1. General considerations

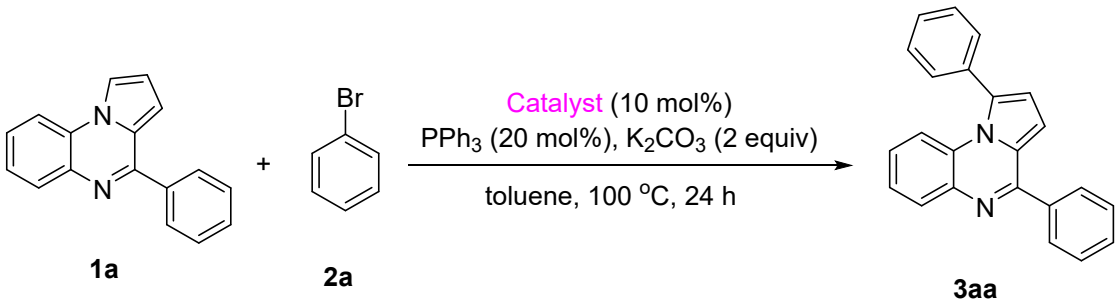
All reagents and starting materials were commercially obtained and were used without further purification unless otherwise noted. The 4-arylpyrrolo[1,2-*a*]quinoxaline substrates were prepared according to the literature.[1]

Gas chromatography (GC) analyses were performed using Shimadzu GC-2010 Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The GC yield was calculated using diphenyl ether as the internal standard. Gas chromatography – mass spectrometry (GC-MS) analyses were performed using Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). Proton and carbon-13 (^{1}H NMR, ^{13}C NMR) spectra were recorded on Bruker AV 600 and 500 spectrometers, respectively, using residual solvent as reference. Splitting is reported with the following symbols: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, and m = multiplet. Coupling constants (*J*) are reported in Hertz. Fourier transform infrared (FT-IR) spectra were obtained from a Shimadzu IRPrestige-21 instrument, with samples being dispersed on potassium bromide pallets. High-resolution mass spectra (HRMS) were recorded by Agilent 6500 Series Q-TOF LC/MS System. The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. For compound **3ai**, mass spectrum was obtained from UPLC Acquity H-Class, Waters.

Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 (Merck), visualized by irradiation with UV light (254 nm and 365 nm). Column chromatography was performed on silica gel (Merck, 15 – 40 μm). To prepare a caffeinated silica gel, silica gel (15 – 40 μm, 40 g), caffeine (8 g), and CH_2Cl_2 (100 mL) were added to a round-bottom flask. The ensuing mixture was stirred for 15 min then evaporated by rotovap until a free-flowing powder was obtained.

2. Optimization of reaction conditions

2.1. Effect of palladium catalyst

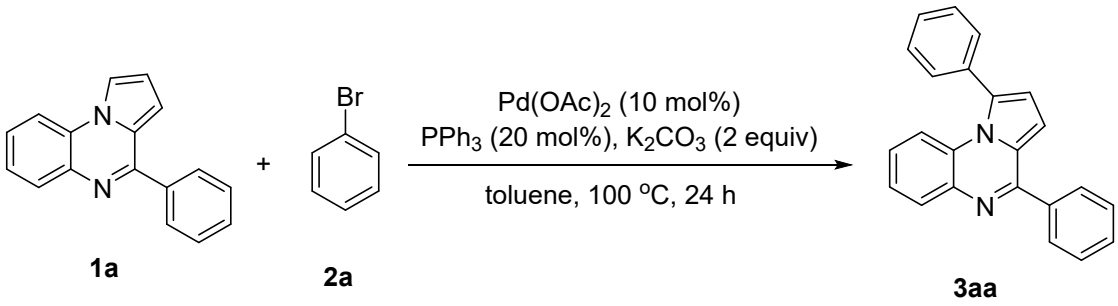


1a + **2a** → **3aa**

Entry [a]	Catalyst	GC yield (%)[b]
1	**$Pd(OAc)_2$**	**55**
2	$Pd(TFA)_2$	0
3	$PdCl_2$	13
4[c]	$PdCl_2(PPh_3)_2$	19
5[c]	$Pd(PPh_3)_4$	16

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (10 mol%), PPh_3 (20 mol%), K_2CO_3 (0.2 mmol), toluene (1 mL), 100 °C, 24 h. [b]GC yields using diphenyl ether as an internal standard. [c]No PPh_3.

2.2. Effect of environment

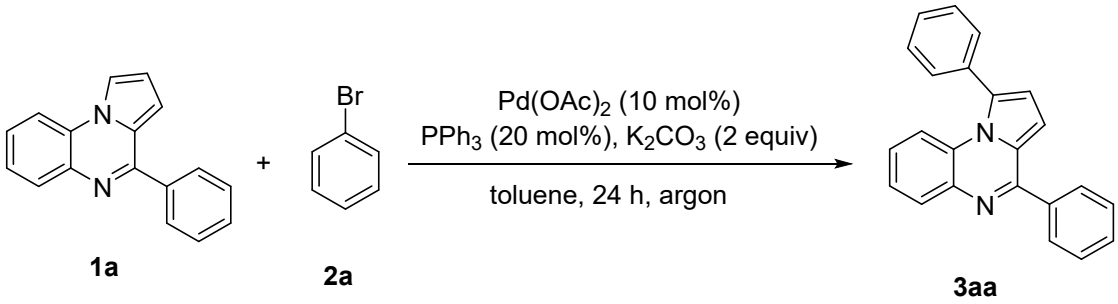


1a + **2a** → **3aa**

Entry	Environment	GC yield (%)[a]
1	Oxygen	35
2	**Argon**	**87**
3	Air	55

[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), K_2CO_3 (0.2 mmol), toluene (1 mL), 100 °C, 24 h. [b]GC yields using diphenyl ether as an internal standard.

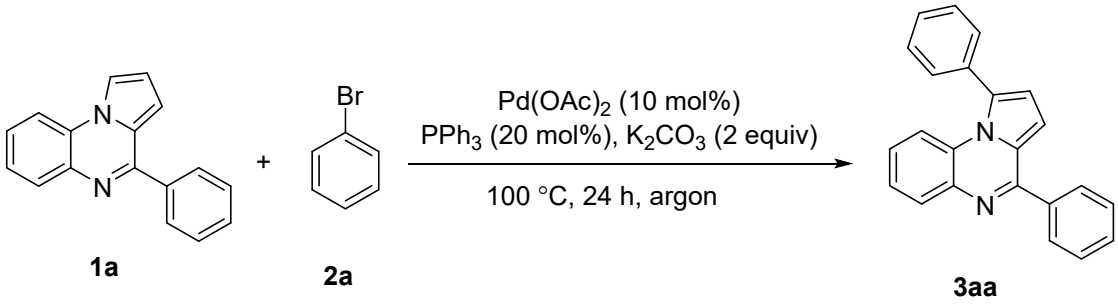
2.3. Effect of temperature



Entry[a]	Temperature (°C)	GC yield (%)[b]
1	40	0
2	60	11
3	80	27
4	**100**	**87**
5	120	78

[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), K_2CO_3 (0.2 mmol), toluene (1 mL), 24 h, under argon. [b]GC yields using diphenyl ether as an internal standard.

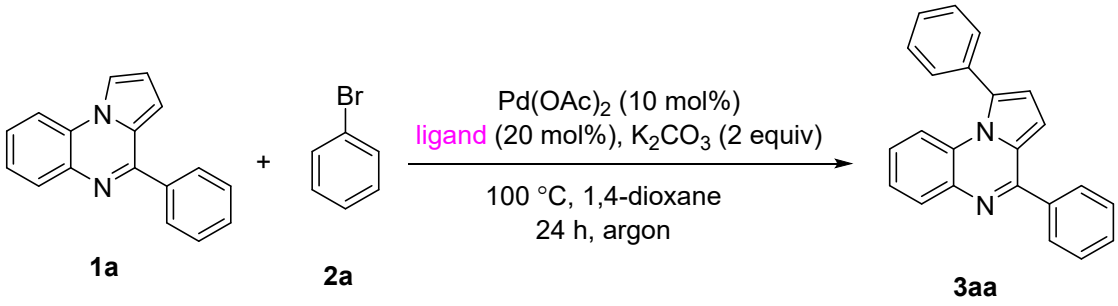
2.4. Effect of solvent



Entry[a]	Solvent	GC yield (%)[b]
1	toluene	87
2	DMSO	12
3	NMP	35
4	**1,4-dioxane**	**97**
5	PhCl	83
6	DMF	89
7	DMAc	96
8	*m*-xylene	70
9	H_2O	78
10	n-butanol	0
11	diethyl carbonate	79

[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), K_2CO_3 (0.2 mmol), solvent (1 mL), 100 °C, 24 h, under argon. [b]GC yields using diphenyl ether as an internal standard.

2.5. Effect of ligand

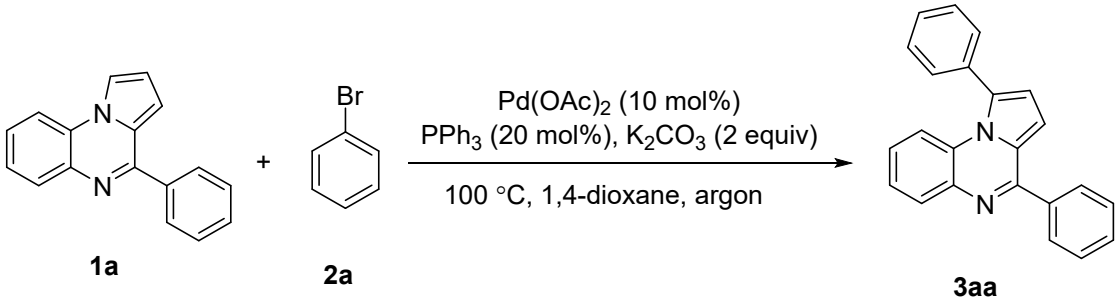


1a **2a** **3aa**

Entry[a]	Ligand	GC yield (%)[b]
1	No ligand	23
2	XPhos	0
3	BINAP	0
4	**PPh_3**	**97**
5	1,10-phenanthroline	13

[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), K_2CO_3 (0.2 mmol), 1,4-dioxane (1 mL), 100 °C, 24 h, under argon. [b]GC yields using diphenyl ether as an internal standard.

2.6. Effect of reaction time

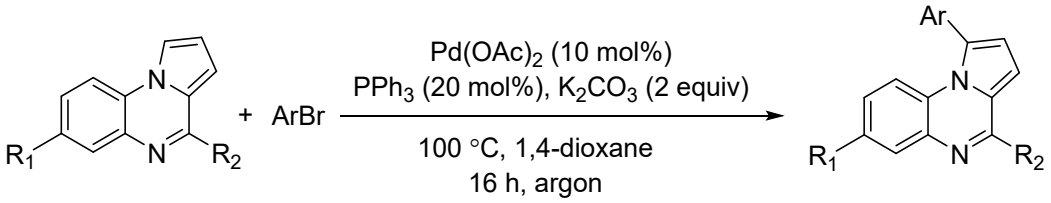


1a **2a** **3aa**

Entry[a]	Time (hour)	GC yield (%)[b]
1	2	23
2	4	45
3	6	85
4	**16**	**98**
5	24	97

[a]Reaction condition: **1a** (0.1 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (10 mol%), ligand (20 mol%), K_2CO_3 (0.2 mmol), 1,4-dioxane (1 mL), 100 °C, under argon. [b]GC yields using diphenyl ether as an internal standard.

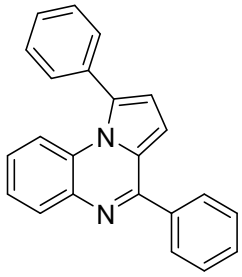
3. General procedure for arylation of 4-arylpyrrolo[1,2-*a*]quinoxalines



In a typical experiment, a 4-mL vial was charged with a derivative of 4-phenyl pyrrolo[1,2-*a*]quinoxaline (0.1 mmol), an aryl bromide (0.15 mmol), $Pd(OAc)_2$ (2.3 mg, 10 mol%), PPh_3 (5.4 mg, 20 mol%), K_2CO_3 (27.8 mg, 0.2 mmol), and 1,4-dioxane (1 mL). The vial was purged with argon, then stirred at 100 °C for 16 h. The mixture was cooled down to room temperature. For GC analysis, diphenyl ether (0.1 mmol) was added at this stage. The obtained mixture was diluted with ethyl acetate (3 mL) and washed with brine (2 x 5 mL). Aqueous phases were further extracted with ethyl acetate (3 x 5 mL). Aliquots of combined organic phases were dried over anhydrous Na_2SO_4, filtered, and analyzed with GC. For isolation, the organic phase was mixed with Celite®, then evaporated by rotovap until a free-flowing powder was obtained. Purification by column chromatography with appropriate eluents afforded the arylation product.

4. Characterization data of products

1,4-Diphenylpyrrolo[1,2-*a*]quinoxaline (3aa)



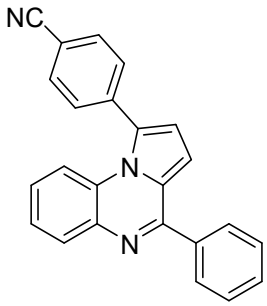
Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/toluene/acid acetic gradient from 115:0:5 to 75:25:20 for 1st column, then eluent: hexanes/ diethyl ether 1:1 for 2nd column) as a pale yellow solid; isolated yield: 96% (30.7 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.1, 1.6 Hz, 1H), 8.02 – 7.99 (m, 2H), 7.58 – 7.53 (m, 5H), 7.54 – 7.51 (m, 3H), 7.44 (dd, J = 8.5, 1.3 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.13 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.04 (d, J = 4.0 Hz, 1H), 6.79 (d, J = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.0, 138.7, 137.7, 134.4, 132.9, 130.4, 129.82, 129.80, 128.87, 128.86, 128.73, 128.69, 128.3, 126.9, 126.3, 125.1, 117.0, 116.6, 109.1.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{17}N_2^+$: 321.1386; found: 321.1390.

4-(4-Phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)benzonitrile (3ab)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ethyl acetate 10:1) as a yellow solid; isolated yield: 74% (25.5 mg).

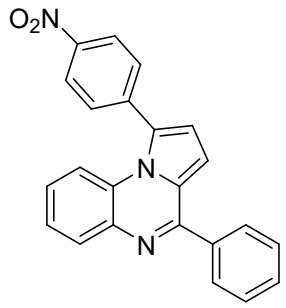
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.0, 1.5 Hz, 1H), 8.00 – 7.96 (m, 2H), 7.80 – 7.77 (m, 2H), 7.70 – 7.65 (m, 2H), 7.59 – 7.52 (m, 3H), 7.41 (ddd, J = 8.0, 7.2, 1.3 Hz, 1H), 7.35 (dd, J = 8.5, 1.3 Hz, 1H), 7.20 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H), 7.06 (d, J = 4.1 Hz, 1H), 6.83 (d, J = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.0, 138.7, 138.3, 137.8, 132.6, 130.7, 130.5, 130.0, 129.9, 128.8, 128.7, 128.0, 127.7, 126.6, 125.6, 118.7, 118.1, 116.5, 112.1, 109.5.

FT-IR (ATR, cm^{-1}) υ 2224.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{16}N_3^+$: 346.1338; found: 346.1341.

1-(4-Nitrophenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3ac)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ chloroform/ethyl acetate gradient from 40:10:0.25 to 40:10:2) as a yellow solid; isolated yield: 80% (29.1 mg).

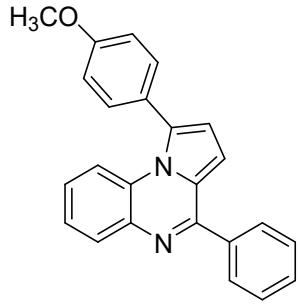
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 – 8.33 (m, 2H), 8.07 (dd, J = 8.0, 1.5 Hz, 1H), 8.01 – 7.95 (m, 2H), 7.77 – 7.71 (m, 2H), 7.60 – 7.52 (m, 3H), 7.42 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 7.37 (dd, J = 8.5, 1.2 Hz, 1H), 7.21 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H), 7.08 (d, J = 4.0 Hz, 1H), 6.88 (d, J = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.0, 147.6, 140.6, 138.3, 137.8, 130.8, 130.2, 130.1, 129.9, 128.8, 128.7, 128.3, 127.6, 126.7, 125.7, 124.1, 118.5, 116.6, 109.7.

FT-IR (ATR, cm^{-1}) υ 1334, 1523.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{16}N_3O_2^+$: 366.1237; found: 366.1246.

1-(4-Methoxyphenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3ad)



Prepared according to the general procedure but extended the reaction time to 24 h. The product was isolated by column chromatography on silica gel (eluent: hexanes/ethyl acetate 20:1) as pale yellow solid; isolated yield: 53% (18.5 mg).

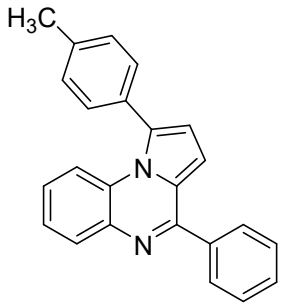
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.0, 1.6 Hz, 1H), 8.00 – 7.98 (m, 2H), 7.58 – 7.51 (m, 3H), 7.51 – 7.45 (m, 3H), 7.36 (ddd, J = 8.0, 7.2, 1.3 Hz, 1H), 7.14 (ddd, J =

8.6, 7.2, 1.6 Hz, 1H), 7.07 – 7.03 (m, 2H), 7.02 (d, J = 4.0 Hz, 1H), 6.74 (d, J = 4.0 Hz, 1H), 3.92 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.1, 155.0, 138.7, 137.7, 132.9, 131.1, 130.3, 129.8, 128.9, 128.7, 128.5, 126.7, 126.2, 125.0, 116.8, 116.5, 114.3, 108.9, 55.5. One carbon signal could not be located.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{19}N_2O^+$: 351.1492; found: 351.1493.

1-(4-Methylphenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (**3ae**)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ethyl acetate/acid acetic 20:1:1) as a pale yellow solid; isolated yield: 74% (24.7 mg); purity: 80%. The product contained 20% of inseparable phenylation product (presumably from PPh_3), thus the true yield of **3ae** should be 60%.

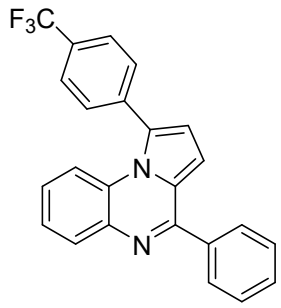
^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.0, 1.6 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.57 – 7.52 (m, 3H), 7.49 (dd, J = 8.6, 1.2 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.13 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 6.76 (d, J = 4.0 Hz, 1H), 2.49 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) due to overlapping of signals, possible peaks are listed δ 155.0, 138.7, 138.6, 137.7, 133.1, 131.5, 130.3, 129.82, 129.78, 129.7, 129.6, 128.9, 128.7, 128.4, 126.8, 126.2, 125.1, 116.9, 116.6, 109.0, 21.6.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{19}N_2^+$: 335.1542; found: 335.1542.

The NMR data reported herein matched with those known.[2]

4-Phenyl-1-(4-(trifluoromethyl)phenyl)pyrrolo[1,2-*a*]quinoxaline (3af)



Prepared according to the general procedure and isolated by column chromatography on caffeinated silica gel (eluent: hexanes/ ethyl acetate gradient from 100:1 to 10:1) as a yellow solid; isolated yield: 65% (25.2 mg).

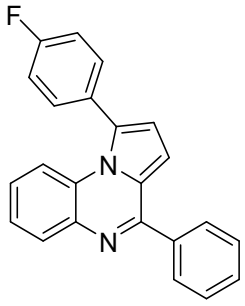
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, J = 7.9, 1.6 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.59 – 7.52 (m, 3H), 7.45 – 7.36 (m, 2H), 7.19 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.06 (d, J = 4.1 Hz, 1H), 6.82 (d, J = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.0, 138.5, 137.9, 137.7, 131.1, 130.65, 130.60 (q, $J_{C\text{-}F}$ = 32.9 Hz), 130.0, 129.8, 128.9, 128.8, 127.9, 127.61, 126.60, 125.8 (q, $J_{C\text{-}F}$ = 3.5 Hz), 125.5, 124.2 (q, $J_{C\text{-}F}$ = 272.2 Hz), 117.8, 116.5, 109.4.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.52.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{16}N_2F_3^+$: 389.1260; found: 389.1263.

1-(4-Fluorophenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3ag)



Prepared according to the general procedure and isolated by column chromatography on caffeinated silica gel (eluent: hexanes/ethyl acetate 20:1) as a yellow solid; isolated yield: 67% (22.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.9, 1.6 Hz, 1H), 8.00 – 7.98 (m, 2H), 7.58 – 7.50 (m, 5H), 7.41 – 7.35 (m, 2H), 7.24 – 7.19 (m, 2H), 7.15 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.03 (d, J = 4.1 Hz, 1H), 6.76 (d, J = 4.1 Hz, 1H).

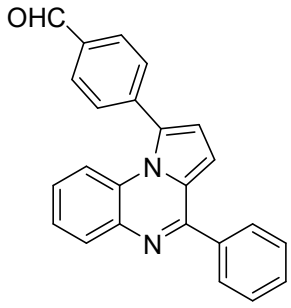
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 249.2 Hz), 155.0, 138.6, 137.71, 131.72, 131.65 (d, $J_{C\text{-}F}$ = 8.2 Hz), 130.49, 130.45, 129.87, 128.85, 128.7, 128.3, 127.0,

126.4, 125.2, 117.1, 116.3, 116.0 (d, J_{C-F} = 21.9 Hz), 109.0. One coupling constant could not be determined due to overlapping and complexity of peaks.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.42.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{16}N_2F^+$: 339.1292; found: 339.1292.

4-(4-Phenylpyrrolo[1,2-*a*]quinoxalin-1-yl)benzaldehyde (3ah)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ chloroform 1/1.25) as a yellow solid; isolated yield: 63% (21.8 mg); purity: 84%. The product presumably contained 16% of inseparable C3-arylation product, thus the true yield should be 53%.

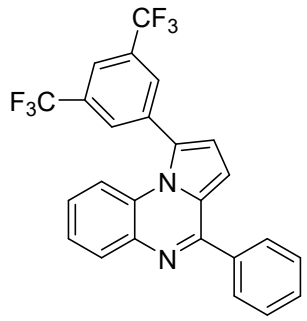
^{1}H NMR (600 MHz, $CDCl_3$) *δ* 10.13 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 8.00 – 7.98 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.53 (m, 3H), 7.44 – 7.39 (m, 2H), 7.20 – 7.14 (m, 1H), 7.07 (d, *J* = 4.1 Hz, 1H), 6.86 (d, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) due to mixture of inseparable isomers, possible peaks are listed *δ* 191.7, 191.6, 155.0, 140.2, 138.4, 137.8, 136.0, 131.3, 130.6, 130.4, 130.1, 130.0, 129.9, 129.4, 128.9, 128.8, 128.2, 127.9, 127.9, 126.6, 125.6, 118.1, 116.7, 109.5.

FT-IR (ATR, cm^{-1}) υ 1693, 1599.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{17}N_2O^+$: 349.1335; found: 349.1339.

1-(3,5-Bis(trifluoromethyl)phenyl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3ai)



Prepared according to the general procedure and isolated by column chromatography on caffeinated silica gel (eluent: hexane/dichloromethane/acetic acid gradient from 100:2.5:1 to 100:20:1 for 1st column, then eluent: hexane/ethyl acetate/acetic acid gradient from 200:0.75:0.25 to 200:4.5:1.5 for 2nd column) as yellow solid; isolated yield: 59% (27.2 mg); purity: 90%. The product presumably contained 10% of inseparable di-arylated product, thus the true yield should be 51%.

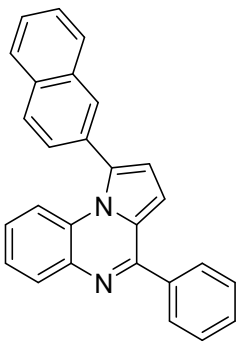
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.0, 1.5 Hz, 1H), 8.05 (d, J = 1.7 Hz, 2H), 8.02 – 7.95 (m, 3H), 7.61 – 7.52 (m, 3H), 7.44 (ddd, J = 8.0, 7.1, 1.5 Hz, 1H), 7.28 (dd, J = 8.5, 1.5 Hz, 1H), 7.22 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H), 7.09 (d, J = 4.1 Hz, 1H), 6.90 (d, J = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) due to overlapping and complexity of peaks, only possible coupling constants are listed δ 155.0, 138.3, 137.8, 136.3, 132.3 (q, $J_{C\text{-}F}$ = 33.6 Hz), 131.0, 130.1, 129.4, 129.4, 129.1, 129.1, 128.9, 128.8, 128.1, 128.1, 127.6, 126.8, 125.9, 123.2 (q, $J_{C\text{-}F}$ = 273.2 Hz), 122.1, 122.0, 118.4, 116.1, 109.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.93.

HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{25}H_{15}F_6N_2^+$: 457.11339, found: 457.11417.

1-(Naphthalen-2-yl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3aj)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/dichloromethane/acetic acid gradient from 50:2.5:10 to 50:10:10 for 1st column), then eluent: hexanes/acetone 20:1 for 2nd column on caffeinated silica gel, then eluent: toluene 100% for 3rd column) as a yellow solid; isolated yield: 32%

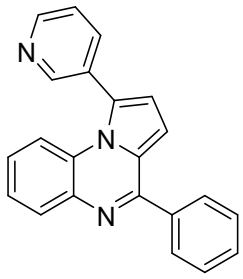
(11.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.08 – 8.02 (m, 3H), 7.96 (dd, J = 9.0, 2.6 Hz, 2H), 7.94 – 7.90 (m, 1H), 7.63 (dd, J = 8.6, 1.7 Hz, 1H), 7.61 – 7.54 (m, 5H), 7.51 (d, J = 8.6 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.09 (d, J = 4.0 Hz, 1H), 7.09 – 7.05 (m, 1H), 6.88 (d, J = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.0, 138.7, 137.8, 133.5, 133.2, 132.8, 131.8, 130.3, 129.8, 128.9, 128.7, 128.6, 128.37, 128.36, 128.0, 127.4, 127.1, 126.9, 126.3, 125.2, 117.4, 116.8, 109.2. Two carbon signals could not be located.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{19}N_2^+$: 371.1542; found: 371.1552.

4-Phenyl-1-(pyridin-3-yl)pyrrolo[1,2-*a*]quinoxaline (3ak)



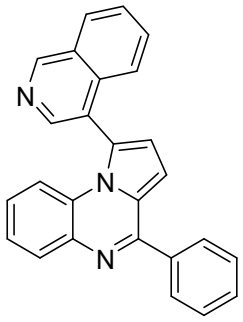
Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ ethyl acetate/triethylamine gradient from 40:1:0.8 to 5:1:0.1) as a yellow solid; isolated yield: 40% (12.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (dd, J = 2.3, 0.9 Hz, 1H), 8.75 (dd, J = 4.9, 1.6 Hz, 1H), 8.05 (dd, J = 8.0, 1.6 Hz, 1H), 8.01 – 7.97 (m, 2H), 7.87 (dt, J = 8.0, 2.3 Hz, 1H), 7.59 – 7.52 (m, 3H), 7.45 (ddd, J = 7.8, 4.8, 0.9 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.17 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.07 (d, J = 4.1 Hz, 1H), 6.83 (d, J = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.0, 150.2, 149.8, 138.5, 137.7, 136.9, 130.7, 130.6, 130.0, 128.9, 128.84, 128.75, 128.1, 127.7, 126.7, 125.5, 123.5, 117.9, 116.2, 109.3.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{16}N_3^+$: 322.1339; found: 322.1351.

1-(Isoquinolin-4-yl)-4-phenylpyrrolo[1,2-*a*]quinoxaline (3al)



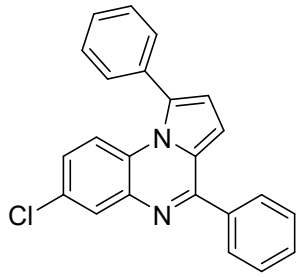
Prepared according to the general procedure and isolated by column chromatography on caffeinated silica gel (eluent: hexanes/ ethyl acetate gradient from 5:1 to 2:1) as a yellow solid; isolated yield: 21% (7.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.82 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.16 – 8.12 (m, 2H), 8.11 (dd, J = 8.0, 1.5 Hz, 1H), 7.74 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 7.71 – 7.63 (m, 4H), 7.51 (d, J = 8.4 Hz, 1H), 7.37 (ddd, J = 8.2, 7.2, 1.3 Hz, 1H), 7.26 (d, J = 4.0 Hz, 1H), 7.07 (dd, J = 8.6, 1.3 Hz, 1H), 7.00 (d, J = 4.0 Hz, 1H), 6.97 (ddd, J = 8.6, 7.1, 1.5 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.9, 153.8, 144.4, 138.5, 137.4, 135.5, 131.6, 130.4, 130.0, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.5, 127.0, 126.9, 126.1, 125.3, 125.1, 118.5, 115.9, 109.1.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{26}H_{18}N_3^+$: 372.1495; found: 372.1506.

7-Chloro-1,4-diphenylpyrrolo[1,2-*a*]quinoxaline (3ba)



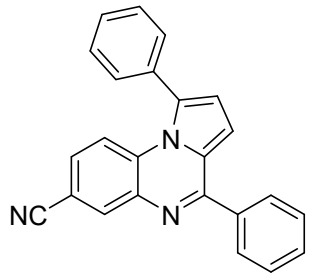
Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ dichloromethane 10:1 for 1st column, then eluent: hexanes/ acetone 50:1 for 2nd column on caffeinated silica gel) as a yellow solid; isolated yield: 70% (24.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 2.5 Hz, 1H), 8.00 – 7.98 (m, 2H), 7.58 – 7.54 (m, 3H), 7.54 – 7.51 (m, 4H), 7.35 (d, J = 9.1 Hz, 1H), 7.08 – 7.06 (m, 2H), 6.80 (d, J = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.9, 138.8, 138.3, 134.0, 133.2, 130.2, 130.1, 129.7, 129.5, 129.03, 129.00, 128.8, 128.7, 126.9, 126.7, 126.2, 117.6, 117.2, 109.7.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{16}N_2Cl^+$: 355.0997; found: 355.1008.

1,4-Diphenylpyrrolo[1,2-*a*]quinoxaline-7-carbonitrile (3ca)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ toluene/ acid acetic/ ethyl acetate gradient from 20:80:0.5:1 to 100:0:0.5:20) as a yellow solid; isolated yield: 70% (24.2 mg).

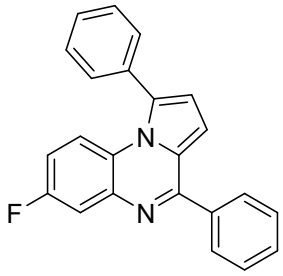
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 2.0 Hz, 1H), 8.00 – 7.97 (m, 2H), 7.59 – 7.56 (m, 3H), 7.56 – 7.52 (m, 5H), 7.47 (d, J = 8.8 Hz, 1H), 7.33 (dd, J = 8.8, 2.0 Hz, 1H), 7.13 (d, J = 4.0 Hz, 1H), 6.86 (d, J = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.7, 137.9, 137.7, 134.6, 134.0, 133.5, 131.3, 130.4, 129.7, 129.4, 129.3, 128.9, 128.8, 128.7, 126.9, 118.6, 118.2, 117.5, 110.6, 108.5.

FT-IR (ATR, cm^{-1}) υ 2229.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{16}N_3^+$: 346.1339; found: 346.1351.

7-Fluoro-1,4-diphenylpyrrolo[1,2-*a*]quinoxaline (3da)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ toluene = 1:1 for 1st column, then eluent: hexanes/acetic acid 4:1 for 2nd column) as a yellow solid; isolated yield: 76% (25.7 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.69 (dd, J = 9.4, 3.0 Hz, 1H), 7.59 – 7.54 (m, 5H), 7.53 – 7.51 (m, 3H), 7.39 (dd, J = 9.4, 5.3 Hz, 1H), 7.06 (d, J = 4.1 Hz, 1H), 6.86 (ddd, J = 9.4, 7.7, 3.0 Hz, 1H), 6.78 (d, J = 4.1 Hz, 1H).

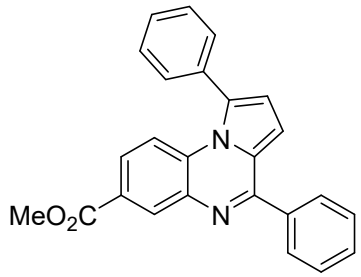
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.6 (d, $J_{C\text{-}F}$ = 244.4 Hz), 156.0, 139.2, 139.1, 138.3, 134.1, 133.0, 130.0, 129.7, 129.0, 128.9, 128.8, 128.7, 126.6, 124.9 (d, $J_{C\text{-}F}$ = 2.5

Hz), 117.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 117.0, 115.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 113.8 (d, $J_{C\text{-}F}$ = 22.7 Hz), 109.5. One coupling signal could not be determined due to overlapping and complexity of peaks.

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.05.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{16}N_2F^+$: 339.1292; found: 339.1289.

Methyl 1,4-diphenylpyrrolo[1,2-*a*]quinoxaline-7-carboxylate (**3ea**)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ ethyl acetate 12:1) as a yellow solid; isolated yield: 52% (19.5 mg).

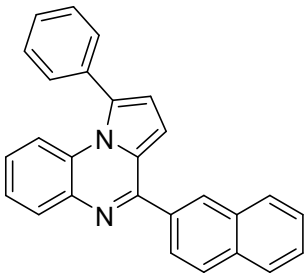
^{1}H NMR (600 MHz, $CDCl_3$) *δ* 8.71 (d, *J* = 2.0 Hz, 1H), 8.00 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.78 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.58 – 7.51 (m, 8H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.09 (d, *J* = 4.1 Hz, 1H), 6.83 (d, *J* = 4.1 Hz, 1H), 3.93 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) *δ* 166.6, 155.7, 138.3, 137.3, 133.9, 133.6, 132.1, 131.4, 130.1, 129.8, 129.1, 129.0, 128.85, 128.76, 127.1, 127.0, 126.8, 117.7, 116.6, 109.8, 52.3.

FT-IR (ATR, cm^{-1}) υ 1715.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{19}N_2O_2^+$: 379.1441; found: 379.1443.

4-(Naphthalen-2-yl)-1-phenylpyrrolo[1,2-*a*]quinoxaline (**3fa**)



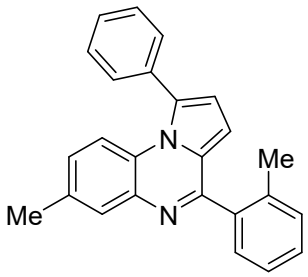
Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/acetone 20:1) as a yellow solid; isolated yield: 45% (15.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.12 (dd, J = 8.5, 1.6 Hz, 1H), 8.07 (dd, J = 8.0, 1.6 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 8.01 – 7.98 (m, 1H), 7.96 – 7.93 (m, 1H), 7.60 – 7.56 (m, 4H), 7.56 – 7.51 (m, 3H), 7.46 (dd, J = 8.5, 1.3 Hz, 1H), 7.39 (ddd, J = 8.0, 7.2, 1.3 Hz, 1H), 7.14 (ddd, J = 8.5, 7.2, 1.6 Hz, 1H), 7.12 (d, J = 4.0 Hz, 1H), 6.82 (d, J = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.9, 137.8, 136.1, 134.4, 134.2, 133.3, 133.0, 130.4, 129.8, 128.89, 128.86, 128.8, 128.6, 128.5, 128.3, 127.9, 127.1, 127.0, 126.5, 126.4, 126.3, 125.2, 117.1, 116.7, 109.1.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{27}H_{19}N_2^+$: 371.1542; found: 371.1542.

