Copper(II)-catalyzed iodinations of carbazoles: An access to functionalized carbazoles

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1g – ^{1}H NMR S61

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1i – ^{1}H NMR....S63
1i – ^{13}C {^{1}H} NMR....S64
1b – ^{1}H NMR....S65
1b – ^{13}C {^{1}H} NMR....S66
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1n – ^{1}H NMR....S69
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1o – ^{13}C {1H} NMR....S72
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1q – ^{13}C {^{1}H} NMR....S76
1h – ^{1}H NMR....S77
1h – ^{13}C {^{1}H} NMR....S78
1l – ^{1}H NMR....S79
1k – ^{1}H NMR....S80
1k -^{13}C {^{1}H} NMR....S81
1m – ^{1}H NMR....S82

1. X-ray crystallographic data

Table S1. *Crystal data and structure refinements for complex* $C_{22}H_{23}B_2CuF_8N_5$

Empirical formula	$C_{22}H_{23}B_2CuF_8N_5$
Formula weight	594.61
Colour	Blue-violet
Temperature/K	250.0
Crystal system	Orthorombic
Space group	Pnc2
a/Å	24.37814(4)
b/Å	9.7029(2)
c/Å	17.2544(3)
α/°	90
β/°	90
γ/°	90
Volume/Å3	4081.33
Z	6
ρcalcmg/mm3	1.482
m/mm-1	0.88
F(000)	1842.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.268 to 52.744°
Index ranges	-30 ≤ h ≤ 30, --9 ≤ k ≤ 12, -21 ≤ l ≤ 21
Reflections collected	56025
Independent reflections	8342[Rint = 0.0326, Rsigma = 0.0287]
Data/restraints/parameters	8342/1/528
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R1 = 0.0539, wR2 = 0.1410
Final R indexes [all data]	R1 = 0.0476, wR2 = 0.1328
Largest diff. peak/hole / e Å-3 0.48/-0.44	0.66/-0.44

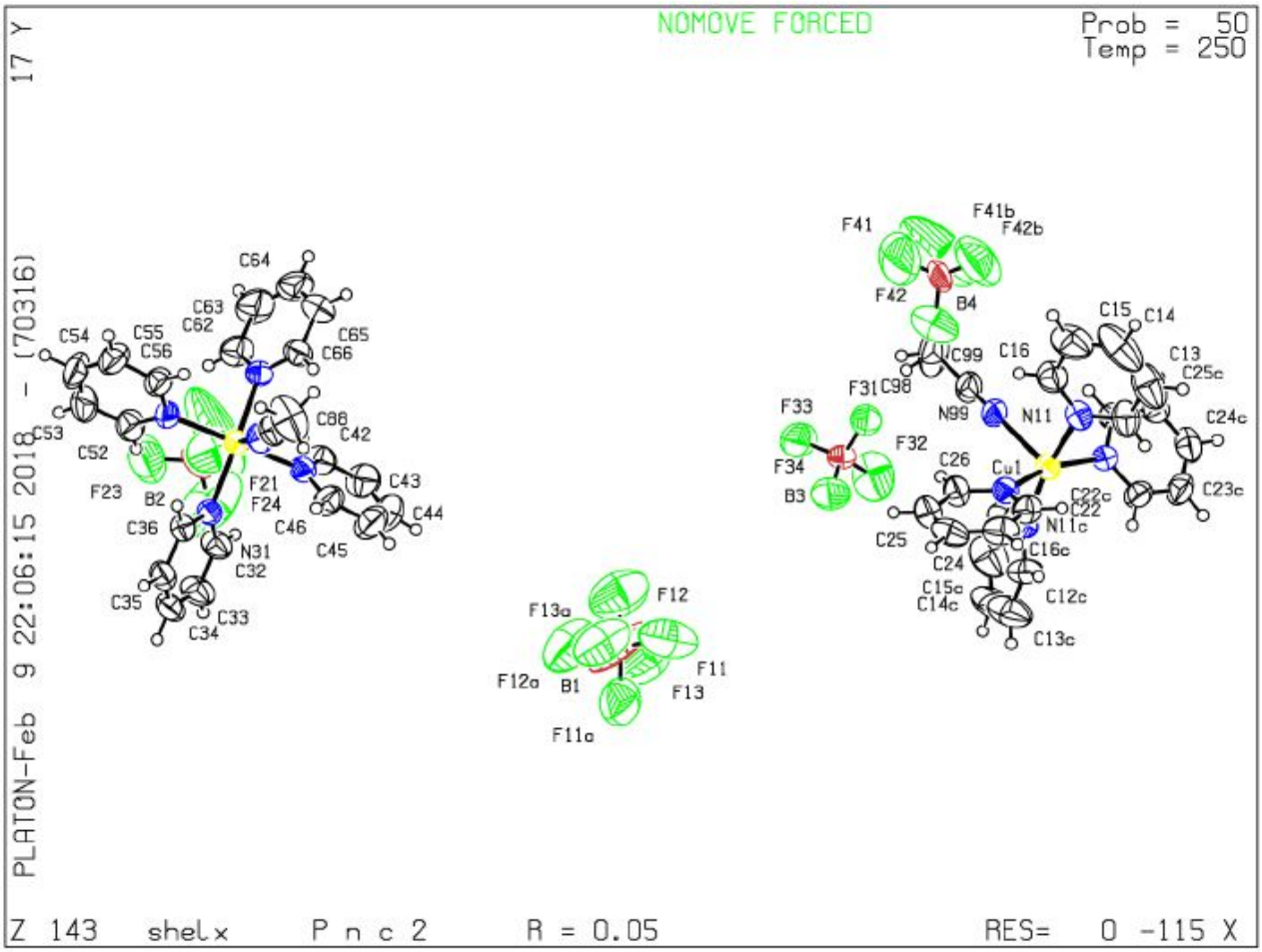


Figure 1. *View of the X-ray crystallographic structure of $C_{22}H_{23}B_2CuF_8N_5$ with 50% probability ellipsoid.*

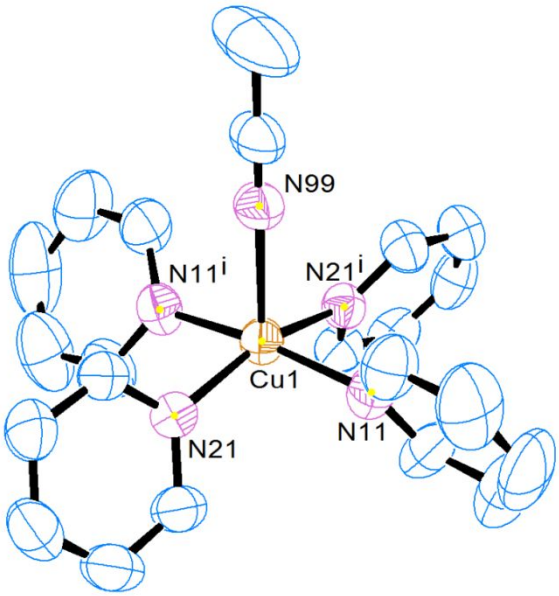


Figure 2. *X-Ray structure of $C_{22}H_{23}B_2CuF_8N_5$ with 50% probability ellipsoids.*

Table S2 *Fractional coordinates and equivalent isotropic atomic displacement parameters (Å2) for complex* $C_{22}H_{23}B_2CuF_8N_5$. *U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.*

	x	y	z	$U_{eq.}$
Cu1	0.0000	0.0000	0.16310(5)	0.0483
N11	-0.0445(2)	0.1744(5)	0.1553(3)	0.0583
C12	-0.0774(3)	0.1988(8)	0.0958(5)	0.0763
H12	-0.0798	0.1310	0.0571	0.0920
C13	-0.1077(4)	0.3132(10)	0.0868(9)	0.1123
H13	-0.1315	0.3245	0.0443	0.1350
C14	-0.1022(4)	0.4117(11)	0.1420(10)	0.1300
H14	-0.1217	0.4949	0.1366	0.1560
C15	-0.0693(4)	0.3937(8)	0.2053(8)	0.1057
H15	-0.0661	0.4620	0.2436	0.1270
C16	-0.0410(3)	0.2708(7)	0.2105(5)	0.0720
H16	-0.0187	0.2545	0.2540	0.0860
N21	0.06896(18)	0.1101(5)	0.1458(3)	0.0493
C22	0.0759(3)	0.1783(6)	0.0790(4)	0.0597
H22	0.0465	0.1822	0.0438	0.0720
C23	0.1236(3)	0.2418(7)	0.0601(4)	0.0713
H23	0.1271	0.2877	0.0124	0.0850
C24	0.1661(3)	0.2387(7)	0.1108(5)	0.0740
H24	0.1997	0.2813	0.0988	0.0890
C25	0.1589(3)	0.1722(8)	0.1795(5)	0.0697
H25	0.1875	0.1690	0.2159	0.0840
C26	0.1098(2)	0.1099(7)	0.1955(4)	0.0603
H26	0.1051	0.0657	0.2435	0.0720
N99	0.0000	0.0000	0.2927(4)	0.0573
C98	0.0000	0.0000	0.4394(8)	0.1953
H98A	-0.0050	-0.0934	0.4582	0.2910
H98B	-0.0297	0.0576	0.4582	0.2910
H98C	0.0347	0.0358	0.4582	0.2910
C99	0.0000	0.0000	0.3550(6)	0.0680
H98A	0.0050	0.0934	0.4582	0.2910
H98B	0.0297	-0.0576	0.4582	0.2910
H98C	-0.0347	-0.0358	0.4582	0.2910
N11	0.0445(2)	-0.1744(5)	0.1553(3)	0.0583
C12	0.0774(3)	-0.1988(8)	0.0958(5)	0.0763
H12	0.0798	-0.1310	0.0571	0.0920
C13	0.1077(4)	-0.3132(10)	0.0868(9)	0.1123
H13	0.1315	-0.3245	0.0443	0.1350

C14	0.1022(4)	-0.4117(11)	0.1420(10)	0.1300
H14	0.1217	-0.4949	0.1366	0.1560
C15	0.0693(4)	-0.3937(8)	0.2053(8)	0.1057
H15	0.0661	-0.4620	0.2436	0.1270
C16	0.0410(3)	-0.2708(7)	0.2105(5)	0.0720
H16	0.0187	-0.2545	0.2540	0.0860
N21	-0.06896(18)	-0.1101(5)	0.1458(3)	0.0493
C22	-0.0759(3)	-0.1783(6)	0.0790(4)	0.0597
H22	-0.0465	-0.1822	0.0438	0.0720
C23	-0.1236(3)	-0.2418(7)	0.0601(4)	0.0713
H23	-0.1271	-0.2877	0.0124	0.0850
C24	-0.1661(3)	-0.2387(7)	0.1108(5)	0.0740
H24	-0.1997	-0.2813	0.0988	0.0890
C25	-0.1589(3)	-0.1722(8)	0.1795(5)	0.0697
H25	-0.1875	-0.1690	0.2159	0.0840
C26	-0.1098(2)	-0.1099(7)	0.1955(4)	0.0603
H26	-0.1051	-0.0657	0.2435	0.0720
Cu2	0.67061(2)	0.15354(6)	0.99730(5)	0.0463
N31	0.73854(18)	0.0687(4)	0.9513(3)	0.0473
C32	0.7411(3)	-0.0679(6)	0.9359(4)	0.0643
H32	0.7100	-0.1227	0.9453	0.0780
C33	0.7866(3)	-0.1275(7)	0.9078(6)	0.0780
H33	0.7867	-0.2226	0.8976	0.0940
C34	0.8324(2)	-0.0520(8)	0.8938(5)	0.0677
H34	0.8642	-0.0938	0.8740	0.0820
C35	0.8312(2)	0.0846(7)	0.9089(4)	0.0610
H35	0.8623	0.1396	0.8997	0.0730
C36	0.7832(2)	0.1426(5)	0.9383(3)	0.0500
H36	0.7826	0.2375	0.9493	0.0600
N41	0.62477(18)	0.0565(5)	0.9166(3)	0.0527
C42	0.5888(3)	-0.0434(7)	0.9374(5)	0.0650
H42	0.5832	-0.0605	0.9905	0.0780
C43	0.5610(4)	-0.1187(8)	0.8856(6)	0.0850
H43	0.5355	-0.1854	0.9019	0.1020
C44	0.5703(4)	-0.0970(11)	0.8099(7)	0.1063
H44	0.5528	-0.1524	0.7726	0.1280
C45	0.6048(4)	0.0041(10)	0.7870(5)	0.0953
H45	0.6098	0.0237	0.7341	0.1140
C46	0.6320(3)	0.0769(8)	0.8421(4)	0.0713
H46	0.6572	0.1448	0.8263	0.0850

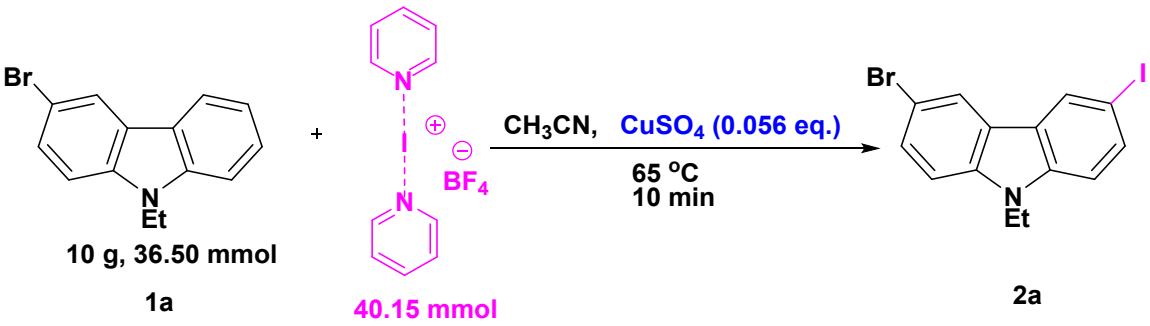
N51	0.71479(19)	0.2265(5)	1.0875(3)	0.0523
C52	0.7426(3)	0.1422(7)	1.1336(4)	0.0693
H52	0.7443	0.0482	1.1207	0.0830
C53	0.7690(4)	0.1862(10)	1.1989(5)	0.0873
H53	0.7886	0.1239	sty.00	0.1050
C54	0.7663(4)	0.3203(11)	1.2177(4)	0.0927
H54	0.7838	0.3527	sty.27	0.1110
C55	0.7378(3)	0.4103(8)	1.1710(4)	0.0793
H55	0.7356	0.5045	1.1835	0.0950
C56	0.7130(3)	0.3601(6)	1.1066(4)	0.0617
H56	0.6939	0.4213	1.0741	0.0740
N61	0.60136(19)	0.1990(5)	1.0561(3)	0.0503
C62	0.5938(4)	0.1420(8)	1.1254(4)	0.0727
H62	0.6221	0.0906	1.1485	0.0870
C63	0.5442(4)	0.1584(11)	1.1631(5)	0.1033
H63	0.5396	0.1195	sty.26	0.1240
C64	0.5036(4)	0.2265(15)	1.1319(6)	0.1080
H64	0.4695	0.2325	1.1572	0.1300
C65	0.5118(3)	0.2910(10)	1.0595(6)	0.0883
H65	0.4842	0.3444	1.0361	0.1060
C66	0.5622(2)	0.2722(7)	1.0246(4)	0.0627
H66	0.5686	0.3136	0.9762	0.0750
N89	0.6739(2)	0.3506(5)	0.9264(3)	0.0560
C88	0.6660(4)	0.5882(9)	0.8602(8)	0.1063
H88A	0.6891	0.6540	0.8872	0.1590
H88B	0.6281	0.6184	0.8626	0.1590
H88C	0.6775	0.5821	0.8064	0.1590
C89	0.6711(2)	0.4532(7)	0.8967(4)	0.0580
B1	0.5000	0.0000	0.3587(8)	0.2030
F11	0.4638(5)	0.0696(10)	0.3022(6)	0.1830
F12	0.4636(6)	0.0377(11)	0.4229(6)	0.2043
F13	0.4715(6)	-0.1241(11)	0.3512(6)	0.1960
F11	0.5362(5)	-0.0696(10)	0.3022(6)	0.1830
F12	0.5364(6)	-0.0377(11)	0.4229(6)	0.2043
F13	0.5285(6)	0.1241(11)	0.3512(6)	0.1960
B2	0.6654(3)	-0.2340(9)	1.1145(6)	0.0737
F21	0.6230(4)	-0.265(3)	1.1454(13)	0.3833
F22	0.6631(4)	-0.1102(8)	1.0813(5)	0.1420
F23	0.7050(3)	-0.2383(10)	1.1719(6)	0.1643
F24	0.6798(8)	-0.3198(9)	1.0658(9)	0.2963

B3	0.1623(3)	0.0014(6)	0.3902(4)	0.0517
F31	0.12665(19)	0.1110(4)	0.3866(3)	0.0820
F32	0.1367(3)	-0.1131(5)	0.3611(5)	0.1400
F33	0.1815(3)	-0.0167(6)	0.4630(3)	0.1010
F34	0.2057(2)	0.0323(7)	0.3433(3)	0.1043
B4	0.0000	0.5000	0.4051(8)	0.0857
F41	0.0265(5)	0.5555(19)	0.4553(12)	0.3320
F42	0.0329(3)	0.4207(13)	0.3649(7)	0.1977
F41	-0.0265(5)	0.4445(19)	0.4553(12)	0.3320
F42	-0.0329(3)	0.5793(13)	0.3649(7)	0.1977

Table S3. *Selected angles for complex* $C_{22}H_{23}B_2CuF_8N_5$

Cu1-N11-C12	121.9
Cu1-N11-C-16	120.4
C12-N11-C16	117.8(6)
N11-C12-H12	117.6
N11-C12-C13	124.8(8)
H12-C12-C13	117.6
C12-C13-H13	122
C12-C13-C14	117(1)
H13-C13-C14	122
N11-C16-C15	121.7(7)
N11-C16-H16	119.2
Cu1-N21-C22	119.7
Cu1-N21-C26	122.3
C22-N21-C26	117.8(5)

2. Gram-scale synthesis



3. Isolation of copper(II) complex $Cu^{II}Py_4(CH_3CN)(BF_4)_2$

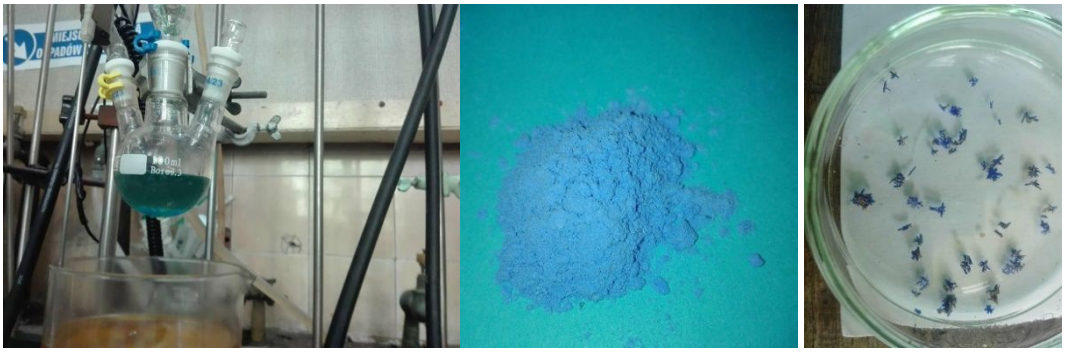
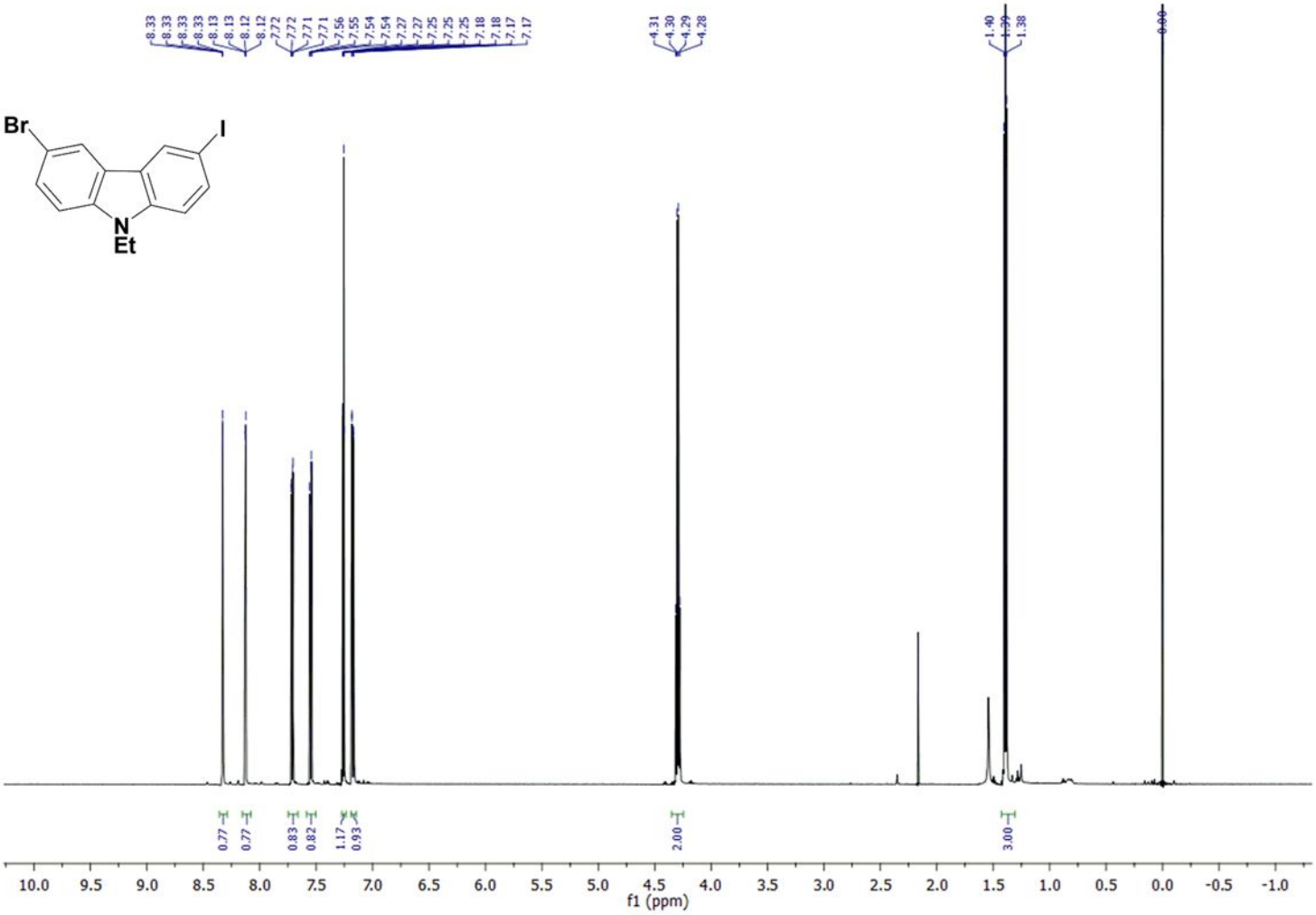


Figure 3. Isolation of copper(II) complex $Cu^{II}Py_4(CH_3CN)(BF_4)_2$

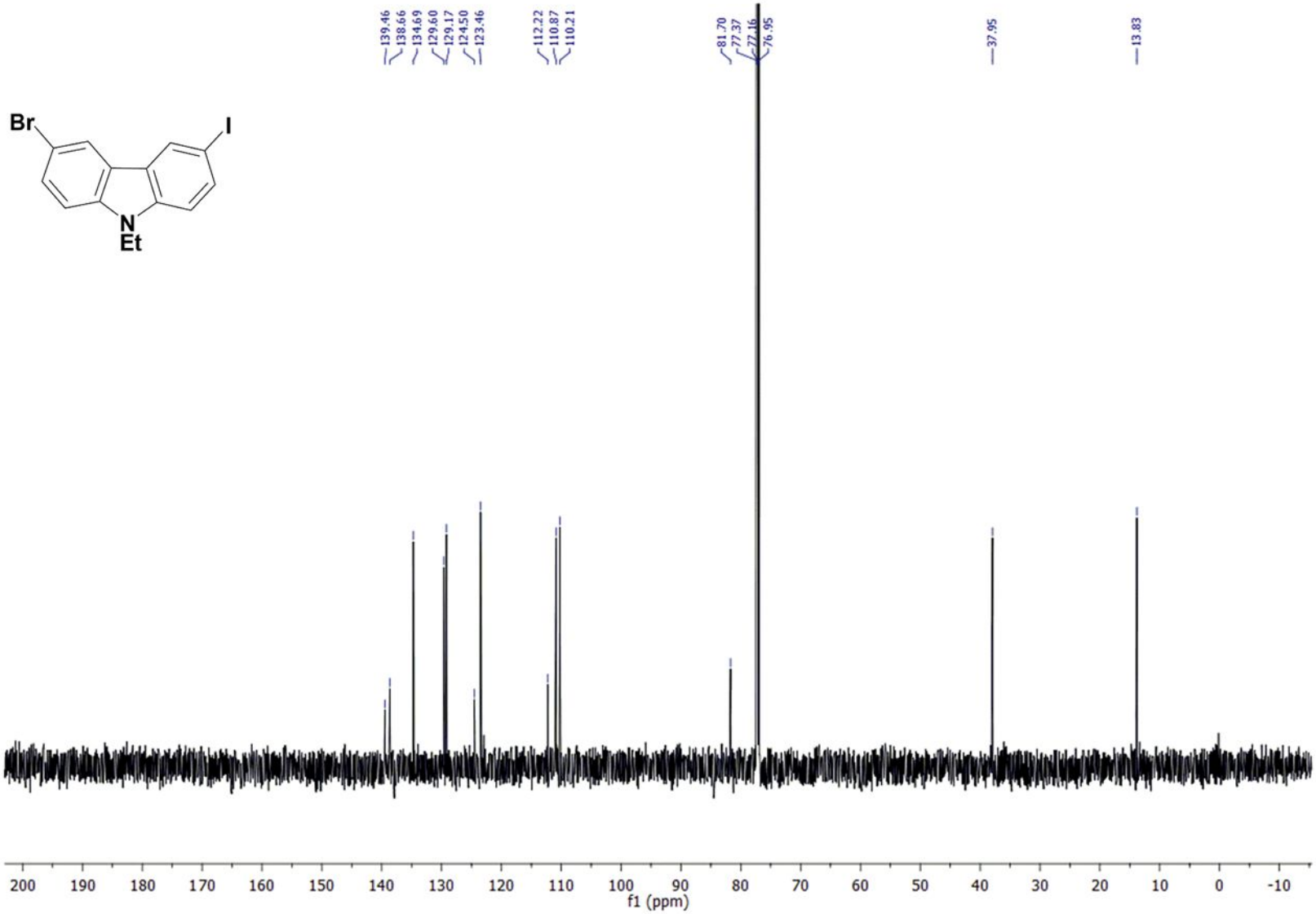
Caution: *X-ray analysis should be performed immediately at nitrogen inlet, because direct oxidation of the metal in the air leads to mixture of cuprous and cupric product.*

4. Copies of NMR spectra

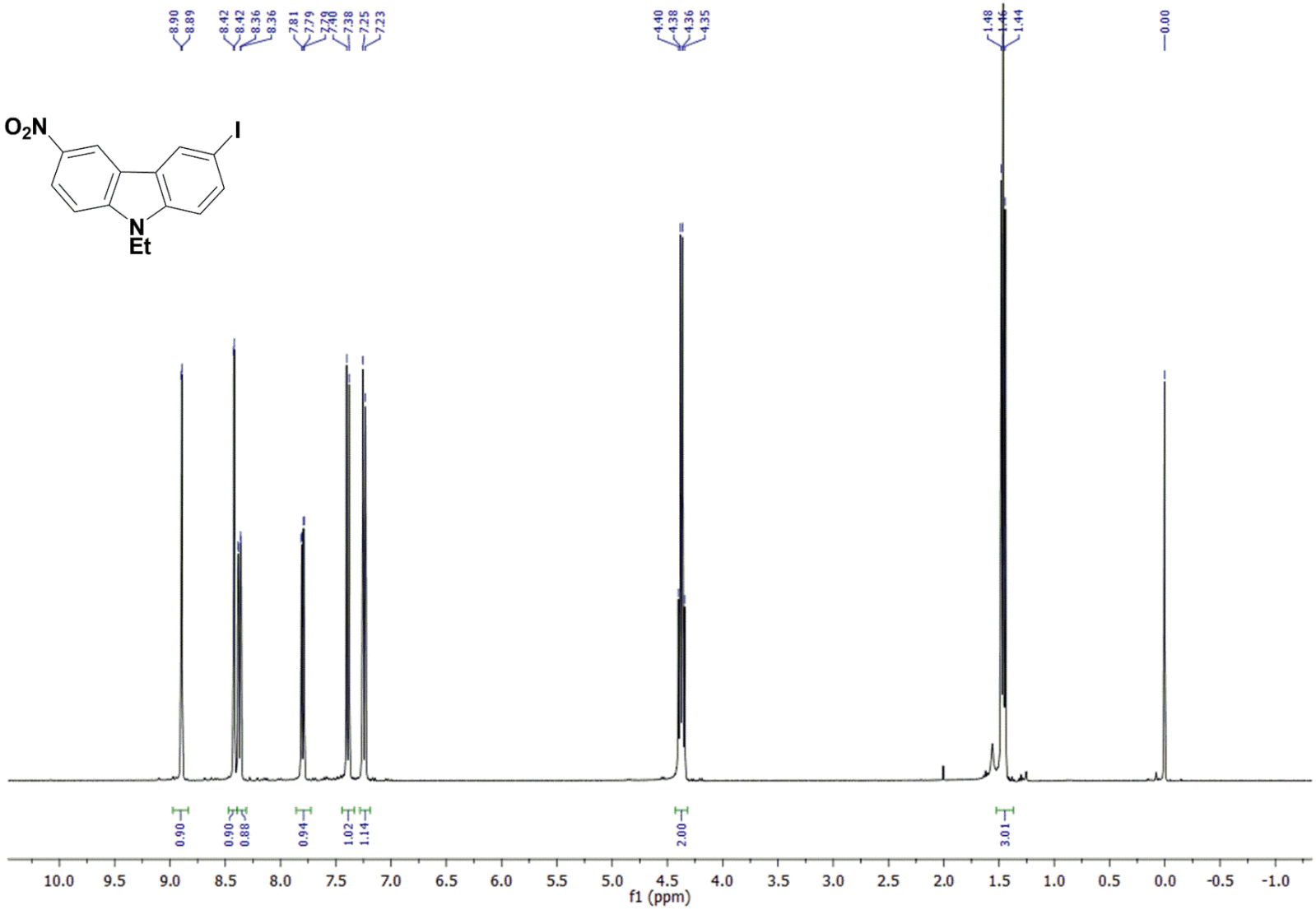
2a -^{1}H NMR



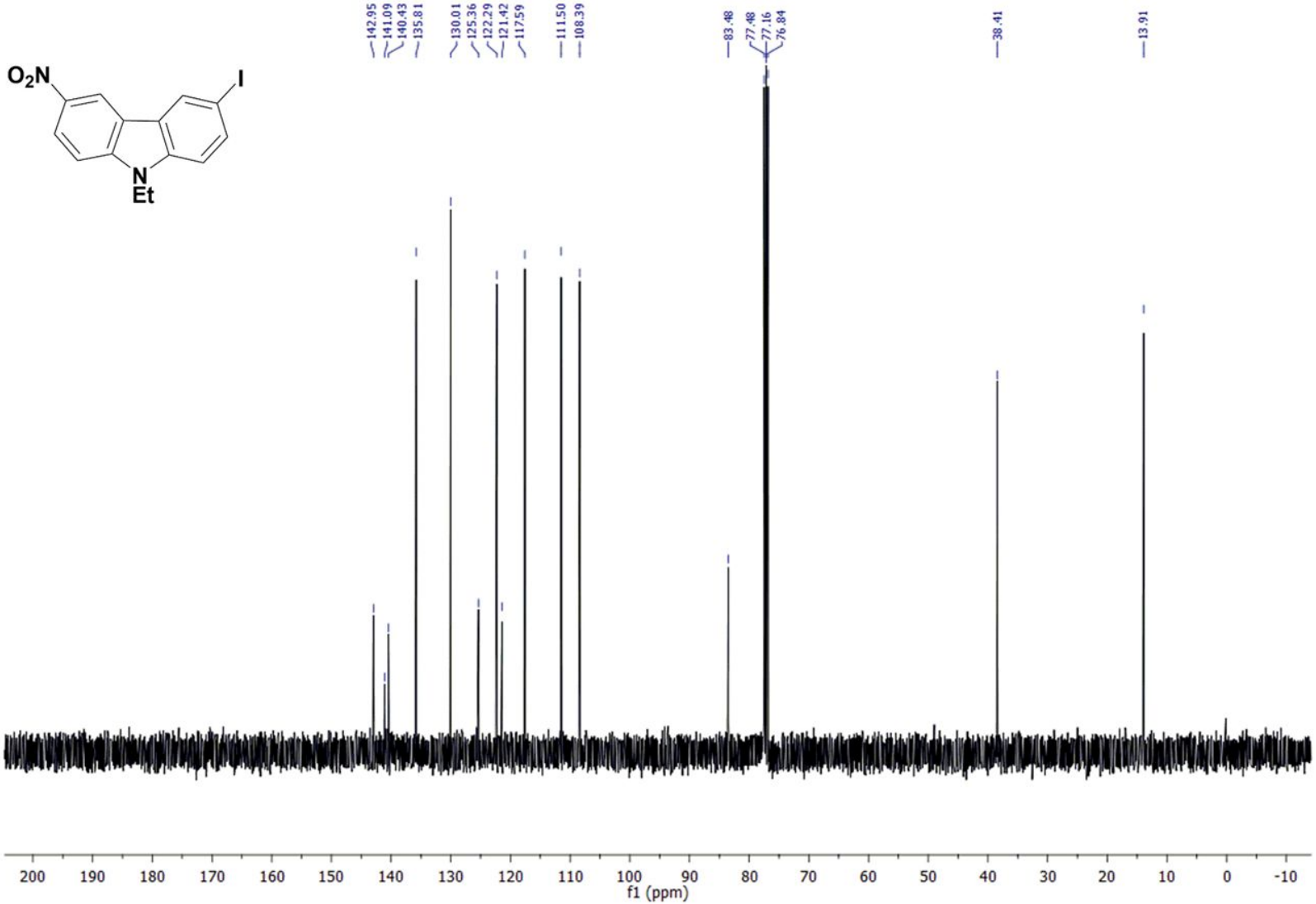
2a -$^{13}C\{^{1}H\}$ NMR


139.46
138.66
134.69
129.60
129.17
124.50
123.46
112.22
110.87
110.21
81.70
77.37
77.16
76.95
37.95
13.83
Br
I
N
Et
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2b -^{1}H NMR


8.90
8.89
8.42
8.42
8.36
8.36
7.81
7.79
7.40
7.38
7.25
7.23
4.40
4.38
4.36
4.35
1.48
1.46
1.44
0.00
O2N
I
N
Et
0.90
0.90
0.88
0.94
1.02
1.14
2.00
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

2b -$^{13}C\{^{1}H\}$ NMR


O2N
I
N
Et
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141.09
140.43
135.81
130.01
125.36
122.29
121.42
117.59
111.50
108.39
83.48
77.48
77.16
76.84
38.41
13.91
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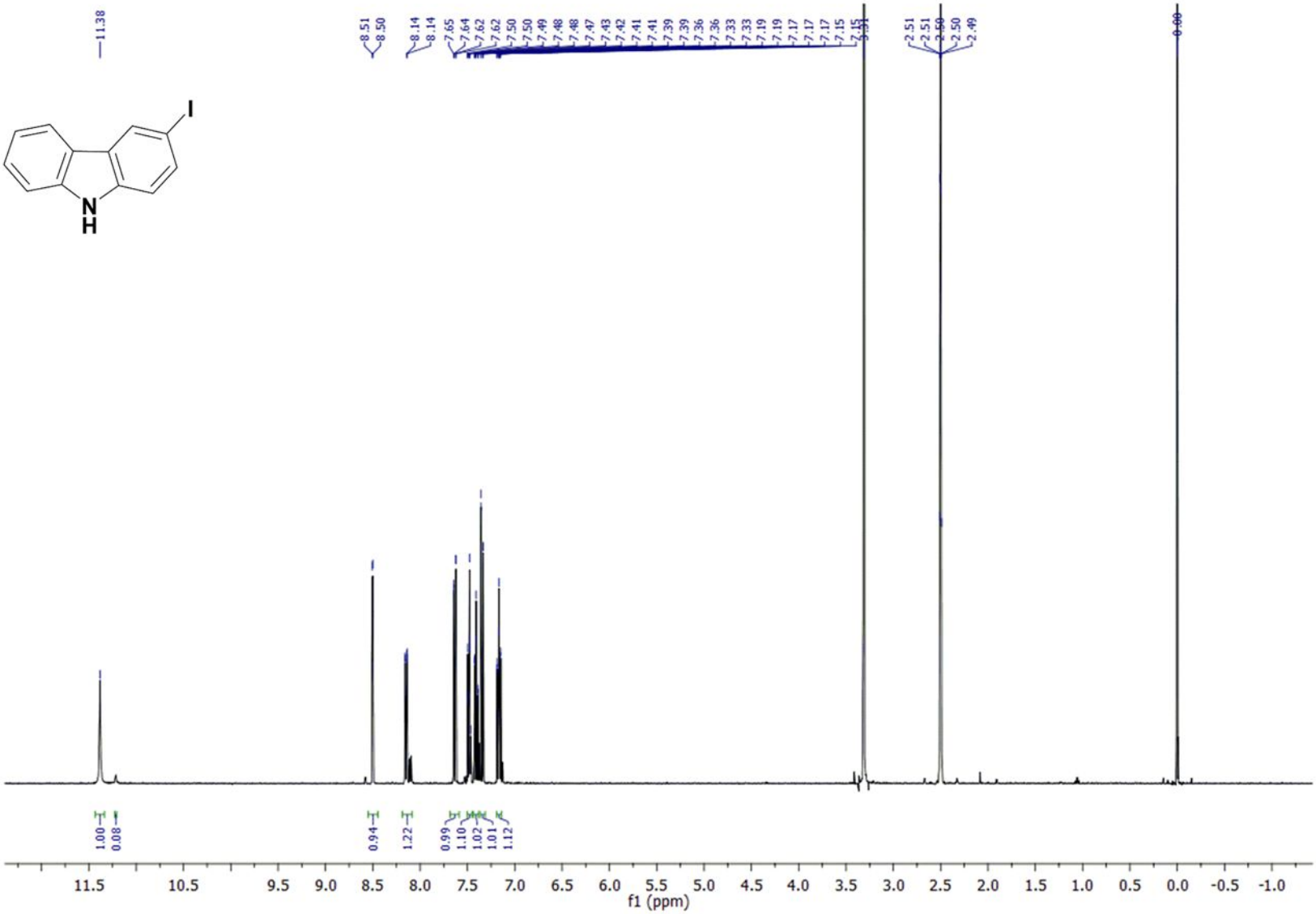
f1 (ppm)

