Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 93–95

Chemical transformations of 2-phenylcyclopropane-1,1-dinitrile under the action of Lewis acids

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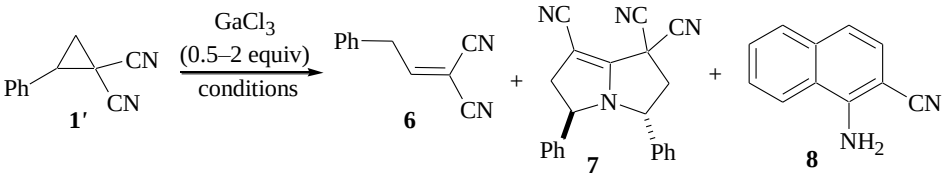
1. Experimental section

1.1. General experimental details

All reagents and solvents were commercial grade chemicals and were without additional purification. All operations with $GaCl_3$ were carried out under dry argon atmosphere. TLC analysis was performed on Silufol chromatographic plates. For preparative chromatography, silica gel 60 (0.040–0.063 mm) was used. ^{1}H, ^{13}C NMR spectra were recorded on a 300 MHz (300.1 and 75.5 MHz MHz respectively) 600 MHz (600.1 and 150.9 MHz respectively) spectrometers in $CDCl_3$, containing 0.05% Me_4Si as the internal standard. Determinations of structures and stereochemistry of obtained compounds and assignments of ^{1}H and ^{13}C signals were made with the aid of 1D and 2D COSY, NOESY, HSQC, HMBC spectra. IR spectra were obtained on a FT-IR spectrometer in $CHCl_3$ solution (1%). High resolution mass spectra were obtained using simultaneous electospray (ESI TOF). Starting 2-phenylcyclopropane-1,1-dinitrile (PCDN) **1′** was synthesized from styrene and bromomalonodinitrile by published synthetic procedure.[S1]

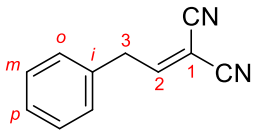
1.2. General synthetic procedures and spectroscopic data for obtained products



All operations were performed under dry argon atmosphere. Solid $GaCl_3$ (0.2–0.8 mmol) was added in one portion to a solution of PCDN **1′** (0.4 mmol, 1.0 equiv.) in dry CH_2Cl_2 or 1,2-DCE (3–4 ml) at room temperature and the reaction mixture was stirred under the conditions given in Table S1. After that, 8–12 ml of aqueous solution of HCl (10%) was added and the reaction mixture was extracted with CH_2Cl_2 (3×15 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was analyzed by NMR spectroscopy and was purified by column chromatography on silica gel (benzene to benzene-EtOAc (20:1)) to afford the compounds **6–8**. The resulting compounds can be additionally purified on a Silufol chromatographic plate (20×20 cm) eluting with hexane–acetone, 2:1 to afford the pure products, if it is necessary.

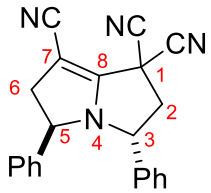
Entry	Solvent	$GaCl_3$ (mol.%)	*T*/°C	*t*/min	Conversion of **1′** (%)
1	DCM	105	25	15	100
2	DCM	105	40	30	100
3	1,2-DCE	105	80	15	100
4	1,2-DCE	200	80	15	100
5	DCM	50	40	30	65
6	DCM	110	0	210	90

2-(2-Phenylethylidene)malononitrile (6)



The title compound was prepared at 25 °C according to the general procedure from 67.3 mg of PCDN **1′** and 74.0 mg $GaCl_3$ in yield 56.0 mg (83%). Red thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3067, 3036, 3020, 2928, 2203 br (C≡N), 1642, 1602, 1496, 1456, 1415, 1257, 1229, 1194 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_8N_2$: *M*+*H*, 169.0760. Found: *m/z* 169.0773. ^1H NMR ($CDCl_3$, 300.1 MHz): δ 3.89 (d, 2H, H(3), ^3J = 8.0 Hz), 6.97–7.61 (m, 6H, 5 H_{Ar} and H(2)) ppm. ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 38.7 (C(3)), 89.8 (C(1)), 110.6 and 111.9 (2 CN), 128.1 (CH_{Ar}), 128.7 (2 CH_{Ar}), 129.4 (2 CH_{Ar}), 133.6 (C_{Ar}), 166.6 (C(2)) ppm.

3,5-Diphenyl-2,3,5,6-tetrahydro-1*H*-pyrrolizine-1,1,7-tricarbonitrile (7)

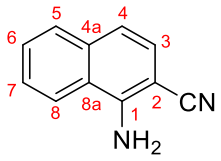


The title compound was prepared at 40 °C according to the general procedure from 67.4 mg of PCDN **1′** and 74.2 mg $GaCl_3$ in yield 8.75 mg (13%) as a single *trans*-

diastereomer. Yellow thick oil. IR ($CHCl_3$) $\tilde{\nu}$ 3068, 3052, 3003, 2956, 2929, 2204 br (C≡N), 1723, 1643, 1603, 1580, 1552, 1496, 1456, 1423, 1367, 1298, 1271, 1249, 1181 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}N_4$: *M+H*, 337.1448; *M+Na*, 359.1267. Found: *m/z* 337.1442; 359.1255.

^{1}H NMR ($CDCl_3$, 600.1 MHz): δ 2.96 (dd, 1H, H(2), ^2J = 13.6 Hz, ^3J = 8.4 Hz), 3.29 (dd, 1H, H(6), ^2J = 15.4 Hz, ^3J = 4.8 Hz), 3.38 (dd, 1H, H(2), ^2J = 13.6 Hz, ^3J = 6.2 Hz), 3.76 (dd, 1H, H(6), ^2J = 15.4 Hz, ^3J = 11.3 Hz), 4.24 (dd, 1H, H(3), ^3J = 8.4 Hz, ^3J = 6.2 Hz), 4.62 (dd, 1H, H(5), ^3J = 11.3 Hz, ^3J = 4.8 Hz), 7.02–7.06 (m, 2H, 2 H_{Ar}), 7.07–7.11 (m, 2H, 2 H_{Ar}), 7.31–7.42 (m, 6H, 6 H_{Ar}) ppm. ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 30.5 (C(1)), 42.6 (C(6)), 49.6 (C(2)), 58.4 (C(3)), 61.7 (C(5)), 73.4 (C(7)), 110.9, 111.3 and 114.6 (3 CN), 126.6 (2 CH_{Ar}), 126.8 (2 CH_{Ar}), 129.3 (2 CH_{Ar}), 129.4 (3 CH_{Ar}), 129.5 (CH_{Ar}), 134.8 and 137.8 (2 C_{Ar}), 155.2 (C(8)) ppm.

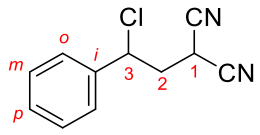
1-Amino-2-naphthonitrile (8)



The title compound was prepared at 80 °C according to the general procedure from 67.2 mg of PCDN **1′** and 140.8 mg $GaCl_3$ in yield 24.9 mg (37%) as red-yellow oil. (See lit. **[S2,S3]**)

^{1}H NMR ($CDCl_3$, 600.1 MHz): δ 7.25 (d, 1H, H_{Ar}, ^3J = 8.6 Hz), 7.37 (d, 1H, H_{Ar}, ^3J = 8.6 Hz), 7.58 (t, 1H, H_{Ar}, ^3J = 8.2 Hz), 7.64 (t, 1H, H_{Ar}, ^3J = 8.2 Hz), 7.83 (d, 1H, H_{Ar}, ^3J = 8.2 Hz), 7.86 (d, 1H, H_{Ar}, ^3J = 8.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 89.5 (C_{Ar}), 118.5 (CH_{Ar}), 118.6 (CN), 121.1 (CH_{Ar}), 121.8 (C_{Ar}), 126.2 (CH_{Ar}), 126.3 (CH_{Ar}), 128.9 (CH_{Ar}), 129.0 (CH_{Ar}), 135.8 (C_{Ar}), 148.2 (C_{Ar}) ppm.