7-Methyl-1-phenyl-4-(*o*-tolyl)pyrrolo[1,2-*a*]quinoxaline (3ga)



Prepared according to the general procedure and isolated by column chromatography on silica gel (eluent: hexanes/ toluene/acetic acid 4:4:1) as a yellow solid; isolated yield: 86% (30.4 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 2.1 Hz, 1H), 7.59 – 7.55 (m, 2H), 7.53 – 7.49 (m, 4H), 7.41 – 7.31 (m, 4H), 6.98 (dd, J = 8.6, 2.1 Hz, 1H), 6.71 (d, J = 4.0 Hz, 1H), 6.59 (d, J = 4.0 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.0, 137.8, 137.5, 136.7, 134.9, 134.4, 132.5, 130.8, 130.1, 129.9, 129.1, 129.0, 128.8, 128.7, 127.7, 127.5, 126.3, 125.7, 116.6, 116.4, 108.8, 21.0, 19.9.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{21}N_2^+$: 349.1699; found: 349.1698.

*X-ray Crystallography of **3ac***

Good quality single crystals of **3ac** suitable for X-ray structure analysis were obtained by slow evaporation of hexanes into a saturated solution of **3ac** in dichloromethane. The

intensities for the X-ray determinations of **3ac** were collected on a Bruker D8-VENTURE instrument with CuKα radiation (λ = 1.54178 Å) at 298 K. Standard procedures were applied for data reduction and absorption correction. Using OLEX,[3] the structure solution and refinement were performed with SHELXT and SHELXL.[4,5] Hydrogen atom positions were calculated for idealized positions and treated with the 'riding mode' option of SHELXL. More details on data collections and structure calculations are contained in Table 1. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre with CCDC code: 2414626.

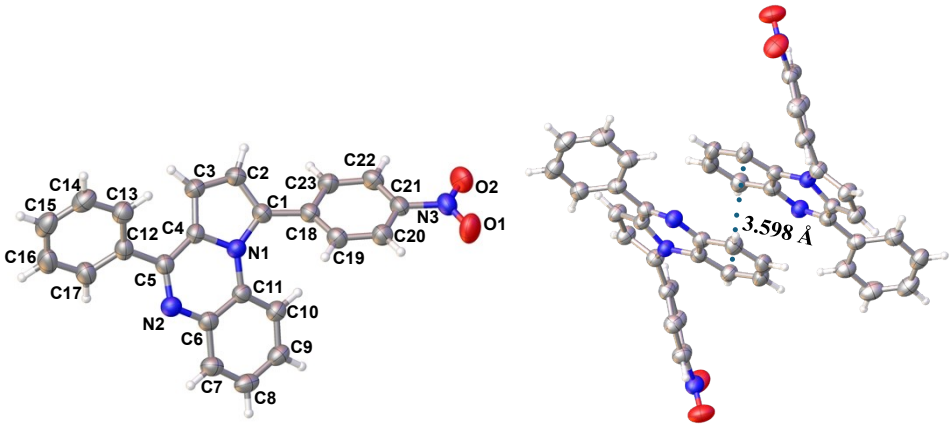


Table 1 Crystal data and structure refinement for **3ac**.

Empirical formula	$C_{23}H_{15}N_3O_2$
Formula weight	365.38
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.3695(2)
b/Å	7.37850(10)
c/Å	18.8523(4)

α/°	90
β/°	92.7020(10)
γ/°	90
Volume/Å^3	1718.71(5)
Z	4
ρ_{calc}g/cm^3	1.412
μ/mm^{-1}	0.746
F(000)	760.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Index ranges	$-14 \leq h \leq 14$, $-8 \leq k \leq 8$, $-22 \leq l \leq 22$
Reflections collected	22227
Independent reflections	2932 [R_{int} = 0.0595, R_{sigma} = 0.0280]
Data/restraints/parameters	2932/0/254
Goodness-of-fit on F^2	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0598, wR_2 = 0.1201
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.1506

References

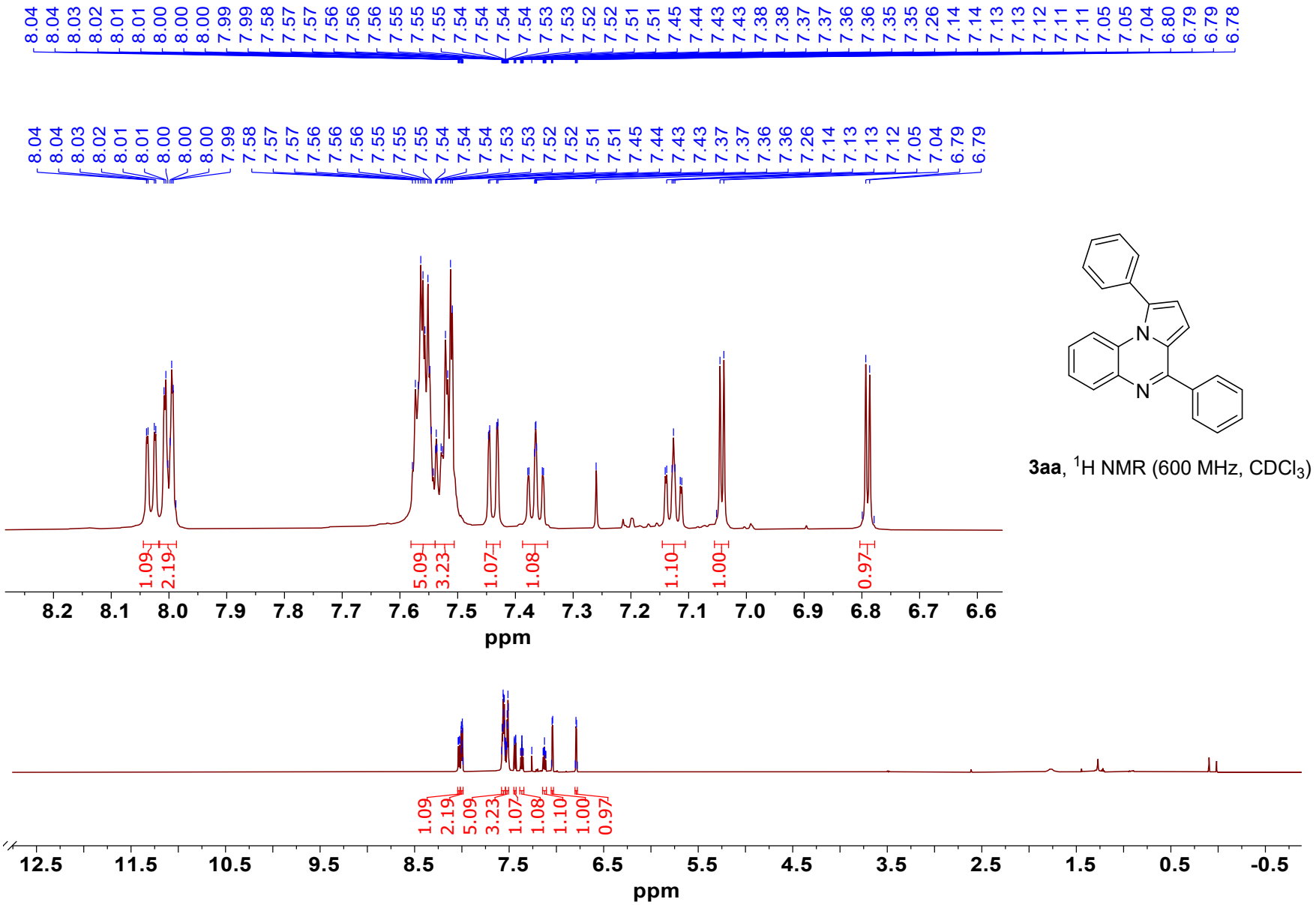
1 (a) C. Xie, L. Feng, W. Li, X. Ma, X. Ma, Y. Liu and C. Ma, *Org. Biomol. Chem.*, 2016, **14**, 8529; (b) B. Budke, W. Tueckmantel, K. Miles, A. P. Kozikowski and P. P. Connell, *ChemMedChem*, 2019, **14**, 1031.

2 D. Hao, Z. Yang, Y. Liu, Y. Li, C. Li, Y. Gu, L. Vaccaro, J. Liu and P. Liu, *Org. Biomol. Chem.*, 2022, **20**, 847.

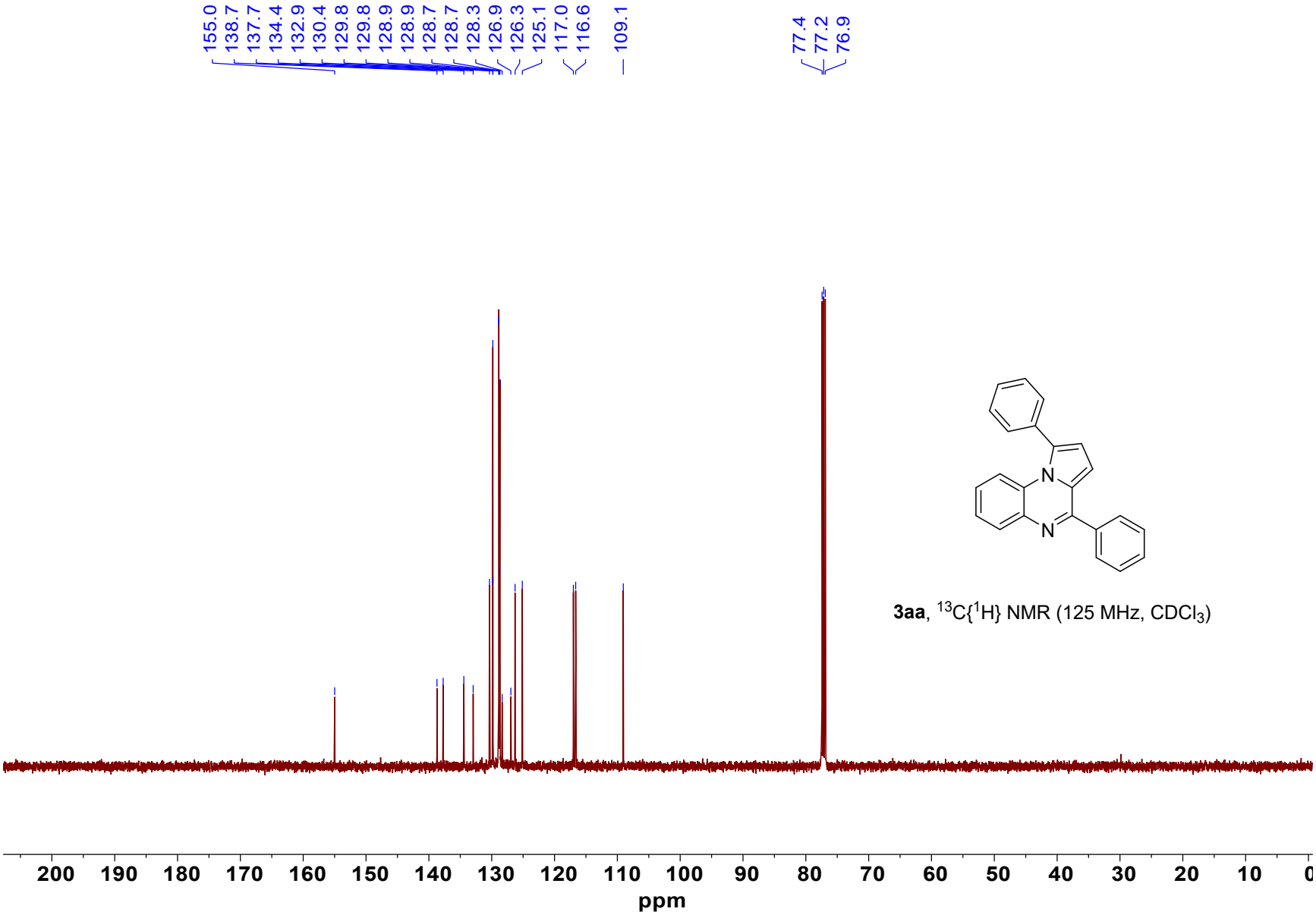
3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

4 S. M. Sheldrick, *Acta Cryst. A71*, 2015, 3.

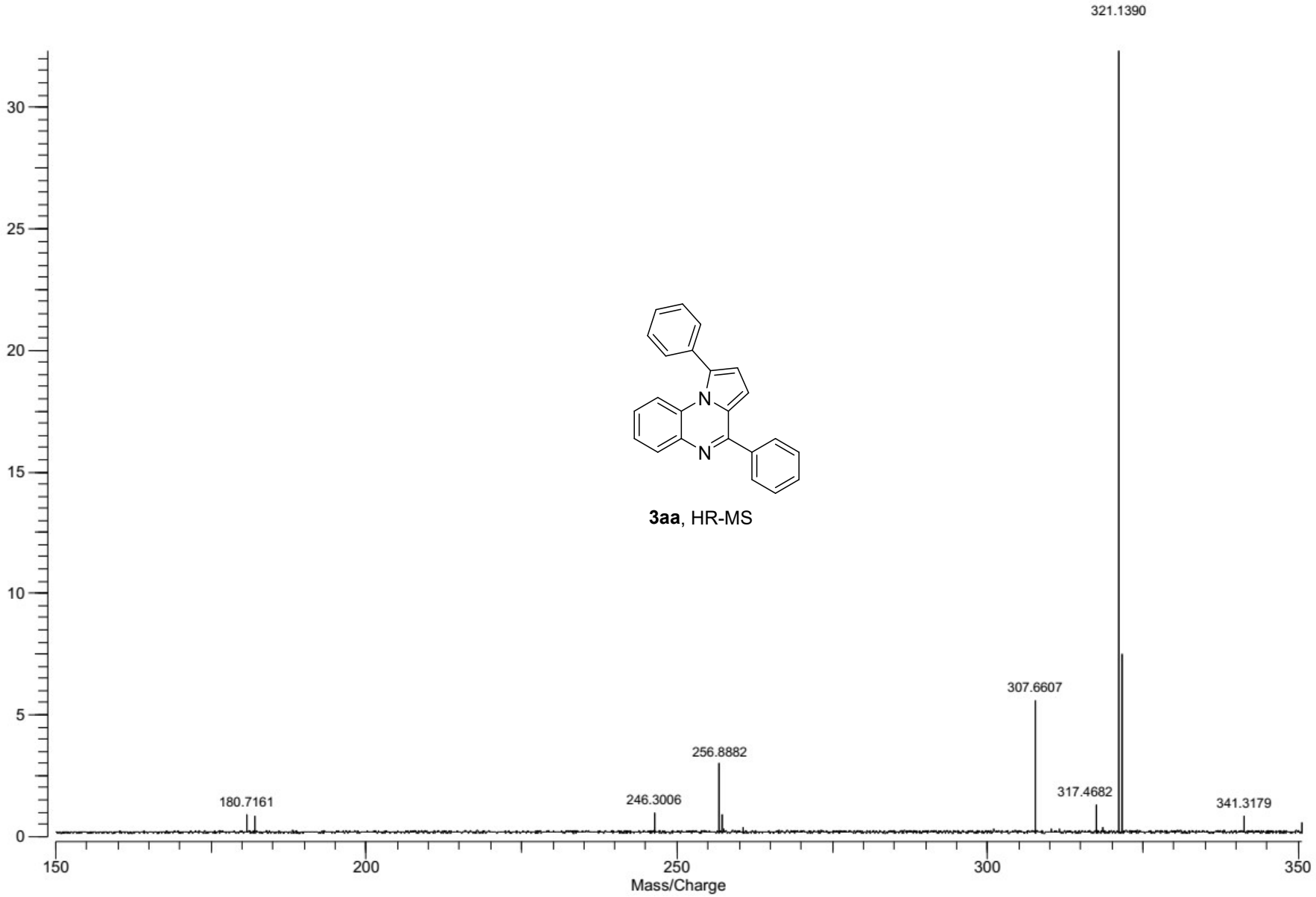
5 S. M. Sheldrick, *Acta Cryst. C71*, 2015, 3.



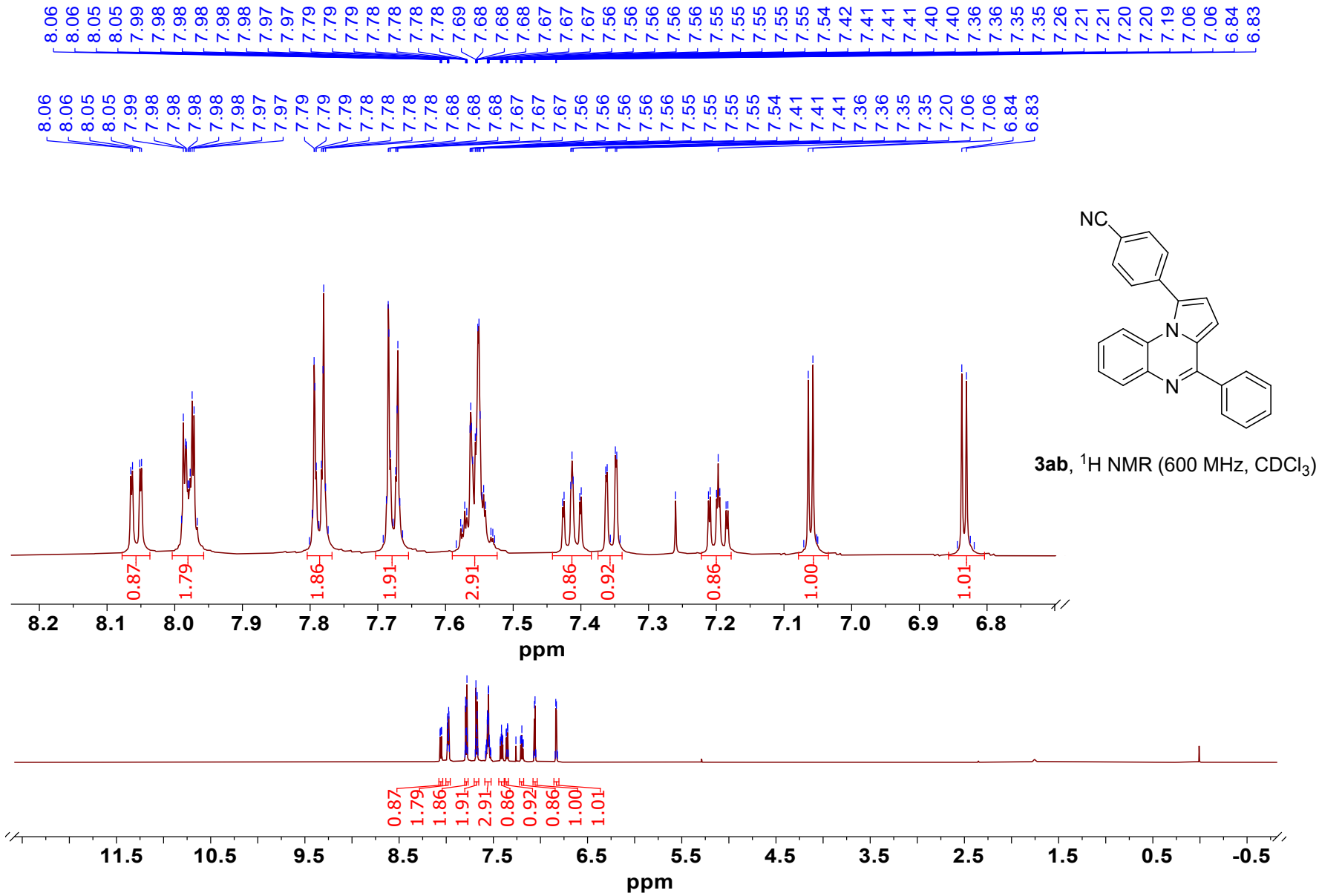
3aa, ^{1}H NMR (600 MHz, $CDCl_3$)



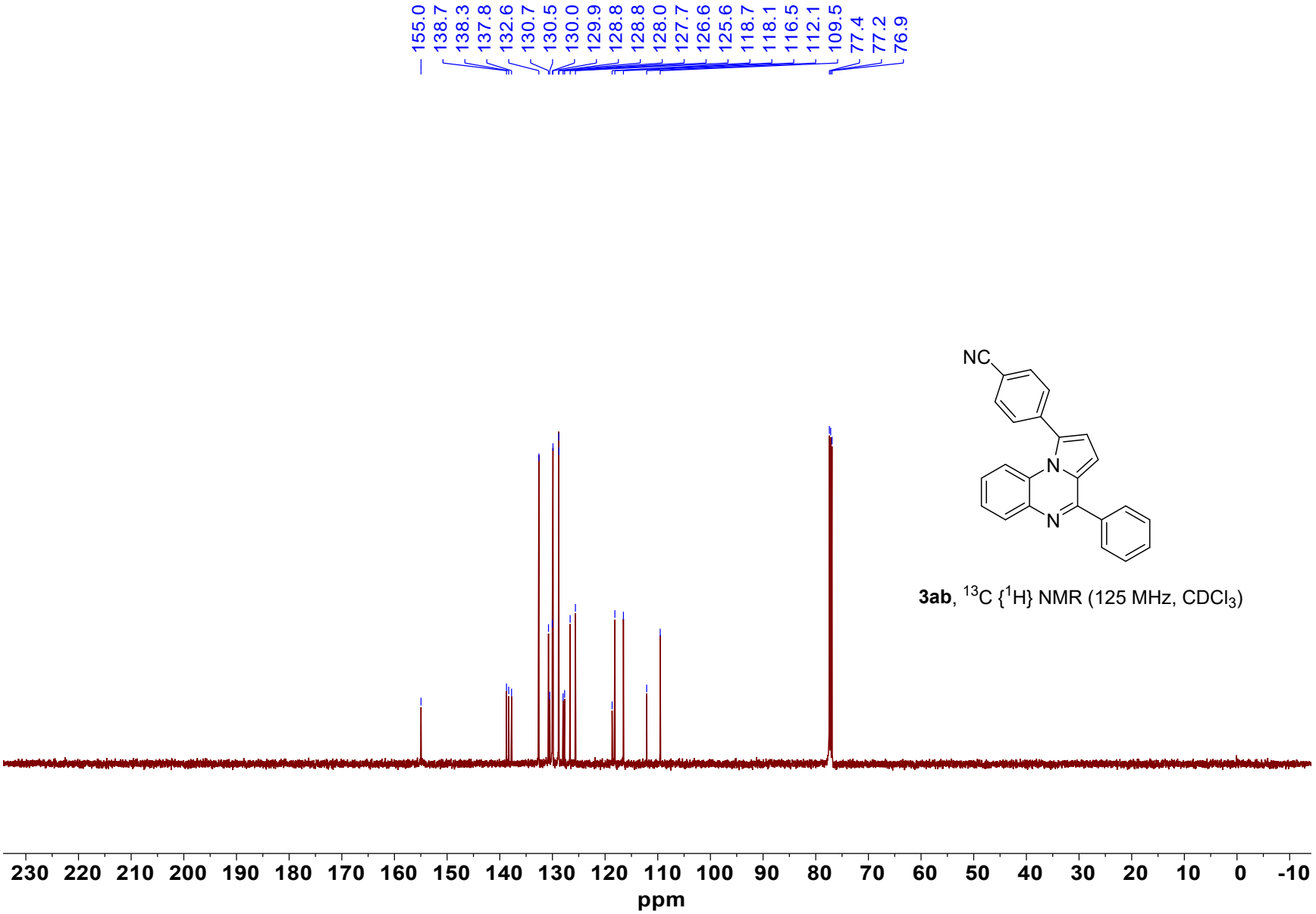
3aa, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


321.1390
30
25
20
15
10
5
0
N
N
307.6607
256.8882
180.7161
246.3006
317.4682
341.3179
150
200
250
300
350
Mass/Charge

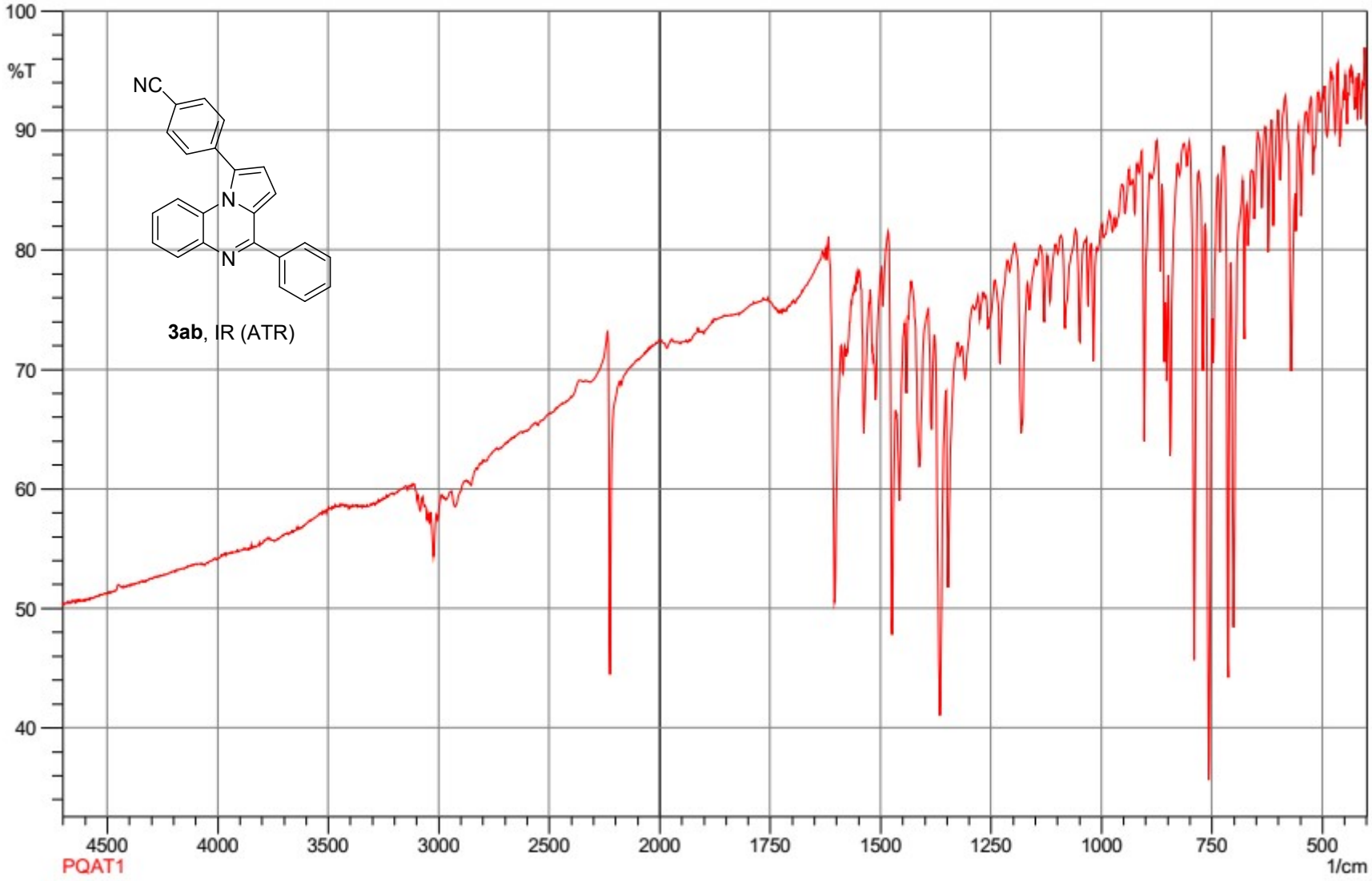
3aa, HR-MS



3ab, ^{1}H NMR (600 MHz, $CDCl_3$)



3ab, $^{13}C\ \{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


NC
N
N
3ab, IR (ATR)
100
%T
90
80
70
60
50
40
4500
4000
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3000
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1750
1500
1250
1000
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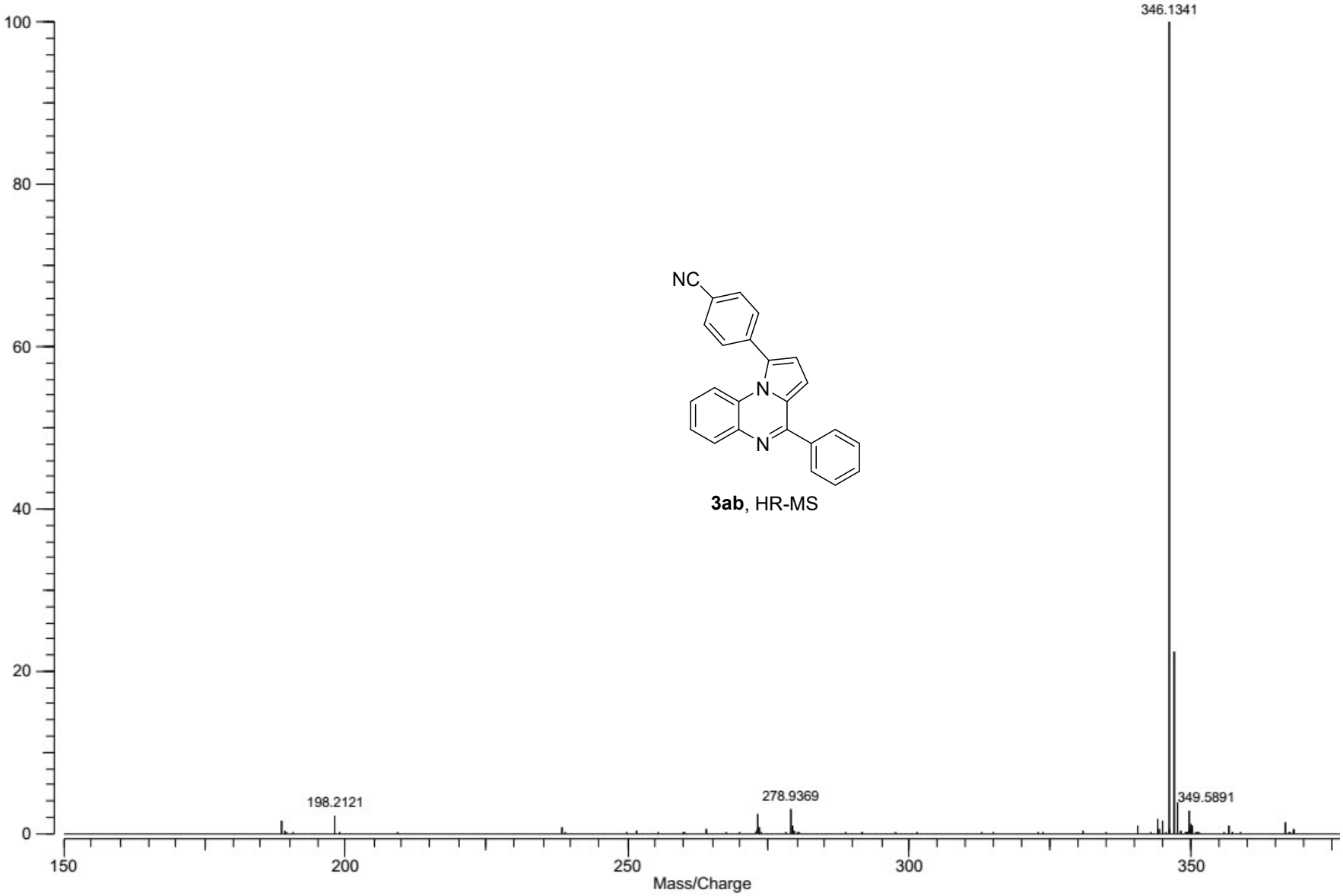
500
1/cm
PQAT1


