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Synthesis and electropolymerization of new N-heterocyclic carbene complexes of Pd and Pt from an emissive imidazolium salt with terthiophene backbone.

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Supporting Information

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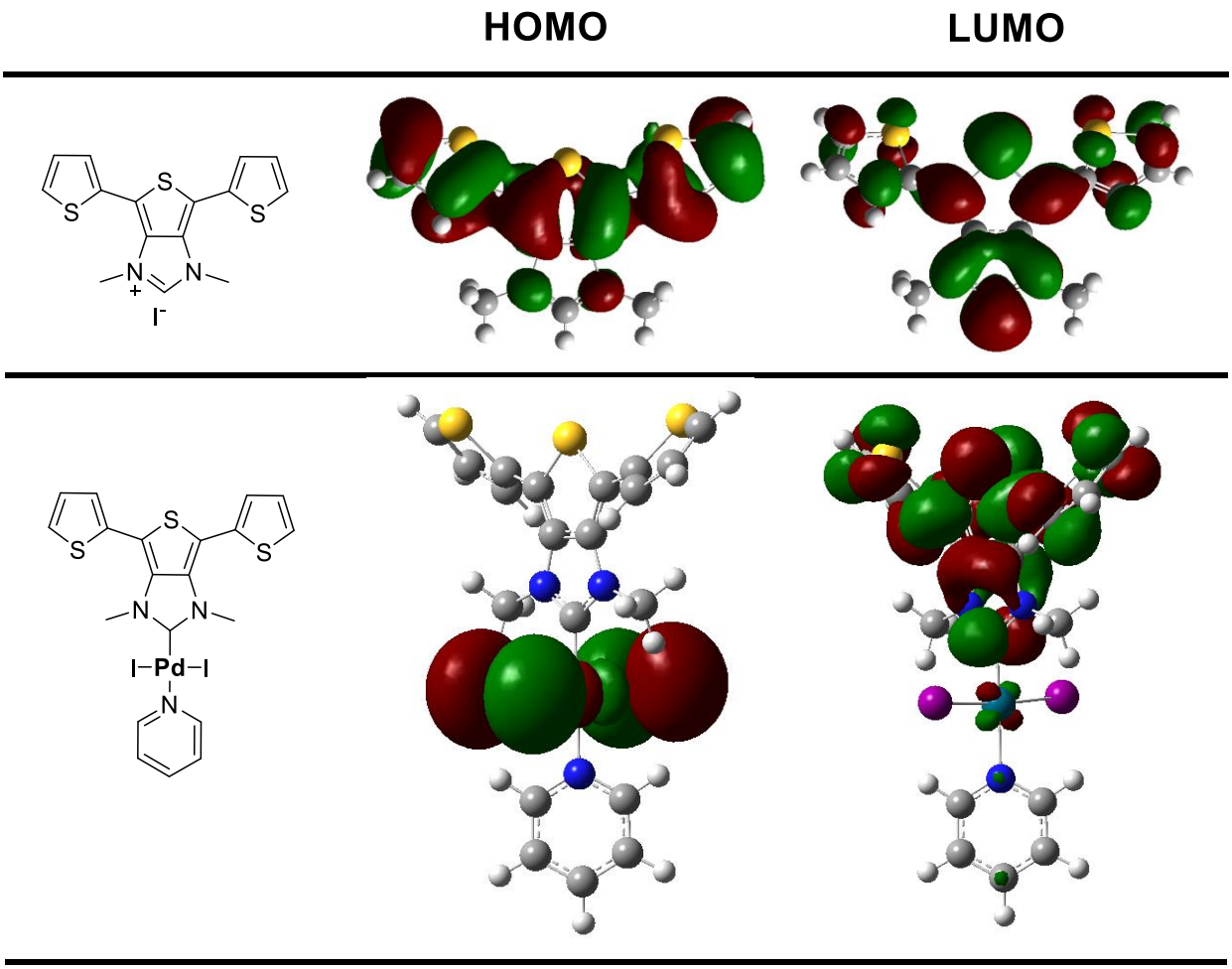


Fig. S1. Calculated frontier molecular orbitals of **4** and **5a**.

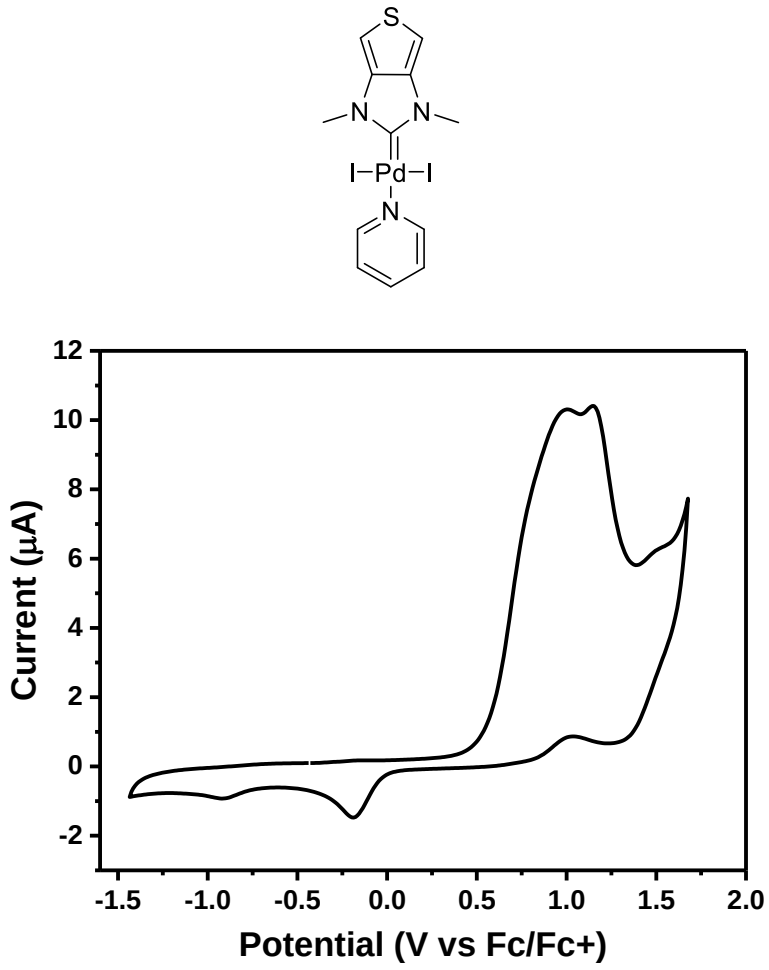


Fig. S2. CV of complex **8** in CH_2Cl_2 using a 1.8 mM solution. All potentials are reported with referenced to Fc/Fc^+ couple as 0 V.