2-(2-Chloro-2-phenylethyl)malononitrile (9)



All operations were performed under dry argon atmosphere. The $TiCl_4$ (~76 mg, 0.4 mmol) was added in one portion to a solution of PCDN **1′** (67.4 mg, 0.4 mmol) in dry CH_2Cl_2 (3 ml) at room temperature and the reaction mixture was stirred at reflux in CH_2Cl_2 during 1 h. After that, the solution was cooled to room temperature, 10 ml of aqueous solution of HCl (10%) was added and the reaction mixture was extracted with CH_2Cl_2 (3×15 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (benzene to benzene-EtOAc (20:1)) to afford title compound **9** in yield 12 mg (15%) as light yellow oil. IR ($CHCl_3$) $\tilde{\nu}$ 3067, 3041, 3025, 2911, 2250 br (C≡N), 1603, 1520, 1498, 1456, 1433, 1249, 1198, 1181 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_9ClN_2$ (*M* for ^{35}Cl): *M+H*, 205.0527. Found: *m/z* 205.0871.

^{1}H NMR ($CDCl_3$, 600.1 MHz): δ 2.68 (ddd, 1H, H(2), ^2J = 14.3 Hz, ^3J = 9.6 Hz, ^3J = 5.0 Hz), 2.77 (ddd, 1H, H(2), ^2J = 14.3 Hz, ^3J = 10.0 Hz, ^3J = 6.0 Hz), 4.03 (dd, 1H, H(1), ^3J = 9.6 Hz, ^3J = 6.0 Hz),

5.06 (dd, 1H, H(3), ^{3}J = 10.0 Hz, ^{3}J = 5.0 Hz), 7.05–7.60 (m, 5H, H_{Ar}) ppm. ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 21.0 (C(1)), 40.3 (C(2)), 58.6 (C(3)), 111.4 and 111.6 (2 CN), 126.8 (2 CH_{Ar}), 129.5 (2 CH_{Ar}), 129.7 (CH_{Ar}), 137.8 (C_{Ar}) ppm.

2. References

S1 P. Boldt, L. Schulz and J. Etzemüller, *Chem. Ber.*, 1967, **100**, 1281.

S2 J. Dong, Z. Wang, Q. Meng, Q. Zhang, G. Huang, J. Cui and S. Li., *RSC Adv.*, 2018, **8**, 15009; https://doi.org/10.1039/C8RA00465J.

S3 Y. Tomioka, K. Ohkubo and M. Yamazaki, *Chem. Pharm. Bull.*, 1985, **33**, 1360; https://doi.org/10.1248/cpb.33.1360.