346.1341
100
80
60
40
20
0
198.2121
278.9369
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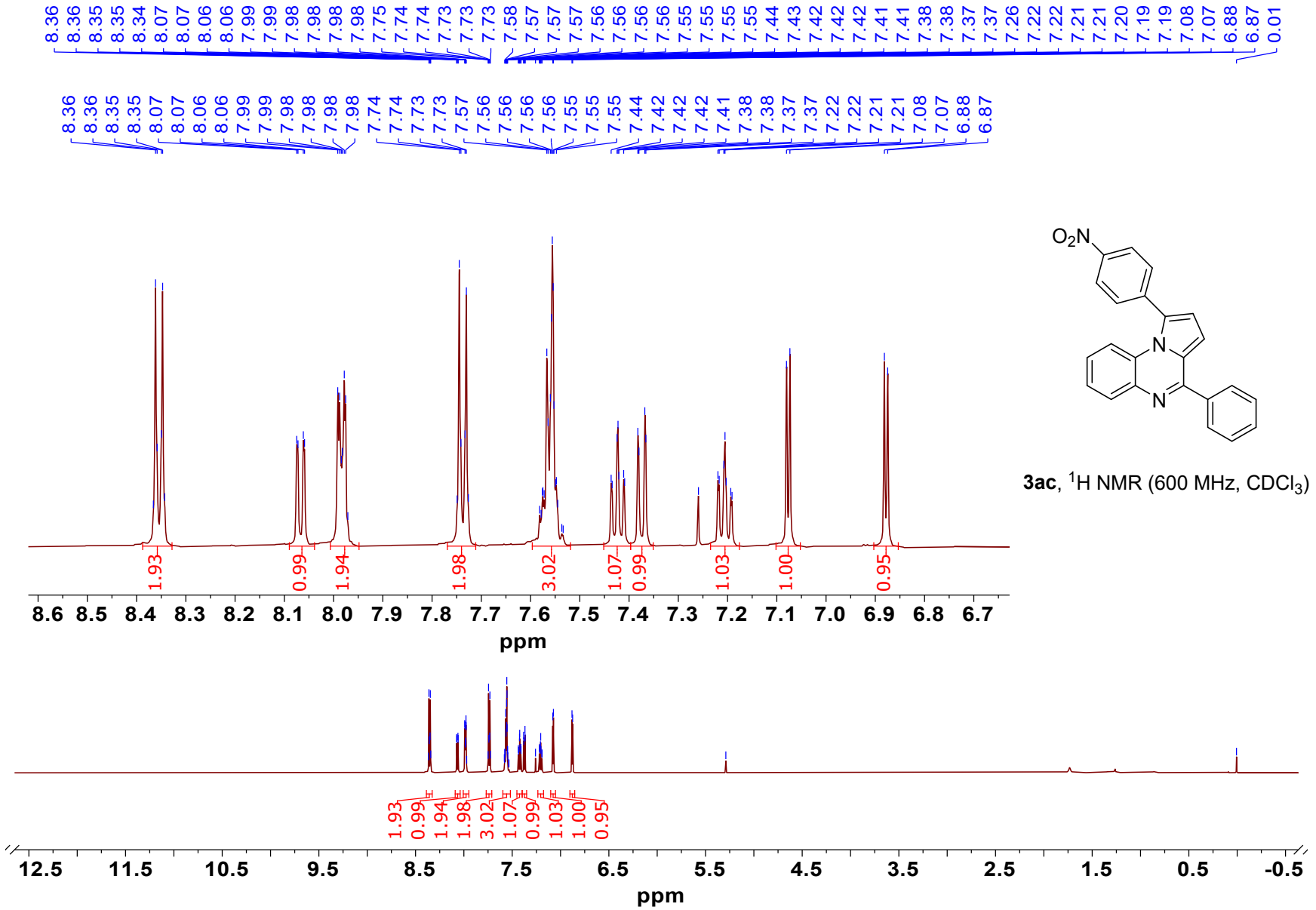
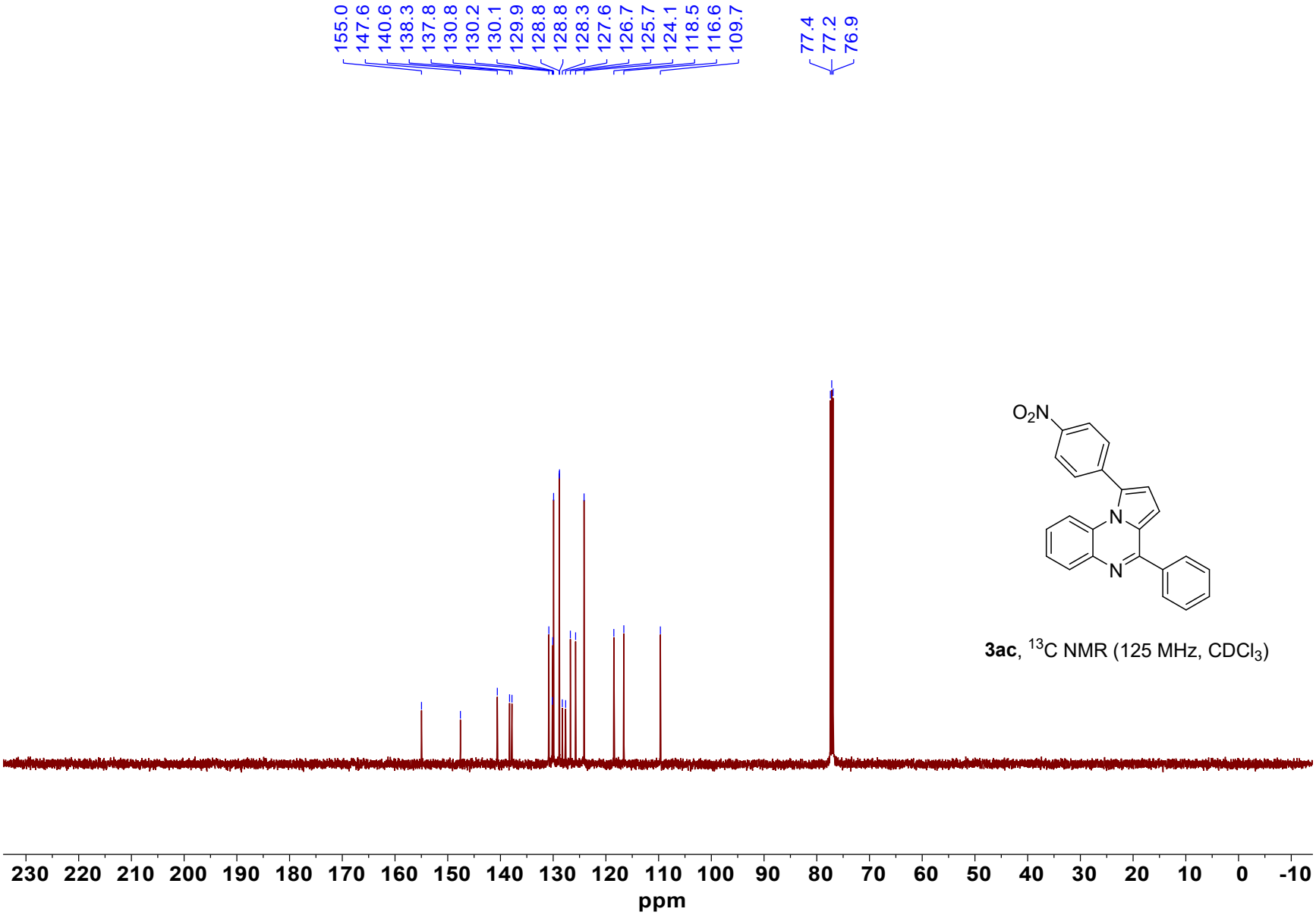
200
250
300
350
Mass/Charge
NC
N
N

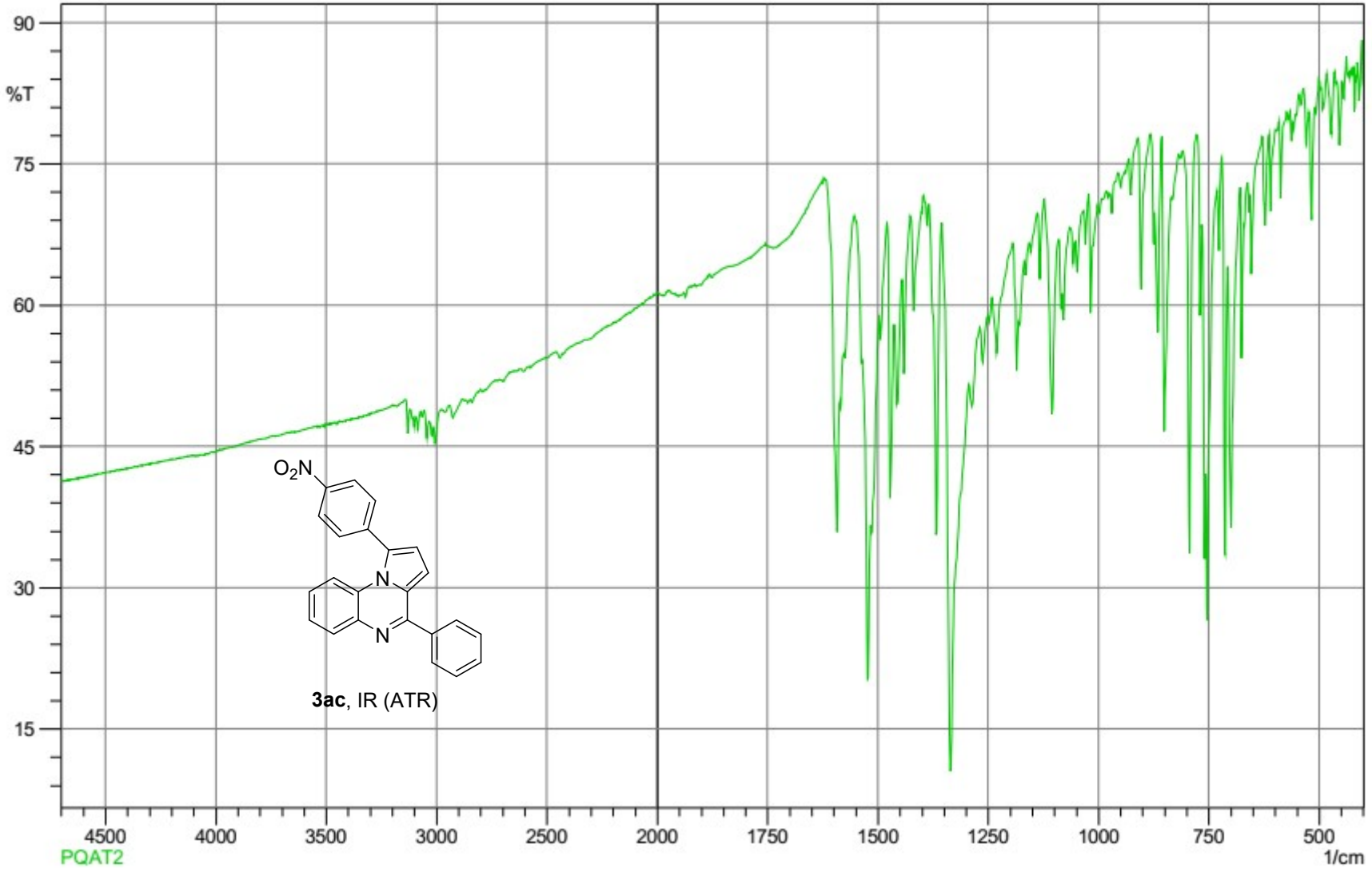
3ab, HR-MS



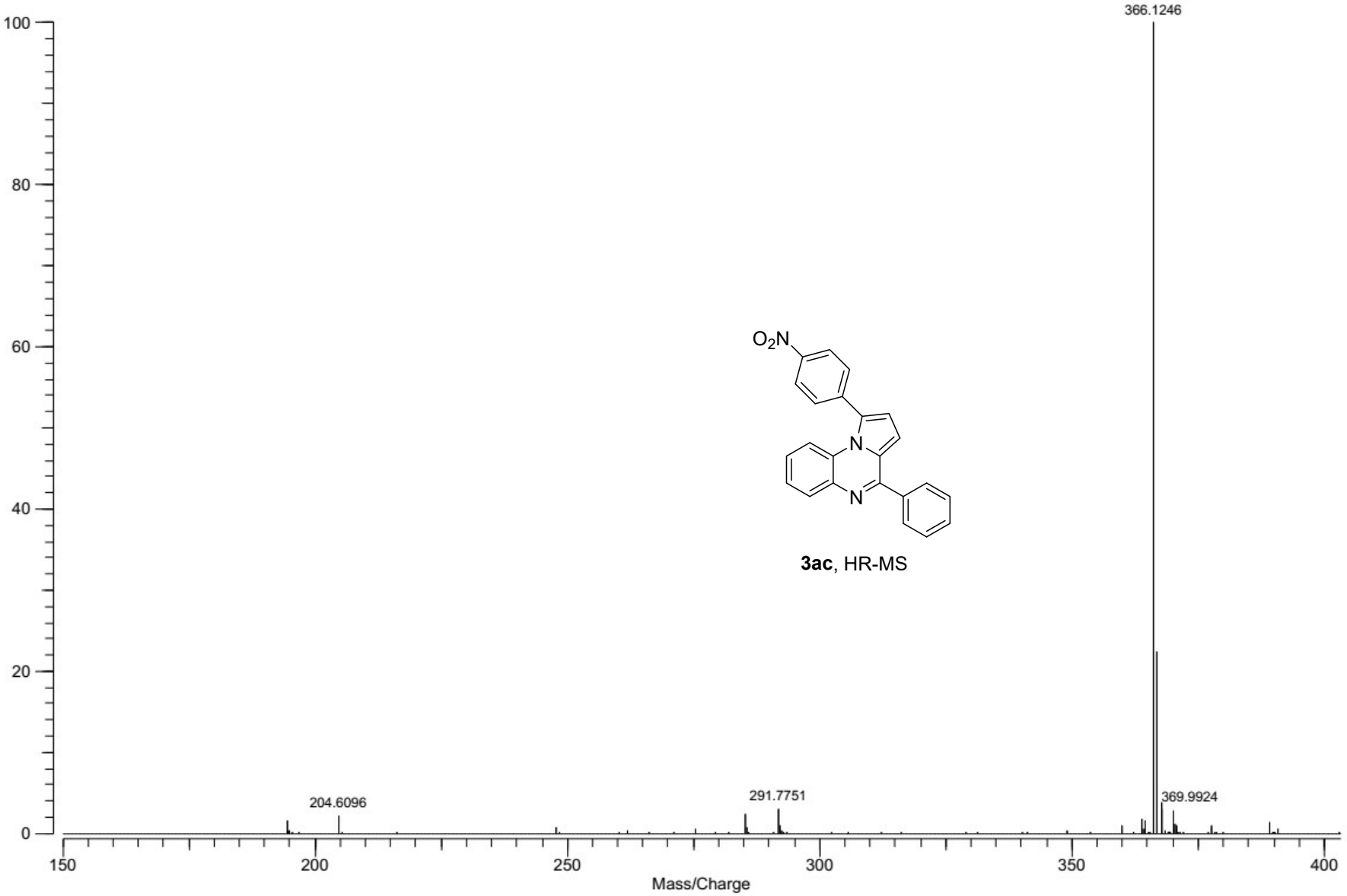
3ac, ^{1}H NMR (600 MHz, $CDCl_3$)



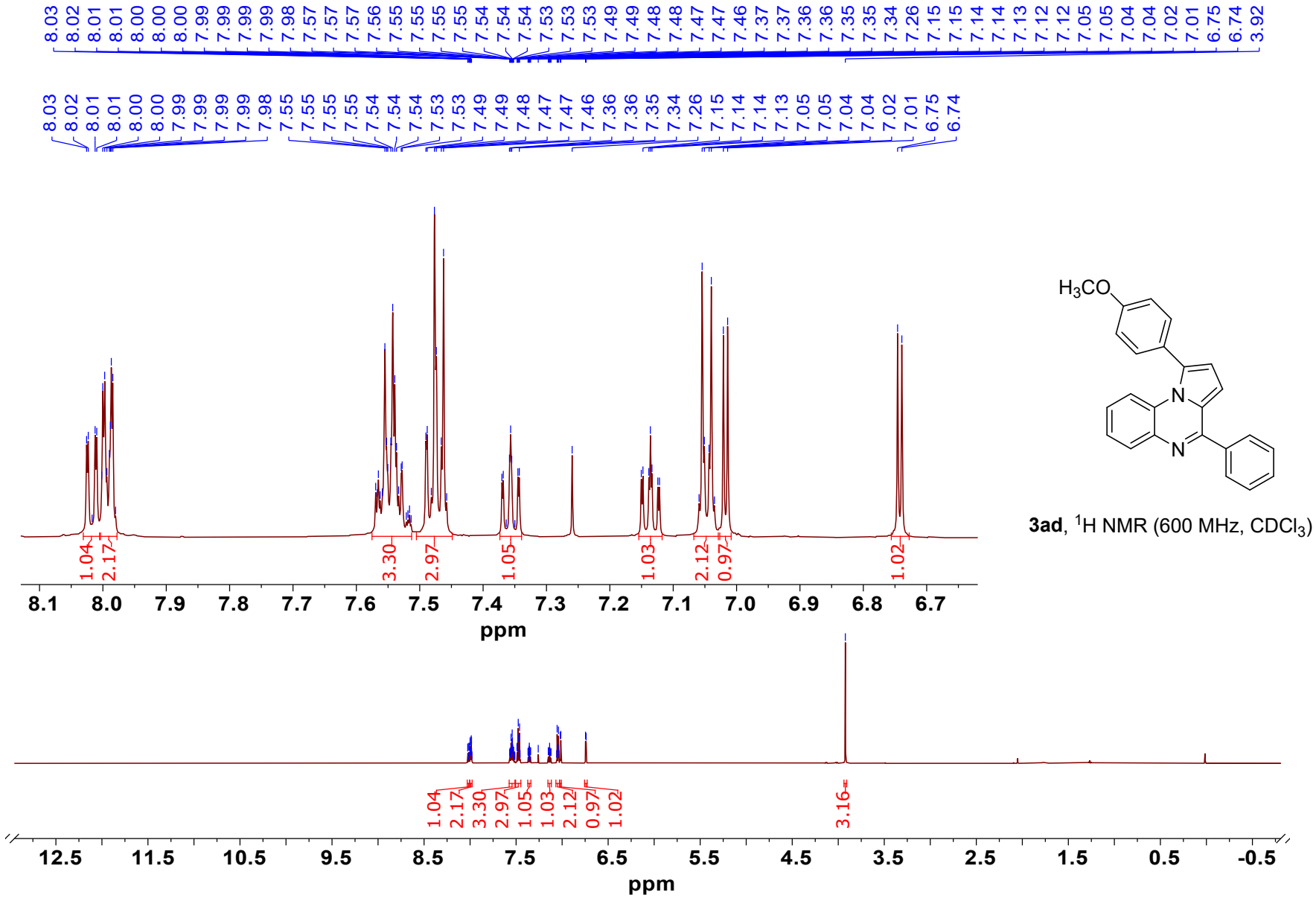
3ac, ^{13}C NMR (125 MHz, $CDCl_3$)


90
%T
75
60
45
30
15
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
PQAT2
O2N
N
N

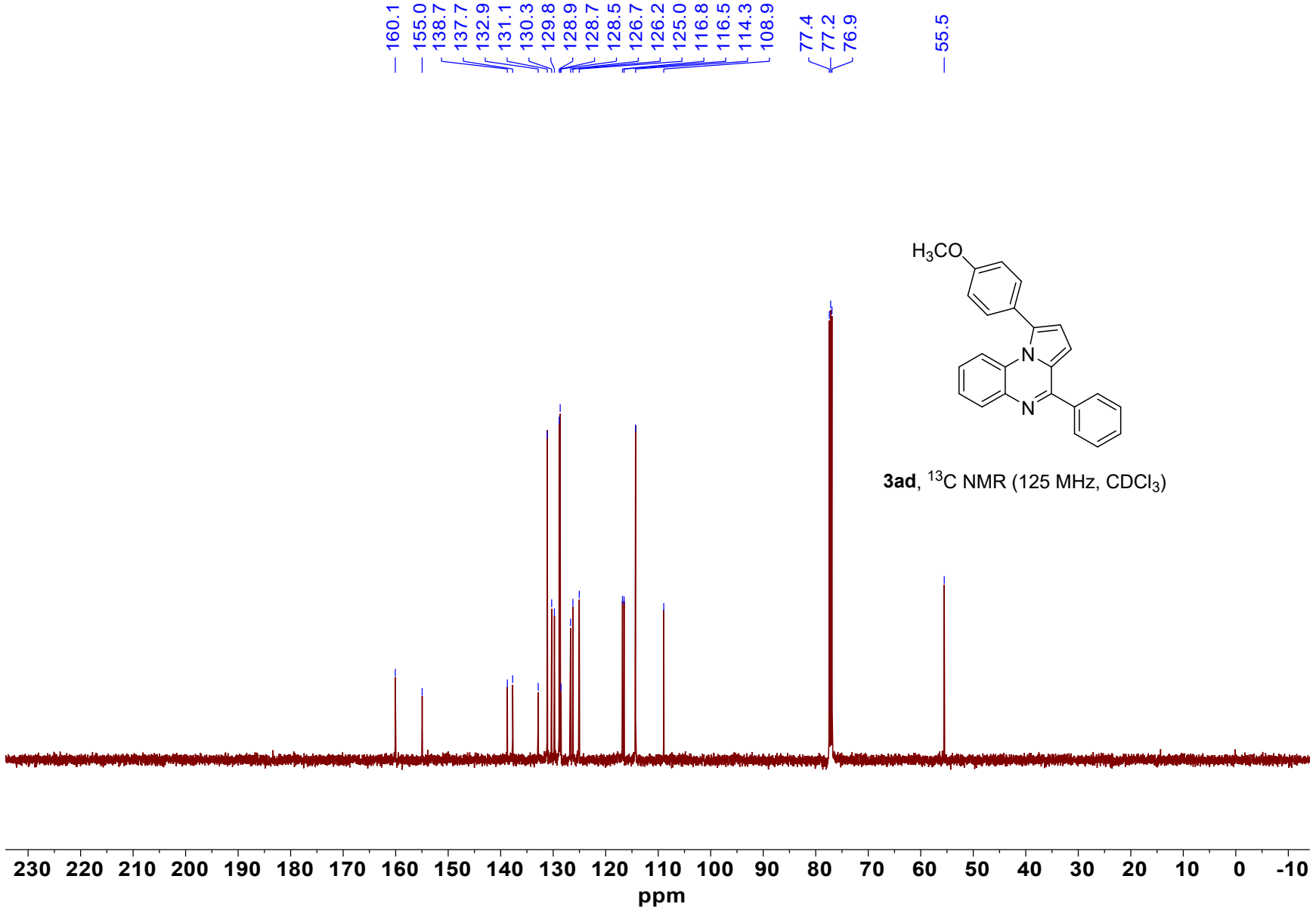
3ac, IR (ATR)


366.1246
100
80
60
40
20
0
204.6096
291.7751
369.9924
150
200
250
300
350
400
Mass/Charge
O2N
N
N

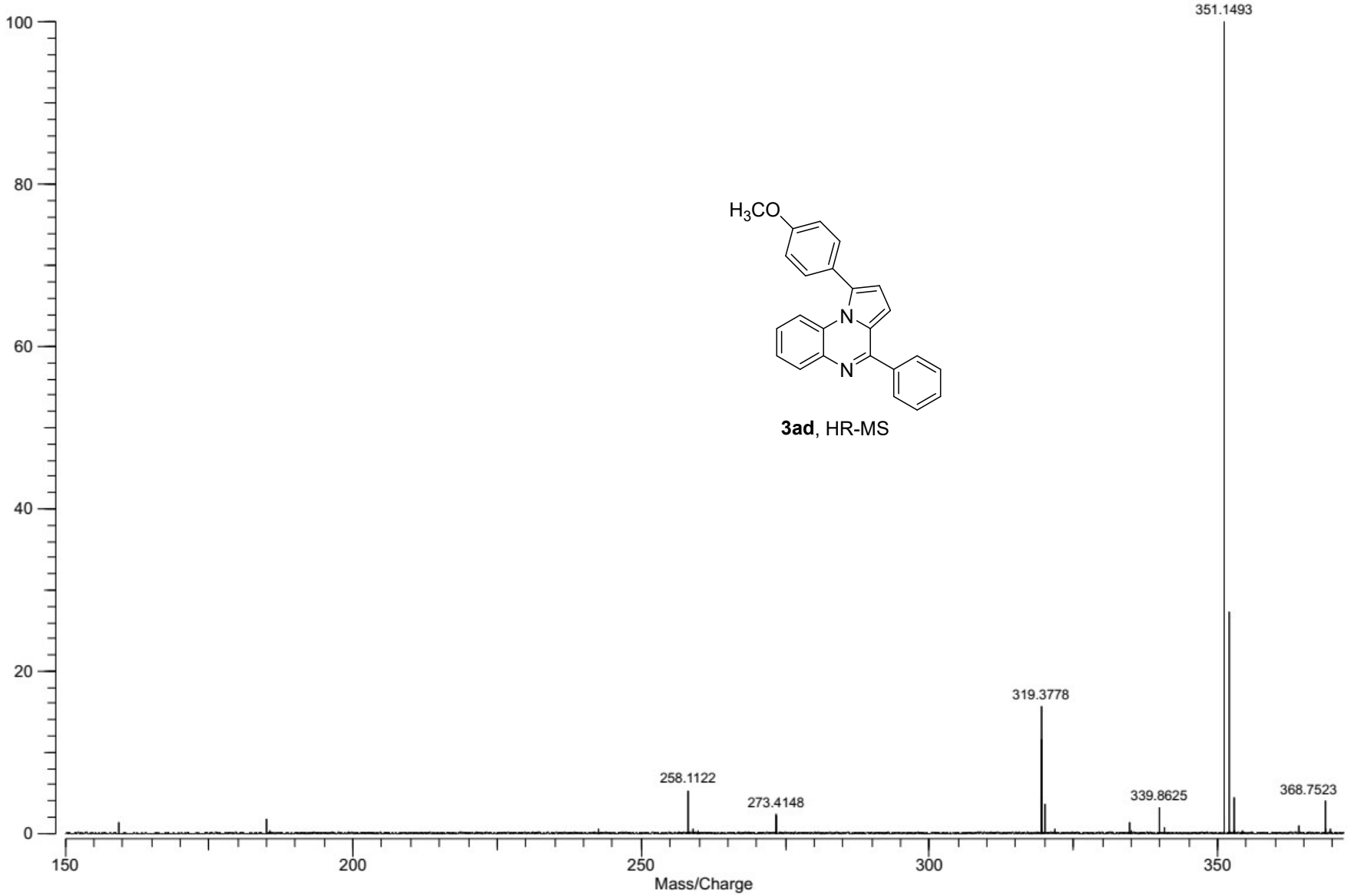
3ac, HR-MS

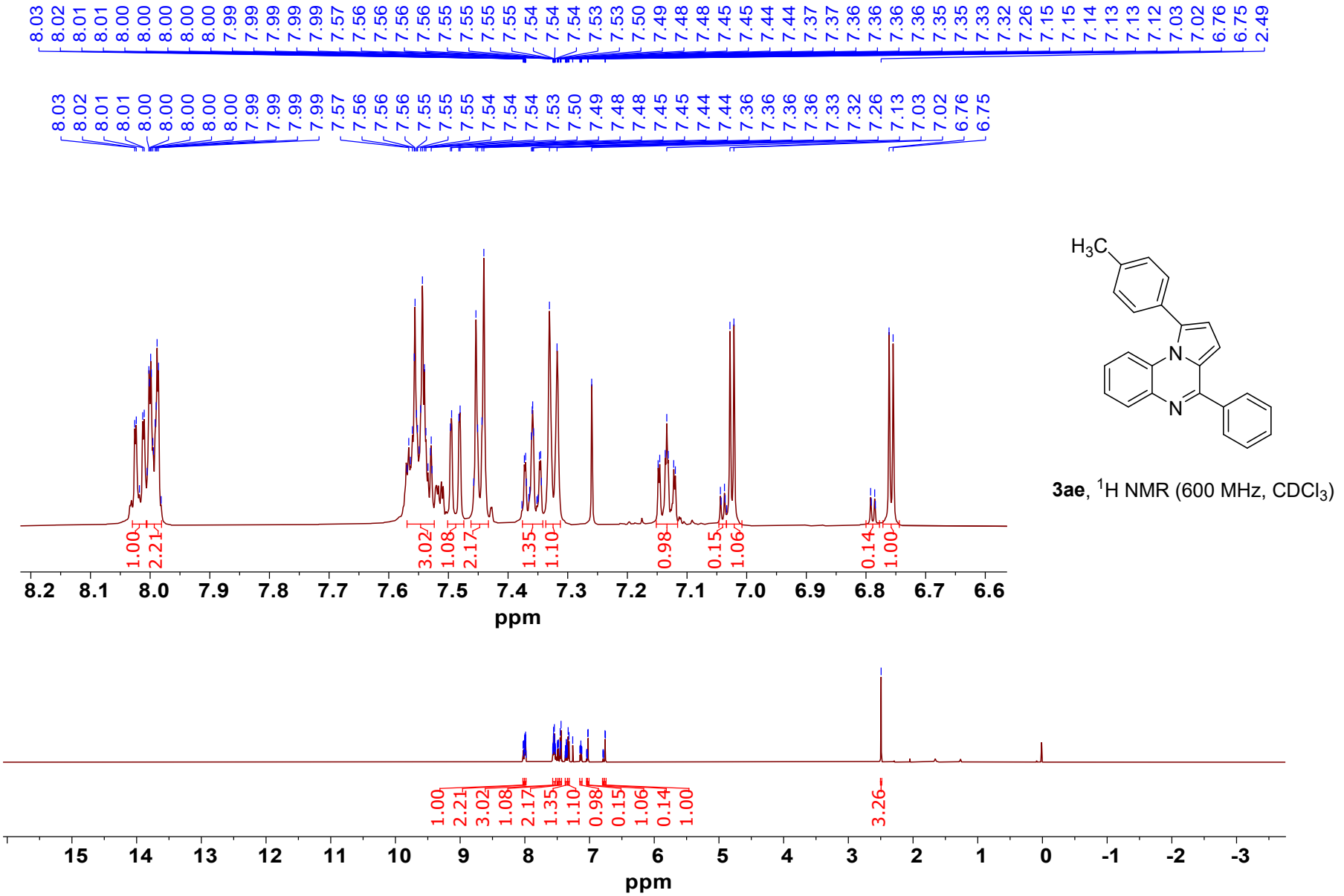


3ad, ^{1}H NMR (600 MHz, $CDCl_3$)

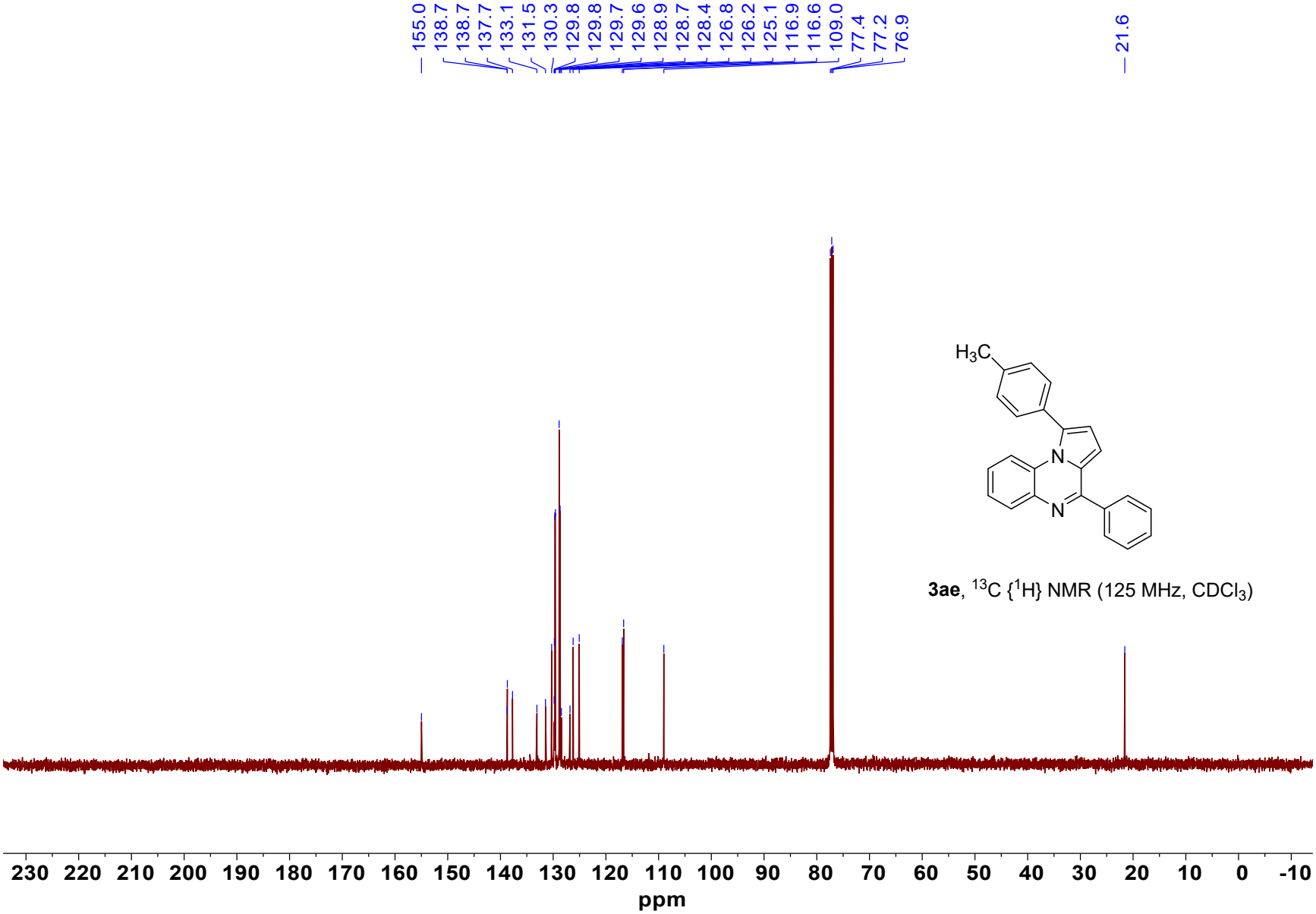


3ad, ^{13}C NMR (125 MHz, $CDCl_3$)

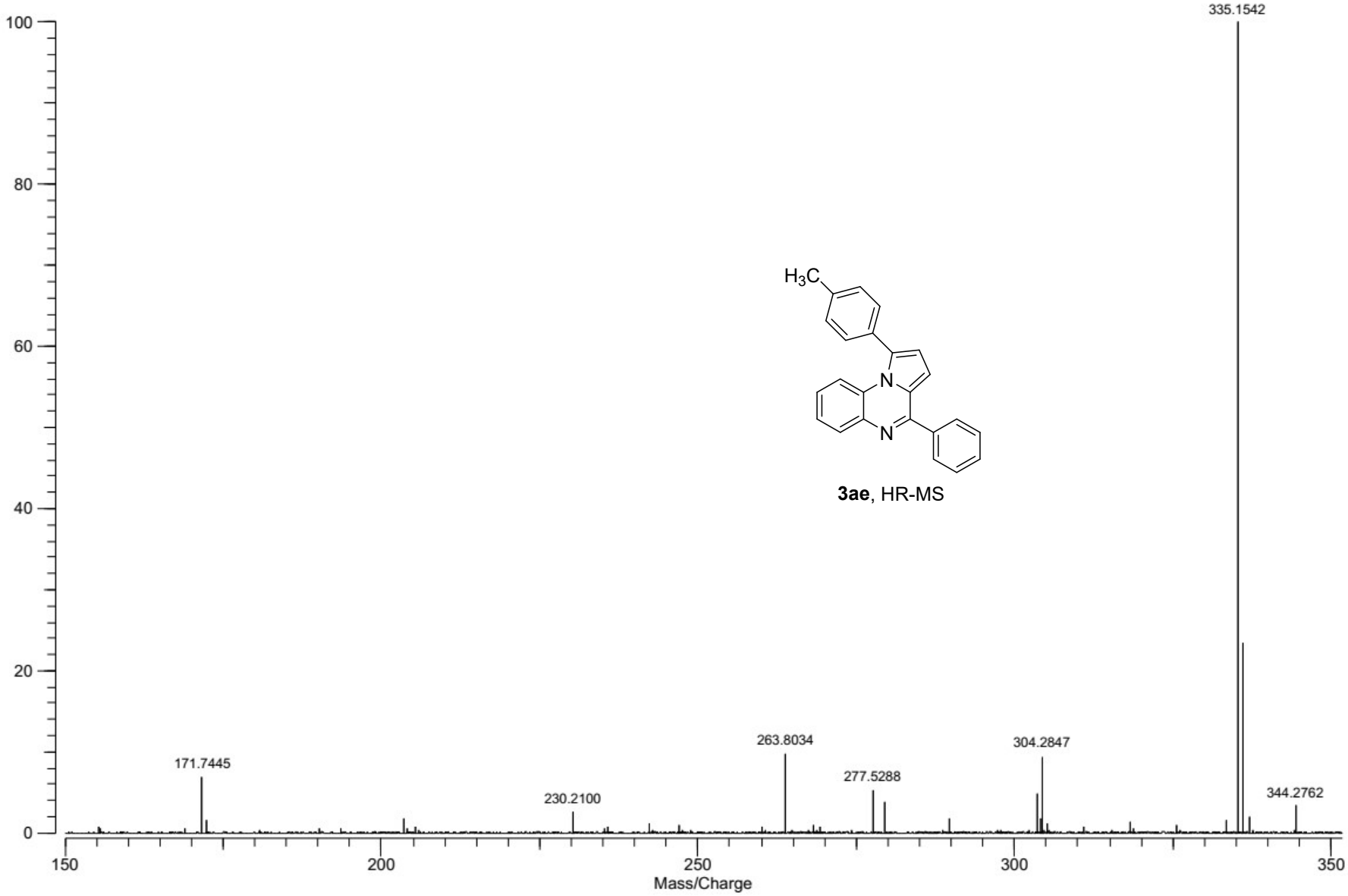

351.1493
100
80
60
40
20
0
H3CO
N
N
3ad, HR-MS
319.3778
258.1122
273.4148
339.8625
368.7523
150
200
250
300
350
Mass/Charge



