Supporting Information To:

Air-stable Pd catalytic systems for sequential one-pot synthesis of challenging unsymmetrical aminoaromatics

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Experimental section

General methods:

All reactions involving water- or air-sensitive material were performed in oven-dried glassware under an argon or nitrogen atmosphere by using Schlenk techniques employing double-line argon-vacuum lines and dry solvents. The synthetic intermediates were co-evaporated twice with toluene and dried in *vacuo* before use. All chemical reagents were obtained from commercial sources and were used as supplied. Anhydrous solvents and amine reagents were obtained by distillation followed by three cycles of degassing (or recrystallization in case of solid nucleophiles) according to standard procedures.[1] Palladium(II) acetate and sodium *tert*-butoxide were bought from Aldrich with respectively a 99.9+% trace metals basis (reference 520764-1G) and a purity of 99.9% (reference 703788-5G). All the ligands were ordered from Aldrich at the except of BINAP which was supplied by ACROS as a (*S*)-isomer. Since the latter displays a purity of 99+%, it provided better coupling yields than *rac*-BINAP from Aldrich presenting a purity of 97%. Thus, most of the reactions described in this report were conducted using (*S*)-BINAP (reference ACROS 26554). The reactions were monitored simultaneously by gas chromatography (GC/MS) and by thin-layer chromatography and visualized both by UV radiation (254 & 365 nm) and by spraying with relevant staining agent ($KMnO_4$ or Ninhydrin) followed by a subsequent warming with a heat gun. Column chromatography[2] was performed with flash silica gel (40–63 μm) with the indicated solvent system, using gradients of increasing polarity in most cases. ^{1}H NMR (200 and 500 MHz), ^{13}C NMR (50 and 125 MHz, recorded with complete proton decoupling) spectra were obtained with samples dissolved in $CDCl_3$, CD_2Cl_2, or TFA-*d*[1], with the residual solvent signals as internal references: 7.26 ppm for C*H*Cl_3, 5.32 ppm for CD*H*Cl_2, 11.50 ppm for CF_3COOH for ^{1}H NMR experiments, and 77.0 ppm for $CDCl_3$, 53.8 ppm for CD_2Cl_z, 164.2 ppm CF_3COOD for ^{13}C NMR experiments.[3] Chemical shifts (δ) are given in ppm to the nearest 0.01 (^{1}H) or 0.1 ppm (^{13}C). The coupling constants (*J*) are given in Hertz (Hz). The signals are reported as follows: (s=singlet, d=doublet, t=triplet, quint=quintet, sext=sextet m=multiplet, br=broad). Assignments of ^{1}H and ^{13}C NMR signals were achieved with the help of D/H exchange, COSY, DEPT, HMQC, HSQC, HMBC experiments. GCMS mass spectra were recorded using an ion trap mass spectrometer with EI source (70eV). LCMS mass spectra were recorded using an ion trap mass spectrometer equipped with an ESI source. HRMS were recorded on a hybrid ion trap−Orbitrap mass spectrometer using ESI. Microwave reactions were conducted using a monowave focused heating model with an internal probe. Systematic nomenclatures were used for the assignments of each spectrum. For fluorene, the assignments followed the systematic nomenclatures for the six-membered rings and alphabetical letters for the central 5-membered ring.

[1] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 7th ed.; Butterworth-Heinemann: Oxford, 2013.
[2] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978,** *43,* 2923–2925.
[3] *a*) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997,** *62,* 7512–7515; *b*) G. R. Fulmer, A. Miller, N. H. Sherden,H. E. Gottlieb, H. E. *Organometallics* **2010,** *29,* 2176–2179.

Mechanistic considerations:

The absence of the undesired reduced products with most ligands can be explained since dialkylbiaryl Buchwald ligands (**L3-6**) display some bidentate character like BINAP forming 4-coordinate complexes suppressing the *β*-hydride elimination.[4] The favored *bis*-amination with Buchwald ligands (**L3-6**) could result from their electron-rich density that facilitates the oxidative addition and their bulkiness that accelerates the reductive elimination.[5] This could have prevented the isolation of the *mono*-aminated intermediate.

On the other hand, the distinct *mono*-amination using BINAP is remarkable. Although computational studies could provide a mechanistic insight, calculations with BINAP are highly demanding. Many intermediates comprising a very bulky ligand with four flexible phenyl groups in different conformations would be involved. A recent study reported different mechanistic possibilities in the catalytic cycle of BINAP.[6] Among all of them, it has been hypothesized that the hemilabililty of this bisphosphine may switch to a monodentate ligand as a possible route. Our experimental data suggest that the bidentate ligands impose a definite influence on the selectivity of *mono*-amination contrary to the monodentate ones. Other parameters related to BINAP are the steric bulkiness and the turnover-limiting step in the catalytic cycle. It is known that the turn-over limiting step of the arylbromide coupling with amines using bisphosphines is the conversion of the Pd(0) complex to an arylpalladium (II) halide complex.[7] This rate-determining step could have played a role.

Emission and absorption of probe 8:

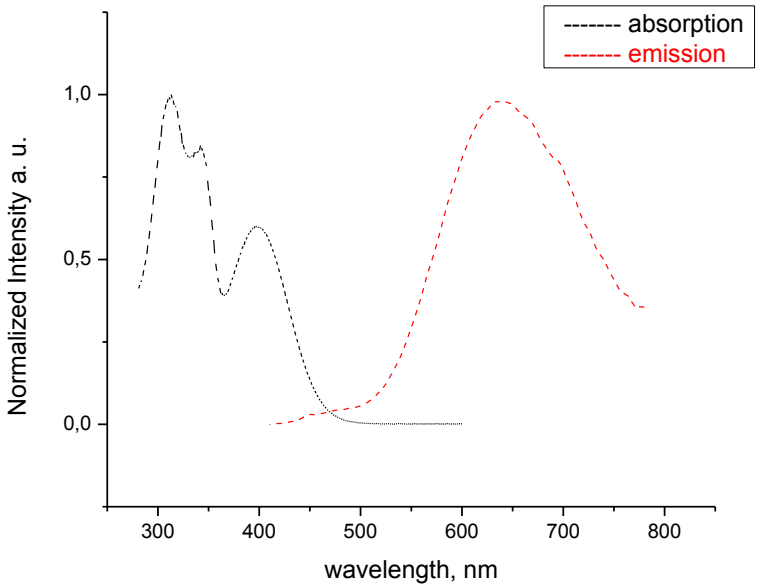

Figure S1: Absorption and emission spectra of the constructed near-IR push-pull probe

4 Hartwig, J. F. *Pure Appl. Chem.* **1999**, *71*, 1417.

5 Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27.

6 Sunesson, Y.; Limé, E.; Nilsson Lill, S. O.; Meadows, R. E.; Norrby, P.-O. *J. Org. Chem.* **2014**, *79*, 11961.

7 (a) Barrios-Landeros, F.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 6944. (b) Shekhar, S.; Ryberg, P.; Hartwig, J. F.; Mathew, J. S.; Blackmond, D. G.; Strieter, E. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 3584.

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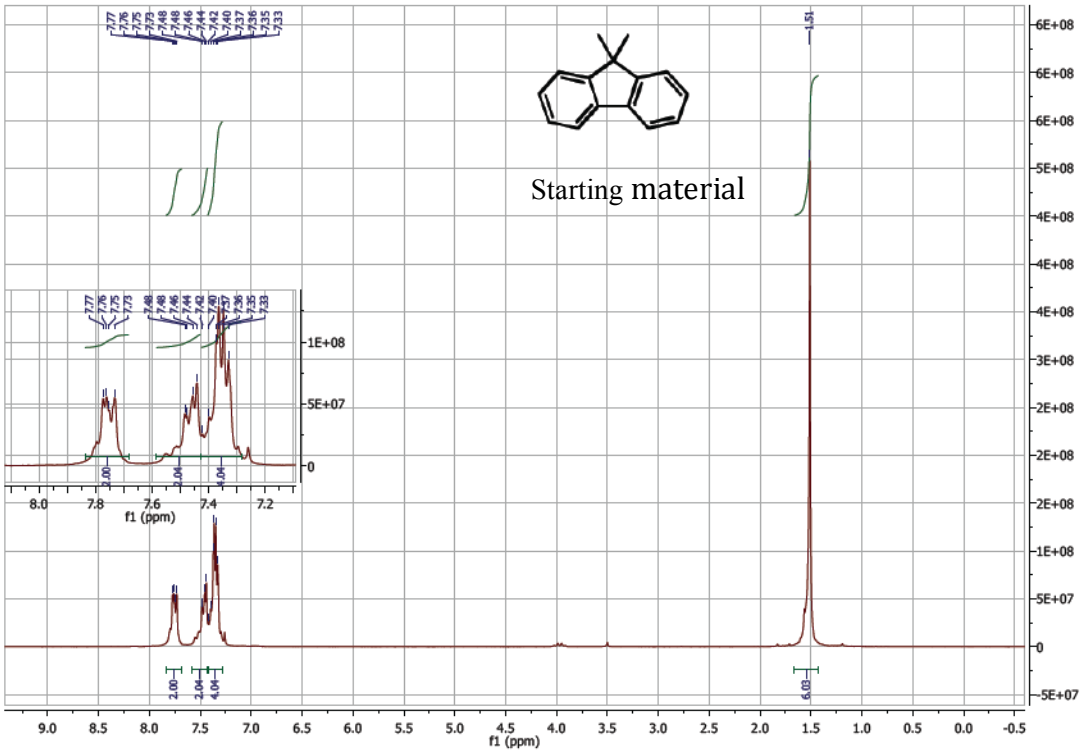

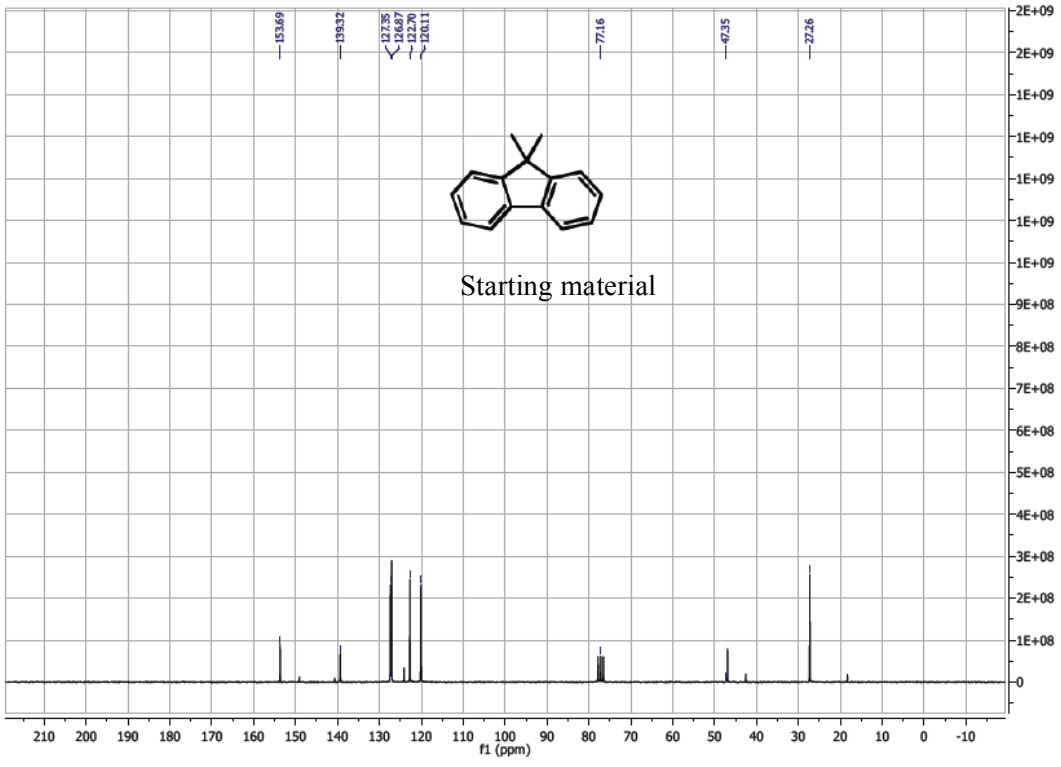

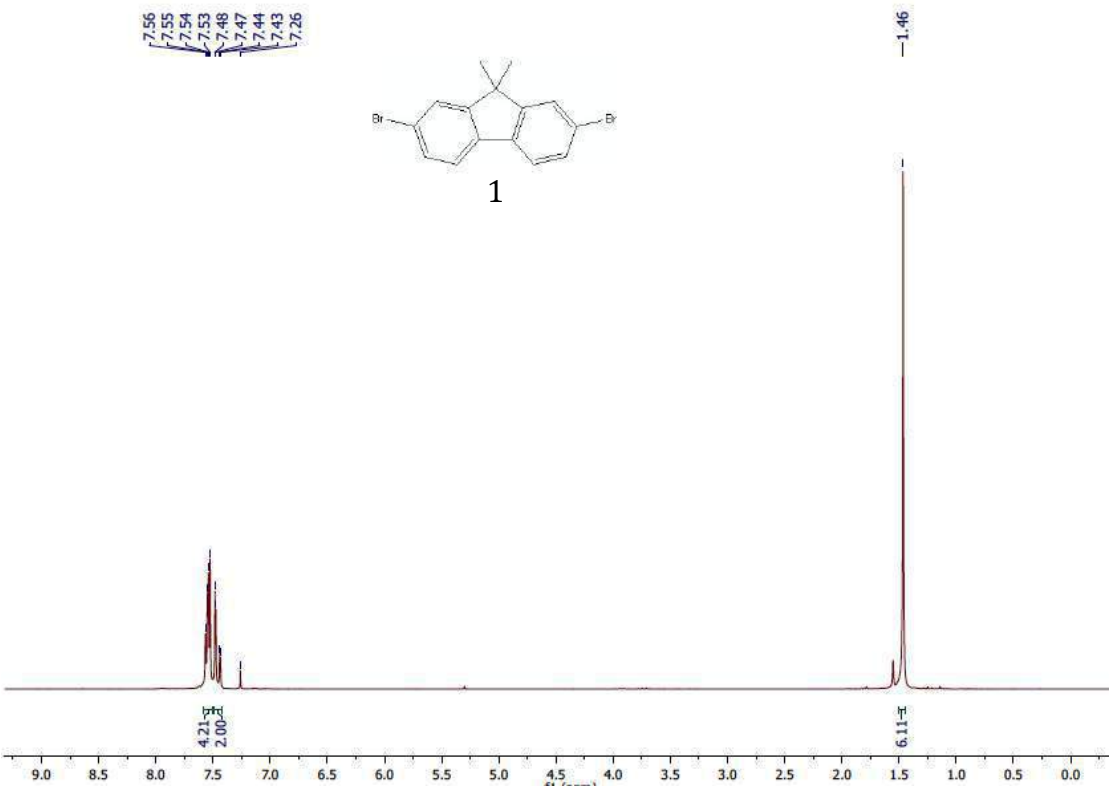
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Br
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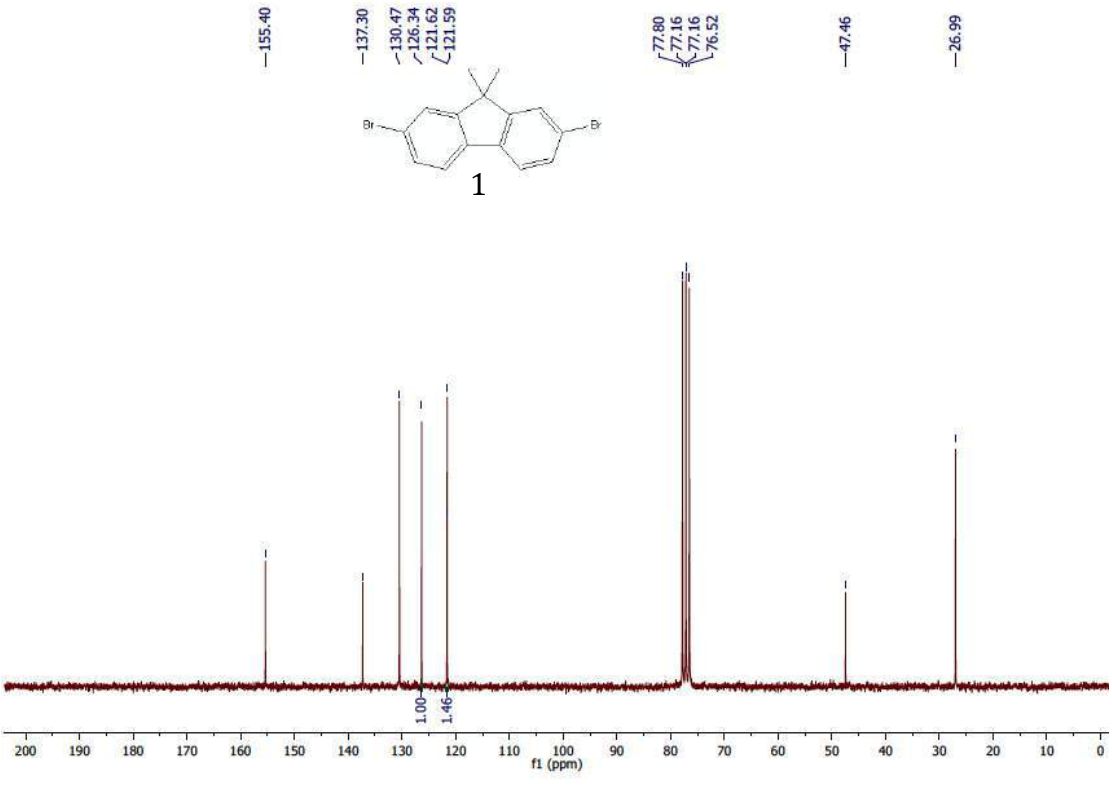
2.00
6.11

1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f1 (ppm)

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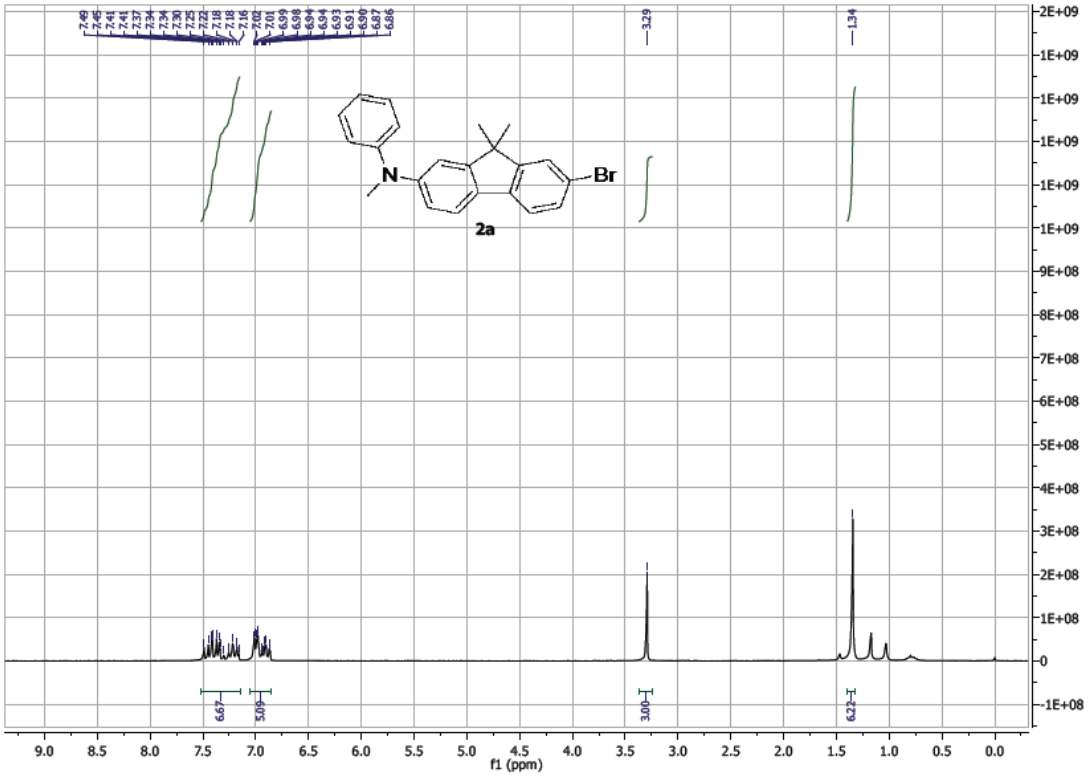
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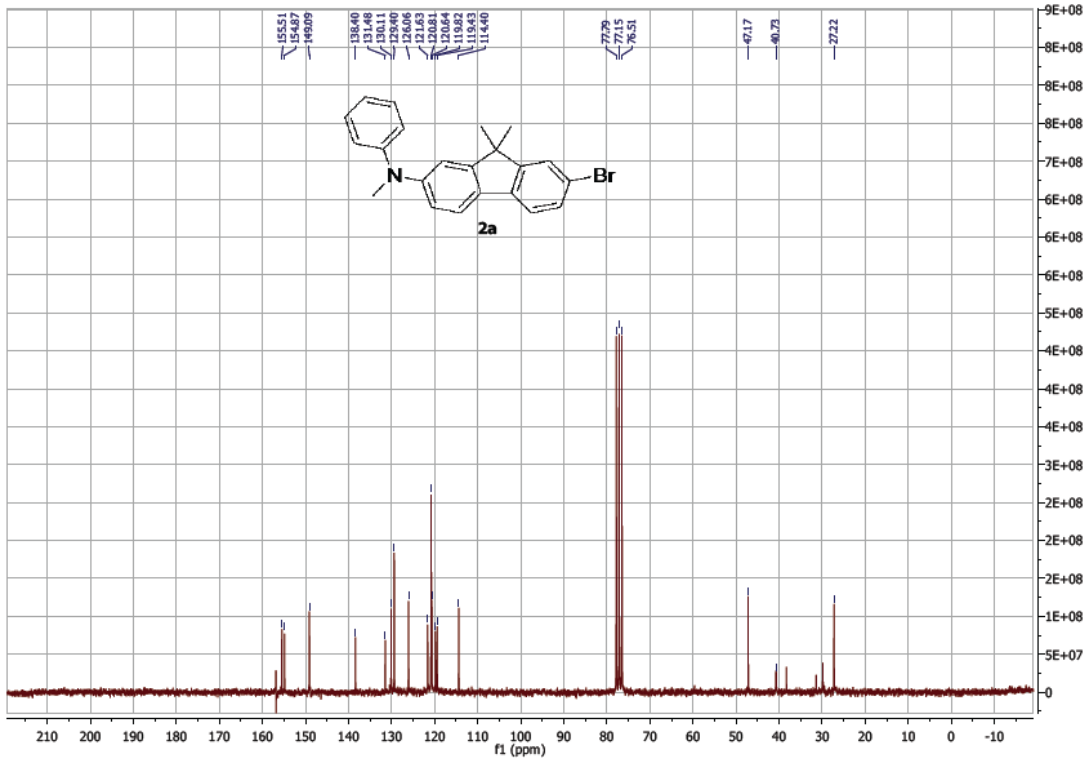
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Br
2a
f1 (ppm)

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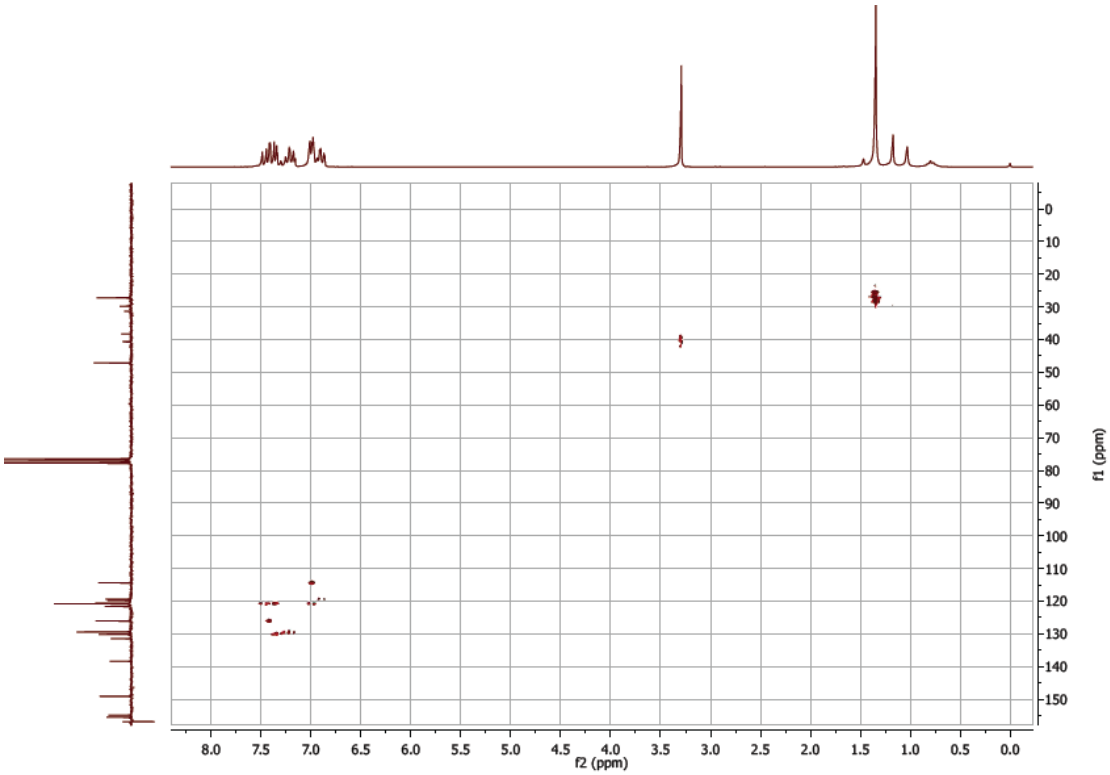

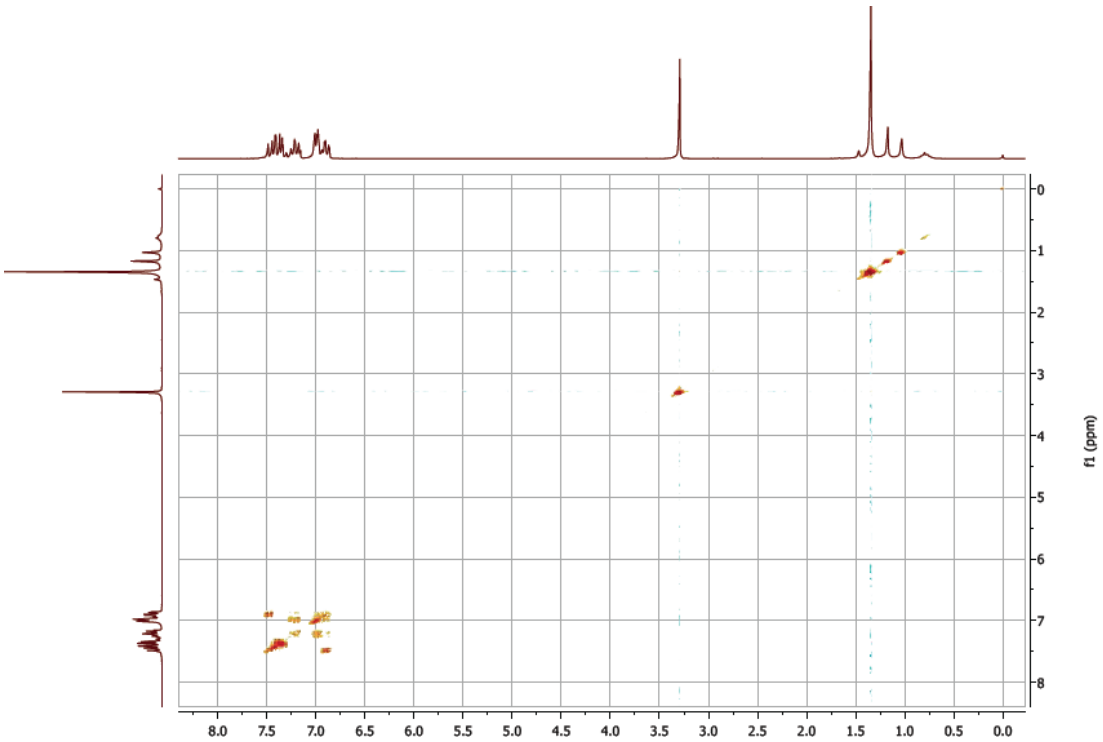

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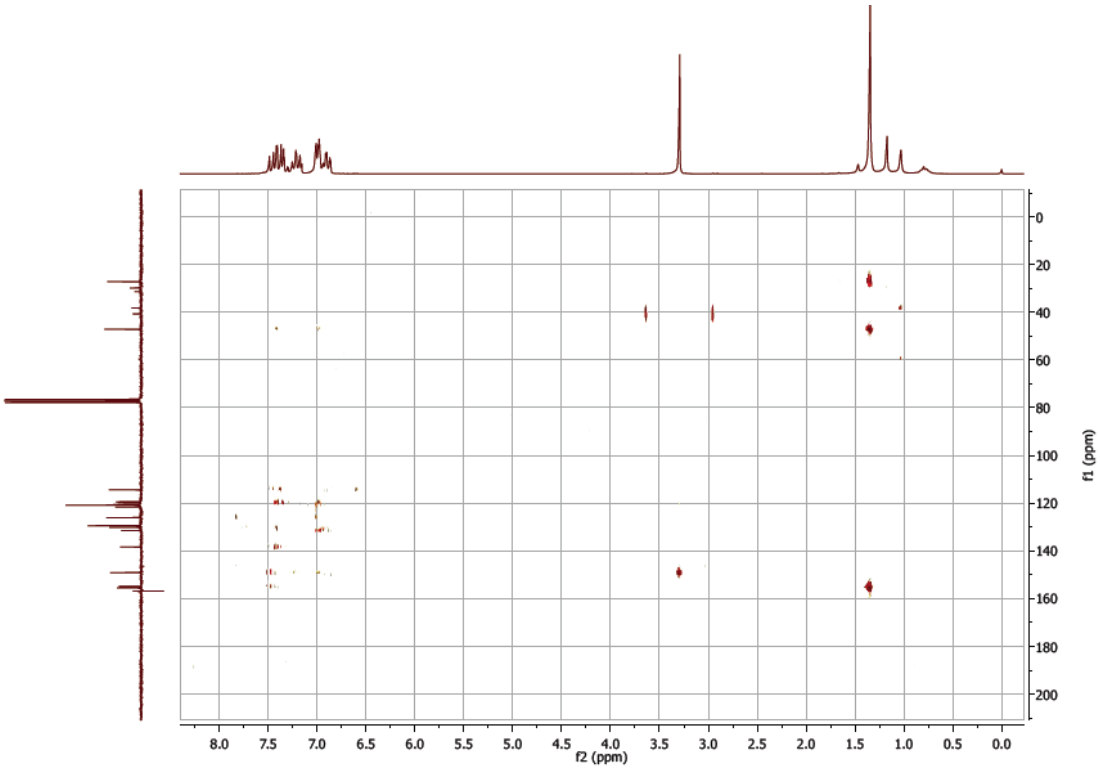