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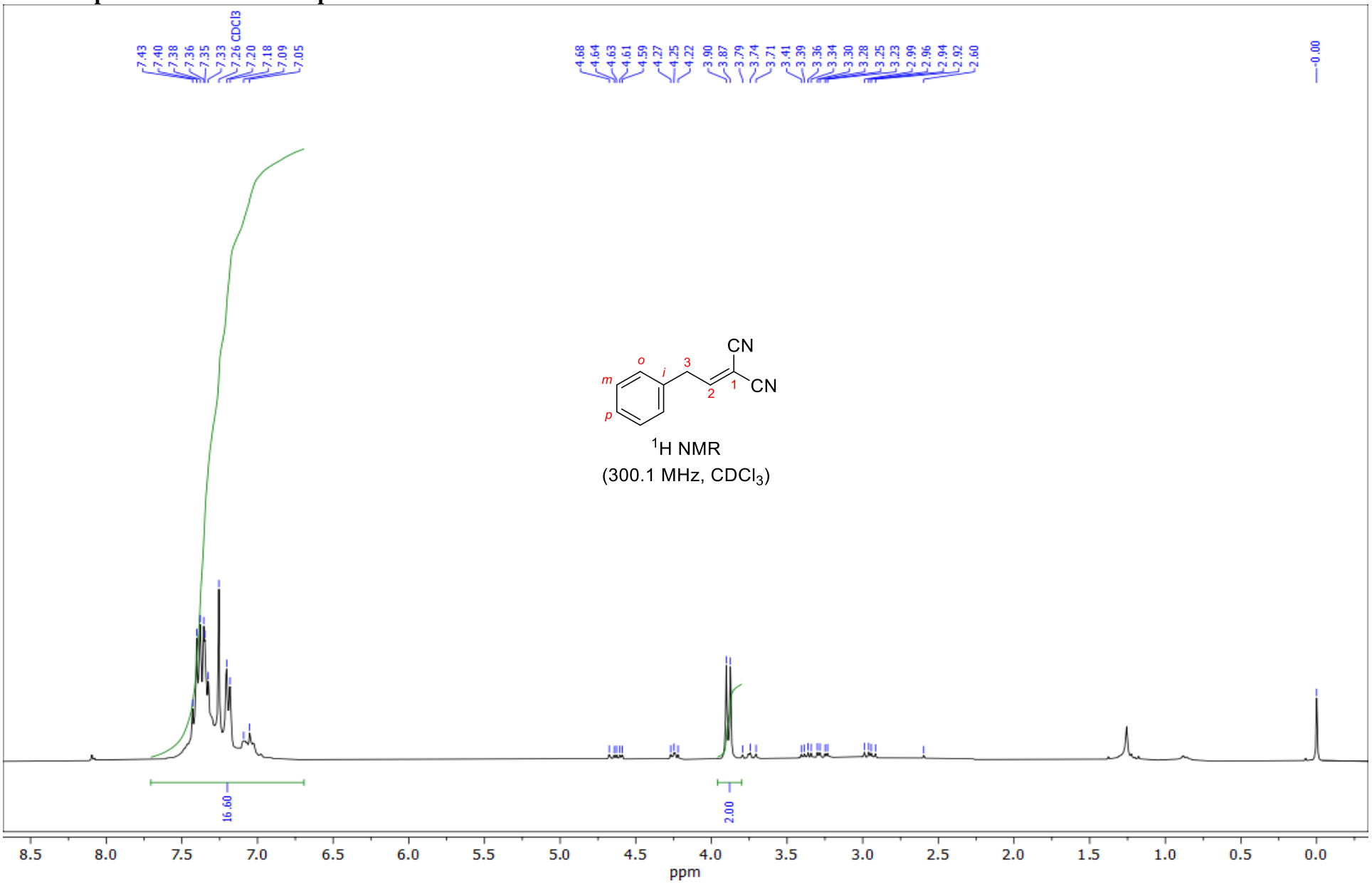
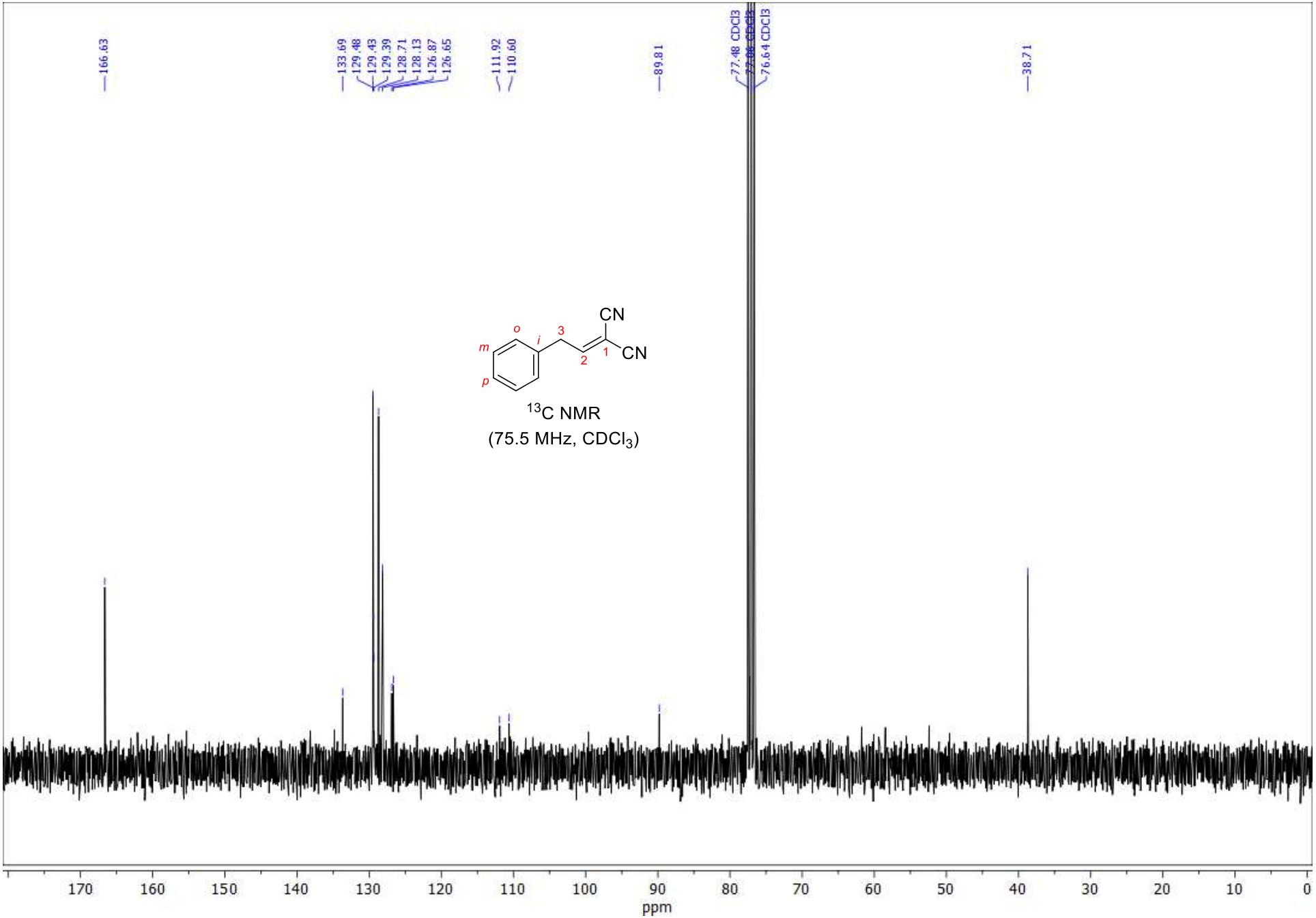
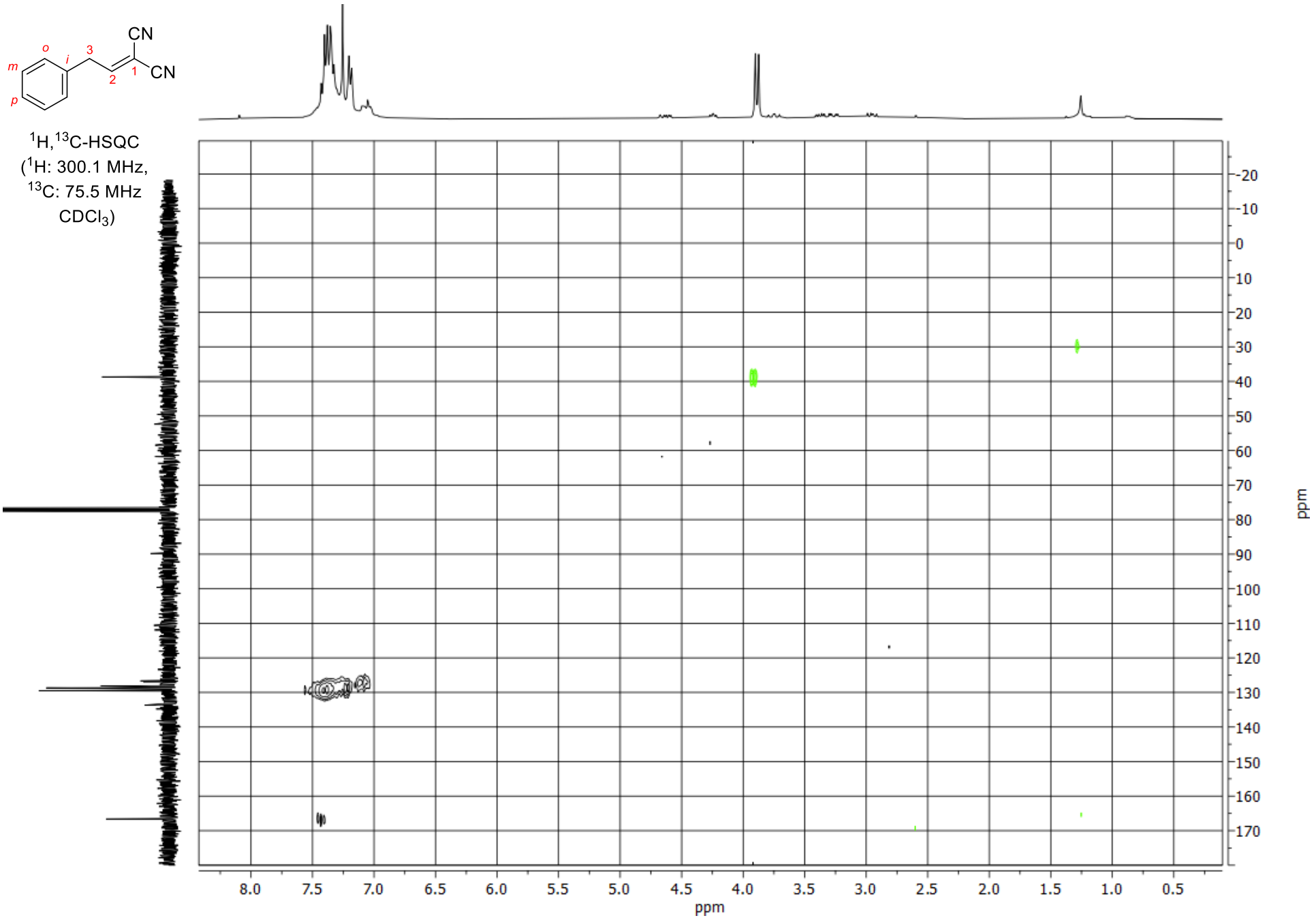
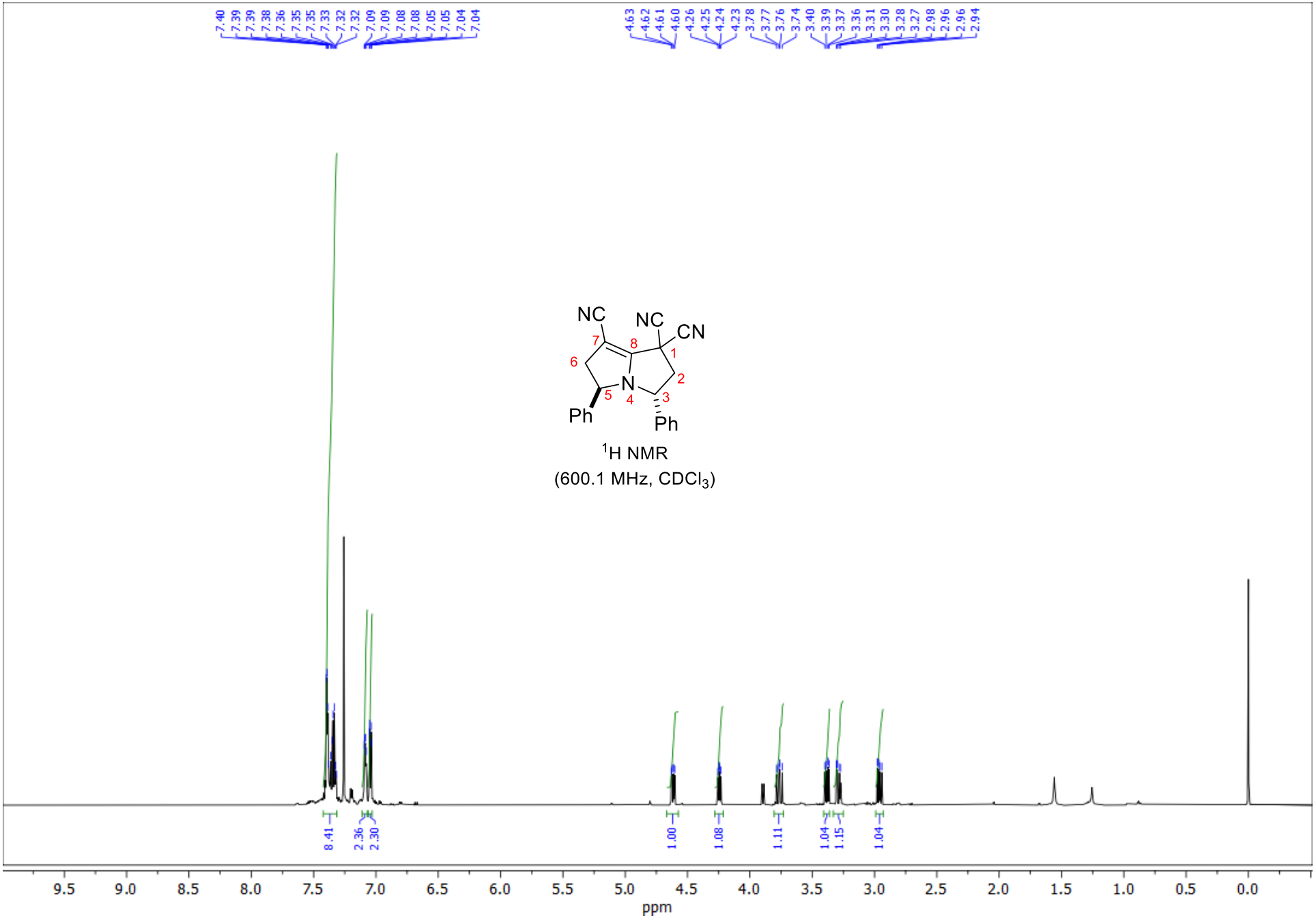
3. NMR spectra of obtained compounds:

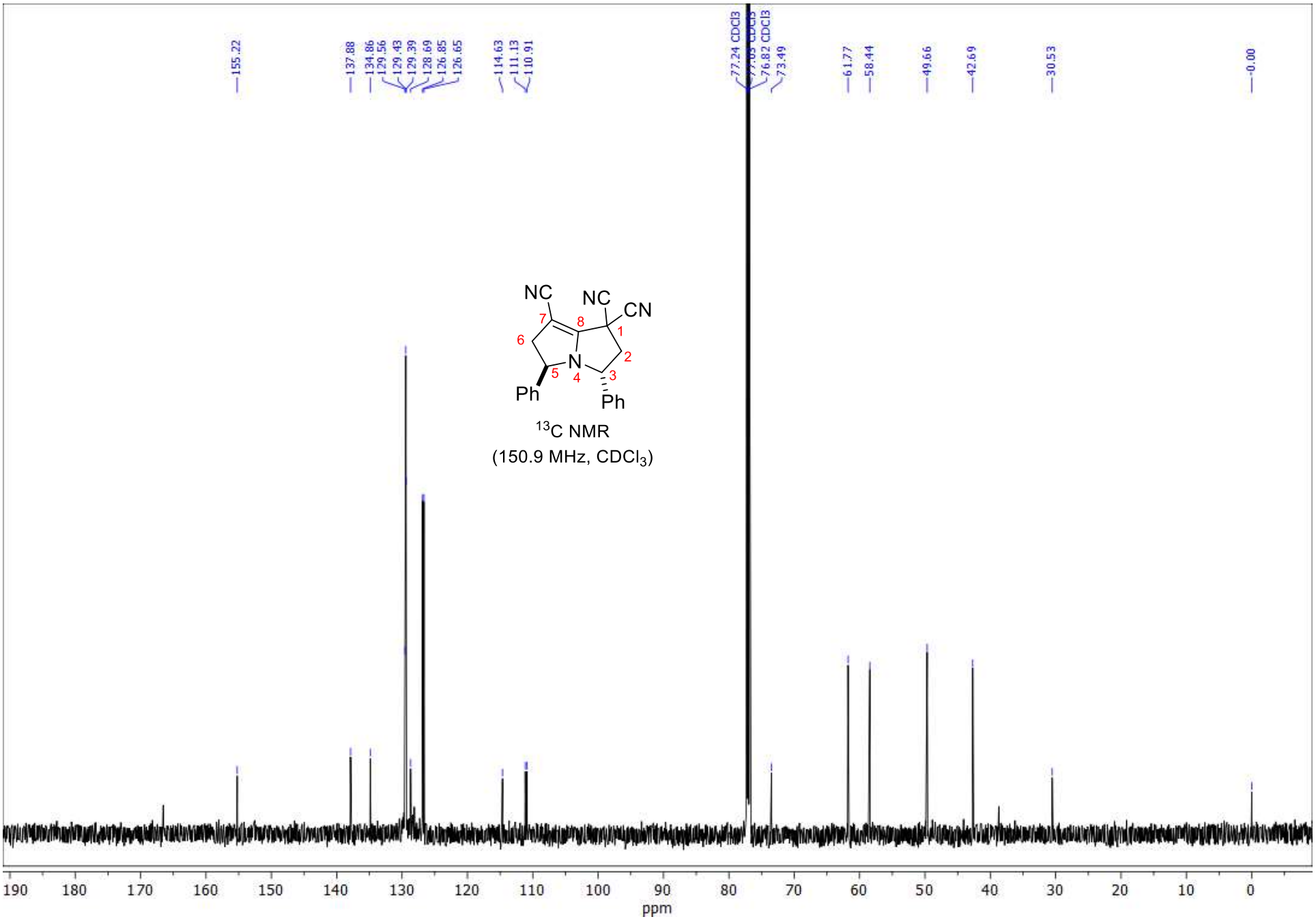



166.63
133.69
129.48
129.43
129.39
128.71
128.13
126.87
126.65
111.92
110.60
89.81
77.48 CDCl3
77.06 CDCl3
76.64 CDCl3
38.71
CN
CN
o
i
3
m
2
1
p
13C NMR
(75.5 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