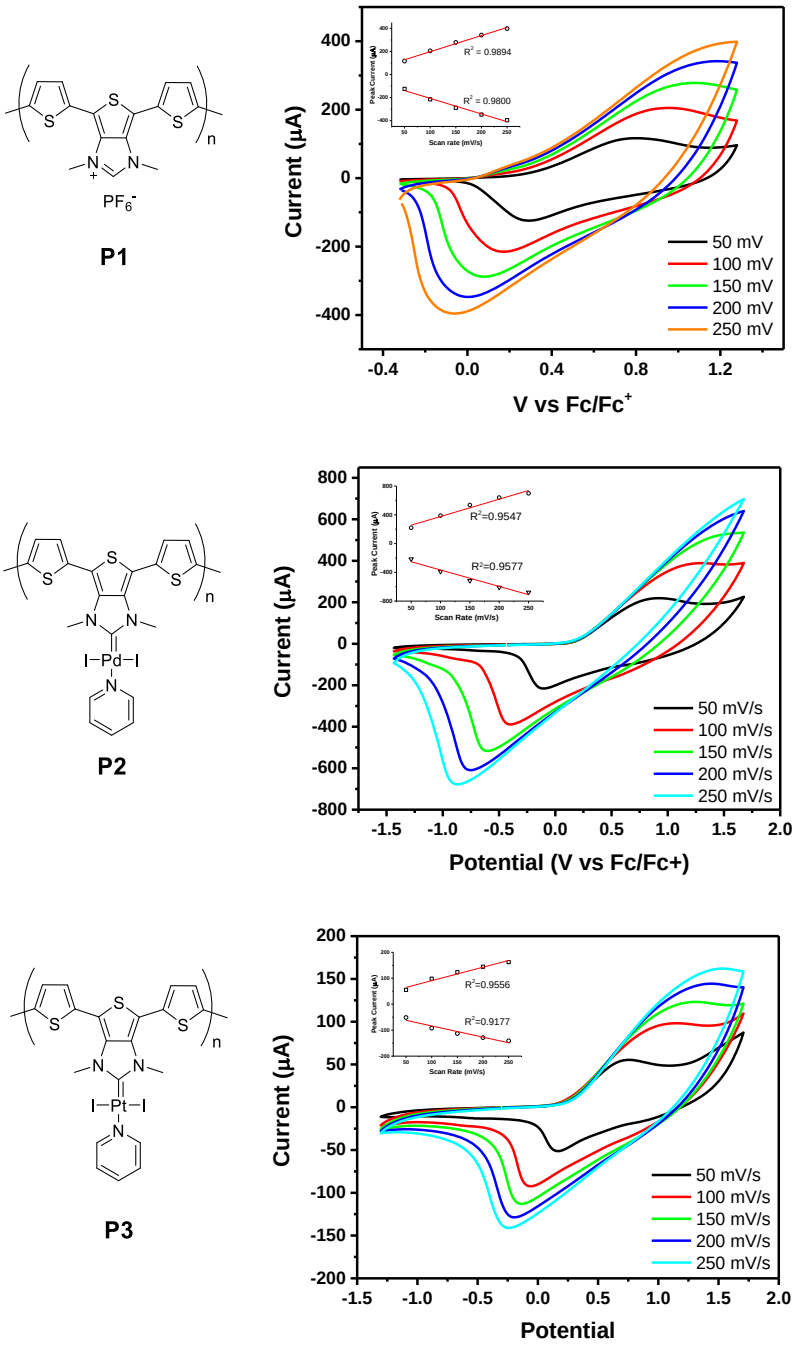


Fig. S3. CV of **P1**, **P2** and **P3** in monomer-free electrolyte solution in CH_2Cl_2. Insets show the linear relationship between current at peak oxidation/reduction potentials and scan rates. All potentials are reported with referenced to Fc/Fc^+ couple as 0 V.

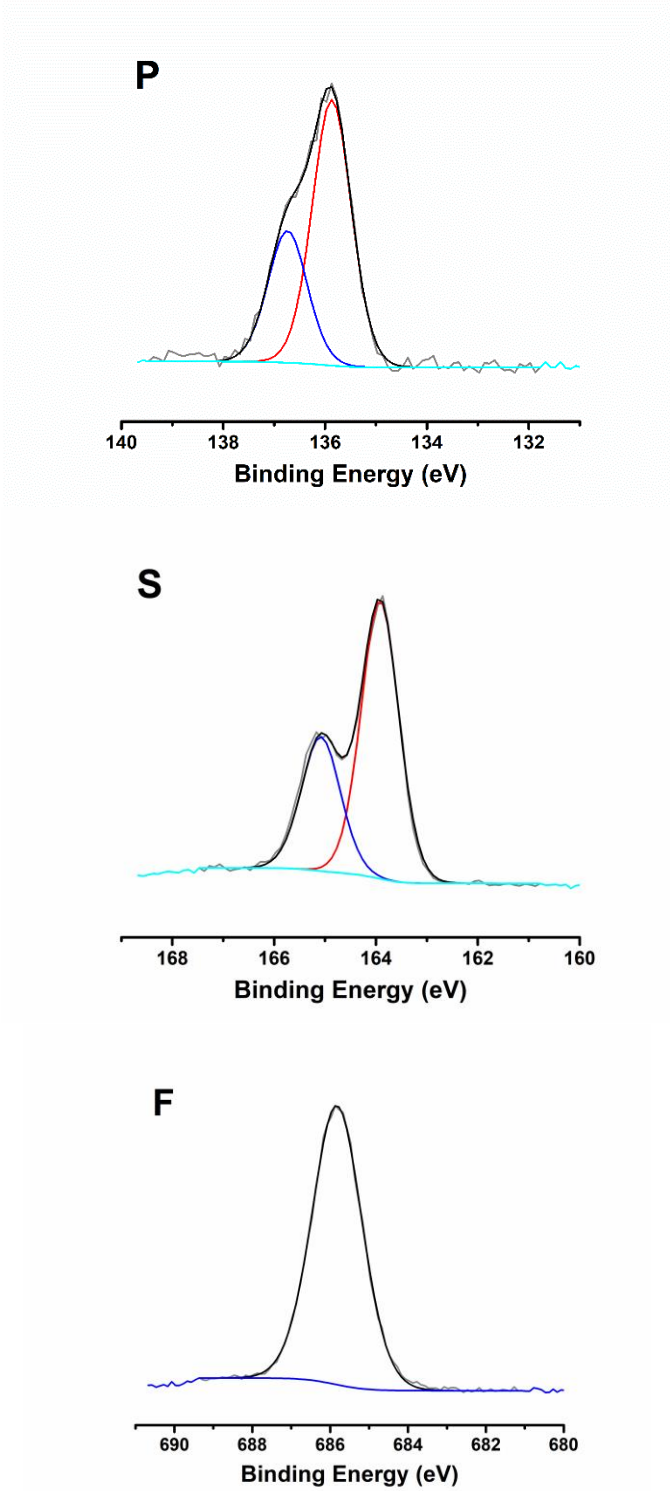


Fig. S4. Deconvoluted F 1s, P 2p and S 2p XPS spectra of **P1**.

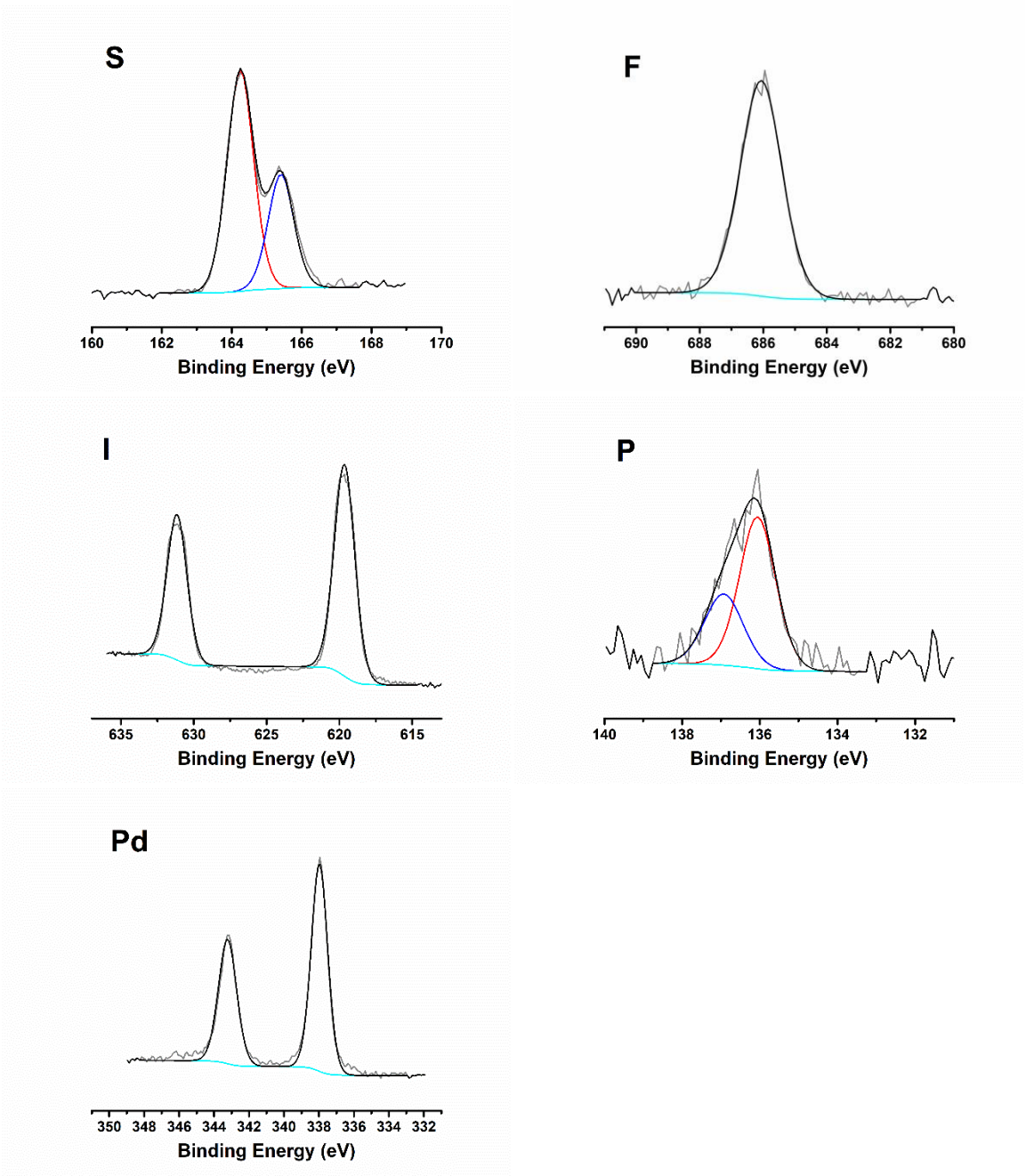


Fig. S5. Deconvoluted F 1s, P 2p, S 2p, Pd 3d and I 3d XPS spectra of **P2**.