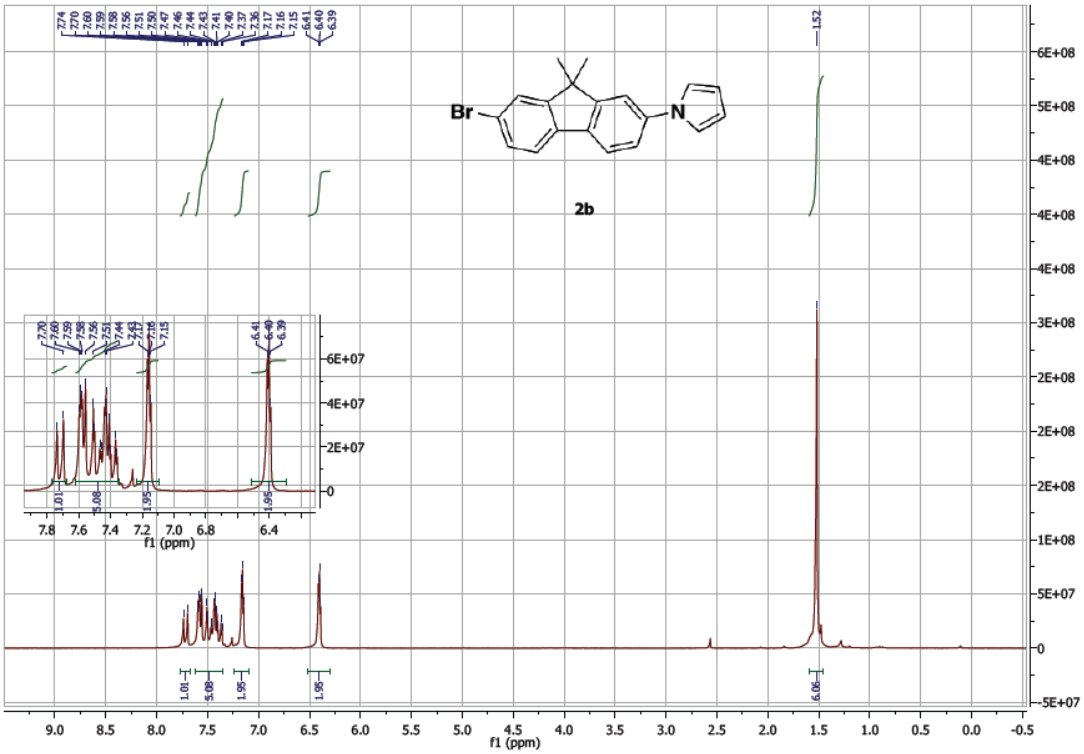

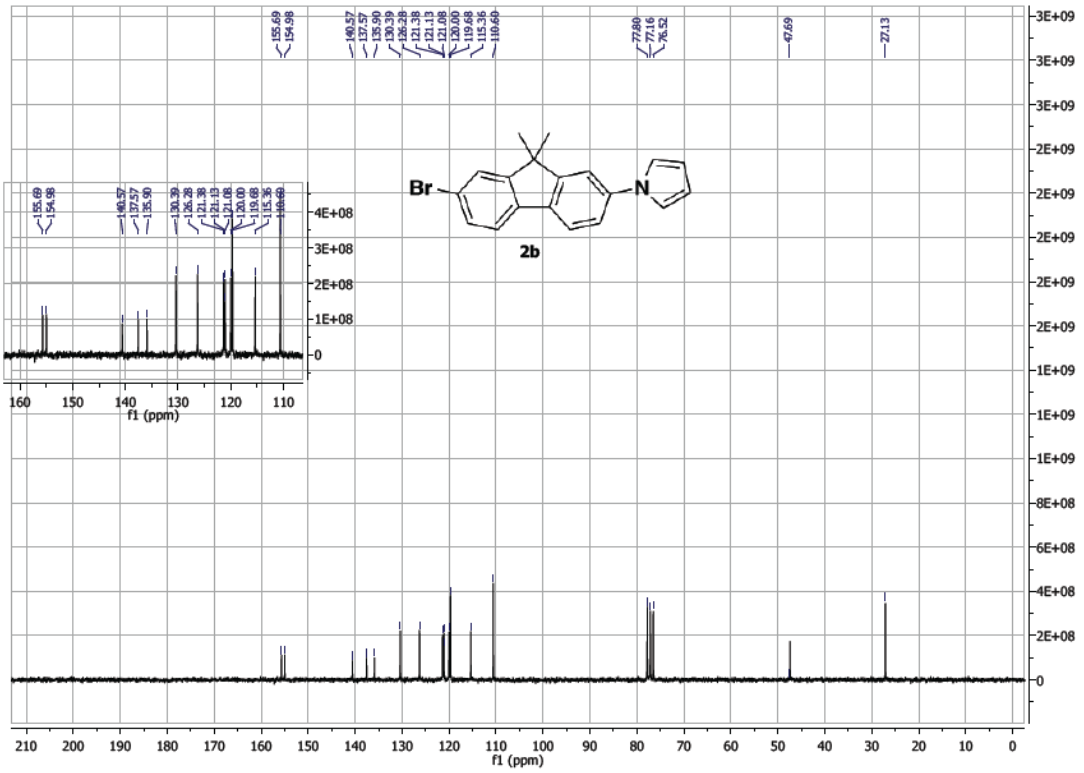
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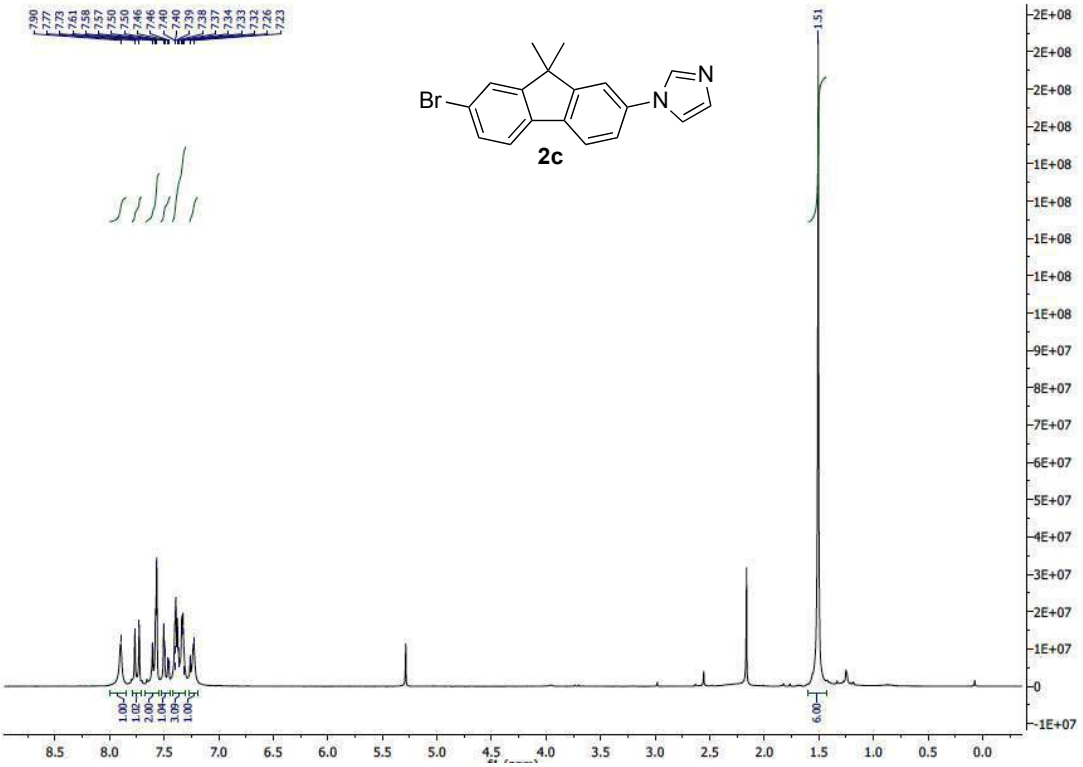
f1 (ppm)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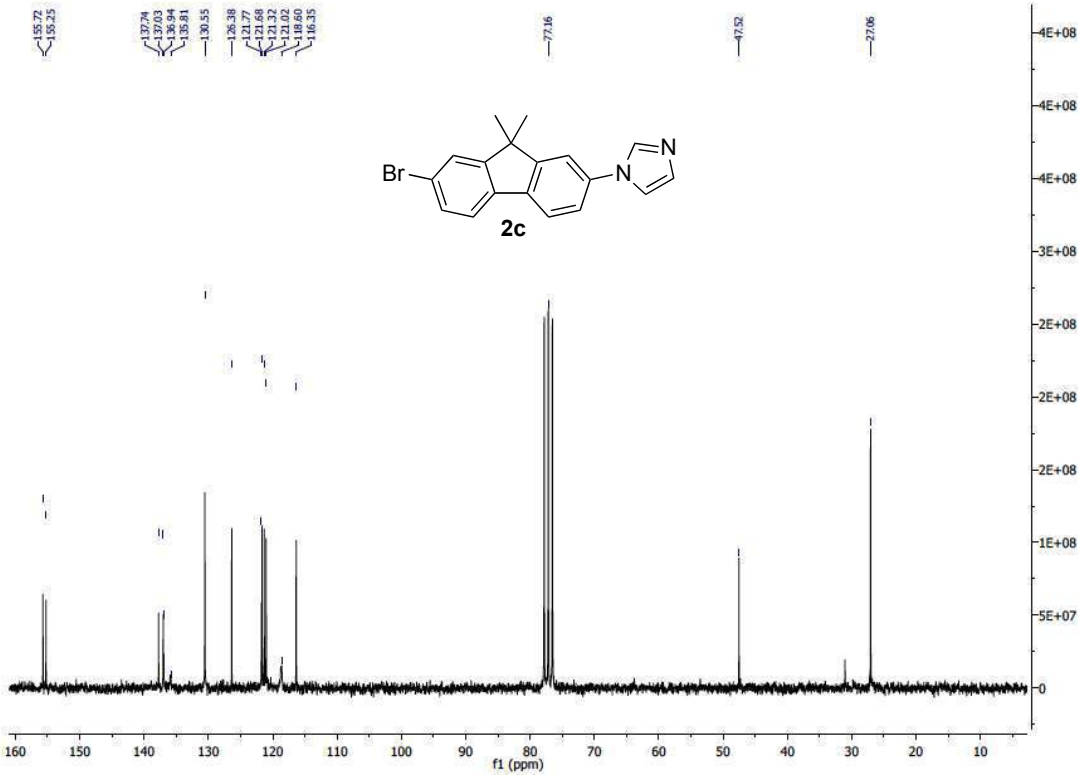
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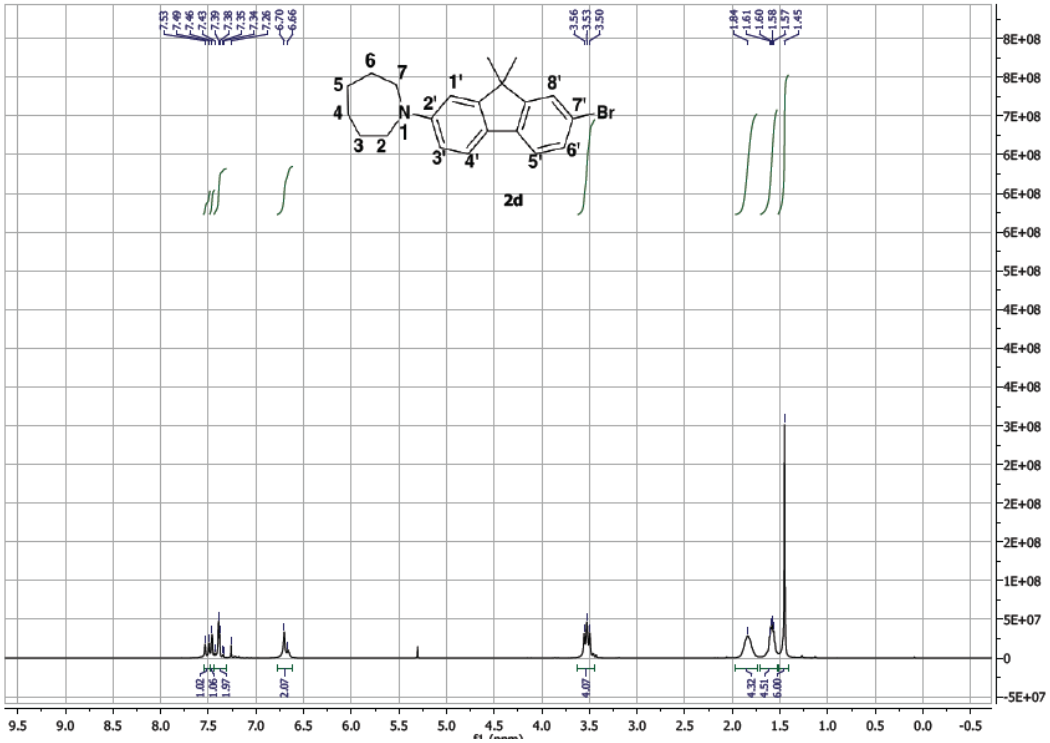
f1 (ppm)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1.61
1.60
1.58
1.57
1.45
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2'
8'
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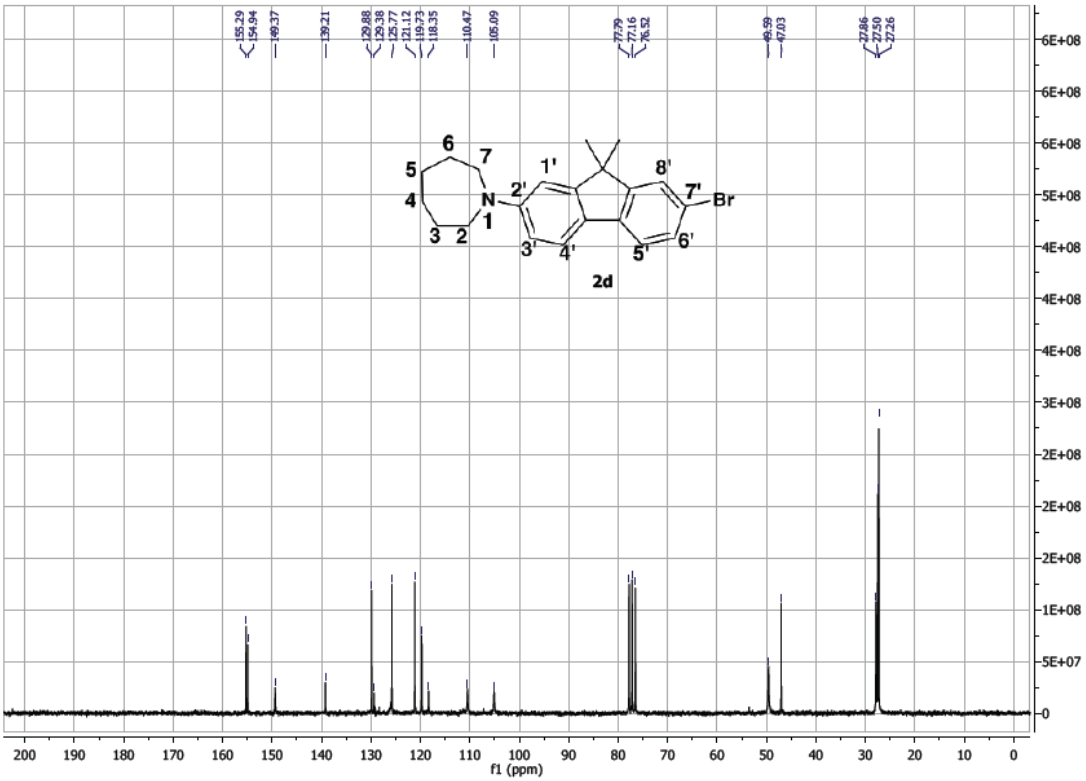
Br
3'
4'
5'
6'
2d



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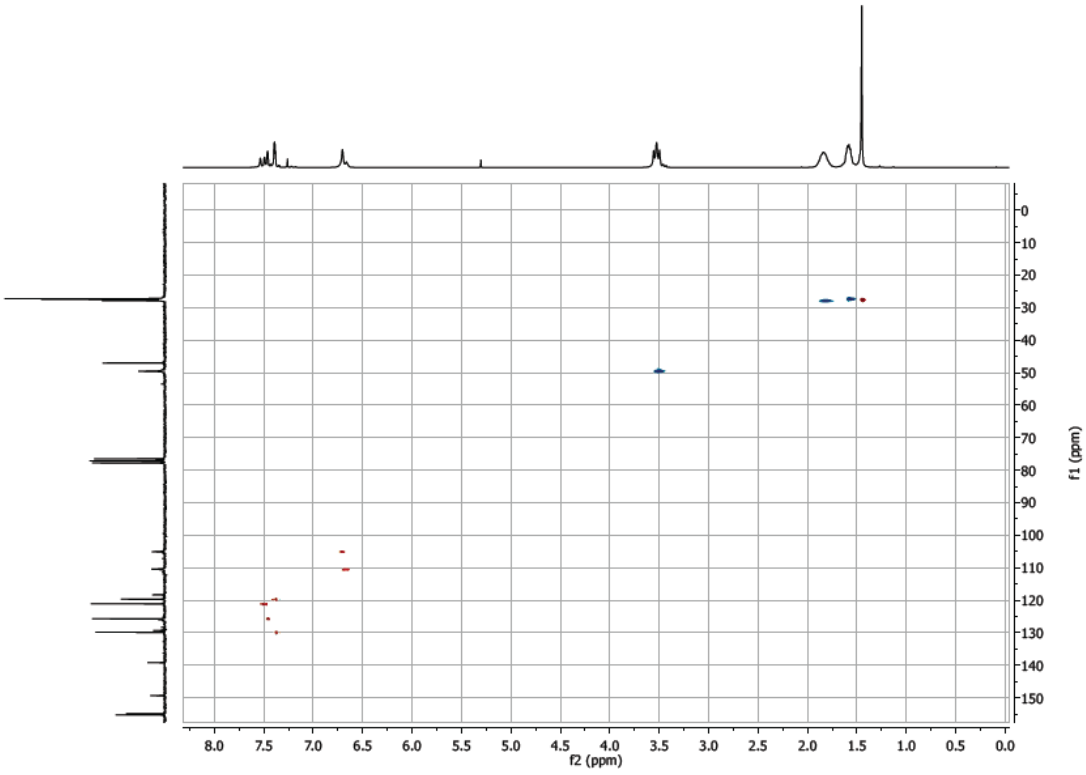

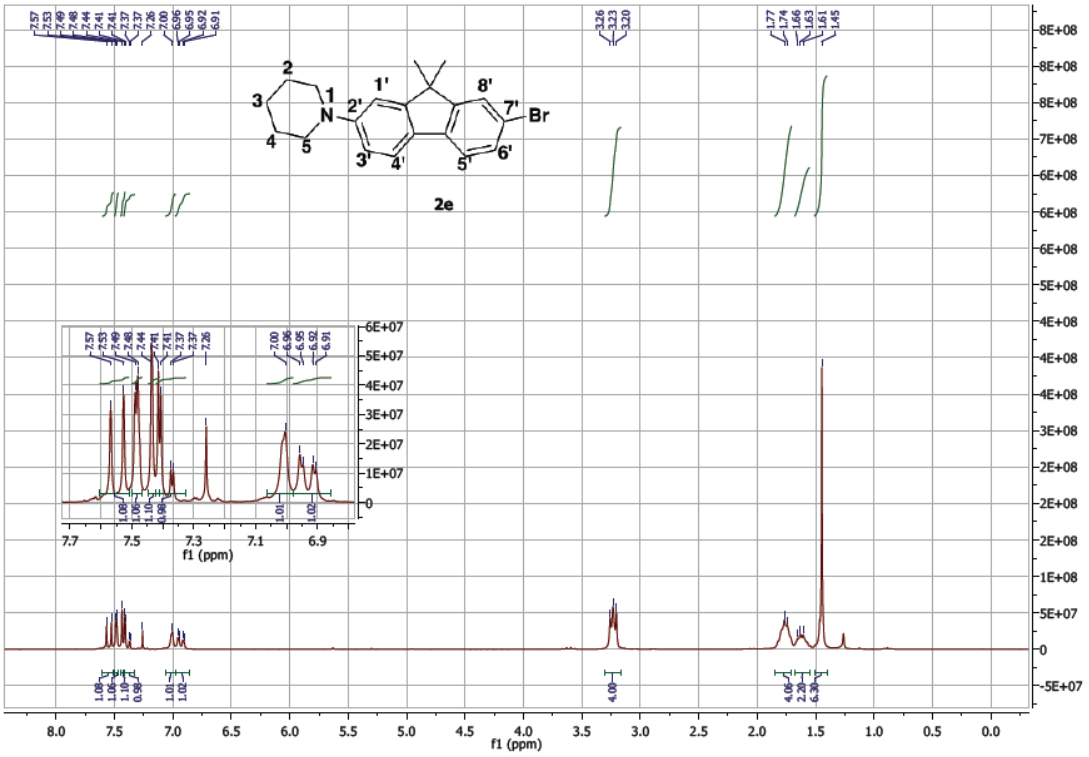
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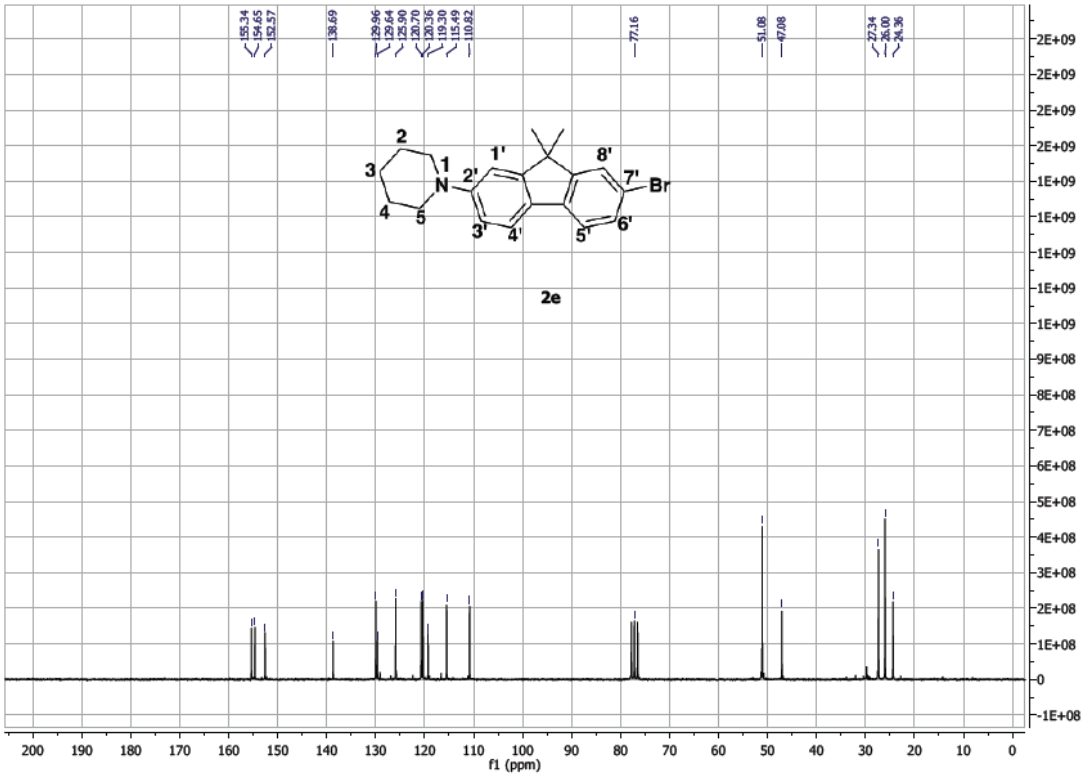
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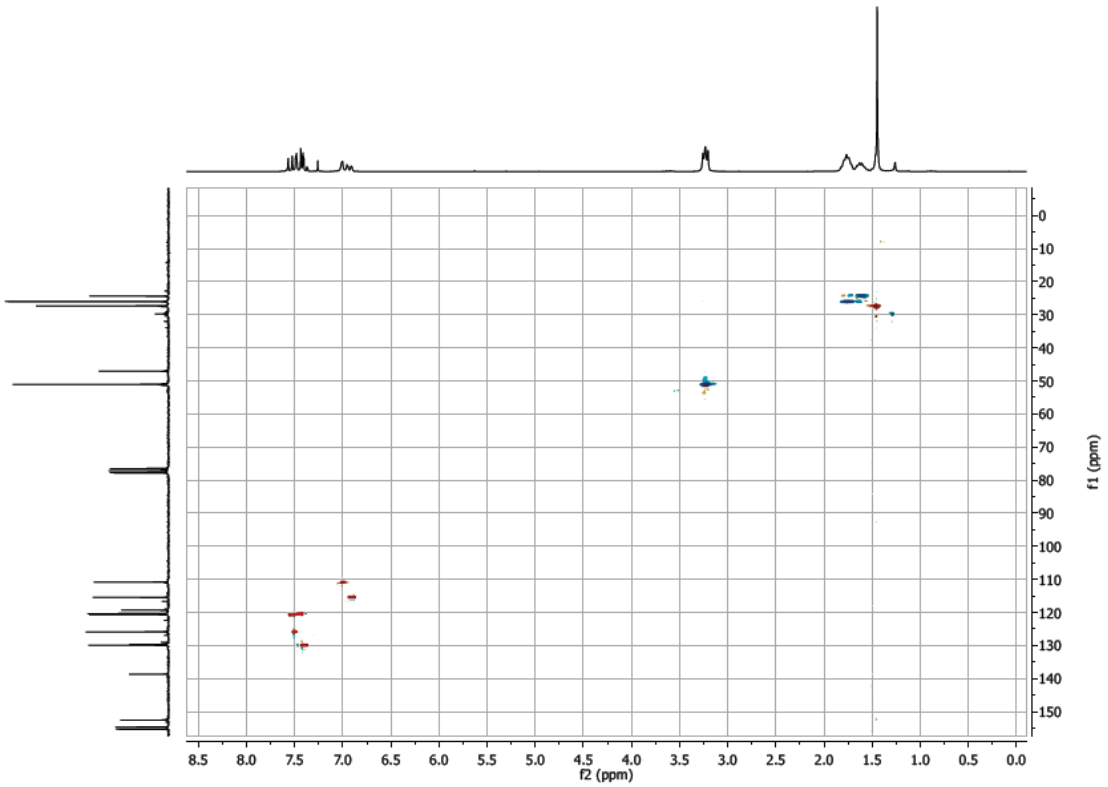

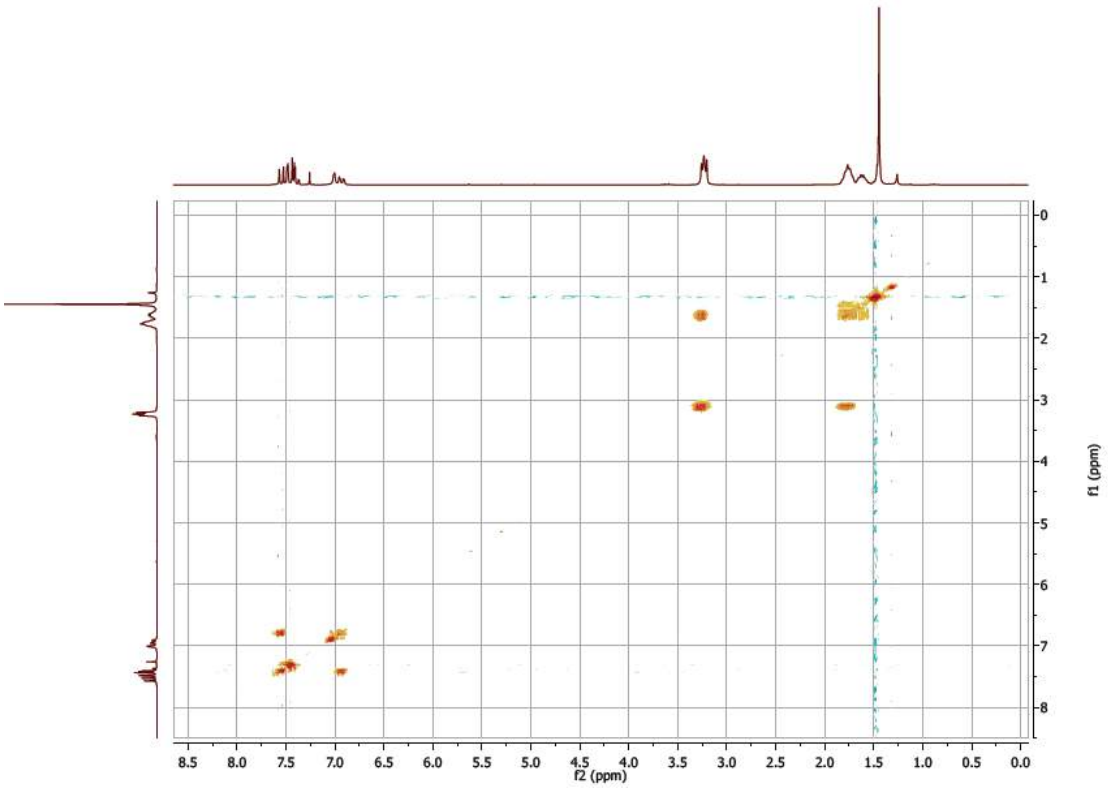

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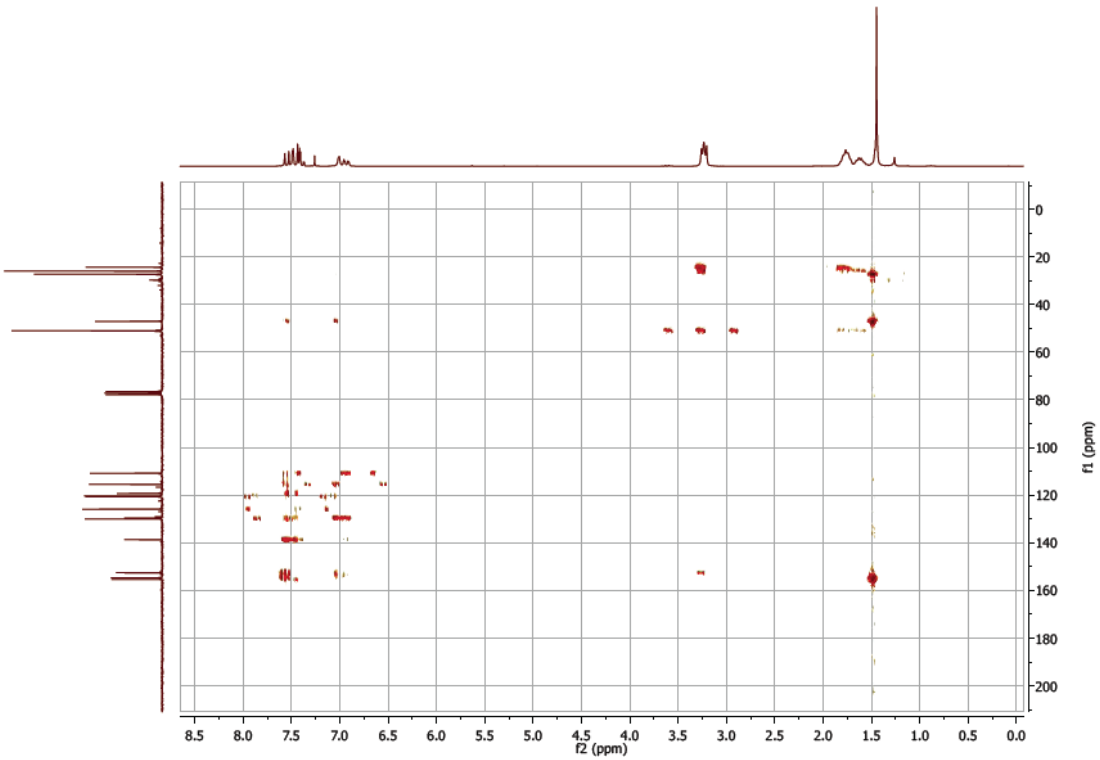

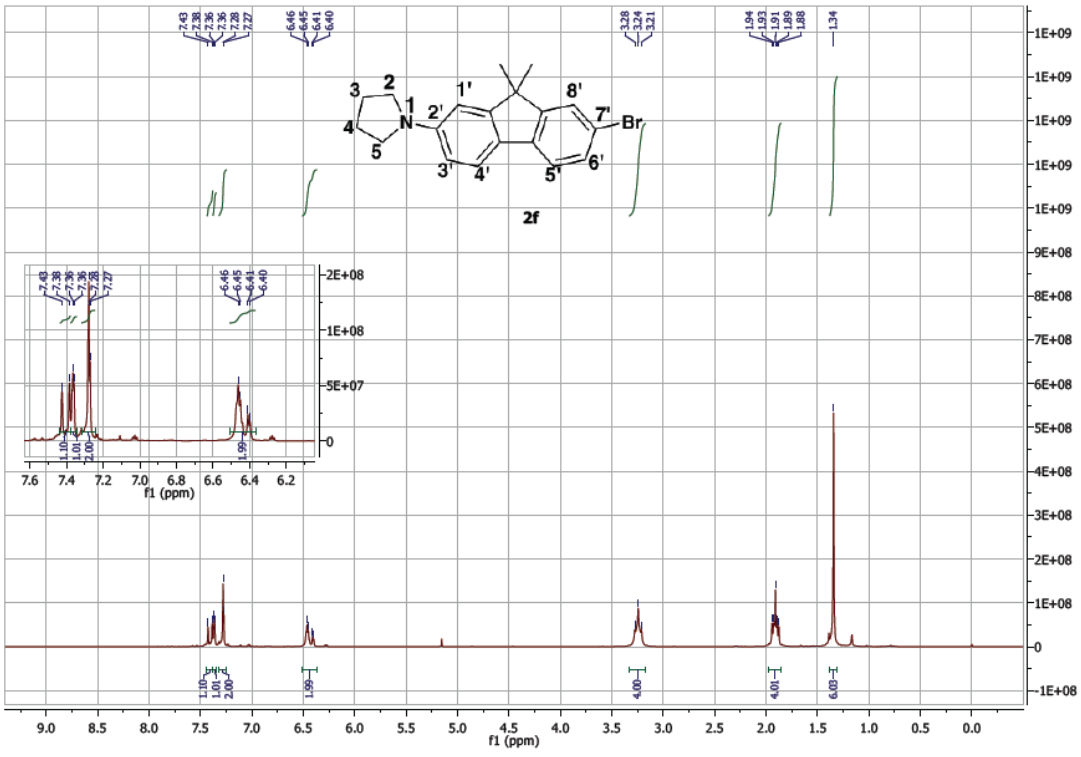

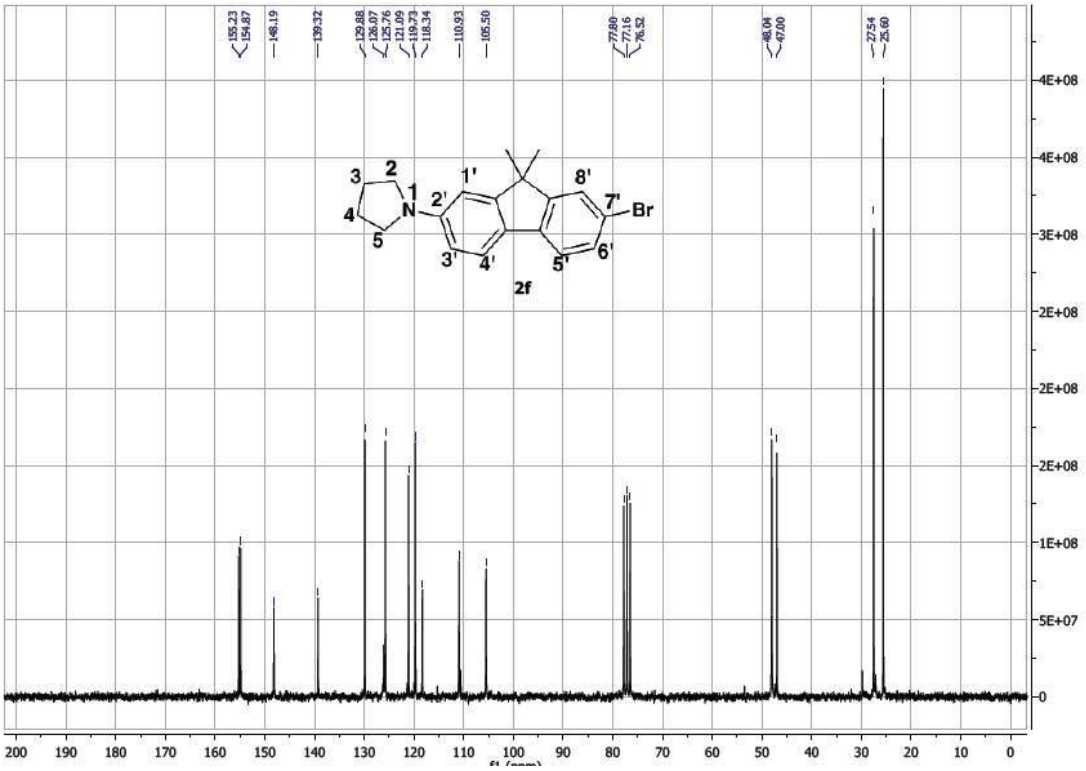

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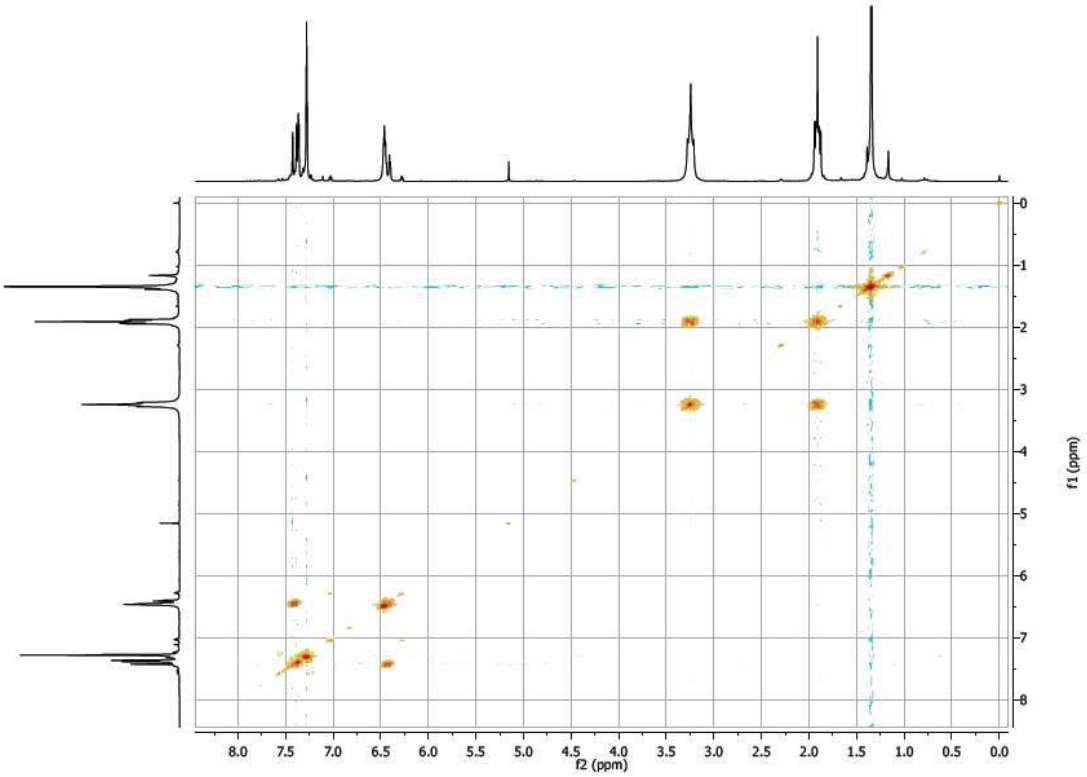

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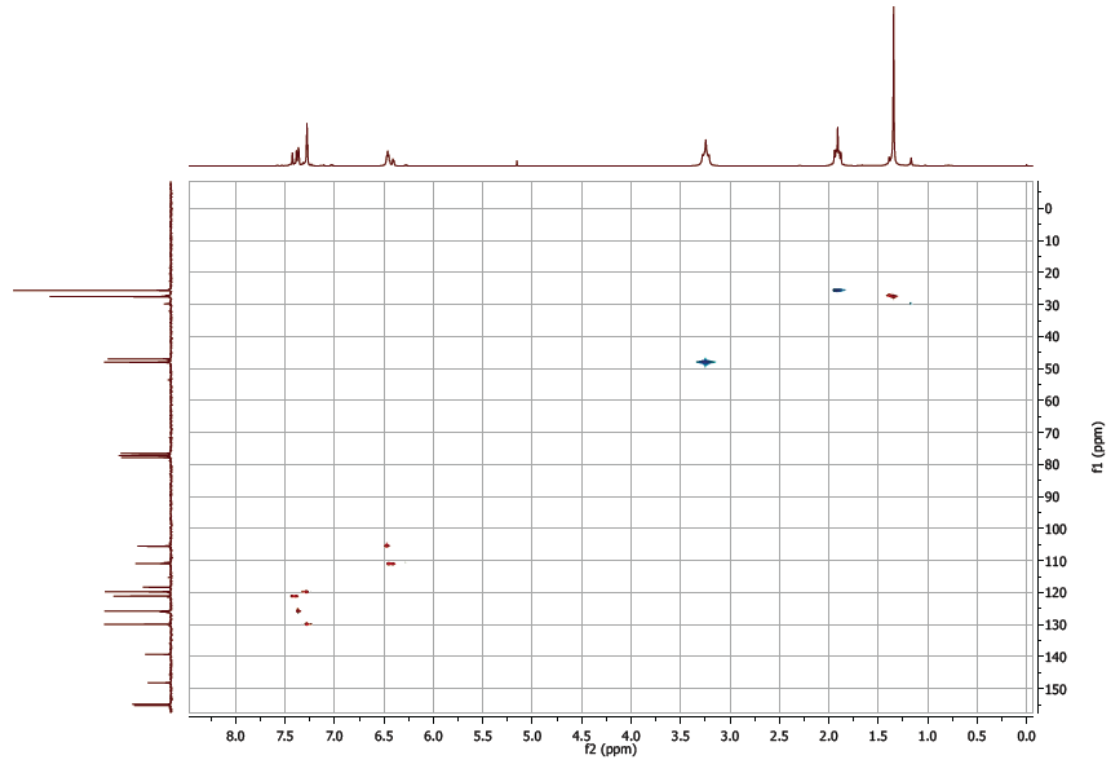

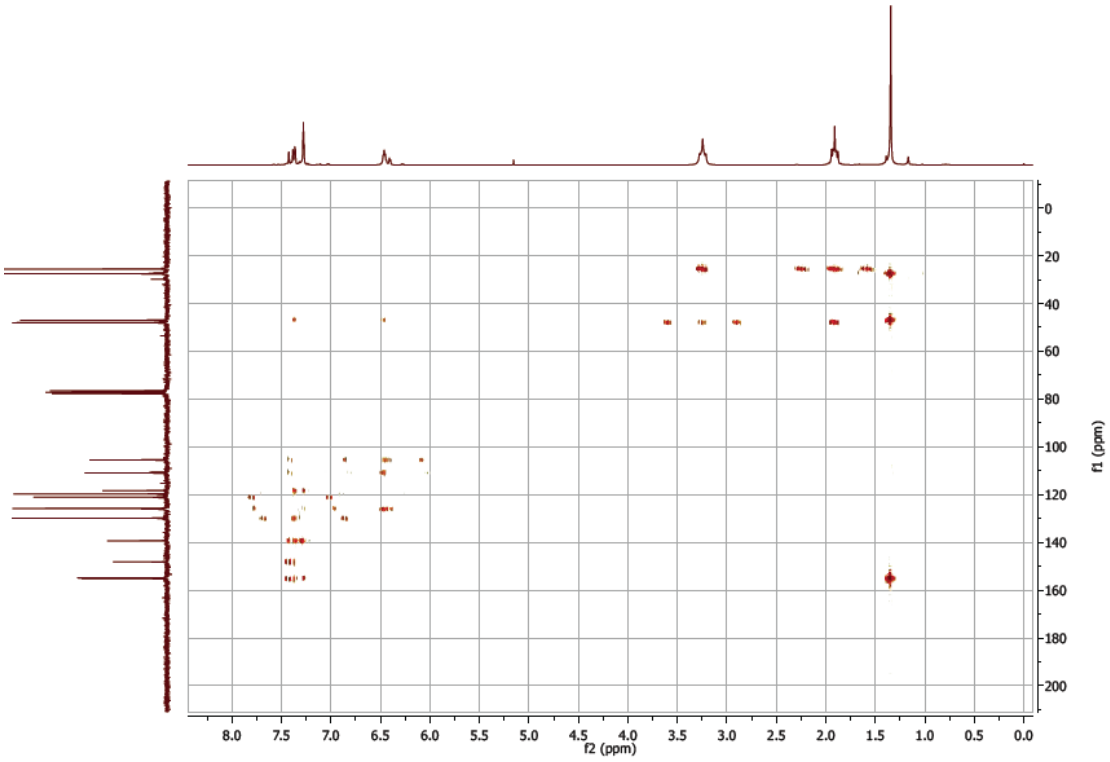

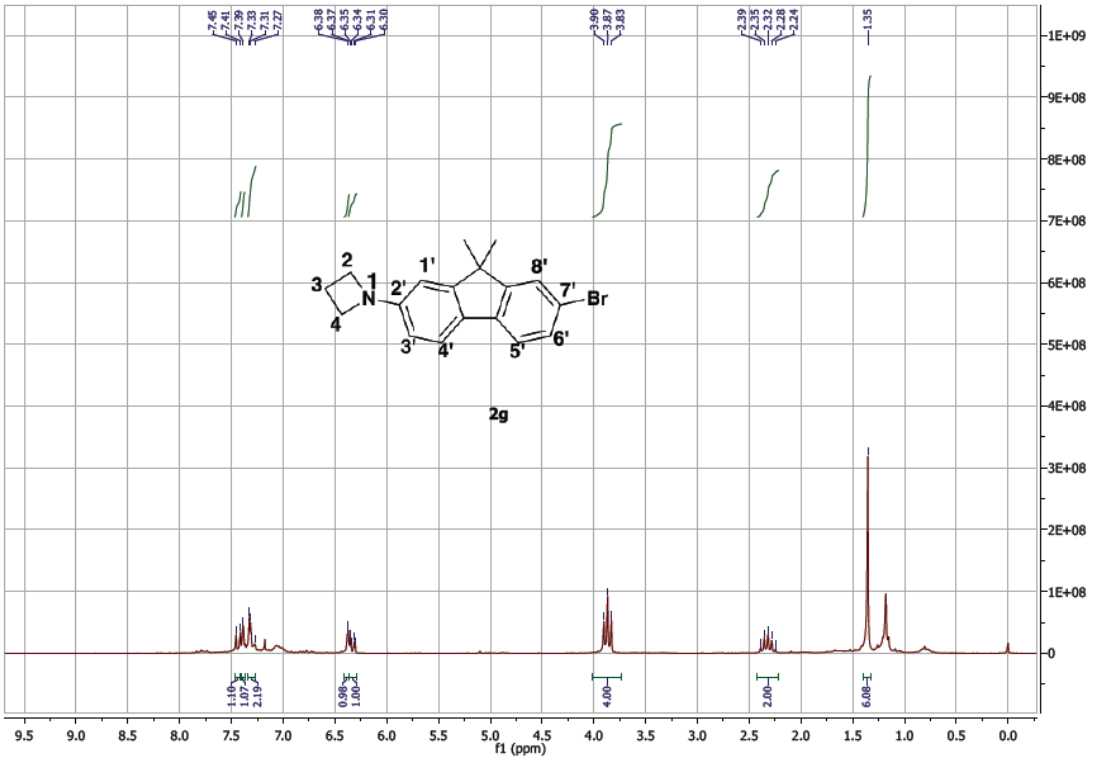
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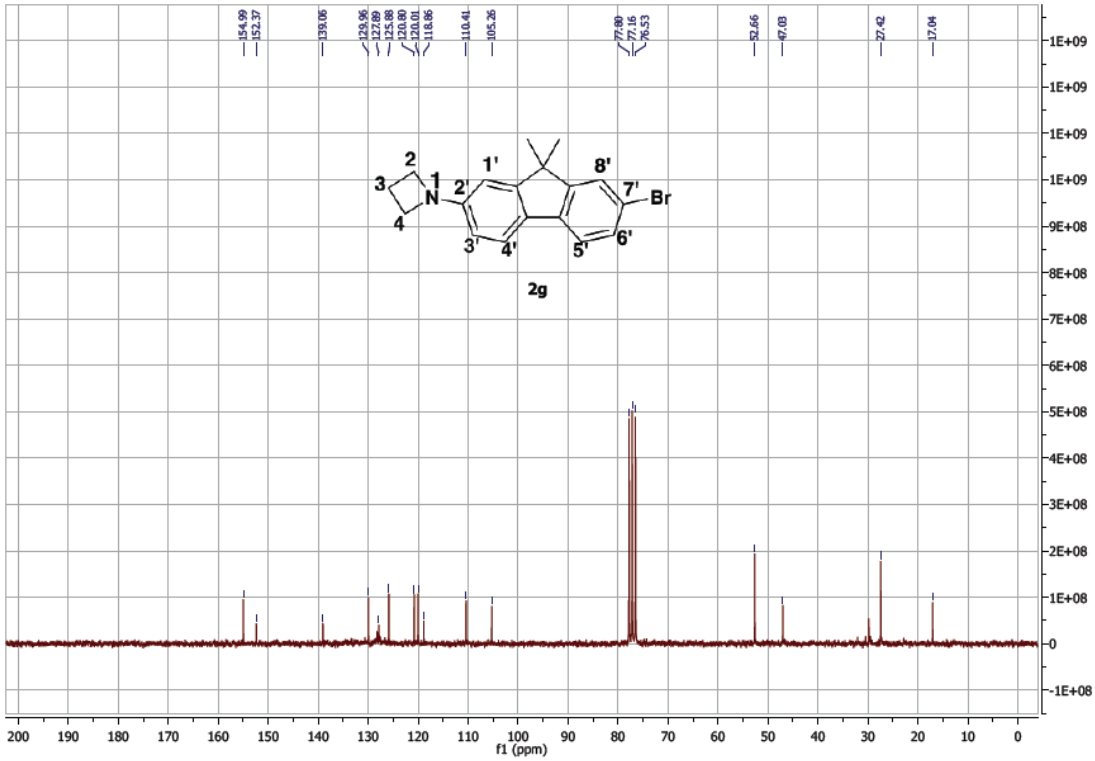
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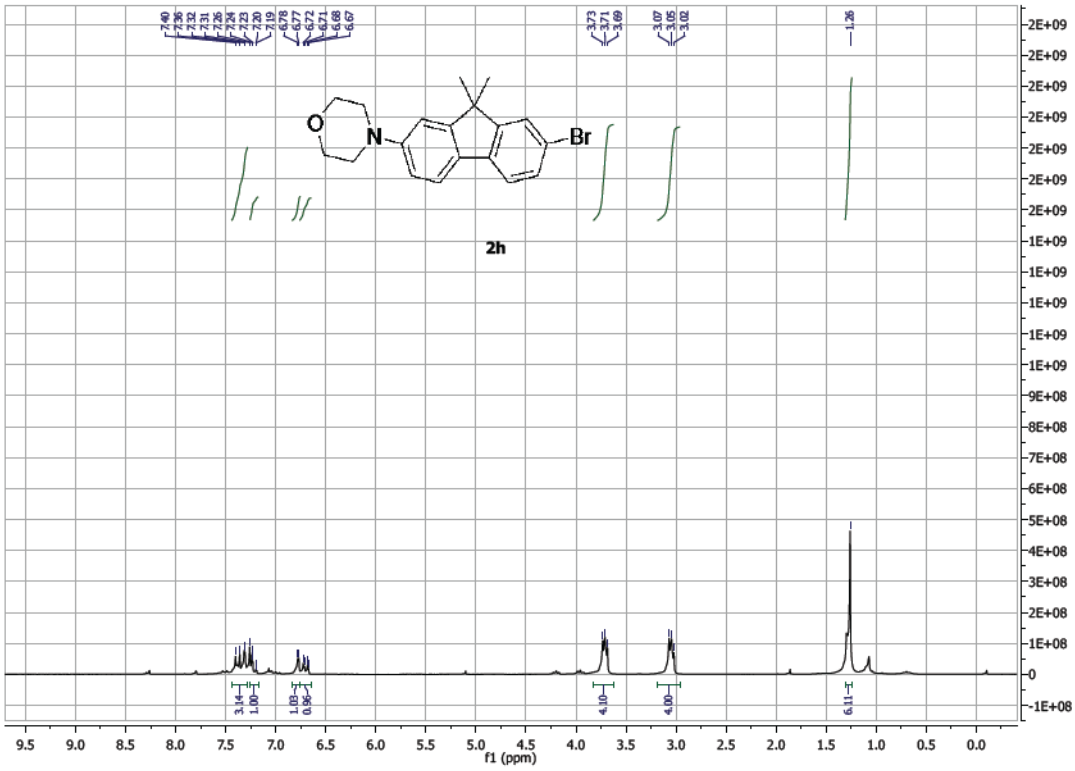
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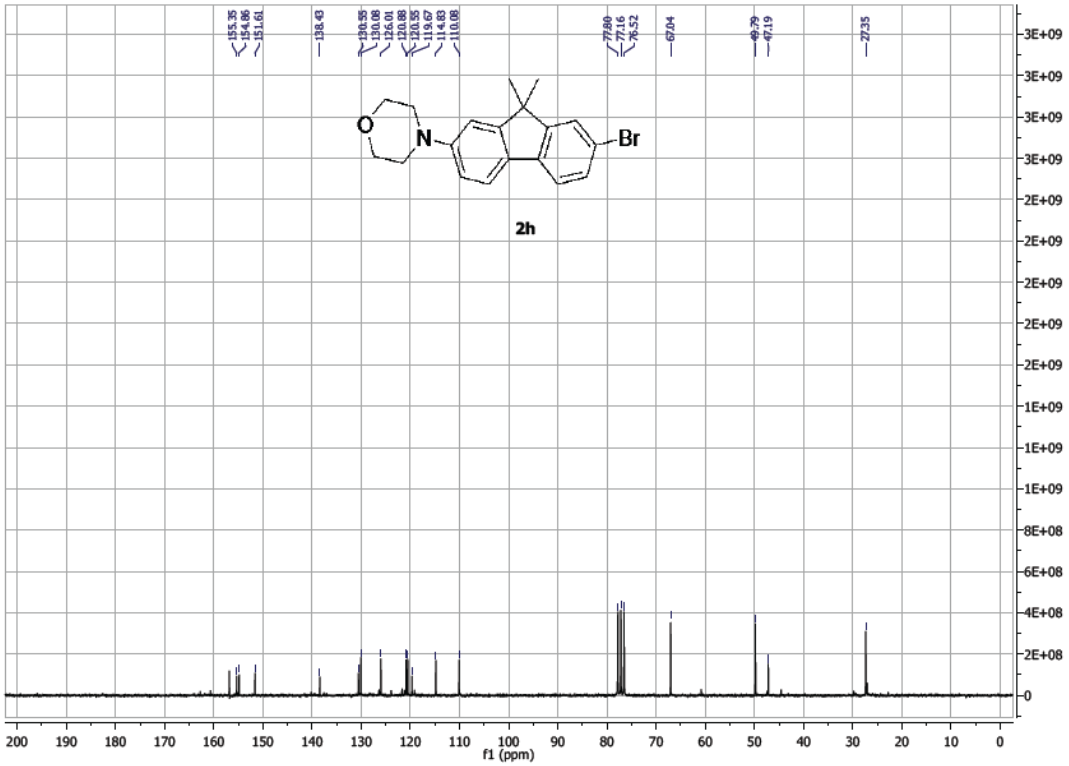
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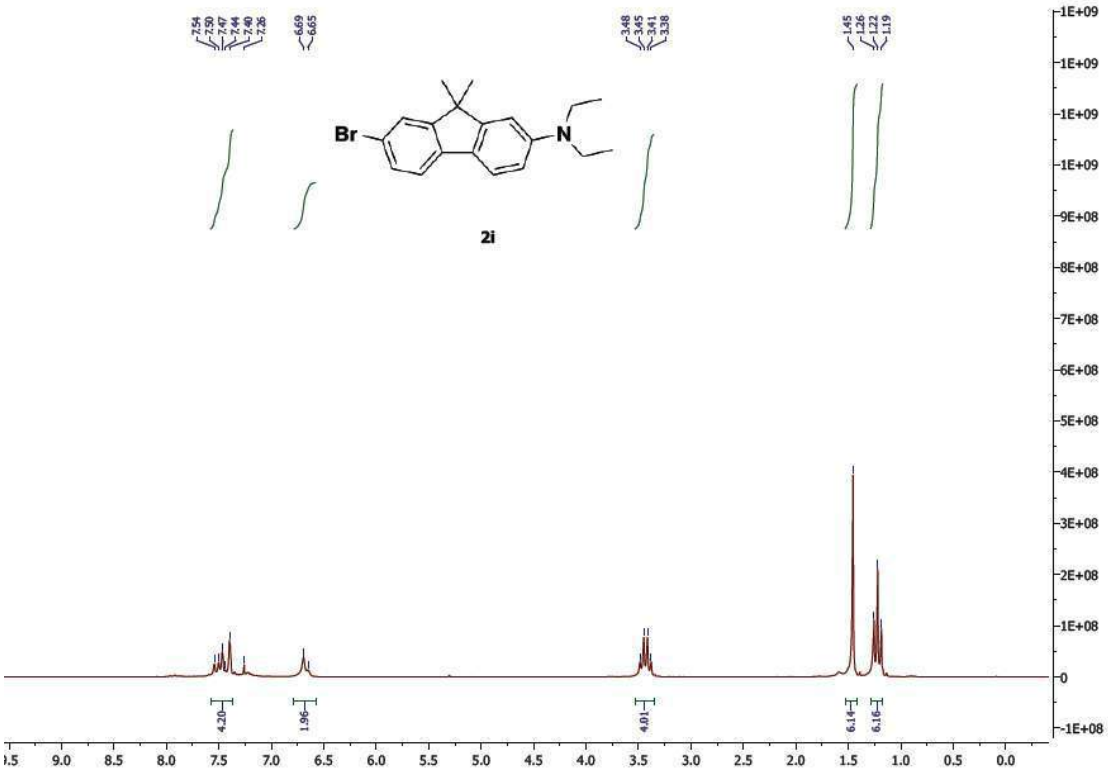
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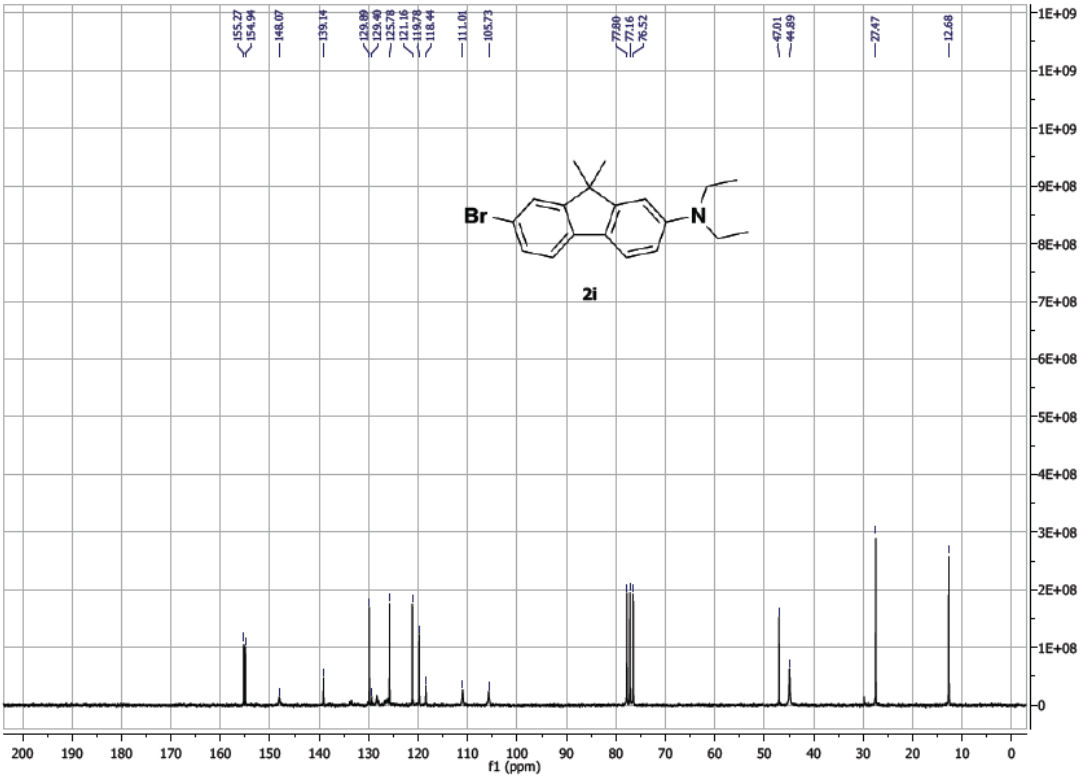
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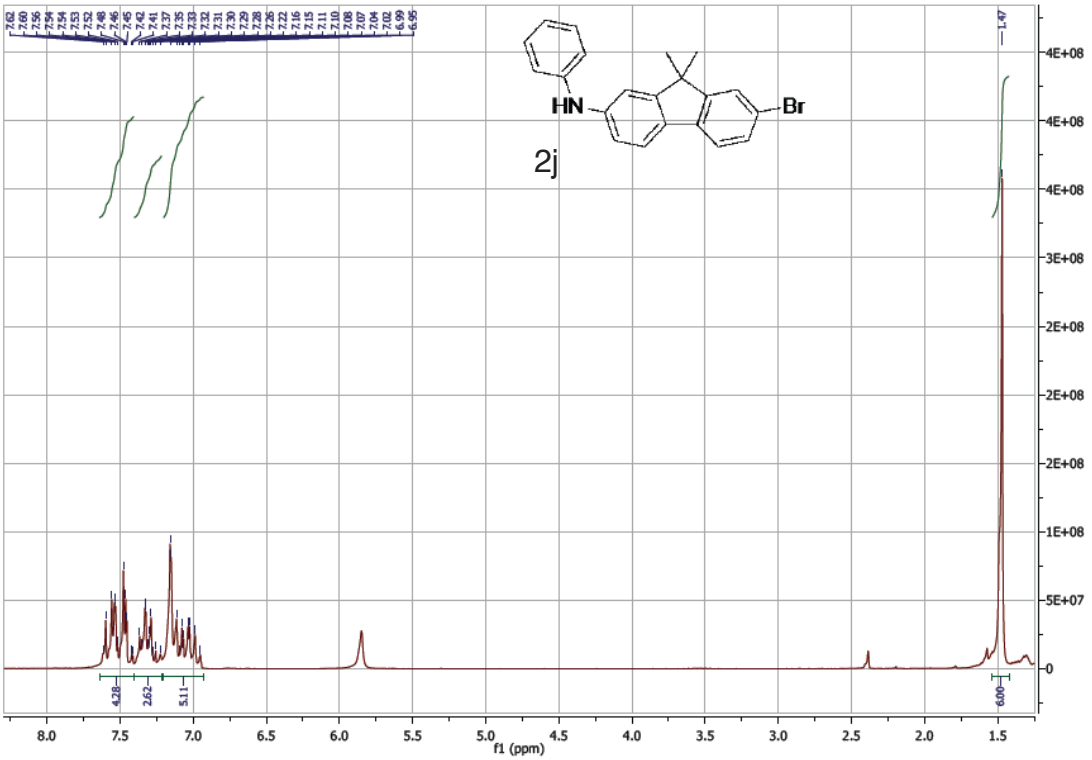
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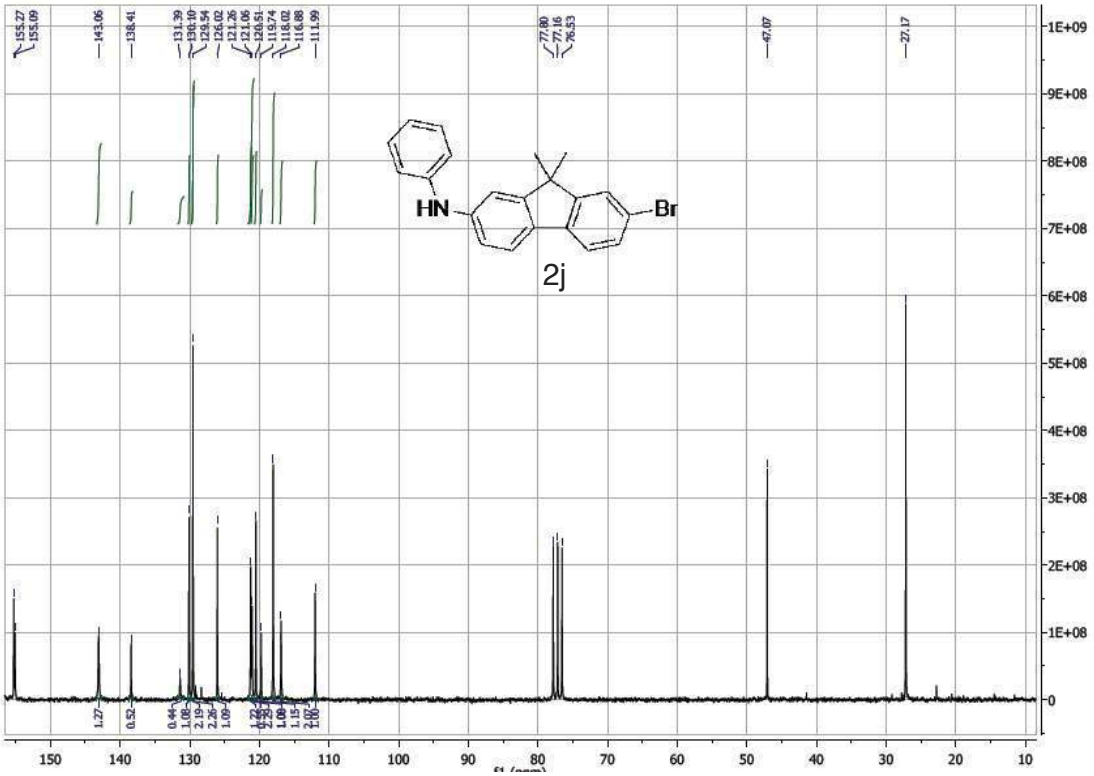
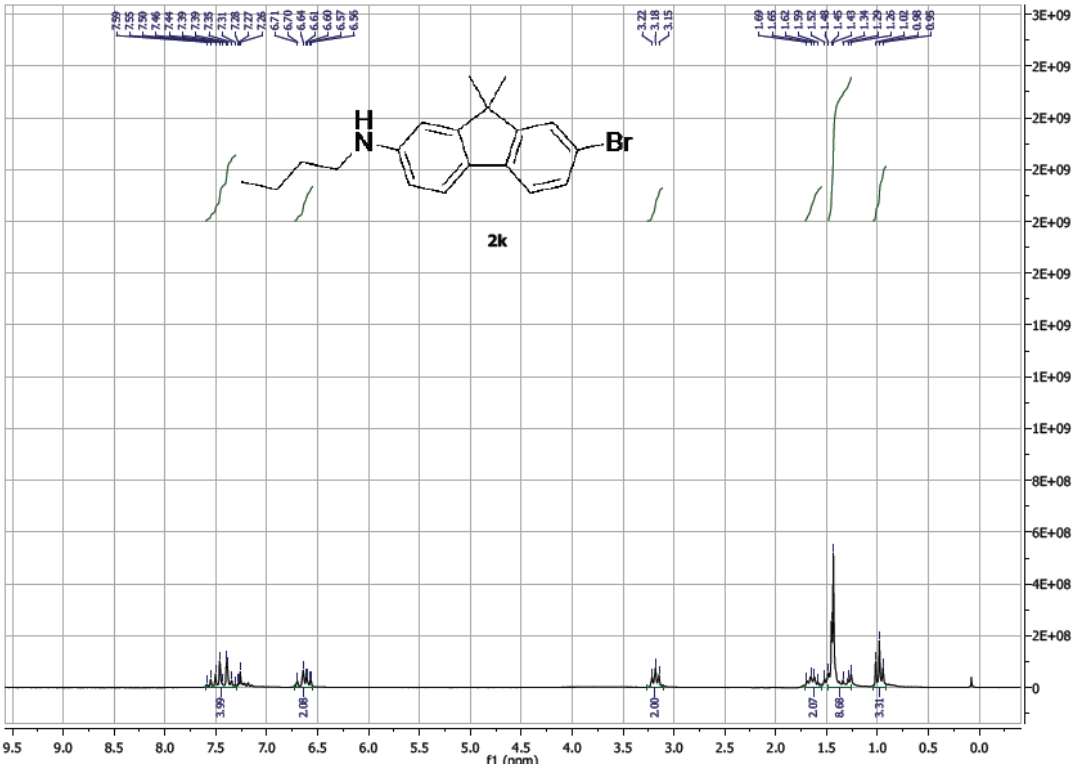
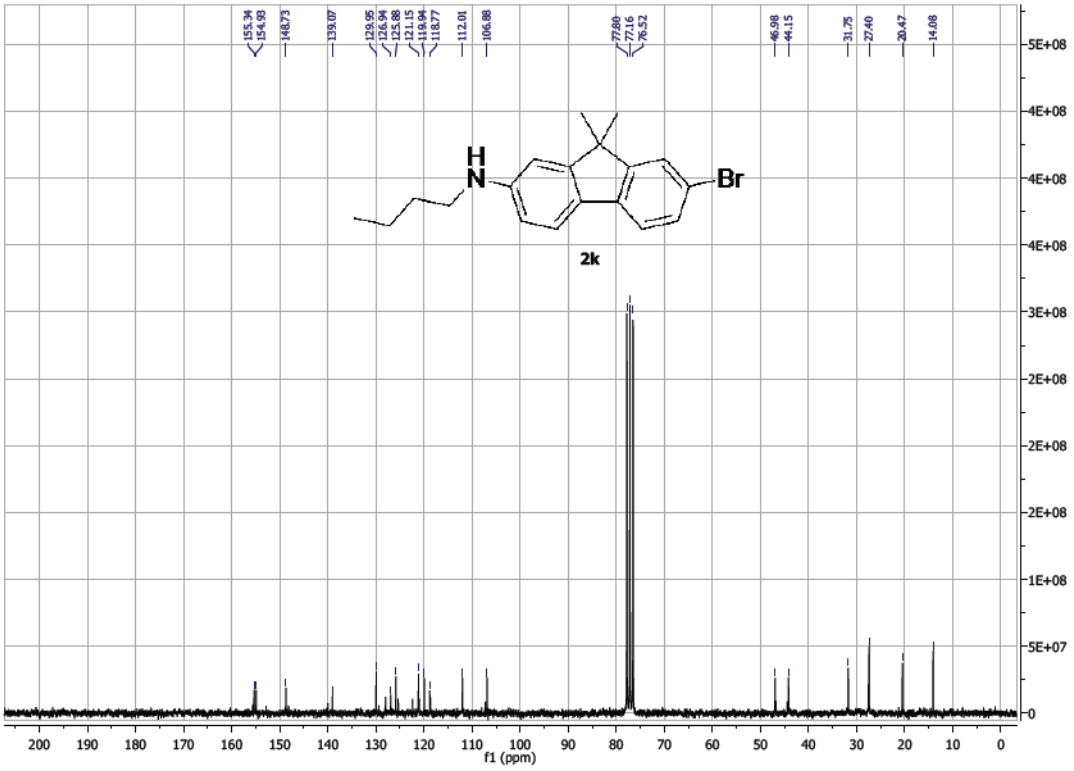
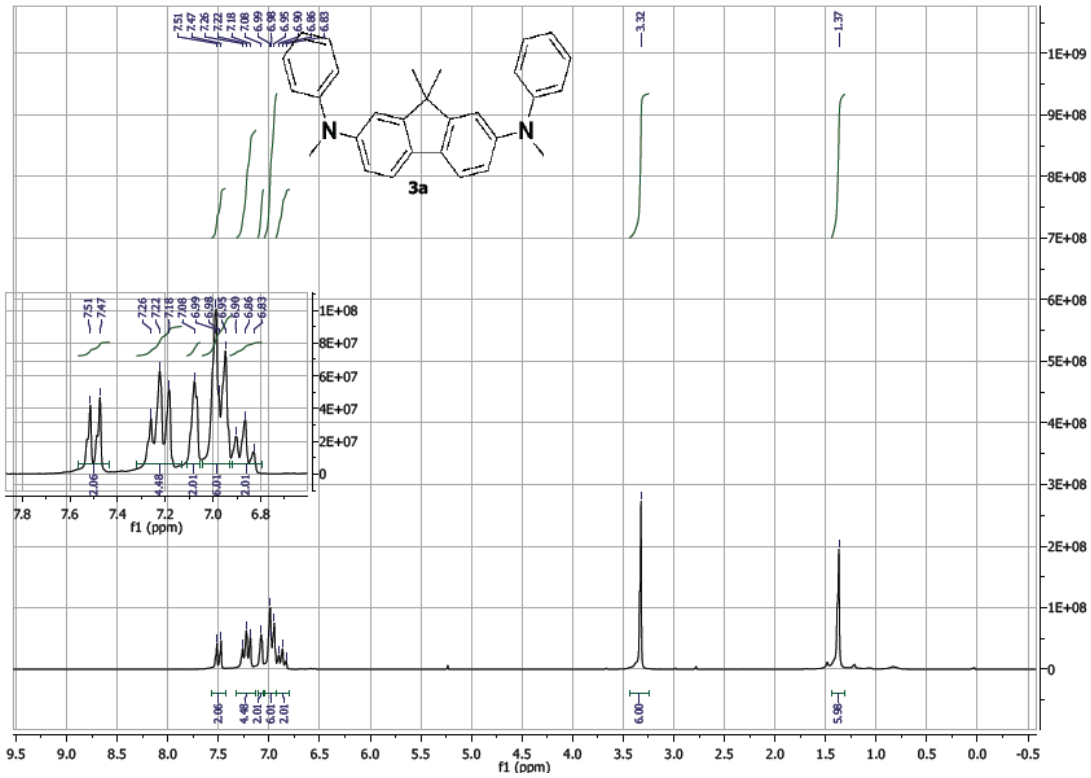
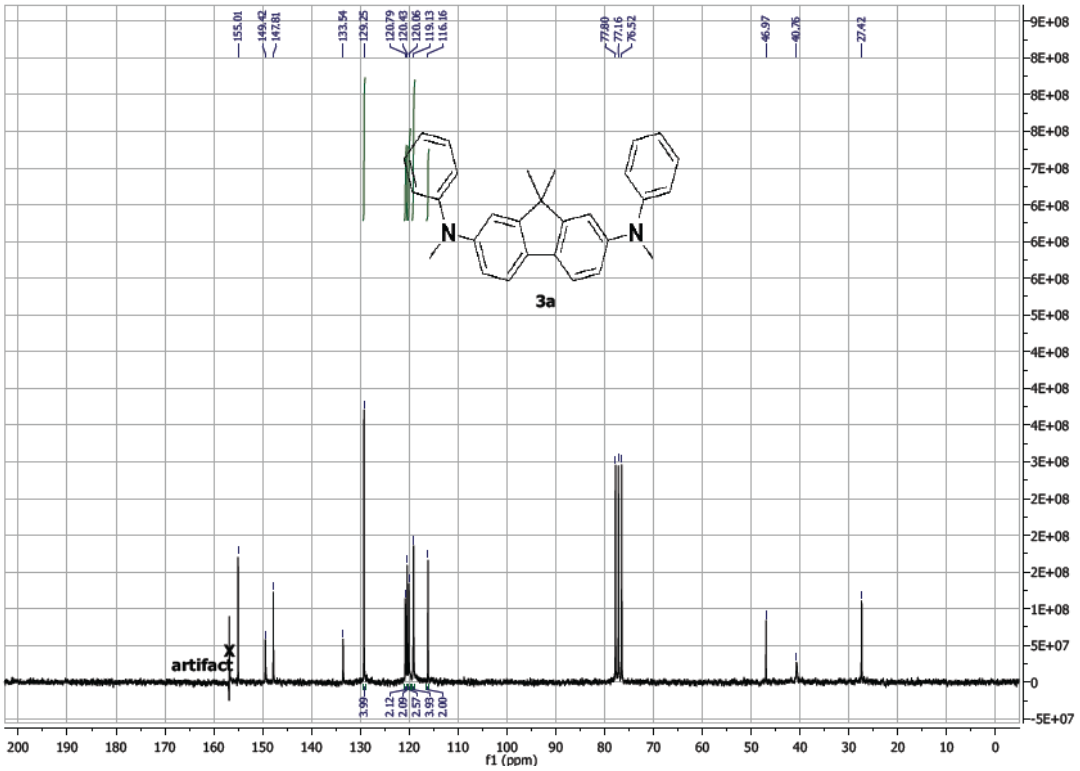
Br
2j
f1 (ppm)

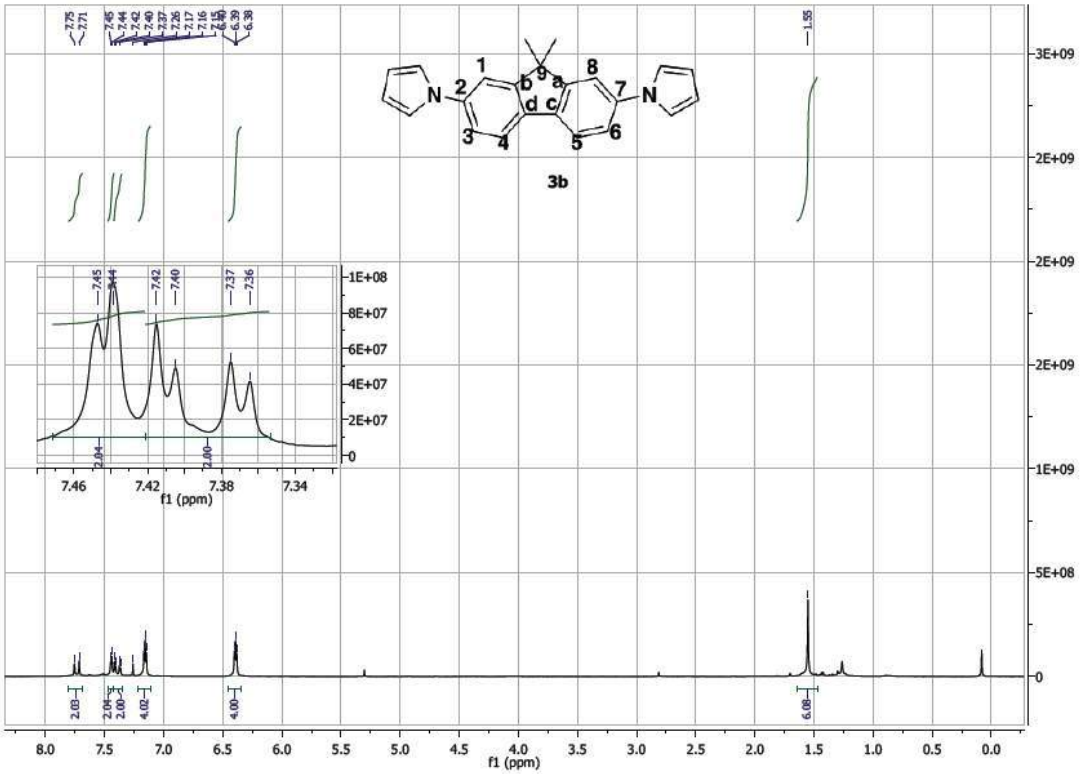

HN
Br
2j

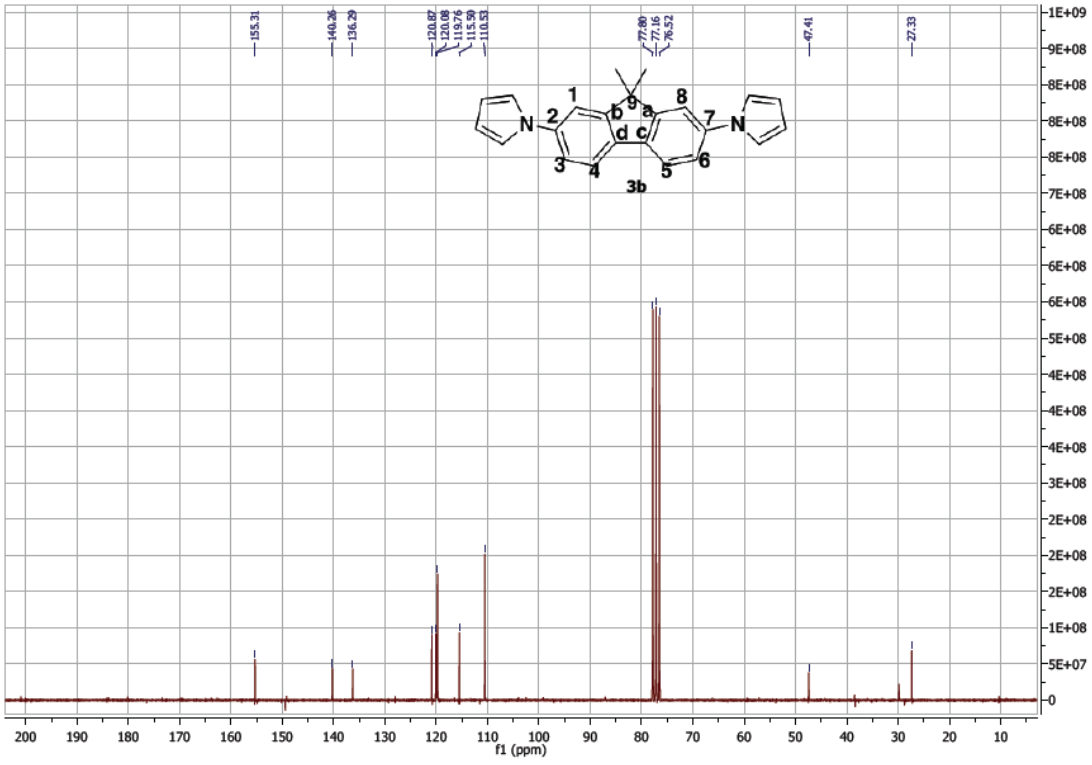

H
N
Br
2k
f1 (ppm)

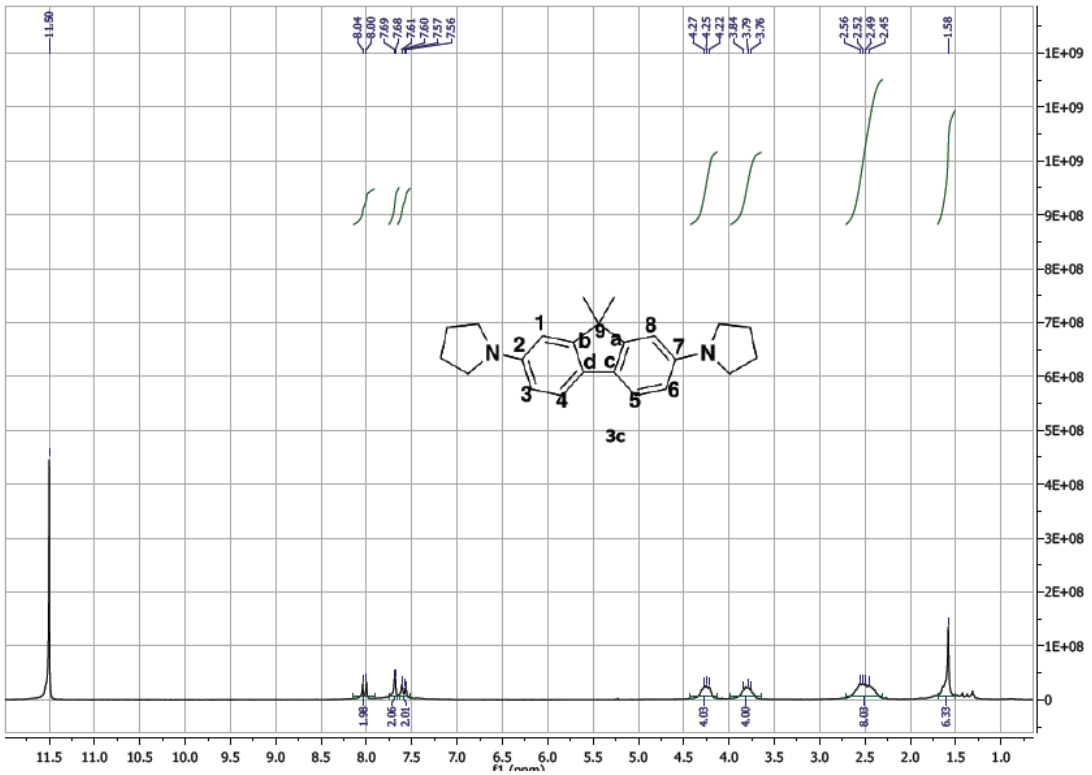

H
N
Br
2k
f1 (ppm)


3a
f1 (ppm)


3a
artifact
f1 (ppm)


3b
f1 (ppm)


3b
f1 (ppm)


11.50
8.04
8.00
7.69
7.68
7.61
7.60
7.57
7.56
4.27
4.25
4.22
3.84
3.79
3.76
2.56
2.52
2.49
2.45
1.58
1
2
3
4
5
6
7
8
9
a
b
c
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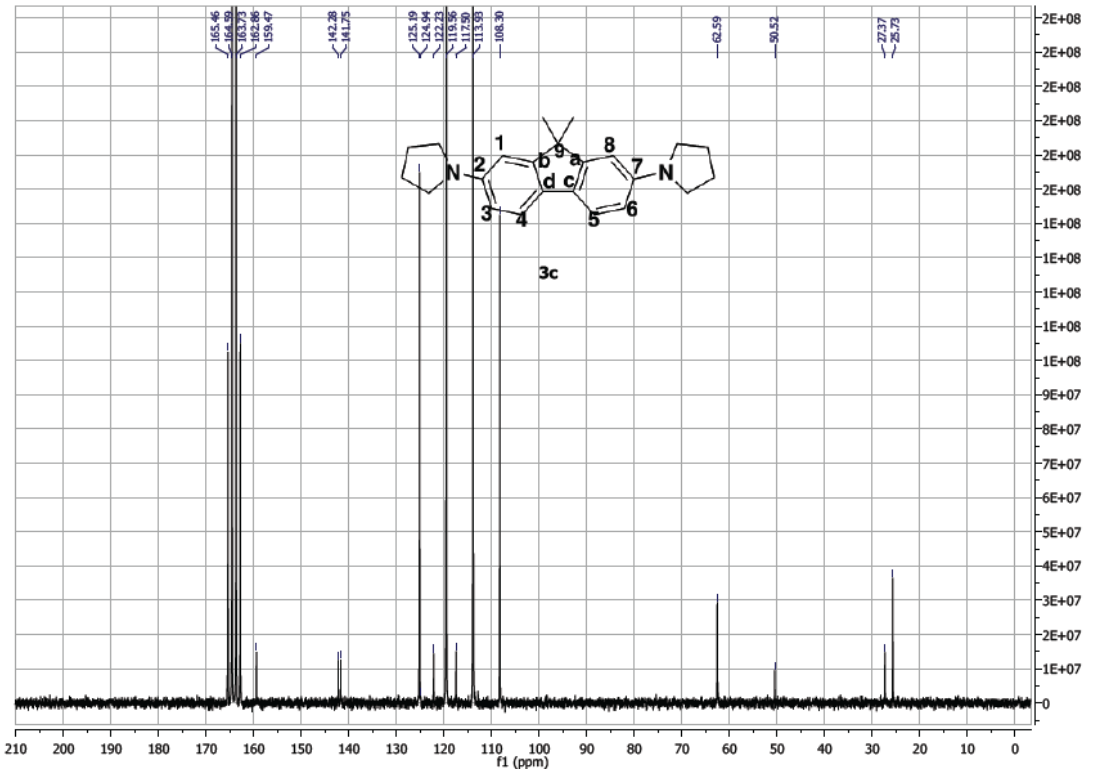
4.03
4.00
8.03
6.33
f1 (ppm)


165.46
164.99
163.77
162.86
159.47
142.28
141.75
125.19
124.94
117.22
116.96
117.30
113.98
108.30
62.59
50.52
27.37
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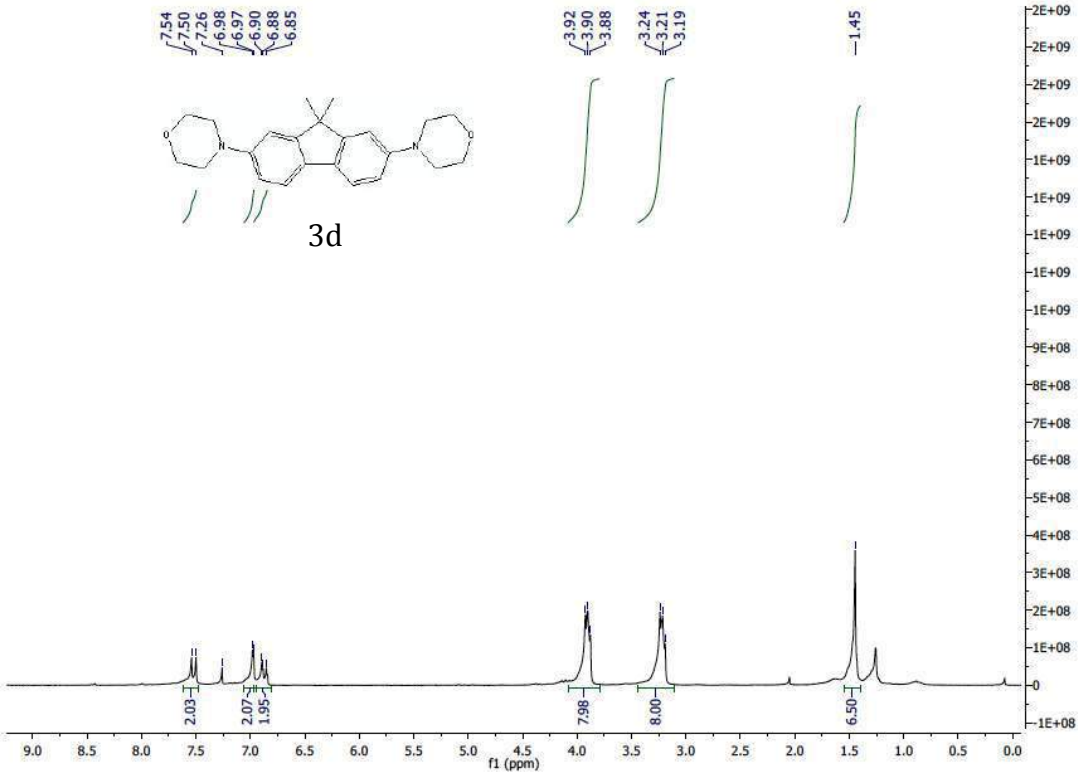
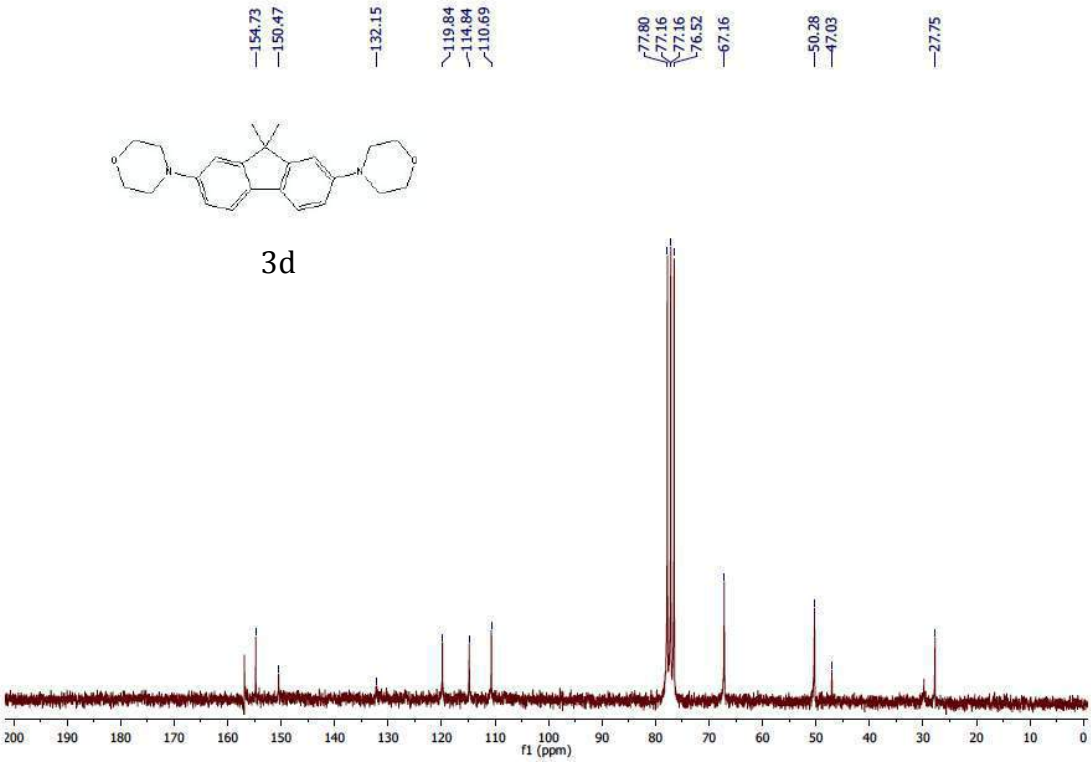
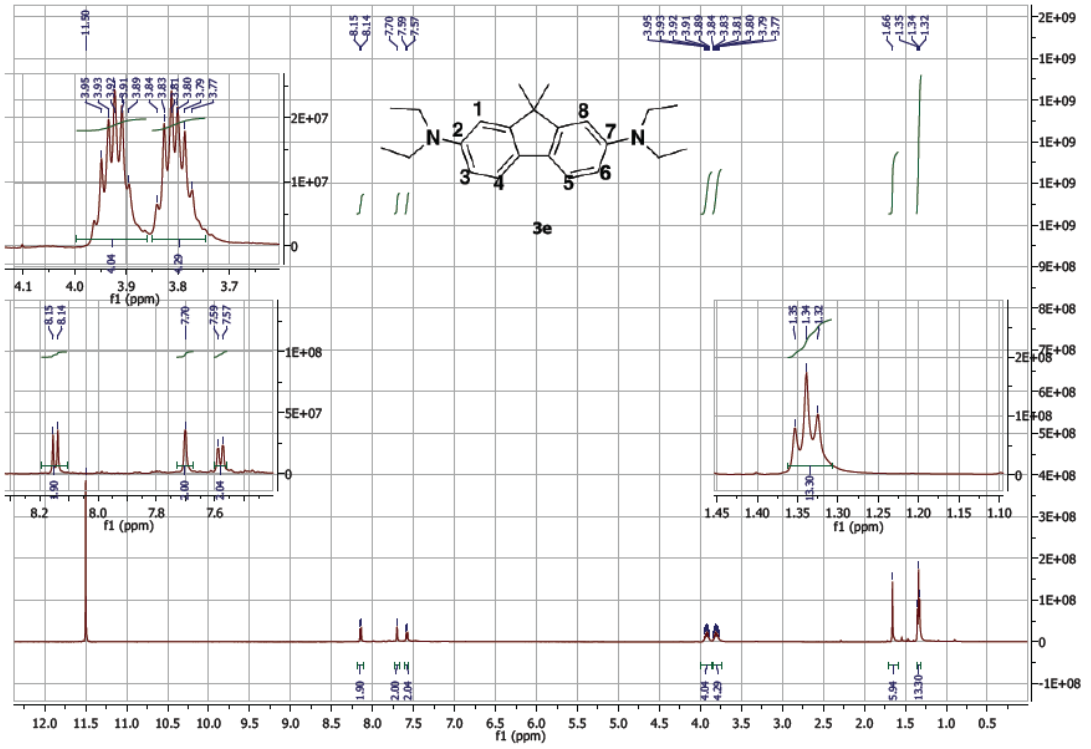
a
b
c
d
N
N
3c
f1 (ppm)

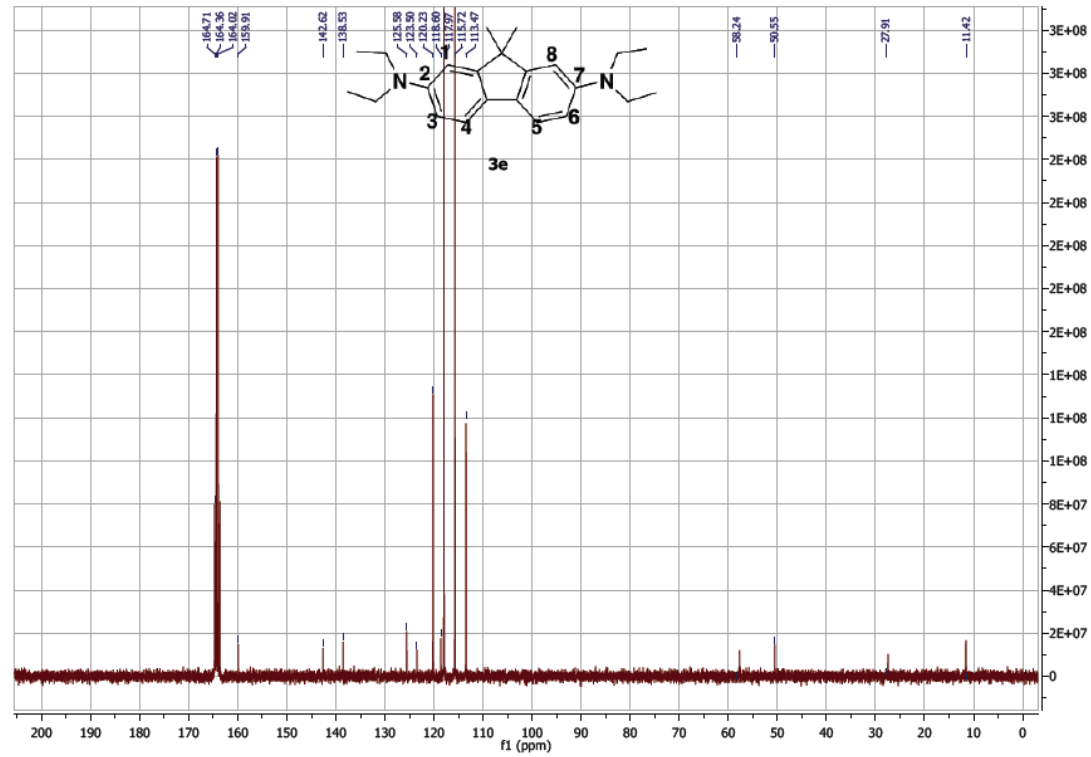

7.54
7.50
7.26
6.98
6.97
6.90
6.88
6.85
3.92
3.90
3.88
3.24
3.21
3.19
1.45
2.03
2.07
1.95
7.98
8.00
6.50
f1 (ppm)

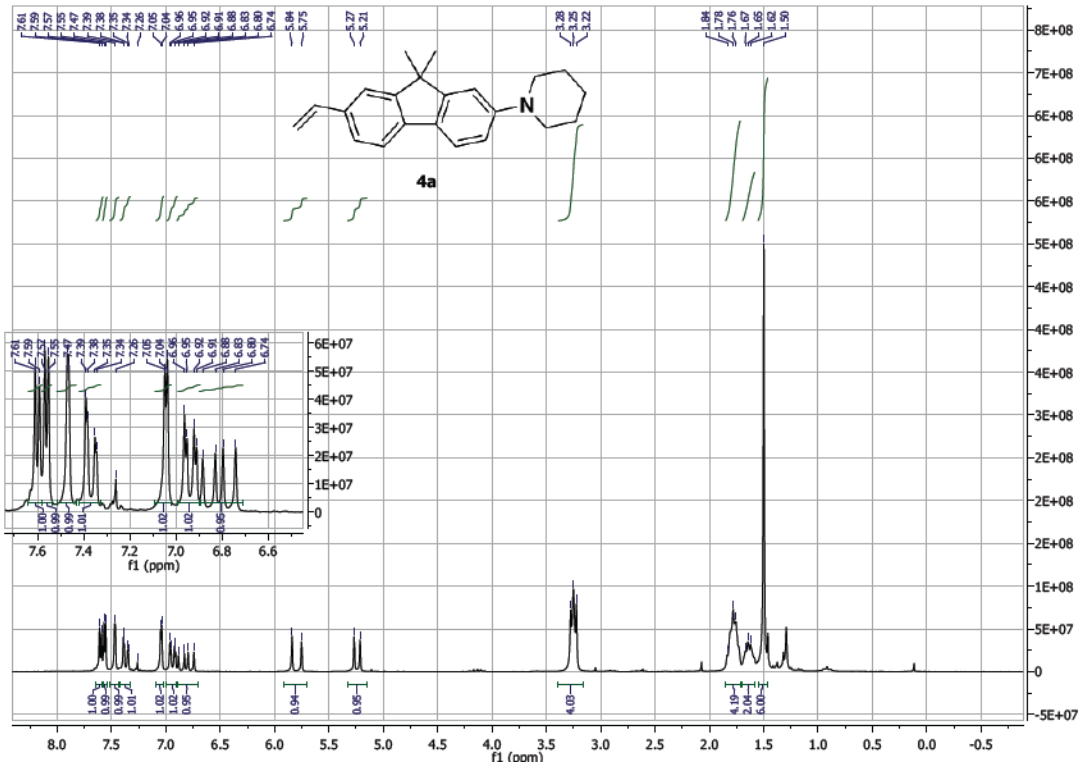
3d

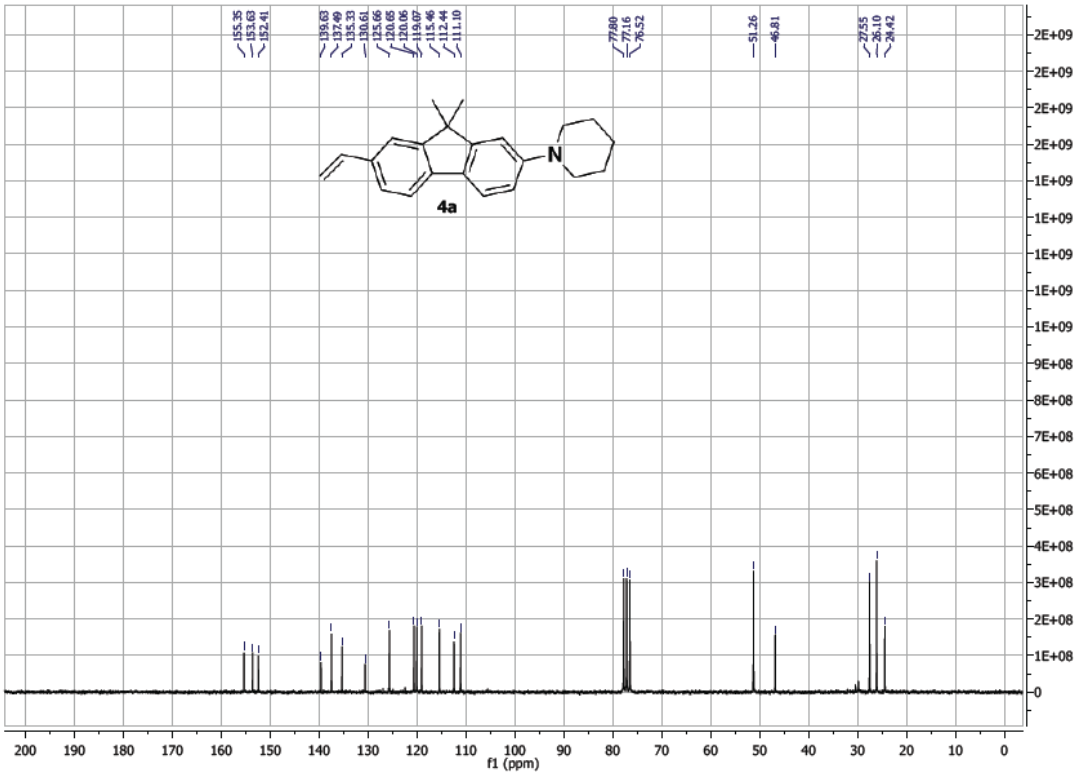

154.73
150.47
132.15
119.84
114.84
110.69
77.80
77.16
77.16
76.52
67.16
50.28
47.03
27.75
f1 (ppm)

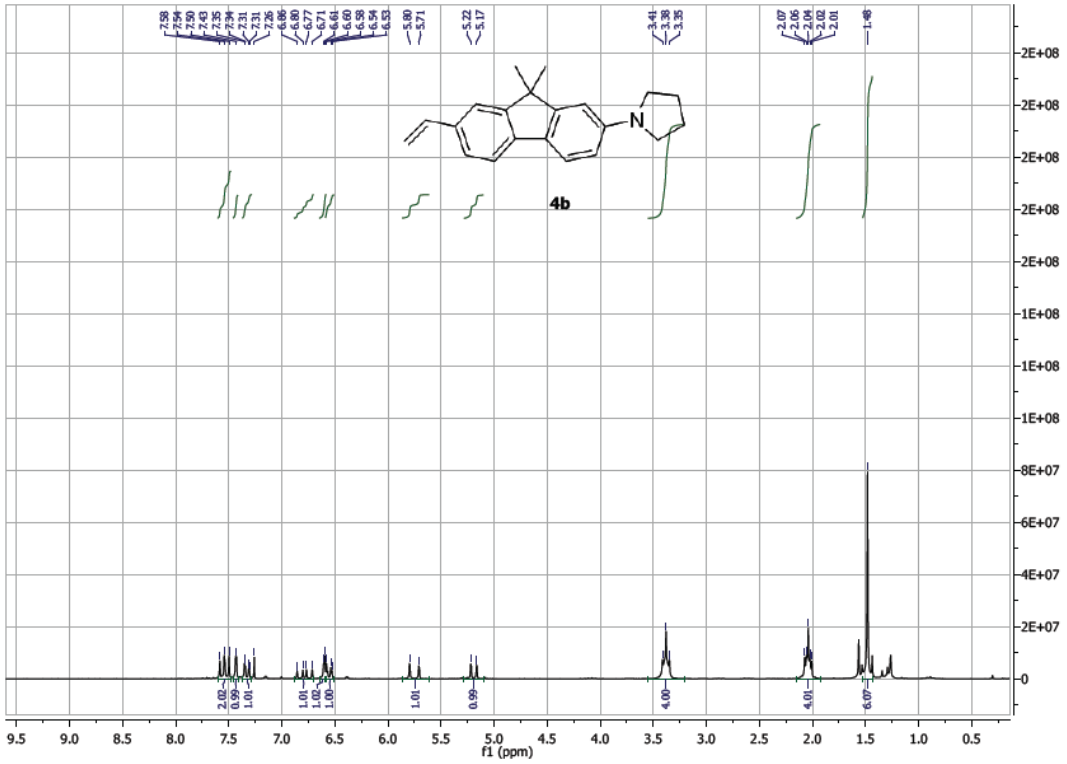
3d

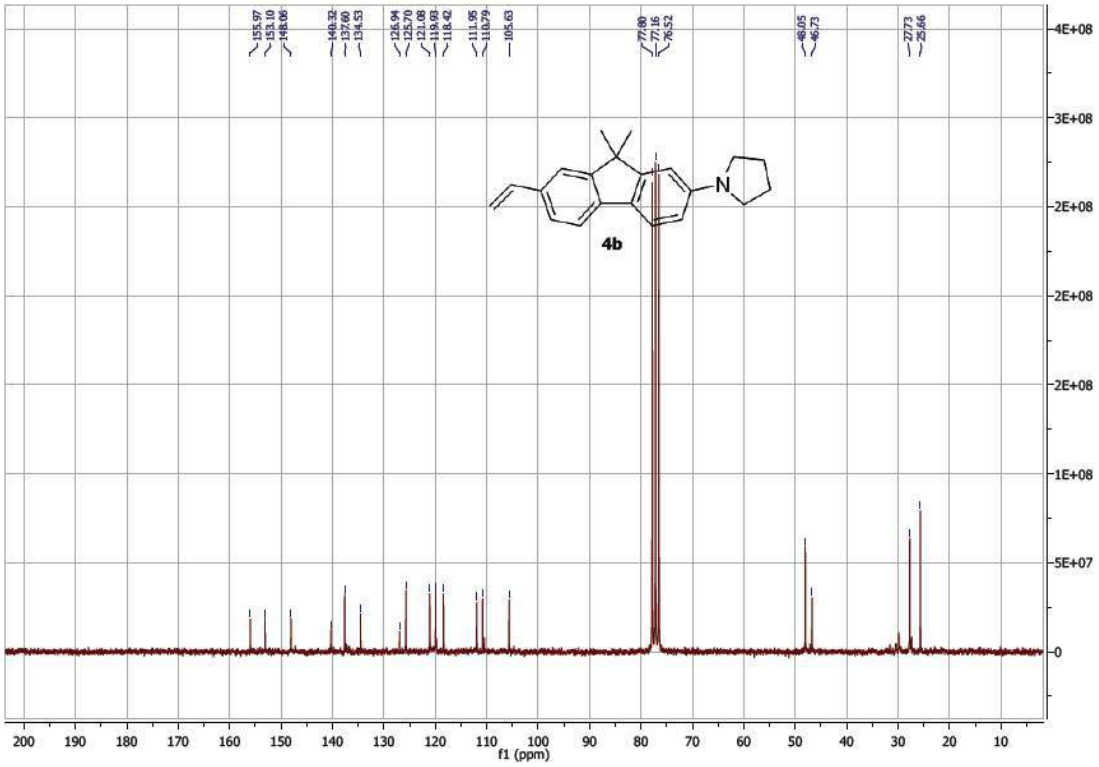

3e
f1 (ppm)

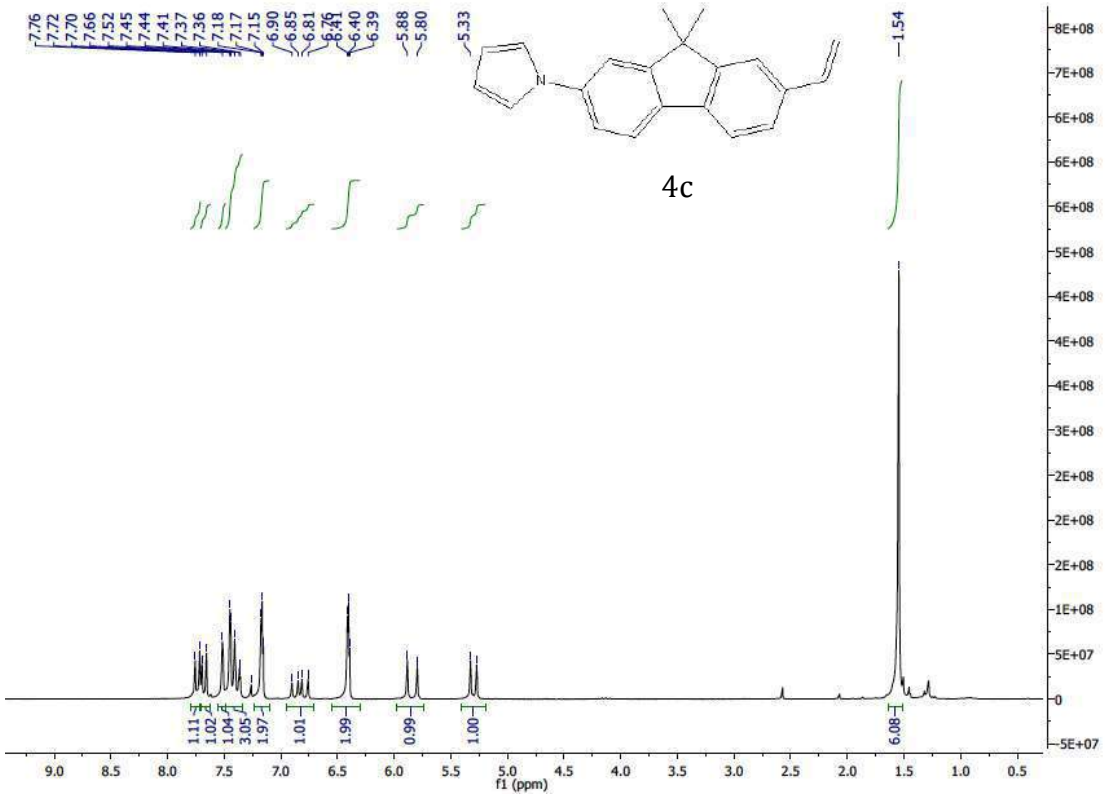

3e
f1 (ppm)


4a
f1 (ppm)

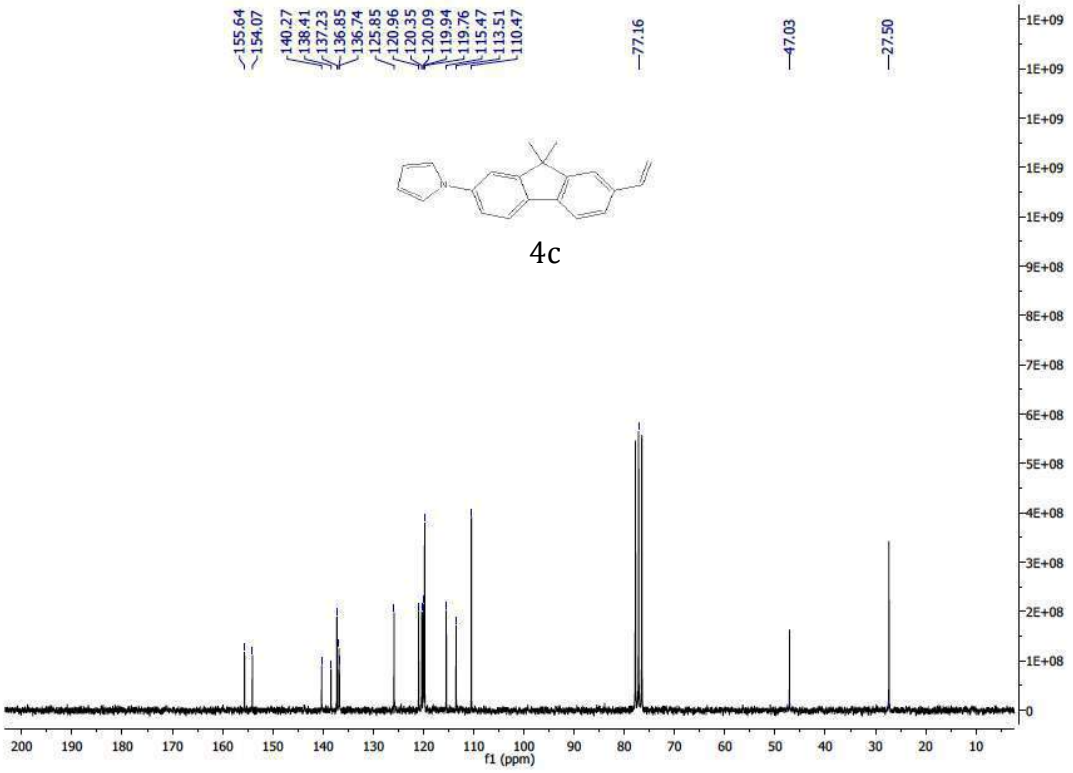

4a
f1 (ppm)


4b
f1 (ppm)

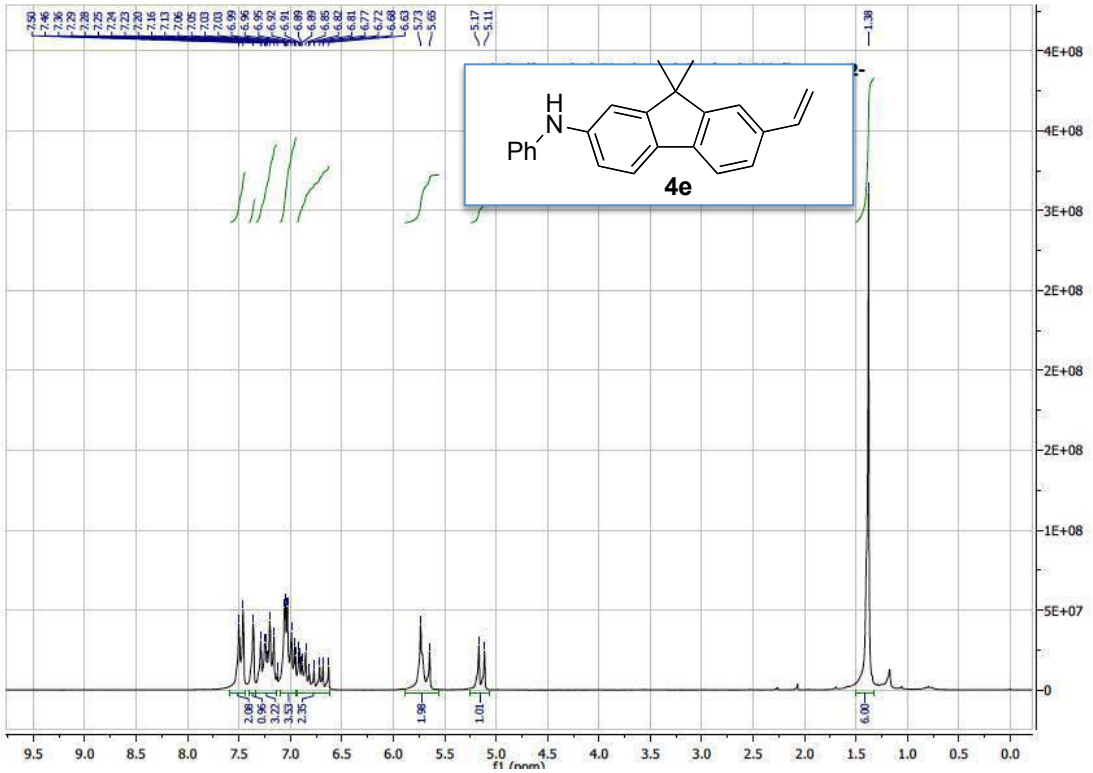

4b
f1 (ppm)

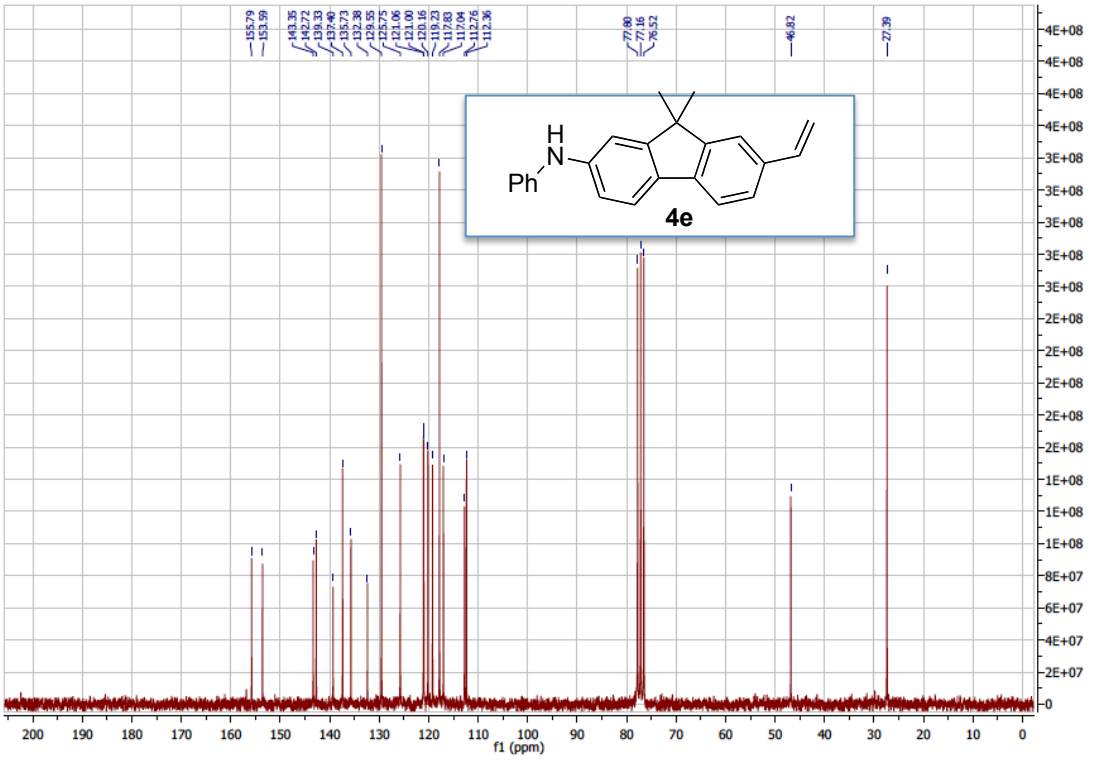

7.76
7.72
7.70
7.66
7.52
7.45
7.44
7.41
7.37
7.36
7.18
7.17
7.15
6.90
6.85
6.81
6.76
6.41
6.40
6.39
5.88
5.80
5.33
1.54
1.11
1.02
1.04
3.05
1.97
1.01
1.99
0.99
1.00
6.08
f1 (ppm)

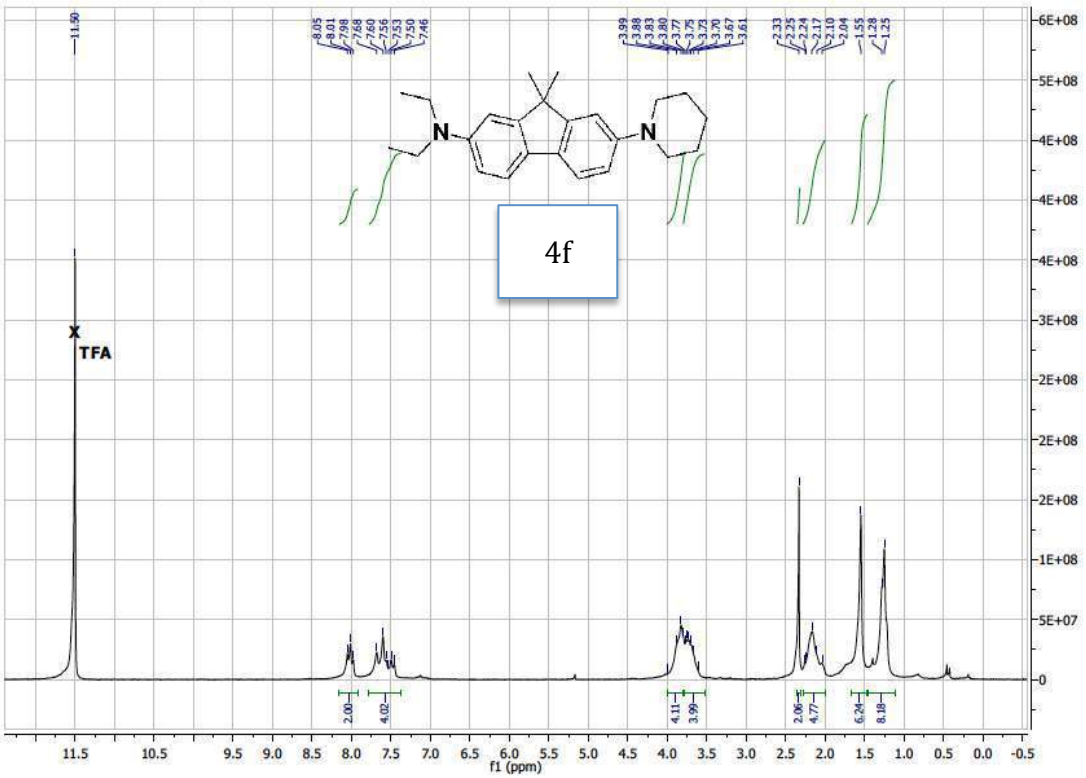
4c

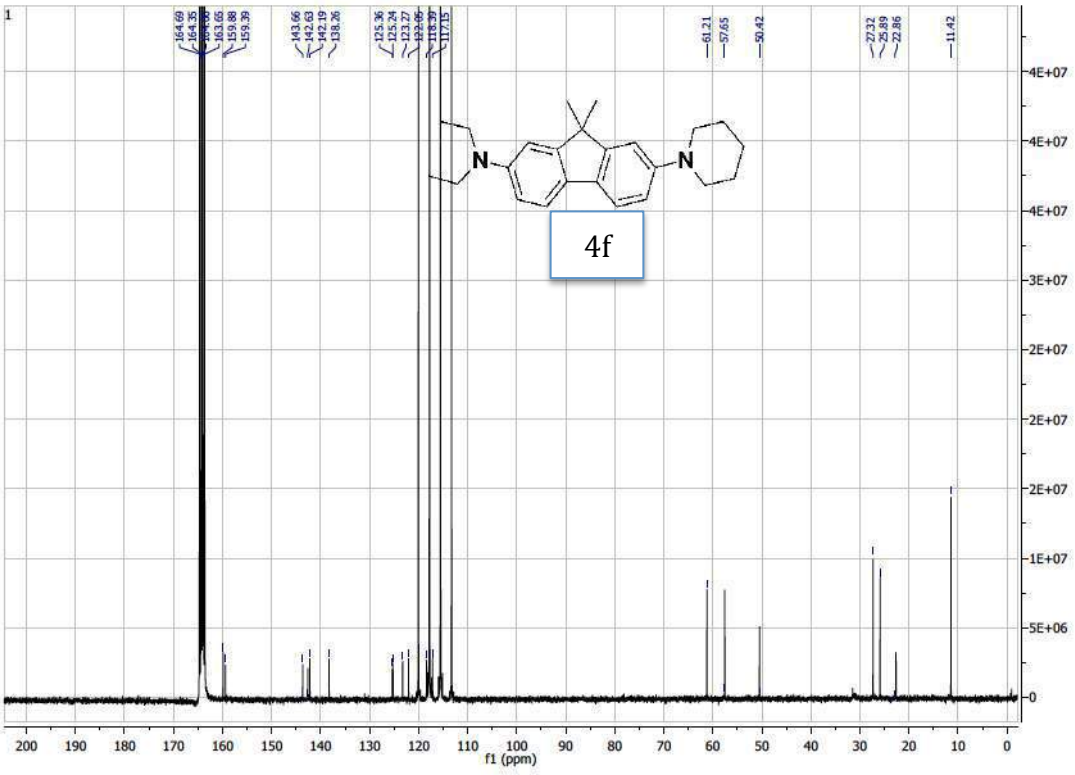

155.64
154.07
140.27
138.41
137.23
136.85
136.74
125.85
120.96
120.35
120.09
119.94
119.76
115.47
113.51
110.47
77.16
47.03
27.50
f1 (ppm)

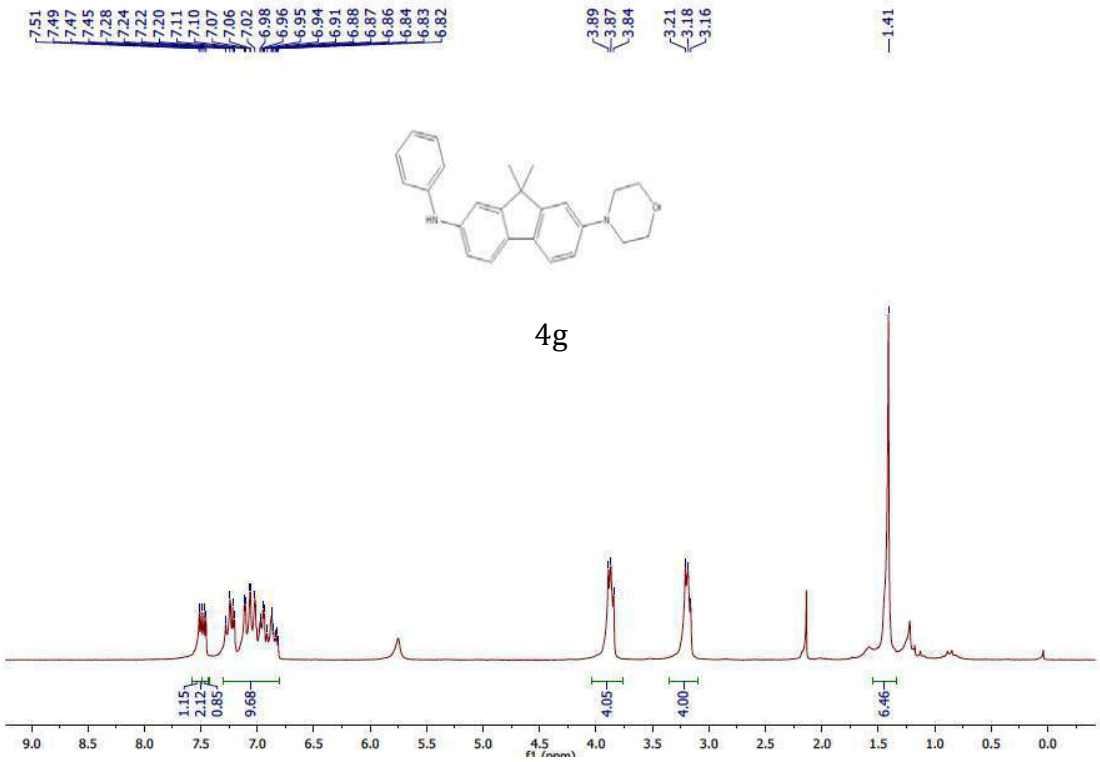
4c


H
N
Ph
4e

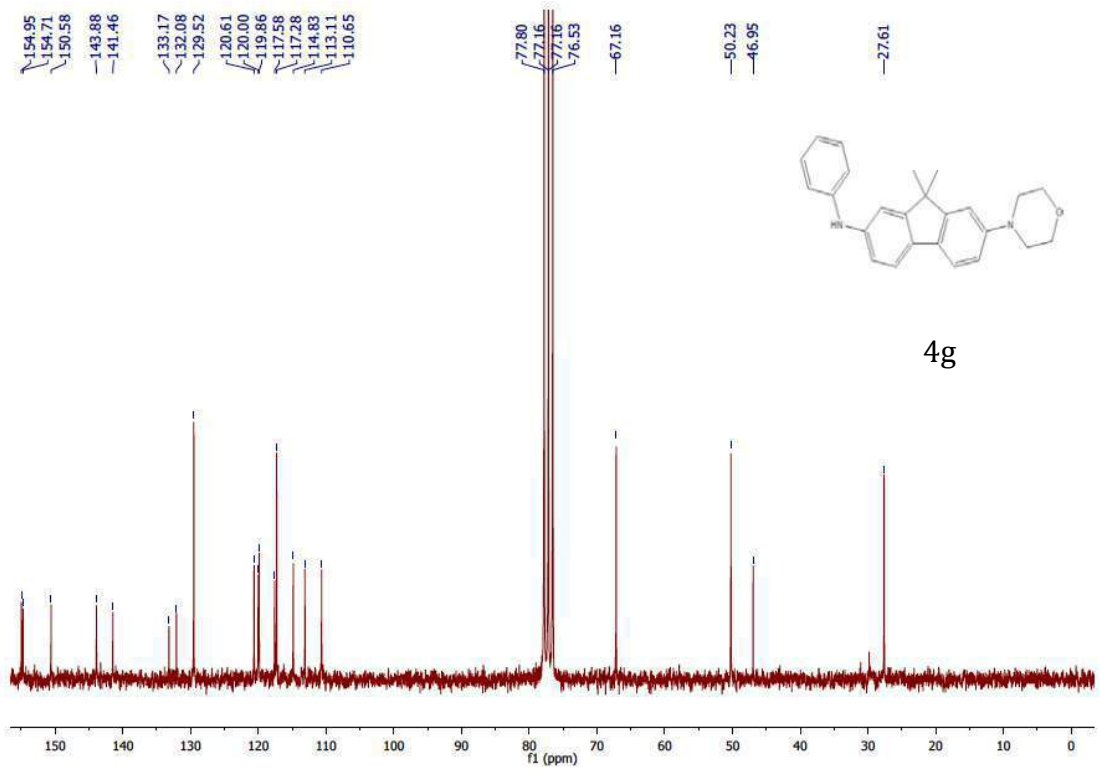

H
N
Ph
4e
f1 (ppm)


11.50
8.05
8.01
7.98
7.68
7.66
7.56
7.53
7.50
7.46
3.99
3.88
3.83
3.80
3.77
3.75
3.73
3.70
3.67
3.61
2.33
2.25
2.24
2.17
2.10
2.04
1.55
1.28
1.25
N
N
4f
X
TFA
2.00
4.02
4.11
3.99
2.06
4.77
6.24
8.18
f1 (ppm)


164.69
164.35
163.66
159.88
159.39
143.66
142.63
142.19
138.26
125.36
125.24
123.27
61.21
57.65
50.42
27.32
25.89
22.86
11.42
N
N
4f
f1 (ppm)


7.51
7.49
7.47
7.45
7.28
7.24
7.22
7.20
7.11
7.10
7.07
7.06
7.02
6.98
6.96
6.95
6.94
6.91
6.88
6.87
6.86
6.84
6.83
6.82
3.89
3.87
3.84
3.21
3.18
3.16
1.41
1.15
2.12
0.85
9.68
4.05
4.00
6.46
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

4g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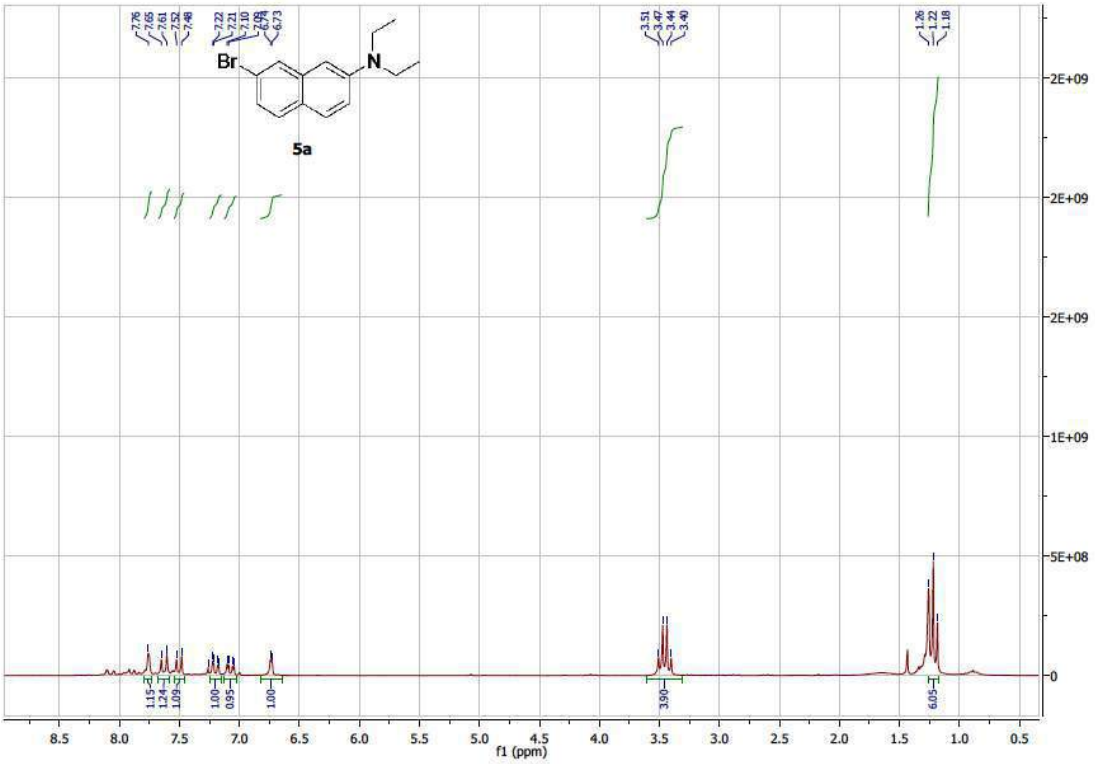
154.71
150.58
143.88
141.46
133.17
132.08
129.52
120.61
120.00
119.86
117.58
117.28
114.83
113.11
110.65
77.80
77.16
76.53
67.16
50.23
46.95
27.61
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4g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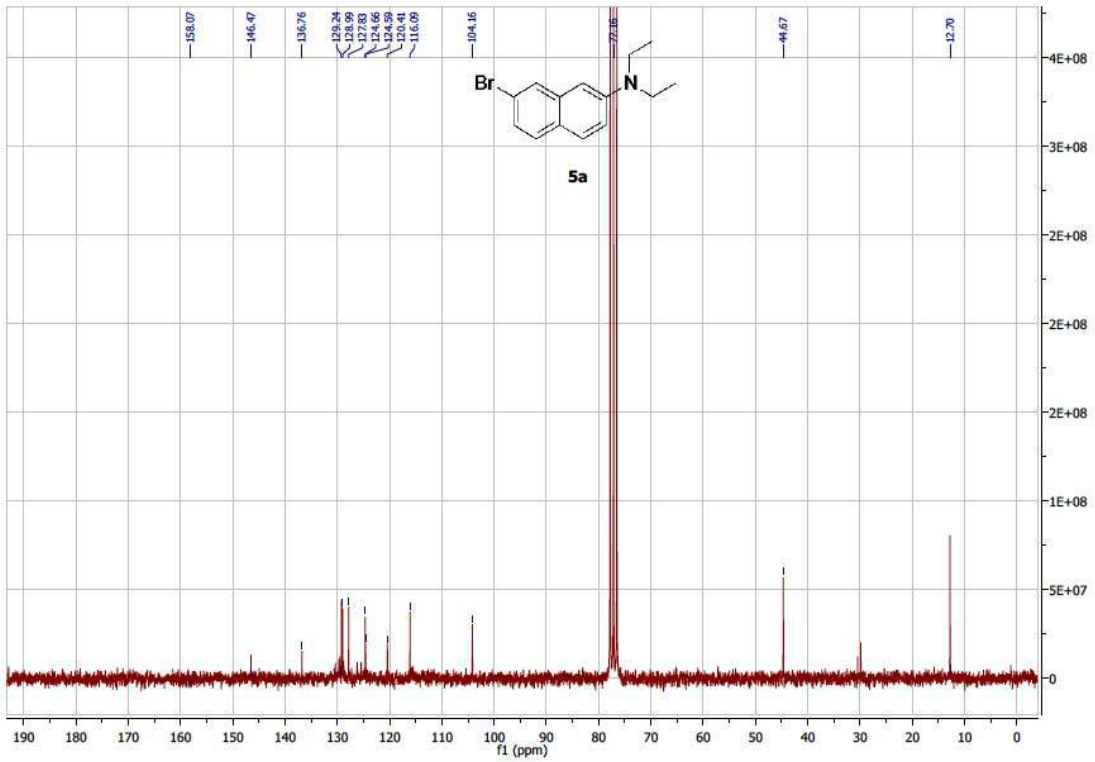
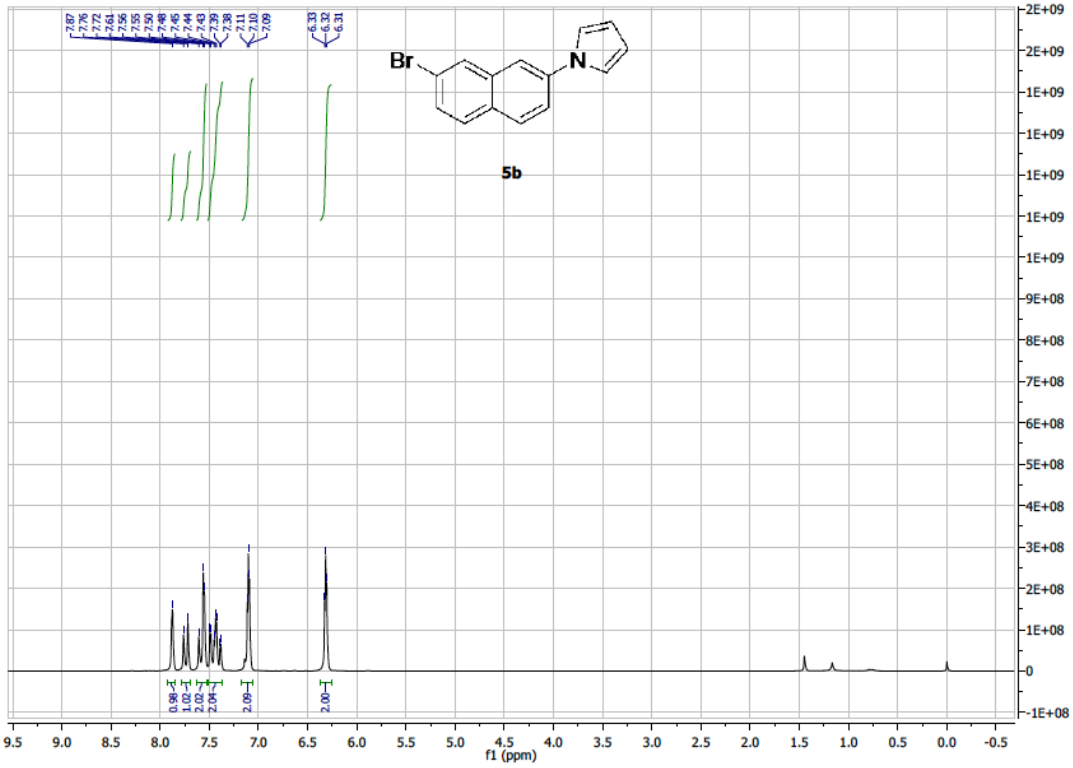
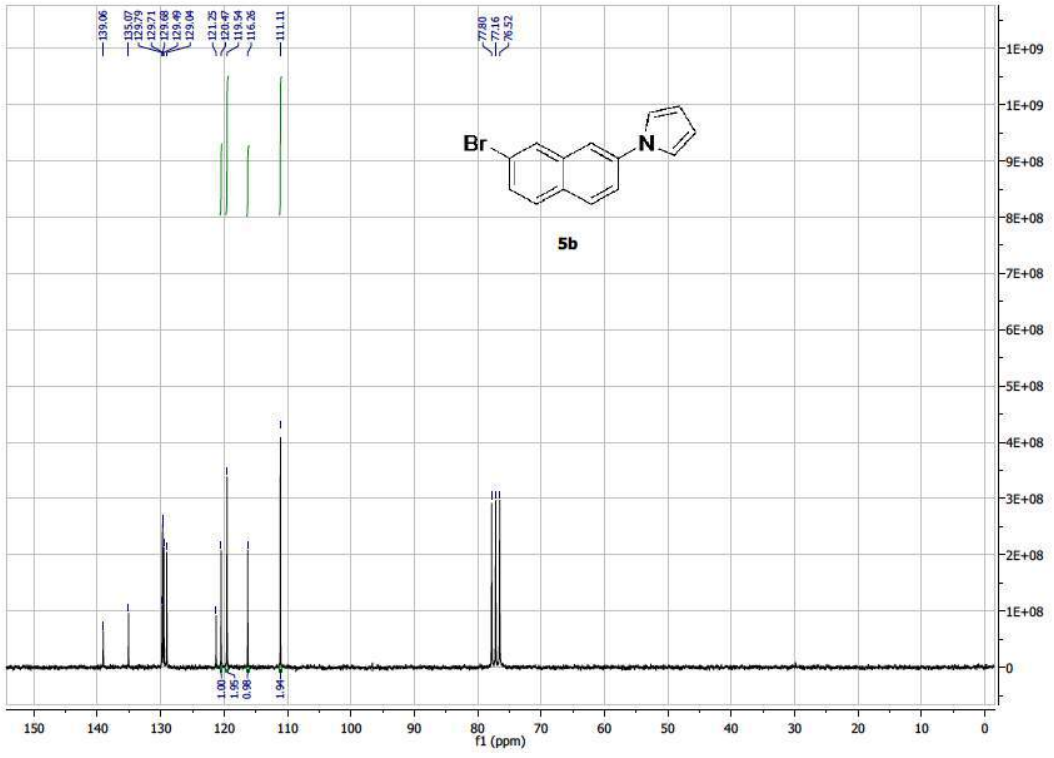
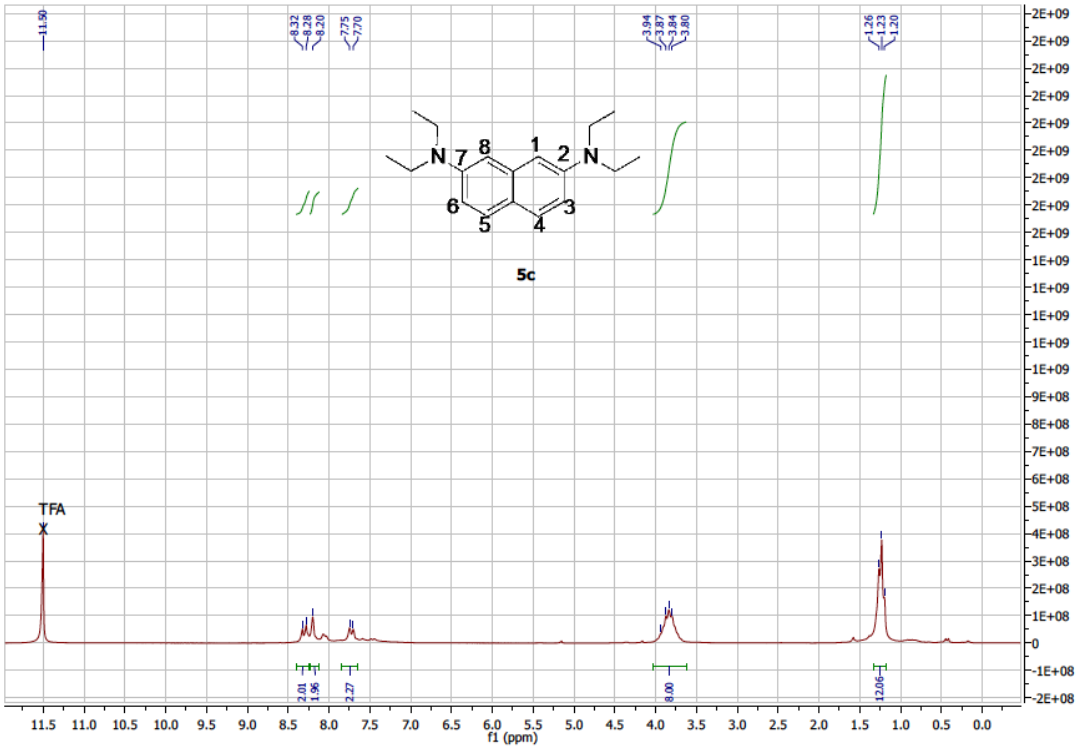
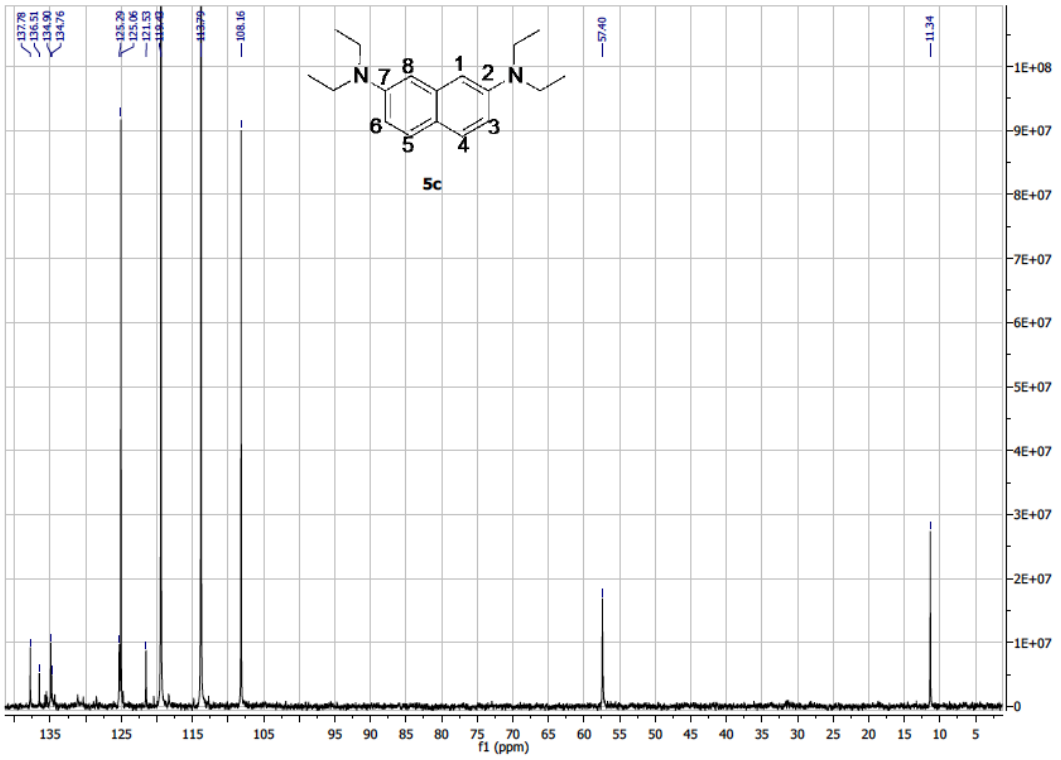
7.65
7.61
7.52
7.48
7.22
7.21
7.10
6.74
6.73
3.51
3.47
3.44
3.40
1.26
1.22
1.18
Br
N
5a
2E+09
2E+09
2E+09
1E+09
5E+08
0
1.15
1.24
1.09
1.00
0.95
1.00
3.90
6.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

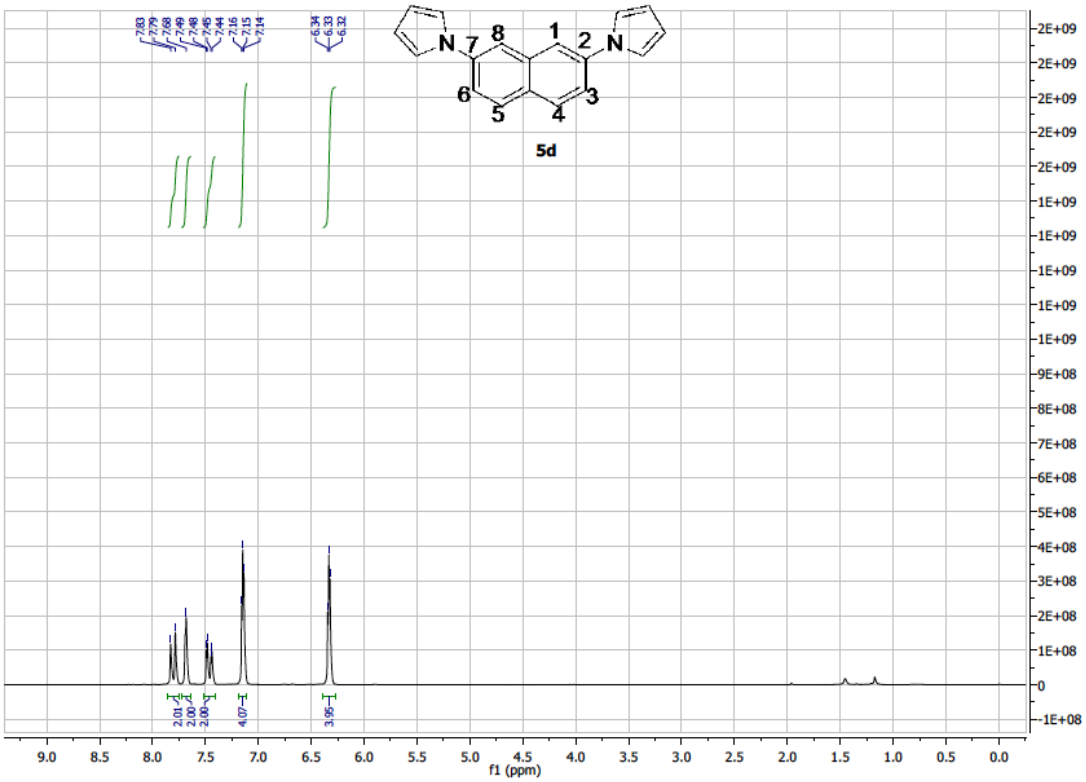

158.07
146.47
136.76
129.24
128.99
127.83
124.66
124.59
120.41
116.09
104.16
77.16
44.67
12.70
Br
N
5a
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

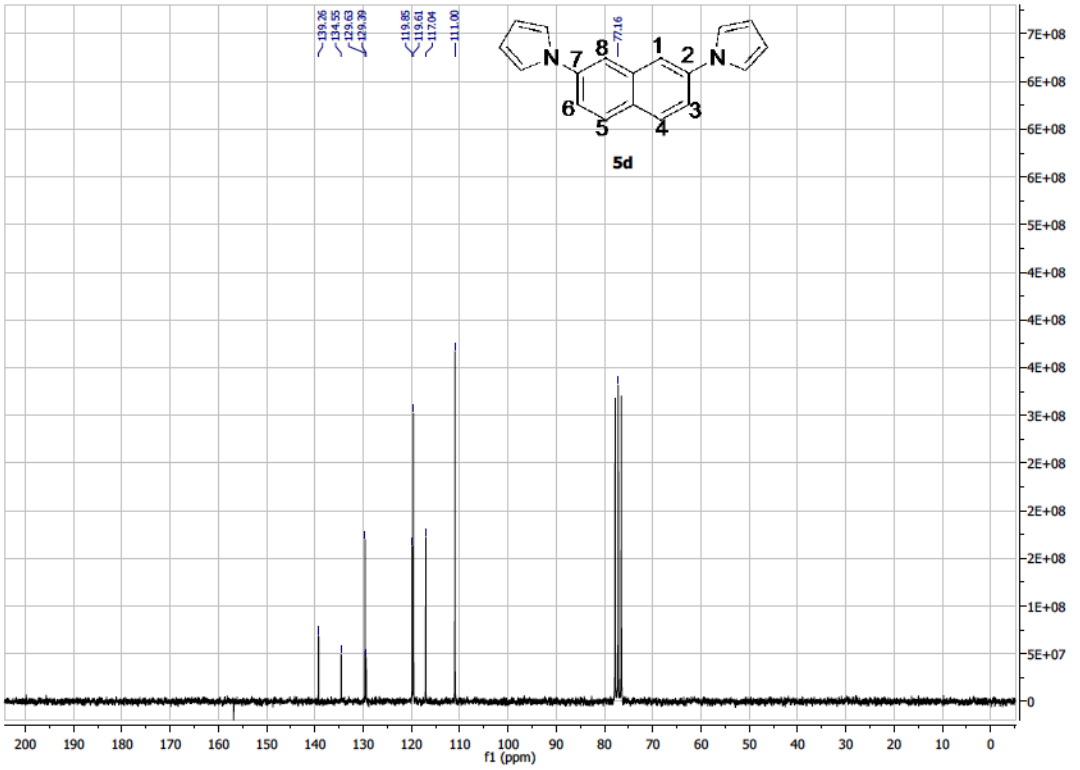

Br
N
5b
f1 (ppm)

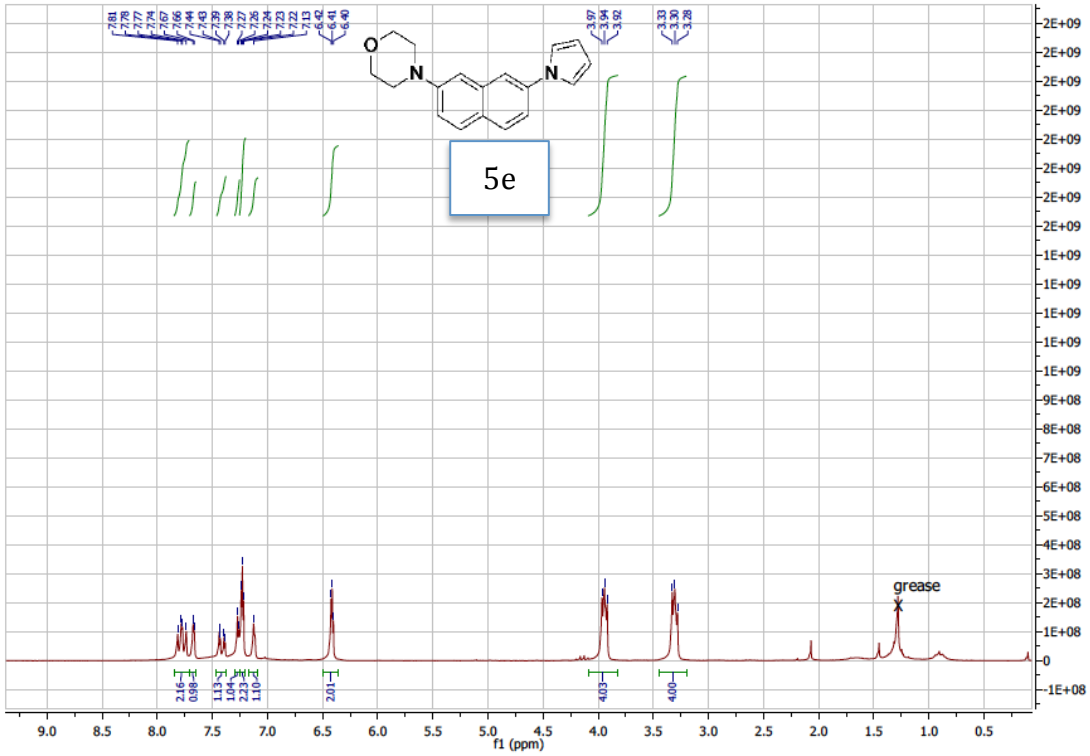

Br
N
5b
f1 (ppm)

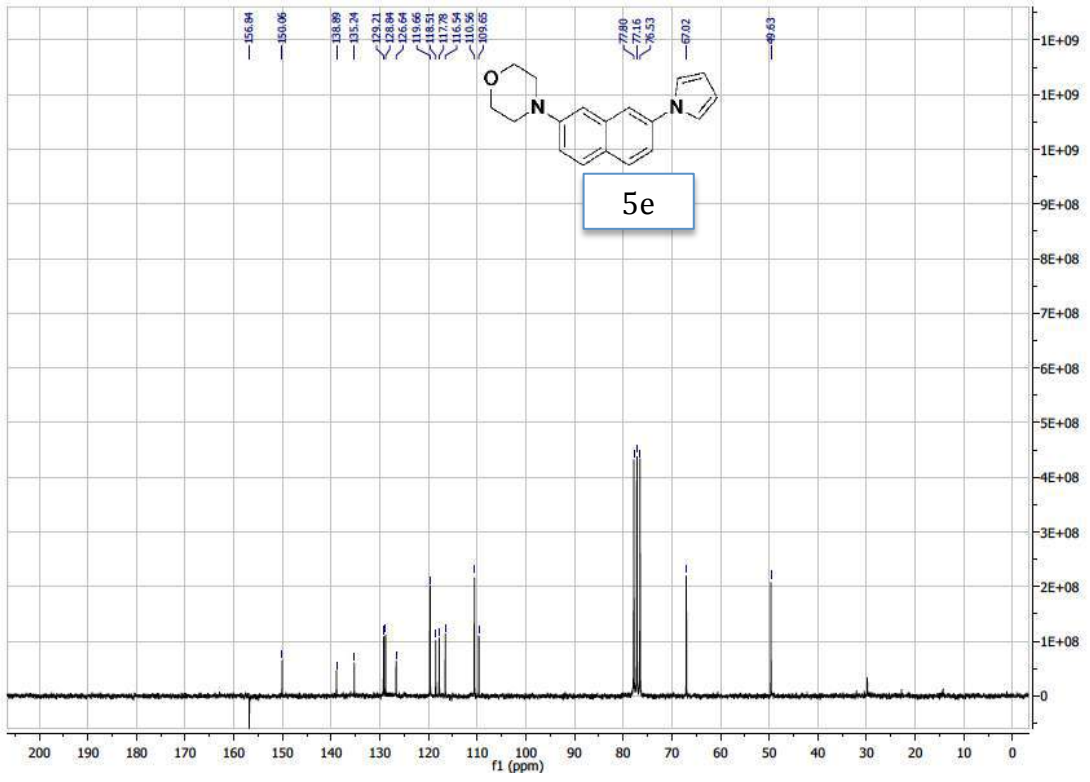

11.90
8.32
8.28
8.20
7.75
7.70
3.94
3.87
3.84
3.80
1.26
1.23
1.20
TFA
5c
2.01
1.96
2.27
8.00
12.06
f1 (ppm)

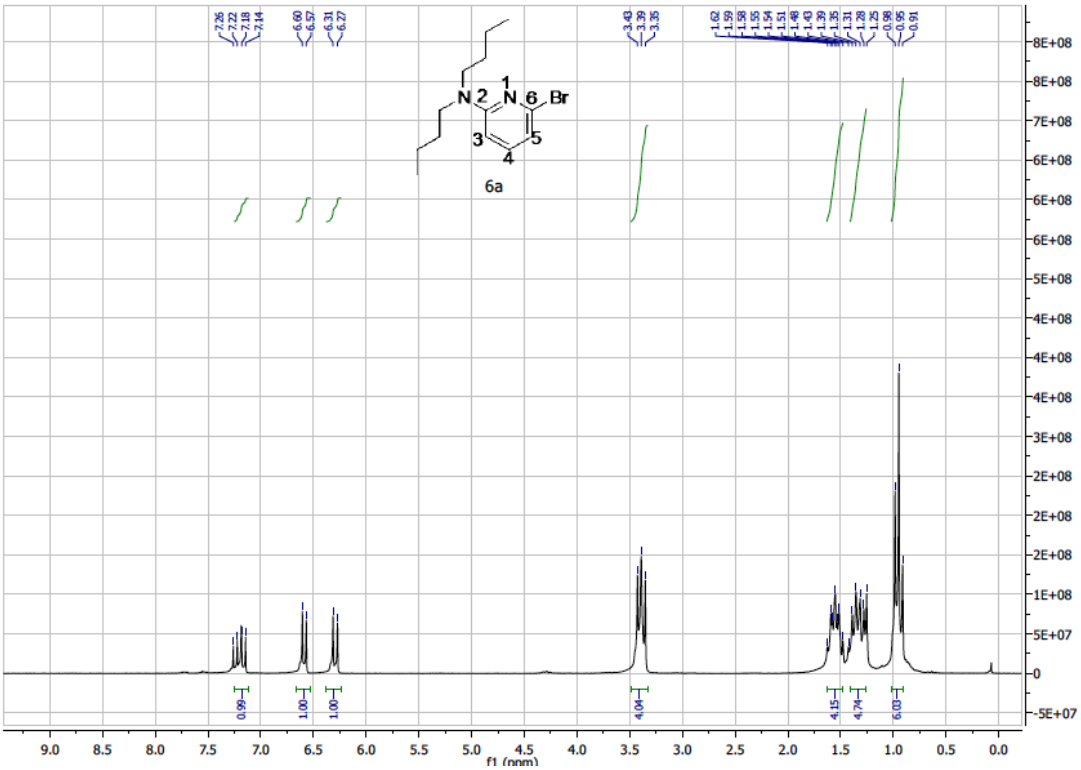

137.78
136.51
134.90
134.76
125.29
125.06
121.53
113.79
108.16
57.40
11.34
5c
f1 (ppm)

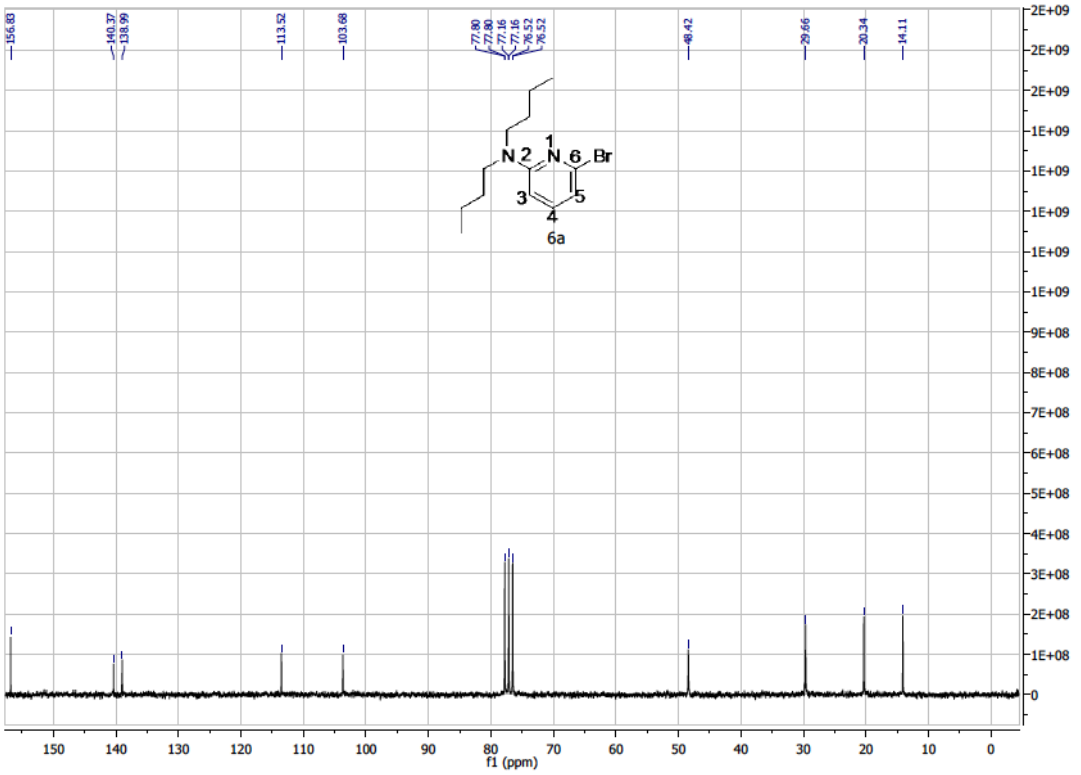

7.83
7.79
7.68
7.49
7.48
7.45
7.44
7.16
7.15
7.14
6.34
6.33
6.32
N
1
2
N
3
4
5
6
7
8
5d
2.01
2.00
2.00
4.07
3.99
f1 (ppm)

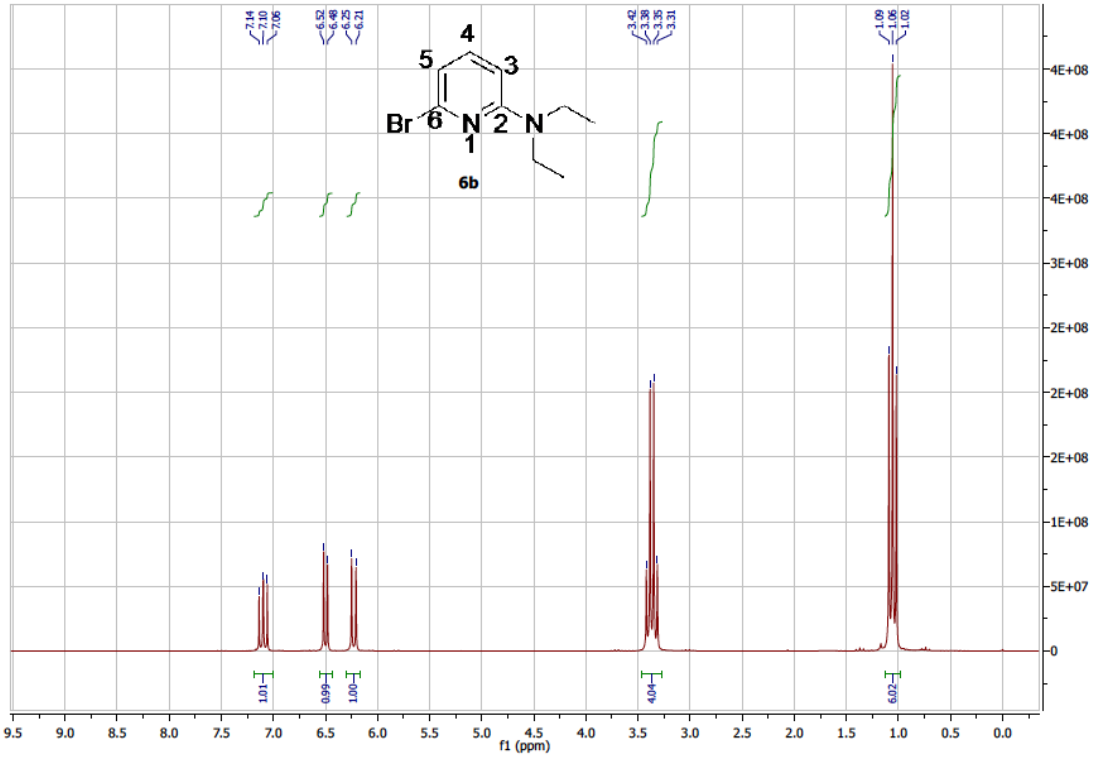

139.26
134.55
129.63
129.39
119.85
119.61
117.04
111.00
77.16
N
1
2
N
3
4
5
6
7
8
5d
f1 (ppm)

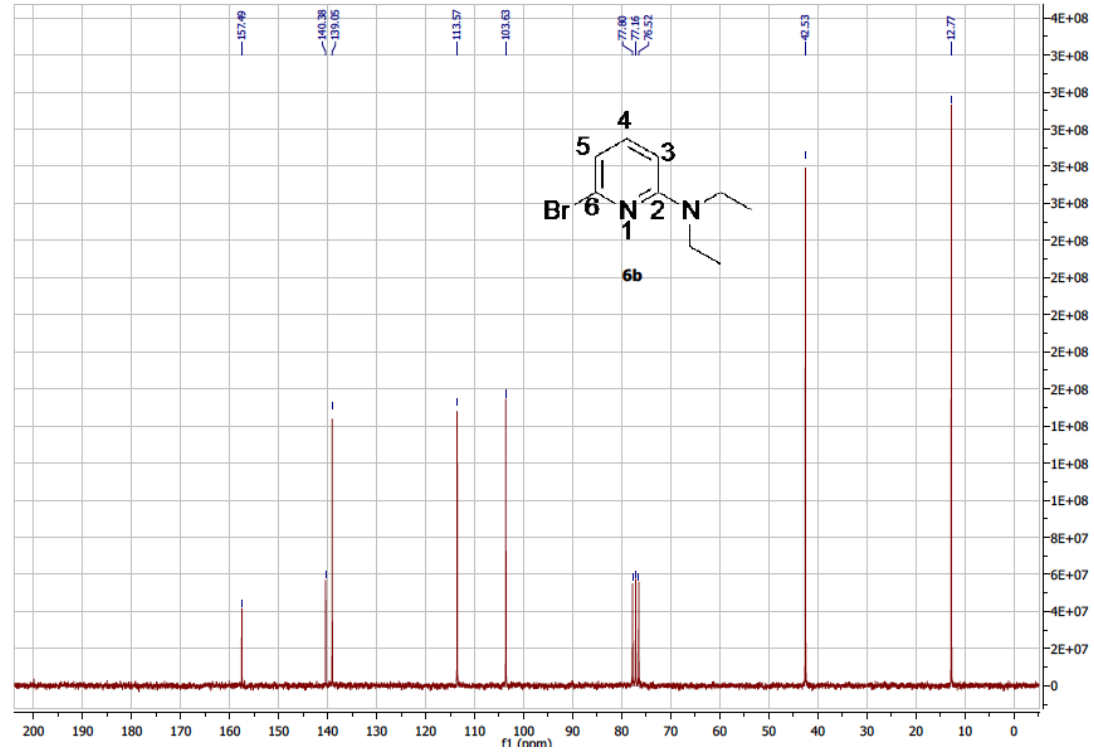

5e
grease
f1 (ppm)

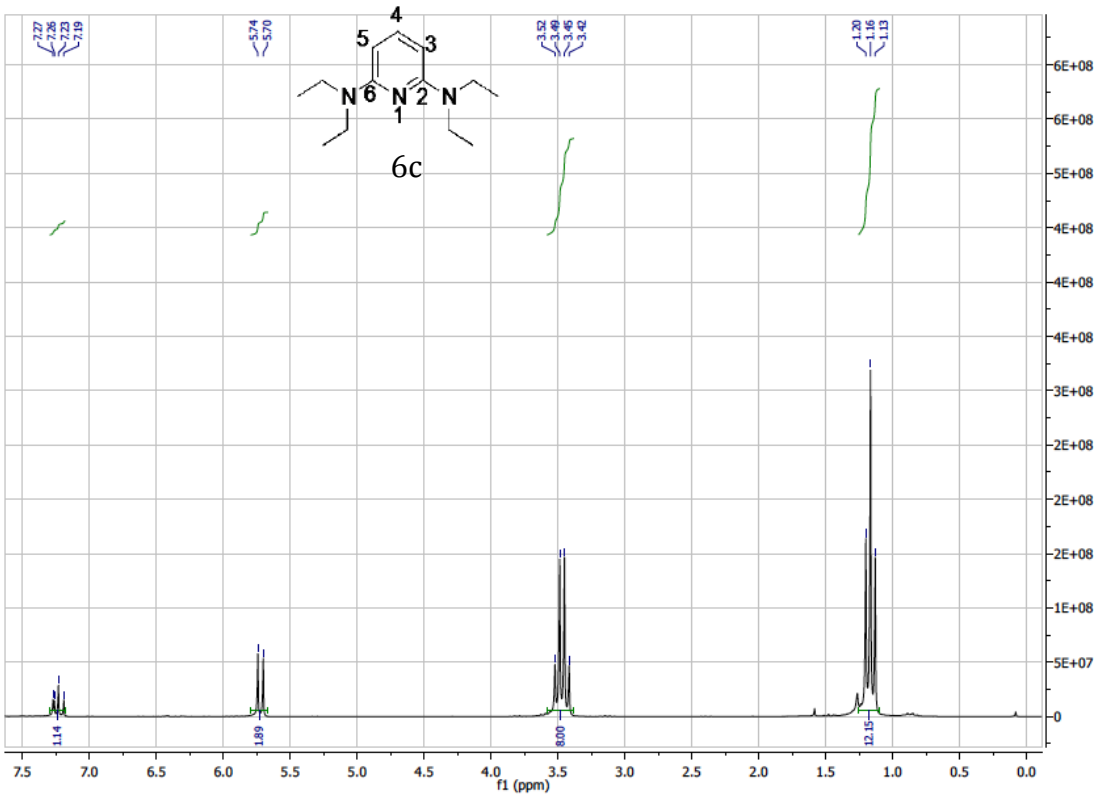

5e
f1 (ppm)


7.26
7.22
7.18
7.14
6.60
6.57
6.31
6.27
3.43
3.39
3.35
1.62
1.59
1.58
1.55
1.54
1.51
1.48
1.45
1.30
1.35
1.31
1.28
1.25
0.98
0.95
0.91
N 2 1 N 6 Br
3 4 5
6a
0.99
1.00
1.00
4.04
4.15
4.74
6.03
f1 (ppm)

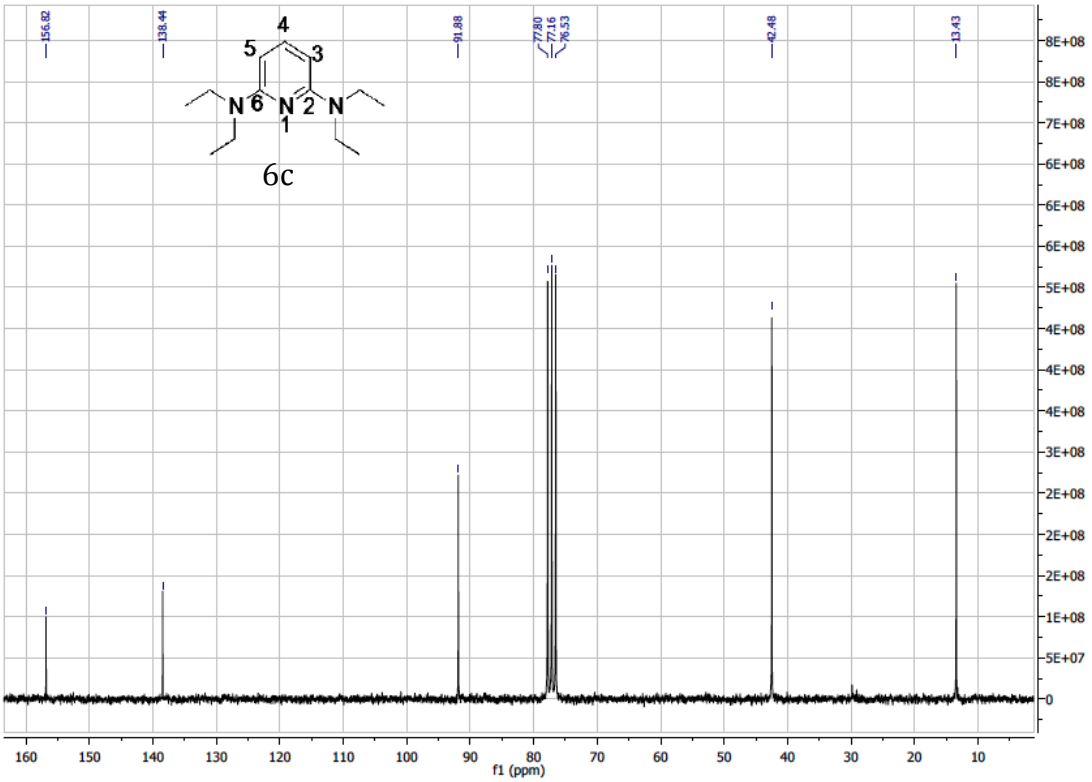

156.83
140.37
138.99
113.52
103.68
77.80
77.80
77.16
77.16
76.53
76.52
48.42
29.66
20.34
14.11
N 2 1 N 6 Br
3 4 5
6a
f1 (ppm)


7.14
7.10
7.06
6.52
6.48
6.25
6.21
3.42
3.38
3.35
3.31
1.09
1.06
1.02
4
5
3
Br
6
N
2
N
1
6b
1.01
0.99
1.00
4.04
6.02
f1 (ppm)


157.49
140.38
139.05
113.57
103.63
77.80
77.16
76.52
42.53
12.77
4
5
3
Br
6
N
2
N
1
6b
f1 (ppm)


7.27
7.26
7.23
7.19
5.74
5.70
3.52
3.49
3.45
3.42
1.20
1.16
1.13
1.14
1.89
8.00
12.15
f1 (ppm)

6c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138.44
91.88
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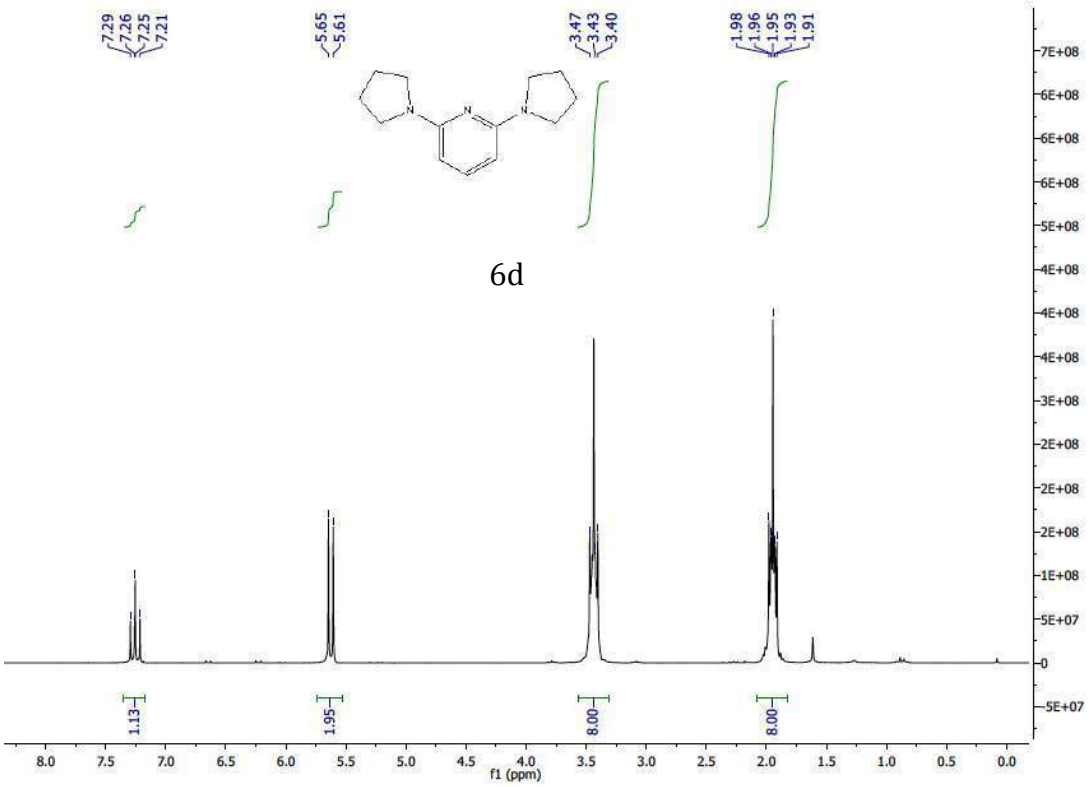
77.16
76.53
42.48
13.43
f1 (ppm)

6c


7.29
7.26
7.25
7.21
5.65
5.61
3.47
3.43
3.40
1.98
1.96
1.95
1.93
1.91
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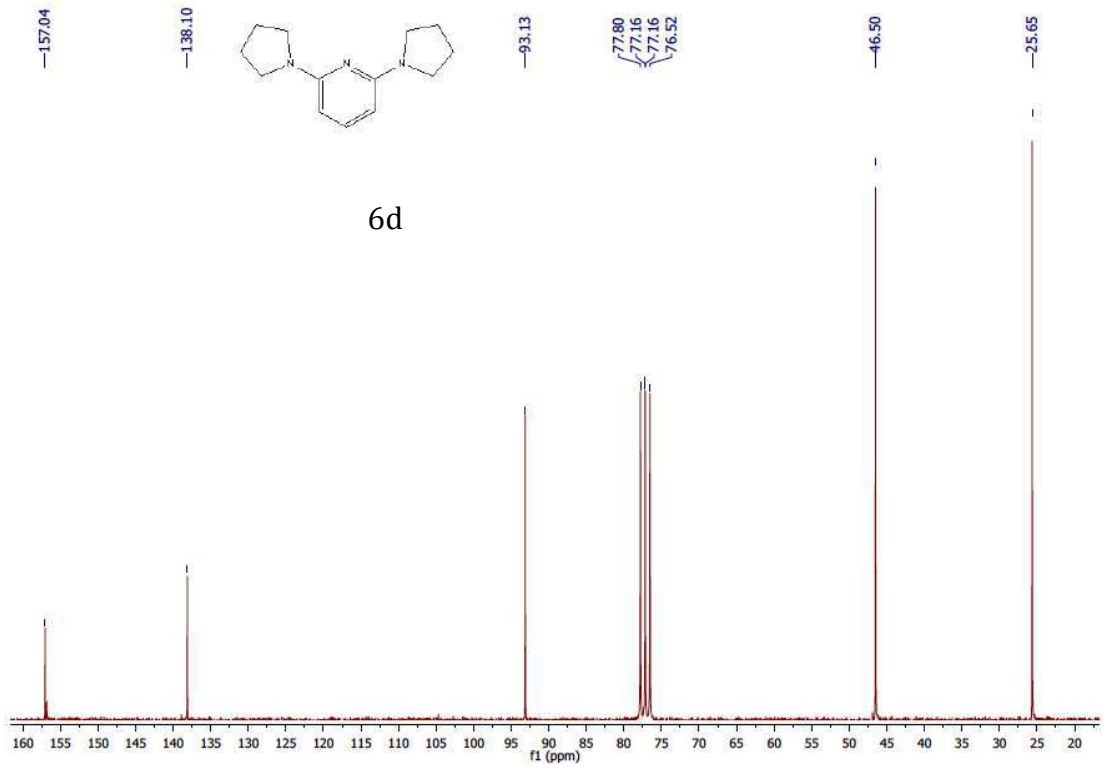
1.95
8.00
8.00
f1 (ppm)

6d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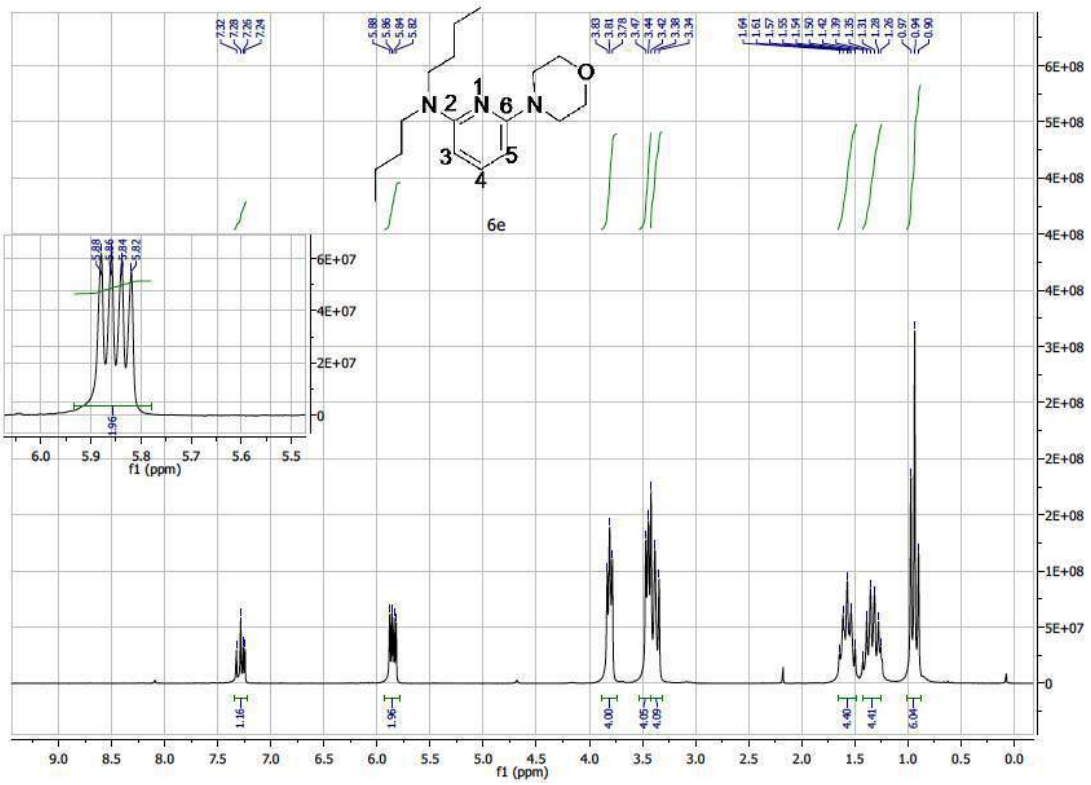
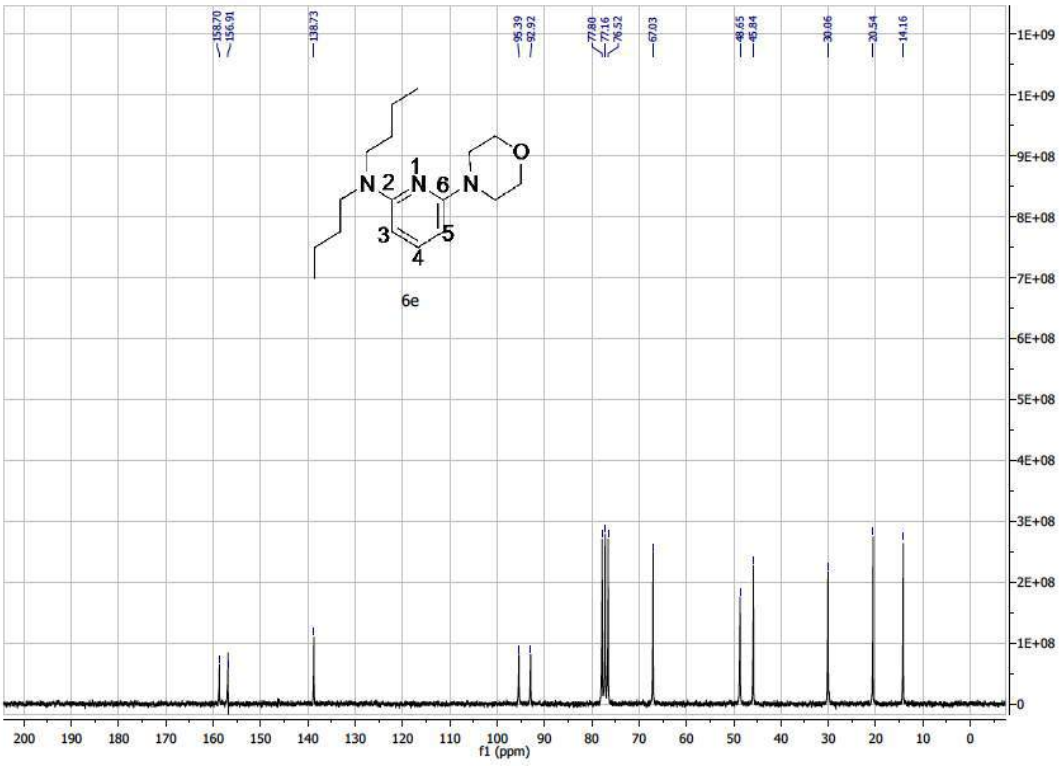
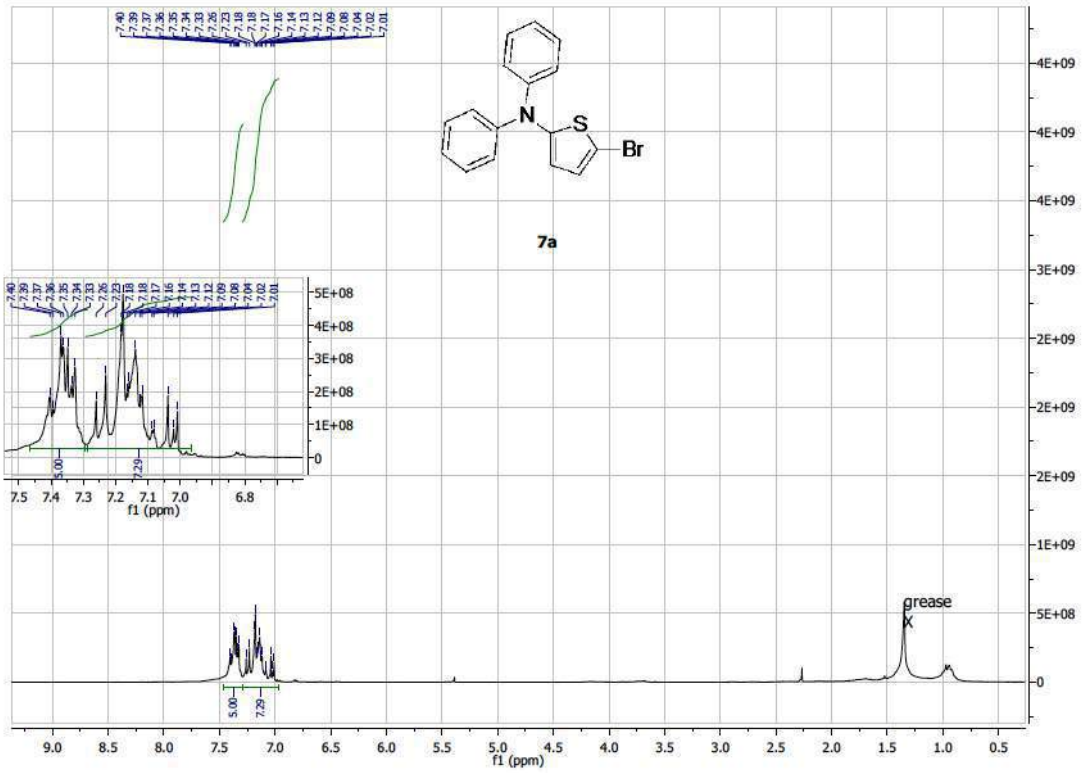
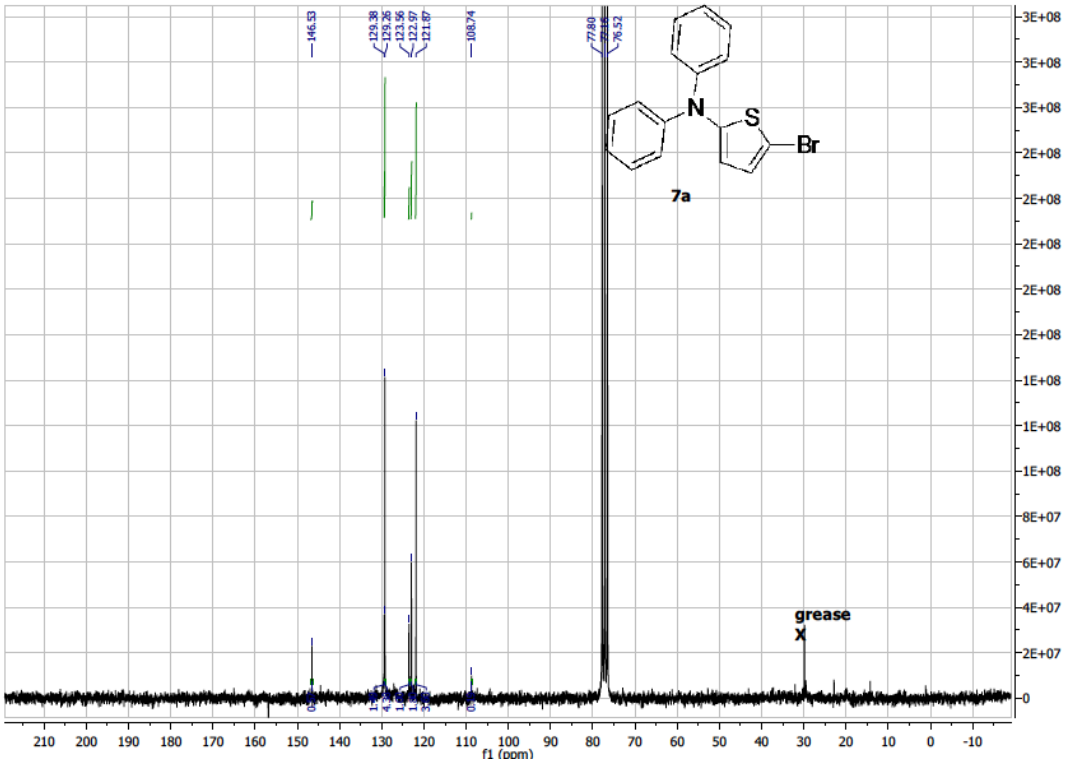
93.13
77.80
77.16
77.16
76.52
46.50
25.65
f1 (ppm)

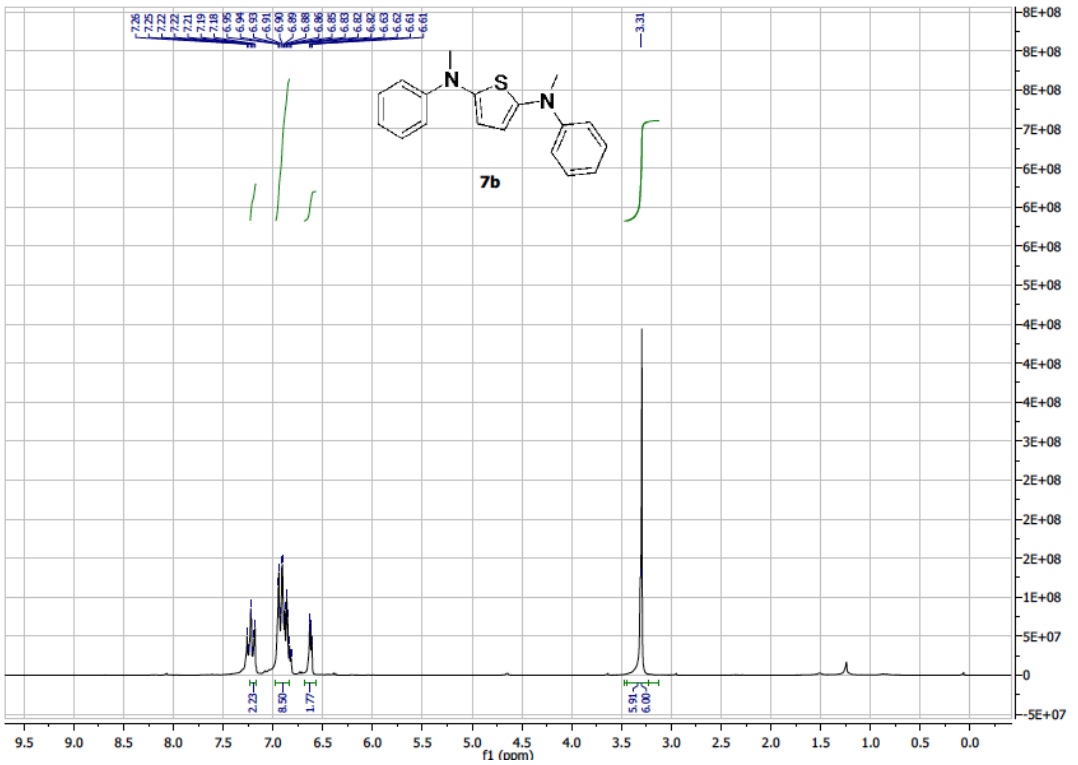
6d

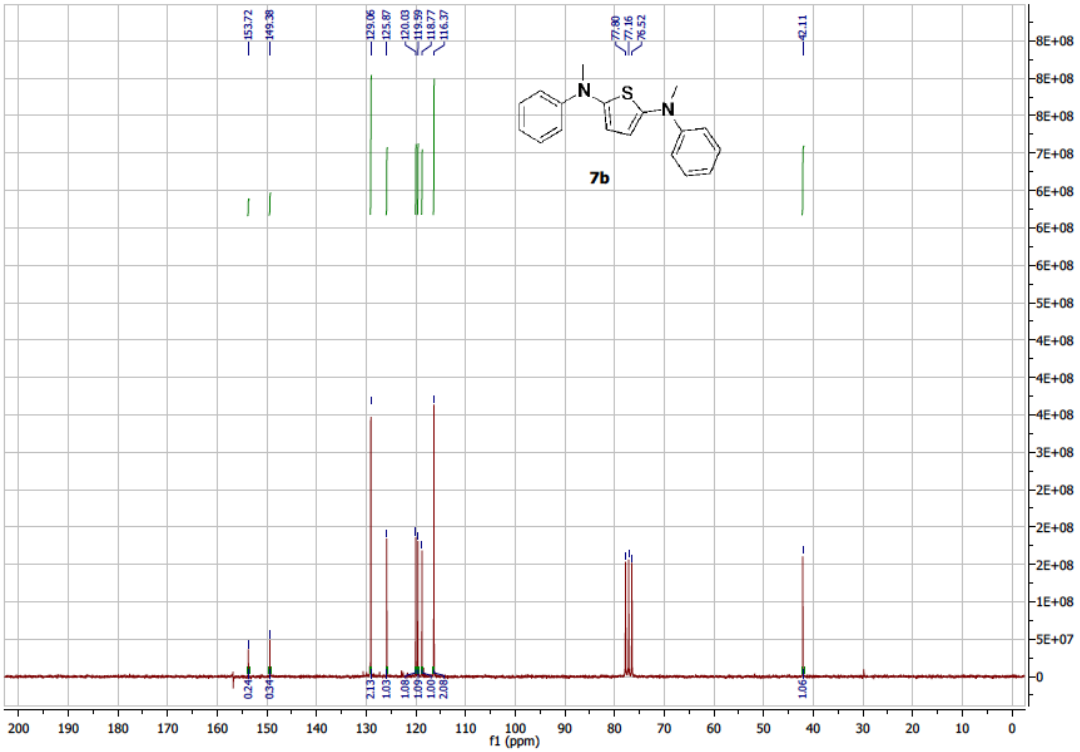

6e
f1 (ppm)

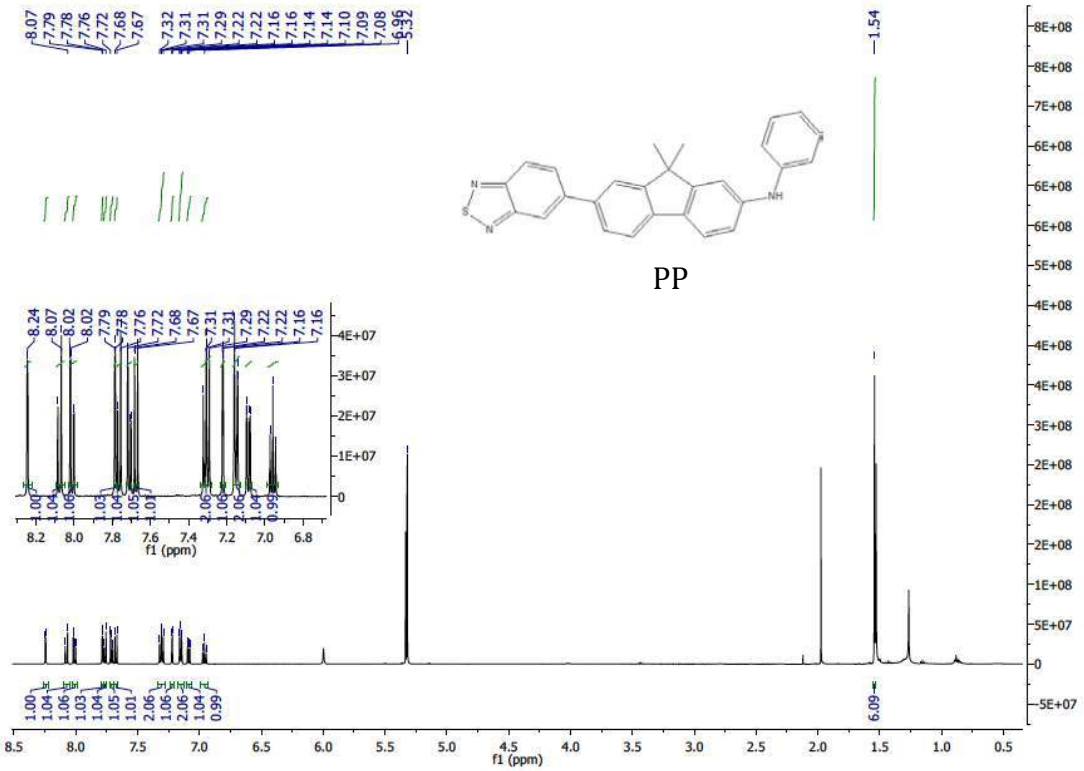

6e
f1 (ppm)


7a
grease
f1 (ppm)

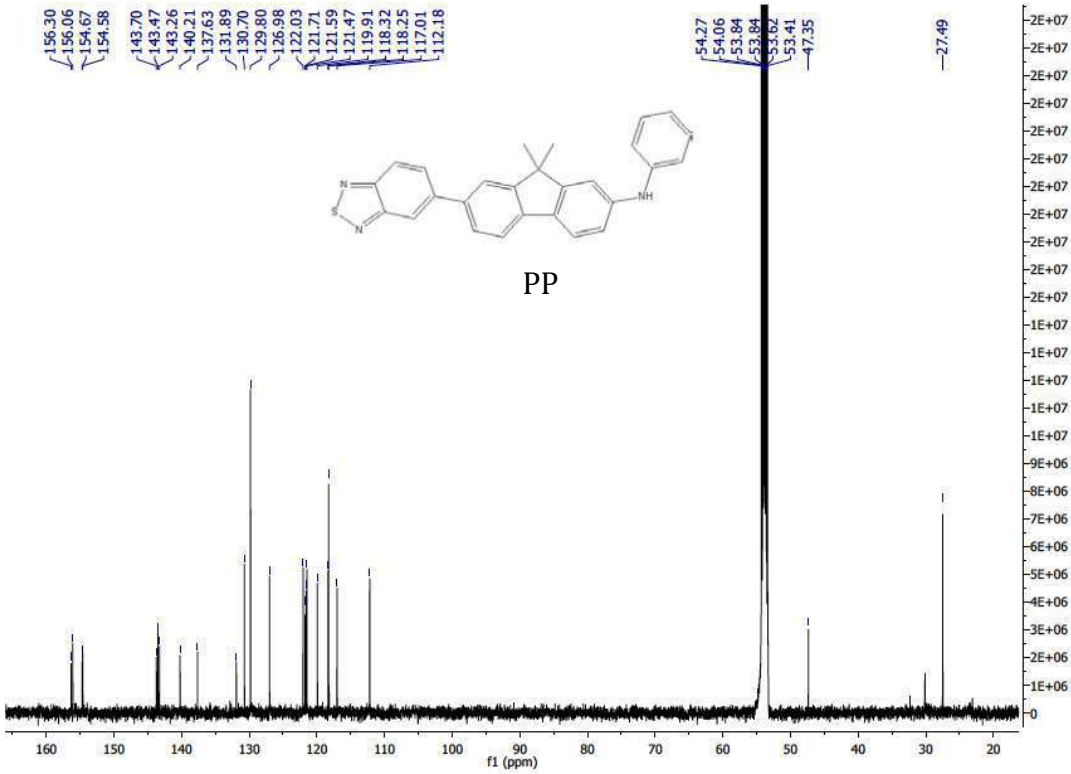

7a
grease
f1 (ppm)


7b
f1 (ppm)


7b
f1 (ppm)



PP



PP