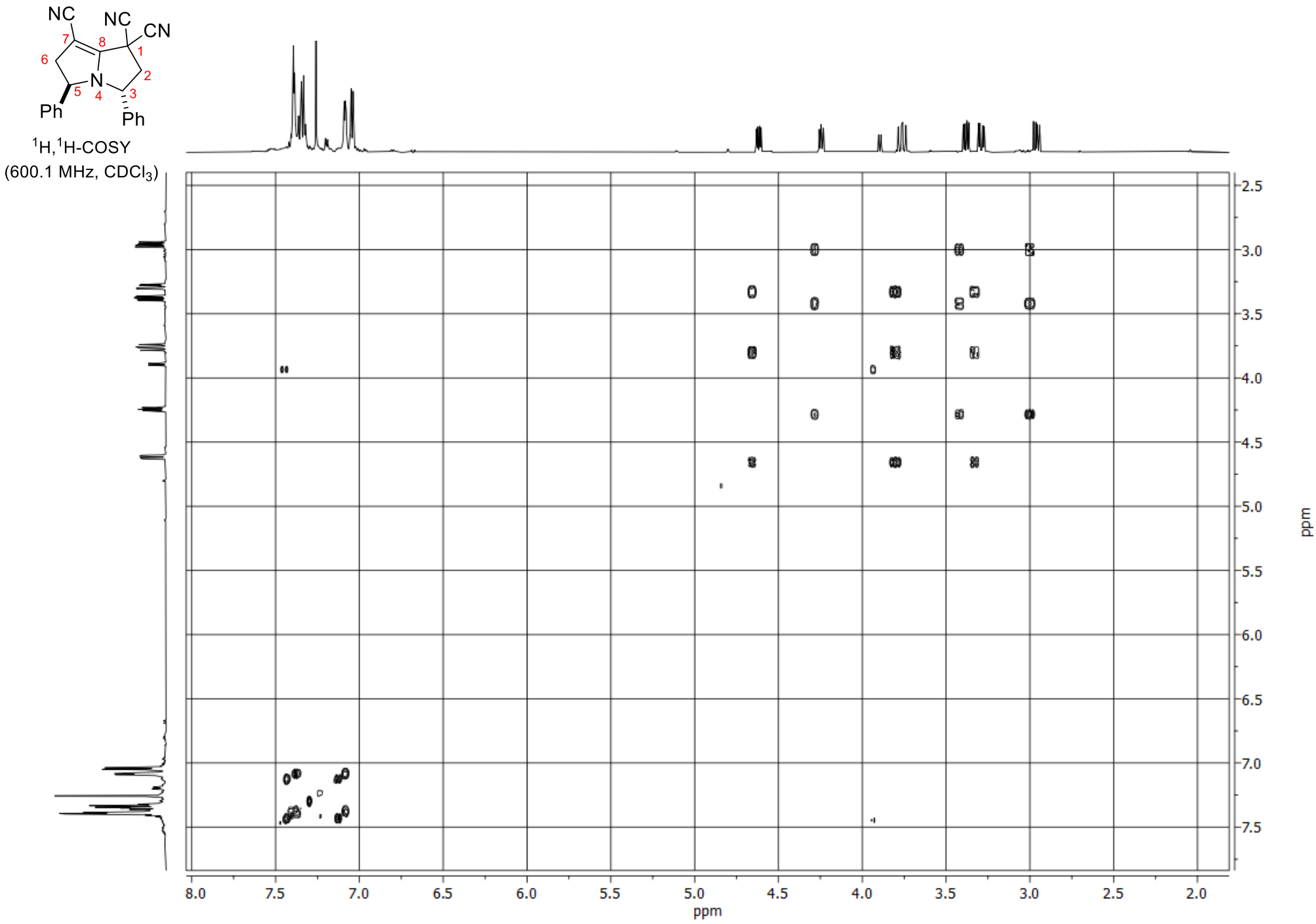

CN
CN
o
i
3
m
2
1
p
^{1}H,^{13}C-HSQC
(^{1}H: 300.1 MHz,
^{13}C: 75.5 MHz
$CDCl_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

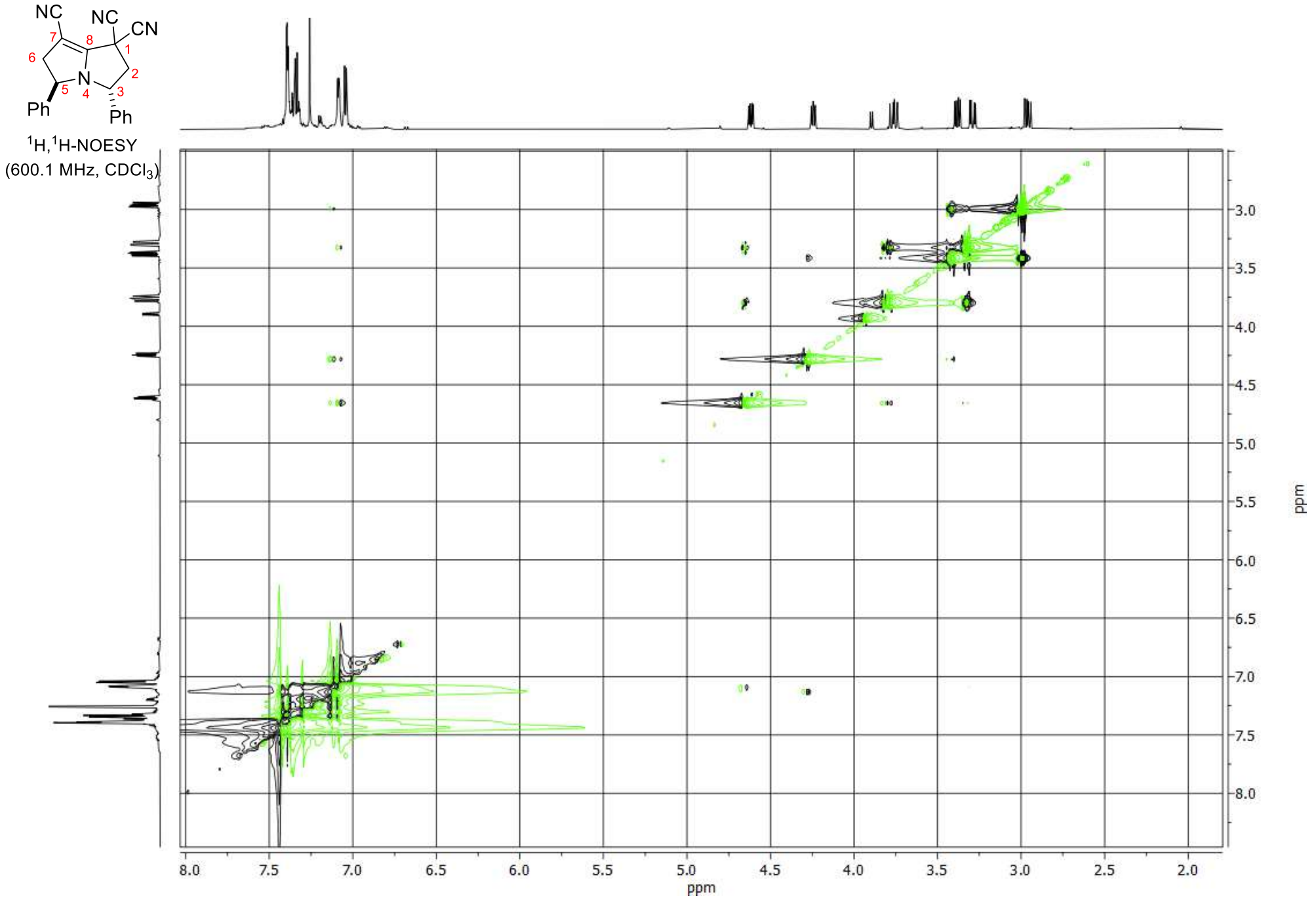


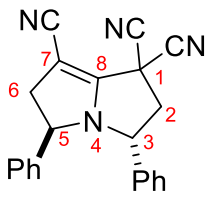
^{1}H NMR
(600.1 MHz, $CDCl_3$)



