# Rh(III)-Catalyzed Intramolecular Redox-Neutral Cyclization of Alkenes via C-H Activation†

## (Supporting Information)

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## CONTENTS:

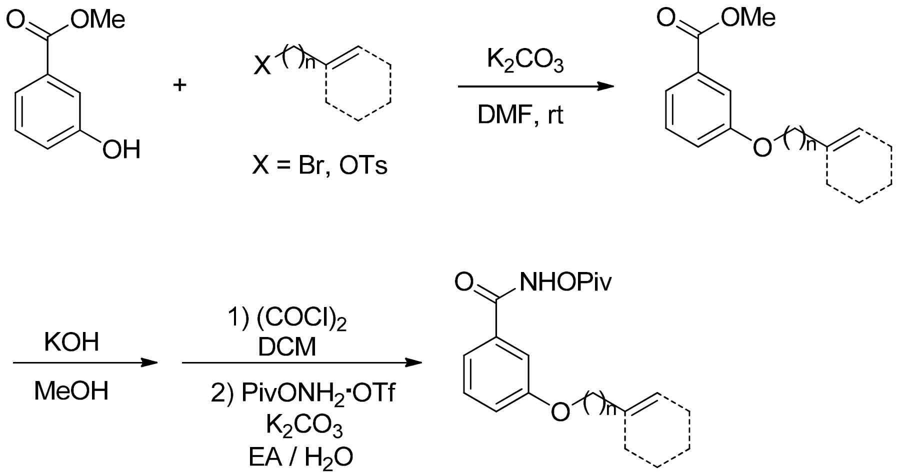
## 1. General Information.

All reactions were carried out in flame-dried reaction vessels with Teflon screw caps under argon. All new compounds were fully characterized. NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or on a Varian Associated, Varian 600 unity plus. ESI mass spectra were recorded on a Bruker Daltonics MicroTof. $[Cp^*RhCl_2]_2$, CsOPiv were purchased from Sigma-Aldrich. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The configuration of compounds **2d** and **2f** were determined by NOE.

## 2. Experimental Procedures and Characterization of Substrates

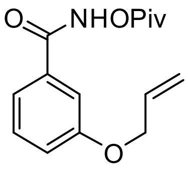
**1a-1f** were generated according to the following route:

Route A:



**1a-1f**

### 3-(Allyloxy)-*N*-(pivaloyloxy)benzamide (1a)

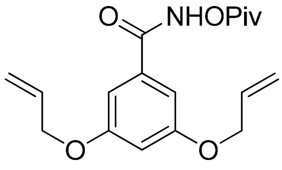


**1a**

To a solution of 3-(allyloxy)benzoic acid[1](891 mg, 5.00 mmol, 1.00 eq) in dry $CH_2Cl_2$ (17 mL) was added oxalylchloride (515 µL, 6.00 mmol, 1.20 eq) at 0 °C under Argon followed by the addition of a catalytic amount of DMF (2 drops). The reaction was stirred for 4 h at rt. The solvent was removed under reduced pressure to afford the crude acid chloride, which was directly engaged in the next step.

*O*-pivaloylhydroxamine (1.60 g, 6.00 mmol, 1.20 eq) was added to a biphasic mixture of $Na_2CO_3$ (1.06 g, 10.0 mmol, 2.00 eq) in EtOAc (33 mL) and $H_2O$ (17 mL). The mixture was cooled to 0 °C, whereupon the unpurified acid chloride was added dropwise as a solution in EtOAc (5 mL). The reaction was allowed to reach rt overnight. After the separation of the organic layer, the aqueos layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography on silica (Pentane:EtOAc, 5:1) to afford 1.27 g (92%) of **1a** as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 9.43 (brs, 1 H), 7.31 – 7.20 (m, 3 H), 7.03 (dt, *J* = 6.8, 2.4 Hz, 1 H), 6.08 – 5.87 (m, 1 H), 5.39 – 5.31 (m, 1 H), 5.26 – 5.21 (m, 1 H), 4.49 (dt, *J* = 5.3, 1.5 Hz, 2 H), 1.29 (s, 9 H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 176.95, 166.47, 158.77, 132.61, 132.06, 129.80, 119.76, 119.45, 118.01, 113.21, 68.87, 38.42, 26.99. **HRMS** m/z (ESI) calcd for **$C_{15}H_{19}NO_4Na$** (M + Na)$^+$ 300.1212, found 300.1209.

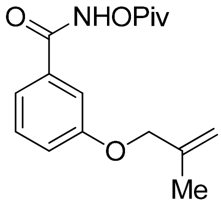
### 3,5-Bis(allyloxy)-*N*-(pivaloyloxy)benzamide (1b)



**1b**

According to the route A, **1b** was synthesized as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 9.38 (brs, 1H), 6.93 (d, *J* = 2.3 Hz, 2 H), 6.65 (t, *J* = 2.3 Hz, 1 H), 6.11 – 5.93 (m, 2 H), 5.47 – 5.35 (m, 2 H), 5.33 – 5.24 (m, 2 H), 4.52 (dt, *J* = 5.3, 1.4 Hz, 4 H), 1.35 (s, 9 H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 176.95, 166.39, 159.84, 132.65, 132.57, 118.06, 106.35, 106.08, 69.04, 38.43, 27.00. **ATR-FTIR** (cm$^{-1}$): **HRMS** m/z (ESI) calcd for **$C_{18}H_{23}NO_5Na$** (M + Na)$^+$ 356.1468, found 356.1456.

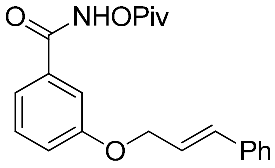
### 3-((2-Methylallyl)oxy)-*N*-(pivaloyloxy)benzamide (1c)



**1c**

According to the route A, **1c** was synthesized as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 9.58 (brs, 1 H), 7.47 – 7.28 (m, 3 H), 7.18 – 7.04 (m, 1 H), 5.08 (s, 1 H), 4.99 (s, 1 H), 4.44 (s, 2 H), 1.81 (s, 3 H), 1.34 (s, 9 H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 177.00, 166.47, 158.93, 140.25, 132.04, 129.76, 119.70, 119.44, 113.34, 113.00, 71.78, 38.42, 26.98, 19.32. **HRMS** m/z (ESI) calcd for **$C_{16}H_{21}NO_4Na$** (M + Na)$^+$ 314.1363, found 314.1367.

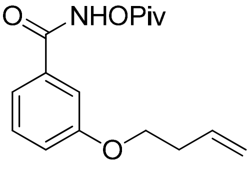
### 3-(cinnamyloxy)-*N*-(pivaloyloxy)benzamide (1d)



**1d**

According to the route A, **1d** was synthesized as a white solid: $^1$H NMR (300 MHz, $CDCl_3$) δ 9.46 (brs, 1H), 7.40 – 7.13 (m, 8H), 7.05 (dt, *J* = 7.3, 2.2 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.76 – 4.51 (m, 2H), 1.27 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 176.92, 166.44, 158.81, 136.19, 133.38, 132.10, 129.85, 128.55, 127.96, 126.56, 123.65, 119.76, 119.51, 113.25, 68.73, 38.41, 26.98. **HRMS** m/z (ESI) calcd for **$C_{21}H_{23}NO_4Na$** (M + Na)$^+$ 376.1525, found 3376.1519.

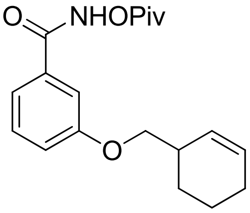
### 3-(But-3-en-1-yloxy)-*N*-(pivaloyloxy)benzamide (1e)



**1e**

According to the route A, **1e** was synthesized as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 9.35 (brs, 1 H), 7.36 – 7.32 (m, 3 H), 7.12 – 7.06 (m, 1 H), 6.02 – 5.76 (m, 1 H), 5.26 – 5.01 (m, 2 H), 4.04 (t, *J* = 6.7 Hz, 2 H), 2.59 – 2.51 (m, 2 H), 1.36 (s, 9 H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 177.00, 166.60, 159.18, 134.10, 132.11, 129.83, 119.62, 119.31, 117.23, 113.07, 67.41, 38.45, 33.47, 27.01. **HRMS** m/z (ESI) calcd for **$C_{16}H_{21}NO_4Na$** $(M + Na)^+$ 314.1363, found 314.1363.

### 3-(Cyclohex-2-en-1-ylmethoxy)-*N*-(pivaloyloxy)benzamide (1f)

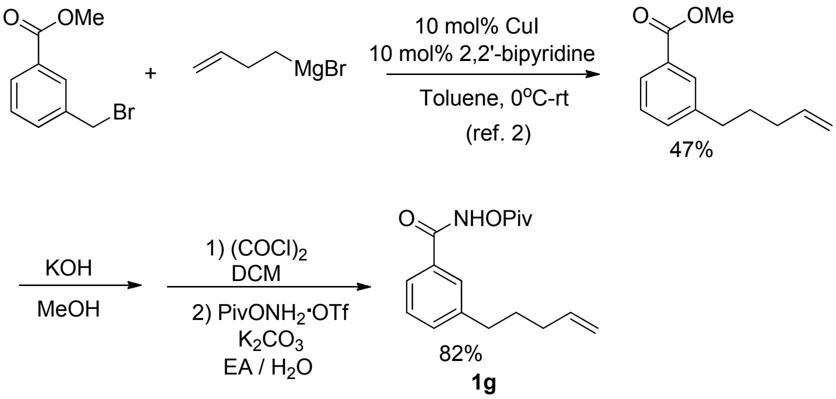


**1f**

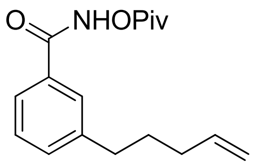
According to the route A, **1f** was synthesized as a white solid: **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 9.46 (brs, 1 H), 7.38 – 7.27 (m, 3 H), 7.09 – 7.06 (m, 1 H), 5.85 – 5.78 (m, 1 H), 5.68 – 5.64 (m, 1 H), 3.93 – 3.76 (m, 2 H), 2.68 – 2.54 (m, 1 H), 2.07 – 1.99 (m, 2 H), 1.93 – 1.82 (m, 1 H), 1.75 – 1.72 (m, 1 H), 1.65 – 1.52 (m, 1 H), 1.52 – 1.39 (m, 1 H), 1.35 (s, 9 H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 176.96, 166.59, 159.40, 132.05, 129.76, 129.43, 127.17, 119.57, 119.20, 113.04, 72.05, 38.42, 35.26, 26.99, 25.70, 25.23, 20.64. **HRMS** m/z (ESI) calcd for **$C_{19}H_{25}NO_4Na$** $(M + Na)^+$ 354.1676, found 354.1674.

**1g** was generated according to the following route:

Route B:



### 3-(Pent-4-en-1-yl)-*N*-(pivaloyloxy)benzamide (1g)

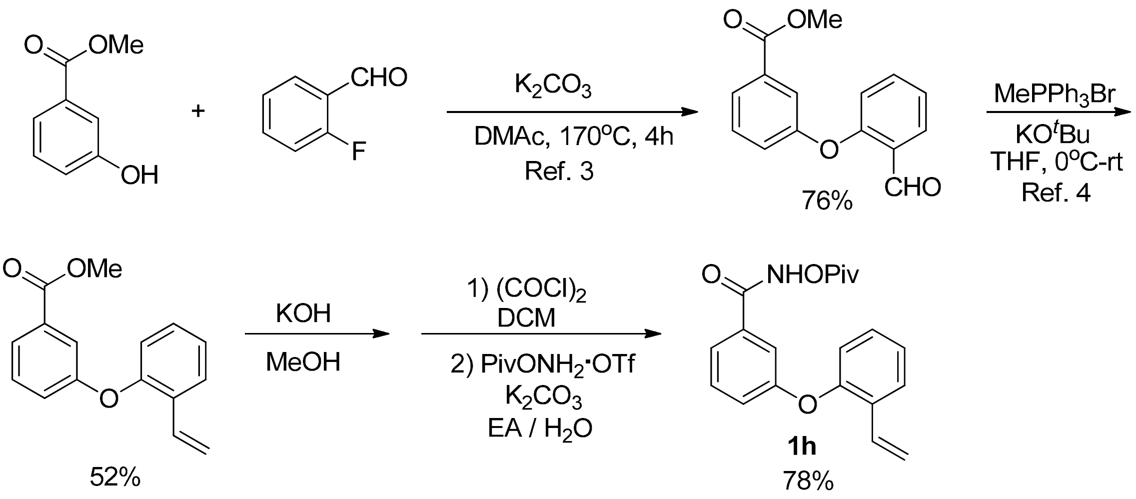


**1g**

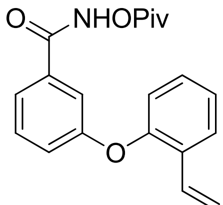
According to the route B, **1g** was synthesized as a white solid: $^1$H NMR (300 MHz, CDCl$_3$) δ 9.34 (brs, 1H), 7.72 – 7.51 (m, 2H), 7.36 (d, *J* = 5.8 Hz, 2H), 5.91 – 5.71 (m, 1H), 5.16 – 4.88 (m, 2H), 2.72 – 2.60 (m, 2H), 2.17 – 1.97 (m, 2H), 1.72 (p, *J* = 7.5 Hz, 2H), 1.36 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 177.06, 167.00, 143.33, 138.18, 132.91, 130.85, 128.72, 127.54, 124.73, 115.01, 38.44, 35.02, 33.13, 30.35, 27.01. **HRMS** m/z (ESI) calcd for **$C_{17}H_{23}NO_3Na$** $(M + Na)^+$ 312.1576, found 312.1570.

**1h** was generated according to the following route:

Route C:



### *N*-(Pivaloyloxy)-3-(2-vinylphenoxy)benzamide (1h)

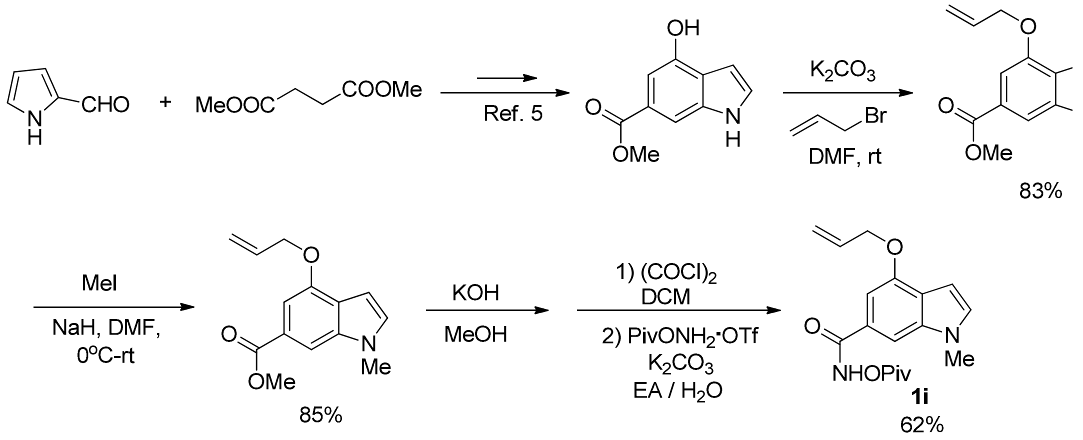


**1h**

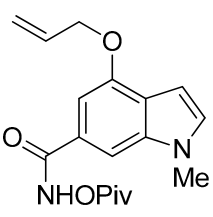
According to the route C, **1g** was synthesized as a white solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 9.22 (brs, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.13 – 7.02 (m, 2H), 6.89 – 6.78 (m, 2H), 5.72 (ddd, *J* = 17.7, 4.0, 1.2 Hz, 1H), 5.20 (dd, *J* = 11.1, 1.2 Hz, 1H), 1.28 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 176.93, 158.49, 152.50, 132.50, 130.53, 130.22, 129.26, 126.86, 124.92, 121.55, 121.23, 120.63, 116.19, 115.93, 38.43, 26.99. **HRMS** m/z (ESI) calcd for **$C_{20}H_{21}NO_4Na$** $(M + Na)^+$ 362.1368, found 362.1363.

**1i** was generated according to the following route:

Route D:



### 4-(Allyloxy)-1-methyl-*N*-(pivaloyloxy)-1H-indole-6-carboxamide (1i)

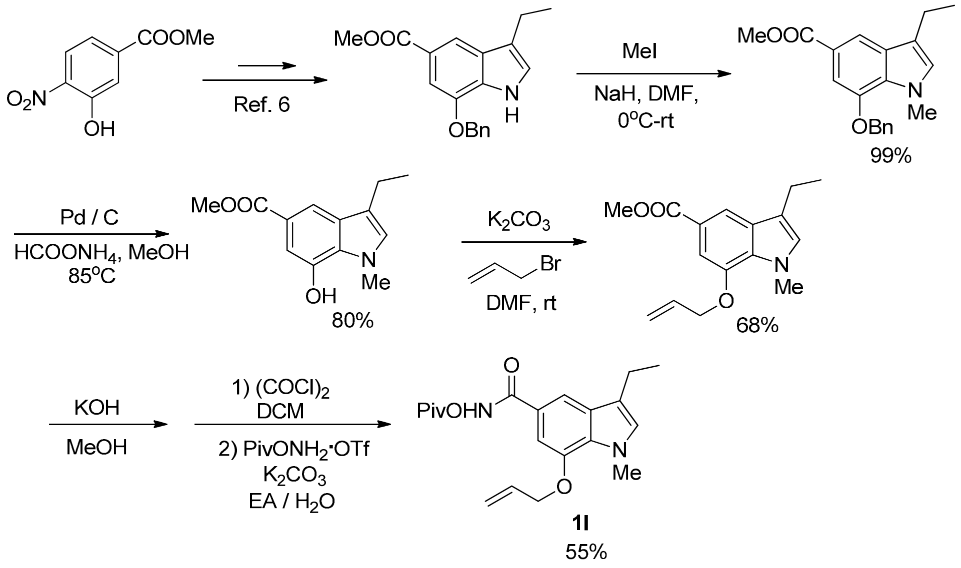


**1i**

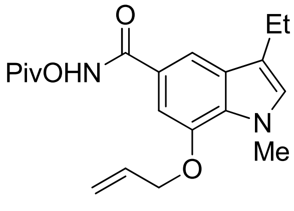
According to the route D, **1i** was synthesized as a white solid: $^1$H NMR (300 MHz, $CDCl_3$) δ 9.53 (brs, 1H), 7.48 (s, 1H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.91 (s, 1H), 6.65 – 6.58 (m, 1H), 6.17 – 6.06 (m, 1H), 5.47 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.31 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.68 (d, *J* = 5.2 Hz, 2H), 3.80 – 3.73 (m, 3H), 1.38 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 177.44, 168.24, 152.11, 137.17, 133.15, 130.24, 124.48, 122.74, 117.53, 103.46, 99.04, 99.01, 68.89, 38.47, 33.15, 27.05. HRMS m/z (ESI) calcd for $C_{18}H_{22}N_2O_4Na$ $(M + Na)^+$ 353.1477, found 353.1472.

**1j** was generated according to the following route:

Route E:



### 7-(Allyloxy)-3-ethyl-1-methyl-*N*-(pivaloyloxy)-1H-indole-5-carboxamide (1j)

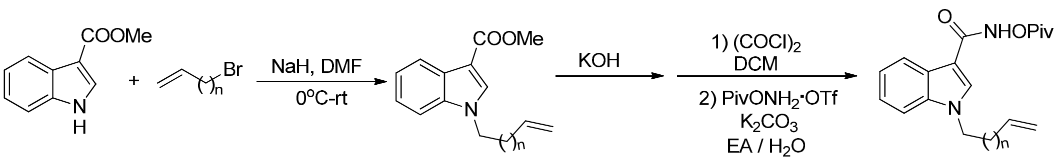


**1j**

According to the route E, **1j** was synthesized as a white solid: $^{1}$H NMR (400 MHz, CDCl$_3$) δ 9.45 (brs, 1H), 7.68 (d, *J* = 1.4 Hz, 1H), 7.08 (d, *J* = 1.2 Hz, 1H), 6.75 (brs, 1H), 6.10 (ddt, *J* = 17.2, 10.5, 5.2 Hz, 1H), 5.44 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.30 (dq, *J* = 10.6, 1.3 Hz, 1H), 4.65 (dt, *J* = 5.2, 1.4 Hz, 2H), 4.02 (s, 3H), 2.71 (qd, *J* = 7.5, 0.8 Hz, 2H), 1.38 (s, 9H), 1.29 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.41, 168.45, 146.49, 132.95, 129.32, 129.07, 127.92, 121.51, 118.85, 117.54, 112.59, 102.38, 69.19, 38.44, 36.28, 27.05, 18.00, 14.55. **HRMS** m/z (ESI) calcd for **$C_{20}H_{26}N_2O_4Na$** (M + Na)$^+$ 381.1790, found 381.1785.

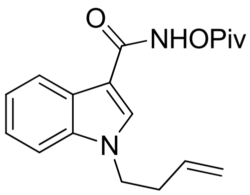
**1k-l** were generated according to the following route:

Route F:



**1k-l**

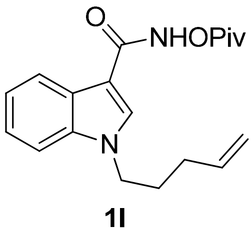
### 1-(but-3-en-1-yl)-*N*-(pivaloyloxy)-1H-indole-3-carboxamide (1k)



**1k**

According to the route F, **1k** was synthesized as a white solid: $^{1}$H NMR (300 MHz, CDCl$_3$) δ 8.69 (brs, 1H), 7.58 – 7.49 (m, 1H), 6.91 – 6.70 (m, 4H), 5.30 – 5.13 (m, 1H), 4.61 – 4.48 (m, 2H), 3.67 (t, *J* = 7.1 Hz, 2H), 2.08 (q, *J* = 7.0 Hz, 2H), 0.87 (s, 9H). $^{13}$C NMR (151 MHz, cdcl$_3$) δ 167.32, 159.05, 135.82, 128.91, 121.90, 121.66, 121.13, 121.03, 110.56, 99.36, 49.46, 47.90, 35.57, 31.93. **HRMS** m/z (ESI) calcd for **$C_{18}H_{22}N_2O_3Na$** (M + Na)$^+$ 337.1528, found 337.1523

### 1-(pent-4-en-1-yl)-*N*-(pivaloyloxy)-1H-indole-3-carboxamide (1l)



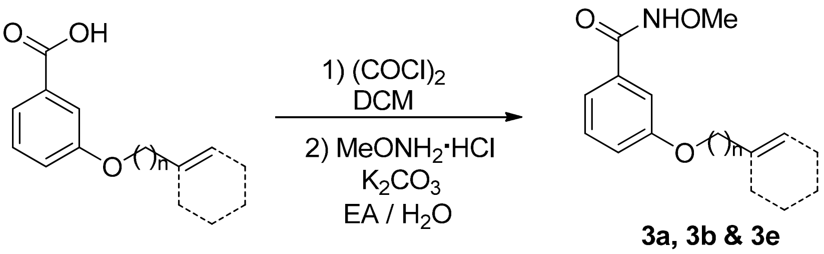
**1l**

According to the route F, **1l** was synthesized as a white solid: $^{1}$H NMR (300 MHz, CDCl$_3$) δ 8.74 (brs, 1H), 7.54 (dt, *J* = 6.0, 2.4

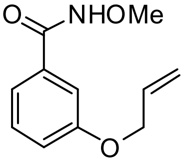
Hz, 1H), 6.89 – 6.65 (m, 4H), 5.25 (ddd, *J* = 17.5, 6.3, 3.4 Hz, 1H), 4.60 – 4.48 (m, 2H), 3.64 – 3.52 (m, 2H), 1.55 (q, *J* = 6.6 Hz, 2H), 1.43 (q, *J* = 7.0 Hz, 2H), 0.86 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 177.65, 165.64, 136.67, 136.38, 132.43, 125.60, 122.91, 122.01, 121.15, 116.12, 110.23, 106.69, 46.14, 38.45, 30.58, 28.68, 27.08. **HRMS** m/z (ESI) calcd for $\mathbf{C_{19}H_{24}N_2O_3Na}$ $(M + Na)^+$ 351.1685, found 351.1679.

**3a**, **3b** & **3e** were generated according to the following route:

Route G:



### 3-(Allyloxy)-*N*-methoxybenzamide (3a)



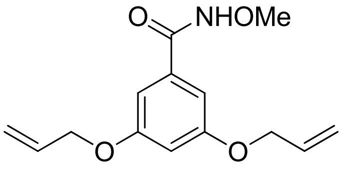
**3a**

To a solution of 3-(allyloxy)benzoic acid (4.45 g, 25.0 mmol, 1.0 eq) in dry $CH_2Cl_2$ (60 mL) was added oxalylchloride (2.6 mL, 30.0 mmol, 1.2 eq) at 0 °C under Argon followed by the addition of a catalytic amount of DMF (2 drops). The reaction was stirred for 4 h at rt. The solvent was removed under reduced pressure to afford the crude acid chloride, which was directly engaged in the next step.

Methoxylamine hydrochloride (2.3 g 27.5 mmol, 1.10 eq) was added to a biphasic mixture of $K_2CO_3$ (6.9 g, 50.0 mmol, 2.00 eq) in EtOAc (80 mL) and $H_2O$ (40 mL). The mixture was cooled to 0 °C, whereupon the unpurified acid chloride was added dropwise as a solution in EtOAc (5 mL). The reaction was allowed to reach rt overnight. After the separation of the organic layer, the aqueos layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude material was purified by column chromatography on silica (Pentane:EtOAc, 1:1) to afford 4.95 g (96%) of **3a** as a white solid: $^1$H NMR (400 MHz, $CDCl_3$) δ 9.20 (brs, 1H), 7.39 – 7.18 (m, 3H), 7.10 – 6.97 (m, 1H), 6.22 – 5.83 (m, 1H), 5.34 (dd, *J* = 46.0, 13.9 Hz, 2H), 4.54 (d, *J* = 4.3

Hz, 2H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.24, 158.73, 133.08, 132.68, 129.67, 119.02, 118.95, 117.92, 113.06, 68.85, 64.44. **HRMS** m/z (ESI) calcd for **$C_{11}H_{13}NO_3Na$** (M + Na)$^+$ 230.0793, found 230.0788.

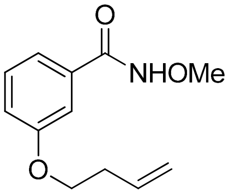
**3,5-Bis(allyloxy)-*N*-methoxybenzamide (3b)**



**3b**

According to the route G, **3b** was synthesized as a white solid: $^1$H NMR (400 MHz, $CDCl_3$) δ 9.05 (brs, 1H), 6.87 (d, *J* = 2.3 Hz, 2H), 6.61 (t, *J* = 2.3 Hz, 1H), 6.01 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 2H), 5.39 (dq, *J* = 17.3, 1.6 Hz, 2H), 5.28 (dq, *J* = 10.5, 1.3 Hz, 2H), 4.51 (dt, *J* = 5.3, 1.5 Hz, 4H), 3.85 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.78, 132.62, 117.98, 105.73, 105.54, 69.00, 64.46. **HRMS** m/z (ESI) calcd for **$C_{14}H_{17}NO_4Na$** (M + Na)$^+$ 286.1055, found 286.1050.

**3-(But-3-en-1-yloxy)-*N*-methoxybenzamide (3e)**

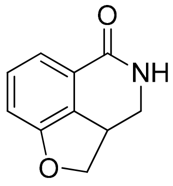


**3e**

According to the route G, **3e** was synthesized as a white solid: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.89 (brs, 1H), 7.38 – 7.21 (m, 3H), 7.08 – 7.00 (m, 1H), 5.89 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.24 – 5.07 (m, 2H), 4.04 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 2.54 (qt, *J* = 6.6, 1.3 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.14, 134.16, 129.71, 118.80, 118.76, 117.20, 112.90, 67.38, 64.48, 33.49. **HRMS** m/z (ESI) calcd for **$C_{12}H_{15}NO_3Na$** (M + Na)$^+$ 244.0950, found 244.0944.

## 3. Experimental Procedures and Characterization of Products

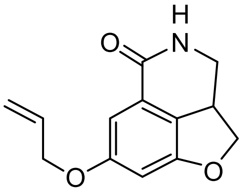
### 3,4-Dihydro-2*H*-furo[4,3,2-*de*]isoquinolin-5(2a*H*)-one (2a)



**2a**

To a 10 mL Schlenk tube was added 3-(allyloxy)-*N*-(pivaloyloxy)benzamide (**1a**) (55.0 mg, 0.20 mmol), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 2.5 mol %), CsOPiv (94.0 mg, 0.20 mmol) and the tube was purged with Ar for three times, followed by addition of CH$_3$CN(4.0 mL). The formed mixture was stirred at room temperature under Ar for 12 h as monitored by TLC. The solution was then removed under vaccum directly. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 25.0 mg (72%) of **2a** as a white solid: **$^1$H NMR** (300 MHz, CDCl$_3$) δ = 7.40 (dd, *J* = 7.7, 0.6 Hz, 1 H), 7.29 (dt, *J* = 7.7, 0.6 Hz, 1 H), 6.97 (t, *J* = 7.9 Hz, 1 H), 6.90 (brs, 1 H), 4.92 (t, *J* = 8.7 Hz, 1 H), 4.28 – 4.22 (m, 1 H), 4.07 – 3.88 (m, 1 H), 3.85 – 3.73 (m, 1 H), 3.61 – 3.52 (m, 1 H). **$^{13}$C NMR** (75 MHz, CDCl$_3$) δ = 166.12, 157.80, 132.00, 129.45, 126.19, 117.60, 112.82, 77.03, 45.79, 36.13. **HRMS** m/z (ESI) calcd for **$C_{10}H_9NO_2Na$** (M + Na)$^+$ 198.0525, found 198.0530.

### 7-(Allyloxy)-3,4-dihydro-2*H*-furo[4,3,2-*de*]isoquinolin-5(2a*H*)-one (2b)

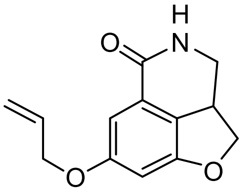


**2b**

The reaction of **1b** (67.0 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (94.0 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 40 mg (87%) of **2b** as a white solid: **$^1$H NMR** (300 MHz, CDCl$_3$) δ = 6.88 (d, *J* = 1.9 Hz, 1 H), 6.55 (d, *J* = 1.9 Hz, 1 H), 6.52 (brs, 1 H), 6.10 – 5.95 (m, 1 H), 5.44 – 5.35 (m, 1 H), 5.31 – 5.24 (m, 1 H), 4.86 (t, *J* = 8.7 Hz, 1 H), 4.56 – 4.49 (m, 2 H), 4.24 – 4.18 (m, 1 H), 3.99 – 3.78 (m, 1 H), 3.74 – 3.67 (m, 1 H), 3.53 – 3.45 (m, 1 H). **$^{13}$C NMR** (75 MHz, CDCl$_3$) δ =

166.02, 160.85, 158.87, 132.81, 125.77, 124.89, 117.83, 102.18, 102.04, 77.73, 69.50, 46.18, 35.49. **HRMS** m/z (ESI) calcd for **$C_{13}H_{13}NO_3Na$** (M + Na)$^+$ 354.0788, found 354.0792.

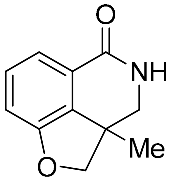
**7-(Allyloxy)-3,4-dihydro-2*H*-furo[4,3,2-*de*]isoquinolin-5(2a*H*)-one (2b)**



**2b**

The reaction of **1b** (67.0 mg, 0.20 mmol, 1.00 eq), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (94.0 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 40 mg (87%) of **2b** as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 6.88 (d, *J* = 1.9 Hz, 1 H), 6.55 (d, *J* = 1.9 Hz, 1 H), 6.52 (brs, 1 H), 6.10 – 5.95 (m, 1 H), 5.44 – 5.35 (m, 1 H), 5.31 – 5.24 (m, 1 H), 4.86 (t, *J* = 8.7 Hz, 1 H), 4.56 – 4.49 (m, 2 H), 4.24 – 4.18 (m, 1 H), 3.99 – 3.78 (m, 1 H), 3.74 – 3.67 (m, 1 H), 3.53 – 3.45 (m, 1 H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 166.02, 160.85, 158.87, 132.81, 125.77, 124.89, 117.83, 102.18, 102.04, 77.73, 69.50, 46.18, 35.49. **HRMS** m/z (ESI) calcd for **$C_{13}H_{13}NO_3Na$** (M + Na)$^+$ 354.0788, found 354.0792.

**2a-Methyl-3,4-dihydro-2*H*-furo[4,3,2-*de*]isoquinolin-5(2a*H*)-one (2c)**

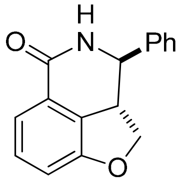


**2c**

The reaction of **1c** (58 mg, 0.20 mmol, 1.00 eq), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5.0 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (2.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 31 mg (81%) of **2c** as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.35 (dd, *J* = 7.7, 0.7 Hz, 1 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.13 (brs, 1 H), 6.92 (dd, *J* = 7.9, 0.6 Hz, 1 H), 4.51 (d, *J* = 8.5 Hz, 1 H), 4.28 (d, *J* = 8.6 Hz, 1 H), 3.70 (d, *J* = 11.9

Hz, 1 H), 3.50 (dd, *J* = 11.8, 5.0 Hz, 1 H), 1.47 (s, 3 H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ = 165.63, 157.12, 136.62, 129.35, 125.34, 117.72, 113.07, 84.11, 51.38, 39.58, 22.42. **HRMS** m/z (ESI) calcd for **$C_{11}H_{11}NO_2Na$** (M + Na)$^+$ 212.0682, found 212.0687.

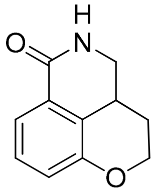
### 3-Phenyl-3,4-dihydro-2*H*-furo[4,3,2-*de*]isoquinolin-5(2a*H*)-one (2d)



**2d**

The reaction of **1d** (36 mg, 0.10 mmol), [Cp$^*$RhCl$_2$]$_2$ (1.6 mg, 2.5 mol %) and CsOPiv (47 mg, 2.0 equiv) in MeCN (2.0 mL) at room temperature under Ar led to full conversion of the starting material after 12 hours. The residue was then purified by silica gel chromatography (pentane / ethyl acetate 1.5:1) affording 22.0 mg (88%) of **2d** as white solid: $^1$H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 6H), 7.29 (td, *J* = 7.8, 0.9 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.73 (s, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.66 (t, *J* = 9.0 Hz, 1H), 4.28 (dd, *J* = 11.3, 9.0 Hz, 1H), 4.03 – 3.98 (m, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 166.1, 158.2, 138.8, 131.4, 129.8, 129.6, 129.4, 126.6, 118.1, 113.3, 76.5, 63.3, 44.6. HRMS m/z (ESI) calcd for $C_{16}H_{13}NO_2Na$ (M + Na)$^+$ 274.0838, found 274.0846.

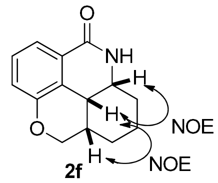
### 3,3a,4,5-tetrahydropyrano[4,3,2-*de*]isoquinolin-6(2*H*)-one (2e)



**2e**

The reaction of **1e** (58 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (2.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over $MgSO_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 29 mg (77%) of **2e** as a white solid: **$^1$H NMR** (300 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 7.6, 1.1 Hz, 1 H), 7.34 – 7.28 (m, 1 H), 7.01 (dd, *J* = 8.2, 1.1 Hz, 1 H), 6.96 (brs, 1 H), 4.54 – 4.47 (m, 1 H), 4.23 – 4.13 (m, 1 H), 3.64 – 3.51 (m, 1 H), 3.39 – 3.22 (m, 2 H), 2.19 – 2.01 (m, 1 H), 1.93 – 1.79 (m, 1 H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 166.40, 152.53, 128.78, 128.09, 123.00, 120.00, 119.89, 65.50, 45.56, 30.56, 25.28. **HRMS** m/z (ESI) calcd for **$C_{11}H_{11}NO_2Na$** (M + Na)$^+$ 212.0682, found 212.0688.

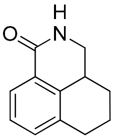
## 5a,6,7,8,8a,9-Hexahydro-5*H*-pyrano[2,3,4,5-lmn]phenanthridin-10(5a1*H*)-one (2f)



**2f**

The reaction of **1f** (66 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (6.2 mg, 0.01 mmol, 5.0 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 23 mg (50%) of **2f** as a white foam: **$^1$H NMR** (400 MHz, CDCl$_3$) δ = 7.59 (dd, *J* = 7.6, 1.1 Hz, 1 H), 7.25 – 7.19 (m, 1 H), 7.16 (brs, 1 H), 6.95 (dd, *J* = 8.2, 1.1 Hz, 1 H), 4.28 – 4.10 (m, 2 H), 3.62 – 3.59 (m, 2 H), 2.05 – 2.01 (m, 1 H), 1.78 – 1.55 (m, 3 H), 1.43 – 1.12 (m, 3 H). **$^{13}$C NMR** (101 MHz, CDCl$_3$) δ = 165.35, 152.82, 128.83, 127.76, 120.04, 119.86, 119.71, 70.06, 52.10, 33.39, 32.13, 28.94, 23.36, 22.93. **HRMS** m/z (ESI) calcd for **$C_{14}H_{15}NO_2Na$** (M + Na)$^+$ 252.0995, found 252.0999.

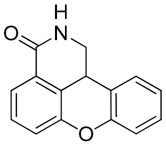
## 2,3,3a,4,5,6-Hexahydro-1*H*-benzo[*de*]isoquinolin-1-one (2g)



**2g**

The reaction of **1g** (58 mg, 0.20 mmol), [Cp$^*$RhCl$_2$]$_2$ (6.2 mg, 5 mol %) and CsOPiv (94 mg, 2.0 equiv) in MeCN (4.0 mL) at room temperature under Ar led to full conversion of the starting material after 12 hours. The residue was then purified by silica gel chromatography (ethyl acetate 100%) affording 15 mg (40%) of **2g** as white solid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.88 (t, *J* = 4.7 Hz, 1H), 7.26 (d, *J* = 4.7 Hz, 2H), 6.43 (brs, 1H), 3.45 (dd, *J* = 11.3, 5.0 Hz, 1H), 3.25 (dd, *J* = 13.2, 11.3 Hz, 1H), 3.20 – 3.01 (m, 1H), 2.97 – 2.71 (m, 2H), 2.15 – 1.95 (m, 2H), 1.87 – 1.67 (m, 1H), 1.47 – 1.29 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.31, 137.78, 135.43, 132.92, 126.55, 125.72, 46.09, 34.54, 28.44, 26.39, 21.99. HRMS m/z (ESI) calcd for $C_{12}H_{13}NONa$ (M + Na)$^+$ 210.0895, found 210.0901.

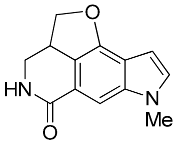
## 1,11b-Dihydrochromeno[4,3,2-*de*]isoquinolin-3(2*H*)-one (2h)



**2h**

The reaction of **1h** (68 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 26.0 mg (56%) of **2h** as a white solid: $^1$H NMR (600 MHz, CDCl$_3$) δ 7.82 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.25 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.32 (brs, 1H), 4.50 (dd, *J* = 13.0, 5.7 Hz, 1H), 4.09 (dt, *J* = 11.4, 5.6 Hz, 1H), 3.71 (dd, *J* = 12.8, 11.7 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 165.37, 151.49, 150.08, 128.85, 128.48, 125.87, 123.70, 122.75, 121.77, 120.10, 119.68, 117.15, 44.75, 30.31. **HRMS** m/z (ESI) calcd for $\mathbf{C_{15}H_{11}NO_2Na}$ (M + Na)$^+$ 260.0687, found 260.0682.

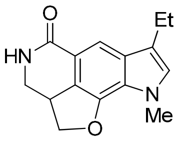
### 7-Methyl-2,2a,3,4-tetrahydrofuro[4,3,2-*de*]pyrrolo[3,2-*g*]isoquinolin-5(7*H*)-one (2i)



**2i**

The reaction of **1i** (66 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 40.0 mg (88%) of **2i** as a white solid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.50 – 7.44 (m, 1H), 7.12 (d, *J* = 3.1 Hz, 1H), 6.57 (brs, 1H), 6.50 – 6.42 (m, 1H), 4.99 (t, *J* = 8.6 Hz, 1H), 4.33 (dd, *J* = 11.4, 8.7 Hz, 1H), 4.06 (tdd, *J* = 11.6, 8.3, 6.0 Hz, 1H), 3.81 (s, 3H), 3.75 (dt, *J* = 11.0, 5.4 Hz, 1H), 3.60 – 3.46 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.51, 149.88, 139.48, 131.18, 119.41, 119.24, 116.99, 100.27, 97.15, 77.88, 46.63, 36.84, 33.65. **HRMS** m/z (ESI) calcd for $\mathbf{C_{13}H_{12}N_2O_2Na}$ (M + Na)$^+$ 251.0796, found 252.0791.

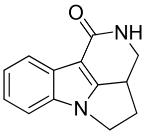
### 7-Ethyl-9-methyl-2,2a,3,4-tetrahydrofuro[4,3,2-*de*]pyrrolo[2,3-*g*]isoquinolin-5(9*H*)-one (2j)



**2j**

The reaction of **1j** (71.6 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 46 mg (90%) of **2j** as a white solid: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.73 (s, 1H), 6.75 (s, 1H), 6.40 (brs, 1H), 4.96 (t, *J* = 8.5 Hz, 1H), 4.29 (dd, *J* = 11.6, 8.6 Hz, 1H), 4.16 – 3.96 (m, 1H), 3.91 (s, 3H), 3.74 (dt, *J* = 10.9, 5.4 Hz, 1H), 3.51 (t, *J* = 11.8 Hz, 1H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.67, 142.18, 131.00, 126.24, 125.44, 123.06, 120.81, 116.86, 110.69, 77.97, 46.46, 37.27, 34.75, 18.39, 14.60. **HRMS** m/z (ESI) calcd for **$C_{15}H_{16}N_2O_2Na$** (M + Na)$^+$ 279.1109, found 279.1104.

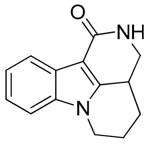
### 3,3a,4,5-Tetrahydrobenzo[*b*]pyrido[3,4,5-*gh*]pyrrolizin-1(2*H*)-one (2k)



**2k**

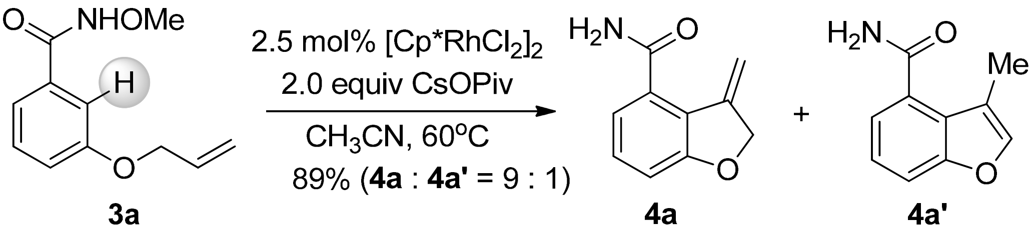
The reaction of **1k** (63 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 26.6 mg (63%) of **2k** as a white solid: $^1$H NMR (300 MHz, CDCl$_3$) δ 8.12 – 7.81 (m, 1H), 7.42 – 7.08 (m, 3H), 5.22 (brs, 1H), 4.53 – 4.13 (m, 2H), 3.99 – 3.60 (m, 2H), 3.34 (t, *J* = 11.2 Hz, 1H), 2.87 (dt, *J* = 12.6, 6.3 Hz, 1H), 2.38 (dq, *J* = 12.7, 9.4 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.32, 159.05, 135.80, 128.88, 121.89, 121.65, 121.01, 110.57, 49.45, 47.89, 35.57, 31.91. **HRMS** m/z (ESI) calcd for **$C_{13}H_{12}N_2ONa$** (M + Na)$^+$ 235.0847, found 235.0842.

### 2,3,3a,4,5,6-Hexahydro-1*H*-indolo[3,2,1-*ij*][1,6]naphthyridin-1-one (2l)



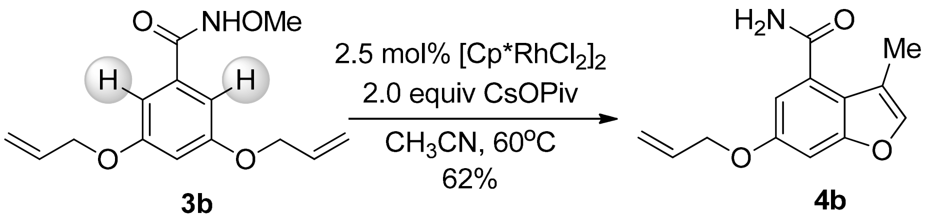
**2l**

The reaction of **1l** (66 mg, 0.20 mmol, 1.00 eq), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol%) and CsOPiv (93.6 mg, 0.40 mmol, 2.00 eq) in acetonitrile (4.0 mL) at rt under Ar was finished by the addition of 1 M NaOH. The phases were separated, the organic layer was extracted with EtOAc (3 x 20 mL), dried over MgSO$_4$, filtered and concentrated. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 2:1) and afforded 27.0 mg (60%) of **2l** as a white solid: $^1$H NMR (300 MHz, CDCl$_3$) δ 8.09 (dd, *J* = 5.7, 2.5 Hz, 1H), 7.33 – 7.20 (m, 3H), 5.78 (s, 1H), 4.22 (dd, *J* = 11.9, 5.5 Hz, 1H), 3.77 (td, *J* = 12.0, 5.0 Hz, 1H), 3.62 – 3.46 (m, 1H), 3.42 – 3.15 (m, 2H), 2.32 (dd, *J* = 13.4, 3.5 Hz, 1H), 2.25 – 2.06 (m, 2H), 1.53 – 1.28 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.21, 145.72, 136.76, 125.50, 122.03, 121.95, 120.62, 109.30, 102.93, 47.22, 41.47, 32.02, 23.65, 22.56. **HRMS** m/z (ESI) calcd for **$C_{14}H_{14}N_2ONa$** (M + Na)$^+$ 249.1004, found 249.1001.



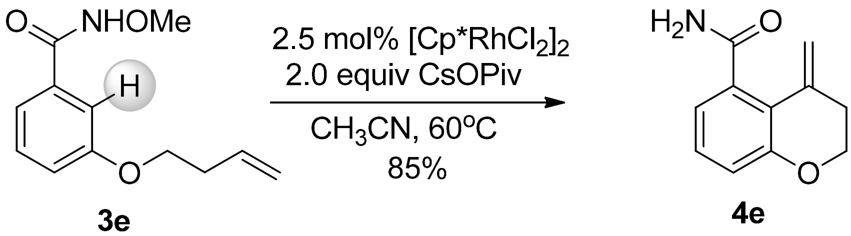
(4)

To a 10 mL Schlenk tube was added 3-(allyloxy)-*N*-methoxybenzamide (**3a**) (41.4 mg, 0.20 mmol), [Cp$^*$RhCl$_2$]$_2$ (3.1 mg, 2.5 mol %), CsOPiv (94.0 mg, 0.40 mmol) and the tube was purged with Ar for three times, followed by addition of CH$_3$CN(4.0 mL). The formed mixture was stirred at 60°C under Ar for 12 h as monitored by TLC. The isomer ratio (**4a** : **4a'** = 9 :1) was determined by crude $^1$H NMR. The pure product **4a** can be formed via recrystallization from Pent/EtOAc in 89% yield (31.0 mg) as a light gray solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.18 (m, 1H), 7.02 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.96 – 6.88 (m, 1H), 6.14(s, 1H), 5.96 (s, 1H), 5.81 (t, *J* = 3.1 Hz, 1H), 5.18 (t, *J* = 2.7 Hz, 1H), 5.12 (t, *J* = 2.9 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 170.28, 164.84, 141.34, 131.51, 130.44, 121.99, 119.75, 112.90, 105.47, 75.63. **HRMS** m/z (ESI) calcd for **$C_{10}H_9NO_2Na$** (M + Na)$^+$ 198.0531, found 198.0525.



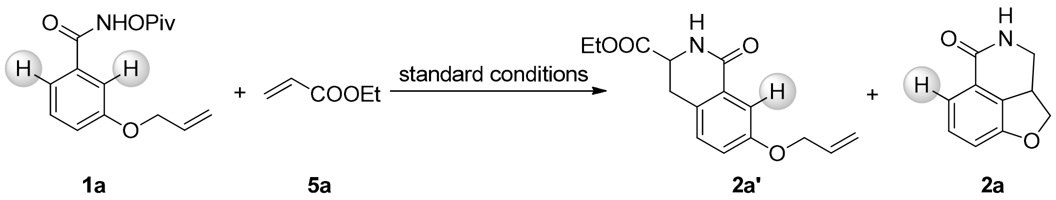
(5)

To a 10 mL Schlenk tube was added 3,5-bis(allyloxy)-*N*-methoxybenzamide (**3b**) (52.6 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), CsOPiv (94.0 mg, 0.40 mmol) and the tube was purged with Ar for three times, followed by addition of $CH_3CN$(4.0 mL). The formed mixture was stirred at 60°C under Ar for 12 h as monitored by TLC The crude material was subjected to column chromatography on silica (Pent:EtOAc, 1:1) and afforded 28.0 mg (62%) of **4b** as a brown solid: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.3 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.12 (s, 1H), 6.10-6.00 (m, 1H), 5.99 (s, 1H), 5.43 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.31 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.57 (dt, *J* = 5.3, 1.4 Hz, 2H), 2.25 (d, *J* = 1.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.15, 157.08, 155.83, 142.36, 132.75, 129.20, 119.53, 118.04, 115.71, 111.05, 99.26, 69.48, 10.01. **HRMS** m/z (ESI) calcd for **$C_{13}H_{13}NO_3Na$** (M + Na)$^+$ 254.0793, found 254.0788.



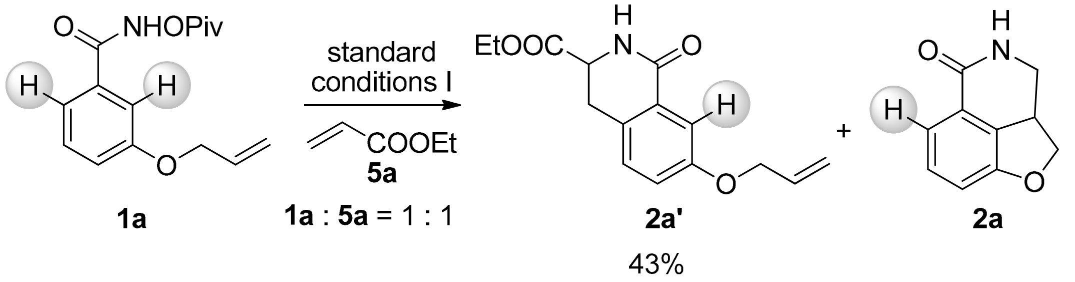
(6)

To a 10 mL Schlenk tube was added 3-(but-3-en-1-yloxy)-*N*-methoxybenzamide (**3e**) (44.2 mg, 0.20 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), CsOPiv (94.0 mg, 0.40 mmol) and the tube was purged with Ar for three times, followed by addition of $CH_3CN$(4.0 mL). The formed mixture was stirred at 60°C under Ar for 12 h as monitored by TLC The crude material was subjected to column chromatography on silica (Pent:EtOAc, 1:1) and afforded 32.0 mg (85%) of **4e** as a white solid: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.08 (m, 1H), 6.94 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.09 (brs, 1H), 5.83 (brs, 1H), 5.57 (s, 1H), 5.12 (s, 1H), 4.31 (t, *J* = 5.7 Hz, 2H), 2.68 (t, *J* = 5.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.92, 154.85, 135.12, 135.05, 128.91, 120.06, 119.19, 118.72, 113.91, 67.68, 32.36. **HRMS** m/z (ESI) calcd for $\mathbf{C_{11}H_{11}NO_2Na}$ $(M + Na)^+$ 212.0687, found 212.0682.



| | | | |
|---|---|---|---|
| **1a** : **5a** = 1 : 4 | 55.0 | : | 45.0 |
| **1a** : **5a** = 1 : 2 | 52.0 | : | 48.0 |
| **1a** : **5a** = 1 : 1 | 49.5 | : | 50.5 |

The ratios were determined directly by analysis of the crude $^1$H NMR. The product **2a**' can be isolated according to the following procedure.



To a 10 mL Schlenk tube was added 3-(allyloxy)-*N*-(pivaloyloxy)benzamide (**1a**) (55.0 mg, 0.20 mmol), ethyl acrylate (22.0 μL, 0.20 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), CsOPiv (94.0 mg, 0.20 mmol) and the tube was purged with Ar for three times, followed by addition of $CH_3CN$ (4.0 mL). The formed mixture was stirred at room temperature under Ar for 12 h as monitored by TLC. The solution was then removed under vaccum directly. The crude material was subjected to column chromatography on silica (Pent:EtOAc, 1:1) and afforded 23.6 mg (43%) of **2a’** as a white solid: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.7 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.64 (s, 1H), 6.04 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.41 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.28 (dd, *J* = 10.5, 1.4 Hz, 1H), 4.57 (dt, *J* = 5.2, 1.4 Hz, 2H), 4.35 (ddd, *J* = 10.2, 5.2, 1.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.36 – 3.03 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.28, 165.22, 158.01, 132.80, 129.30, 128.60, 128.51, 120.70, 117.87, 112.19, 68.96, 62.06, 53.29, 30.42, 14.09. **HRMS** m/z (ESI) calcd for $\mathbf{C_{15}H_{17}NO_4Na}$ $(M + Na)^+$ 298.1055, found 298.1050

## 4. References

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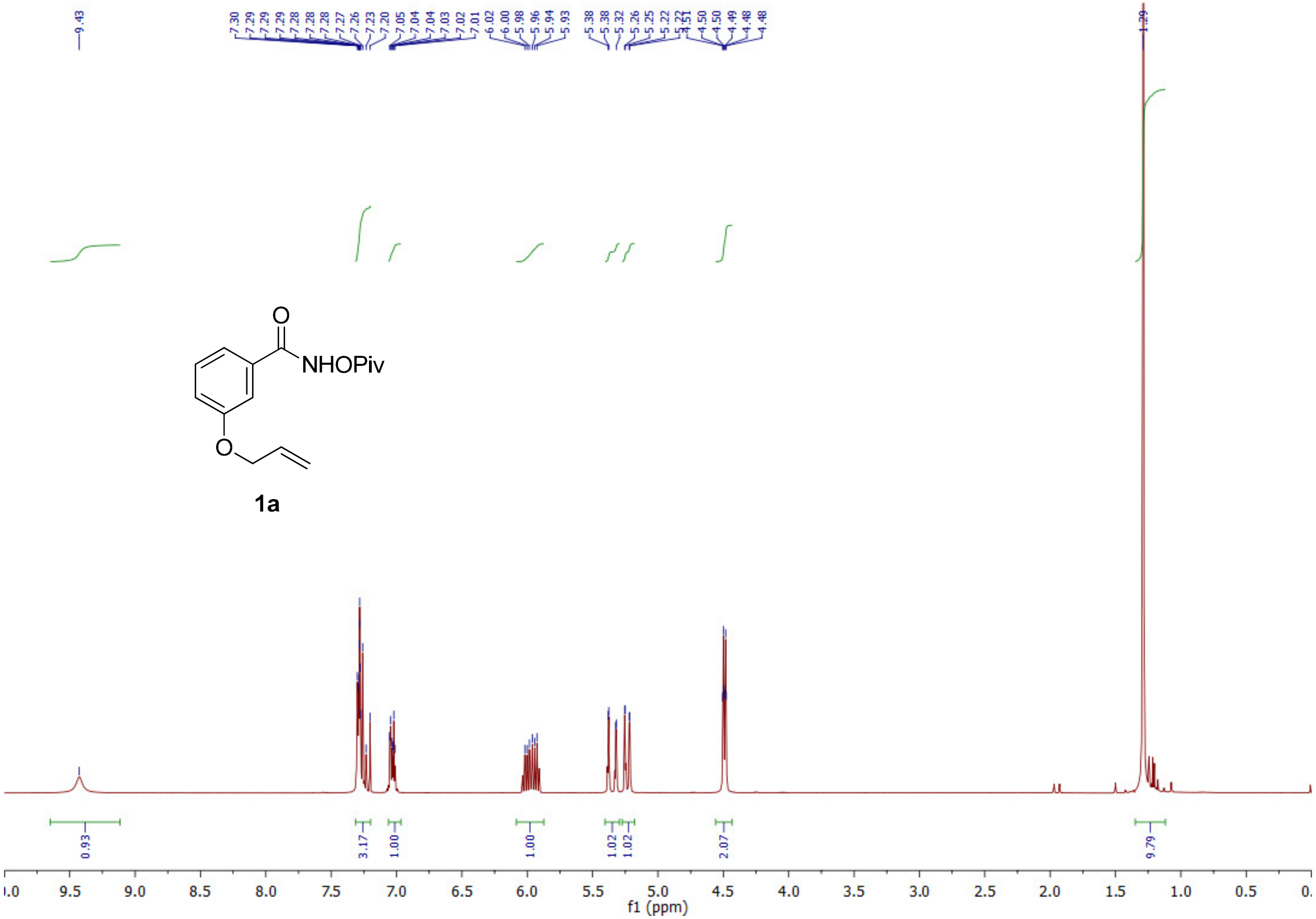
# 5. $^1$H NMR and $^{13}$C NMR spectra of those compounds



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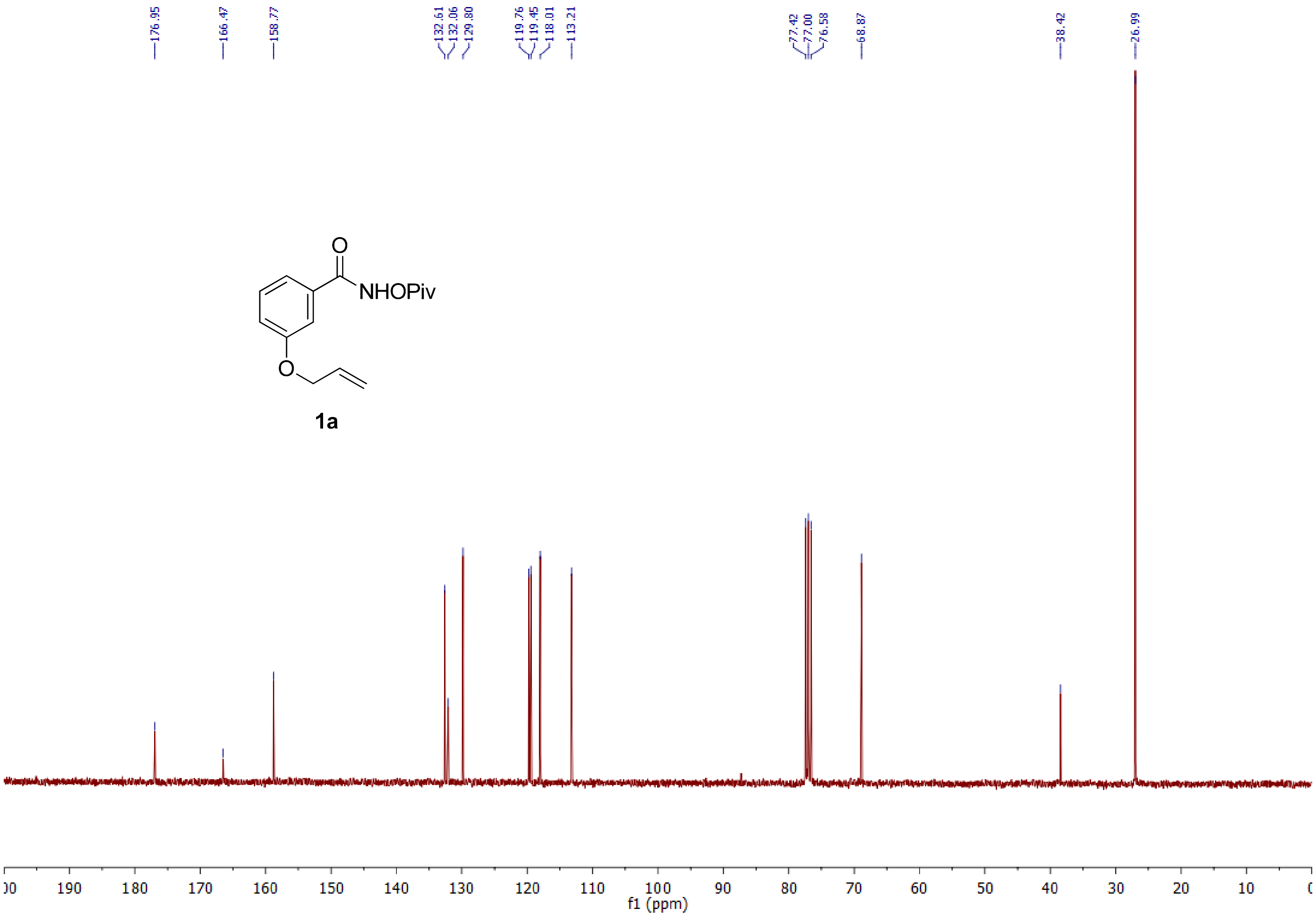
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26.99
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NHOPiv
O
1a
190
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140
130
120
110
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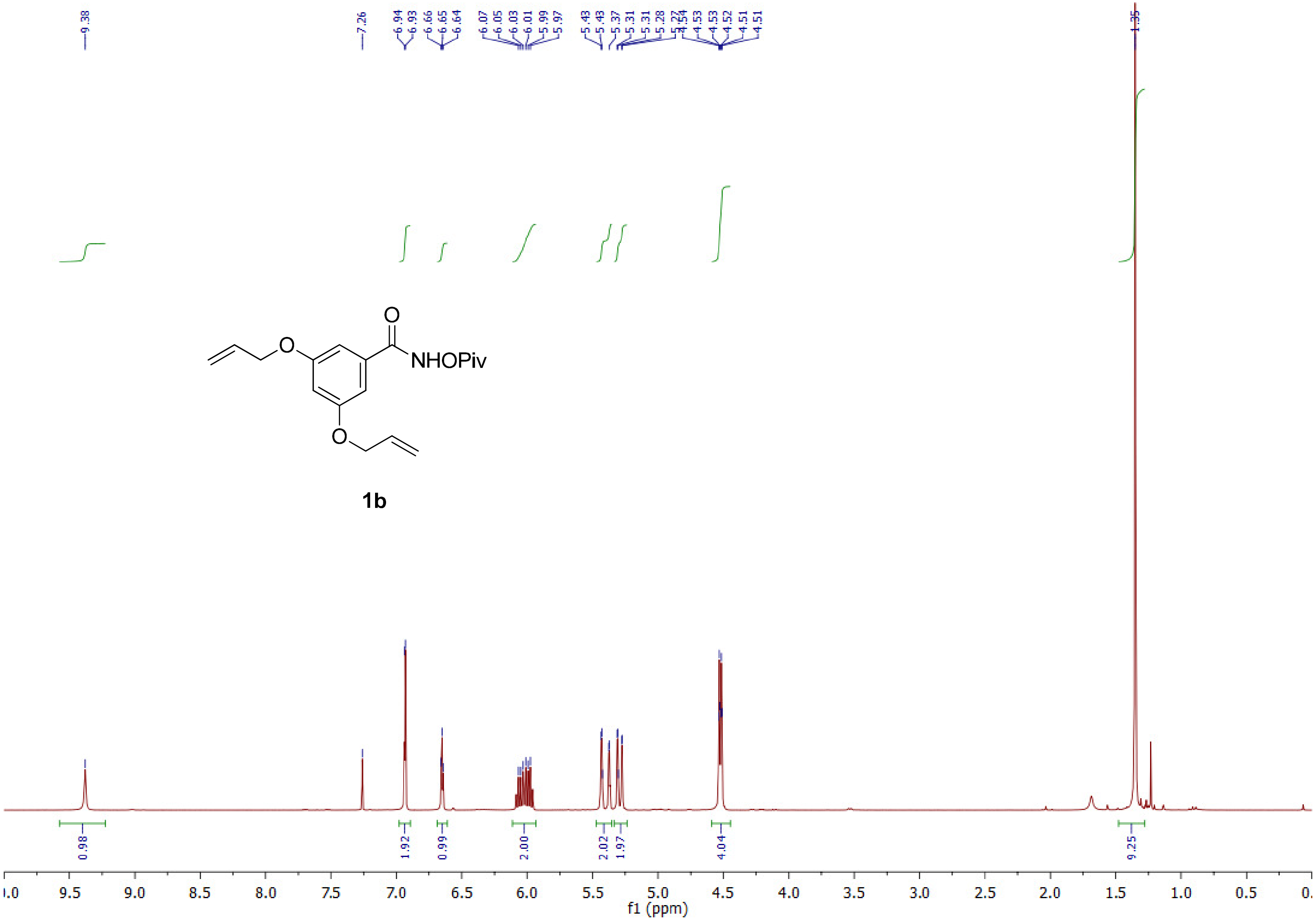
60
50
40
30
20
10
f1 (ppm)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f1 (ppm)

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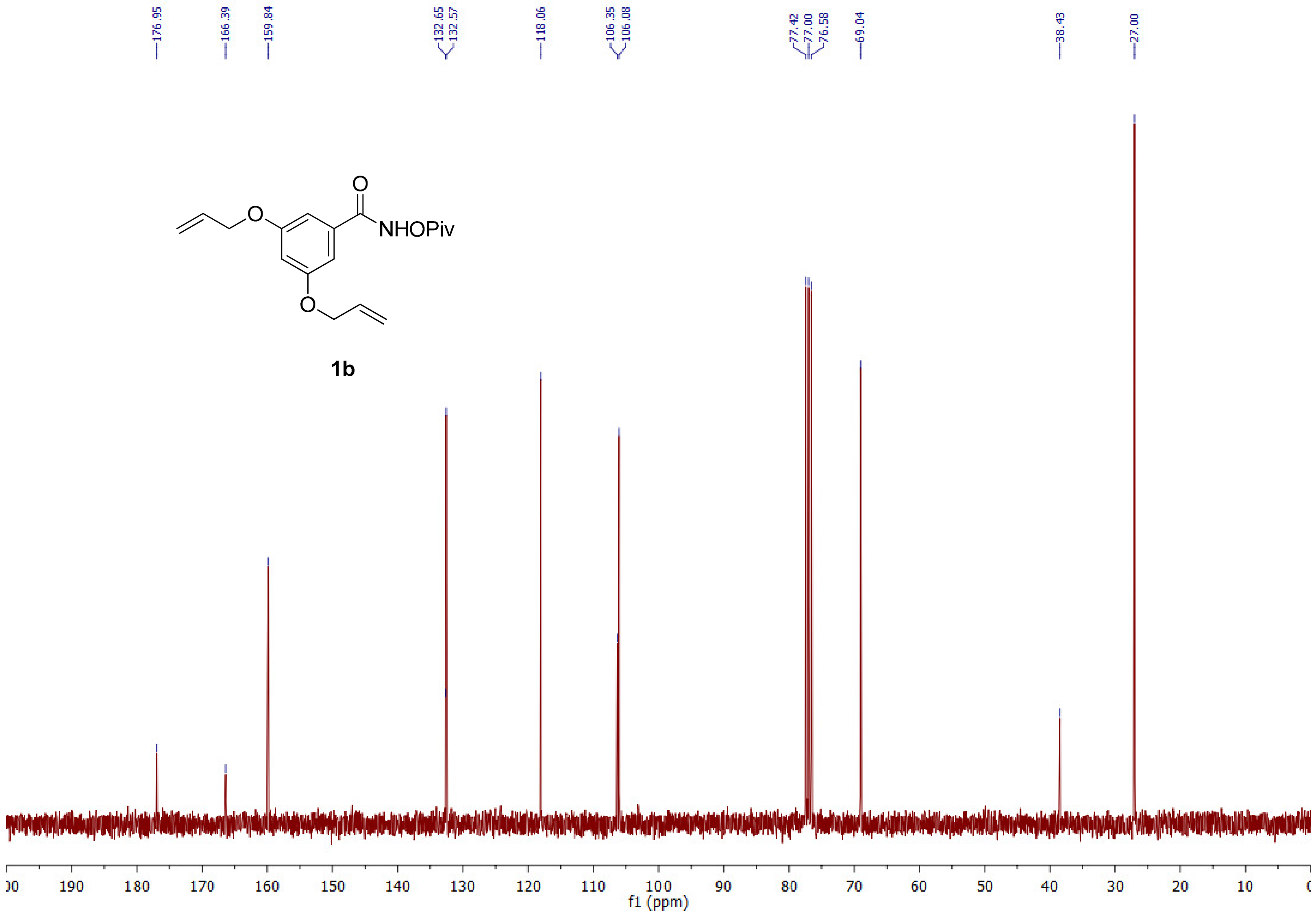
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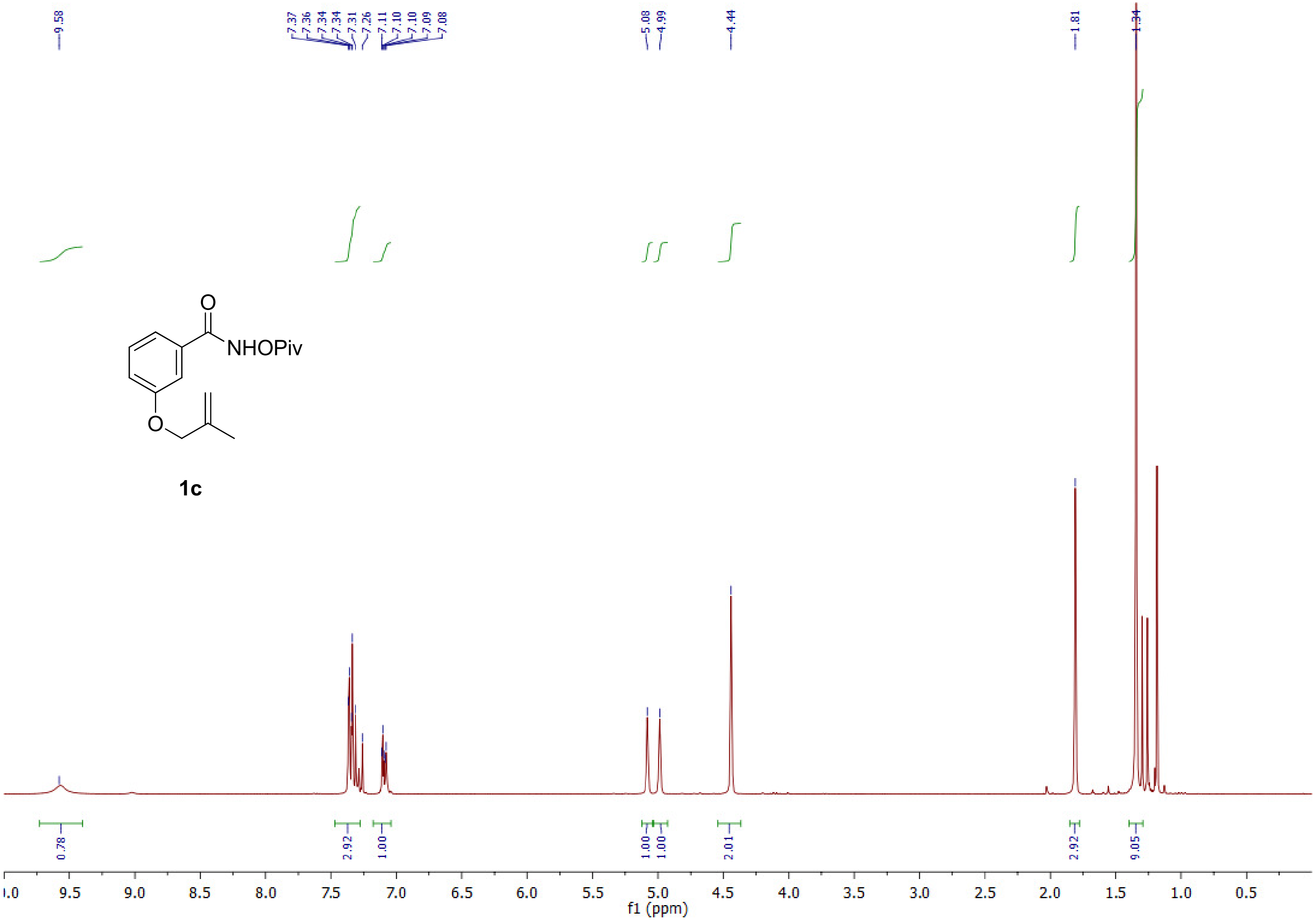
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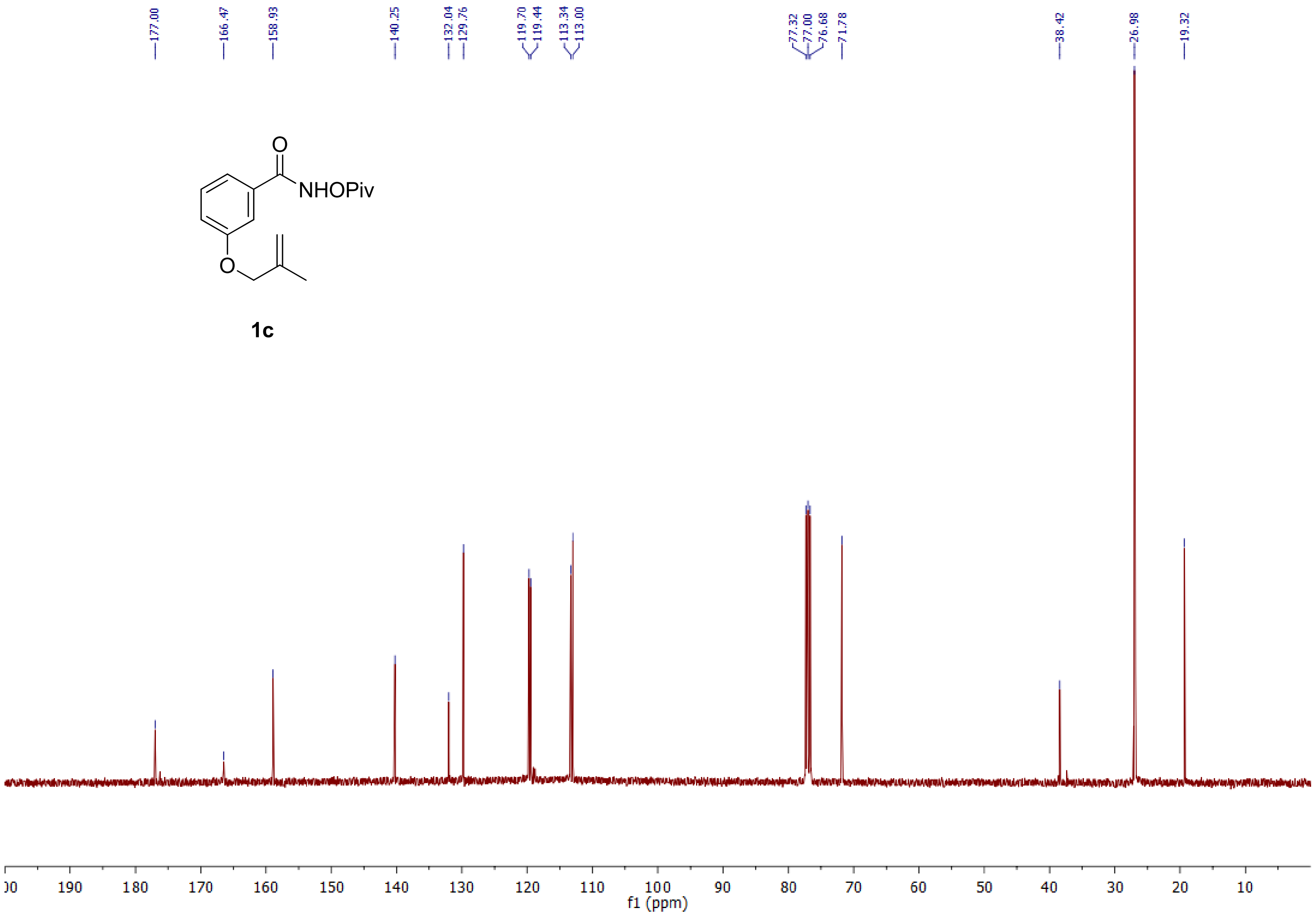
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1c
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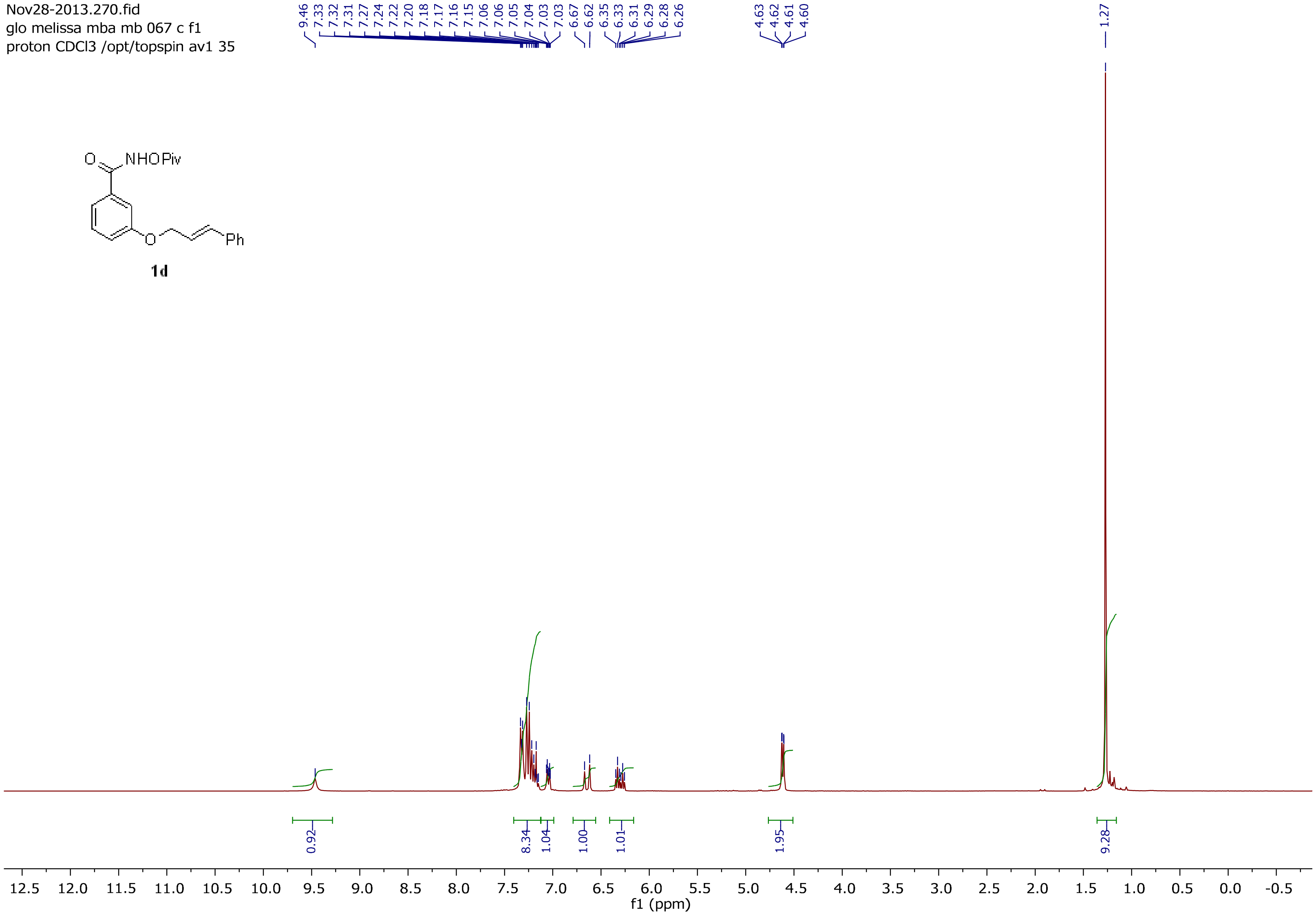
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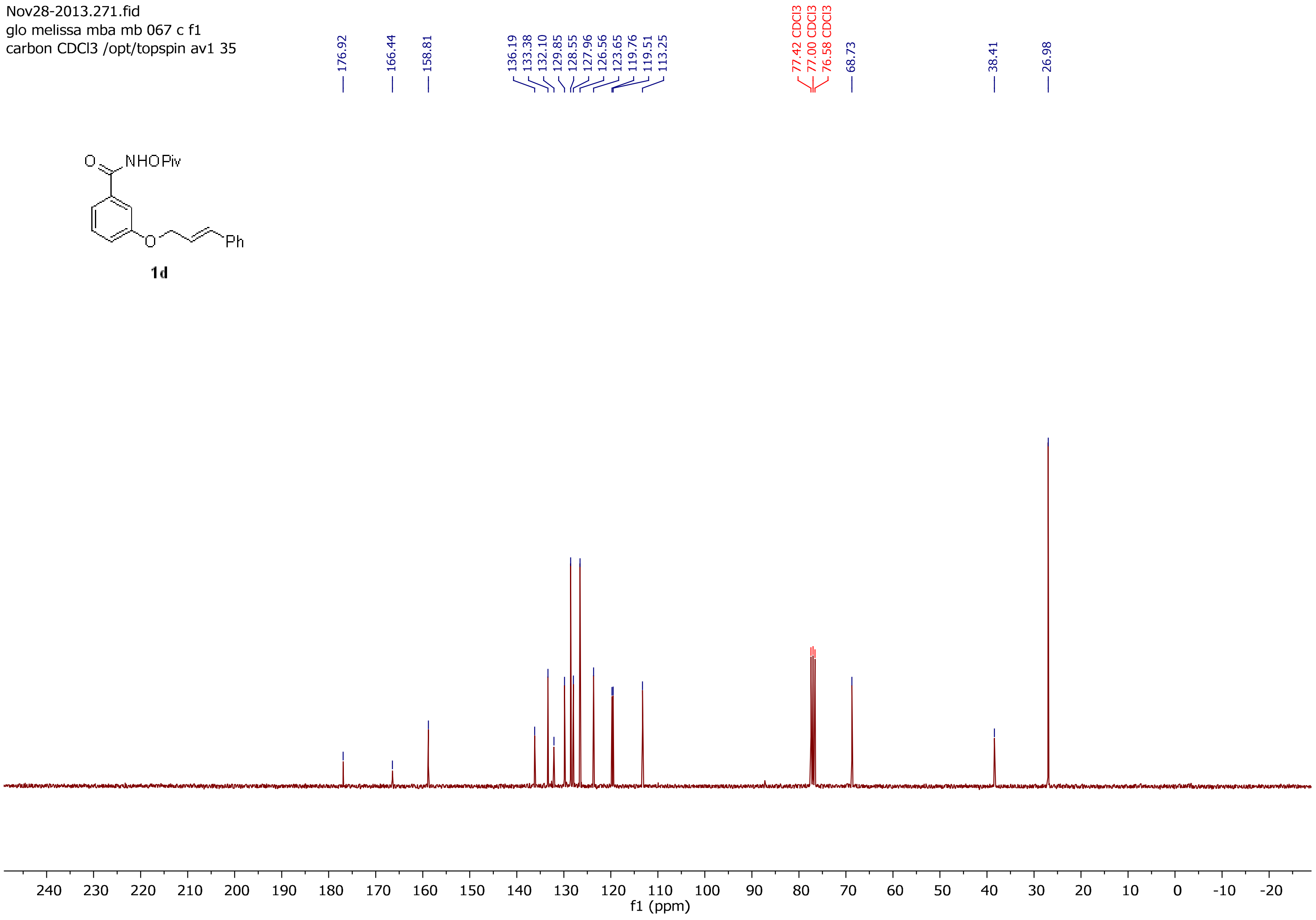
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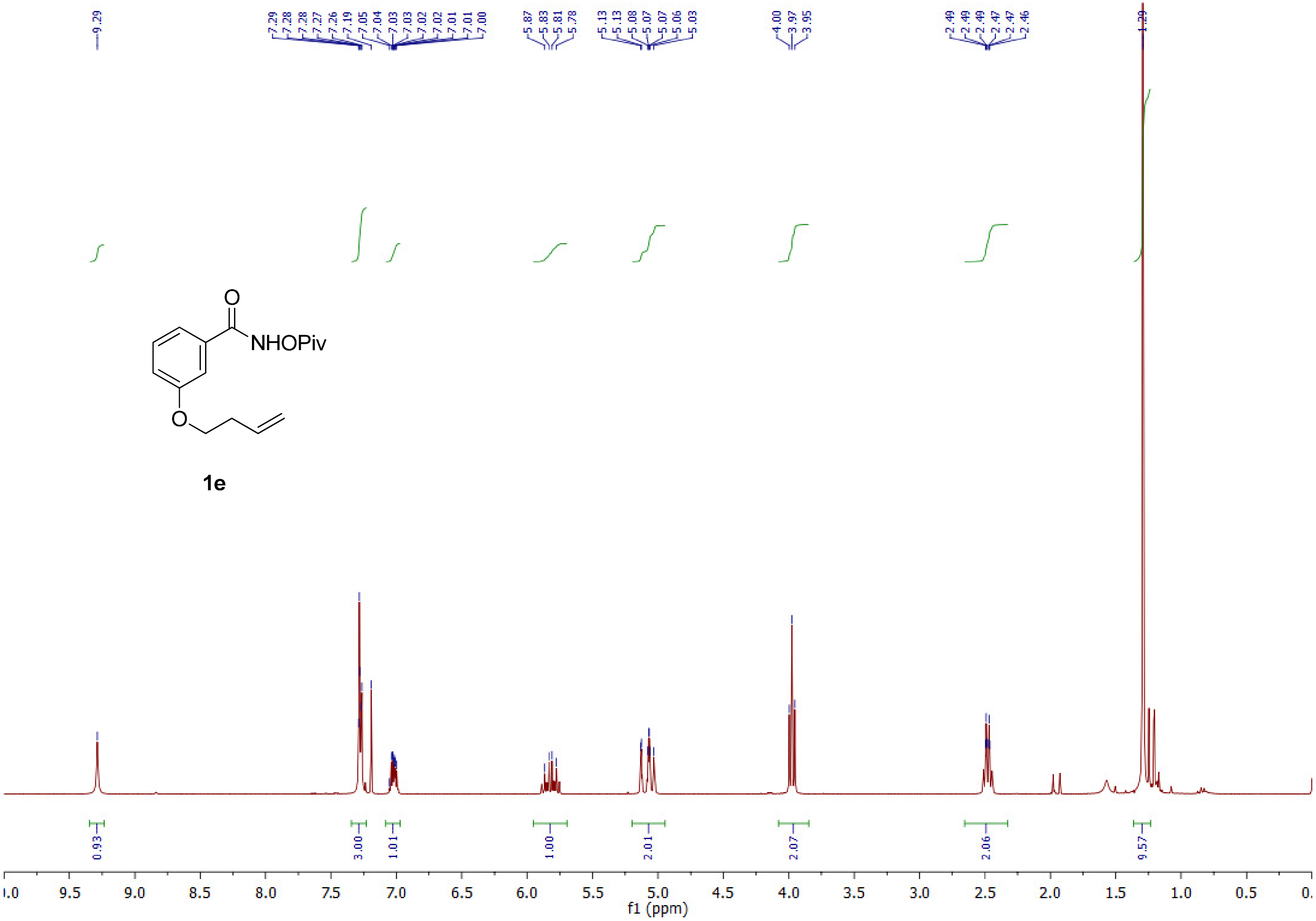
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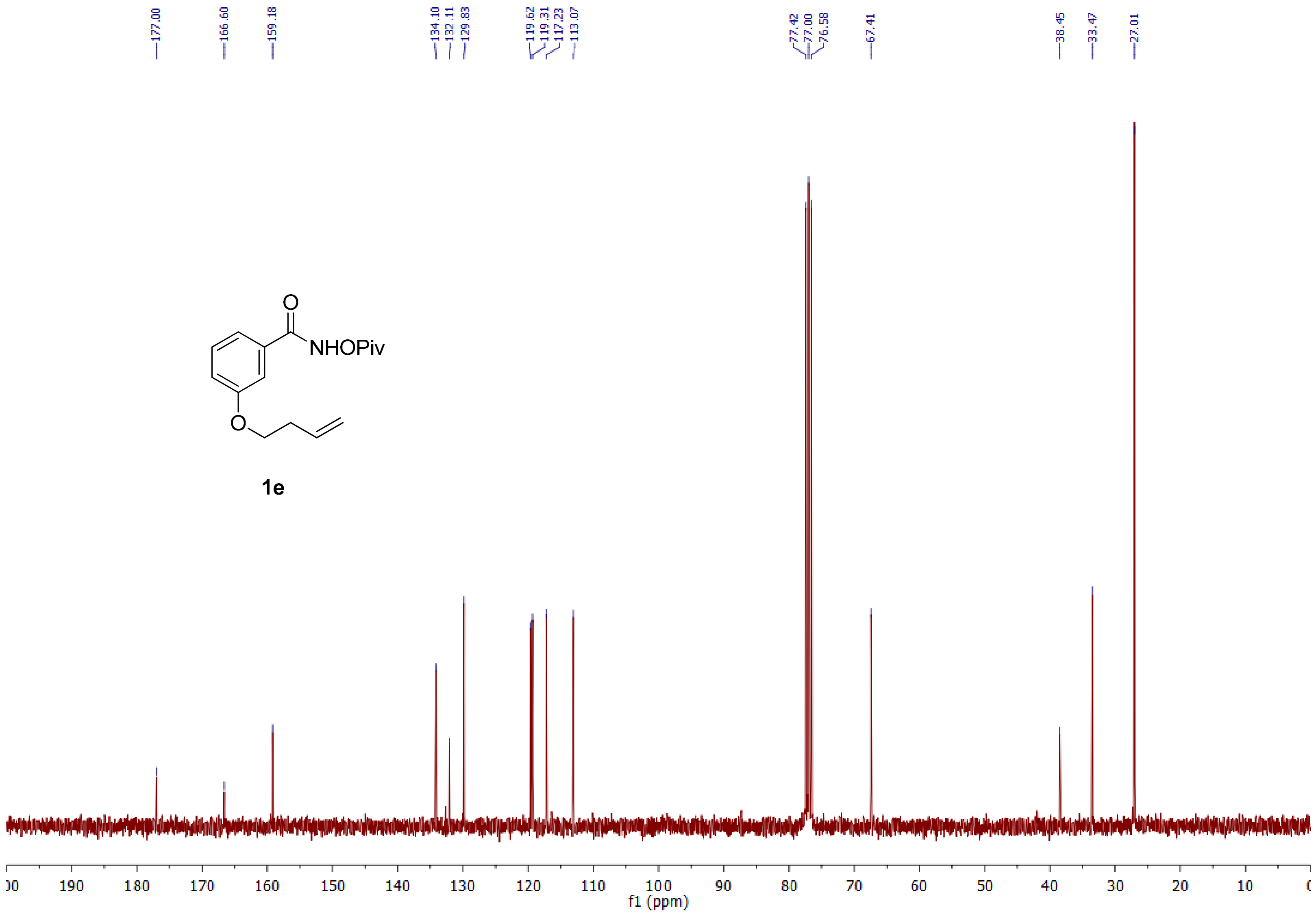
**1e**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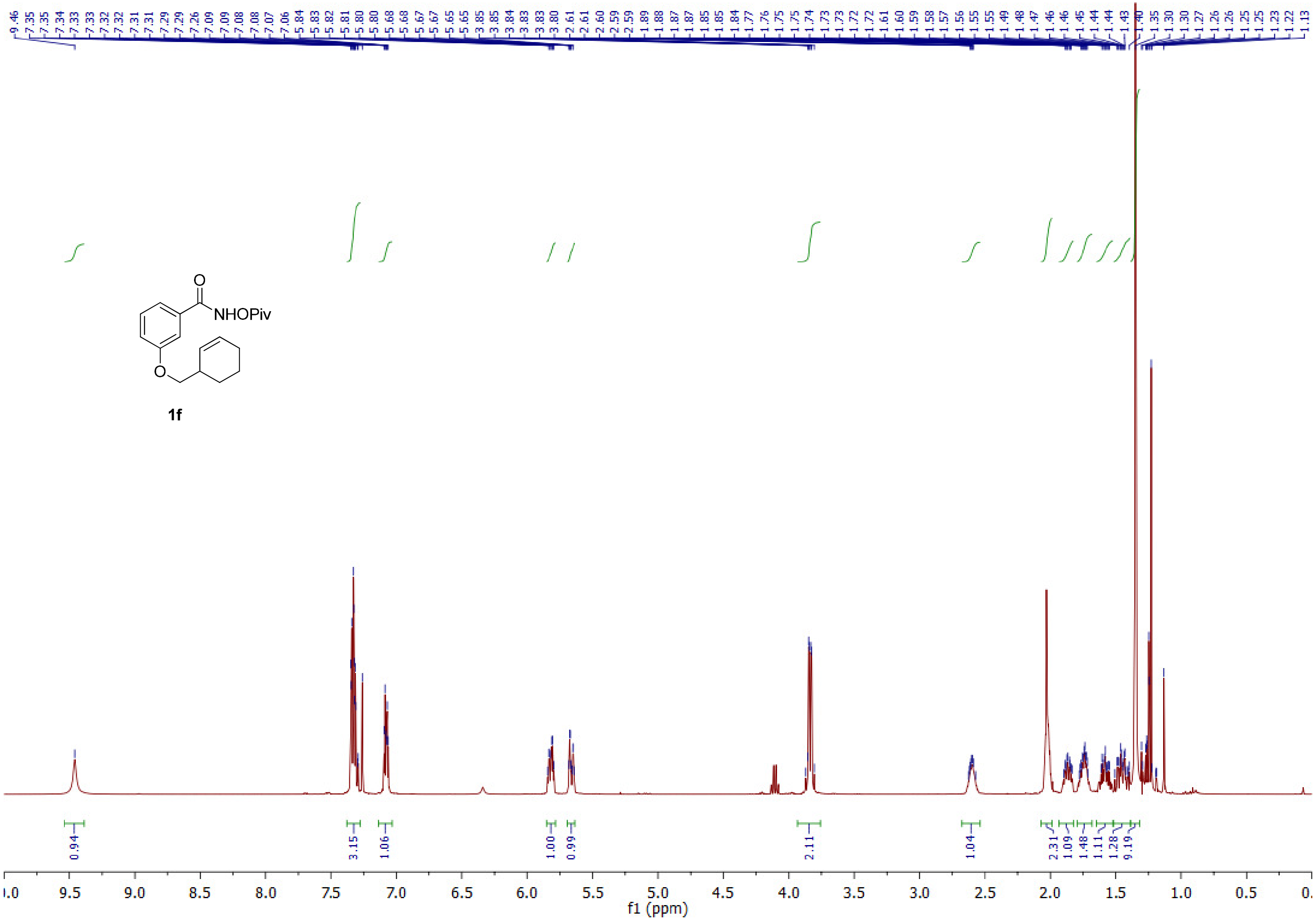
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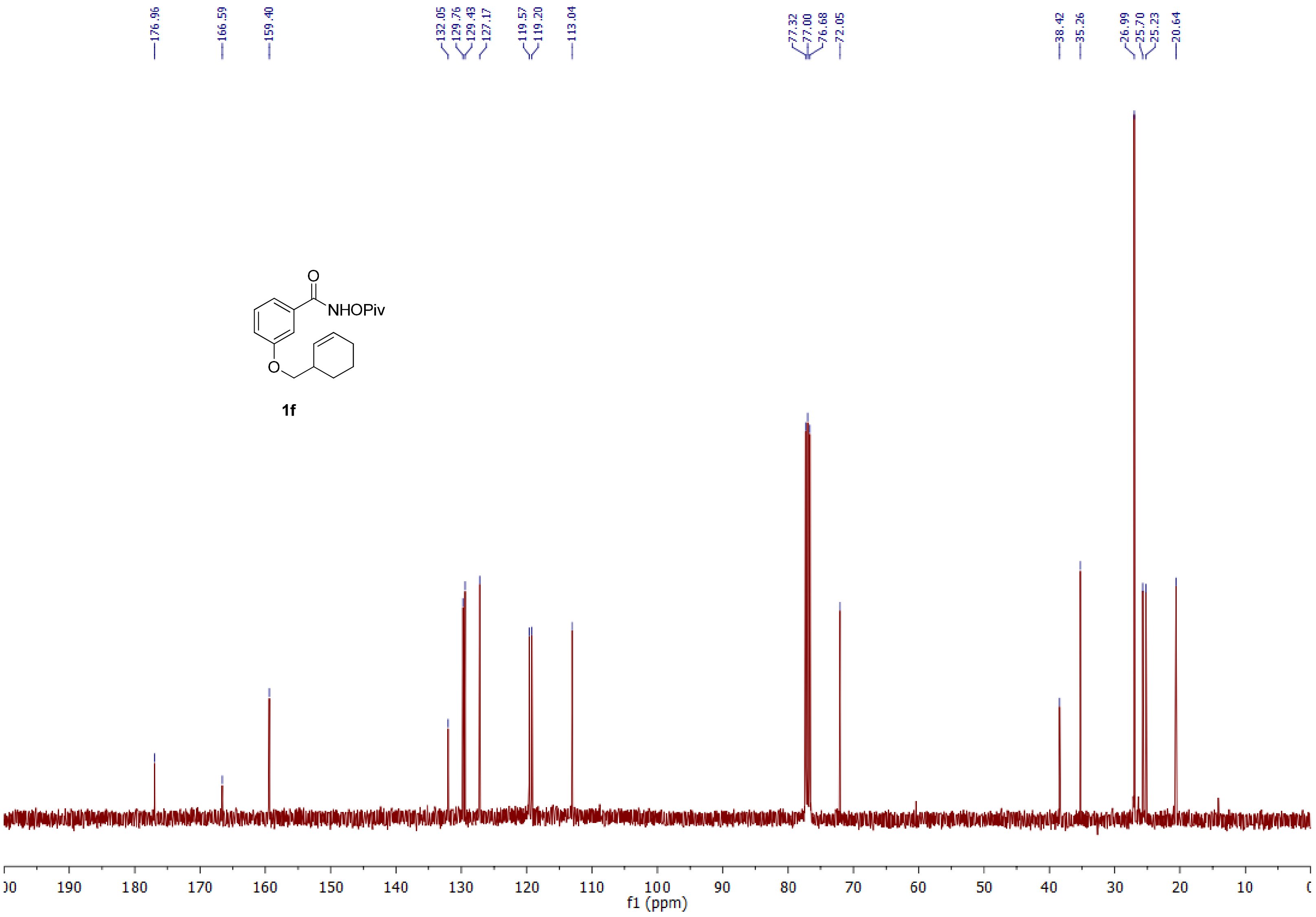
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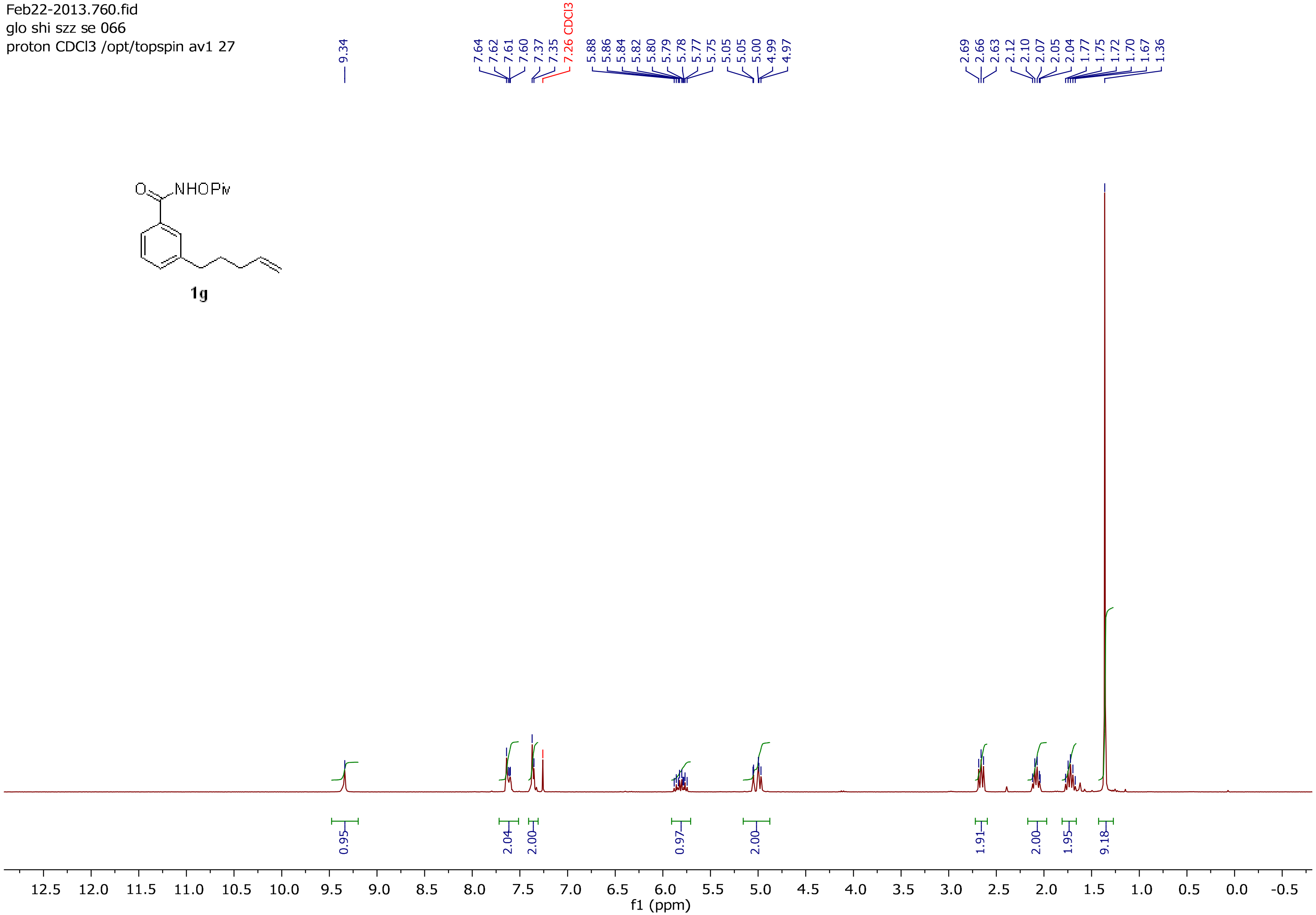
f1 (ppm)

**1f**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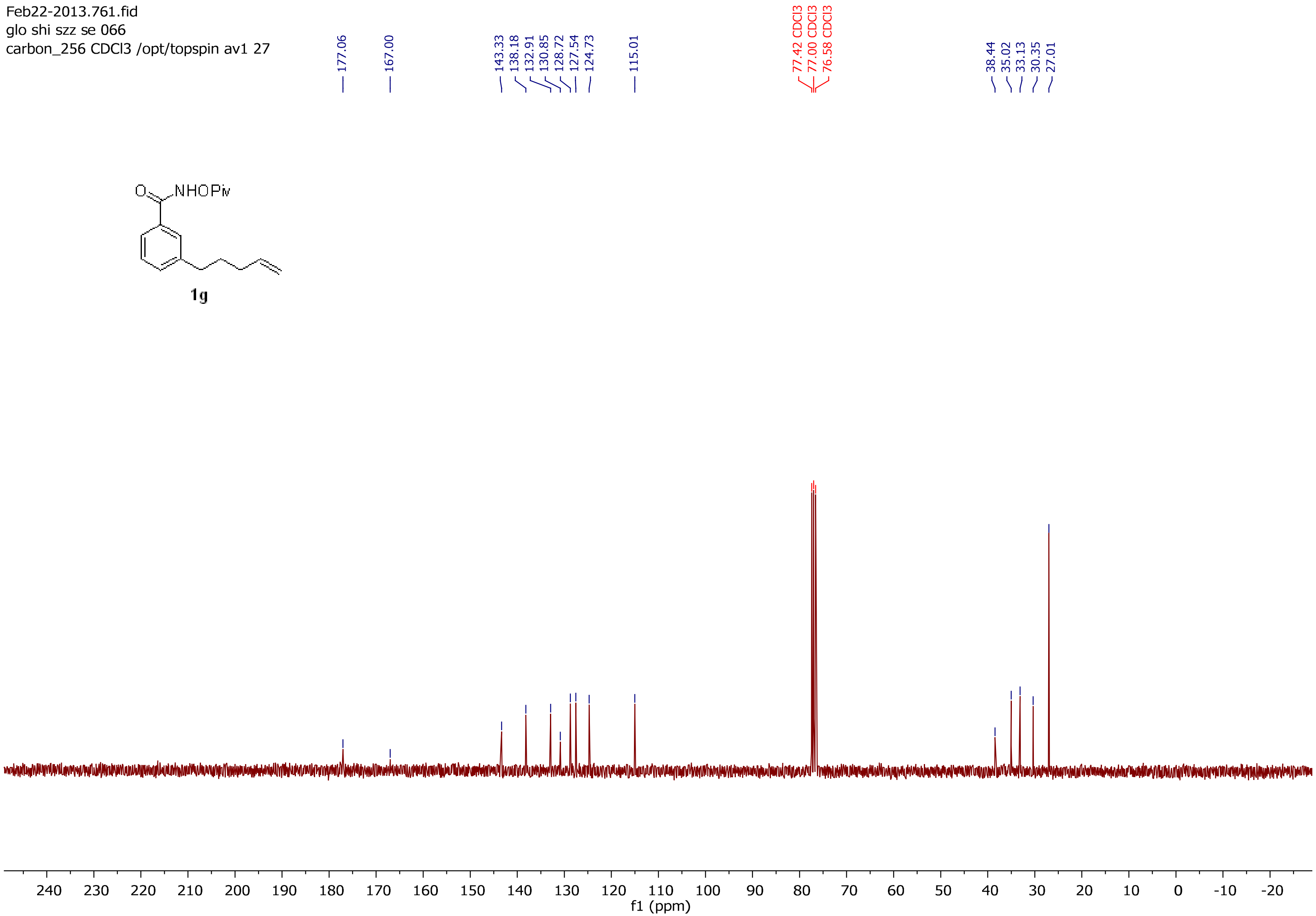
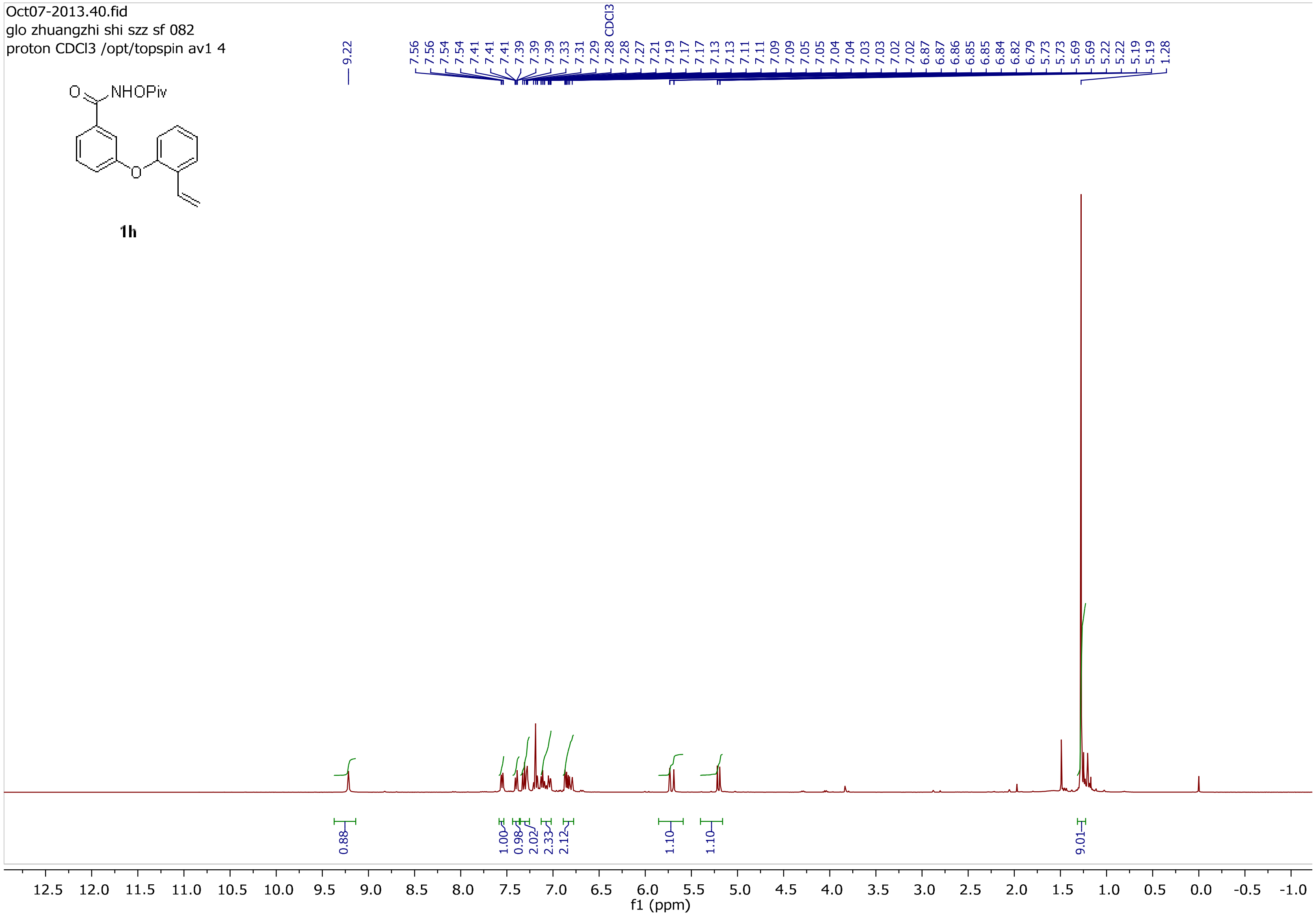
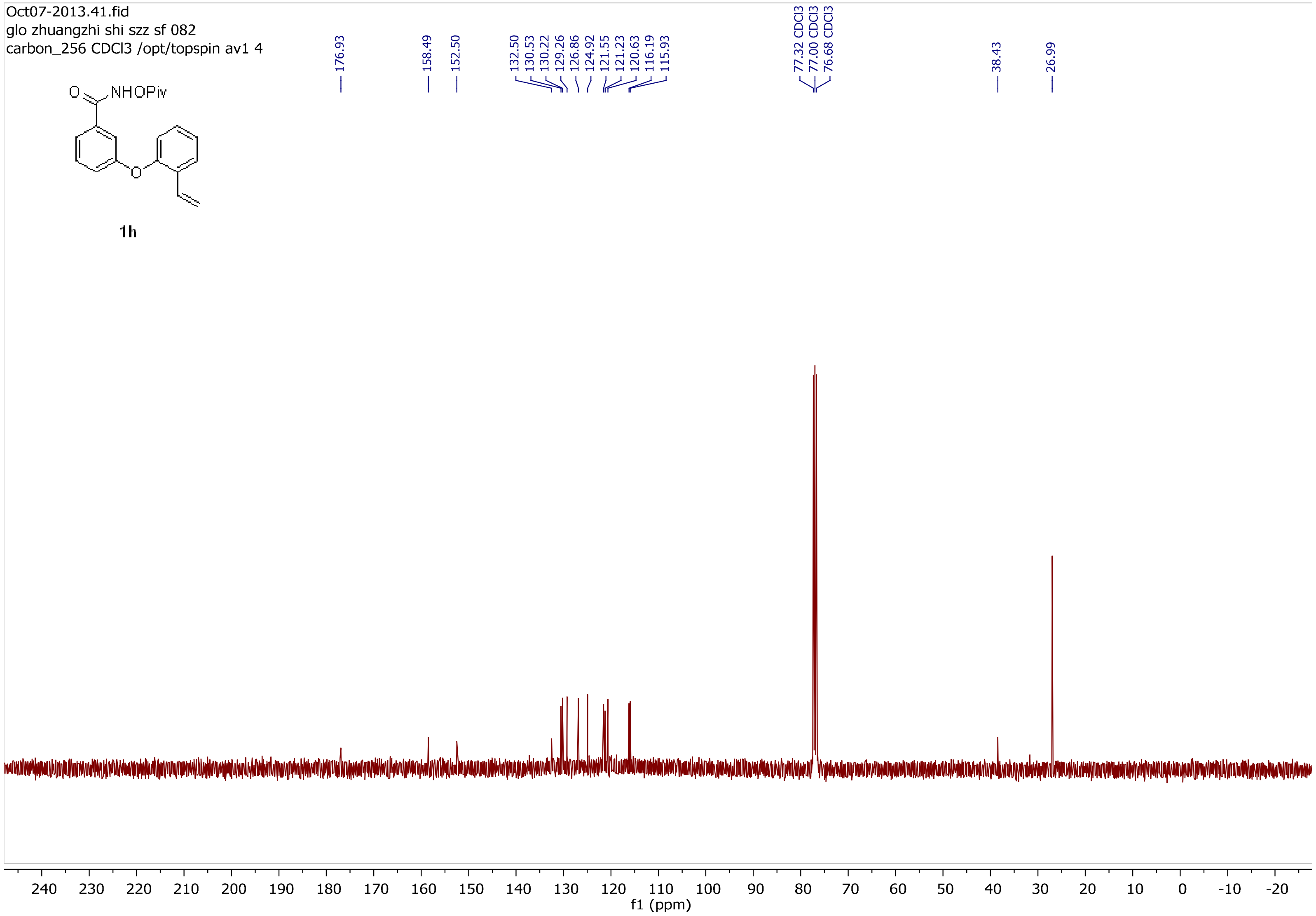
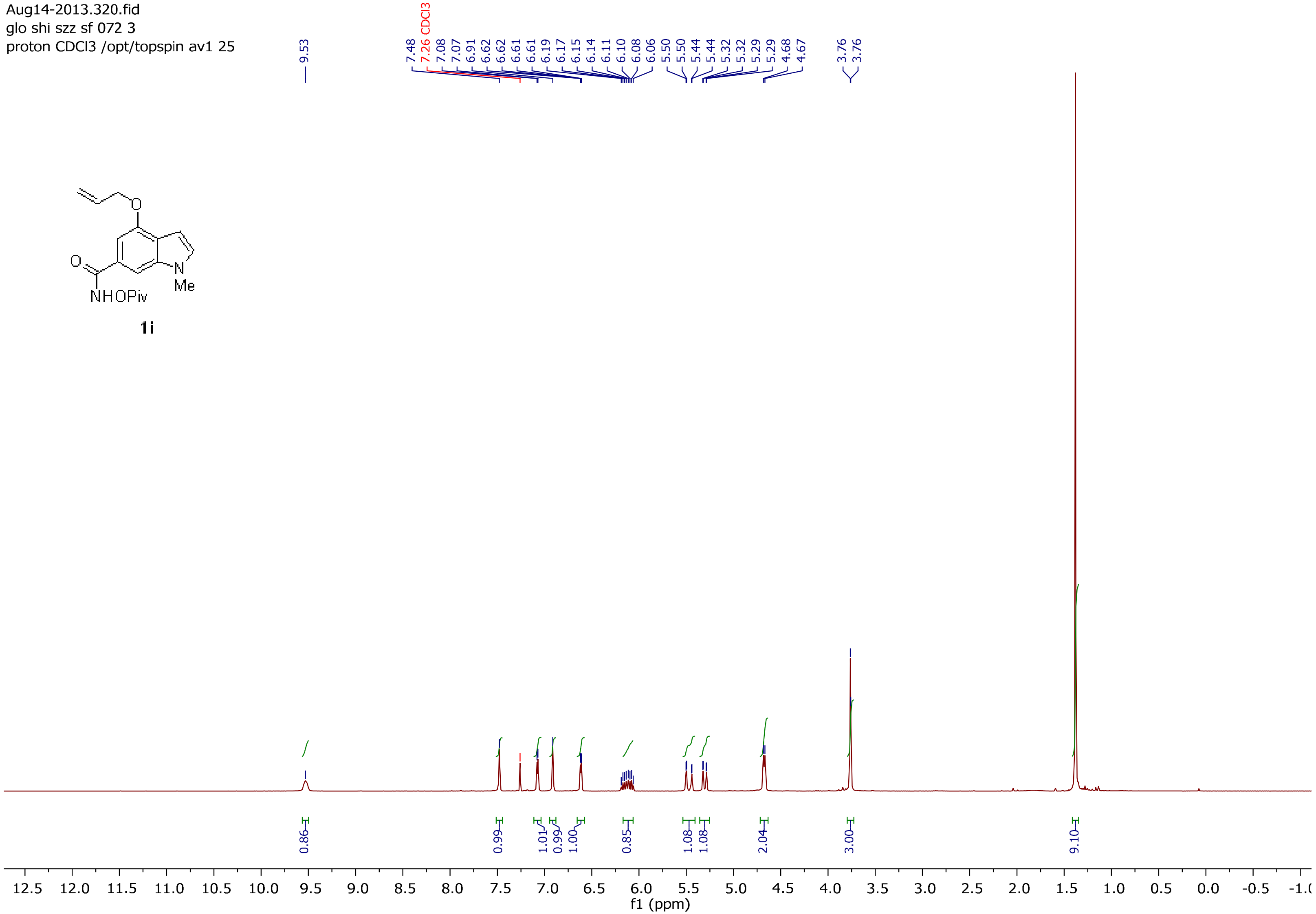
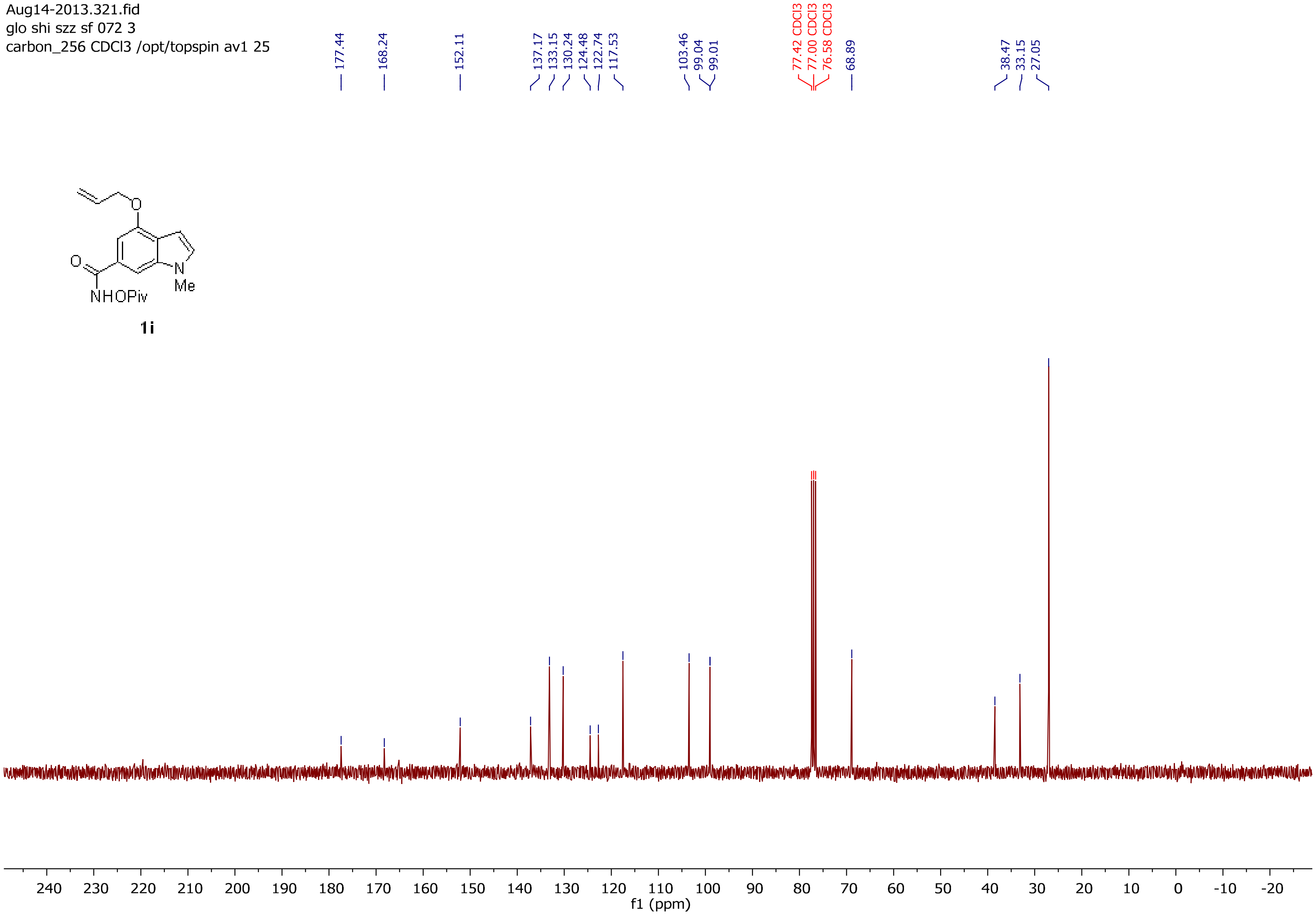
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

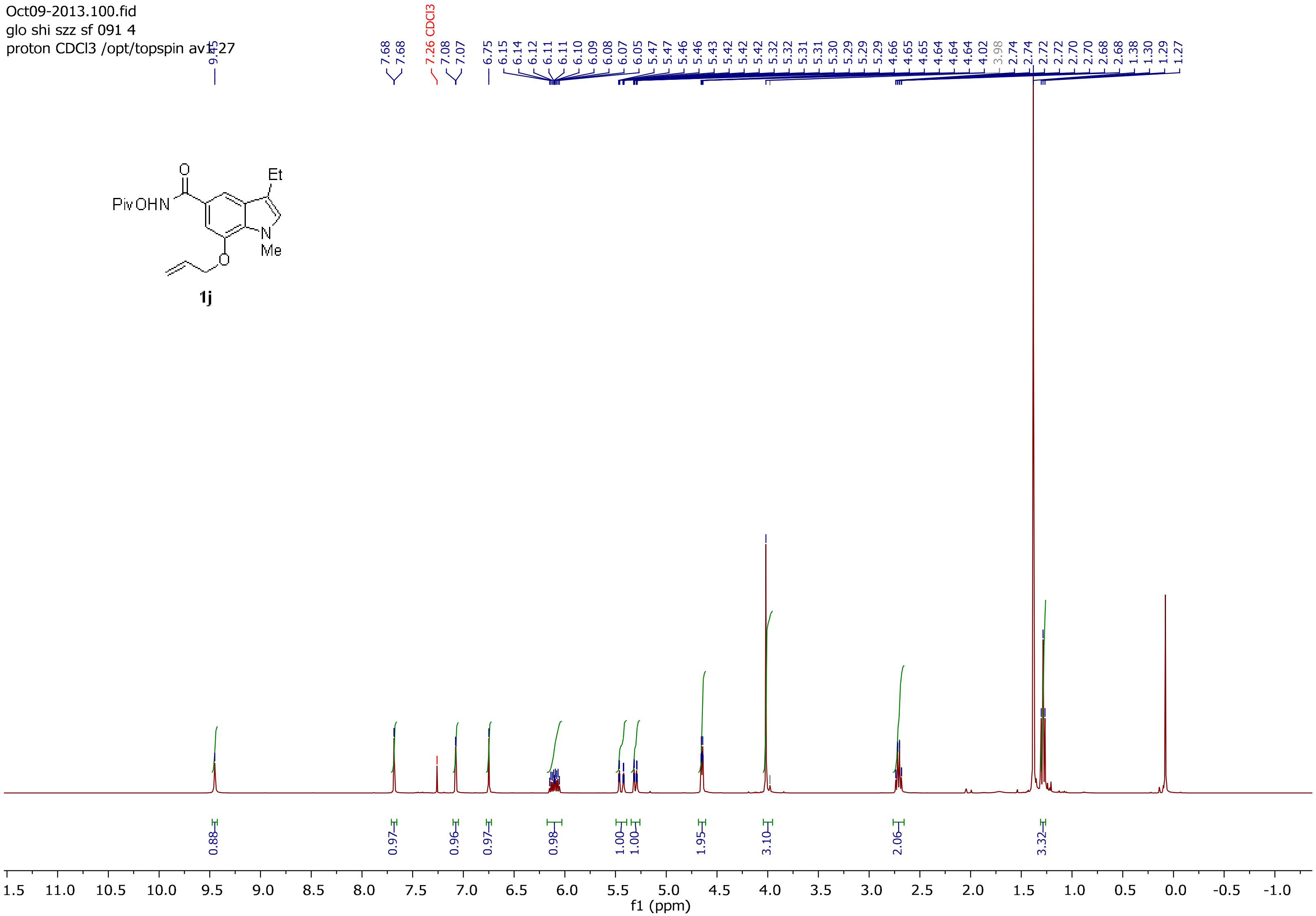

Feb22-2013.761.fid
glo shi szz se 066
carbon_256 CDCl3 /opt/topspin av1 27
177.06
167.00
143.33
138.18
132.91
130.85
128.72
127.54
124.73
115.01
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
38.44
35.02
33.13
30.35
27.01
O
NHOPiv
1g
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

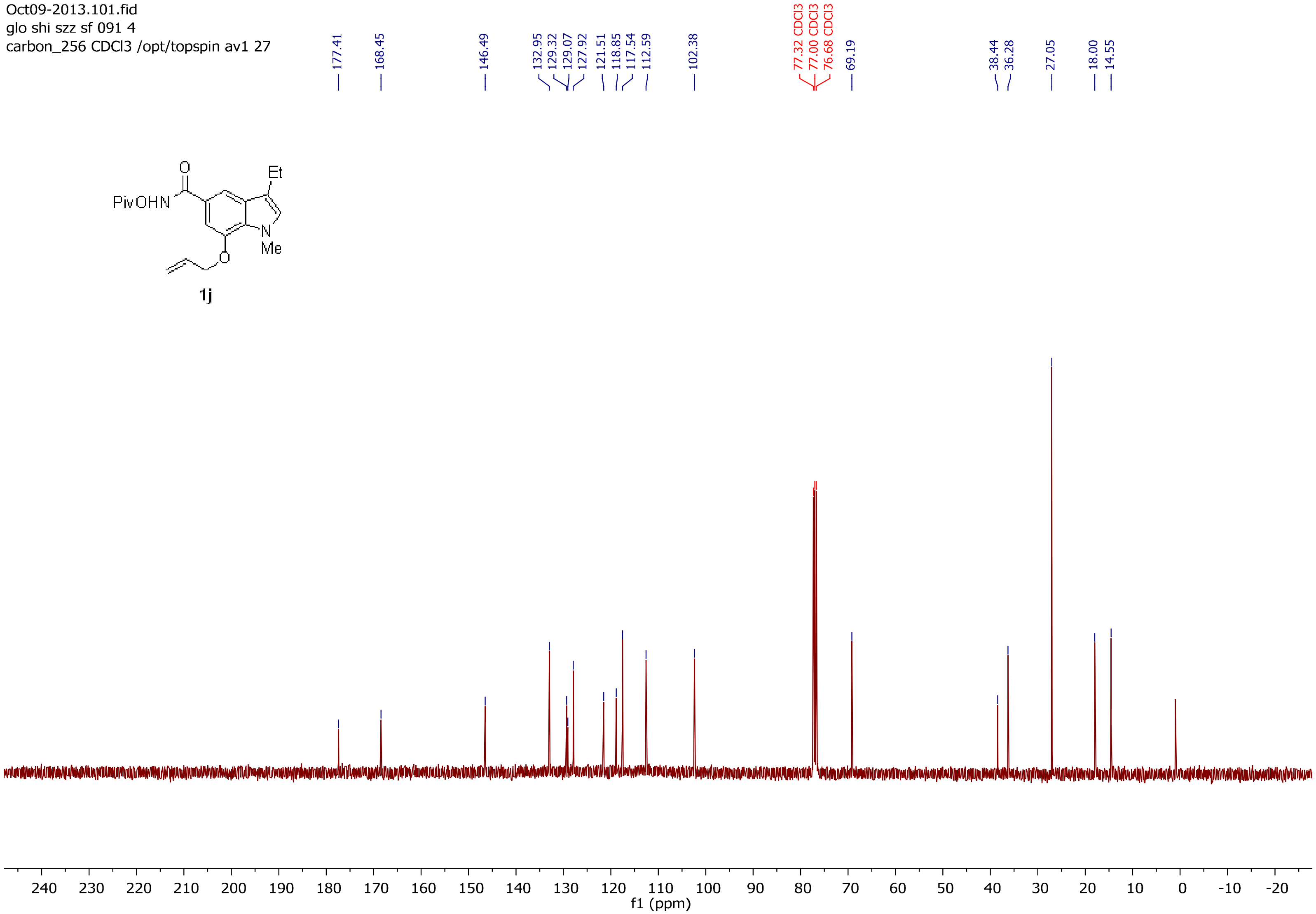

Oct07-2013.40.fid
glo zhuangzhi shi szz sf 082
proton CDCl3 /opt/topspin av1 4
O
NHOPiv
O
1h
9.22
7.56
7.56
7.54
7.54
7.41
7.41
7.39
7.39
7.39
7.33
7.31
7.29
7.28 CDCl3
7.28
7.27
7.21
7.19
7.17
7.17
7.13
7.13
7.11
7.11
7.09
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
6.87
6.87
6.86
6.85
6.85
6.84
6.82
6.79
5.73
5.73
5.69
5.69
5.22
5.22
5.19
5.19
1.28
0.88
1.00
0.98
2.02
2.33
2.12
1.10
1.10
9.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


Oct07-2013.41.fid
glo zhuangzhi shi szz sf 082
carbon_256 CDCl3 /opt/topspin av1 4
O
NHOPiv
O
1h
176.93
158.49
152.50
132.50
130.53
130.22
129.26
126.86
124.92
121.55
121.23
120.63
116.19
115.93
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
38.43
26.99
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

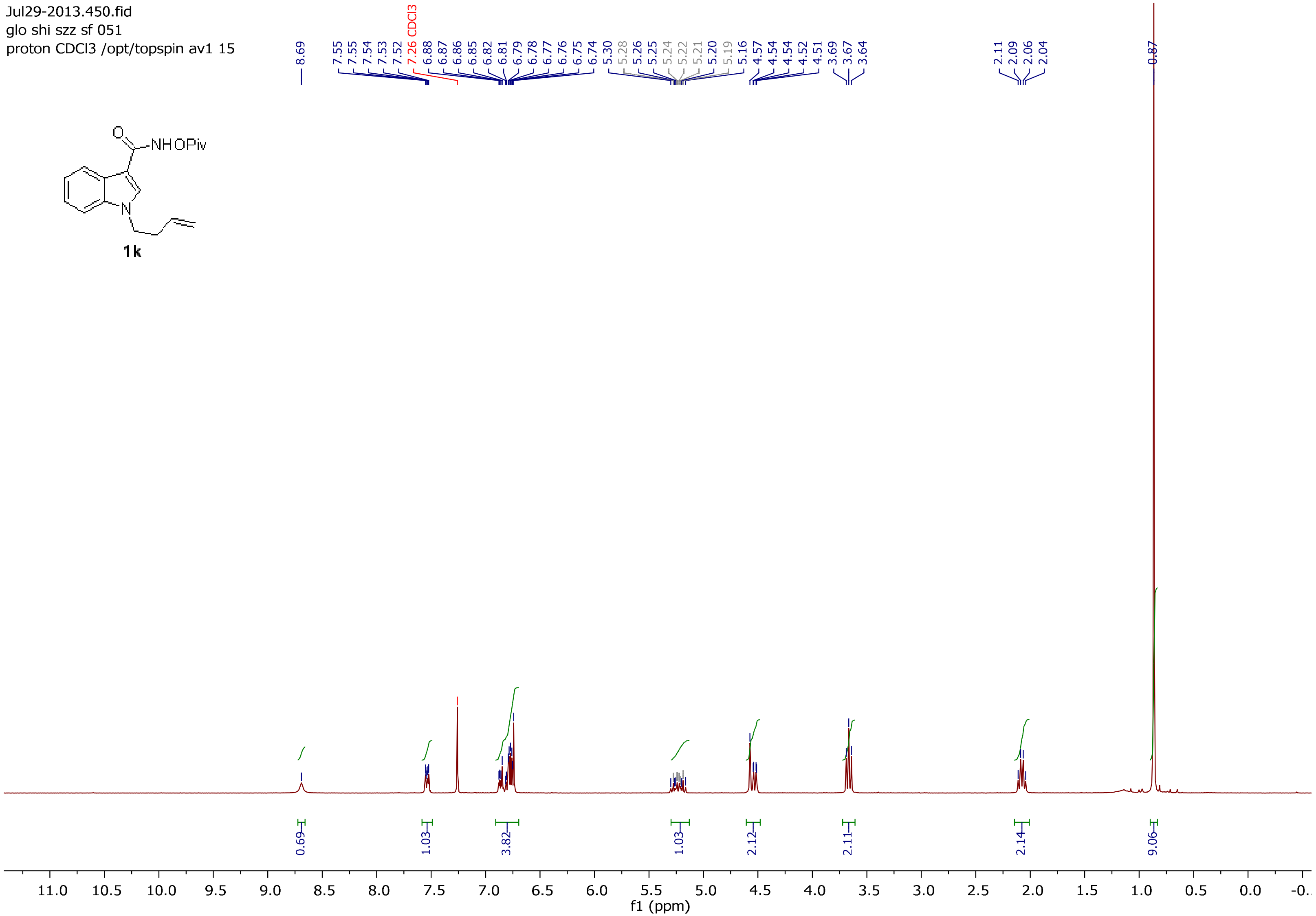

Aug14-2013.320.fid
glo shi szz sf 072 3
proton CDCl3 /opt/topspin av1 25
9.53
7.48
7.26 CDCl3
7.08
7.07
6.91
6.62
6.61
6.61
6.19
6.17
6.15
6.14
6.11
6.10
6.08
6.06
5.50
5.50
5.44
5.44
5.32
5.32
5.29
5.29
4.68
4.67
3.76
3.76
O
O
N
Me
NHOPiv
1i
0.86
0.99
1.01
0.99
1.00
0.85
1.08
1.08
2.04
3.00
9.10
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

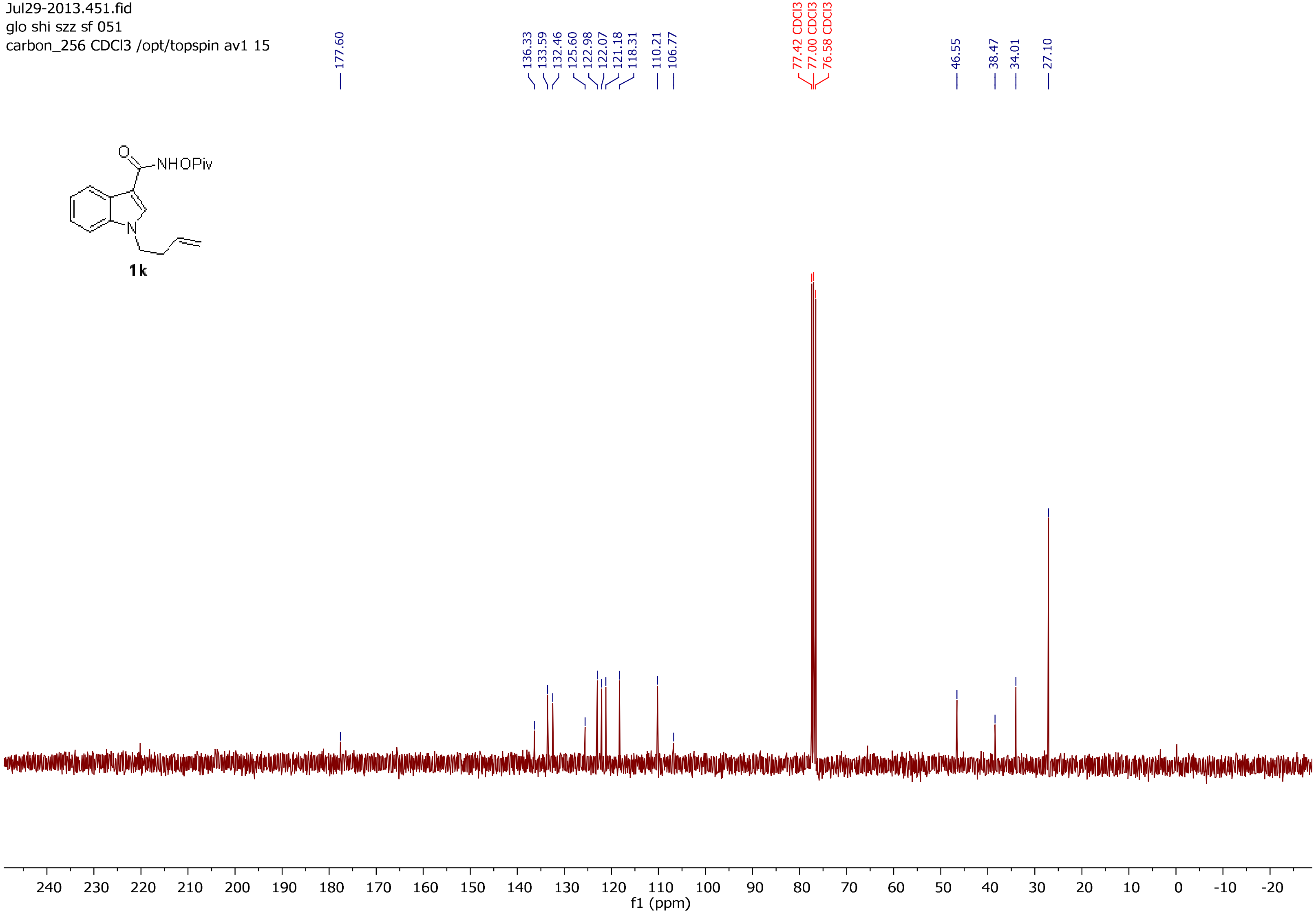

Aug14-2013.321.fid
glo shi szz sf 072 3
carbon_256 CDCl3 /opt/topspin av1 25
177.44
168.24
152.11
137.17
133.15
130.24
124.48
122.74
117.53
103.46
99.04
99.01
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
68.89
38.47
33.15
27.05
O
O
N
Me
NHOPiv
1i
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Oct09-2013.100.fid
glo shi szz sf 091 4
proton CDCl3 /opt/topspin av127
9.45
7.68
7.68
7.26 CDCl3
7.08
7.07
6.75
6.15
6.14
6.12
6.11
6.11
6.10
6.09
6.08
6.07
6.05
5.47
5.47
5.46
5.43
5.42
5.42
5.42
5.32
5.32
5.31
5.31
5.30
5.29
5.29
5.29
4.66
4.65
4.65
4.64
4.64
4.64
4.02
3.98
2.74
2.74
2.72
2.72
2.70
2.70
2.68
2.68
1.38
1.30
1.29
1.27
O
Et
PivOHN
N
Me
O
1j
0.88
0.97
0.96
0.97
0.98
1.00
1.00
1.95
3.10
2.06
3.32
1.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

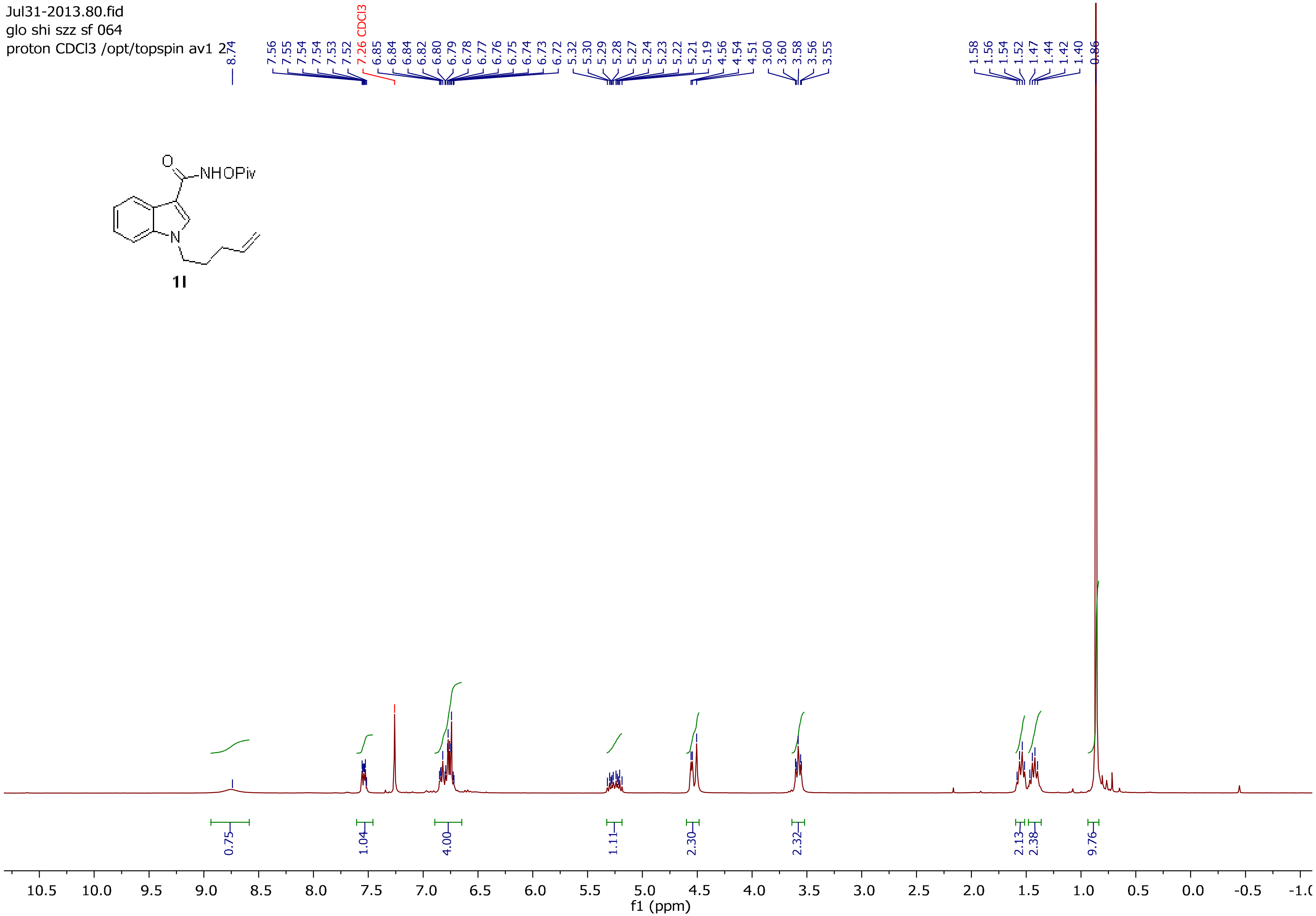

Oct09-2013.101.fid
glo shi szz sf 091 4
carbon_256 CDCl3 /opt/topspin av1 27
177.41
168.45
146.49
132.95
129.32
129.07
127.92
121.51
118.85
117.54
112.59
102.38
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.19
38.44
36.28
27.05
18.00
14.55
O
Et
PivOHN
N
Me
O
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

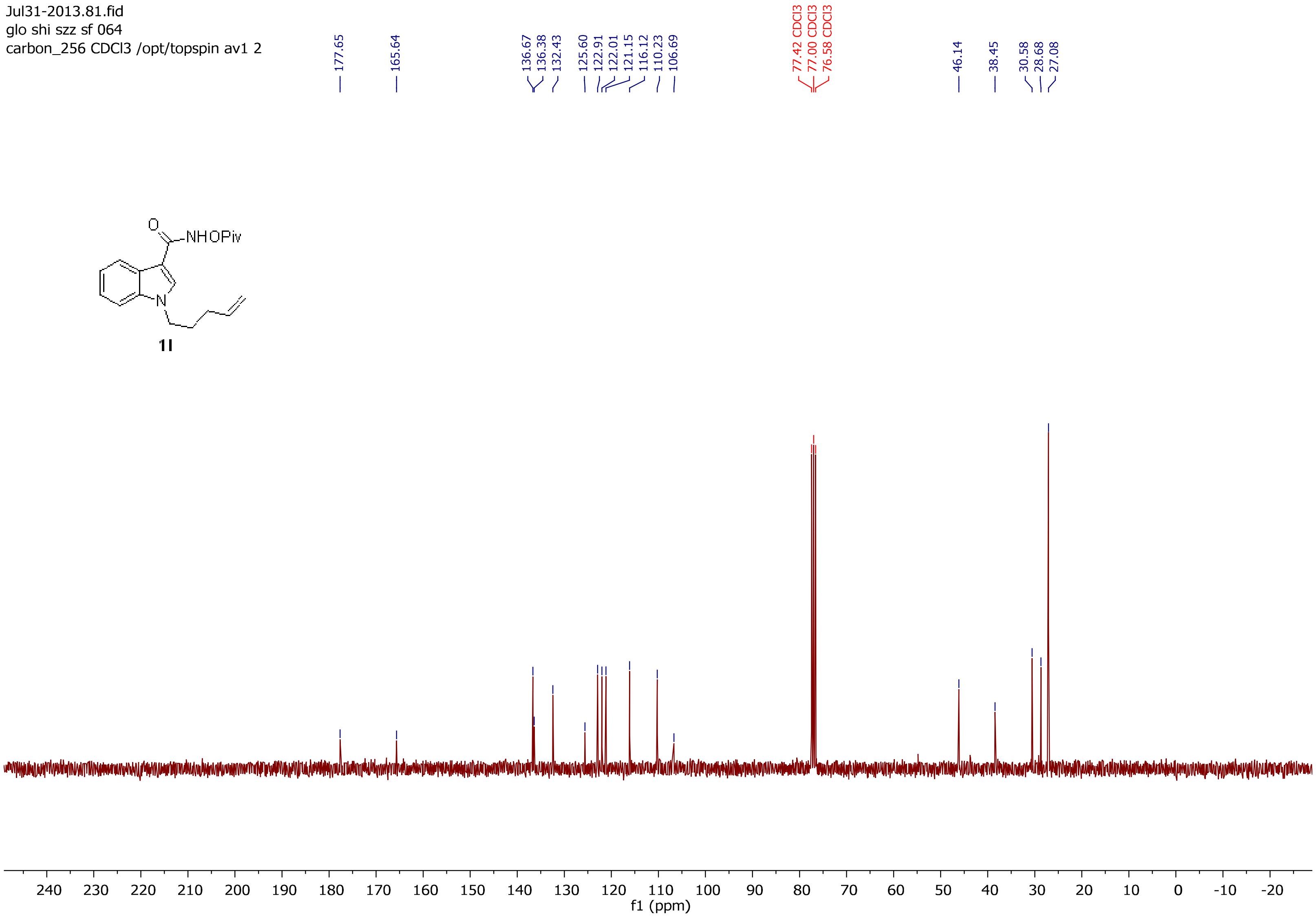
**1j**


Jul29-2013.450.fid
glo shi szz sf 051
proton CDCl3 /opt/topspin av1 15
O
NHOPiv
N
1k
8.69
7.55
7.55
7.54
7.53
7.52
7.26 CDCl3
6.88
6.87
6.86
6.85
6.82
6.81
6.79
6.78
6.77
6.76
6.75
6.74
5.30
5.28
5.26
5.25
5.24
5.22
5.21
5.20
5.19
5.16
4.57
4.54
4.54
4.52
4.51
3.69
3.67
3.64
2.11
2.09
2.06
2.04
0.87
0.69
1.03
3.82
1.03
2.12
2.11
2.14
9.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

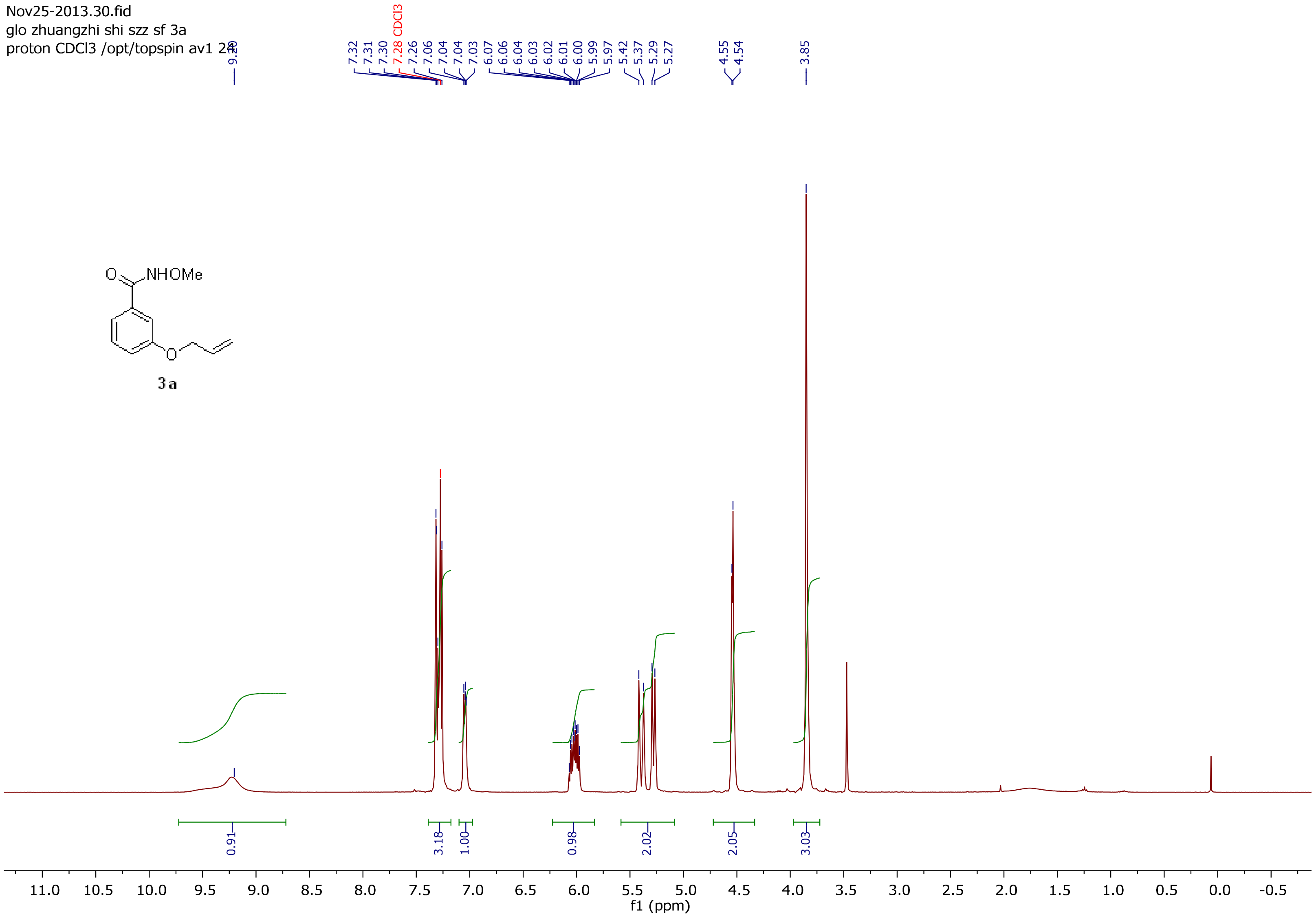

Jul29-2013.451.fid
glo shi szz sf 051
carbon_256 CDCl3 /opt/topspin av1 15
177.60
136.33
133.59
132.46
125.60
122.98
122.07
121.18
118.31
110.21
106.77
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
46.55
38.47
34.01
27.10
NHOPiv
O
N
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

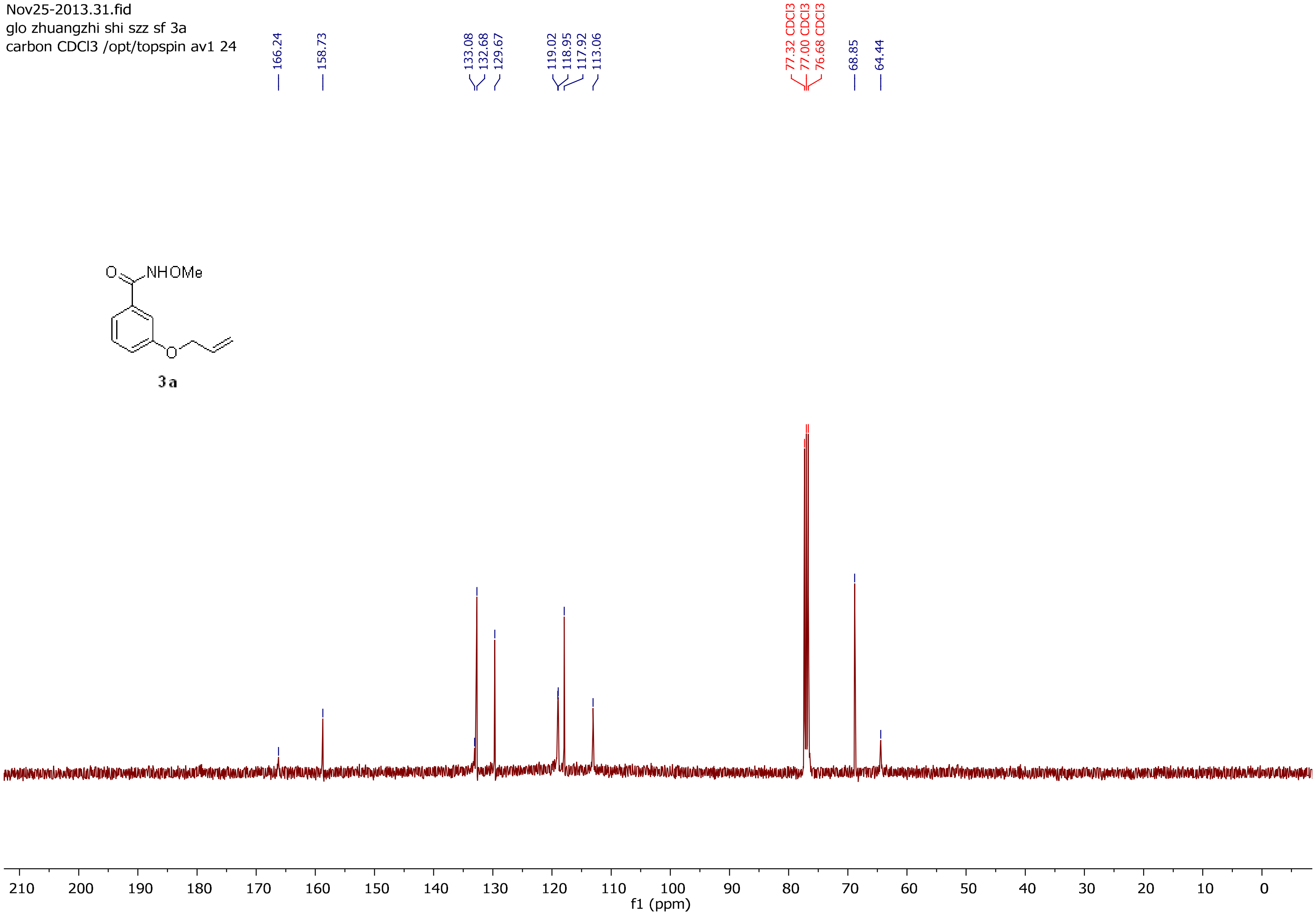
**1k**

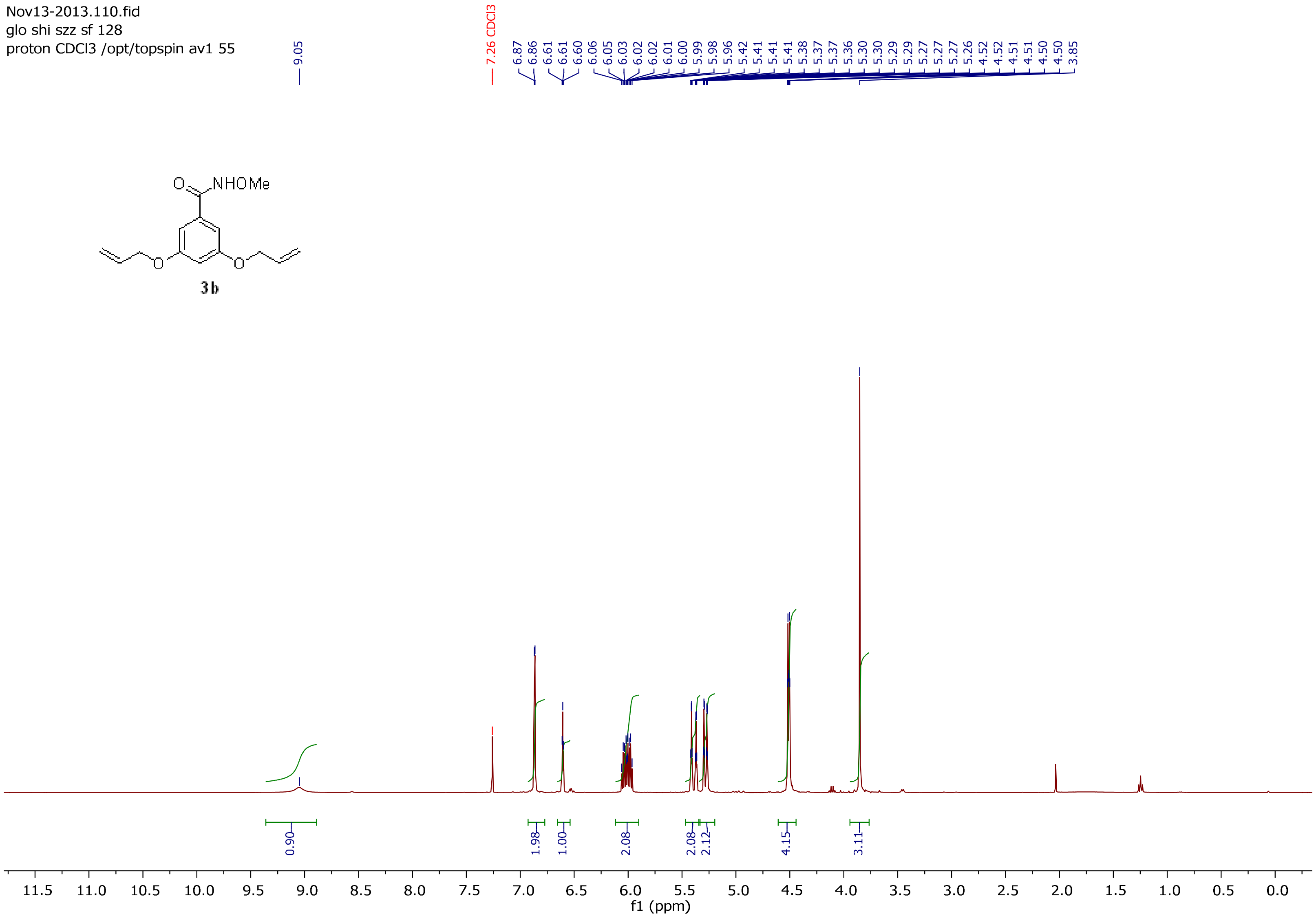

Jul31-2013.80.fid
glo shi szz sf 064
proton CDCl3 /opt/topspin av1 2
8.74
7.56
7.55
7.54
7.54
7.53
7.52
7.26 CDCl3
6.85
6.84
6.82
6.80
6.79
6.78
6.77
6.76
6.75
6.74
6.73
6.72
5.32
5.30
5.29
5.28
5.27
5.24
5.23
5.22
5.21
5.19
4.56
4.54
4.51
3.60
3.60
3.58
3.56
3.55
1.58
1.56
1.54
1.52
1.47
1.44
1.42
1.40
0.86
O
NHOPiv
N
1l
0.75
1.04
4.00
1.11
2.30
2.32
2.13
2.38
9.76
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.(
f1 (ppm)


Jul31-2013.81.fid
glo shi szz sf 064
carbon_256 CDCl3 /opt/topspin av1 2
177.65
165.64
136.67
136.38
132.43
125.60
122.91
122.01
121.15
116.12
110.23
106.69
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
46.14
38.45
30.58
28.68
27.08
O
NHOPiv
N
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

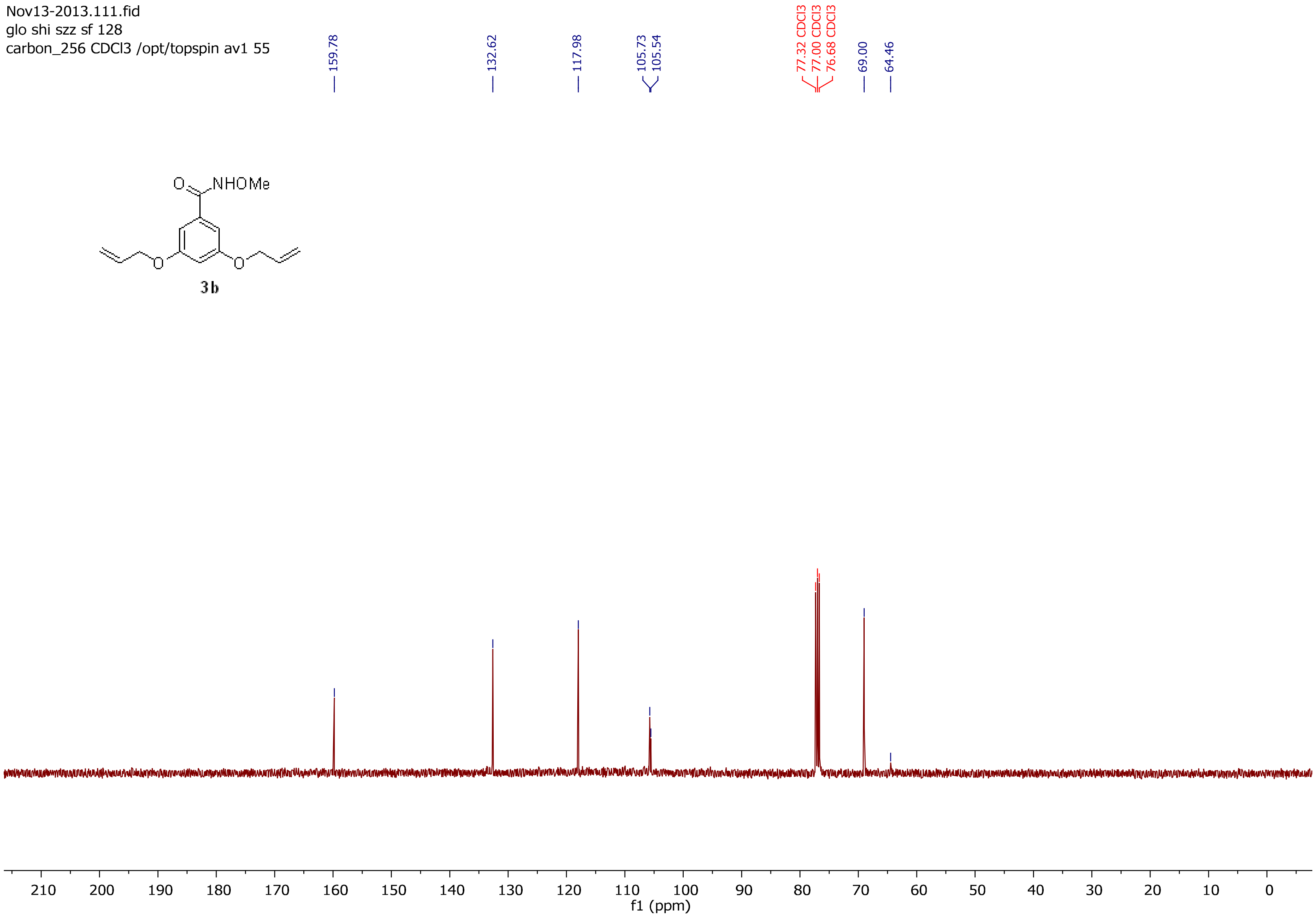
**1l**

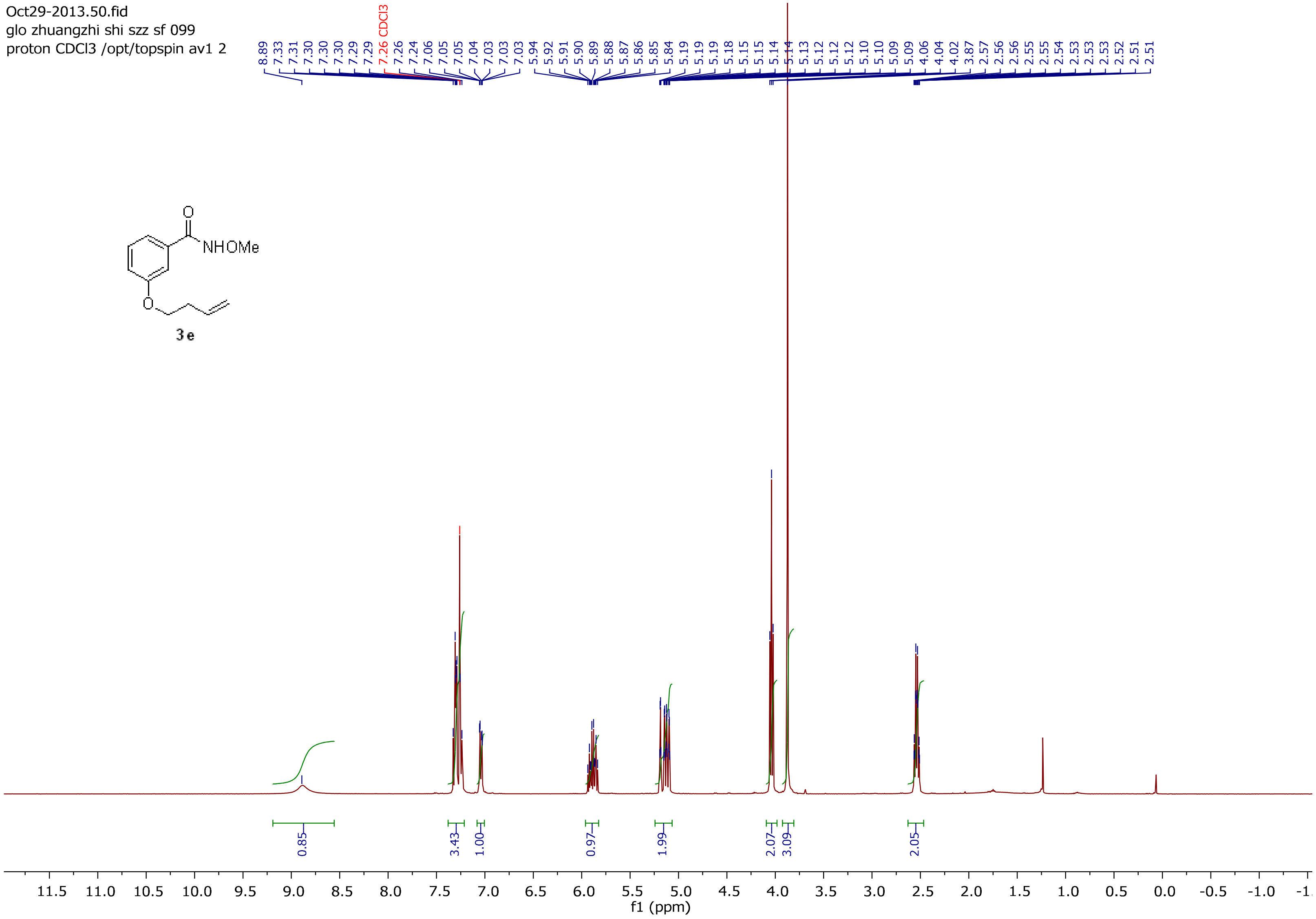

Nov25-2013.30.fid
glo zhuangzhi shi szz sf 3a
proton CDCl3 /opt/topspin av1 28
9.20
7.32
7.31
7.30
7.28 CDCl3
7.26
7.06
7.04
7.04
7.03
6.07
6.06
6.04
6.03
6.02
6.01
6.00
5.99
5.97
5.42
5.37
5.29
5.27
4.55
4.54
3.85
O
NHOMe
O
3a
0.91
3.18
1.00
0.98
2.02
2.05
3.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

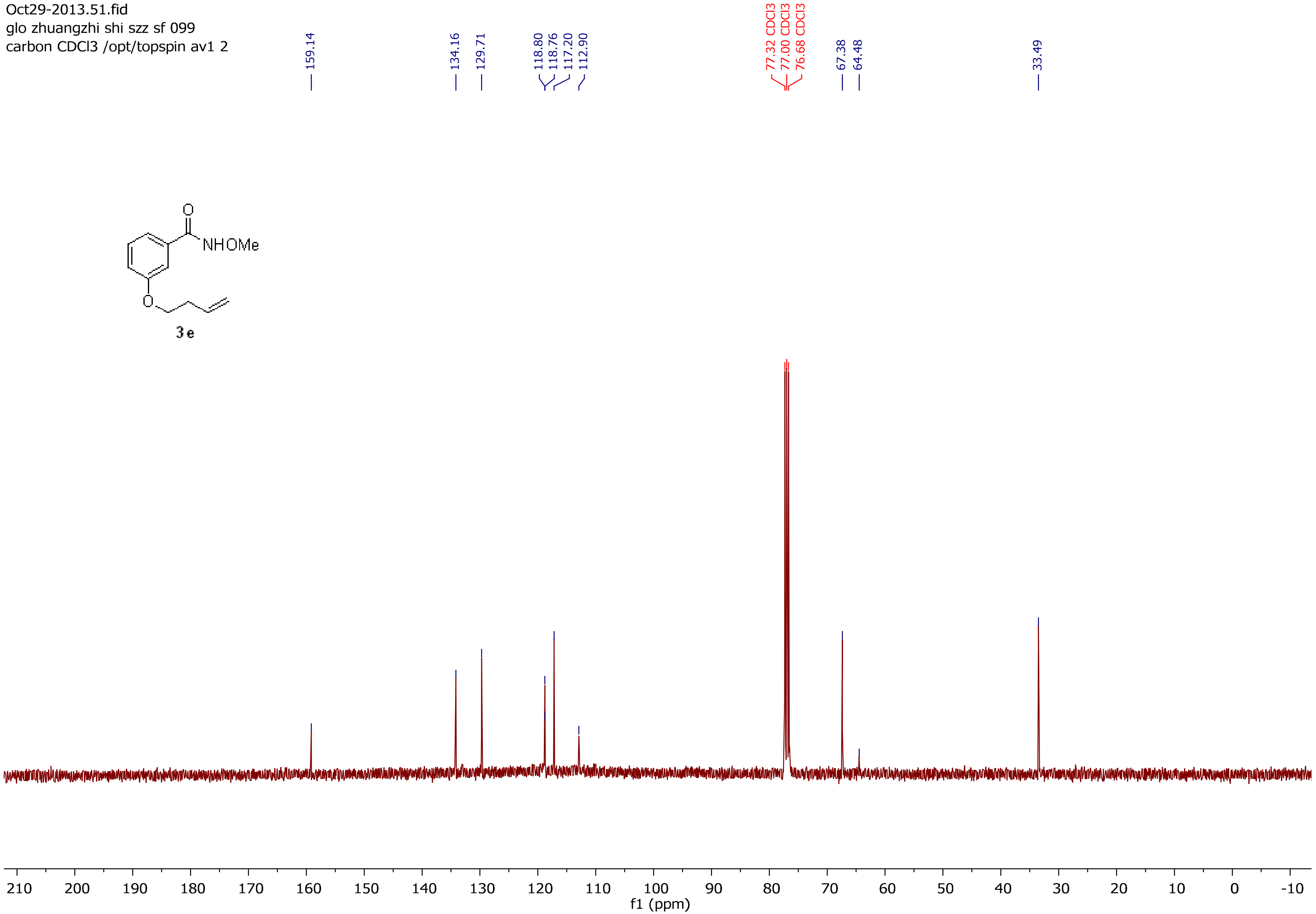

Nov25-2013.31.fid
glo zhuangzhi shi szz sf 3a
carbon CDCl3 /opt/topspin av1 24
166.24
158.73
133.08
132.68
129.67
119.02
118.95
117.92
113.06
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
68.85
64.44
O
NHOMe
O
3a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

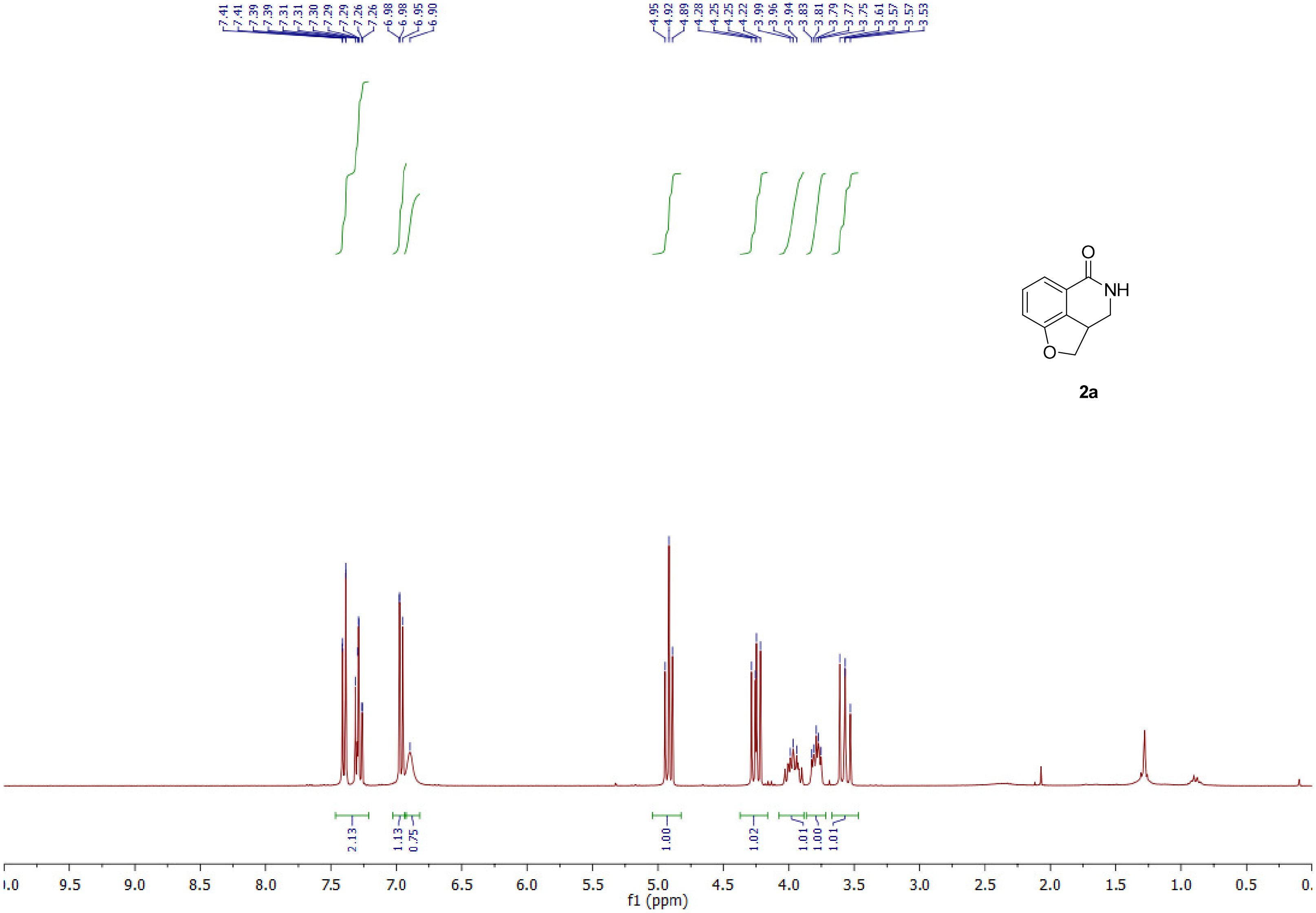

Nov13-2013.110.fid
glo shi szz sf 128
proton CDCl3 /opt/topspin av1 55
9.05
7.26 CDCl3
6.87
6.86
6.61
6.61
6.60
6.06
6.05
6.03
6.02
6.02
6.01
6.00
5.99
5.98
5.96
5.42
5.41
5.41
5.38
5.37
5.37
5.36
5.30
5.30
5.29
5.29
5.27
5.27
5.26
4.52
4.52
4.51
4.51
4.50
4.50
3.85
O
NHOMe
O
O
0.90
1.98
1.00
2.08
2.08
2.12
4.15
3.11
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**3b**

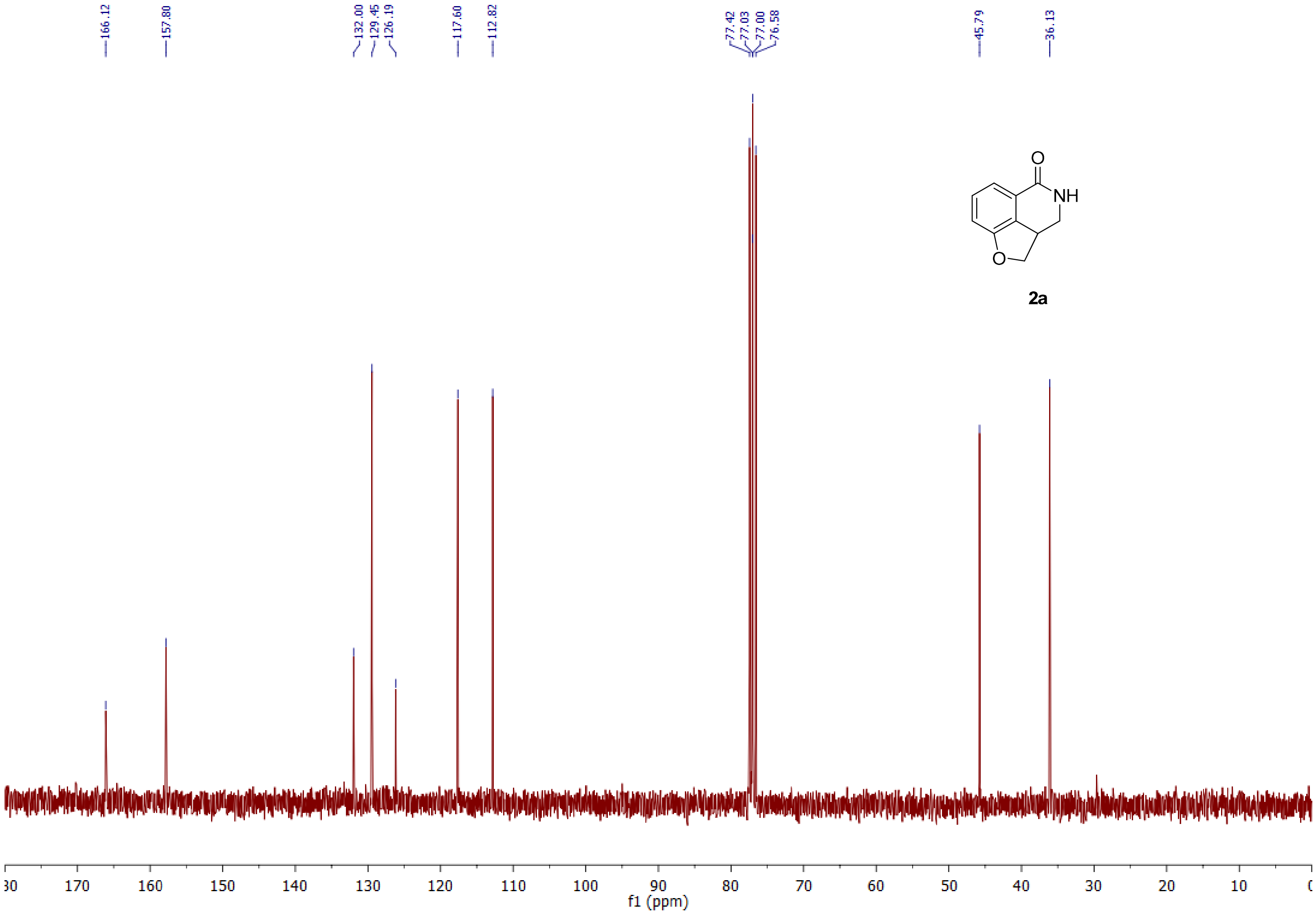

Nov13-2013.111.fid
glo shi szz sf 128
carbon_256 CDCl3 /opt/topspin av1 55
159.78
132.62
117.98
105.73
105.54
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.00
64.46
O
NHOMe
O
O
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Oct29-2013.50.fid
glo zhuangzhi shi szz sf 099
proton CDCl3 /opt/topspin av1 2
8.89
7.33
7.31
7.30
7.30
7.30
7.29
7.29
7.26 CDCl3
7.26
7.24
7.06
7.05
7.05
7.04
7.03
7.03
7.03
5.94
5.92
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.84
5.19
5.19
5.19
5.18
5.15
5.15
5.14
5.14
5.13
5.12
5.12
5.12
5.10
5.10
5.09
5.09
4.06
4.04
4.02
3.87
2.57
2.56
2.56
2.55
2.55
2.54
2.53
2.53
2.52
2.51
2.51
NHOMe
O
O
3e
0.85
3.43
1.00
0.97
1.99
2.07
3.09
2.05
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

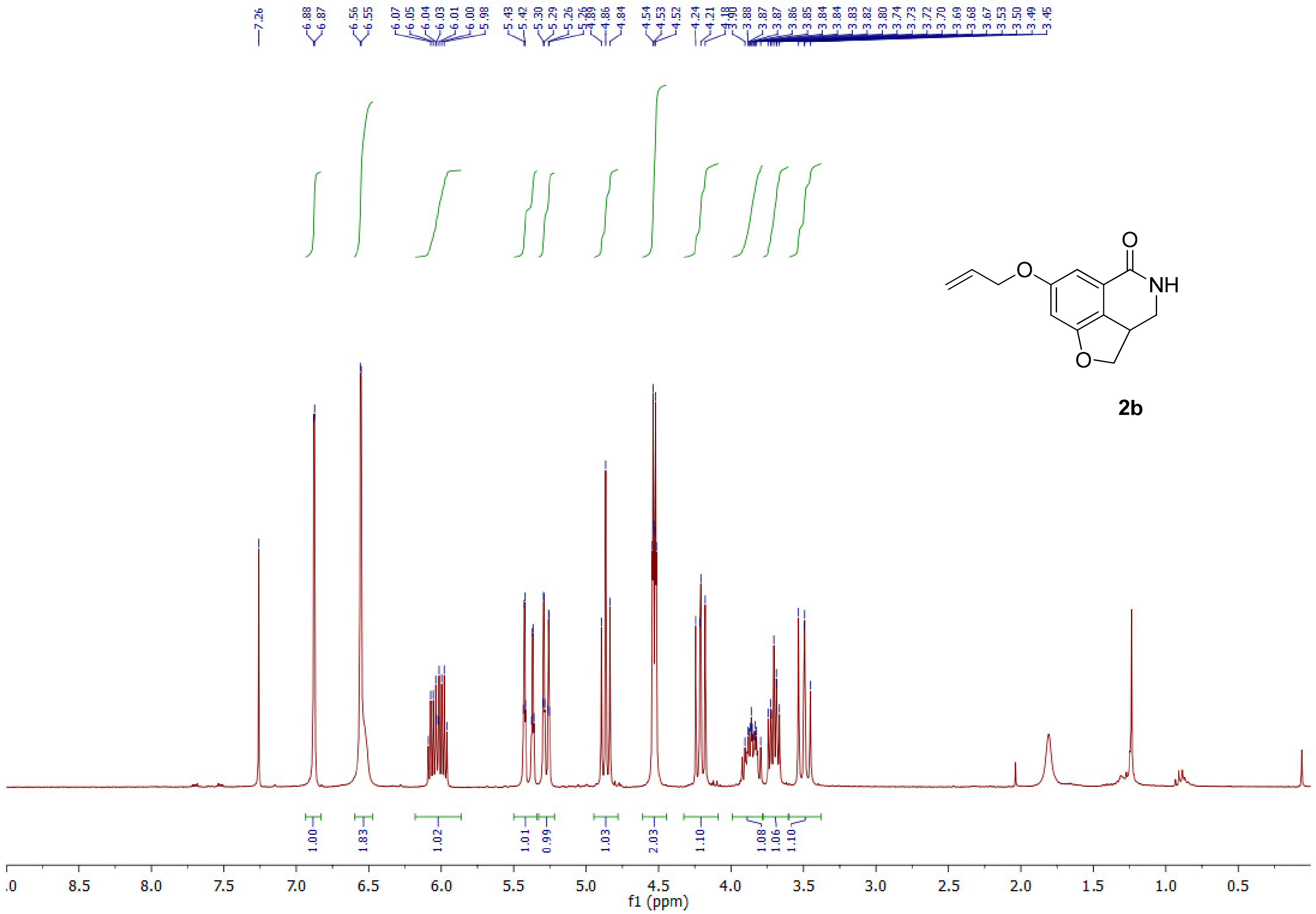

Oct29-2013.51.fid
glo zhuangzhi shi szz sf 099
carbon CDCl3 /opt/topspin av1 2
159.14
134.16
129.71
118.80
118.76
117.20
112.90
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.38
64.48
33.49
O
NHOMe
O
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.41
7.41
7.39
7.39
7.31
7.31
7.30
7.29
7.29
7.26
7.26
6.98
6.98
6.95
6.90
4.95
4.92
4.89
4.28
4.25
4.25
4.22
3.99
3.96
3.94
3.83
3.81
3.79
3.77
3.75
3.61
3.57
3.57
3.53
O
NH
O
2.13
1.13
0.75
1.00
1.02
1.01
1.00
1.01
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

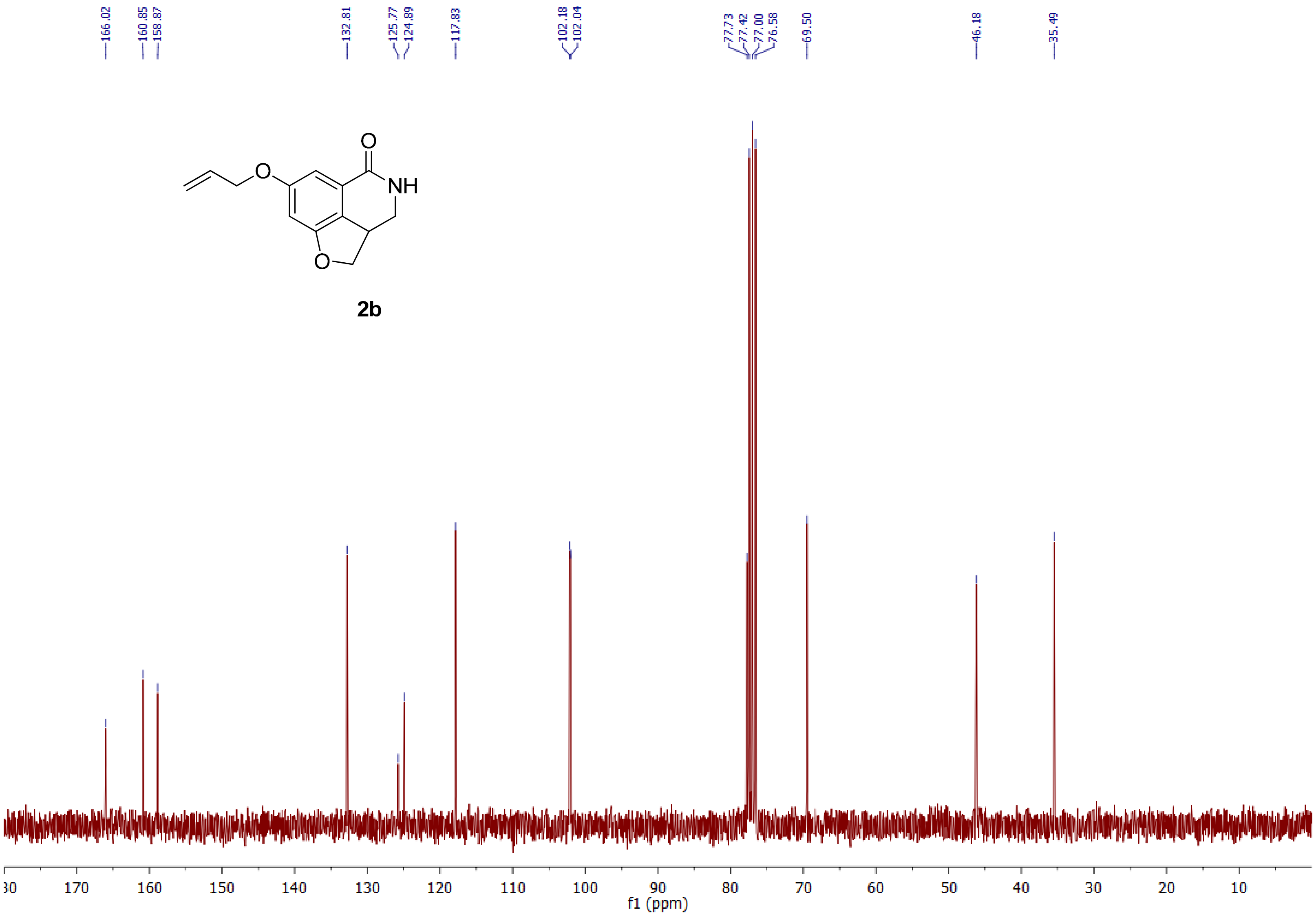
**2a**


166.12
157.80
132.00
129.45
126.19
117.60
112.82
77.42
77.03
77.00
76.58
45.79
36.13
O
NH
O
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

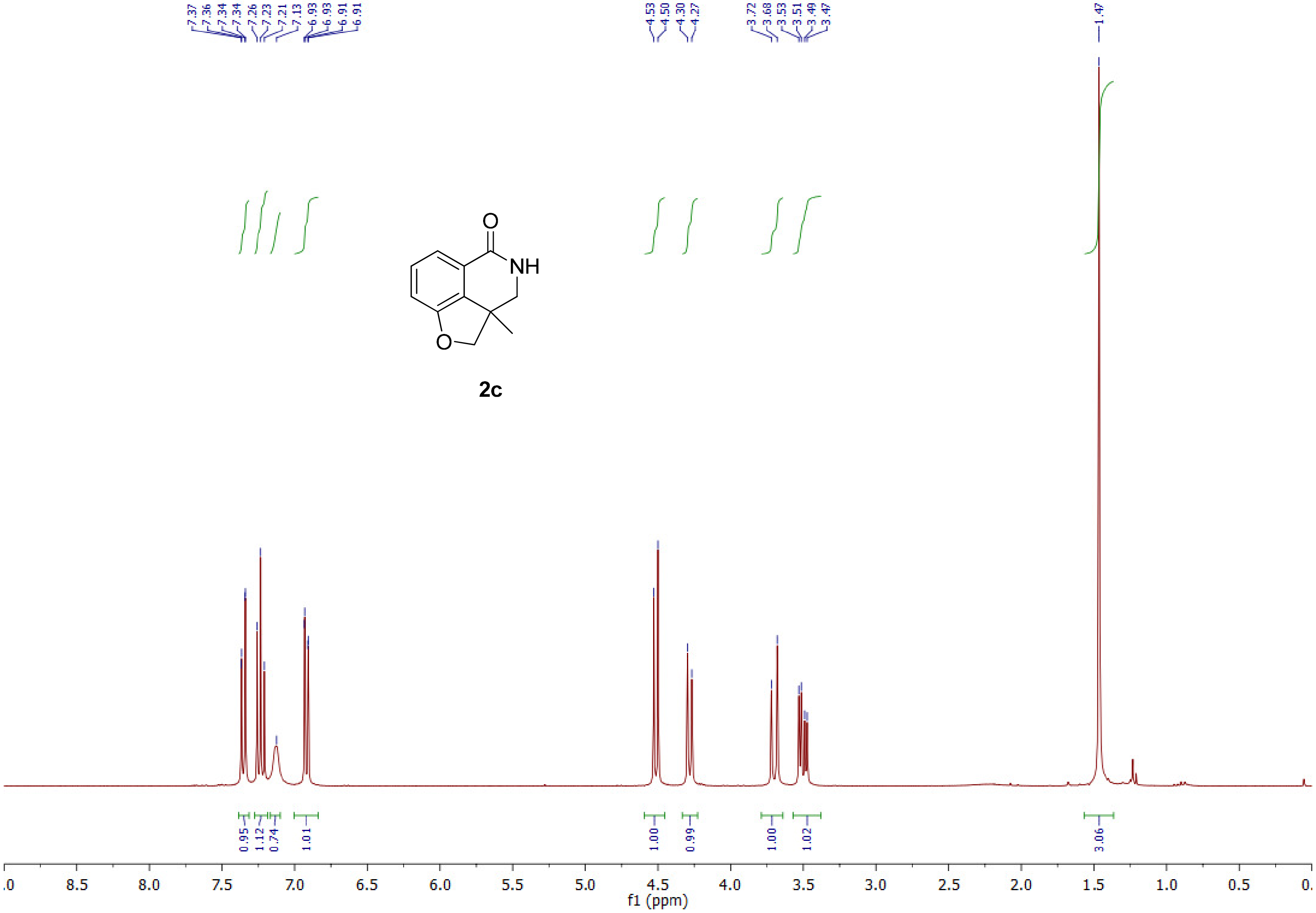
**2a**


7.26
6.88
6.87
6.56
6.55
6.07
6.05
6.04
6.03
6.01
6.00
5.98
5.43
5.42
5.30
5.29
5.26
5.26
4.89
4.86
4.84
4.54
4.53
4.52
4.24
4.21
4.18
3.90
3.88
3.87
3.87
3.86
3.85
3.84
3.84
3.83
3.82
3.80
3.74
3.73
3.72
3.70
3.69
3.68
3.67
3.53
3.50
3.49
3.45
1.00
1.83
1.02
1.01
0.99
1.03
2.03
1.10
1.08
1.06
1.10
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
O
O
NH
O

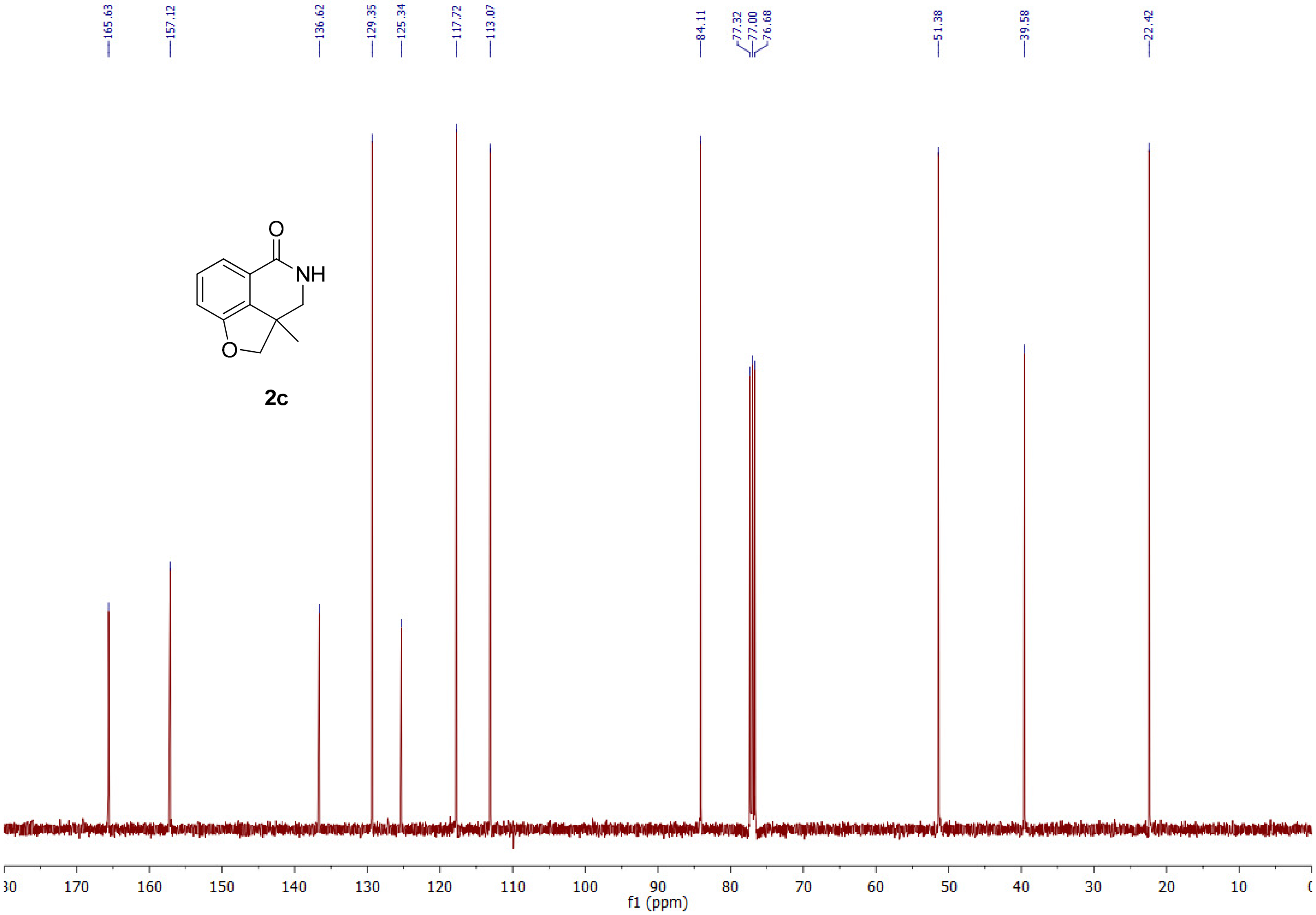
**2b**


166.02
160.85
158.87
132.81
125.77
124.89
117.83
102.18
102.04
77.73
77.42
77.00
76.58
69.50
46.18
35.49
O
NH
O
O
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

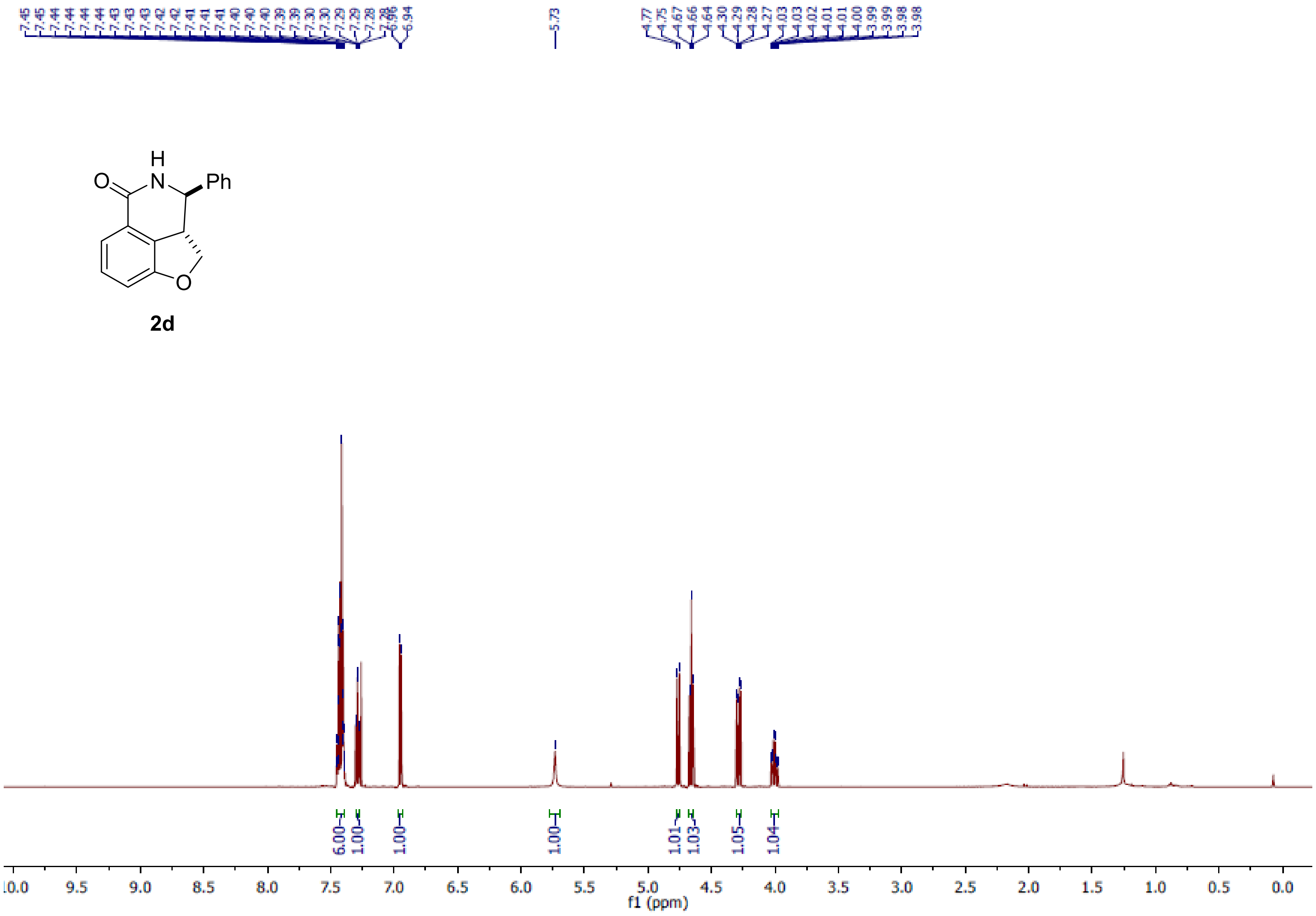
**2b**


7.37
7.36
7.34
7.34
7.26
7.23
7.21
7.13
6.93
6.93
6.91
6.91
4.53
4.50
4.30
4.27
3.72
3.68
3.53
3.51
3.49
3.47
1.47
O
NH
O
0.95
1.12
0.74
1.01
1.00
0.99
1.00
1.02
3.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

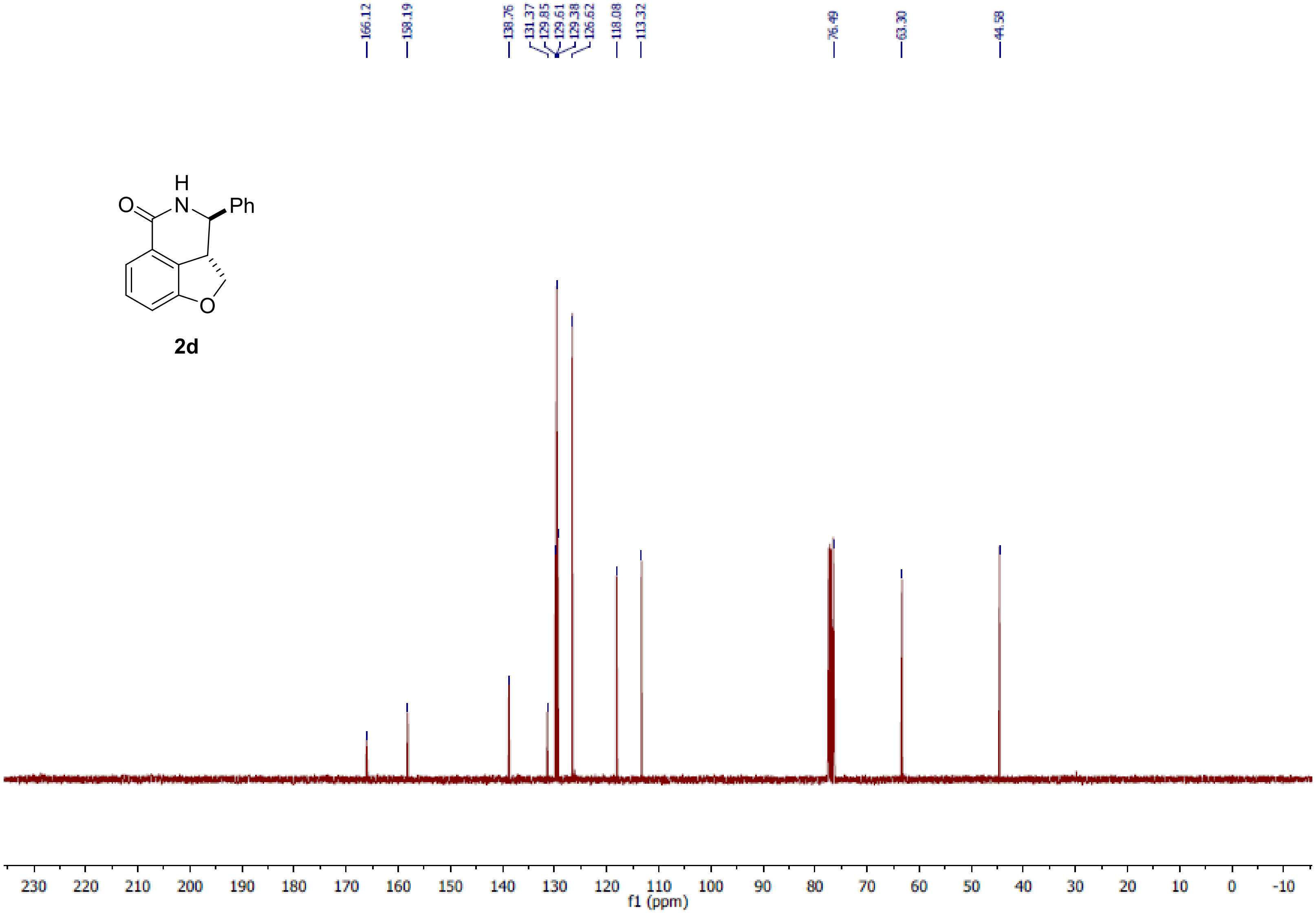
**2c**

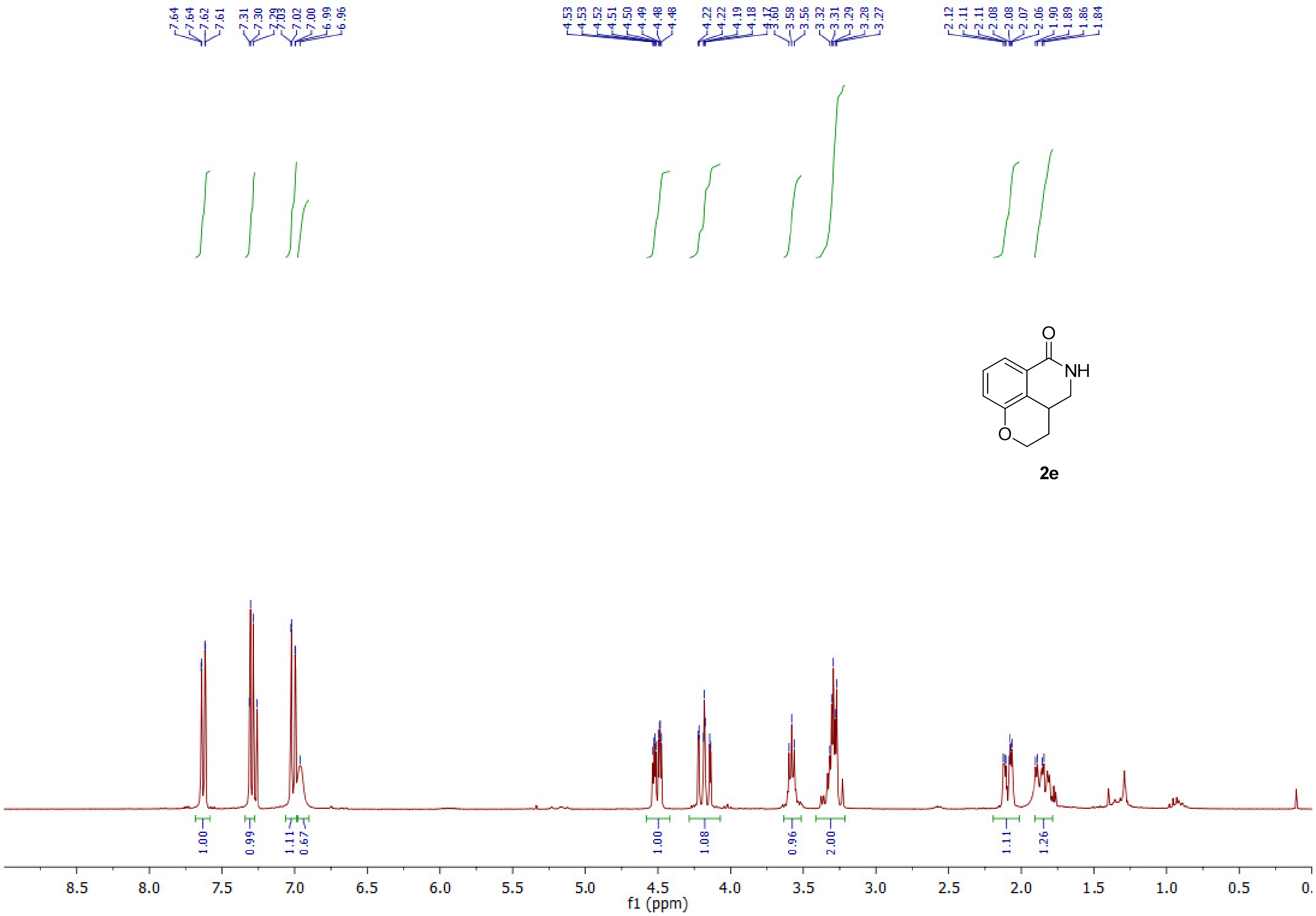

165.63
157.12
136.62
129.35
125.34
117.72
113.07
84.11
77.32
77.00
76.68
51.38
39.58
22.42
O
NH
O
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

**2c**

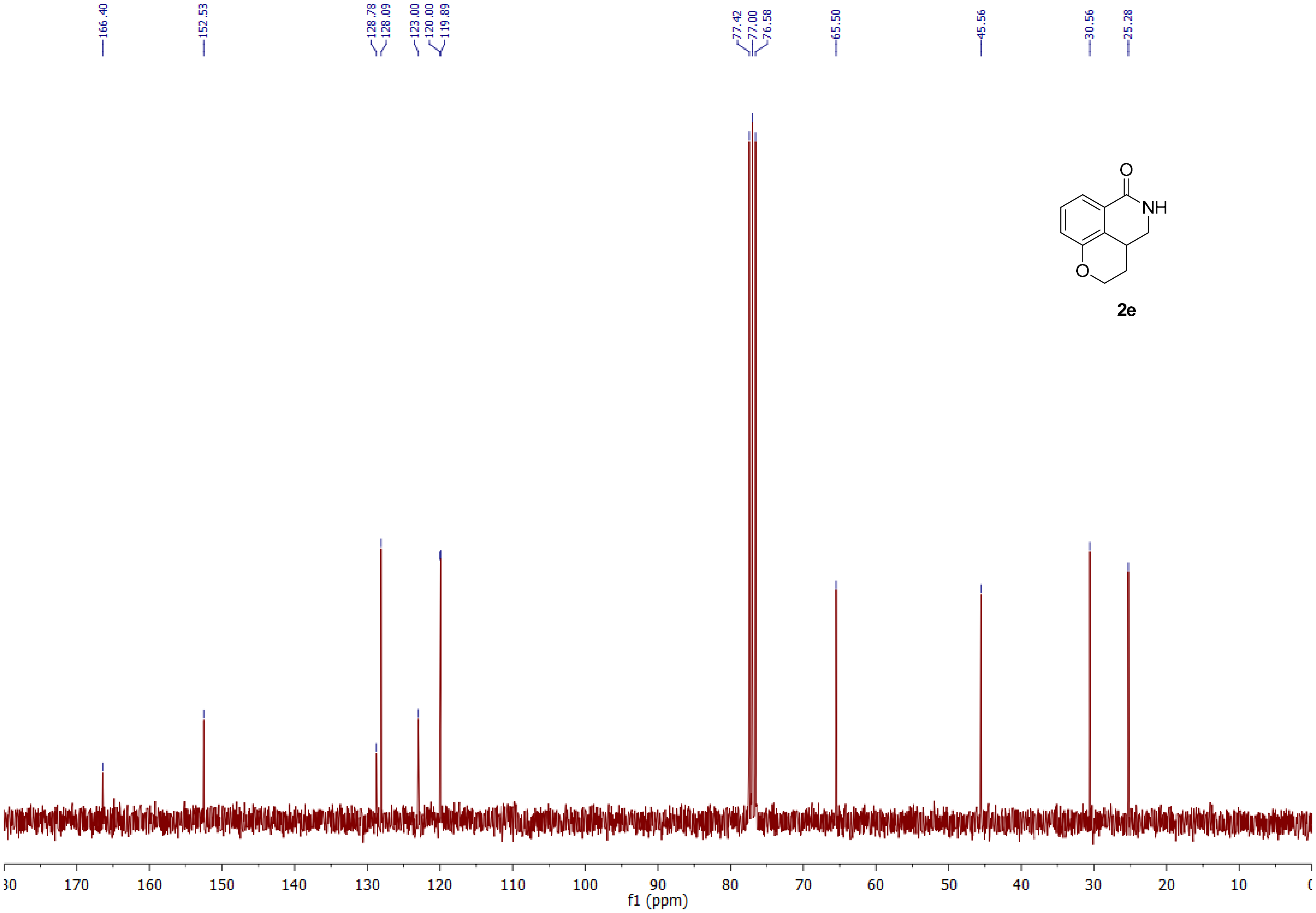

7.45
7.45
7.44
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.30
7.30
7.29
7.29
7.28
7.28
6.96
6.94
5.73
4.77
4.75
4.67
4.66
4.64
4.30
4.29
4.28
4.27
4.03
4.03
4.02
4.01
4.01
4.00
3.99
3.99
3.98
3.98
H
O
N
Ph
O
6.00
1.00
1.00
1.00
1.01
1.03
1.05
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

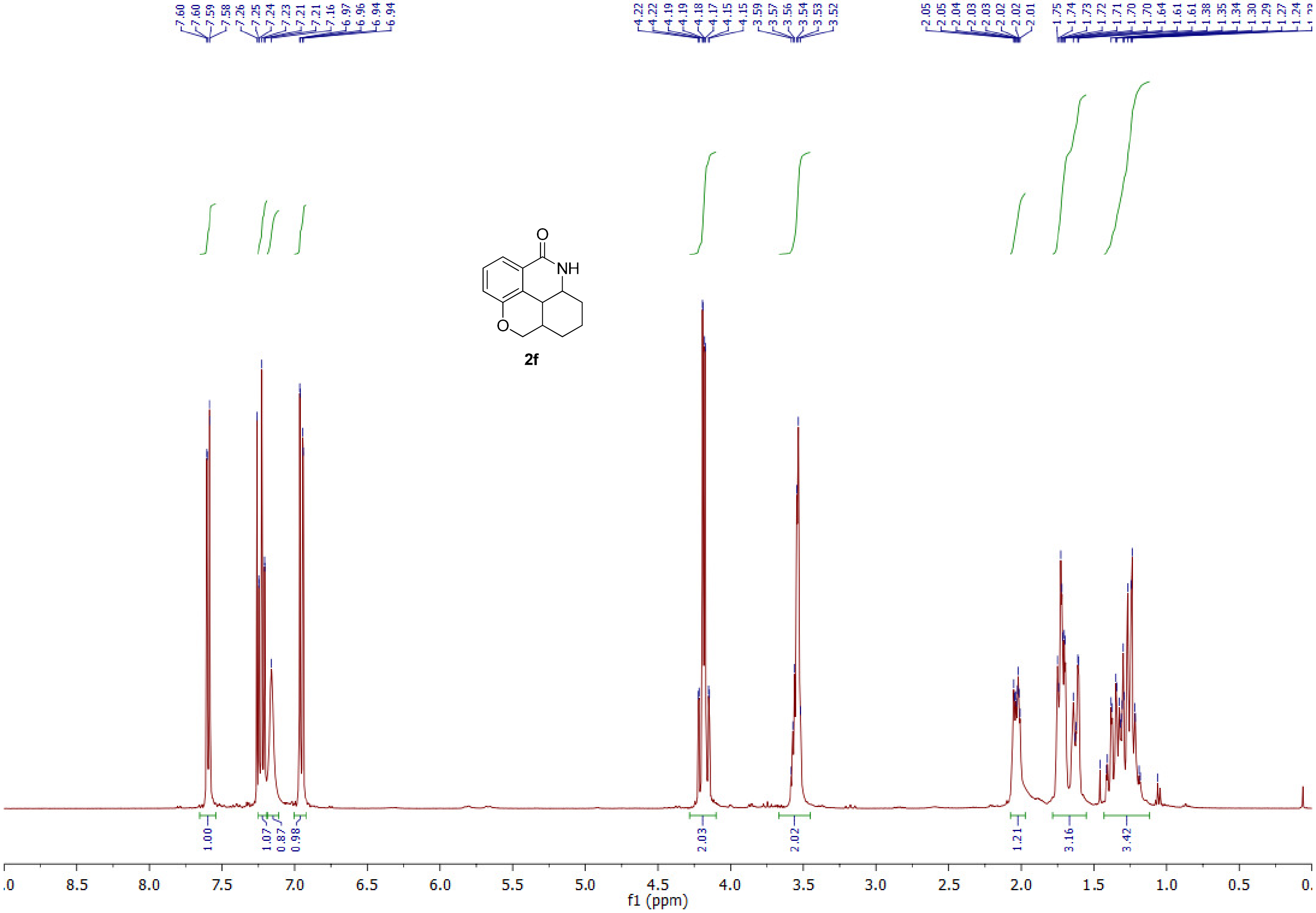
**2d**

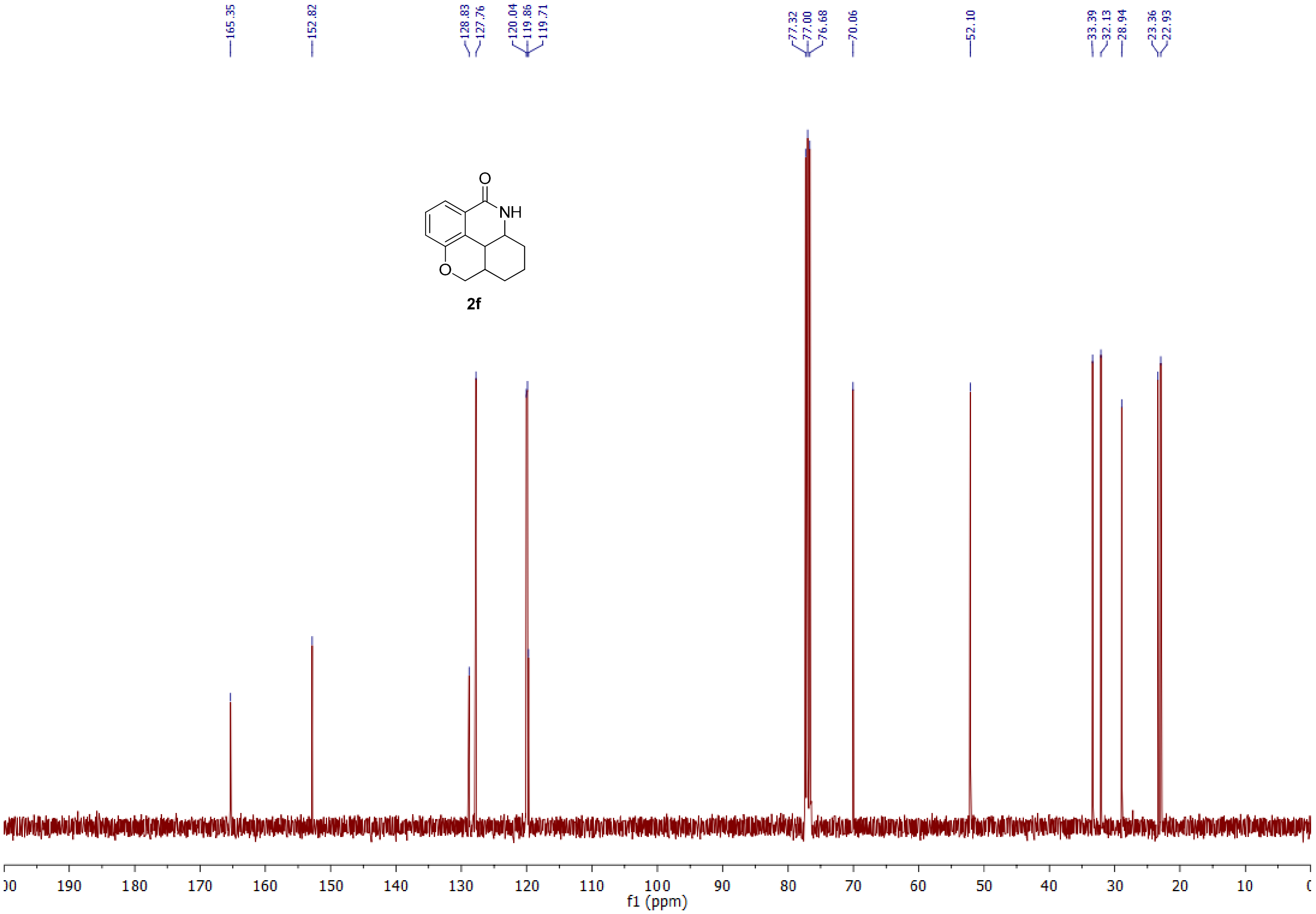

166.12
158.19
138.76
131.37
129.85
129.61
129.38
126.62
118.08
113.32
76.49
63.30
44.58
H
O
N
Ph
O
2d
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

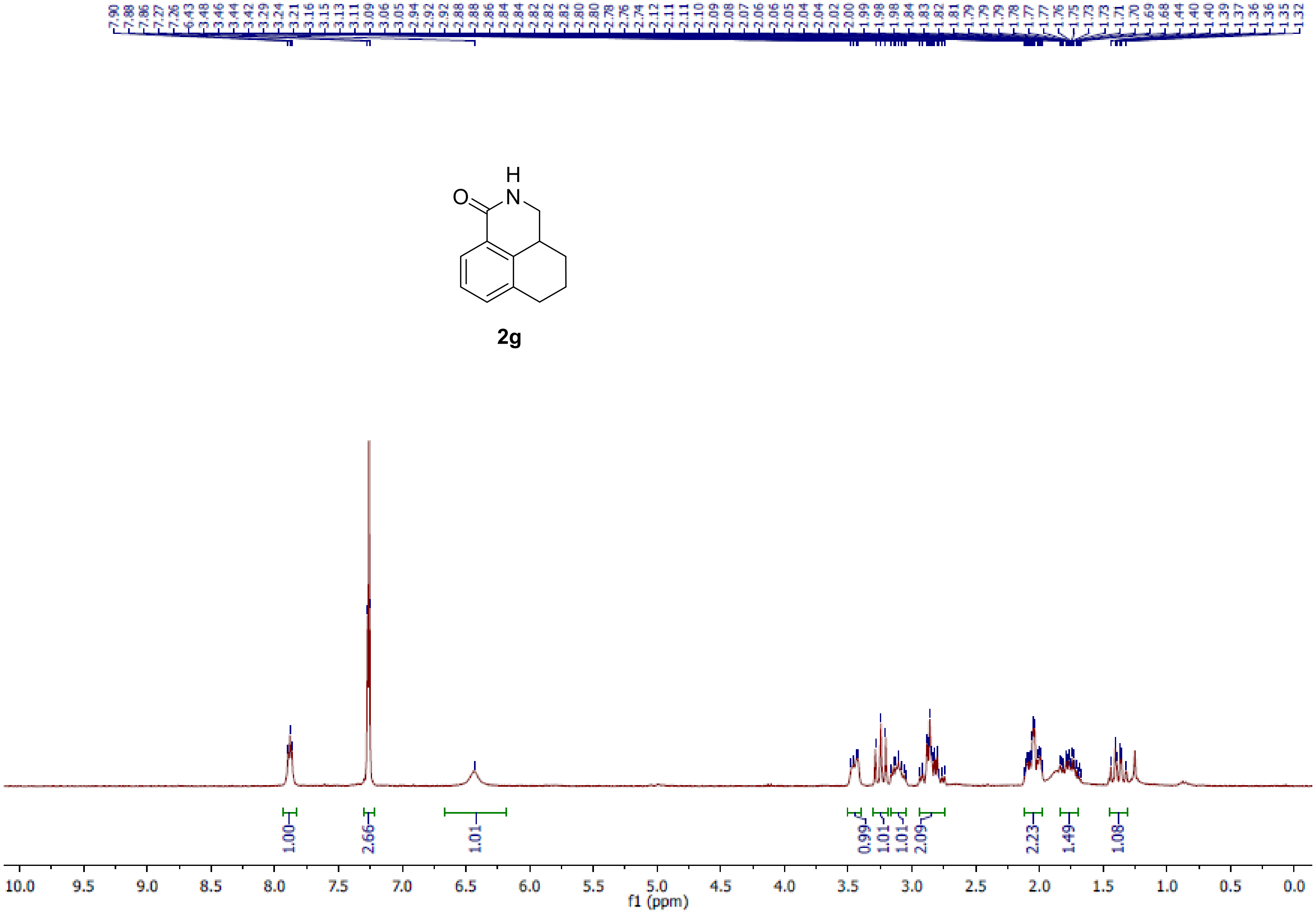

7.64
7.64
7.62
7.61
7.31
7.30
7.28
7.03
7.02
7.00
6.99
6.96
4.53
4.53
4.52
4.51
4.50
4.49
4.48
4.48
4.22
4.22
4.19
4.18
4.17
3.60
3.58
3.56
3.32
3.31
3.29
3.28
3.27
2.12
2.11
2.11
2.08
2.08
2.07
2.06
1.90
1.89
1.86
1.84
O
NH
O
1.00
0.99
1.11
0.67
1.00
1.08
0.96
2.00
1.11
1.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

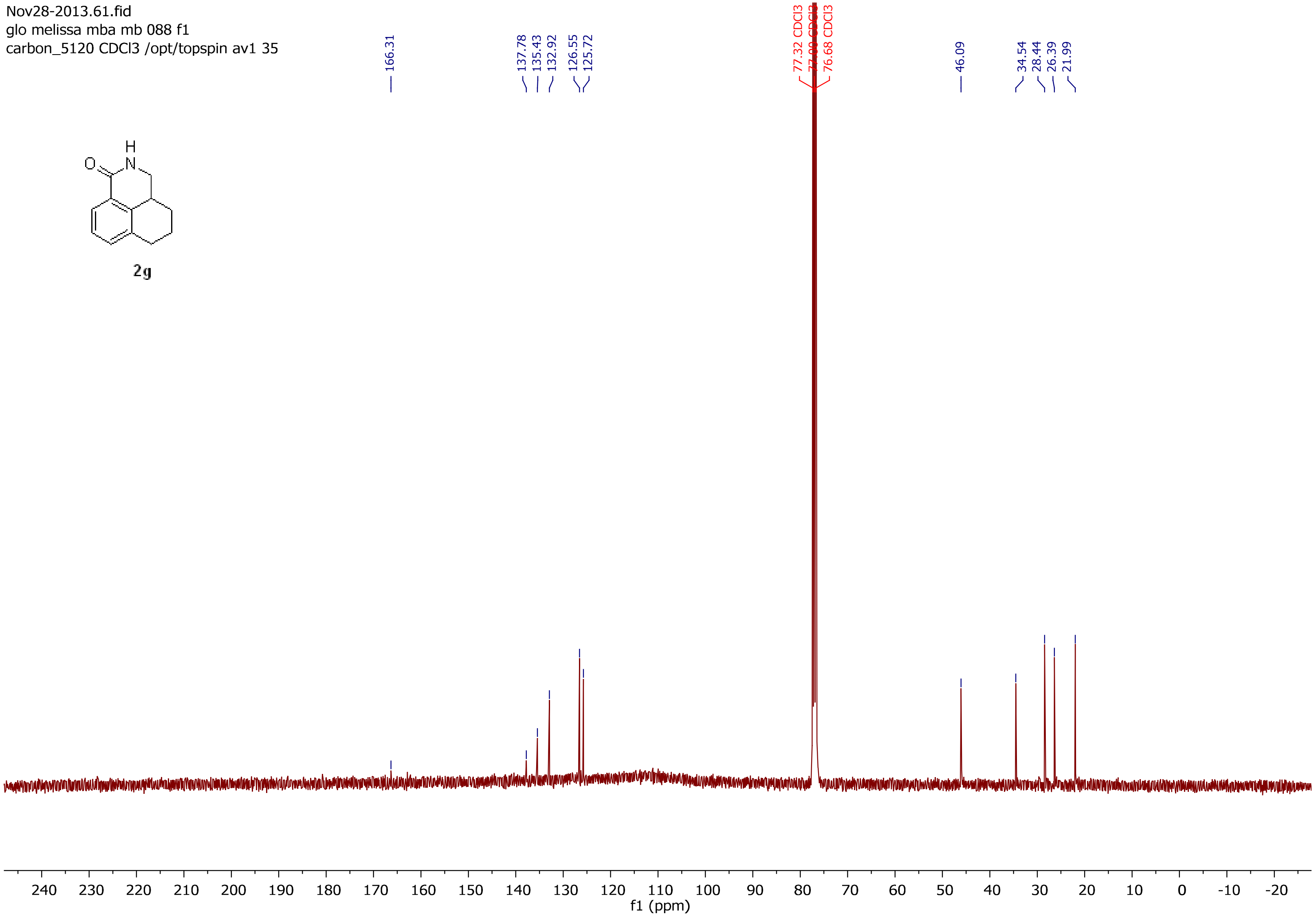
**2e**

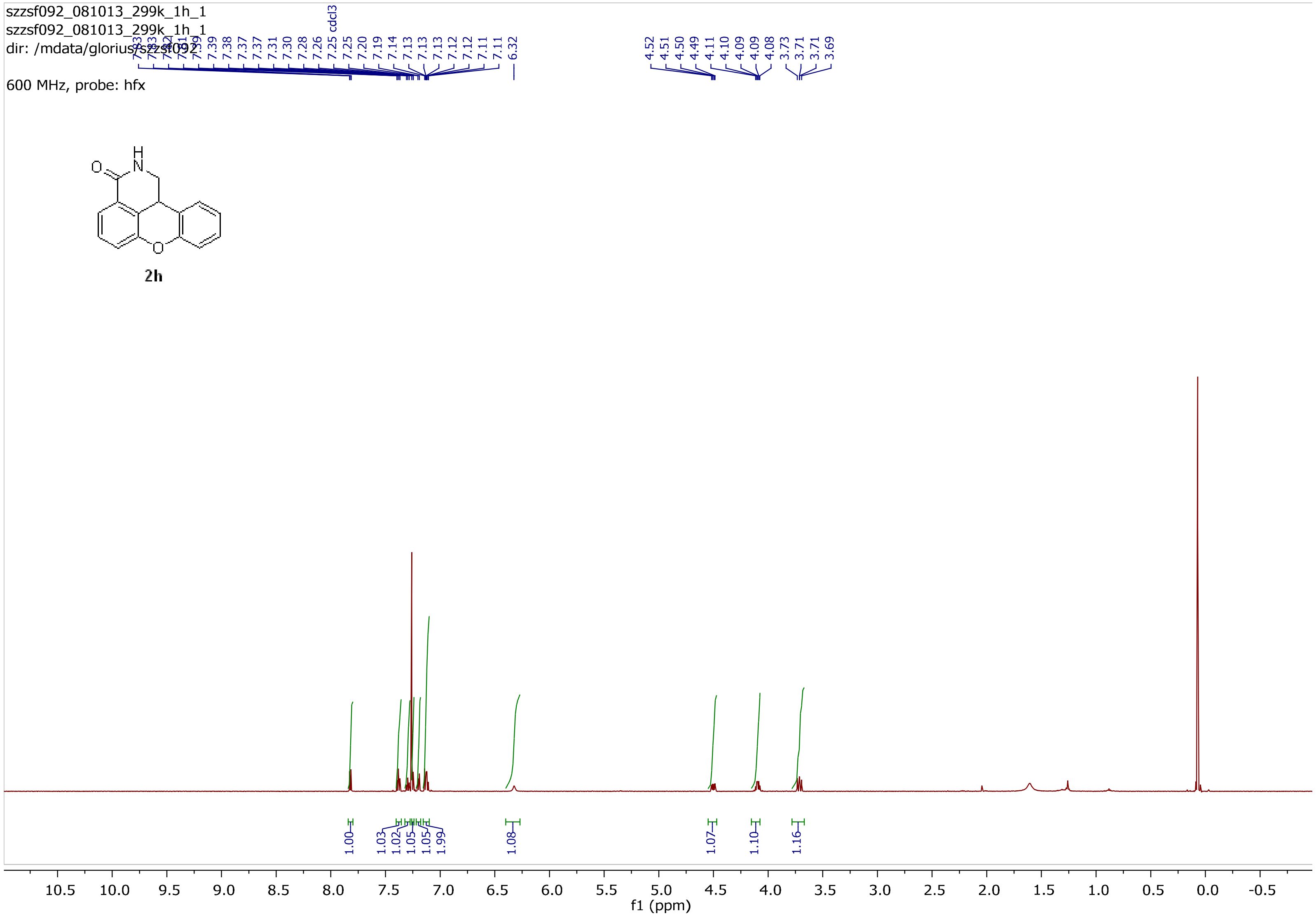

166.40
152.53
128.78
128.09
123.00
120.00
119.89
77.42
77.00
76.58
65.50
45.56
30.56
25.28
O
NH
O
2e
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

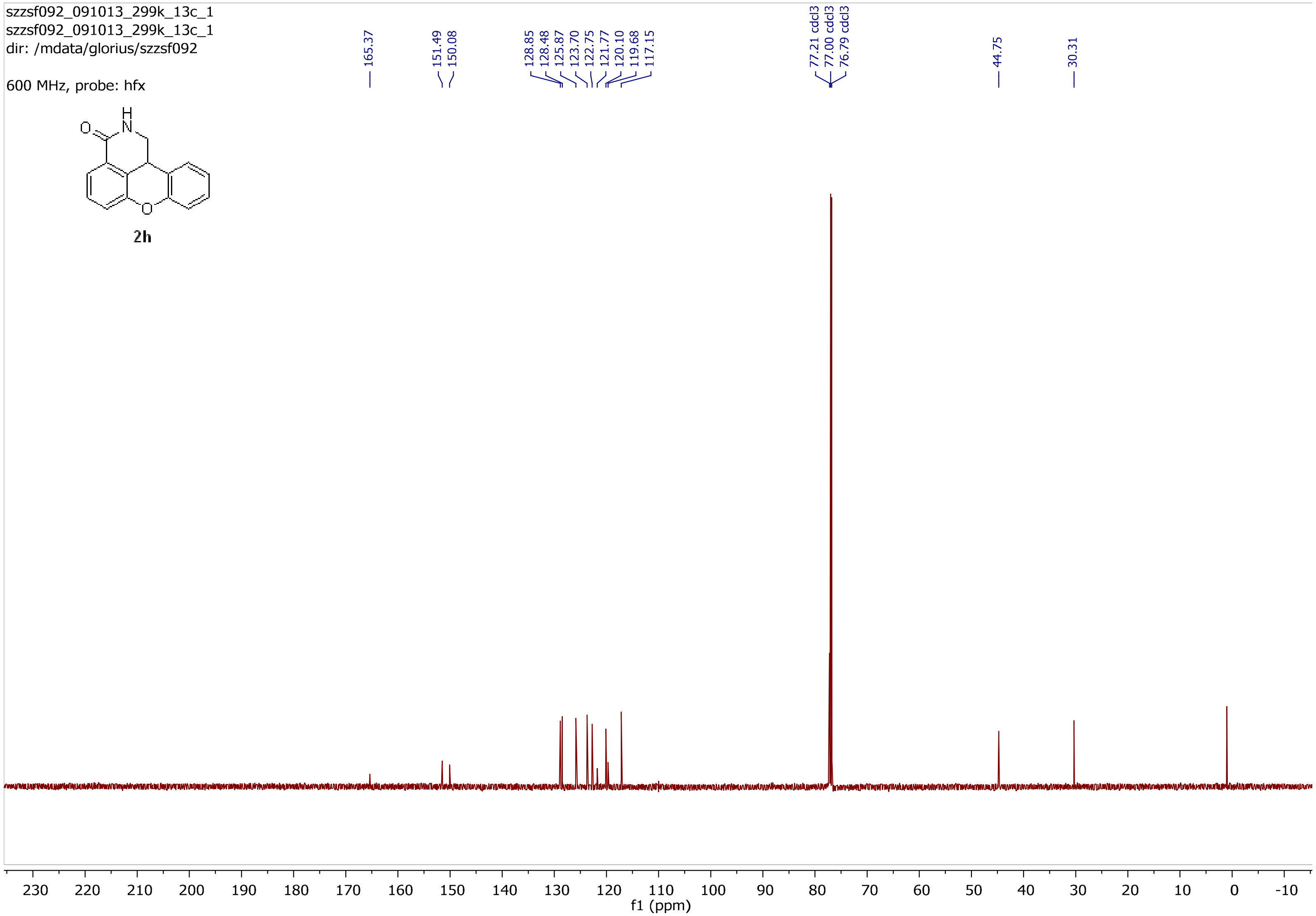

7.60
7.60
7.59
7.58
7.26
7.25
7.24
7.23
7.21
7.21
7.16
6.97
6.96
6.94
6.94
4.22
4.22
4.19
4.19
4.18
4.17
4.15
4.15
3.59
3.57
3.56
3.54
3.53
3.52
2.05
2.05
2.04
2.03
2.03
2.02
2.02
2.01
1.75
1.74
1.73
1.72
1.71
1.70
1.70
1.64
1.61
1.61
1.38
1.35
1.34
1.30
1.29
1.27
1.24
O
NH
O
2f
1.00
1.07
0.87
0.98
2.03
2.02
1.21
3.16
3.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

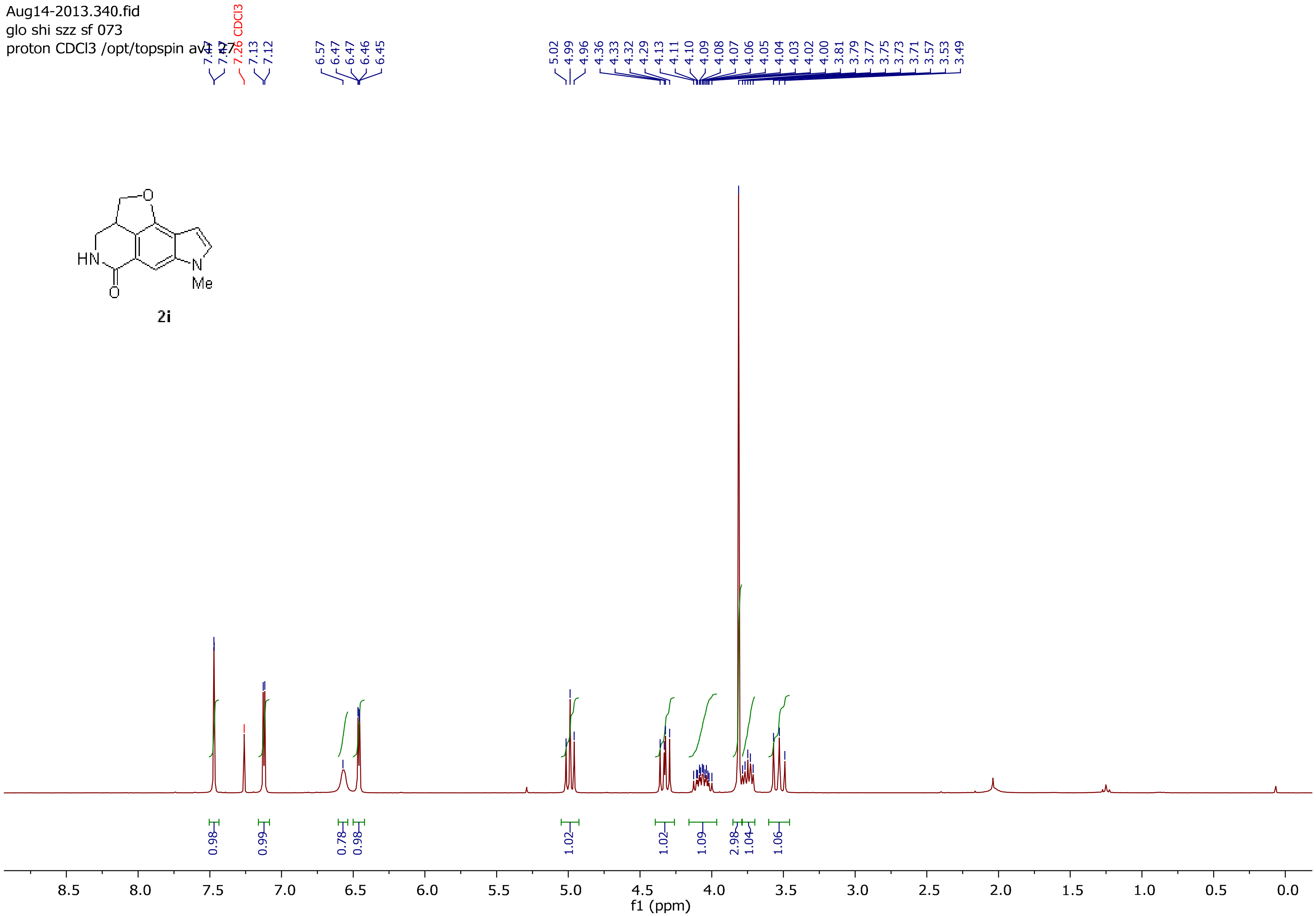

165.35
152.82
128.83
127.76
120.04
119.86
119.71
77.32
77.00
76.68
70.06
52.10
33.39
32.13
28.94
23.36
22.93
O
NH
O
2f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.90
7.88
7.86
7.27
7.26
6.43
3.48
3.46
3.44
3.42
3.29
3.24
3.21
3.16
3.15
3.13
3.11
3.09
3.06
3.05
2.94
2.92
2.92
2.88
2.88
2.86
2.84
2.84
2.82
2.82
2.82
2.80
2.80
2.78
2.76
2.74
2.12
2.11
2.11
2.10
2.09
2.08
2.07
2.06
2.06
2.05
2.04
2.04
2.02
2.00
1.99
1.98
1.98
1.84
1.83
1.82
1.81
1.79
1.79
1.79
1.78
1.77
1.77
1.76
1.75
1.73
1.73
1.71
1.70
1.69
1.68
1.44
1.40
1.40
1.39
1.37
1.36
1.36
1.35
1.32
H
O
N
2g
1.00
2.66
1.01
0.99
1.01
1.01
2.09
2.23
1.49
1.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

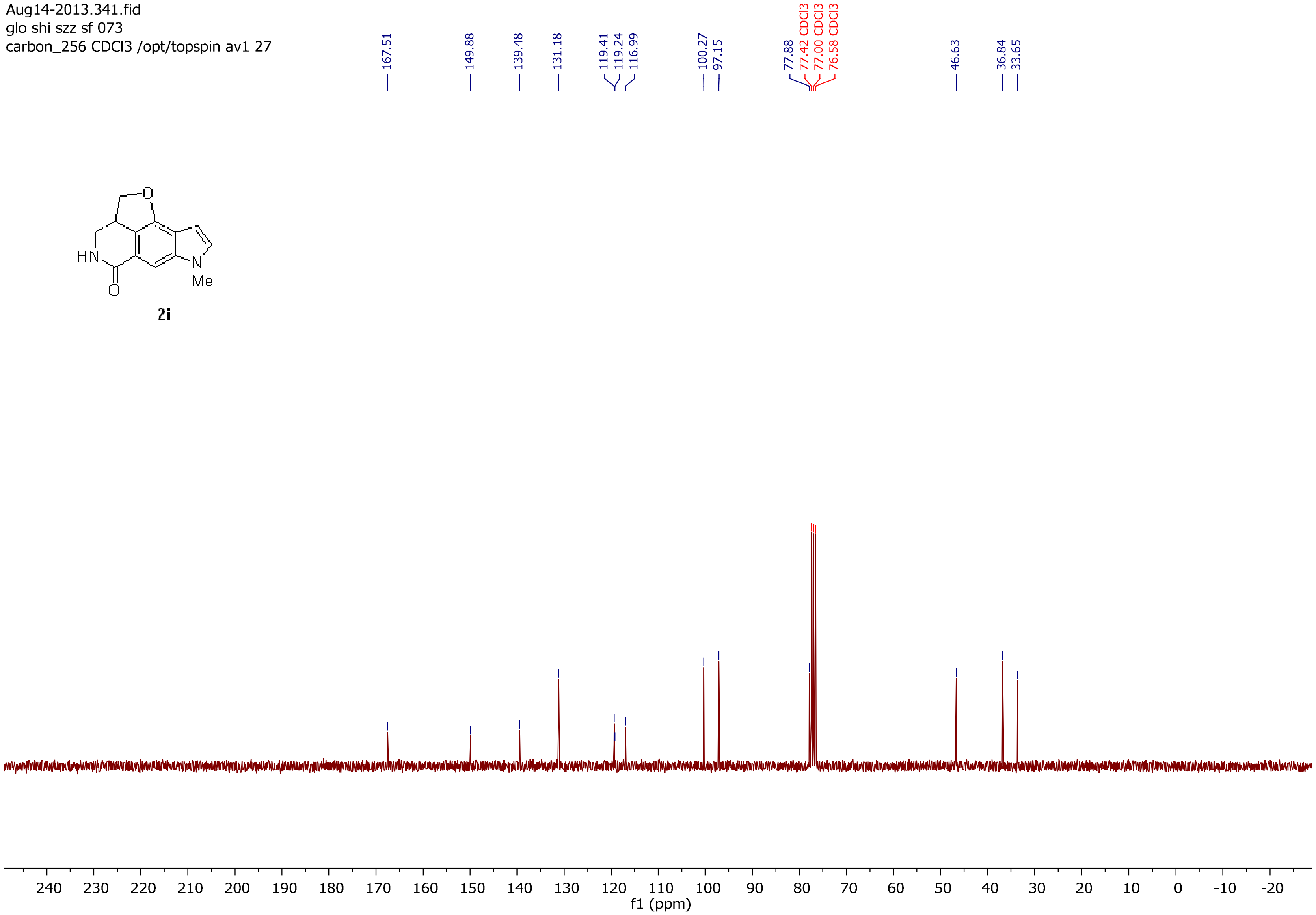

Nov28-2013.61.fid
glo melissa mba mb 088 f1
carbon_5120 CDCl3 /opt/topspin av1 35
166.31
137.78
135.43
132.92
126.55
125.72
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
46.09
34.54
28.44
26.39
21.99
O
H
N
2g
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

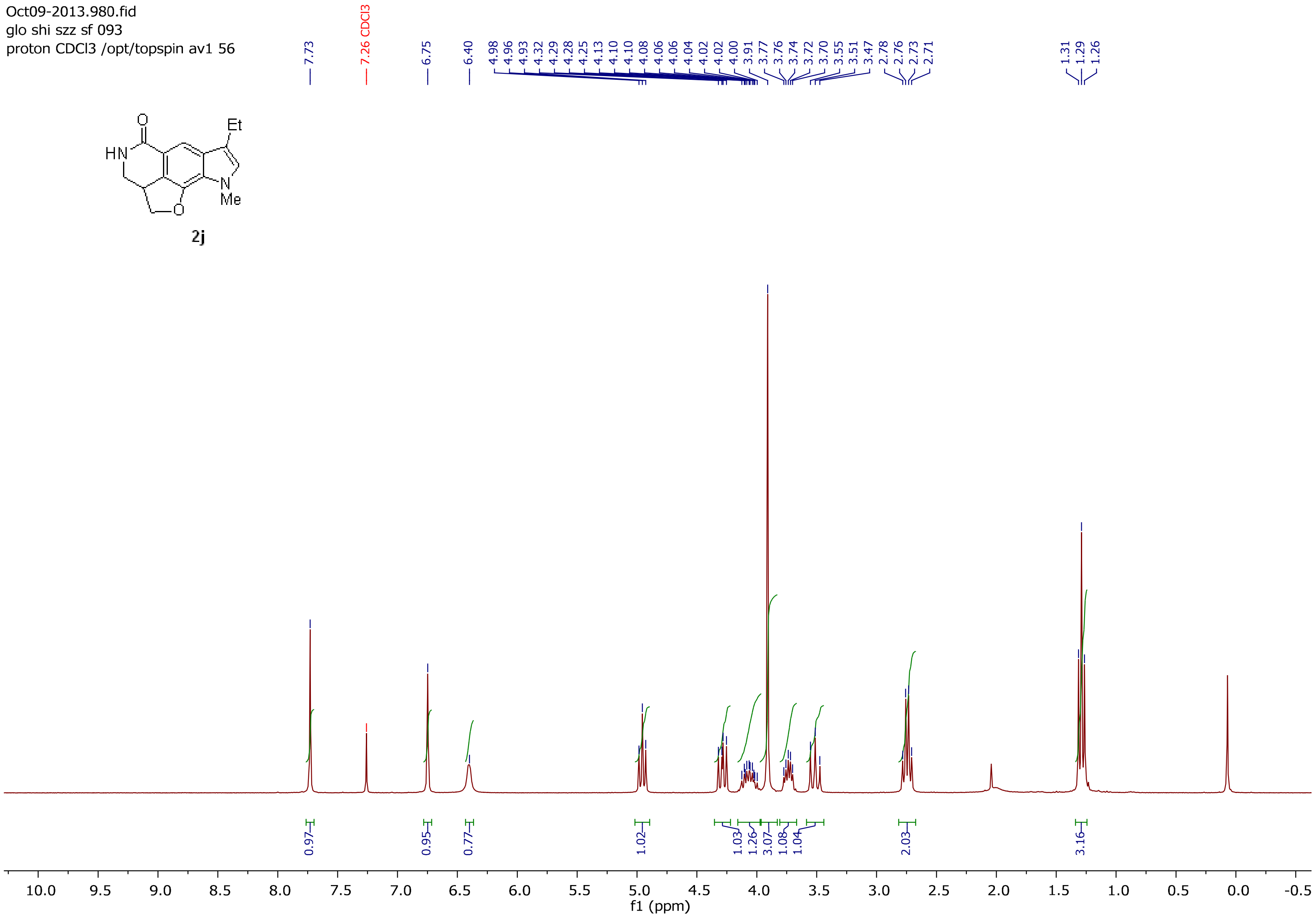

szzsf092_081013_299k_1h_1
szzsf092_081013_299k_1h_1
dir: /mdata/glorius/szzsf092
600 MHz, probe: hfx
7.83 7.83 7.82 7.81 7.39 7.39 7.38 7.37 7.37 7.31 7.30 7.28 7.26 7.25 cdcl3 7.25 7.20 7.19 7.14 7.13 7.13 7.13 7.12 7.12 7.11 7.11 6.32
4.52 4.51 4.50 4.49 4.11 4.10 4.09 4.09 4.08 3.73 3.71 3.71 3.69
2h
1.00 1.03 1.02 1.05 1.05 1.99 1.08 1.07 1.10 1.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


szzsf092_091013_299k_13c_1
szzsf092_091013_299k_13c_1
dir: /mdata/glorius/szzsf092
600 MHz, probe: hfx
2h
165.37
151.49
150.08
128.85
128.48
125.87
123.70
122.75
121.77
120.10
119.68
117.15
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
44.75
30.31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Aug14-2013.340.fid
glo shi szz sf 073
proton CDCl3 /opt/topspin av1 27
7.47
7.47
7.26 CDCl3
7.13
7.12
6.57
6.47
6.47
6.46
6.45
5.02
4.99
4.96
4.36
4.33
4.32
4.29
4.13
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.00
3.81
3.79
3.77
3.75
3.73
3.71
3.57
3.53
3.49
O
HN
N
Me
O
0.98
0.99
0.78
0.98
1.02
1.02
1.09
2.98
1.04
1.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

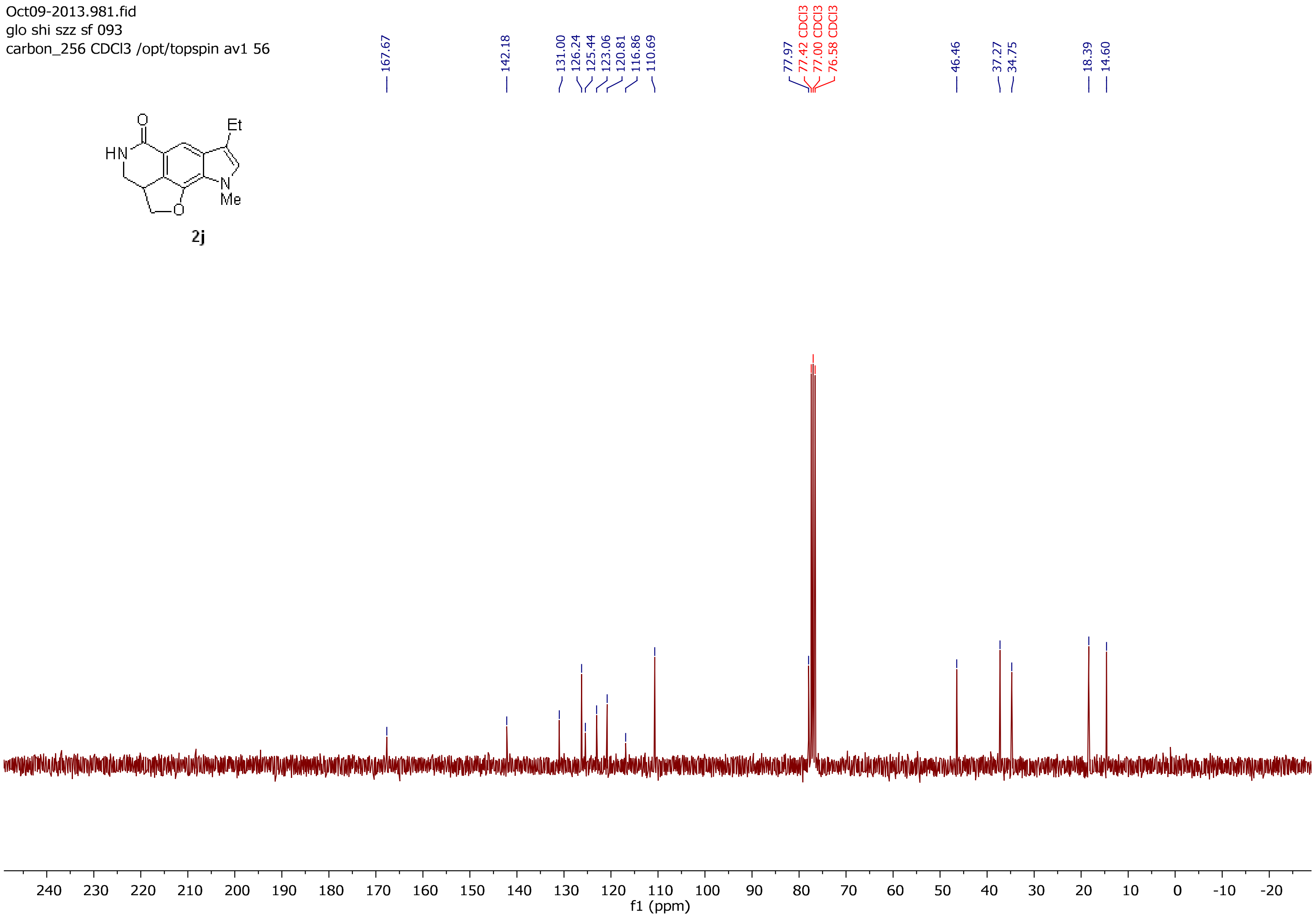
**2i**

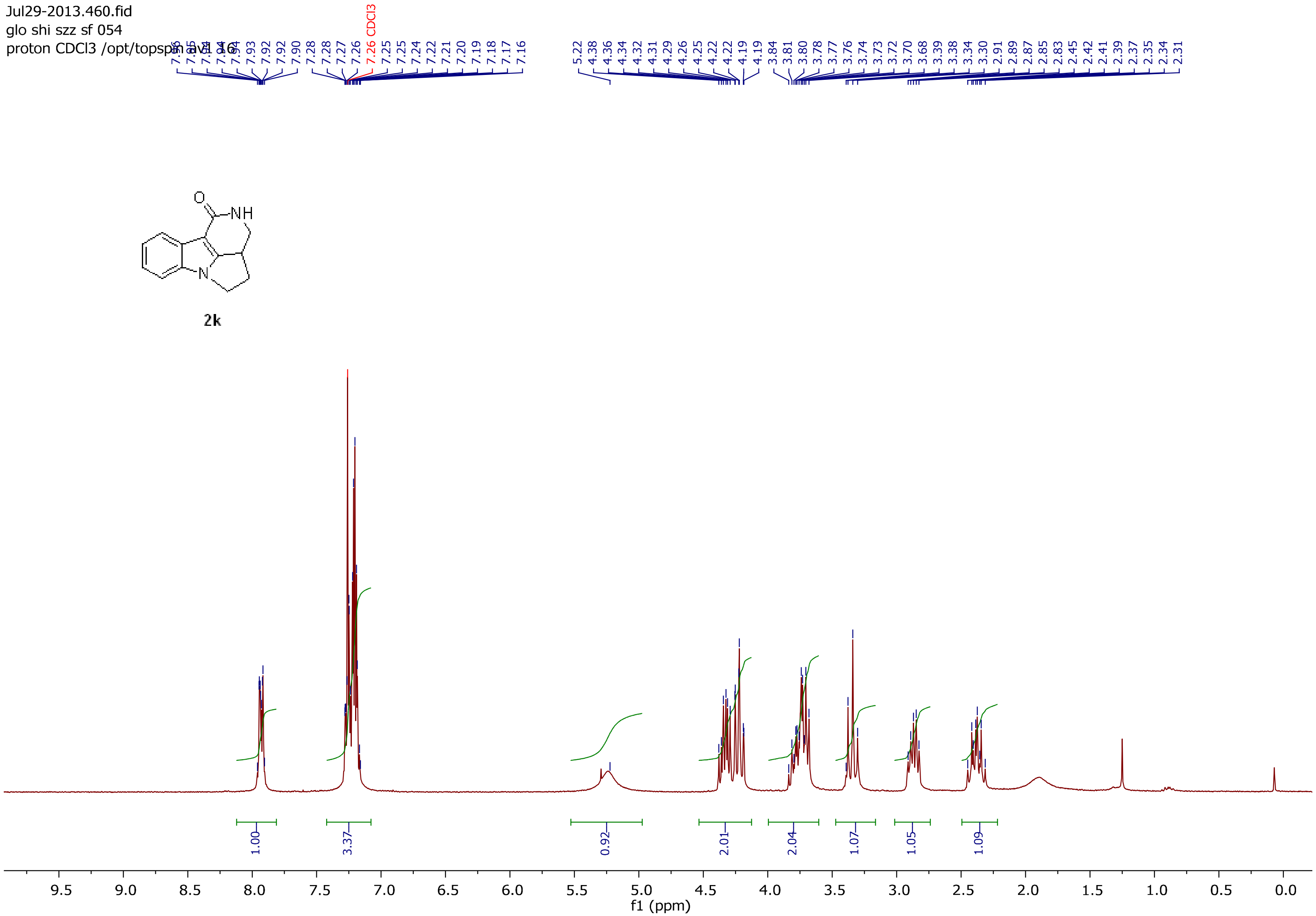

Aug14-2013.341.fid
glo shi szz sf 073
carbon_256 CDCl3 /opt/topspin av1 27
167.51
149.88
139.48
131.18
119.41
119.24
116.99
100.27
97.15
77.88
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
46.63
36.84
33.65
O
HN
N
Me
O
2i
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

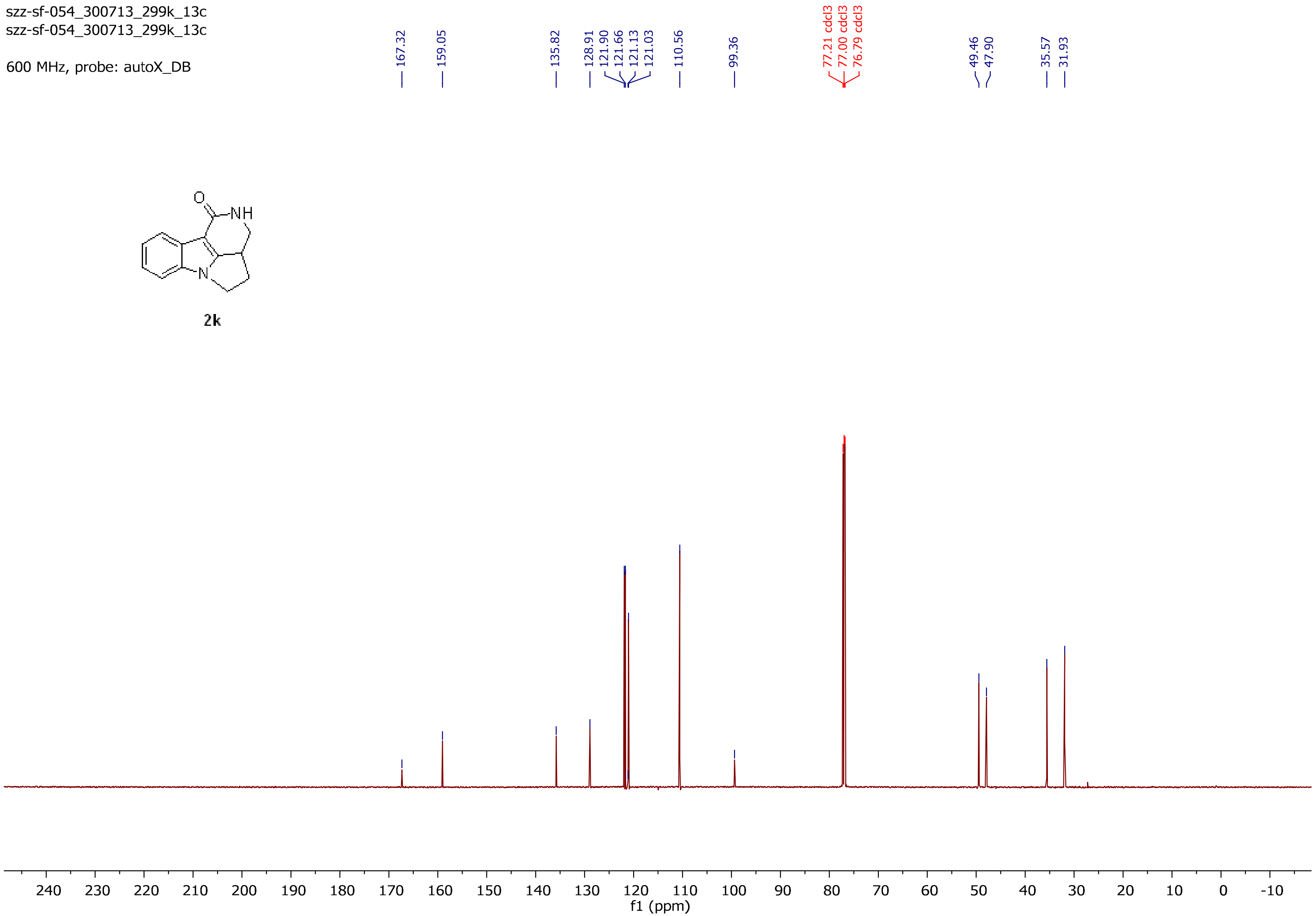


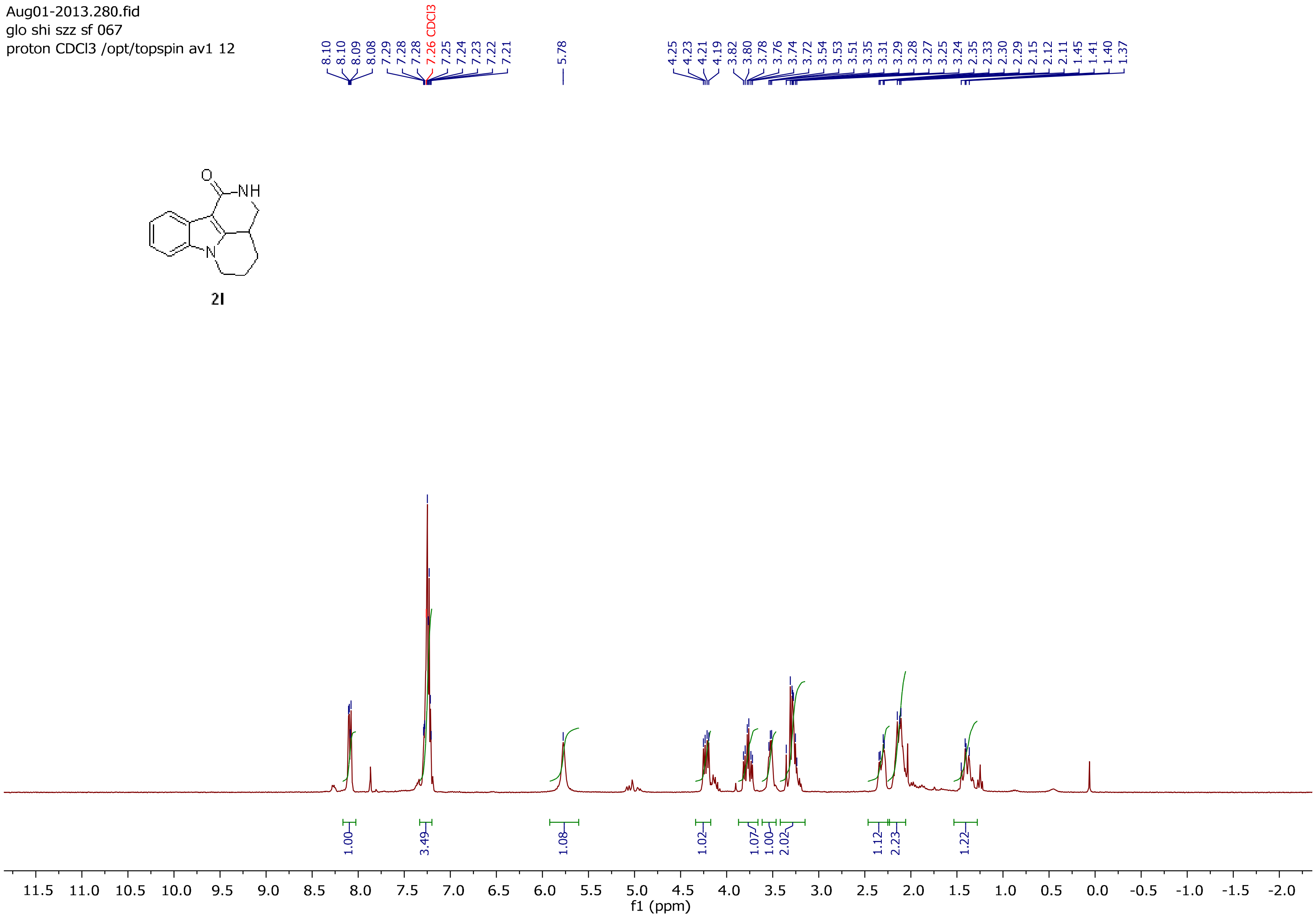
**2j**

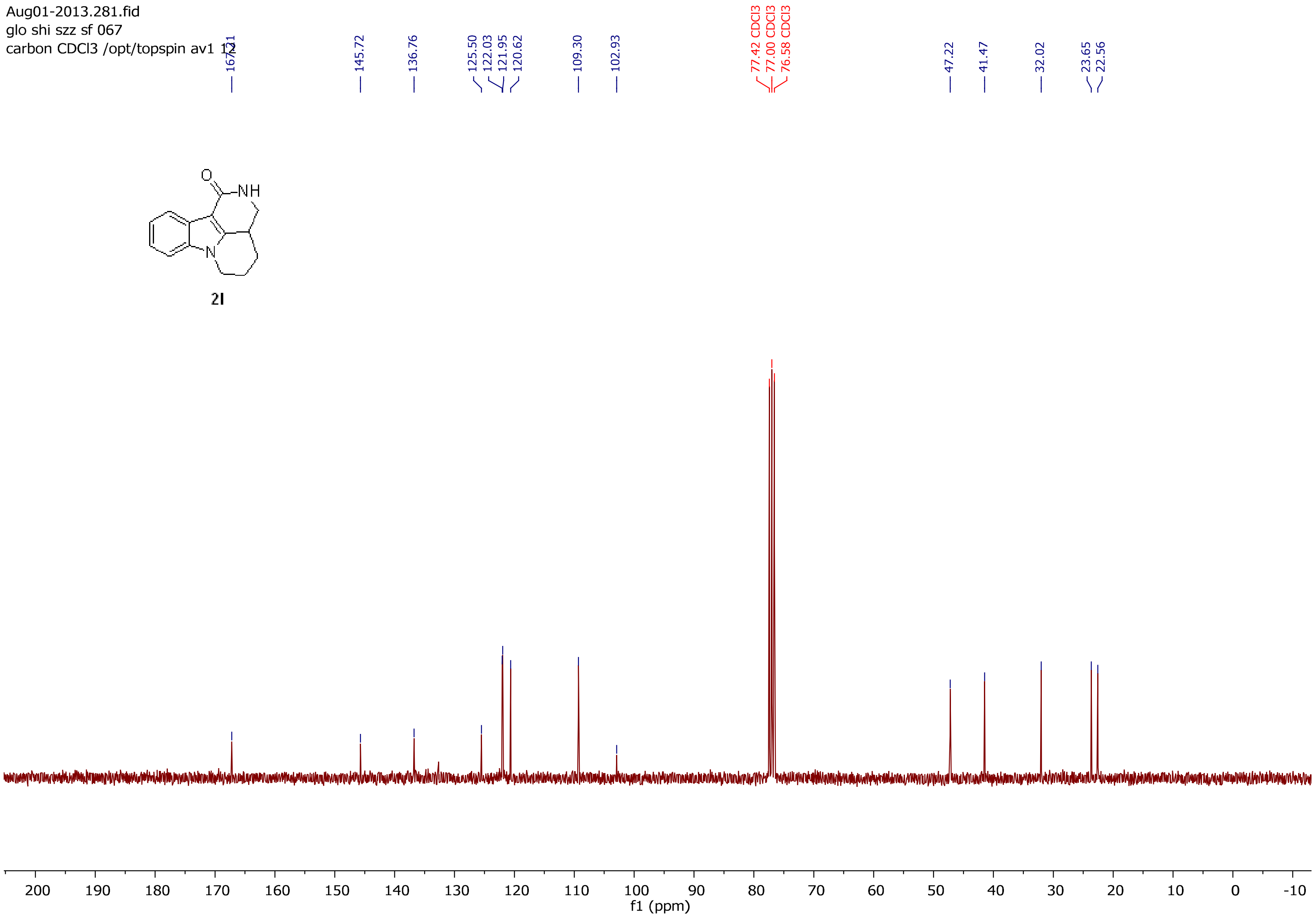
Oct09-2013.980.fid
glo shi szz sf 093
proton CDCl3 /opt/topspin av1 56
7.73
7.26 CDCl3
6.75
6.40
4.98
4.96
4.93
4.32
4.29
4.28
4.25
4.13
4.10
4.10
4.08
4.06
4.06
4.04
4.02
4.02
4.00
3.91
3.77
3.76
3.74
3.72
3.70
3.55
3.51
3.47
2.78
2.76
2.73
2.71
1.31
1.29
1.26
O
HN
Et
N
Me
O
0.97
0.95
0.77
1.02
1.03
1.26
3.07
1.08
1.04
2.03
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Oct09-2013.981.fid
glo shi szz sf 093
carbon_256 CDCl3 /opt/topspin av1 56
167.67
142.18
131.00
126.24
125.44
123.06
120.81
116.86
110.69
77.97
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
46.46
37.27
34.75
18.39
14.60
O
Et
HN
N
Me
O
2j
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


Jul29-2013.460.fid
glo shi szz sf 054
proton CDCl3 /opt/topspin av1 16
7.96
7.95
7.94
7.94
7.94
7.93
7.92
7.92
7.90
7.28
7.28
7.27
7.26
7.26 CDCl3
7.25
7.25
7.24
7.22
7.21
7.20
7.19
7.18
7.17
7.16
5.22
4.38
4.36
4.34
4.32
4.31
4.29
4.26
4.25
4.22
4.22
4.19
4.19
3.84
3.81
3.80
3.78
3.77
3.76
3.74
3.73
3.72
3.70
3.68
3.39
3.38
3.34
3.30
2.91
2.89
2.87
2.85
2.83
2.45
2.42
2.41
2.39
2.37
2.35
2.34
2.31
O
NH
N
2k
1.00
3.37
0.92
2.01
2.04
1.07
1.05
1.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


szz-sf-054_300713_299k_13c
szz-sf-054_300713_299k_13c
600 MHz, probe: autoX_DB
167.32
159.05
135.82
128.91
121.90
121.66
121.13
121.03
110.56
99.36
77.21 cdcl3
77.00 cdcl3
76.79 cdcl3
49.46
47.90
35.57
31.93
O
NH
N
2k
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Aug01-2013.280.fid
glo shi szz sf 067
proton CDCl3 /opt/topspin av1 12
8.10
8.10
8.09
8.08
7.29
7.28
7.28
7.26 CDCl3
7.25
7.24
7.23
7.22
7.21
5.78
4.25
4.23
4.21
4.19
3.82
3.80
3.78
3.76
3.74
3.72
3.54
3.53
3.51
3.35
3.31
3.29
3.28
3.27
3.25
3.24
2.35
2.33
2.30
2.29
2.15
2.12
2.11
1.45
1.41
1.40
1.37
O
NH
N
2l
1.00
3.49
1.08
1.02
1.07
1.00
2.02
1.12
2.23
1.22
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)


Aug01-2013.281.fid
glo shi szz sf 067
carbon CDCl3 /opt/topspin av1 12
167.21
145.72
136.76
125.50
122.03
121.95
120.62
109.30
102.93
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
47.22
41.47
32.02
23.65
22.56
O
NH
N
2l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Electronic Supplementary Material (ESI) for Chemical Communications
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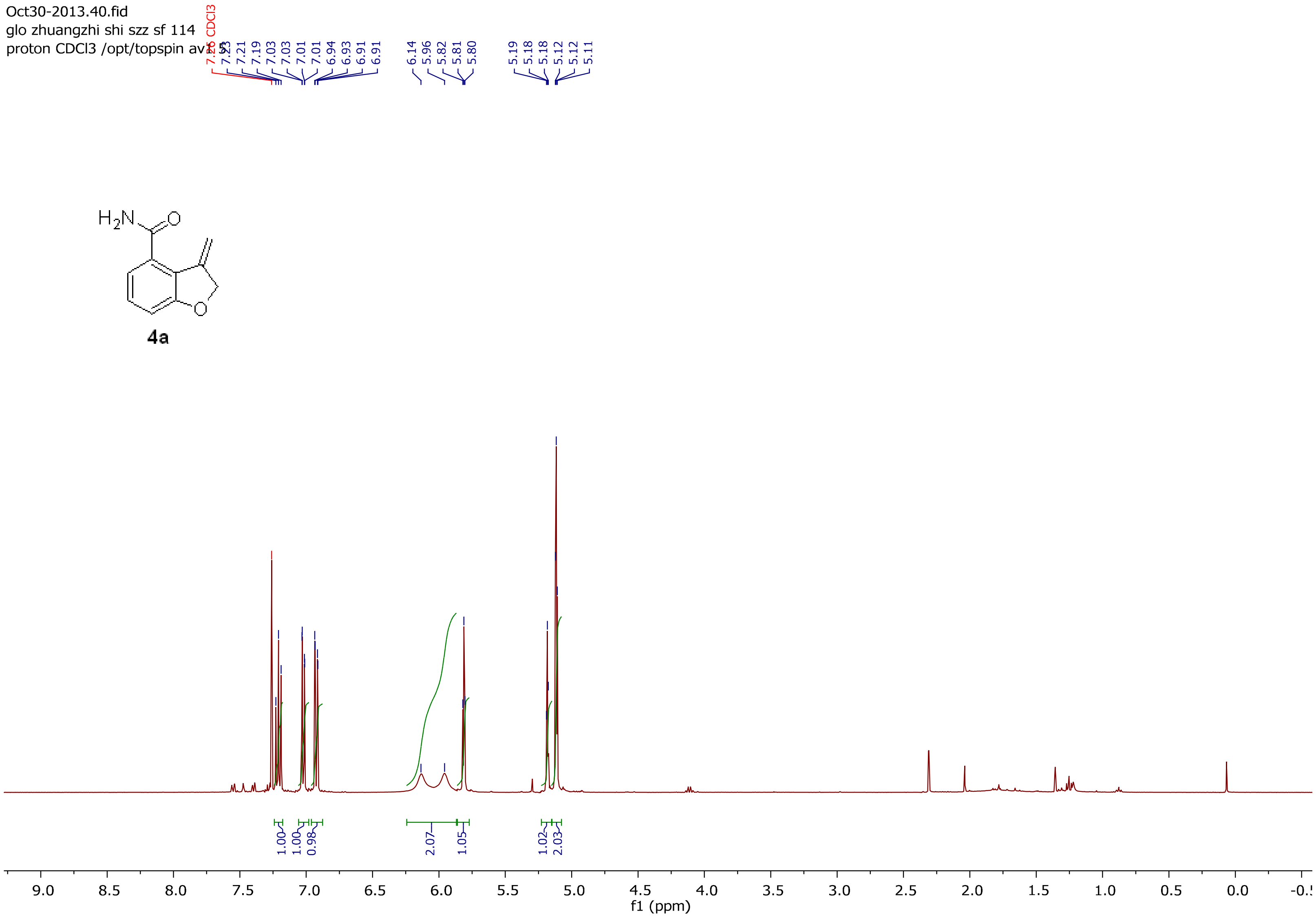
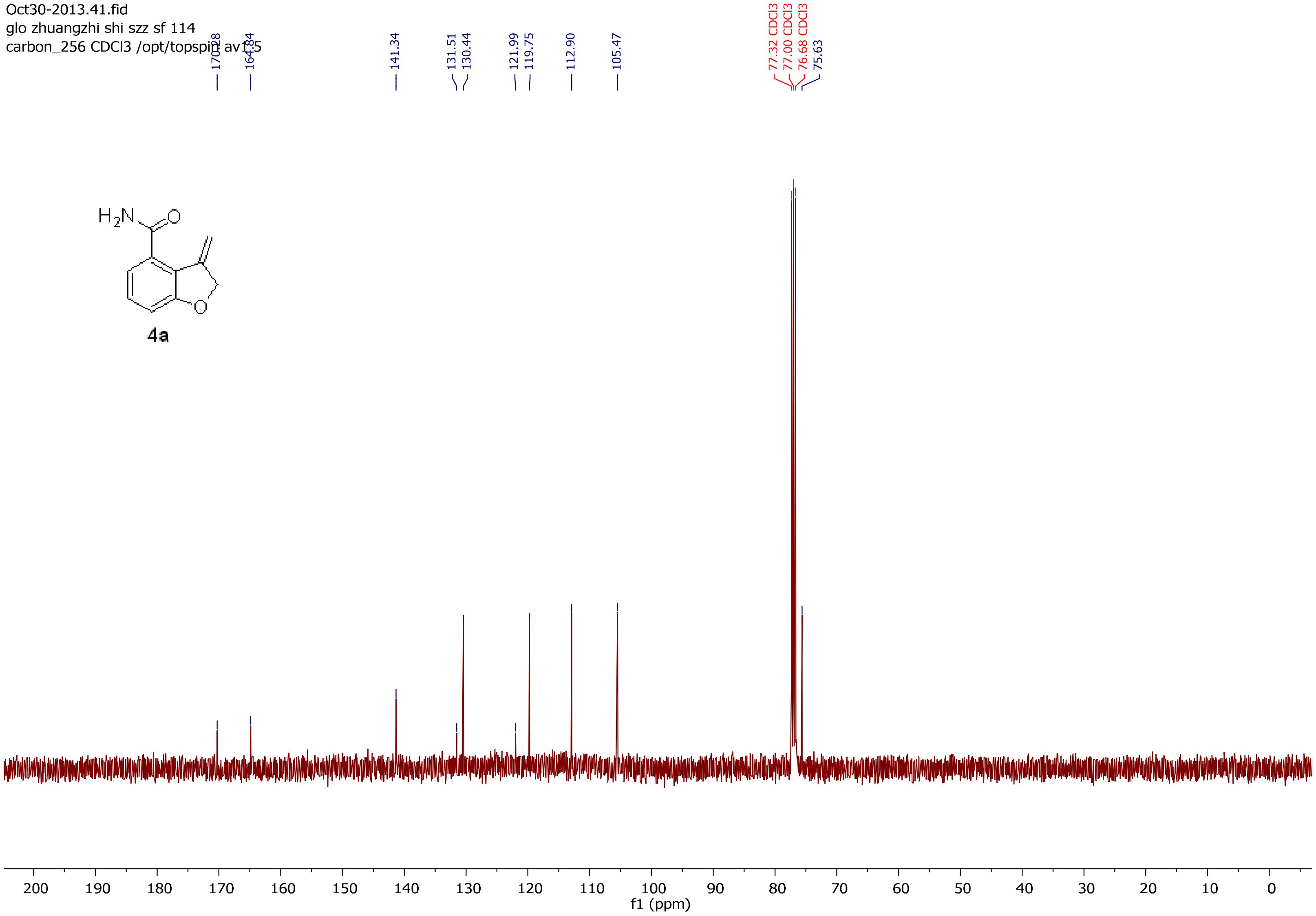
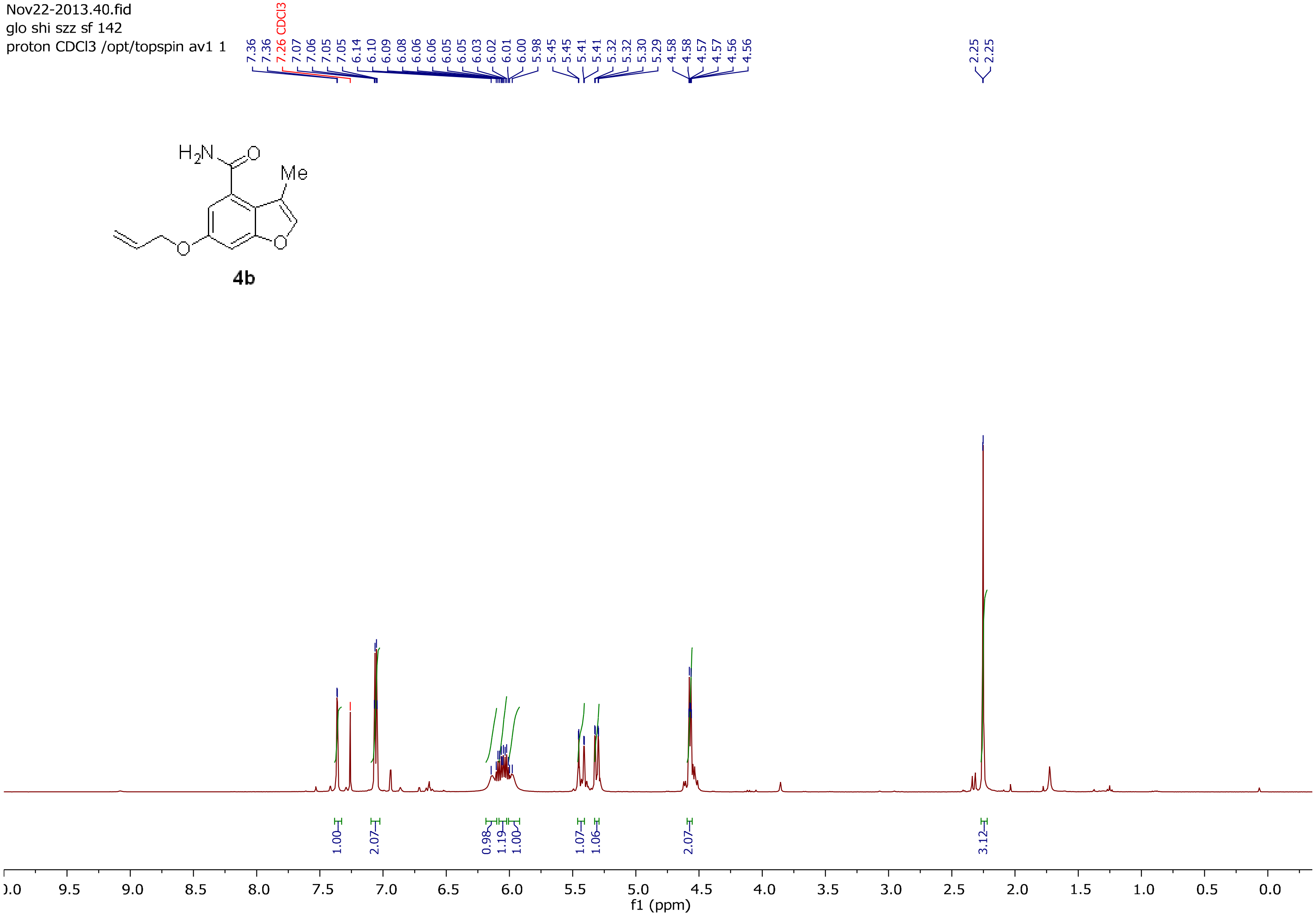
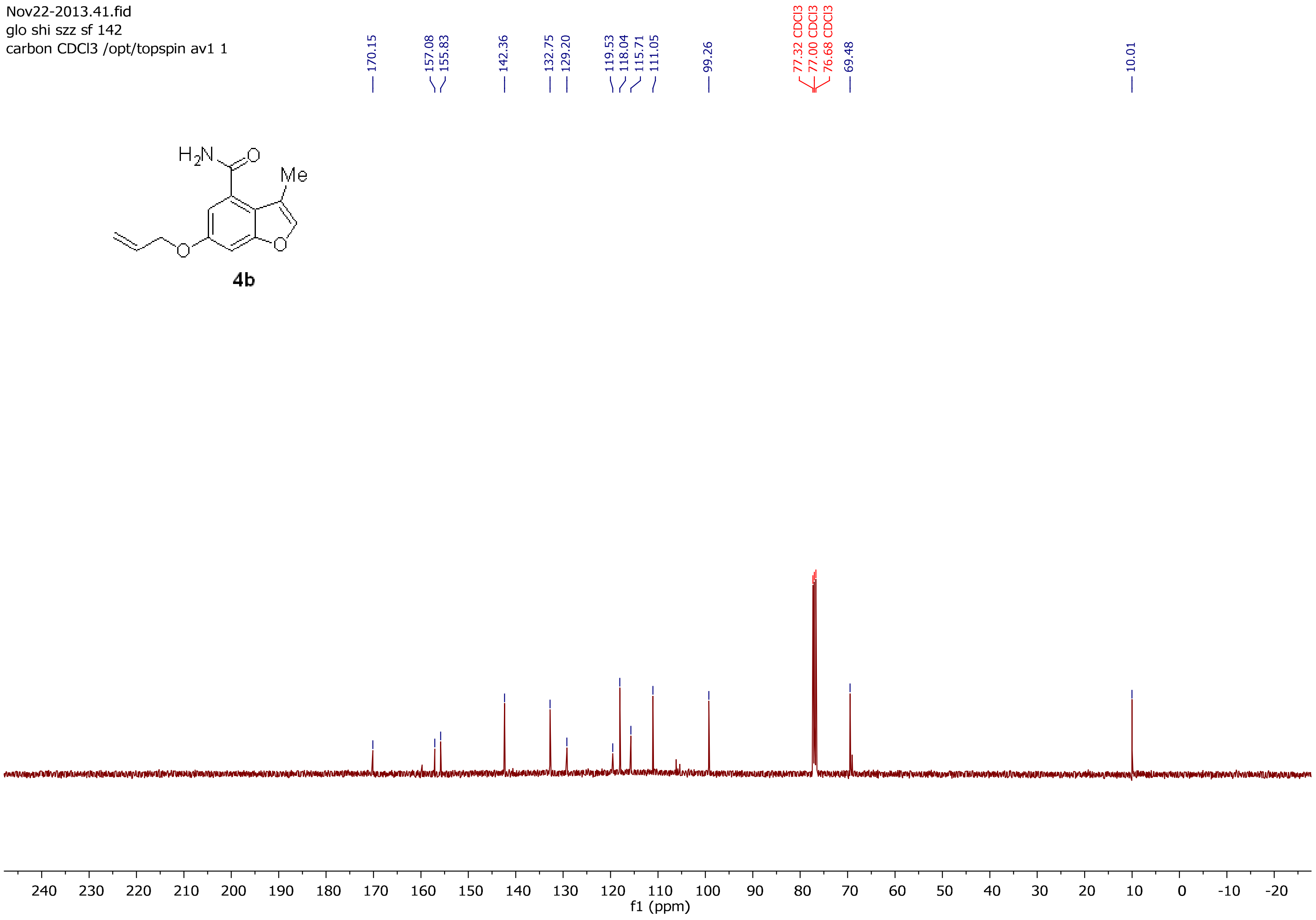


**4a**

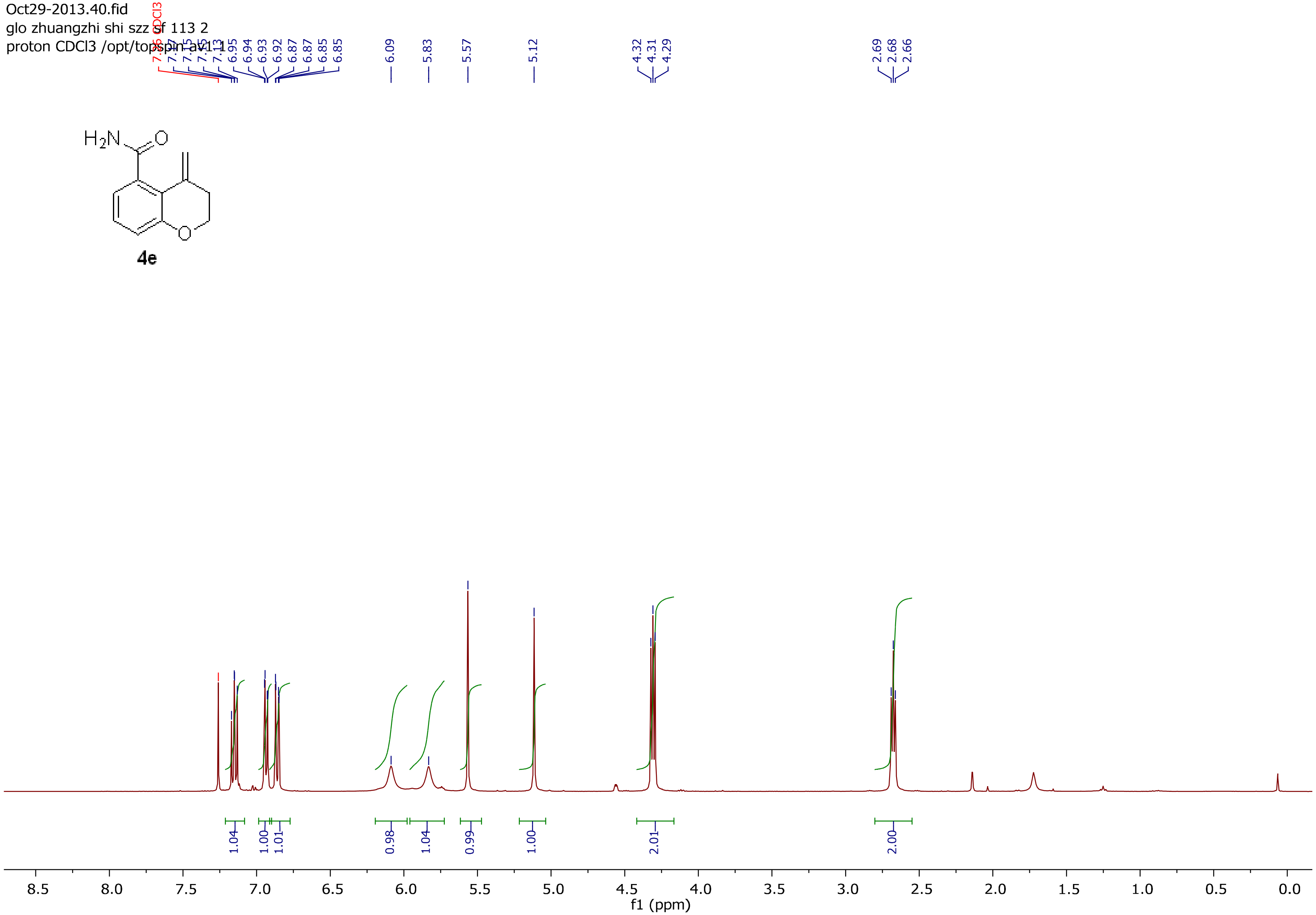

Oct30-2013.41.fid
glo zhuangzhi shi szz sf 114
carbon_256 CDCl3 /opt/topspin av1.5
170.28
164.84
141.34
131.51
130.44
121.99
119.75
112.90
105.47
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
75.63
H2N
O
O
4a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Nov22-2013.40.fid
glo shi szz sf 142
proton CDCl3 /opt/topspin av1 1
7.36
7.36
7.26 CDCl3
7.07
7.06
7.05
7.05
6.14
6.10
6.09
6.08
6.06
6.06
6.05
6.05
6.03
6.02
6.01
6.00
5.98
5.45
5.45
5.41
5.41
5.32
5.32
5.30
5.29
4.58
4.58
4.57
4.57
4.56
4.56
2.25
2.25
H2N
O
Me
O
O
4b
1.00
2.07
0.98
1.19
1.00
1.07
1.06
2.07
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

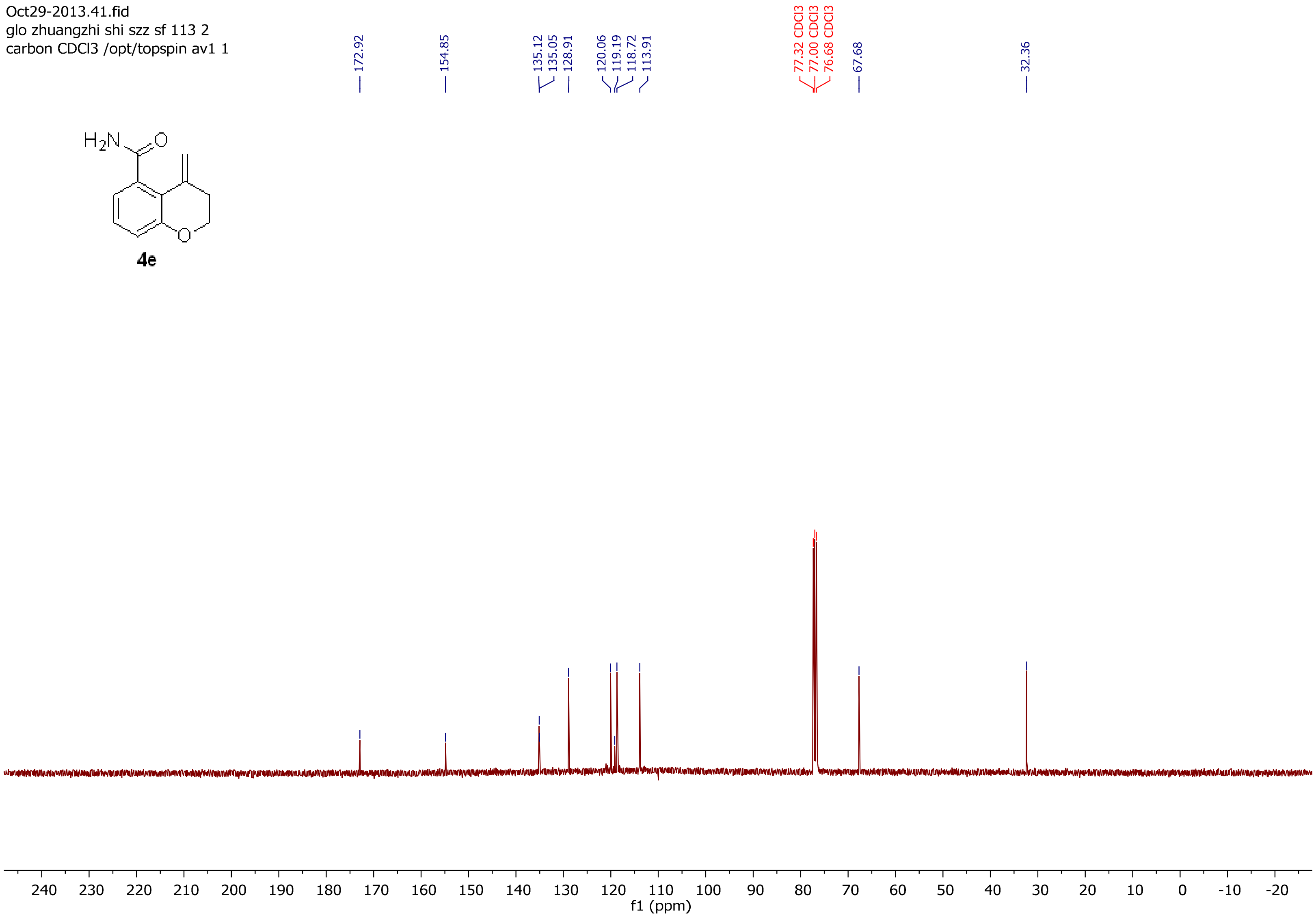


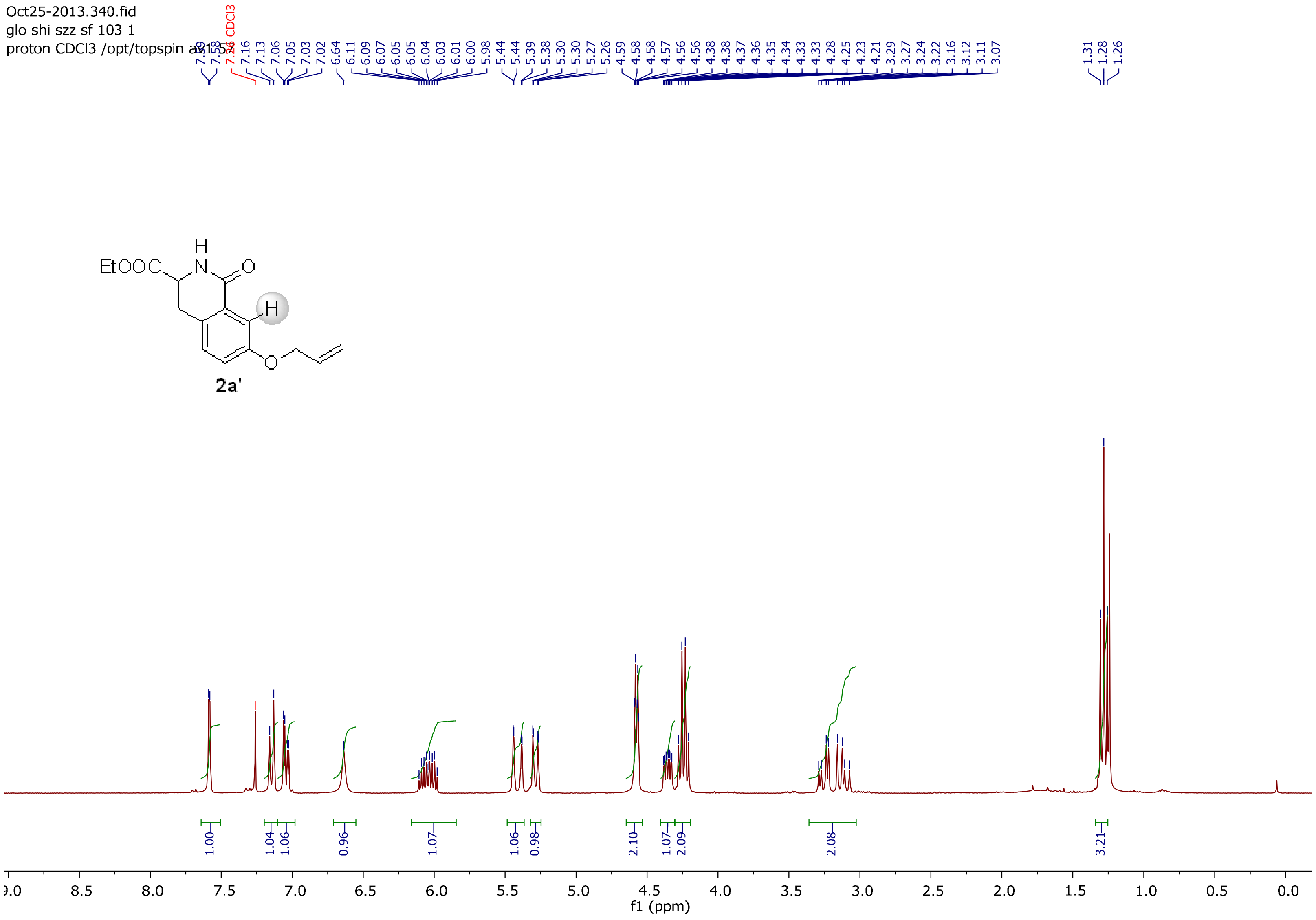
**4b**

Nov22-2013.41.fid
glo shi szz sf 142
carbon CDCl3 /opt/topspin av1 1
H2N
O
Me
O
O
170.15
157.08
155.83
142.36
132.75
129.20
119.53
118.04
115.71
111.05
99.26
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
69.48
10.01
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

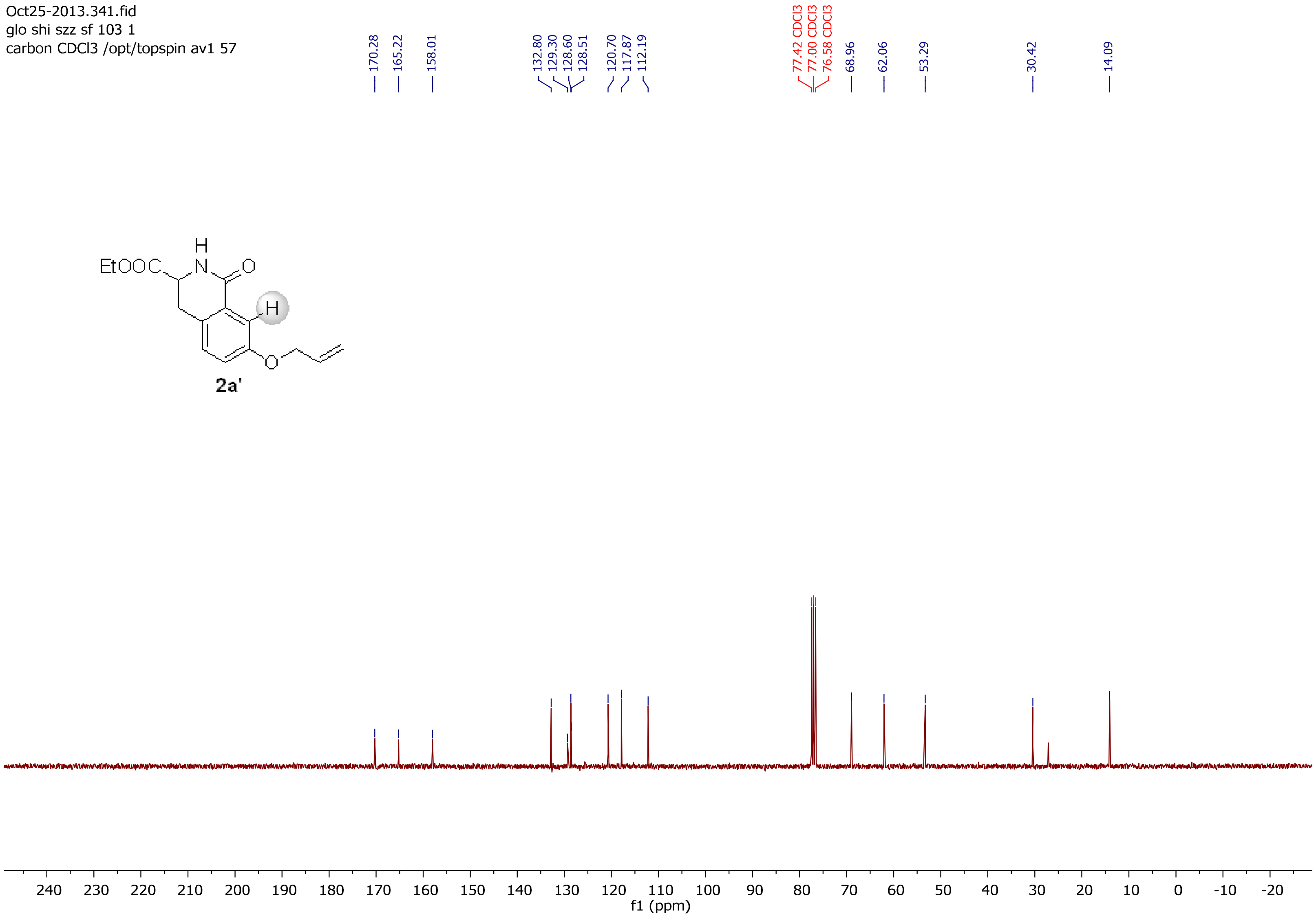

Oct29-2013.40.fid
glo zhuangzhi shi szz sf 113 2
proton CDCl3 /opt/topspin av11
7.26 CDCl3
7.17
7.15
7.15
7.13
7.13
6.95
6.94
6.93
6.92
6.87
6.87
6.85
6.85
6.09
5.83
5.57
5.12
4.32
4.31
4.29
2.69
2.68
2.66
H2N
O
O
1.04
1.00
1.01
0.98
1.04
0.99
1.00
2.01
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**4e**


Oct29-2013.41.fid
glo zhuangzhi shi szz sf 113 2
carbon CDCl3 /opt/topspin av1 1
H2N
O
O
4e
172.92
154.85
135.12
135.05
128.91
120.06
119.19
118.72
113.91
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
67.68
32.36
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


Oct25-2013.340.fid
glo shi szz sf 103 1
proton CDCl3 /opt/topspin av
7.59
7.58
7.26 CDCl3
7.16
7.13
7.06
7.05
7.03
7.02
6.64
6.11
6.09
6.07
6.05
6.05
6.04
6.03
6.01
6.00
5.98
5.44
5.44
5.39
5.38
5.30
5.30
5.27
5.26
4.59
4.58
4.58
4.57
4.56
4.56
4.38
4.38
4.37
4.36
4.35
4.34
4.33
4.33
4.28
4.25
4.23
4.21
3.29
3.27
3.24
3.22
3.16
3.12
3.11
3.07
1.31
1.28
1.26
EtOOC
H
N
O
H
O
1.00
1.04
1.06
0.96
1.07
1.06
0.98
2.10
1.07
2.09
2.08
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**2a'**


Oct25-2013.341.fid
glo shi szz sf 103 1
carbon CDCl3 /opt/topspin av1 57
170.28
165.22
158.01
132.80
129.30
128.60
128.51
120.70
117.87
112.19
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
68.96
62.06
53.29
30.42
14.09
EtOOC
H
N
O
H
O
2a'
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)