

## Supporting Information

# Phosphoric Acid-Catalyzed Asymmetric N-propargylation of Pyridazinones and 2-Pyridones

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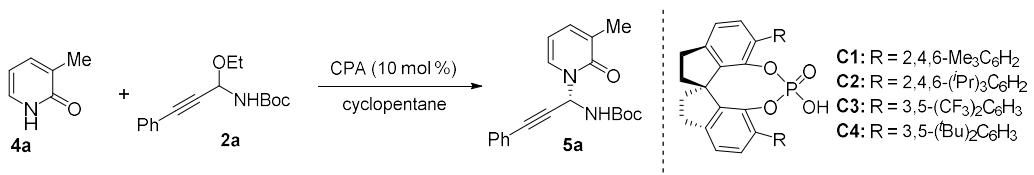
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## General information

All of the reactions were carried out in flame-dried tubes under an argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F<sub>254</sub> indicator. For column chromatography, 200-300 mesh silica gel was used. <sup>1</sup>H NMR spectra were recorded on Bruker 300 MHz, or 400 MHz spectrometer in CDCl<sub>3</sub> or DMSO-d6. <sup>13</sup>C NMR spectra were recorded on Bruker 75 MHz, or 100 MHz spectrometer in CDCl<sub>3</sub> or DMSO-d6. <sup>19</sup>F NMR spectra were recorded on Bruker 376 MHz spectrometer in CDCl<sub>3</sub> or DMSO-d6. Data for <sup>1</sup>H NMR spectra were reported relative to tetramethylsilane (TMS) as an internal standard (0 ppm) and were reported as follows: chemical shift ( $\delta$  ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, and m = multiplet. Data for <sup>13</sup>C NMR spectra were reported relative to CDCl<sub>3</sub> as an internal standard (77.16 ppm) and were reported in terms of chemical shift ( $\delta$  ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 Q-TOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were uncorrected and determined on a SGW X-4B melting point apparatus. Enantiomeric excess (ee) values were determined by chiral HPLC analysis on Daicel Chiraldex IA, IC, OD-H, AS-H, ID column. Optical rotations were determined on a Shanghai Shenguang® polarimeter and reported as follows:  $[\alpha]_D^T$  (c: g/100 mL, solvent).

All of the CPA were known compounds and were purchased from Daicel Chiral Technologies (China) Co., Ltd. All of the Pyridazinones **1** and Pyridones **4** were known compounds and were purchased from Aladdin, Bide pharm and Energy Chemical. All of the C-alkynyl N,O-acetals **2** were known and prepared according to the literature procedures.<sup>1</sup>

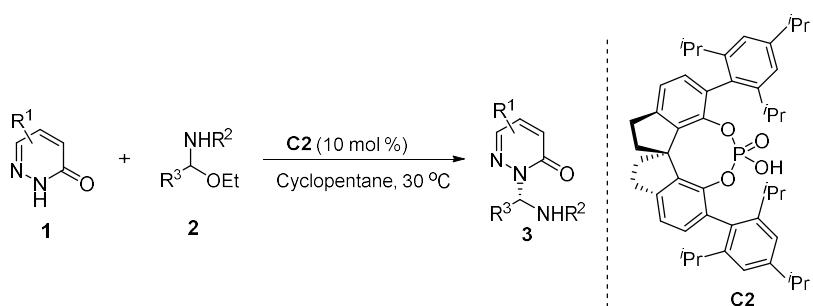
## Optimization of the reaction conditions for **5<sup>a</sup>**



entry	CPA	solvent	<b>1a:2a</b>	t (°C)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1	<b>C1</b>	cyclopentane	1:4	30	23	0
2	<b>C2</b>	cyclopentane	1:4	30	83	83
3	<b>C3</b>	cyclopentane	1:4	30	<5	0
4	<b>C4</b>	cyclopentane	1:4	30	23	26
5	<b>C2</b>	DCM	1:4	30	56	76
6	<b>C2</b>	DCE	1:4	30	43	70
7	<b>C2</b>	Et <sub>2</sub> O	1:4	30	32	72
8	<b>C2</b>	MeCN	1:4	30	27	60
9	<b>C2</b>	Hexane	1:4	30	16	86
10	<b>C2</b>	PhMe	1:4	30	68	78
11	<b>C2</b>	THF	1:4	30	61	78
12	<b>C2</b>	cyclohexane	1:4	30	72	82
13	<b>C2</b>	cyclopentane	1:4	25	79	88
14	<b>C2</b>	cyclopentane	1:4	20	58	90
15	<b>C2</b>	cyclopentane	1:4	10	<10	94
16	<b>C2</b>	cyclopentane	1:4	0	<5	94
17 <sup>d</sup>	<b>C2</b>	Cyclopentane	1:4	25	79	88
18 <sup>e</sup>	<b>C2</b>	cyclopentane	1:4	25	78	93
19 <sup>f</sup>	<b>C2</b>	cyclopentane	1:4	25	78	88
20 <sup>g</sup>	<b>C2</b>	cyclopentane	1:4	25	35	93

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), catalyst (10 mol %) in solvent (2 mL) under Ar. The reaction was stirred at 25 °C for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>ee was determined by chiral HPLC analysis. <sup>d</sup>3ÅMS (50 mg) was added. <sup>e</sup>4ÅMS (50 mg) was added. <sup>f</sup>5ÅMS (50 mg) was added. <sup>g</sup>5 mol % of **C2** was used.

## General procedure for Scheme 2

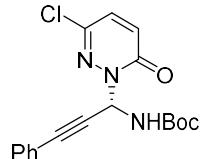


To a 10 mL of dry Schlenk tube were added **C2** (7.2 mg, 0.01 mmol, 10 mol %), **1** (0.1 mmol, 1.0 equiv) and **2** (0.4 mmol, 4.0 equiv), then Cyclopentane (2 mL) was added under argon atmosphere. The resulting mixture was stirred at 30 °C for 24 hours. The reaction mixture was concentrated

under vacuum; the crude residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 10:1-3:1) to give **3**.

[Note: racemic samples were prepared by using BNDHP instead of **C2**.]

**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3a)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (31.6 mg, 88%), mp: 159-161 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

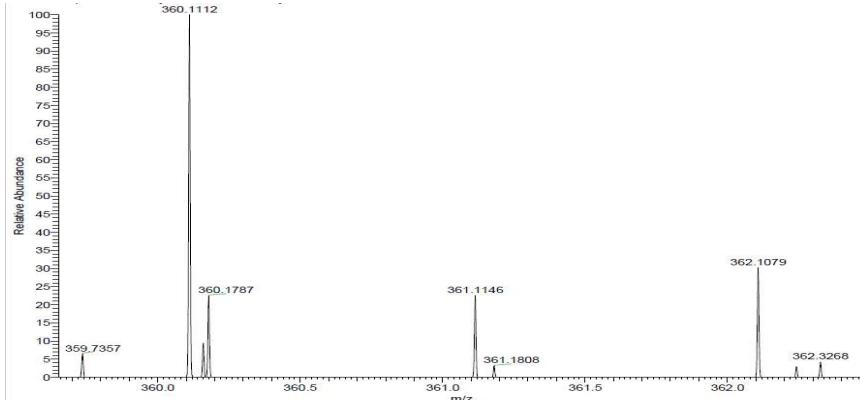
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 8.84 min (major), 10.79 min (minor), 94% ee.

[ $\alpha$ ]<sub>D</sub><sup>25</sup>: +29.76 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

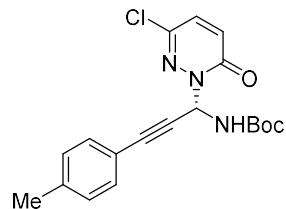
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.39 (m, 2H), 7.37-7.22 (m, 4H), 7.16 (d, *J* = 9.6 Hz, 1H), 6.93 (d, *J* = 9.6 Hz, 1H), 6.23 (s, 1H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 153.5, 138.1, 134.2, 132.8, 132.1, 129.2, 128.4, 121.4, 85.1, 82.8, 81.3, 59.0, 28.3.

**HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>19</sub>ClN<sub>3</sub>O<sub>3</sub> 360.1109; Found 360.1112.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)carbamate (3b)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(*p*-tolyl)prop-2-yn-1-yl)carbamate (115.7 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel

column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (34.7 mg, 93%), mp: 177-179 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

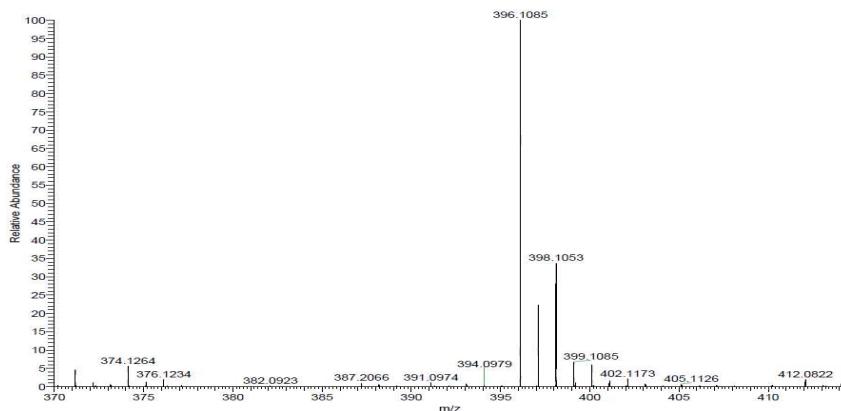
**HPLC** (IC, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 11.07 min (major), 14.23 min (minor), 96% ee.

[ $\alpha$ ]D<sup>25</sup>: +8.96 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

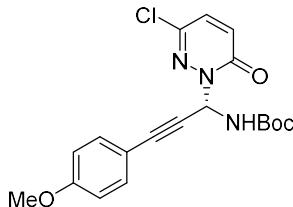
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.35-7.30 (m, 2H), 7.25 (d, *J* = 9.6 Hz, 1H), 7.16 (d, *J* = 9.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 9.6 Hz, 1H), 6.19 (s, 1H), 2.33 (s, 3H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 153.5, 139.5, 138.0, 134.2, 132.8, 132.0, 129.2, 118.3, 85.3, 82.1, 81.3, 59.1, 28.3, 21.6.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>ClN<sub>3</sub>NaO<sub>3</sub> 396.1085; Found 396.1085.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-(4-methoxyphenyl)prop-2-yn-1-yl)carbamate (3c)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(4-methoxyphenyl)prop-2-yn-1-yl)carbamate (122.1 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 2:1) and was obtained as a white solid (34.6 mg, 89%), mp: 135-137 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.1.

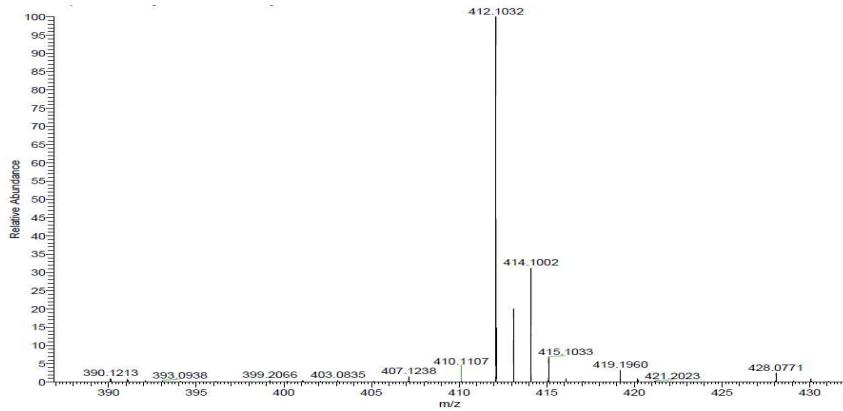
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 9.08 min (major), 13.13 min (minor), 90% ee.

[ $\alpha$ ]D<sup>25</sup>: +35.68 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

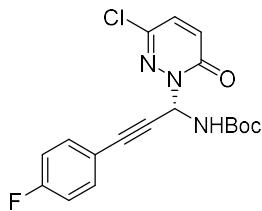
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40-7.32 (m, 2H), 7.25 (d, *J* = 9.6 Hz, 1H), 7.16 (d, *J* = 9.6 Hz, 1H), 6.92 (d, *J* = 9.6 Hz, 1H), 6.85-6.78 (m, 2H), 6.25 (s, 1H), 3.79 (s, 3H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 160.3, 157.6, 153.6, 138.0, 134.2, 133.6, 132.8, 114.0, 113.4, 85.2, 81.5, 81.2, 59.1, 55.4, 28.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>ClN<sub>3</sub>NaO<sub>4</sub> 412.1035; Found 412.1032.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-(4-fluorophenyl)prop-2-yn-1-yl)carbamate (3d)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(4-fluorophenyl)prop-2-yn-1-yl)carbamate (117.2 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (27.5 mg, 73%), mp: 139-141 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

**HPLC** (IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 12.70 min (major), 14.04 min (minor), 92% ee.

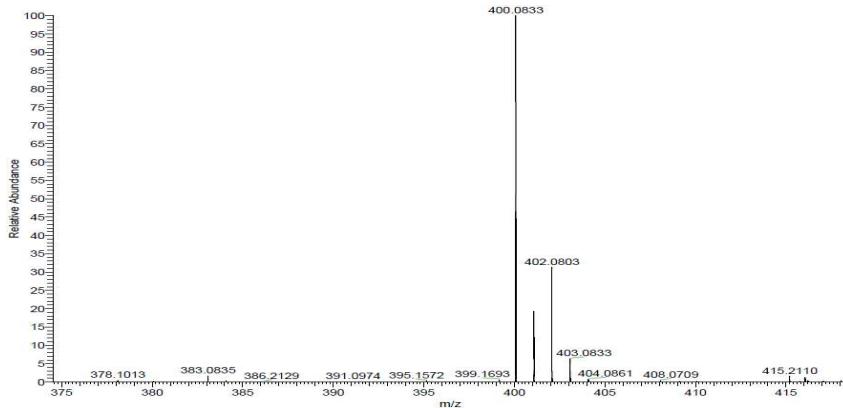
[**a**]D<sup>25</sup>: +24.32 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47-7.38 (m, 2H), 7.24 (d, *J* = 9.6 Hz, 1H), 7.19 (d, *J* = 9.6 Hz, 1H), 7.04-6.97 (m, 2H), 6.94 (d, *J* = 9.6 Hz, 1H), 6.20 (s, 1H), 1.45 (s, 9H).

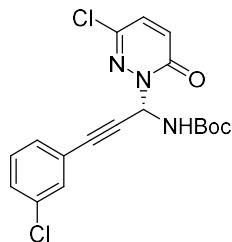
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 163.0 (d, *J* = 250.0 Hz), 157.6, 153.5, 138.1, 134.3, 134.1 (d, *J* = 9.0 Hz), 132.8, 117.5 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 22.0 Hz), 84.1, 82.5, 81.4, 59.1, 28.3.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -109.2 (s).

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>ClFN<sub>3</sub>NaO<sub>3</sub> 400.0835; Found 400.0833.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-(3-chlorophenyl)prop-2-yn-1-yl)carbamate (3e)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (3-(3-chlorophenyl)-1-ethoxyprop-2-yn-1-yl)carbamate (123.6 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (18.5 mg, 47%), mp: 139-141 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.4.

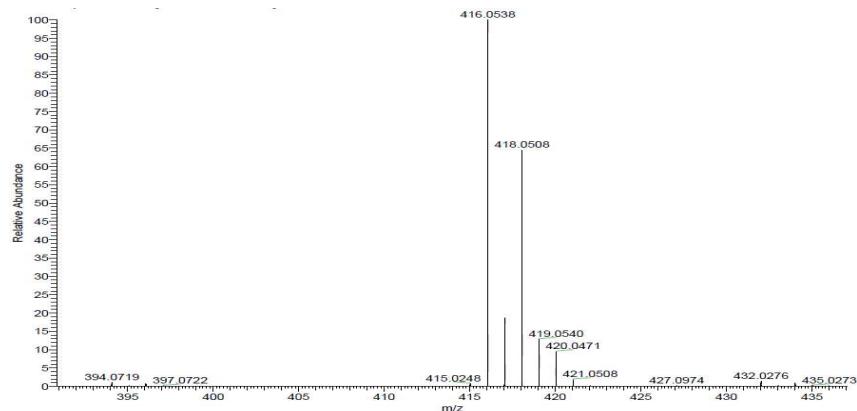
**HPLC** (IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 13.56 min (minor), 15.50 min (major), 92% ee.

[ $\alpha$ ]<sub>D</sub><sup>25</sup>: +17.60 (c = 0.10, CH<sub>2</sub>Cl<sub>2</sub>).

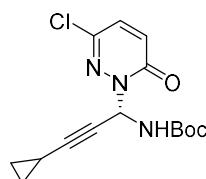
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.43 (t, *J* = 1.6 Hz, 1H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 2H), 7.19 (d, *J* = 9.6 Hz, 1H), 6.94 (d, *J* = 9.6 Hz, 1H), 6.14 (s, 1H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 153.4, 138.1, 134.3, 134.2, 132.8, 131.9, 130.2, 129.6, 129.5, 123.0, 83.8, 83.6, 81.4, 59.0, 28.2.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>3</sub> 416.0539; Found 416.0538.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-cyclopropylprop-2-yn-1-yl)carbamate (3f)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (3-cyclopropyl-1-ethoxyprop-2-yn-1-yl)carbamate (95.7 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid

(29.7 mg, 92%), mp: 149-151 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.2.

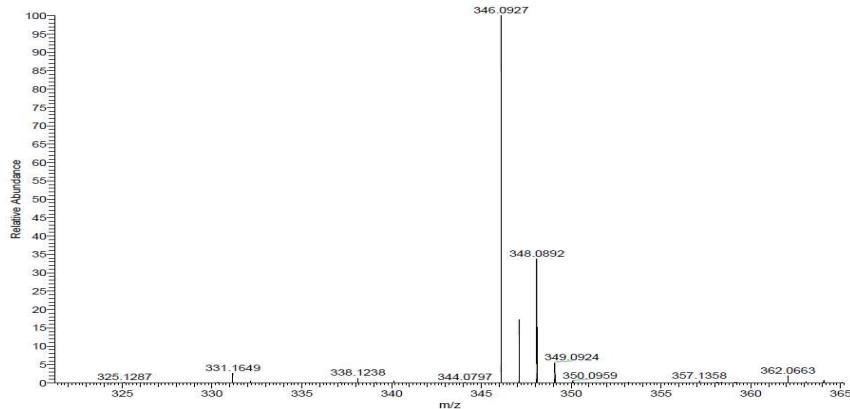
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.57 min (major), 9.72 min (minor), 80% ee.

[ $\alpha$ ]D<sup>25</sup>: +18.88 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

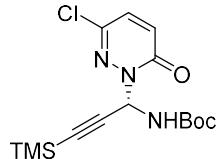
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.17 (d, *J* = 9.6 Hz, 1H), 6.95 (dd, *J* = 9.2, 1.6 Hz, 1H), 6.91 (d, *J* = 9.6 Hz, 1H), 6.02 (s, 1H), 1.42 (s, 9H), 1.31-1.14 (m, 1H), 0.82-0.74 (m, 2H), 0.74-0.67 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 153.4, 137.8, 134.1, 132.8, 89.4, 81.1, 69.1, 58.8, 28.3, 8.4, 8.3, -0.6.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>18</sub>ClN<sub>3</sub>NaO<sub>3</sub> 346.0929; Found 346.0927.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-(trimethylsilyl)prop-2-yn-1-yl)carbamate (3g)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(trimethylsilyl)prop-2-yn-1-yl)carbamate (108.5 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (20.6 mg, 58%), mp: 169-171 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

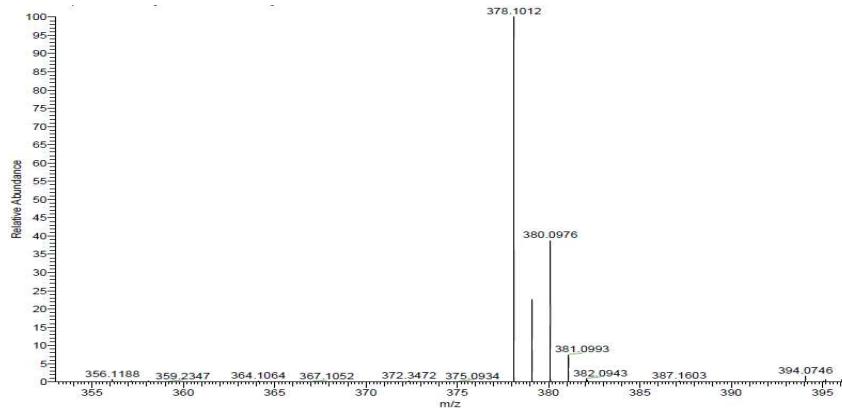
**HPLC** (IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.86 min (major), 8.21 min (minor), 90% ee.

[ $\alpha$ ]D<sup>25</sup>: +4.00 (c = 0.15, CH<sub>2</sub>Cl<sub>2</sub>).

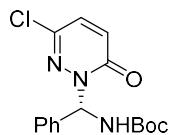
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.18 (d, *J* = 9.6 Hz, 1H), 7.01 (d, *J* = 10.0 Hz, 1H), 6.92 (d, *J* = 9.6 Hz, 1H), 6.04 (s, 1H), 1.43 (s, 9H), 0.16 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.5, 153.5, 137.9, 134.2, 132.8, 97.9, 90.8, 81.3, 58.7, 28.3, -0.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>22</sub>ClN<sub>3</sub>NaO<sub>3</sub>Si 378.1011; Found 378.1012.



**tert-Butyl (S)-((3-chloro-6-oxopyridazin-1(6H)-yl)(phenyl)methyl)carbamate (3h)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (ethoxy(phenyl)methyl)carbamate (100.5 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (10.1 mg, 30%), mp: 154-156 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

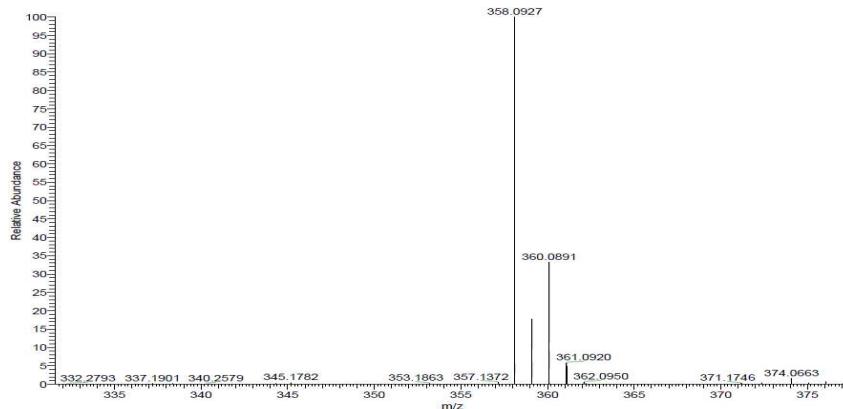
**HPLC** (OD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 8.89 min (major), 10.11 min (minor), 24% ee.

[**a**]D<sup>25</sup>: +9.80 (c = 0.1, CH<sub>2</sub>Cl<sub>2</sub>).

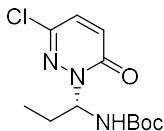
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 10.0 Hz, 1H), 7.40-7.29 (m, 5H), 7.16 (d, *J* = 9.6 Hz, 1H), 6.89 (d, *J* = 9.6 Hz, 1H), 6.16 (s, 1H), 1.46 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.3, 154.3, 137.9, 136.6, 133.8, 132.6, 128.8, 126.3, 80.9, 68.3, 28.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>NaO<sub>3</sub> 358.0929; Found 358.0927.



**tert-Butyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)propyl)carbamate (3i)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxypropyl)carbamate (81.3 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (13.2 mg, 46%), mp: 135-137 °C.

**R<sub>f</sub>** (Petroleum ether/EtOAc = 3:1) = 0.3.

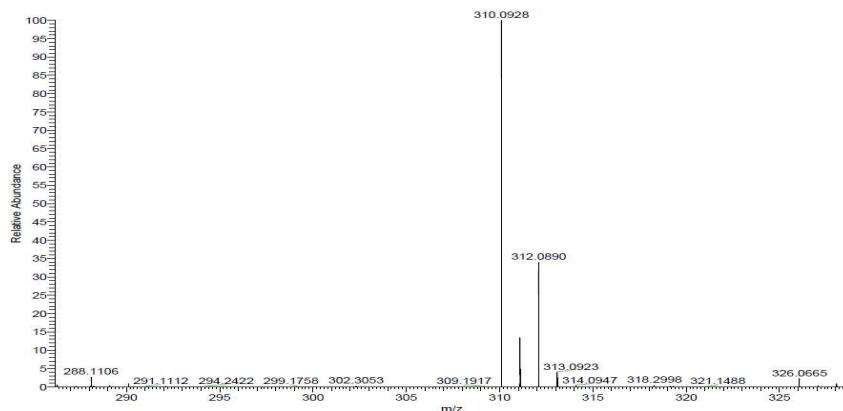
**HPLC** (OD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.49 min (major), 7.76 min (minor), 70% ee.

[ $\alpha$ ]D<sup>25</sup>: +12.00 (c = 0.1, CH<sub>2</sub>Cl<sub>2</sub>).

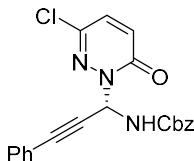
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.16 (d, *J* = 9.6 Hz, 1H), 6.90 (d, *J* = 9.6 Hz, 1H), 6.35-6.18 (m, 1H), 5.65 (s, 1H), 2.02-1.79 (m, 2H), 1.42 (s, 9H), 0.95 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.5, 154.4, 137.6, 133.5, 132.6, 80.5, 68.0, 28.3, 27.2, 9.7.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>18</sub>ClN<sub>3</sub>NaO<sub>3</sub> 310.0929; Found 310.0928.



#### Benzyl (S)-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3j)



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and benzyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (123.6 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc c = 10:1 to 3:1) and was obtained as a white solid (16.1 mg, 41%), mp: 136-138 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.3.

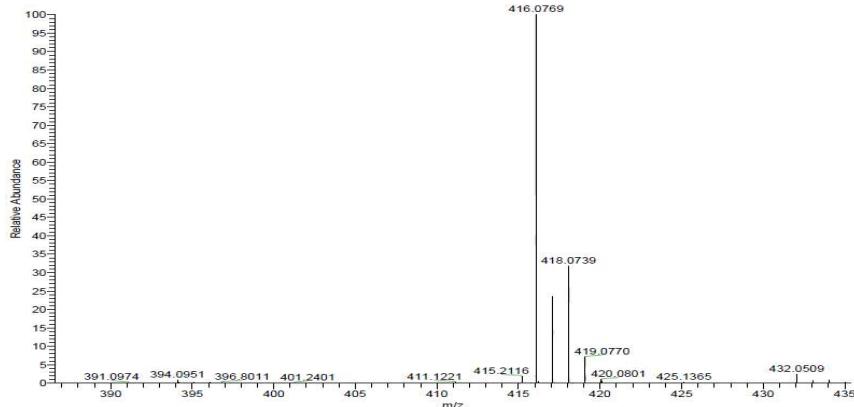
**HPLC** (IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.12 min (minor), 8.54 min (major), 92% ee.

[ $\alpha$ ]D<sup>25</sup>: +13.12 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

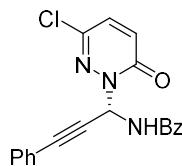
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.38 (m, 2H), 7.37-7.22 (m, 9H), 7.11 (d, *J* = 9.6 Hz, 1H), 6.90 (d, *J* = 9.6 Hz, 1H), 6.57 (d, *J* = 7.2 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.0 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 154.5, 138.3, 135.8, 134.3, 132.8, 132.1, 129.4, 128.7, 128.5, 128.4, 121.3, 85.5, 82.3, 67.7, 59.4.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>16</sub>ClN<sub>3</sub>NaO<sub>3</sub> 416.0772; Found 416.0769.



**(S)-N-(1-(3-chloro-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)benzamide (3k)**



Prepared from 6-chloropyridazin-3(2H)-one (13.0 mg, 0.1 mmol, 1.0 equiv) and N-(1-ethoxy-3-phenylprop-2-yn-1-yl)benzamide (111.6 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (18.5 mg, 51%), mp: 196–198 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.2.

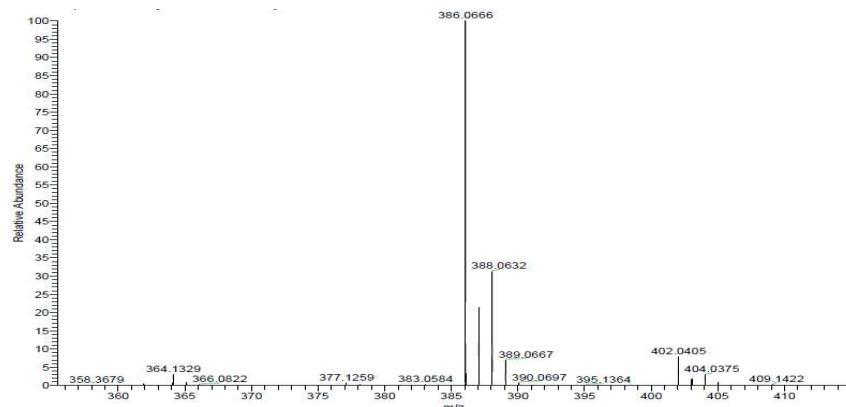
**HPLC** (IC, *n*-hexane/*i*-PrOH = 40/60, flow rate = 3.0 mL/min, I = 215 nm) t<sub>R</sub> = 14.07 min (major), 20.97 min (minor), 88% ee.

[**α**]D<sup>25</sup>: +8.53 (c = 0.15, CH<sub>2</sub>Cl<sub>2</sub>).

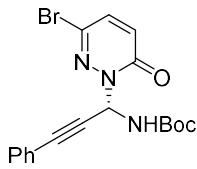
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48–7.39 (m, 4H), 7.37–7.24 (m, 3H), 7.14 (d, *J* = 10.0 Hz, 1H), 6.96 (d, *J* = 10.0 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 165.9, 157.9, 138.2, 134.3, 132.9, 132.7, 132.5, 132.1, 129.3, 128.7, 128.4, 127.6, 121.2, 85.5, 82.5, 58.4.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>14</sub>ClN<sub>3</sub>NaO<sub>2</sub> 386.0667; Found 386.0666.



**tert-Butyl (S)-(1-(3-bromo-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3l)**



Prepared from 6-bromopyridazin-3(2H)-one (17.4 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (32.7mg, 81%), mp: 162-164 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

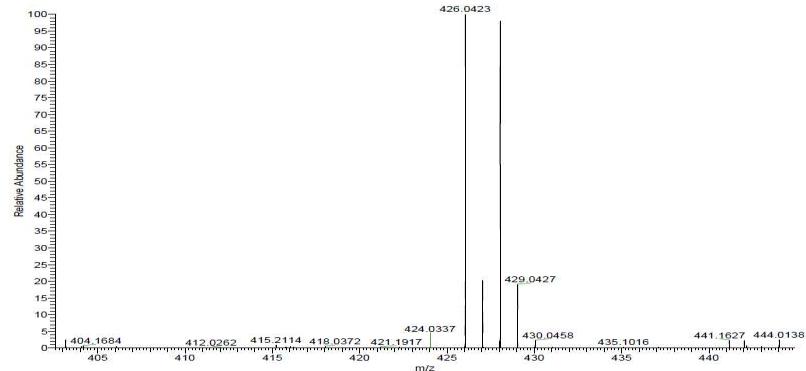
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 9.48 min (major), 11.97 min (minor), 94% ee.

[ $\alpha$ ]D<sup>25</sup>: +22.16 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

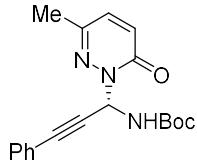
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.46-7.41 (m, 2H), 7.36-7.20 (m, 5H), 6.83 (d, *J* = 9.6 Hz, 1H), 6.25 (s, 1H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.6, 153.5, 136.9, 132.5, 132.1, 129.2, 128.4, 127.0, 121.4, 85.1, 82.8, 81.3, 59.2, 28.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>BrN<sub>3</sub>NaO<sub>3</sub> 426.0424; Found 426.0423.



**tert-Butyl (S)-(1-(3-methyl-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3m)**



Prepared from *tert*-butyl 6-methylpyridazin-3(2H)-one (11.0 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 2:1) and was obtained as a white solid (7.5 mg, 22%), mp: 163-165 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 2:1) = 0.2.

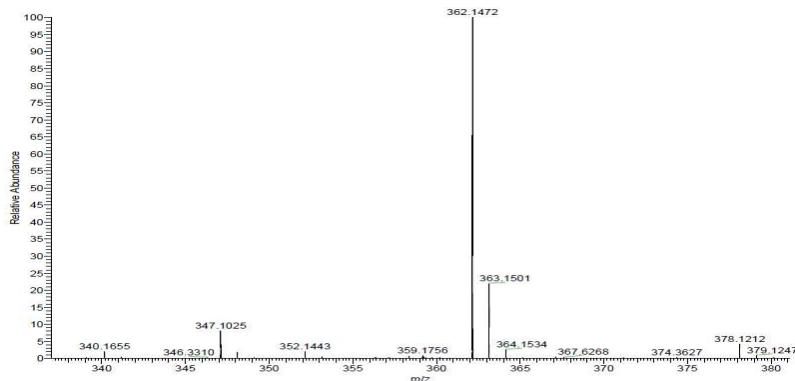
**HPLC** (IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.06 min (minor), 7.16 min (major), 92% ee.

[ $\alpha$ ]D<sup>25</sup>: +81.52 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

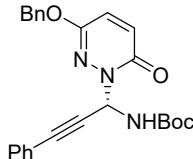
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.48-7.38 (m, 2H), 7.36-7.26 (m, 3H), 7.25-7.12 (m, 1H), 7.08 (d, *J* = 9.6 Hz, 1H), 6.87 (d, *J* = 9.6 Hz, 1H), 6.33 (s, 1H), 2.36 (s, 3H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.5, 153.7, 144.7, 133.8, 132.0, 130.6, 128.9, 128.2, 121.7, 84.2, 83.6, 80.9, 59.9, 28.3, 20.9.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>NaO<sub>3</sub> 362.1475; Found 362.1472.



**tert-Butyl (S)-(1-(3-(benzyloxy)-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3n)**



Prepared from 6-(benzyloxy)pyridazin-3(2H)-one (20.2 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 2:1) and was obtained as colorless oil (28.9 mg, 67%).

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.1.

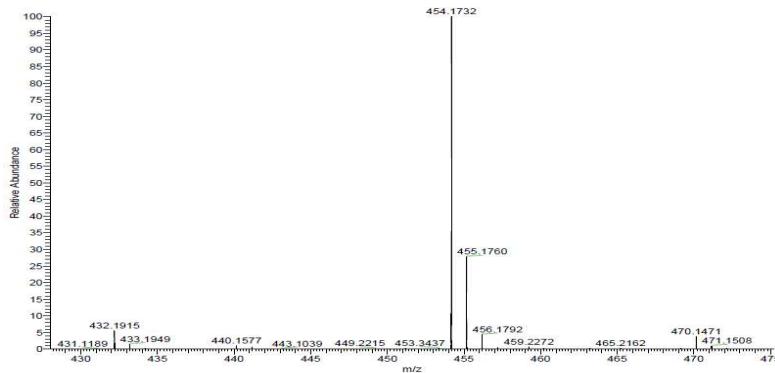
**HPLC** (IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 21.16 min (major), 24.15 min (minor), 94% ee.

[ $\alpha$ ]D<sup>25</sup>: +23.92 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

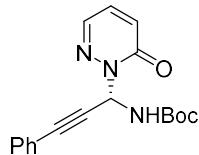
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.49-7.40 (m, 4H), δ 7.40-7.27 (m, 6H), 7.22 (s, 1H), 6.96 (d, *J* = 10.0 Hz, 1H), 6.91 (d, *J* = 10.0 Hz, 1H), 6.19 (s, 1H), 5.27 (d, *J* = 12.0 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 1.46 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.9, 153.7, 152.4, 135.9, 133.6, 132.1, 129.0, 128.7, 128.5, 128.4, 127.5, 121.8, 84.4, 83.6, 81.0, 69.3, 58.9, 28.4.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>25</sub>N<sub>3</sub>NaO<sub>4</sub> 454.1737; Found 454.1732.



**tert-Butyl (S)-(1-(6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3o)**



Prepared from pyridazin-3(2H)-one (9.6 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 2:1) and was obtained as a white solid (13.3 mg, 41%), mp: 164–166 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 2:1) = 0.2.

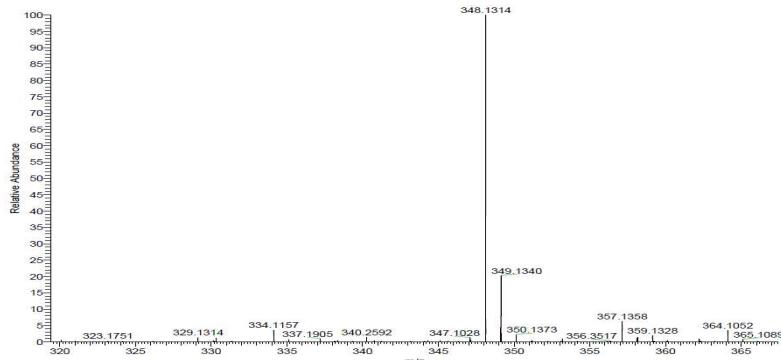
**HPLC** (IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 17.64 min (minor), 20.11 min (major), 94% ee.

[**α**]<sub>D</sub><sup>25</sup>: +46.72 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

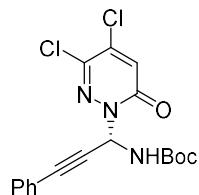
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.81 (dd, *J* = 3.6, 1.6 Hz, 1H), 7.48–7.38 (m, 2H), 7.36–7.25 (m, 4H), 7.19 (dd, *J* = 9.2, 3.6 Hz, 1H), 6.95 (dd, *J* = 9.2, 1.6 Hz, 1H), 6.30 (s, 1H), 1.44 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.2, 153.7, 136.5, 132.1, 131.7, 130.9, 129.1, 128.3, 121.6, 84.7, 83.2, 81.1, 60.0, 28.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>NaO<sub>3</sub> 348.1319; Found 348.1314.



**tert-Butyl (S)-(1-(3,4-dichloro-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3p)**



Prepared from 5,6-dichloropyridazin-3(2H)-one (16.4 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 30:1 to 10:1) and was obtained as a white solid (36.2 mg, 92%), mp: 191–193 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 10:1) = 0.3.

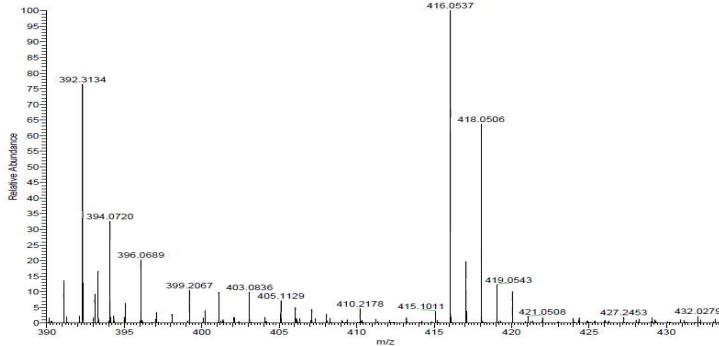
**HPLC** (OD-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.73 min (minor), 8.85 min (major), 86% ee.

[**α**]<sub>D</sub><sup>25</sup>: +30.13 (c = 0.15, CH<sub>2</sub>Cl<sub>2</sub>).

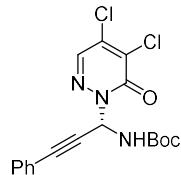
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.48-7.38 (m, 2H), 7.38-7.27 (m, 3H), 7.24 (d, *J* = 9.6 Hz, 1H), 7.11 (s, 1H), 6.15 (s, 1H), 1.46 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.0, 153.4, 140.1, 137.0, 132.0, 130.1, 129.3, 128.4, 121.1, 85.4, 82.3, 81.5, 59.1, 28.2.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>3</sub> 416.0539; Found 416.0537.



**tert-Butyl (S)-(1-(4,5-dichloro-6-oxopyridazin-1(6H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (3q)**



Prepared from 4,5-dichloropyridazin-3(2H)-one (16.4 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 5:1) and was obtained as a colorless oil (19.7 mg, 50%).

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.5.

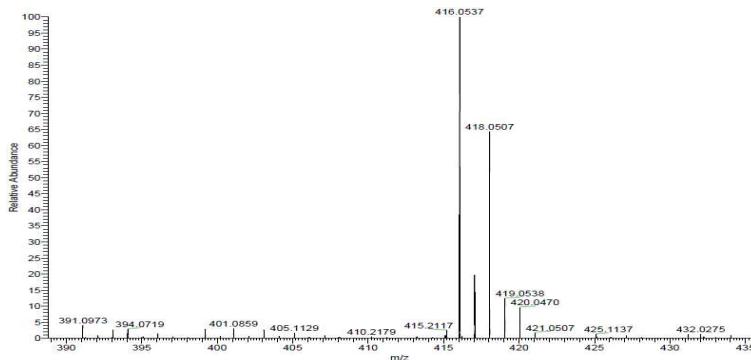
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, *I* = 215 nm) t<sub>R</sub> = 6.11 min (major), 7.62 min (minor), 88% ee.

[ **$\alpha$** ]<sub>D</sub><sup>25</sup>: +59.60 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

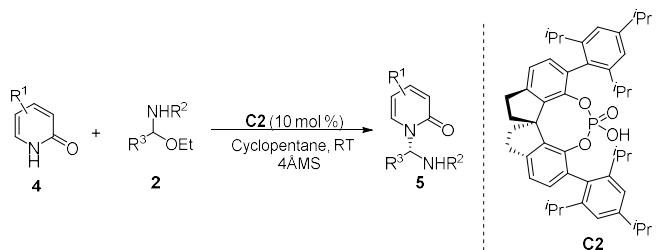
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.83 (s, 1H), 7.47-7.38 (m, 2H), 7.38-7.27 (m, 3H), 7.25-7.17 (m, 1H), 6.24 (s, 1H), 1.45 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 155.4, 153.6, 137.0, 136.1, 135.0, 132.1, 129.3, 128.4, 121.2, 85.5, 82.1, 81.5, 61.3, 28.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>3</sub> 416.0539; Found 416.0537.



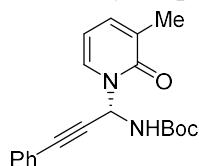
### General procedure for Scheme 3



To a 10 mL of dry Schlenk tube were added **C2** (7.2 mg, 0.01 mmol, 10 mol %), 4ÅMS (50 mg), **4** (0.1 mmol, 1.0 equiv) and **2** (0.4 mmol, 4.0 equiv), then Cyclopentane (2 mL) was added under argon atmosphere. The resulting mixture was stirred at RT for 24 hours. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 10:1-3:1) to give **5**.

[Note: racemic samples were prepared by using BNDHP instead of **C2**.]

#### *tert*-Butyl (*S*)-(1-(3-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylprop-2-yn-1-yl)carbamate (**5a**)



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (26.4 mg, 78%), mp: 90-92 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.5.

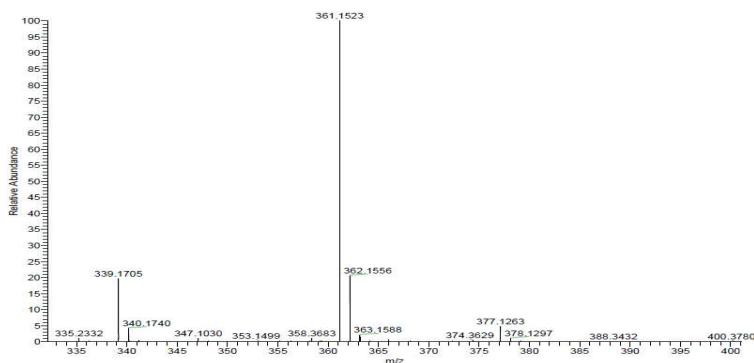
**HPLC** (IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) *t*<sub>R</sub> = 10.73 min (minor), 12.67 min (major), 93% ee.

[\alpha]<sub>D</sub><sup>25</sup>: -35.12 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

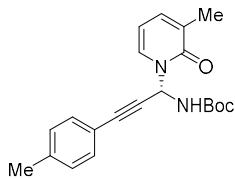
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 (d, *J* = 6.4 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.36-7.25 (m, 3H), 7.20 (d, *J* = 6.4 Hz, 1H), 6.76 (s, 1H), 6.61 (s, 1H), 6.13 (t, *J* = 6.8 Hz, 1H), 2.17 (s, 3H), 1.43 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.3, 154.0, 137.2, 133.4, 132.0, 130.4, 129.0, 128.3, 121.6, 105.6, 85.0, 83.1, 81.0, 59.3, 28.2, 17.0.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub> 361.1523; Found 361.1523.



**tert-Butyl (S)-(1-(3-methyl-2-oxopyridin-1(2H)-yl)-3-(*p*-tolyl)prop-2-yn-1-yl)carbamate (5b)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(*p*-tolyl)prop-2-yn-1-yl)carbamate (115.7 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (27.5 mg, 78%), mp: 153–155 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.4.

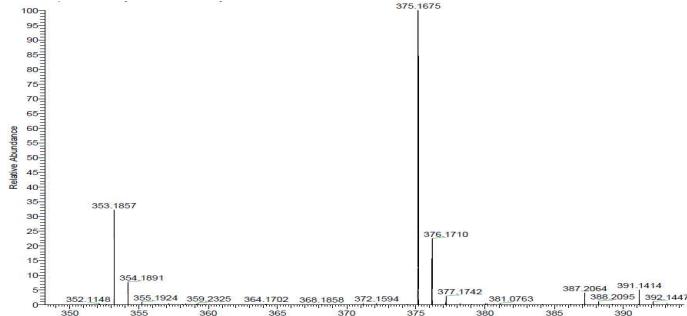
**HPLC** (IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 9.46 min (minor), 12.13 min (major), 92% ee.

[**α**]<sub>D</sub><sup>25</sup>: +2.00 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

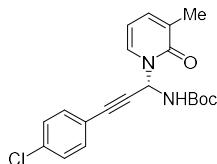
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 6.4 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.23–7.15 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 6.75 (s, 1H), 6.54 (s, 1H), 6.12 (t, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.16 (s, 3H), 1.42 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.2, 154.0, 139.2, 137.2, 133.3, 131.9, 130.4, 129.0, 118.5, 105.6, 85.2, 82.4, 81.0, 59.4, 28.2, 21.5, 17.0.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>3</sub> 375.1679; Found 375.1675.



**tert-Butyl (S)-(3-(4-chlorophenyl)-1-(3-methyl-2-oxopyridin-1(2H)-yl)prop-2-yn-1-yl)carbamate (5c)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (3-(4-chlorophenyl)-1-ethoxyprop-2-yn-1-yl)carbamate (123.6 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (23.8 mg, 64%), mp: 173–175 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.4.

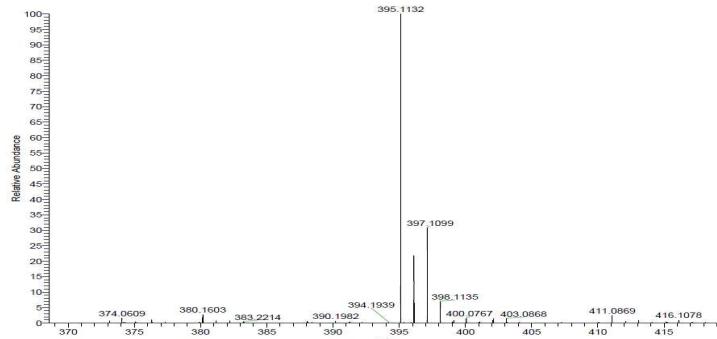
**HPLC** (IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 5.56 min (major), 6.10 min (minor), 82% ee.

[**α**]<sub>D</sub><sup>25</sup>: -12.43 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

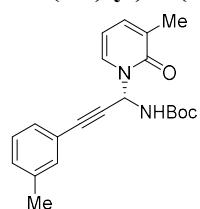
**<sup>1</sup>H NMR** (400 MHz, DMSO-d6) δ 8.84 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 6.4 Hz, 1H), 7.55-7.43 (m, 4H), 7.39-7.27 (m, 2H), 6.30 (t, *J* = 6.8 Hz, 1H), 2.02 (s, 3H), 1.39 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, DMSO-d6) δ 165.7, 158.9, 142.3, 139.4, 138.7, 136.4, 134.2, 133.6, 124.9, 111.3, 91.2, 87.9, 85.1, 58.3, 33.2, 22.1.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>21</sub>ClN<sub>2</sub>NaO<sub>3</sub> 395.1133; Found 395.1132.



**tert-Butyl (S)-(1-(3-methyl-2-oxopyridin-1(2H)-yl)-3-(m-tolyl)prop-2-yn-1-yl)carbamate (5d)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(m-tolyl)prop-2-yn-1-yl)carbamate (115.7 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (31.0 mg, 88%), mp: 148-150 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.4.

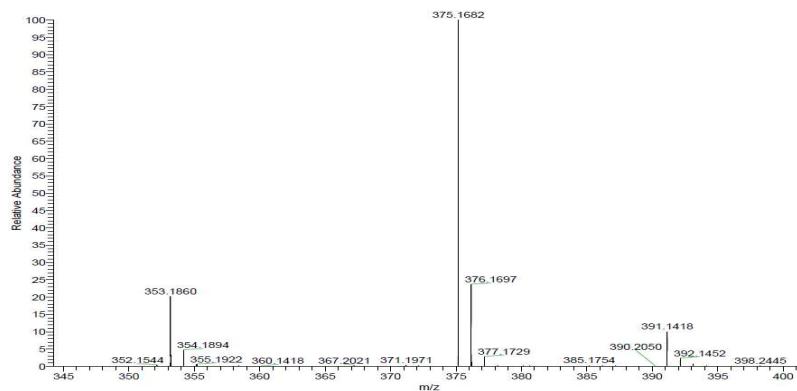
**HPLC** (IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 14.09 min (minor), 16.42 min (major), 90% ee.

[ $\alpha$ ]<sub>D</sub><sup>25</sup>: -16.64 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

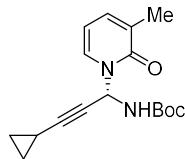
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.52 (d, *J* = 6.4 Hz, 1H), 7.27-7.06 (m, 5H), 6.76 (s, 1H), 6.66 (s, 1H), 6.12 (t, *J* = 6.8 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 1.43 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.2, 154.0, 137.9, 137.2, 133.4, 132.6, 130.2, 129.8, 129.0, 128.1, 121.4, 105.7, 85.2, 82.9, 80.9, 59.0, 28.2, 21.2, 17.1.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>3</sub> 375.1679; Found 375.1682.



**tert-Butyl (S)-(3-cyclopropyl-1-(3-methyl-2-oxopyridin-1(2H)-yl)prop-2-yn-1-yl)carbamate (5e)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (3-cyclopropyl-1-ethoxyprop-2-yn-1-yl)carbamate (95.7 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (26.3 mg, 87%), mp: 176-178 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

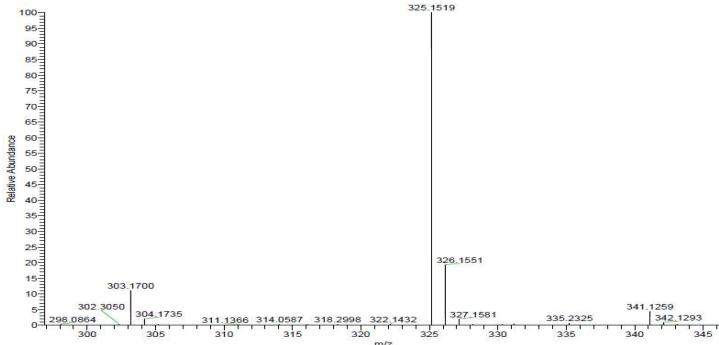
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 6.70 min (minor), 11.15 min (major), 94% ee.

[ $\alpha$ ]<sub>D</sub><sup>25</sup>: -44.80 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

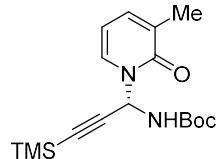
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.22-7.12 (m, 1H), 6.46 (s, 1H), 6.32 (s, 1H), 6.10 (t, *J* = 6.8 Hz, 1H), 2.15 (s, 3H), 1.40 (s, 9H), 1.31-1.22 (m, 1H), 0.82-0.73 (m, 2H), 0.73-0.66 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.7, 154.5, 137.6, 133.9, 130.8, 106.0, 89.7, 81.4, 70.0, 59.6, 28.8, 17.6, 8.9, 8.8, 0.0.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub> 325.1523; Found 325.1519.



**tert-Butyl (S)-(1-(3-methyl-2-oxopyridin-1(2H)-yl)-3-(trimethylsilyl)prop-2-yn-1-yl)carbamate (5f)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-(trimethylsilyl)prop-2-yn-1-yl)carbamate (108.5 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (27.1 mg, 81%), mp: 165-167 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.5.

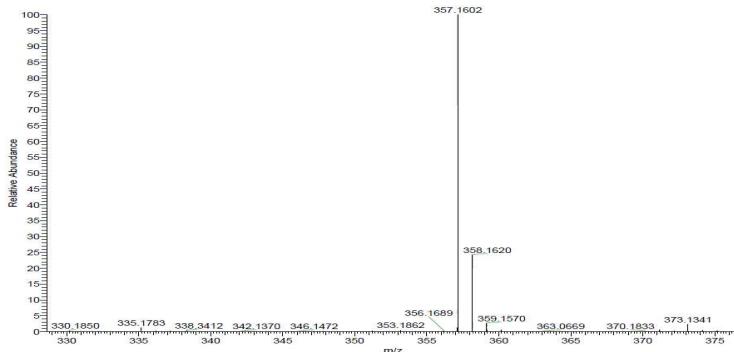
**HPLC** (IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 7.24 min (minor), 9.87 min (major), 89% ee.

$[\alpha]_D^{25}$ : -37.04 ( $c = 0.25$ ,  $\text{CH}_2\text{Cl}_2$ ).

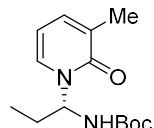
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 6.0$  Hz, 1H), 7.22-7.16 (m, 1H), 6.58 (s, 1H), 6.27 (s, 1H), 6.11 (t,  $J = 6.8$  Hz, 1H), 2.15 (s, 3H), 1.41 (s, 9H), 0.17 (s, 9H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 154.2, 137.4, 133.5, 130.5, 105.9, 98.9, 91.0, 81.3, 58.5, 28.6, 17.5, 0.0.

**HRMS (ESI)** m/z:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{26}\text{N}_2\text{NaO}_3\text{Si}$  357.1605, Found 357.1602.



### tert-Butyl (S)-(1-(3-methyl-2-oxopyridin-1(2H)-yl)propyl)carbamate (5g)



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxypropyl)carbamate (81.3 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (5.6 mg, 21%), mp: 144-146 °C.

$R_f$  (Petroleum ether/ EtOAc = 3:1) = 0.3.