^{13}C NMR
(150.9 MHz, $CDCl_3$)

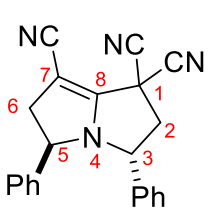

NC
NC
CN
Ph
Ph
N
1
2
3
4
5
6
7
8
^{1}H,^{1}H-COSY
(600.1 MHz, $CDCl_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
ppm


NC
NC
CN
7
8
1
6
2
N
5
4
3
Ph
Ph
^{1}H,^{1}H-NOESY
(600.1 MHz, $CDCl_3$)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
ppm

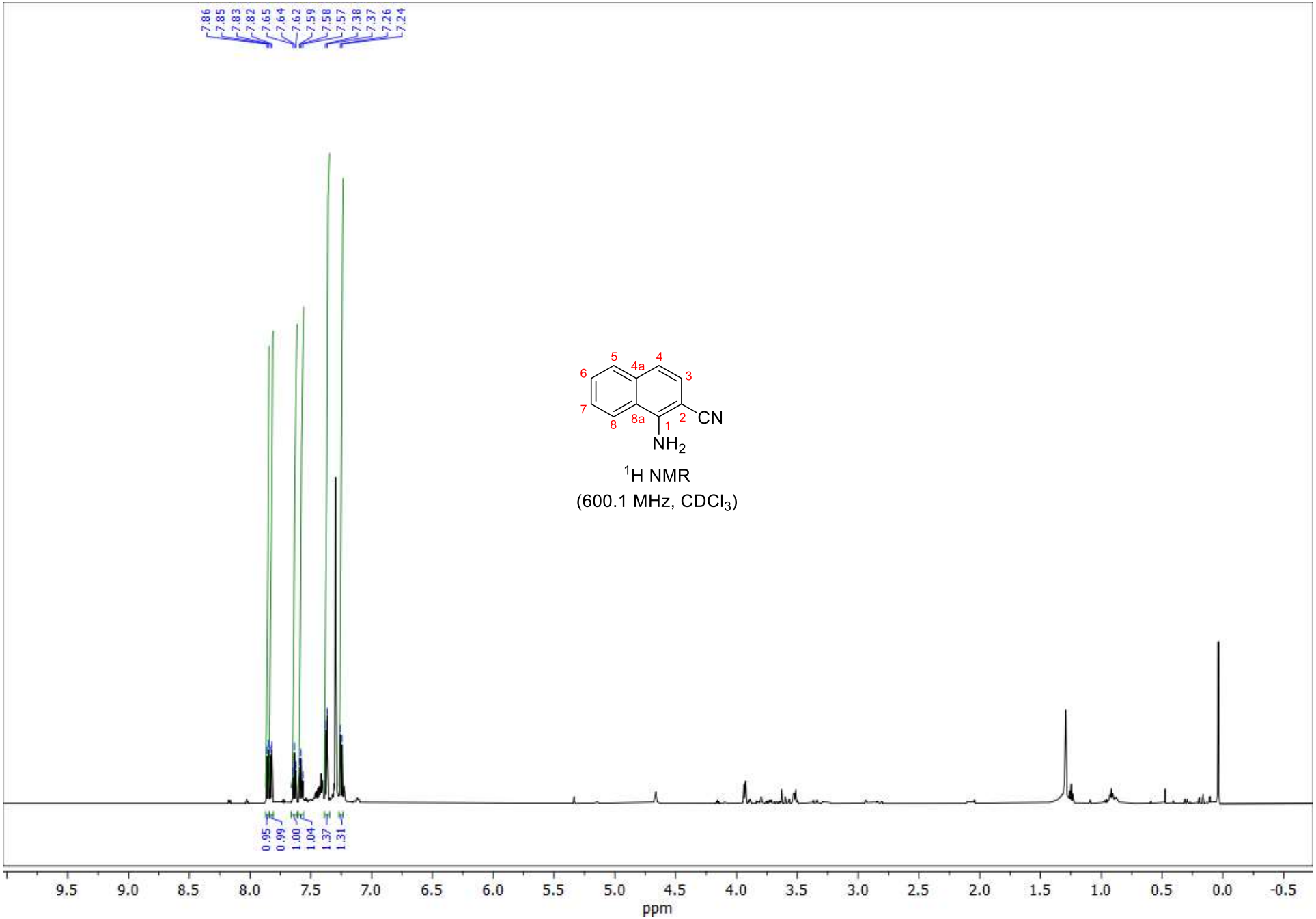


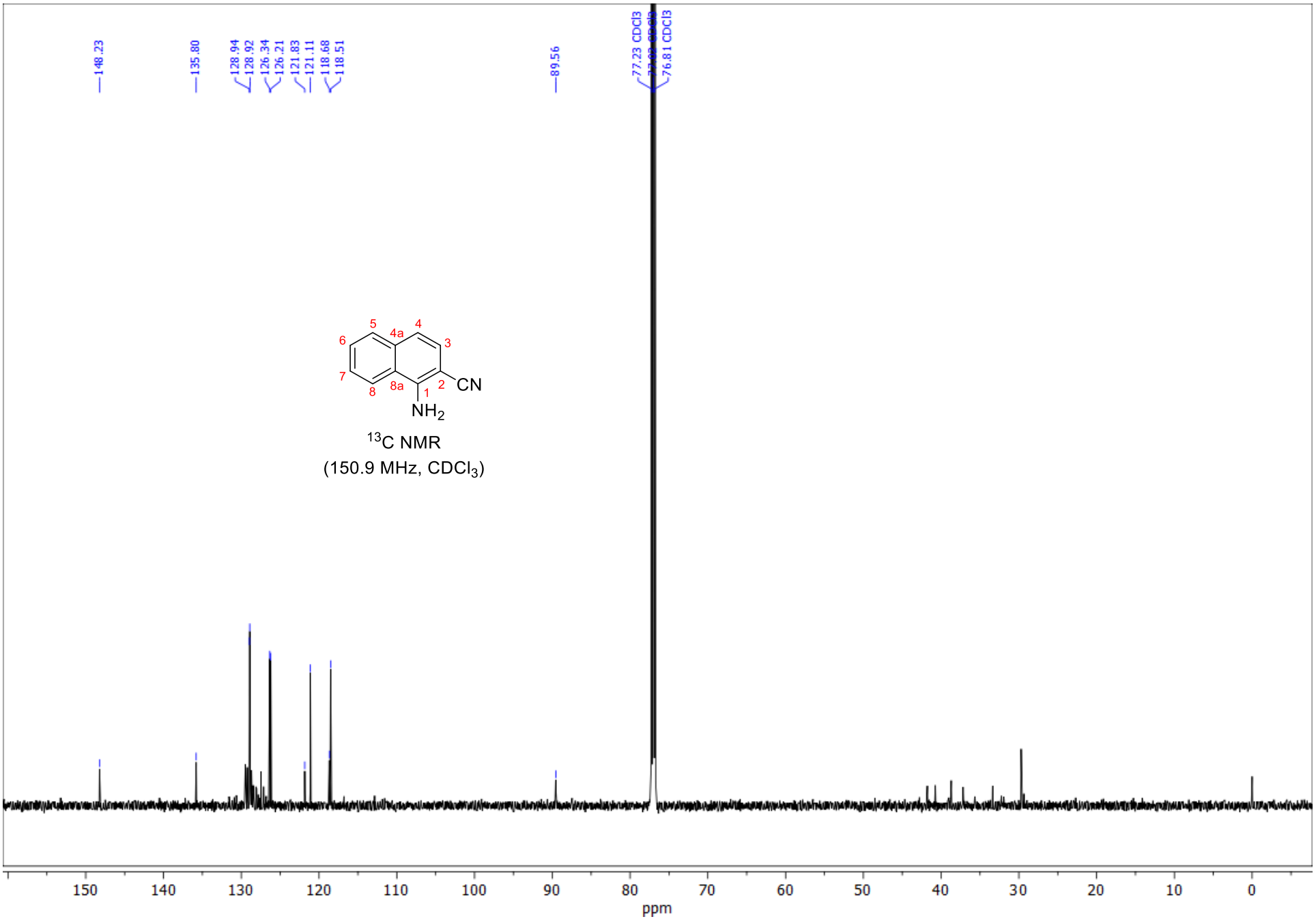
$^{1}H,^{13}C$-HSQC
(^{1}H: 600.1 MHz,
^{13}C: 150.9 MHz
$CDCl_3$)