2c - ^{1}H NMR


11.38
8.51
8.50
8.14
8.14
7.65
7.64
7.62
7.62
7.50
7.50
7.49
7.48
7.48
7.47
7.43
7.42
7.41
7.41
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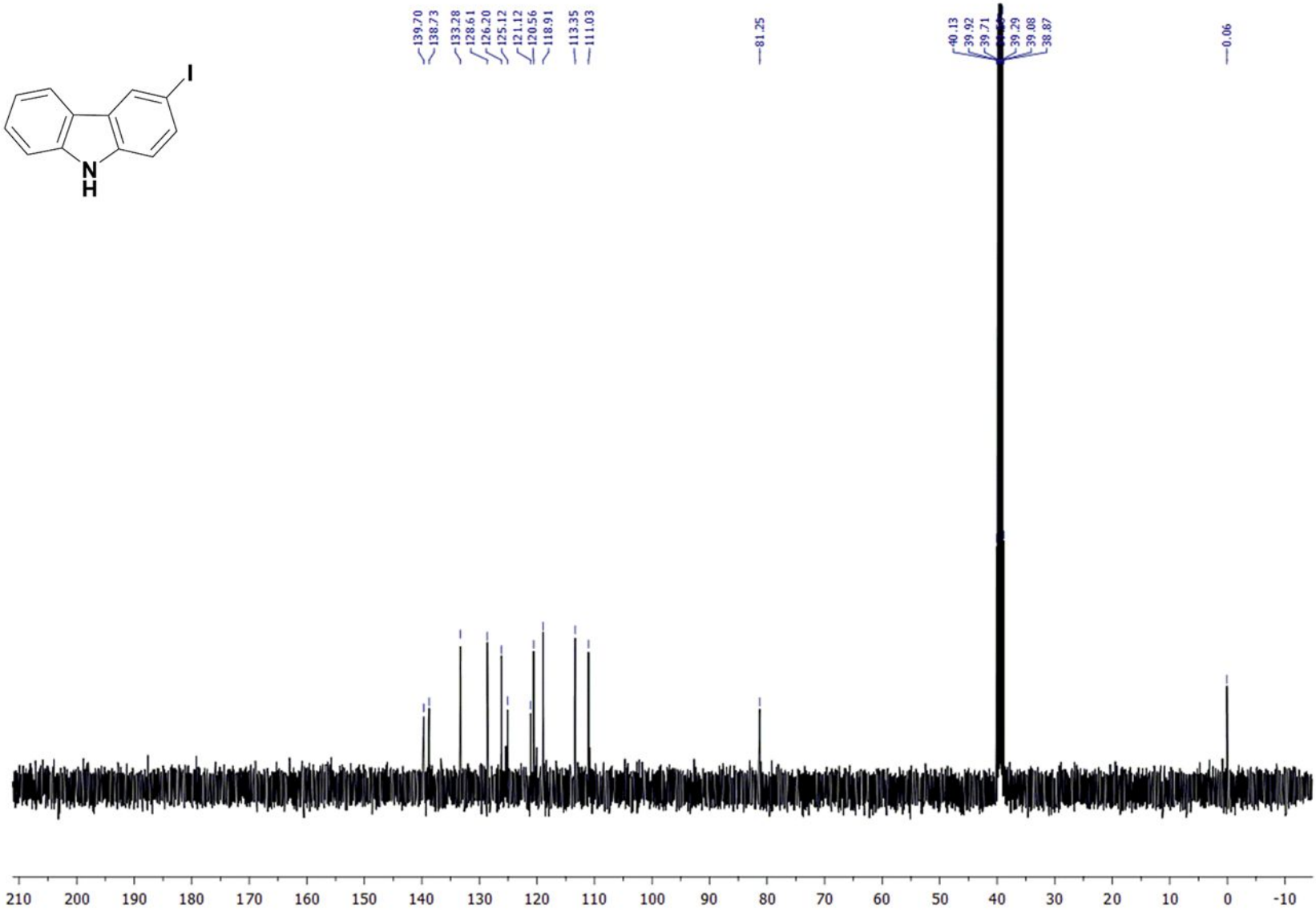
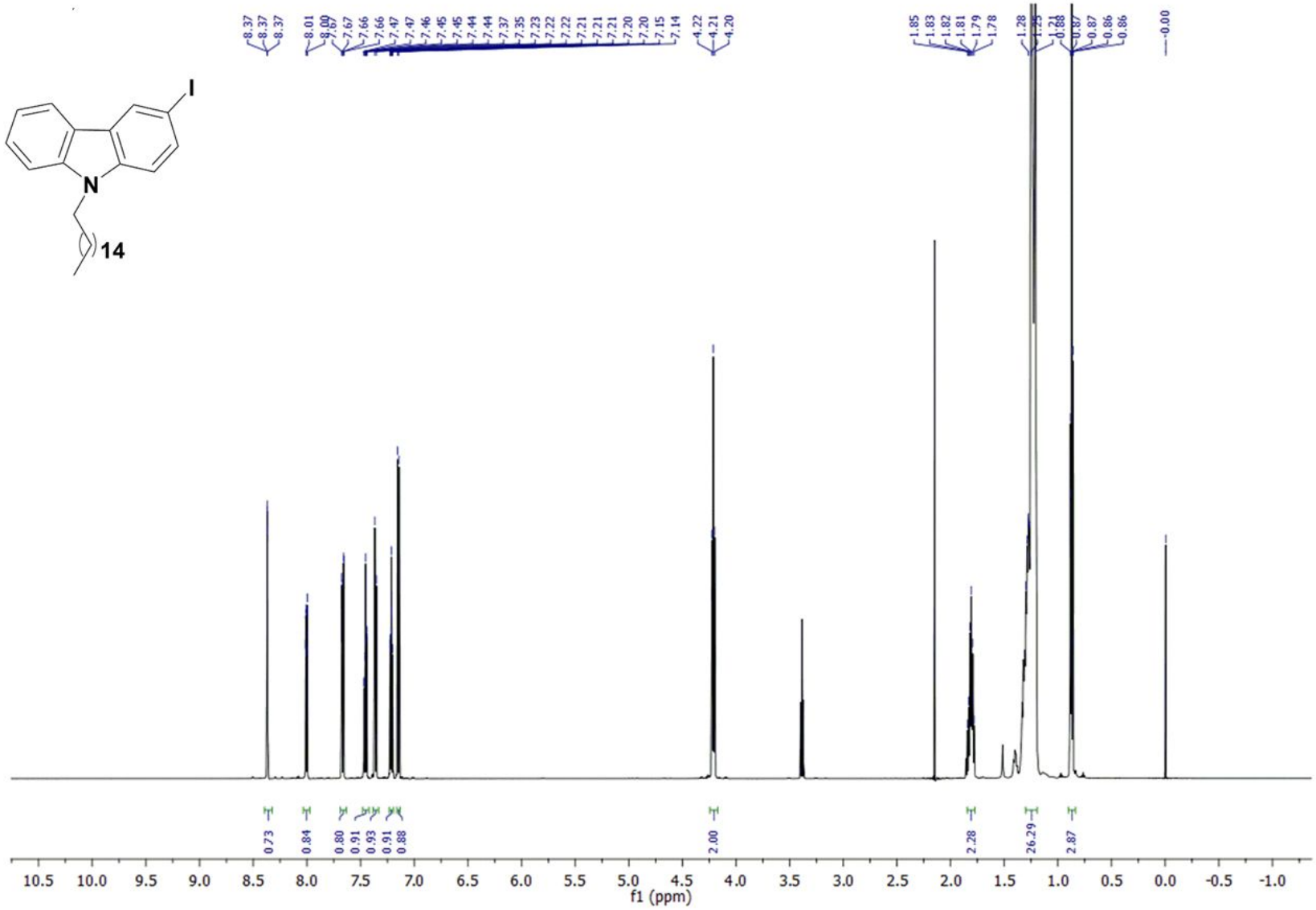
7.17
7.17
7.15
7.15
2.51
2.51
2.50
2.50
2.49
0.00
I
N
H
1.00
0.08
0.94
1.22
0.99
1.10
1.02
1.01
1.12
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

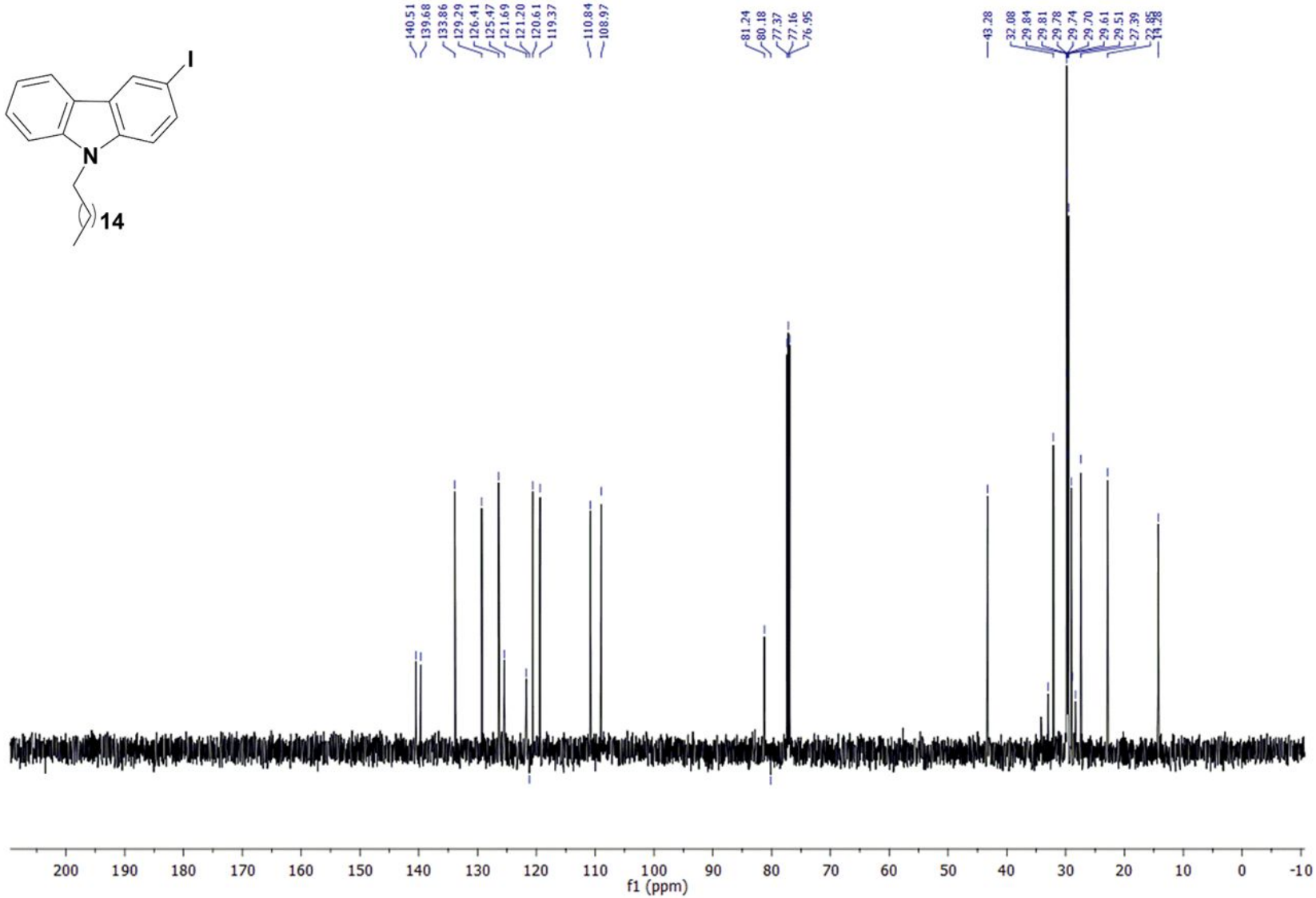
2c -$^{13}C\{^{1}H\}$ NMR


I
N
H
139.70
138.73
133.28
128.61
126.20
125.12
121.12
120.56
118.91
113.35
111.03
81.25
40.13
39.92
39.71
39.29
39.08
38.87
0.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

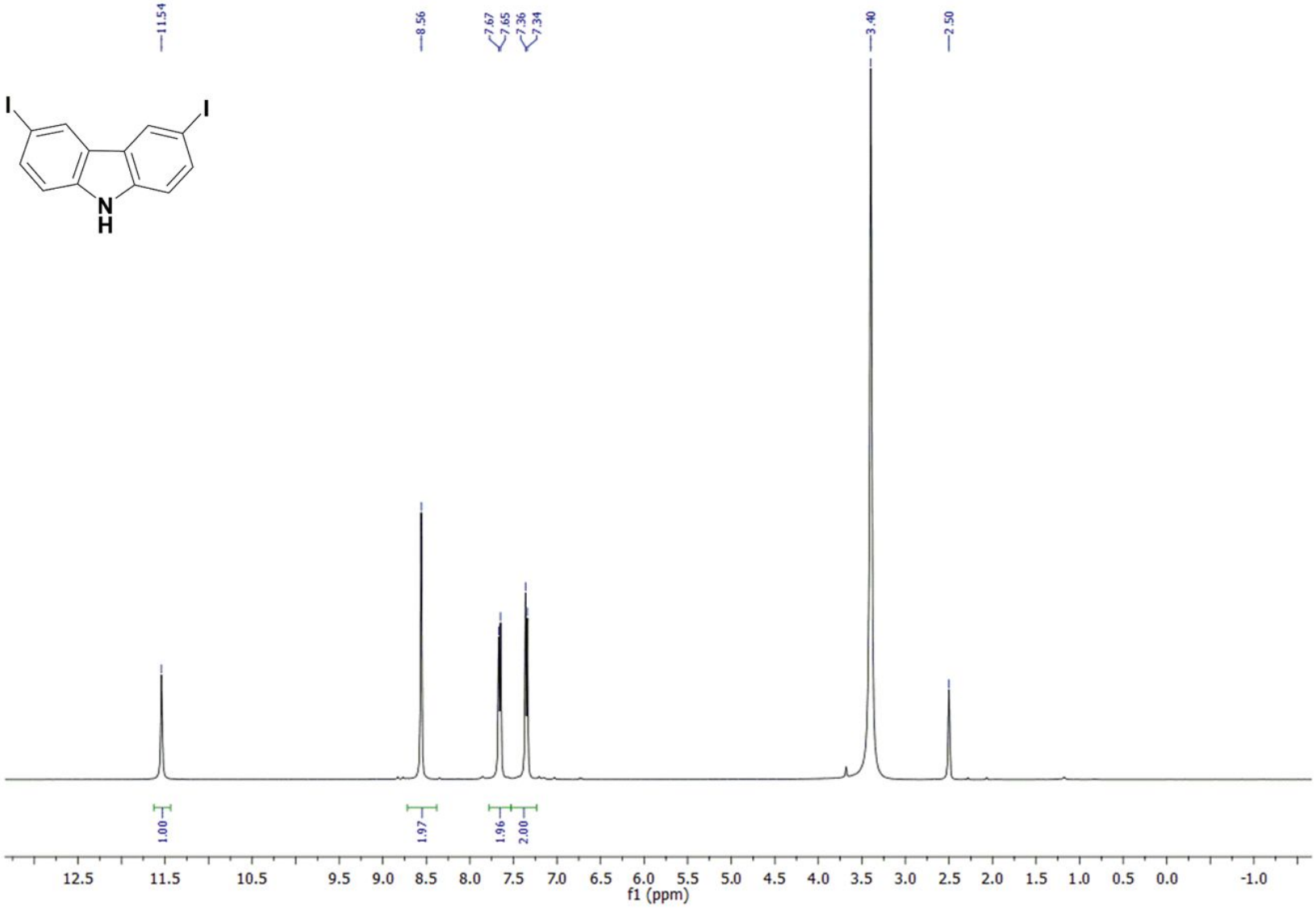
2d - ^{1}H NMR



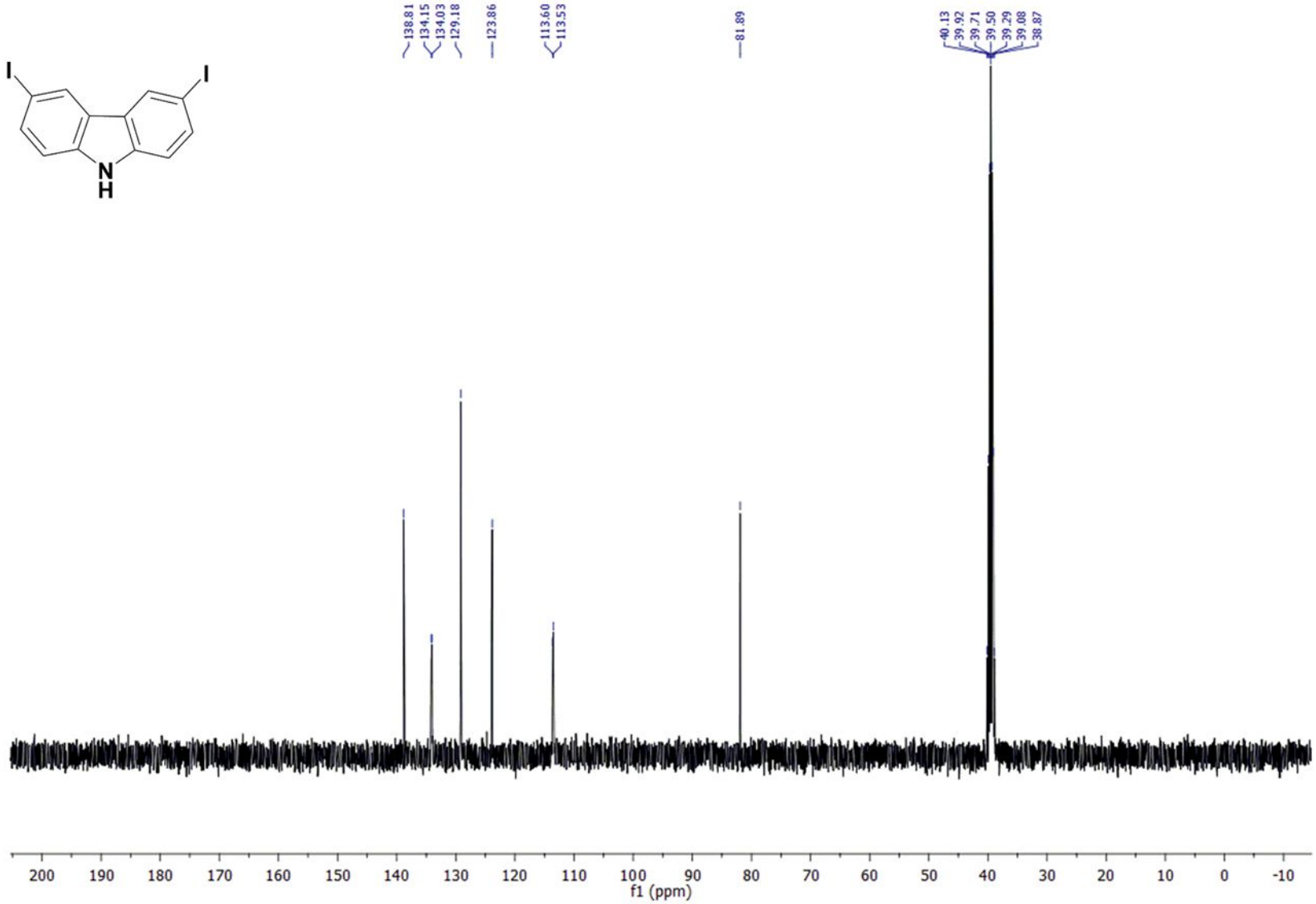
2d -$^{13}C\{^{1}H\}$ NMR


I
N
14
140.51
139.68
133.86
129.29
126.41
125.47
121.69
121.20
120.61
119.37
110.84
108.97
81.24
80.18
77.37
77.16
76.95
43.28
32.08
29.84
29.81
29.78
29.74
29.70
29.61
29.51
27.39
14.28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

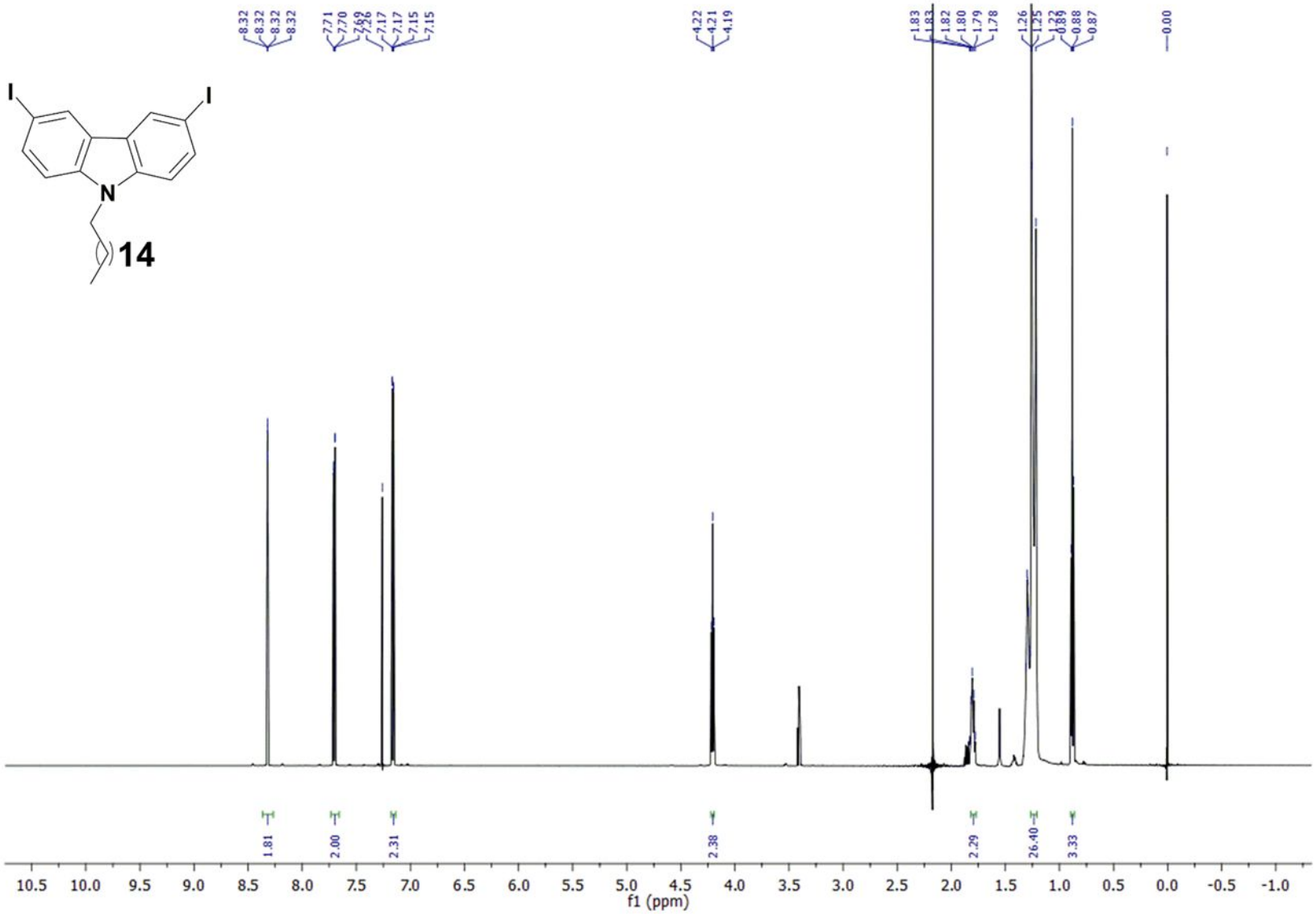
2e -^{1}H NMR


11.54
8.56
7.67
7.65
7.36
7.34
3.40
2.50
I
I
N
H
1.00
1.97
1.96
2.00
12.5
11.5
10.5
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
-1.0
f1 (ppm)

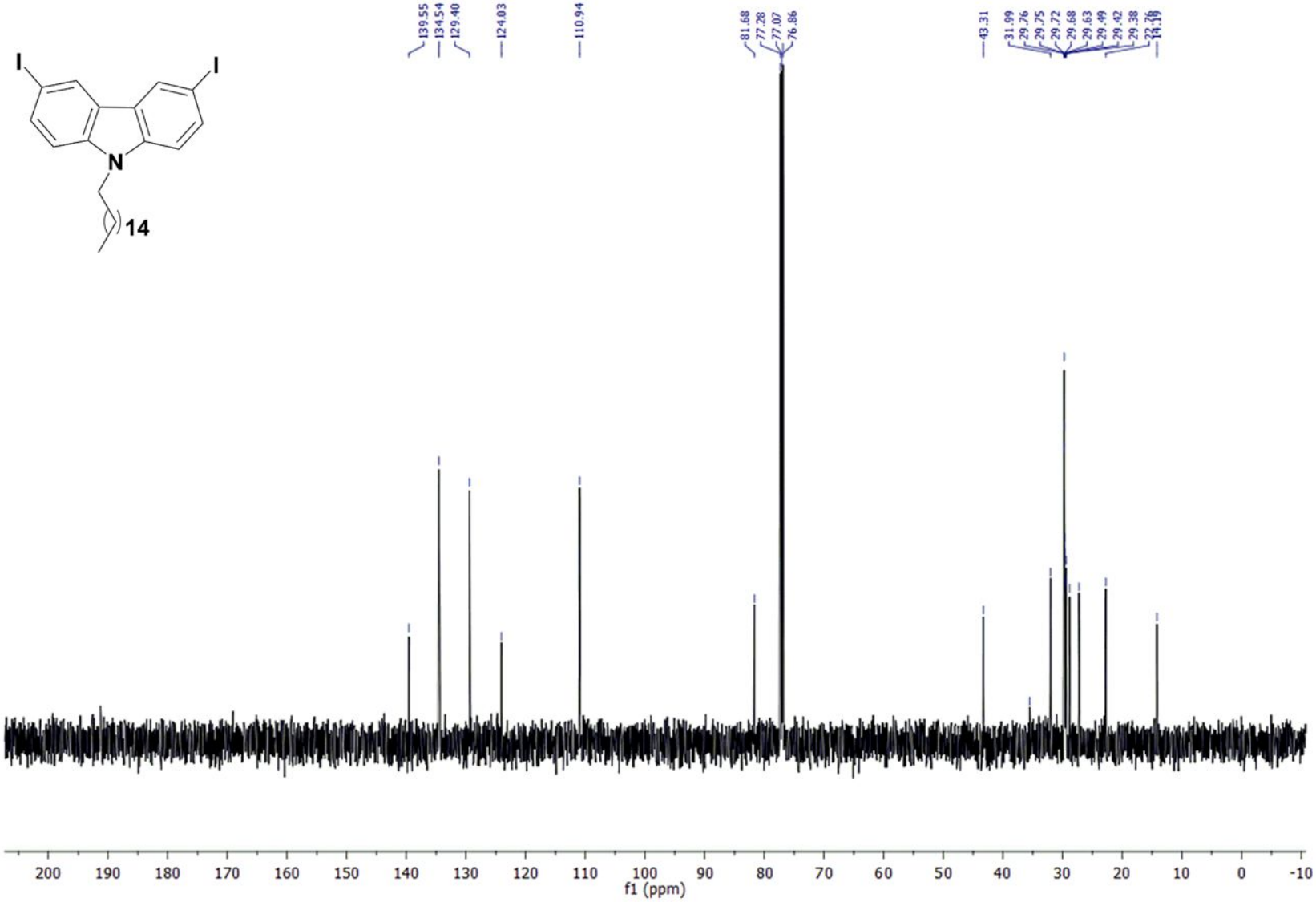
2e -$^{13}C\{^{1}H\}$ NMR


138.81
134.15
134.03
129.18
123.86
113.60
113.53
81.89
40.13
39.92
39.71
39.50
39.29
39.08
38.87
I
I
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

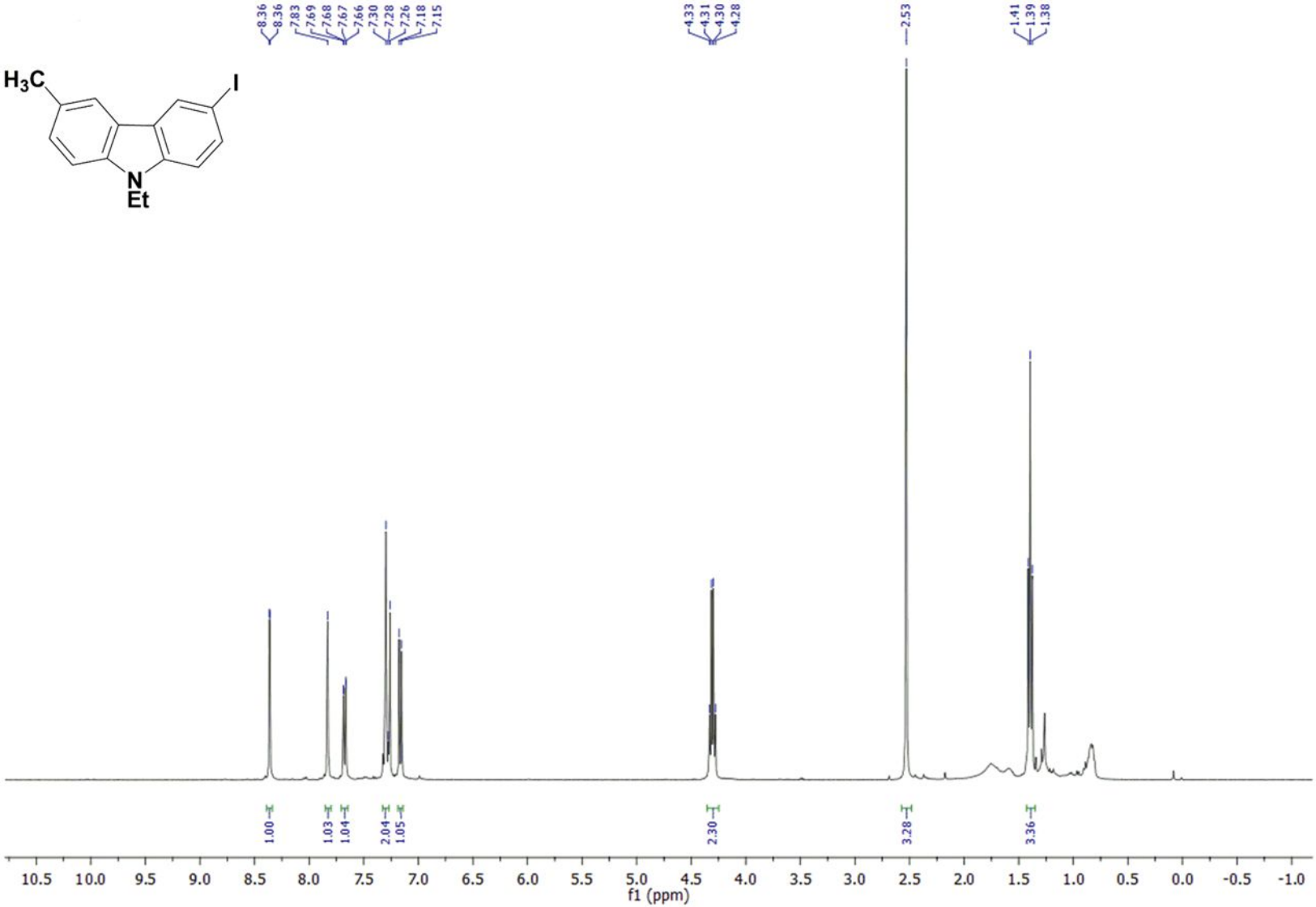
2f -^{1}H NMR


I
I
N
14
8.32
8.32
8.32
8.32
7.71
7.70
7.17
7.17
7.15
7.15
4.22
4.21
4.19
1.83
1.83
1.82
1.80
1.79
1.78
1.26
1.25
0.88
0.87
0.00
1.81
2.00
2.31
2.38
2.29
26.40
3.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

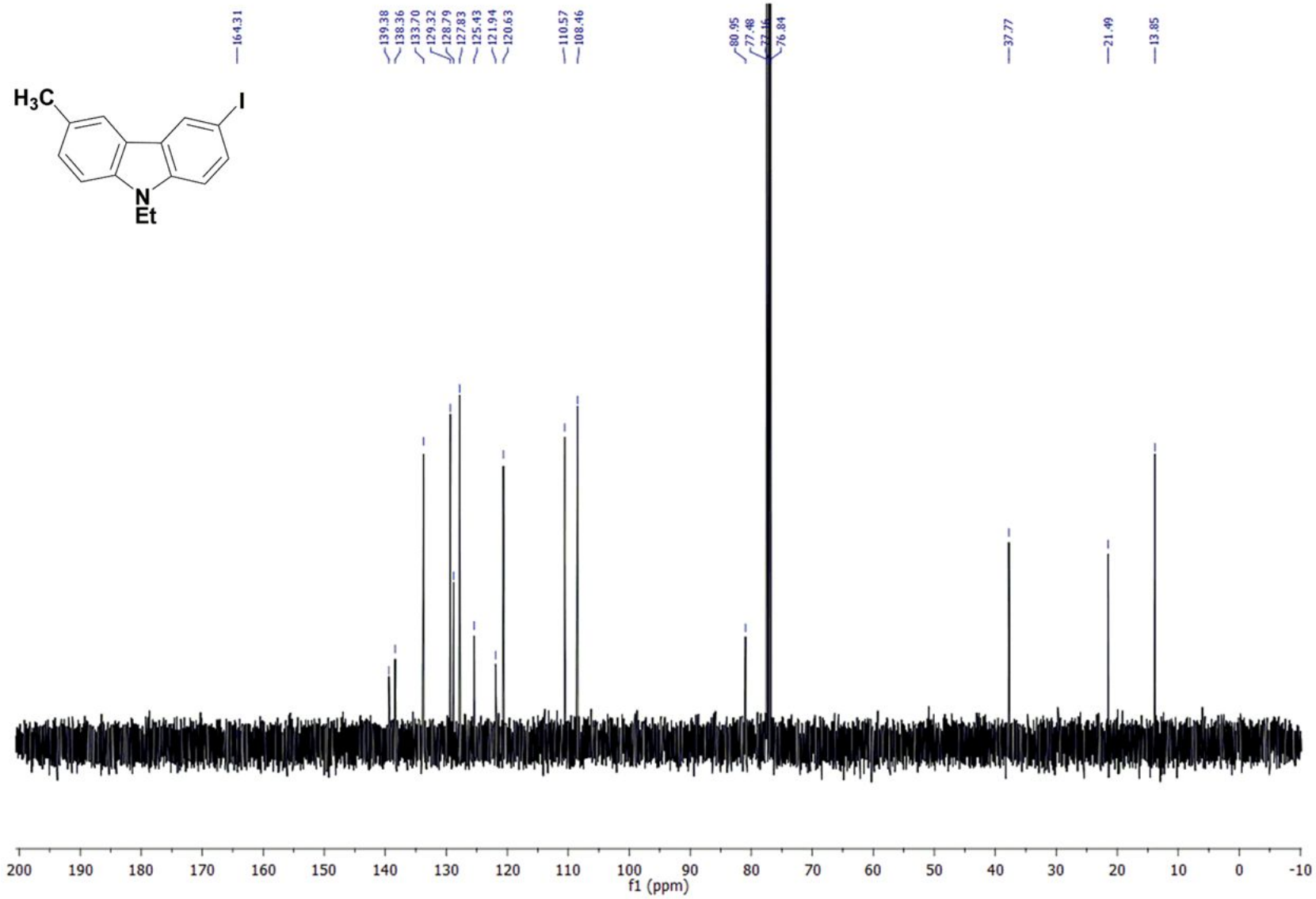
2f -$^{13}C\{^{1}H\}$ NMR


I
I
N
14
139.55
134.54
129.40
124.03
110.94
81.68
77.28
77.07
76.86
43.31
31.99
29.76
29.75
29.72
29.68
29.63
29.49
29.42
29.38
23.78
14.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

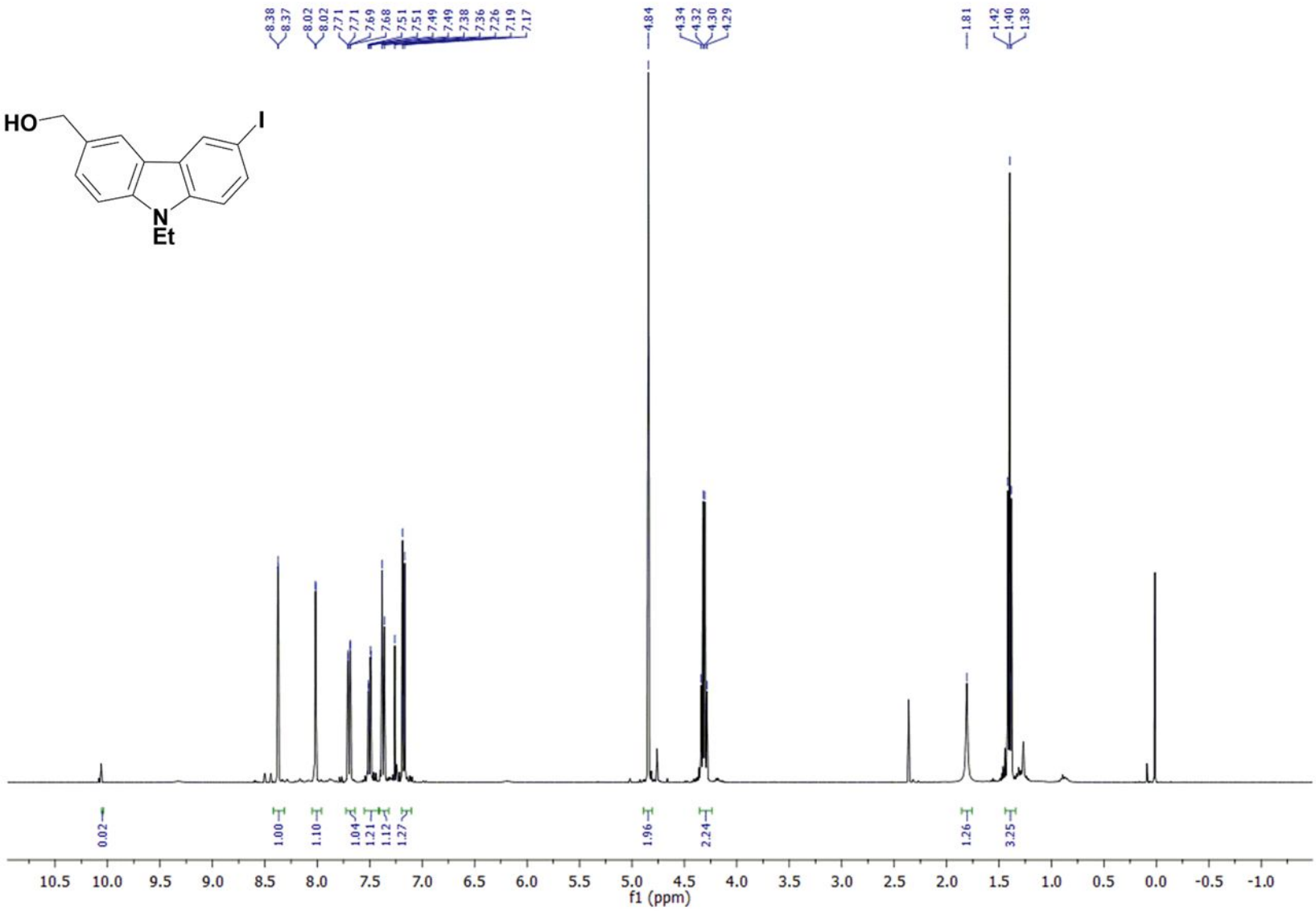
2g -^{1}H NMR


8.36
8.36
7.83
7.69
7.68
7.67
7.66
7.30
7.28
7.26
7.18
7.15
4.33
4.31
4.30
4.28
2.53
1.41
1.39
1.38
H3C
I
N
Et
1.00
1.03
1.04
2.04
1.05
2.30
3.28
3.36
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

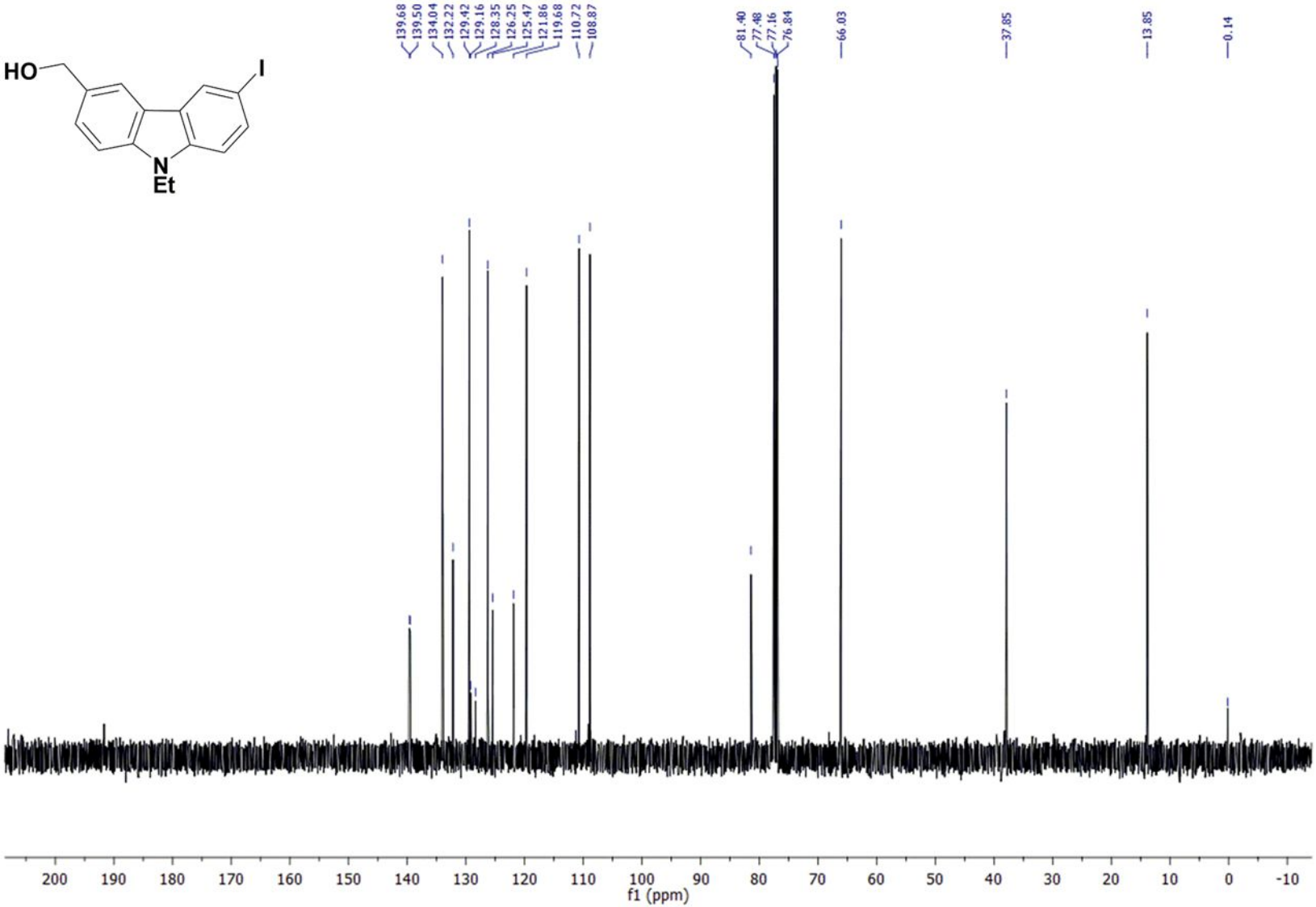
2g -$^{13}C\{^{1}H\}$ NMR


164.31
139.38
138.36
133.70
129.32
128.79
127.83
125.43
121.94
120.63
110.57
108.46
80.95
77.48
77.16
76.84
37.77
21.49
13.85
H3C
I
N
Et
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

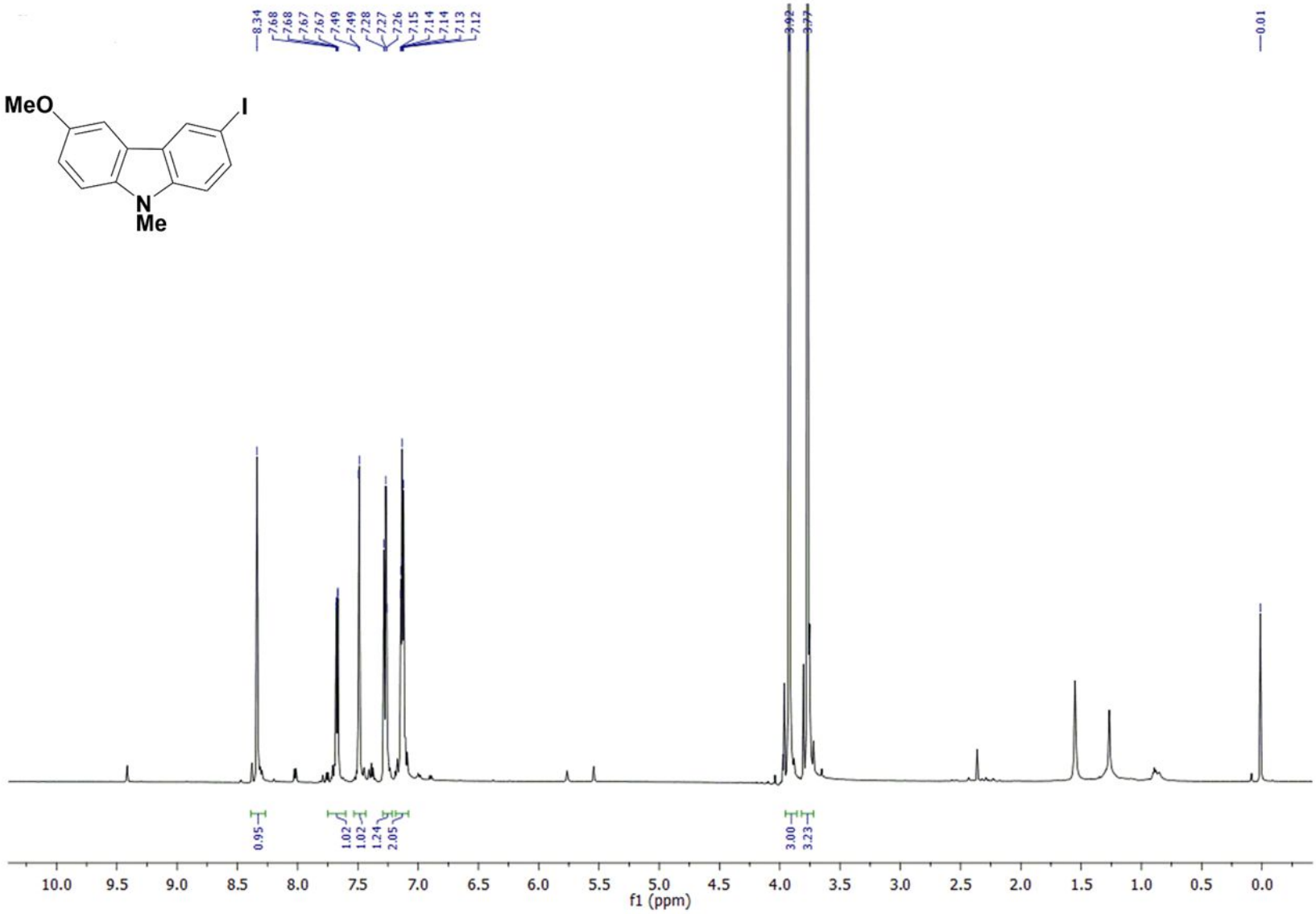
2h-^{1}H NMR


HO
I
N
Et
8.38
8.37
8.02
8.02
7.71
7.71
7.69
7.68
7.51
7.51
7.49
7.49
7.38
7.36
7.26
7.19
7.17
4.84
4.34
4.32
4.30
4.29
1.81
1.42
1.40
1.38
0.02
1.00
1.10
1.04
1.21
1.12
1.27
1.96
2.24
1.26
3.25
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

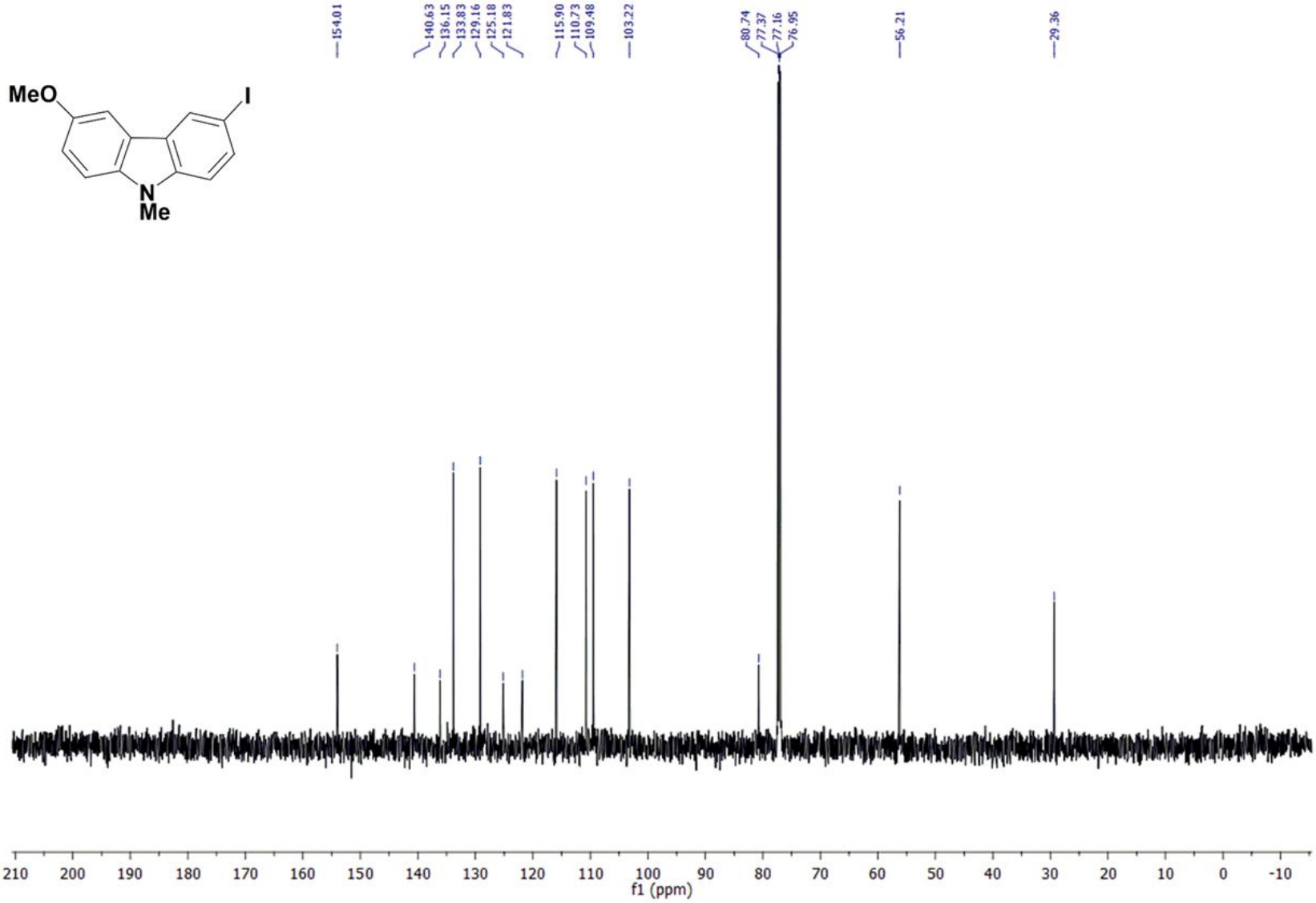
2h -$^{13}C\{^{1}H\}$ NMR


HO
I
N
Et
139.68
139.50
134.04
132.22
129.42
129.16
128.35
126.25
125.47
121.86
119.68
110.72
108.87
81.40
77.48
77.16
76.84
66.03
37.85
13.85
0.14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

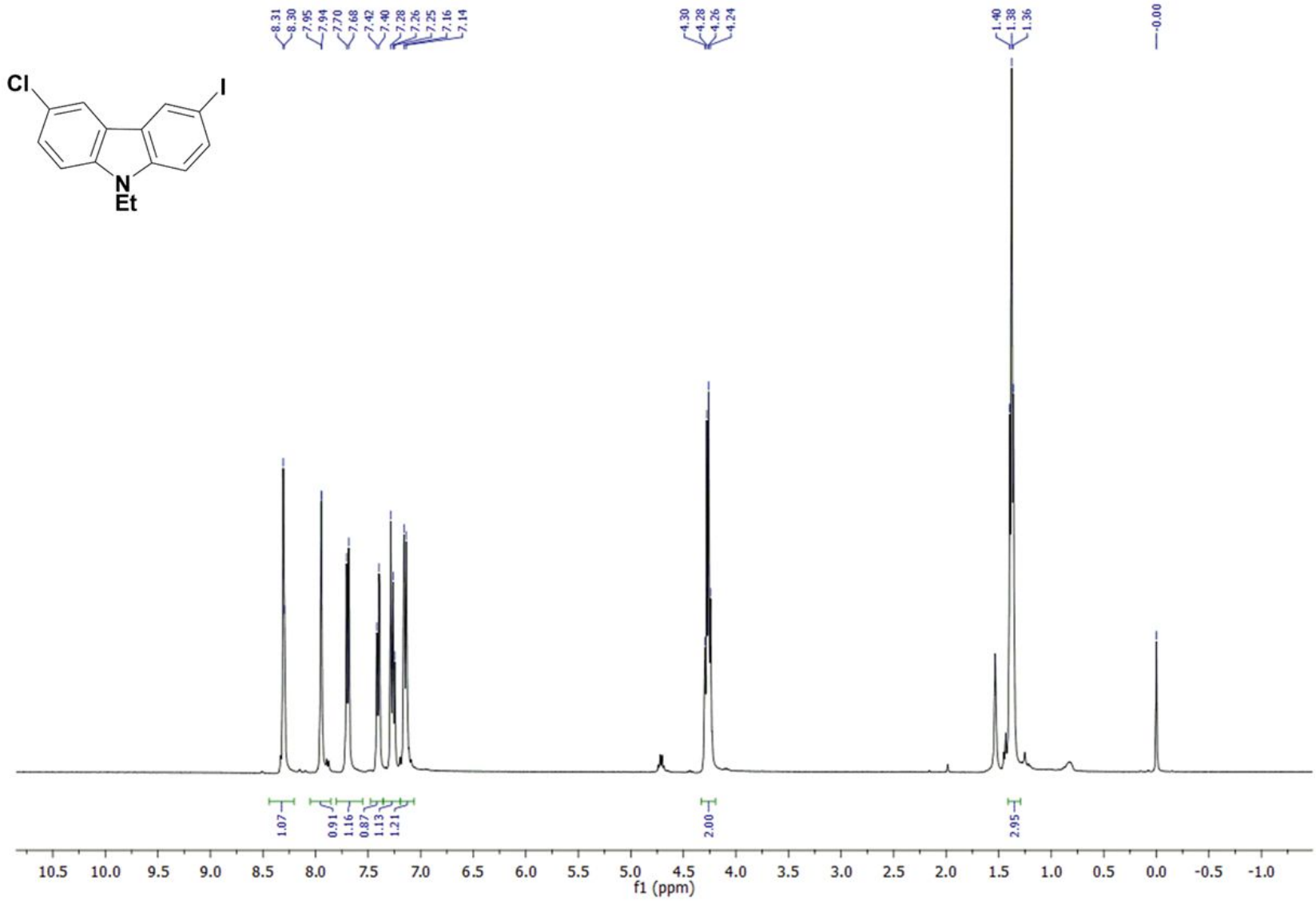
2i – ^{1}H NMR


MeO
I
N
Me
8.34
7.68
7.68
7.67
7.67
7.49
7.49
7.28
7.27
7.26
7.15
7.14
7.14
7.13
7.12
3.92
3.77
0.01
0.95
1.02
1.02
1.24
2.05
3.00
3.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

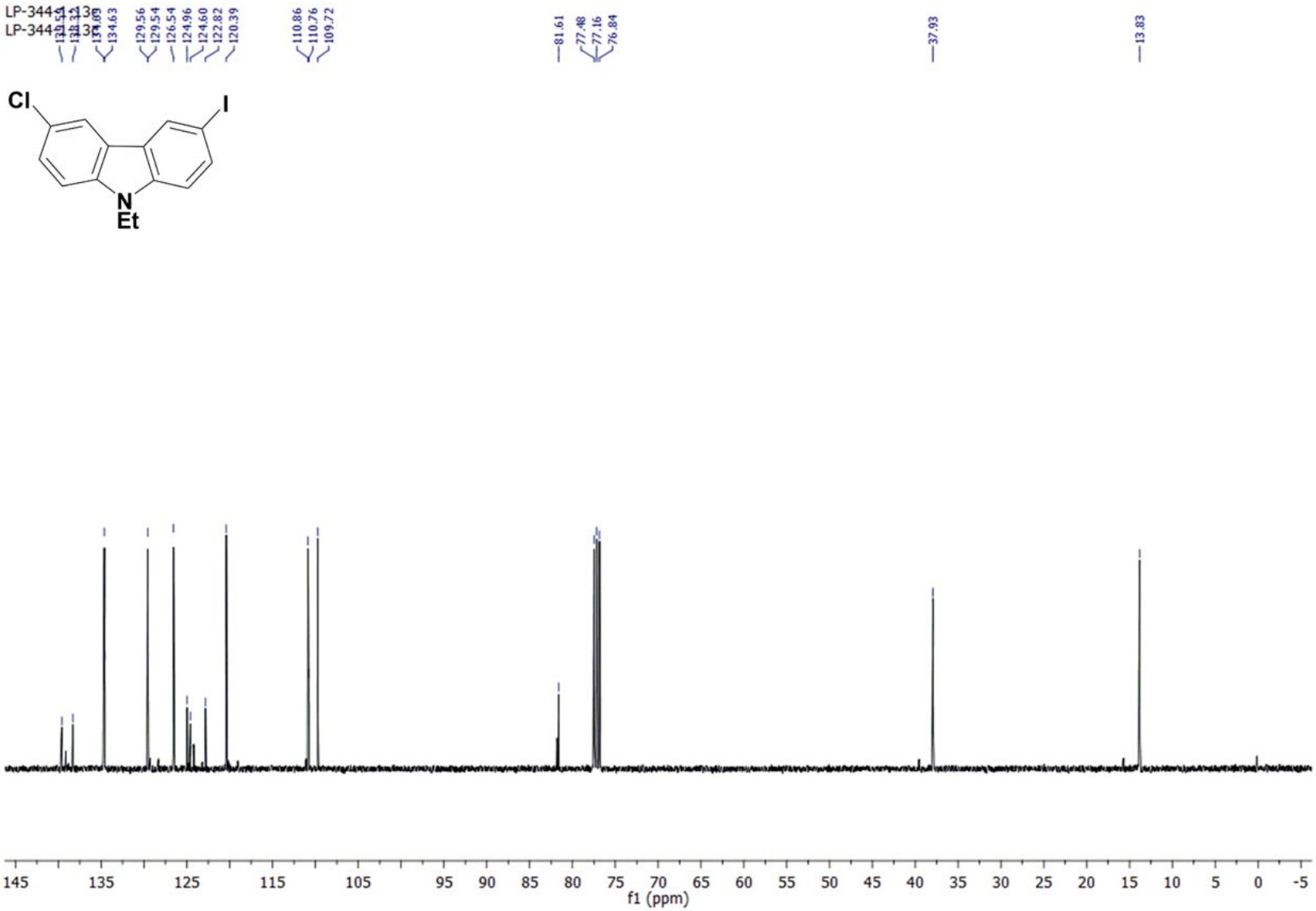
2i – ^{13}C {^{1}H} NMR


154.01
140.63
136.15
133.83
129.16
125.18
121.83
115.90
110.73
109.48
103.22
80.74
77.37
77.16
76.95
56.21
29.36
MeO
I
N
Me
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)

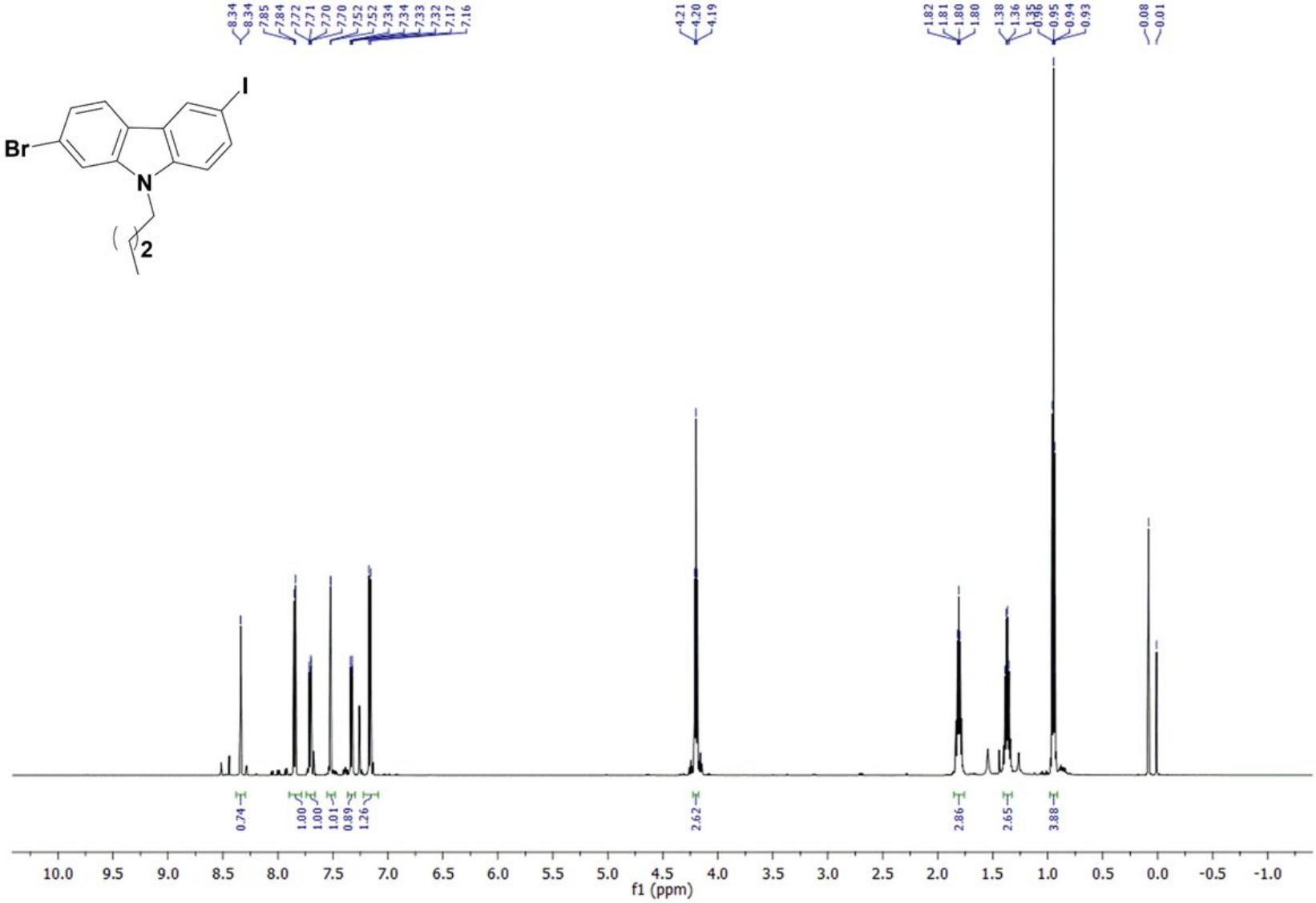
2j - ^{1}H NMR


Cl
I
N
Et
8.31
8.30
7.95
7.94
7.70
7.68
7.42
7.40
7.28
7.26
7.25
7.16
7.14
4.30
4.28
4.26
4.24
1.40
1.38
1.36
-0.00
1.07
0.91
1.16
0.87
1.13
1.21
2.00
2.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

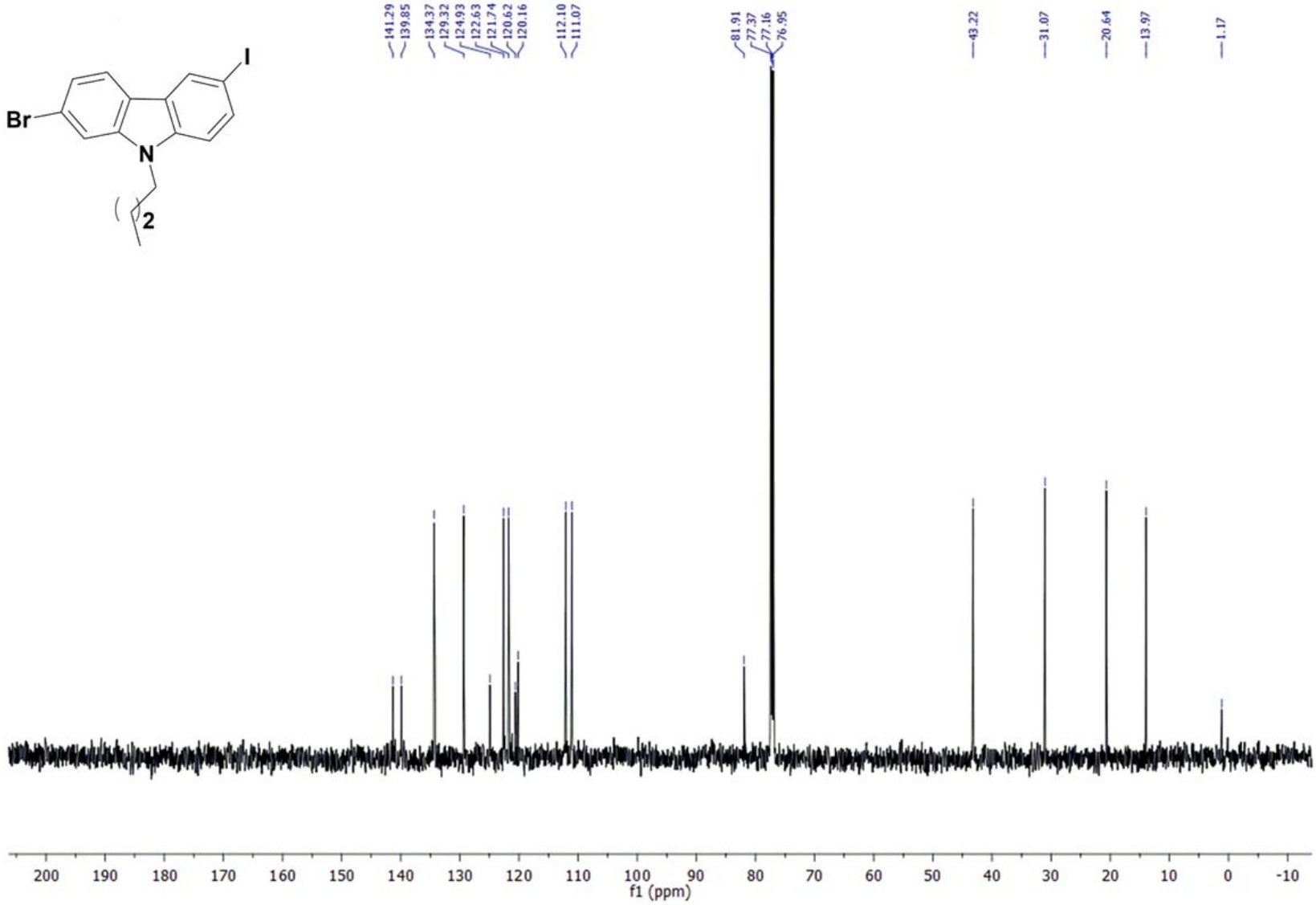
2j -^{13}C{1H} NMR


LP-344
LP-344
134.63
129.56
129.54
126.54
124.96
124.60
122.82
120.39
110.86
110.76
109.72
81.61
77.48
77.16
76.84
37.93
13.83
Cl
I
N
Et
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
f1 (ppm)

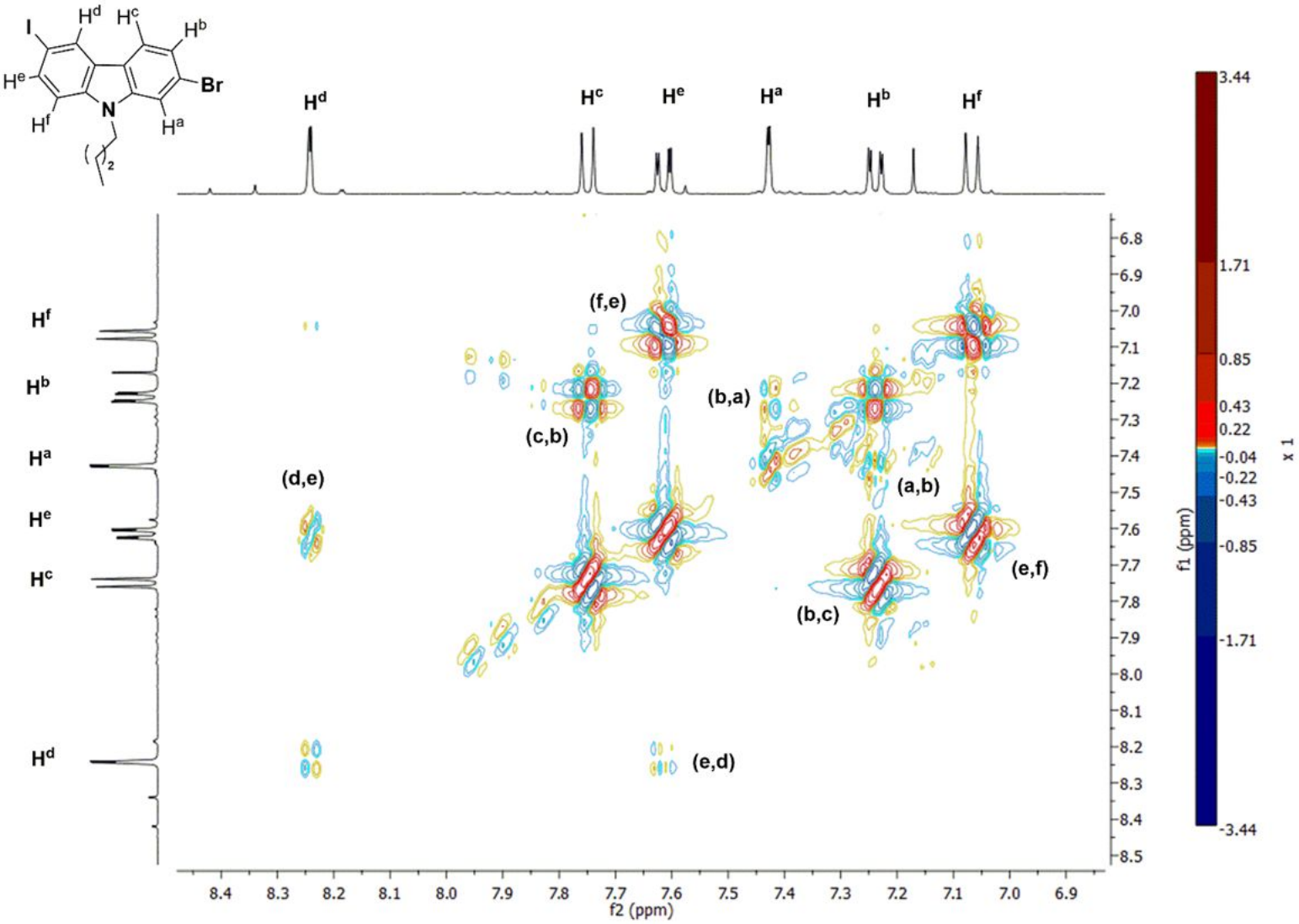
2k - ^{1}H NMR


Br
I
N
2
8.34
8.34
7.85
7.84
7.72
7.71
7.70
7.70
7.52
7.52
7.34
7.34
7.33
7.32
7.17
7.16
4.21
4.20
4.19
1.82
1.81
1.80
1.80
1.38
1.36
1.35
0.95
0.94
0.93
0.08
0.01
0.74
1.00
1.00
1.01
0.89
1.26
2.62
2.86
2.65
3.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

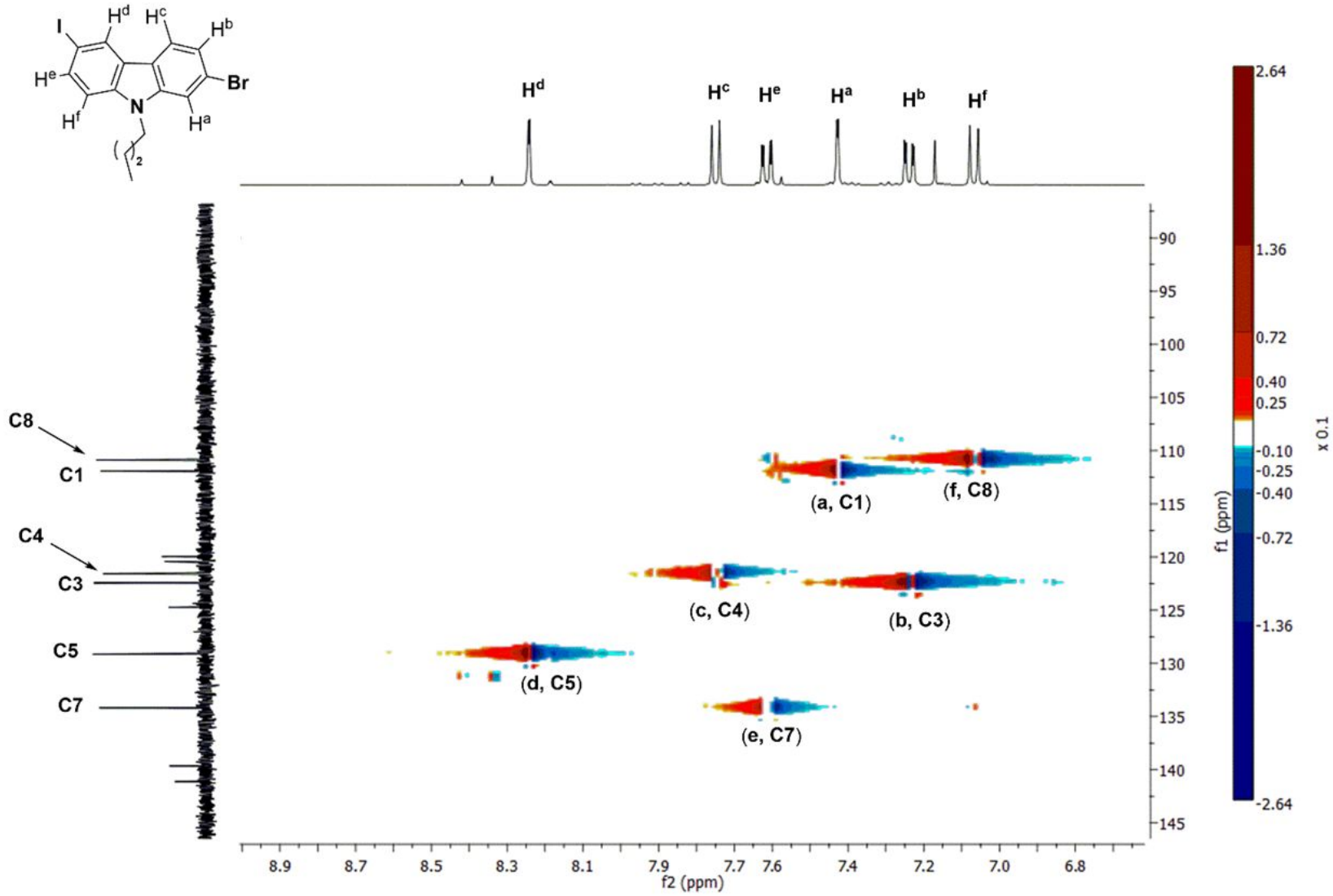
2k -$^{13}C\{^{1}H\}$ NMR


141.29
139.85
134.37
129.32
124.93
122.63
121.74
120.62
120.16
112.10
111.07
81.91
77.37
77.16
76.95
43.22
31.07
20.64
13.97
1.17
Br
I
N
2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

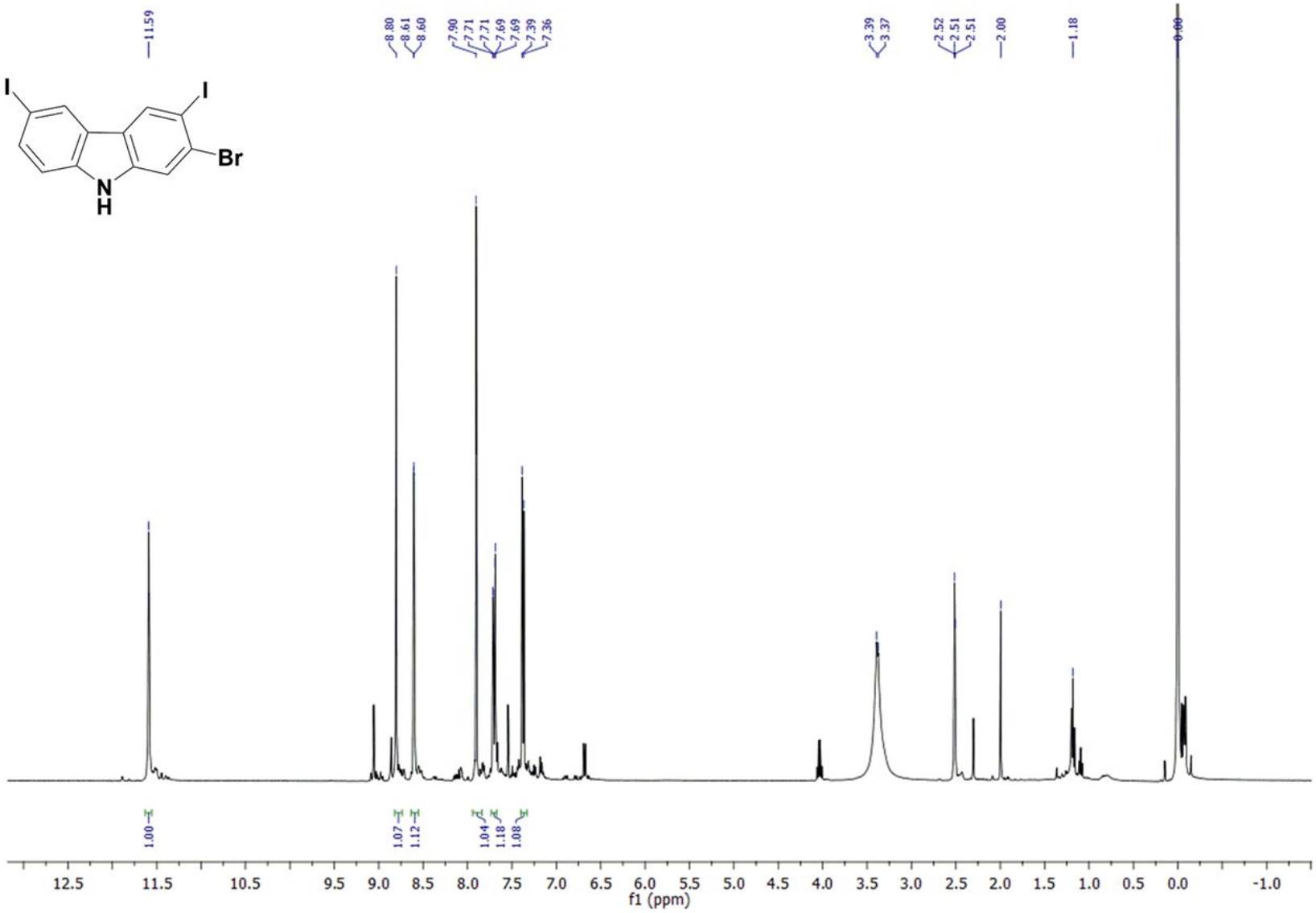
2k – 2D gDQFCOSY NMR



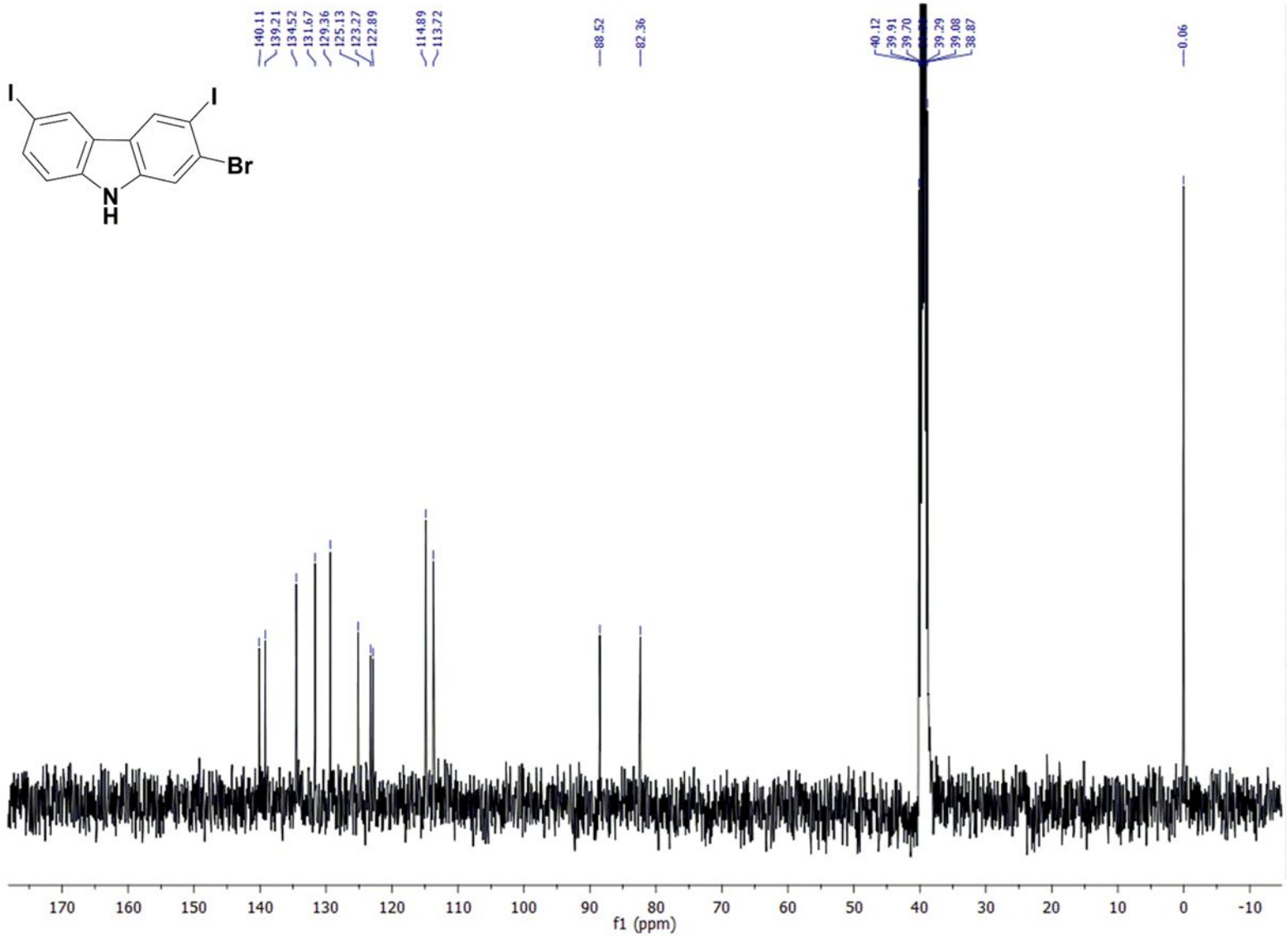
2k - gHSQAD NMR



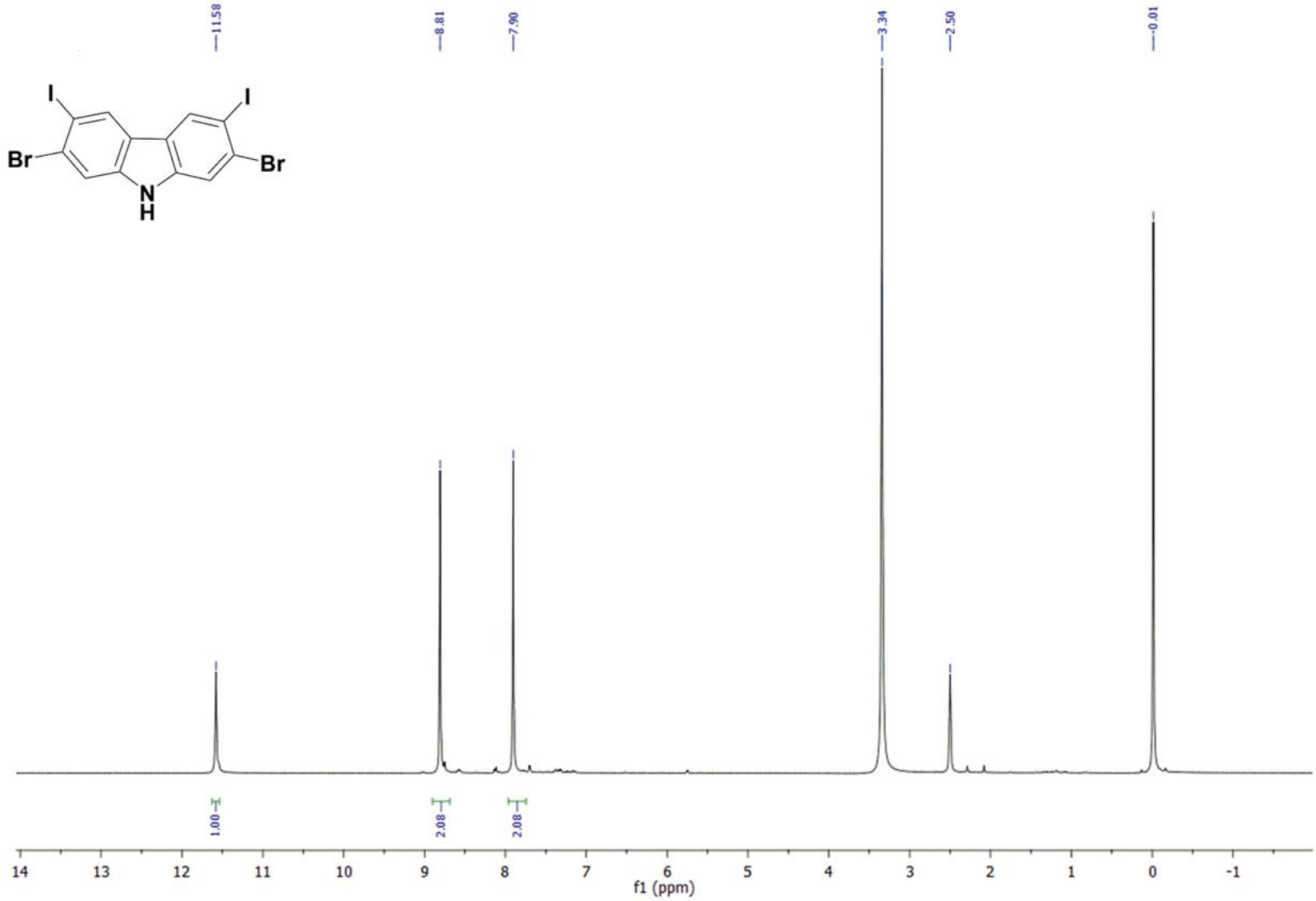
2l -^{1}H NMR


11.59
8.80
8.61
8.60
7.90
7.71
7.71
7.69
7.69
7.39
7.36
3.39
3.37
2.52
2.51
2.51
2.00
1.18
0.00
I
I
Br
N
H
1.00
1.07
1.12
1.04
1.18
1.08
12.5
11.5
10.5
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
-1.0
f1 (ppm)

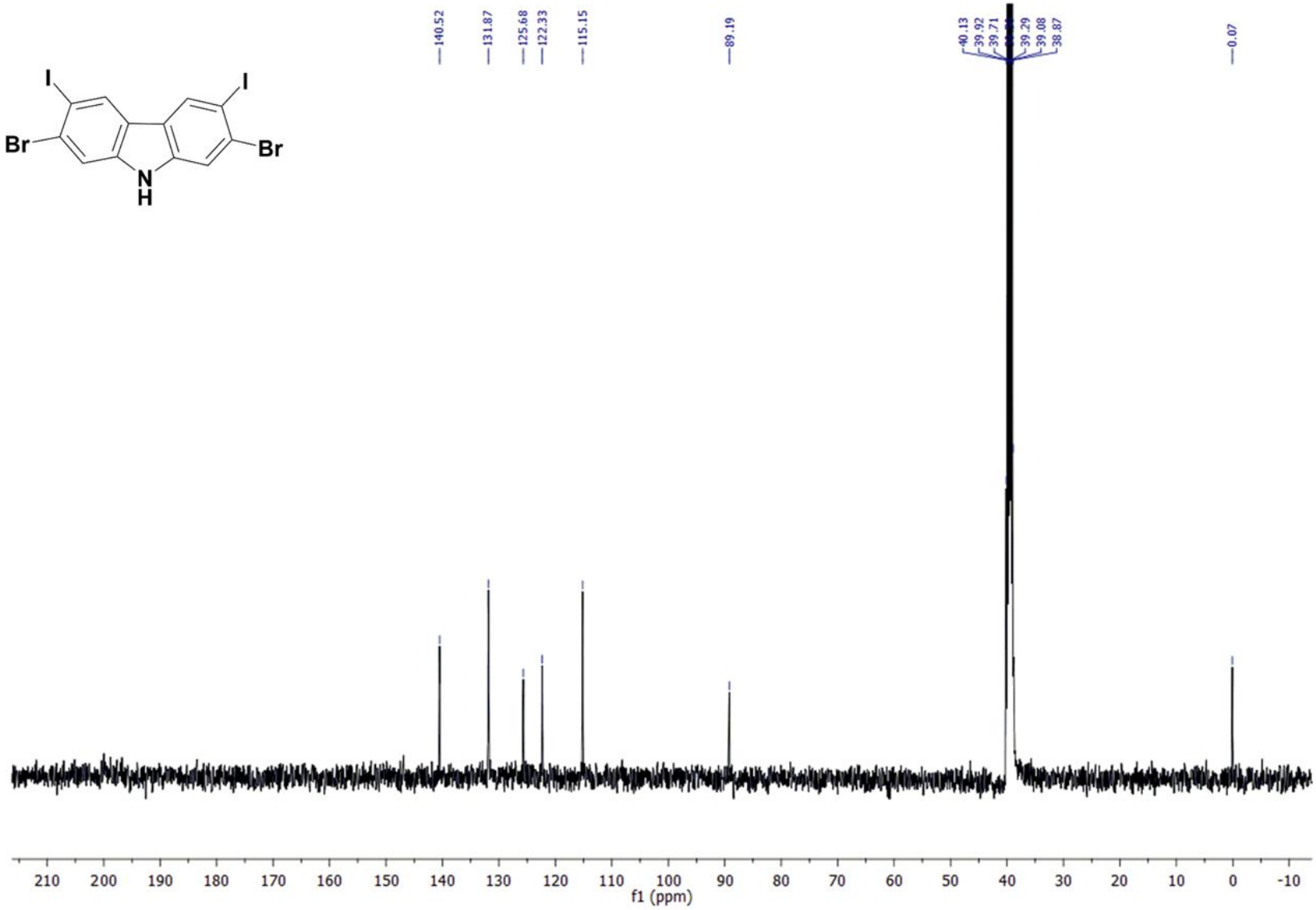
2l-$^{13}C\{^{1}H\}$ NMR


140.11
139.21
134.52
131.67
129.36
125.13
123.27
122.89
114.89
113.72
88.52
82.36
40.12
39.91
39.70
39.29
39.08
38.87
0.06
I
I
Br
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

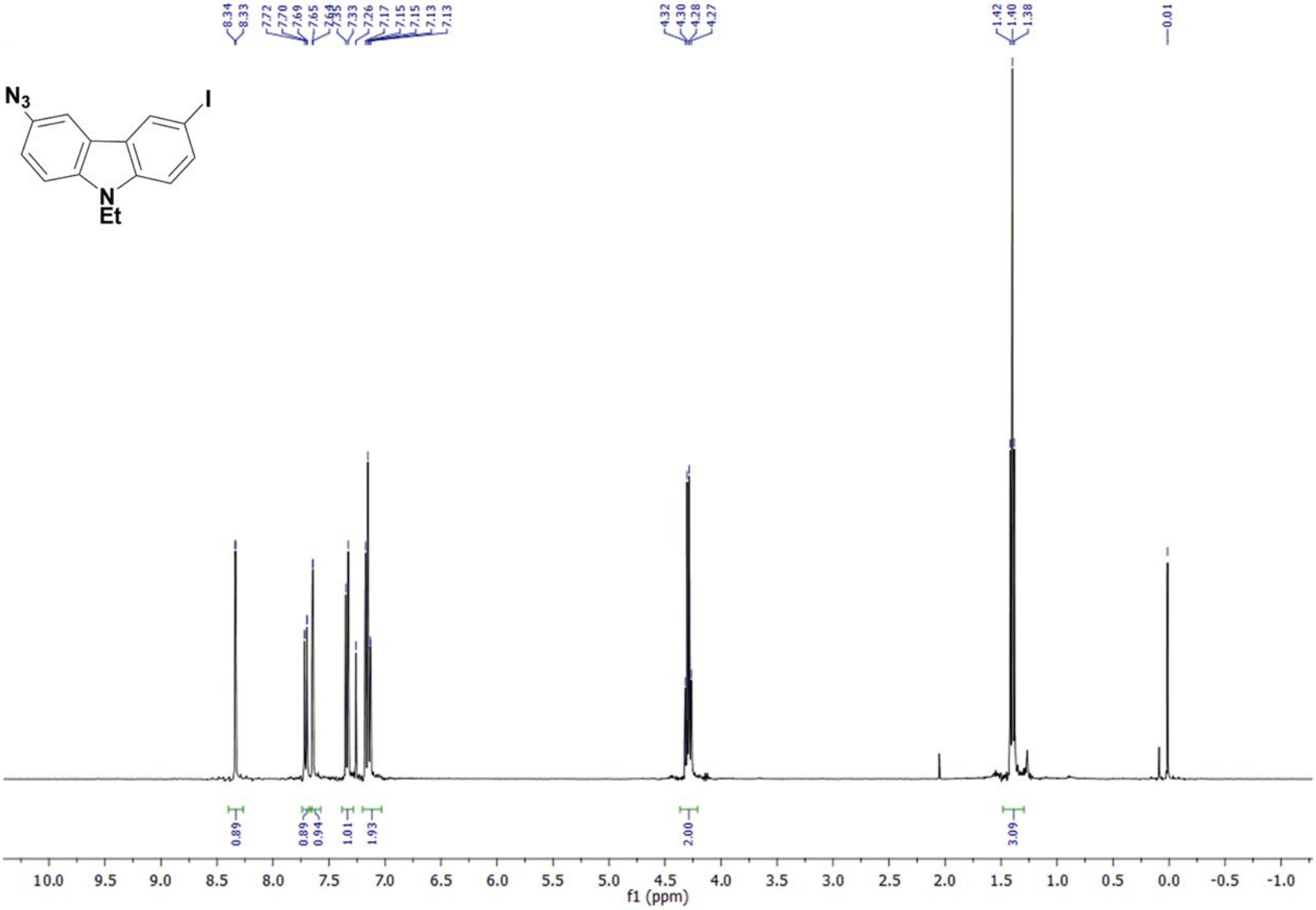
2m -^{1}H NMR


11.58
8.81
7.90
3.34
2.50
0.01
I
I
Br
Br
N
H
1.00
2.08
2.08
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

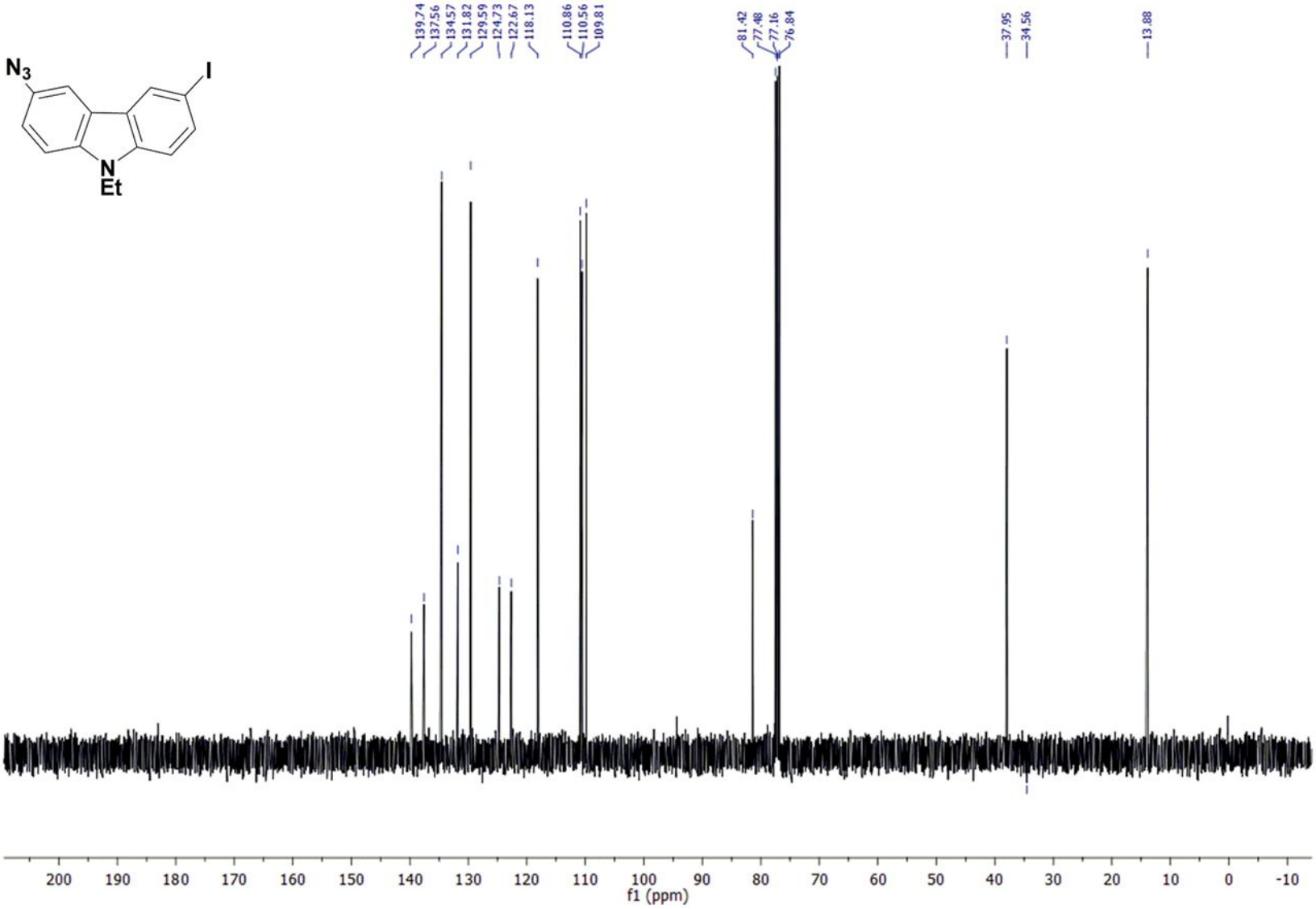
2m -^{13}C {^{1}H} NMR


140.52
131.87
125.68
122.33
115.15
89.19
40.13
39.92
39.71
39.29
39.08
38.87
0.07
I
I
Br
Br
N
H
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)

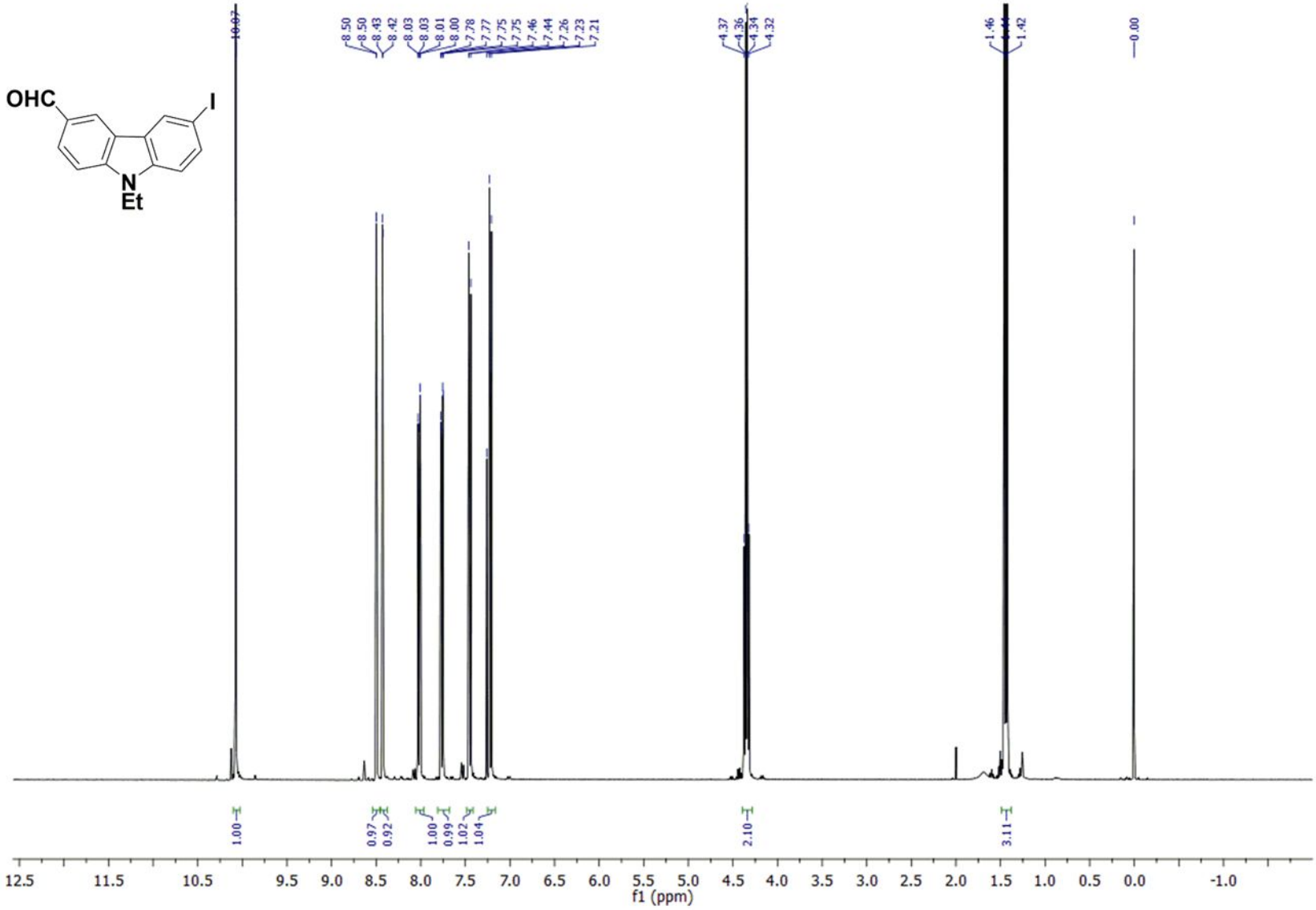
2n -^{1}H NMR


N3
I
N
Et
8.34
8.33
7.72
7.70
7.69
7.65
7.33
7.26
7.17
7.15
7.15
7.13
7.13
4.32
4.30
4.28
4.27
1.42
1.40
1.38
0.01
0.89
0.89
0.94
1.01
1.93
2.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

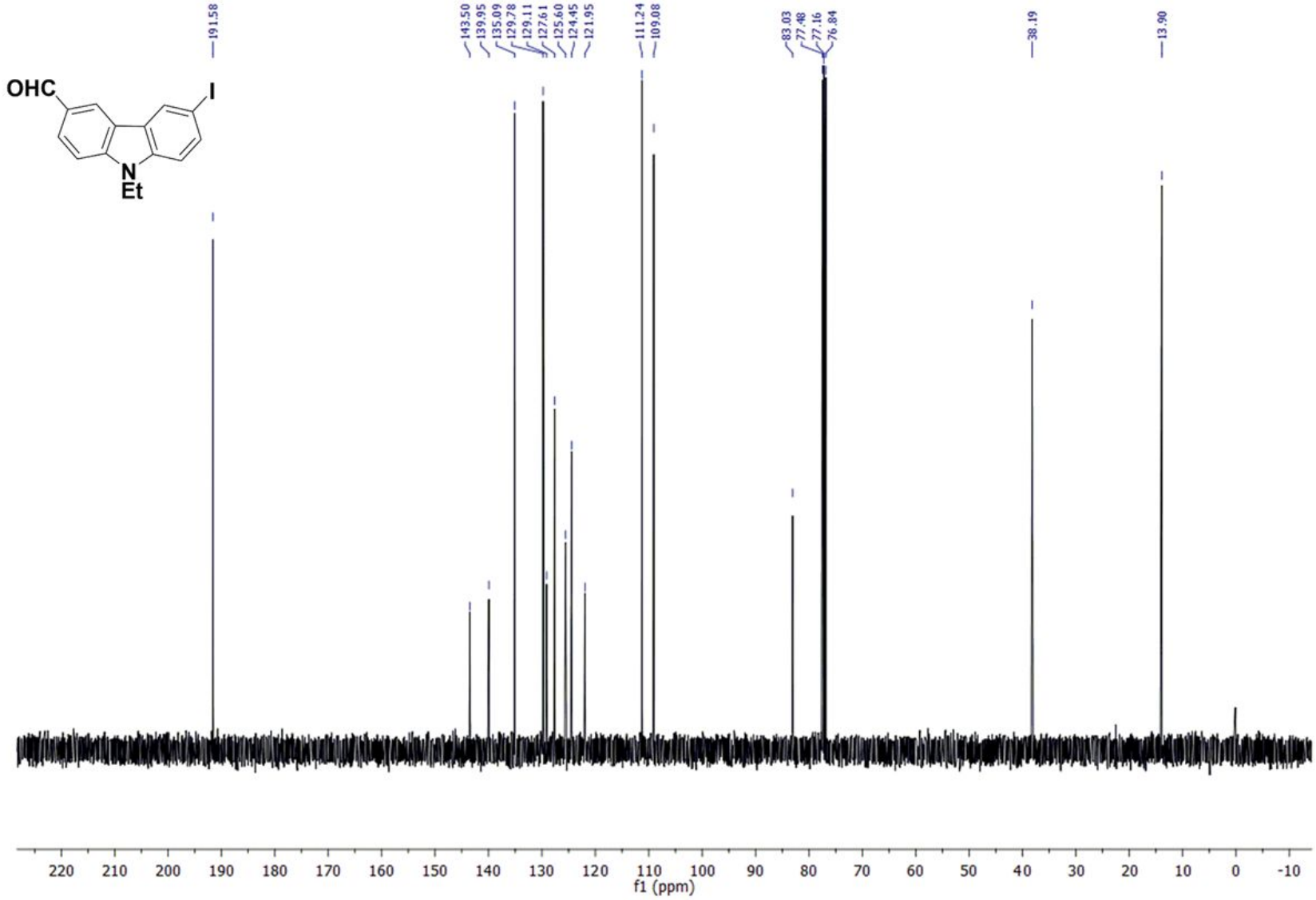
2n -^{13}C {^{1}H} NMR


N3
I
N
Et
139.74
137.56
134.57
131.82
129.59
124.73
122.67
118.13
110.86
110.56
109.81
81.42
77.48
77.16
76.84
37.95
34.56
13.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

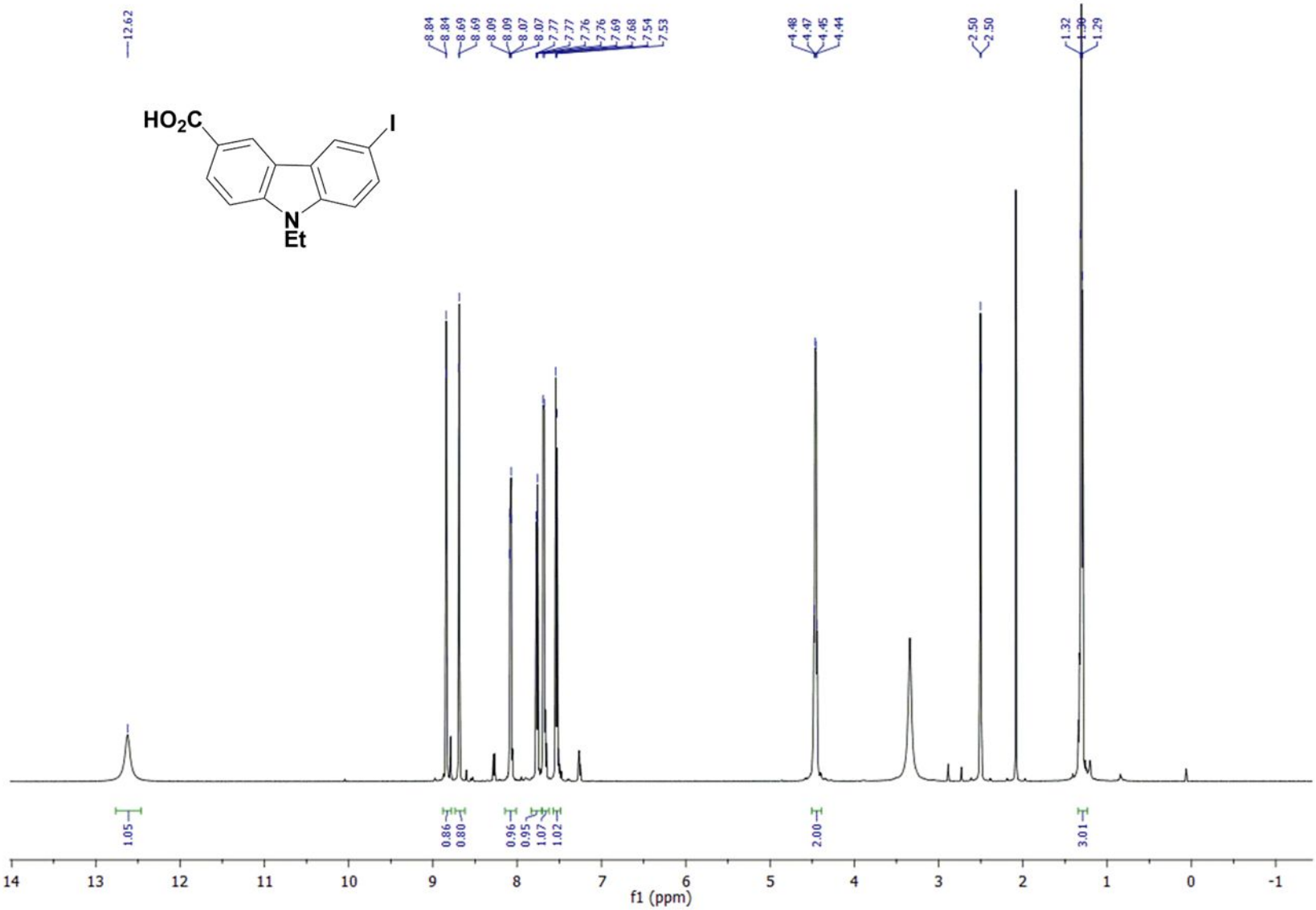
2o -^{1}H NMR


OHC
I
N
Et
10.07
8.50
8.50
8.43
8.42
8.03
8.03
8.01
8.00
7.78
7.77
7.75
7.75
7.46
7.44
7.26
7.23
7.21
4.37
4.36
4.34
4.32
1.46
1.42
0.00
1.00
0.97
0.92
1.00
0.99
1.02
1.04
2.10
3.11
12.5
11.5
10.5
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
-1.0
f1 (ppm)

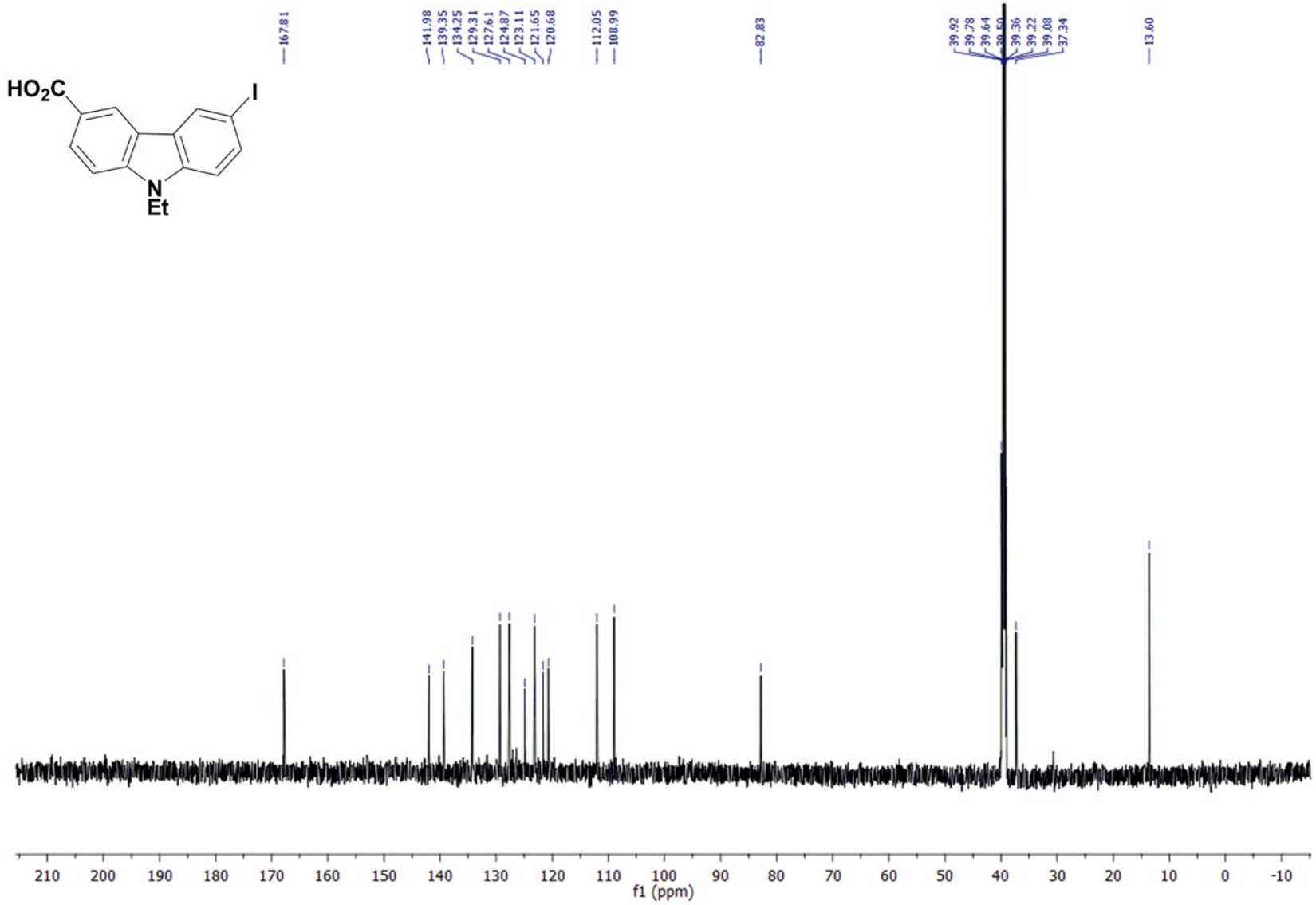
2o – ^{13}C {^{1}H} NMR


OHC
I
N
Et
191.58
143.50
139.95
135.09
129.78
129.11
127.61
125.60
124.45
121.95
111.24
109.08
83.03
77.48
77.16
76.84
38.19
13.90
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

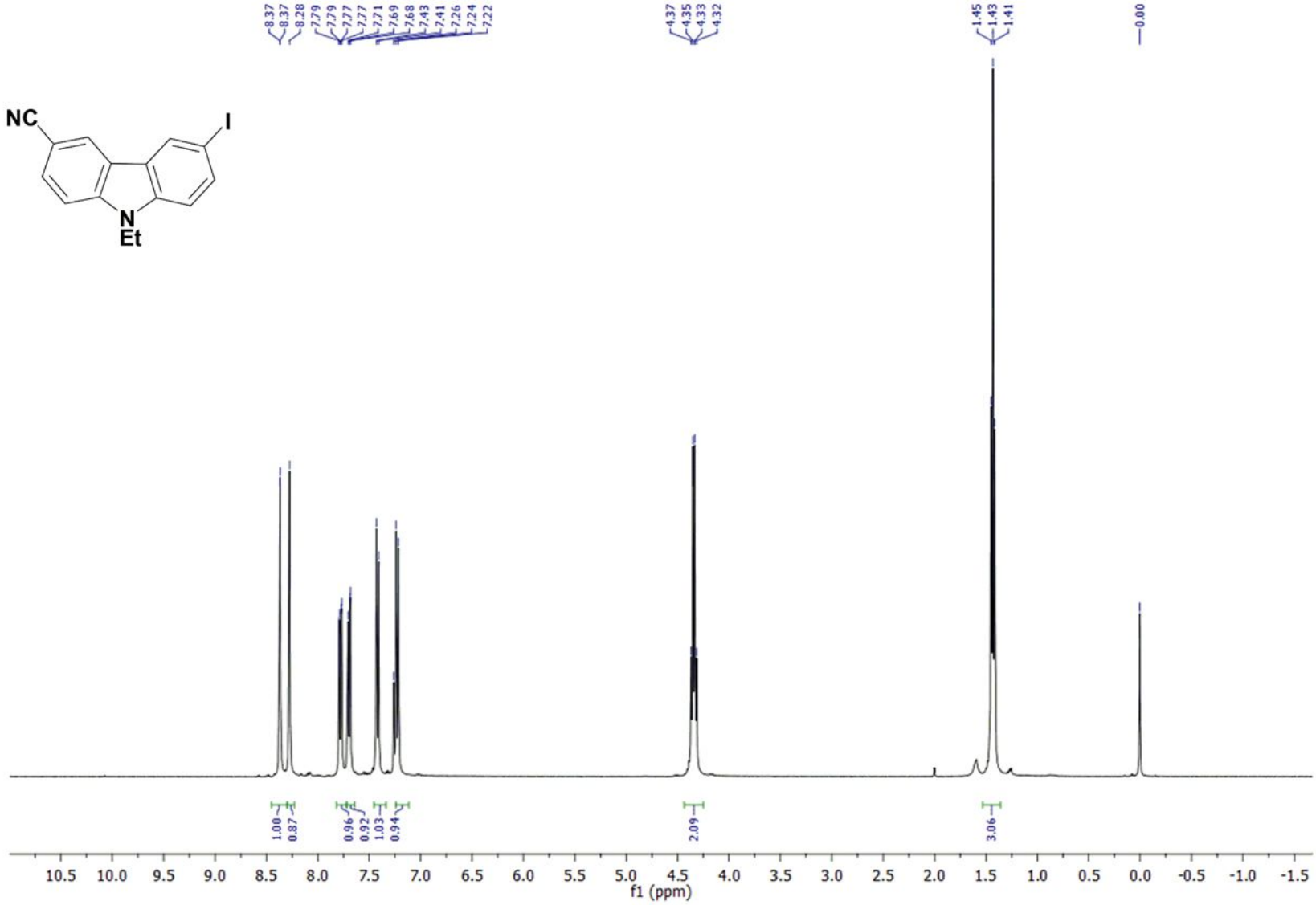
2p -^{1}H NMR


12.62
8.84
8.84
8.69
8.69
8.09
8.09
8.07
8.07
7.77
7.77
7.76
7.76
7.69
7.68
7.54
7.53
4.48
4.47
4.45
4.44
2.50
2.50
1.32
1.30
1.29
HO2C
I
N
Et
1.05
0.86
0.80
0.96
0.95
1.07
1.02
2.00
3.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

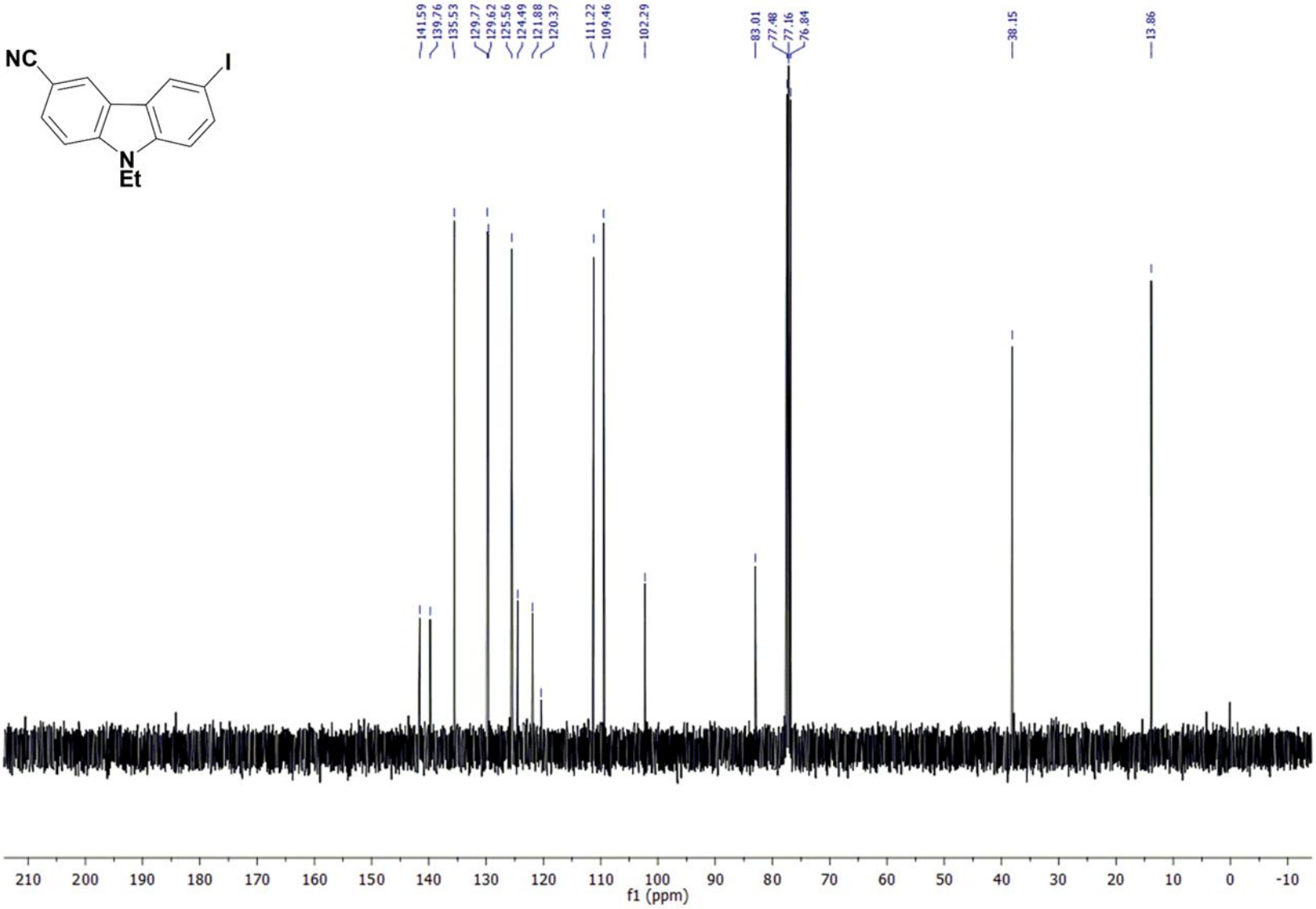
2p – ^{13}C {^{1}H} NMR


HO2C
I
N
Et
167.81
141.98
139.35
134.25
129.31
127.61
124.87
123.11
121.65
120.68
112.05
108.99
82.83
39.92
39.78
39.64
39.36
39.22
39.08
37.34
13.60
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)

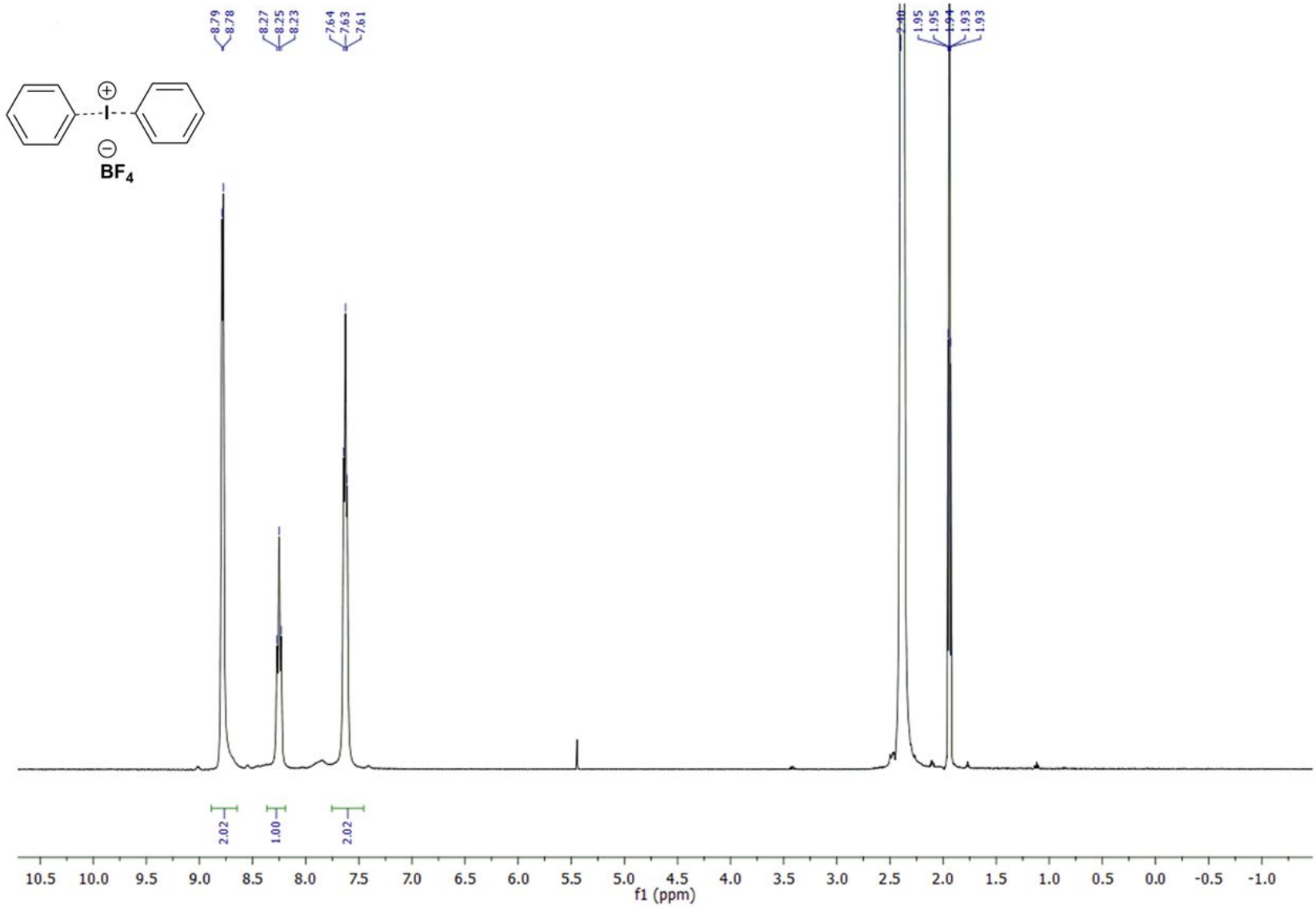
2q -^{1}H NMR


8.37
8.37
8.28
7.79
7.79
7.77
7.77
7.77
7.71
7.69
7.68
7.43
7.41
7.26
7.24
7.22
4.37
4.35
4.33
4.32
1.45
1.43
1.41
0.00
NC
I
N
Et
1.00
0.87
0.96
0.92
1.03
0.94
2.09
3.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

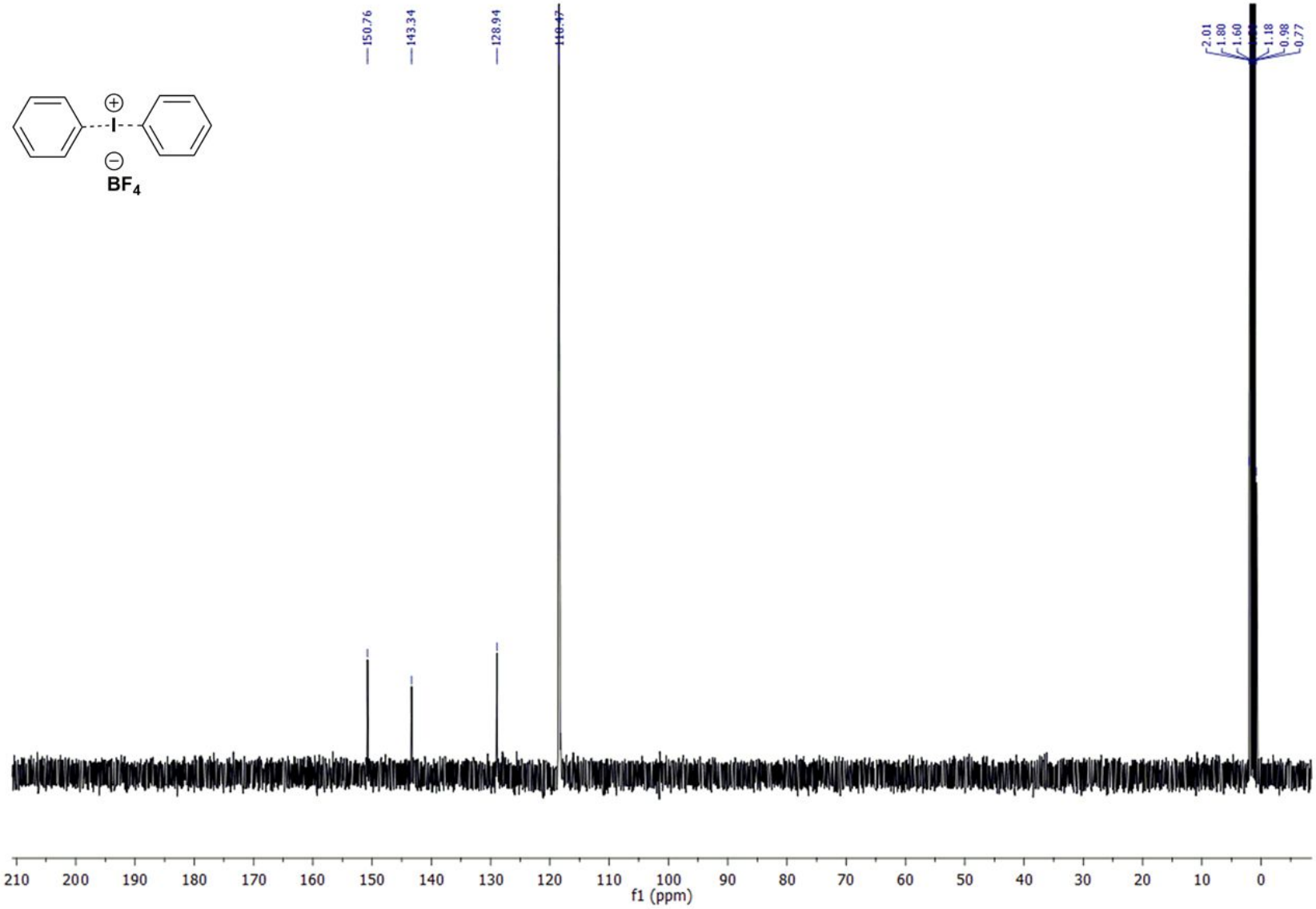
2q – ^{13}C {^{1}H} NMR


NC
I
N
Et
141.59
139.76
135.53
129.77
129.62
125.56
124.49
121.88
120.37
111.22
109.46
102.29
83.01
77.48
77.16
76.84
38.15
13.86
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)

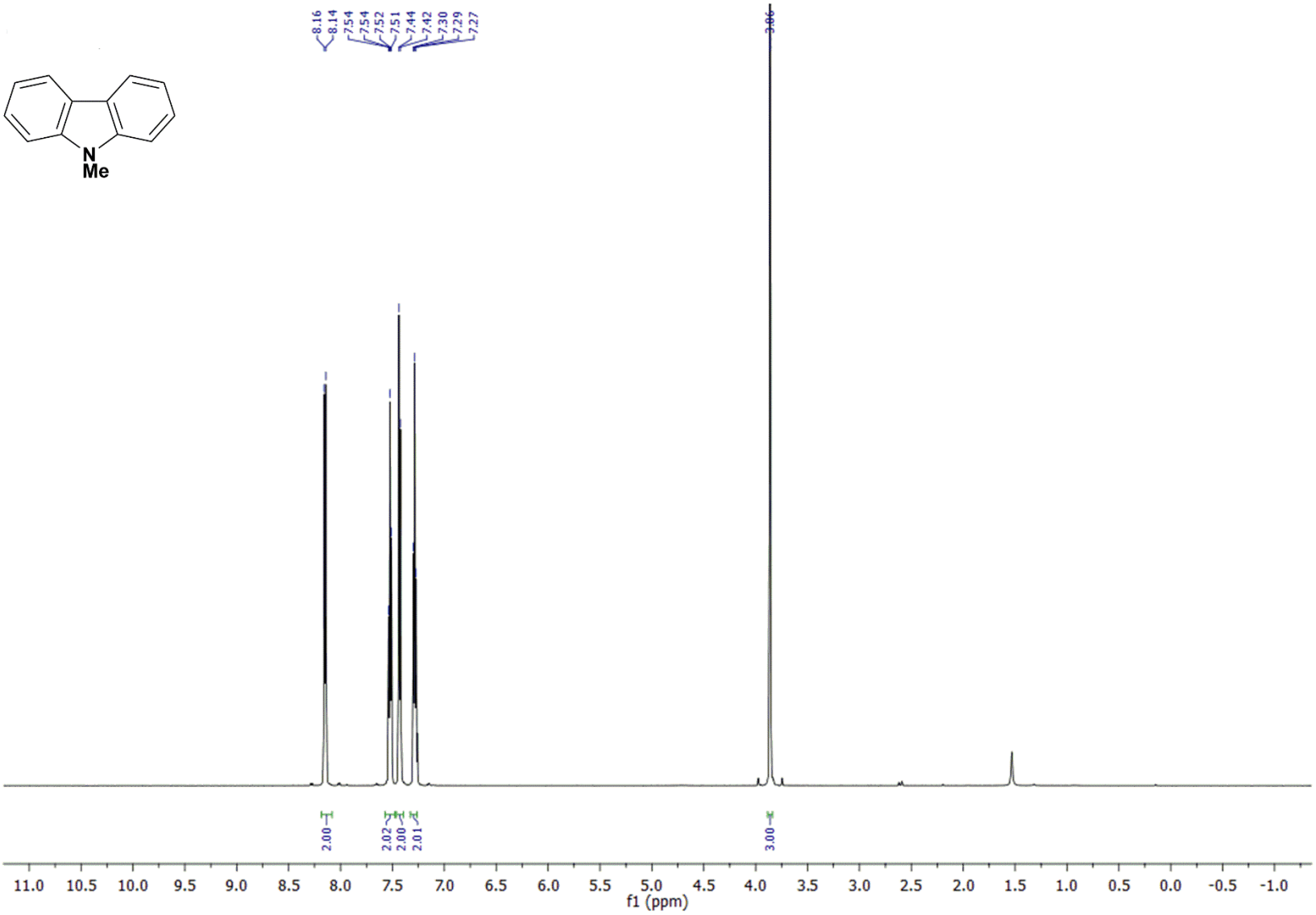
Barluenga's reagent IPy_2BF_4 – ^1H NMR



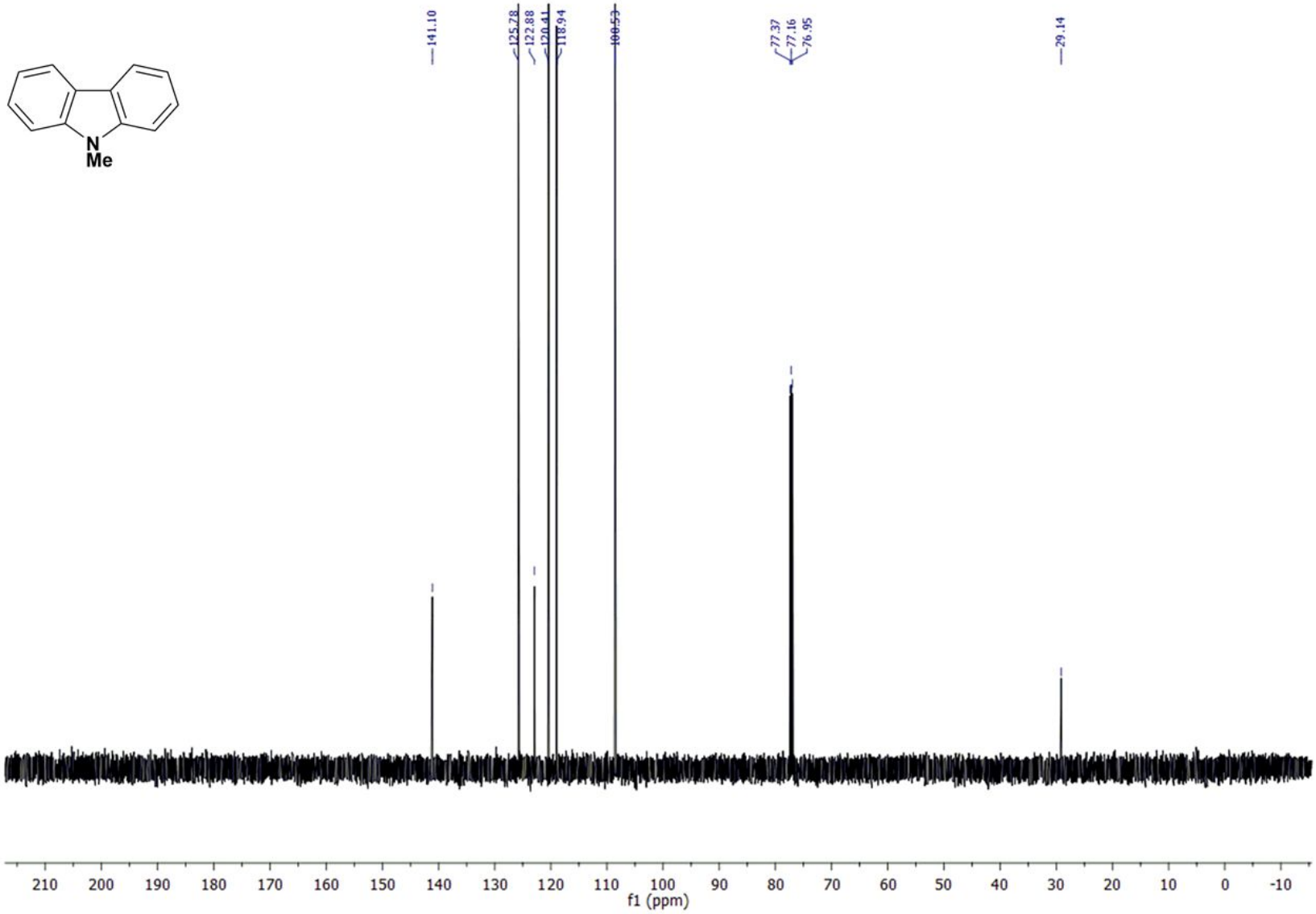
Barluenga's reagent IPy_2BF_4 – ^{13}C {^1H} NMR



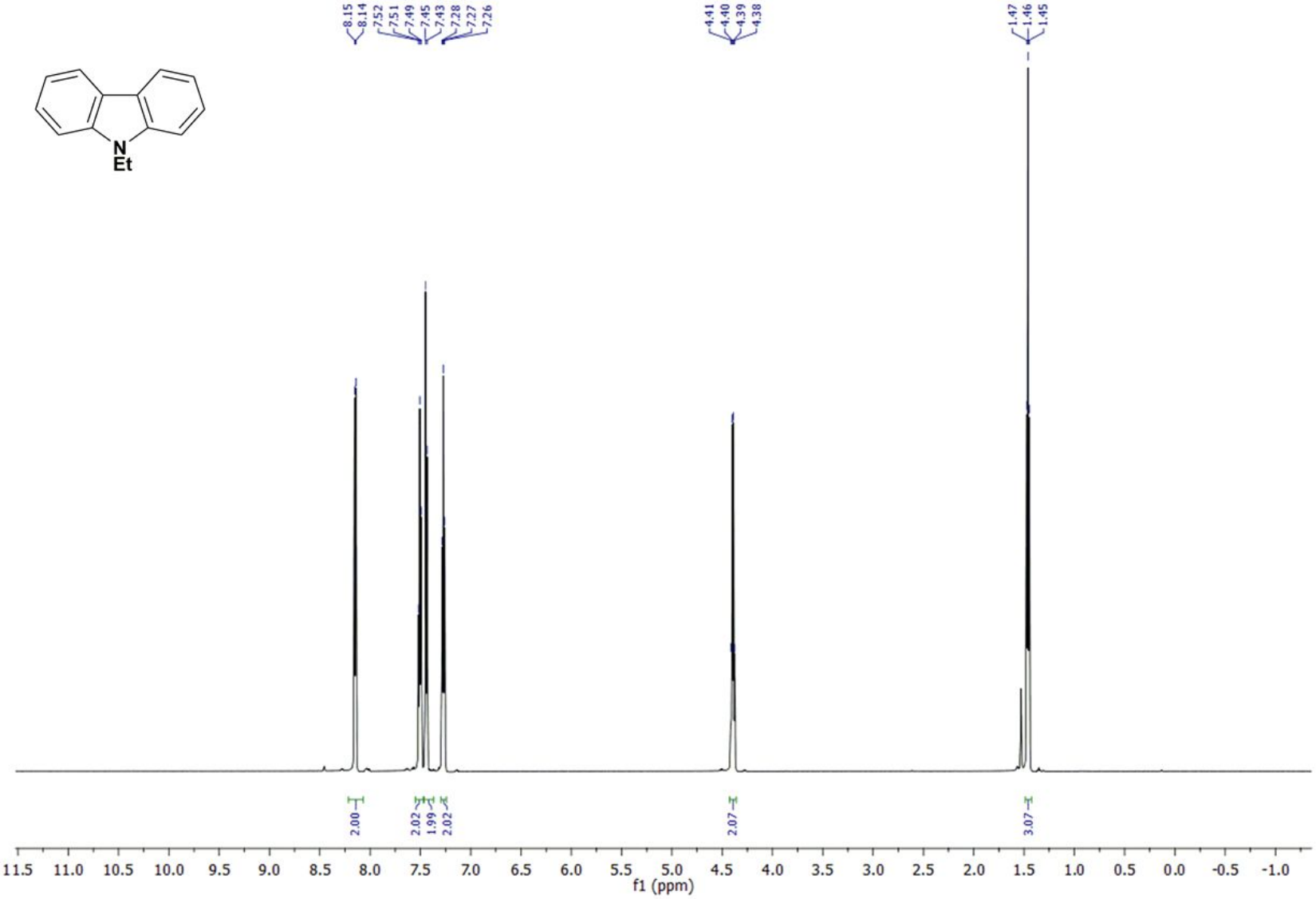
9-Methylcarbazole – ^{1}H NMR



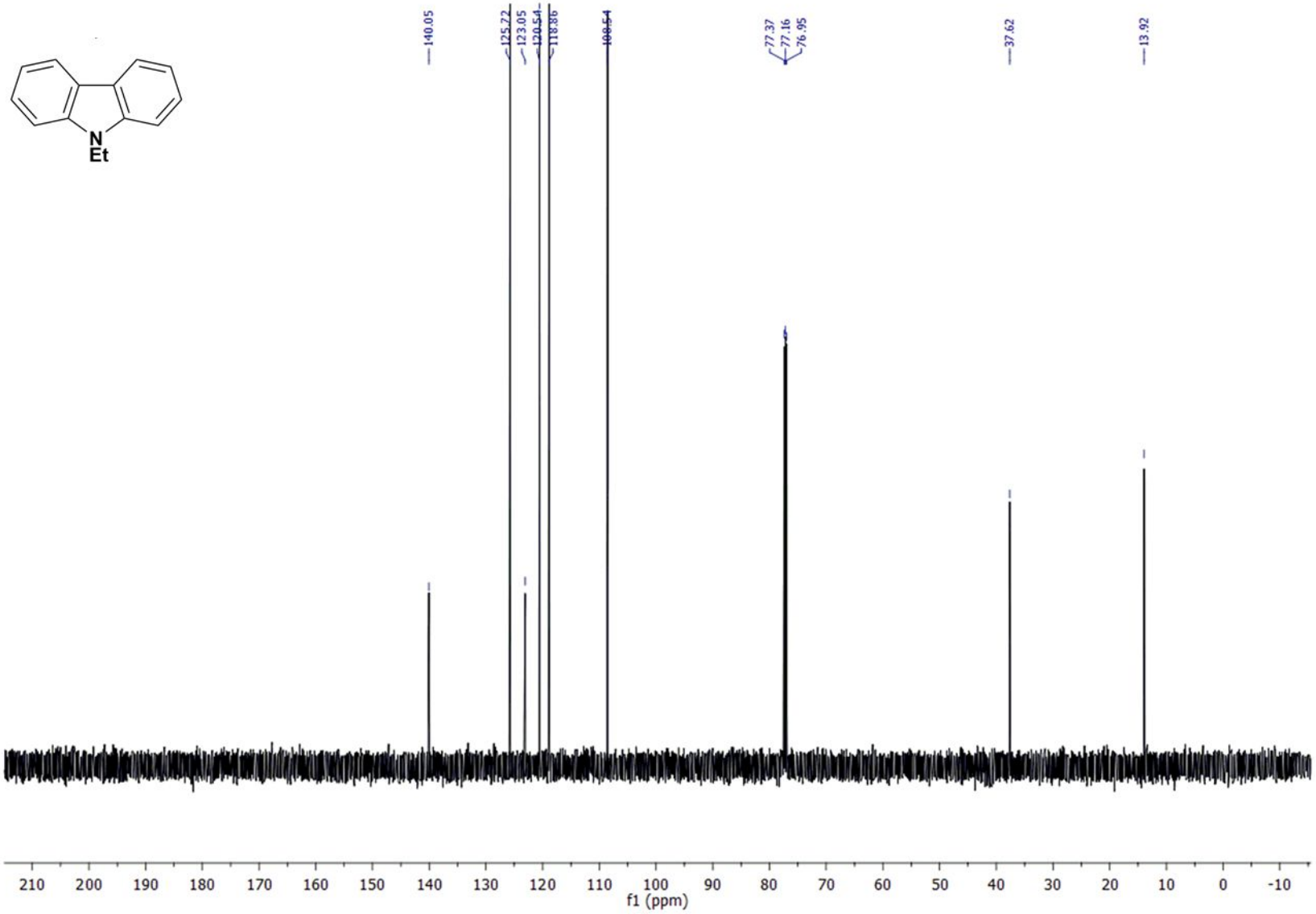
9-Methylcarbazole – ^{13}C {^{1}H} NMR



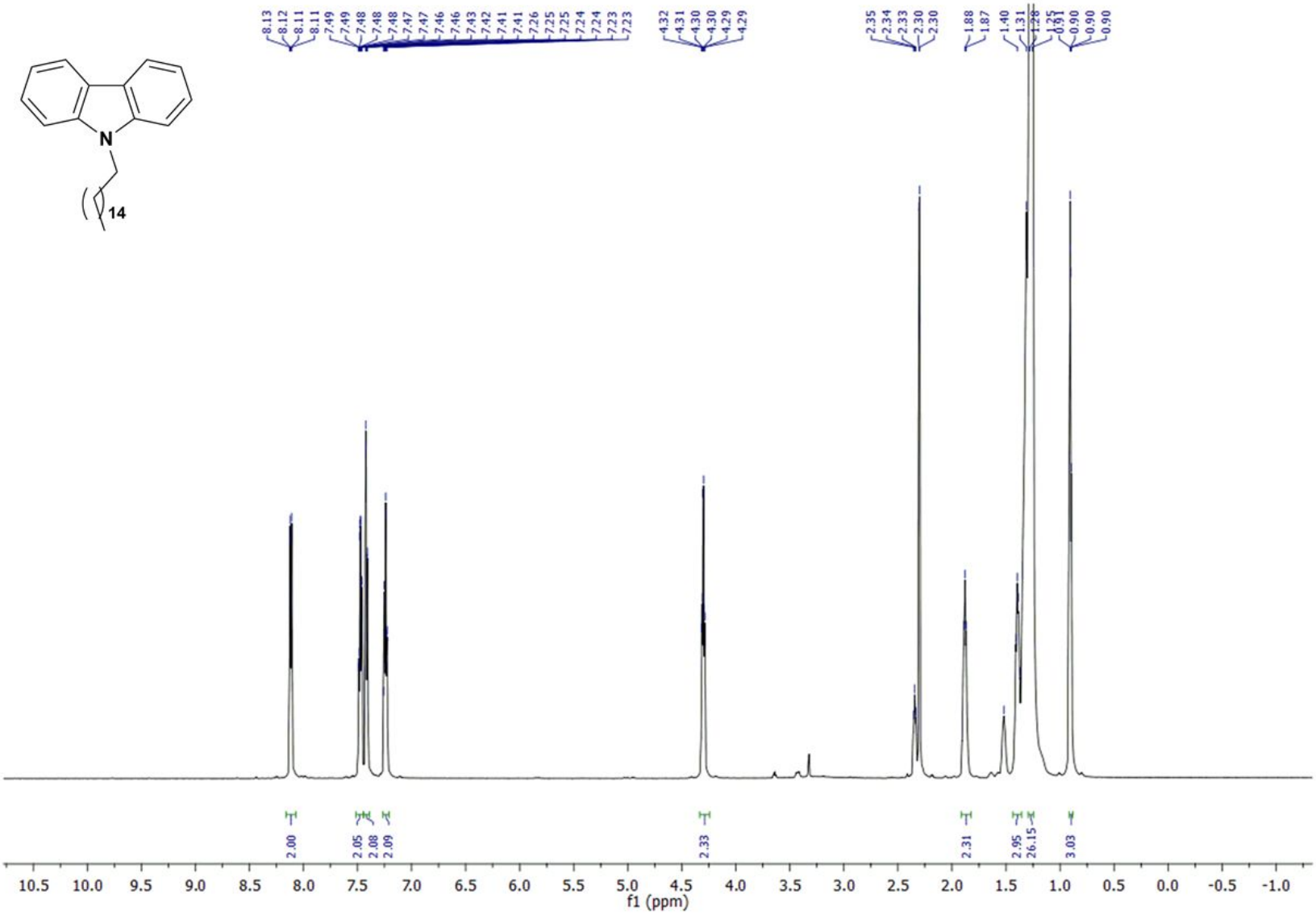
9-Ethylcarbazole – ^{1}H NMR



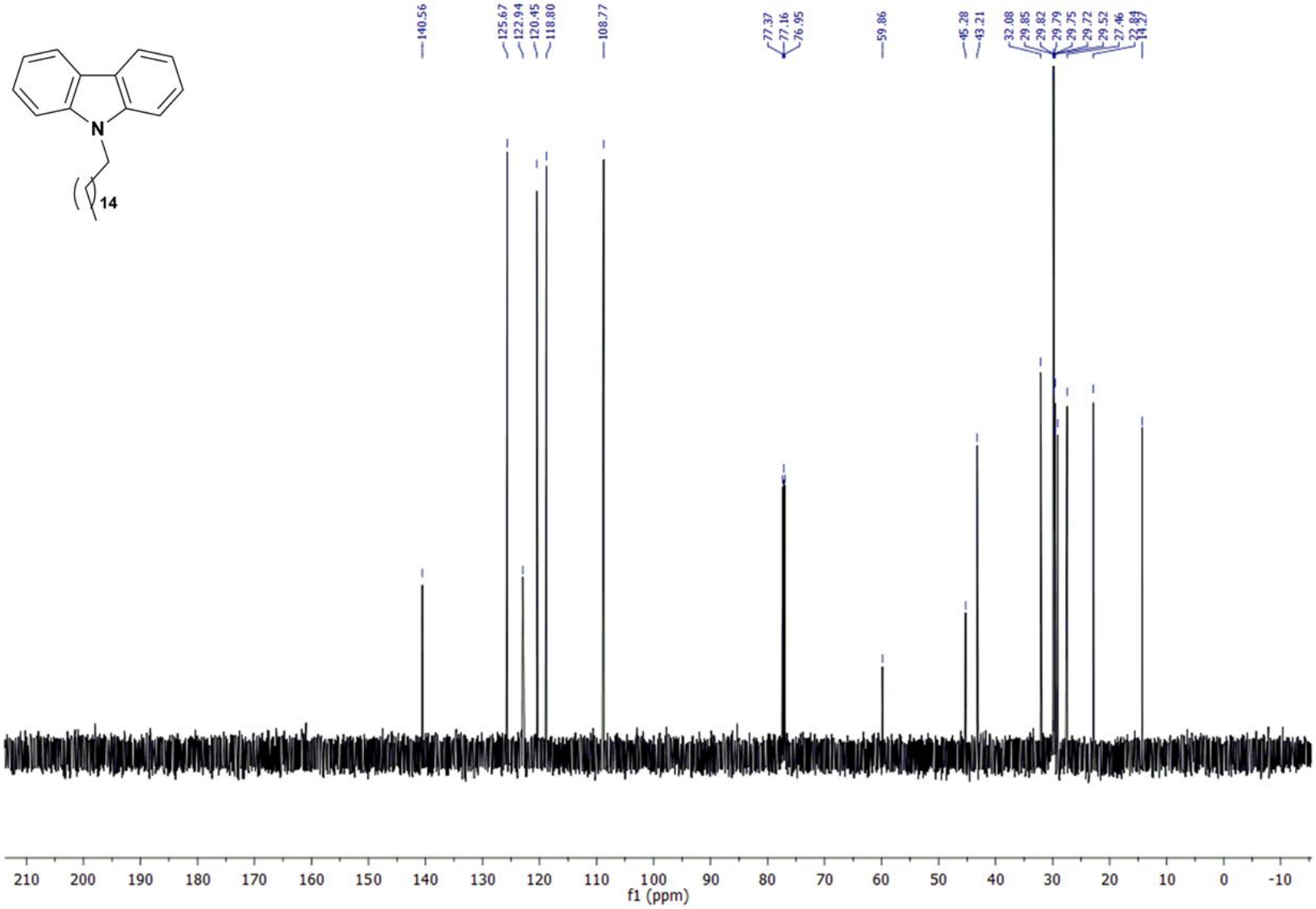
9-Ethylcarbazole – $^{13}C\ \{^{1}H\}$ NMR



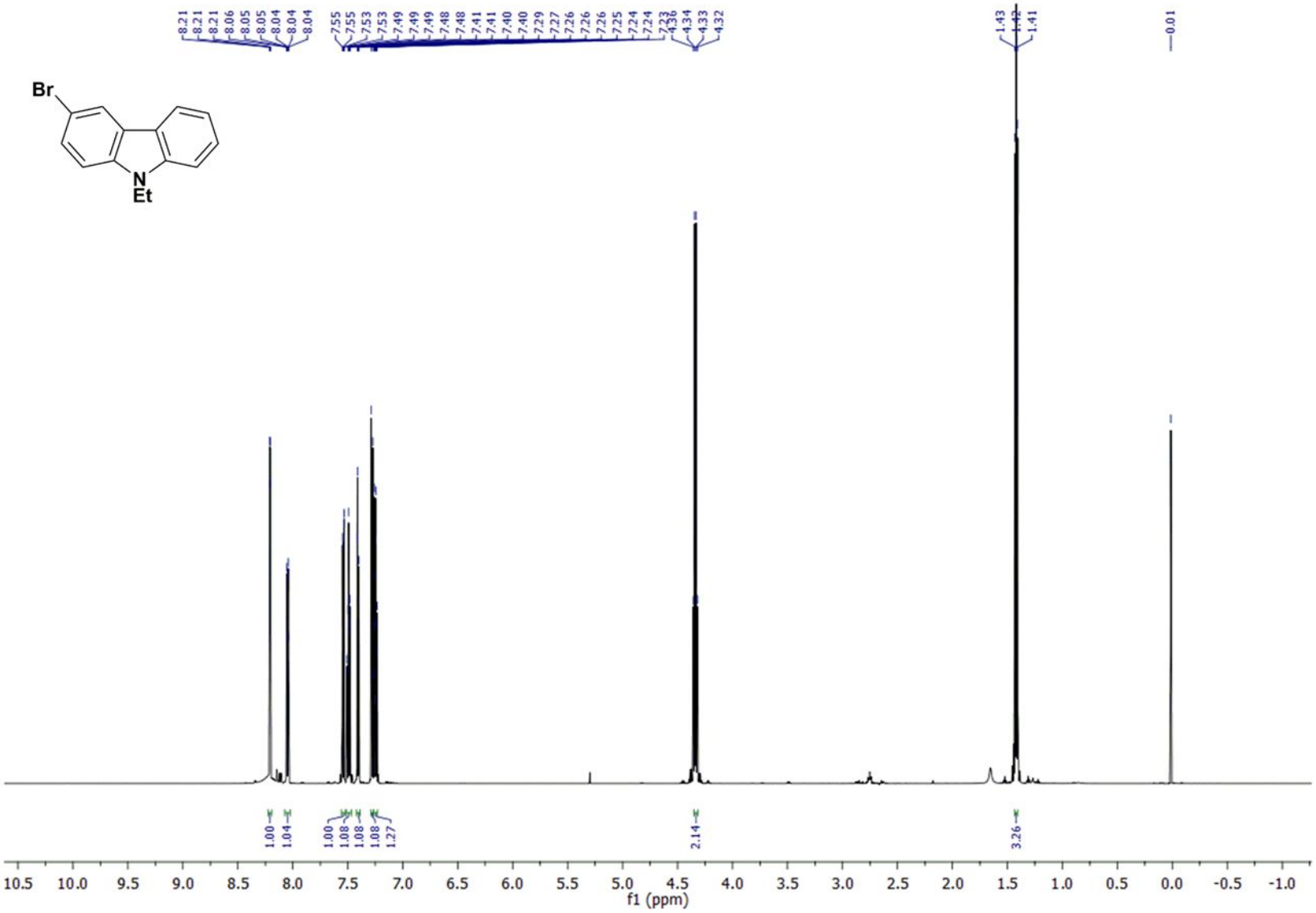
9-Hexadecylcarbazole – ^{1}H NMR



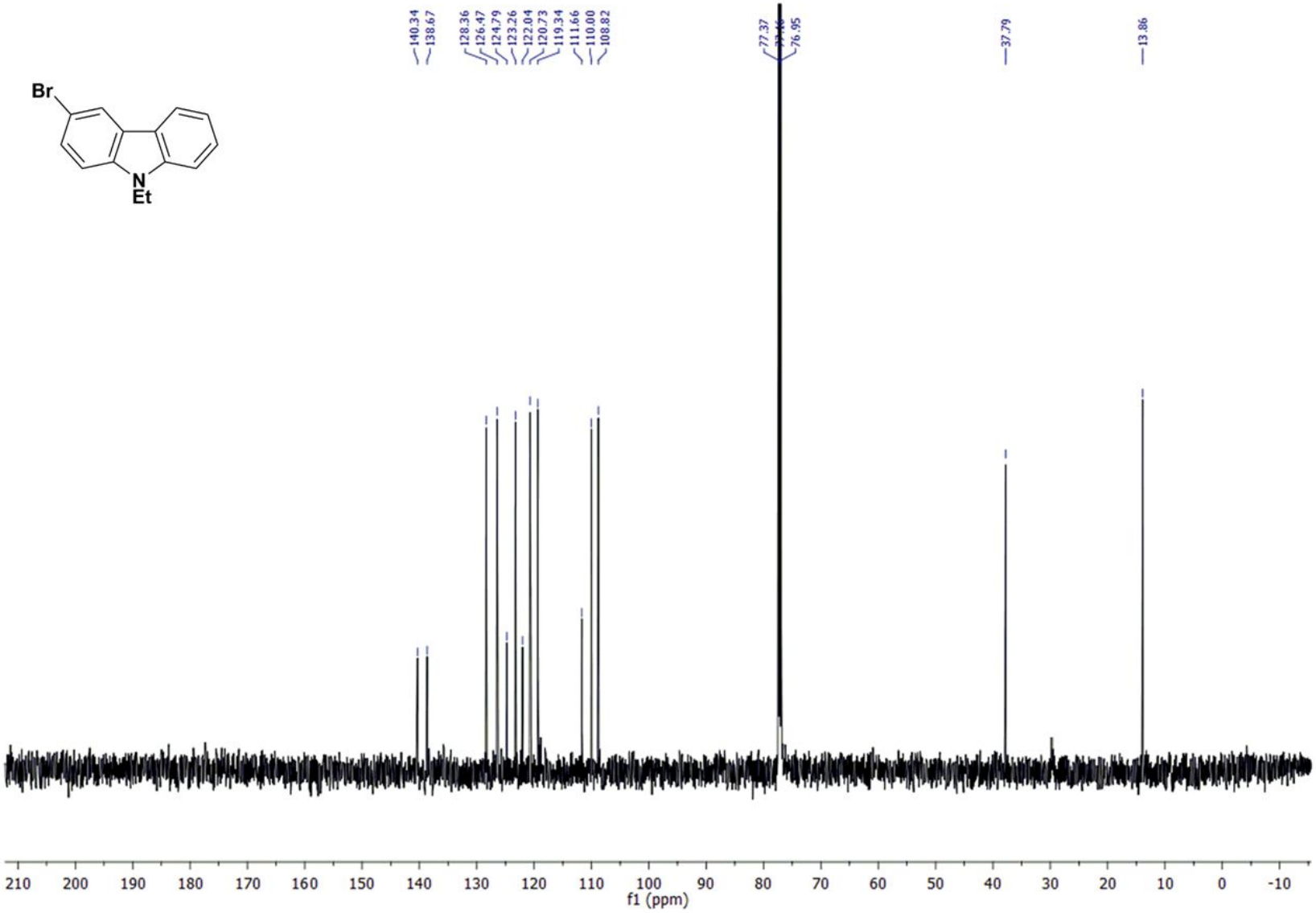
9-Hexadecylcarbazole – ^{13}C {^{1}H} NMR



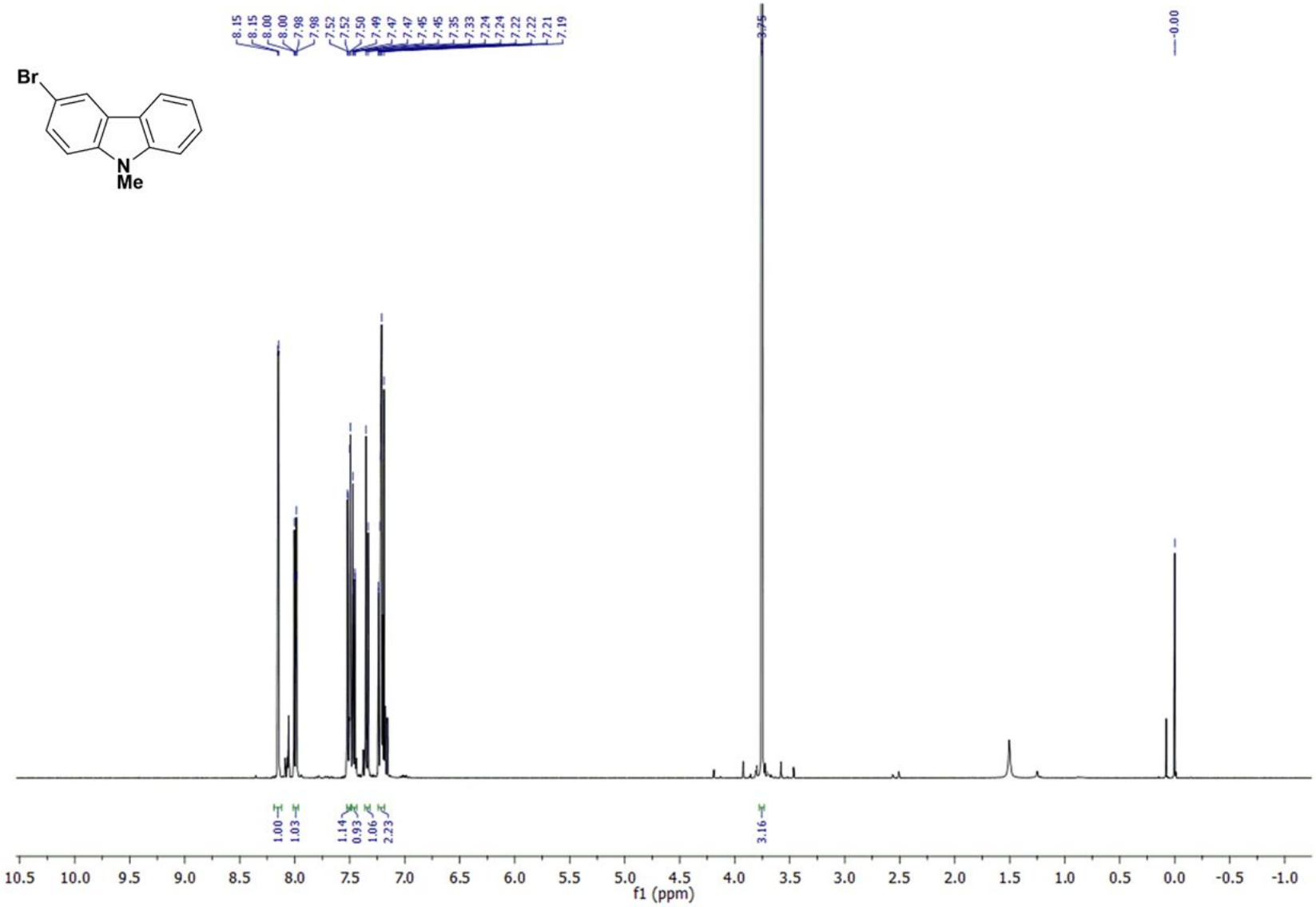
1a – ^{1}H NMR


Br
N
Et
8.21
8.21
8.21
8.06
8.05
8.05
8.04
8.04
8.04
7.55
7.55
7.53
7.53
7.49
7.49
7.49
7.48
7.48
7.41
7.41
7.40
7.40
7.29
7.27
7.26
7.26
7.26
7.25
7.24
7.24
7.23
4.36
4.34
4.33
4.32
1.43
1.42
1.41
0.01
1.00
1.04
1.00
1.08
1.08
1.08
1.27
2.14
3.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

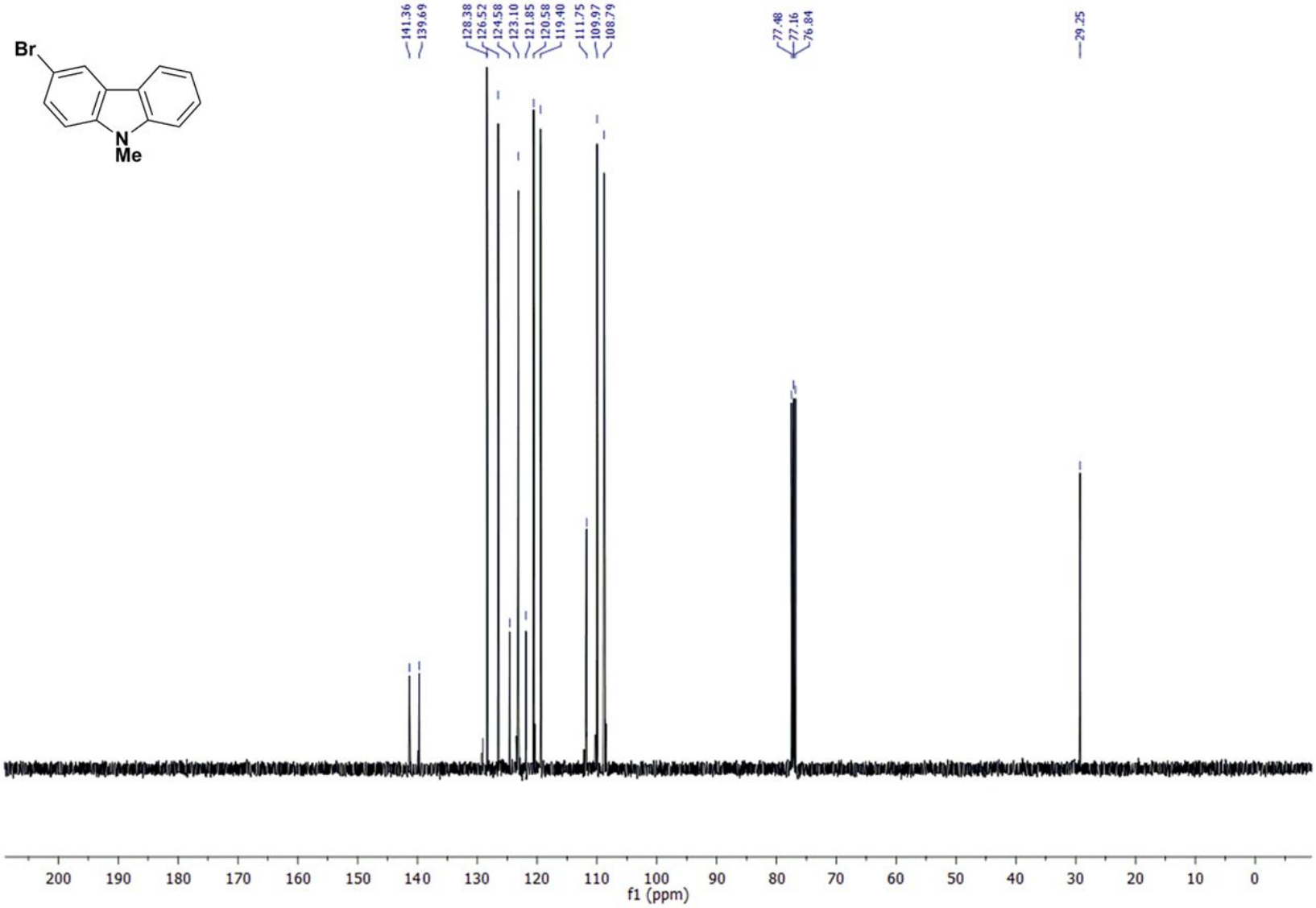
1a – ^{13}C {^{1}H} NMR


Br
N
Et
140.34
138.67
128.36
126.47
124.79
123.26
122.04
120.73
119.34
111.66
110.00
108.82
77.37
76.95
37.79
13.86
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)

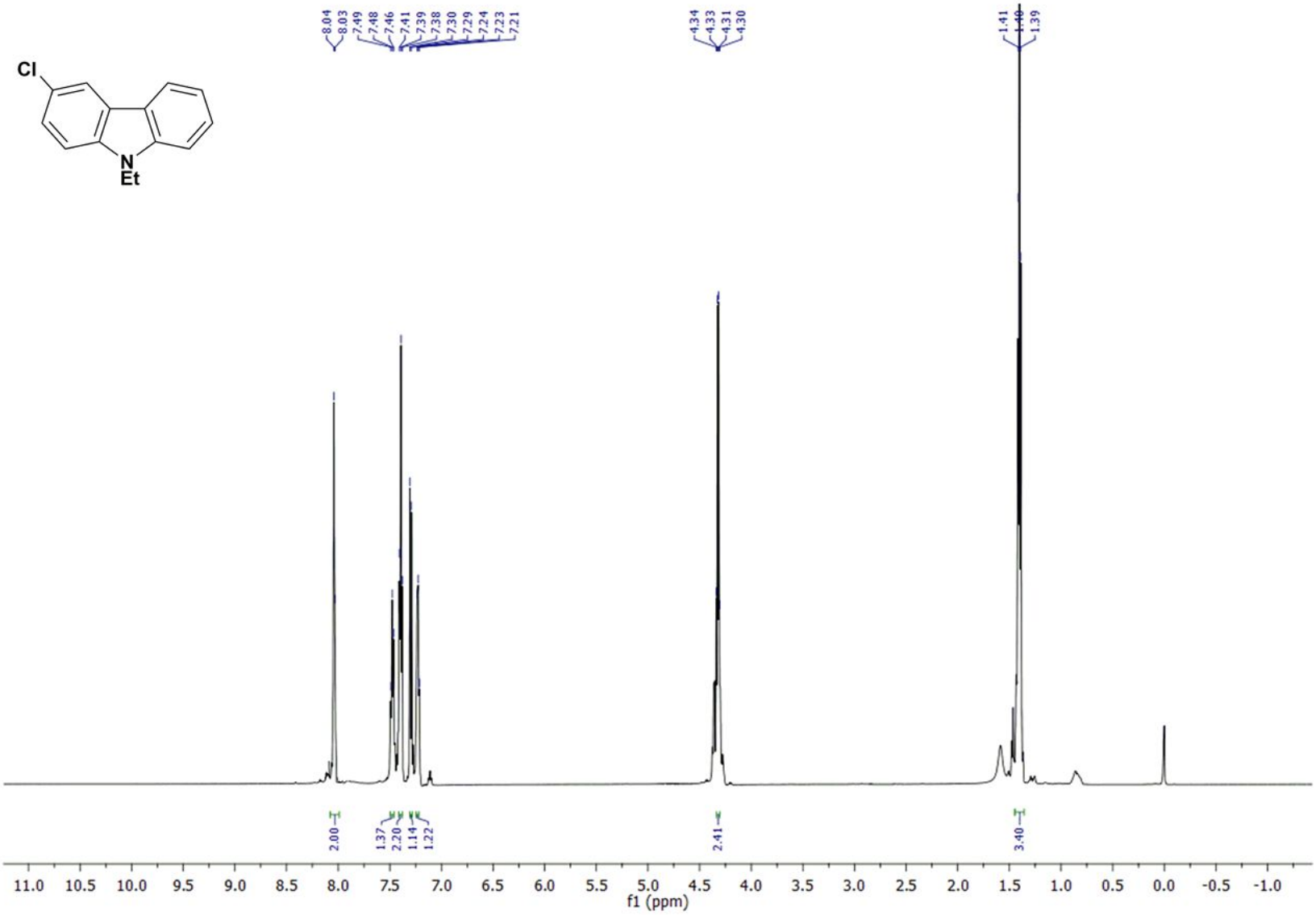
3-Bromo-9-methylcarbazole – ^{1}H NMR



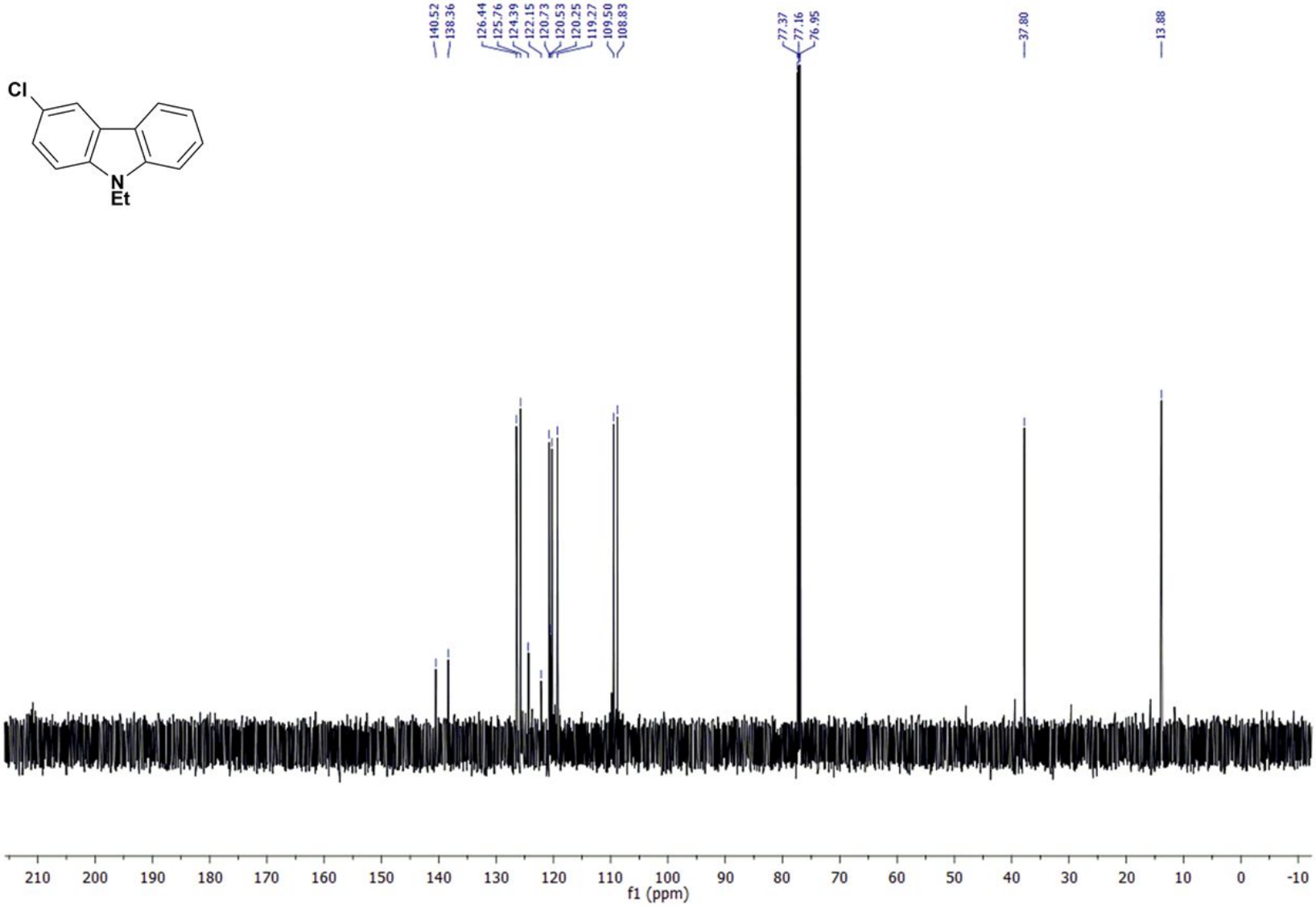
3-Bromo-9-methylcarbazole – $^{13}C\ \{^{1}H\}$ NMR



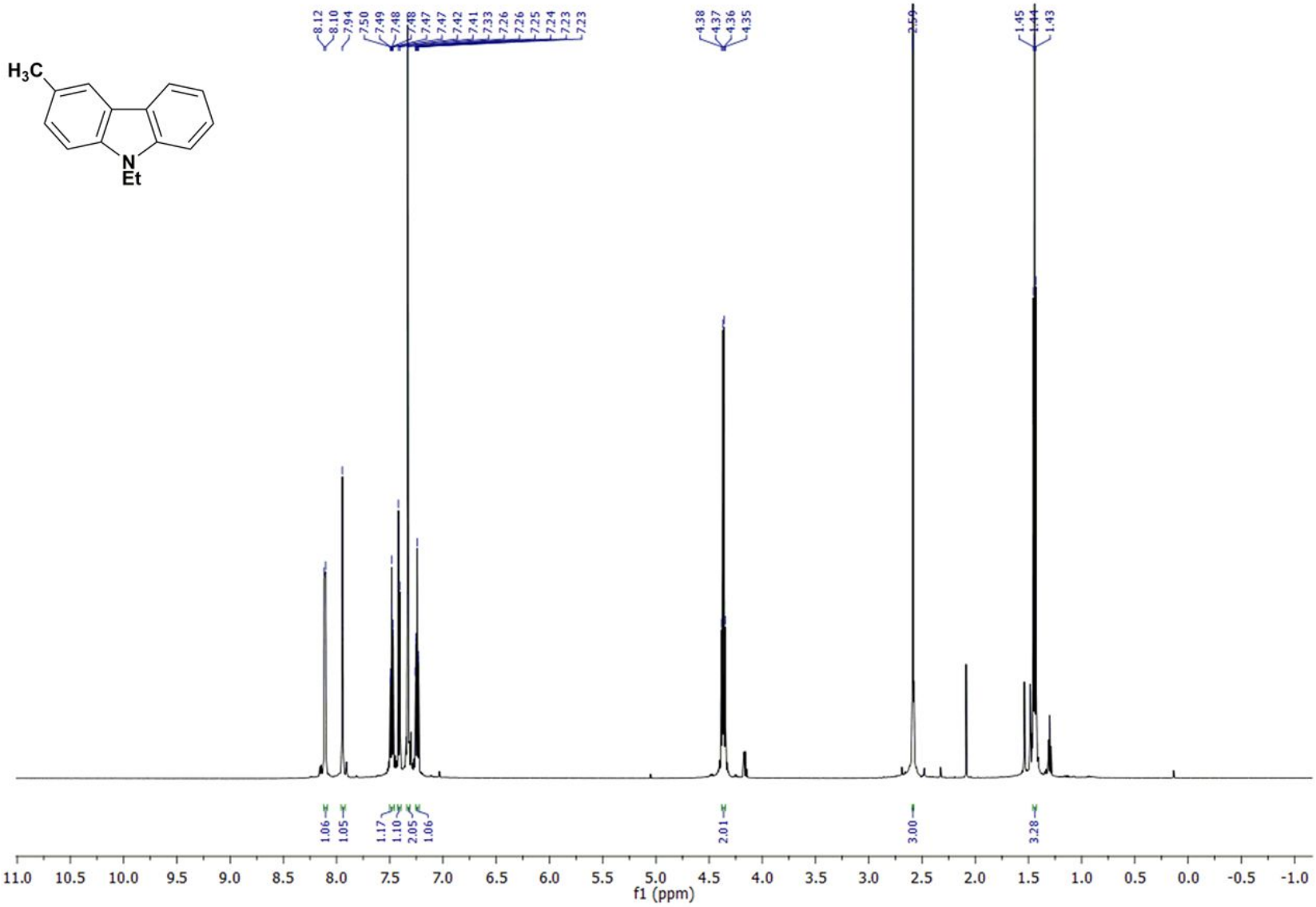
1j – ^{1}H NMR


Cl
N
Et
8.04
8.03
7.49
7.48
7.46
7.41
7.39
7.38
7.30
7.29
7.24
7.23
7.21
4.34
4.33
4.31
4.30
1.41
1.40
1.39
2.00
1.37
2.20
1.14
1.22
2.41
3.40
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

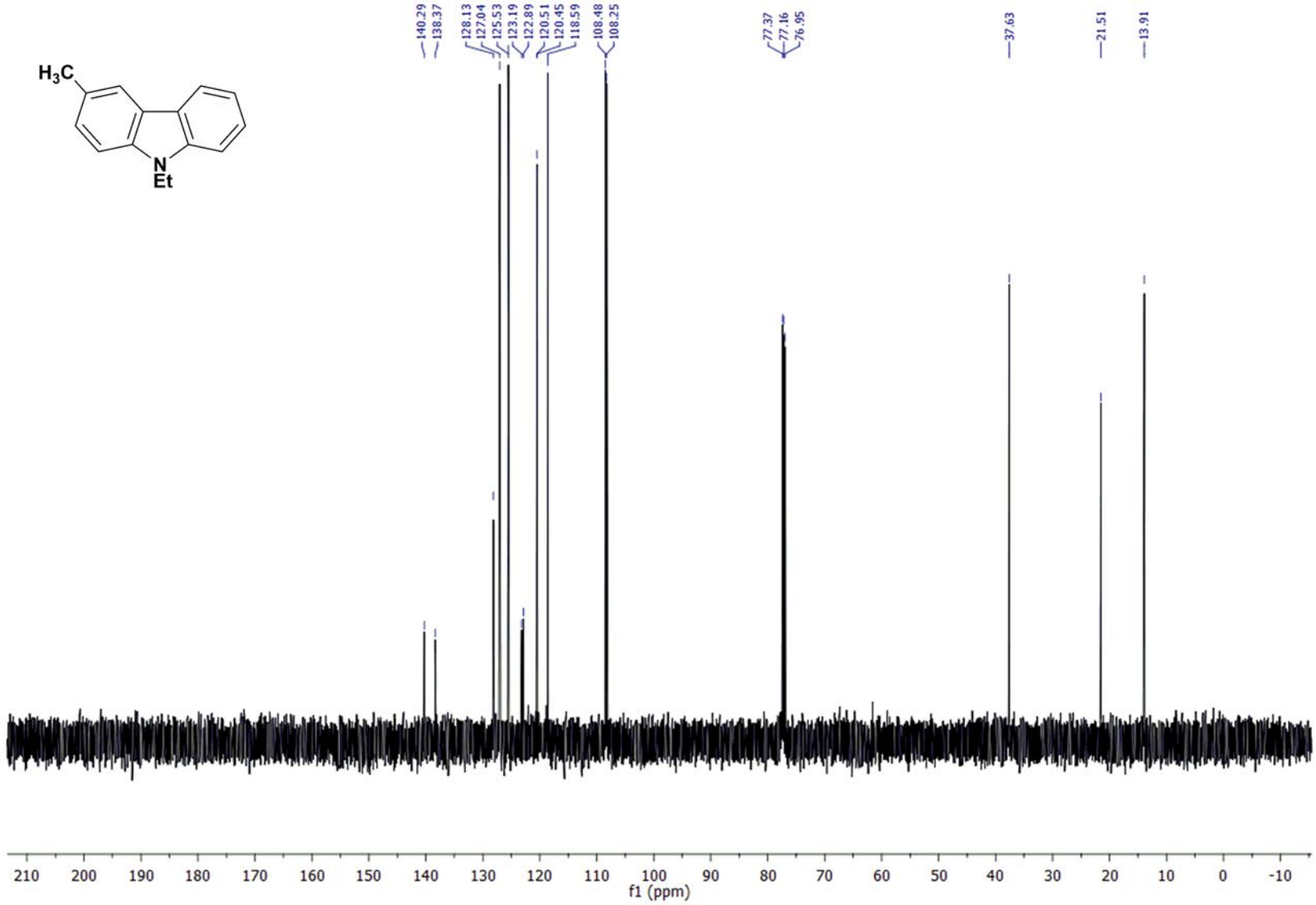
1j – ^{13}C {^{1}H} NMR


140.52
138.36
126.44
125.76
124.39
122.15
120.73
120.53
120.25
119.27
109.50
108.83
77.37
77.16
76.95
37.80
13.88
Cl
N
Et
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)

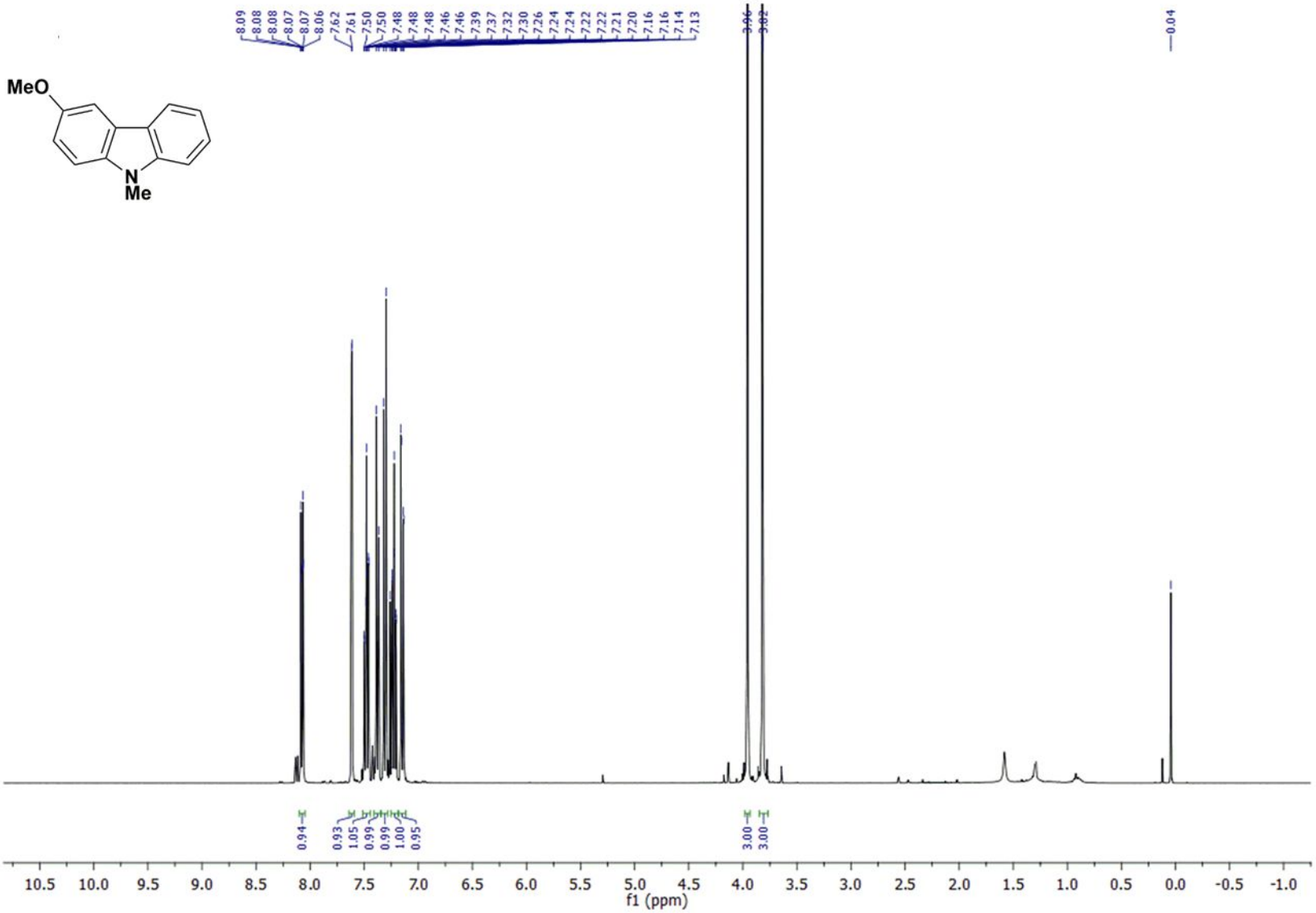
1g – ^{1}H NMR


H3C
N
Et
8.12
8.10
7.94
7.50
7.49
7.48
7.48
7.47
7.47
7.42
7.41
7.33
7.26
7.26
7.25
7.24
7.23
7.23
4.38
4.37
4.36
4.35
2.59
1.45
1.44
1.43
1.06
1.05
1.17
1.10
2.05
1.06
2.01
3.00
3.28
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

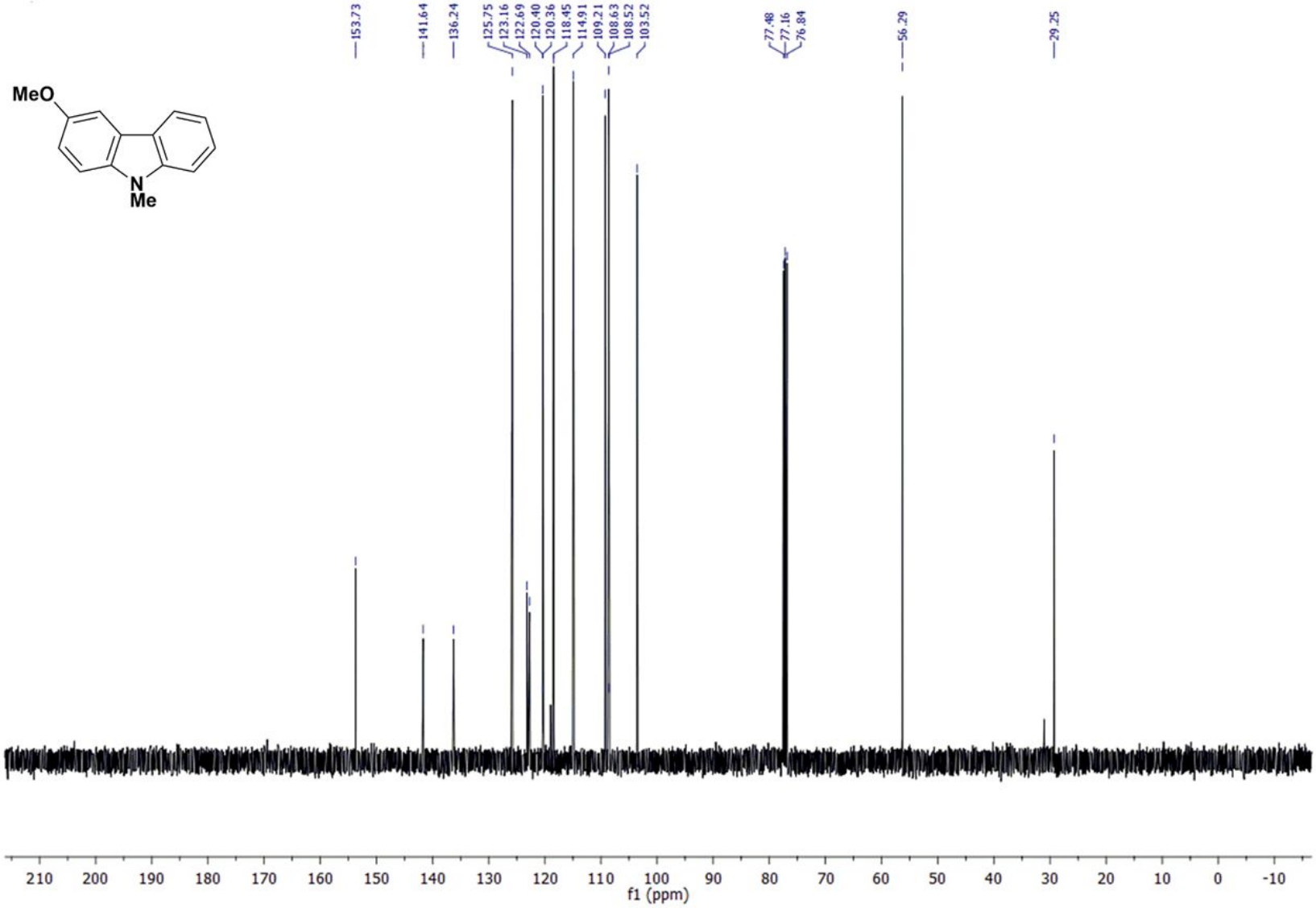
1g – ^{13}C {^{1}H} NMR


H3C
N
Et
140.29
138.37
128.13
127.04
125.53
123.19
122.89
120.51
120.45
118.59
108.48
108.25
77.37
77.16
76.95
37.63
21.51
13.91
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)

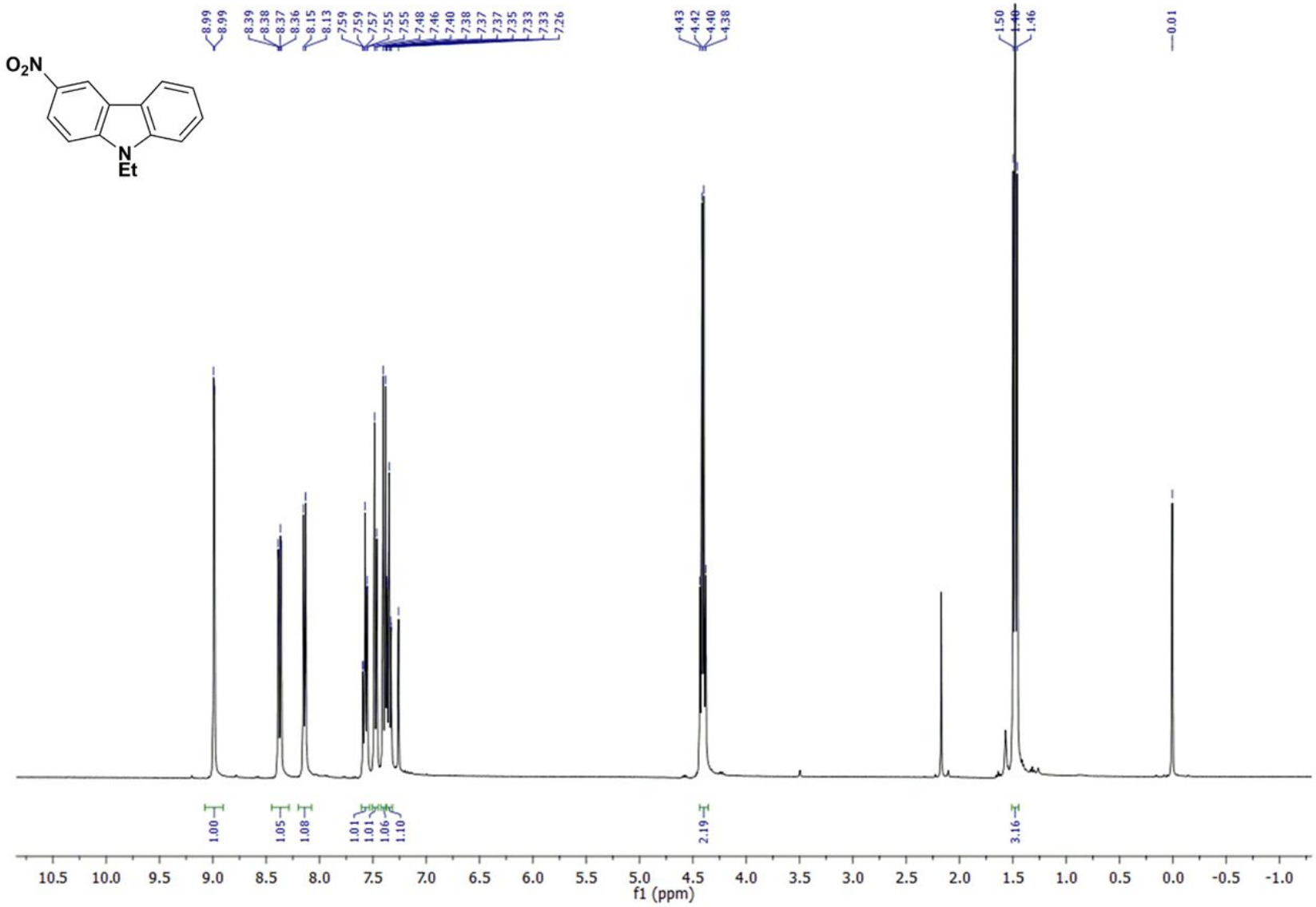
1i – ^{1}H NMR


MeO
N
Me
8.09
8.08
8.08
8.07
8.07
8.06
7.62
7.61
7.50
7.50
7.48
7.48
7.48
7.46
7.46
7.39
7.37
7.32
7.30
7.26
7.24
7.24
7.22
7.22
7.21
7.20
7.16
7.16
7.14
7.13
3.96
3.82
0.04
0.94
0.93
1.05
0.99
0.99
1.00
0.95
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

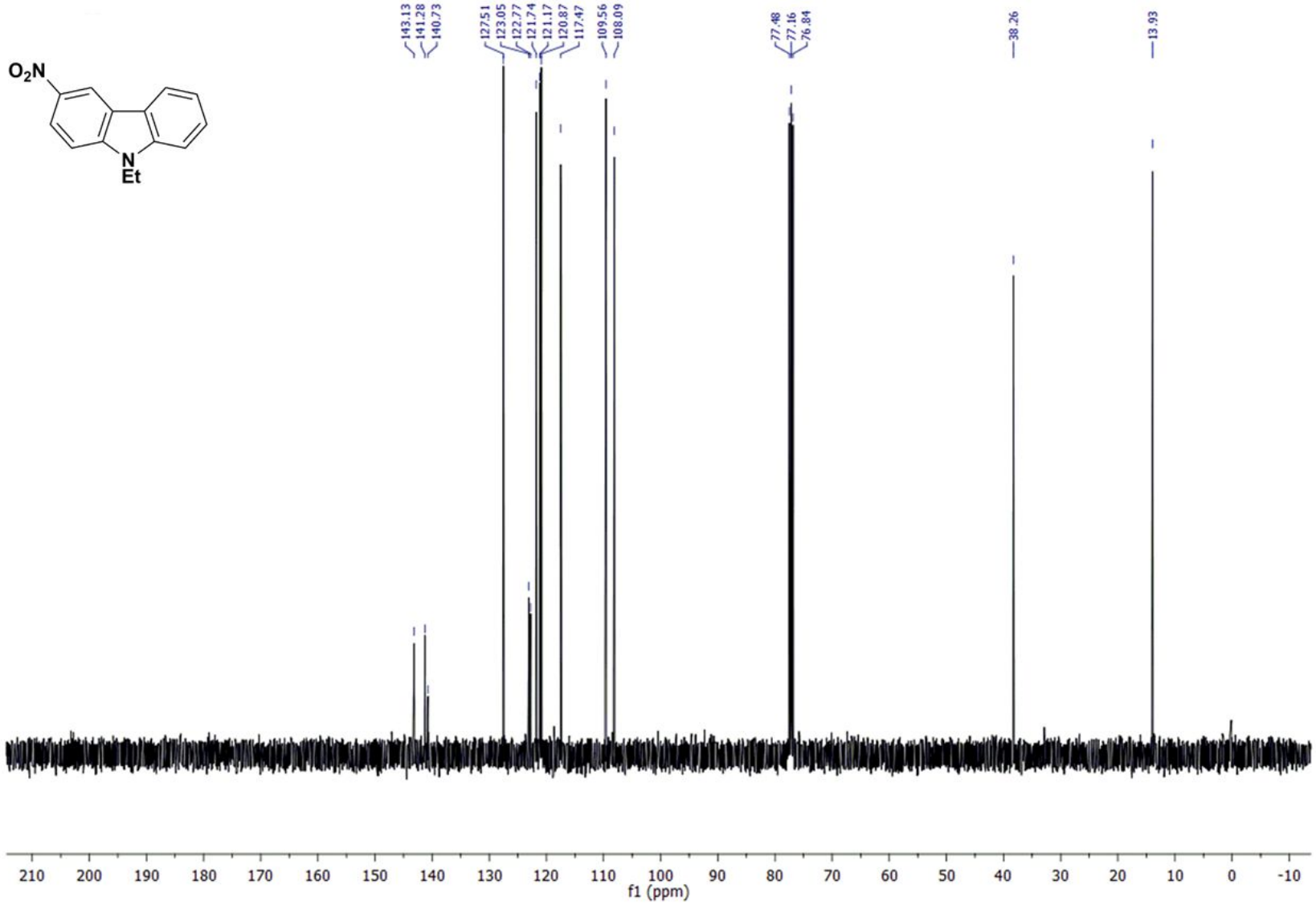
1i – ^{13}C {^{1}H} NMR


153.73
141.64
136.24
125.75
123.16
122.69
120.40
120.36
118.45
114.91
109.21
108.63
108.52
103.52
77.48
77.16
76.84
56.29
29.25
MeO
N
Me
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)

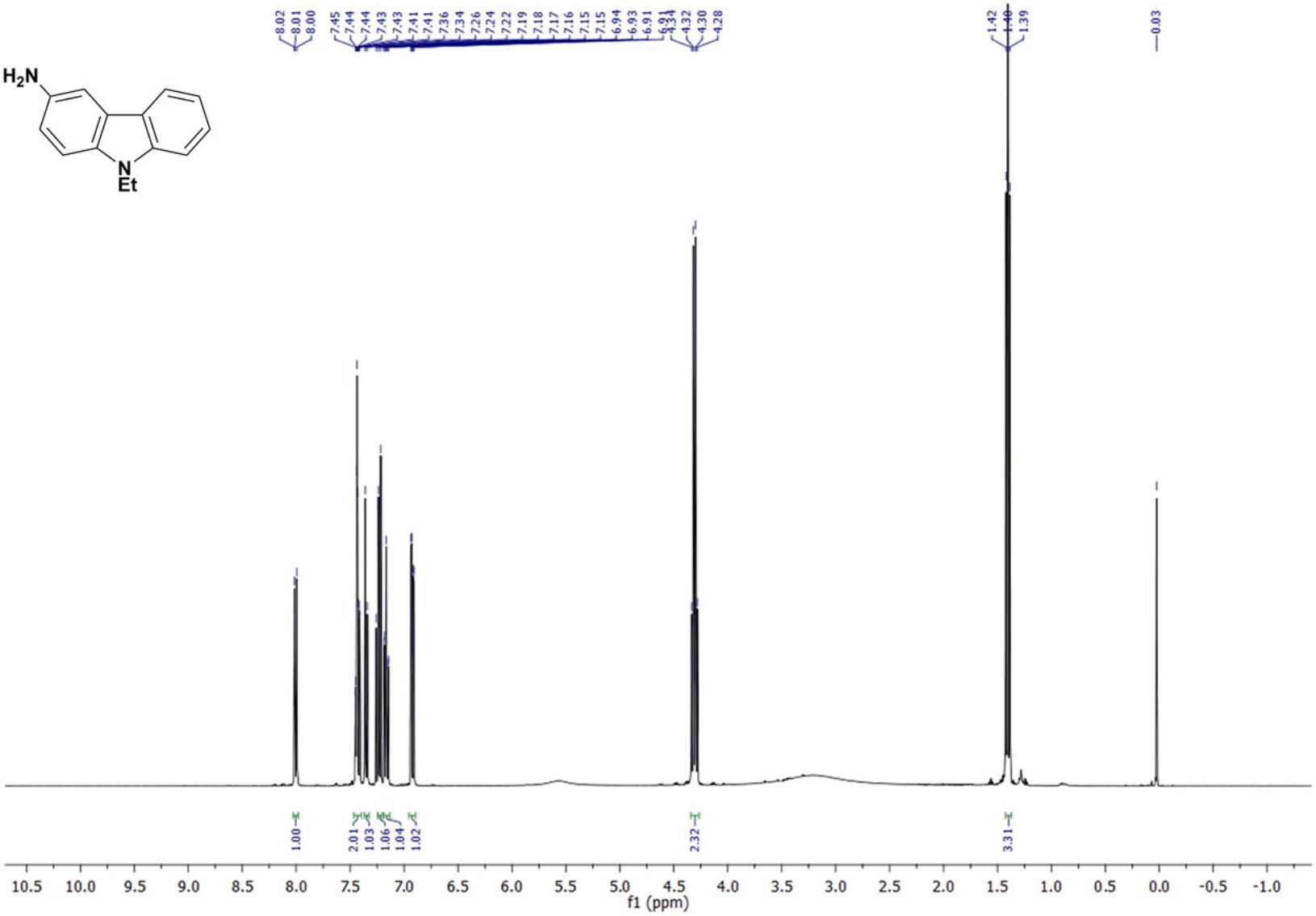
1b – ^{1}H NMR


O2N
N
Et
8.99
8.99
8.39
8.38
8.37
8.36
8.15
8.13
7.59
7.59
7.57
7.55
7.55
7.48
7.46
7.40
7.38
7.37
7.37
7.35
7.33
7.33
7.26
4.43
4.42
4.40
4.38
1.50
1.48
1.46
0.01
1.00
1.05
1.08
1.01
1.01
1.06
1.10
2.19
3.16
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

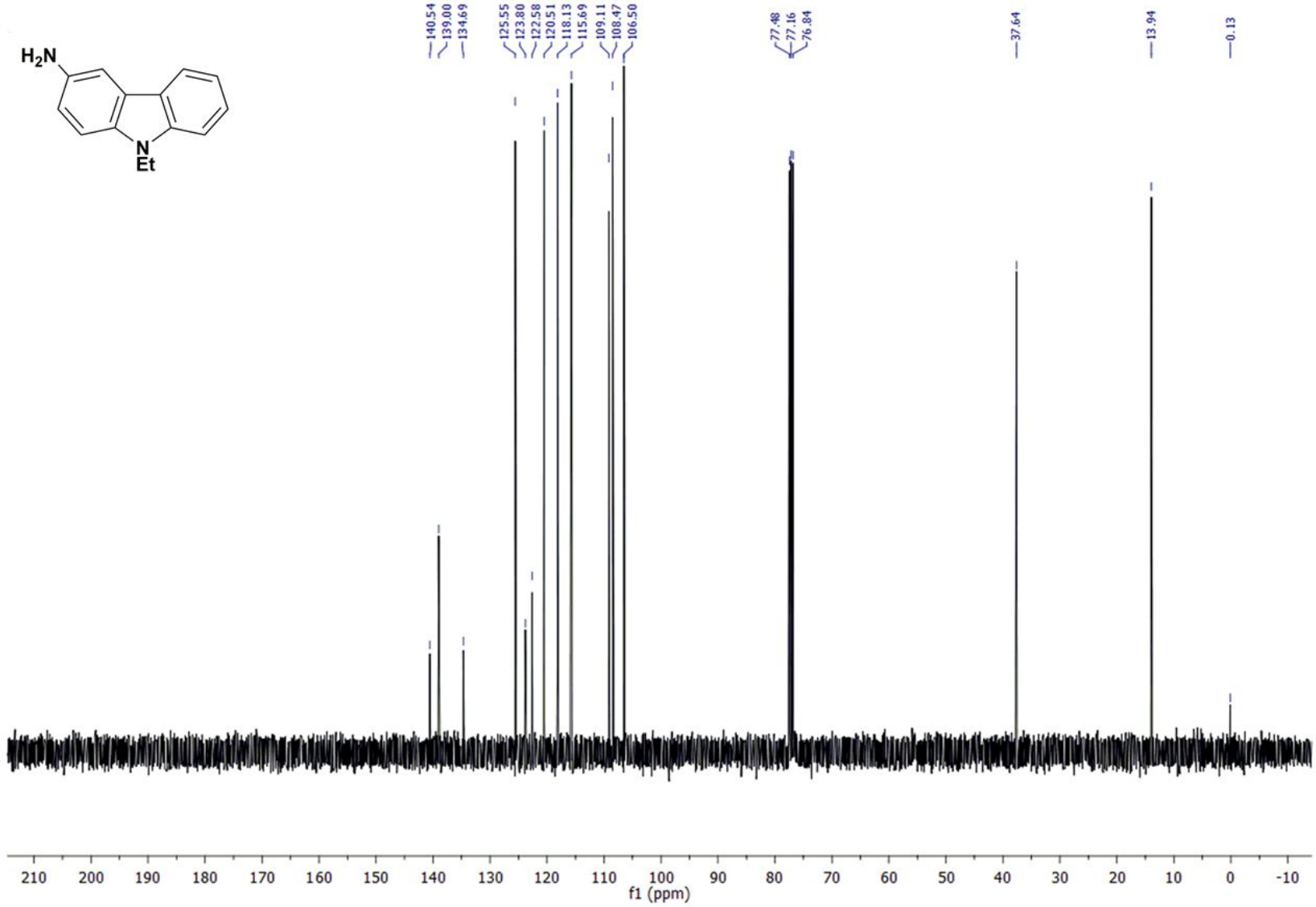
1b – ^{13}C {^{1}H} NMR


143.13
141.28
140.73
127.51
123.05
122.77
121.74
121.17
120.87
117.47
109.56
108.09
77.48
77.16
76.84
38.26
13.93
O2N
N
Et
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)

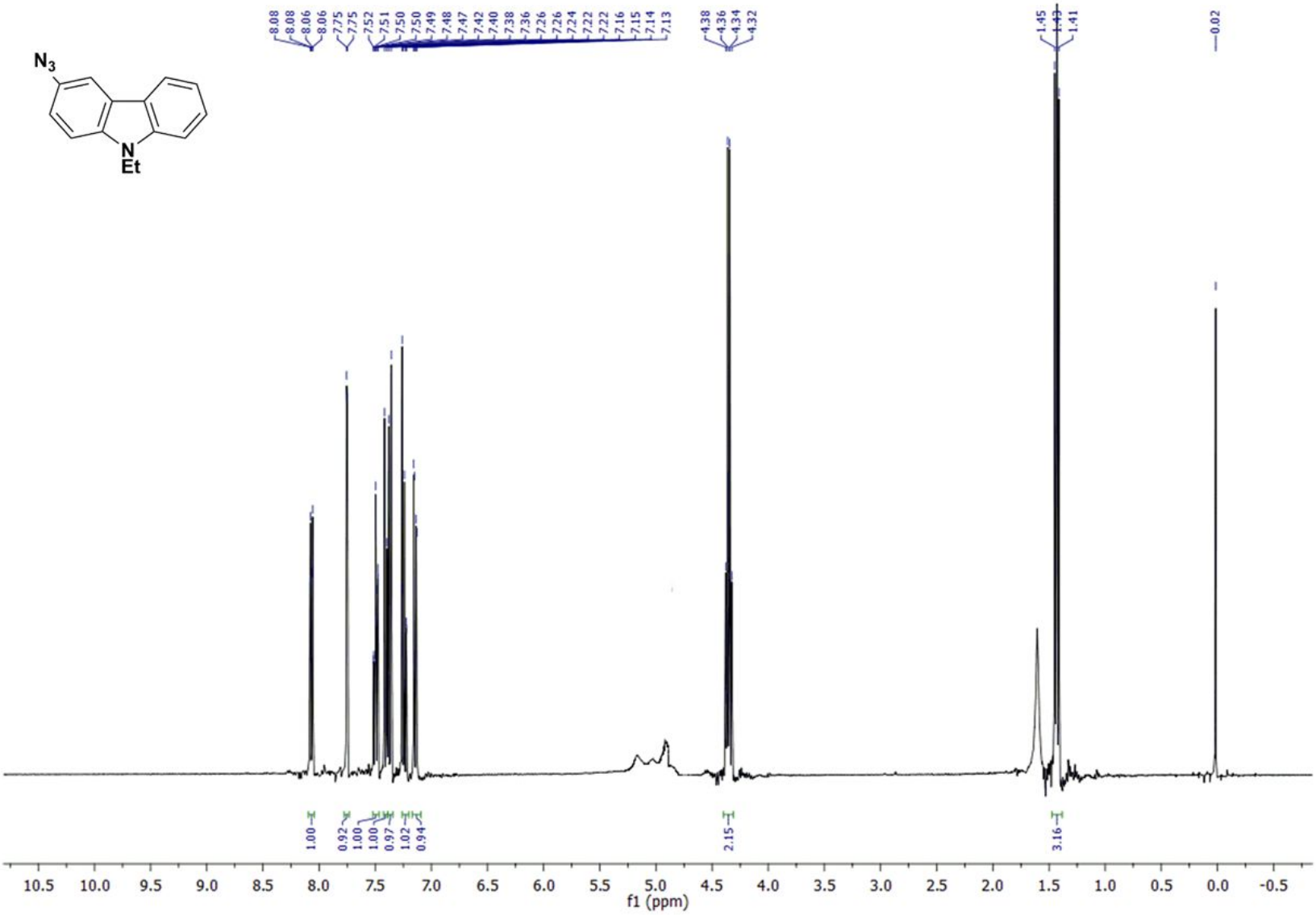
3-Amino-9-ethylcarbazole – ^{1}H NMR



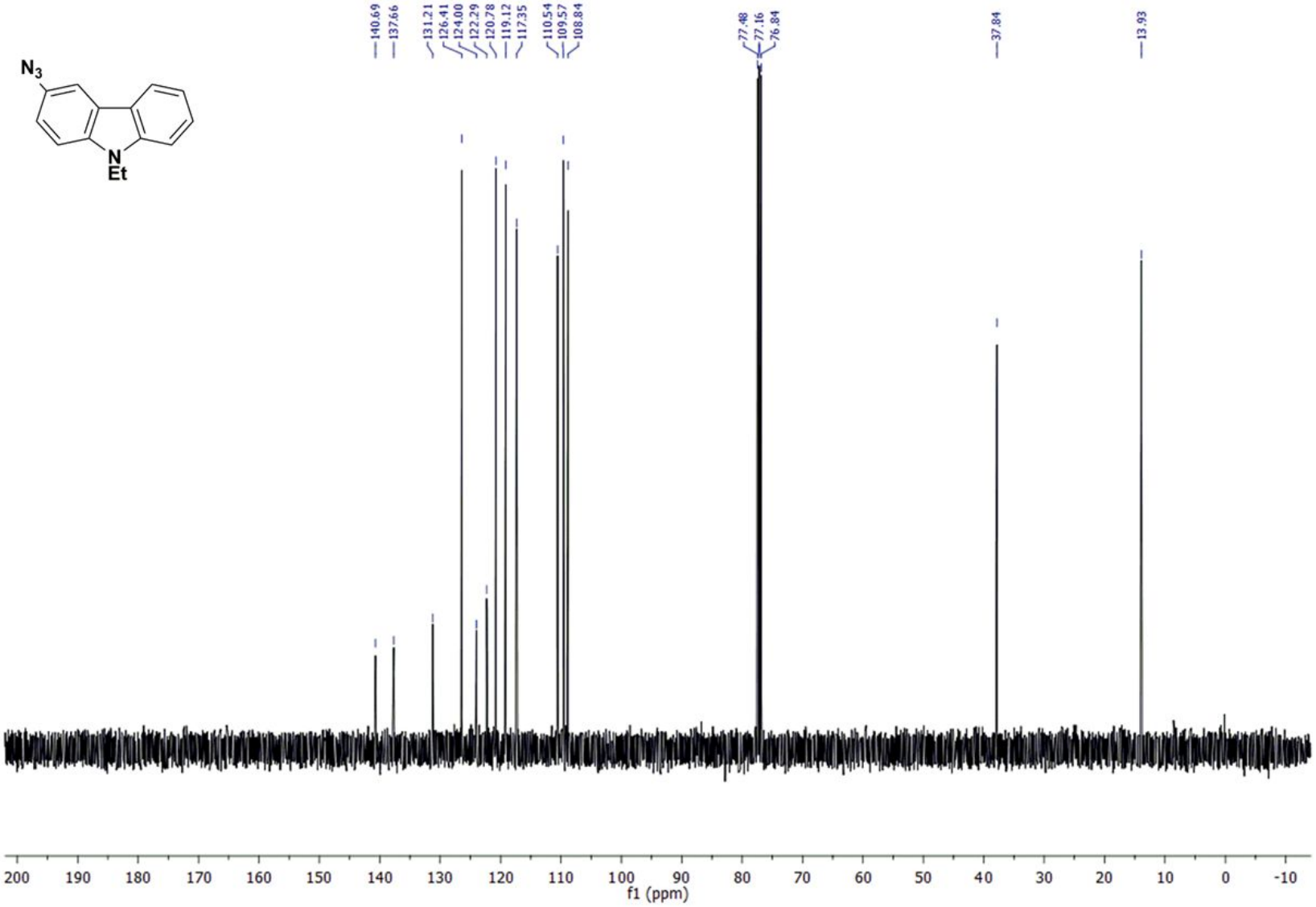
3-Amino-9-ethylcarbazole – $^{13}C\ \{^{1}H\}$ NMR



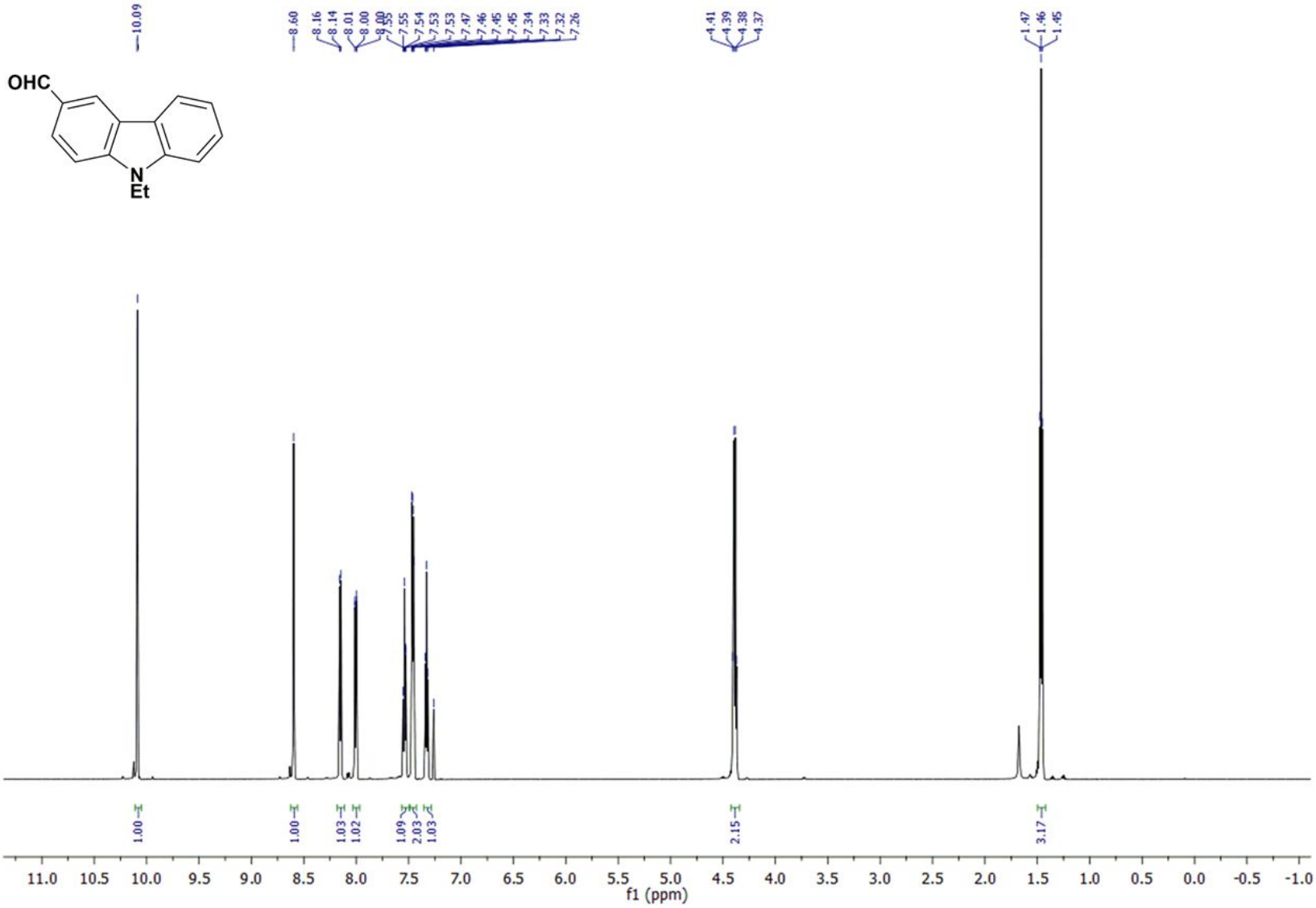
1n – ^{1}H NMR


N3
N
Et
8.08
8.08
8.06
8.06
7.75
7.75
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.42
7.40
7.38
7.36
7.26
7.26
7.24
7.22
7.22
7.16
7.15
7.14
7.13
4.38
4.36
4.34
4.32
1.45
1.43
1.41
0.02
1.00
0.92
1.00
1.00
0.97
1.02
0.94
2.15
3.16
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

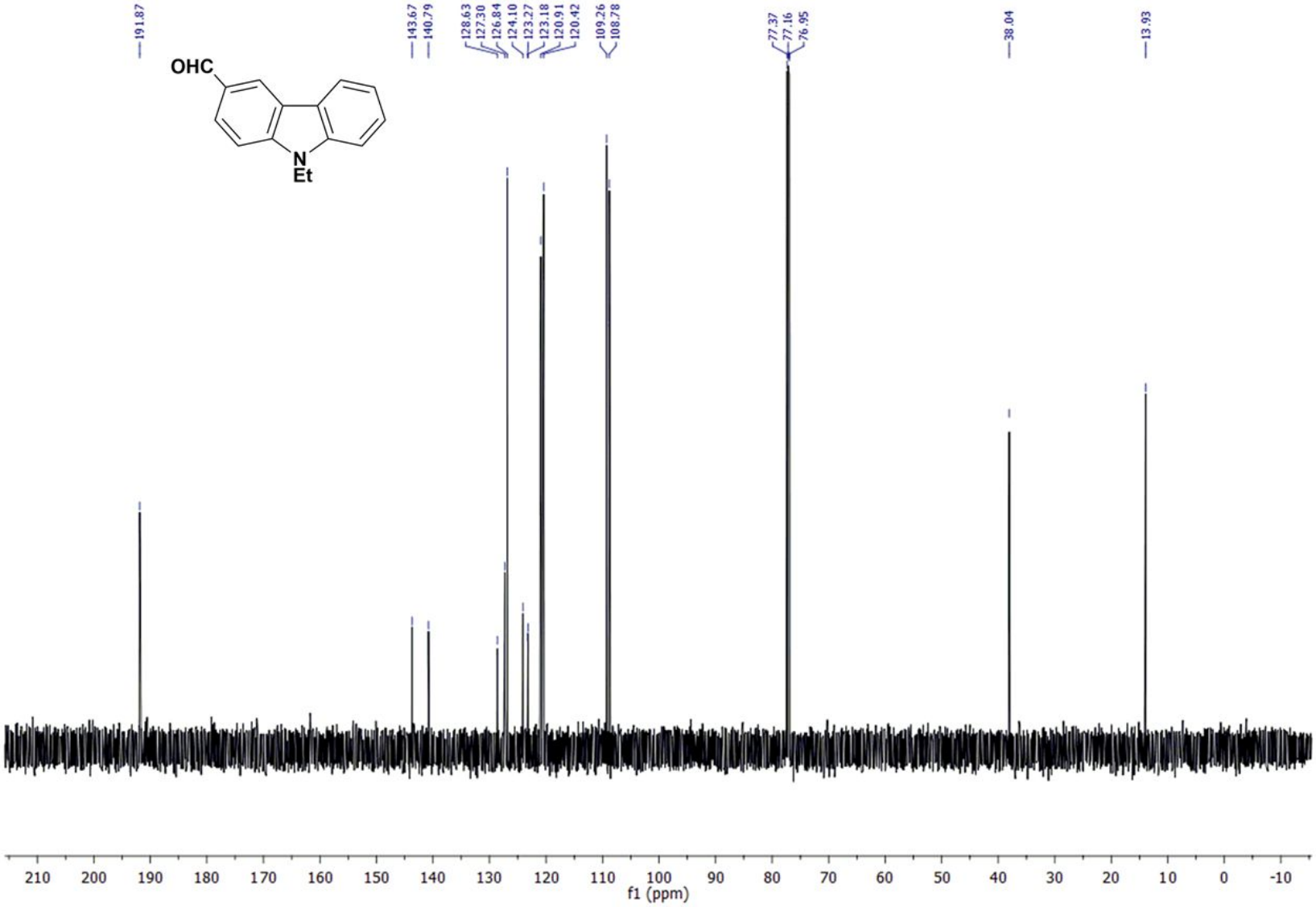
1n – ^{13}C {^{1}H} NMR


140.69
137.66
131.21
126.41
124.00
122.29
120.78
119.12
117.35
110.54
109.57
108.84
77.48
77.16
76.84
37.84
13.93
N3
N
Et
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

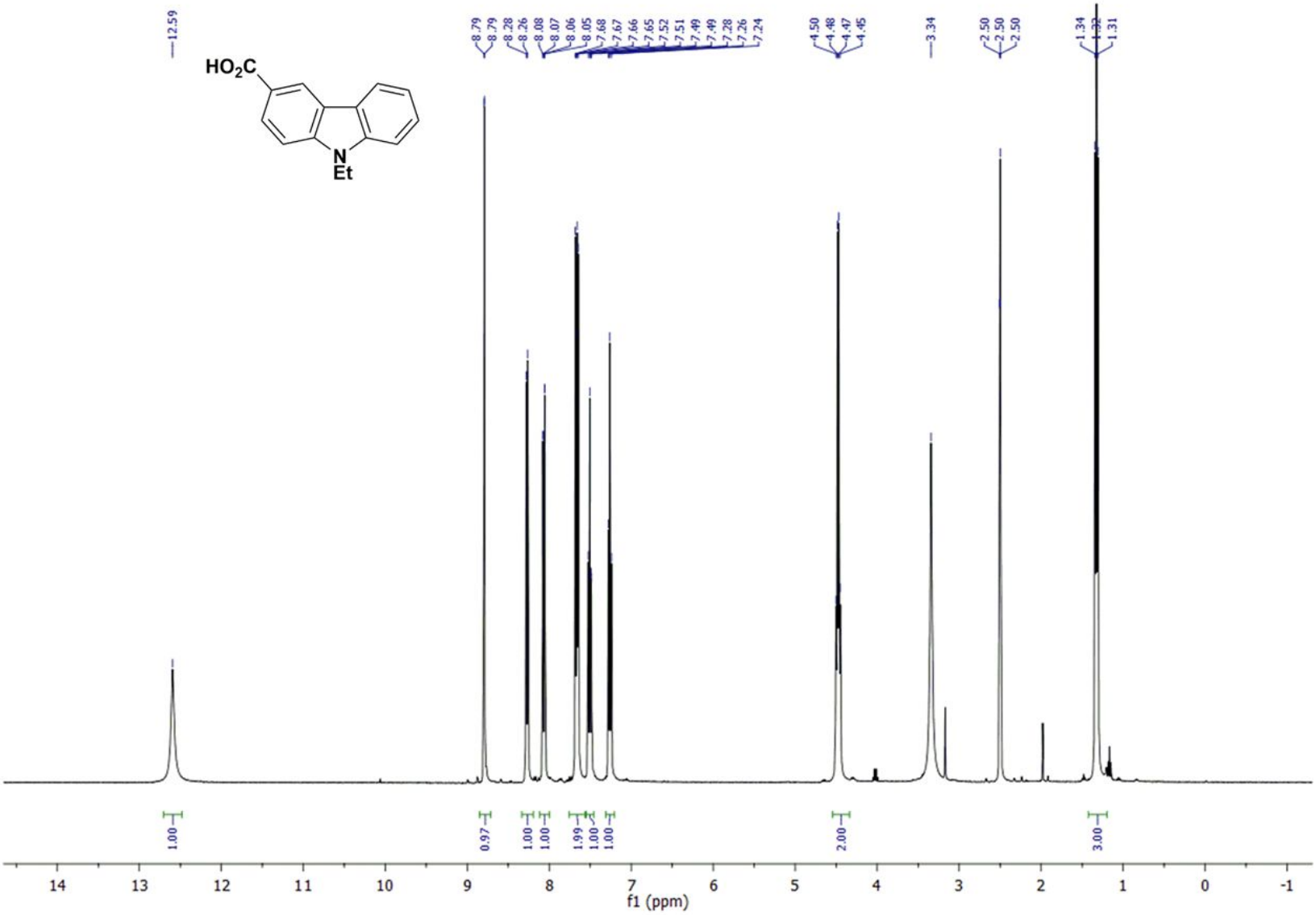
1o – ^{1}H NMR


OHC
N
Et
10.09
8.60
8.16
8.14
8.01
8.00
7.55
7.54
7.53
7.47
7.46
7.45
7.45
7.34
7.33
7.32
7.26
4.41
4.39
4.38
4.37
1.47
1.46
1.45
1.00
1.00
1.03
1.02
1.09
2.03
1.03
2.15
3.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

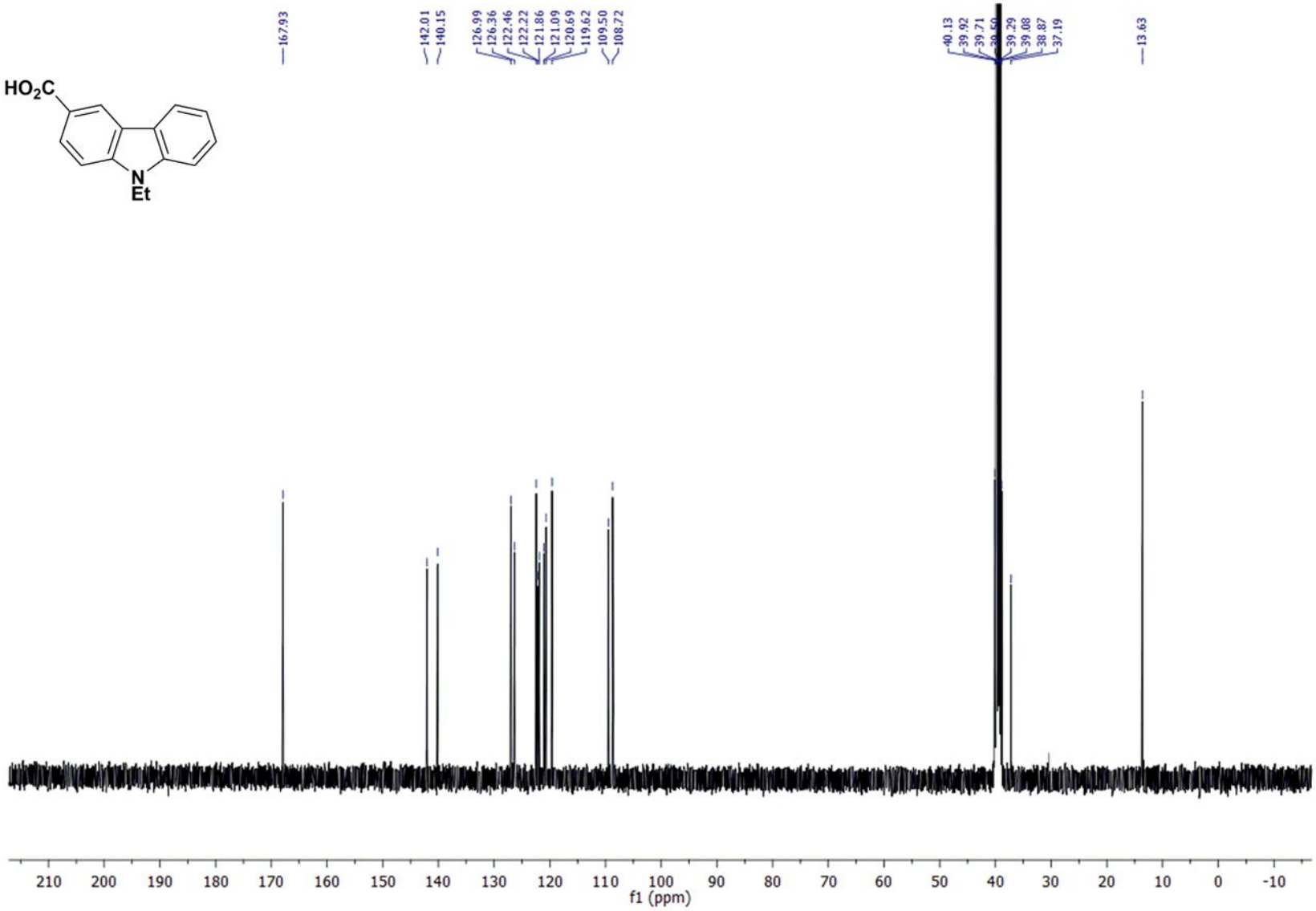
1o – ^{13}C {1H} NMR


191.87
143.67
140.79
128.63
127.30
126.84
124.10
123.27
123.18
120.91
120.42
109.26
108.78
77.37
77.16
76.95
38.04
13.93
OHC
N
Et
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)

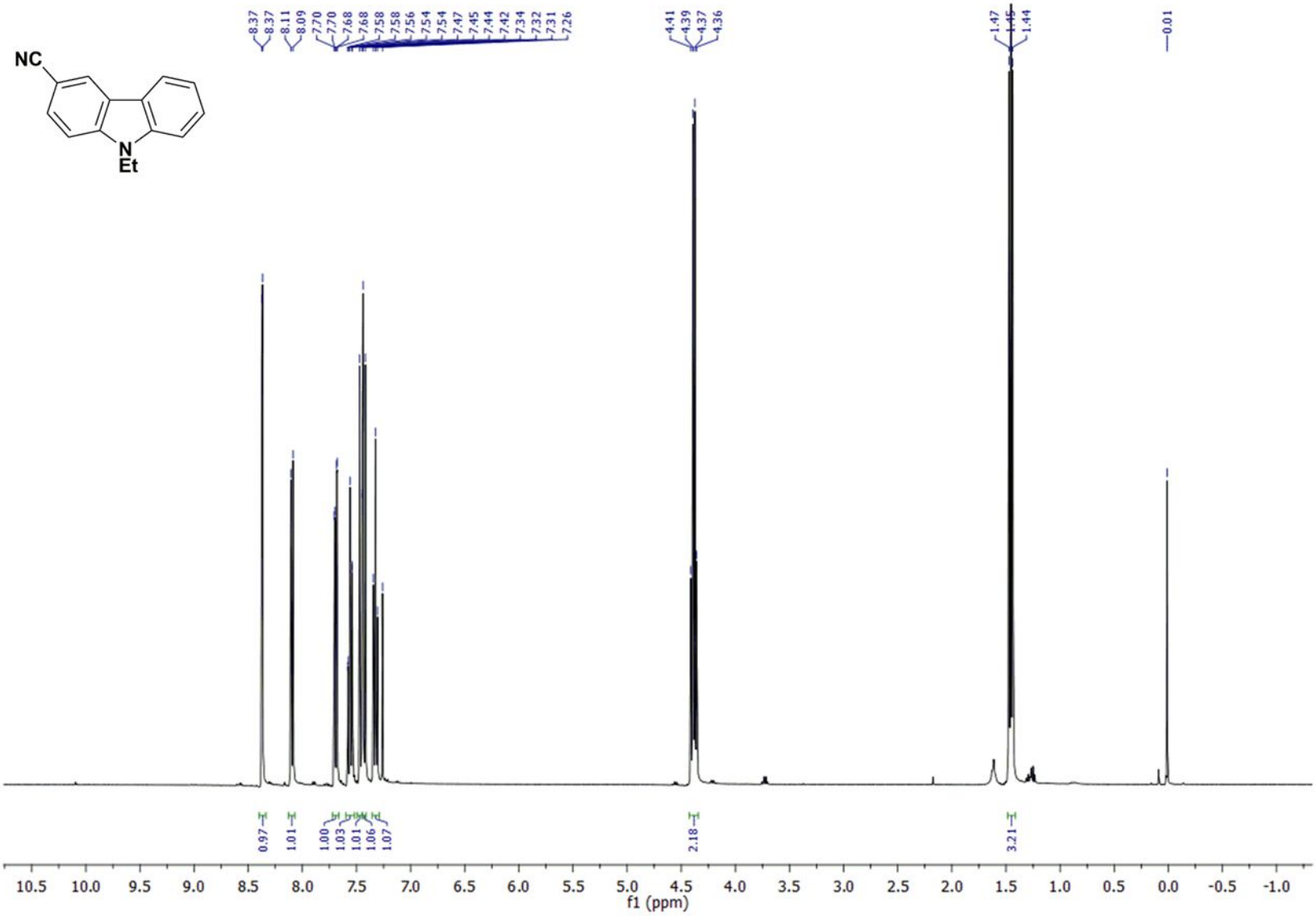
1p – ^{1}H NMR


HO2C
N
Et
12.59
8.79
8.79
8.28
8.26
8.08
8.07
8.06
8.05
7.68
7.67
7.66
7.65
7.52
7.51
7.49
7.49
7.28
7.26
7.24
4.50
4.48
4.47
4.45
3.34
2.50
2.50
2.50
1.34
1.32
1.31
1.00
0.97
1.00
1.00
1.99
1.00
1.00
2.00
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

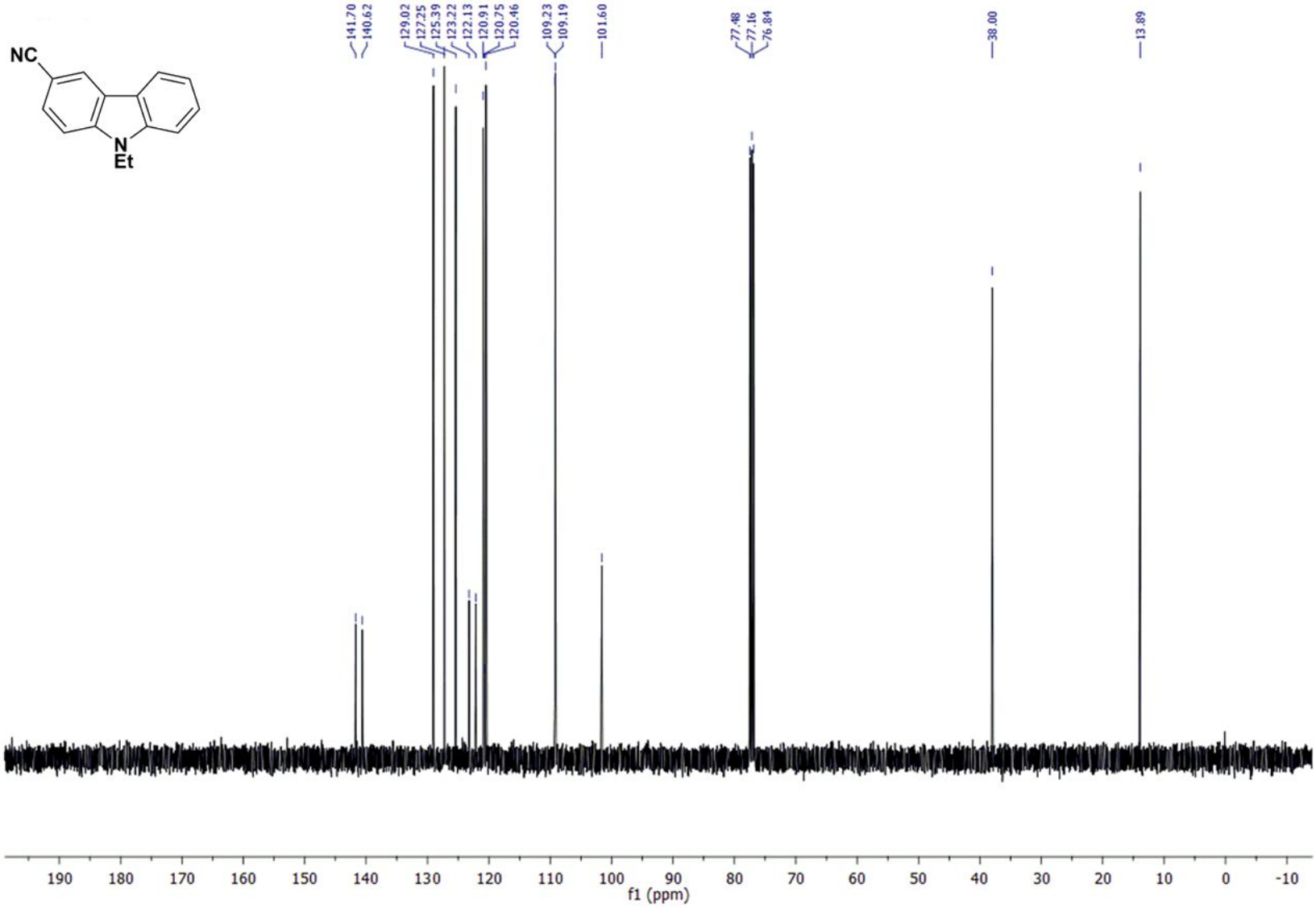
1p – ^{13}C {^{1}H} NMR


HO2C
N
Et
167.93
142.01
140.15
126.99
126.36
122.46
122.22
121.86
121.09
120.69
119.62
109.50
108.72
40.13
39.92
39.71
39.29
39.08
38.87
37.19
13.63
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)

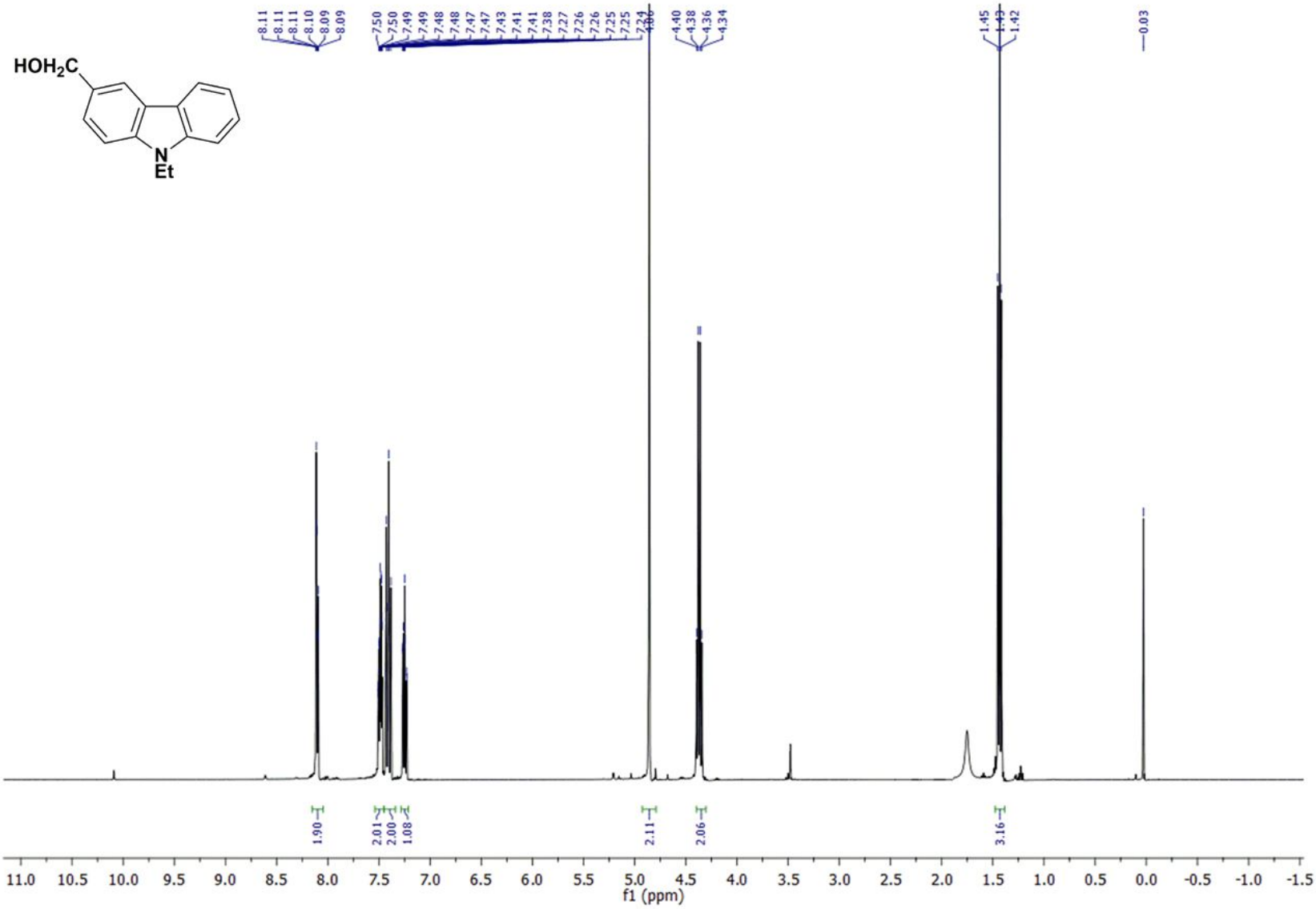
1q – ^{1}H NMR


NC
N
Et
8.37
8.37
8.11
8.09
7.70
7.70
7.68
7.68
7.58
7.58
7.56
7.54
7.54
7.47
7.45
7.44
7.42
7.34
7.32
7.31
7.26
4.41
4.39
4.37
4.36
1.47
1.45
1.44
0.01
0.97
1.01
1.00
1.03
1.01
1.06
1.07
2.18
3.21
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

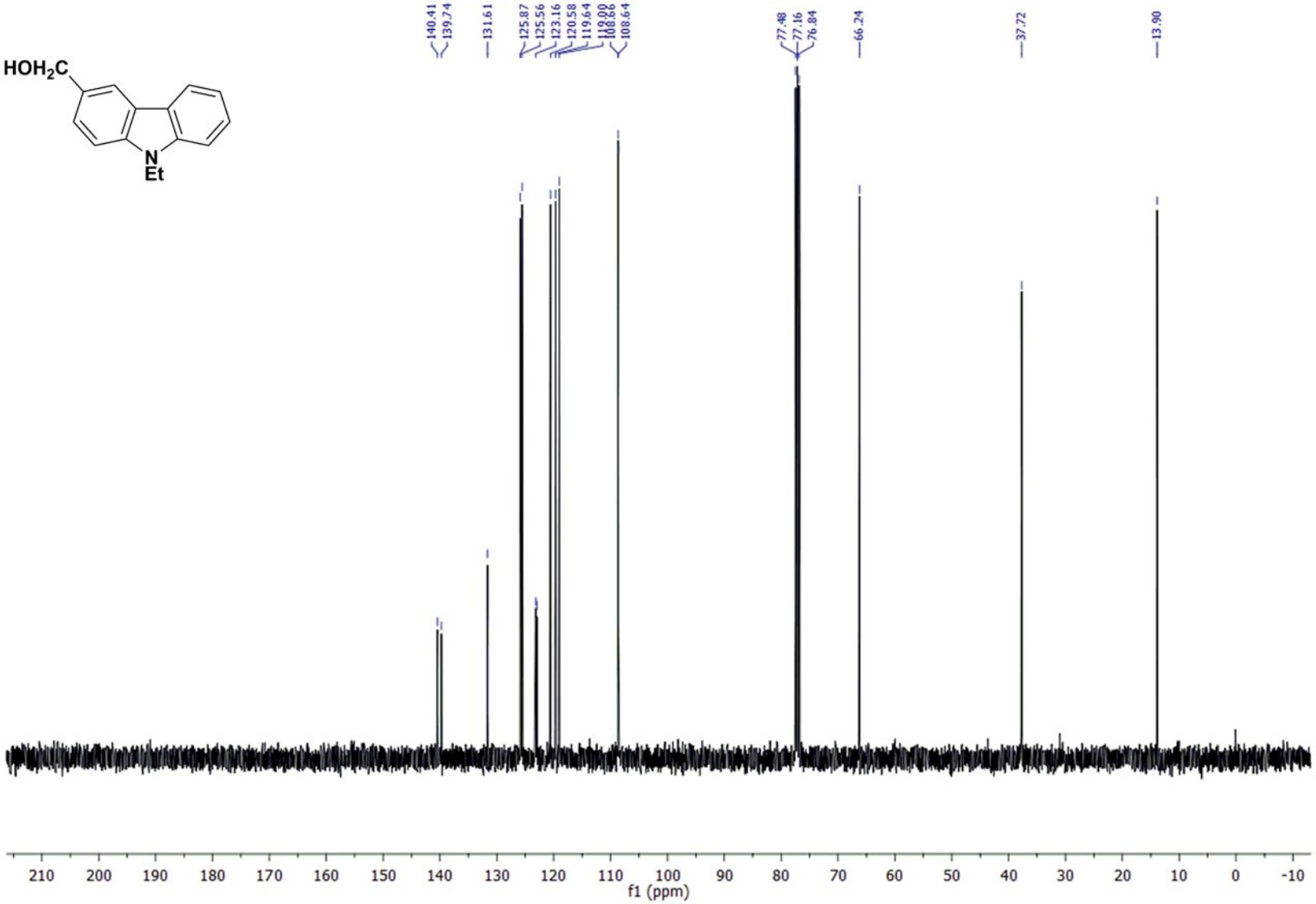
1q – ^{13}C {^{1}H} NMR


NC
N
Et
141.70
140.62
129.02
127.25
125.39
123.22
122.13
120.91
120.75
120.46
109.23
109.19
101.60
77.48
77.16
76.84
38.00
13.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

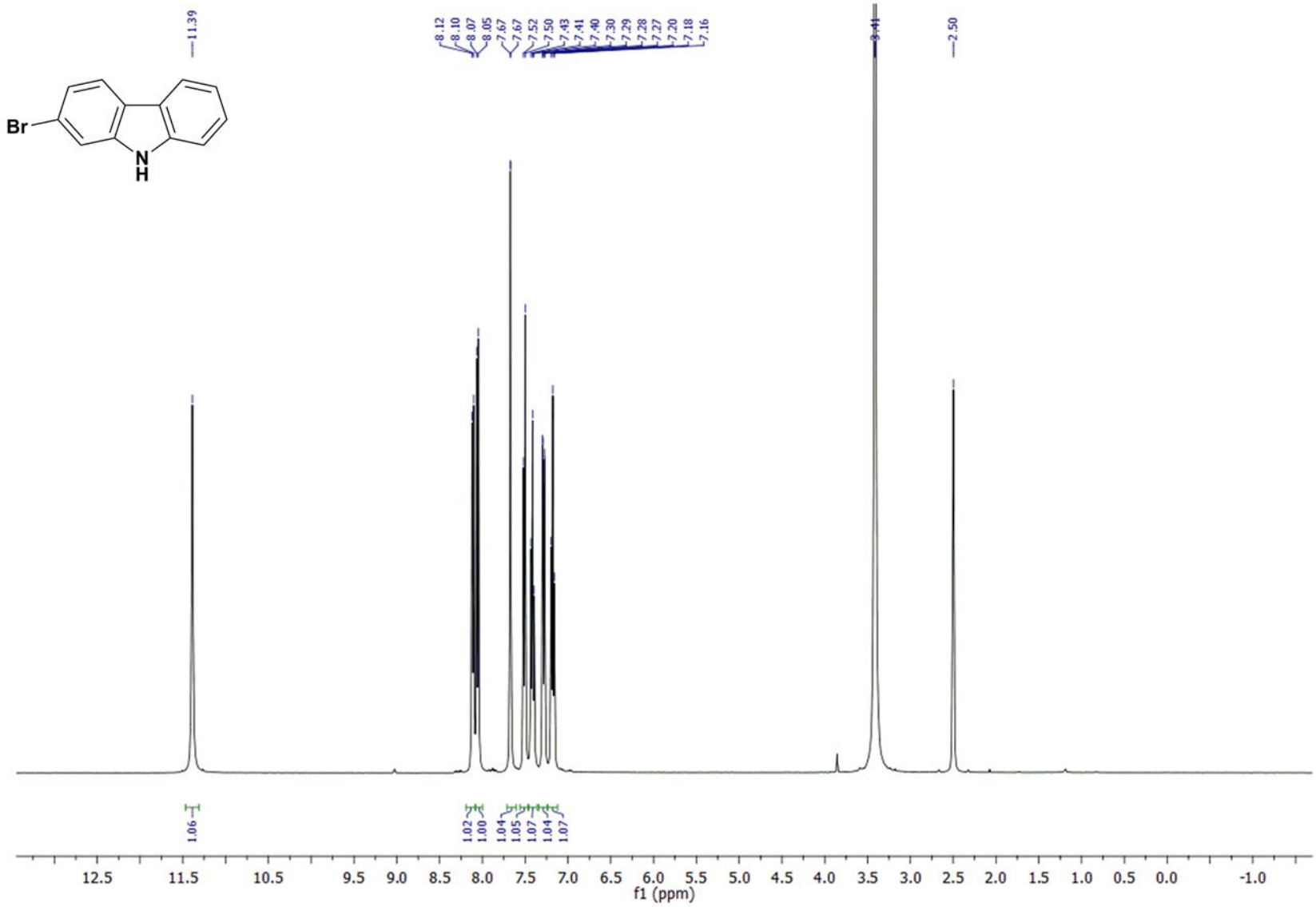
1h – ^{1}H NMR


HOH2C
N
Et
8.11
8.11
8.11
8.10
8.09
8.09
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.43
7.41
7.41
7.38
7.27
7.26
7.26
7.25
7.25
7.24
4.40
4.38
4.36
4.34
1.45
1.43
1.42
0.03
1.90
2.01
2.00
1.08
2.11
2.06
3.16
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

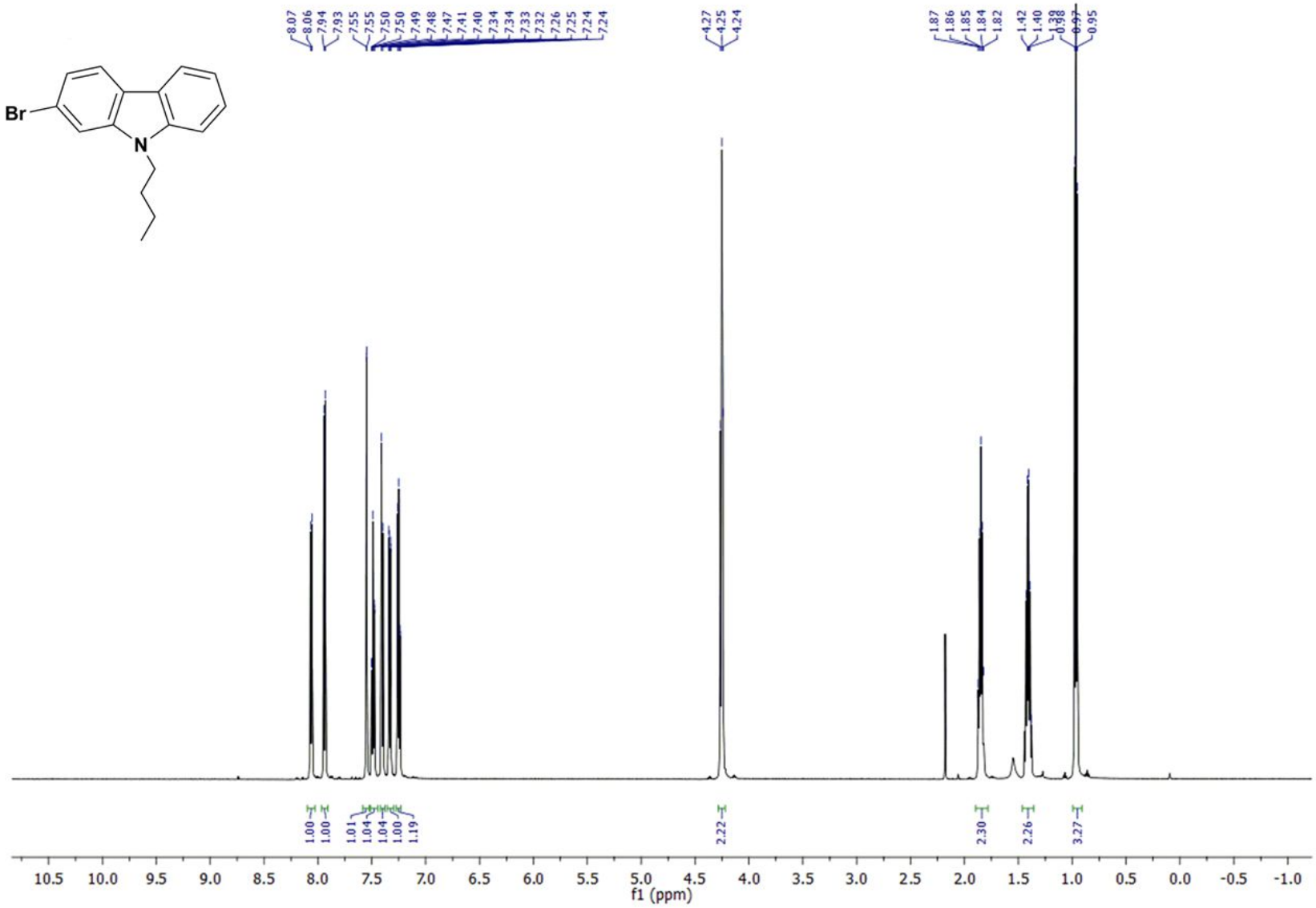
1h – ^{13}C {^{1}H} NMR


HOH2C
N
Et
140.41
139.74
131.61
125.87
125.56
123.16
120.58
119.64
108.64
77.48
77.16
76.84
66.24
37.72
13.90
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)

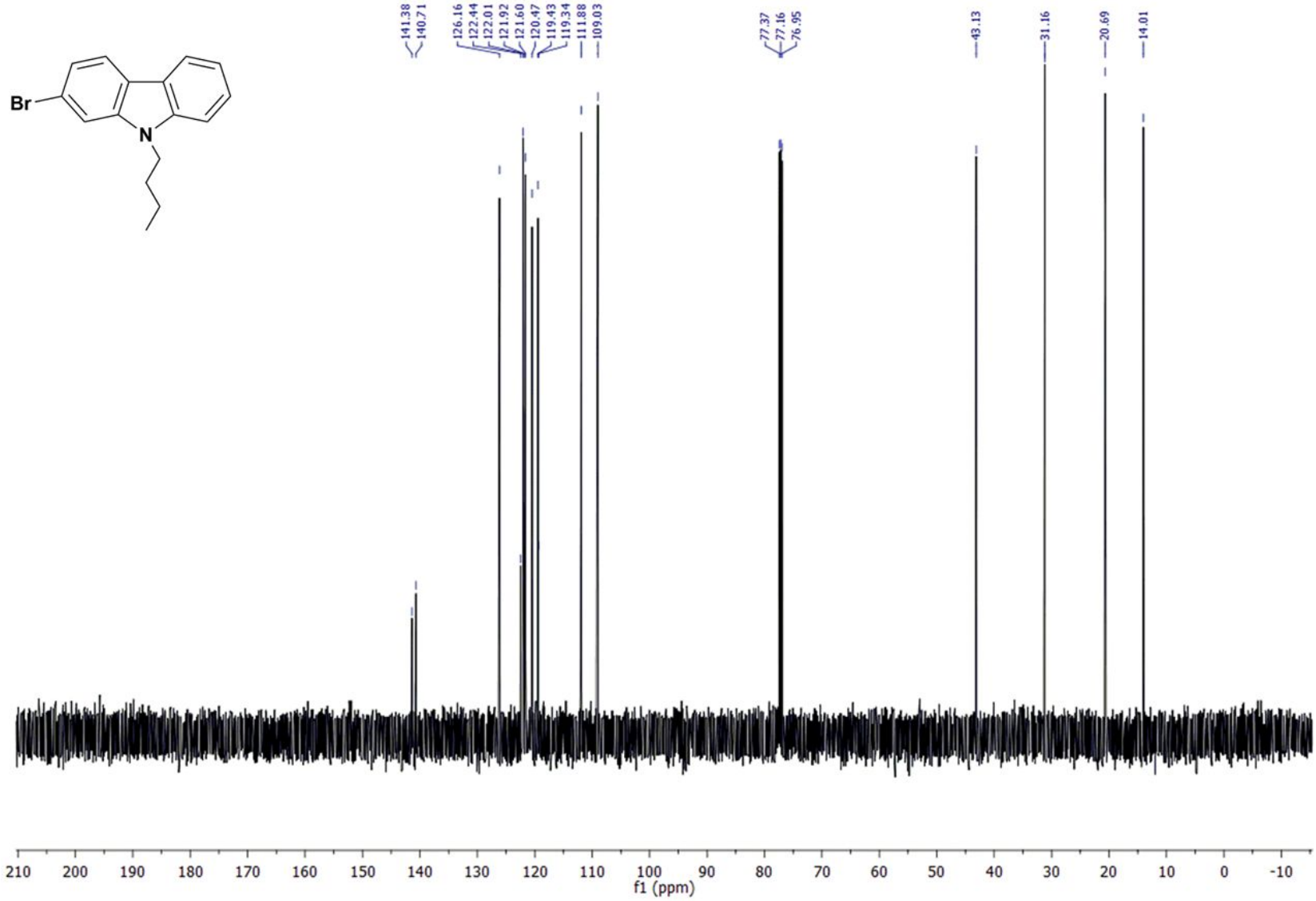
11 – ^{1}H NMR


11.39
8.12
8.10
8.07
8.05
7.67
7.67
7.52
7.50
7.43
7.41
7.40
7.30
7.29
7.28
7.27
7.20
7.18
7.16
3.41
2.50
Br
N
H
1.06
1.02
1.00
1.04
1.05
1.07
1.04
1.07
12.5
11.5
10.5
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
-1.0
f1 (ppm)

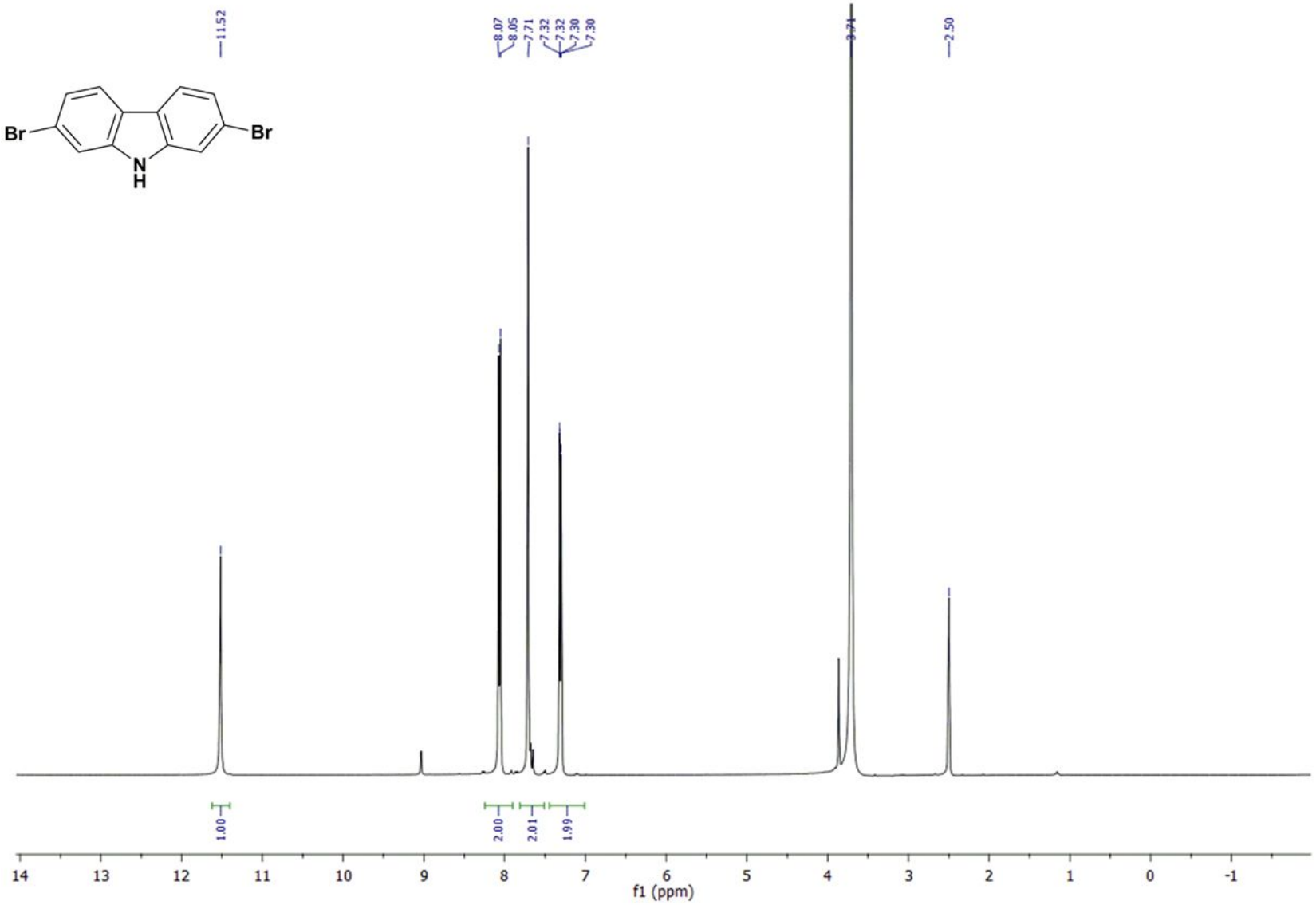
1k – ^{1}H NMR


Br
N
8.07
8.06
7.94
7.93
7.55
7.55
7.50
7.50
7.49
7.48
7.47
7.41
7.40
7.34
7.34
7.33
7.32
7.26
7.25
7.24
7.24
4.27
4.25
4.24
1.87
1.86
1.85
1.84
1.82
1.42
1.40
1.39
1.38
0.97
0.95
1.00
1.00
1.01
1.04
1.04
1.00
1.19
2.22
2.30
2.26
3.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

1k -^{13}C {^{1}H} NMR


Br
N
141.38
140.71
126.16
122.44
122.01
121.92
121.60
120.47
119.43
119.34
111.88
109.03
77.37
77.16
76.95
43.13
31.16
20.69
14.01
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)

1m – ^{1}H NMR


11.52
8.07
8.05
7.71
7.32
7.32
7.30
7.30
3.71
2.50
Br
Br
N
H
1.00
2.00
2.01
1.99
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)