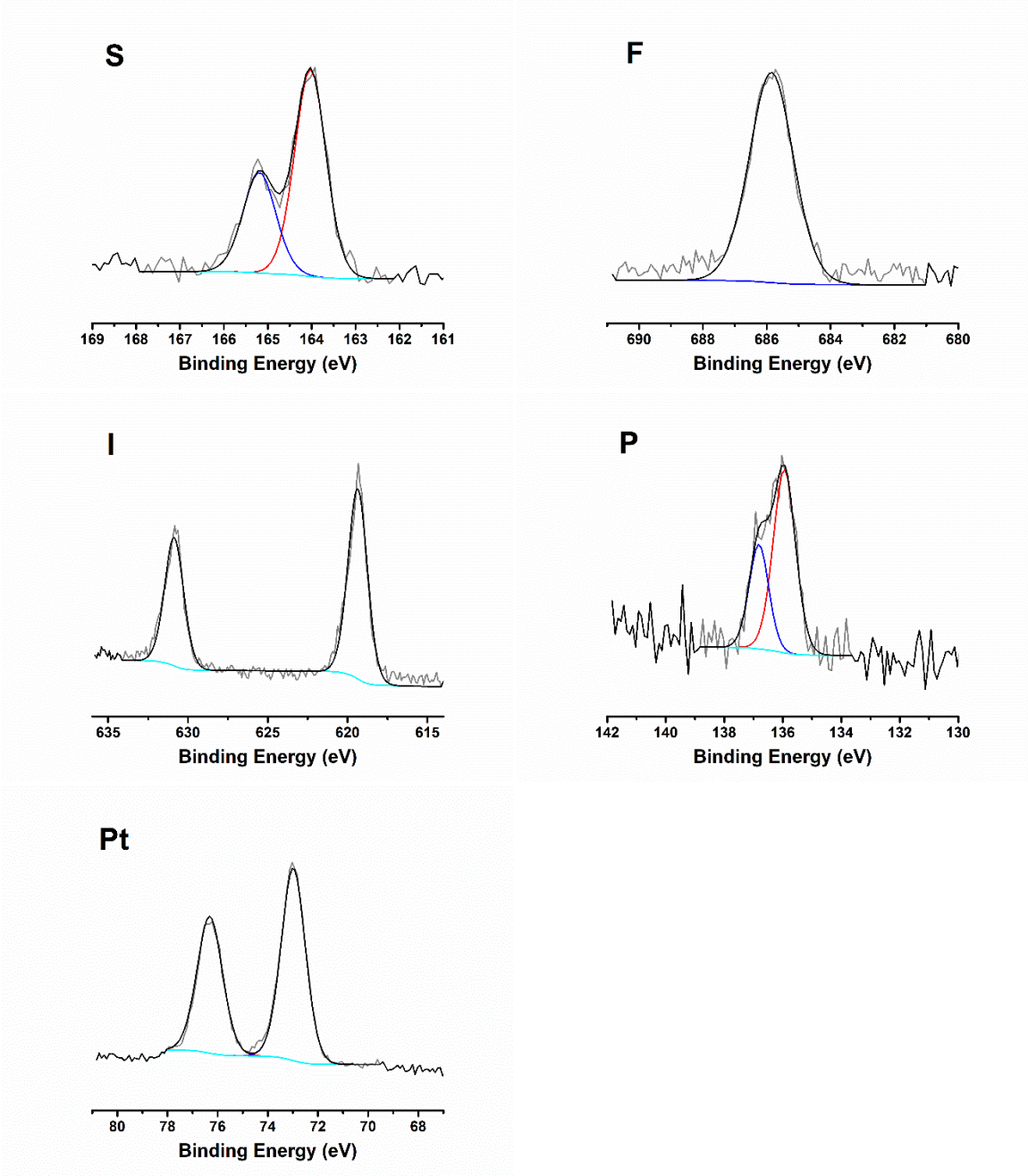


Fig. S6. Deconvoluted F 1s, P 2p, S 2p, Pd 3d and I 3d XPS spectra of **P3**.

Table S1. Crystal data and structure refinement for **4**, **5a**, **5b** and **8**.

Compound	4	5a	5b	8
CCDC Number				
Chemical formula	$C_{15}H_{13}N_2S_3I$	$C_{20}H_{17}I_2N_3PdS_3$	$C_{20}H_{17}I_2N_3PtS_3$	$C_{13}H_{15}Cl_2I_2N_3PdS$
Formula weight	444.35	755.75	844.43	676.44
Crystal system	triclinic	monoclinic		
Space group	$P\bar{1}$	$P2_1/c$		
a/Å	10.5465(14)	22.1504(19)	21.932(3)	16.423(2)
b/Å	12.5852(17)	11.3508(9)	11.3524(13)	7.9595(10)
c/Å	13.9485(18)	19.5686(17)	19.528(2)	15.932(2)
α/°	73.117(3)	90	90	90
β/°	73.645(4)	98.853(2)	99.221(6)	108.871(5)
γ/°	87.820(4)	90	90	90
Volume/$Å^3$	1698.0(4)	4861.4(7)	4799.2(10)	1970.6(4)
Z	4	8	8	4
ρ_{calc},g/cm^3	1.738	2.065	2.337	2.28
μ/mm^{-1}	2.249	3.574	8.694	4.451
F(000)	872	2864	3120	1264
Crystal size/mm^3	0.2 × 0.2 × 0.2	0.23 × 0.15 × 0.09	0.237 × 0.2 × 0.173	0.176 × 0.133 × 0.094
2Θ range for	4.372 to 54.96	4.162 to 54.906	1.882 to 54.97	5.188 to 56.886

data collection/°				
Index ranges	$-13 \le h \le 13$ $-16 \le k \le 16$ $-18 \le l \le 18$	$-28 \le h \le 28$ $-14 \le k \le 14$ $-25 \le l \le 25$	$-28 \le h \le 28$ $-14 \le k \le 14$ $-25 \le l \le 25$	$-21 \le h \le 21$ $-10 \le k \le 10$ $-21 \le l \le 21$
Reflections collected	31993	89157	69261	47017
Independent reflections	7766 $R_{int} = 0.0472$ $R_{sigma} = 0.0406$	11098 $R_{int} = 0.0447$ $R_{sigma} = 0.0251$	11000 $R_{int} = 0.0525$ $R_{sigma} = 0.0343$	4954 $R_{int} = 0.0394$ $R_{sigma} = 0.0185$
Data/restraints/ parameters	7766/244/396	11098/223/628	11000/407/580	4954/0/201
GOF on F^2	1.053	1.161	1.057	1.075
R_1, wR_2 [$I>=2\sigma(I)$]	0.0404, 0.1000	0.0375, 0.0861	0.0270, 0.0590	0.0168, 0.0406
R_1, wR_2 [all data]	0.0492, 0.1045	0.0412, 0.0876	0.0344, 0.0612	0.0193, 0.0412
Largest diff. peak and hole / e $Å^{-3}$	1.25/-1.11	1.63/-1.07	1.74/-1.26	0.85/-0.81

Table S2. DFT Optimized Atomic Coordinates for **4**.

Compound 2	X	Y	Z
S	-0.0057	-0.02775	-0.01494
C	-0.14939	-0.08058	-0.10181
H	0.137408	0.042912	0.077002
C	0.061584	-0.13443	-0.02955
H	-0.01048	0.151721	0.061962
C	0.097776	-0.05944	0.014205
H	-0.14557	0.065088	-0.03432
S	-0.0016	-0.0002	-0.00502
S	-0.0012	0.005893	-0.00769
N	0.001618	-0.00308	-0.00499
N	-0.00195	-0.00846	-0.00531
C	0.000901	-0.00415	-0.01067
C	0.003659	-0.00537	-0.00274
C	-0.00298	0.008982	0.00712
C	-0.00019	-0.00017	-0.00085
C	-0.00712	0.015103	0.006161
C	0.008257	0.07396	-0.13524
H	-0.00804	-0.07701	0.142657
C	0.020398	0.031007	0.026735
C	-0.06546	0.033428	-0.12863

H	0.06969	-0.02695	0.144054
C	-0.07407	0.086445	0.00033
H	-0.06593	-0.10578	-0.00264
H	0.070112	0.005619	0.101313
H	0.069646	0.011524	-0.10148
C	-0.03088	0.042947	0.144521
H	0.032389	-0.03727	-0.15604
C	-0.04275	0.149492	0.023491
H	0.042509	-0.15834	-0.00972
C	0.035523	-0.06927	-0.0805
H	0.035674	0.115988	-0.03001
H	0.049274	-0.03391	0.109463
H	-0.12313	-0.00795	0.003155

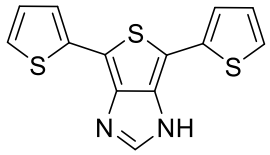
Table S3. DFT Optimized Atomic Coordinates for **5a**.

Compound 5a	X	Y	Z
C	-0.000008345	-0.000001168	-0.000004891
H	-0.000009377	0.00000075	-0.000005199
C	-0.000012216	-0.000003321	-0.000005393
H	-0.000014948	-0.000001793	-0.000006694
C	-0.000012314	-0.000004444	-0.000003321
H	-0.000013953	-0.000006575	-0.000004078
S	-0.000005914	-0.000006099	-0.000002359
I	-0.000001959	0.000005568	-0.00000438
I	0.000001357	-0.000006315	0.000003914
Pd	-0.000001036	0.000001896	0.00000003
S	-0.000000665	0.000001502	-0.000000797
S	0.000008038	0.000005053	0.000001035
N	0.000003348	-0.000002524	0.00000311
N	0.000001959	0.000000641	0.000001946
N	-0.00000169	-0.000000434	0.000000256
C	-0.000009798	-0.000000872	-0.000001725
C	0.000008694	0.000001499	0.000004513
H	0.000009444	-0.000000913	0.000004711
C	0.000004297	-0.000000027	0.000000329
C	-0.000000888	-0.000001025	-0.000001897

C	0.000001522	0.000003155	-0.000001733
H	0.000003125	0.000004817	-0.00000063
C	-0.00000157	-0.000002672	0.000000524
H	-0.00000359	-0.000004702	0.000000398
C	-0.000002196	-0.000002198	0.000000454
C	0.00000689	0.000001885	0.000003302
C	-0.000003342	-0.000000328	-0.00000205
C	0.000001959	0.000000274	0.000001398
C	-0.000000181	0.000000099	0.000000156
H	0.00000013	-0.000000071	-0.000000188
C	0.000001612	0.00000281	-0.000000651
H	0.000003606	0.0000047	-0.000000395
C	-0.000002975	-0.000001535	0.000000224
H	-0.000003239	-0.000004823	0.000000369
C	-0.000005802	-0.000002469	-0.000001487
H	-0.000007303	-0.000000435	-0.000003581
H	-0.000007508	-0.000004675	-0.000001303
H	-0.00000566	-0.000003553	-0.000001498
C	0.000012685	0.000002704	0.000004485
H	0.000014914	0.000001828	0.00000681
C	0.000005767	0.000003005	0.000001592
H	0.000006325	0.000003498	0.00000122
H	0.000007644	0.000001211	0.000003805

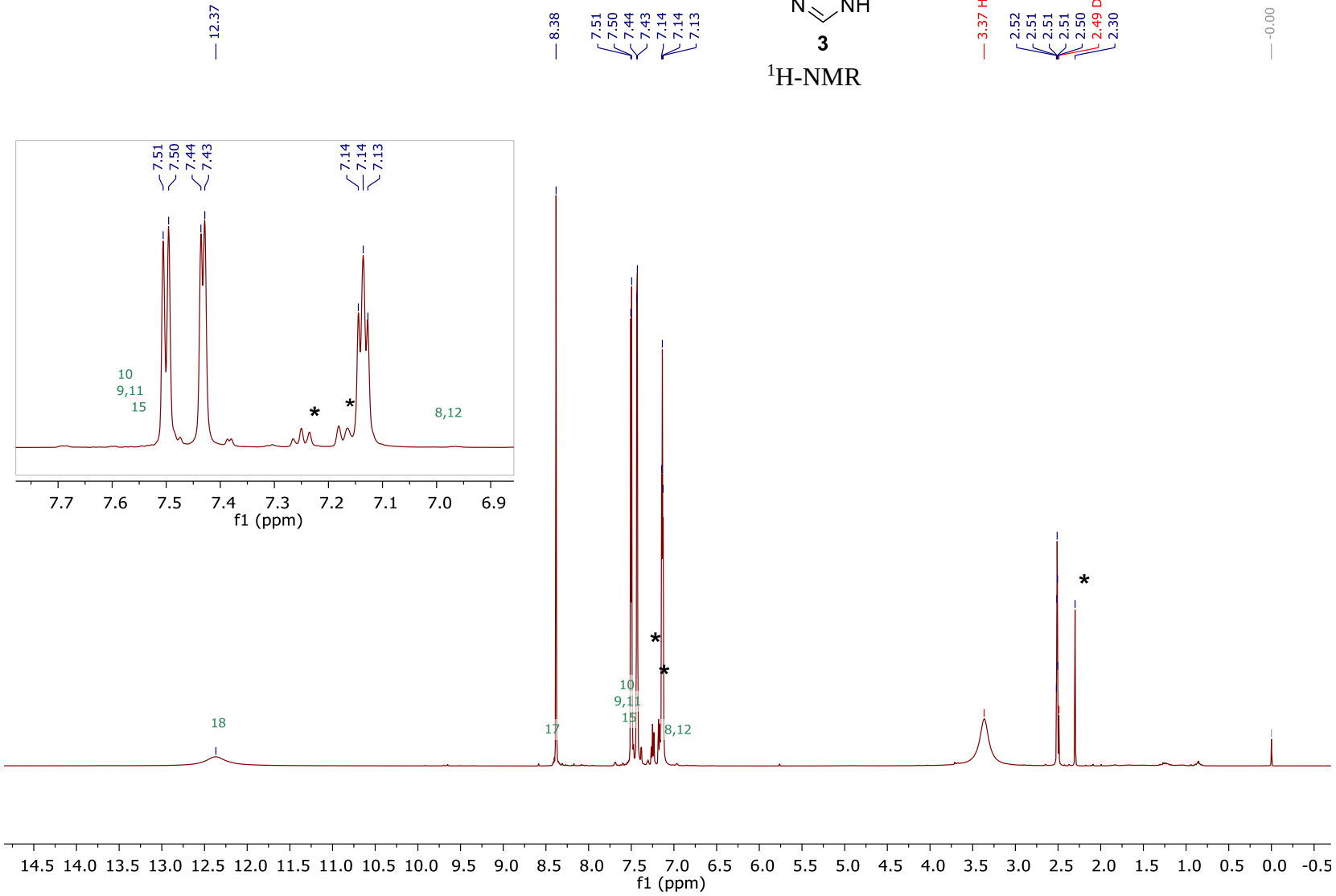
H	0.000007222	0.000004521	0.000001396
C	0.000011956	0.000005153	0.000004131
H	0.000013978	0.000006406	0.000004142

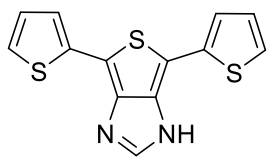
^{1}H and ^{13}C NMR spectra



3

^{1}H-NMR

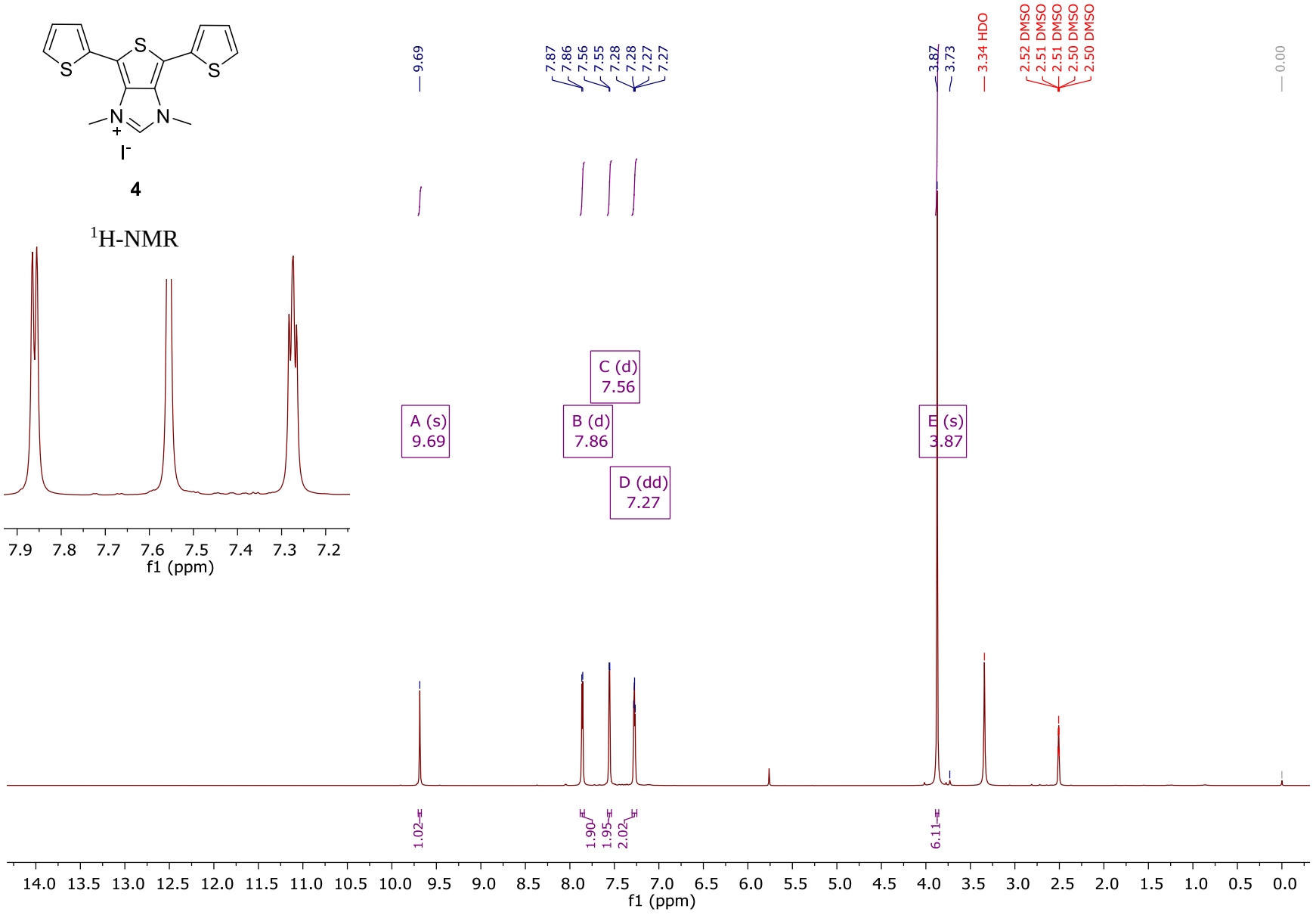


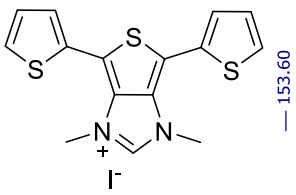

S
S
S
N
NH

3

^{13}C-NMR

152.97
134.75
128.29
124.61
123.32
123.09
39.85
39.69
39.52
39.35
39.19
*
*
*
*
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)

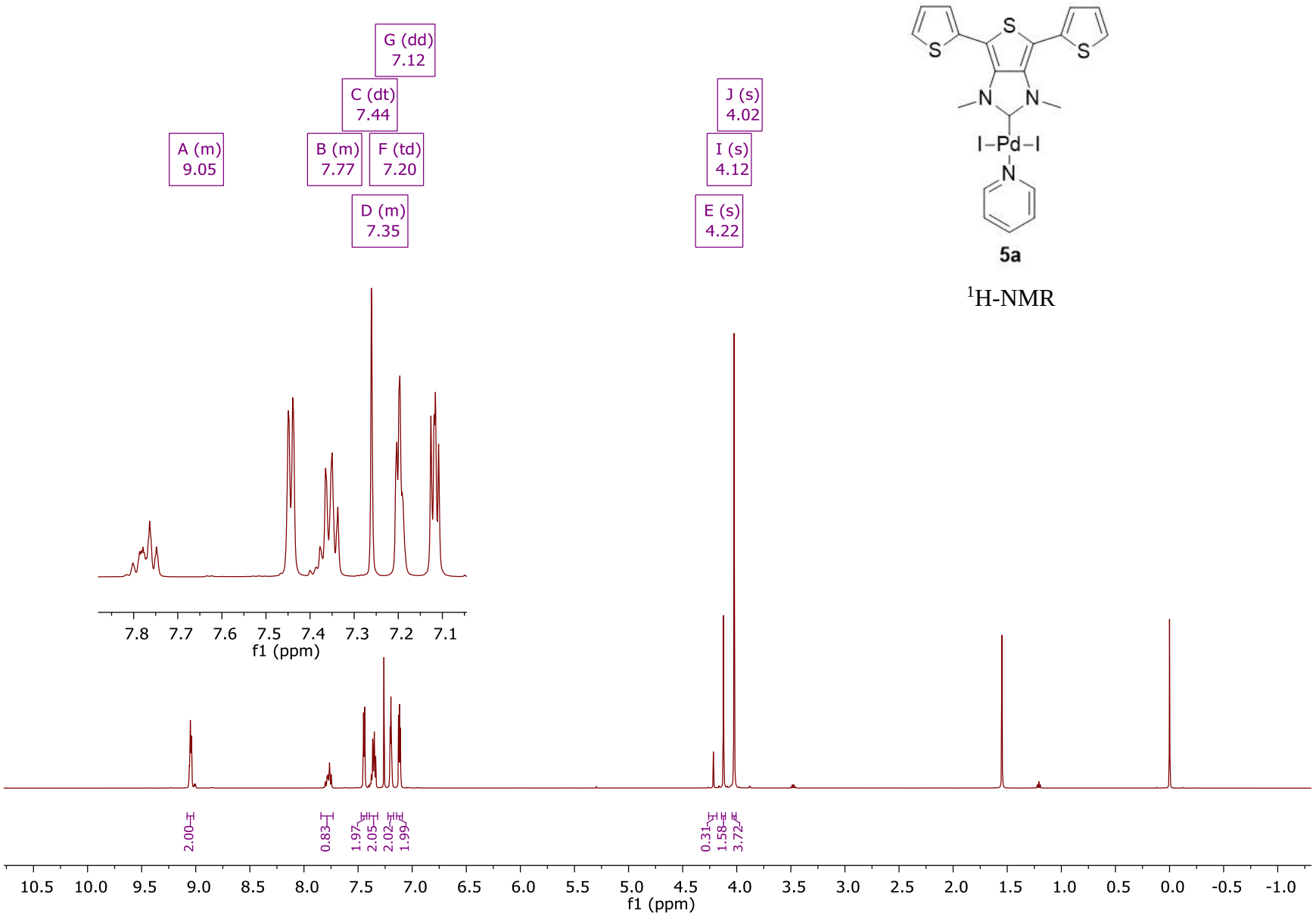

4
^{1}H-NMR
9.69
7.87
7.86
7.56
7.55
7.28
7.28
7.27
7.27
3.87
3.73
3.34 HDO
2.52 DMSO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
0.00
A (s)
9.69
B (d)
7.86
C (d)
7.56
D (dd)
7.27
E (s)
3.87
1.02
1.90
1.95
2.02
6.11
f1 (ppm)


S
S
S
N
+
N
I-

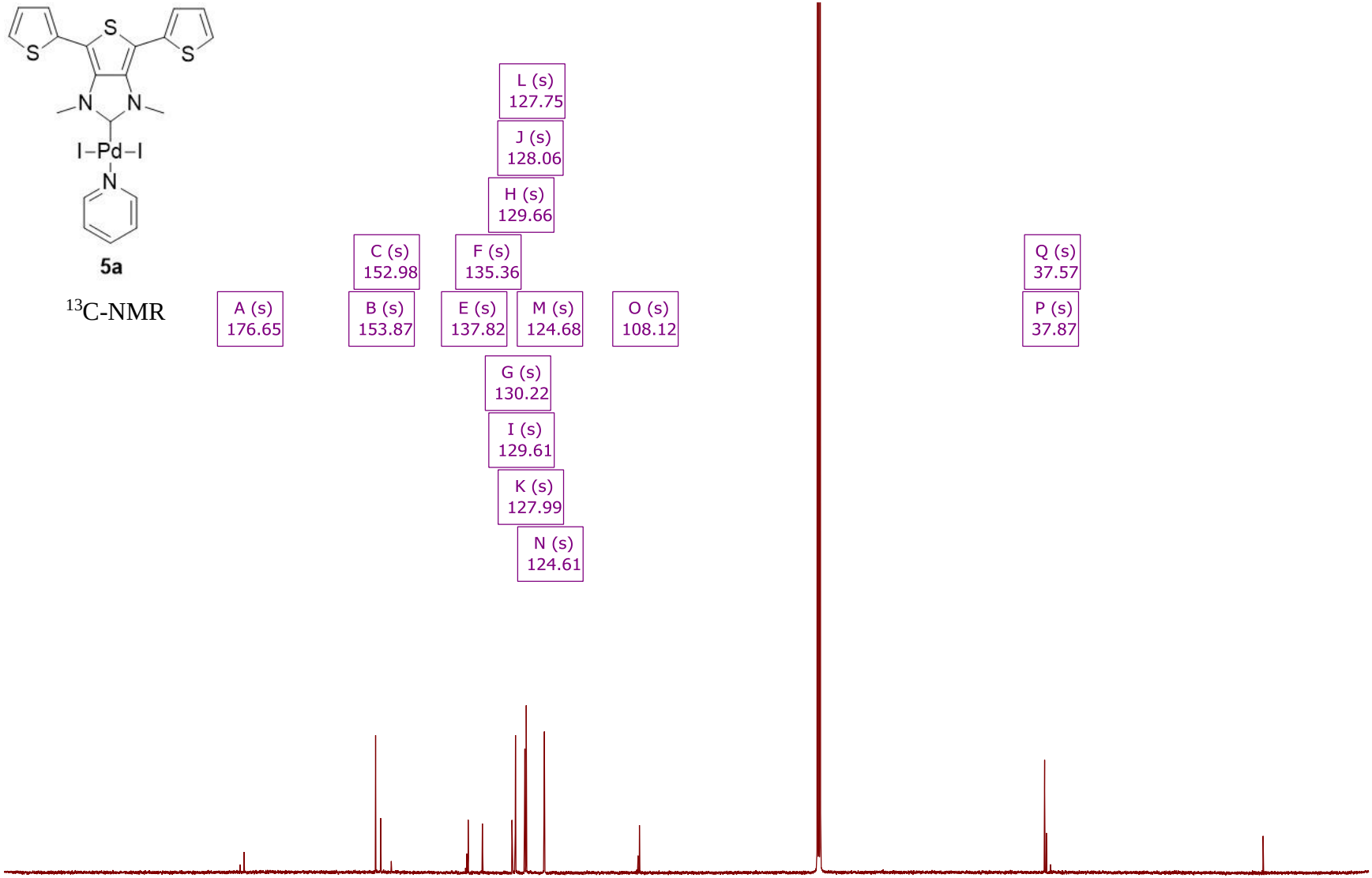
4

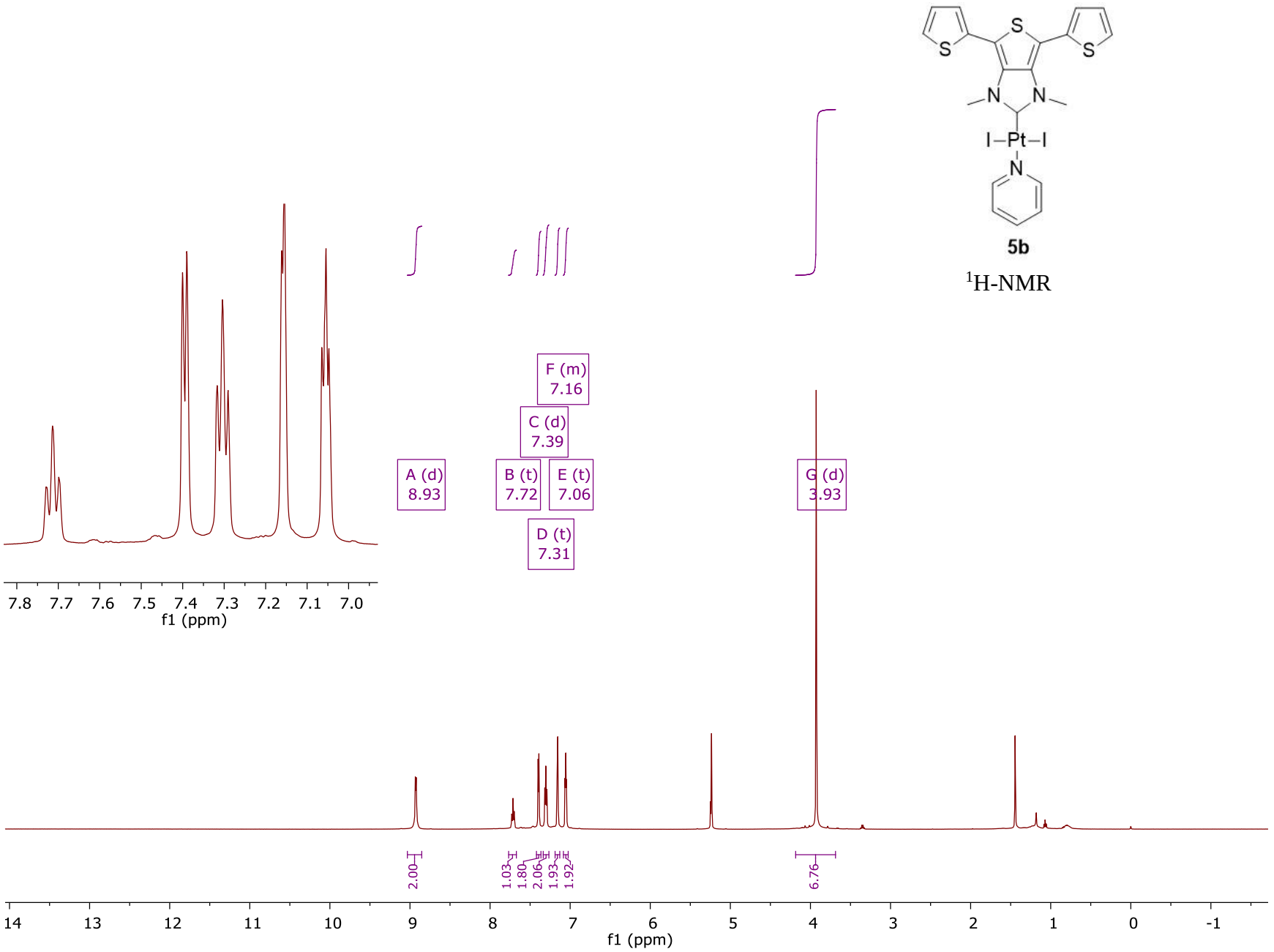
^{13}C-NMR

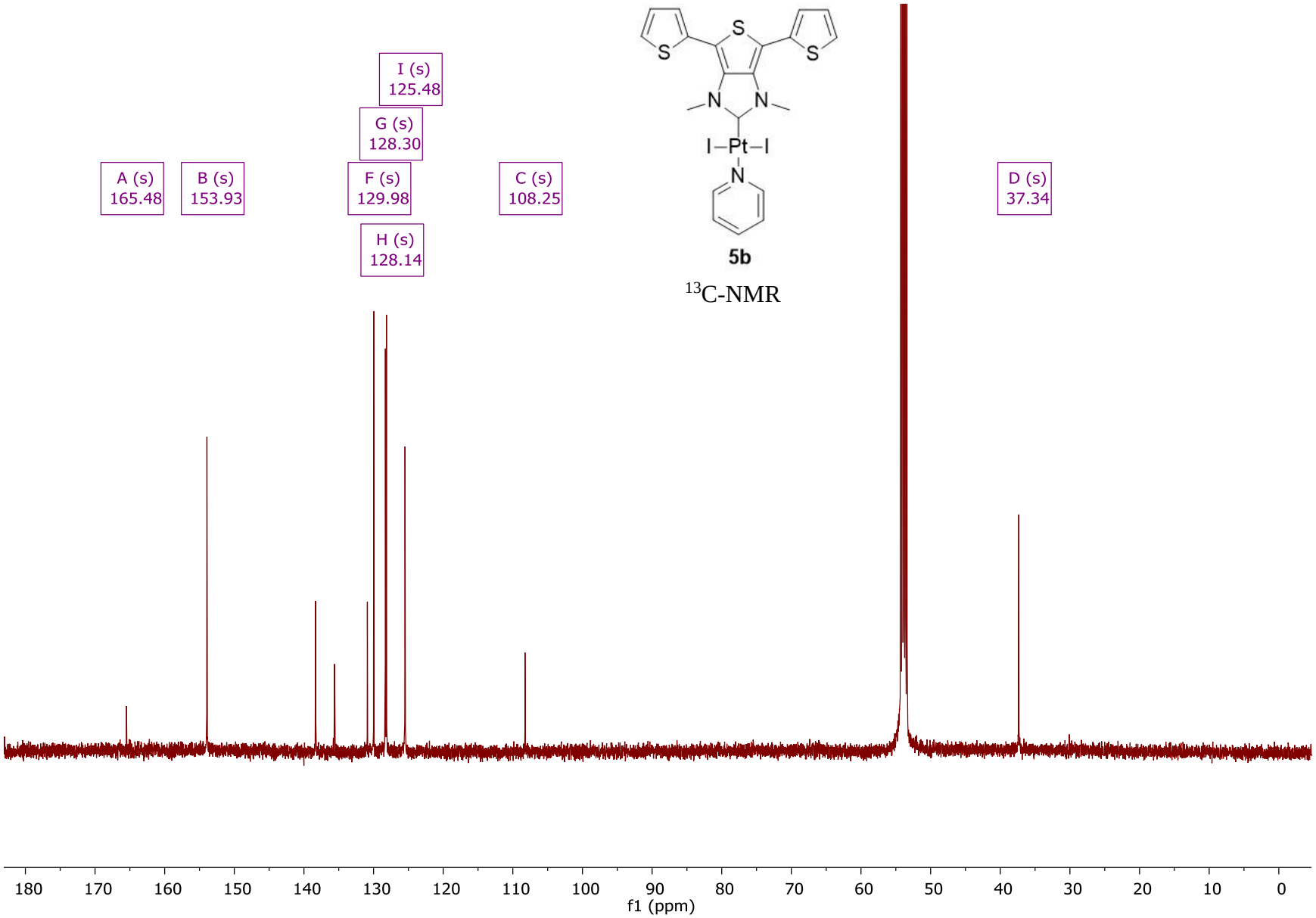
153.60
131.65
130.31
129.89
128.81
128.25
113.12
40.02 DMSO
39.85 DMSO
39.69 DMSO
39.52 DMSO
39.35 DMSO
39.19 DMSO
39.02 DMSO
35.46
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


A (m)
9.05
B (m)
7.77
C (dt)
7.44
D (m)
7.35
E (s)
4.22
F (td)
7.20
G (dd)
7.12
I (s)
4.12
J (s)
4.02
S
S
S
N
N
I–Pd–I
N
5a
f1 (ppm)
2.00
0.83
1.97
2.05
2.02
1.99
0.31
1.58
3.72

^{1}H-NMR


5a
^{13}C-NMR
A (s) 176.65
B (s) 153.87
C (s) 152.98
E (s) 137.82
F (s) 135.36
M (s) 124.68
O (s) 108.12
G (s) 130.22
H (s) 129.66
I (s) 129.61
J (s) 128.06
K (s) 127.99
L (s) 127.75
N (s) 124.61
P (s) 37.87
Q (s) 37.57


S
S
S
N
N
I–Pt–I
N
5b
1H-NMR
A (d)
8.93
B (t)
7.72
C (d)
7.39
D (t)
7.31
E (t)
7.06
F (m)
7.16
G (d)
3.93
2.00
1.03
1.80
2.06
1.93
1.92
6.76
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)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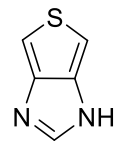
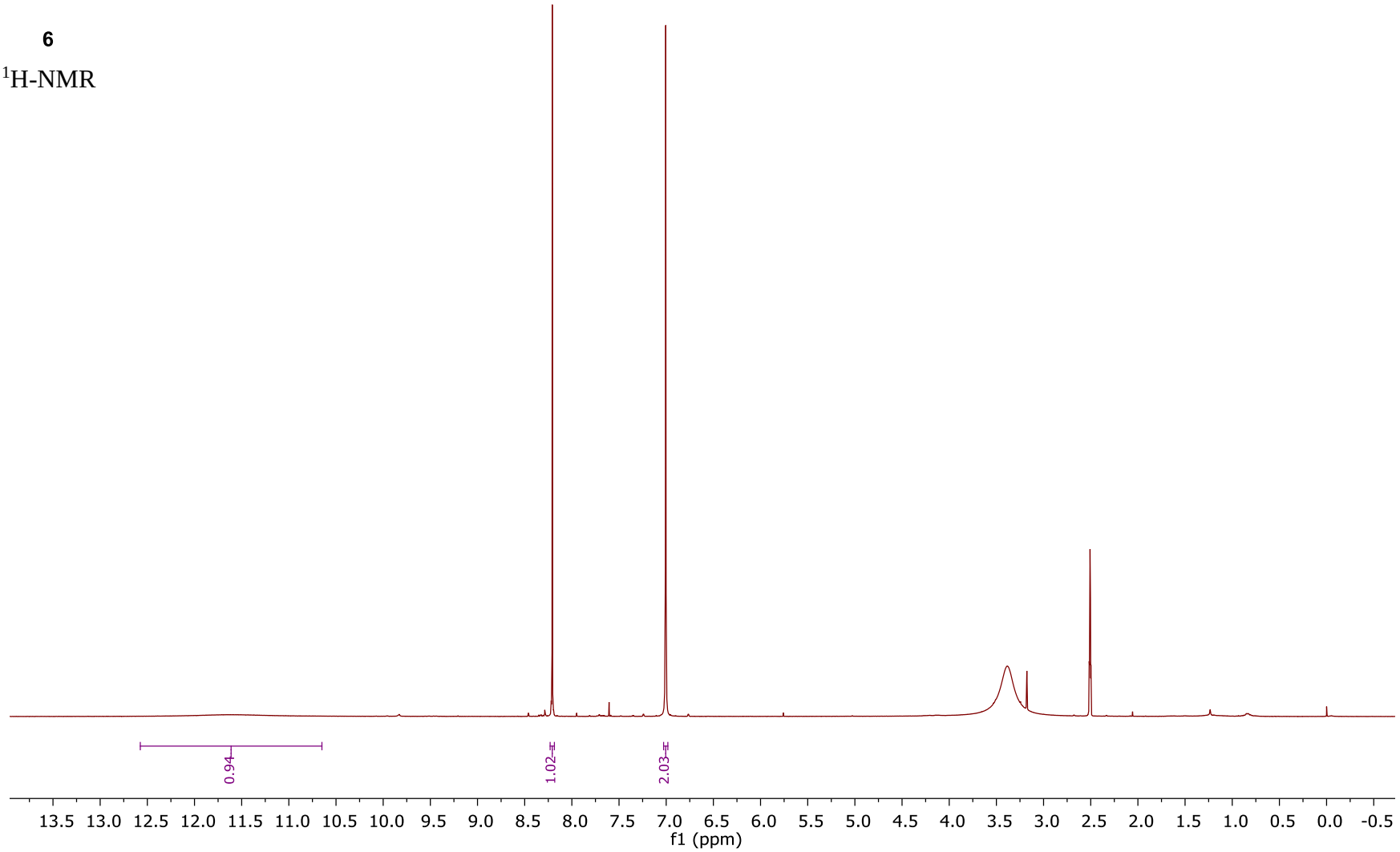
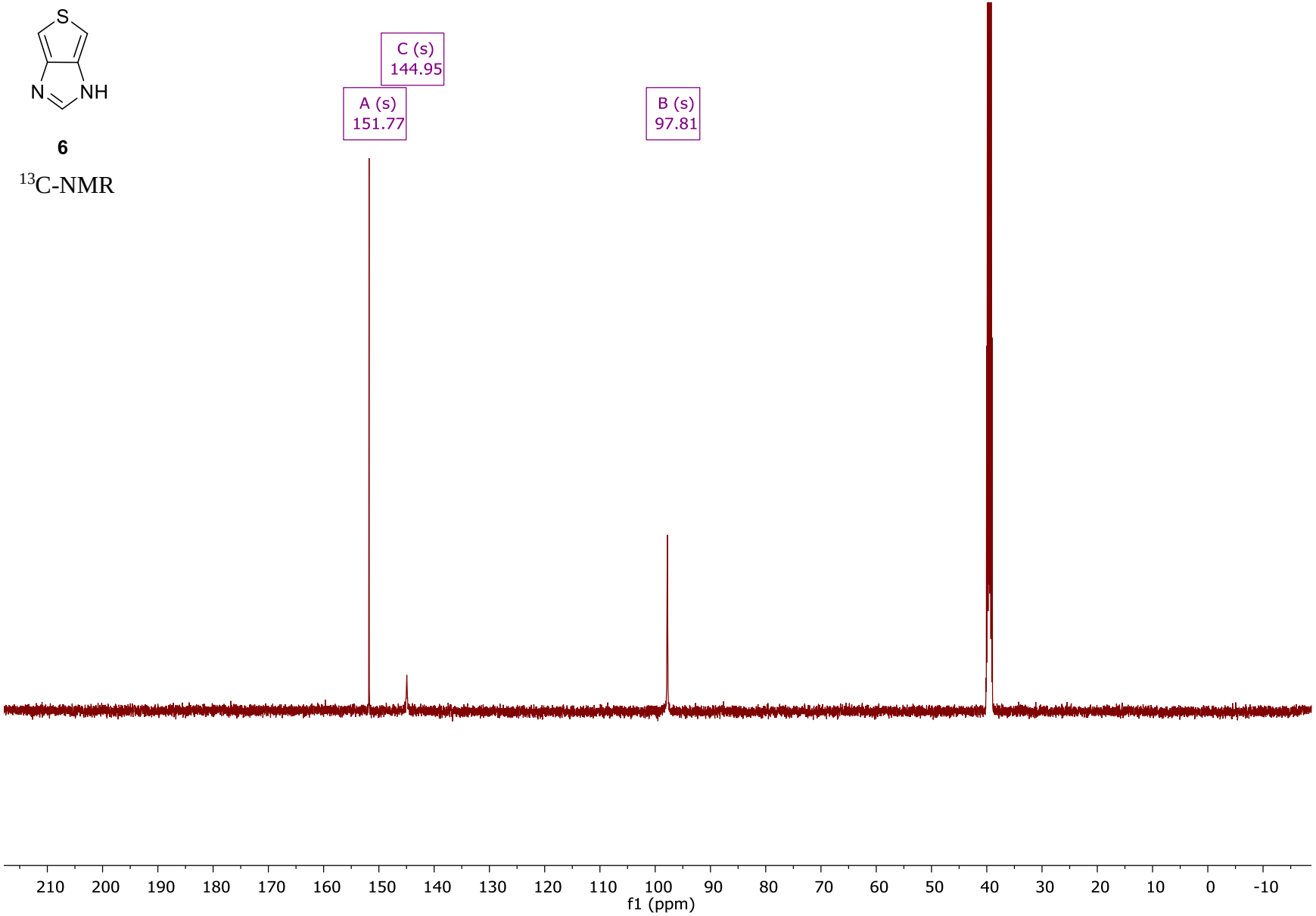
B (s)
153.93
I (s)
125.48
G (s)
128.30
F (s)
129.98
H (s)
128.14
C (s)
108.25
D (s)
37.34
S
S
S
N
N
I–Pt–I
N
5b
13C-NMR
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

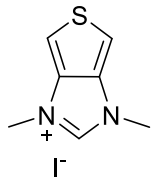

S
N
NH

6

^{1}H-NMR

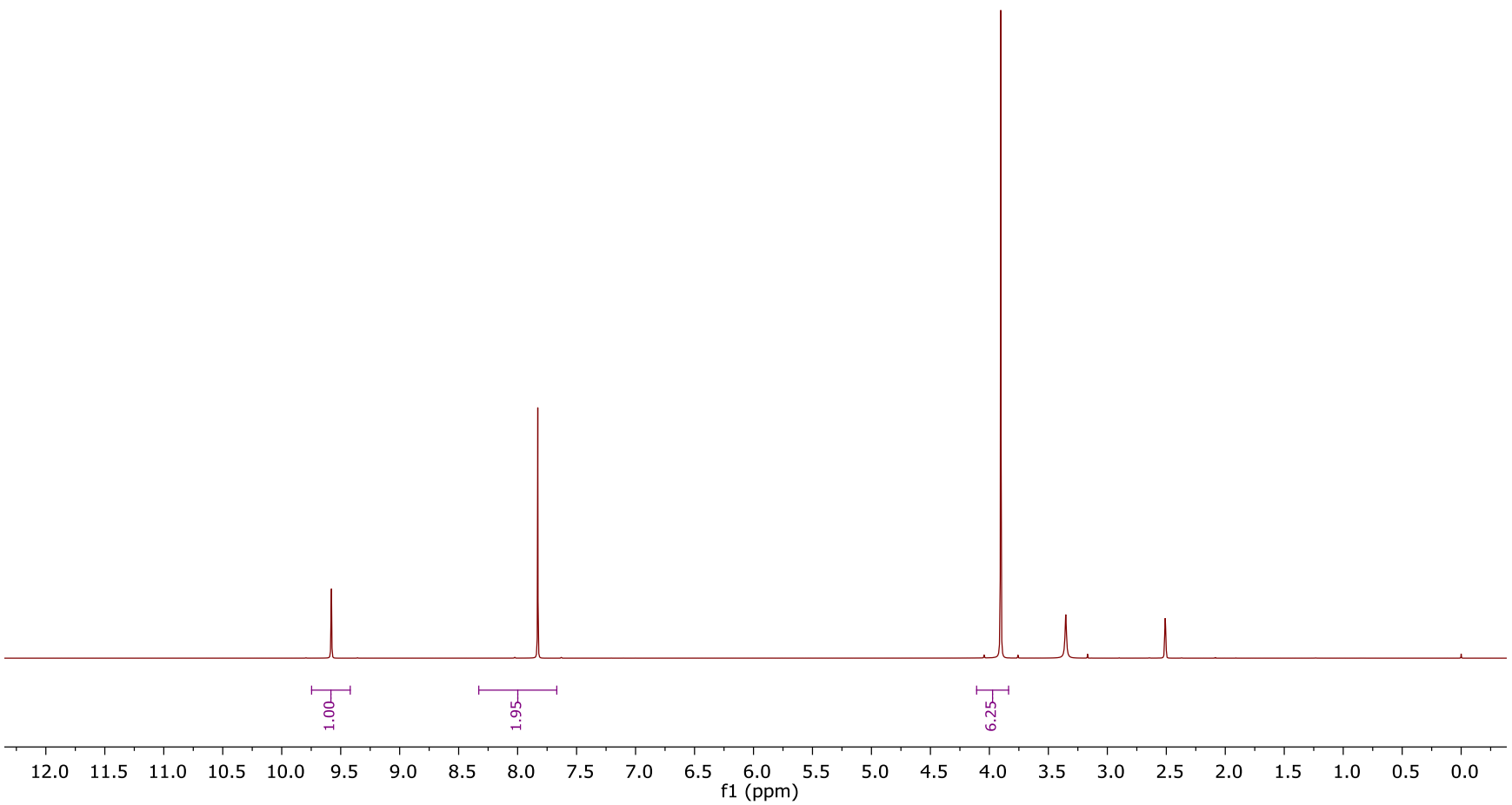

A (s)
11.62
B (s)
8.21
C (s)
7.01
0.94
1.02
2.03
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

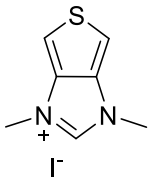

S
N
NH
6
13C-NMR
C (s)
144.95
A (s)
151.77
B (s)
97.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


S
N
+
N
I-

7

^{1}H-NMR

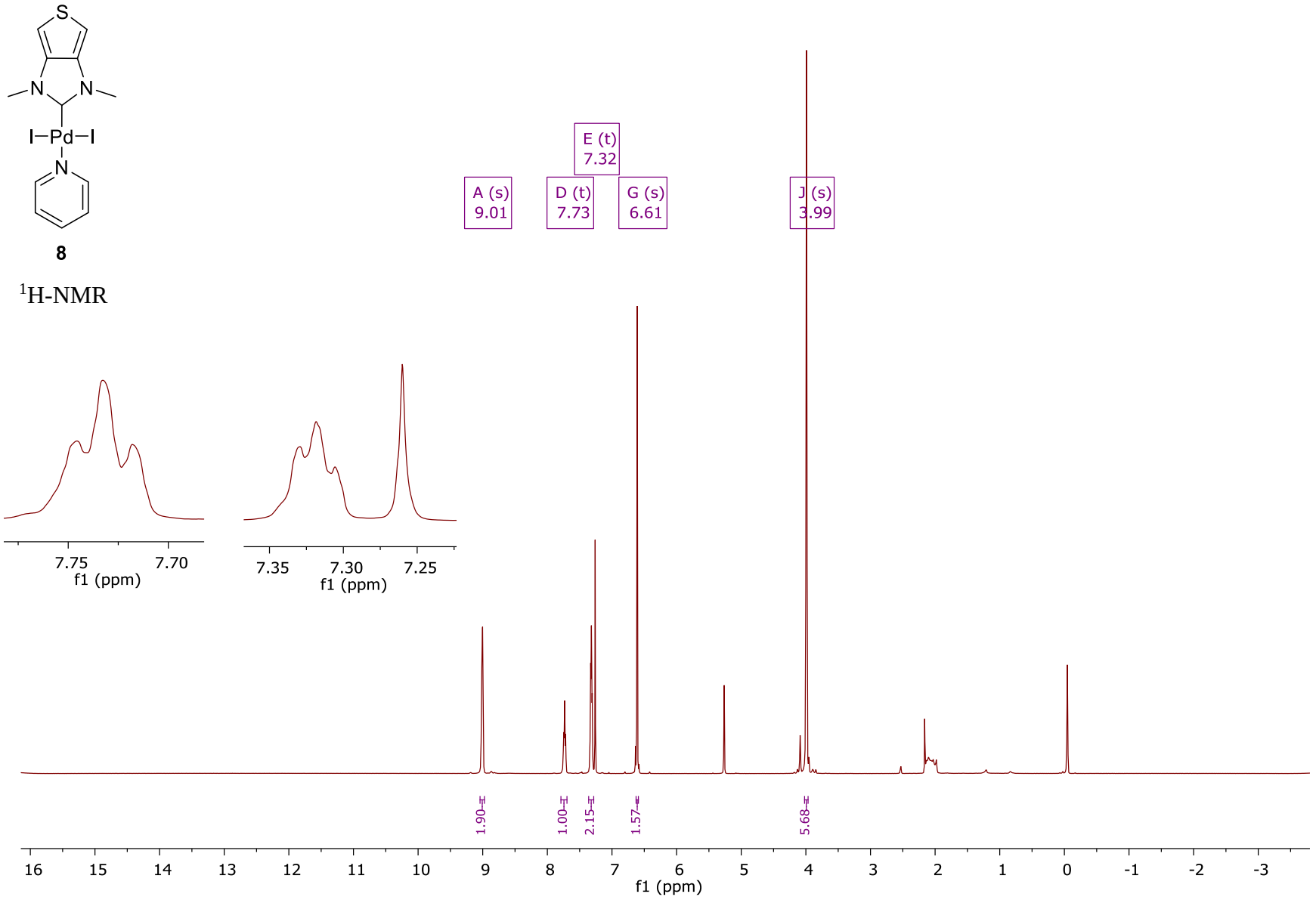

A (s)
9.58
B (s)
7.83
C (s)
3.90
1.00
1.95
6.25
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

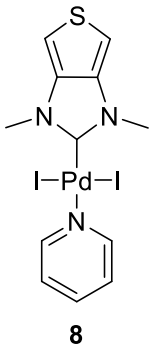

S
N
+
N
I-

7

^{13}C-NMR

152.25
136.44
104.15
40.53 DMSO
40.36 DMSO
40.19 DMSO
40.03 DMSO
39.86 DMSO
39.69 DMSO
39.52 DMSO
34.77
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)


S
N
N
I—Pd—I
N
8
1H-NMR
A (s)
9.01
D (t)
7.73
E (t)
7.32
G (s)
6.61
J (s)
3.99
7.75
7.70
f1 (ppm)
7.35
7.30
7.25
f1 (ppm)
1.90
1.00
2.15
1.57
5.68
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


S
N
N
I—Pd—I
N

8

^{13}C-NMR

A (d)
174.99
B (s)
153.77
D (s)
137.84
C (s)
139.87
E (s)
124.59
F (s)
96.12
G (s)
36.91
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)