

# **Isomerization of N-Allyl Amides to Form Geometrically Defined Di-, Tri-, and Tetrasubstituted Enamides.**

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## Experimental:

### A. General Methods

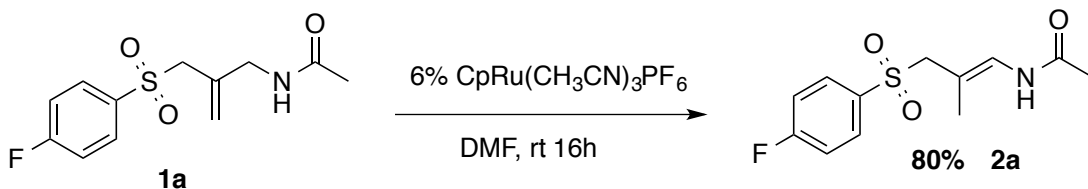
Compounds were purchased from commercial sources unless otherwise noted and used without further purification. DMF was used from a Sureseal Acros bottle. For NMR experiments deuterated solvent ampules were used immediately after opening. Thin layer chromatography was carried out on glass plates coated with silica gel SiO<sub>2</sub> 60 F254 from Merck; visualization with a UV lamp (254 nm) or by staining with a p-anisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO<sub>2</sub> 60 (0.040–0.063  $\mu$ m, 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Melting points were measured on a Thomas Hoover capillary melting point apparatus in open capillaries. Chemical shifts are reported in ppm relative to the residual protonated solvent (CDCl<sub>3</sub>:  $\delta$ H = 7.26 ppm,  $\delta$ C = 77.16 ppm) Benzene-*d*<sub>6</sub>:  $\delta$ H = 7.16 ppm (Toluene-*d*<sub>8</sub>:  $\delta$ H = 2.08 ppm)(CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ H = 5.32 ppm)(DMF-*d*<sub>7</sub>,  $\delta$ H = 2.75 ppm) (Acetone-*d*<sub>6</sub>,  $\delta$ H = 2.09 ppm). All <sup>13</sup>C NMR spectra are proton decoupled. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Infrared spectroscopic (IR) data was taken as thin films on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorption bands are reported in wavenumbers (cm<sup>-1</sup>) in the range of 4000–600 cm<sup>-1</sup>. High-resolution mass spectrometry (HRMS) was measured on a Bruker micrOTOF-Q II electrospray ionization (ESI) mass spectrometer by the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University. Mass peaks are reported in m/z units. Boron NMR was reference to BF<sub>3</sub> (OEt<sub>2</sub>) using an external standard.

## B. Isomerizations of allyl amides

All enamide geometries were determined by NOE experiments. Geometric selectivities were assigned by NMR analysis. For all enamide spectra if any small peaks were observed that could be assigned to a rotamer or minor olefin isomer the region was enlarged and integrated relative to the major. Since the selectivity in these case was still >20:1 whether you consider the small impurities (<5%) minor olefin isomers or not we did not investigate it any further. To illustrate that the selectivities were in fact excellent (>20:1) and were not being enriched through chromatography we have include a crude spectra after an aqueous workup to remove DMF (**2a**)(S58), and run a number of the reactions in *d*<sub>7</sub>-DMF (**4a** (S70), **10b** (S106), **11b** (S111), **12b/12c** (S118-S122). For compound **4h** (S80) we accounted for rotamers and the minor trans isomer to give a ratio of 18.7:1 (Z:E)(S80).

Synthesis of (**Z**)-*N*-(prop-1-en-1-yl)benzamide (**4a**) under atmospheric conditions without dry glassware showed no significant difference in terms of conversion, yield, or selectivity compared to that run under inert atmosphere and with dry glassware. Additionally for enamides **6b**, **7b**, **9a**, **9b**, **9c** reactions were run under atmospheric conditions and without dry glassware. DMF was used directly without degassing.

CpRu(CH<sub>3</sub>CN)<sub>3</sub>PF<sub>6</sub> was synthesized according to previous reports<sup>1</sup> but is also commercially available from Aldrich and Strem. The catalyst was stored in a capped vial in the freezer when not being used. While we initially would fill the vial with argon and parafilm after using we found that this was not necessary and the catalyst maintained the same orange color for long periods (months) if simply stored cold under atmospheric conditions in a capped vial. The vial was parafilmed to avoid excess moisture. For weighing the catalyst no precautions were taken and the catalyst was weighed directly under air. While a sure seal bottle was used for the DMF source this was done for convenience. For the reactions run under atmospheric conditions a positive pressure of inert gas was used to remove the solvent from the Sureseal bottle but after this no inert atmosphere was used and the reaction was run without any additional precautions. The runs using 6 mol% catalyst in which 2 mol% were added in portions was done in order to help find the minimum catalyst loading (using TLC to indicate conversion) and does not seem to increase conversion relative to one catalyst addition. The catalyst was always added last (as a solid) or dissolved with the substrate. In these cases the color becomes a dark orange/brown. As the reaction progresses the solution will slowly turn dark brown, even blackish if left long enough. Oftentimes the reaction is done before this point.



**(*E*)-*N*-(3-((4-fluorophenyl)sulfonyl)-2-methylprop-1-en-1-yl)acetamide (2a).**

To a test tube, *N*-(2-(((4-fluorophenyl)sulfonyl)methyl) allyl)acetamide (635 mg, 2.3 mmol) (**1a**) and [CpRu(CH<sub>3</sub>CN)<sub>3</sub>]PF<sub>6</sub> (23 mg, 0.054 mmol, 2% mol) were added. The test tube was then flushed with argon and kept under argon atmosphere, then dry DMF (4 mL) was added. The reaction mixture was stirred at rt, and 2% mol catalyst was added hourly as a solid to the reaction mixture until the total catalyst loading was 6% mol. Afterwards, the reaction was monitored by TLC (70:30 EtOAc: pet. ether). After 16 h, the reaction mixture was diluted with EtOAc (~20 mL), and washed with saturated LiCl (5x15 mL). The aqueous layer was then extracted with EtOAc (2 X 10 mL). The combined organic layers were then dried with MgSO<sub>4</sub>, and the solvent evaporated to yield a brown oil. NMR analysis of the crude mixture showed that the crude oil was >95% pure however to increase purity the compound could be purified by silica gel column chromatography (eluting with 70:30 EtOAc: pet. ether) to yield 505 mg (80% yield) of (*E*)-*N*-(3-((4-fluorophenyl)sulfonyl)-2-methylprop-1-en-1-yl)acetamide.

R<sub>f</sub> = 0.43 70:30 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 124-125°C

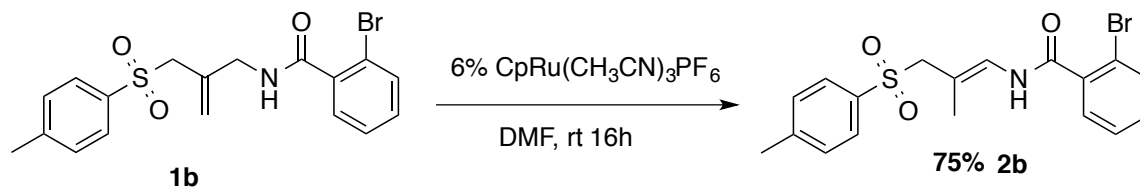
HRMS-ESI [C<sub>12</sub>H<sub>14</sub>FNNO<sub>3</sub>S+Na]<sup>+</sup> calcd 294.0576, Found: 294.0574.

IR(thin film, cm<sup>-1</sup>): 3228, 3157, 3018, 2939, 2888, 1634, 1512, 1296, 1269, 1133, 1071, 832, 732 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.81 (s, 3H), 2.04 (s, 3H), 3.73 (s, 2H), 6.50 (d, J=10.7 Hz, 1H), 7.22 (t, J=7.5 Hz, 2H), 7.33-7.43 (m, 1H), 7.85 (d, J=5.1 Hz, 2H)

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 15.4, 23.1, 64.3, 104.7, 116.5 (d, J=22.6 Hz), 125.8, 131.0 (d, J=9.6 Hz), 134.4 (d, J=3.0 Hz), 165.8 (d, J=257 Hz), 167.4

1D NOE: Irradiation of the vinyl proton (6.50 ppm) yields a 13% enhancement of the methylene protons at 3.73 ppm, indicative of the *E* isomer.



**2-bromo-*N*-(2-(((4-fluorophenyl)sulfonyl)methyl)allyl)benzamide(2b):** To a test tube, benzamide **1b** (84 mg, 0.21 mmol) and [CpRu(MeCN)<sub>3</sub>]PF<sub>6</sub> (2 mg, 0.0044 mmol, 2.1% mol) were added. The test tube was then flushed with argon and kept under inert atmosphere. Dry DMF (0.4 mL) was then added and the solution stirred

at rt. 2% mol catalyst was added as a solid hourly until the total catalyst loading was 6% mol. After 16 h, the reaction mixture was diluted with ethyl acetate (3 mL). This mixture was washed with 5x3 mL saturated LiCl. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation yielded crude (*E*)-2-bromo-*N*-(2-methyl-3-tosylprop-1-en-1-yl)benzamide as an oil. Purification by silica column chromatography, eluting with 50:50 ethyl acetate:petroleum ether, afforded 63 mg (75% yield) pure (*E*)-2-bromo-*N*-(2-methyl-3-tosylprop-1-en-1-yl)benzamide as a crystalline white solid.

$R_f = 0.38$  50:50 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 108-109°C

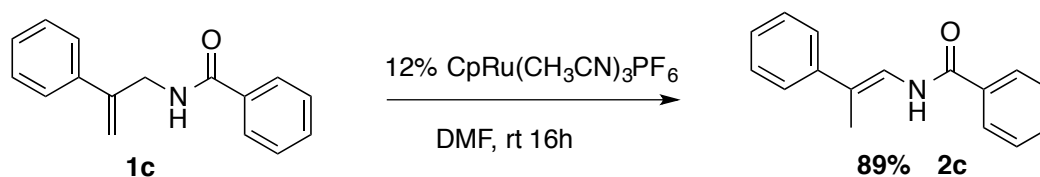
HRMS-ESI [C<sub>18</sub>H<sub>18</sub>BrNO<sub>3</sub>S+H]<sup>+</sup> calcd. 408.0269, Found: 408.0264

IR(thin film, cm<sup>-1</sup>): 3268, 3144, 3022, 2936, 2881, 1637, 1570, 1492, 1272, 1235, 1071, 900, 722, 681 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  1.86 (d, *J*=1.2 Hz, 3H), 2.43 (s, 3H), 3.74 (s, 2H), 6.56-6.63 (m, 1H), 7.27-7.38 (m, 4H), 7.53-7.60 (m, 2H), 7.70 (d, *J*=8.1 Hz, 2H), 7.84 (d, *J*=10.5 Hz, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  15.6, 21.6, 64.1, 107.5, 119.1, 125.2, 127.7, 128.2, 129.7, 130.3, 131.9, 133.5, 135.2, 135.9, 144.8, 163.9.

1D NOE: Irradiation of the methylene protons (3.74 ppm) gave a 14% enhancement of the vinyl proton (6.59 ppm), which is characteristic of the *E* isomer



**(*E*)-*N*-(2-phenylprop-1-en-1-yl)benzamide(2c):** To a test tube, *N*-(2-phenylallyl)benzamide (24 mg 0.1 mmol)(**1c**) and the [CpRu(MeCN)<sub>3</sub>]PF<sub>6</sub> (5.2 mg, 0.012 mmol, 12%) were added. The test tube was then purged with Ar, then dry DMF (0.5M, 0.2 mL) added. The reaction was stirred at rt for 16 h. After 16 h, the reaction mixture was diluted with ethyl acetate (~3 mL), and the organic layer was washed with 5x3mL saturated LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation of the solvent yielded a light brown solid. Purification by silica column chromatography, eluting with 20:80 EA:PE, yield pure (*E*)-*N*-(2-phenylprop-1-en-1-yl)benzamide as a white solid (21 mg, 89% yield).

$R_f = 0.68$  30:70 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 113-114°C

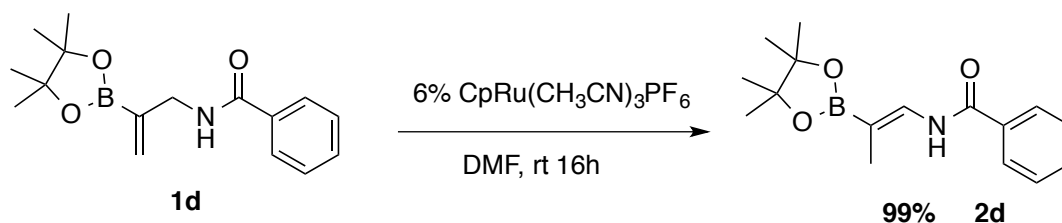
HRMS-ESI [C<sub>16</sub>H<sub>15</sub>NO+H]<sup>+</sup> calcd 238.1232, Found: 238.1229

IR (thin film, cm<sup>-1</sup>): 3210, 1610, 1554, 1498, 1464, 1266, 744, 687 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.17 (d, J=1.2 Hz, 3H), 7.27-7.32 (m, 2H), 7.38 (t, J=7.7 Hz, 2H), 7.47 (s, 2H), 7.53 (d, J=7.8 Hz, 2H), 7.59 (s, 1H), 7.83 (d, J=10.7 Hz, 1H), 7.87-7.92 (m, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 14.5, 118.4, 119.9, 125.4, 126.7, 127.0, 128.4, 128.8, 132.0, 133.8, 140.8, 164.3

<sup>1</sup>H NOE: Irradiation of the methyl protons (2.17 ppm) gave a 7% enhancement of the N-H proton (6.82 ppm), which is characteristic of the E isomer.



**(Z)-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)benzamide (2d):** To a test tube, *N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide (**1d**) (58 mg, 2.0 mmol) and [CpRu(MeCN)<sub>3</sub>]PF<sub>6</sub> (2 mg, 0.004 mmol, 2% mol) were added. The test tube was then flushed with argon and kept under argon atmosphere. Solvent (0.4 mL) was added and the reaction was stirred. Every hour after the solvent was added, ~2% mol catalyst was added as a solid to the reaction mixture until the total catalyst loading was ~6% mol. The reaction progress was monitored by TLC (20:80 EtOAc:pet. ether). Purification of the crude (*Z*)-*N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)benzamide (**2d**) was done by directly columning the DMF solution eluting with 20:80 EA:PE to afford pure isomerized product (58 mg, 99% yield).

R<sub>f</sub> = 0.48 20:80 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 128-129°C

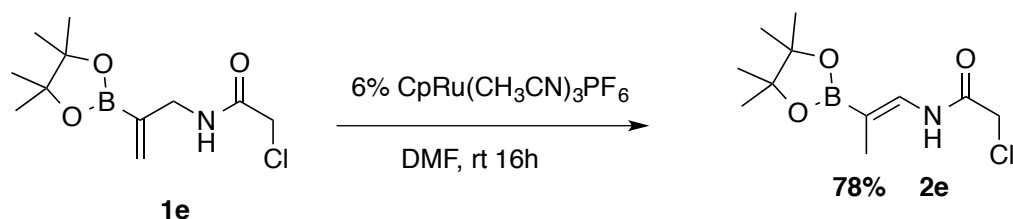
HRMS-ESI [C<sub>16</sub>H<sub>22</sub>BNO<sub>3</sub>+H]<sup>+</sup> calcd. 288.1771, Found: 288.1771

IR(thin film, cm<sup>-1</sup>): 3312, 2936, 2884, 1645, 1609, 1493, 1463, 1359, 1305, 1276, 1171, 1135, 1113, 679, 658 cm<sup>-1</sup>.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.27 (s, 12H), 1.75 (d,  $J=1.5$  Hz, 3H), 7.43-7.50 (m, 2 H), 7.55 (s, 1H), 7.68 (d,  $J=11.2$  Hz, 1H), 7.82 (d,  $J=7.08$  Hz, 2H), 7.84-7.91 (m, 1H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  11.6, 24.7, 83.2, 127.1, 128.8, 132.1, 133.2, 133.7, 164.0  
Note: Signal from the carbon adjacent to B not observed due to low intensity in  $^{13}\text{C}$  NMR

1D NOE: Irradiation of the methyl H's at 1.74 ppm yielded a 10% enhancement in the N-H signal at 7.88 ppm.



**(Z)-2-chloro-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)acetamide (2e):** In a test tube, 2-chloro-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)acetamide (**1e**) (218 mg, 0.83 mmol) was dissolved in dry DMF (0.7 mL). The test tube was flushed with argon, and kept under argon atmosphere.  $[\text{CpRu}(\text{MeCN})_3]\text{PF}_6$  (7 mg, 0.015 mmol, 2% mol) was added to the reaction mixture as a solid and the reaction stirred at rt. Every hour after the initial addition of catalyst, ~2% mol catalyst was added by solid addition until the total catalyst loading was ~6% mol. The reaction progress was monitored by TLC (boric acid treated silica TLC plate<sup>6</sup>; 20:80 ethyl acetate:petroleum ether). After 16 h, the reaction mixture was diluted with ethyl acetate (~20 mL). The solution was washed with 5x15 mL saturated LiCl, then dried with  $\text{MgSO}_4$ . Evaporation of the solvent yielded a light brown solid. The crude isomerization product was purified by boric acid treated silica gel column chromatography,<sup>16</sup> eluting with 20:80 EtOAc:pet. ether, to afford 170 mg (0.66 mmol, 78.4% yield) of (Z)-2-chloro-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)acetamide as a white powder.

$R_f = 0.50$  20:80 EA:PE (UV/ $\text{KMnO}_4$ )

Mp = 138-139°C

HRMS-ESI  $[\text{C}_{16}\text{H}_{22}\text{BNO}_3+\text{H}]^+$  calcd. 260.1225, Found: 260.1225

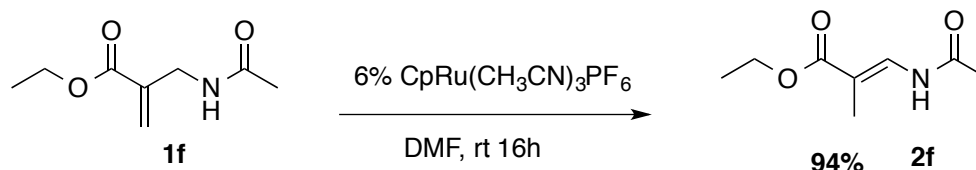
IR(thin film,  $\text{cm}^{-1}$ ): 3238, 2937, 2902, 1645, 1615, 1505, 13456, 1204, 1128, 1084, 661  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (s, 12H), 1.68 (d,  $J=1.7$  Hz, 3H), 4.14 (s, 2H), 7.38 (dd,  $J=11.23, 1.7$  Hz, 1H), 8.30 (d,  $J=10.5$  Hz, 1H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  11.5, 24.7, 42.6, 83.3, 131.5, 162.9

Note: Signal from the carbon adjacent to B not observed due to low intensity.

1D NOE: Irradiation of the methyl protons at 1.68 ppm yielded an 8% enhancement in the N-H signal at 8.30 ppm.



**Ethyl (*E*)-3-acetamido-2-methylacrylate (2f):** To a dry test tube, ethyl 2-(acetamidomethyl)acrylate (35.1 mg, 0.20 mmol, 1 equiv) (**2f**) and  $[\text{CpRu}(\text{CH}_3\text{CN})]\text{PF}_6$  (5.3 mg, 0.012 mmol, 6% mol) were added as solids. The test was then flushed with Ar, then 0.4 mL of dry DMF added. The reaction was stirred at rt for 16h and monitored by TLC (90:10 EtOAc:pet. ether). After 16h, the reaction was diluted with 3mL ethyl acetate and 3mL of saturated LiCl. The aqueous layer was then removed. The organic layer was washed with 4x3mL saturated LiCl. The aqueous layer was then extracted with EtOAc (2 X 2 ml). The combined organic layers were dried with  $\text{MgSO}_4$ . Evaporation of the solvent yielded ethyl (*E*)-3-acetamido-2-methylacrylate as an off-white solid. Purification of the crude ethyl (*E*)-3-acetamido-2-methylacrylate by eluting with 80:20 EA:PE gave (33.2 mg, 94.6% yield) of (*E*)-3-acetamido-2-methylacrylate as a white solid. Characterization data was consistent with those previously reported in the literature.<sup>2</sup>

$R_f$  = 0.56 in 80:20 EA:PE (UV/ $\text{KMnO}_4$ )

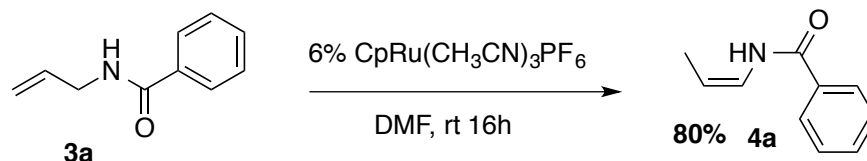
$M_p$  = 90-92°C

IR(thin film,  $\text{cm}^{-1}$ ): 3264.0, 2884.2, 1661.3, 1627.5, 1500.8, 1251.5, 1115.9, 740.9  $\text{cm}^{-1}$ .

$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.27 (td,  $J=7.1$ , 0.86 Hz, 3H), 1.80 (d,  $J=1.0$  Hz, 3H), 2.16 (s, 3H), 4.17 (q,  $J=7.1$  Hz, 2H), 7.67 (d,  $J=11.7$ , 1H), 7.98 (dt,  $J=11.9$ , 1.15 Hz, 1H).

$^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  10.6, 14.3, 23.4, 60.5, 107.8, 131.6, 168.0, 168.3

1D NOE: Irradiation of the methyl H's adjacent to the ester (1.80 ppm) resulted in a 5.49% enhancement of the N-H signal at 7.67 ppm, which is characteristic of the *E* isomer.





**(Z)-N-(prop-1-en-1-yl)benzamide (4a):** To a small test tube, N-allylbenzamide (0.0375g, 0.2 mmol) (**3a**) was added and the test tube purged with argon. DMF (0.4 mL, 0.5 M) was added, followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (5.2 mg, 0.012 mmol, 6% mol) as a solid. The reaction was stirred at rt for 16 h. After 16 h, the reaction mixture was diluted with 3 mL ethyl acetate, then washed 5x3 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with  $\text{MgSO}_4$ , and the solvent evaporated. The crude product was purified by silica column chromatography, eluting along a gradient starting with 10:90 EtOAc:pet. ether and ending with 20:80 EA:PE. Evaporation yielded (Z)-N-(prop-1-en-1-yl)benzamide (30 mg, 80% yield) as a white solid. Characterization data was consistent with those previously reported in the literature.<sup>3</sup>

$R_f = 0.70$  in 20:80 EA:PE (UV/ $\text{KMnO}_4$ )

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.71 (dd,  $J=7.1, 1.7$  Hz, 3H), 4.94 (dq,  $J = 8.5, 7.2$ , 1H), 6.93 (t,  $J=9.8$  Hz, 1H), 7.46 (t,  $J=7.4$  Hz, 2H), 7.53 (t,  $J=7.3$  Hz, 1H), 7.64 (bs, 1H), 7.81 (d,  $J=7.1$  Hz, 2H).

$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ , rt)  $\delta$  11.0, 106.1, 127.0, 128.7, 131.9, 133.9, 164.3.

1D NOE: Irradiation of the vinyl H (6.93 ppm) resulted in a 5% enhancement of the other vinylic signal at 4.90-4.98 ppm.

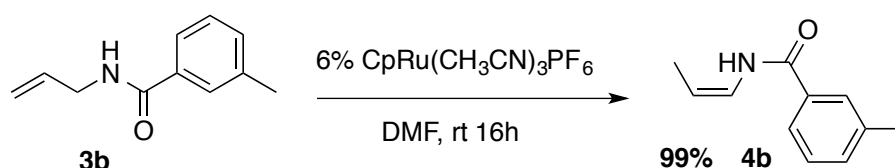
#### NMR Experiments for **3a** to **4a**:

**(Z)-N-(prop-1-en-1-yl)benzamide (4a):** N-allylbenzamide (37.5 mg, 0.2 mmol) (**3a**) and  $d_7$ -DMF (0.4 mL, 0.5 M) were added to an NMR tube, followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (5.2 mg, 0.012 mmol, 6% mol) or by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (2.6 mg, 0.006 mmol, 3% mol) as a solid. The reaction was monitored by NMR. No attempts to exclude atmosphere or  $\text{H}_2\text{O}$  were made.

6% cat: Reaction was complete within 1h.

3% cat: Reaction was complete within 3h.

$^1\text{H NMR}$  (600 MHz; DMF):  $\delta$  9.61 (s, 1H), 7.99 (dd,  $J = 8.3, 1.1$ , 2H), 7.57 (t,  $J = 7.4$ , 1H), 7.50 (t,  $J = 7.6$ , 2H), 6.87 (ddd,  $J = 9.8, 9.1, 1.7$ , 1H), 4.92-4.87 (m, 1H), 1.80 (dd,  $J = 7.1, 1.8$ , 3H)



**(Z)-3-methyl-N-(prop-1-en-1-yl)benzamide (4b):** To a test tube, *N*-allyl-3-methylbenzamide (37 mg, 0.21 mmol) (**3b**) was added, then the test tube was purged with argon. DMF (0.4 mL, 0.5M) was then added, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (5.4 mg, 0.01 mmol, 6% mol). The reaction was allowed to stir at rt for 16 h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with (2 X 2 mL). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation of solvent yielded crude (Z)-3-methyl-N-(prop-1-en-1-yl)benzamide as an oil. The crude product was purified by column chromatography, eluting with 20:80 EA:PE to give (Z)-3-methyl-N-(prop-1-en-1-yl)benzamide (37 mg, 99% yield) as a white solid.

R<sub>f</sub> = 0.50 in 20:80 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 58-60°C

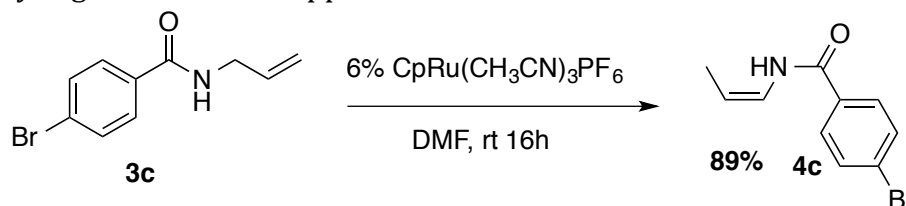
HRMS-ESI [C<sub>11</sub>H<sub>13</sub>NO + Na]<sup>+</sup> calcd. 198.0895 found: 198.0890

IR(thin film, cm<sup>-1</sup>): 3254.8, 2879.4, 1623.2, 1491.47, 1265.1, 1192.3, 1131.1 cm<sup>-1</sup>.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 1.70 (dd, J=7.1, 1.7 Hz, 3H), 2.40 (s, 3H), 4.93 (dq, J = 8.8, 7.1, 1H), 6.92 (ddq, J = 10.7, 9.0, 1.7, 1H), 7.33 (d, J=4.7 Hz, 2H), 7.57 (t, J=3.5 Hz, 1H), 7.62 (s, 1H), 7.64 (bs, 1H).

<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>, rt) δ 21.7, 106.3, 106.4, 122.5, 124.2, 128.1, 128.9, 132.9, 134.2, 138.9, 164.8.

1D NOE: Irradiation of the vinyl H (6.90-6.95 ppm) resulted in a 6.0% enhancement of the vinyl signal at 4.89-4.95 ppm.



**(Z)-4-bromo-N-(prop-1-en-1-yl)benzamide (4c):** To a test tube, *N*-allyl-4-bromobenzamide (52.3 mg, 0.21 mmol) (**3c**) was added, then the test tube was purged with argon. DMF (0.4 mL, 0.5M) was added, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (5.5 mg, 0.01 mmol, 6% mol). The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation of solvent yielded crude (Z)-4-bromo-N-(prop-1-en-1-yl)benzamide as a cream solid. The crude product was purified by column chromatography, eluting with 20:80 EtOAc:pet. ether. Evaporation yielded (Z)-4-bromo-N-(prop-1-en-1-yl)benzamide (47 mg, 88.9% yield) as a white solid.

R<sub>f</sub> = 0.55 in 20:80 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 68-69°C

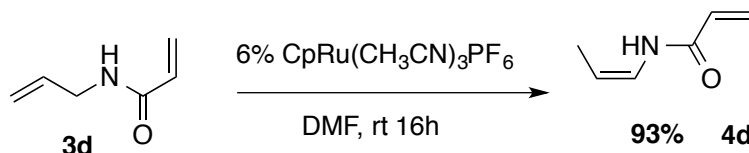
IR(thin film, cm<sup>-1</sup>): 3287.4, 2879.6, 1630.6, 1488.04, 1371.7, 1258.4, 832.8, 721.9 cm<sup>-1</sup>.

HRMS-ESI [C<sub>10</sub>H<sub>10</sub>BrNO+Na]<sup>+</sup> calcd. 261.9843:263.9824 found 261.9836:263.9814

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 1.70 (dd, J=7.1, 1.8 Hz, 3H), 4.92-4.98 (m, 1H), 6.86 (ddq, J=10.7, 8.9, 1.8 Hz, 1H), 7.54-7.56 (m, 2H), 7.63-7.66 (m, 2H), 7.73 (broad d, J=8.5 Hz, 1H).

<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 11.0, 106.9, 122.0, 126.6, 128.6, 131.9, 132.7, 163.5.

1D NOE: Irradiation of the vinyl H (6.86 ppm) resulted in a 5% enhancement of the vinyl signal at 4.92-4.98 ppm.



**(Z)-N-(prop-1-en-1-yl)acrylamide (4d):** To a test tube, *N*-allylacrylamide (26 mg, 0.20 mmol) was added, then the test tube was purged with argon. DMF (0.4 mL, 0.5M) was added, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (6.5 mg, 0.01 mmol, 6% mol). The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 ml). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation of solvent yielded crude (Z)-N-(prop-1-en-1-yl)acrylamide as a cream solid. The crude product was purified by column chromatography, eluting along a gradient (start 20:80 EtOAc:pet. ether and ending with 40:60 EtOAc:pet ether). Evaporation of the appropriate fractions yielded (Z)-N-(prop-1-en-1-yl)acrylamide (24 mg, 93 % yield) as a white solid.

R<sub>f</sub> = 0.48 in 50:50 EA:PE (UV/KMNO<sub>4</sub>)

Mp = 78-79 °C

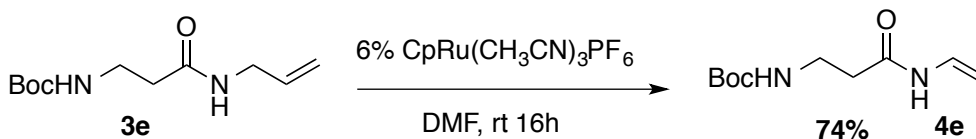
HRMS-ESI [C<sub>6</sub>H<sub>9</sub>NO+Na]<sup>+</sup> calcd. 134.0582 found 134.0578

IR(thin film, cm<sup>-1</sup>): 3247.4, 1631.4, 1601.6, 1506.5, 1388.6, 1291.0, 1211.1, 1132.2, 975.2.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, rt) δ 1.62 (s, 1H), 1.65 (dd, J=7.1, 1.6 Hz, 3H), 4.89 (dq, J = 8.7, 7.1, 1H), 5.74 (dd, J=10.3, 1.0 Hz, 1H), 6.16 (dd, J=16.9, 10.3 Hz, 1H), 6.39 (dd, J=16.9, 0.8 Hz, 1H), 6.79-6.85 (m, 1H), 7.05 (bs, 1H).

$^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ , rt)  $\delta$  10.9, 106.2, 121.8, 128.0, 130.1, 162.3.

1D-NOE: Irradiation of the vinyl H (6.79-6.85 ppm) resulted in a 3.0% enhancement of the vinyl signal at 4.86-4.92 ppm.



***tert*-butyl (*Z*)-(3-oxo-3-(prop-1-en-1-ylamino)propyl)carbamate (**4e**):** To a test tube, *tert*-butyl (3-(allylamino)-3-oxopropyl)carbamate (47 mg, 0.20 mmol) (**3e**) was added, then the test tube was purged with argon. DMF (0.4 mL, 0.5M) was added, followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (5.5 mg, 0.01 mmol, 6% mol). The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with  $\text{MgSO}_4$ . Evaporation of solvent yielded crude *tert*-butyl (*Z*)-(3-oxo-3-(prop-1-en-1-ylamino)propyl)carbamate as a cream solid. The crude product was purified by column chromatography, eluting with 50:50 EA:PE. Evaporation of the appropriate fractions yielded *tert*-butyl (*Z*)-(3-oxo-3-(prop-1-en-1-ylamino)propyl)carbamate (35 mg, 74.3% yield) as a white solid.

$R_f$  = 0.44 in 50:50 EA:PE (UV/ $\text{KMnO}_4$ )

$\text{Mp}$  = 109-110°C

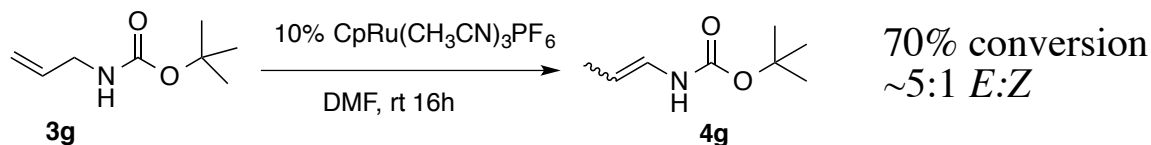
HRMS-ESI [ $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_3 + \text{Na}$ ] $^+$  calcd. 251.1372 found 251.1363

IR(thin film,  $\text{cm}^{-1}$ ): 3266.7, 2937.5, 1638.2, 1492.5, 1345.6, 1235.1, 1151.1  $\text{cm}^{-1}$

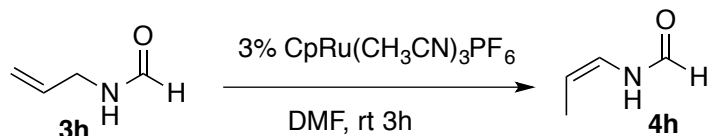
$^1\text{H}$ -NMR (500 MHz,  $\text{CDCl}_3$ , rt)  $\delta$  1.40 (s, 9H), 1.61 (dd,  $J=7.1, 1.5$  Hz, 3H), 2.49 (t,  $J=5.9$  Hz, 2H), 3.41 (q,  $J=6.0$  Hz, 2H), 4.79 (dq,  $J = 8.9, 7.0$ , 1H), 5.23 (bs, 1H), 6.65-6.70 (m, 1H), 7.56 (bs, 1H).

$^{13}\text{C}$ -NMR (125 MHz,  $\text{CDCl}_3$ , rt)  $\delta$  10.9, 28.3, 36.3, 79.4, 105.8, 121.5, 156.2, 168.8,

1D-NOE: Irradiation of the vinyl H (6.65-6.70 ppm) resulted in a 6% enhancement of the vinyl signal at 4.76-4.82 ppm.



***tert*-butyl prop-1-en-1-ylcarbamate (4g):** To a test tube, allyl amide (**3g**) (170 mg, 1 equiv.) was added, then the test tube was purged with argon. DMF (1.9 mL, 0.5M) was added, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (43 mg, 10% mol). The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 5 mL EtOAc, then washed with 3x5 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 5 ml). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation of solvent yielded crude (5:1) (E:Z) *tert*-butyl prop-1-en-1-ylcarbamate. NMR of crude mixture showed ~70% conversion. Z and E isomers were assigned by comparison to known spectra for the respective Z and E isomers.<sup>4</sup>



**(Z)-N-(prop-1-en-1-yl)formamide (4h):** To an NMR tube, allyl formamide (**3h**) (17mg, 0.2 mmol, 1 equiv.) was added. Deuterated DMF (0.4 mL, 0.5M) was added, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (2.6 mg, 0.006 mmol, 3% mol). The reaction was monitored by NMR and complete within 3h. The ratio of Z:E was ~19:1 by NMR. The Z isomer appeared as a resolved set of rotamers (~6:1). The major isomer was assigned by coupling constants and NOE effects.

Z- isomer Major rotamer:

<sup>1</sup>H NMR (400 MHz; DMF): δ 9.74 (s, 1H), 8.16 (s, 1H), 6.69 (t, J = 9.9, 1H), 4.78 (apparent quintet, J = 7.5, 1H), 1.66 (dd, J = 7.0, 1.4, 3H).

1D-NOE: Irradiation of the vinyl H (4.78ppm) resulted in a 9% enhancement of the vinyl signal at 6.69 ppm.

Z-isomer Minor rotamer resolved peaks:

<sup>1</sup>H NMR (400 MHz; DMF): δ 6.49 (t, J = 10.0, 1H), 4.61 (quintet, J = 7.7, 1H)

E-isomer:

<sup>1</sup>H NMR (400 MHz; DMF): δ 5.31 (dq, J = 14.1, 7.0).



**methyl(*S*)-3-((*tert*-butoxycarbonyl)amino)-4-(((*S*)-3-((*tert*-butyldimethylsilyl)oxy)-1-oxo-1-(((*Z*)-prop-1-en-1-yl)amino)propan-2-**

**yl)amino)-4-oxobutanoate (5b):** Dipeptide (**5a**) (243 mg, 0.05 mmol, 1 equiv.) was added to a dry test tube. The test tube was purged with argon, and DMF (1 mL, 0.5M) was added, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (26 mg, 0.06 mmol, 12% mol). The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, and washed with 3x2 mL saturated LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with MgSO<sub>4</sub>. Evaporation of the solvent and purification by column chromatography, eluting with 33% EA:PE, gave enamide **5b** as a colorless oil (168 mg, 69% yield).

R<sub>f</sub> = 0.4 30% EA:PE (UV/KMnO<sub>4</sub>)

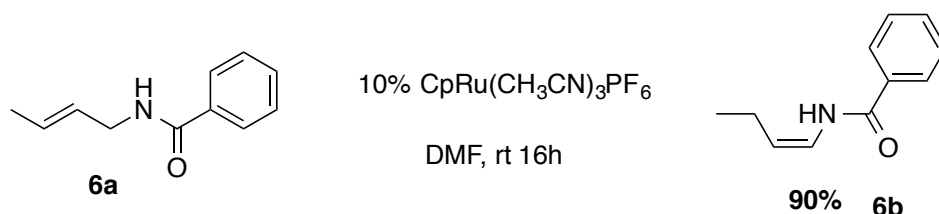
HRMS-ESI [C<sub>22</sub>H<sub>41</sub>N<sub>3</sub>O<sub>7</sub>Si+Na]<sup>+</sup> calcd. 510.2606 found 510.2606

IR(thin film, cm<sup>-1</sup>): 3312, 2954, 2930, 2857, 1718, 1697, 1655, 1517, 1367, 1257, 1168, 838.

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 8.05-8.03 (m, 1H), 7.24 (s, 1H), 6.66 (ddd, J = 10.6, 8.9, 1.7, 1H), 5.54-5.52 (m, 1H), 4.84 (dq, J = 8.6, 7.2, 1H), 4.52-4.49 (m, 1H), 4.42 (td, J = 6.9, 3.5, 1H), 4.14-4.10 (m, 1H), 3.69 (s, 3H), 3.64 (dd, J = 9.8, 6.8, 1H), 3.00 (dd, J = 17.1, 4.5, 1H), 2.75 (dd, J = 17.0, 6.2, 1H), 1.61 (dd, J = 7.1, 1.7, 3H), 1.44 (s, 9H), 0.90 (s, 9H), 0.09 (d, J = 5.0, 6H).

<sup>13</sup>C NMR (101 MHz; CDCl<sub>3</sub>): δ 172.1, 171.2, 167.5, 155.6, 121.7, 107.1, 80.9, 62.8, 54.8, 52.2, 51.30, 51.28, 51.24, 36.1, 28.4, 26.0, 18.5, 11.2, -5.24, -5.34.

1D NOE: Irradiation of C-H (6.66 ppm) gives 8.5 % NOE to C-H (4.84 ppm).



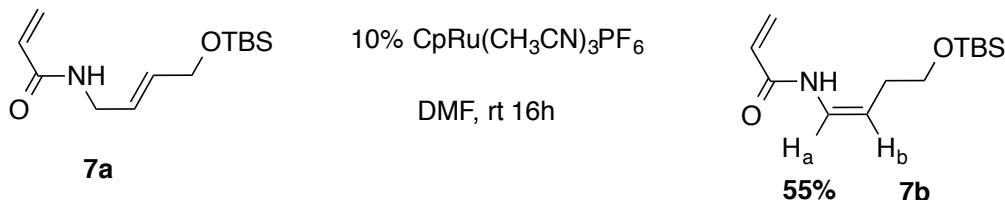
**(Z)-N-(but-1-en-1-yl)benzamide (6b):** A test tube was charged with alkene **6a** (35 mg, 0.20 mmol) and DMF (0.4 mL, 0.5M), followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (8.8 mg, 0.01 mmol, 10% mol) as a solid. The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL saturated LiCl solution. The organic layer was then dried with MgSO<sub>4</sub>. The crude product was purified by column chromatography, eluting with 20:80 EtOAc:pet ether to give a white solid (31.5 mg, 90% yield). Characterization data was consistent with those previously reported in the literature.<sup>4</sup>

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.79 (d, J = 7.2, 2H), 7.67 (s, 1H), 7.52 (t, J = 7.4, 1H), 7.45 (t, J = 7.5, 2H), 6.88 (dd, J = 10.7, 9.1, 1H), 4.86 (q, J = 8.1, 1H), 2.11 (quintet, J = 7.4, 1.6, 2H), 1.07 (t, J = 7.5, 3H)

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ):  $\delta$  164.5, 134.1, 132.0, 128.8, 127.1, 120.7, 114.1, 19.3, 14.1

HRMS-ESI [ $\text{C}_{11}\text{H}_{13}\text{NO}$ ] $^+$  calcd 176.1070 found: 176.1068.

1D-NOE: Irradiation of the vinyl H (4.86 ppm) resulted in a 6.2% enhancement of the vinyl proton at 6.88 ppm which is characteristic of the Z isomer.



**(Z)-N-(4-((tert-butyldimethylsilyl)oxy)but-1-en-1-yl)acrylamide (7b):**

**7b**: A test tube was charged with alkene **7a** using (43 mg, 0.17 mmol, 1 equiv) and DMF (0.4 mL, 0.5M), followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (8.8 mg, 0.01 mmol, 10% mol) as a solid. The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with  $\text{MgSO}_4$ . The crude product was purified by column chromatography, eluting with 20% to 40% Ethyl Acetate:Pet ether to give a white solid (24 mg, 55% yield). There was a minor impurity, which could not be removed from the product (<10%). However this impurity did not appear to be the trans isomer, since trans and cis enamide isomers have characteristic  $H_b$  shifts, where  $H_b$  appears between  $\sim 5$ -4.7 ppm for cis, and trans appears between  $\sim 5.4$  to 5.15 ppm. Previous literature reports containing similar products are referenced.<sup>5,6</sup> The impurity had no signals in the region between 5.4 and 5.2 ppm. Additionally the impurity is inconsistent with isomerization towards the silyl ether to give an enol silane.

$R_f = 0.6$  30% EA:PE (UV/ $\text{KMnO}_4$ ).

$M_p = 29$ -31  $^\circ\text{C}$

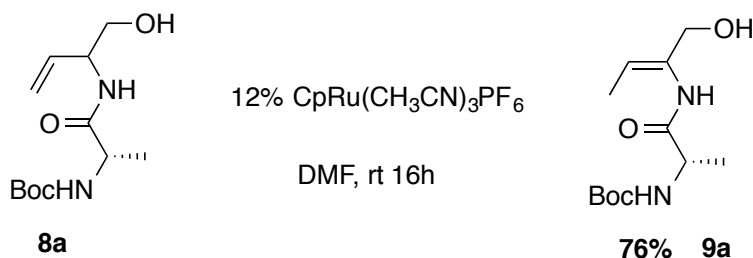
HRMS-ESI [ $\text{C}_{13}\text{H}_{25}\text{NO}_2\text{Si}+\text{Na}$ ] $^+$  calcd 278.1552 found: 278.1545

IR(thin film,  $\text{cm}^{-1}$ ): 3273, 2954, 2928, 2856, 1655, 1515, 1253, 1224, 1096, 834, 775.

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1H), 6.89 (t,  $J = 9.6$ , 1H), 6.37 (dd,  $J = 16.9$ , 1.2, 1H), 6.10 (dd,  $J = 16.9$ , 10.3, 1H), 5.70 (dd,  $J = 10.3$ , 1.2, 1H), 4.92 (q,  $J = 8.2$ , 1H), 3.72 (t,  $J = 5.6$ , 2H), 2.26 (q,  $J = 6.6$ , 2H), 0.89 (s, 9H), 0.07 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz;  $\text{CDCl}_3$ ):  $\delta$  162.8, 130.5, 127.9, 124.1, 109.5, 63.8, 29.7, 26.2, 26.0, -5.1.

1D-NOE: Irradiation of the vinyl H (4.92 ppm) resulted in a 8.6% enhancement of the vinyl proton at 6.89 ppm, which is characteristic of the Z isomer.



**tert-butyl(*S,Z*)-(1-((1-hydroxybut-2-en-2-yl)amino)-1-oxopropan-2-yl)carbamate (9a):** A test tube was charged with alkene **8a** (31 mg, 0.12 mmol, 1 equiv), DMF (0.24 mL, 0.5M) followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (6.2 mg, 0.14 mmol, 12% mol) as a solid. The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 mL). The combined organic layers were dried with  $\text{MgSO}_4$ , and the solvent was evaporated. The crude product was purified by column chromatography, eluting with 70% ethyl acetate:pet ether to give a white solid (23.5 mg, 76% yield).

$R_f = 0.4$  70% EA:PE (UV/ $\text{KMnO}_4$ )

$M_p = 91-92^\circ\text{C}$

HRMS-ESI [ $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4 + \text{Na}$ ] $^+$  calcd 281.1477 found: 281.1464

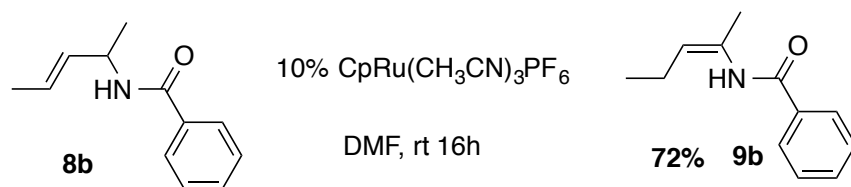
IR(thin film,  $\text{cm}^{-1}$ ): 3329, 2979, 2922, 1662, 1518, 1366, 1251, 1163, 1017, 801, 732.

$^1\text{H}$ -NMR (400 MHz;  $\text{CDCl}_3$ ) taken at  $50^\circ\text{C}$ :  $\delta$  7.98 (s, 1H), 5.10 (q,  $J = 7.0$  Hz, 1H), 4.94 (d,  $J = 6.3$  Hz, 1H), 4.24 (quintet,  $J = 7.1$  Hz, 1H), 4.17 (d,  $J = 12.7$  Hz, 1H), 4.14 (d,  $J = 12.8$  Hz, 1H), 1.62 (d,  $J = 7.0$  Hz, 3H), 1.46 (s, 9H), 1.40 (d,  $J = 7.1$  Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz;  $\text{CDCl}_3$ ):  $\delta$  171.5, 156.1, 136.3, 113.4, 81.1, 64.3, 51.0, 28.5, 17.4, 11.5

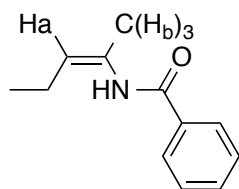
1D-NOESY: Irradiation on  $\text{CH}_2(\text{OH})$  gave a 6.3% noe enhancement vinyl C-H (5.10 ppm).



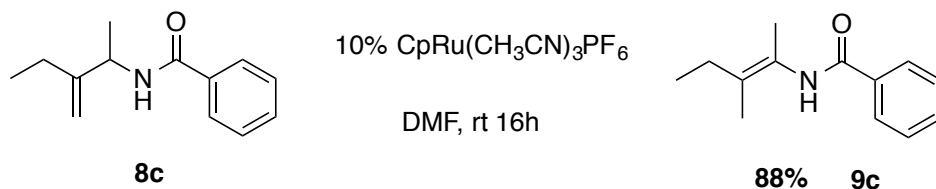


**(Z)-N-(pent-2-en-2-yl)benzamide (9b):** To a test tube, alkene **8b** (38 mg, 0.20 mmol, 1 equiv.) was added, and the test tube was purged with argon. DMF (0.4 mL, 0.5M) was added, followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (8.8 mg, 0.01 mmol, 10% mol) as a solid. The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 ml). The combined organic layers were dried with  $\text{MgSO}_4$ , and the solvent was evaporated. The crude product was purified by column chromatography, eluting with 20:80 EtOAc:pet ether to give an oil (27 mg, 72%). The compound was prone to decomposition therefore the only characterization data taken was a  $^1\text{H}$ NMR and a 1D NOE spectrum.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.83-7.82 (m, 2H), 7.56-7.53 (m, 1H), 7.49-7.46 (m, 2H), 7.18 (bs, 1H), 5.03 (t,  $J = 7.0$ , 1H), 2.14 (s, 3H), 2.09-2.02 (m, 2H), 1.03 (t,  $J = 7.5$ , 3H).



1D-NOESY: Irradiation of vinyl C-H<sub>a</sub> (5.03 ppm) gave 4% enhancement of C(H<sub>b</sub>)<sub>3</sub> (2.14 ppm).



**(E)-N-(3-methylpent-2-en-2-yl)benzamide (9c):** A test tube was charged with alkene **8c** (41 mg, 0.20 mmol, 1 equiv.), and DMF (0.4 mL, 0.5M), followed by  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (8.8 mg, 0.01 mmol, 10% mol) as a solid. The reaction was allowed to stir at rt for 16h, after which the reaction mixture was diluted 2 mL EtOAc, then washed with 3x2 mL LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 ml). The combined organic layers were dried with  $\text{MgSO}_4$ . The crude product was purified by column chromatography, eluting with 15:85 EtOAc:pet ether to give a white solid (36 mg, 88% yield). Minor impurities (<10%) remaining from ~3% SM and impurities within the SM account for small signals not attributed to the product. See spectra for analysis. Additional chromatography was unable to remove these as they cospot with the product.

$R_f = 0.65$  30% EA:PE (UV/KMNO<sub>4</sub>)

Mp = 89-90 °C.

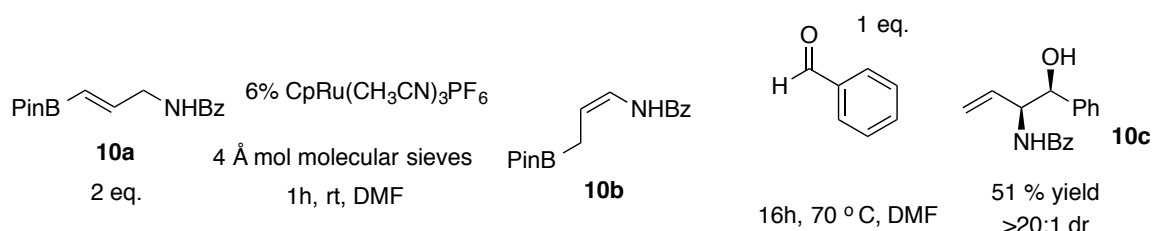
IR(thin film, cm<sup>-1</sup>): 3286, 2965, 2929, 1637, 1518, 1487, 1290, 713.

HRMS-ESI [C<sub>13</sub>H<sub>17</sub>NO+Na]<sup>+</sup> calcd 226.1208, found 226.1207

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.83 (d, J = 7.4, 2H), 7.54-7.51 (m, 1H), 7.46 (t, J = 7.5, 2H), 7.13 (s, 1H), 2.15 (q, J = 7.5, 2H), 2.03 (s, 3H), 1.70 (s, 3H), 1.04 (t, J = 7.5, 3H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 165.9, 135.2, 131.7, 130.6, 128.8, 127.3, 124.5, 26.9, 17.2, 17.1, 12.7.

1D NOE: Irradiation of methyl at C-H (2.03 ppm) gave a 3% NOE of CH<sub>2</sub> at (2.15 ppm). Additionally there was no NOE effect between the methyl groups at 2.03 ppm and 1.7 ppm that would be expected for the opposite isomer.



**(Z)-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)benzamide (10b):** Allyl amide **10a** (86 mg, 0.3 mmol, 2 equiv.) and CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (3.9 mg, 0.009 mmol, 6% mol) were added to a dry NMR tube containing 20 mg powdered 4A molecular sieves, and d<sub>7</sub>-DMF was added (0.4 mL). The tube was flushed with argon, capped and parafilm. After 1h the reaction was almost complete and the crude NMR for **10b** in DMF is listed below.

<sup>1</sup>H NMR (500 MHz; DMF): δ 9.54 (d, J = 9.5, 1H), 8.03-8.00 (m, 2H), 7.63-7.59 (m, 1H), 7.56-7.52 (m, 2H), 6.88-6.84 (m, 1H), 4.94 (q, J = 8.4, 1H), 1.91 (s, 2H), 1.25 (s, 12H).

NOE of crude **10b** in DMF indicated the product was the cis isomer. Irradiation of vinyl C-H(6.88-6.84 ppm) gave a 10% enhancement of the olefin peak at 4.94 ppm.

**N-(cis(1,2)-1-hydroxy-1-phenylbut-3-en-2-yl)benzamide (10c):** To crude solution of **10b** in DMF was added benzaldehyde (0.015 mL, 0.15 mmol, 1 equiv.). The reaction was heated at 70 °C for 16h. The solution was then cooled to rt and diluted with diethyl ether (2 ml) and stirred with 2ml saturated sodium bicarbonate for 30 mins. The aqueous layer was extracted with ether (2X2mL). The combine organic fractions were washed with brine (1X3mL), and dried with MgSO<sub>4</sub>. The

solution was evaporated and the crude mixture was purified by column chromatography, eluting with 35:65 EtOAc:pet ether to give a white solid (22 mg, 51 % yield).

$R_f$  = 0.22 30% EA:PE (UV/KMNO<sub>4</sub>).

Mp = 78-79 °C

IR(thin film, cm<sup>-1</sup>): 3334, 3062, 1636, 1536, 1487, 1334, 700.

HRMS-ESI [C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>+Na]<sup>+</sup> calcd 290.1157, found 290.1152

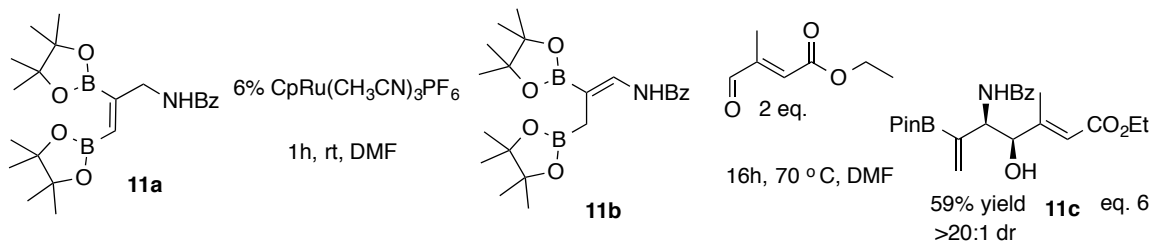
<sup>1</sup>H NMR (600 MHz; CDCl<sub>3</sub>): δ 7.68 (d, J = 7.8, 2H), 7.49-7.46 (m, 1H), 7.38 (dd, J = 10.7, 7.8, 4H), 7.32 (t, J = 7.5, 2H), 7.26 (t, J = 7.2, 1H), 6.55 (d, J = 7.1, 1H), 5.98 (ddd, J = 16.8, 10.9, 5.4, 1H), 5.27 (m, 2H), 4.93 (m, 2H).

NMR was taken in benzene was taken to ascertain the coupling constants for the vicinal amino alcohol.

<sup>1</sup>H NMR (600 MHz; Benzene): δ 7.60-7.59 (m, 2H), 7.26 (d, J = 7.5, 2H), 7.05 (t, J = 7.6, 2H), 6.99-6.96 (m, 2H), 6.92-6.89 (m, 2H), 6.48 (dd, J = 7.0, 0.3, 1H), 5.84 (ddd, J = 17.1, 10.5, 5.5, 1H), 5.11 (dt, J = 17.2, 1.4, 1H), 5.08-5.05 (m, 1H), 4.98 (dt, J = 10.5, 1.4, 1H), 4.68 (d, J = 4.4, 1H), 3.53 (s, 1H).

C-H at 4.68 ppm with J=4.4 is consistent with cis relationship as would be the expected under traditional Zimmerman Traxler type transition states.<sup>7,8,9</sup>

<sup>13</sup>C NMR (101 MHz; CDCl<sub>3</sub>): δ 167.9, 140.8, 135.4, 134.4, 131.9, 128.80, 128.63, 128.1, 127.2, 126.4, 117.3, 75.5, 57.9.



**(Z)-N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)benzamide (11b):** To a dry nmr tube containing CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (5.2 mg, 0.012 mmol, 6% mol), under argon, was charged alkene **11a** (82 mg, 0.2 mmol, 1 equiv.) as a solution in d<sub>7</sub>-DMF (0.4 mL, 0.5 M) (freshly opened ampule). The mixture was inverted 5 times to create a homogeneous solution. The cap was sealed with parafilm. The reaction was monitored by NMR and after 1h was complete.

<sup>1</sup>H NMR (400 MHz; d<sub>7</sub>-dmf): δ 9.69 (d, J = 10.9, 1H), 7.99 (d, J = 7.5, 2H), 7.62-7.59 (m, 2H), 7.54 (t, J = 7.4, 2H), 1.94 (s, 2H), 1.27 (s, 12H), 1.21 (s, 15H).

**ethyl syn-(4,5)(E)-5-benzamido-4-hydroxy-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-2,6-dienoate (11c):** To crude solution of **11b** in d7-DMF was added Ethyl 3-methyl-4-oxocrotonate (0.054 mL, 0.4 mmol, 2 equiv.). The reaction was heated at 70 °C for 16h. The solution was then cooled to rt and diluted with diethyl ether (2 mL). The aqueous layer was extracted with ether (2X2mL). The combine organic fractions were washed with brine (1X3mL), and dried with MgSO<sub>4</sub>. The solution was evaporated and the crude mixture was purified by column chromatography, eluting with 35:65 EtOAc:pet ether to give an oil (50 mg, 59% yield). The compound was prone to decomposition on silica therefore the amount of silica was limited to 3 inches and run rapidly.

R<sub>f</sub> = 0.25 30% EA:PE (UV/KMnO<sub>4</sub>).

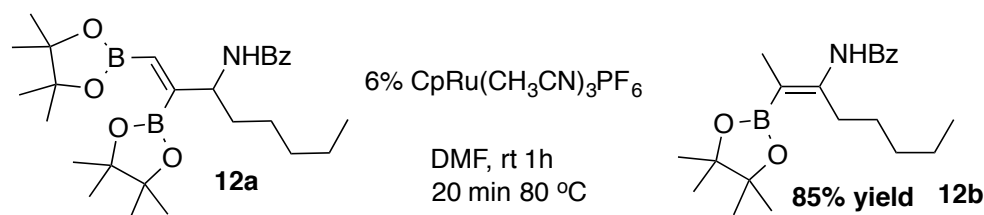
HRMS-ESI [C<sub>23</sub>H<sub>32</sub>BN<sub>2</sub>O<sub>6</sub> +Na]<sup>+</sup> calcd 452.2221, found 451.2242

IR(thin film, cm<sup>-1</sup>): 3400, 2978, 2922, 1715, 1649, 1529, 1371, 1314, 1141, 713.

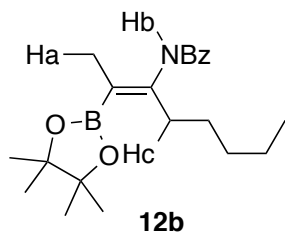
<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 7.77 (d, J = 7.7, 2H), 7.50 (d, J = 6.9, 1H), 7.45-7.41 (m, 2H), 7.15 (d, J = 8.4, 1H), 6.03 (s, 1H), 5.93 (s, 1H), 5.90 (s, 1H), 5.00 (dd, J = 8.3, 4.4, 1H), 4.33 (d, J = 4.1, 1H), 4.14-4.09 (m, 2H), 3.16 (s, 1H), 2.20 (s, 3H), 1.31 (s, 12H), 1.23 (m, 13H). Due to instability on the column, the impurity present at multiplet 1.23 ppm could not be removed. The alcohol broad singlet at 3.16 suggests that it is not due to incomplete cleavage of the alcohol boronic ester, which could account for the excess protons.

C-H at 4.33 ppm with J=4.1 is consistent with cis relationship as would be expected under traditional zimmerman traxler type transition states.<sup>7,8,9</sup>

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 167.7, 166.6, 156.9, 134.5, 133.3, 131.9, 128.8, 127.2, 117.1, 84.5, 79.3, 60.0, 58.1, 25.0, 15.9, 14.5.

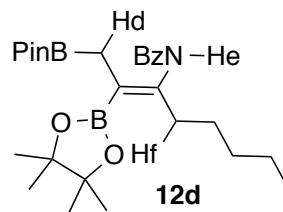


**(Z)-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-en-3-yl)benzamide (12b):** To a dry nmr tube containing CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (0.6 mg, 0.0012 mmol, 6% mol), was charged alkene **12a** (10 mg, 0.02 mmol, 1 equiv.) as a solution in d7-DMF (0.4 mL, 0.05M). The mixture was inverted 5 times to create a homogeneous solution. The cap was sealed with parafilm. The reaction was monitored by NMR and after 1h was complete. At this time NMR showed a ratio of 3:1 of **12b** to compound **12d** (spectrum 1).

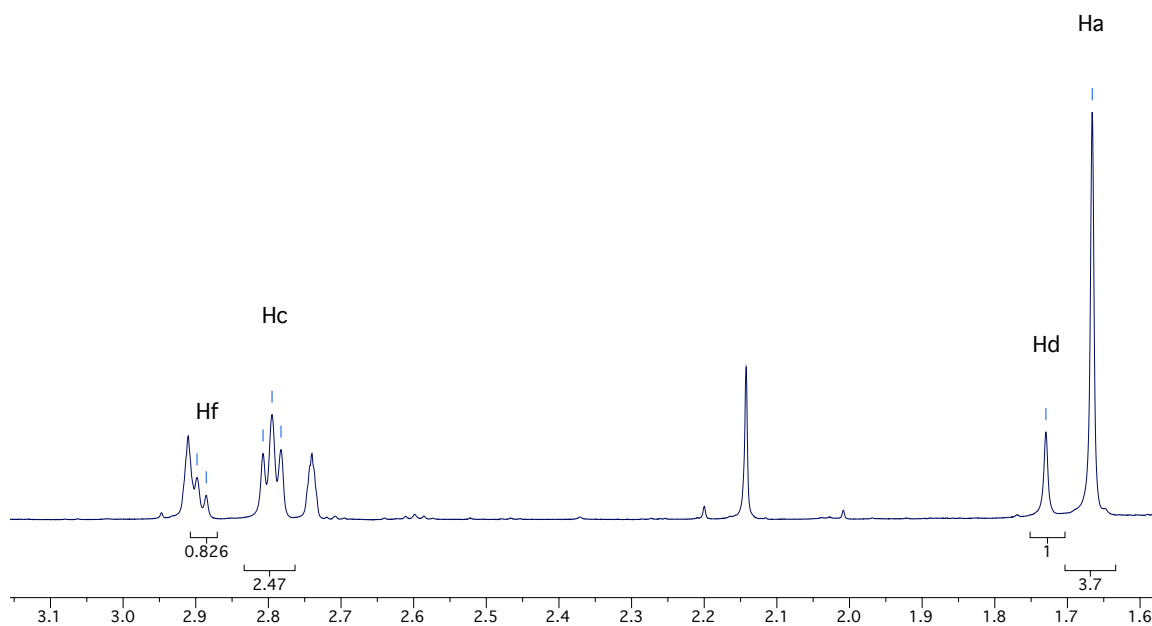
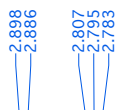


3

at rt 1h

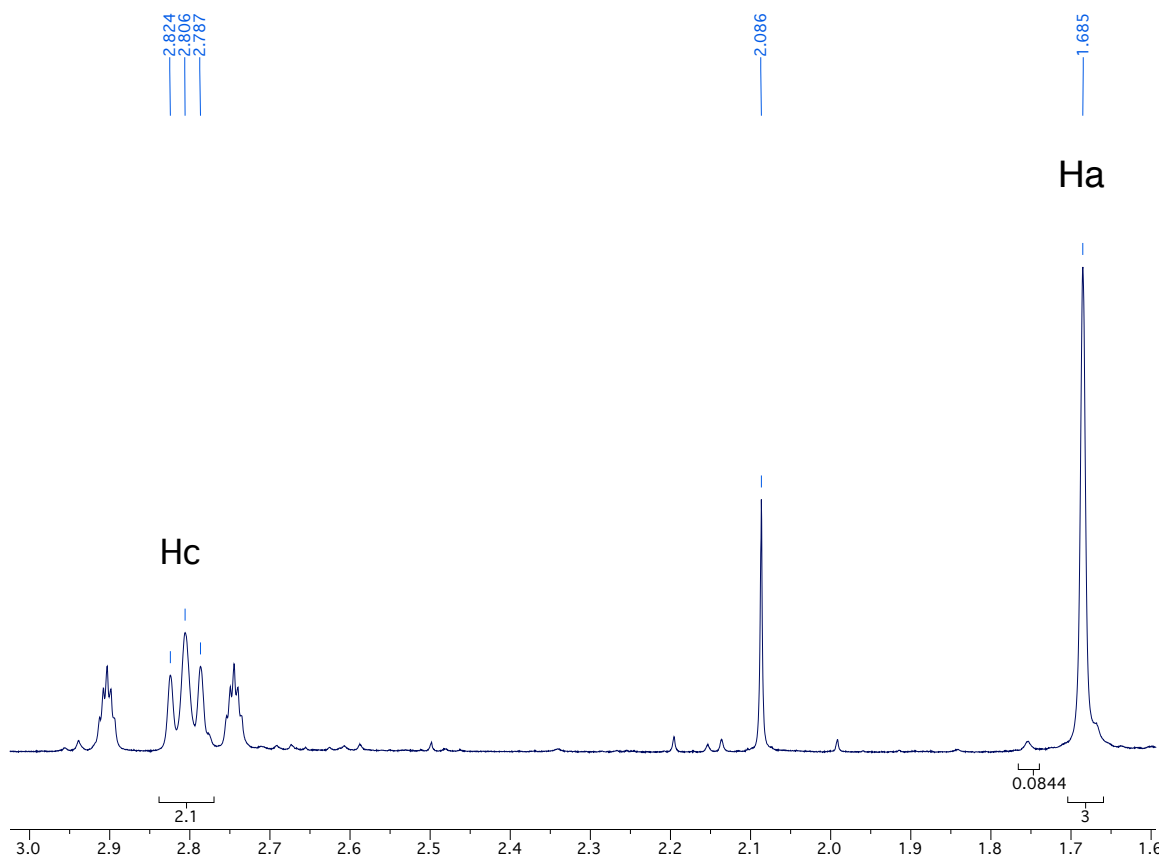


1



### Spectrum 1: NMR after 1h in d7-DMF at rt

The reaction was then heated to 80 °C over 20 mins. NMR at this time showed conversion of remaining allyl boron species to **12b** (>20:1)(**spectrum 2**).



**Spectrum 2: NMR after heating to 80 °C over 20 minutes in d7-DMF.**

The reaction was cooled to rt, diluted with 2 mL EtOAc, and then washed with saturated (3x2 ml) LiCl solution. The aqueous layer was then extracted with EtOAc (2 X 2 ml). The combined organic layers were dried with MgSO<sub>4</sub>. The crude product was purified by column chromatography, eluting with 20:80 EtOAc:pet ether to give a colorless oil (6.5 mg, 85%yield).

R<sub>f</sub> = 0.35 EA:PE (UV/KMnO<sub>4</sub>).

IR: 3257.2, 2867.3, 2807.9, 1613.7, 1593.7, 1487.4, 1457.5, 1330.3, 1276.9, 1108.5.

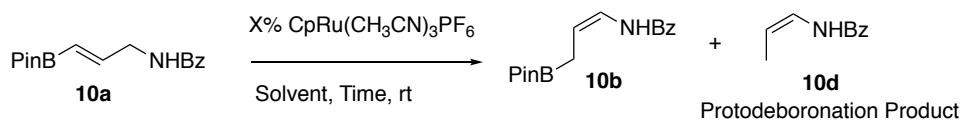
HRMS-ESI [C<sub>21</sub>H<sub>32</sub>BN<sub>3</sub>O<sub>3</sub>+Na]<sup>+</sup> calcd 380.2373, found 380.2369

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>): δ 7.81 (d, J = 7.5, 2H), 7.52 (t, J = 7.5, 1H), 7.46 (t, J = 7.5, 2H), 7.29 (s, 1H), 2.97 (t, J = 7.6, 2H), 1.72 (s, 3H), 1.52-1.48 (m, 2H), 1.33-1.31 (m, 4H), 1.276 (s, 12H), 1.25 (s, 2H), 0.88 (t, J = 6.3, 3H).

<sup>13</sup>C NMR (101 MHz; CDCl<sub>3</sub>): δ 164.8, 149.8, 135.4, 131.8, 128.9, 127.2, 83.2, 32.1, 31.7, 29.4, 25.0, 22.6, 15.0, 14.3. Note: Signal from the carbon adjacent to B not observed due to low intensity in <sup>13</sup>C NMR.

1D-NOE: Irradiation of vinyl Methyl (1.72 ppm) gave 7% enhancement of N-H(7.29 ppm).

## Proteodeborylation Optimization:

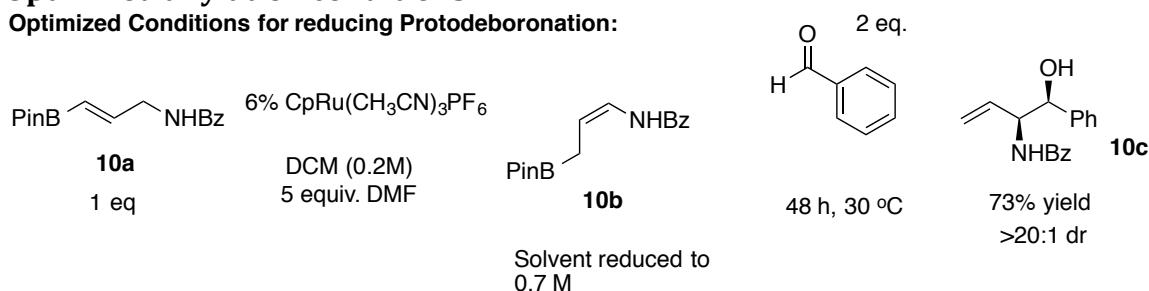


Entry	Solvent	Ru%	Concentration	Time	Conversion	10b:10d	Mol. Sieves
1	DMF	3	0.75 M	1h	88%	10:1 4:1 <sup>a</sup>	Yes
2	Acetone:DMF 7:1	6	0.175 M	20 mins 1.5 h	90% >95%	>10:1 6.5:1 <sup>b</sup>	No
3	DCM:DMF 7:1	6	0.175 M	25 mins 80 mins	33% 75%	>20:1 >20:1 >20:1 <sup>b</sup>	No
4	DCM:DMF 12:1 5 equiv DMF	6	0.2 M	1h	30%	>20:1	No
5	DCM	6	0.13 M	30 mins	<10%		No
6	DCM 15:1	6	0.5 M	1h	<10%		No
8	DCM:Acetone 7:1	6	0.13 M	1h	<10%		No

a) 1h After addition of aldehyde heating at 70 °C b) 1h After addition of aldehyde heating at rt

## Optimized allylation conditions:

Optimized Conditions for reducing Protodeborylation:



**N-(syn-(1,2)-1-hydroxy-1-phenylbut-3-en-2-yl)benzamide (10c):** Allyl amide **10a** (29 mg, 0.1 mmol, 1 equiv.) and  $\text{CpRu}(\text{MeCN})_3\text{PF}_6$  (2.6 mg, 0.006 mmol, 6% mol) were added to a dry vial. The tube was flushed with argon, and charged with DCM (0.5 ml, 0.2M), and DMF (0.077 ml, 5 equiv.). The reaction was stirred at room temperature for 5h. The solution was evaporated to a total volume of 0.15 ml.

Freshly distilled benzaldehyde (21.2 mg, 2 equiv, 0.2 mmol) was added neat and the reaction was stirred for 48 h at 30 °C. The solution was charged with DCM (1 ml) and stirred with 1 ml saturated sodium bicarbonate for 30 mins. The aqueous layer was extracted with DCM (2X2mL). The combine organic fractions were washed with brine (1X3mL), and dried with MgSO<sub>4</sub>. The solution was evaporated and the crude mixture was purified by column chromatography, eluting with 35:65 EA:PE to give a white solid (19.5 mg, 73 % yield, >20:1 dr.).

R<sub>f</sub> = 0.22 30% EA:PE (UV/KMNO<sub>4</sub>).

Mp = 78-79 °C

IR(thin film, cm<sup>-1</sup>): 3334, 3062, 1636, 1536, 1487, 1334, 700.

HRMS-ESI [C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>+Na]<sup>+</sup> calcd 290.1157, found 290.1152

<sup>1</sup>H NMR (600 MHz; CDCl<sub>3</sub>): δ 7.68 (d, J = 7.8, 2H), 7.49-7.46 (m, 1H), 7.38 (dd, J = 10.7, 7.8, 4H), 7.32 (t, J = 7.5, 2H), 7.26 (t, J = 7.2, 1H), 6.55 (d, J = 7.1, 1H), 5.98 (ddd, J = 16.8, 10.9, 5.4, 1H), 5.27 (m, 2H), 4.93 (m, 2H).

NMR was taken in benzene was taken to ascertain the coupling constants for the vicinal amino alcohol.

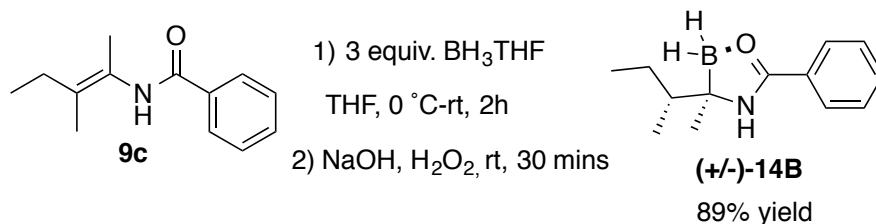
<sup>1</sup>H NMR (600 MHz; Benzene): δ 7.60-7.59 (m, 2H), 7.26 (d, J = 7.5, 2H), 7.05 (t, J = 7.6, 2H), 6.99-6.96 (m, 2H), 6.92-6.89 (m, 2H), 6.48 (dd, J = 7.0, 0.3, 1H), 5.84 (ddd, J = 17.1, 10.5, 5.5, 1H), 5.11 (dt, J = 17.2, 1.4, 1H), 5.08-5.05 (m, 1H), 4.98 (dt, J = 10.5, 1.4, 1H), 4.68 (d, J = 4.4, 1H), 3.53 (s, 1H).

C-H at 4.68 ppm with J=4.4 is consistent with cis relationship as would be the expected under traditional zimmerman traxler type transition states.<sup>7,8,9</sup>

<sup>13</sup>C NMR (101 MHz; CDCl<sub>3</sub>): δ 167.9, 140.8, 135.4, 134.4, 131.9, 128.80, 128.63, 128.1, 127.2, 126.4, 117.3, 75.5, 57.9.



## Hydroboration:



A dry vial under argon was charged with alkene (12.2 mg, 0.06 mmol, 1 equiv.) **9c**, and 0.6 ml THF (0.1M). The solution was brought to 0 °C, followed by dropwise addition of  $\text{BH}_3\text{THF}$  (1M in THF) (0.18 mmol, 3 equiv., 0.18 ml) over 5 mins. After a stirring for 45 minutes at that temperature it was removed from the ice bath and allowed to stir at room temperature for 75 minutes. The excess  $\text{BH}_3$  was quenched by the addition of 1 ml  $\text{H}_2\text{O}$  at 0 °C. When bubbling stopped, 1 ml NaOH (1.5 M) and 1ml 30%  $\text{H}_2\text{O}_2$  were added at the same temperature. The solution was allowed to warm to room temperature and after stirring for 30 minutes the reaction was cooled back 0 °C and quenched by slow addition of saturated aqueous sodium thiosulfate the solution was extracted with EtOAc (5X3 ml), and washed with saturated sodium bicarbonate (1X5 ml). The organic fractions were dried with  $\text{MgSO}_4$ . The crude product was purified by column chromatography, eluting with 25:75 EtOAc:pet ether to give **14b** as a white solid (11.5 mg, 89%yield).

$R_f = 0.3$  25% EA:PE (UV,  $\text{KMnO}_4$ )

Mp = 110 – 112 °C

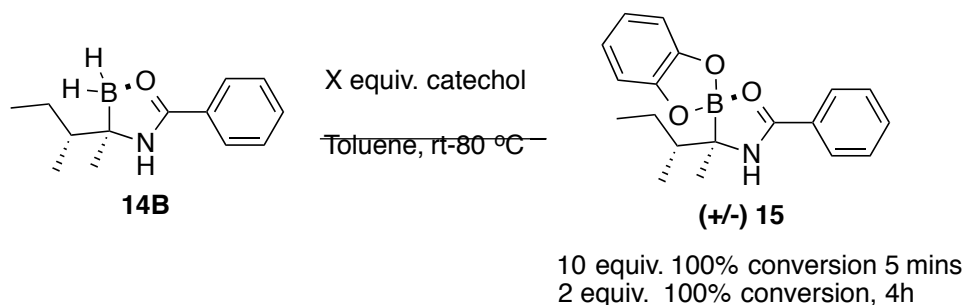
HRMS-ESI [ $\text{C}_{13}\text{H}_{20}\text{BNO-H}$ ]- calcd 215.1596 (24.8 %) and 216.1560 (100%), found 215.1591 (26%), 216.1559 (100 %).

IR(thin film,  $\text{cm}^{-1}$ ): 3314, 2960, 2923, 1874, 2343, 1610, 1599, 1574, 1521, 1485, 1206, 1148, 687. The IR spectras is include in the spectra portion of this supporting information.

$^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.84 (dd,  $J = 8.4, 1.2$ , 2H), 7.66-7.62 (m, 1H), 7.51 (t,  $J = 7.8$ , 2H), 7.15 (s, 1H), 3.5-2.5 (very broad s, 2H), 1.57-1.50 (m, 1H), 1.47 (dtd,  $J = 13.7, 7.1, 2.4$ , 1H), 1.28 (s, 3H), 1.11 (ddq,  $J = 13.6, 10.6, 6.9$ , 1H), 0.91 (m, 6H). Peak at 1.25 is from grease.

$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  171.7, 134.1, 129.2, 128.3, 125.8, 45.1, 25.4, 25.1, 13.6, 12.9

$^{11}\text{B}$  NMR (96 MHz;  $\text{CDCl}_3$ ):  $\delta$  4.35 bs



Amide borane **14b** (2.2 mg, 0.01 mmol, 1 equiv.) and catechol (2.2 mg, 0.02 mmol, 2 equiv.) or (11 mg, 0.1 mmol, 10 equiv.) were dissolved in toluene- $d_8$  (0.385 ml, 0.026 M) in a dry NMR tube. The solution was heated to 80 °C and monitored by  $^1\text{H}$  NMR and  $^{11}\text{B}$  NMR. After 4 hours (2 equiv. catechol) or 5 minutes (10 equiv. catechol) conversion of **14b** was complete. The toluene was removed and  $\text{CDCl}_3$  (0.4 ml) was added and  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded. Peaks corresponding to catechol are noted.

$R_f$  (**15**) = 0.37 30% EA:PE ( $\text{KMnO}_4$ , UV).  $R_f$  (catechol) = 0.35 30% EA:PE ( $\text{KMnO}_4$ , UV).

$M_p$  = 99-102 °C

IR(thin film,  $\text{cm}^{-1}$ ): 3300, 2960, 2924, 1663, 1608, 1482, 1239, 1071.

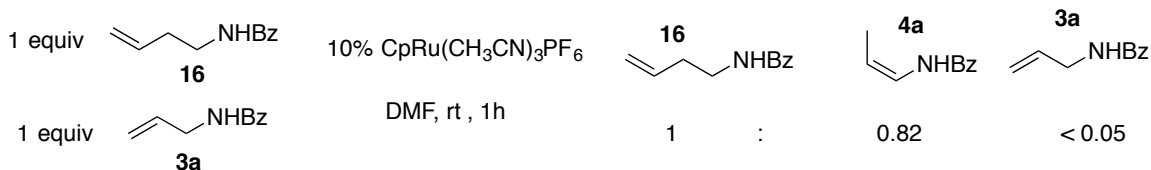
$^1\text{H}$  NMR (600 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.86 (d,  $J$  = 7.5, 2H), 7.67 (t,  $J$  = 7.5, 1H), 7.51 (t,  $J$  = 7.8, 2H), 7.33 (s, 1H), 6.86 (overlapping (**15**) and catechol.  $J$  = 5.7, 3.5, 3H), 6.79 (catechol dt,  $J$  = 6.2, 3.3, 2H), 6.76 (dd,  $J$  = 5.5, 3.4, 2H), 5.28 (s, 2H), 1.89-1.83 (m, 1H), 1.39-1.34 (m, 1H), 1.32 (s, 3H), 1.12-1.05 (m, 1H), 1.01 (d,  $J$  = 6.7, 3H), 0.90 (t,  $J$  = 7.3, 3H).

$^{13}\text{C}$  NMR (126 MHz;  $\text{CDCl}_3$ ):  $\delta$  171.3, 143.7 (catechol), 135.1, 129.4, 128.5, 124.9, 121.3 (catechol), 119.4, 115.6 (catechol), 109.91, 109.87, 40.5, 26.0, 18.3, 13.3, 12.8.

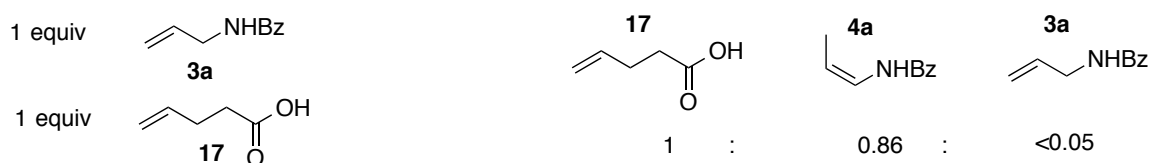
$^{11}\text{B}$  NMR (96 MHz; Toluene):  $\delta$  17.66 bs.

HRMS-ESI [ $\text{C}_{19}\text{H}_{22}\text{BN}_3 + \text{Na}$ ] $^+$  calcd 346.1591, found 346.1586

### Competition Experiments:



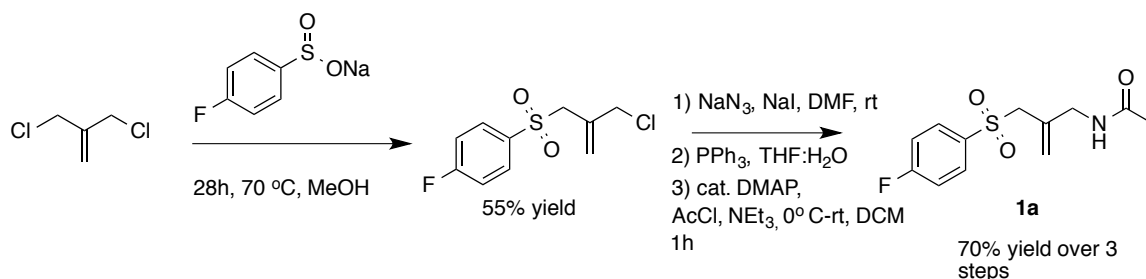
**(Z)-N-(prop-1-en-1-yl)benzamide (4a):** N-allylbenzamide (11.3 mg, 0.07 mmol, 1 equiv.) (**3a**), N-(but-3-en-1-yl)benzamide (12.3 mg, 0.07 mmol, 1 equiv.) **16** and d<sub>7</sub>-DMF (0.46 mL, 0.15 M) were added to an NMR tube, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (3 mg, 0.007 mmol, 10 mol%). The reaction was monitored by NMR and <5% of **3a** remained after 1h. Relative ratios were assigned by comparison of N-H in **16** and N-H in compound **4a**. See Spectra for additional detail.



**(Z)-N-(prop-1-en-1-yl)benzamide (4a):** N-allylbenzamide (11.3 mg, 0.07 mmol, 1 equiv.) (**3a**), acid **17** (12.3 mg, 0.07 mmol, 1 equiv.) and d<sub>7</sub>-DMF (0.46 mL, 0.15 M) were added to an NMR tube, followed by CpRu(MeCN)<sub>3</sub>PF<sub>6</sub> (3 mg, 0.007 mmol, 10 mol%). The reaction was monitored by NMR and <5% of **3a** remained after 1h. Relative ratios were assigned by comparison of CH<sub>2</sub> at 2.3 ppm in compound **17** and N-H in compound **4a**. See Spectra for additional detail.

## Substrate Synthesis:

Compounds **3a** and **3f** commercial. For synthesis of compounds **3b**<sup>10</sup>, **3c**<sup>11</sup>, **3d**<sup>12</sup>, and **3e**<sup>13</sup> see the appropriate reference.



**N-(2-(((4-fluorophenyl)sulfonyl)methyl)allyl)acetamide (1a).** In a dry round bottom flask, sodium 4-fluorobenzenesulfonate (1.76 g, 1 equiv) was added. The flask was then flushed with argon, and dry methanol (25 mL) added. Freshly distilled 3-chloro-2-(chloromethyl)prop-1-ene (1.2 mL, 1 equiv.) was added to reaction mixture, then the solution was stirred at reflux (~70°C). The reaction was monitored by TLC (20:80 EtOAc: pet. ether). After 28 h, the reaction mixture was cooled to rt and the solvent evaporated to afford a white solid. To the solid, water (30 mL) and DCM (20 mL) were added and agitated thoroughly to dissolve all solids. The organic layer was then separated and the aqueous layer was further extracted with 2x20 mL DCM. The DCM layers were then combined and dried with MgSO<sub>4</sub>. Evaporation of the DCM yielded crude 1-((2-(chloromethyl)allyl)sulfonyl)-4-fluorobenzene (1.33 g, 55% yield).

To a dry round bottom flask, crude 1-((2-(chloromethyl)allyl)sulfonyl)-4-fluorobenzene (0.93 g, 3.7 mmol), sodium azide (0.74 g, 11.3 mmol), and sodium iodide (29 mg, 0.2 mmol) were added. The flask was then flushed with argon, then DMF (15 mL) added. The reaction was monitored by TLC (20:80 EtOAc: pet. ether). After 24 h at rt, no more starting chloride was detected. Diethyl ether (20 mL) and water (20 mL) were added to the reaction mixture. The organic layer was separated and the aqueous layer was further extracted with 3x20 mL diethyl ether. The ether layers were combined and washed with 5x40 mL saturated LiCl, then washed with saturated NaCl (1x40 mL). The ether layer was dried with MgSO<sub>4</sub>, then the ether evaporated to yield 1-((2-(azidomethyl)allyl)sulfonyl)-4-fluorobenzene as an oil with solid inclusions.

The flask containing the 1-((2-(azidomethyl)allyl)sulfonyl)-4-fluorobenzene was then flushed with argon then THF (17 mL) and H<sub>2</sub>O (4.3 mL) were added to dissolve the azide. A solution of PPh<sub>3</sub> (1.57 g, 6.0 mmol) in THF (7 mL) was added dropwise over 20 mins with stirring. After 16 h, no more starting azide was detected by TLC (40:60 EtOAc: pet. ether). To the reaction mixture, saturated NaHSO<sub>4</sub> (8 mL), H<sub>2</sub>O (12 mL), and diethyl ether (50 mL) were added, which resulted in precipitation of yellow solids, which dissolved upon further addition of water (~15 mL). The layers were then separated and the aqueous layer was further washed with 2x35 mL diethyl ether. The aqueous layer was then basified with 10% NaOH solution

until white precipitate stopped forming and the solution was basic to pH paper. The aqueous layer was extracted with diethyl ether (3x50 mL). The ether extracts were then combined and dried with  $\text{MgSO}_4$ . Evaporation of the ether yielded 0.76 g of crude 2-(((4-fluorophenyl)sulfonyl)methyl)prop-2-en-1-amine as a fluffy white powder.

To the flask containing the crude 2-(((4-fluorophenyl)sulfonyl)methyl)prop-2-en-1-amine, DCM (30 mL), triethylamine (2 mL, 14.3 mmol), and 4-N,N-dimethylaminopyridine (82 mg, 0.67 mmol) were added. The reaction mixture was cooled to  $0^\circ\text{C}$  in an ice bath, then acetyl chloride (0.8 mL, 11.2 mmol) was added dropwise to the reaction. Once the addition was complete, the reaction mixture was warmed to rt and allowed to stir for 1 h. After 1 h, saturated  $\text{NaHSO}_4$  (13 mL) and  $\text{H}_2\text{O}$  (51 mL) were added to the reaction mixture. The layers were separated, then the aqueous layer was further extracted with 3x25 mL DCM. The DCM extracts were combined and dried with  $\text{MgSO}_4$ . Evaporation of the DCM yielded 0.63g (2.3 mmol, 70.2% yield) of *N*-(2-(((4-fluorophenyl)sulfonyl)methyl)allyl)acetamide as a yellow solid, which is pure enough to use for the subsequent isomerization. For further purification, the crude amide was purified by silica column chromatography, eluting with 90:10 ethyl acetate:petroleum ether.

$R_f = 0.29$  (90:10 EtOAc: pet. ether) (UV,  $\text{KMnO}_4$ )

$\text{Mp} = 108\text{-}109^\circ\text{C}$

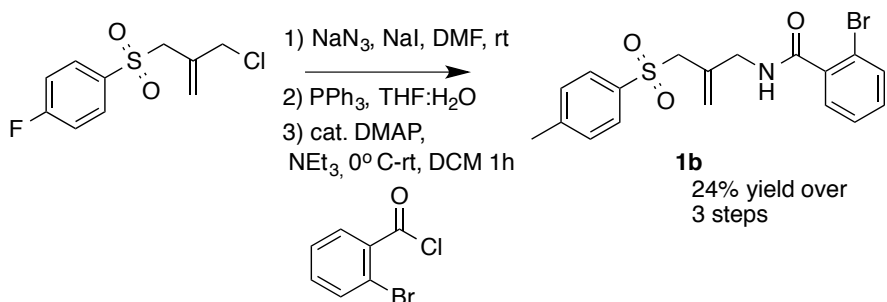
HRMS-ESI  $[\text{C}_{12}\text{H}_{14}\text{FNO}_3\text{S}+\text{H}]^+$ : 272.0756, Found: 272.0759

IR(thin film,  $\text{cm}^{-1}$ ): 3246, 2943, 1605, 1296, 1271, 1132, 1070, 832  $\text{cm}^{-1}$ .

<sup>1</sup>

<sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.07 (s, 3H), 3.86 (s, 2H), 4.02 (d,  $J=4.88$  Hz, 2H), 4.99 (s, 1H), 5.34 (s, 1H), 6.23 (br. s., 1H), 7.29 (d,  $J=7.32$  Hz, 2H), 7.94 (d,  $J=4.88$  Hz, 2H).

<sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  23.2, 44.0, 60.9, 116.5, 116.6, 121.8, 131.3, 133.4, 134.1, 164.9, 167.0, 170.3



**2-bromo-N-(2-(tosylmethyl)allyl)benzamide (1b):** To a dry round bottom flask, 1-((2-(chloromethyl)allyl)sulfonyl)-4-methylbenzene<sup>2</sup> (3.29 g, 13.4 mmol) added. The flask was then flushed with argon and dry DMF (34 mL) was added and the mixture stirred at rt for 16 h. After 16 h, no more starting chloride was detected by TLC

(20:80 EtOAc: pet. ether), so H<sub>2</sub>O (60 mL) was added to the reaction mixture. The aqueous mixture was extracted with diethyl ether (3x60 mL). The ether layers were combined and washed with saturated LiCl (5x75 mL), followed by saturated NaCl washes (3x75 mL). The organic layer was then dried with MgSO<sub>4</sub>. Evaporation of the ether yielded crude 1-((2-(azidomethyl)allyl)sulfonyl)-4-methylbenzene as an oil with solid inclusions. To the flask containing the crude azide, 5.58 g (21.2 mmol, 1.6 equiv) of triphenylphosphine was added, followed by THF (60 mL) and H<sub>2</sub>O (16 mL). The reaction mixture was allowed to stir at rt for 16 h. After 16 h, no more of the starting azide was detected by TLC (40:60 EtOAc: pet. ether), so the THF was evaporated. 2M HCl (50 mL) was added to the mixture, precipitating a white solid. The resulting mixture was then washed with diethyl ether (3x75 mL), then 10% aqueous NaOH was added to the aqueous phase until the solution was basic to pH paper and a white precipitate formed. The aqueous mixture was extracted with diethyl ether (3x75 mL), then the ether extracts were combined and dried with MgSO<sub>4</sub>. Evaporation of the ether resulted in 1.78 g of crude 2-(tosylmethyl)prop-2-en-1-amine as an oil (59% crude yield).

To a test tube, DCM (10 mL), triethylamine (0.35 mL, 2.5 mmol), and crude 2-(tosylmethyl)prop-2-en-1-amine (0.35 g, 1.6 mmol) were added. The solution was cooled to 0°C with stirring, and then 2-bromobenzoyl chloride (0.22 mL, 1.7 mmol) added dropwise. Once the addition was complete, the reaction mixture was warmed to rt. After 1h, no more starting amine was detected by TLC (60:40 EtOAc: pet. ether), so the reaction mixture was dumped into 2M HCl (20 mL) and the layers separated. The aqueous layer was further extracted with DCM (2x10 mL). The DCM extracts were combined and washed with saturated NaCl (1x20 mL), then dried with MgSO<sub>4</sub>. Evaporation yielded a brown oil mixture. The crude 2-bromo-*N*-(2-(tosylmethyl)allyl)benzamide was purified by silica column chromatography, eluting with 50:50 ethyl acetate: petroleum ether, to yield 258 mg (40.7% yield) of the desired amide.

R<sub>f</sub> = 0.50 (50:50 ethyl acetate:pet. ether) (UV, KMnO<sub>4</sub>)

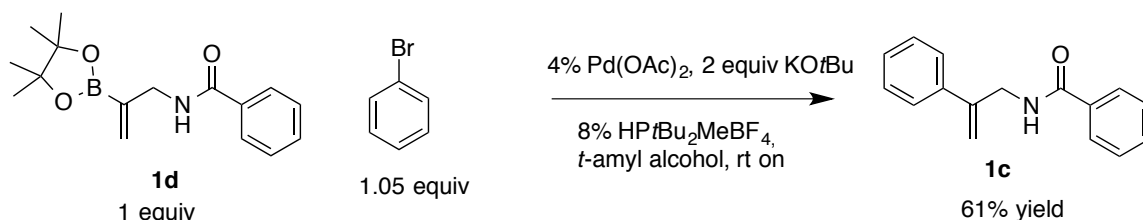
Mp= 144-145°C

HRMS-ESI [C<sub>18</sub>H<sub>18</sub>BrNO<sub>3</sub>S+H]<sup>+</sup>: expected 408.0269, Found: 408.0264

IR(thin film, cm<sup>-1</sup>): 3290, 3008, 2876, 1626, 1572, 1512, 1408, 1288, 1135, 1071, 900, 666 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.45 (s, 3H), 3.91 (s, 2H), 4.20 (d, J=5.86 Hz, 2H), 5.04 (s, 1H), 5.45 (s, 1H), 6.60 (br. s., 1H), 7.27-7.31 (m, 1H), 7.33-7.39 (m, 3H), 7.53 (dd, J=7.57, 1.71 Hz, 1H), 7.60 (dd, J=7.93, 1.10 Hz, 1H), 7.76 (d, J=8.30 Hz, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 21.7, 44.4, 60.6, 119.2, 122.1, 127.6, 128.4, 129.4, 129.8, 131.4, 133.1, 133.4, 135.1, 137.5, 145.0, 167.5



***N*-(2-phenylallyl)benzamide (1c):**<sup>14</sup> To a test tube, palladium(II) acetate (5 mg, 0.02 mmol, 4%), di-*tert*-butyl-methylphosphonium tetrafluoroborate (9 mg, 0.04 mmol, 8%), and *N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide (**1d**) (156 mg, 0.54 mmol) were added. In the nitrogen glovebox, potassium *tert*-butoxide (118 mg, 1.0 mmol) was added to the test tube. The test tube was then placed under argon atmosphere, and *tert*-amyl alcohol (2 mL) added, immediately followed by bromobenzene (0.06 mL, 0.57 mmol). The reaction was then stirred at rt. After 16h, no more starting boronic ester was detected by TLC (20:80 EtOAc:pet. ether) and the reaction mixture was poured into diethyl ether (10 mL). The resulting gray suspension was passed through a short plug of silica and washed with copious amounts of ethyl acetate (~10 mL). Evaporation of the solvent yielded crude *N*-(2-phenylallyl)benzamide as yellow oil. Purification by silica column chromatography, eluting with 20:80 ethyl acetate:petroleum ether yielded 76 mg (0.32 mmol, 61.1% yield) pure *N*-(2-phenylallyl)benzamide as a white crystalline solid.

R<sub>f</sub> = 0.27 (20:80 ethyl acetate:petroleum ether) (UV, KMNO<sub>4</sub>)

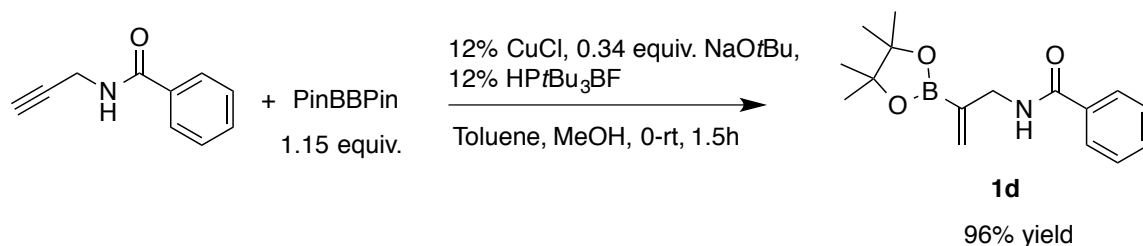
HRMS-ESI [C<sub>16</sub>H<sub>15</sub>NO +H]<sup>+</sup>: expected:238.1232, Found: 238.1229

Mp = 111-112°C

IR(thin film, cm<sup>-1</sup>): 3275, 1624, 1609, 1556, 1523, 1401, 1247, 900, 684 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.53 (d, J=5.86 Hz, 2H), 5.31 (d, J=0.73 Hz, 1H), 5.52 (d, J=0.73 Hz, 1H), 6.47 (br. s., 1H), 7.28-7.43 (m, 5H), 7.45-7.51 (m, 3H), 7.73 (dd, J=8.18, 1.10 Hz, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 43.6, 113.9, 126.0, 126.8, 128.0, 128.5, 128.5, 131.4, 134.3, 138.2, 144.1, 167.4



***N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide (1d)**<sup>15</sup>: To a dry round bottom flask, *N*-(prop-2-yn-1-yl)benzamide (669 mg, 4.2 mmol), CuCl (76.1 mg, 0.5 mmol), sodium *tert*-butoxide (139 mg, 1.44 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (142 mg, 0.5 mmol), bis(pinacolato)diboron (1227 mg, 4.8 mmol) were added in the nitrogen glovebox. Dry toluene (14mL) was added to the flask, then the reaction mixture was cooled to 0°C with stirring. Dry methanol (0.24 mL, 5.55 mmol) was added dropwise to the reaction mixture. Once the addition was complete, the reaction mixture was warmed to rt. The reaction was monitored by TLC (silica TLC plate treated with boric acid<sup>16</sup>)(50:50 EtOAc: pet. ether). After 1.5 h, the reaction was quenched with MeOH (34 mL), and the solution passed through a pad of Celite, rinsing the Celite with DCM (~15 mL). The solvent was then evaporated to yield a clear-pale yellow mixture of oil and solids. CHCl<sub>3</sub> (~20-25 mL) was added to the mixture and thoroughly agitated and sonicated to get as much solid to go into solution. The resulting suspension was then passed through a pad of Celite and rinsed with more CHCl<sub>3</sub>. Evaporation of the CHCl<sub>3</sub> resulted in an oil/solid mixture. This crude *N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide **6** was purified by boric acid treated silica column chromatography<sup>16</sup> eluting with 20:80 ethyl acetate:petroleum ether. Evaporation of the desired fractions yielded 1.16 g (4.0 mmol, 95.8% yield) of pure *N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide **6** as a white crystalline solid.

R<sub>f</sub> = 0.39 (50:50 EA:PE) (UV, KMNO<sub>4</sub>)

Mp = 109-110°C

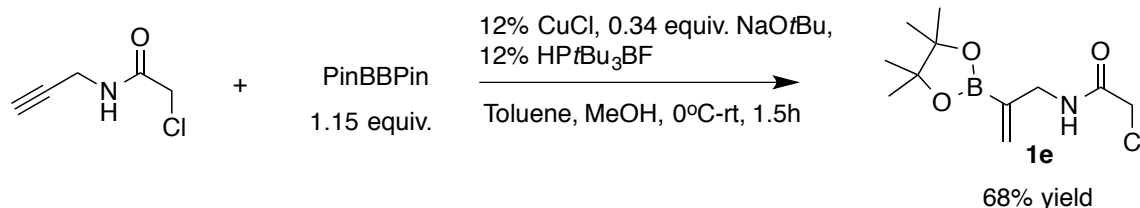
HRMS-ESI [C<sub>16</sub>H<sub>22</sub>BNO<sub>3</sub>+H]<sup>+</sup> expected: 288.1771, Found: 288.1775

IR(thin film, cm<sup>-1</sup>): 3289, 3022, 2941, 1622, 1532, 1400, 1354, 1324, 1297, 1117 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.30 (s, 12 H), 4.21 (d, J=4.39 Hz, 2H), 5.86-5.90 (m, 1H), 5.94-5.98 (m, 1H), 6.71-6.82 (m, 1H), 7.41-7.47 (m, 2H), 7.47-7.53 (m, 1H), 7.78-7.83 (m, 2H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 24.8, 44.2, 83.9, 126.8, 128.5, 131.0, 131.2, 134.9, 166.9. The carbon attached to boron was not observed.





**2-chloro-*N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)acetamide**

**(1e)**<sup>15</sup>: To a dry round bottom flask, 2-chloro-*N*-(prop-2-yn-1-yl)acetamide (966 mg, 7.3 mmol), CuCl (79 mg, 0.8 mmol), sodium *tert*-butoxide (245.7 mg, 2.6 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (296 mg, 1.0 mmol), and bis(pinacolato)diboron (2181 mg, 8.1 mmol) were added in the nitrogen glovebox. Dry toluene (35 mL) was added to the flask, then the reaction mixture cooled to 0°C with stirring. Dry methanol (0.7 mL, 17.3 mmol) was added dropwise to the reaction mixture. Once the addition was complete, the reaction mixture was warmed to rt. After 1 h, no more starting amide was detected by TLC (20:80 EtOAc:pet. ether), so the reaction was quenched with MeOH (60 mL), and the solution passed through a pad of Celite, rinsing the Celite with DCM (~15 mL). The solvent was then evaporated to yield a clear-pale yellow mixture of oil and solids. CHCl<sub>3</sub> (~20-25 mL) was added to the mixture and thoroughly agitated and sonicated to get as much solid to go into solution. The resulting suspension was then passed through a pad of Celite and rinsed with more CHCl<sub>3</sub>. Evaporation of the CHCl<sub>3</sub> resulted in an oil/solid mixture. This crude 2-chloro-*N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)acetamide was purified with boric acid treated silica column chromatography<sup>16</sup>, eluting with 20:80 ethyl acetate:petroleum ether, affording a 1.29 g (4.9 mmol, 68% yield) clear oil.

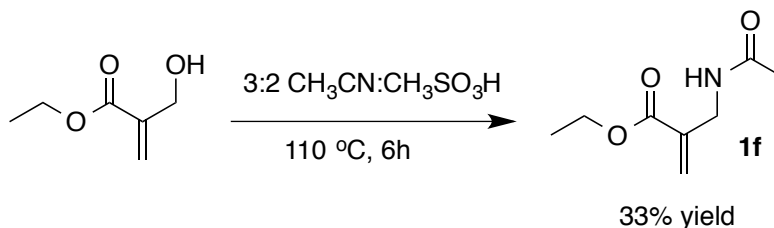
R<sub>f</sub> = 0.23 (20:80 ethyl EA:PE)(KMNO<sub>4</sub>)

HRMS-ESI [C<sub>11</sub>H<sub>19</sub>BClNO<sub>3</sub>+H]<sup>+</sup> expected: 260.1225, Found: 260.1229

IR(thin film, cm<sup>-1</sup>): 3254, 3033, 2938, 2891, 1643, 1517, 1404, 1354, 1297, 1125, 956, 849 cm<sup>-1</sup>.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.29 (s, 12H), 4.05 (d, J=5.86 Hz, 2H), 4.07 (s, 2H), 5.81 (s, 1H), 5.93 (s, 1H), 7.14-7.25 (br. s., 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 24.5, 24.8, 42.7, 44.0, 83.9, 131.1, 165.4. The carbon attached to boron was not observed.



**Ethyl 2-(acetamidomethyl)acrylate (1f):** To a dry 250 mL round-bottom flask, 32 mL of dry acetonitrile and 2-(hydroxymethyl)acrylate (0.978g, 7.51 mmol, 1 equiv) were added. A reflux condenser was placed on the flask, and then the reaction mixture was heated to 60°C. Methanesulfonic acid (21 mL, 323 mmol, 43 equiv) was added dropwise through the top of the condenser. The flask was then heated to 110°C to reflux for 6 h. After 6h, the flask was cooled to rt, then 30 mL of water was slowly added to the mixture. The flask was then placed in an ice bath, then solid K<sub>2</sub>CO<sub>3</sub> added slowly until the pH>7. The mixture was extracted with 3x150 mL diethyl ether. The ether layers were combined and dried with MgSO<sub>4</sub>. Evaporation of the solvent yielded a yellow liquid that subsequently crystallized into a cream-colored solid. The crude ethyl 2-(acetamidomethyl)acrylate was purified by silica column chromatography, eluting with 90:10 EtOAc:pet. ether. To give 0.428g (33 % yield) of ethyl 2-(acetamidomethyl)acrylate as a cream-colored solid.

R<sub>f</sub> = 0.35 in 90:10 ethyl acetate:petroleum ether

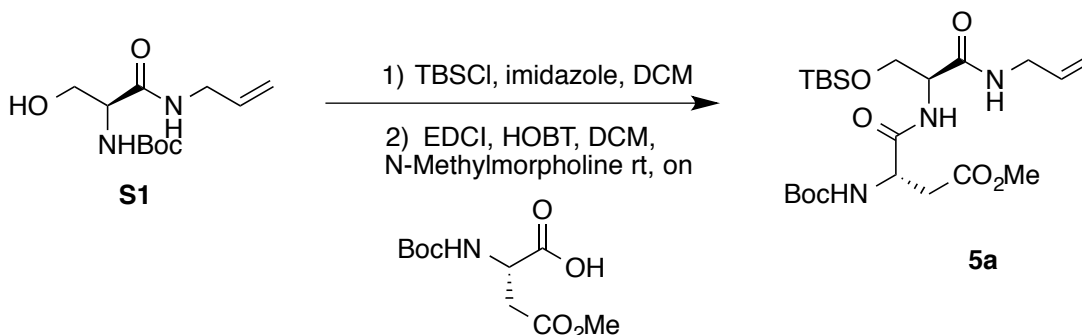
Mp = 40-41°C

IR(thin film, CHCl<sub>3</sub>): 3243.5, 3036.1, 2941.8, 1691.0, 1636.3, 1527.8, 1351.9, 1282.5, 1139.2, 1085.7, 1014.5, 936.2, 805.0 cm<sup>-1</sup>.

HRMS-ESI [C<sub>8</sub>H<sub>13</sub>NO<sub>3</sub>+Na]<sup>+</sup> expected: 194.0793 found: 194.0796

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 1.23 (t, J=7.14 Hz, 3H), 1.91 (s, 3H), 3.98 (d, J=6.15 Hz, 2H), 4.14 (q, J= 7.14 Hz, 2H), 5.70 (s, 1H), 6.17 (s, 1H), 6.57 (bs, 1H).

<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ 13.9, 22.9, 40.2, 60.8, 126.2, 136.5, 166.1, 170.1



**methyl(S)-4-(((S)-1-(allylamino)-3-((tert-butyldimethylsilyl)oxy)-1-oxopropan-2-yl)amino)-3-((tert-butoxycarbonyl)amino)-4-oxobutanoate**

**(5a):** *tert*-butyl (*S*)-(1-(allylamino)-3-hydroxy-1-oxopropan-2-yl)carbamate (**S1**)<sup>17</sup> (976 mg, 4 mmol, 1 equiv.) and imidazole (816 mg, 3 equiv, 12 mmol) were dissolved in 8 ml DCM (0.5 M) followed by addition of TBSCl (906 mg, 6 mmol, 1.5 equiv). The reaction was allowed to stir for 2h and quenched with saturated aqueous sodium bicarbonate (10 ml). The aqueous layer was extracted with DCM (3X10 ml). The combined organic layers were dried with MgSO<sub>4</sub>, and the solvent was evaporate to give the crude TBS protected alcohol. The material was directly deprotected by dissolving in TFA:DCM (1:1) 10 mL and stirring at room temperature for 30 minutes. The solvent was evaporated and redissolved in DCM (10 mL) followed by addition of saturated aqueous sodium bicarbonate until there was no more bubbling. The organic layer was removed and the aqueous layer was extracted with DCM (3X10 ml). The combined organic layers were dried with MgSO<sub>4</sub>, and the solvent was evaporated to give the crude amine. The amine was dissolved in 12.3 ml DCM (0.3 M) and HOBT (795 mg, 5.3 mmol, 1.3 equiv), Boc-L-aspartic acid 4-methyl ester (1.284 g, 5.3 mmol, 1.3 equiv), and N-Methylmorpholine (0.57 ml, 5.3 mmol, 1.3 equiv.) were added sequentially. The solution was placed in an ice bath and allowed to cool for 10 minutes before EDCI (993 mg, 5.2, 1.3 equiv.) was added as a solid. The reaction was allowed to warm to room temperature overnight. After 16h saturated aqueous sodium bicarbonate (15 ml) was added and the aqueous layer was extracted with DCM (3X10 ml). The combined organic fractions were dried with MgSO<sub>4</sub>, the solvent was evaporated, and the crude product was purified by column chromatography eluting with 55% EA:PE to give **5a** as a foam (1.44 g, 50% yield).

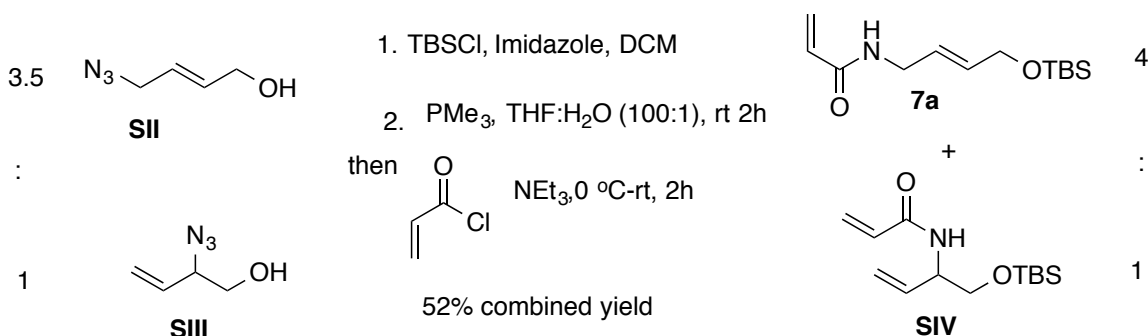
R<sub>f</sub> = 0.15 30% EA:PE (KMNO<sub>4</sub>).

HRMS-ESI [C<sub>22</sub>H<sub>41</sub>N<sub>3</sub>O<sub>7</sub>Si+Na]<sup>+</sup> expected: 510.2612, Found: 510.2611

IR(thin film, cm<sup>-1</sup>): 3304, 2953, 2930, 2857, 1721, 1651, 1518, 1252, 1166, 838.

<sup>1</sup>H NMR (600 MHz; CDCl<sub>3</sub>): δ 7.16 (d, J = 7.0, 1H), 6.76 (s, 1H), 5.81 (ddt, J = 16.8, 10.8, 5.7, 1H), 5.51 (d, J = 6.8, 1H), 5.17 (dd, J = 17.1, 1.4, 1H), 5.10 (d, J = 10.2, 1H), 4.47 (q, J = 6.1, 1H), 4.40 (ddd, J = 7.7, 5.6, 2.5, 1H), 4.18 (d, J = 7.9, 1H), 3.92-3.83 (m, 2H), 3.69 (s, 3H), 3.63 (dd, J = 9.7, 5.8, 1H), 2.96 (dd, J = 17.0, 4.7, 1H), 2.79 (dd, J = 17.0, 6.4, 1H), 1.45 (s, 9H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 172.09, 170.80, 169.62, 155.74, 133.83, 116.36, 80.93, 62.74, 54.64, 52.22, 51.38, 42.13, 35.86, 28.34, 25.90, 18.25, -5.42.



**(*E*)-*N*-(4-((*tert*-butyldimethylsilyl)oxy)but-2-en-1-yl)acrylamide (**7a**):** A ~3.5:1 mixture of (*E*)-4-azidobut-2-en-1-ol to 2-azidobut-3-en-1-ol (590 mg, 5.2 mmol, 1 equiv.) (**SII**) and branched compound **SIII**<sup>18</sup> was dissolved in 26 ml DCM (0.2 M). Imidazole (1.23g, 18.2 mmol, 3.5 equiv) and TBSCl (1.1g, 7.3 mmol, 1.4 equiv) were added. After stirring for 2h the reaction was quenched with saturated sodium bicarbonate (30 mL). The DCM layer was removed and the aqueous layer was extracted with DCM (2X20 ml). The combined organic fractions were dried with  $\text{MgSO}_4$ , and the solution was evaporated to give a crude oil (0.98 g, 83% yield). A portion of the crude oil (432 mg, 1.9 mmol, 1 equiv.) was dissolved in THF:H<sub>2</sub>O (5 mL:0.05 mL), and  $\text{PMe}_3$  (1M in Toluene)(2.09 mmol, 1.1 equiv., 2.1 ml) was then added dropwise over 5 minutes causing vigorous bubbling. The reaction was let stir for 2h. The solution was cooled to 0 °C and  $\text{NEt}_3$  (4.75 mmol, 2.5 equiv., 0.67 ml) was added followed by dropwise addition of acryloyl chloride (3.8 mmol, 2 equiv, 0.31 ml). The reaction was taken out of the ice bath and allowed to react for 2h. The reaction was then diluted with saturated sodium bicarbonate and extracted with ether (3X10 ml). The ether layer was dried with  $\text{MgSO}_4$ , evaporated, and chromatographed using 20% ethyl acetate to 40% ethyl acetate:pet ether to give a yellow oil **7a** (235 mg) and 64 mg of the branched *N*-(1-((*tert*-butyldimethylsilyl)oxy)but-3-en-2-yl)acrylamide (**SIV**) (52% yield over 2 steps).

**7a:**  $R_f$ : 0.25 30% EA:PE ( $\text{KMnO}_4$ )

IR(thin film  $\text{cm}^{-1}$ ): 3271, 3077, 2922, 1655, 1622, 1545, 1408, 1244, 965.

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  6.28 (dd,  $J$  = 17.0, 1.4, 1H), 6.09 (dd,  $J$  = 17.0, 10.3, 1H), 5.73-5.71 (m, 3H), 5.64 (dd,  $J$  = 10.3, 1.4, 1H), 4.15 (d,  $J$  = 2.8, 2H), 3.95 (td,  $J$  = 4.4, 1.3, 2H), 0.89 (s, 9H), 0.06 (s, 6H).

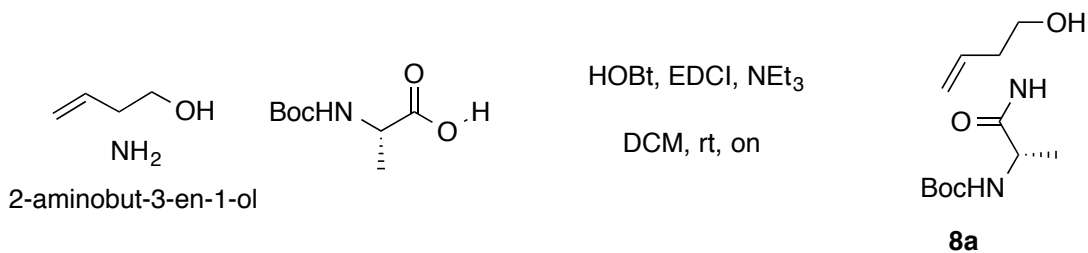
$^{13}\text{C}$  NMR (101 MHz;  $\text{CDCl}_3$ ):  $\delta$  165.39, 132.34, 130.83, 126.70, 125.66, 63.18, 41.07, 26.07, 18.55, -5.13.

HRMS-ESI [ $\text{C}_{13}\text{H}_{25}\text{NO}_2\text{Si}+\text{Na}$ ]<sup>+</sup> expected: 278.1553, Found: 278.1546

**SIV** ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR)

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.09 (d, 1H), 6.29 (dd, 1H), 6.15 (d, 1H), 5.94 (s, 1H), 5.90-5.81 (m, 1H), 5.66 (dd, 1H), 5.22 (dt, 1H), 5.18 (dt, 1H), 4.68 (d, 1H), 4.61-4.58 (m, 1H), 3.75-3.68 (m, 2H), 0.88 (s, 9H), 0.05 (s, 5H).

$^{13}\text{C}$  NMR (101 MHz;  $\text{CDCl}_3$ ):  $\delta$  165.0, 135.9, 131.0, 126.7, 116.4, 65.1, 52.8, 26.0, 18.4, -5.3



***tert*-butyl((2*S*)-1-((1-hydroxybut-3-en-2-yl)amino)-1-oxopropan-2-yl)carbamate (**8a**):** Racemic 2-aminobut-3-en-1-ol (164 mg, 1 equiv., 1.7 mmol) was dissolved in DCM (0.3M, 5.7 ml). HOBT (260 mg, 1.7 mmol, 1 equiv.),  $\text{NEt}_3$  (0.55 ml, 4 mmol, 2.1 equiv) and (*tert*-butoxycarbonyl)-*L*-alanine (340 mg, 1.8 mmol, 1.1 equiv.) were added followed by EDCI (345 mg, 1.8 mmol, 1.1 equiv) at room temperature. The reaction was stirred overnight and diluted with water (15 ml). The organic layer was removed and the aqueous layer was extracted with DCM (2X10 ml). The combined organic layers were dried with  $\text{MgSO}_4$ , evaporated, and chromatographed using 70% EA:PE to give product **8a** (1:1 Mixture of diastereomers) as a white foam (283 mg, 58% yield).

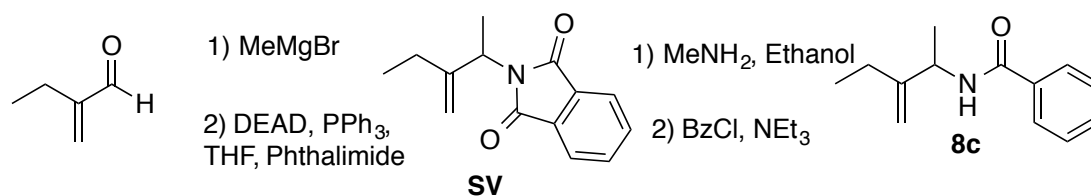
Rf: 0.2 70% EA:PE ( $\text{KMnO}_4$ )

HRMS-ESI [ $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4 + \text{Na}$ ] $^+$  expected: 281.1477, found: 281.1466.

IR(thin film,  $\text{cm}^{-1}$ ): 3254.9, 1638.1, 1505.7, 1348.2, 1152  $\text{cm}^{-1}$ .

(1:1 Mixture of diastereomers, most signals overlap)  $^1\text{H}$ -NMR (500 MHz;  $\text{CDCl}_3$ ):  $\delta$  6.66 (s, 1H), 5.83 (ddd,  $J = 16.9, 10.9, 5.6$  Hz, 1H), 5.27-5.22 (m, 3H), 4.57-4.53 (m, 1H), 4.18-4.14 (m, 1H), 3.75-3.72 (m, 1H), 3.65-3.61 (m, 1H), 1.43 (d,  $J = 1.7$  Hz, 9H), 1.37 (dd,  $J = 7.0, 2.5$  Hz, 3H).

(1:1 Mixture of diastereomers, most signals are resolved)  $^{13}\text{C}$ -NMR (101 MHz;  $\text{CDCl}_3$ ):  $\delta$  173.33, 155.92, 134.93, 134.83, 116.80, 116.70, 80.36, 64.76, 64.68, 53.72, 53.56, 50.48, 50.47, 28.40, 18.64, 18.27.



**2-(3-methylenepentan-2-yl)isoindoline-1,3-dione (SV):** A dry round bottom, under argon, was charged with 2-methylenepentanal (841 mg, 10 mmol, 1 equiv.), and diethyl ether (50 ml, 0.2 M), and cooled to 0 °C. MeMgBr (2M in diethyl ether) (15 mmol, 7.5 ml) was added dropwise over 30 mins at 0 °C. The reaction was removed from the ice bath, allowed to warm to room temperature and stir for an additional hour. The reaction was quenched with saturated sodium bicarbonate (30 mL) by slow addition at 0 °C. The ether layer was removed and the aqueous layer was extracted with diethyl ether (2X10 ml). The combined organic fractions were dried with MgSO<sub>4</sub>, and the solution was evaporated at 0 °C to give crude 3-methylenepentan-2-ol (705 mg, 70% crude yield, 7 mmol). The alcohol was dissolved in THF (28 ml, 0.25 M). PPh<sub>3</sub> (2.2g, 8.4 mmol, 1.2 equiv.) and Phthalimide (1.13g, 7.7 mmol, 1.1 equiv) were added, followed by the dropwise addition of DEAD (40% in Toluene)(3.65 ml, 8.4 mmol, 1.2 equiv). The reaction was stirred overnight at room temperature. The solvent was evaporated and a 1:1 mixture of Et<sub>2</sub>O:PE (50 ml) was added in order to precipitate triphenylphosphine oxide. The precipitate was filtered and washed with Et<sub>2</sub>O. The combined filtrate was evaporated and the crude material was purified by column chromatography eluting with 5-10% EA:PE to give **SV** as a clear viscous oil (689 mg, 43% yield).

Rf: 0.45 10% EA:PE (KMNO<sub>4</sub>)

IR(thin film, cm<sup>-1</sup>): 2967, 2938, 1704, 1383, 1351, 1329, 1146, 880.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.83-7.81 (m, 2H), 7.70 (dd, J = 5.5, 3.0, 2H), 5.09 (dd, J = 1.6, 0.7, 1H), 5.01 (d, J = 0.8, 1H), 4.89 (q, J = 7.1, 1H), 2.08-1.95 (m, 2H), 1.64 (d, J = 7.1, 3H), 1.04 (t, J = 7.4, 3H).

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 187.9, 168.4, 148.5, 134.0, 132.0, 123.3, 110.2, 49.6, 26.6, 16.6, 12.3

**N-(3-methylenepentan-2-yl)benzamide (8c):** 2-(3-methylenepentan-2-yl)isoindoline-1,3-dione (**SV**) (275 mg, 1.2 mmol, 1 eq) was dissolved in 3 mL of 33% MeNH<sub>2</sub> in ethanol and heated at 80 °C for 30 mins. The reaction was allowed to cool and the solution was filtered to remove any solids and washed with ether. The solution was evaporated at 0 °C to half volume and 2 mL of 1M HCL in ether was added and stirred for 5 minutes. The solution was evaporated to give the crude amine salt. The salt was dissolved in DCM (3.3 mL, 0.3M) and placed in an ice bath. To the solution was added NEt<sub>3</sub> (5 eq, 0.7 mL), and then Benzoyl chloride (2 eq, 0.235 ml) was added dropwise. The solution was allowed to stir for 3h after which saturated sodium bicarbonate was added (20 mL). The biphasic mixture was

extracted with DCM 3 X 10 mL and washed with brine 1X10 mL. The organic layer was dried and the solvent evaporated to give a crude oil. The oil was purified by flash column chromatography eluting with 15% to 25% ethyl acetate:pet ether to give oil **8c** (139 mg, 57% yield).<sup>19</sup>

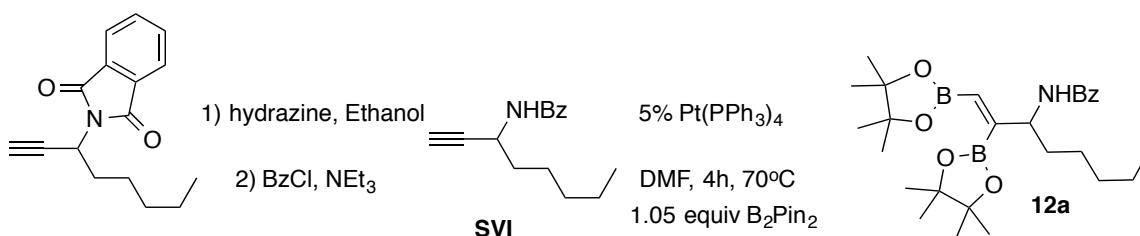
$R_f$  = 0.65 30% EA:PE (UV/KMNO<sub>4</sub>)

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>):  $\delta$  7.80 (dd,  $J$  = 8.3, 1.3, 2H), 7.53-7.49 (m, 1H), 7.48-7.44 (m, 2H), 6.13-6.11 (m, 1H), 5.04 (t,  $J$  = 1.0, 1H), 4.92 (dt,  $J$  = 1.5, 0.8, 1H), 4.75 (t,  $J$  = 7.3, 1H), 2.17-2.15 (m, 2H), 1.40 (d,  $J$  = 6.8, 3H), 1.12 (t,  $J$  = 7.4, 3H).

Minor impurity, which could not be removed, corresponds to signals seen at 8.13 (dd,  $J$  = 8.4, 1.3)(relative integration = 0.33) and 7.64-7.60 (m) (relative integration = 0.19)

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>):  $\delta$  166.8, 152.4, 134.8, 131.6, 128.7, 127.0, 108.2, 49.2, 26.6, 20.1, 12.4.

Minor impurity, which could not be removed, corresponds to signals seen at <sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>):  $\delta$  133.6, 130.2, 128.5



***N*-(oct-1-yn-3-yl)benzamide (SVI):** 2-(oct-1-yn-3-yl)isoindoline-1,3-dione<sup>20</sup> (1.79 g, 7 mmol, 1 equiv.) was dissolved in EtOH (35 ml, 0.2 M). Hydrazine hydrate (0.88 ml, 2.2 equiv.) was then added and the reaction was heated at reflux for 2h. The reaction was then cooled and the solid precipitates were removed by filtration. The precipitate was washed with ether. 15 ml of 1M HCL in ether was added to the combined filtrate and the solution was evaporated to give the crude amine salt. The salt was dissolved in DCM (35 ml, 0.2M) and placed in an ice bath. To the solution was added NEt<sub>3</sub> (2 eq, 1.8 ml), followed by the dropwise addition of Benzoyl chloride (1.5 eq, 1.225 ml). The solution was allowed to stir for 3h after which saturated sodium bicarbonate was added (20 mL). The biphasic mixture was extracted with DCM 3 X 20 ml and washed with brine 1X10 ml. The organic layer was dried and the solvent evaporated to give a crude oil. The oil was purified by flash column chromatography eluting with 15% EA:PE to give a white solid **SVI** (1.03 g, 52% yield).

$R_f = 0.25$  20% EA:PE (UV,  $\text{KMnO}_4$ ).

$M_p = 55\text{-}56\text{ }^\circ\text{C}$

IR(thin film,  $\text{cm}^{-1}$ ): 3332, 3267, 2923, 2859, 1632, 1516, 1304, 1074.

HRMS-ESI [ $\text{C}_{15}\text{H}_{19}\text{NO}+\text{H}$ ] $^+$  expected: 230.1545 Found: 230.1542.

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.79-7.77 (m, 2H), 7.52-7.47 (m, 1H), 7.46-7.40 (m, 2H), 6.40 (d,  $J = 6.6$ , 1H), 4.98-4.92 (m, 1H), 2.30 (d,  $J = 2.3$ , 1H), 1.77 (td,  $J = 12.2$ , 6.2, 2H), 1.51-1.47 (m, 2H), 1.32 (dq,  $J = 7.2$ , 3.6, 4H), 0.90-0.87 (m, 3H).

$^{13}\text{C}$  NMR (101 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.6, 134.1, 131.8, 128.7, 127.1, 83.4, 71.5, 42.0, 35.9, 31.4, 25.4, 22.6, 14.1

**(*E*)-*N*-(1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-3-yl)benzamide (12a):** Alkyne **SVI** (137.5 mg, 0.6 mmol, 1 equiv) was combined with  $\text{Pt}(\text{PPh}_3)_4$  (37.3 mg, 0.03 mmol, 0.05 equiv) and PinBBPin (160 mg, 0.63 mmol, 1.05 equiv) in a dry vial under argon. The solids were dissolved in 1.2 ml DMF (0.5 M) and the reaction was heated for 4h at 70  $^\circ\text{C}$ . The solution was directly loaded on a silica column and purified using 20% EA:PE to give **12a** as a yellow oil (120 mg, 41% yield).

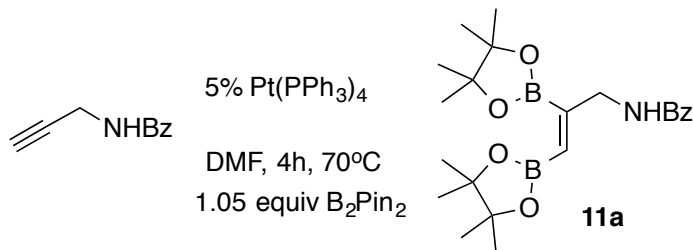
$R_f = 0.25$  20% EA:PE (UV,  $\text{KMnO}_4$ ).

HRMS-ESI [ $\text{C}_{15}\text{H}_{19}\text{NO}+\text{H}$ ] $^+$  expected: 484.3405 Found: 484.3408.

IR(thin film,  $\text{cm}^{-1}$ ): 3332, 2977, 2929, 2858, 1646, 1579, 1336, 1217, 1140, 969.

$^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.81-7.79 (m, 2H), 7.48-7.39 (m, 3H), 7.02 (d,  $J = 8.9$ , 1H), 6.15 (s, 1H), 4.72 (q,  $J = 7.7$ , 1H), 1.66-1.57 (m, 2H), 1.34 (s, 12H), 1.30 (s, 12H), 1.27-1.24 (m, 4H), 0.86 (t,  $J = 6.4$ , 3H).

$^{13}\text{C}$  NMR (75 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.2, 135.4, 131.3, 128.6, 127.1, 84.4, 83.9, 58.8, 36.0, 32.0, 26.0, 25.23, 25.20, 25.14, 25.06, 22.7, 14.4. The carbons attached to boron were not observed.





**(E)-N-(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide**

**(11a):** N-(prop-2-yn-1-yl)benzamide (318mg, 2 mmol, 1 equiv) was combined with Pt(PPh<sub>3</sub>)<sub>4</sub> (124 mg, 0.1 mmol, 0.05 equiv) and PinBBPin (533 mg, 2.1 mmol, 1.05 equiv.) in a dry vial under argon. The solids were dissolved in 4 ml DMF (0.5 M) and the reaction was heated for 4h at 70 °C. The solution was directly loaded on a silica column and purified using 20% EA:PE to give **12a** as a yellow oil (145 mg, 30% yield).

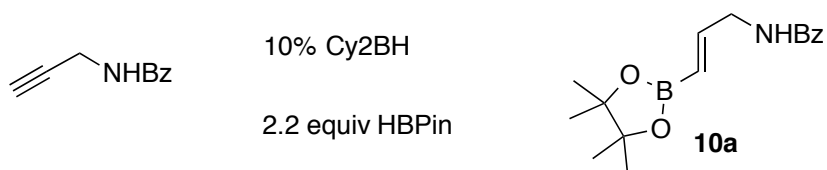
R<sub>f</sub> = 0.32 20% EA:PE

IR(thin film, cm<sup>-1</sup>): 3277.7, 2921.7, 2874.4, 1614.6, 1509.2, 1376.4, 1345.9, 1291.3, 1192.8, 1119.5.

HRMS-ESI [C<sub>22</sub>H<sub>33</sub>B<sub>2</sub>NO<sub>5</sub>+Na]<sup>+</sup> calcd 414.2623, found: 414.2615.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): δ 7.78 (d, J = 7.1, 2H), 7.48 (t, J = 7.3, 1H), 7.42 (t, J = 7.5, 2H), 6.52 (s, 1H), 6.14 (s, 1H), 4.24 (dd, J = 5.6, 1.6, 2H), 1.29 (2 singlets, 24H)

<sup>13</sup>C NMR (126 MHz; CDCl<sub>3</sub>): δ 167.0, 134.7, 131.4, 128.5, 127.0, 84.3, 83.8, 47.3, 25.0. The carbons attached to boron were not observed.

**(E)-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)benzamide (10a):**

A dry vial was charged with dicyclohexyl borane (90 mg, 0.1 equiv, 0.5 mmol) and N-(prop-2-yn-1-yl)benzamide (795 mg, 5 mmol, 1 equiv) under nitrogen. Neat HBPIn (1.6 ml, 2.2 equiv.) was added and the reaction was stirred at room temperature for 1h. The solution was diluted with diethyl ether (10 ml) and excess borane was quenched by dropwise addition of water (2 ml). After stirring for 10 minutes saturated aqueous bicarbonate (10 ml) was added and the ether layer was removed. The aqueous layer was extracted with diethyl ether (3X10 ml). The combined organic layers were dried with MgSO<sub>4</sub>, evaporated, and chromatographed using 30% EA:PE to give product **10a** as a white solid (1.32 g, 92% yield).

R<sub>f</sub> = 0.32 20% EA:PE

Mp = 79-80 °C

IR(thin film, cm<sup>-1</sup>): 3319, 2978, 1639, 1537, 1364, 1324, 1144, 972, 850.

HRMS-ESI [C<sub>16</sub>H<sub>22</sub>BNO<sub>3</sub>+Na]<sup>+</sup> calcd 310.1591, found: 310.1593

$^1\text{H}$  NMR (600 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.73 (d,  $J$  = 7.3, 2H), 7.49 (t,  $J$  = 7.4, 1H), 7.40 (t,  $J$  = 7.7, 2H), 6.64 (dt,  $J$  = 18.1, 4.8, 2H, overlapping N-H), 5.62 (dt,  $J$  = 18.0, 1.6, 1H), 4.15 (t,  $J$  = 4.4, 2H), 1.25 (s, 12H)

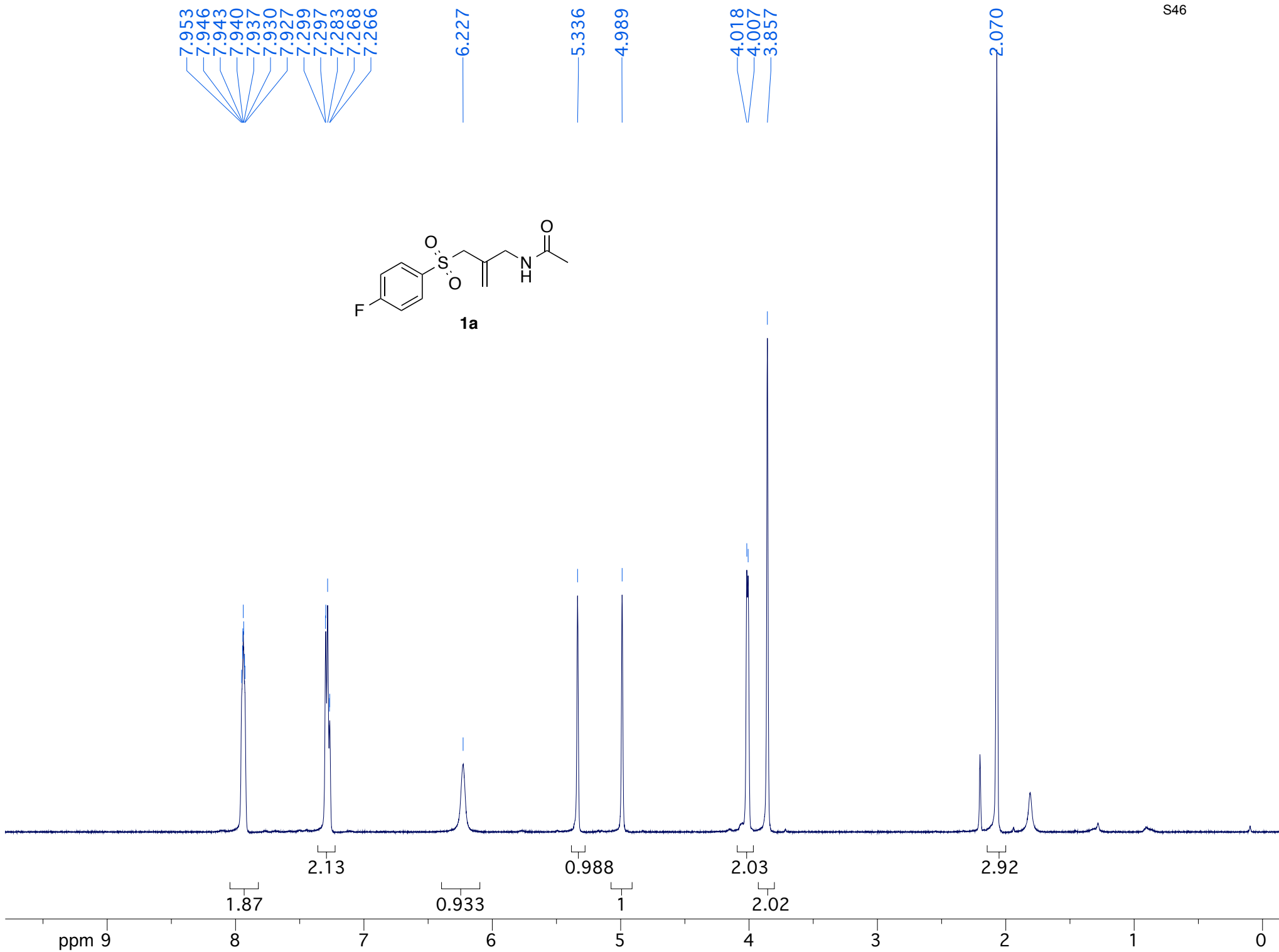
$^{13}\text{C}$  NMR (151 MHz;  $\text{CDCl}_3$ ):  $\delta$  168.4, 147.9, 133.7, 132.0, 128.8, 127.2, 83.6, 43.7, 24.9

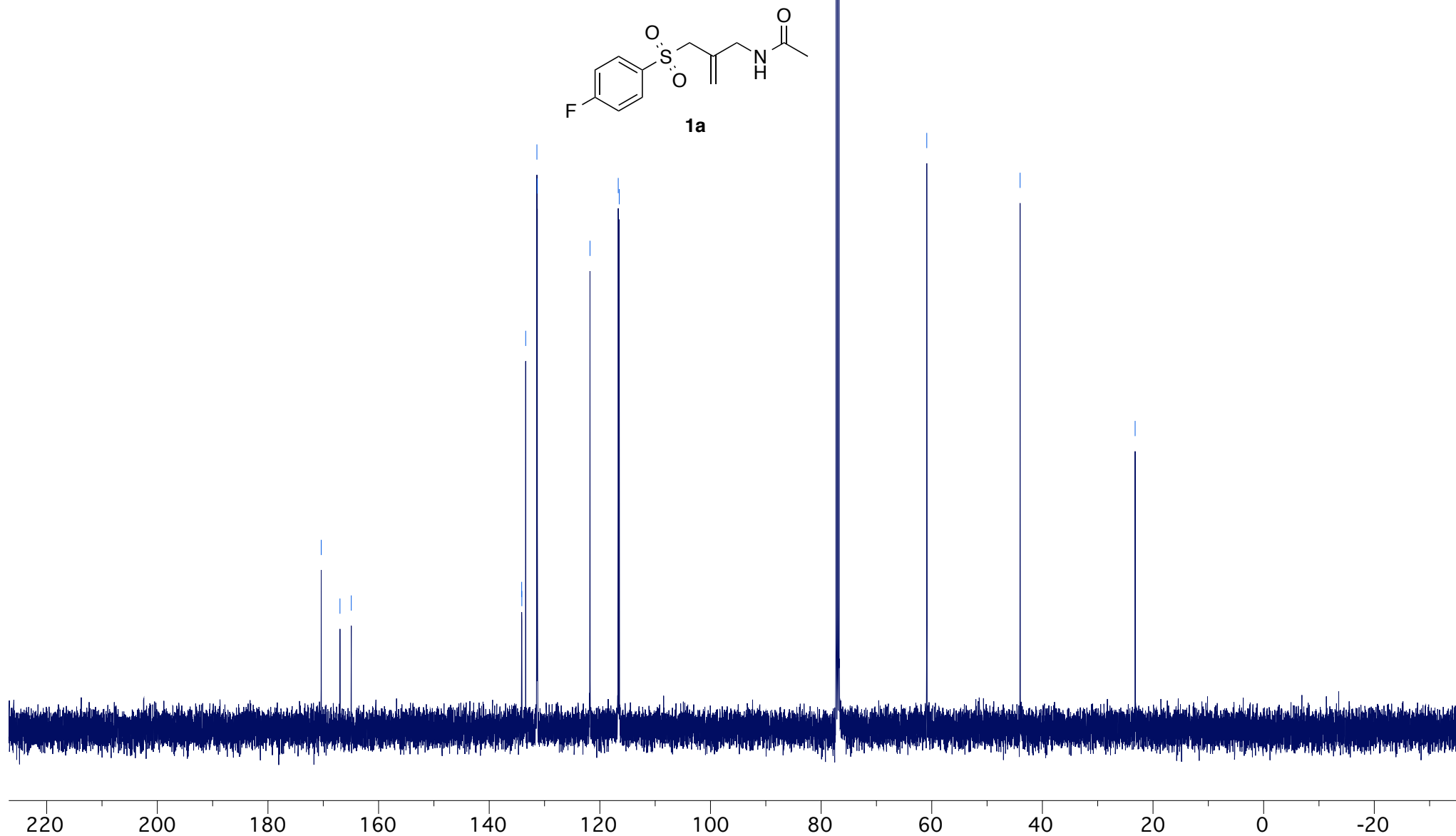


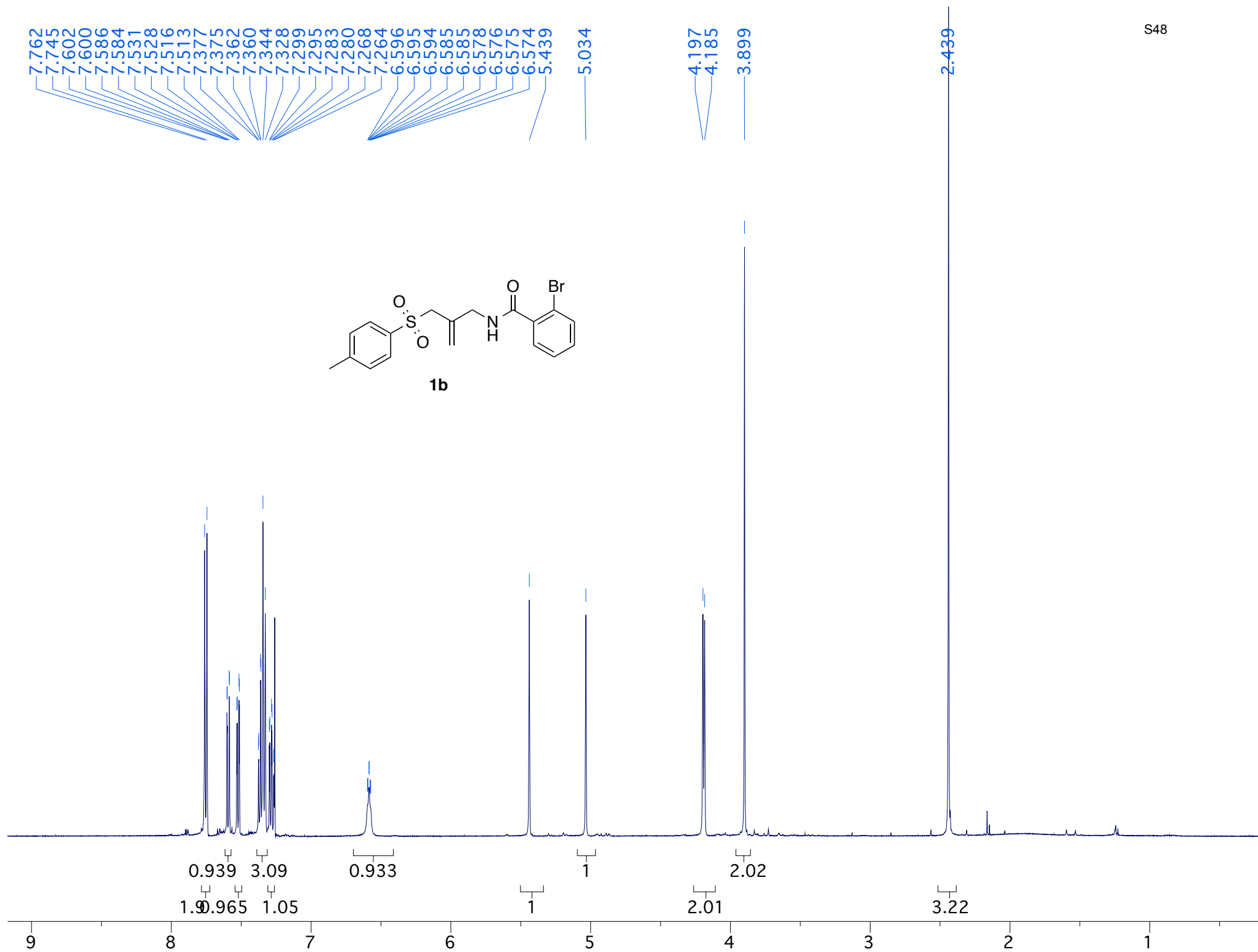
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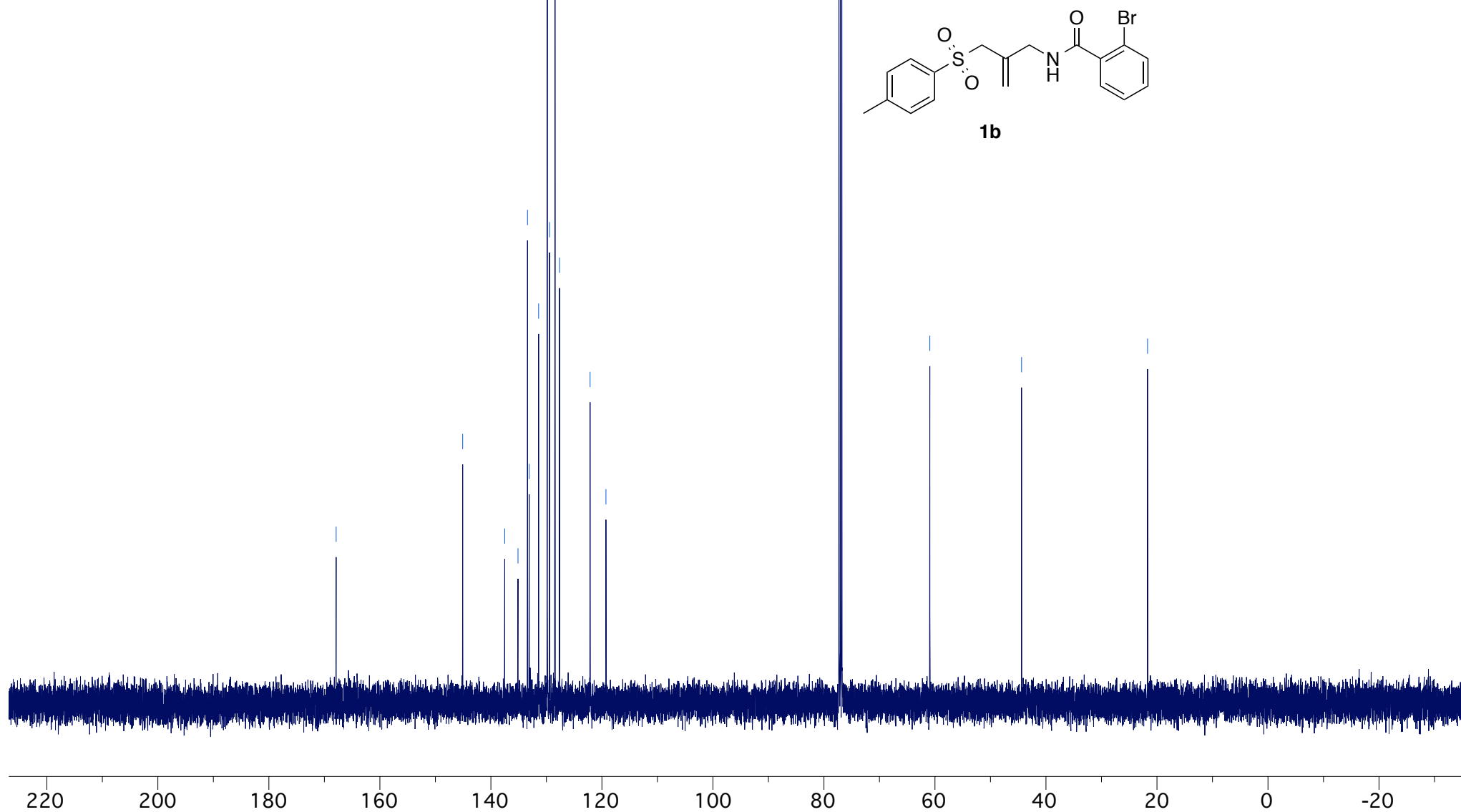
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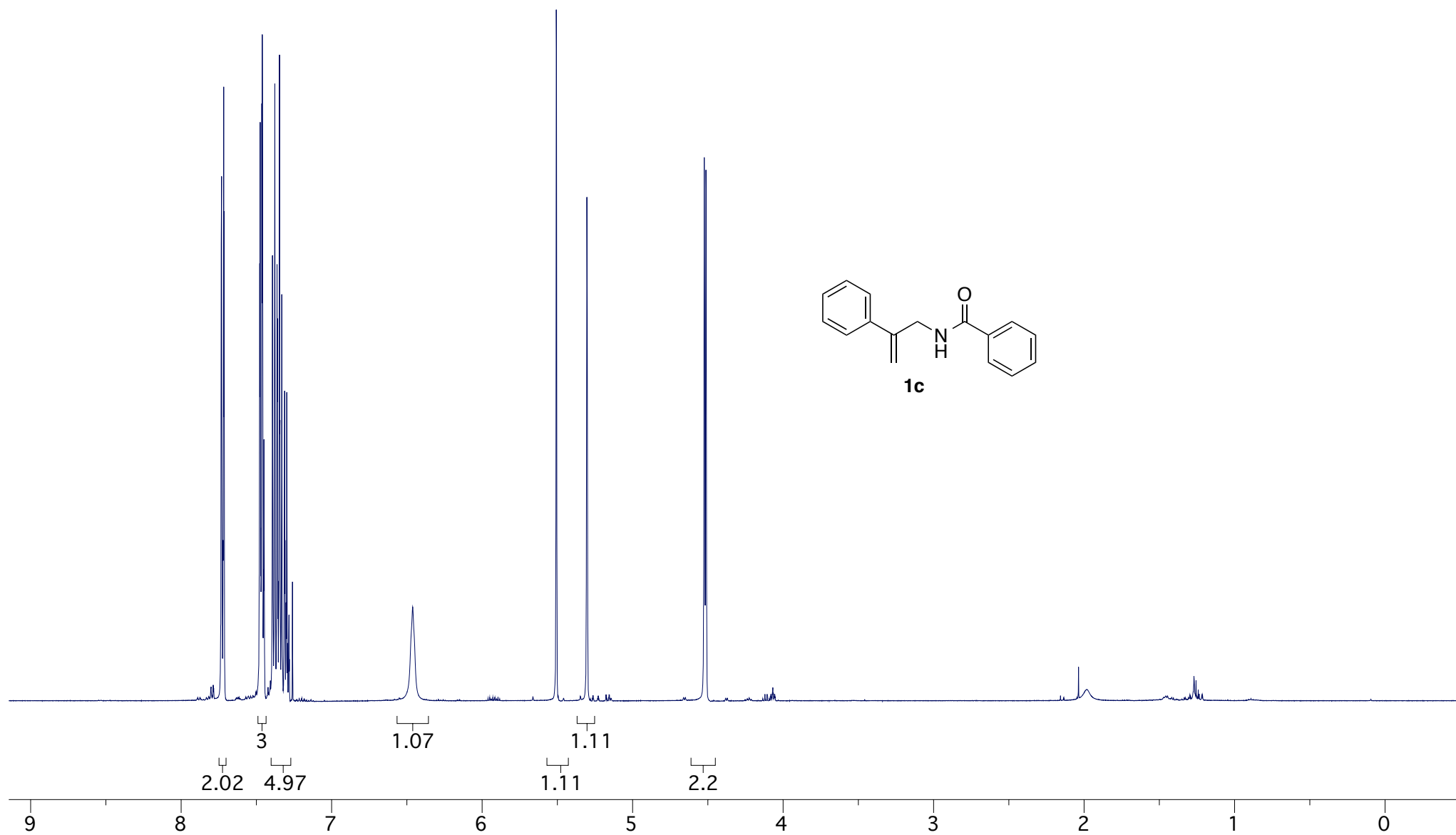


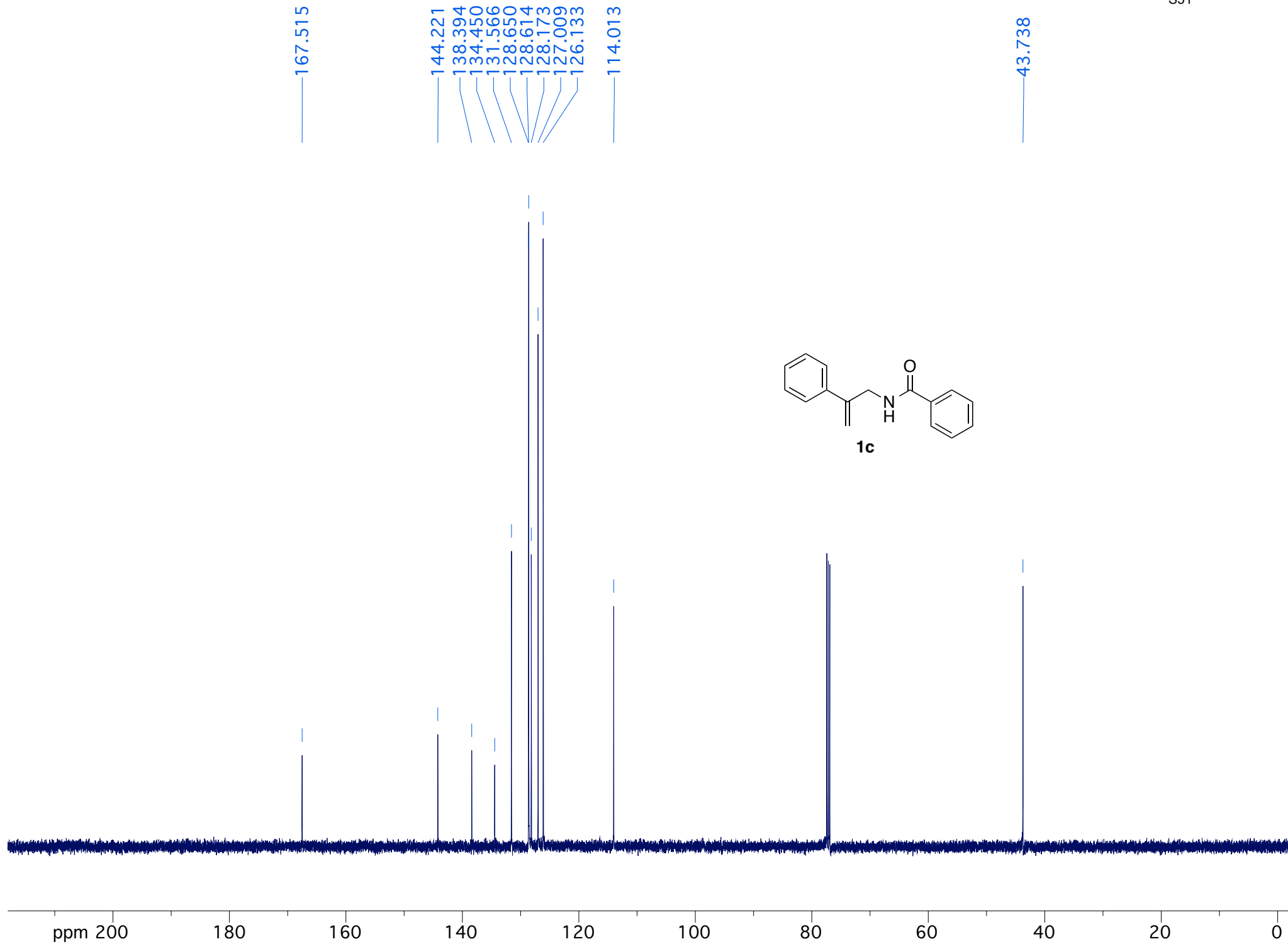


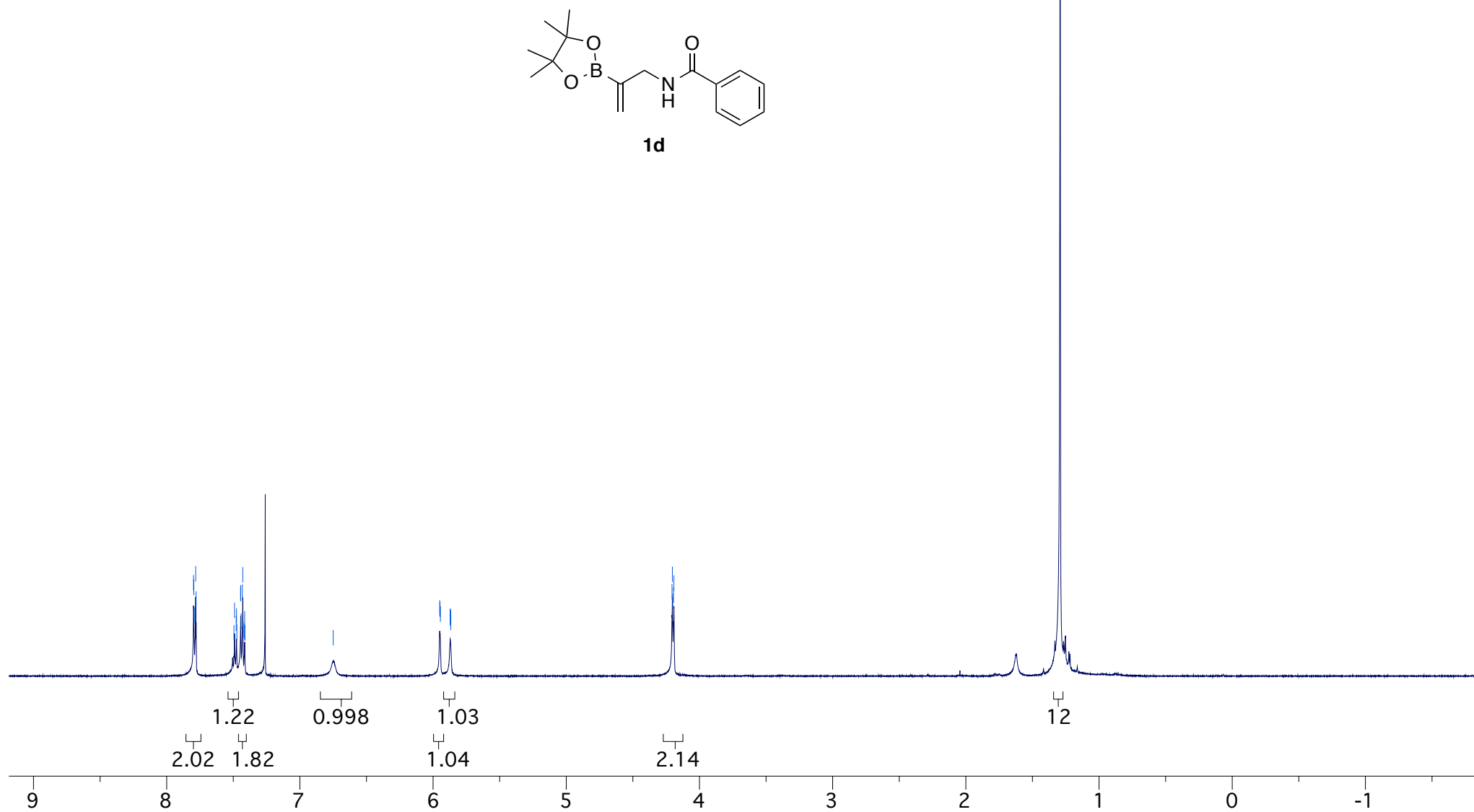












167.045

135.053

131.393

131.123

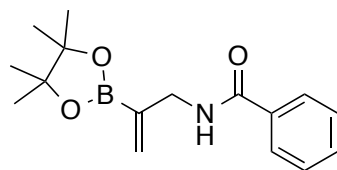
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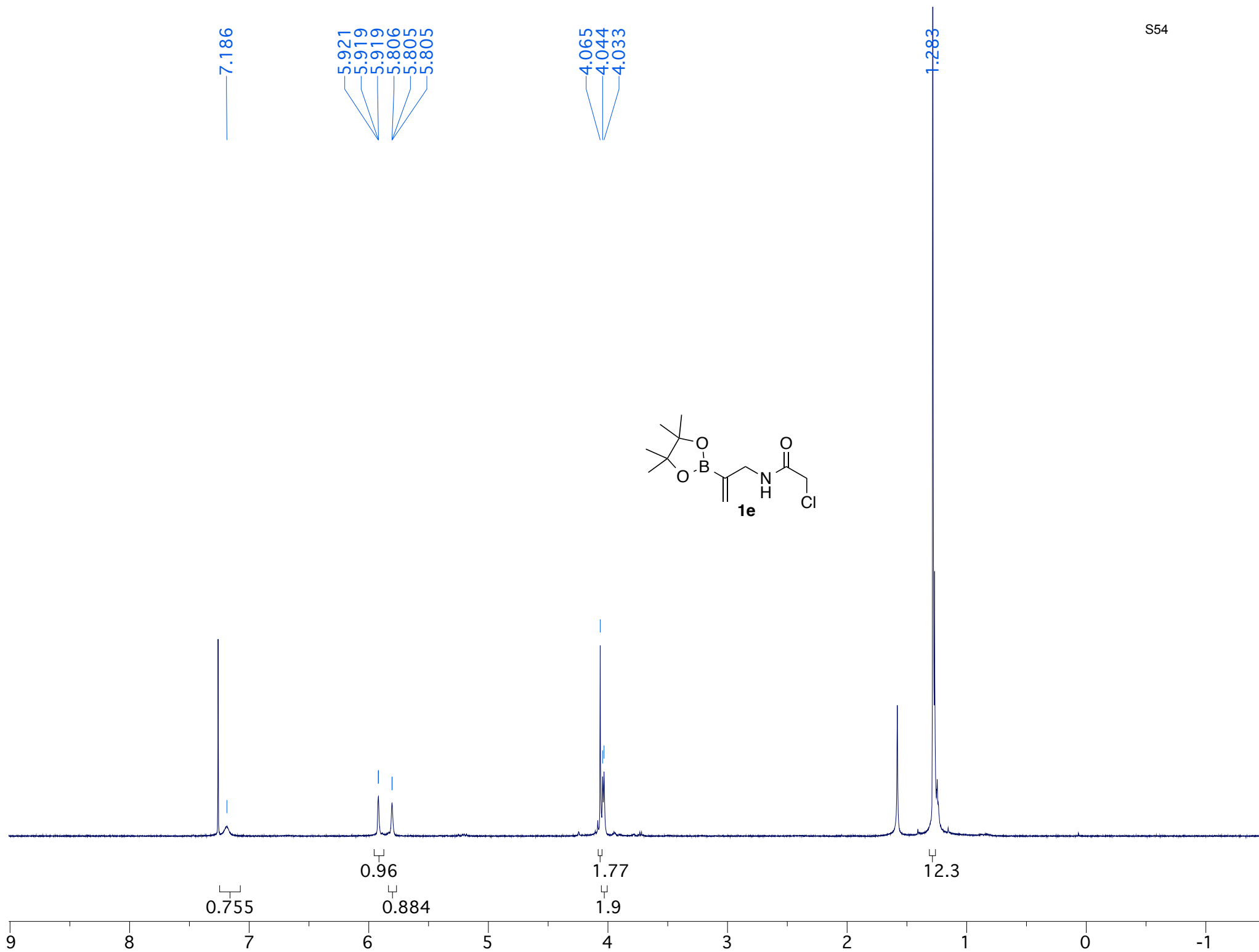
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44.363

25.001

**1d**

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165.578

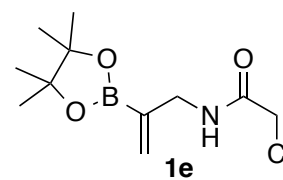
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84.087

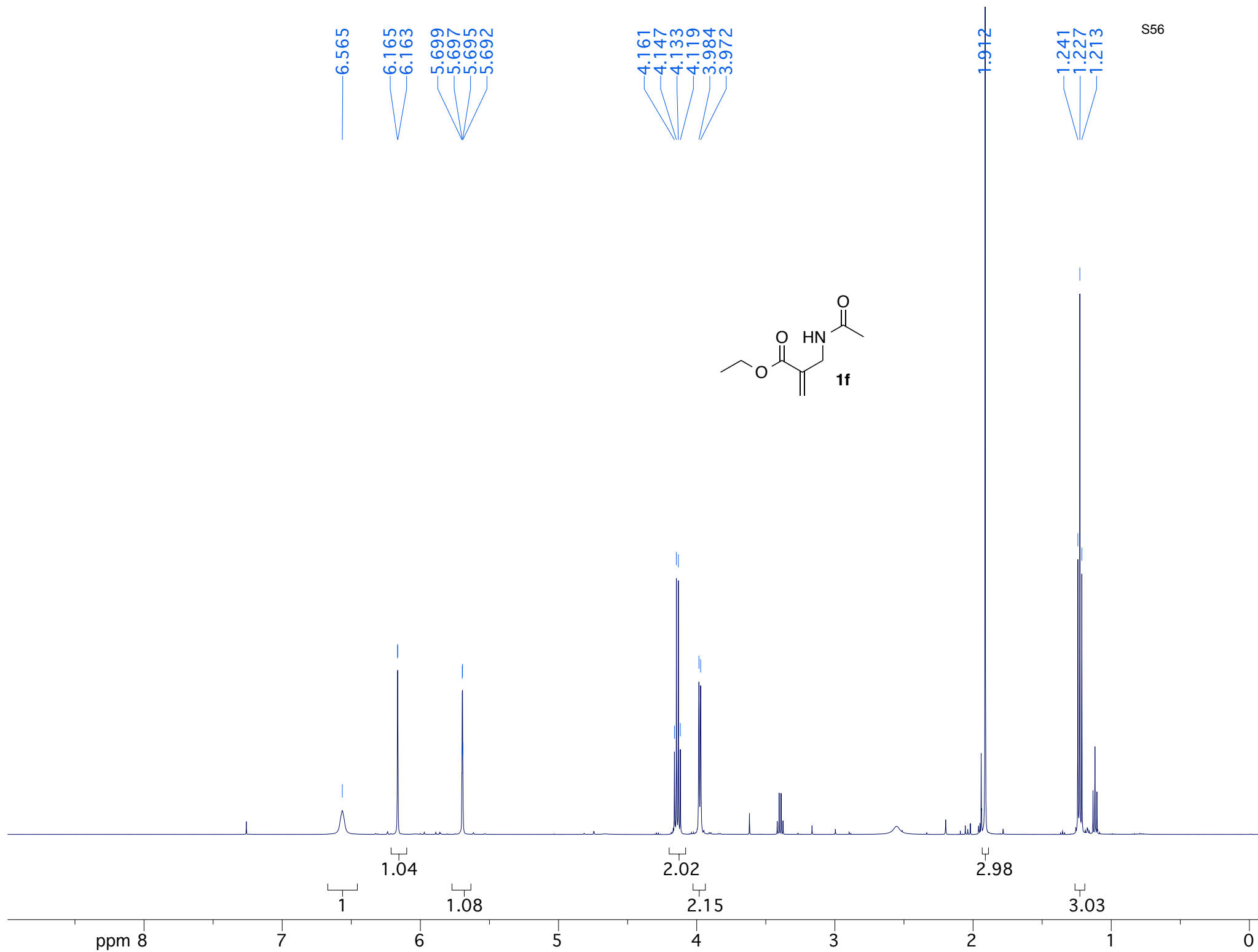
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42.890

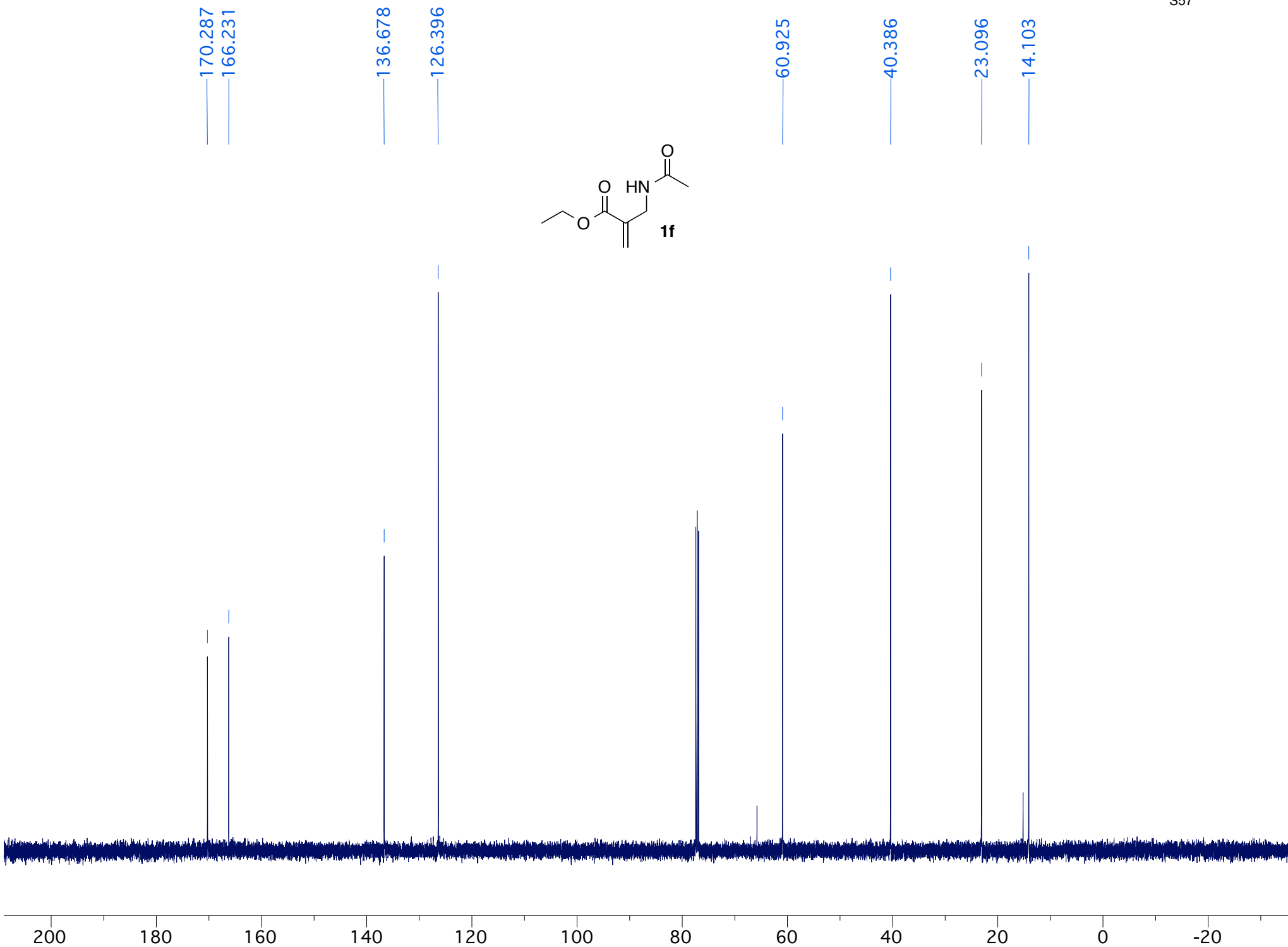
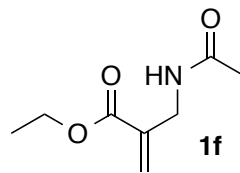
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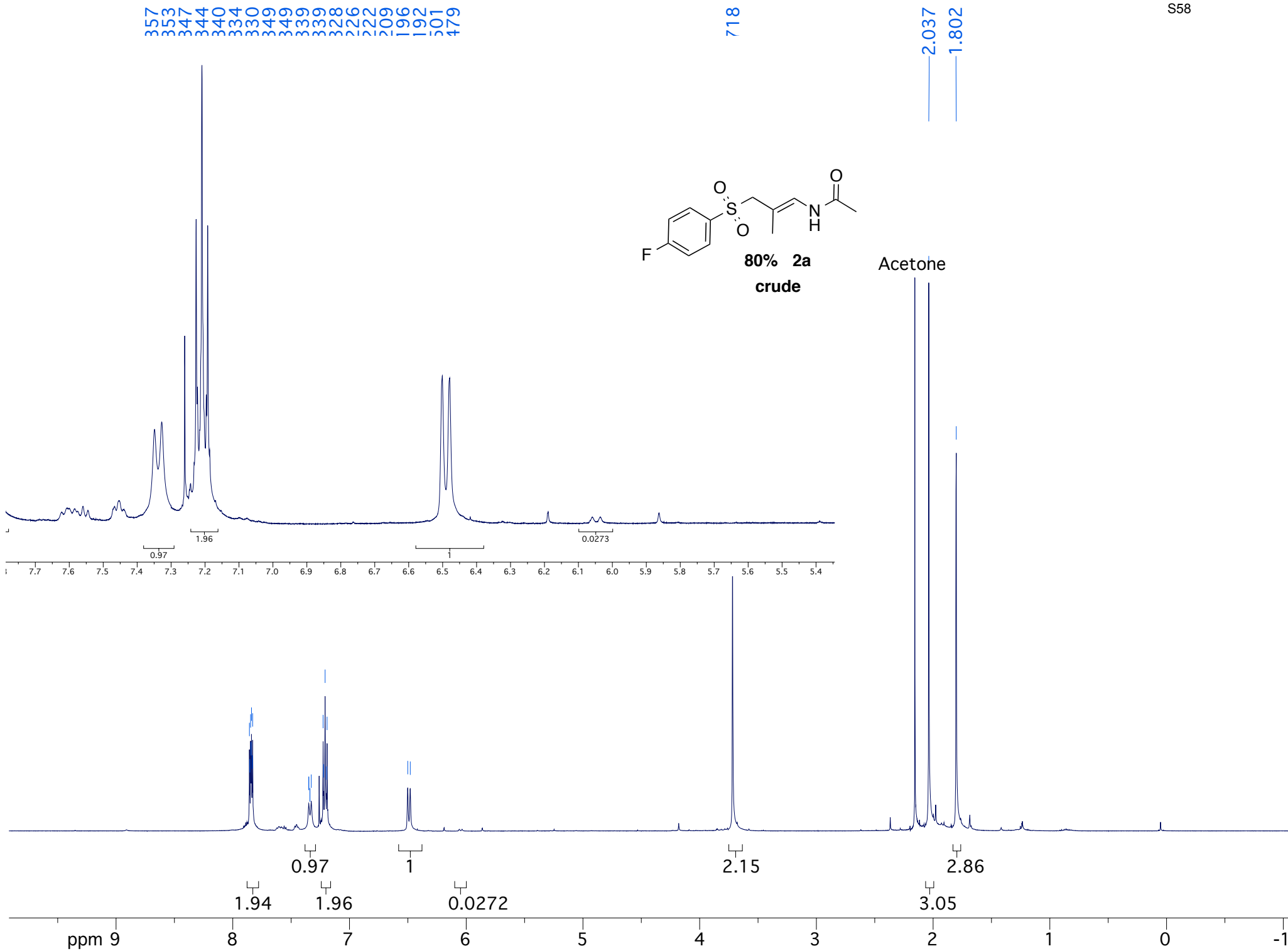


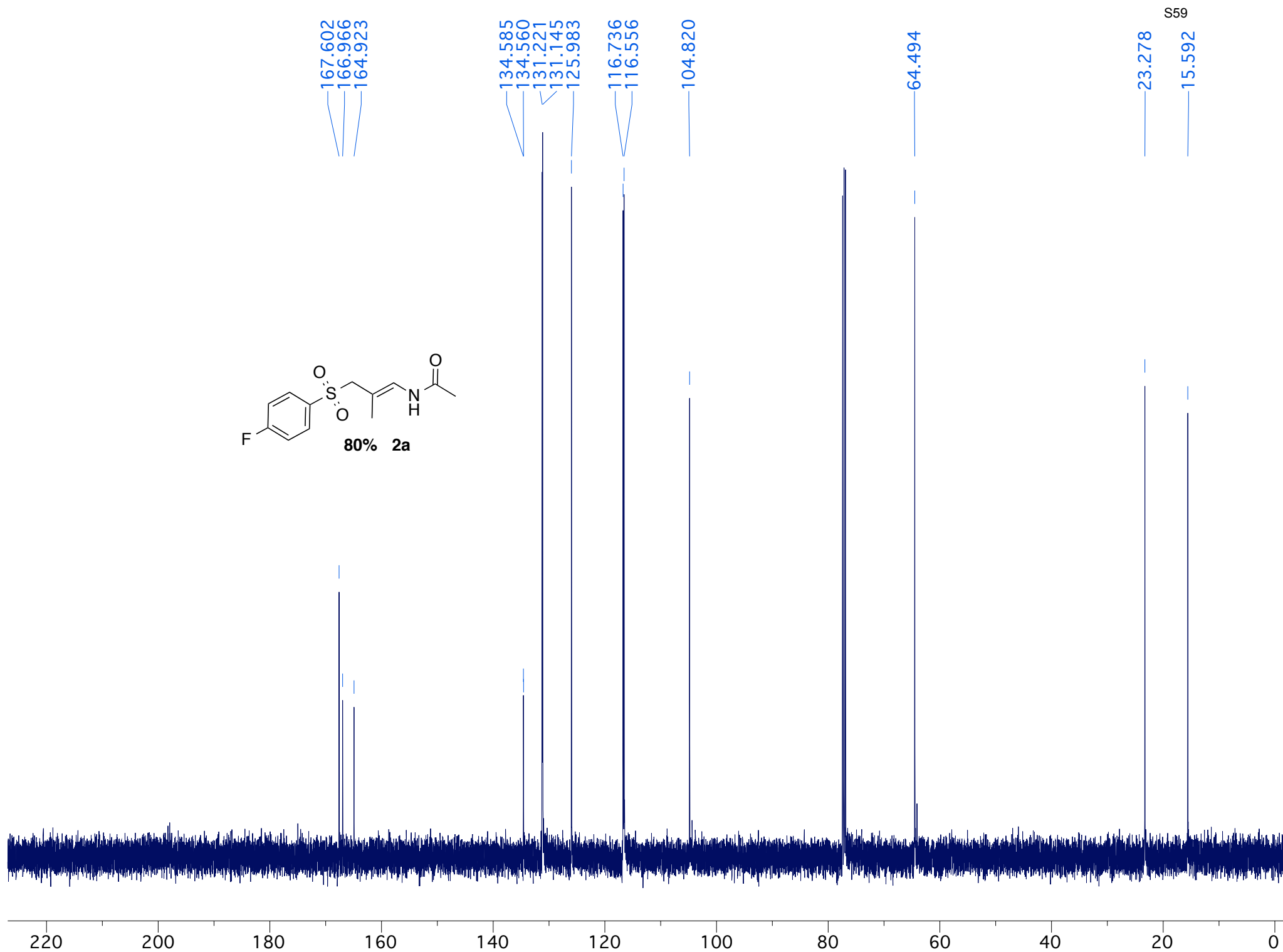
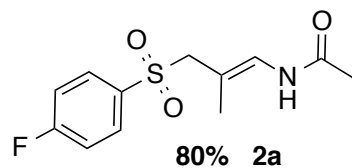
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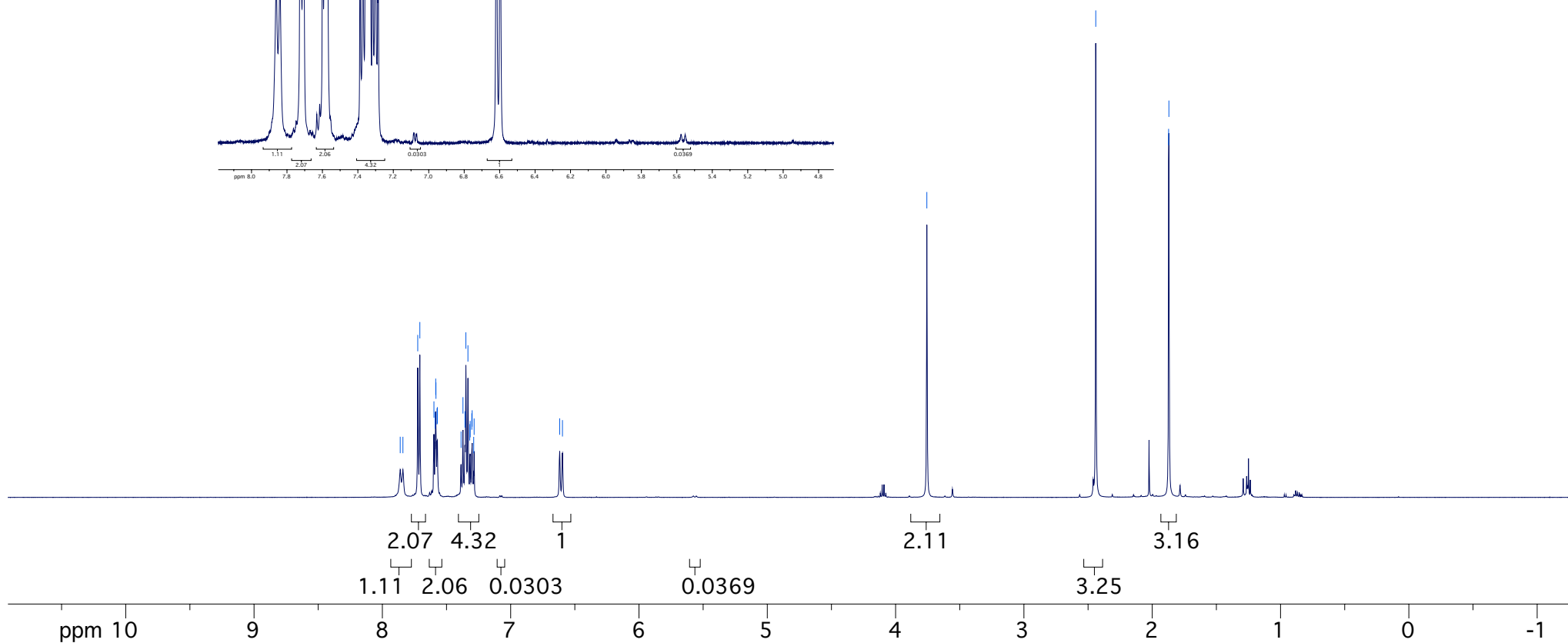
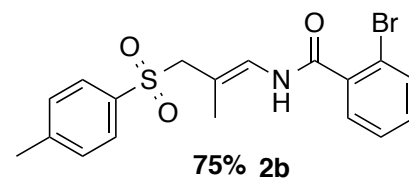
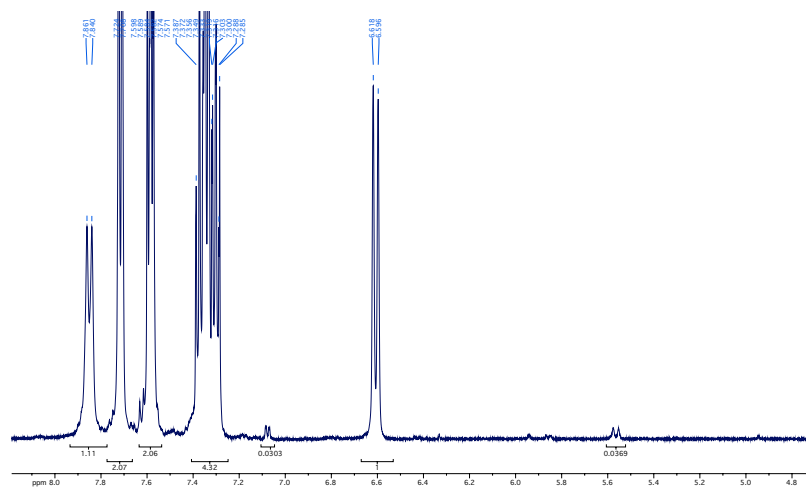


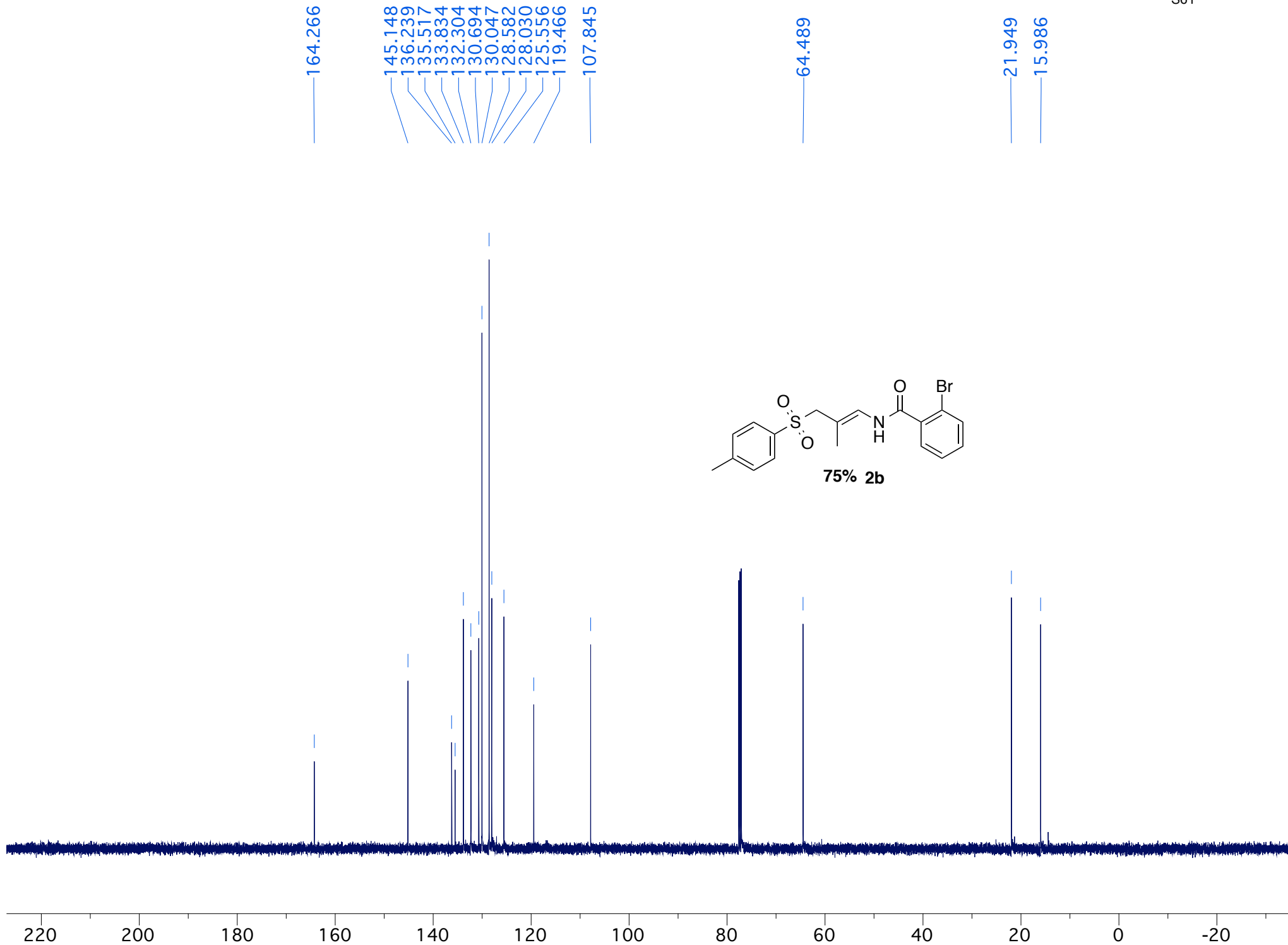
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7.724  
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7.598  
7.589  
7.584  
7.582  
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7.571  
7.387  
7.372  
7.356  
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7.303  
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6.596

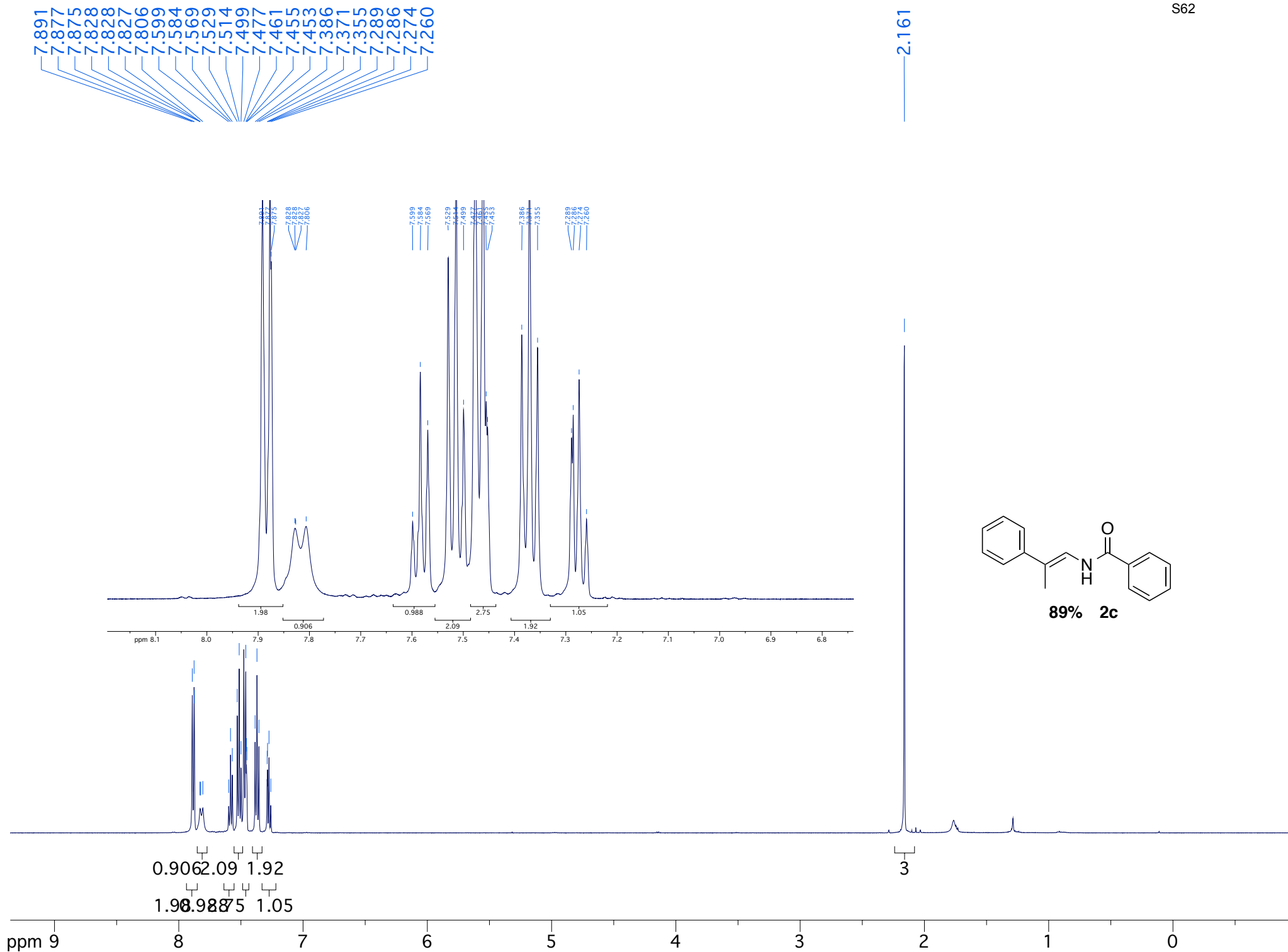
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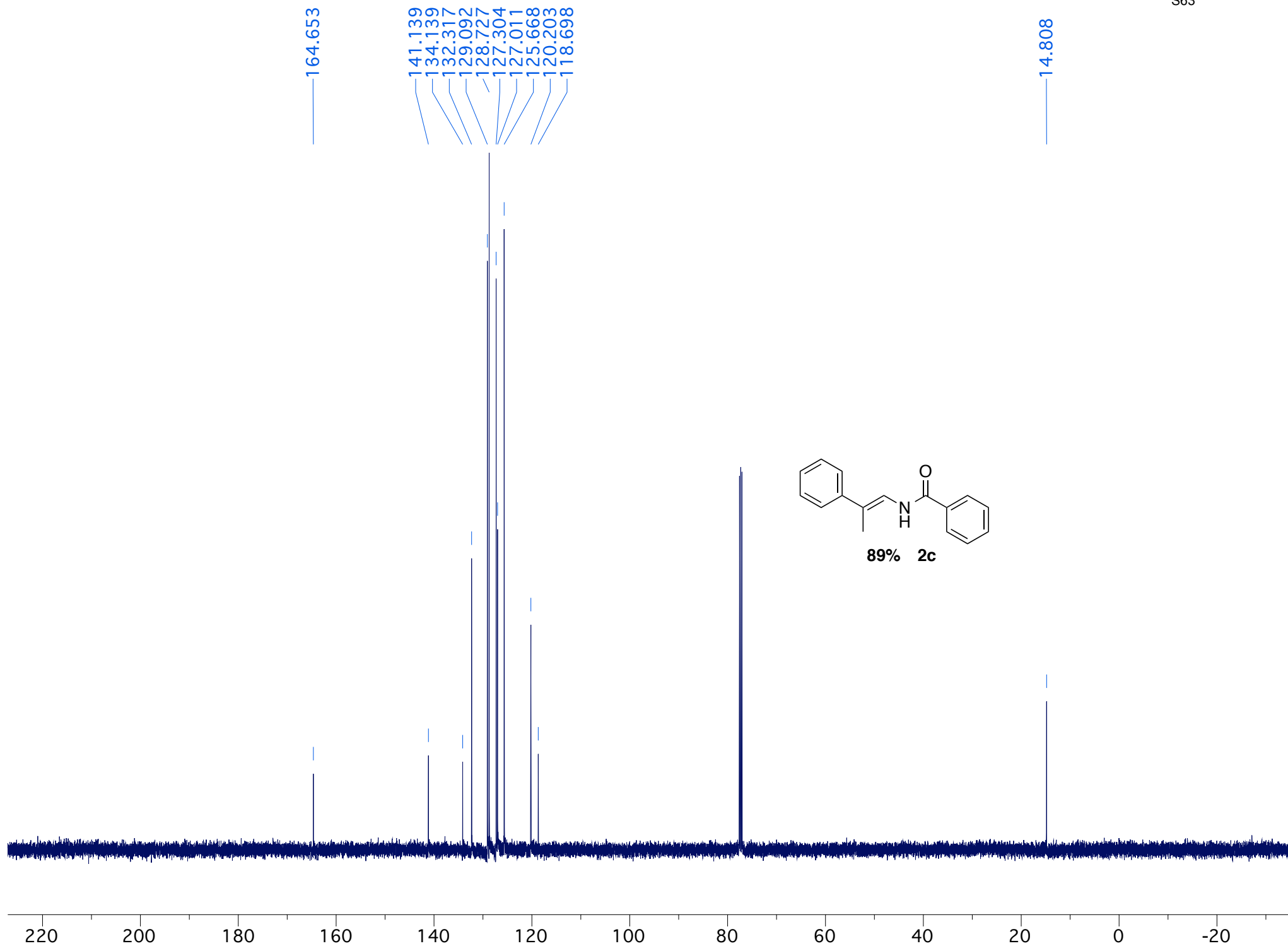
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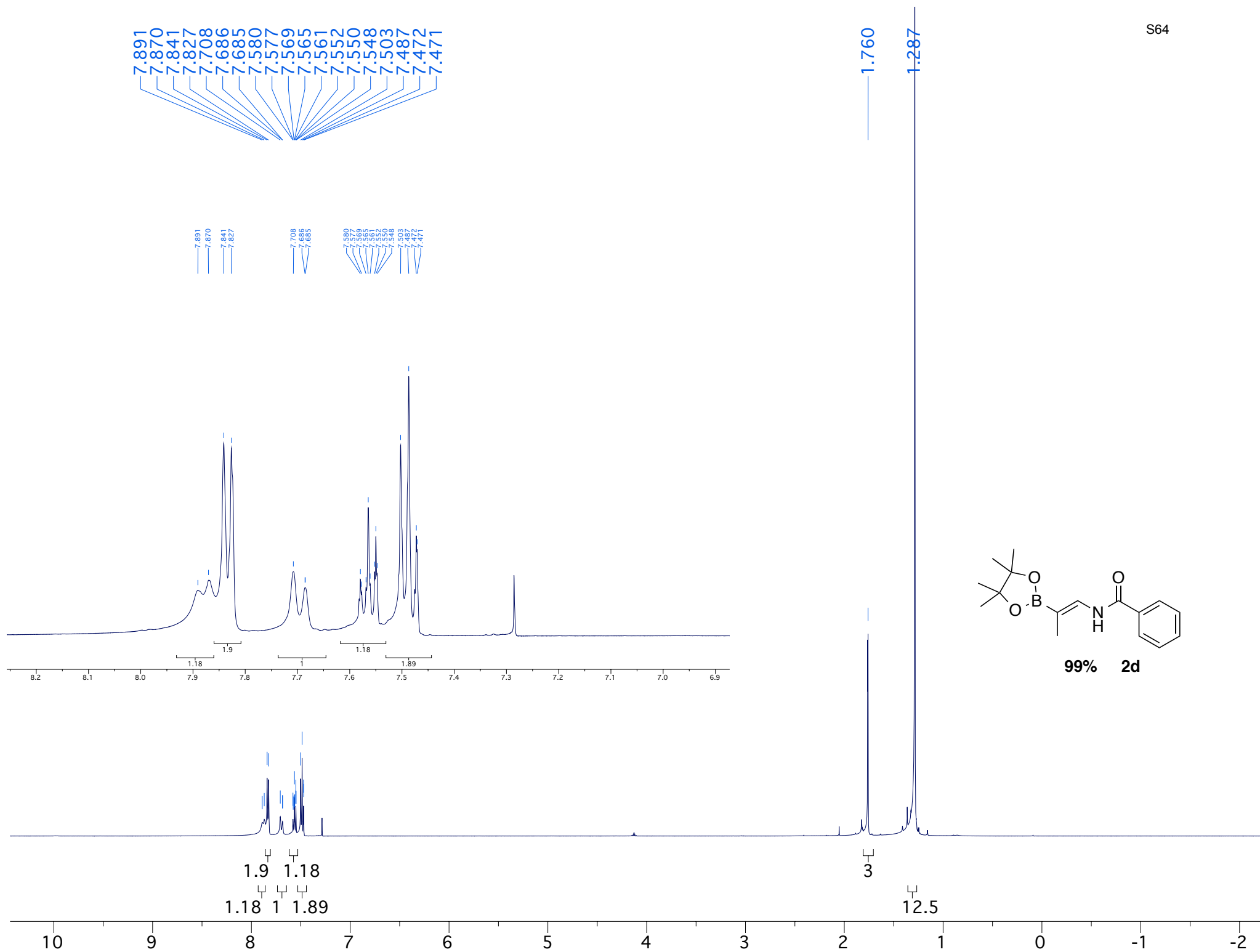
1.872  
1.870



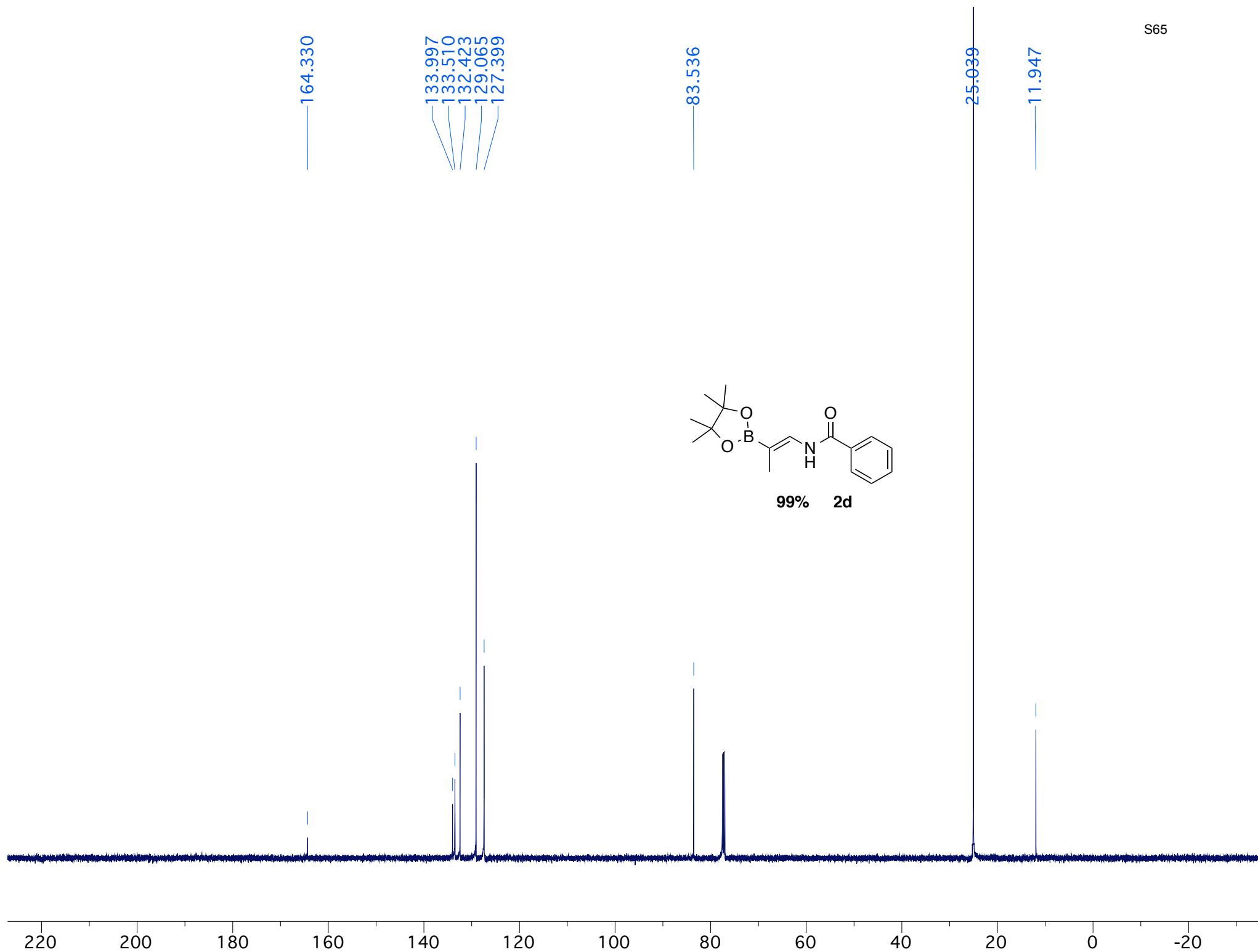


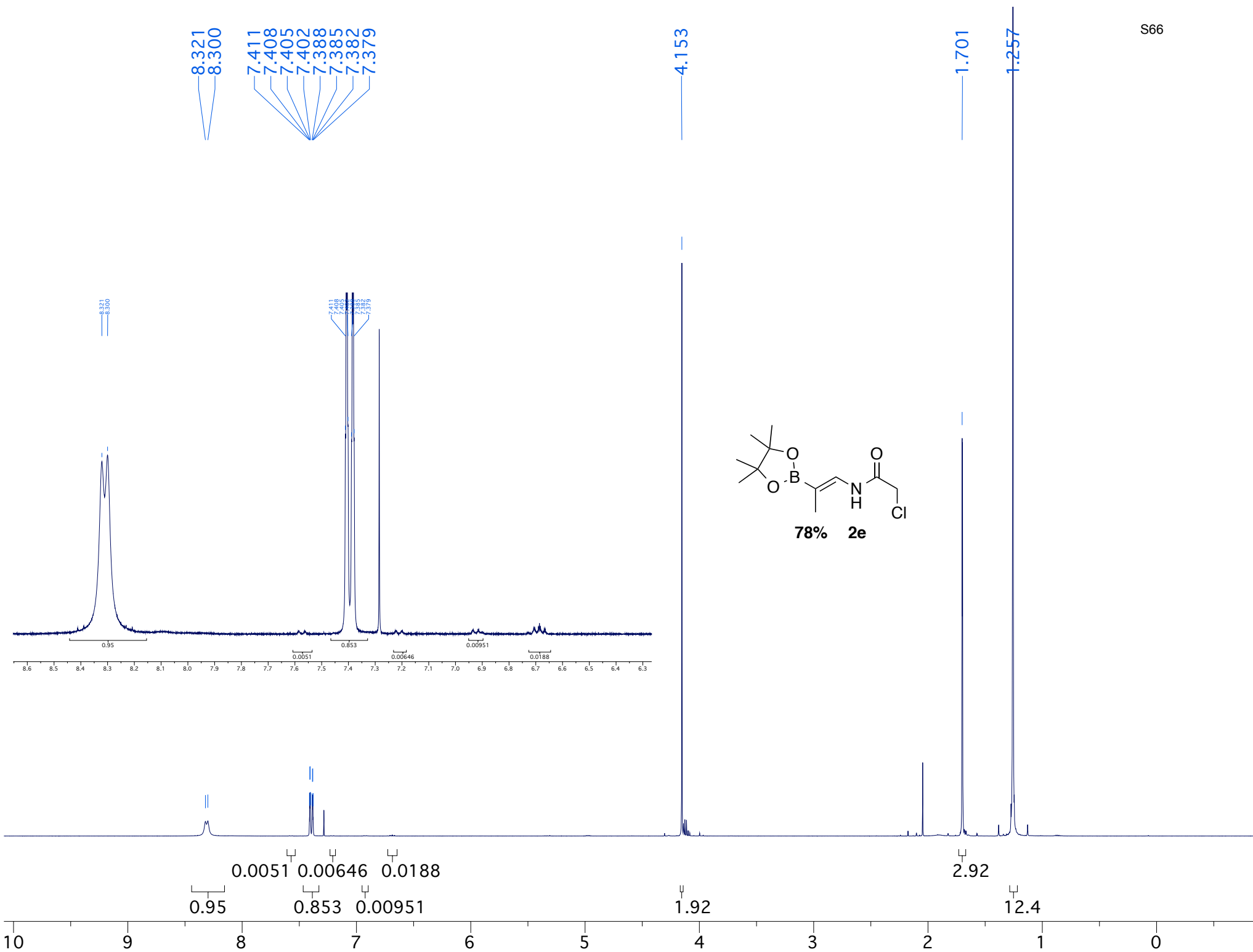


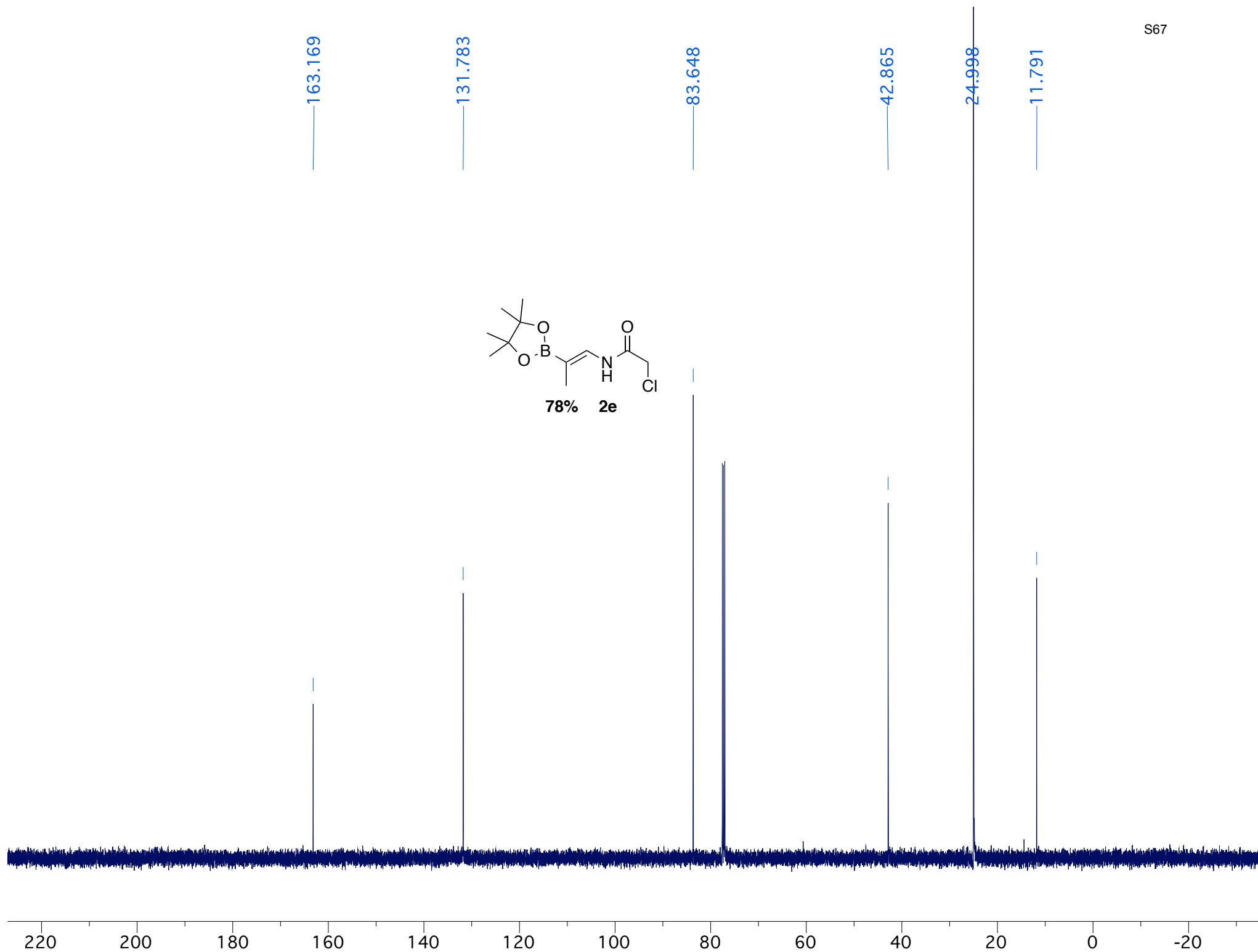
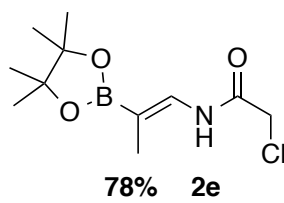


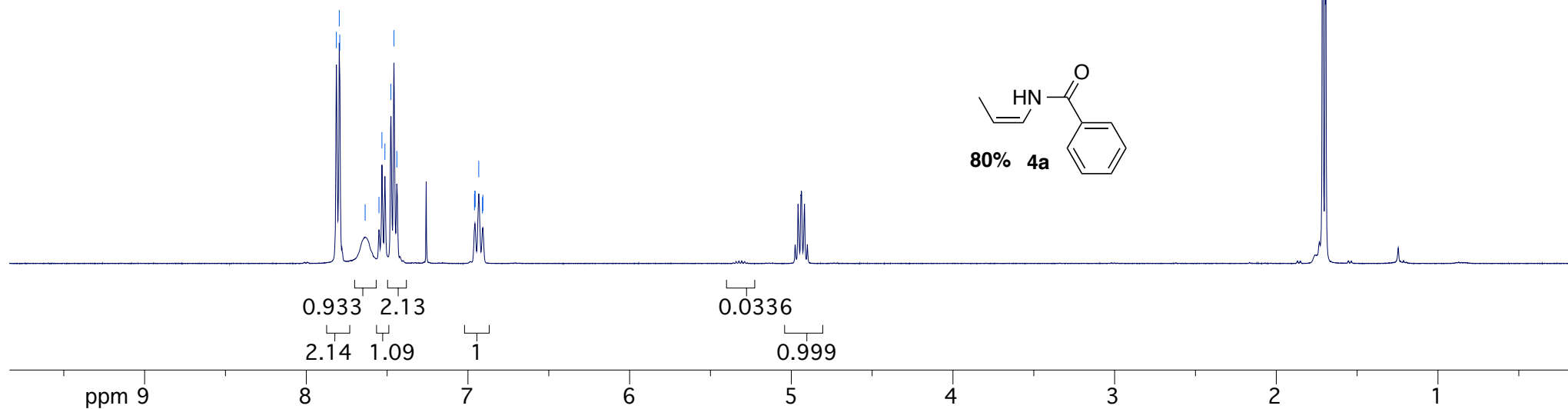
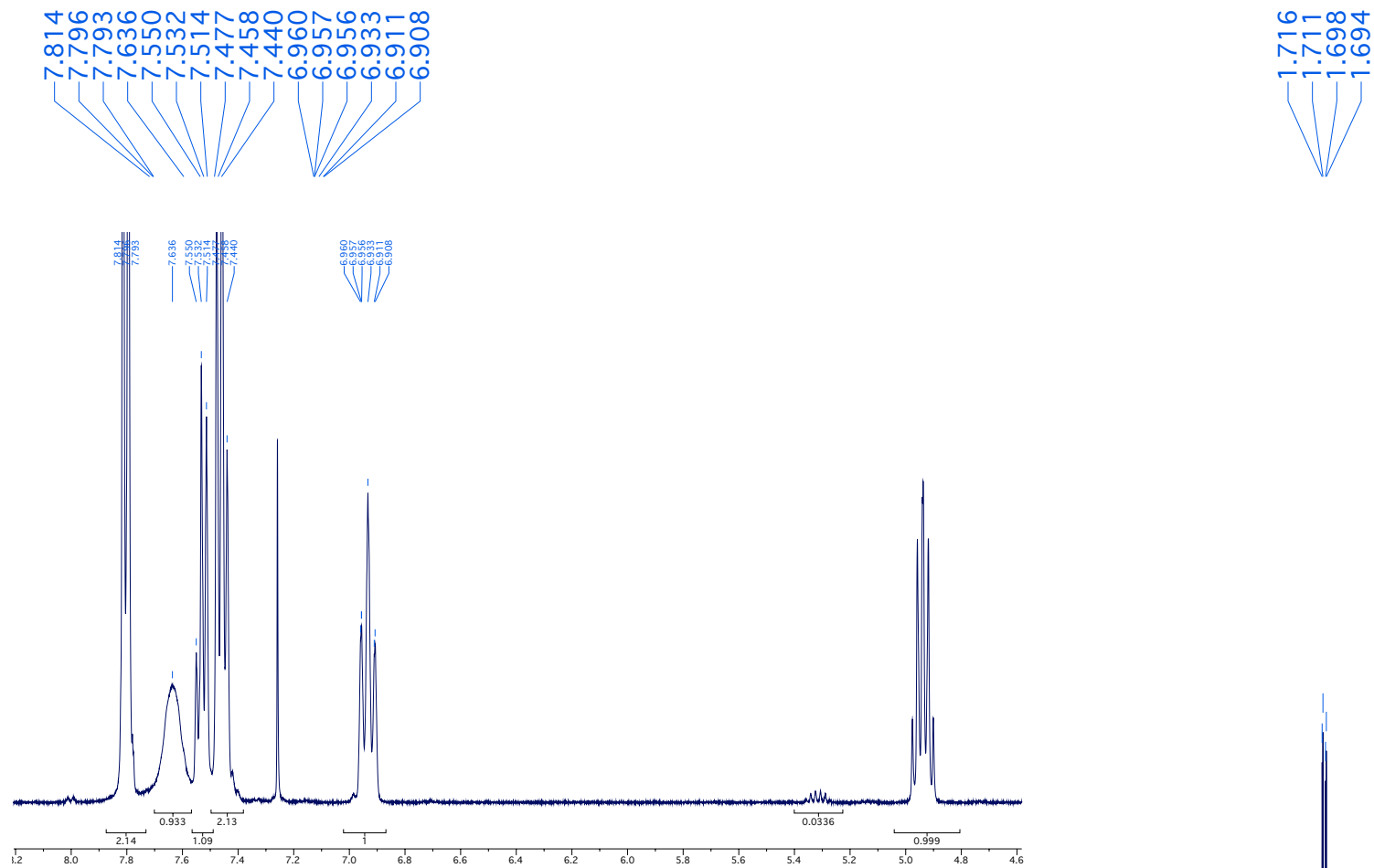


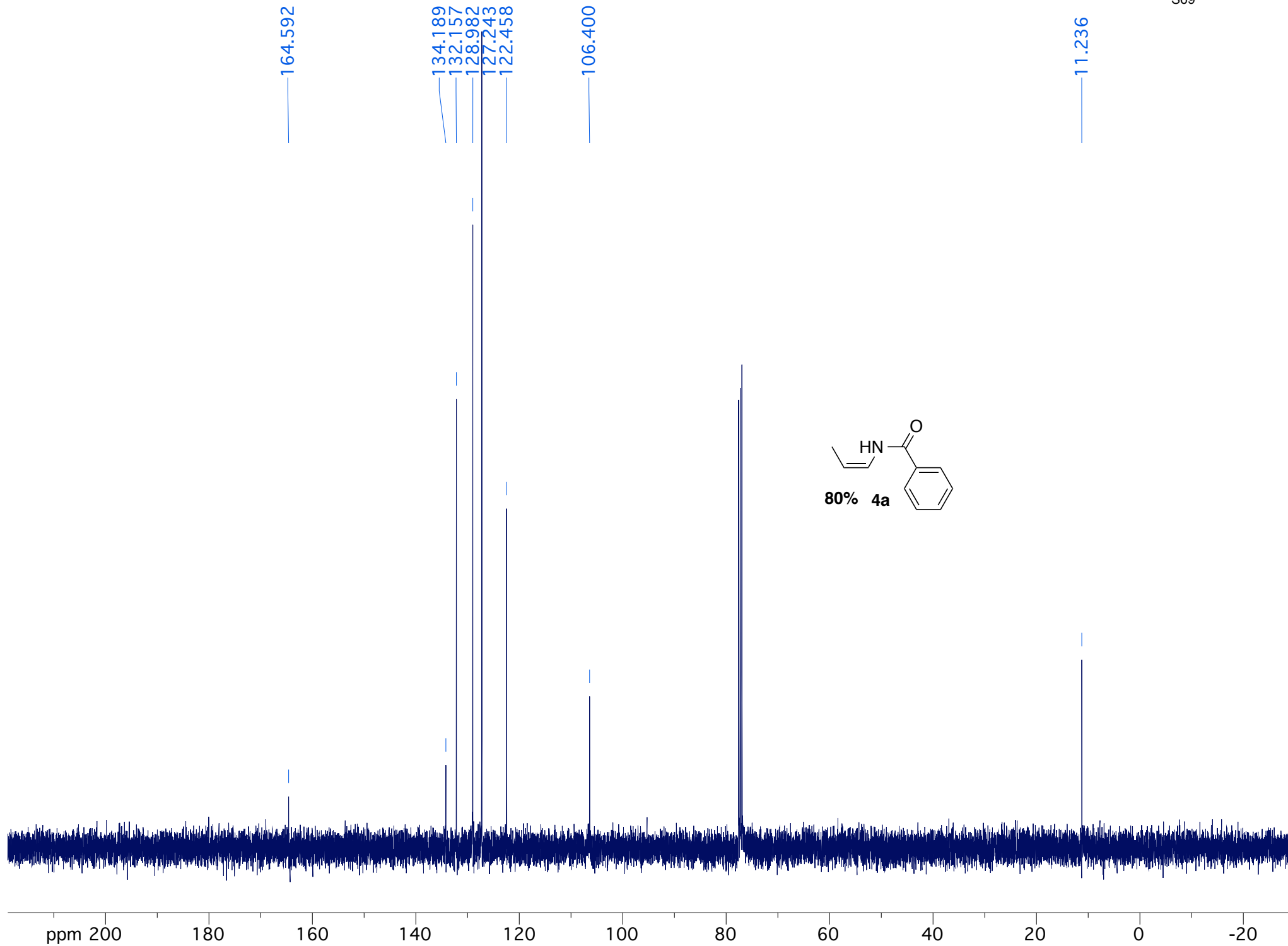


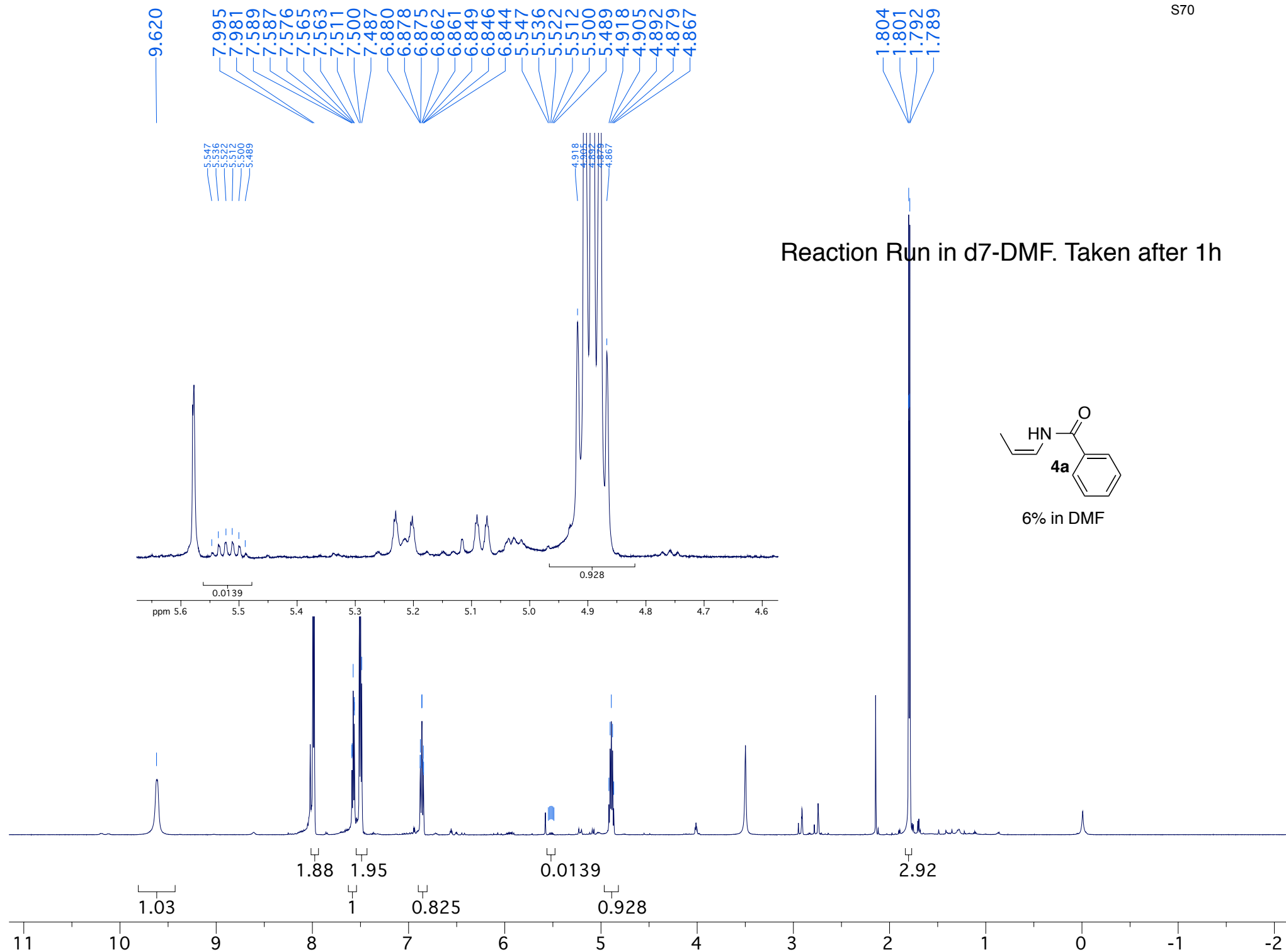


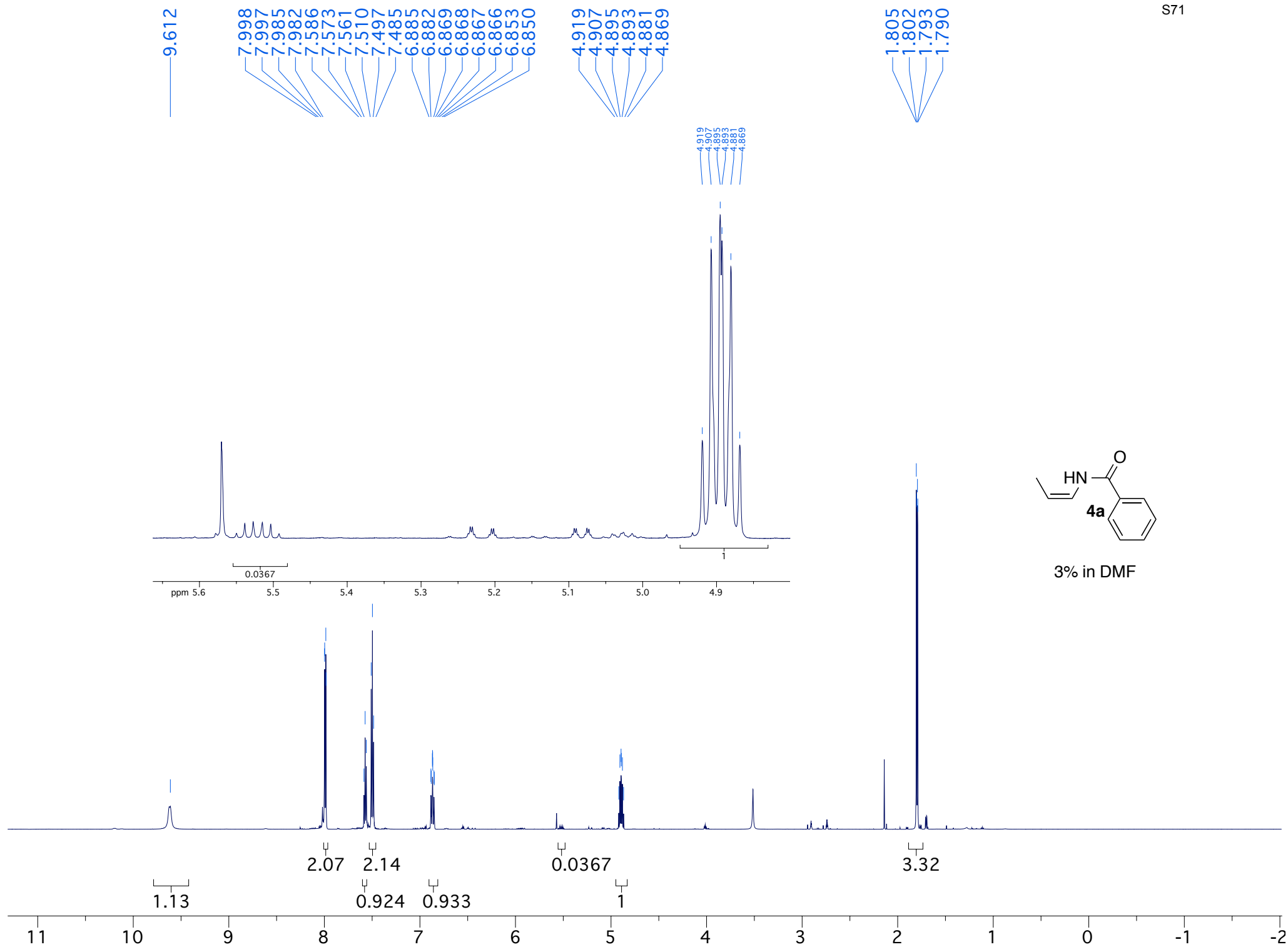


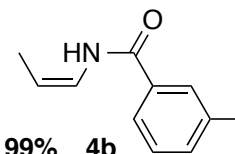
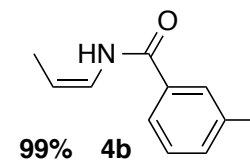
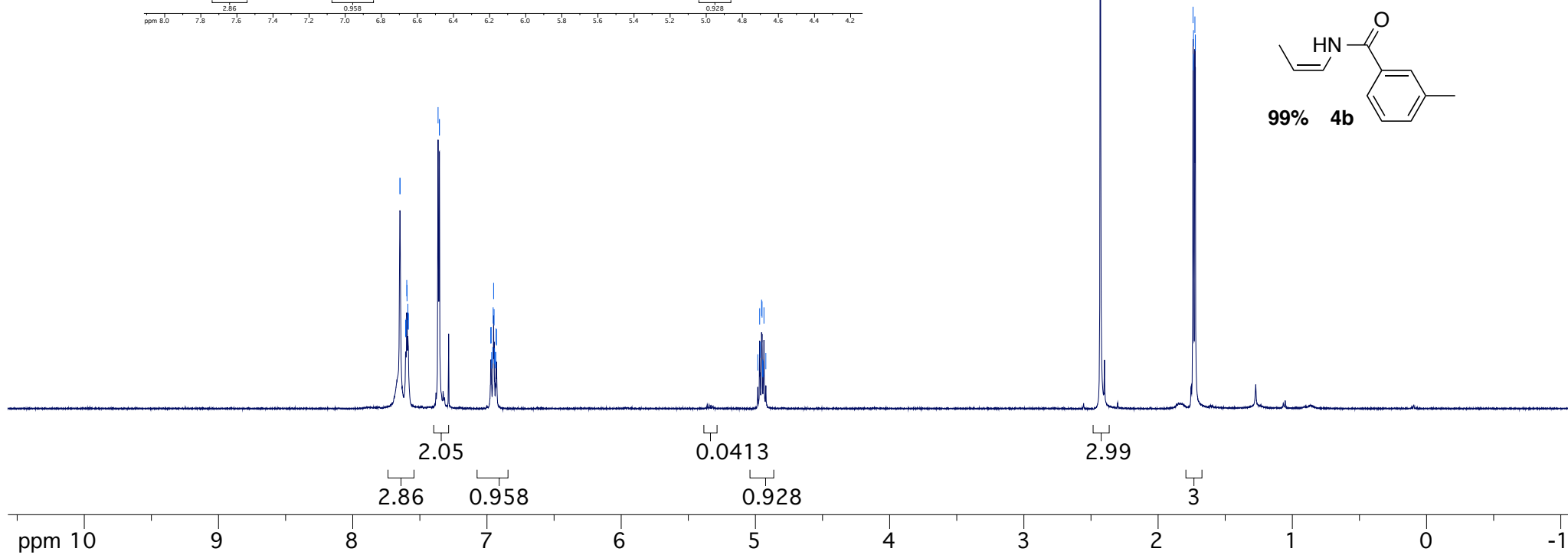
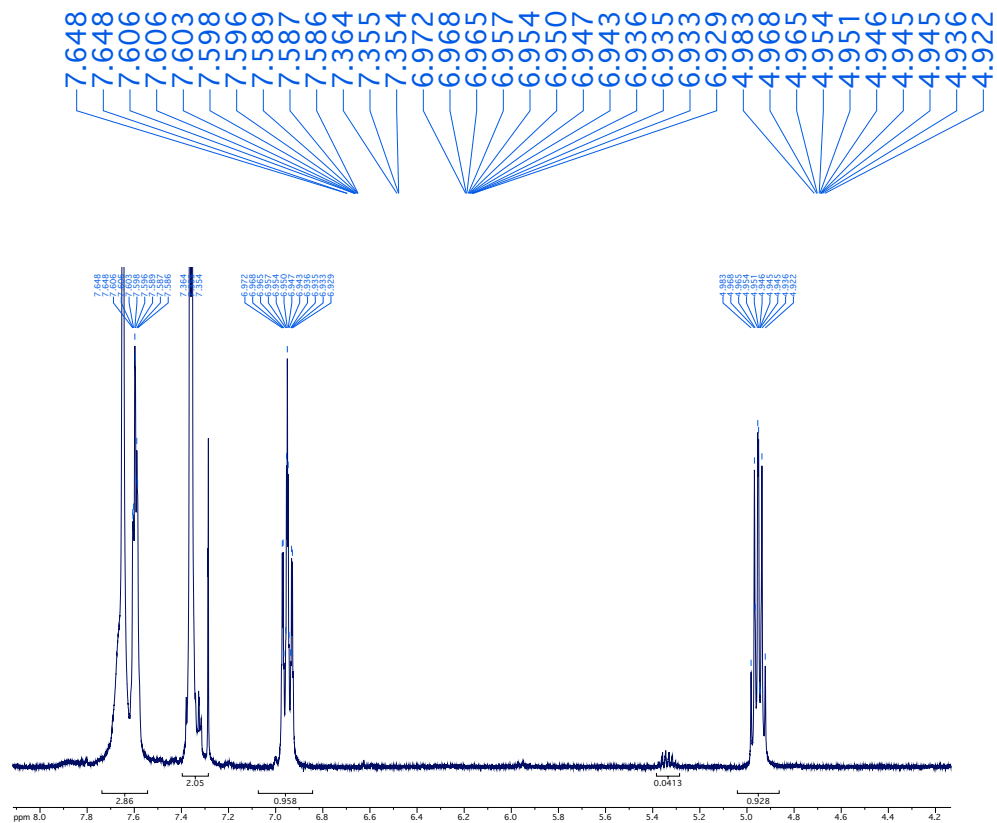




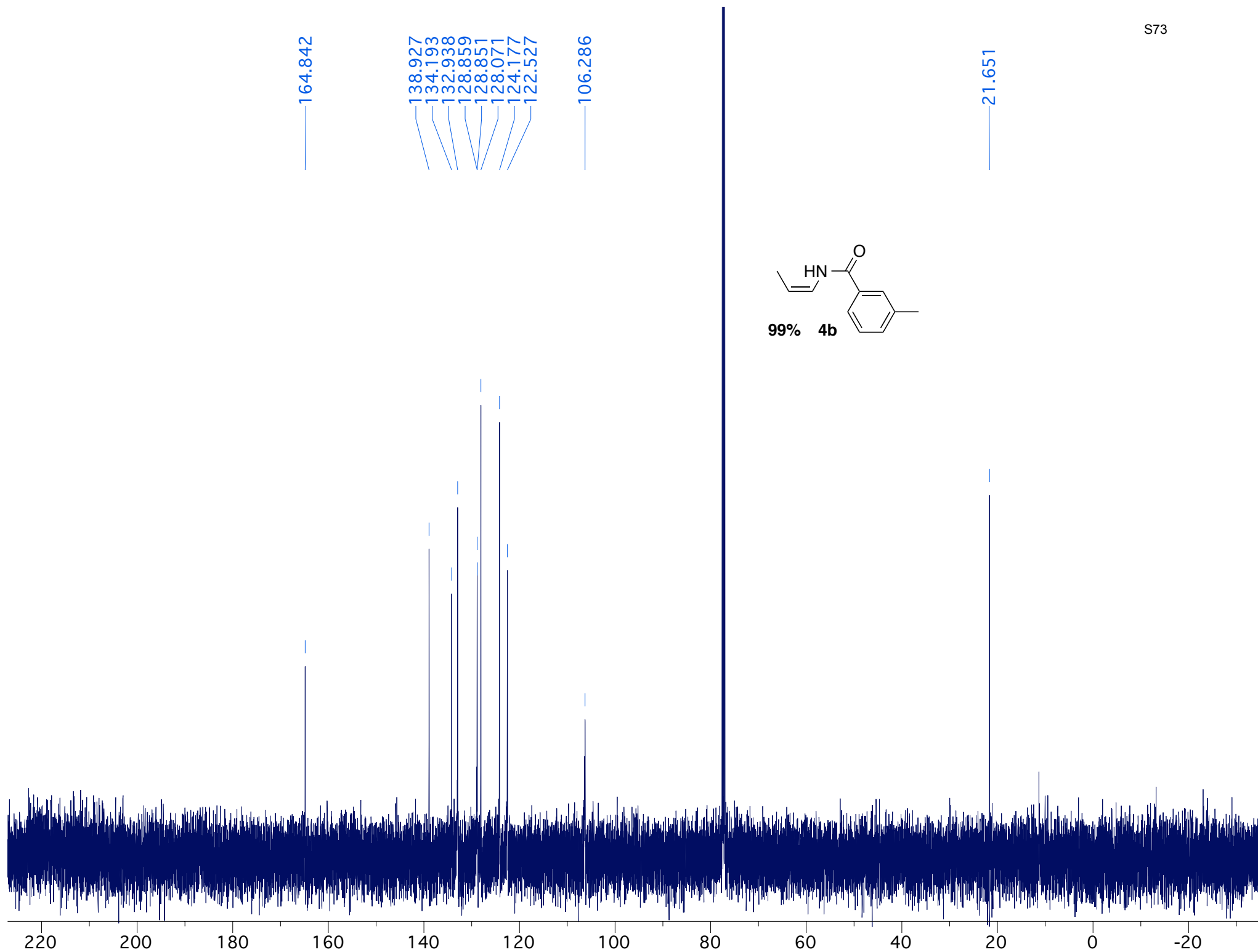


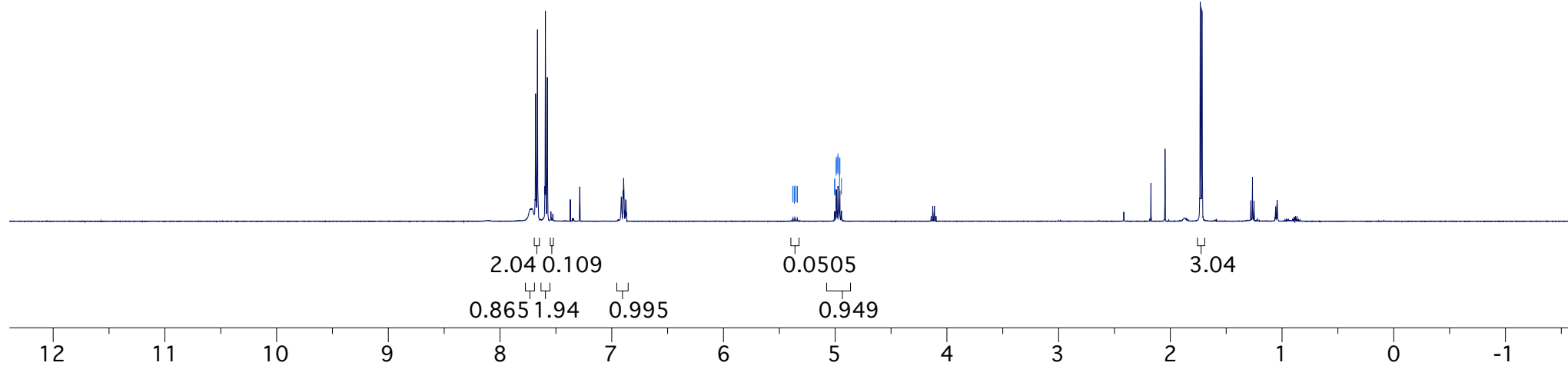
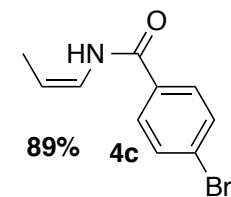
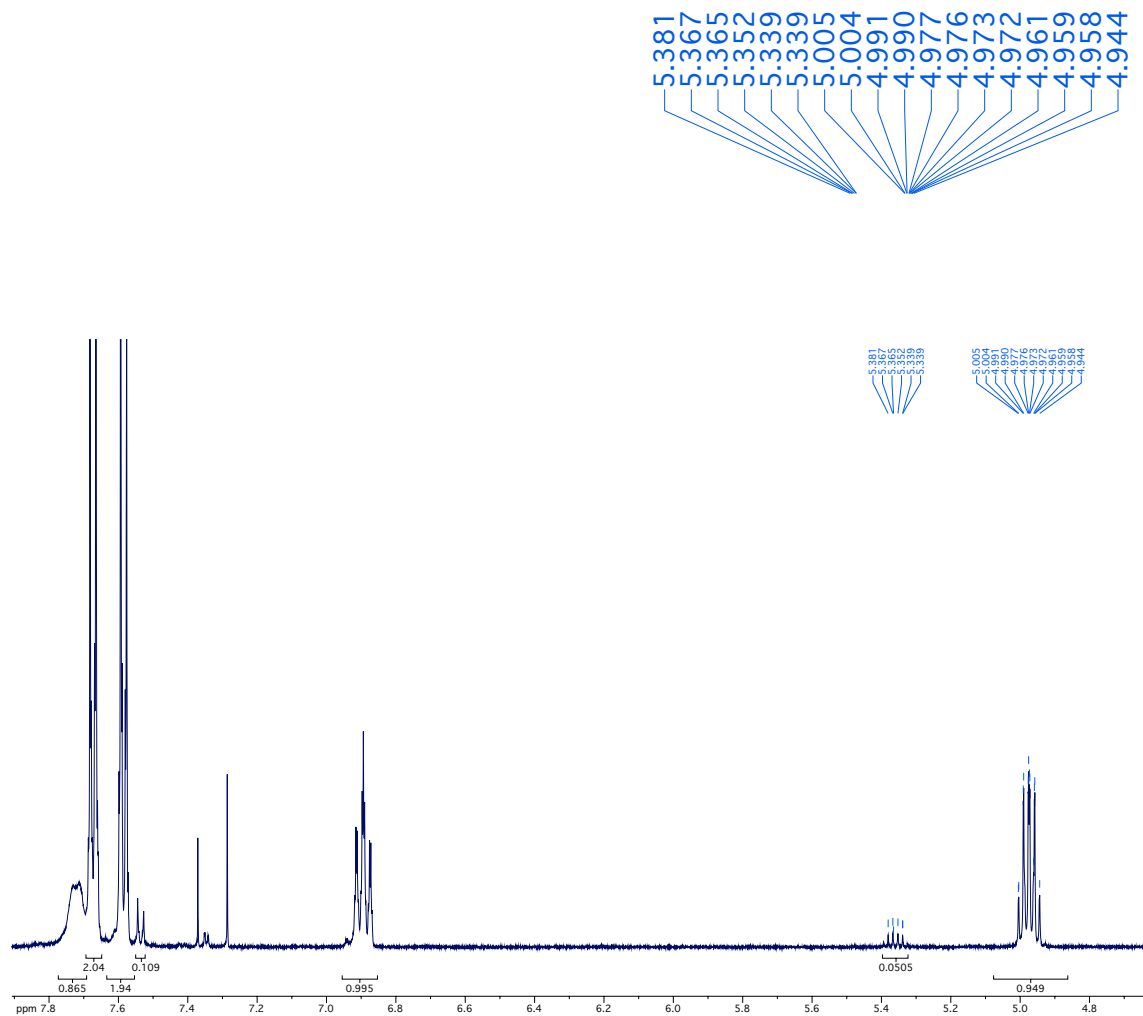


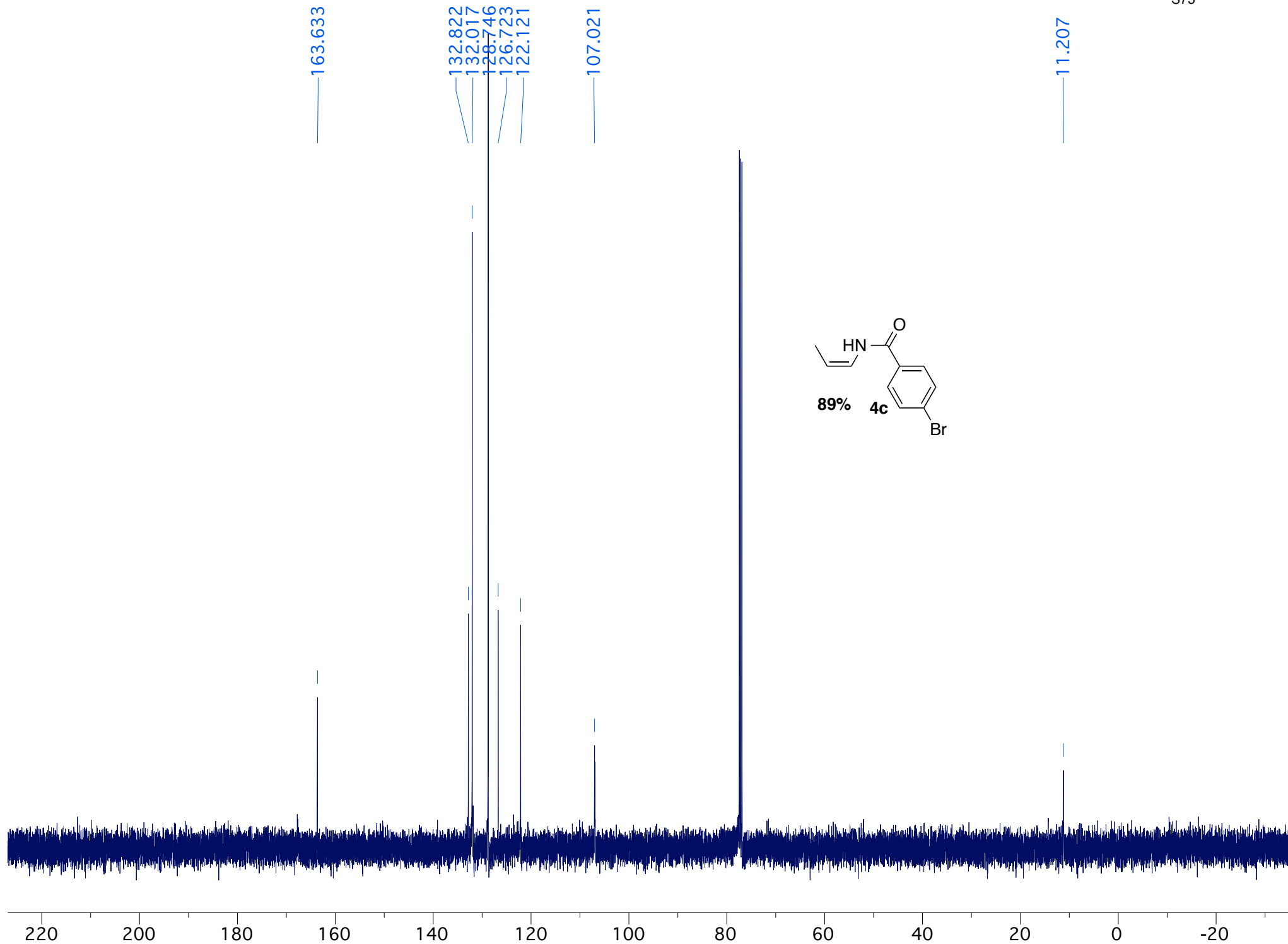


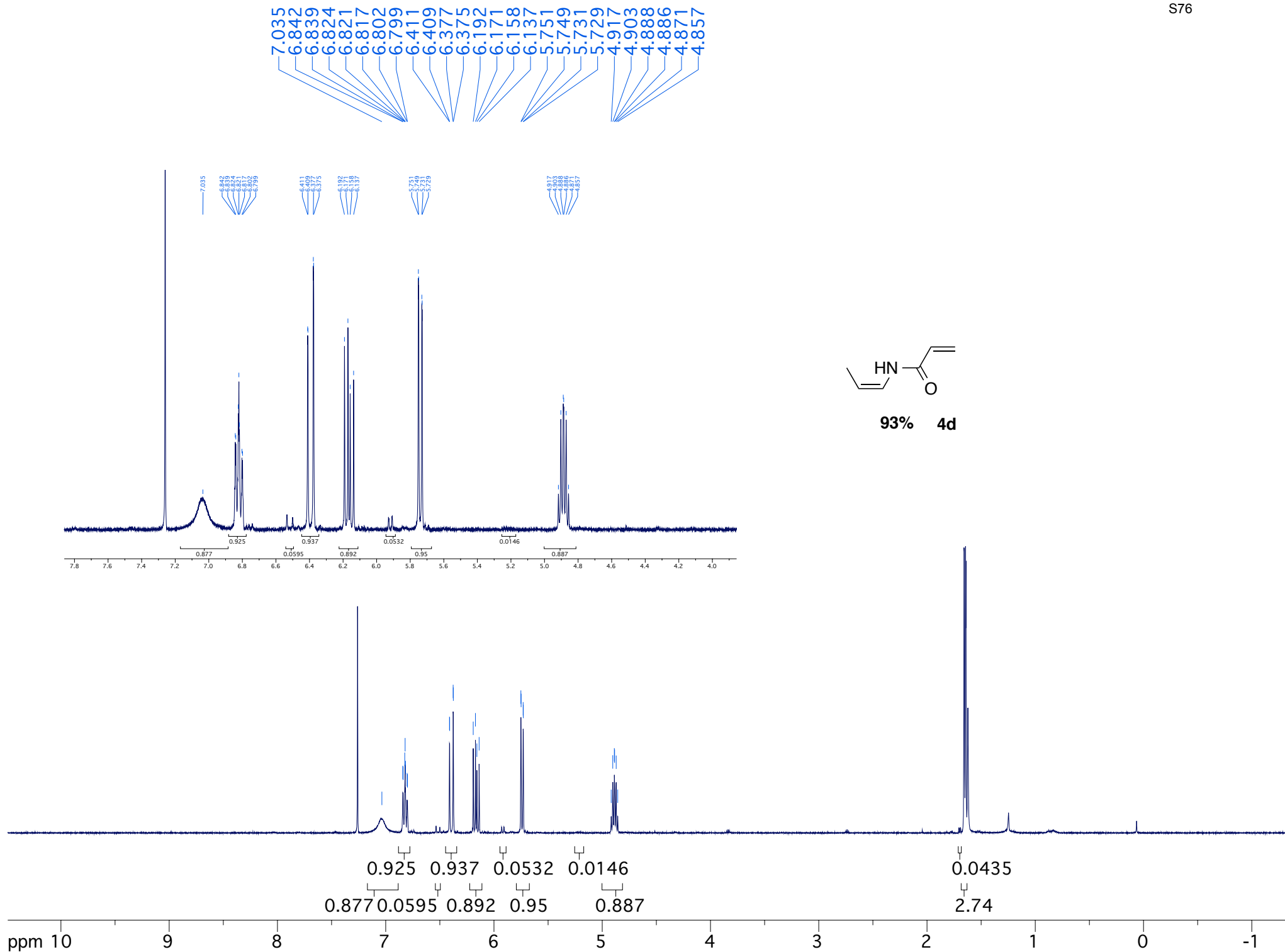


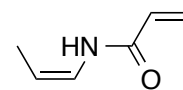




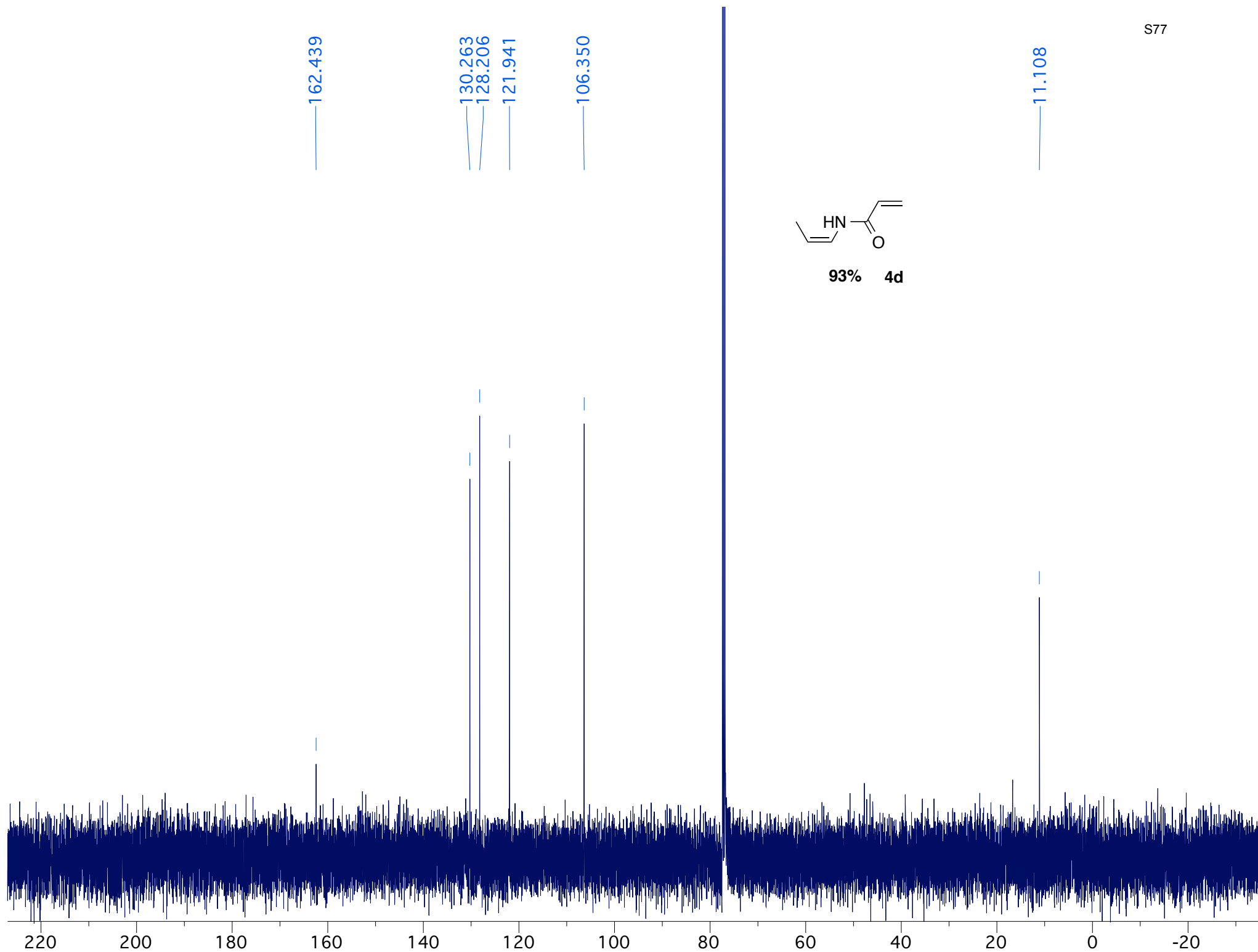


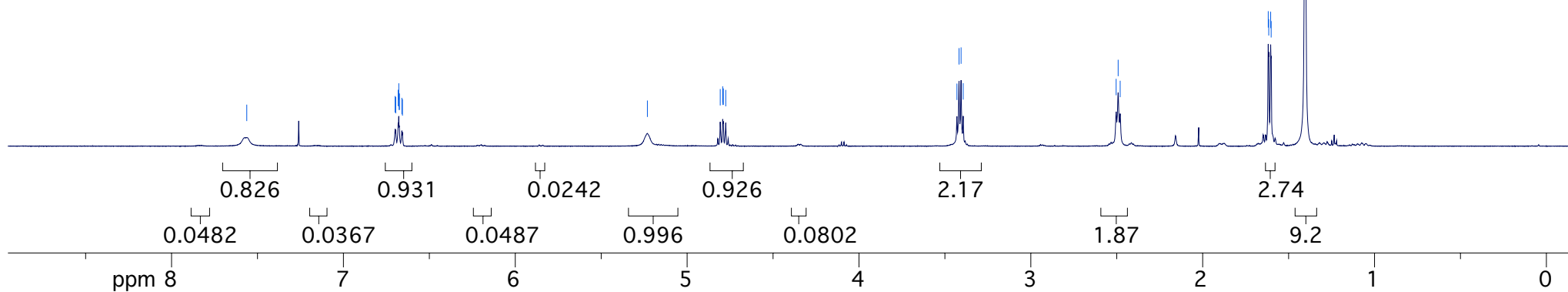
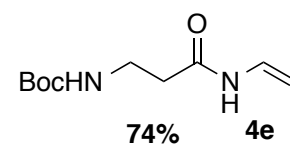
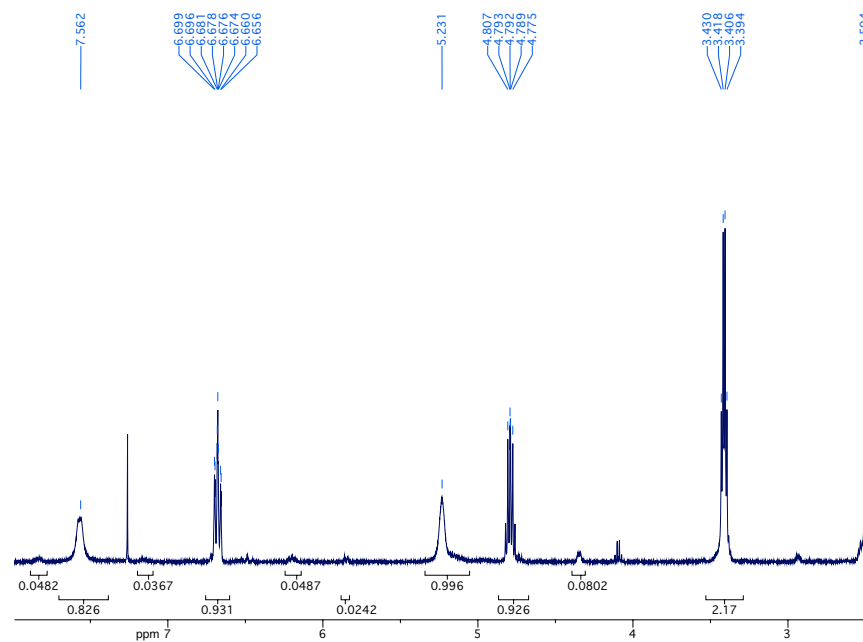
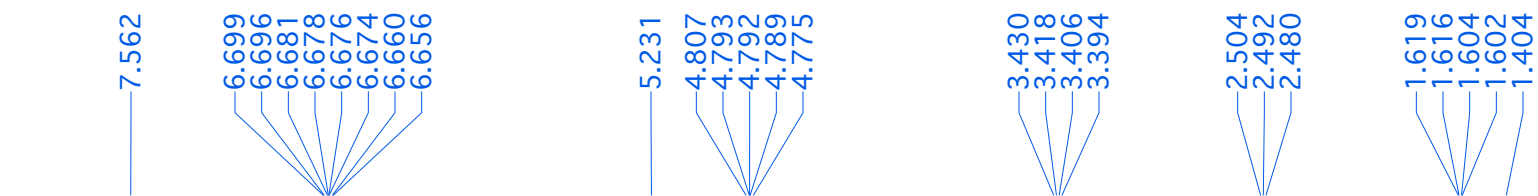


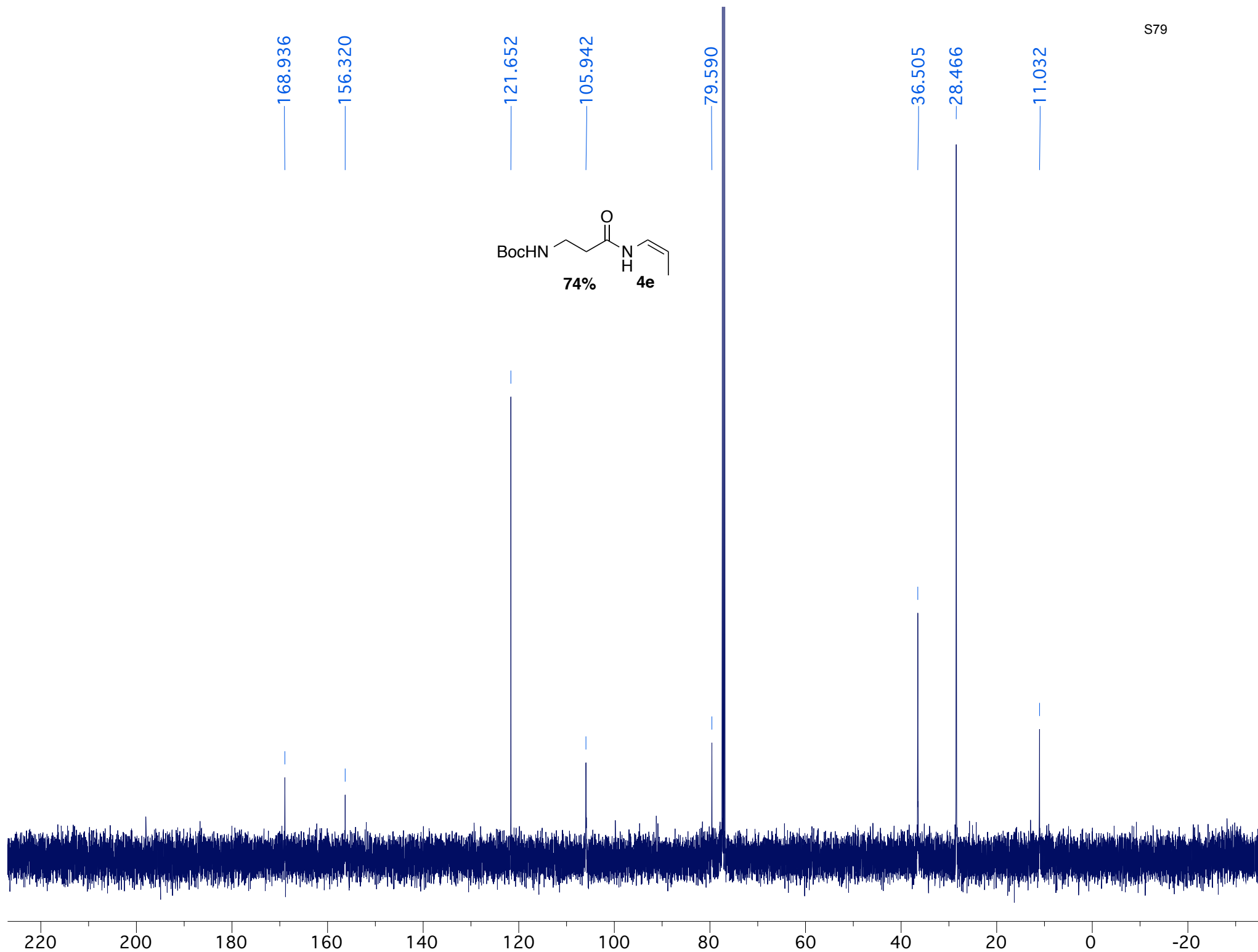
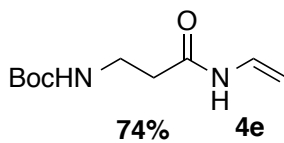


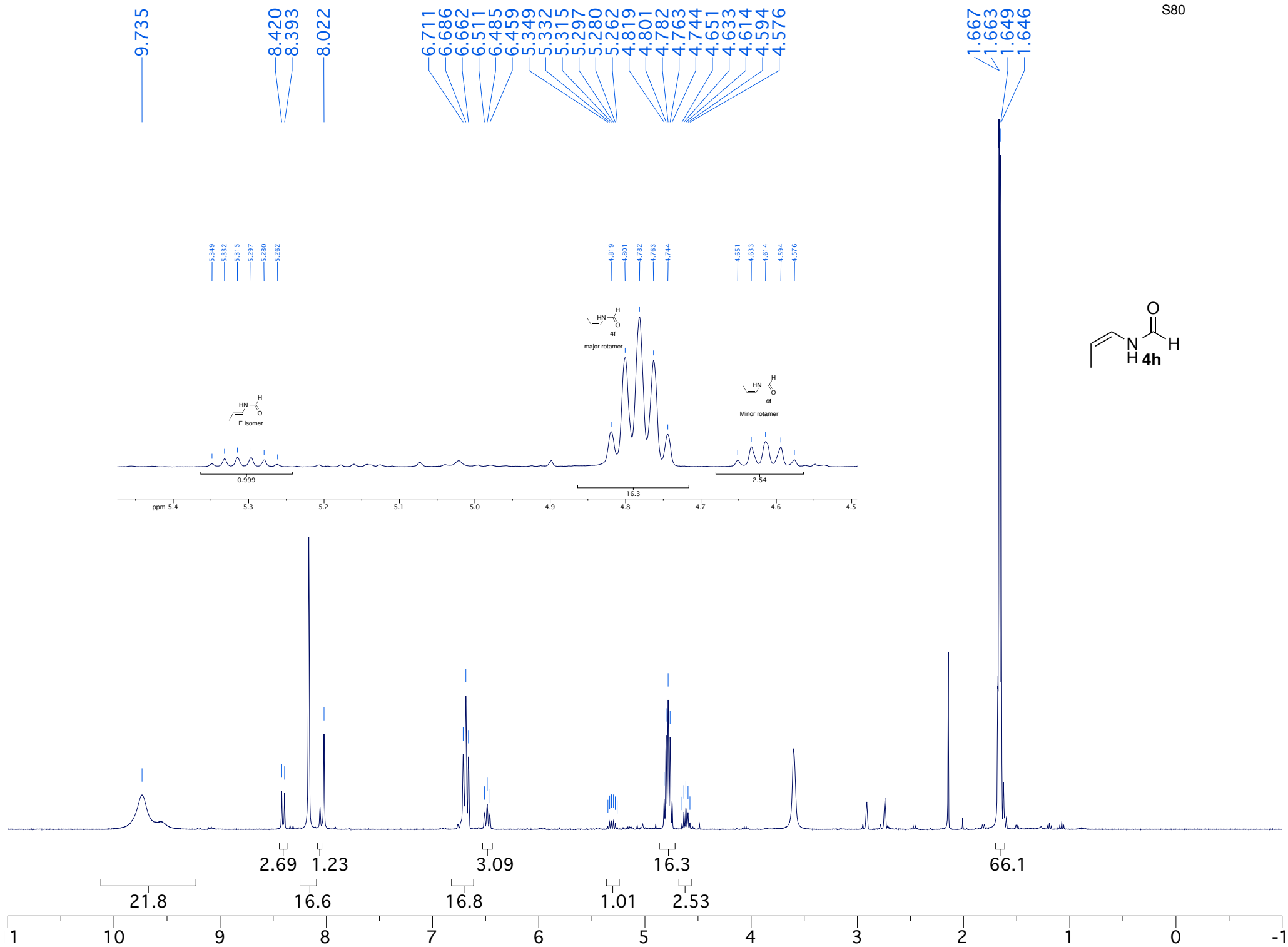


93% 4d

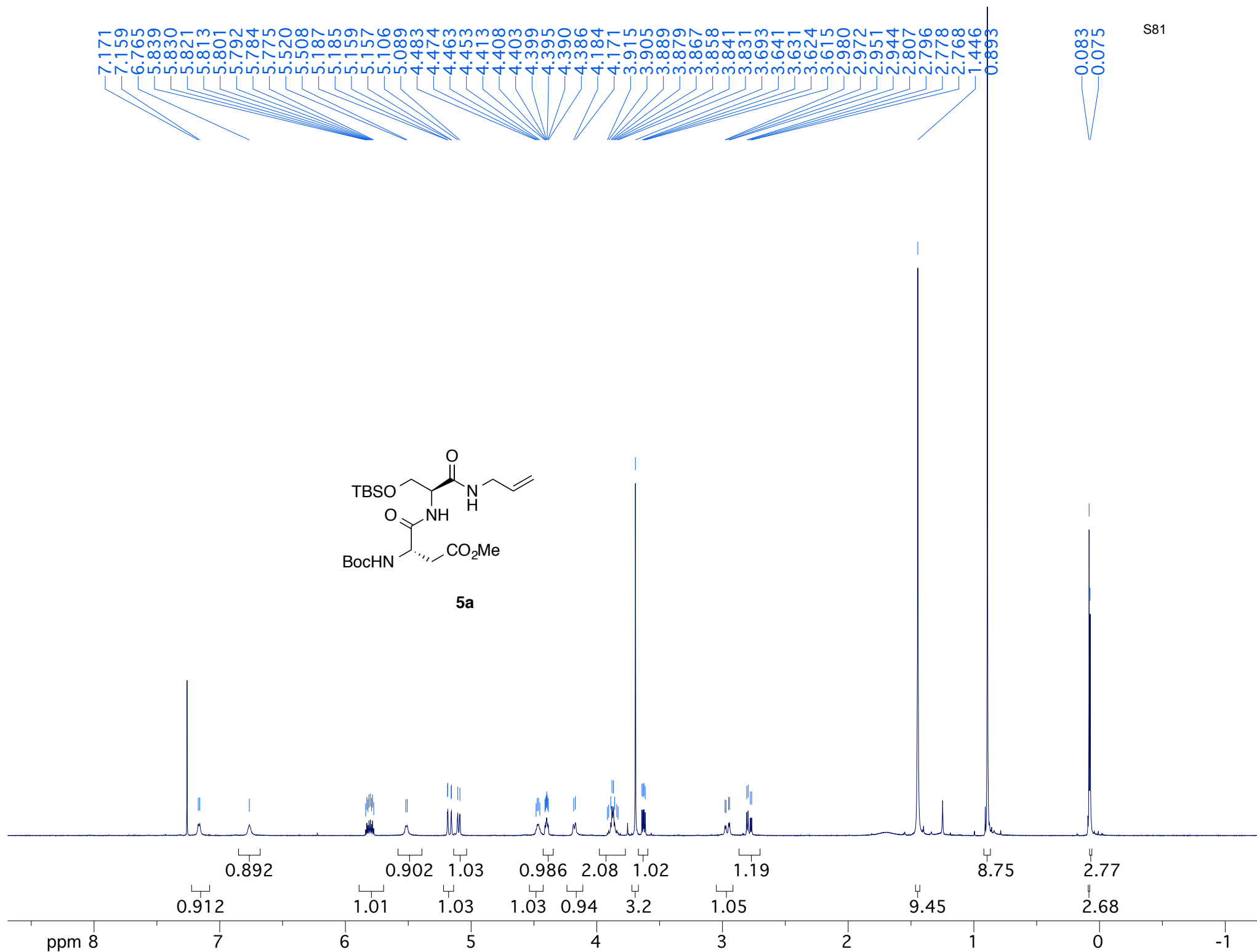


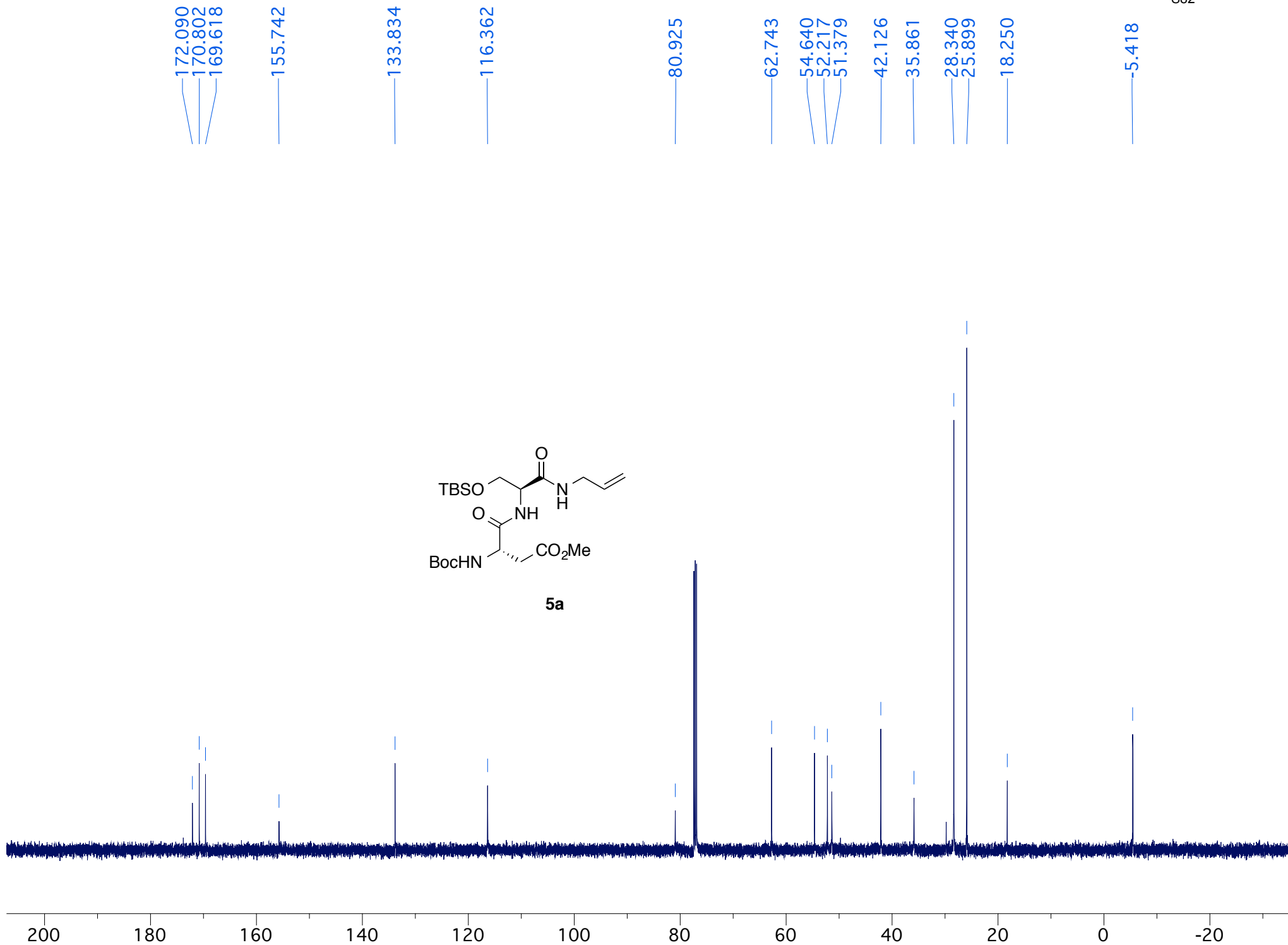


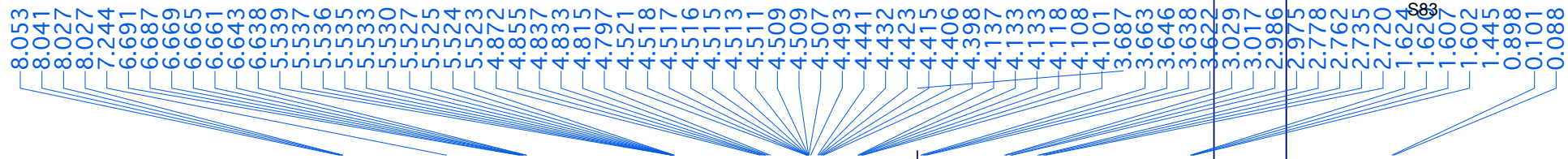
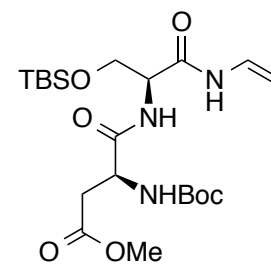


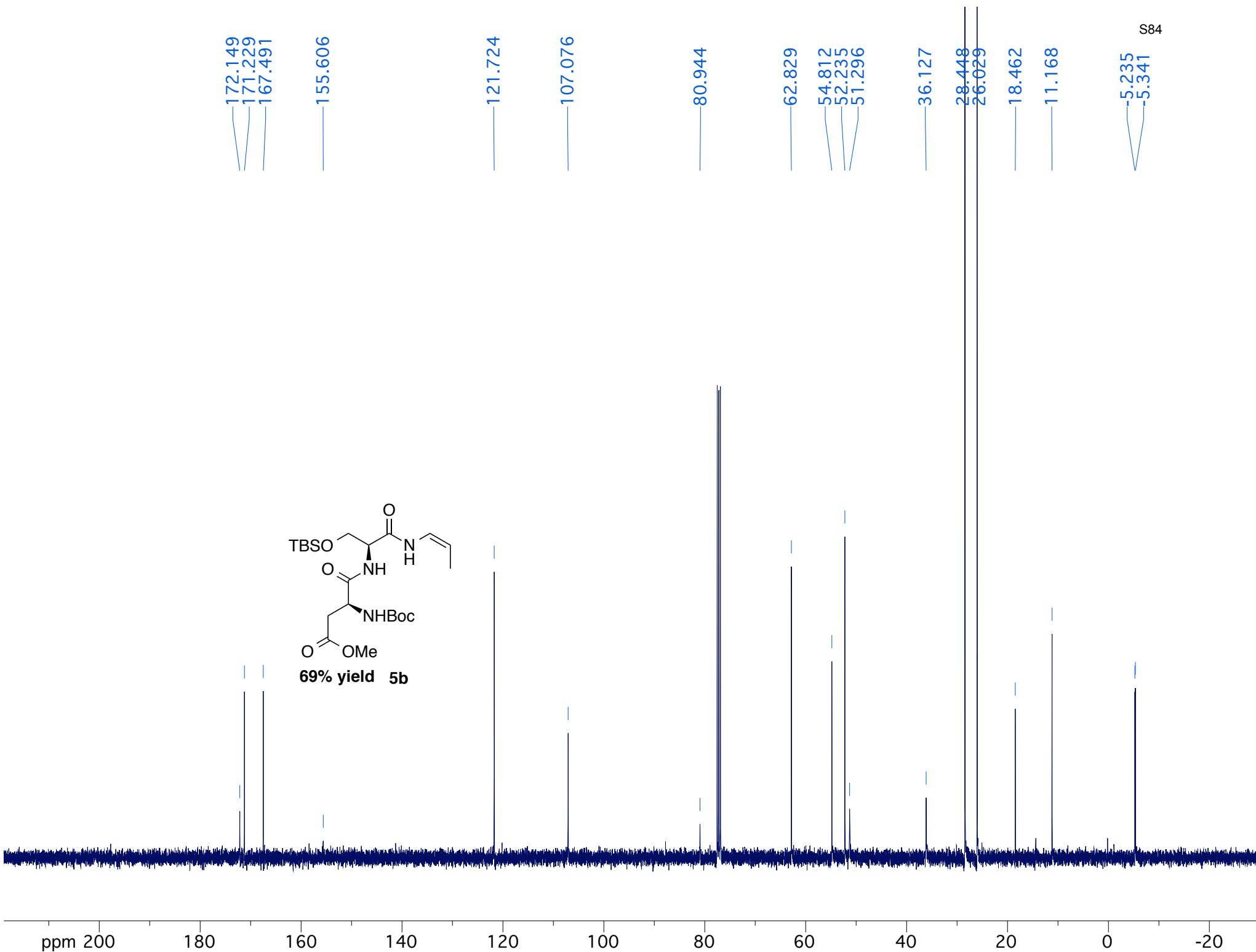


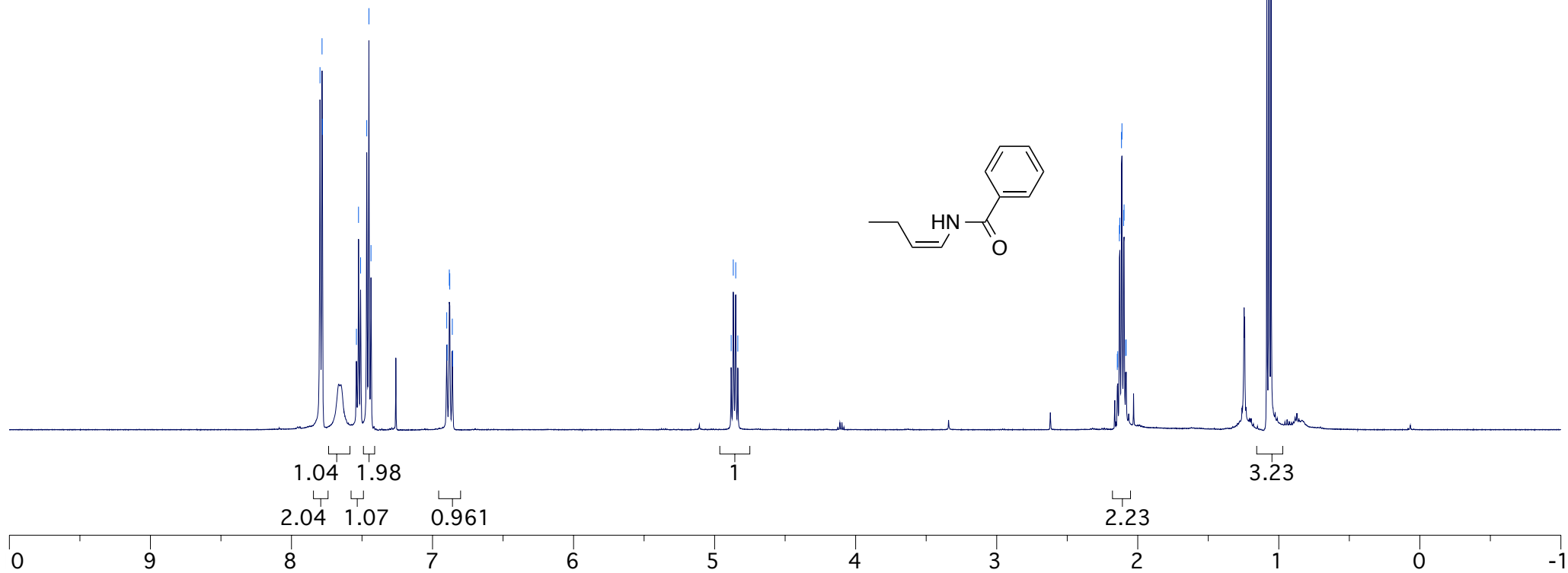
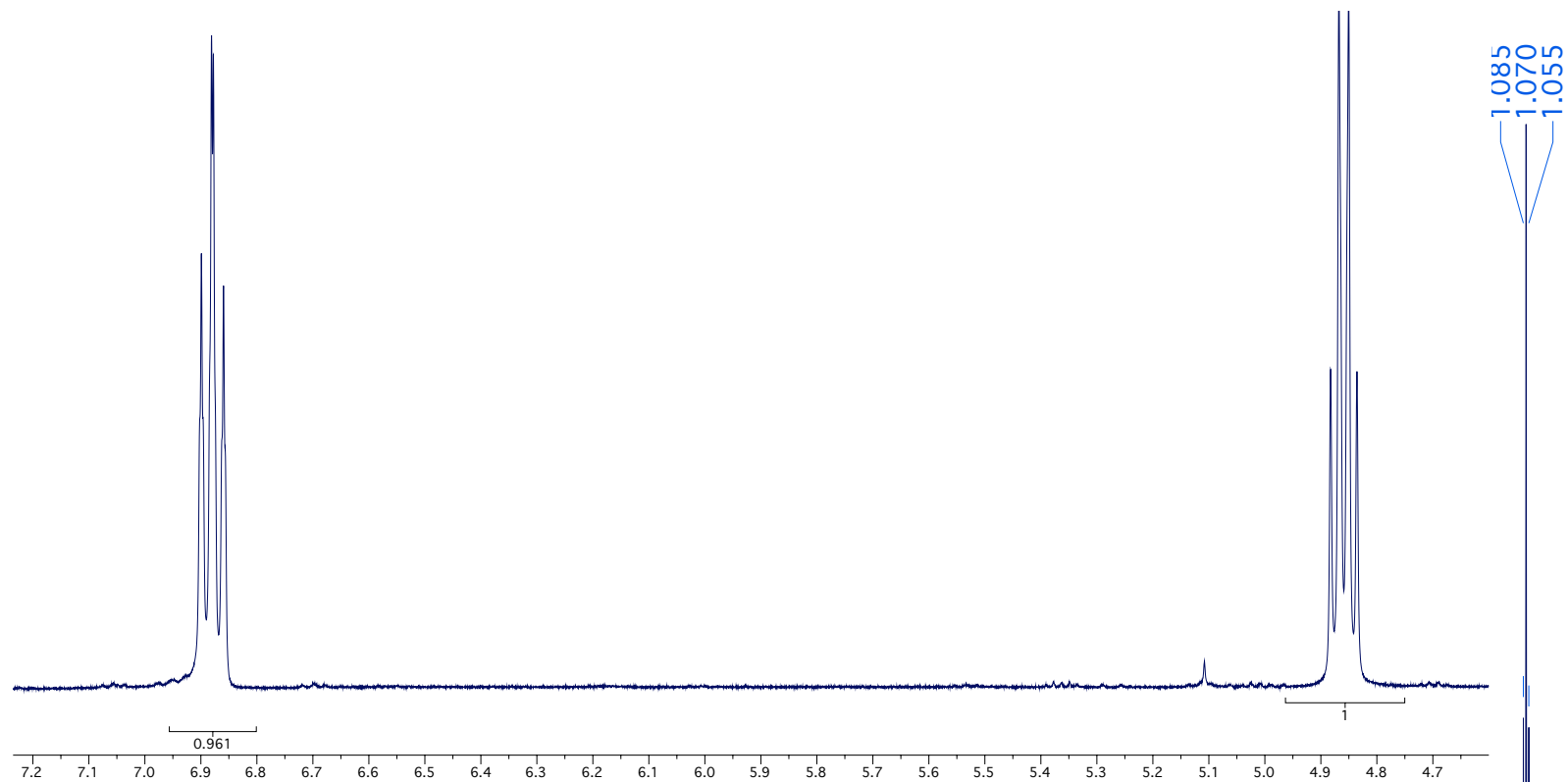


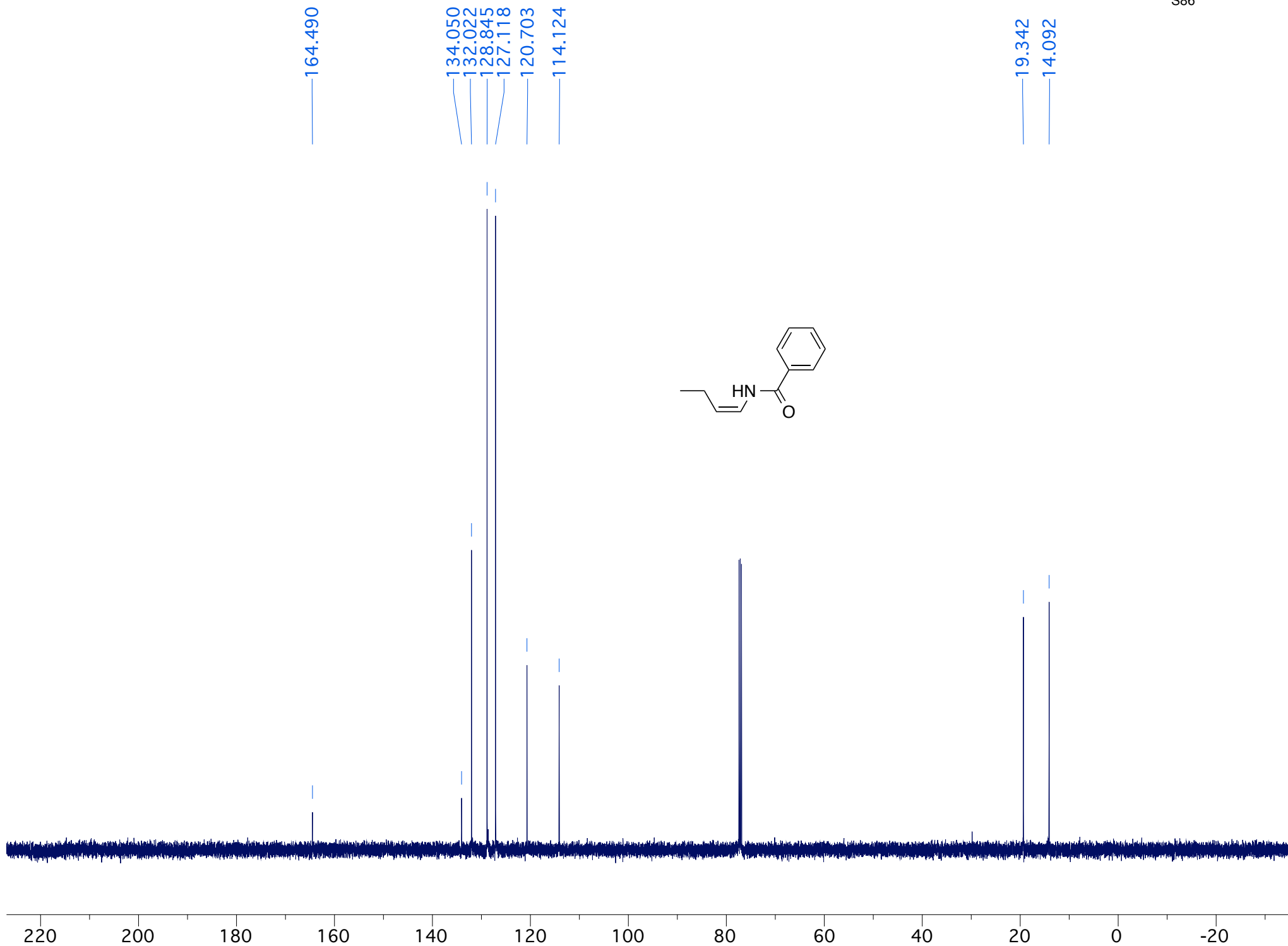
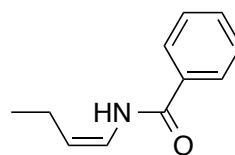










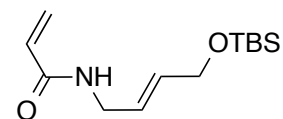


6.301  
6.298  
6.259  
6.255  
6.124  
6.099  
6.082  
6.056  
5.730  
5.725  
5.721  
5.716  
5.706  
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5.623

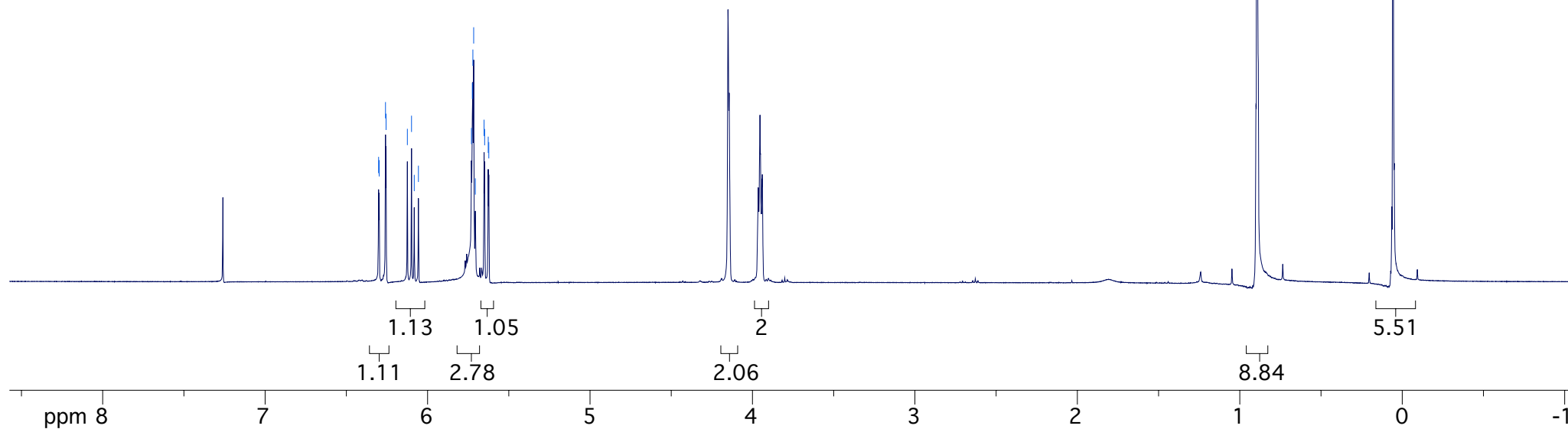
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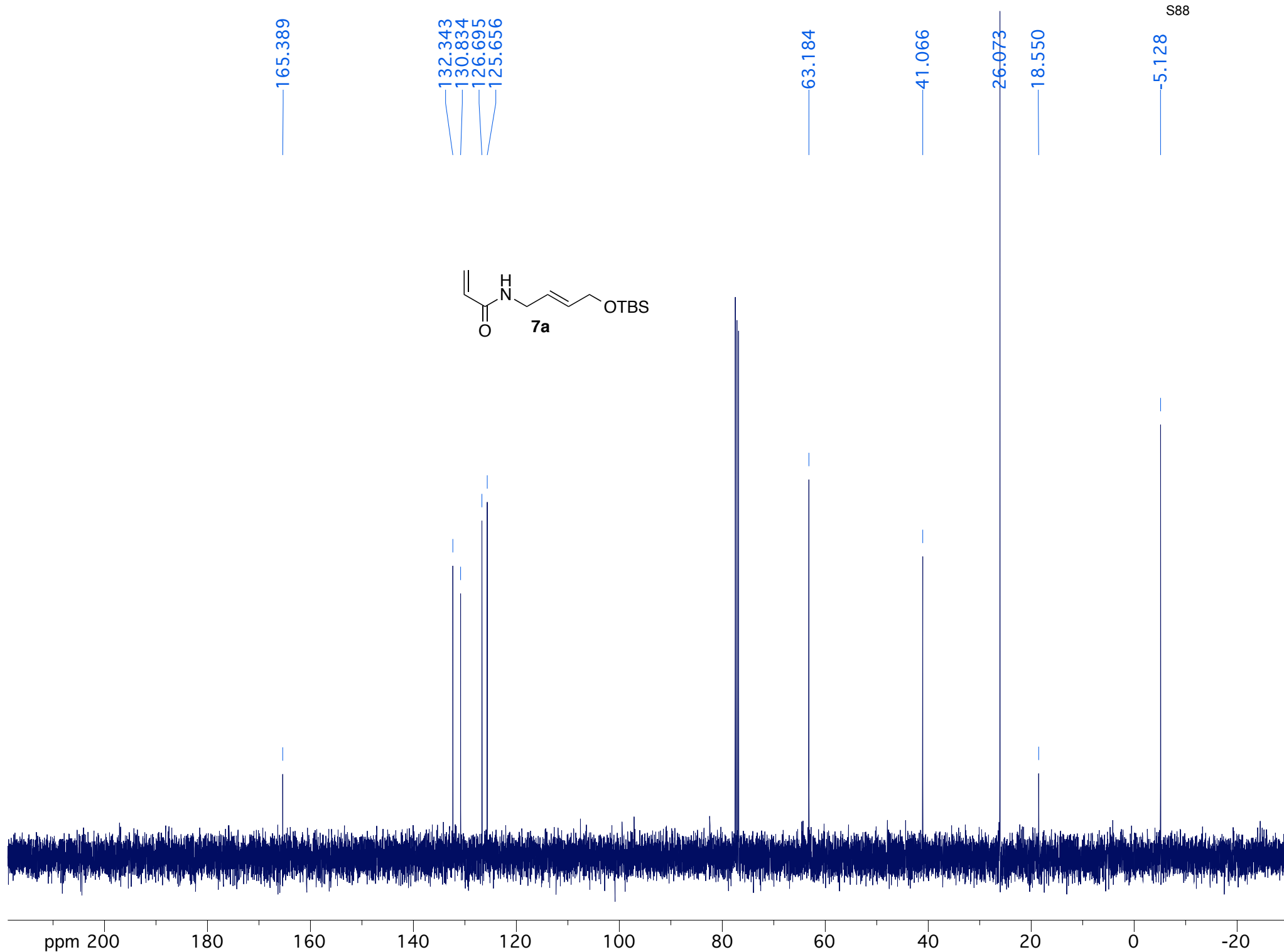
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S87

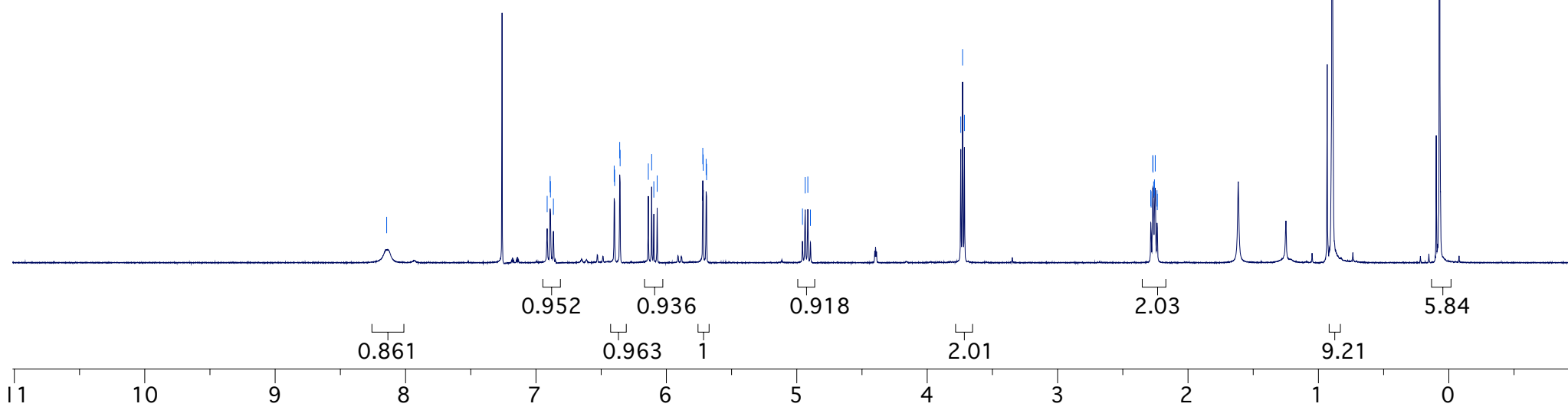
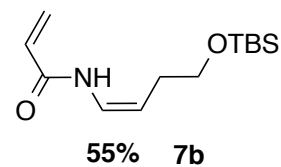
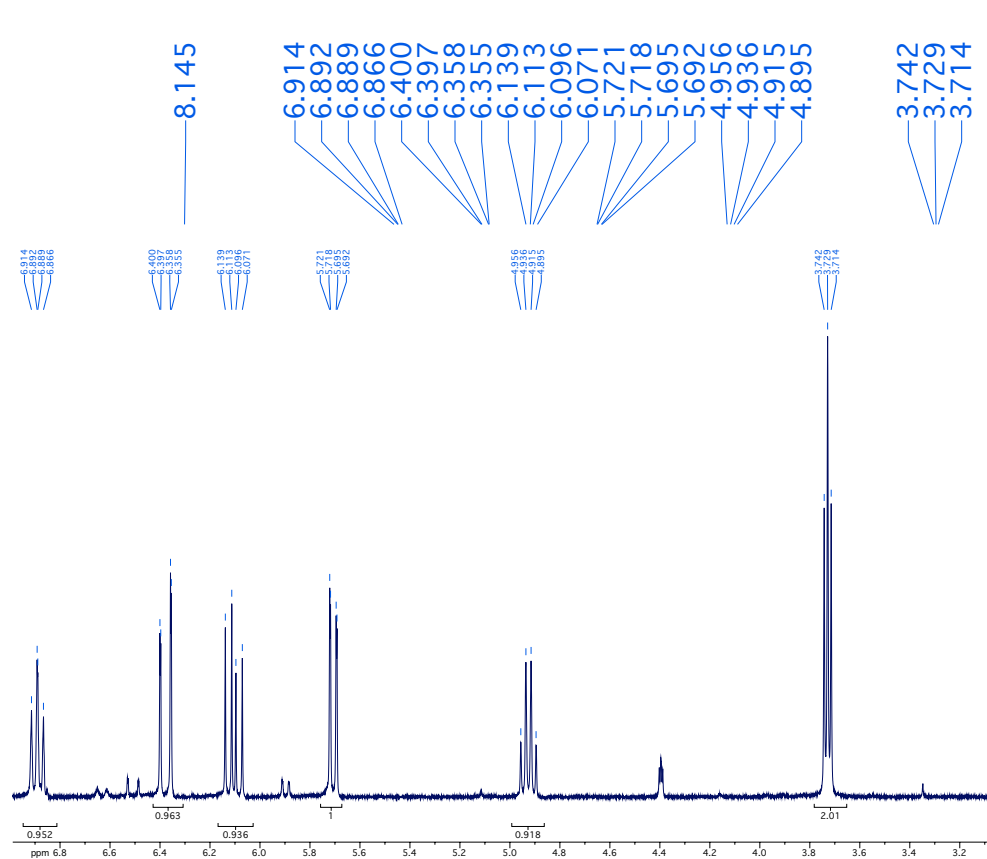


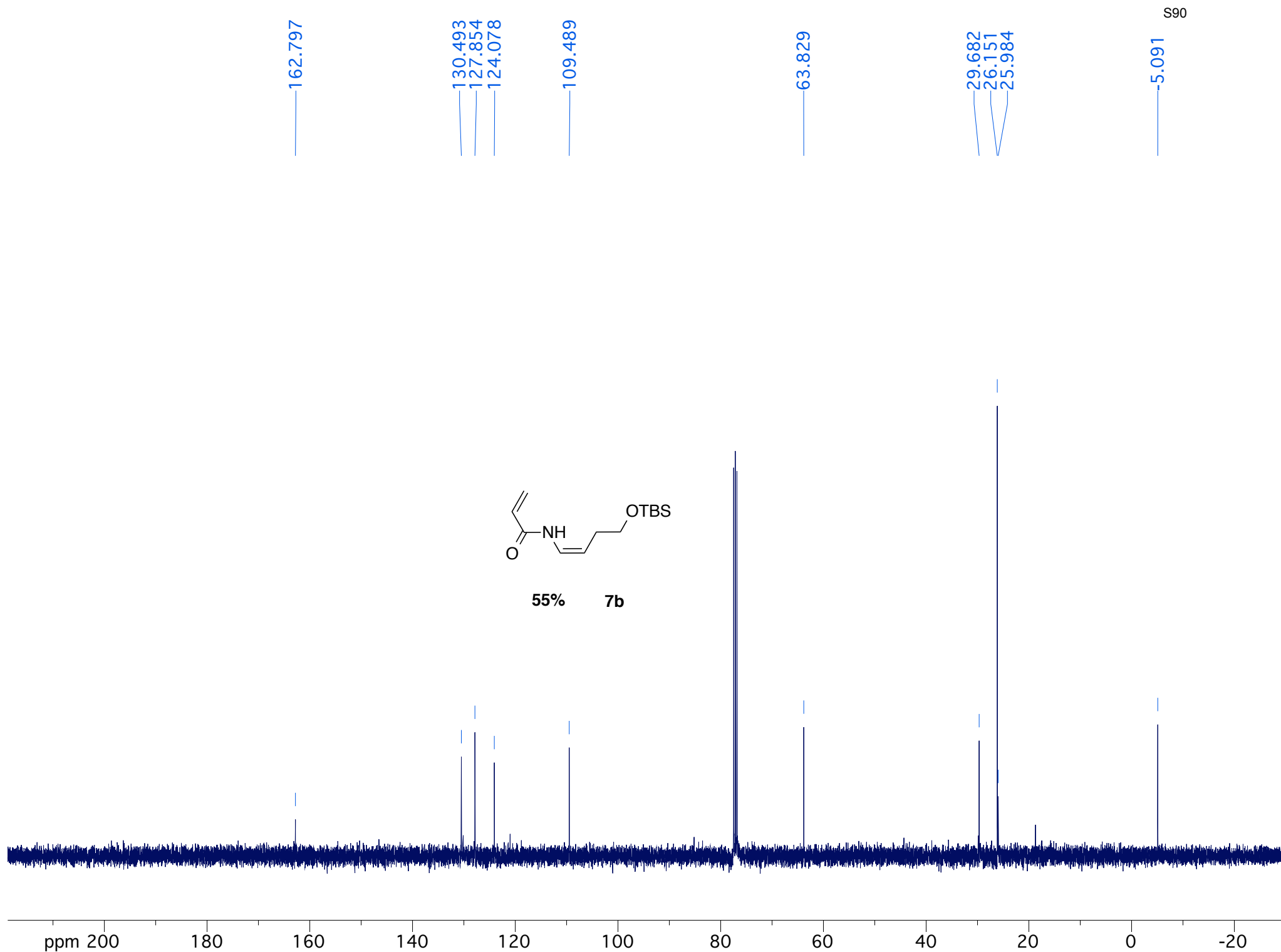
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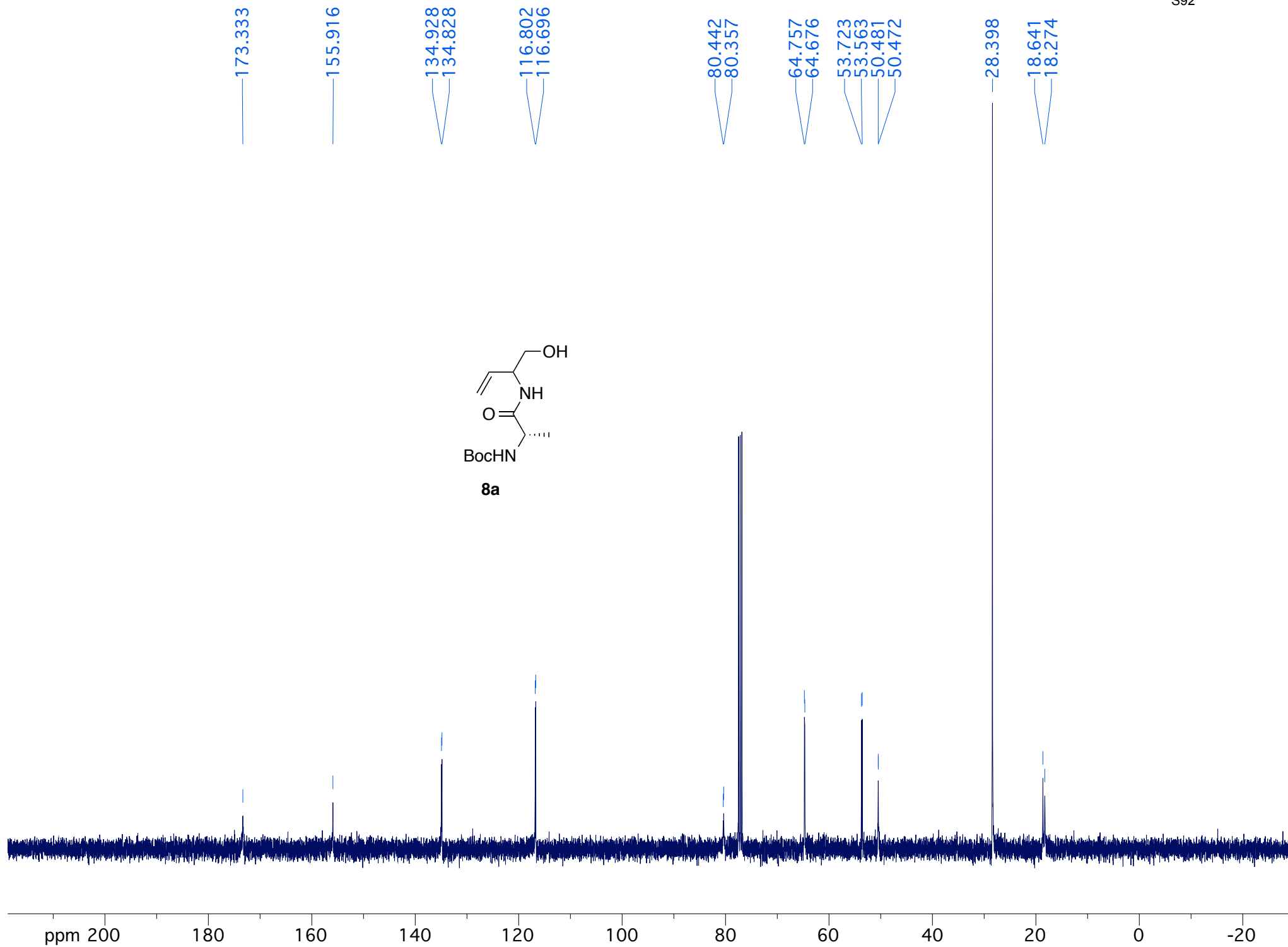


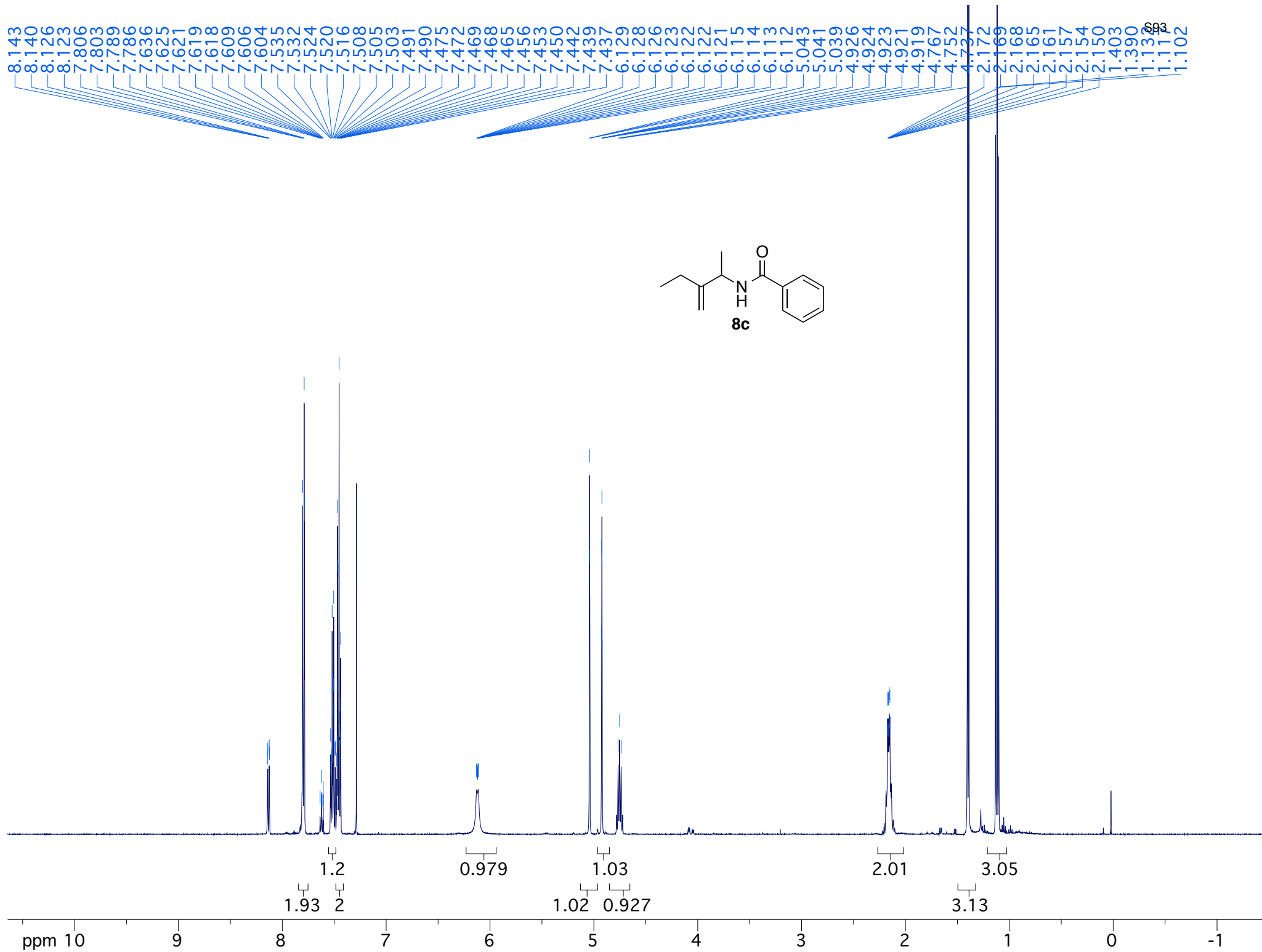


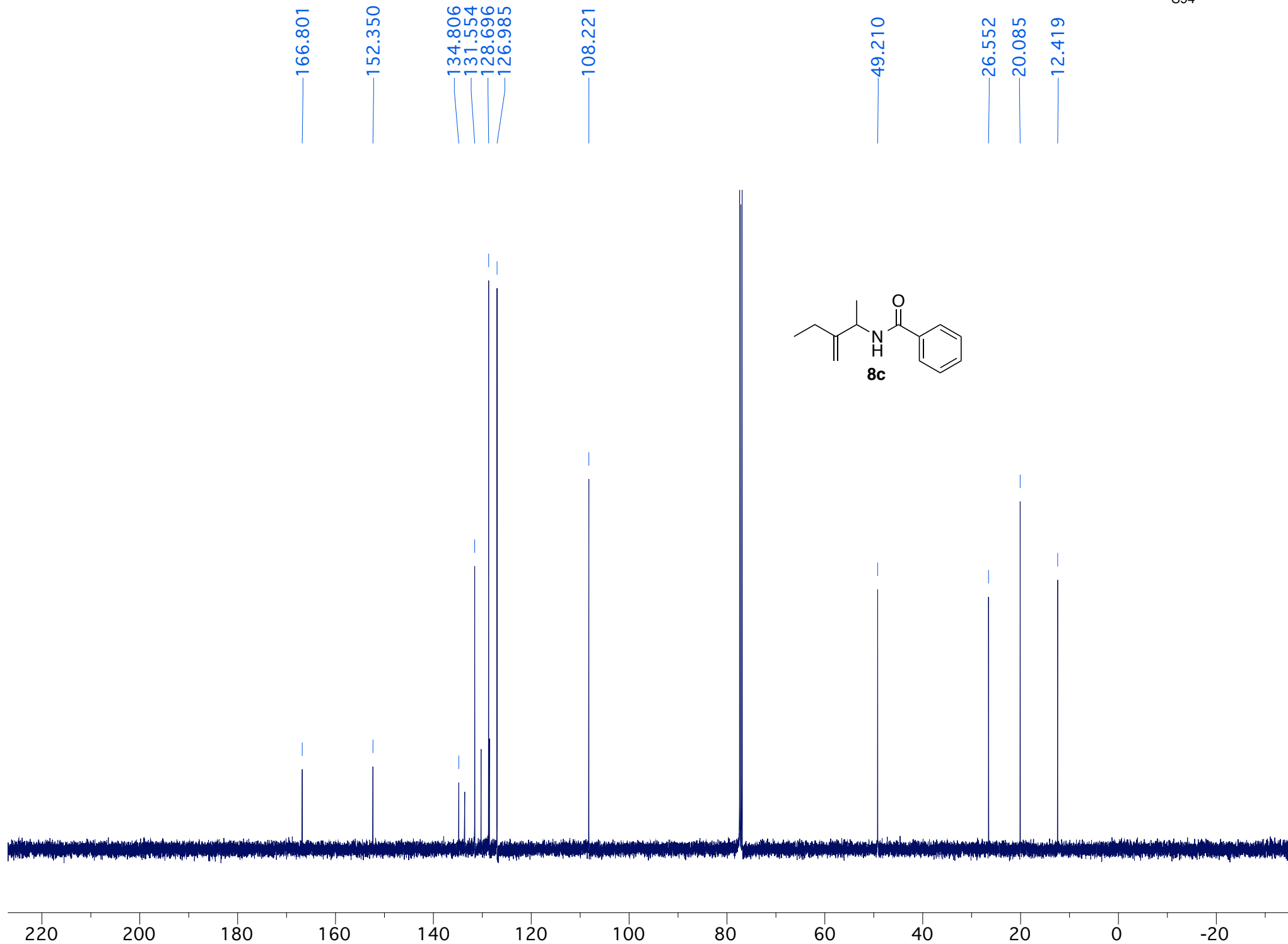


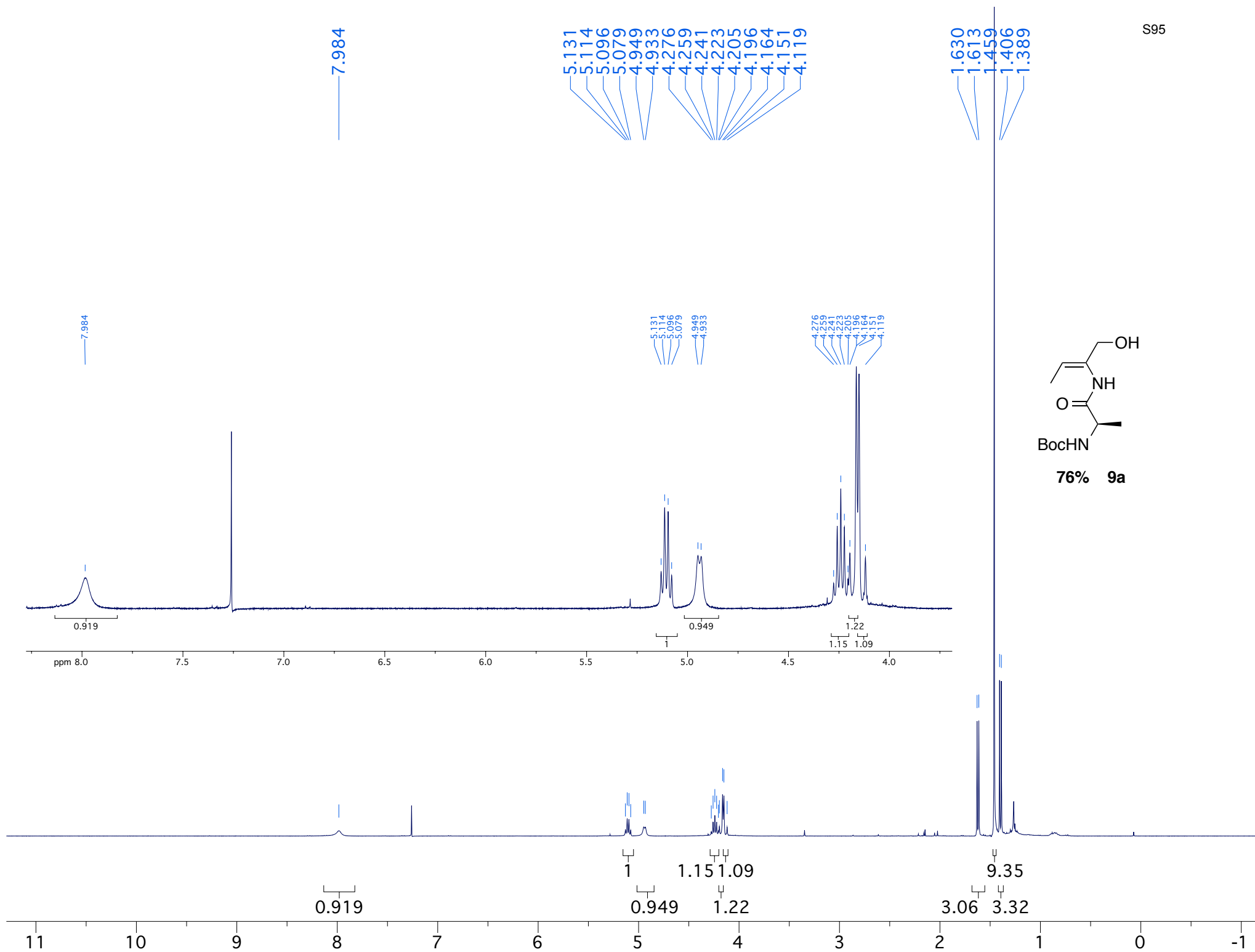


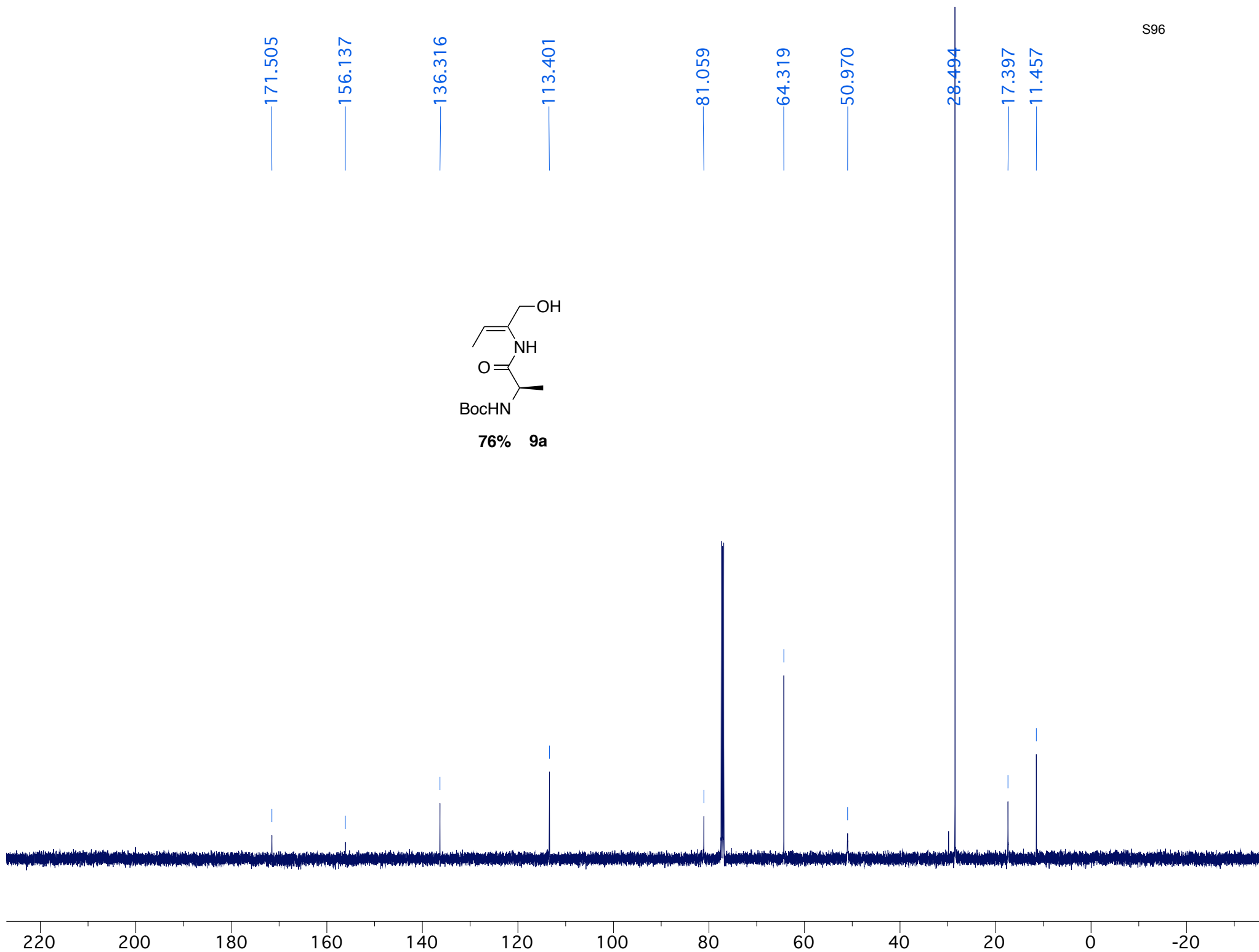
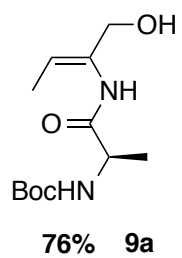




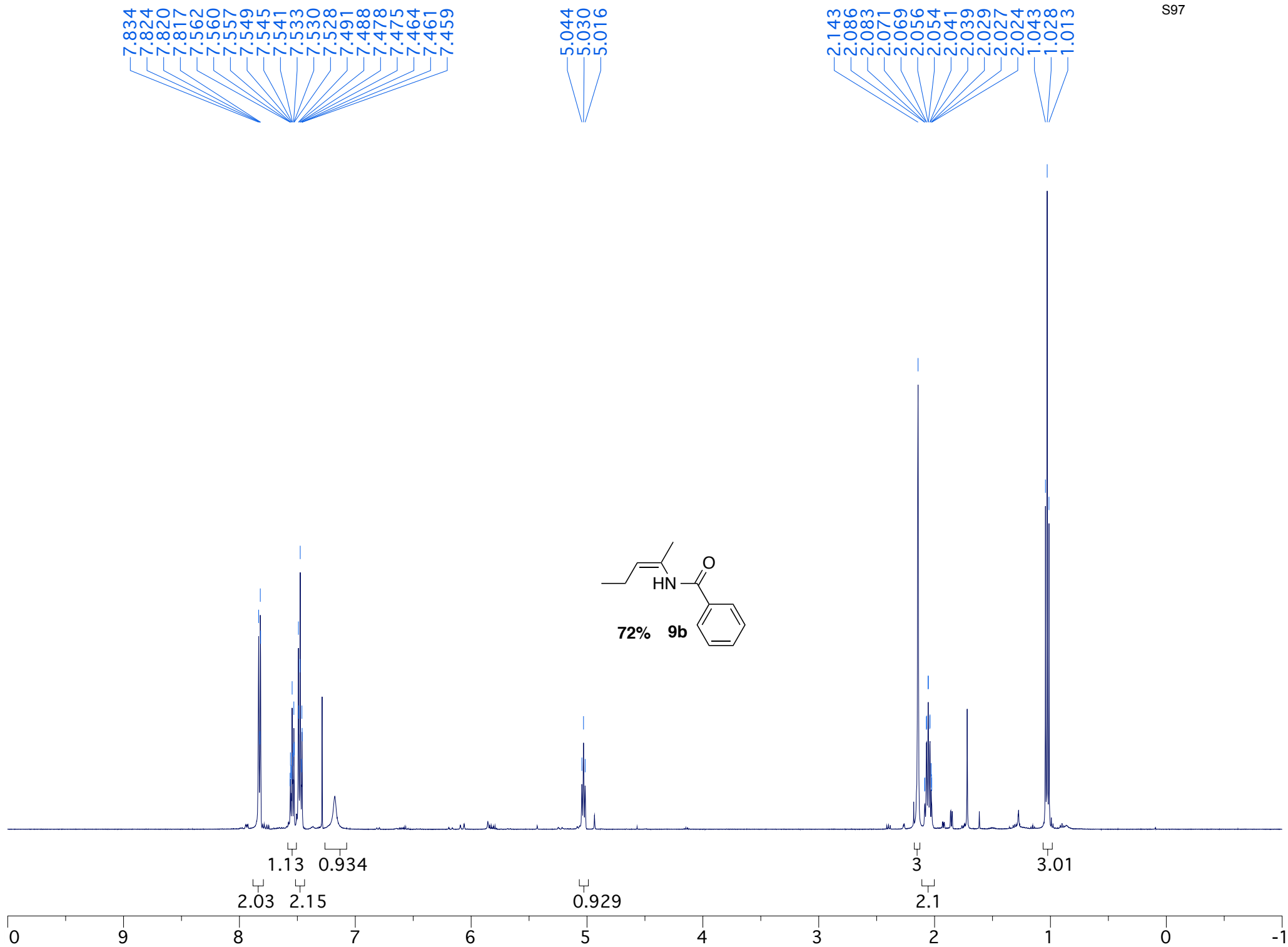








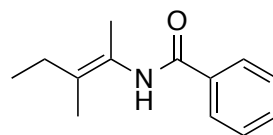




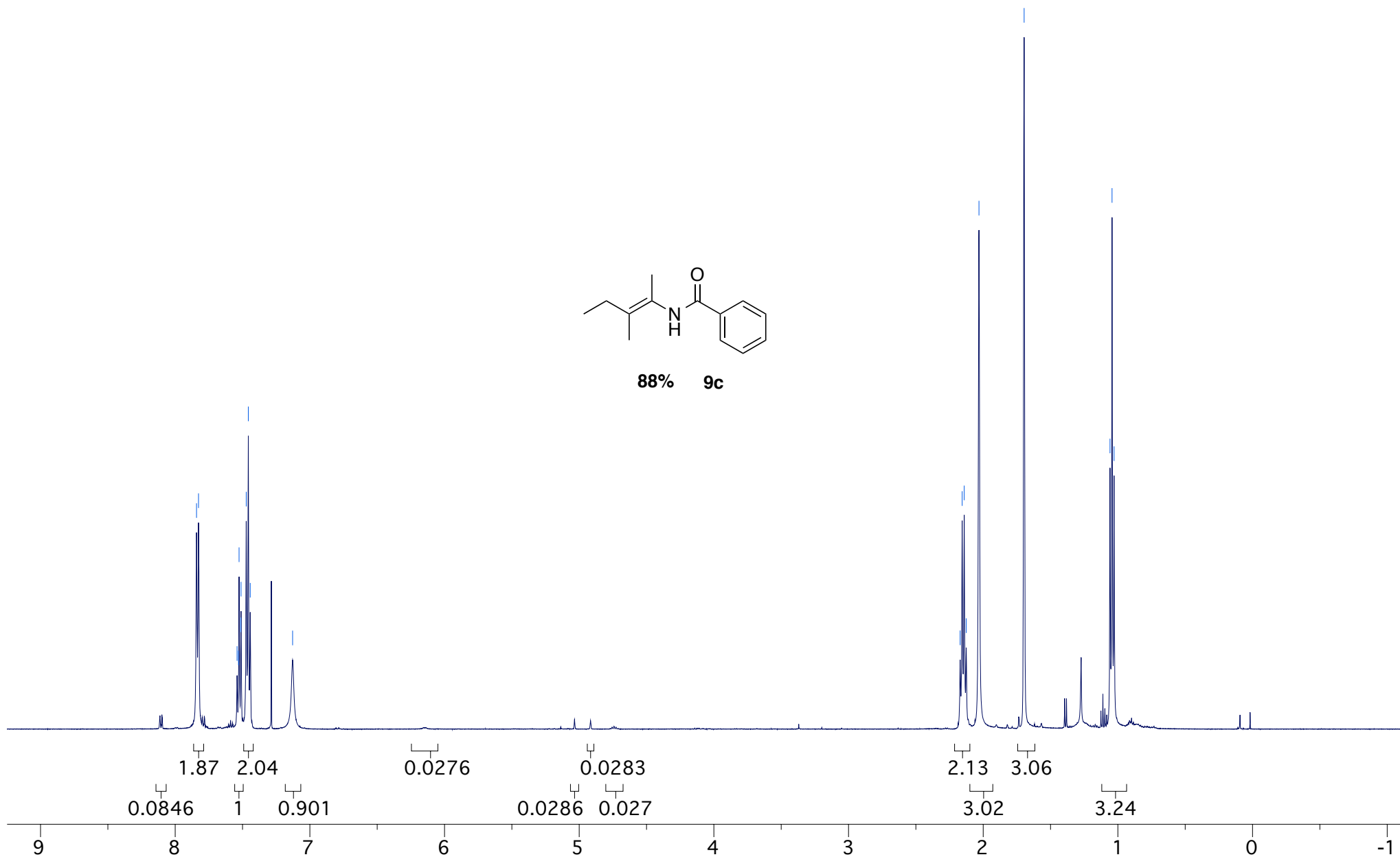
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7.128

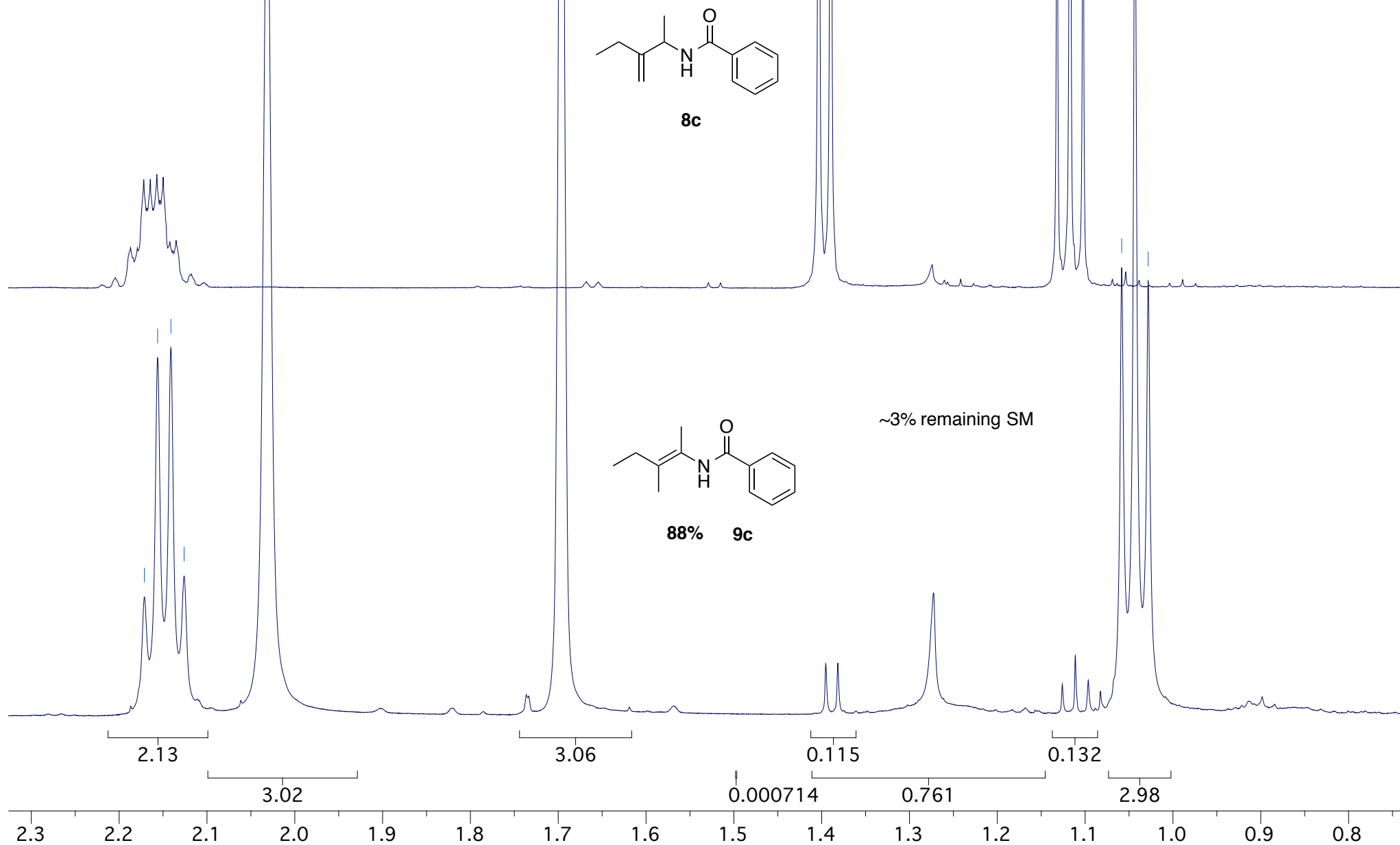
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2.126  
2.031  
1.696

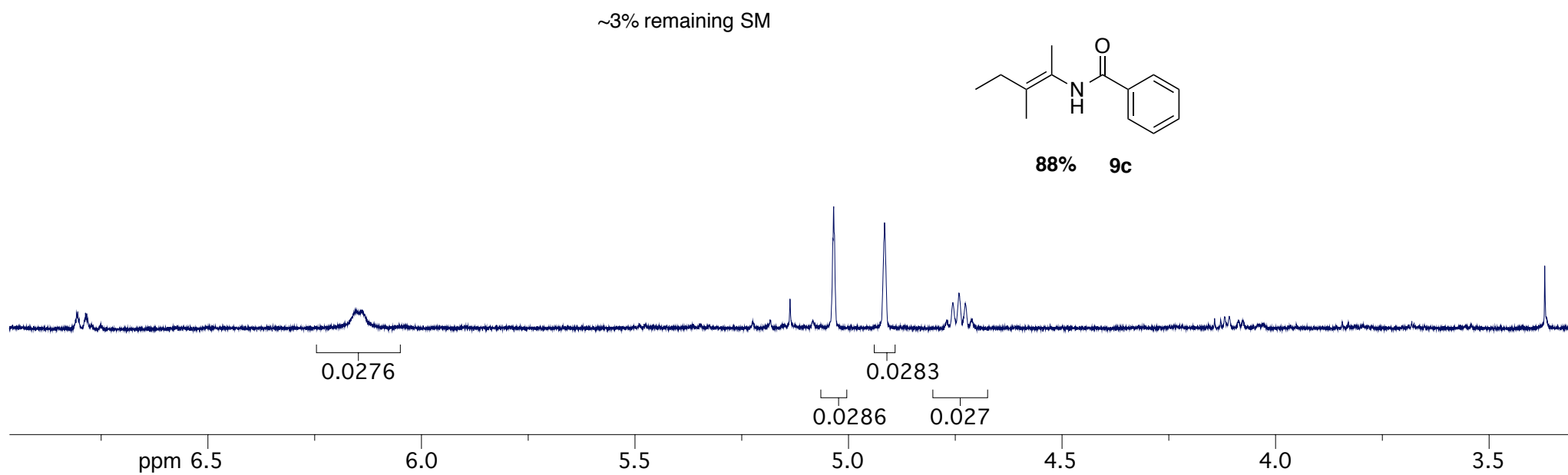
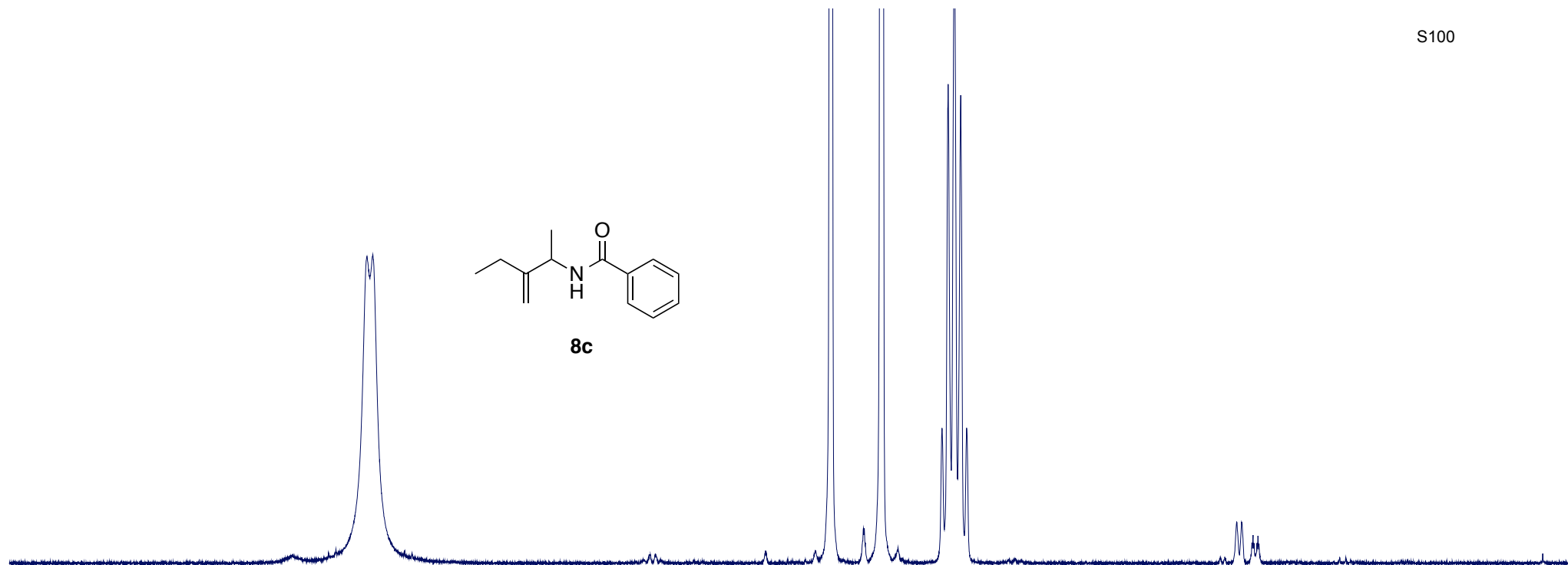
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1.043  
1.028

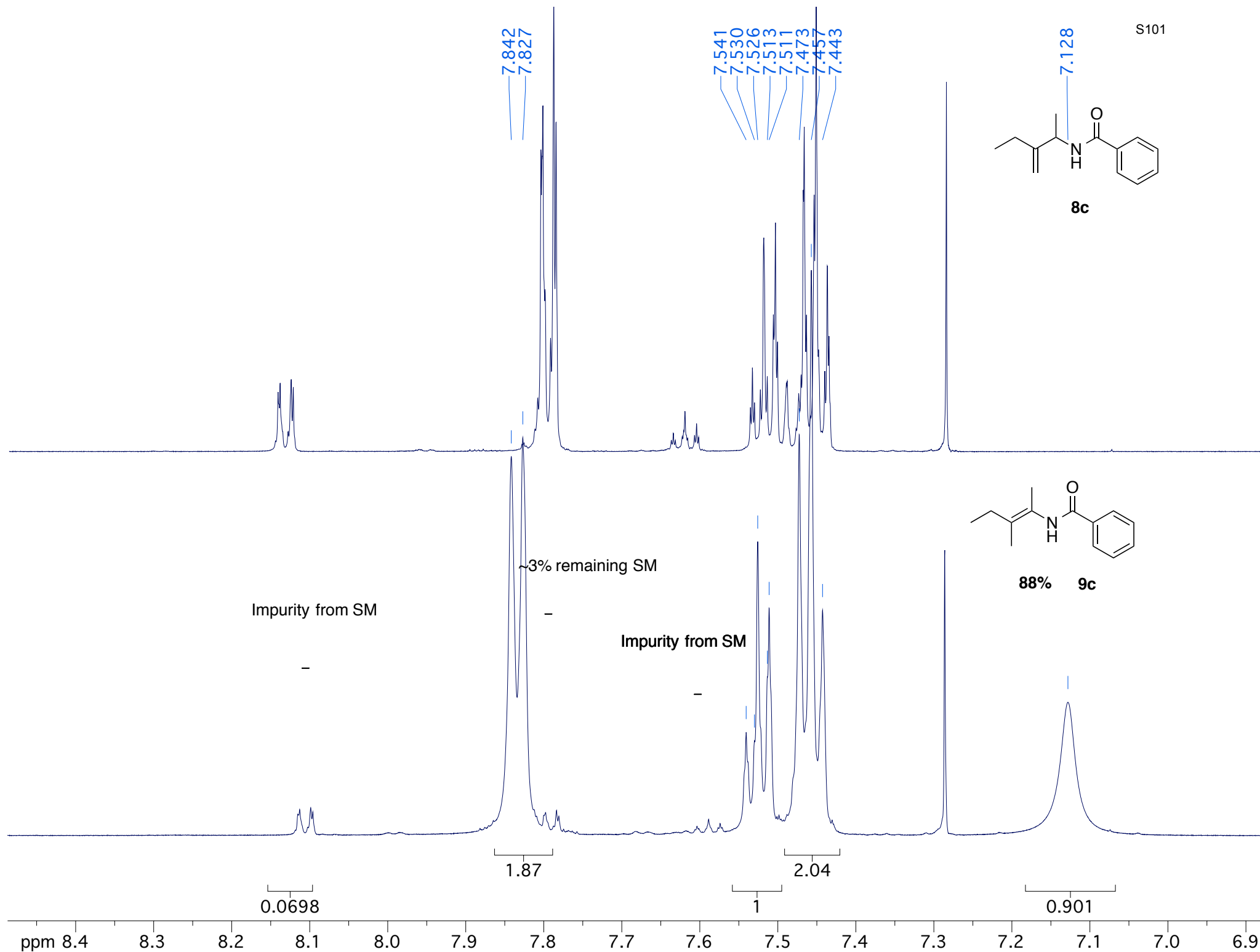


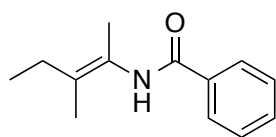
88% 9c



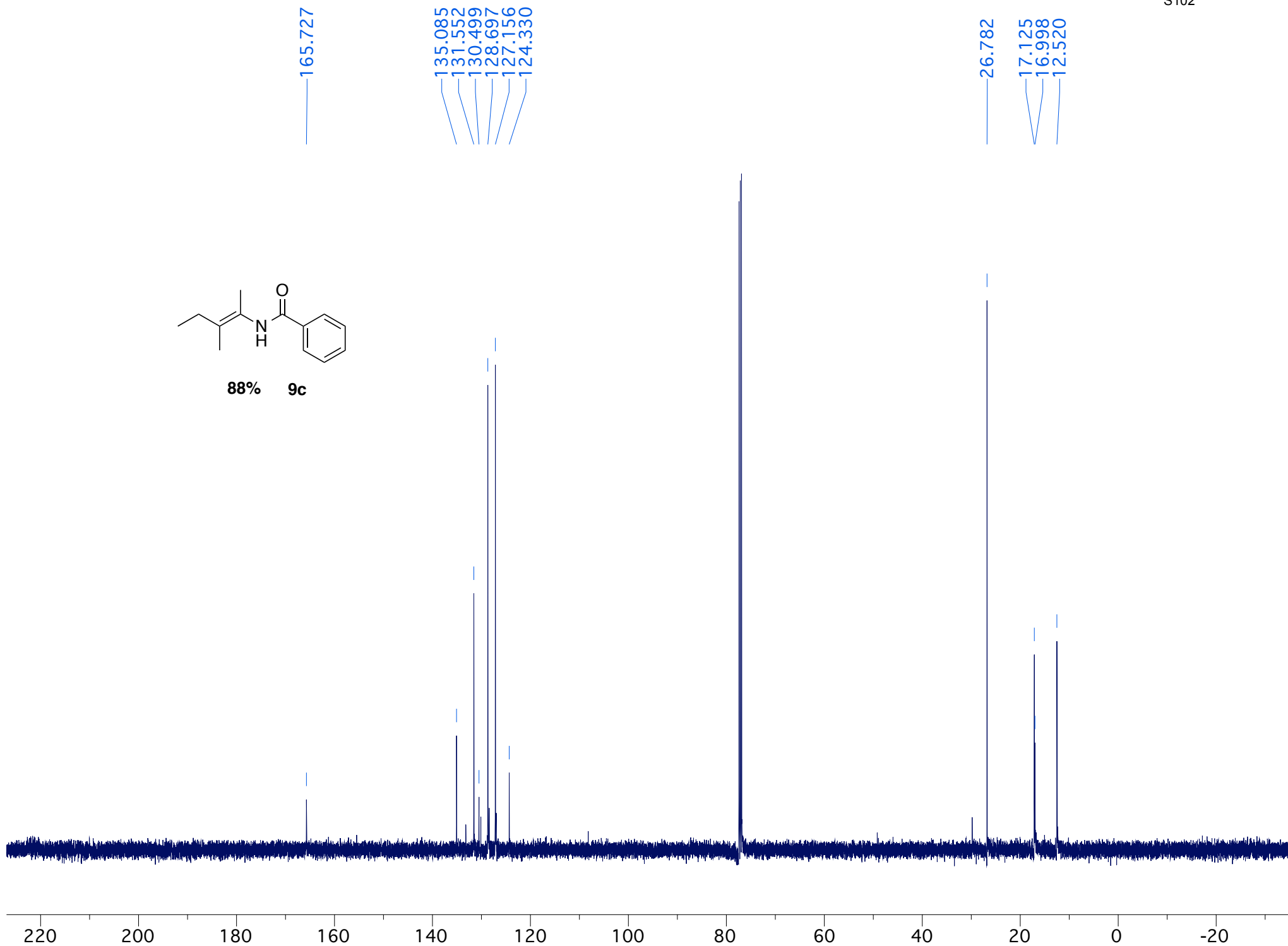


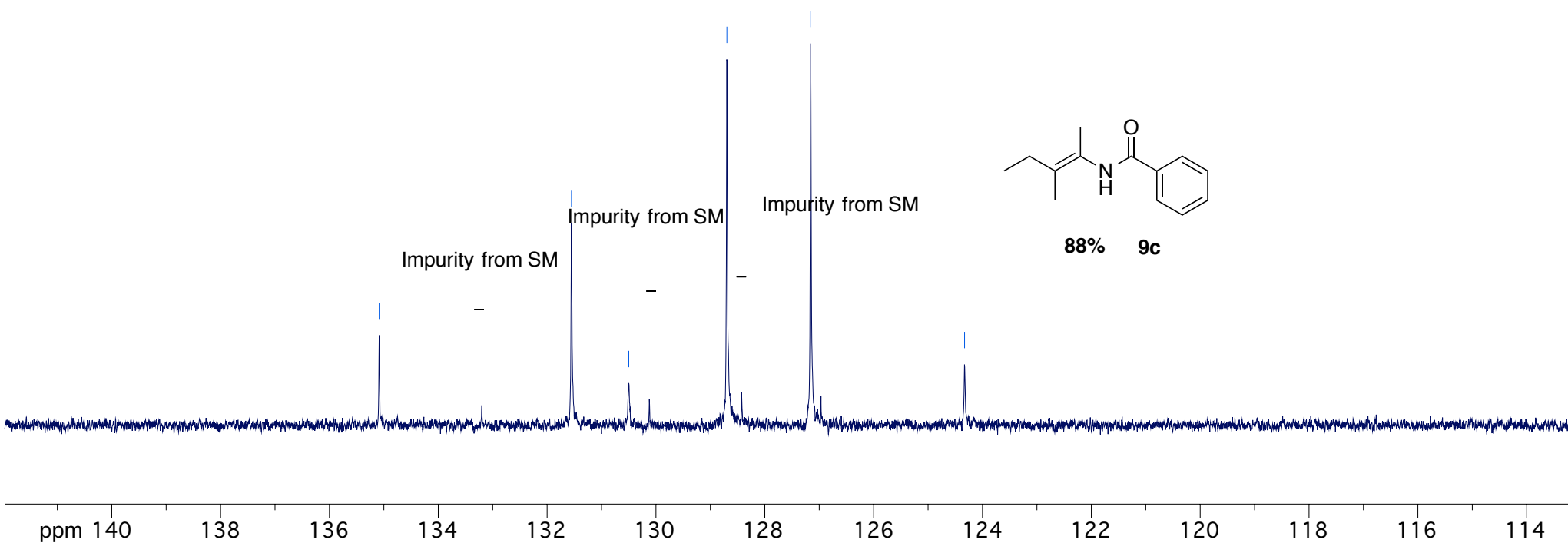
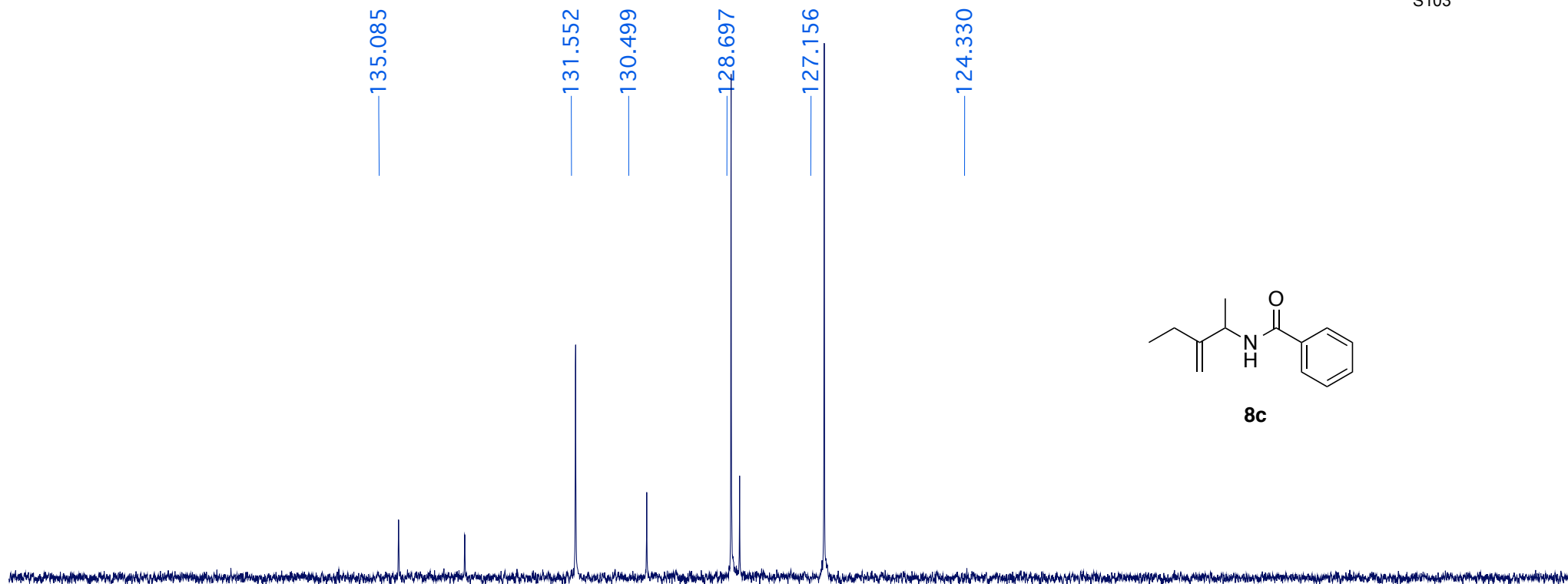


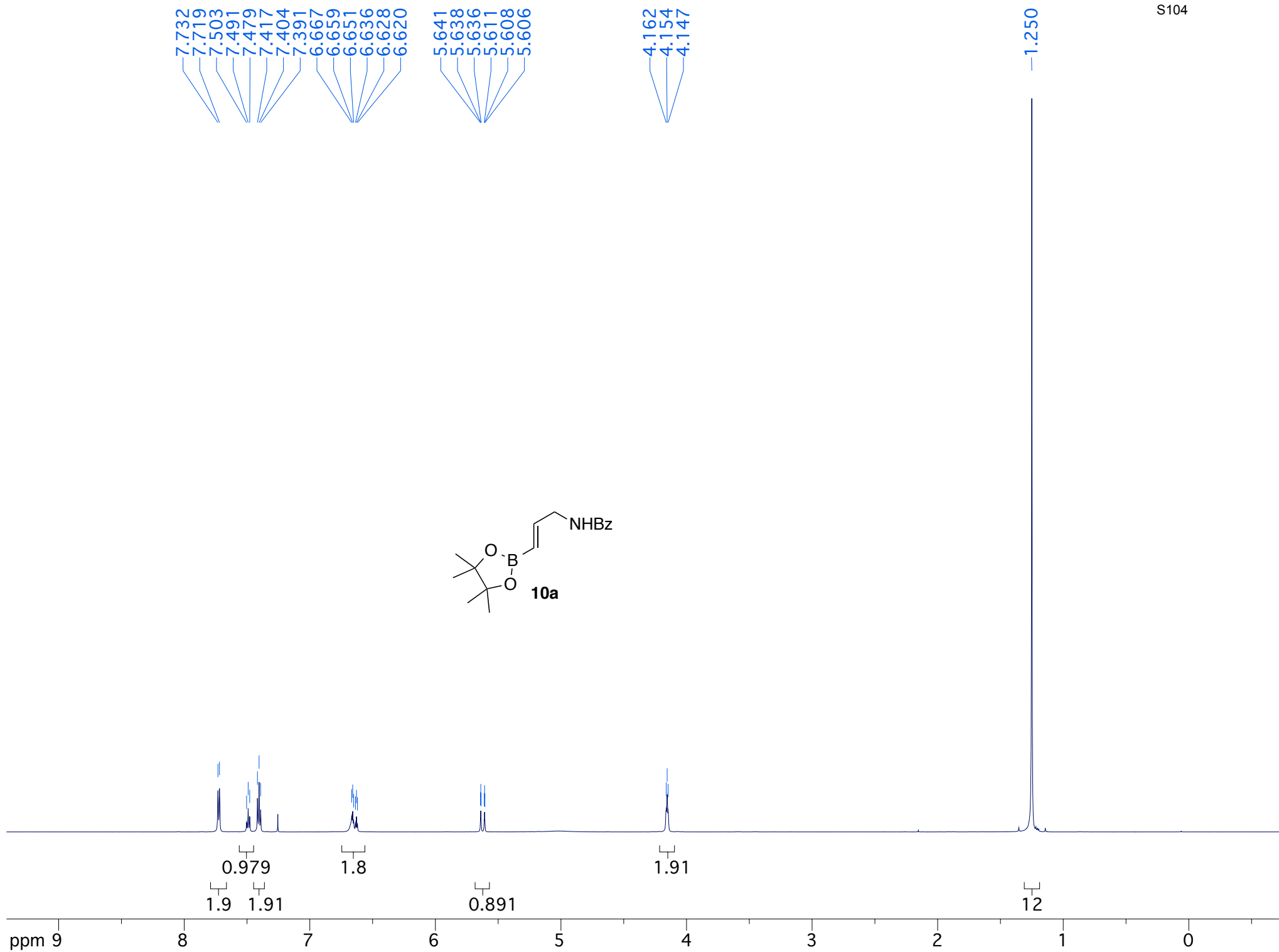




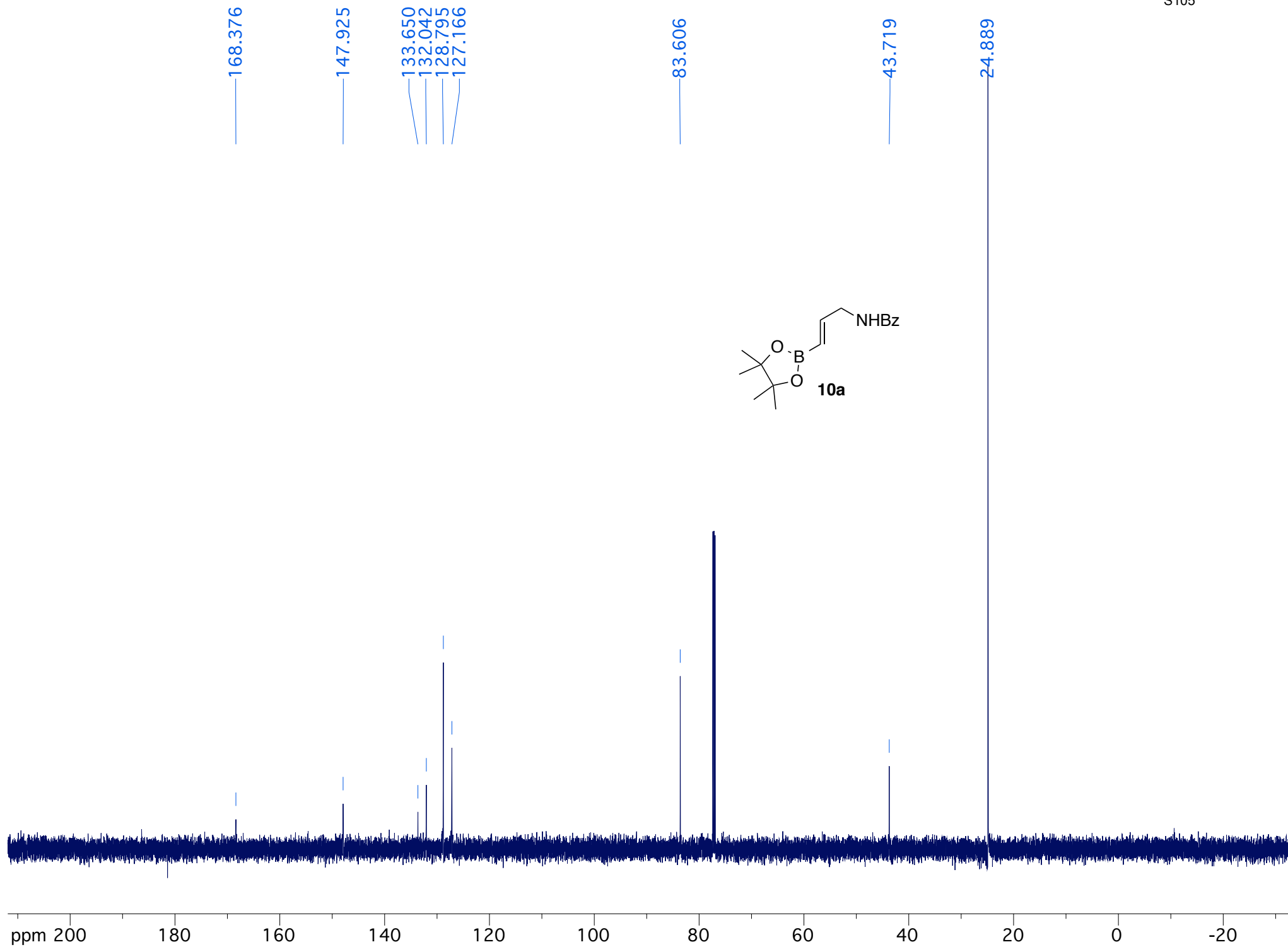
88% **9c**

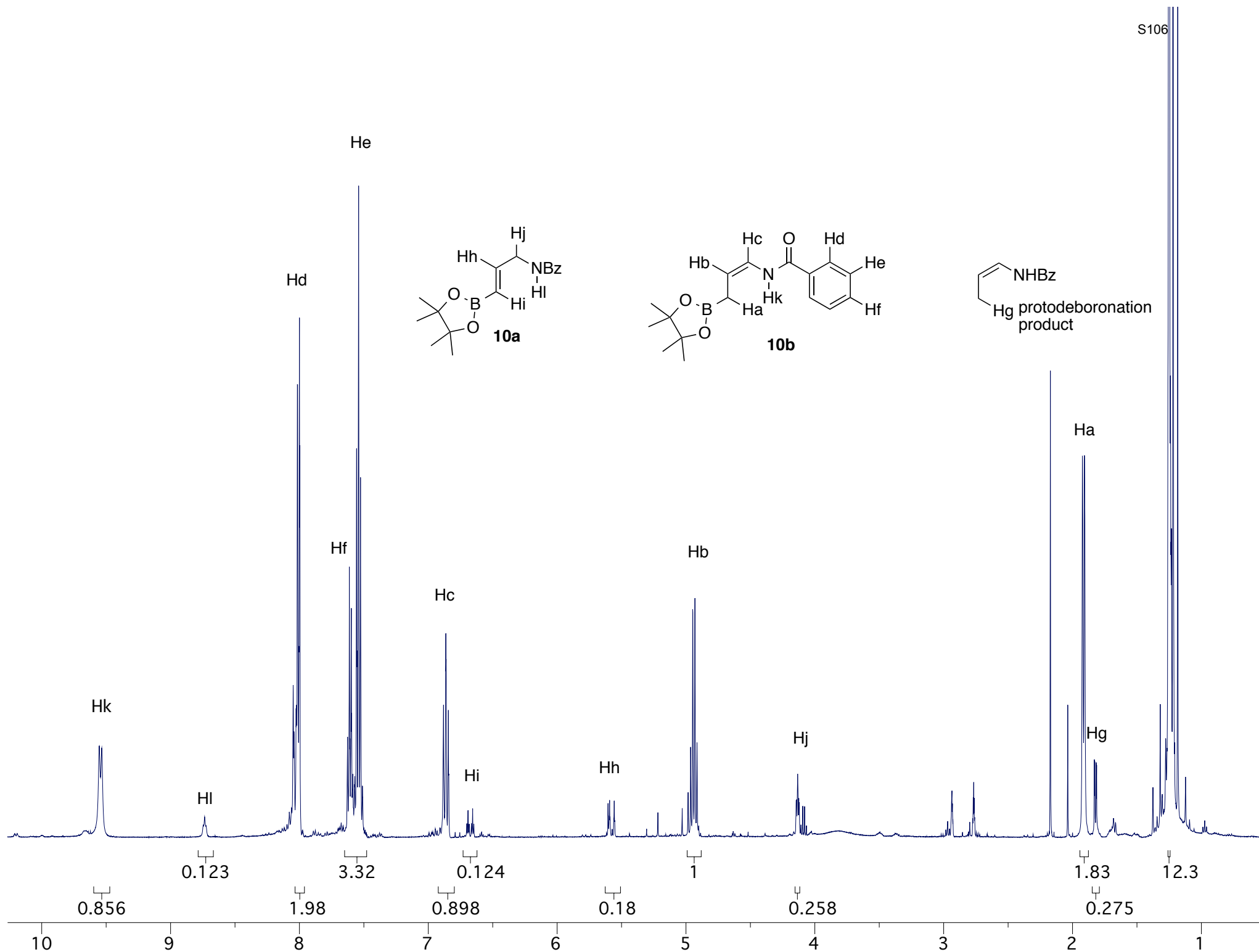


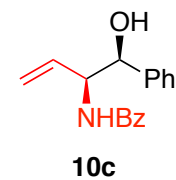
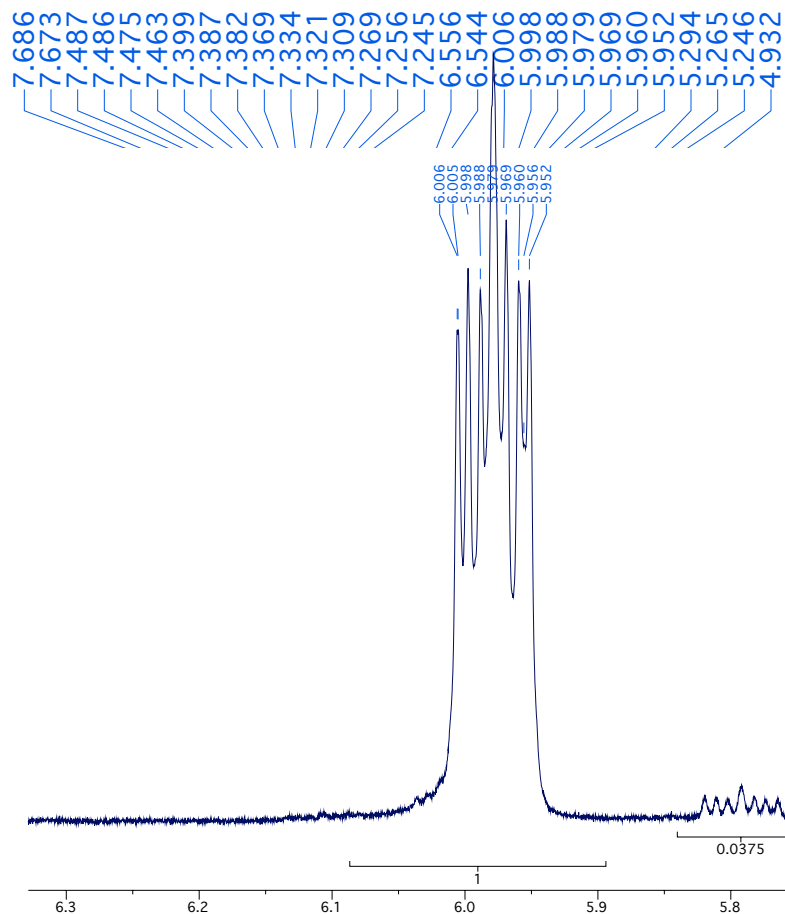




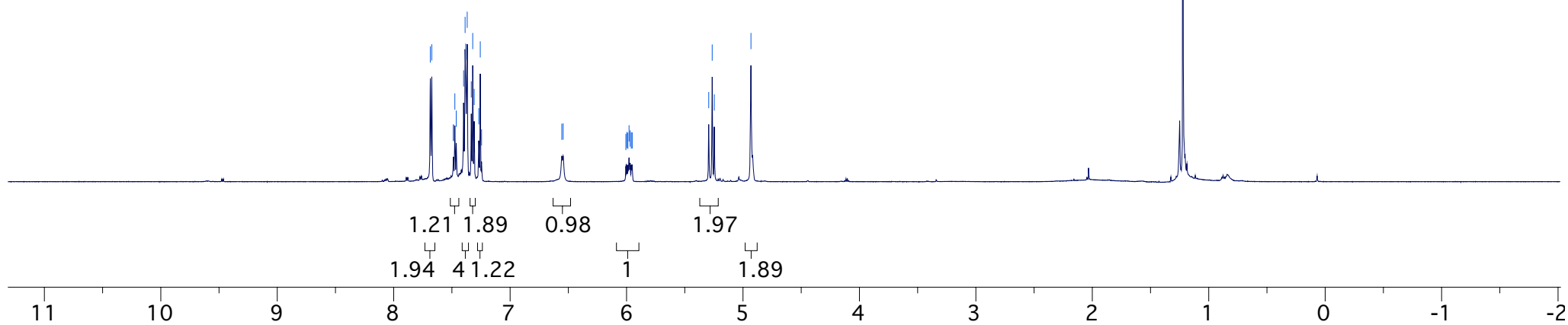


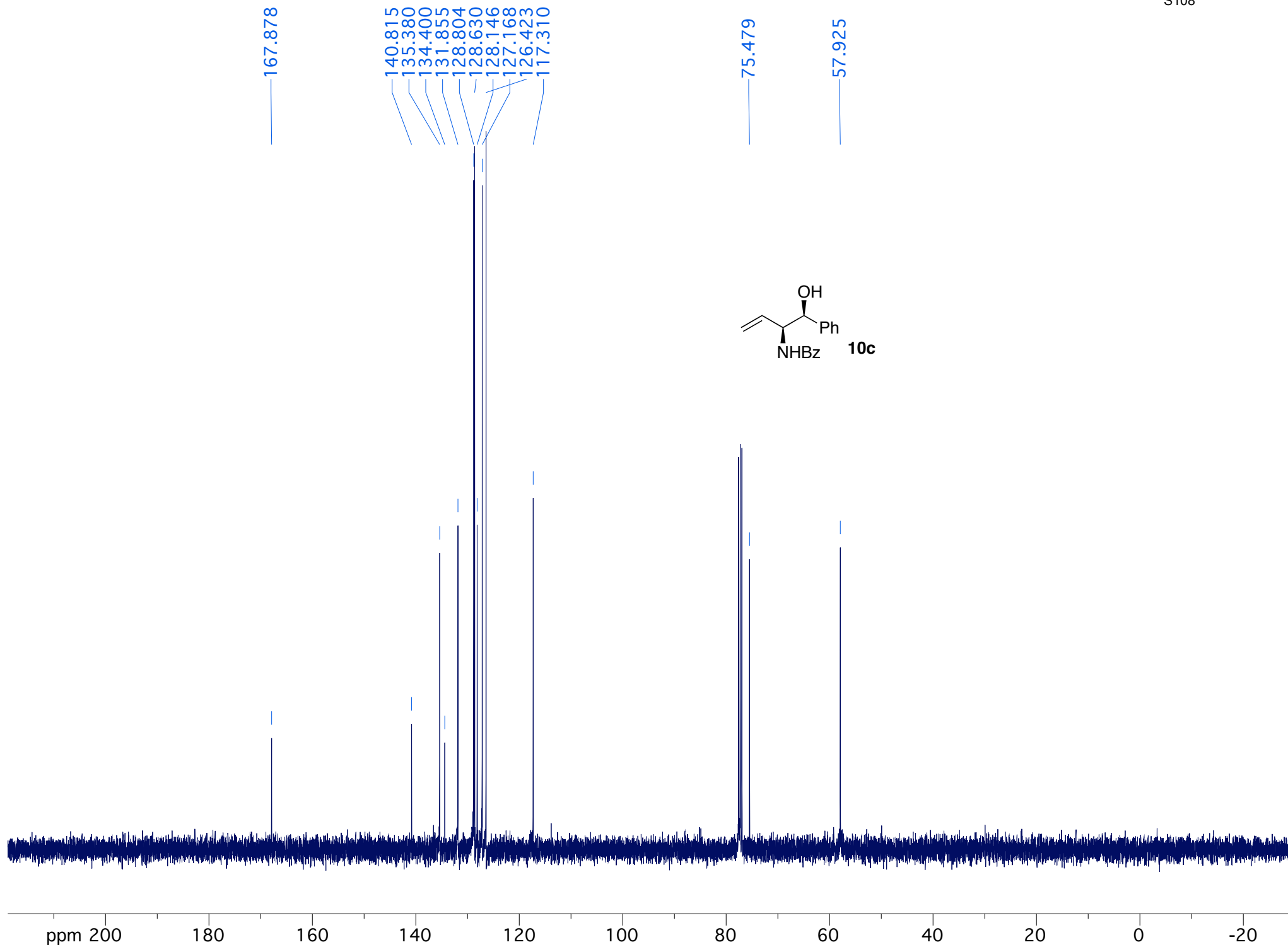


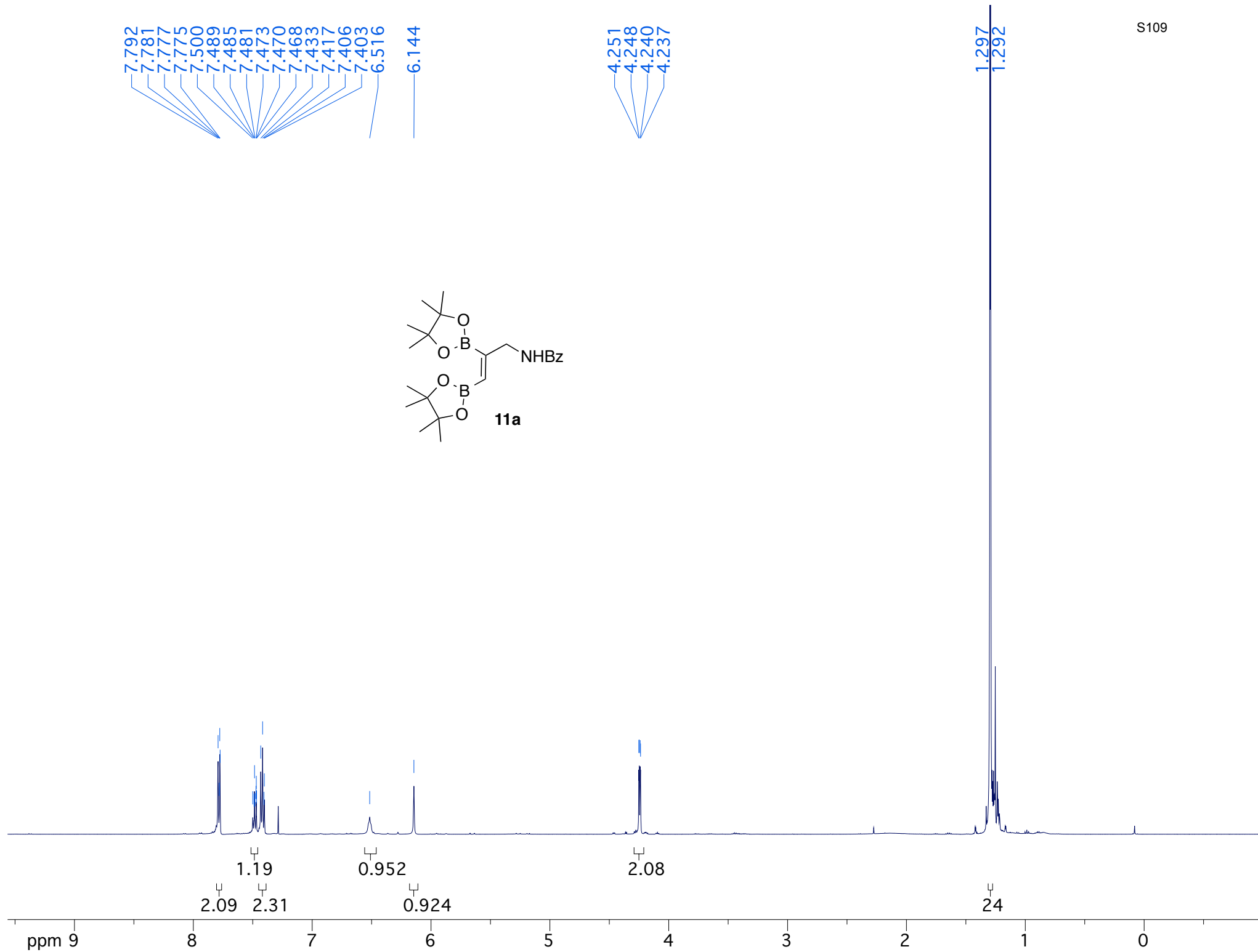
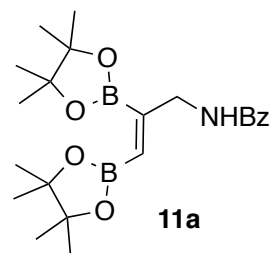
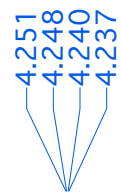
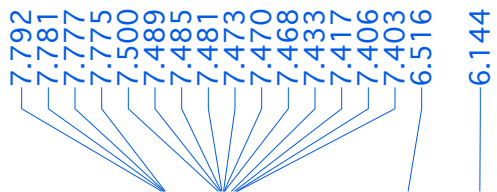


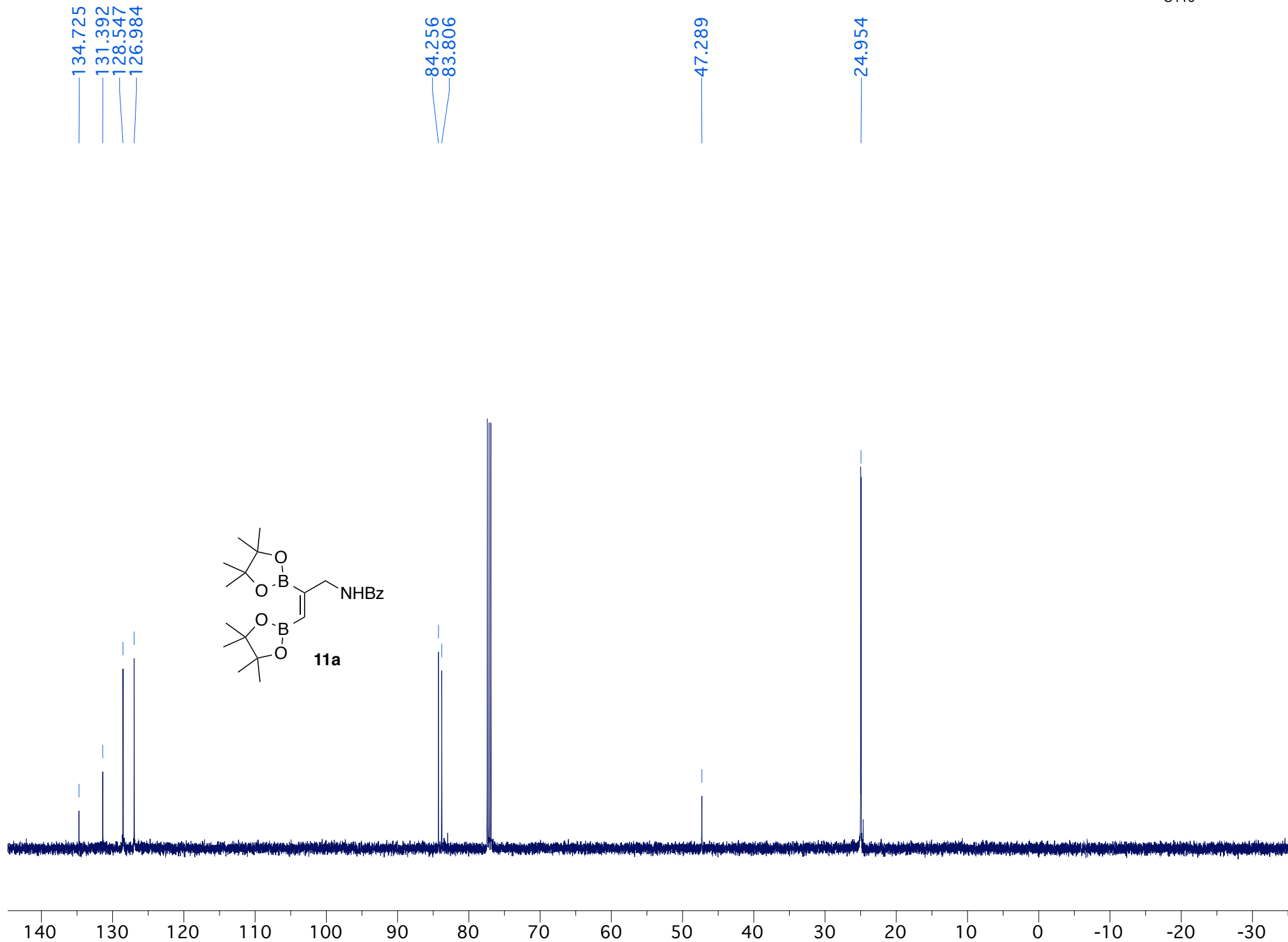


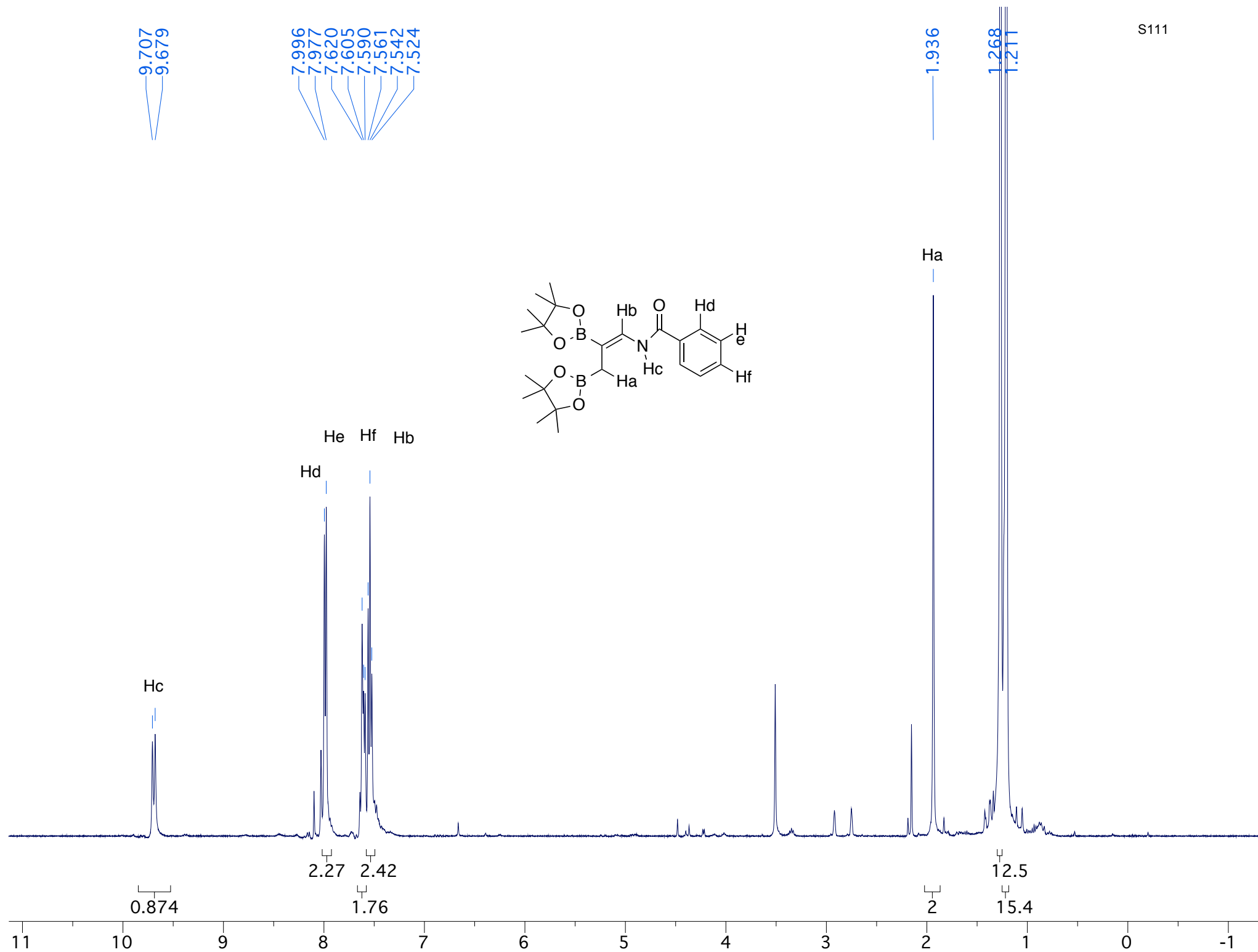
73% yield  
>20:1 dr

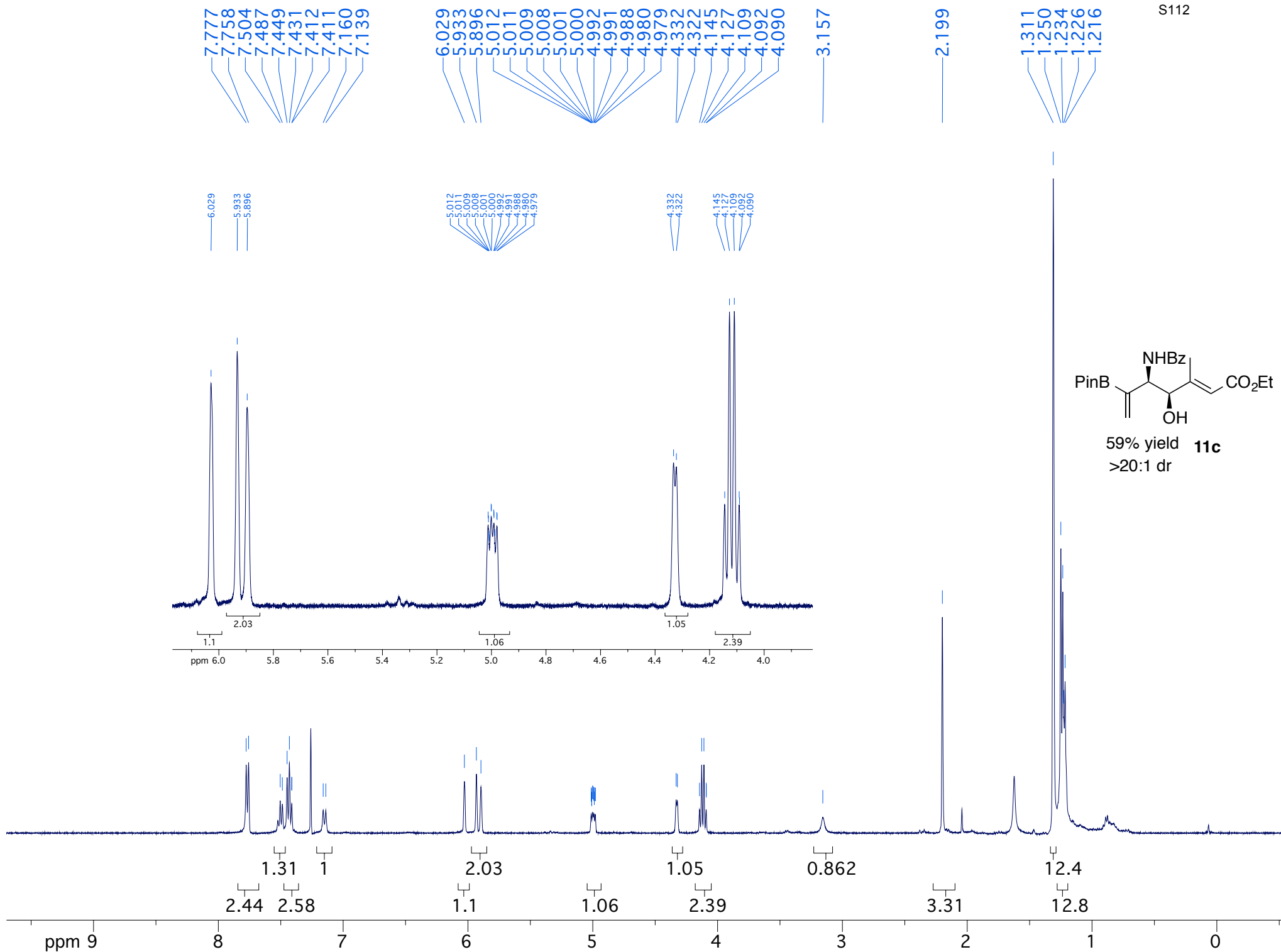




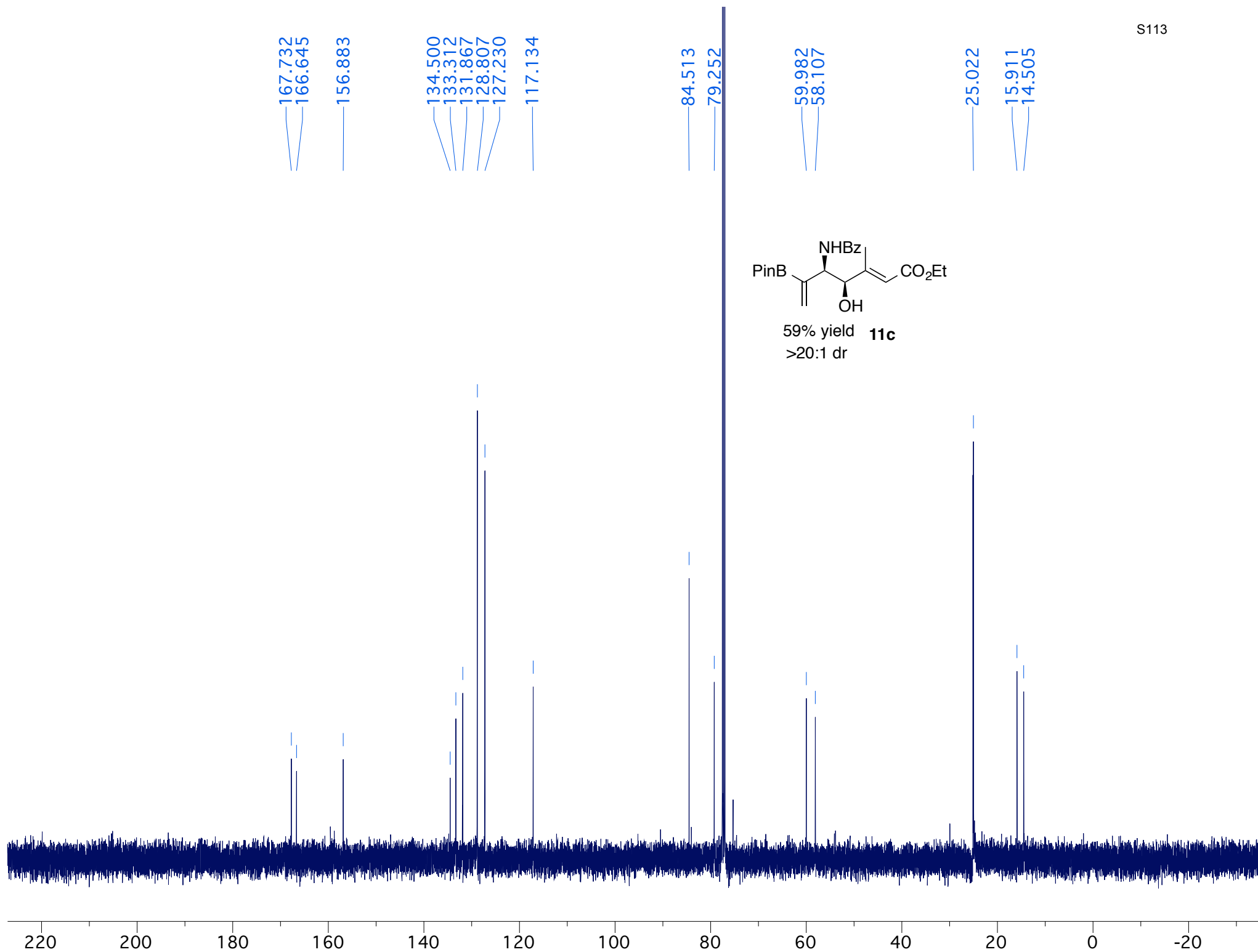


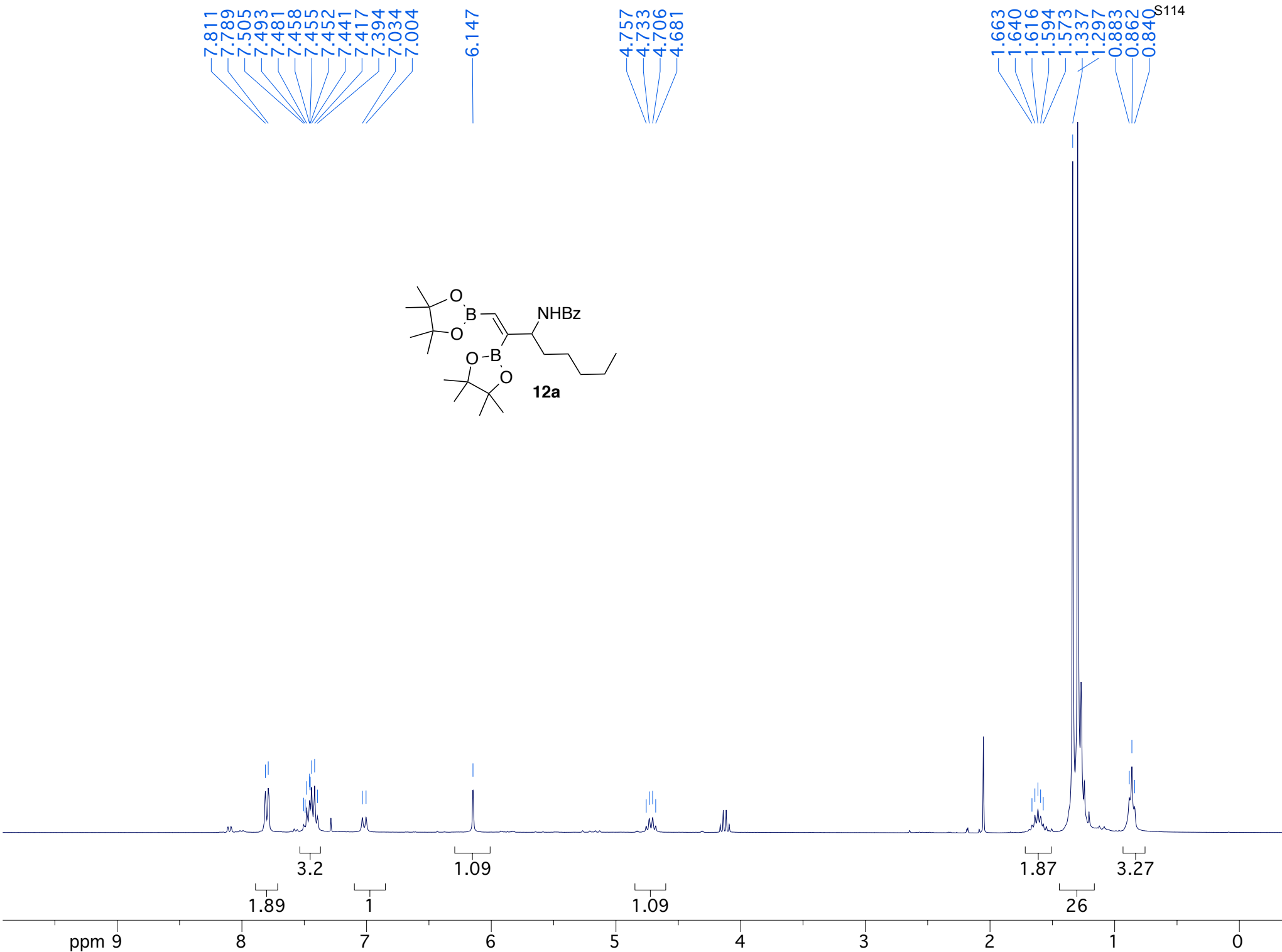




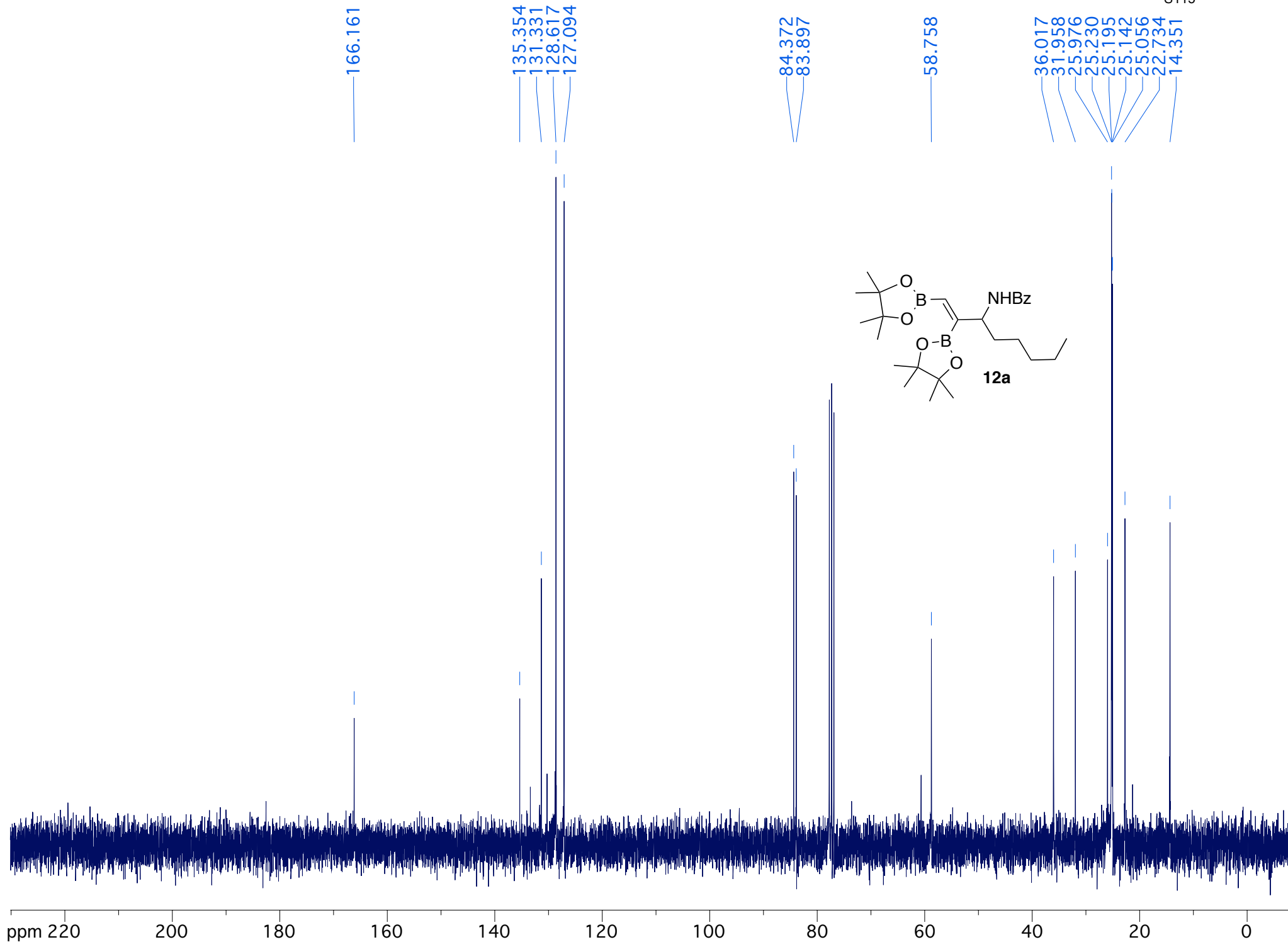


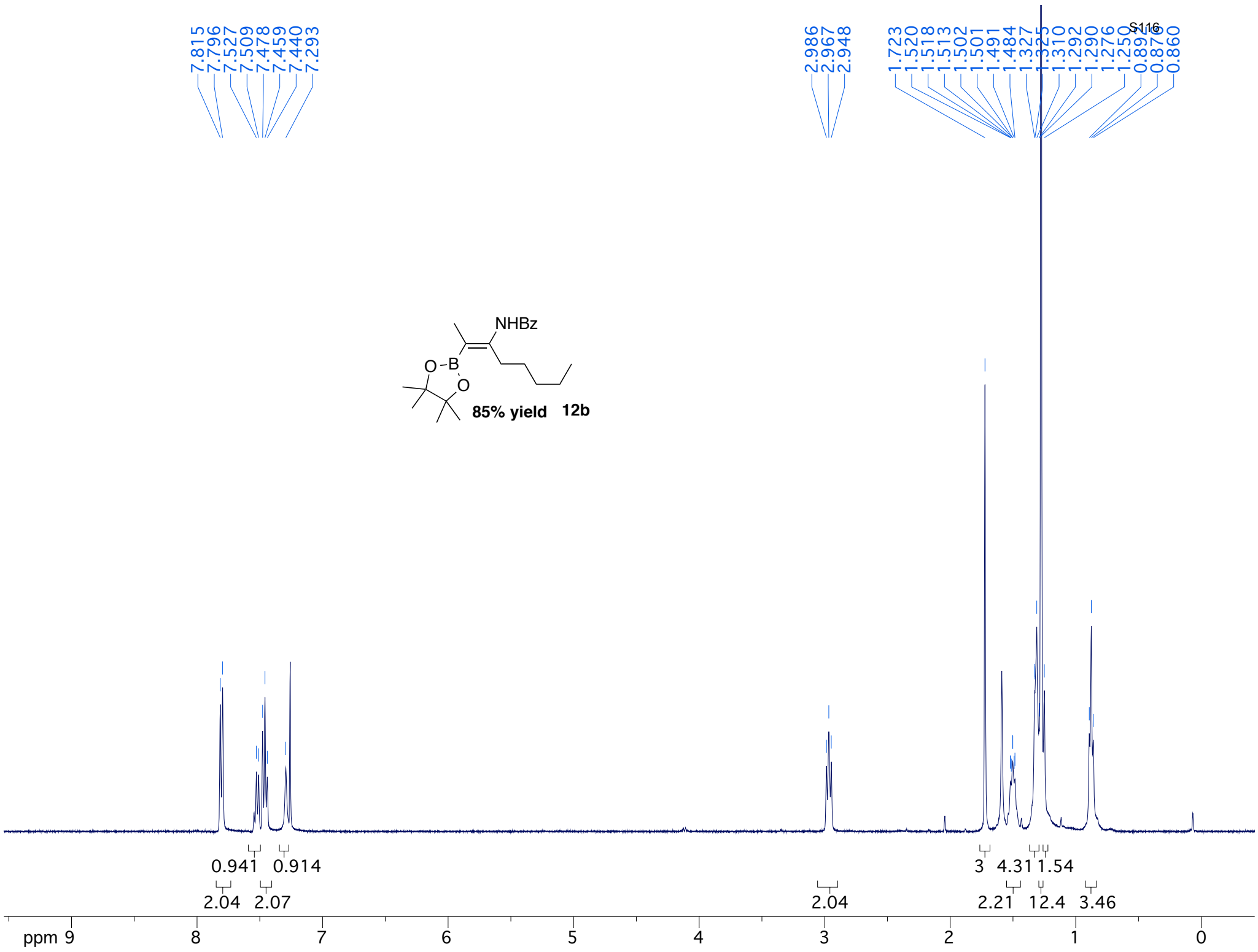


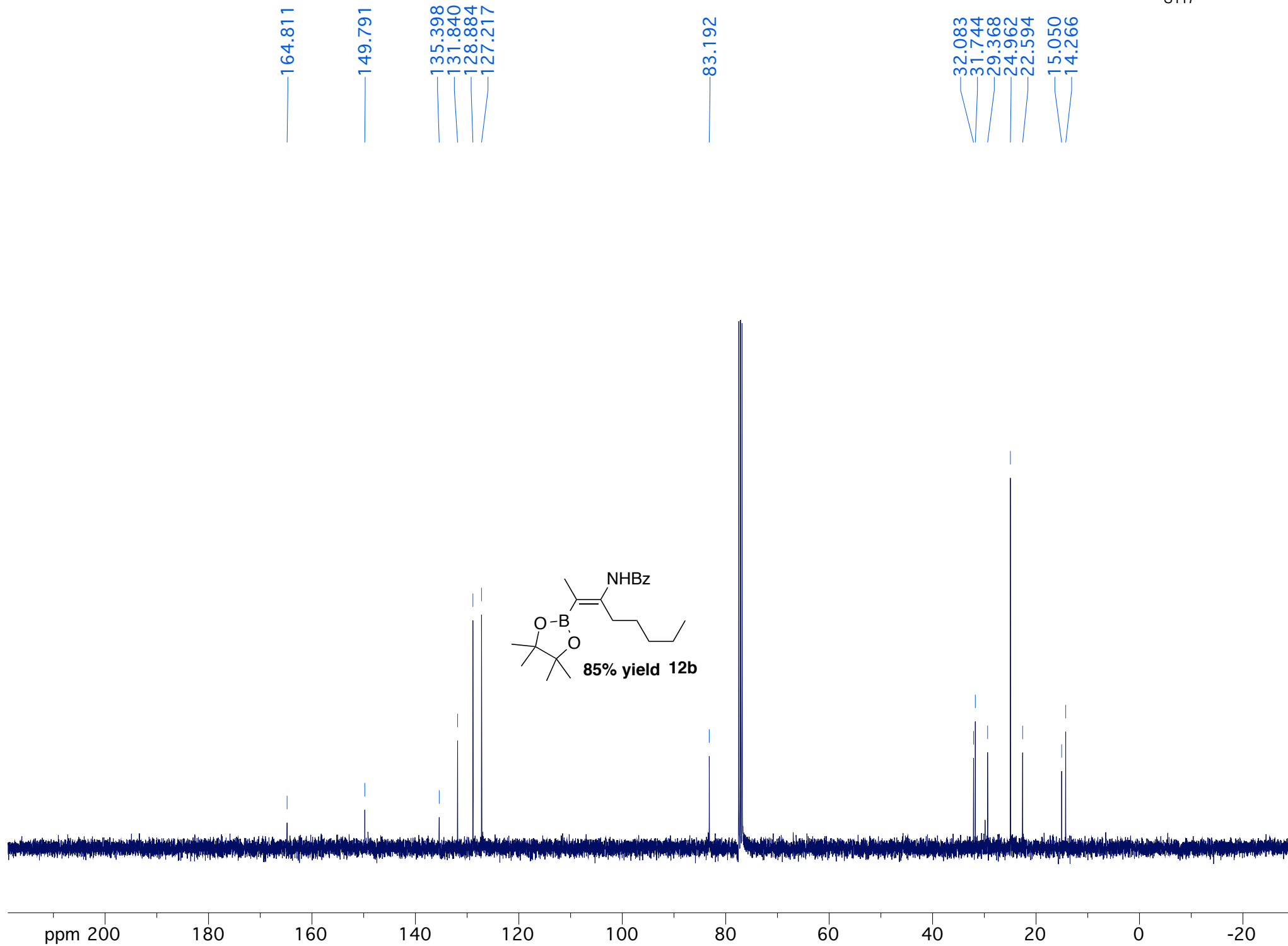


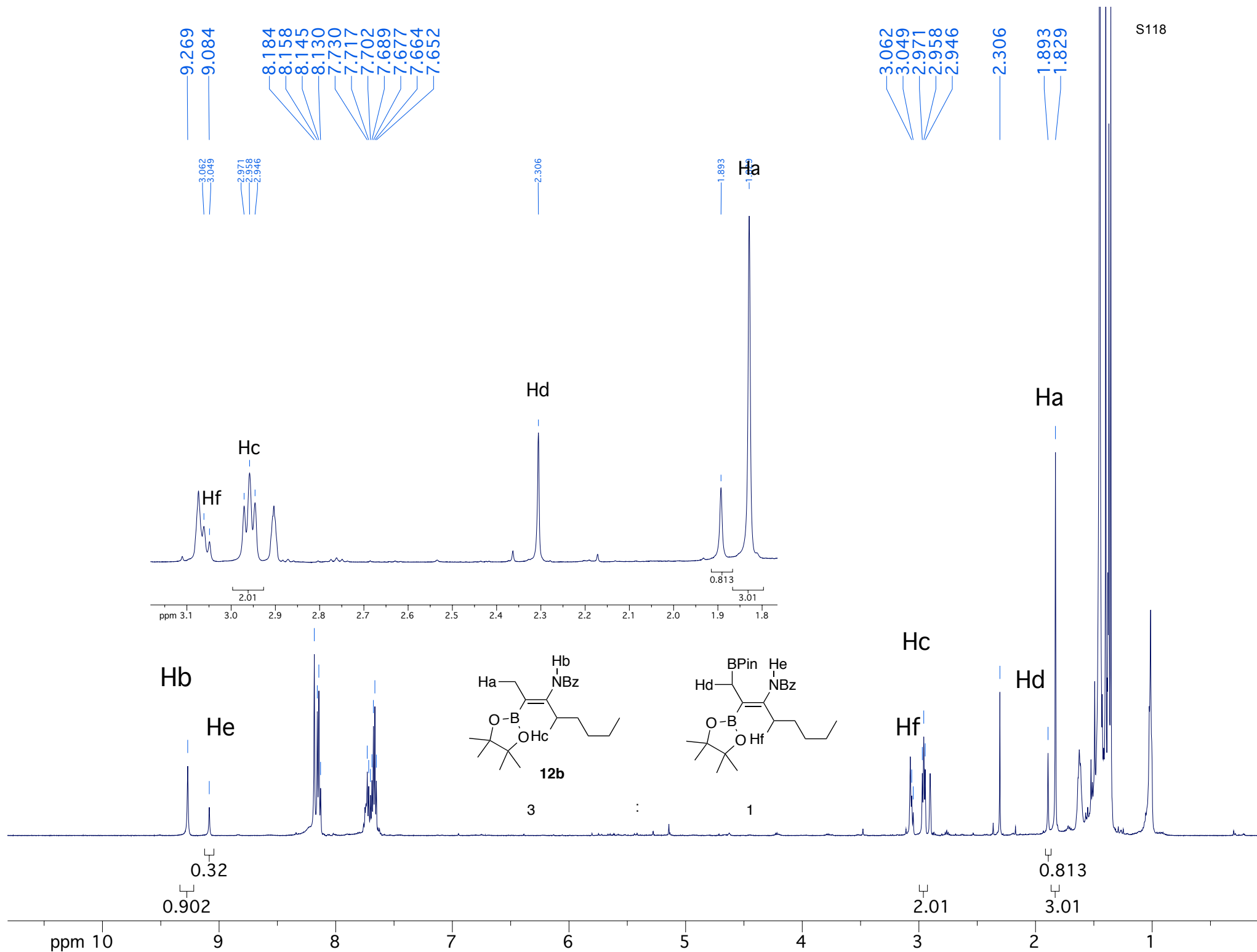


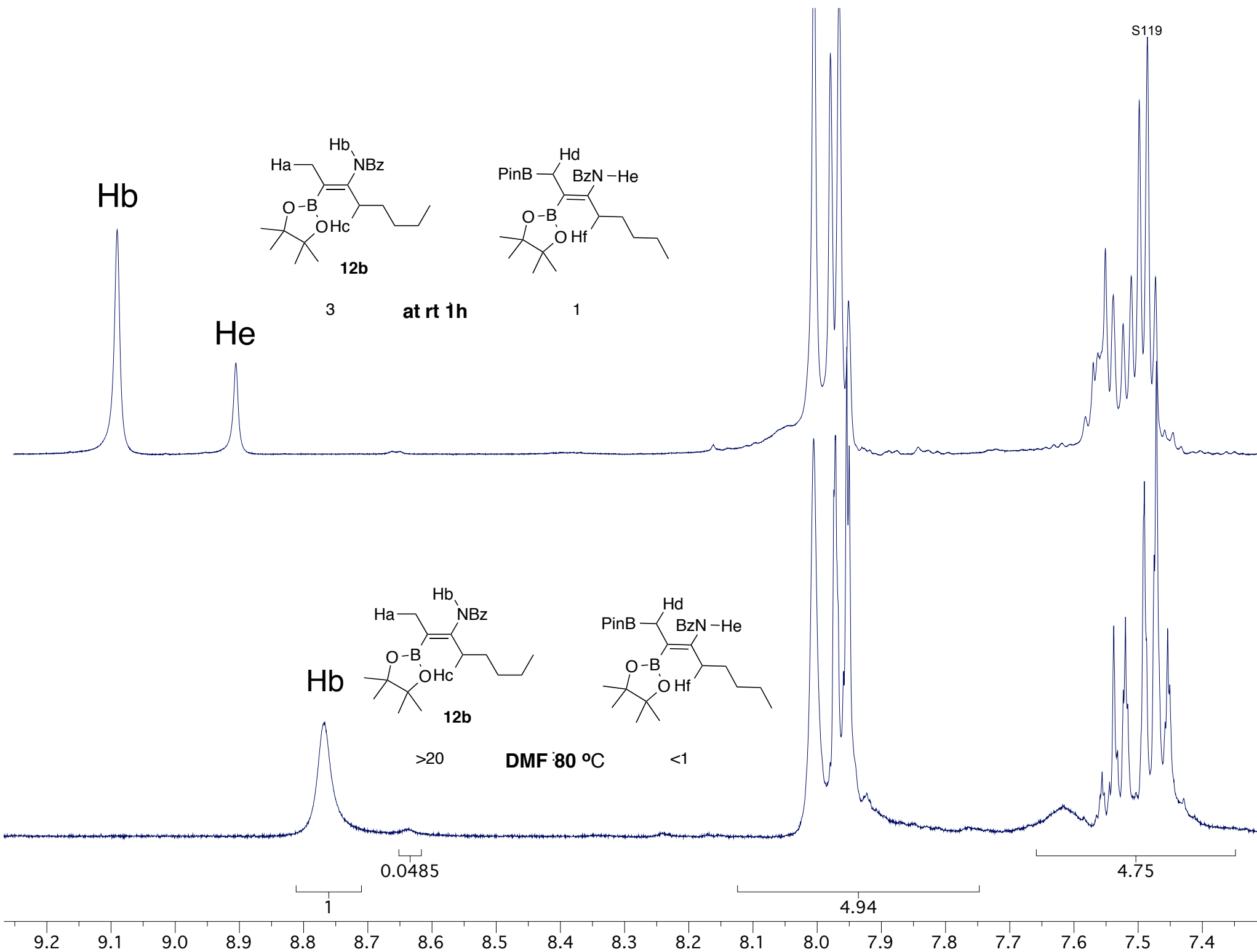
S115

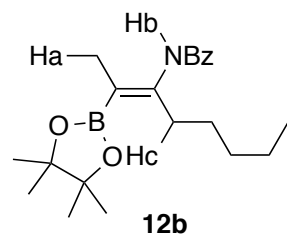






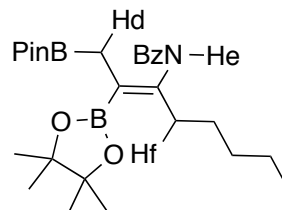




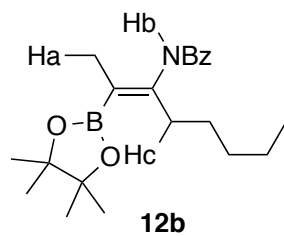
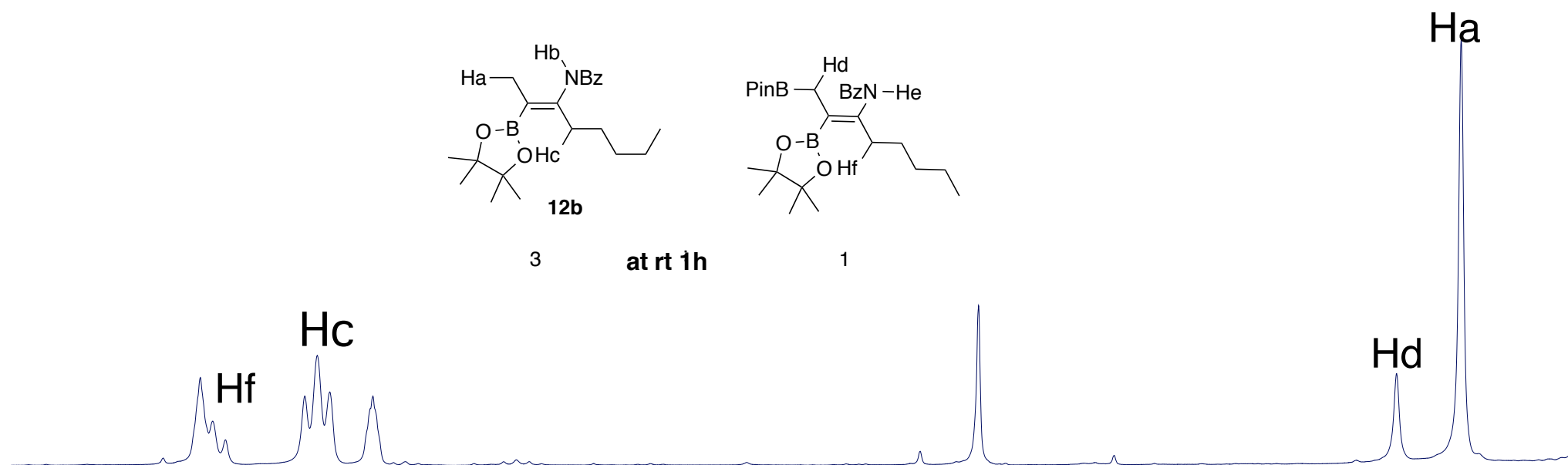


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at rt 1h

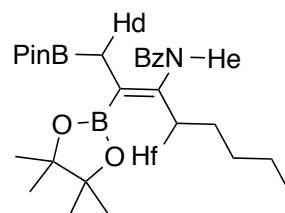


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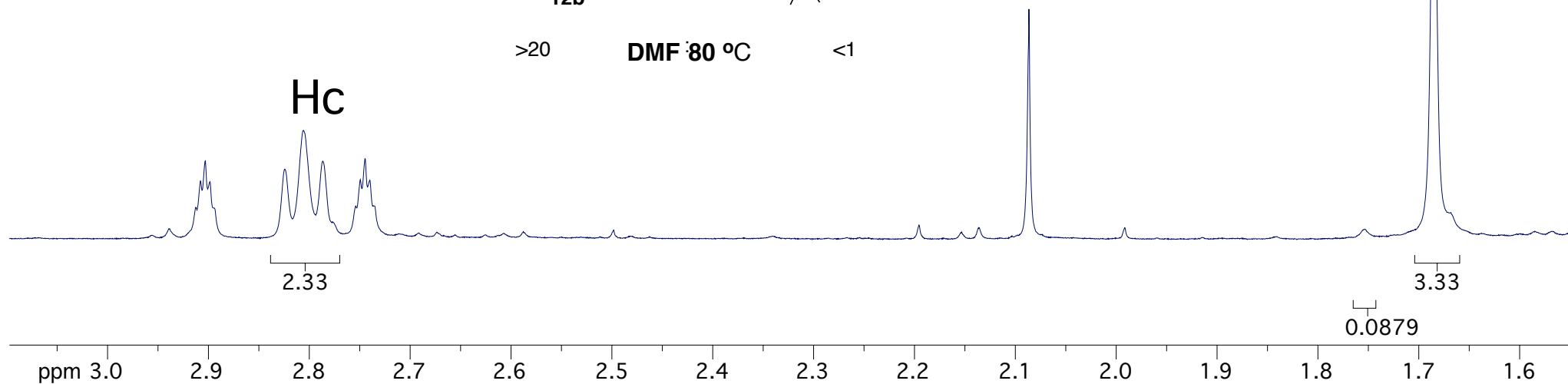


&gt;20

DMF 80 °C



&lt;1

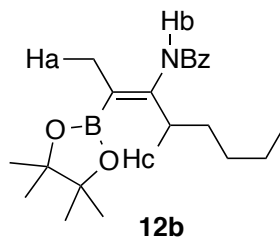




2.898  
2.886  
2.807  
2.795  
2.783

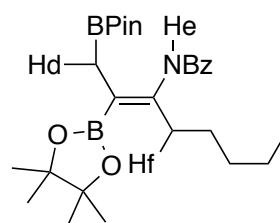
1.730  
1.666

Ha

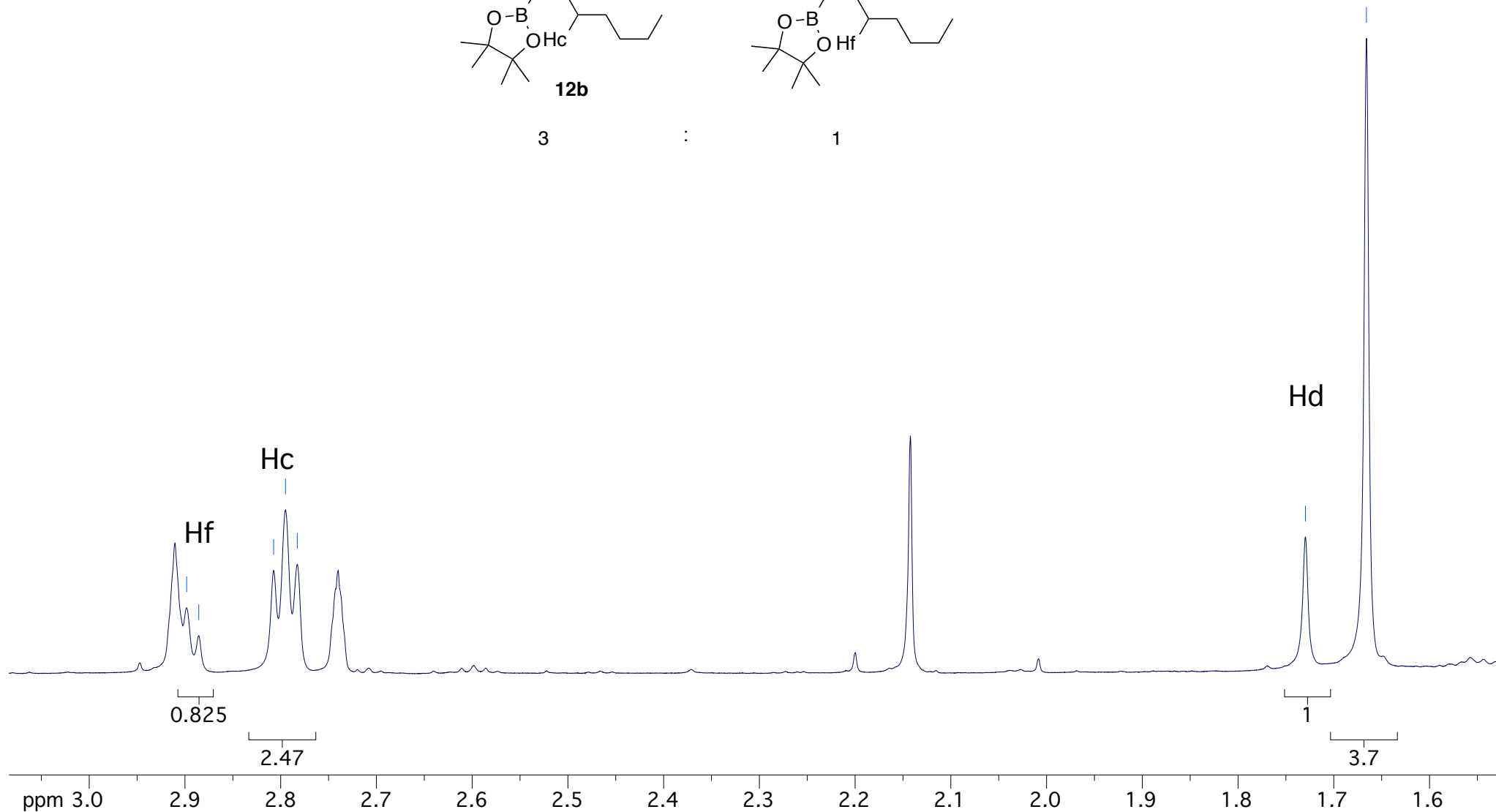


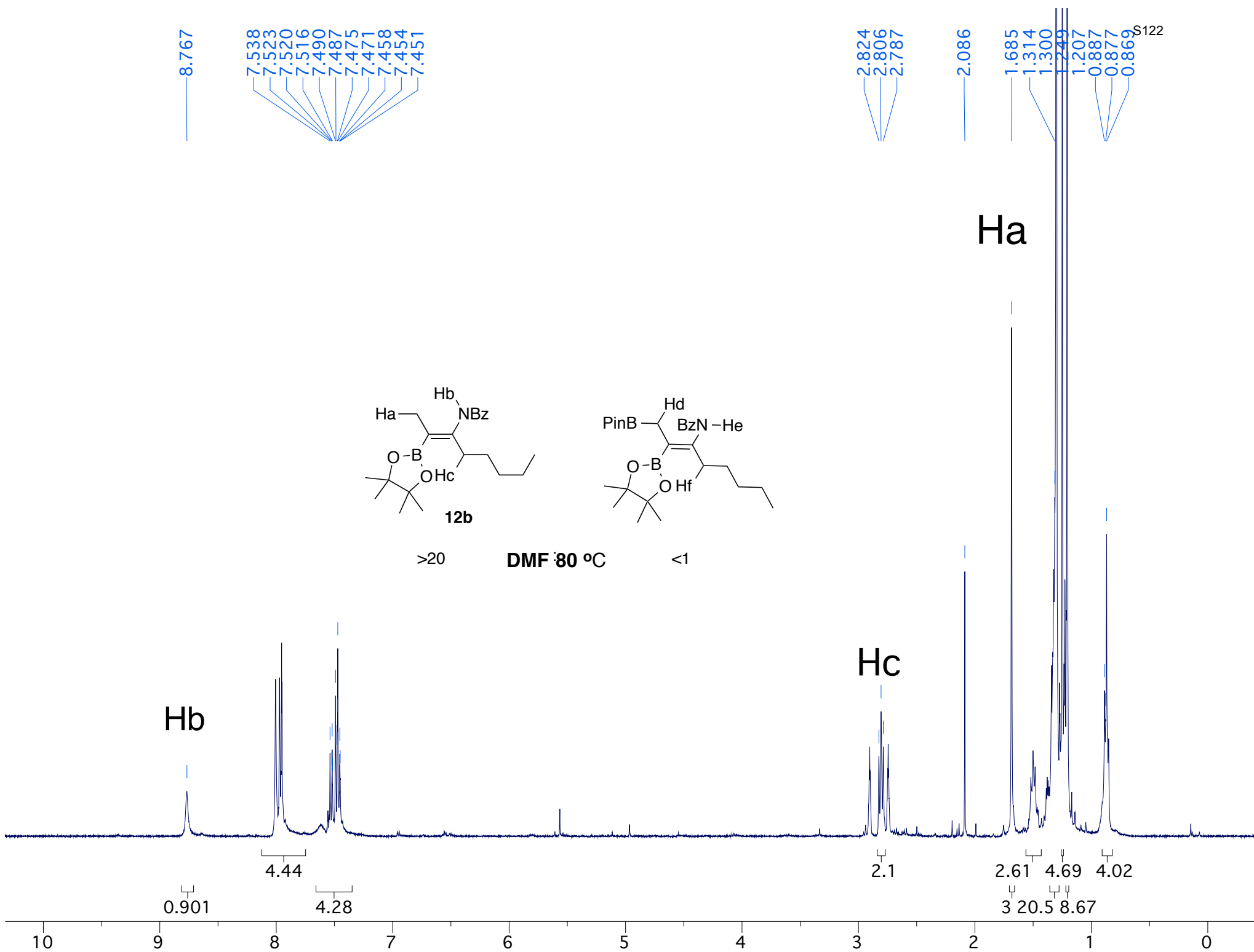
3

:



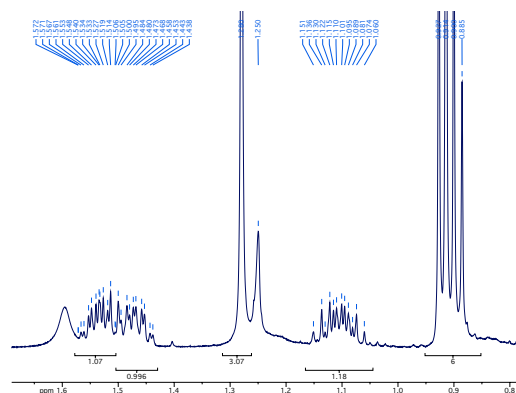
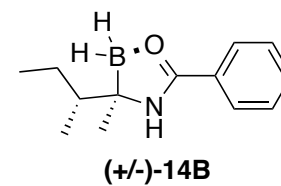
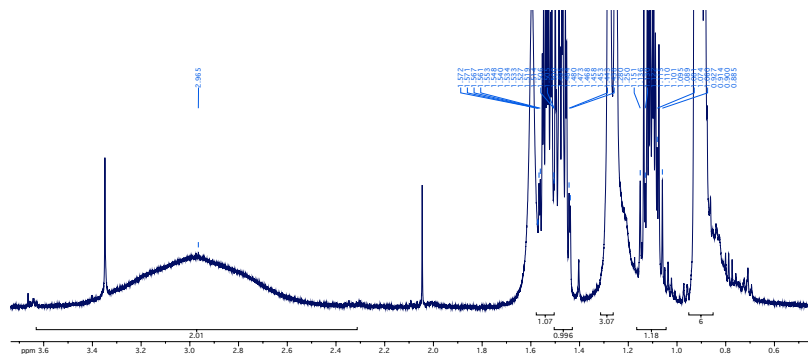
1





7.854  
7.851  
7.837  
7.834  
7.659  
7.657  
7.655  
7.642  
7.629  
7.627  
7.625  
7.529  
7.513  
7.498  
7.147

2.965  
1.572  
1.571  
1.567  
1.561  
1.553  
1.548  
1.540  
1.534  
1.533  
1.527  
1.519  
1.514  
1.506  
1.505  
1.495  
1.484  
1.480  
1.473  
1.468  
1.458  
1.453  
1.443  
1.438  
1.280  
1.250  
1.151  
1.136  
1.130  
1.122  
1.115  
1.110  
1.101  
1.095  
1.089  
1.081  
1.074  
1.060  
0.923  
0.914  
0.900  
0.885

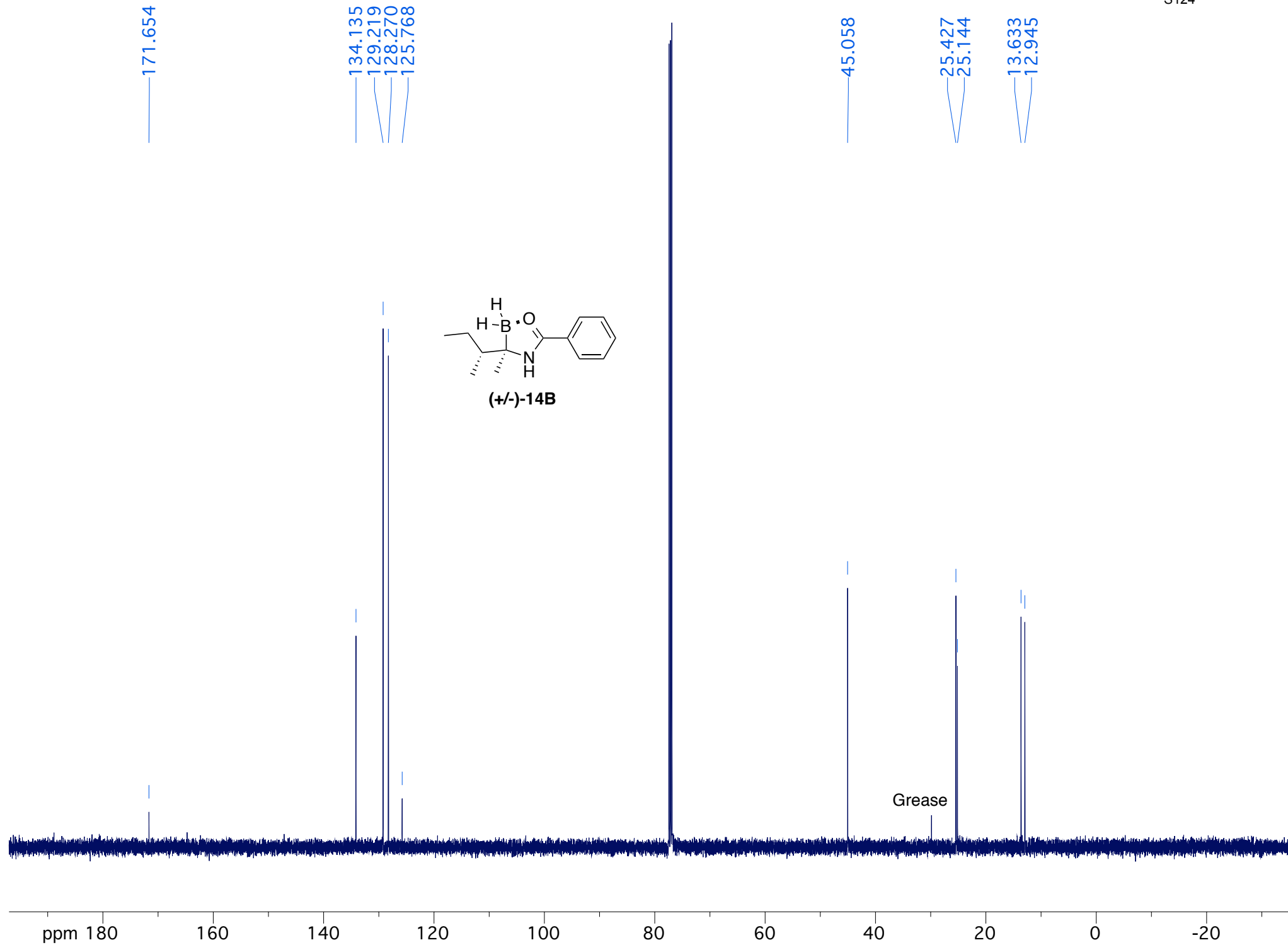


0.881 0.883  
1.78 1.79

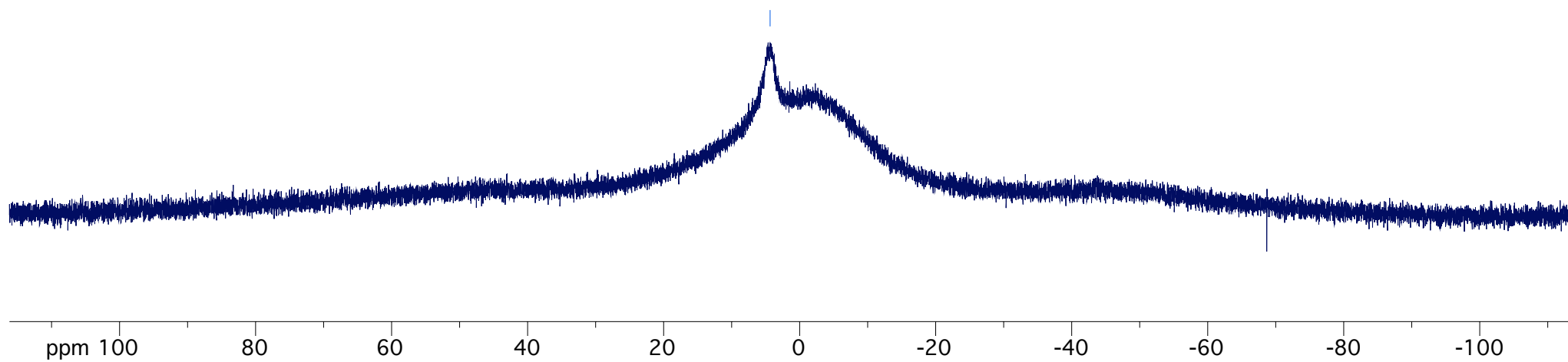
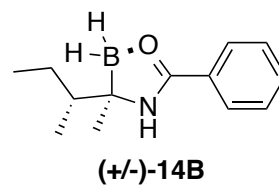
2.01

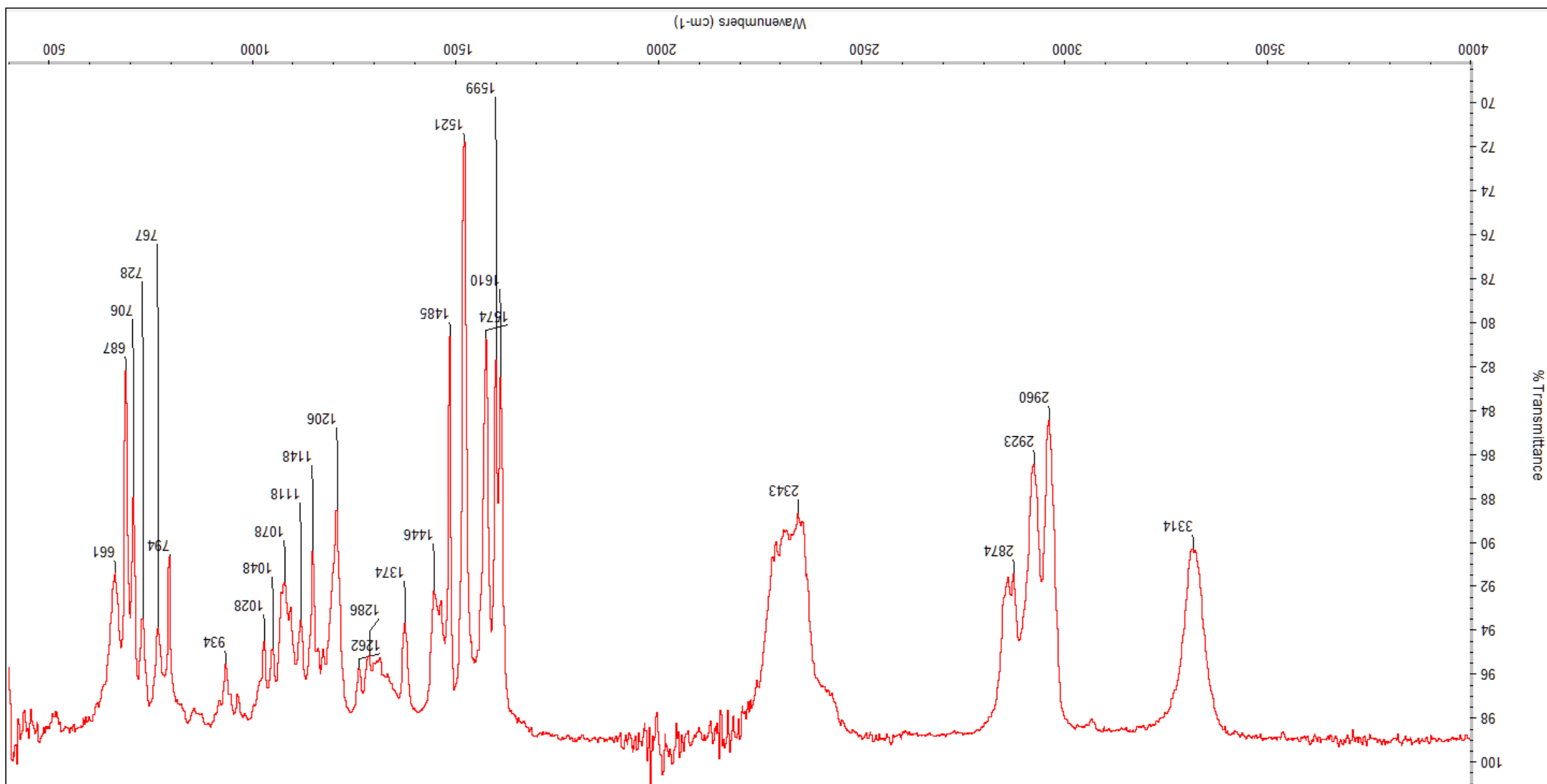
1.07 3.07 6  
0.996 1.18

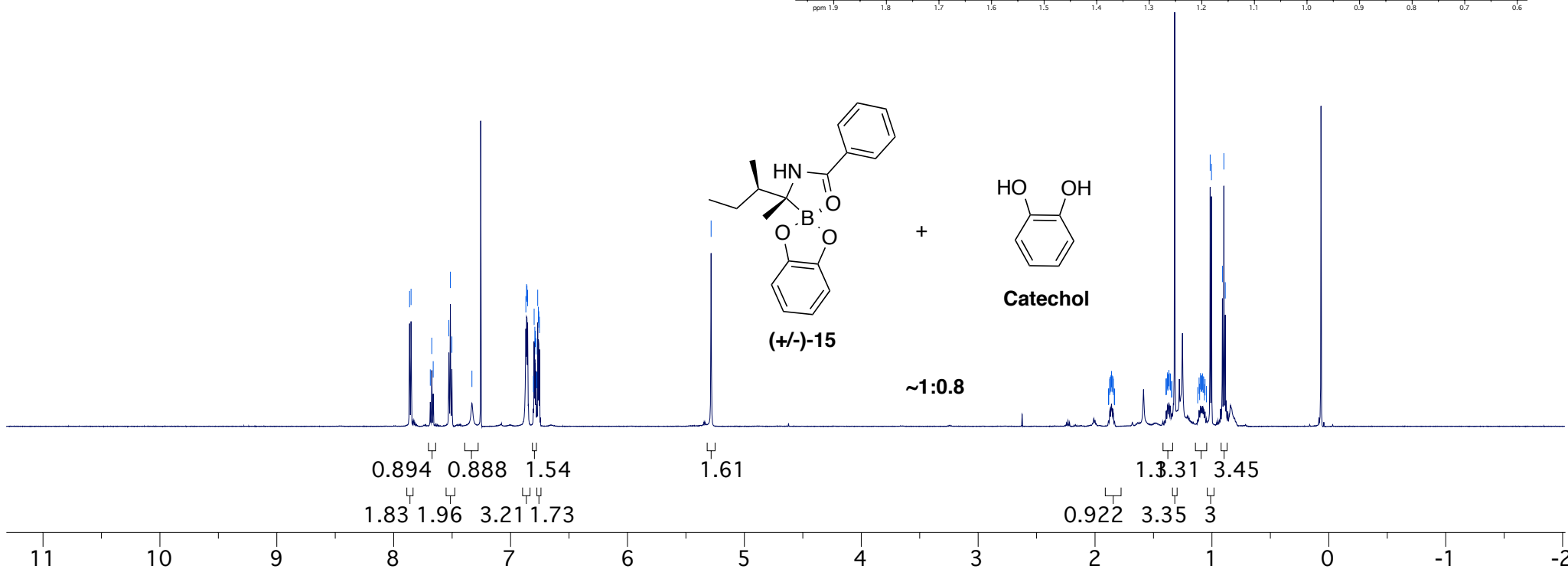
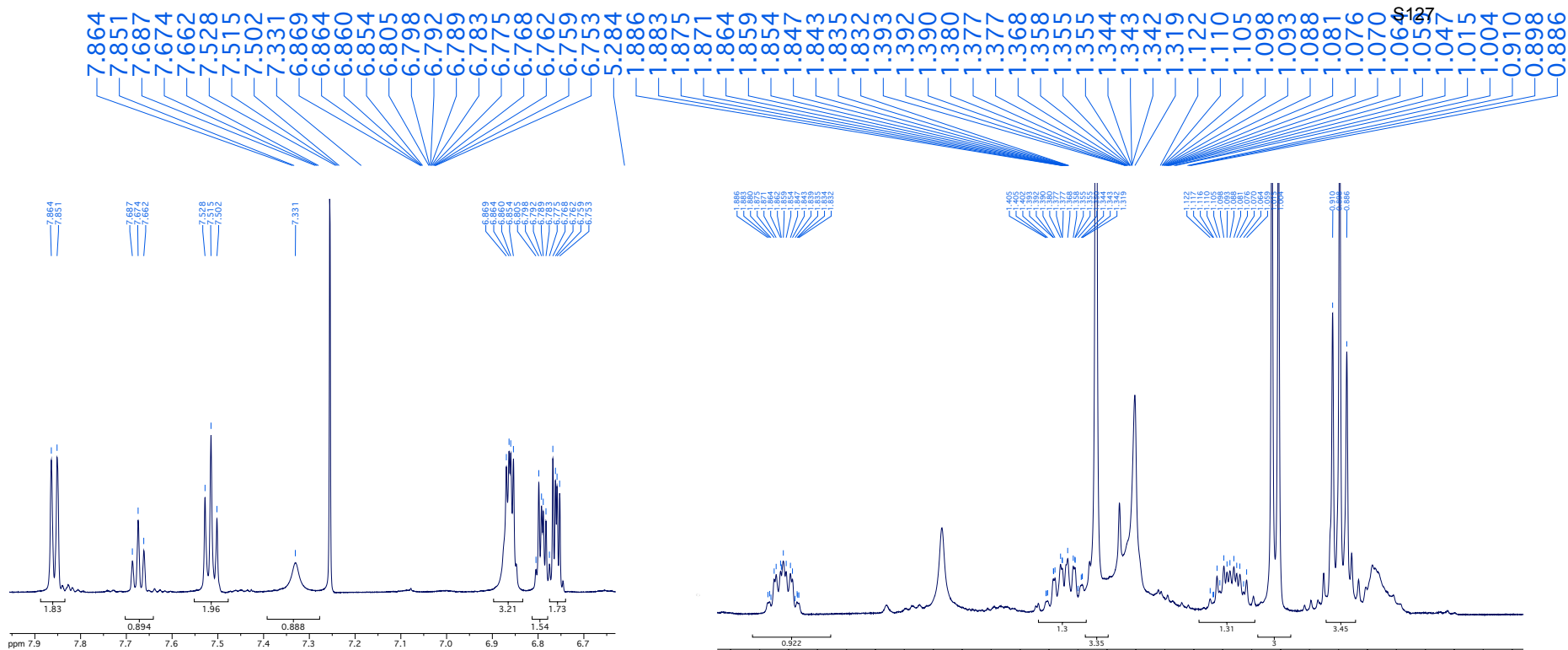
ppm 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

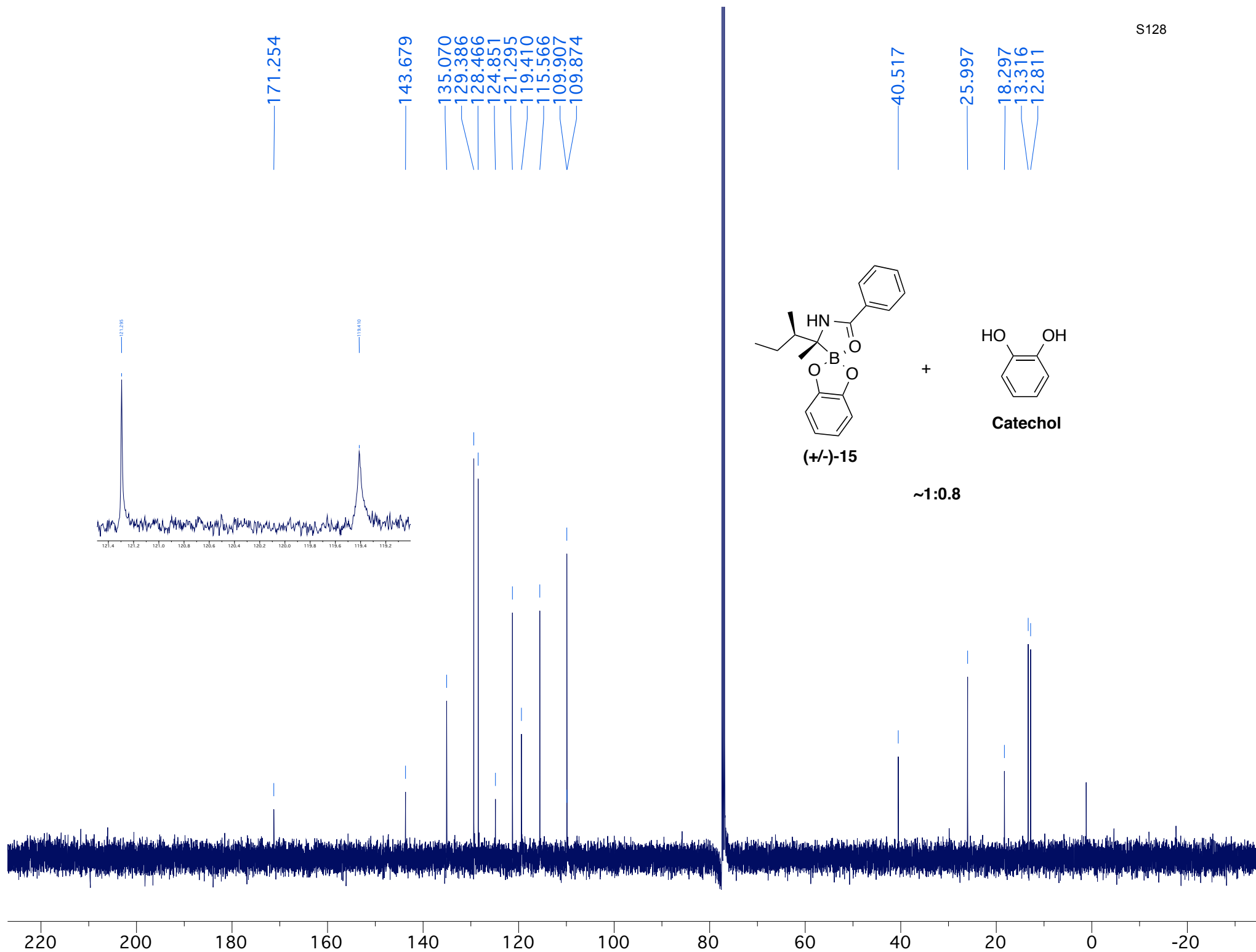


4.346



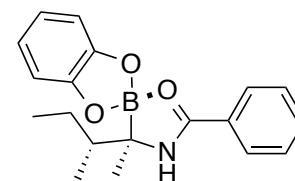




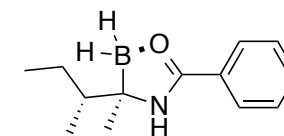




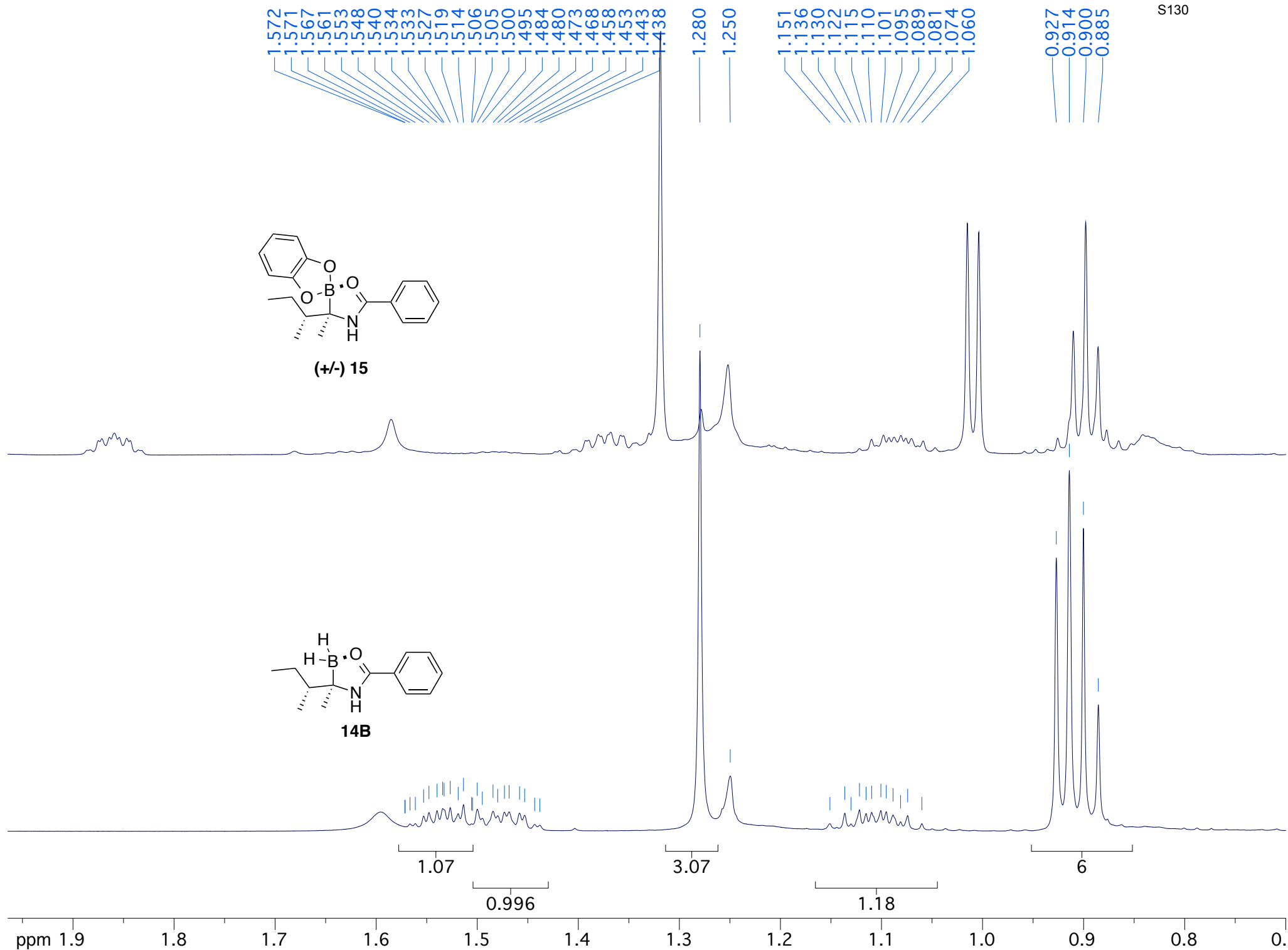
S129

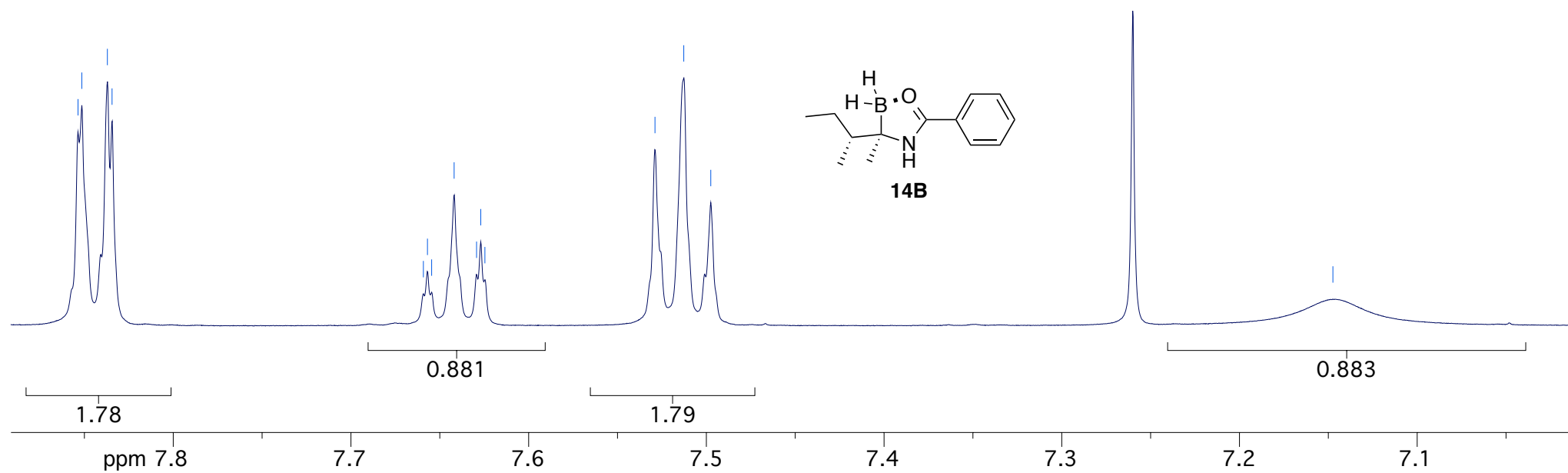
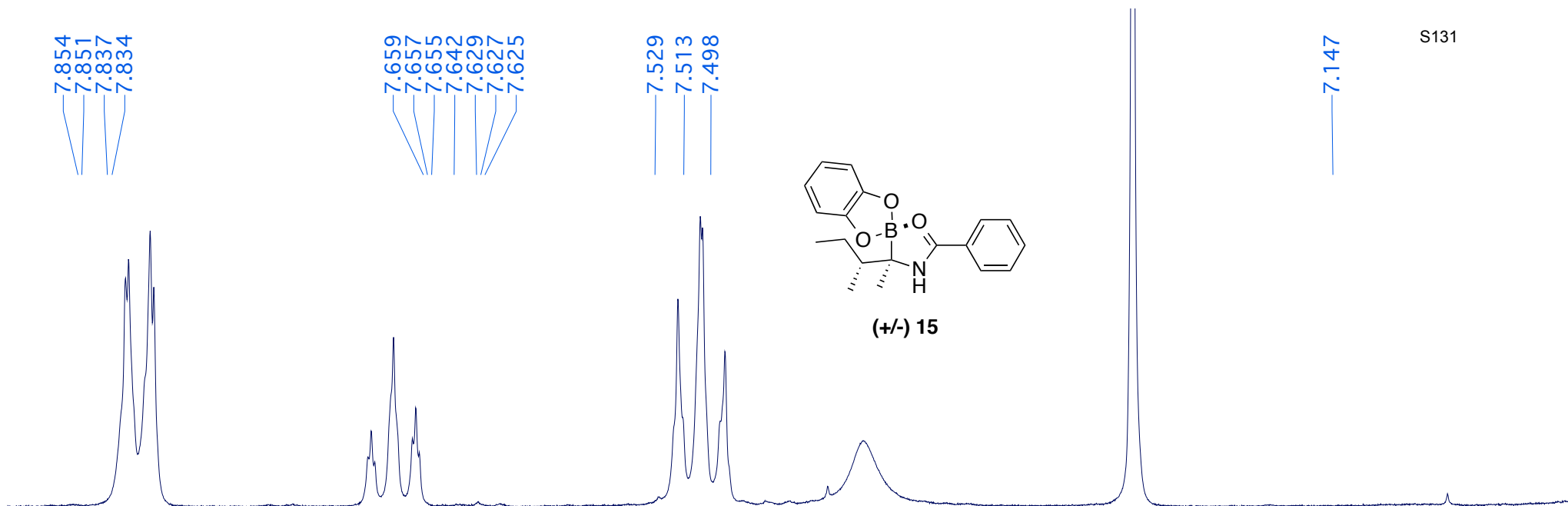
**(+/-) 15**

2.965

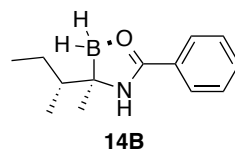
**14B**

2.01



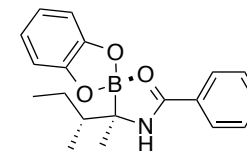


17.656  
5.104

**14B**<sup>11</sup>B NMR 5.10 ppm (toluene)

1.8 equiv. catechol

Toluene, 80 °C

**(+/-) 15**<sup>11</sup>B NMR 17.66 ppm (toluene)