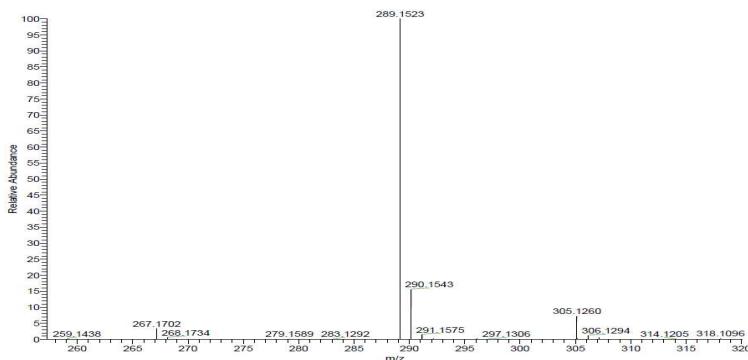
**HPLC** (IC, *n*-hexane/*i*-PrOH = 70/30, flow rate = 2.0 mL/min,  $\lambda = 215$  nm)  $t_R$  = 3.46 min (major), 4.33 min (minor), 66% ee.

$[\alpha]_D^{25}$ : +70.80 ( $c = 0.05$ ,  $\text{CH}_2\text{Cl}_2$ ).

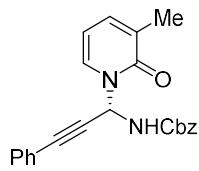
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (d,  $J = 6.8$  Hz, 1H), 7.16 (d,  $J = 6.8$  Hz, 1H), 6.46 (d,  $J = 7.2$  Hz, 1H), 6.09 (t,  $J = 6.8$  Hz, 1H), 5.36 (d,  $J = 5.6$  Hz, 1H), 2.38-2.18 (m, 1H), 2.13 (s, 3H), 2.11-1.95 (m, 1H), 1.41 (s, 9H), 0.88 (t,  $J = 7.2$  Hz, 3H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 155.0, 137.0, 134.9, 130.5, 105.4, 80.1, 73.4, 28.2, 26.1, 16.9, 10.4.

**HRMS (ESI)** m/z:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{14}\text{H}_{22}\text{N}_2\text{NaO}_3$  289.1523; Found 289.1523.



**Benzyl (S)-(1-(3-methyl-2-oxopyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5h)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and benzyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (123.6 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as colorless oil (16.0 mg, 43%).

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.3.

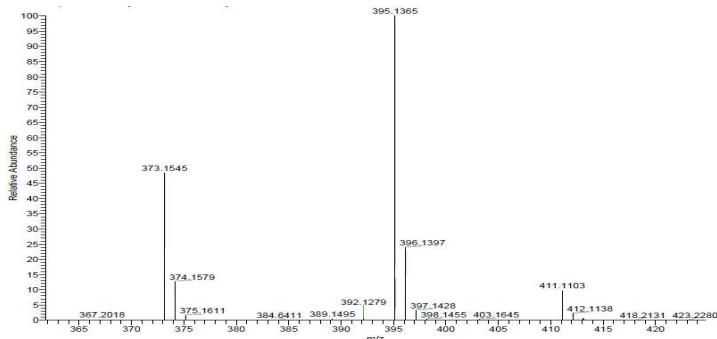
**HPLC** (IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 7.35 min (minor), 8.02 min (major), 76% ee.

[**a**]D<sup>25</sup>: -27.69 (c = 0.15, CH<sub>2</sub>Cl<sub>2</sub>).

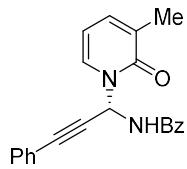
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 6.4 Hz, 1H), 7.46-7.40 (m, 2H), 7.38-7.25 (m, 8H), 7.20 (d, *J* = 6.0 Hz, 1H), 6.88 (s, 1H), 6.81 (s, 1H), 6.12 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 2.15 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.2, 155.0, 137.4, 135.8, 133.5, 132.0, 130.4, 129.1, 128.5, 128.31, 128.27, 128.2, 121.5, 105.8, 85.6, 82.7, 67.4, 59.2, 17.1.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>3</sub> 395.1366; Found 395.1365.



**(S)-N-(1-(3-methyl-2-oxopyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)benzamide (5i)**



Prepared from 3-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and N-(1-ethoxy-3-phenylprop-2-yn-1-yl)benzamide (111.6 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (28.1 mg, 82%), mp: 193-195 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.2.

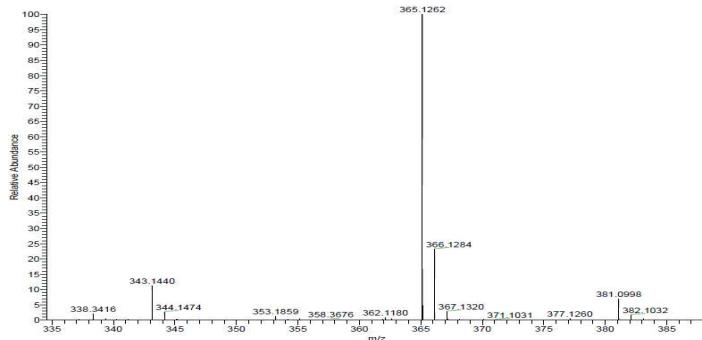
**HPLC** (IA, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 13.53 min (minor), 14.87 min (major), 54% ee.

[**a**]D<sup>25</sup>: +5.36 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

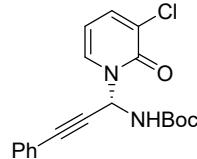
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 8.4 Hz, 1H), 7.93-7.79 (m, 2H), 7.66 (d, *J* = 6.4 Hz, 1H), 7.51-7.36 (m, 5H), 7.34-7.24 (m, 3H), 7.20 (d, *J* = 6.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.14 (t, *J* = 6.8 Hz, 1H), 2.13 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 166.4, 162.6, 137.6, 134.5, 132.8, 132.3, 132.1, 130.6, 129.0, 128.6, 128.3, 127.6, 121.6, 105.8, 85.2, 82.9, 59.1, 16.9.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>2</sub> 365.1260; Found 365.1262.



#### **tert-Butyl (S)-(1-(3-chloro-2-oxopyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5j)**



Prepared from 3-chloropyridin-2(1H)-one (12.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (22.9 mg, 64%), mp: 189-191 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.4.

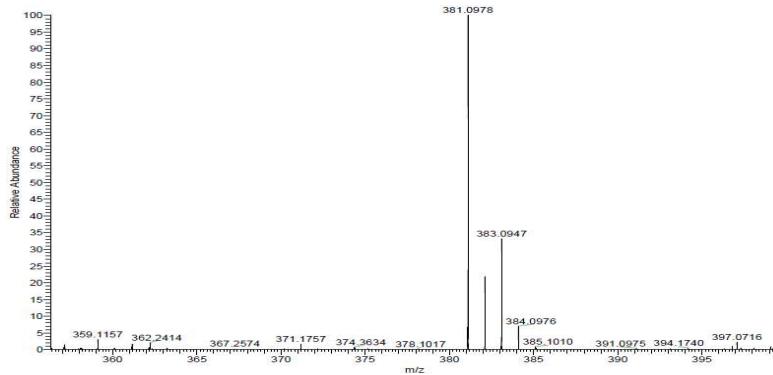
**HPLC** (IC, *n*-hexane/*i*-PrOH = 90/10, flow rate = 2.0 mL/min, I = 215 nm) t<sub>R</sub> = 13.93 min (minor), 16.17 min (major), 76% ee.

[ $\alpha$ ]<sub>D</sub><sup>25</sup>: -16.88 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

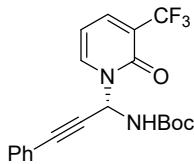
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70-7.59 (m, 1H), 7.54 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.48-7.40 (m, 2H), 7.37-7.26 (m, 3H), 6.72 (s, 1H), 6.57 (s, 1H), 6.18 (t, *J* = 7.2 Hz, 1H), 1.43 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.2, 153.9, 138.1, 134.9, 132.0, 129.2, 128.3, 126.6, 121.3, 105.3, 85.7, 82.1, 81.3, 60.3, 28.2.

**HRMS (ESI)** m/z: [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>19</sub>ClN<sub>2</sub>NaO<sub>3</sub> 381.0976; Found 381.0978.



**tert-Butyl (S)-(1-(2-oxo-3-(trifluoromethyl)pyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5k)**



Prepared from 3-(trifluoromethyl)pyridin-2(1H)-one (16.3 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as colorless oil (23.5 mg, 60%).

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.5.

**HPLC** (IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 9.89 min (major), 11.96 min (minor), 72% ee.

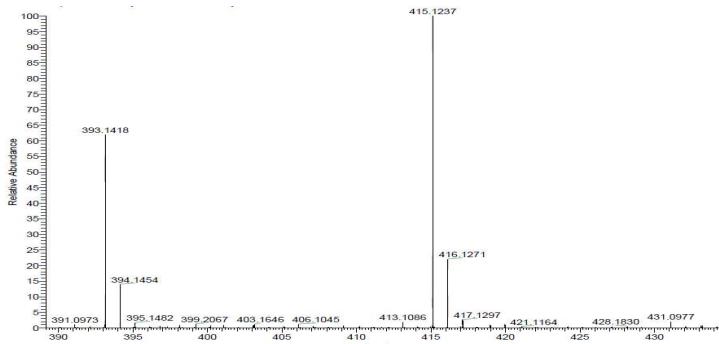
[**α**]<sub>D</sub><sup>25</sup>: -6.08 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 6.8 Hz, 1H), 7.74 (d, *J* = 6.8 Hz, 1H), 7.45-7.39 (m, 2H), 7.37-7.25 (m, 3H), 6.81 (s, 2H), 6.28 (t, *J* = 6.8 Hz, 1H), 1.43 (s, 9H).

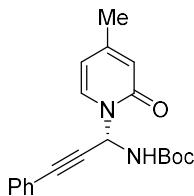
**<sup>13</sup>C NMR** (75 MHz, DMSO-d6) δ 156.6, 154.1, 140.9 (q, *J* = 4.5 Hz), 139.4, 132.2, 130.0, 129.2, 123.3 (q, *J* = 270.0 Hz), 121.0, 118.6 (q, *J* = 30.0 Hz), 105.6, 85.1, 84.2, 80.6, 54.4, 28.3.

**<sup>19</sup>F NMR** (376 MHz, DMSO-D6) δ -70.2.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>NaO<sub>3</sub> 415.1240; Found 415.1237.



**tert-Butyl (S)-(1-(4-methyl-2-oxopyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5l)**



Prepared from 4-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (20.3 mg, 60%), mp: 213-215 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.2.

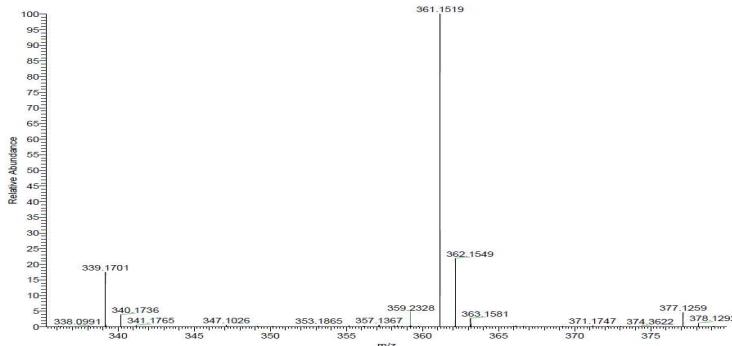
**HPLC** (IC, *n*-hexane/*i*-PrOH = 50/50, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 7.84 min (minor), 9.89 min (major), 83% ee.

$[\alpha]_D^{25}$ : +8.24 ( $c = 0.25$ ,  $\text{CH}_2\text{Cl}_2$ ).

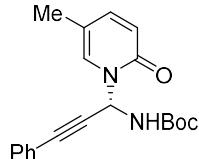
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 6.8$  Hz, 1H), 7.47-7.42 (m, 2H), 7.37-7.26 (m, 3H), 6.67 (s, 1H), 6.53 (s, 1H), 6.37 (s, 1H), 6.04 (dd,  $J = 7.2, 2.0$  Hz, 1H), 2.17 (s, 3H), 1.43 (s, 9H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 154.0, 151.9, 134.9, 132.0, 129.0, 128.3, 121.6, 119.8, 108.6, 85.2, 82.9, 81.0, 58.9, 28.3, 21.4.

**HRMS (ESI)** m/z:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{NaO}_3$  361.1523; Found 361.1519.



#### **tert-Butyl (S)-(1-(5-methyl-2-oxopyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5m)**



Prepared from 5-methylpyridin-2(1H)-one (10.9 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (30.8 mg, 91%), mp: 176-178 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.2.

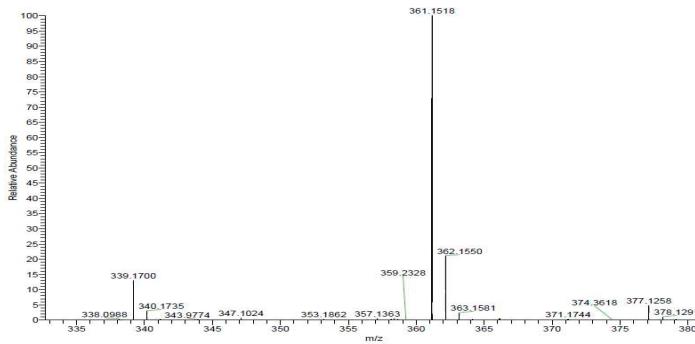
**HPLC** (AS-H, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min,  $\lambda = 215$  nm)  $t_R$  = 7.74 min (major), 10.97 min (minor), 88% ee.

$[\alpha]_D^{25}$ : +5.44 ( $c = 0.25$ ,  $\text{CH}_2\text{Cl}_2$ ).

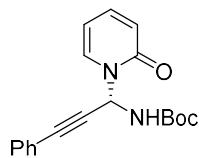
**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.41 (m, 2H), 7.37-7.25 (m, 4H), 7.20 (dd,  $J = 9.2, 2.4$  Hz, 1H), 6.65 (s, 2H), 6.53 (d,  $J = 9.2$  Hz, 1H), 2.09 (s, 3H), 1.43 (s, 9H).

**$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 154.0, 142.8, 133.3, 132.0, 129.0, 128.3, 121.6, 121.1, 115.1, 84.9, 83.2, 81.0, 59.2, 28.3, 17.2.

**HRMS (ESI)** m/z:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{NaO}_3$  361.1523, Found 361.1518.



**tert-Butyl (S)-(1-(2-oxopyridin-1(2H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5n)**



Prepared from pyridin-2(1H)-one (9.5 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 10:1 to 3:1) and was obtained as a white solid (28.2 mg, 87%), mp: 188-190 °C.

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 3:1) = 0.2.

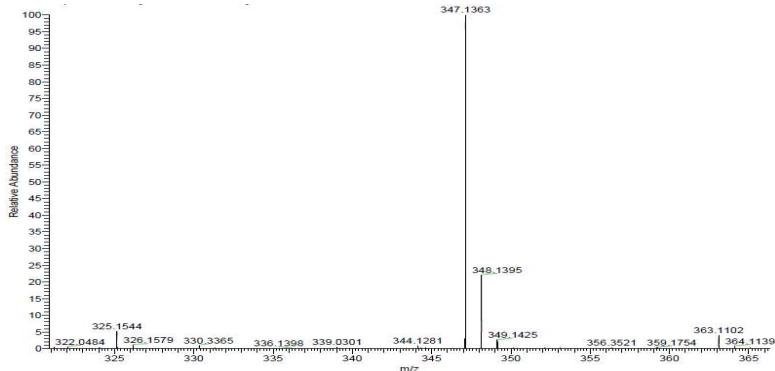
**HPLC** (IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.2 mL/min, I = 215 nm) t<sub>R</sub> = 17.46 min (minor), 19.19 min (major), 82% ee.

[**α**]<sub>D</sub><sup>25</sup>: +26.16 (c = 0.25, CH<sub>2</sub>Cl<sub>2</sub>).

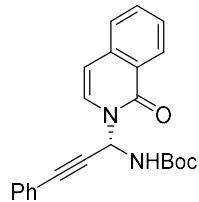
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.64 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.48-7.40 (m, 2H), 7.39-7.27 (m, 4H), 6.72 (s, 1H), 6.58 (dd, *J* = 9.2, 0.4 Hz, 2H), 6.20 (td, *J* = 6.8, 1.2 Hz, 1H), 1.43 (s, 9H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.9, 153.9, 140.1, 136.0, 132.0, 129.1, 128.3, 121.53, 121.47, 105.9, 85.3, 82.7, 81.1, 59.4, 28.2.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>3</sub> 347.1366; Found 347.1363.



**tert-Butyl (S)-(1-(1-oxoisoquinolin-2(1H)-yl)-3-phenylprop-2-yn-1-yl)carbamate (5o)**



Prepared from isoquinolin-1(2H)-one (14.5 mg, 0.1 mmol, 1.0 equiv) and *tert*-butyl (1-ethoxy-3-phenylprop-2-yn-1-yl)carbamate (110.0 mg, 0.4 mmol, 4.0 equiv) according to the general procedure in the presence of **C2** (7.2 mg, 0.01 mmol, 10 mol %), purified by silica gel column chromatography (petroleum ether/ EtOAc = 20:1 to 5:1) and was obtained as colorless oil (10.1 mg, 27%).

**R<sub>f</sub>** (Petroleum ether/ EtOAc = 5:1) = 0.3.

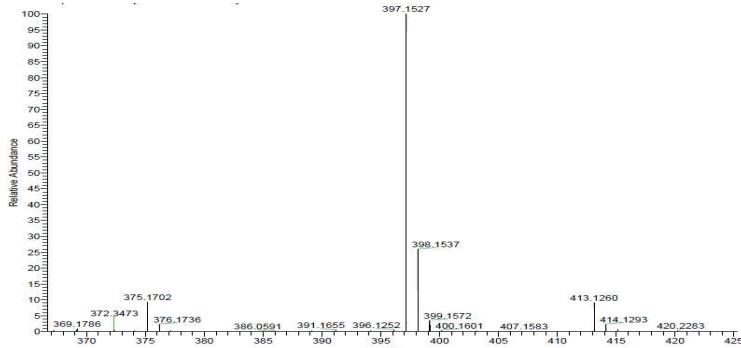
**HPLC** (ID, *n*-hexane/*i*-PrOH = 60/40, flow rate = 1.0 mL/min, I = 215 nm) t<sub>R</sub> = 9.90 min (major), 12.20 min (minor), 96% ee.

[**α**]<sub>D</sub><sup>25</sup>: -8.40 (c = 0.1, CH<sub>2</sub>Cl<sub>2</sub>).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.48-8.41 (m, 1H), 7.69-7.57 (m, 1H), 7.55-7.37 (m, 5H), 7.36-7.25 (m, 3H), 6.89 (s, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 6.45 (s, 1H), 1.42 (s, 9H).

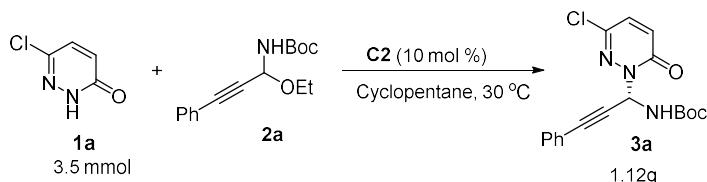
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.5, 154.1, 137.0, 132.6, 132.0, 129.7, 129.0, 128.3, 128.0, 127.0, 126.4, 126.0, 121.6, 106.4, 84.8, 83.3, 80.8, 58.5, 28.3.

**HRMS (ESI)** m/z: [M+Na]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub> 397.1523; Found 397.1527.



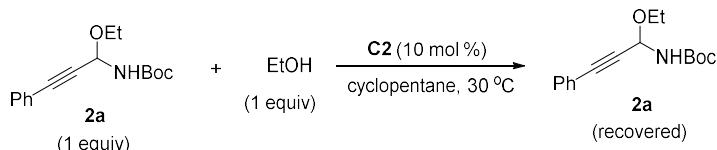
## Control Experiments for Scheme 4

### Gram-scale reaction



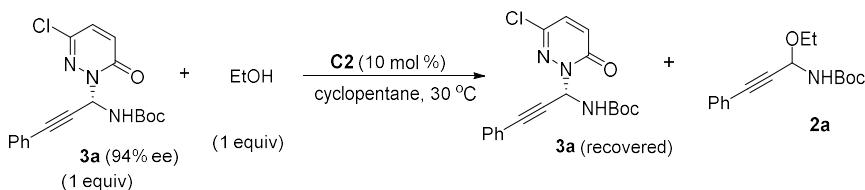
To a 100 mL of dry three-neck flask were added **C2** (251.6 mg, 0.35 mmol, 10 mol %), **1a** (455 mg, 3.5 mmol, 1.0 equiv) and **2a** (3.85 g, 14 mmol, 4.0 equiv), then Cyclopentane (50 mL) was added under argon atmosphere. The resulting mixture was stirred at 30 °C for 24 hours. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 10:1-3:1) to give **3a** (1.12 g, 89 %, 94% ee).

### Scheme 4a



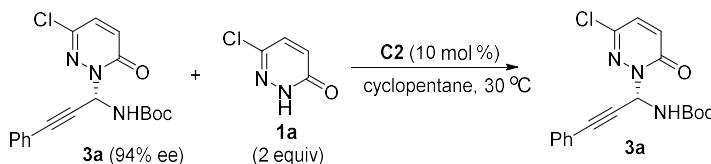
To a 10 mL of dry schlenk tube were added **2a** (13.8 mg, 0.05 mmol, 1.0 equiv) and EtOH (2.3 mg, 0.05 mmol, 1.0 equiv), then Cyclopentane (1 mL) was added under argon atmosphere. The resulting mixture was stirred at 30 °C. After a period of time, the reaction solution was monitored and the ee values were determined by HPLC.

entry	t (h)	ee of recovered <b>2a</b> (%)
1	1	0
2	3	0
3	6	0
4	12	0
5	24	0

**Scheme 4b**

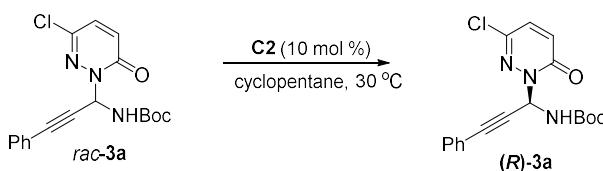
To a 10 mL of dry schlenk tube were added **3a** (18.0 mg, 0.05 mmol, 1.0 equiv), EtOH (2.3 mg, 0.05 mmol, 1.0 equiv) and **C2** (3.6 mg, 0.005 mmol, 10 mol %), then Cyclopentane (1 mL) was added under argon atmosphere. The resulting mixture was stirred at 30 °C. After a period of time, the reaction solution was monitored an the ee values were determined by HPLC.

Entry	t (h)	ee of recovered <b>3a</b> (%)	yield of <b>2a</b> (%)	ee of <b>2a</b> (%)
1	6	94	<5	0
2	12	94	6	0
3	18	92	8	0
4	24	92	17	0
5	48	92	22	0

**Scheme 4c**

To a 10 mL of dry schlenk tube were added **3a** (18.0 mg, 0.05 mmol, 1.0 equiv), **1a** (13.0 mg, 0.1 mmol, 2.0 equiv) and **C2** (3.6 mg, 0.005 mmol, 10 mol %), then Cyclopentane (1 mL) was added under argon atmosphere. The resulting mixture was stirred at 30 °C. After a period of time, the reaction solution was monitored an the ee values were determined by HPLC.

entry	t (h)	ee of <b>3a</b>
1	6	94
2	12	94
3	18	92
4	24	92
5	48	92
6	96	92

**Scheme 4d**

To a 10 mL of dry schlenk tube were added *rac*-**3a** (18.0 mg, 0.05 mmol, 1.0 equiv) and **C2** (3.6 mg, 0.005 mmol, 10 mol %), then Cyclopentane (1 mL) was added under argon atmosphere. The resulting mixture was stirred at 30 °C. After a period of time, the reaction solution was monitored an the ee values were determined by HPLC.

entry	t (h)	ee of ( <i>R</i> )-3a
1	6	-6
2	12	-6
3	18	-10
4	24	-10
5	48	-15

## X-ray crystallographic data of 5f

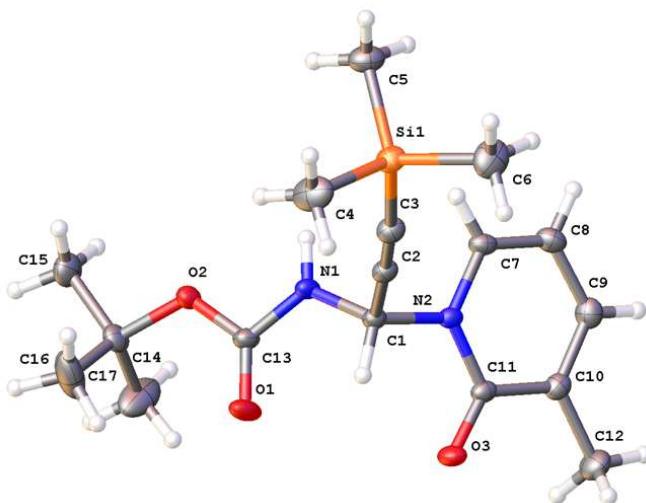
The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2268745 (**5f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at [www.ccdc.cam.ac.uk/data-request/cif](http://www.ccdc.cam.ac.uk/data-request/cif).

The measurements were taken in a Bruker D8 Venture diffractometer. The data were integrated by Bruker D8 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL.

## X-ray crystallographic data for 5f

**Method of crystallization:** A solution of **5f** in dichloromethane and petroleum ether was evaporated the solvent slowly at room temperature.

## Crystal data and structure for 5f



X-ray structure of **5f**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{17}H_{26}N_2O_3Si$	
Formula weight	334.49	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	$a = 9.3045(2)$ Å	$\alpha = 90^\circ$
	$b = 11.4846(2)$ Å	$\beta = 115.1230(10)^\circ$

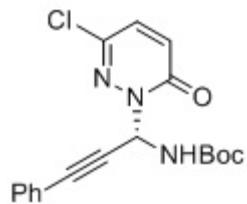
	$c = 10.1085(2) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$977.99(3) \text{ \AA}^3$	
Z	2	
Density (calculated)	$1.136 \text{ Mg/m}^3$	
Absorption coefficient	$0.764 \text{ mm}^{-1}$	
F(000)	360	
Crystal size	$0.07 \times 0.07 \times 0.05 \text{ mm}^3$	
$\theta$ range for data collection	$4.203 \text{ to } 54.886^\circ$	
Index ranges	$-11 \leq h \leq 11, -13 \leq k \leq 13, -12 \leq l \leq 12$	
Reflections collected	11863	
Independent reflections	3679 ( $R_{\text{int}} = 0.0473$ )	
Completeness to $\theta = 25.242^\circ$	99.7 %	
Max. and min. transmission	0.7508 and 0.5632	
Data / restraints / parameters	3679 / 1 / 215	
Goodness-of-fit on $F^2$	1.052	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0351, wR_2 = 0.0804$	
R indices (all data)	$R_1 = 0.0336, wR_2 = 0.0819$	
Largest diff. peak and hole	0.134 and $-0.202 \text{ e.\AA}^{-3}$	
Flack parameter	0.049(17)	

## References

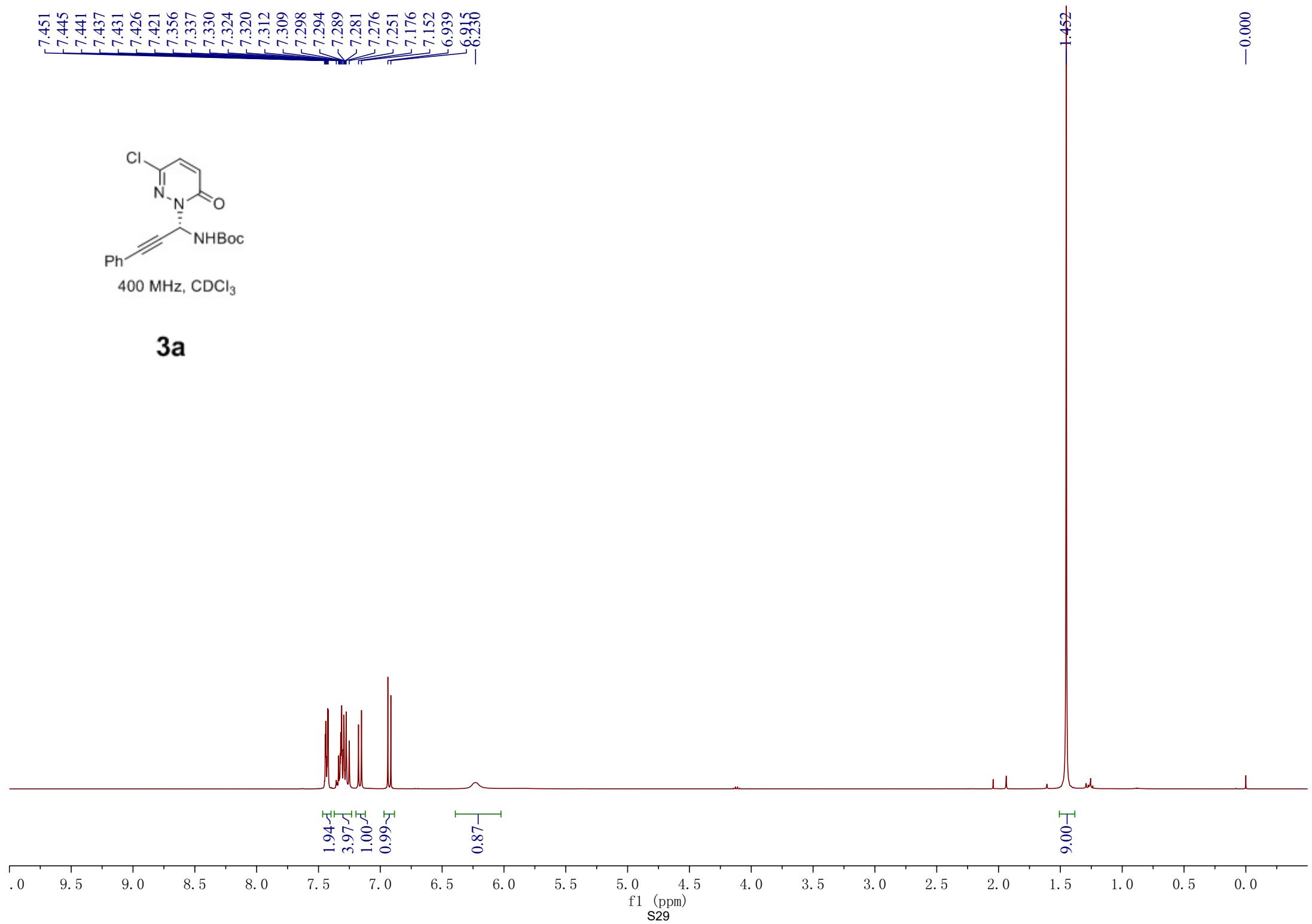
- [1] (a) Wang, Y.; Wang, S.; Shan, W.; Shao, Z. *Nat. Commun.* **2020**, *11*, 226. (b) Sun, Z.; Chen, L.; Qiu, K.; Liu, B.; Li, H.; Yu, F. *Chem. Commun.*, **2022**, *58*, 3035-3038. (c) Ma, X.-Y.; Zhang, C.-F.; Hu, X.; Zou, W.; Li, Y. *Tetrahedron*, **2020**, *76*, 131085.

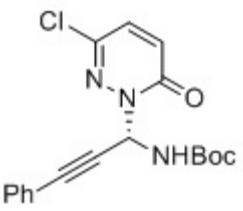
7.451  
7.445  
7.441  
7.437  
7.431  
7.426  
7.421  
7.356  
7.337  
7.330  
7.324  
7.320  
7.312  
7.309  
7.298  
7.294  
7.289  
7.281  
7.276  
7.251  
6.939  
6.915  
6.230

—0.000



**3a**





100 MHz, CDCl<sub>3</sub>

**3a**

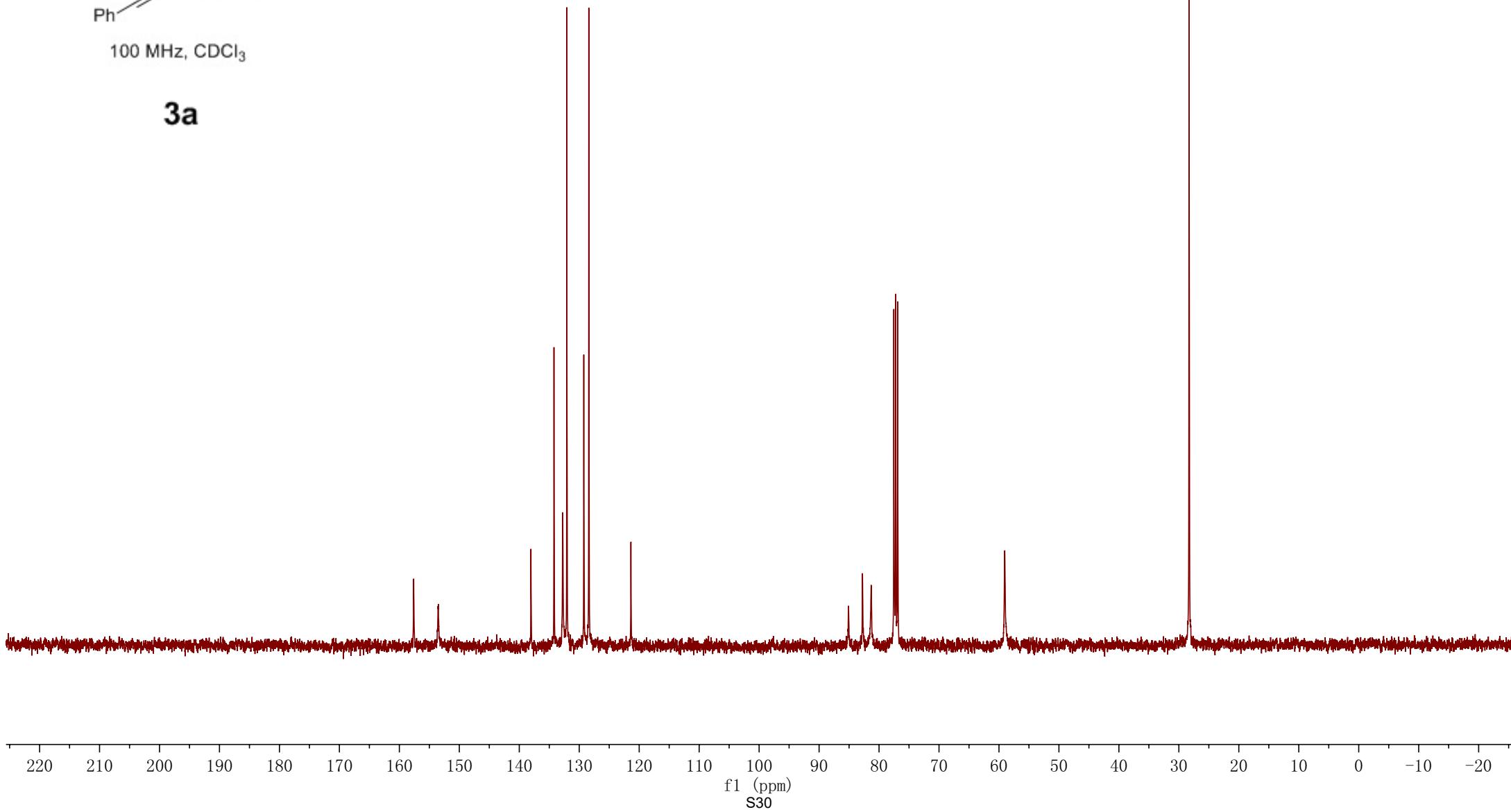
— 157.61  
— 153.50

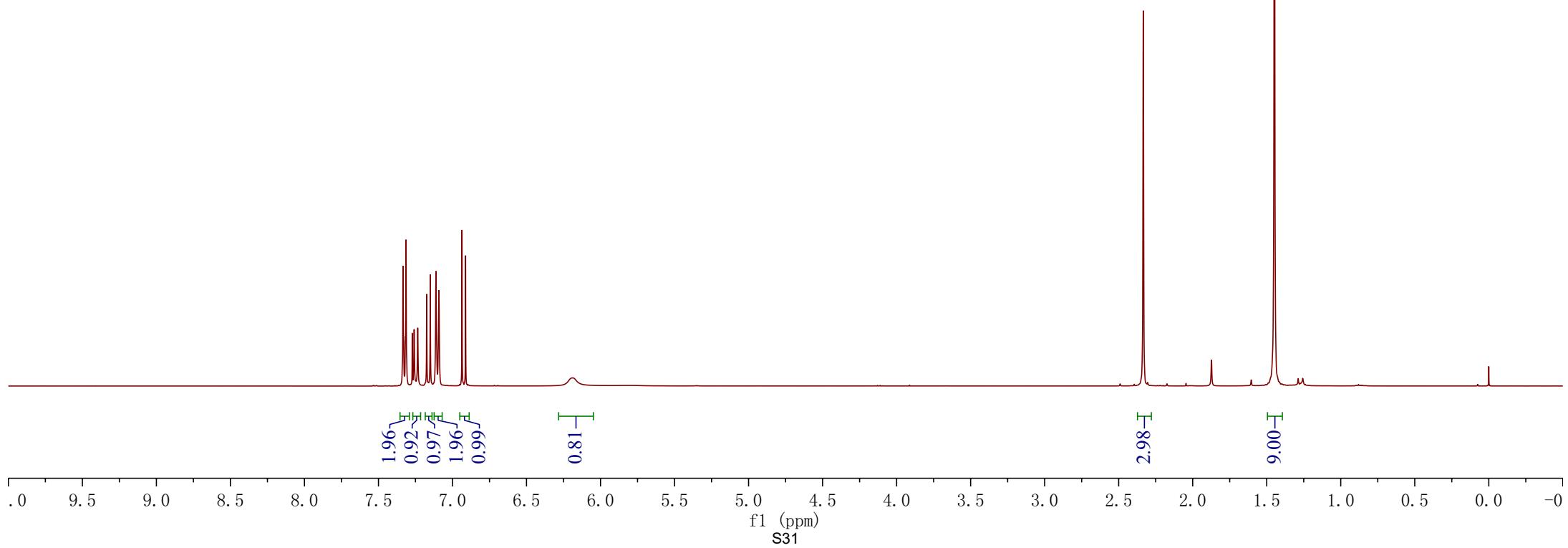
✓ 138.06  
✓ 134.21  
✓ 132.76  
✓ 132.07  
✓ 129.24  
✓ 128.40  
✓ 121.38

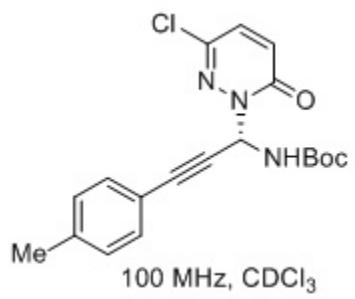
✓ 85.10  
✓ 82.76  
✓ 81.32

— 59.04

— 28.30

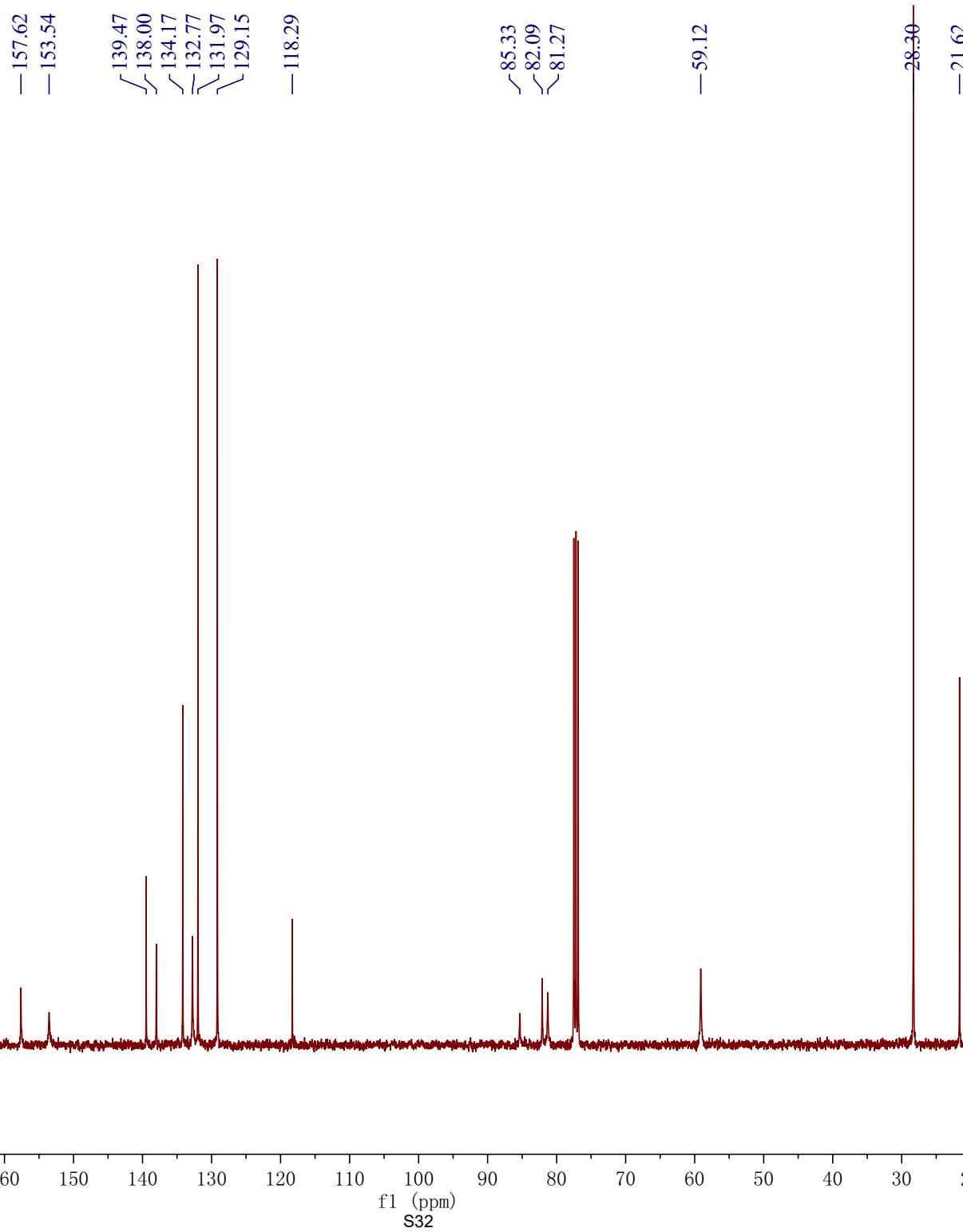






100 MHz, CDCl<sub>3</sub>

**3b**

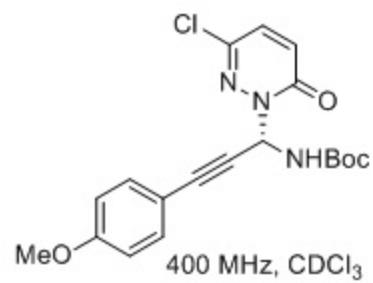


7.386  
7.381  
7.374  
7.369  
7.357  
7.352  
7.345  
7.260  
7.236  
7.173  
7.148  
6.936  
6.912  
6.835  
6.828  
6.823  
6.811  
6.806  
6.799  
6.254

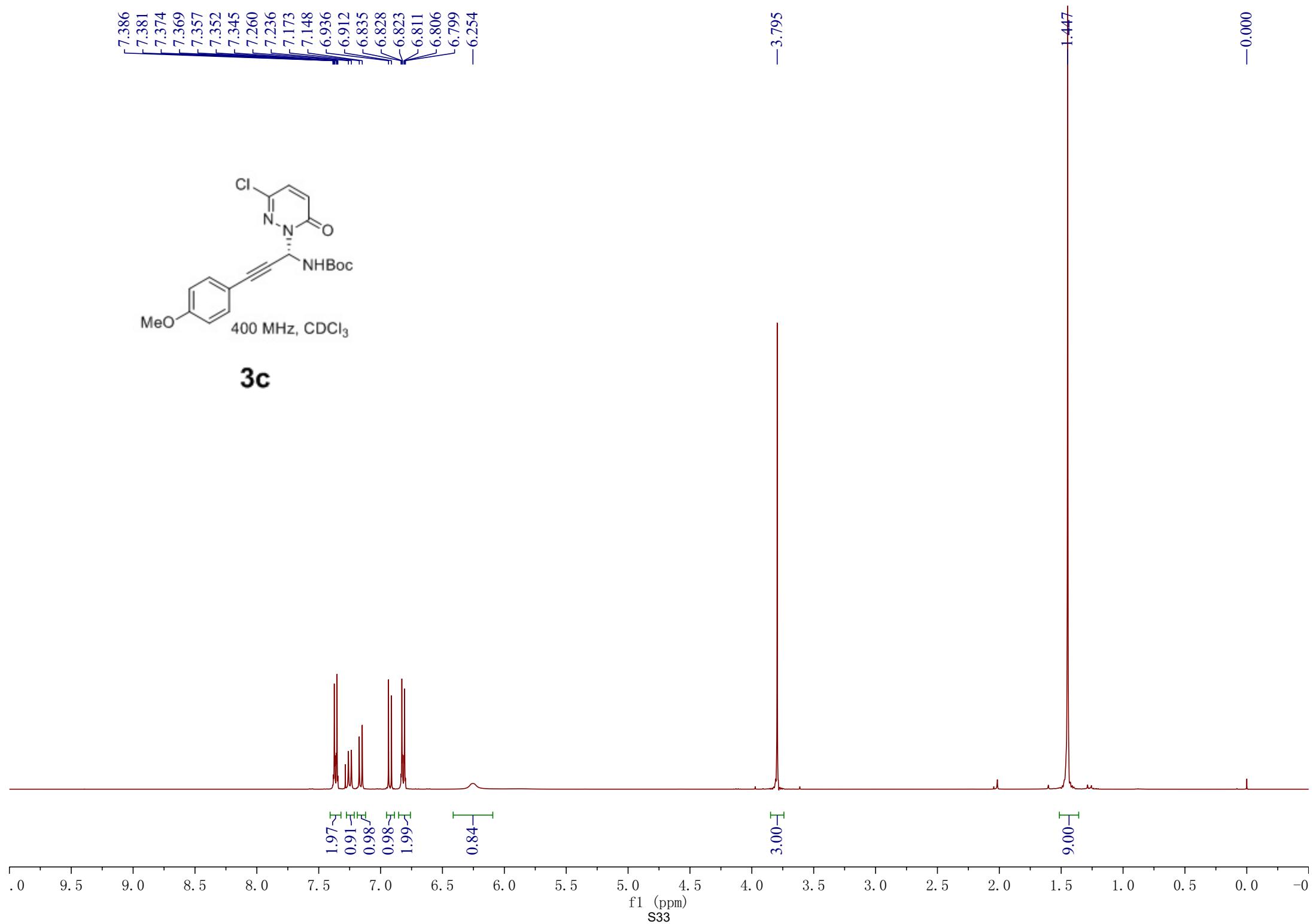
-3.795

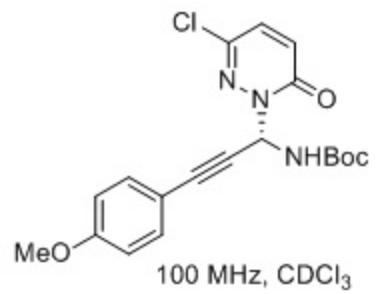
1.447

-0.000



**3c**





**3c**

— 160.26  
~ 157.62  
— 153.57

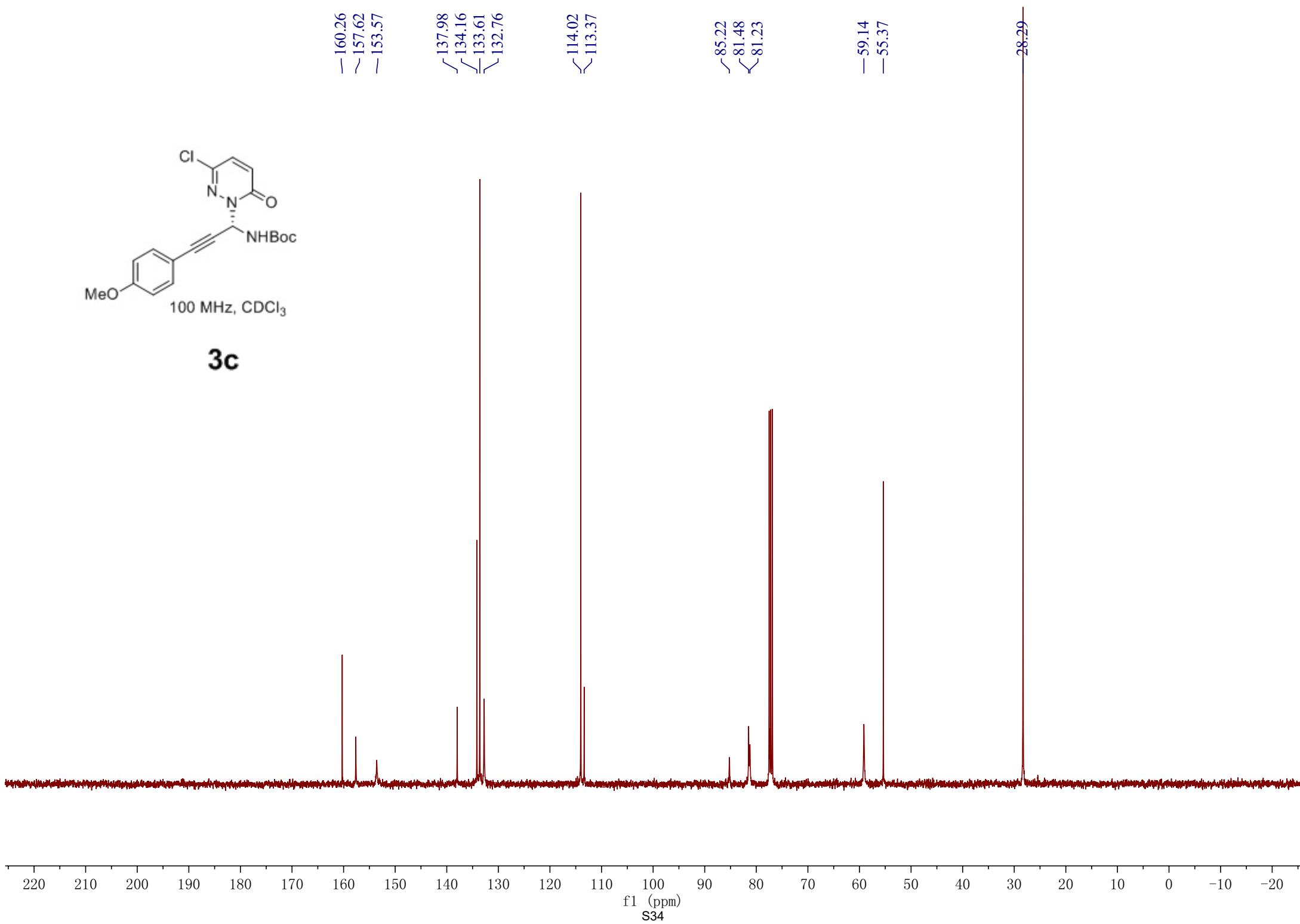
✓ 137.98  
✓ 134.16  
✓ 133.61  
✓ 132.76

✓ 114.02  
✓ 113.37

✓ 85.22  
✓ 81.48  
✓ 81.23

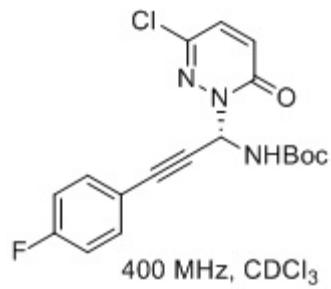
— 59.14  
— 55.37

✓ 28.29



7.451  
7.444  
7.438  
7.430  
7.425  
7.422  
7.414  
7.408  
7.401  
7.250  
7.226  
7.197  
7.173  
7.029  
7.022  
7.017  
7.005  
7.000  
6.996  
6.990  
6.984  
6.929  
6.198

—0.000

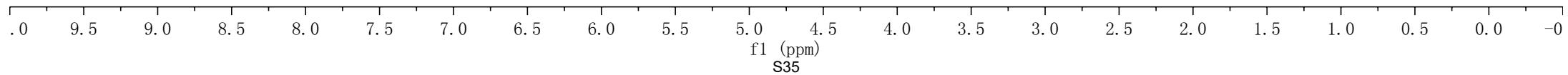


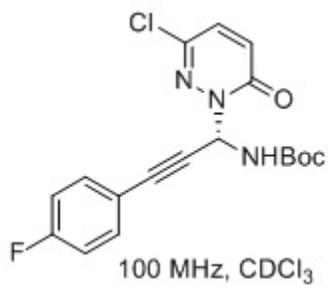
**3d**

2.07 [ 0.93 [ 1.01 [ 2.08 [ 1.00 [

0.91 [

9.00 [





**3d**

— 164.29  
— 161.79  
— 157.63  
— 153.53

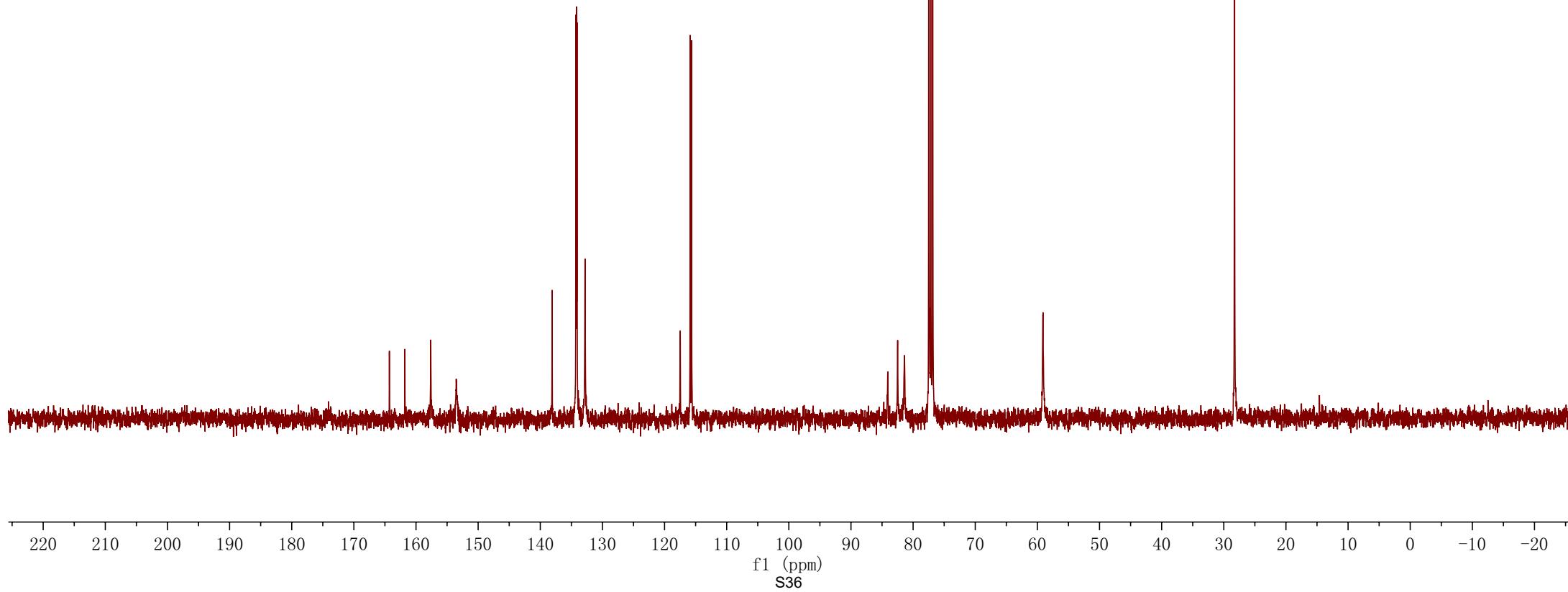
138.09  
134.27  
134.17  
134.08  
132.80