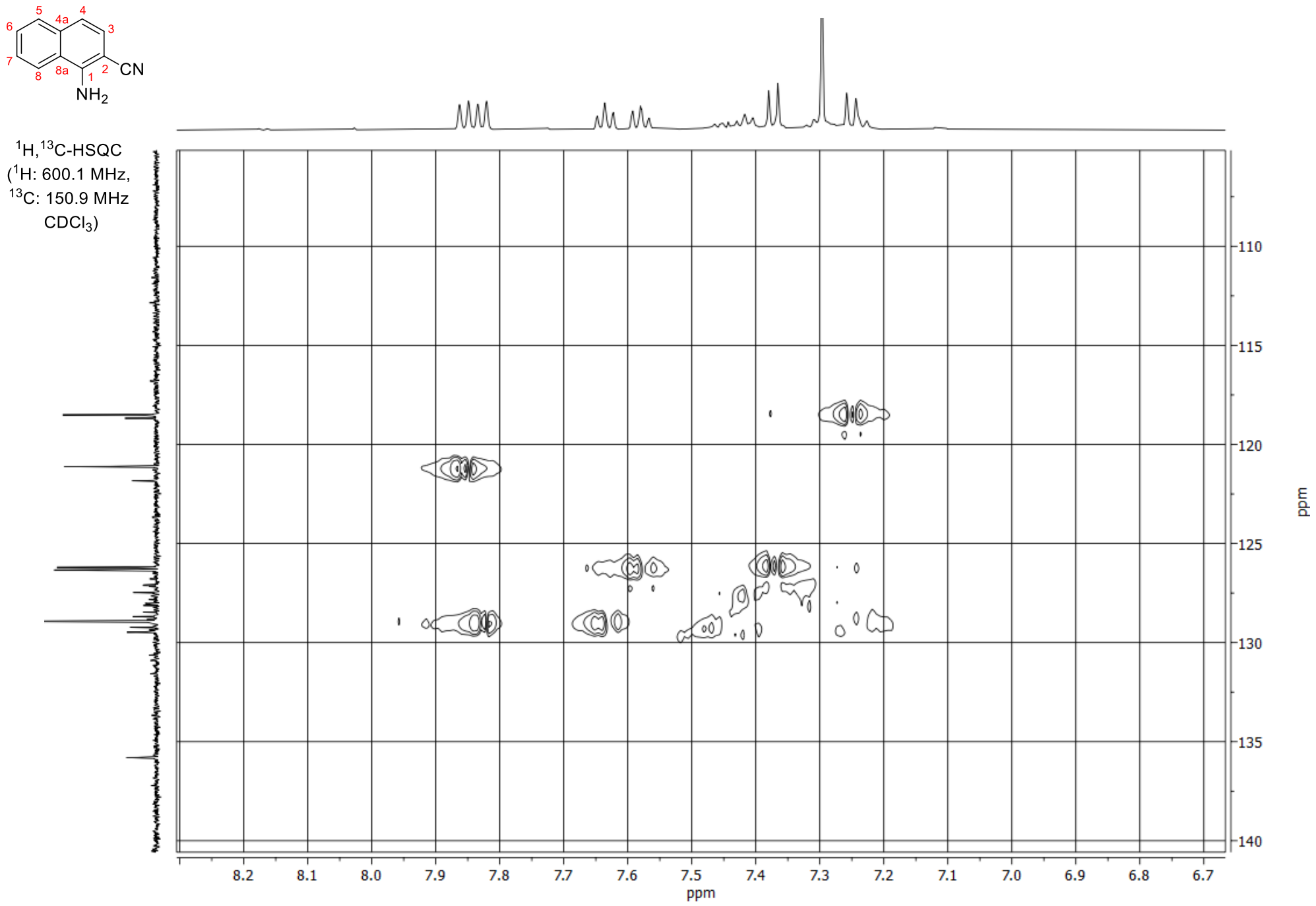
*

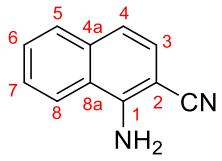


$^{1}H,^{13}C$-HMBC
(^{1}H: 600.1 MHz,
^{13}C: 150.9 MHz
$CDCl_3$)