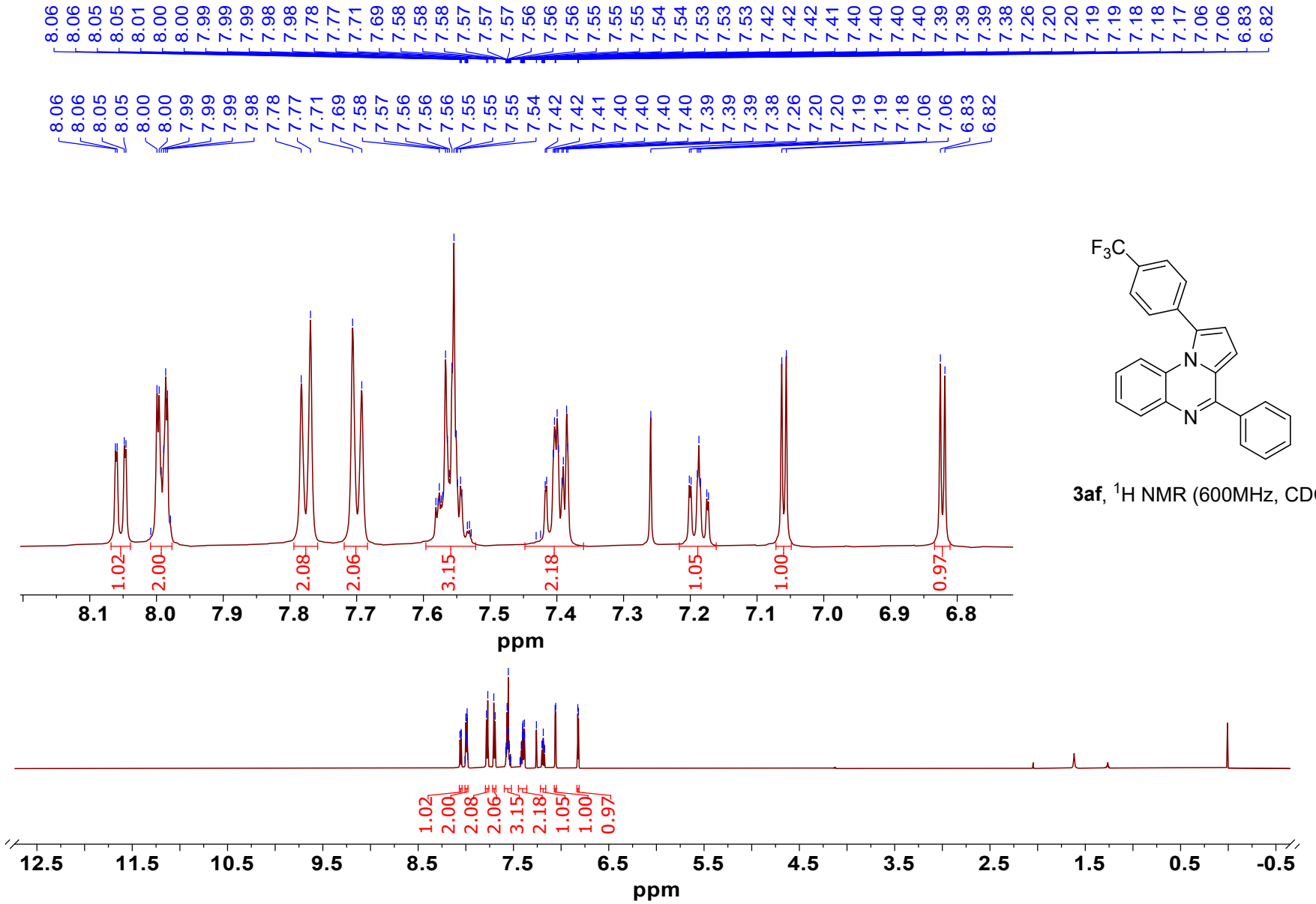
3ae, ^{1}H NMR (600 MHz, $CDCl_3$)



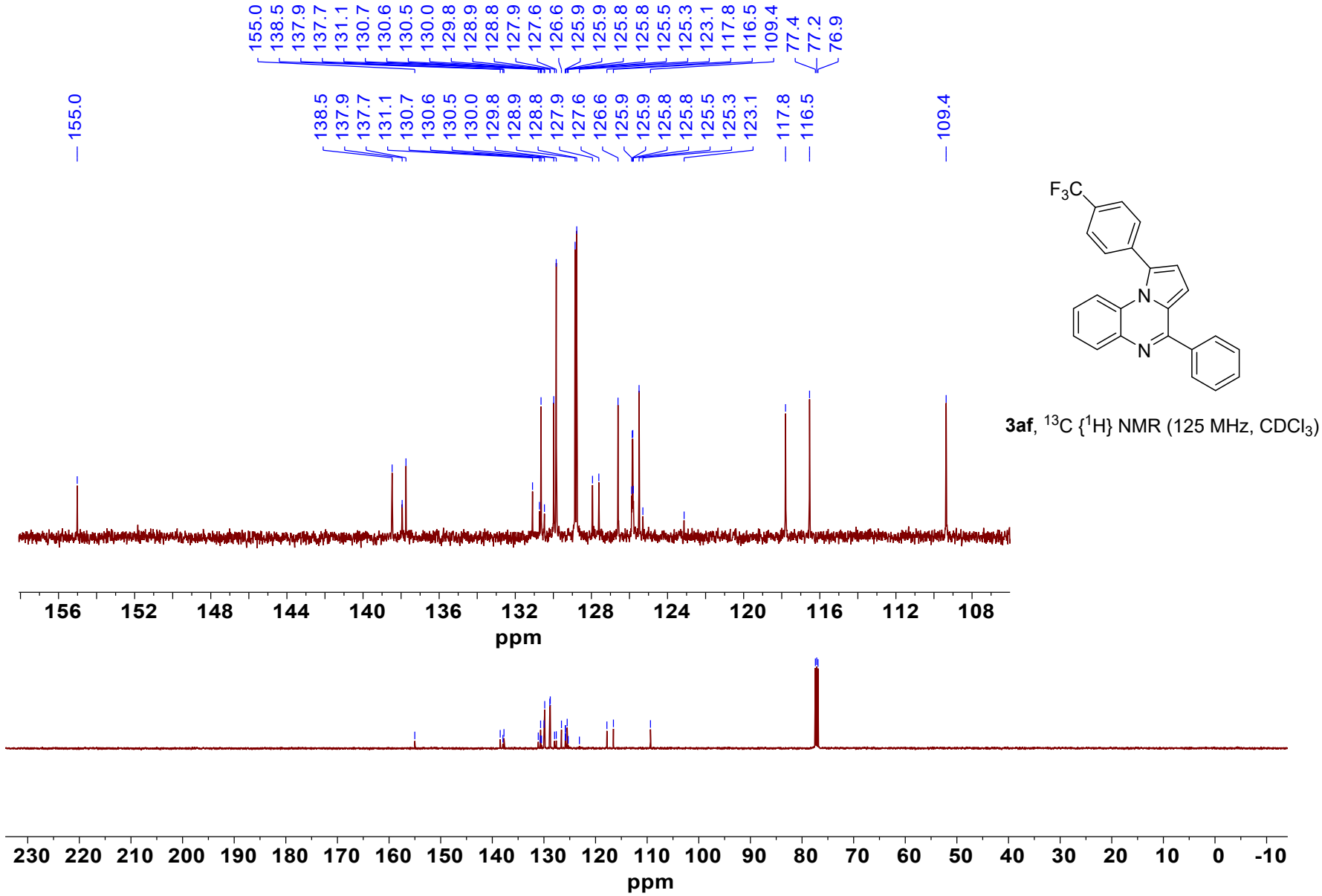
3ae, ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)


335.1542
100
80
60
40
20
0
171.7445
230.2100
263.8034
277.5288
304.2847
344.2762
150
200
250
300
350
Mass/Charge
H3C
N
N

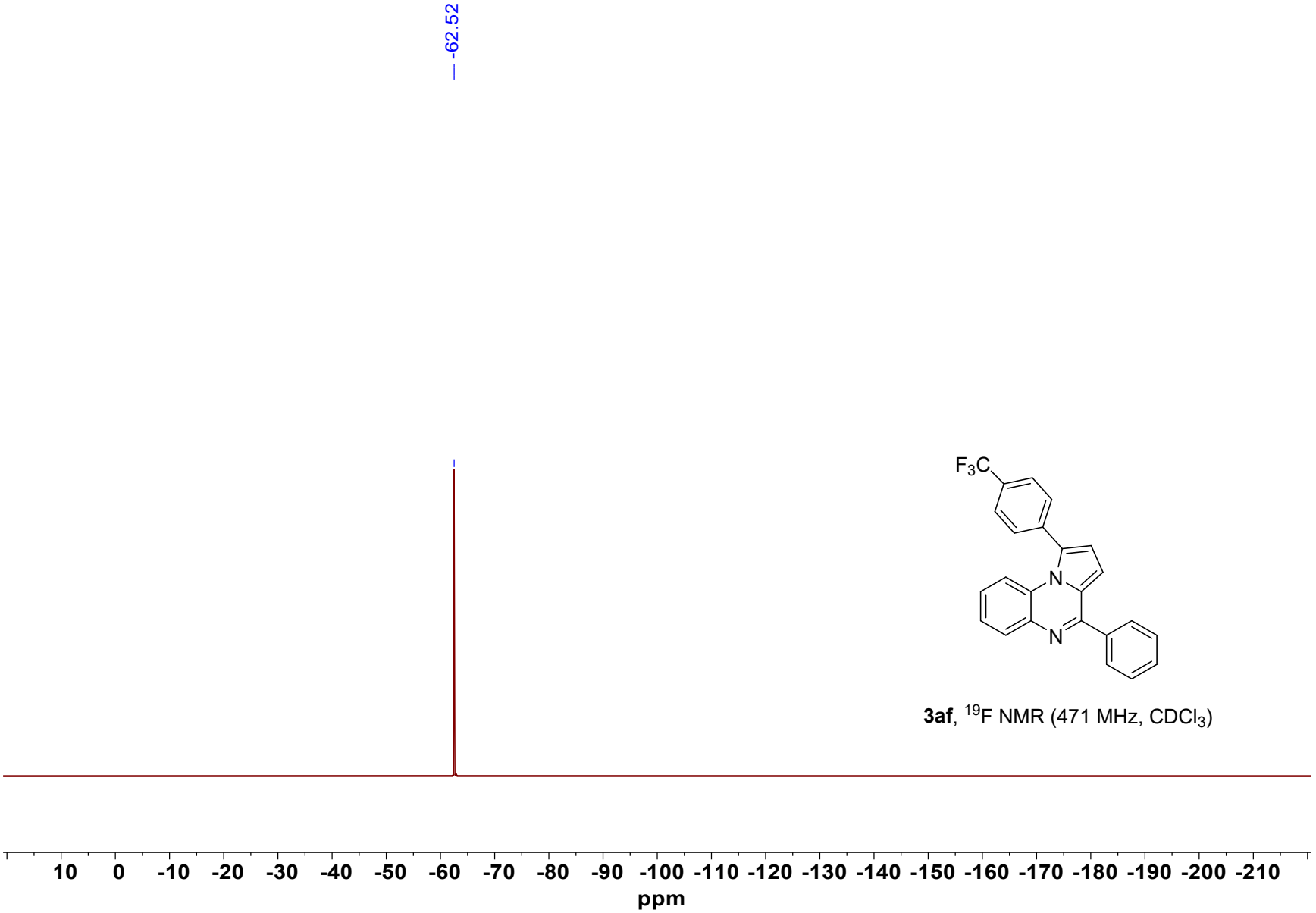
3ae, HR-MS



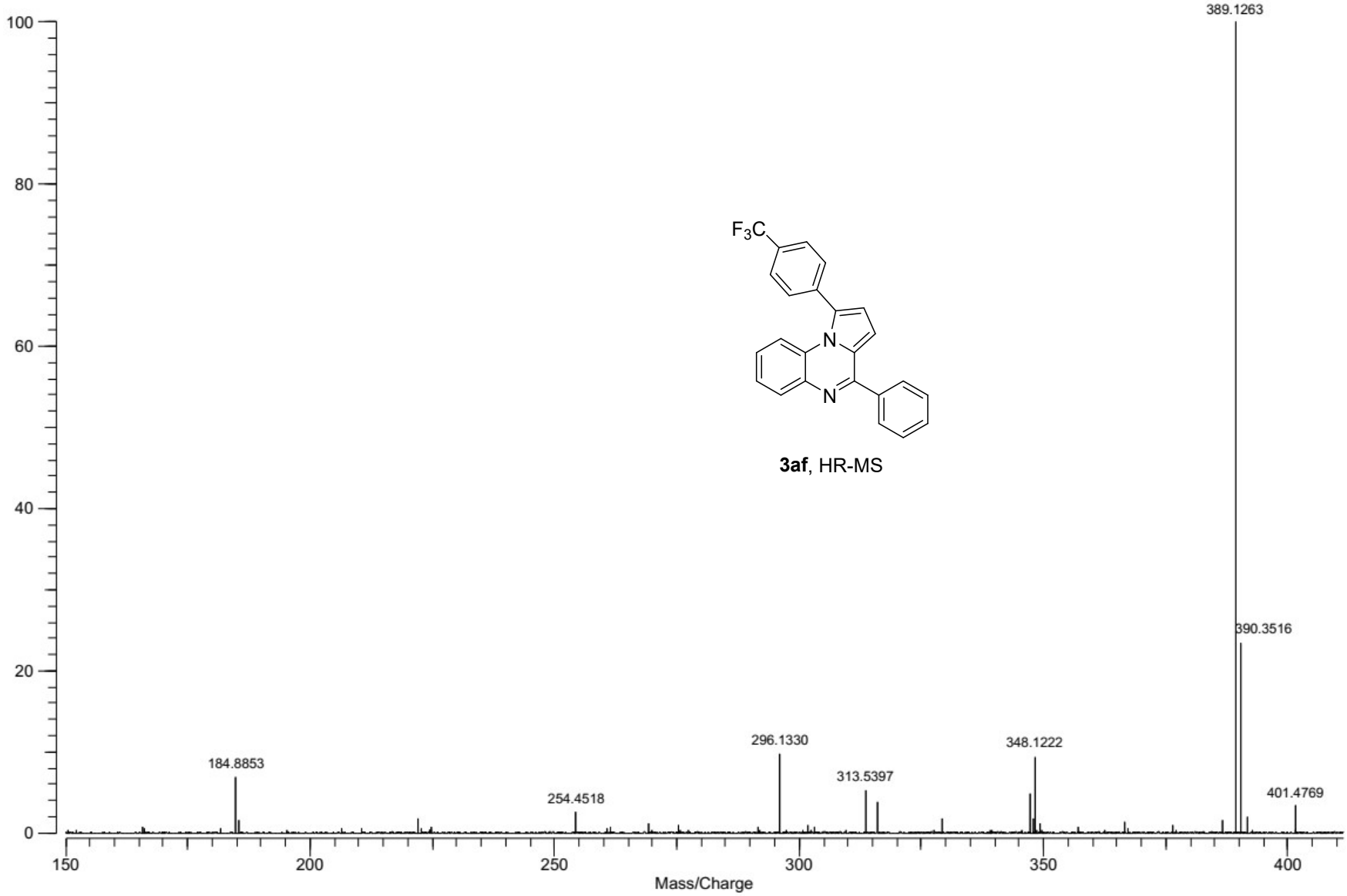
3af, ^{1}H NMR (600MHz, $CDCl_3$)



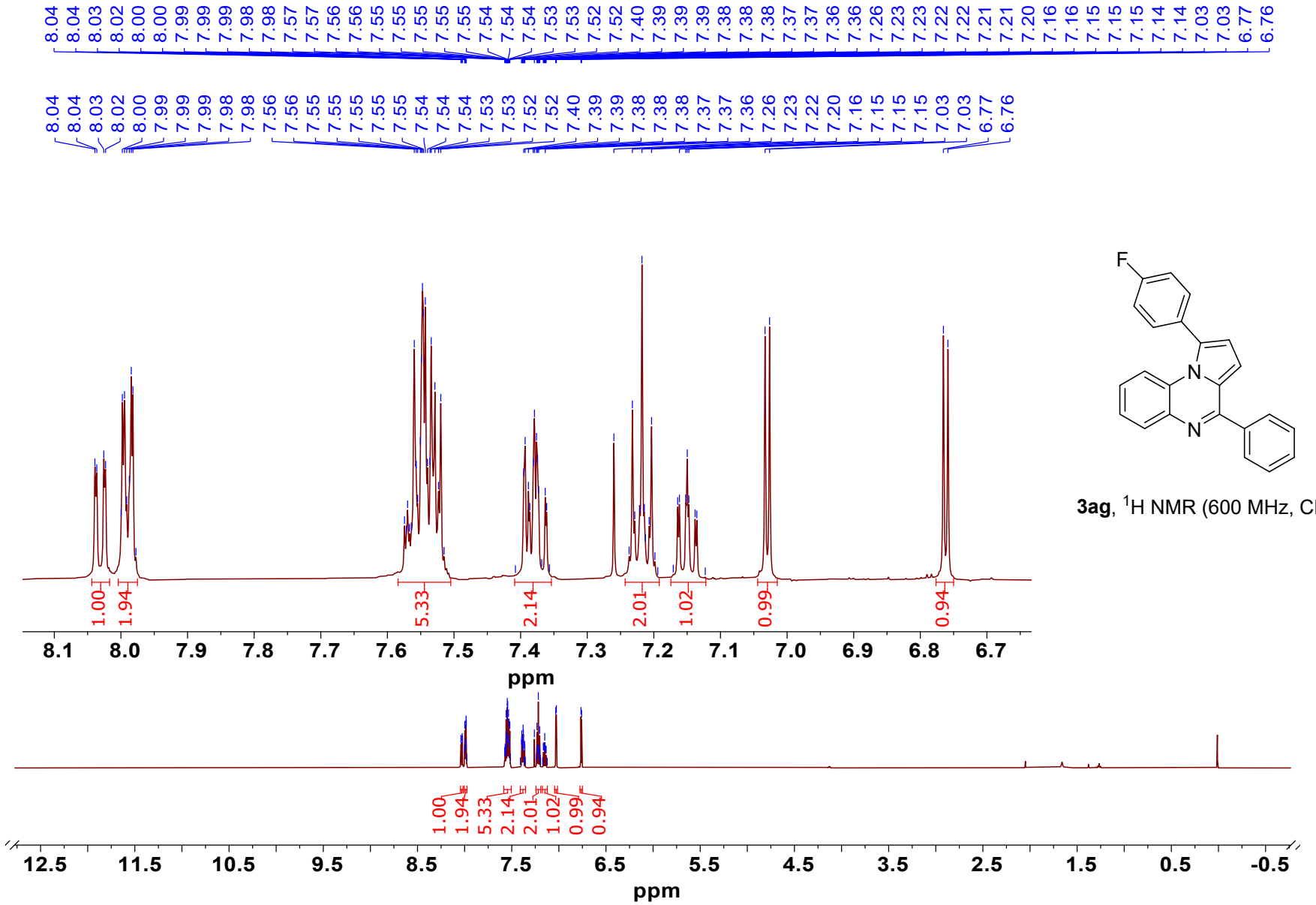
3af, $^{13}C\ \{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



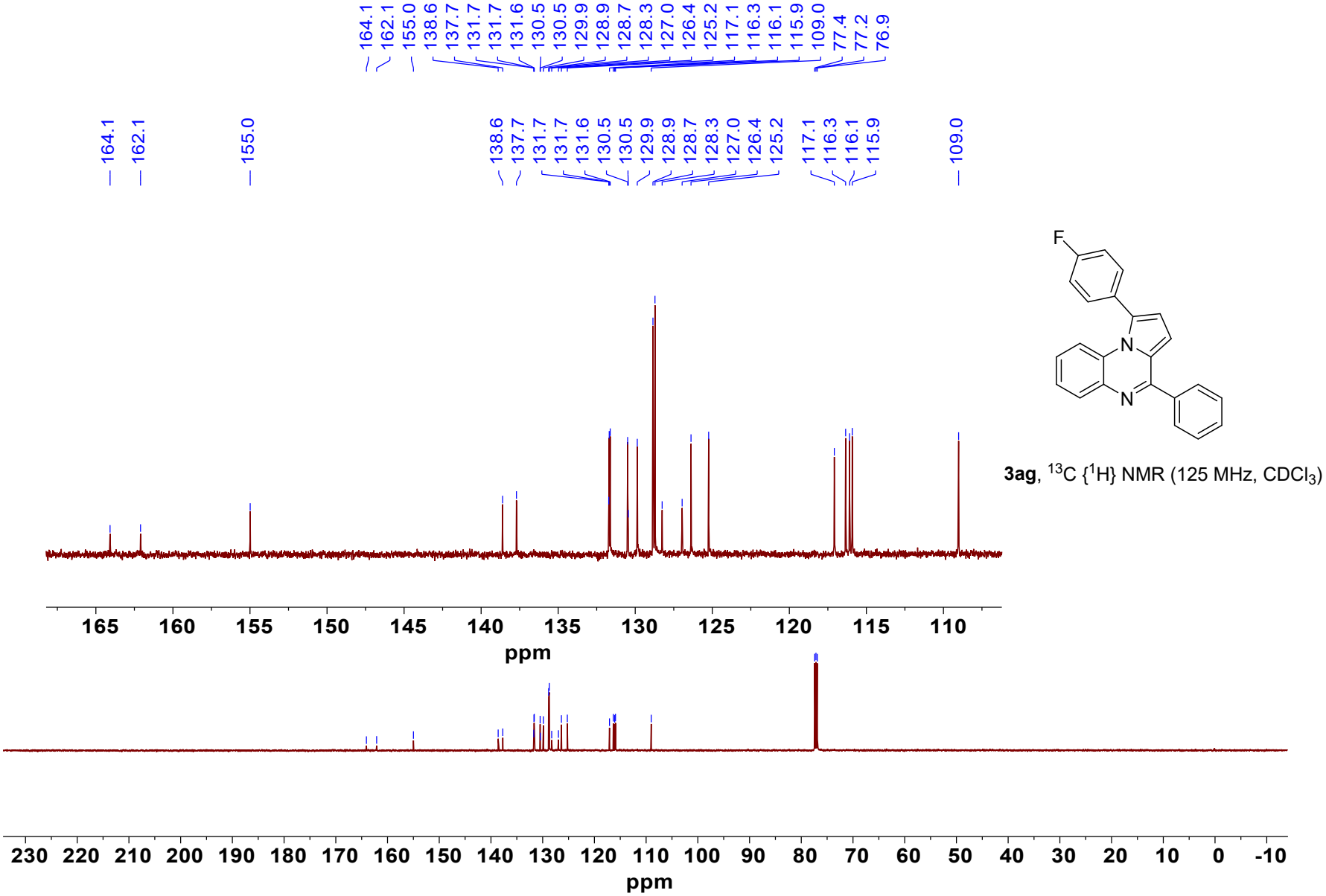
3af, ^{19}F NMR (471 MHz, $CDCl_3$)


389.1263
390.3516
296.1330
348.1222
313.5397
184.8853
254.4518
401.4769
100
80
60
40
20
0
150
200
250
300
350
400
Mass/Charge
F3C
N
N

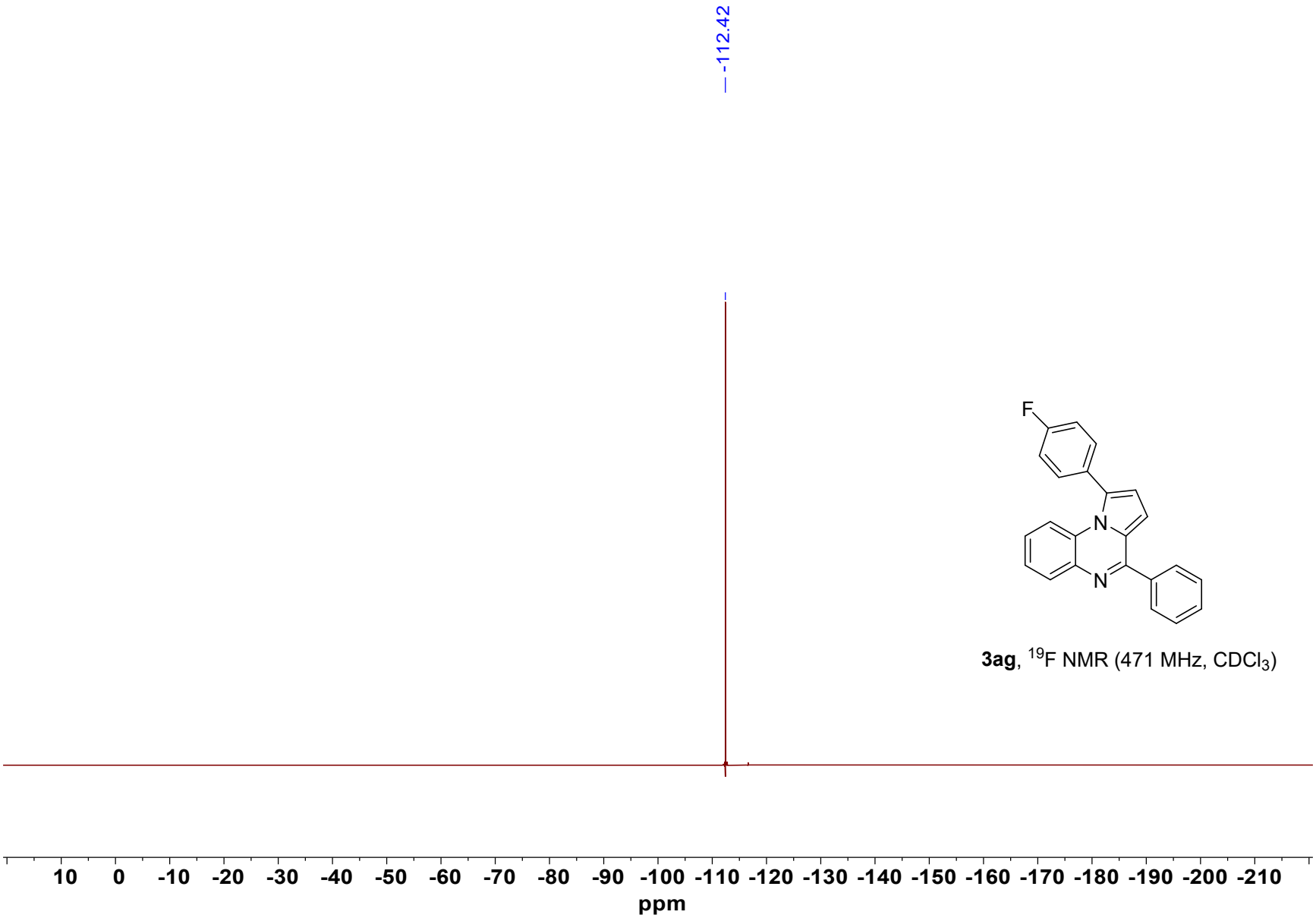
3af, HR-MS



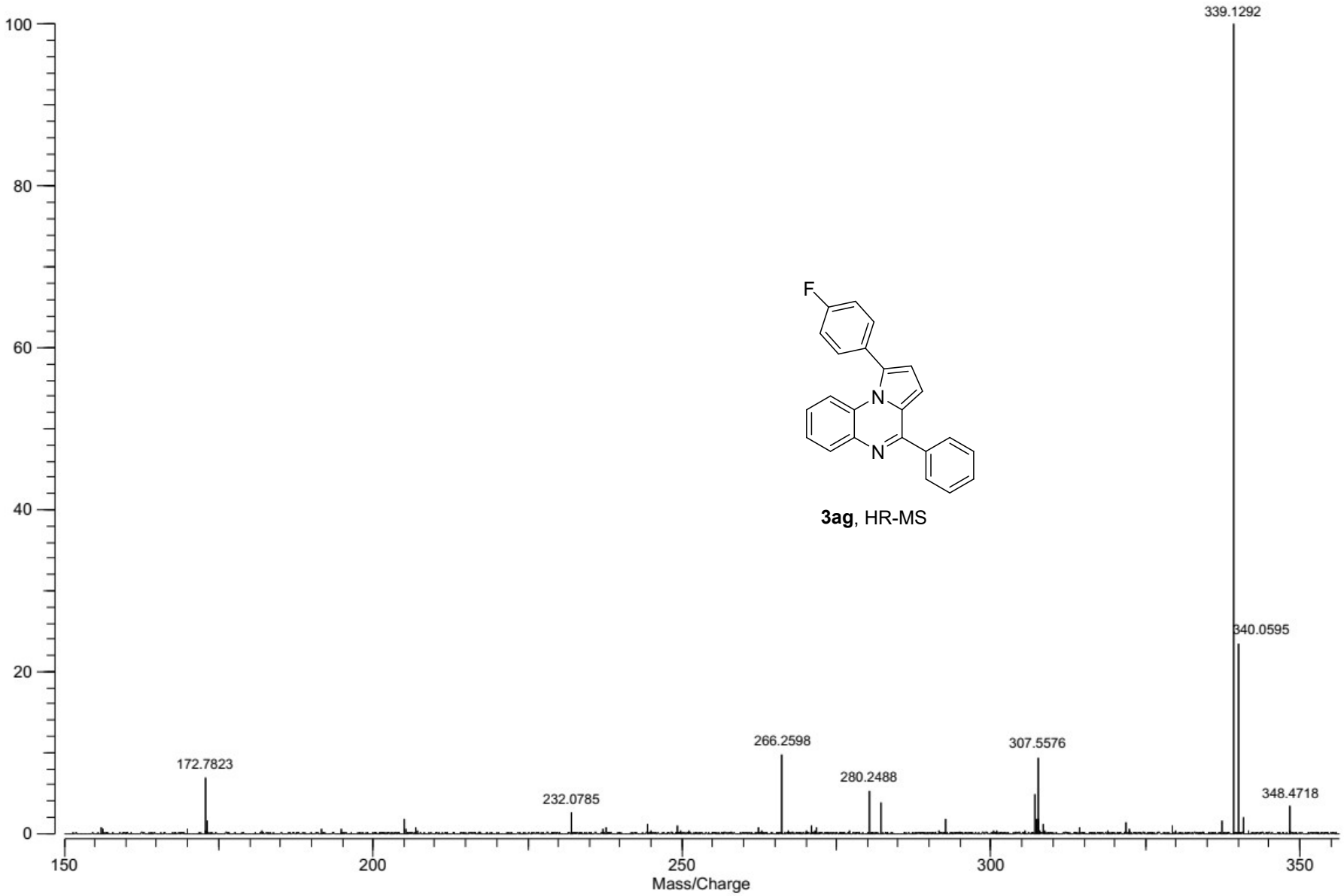
3ag, ^{1}H NMR (600 MHz, $CDCl_3$)



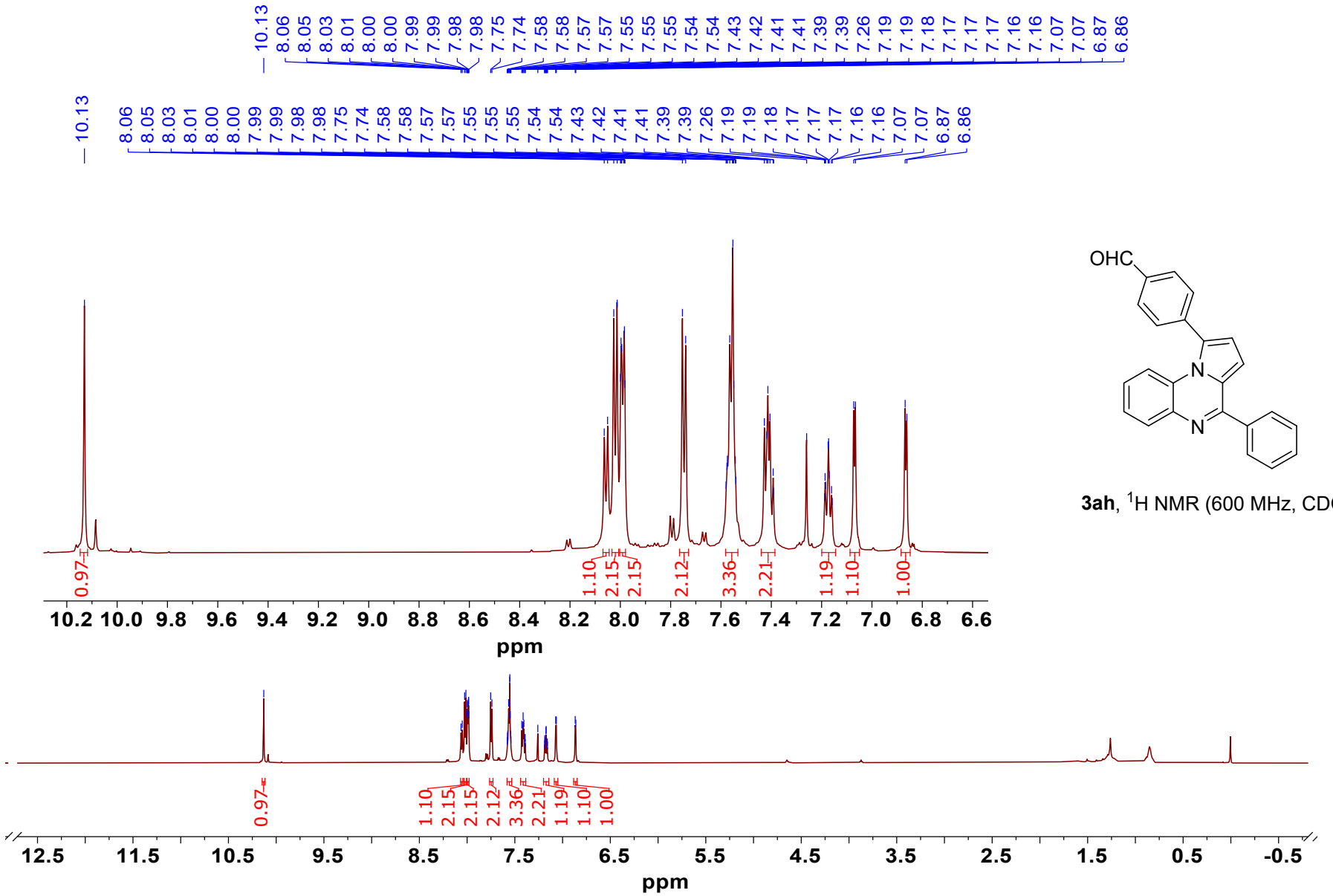
3ag, ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)



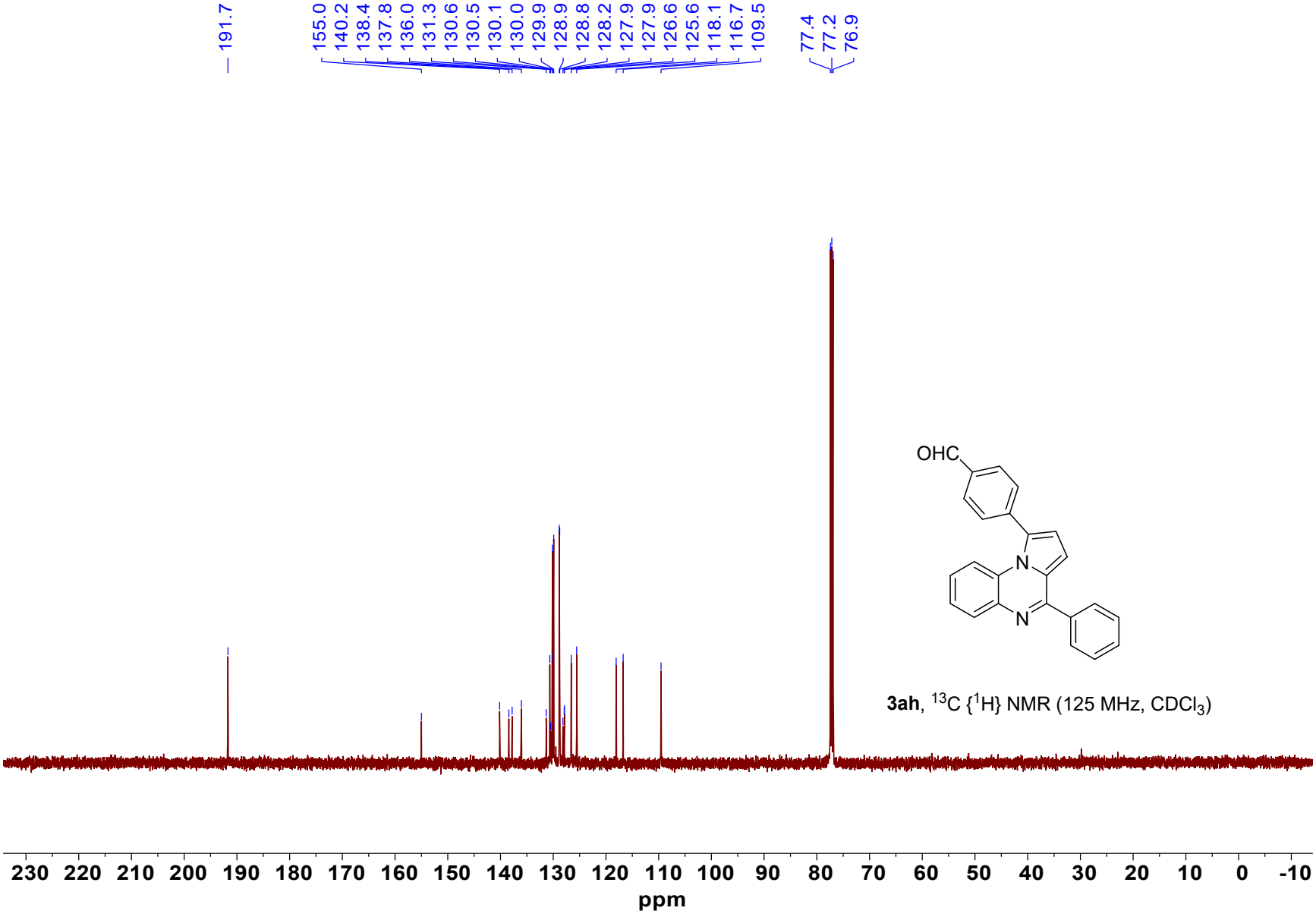
3ag, ^{19}F NMR (471 MHz, $CDCl_3$)


339.1292
340.0595
266.2598
307.5576
280.2488
348.4718
232.0785
172.7823
100
80
60
40
20
0
150
200
250
300
350
Mass/Charge
F
N
N

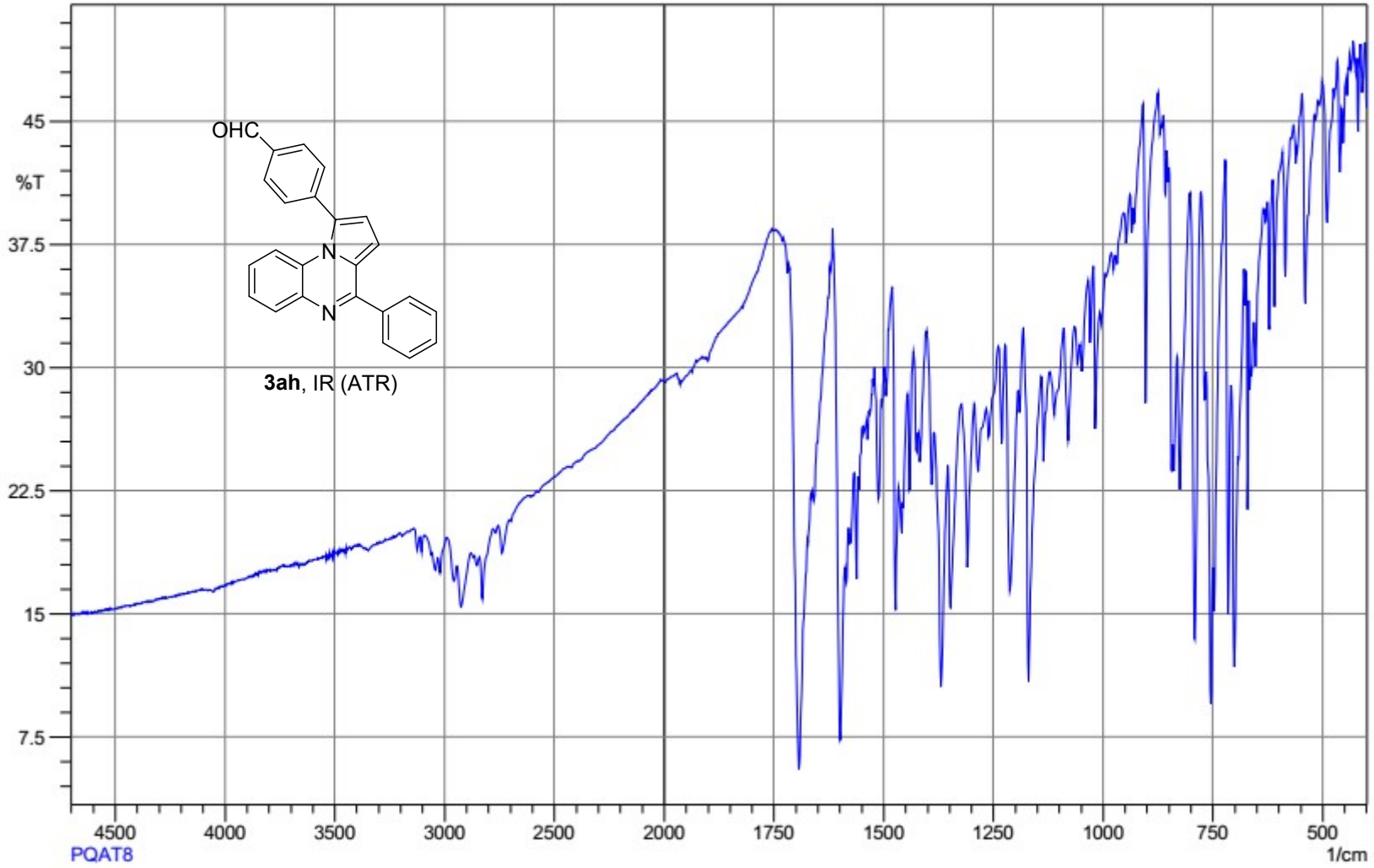
3ag, HR-MS



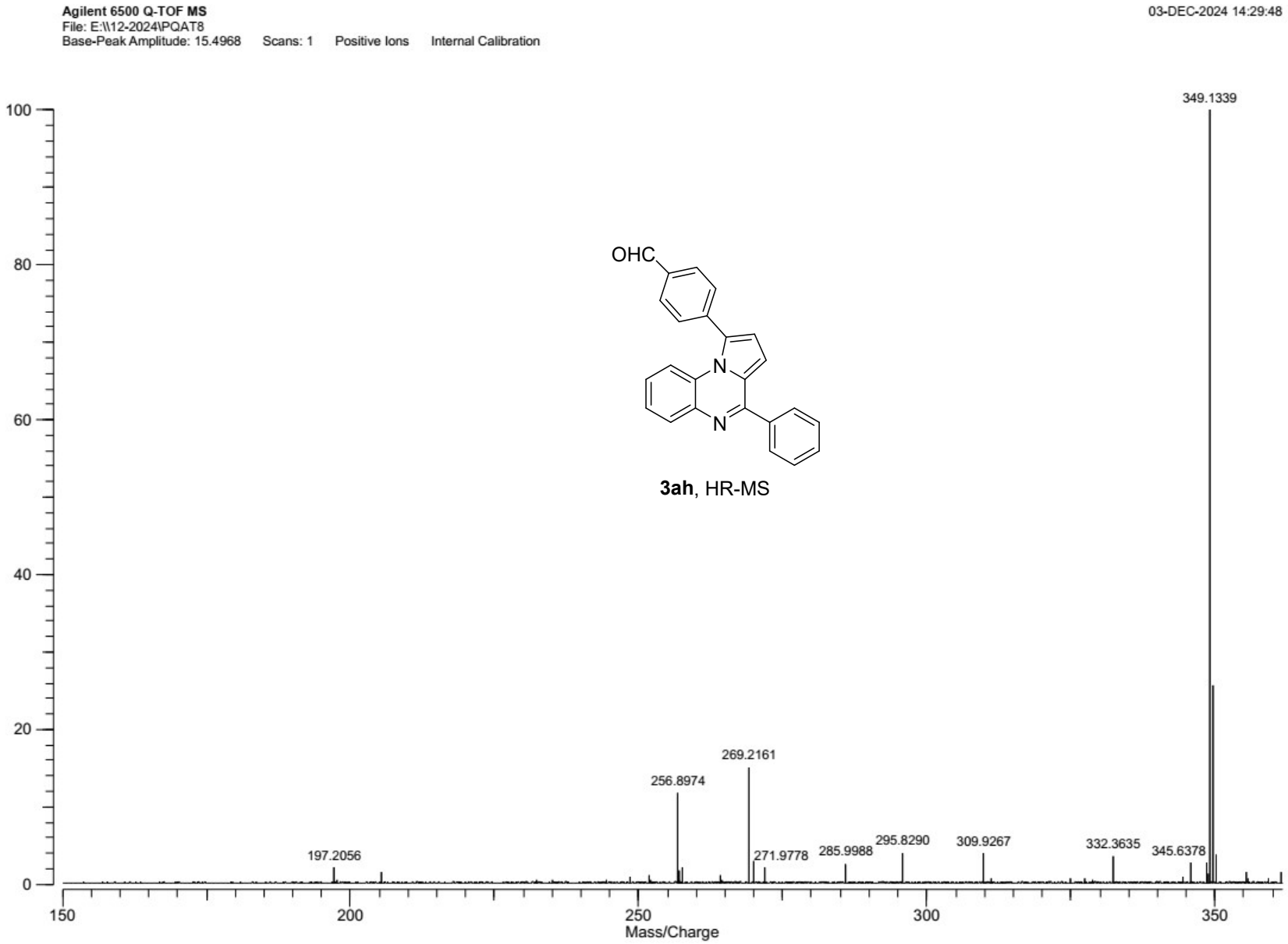
3ah, ^{1}H NMR (600 MHz, $CDCl_3$)

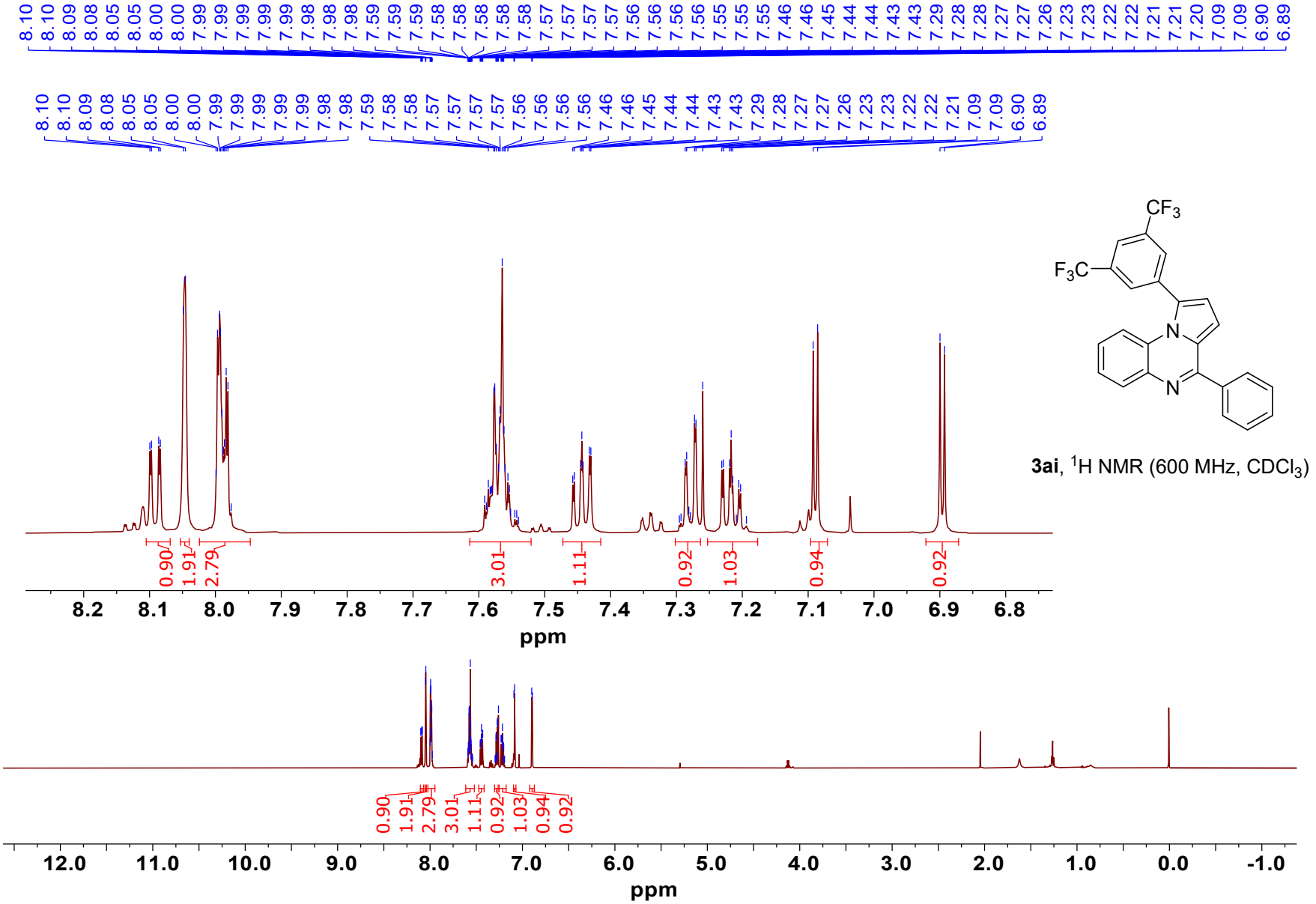


3ah, ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$)

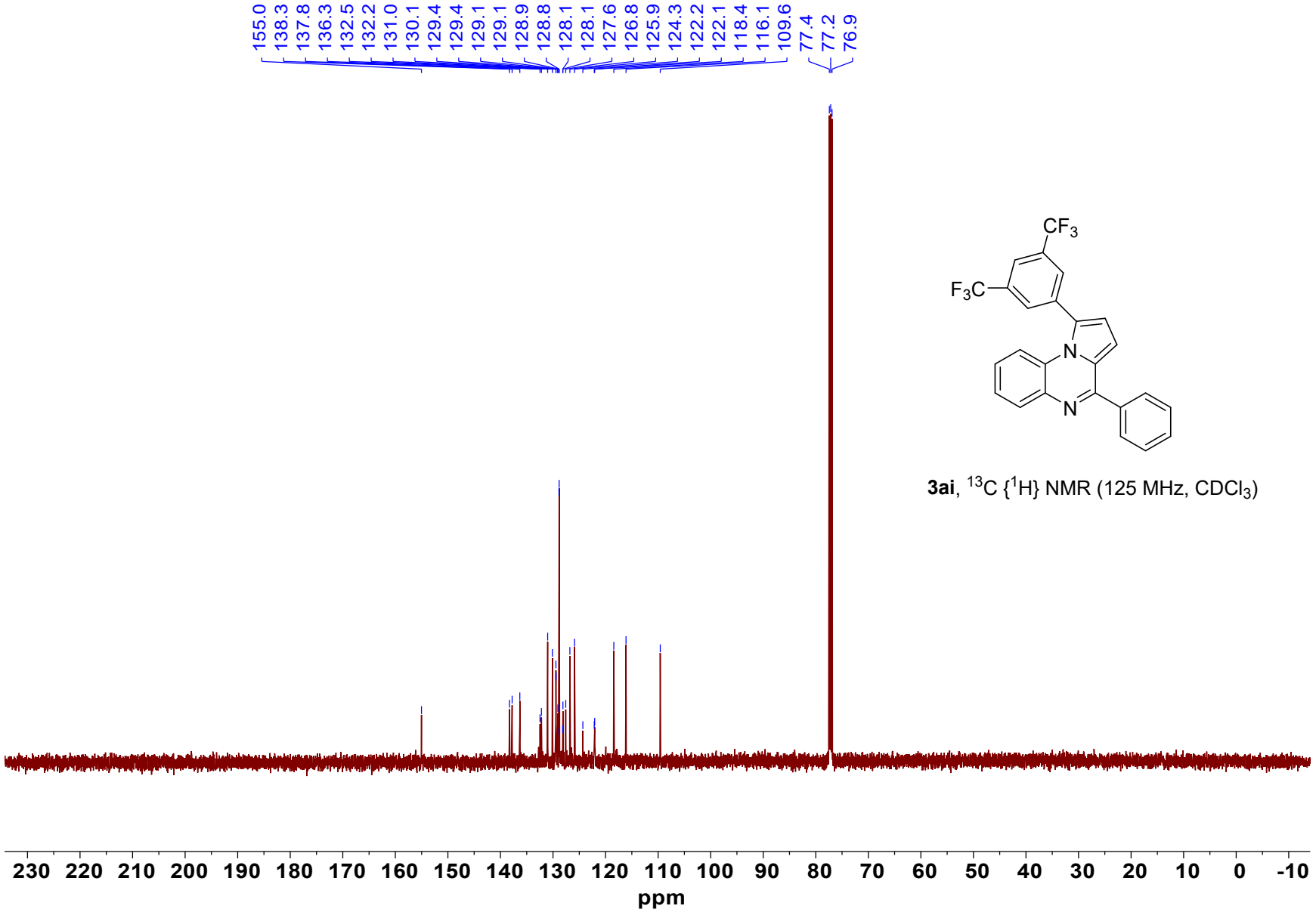

OHC
N
N
45
%T
37.5
30
22.5
15
7.5
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
PQAT8

3ah, IR (ATR)

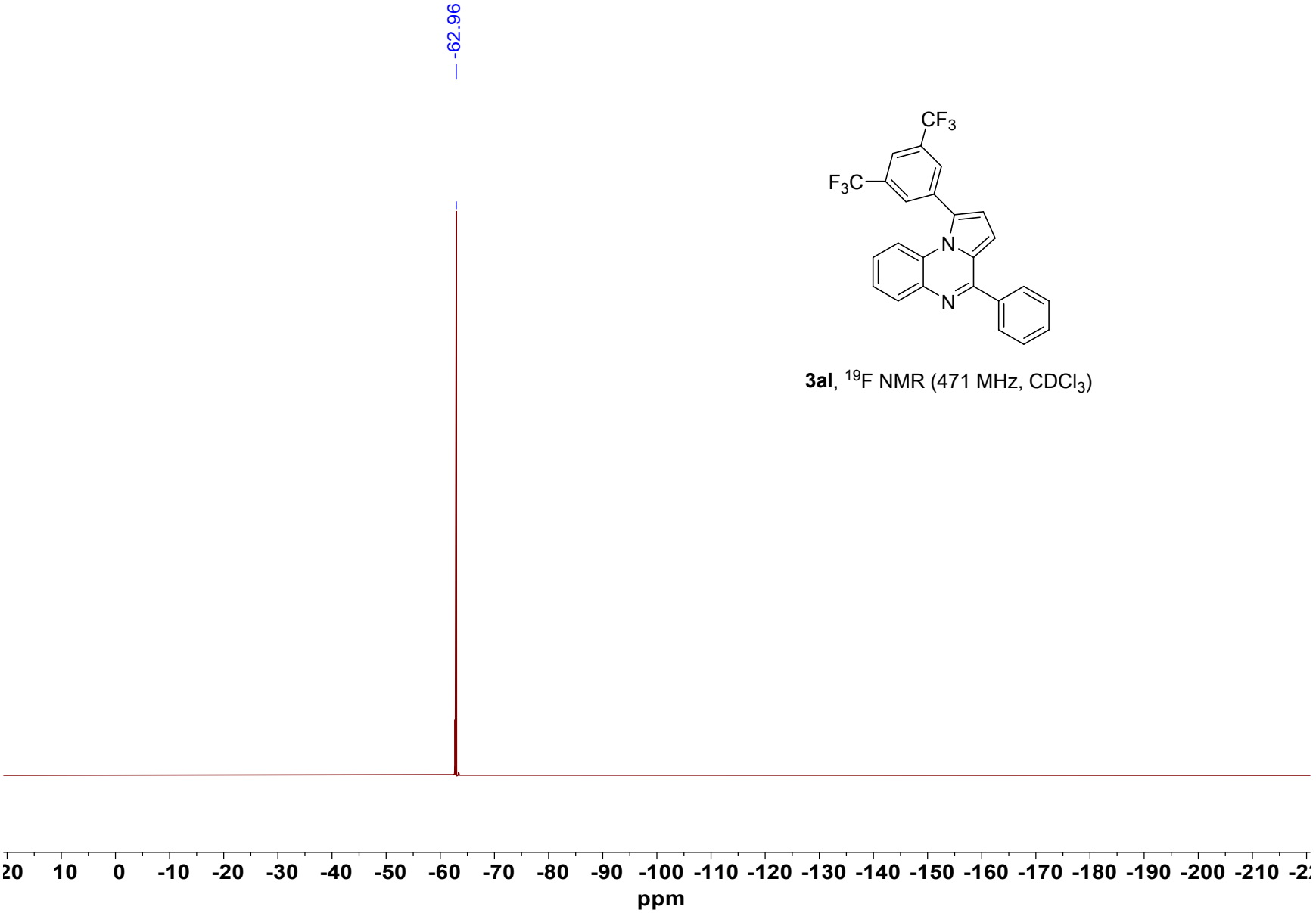

Agilent 6500 Q-TOF MS
File: E:\\12-2024\PQAT8
Base-Peak Amplitude: 15.4968 Scans: 1 Positive Ions Internal Calibration
03-DEC-2024 14:29:48
OHC
N
N
3ah, HR-MS
349.1339
269.2161
256.8974
197.2056
271.9778
285.9988
295.8290
309.9267
332.3635
345.6378
100
80
60
40
20
0
150
200
250
300
350
Mass/Charge



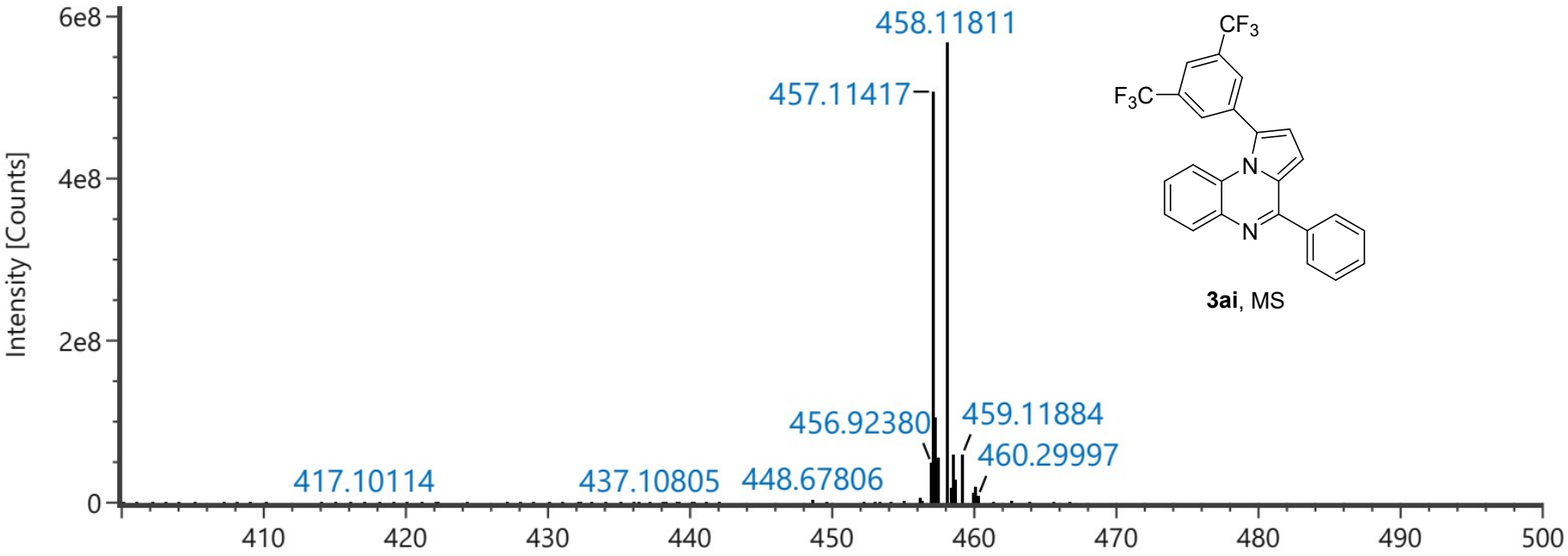
3ai, ^{1}H NMR (600 MHz, $CDCl_3$)



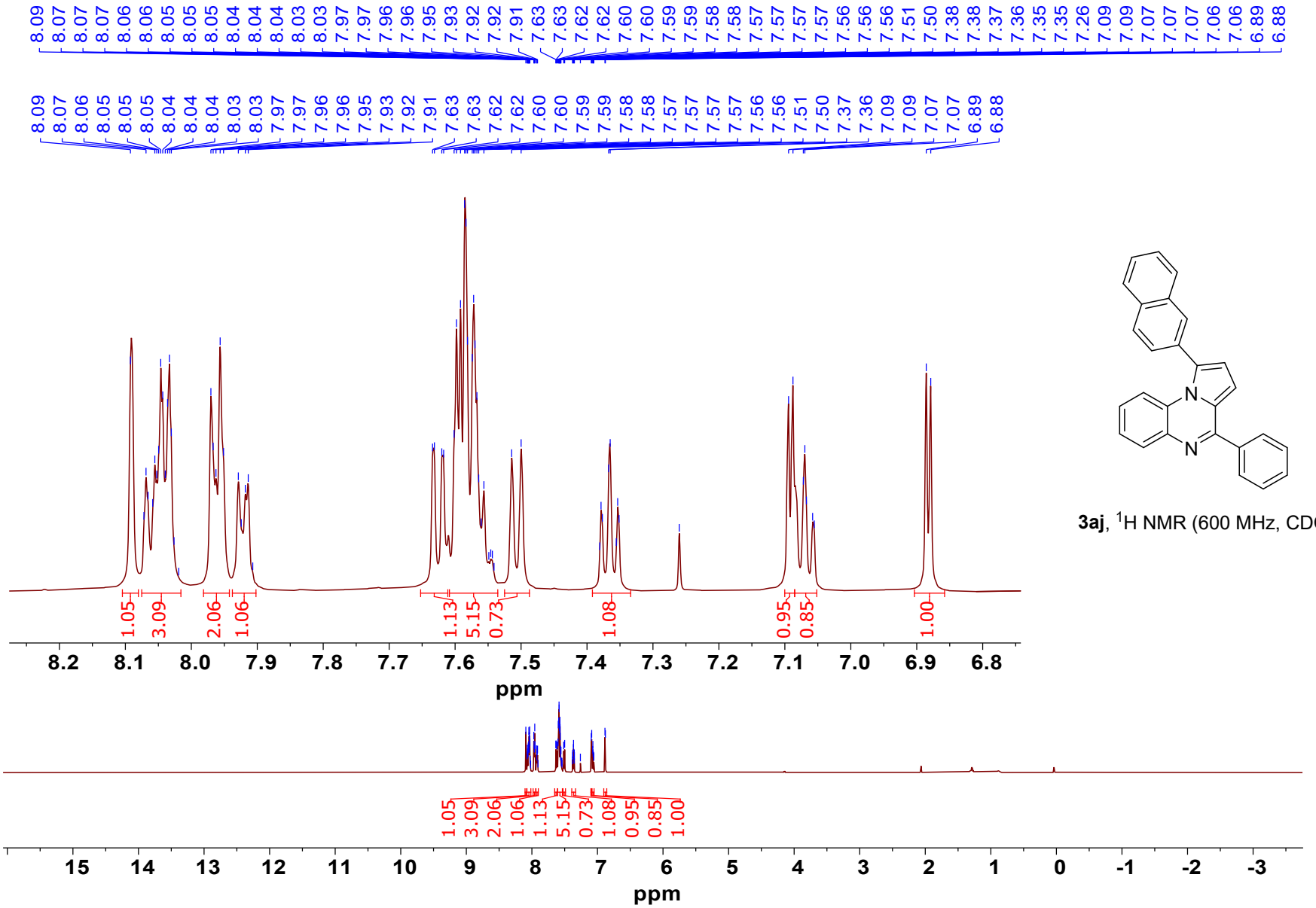
3ai, $^{13}C\ \{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



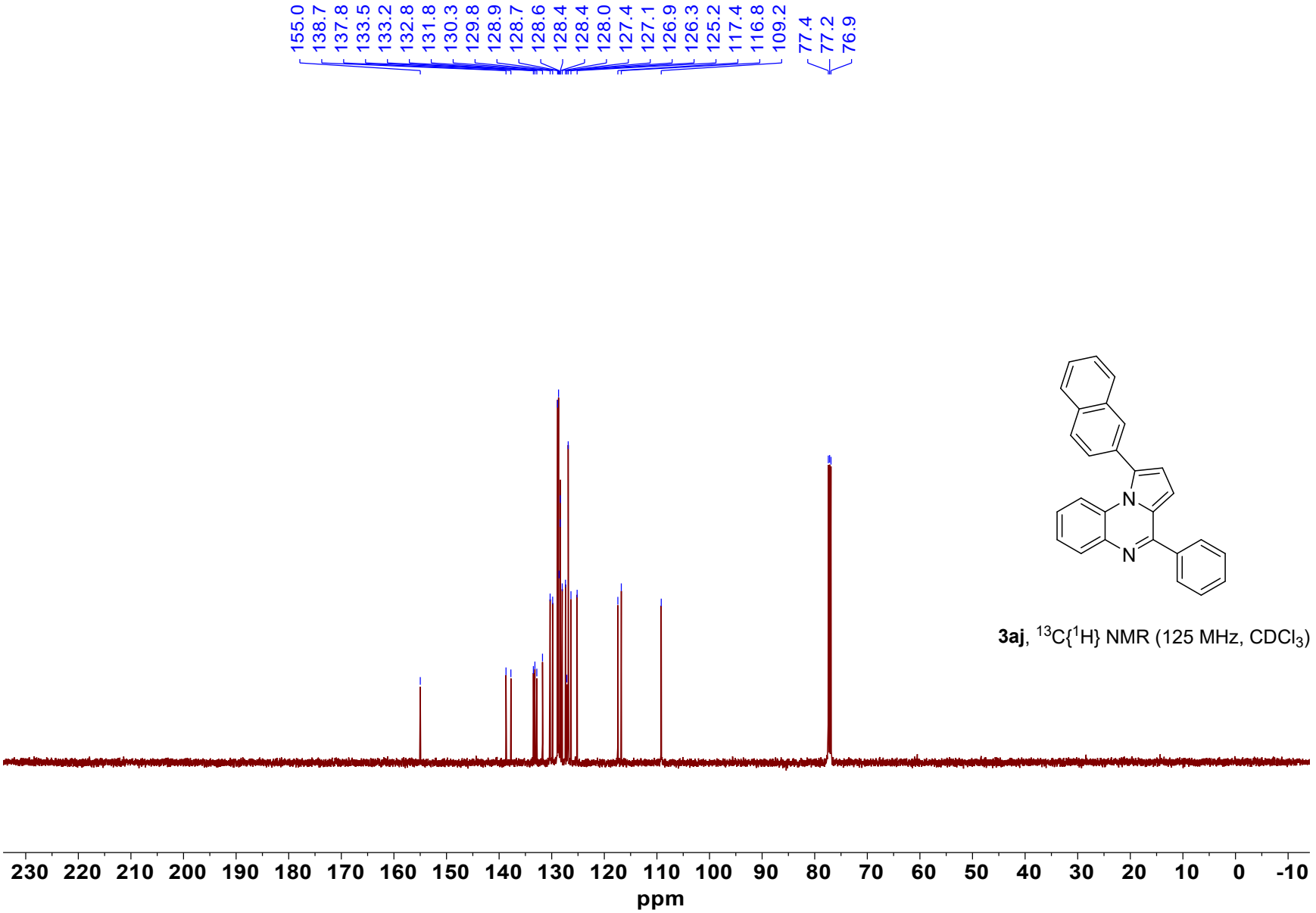
3al, ^{19}F NMR (471 MHz, $CDCl_3$)


6e8
4e8
2e8
0
Intensity [Counts]
458.11811
457.11417
456.92380
459.11884
460.29997
417.10114
437.10805
448.67806
410
420
430
440
450
460
470
480
490
500
CF3
F3C
N
N

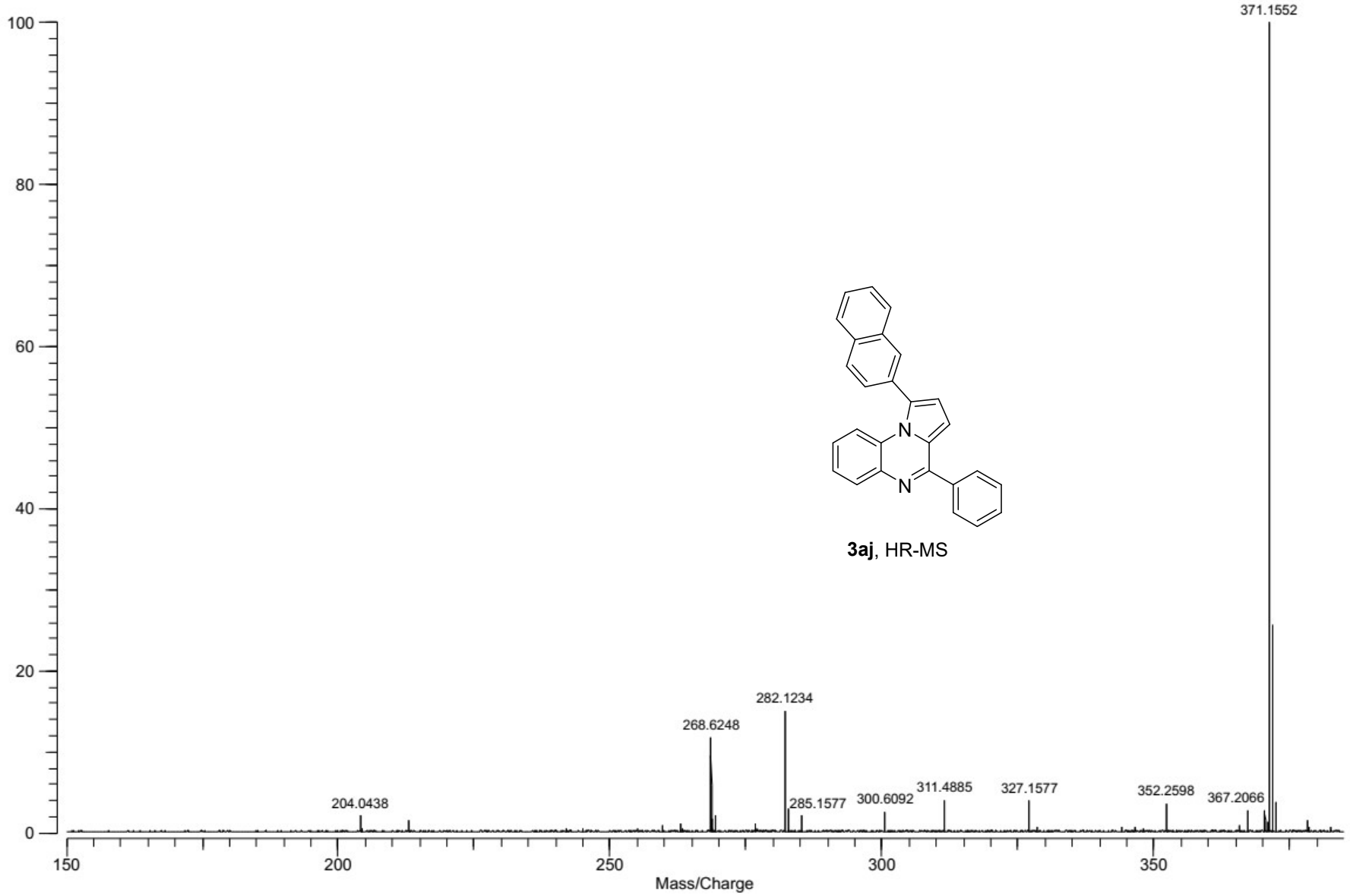
3ai, MS



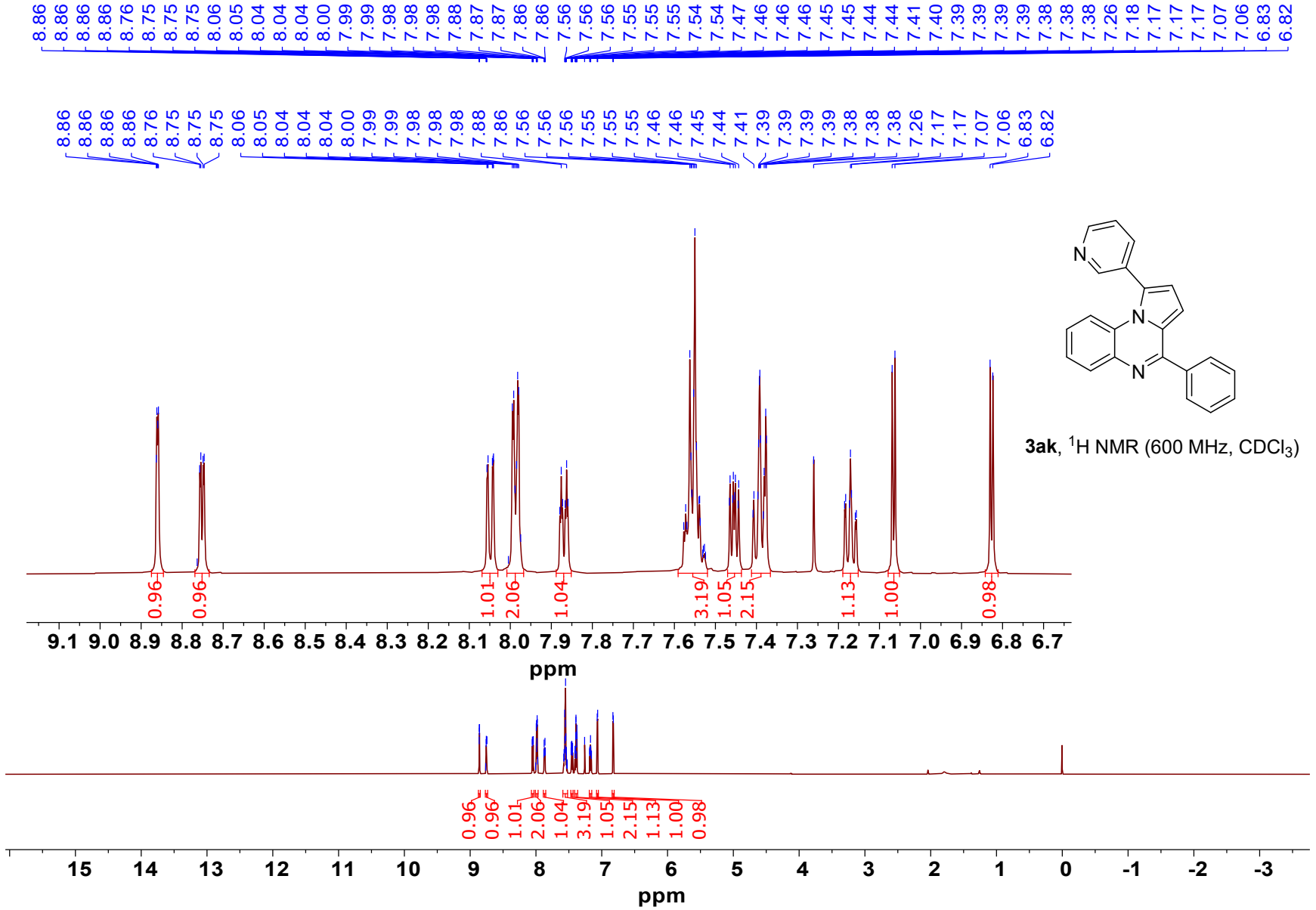
3aj, ^{1}H NMR (600 MHz, $CDCl_3$)



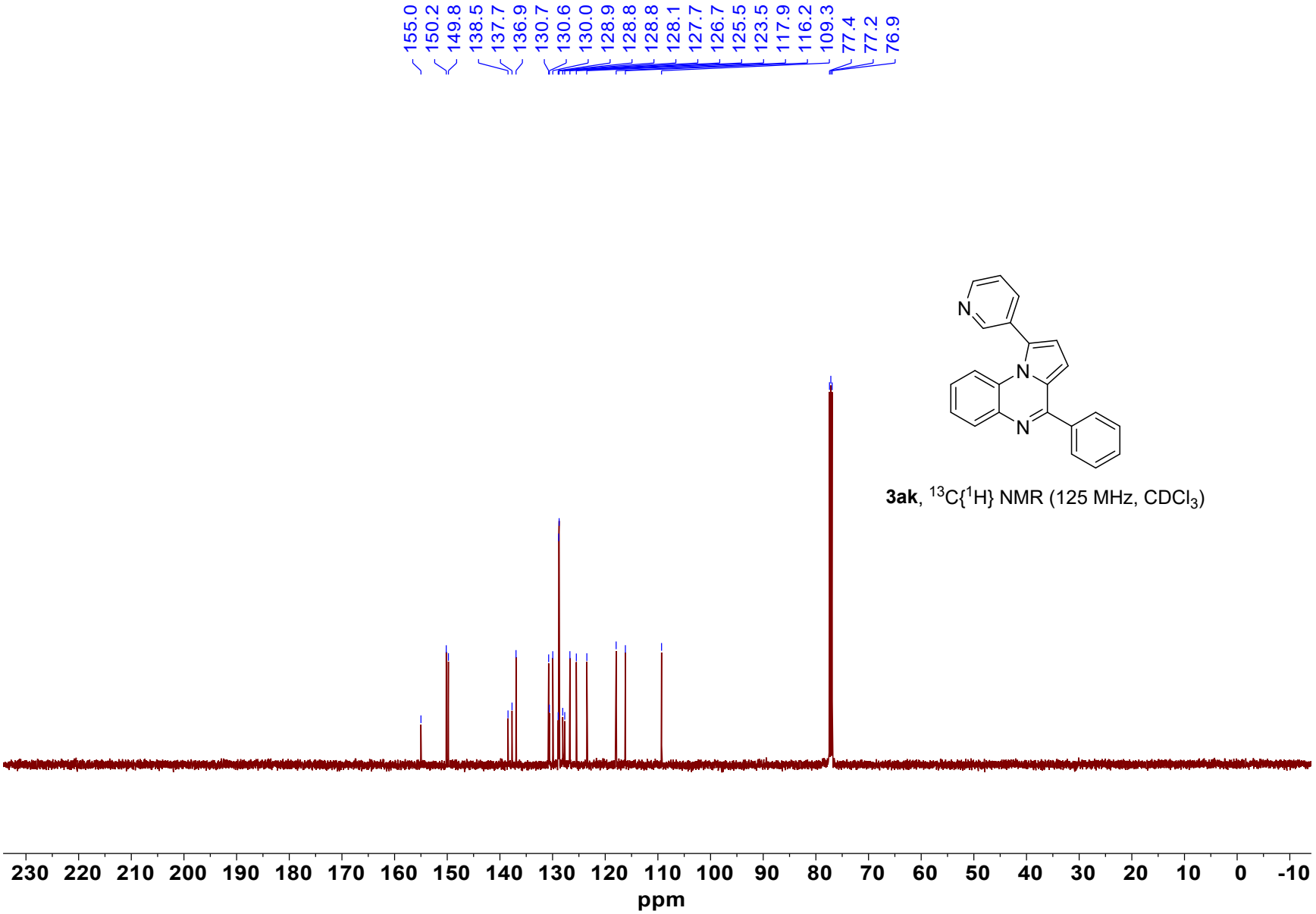
3aj, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


371.1552
100
80
60
40
20
0
N
N
282.1234
268.6248
204.0438
285.1577
300.6092
311.4885
327.1577
352.2598
367.2066
150
200
250
300
350
Mass/Charge

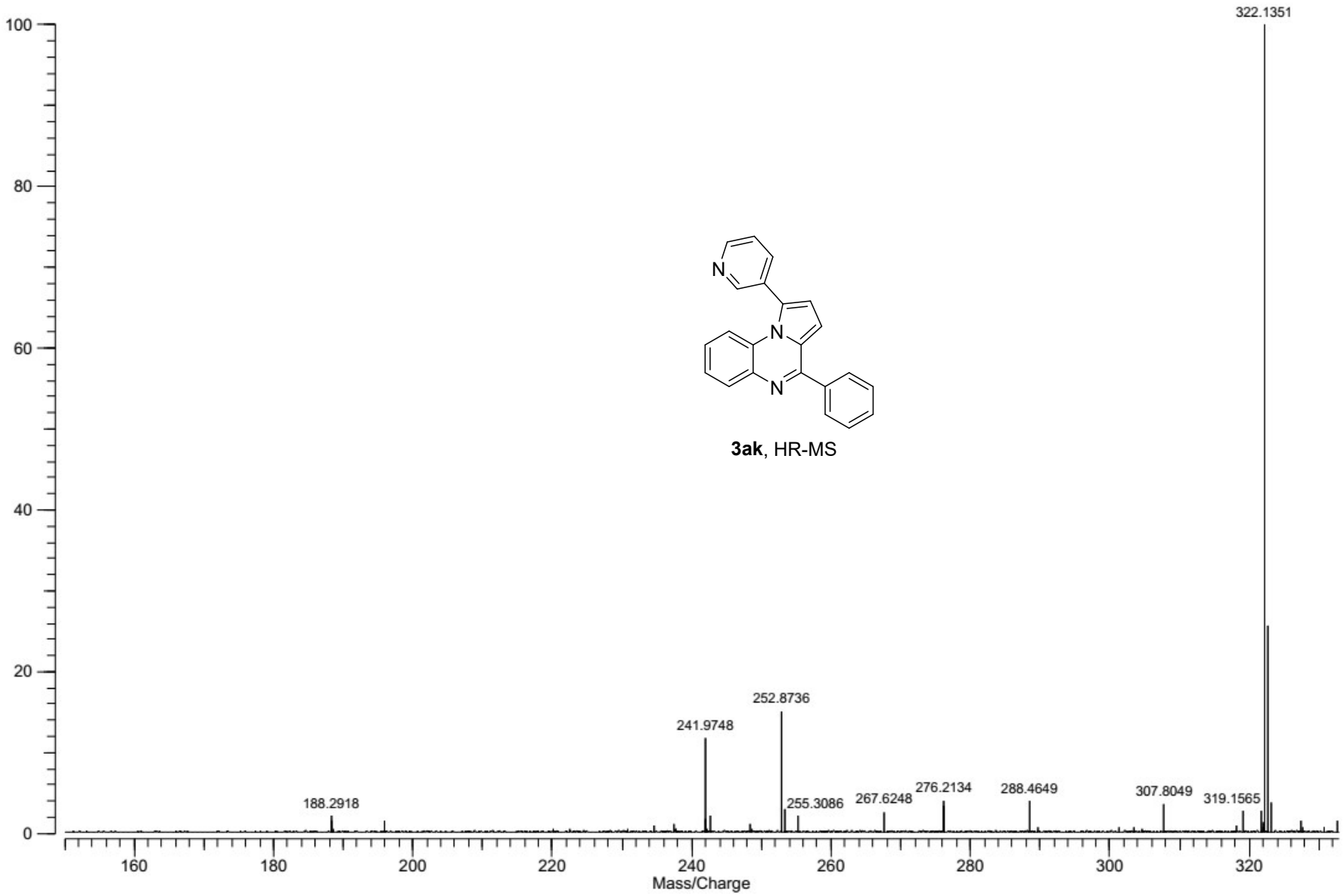
3aj, HR-MS



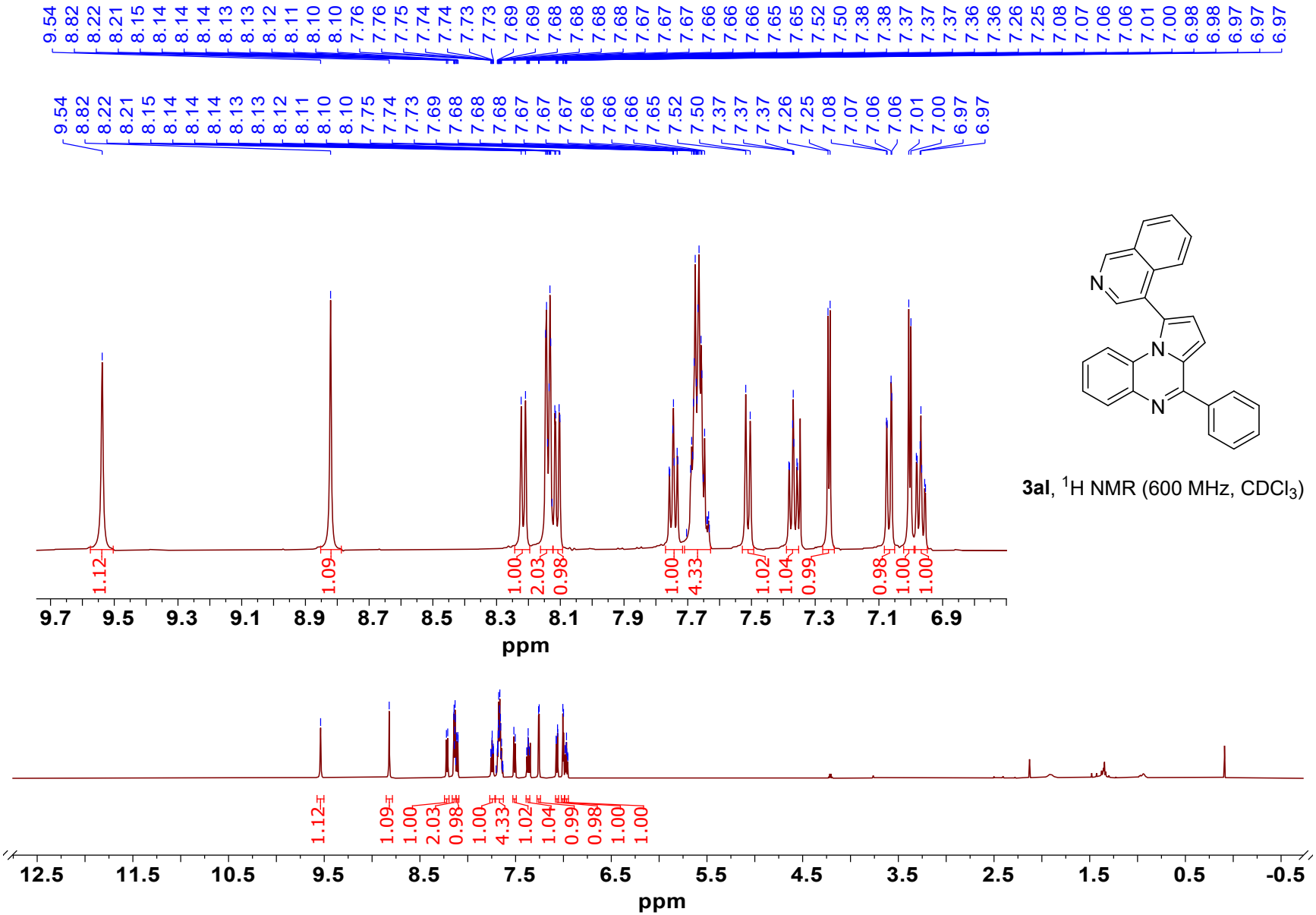
3ak, ^{1}H NMR (600 MHz, $CDCl_3$)



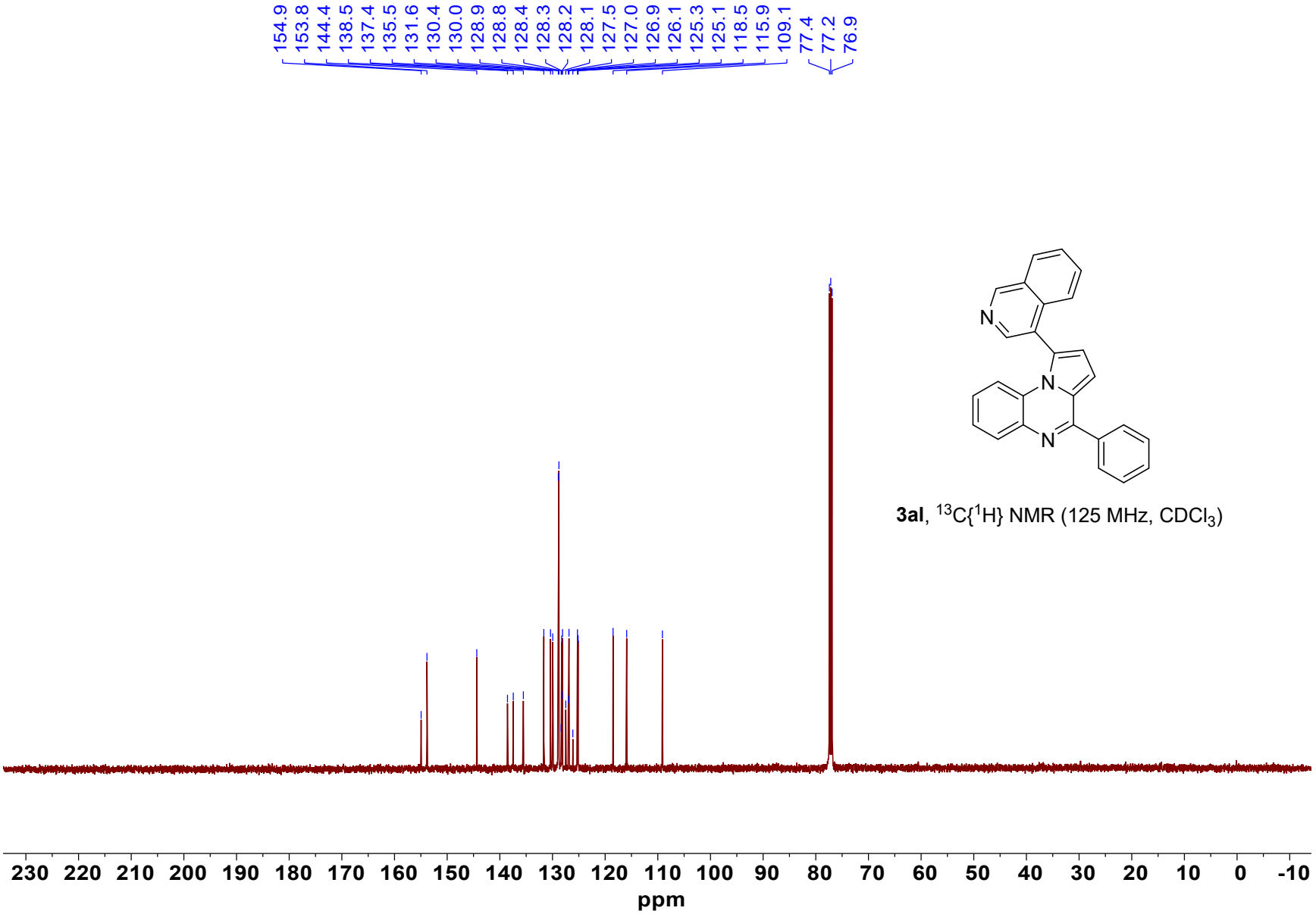
3ak, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


322.1351
100
80
60
40
20
0
N
N
N
252.8736
241.9748
188.2918
255.3086
267.6248
276.2134
288.4649
307.8049
319.1565
160
180
200
220
240
260
280
300
320
Mass/Charge

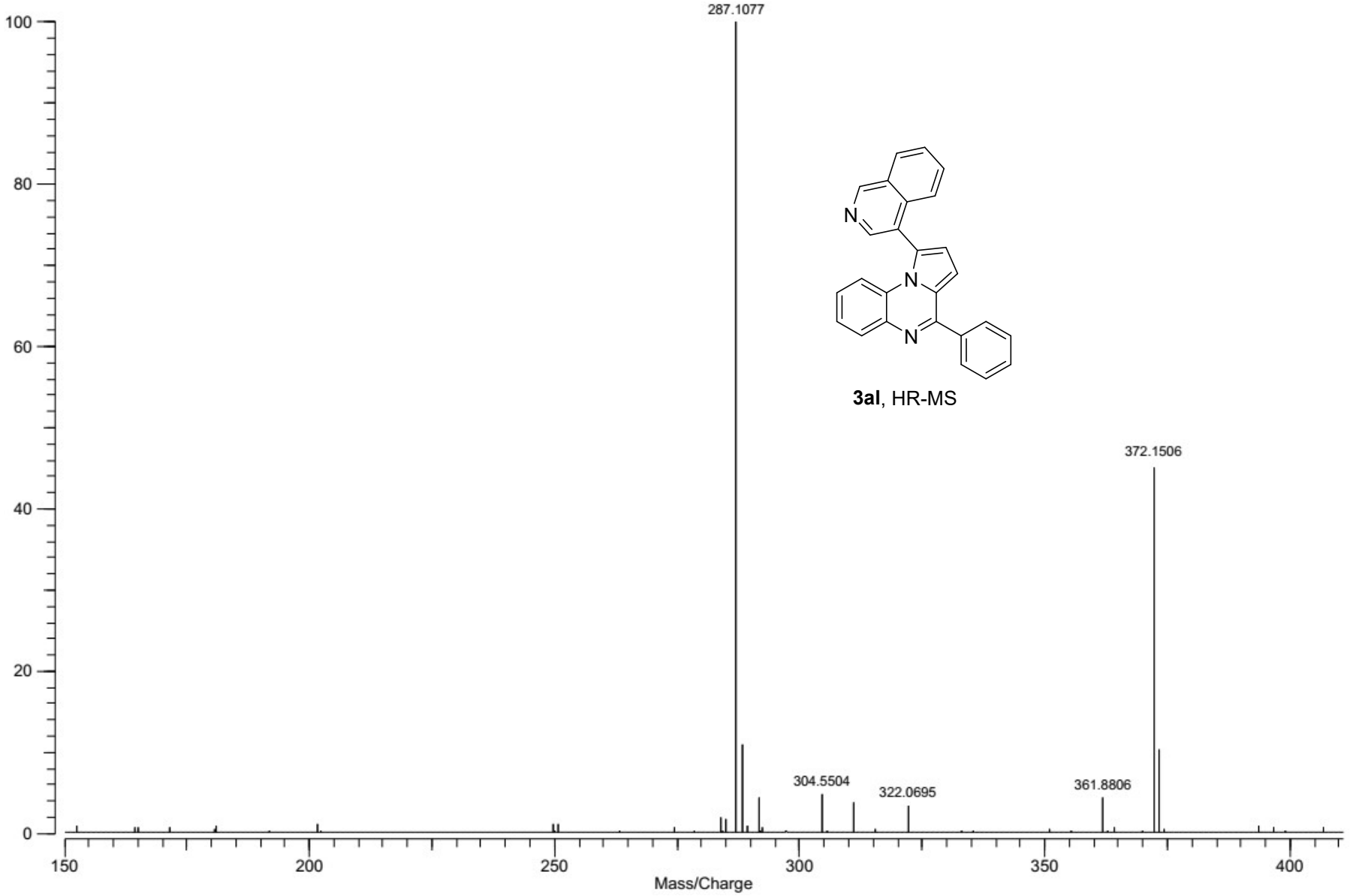
3ak, HR-MS



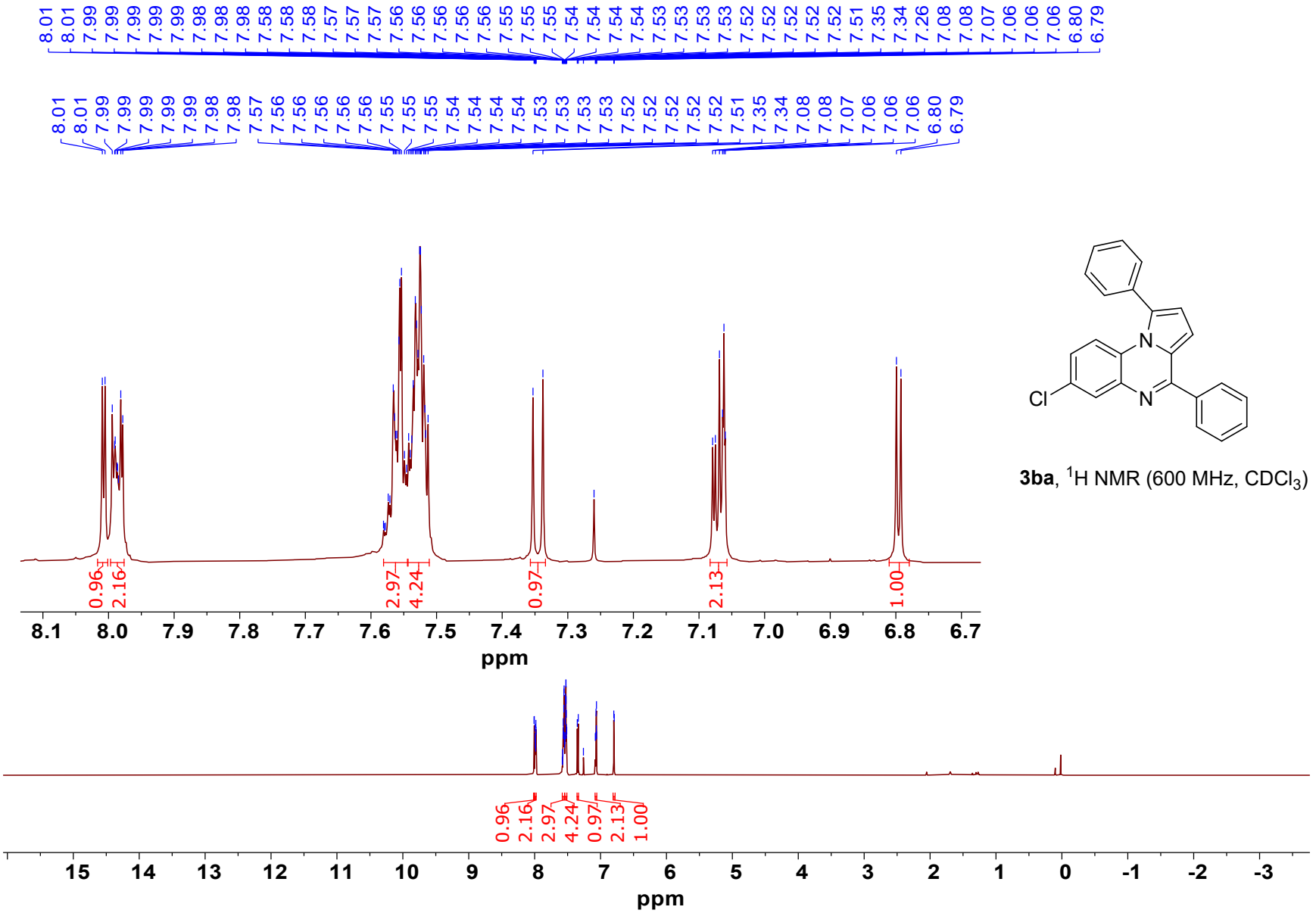
3al, ^{1}H NMR (600 MHz, $CDCl_3$)



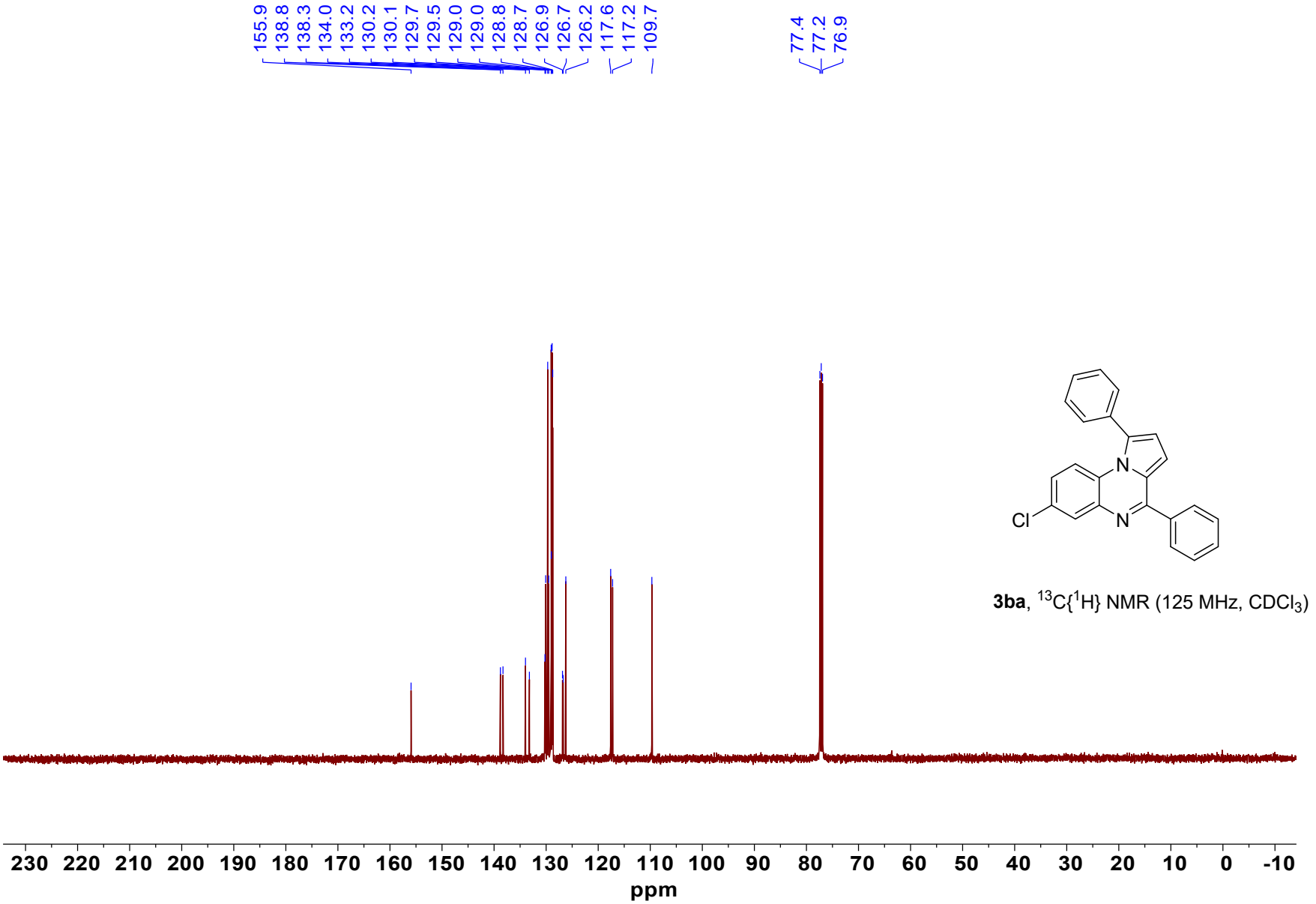
3al, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


287.1077
372.1506
304.5504
322.0695
361.8806
100
80
60
40
20
0
150
200
250
300
350
400
Mass/Charge
N
N
N

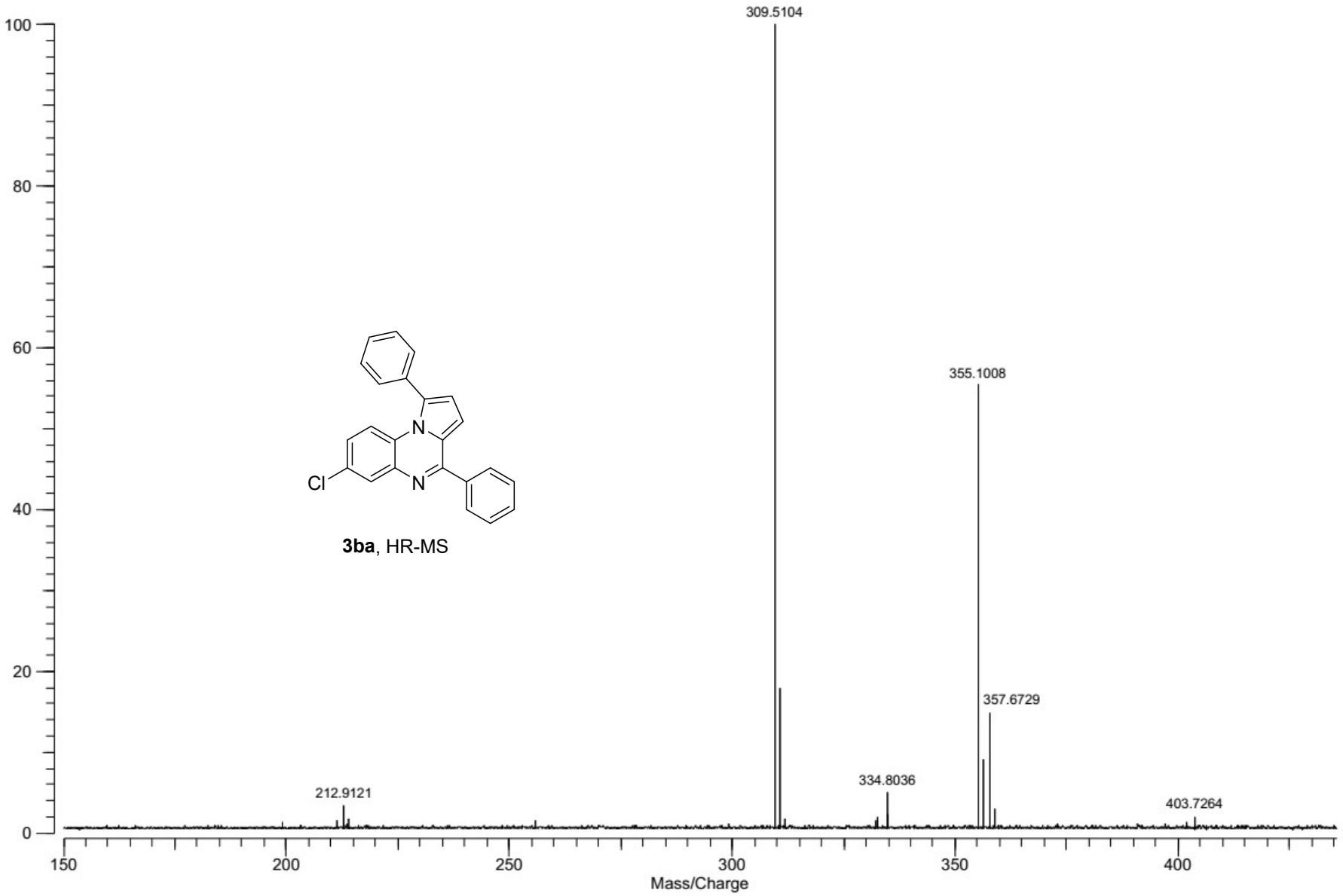
3al, HR-MS



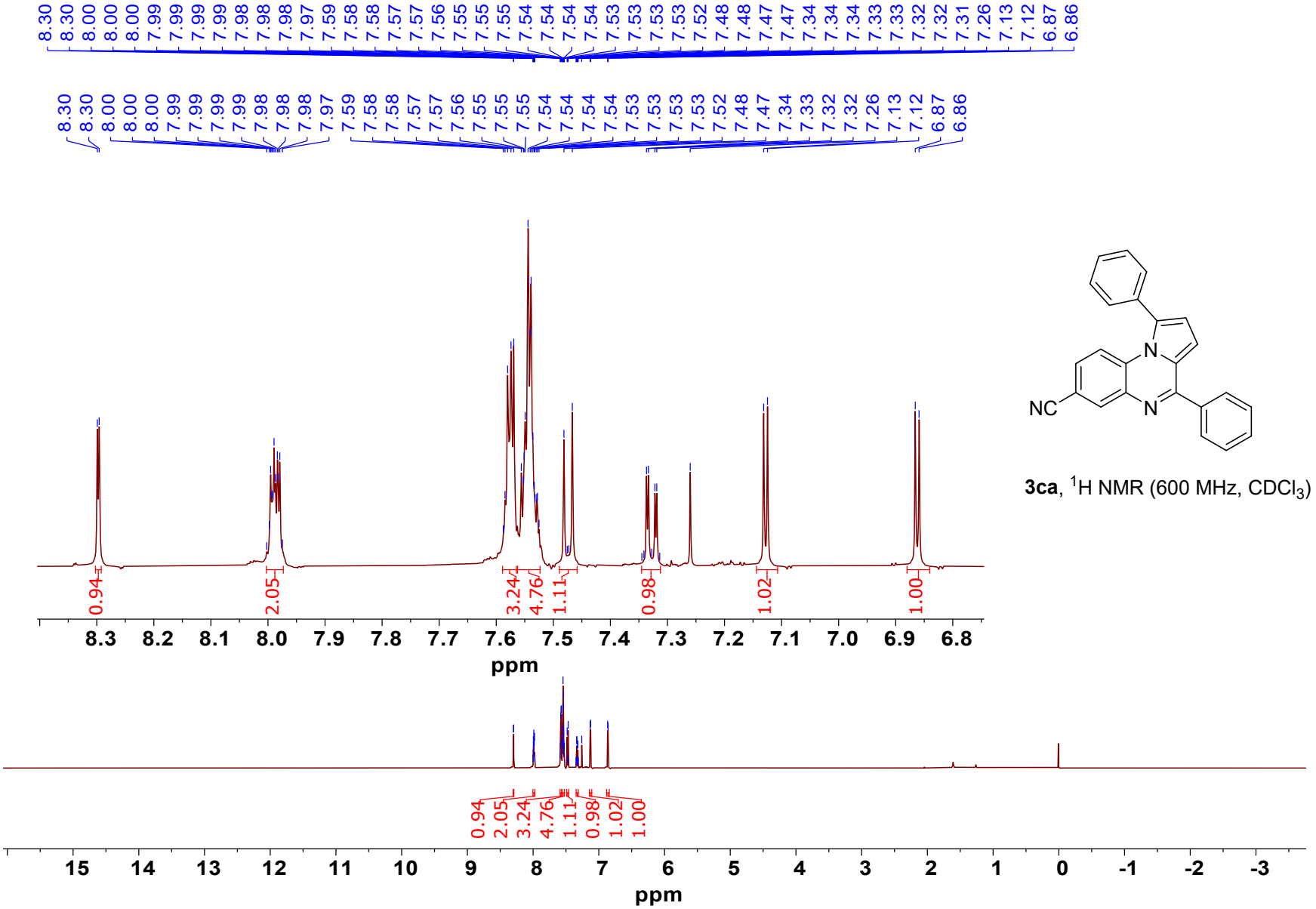
3ba, ^{1}H NMR (600 MHz, $CDCl_3$)



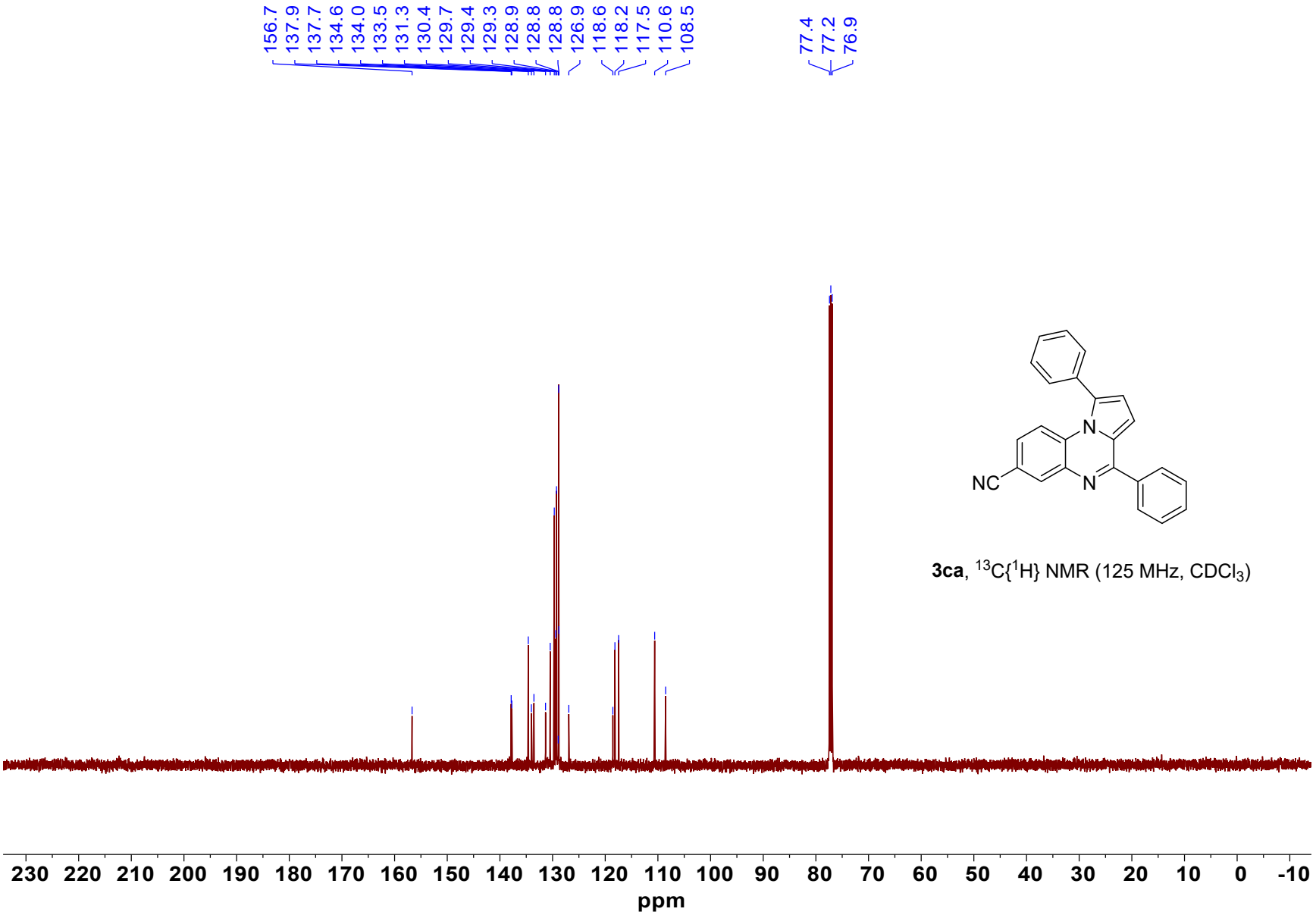
3ba, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


309.5104
355.1008
357.6729
334.8036
212.9121
403.7264
100
80
60
40
20
0
150
200
250
300
350
400
Mass/Charge
N
N
Cl

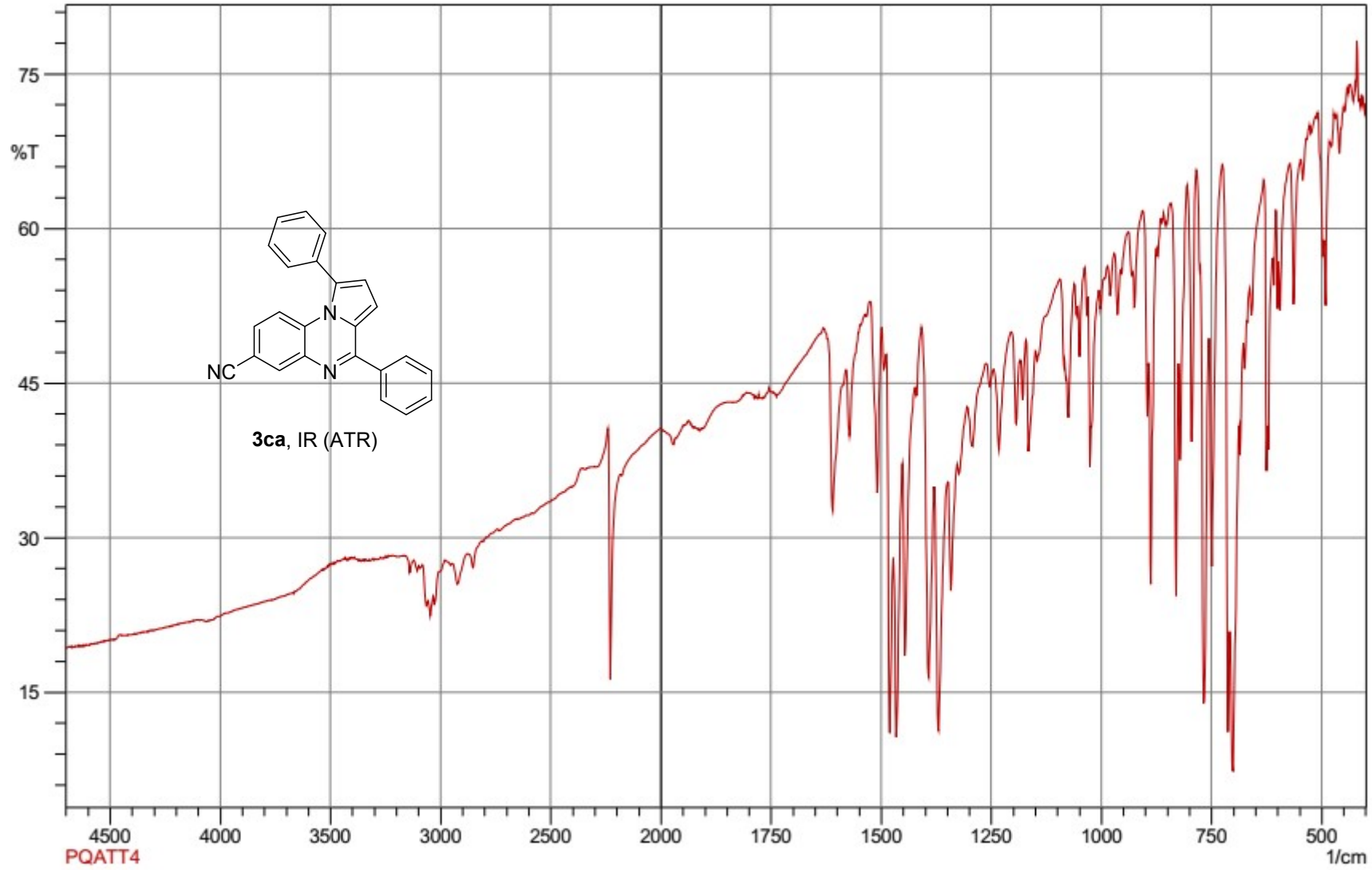
3ba, HR-MS



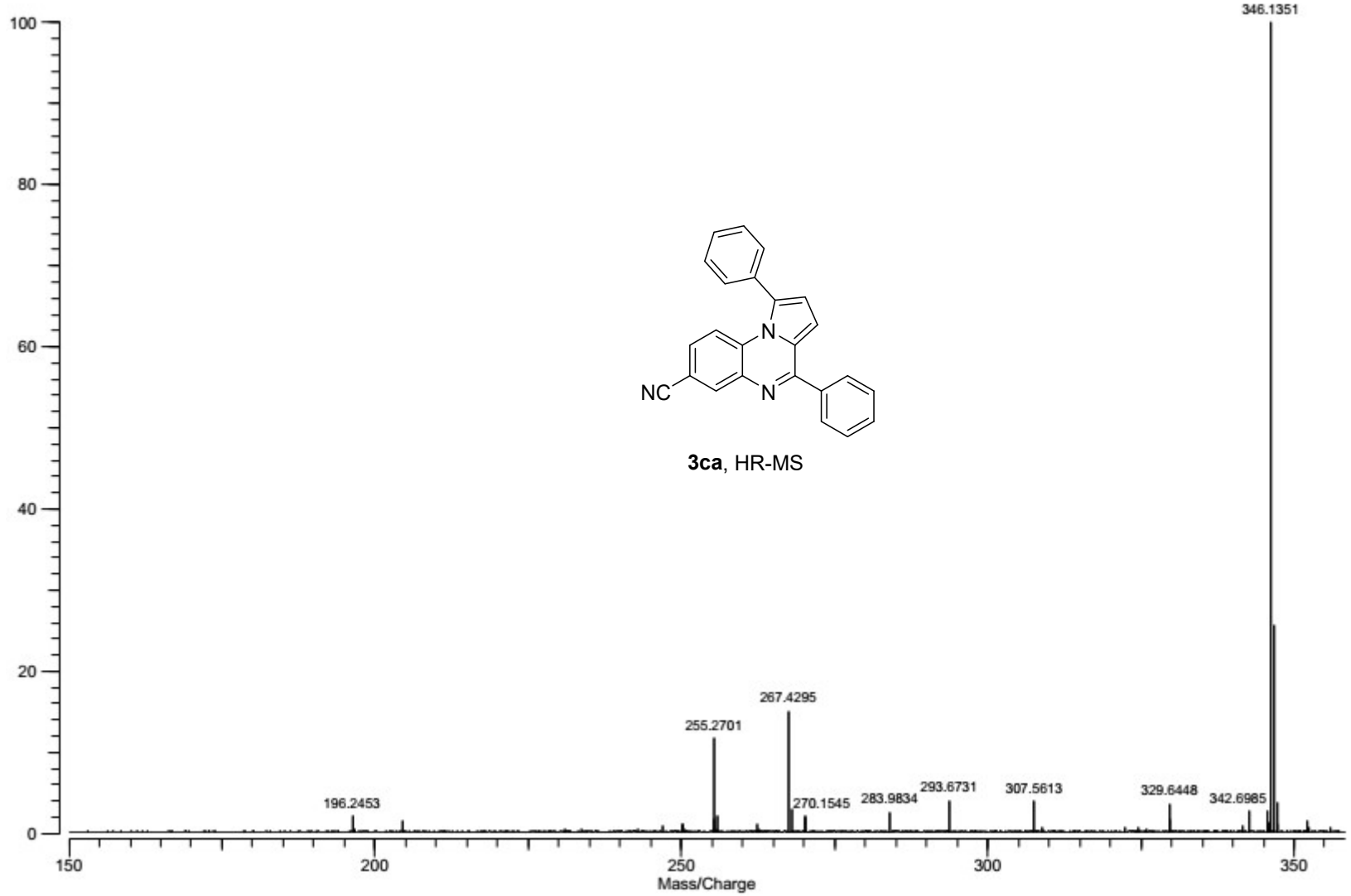
3ca, ^{1}H NMR (600 MHz, $CDCl_3$)



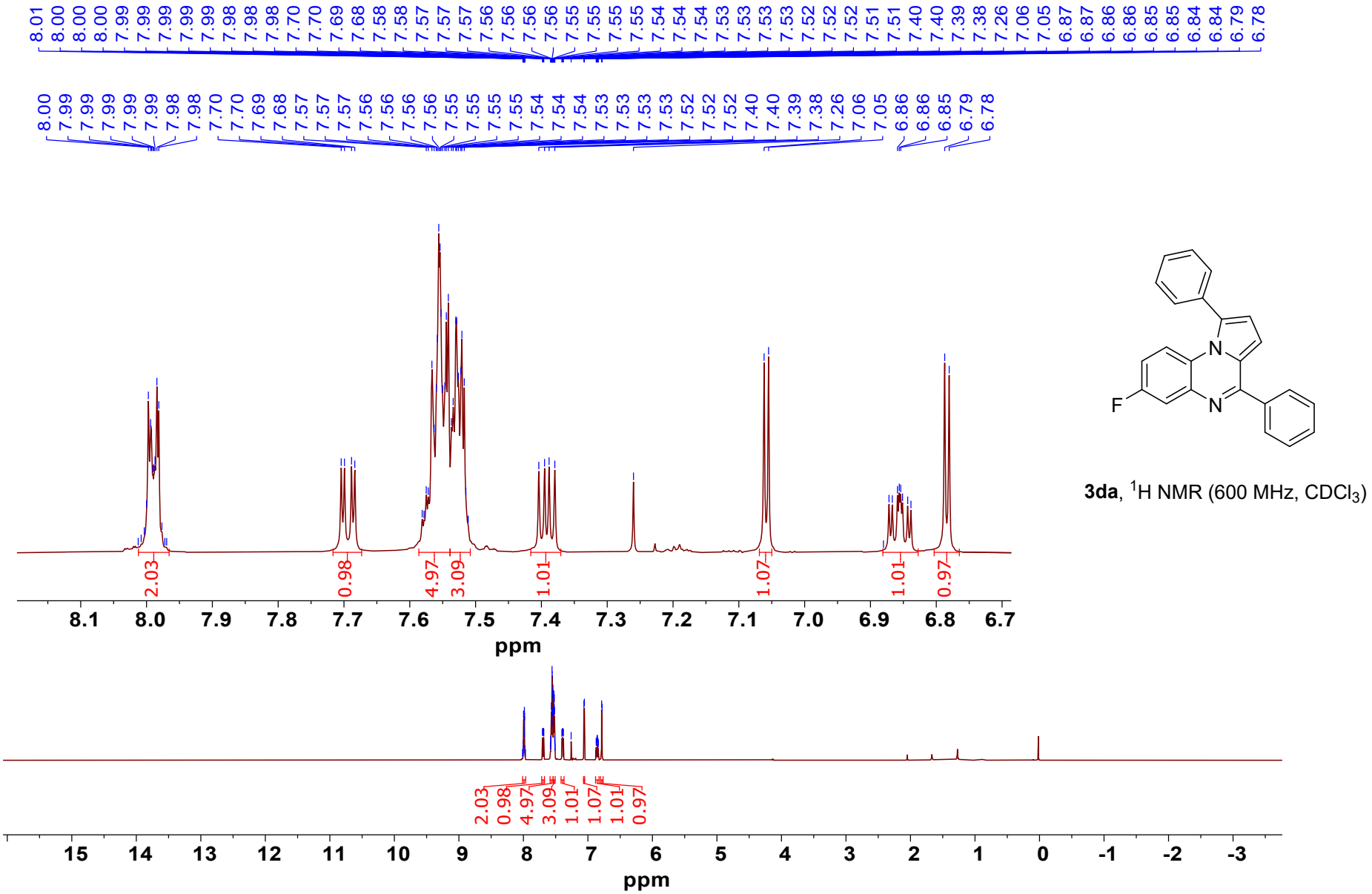
3ca, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


75
%T
60
45
30
15
NC
N
N
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
PQATT4

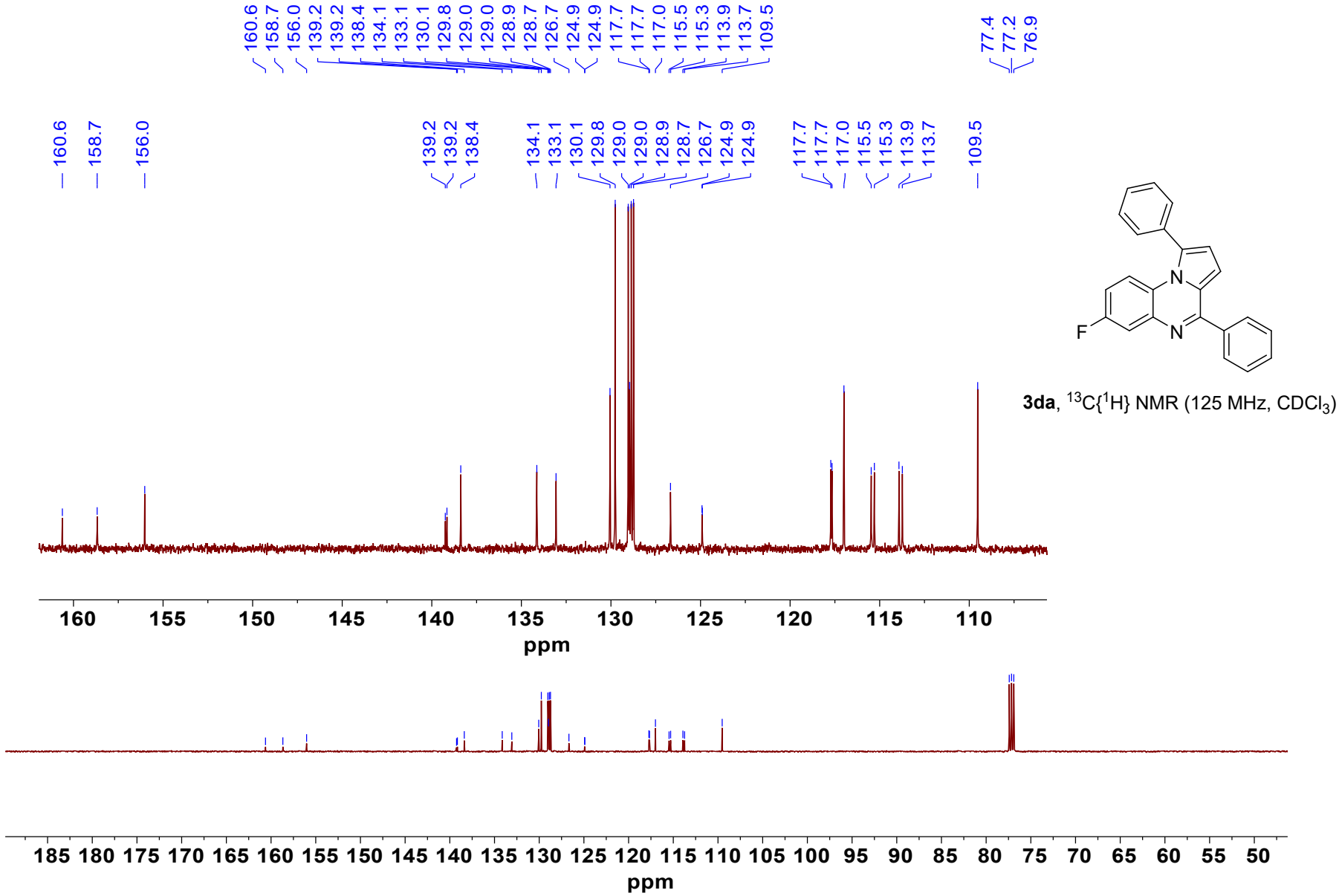
3ca, IR (ATR)


346.1351
100
80
60
40
20
0
NC
N
N
267.4295
255.2701
196.2453
270.1545
283.9834
293.6731
307.5613
329.6448
342.6985
150
200
250
300
350
Mass/Charge

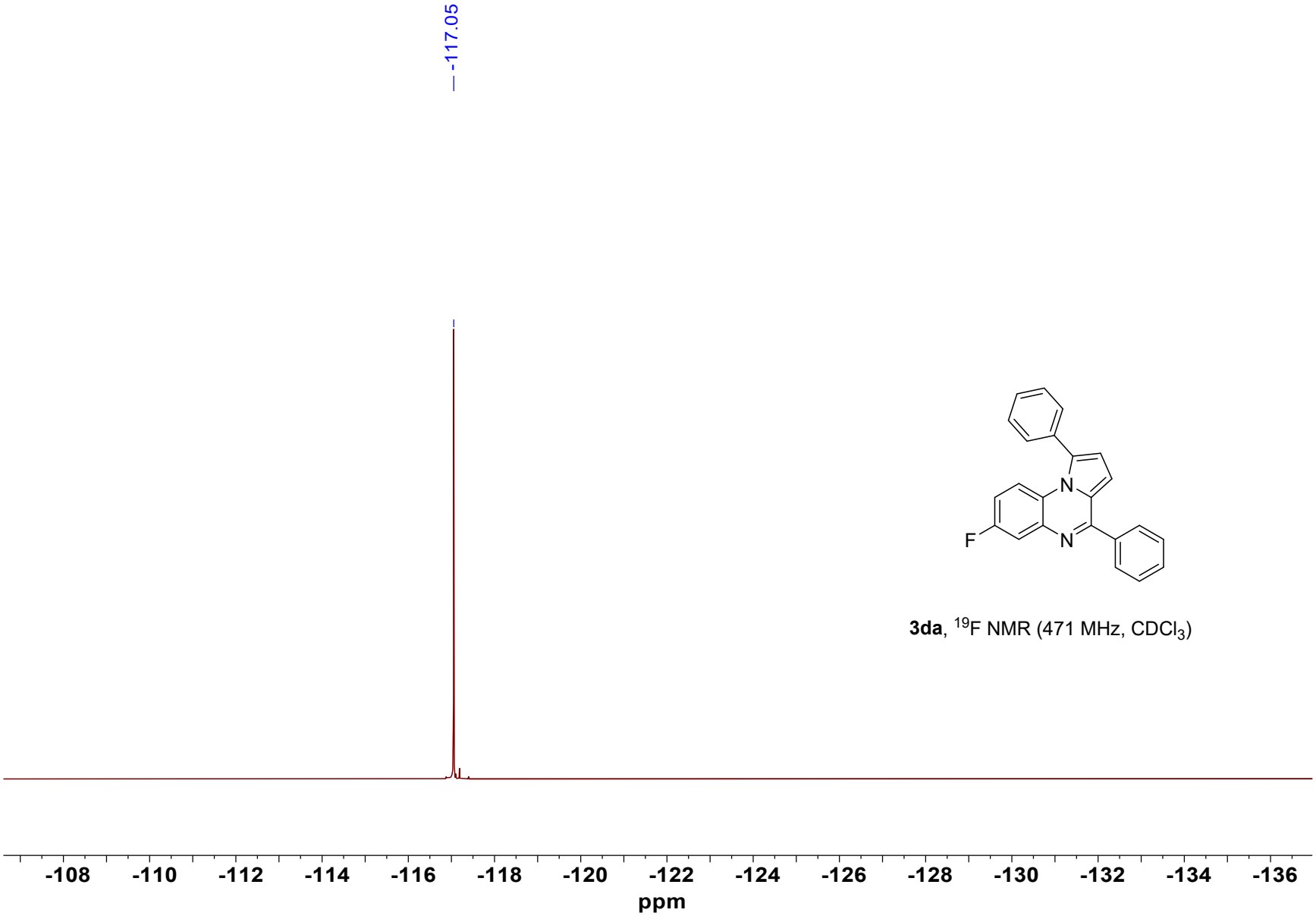
3ca, HR-MS



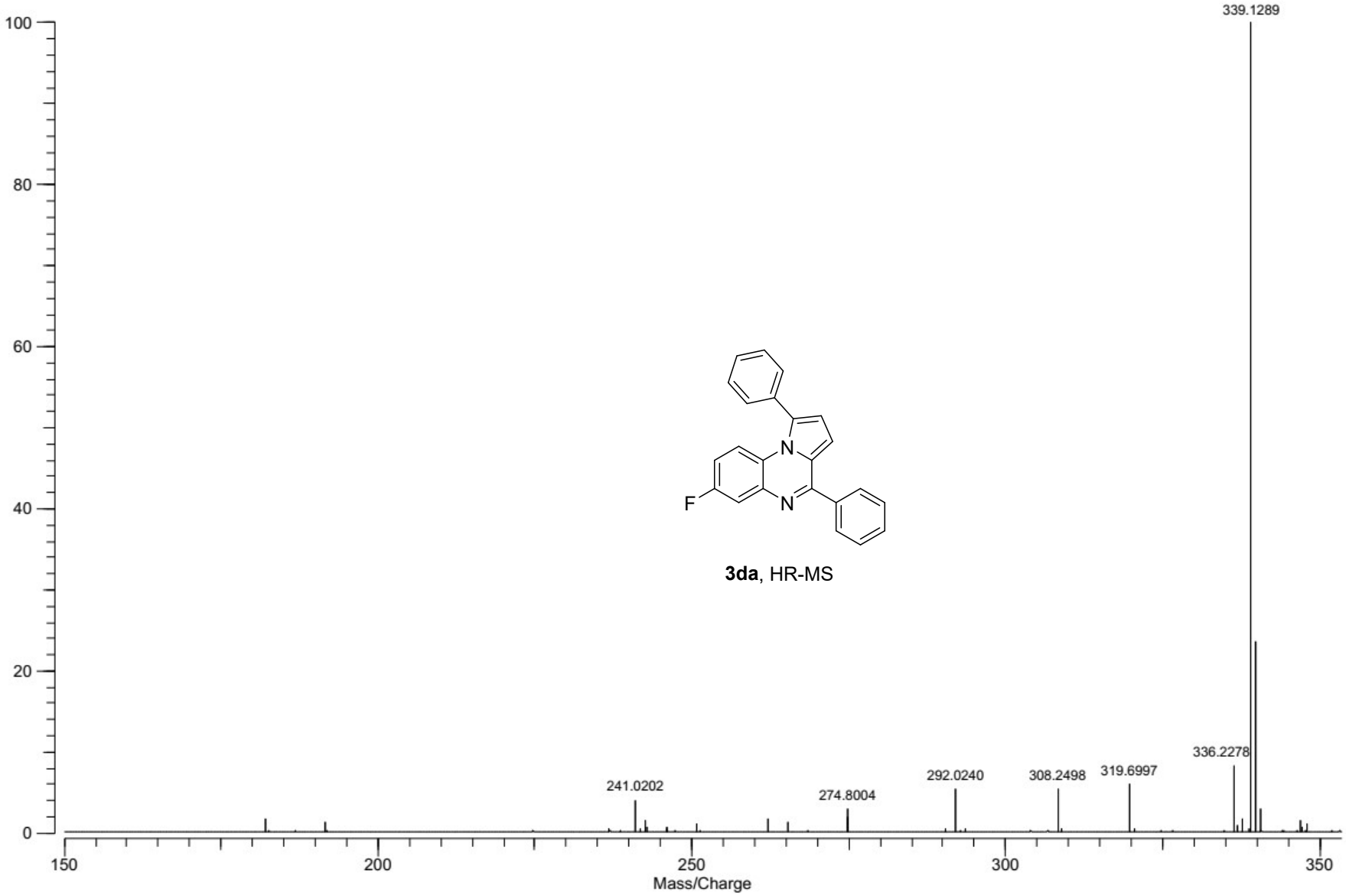
3da, ^{1}H NMR (600 MHz, $CDCl_3$)



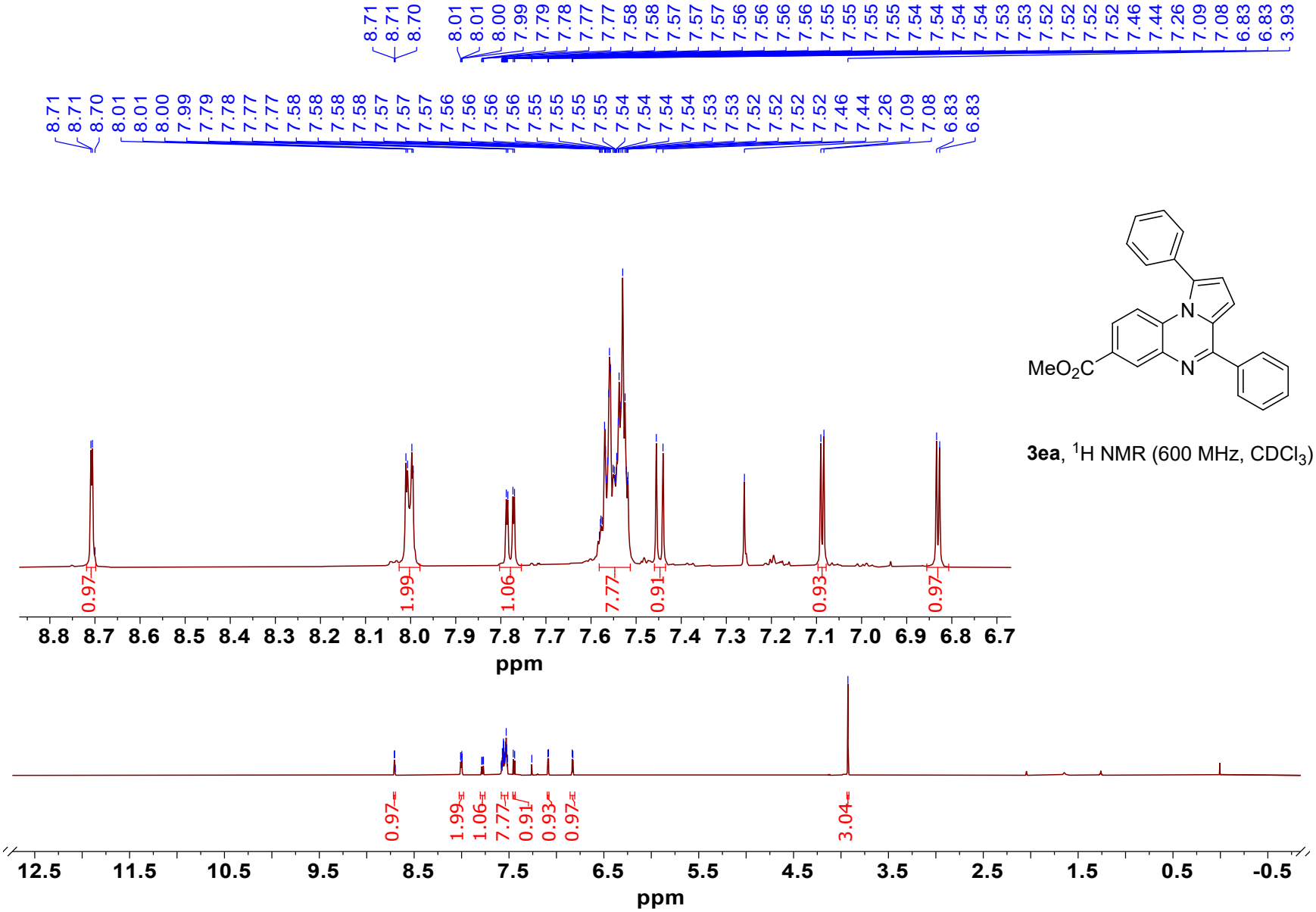
3da, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



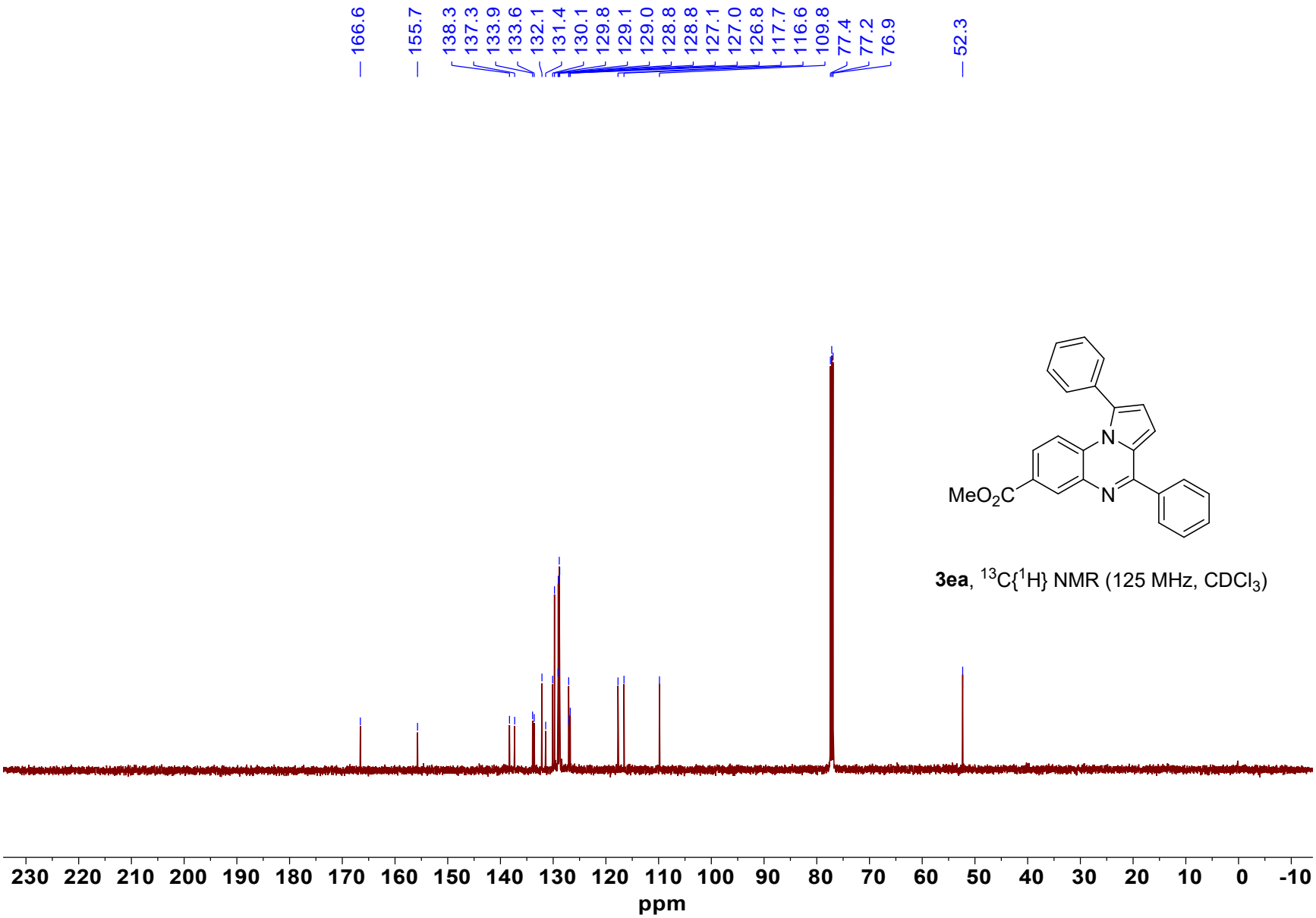
3da, ^{19}F NMR (471 MHz, $CDCl_3$)


339.1289
100
80
60
40
20
0
241.0202
274.8004
292.0240
308.2498
319.6997
336.2278
150
200
250
300
350
Mass/Charge
F
N
N

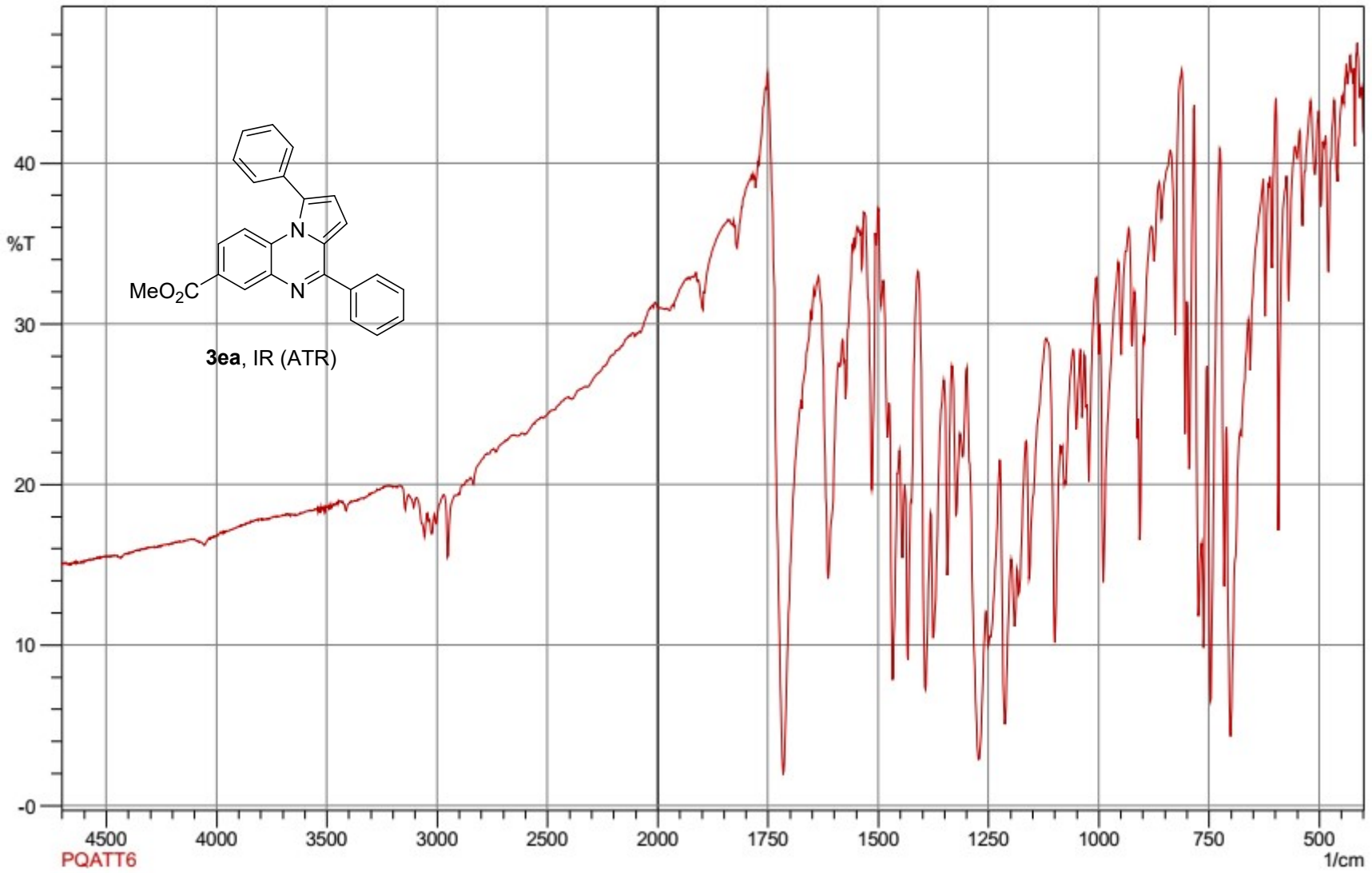
3da, HR-MS



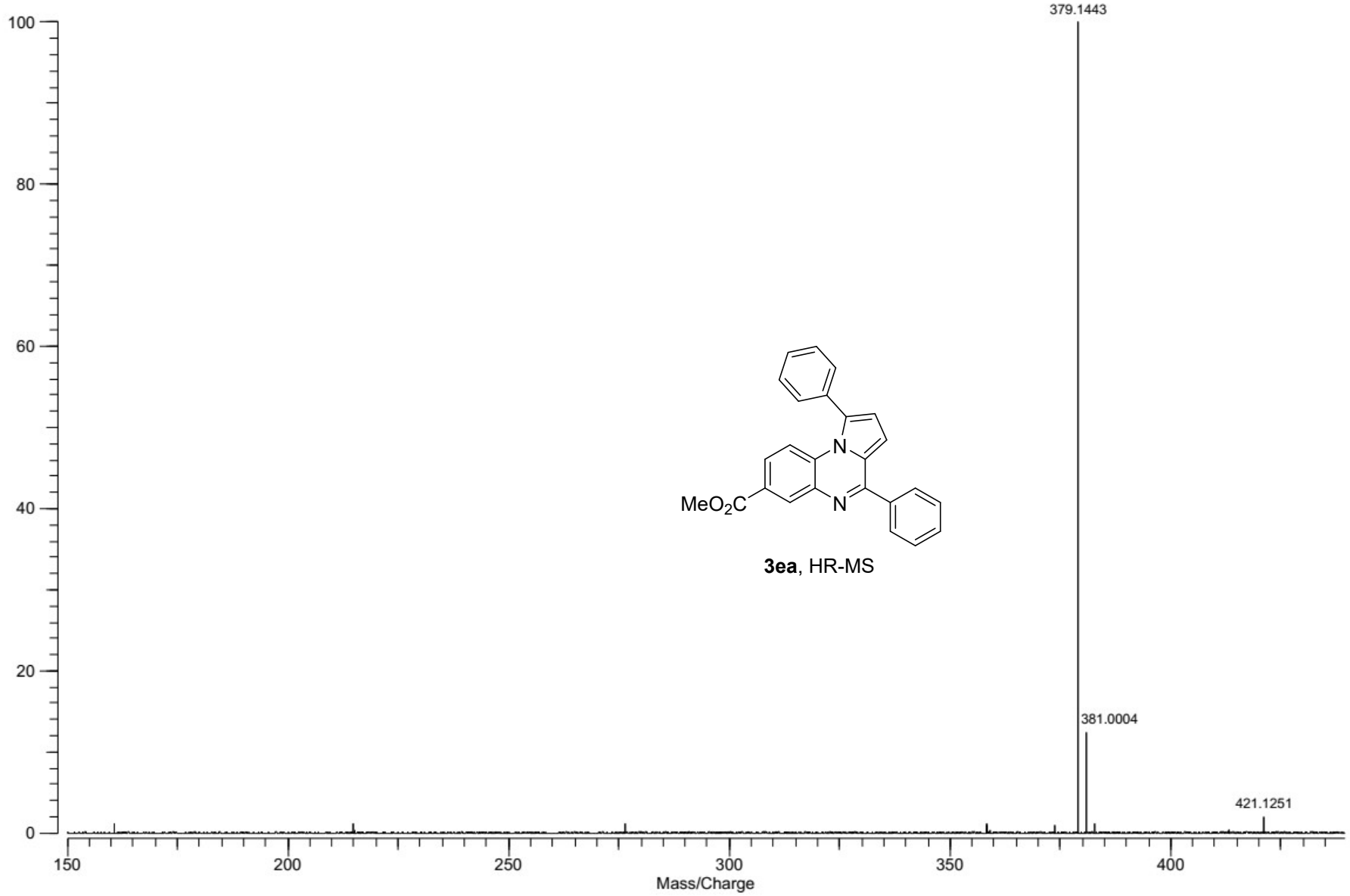
3ea, ^{1}H NMR (600 MHz, $CDCl_3$)



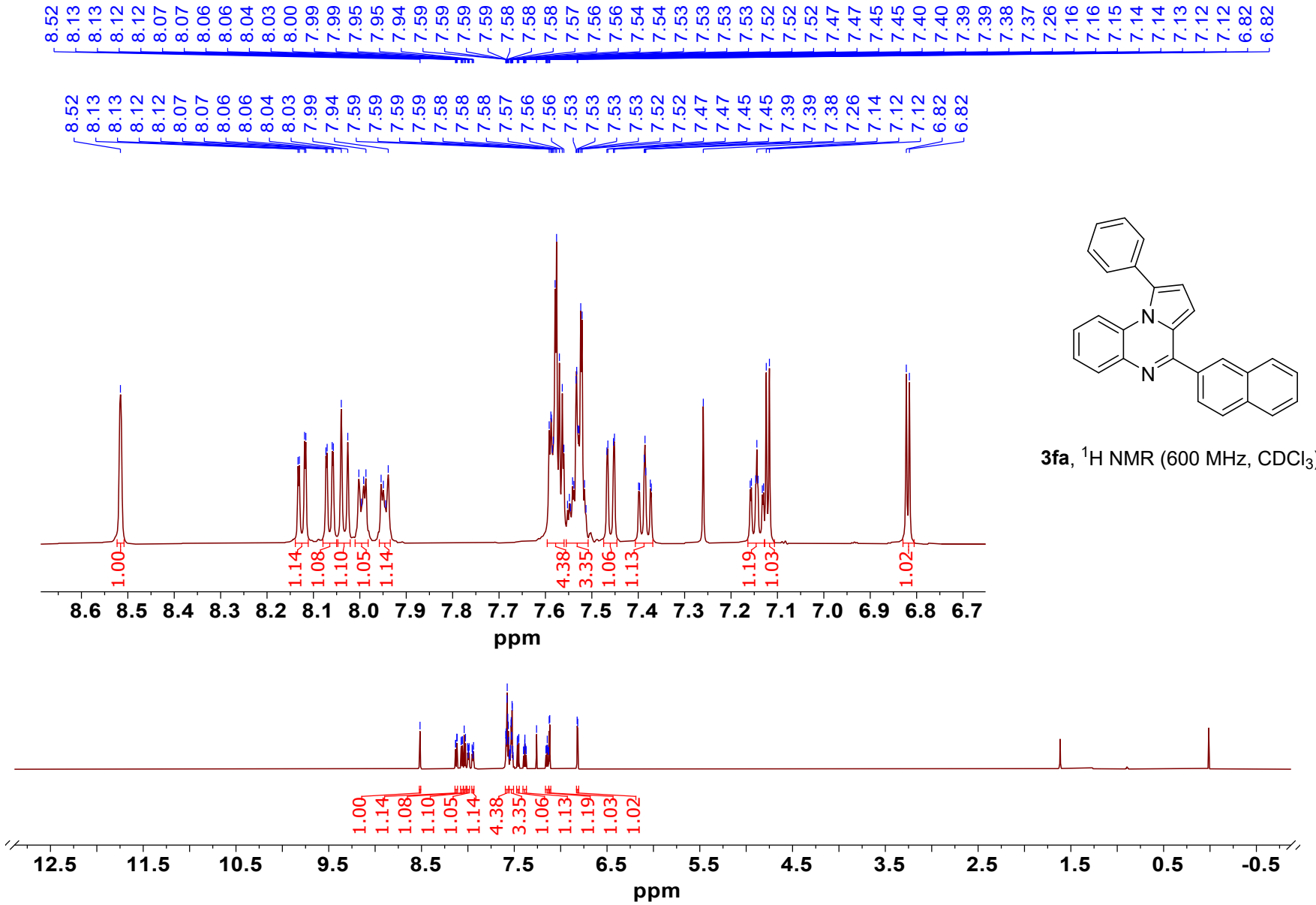
3ea, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


%T
40
30
20
10
-0
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
PQATT6
N
N
MeO2C

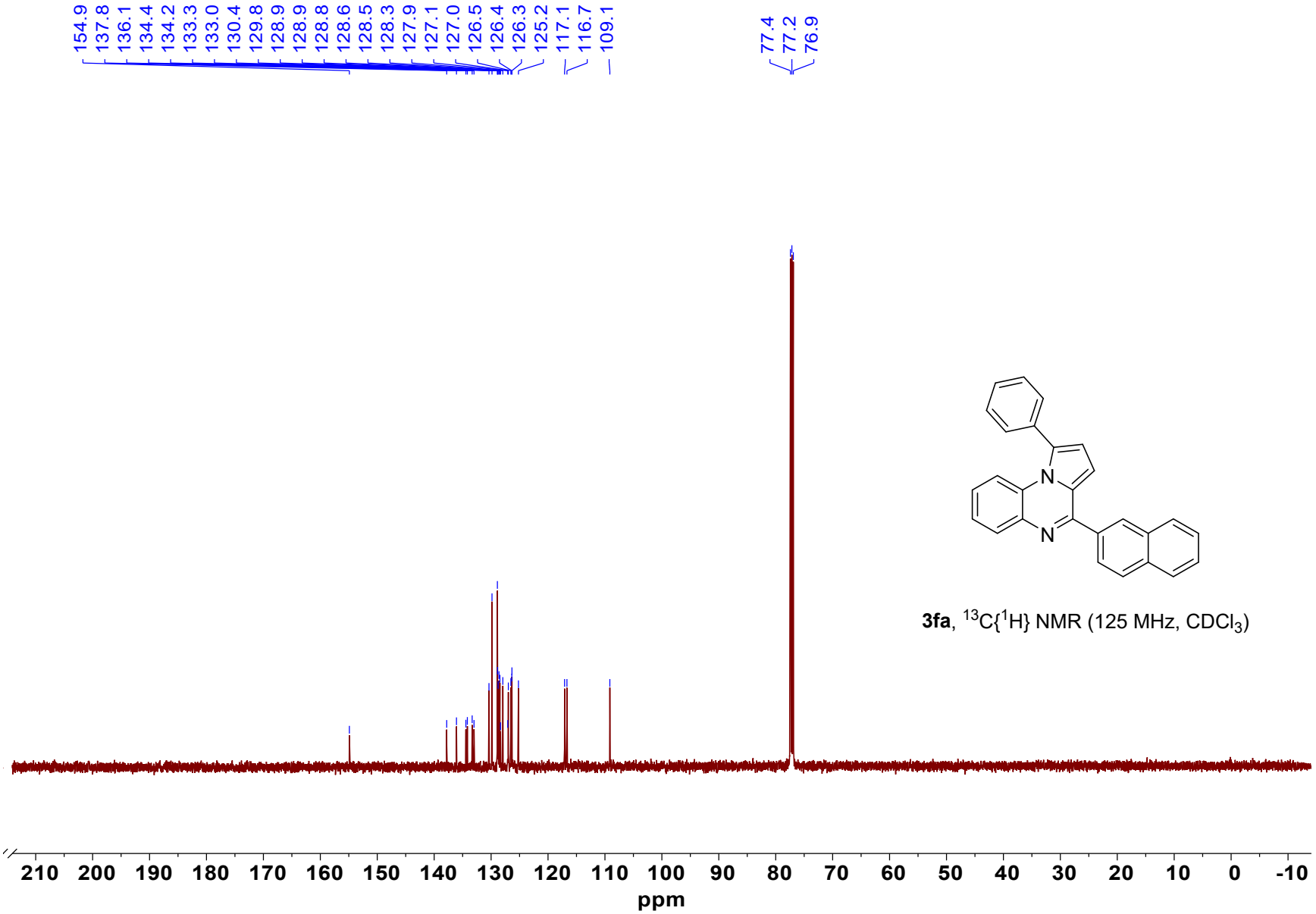
3ea, IR (ATR)


379.1443
381.0004
421.1251
100
80
60
40
20
0
150
200
250
300
350
400
Mass/Charge
MeO2C
N
N

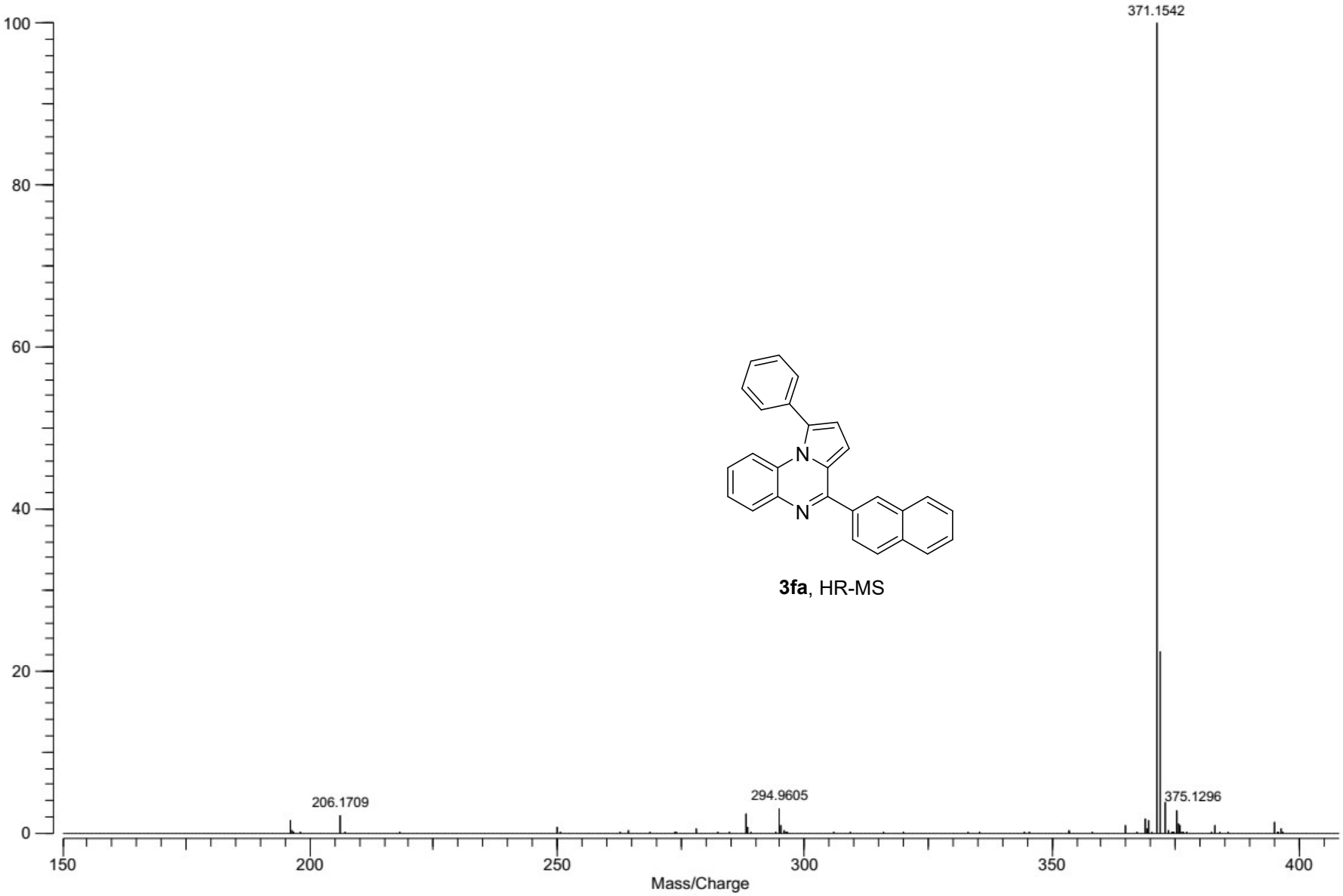
3ea, HR-MS



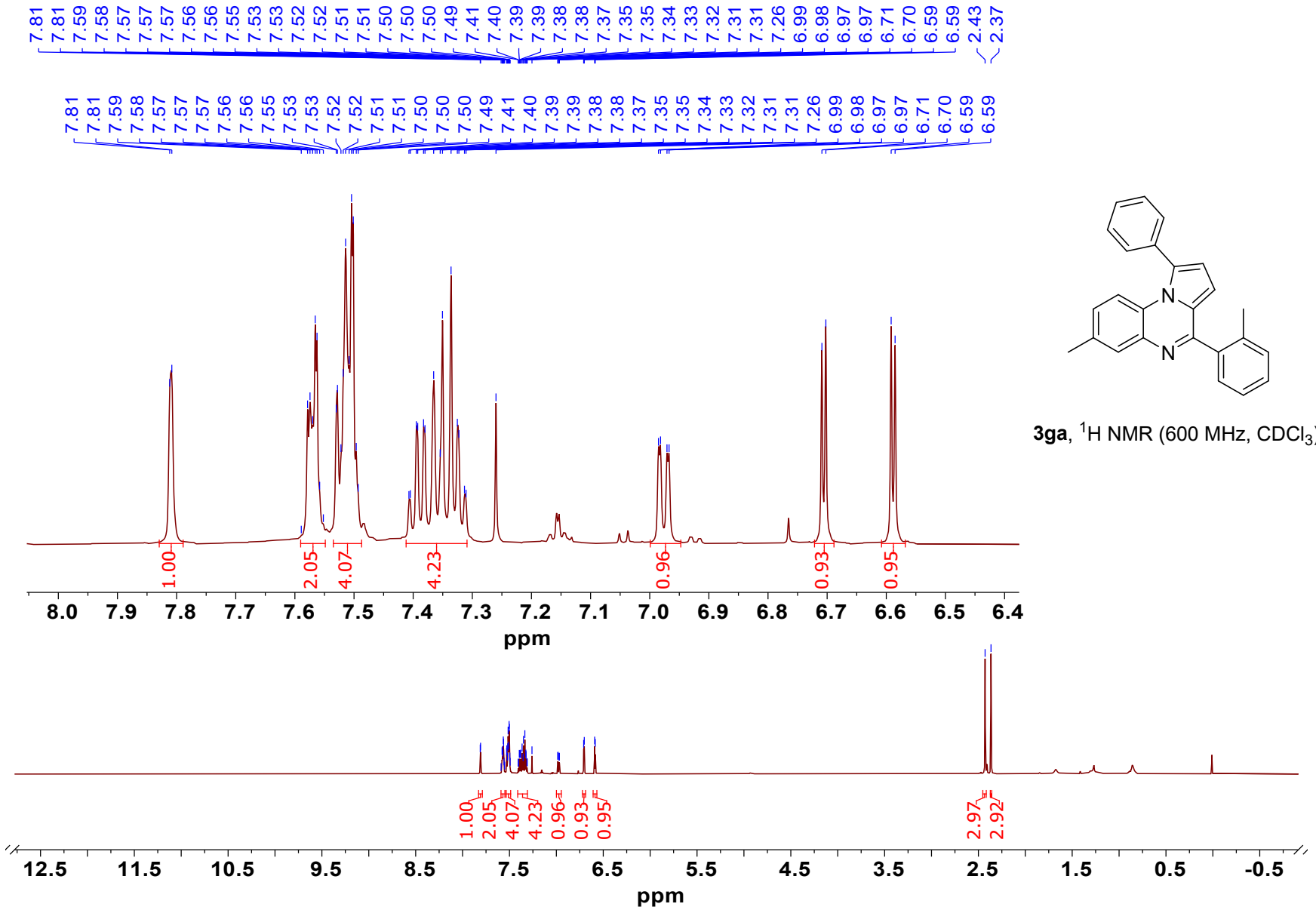
3fa, ^{1}H NMR (600 MHz, $CDCl_3$)



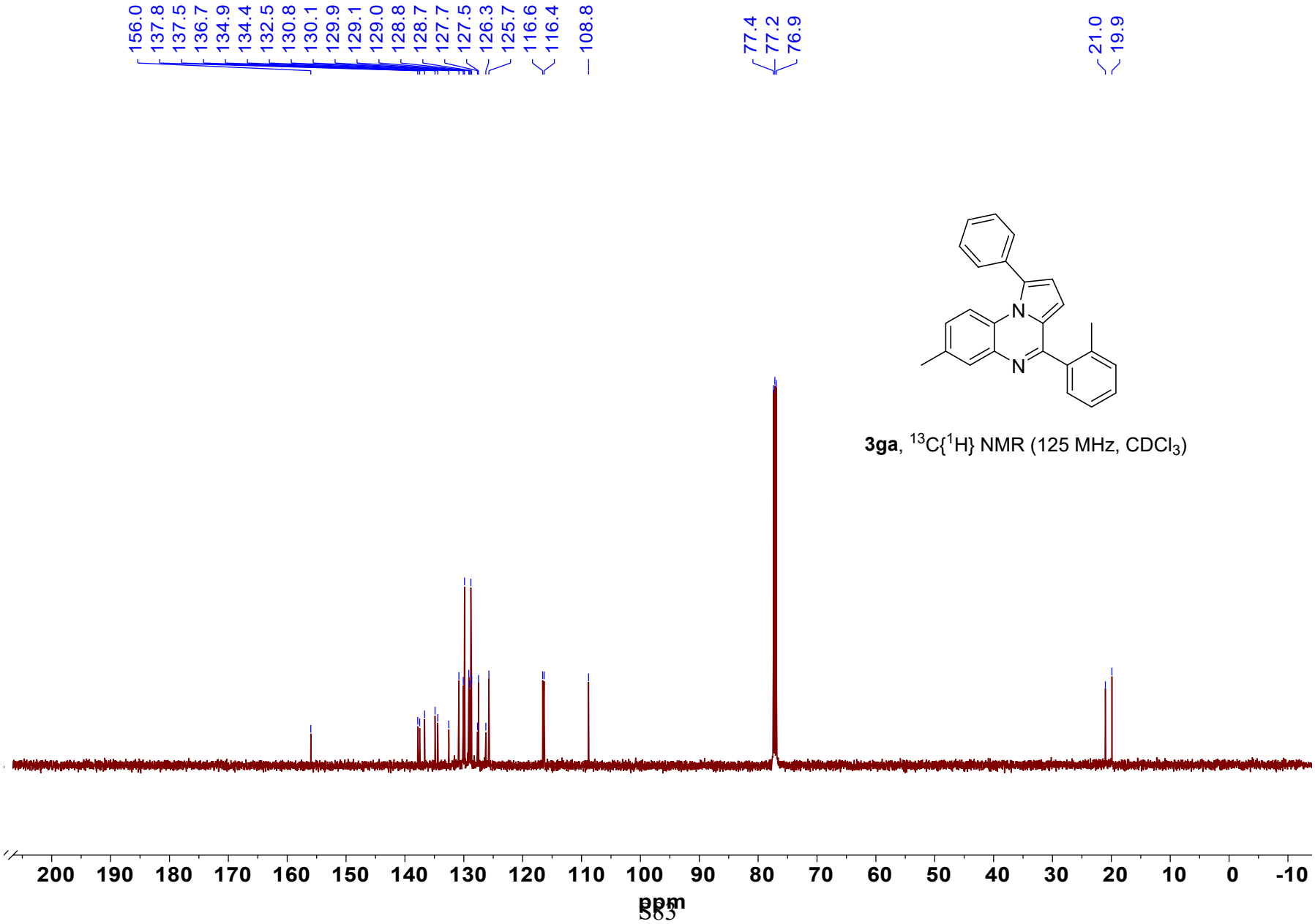
3fa, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


371.1542
100
80
60
40
20
0
206.1709
294.9605
375.1296
150
200
250
300
350
400
Mass/Charge
N
N

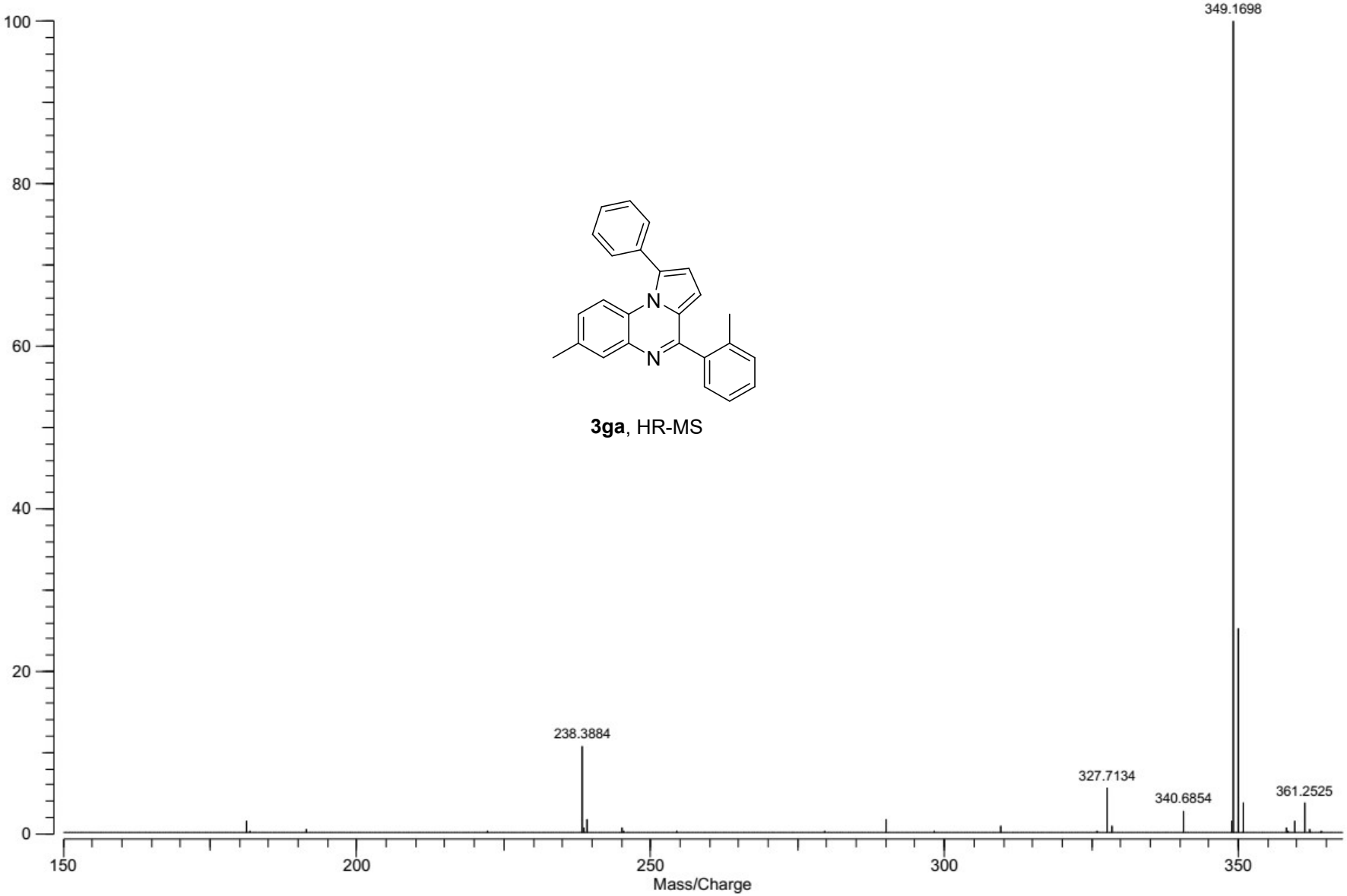
3fa, HR-MS



3ga, ^{1}H NMR (600 MHz, $CDCl_3$)



3ga, $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


349.1698
100
80
60
40
20
0
N
N
238.3884
327.7134
340.6854
361.2525
150
200
250
300
350
Mass/Charge

3ga, HR-MS