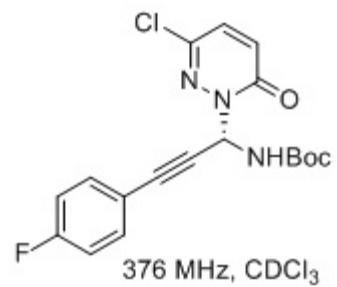
117.50  
117.47  
115.88  
115.66

84.07  
82.49  
81.40

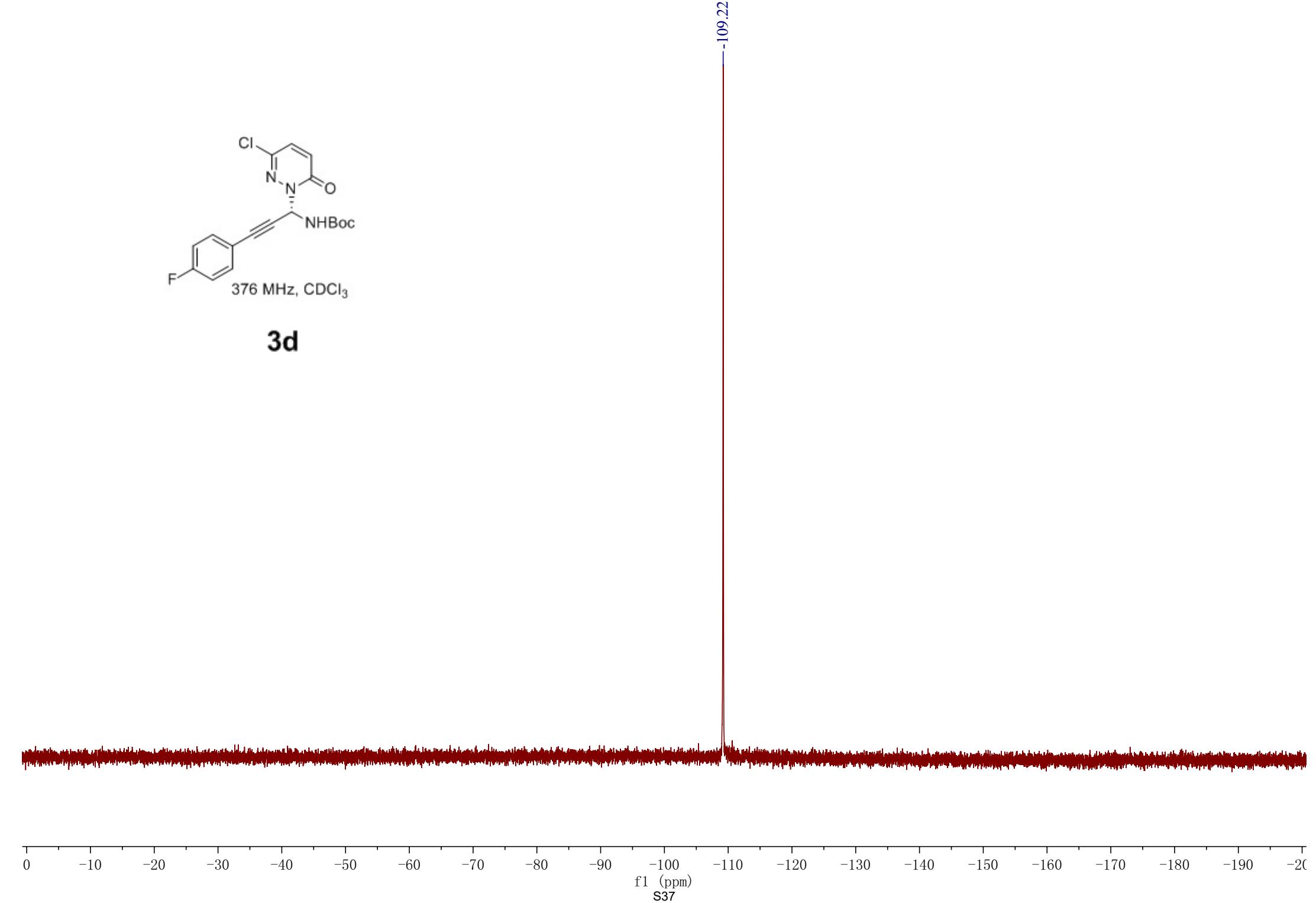
— 59.09

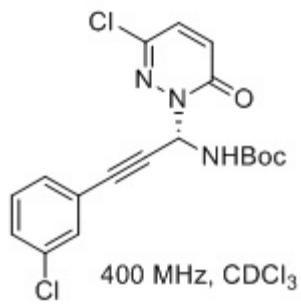
28.28





**3d**



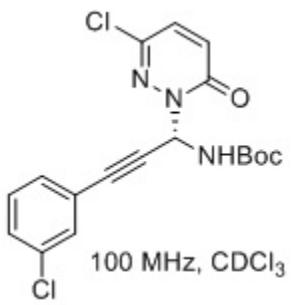


**3e**

0.95  
1.95  
1.96  
1.01  
1.04

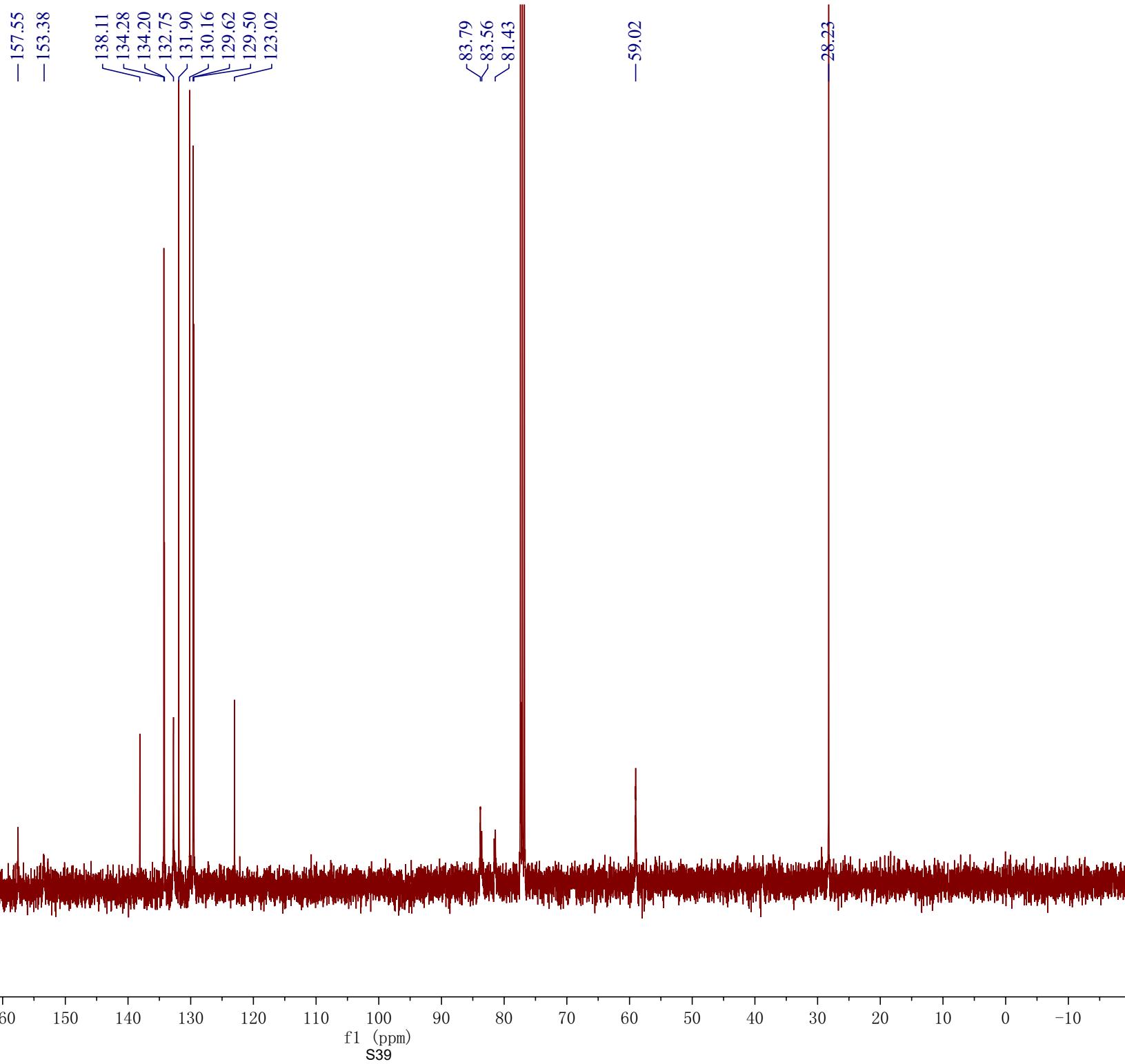
0.97

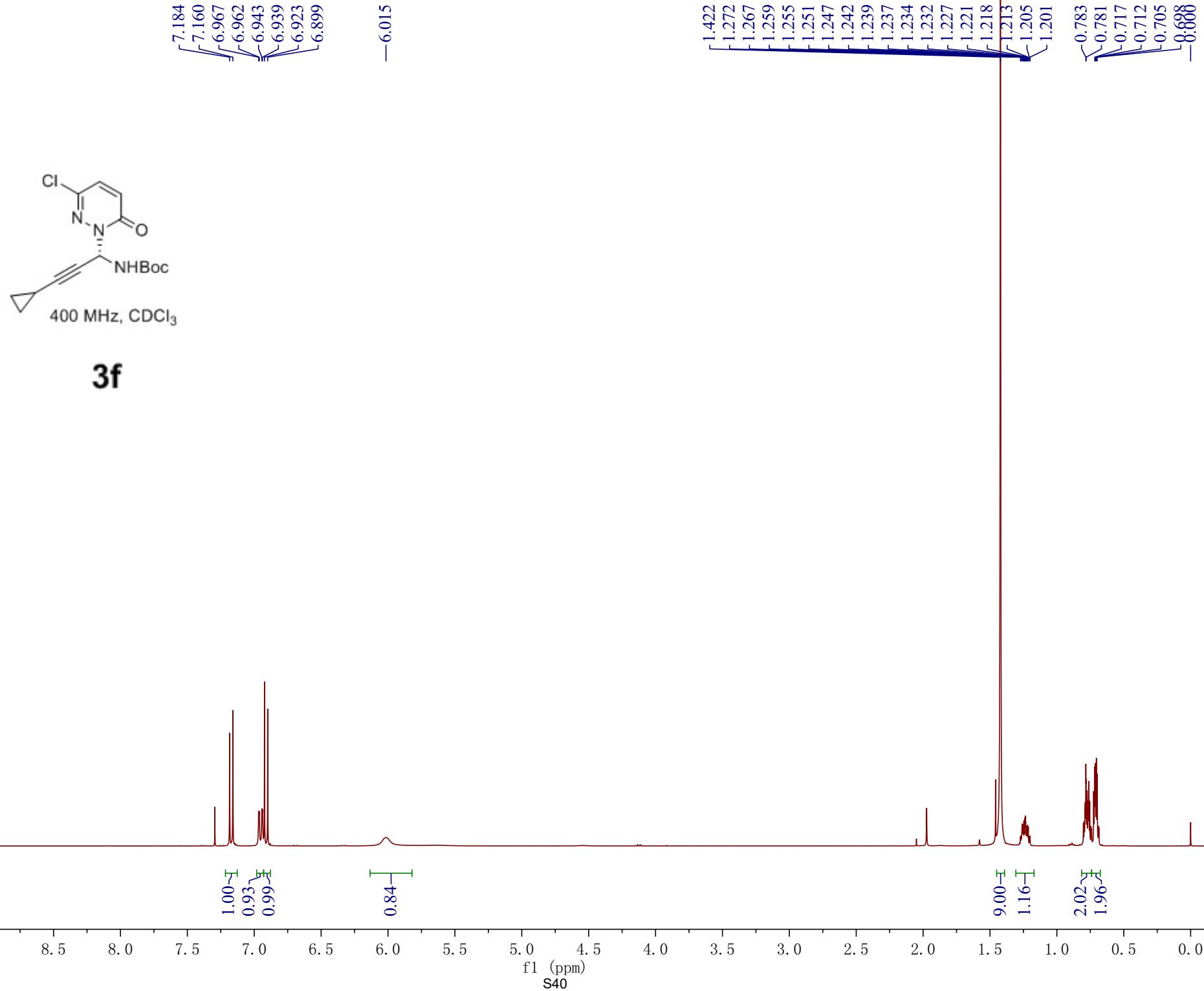
9.00

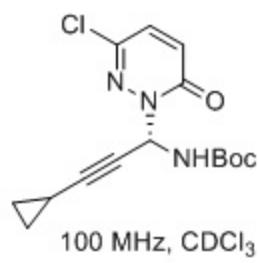


100 MHz, CDCl<sub>3</sub>

**3e**

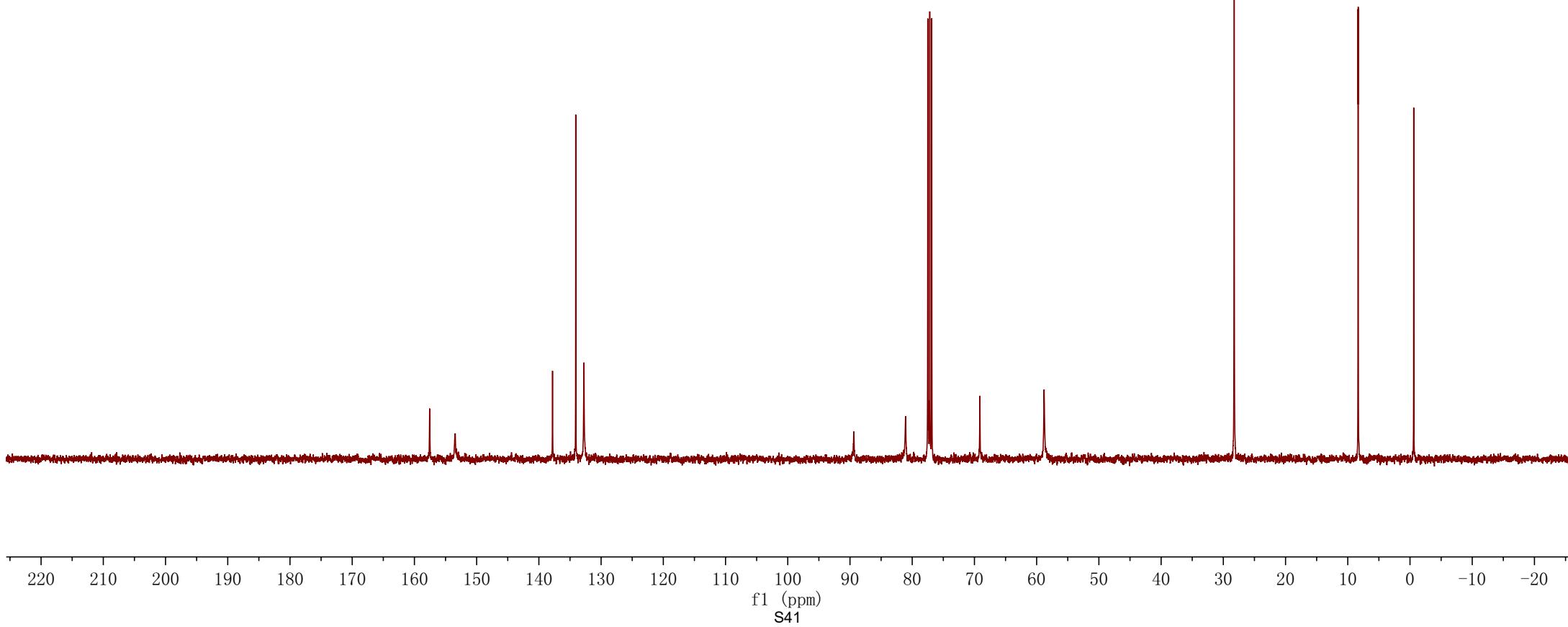


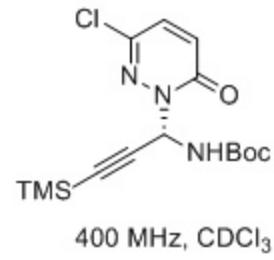




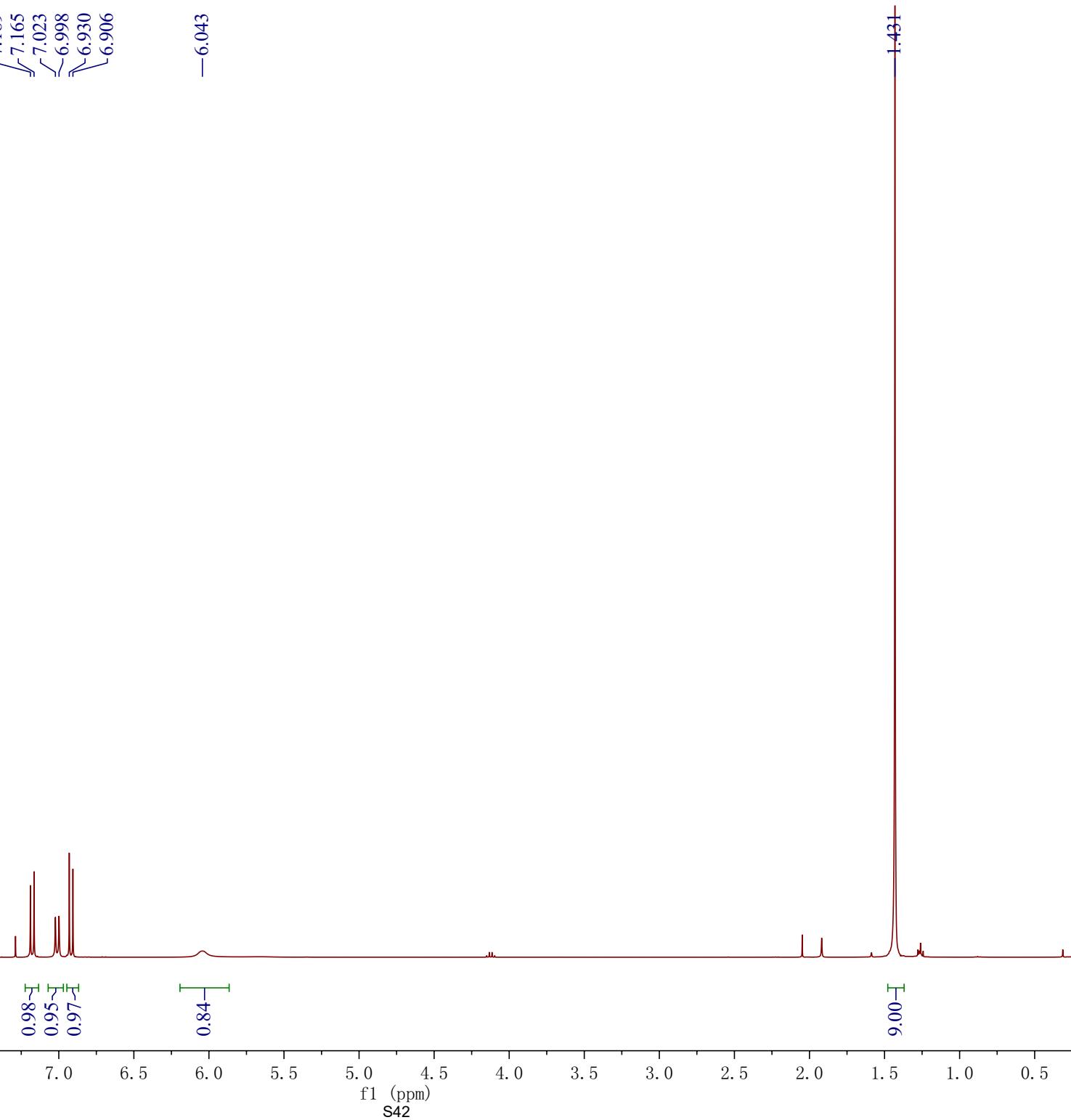
**3f**

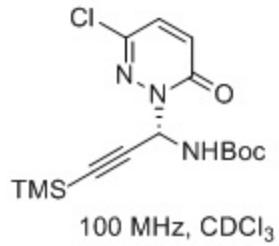
— 157.55  
— 153.44  
— 137.80  
— 134.07  
— 132.76  
— 89.39  
— 81.07  
— 69.13  
— 58.80  
— 28.25  
— 8.35  
— 8.32  
— 0.60





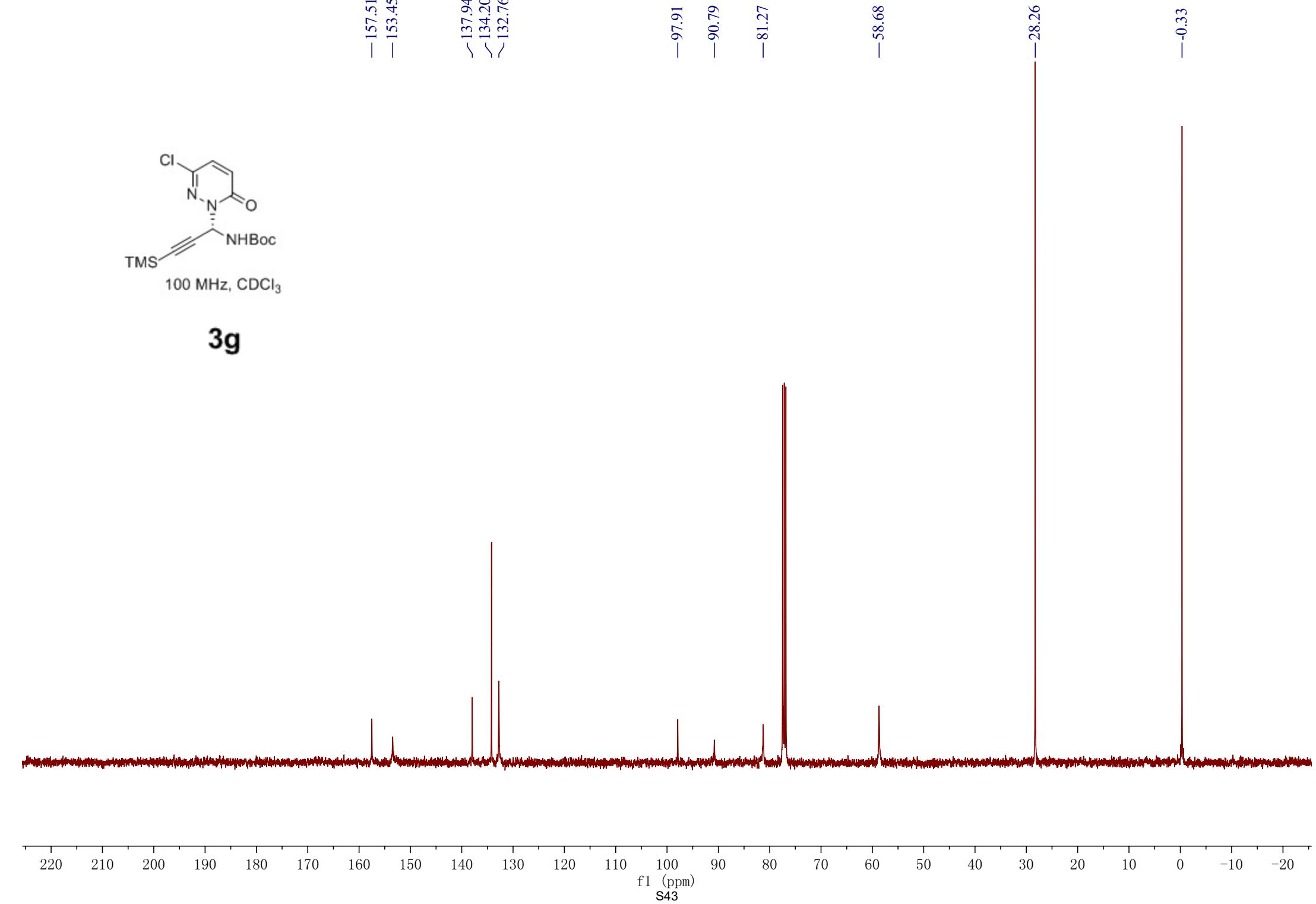
**3g**





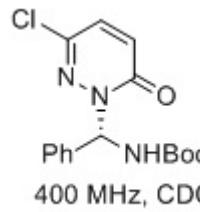
100 MHz, CDCl<sub>3</sub>

3g

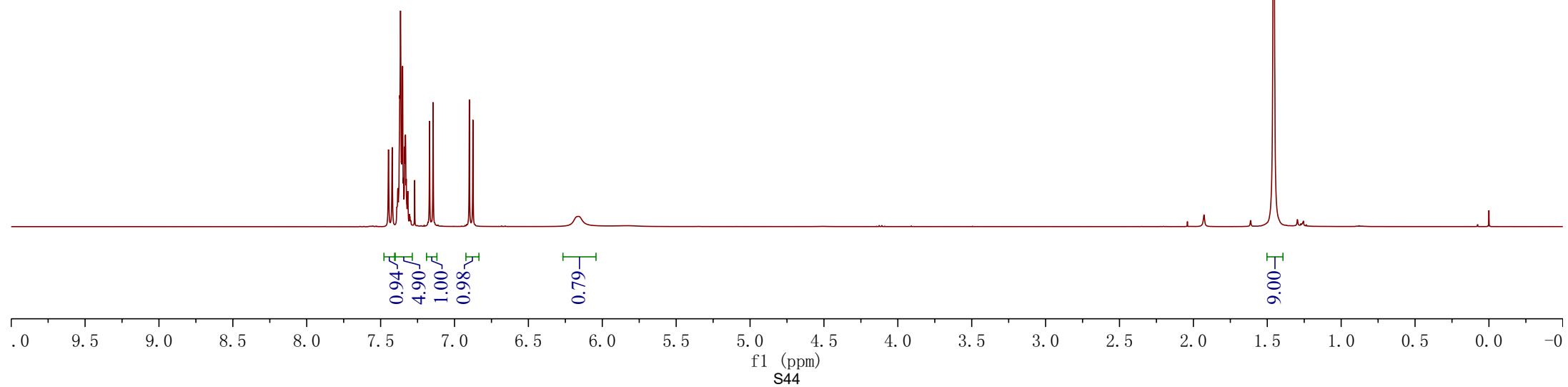


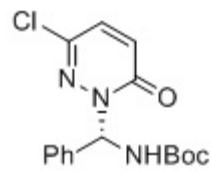
7.447  
7.422  
7.390  
7.383  
7.370  
7.365  
7.359  
7.351  
7.345  
7.338  
7.332  
7.327  
7.316  
7.305  
7.302  
6.900  
6.875  
6.163

—0.000



**3h**





100 MHz,  $\text{CDCl}_3$

**3h**

— 158.26  
— 154.25

137.87  
136.59  
133.80  
132.62  
128.83  
126.34

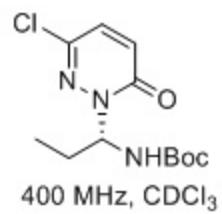
— 80.85

— 68.31

— 28.28

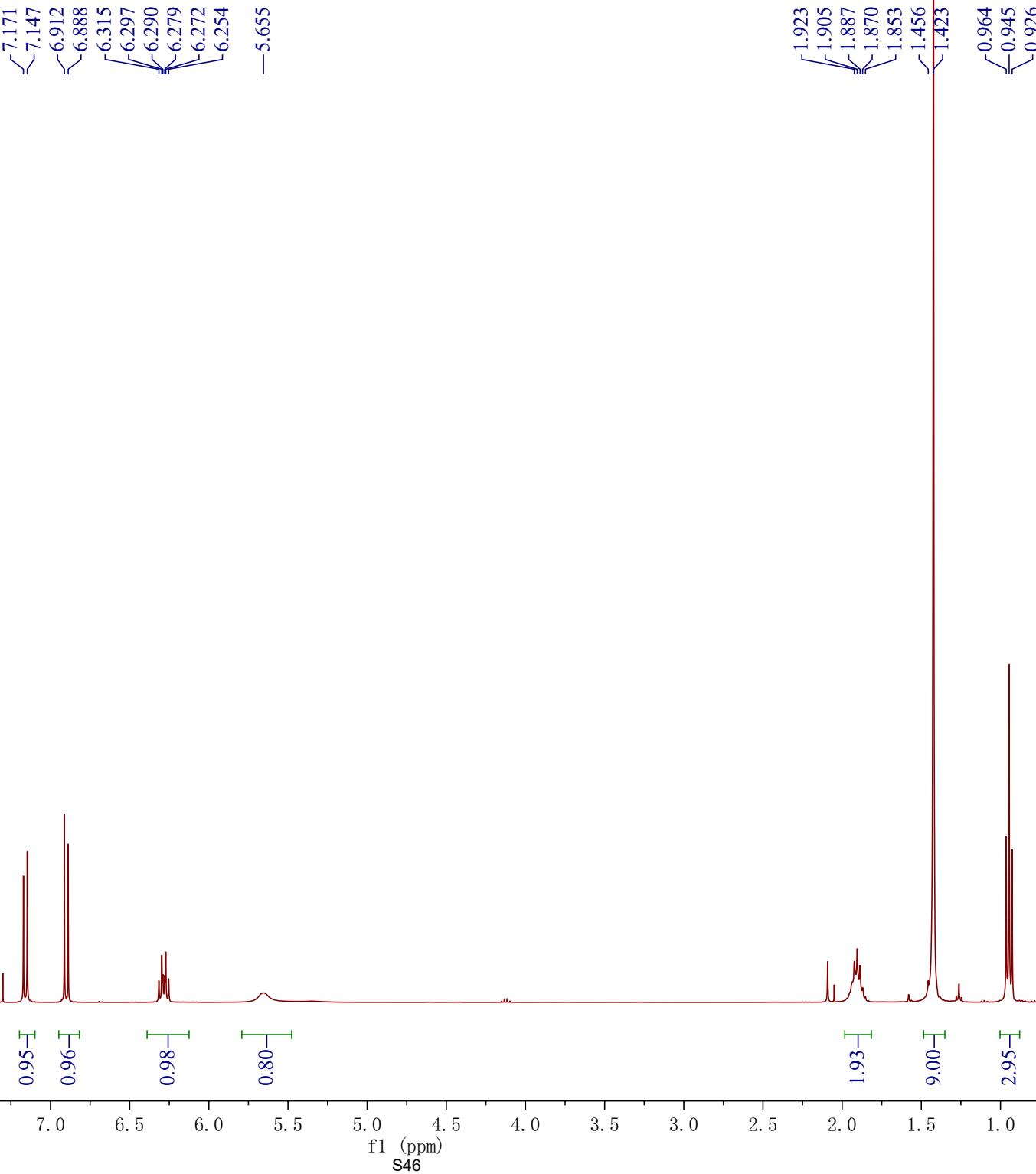
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

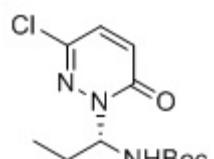
f1 (ppm)  
S45



400 MHz,  $\text{CDCl}_3$

**3i**

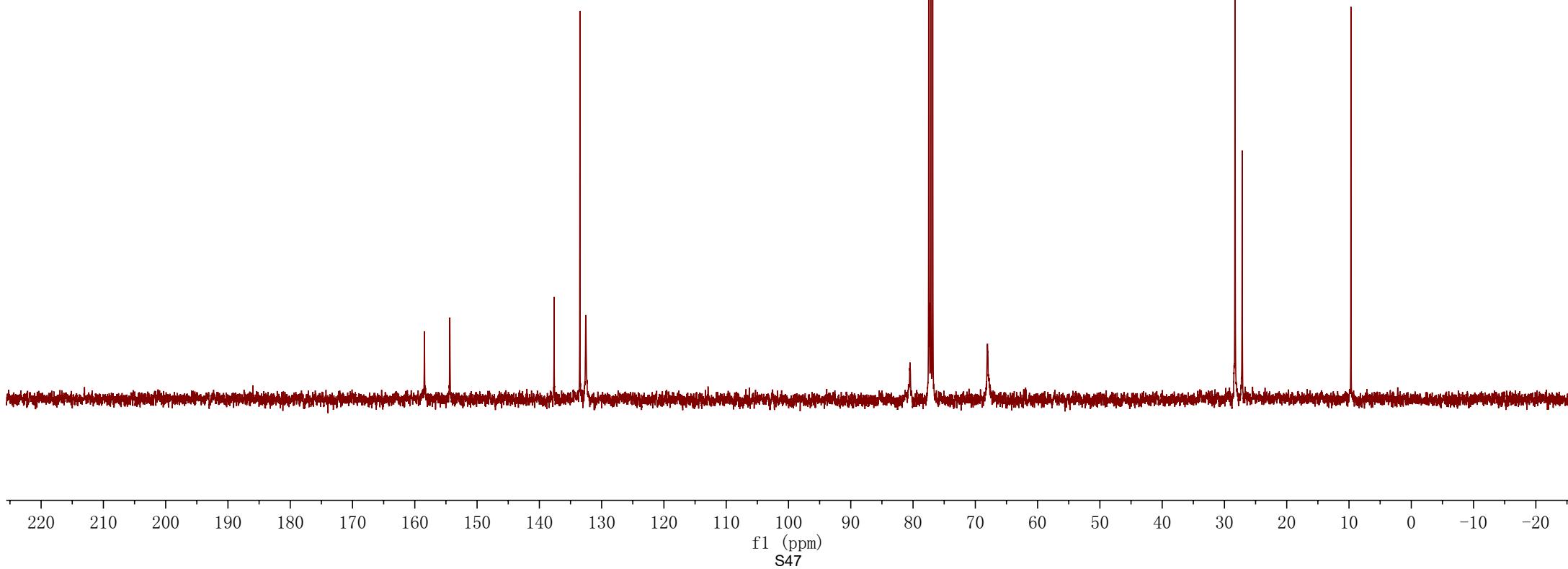




100 MHz, CDCl<sub>3</sub>

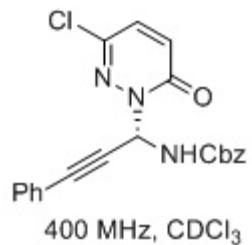
**3i**

— 158.46  
— 154.38  
— 137.63  
— 133.50  
— 132.56  
— 80.50  
— 68.04  
— 28.30  
— 27.15  
— 9.69



7.427  
7.423  
7.419  
7.407  
7.402  
7.346  
7.344  
7.342  
7.335  
7.326  
7.319  
7.313  
7.308  
7.304  
7.300  
7.295  
7.292  
7.281  
7.277  
7.260  
7.122  
6.988  
6.581  
6.563

—0.000

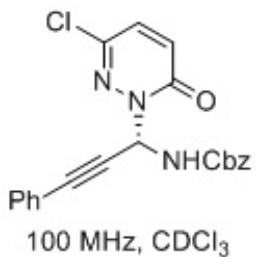


400 MHz, CDCl<sub>3</sub>

**3j**

2.02  
8.77  
1.02  
0.95~  
0.85

5.195  
5.165  
5.099  
5.069



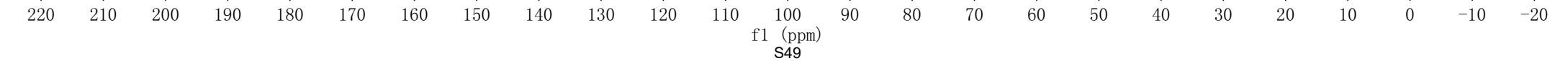
100 MHz,  $\text{CDCl}_3$

**3j**

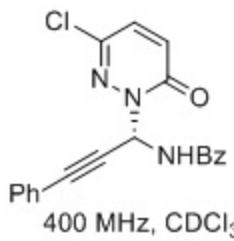


Chemical shift assignments for the  $^{13}\text{C}$  NMR spectrum of compound **3j**:

- 157.61
- 154.53
- 135.77
- 134.29
- 132.80
- 132.11
- 129.35
- 128.68
- 128.45
- 128.37
- 85.51
- 82.34
- 67.71
- 59.42

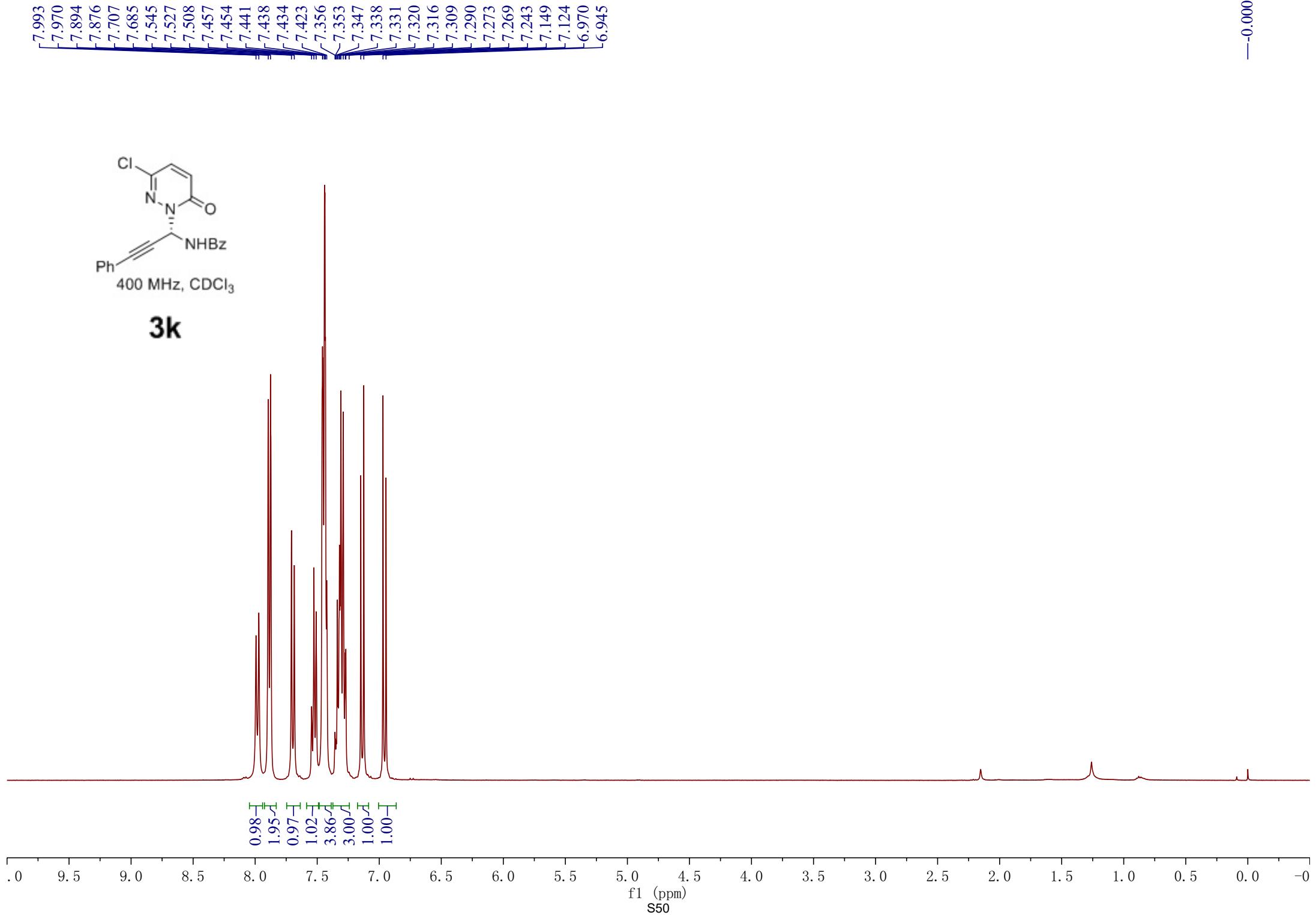


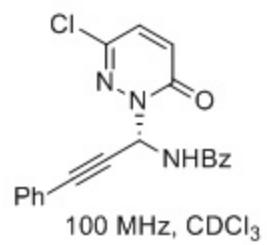
-0.000



**3k**

0.98  
1.95  
1.97  
1.02  
3.86  
3.00  
1.00  
1.00





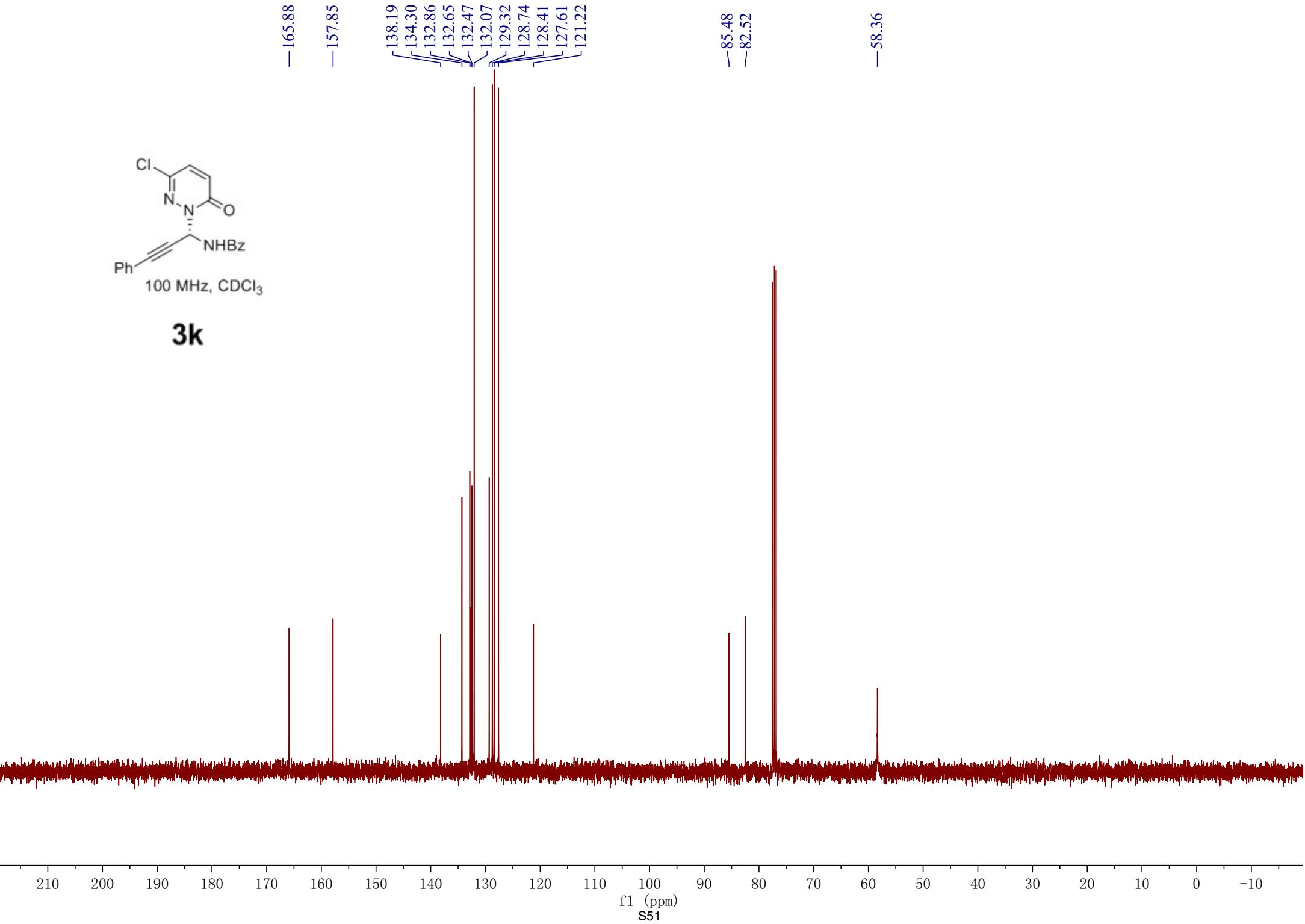
**3k**

— 165.88  
— 157.85

138.19  
134.30  
132.86  
132.65  
132.47  
132.07  
129.32  
128.74  
128.41  
127.61  
121.22

— 85.48  
— 82.52

— 58.36

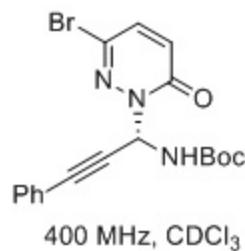


7.446  
7.442  
7.439  
7.432  
7.427  
7.422  
7.337  
7.330  
7.325  
7.321  
7.313  
7.298  
7.295  
7.282  
7.277  
7.273  
7.263  
7.253  
7.239  
7.229  
7.222  
6.842  
6.818

—6.253

1.454

—0.000



400 MHz,  $\text{CDCl}_3$

**3l**

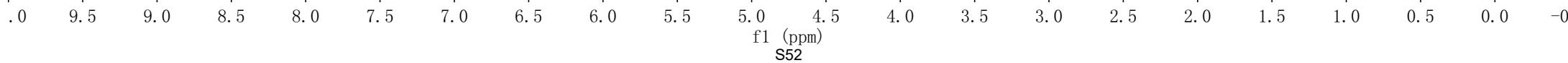
1.91

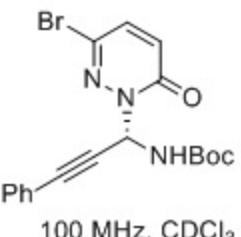
4.92

0.98

0.85

9.00





100 MHz,  $\text{CDCl}_3$

**3l**

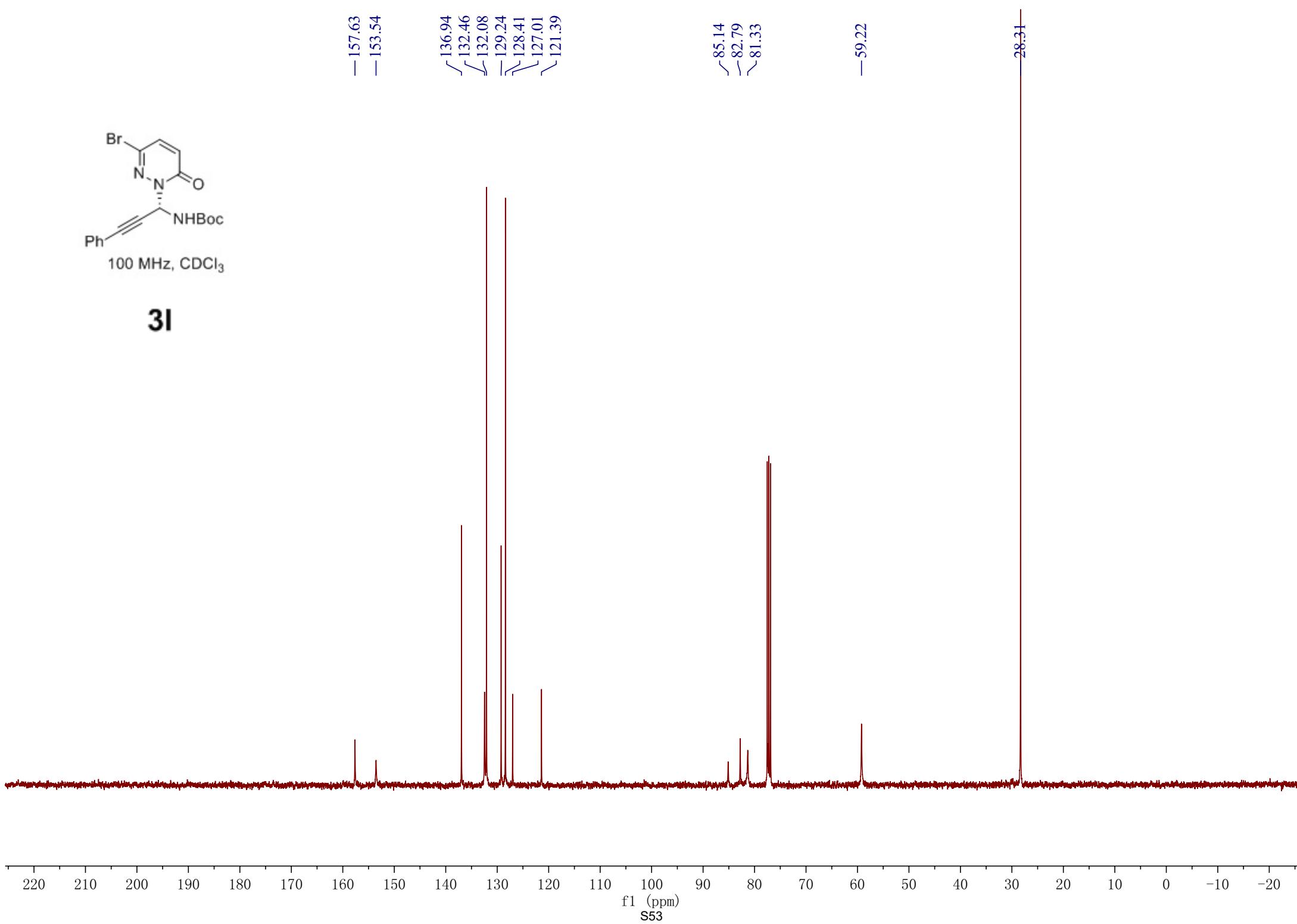
— 157.63  
— 153.54

136.94  
132.46  
132.08  
129.24  
128.41  
127.01  
121.39

— 85.14  
— 82.79  
— 81.33

— 59.22

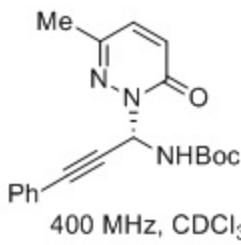
— 28.31



7.448  
7.445  
7.434  
7.429  
7.424  
7.322  
7.320  
7.313  
7.309  
7.305  
7.302  
7.290  
7.287  
7.283  
7.270  
7.203  
7.087  
7.063  
6.880  
6.856  
6.330

-2.355  
-1.447

-0.000

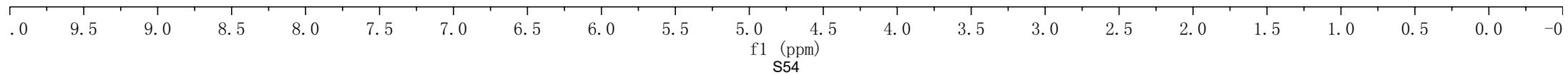


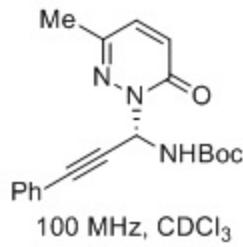
400 MHz, CDCl<sub>3</sub>

**3m**

2.02  
3.20  
0.86  
1.03  
1.00  
0.87

3.05  
9.00





**3m**

— 158.51  
— 153.67  
— 144.73  
— 133.78  
— 132.00  
— 130.60  
— 128.90  
— 128.24  
— 121.69  
— 84.24  
— 83.56  
— 80.86  
— 59.91  
— 28.25  
— 20.91

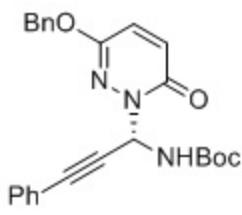
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)  
S55

7.461  
7.456  
7.448  
7.444  
7.441  
7.429  
7.424  
7.424  
7.380  
7.365  
7.347  
7.344  
7.339  
7.335  
7.327  
7.322  
7.318  
7.313  
7.302  
7.299  
7.280  
7.295  
6.970  
6.945  
6.921  
6.894