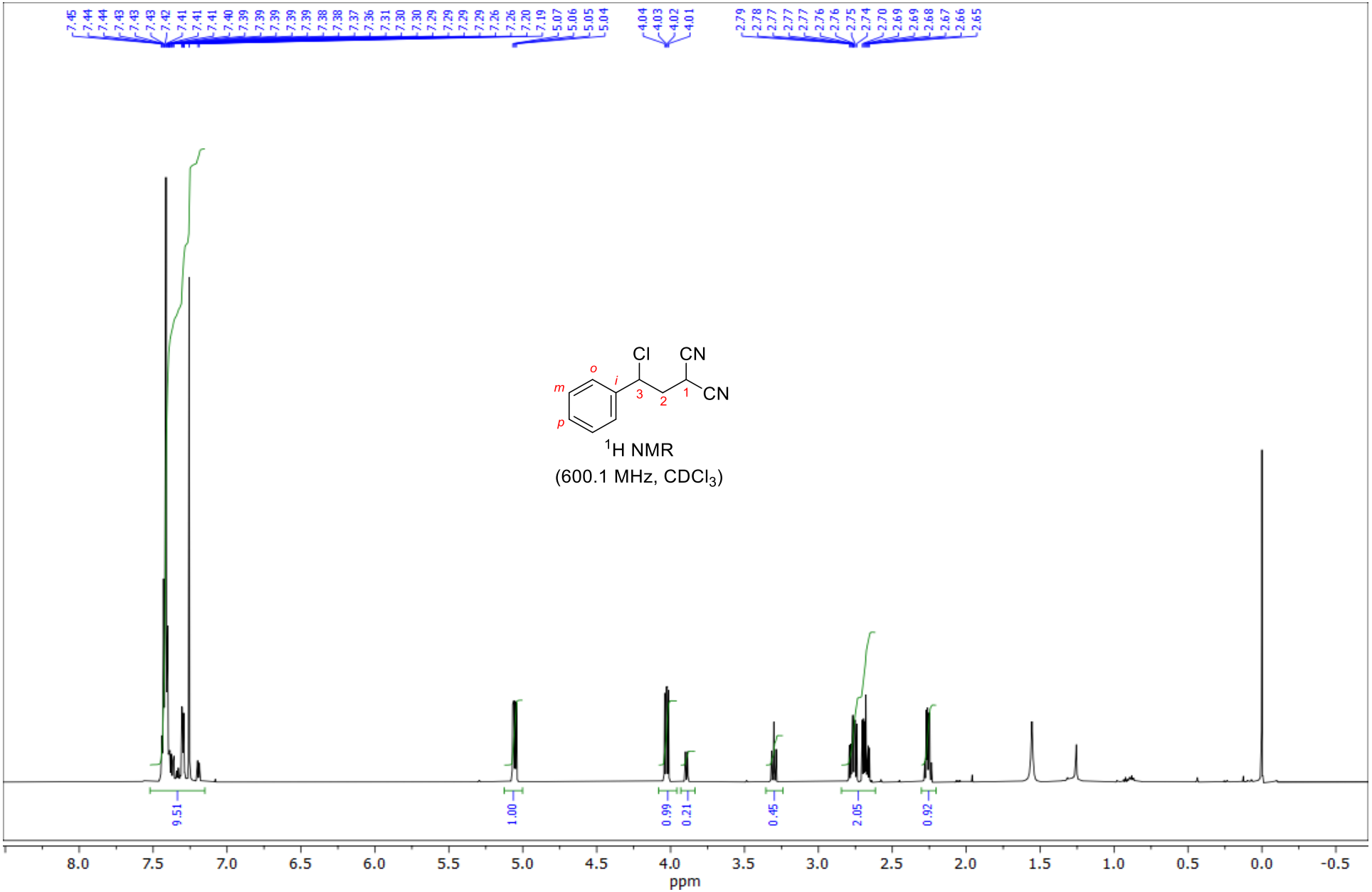

7.86
7.85
7.83
7.82
7.65
7.64
7.62
7.59
7.58
7.57
7.38
7.37
7.26
7.24
5
4a
4
6
3
7
8
8a
1
2
CN
NH2
1H NMR
(600.1 MHz, CDCl3)
0.95
0.99
1.00
1.04
1.37
1.31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

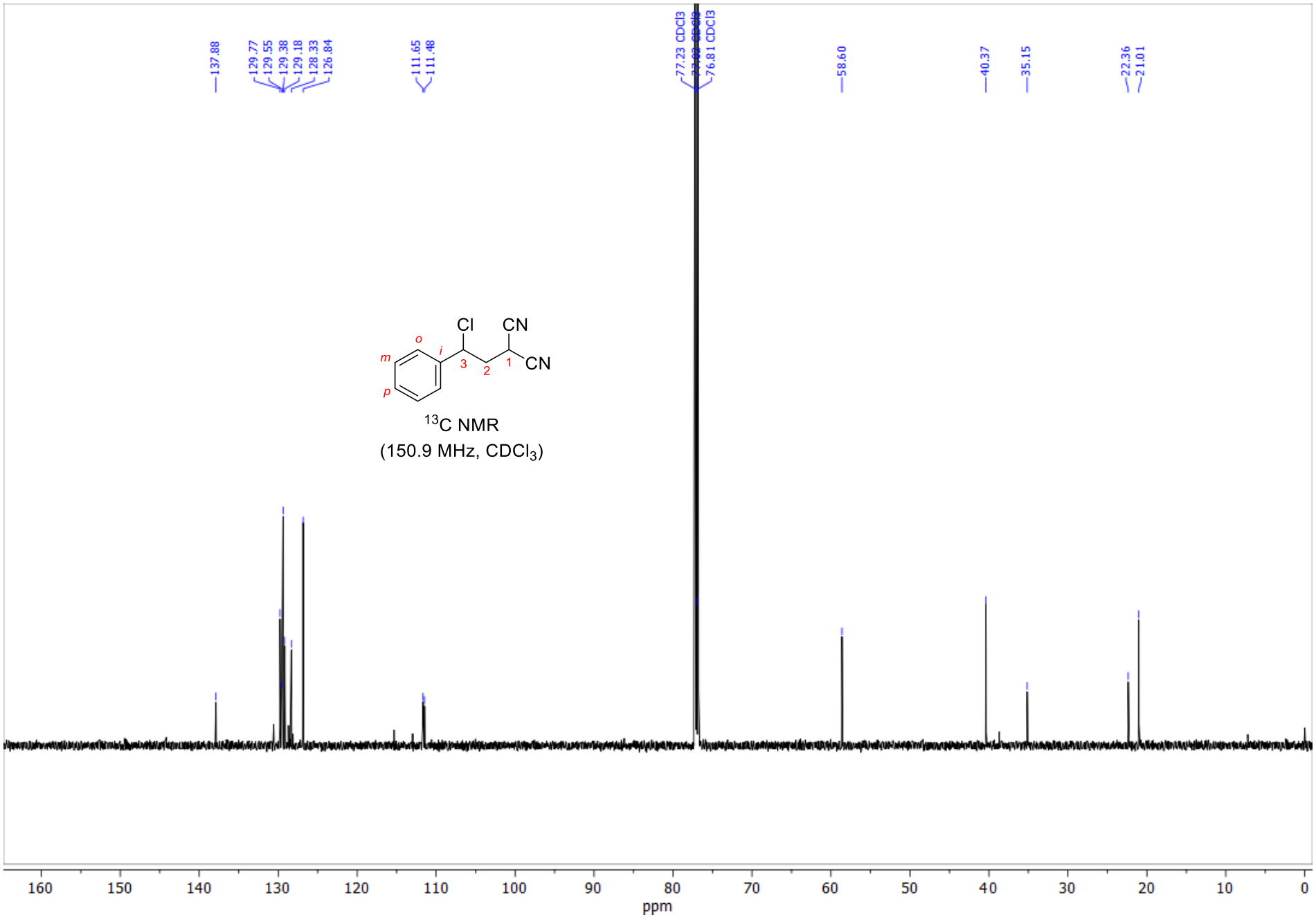

148.23
135.80
128.94
128.92
126.34
126.21
121.83
121.11
118.68
118.51
89.56
77.23 CDCl3
76.81 CDCl3
5
4a
4
6
3
7
8
8a
1
2
CN
NH2
13C NMR
(150.9 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


5
4a
4
6
3
7
2
CN
8
8a
1
NH2
1H,13C-HSQC
(1H: 600.1 MHz,
13C: 150.9 MHz
CDCl3)
110
115
120
125
130
135
140
ppm
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
ppm



$^{1}H,^{13}C$-HMBC
(^{1}H: 600.1 MHz,
^{13}C: 150.9 MHz
$CDCl_3$)


Cl
CN
CN
o
m
i
p
3
2
1
^{1}H NMR
(600.1 MHz, $CDCl_3$)
9.51
1.00
0.99
0.21
0.45
2.05
0.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


137.88
129.77
129.55
129.38
129.18
128.33
126.84
111.65
111.48
77.23 CDCl3
76.81 CDCl3
58.60
40.37
35.15
22.36
21.01
Cl
CN
CN
o
m
p
i
3
2
1
13C NMR
(150.9 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm