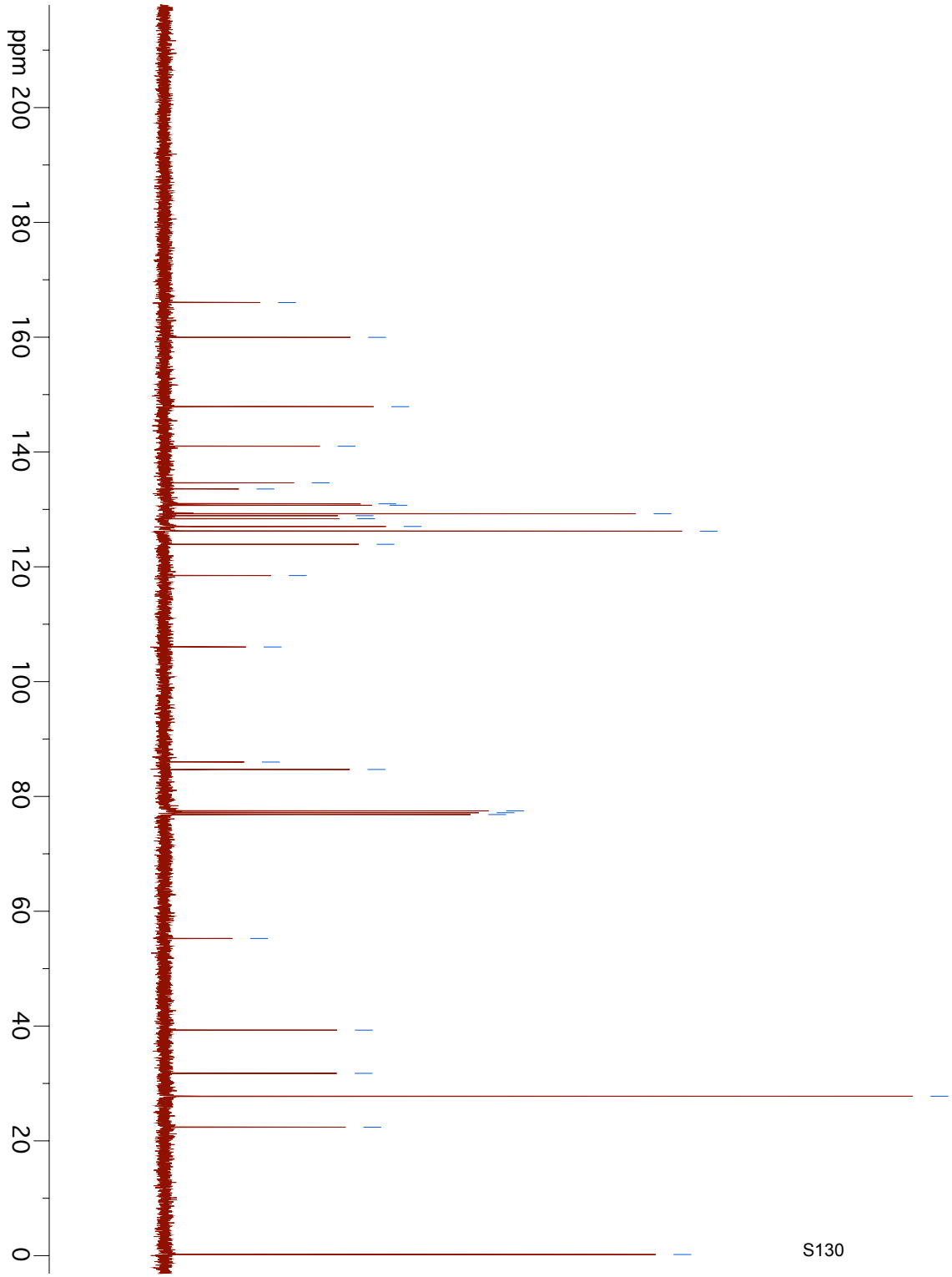
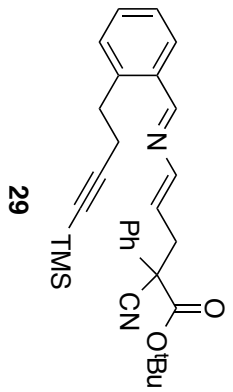
2.931
2.915
2.912


O
N
O
tBu
Ph
CN
TMS

29

S129
0.998
3.08
2.31
0.997
1.99
2.03
7.4
1.02
1.05
1.06
1.07
8.95
10
9
8
7
6
5
4
3
2
1
0





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159.975
147.894
141.010
134.633
133.559
130.971
130.720
129.242
128.906
128.375
127.028
126.209
123.918
118.475
106.034

85.991
84.693
77.477
77.160
76.843

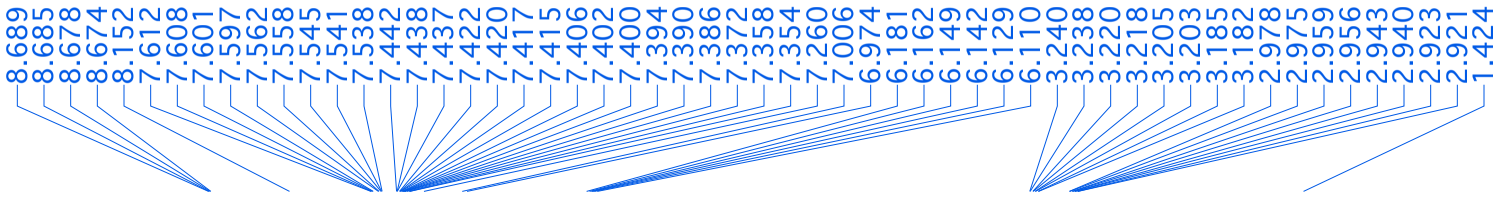
55.255

39.288

31.762
27.772

22.385

0.194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8.685
8.678
8.674
8.152
7.612
7.608
7.601
7.597
7.562
7.558
7.545
7.541
7.538
7.442
7.438
7.437
7.422
7.420
7.417
7.415
7.406
7.402
7.400
7.394
7.390
7.386
7.372
7.358
7.354
7.260
7.006
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6.181
6.162
6.149
6.142
6.129
6.110
3.240
3.238
3.220
3.218
3.205
3.203
3.185
3.182
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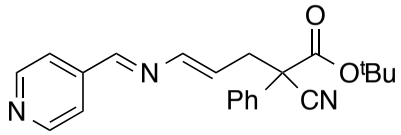
2.975
2.959
2.956
2.943
2.940
2.923
2.921
1.424


O
N
O^{t}Bu
N
Ph
CN

30

S131
1.13
1.63
1.06
1.08
9.29
2.06
1.34
3.35
0.982
1.08
10
9
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7
6
5
4
3
2
1
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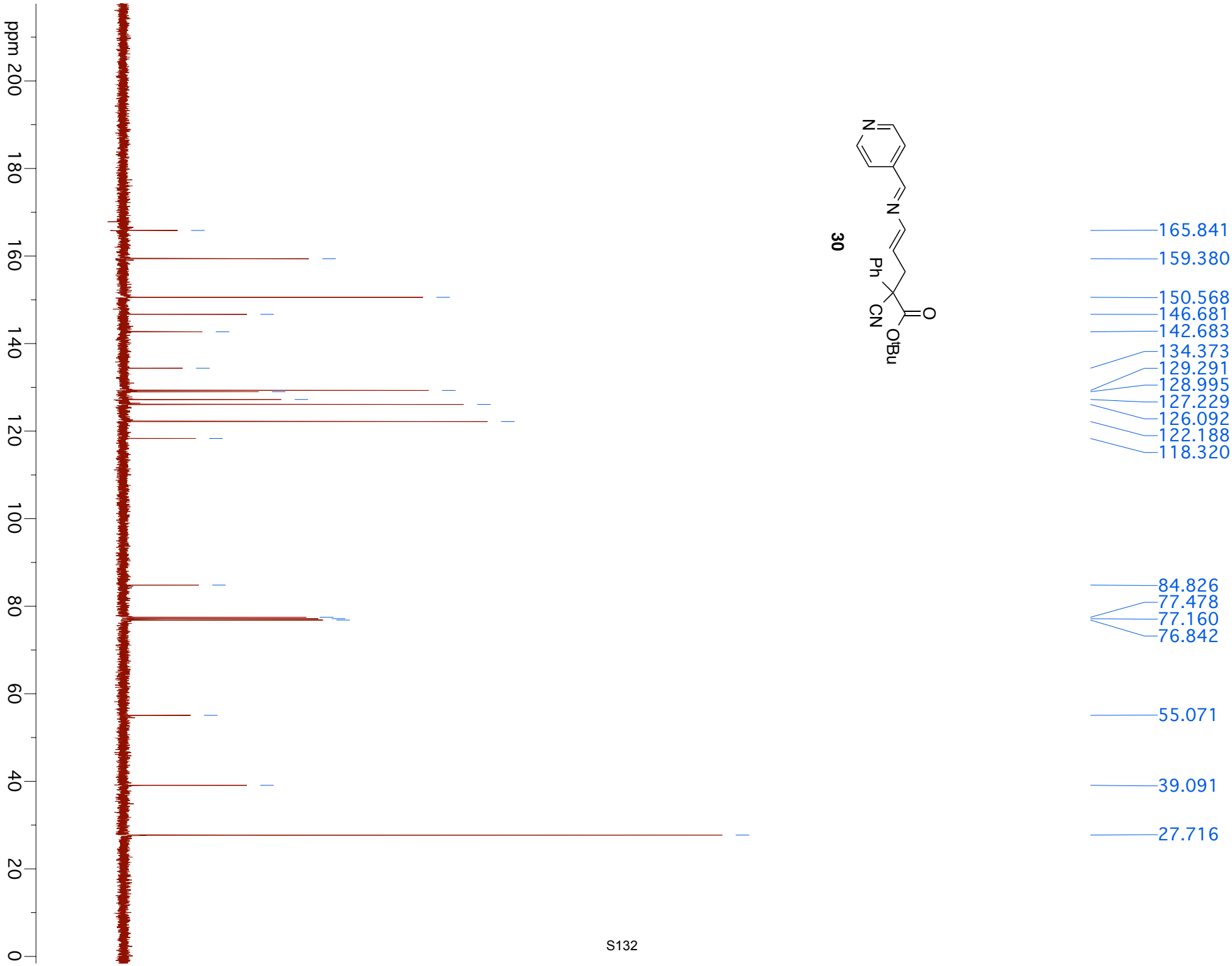
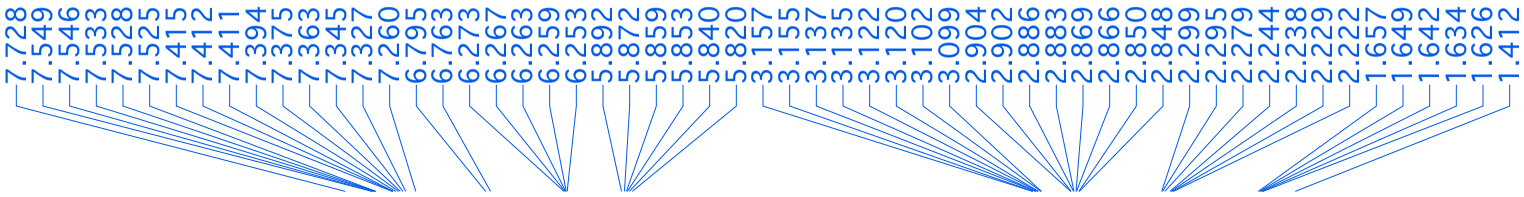

ppm
200
180
160
140
120
100
80
60
40
20
0
N
N
Ph
CN
O
O
tBu
30
165.841
159.380
150.568
146.681
142.683
134.373
129.291
128.995
127.229
126.092
122.188
118.320
84.826
77.478
77.160
76.842
55.071
39.091
27.716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7.525
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7.412
7.411
7.394
7.375
7.363
7.345
7.327
7.260
6.795
6.763
6.273
6.267
6.263
6.259
6.253
5.892
5.872
5.859
5.853
5.840
5.820
3.157
3.155
3.137
3.135
3.122
3.120
3.102
3.099
2.904
2.902
2.886
2.883
2.869
2.866
2.850
2.848
2.299
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2.238
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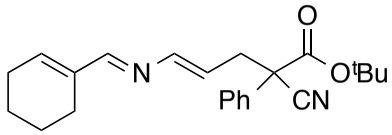
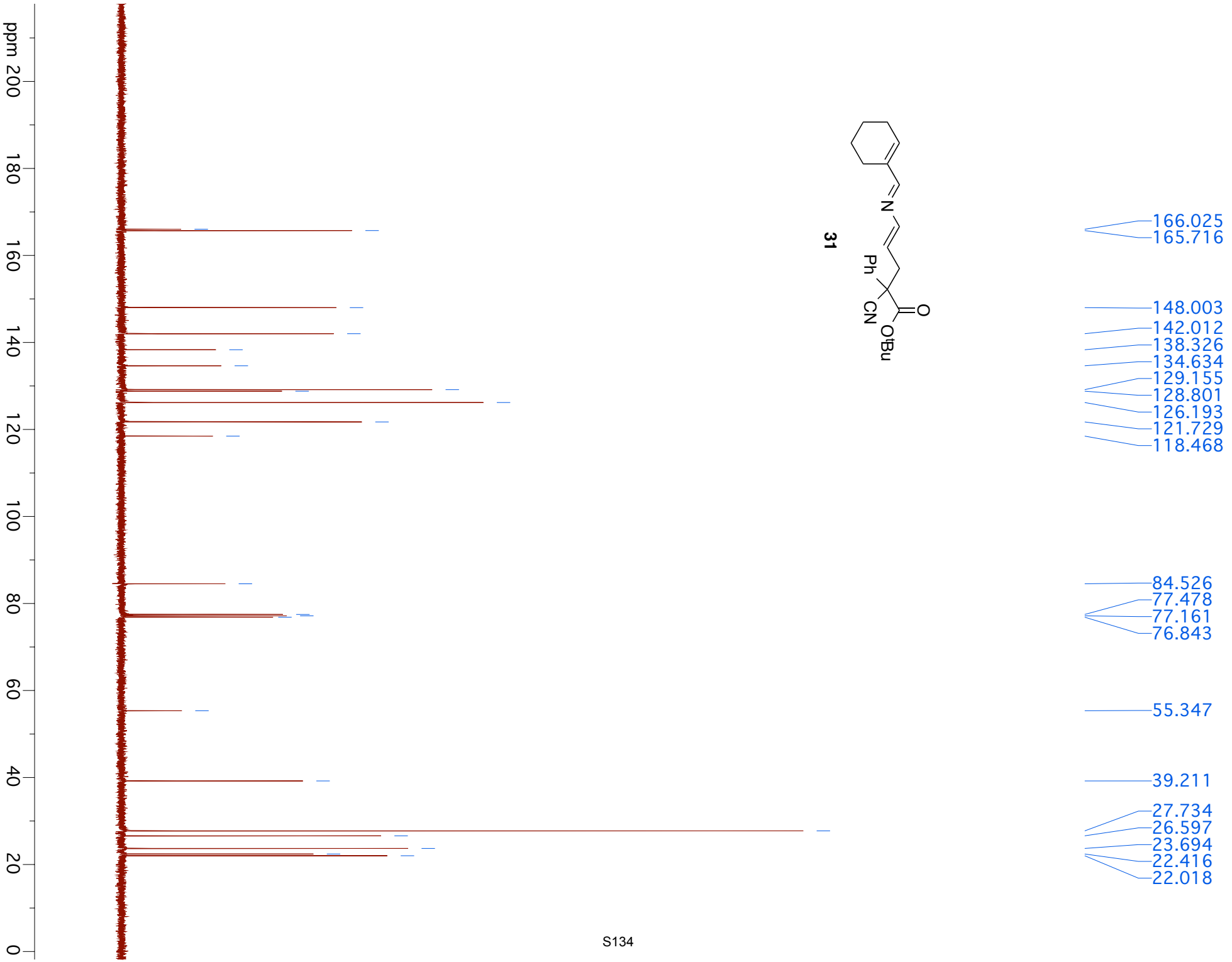
1.634
1.626
1.412


O
N
O
tBu
Ph
CN

31

S133

1.88
1.07
0.989
1.07
2.06
8.83
1
2.85
1.04
1.09
2.01
4.02
10
9
8
7
6
5
4
3
2
1
0


ppm
200
180
160
140
120
100
80
60
40
20
0
N
Ph
CN
O
O
tBu
166.025
165.716
148.003
142.012
138.326
134.634
129.155
128.801
126.193
121.729
118.468
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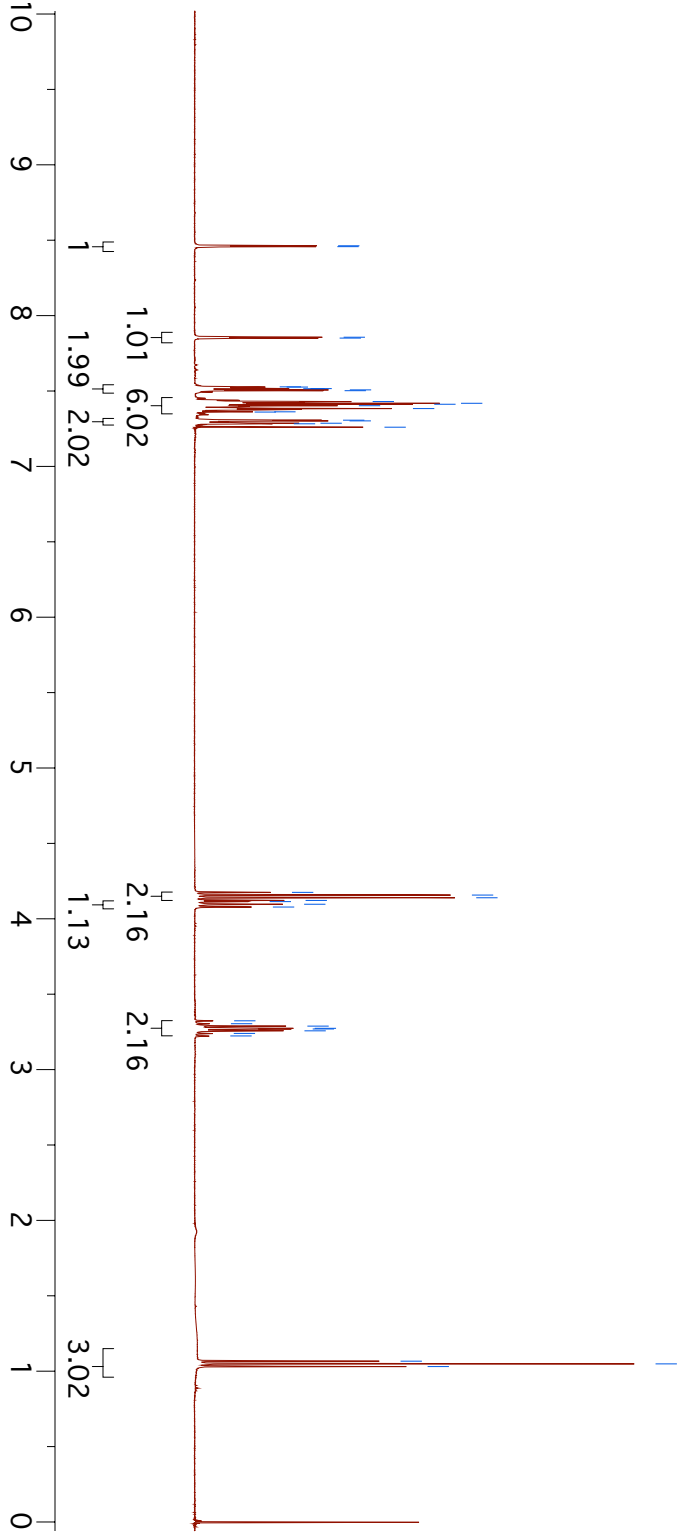
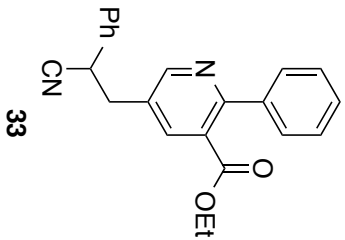
77.161
76.843
55.347
39.211
27.734
26.597
23.694
22.416
22.018

31





33

8.463
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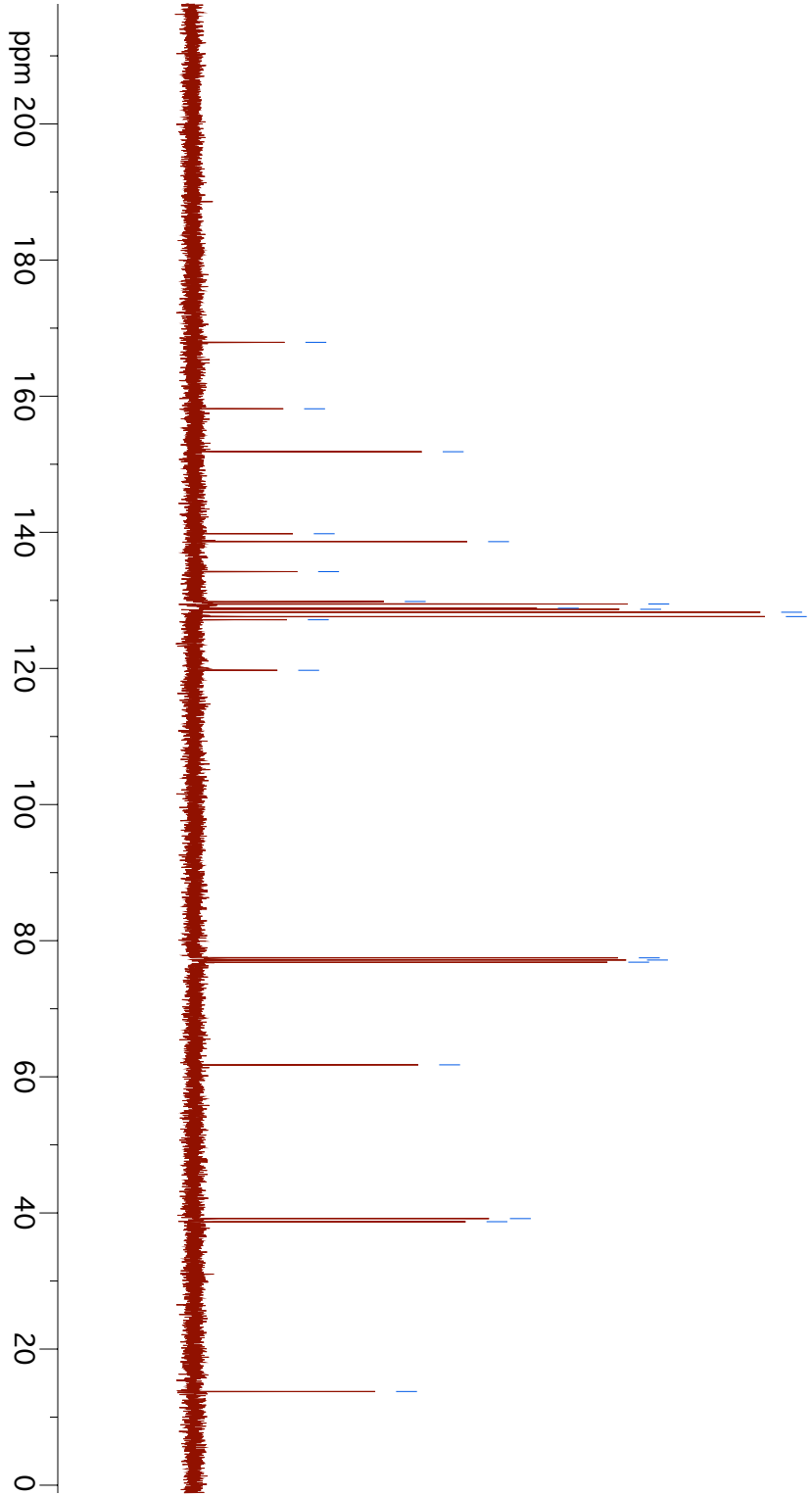
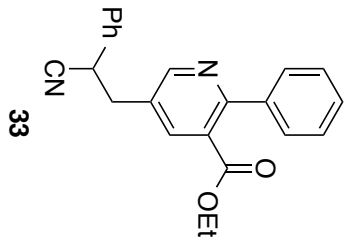
7.528
7.526
7.516
7.515
7.507
7.502
7.430
7.419
7.412
7.402
7.383
7.362
7.360
7.307
7.302
7.286
7.283
7.260

4.175
4.157
4.139
4.122
4.114
4.097
4.078

3.324
3.304
3.288
3.274
3.269
3.257
3.240
3.223

1.066
1.048
1.031





33

167.916
158.148
151.841
139.792
138.630
134.225
129.835
129.465
128.847
128.687
128.258
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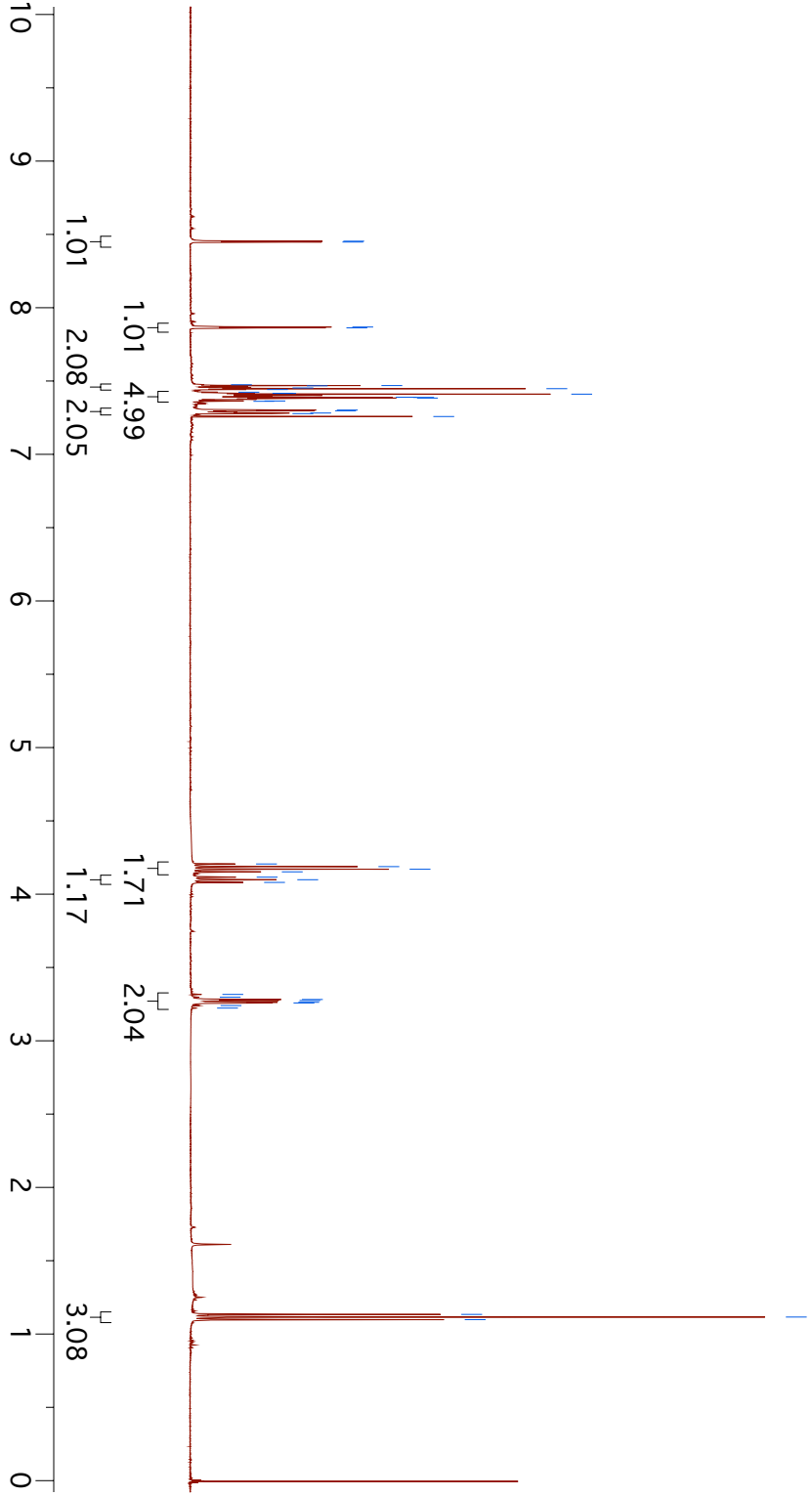
127.150
119.725

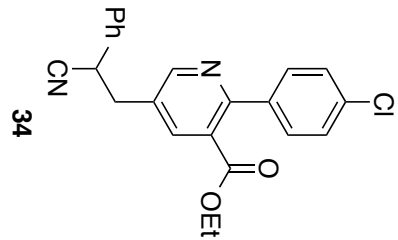
77.478
77.160
76.842

61.759

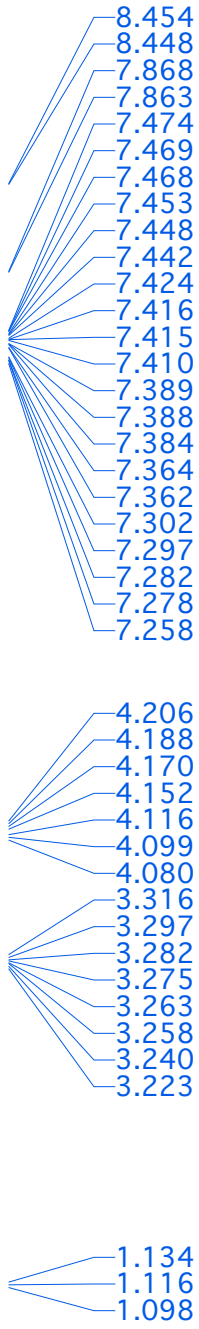
39.170
38.714

13.764


10
9
8
7
6
5
4
3
2
1
0
1.01
1.01
2.08
4.99
2.05
1.71
1.17
2.04
3.08


Ph
CN
N
Cl
O
OEt

34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7.424
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7.415
7.410
7.389
7.388
7.384
7.364
7.362
7.302
7.297
7.282
7.278
7.258
4.206
4.188
4.170
4.152
4.116
4.099
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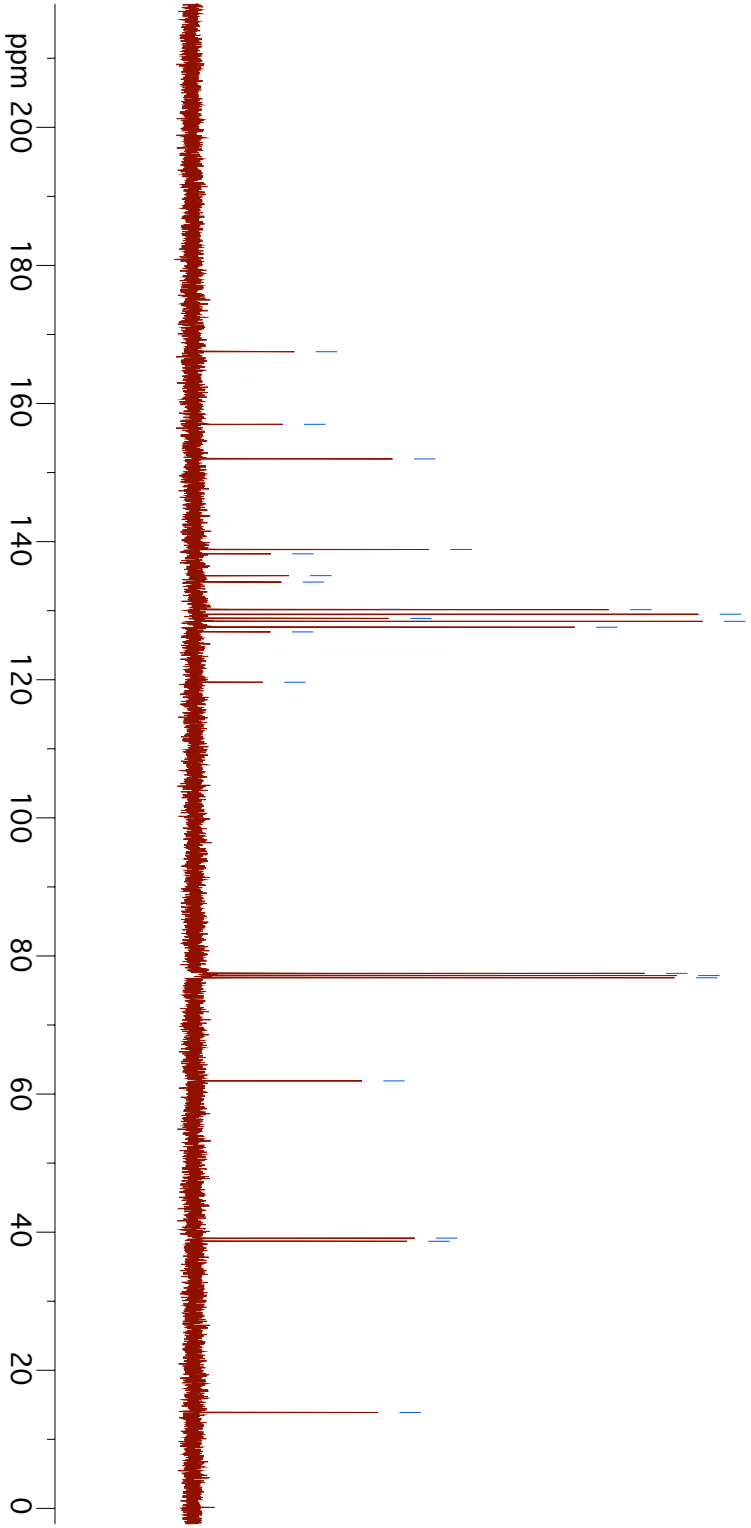
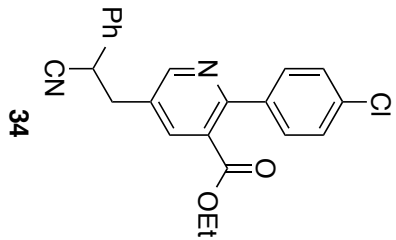
3.258
3.240
3.223
1.134
1.116
1.098





34

167.501
156.991
151.978
138.862
138.232
135.077
134.144
130.194
130.148
129.489
128.882
128.458
127.608
126.927
119.642

77.478
77.160
76.842

61.907

39.136
38.680

13.892