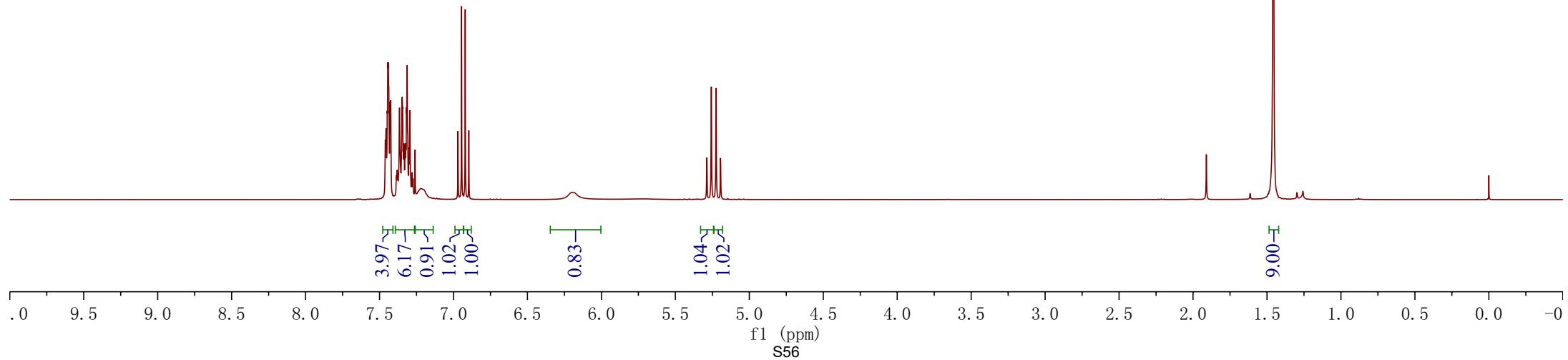
5.287  
5.257  
5.225  
5.194

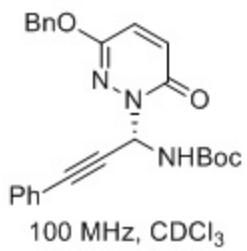
1.457  
—0.000



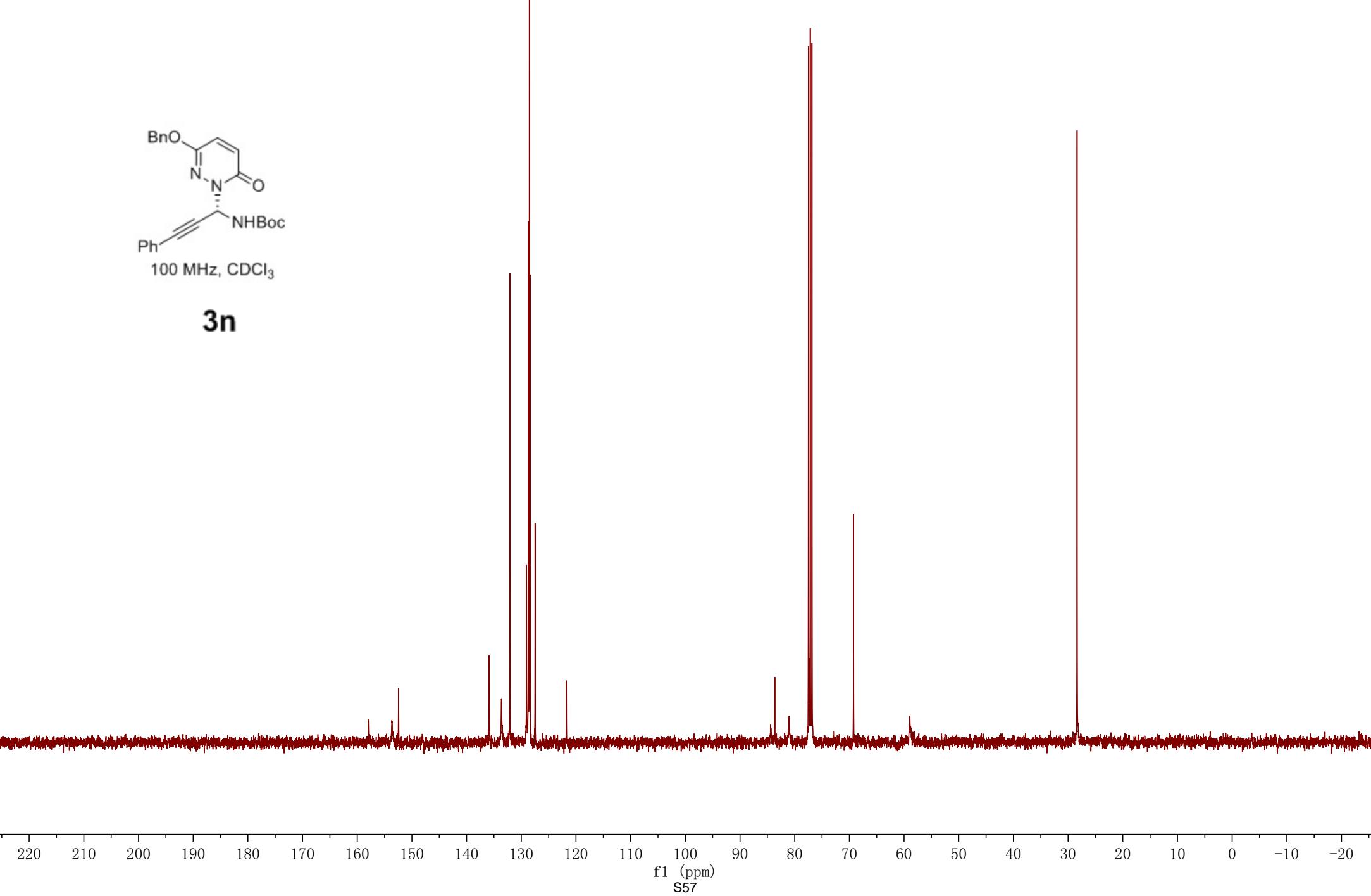
400 MHz, CDCl<sub>3</sub>

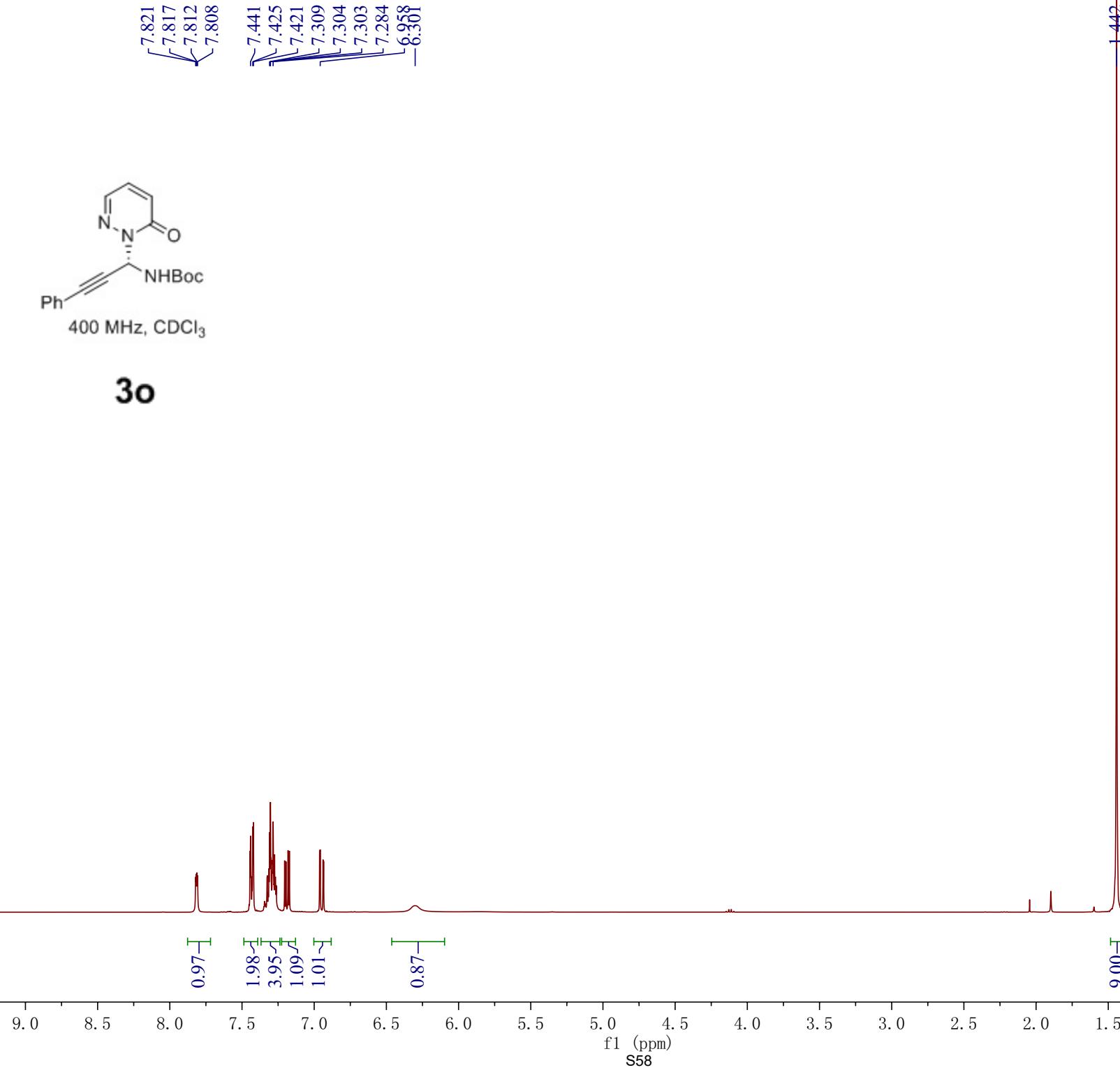
**3n**

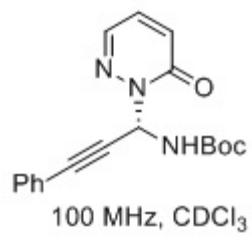




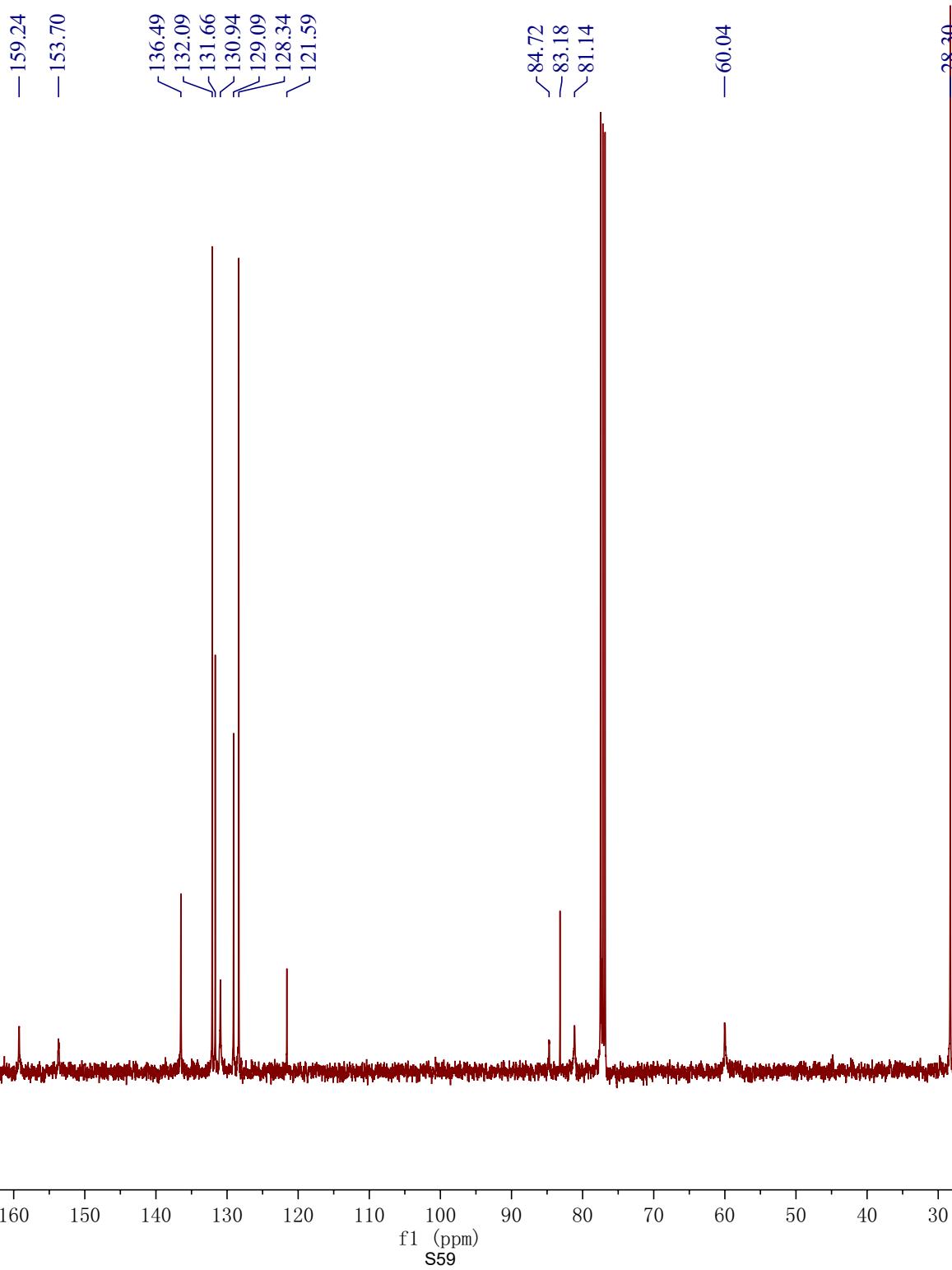
**3n**





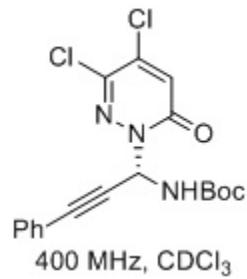


**3o**



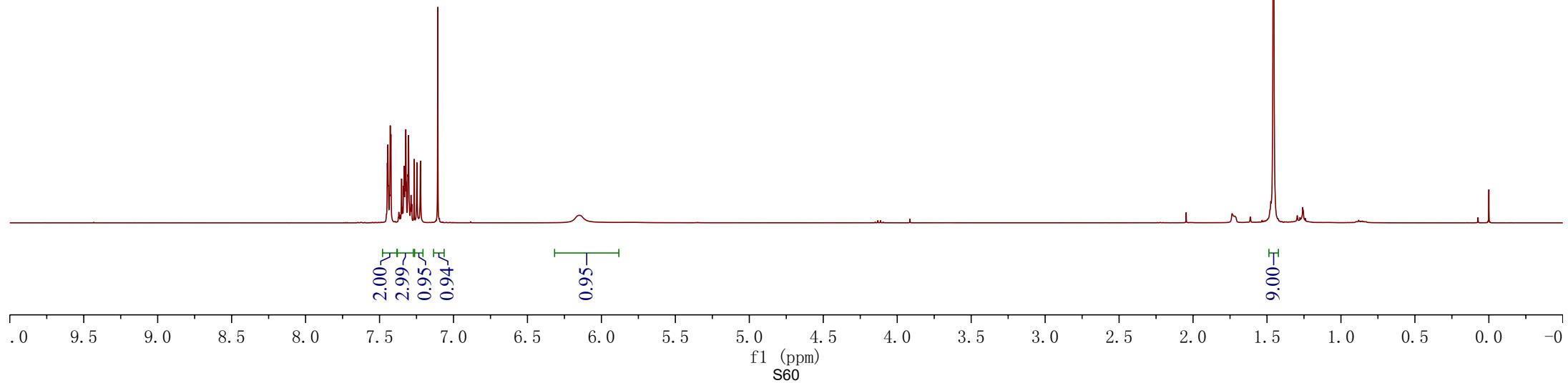
7.453  
7.447  
7.444  
7.440  
7.433  
7.428  
7.423  
7.369  
7.366  
7.360  
7.351  
7.344  
7.337  
7.333  
7.329  
7.322  
7.308  
7.304  
7.291  
7.287  
7.282  
7.247  
7.223  
7.106  
6.149

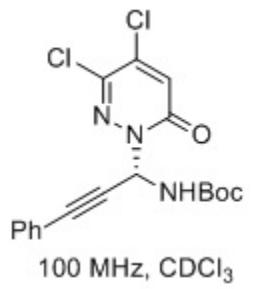
—0.000



400 MHz, CDCl<sub>3</sub>

**3p**



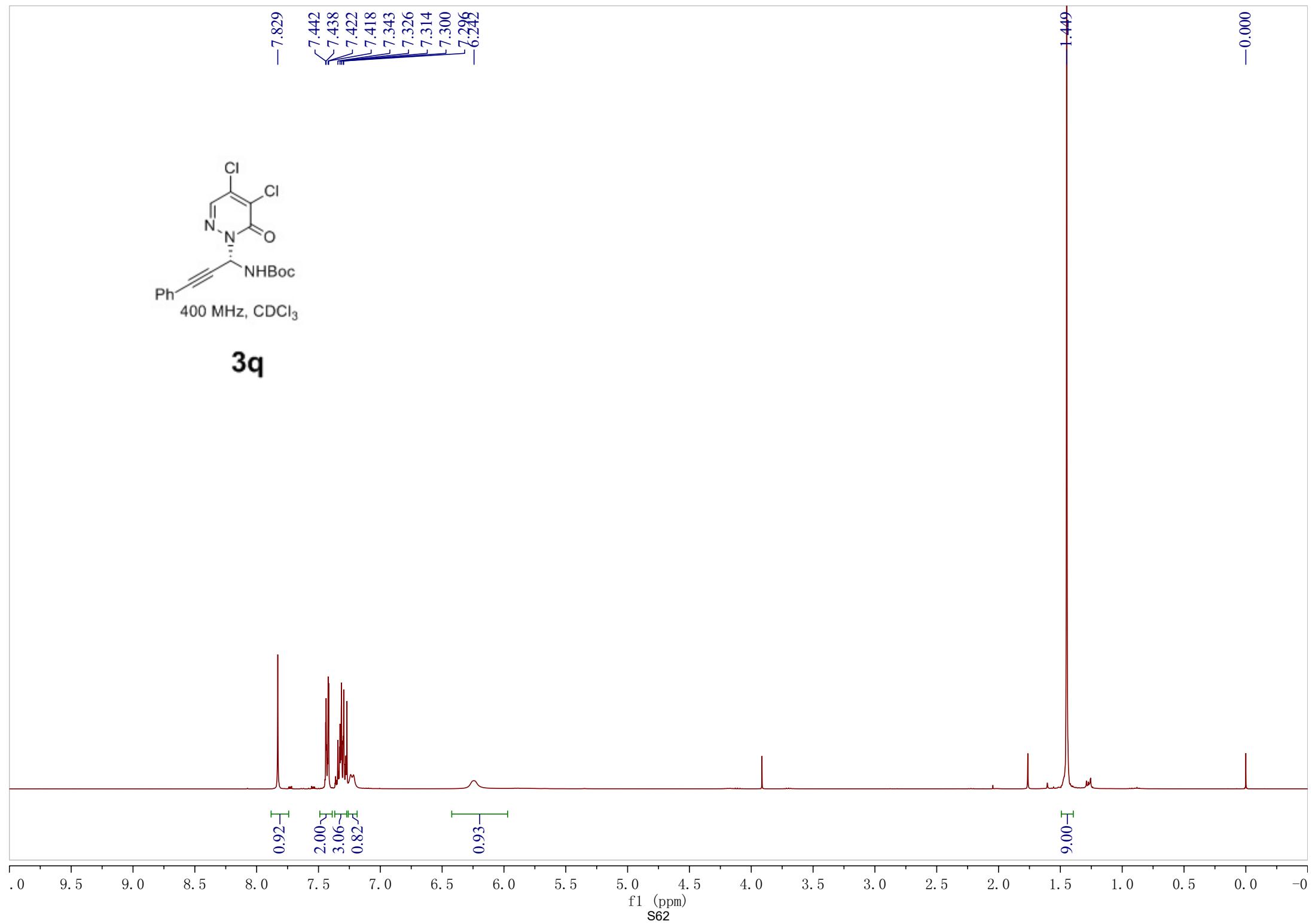


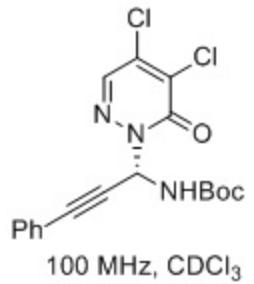
**3p**

— 156.99  
— 153.44  
— 140.13  
— 137.02  
— 132.01  
— 130.11  
— 129.30  
— 128.38  
— 121.14  
— 85.44  
— 82.25  
— 81.46  
— 59.07  
— 28.24



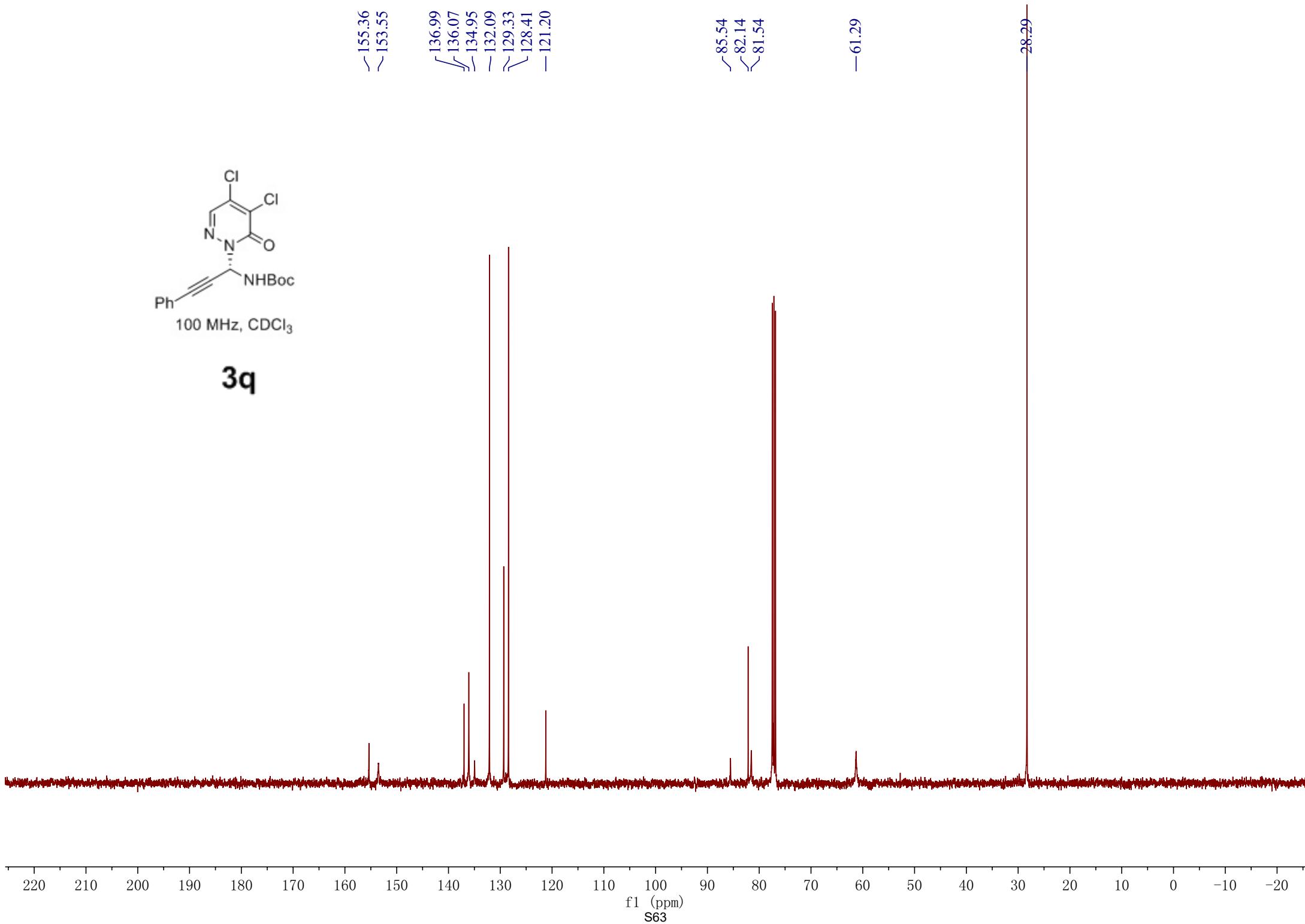
**3q**





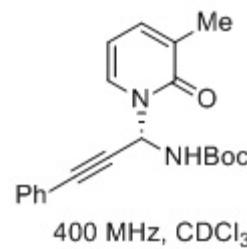
**3q**

155.36  
153.55  
136.99  
136.07  
134.95  
132.09  
129.33  
128.41  
121.20  
85.54  
82.14  
81.54  
-61.29  
28.29



7.520  
7.504  
7.445  
7.427  
7.343  
7.325  
7.303  
7.285  
7.271  
7.210  
7.194  
6.757  
6.612  
6.144  
6.127  
6.110

-2.166  
1.428  
-0.000

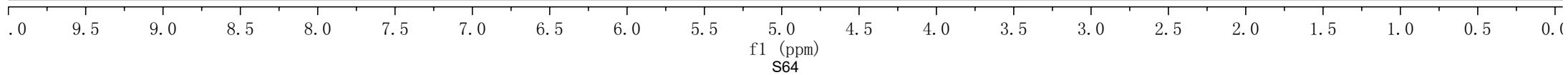


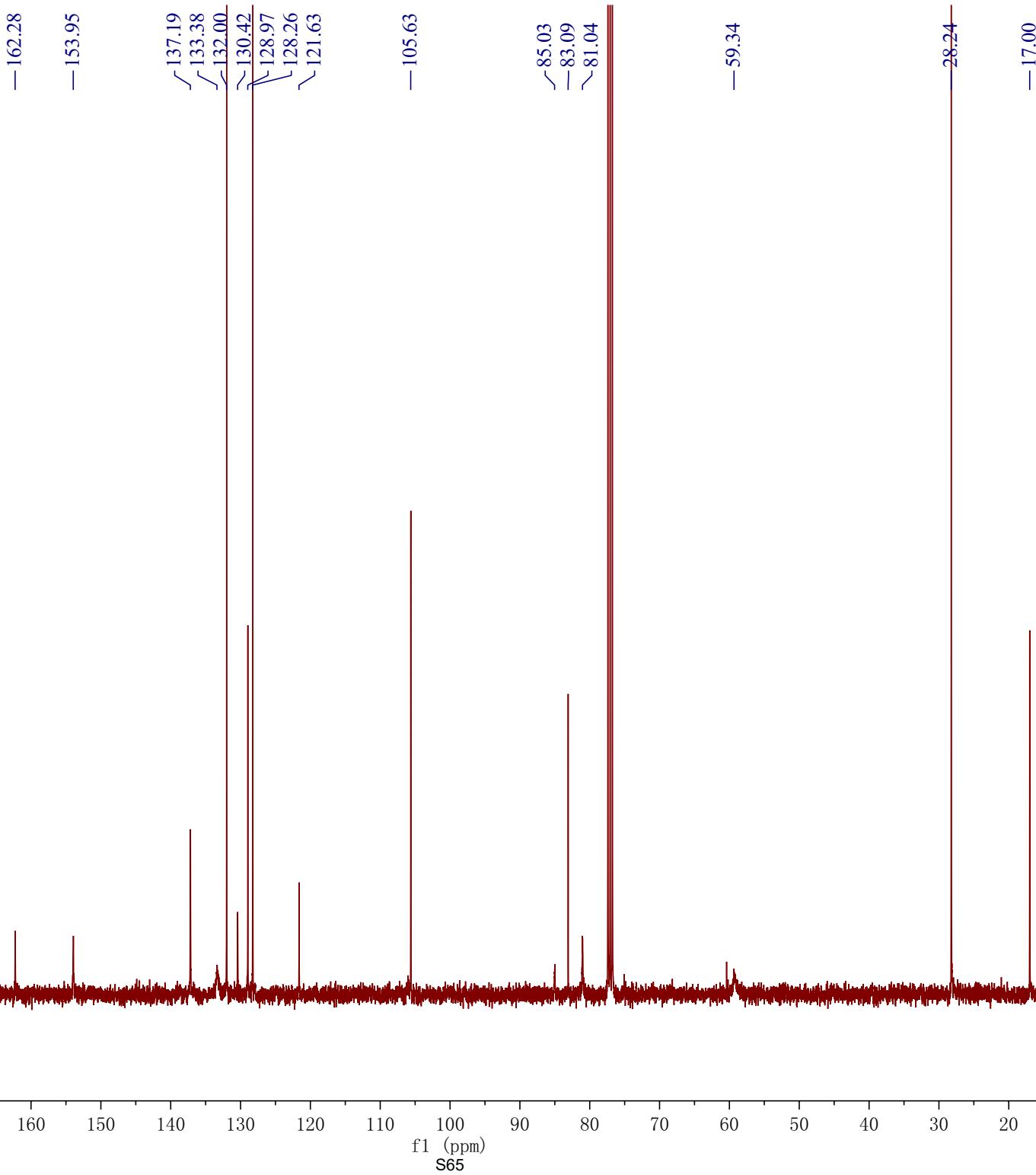
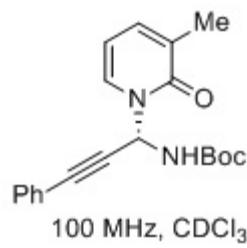
400 MHz, CDCl<sub>3</sub>

**5a**

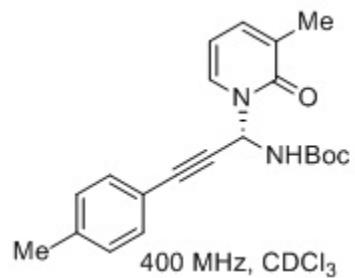
0.96  
1.97  
3.12  
1.01  
0.96  
0.86  
1.02

3.00  
9.14

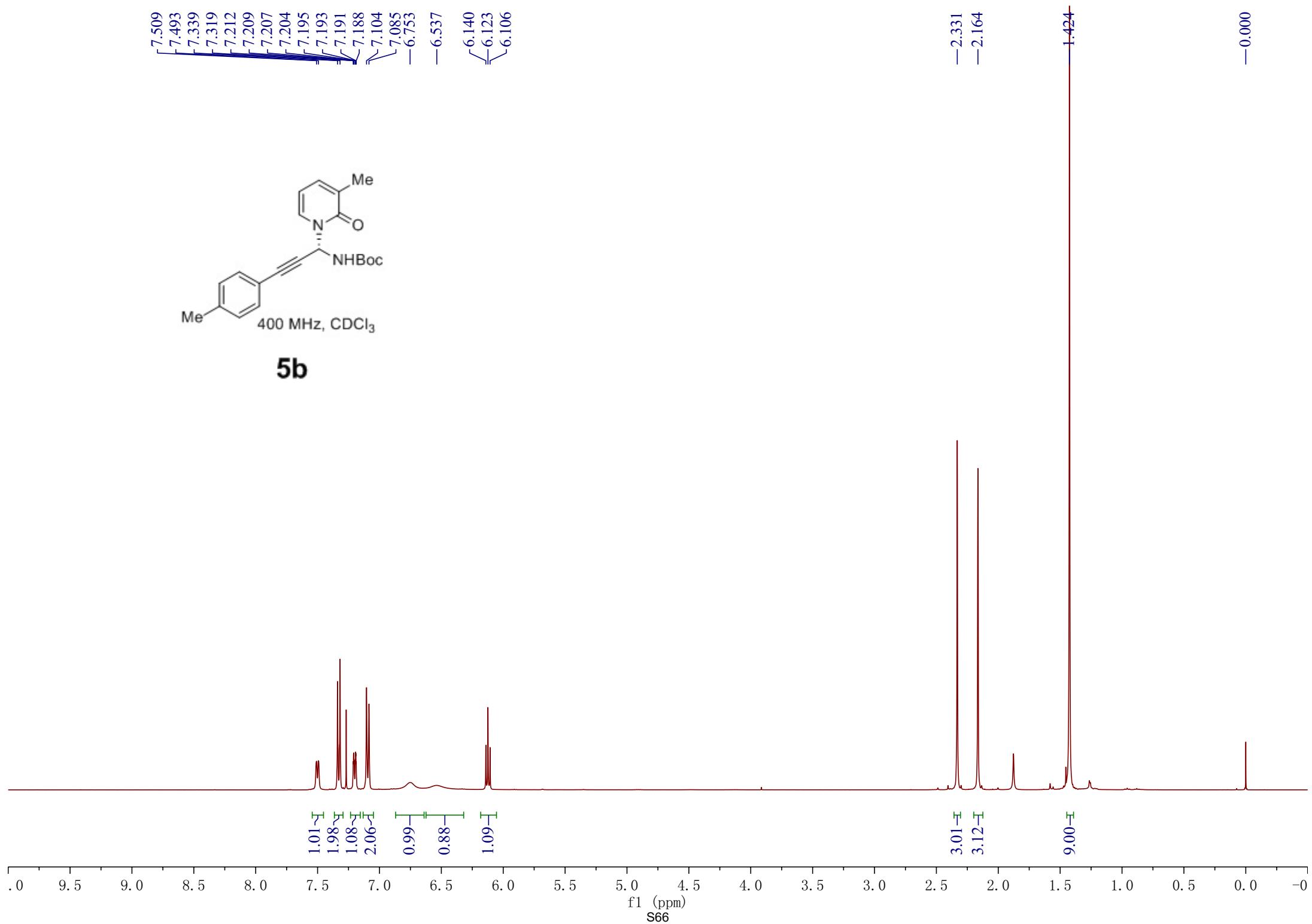


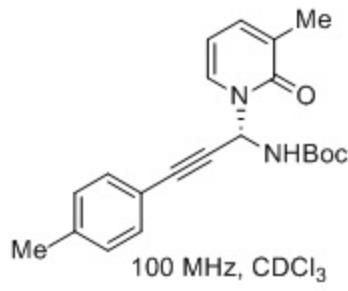


7.509  
7.493  
7.339  
7.319  
7.212  
7.209  
7.207  
7.204  
7.195  
7.193  
7.191  
7.188  
7.104  
7.085  
6.753  
6.537  
  
6.140  
6.123  
6.106  
  
-2.331  
-2.164  
-1.424  
  
—0.000



**5b**





100 MHz, CDCl<sub>3</sub>

**5b**

—162.24  
—153.95

139.15  
137.17  
133.34  
131.87  
130.36  
129.01

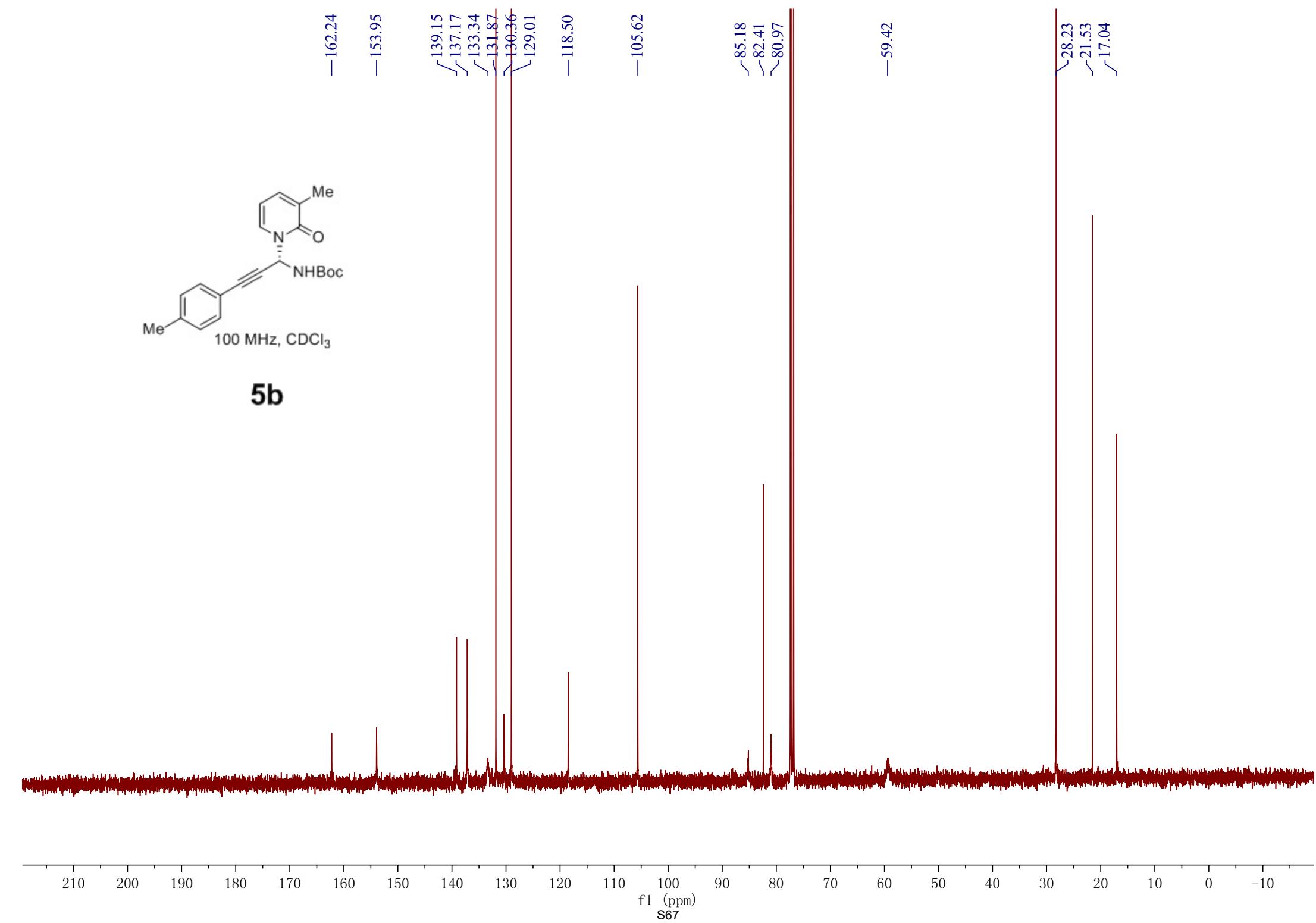
—118.50

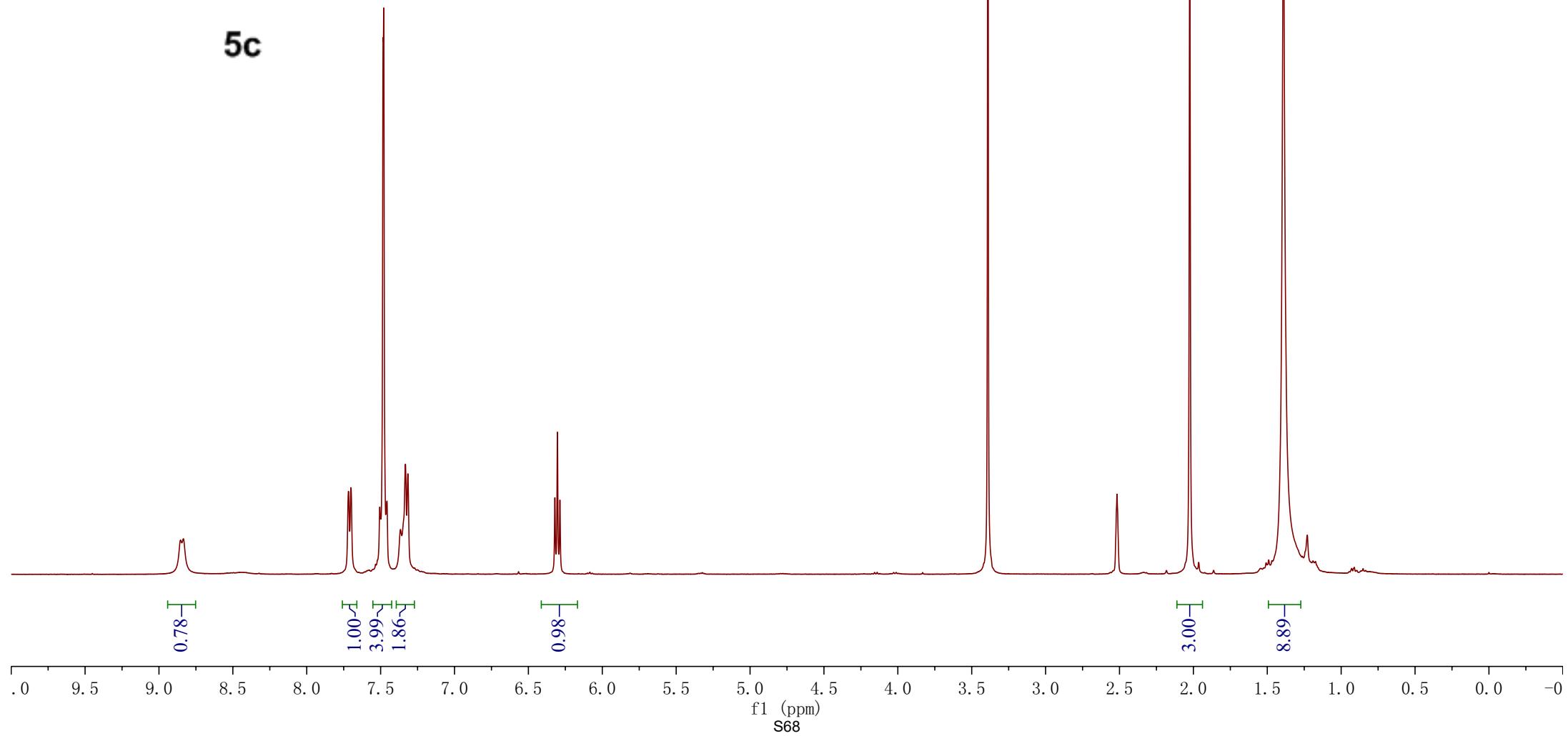
—105.62

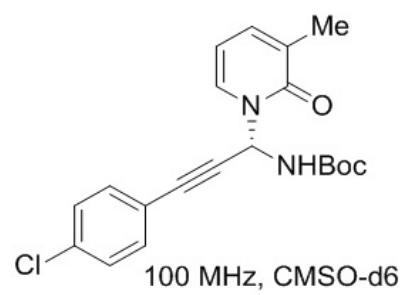
—85.18  
—82.41  
—80.97

—59.42

28.23  
21.53  
17.04







**5c**

— 165.67  
— 158.88

142.33  
139.44  
138.65  
— 136.42  
134.19  
133.60  
— 124.87

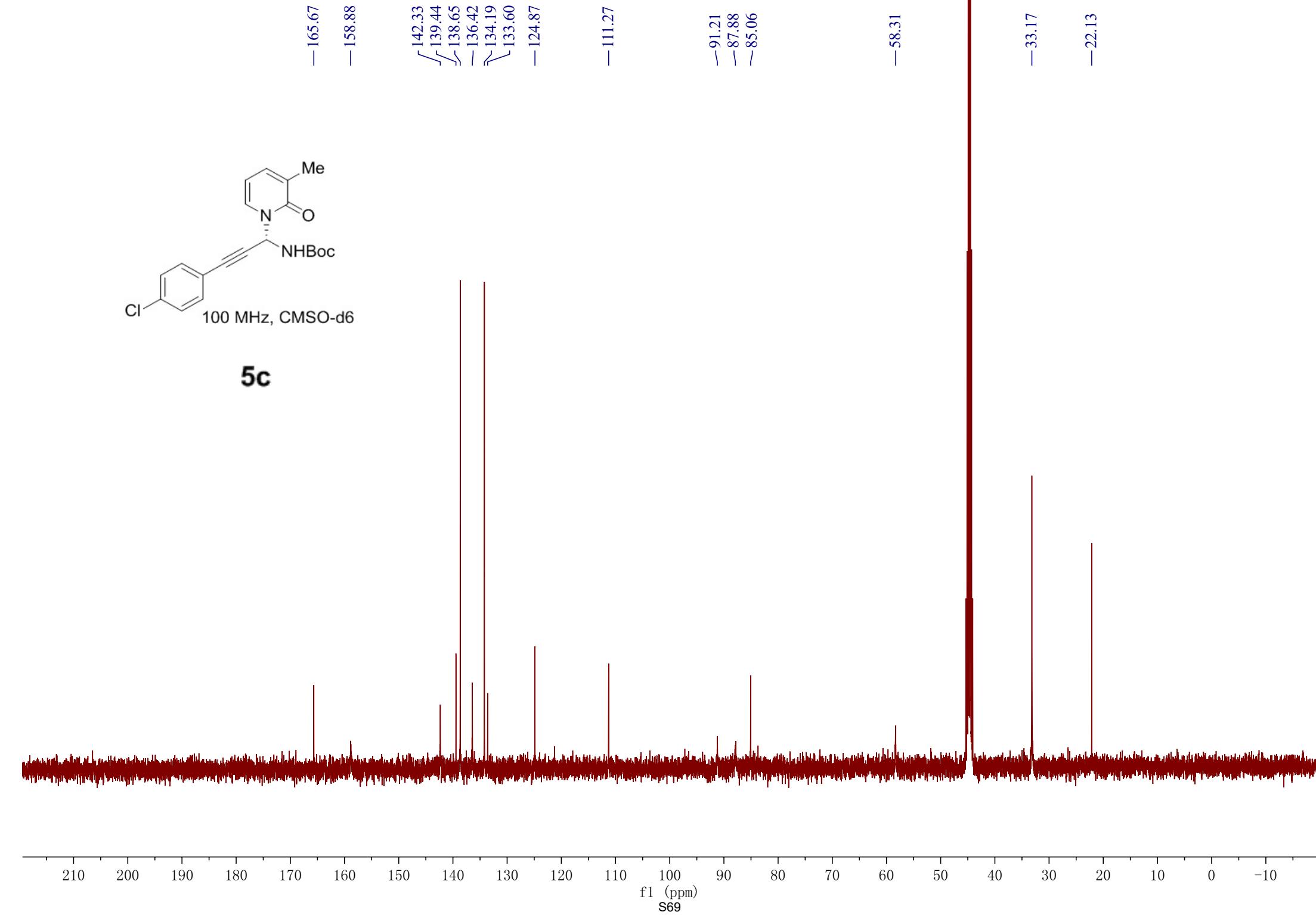
— 111.27

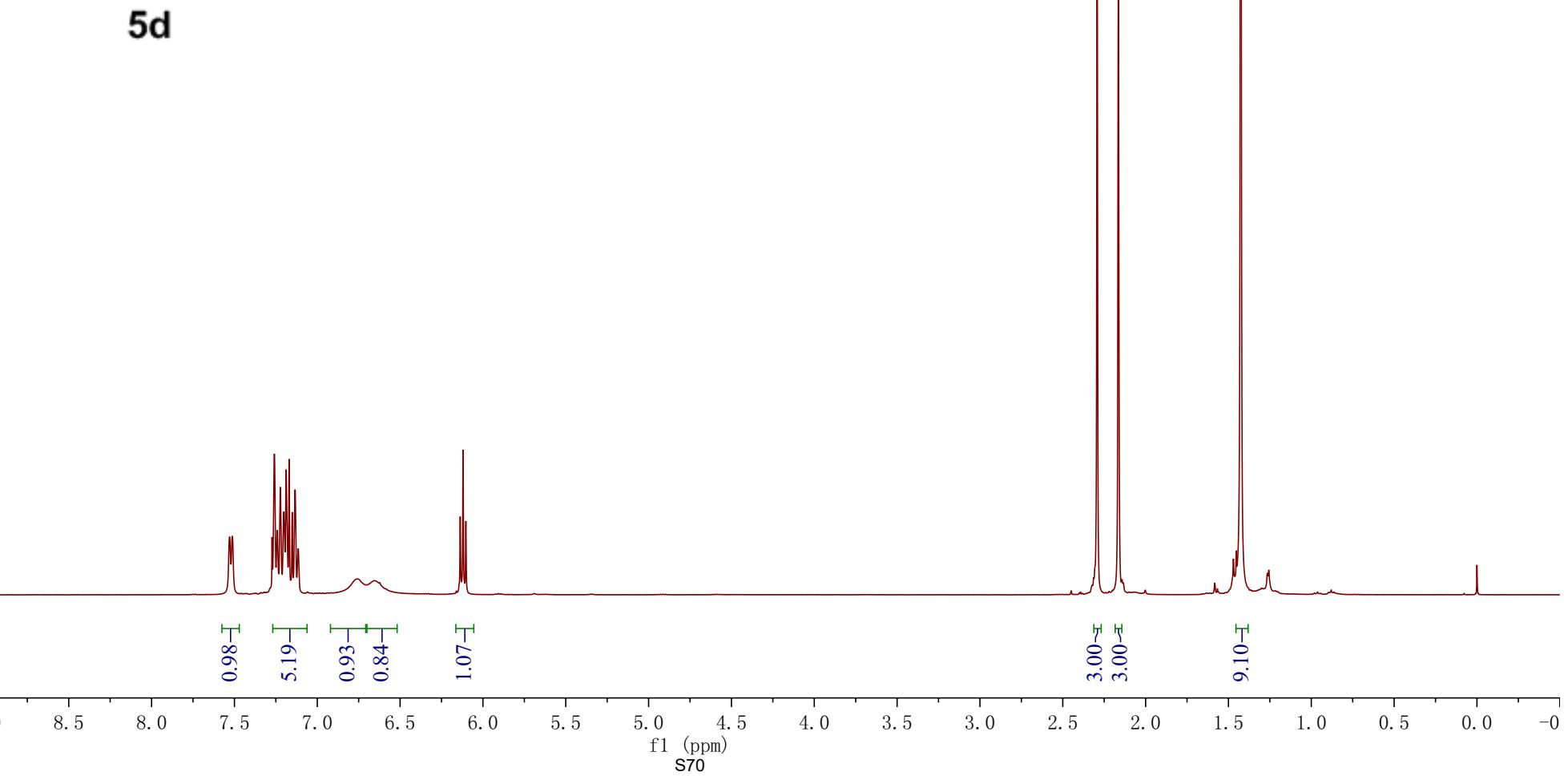
— 91.21  
— 87.88  
— 85.06

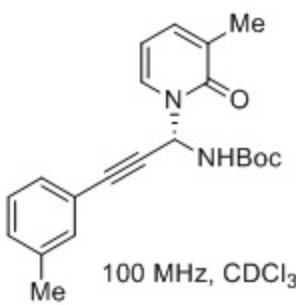
— 58.31

— 33.17

— 22.13



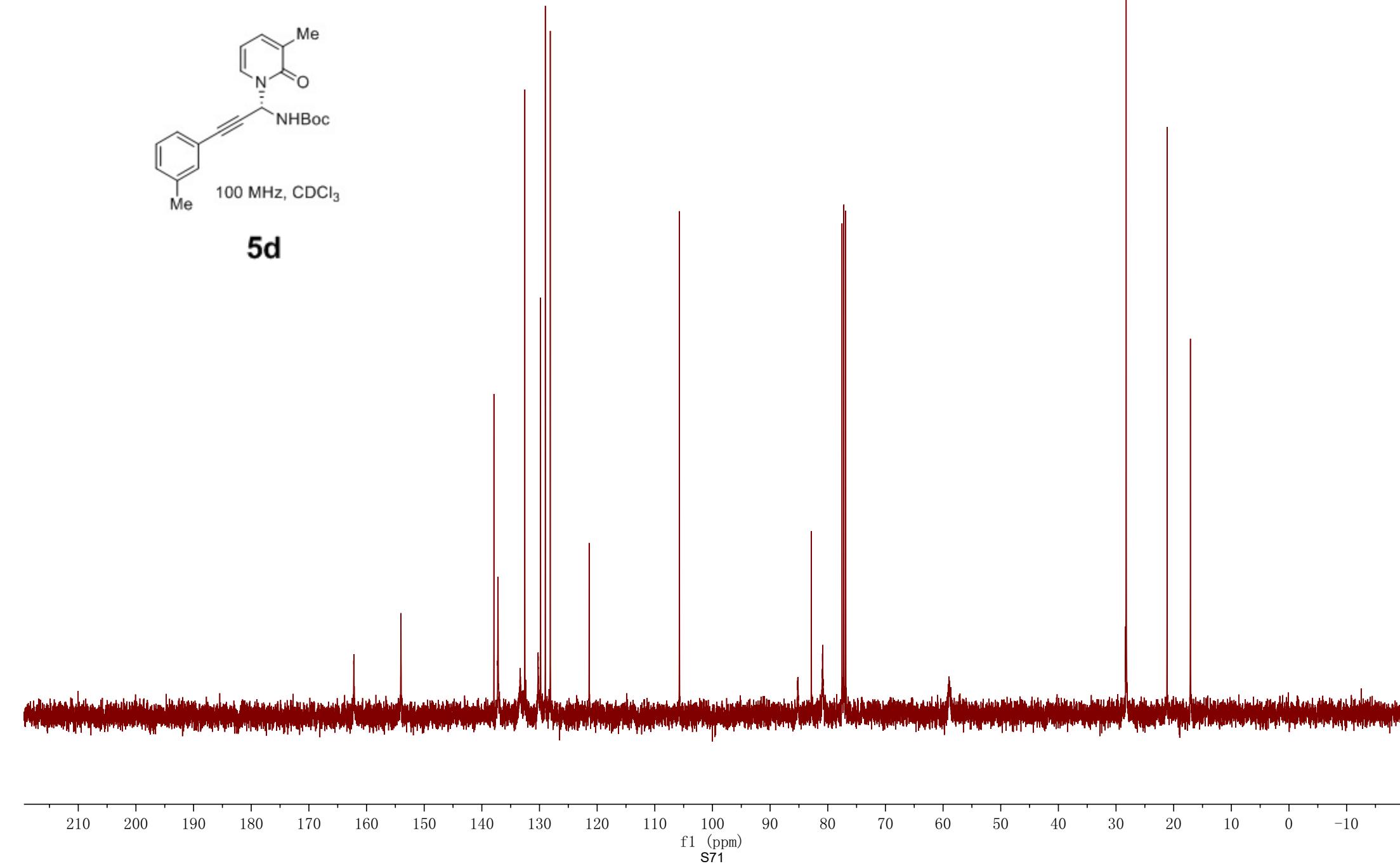




**5d**

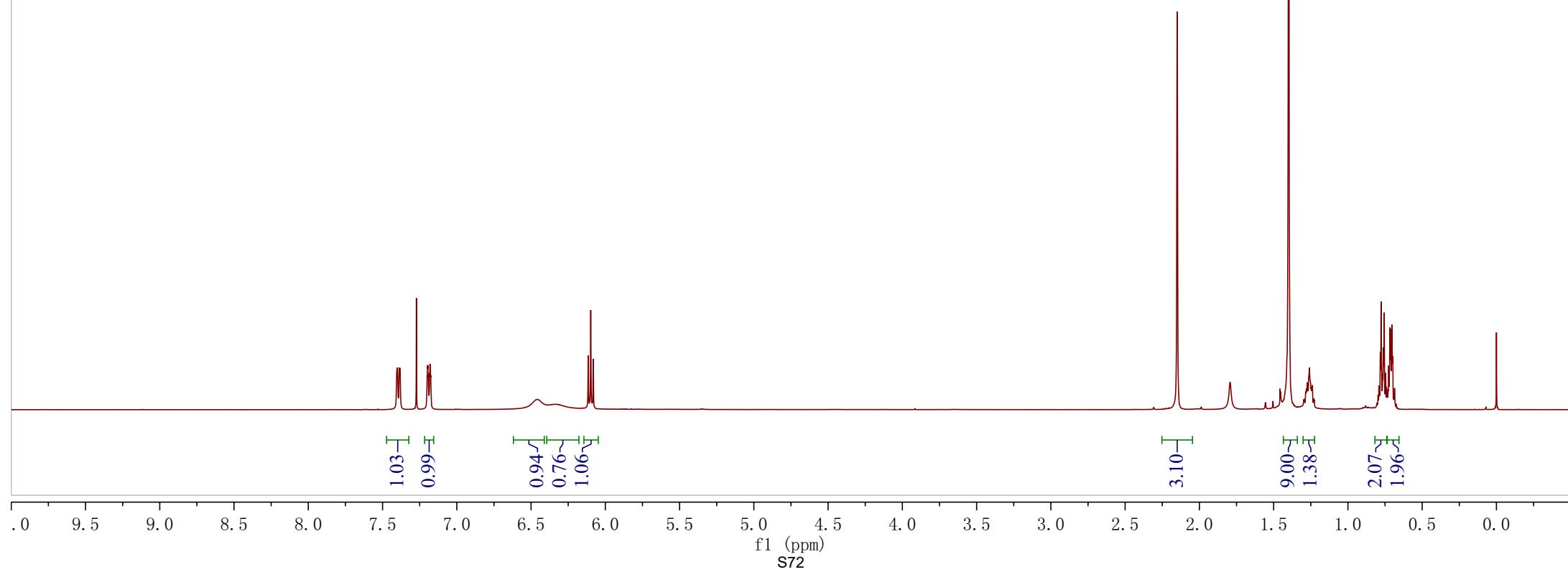
100 MHz, CDCl<sub>3</sub>

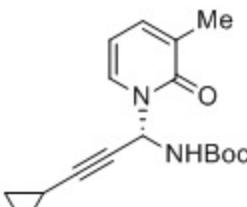
—162.19  
—154.03  
  
137.91  
137.20  
133.37  
132.55  
130.24  
129.82  
128.99  
128.13  
121.39  
  
—105.73  
  
—85.17  
—82.86  
—80.87  
  
—58.99  
  
28.24  
—21.15  
—17.10





**5e**

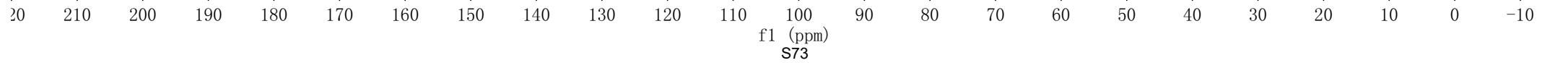


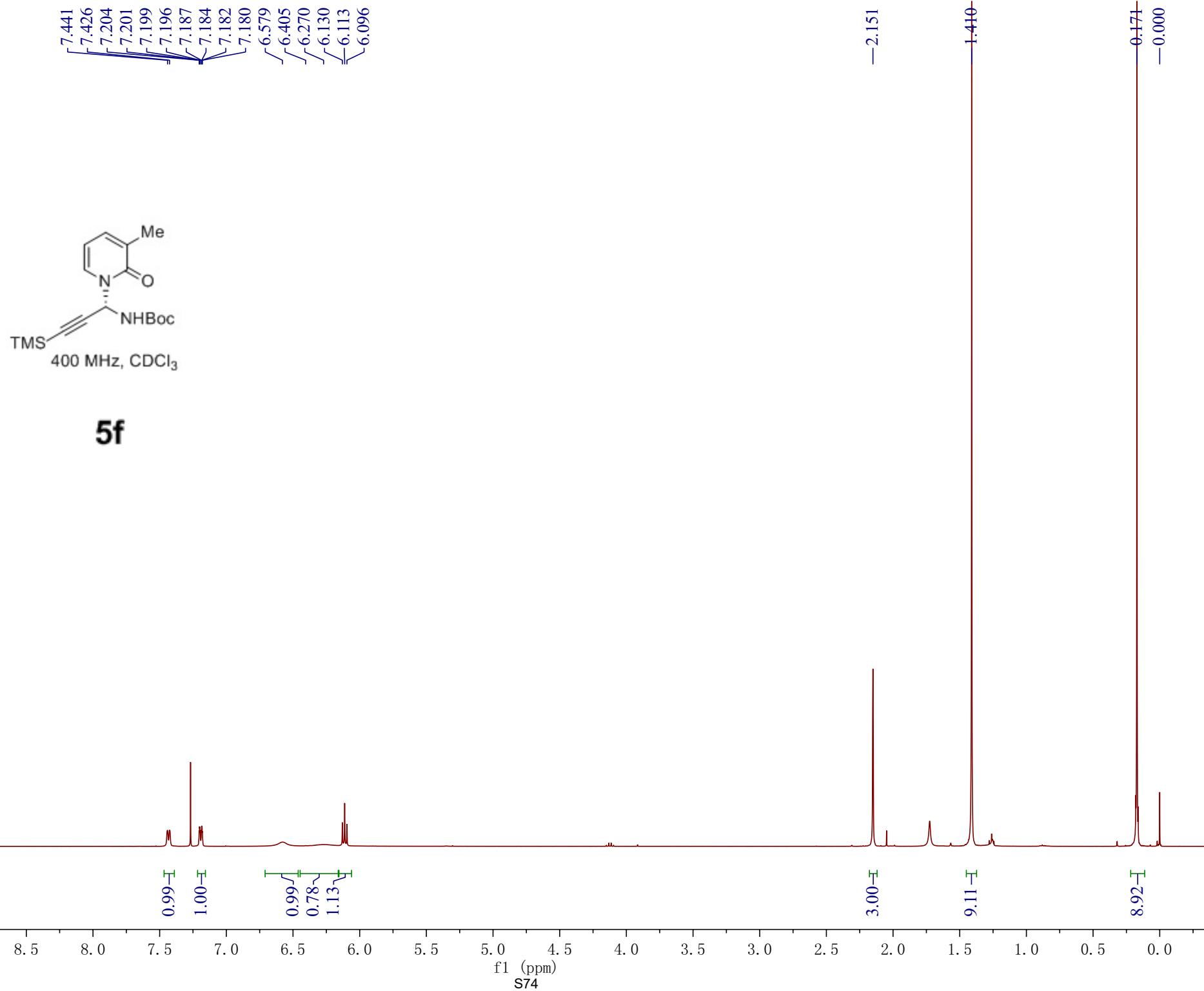


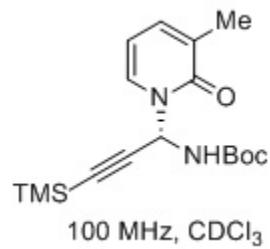
100 MHz, CDCl<sub>3</sub>

**5e**

—162.73  
—154.45  
  
—137.61  
—133.86  
—130.84  
  
—106.04  
  
—89.72  
—81.35  
  
—69.98  
—59.61  
  
28.78  
  
—17.57  
—8.85  
—8.82  
—0.00







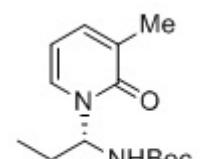
100 MHz,  $\text{CDCl}_3$

**5f**

— 162.36  
— 154.17  
— 137.44  
— 133.47  
— 130.47  
— 105.93  
— 98.92  
— 90.95  
— 81.26  
— 58.46  
— 28.55  
— 17.45  
— 0.00

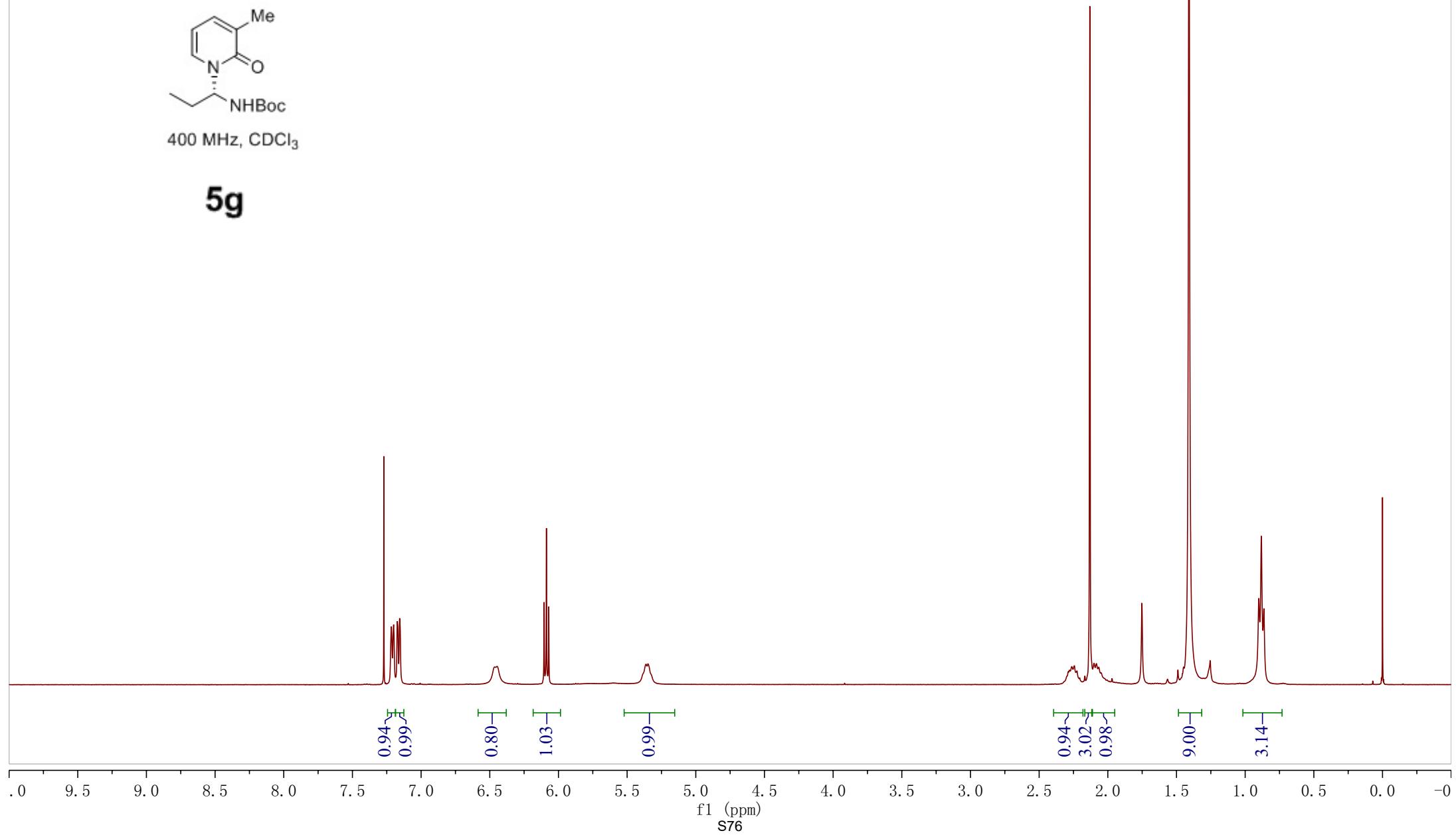
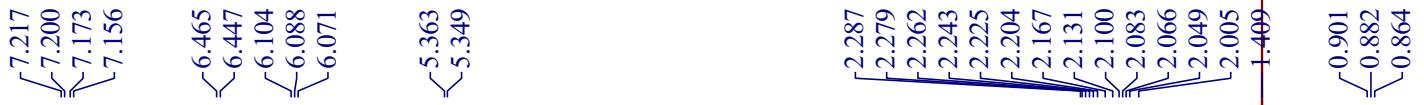
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

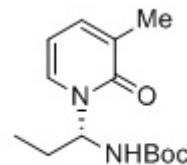
f1 (ppm)  
S75



400 MHz, CDCl<sub>3</sub>

**5g**





100 MHz, CDCl<sub>3</sub>

**5g**

— 163.22  
— 155.00  
— 137.02  
~ 134.89  
— 130.50  
— 105.37  
— 80.12  
— 73.38  
— 28.24  
~ 26.08  
— 16.87  
— 10.35

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)  
S77

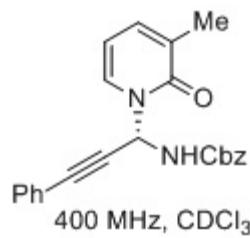
7.567  
7.551  
7.438  
7.422  
7.419  
7.347  
7.323  
7.315  
7.312  
7.307  
7.302  
7.299  
7.288  
7.284  
7.279  
7.268  
7.262  
7.208  
6.879  
6.807

6.138  
6.121  
6.104

5.157  
5.127  
5.080  
5.049

-2.148

-0.000



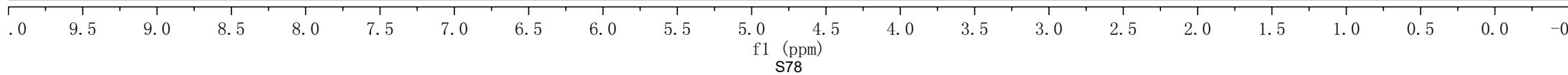
**5h**

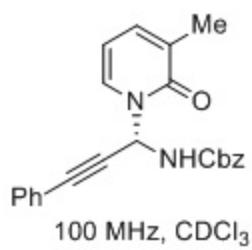
1.02  
1.99  
7.97  
1.03  
0.85  
0.99

1.01

1.00  
0.99

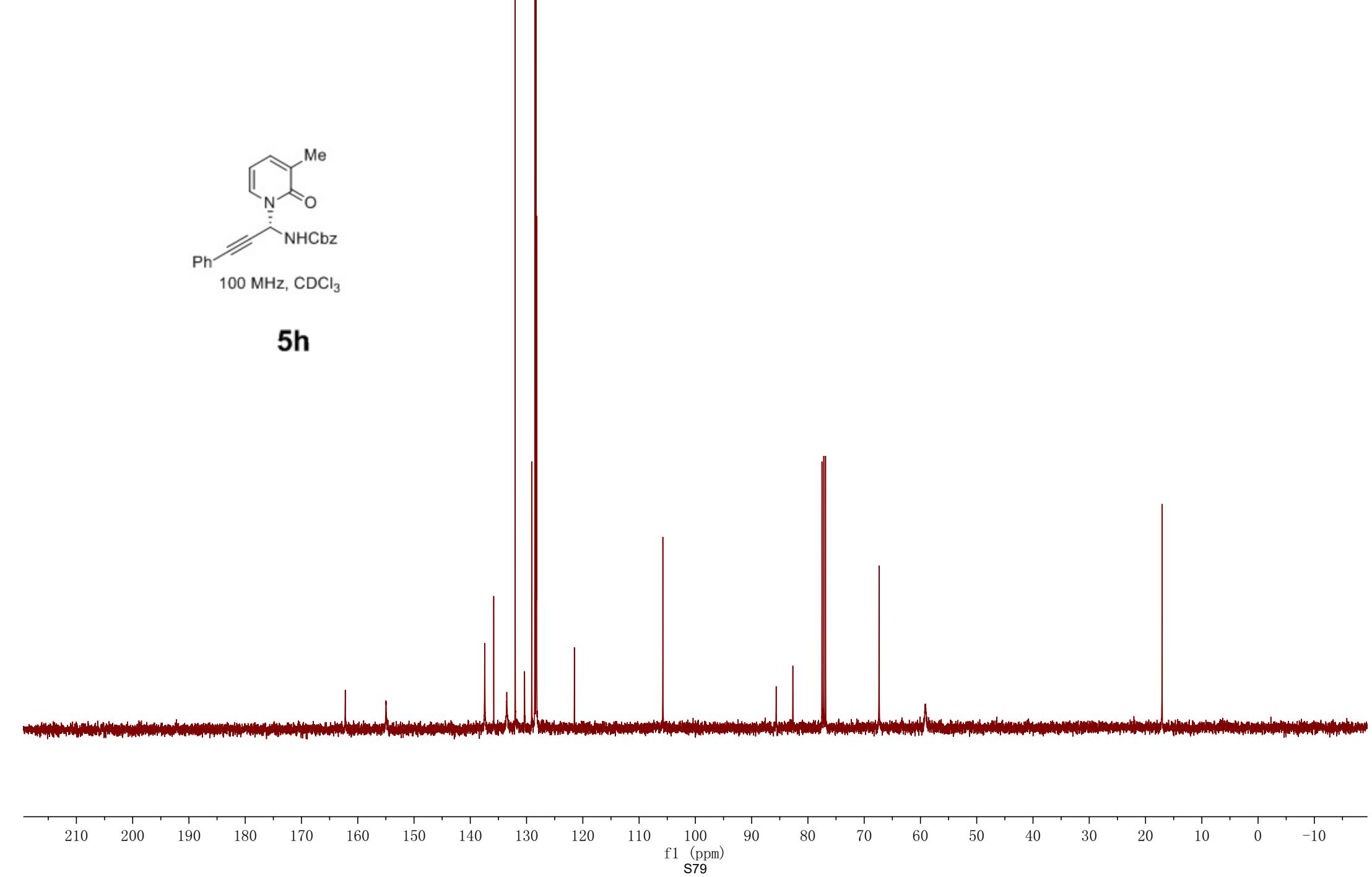
3.00



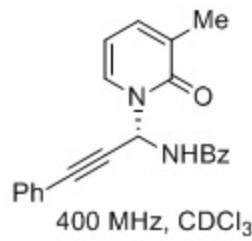


**5h**

—162.22  
—154.99  
137.43  
135.84  
133.52  
132.02  
130.36  
129.07  
128.54  
128.31  
128.27  
128.22  
121.50  
—105.78  
—85.64  
—82.68  
—67.36  
—59.17  
—17.06

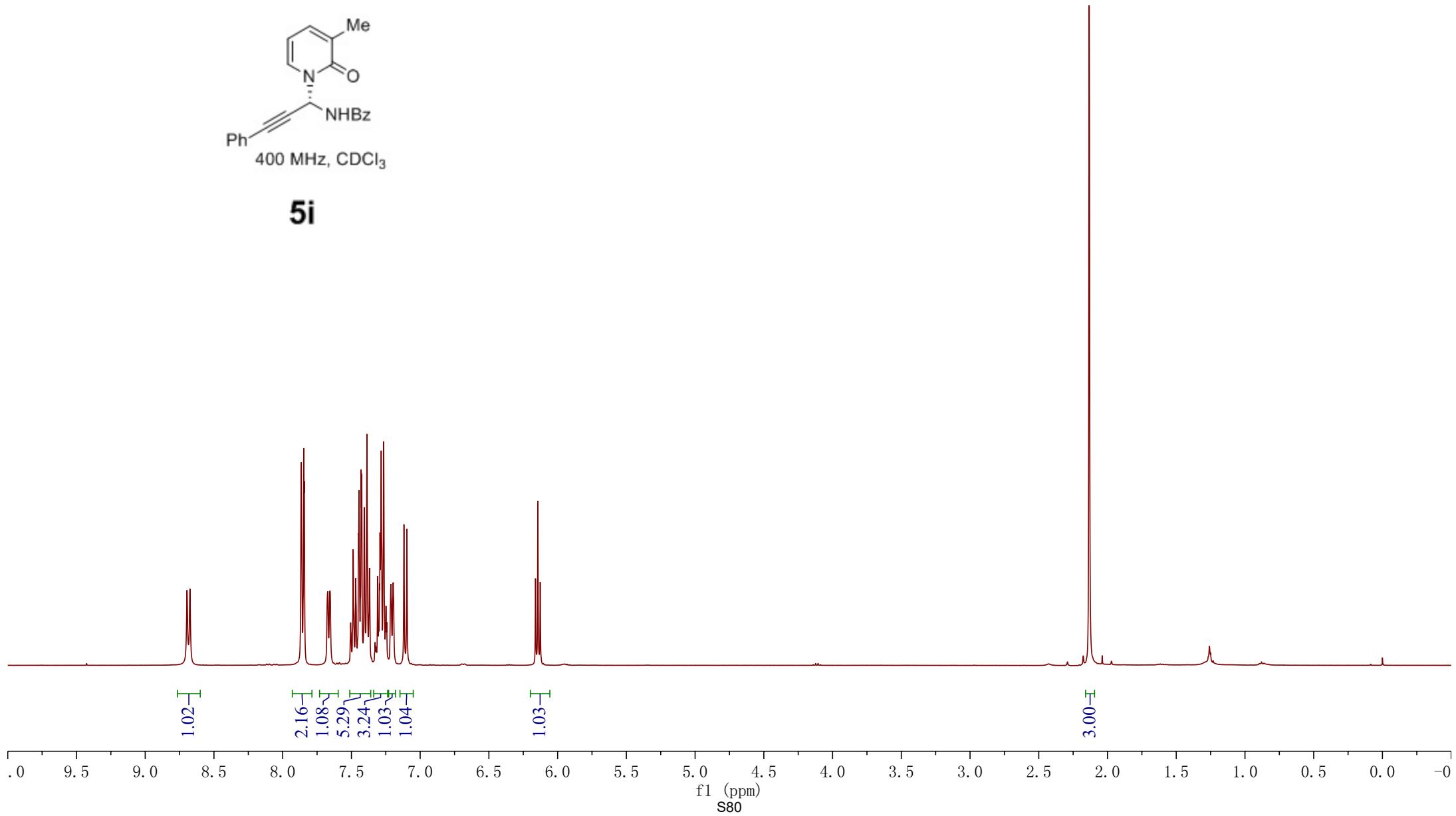


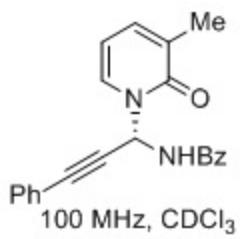
8.696  
8.675  
7.864  
7.846  
7.843  
7.449  
7.445  
7.429  
7.425  
7.407  
7.387  
7.292  
7.283  
7.265  
7.118  
7.097  
6.961  
6.144  
6.127  
-2.133  
-0.000



400 MHz, CDCl<sub>3</sub>

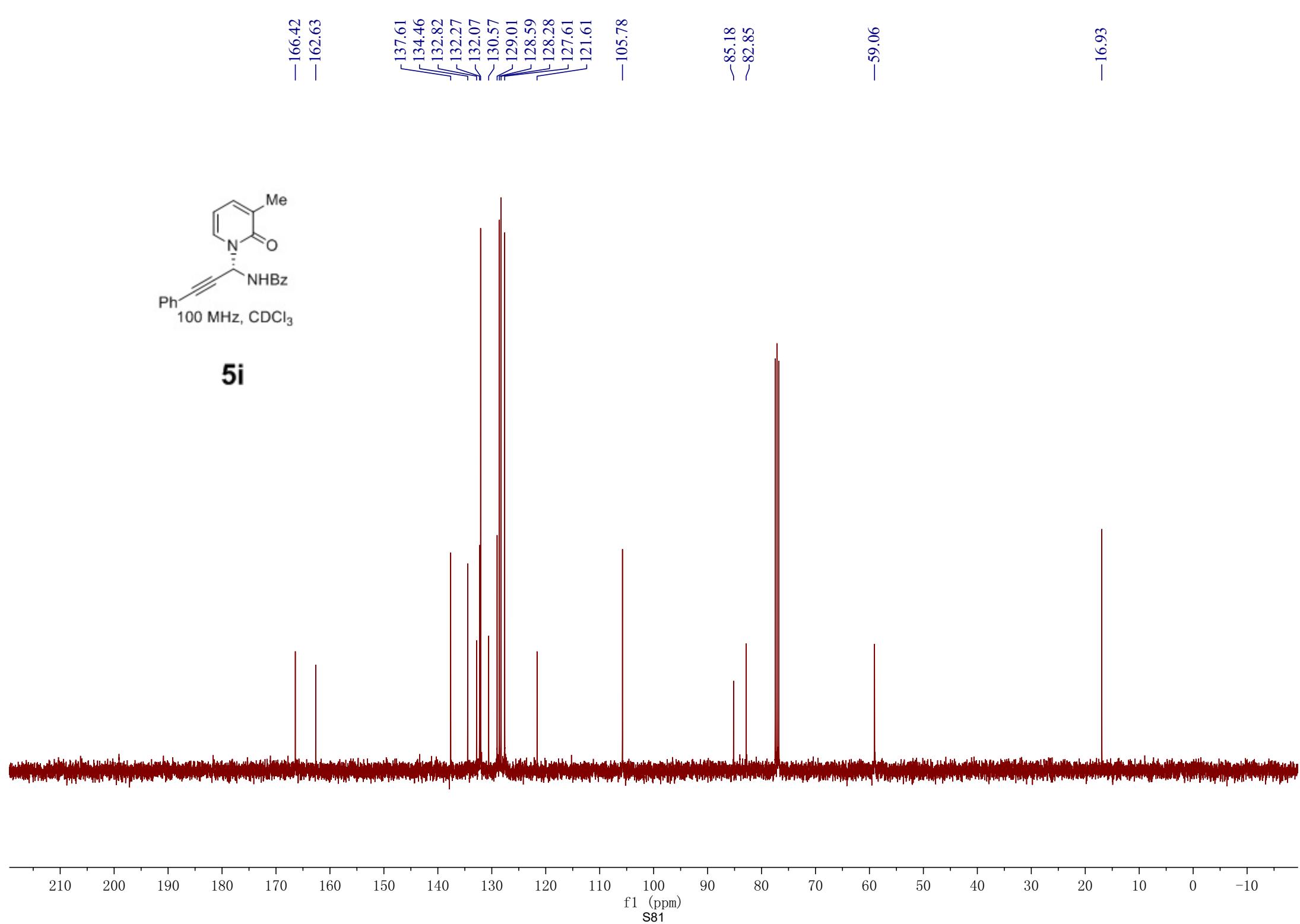
**5i**

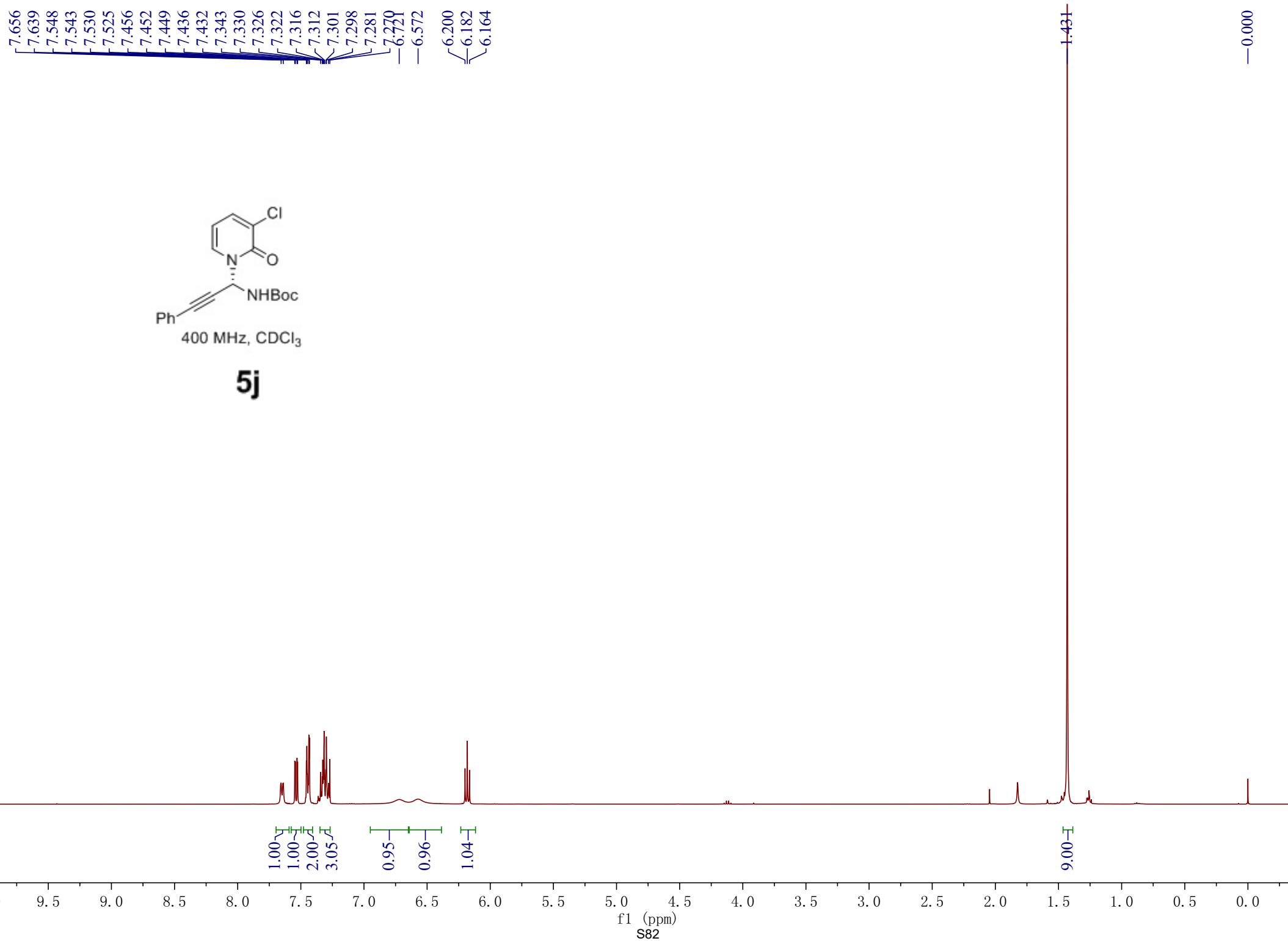


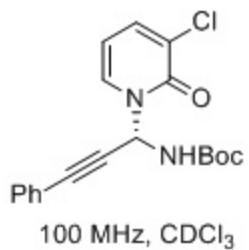


**5i**

100 MHz, CDCl<sub>3</sub>







100 MHz, CDCl<sub>3</sub>

**5j**

— 158.16  
— 153.92

— 138.11  
— 134.88  
— 132.01  
— 129.19

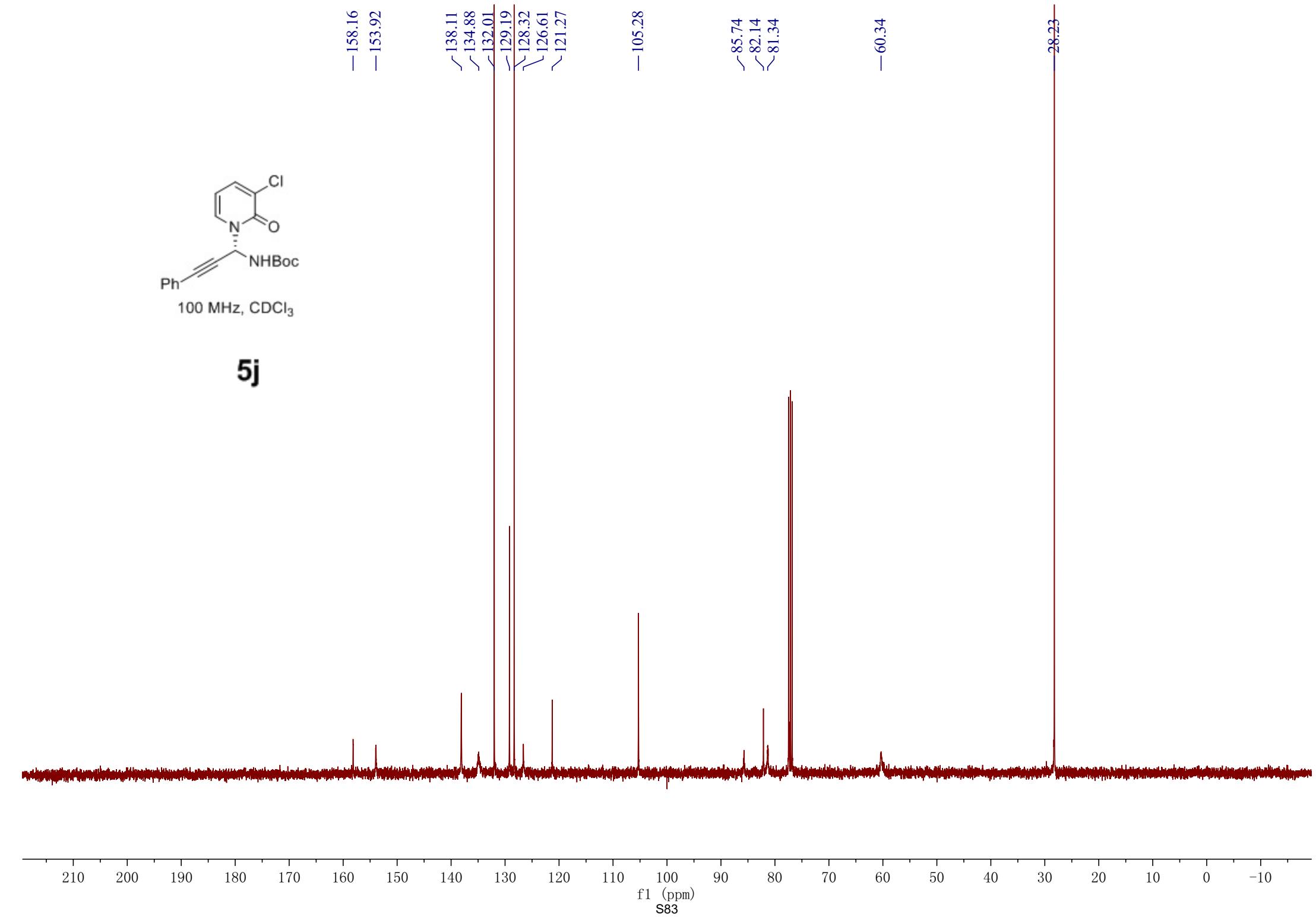
— 128.32  
— 126.61  
— 121.27

— 105.28

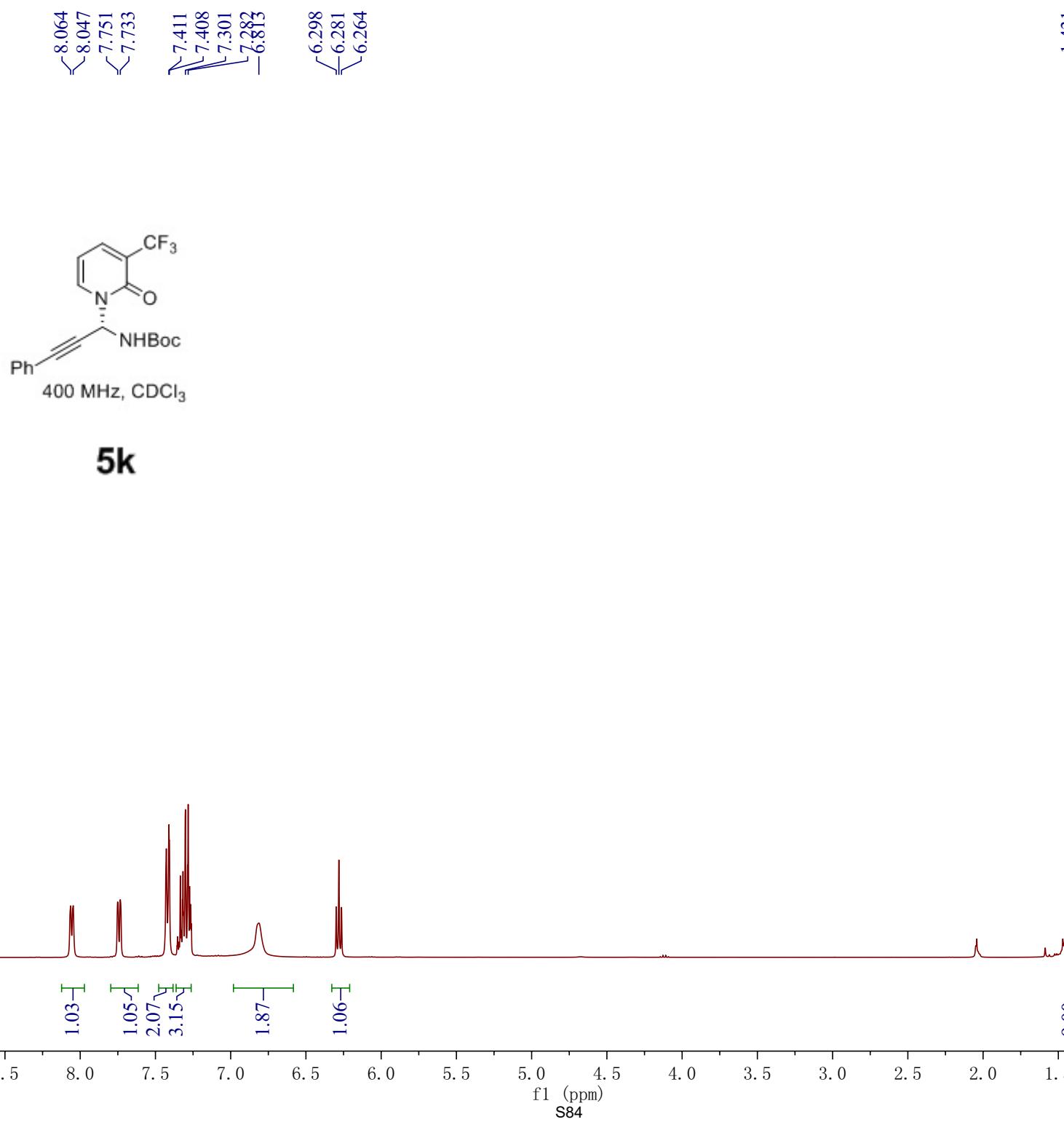
— 85.74  
— 82.14  
— 81.34

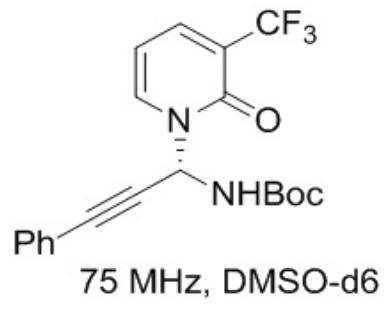
— 60.34

— 28.23



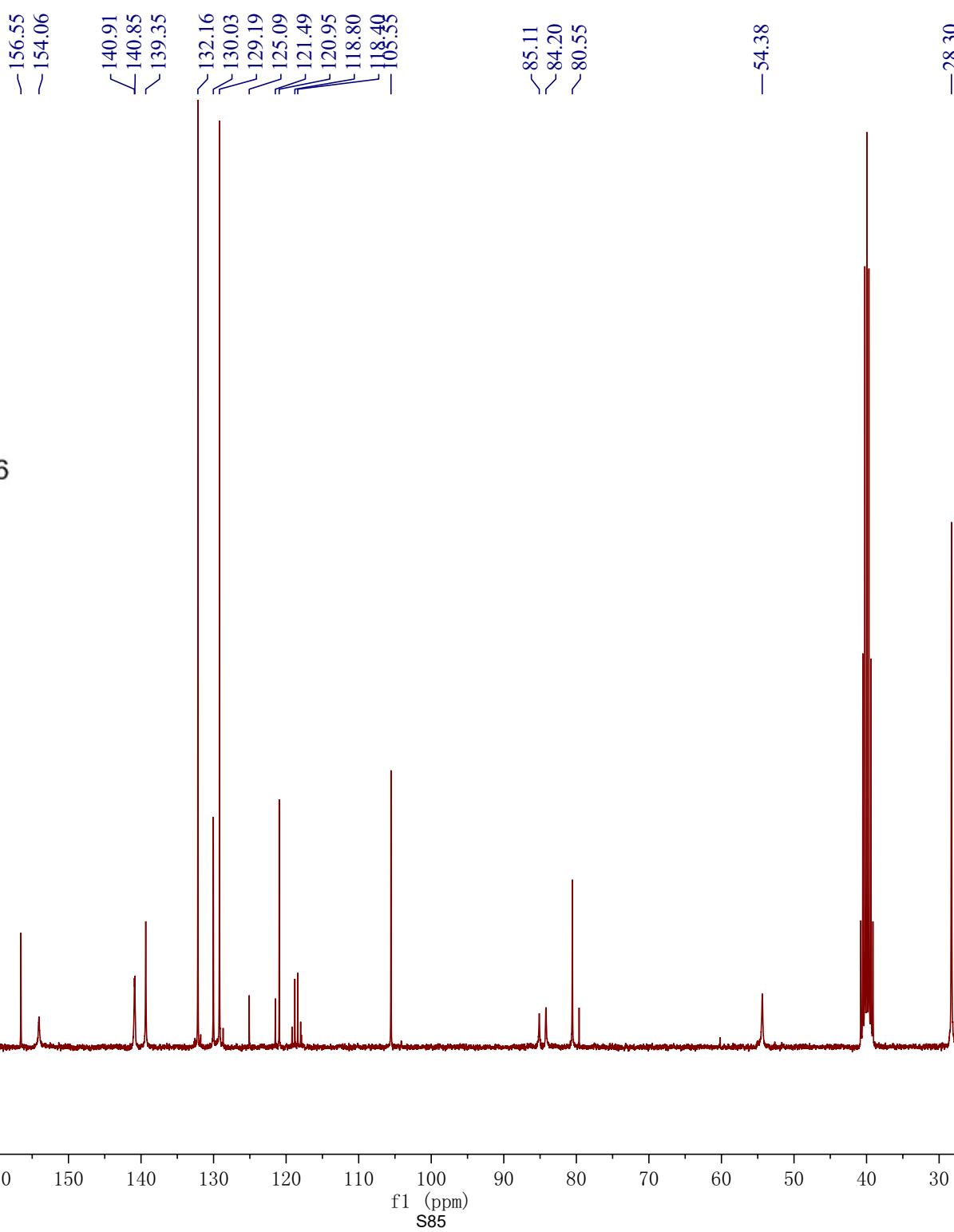
—0.000

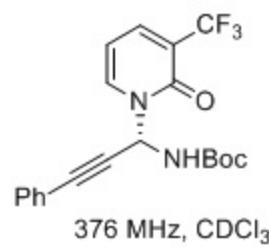




75 MHz, DMSO-d<sub>6</sub>

**5k**





**5k**

70.219

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

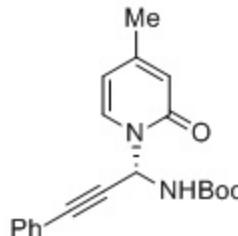
f1 (ppm)

S86

7.523  
7.506  
7.453  
7.450  
7.445  
7.439  
7.434  
7.429  
7.350  
7.331  
7.324  
7.319  
7.315  
7.309  
7.305  
7.297  
7.294  
7.291  
7.279  
7.275  
7.269  
6.534  
6.373  
6.055  
6.050  
6.037  
6.032

-2.173  
-1.428

-0.000



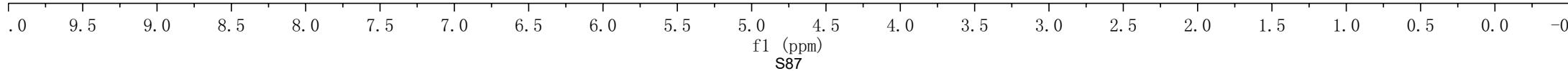
400 MHz, CDCl<sub>3</sub>

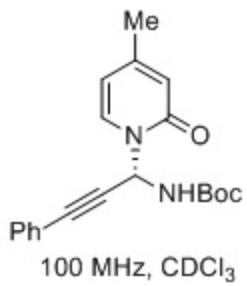
**5l**

0.99  
1.95  
3.17

0.94  
0.78  
1.08  
1.01

3.00  
9.00





**5l**

— 161.90  
— 153.97  
~ 151.91

— 134.91  
— 132.00  
— 129.01  
— 128.29  
— 121.57  
~ 119.77

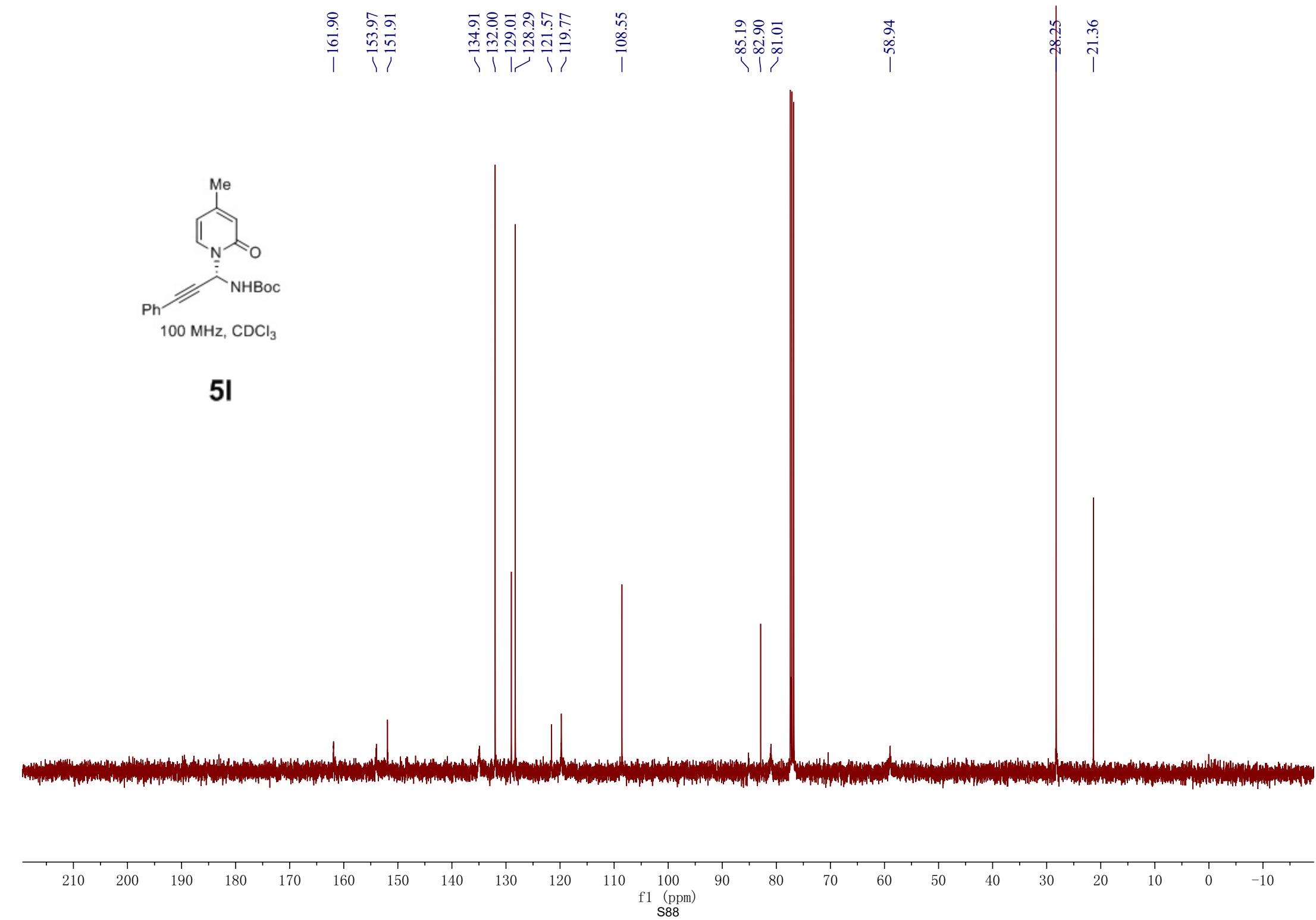
— 108.55

— 85.19  
— 82.90  
~ 81.01

— 58.94

— 28.25

— 21.36

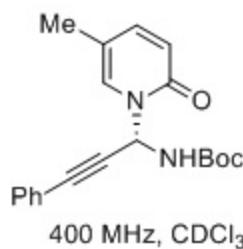


7.452  
7.448  
7.444  
7.438  
7.433  
7.428  
7.422  
7.348  
7.339  
7.329  
7.317  
7.312  
7.306  
7.302  
7.294  
7.292  
7.288  
7.272  
7.266  
7.215  
7.209  
7.192  
6.186  
6.649  
6.540  
6.517

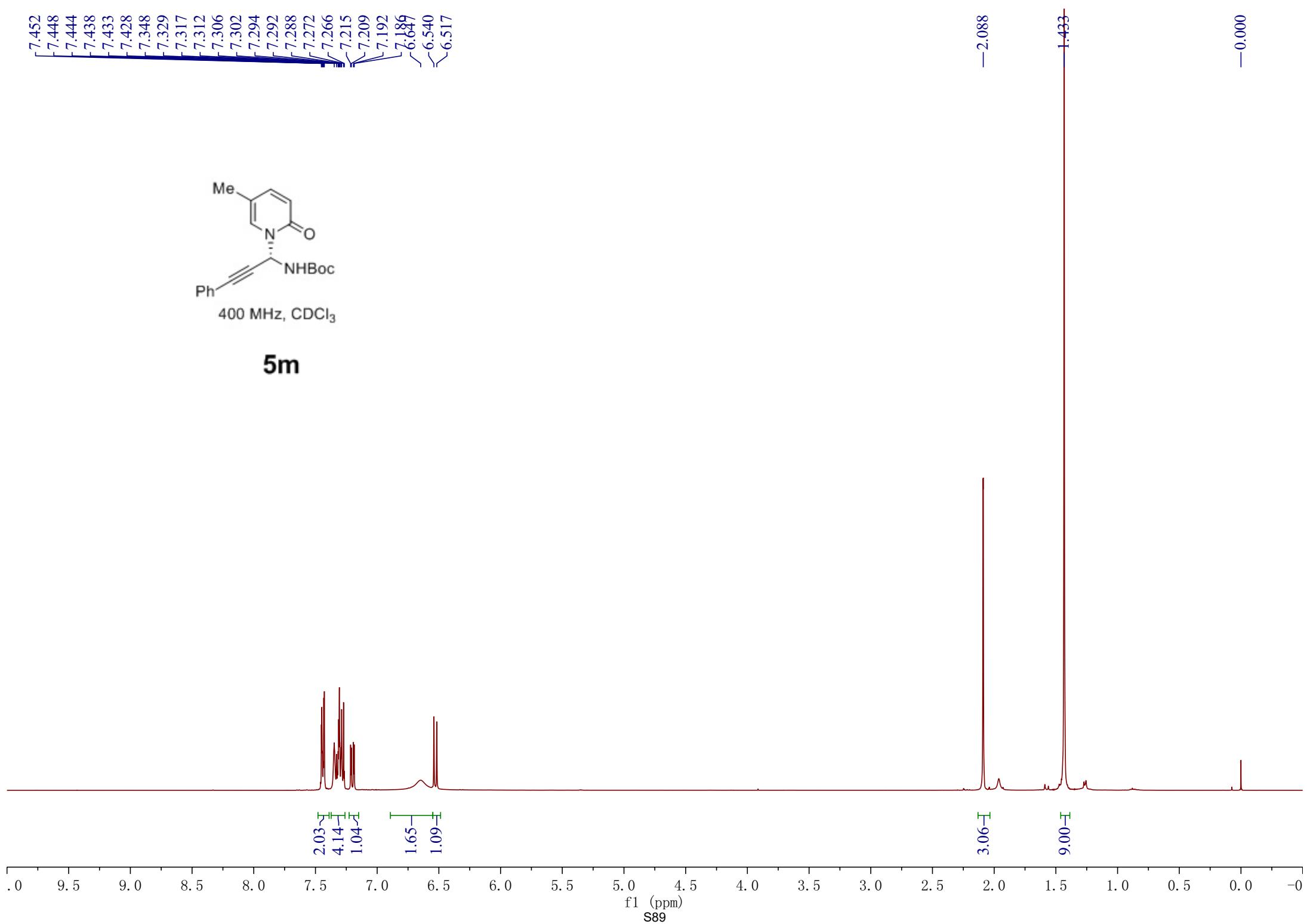
-2.088

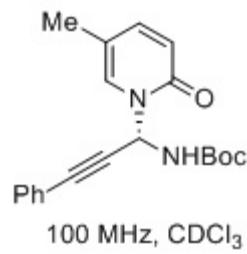
-1.433

-0.000



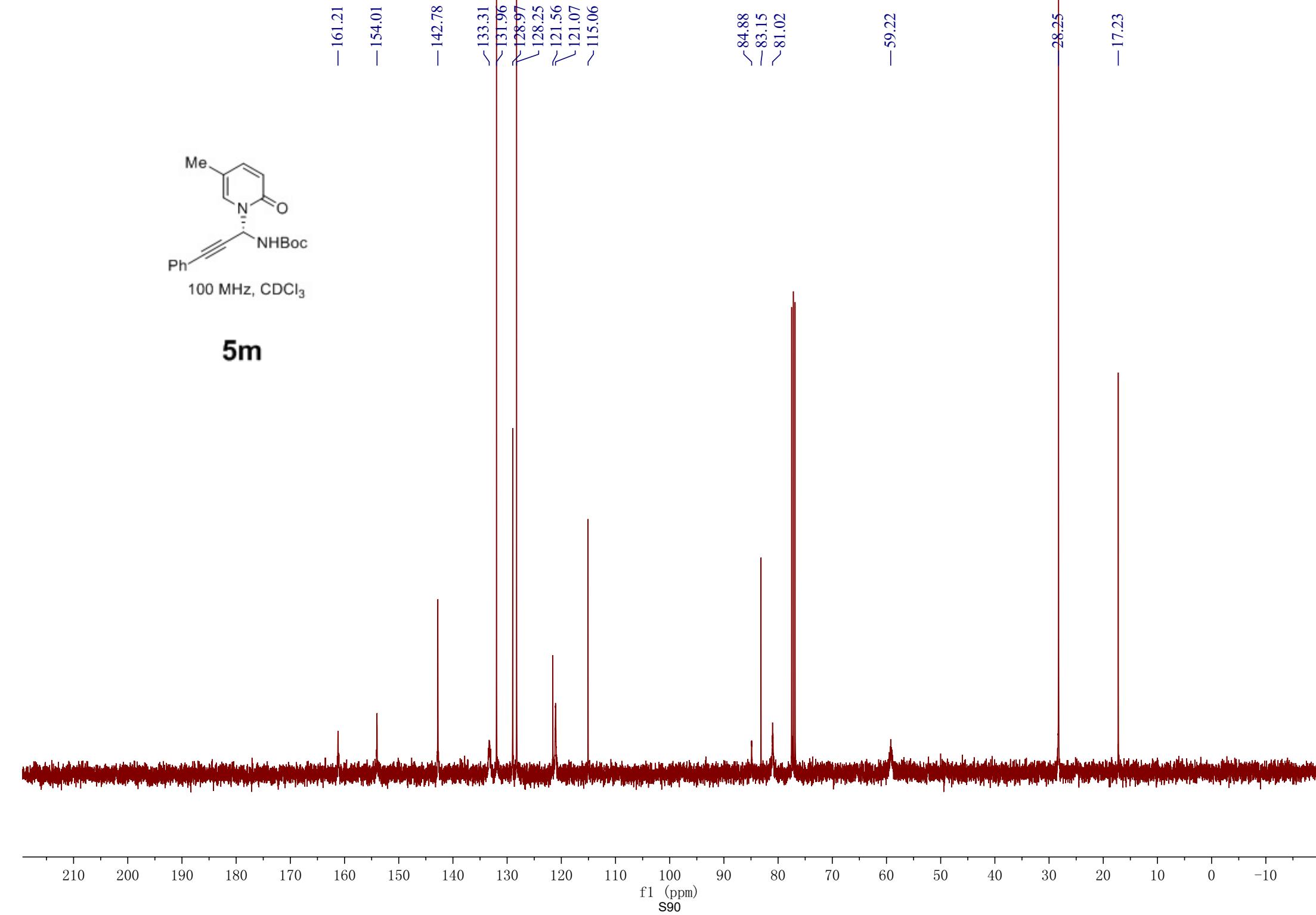
**5m**





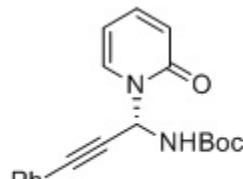
**5m**

— 161.21  
— 154.01  
— 142.78  
— 133.31  
— 131.96  
— 128.97  
— 128.25  
— 121.56  
— 121.07  
— 115.06  
— 84.88  
— 83.15  
— 81.02  
— 59.22  
— 28.25  
— 17.23



7.651  
7.638  
7.634  
7.458  
7.454  
7.450  
7.438  
7.434  
7.357  
7.346  
7.339  
7.334  
7.323  
7.318  
7.312  
7.308  
7.300  
7.297  
7.294

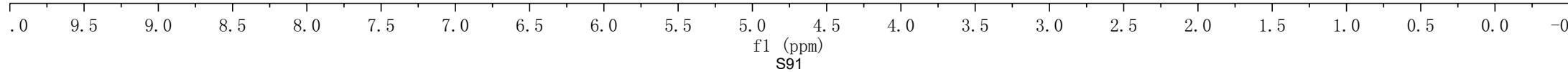
1.428  
—0.000

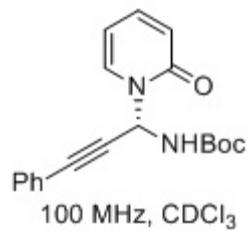


400 MHz, CDCl<sub>3</sub>

**5n**

1.01 —H  
2.01 —H  
4.02 —H  
0.91 —H  
1.79 —H  
1.07 —H  
9.00 —H





—161.89  
—153.93

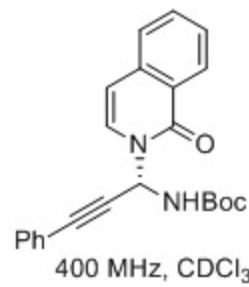
—140.05  
—135.97  
—131.99  
—129.06  
—128.29  
—121.53  
—121.47

—105.92

—85.27  
—82.69  
—81.10

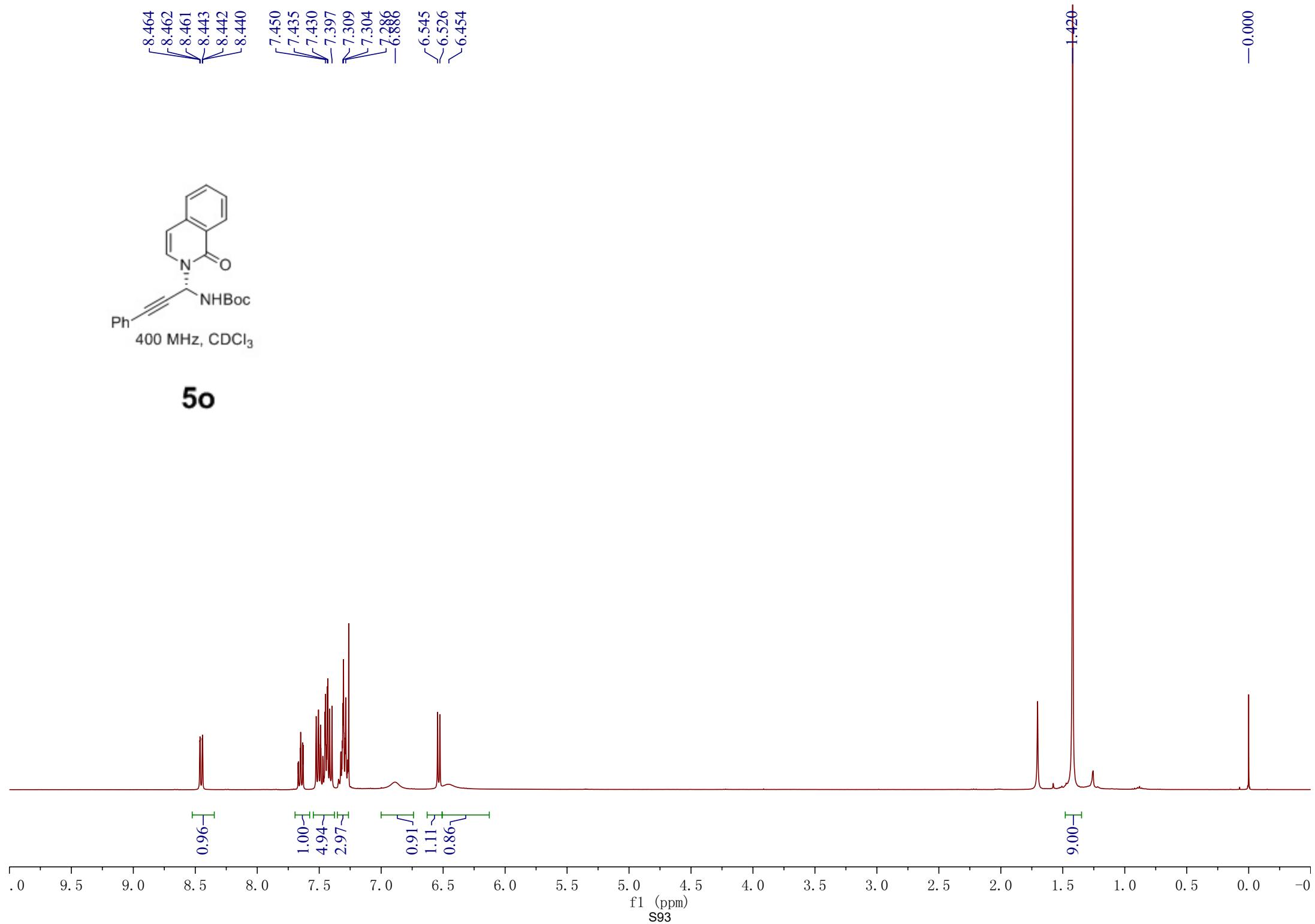
—59.44

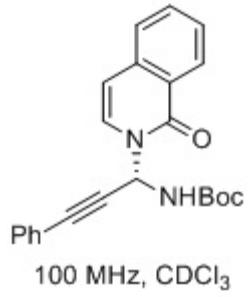
28.22



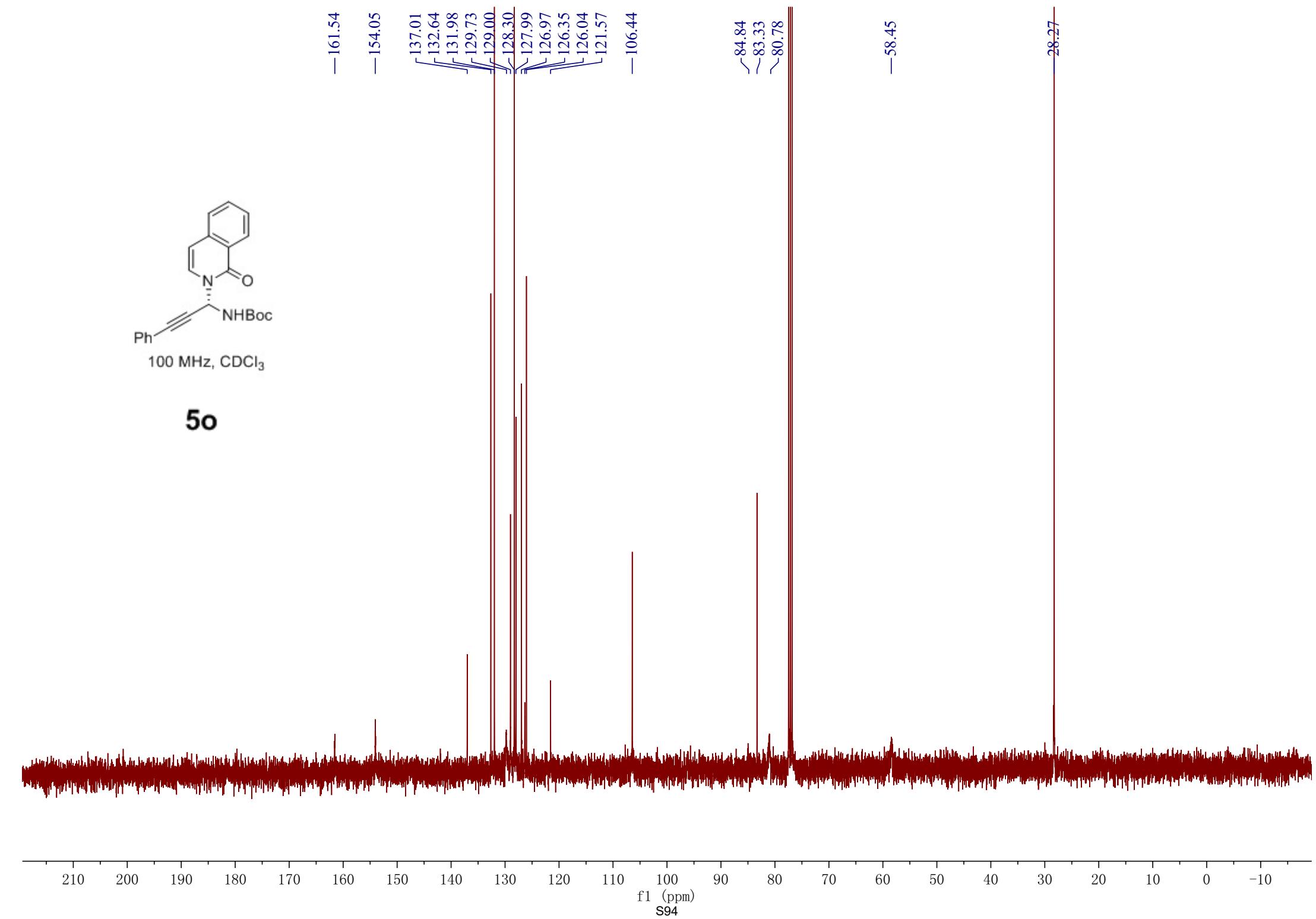
400 MHz,  $\text{CDCl}_3$

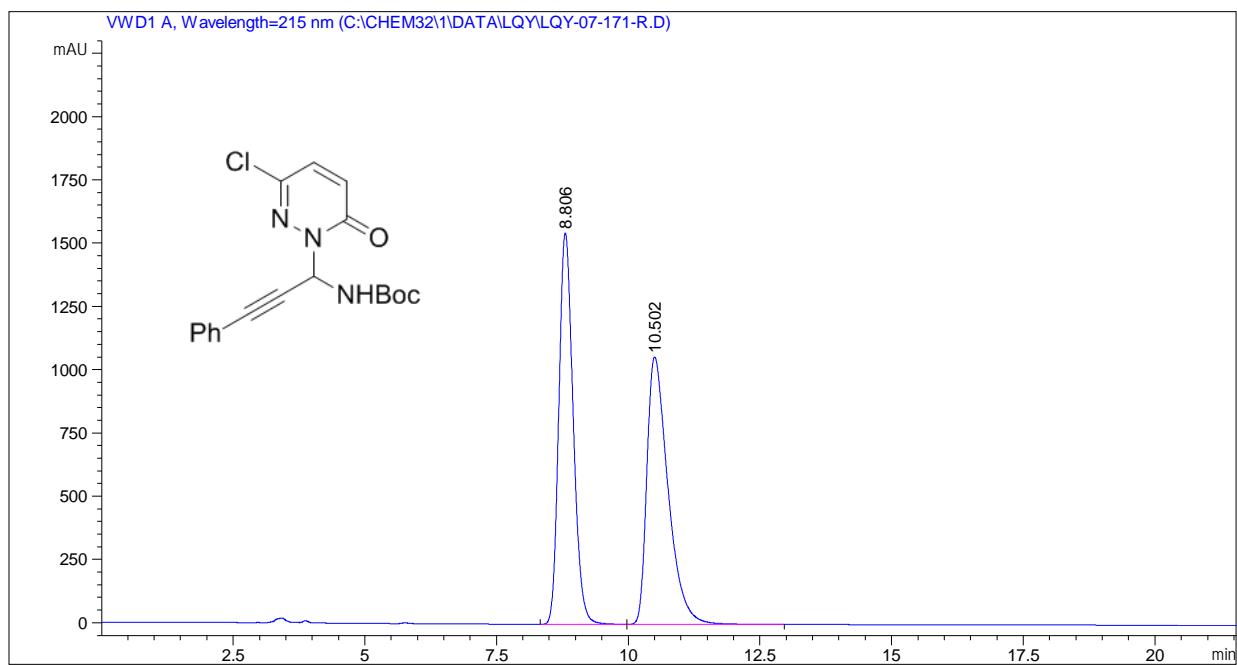
**5o**





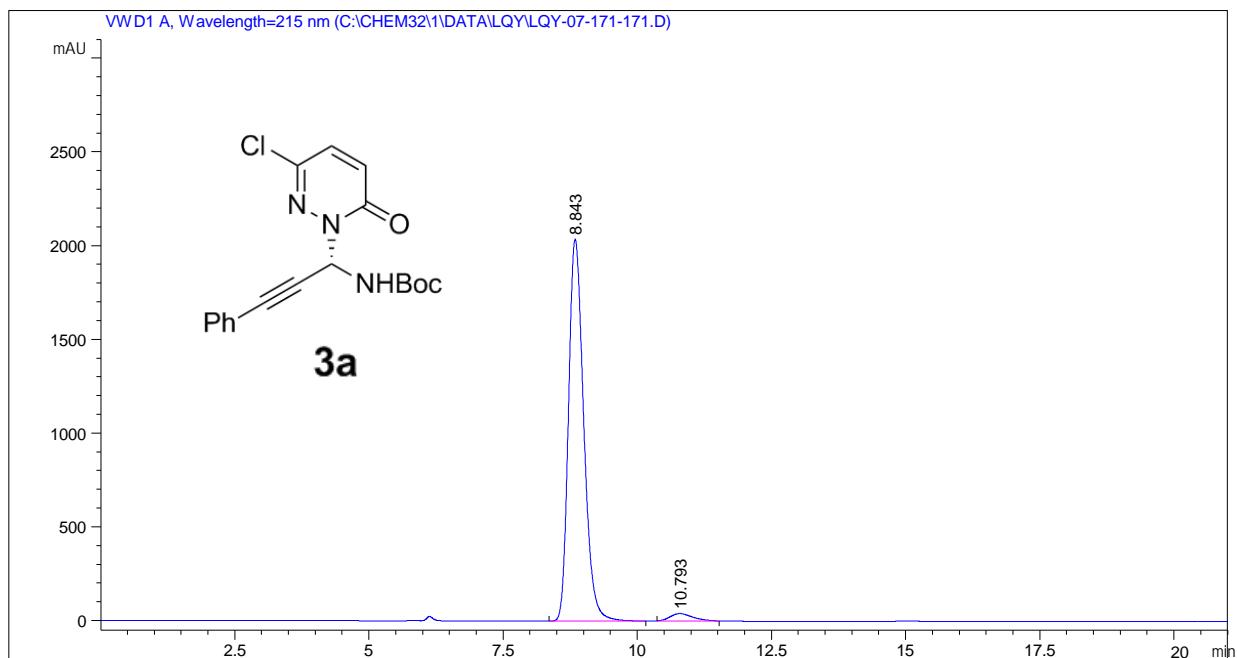
**5o**





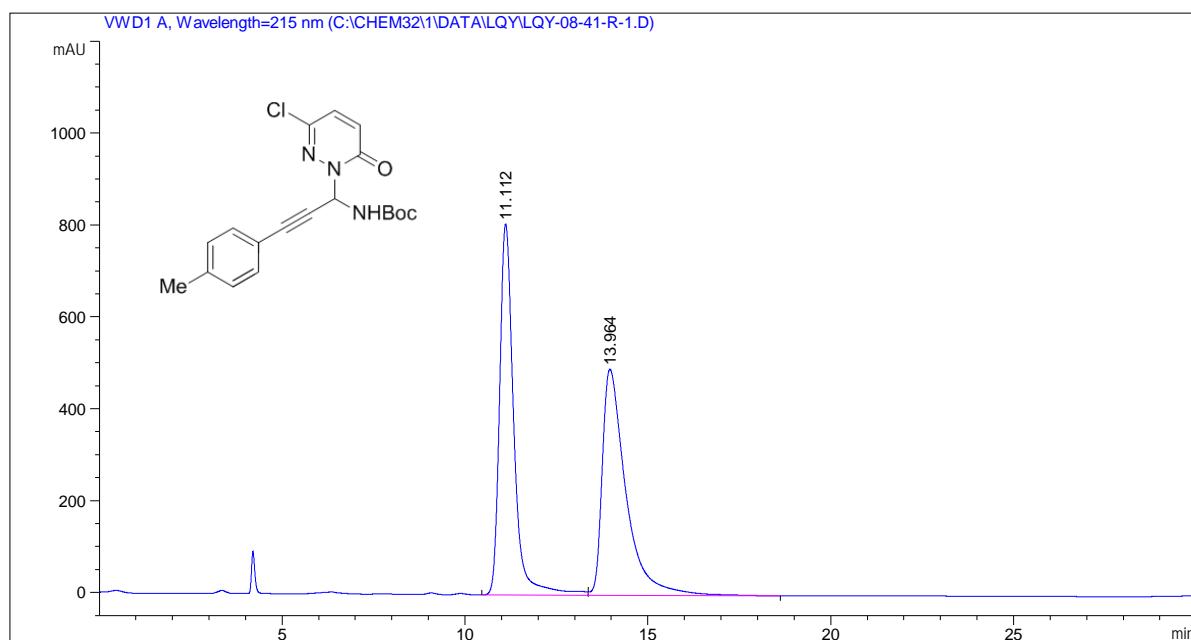
DYU FYhH aY H<sub>4</sub>dY KjXh\ 5f YU <Y] [\h\ 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.806	BB	0.2934	2.92104e4	1545.91370
2	10.502	BB	0.4243	2.95454e4	1056.23389

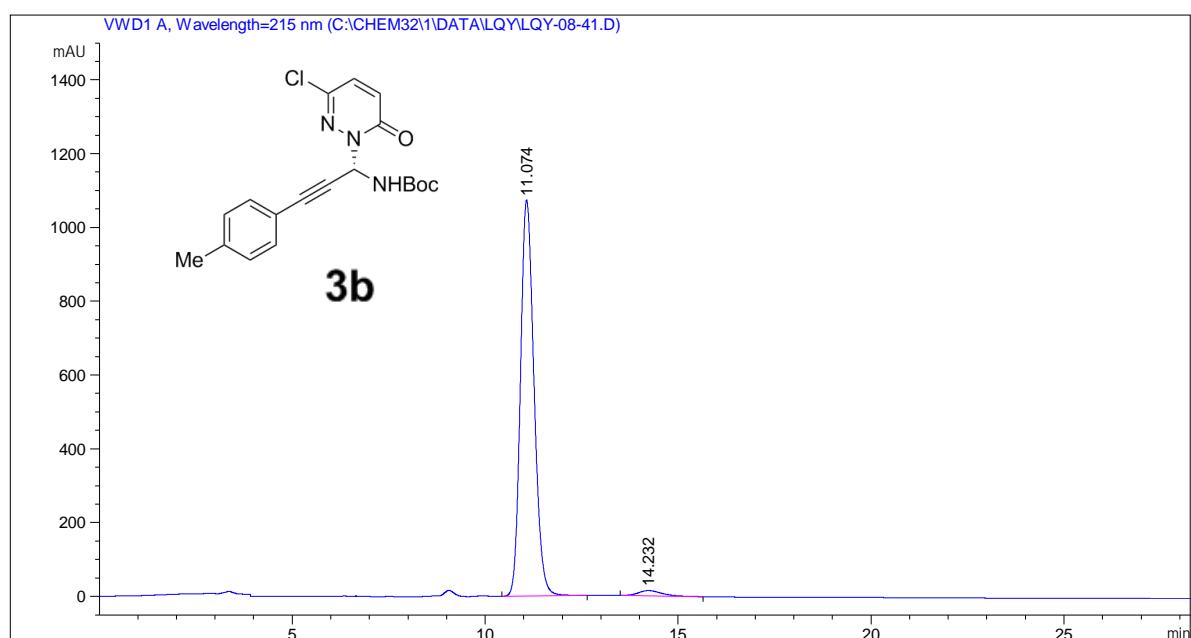


DYU FYhH aY H<sub>4</sub>dY KjXh\ 5f YU <Y] [\h\ 5f YU

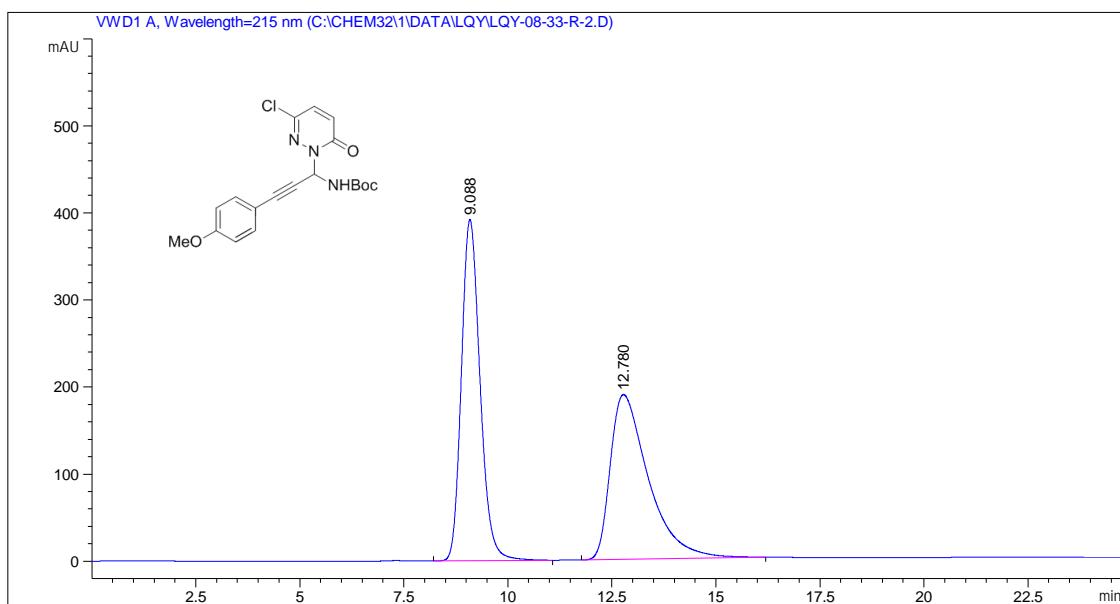
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.843	MM	0.3287	4.01724e4	2036.99768
2	10.793	MM	0.4896	1162.04663	39.55899



	DNU	FYH	aY	HdY	K	Xh\	5f	YU	<Y>	\h	5f	YU
#	[m i n]	[m i n]	[mAU*s]	[mAU]	%							
1	11.112	BV	R	0.4083	2.18504e4	807.	78693	49.	647			
2	13.964	VB		0.6655	2.21611e4	491.	99591	50.	353			

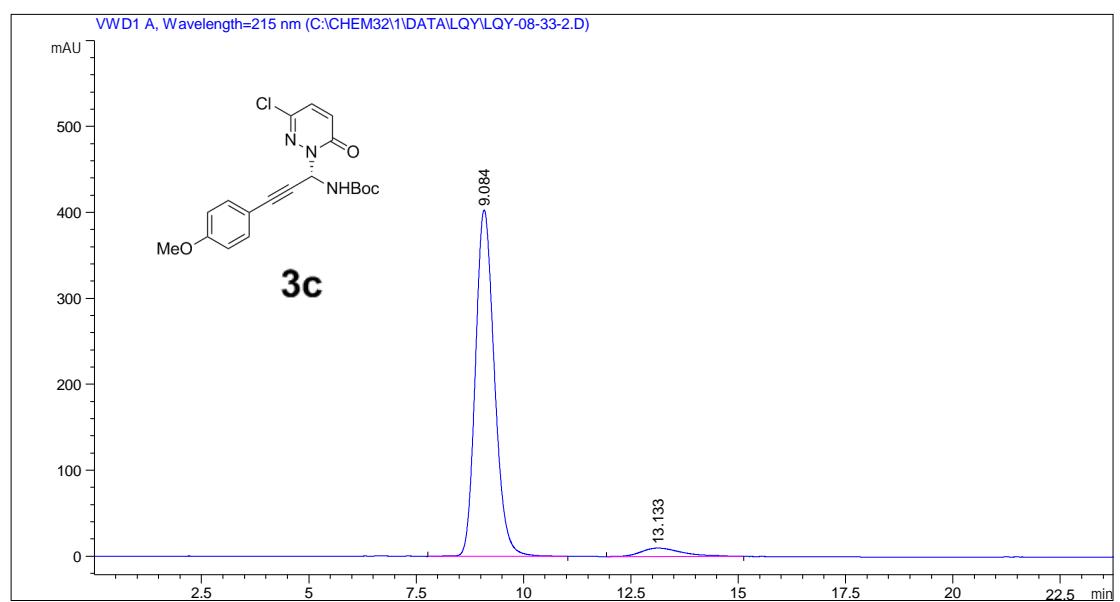


DYU	FYhH	aY	HhdY	KJ	Xh\	5f	YU	5f	YU	<Y>	\h	5f	YU
#	[m i n]		[m i n]		[mAU*s]		[mAU]		%				
1	11.074	BB	0.3775	2.61821e4	1073.	79468	97.	7482					
2	14.232	BB	0.6489	603.	15656	14.	24609	2.	2518				



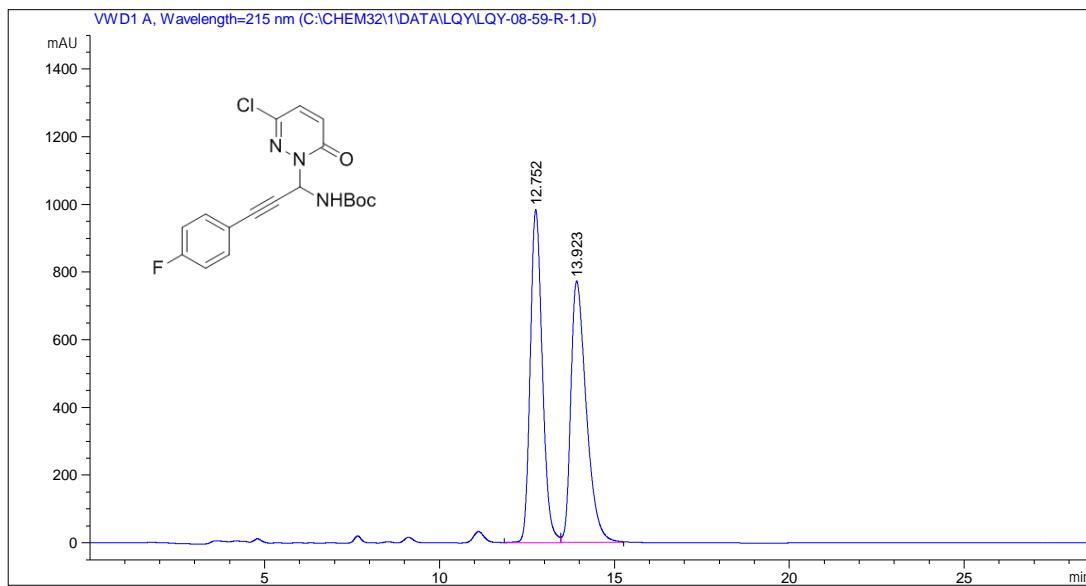
DYU\_ FYhH aY HhdY K] Xh\ \ \ \ \ \ 5f YU \ \ \ \ \ \ <Y] [\h\ \ \ \ \ \ 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%	
1	9.088	BB	0.4817	1.22173e4	391.94629	50.2893
2	12.780	BB	0.9601	1.20768e4	189.36020	49.7107



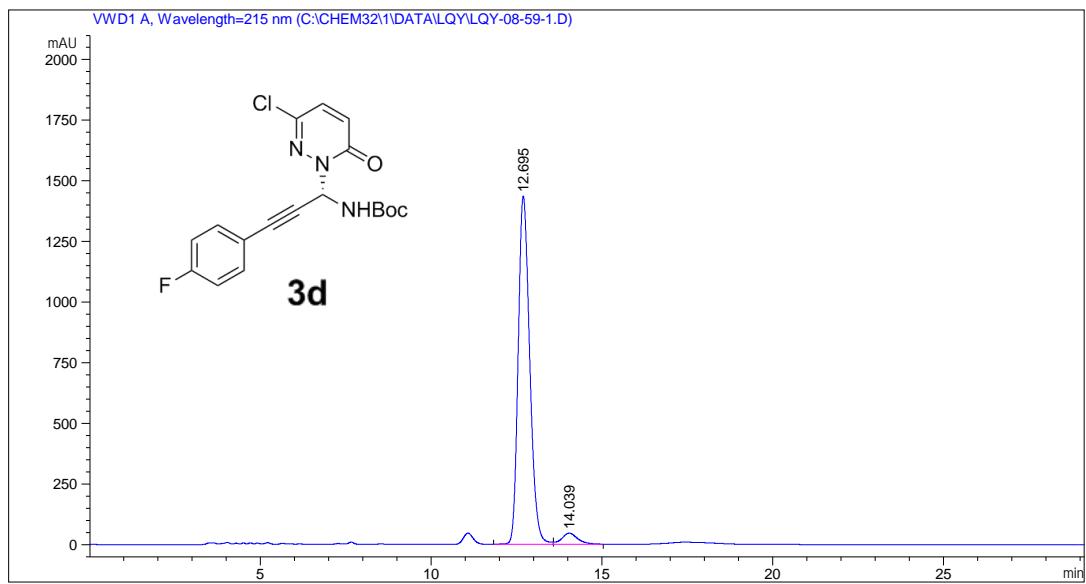
DYU\_ FYhH aY HhdY K] Xh\ \ \ \ \ \ 5f YU \ \ \ \ \ \ <Y] [\h\ \ \ \ \ \ 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%	
1	9.084	BB	0.4753	1.23838e4	403.28482	94.9234
2	13.133	BB	0.9599	662.29431	9.81979	5.0766



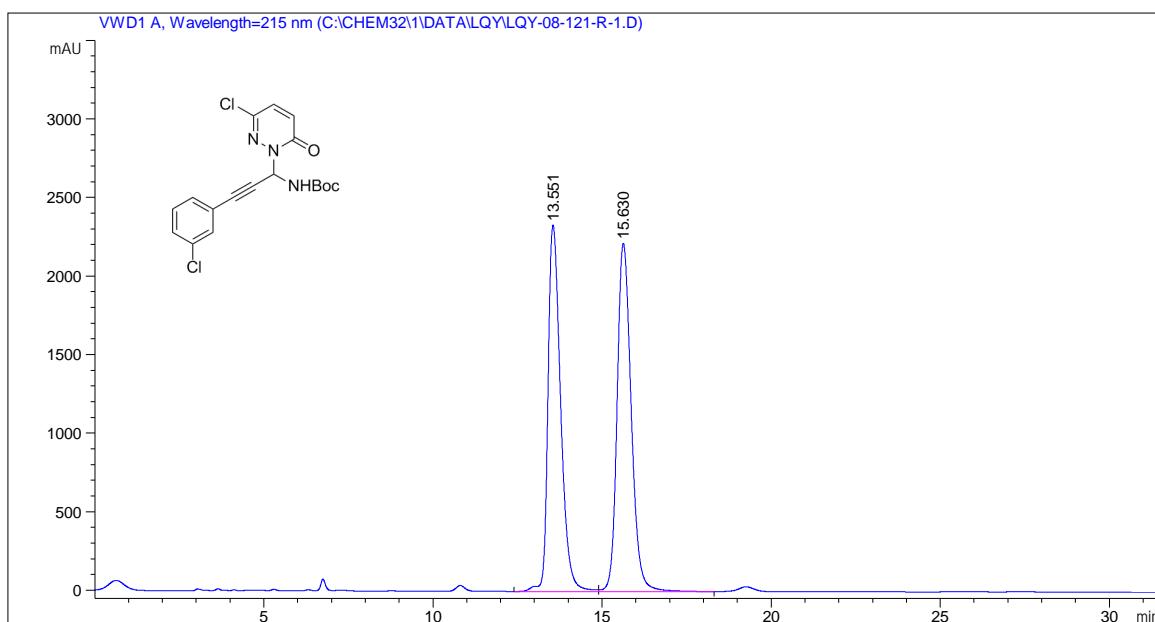
DYU\_·FYhH]aY HhdY ·K]Xh\ · · · 5f YU · · · <Y] [\h · · · 5f YU

#	[min]	[min]	[mAUs]	[mAUs]	%
1	12.752	VV	0.3719	2.37278e4	985.34229
2	13.923	MM	0.5121	2.37289e4	772.22656

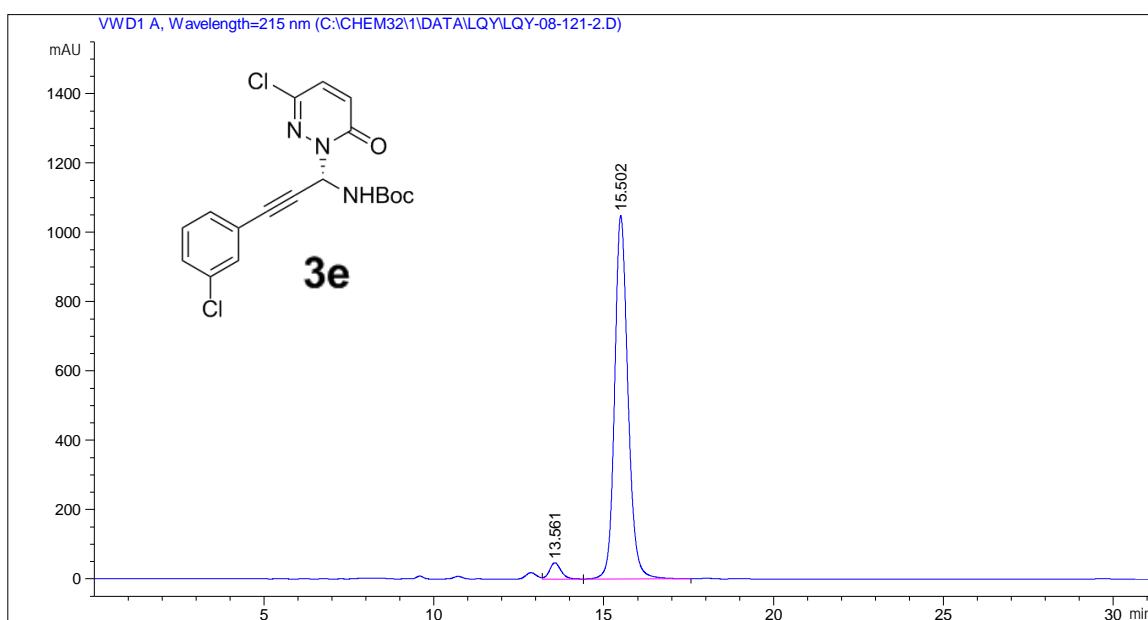


DYU\_·FYhH]aY HhdY ·K]Xh\ · · · · 5f YU · · · · <Y] [\h · · · · 5f YU

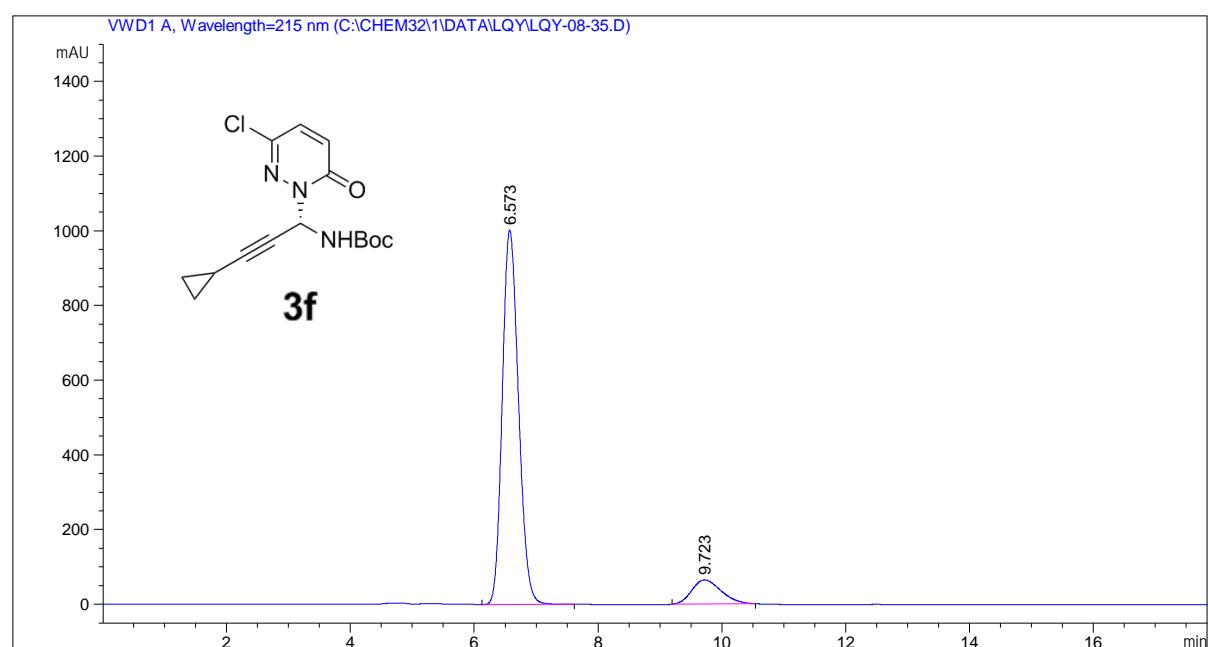
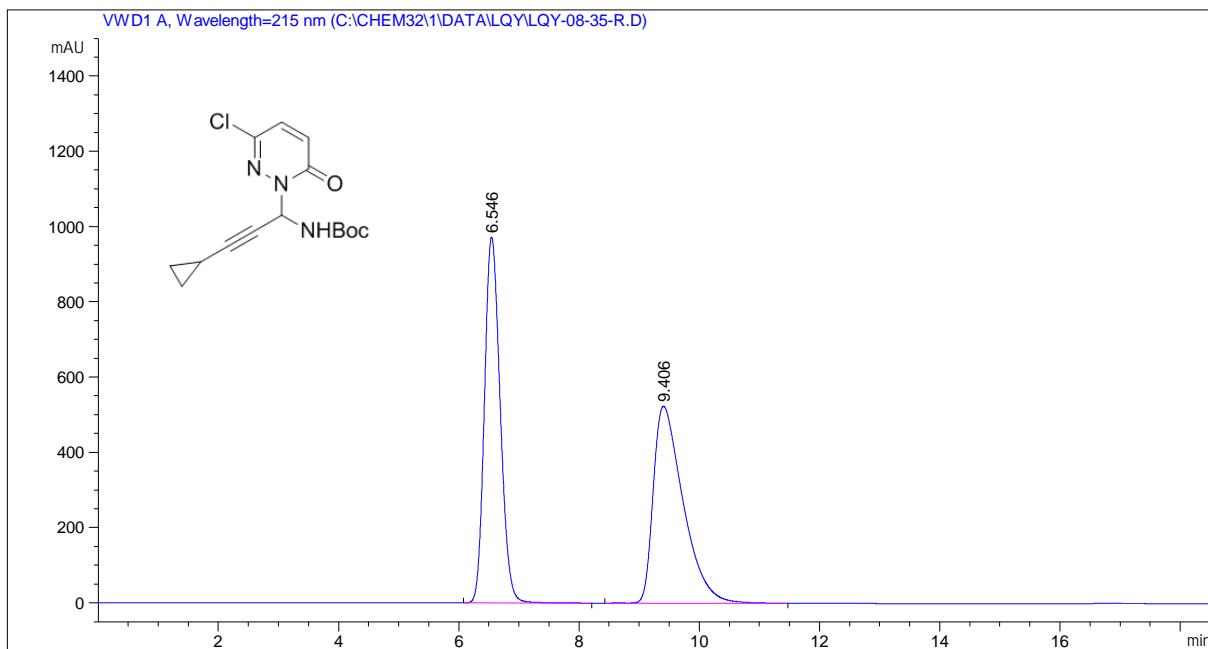
#	[mi n]	[mi n]	[mAU*s]	[mAU]	%
1	12.695 MM	0.3900	3.36248e4	1437.00769	95.6994
2	14.039 MM	0.5489	1511.06738	45.88544	4.3006

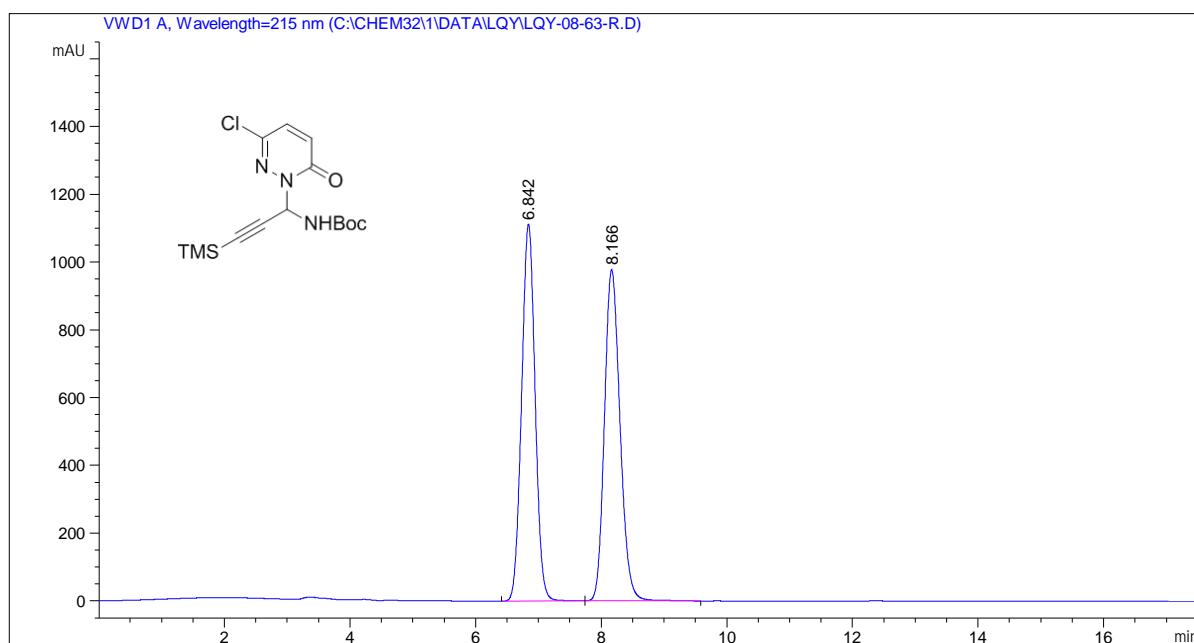


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.551	VV R	0.3982	6.05814e4	2331.77954	48.5467
2	15.630	VB	0.4480	6.42085e4	2216.45508	51.4533



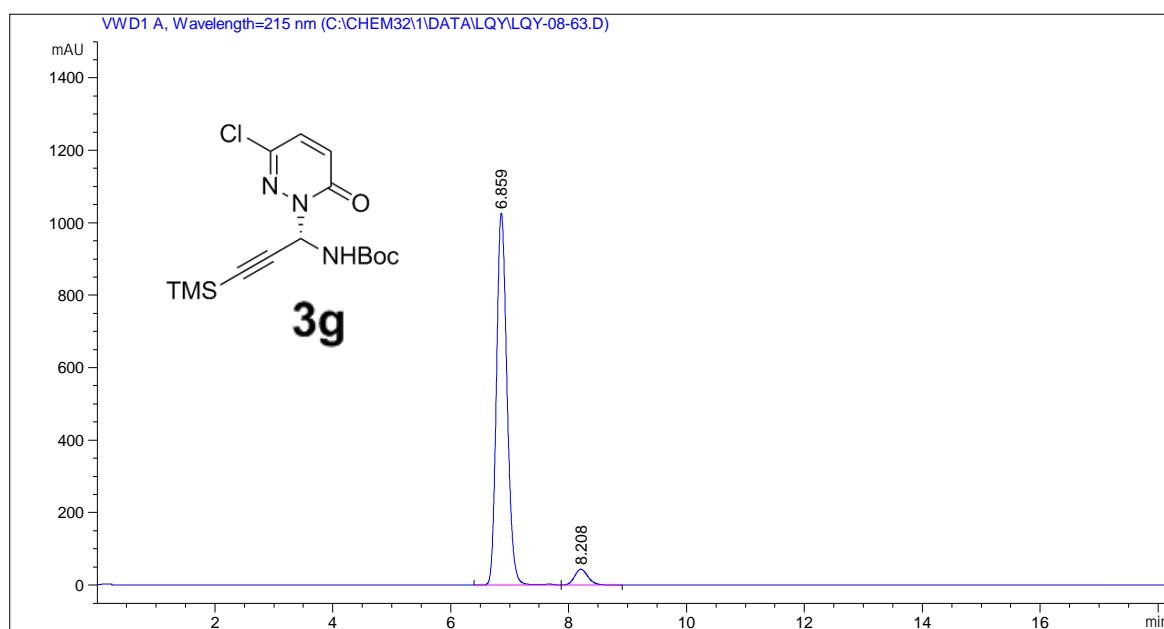
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.561	VB	0.3563	1101.51282	47.19630	3.7118
2	15.502	BB	0.4159	2.85748e4	1048.71362	96.2882





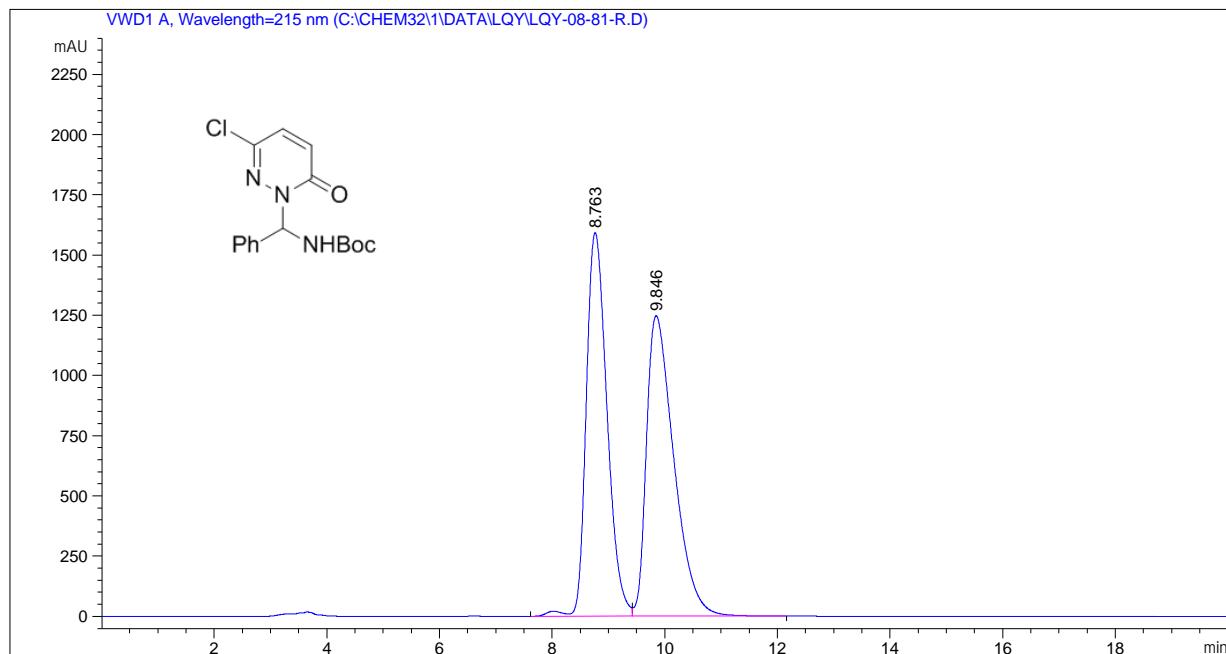
DYU\_FYhH aY HhdY KjXh\ 5f YU <Y] [\h 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%
1	6.842	BB	0.2322	1.66073e4	1112.35486 49.6510
2	8.166	BB	0.2670	1.68408e4	977.25244 50.3490

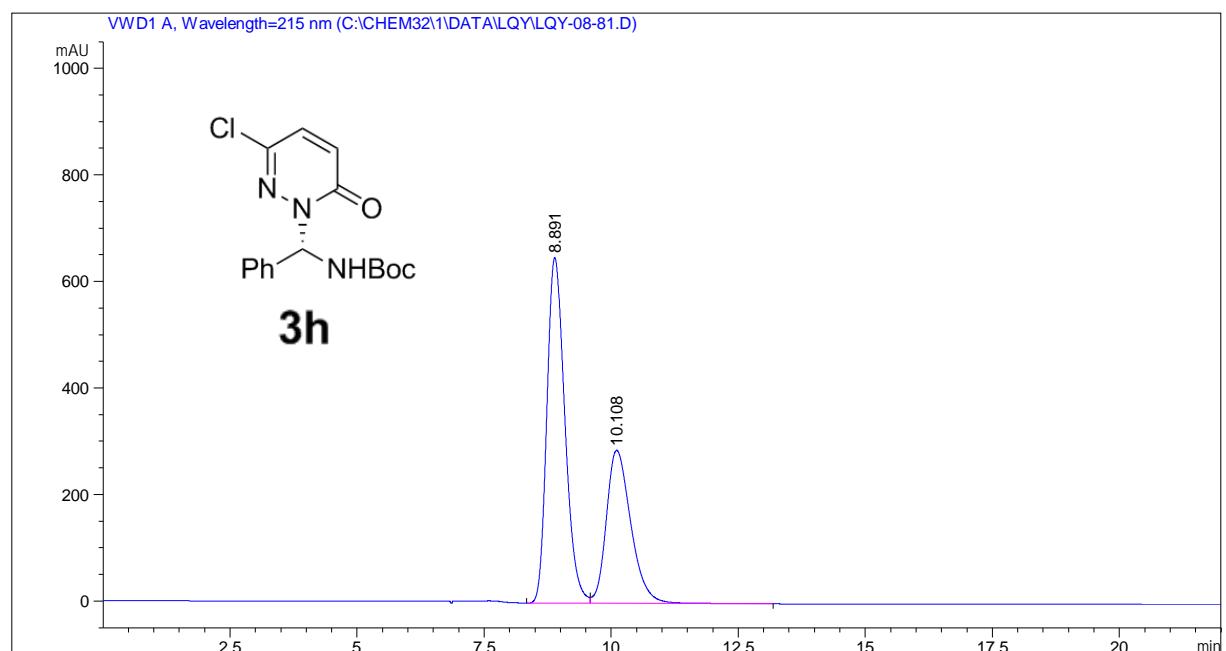


DYU\_FYhH aY HhdY KjXh\ 5f YU <Y] [\h 5f YU

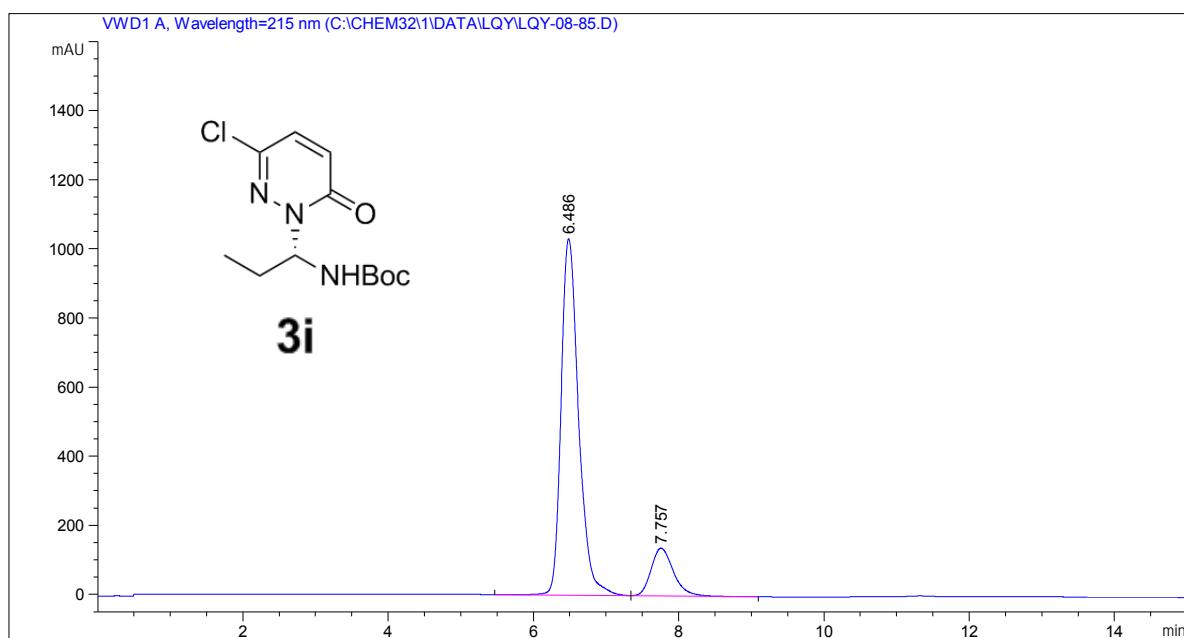
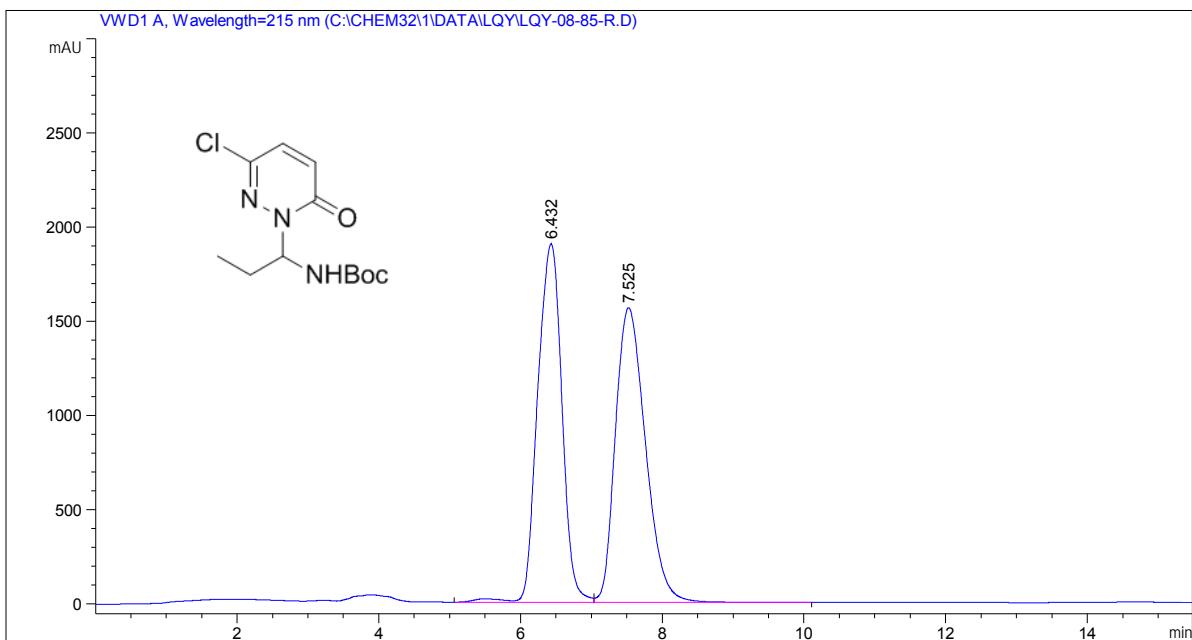
#	[min]	[min]	[mAU*s]	[mAU]	%
1	6.859	BV R	0.1930	1.27776e4	1026.81482 94.8457
2	8.208	VB	0.2457	694.38489	43.62417 5.1543

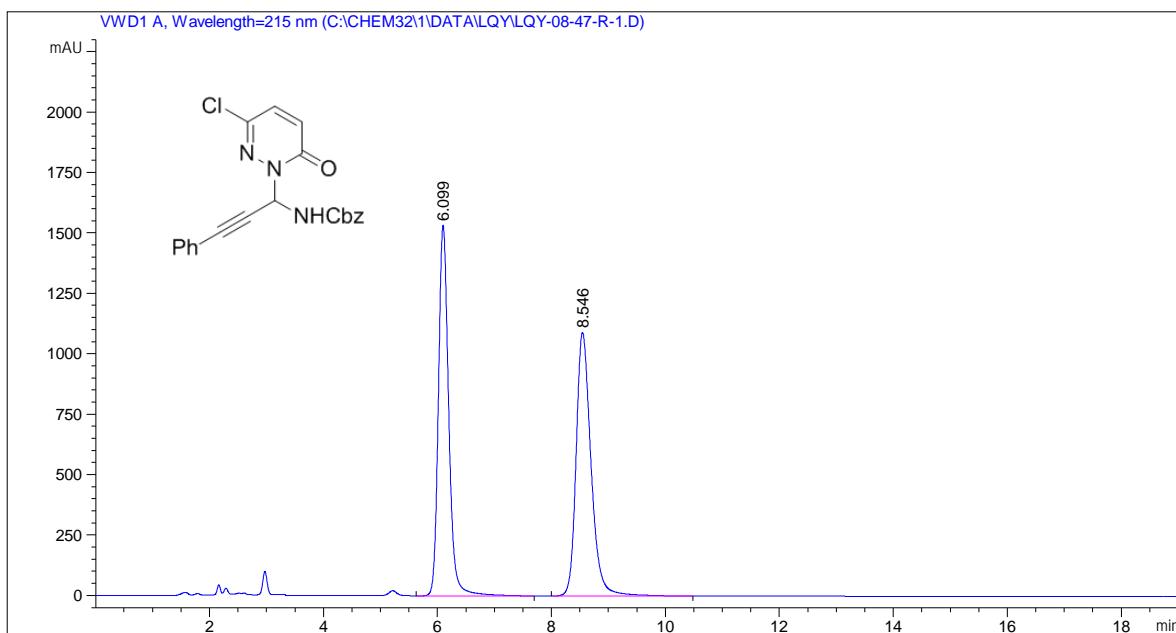


DYU_ · FYhH aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU					
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.763	VW R	0.3982 4.08560e4	1592.40771	49.2159
2	9.846	VB	0.5173 4.21579e4	1247.26355	50.7841

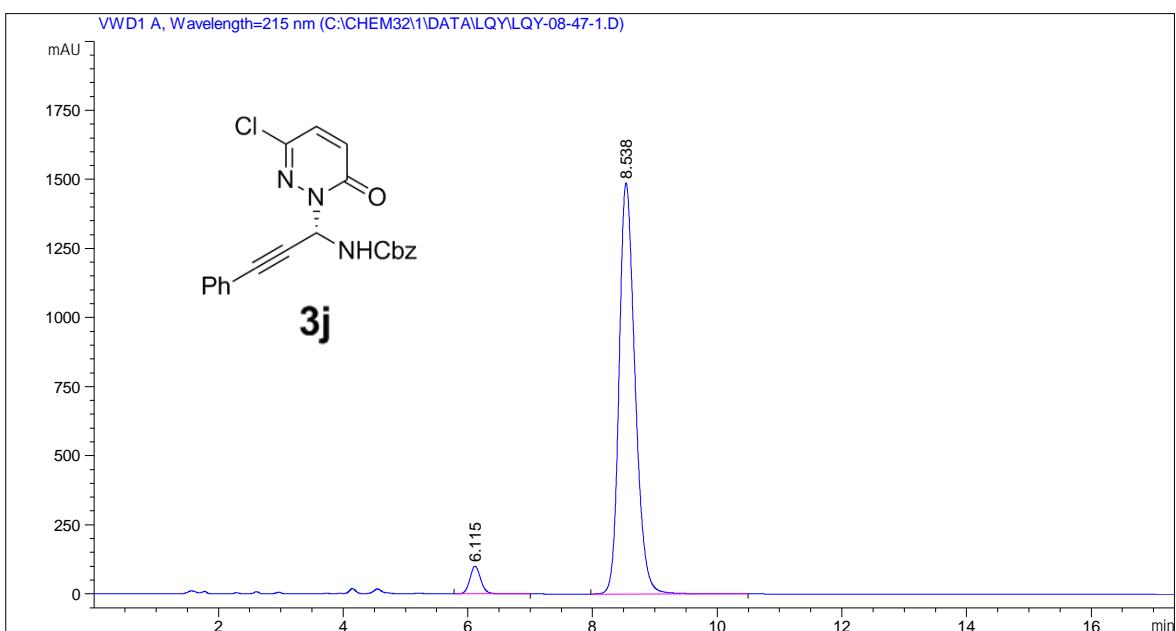


DYU_ · FYhH aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU					
#	[min]	[min]	[mAU*s]	[mAU]	%
1	8.891	BV	0.3809 1.59569e4	648.88745	62.2837
2	10.108	VB	0.5151 9662.78125	287.51392	37.7163

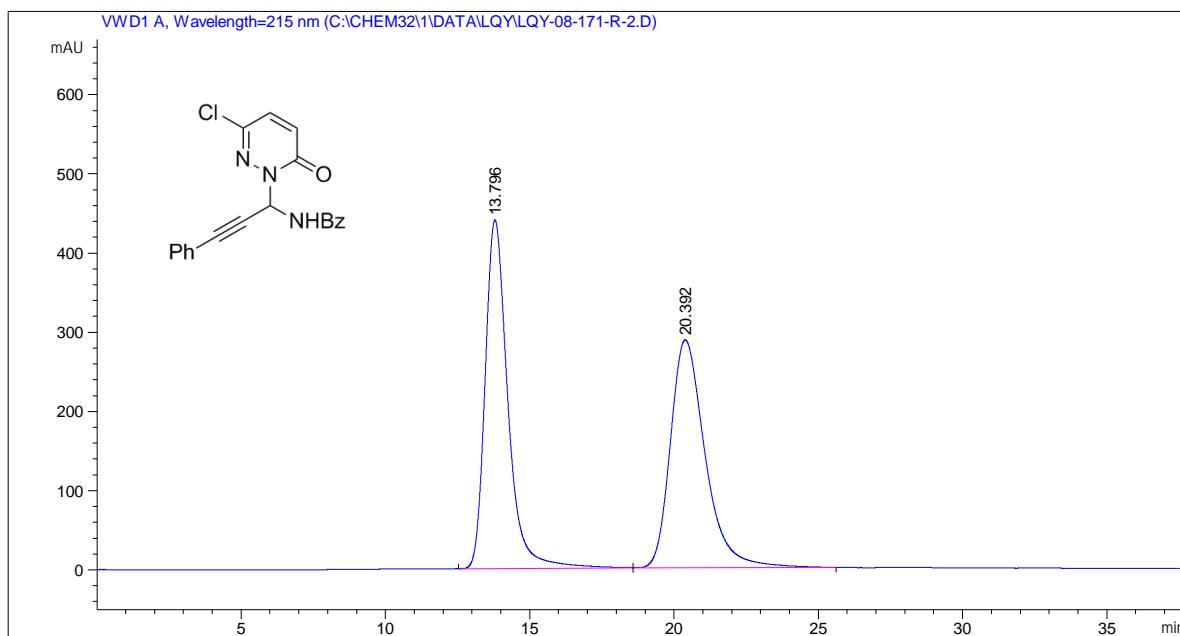




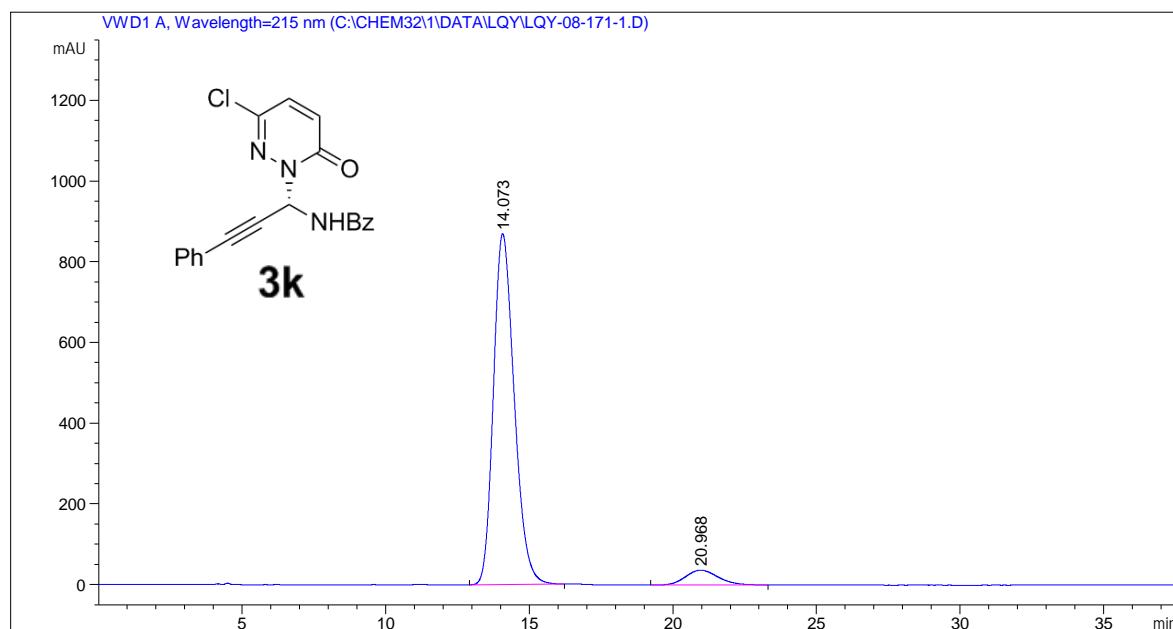
	DU	FYhH	aY	HhdY	KJXh	5f YU	<Y>	\h	5f YU
#	[m i n]	[m i n]	[mAU*s]	[mAU]					%
1	6.099	BB	0.1927	1.92867e4	1533.	41492	49.	3974	
2	8.546	BB	0.2765	1.97573e4	1089.	68945	50.	6026	



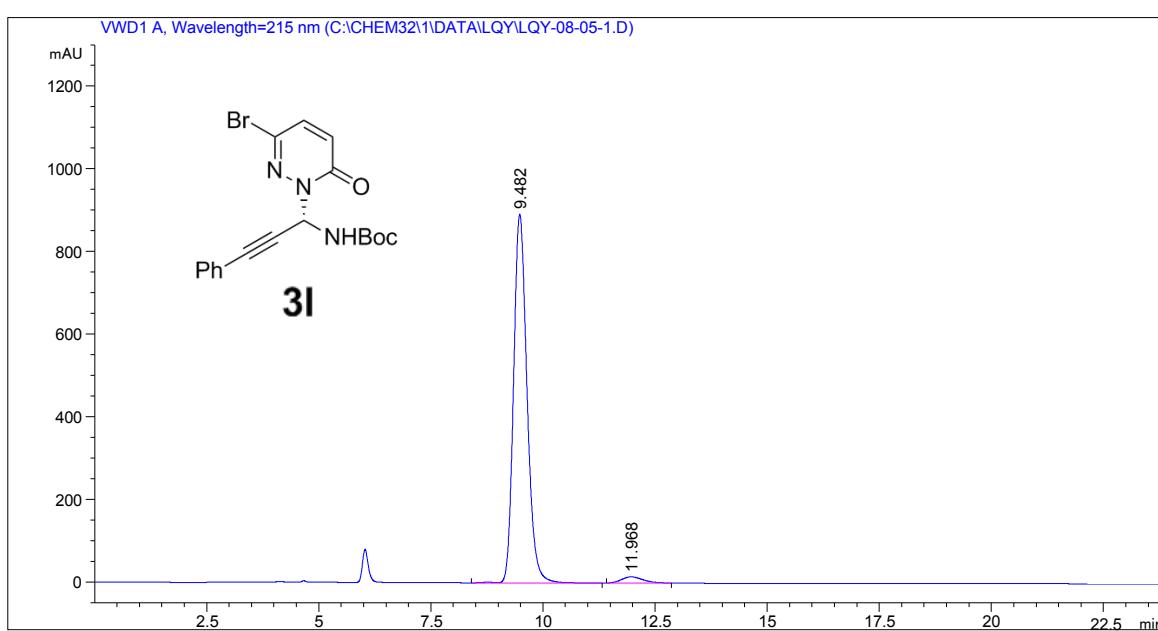
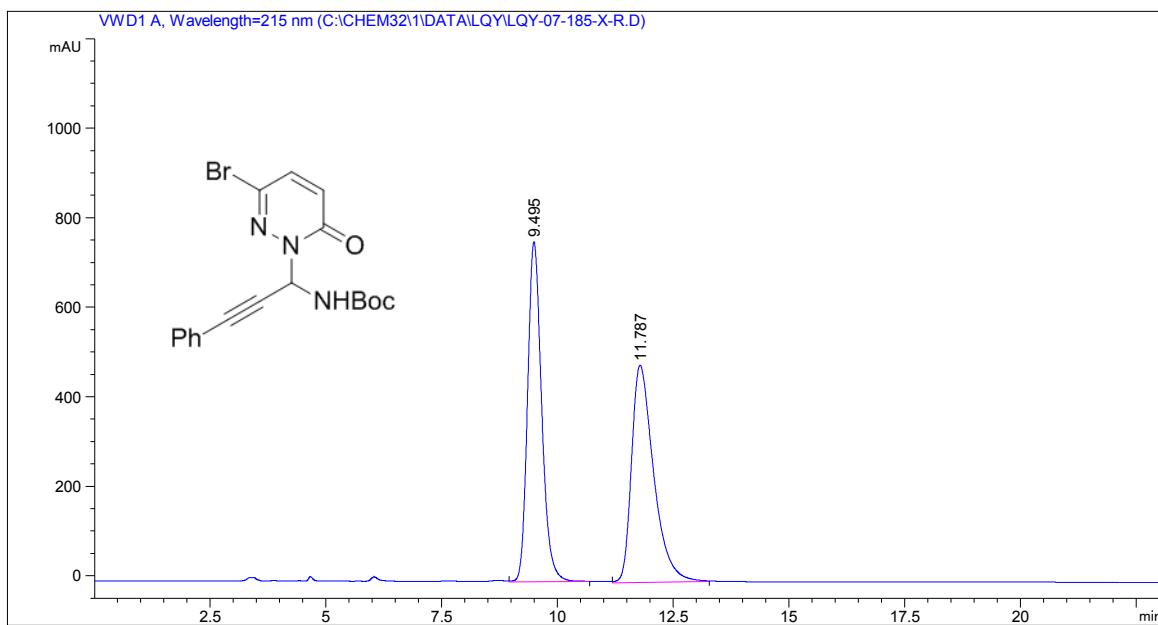
	DYU	FYH	HaY	HdY	KJXh\	5f YU	<Y>	\h	5f YU
#	[mIn]	[mIn]	[mAU*s]	[mAU]					%
1	6.115	BB	0.1861	1214.56812	100.	40508	4.	3998	
2	8.538	BB	0.2720	2.63904e4	1487.	71179	95.	6002	

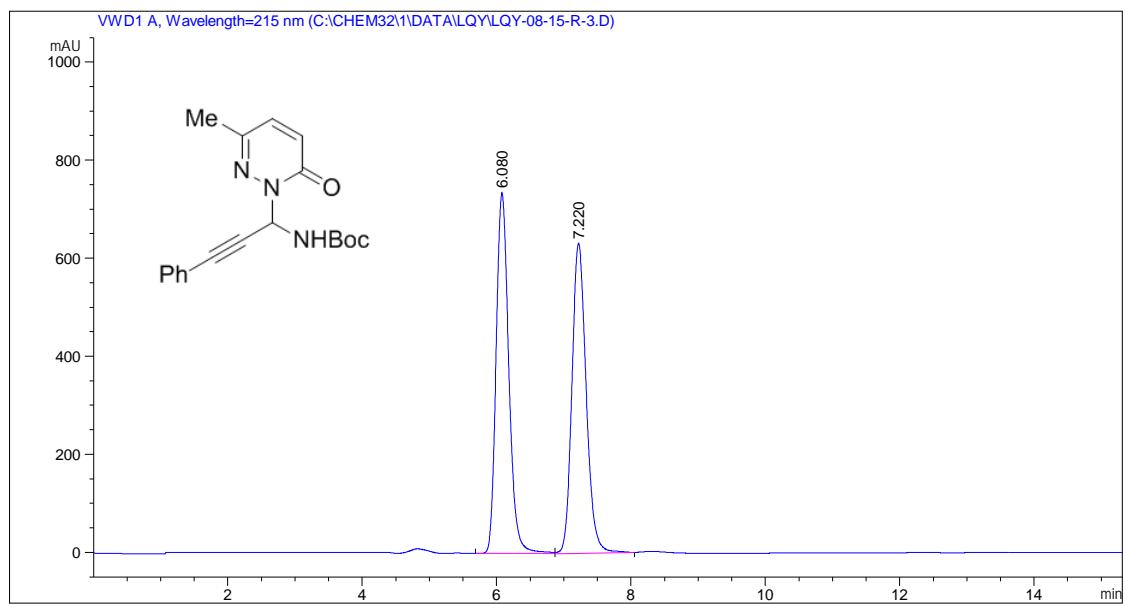


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.796	BB	0.8311	2.40085e4	440.35574	49.9961
2	20.392	BB	1.2674	2.40122e4	287.49829	50.0039



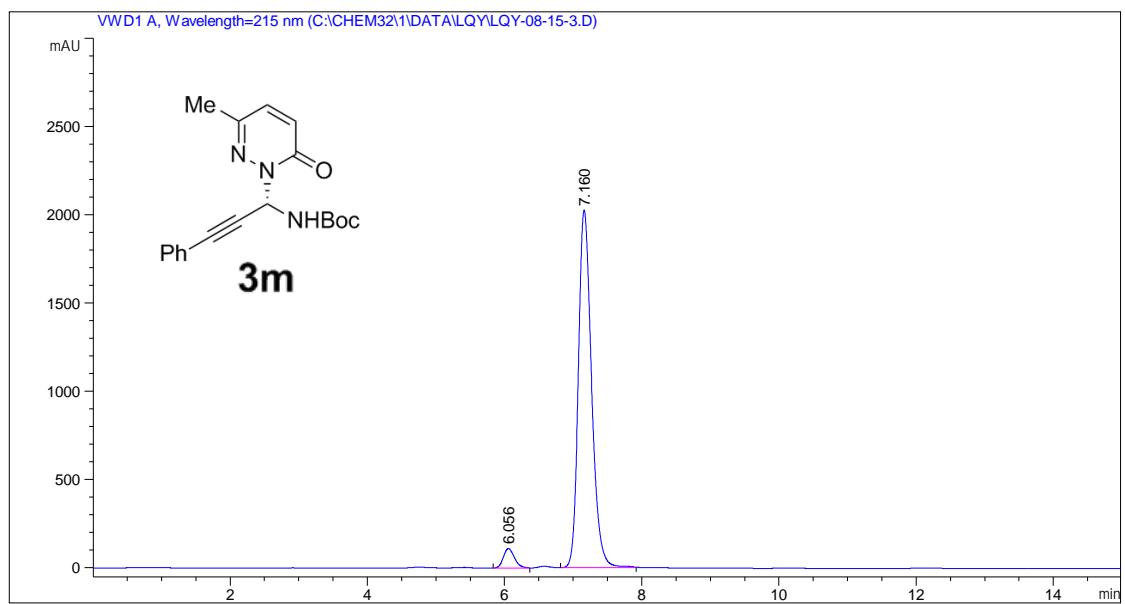
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.073	BB	0.7816	4.37153e4	869.48621	93.7963
2	20.968	BB	1.1839	2891.34961	36.74792	6.2037





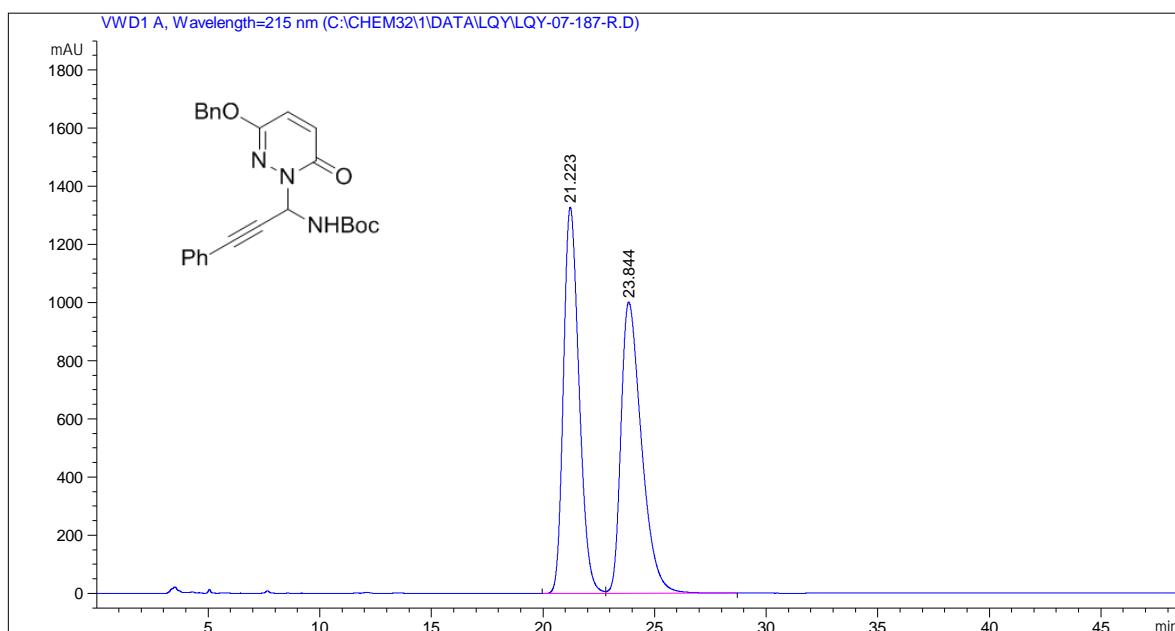
DYU\_ · FYhH] aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU

#	[min]	[min]	[mAUs]	[mAUs]	%	
1	6.080	BV	0.2028	9636.93945	735.68634	50.7219
2	7.220	MM	0.2466	9362.63770	632.67725	49.2781

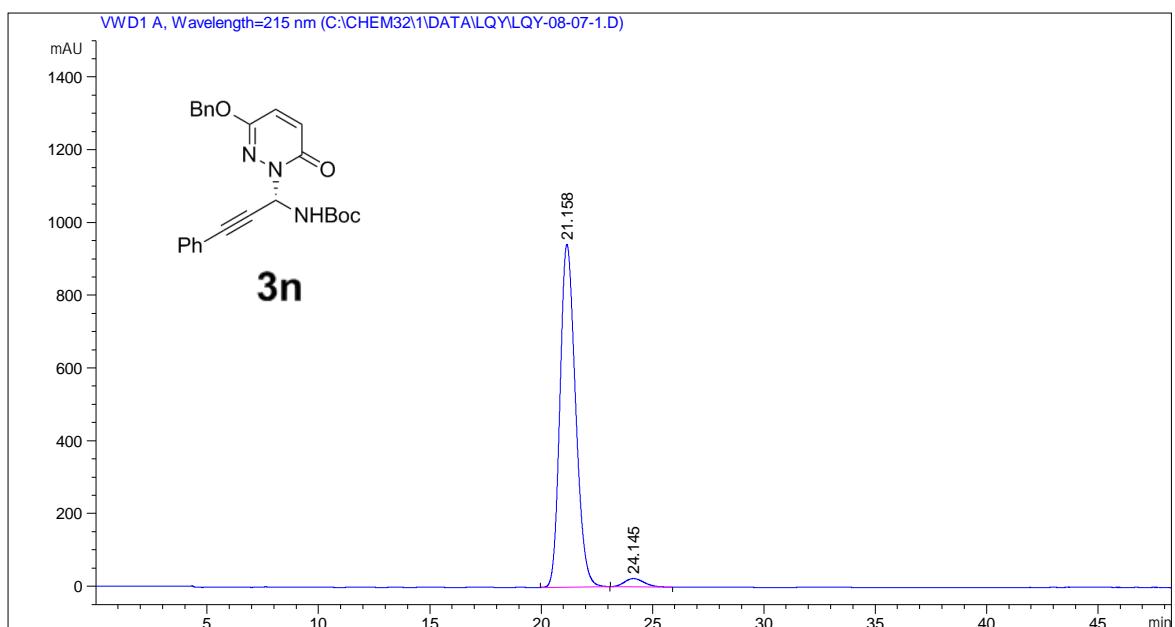


DYU\_ · FYhH] aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU

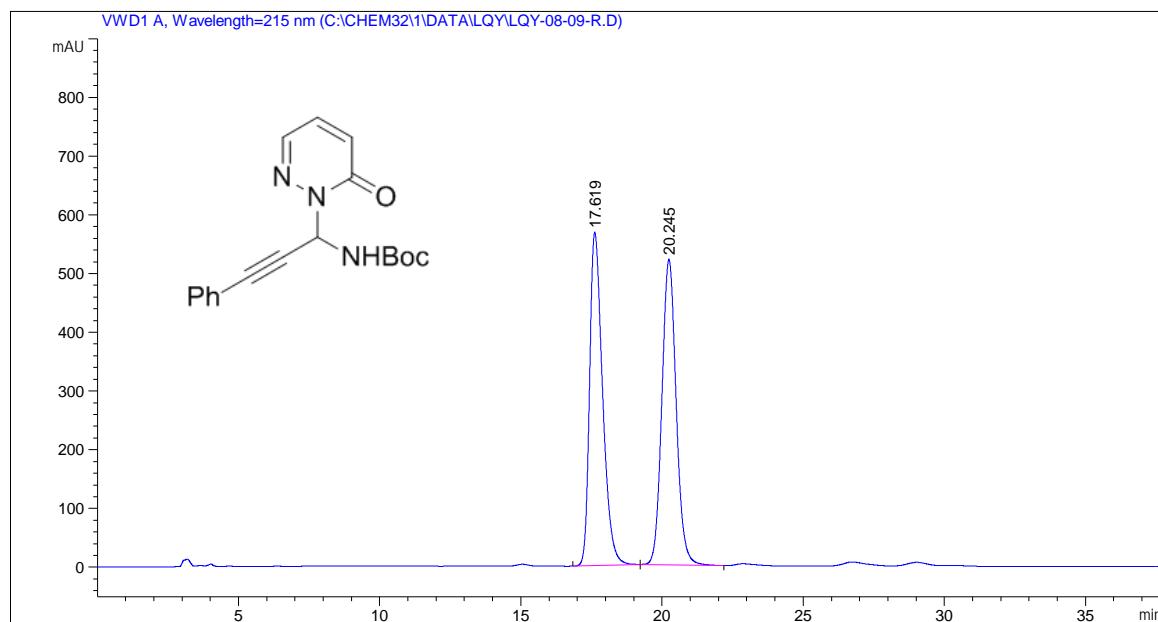
#	[min]	[min]	[mAUs]	[mAUs]	%
1	6.056 MM	0.1853	1226.41675	110.30167	4.3519
2	7.160 MM	0.2219	2.69548e4	2024.46106	95.6481



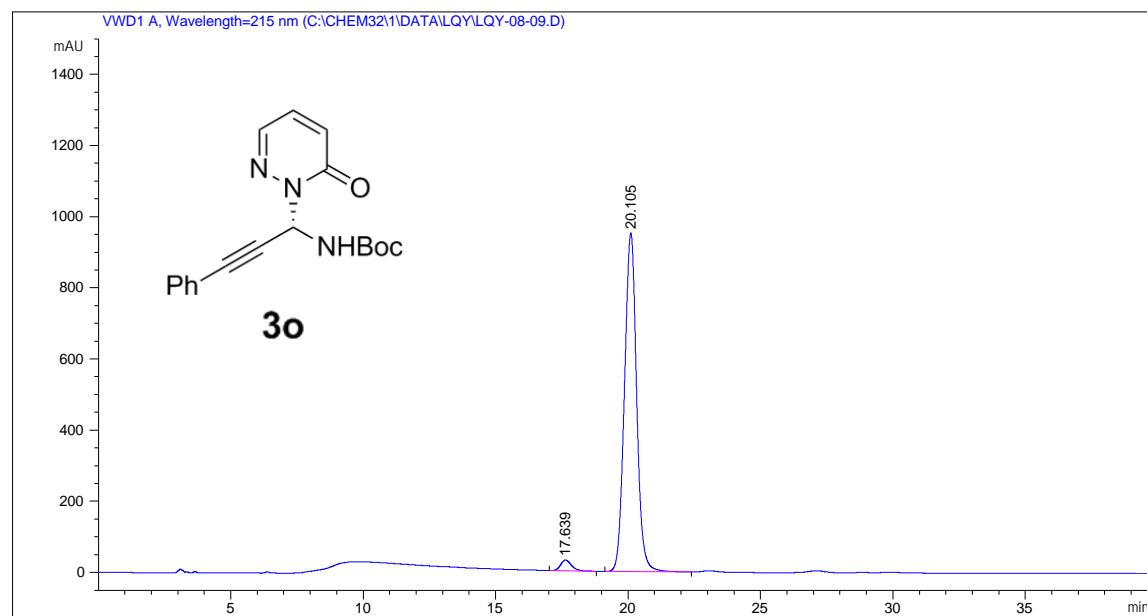
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.223	BV	0.7520	6.44654e4	1328.69922	50.1330
2	23.844	VB	0.9757	6.41235e4	1001.86029	49.8670



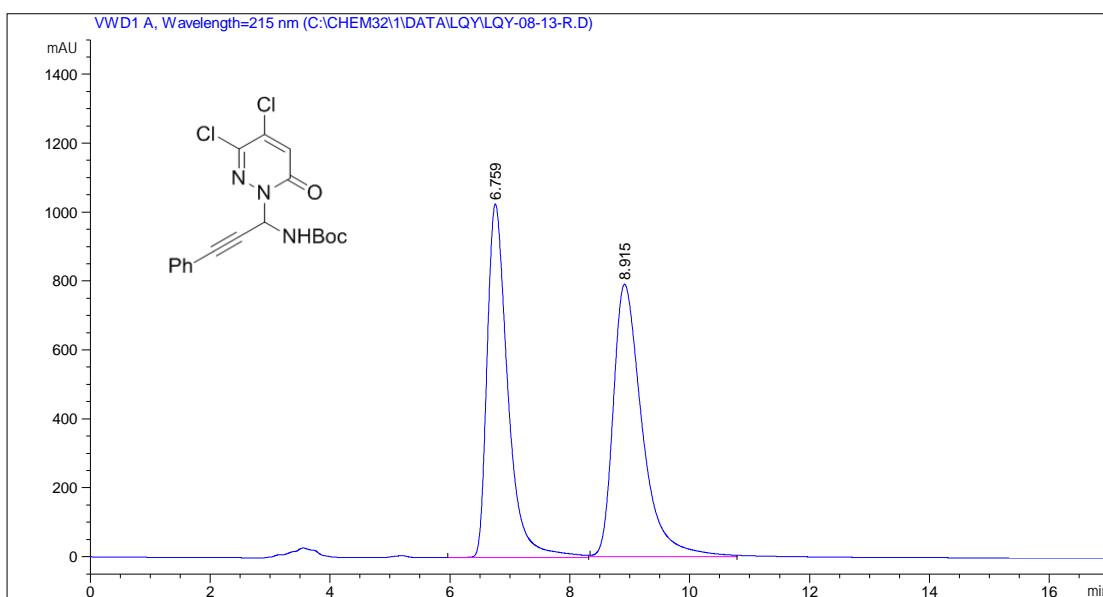
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.158	BB	0.7504	4.56736e4	942.41882	97.0787
2	24.145	BB	0.9230	1374.42297	22.71358	2.9213



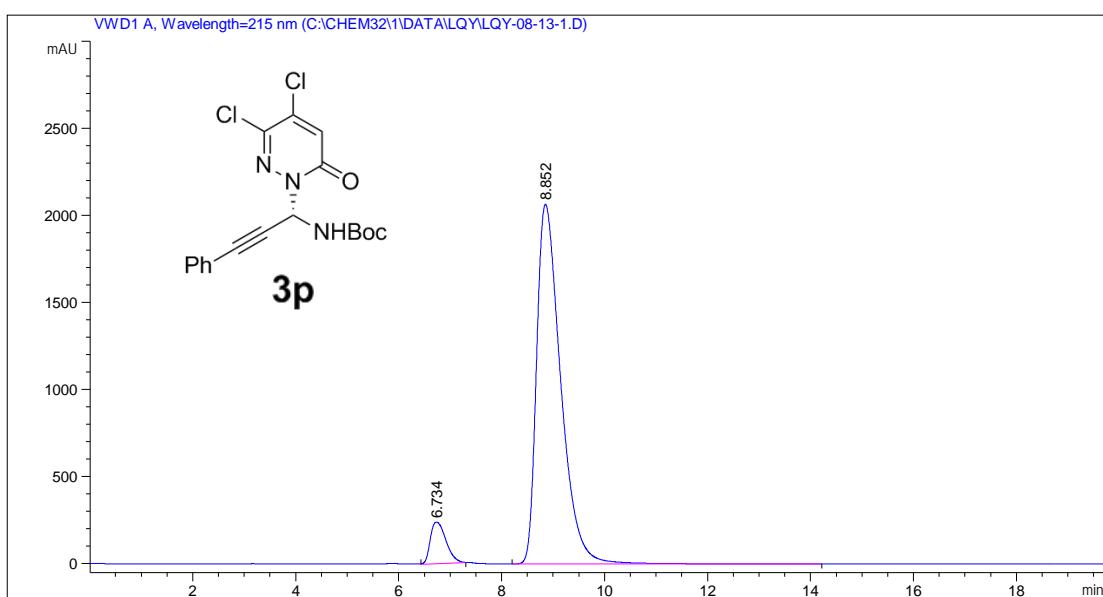
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.619	BB	0.4874	1.81186e4	567.64630	49.8163
2	20.245	BB	0.5433	1.82523e4	520.20465	50.1837



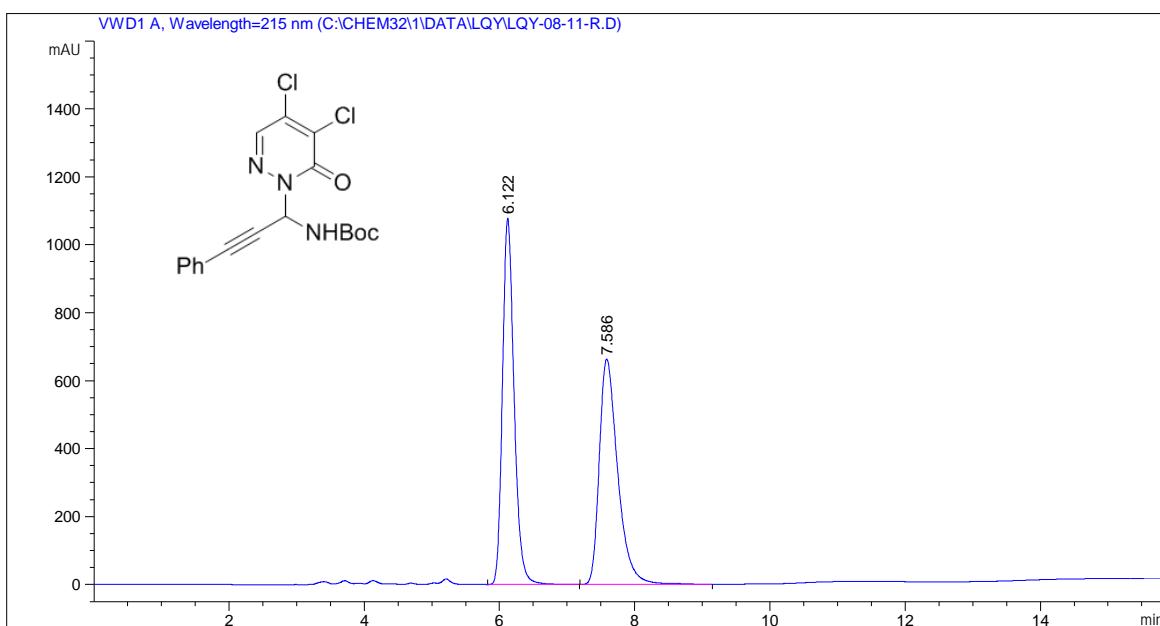
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.639	BB	0.4345	861.66656	30.23155	2.7676
2	20.105	BB	0.4942	3.02721e4	951.46997	97.2324



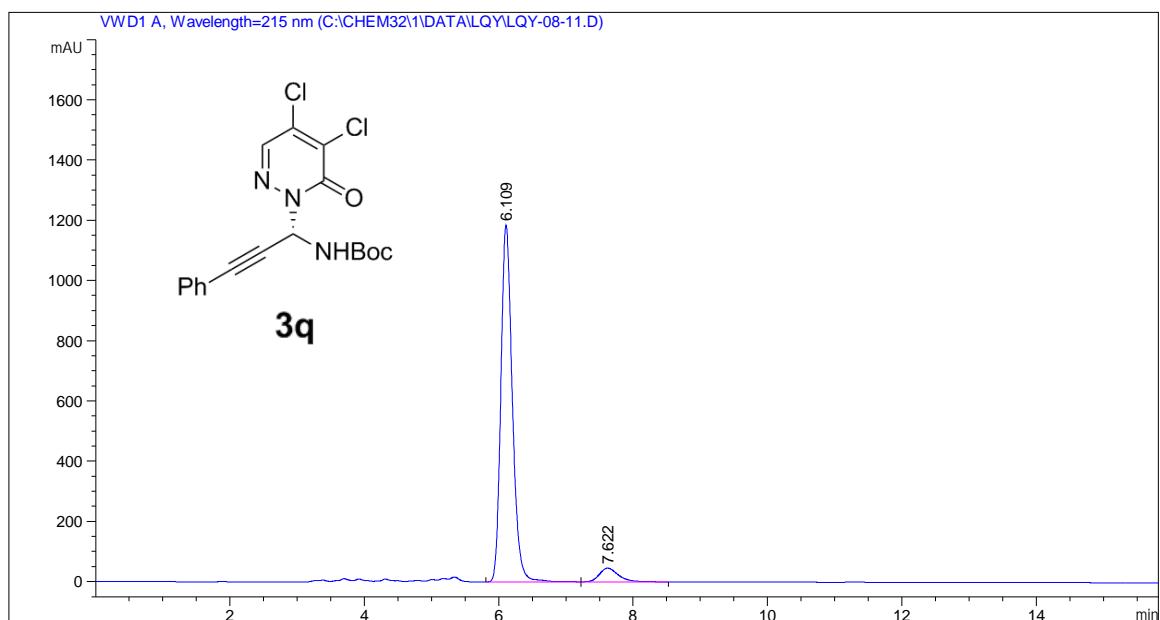
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6. 759	BV	0. 3671	2. 46307e4	1025. 82715	48. 2583
2	8. 915	MM	0. 5570	2. 64085e4	790. 22650	51. 7417



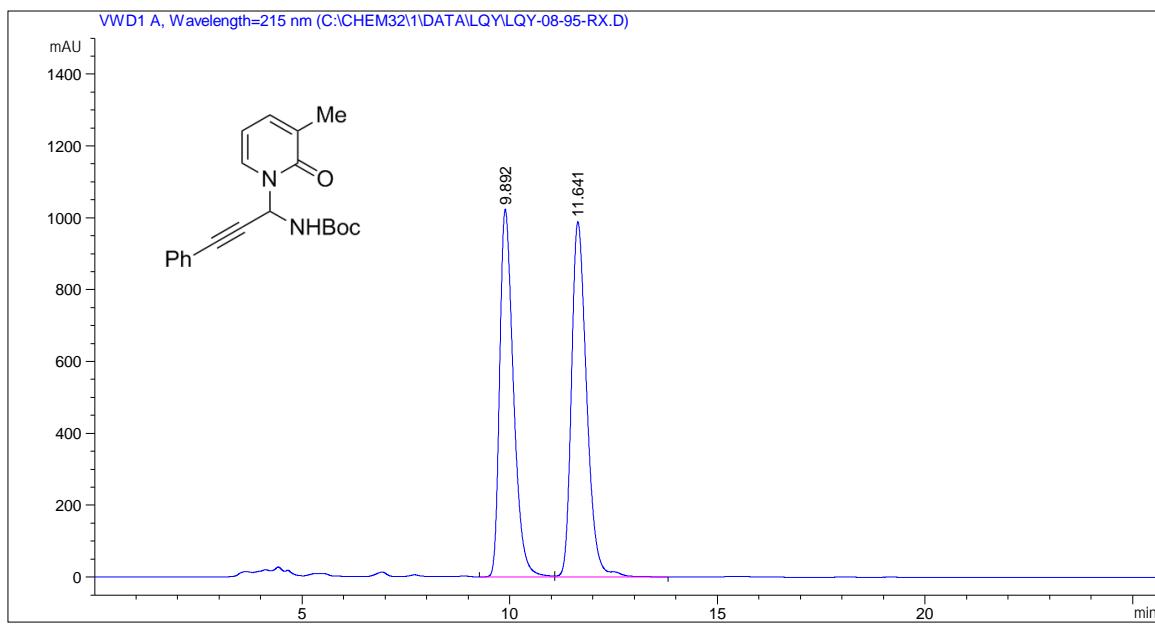
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6. 734	MM	0. 3537	5093. 09863	239. 99750	7. 0609
2	8. 852	BB	0. 4958	6. 70378e4	2064. 76172	92. 9391



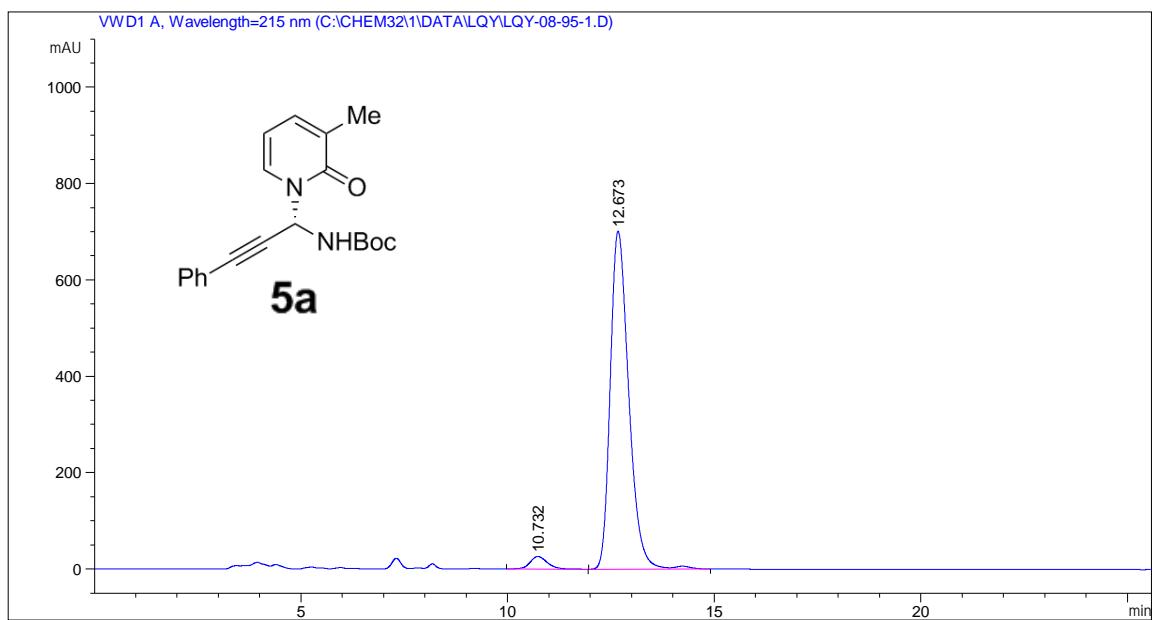
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6. 122	BB	0. 1823	1. 28656e4	1077. 32642	50. 5592
2	7. 586	BV R	0. 2883	1. 25810e4	663. 24408	49. 4408



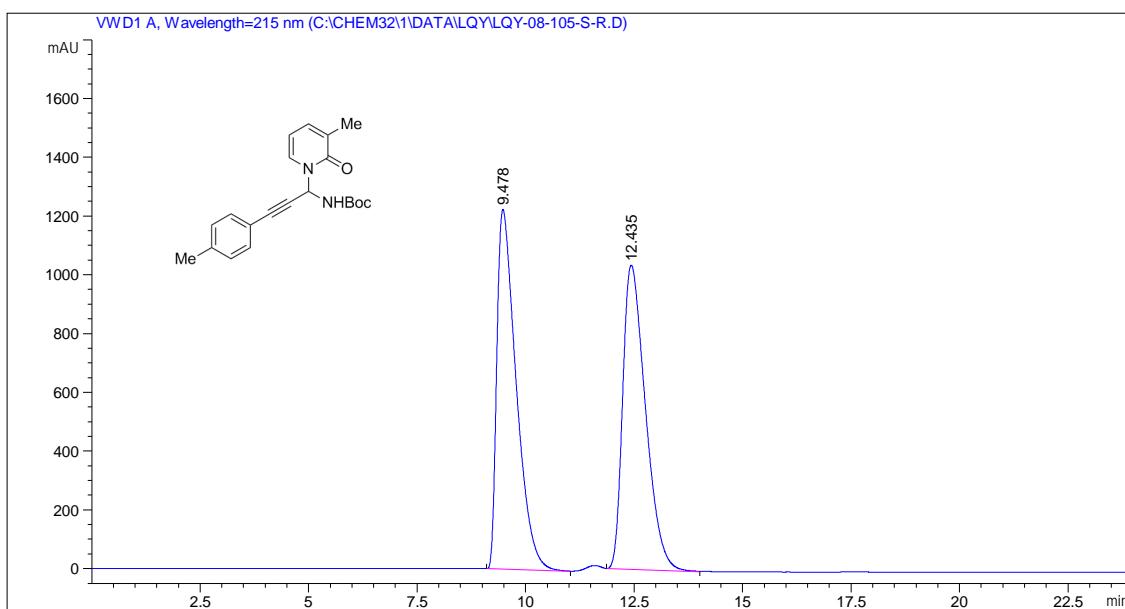
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6. 109	BV	0. 1820	1. 40047e4	1184. 01758	93. 9780
2	7. 622	VB	0. 3002	897. 40613	45. 47625	6. 0220



DYU	FYH	aY	HdY	KJXh	5fYU	<Y>	\h	5fYU
#	[m i n]	[m i n]	[mAU*s]	[mAU]			%	
1	9.892	BV	0.3536	2.35565e4	1023.	03162	48.	3775
2	11.641	VV	R	0.3889	2.51366e4	988.	15271	51.6225

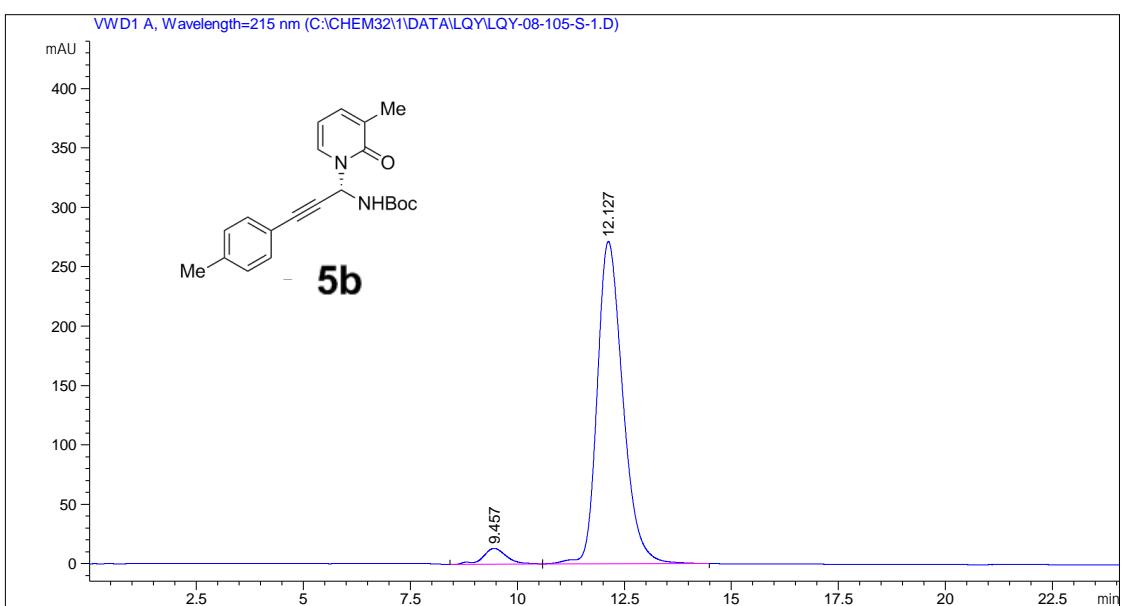


DUU	FYH	aY	HdY	KJ	Xh	5f	YU	<Y>	\h	5f	YU
#	[m i n]		[m i n]		[mAU*s]		[mAU]		%		
- - -   - - - -   - - -   - - - -   - - - - -   - - - -   - - - -											
1	10.732	BB	0.4510	780.	96393	26.	33418	3.	4528		
2	12.673	BV R	0.4752	2.	18376e4	701.	65155	96.	5472		



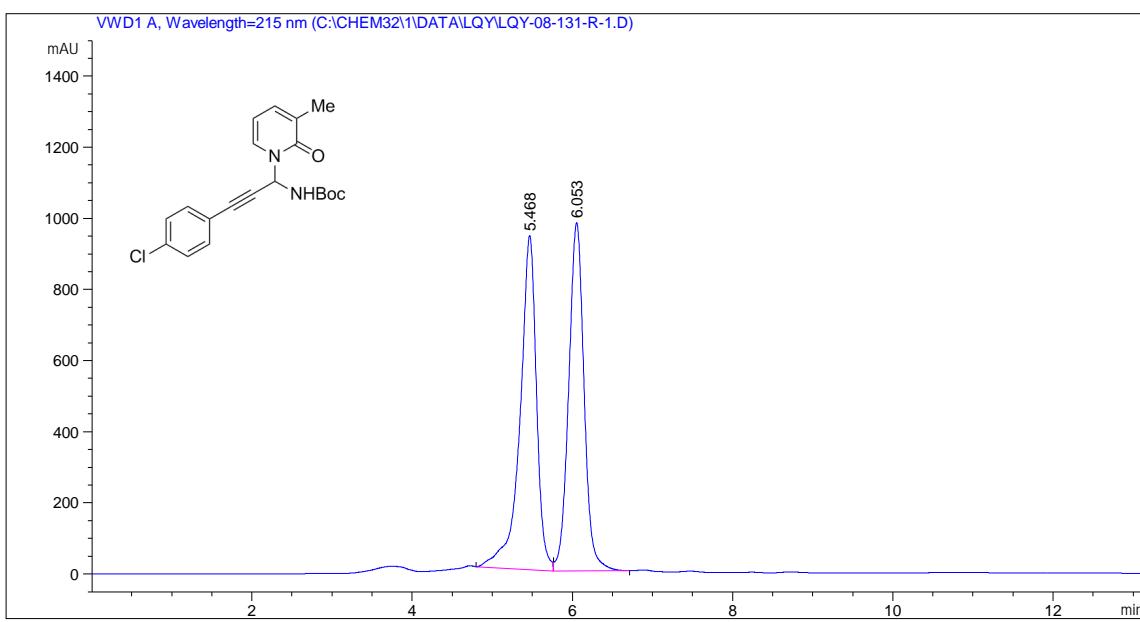
DYU\_FYhH aY HhdY KjXh\ \ \ \ \ \ 5f YU \ \ \ \ \ \ <Y] [ \h \ \ \ \ \ \ 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%
1	9.478	BB	0.4710	3.77713e4	1223.91370
2	12.435	MM	0.6061	3.76599e4	1035.52917

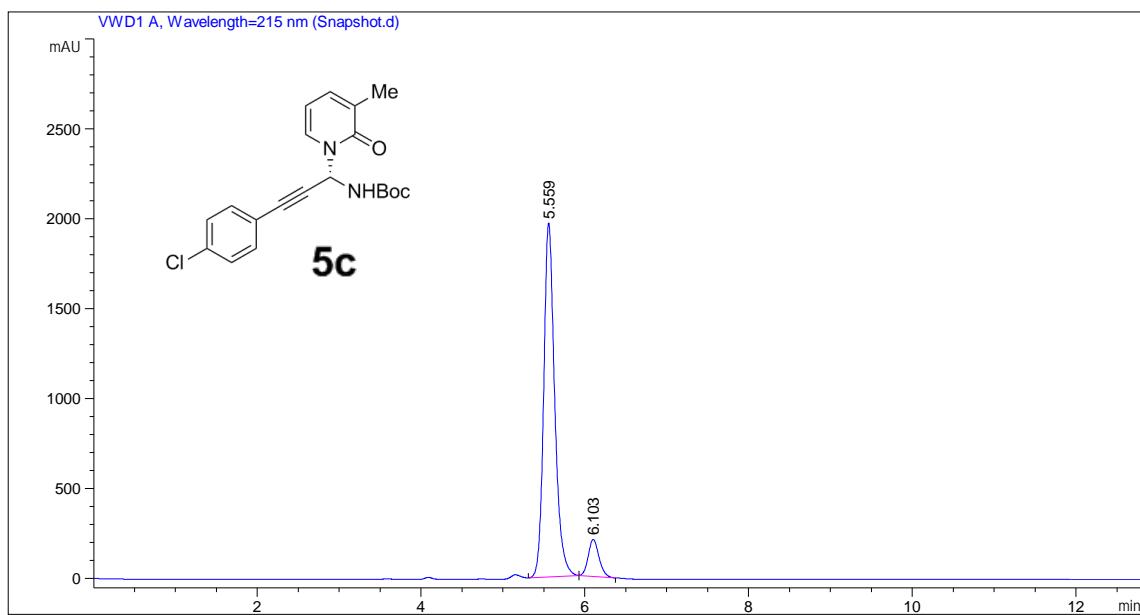


DYU\_FYhH aY HhdY KjXh\ \ \ \ \ \ 5f YU \ \ \ \ \ \ <Y] [ \h \ \ \ \ \ \ 5f YU

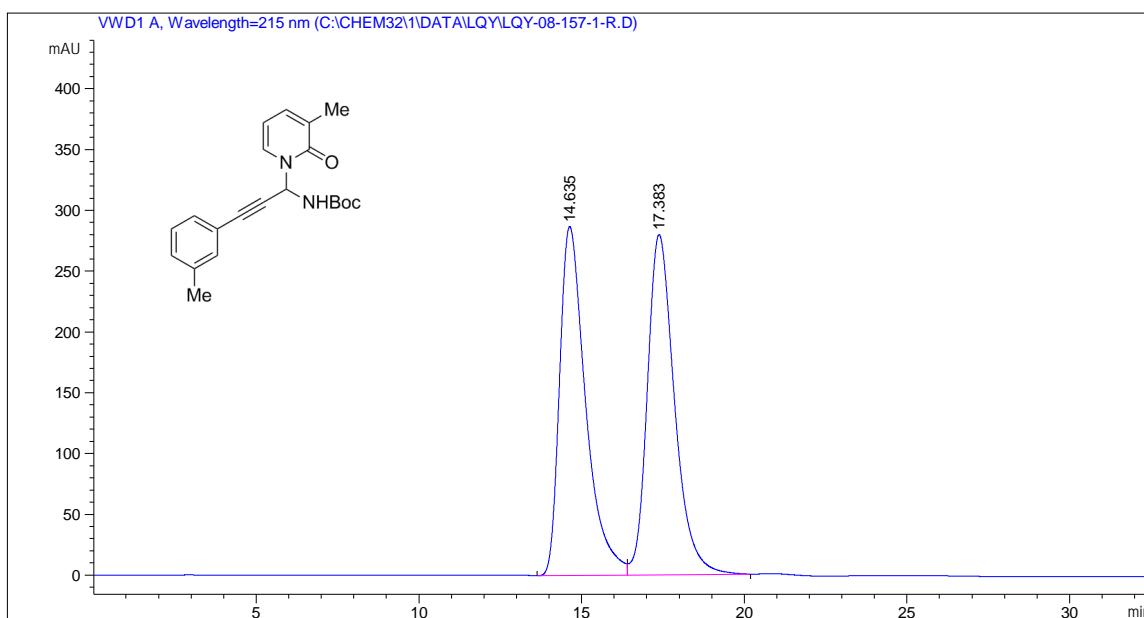
#	[min]	[min]	[mAU*s]	[mAU]	%
1	9.457	VB R	0.5679	505.45255	13.31378
2	12.127	BB	0.6398	1.12516e4	271.30576



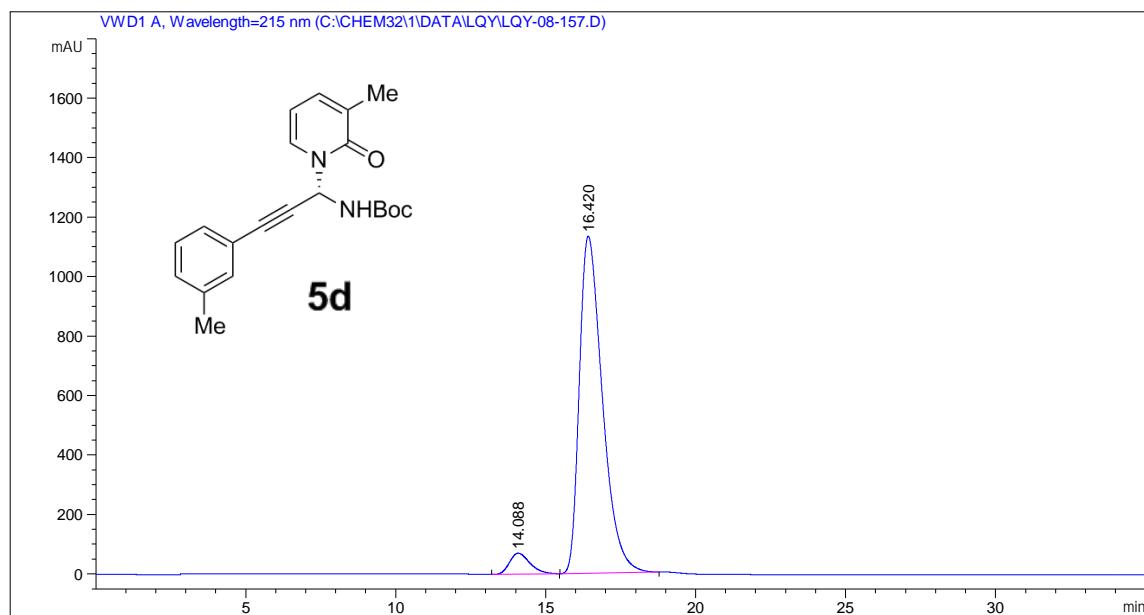
DYU	FYhH	aY	HdY	K	Xh\	5f	YU	<Y>	[\h	5f	YU
#	[min]	[min]				[mAU*s]	[mAU]				%
1	5.468	MM	0.2397	1.35316e4		940.	80920	50.	8477		
2	6.053	VB	0.2038	1.30805e4		979.	35138	49.	1523		



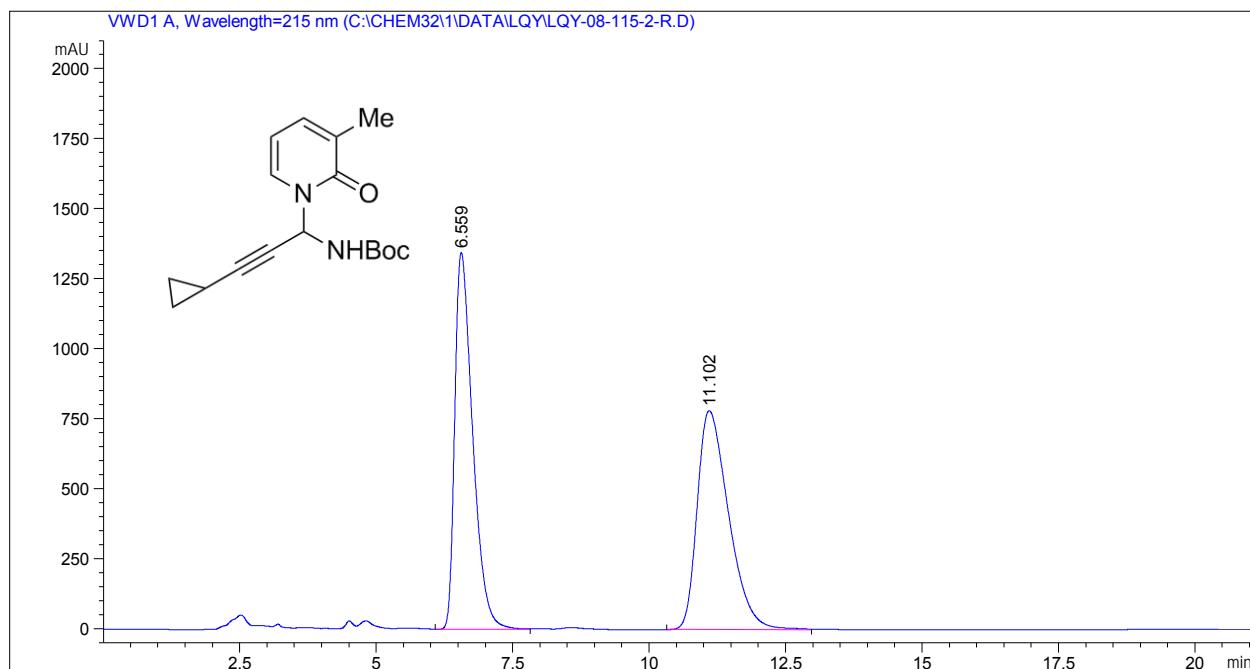
DYU	FYhH	aY	HhdY	KjXh\	5fYU	<Y>	\h	5fYU	
#	[min]		[min]	[mAU*s]	[mAU]		%		
1	5.559	MM	0.1549	1.82867e4	1967.	73901	90.	6805	
2	6.103	MM	0.1521	1879.	38477	205.	95634	9.	3195



DYU_<Y>[h]<Y>5f YU				
#	[min]	[min]	[mAU*s]	[mAU]
1	14.635	BV	0.8388 1.59665e4	287.09940 49.5697
2	17.383	VB	0.8883 1.62437e4	279.80981 50.4303



DYU_<Y>[h]<Y>5f YU				
#	[min]	[min]	[mAU*s]	[mAU]
1	14.088	BB	0.7265 3357.64209	70.77703 5.2640
2	16.420	BB	0.8240 6.04279e4	1133.43201 94.7360

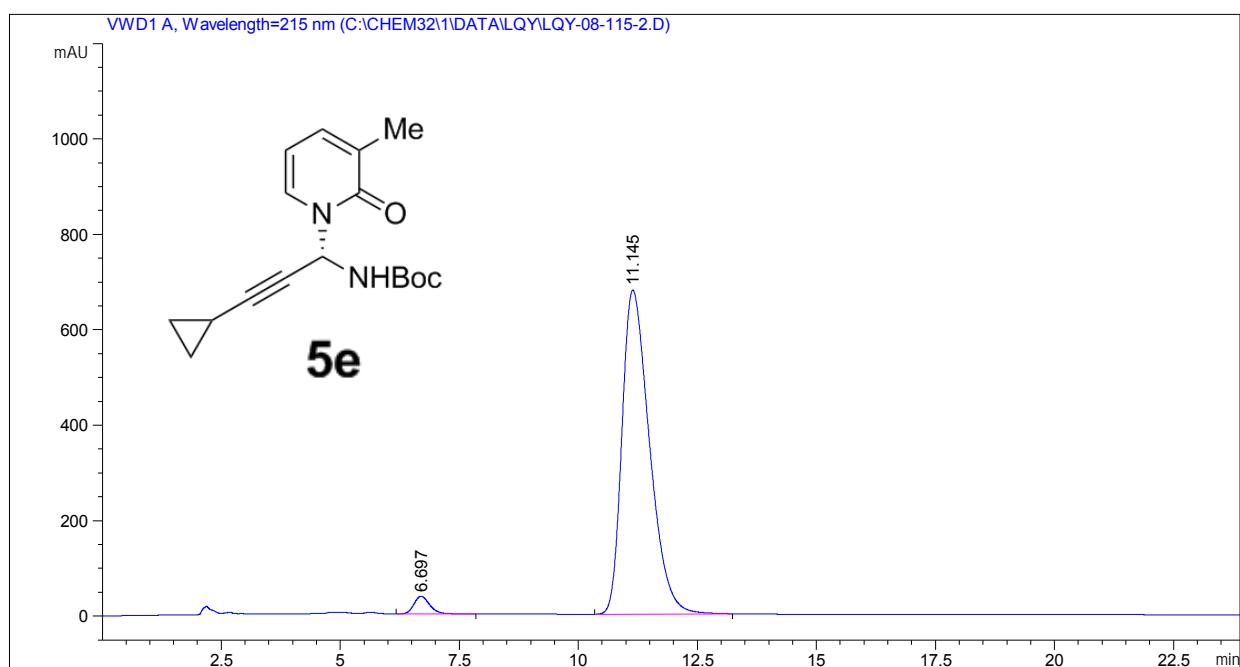


DYU\_ · FYhH] aY HhdY · K| Xh\ · · · 5f YU · · · · <Y| \h · · · · 5f YU

# [min] [min] [mAU\*s] [mAU] %

1 6.559 MM 0.3800 3.06810e4 1345.70300 49.4692

2 11.102 MM 0.6680 3.13394e4 781.96362 50.5308



DYU · FYhH] aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%
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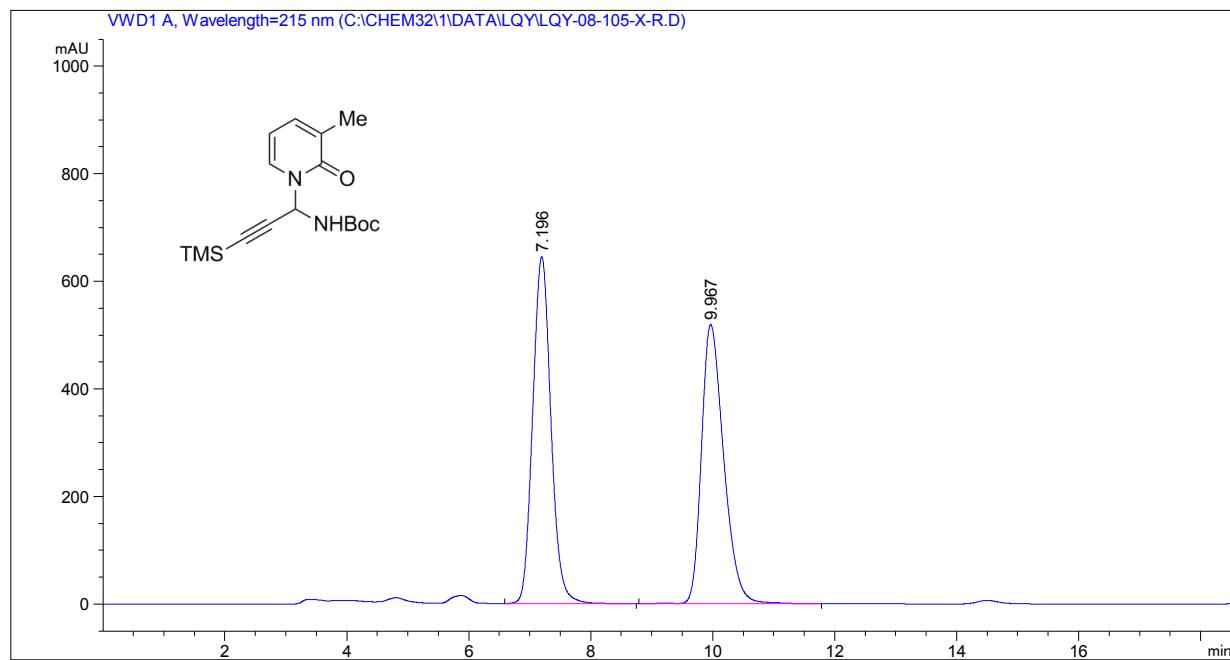
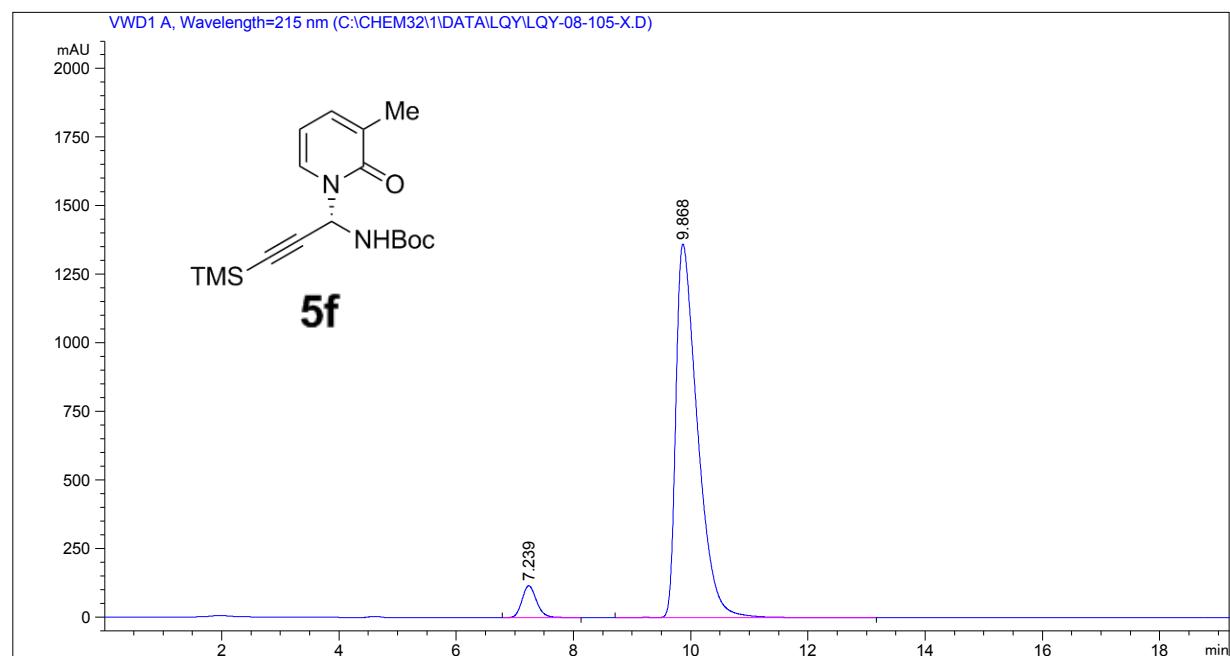
-----|-----|-----|-----|-----|-----|-----|

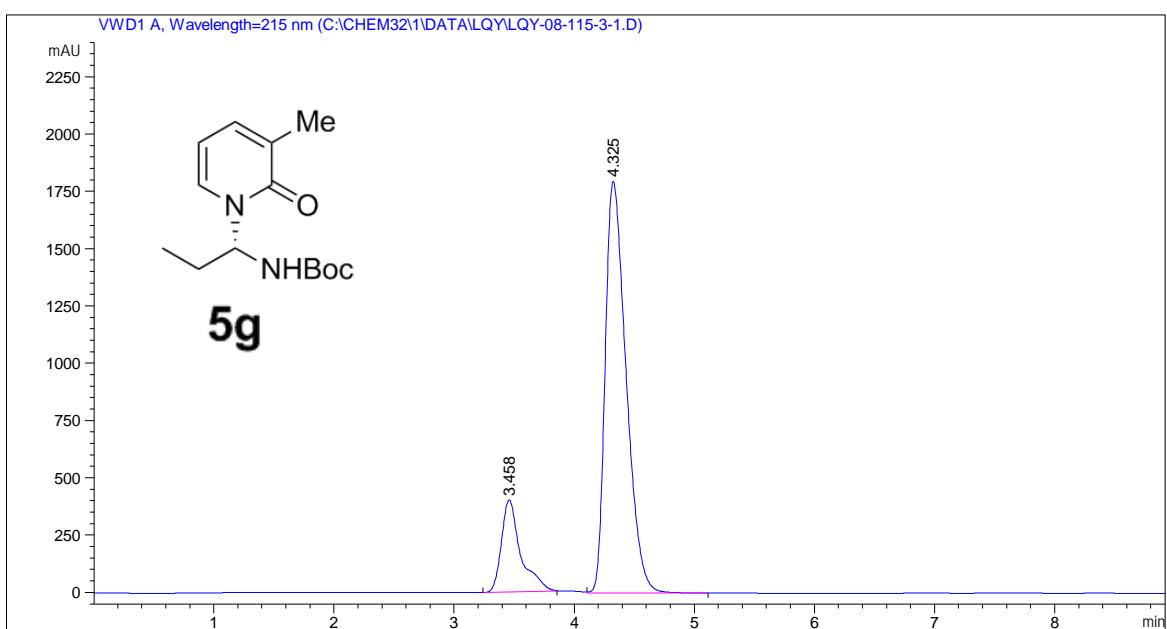
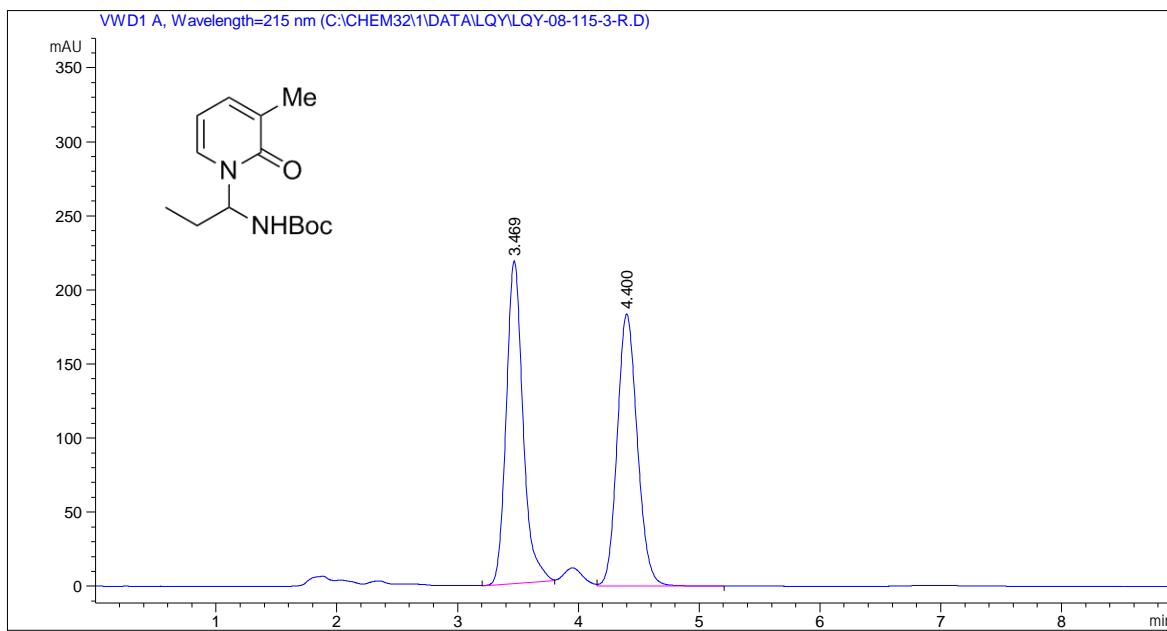
1 6 697 BB 0 3521 845 15936 36 91849 2 9985

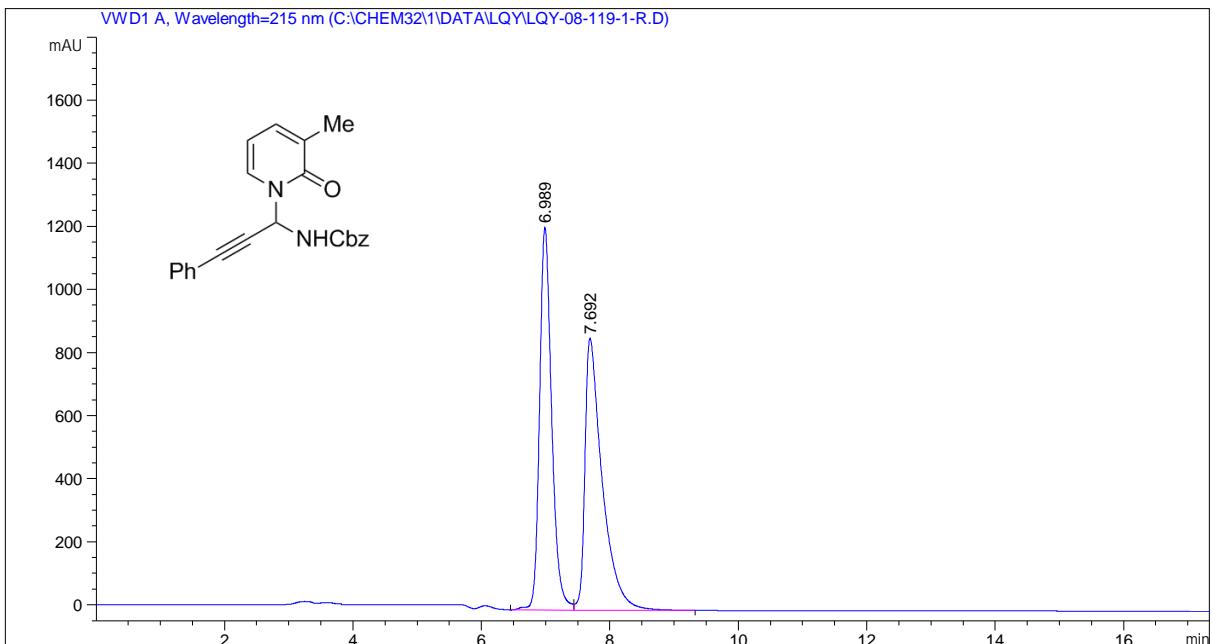
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1 0.097 DB 0.3321 845.15938 38.91847 2.9983
2 11 145 MM 0.67032 73409e4 679.79895 97.0015

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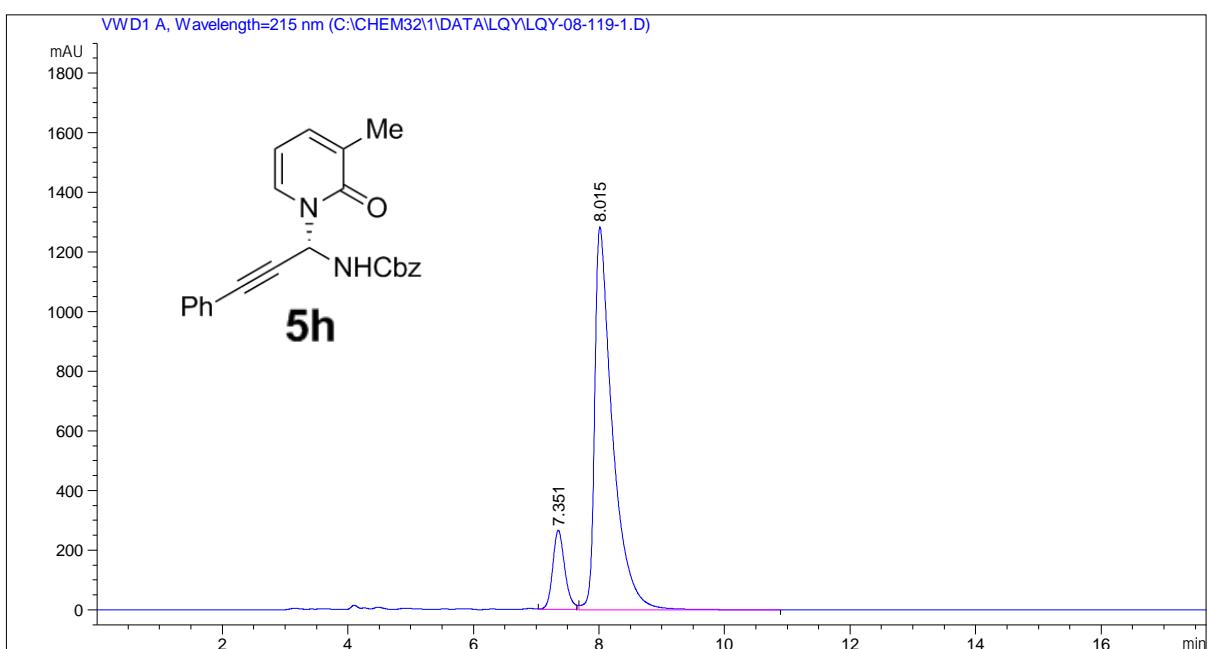







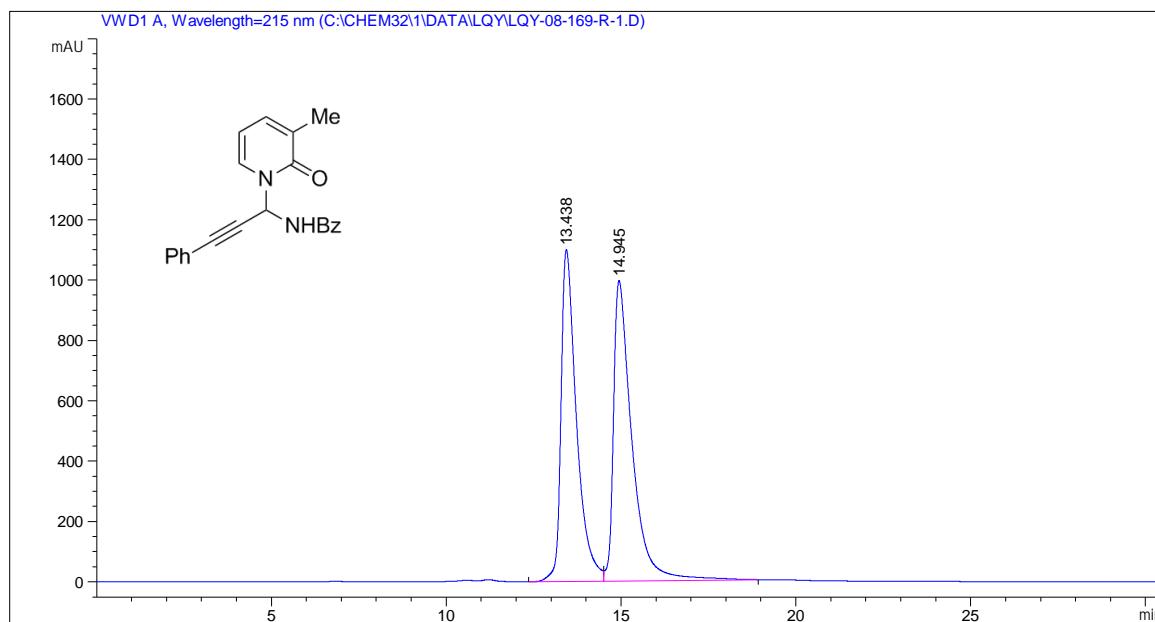
DMU\_ FYhH] aY H\o dY · K] Xh\ · · · · 5f YU · · · · <Y] [\h · · · · 5f YU

#	[min]	[min]	[mAU*s]	[mAU]	%	
1	6.989	VV R	0.1989	1.58923e4	1212.43835	49.5567
2	7.692	VB	0.2708	1.61766e4	862.37329	50.4433

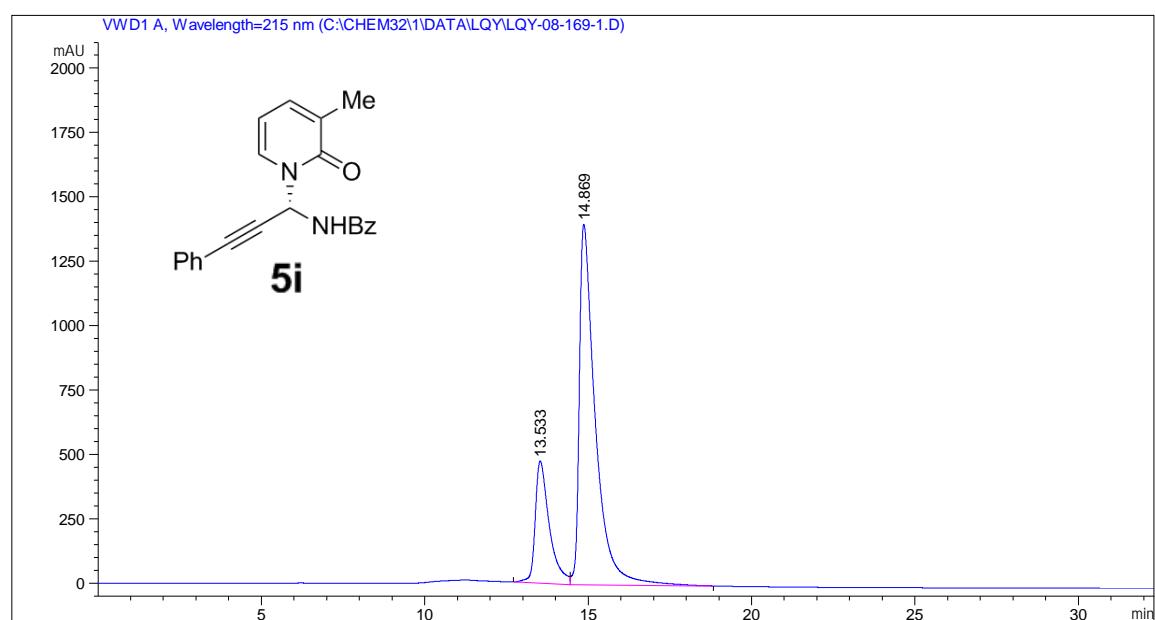


DYU\_ · FYhH] aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU

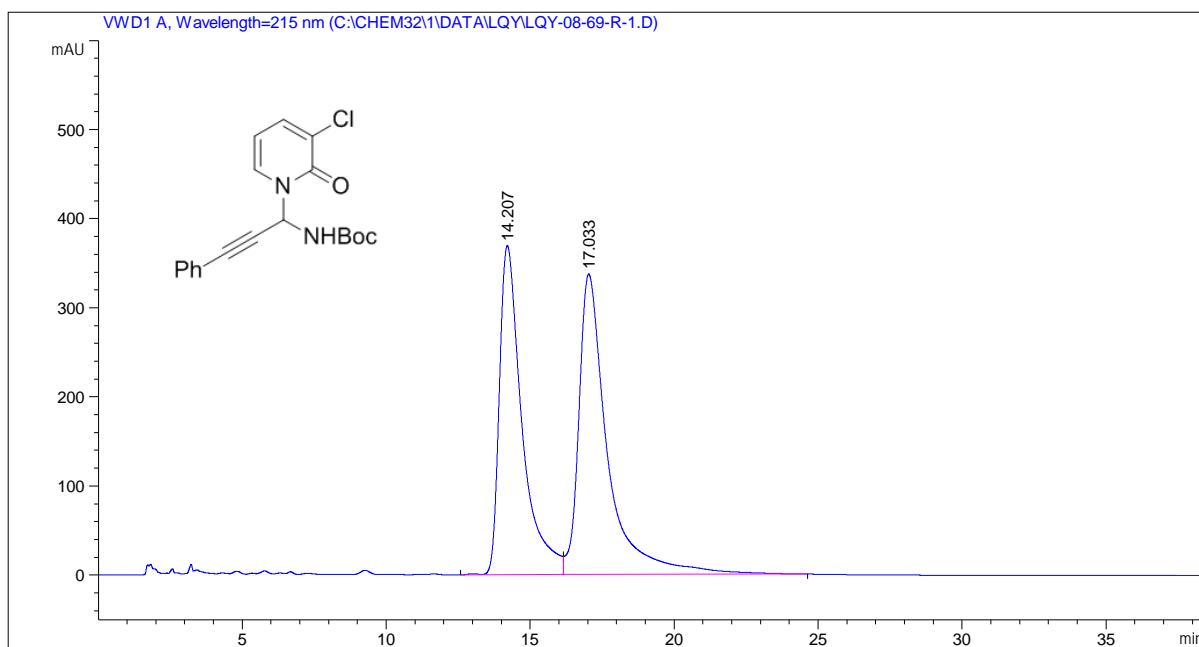
#	[min]	[min]	[mAUs]	[mAU]	%
1	7.351 MM	0.22263554	34644	266.09863	12.3308
2	8.015 VB	0.282725	52707e4	1283.75549	87.6692



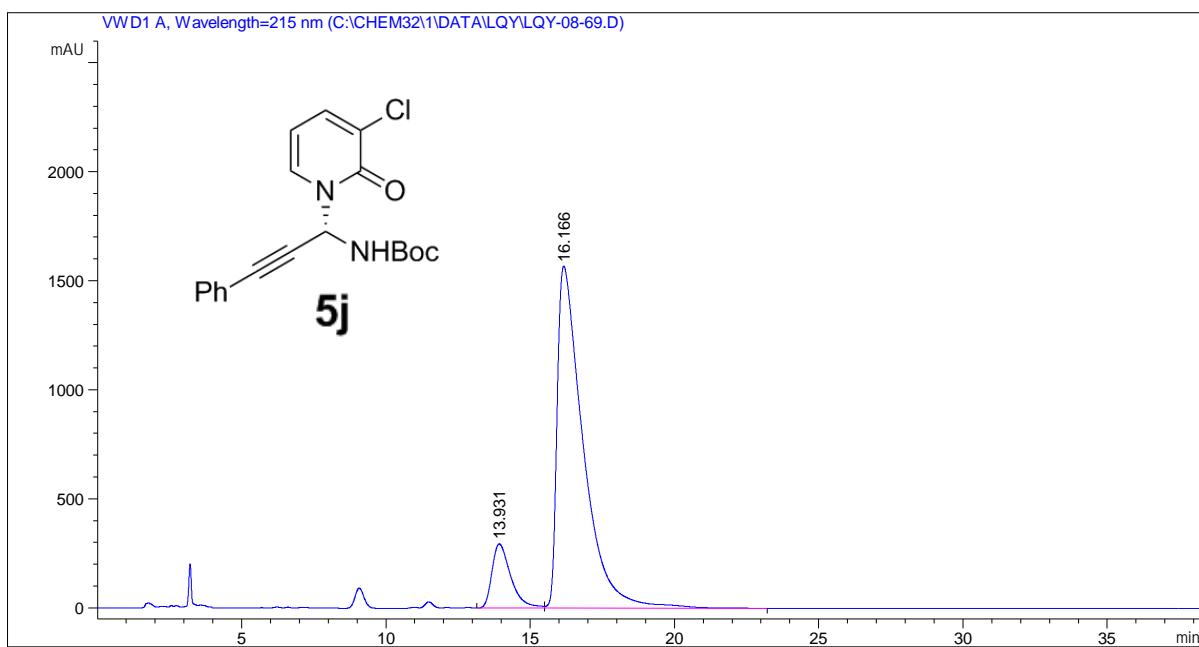
	DYU	FYhH	aY	HdY	KJ	Xh\	5f	YU	<Y	\h	5f	YU
#	[min]	[min]					[mAU*s]	[mAU]				%
1	13.438	MM	0.5133	3.38782e4	1099.	95325	48.087					
2	14.945	MM	0.6125	3.65731e4	995.	24701	51.912					



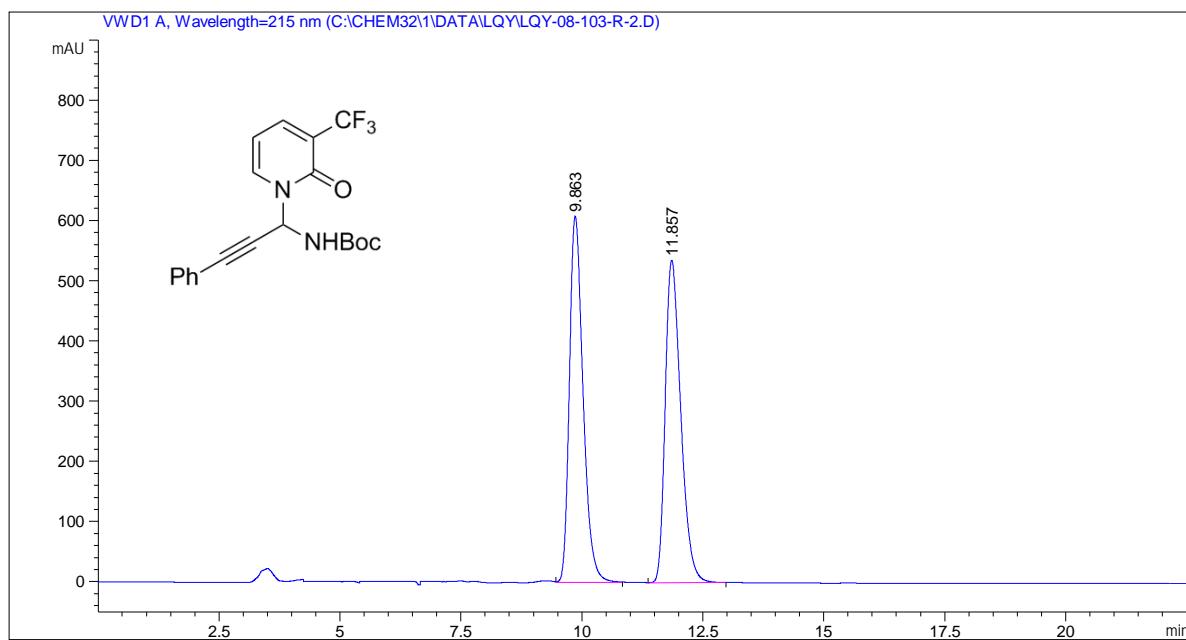
DYU	FYH	aY	HndY	K	Xh	5f	YU	<Y	\h	5f	YU
#	[m i n]	[m i n]	[mAU*s]	[mAU]							%
1	13.533	MM	0.5022	1.43179e4	475.	13943	23.	0375			
2	14.869	MM	0.5692	4.78327e4	1400.	56360	76.	9625			



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14. 207	VV R	0. 7978	2. 02276e4	369. 42578	46. 3217
2	17. 033	VB	0. 9899	2. 34400e4	337. 23438	53. 6783

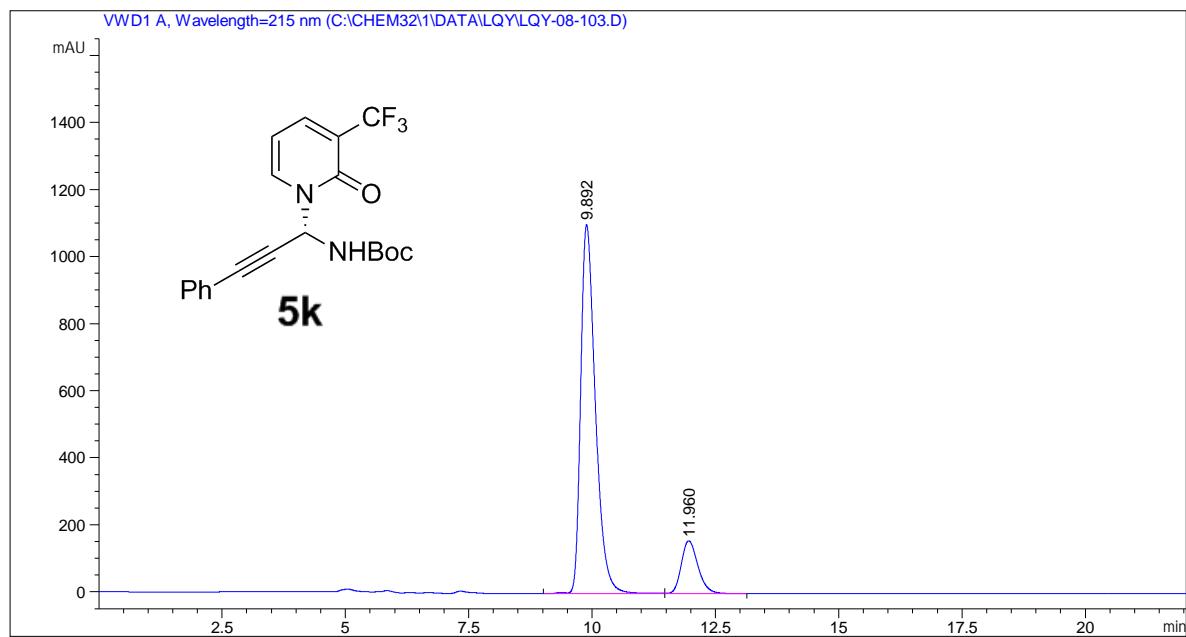


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13. 931	BV	0. 6961	1. 33869e4	294. 64618	12. 0267
2	16. 166	VB	0. 9071	9. 79231e4	1569. 15857	87. 9733



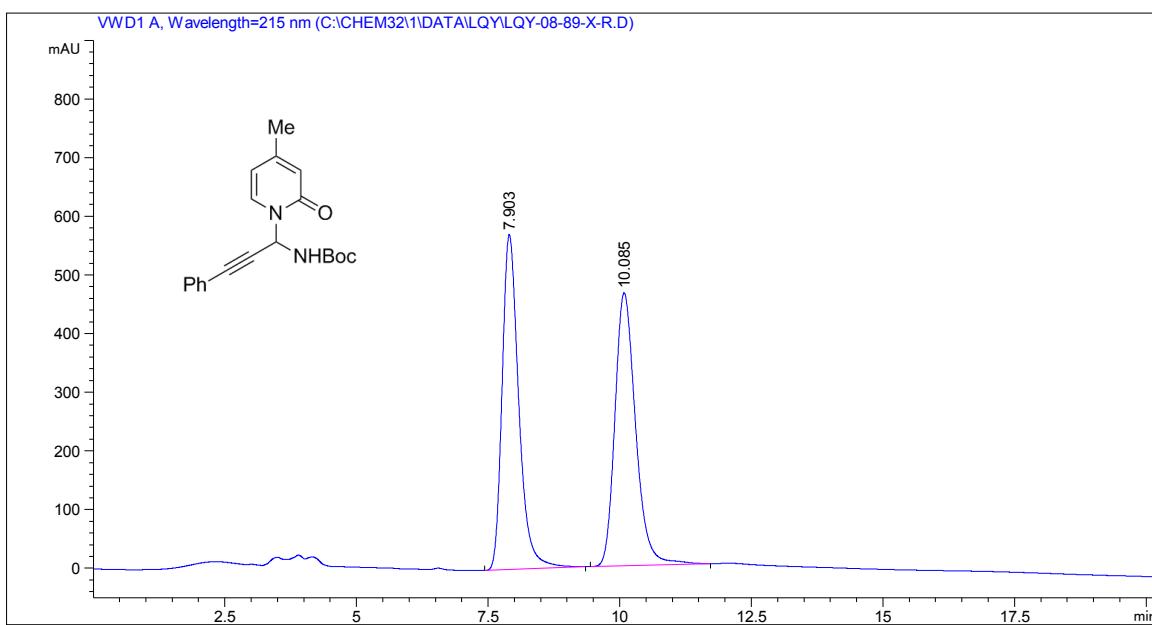
DYU\_ · FYhH] aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU

#	[min]	[min]	[mAUs]	[mAU]	%	
1	9.863	MM	0.3271	1.19437e4	608.49042	49.9623
2	11.857	BB	0.3446	1.19617e4	535.50598	50.0377

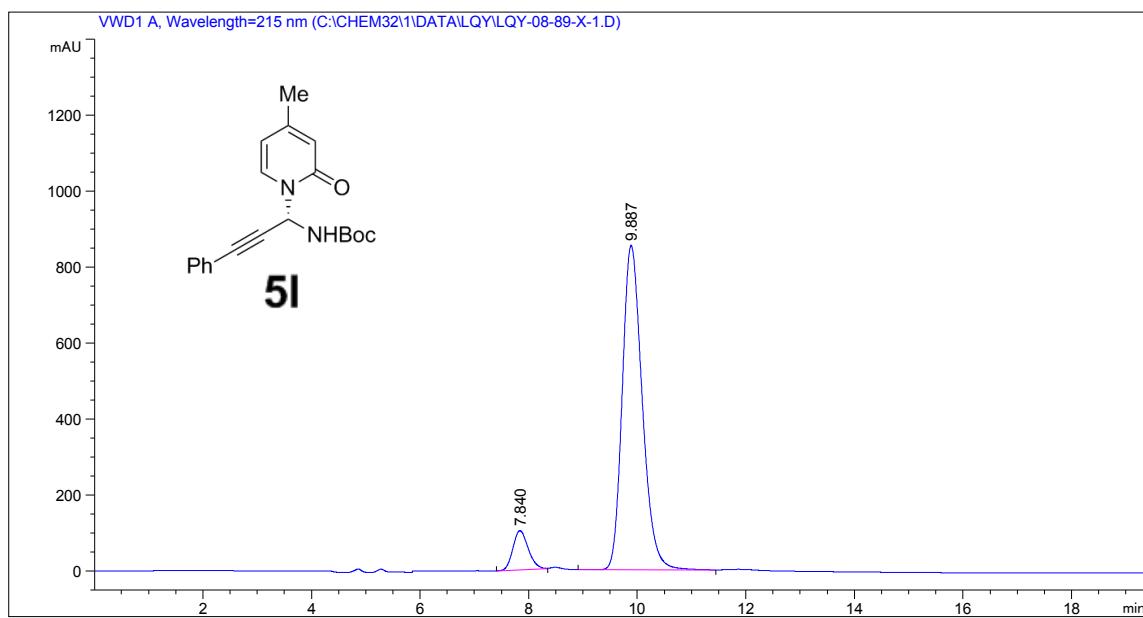


DYU\_ · FYhH] aY HhdY · K] Xh\ · · · 5f YU · · · <Y] [ \h · · · 5f YU

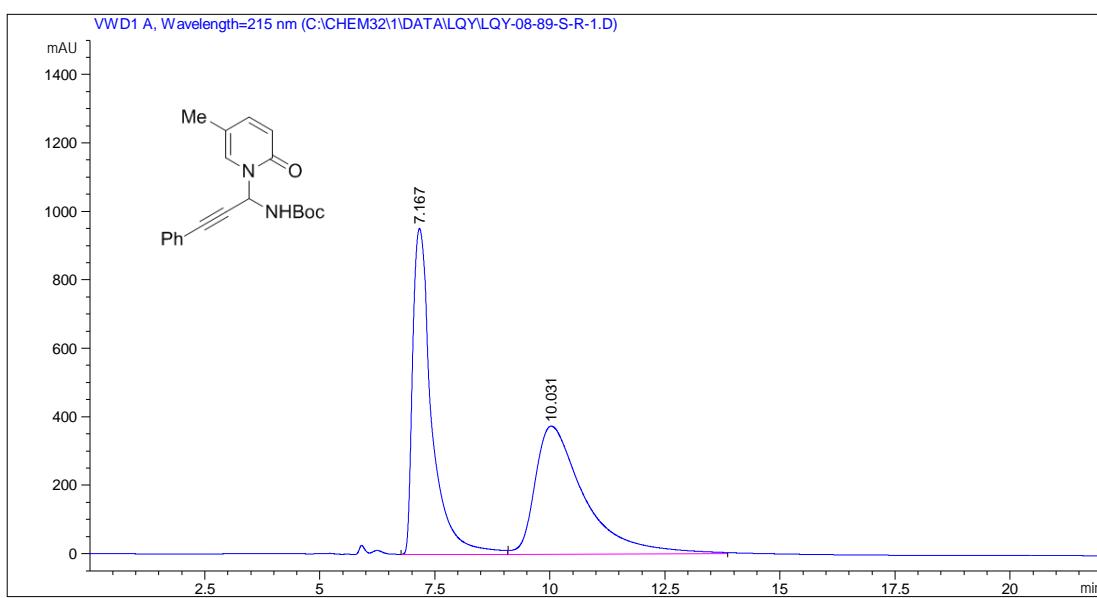
#	[min]	[min]	[mAUs]	[mAUs]	%
1	9.892	VW R	0.3170	2.27945e4	1100.88086
2	11.960	VB	0.3606	3699.98804	157.78110



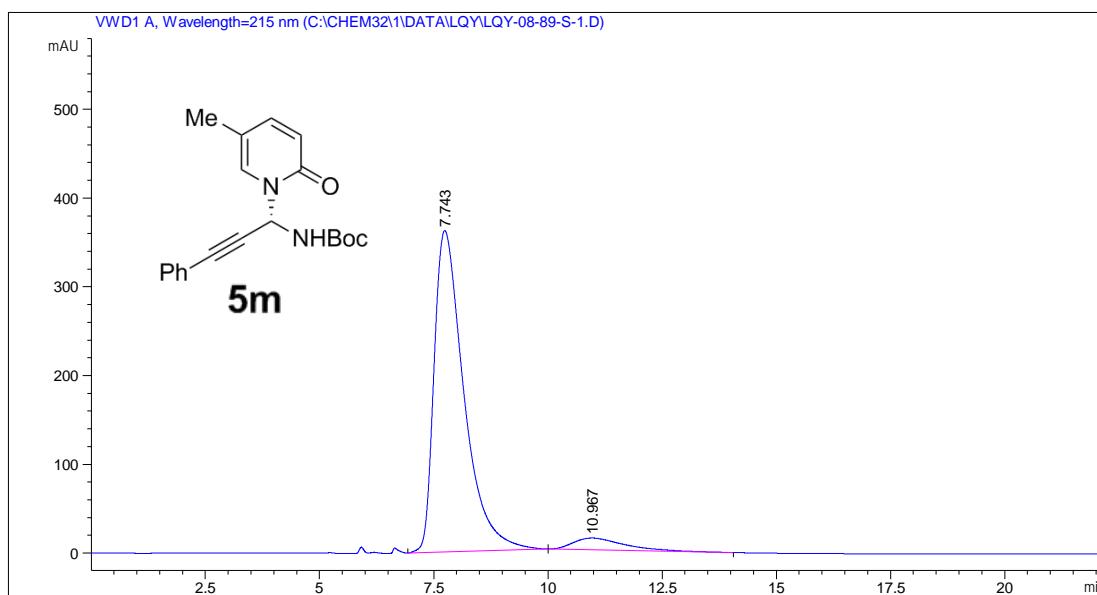
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.903	BB	0.3352	1.25375e4	570.89581	49.6493
2	10.085	BB	0.4199	1.27146e4	465.19318	50.3507



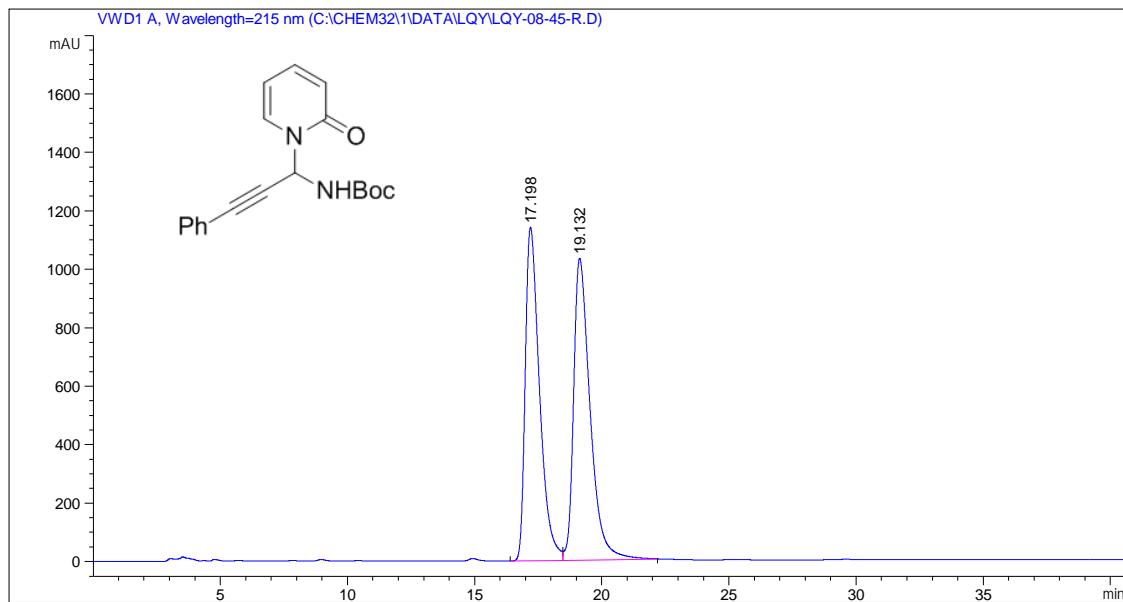
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.840	MM	0.3291	2046.23303	103.63663	8.5911
2	9.887	VB R	0.3935	2.17718e4853.83411	91.4089	



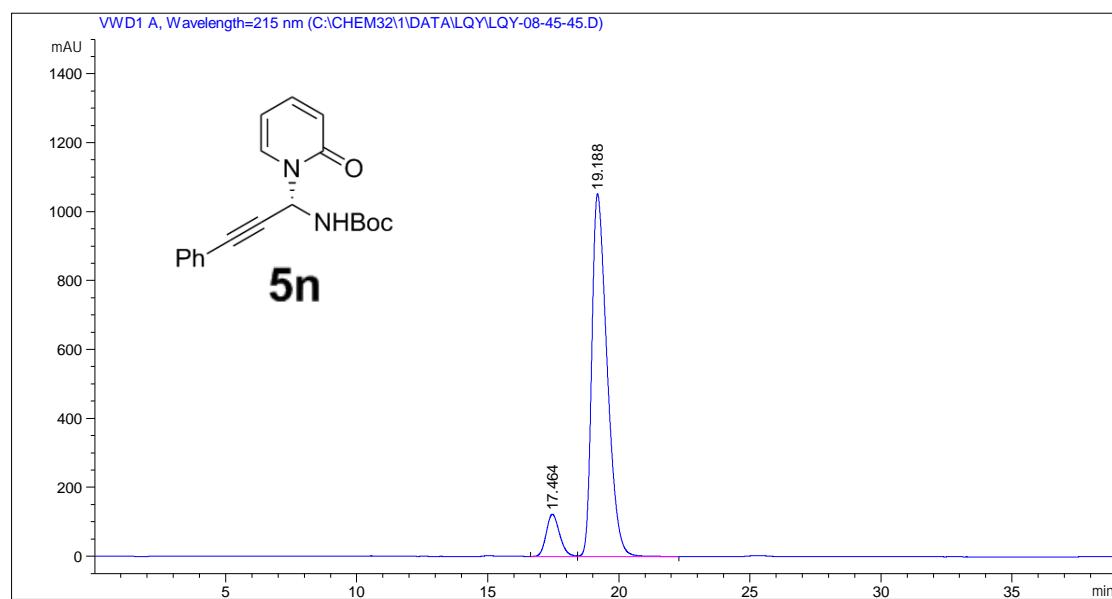
DYU_FYhH aY HhdY K] Xh\ \ \ \ \ \ 5f YU \ \ \ \ \ \ <Y] [\ h\ \ \ \ \ \ 5f YU					
#	[min]	[min]	[mAU*s]	[mAU]	%
1	7.167	BV	0.4341	2.75061e4	952.08728
2	10.031	MM	1.2391	2.78185e4	374.17365



DYU_FYhH aY HhdY K] Xh\ \ \ \ \ \ 5f YU \ \ \ \ \ \ <Y] [\ h\ \ \ \ \ \ 5f YU					
#	[min]	[min]	[mAU*s]	[mAU]	%
1	7.743	BB	0.6900	1.64497e4	362.12421
2	10.967	BB	1.1497	1054.02502	13.34138



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.198	BV	0.5926	4.46036e4	1142.12146	48.8387
2	19.132	MM	0.7535	4.67247e4	1033.51782	51.1613



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.464	BV	0.5475	4334.63232	122.59177	9.2154
2	19.188	VB	0.6185	4.27024e4	1052.22437	90.7846

